

Supporting Information

Ruthenium-Catalyzed Amination of Secondary Alcohols using Borrowing Hydrogen Methodology

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General information.

All reactions were carried out under an atmosphere of dry nitrogen. Dichloromethane (DCM), tetrahydrofuran (THF), and toluene were freshly distilled under the following conditions: toluene and THF from sodium/benzophenone and DCM from calcium hydride. Dichloro(*p*-cymene)ruthenium(II) dimer of 98% purity was purchased from Alpha Aesar and used as received in complexation reactions. All other chemicals were used as received from suppliers. NMR spectra were recorded on 300 MHz or 700 MHz Bruker Avance III HD NMR spectrometers using residue CDCl₃ (δ 7.26 ppm) or H₂O (δ 1.56 ppm) for ¹H NMR reference and the central CDCl₃ resonance (δ 77.16 ppm) for ¹³C NMR reference. ¹H NMR spectra are reported as follows (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = unresolved multiplet). Flash chromatography was carried out using EMD Silica Gel 60 Geduran®. Thin Layer Chromatography analyses were performed on Analtech Silica Gel HLF (0.25 mm) pre-coated analytical plates and visualized with use of handheld short wavelength UV light, iodine stain (I₂ and EMD Silica Gel 60 Geduran®) and/or vanillin stain (ethanol, H₂SO₄, and vanillin). Chiral HPLC analyses were performed on an ISCO model 2360 HPLC with Daicel chemical industries, LTD. Chiralcel OJ-H and Chiralpak AD or IC columns (0.46 x 25 cm). Data were recorded and analyzed with ChromPerfect chromatography software (version 5.1.0). IR spectra were recorded using an Avatar 360 FT-IR. Optical rotations were measured as solutions in dichloromethane or chloroform, and recorded using an Autopol III automatic polarimeter; the concentration, *c*, is reported in g/100 mL. HRMS analyses were performed by the Nebraska Center for Mass Spectrometry.

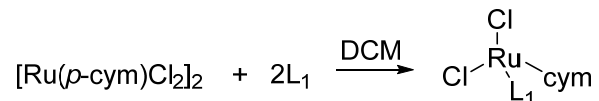
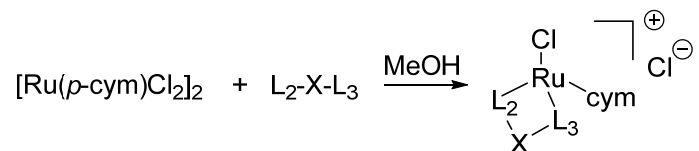


Figure S1. The synthesis of neutral ruthenium(II) complexes.

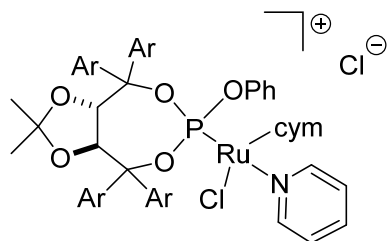
Two general routes to the neutral (Figure S1) and cationic ruthenium(II) complexes (Figure S2) employed ligands prepared according to literature procedures; these included (*S*)-2-(2-(diphenylphosphanyl)phenyl)-4-phenyl-4,5-dihydrooxazole¹ for complex **1**, (3*aS*,8*aS*)-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-dimethyl-6-phenoxytetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepine ((*S*)-xTADDOL)² for complexes **2** and **8**, (*S,S*)-2,2'-methylenebis(4-phenyl-2-oxazoline)³ and (*S,S*)-2,2'-dibenzylmethylenebis(4-phenyl-2-oxazoline)⁴ for complexes **4** and **5**, bis((4*S*,5*S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)methane⁵ for complex **6**. Other ruthenium(II) complexes (i.e., **3**⁶, **7**⁷ and **9**⁸) were synthesized according to published procedures.



L₂-X-L₃ – bidentate ligand; X = linker

Figure S2. Preparation of cationic ruthenium(II) complexes.

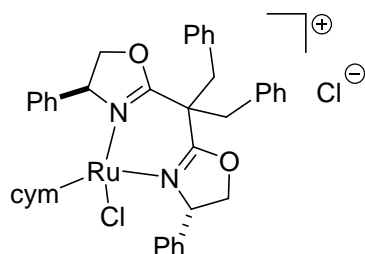
General procedure. A mixture of dichloro(*p*-cymene)ruthenium(II) dimer (0.10 mmol), mono- or bidentate ligand (0.20 mmol) in 10 mL of dichloromethane (for covalent complexes) or methanol (for cationic complexes) was stirred at room temperature for 3 h. The solvent was evaporated. Flash chromatography on silica gel affords the ruthenium(II) complex.



Ar = 3,5-dimethylphenyl

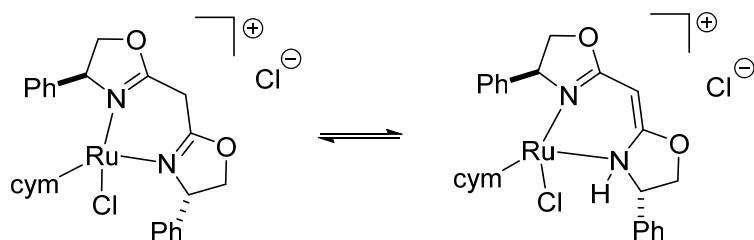
Chloro(*p*-cymene)(pyridine)[(3*aS*,8*aS*)-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-dimethyl-6-phenoxytetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepine]ruthenium(II) chloride (2).

Prepared from dichloro(*p*-cymene)ruthenium(II) dimer, [(3*aS*,8*aS*)-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-dimethyl-6-phenoxytetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepine ((*S,S*)-xylyl-TADDOLPOPh) and pyridine: 126 mg (58%); yellow-green solid; mp 152-154 °C; $R_f = 0.3$ (dichloromethane/methanol 9:1); $[\alpha]_D^{25} = +94.5$ (c 0.67, CH_2Cl_2); NMR signals reported for the mixture of two diastereomers (ratio 5:4); ^1H NMR (700 MHz, CDCl_3) δ 8.96 (d, $J = 4.9$ Hz, 2H), 8.83 (d, $J = 4.9$ Hz, 2H), 7.86 (t, $J = 7.0$ Hz, 1H), 7.67 (t, $J = 7.0$ Hz, 1H), 7.27-7.21 (m, 7H), 7.10-6.76 (m, 33H), 6.54 (s, 2H), 6.31 (d, $J = 7.7$ Hz, 2H), 6.20 (d, $J = 6.3$ Hz, 2H), 6.03-5.98 (m, 3H), 5.85 (d, $J = 7.7$ Hz, 1H), 5.81 (d, $J = 7.7$ Hz, 1H), 5.77 (s, 1H), 5.08 (dd, $J = 7.7, 3.5$ Hz, 2H), 2.59 (m, 2H), 2.38 (s, 8H), 2.33-2.31 (m, 24H), 2.23 (s, 8H), 2.17-2.15 (m, 24H), 2.04 (s, 12H), 1.31-1.20 (m, 8H), 1.18 (dd, $J = 15.4, 7.0$ Hz, 8H), 1.11 (s, 3H), 1.00-0.96 (m, 11H), 0.90-0.85 (m, 7H), 0.43 (s, 3H), 0.29 (s, 3H) ppm; ^{13}C NMR (175 MHz, CDCl_3) δ 156.4, 156.3, 150.7, 150.5, 144.0, 143.9, 143.8, 142.9, 139.6, 139.5, 138.9, 138.5, 138.1, 137.5, 137.4, 136.9, 136.7, 136.6, 136.5, 136.3, 130.5, 130.3, 130.0, 129.9, 129.8, 129.7, 129.6, 129.4, 129.3, 129.1, 127.3, 127.1, 126.8, 126.1, 125.9, 125.5, 125.0, 124.6, 120.8, 119.9, 119.5, 113.8, 113.5, 103.0, 102.4, 94.2, 93.3, 93.2, 92.8, 92.7, 92.4, 92.3, 91.6, 91.5, 88.9, 85.2, 84.6, 80.2, 80.1, 77.5, 31.6, 30.8, 29.1, 27.5, 27.2, 26.2, 25.9, 25.3, 22.7, 22.4, 21.9, 21.7, 21.6, 21.5, 21.4, 21.3, 21.2, 18.4, 18.0, 14.1, 11.4 ppm; ^{31}P NMR (283.4 MHz, CDCl_3) δ 103.2 (56%), 102.7 (44%) ppm; IR (neat) 2162, 2025, 1603, 1485, 1447, 1372, 1161, 1009, 947, 907, 723, 690, 595 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{60}\text{H}_{68}\text{NO}_5\text{P}^{35}\text{Cl}^{96}\text{Ru} [(\text{M}-\text{Cl})^+]$, 1044.3600; found, 1044.3615 m/z .

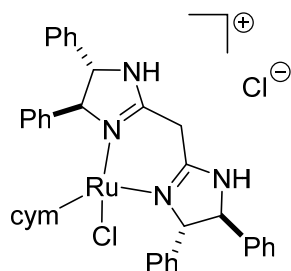


Chloro(*p*-cymene)[(*S,S*)-2,2'-dibenzylmethylenebis(4-phenyl-2-oxazoline)]ruthenium(II) chloride (4). Prepared from dichloro(*p*-cymene)ruthenium(II) dimer and (*S,S*)-2,2'-dibenzylmethylenebis(4-phenyl-2-oxazoline): 148 mg (87%); orange solid; mp 125-127 °C; $R_f =$

0.4 (dichloromethane/methanol 9:1); $[\alpha]_D^{25} = +132.0$ (c 0.67, CH_2Cl_2); ^1H NMR (700 MHz, CDCl_3) δ 7.83 (d, $J = 21.0$ Hz, 2H), 7.50-7.27 (m, 18H), 5.49 (br s, 2H), 4.69 (t, $J = 9.8$ Hz, 1H), 4.18 (dd, $J = 8.4, 5.6$ Hz, 1H), 4.03 (br s, 4H), 3.65 (dd, $J = 56.0, 13.3$ Hz, 4H), 3.27 (d, $J = 14.0$ Hz, 2H), 2.46 (m, 1H), 1.92 (br s, 3H), 1.04 (br s, 3H), 0.69 (d, $J = 5.6$ Hz, 3H) ppm; ^{13}C NMR (175 MHz, CDCl_3) δ 173.1, 170.3, 139.7, 139.3, 134.6, 130.6, 130.0, 129.7, 128.8, 128.7, 128.5, 128.3, 128.0, 127.8, 126.7, 88.4, 76.4, 76.2, 73.2, 72.0, 46.0, 42.7, 30.8, 22.4, 20.1, 18.1 ppm; IR (neat) 2159, 2021, 1651, 1455, 1083, 1053, 926, 726, 700, 635 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{43}\text{H}_{44}\text{N}_2\text{O}_2^{35}\text{Cl}^{96}\text{Ru} [(\text{M}-\text{Cl})^+]$, 751.2167; found, 751.2180 m/z .

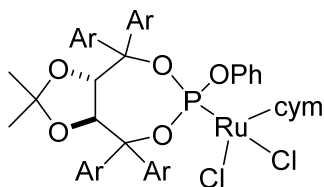


Chloro(*p*-cymene)[(*S,S*)-2,2'-methylenebis(4-phenyl-2-oxazoline)]ruthenium(II) chloride (5). Prepared from dichloro(*p*-cymene)ruthenium(II) dimer and (*S,S*)-2,2'-methylenebis(4-phenyl-2-oxazoline): 109 mg (89%); dark orange solid; mp 155-157 °C (dec); $R_f = 0.25$ (dichloromethane/methanol 9:1); $[\alpha]_D^{25} = +168.0$ (c 0.67, CH_2Cl_2); ^1H NMR (700 MHz, CDCl_3) signals for two forms: δ 7.60-7.38 (m, 20H), 6.37-6.26 (m, 3H), 6.00-5.93 (m, 1H), 5.74 (br s, 1H), 5.44 (m, 1H), 5.25 (br s, 1H), 4.90 (m, 4H), 4.73 (br s, 1H), 4.57 (d, $J = 33.6$ Hz, 2H), 4.40-4.20 (m, 7H), 3.86 (d, $J = 17.5$ Hz, 1H), 2.41 (m, 2H), 1.99 (br s, 3H), 1.68 (br s, 3H), 1.11 (br s, 3H), 1.03 (br s, 3H), 0.87 (br s, 6H) ppm; ^{13}C NMR (175 MHz, CDCl_3) δ 168.3, 167.2, 139.6, 138.9, 130.0, 129.8, 129.2, 128.8, 128.6, 128.5, 128.3, 128.2, 127.8, 126.8, 126.5, 83.6, 77.8, 75.8, 74.9, 73.22, 30.7, 23.1, 22.7, 21.9 ppm; IR (neat) 2159, 2017, 1562, 1454, 1394, 1031, 940, 723, 701 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{29}\text{H}_{31}\text{N}_2\text{O}_2^{102}\text{Ru} [(\text{M}-\text{Cl}-\text{HCl})^+]$, 541.1196; found, 541.1145 m/z .



Chloro(*p*-cymene)[bis((*4S,5S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)methane]-ruthenium(II) chloride (6). Prepared from dichloro(*p*-cymene)ruthenium(II) dimer and bis((*4S,5S*)-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)methane: 110 mg (72%); dark brown solid; mp 184-186 °C (dec); $R_f = 0.35$ (dichloromethane/methanol 9:1); $[\alpha]_D^{25} = +144.0$ (c 0.67, CH_2Cl_2); ^1H NMR (700 MHz, CDCl_3) δ 7.56-7.28 (m, 20H), 5.33 (br s, 1H), 5.17 (br s, 1H), 4.85 (d, $J = 11.9$ Hz, 2H), 4.68-4.45 (m, 4H), 4.13 (br s, 1H), 2.37 (m, 1H), 1.79 (br s, 3H), 1.02 (br s, 3H), 0.92 (br s, 3H) ppm; ^{13}C NMR (175 MHz, CDCl_3) δ 166.1, 164.5, 143.3, 142.0, 141.7, 141.6, 129.5, 129.2, 129.1, 129.0, 128.9, 128.4, 128.3, 127.1, 126.7, 126.6, 126.2, 84.5, 84.4, 82.1, 80.3, 69.1, 69.0, 30.7, 24.1, 22.9, 21.8 ppm; IR (neat) 3027, 2162, 1978, 1613, 1394, 1452,

751, 696 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{41}\text{H}_{41}\text{N}_4^{102}\text{Ru}$ $[(\text{M}-\text{Cl}-\text{HCl})^+]$, 691.2982; found, 691.3012 m/z .



Ar = 3,5-dimethylphenyl

Dichloro(*p*-cymene)(3*aS*,8*aS*)-4,4,8,8-tetrakis(3,5-dimethylphenyl)-2,2-dimethyl-6-phenoxytetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphine) ruthenium(II) (8). Prepared from dichloro(*p*-cymene)ruthenium(II) dimer and (*S,S*)-xylyl-TADDOLPOPh: 191 mg (96%); pale red solid; mp 143-145 °C; $R_f = 0.7$ (dichloromethane/ethyl acetate 4:1); $[\alpha]_D^{25} = +52.5$ (c 0.67, CH_2Cl_2); ^1H NMR (700 MHz, CDCl_3) δ 7.53 (s, 2H), 7.30 (s, 2H), 7.20 (s, 2H), 6.92-6.83 (m, 9H), 6.24 (d, $J = 7.7$ Hz, 2H), 5.96 (d, $J = 9.1$ Hz, 1H), 5.36 (d, $J = 6.3$ Hz, 1H), 5.30 (d, $J = 6.3$ Hz, 1H), 5.14 (d, $J = 5.6$ Hz, 1H), 4.85 (d, $J = 6.3$ Hz, 1H), 4.82 (d, $J = 8.4$ Hz, 1H), 2.76 (septet, $J = 7.0$ Hz, 1H), 2.33 (s, 6H), 2.31 (s, 6H), 2.27 (m, 12H), 1.75 (s, 3H), 1.51 (s, 3H), 1.12 (dd, $J = 8.4, 7.7$ Hz, 6H), 0.24 (s, 3H) ppm; ^{13}C NMR (175 MHz, CDCl_3) δ 151.1 (d, $J = 1.8$ Hz), 144.4, 141.3, 137.1, 136.5 (d, $J = 5.3$ Hz), 136.3, 129.5, 129.0 (t, $J = 7.0$ Hz), 128.7, 126.6, 126.2, 125.9, 123.4, 119.9 (d, $J = 3.6$ Hz), 111.9, 90.2, 90.1, 87.8, 82.6, 78.2, 30.2, 27.9, 25.7, 22.8, 22.0, 21.6, 21.5 (d, $J = 8.8$ Hz), 21.3, 18.0 ppm; ^{31}P NMR (283.4 MHz, CDCl_3) δ 96.6 ppm; IR (neat) 2915, 2161, 2031, 1601, 1490, 1372, 1213, 1161, 1020, 906, 693, 590 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{55}\text{H}_{63}\text{O}_5\text{PCl}_2^{102}\text{RuNa}$ $[(\text{M}+\text{Na})^+]$, 1029.2731; found, 1029.2742 m/z .

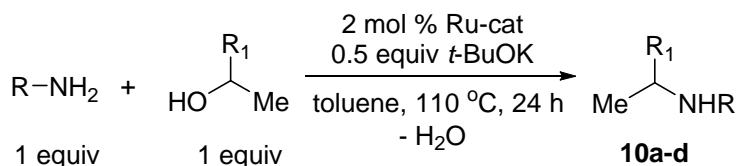
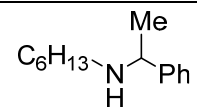
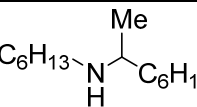
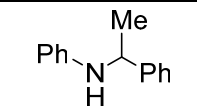
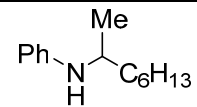


Figure S3. Aminations of secondary alcohols.

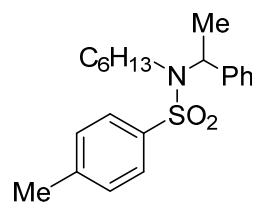
General procedure for the amination of secondary alcohols (Figure S3). In a nitrogen-filled glovebox an 8 mL oven-dried sample vial was charged with ruthenium(II) complex (0.01 mmol, 2 mol%), monoalcohol (0.50 mmol), amine (0.50 mmol), and potassium *tert*-butoxide (28 mg, 0.25 mmol). Toluene (1 mL) was added and the vial sealed with a teflon-lined septum/screw cap. The reaction mixture was taken outside the glovebox and heated to 110 °C for 24 h after which the mixture was cooled to room temperature. Water (5 mL) was added, products were extracted with ethyl acetate (3 x 5 mL), dried (anhyd Na_2SO_4), and the solvent was removed under vacuum. Purification by flash chromatography on silica afforded the target products. Chiral HPLC analysis shows that all obtained products were obtained as near racemic mixtures (See chiral HPLC data below).

Table S1. Catalyst screening results.

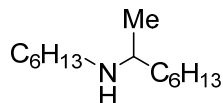
Product	Yields of products with different catalysts, % ^a								
	1	2	3	4	5	6	7	8	9
	71	55	53	74	65	63	47	59	55
	78	71	62	69	61	34	32	55	33
	72	62	68	68	56	53	28	59	68
	88	64	84	74	76	40	21	73	68

^a Reported in Table S1 are isolated yields of products, the results are average of two runs. *Reaction conditions:* Alcohol/amine ratio 1:1, solvent: toluene, 110 °C, 24 h, base: *t*-BuOK (0.5 equiv.), Ru(II) catalyst loading 2%.

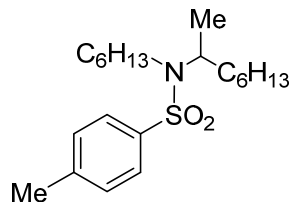
Characterization Data



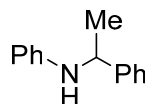
***N*-Hexyl-4-methyl-*N*-(1-phenylethyl)benzenesulfonamide (10a').** (Note: Prepared from **10a** for chiral HPLC analysis.) To a cooled (0 °C), stirred mixture of *N*-(1-phenylethyl)hexan-1-amine **10a** (100 mg, 0.487 mmol, prepared using **1**) and 4-methylbenzenesulfonyl chloride 102 mg (0.537 mmol) in 1 mL of dry DCM was added triethylamine (0.075 mL, 0.537 mmol) in one portion. The resulting solution was warmed to room temperature and stirred for 3 h, and then partitioned with water (2 mL). The aqueous phase was extracted with additional DCM (2 x 1 mL). The combined organic layers were dried (anhyd Na₂SO₄) and the solvent evaporated. Flash chromatography of the residue on silica (first eluting with a mixture of hexanes/DCM 1:1 followed by DCM) afforded the title compound as a colorless oil (158 mg, 90%); R_f = 0.5 (dichloromethane); chiral HPLC analysis (Chiralpak AD with AD guard, hexanes/isopropanol 99:1, flow rate = 2.0 mL/min) showed peaks at 27.4 min (49.6%) and 35.7 min (50.4%); ¹H NMR (300 MHz, CDCl₃) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.33-7.23 (m, 7H), 7.20 (s, 2H), 5.20 (q, *J* = 7.2 Hz, 1H), 3.04-2.98 (m, 2H), 2.46 (s, 3H), 1.41 (d, *J* = 6.9 Hz, 3H overlapping with m, 1H), 1.22-1.04 (m, 7H), 0.82 (t, *J* = 6.6 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 142.9, 140.4, 138.5, 129.6, 128.3, 127.6 (d, *J* = 1.5 Hz), 127.1, 55.3, 44.3, 31.2, 30.6, 26.6, 22.5, 21.5, 16.7, 14.0 ppm; IR (neat) 2923, 2857, 1495, 1451, 1315, 1160, 1142, 1089, 1049, 952, 727, 697, 655, 612, 555 cm⁻¹; HRMS (ESI) calcd. for C₂₁H₂₉NO₂Na [(M+Na)⁺], 382.1817; found, 382.1830 *m/z*.



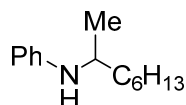
***N*-Hexyloctan-2-amine (10b):**⁹ pale yellow oil (yield reported in Table S1); $R_f = 0.55$ (hexanes/dichloromethane 1:1); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 2.68-2.50 (m, 3H), 1.50-1.44 (m, 3H), 1.40-1.20 (m, 16H), 1.04 (d, $J = 6.3$ Hz, 3H), 0.90 (dt, overlapping, $J = 6.9, 5.7$ Hz, 6H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 53.3, 47.4, 37.1, 31.9, 31.8, 30.4, 29.5, 27.2, 26.1, 22.6, 20.3, 14.1 (d, $J = 3.0$ Hz) ppm.



***N*-Hexyl-4-methyl-*N*-(octan-2-yl)benzenesulfonamide (10b').** Prepared from **10b** for chiral HPLC analysis using the same procedure as for *N*-hexyl-4-methyl-*N*-(1-phenylethyl)benzenesulfonamide **10a'** using complex **1**: 160 mg (93%); colourless oil; $R_f = 0.6$ (dichloromethane); chiral HPLC analysis (Chiralpak IC with AD guard, hexanes/isopropanol 90:10, flow rate = 1.0 mL/min) showed peaks at 30.5 min (49.7%) and 33.8 min (50.3%); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.72 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 2H), 3.84 (sextet, $J = 6.9$ Hz, 1H), 3.13-2.94 (m, 2H), 2.43 (s, 3H), 1.76-1.56 (m, 2H), 1.45-1.10 (m, 16H), 0.98 (d, $J = 6.6$ Hz, 3H), 0.92 (dt, overlapping, $J = 6.6, 5.4$ Hz, 6H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 142.7, 138.5, 129.5, 127.1, 53.9, 43.3, 35.6, 31.7 (d, $J = 3.0$ Hz), 31.5, 29.1, 26.9, 26.6, 22.6 (d, $J = 4.5$ Hz), 21.5, 19.0, 14.1, 14.0 ppm; IR (neat) 2926, 2856, 1338, 1130, 1090, 956, 814, 635, 586, 554 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{37}\text{NO}_2\text{SNa}$ [(M+Na)⁺], 390.2443; found, 390.2426 m/z .



***N*-(1-Phenylethyl)aniline (10c):**^{10,11} pale yellow liquid (yield reported in Table S1, data for the product obtained using complex **1**): $R_f = 0.3$ (hexanes/dichloromethane 1:1); chiral HPLC analysis (Chiralcel OJ-H with AD guard, hexanes/isopropanol 70:30, flow rate = 1.0 mL/min) showed peaks at 21.6 min (49.2%) and 26.2 min (50.8%); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.42-7.33 (m, 4H), 7.28-7.23 (m, 1H), 7.12 (td, $J = 7.5, 2.1$ Hz, 2H), 6.68 (td, $J = 8.4, 0.9$ Hz, 1H), 6.54 (dd, $J = 8.7, 2.1$ Hz, 2H), 4.52 (q, $J = 6.9$ Hz, 1H), 4.06 (br s, 1H), 1.55 (d, $J = 6.6$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 147.3, 145.3, 129.1, 128.7, 126.9, 125.9, 117.2, 113.3, 53.5, 25.1 ppm.



***N*-(Octan-2-yl)aniline (10d):**¹² pale yellow liquid (yield reported in Table S1, data reported for the product obtained using complex **1**): $R_f = 0.4$ (hexanes/dichloromethane 1:1); chiral HPLC analysis (Chiralpak IC with AD guard, hexanes, flow rate = 0.5 mL/min) showed peaks at 29.5 min (50.7%) and 32.4 min (49.3%); ¹H NMR (300 MHz, CDCl₃) δ 7.21 (td, $J = 7.2, 1.8$ Hz, 2H), 6.70 (td, $J = 7.5, 0.9$ Hz, 1H), 6.62 (dd, $J = 8.4, 0.9$ Hz, 2H), 3.49 (septet, $J = 6.0$ Hz, 1H overlapping with br s, 1H), 1.64-1.59 (m, 1H), 1.51-1.25 (m, 9H), 1.22 (d, $J = 6.3$ Hz, 3H), 0.95 (t, $J = 6.9$ Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 147.8, 129.3, 116.8, 113.1, 48.5, 37.3, 31.9, 29.4, 26.2, 22.7, 20.8, 14.1 ppm.

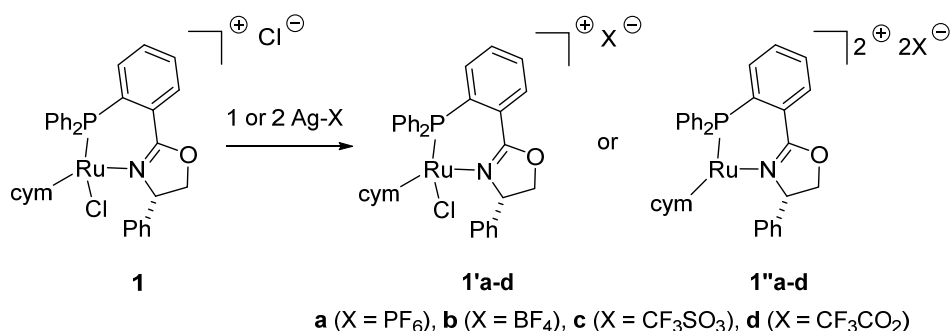


Figure S4. Anion-exchanged complexes based on **1**.

General Procedure to Probe the Effect of Counter-Anion Exchange with Complex 1. The anion exchange reactions (Figure S4) were carried out with **1** as described in the *General procedure for the amination of secondary alcohols* with the following modification: one or two equivalents of appropriate silver salt dissolved in the mixture of DCM and THF was added to complex **1**. Precipitated silver chloride was filtered off, solvents were evaporated, and the resulting Ru(II)-complexes used directly.

Table S2. The effect of counter-anion exchange on the BH reactivity.

Product	Yields of products using 1 with different anions, % ^a								
	1	1'a	1''a	1'b	1''b	1'c	1''c	1'd	1''d
	Cl ⁻	PF ₆ ⁻	2PF ₆ ⁻	BF ₄ ⁻	2BF ₄ ⁻	CF ₃ SO ₃ ⁻	2CF ₃ SO ₃ ⁻	CF ₃ COO ⁻	2CF ₃ COO ⁻
	71	58	41	44	28	22	18	11	8
	78	61	45	38	26	24	24	35	31
	72	40	36	48	31	34	18	26	28
	88	43	28	54	35	28	12	16	9

^a Reported in Table S2 are isolated yields of products, the results are average of two runs. *Reaction conditions*: Alcohol/amine ratio 1:1, solvent: toluene, 110 °C, 24 h, base: *t*-BuOK (0.5 equiv.), Ru(II) catalyst loading 2%.

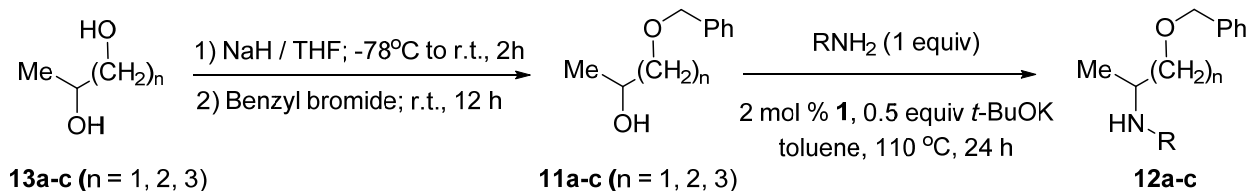
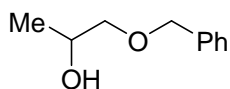
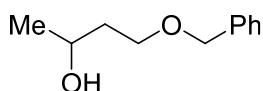


Figure S5. Aminations of secondary alcohols **11a-c** using complex **1**.

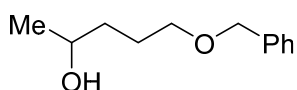
General procedure for the monobenzylation of primary-secondary diols (Figure S5). To a cold (-78 °C), vigorously stirred suspension of NaH (24 mmol) in dry THF (40 mL) was added a solution of diol (20 mmol) in THF (8 mL). The resulting suspension was then slowly warmed up to room temperature with stirring over 2 h. The mixture was re-cooled (0 °C) and neat benzyl bromide (22 mmol) added dropwise. Afterwards, the reaction mixture was warmed and stirred at room temperature (12 h). The resulting mixture was quenched by the careful addition of saturated aq NH₄Cl (ca. 20 mL) and then extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were dried (anhyd Na₂SO₄), filtered and the solvents removed via rotovap yielding a crude mixture of mono- and dibenzyl ethers and starting material. The desired monobenzyloxy ether was obtained by flash-chromatography on silica.



1-(Benzyloxy)propan-2-ol (11a).¹³ Chromatography affords the title compound as colorless oil: 1.76 g (53%); *R*_f = 0.35 (hexanes/ethyl acetate 7:3); ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.30 (m, 5H), 4.58 (s, 2H), 4.08-3.97 (m, 1H), 3.50 (dd, *J* = 9.3, 3.0 Hz, 1H), 3.31 (dd, *J* = 9.3, 8.1 Hz, 1H), 2.48 (br s, 1H), 1.17 (d, *J* = 6.6 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 138.0, 128.5, 127.8 (d, *J* = 3.8 Hz), 75.8, 73.3, 66.5, 18.6 ppm.



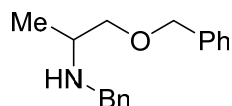
4-(Benzyloxy)butan-2-ol (11b).¹⁴ Chromatography yields the title compound as colorless oil: 2.02 g (56%); *R*_f = 0.45 (hexanes/ethyl acetate 7:3); ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.28 (m, 5H), 4.54 (s, 2H), 4.02 (sextet, *J* = 6.3 Hz, 1H), 3.76-3.62 (m, 2H), 3.00 (br s, 1H), 1.86-1.68 (m, 2H), 1.22 (d, *J* = 6.0 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 138.0, 128.5, 127.8, 127.7, 73.3, 69.1, 67.4, 38.2, 23.4 ppm.



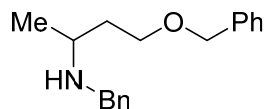
5-(Benzyloxy)pentan-2-ol (11c).¹⁵ Chromatography affords the title compound as colorless oil: 1.82 g (47%); *R*_f = 0.55 (hexanes/ethyl acetate 7:3); ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.27 (m,

5H), 4.54 (s, 2H), 3.80 (tq, $J = 6.3$ Hz, 1H), 3.52 (t, $J = 6.0$ Hz, 2H), 2.65 (br s, 1H), 1.79-1.66 (m, 2H), 1.64-1.46 (m, 2H), 1.20 (d, $J = 6.0$ Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 138.2, 128.4, 127.7, 127.6, 73.0, 70.6, 67.7, 36.5, 26.3, 23.5 ppm.

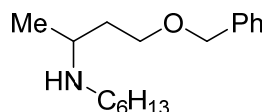
General procedure for the amination of benzyloxyalcohols 11a-c (Figure S5). To a nitrogen-flushed flask equipped with reflux condenser was added **1** (26.0 mg, 0.036 mmol), monobenzyl alcohol **11** (1.80 mmol), amine (1.80 mmol) and potassium *tert*-butoxide (0.90 mmol). Toluene (4 mL) was added, and the resulting reaction mixture was heated and stirred (110 °C, 24 h). Afterwards, the mixture was cooled (RT) and partitioned with water (8 mL). The aqueous layer was extracted with ethyl acetate (2 x 5 mL) and the combined organic layers dried (anhyd. Na_2SO_4), filtered and the solvents evaporated. Flash chromatography on silica gel affords the desired amine product.



N-Benzyl-1-(benzyloxy)propan-2-amine (12b): 239 mg (52%); pale yellow liquid; $R_f = 0.3$ (ethyl acetate/dichloromethane 1:1); ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.26 (m, 10H), 4.54 (s, 2H), 3.91 (d, $J = 13.2$ Hz, 1H), 3.78 (d, $J = 13.2$ Hz, 1H), 3.51-3.39 (m, 2H), 3.08-2.98 (m, 1H), 2.03 (br s, 1H), 1.12 (d, $J = 6.3$ Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 140.7, 138.4, 128.4 (d, $J = 0.8$ Hz), 128.2, 127.7, 127.6, 126.9, 74.7, 73.2, 52.0, 51.3, 17.2 ppm; IR (neat) 2852, 1495, 1452, 1368, 1093, 1028, 731, 695 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{21}\text{NONa}$ [(M+Na) $^+$], 278.1521; found, 278.1512 m/z ; calcd. for $\text{C}_{17}\text{H}_{22}\text{NO}$ [(M+H) $^+$], 256.1701; found, 256.1697 m/z .

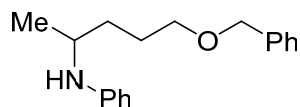


N-Benzyl-4-(benzyloxy)butan-2-amine (12c): 330 mg (68%); colorless liquid; $R_f = 0.35$ (ethyl acetate/dichloromethane 1:1); ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.25 (m, 10H), 4.53 (s, 2H), 3.88 (d, $J = 12.9$ Hz, 1H), 3.76 (d, $J = 12.9$ Hz, 1H), 3.68-3.55 (m, 2H), 2.93 (tq, $J = 6.3$ Hz, 1H), 1.92-1.81 (m, 1H), 1.75-1.65 (m, 1H overlapping with br s, 1H), 1.16 (d, $J = 6.3$ Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 140.8, 138.5, 128.4, 128.2, 127.7, 127.6, 126.8, 73.1, 68.2, 51.4, 50.7, 36.9, 20.6 ppm; IR (neat) 2853, 2159, 1494, 1452, 1363, 1097, 1027, 731, 695 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{NONa}$ [(M+Na) $^+$], 292.1677; found, 292.1664 m/z .

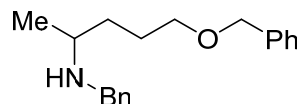


N-(4-(benzyloxy)butan-2-yl)hexan-1-amine (12d): 393 mg (83%); colorless liquid; $R_f = 0.35$ (ethyl acetate/dichloromethane 1:1); ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.27 (m, 5H), 4.51 (s, 2H), 3.63-3.51 (m, 2H), 2.82 (tq, $J = 6.3$ Hz, 1H), 2.69-2.49 (m, 2H), 1.86-1.75 (m, 1H), 1.67-1.39 (m, 3H), 1.38-1.20 (m, 7H), 1.07 (d, $J = 6.3$ Hz, 3H), 0.90 (t, $J = 6.9$ Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 138.5, 128.4, 127.6, 127.5, 73.0, 68.2, 51.2, 47.4, 36.9, 31.8,

30.4, 27.2, 22.6, 20.6, 14.1 ppm; IR (neat) 2956, 2924, 2855, 1454, 1364, 1099, 1027, 732, 695 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{29}\text{NONa}$ $[(\text{M}+\text{Na})^+]$, 286.2147; found, 286.2135 m/z ; calcd. for $\text{C}_{17}\text{H}_{30}\text{NO}$ $[(\text{M}+\text{H})^+]$, 264.2327; found, 264.2320 m/z .



***N*-(5-(Benzyloxy)pentan-2-yl)aniline (12e)**: 426 mg (88%); orange liquid; $R_f = 0.5$ (hexanes/dichloromethane 1:2); ^1H NMR (300 MHz, CDCl_3) δ 7.42-7.30 (m, 5H), 7.19 (t, $J = 8.1$ Hz, 2H), 6.70 (t, $J = 7.2$ Hz, 1H), 6.59 (d, $J = 7.8$ Hz, 2H), 4.55 (s, 2H), 3.66-3.50 (m, 2H overlapping with t, $J = 5.7$ Hz, 2H), 1.84-1.56 (m, 4H), 1.23 (d, $J = 6.0$ Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 147.7, 138.6, 129.3, 128.4, 127.7, 127.6, 116.8, 113.1, 73.0, 70.3, 48.3, 33.8, 26.4, 20.9 ppm; IR (neat) 2863, 2168, 2019, 1605, 1489, 1463, 1076, 748, 696 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{NONa}$ $[(\text{M}+\text{Na})^+]$, 292.1677; found, 292.1669 m/z .



***N*-Benzyl-5-(benzyloxy)pentan-2-amine (12f)**: 433 mg (85%); colorless liquid; $R_f = 0.4$ (ethyl acetate/dichloromethane 1:1); ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.23 (m, 10H), 4.52 (s, 2H), 3.85 (d, $J = 12.9$ Hz, 1H), 3.76 (d, $J = 12.9$ Hz, 1H), 3.49 (t, $J = 6.3$ Hz, 2H), 2.73 (tq, $J = 6.3$ Hz, 1H), 1.74-1.52 (m, 2H), 1.50-1.38 (m, 2H overlapping with br s, 1H), 1.12 (d, $J = 6.3$ Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 140.8, 138.6, 128.4, 128.3, 128.1, 127.7, 127.5, 126.8, 72.9, 70.6, 52.3, 51.4, 33.6, 26.3, 20.3 ppm; IR (neat) 2855, 1495, 1453, 1372, 1203, 1094, 731, 695 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{25}\text{NONa}$ $[(\text{M}+\text{Na})^+]$, 306.1834; found, 306.1830 m/z .

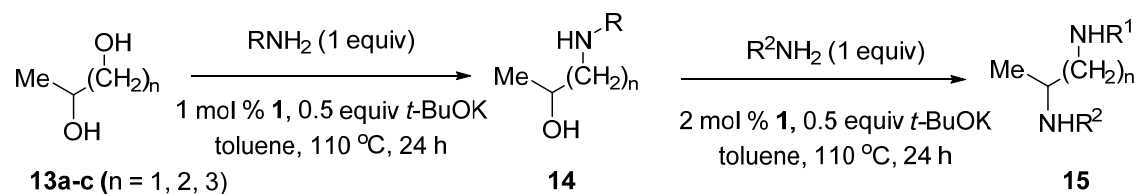
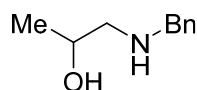
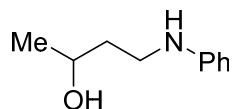


Figure S6. Regioselective mono- and sequential diaminations of diols **13a-c**.

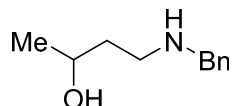
General procedure for the regioselective monoamination of primary-secondary diols 13a-c (Figure S6). To a nitrogen-flushed flask equipped with reflux condenser was added **1** (21.4 mg, 0.030 mmol), diol (3.00 mmol), amine (3.00 mmol) and potassium *tert*-butoxide (168 mg, 1.50 mmol). Toluene (5 mL) was added, and the resulting reaction mixture was heated and stirred (110 °C, 24 h). Afterwards, the mixture was cooled (RT) and partitioned with water (10 mL). The aqueous layer was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers dried (anhyd Na_2SO_4), filtered, and the solvents evaporated via rotvap. Flash chromatography on silica gel affords the desired aminoalcohol **14**.



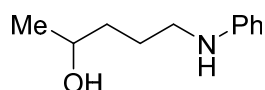
1-(Benzylamino)propan-2-ol (14b):¹⁶ 357 mg (72%); pale yellow liquid; $R_f = 0.25$ (ethyl acetate/methanol 9:1); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.38-7.25 (m, 5H), 3.88-3.77 (m, 3H), 2.74 (dd, $J = 12.0, 3.0$ Hz, 1H), 2.46 (dd, $J = 12.0, 9.3$ Hz, 1H overlapping with br s, 2H), 1.16 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 140.1, 128.5, 128.1, 127.1, 65.7, 56.3, 53.7, 20.5 ppm.



4-(Phenylamino)butan-2-ol (14c):¹⁷ 426 mg (86%); pale yellow solid; mp 61-63 °C (61-63 °C lit.); $R_f = 0.55$ (ethyl acetate/hexanes 1:1); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.22 (dd, $J = 8.4, 7.5$ Hz, 2H), 6.76 (t, $J = 7.5$ Hz, 1H), 6.68 (d, $J = 7.5$ Hz, 2H), 4.08-3.97 (m, 1H), 3.37-3.23 (m, 2H), 1.87-1.68 (m, 2H), 1.27 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 148.4, 129.3, 117.8, 113.3, 67.4, 41.9, 38.1, 23.9 ppm; IR (neat) 3261, 1603, 1476, 1143, 1097, 865, 745, 695, 590 cm^{-1} .



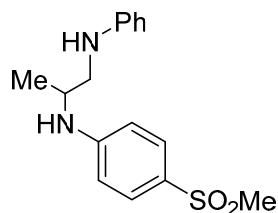
4-(Benzylamino)butan-2-ol (14d):¹⁸ 403 mg (75%); pale yellow liquid; $R_f = 0.3$ (ethyl acetate/methanol 9:1); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.37-7.25 (m, 5H), 4.03-3.97 (m, 1H), 3.84 (d, $J = 12.9$ Hz, 1H), 3.75 (d, $J = 12.9$ Hz, 1H), 3.54 (br s, 2H), 3.06-2.99 (m, 1H), 2.85-2.76 (m, 1H), 1.67-1.52 (m, 2H), 1.19 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 139.3, 128.5, 128.2, 127.2, 69.6, 53.8, 48.3, 36.8, 23.6 ppm; IR (neat) 3275, 2964, 2923, 2839, 1453, 1103, 1028, 733, 695, 602 cm^{-1} .



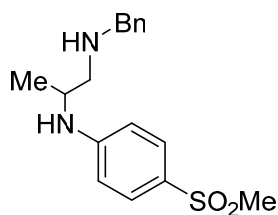
5-(Phenylamino)pentan-2-ol (14e):¹⁹ 489 mg (91%) on an 8.0 mmol scale: 1.19 g (83%); pale brown liquid; $R_f = 0.55$ (ethyl acetate/hexanes 1:1); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.21 (dd, $J = 8.4, 7.5$ Hz, 2H), 6.74 (t, $J = 7.2$ Hz, 1H), 6.64 (d, $J = 7.8$ Hz, 2H), 3.85 (tq, $J = 6.3$ Hz, 1H), 3.16 (t, $J = 6.9$ Hz, 2H), 1.81-1.63 (m, 2H), 1.61-1.54 (m, 2H), 1.23 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 148.4, 129.3, 117.4, 113.0, 67.8, 44.1, 36.8, 25.9, 23.7 ppm; IR (neat) 3361, 2928, 1605, 1504, 1318, 1258, 746, 691 cm^{-1} .

General procedure for the amination of secondary aminoalcohols 14 (Figure S6). To a nitrogen-flushed flask equipped with reflux condenser was added **1** (11.4 mg, 0.016 mmol), secondary aminoalcohol (0.80 mmol), amine (0.80 mmol) and potassium *tert*-butoxide (44.8 mg, 0.40 mmol). Toluene (2 mL) was added, and the resulting reaction mixture was heated and stirred (110 °C, 24 h). Afterwards, the mixture was cooled (RT) and partitioned with water

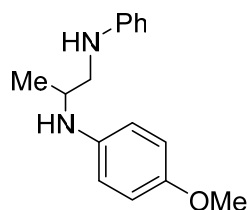
(5 mL). The aqueous layer was extracted with ethyl acetate (2 x 5 mL) and the combined organic layers dried (anhyd Na₂SO₄), filtered, and the solvents evaporated. Flash chromatography on silica gel affords the desired diamine product **15**.



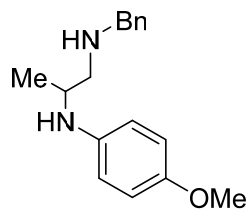
N²-(4-(Methylsulfonyl)phenyl)-N¹-phenylpropane-1,2-diamine (15a): 226 mg (93%); dark yellow oil; R_f = 0.25 (ethyl acetate/hexanes 1:1); ¹H NMR (300 MHz, CDCl₃) δ 7.62 (dd, *J* = 8.7, 1.8 Hz, 3H), 7.16 (dd, *J* = 8.4, 7.5 Hz, 1H), 6.74-6.57 (m, 5H), 4.04-3.96 (m, 1H), 3.20 (dd, *J* = 12.9, 3.3 Hz, 1H), 3.02-2.94 (m, 3H), 2.98 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 151.9, 148.4, 129.4, 129.3, 127.9, 117.7, 114.1, 113.2, 66.3, 51.6, 45.0, 20.9 ppm; IR (neat) 3478, 3364, 1625, 1591, 1508, 1264, 1121, 1089, 965, 775, 691 cm⁻¹; HRMS (ESI) calcd. for C₁₆H₂₀N₂O₂SNa [(M+Na)⁺], 327.1164; found, 327.1159 *m/z*.



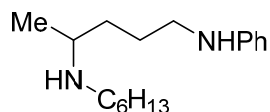
N¹-Benzyl-N²-(4-(methylsulfonyl)phenyl)propane-1,2-diamine (15b): 196 mg (77%); pale yellow oil; R_f = 0.2 (ethyl acetate/methanol 9:1); ¹H NMR (300 MHz, CDCl₃) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.42-7.20 (m, 5H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.37 (br s, 1H), 3.81 (m, 2H), 3.00 (s, 3H), 2.75-2.64 (m, 3H), 2.50-2.42 (m, 1H), 1.15 (d, *J* = 6.0 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 151.7, 139.9, 129.4, 128.5, 128.4, 128.2, 127.2, 114.0, 65.6, 56.3, 53.6, 45.0, 20.5 ppm; IR (neat) 3465, 3338, 1615, 1591, 1280, 1105, 1093, 965, 691 cm⁻¹; HRMS (ESI) calcd. for C₁₇H₂₂N₂O₂SNa [(M+Na)⁺], 341.1323; found, 341.1320 *m/z*.



N²-(4-Methoxyphenyl)-N¹-phenylpropane-1,2-diamine (15c): 115 mg (56%); brown oil; R_f = 0.4 (ethyl acetate/hexanes 1:2); ¹H NMR (300 MHz, CDCl₃) δ 7.24 (t, *J* = 7.5 Hz, 2H), 6.86-6.74 (m, 3H), 6.71-6.63 (m, 4H), 3.81 (s, 3H), 3.74-3.70 (m, 1H), 3.36-3.27 (m, 1H), 3.14-3.07 (m, 1H), 1.29 (d, *J* = 6.0 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 152.5, 152.3, 148.4, 147.5, 142.6, 141.5, 129.4, 129.3, 117.8, 117.6, 115.5, 115.1, 115.0, 114.5, 113.7, 113.1, 55.8, 49.8, 48.7, 19.3 ppm; IR (neat) 3382, 2959, 2830, 2161, 2033, 1601, 1504, 1313, 1231, 1033, 818, 748, 692 cm⁻¹; HRMS (ESI) calcd. for C₁₆H₂₀N₂ONa [(M+Na)⁺], 279.1473; found, 279.1468 *m/z*.

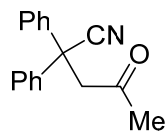


***N*¹-Benzyl-*N*²-(4-methoxyphenyl)propane-1,2-diamine (15d):** 138 mg (64%); brown oil; *R*_f = 0.35 (ethyl acetate/methanol 9:1); ¹H NMR (300 MHz, CDCl₃) δ 7.34-7.23 (m, 5H), 6.72 (dd, *J* = 49.2, 9.0 Hz, 4H), 3.82 (d, *J* = 2.7 Hz, 2H), 3.78 (s, 3H), 3.54 (tq, *J* = 6.3 Hz, 1H), 2.78 (dd, *J* = 11.7, 4.5 Hz, 1H), 2.66 (dd, *J* = 12.0, 7.2 Hz, 1H), 1.18 (d, *J* = 6.3 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 152.2, 142.0, 140.4, 128.4, 128.1, 127.0, 115.3, 114.9, 55.8, 54.8, 54.0, 49.8, 19.3 ppm; IR (neat) 3365, 2960, 2849, 2048, 1605, 1511, 1233, 1034, 823, 752, 695 cm⁻¹; HRMS (ESI) calcd. for C₁₇H₂₂N₂ONa [(M+Na)⁺], 293.1630; found, 293.1623 *m/z*.

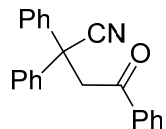


***N*⁴-Hexyl-*N*¹-phenylpentane-1,4-diamine (15f):** 157 mg (75%); dark yellow oil; *R*_f = 0.4 (ethyl acetate/methanol 9:1); ¹H NMR (300 MHz, CDCl₃) δ 7.19-7.13 (m, 2H), 6.67 (td, *J* = 7.2, 0.9 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 2H), 3.79 (tq, *J* = 6.0 Hz, 1H), 3.12 (t, *J* = 6.9 Hz, 2H), 2.66 (t, *J* = 6.0 Hz, 2H), 1.95-1.61 (m, 3H), 1.56-1.49 (m, 1H), 1.45-1.36 (m, 2H), 1.45-1.36 (m, 2H), 1.33-1.25 (m, 7H), 1.18 (d, *J* = 6.3 Hz, 3H), 0.89-0.86 (m, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 148.4, 129.2, 117.2, 112.8, 67.1, 44.0, 42.2, 36.8, 33.8, 31.7, 26.6, 25.9, 23.7, 22.6, 14.0 ppm; IR (neat) 2958, 2918, 2855, 1453, 1358, 1100, 864, 732, 695 cm⁻¹; HRMS (ESI) calcd. for C₁₇H₃₀N₂Na [(M+Na)⁺], 285.2312; found, 285.2309 *m/z*.

Key procedures and/or characterization data for the aminoalcohols used for the BH cyclization to heterocycles that follow.

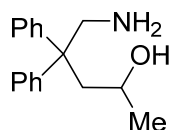


4-Oxo-2,2-diphenylvaleronitrile (17a-1):²⁰ 1.43 g (76%); white solid, mp 106-108 °C (105-107 °C lit.); *R*_f = 0.6 (dichloromethane); ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.30 (m, 10H), 3.59 (s, 2H), 2.16 (s, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 202.3, 139.5, 129.0, 128.1, 126.7, 122.1, 52.0, 47.7, 30.5 ppm.

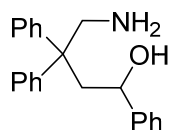


4-Oxo-2,2,4-triphenylbutanenitrile (17a-2). To a cooled (-78 °C) stirred solution of diphenylacetone nitrile (600 mg, 3.10 mmol) in dry THF (10 mL) was added NaHMDS (2M, 1.70 mL, 3.40 mmol) dropwise. The reaction mixture was warmed to room temperature and stirred for 1 h. 2-Bromoacetophenone (676 mg, 3.40 mmol) in 10 mL of dry THF was added

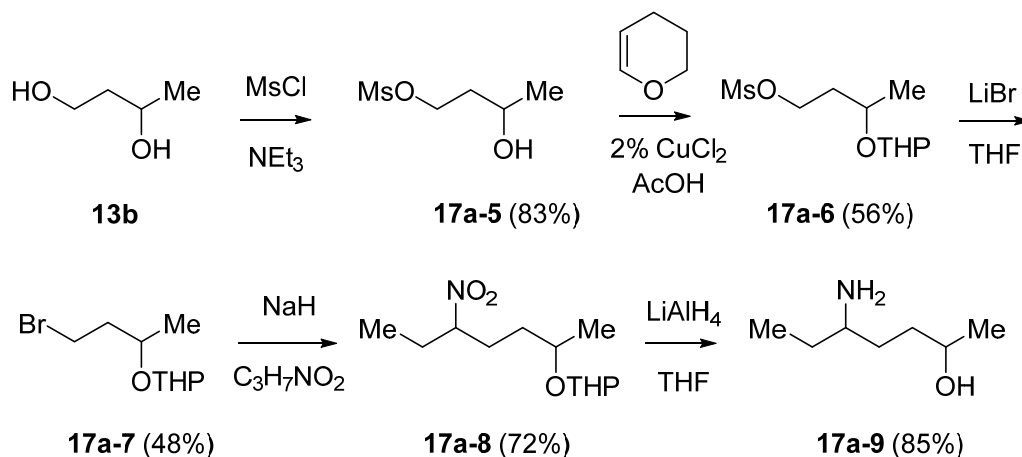
dropwise at room temperature, and the reaction mixture stirred (6 h). Afterwards, the THF was evaporated and the mixture partitioned with DCM (10 mL) and water (10 mL). The water layer was extracted with DCM (2 x 10 mL). The combined organic layers were dried (anhyd Na₂SO₄), filtered through a short pad of silica gel, and concentrated to yield a pale yellow crystalline product which was washed with hexanes (2 x 4 mL) to afford the title compound as a white solid (696 mg, 72%): mp 136-138 °C; R_f = 0.8 (dichloromethane); ¹H NMR (300 MHz, CDCl₃) δ 7.96 (d, *J* = 6.9 Hz, 2H), 7.62-7.59 (m, 1H), 7.51-7.28 (m, 12H), 4.14 (s, 2H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 193.5, 139.7, 136.1, 133.7, 129.0, 128.8, 128.0 (d, *J* = 2.3 Hz), 126.8, 122.2, 48.0, 47.8 ppm; IR (neat) 2161, 1977, 1685, 1596, 1490, 1448, 1348, 1220, 980, 752, 695, 608 cm⁻¹; HRMS (ESI) calcd. for C₂₂H₁₇NONa [(M+Na)⁺], 334.1208; found, 334.1197 *m/z*.



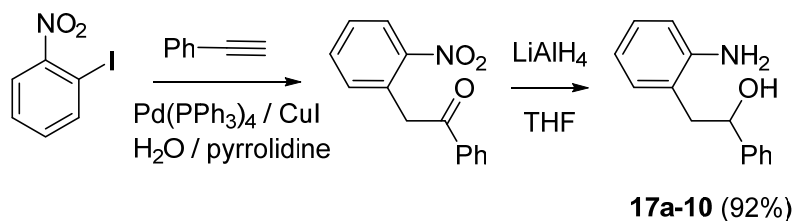
5-Amino-4,4-diphenylpentan-2-ol (17a-3).²¹ To a nitrogen-blanketed, cooled (-78 °C), stirred solution of 4-oxo-2,2-diphenylvaleronitrile **17a-1** (800 mg, 3.21 mmol) in dry THF (20 mL) was carefully added LiAlH₄ (304 mg, 8.00 mmol) in portions. The reaction mixture was slowly warmed to room temperature and stirred (12 h). The reaction was quenched by the careful addition of water (10 mL) and treated with 3M NaOH solution (15 mL). After stirring (0.5 h), ethyl acetate (20 mL) was added, and the resulting two layer mixture filtered through celite. The organic phase was separated, and the water layer extracted with additional ethyl acetate (2 x 20 mL). The combined organic layers were dried (anhyd Na₂SO₄), filtered and concentrated. Flash chromatography on silica afforded the title compound as a white solid (704 mg, 86%): mp 85-87 °C (85-86.5 °C lit.); R_f = 0.25 (dichloromethane/methanol 9:1); ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.11 (m, 10H), 3.83 (tq, *J* = 6.6 Hz, 1H), 3.76 (d, *J* = 12.0 Hz, 1H), 3.42 (d, *J* = 12.0 Hz, 1H), 2.98 (br s, 3H), 2.49 (dd, *J* = 15.0, 8.4 Hz, 1H), 2.33 (d, *J* = 14.7 Hz, 1H), 1.18 (d, *J* = 6.3 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 148.3, 145.2, 128.6, 128.3, 128.1, 127.4, 126.3, 126.2, 63.7, 51.1, 48.8, 47.9, 25.0 ppm; IR (neat) 3378, 3088, 2968, 2160, 2033, 1493, 1444, 1371, 1331, 1085, 917, 774, 752, 699 cm⁻¹; HRMS (ESI) calcd. for C₁₇H₂₁NONa [(M+Na)⁺], 278.1521; found, 278.1516 *m/z*; calcd. for C₁₇H₂₂NO [(M+H)⁺], 256.1701; found, 256.1706 *m/z*.



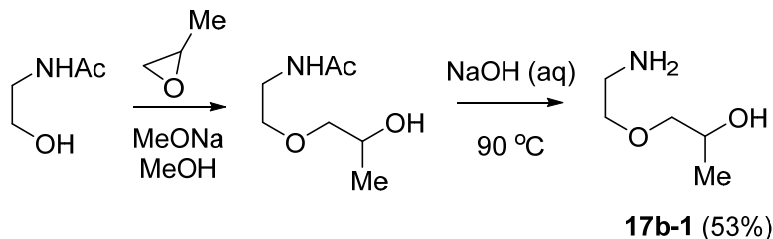
4-Amino-1,3,3-triphenylbutan-1-ol (17a-4). Synthesized according to the procedure reported for aminoalcohol **17a-3**: 515 mg (84%); white solid, mp 76-77 °C, R_f = 0.4 (dichloromethane/methanol 9:1); ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.09 (m, 15H), 4.52 (d, *J* = 9.0 Hz, 1H), 4.33 (br s, 3H), 4.12 (d, *J* = 12.3 Hz, 1H), 3.43 (d, *J* = 12.0 Hz, 1H), 2.93 (dd, *J* = 15.0, 9.3 Hz, 1H), 2.41 (d, *J* = 14.7 Hz, 1H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 146.7, 146.1, 145.2, 128.7, 128.5, 128.4, 127.9, 127.6, 127.0, 126.7, 125.4, 70.5, 50.6, 48.0, 47.3 ppm; IR (neat) 3025, 2160, 2027, 1598, 1493, 1445, 1054, 907, 753, 696 cm⁻¹; HRMS (ESI) calcd. for C₂₂H₂₃NONa [(M+Na)⁺], 340.1677; found, 340.1675 *m/z*; calcd. for C₂₂H₂₄NO [(M+H)⁺], 318.1858; found, 318.1853 *m/z*.



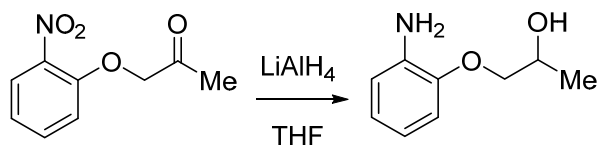
5-Aminoheptan-2-ol (17a-9). Synthesized in 5 steps from 1,3-butanediol according to the above scheme. To a cooled (-78 °C) stirred solution of 2-((5-nitroheptan-2-yl)oxy)tetrahydro-2*H*-pyran **17a-8** as a mixture of diastereomers (1.20 g, 4.89 mmol) in dry THF (40 mL) LiAlH₄ (0.560 g, 14.7 mmol) was added in portions. The reaction mixture was slowly warmed up to room temperature and refluxed under nitrogen atmosphere for 4 h. The reaction was quenched with 40 mL of water and treated with 3*M* NaOH solution (20 mL). After 30 min of stirring ethyl acetate (40 mL) was added, and two-layer system filtered through celite. Organic phase separated, and water phase extracted with additional ethyl acetate (2 x 30 mL). Combined organic fractions dried (anhyd Na₂SO₄), and solvents evaporated. Flash chromatography on silica afforded the title compound as a yellow-green liquid (488 mg, 76%); R_f = 0.4 (dichloromethane/methanol 1:1); NMR spectra showed a mixture of diastereomers in ratio 3:2; ¹H NMR (300 MHz, CDCl₃) δ 3.77-3.63 (m, 1H), 2.98 (br s, 3H), 2.73-2.65 and 2.58-2.52 (m, 1H), 1.69-1.22 (m, 6H), 1.16 (d, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 67.8, 67.1, 53.7, 52.3, 37.6, 35.3, 34.7, 32.8, 32.0, 30.1, 23.7, 23.4, 10.4, 10.3 ppm; IR (neat) 3361, 2968, 2922, 2875, 1595, 1459, 1371, 1119, 1068, 923 cm⁻¹. HRMS (ESI) calcd. for C₇H₁₇NONa [(M+Na)⁺], 154.1208; found, 154.1203 *m/z*; calcd. for C₇H₁₈NO [(M+H)⁺], 132.1388; found, 132.1391 *m/z*.



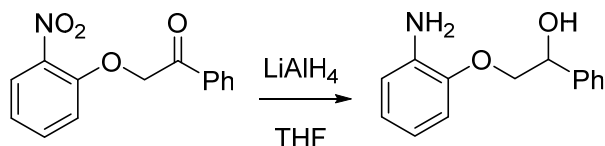
2-(2-Aminophenyl)-1-phenylethan-1-ol (17a-10).^{22,23} 2-(2-Nitrophenyl)-1-phenylethan-1-one was obtained according to literature procedure²⁴ and used in the general procedure for the LiAlH₄ reduction in the synthesis of **17a-9**: 813 mg (92%); pale yellow solid, mp 100-102 °C (98-99 °C lit.); R_f = 0.4 (ethyl acetate/hexanes 1:2); ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.28 (m, 5H), 7.10 (td, *J* = 15.6, 1.2 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.96 (dd, *J* = 8.7, 3.9 Hz, 1H), 3.43 (br s, 3H), 3.02 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.89 (dd, *J* = 14.1, 4.2 Hz, 1H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 145.4, 144.4, 131.3, 128.5, 127.8, 127.7, 125.7, 124.2, 119.3, 116.7, 75.7, 41.9 ppm; IR (neat) 3590, 3480, 3010, 1640, 1500, 1240, 1050, 800 cm⁻¹.



1-(2-Aminoethoxy)propan-2-ol (17b-1). An oven-dried sample vial was charged with *N*-(2-hydroxyethyl)acetamide (1.20 g, 11.6 mmol) and propylene oxide (2.00 g, 34.8 mmol) as a solution in methanol (6 mL). Sodium methoxide (648 mg, 12.0 mmol) was added, the vial flushed with nitrogen, sealed with a teflon-lined septum/screw cap and then heated at 50 °C for 16 h. Afterwards, the mixture was cooled (RT) and the volatiles were evaporated under vacuum. NaOH (520 mg, 13.0 mmol) in aq ethanol (8 mL) was added, and the reaction mixture heated at 90 °C for 4 h. The mixture was then cooled (RT), quenched by the addition of saturated aq NH₄Cl (2 mL), and solvents evaporated. Vacuum distillation at 155 °C/16 mmHg afforded the title compound as a colorless liquid (731 mg, 53%): *R*_f = 0.4 (ethyl acetate/methanol 1:1); ¹H NMR (300 MHz, CDCl₃) δ 4.00-3.90 (m, 1H), 3.60-3.33 (m, 5H), 3.26 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.73 (br s, 3H), 1.13 (d, *J* = 6.3 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 76.6, 69.9, 66.3, 39.3, 18.8 ppm; IR (neat) 3345, 2952, 2870, 1594, 1459, 1368, 1121, 1065, 921 cm⁻¹; HRMS (ESI) calcd. for C₅H₁₃NO₂Na [(M+Na)⁺], 142.0823; found, 142.0818 *m/z*.

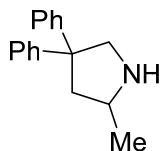


1-(2-Aminophenoxy)propan-2-ol (17b-2).²⁵ 1-(2-Nitrophenoxy)propan-2-one was synthesized according to literature procedure²⁶ and reduced following the general procedure for LiAlH₄ reduction described above yielding the title compound (447 mg, 87%) as a white solid: mp 68-70 °C (66-67 °C lit.); *R*_f = 0.4 (ethyl acetate/hexanes 1:1); ¹H NMR (300 MHz, CDCl₃) δ 6.87-6.72 (m, 4H), 4.27-4.16 (m, 1H), 3.99 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.87 (dd, *J* = 9.6, 7.5 Hz, 1H), 3.66 (br s, 3H), 1.29 (d, *J* = 6.3 Hz, 3H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 148.5, 137.9, 122.2, 120.1, 116.9, 112.1, 75.1, 67.2, 19.7 ppm.

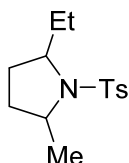


2-(2-Aminophenoxy)-1-phenylethan-1-ol (17b-3). 2-(2-Nitrophenoxy)-1-phenylethan-1-one was obtained according to literature procedure²⁸ and reduced following the general procedure for LiAlH₄ reduction described above yielding the title compound (695 mg, 78%) as a pale yellow solid: mp 120-122 °C; *R*_f = 0.5 (ethyl acetate/hexanes 1:1); ¹H NMR (300 MHz, CDCl₃) δ 7.46-7.32 (m, 5H), 6.91-6.85 (m, 1H), 6.80-6.68 (m, 3H), 4.96 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.46-3.33 (m, 2H) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 146.8, 141.9, 136.7, 128.6, 128.0, 125.9, 121.6, 118.9, 114.9, 113.6, 72.7, 52.5 ppm; IR (neat) 3438, 3313, 2161, 1977, 1607, 1516, 1260, 1197, 736, 698 cm⁻¹; HRMS (ESI) calcd. for C₁₄H₁₅NO₂Na [(M+Na)⁺], 252.1000; found, 252.0991 *m/z*.

Characterization data for heterocycles prepared via BH cyclizations of aminoalcohols and diol/diamine pairs.

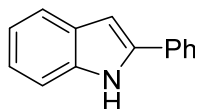


2-Methyl-4,4-diphenylpyrrolidine (18):²⁷ 206 mg (87%); colorless oil; $R_f = 0.35$ (ethyl acetate); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.32-7.12 (m, 10H), 4.00 (d, $J = 12.0$ Hz, 1H), 3.62 (d, $J = 12.0$ Hz, 1H), 3.57-3.48 (m, 1H), 2.75 (dd, $J = 12.9, 6.0$ Hz, 1H), 2.28 (dd, $J = 12.9, 10.2$ Hz, 1H), 1.40 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 146.2, 145.4, 128.7, 128.6, 126.9, 126.8, 126.6, 56.1, 55.8, 53.9, 46.3, 20.0 ppm.



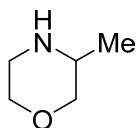
2-Ethyl-5-methyl-1-(4-toluenesulfonyl)pyrrolidine (20). An oven-dried sample vial with a mixture of complex **1** (14.3 mg, 0.020 mmol), **17a-9** (131 mg, 1.00 mmol), potassium *tert*-butoxide (56.0 mg, 0.500 mmol) and toluene (3 mL) was flushed with nitrogen. The vial was sealed with a teflon-lined septum/screw cap, and the reaction mixture was stirred at 110 °C for 24 h. Afterwards, the reaction the mixture was partitioned with water (5 mL), and the aqueous phase extracted with hexanes (2 x 5 mL). The combined organic layers were dried (anhyd Na_2SO_4), filtered and concentrated under vacuum at room temperature.

To the residue was added hexanes (2 mL), 4-toluenesulfonyl chloride (191 mg, 1.00 mmol), and triethylamine (120 mg, 1.20 mmol). The resulting mixture was stirred at room temperature for 4 h and then partitioned with water (5 mL). The aqueous phase was extracted with additional hexanes (2 x 5 mL) and the combined organic extracts dried (anhyd Na_2SO_4), filtered and concentrated. Flash chromatography on silica afforded the title compound (142 mg, 53%) as a pale yellow oil: $R_f = 0.6$ (dichloromethane); (Note: the NMR spectra showed mixture of *cis:trans* isomers in ratio 4:1 based on data reported for the ^{13}C NMR spectra of homologous structures.^{28,29,30,31}) $^1\text{H NMR}$ (300 MHz, CDCl_3) *cis-isomer* δ 7.71 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), 3.67 (tq, $J = 6.6$ Hz, 1H), 3.56-3.47 (m, 1H), 2.42 (s, 3H), 1.93-1.78 (m, 2H), 1.63-1.42 (m, 4H), 1.32 (d, $J = 6.3$ Hz, 3H), 0.93 (t, $J = 7.5$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) *cis-isomer* δ 143.1, 135.3, 129.6, 127.5, 63.3, 57.3, 32.0, 29.9, 29.0, 23.5, 21.5, 10.5 ppm; *trans-isomer* δ 142.6, 139.8, 129.4, 126.9, 62.0, 56.4, 31.4, 27.2, 27.0, 21.5, 21.0, 10.6 ppm; IR (neat) 2967, 1461, 1337, 1202, 1156, 1091, 814, 710, 660 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}_2\text{NaS}$ [(M+Na)⁺], 290.1191; found, 290.1181 m/z .

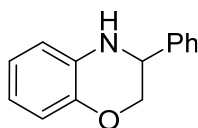


2-Phenyl-1H-indole (21):³² 182 mg (94%); white solid; mp 187-189 °C (mp 188-190 °C lit.); $R_f = 0.45$ (ethyl acetate/hexanes 1:9); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.35 (br s, 1H), 7.72-7.66 (m,

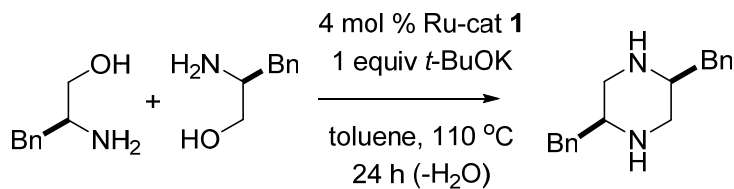
3H), 7.51-7.42 (m, 3H), 7.39-7.33 (m, 1H), 7.26-7.13 (m, 2H), 6.87 (d, $J = 1.5$ Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 137.9, 136.8, 132.4, 129.3, 129.1, 127.7, 125.2, 122.4, 120.7, 120.3, 110.9, 100.0 ppm.



3-Methylmorpholine (22):³³ 87 mg (86%); colorless oil; $R_f = 0.3$ (ethyl acetate); ^1H NMR (300 MHz, CDCl_3) δ 3.82-3.68 (m, 2H), 3.50-3.39 (m, 1H), 3.11-2.82 (m, 4H), 0.95 (d, $J = 6.3$ Hz, 3H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 72.8, 68.1, 52.9, 43.6, 18.8 ppm.

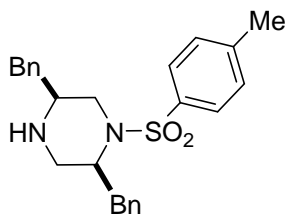


3-Phenyl-3,4-dihydro-2H-benzo[b][1,4]oxazine (24):^{34, 35} 120 mg (57%); yellow oil; $R_f = 0.5$ (ethyl acetate/hexanes 1:9); ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.33 (m, 5H), 6.86-6.78 (m, 2H), 6.72-6.65 (m, 2H), 4.50 (dd, $J = 8.6, 2.8$ Hz, 1H), 4.28 (dd, $J = 10.6, 2.8$ Hz, 1H), 4.07 (br s, 1H), 4.03-3.94 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 143.7, 139.3, 134.1, 129.0, 128.5, 127.4, 121.7, 119.1, 116.8, 115.5, 71.1, 54.4 ppm.

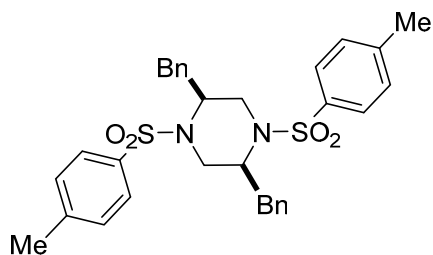


(2S,5S)-2,5-Dibenzylpiperazine (26b):³⁶ 152 mg (57%); pale yellow oil; $R_f = 0.25$ (methanol); $[\alpha]_D^{25} = +38.7$ (c 1.0, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.21 (m, 10H), 3.07-2.79 (m, 10H), 1.65 (br s, 2H) ppm; ^{13}C NMR (75.5 MHz, CDCl_3) δ 139.4, 129.2, 128.6, 126.2, 55.7, 48.1, 38.6 ppm.

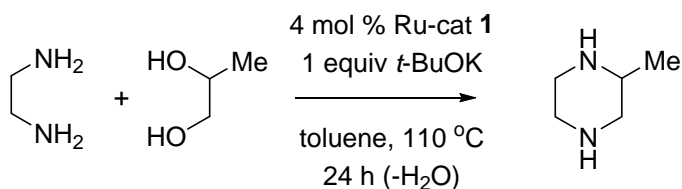
Proof of optical purity: In order to assay the products via chiral HPLC, (2S,5S)-2,5-dibenzylpiperazine **26b** and (2R,5R)-2,5-dibenzylpiperazine *ent*-**26b** (synthesized starting from enantiomeric (*R*)-aminoalcohol; all spectra are identical to *S*-isomer) were converted to a mixture of their corresponding monotosyl- and ditosyl-derivatives via the procedure described above using 1.0 or 2.0 equivalents of TsCl as appropriate.



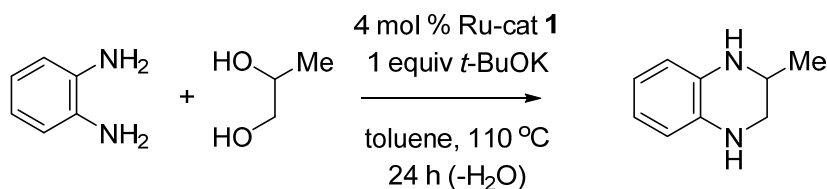
(2*S*,5*S*)-2,5-Dibenzyl-1-tosylpiperazine (26b'): 69 mg (88%); white solid; mp 153-155 °C; $R_f = 0.4$ (dichloromethane/ethyl acetate 4:1); $[\alpha]_D^{25} = +30.5$ (c 1.0, CH_2Cl_2); chiral HPLC analysis (Chiralpak AD with AD guard, hexanes/isopropanol 90:10, flow rate = 1.5 mL/min) showed single peak (100%) at 36.5 min for (2*S*,5*S*)-2,5-Dibenzyl-1-tosylpiperazine (**26b'**) (Under these conditions, the enantiomer (2*R*,5*R*)-2,5-Dibenzyl-1-tosylpiperazine (*ent*-**26b'**) showed a single peak (100%) at 31.2 min.); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.60 (d, $J = 8.4$ Hz, 2H), 7.37-7.18 (m, 12H), 4.14-4.08 (m, 1H), 3.70 (dd, $J = 12.0, 2.1$ Hz, 1H), 3.19 (dd, $J = 12.9, 9.9$ Hz, 1H), 2.93 (dd, $J = 12.3, 10.8$ Hz, 1H), 2.81-2.75 (m, 4H), 2.52-2.62 (m, 2H), 2.43 (s, 3H), 1.54 (br s, 1H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 143.1, 138.7, 138.1, 137.5, 129.7, 129.5, 129.2, 128.7, 128.5, 127.1, 126.7, 126.4, 56.1, 54.8, 46.8, 46.6, 40.2, 34.5, 21.5 ppm; IR (neat) 2963, 2872, 1586, 1487, 1328, 1245, 725, 693 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_2\text{NaS}$ [(M+Na) $^+$], 443.1769; found, 443.1754 m/z .



(2*S*,5*S*)-2,5-Dibenzyl-1,4-ditosylpiperazine (26b''): 102 mg (95%); white foamy solid; mp 56-58 °C; $R_f = 0.6$ (dichloromethane); $[\alpha]_D^{25} = +16.4$ (c 1.0, CH_2Cl_2); chiral HPLC analysis (Chiralpak AD with AD guard, hexanes/isopropanol 97:3, flow rate = 1.0 mL/min) showed no separation of enantiomers; a single peak (100%) at 34.1 min was observed for both the (2*S*,5*S*)- and (2*R*,5*R*)-enantiomers; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.59 (d, $J = 8.1$ Hz, 4H), 7.34-7.27 (m, 10H), 7.17 (d, $J = 7.8$ Hz, 4H), 3.83-3.75 (m, 2H), 3.30-3.16 (m, 4H), 3.08-2.92 (m, 4H), 2.45 (s, 6H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 143.9, 137.2, 135.3, 129.9, 129.6, 128.7, 127.5, 126.8, 56.9, 43.6, 39.4, 21.6 ppm; IR (neat) 2933, 2864, 1495, 1320, 1175, 1093, 952, 733, 695, 656, 615, 560 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}_4\text{NaS}_2$ [(M+Na) $^+$], 597.1858; found, 597.1873 m/z .



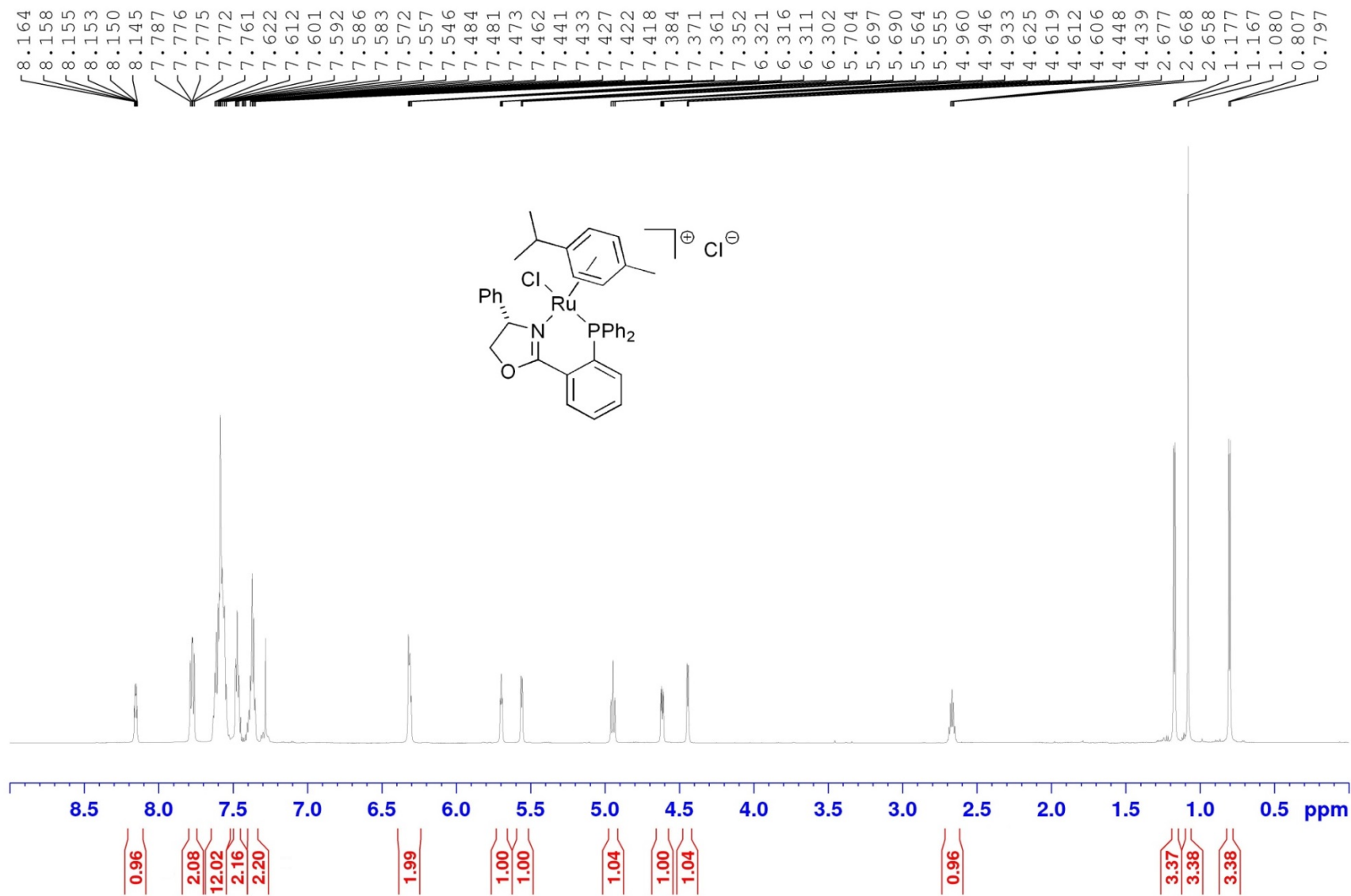
2-Methylpiperazine (28):³⁷ 50 mg (42%); pale yellow liquid; $R_f = 0.2$ (methanol); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 3.07-2.79 (m, 7H), 1.98 (br s, 2H), 1.06 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 54.5, 52.2, 47.8, 47.1, 20.4 ppm.



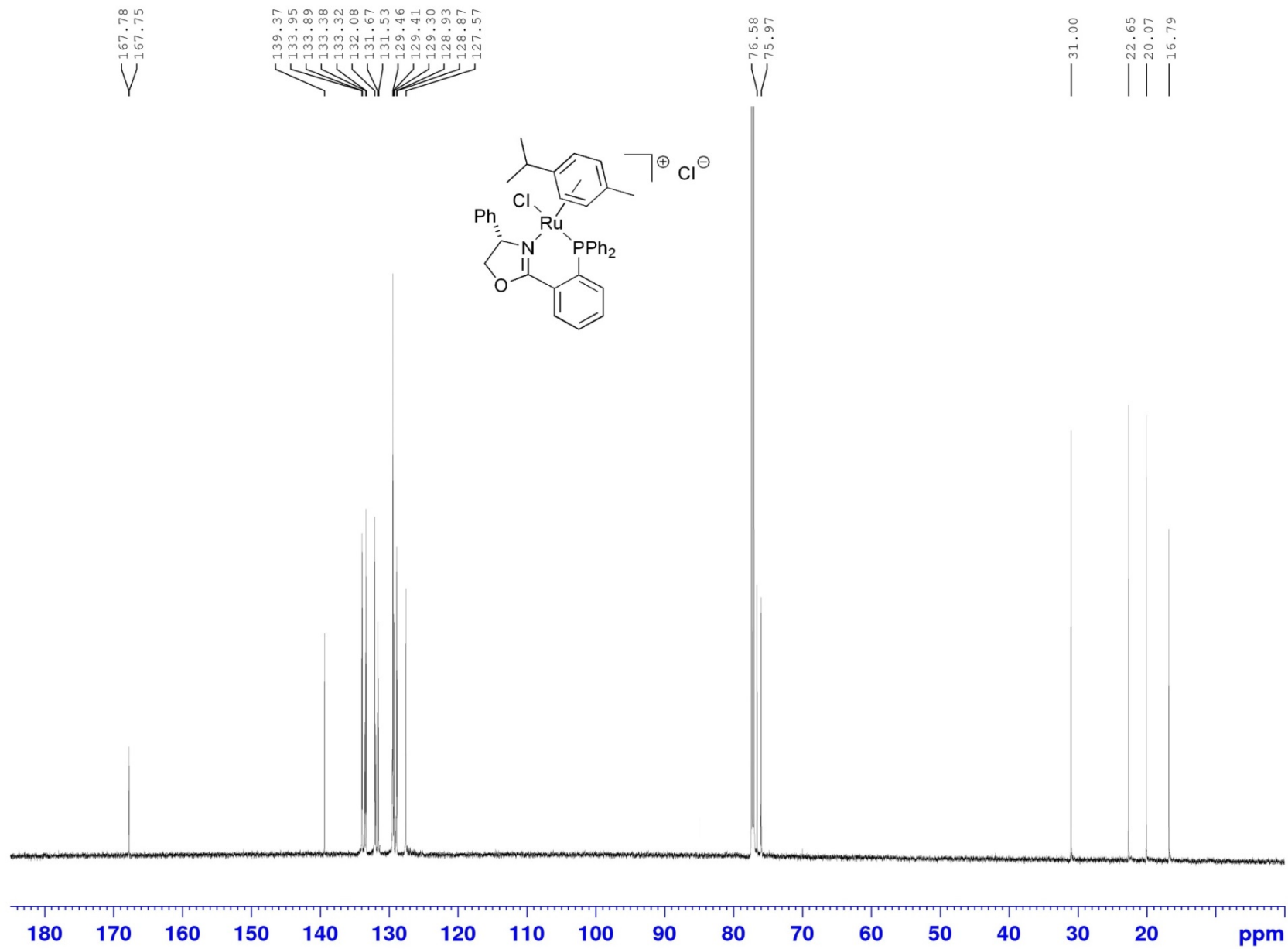
2-Methyl-1,2,3,4-tetrahydroquinoxaline (29):^{38,39} 76 mg (43%); yellow solid, mp 86-88 °C (88-89 °C lit.); $R_f = 0.25$ (ethyl acetate/hexanes 1:2); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 6.57-6.55 (m, 2H), 6.50-6.48 (m, 2H), 3.63 (br s, 2H), 3.50-3.45 (m, 1H), 3.27 (dd, $J = 10.5, 2.1$ Hz, 1H), 2.99 (dd, $J = 10.5, 9.0$ Hz, 1H), 1.15 (d, $J = 6.3$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (75.5 MHz, CDCl_3) δ 133.6, 133.2, 118.7, 118.7, 114.5, 114.4, 48.2, 45.7, 19.9 ppm.

7. NMR Spectra of compounds.

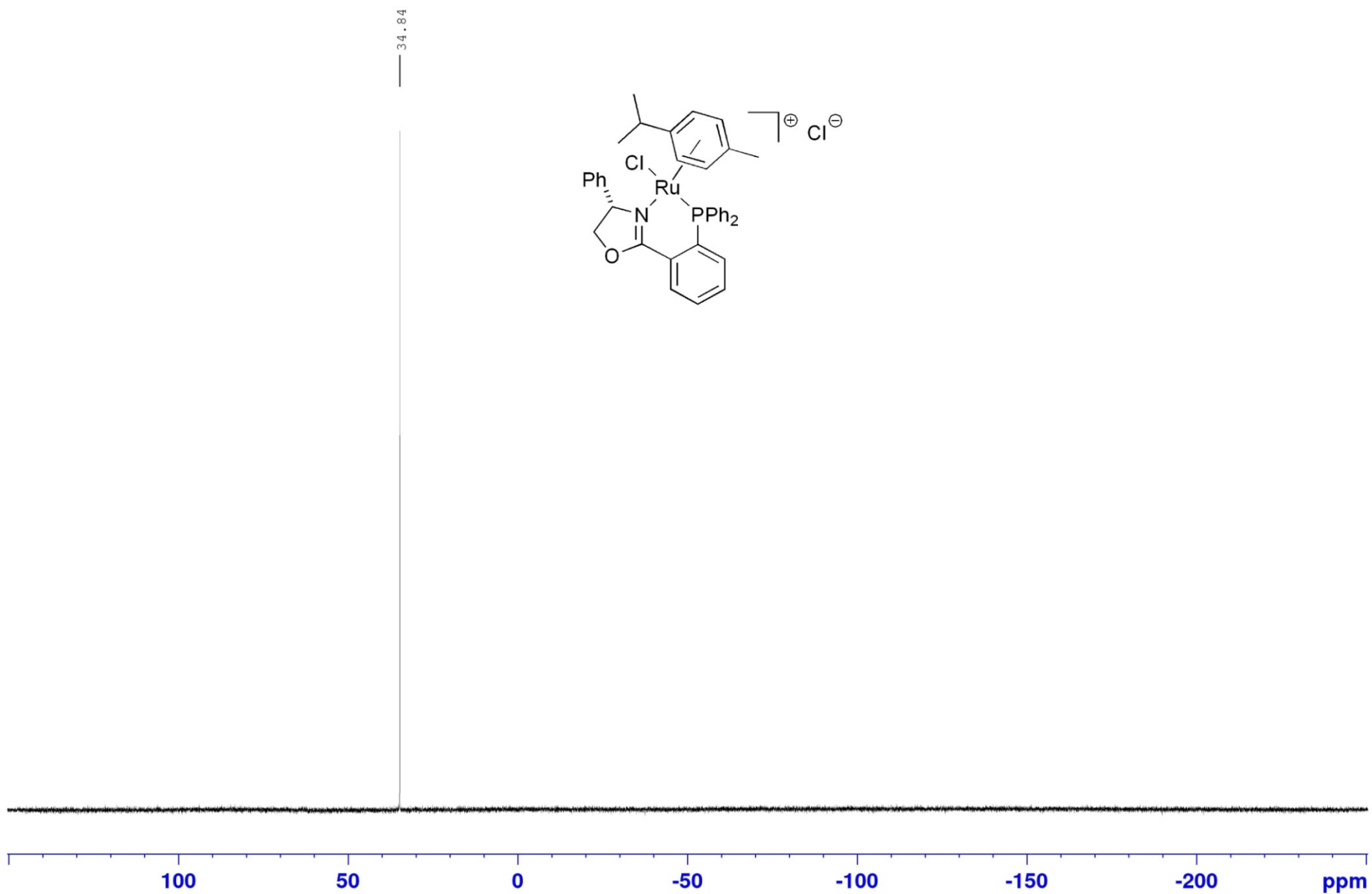
^1H NMR of 1



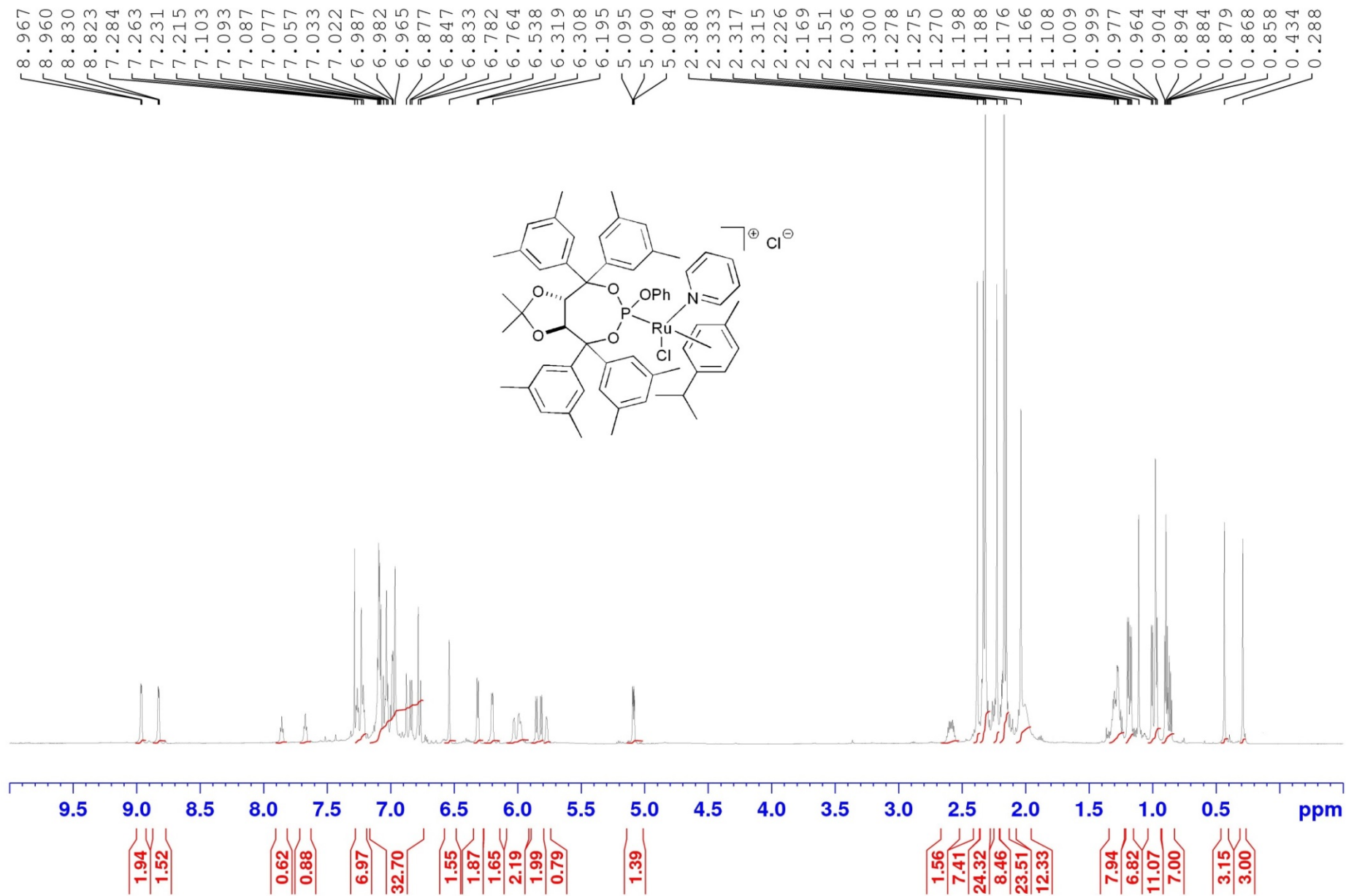
^{13}C NMR of **1**



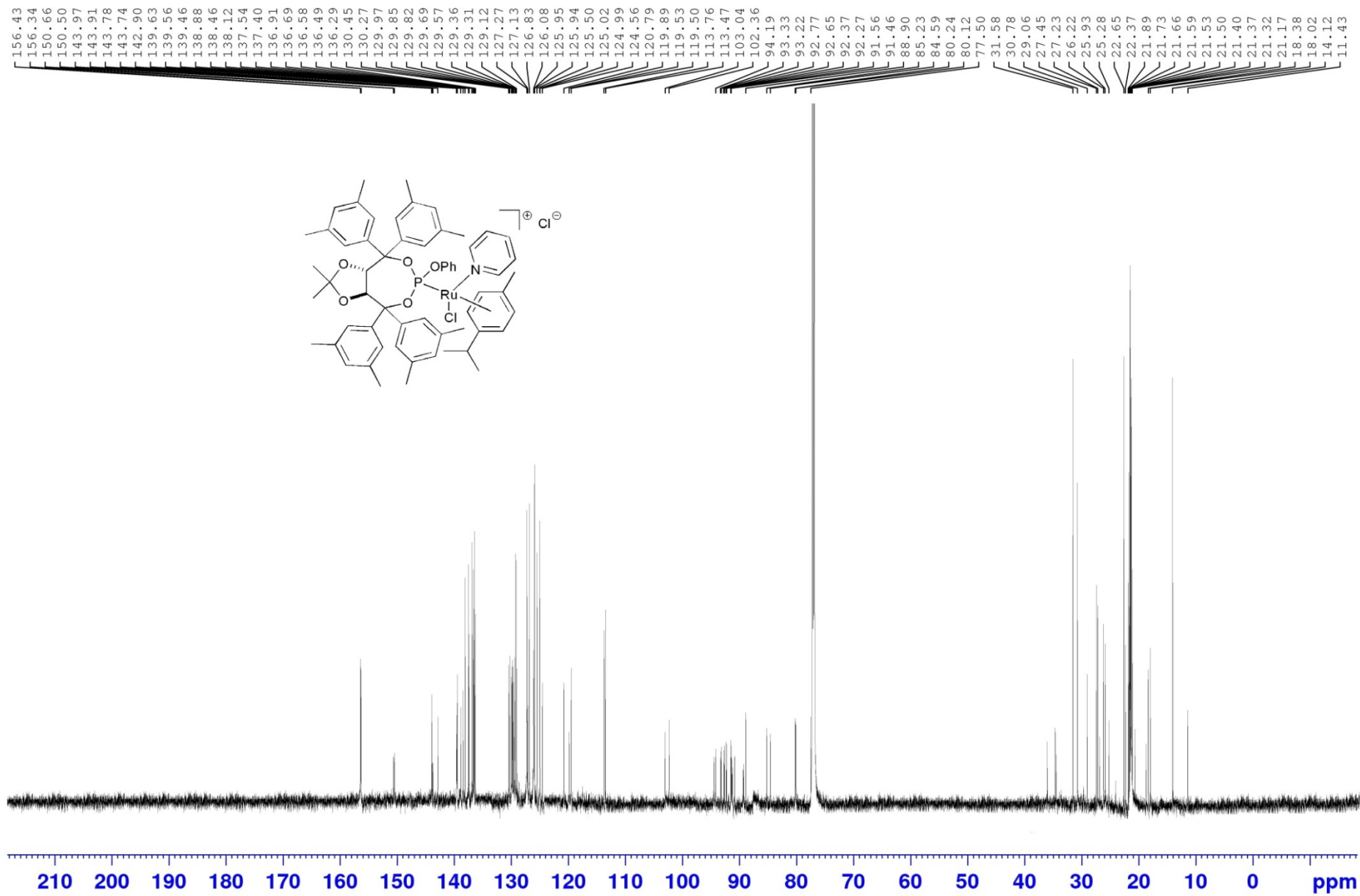
^{31}P NMR of **1**



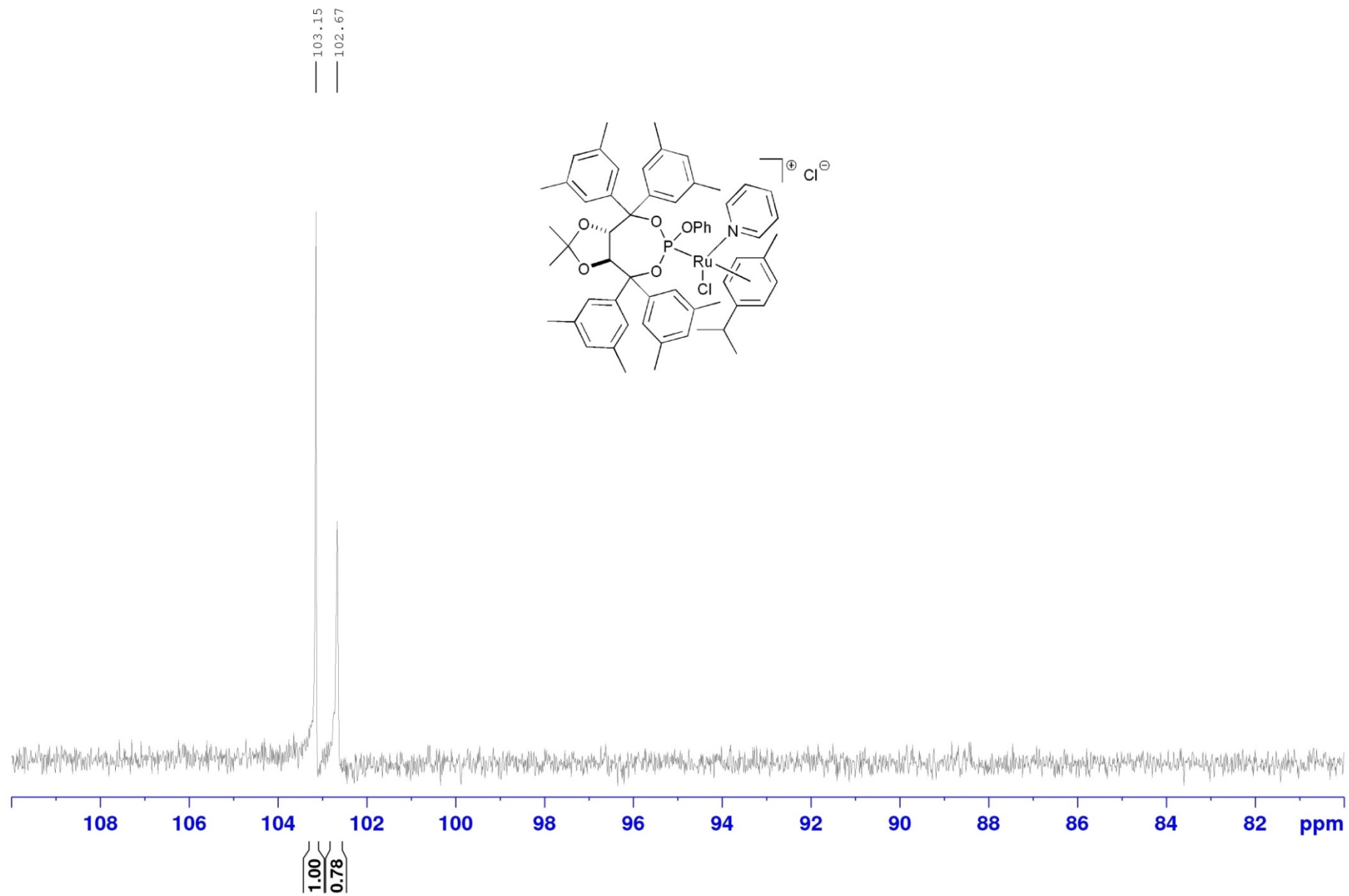
¹H NMR of 2



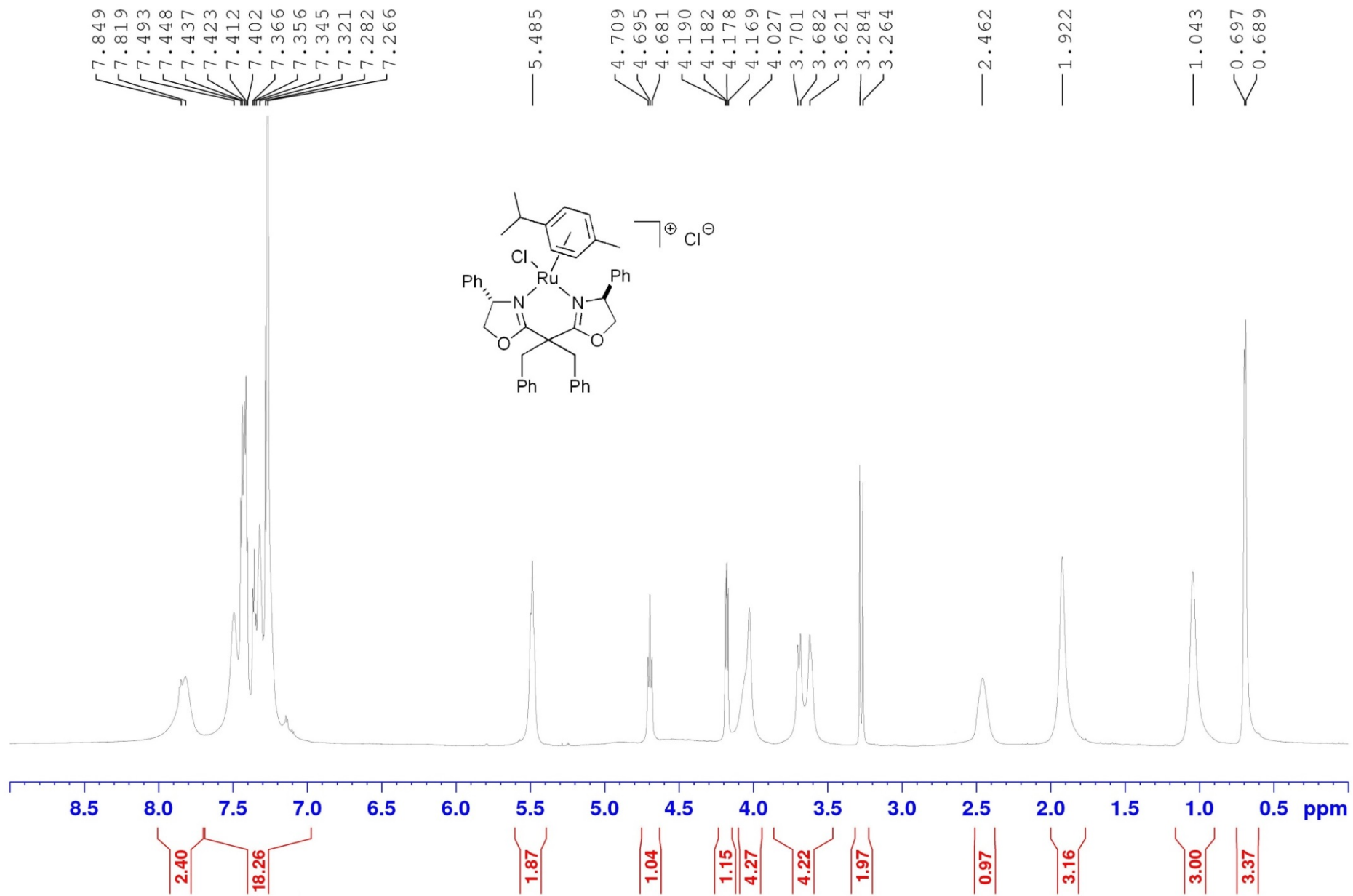
¹³C NMR of 2



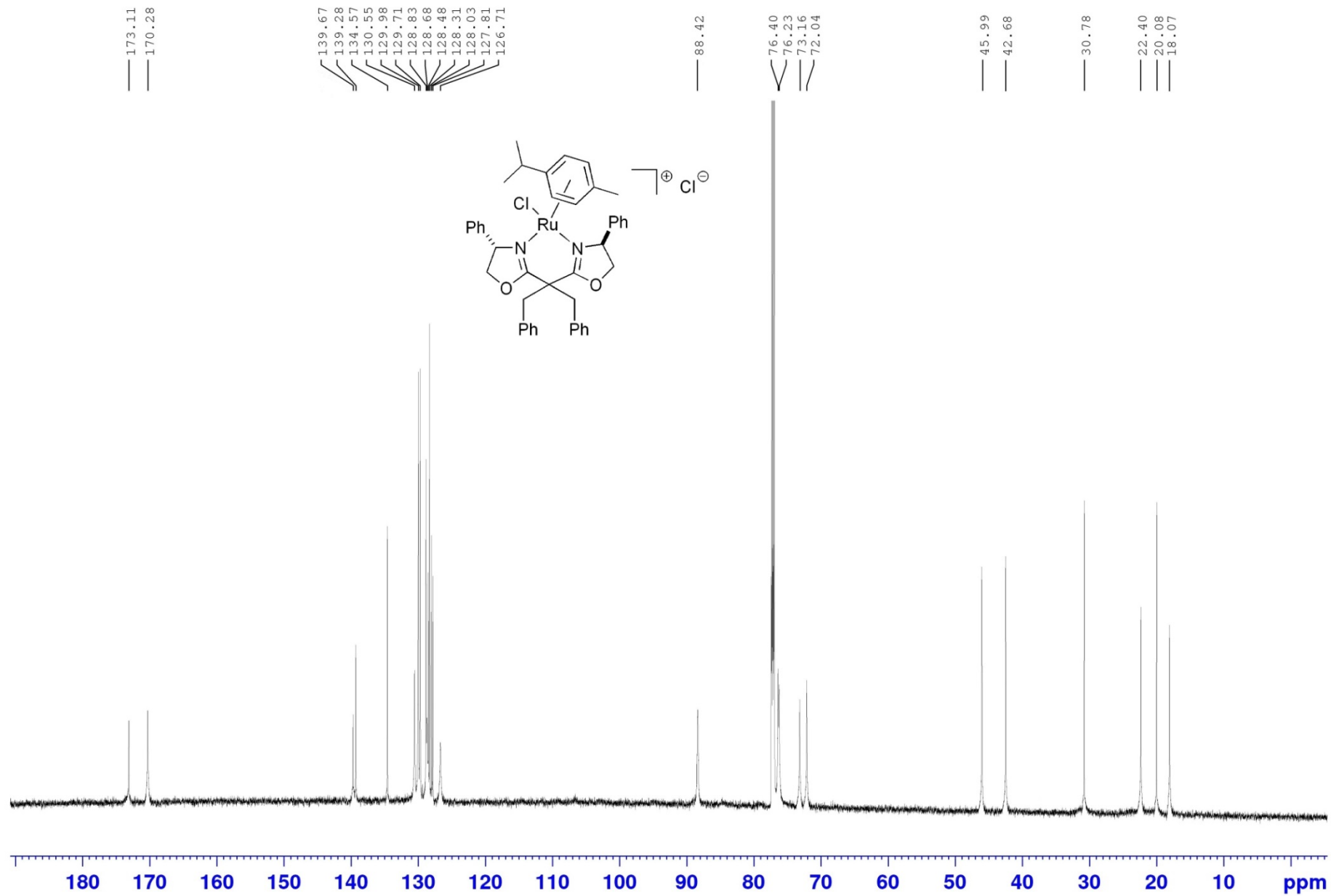
^{31}P NMR of **2**



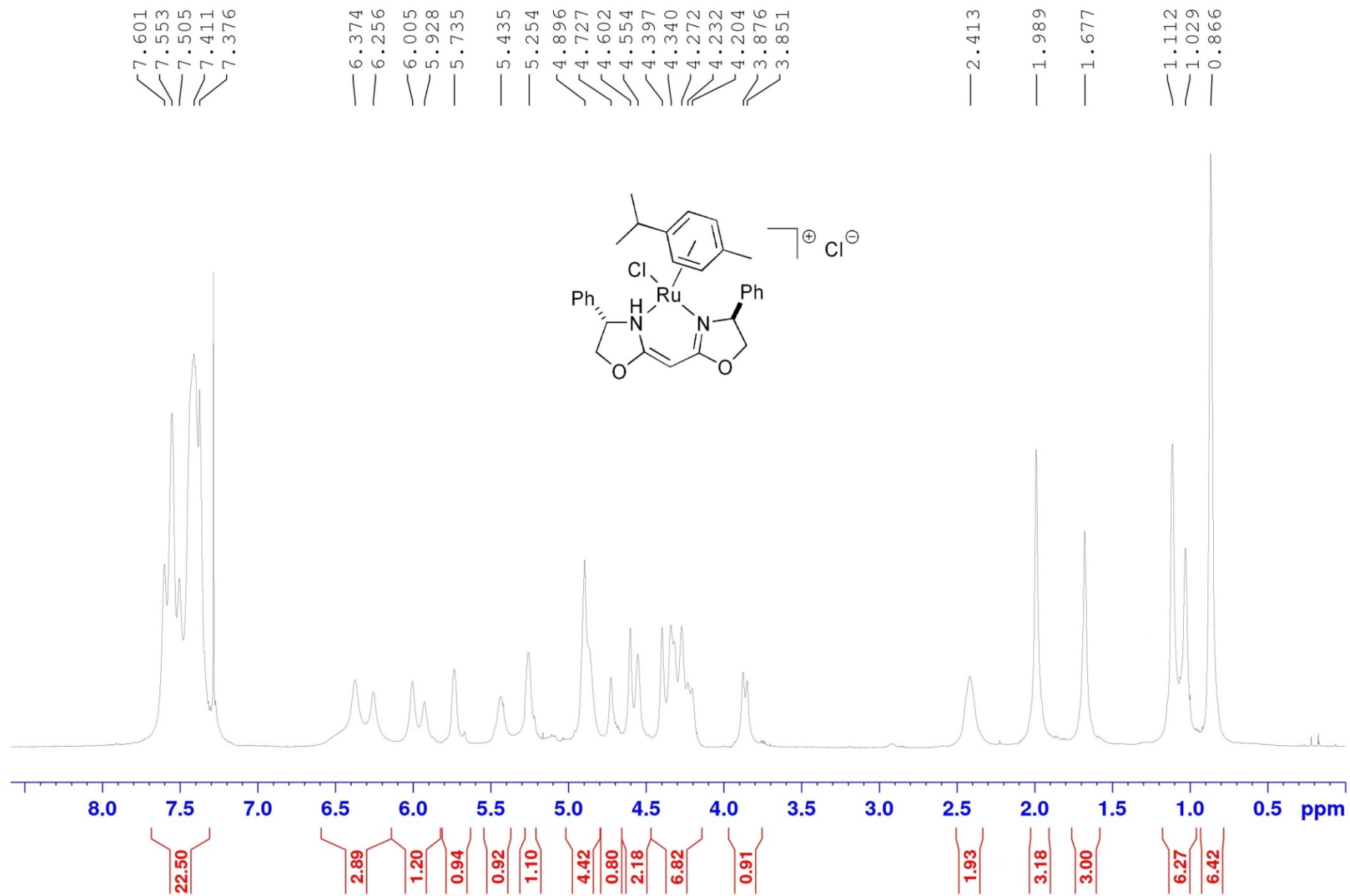
¹H NMR of 4



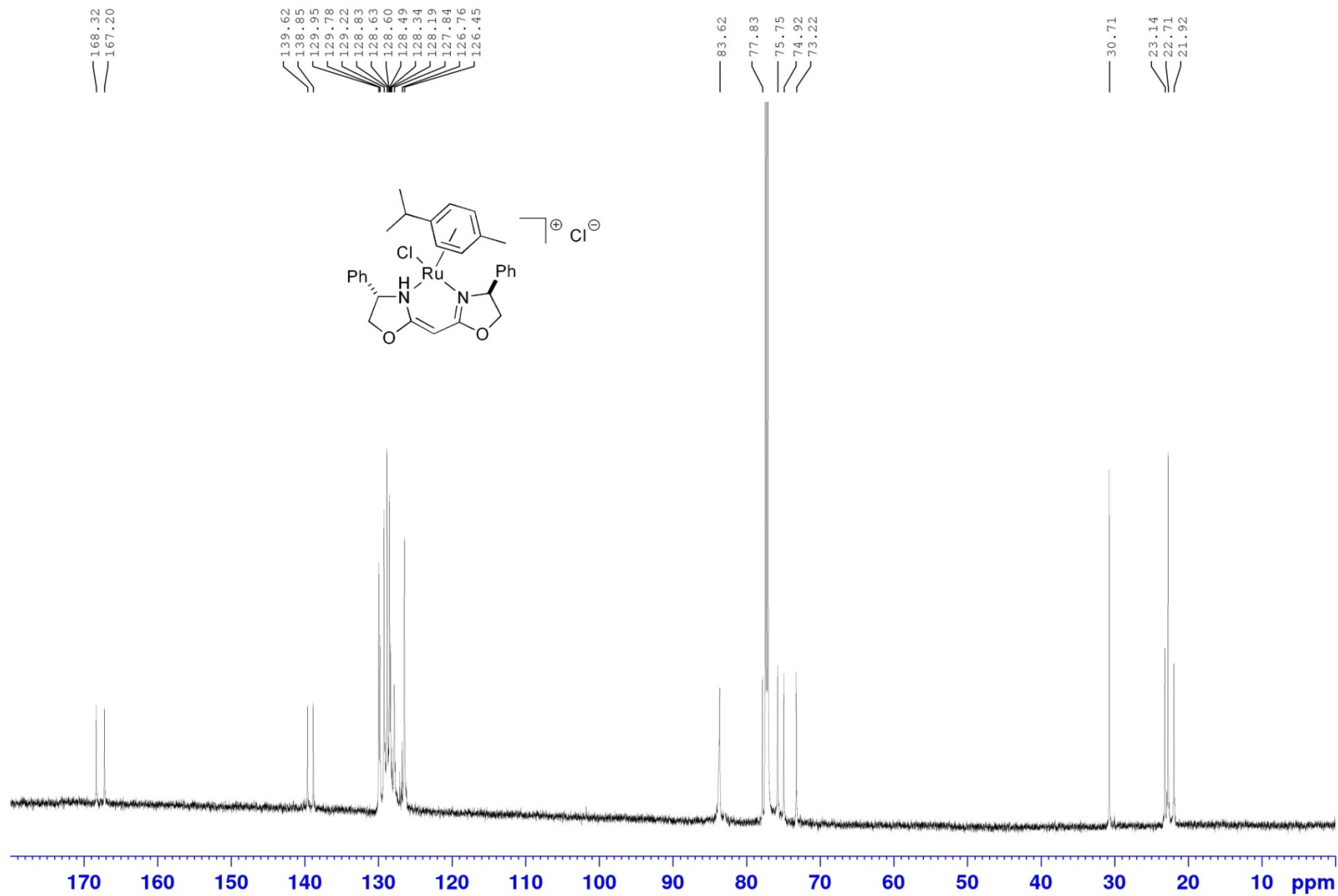
¹³C NMR of 4



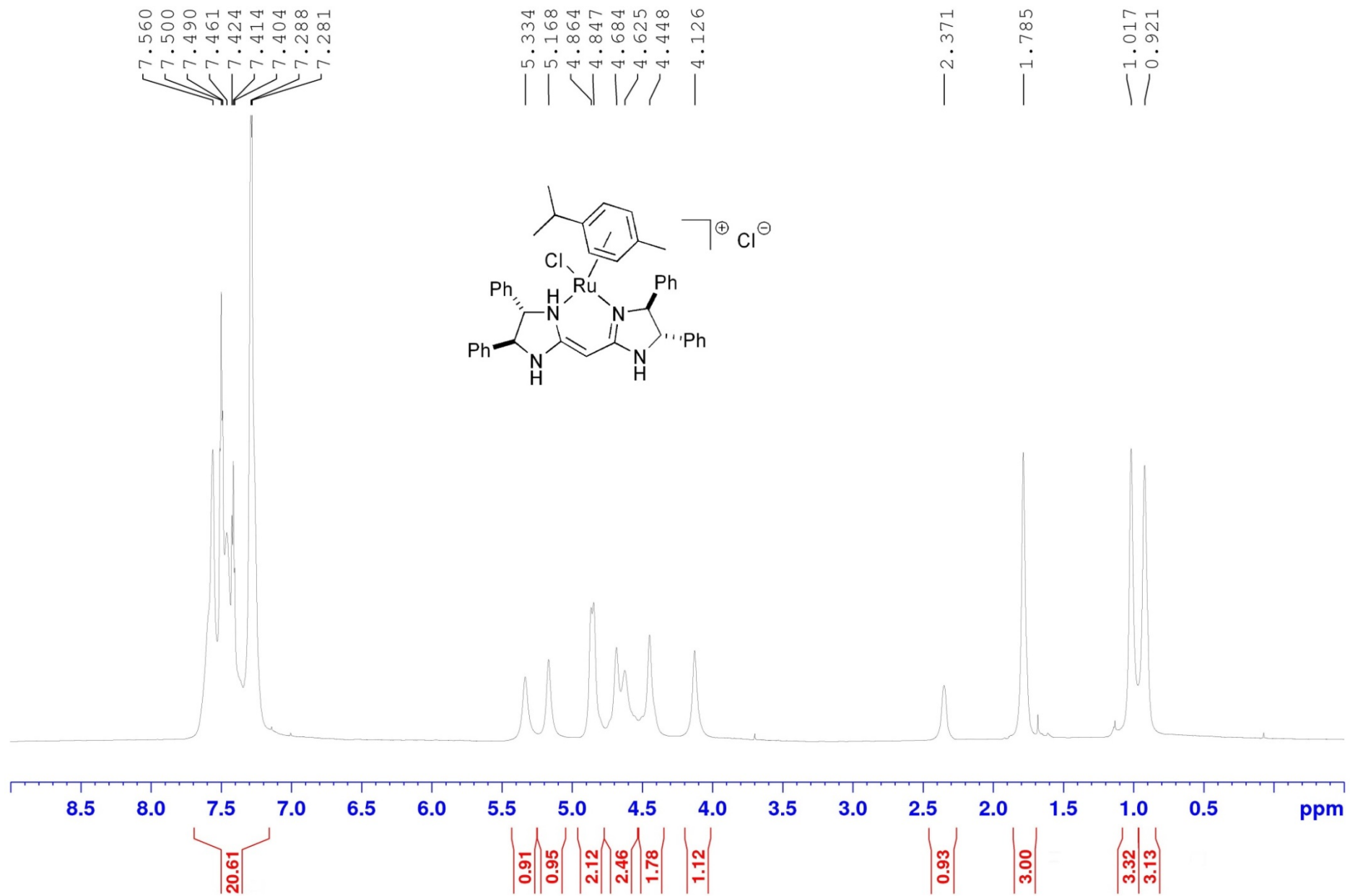
¹H NMR of 5



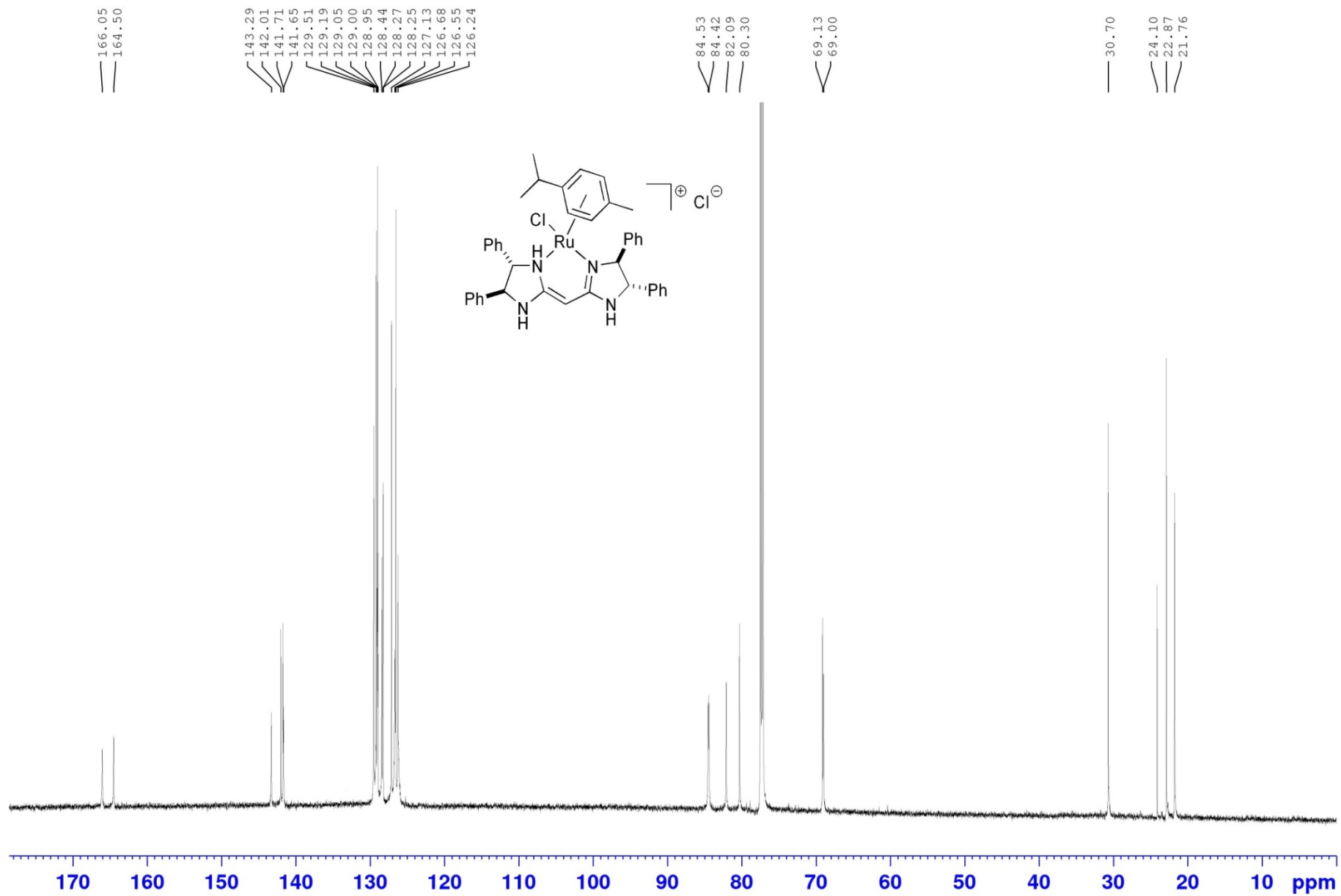
^{13}C NMR of **5**



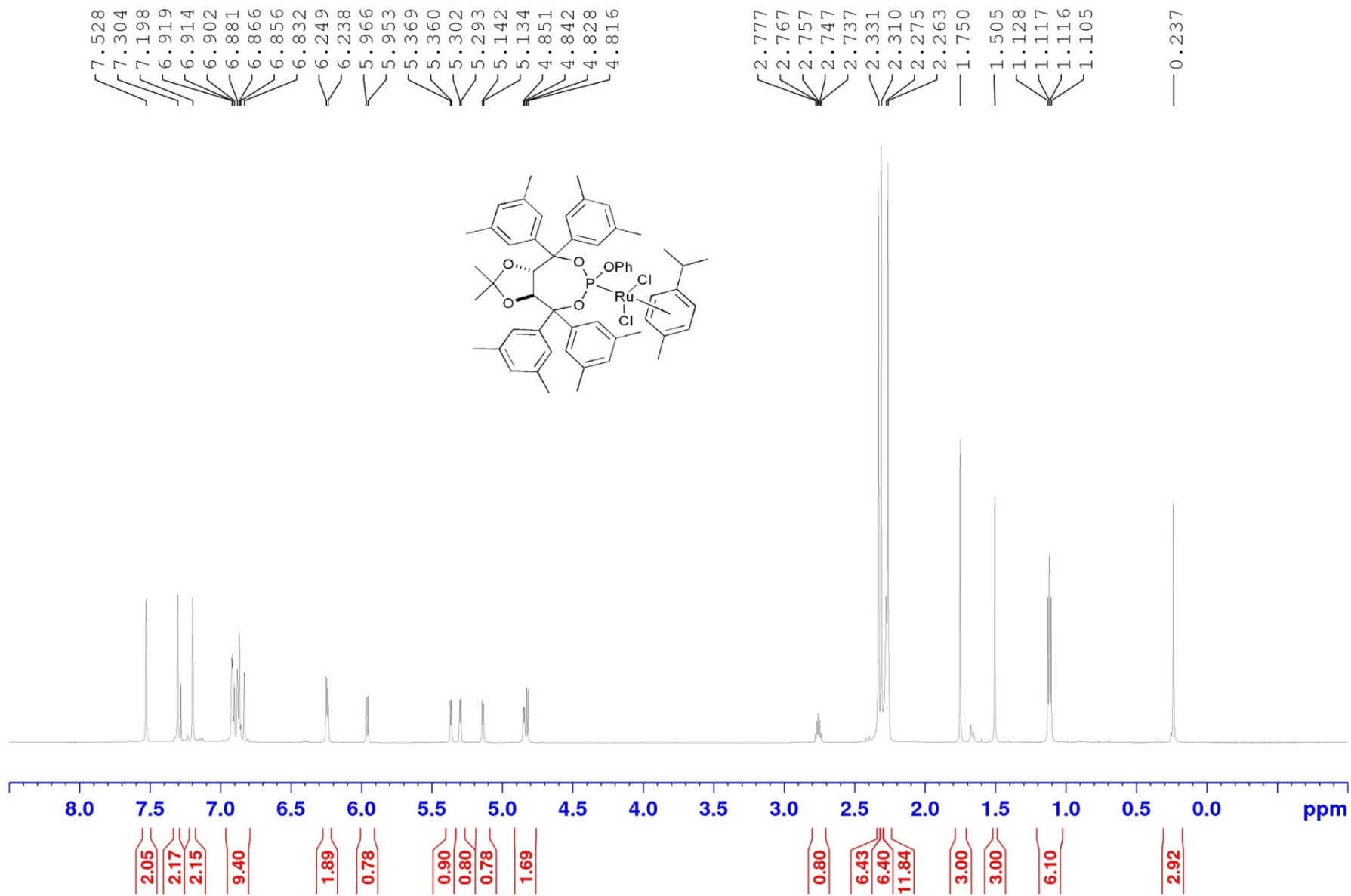
¹H NMR of **6**



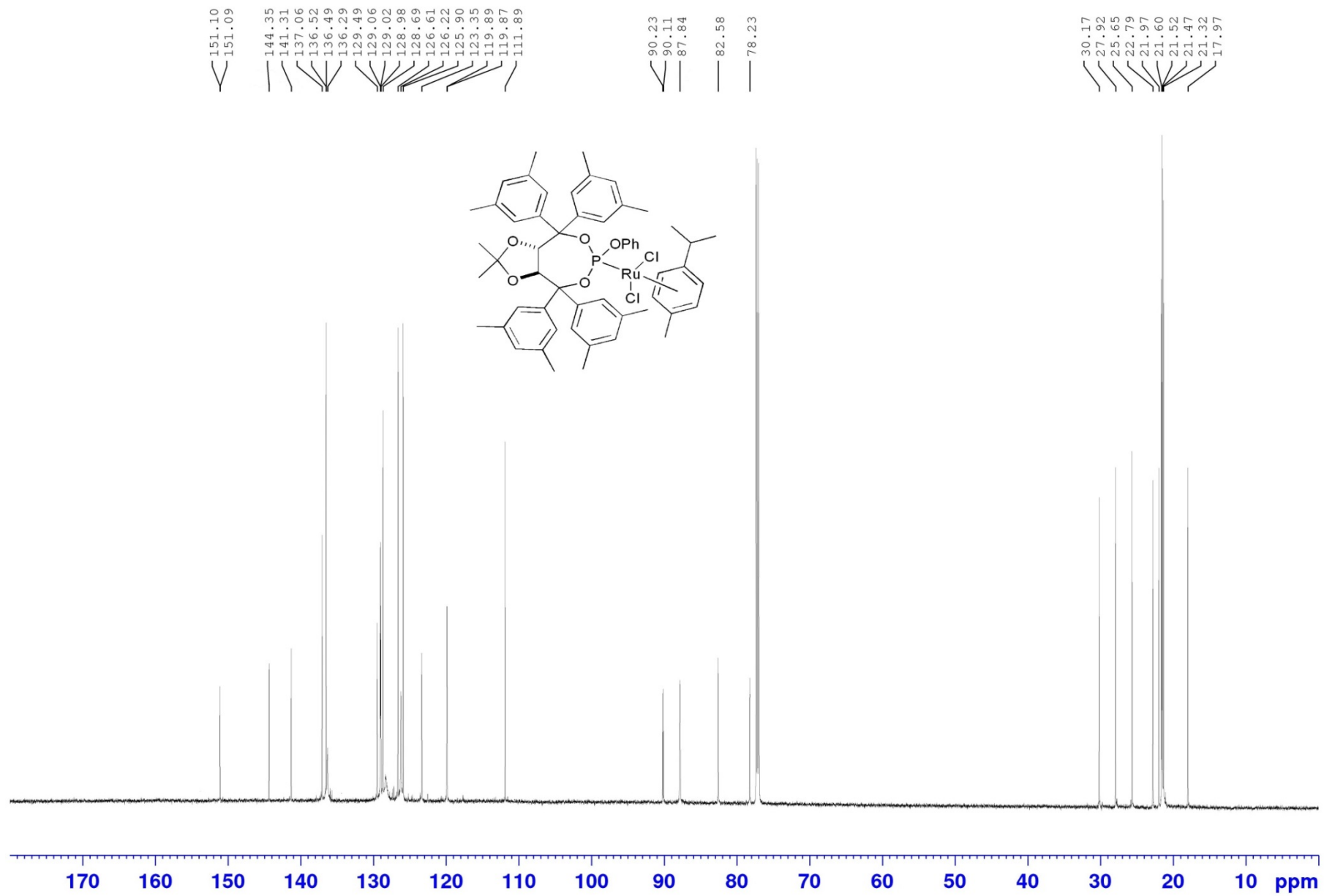
¹³C NMR of 6



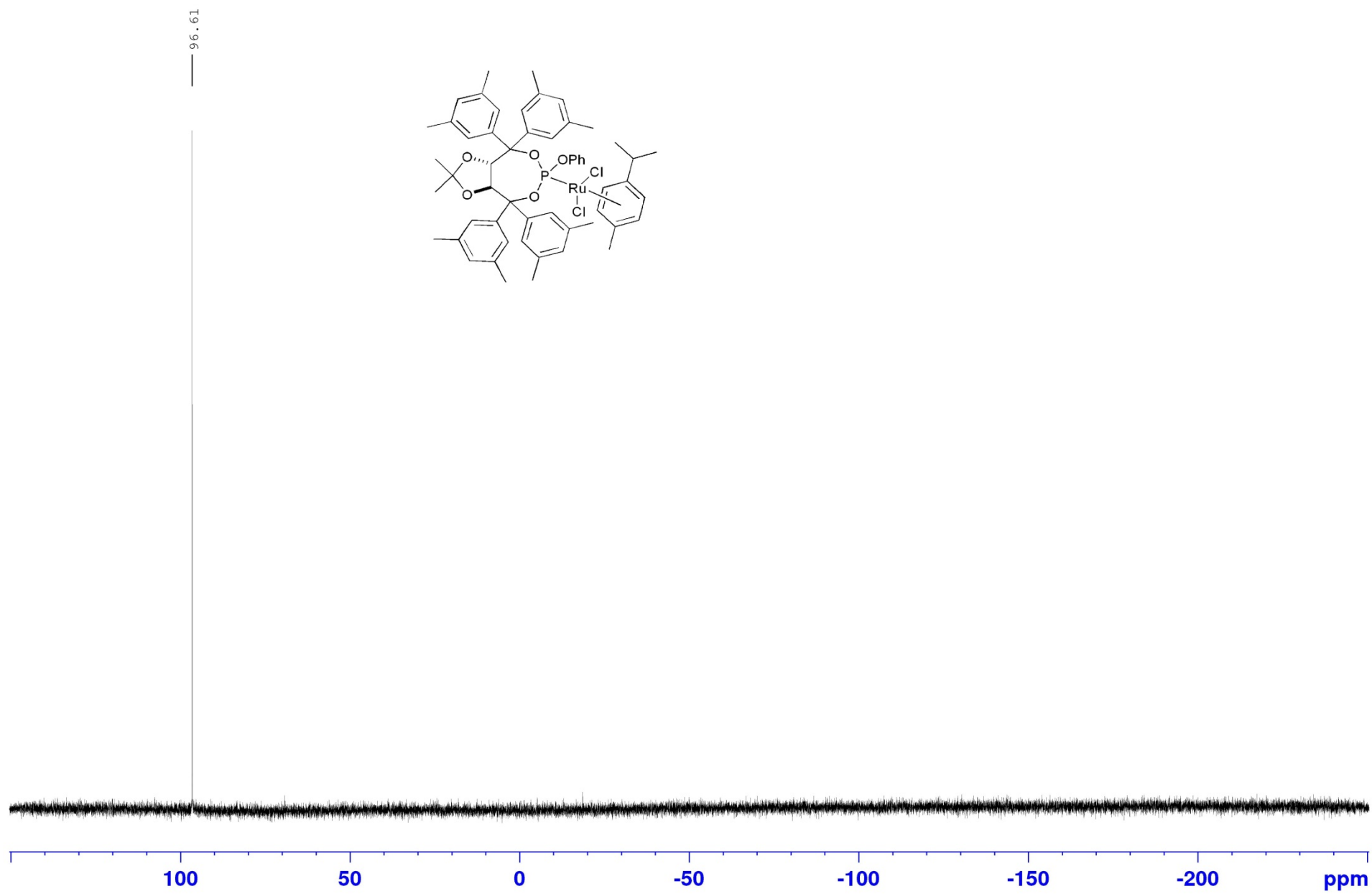
^1H NMR of **8**



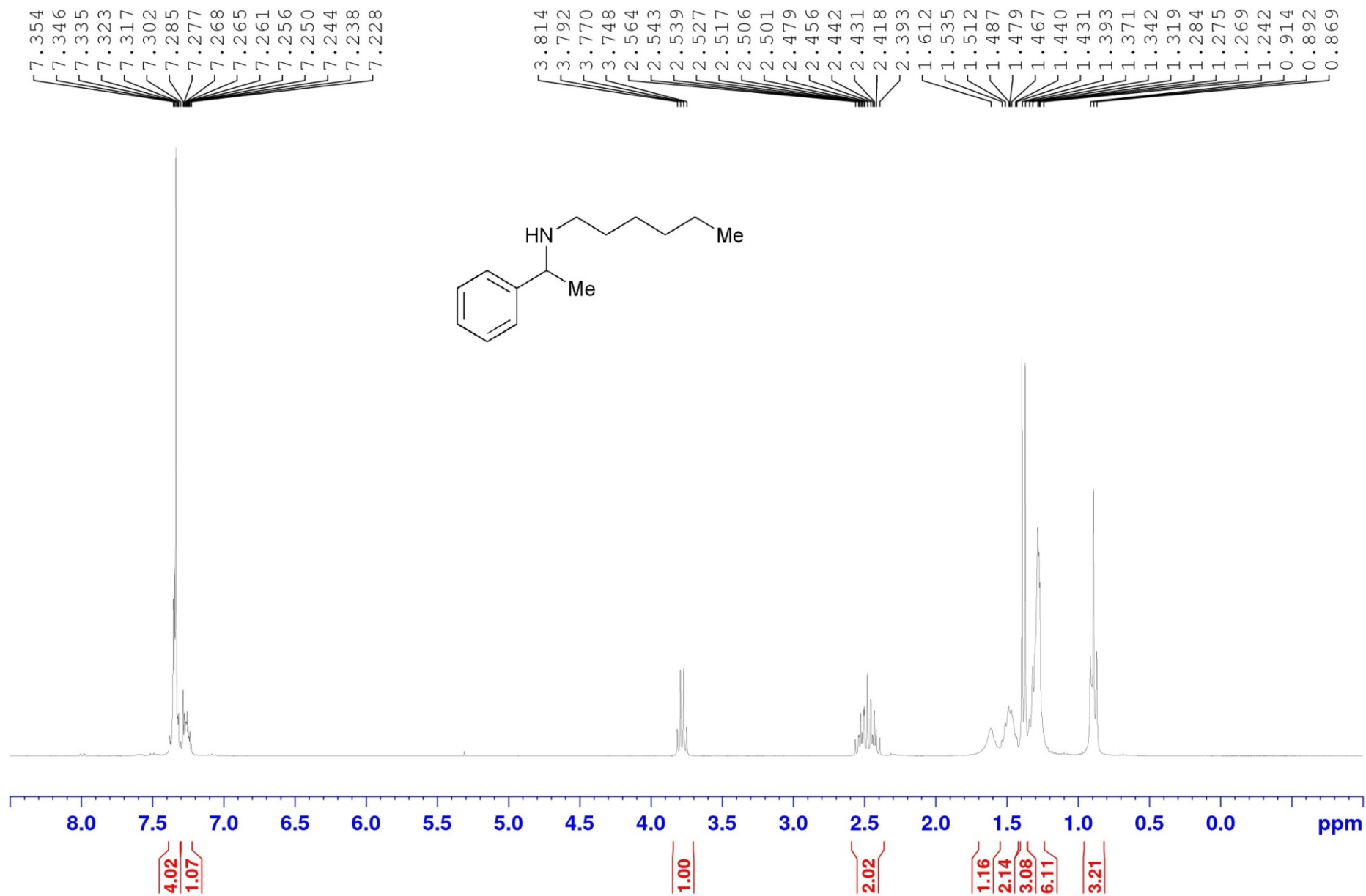
^{13}C NMR of **8**



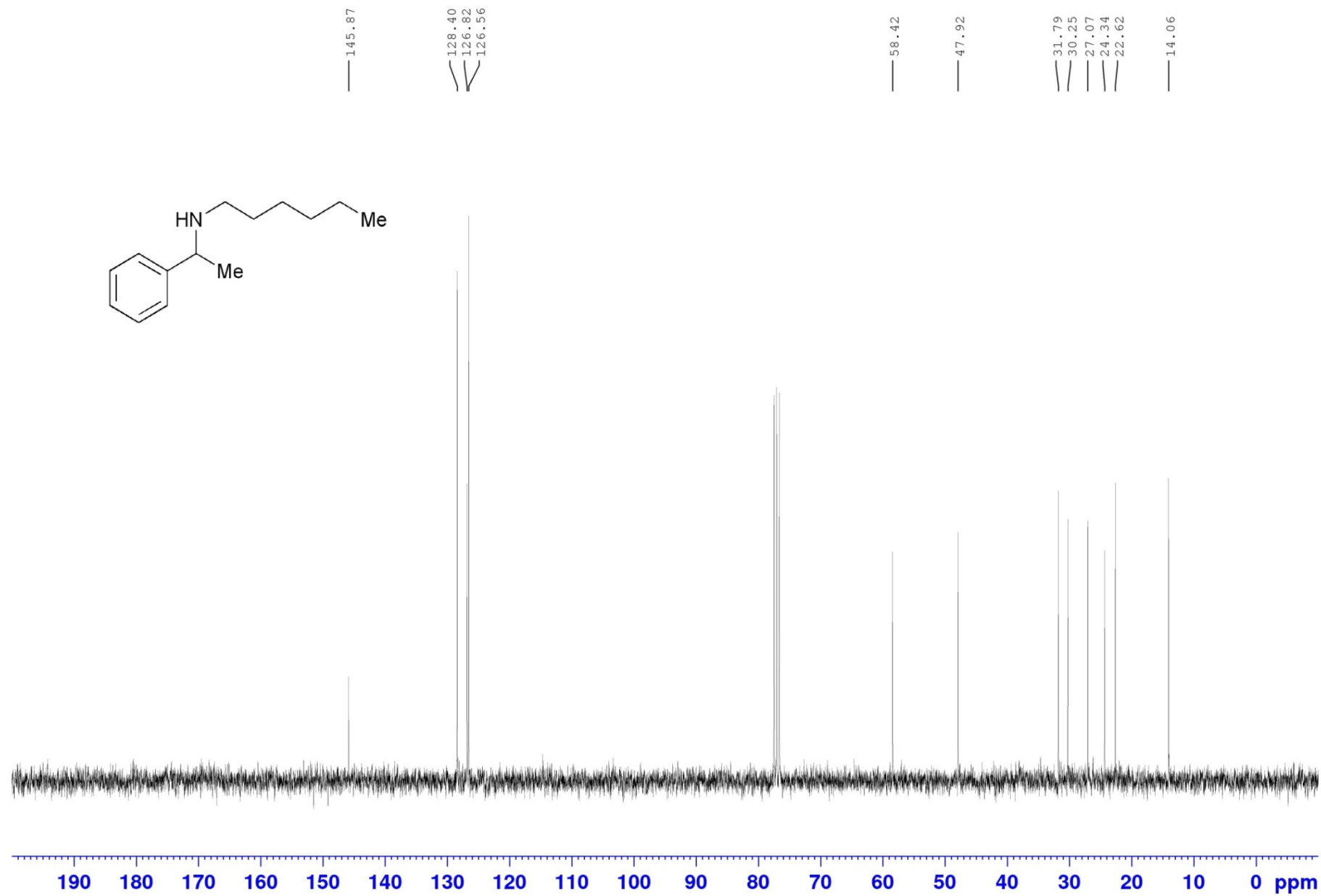
^{31}P NMR of **8**



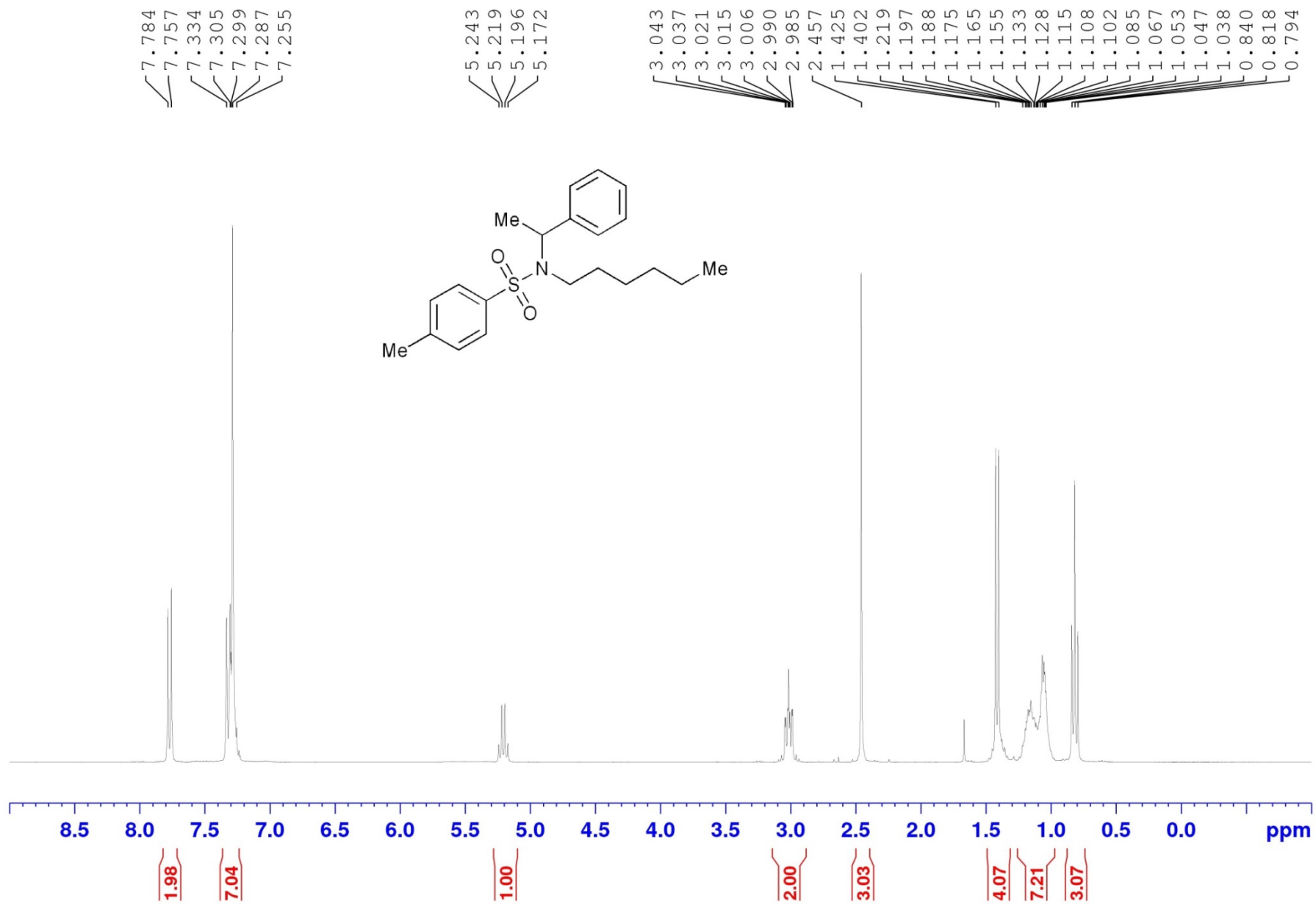
¹H NMR of 10a



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



¹H NMR of 10a'



^{13}C NMR of **10a'**

142.94
140.41
138.50

129.62
128.28
127.57
127.55
127.14

55.25

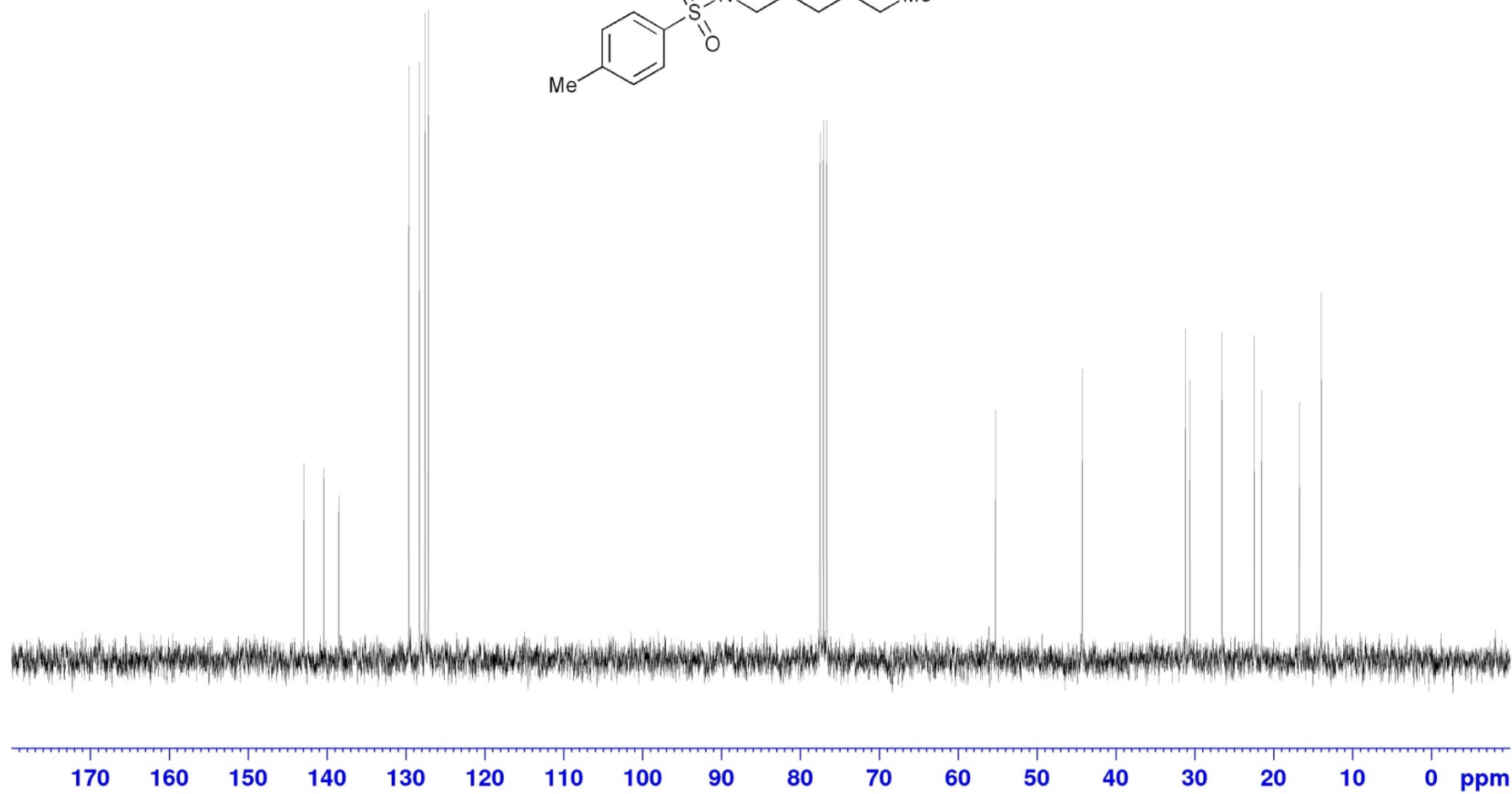
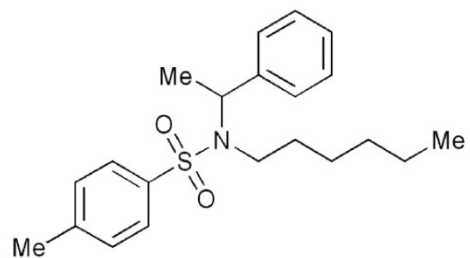
44.25

31.19
30.60

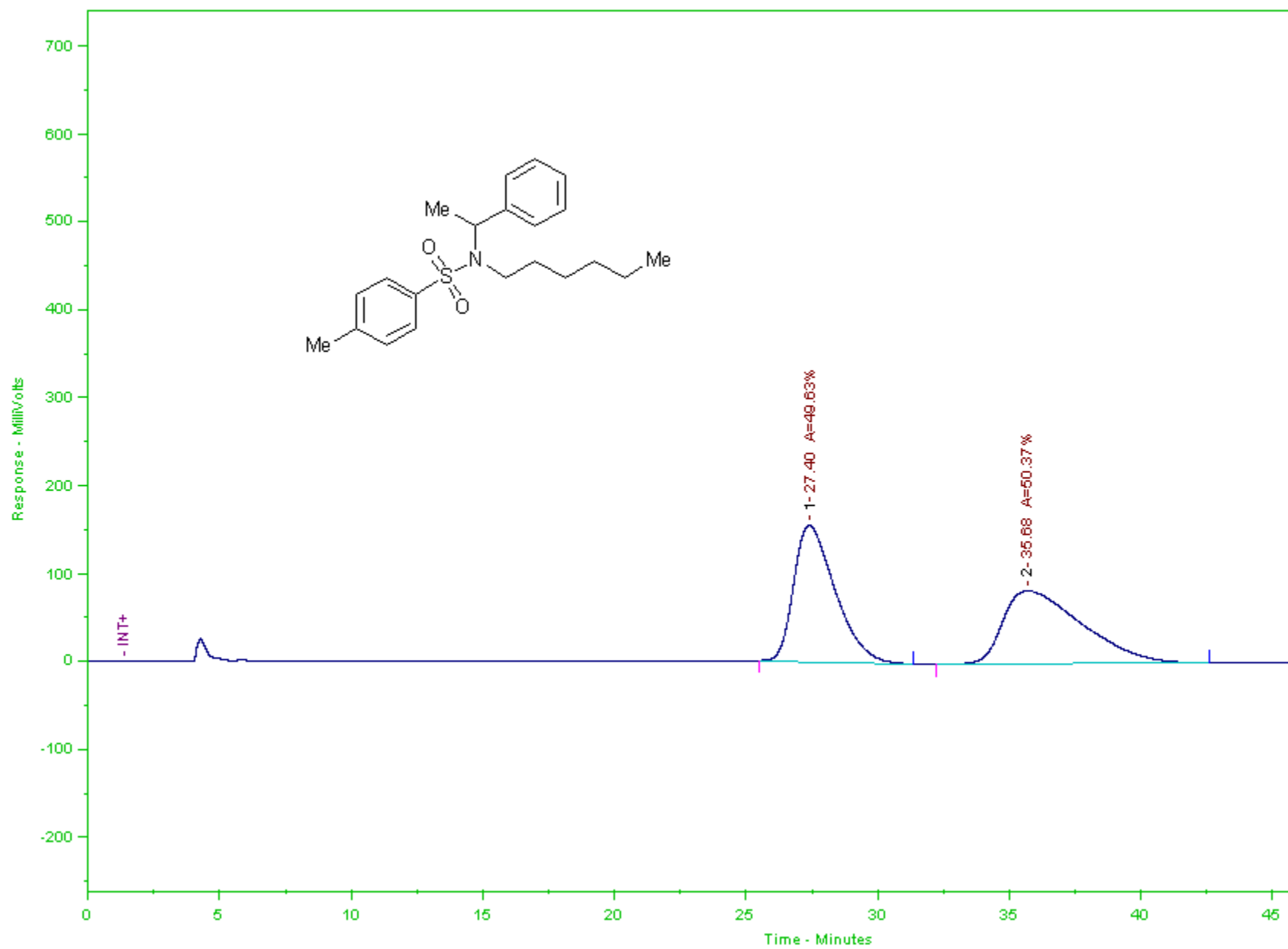
26.55

22.45
21.52

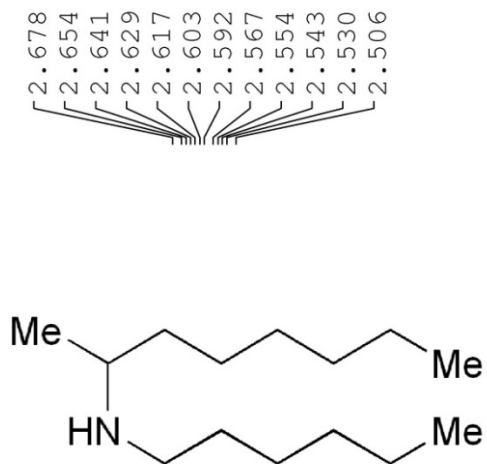
16.74
13.95



Chiral HPLC Analysis: 10a'

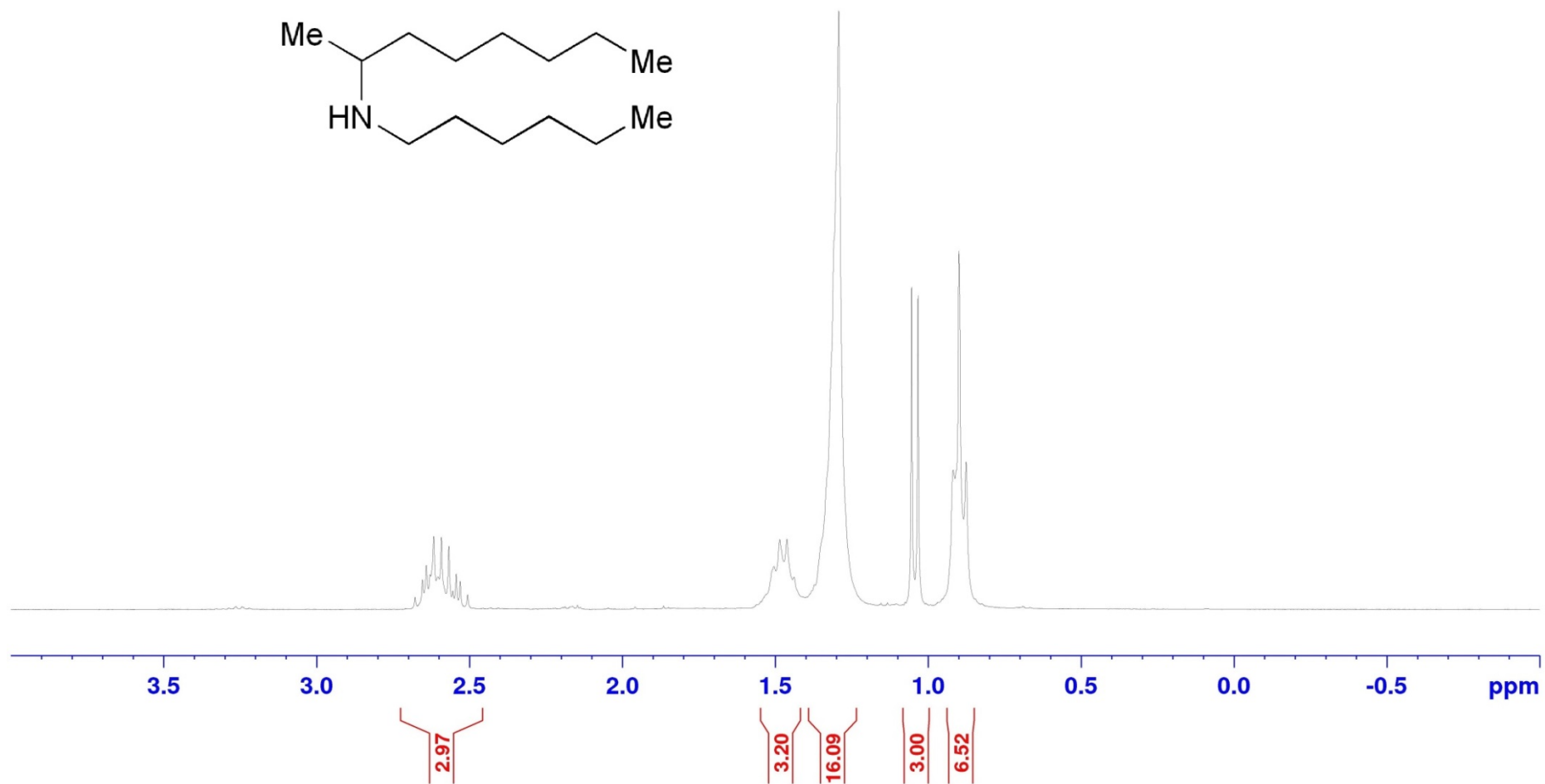


¹H NMR of **10b**

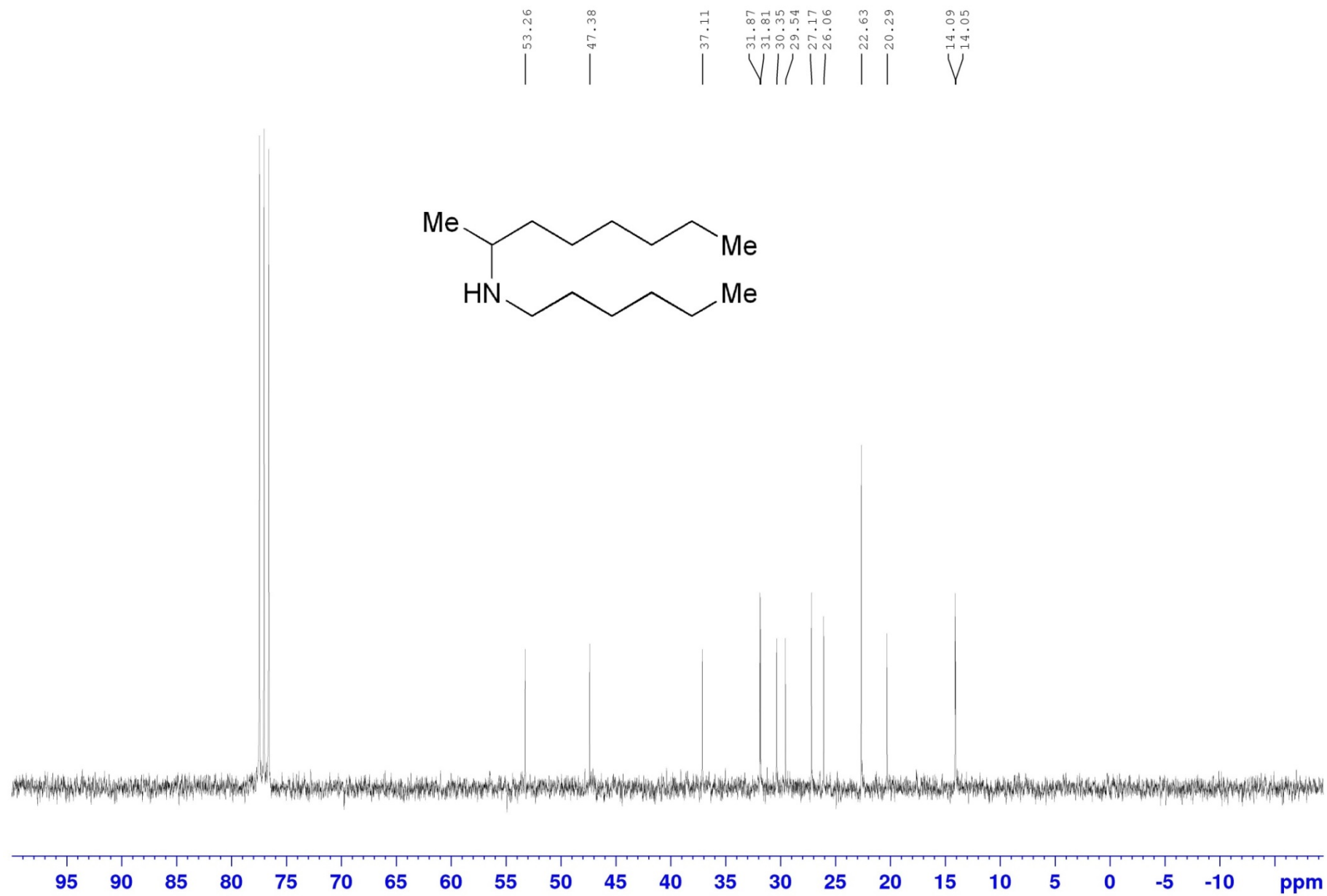


2.678
2.654
2.641
2.629
2.617
2.603
2.592
2.567
2.554
2.543
2.530
2.506

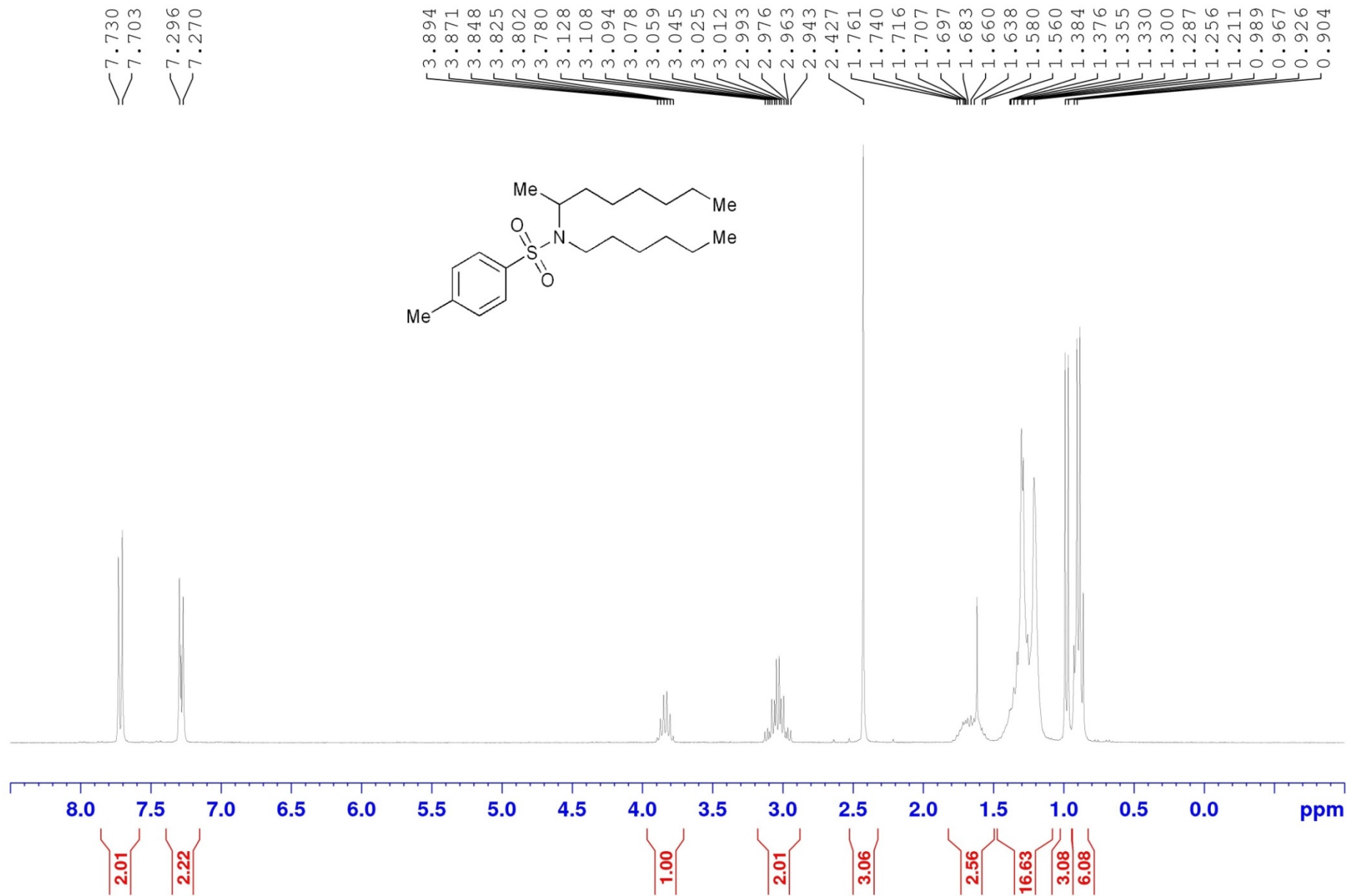
1.504
1.485
1.462
1.438
1.372
1.292
1.054
1.033
0.918
0.899
0.876



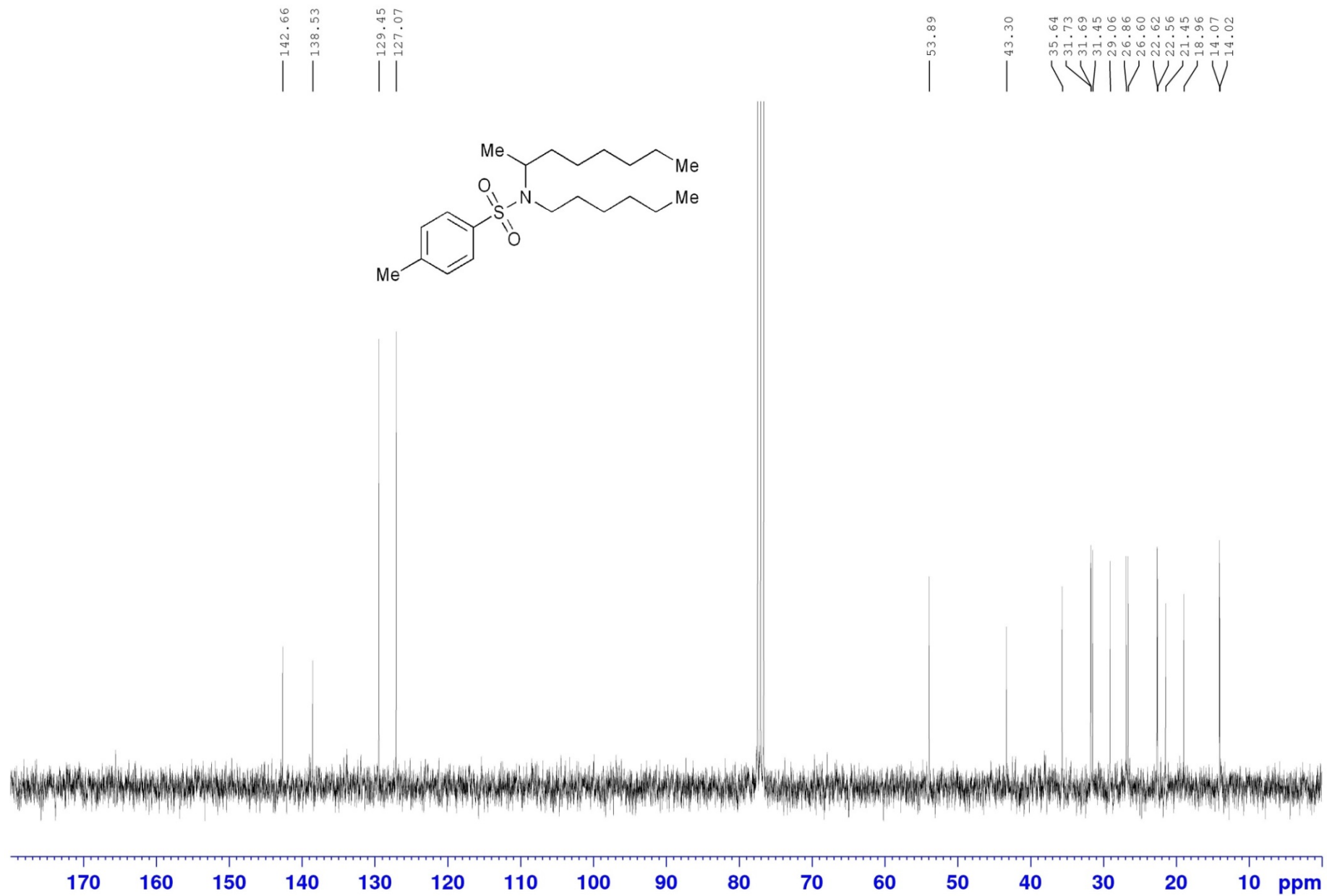
^{13}C NMR of **10b**



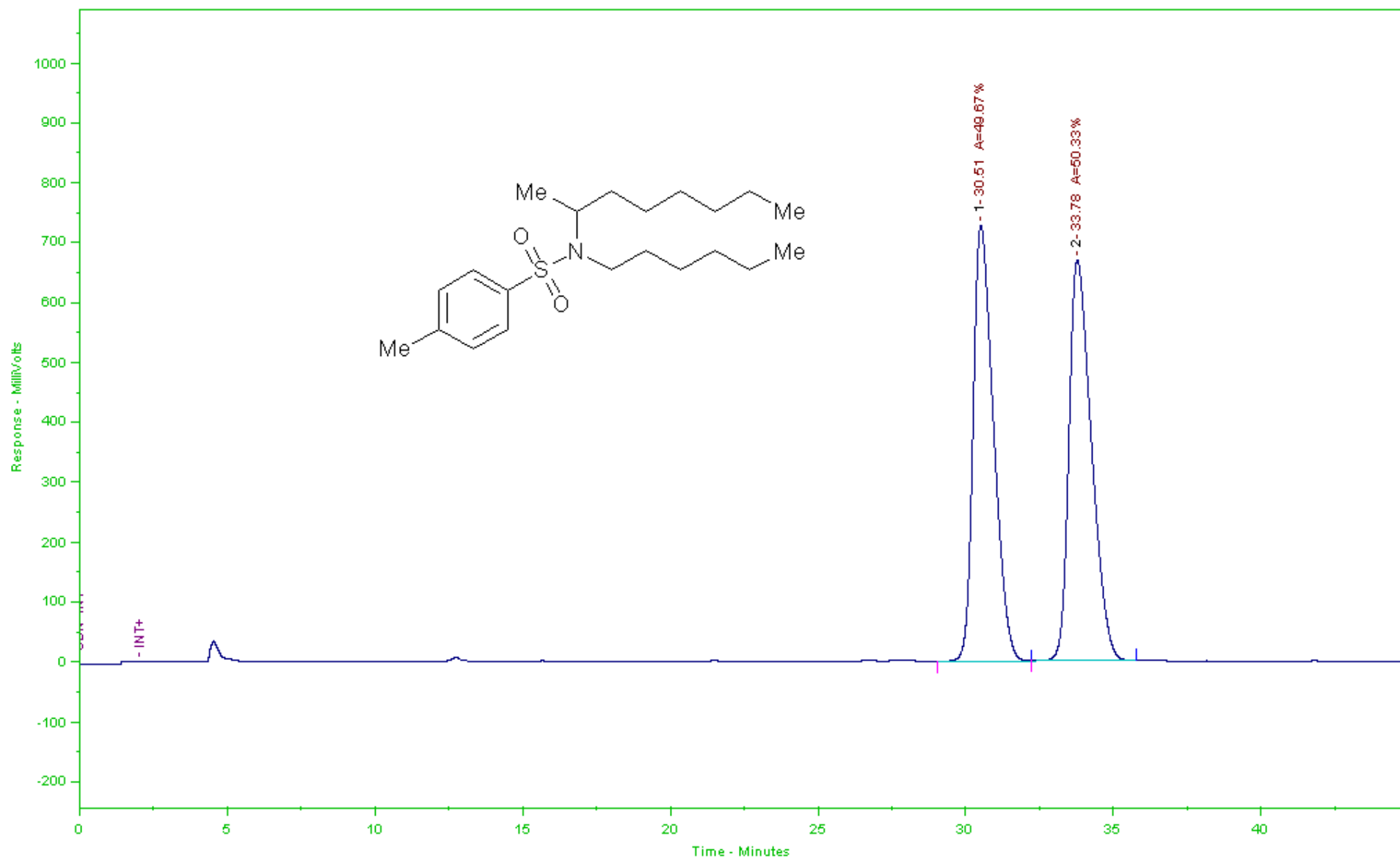
¹H NMR of 10b'



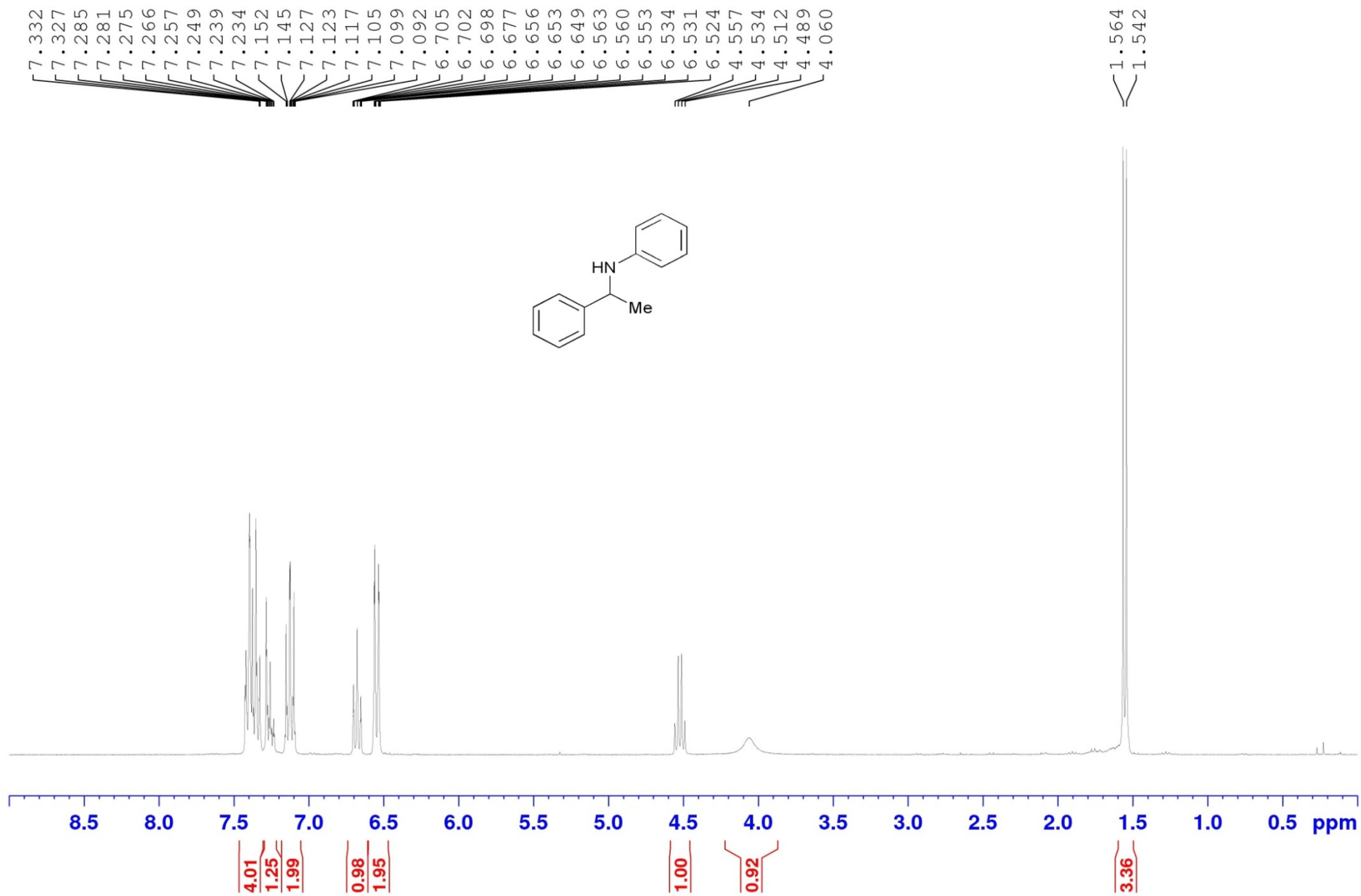
^{13}C NMR of **10b'**



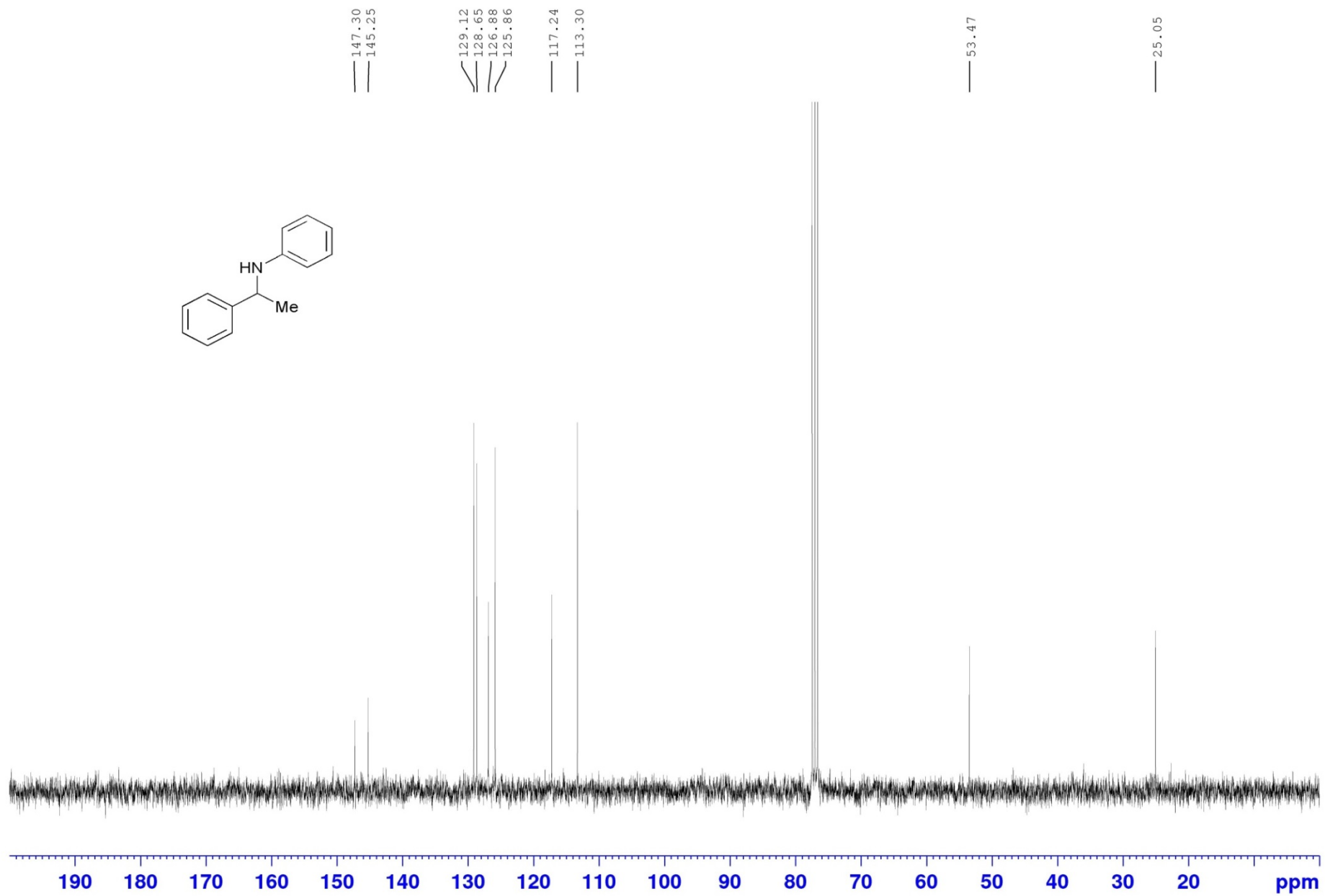
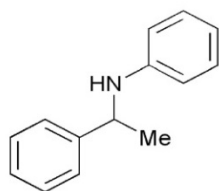
Chiral HPLC Analysis: 10b'



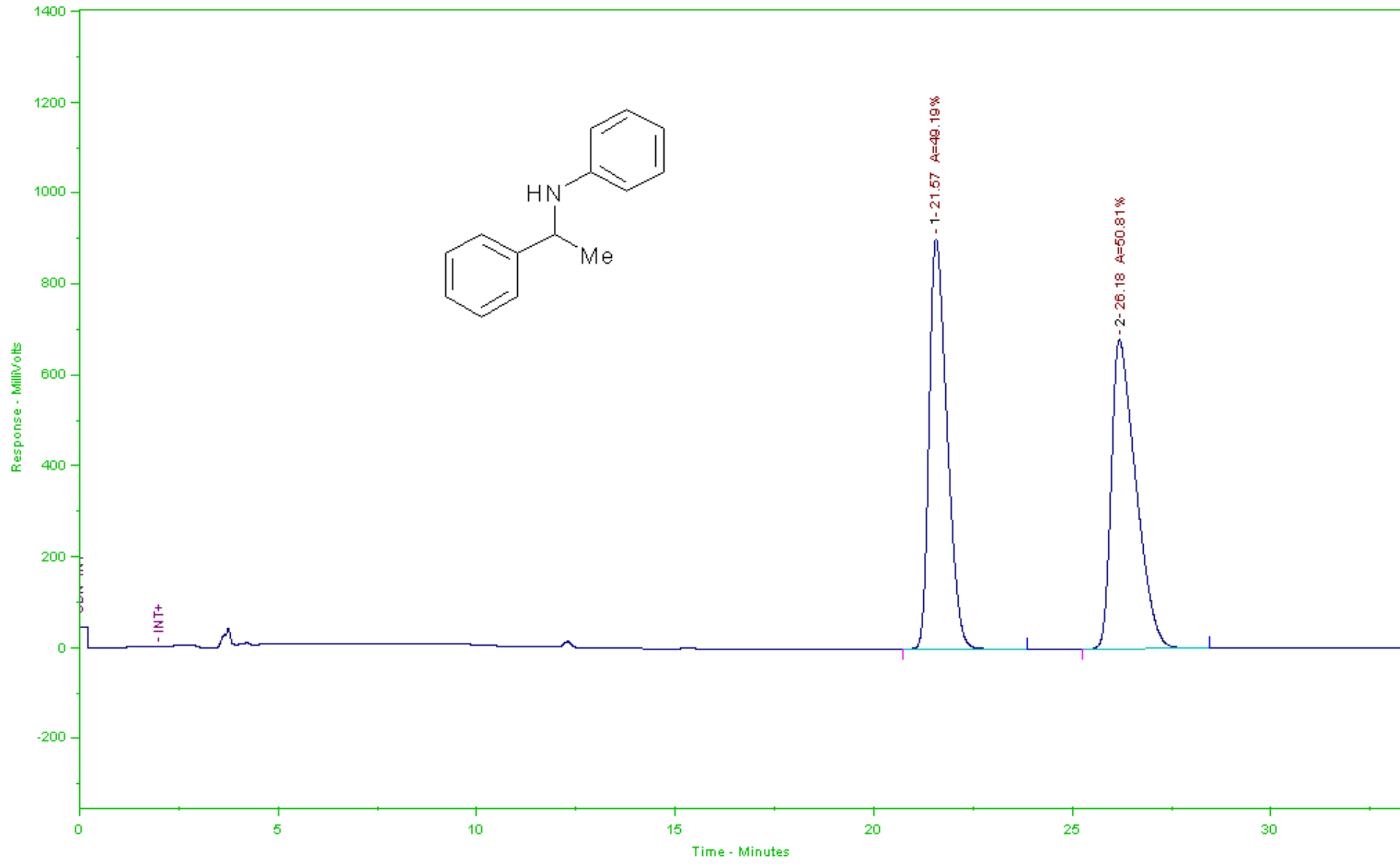
¹H NMR of 10c



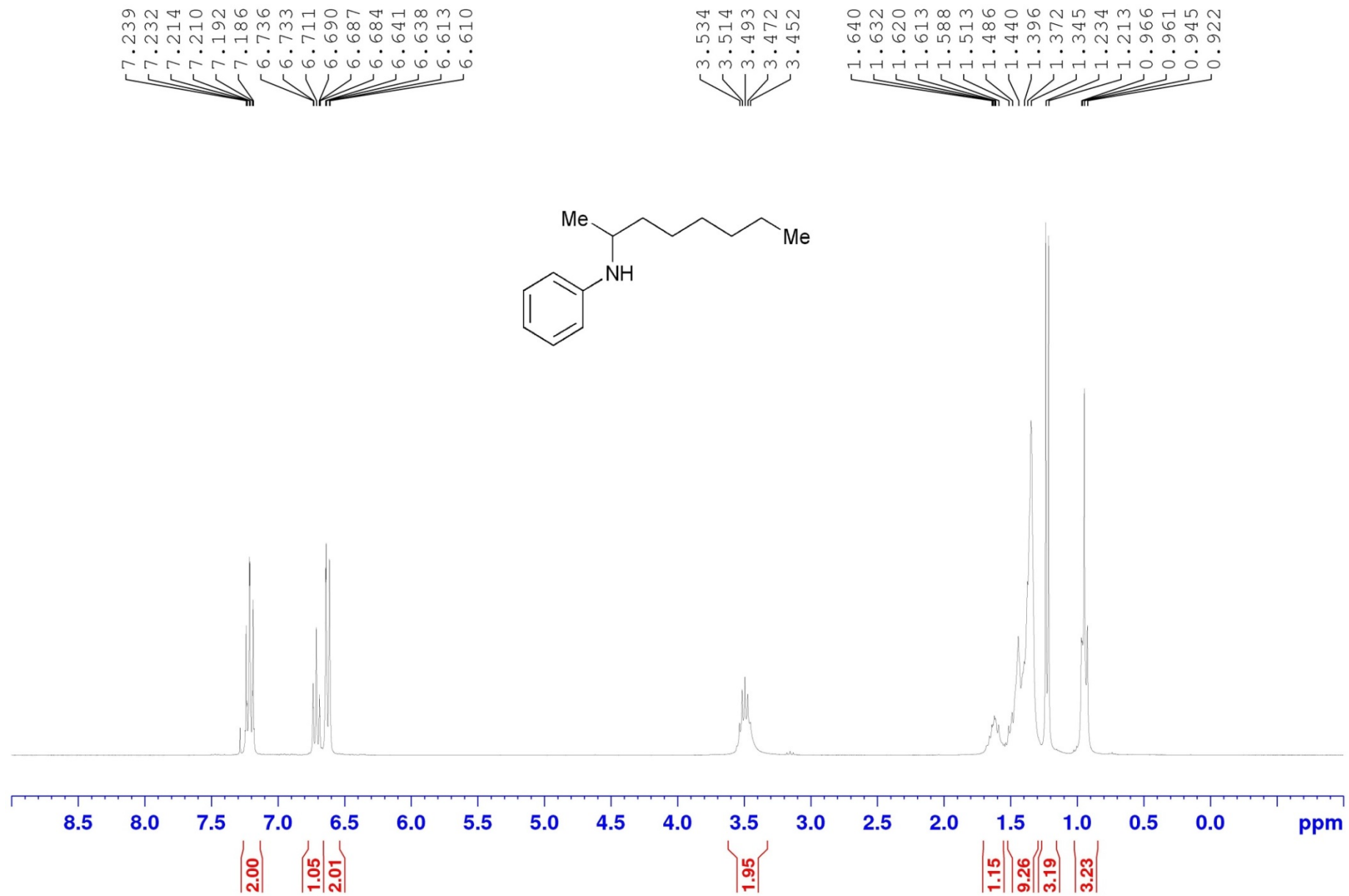
^{13}C NMR of **10c**



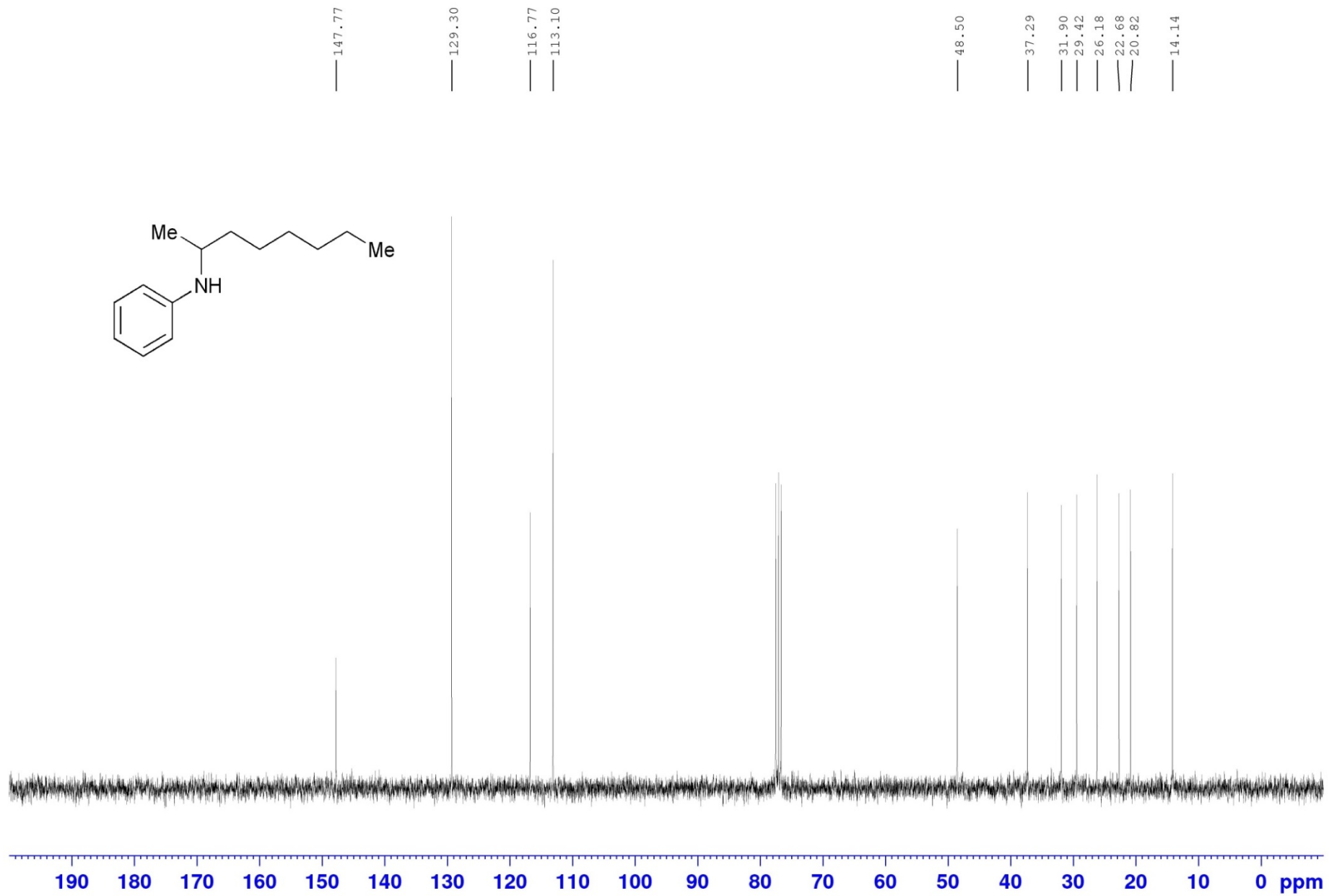
Chiral HPLC Analysis: 10c



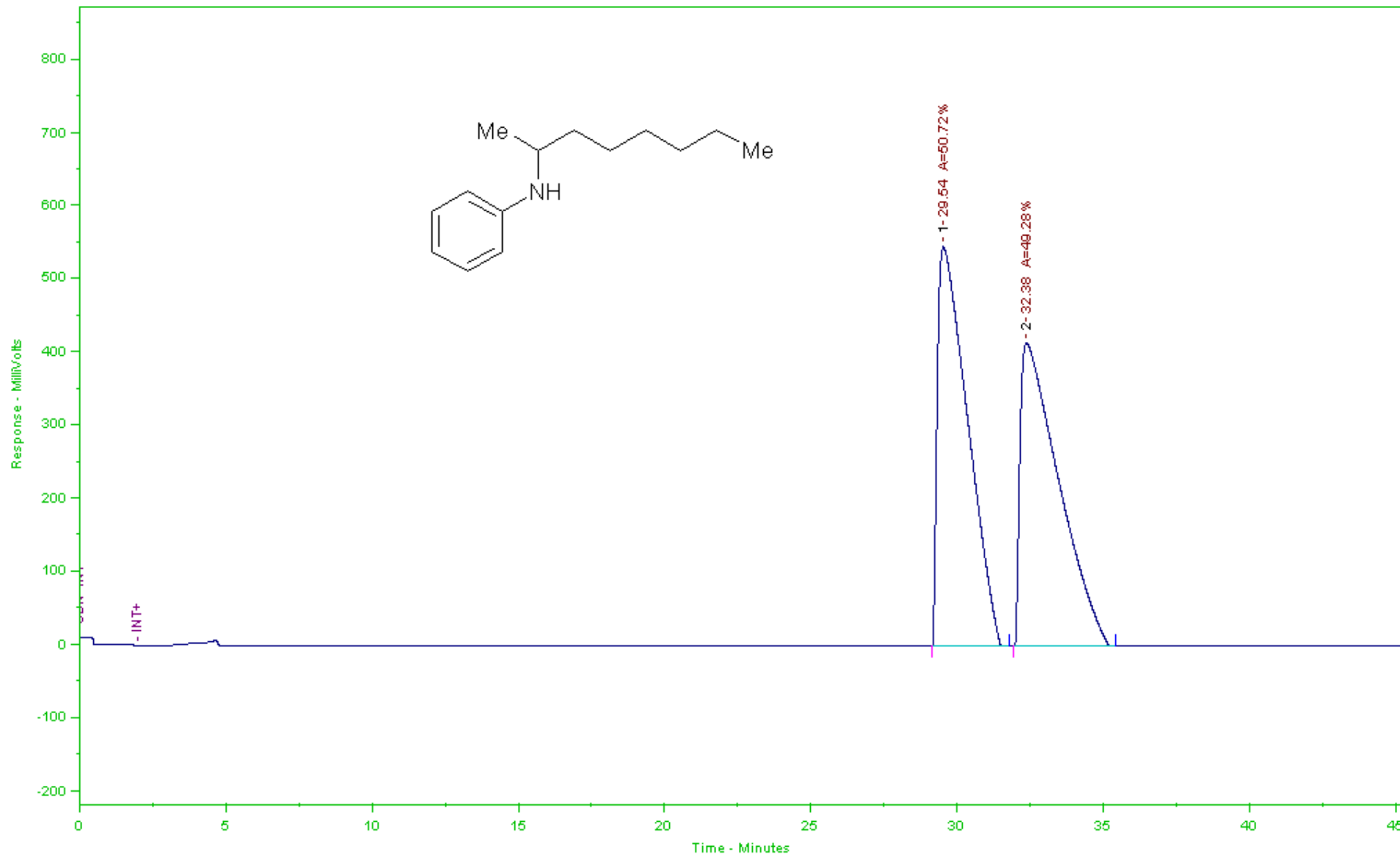
¹H NMR of 10d



¹³C NMR of **10d**



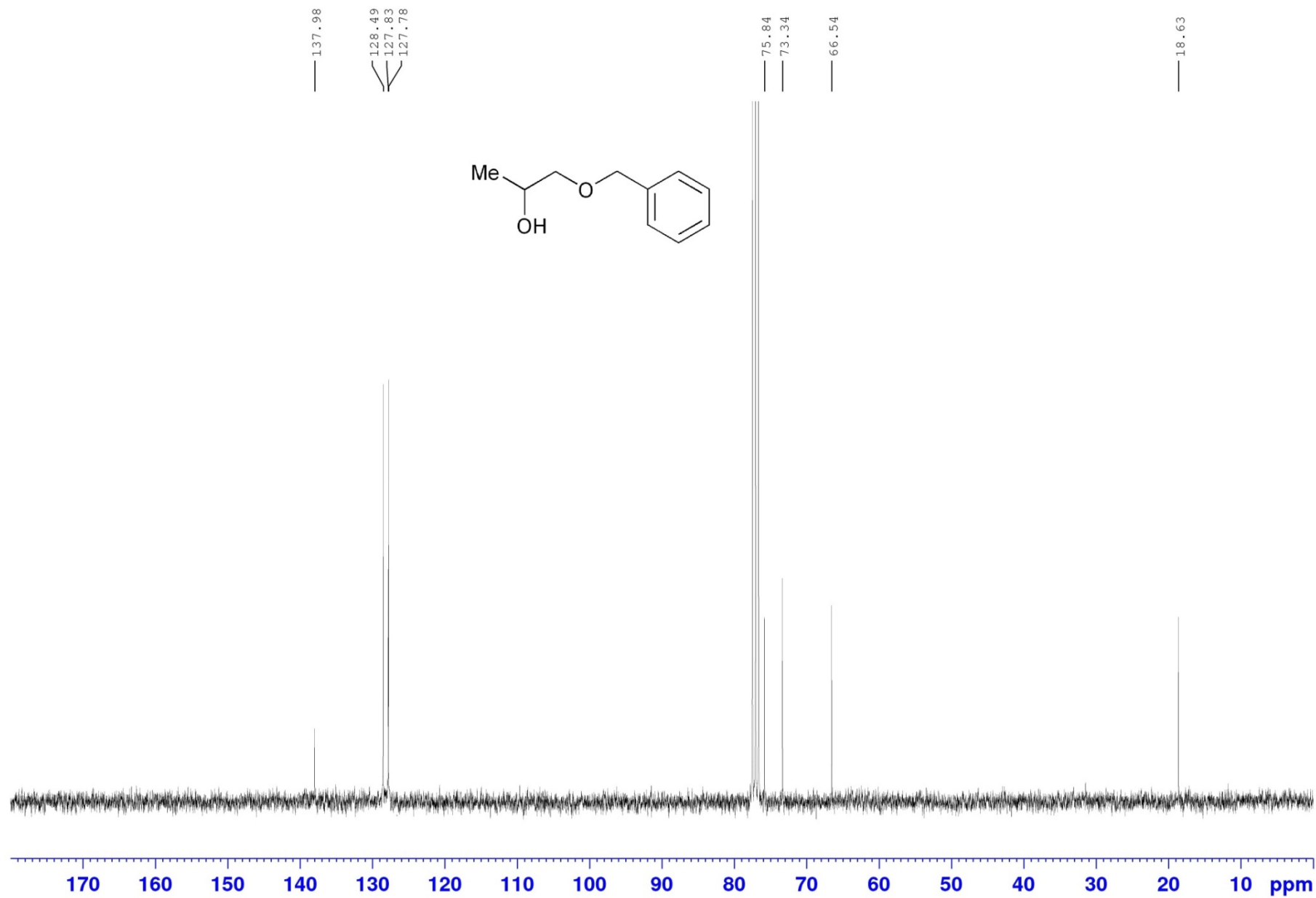
Chiral HPLC Analysis: 10d



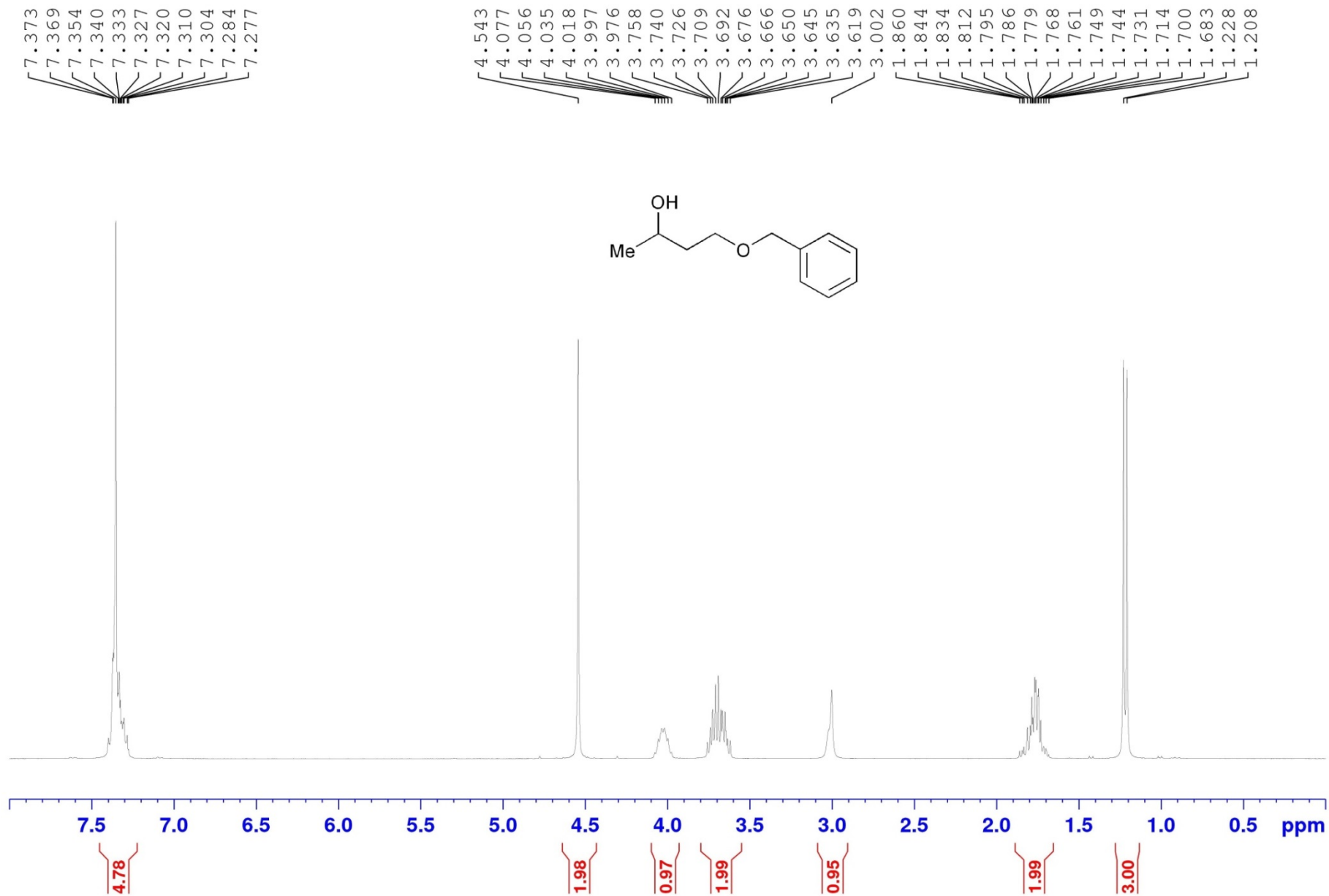
¹H NMR of **11a**



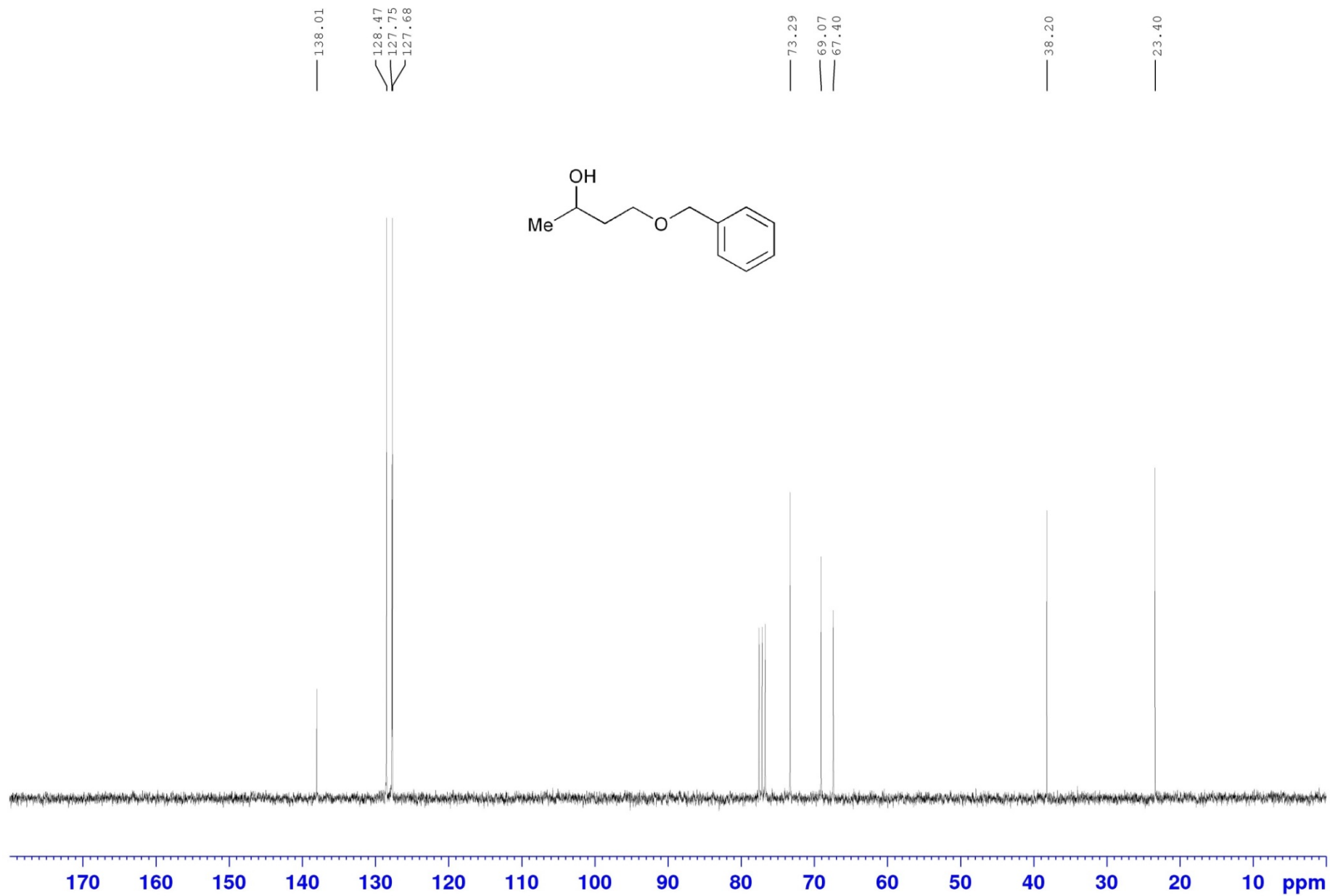
^{13}C NMR of **11a**



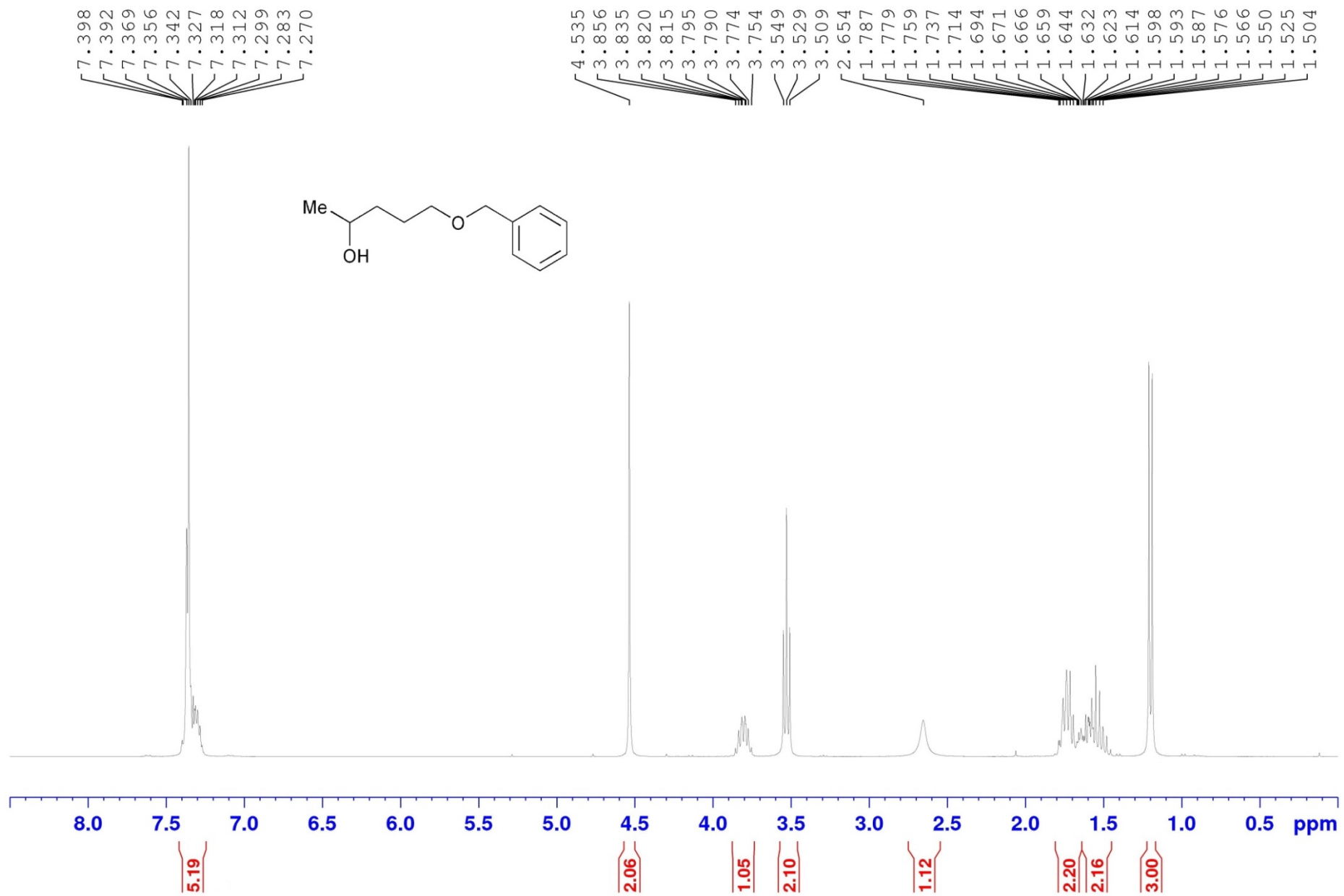
¹H NMR of 11b



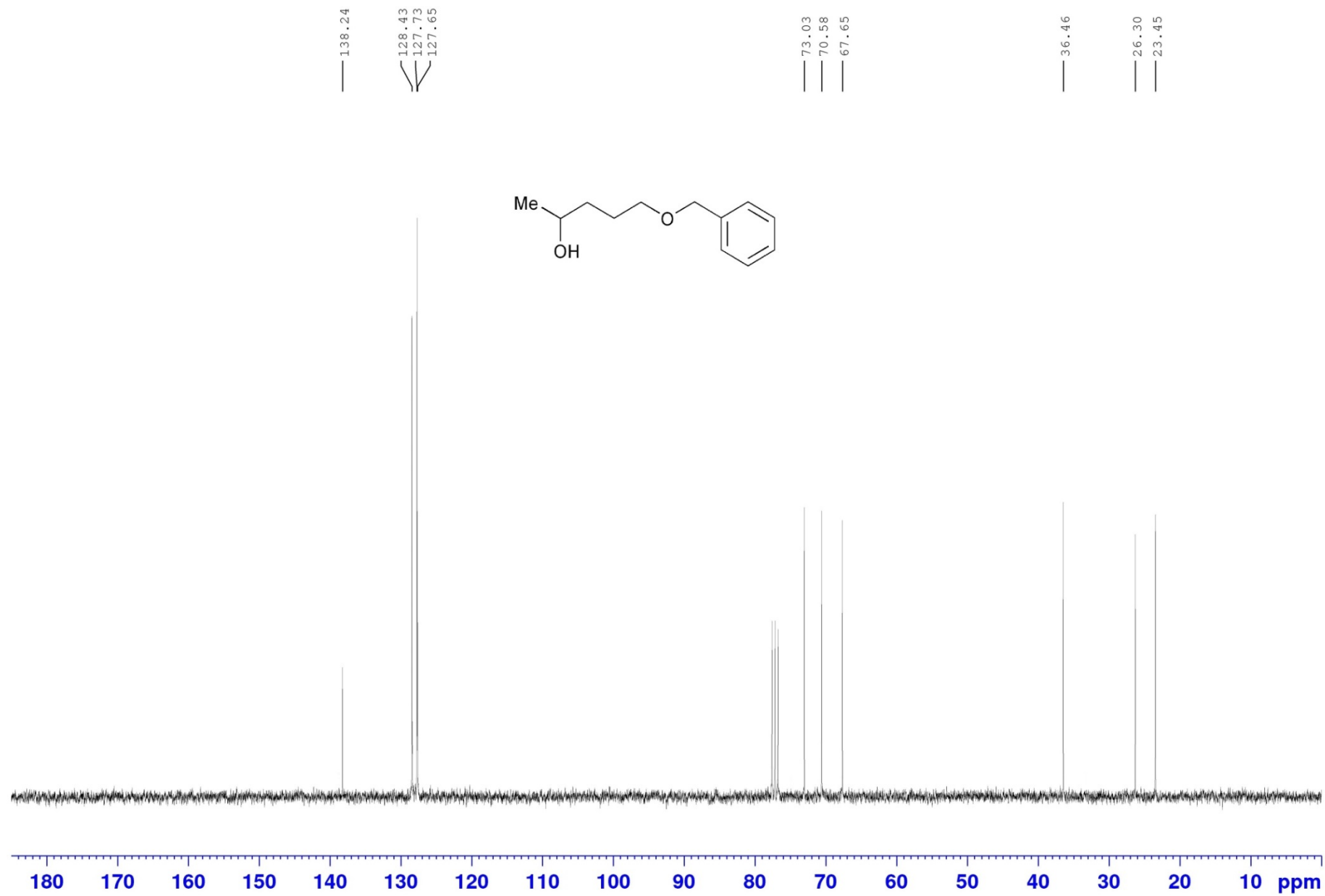
¹³C NMR of **11b**



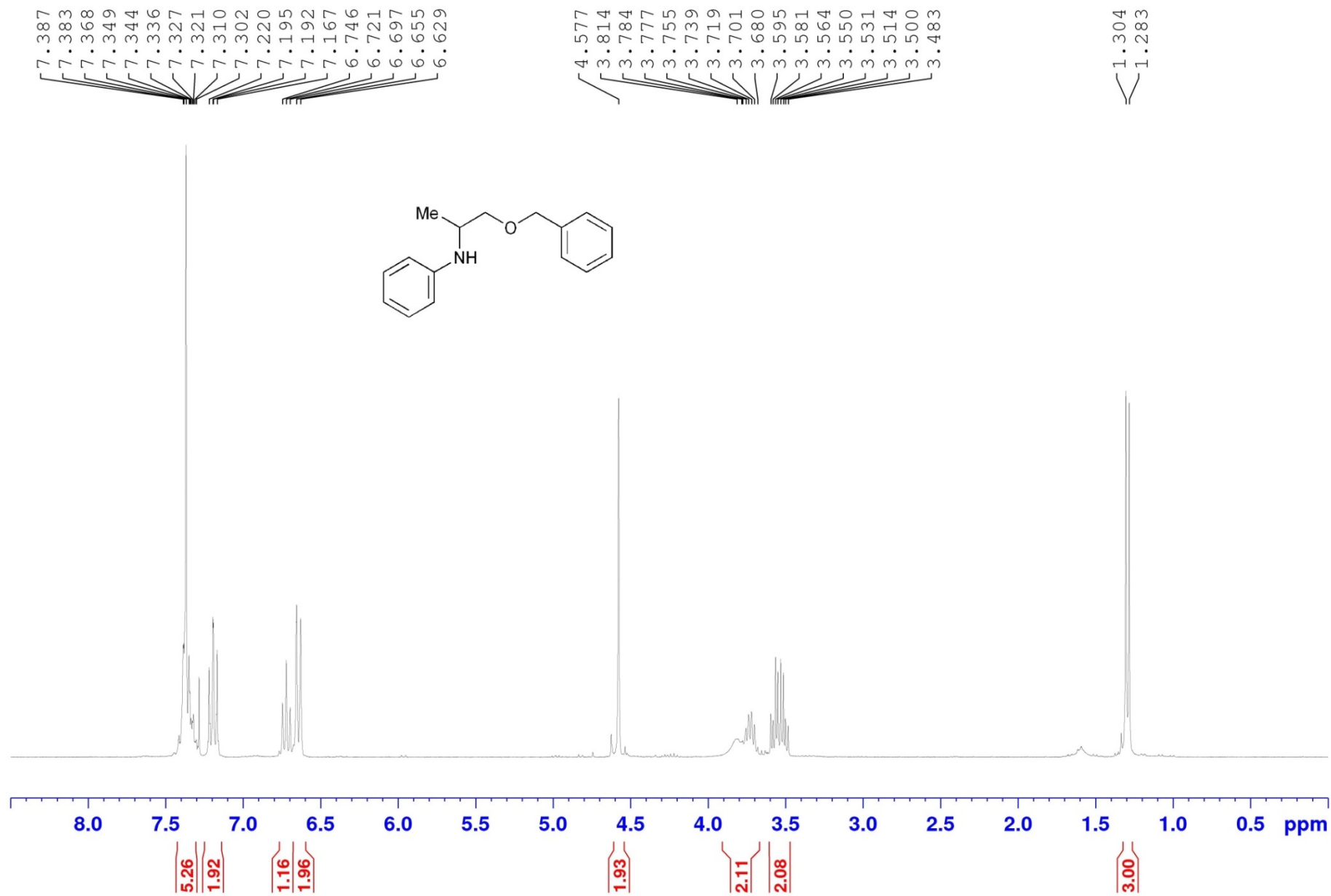
¹H NMR of 11c



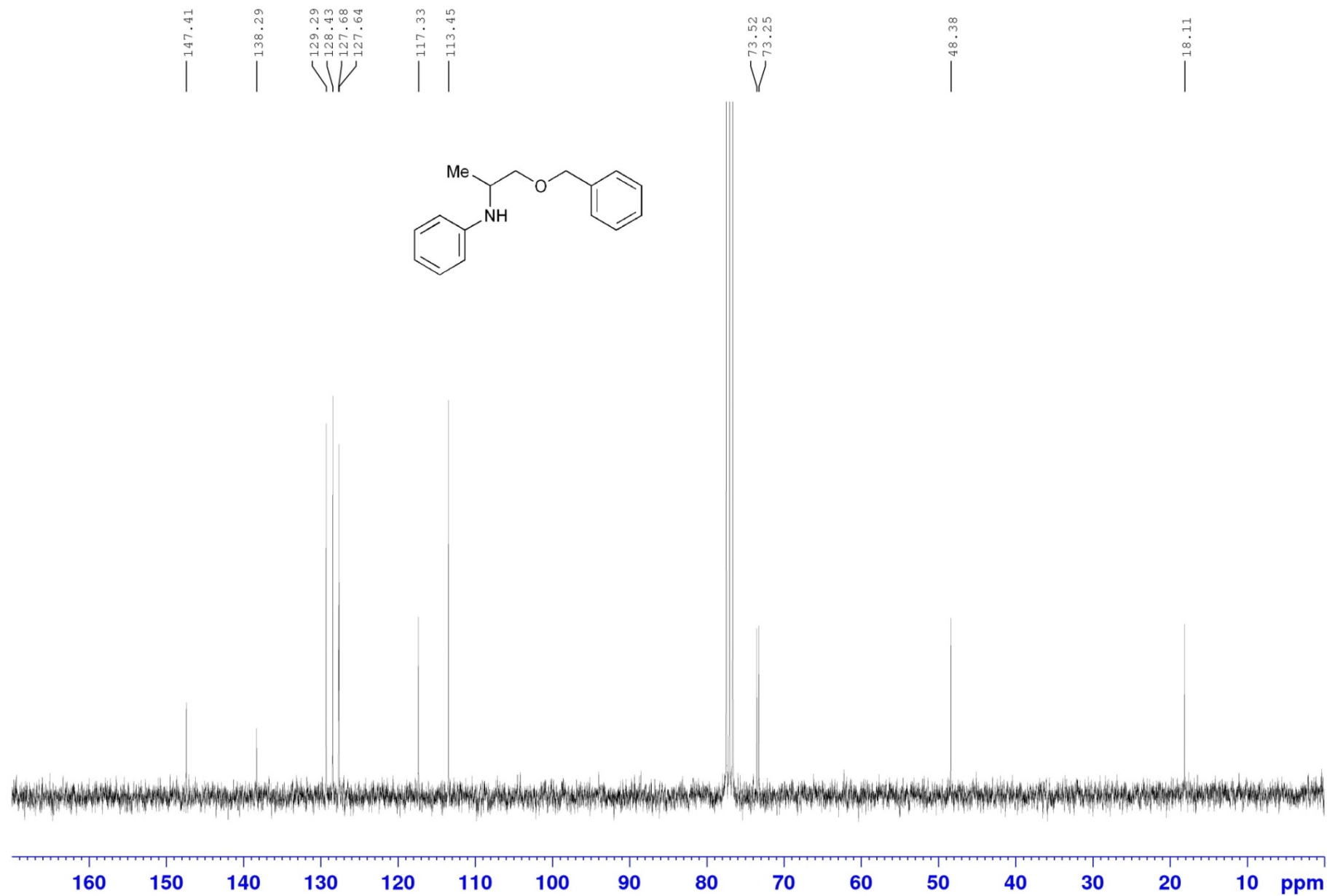
^{13}C NMR of **11c**



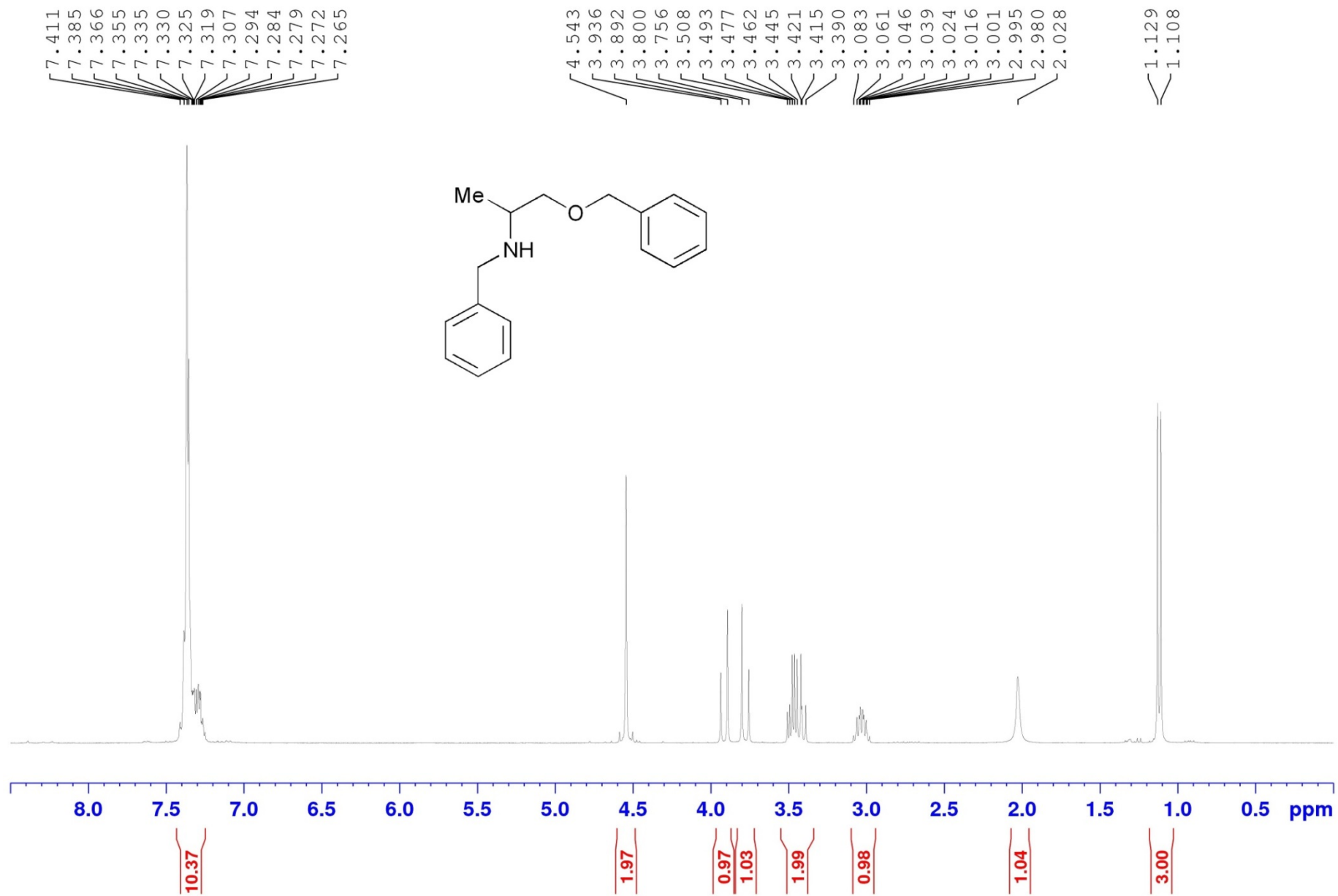
¹H NMR of **12a**



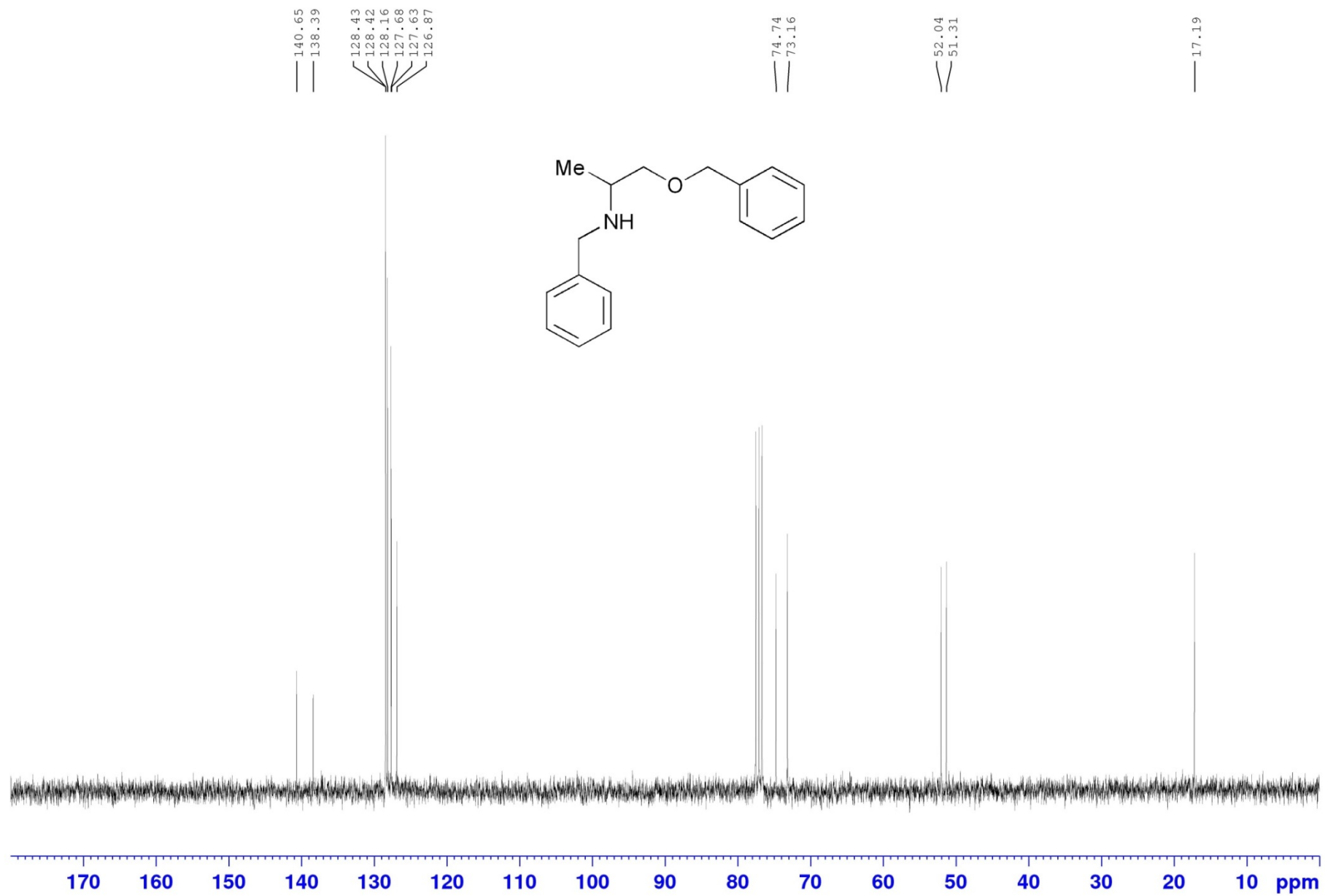
¹³C NMR of **12a**



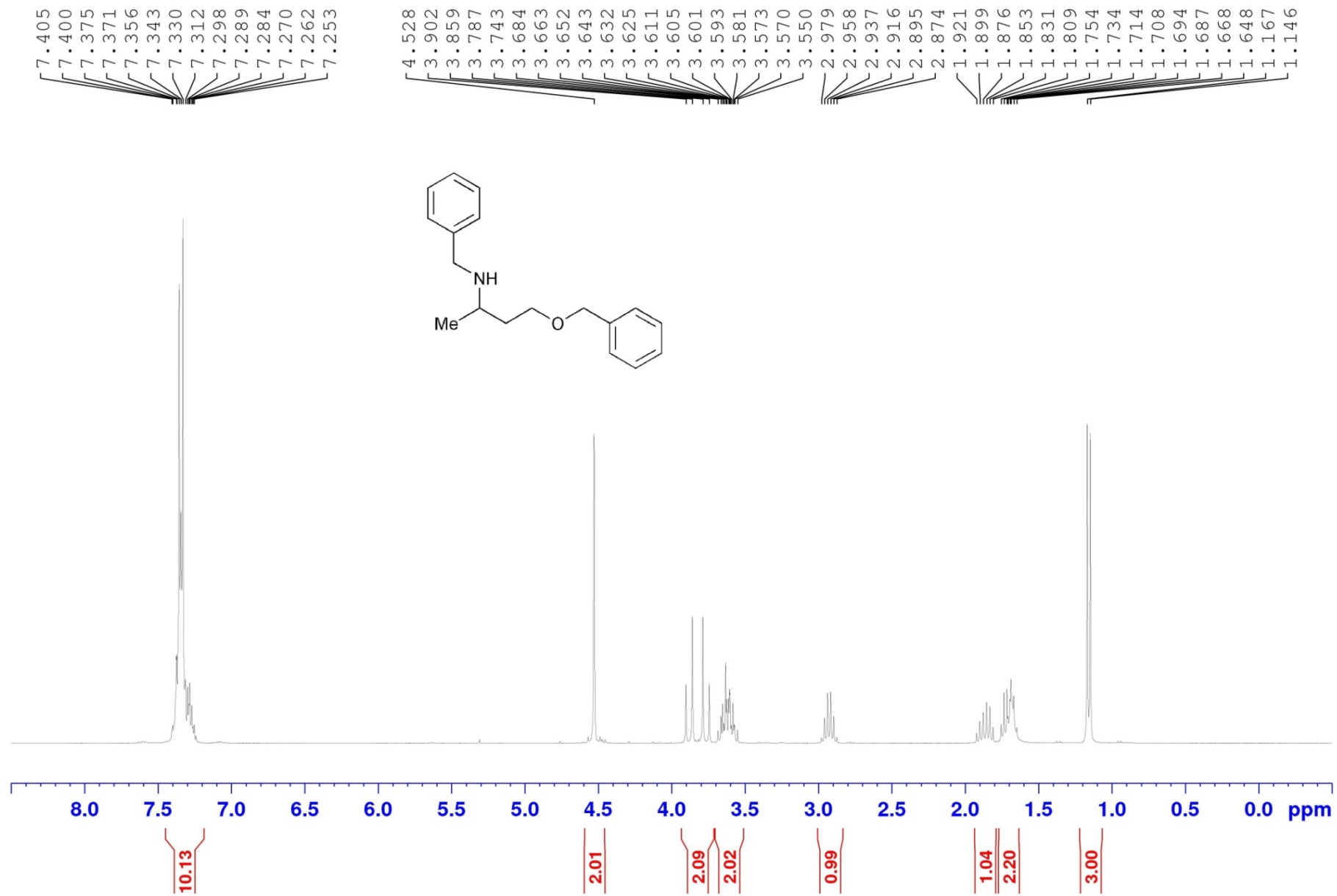
¹H NMR of **12b**



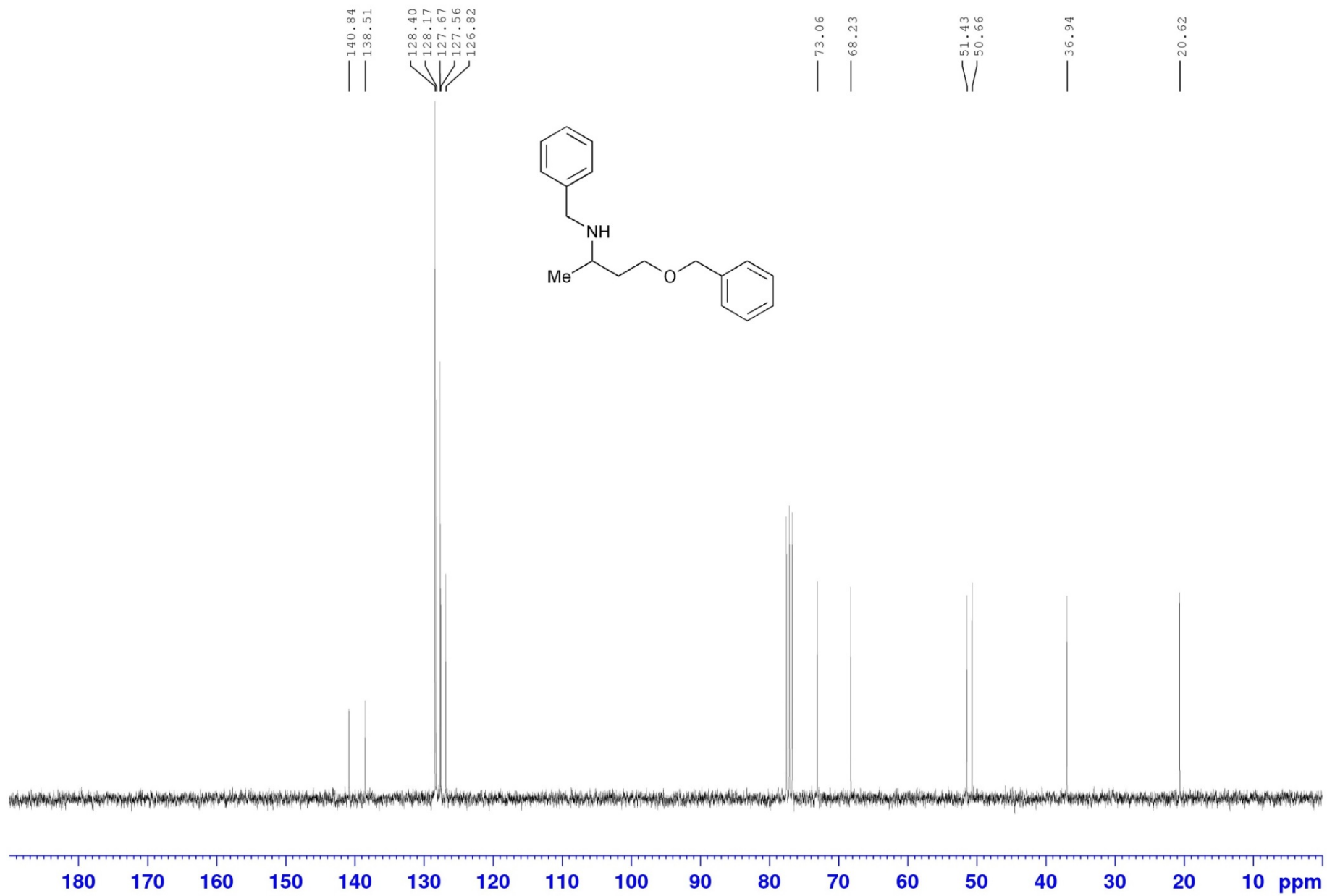
^{13}C NMR of **12b**



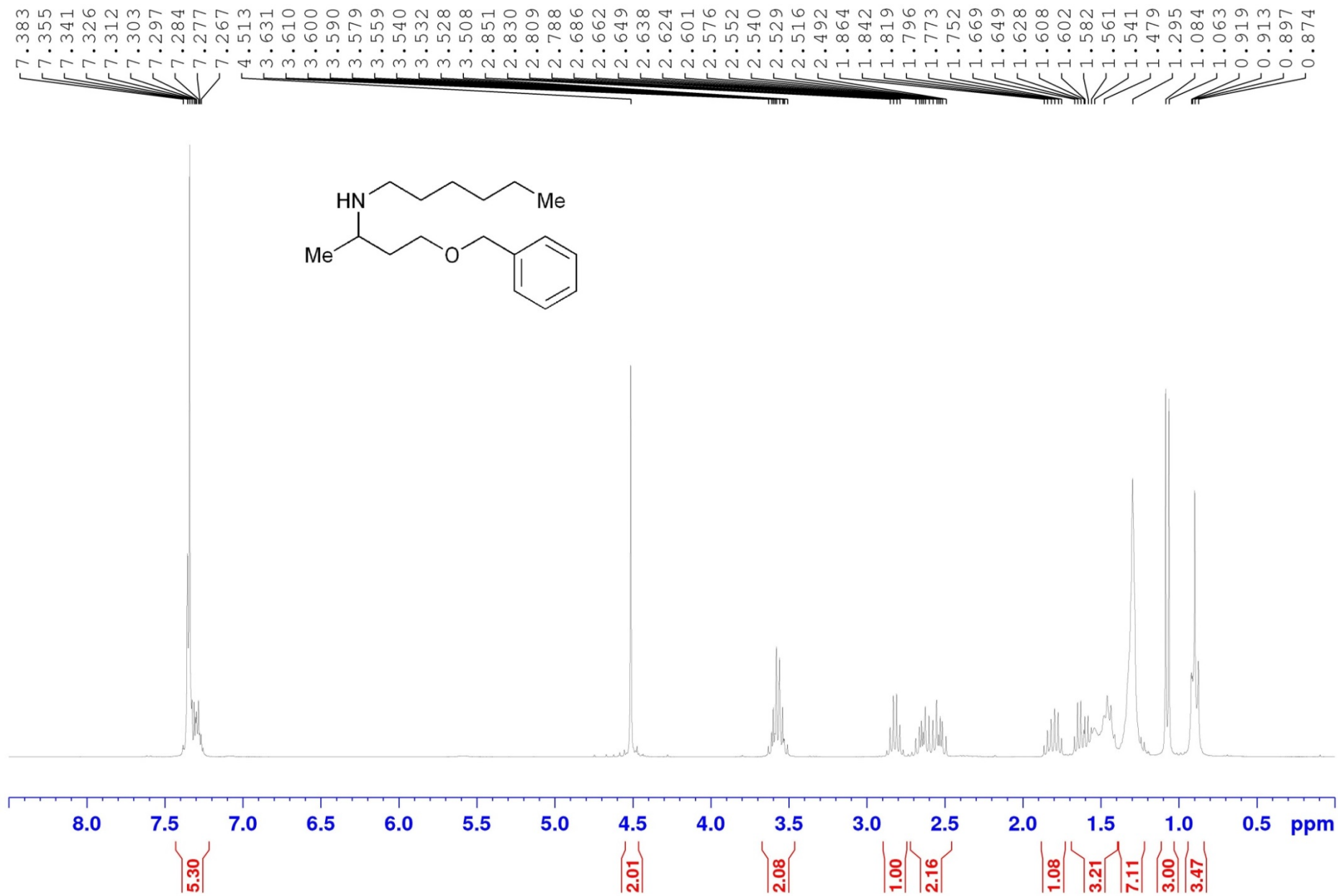
¹H NMR of 12c



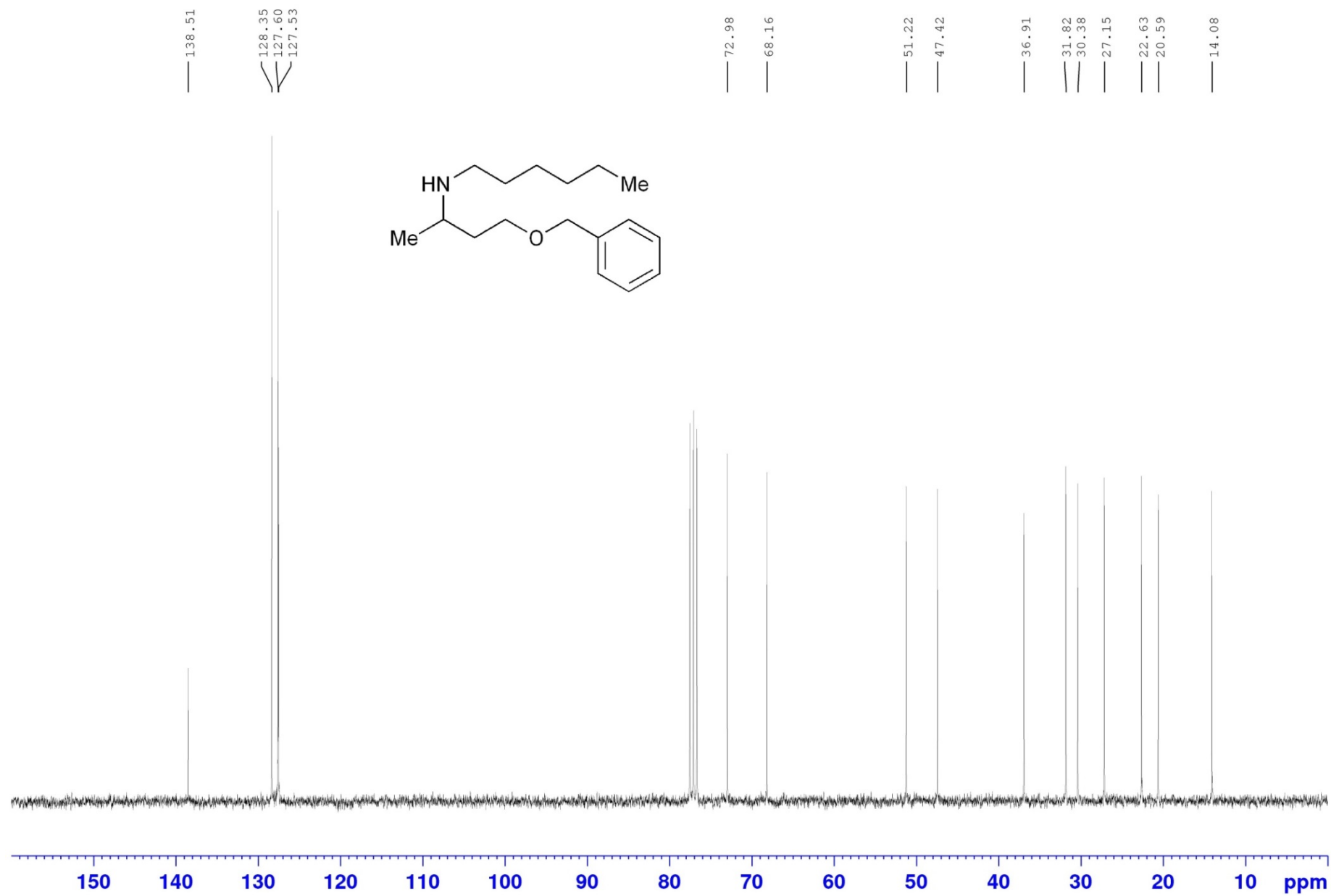
^{13}C NMR of **12c**



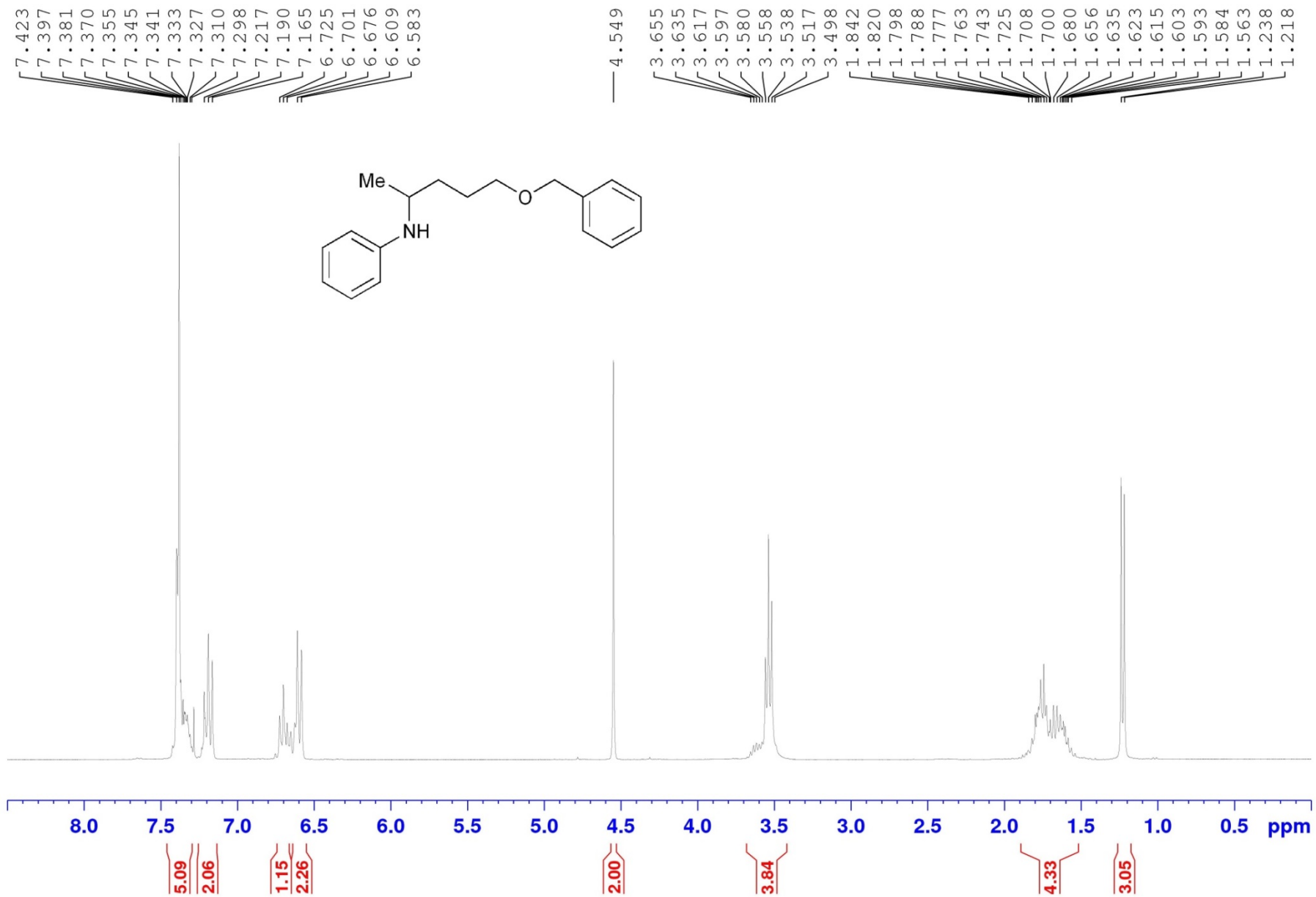
¹H NMR of **12d**



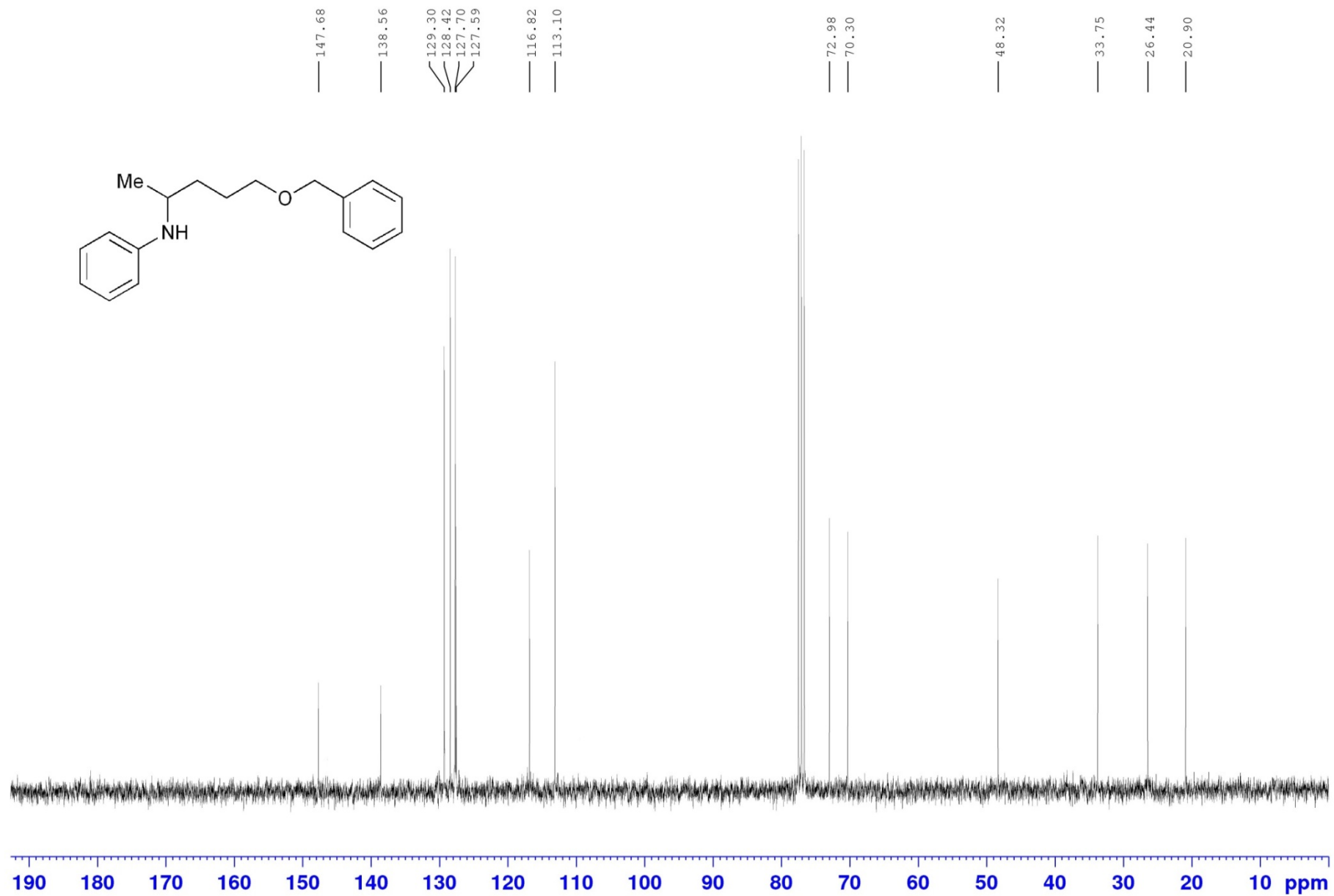
¹³C NMR of **12d**



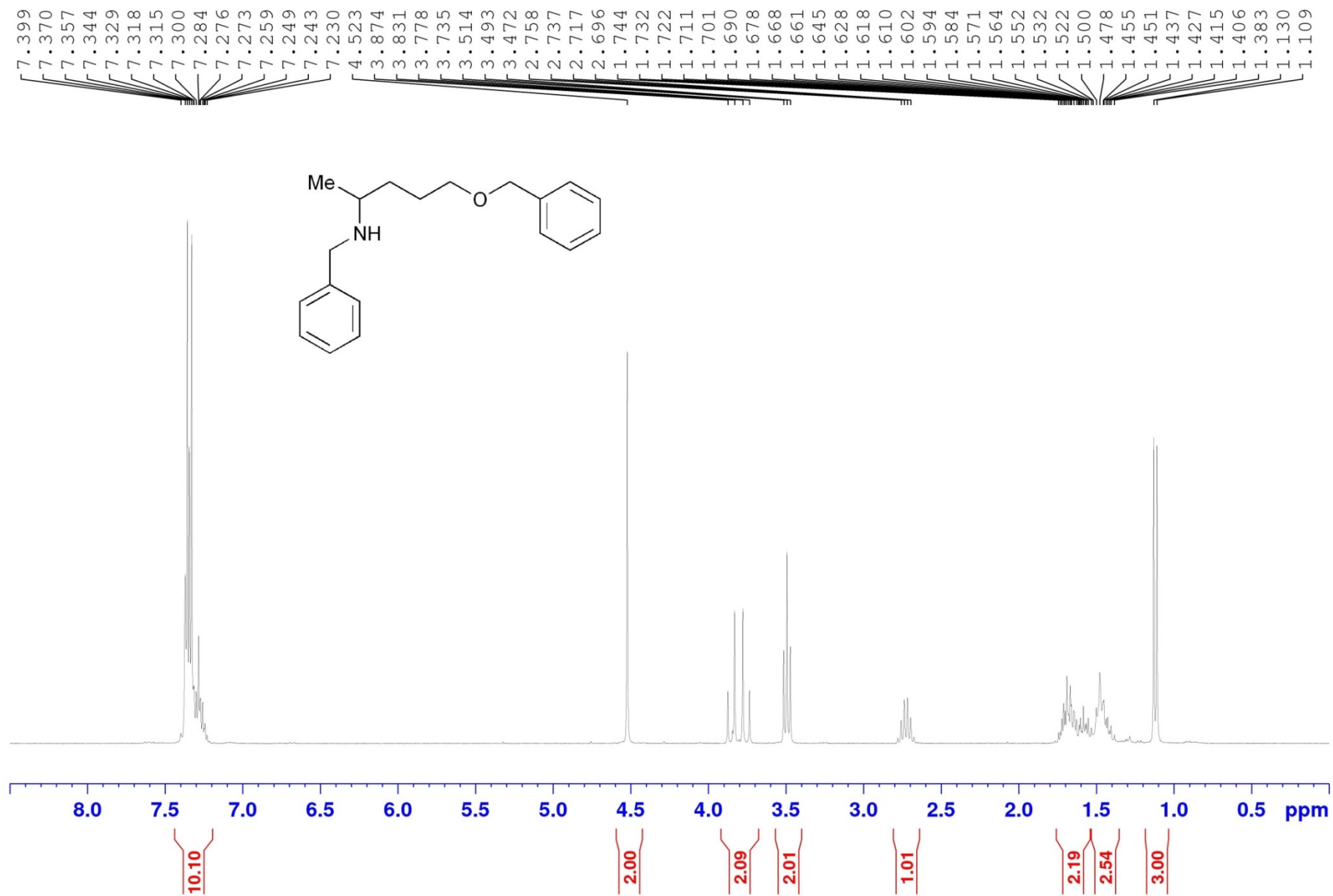
¹H NMR of 12e



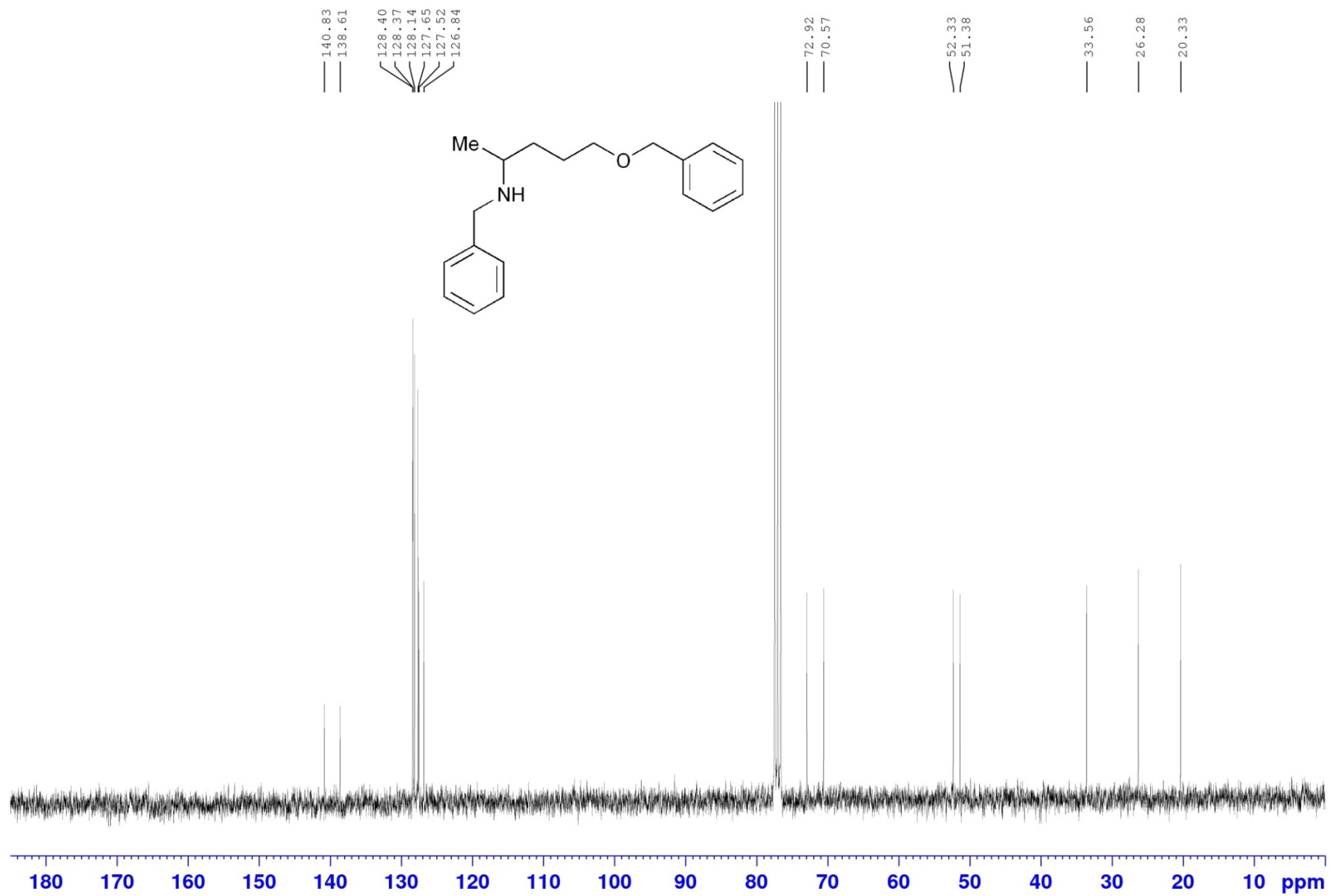
^{13}C NMR of **12e**



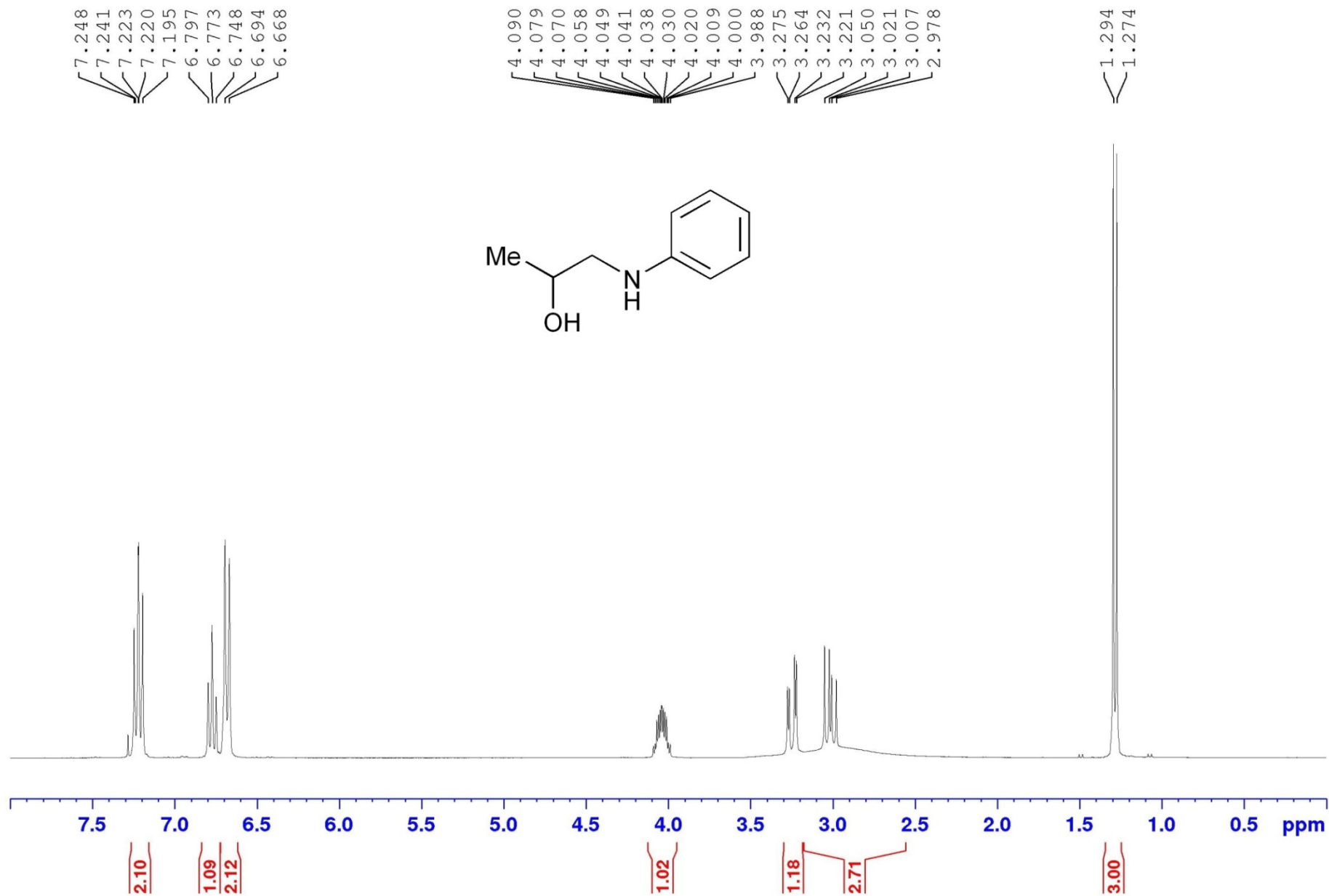
¹H NMR of **12f**



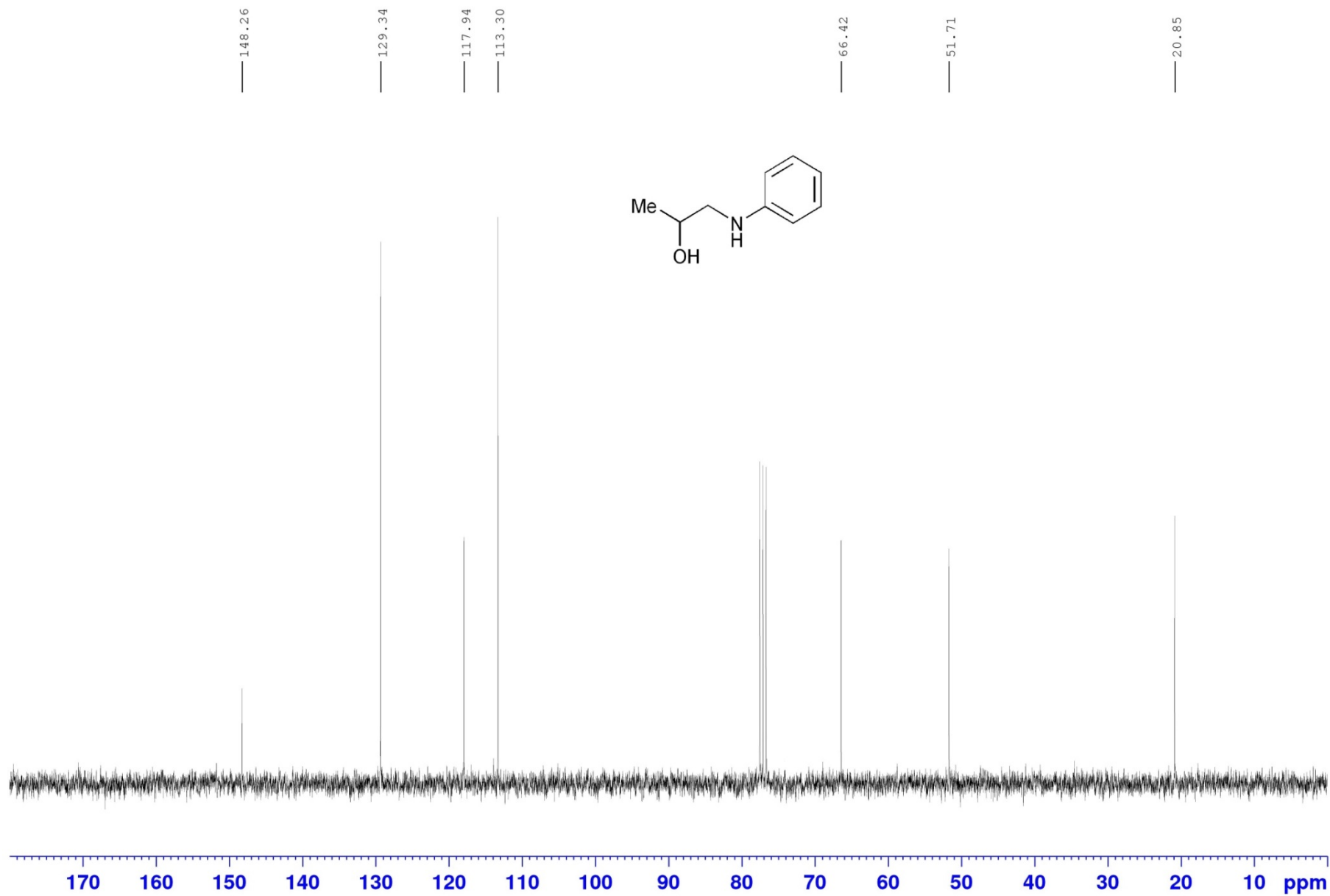
^{13}C NMR of **12f**



¹H NMR of **14a**



^{13}C NMR of **14a**

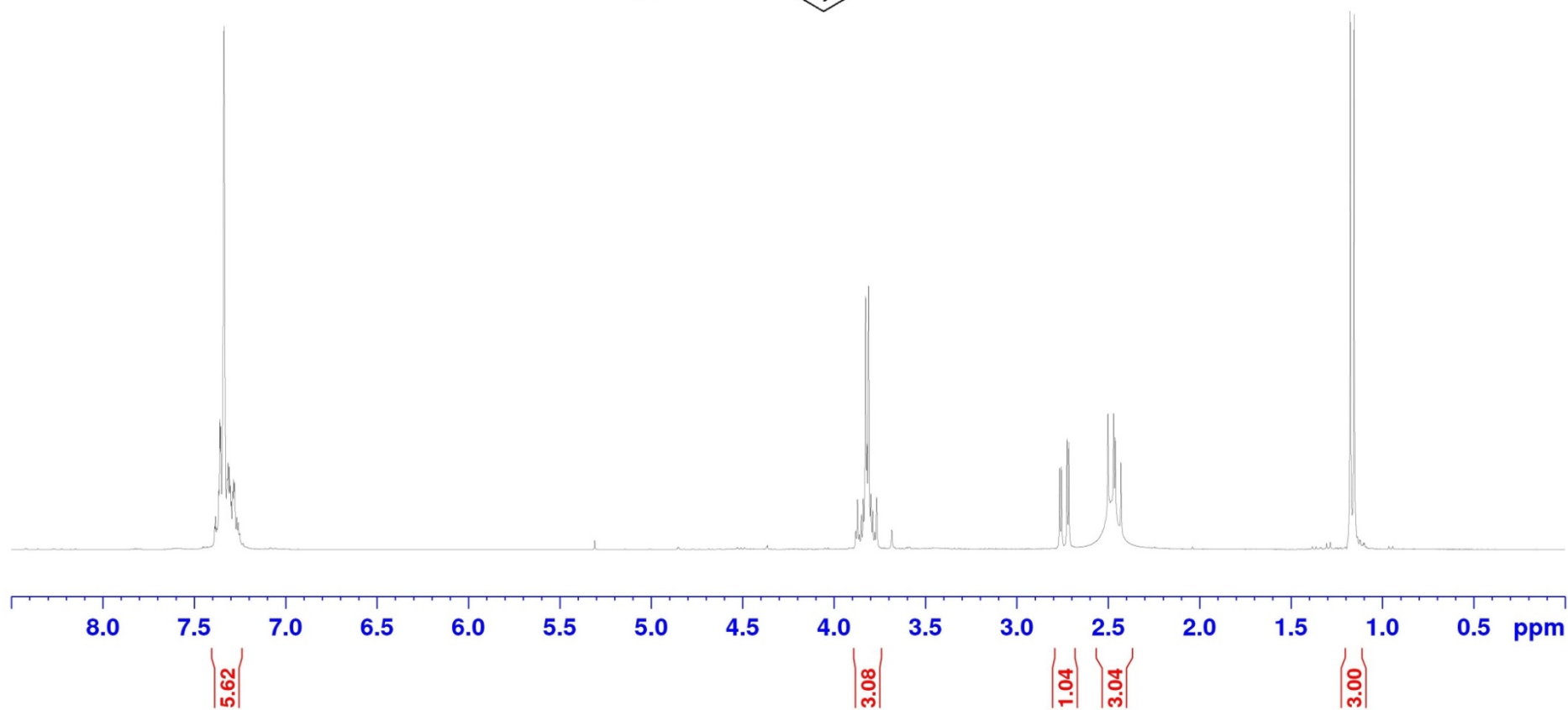
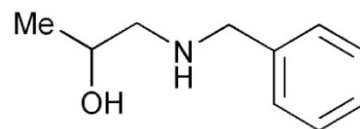


¹H NMR of 14b

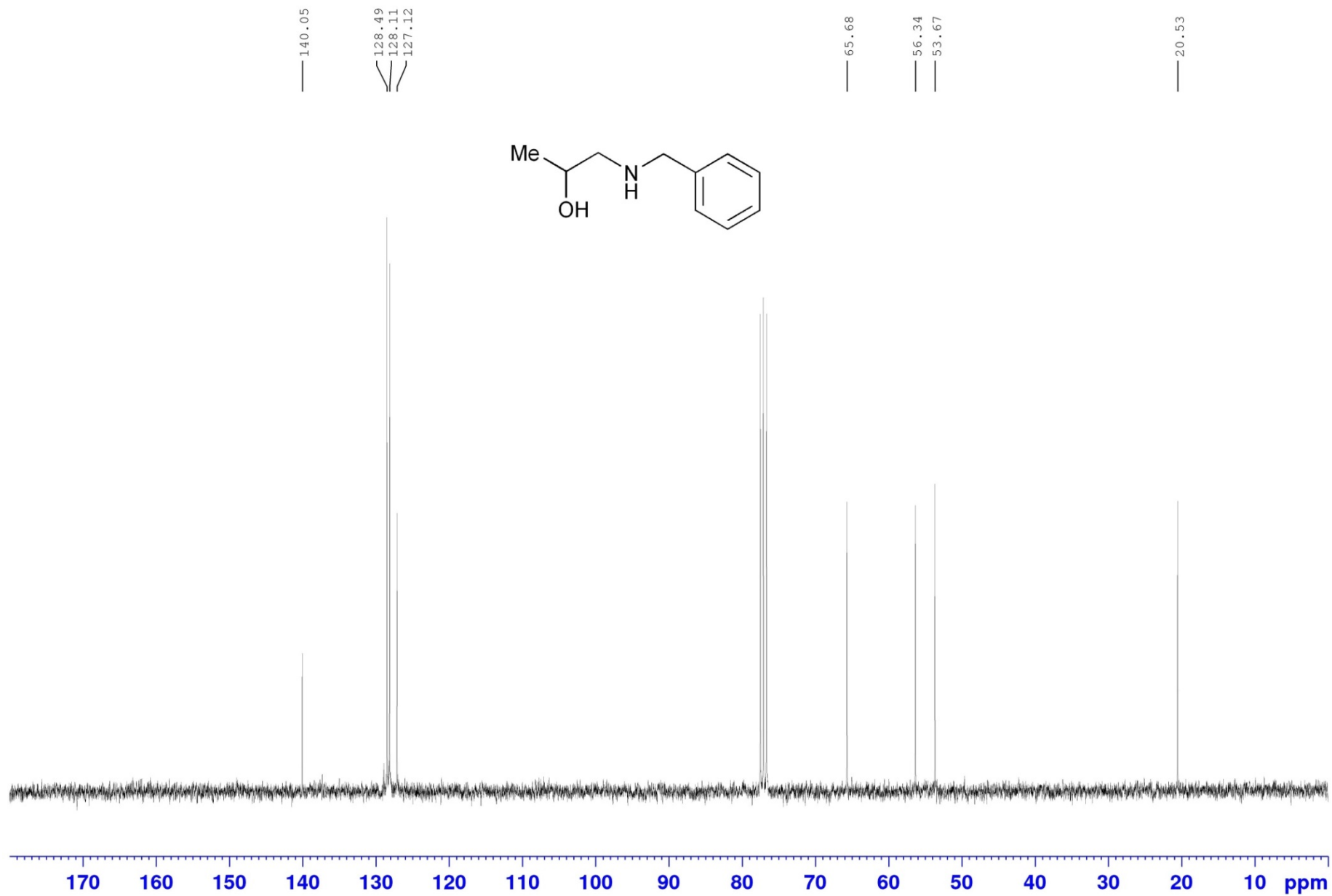
7.384
7.378
7.365
7.360
7.355
7.337
7.321
7.315
7.308
7.302
7.297
7.289
7.284
7.279
7.267
7.259
7.251

3.881
3.871
3.861
3.850
3.840
3.827
3.819
3.810
3.798
3.788
3.777
3.767
2.765
2.755
2.725
2.715
2.501
2.470
2.461
2.430

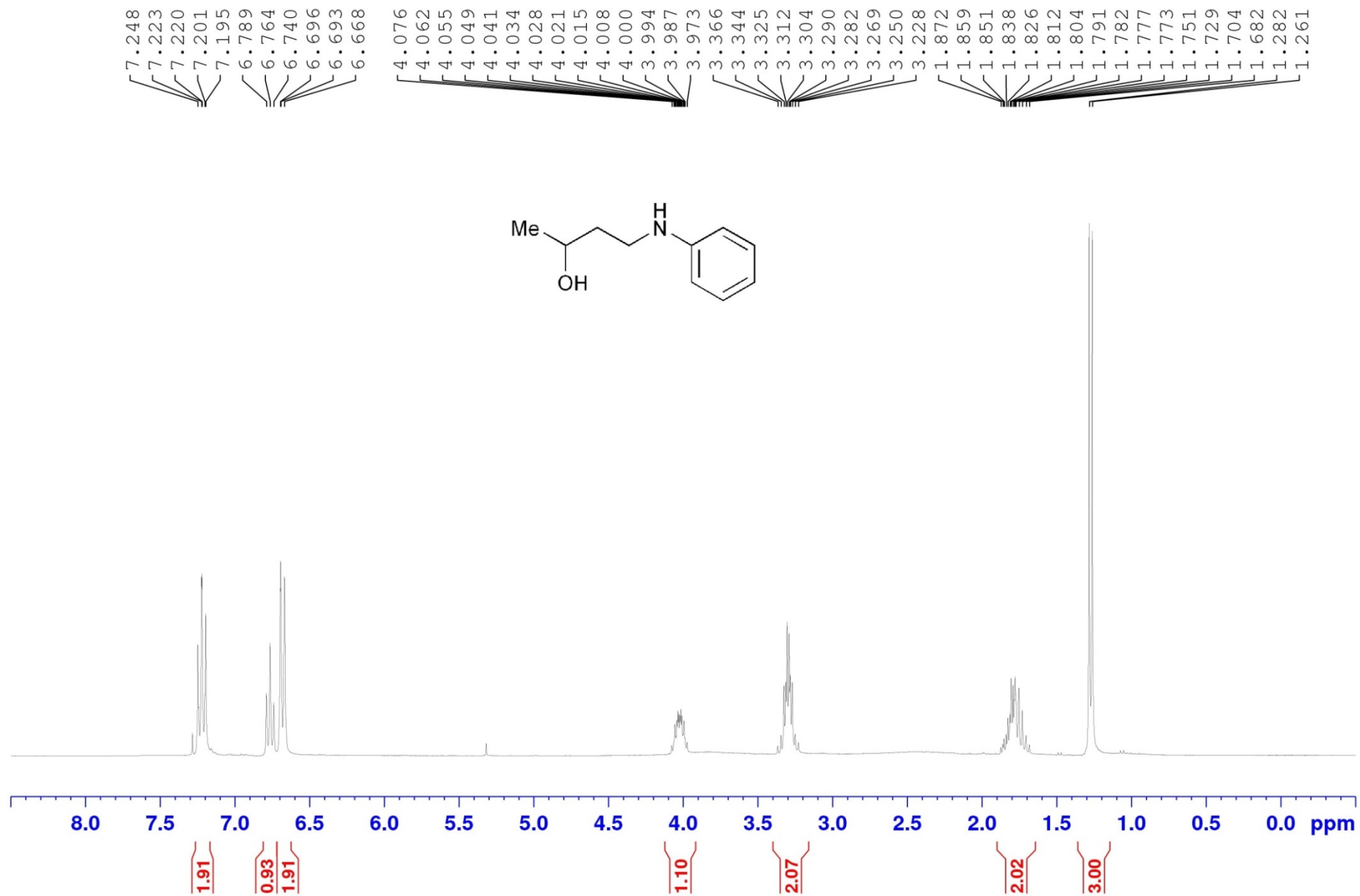
1.175
1.154



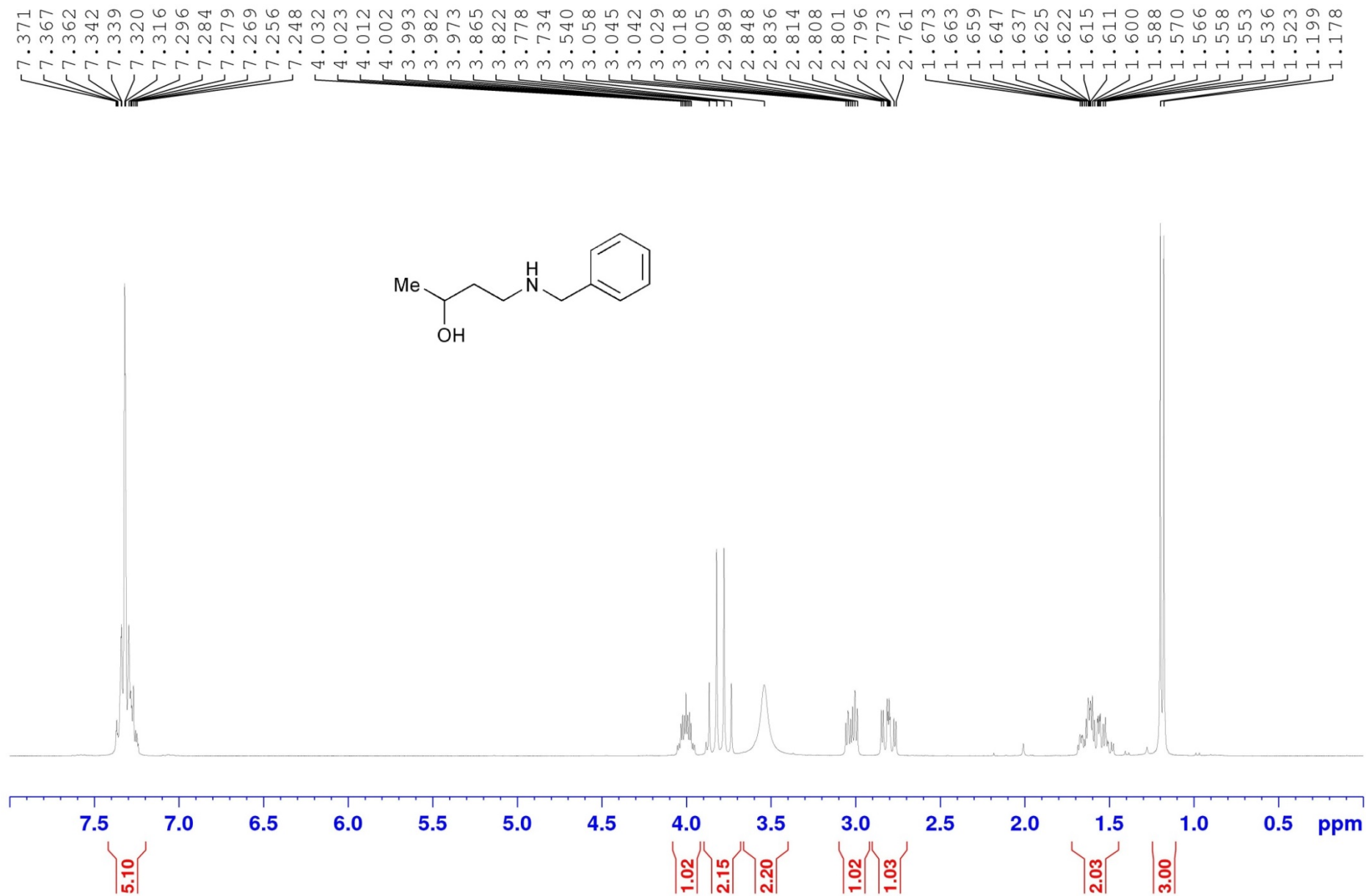
^{13}C NMR of **14b**



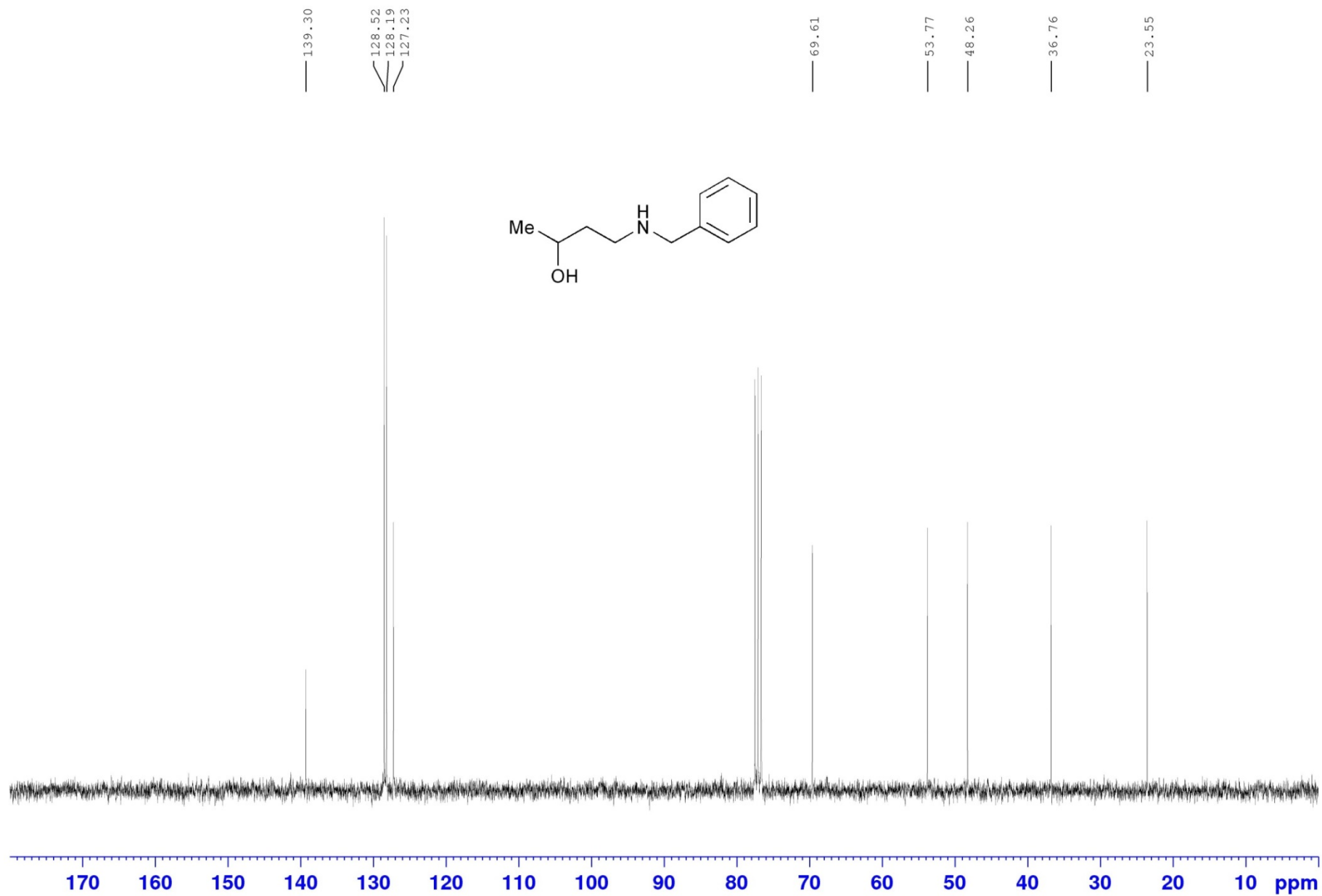
¹H NMR of 14c



¹H NMR of 14d



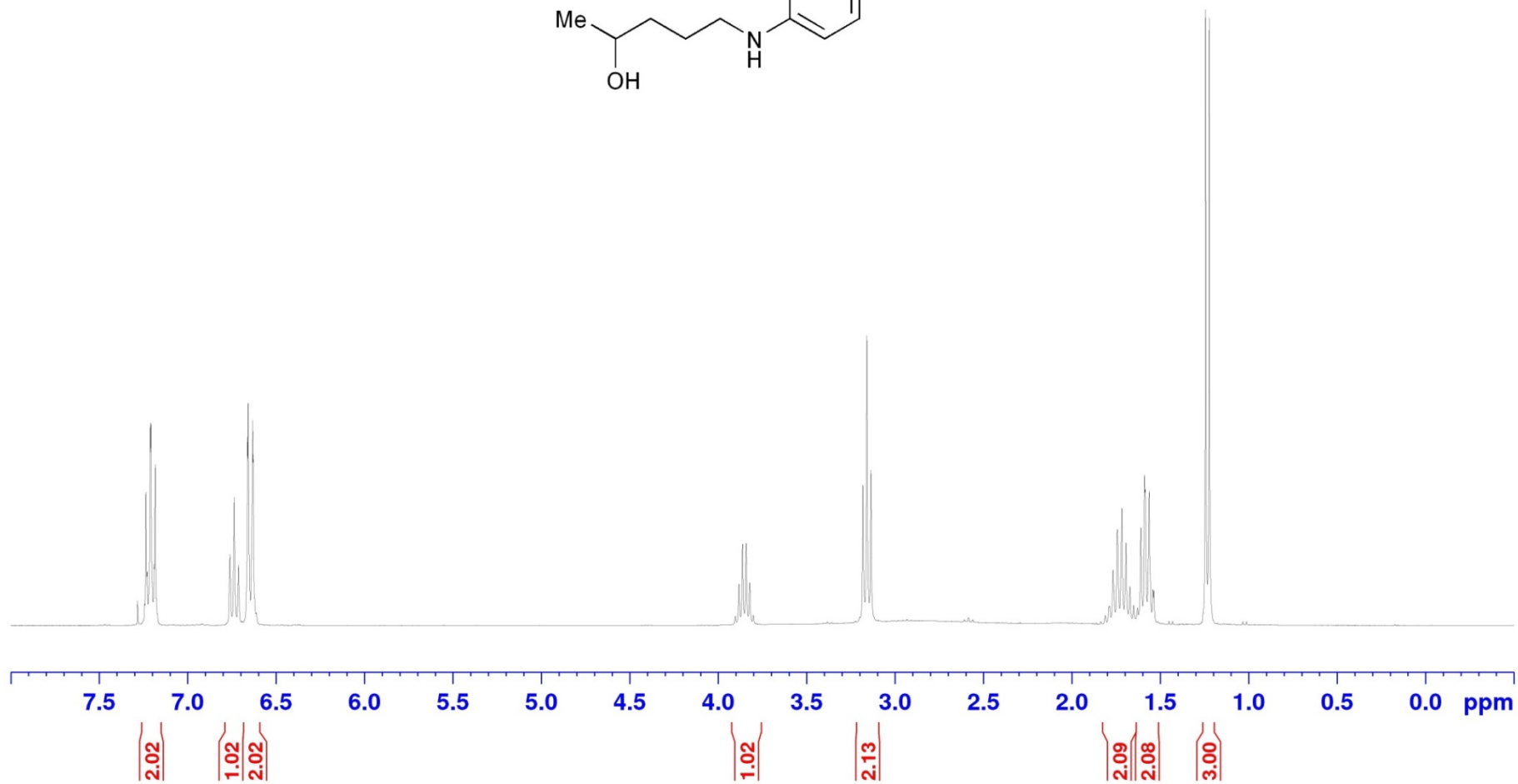
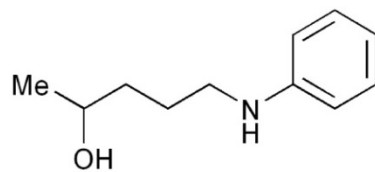
^{13}C NMR of **14d**



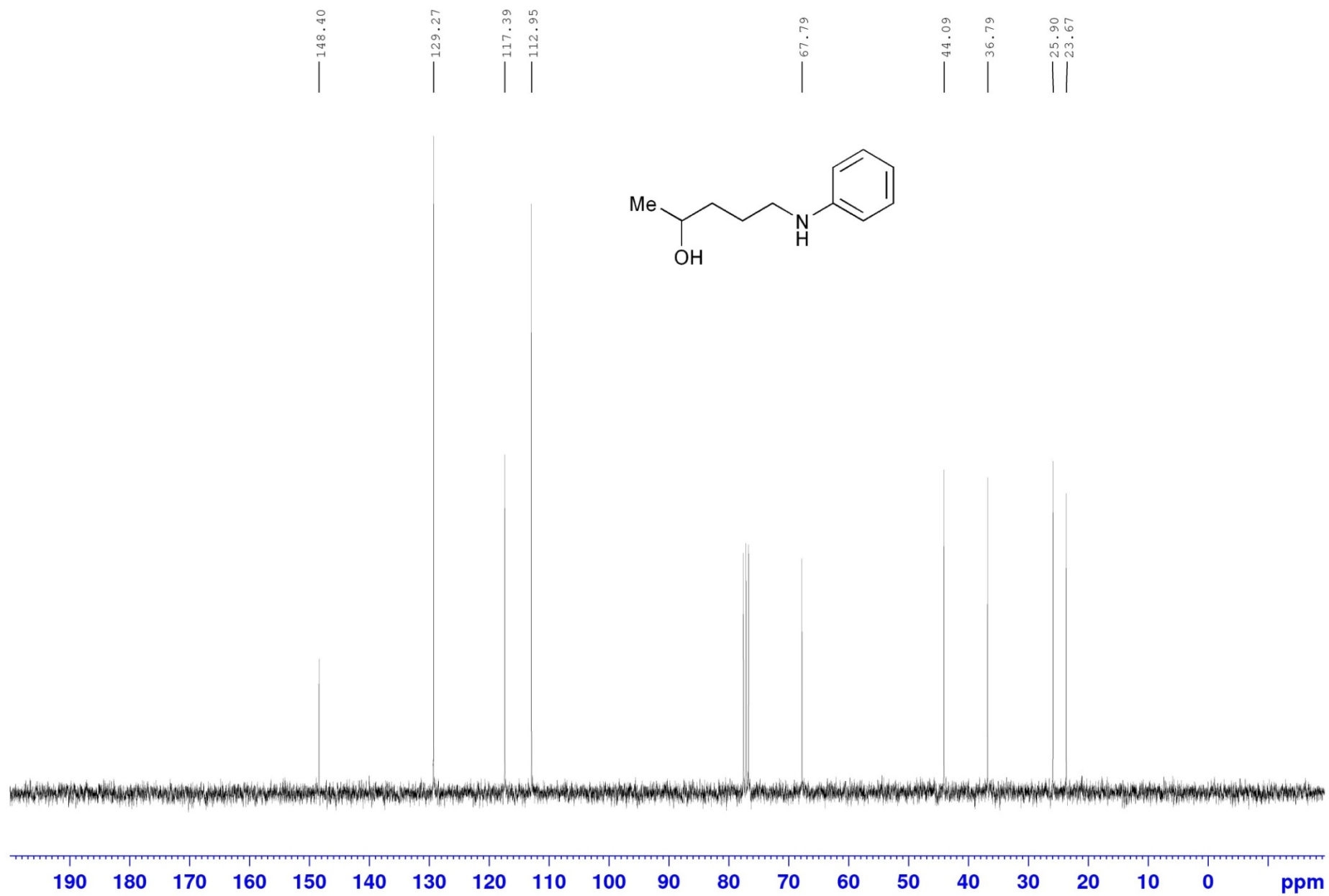
¹H NMR of 14e

7.237
7.230
7.212
7.209
7.190
7.184
6.762
6.738
6.713
6.662
6.659
6.633
6.630

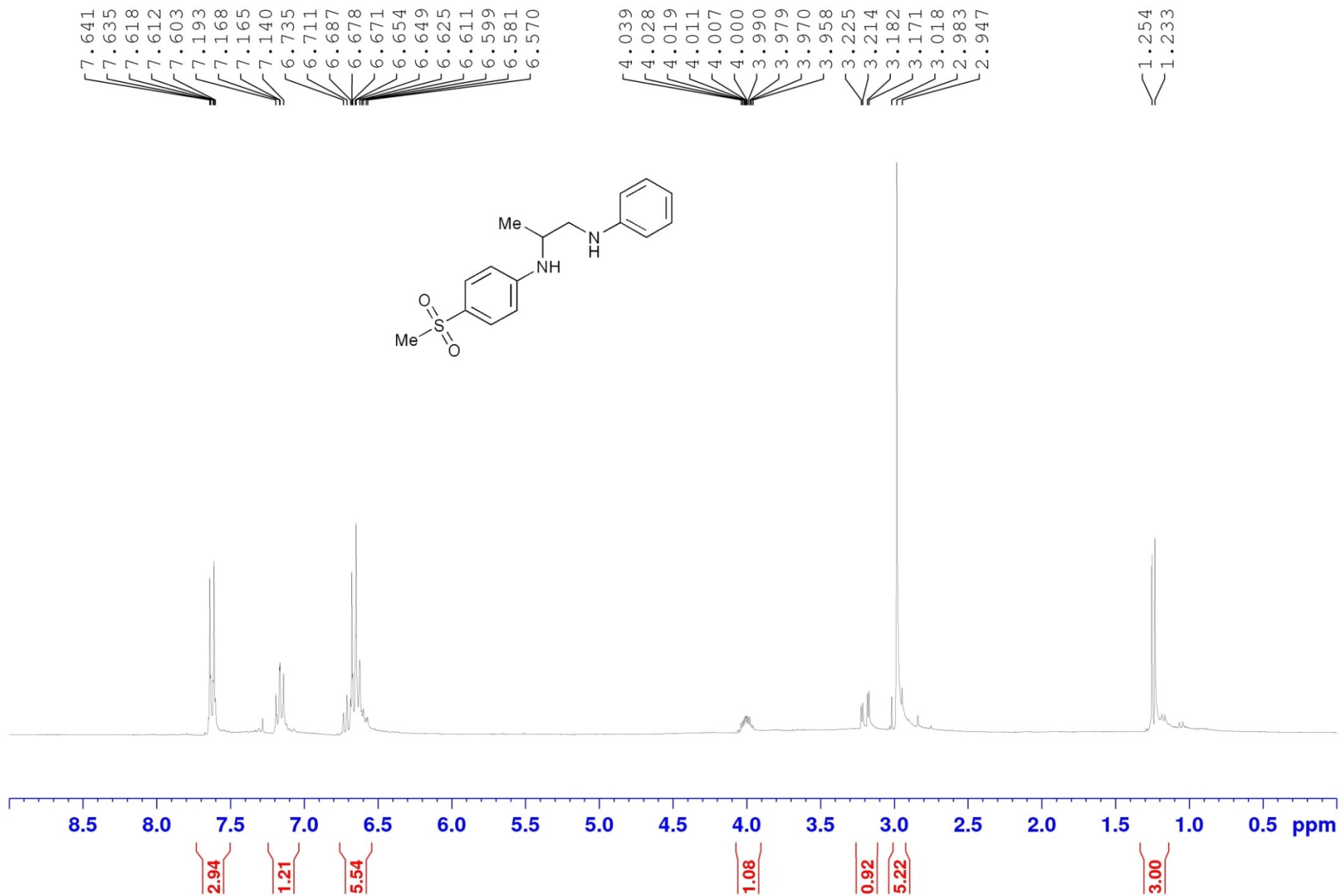
3.904
3.883
3.863
3.842
3.822
3.802
3.182
3.160
3.137
1.811
1.792
1.788
1.768
1.743
1.717
1.694
1.672
1.651
1.629
1.610
1.589
1.586
1.563
1.542
1.536
1.244
1.223



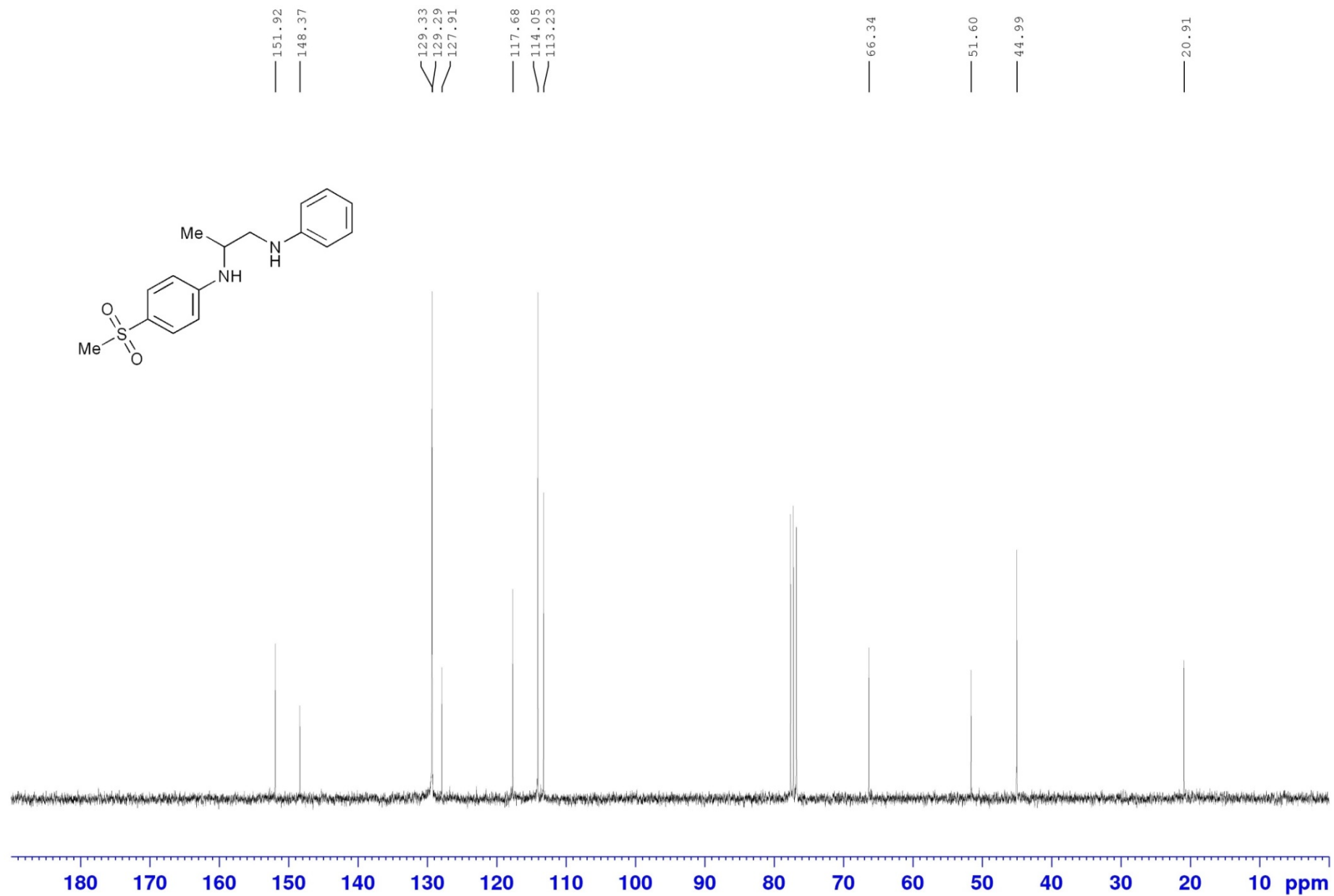
¹³C NMR of **14e**



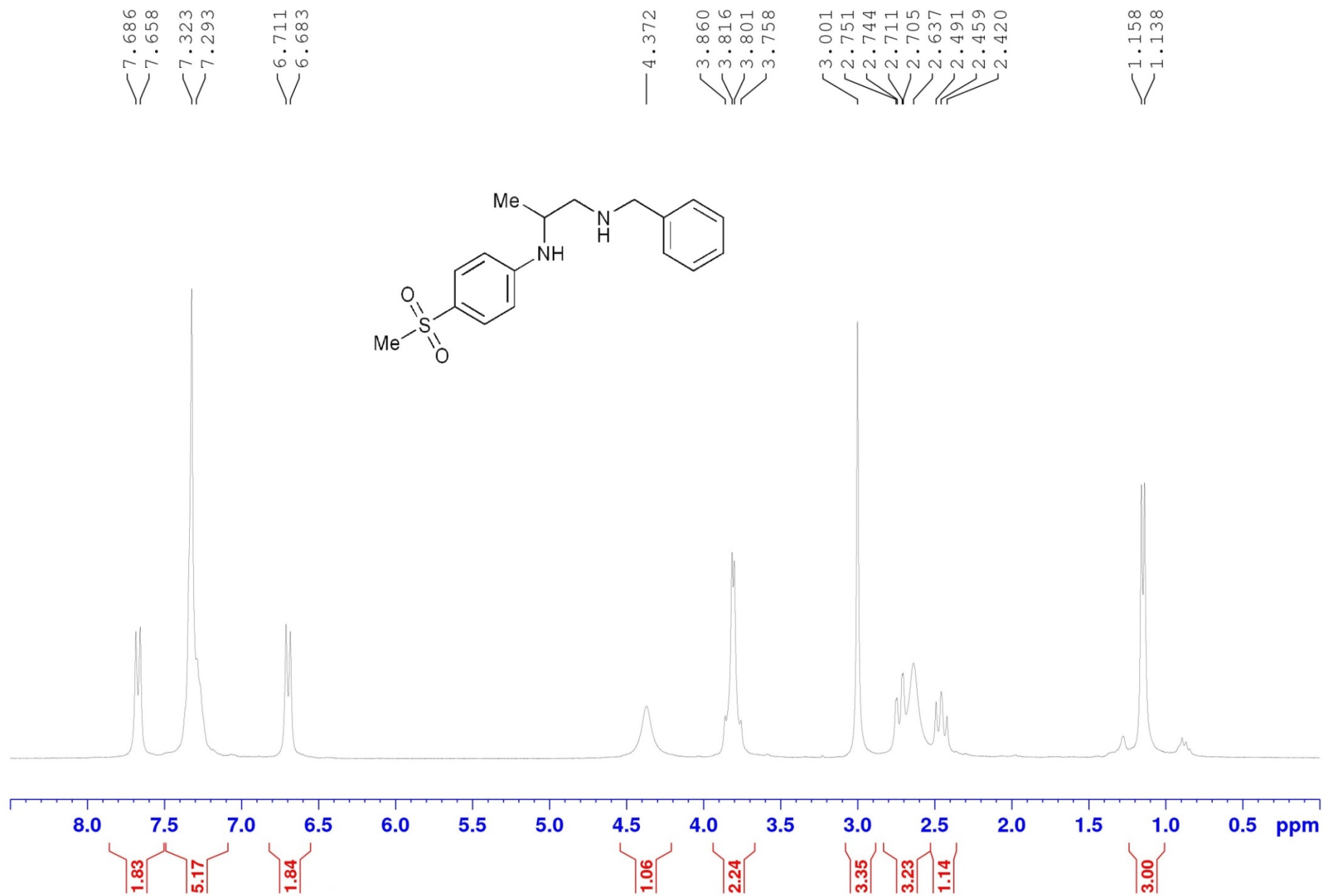
¹H NMR of **15a**



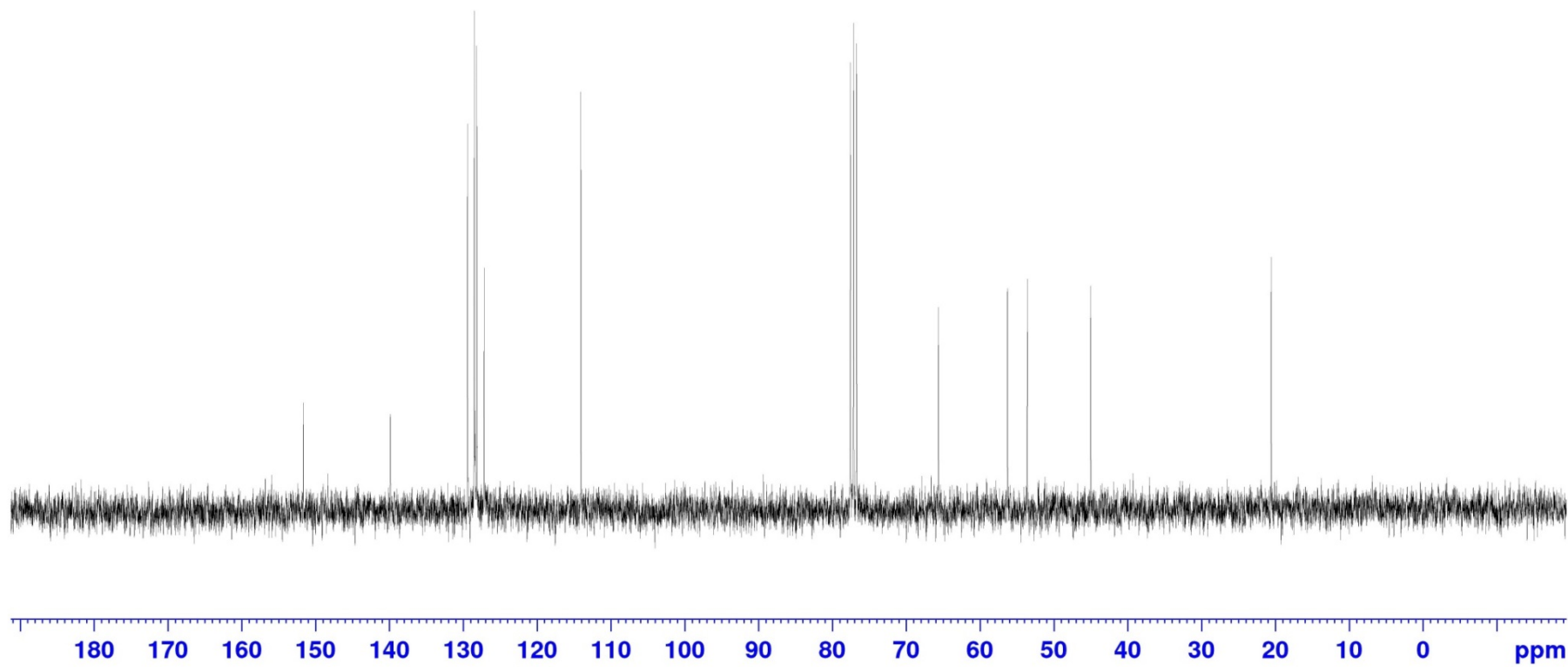
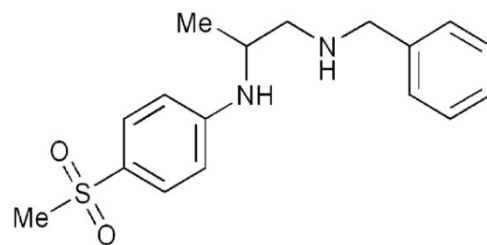
^{13}C NMR of **15a**



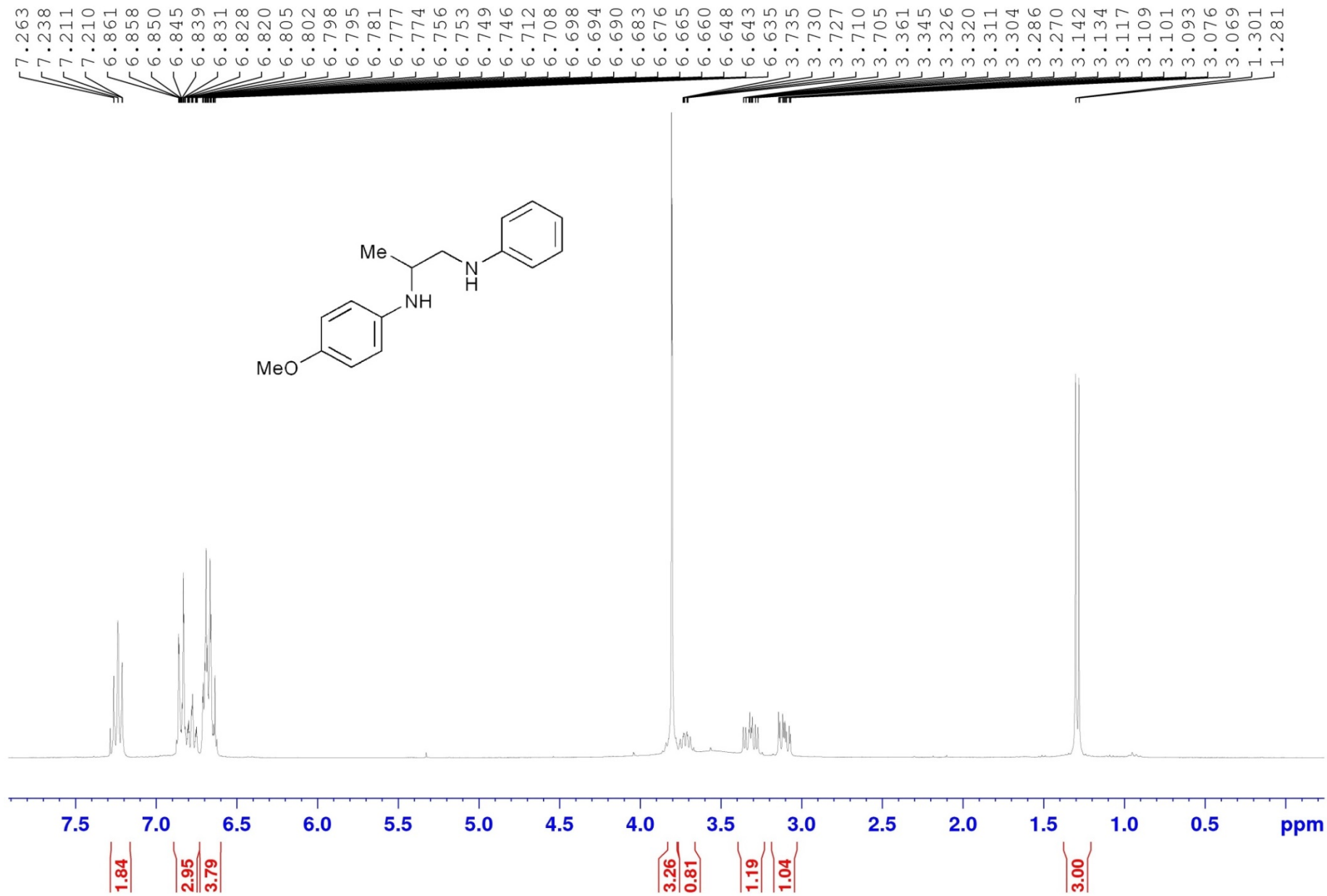
¹H NMR of **15b**



^{13}C NMR of **15b**



¹H NMR of **15c**



^{13}C NMR of **15c**

152.53
152.33
148.40
147.54
142.56
141.52

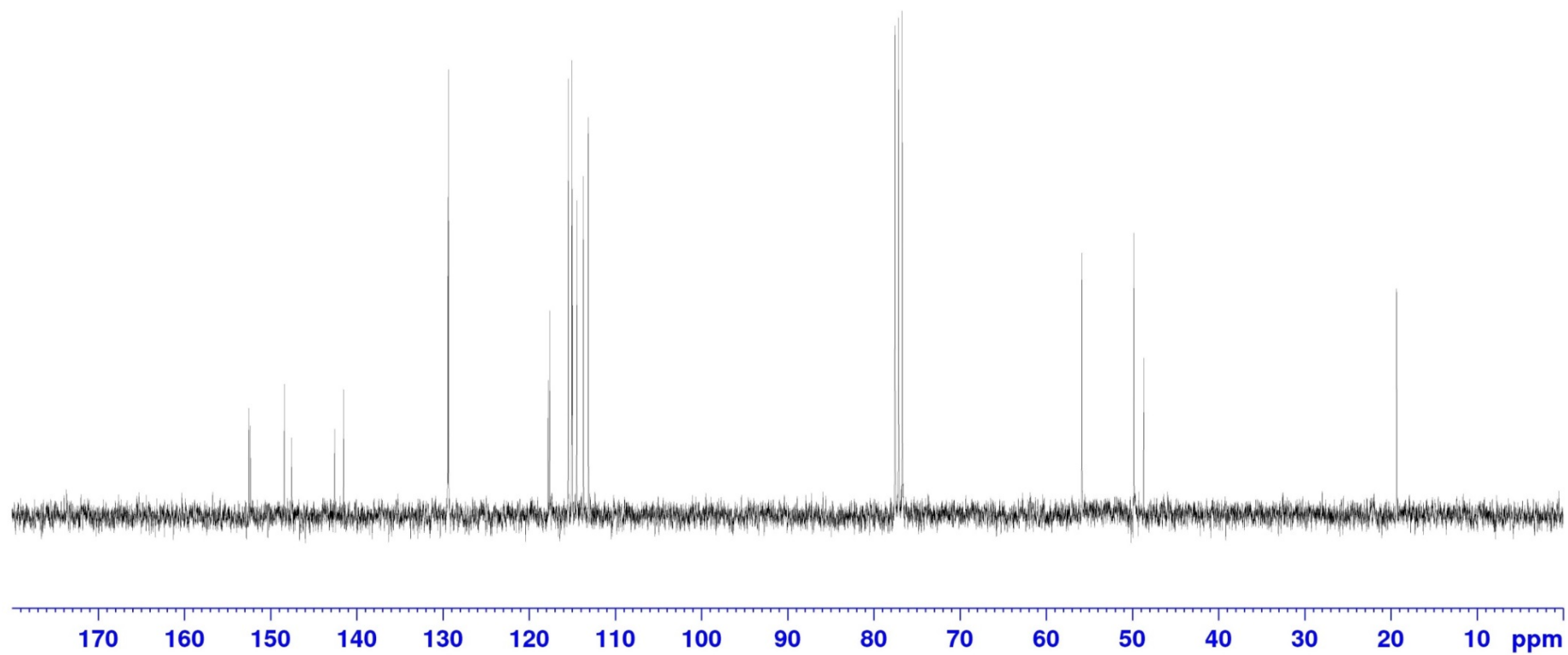
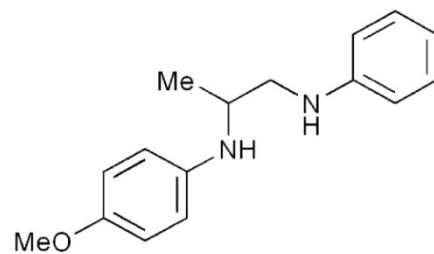
129.44
129.33

117.78
117.61
115.45
115.04
114.98
114.46
113.69
113.11

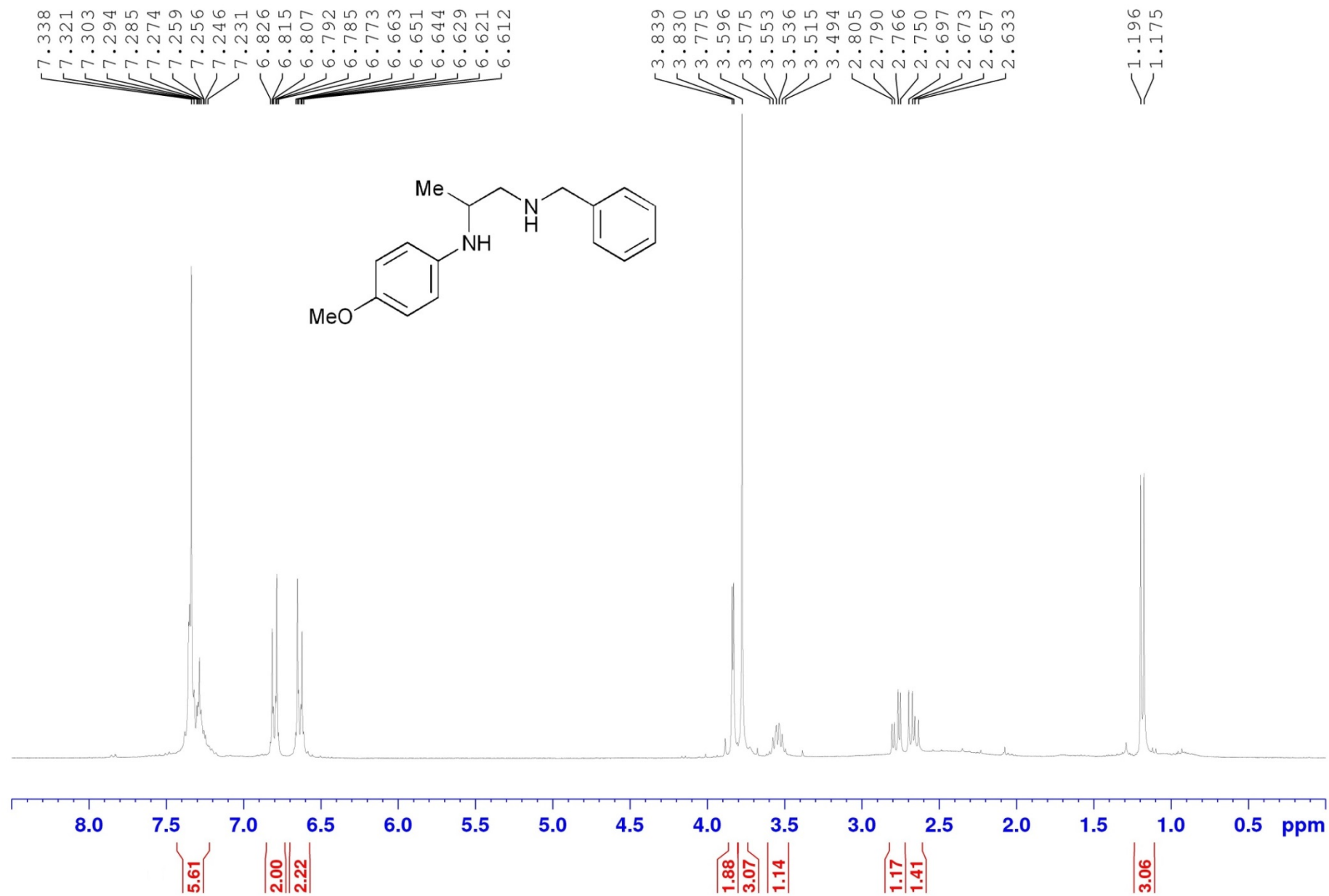
55.84

49.80
48.67

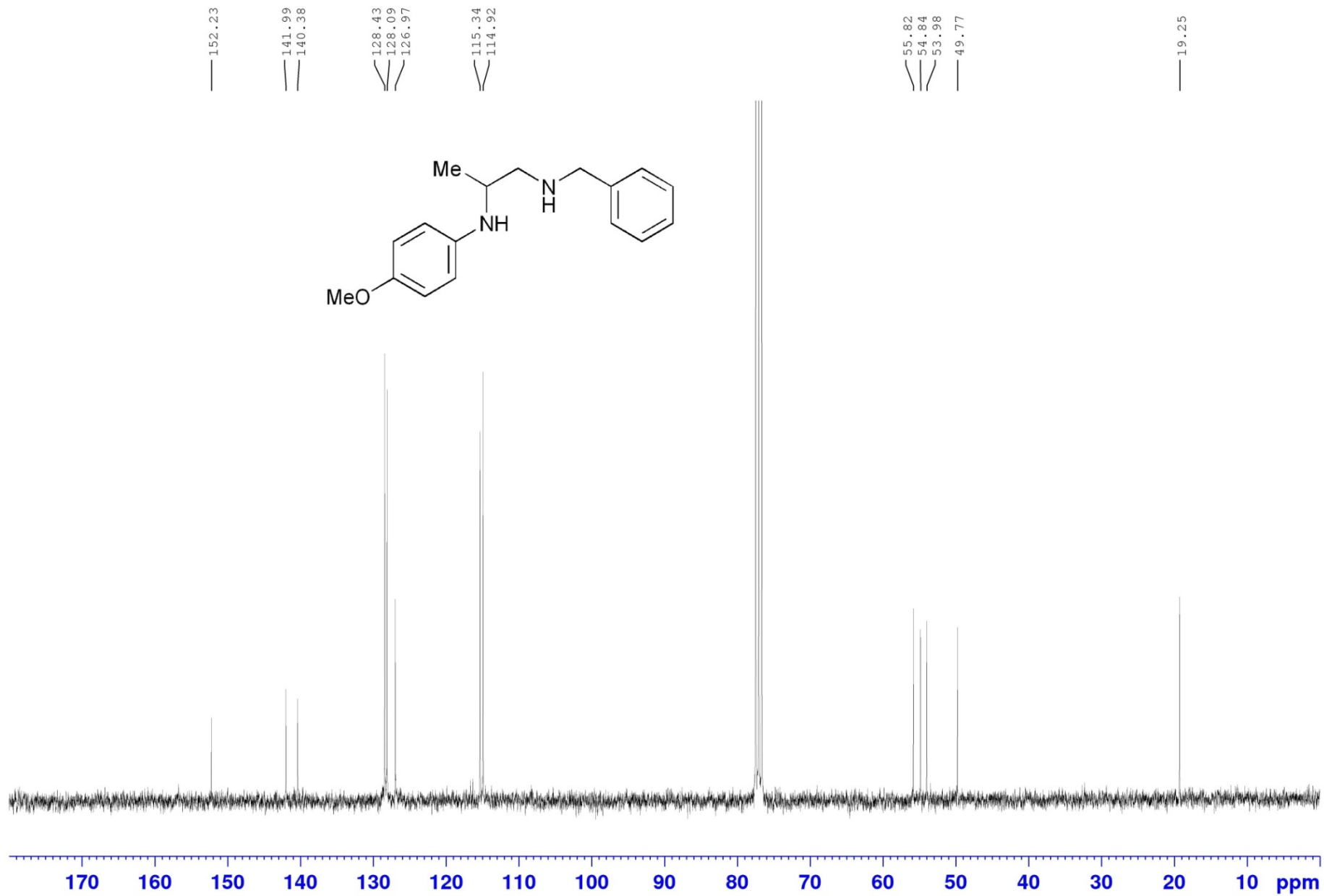
19.32



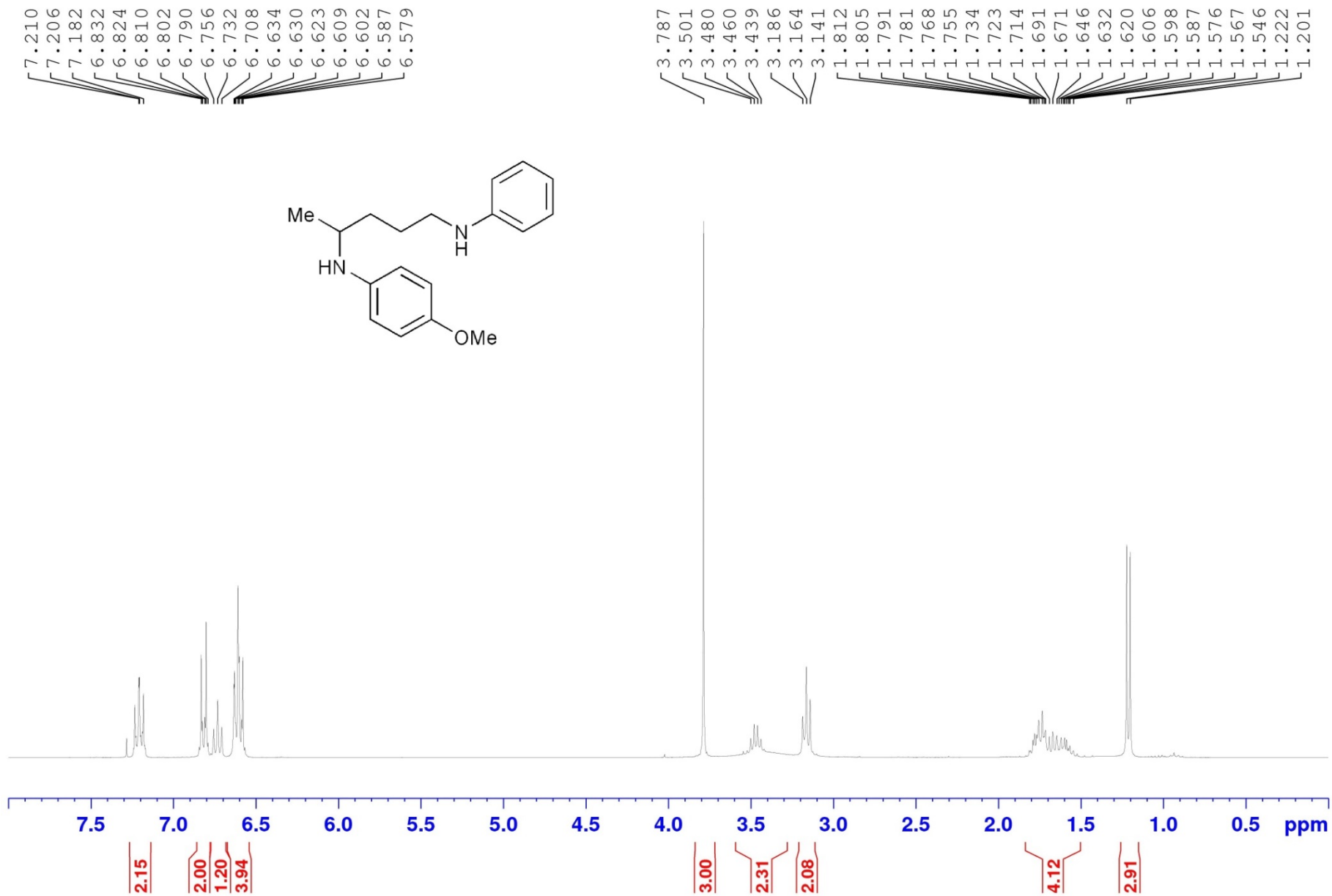
¹H NMR of 15d



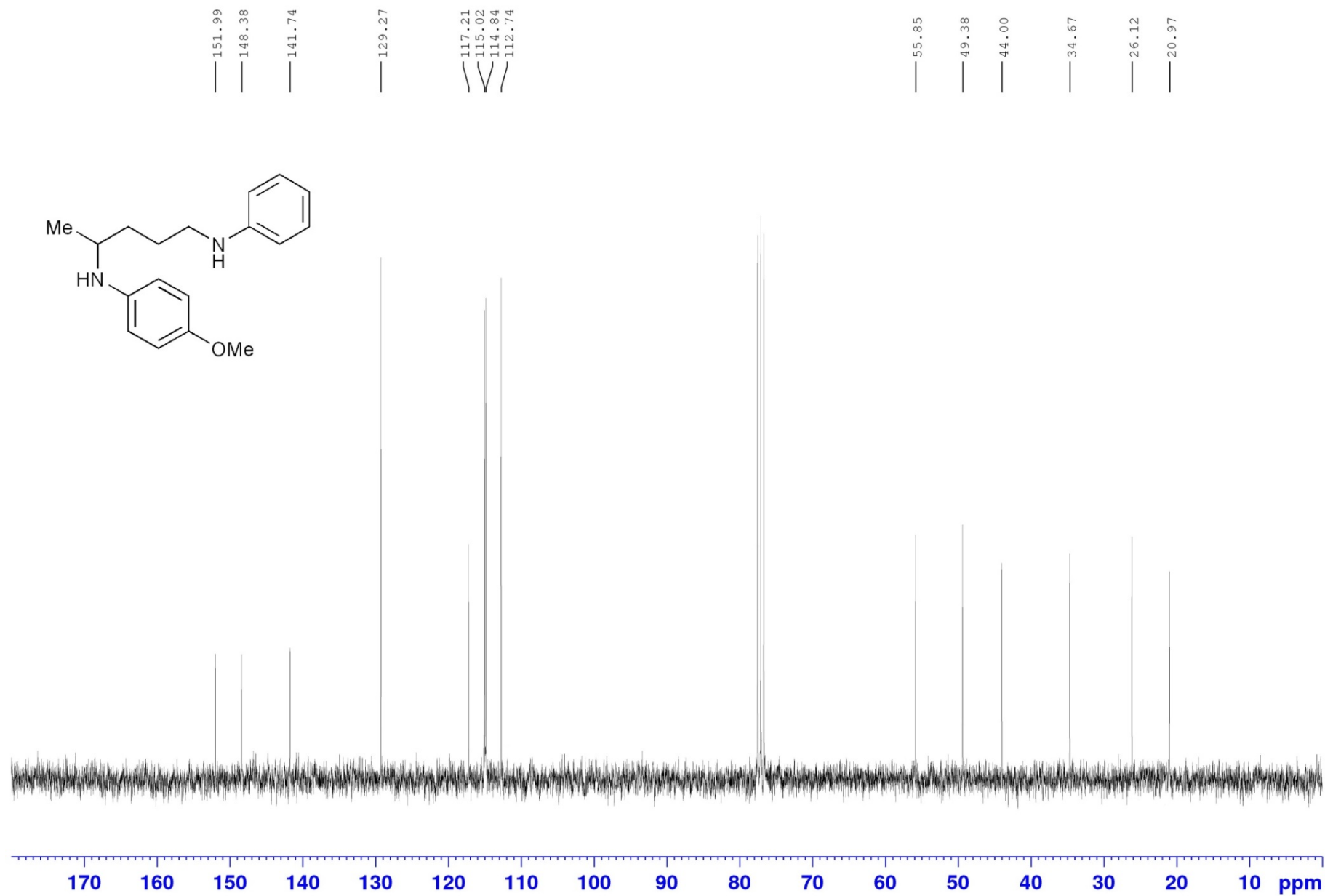
¹³C NMR of **15d**



¹H NMR of **15e**



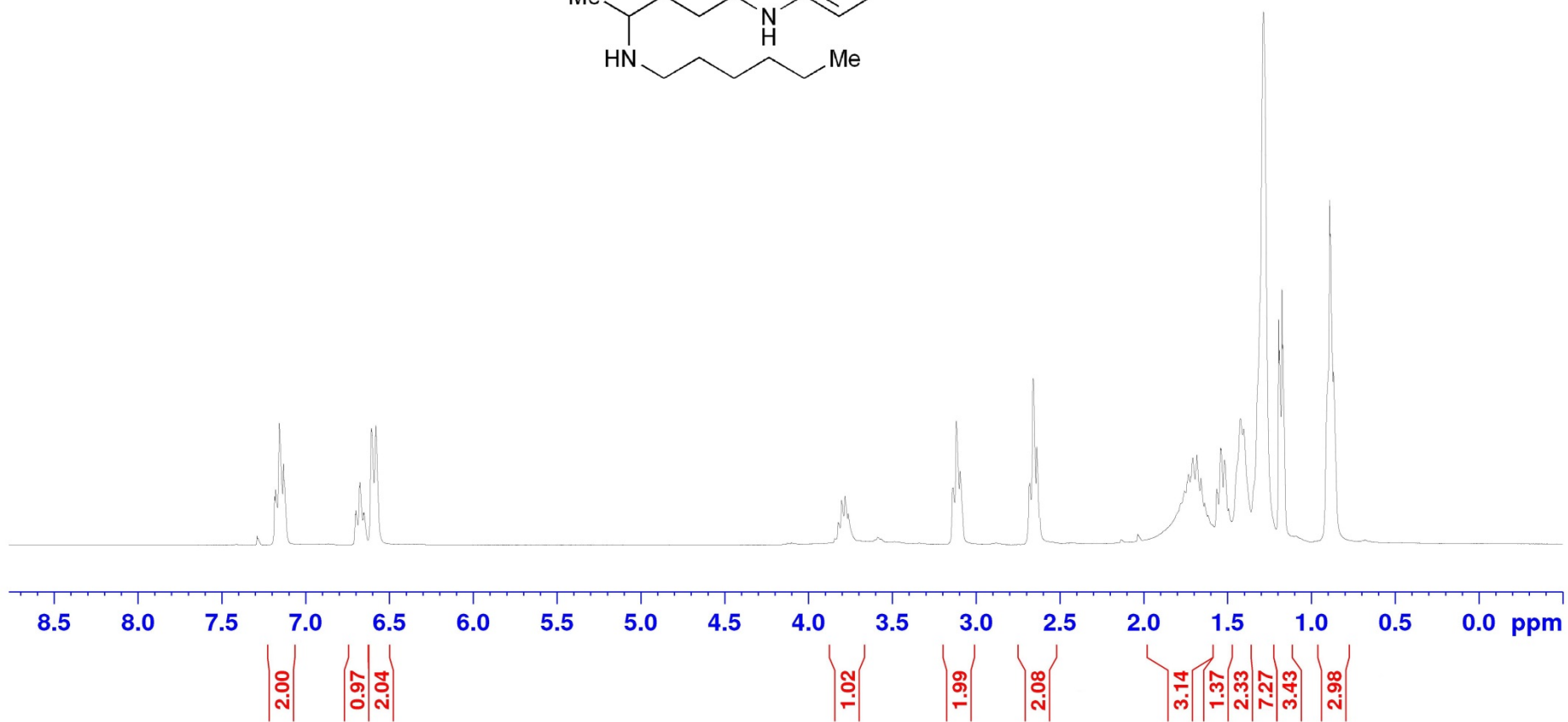
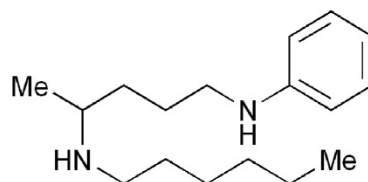
^{13}C NMR of **15e**



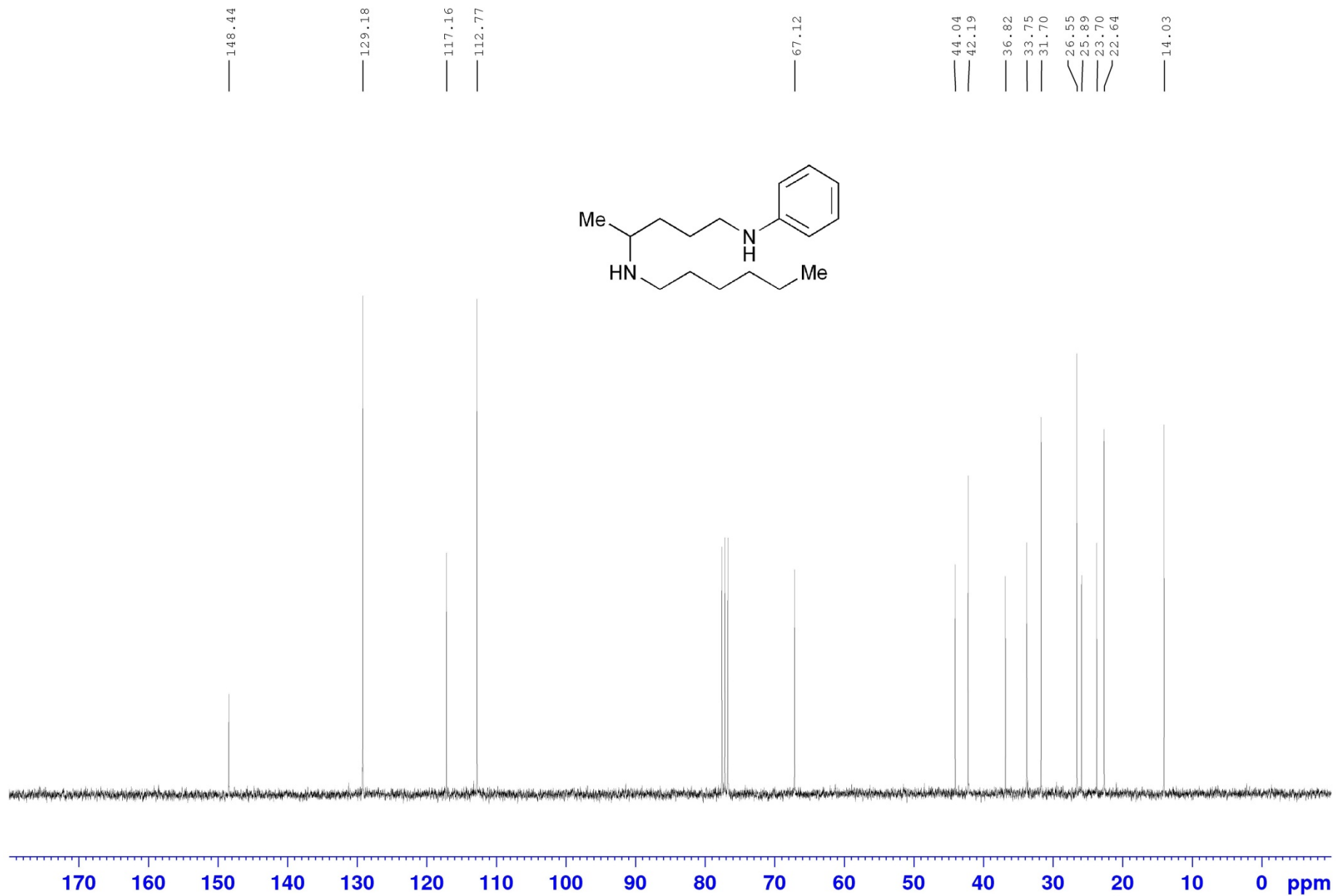
¹H NMR of **15f**

7.185
7.178
7.156
7.132
6.703
6.700
6.679
6.675
6.654
6.651
6.608
6.606
6.580

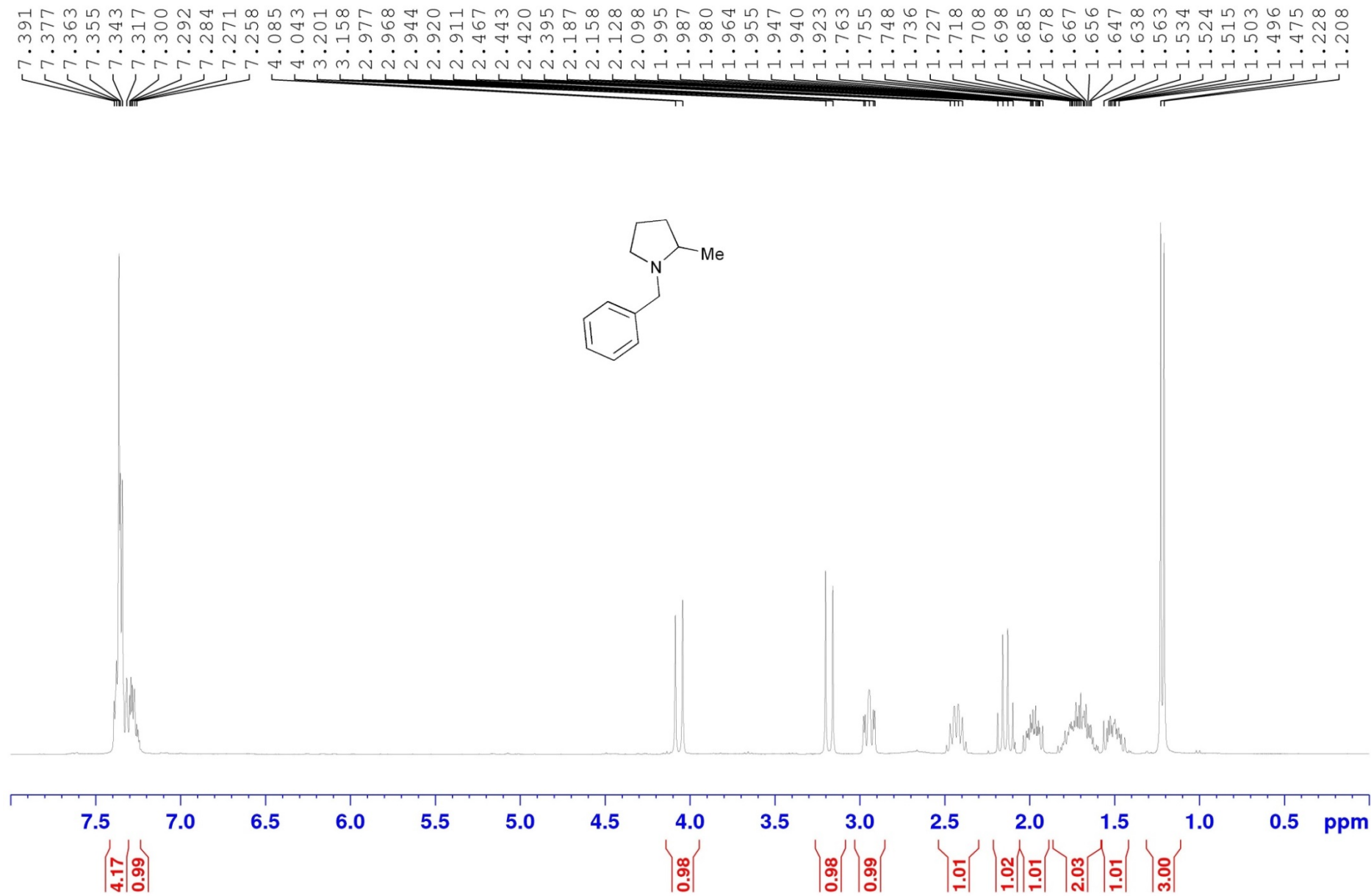
3.823
3.802
3.782
3.762
3.137
3.118
3.095
2.679
2.659
2.638
1.755
1.732
1.706
1.682
1.658
1.636
1.615
1.565
1.541
1.537
1.518
1.492
1.424
1.403
1.285
1.195
1.174
0.890
0.886
0.867



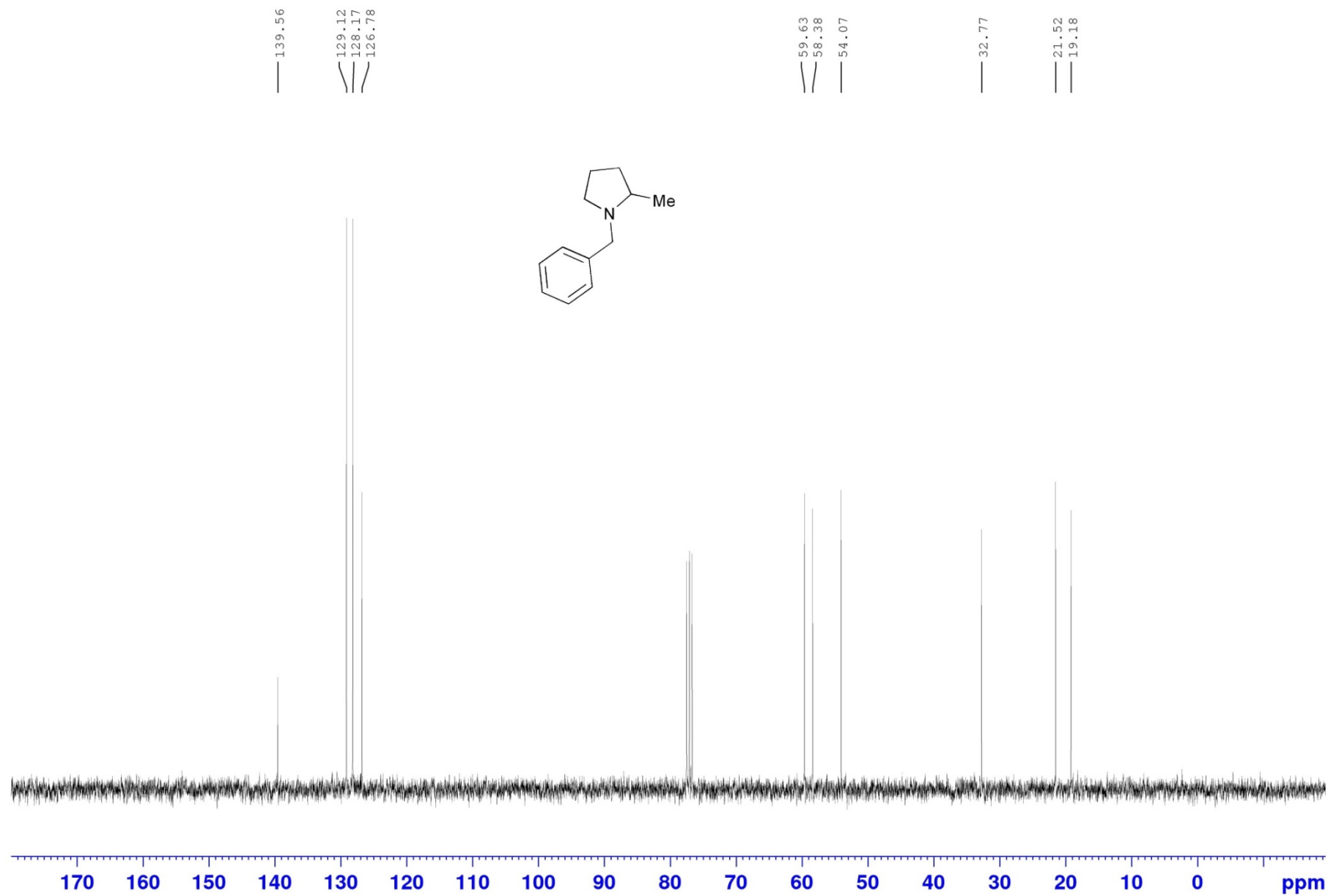
^{13}C NMR of **15f**



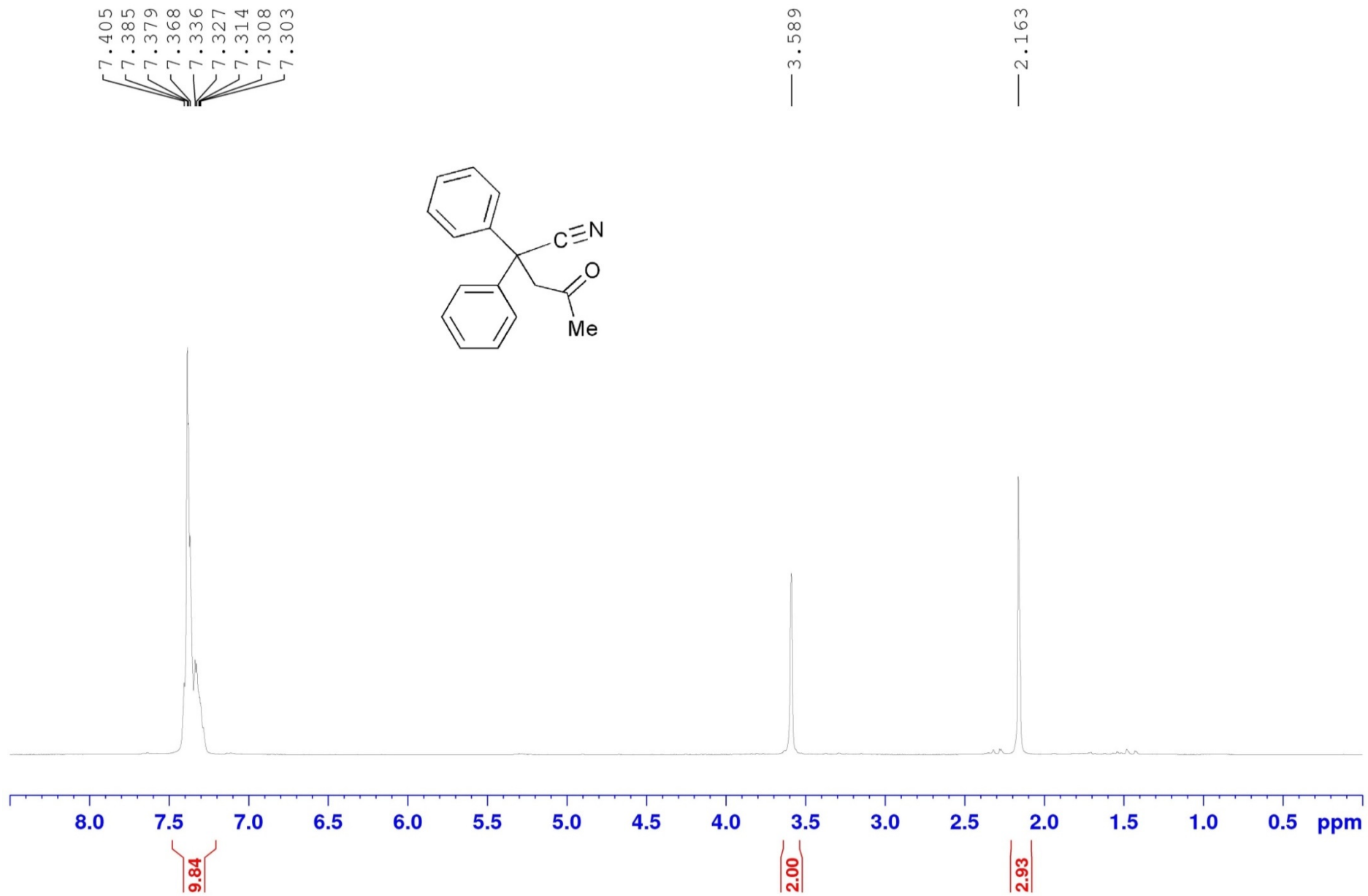
¹H NMR of 16



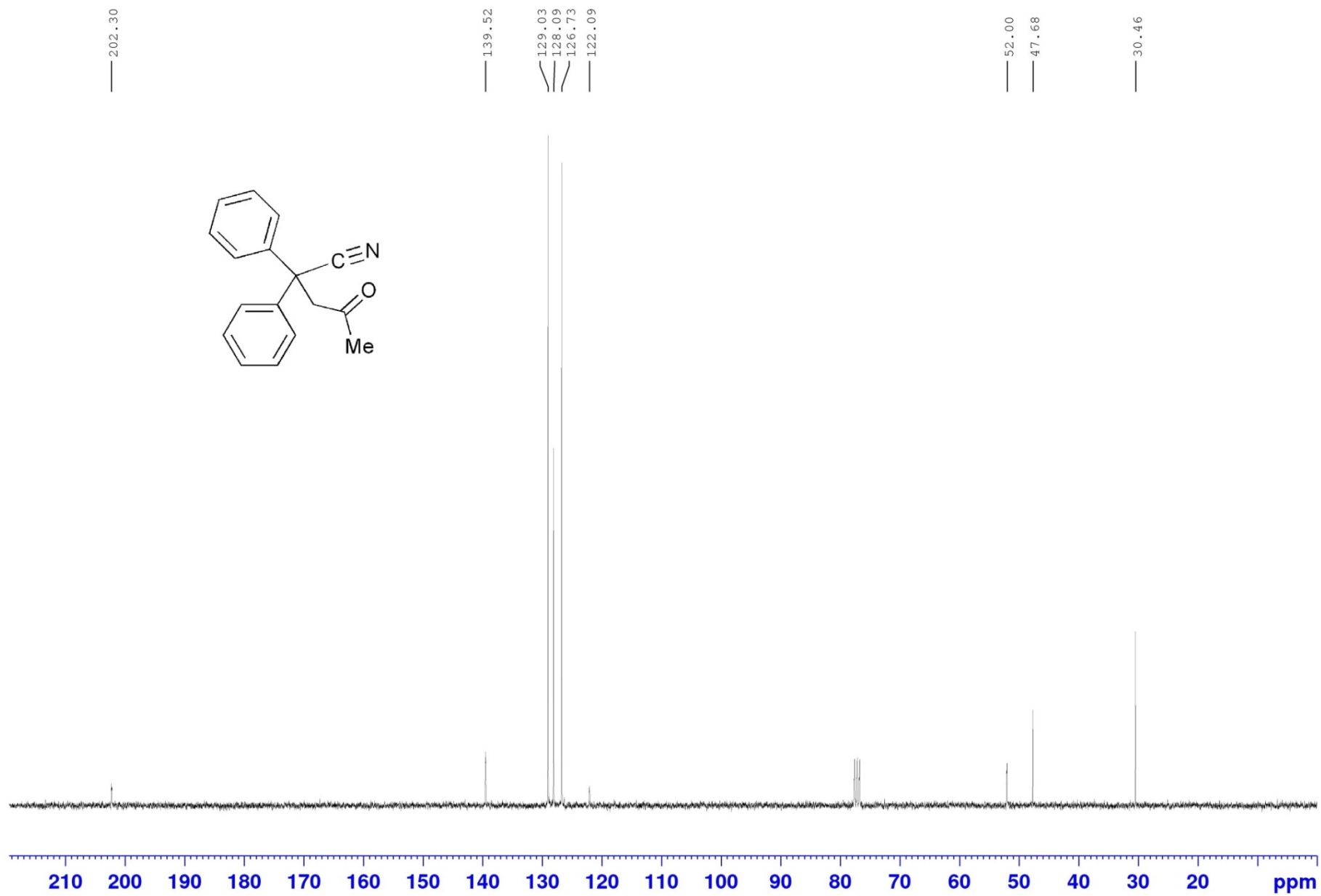
^{13}C NMR of **16**



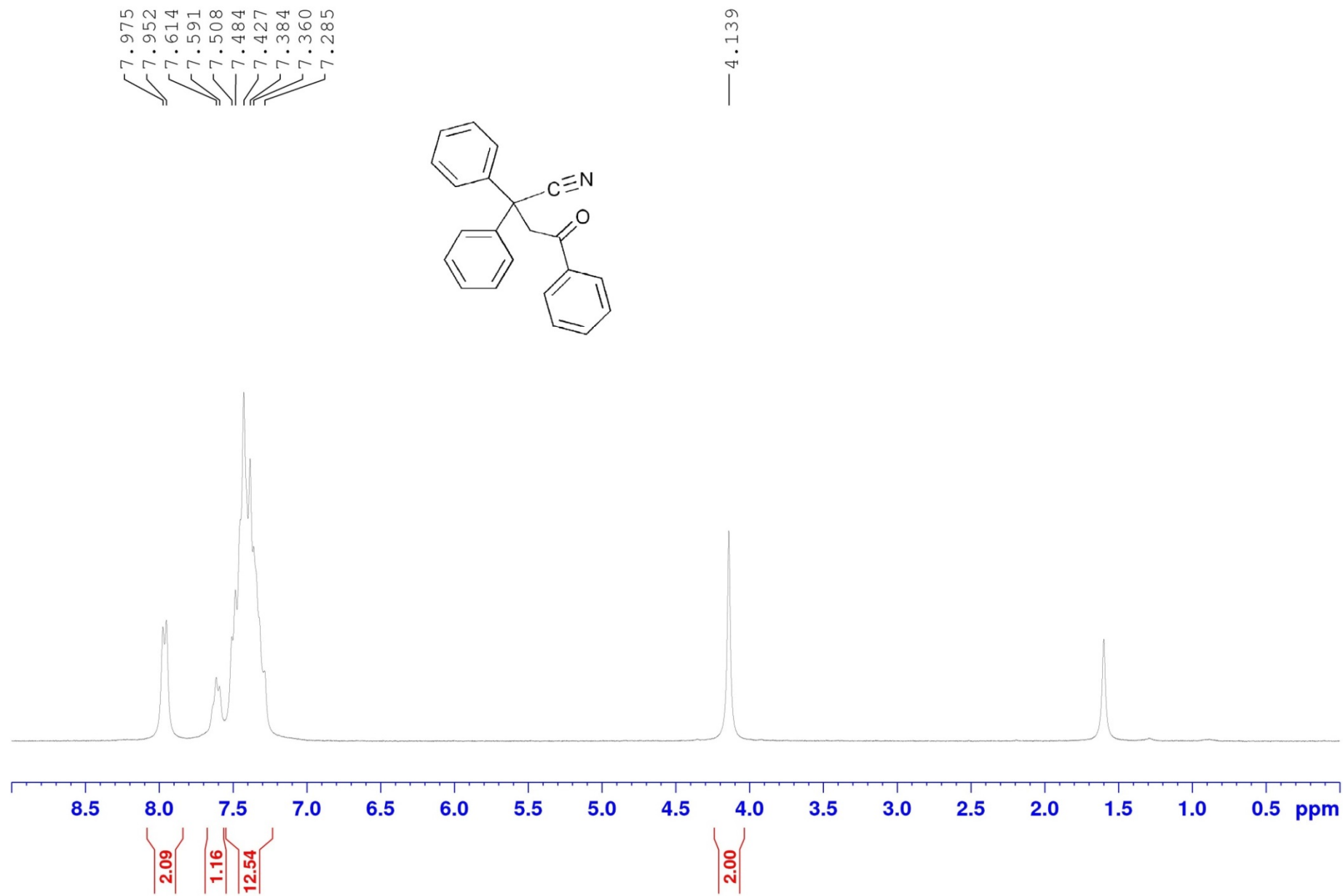
¹H NMR of **17a-1**



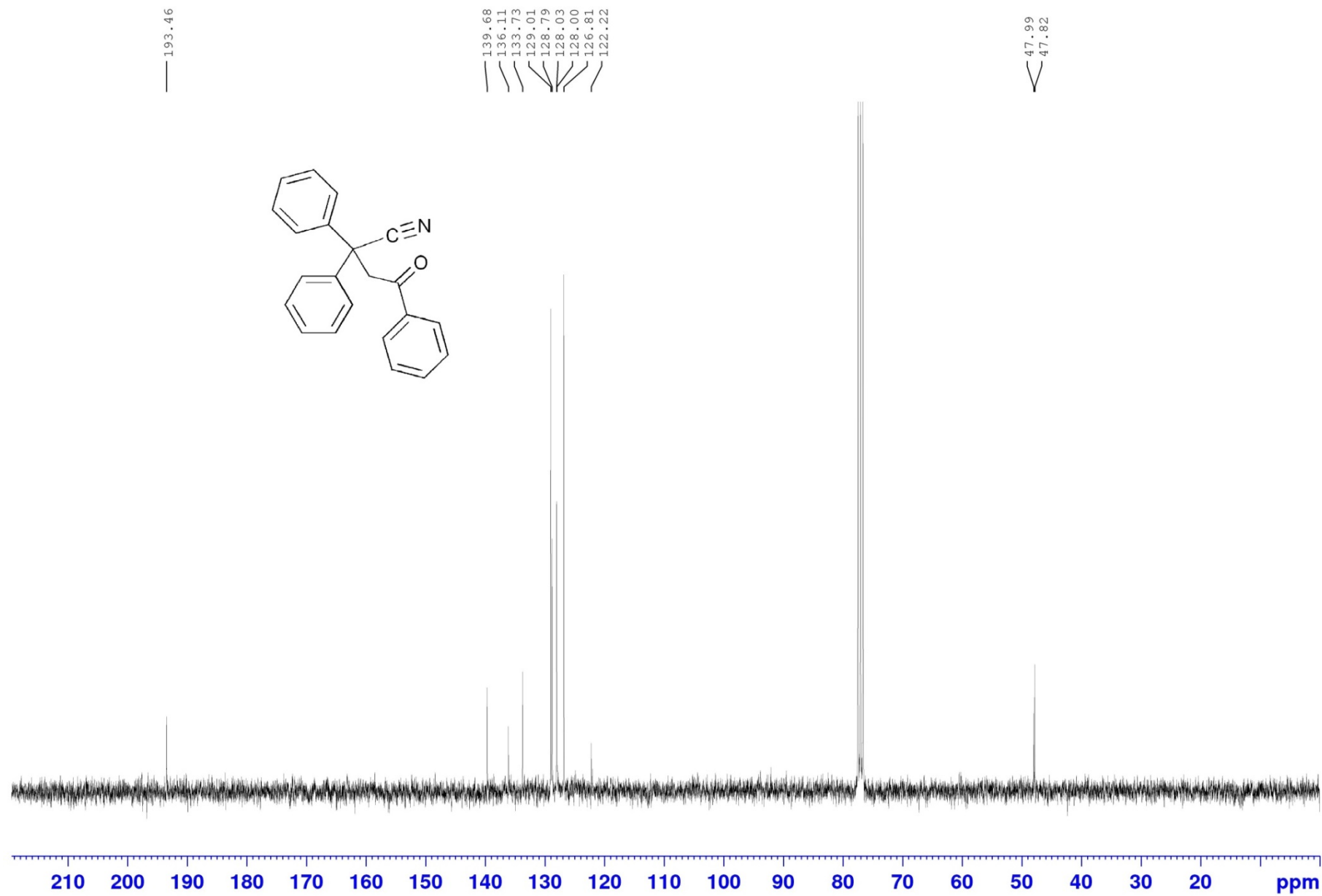
¹³C NMR of **17a-1**



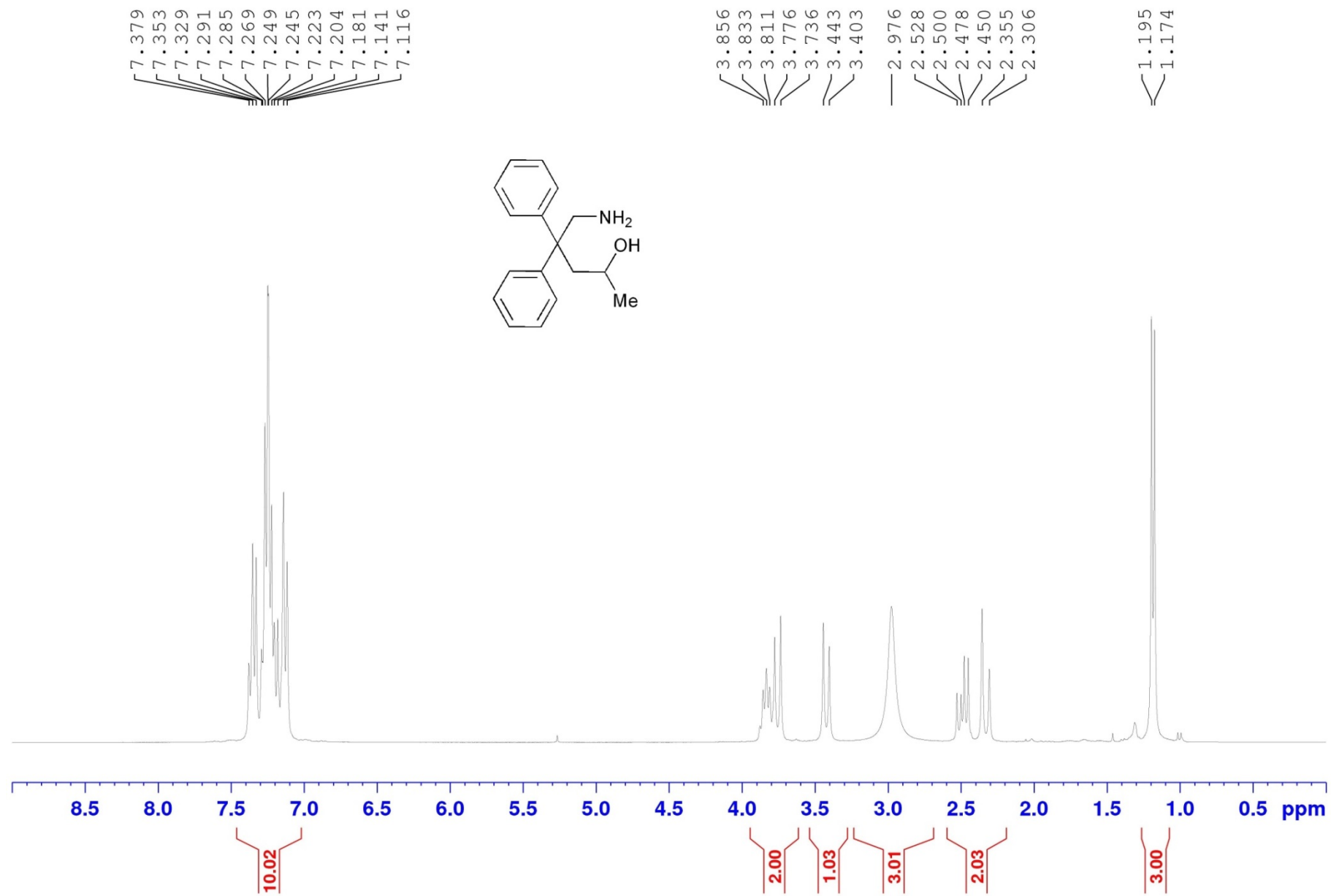
¹H NMR of **17a-2**



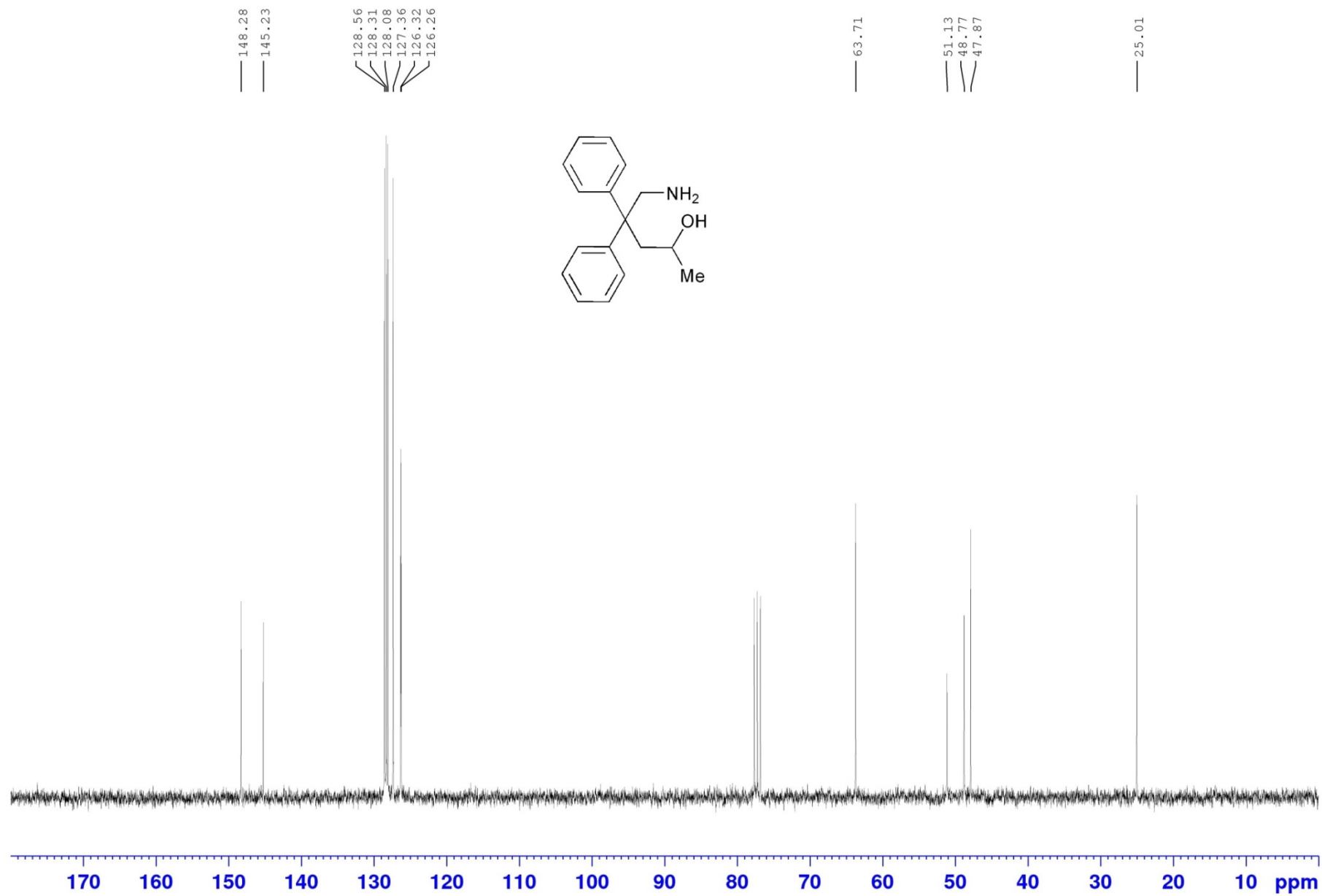
^{13}C NMR of **17a-2**



¹H NMR of **17a-3**



^{13}C NMR of **17a-3**

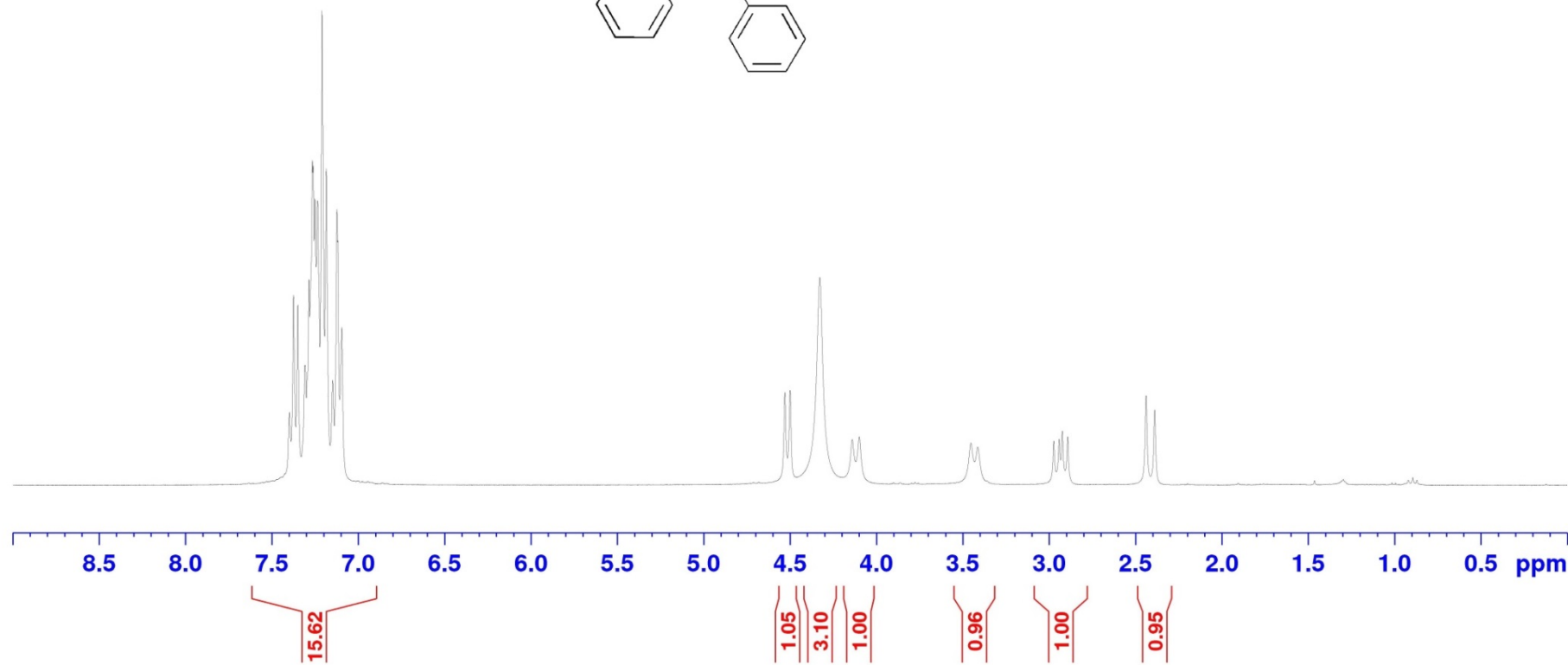
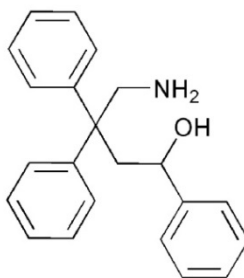


¹H NMR of **17a-4**

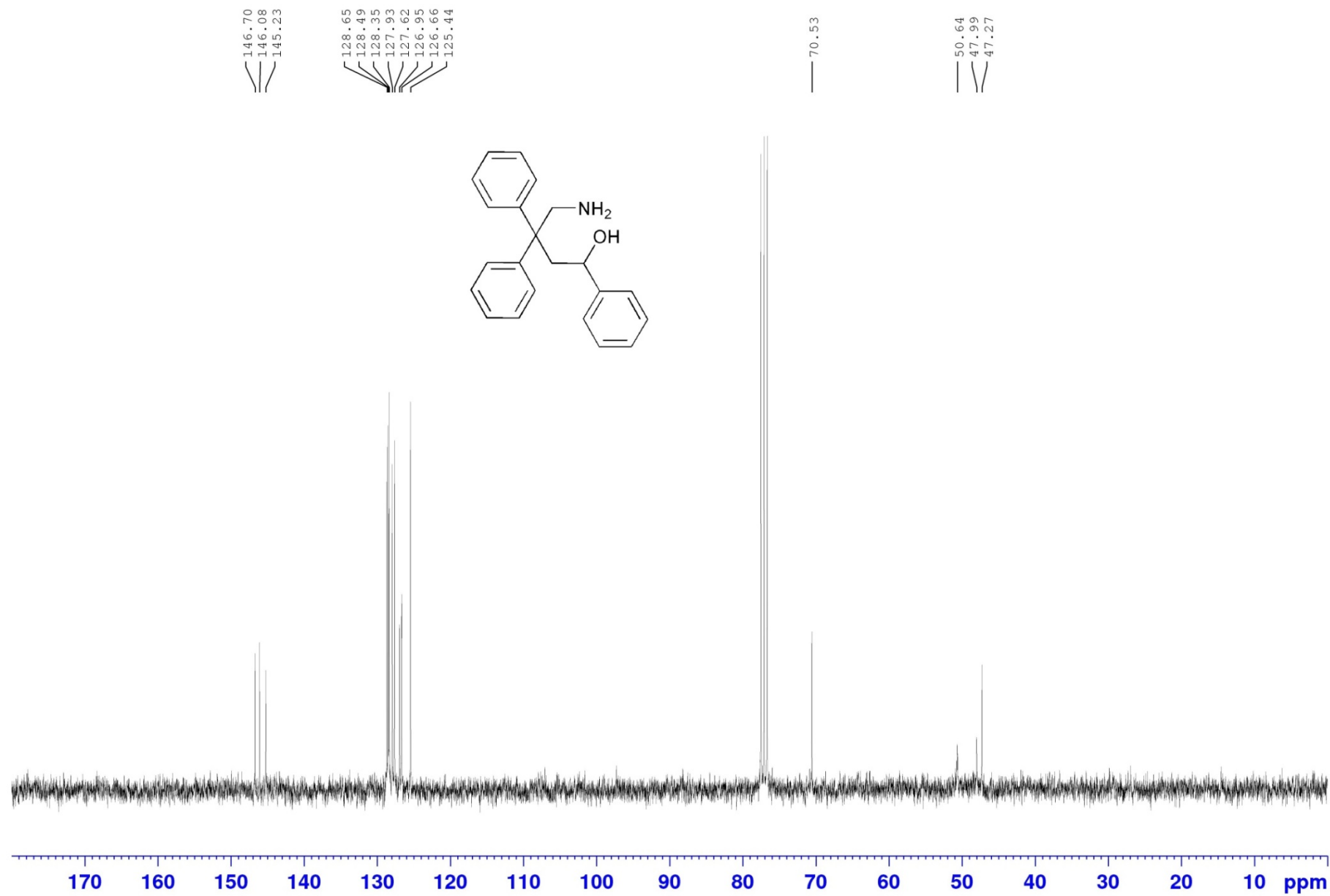
7.399
7.376
7.350
7.309
7.285
7.266
7.262
7.251
7.237
7.210
7.185
7.149
7.124
7.119
7.095

4.530
4.500
4.328
4.140
4.099

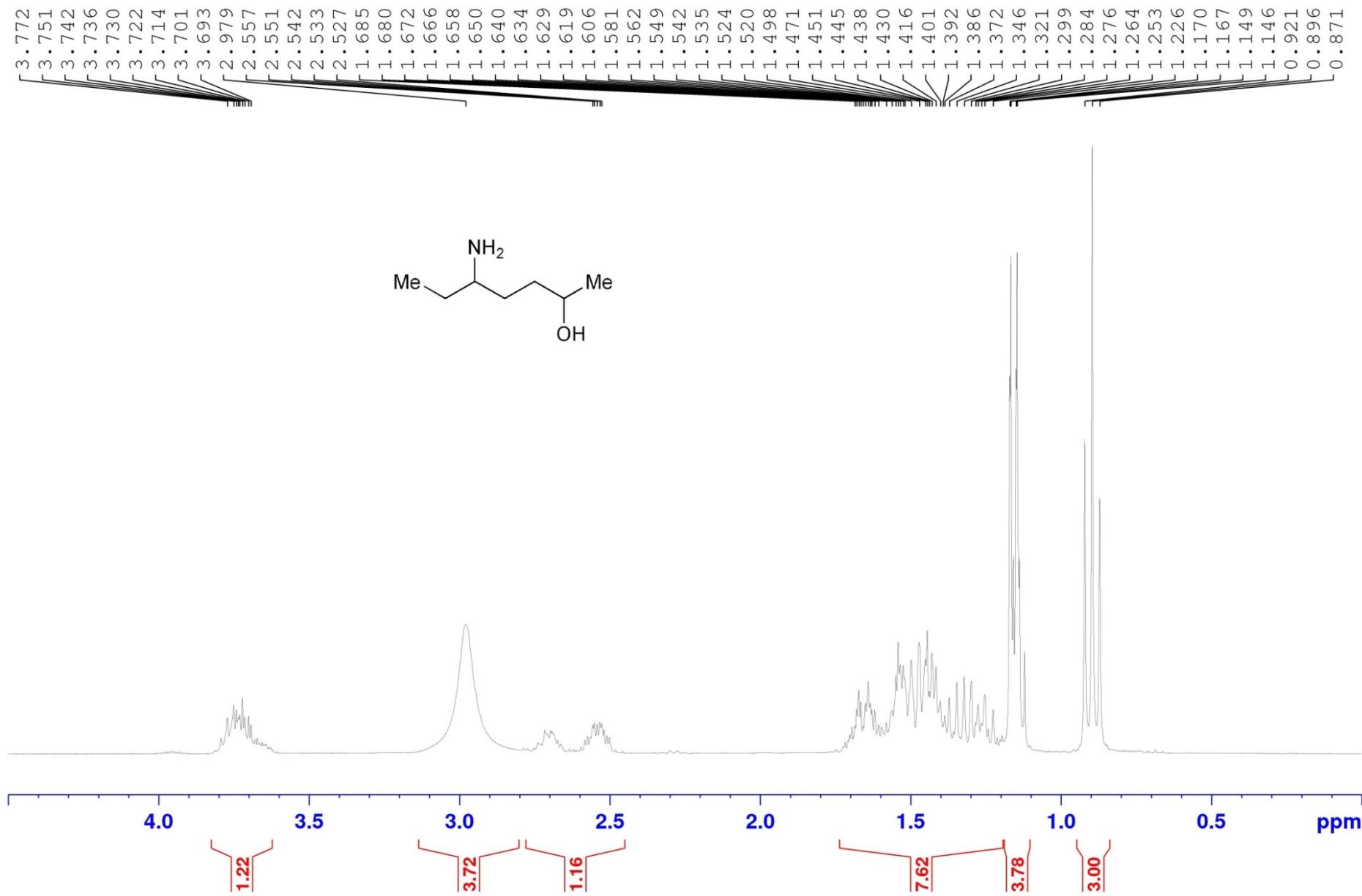
3.453
3.413
2.973
2.942
2.923
2.892
2.438
2.389



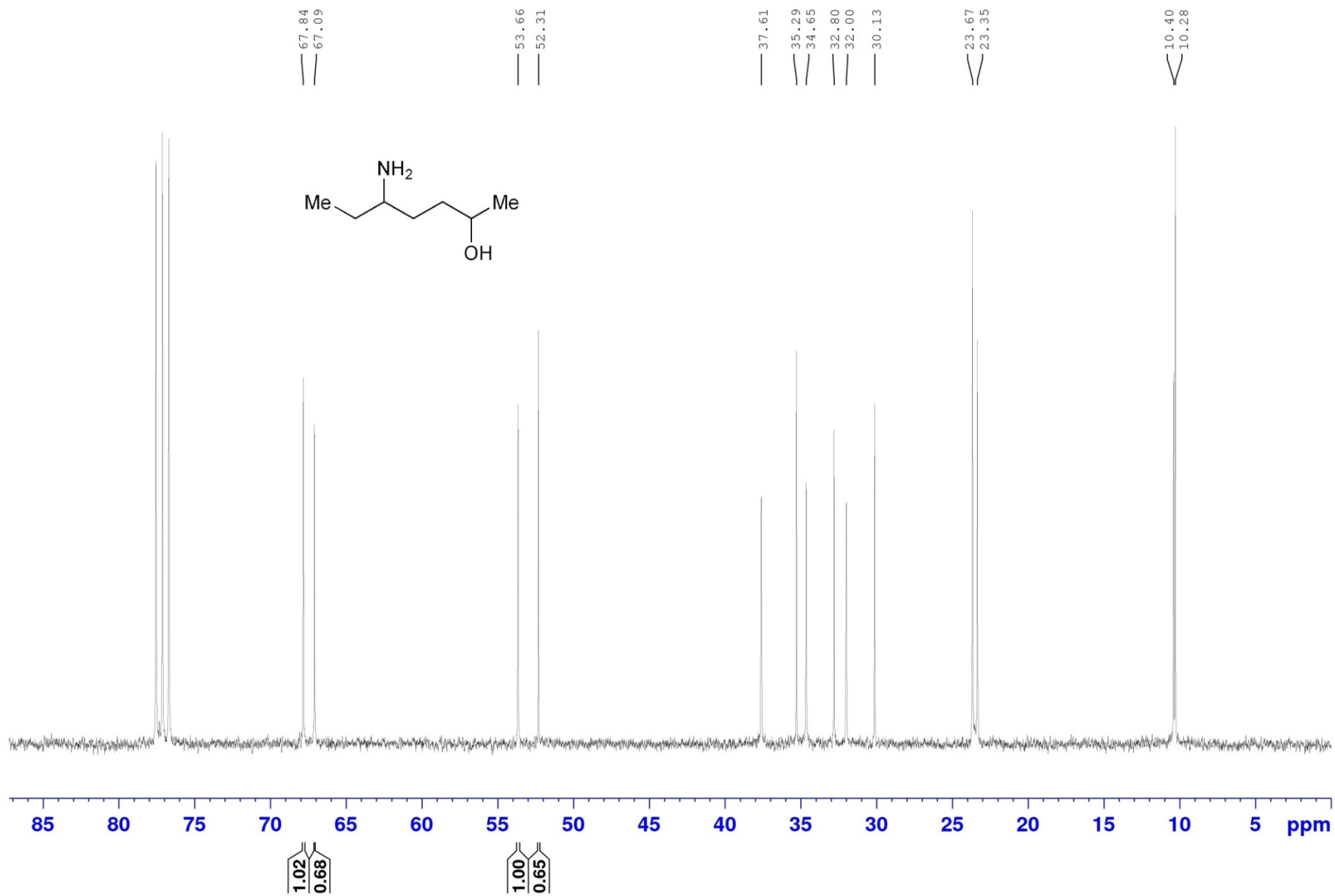
^{13}C NMR of **17a-4**



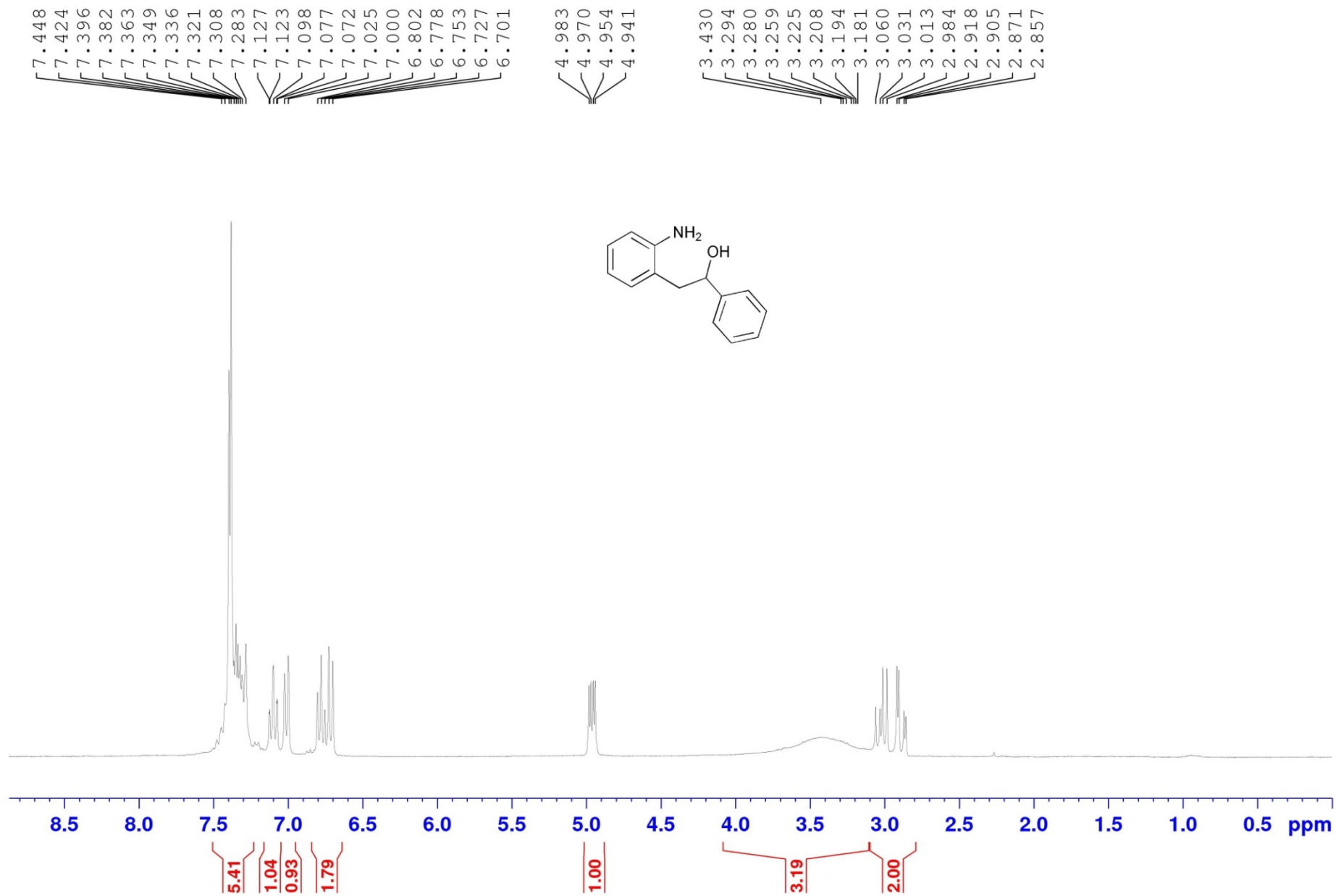
¹H NMR of 17a-9



^{13}C NMR of 17a-9



¹H NMR of **17a-10**

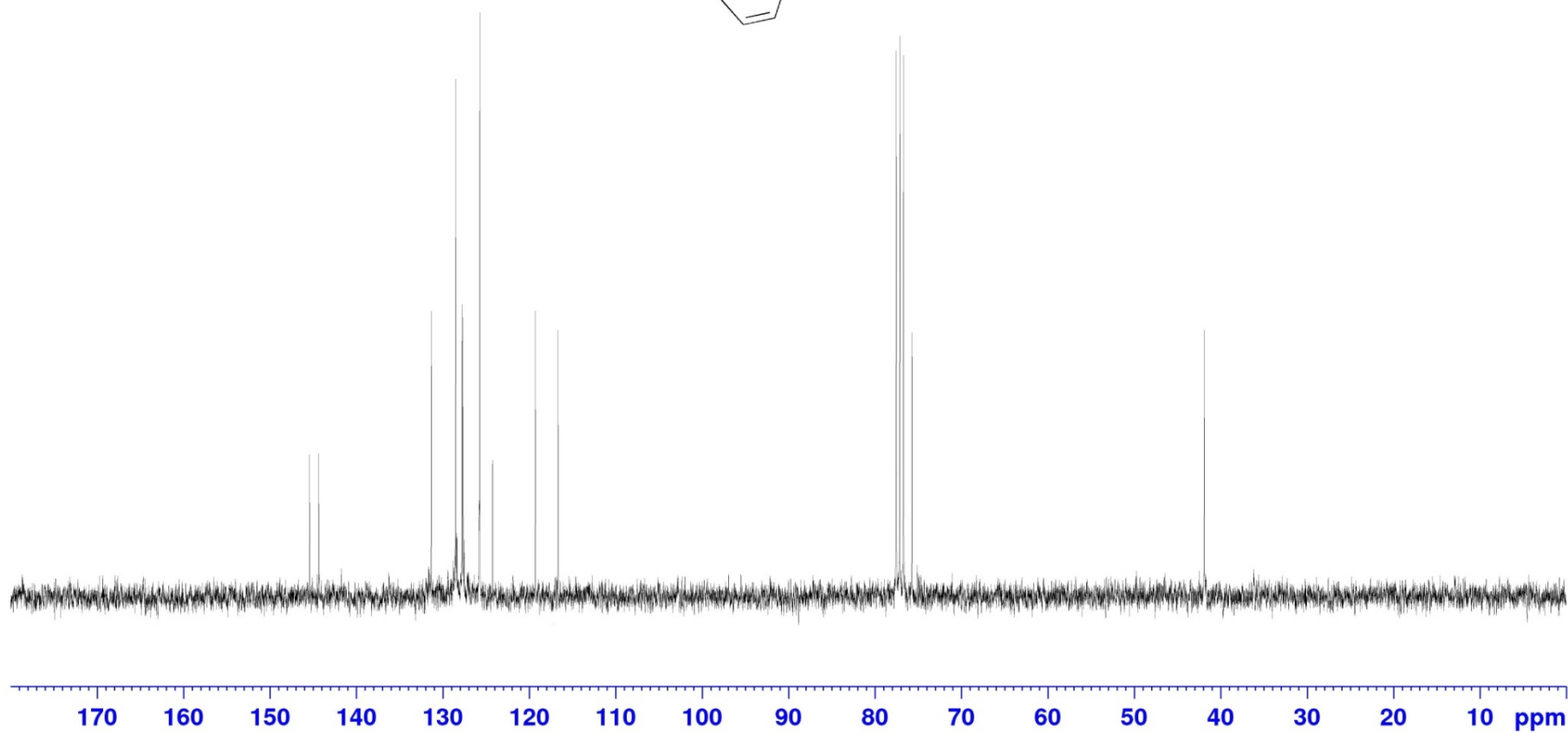
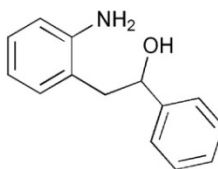


^{13}C NMR of **17a-10**

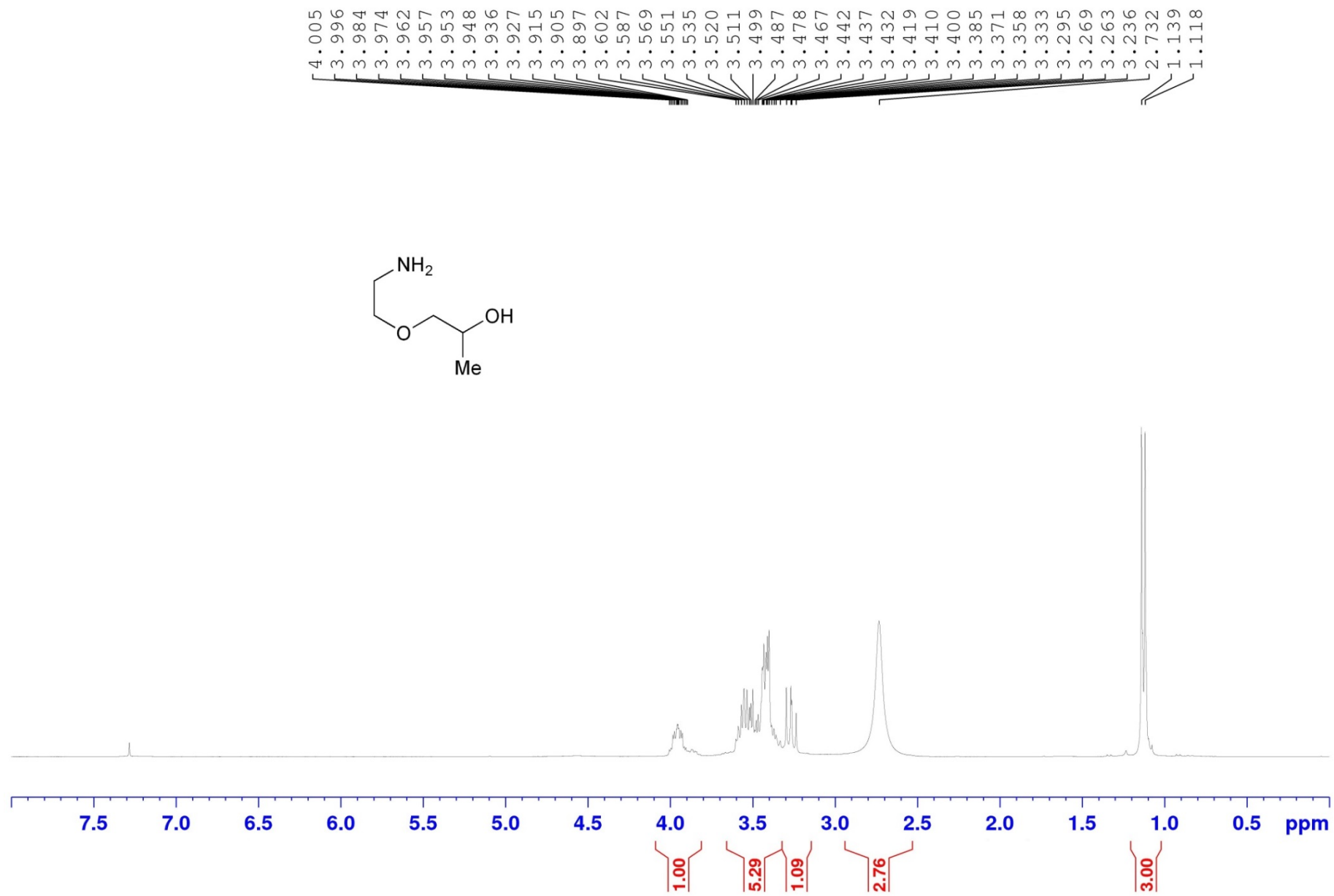
145.41
144.35
131.32
128.50
127.78
127.65
125.72
124.24
119.28
116.65

75.70

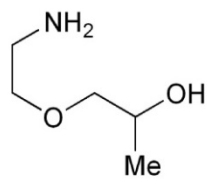
41.87



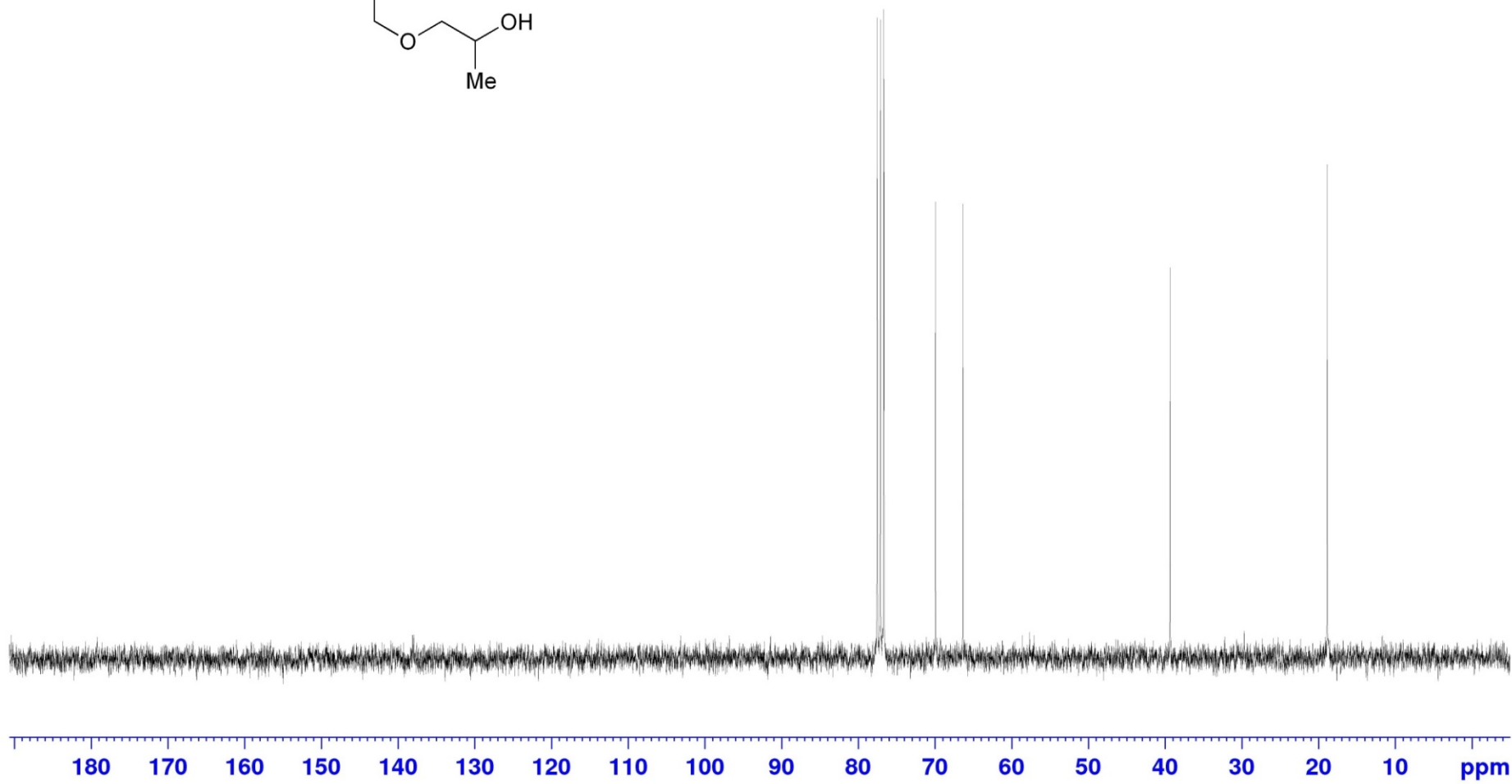
¹H NMR of 17b-1



^{13}C NMR of **17b-1**



76.62
69.92
66.34
39.33
18.84

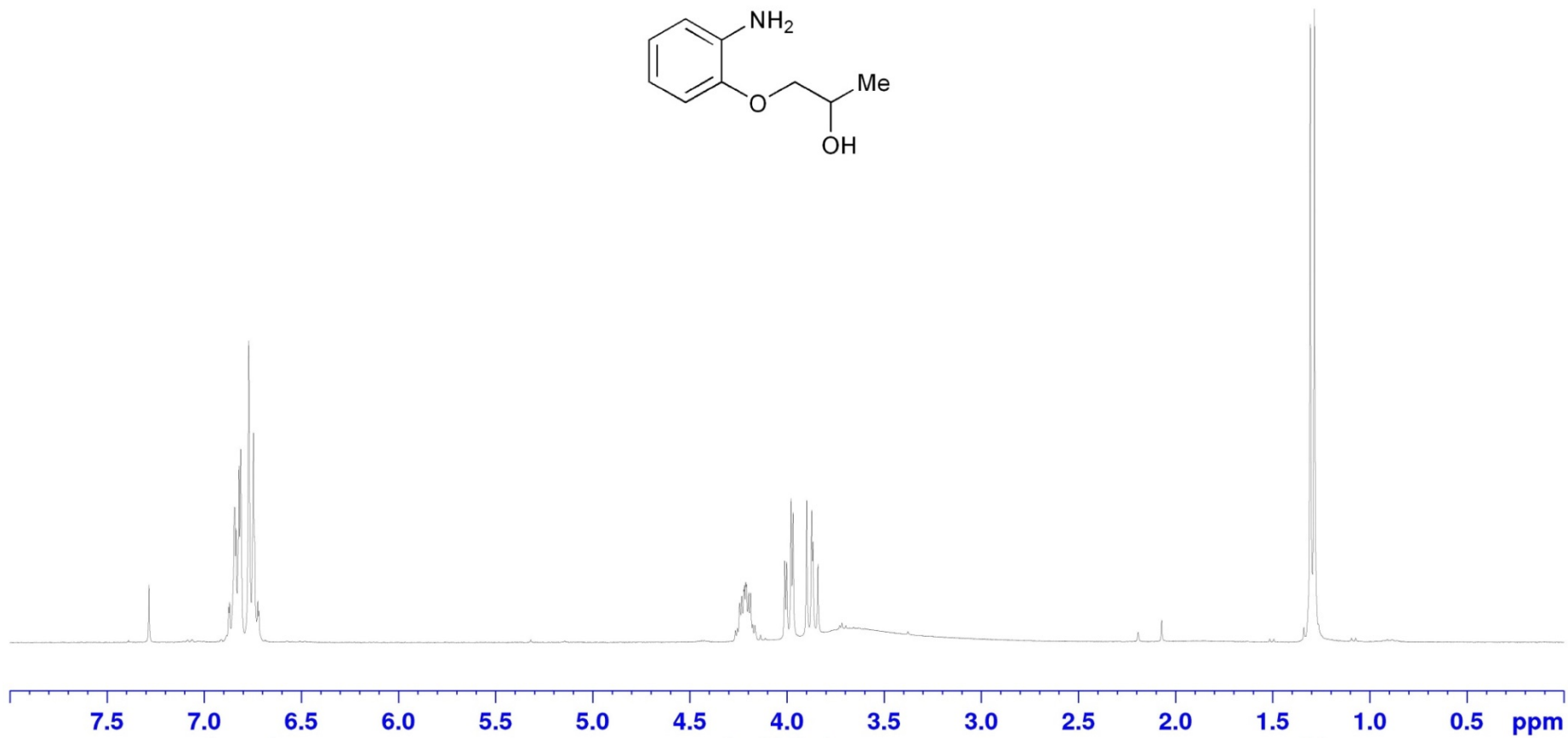
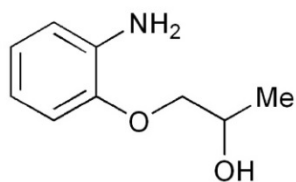


¹H NMR of **17b-2**

6.874
6.869
6.843
6.836
6.821
6.813
6.771
6.746
6.724
6.719

4.266
4.255
4.244
4.234
4.222
4.219
4.212
4.208
4.197
4.187
4.176
4.165
4.011
4.001
3.979
3.969
3.898
3.873
3.866
3.841
3.656

1.306
1.285

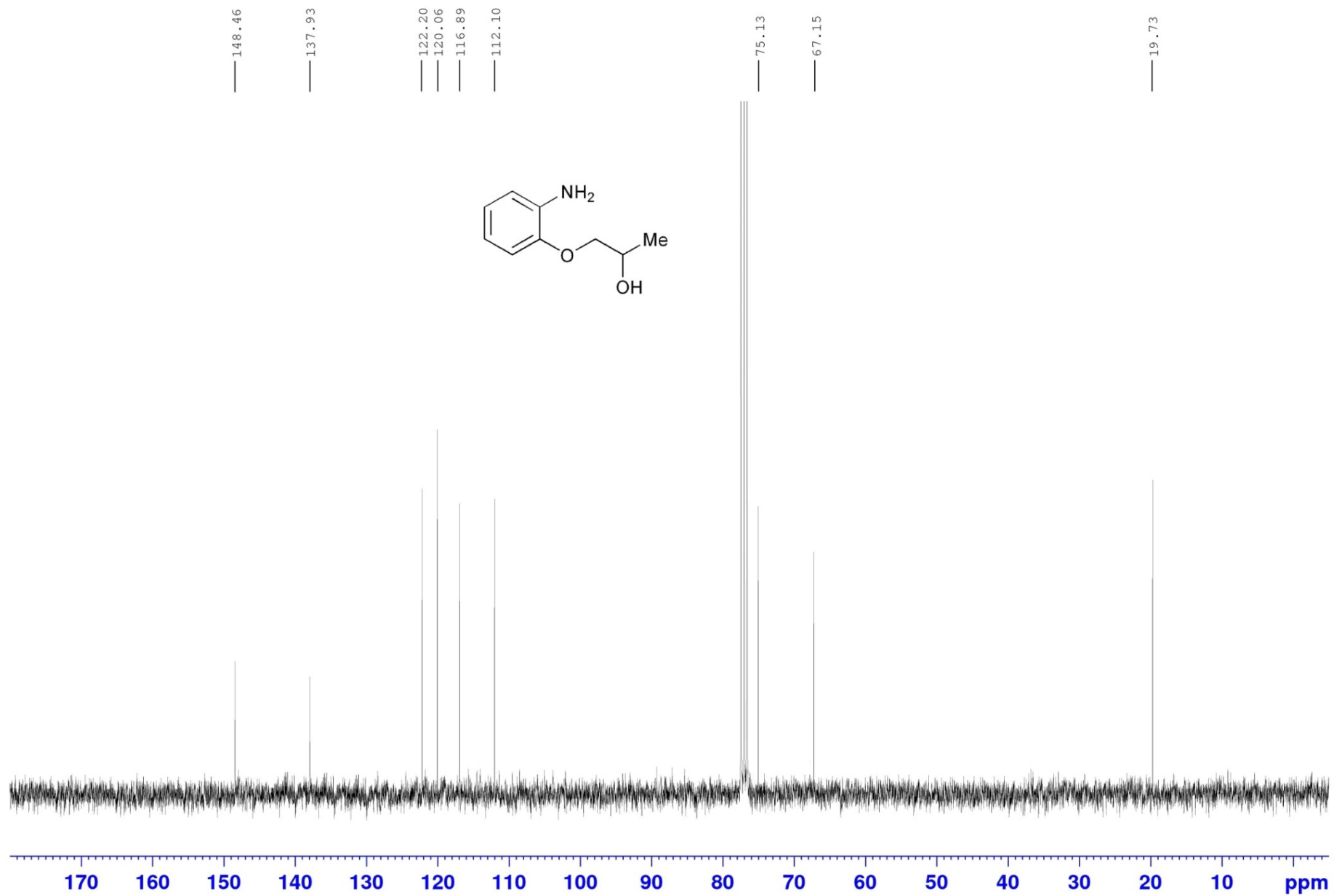


3.87

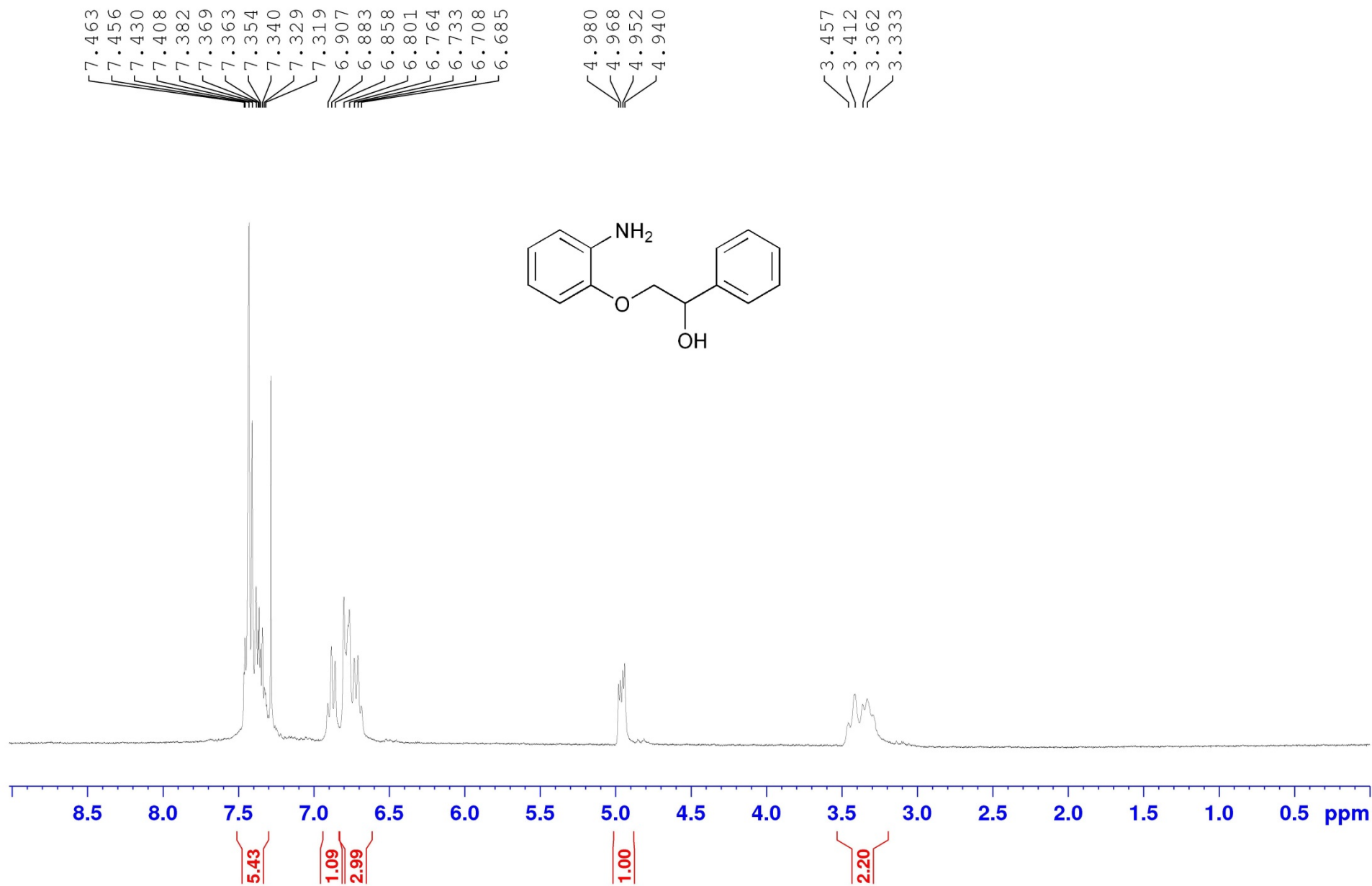
1.05
1.06
1.31

3.00

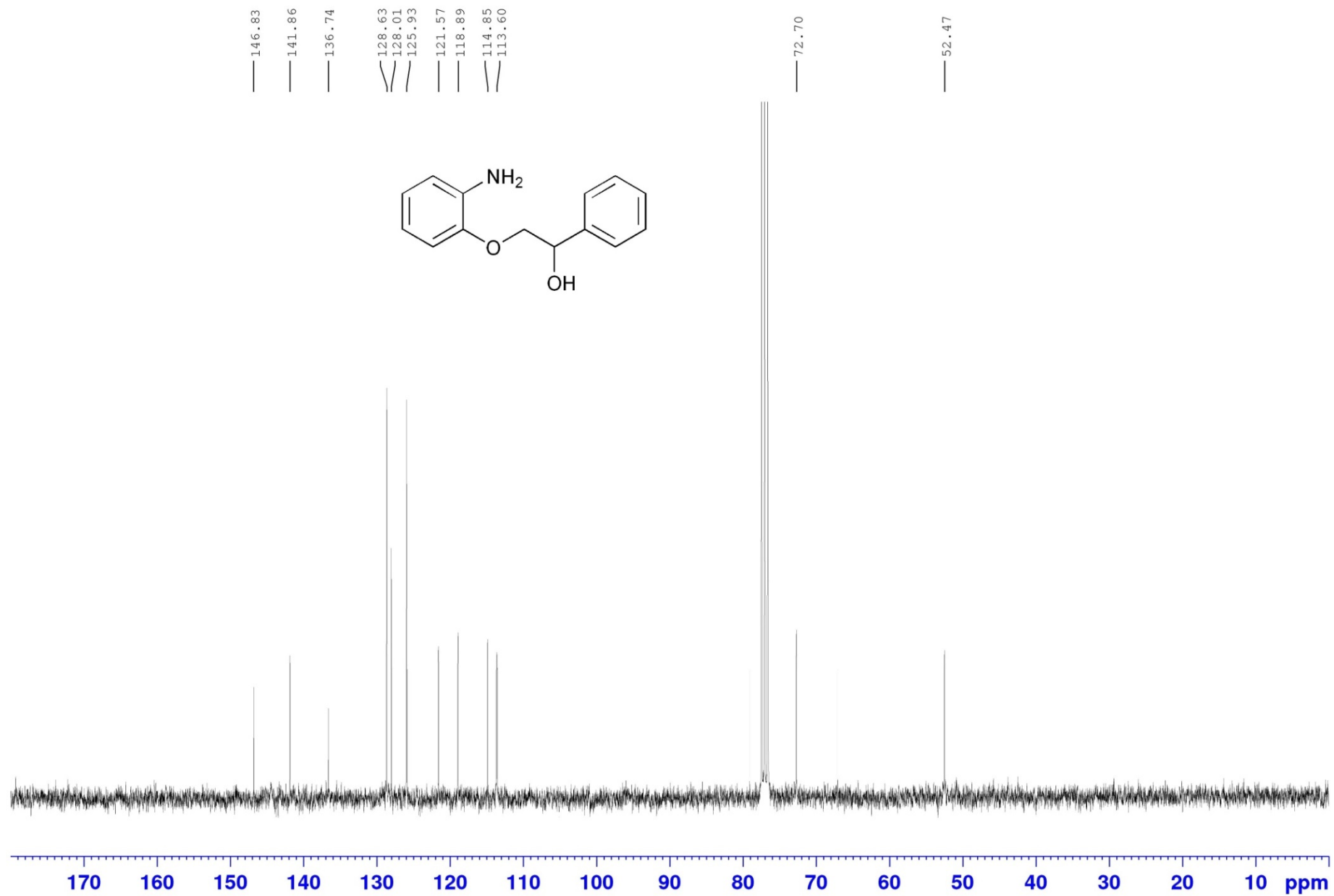
^{13}C NMR of **17b-2**



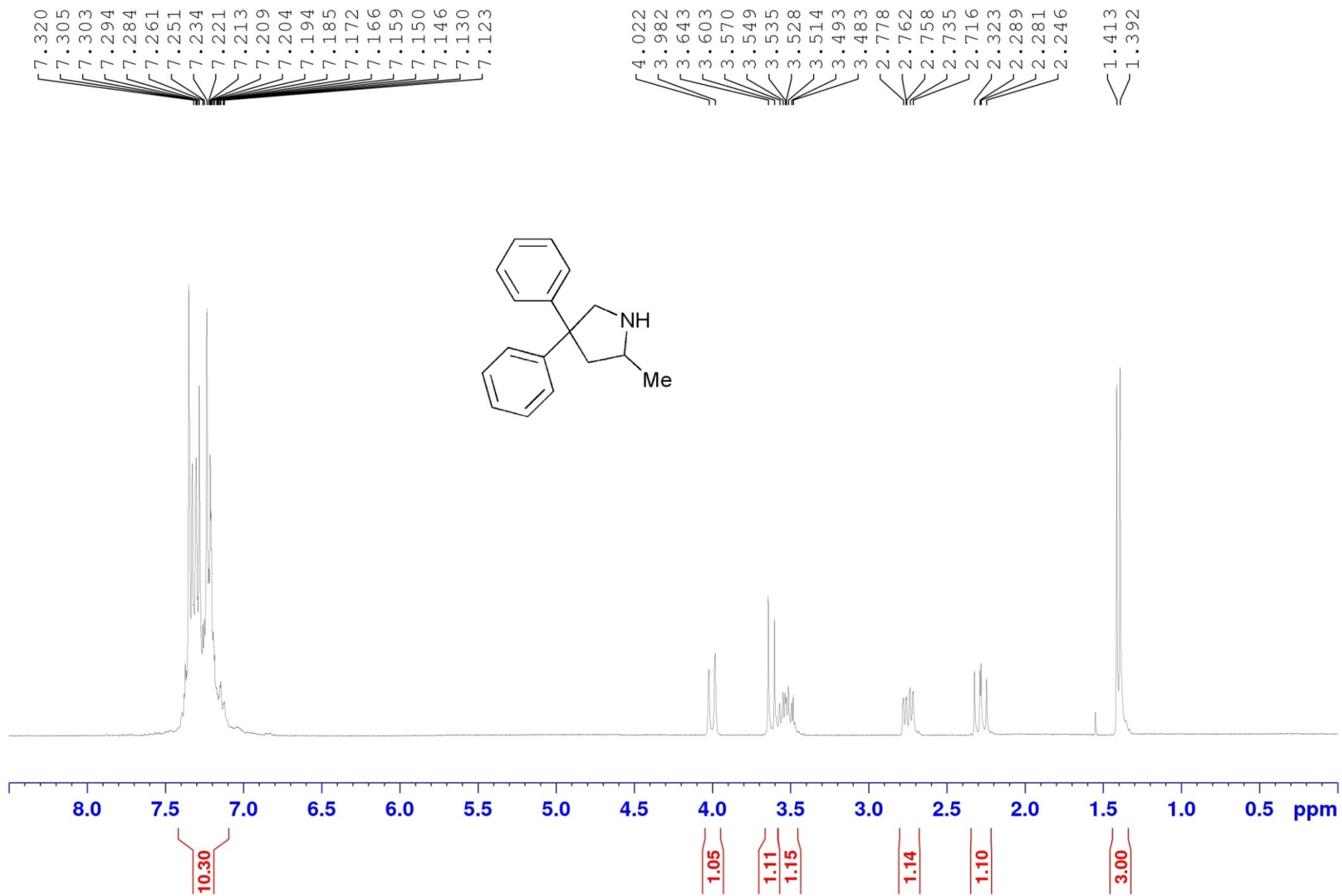
¹H NMR of **17b-3**



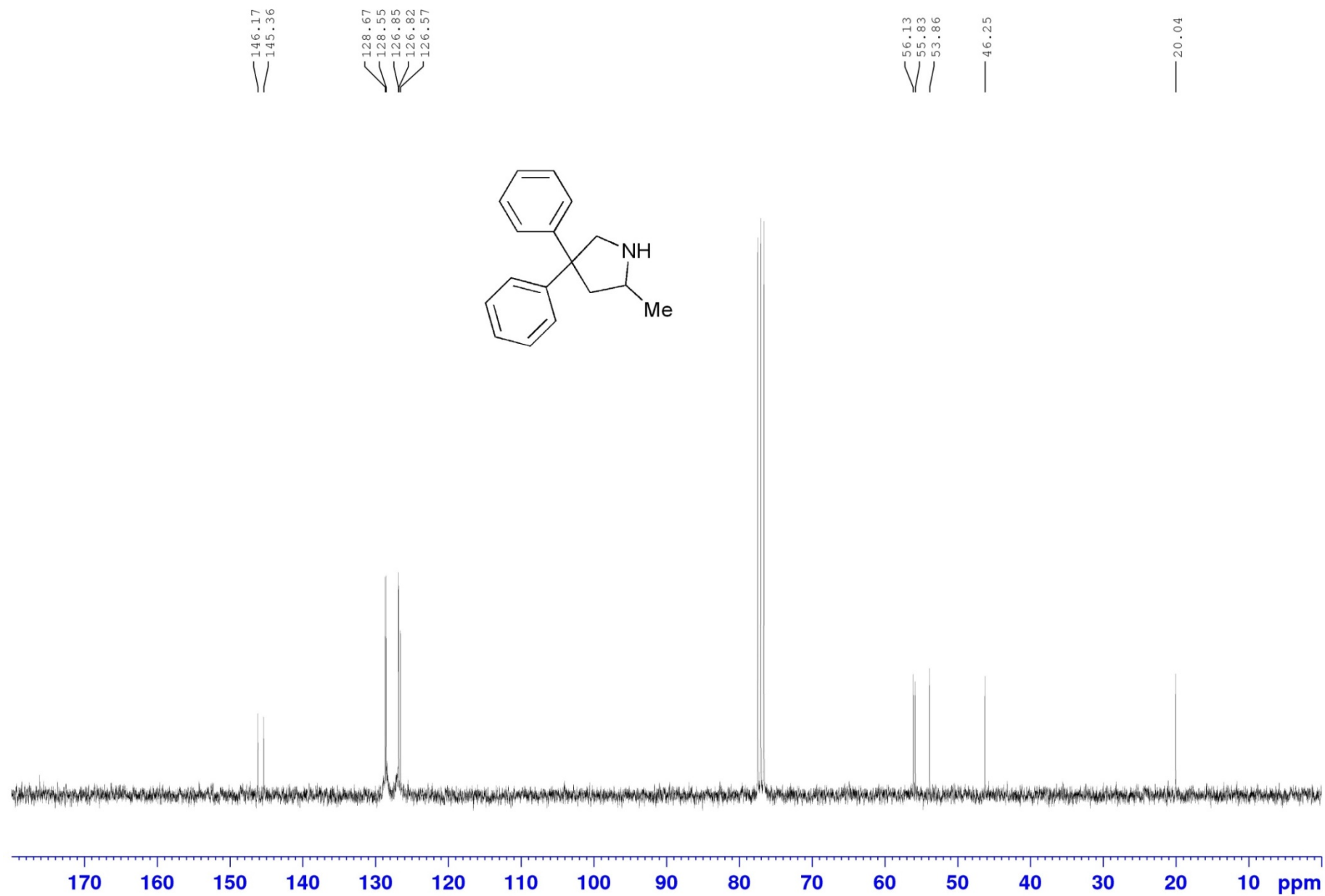
^{13}C NMR of **17b-3**



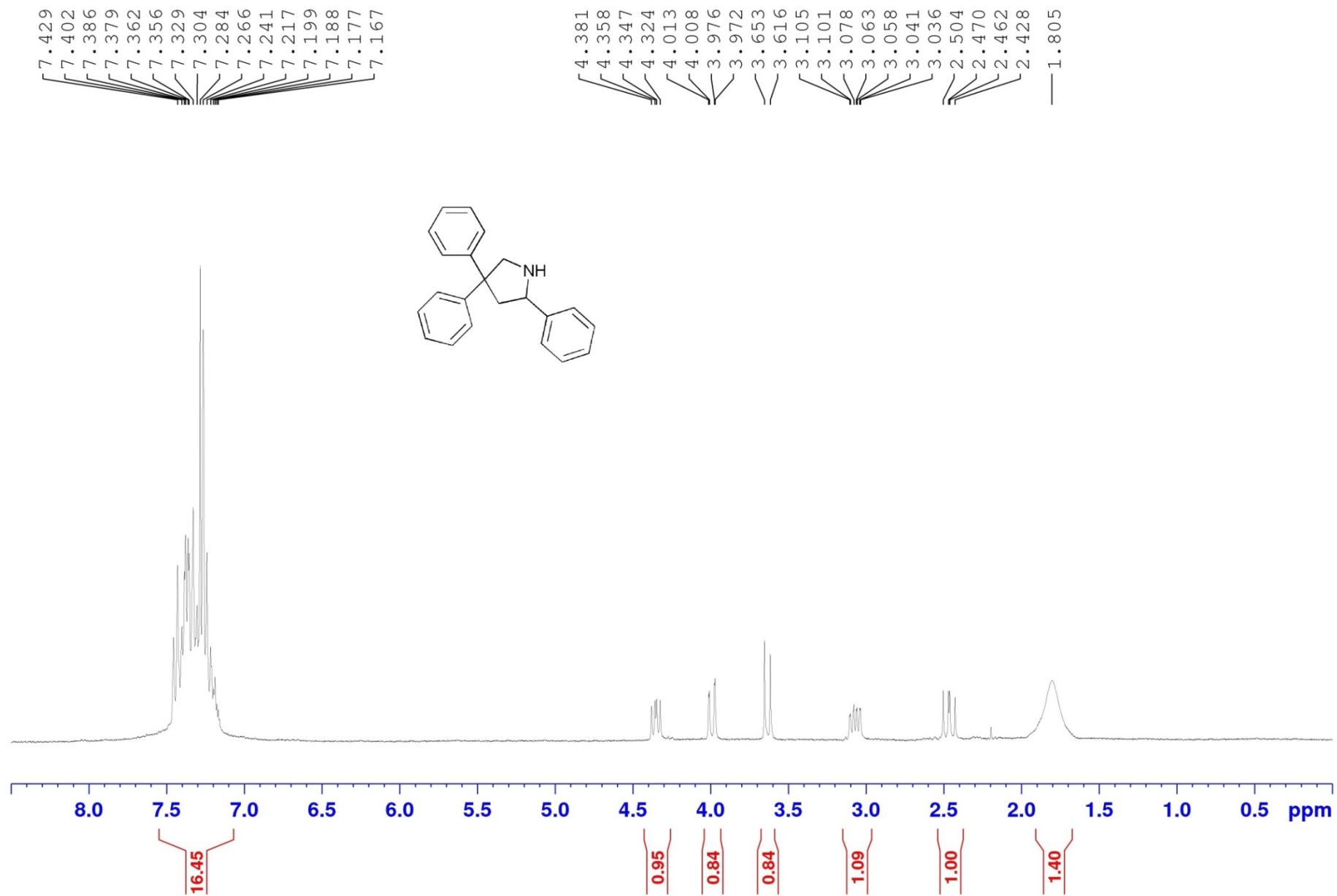
¹H NMR of 18



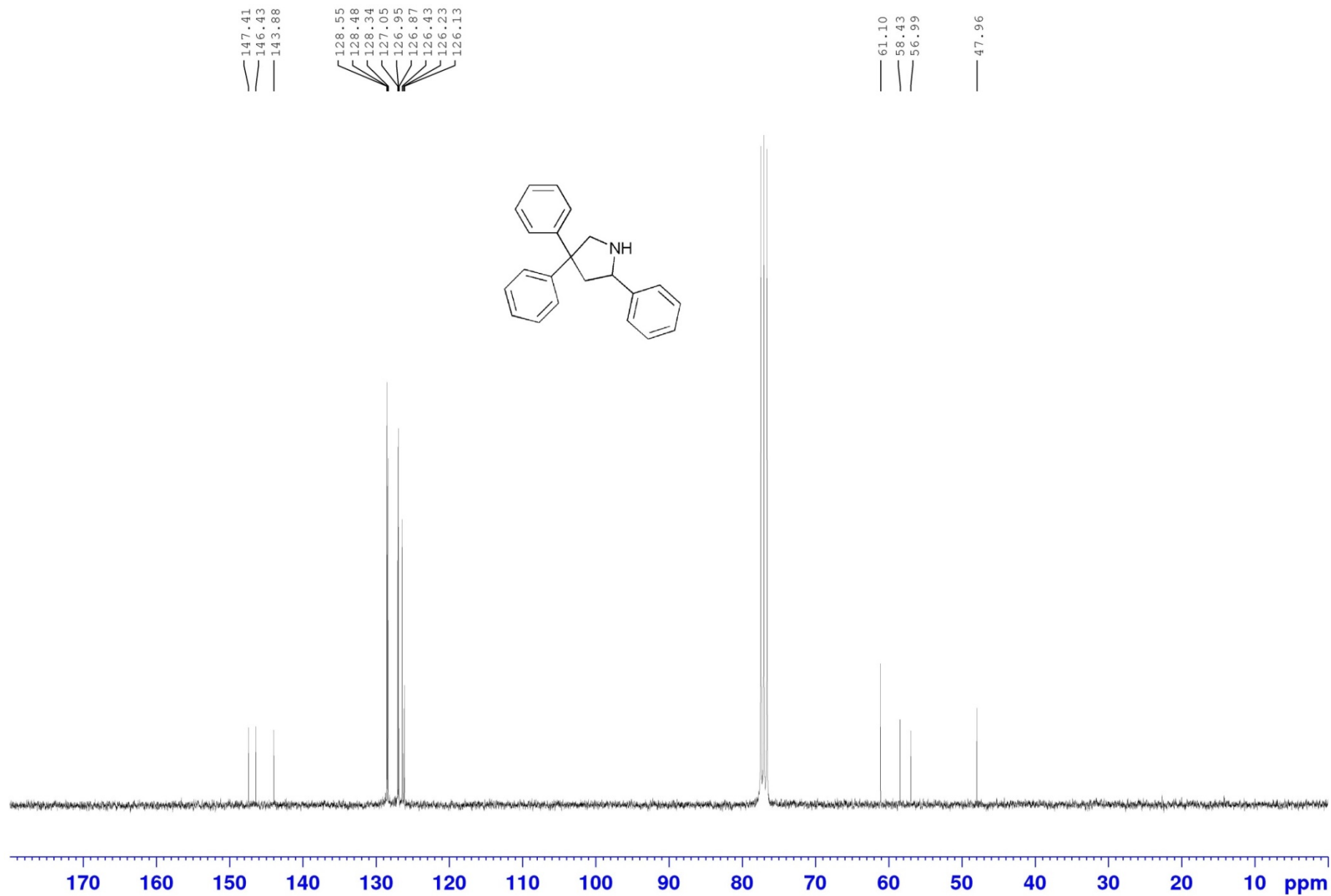
^{13}C NMR of **18**



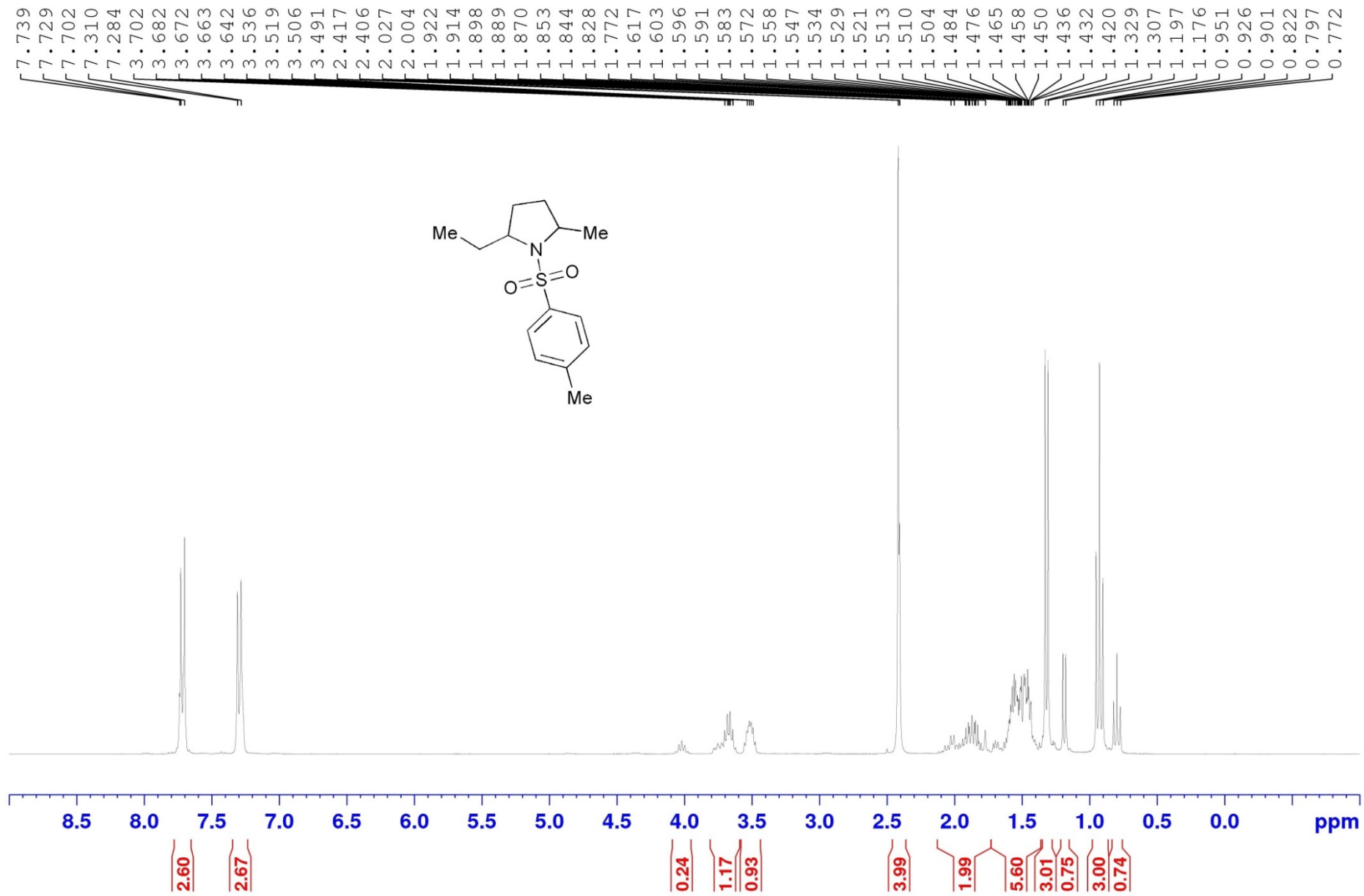
¹H NMR of 19



^{13}C NMR of **19**

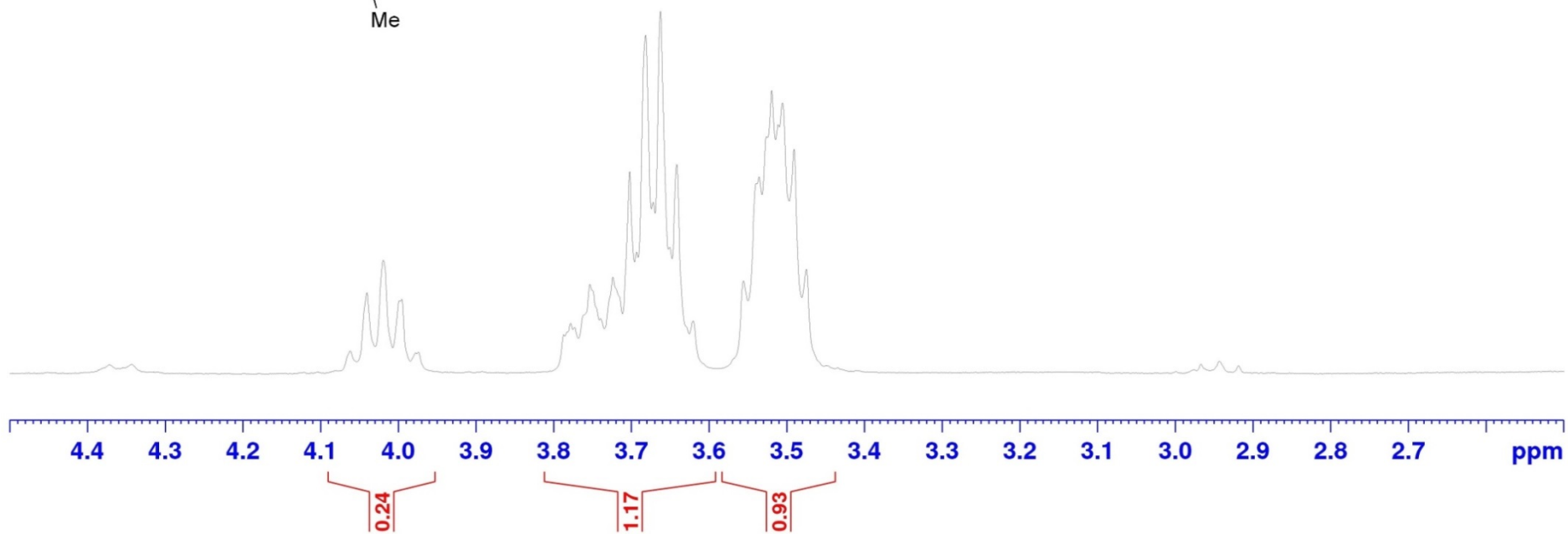
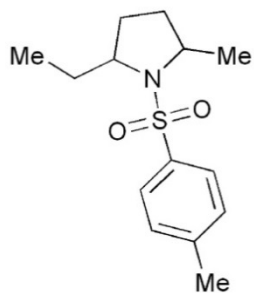


¹H NMR of **20**

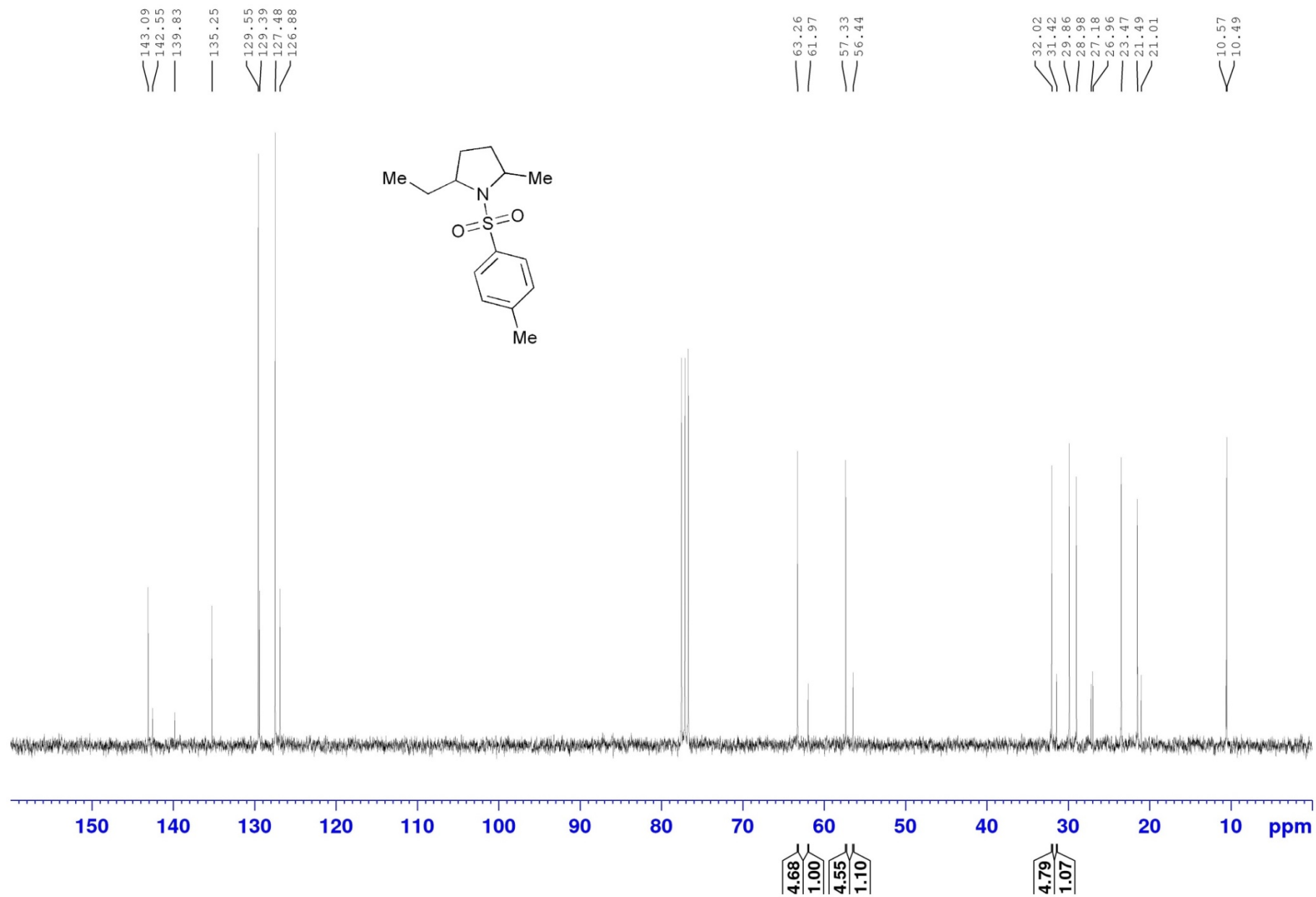


^1H NMR of **20** (zoomed in)

4.062
4.041
4.019
3.996
3.974
3.778
3.753
3.724
3.702
3.693
3.682
3.672
3.663
3.642
3.620
3.556
3.536
3.519
3.506
3.491
3.475

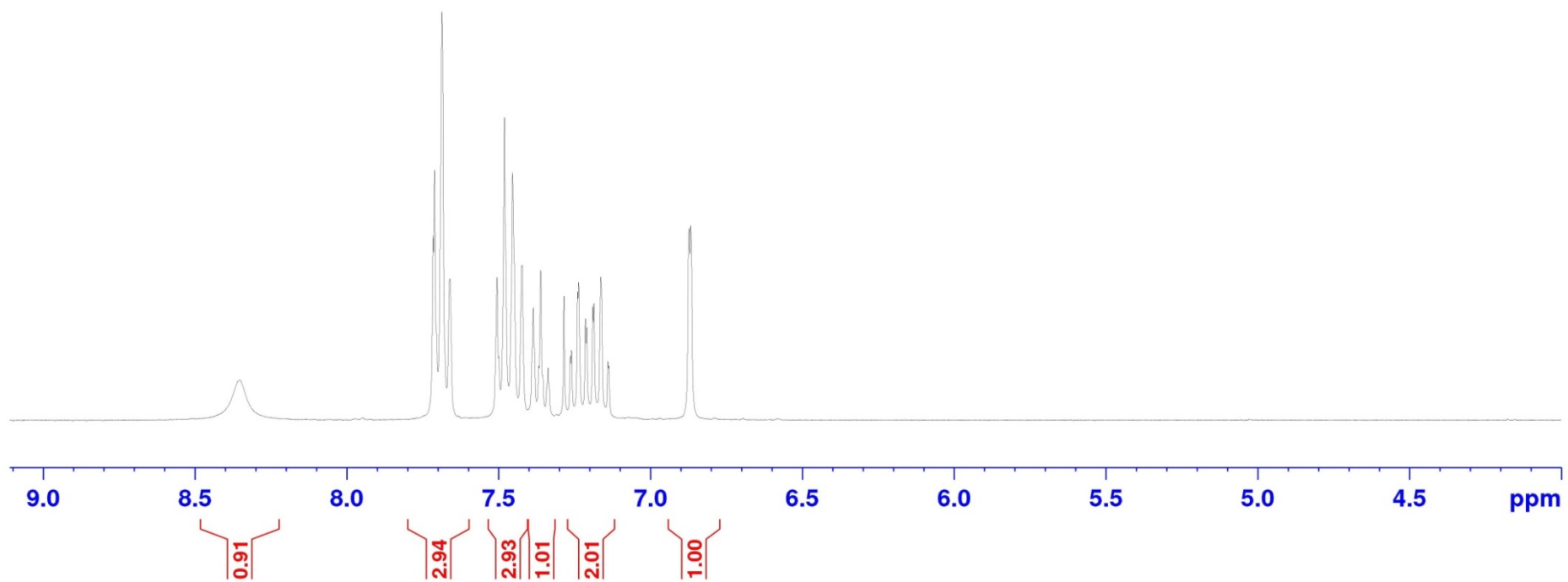
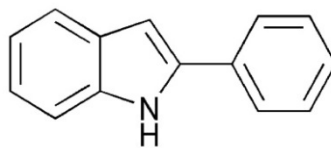


¹³C NMR of **20**

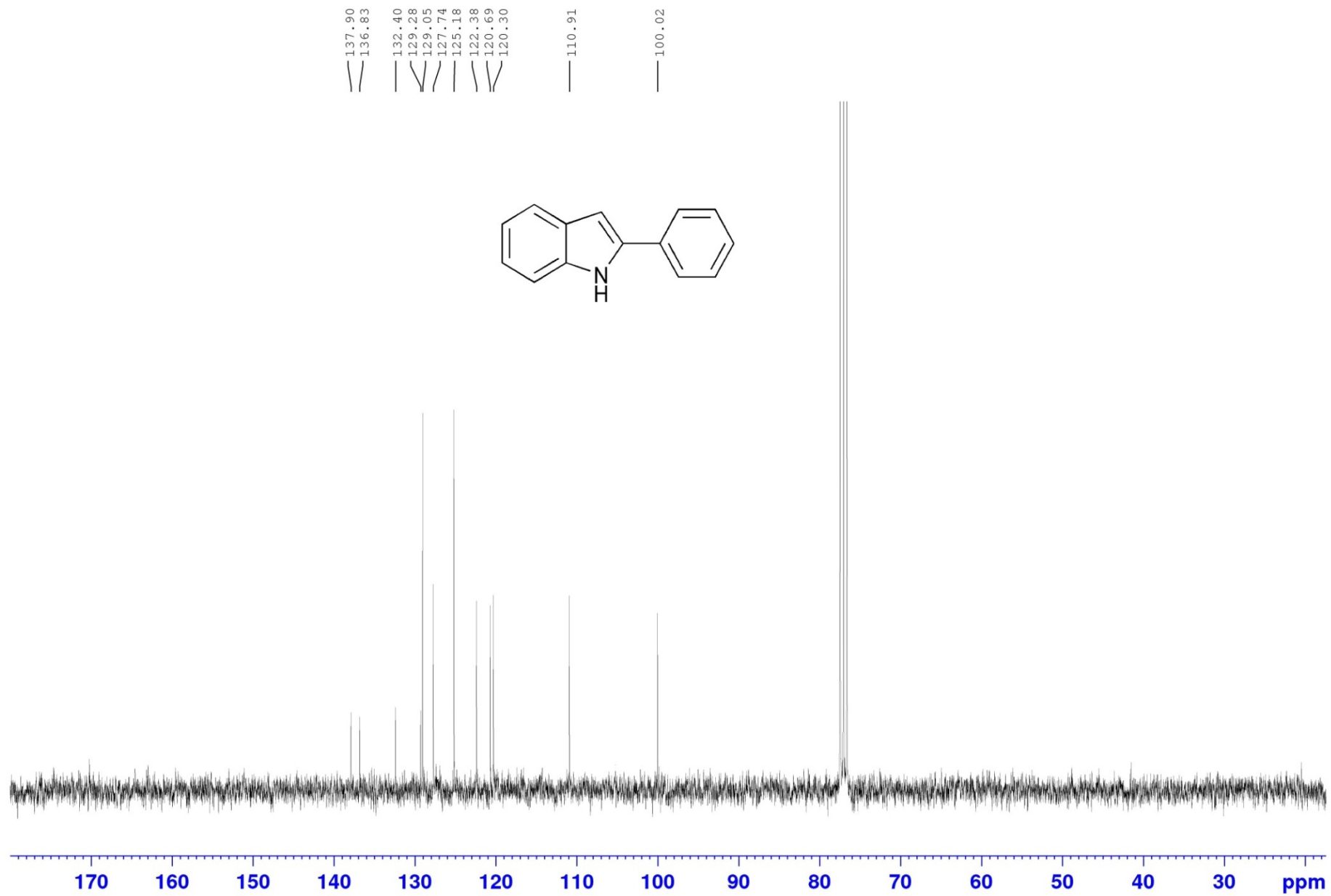


¹H NMR of **21**

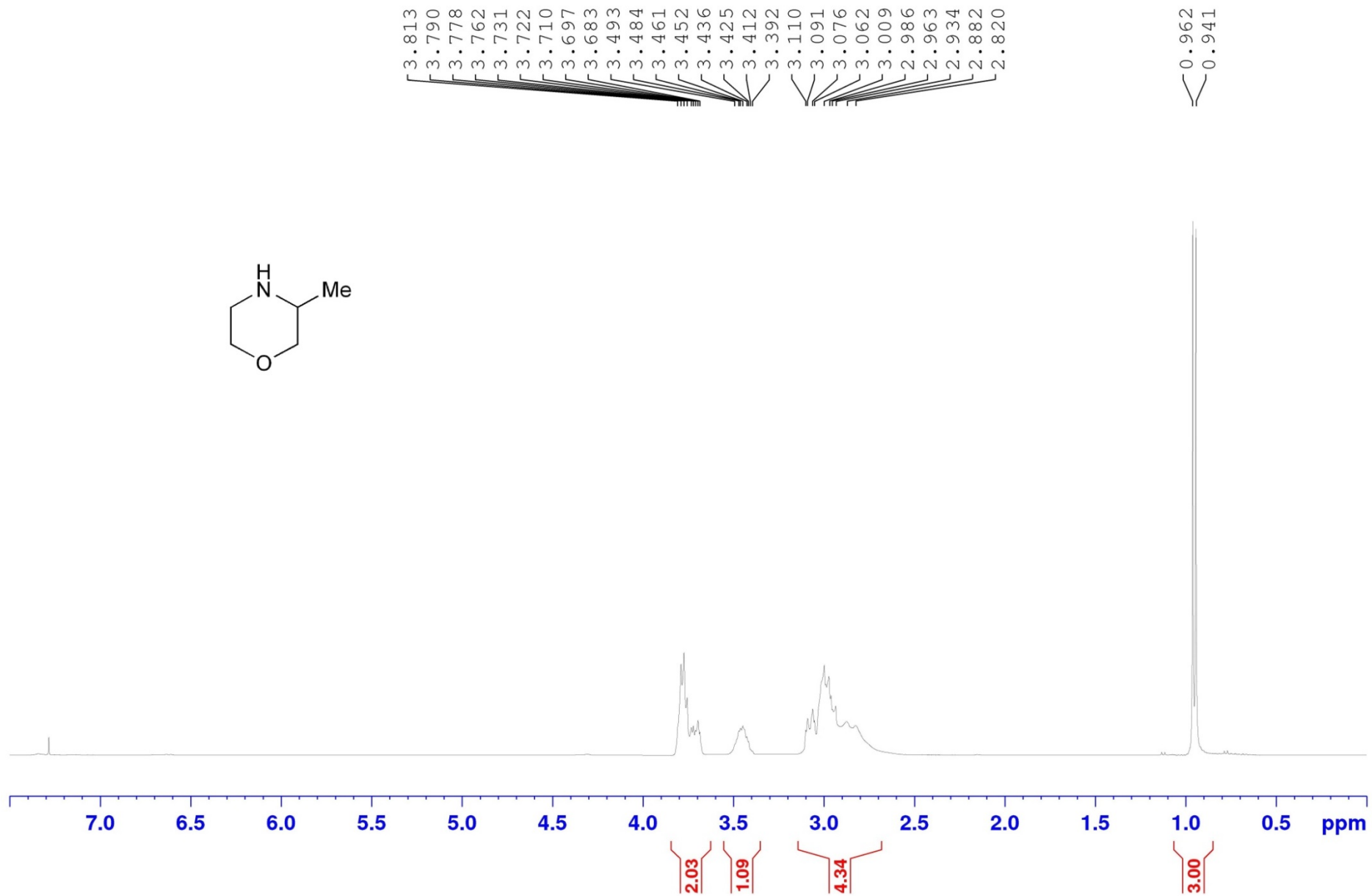
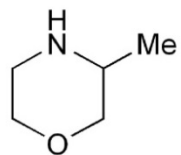
8.353
7.715
7.711
7.687
7.660
7.505
7.499
7.480
7.454
7.422
7.386
7.367
7.361
7.337
7.284
7.263
7.260
7.240
7.236
7.214
7.209
7.189
7.186
7.163
7.140
7.137
6.872
6.867



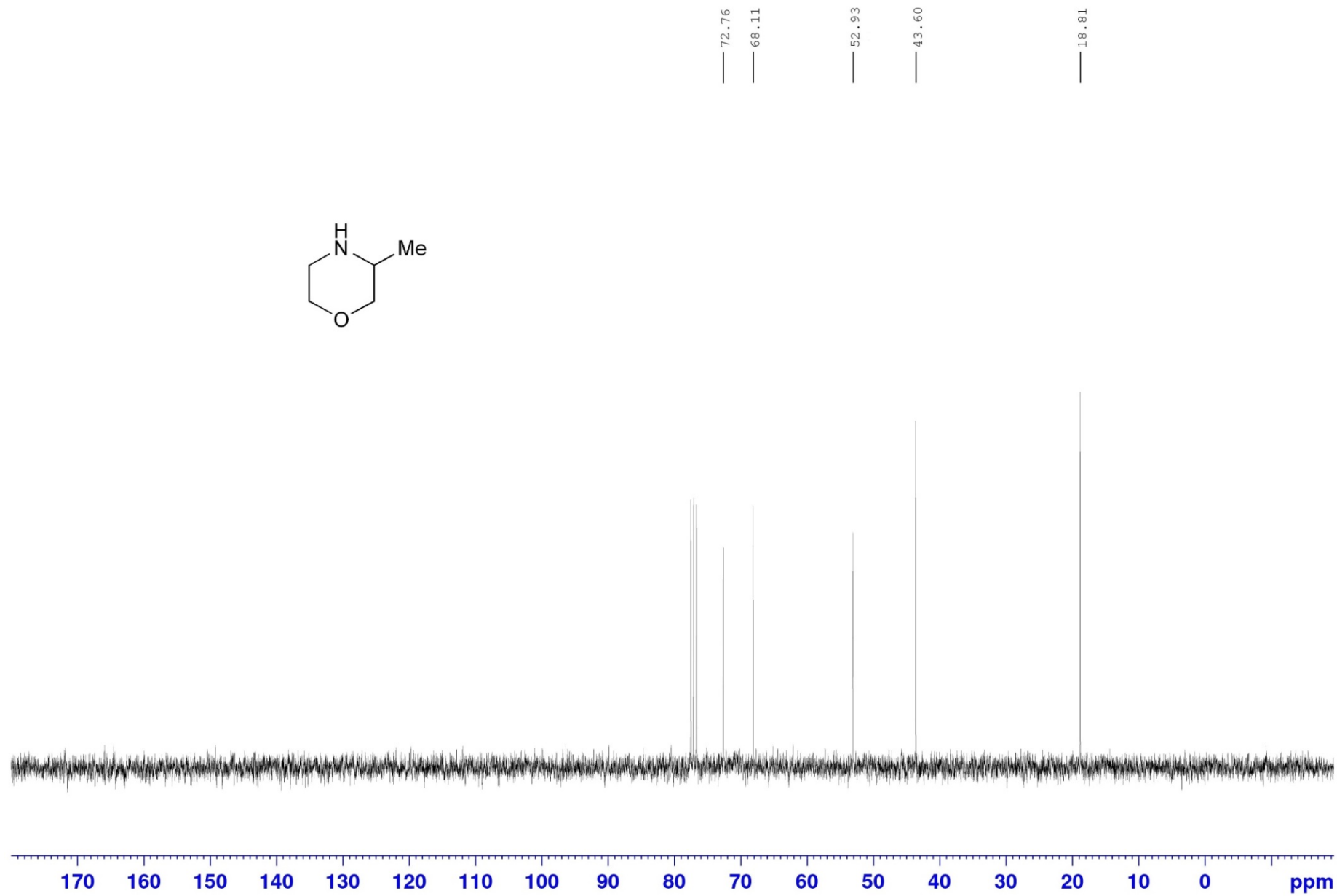
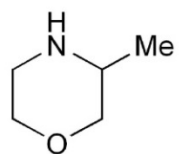
^{13}C NMR of **21**



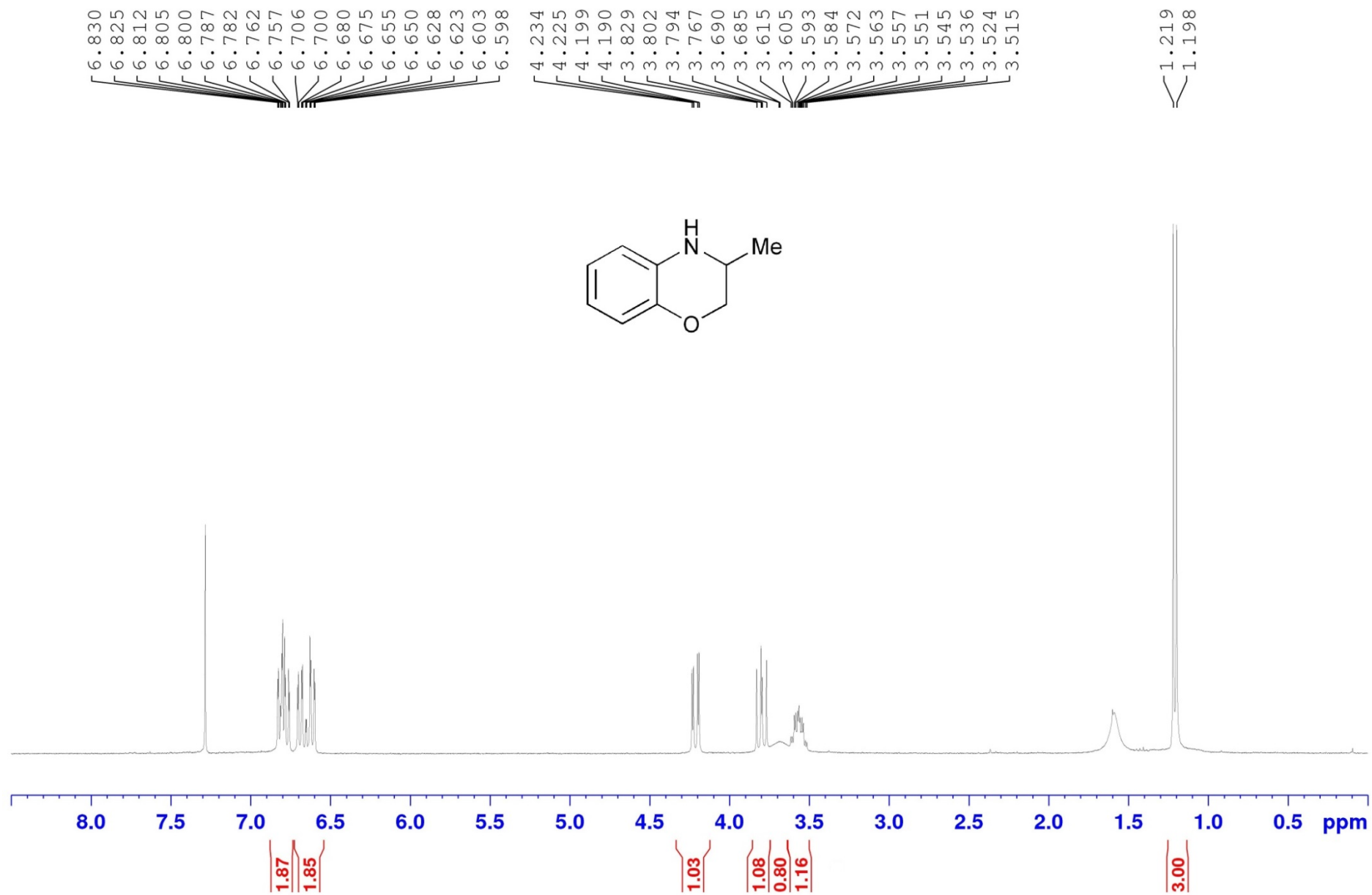
¹H NMR of 22



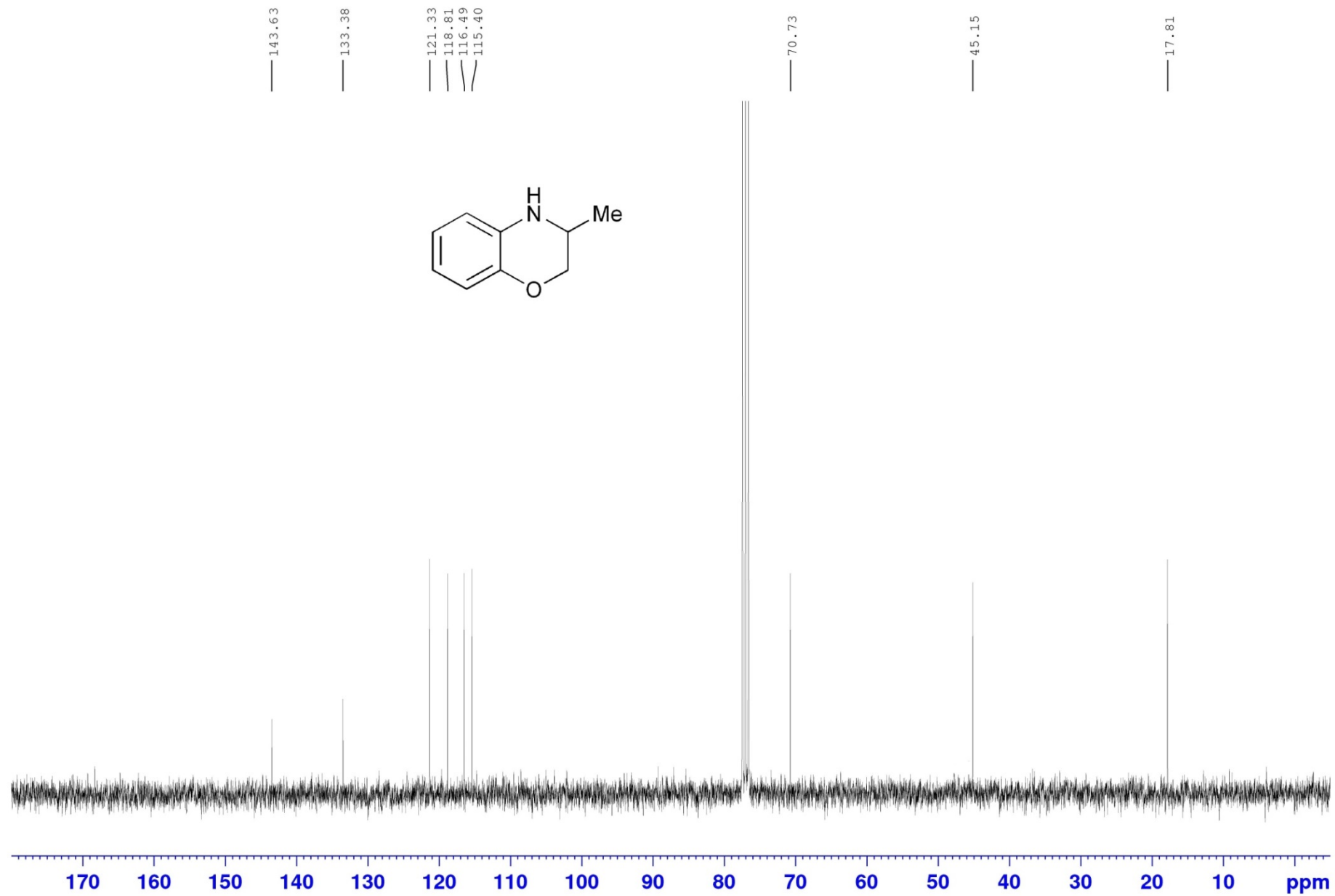
^{13}C NMR of **22**



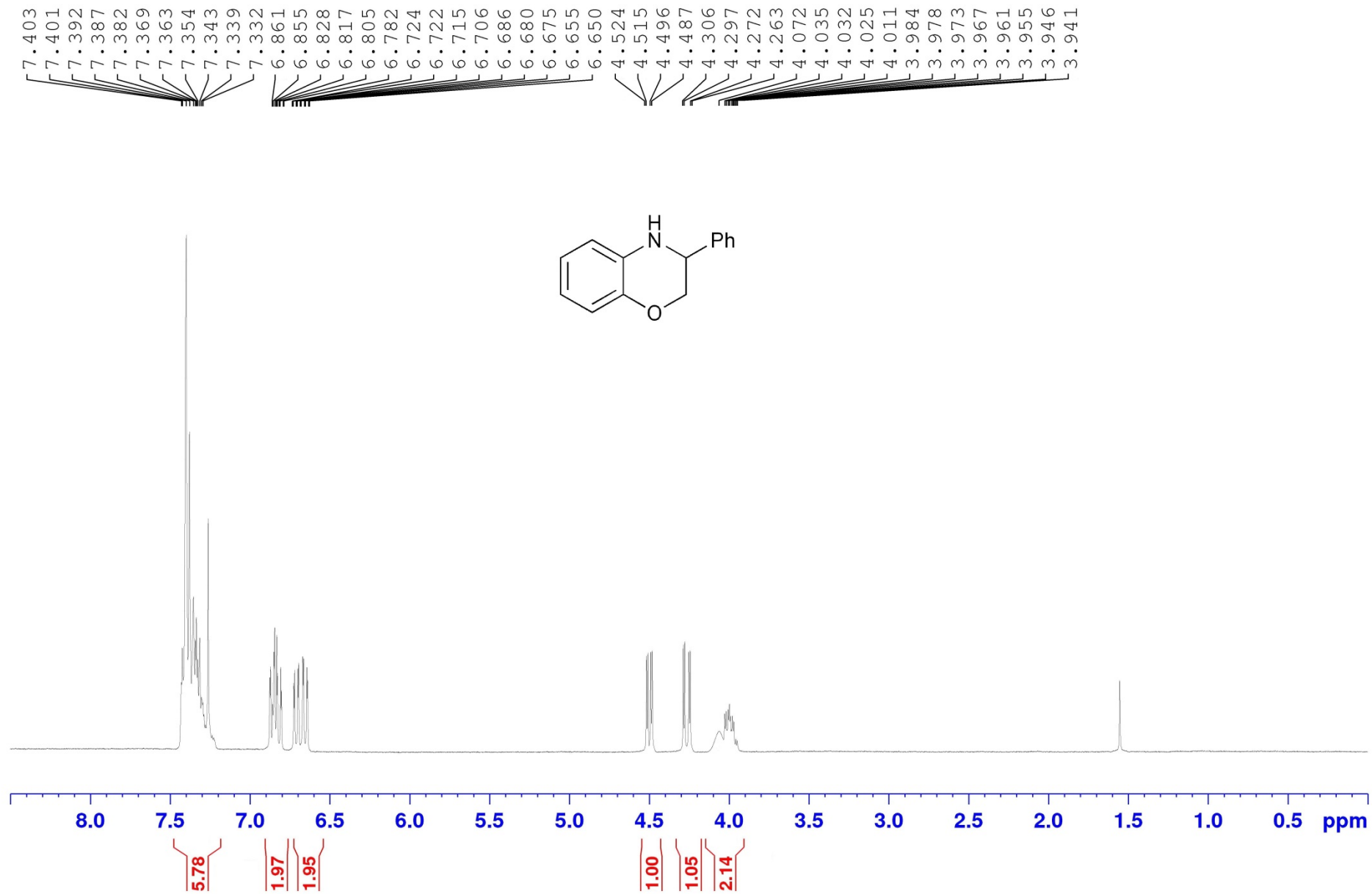
¹H NMR of **23**



¹³C NMR of **23**



¹H NMR of 24

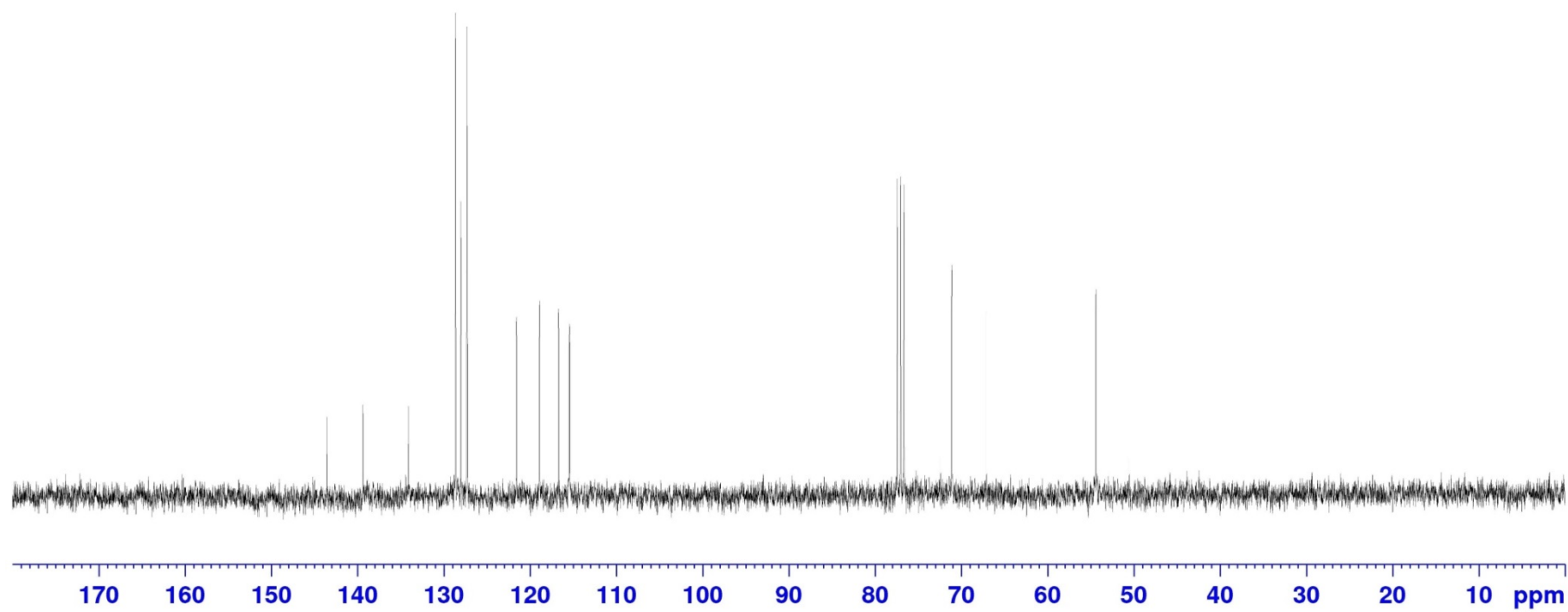
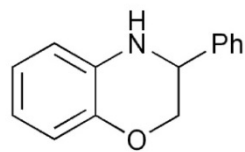


^{13}C NMR of **24**

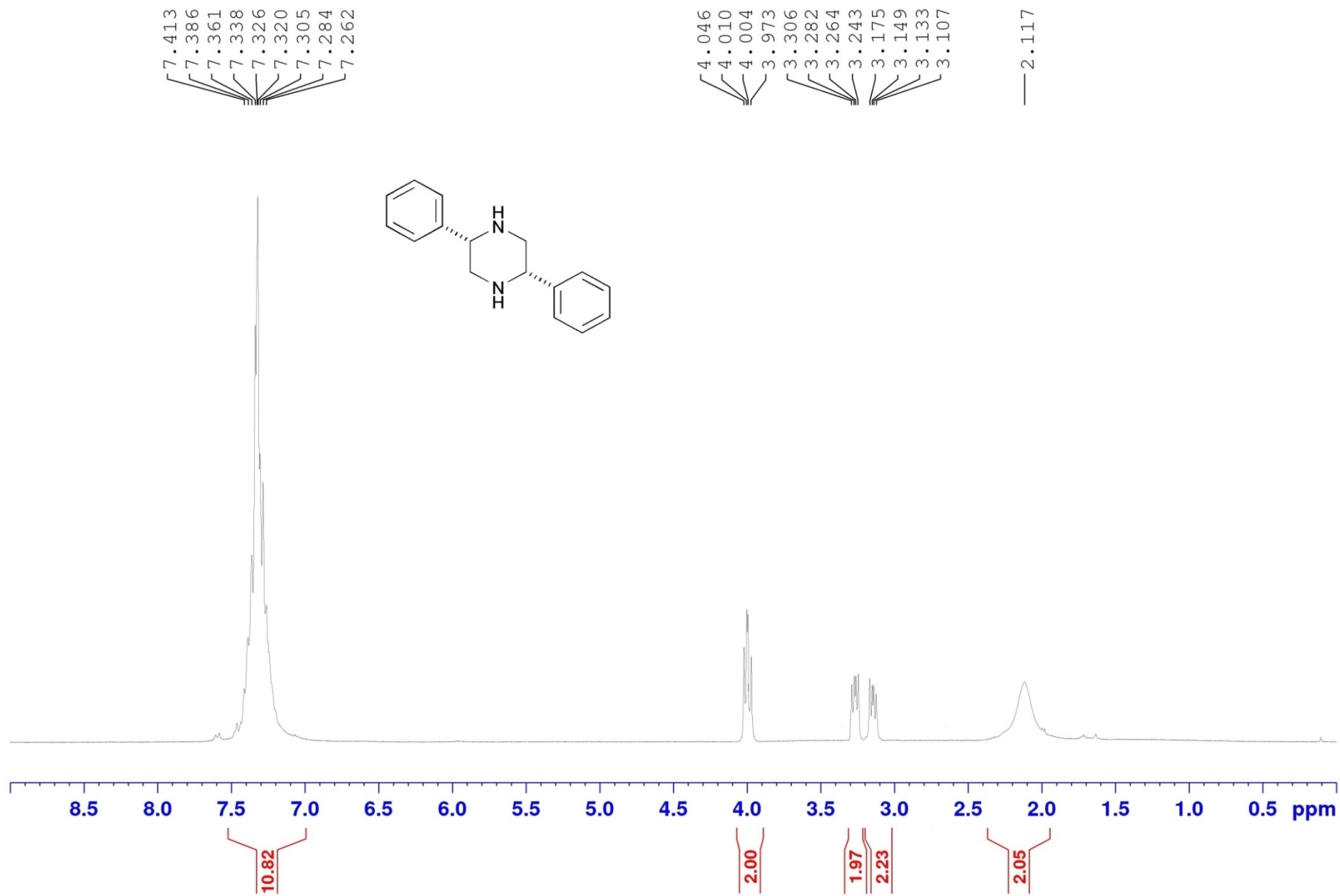
— 143.73
— 139.31
— 134.10
— 128.97
— 128.51
— 127.43
— 121.72
— 119.09
— 116.83
— 115.50

— 71.14

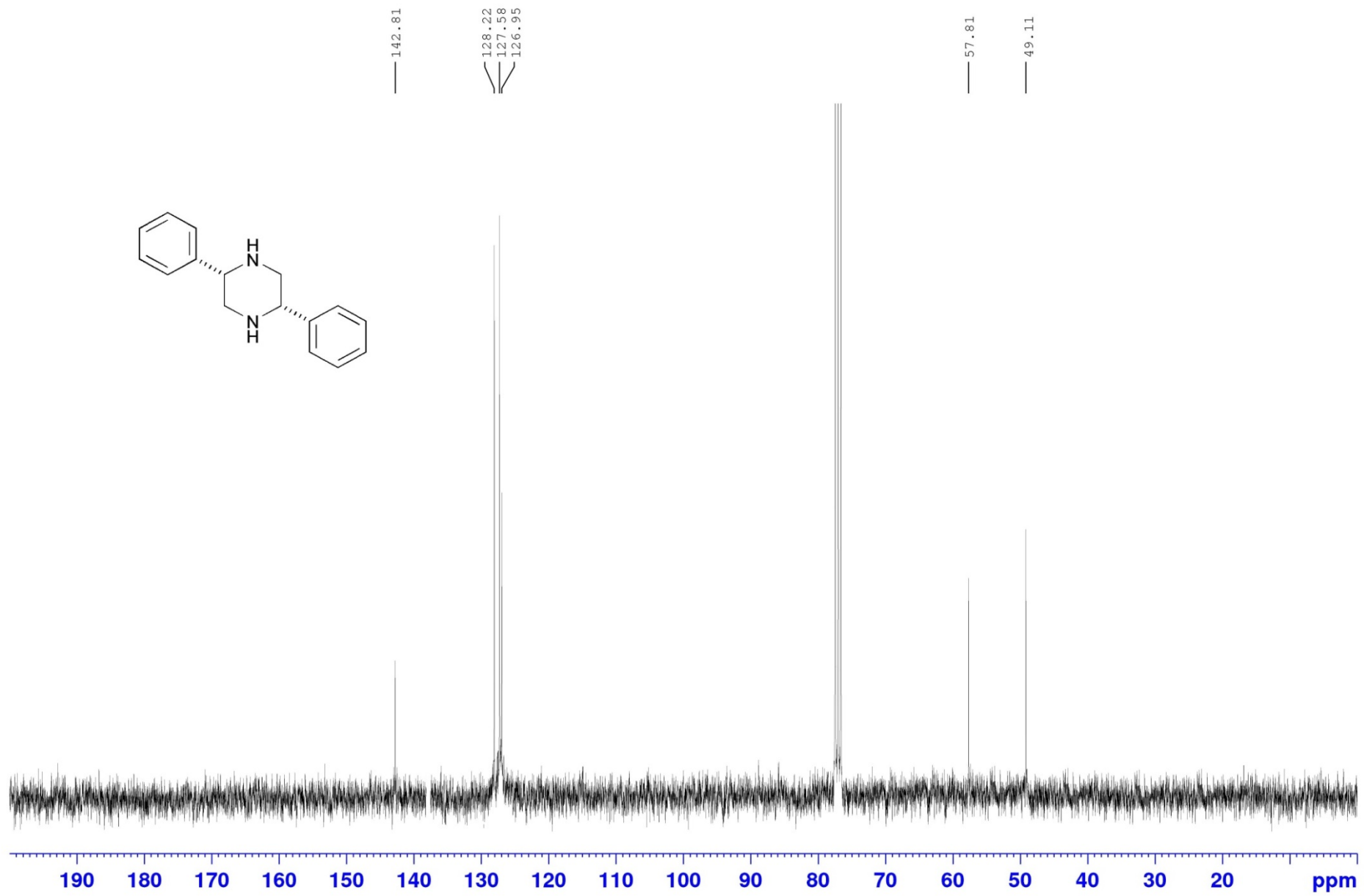
— 54.41



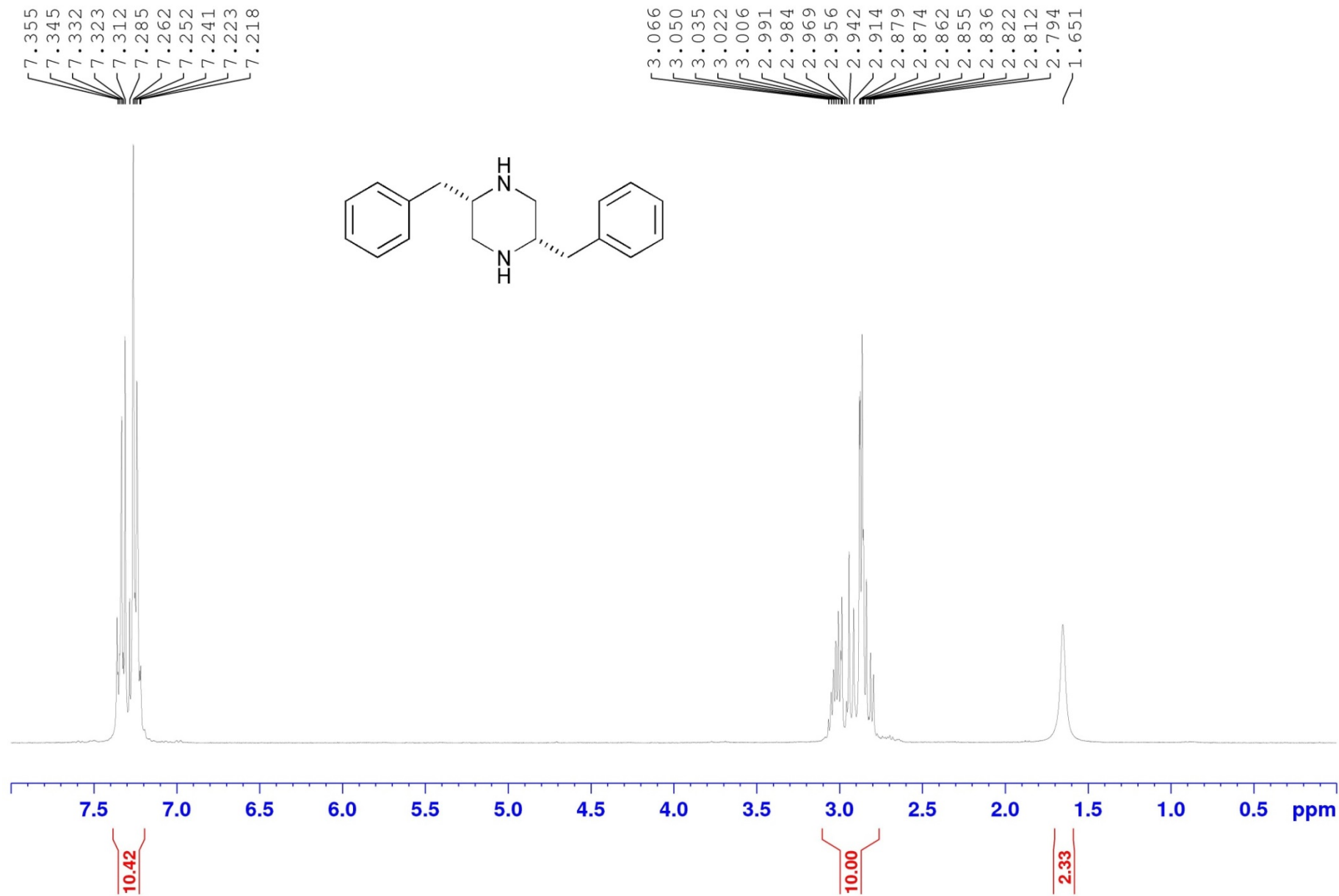
¹H NMR of **26a**



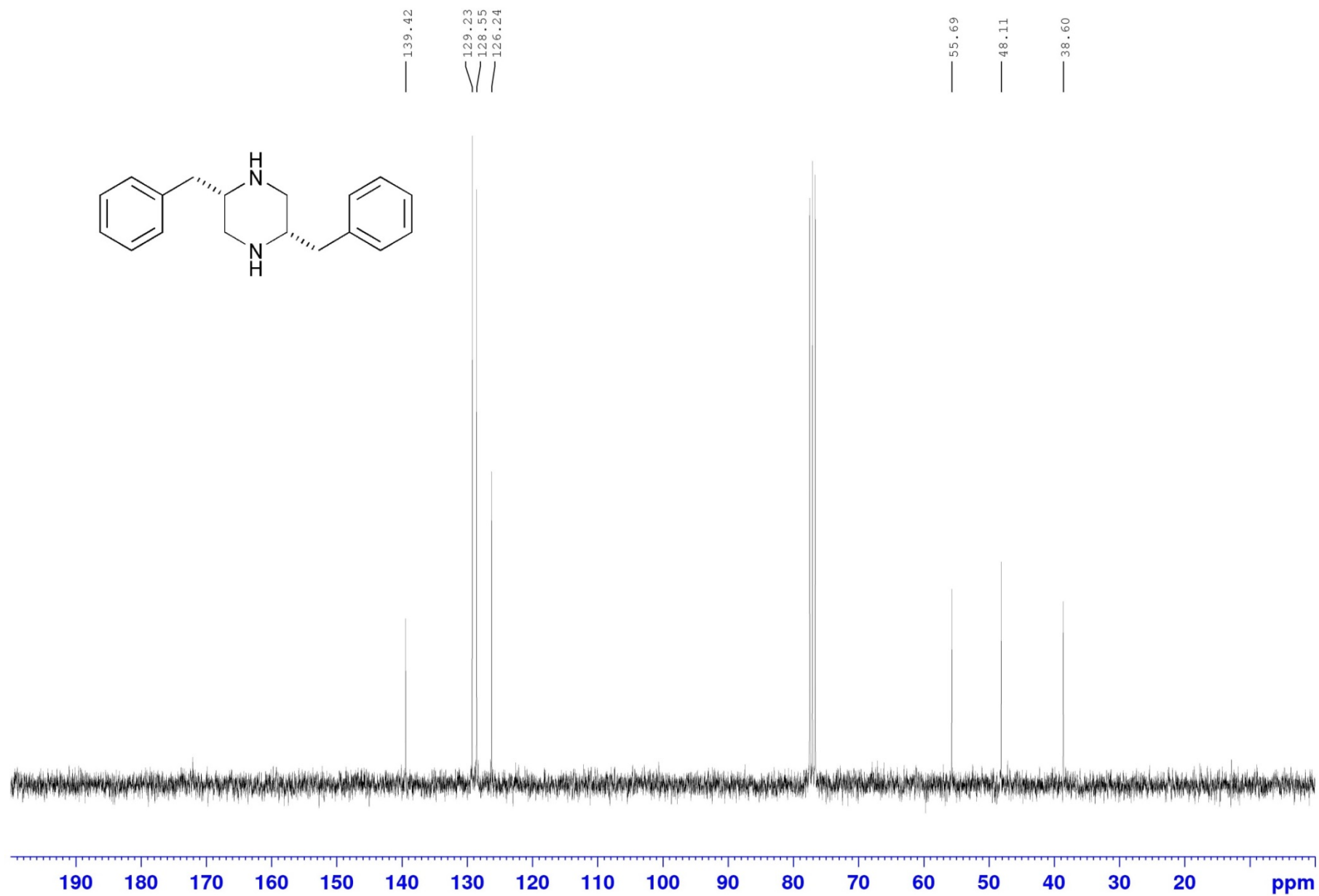
^{13}C NMR of **26a**



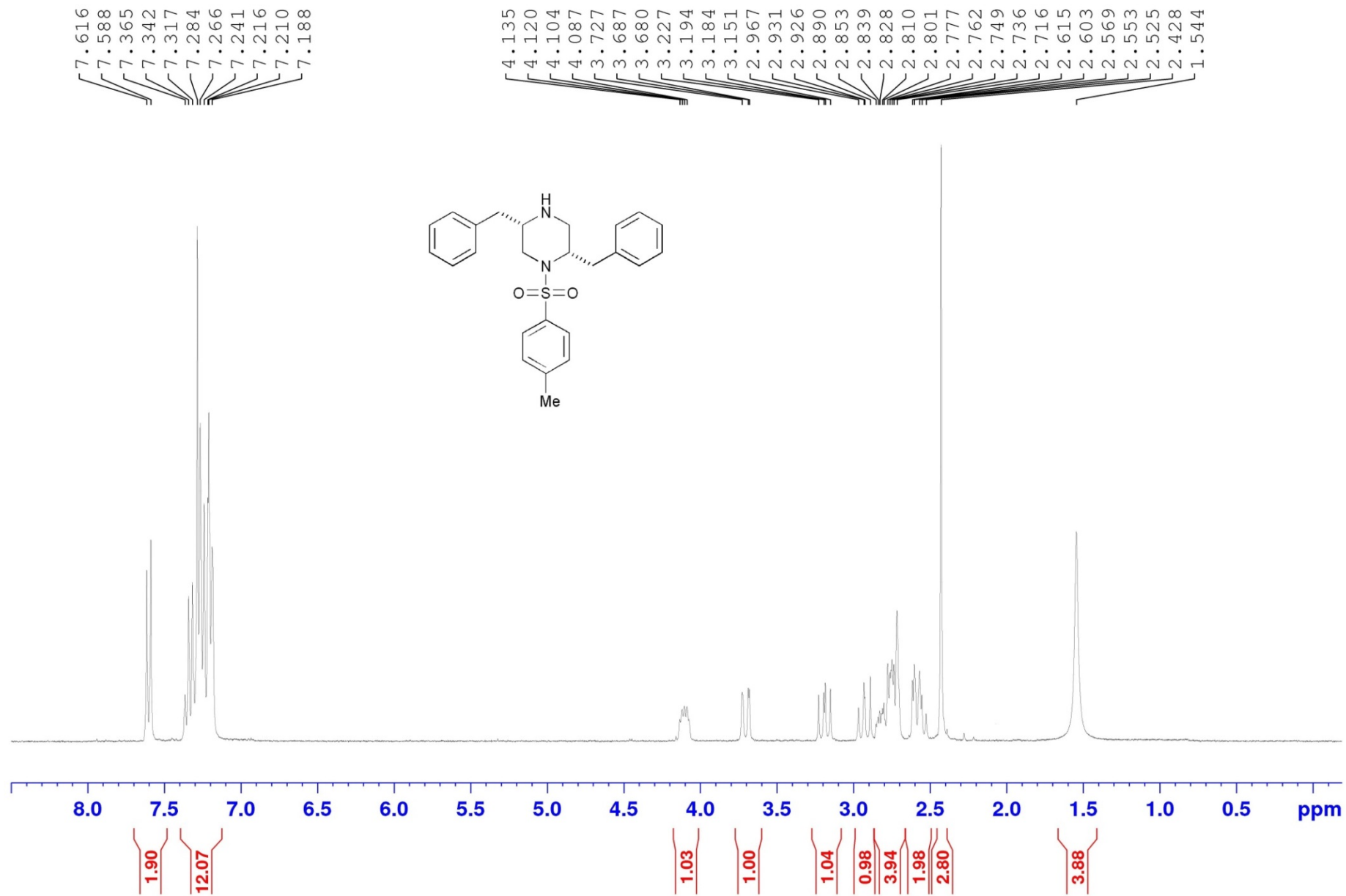
¹H NMR of **26b**



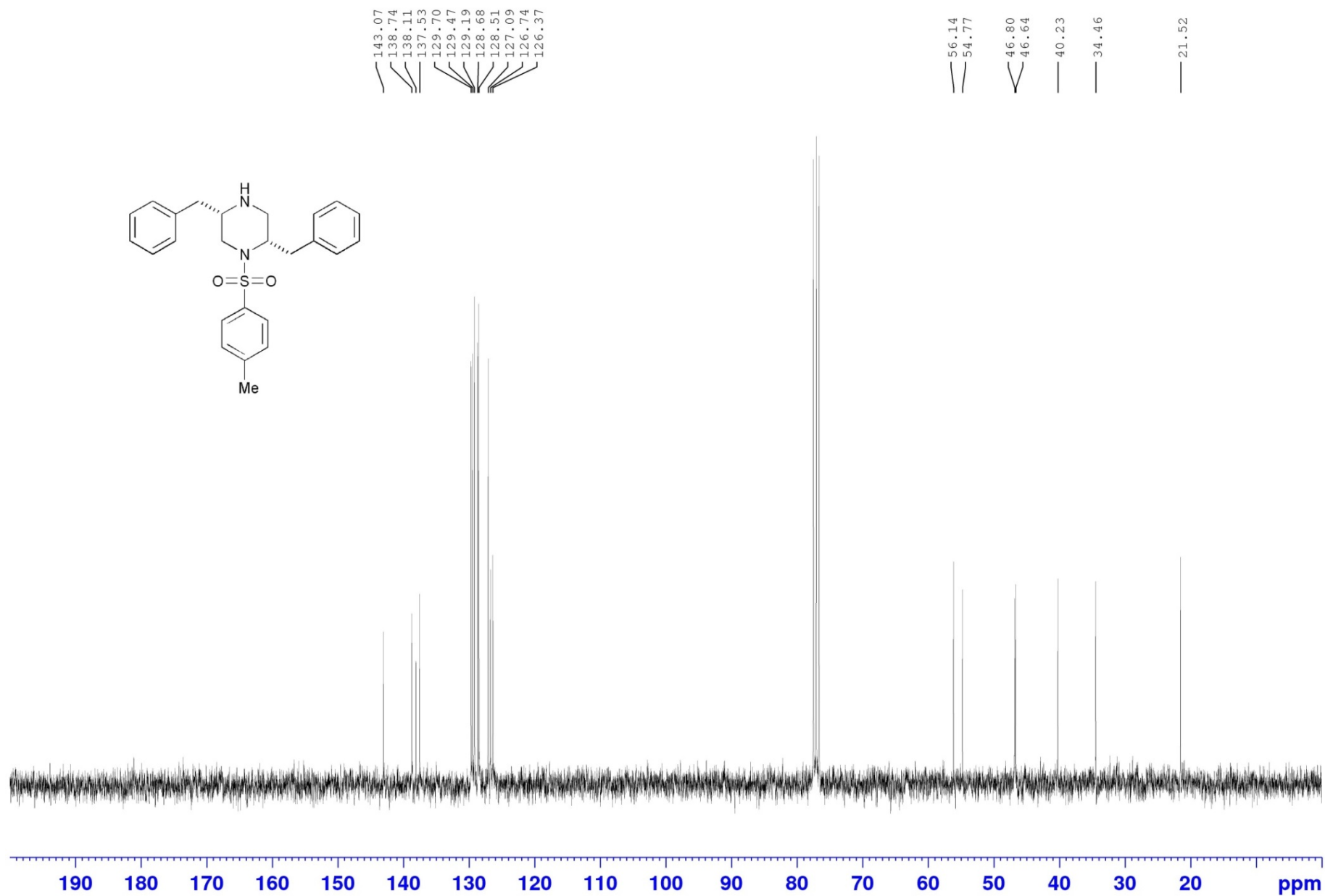
¹³C NMR of **26b**



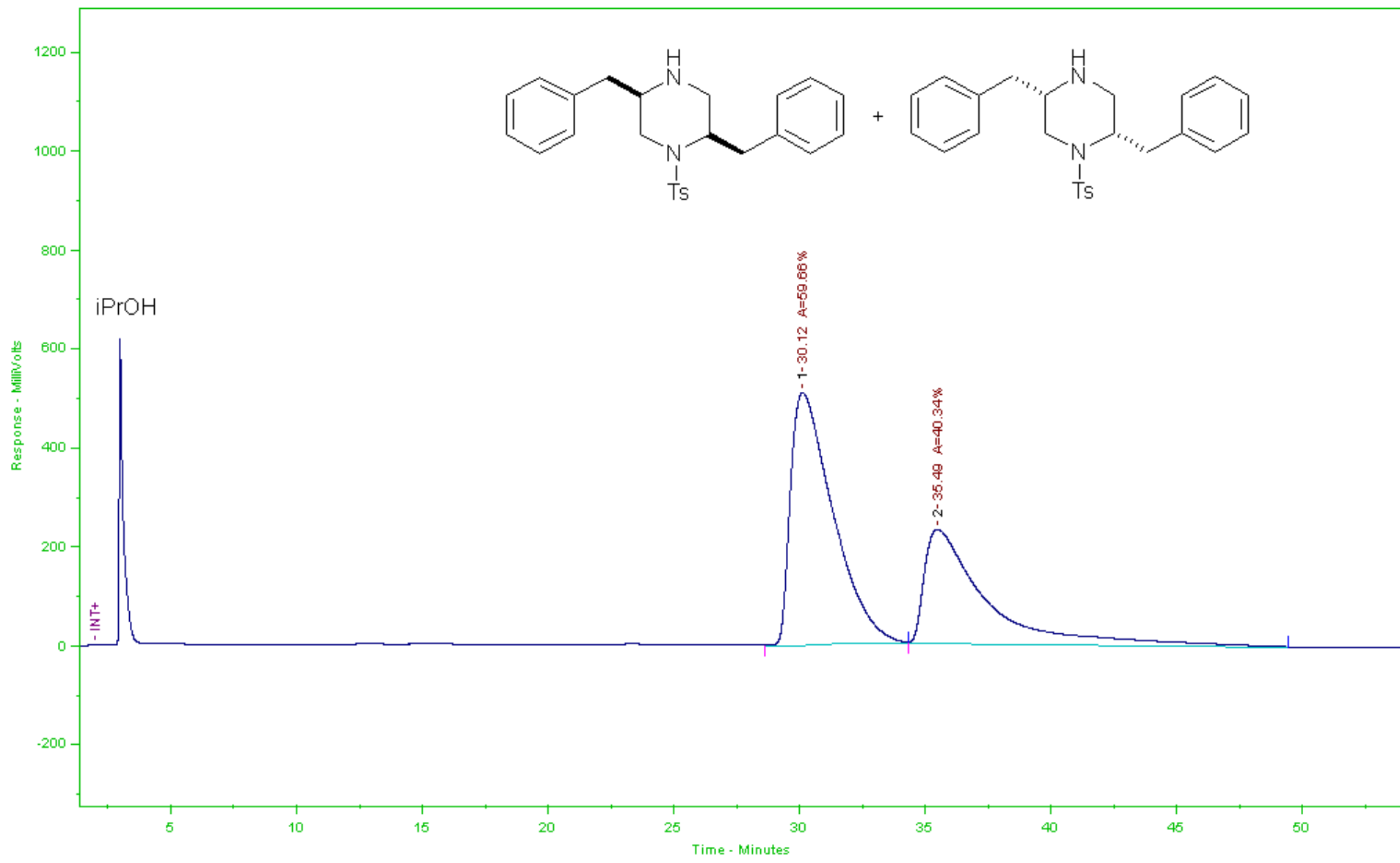
¹H NMR of 26b'



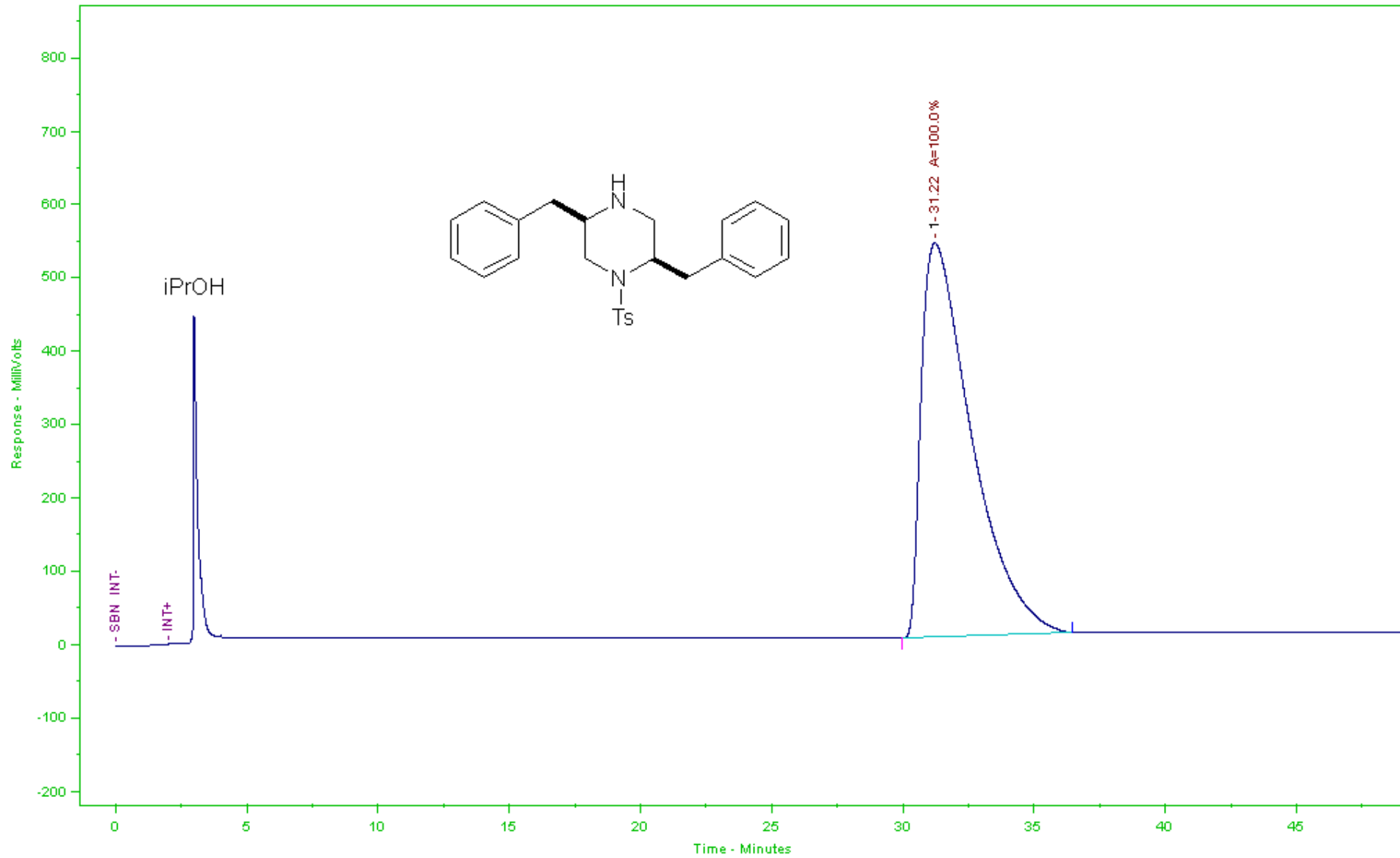
^{13}C NMR of **26b'**



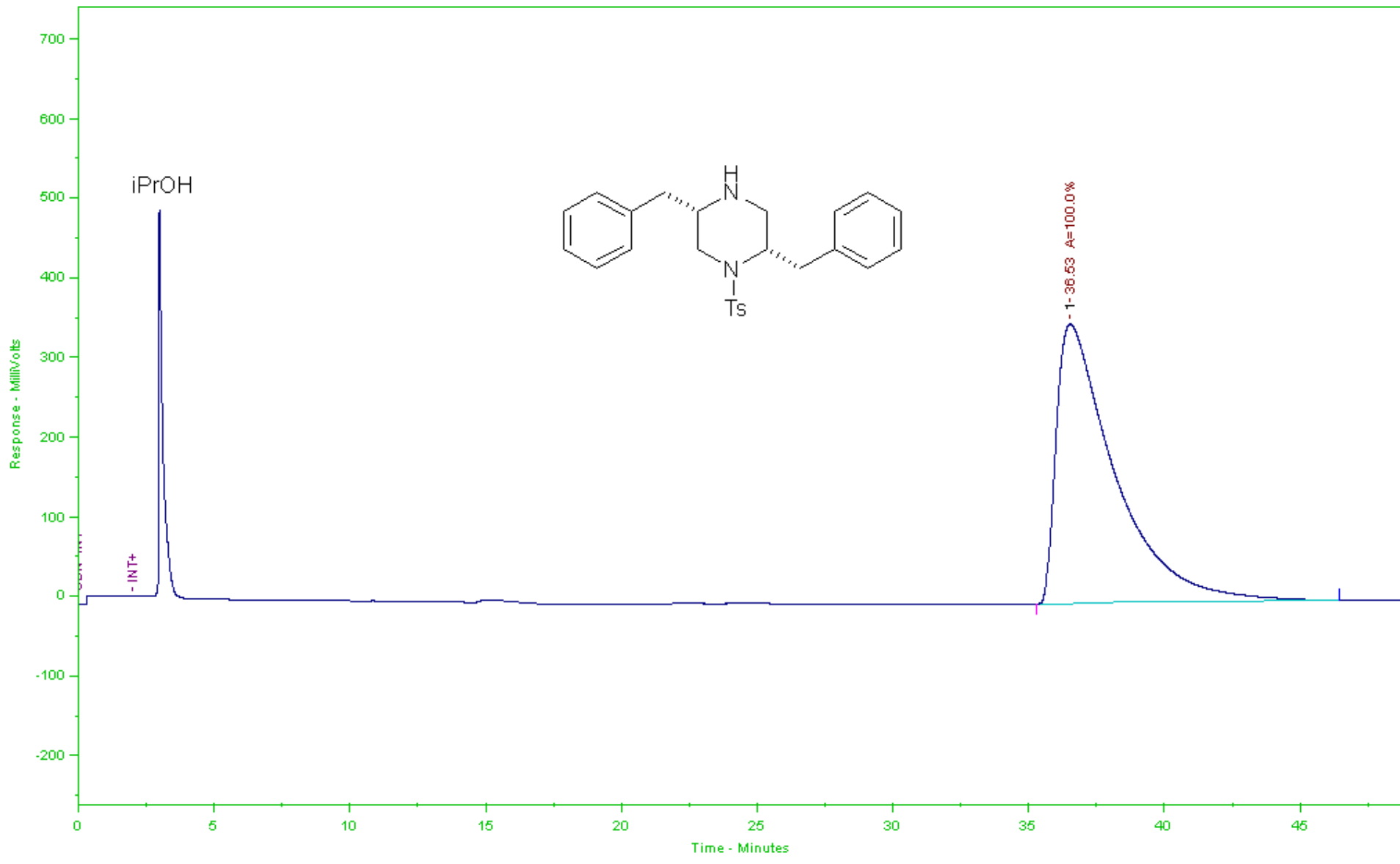
Chiral HPLC Analysis: Mixture of 26b' and *ent*-26b'



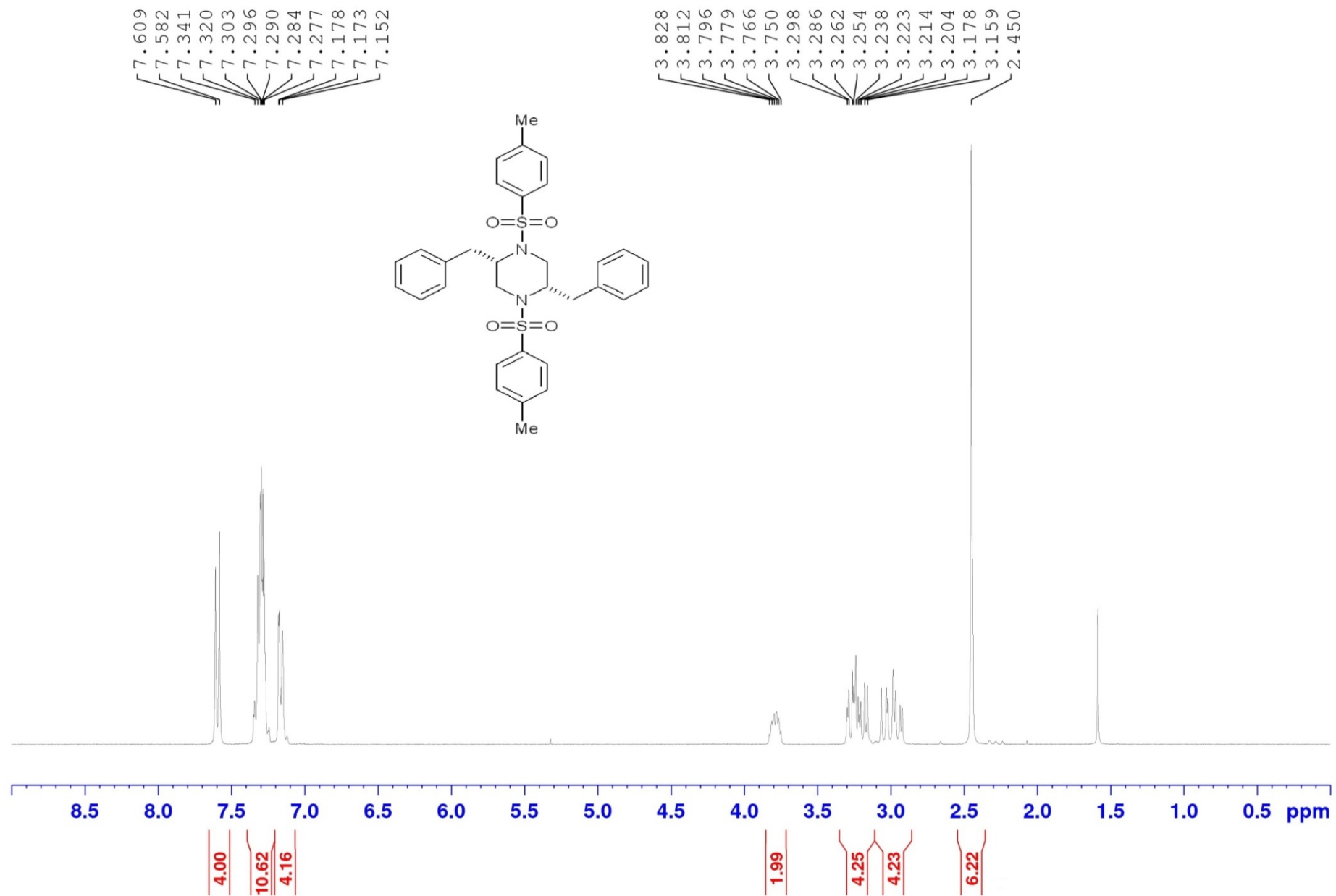
Chiral HPLC Analysis: 26b'



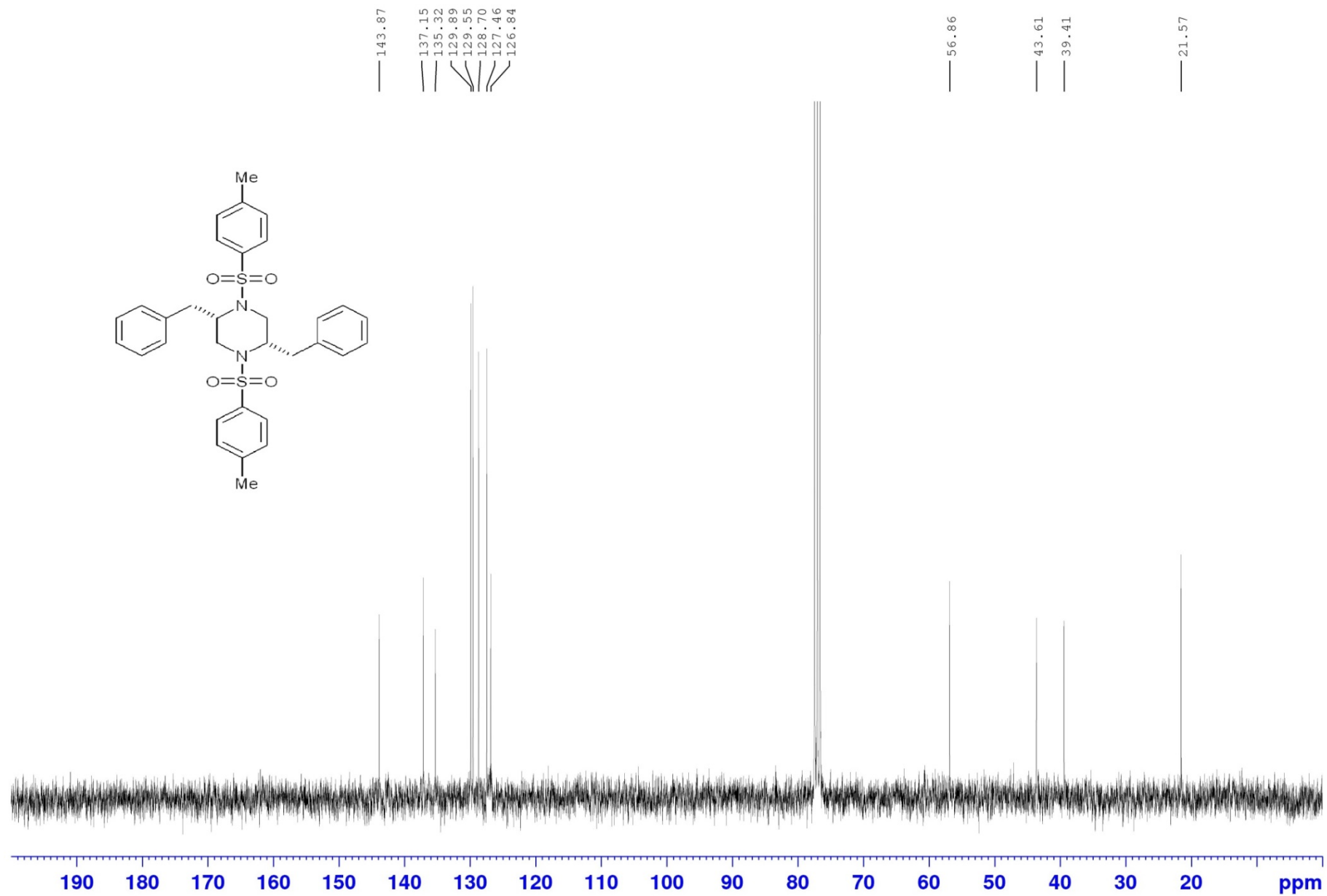
Chiral HPLC Analysis: *ent*-26b'



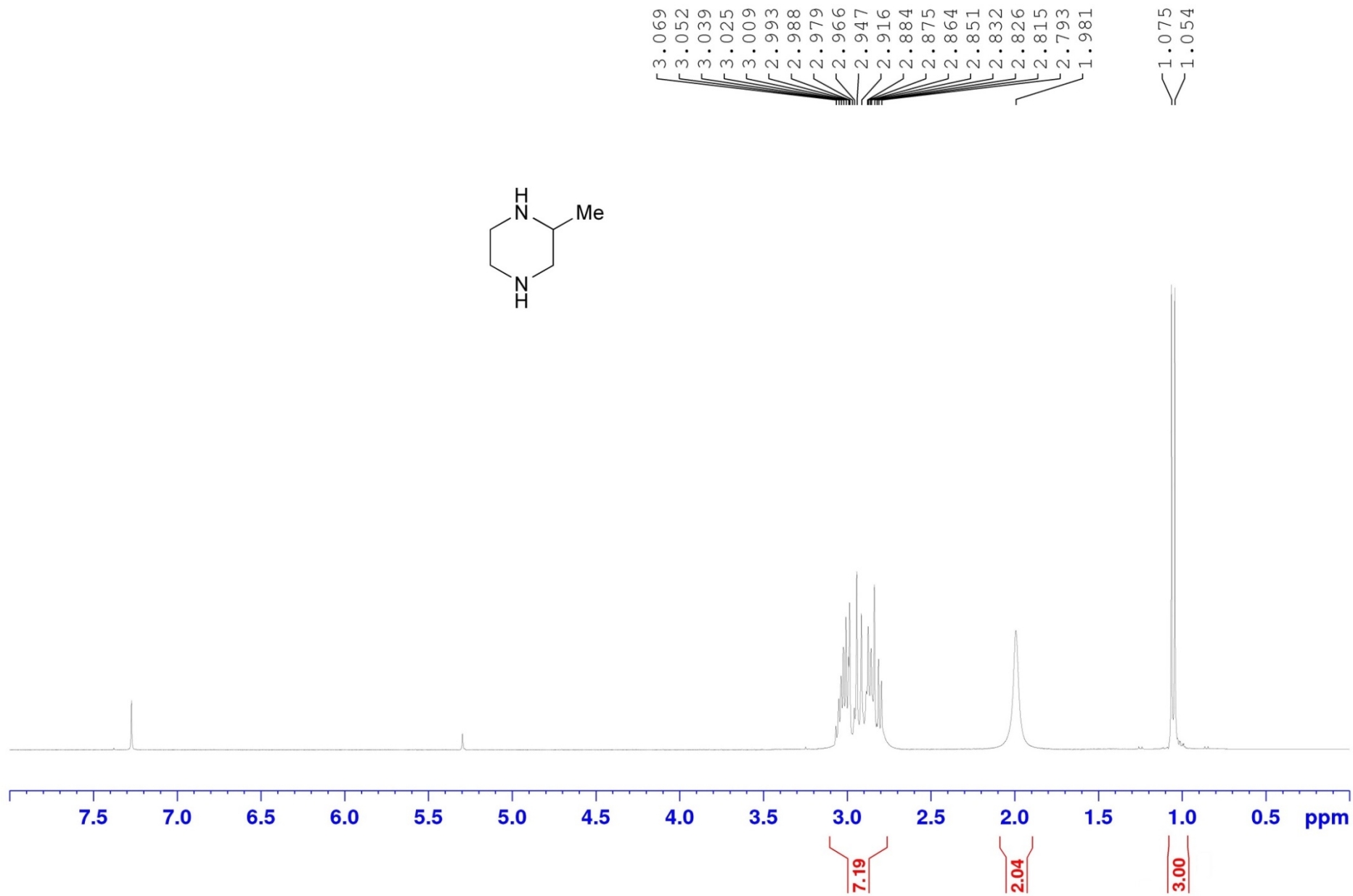
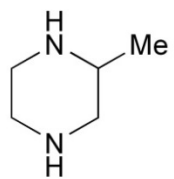
¹H NMR of 26b''



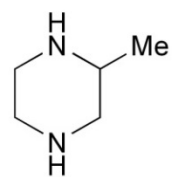
^{13}C NMR of **26b''**



^1H NMR of **28**

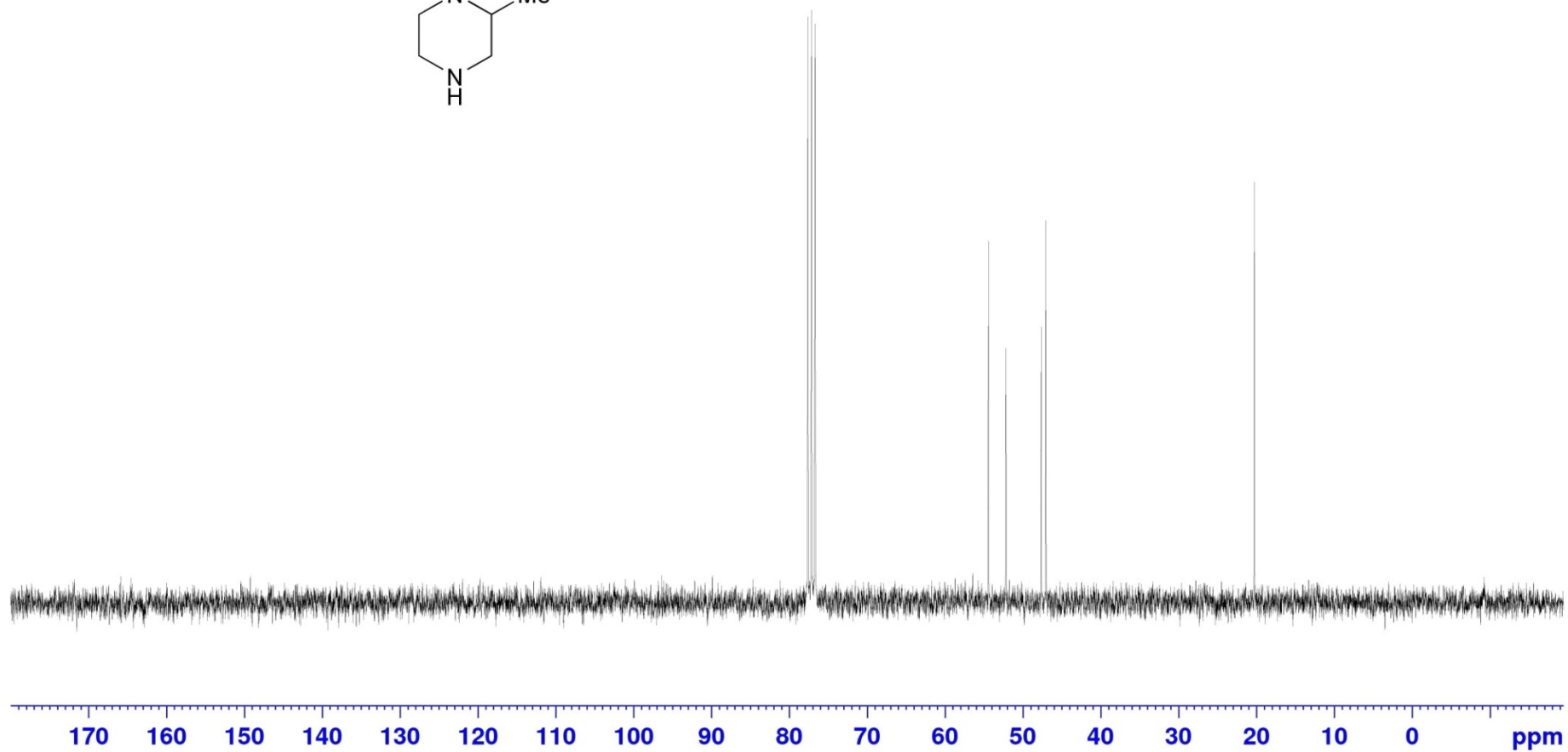


^{13}C NMR of **28**



54.47
52.19
47.78
47.12

20.36

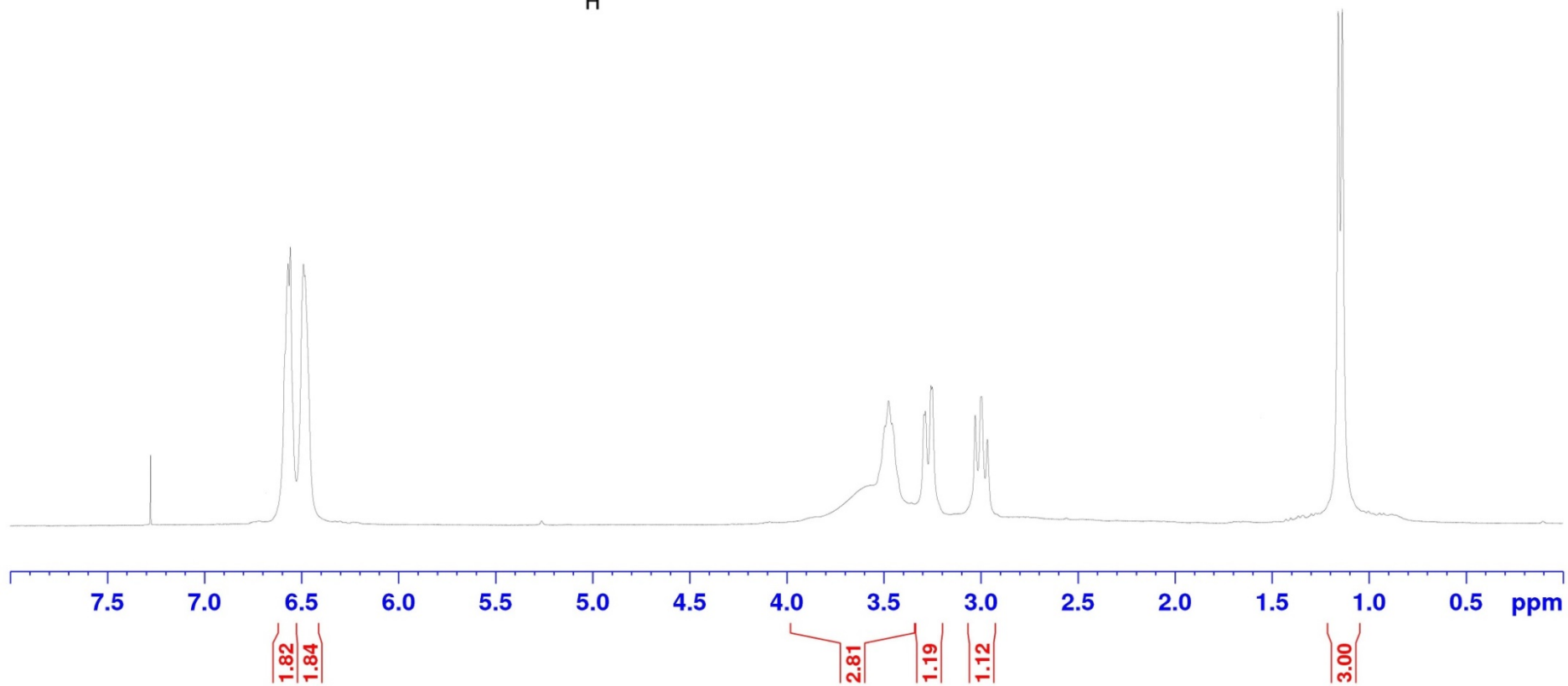
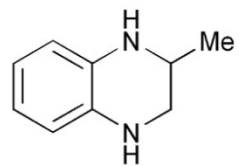


¹H NMR of 29

6.569
6.558
6.490
6.482

3.494
3.475
3.457
3.292
3.285
3.257
3.250
3.029
2.996
2.966

1.158
1.137



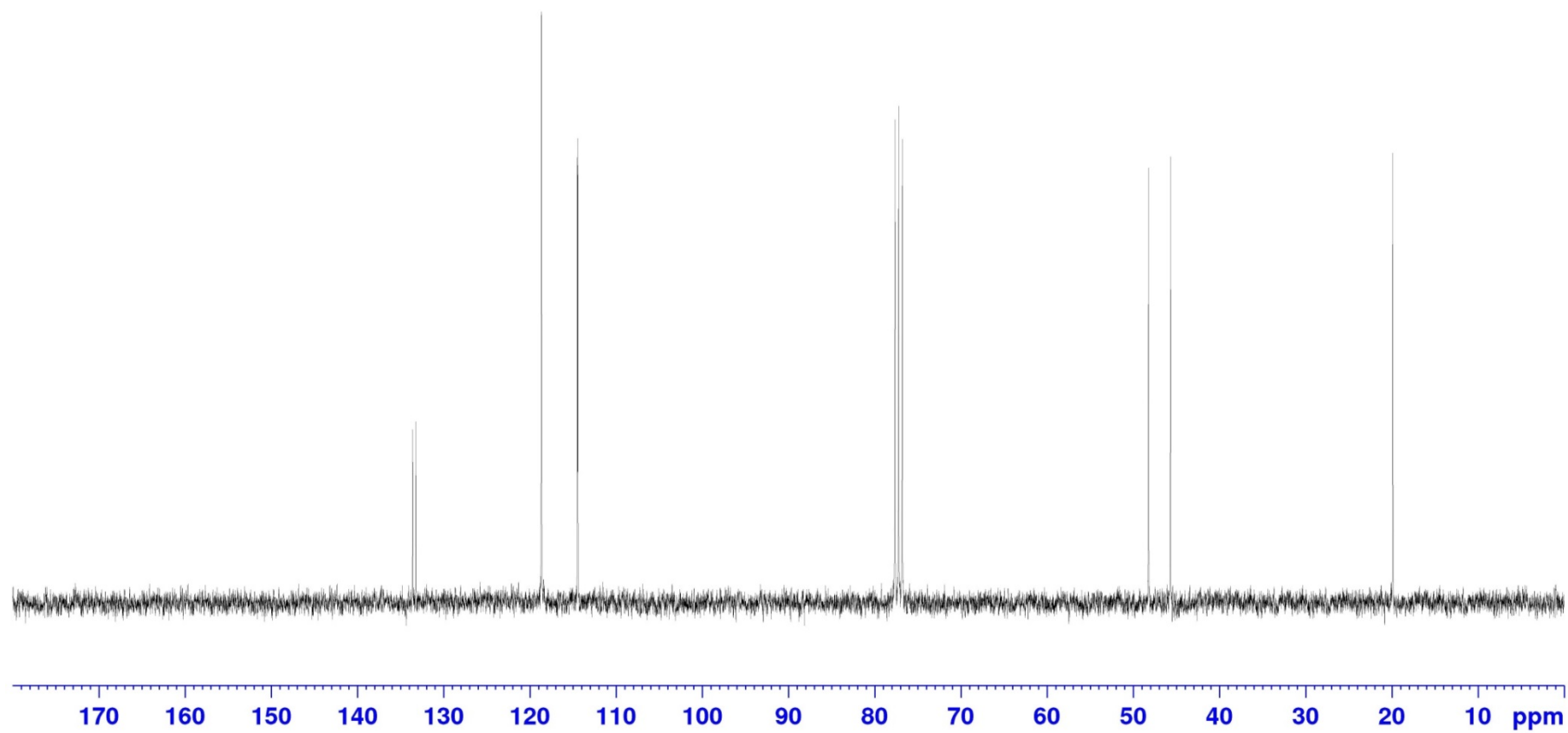
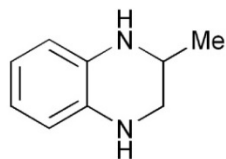
¹³C NMR of **29**

133.58
133.22

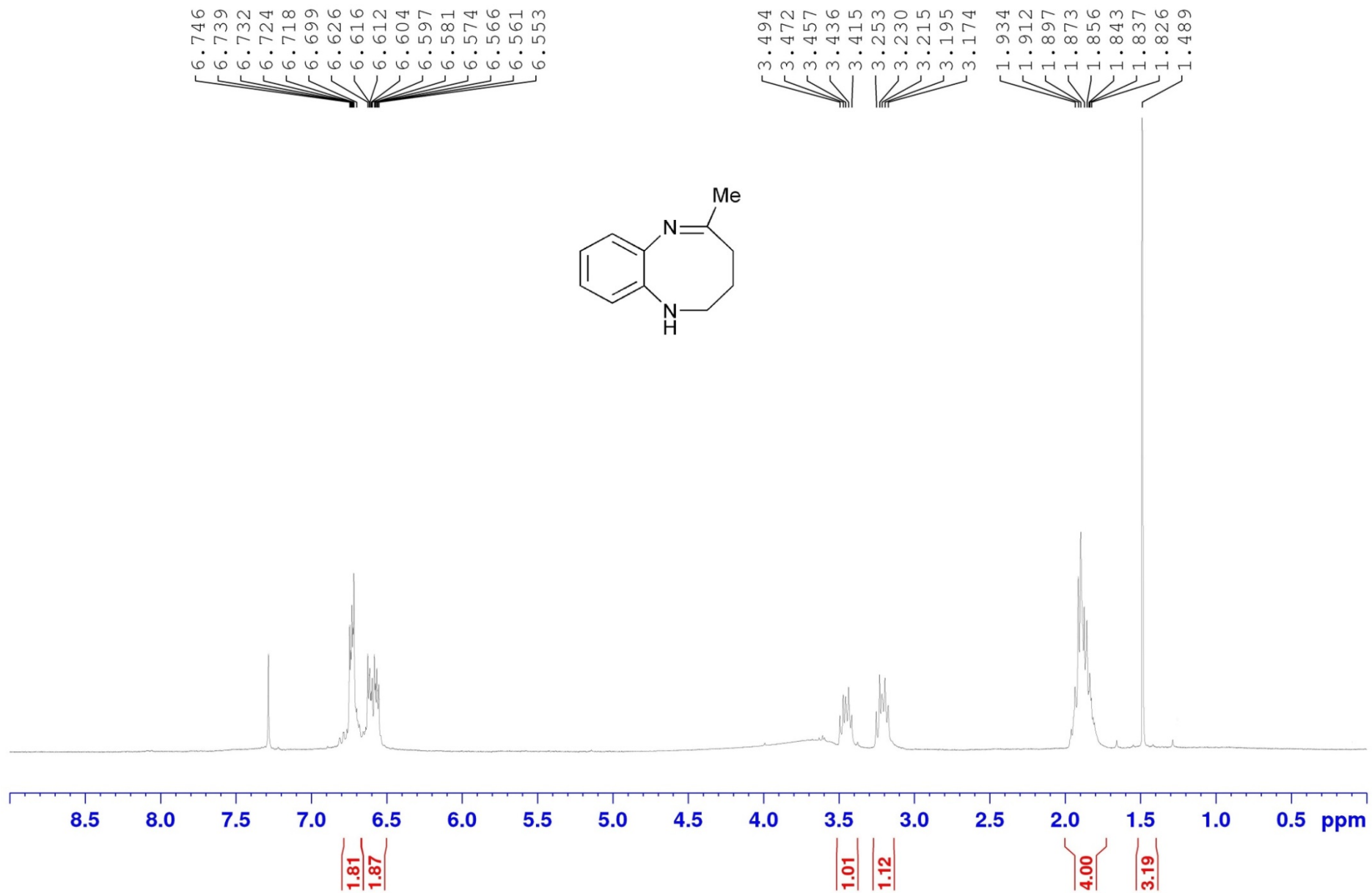
118.65
114.47
114.41

46.21
45.66

19.86



¹H NMR of **30**



^{13}C NMR of **30**

— 144.43
— 141.24

— 121.13
— 120.34

— 112.01
— 109.49

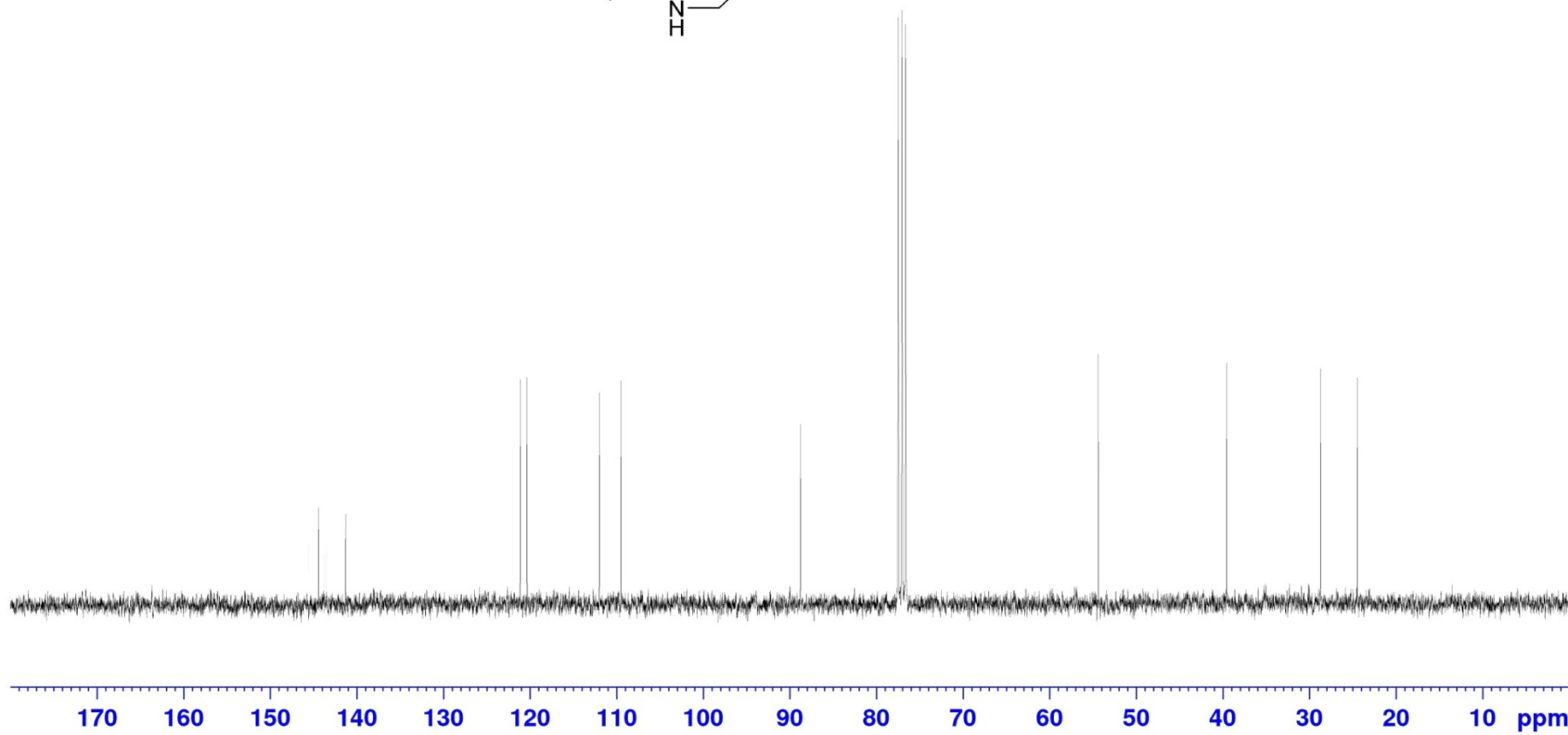
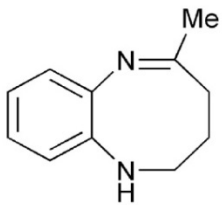
— 88.77

— 54.38

— 39.54

— 28.71

— 24.47



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