

Electronic Supplementary Information for

Efficient Palladium-Catalyzed Synthesis of Substituted Indoles Employing a New (Silanyloxyphenyl)phosphine Ligand

Christopher B. Lavery,^a Robert McDonald^b and Mark Stradiotto^{a,*}

^aDepartment of Chemistry, Dalhousie University, 6274 Coburg Road, P.O. Box 15000, Halifax, NS, Canada B3H 4R2.

^bX-Ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2.

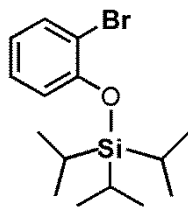
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General Considerations:

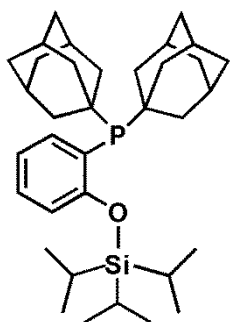
Unless otherwise noted, all reactions were set up inside a dinitrogen-filled inert atmosphere glovebox and worked up in air using benchtop procedures. Toluene used in the synthesis of **L1** and the catalytic transformations was deoxygenated by sparging with dinitrogen followed by passage through an mBraun double column solvent purification system packed with alumina and copper-Q5 reactant. $[\text{Pd}(\text{cinnamyl})\text{Cl}]_2$,¹ di(1-adamantyl)phosphine,² and (4-bromophenoxy)triisopropylsilane³ were prepared according to literature protocols. The 2-alkynylbromoarene substrates were prepared by using literature synthetic protocols involving Sonogashira reactions of aryl iodides^{4, 5} or bromides⁶ with appropriate terminal alkyne precursors. Reactions employing methylamine were conducted using commercially available 2.0 M solutions of methylamine in tetrahydrofuran. C_6D_6 was degassed by using at least three repeated freeze-pump-thaw cycles and stored over 4 Å molecular sieves for 24 h prior to use. All other chemicals were obtained from commercial sources in high purity and used as received. Column chromatography was carried out using Silicycle SiliaFlash 60 with particle size 40-63 μm (230-400 mesh). Gas chromatography (GC) data were obtained on a Shimadzu GC-2014 equipped with a SGE BP-5 30 m, 0.25 mm I.D. column. In the case where conversions and yields are given on the basis of gas chromatography experiments, the data were corrected by calibration using dodecane as an internal standard and product identity was confirmed by comparison with authentic samples. All ^1H , ^{13}C , and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe_4 (for ^1H and ^{13}C) or 85% H_3PO_4 in D_2O (for ^{31}P). NMR data were acquired with the technical assistance of Dr. Michael Lumsden (NMR-3, Dalhousie University), while mass spectrometric data were acquired by Mr. Xiao Feng (Mass Spectrometry Laboratory, Dalhousie University).

Synthesis and characterization of **L1**:



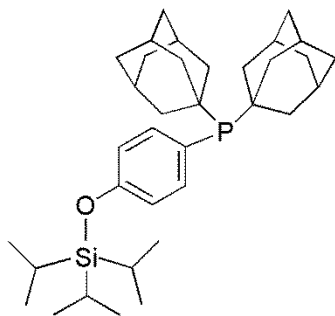
Step 1. To an oven dried screw-capped vial was added a magnetic stir bar, imidazole (629 mg, 9.2 mmol), 2-bromophenol (536 μL , 4.6 mmol) and 9.0 mL of methylene chloride. Triisopropylchlorosilane (1.1 mL, 5.1 mmol) was then added dropwise with constant magnetic stirring. The vial was sealed under dinitrogen with a cap containing a PTFE septum and was removed from the glovebox and stirred vigorously at ambient temperature. Full consumption of starting material and quantitative formation of one new product was observed after 16 h by removing a 50 μL aliquot of the reaction mixture by syringe and filtering through a Celite plug, followed by dilution of the eluent with methylene chloride for GC and thin layer chromatography (TLC) analysis. At this point, the reaction mixture was diluted with ethyl acetate (100 mL) and water (50 mL). The layers were separated and the organic layer was washed with water (3 x 50

mL). The organic layer was dried over sodium sulfate, filtered and concentrated to afford a light yellow oil. The crude oil was purified by column chromatography with hexanes to afford the target product as a colorless oil (1.3 g, 93 %). ^1H NMR (CDCl_3): δ 7.52 (dd, $J = 7.9$ Hz, 1.7 Hz, 1H), 7.15 (m, 1H), 6.90 (d,d, $J = 8.1$ Hz, 1.4 Hz, 1H), 6.80 (m, 1H), 1.34 (sept, $J = 7.4$ Hz, 3H), 1.14 (d, $J = 7.4$ Hz, 18H); ^{13}C NMR (CDCl_3) δ 153.3, 133.8, 128.5, 122.3, 120.0, 115.4, 18.3, 13.3. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.⁷



Step 2. To an oven dried screw-capped vial was added a stir bar, (2-bromophenoxy)-triisopropylsilane (703 mg, 2.1 mmol), $\text{Pd}(\text{OAc})_2$ (14.4 mg, 0.0640 mmol, 3 mol%), 1,1'-bis(diisopropylphosphino)ferrocene (31.3 mg, 0.0747 mmol, 3.5 mol%), NaOt-Bu (246 mg, 2.5 mmol) and 5 mL of toluene. The resulting suspension was stirred until apparently homogeneous and then di(1-adamantyl)phosphine (645 mg, 2.1 mmol) was added. The vial was sealed under dinitrogen with a cap containing a PTFE septum, removed from the glovebox, placed in a temperature-controlled aluminum heating block set at 110 °C and vigorous magnetic stirring was initiated. After 12 h, ^{31}P NMR analysis of the reaction mixture confirmed the consumption of di(1-adamantyl)phosphine and the quantitative formation of one new phosphorus-containing product. The vial containing the reaction mixture was then cooled and opened to air, and on the benchtop the reaction mixture was then filtered through a plug of silica, which in turn was washed with methylene chloride. Removal of the solvent from the combined eluent afforded the target product, which was further purified by recrystallization from cold hexanes as a beige powder (950 mg, 83 %). ^1H NMR (CDCl_3): δ 7.65 (dt, $J_{\text{HH}} = 7.65$ Hz, 1.7 Hz, 1H), 7.18 (m, 1H), 6.88 (m, 1H), 6.80 (m, 1H), 1.96 (m, 6H), 1.90 (m, 12H), 1.67 (s, 12H), 1.34 (sept, $J = 7.6$ Hz, 3H), 1.15 (d, $J_{\text{HH}} = 7.5$ Hz, 18H); ^{13}C NMR (CDCl_3) δ 161.4 (d, $J_{\text{P,C}} = 20.1$ Hz), 137.7, 129.7, 125.6 (d, $J_{\text{P,C}} = 26.4$ Hz), 119.2, 118.7, 42.1 (d, $J_{\text{P,C}} = 13.8$ Hz), 37.5, 37.0 (d, $J_{\text{P,C}} = 27.7$ Hz), 29.3 (d, $J_{\text{P,C}} = 7.5$ Hz), 18.6, 13.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 12.2. HRMS (ESI/[M+H]⁺) calcd. for $\text{C}_{35}\text{H}_{56}\text{O}_1\text{P}_1\text{Si}_1$: 551.3833. Found: 551.3835. *Note:* Two control experiments were performed using **L1** to investigate if O-Si bond cleavage occurred readily under catalytic conditions. In the first control experiment, a toluene solution of **L1** was heated at 120 °C in the presence of 60 equivalents of KOt-Bu for 14 h and using trimesitylphosphine as an internal standard; no ligand degradation was observed by use of ^{31}P NMR analysis. In the second control experiment a catalytic reaction was run using similar conditions to those reported herein but at a 50 mol% catalyst loading which would allow for loss of the silane moiety from **L1** (e.g. as triisopropylsilyl chloride) to be observed by GC analysis; no such ligand degradation was observed.

Synthesis and characterization of **L1'**:



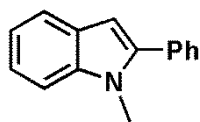
To an oven dried screw-capped vial was added a stir bar, (4-bromophenoxy)triisopropylsilane (844 mg, 2.5 mmol), Pd(OAc)₂ (17.4 mg, 0.0768 mmol, 3 mol%), 1,1'-bis(diisopropylphosphino)ferrocene (37.5 mg, 0.0896 mmol, 3.5 mol%), NaO*t*-Bu (295 mg, 3.0 mmol) and 6 mL of toluene. The resulting suspension was stirred until apparently homogeneous and then di(1-adamantyl)phosphine (774 mg, 2.5 mmol) was added. The vial was sealed under dinitrogen with a cap containing a PTFE septum, removed from the glovebox, placed in a temperature-controlled aluminum heating block set at 110 °C and vigorous magnetic stirring was initiated. After 8 h, ³¹P NMR analysis of the reaction mixture confirmed the consumption of di(1-adamantyl)phosphine and the quantitative formation of one new phosphorus-containing product. The vial containing the reaction mixture was allowed to cool to room temperature and was brought back inside the glovebox for workup under inert atmosphere; attempts to isolate and purify **L1'** under the benchtop conditions that proved effective for **L1** resulted in degradation of **L1'**. The reaction mixture was filtered through a plug of Celite and alumina, which in turn was washed with methylene chloride. Removal of the solvent from the combined eluent afforded the target product, which was further purified by washing with cold pentane (3 x 3 mL) to give a beige powder (986 mg, 72 %). ¹H NMR (C₆D₆): δ 7.73-7.70 (m, 2H), 6.95 (br m, 2H), 2.11-2.03 (m, 12H), 1.87 (br s, 6H), 1.64 (s, 12H), 1.19-1.12 (m, 21H); ¹³C NMR (C₆D₆) δ 158.0, 142.6 (br), 137.1 (br), 127.6 (d, *J*_{P,C} = 30.2 Hz), 120.2, 120.1, 42.8 (d, *J*_{P,C} = 12.6 Hz), 37.9, 37.4 (d, *J*_{P,C} = 23.9 Hz), 29.9 (d, *J*_{P,C} = 7.5 Hz), 18.7, 13.6; ³¹P{¹H} NMR (C₆D₆): δ 38.5. HRMS (ESI/[M+H]⁺) calcd. for C₃₅H₅₆O₁P₁Si₁: 551.3833. Found: 551.3822.

Representative catalytic protocol (synthesis of **2**):

To an oven dried screw-capped vial was added a stir bar, [Pd(cinnamyl)Cl]₂ (3.2 mg, 0.0063 mmol, 1.25 mol%), **L1** (6.8 mg, 0.013 mmol, 2.5 mol%), and 2.0 mL of toluene. The mixture was then stirred magnetically for 2 minutes at which point KO*t*Bu (168 mg, 1.5 mmol) was added. The mixture was then stirred briefly followed by the addition of 1-bromo-2-(phenylethynyl)benzene (128.6 mg, 0.5 mmol) in 3 x 1.0 mL portions of toluene, as well as 1-adamantylamine (83.1mg, 0.55 mmol). The vial was sealed under dinitrogen with a cap containing a PTFE septum, removed from the glovebox, placed in a temperature-controlled aluminum heating block set at 90 °C and vigorous magnetic stirring was initiated. Reaction progress was monitored by use of TLC or GC methods and after complete consumption of the aryl bromide (12 h), the reaction mixture was cooled, diluted with ethyl acetate (50 mL) and

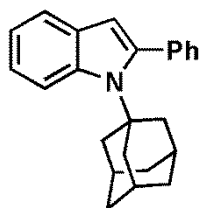
washed with water (50 mL). The layers were separated and the organic layer was washed with water (3 x 50 mL). The organic layer was dried over sodium sulfate, filtered and concentrated to afford a brown solid. The crude solid was purified by column chromatography with a hexanes:ethyl acetate (100:1) eluent system to afford 1-Adamantan-1-yl-2-phenyl-1*H*-indole (**2**) as a white crystalline solid (146 mg, 89 %).

Synthesis and characterization of reaction products:



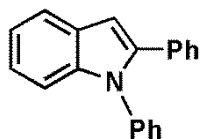
(1) 1-methyl-2-phenyl-1*H*-indole.

Representative catalytic protocol A was followed, however, addition via syringe of methylamine as a 2.0 M solution in tetrahydrofuran (0.300 mL, 0.55 mmol) was performed outside of the glovebox. ^1H NMR (CDCl_3): δ 7.68 (d, $J = 7.8$ Hz, 1H), 7.57-7.55 (m, 2H), 7.53-7.49 (m, 2H), 7.44 (m, 1H), 7.41 (d, $J = 8.5$ Hz, 1H), 7.30 (m, 1H), 7.20 (m, 1H), 6.62 (s, 1H), 3.79 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.9, 138.7, 133.2, 129.7, 128.8, 128.3, 128.2, 122.0, 120.8, 120.2, 109.9, 102.0, 31.5. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.⁸



(2) 1-Adamantan-1-yl-2-phenyl-1*H*-indole.

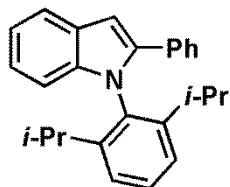
^1H NMR (CDCl_3): δ 7.85 (d, $J = 8.4$ Hz, 1H), 7.59 (dd, $J = 7.7$ Hz, 0.6 Hz, 1H), 7.44-7.40 (m, 2H), 7.37-7.33 (m, 3H), 7.19-7.15 (m, 1H), 7.12-7.09 (m, 1H), 6.30 (s, 1H), 2.30 (d, $J = 5.0$ Hz, 6H), 2.11 (s, 3H), 1.72-1.65 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.8, 139.9, 136.8, 130.5, 129.5, 127.7, 127.6, 120.9, 120.6, 119.6, 116.1, 107.0, 61.2, 43.7, 36.5, 30.6. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.⁹



(3) 1,2-Diphenyl-1*H*-indole.

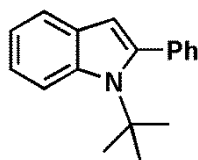
^1H NMR (CDCl_3): δ 7.77(m, 1H), 7.46 (m, 1H), 7.41 (m, 1H), 7.37 (m, 1H), 7.35-7.28 (m, 7H), 7.27-7.23 (m, 2H), 6.88 (d, $J = 0.7$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.0, 139.3, 138.8, 132.8,

129.6, 129.2, 128.6, 128.5, 128.4, 127.6, 127.5, 122.7, 121.0, 120.8, 111.0, 104.0. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹⁰



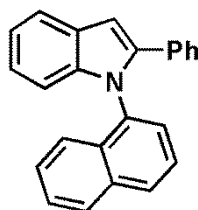
(4) 2-phenyl-1-(2,6-di-iso-propylphenyl)-1H-indole.

^1H NMR (CDCl_3): δ 7.81 (d, $J = 7.8$ Hz, 1H), 7.57 (t, $J = 7.7$ Hz, 1H), 7.41–7.39 (m, 3H), 7.37 (s, 1H), 7.31–7.21 (m, 5H), 7.08 (s, 1H), 6.97 (d, $J = 8.3$ Hz, 1H), 2.47 (sept., $J = 6.9$ Hz, 2H), 1.08 (d, $J = 6.8$ Hz, 6H), 0.96 (d, $J = 6.8$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 148.2, 141.3, 140.1, 134.0, 132.8, 129.8, 128.5, 128.1, 128.0, 127.6, 124.6, 122.3, 120.7, 120.7, 111.5, 102.2, 28.5, 25.4, 23.4. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.⁹



(5) 1-tert-Butyl-2-phenyl-1H-indole.

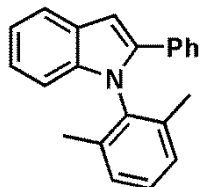
^1H NMR (CDCl_3): δ 7.74 (dd, $J = 8.5$ Hz, 0.7 Hz, 1H), 7.59 (d,d, $J = 7.6$ Hz, 0.4 Hz, 1H), 7.43–7.42 (m, 2H), 7.38–7.35 (m, 3H), 7.19 (m, 1H), 7.12 (m, 1H), 6.32 (d, $J = 0.7$ Hz, 1H), 1.61 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 142.2, 138.5, 137.6, 130.5, 129.3, 127.9, 127.7, 121.0, 120.8, 119.7, 115.4, 106.5, 59.2, 32.4. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹¹



(6) 1-Naphthalen-1-yl-2-phenyl-1H-indole.

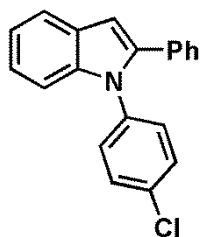
Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. ^1H NMR (CDCl_3): δ 8.01–7.98 (m, 2H), 7.83 (dt, $J = 7.9$ Hz, 1.0 Hz, 1H), 7.59–7.52 (m, 3H), 7.44 (m, 1H), 7.41 (m, 1H), 7.33–7.30 (m, 2H), 7.27 (m, 1H), 7.19–7.14 (m, 4H), 7.03 (d, $J = 1$ Hz, 1H), 6.90 (dd, $J = 8.25$ Hz, 0.8 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 142.5, 140.6, 135.7, 134.7, 132.9, 131.7, 128.9, 128.6, 128.5, 128.4, 127.6, 127.5, 127.4, 126.9, 125.8, 124.0, 122.6, 121.0, 120.8, 111.6, 103.6.

In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹⁰



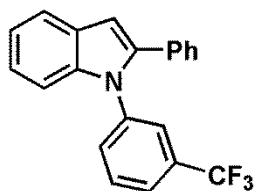
(7) 2-phenyl-1-(2,6-dimethyl)-1H-indole.

^1H NMR (CDCl_3): δ 7.74 (dd, $J = 6.7$ Hz, 1.4 Hz, 1H), 7.32-7.29 (m, 2H), 7.28-7.23 (m, 4H), 7.22-7.15 (m, 4H), 6.92 (s, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 1.91 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 140.8, 138.1, 137.7, 136.9, 133.1, 128.9, 128.8, 128.7, 128.6, 127.8, 127.7, 122.5, 120.8, 120.7, 110.8, 102.5, 18.2. HRMS (ESI/[M+H]⁺) calcd. for $\text{C}_{22}\text{H}_{20}\text{N}$: 298.1590. Found: 298.1279.



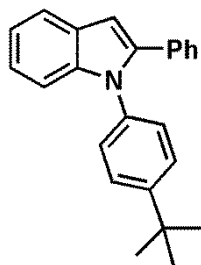
(8) 1-(4-Chloro-phenyl)-2-phenyl-1H-indole.

^1H NMR (CDCl_3): δ 7.72 (m, 1H), 7.42-7.40 (m, 2H), 7.31-7.27 (m, 6H), 7.24-7.20 (m, 4H), 6.83 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 140.9, 139.1, 137.4, 133.2, 132.5, 129.8, 129.5, 129.3, 128.7, 127.8, 122.9, 121.3, 121.0, 110.7, 104.5. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹²



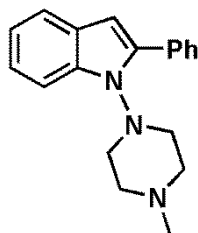
(9) 2-Phenyl-1-(3-trifluoromethyl-phenyl)-1H-indole.

Column chromatography using a hexanes:ethyl acetate (20:1) eluent system. ^1H NMR (CDCl_3): δ 7.71 (m, 1H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.58 (s, 1H), 7.53 (d, $J = 7.9$ Hz, 1H), 7.39 (d, $J = 7.9$ Hz, 1H), 7.31-7.22 (m, 7H), 6.84 (d, $J = 0.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 140.9, 139.5, 138.9, 132.3, 132.1 ($J_{\text{C,F}} = 66$ Hz), 131.5, 130.2, 129.3, 128.8, 128.7, 128.0, 125.0 ($J_{\text{C,F}} = 4$ Hz), 124.1 ($J_{\text{C,F}} = 4$ Hz), 123.1, 121.8 ($J_{\text{C,F}} = 272$ Hz), 121.5, 121.2, 110.5, 104.9. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹⁰



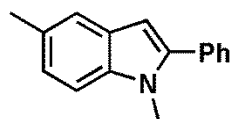
(10) 1-(4-*tert*-Butyl-phenyl)-2-phenyl-1*H*-indole.

^1H NMR (CDCl_3): δ 7.73 (m, 1H), 7.47-7.44 (m, 2H), 7.36-7.26 (m, 6H), 7.23-7.20 (m, 4H), 6.84 (s, 1H), 1.40 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 150.5, 141.1, 139.4, 136.1, 133.0, 129.1, 128.5, 128.4, 127.8, 127.5, 126.4, 122.5, 120.8, 120.8, 111.1, 103.8, 35.0, 31.8. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹³



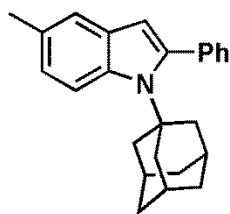
(11) 1-(4-Methyl-piperazin-1-yl)-2-phenyl-1*H*-indole.

Column chromatography using a dichloromethane:ethyl acetate (6:4) eluent system. ^1H NMR (CDCl_3): δ 7.75 (d, $J = 8.2$ Hz, 1H), 7.68-7.67 (m, 2H), 7.63 (d, $J = 7.7$ Hz, 1H), 7.46-7.43 (m, 2H), 7.37 (m, 1H), 7.19 (m, 1H), 7.14 (m, 1H), 6.54 (s, 1H), 4.01 (dt, $J = 2.2$ Hz, 10.9 Hz, 2H), 3.12 (d, $J = 11.1$ Hz, 2H), 2.83 (d, $J = 11.8$ Hz, 2H), 2.37 (s, 3H), 2.31 (dt, $J = 2.6$ Hz, 11.2 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 140.7, 135.7, 132.7, 129.5, 128.1, 127.8, 127.3, 121.7, 121.4, 120.3, 112.1, 100.2, 55.6, 52.1, 46.3. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹⁴



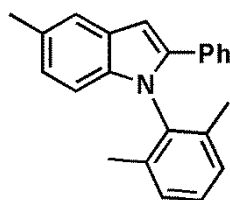
(12) 1,5-Dimethyl-2-phenyl-1*H*-indole.

Representative catalytic protocol A was followed, however, addition via syringe of methylamine as a 2.0 M solution in tetrahydrofuran (0.300 mL, 0.55 mmol) was performed outside of the glovebox. ^1H NMR (CDCl_3): δ 7.56-7.53 (m, 2H), 7.51-7.48 (m, 2H), 7.46 (m, 1H), 7.42 (m, 1H), 7.29 (d, $J = 8.3$ Hz, 1H), 7.11 (dd, $J = 8.4$ Hz, 1.3 Hz, 1H), 6.52 (d, $J = 0.7$ Hz, 1H), 3.76 (s, 3H), 2.51 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.9, 137.2, 133.3, 129.6, 129.4, 128.8, 128.5, 128.1, 123.6, 120.5, 109.6, 101.5, 31.5, 21.8. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹⁵



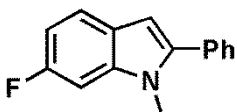
(13) 1-Adamantan-1-yl-5-methyl-2-phenyl-1H-indole.

^1H NMR (CDCl_3): δ 7.72 (d, $J = 8.6$ Hz, 1H), 7.42-7.40 (m, 2H), 7.37 (s, 1H), 7.34-7.33 (m, 3H), 6.99 (d, $J = 8.6$ Hz, 1H), 6.21 (s, 1H), 2.44 (s, 3H), 2.28 (d, $J = 2.3$ Hz, 6H), 2.09 (s, 3H), 1.71-1.64 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 142.0, 139.1, 135.2, 130.5, 129.8, 128.8, 127.6, 127.5, 122.2, 120.6, 115.7, 106.5, 61.0, 43.7, 36.6, 30.5, 21.4. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{25}\text{H}_{28}\text{N}_1$: 342.2216. Found: 342.2219.



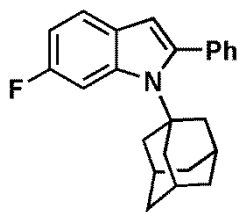
(14) 1-(2,6-Dimethyl-phenyl)-5-methyl-2-phenyl-1H-indole.

^1H NMR (CDCl_3): δ 7.57 (s, 1H), 7.34-7.26 (m, 6H), 7.21-7.20 (m, 2H), 7.04 (dd, $J = 8.3$ Hz, 1.1 Hz, 1H), 6.87 (d, $J = 0.4$ Hz, 1H), 6.80 (d, $J = 0.4$ Hz, 1H), 2.55 (s, 3H), 1.95 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 140.8, 137.8, 137.0, 136.5, 133.2, 129.9, 128.8, 128.7, 128.6, 127.7, 127.6, 124.1, 120.5, 110.5, 102.0, 21.8, 18.1. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{23}\text{H}_{22}\text{N}_1$: 312.1747. Found: 312.1753.



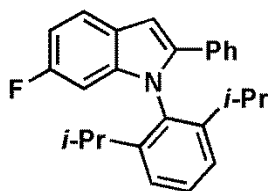
(15) 6-Fluoro-1-methyl-2-phenyl-1H-indole.

Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. Representative catalytic protocol A was followed, however, addition via syringe of methylamine as a 2.0 M solution in tetrahydrofuran (0.300 mL, 0.55 mmol) was performed outside of the glovebox. ^1H NMR (CDCl_3): δ 7.54-7.49 (m, 4H), 7.44 (m, 1H), 7.32-7.27 (m, 2H), 7.02 (dt, $J = 2.5$ Hz, 9.2 Hz, 1H), 6.54 (s, 1H), 3.76 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 158.3 (d, $J_{\text{C,F}} = 234.3$ Hz), 143.5, 135.3, 132.8, 129.7, 128.9, 128.5, 128.4, 110.5 (d, $J_{\text{C,F}} = 12.6$ Hz), 110.2 (d, $J_{\text{C,F}} = 26.3$ Hz), 105.5 (d, $J_{\text{C,F}} = 23.4$ Hz), 101.9 (d, $J_{\text{C,F}} = 23.4$ Hz), 31.7. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_1\text{N}_1$: 226.1027. Found: 226.1026.



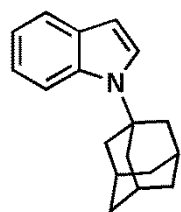
(16) 1-Adamantan-1-yl-6-fluoro-2-phenyl-1H-indole.

Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. ^1H NMR (CDCl_3): δ 7.75 (dd, $J = 9.2$ Hz, 4.3 Hz, 1H), 7.42-7.40 (m, 2H), 7.37-7.35 (m, 3H), 7.21 (dd, $J = 9.2$ Hz, 2.7 Hz, 1H), 6.91 (dt, $J = 2.8$ Hz, 9.1 Hz, 1H), 6.25 (d, $J = 0.6$ Hz, 1H), 2.27 (d, $J = 2.9$ Hz, 6H), 2.11 (s, 3H). 1.69-1.66 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 157.6 (d, $J_{\text{C,F}} = 235.4$ Hz), 143.5, 138.6, 133.4, 130.4, 129.9 (d, $J_{\text{C,F}} = 9.8$ Hz), 127.9, 127.6, 116.6 (d, $J_{\text{C,F}} = 9.1$ Hz), 108.8 (d, $J_{\text{C,F}} = 25.4$ Hz), 106.8 (d, $J_{\text{C,F}} = 3.8$ Hz), 105.3 (d, $J_{\text{C,F}} = 22.4$ Hz), 61.4, 43.8, 36.5, 30.5. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{24}\text{H}_{25}\text{F}_1\text{N}_1$: 346.1966. Found: 346.1954.



(17) 1-(2,6-Diisopropyl-phenyl)-6-fluoro-2-phenyl-1H-indole.

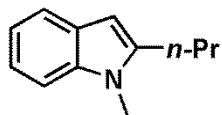
Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. ^1H NMR (CDCl_3): δ 7.54 (t, $J = 7.7$ Hz, 1H), 7.41 (dd, $J = 9.4$ Hz, 2.4 Hz, 1H), 7.36-7.33 (m, 4H), 7.29-7.24 (m, 3H), 6.99 (d, $J = 0.7$ Hz, 1H), 6.93 (dt, $J = 2.5$ Hz, 9.1 Hz, 1H), 6.83 (dd, $J = 8.9$ Hz, 4.5 Hz, 1H), 2.40 (sept, $J = 6.9$ Hz, 2H), 1.04 (d, $J = 6.9$ Hz, 6H), 0.93 (d, $J = 6.9$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 158.6 (d, $J_{\text{C,F}} = 235.0$ Hz), 148.1, 142.9, 136.7, 133.8, 132.5, 130.0, 128.5, 128.3, 128.1, 127.9, 124.7, 112.1 (d, $J_{\text{C,F}} = 26.3$ Hz), 110.6 (d, $J_{\text{C,F}} = 25.1$ Hz), 105.4 (d, $J_{\text{C,F}} = 23.6$ Hz), 102.1 (d, $J_{\text{C,F}} = 4.4$ Hz), 28.5, 25.4, 23.4. HRMS (ESI/[M+Na] $^+$) calcd. for $\text{C}_{26}\text{H}_{26}\text{F}_1\text{N}_1\text{Na}_1$: 394.1941. Found: 394.1946.



(18) 1-Adamantan-1-yl-1H-indole.

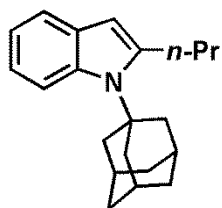
^1H NMR (CDCl_3): δ 7.74 (m, 1H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 3.4$ Hz, 1H), 7.14 (m, 1H), 7.07 (m, 1H), 6.46 (dd, $J = 8.3$ Hz, 0.6 Hz, 1H), 2.38 (d, $J = 2.9$ Hz, 6H), 2.29 (s, 3H), 1.86-1.81 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 134.8, 130.6, 124.6, 121.6, 120.6, 119.1, 114.1, 100.4,

57.0, 42.5, 36.8, 30.2. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹⁶



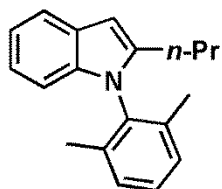
(19) 1-Methyl-2-propyl-1H-indole.

Representative catalytic protocol A was followed, however, addition via syringe of methylamine as a 2.0 M solution in tetrahydrofuran (0.300 mL, 0.55 mmol) was performed outside of the glovebox. ^1H NMR (CDCl_3): δ 7.54 (d, $J = 9.2$ Hz, 1H), 7.28 (s, 1H), 7.15 (m, 1H), 7.07 (m, 1H), 6.26 (d, $J = 0.7$ Hz, 1H), 3.67 (s, 3H), 2.72 (t, $J = 7.6$ Hz, 2H), 1.76 (m, 2H), 1.06 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.6, 137.8, 128.4, 120.9, 120.2, 119.6, 109.1, 99.2, 29.7, 29.3, 22.4, 14.3. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹⁷



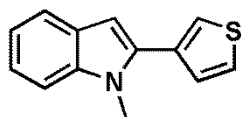
(20) 1-Adamantan-1-yl-2-propyl-1H-indole.

^1H NMR (CDCl_3): δ 7.77 (d, $J = 8.4$ Hz, 1H), 7.49 (m, 1H), 7.04 (m, 2H), 6.68 (s, 1H), 2.98 (t, $J = 7.7$ Hz, 2H), 2.56 (d, $J = 2.5$ Hz, 6H), 2.27 (s, 3H), 1.87-1.73 (m, 8H), 1.04 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 143.1, 136.8, 129.6, 120.3, 119.8, 118.8, 115.6, 103.4, 61.3, 42.6, 36.7, 34.7, 30.6, 24.4, 14.7. HRMS (ESI/[M+H]⁺) calcd. for $\text{C}_{21}\text{H}_{28}\text{N}_1$: 294.2216. Found: 294.2218.



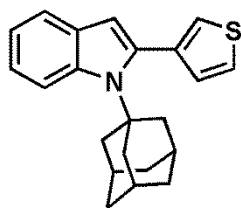
(21) 1-(2,6-Dimethyl-phenyl)-2-propyl-1H-indole.

^1H NMR (CDCl_3): δ 7.65 (m, 1H), 7.32 (m, 1H), 7.26-7.23 (m, 2H), 7.13 (dt, $J = 1.0$ Hz, 7.1 Hz, 1H), 7.08 (m, 1H), 6.77 (m, 1H), 6.48 (d, $J = 0.9$ Hz, 1H), 2.39 (t, $J = 8.0$ Hz, 2H), 1.90 (s, 6H), 1.70 (m, 2H), 0.98 (t, $J = 7.35$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.3, 138.1, 136.9, 136.0, 128.7, 128.6, 121.2, 119.9, 119.9, 100.8, 99.7, 29.1, 21.5, 17.6, 14.2. HRMS (ESI/[M+H]⁺) calcd. for $\text{C}_{19}\text{H}_{22}\text{N}_1$: 264.1747. Found: 264.1747.



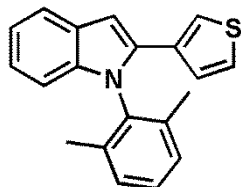
(22) 1-Methyl-2-thiophen-3-yl-1H-indole.

Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. Representative catalytic protocol A was followed, however, addition via syringe of methylamine as a 2.0 M solution in tetrahydrofuran (0.300 mL, 0.55 mmol) was performed outside of the glovebox. ^1H NMR (CDCl_3): δ 7.62 (dt, $J = 7.8$ Hz, 0.9 Hz, 1H), 7.44 (m, 1H), 7.40 (m, 1H), 7.36 (m, 1H), 7.30 (m, 1H), 7.24 (m, 1H), 7.14 (m, 1H), 6.60 (d, $J = 0.7$ Hz, 1H), 3.80 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 138.4, 136.7, 133.7, 128.7, 128.0, 126.1, 123.5, 122.0, 120.7, 120.2, 109.8, 101.7, 31.4. In good agreement with previously reported ^1H and ^{13}C characterization data for the title compound.¹⁸



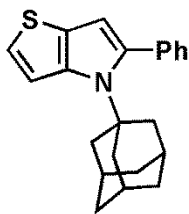
(23) 1-Adamantan-1-yl-2-thiophen-3-yl-1H-indole.

Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. ^1H NMR (CDCl_3): δ 7.87 (d, $J = 8.5$ Hz, 1H), 7.60 (dd, $J = 7.7$ Hz, 0.6 Hz, 1H), 7.31 (m, 1H), 7.30 (m, 1H), 7.20 (m, 1H), 7.15 (dd, $J = 4.6$ Hz, 1.5 Hz, 1H), 7.12 (m, 1H), 6.39 (s, 1H), 2.38 (d, $J = 2.7$ Hz, 6H), 2.17 (s, 3H), 1.78-1.72 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 138.5, 136.9, 136.0, 113.0, 129.3, 124.2, 124.1, 120.9, 120.8, 119.5, 116.0, 107.2, 61.1, 43.1, 36.6, 30.6. HRMS (ESI/[M+H]⁺) calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_1\text{S}_1$: 334.1624. Found: 334.1609.



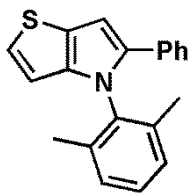
(24) 1-(2,6-Dimethyl-phenyl)-2-thiophen-3-yl-1H-indole.

Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. ^1H NMR (CDCl_3): δ 7.69 (m, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.23-7.22 (m, 4H), 6.93 (d, $J = 0.7$ Hz, 1H), 6.81 (m, 1H), 6.59 (t, $J = 2.1$ Hz, 1H), 1.87 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 138.3, 137.7, 137.0, 135.6, 133.4, 129.2, 129.0, 128.4, 125.5, 122.6, 120.7, 120.2, 110.4, 101.7, 17.9. HRMS (ESI/[M+H]⁺) calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_1\text{S}_1$: 304.1154. Found: 304.1140.



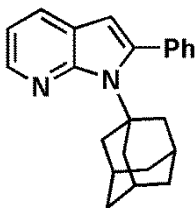
(25) 4-Adamantan-1-yl-5-phenyl-4H-thieno[3,2-*b*]pyrrole.

Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. ^1H NMR (CDCl_3): δ 7.47-7.45 (m, 2H), 7.37-7.36 (m, 3H), 7.29 (m, 1H), 7.08 (d, $J = 5.4$ Hz, 1H), 6.23 (d, $J = 0.4$ Hz, 1H), 2.22 (d, $J = 2.9$ Hz, 6H), 2.11 (s, 3H), 1.70-1.64 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 139.8, 139.0, 138.3, 131.5, 127.8, 127.5, 124.0, 121.2, 115.9, 104.4, 61.7, 44.2, 36.4, 30.4. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{22}\text{H}_{24}\text{N}_1\text{S}_1$: 334.1624. Found: 334.1632.



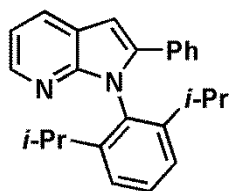
(26) 4-(2,6-Dimethyl-phenyl)-5-phenyl-4H-thieno[3,2-*b*]pyrrole.

Column chromatography using a hexanes:ethyl acetate (50:1) eluent system. ^1H NMR (CDCl_3): δ 7.27 (m, 1H), 7.24-7.19 (m, 4H), 7.16-7.15 (m, 2H), 7.09 (d, $J = 5.2$ Hz, 1H), 6.83 (s, 1H), 6.59 (d,d, $J = 5.2$ Hz, 0.3 Hz, 1H), 1.98 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 141.8, 139.4, 138.0, 137.0, 133.5, 128.7, 128.6, 127.0, 126.9, 124.0, 123.8, 111.4, 101.3, 18.2. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_1\text{S}_1$: 304.1154. Found: 304.1152.



(27) 1-Adamantan-1-yl-2-phenyl-1H-pyrrolo[2,3-*b*]pyridine.

Column chromatography using a hexanes:ethyl acetate (20:1) eluent system. Representative catalytic protocol A was followed, however, 2.5 mol% [$\text{Pd}(\text{cinnamyl})\text{Cl}$] $_2$ (6.4 mg, 0.013 mmol) and 5 mol % **L1** (13.6 mg, 0.026 mmol) was used; reaction was also performed at 110 $^\circ\text{C}$. ^1H NMR (CDCl_3): δ 8.32 (dd, $J = 4.6$ Hz, 1.7 Hz, 1H), 7.80 (dd, $J = 7.8$ Hz, 1.7 Hz, 1H), 7.44-7.42 (m, 2H), 7.37-7.35 (m, 3H), 7.03 (dd, $J = 7.8$ Hz, 4.6 Hz, 1H), 6.21 (s, 1H), 2.48 (d, $J = 2.6$ Hz, 6H), 2.07 (s, 3H), 1.75-1.62 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 150.5, 142.3, 141.3, 138.4, 130.6, 128.1, 127.7, 121.3, 115.9, 104.2, 62.5, 43., 36.6, 30.6. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{23}\text{H}_{25}\text{N}_2$: 329.2012. Found: 329.2010.



(28) 1-(2,6-Diisopropyl-phenyl)-2-phenyl-1H-pyrrolo[2,3-b]pyridine.

Column chromatography using a hexanes:ethyl acetate (20:1) eluent system. Representative catalytic protocol A was followed, however, 2.5 mol% [Pd(cinnamyl)Cl]₂ (6.4 mg, 0.013 mmol) and 5 mol % **L1** (13.6 mg, 0.026 mmol) was used; reaction was also performed at 110 °C. ¹H NMR (CDCl₃): δ 8.40 (dd, *J* = 4.7 Hz, 1.5 Hz, 1H), 7.99 (dd, *J* = 7.8 Hz, 1.6 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.33-7.32 (m, 2H), 7.30-7.28 (m, 2H), 7.24-7.23 (m, 3H), 7.11 (dd, *J* = 7.8 Hz, 4.7 Hz, 1H), 6.91 (s, 1H), 2.36 (sept, *J* = 6.8 Hz, 2H), 1.03 (d, *J* = 6.9 Hz, 6H), 0.90 (d, *J* = 6.9 Hz, 6H); ¹³C{¹H} NMR (CDCl₃): δ 150.8, 147.7, 143.9, 141.7, 133.0, 132.3, 130.1, 128.4, 128.1, 124.5, 120.5, 116.9, 100.1, 28.9, 25.0, 23.2. HRMS (ESI/[M+H]⁺) calcd. for C₂₅H₂₇N₂: 355.2169. Found: 355.2174.

Crystallographic Solution and Refinement Details for L1:

Crystallographic data were obtained at 173(±2) K on a Bruker D8/APEX II CCD diffractometer using a graphite-monochromated Mo K α (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Gaussian integration (face-indexed) was employed as the absorption correction method and the structure was solved by use of direct methods. The structure was refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed for all the non-hydrogen atoms. All hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information is provided in Table S1 and in the accompanying CIF (CCDC 871158).

Table S1. Crystallographic Experimental Details for **L1**

A. Crystal Data

formula	C ₃₅ H ₅₅ OPSi
formula weight	550.85
crystal dimensions (mm)	0.61 × 0.14 × 0.04
crystal system	orthorhombic
space group	<i>Pbca</i> (No. 61)
unit cell parameters ^a	
<i>a</i> (Å)	8.7730 (1)
<i>b</i> (Å)	23.8938 (4)
<i>c</i> (Å)	30.2150 (5)
<i>V</i> (Å ³)	6333.68 (17)
<i>Z</i>	8
ρ_{calcd} (g cm ⁻³)	1.155
μ (mm ⁻¹)	1.306

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD ^b
radiation (λ [Å])	graphite-monochromated Cu K α (1.54178)
temperature (°C)	-100
scan type	ω scans (0.75°) (5 s exposures)
data collection 2θ limit (deg)	140.14
total data collected	40496 ($-10 \leq h \leq 10$, $-29 \leq k \leq 29$, $-36 \leq l \leq 36$)
independent reflections	5997 ($R_{\text{int}} = 0.0463$)
number of observed reflections (<i>NO</i>)	5393 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXD</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-97</i> ^d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9545–0.5046
data/restraints/parameters	5997 / 0 / 343
goodness-of-fit (<i>S</i>) ^e [all data]	1.035
final <i>R</i> indices ^f	
<i>R</i> ₁ [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0371
<i>wR</i> ₂ [all data]	0.1057
largest difference peak and hole	0.569 and -0.284 e Å ⁻³

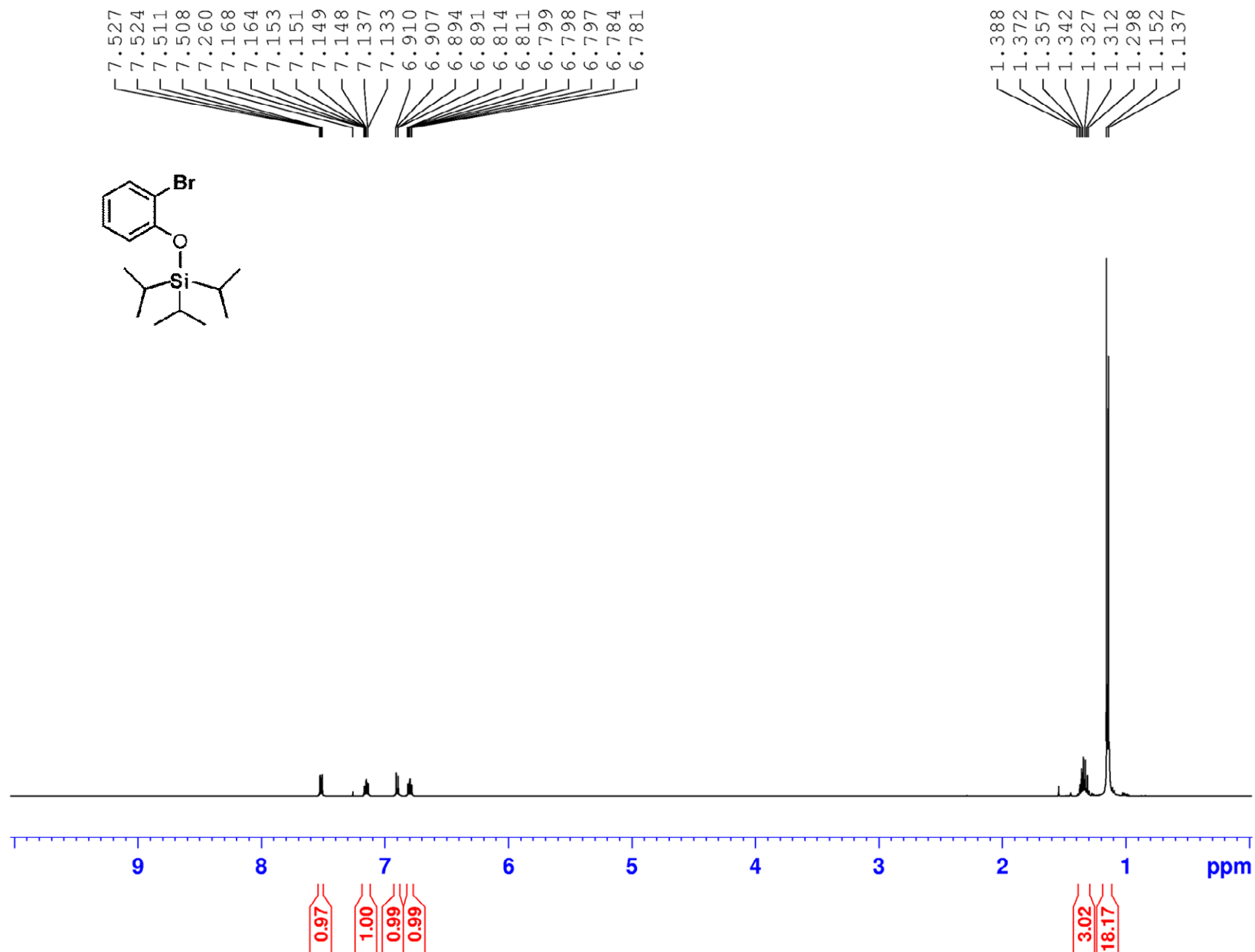
^aObtained from least-squares refinement of 9967 reflections with $5.84^\circ < 2\theta < 139.04^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. ^cSchneider, T. R.; Sheldrick, G. M. *Acta Crystallogr.* **2002**, *D58*, 1772-1779. ^dSheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112-122. ^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0592P)^2 + 2.7697P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). ^f $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

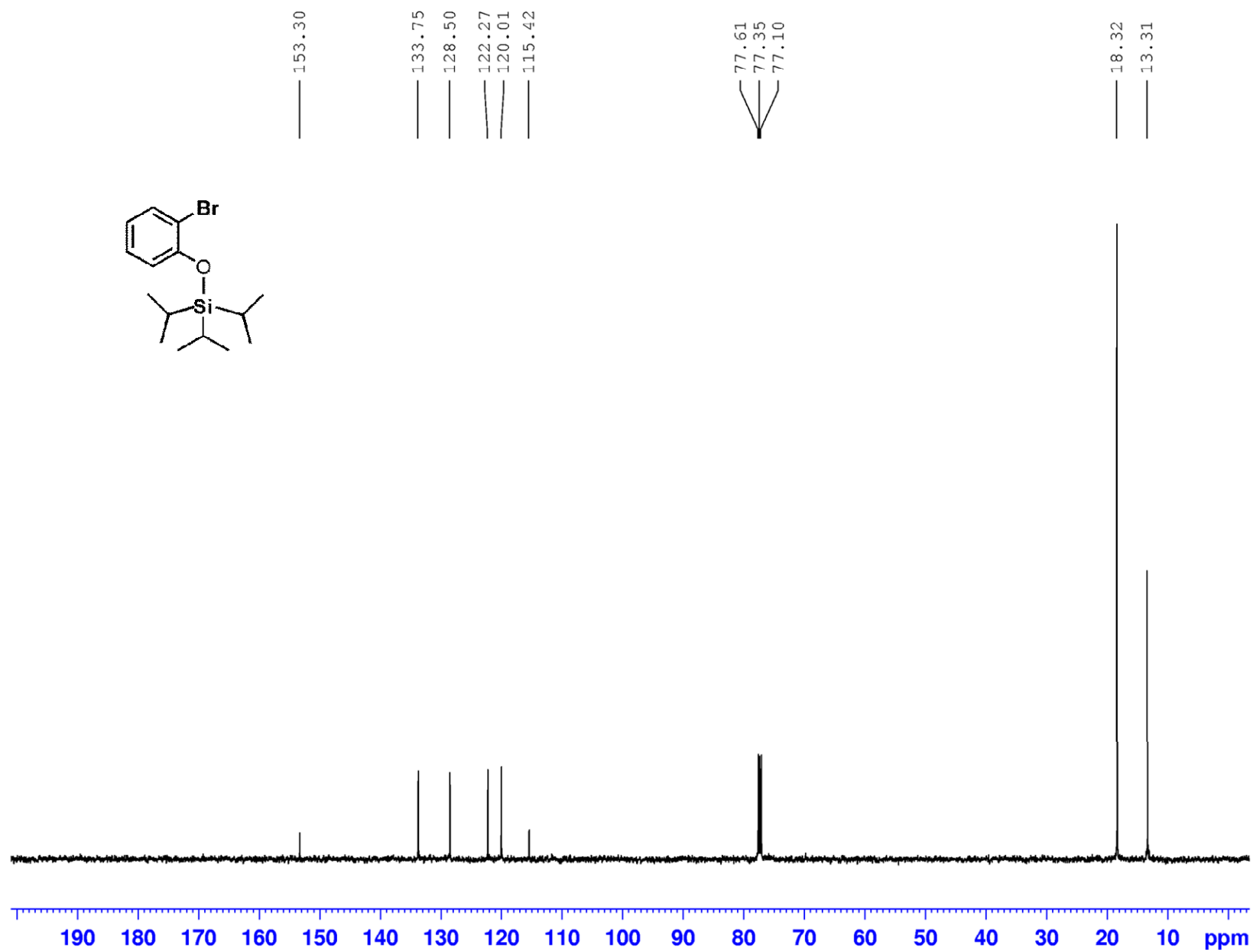
ESI References

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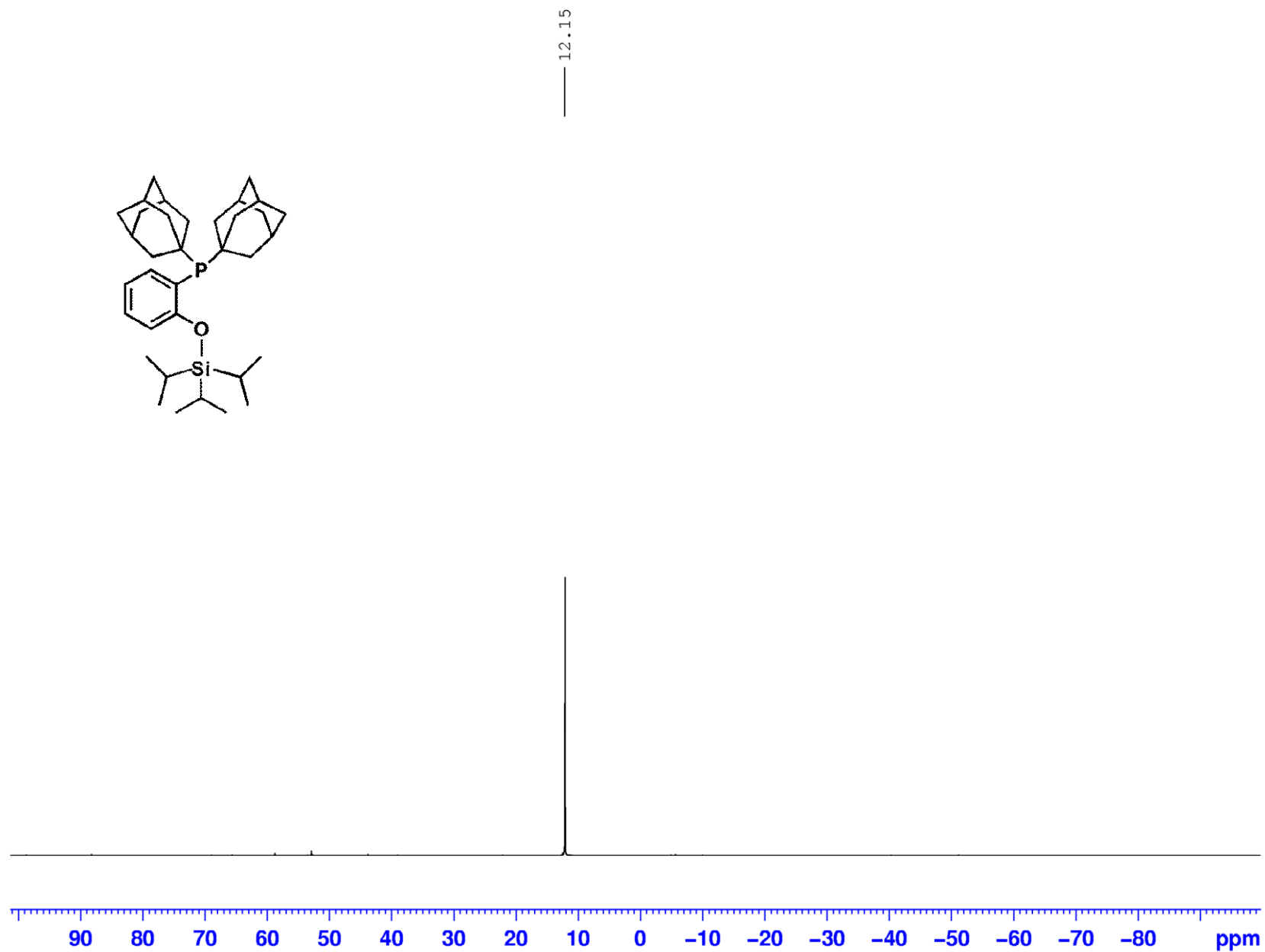
^1H NMR of (2-Bromo-phenoxy)triisopropylsilane (CDCl_3 , 500 MHz, 300 K)



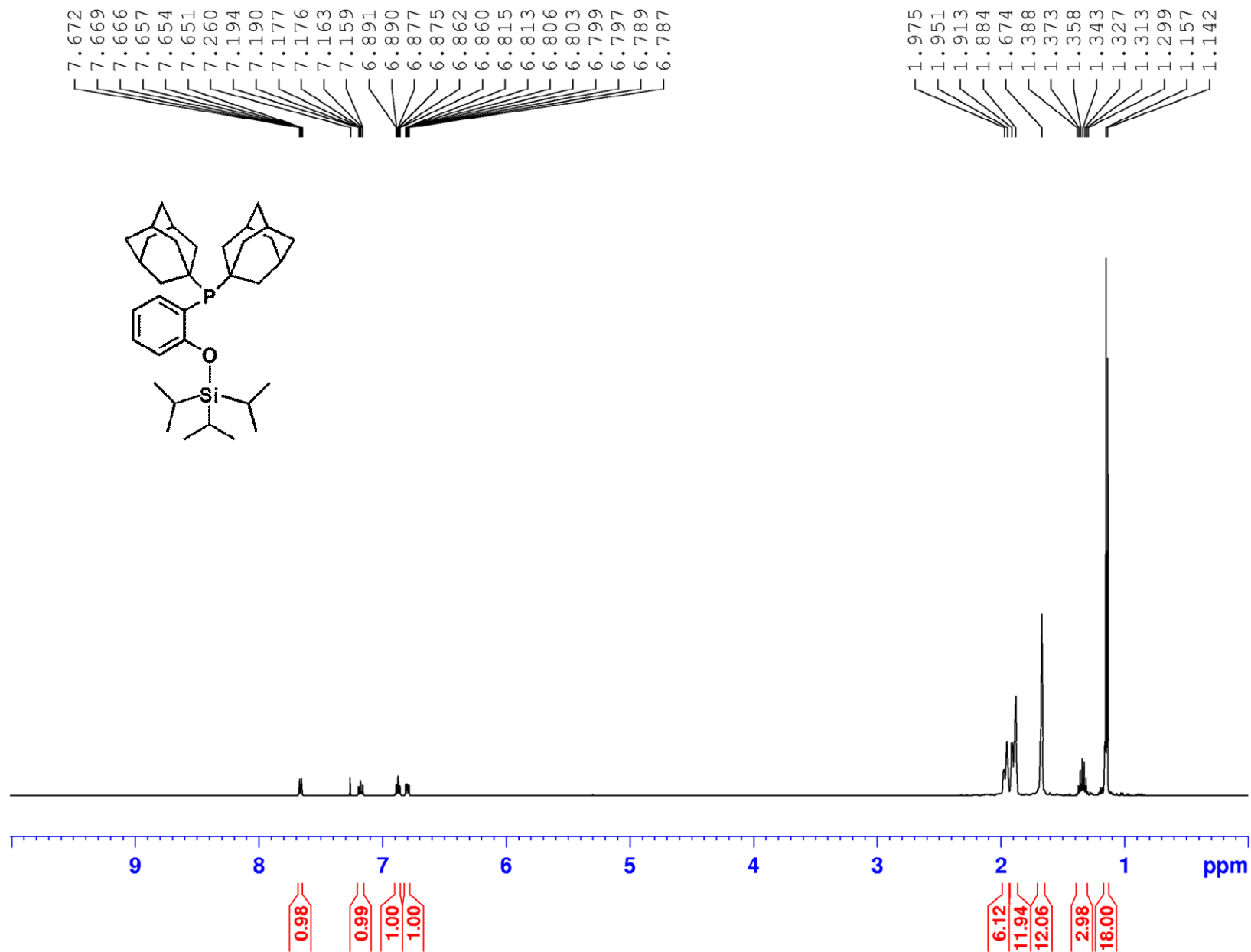
$^{13}\text{C}\{^1\text{H}\}$ NMR of (2-Bromo-phenoxy)triisopropylsilane (CDCl_3 , 125.8 MHz, 300 K)



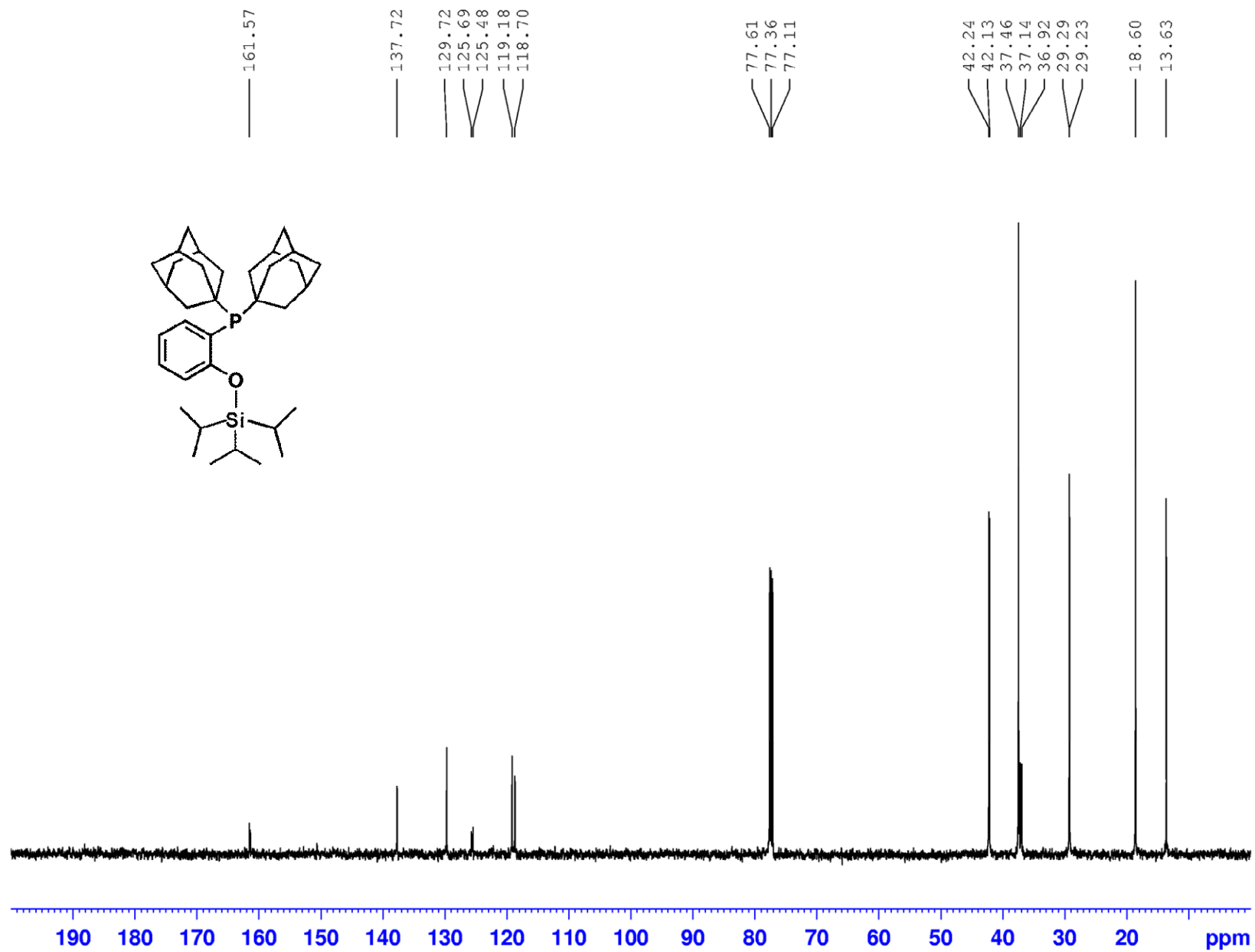
$^{31}\text{P}\{^1\text{H}\}$ NMR of **L1** (CDCl_3 , 202.5 MHz, 300 K)



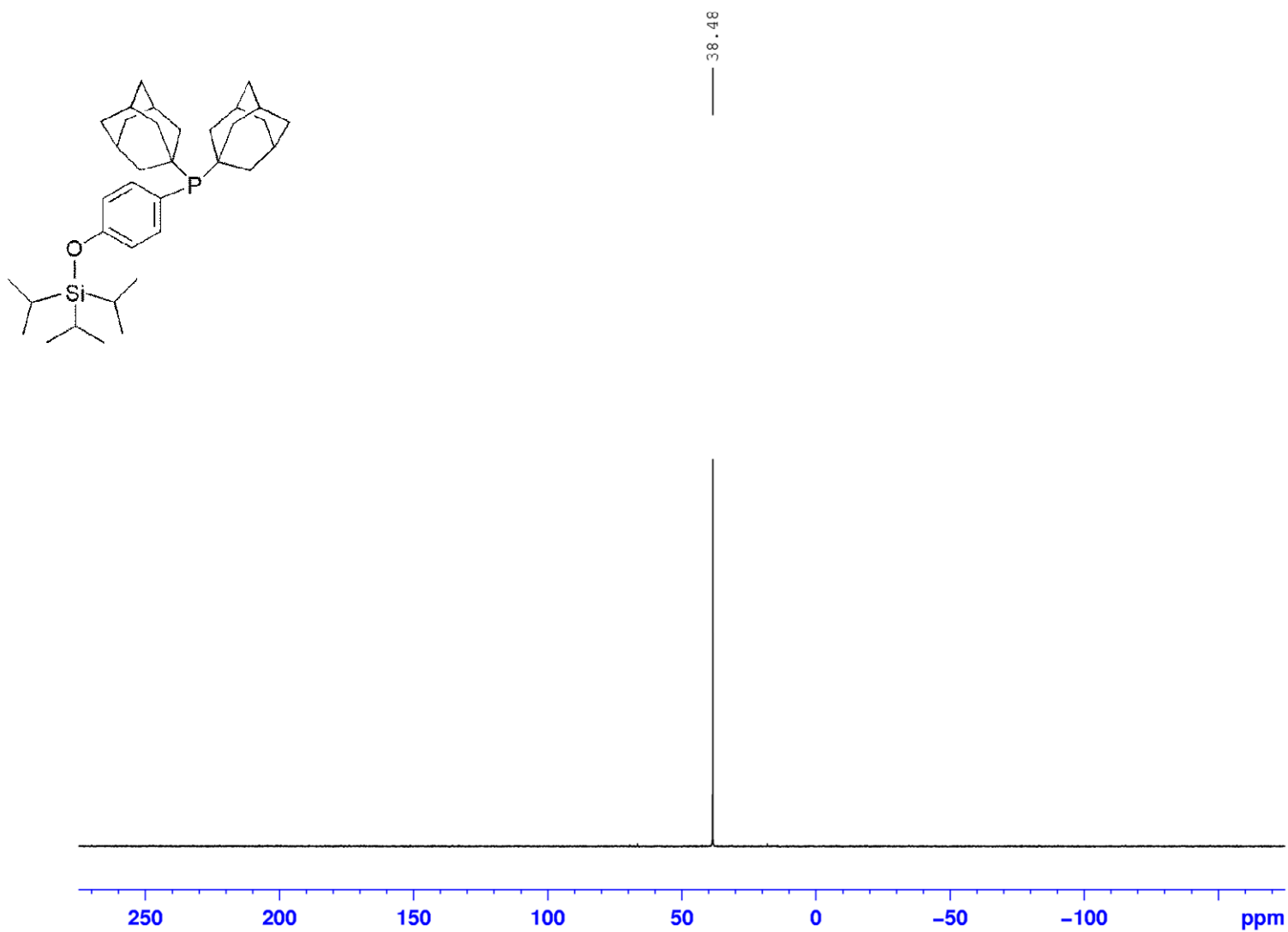
^1H NMR of **L1** (CDCl_3 , 500 MHz, 300 K)



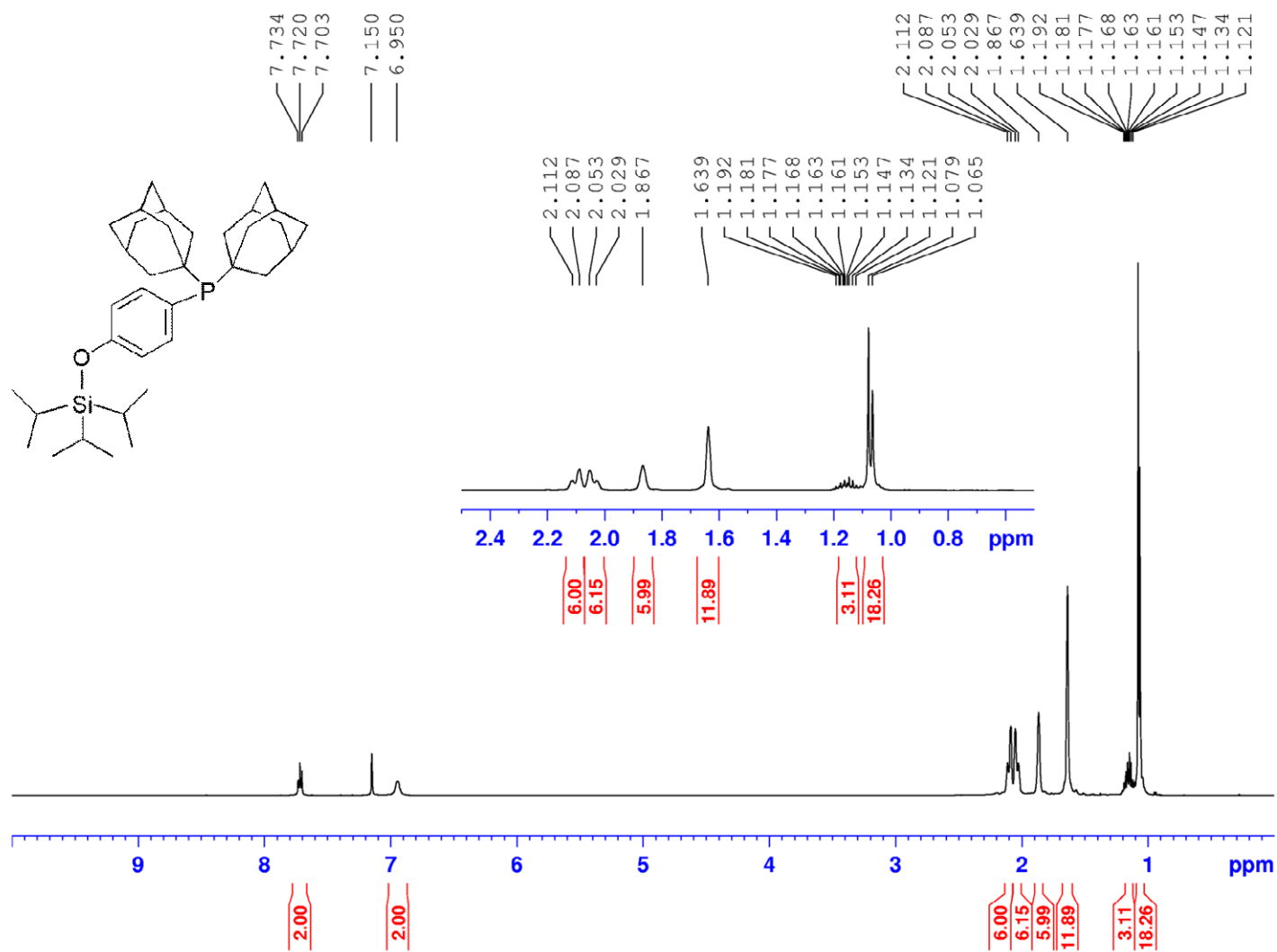
$^{13}\text{C}\{^1\text{H}\}$ NMR of **L1** (CDCl_3 , 125.8 MHz, 300 K)



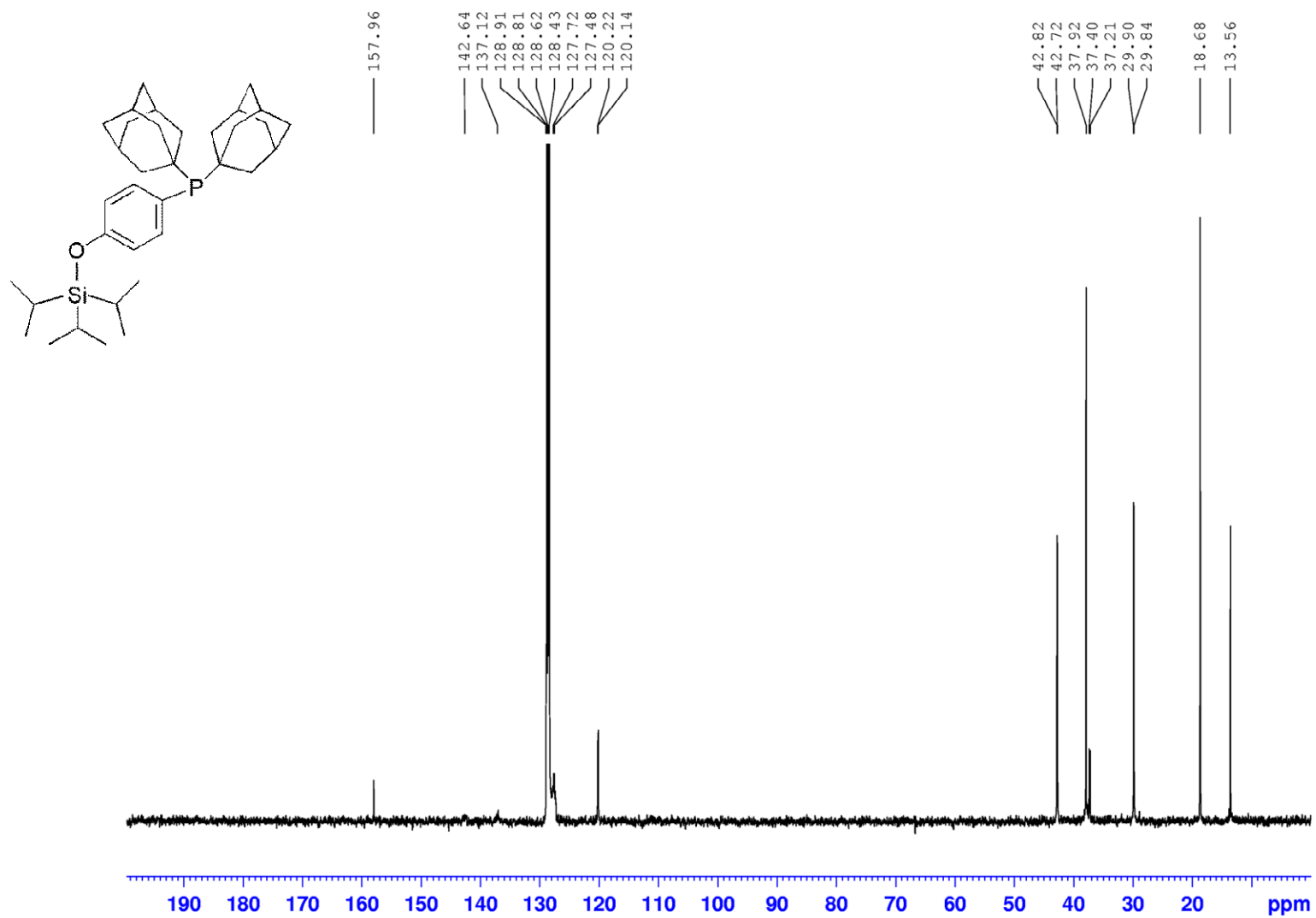
$^{31}\text{P}\{^1\text{H}\}$ NMR of **L1'** (C_6D_6 , 202.5 MHz, 300 K)



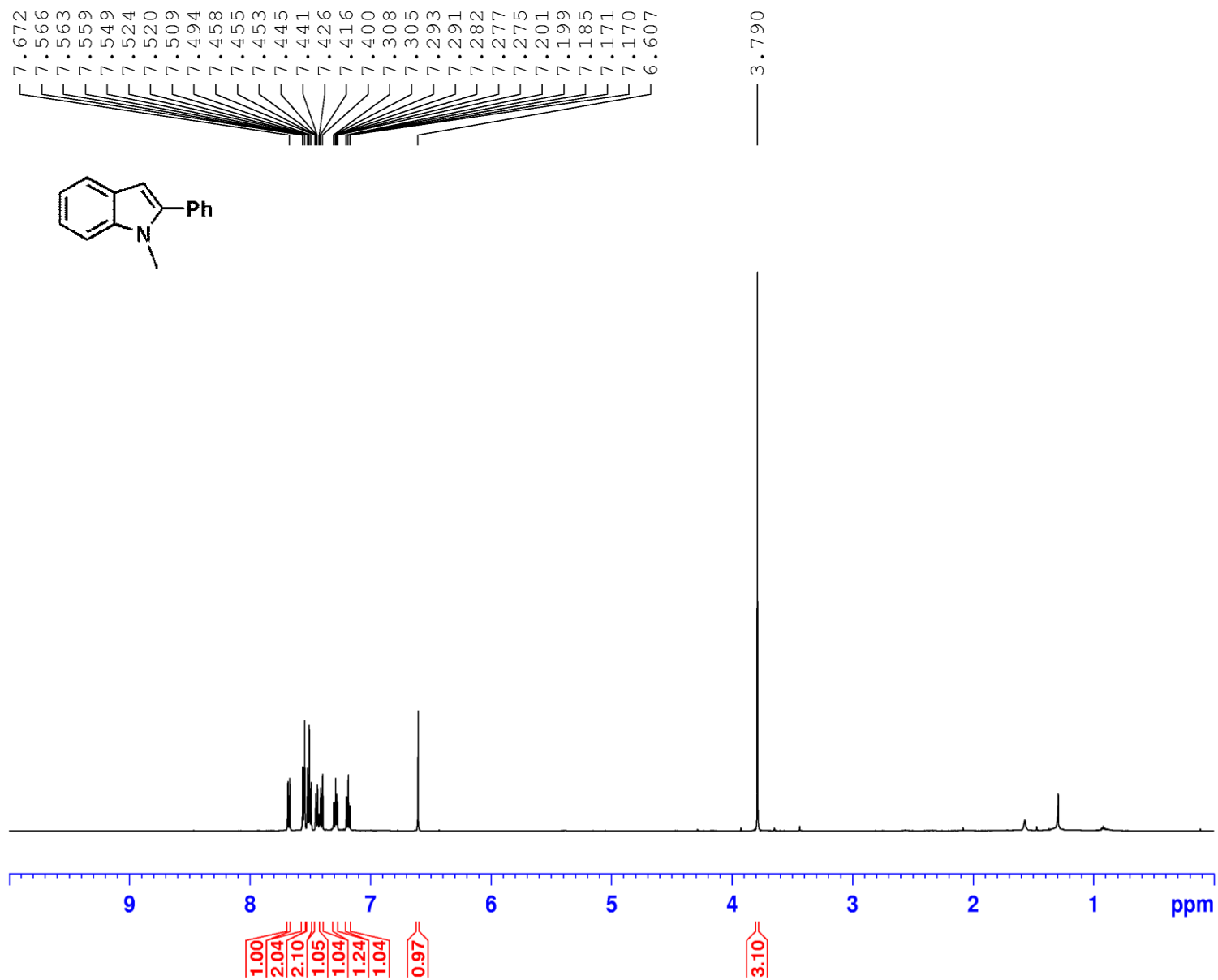
^1H NMR of **L1'** (C_6D_6 , 500 MHz, 300 K)



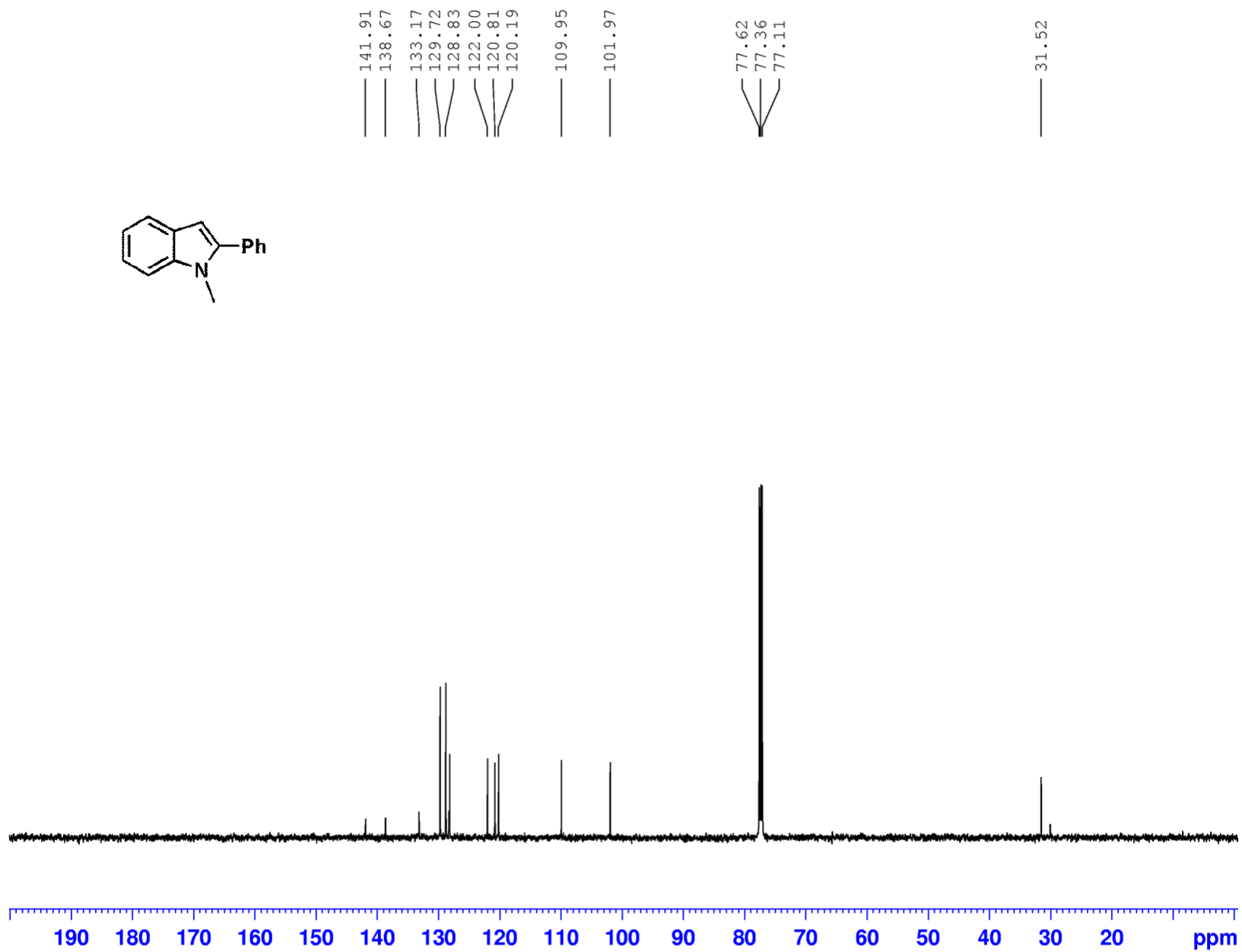
$^{13}\text{C}\{^1\text{H}\}$ NMR of **L1'** (C_6D_6 , 125.8 MHz, 300 K)



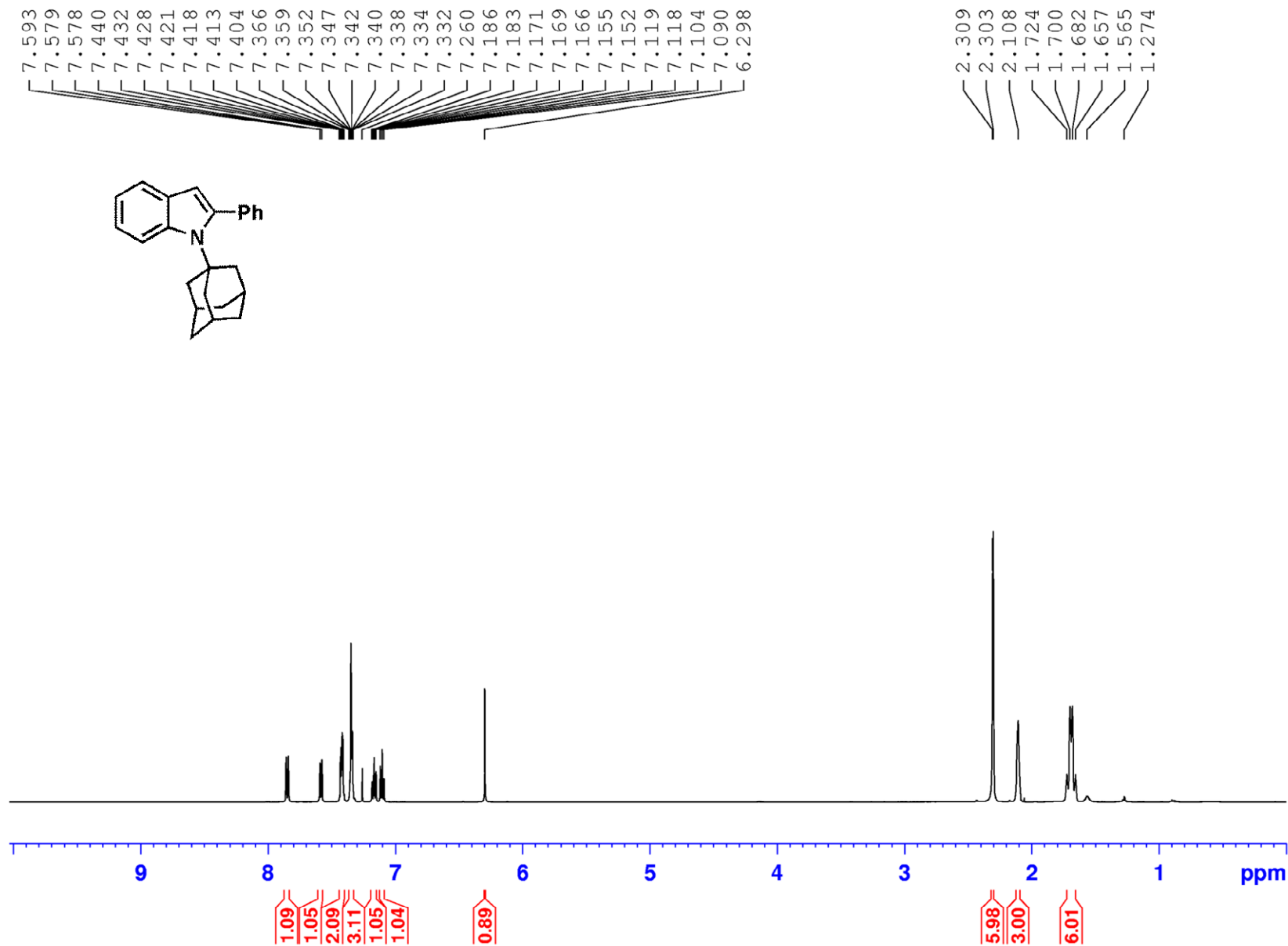
^1H NMR of **1**, 1-Methyl-2-phenyl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



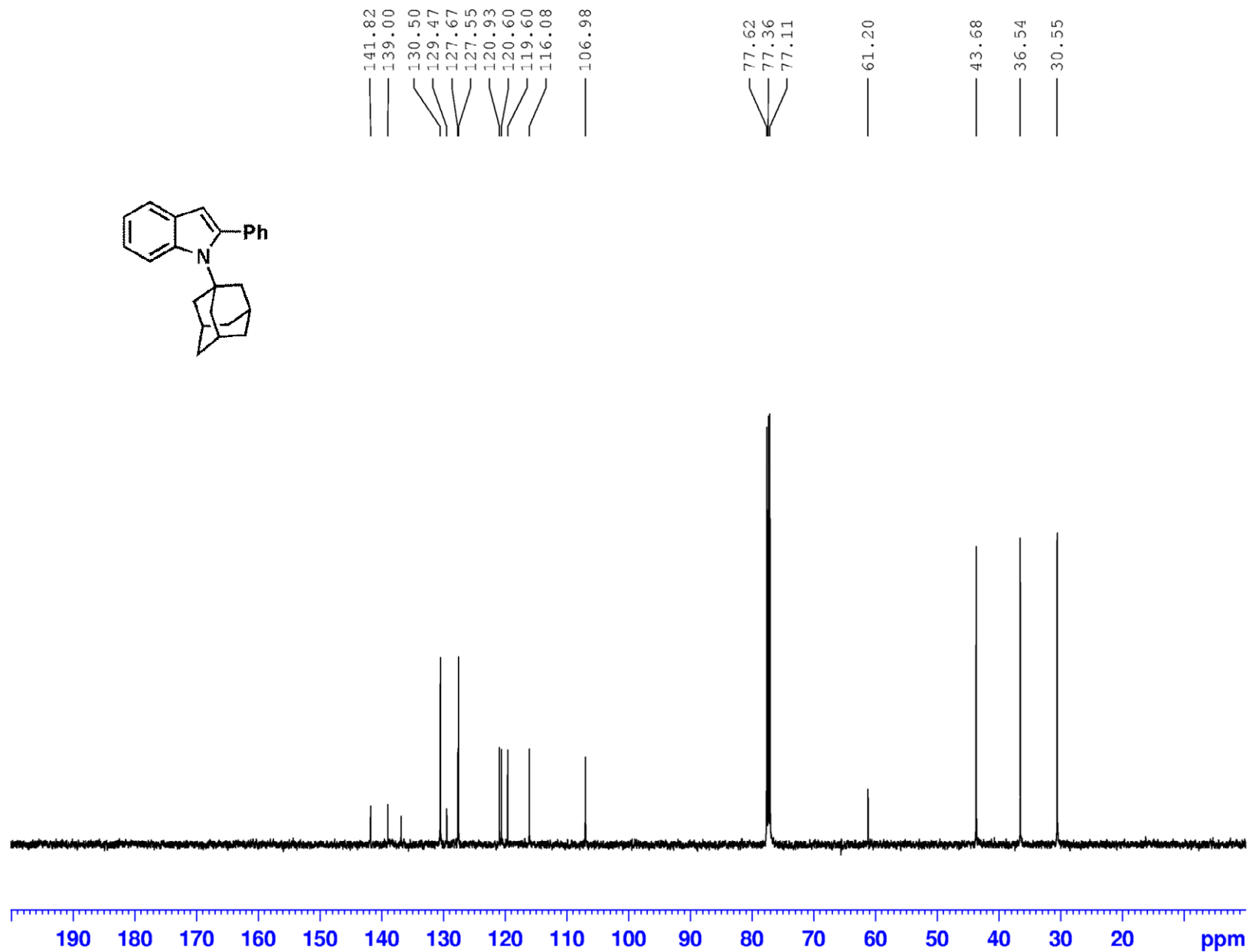
$^{13}\text{C}\{^1\text{H}\}$ NMR of **1**, 1-Methyl-2-phenyl-1*H*-indole (CDCl_3 , 125.8 MHz, 300 K)



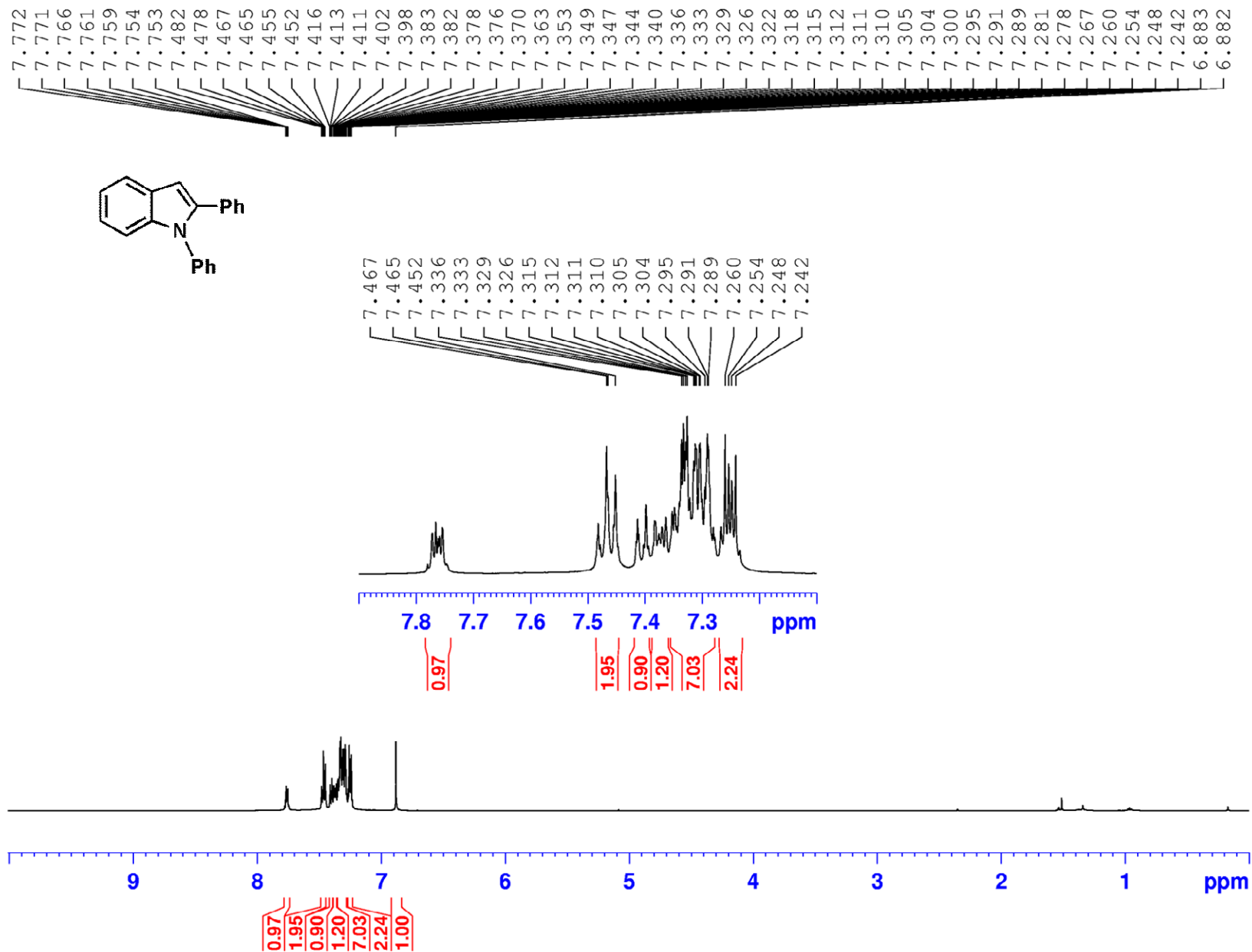
^1H NMR of **2**, 1-Adamantan-1-yl-2-phenyl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



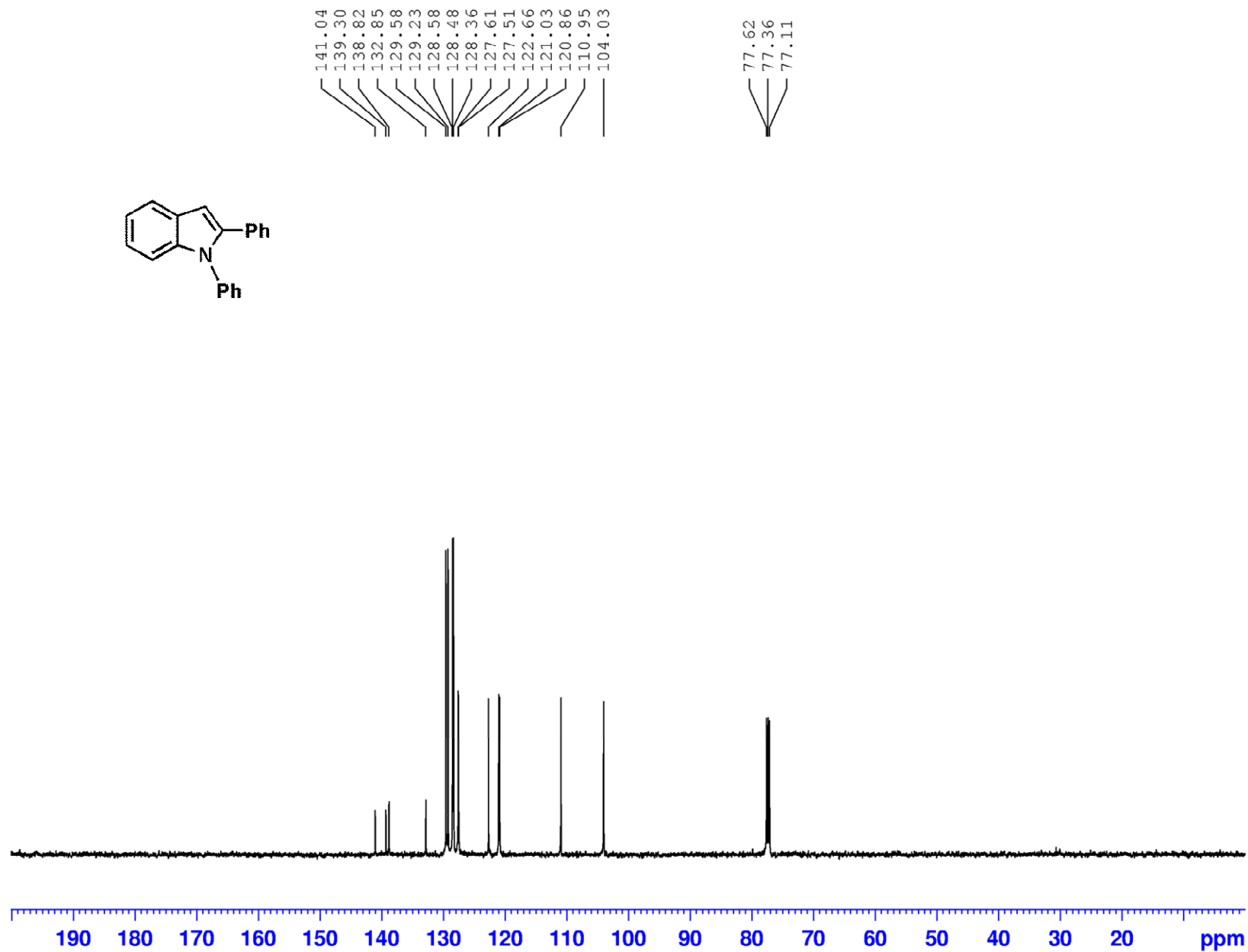
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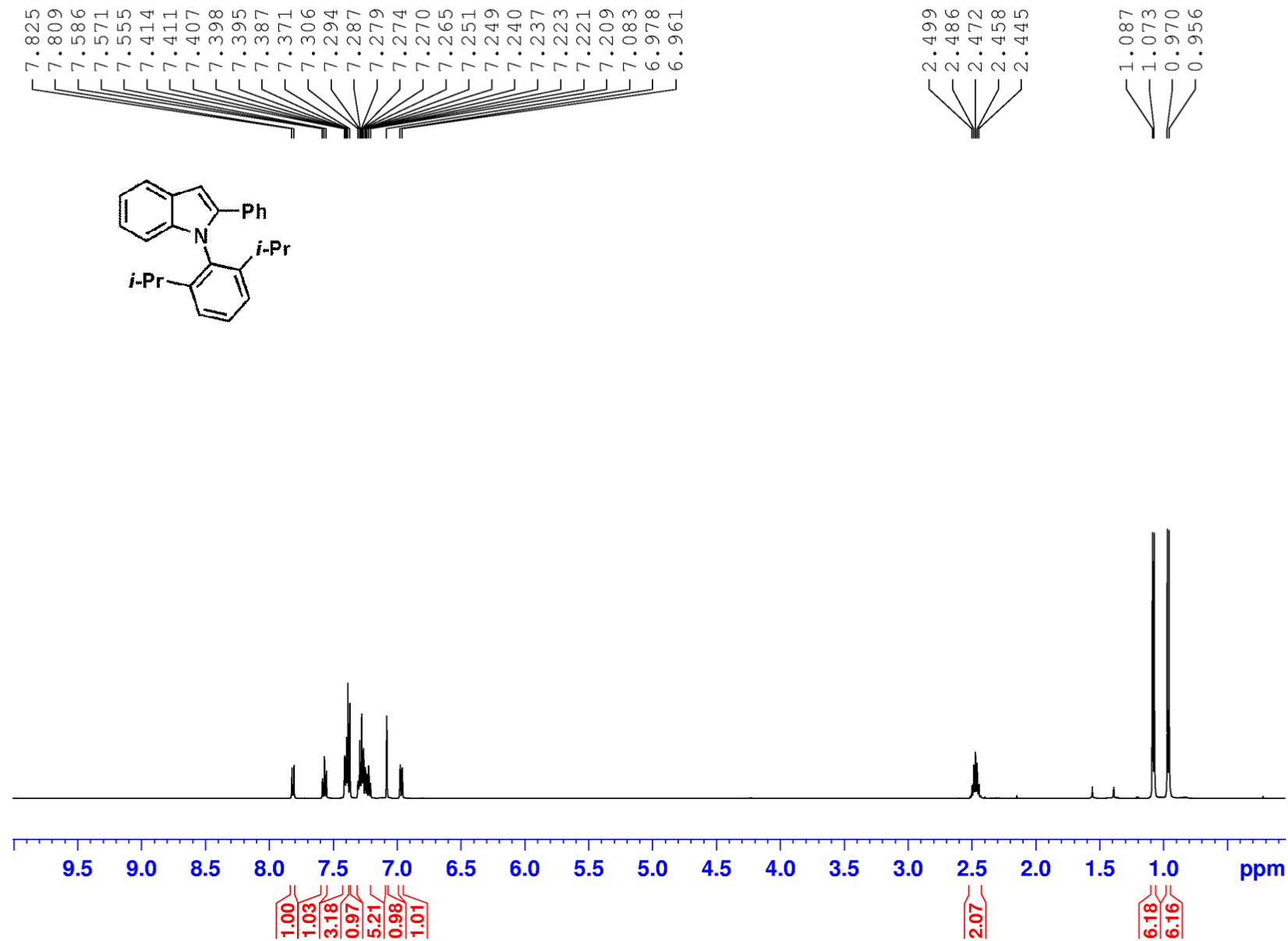
^1H NMR of **3**, 1,2-Diphenyl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



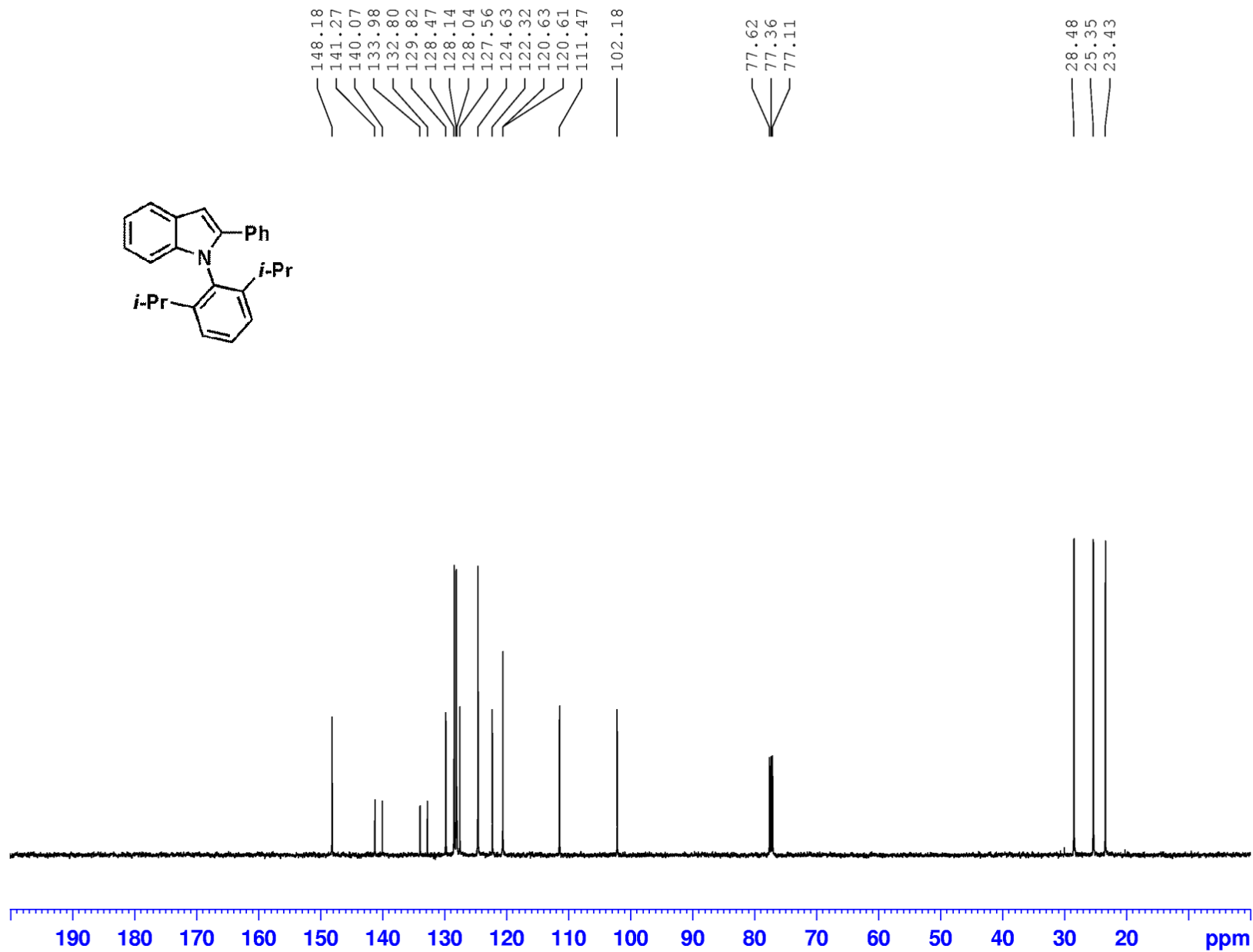
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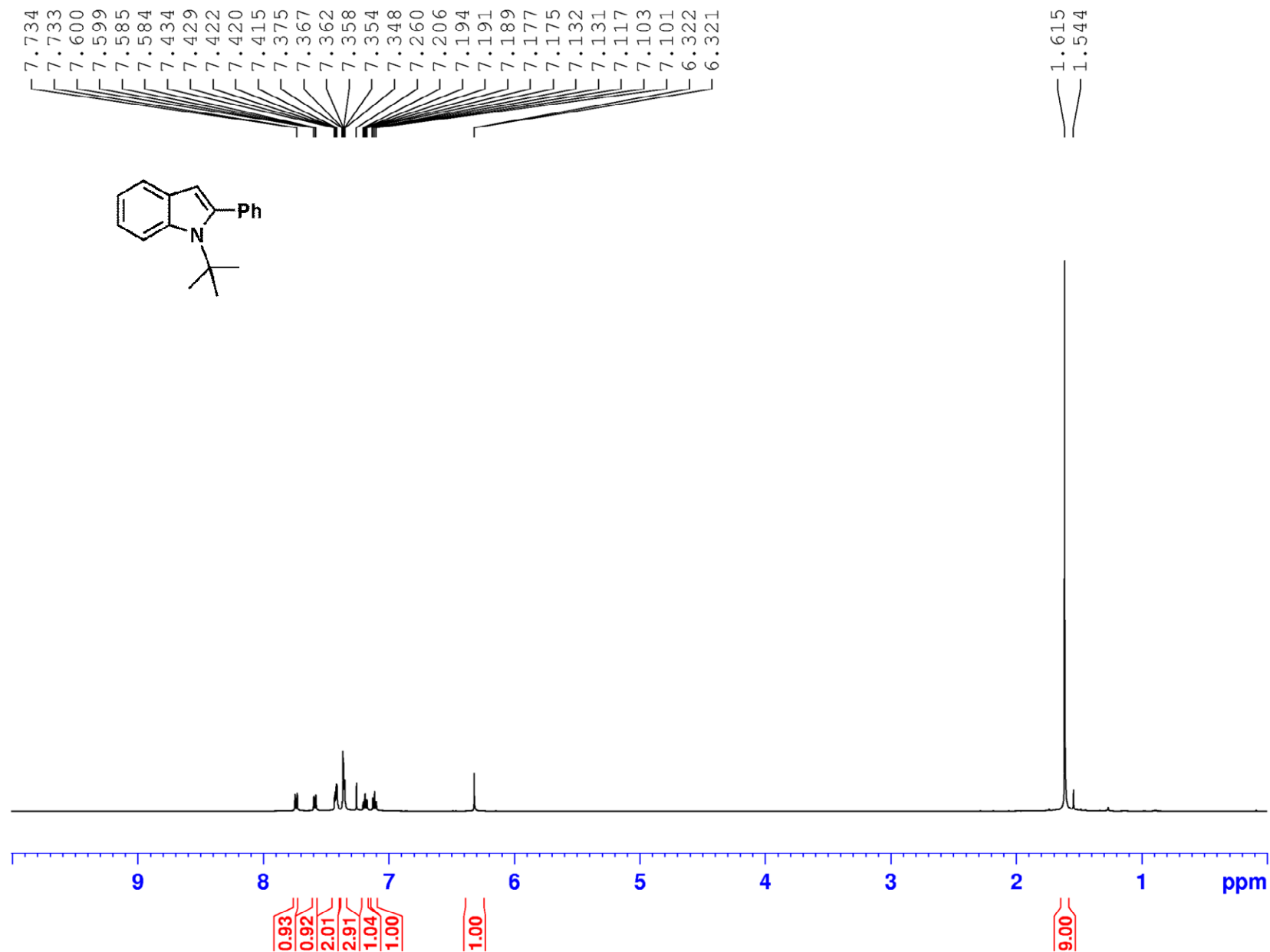
^1H NMR of **4**, 1-(2,6-Diisopropyl-phenyl)-2-phenyl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



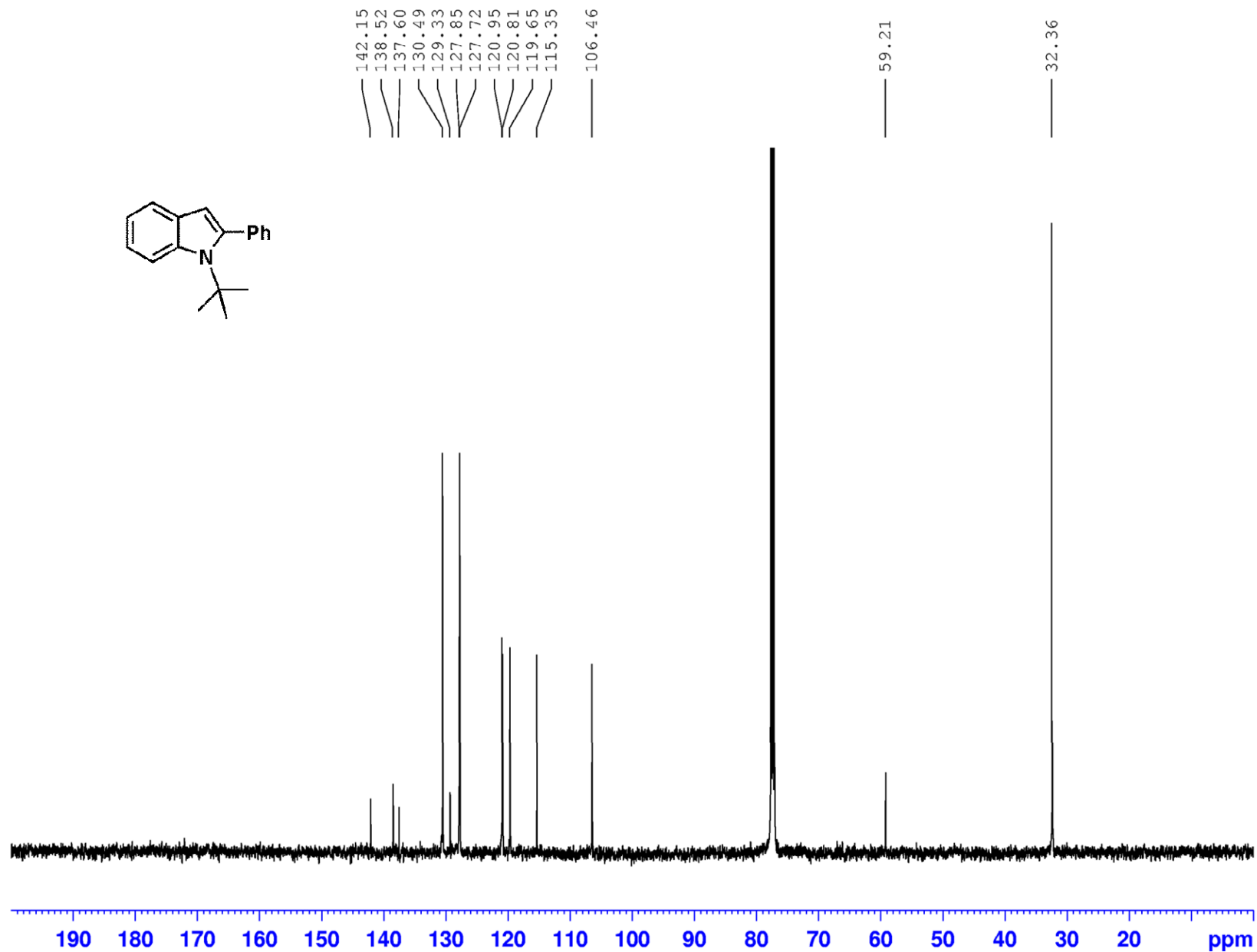
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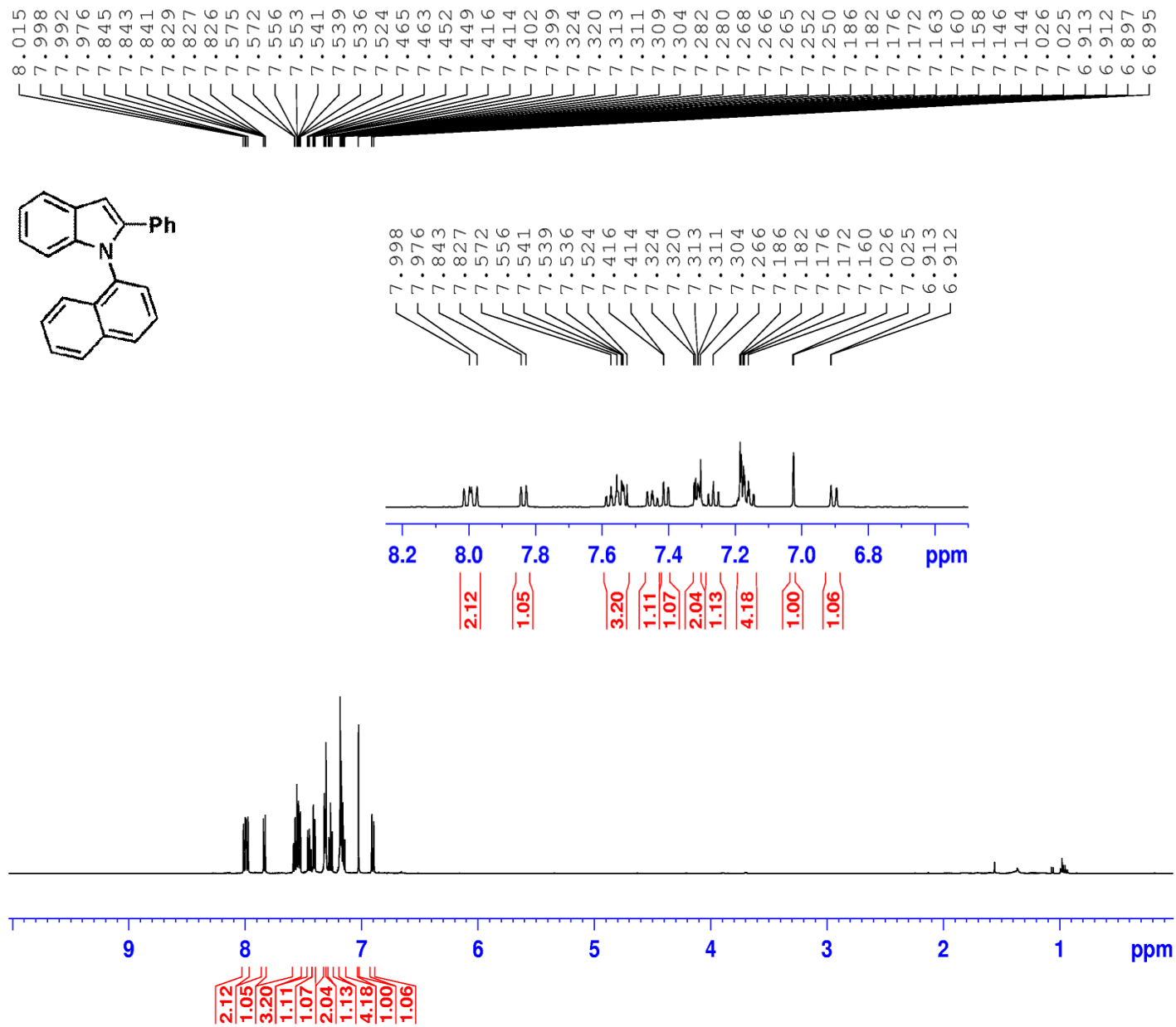
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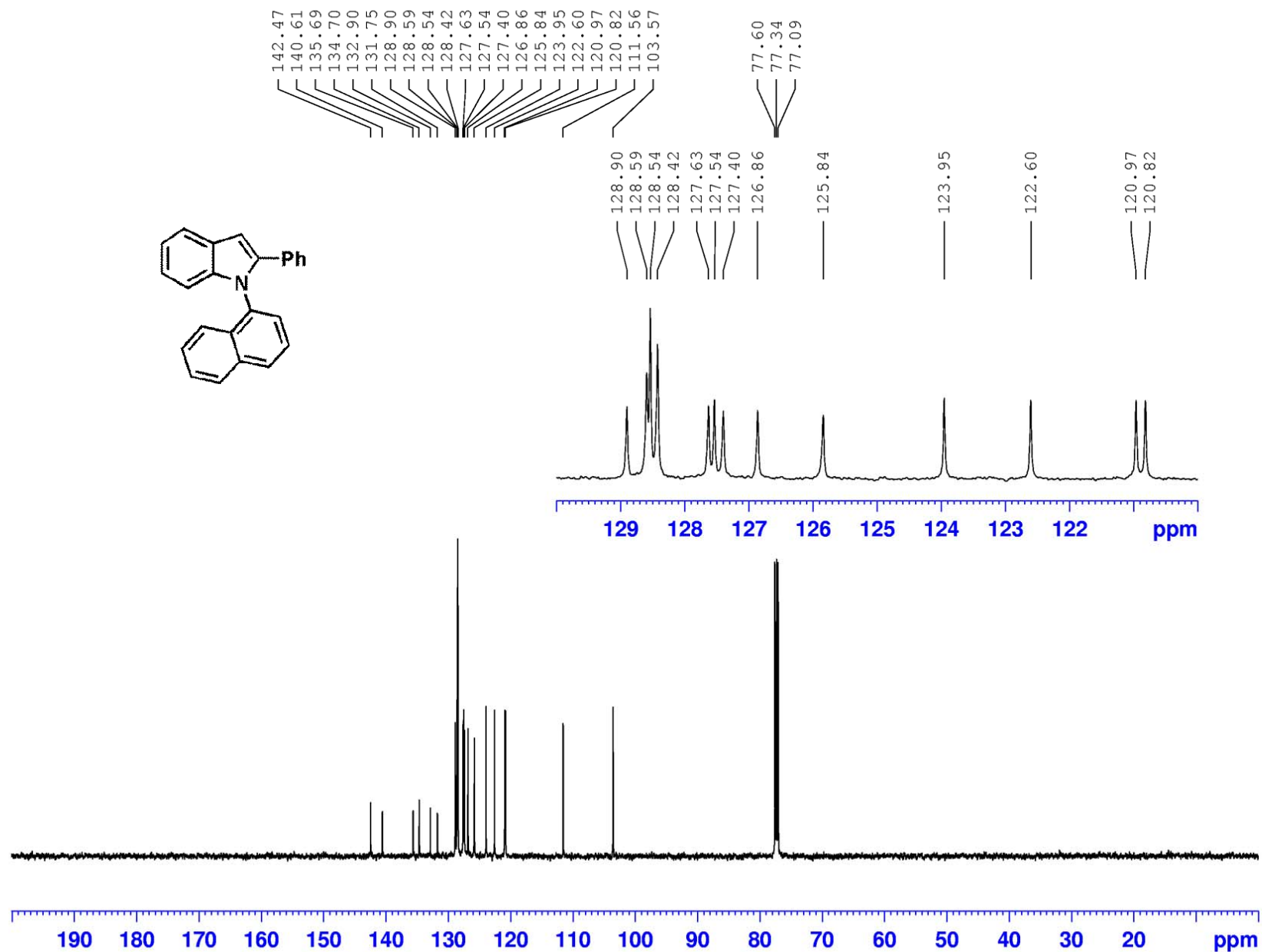
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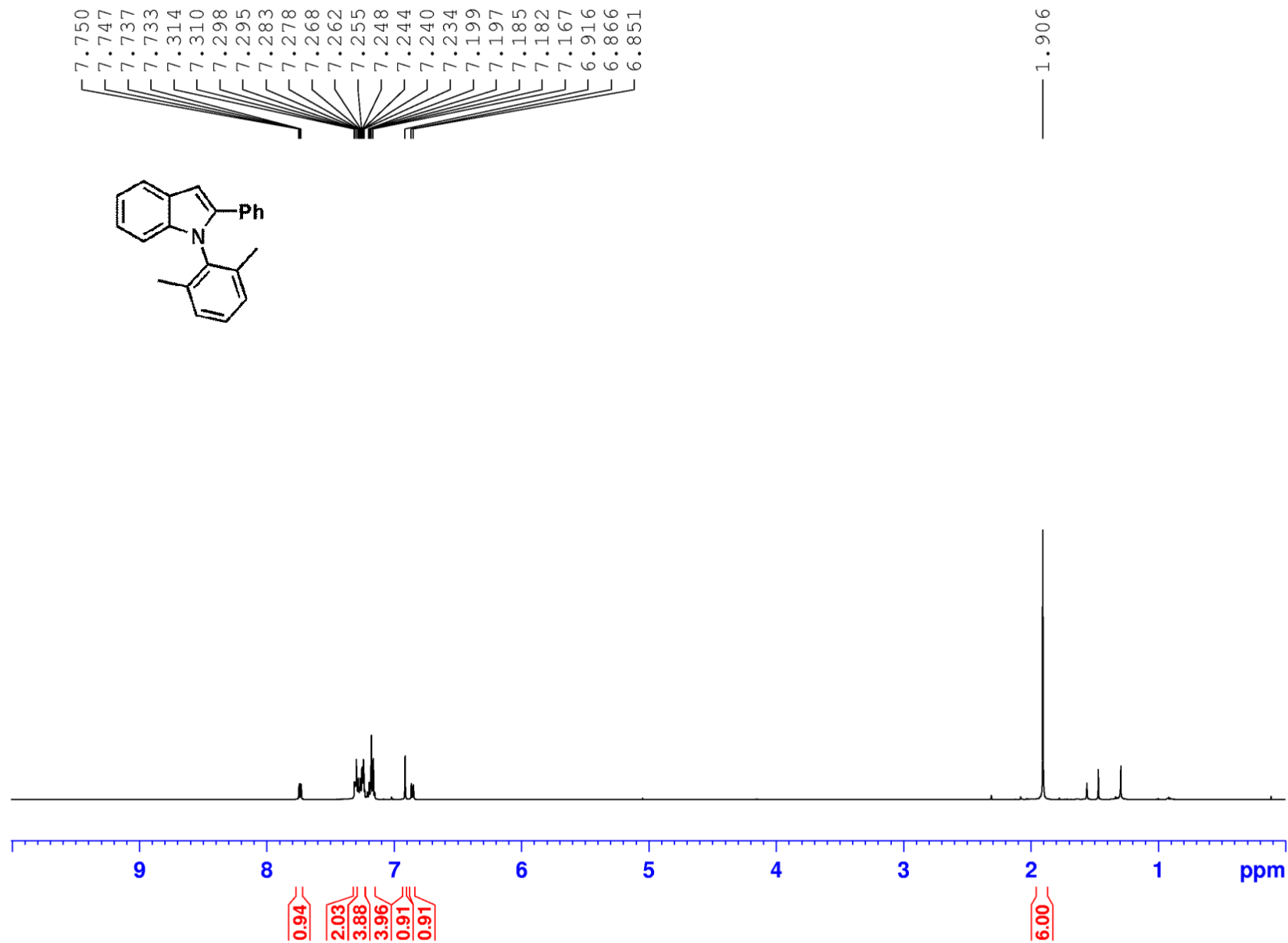
^1H NMR of **6**, 1-Naphthalen-1-yl-2-phenyl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



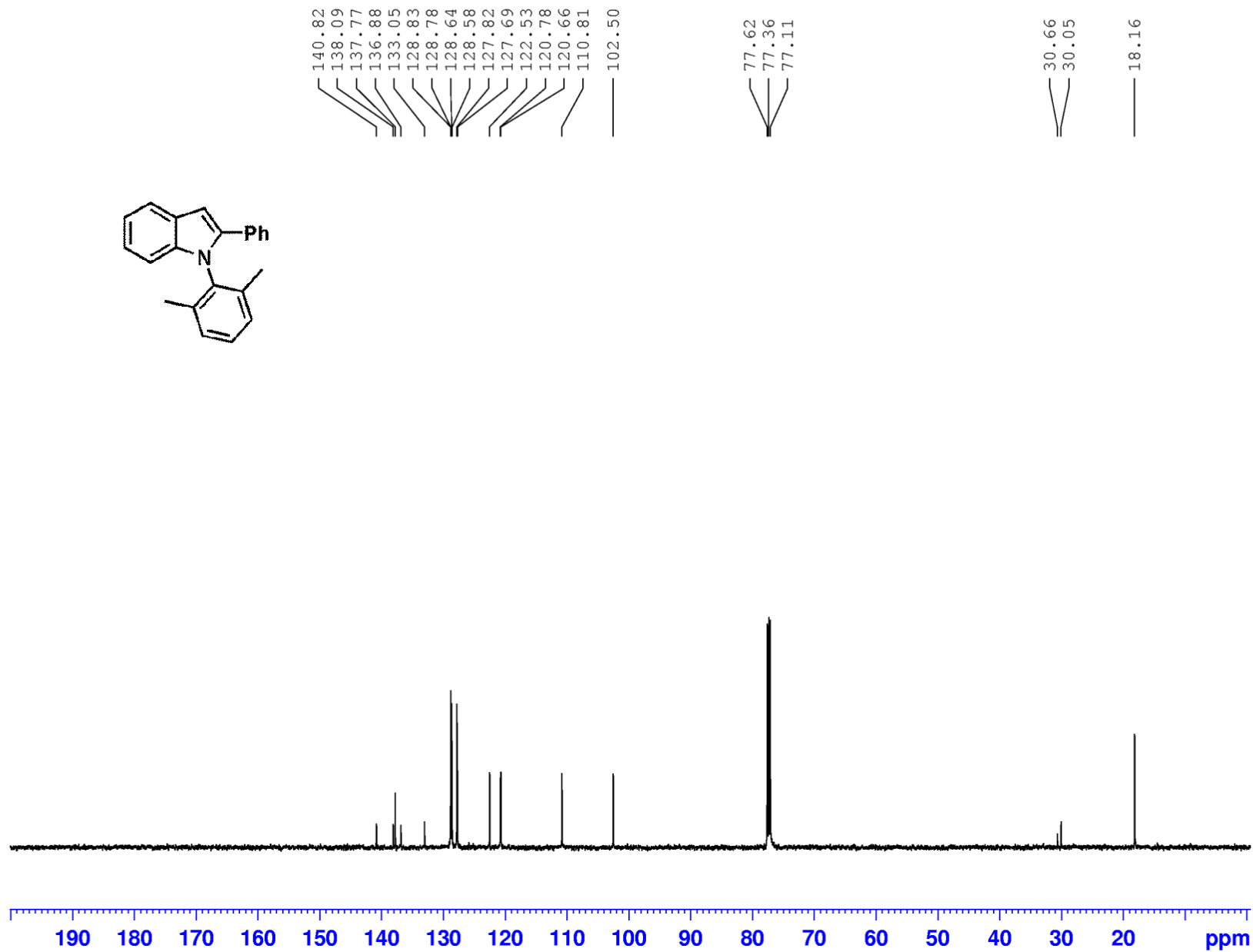
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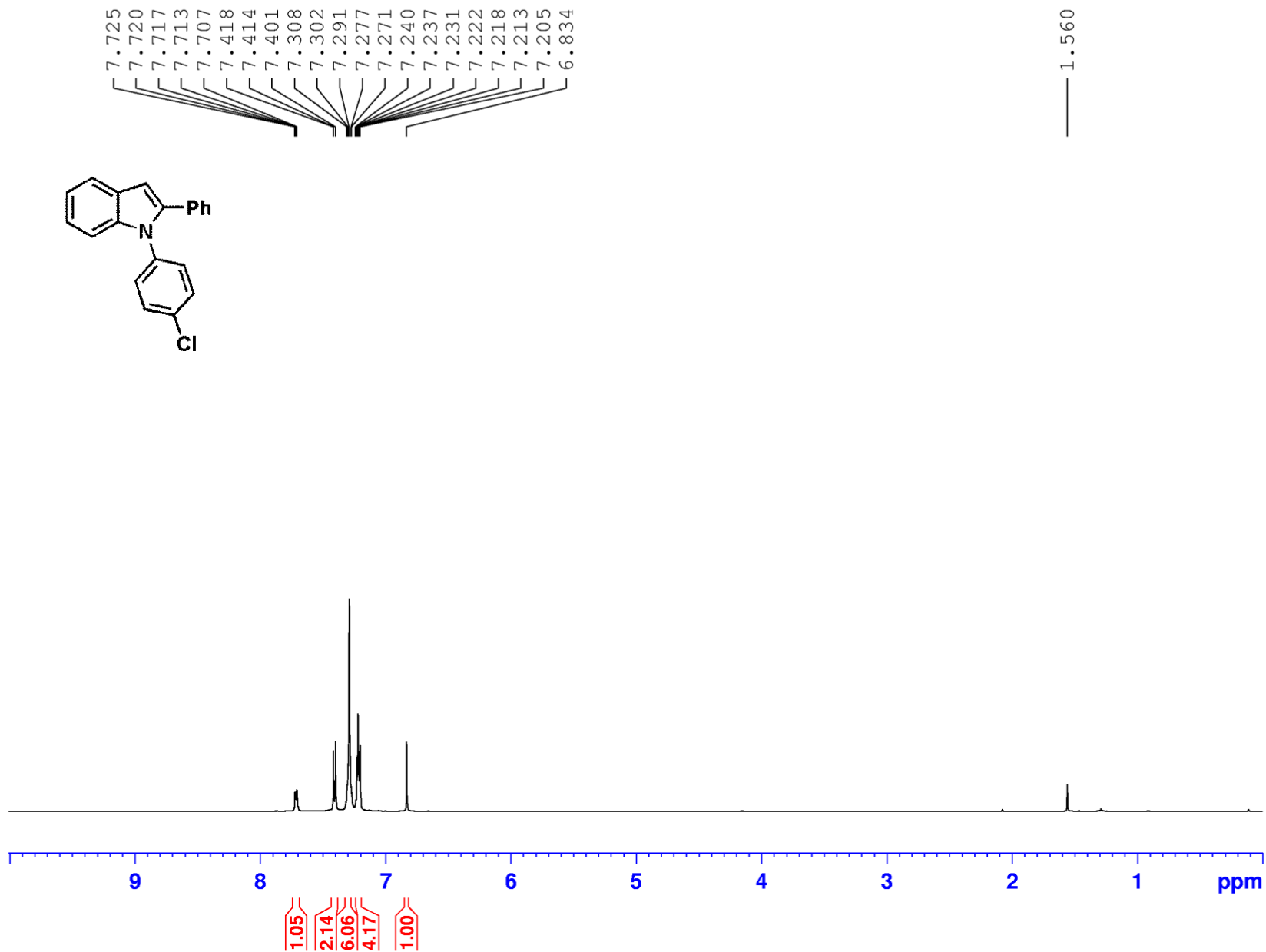
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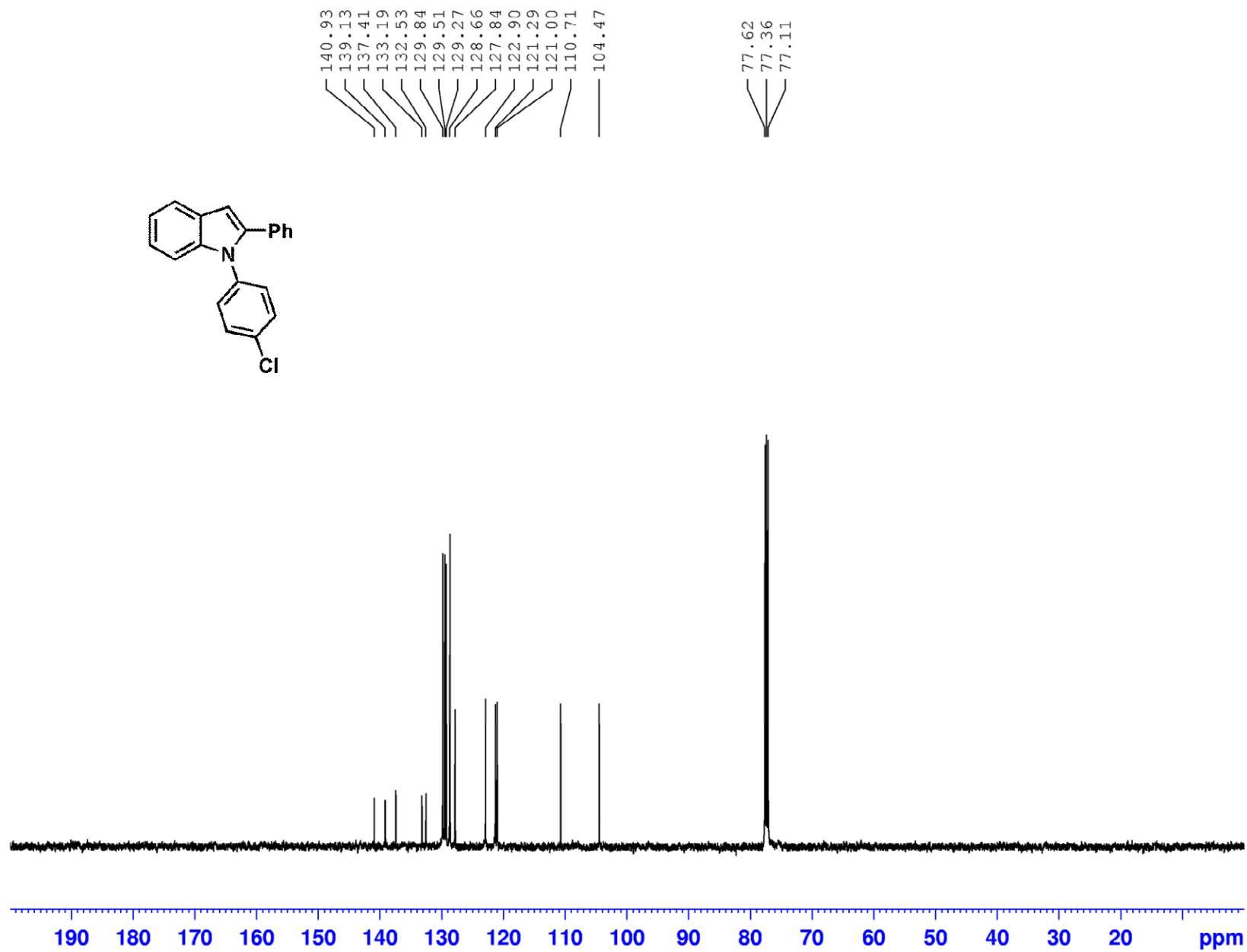
$^{13}\text{C}\{^1\text{H}\}$ NMR of **7**, 1-(2,6-Dimethyl-phenyl)-2-phenyl-1*H*-indole (CDCl_3 , 125.8 MHz, 300 K)



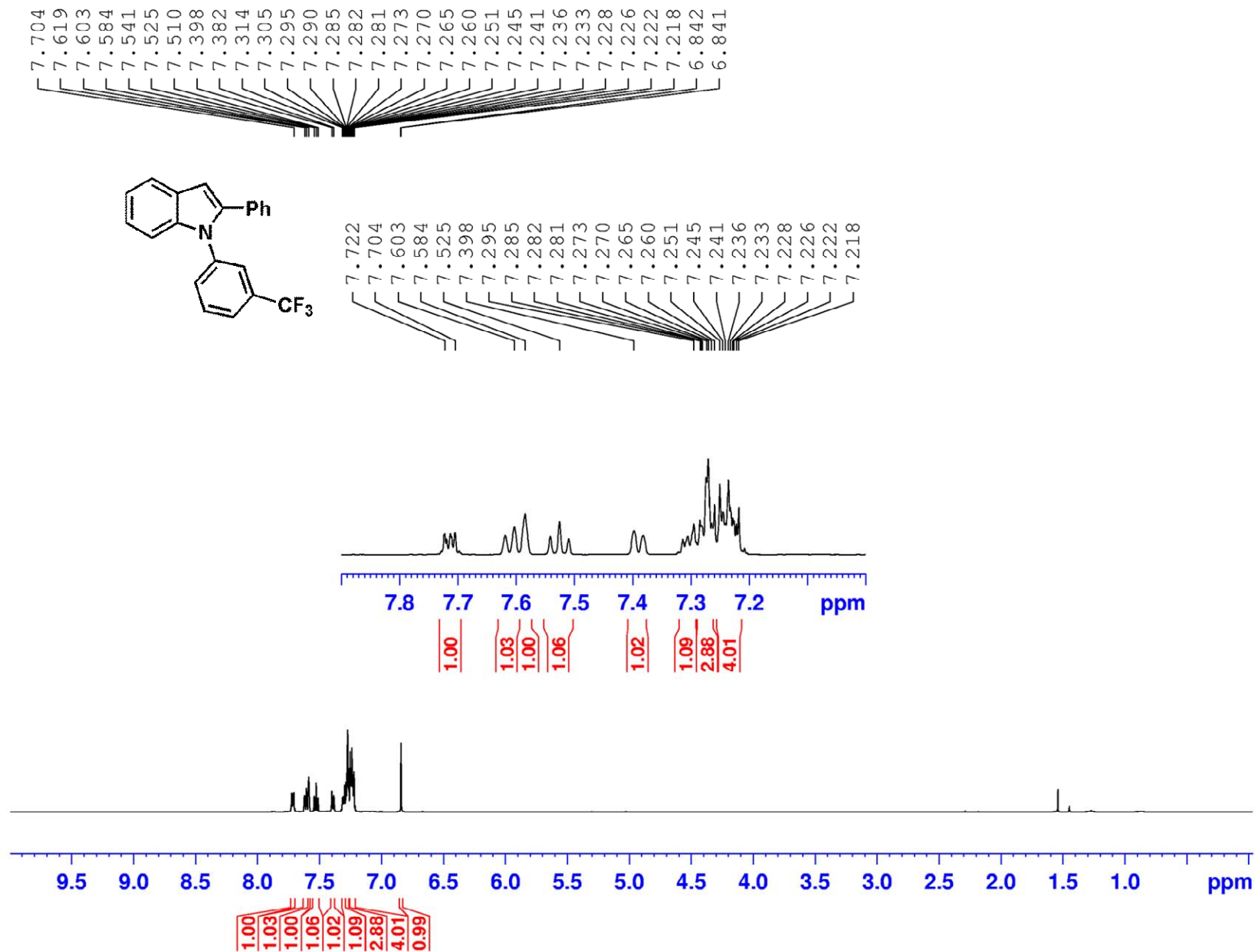
^1H NMR of **8**, 1-(4-Chloro-phenyl)-2-phenyl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



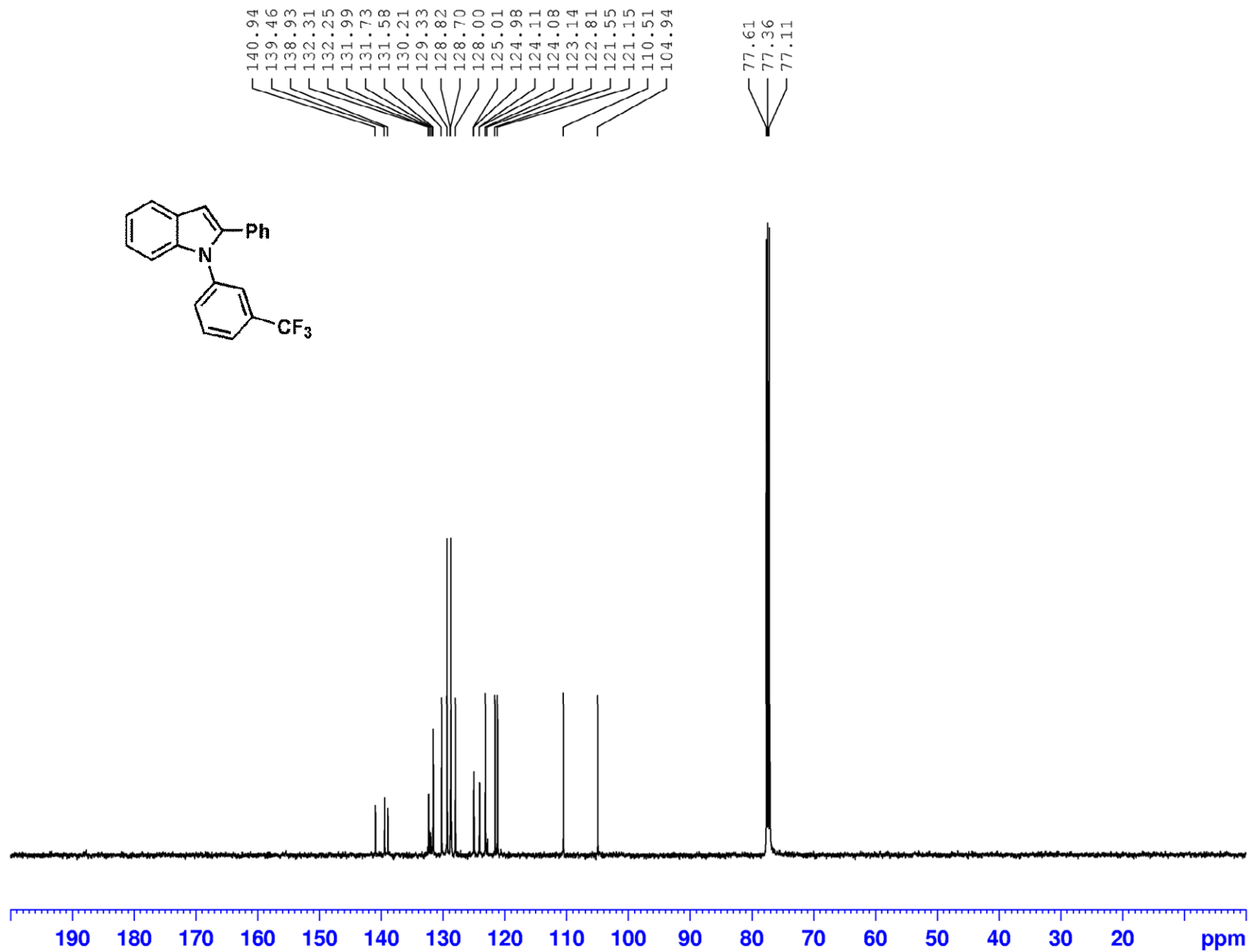
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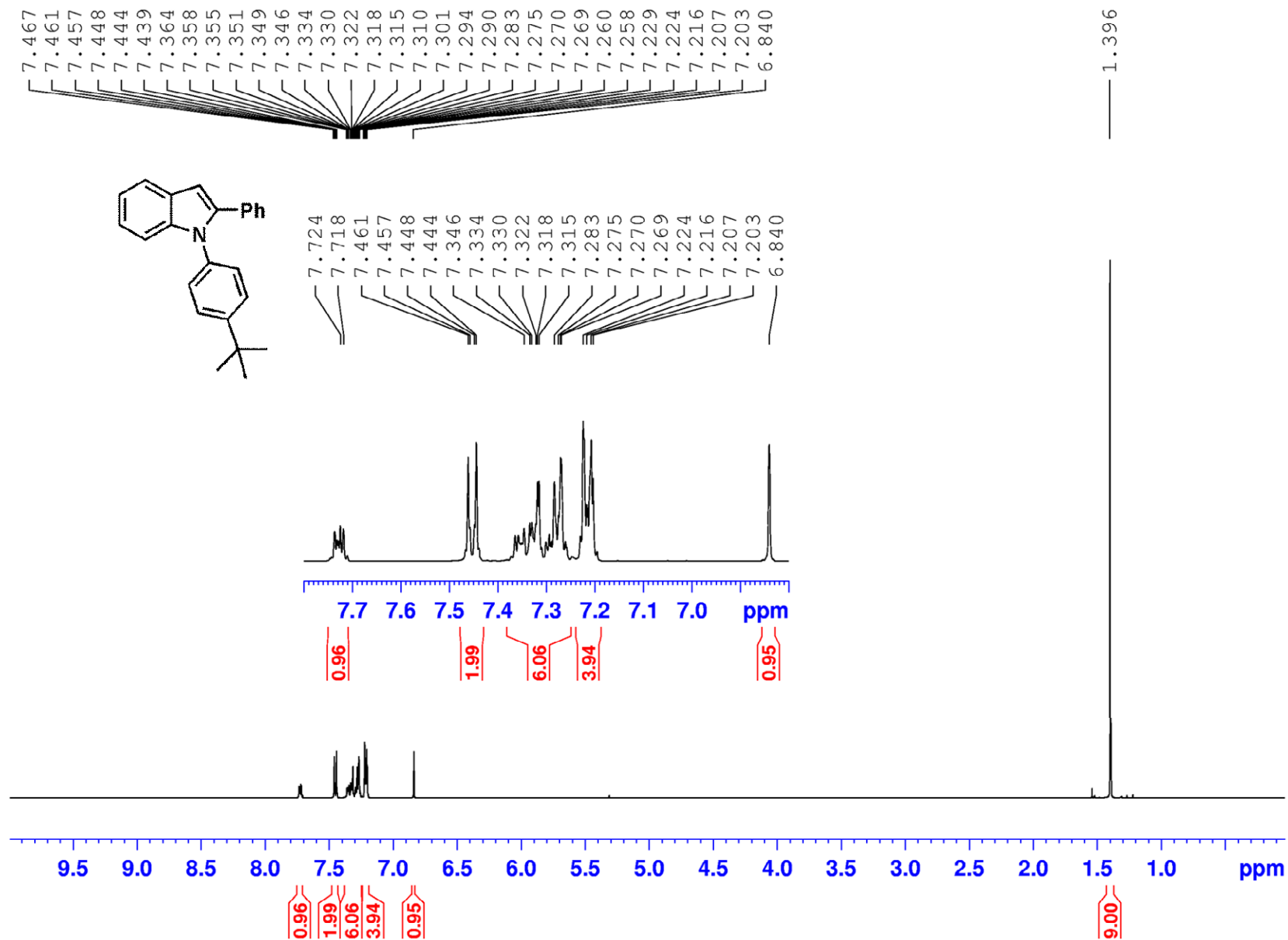
^1H NMR of **9**, 2-Phenyl-1-(3-trifluoromethyl-phenyl)-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



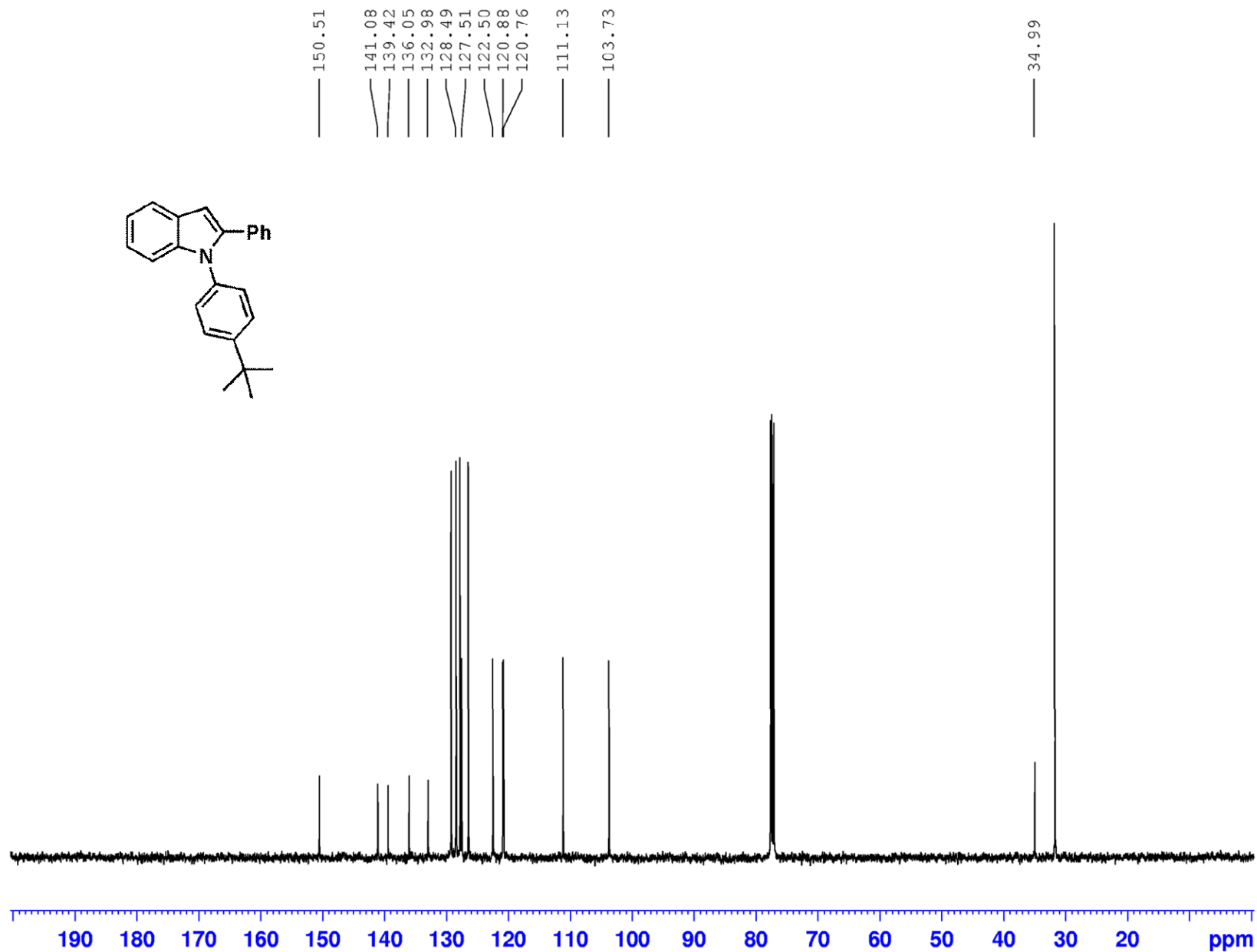
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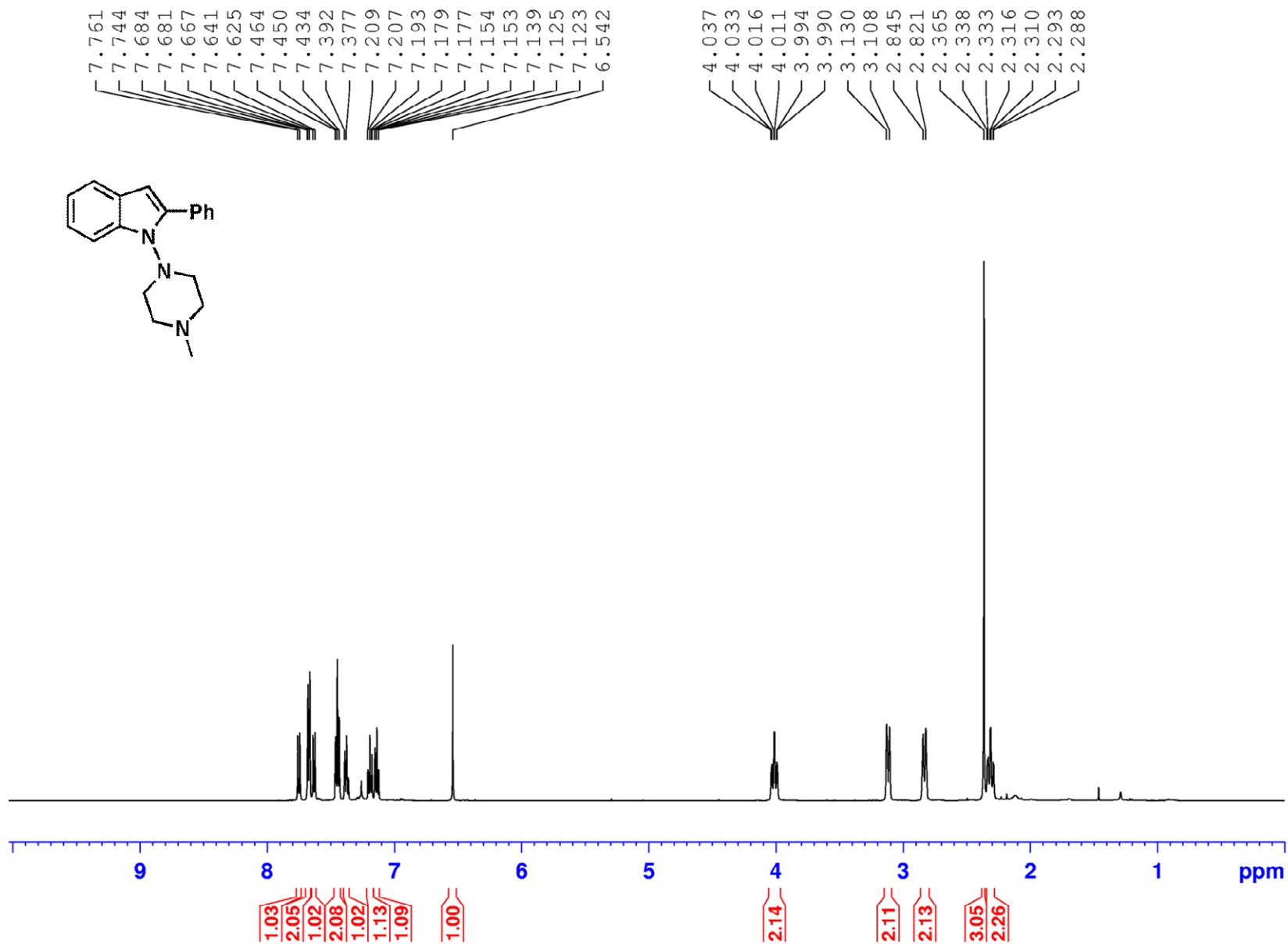
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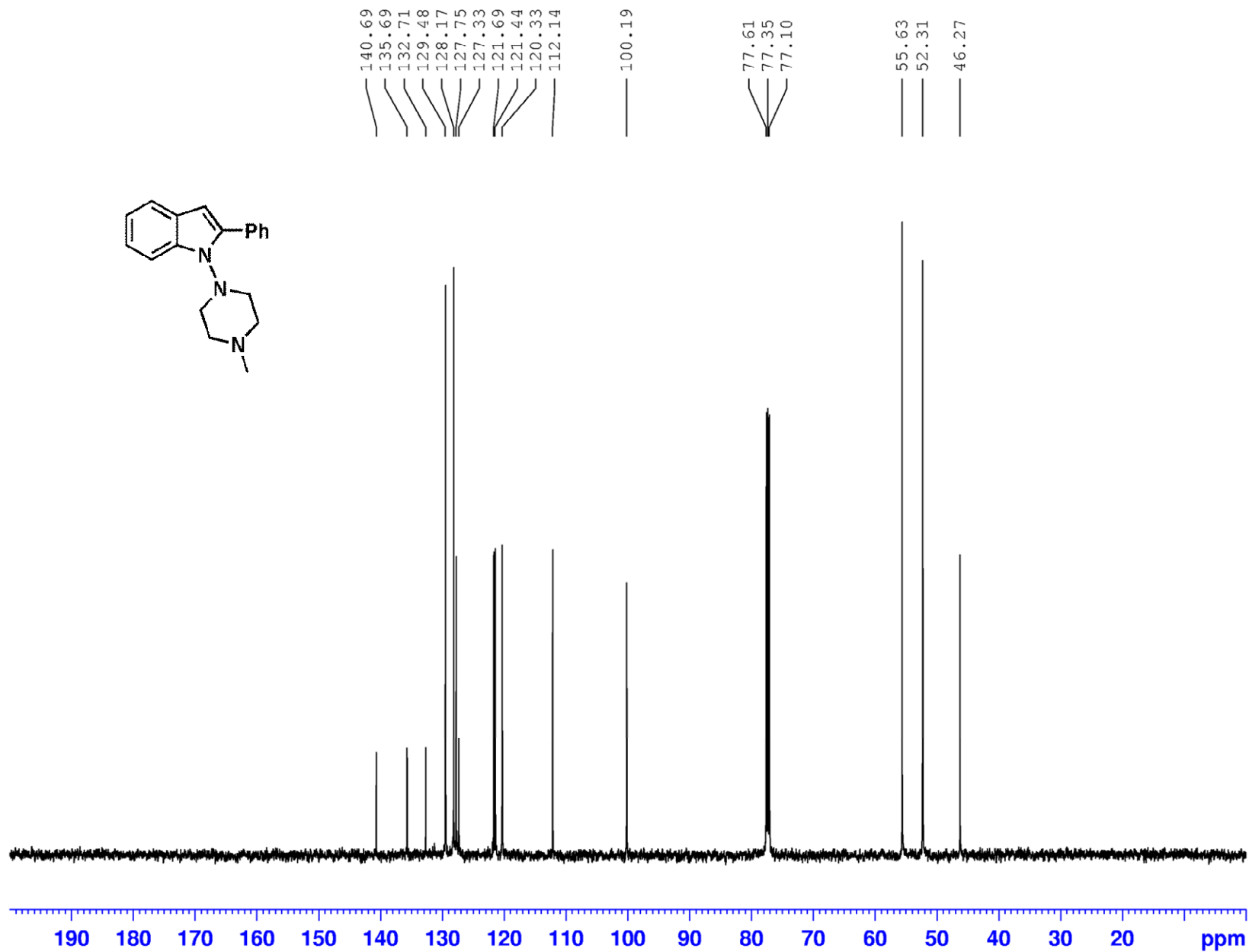
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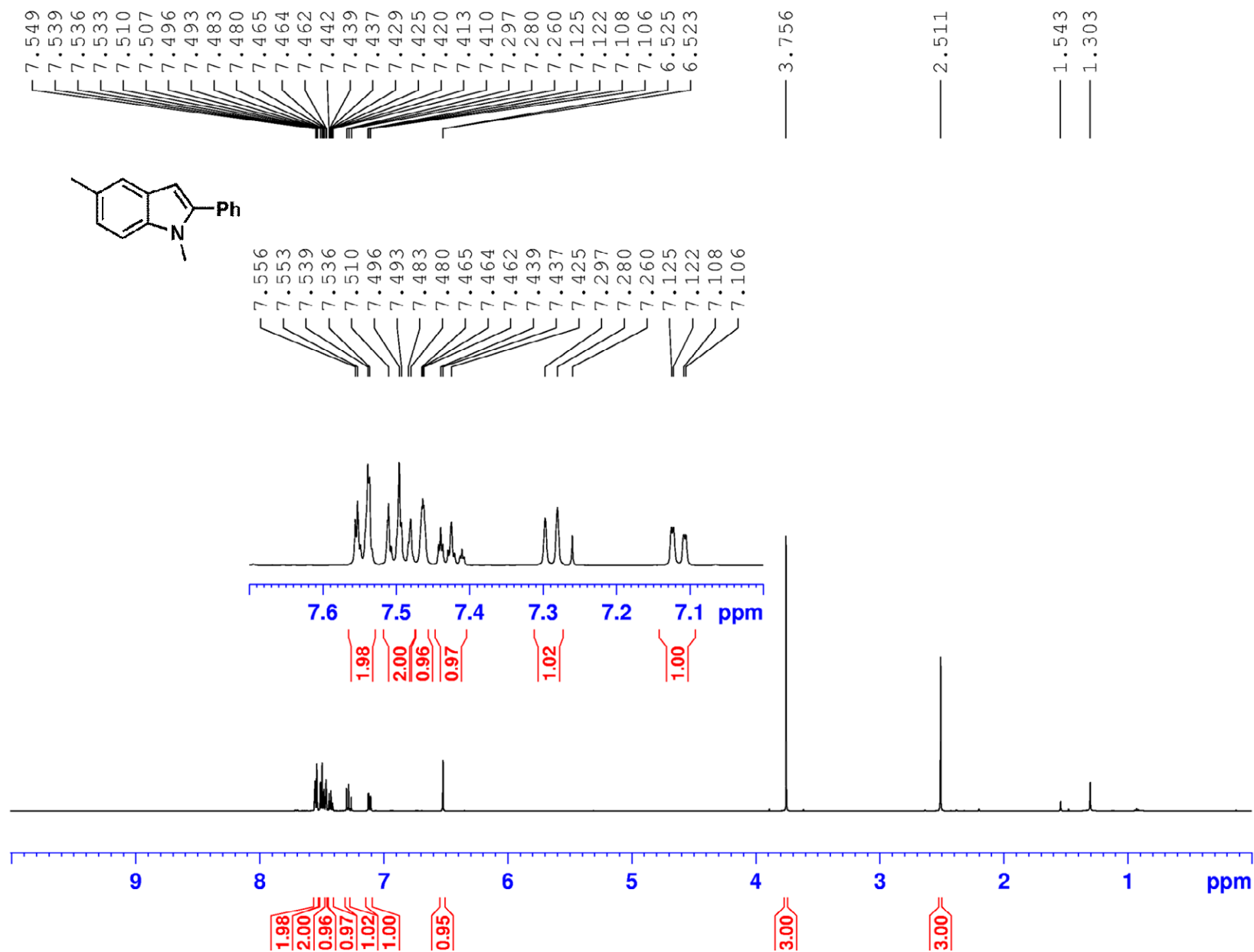
^1H NMR of **11**, 1-(4-Methyl-piperazin-1-yl)-2-phenyl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



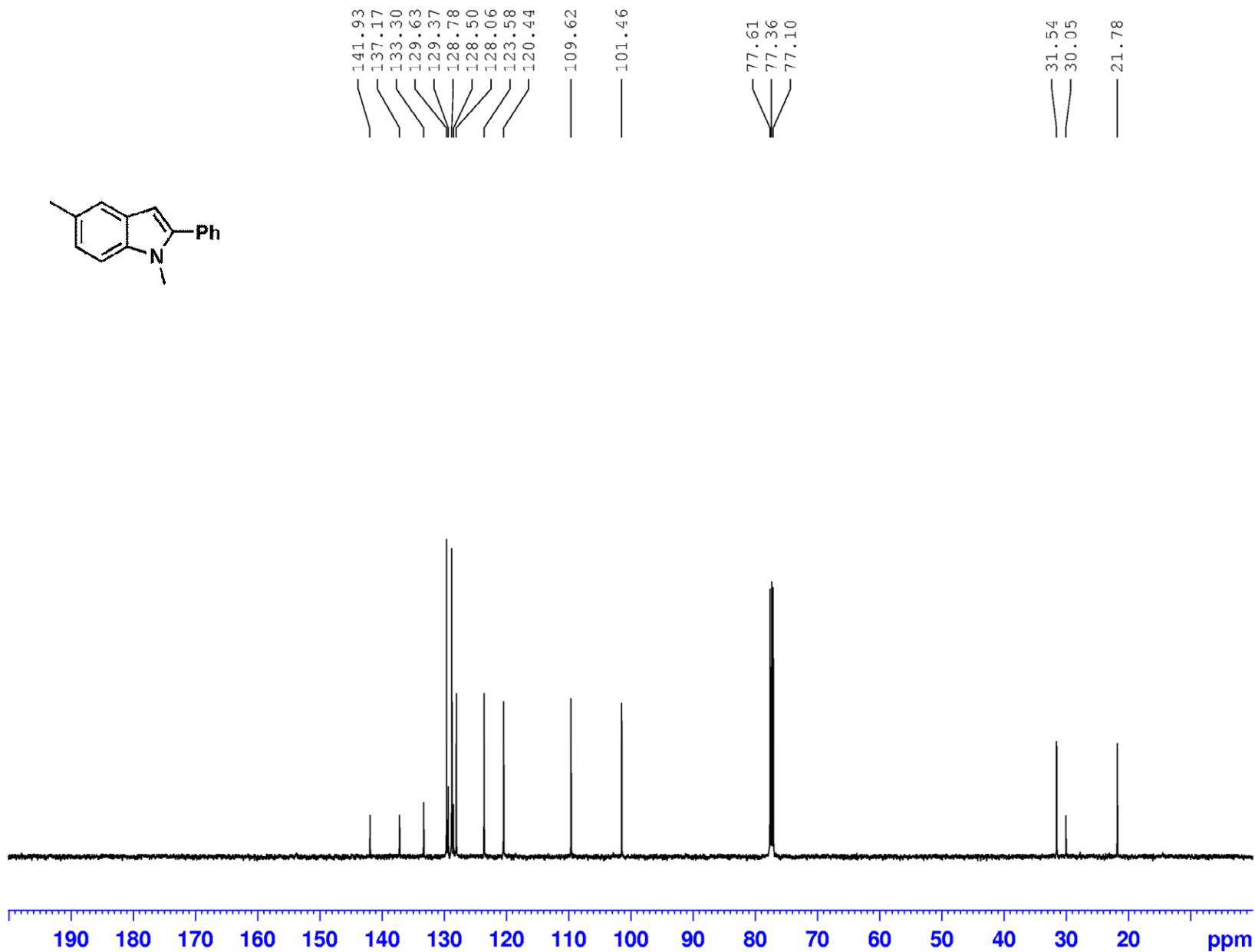
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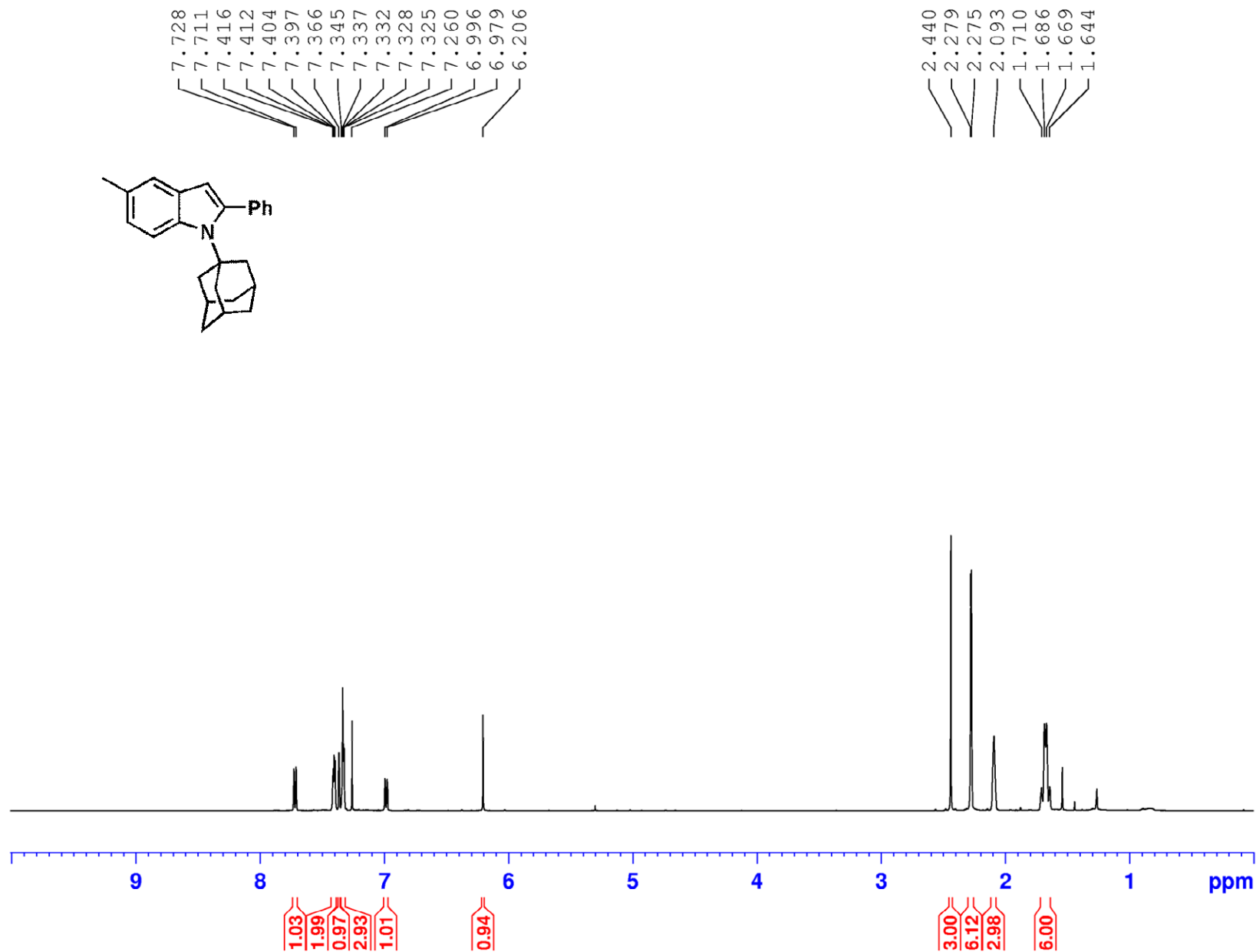
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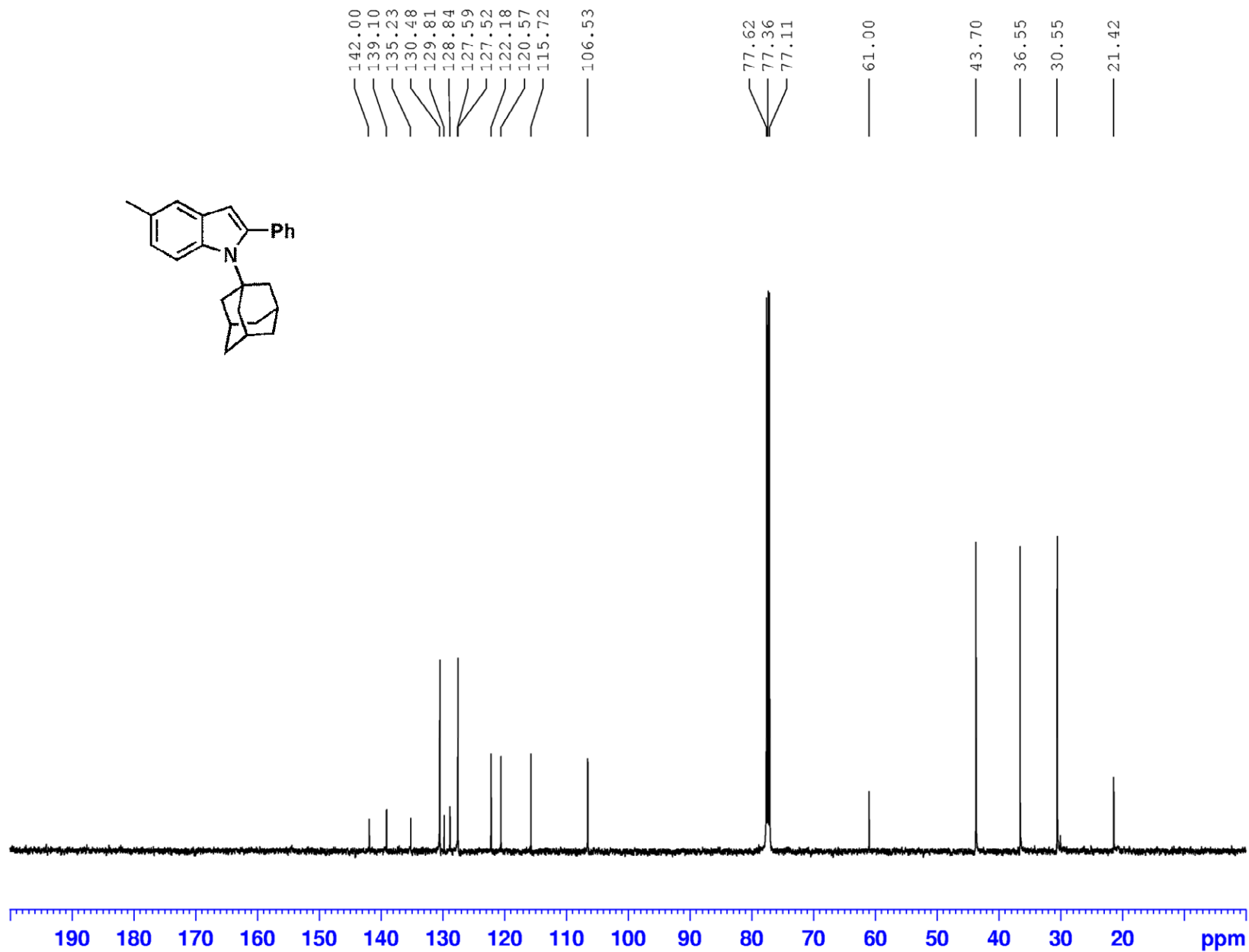
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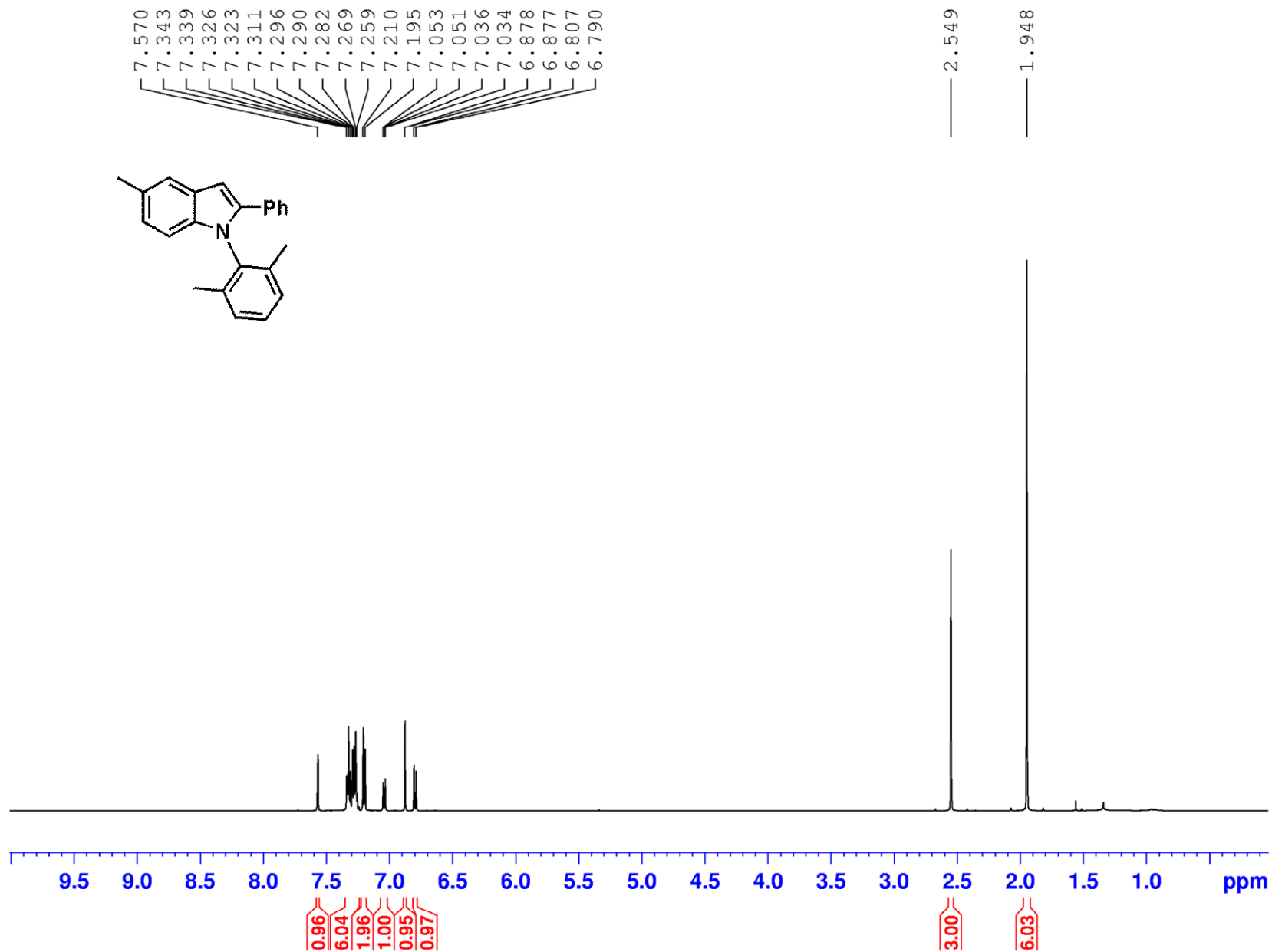
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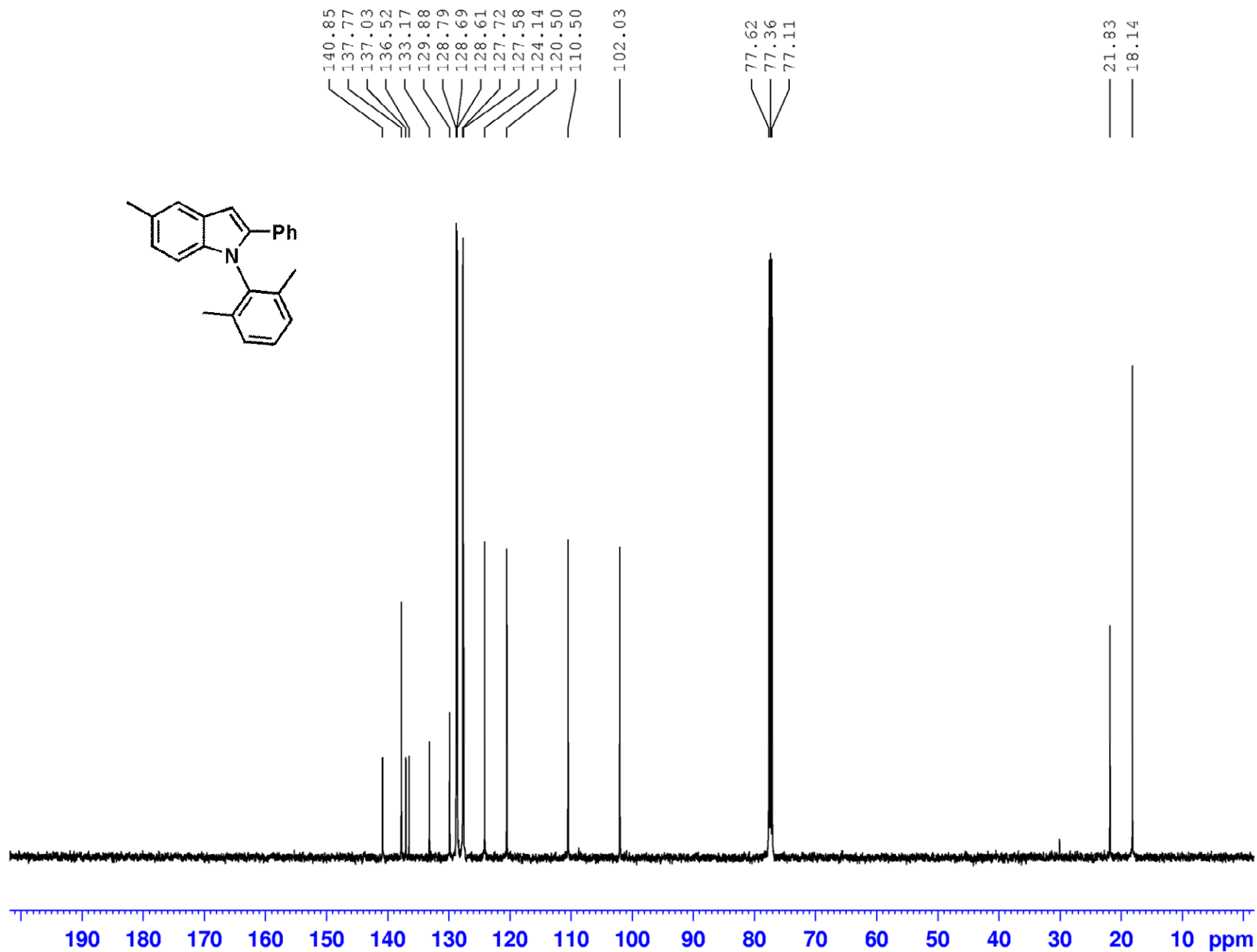
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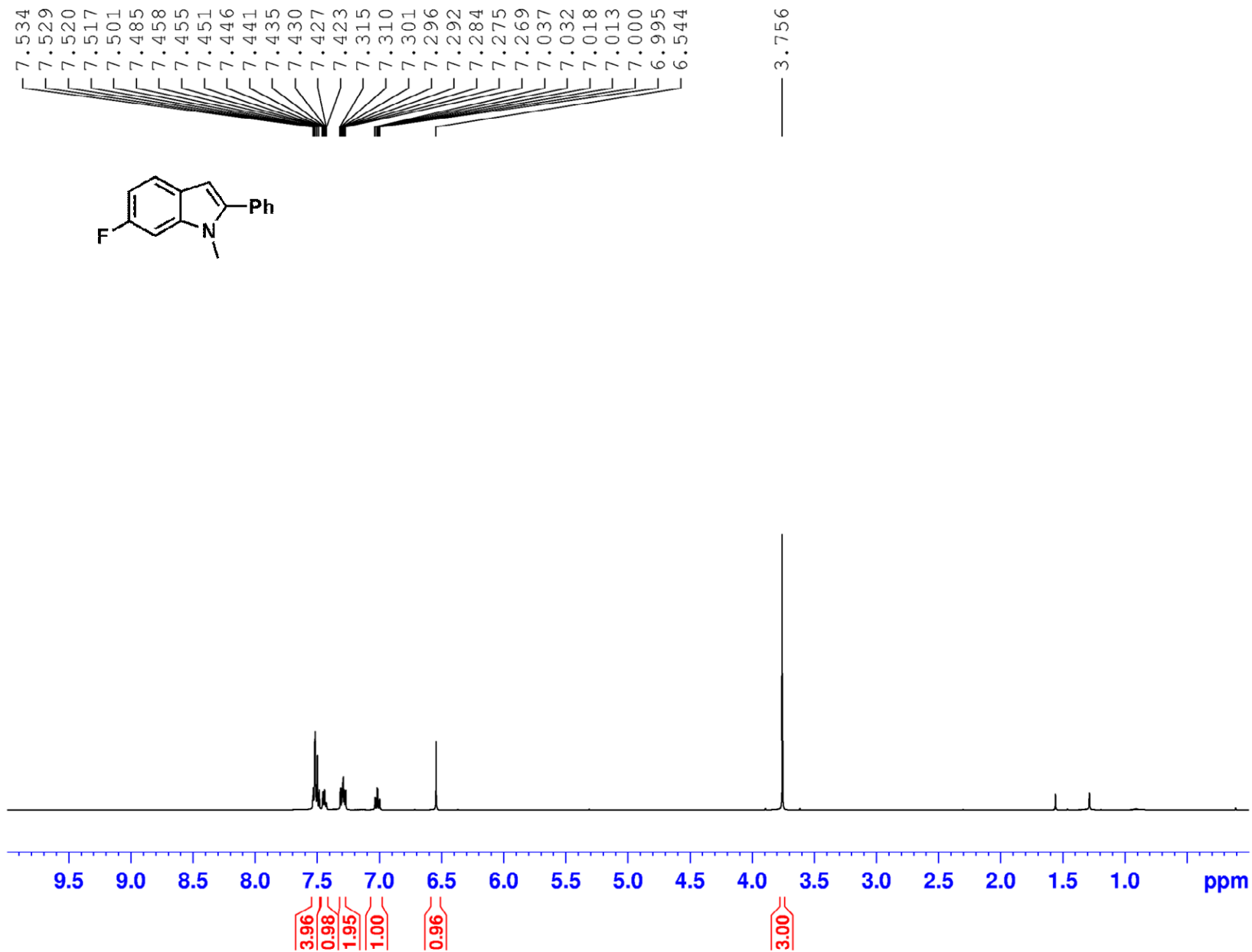
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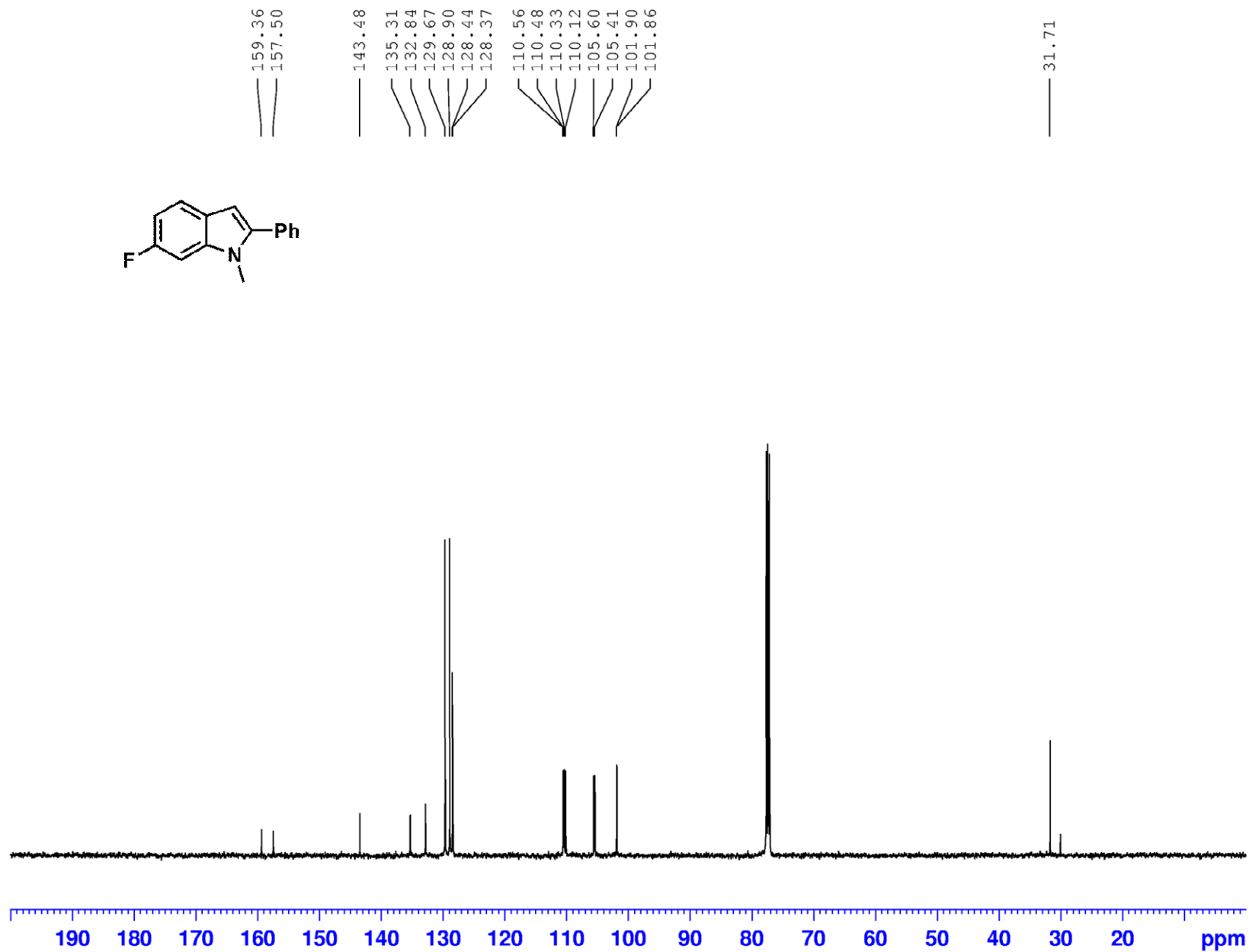
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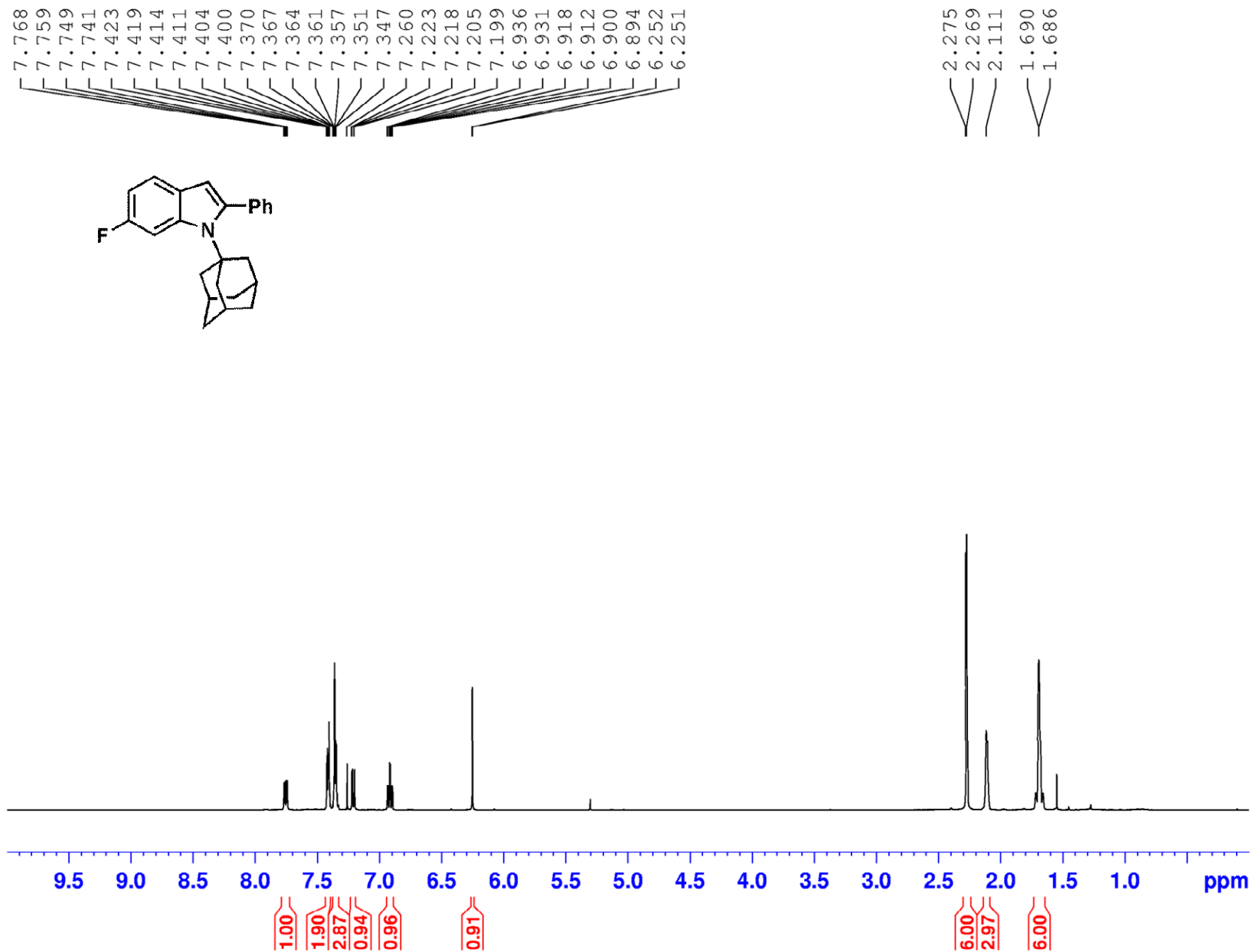
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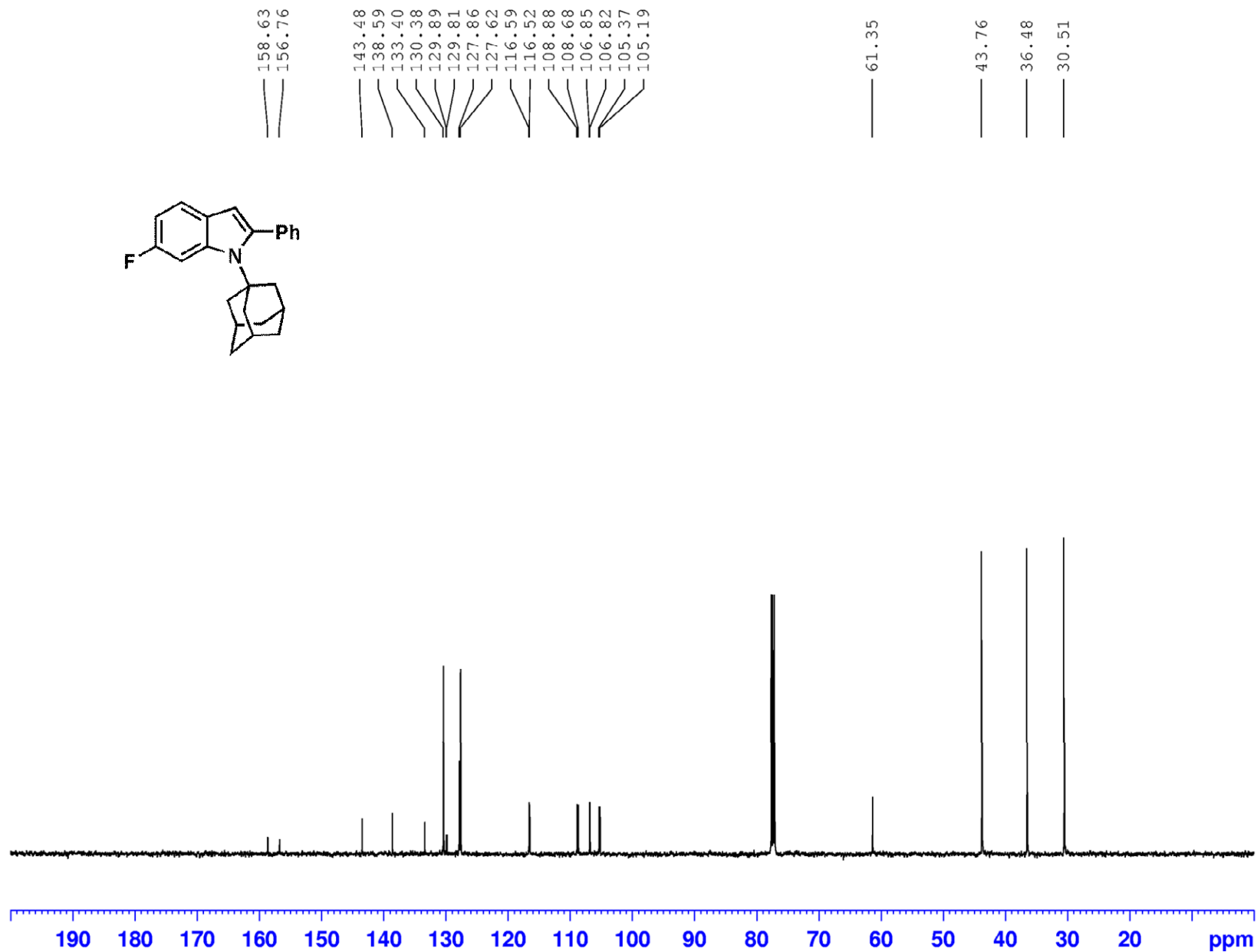
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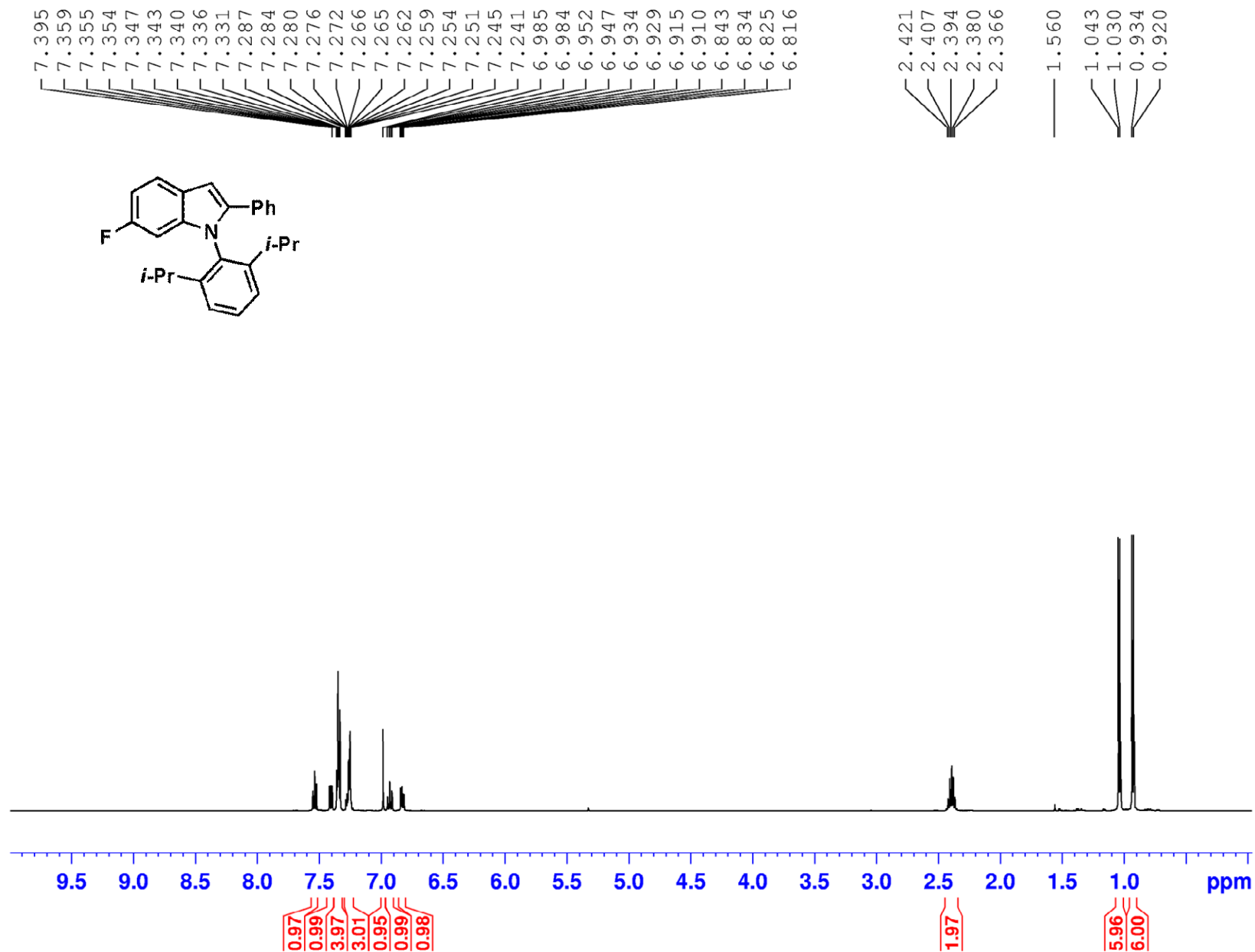
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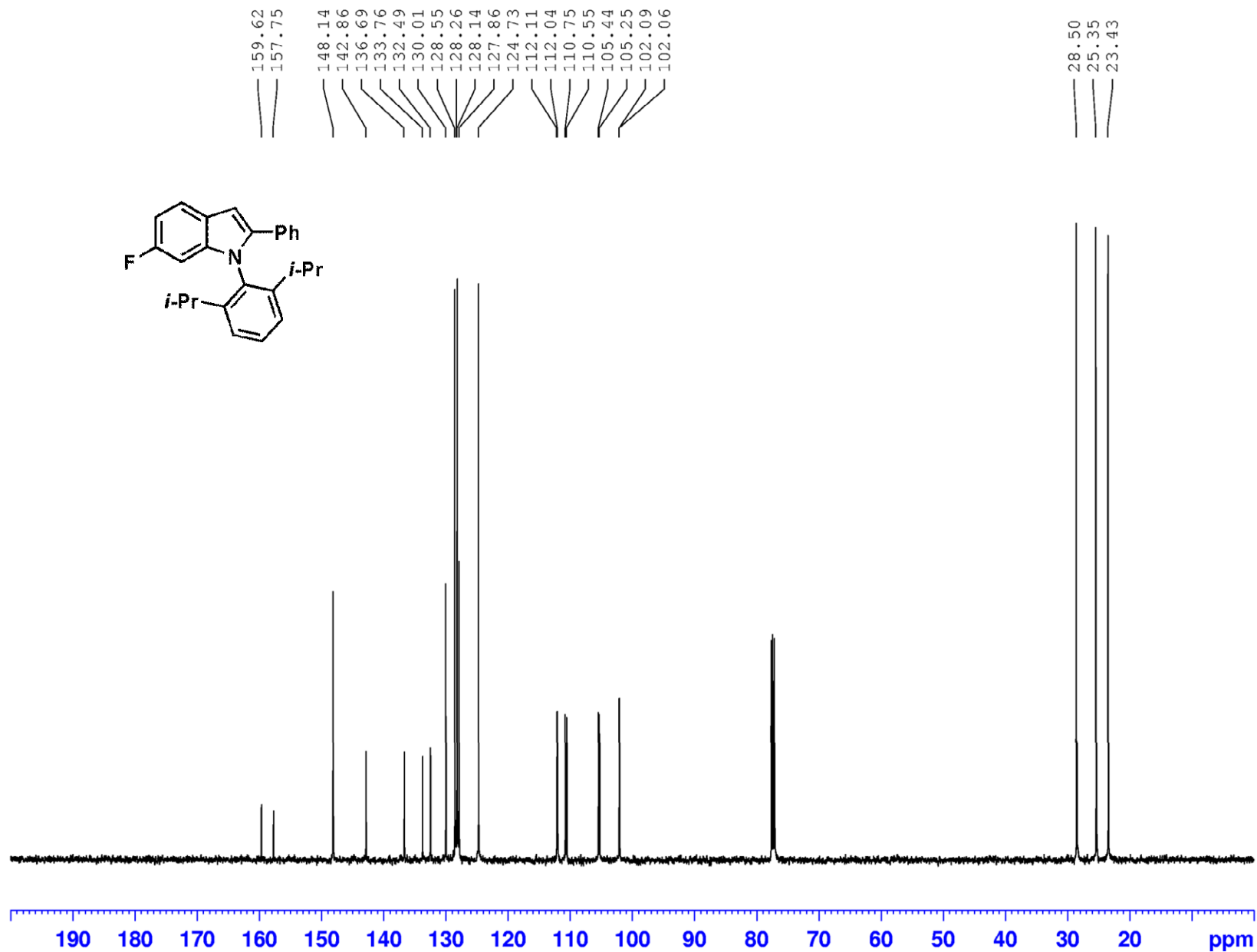
$^{13}\text{C}\{^1\text{H}\}$ NMR of **16**, 1-Adamantan-1-yl-6-fluoro-2-phenyl-1*H*-indole (CDCl_3 , 125.8 MHz, 300 K)



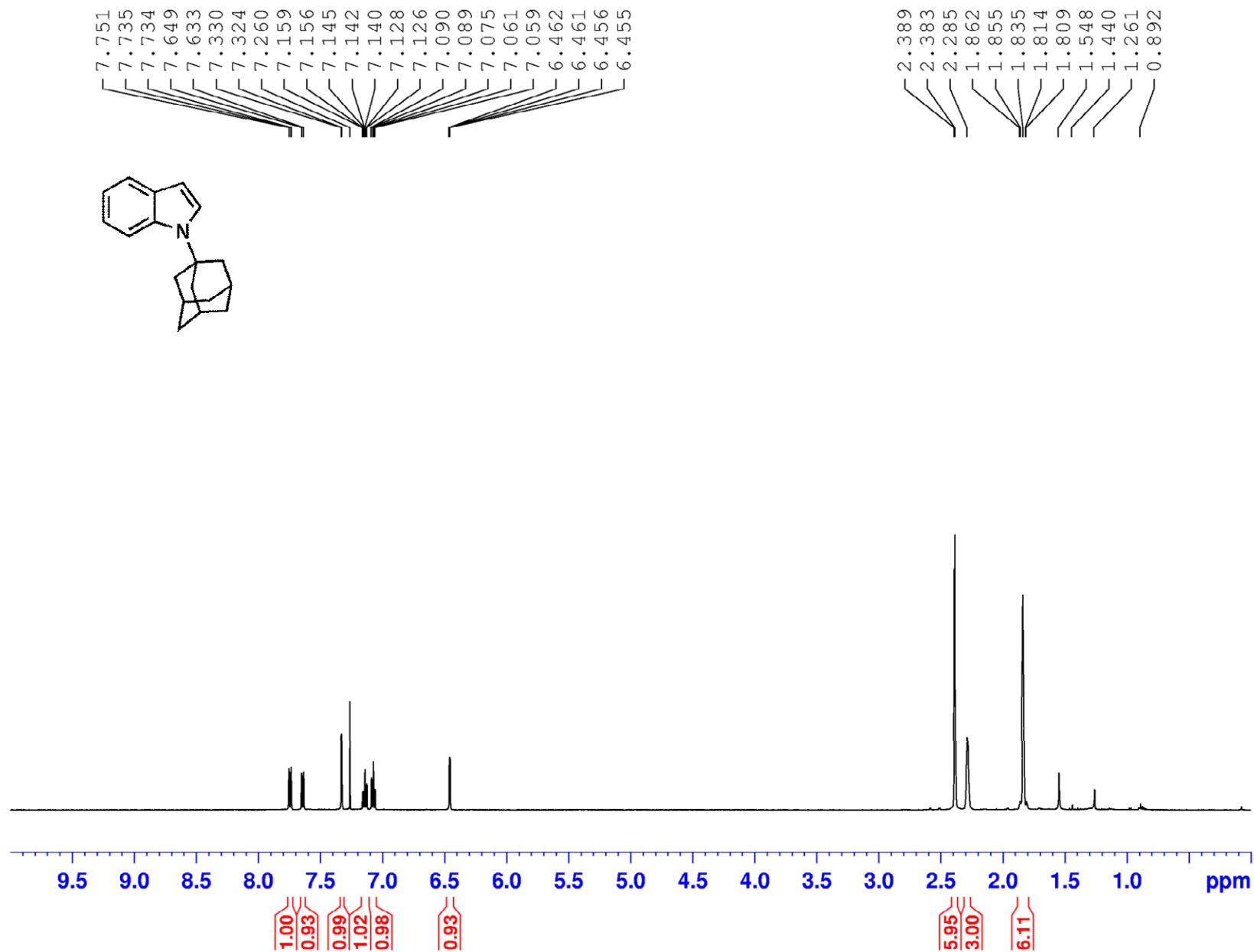
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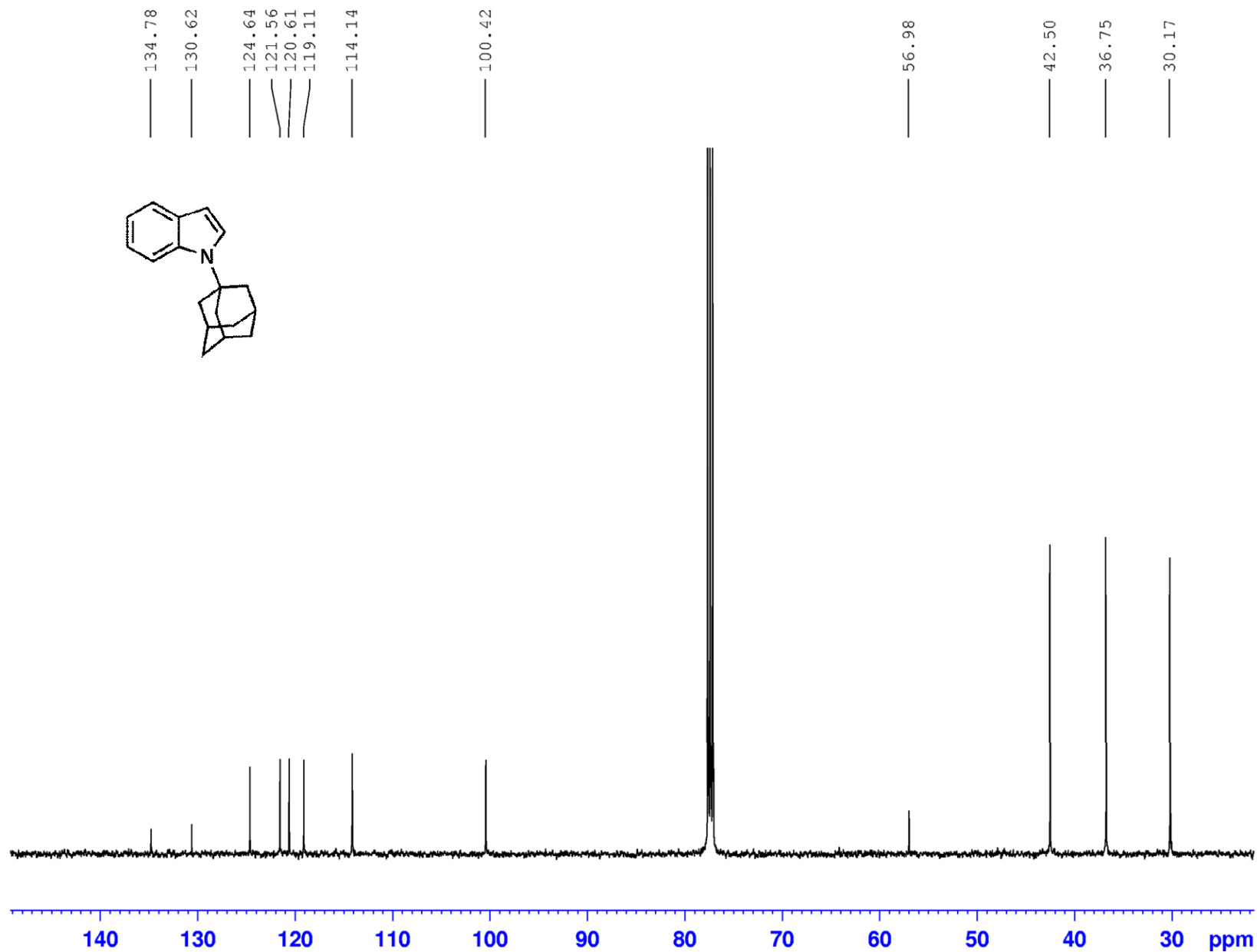
$^{13}\text{C}\{^1\text{H}\}$ NMR of **17**, 1-(2,6-Diisopropyl-phenyl)-6-fluoro-2-phenyl-1*H*-indole (CDCl_3 , 125.8 MHz, 300 K)



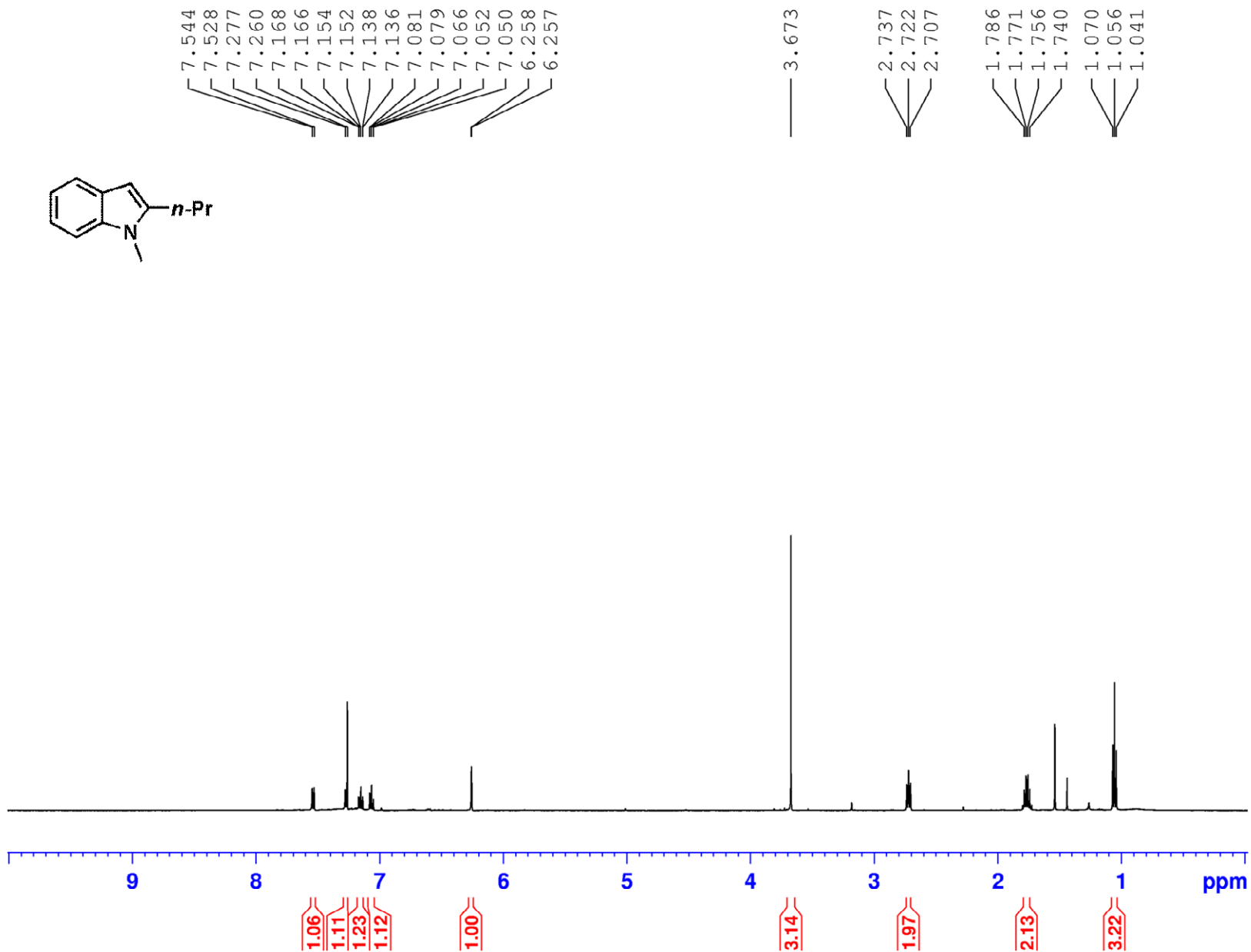
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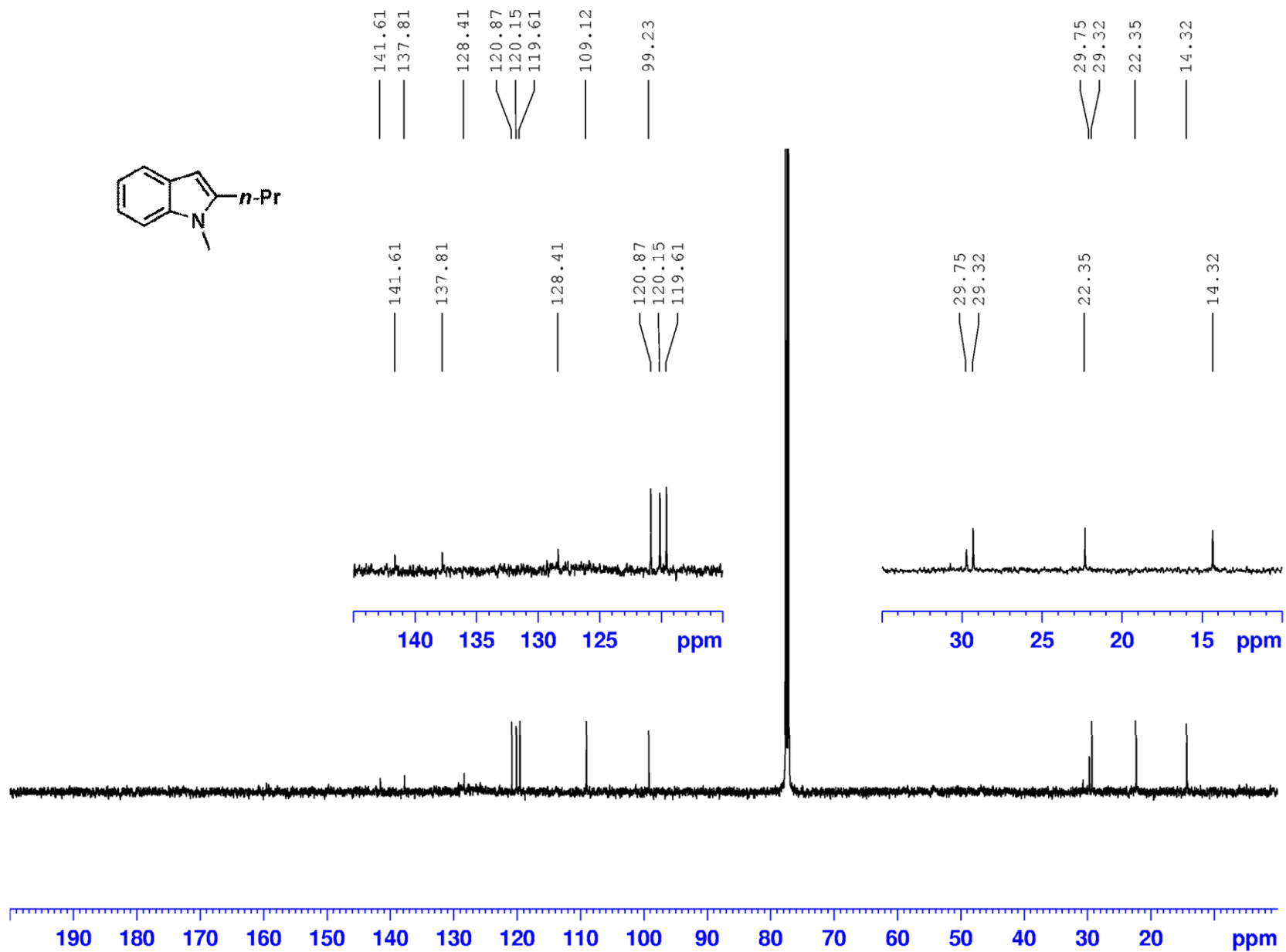
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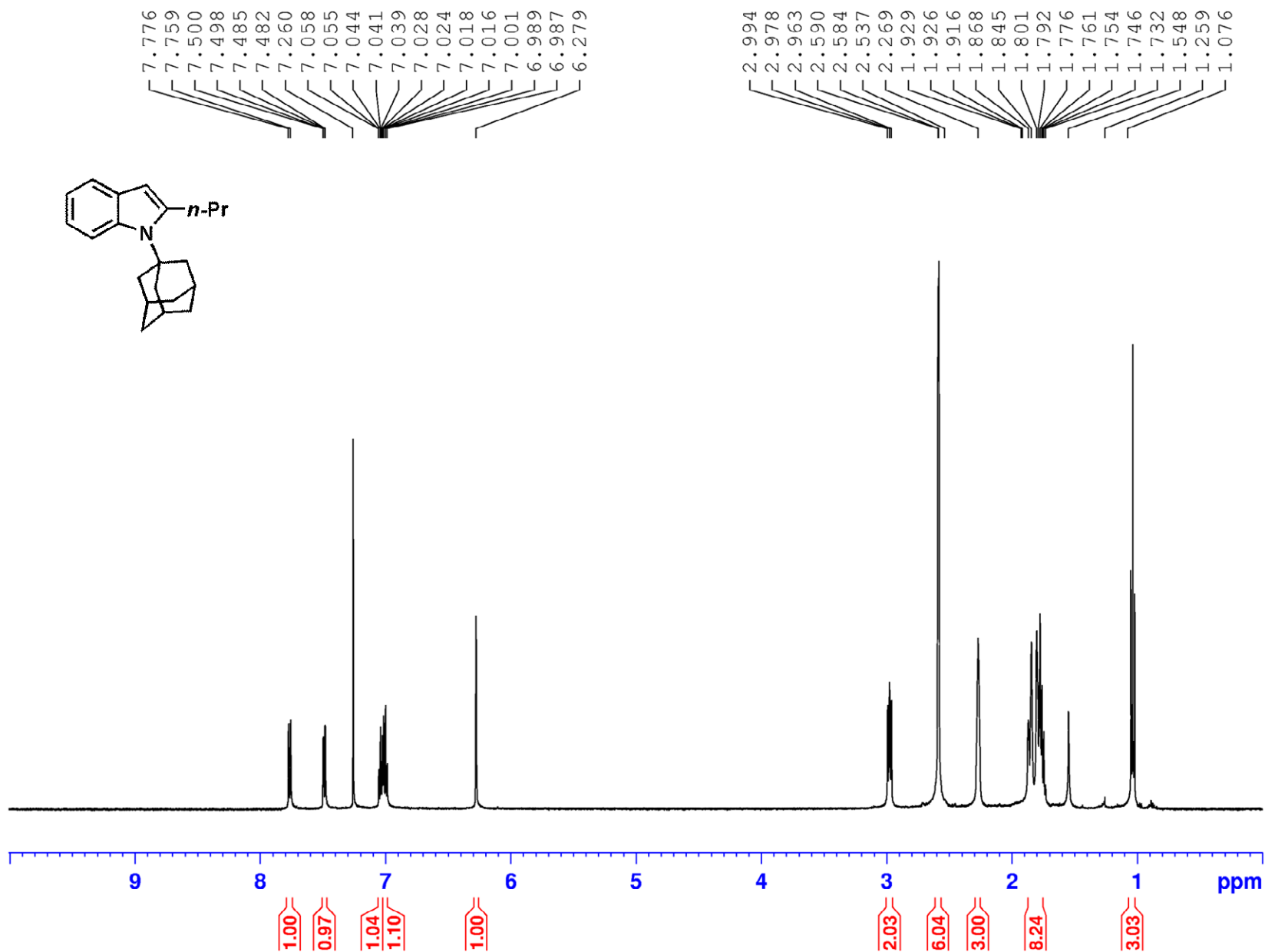
^1H NMR of **19**, 1-Methyl-2-propyl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



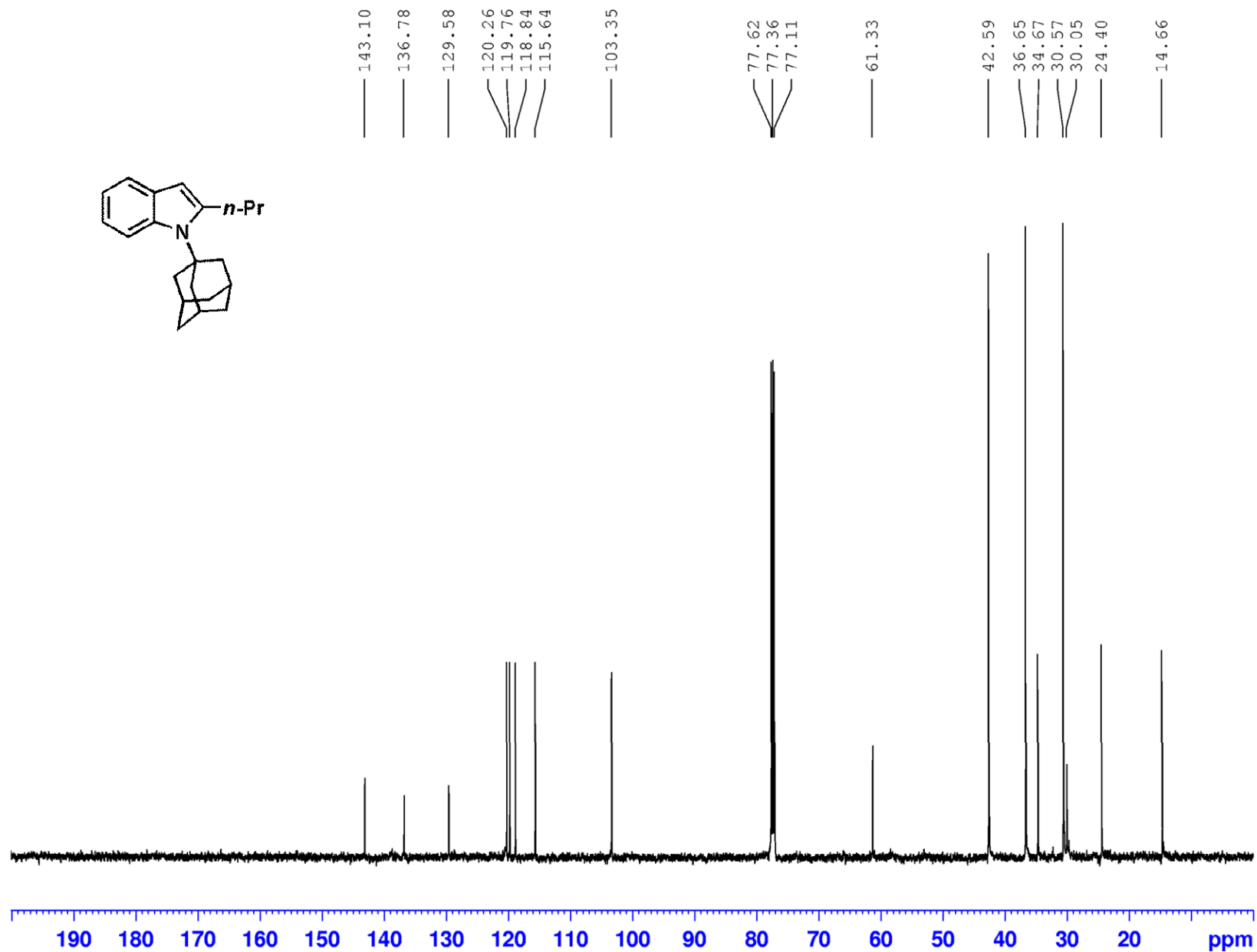
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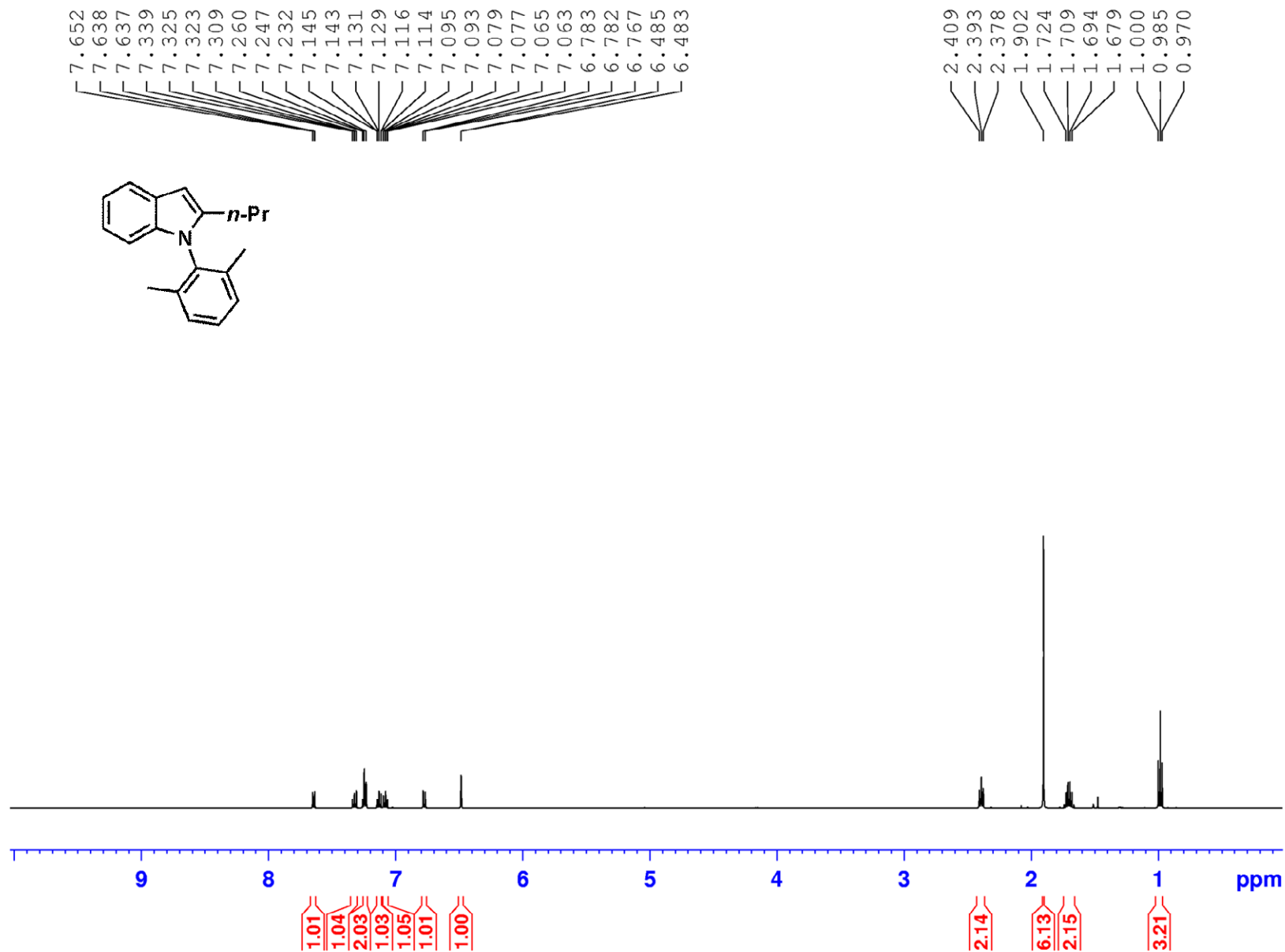
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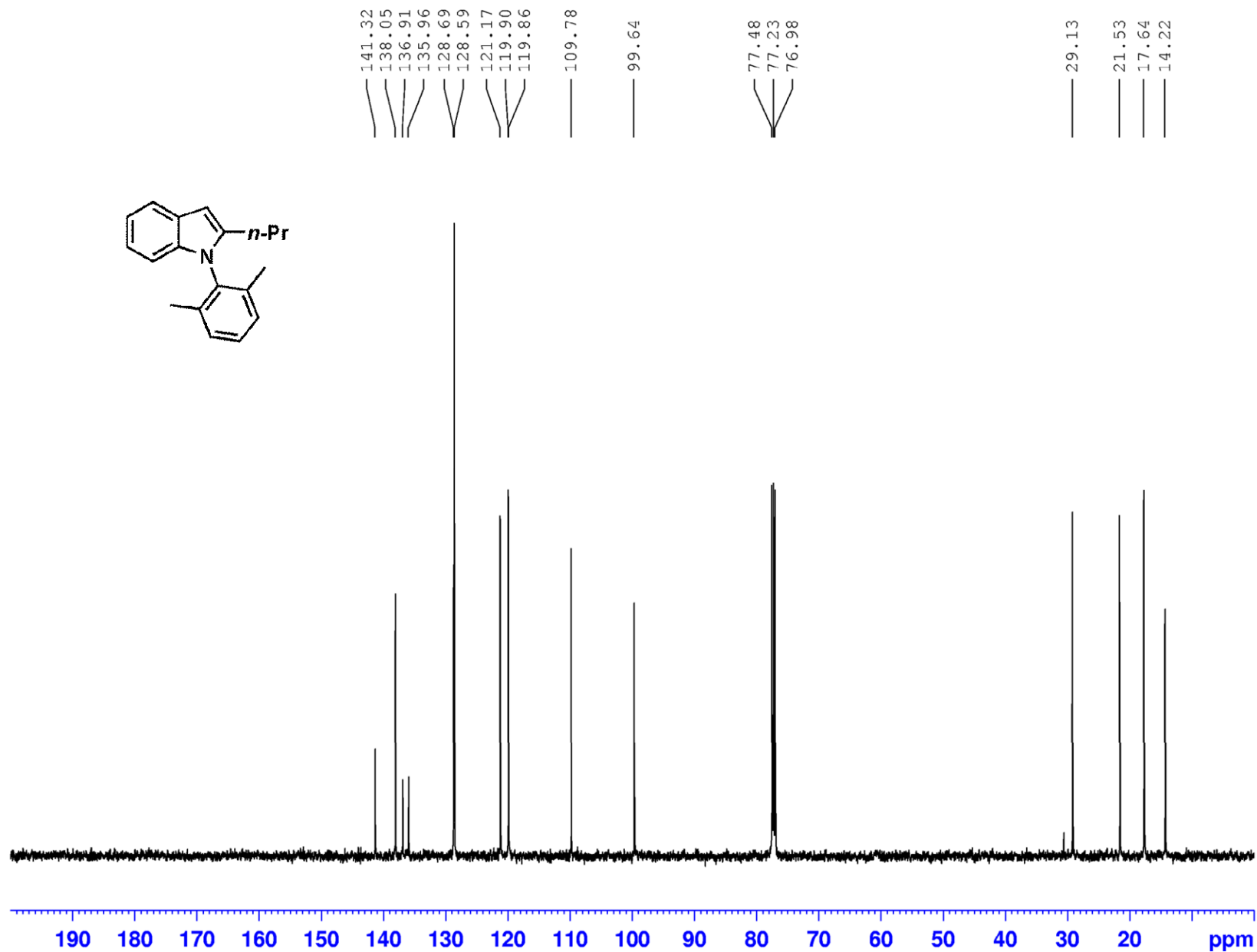
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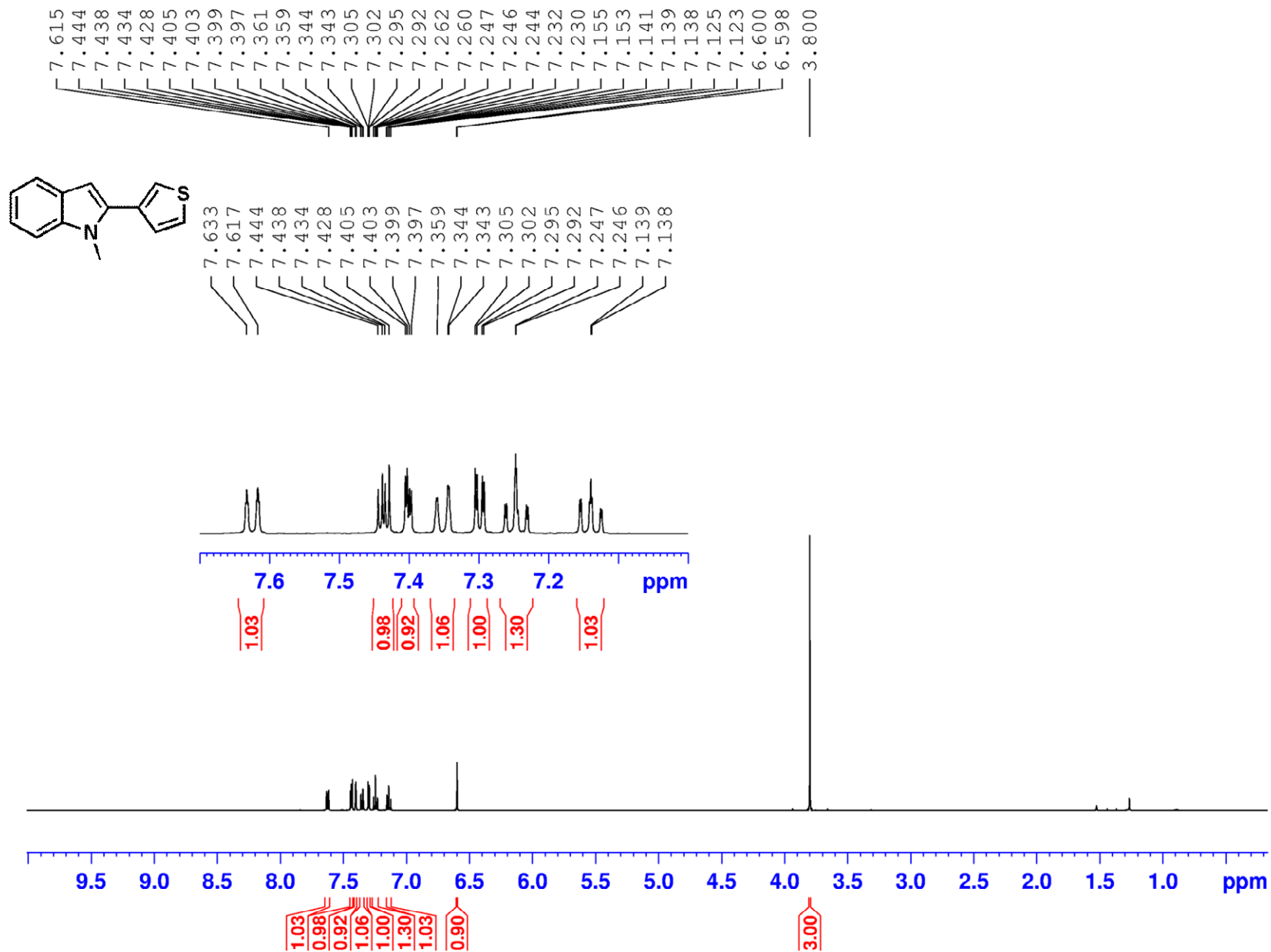
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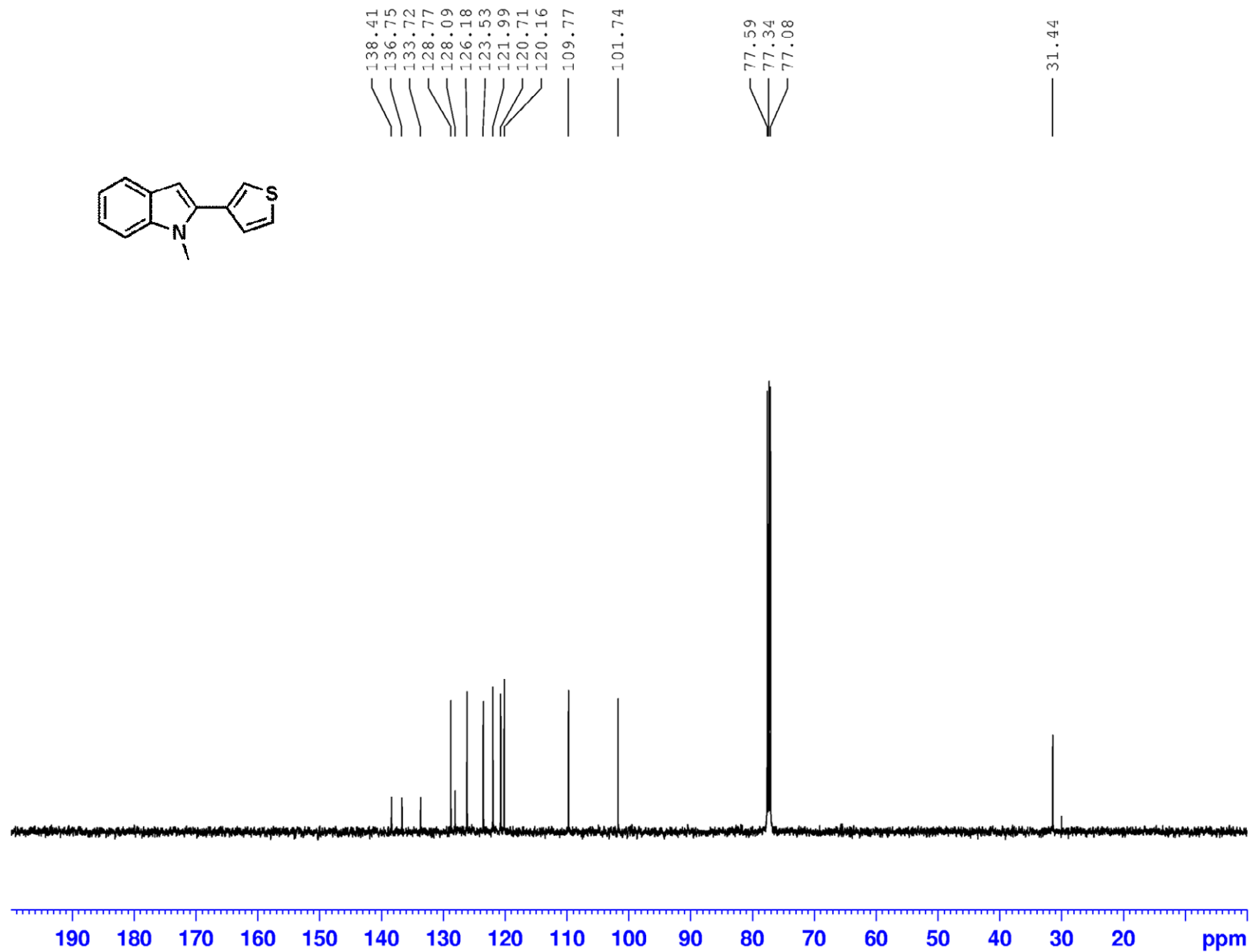
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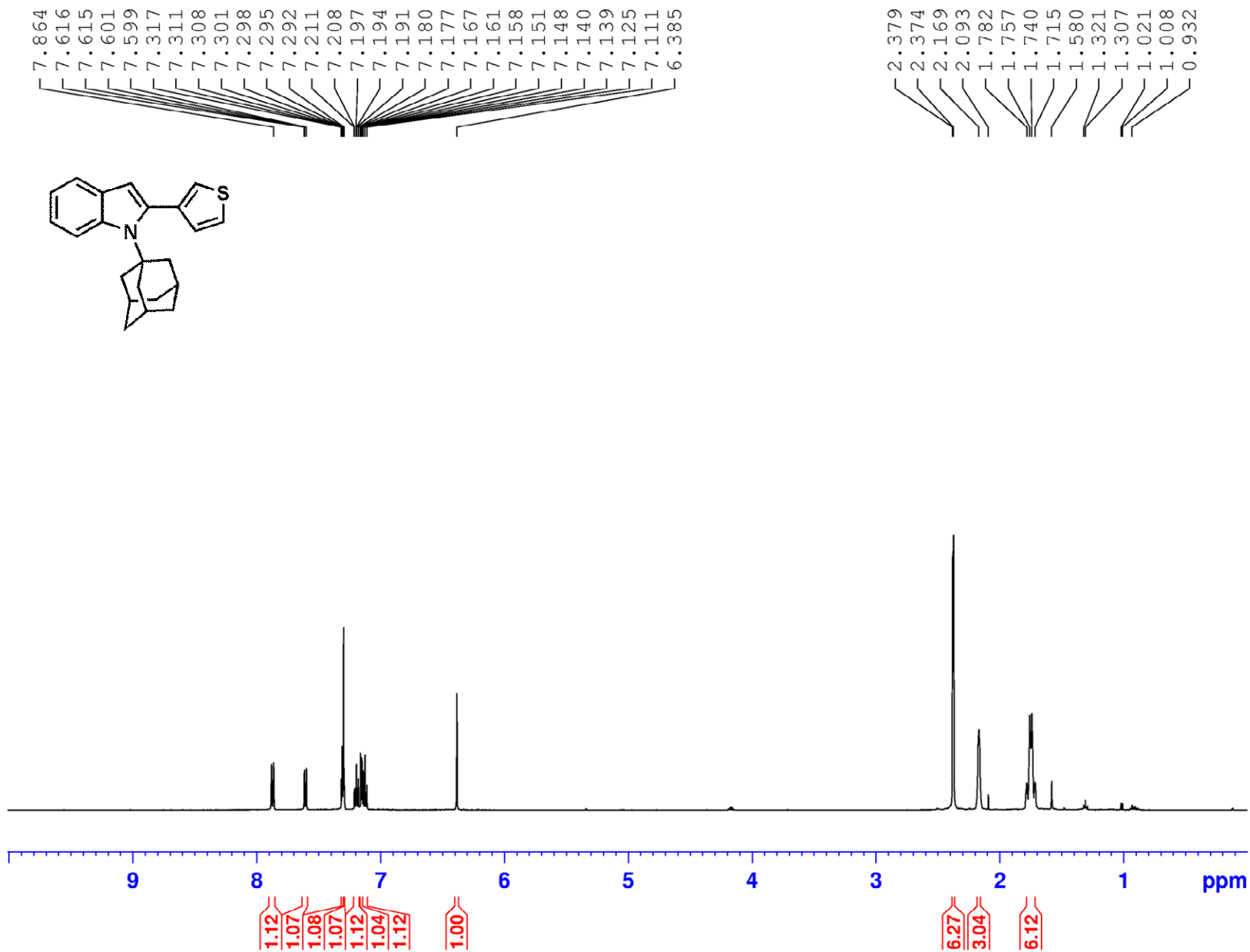
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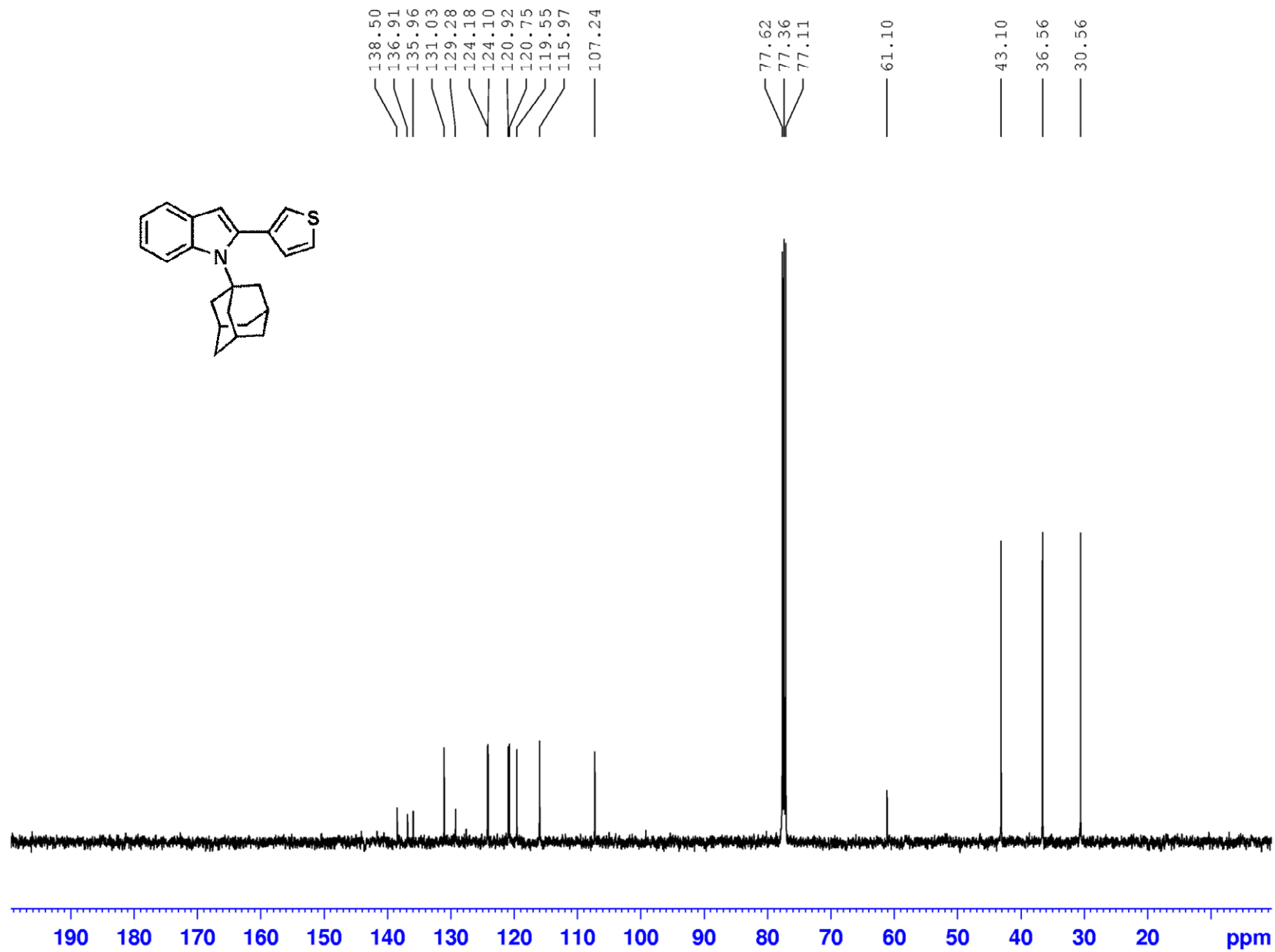
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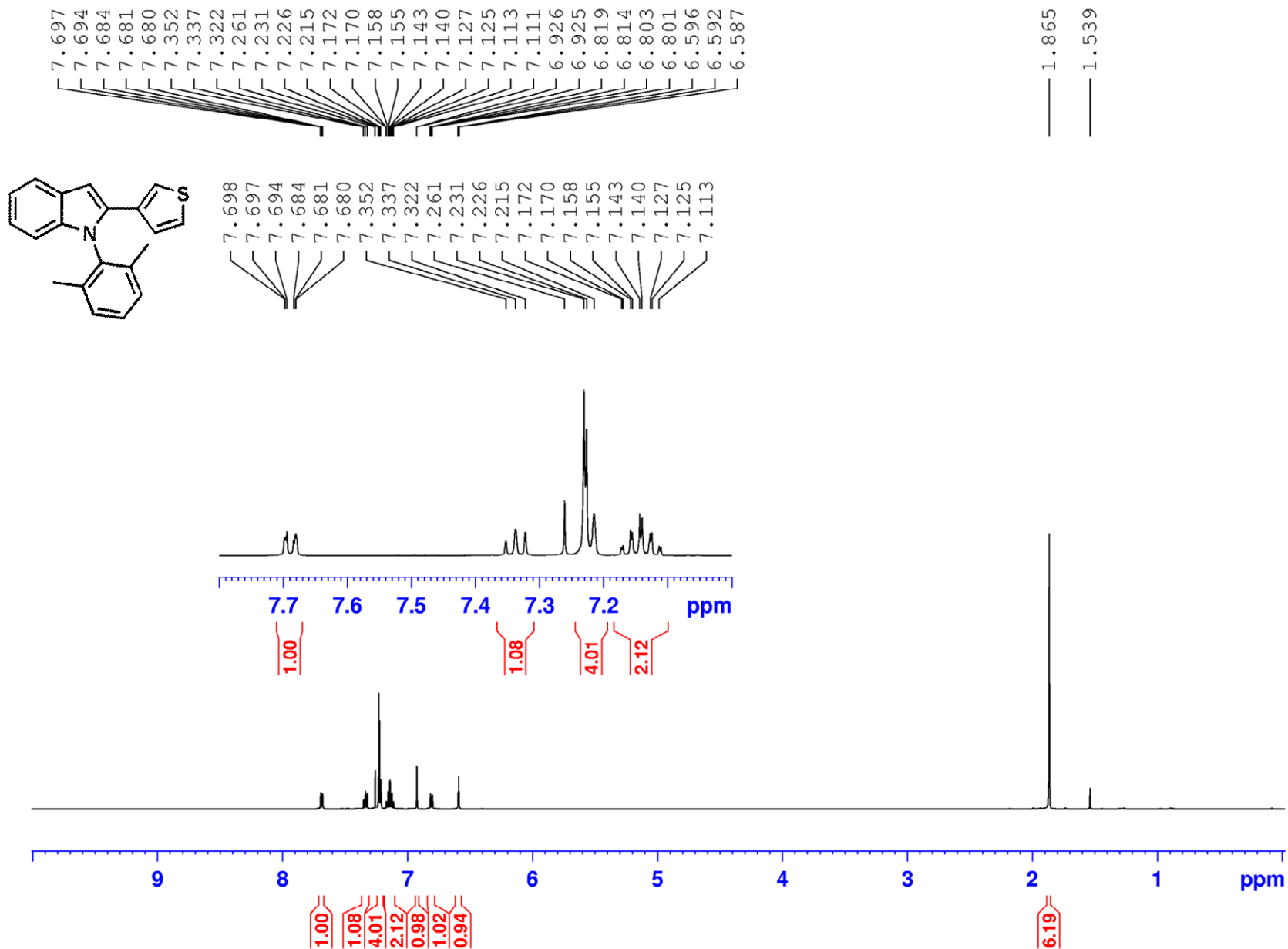
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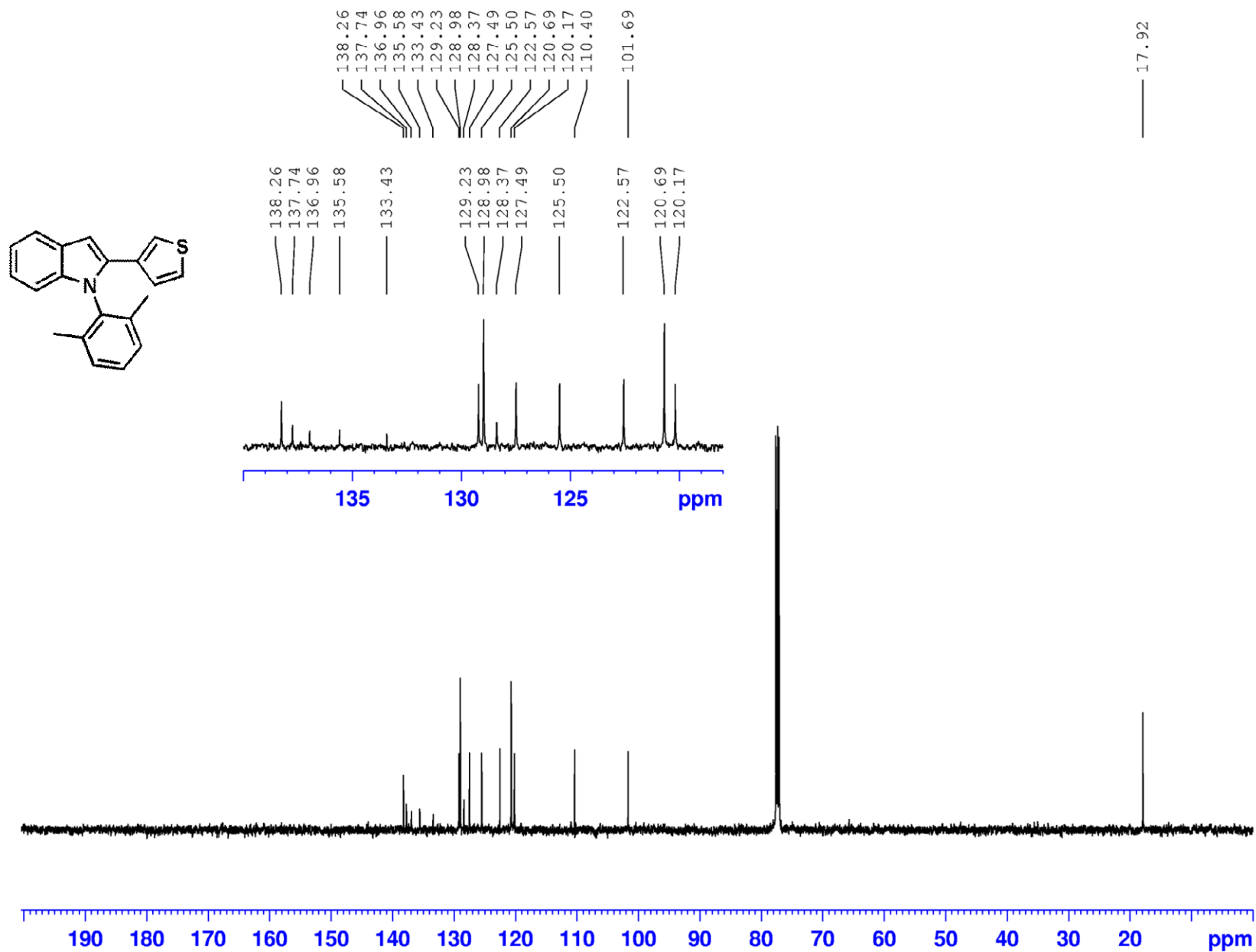
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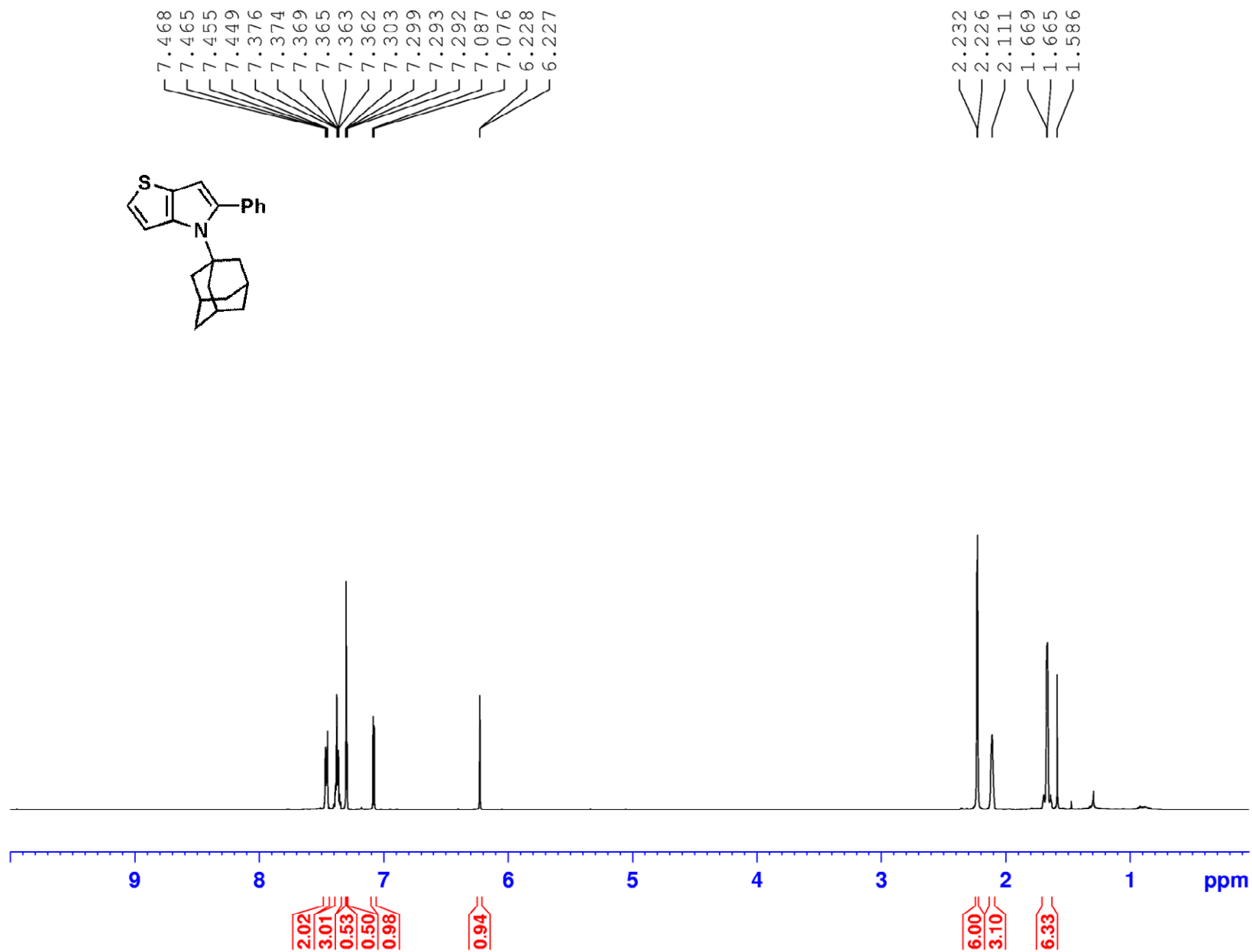
^1H NMR of **24**, 1-(2,6-Dimethyl-phenyl)-2-thiophen-3-yl-1*H*-indole (CDCl_3 , 500 MHz, 300 K)



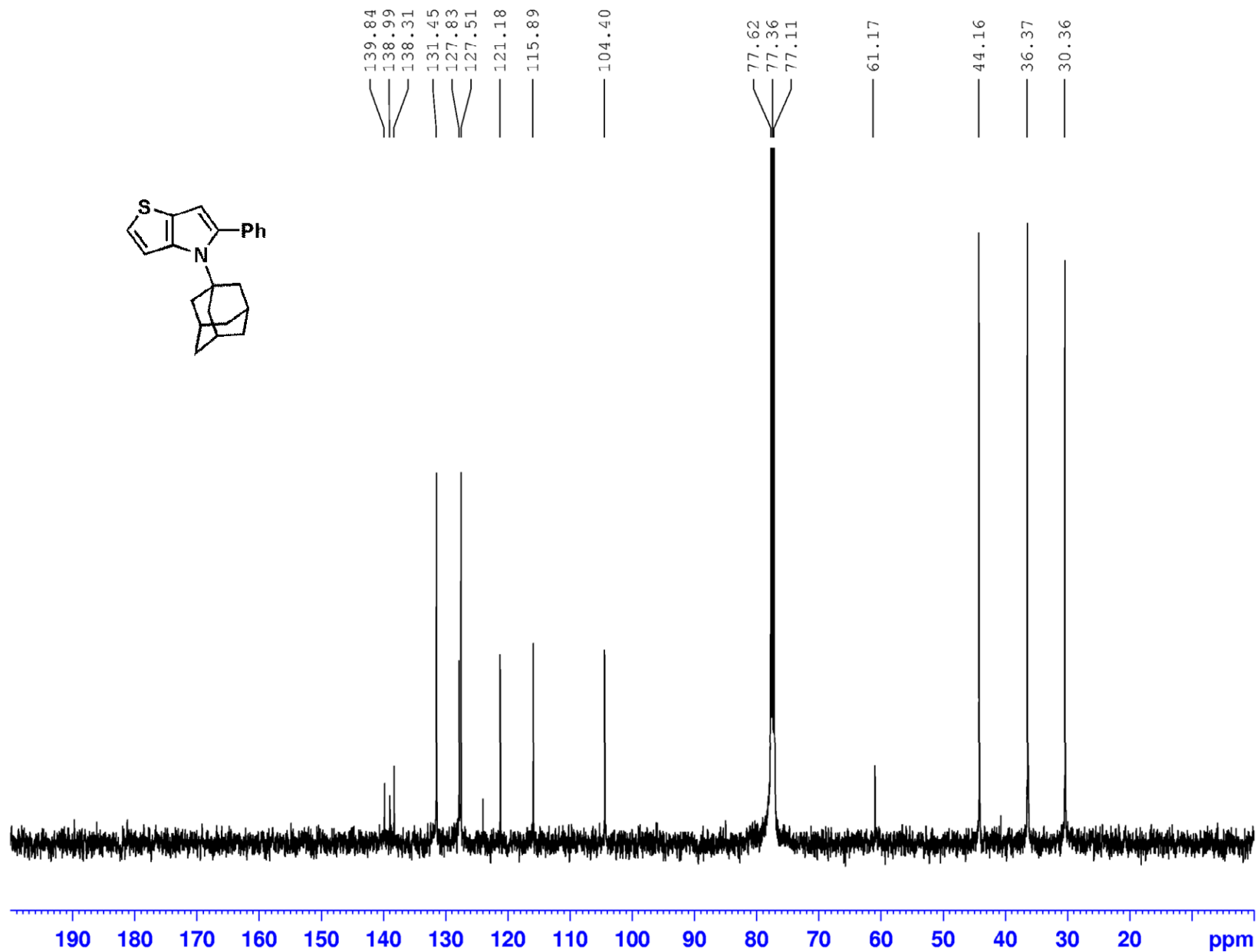
$^{13}\text{C}\{^1\text{H}\}$ NMR of **24**, 1-(2,6-Dimethyl-phenyl)-2-thiophen-3-yl-1*H*-indole (CDCl_3 , 125.8 MHz, 300 K)



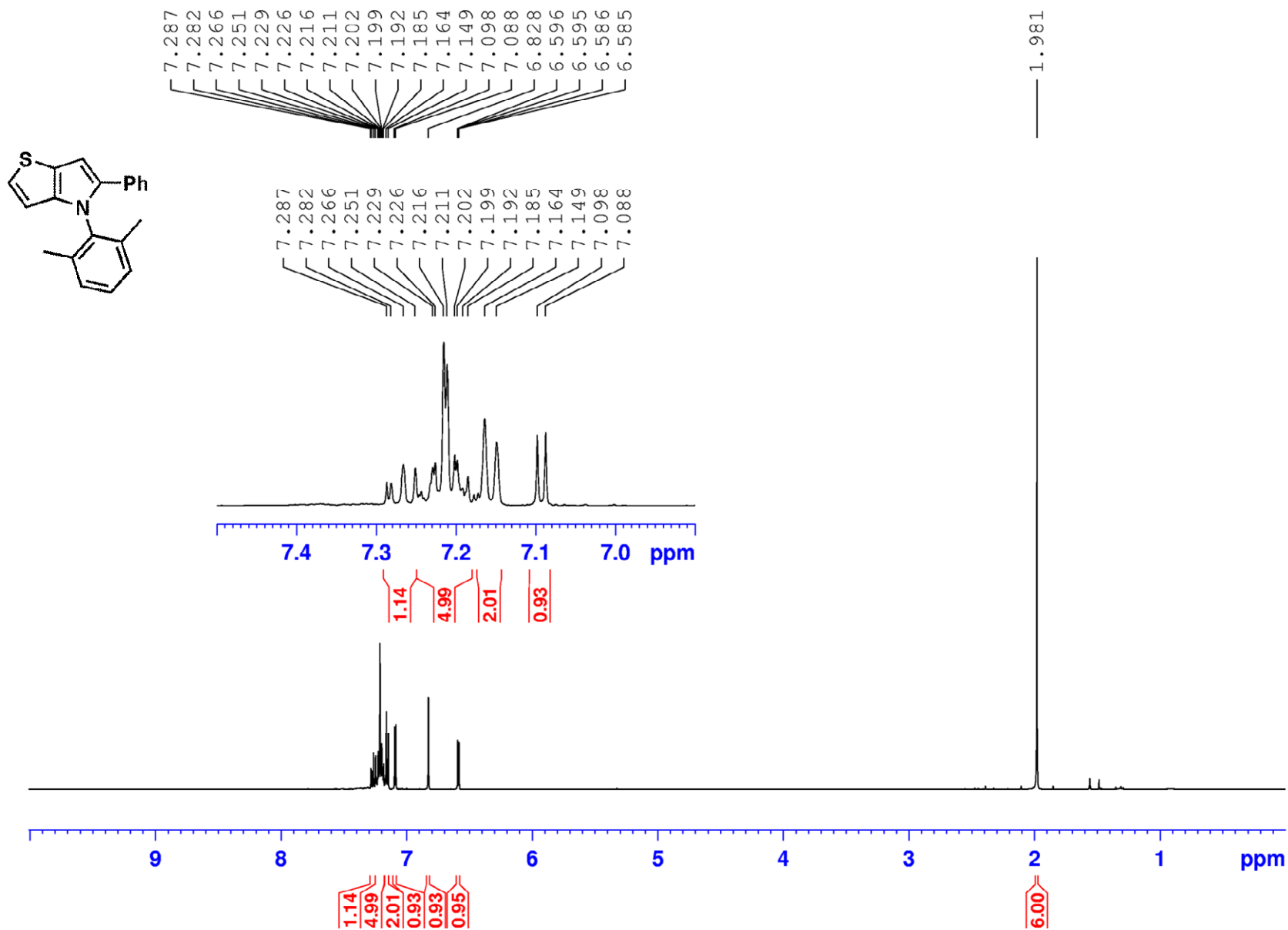
^1H NMR of **25**, 4-Adamantan-1-yl-5-phenyl-4*H*-thieno[3,2-*b*]pyrrole (CDCl_3 , 500 MHz, 300 K)



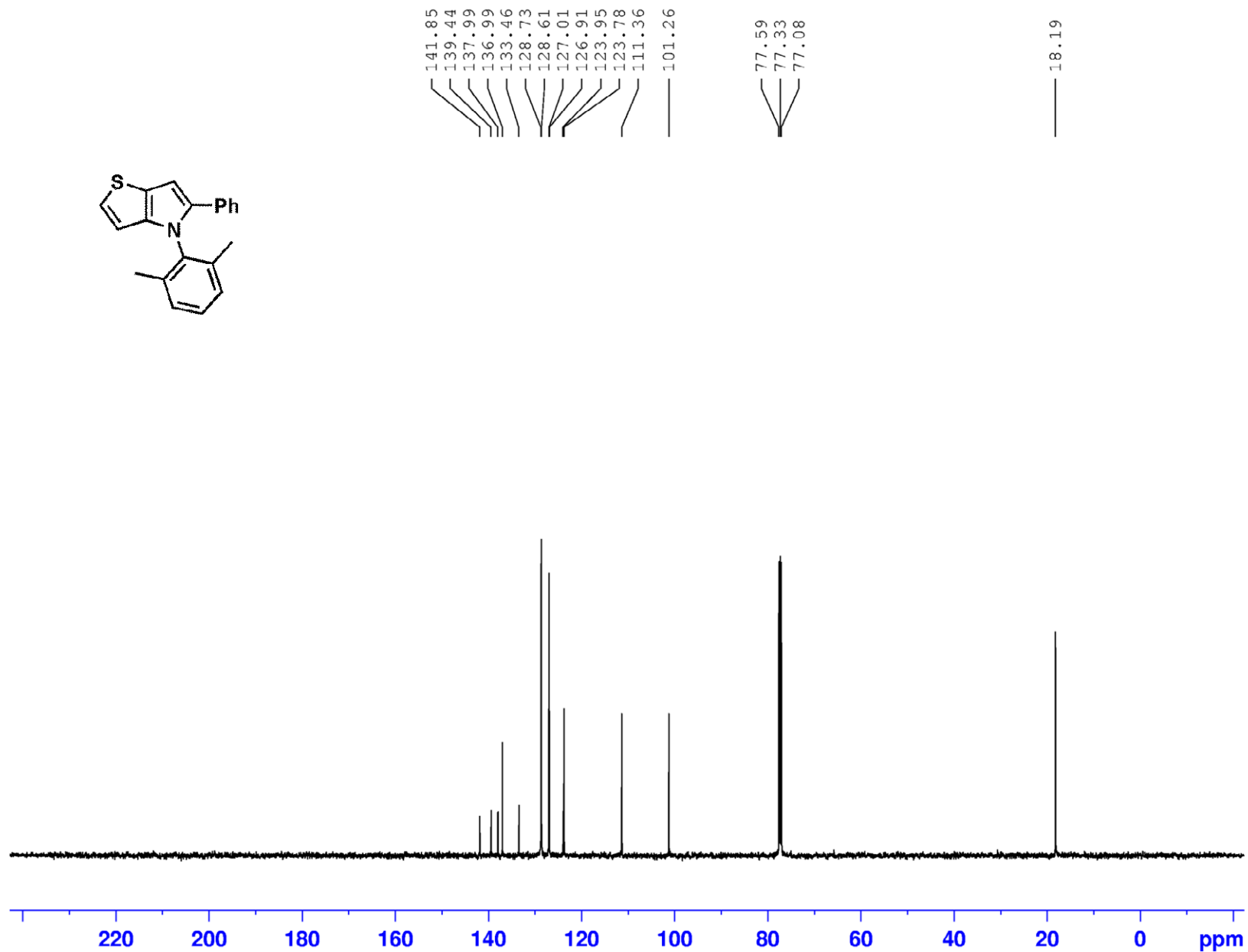
$^{13}\text{C}\{^1\text{H}\}$ NMR of **25**, 4-Adamantan-1-yl-5-phenyl-4*H*-thieno[3,2-*b*]pyrrole (CDCl₃, 125.8 MHz, 300 K)



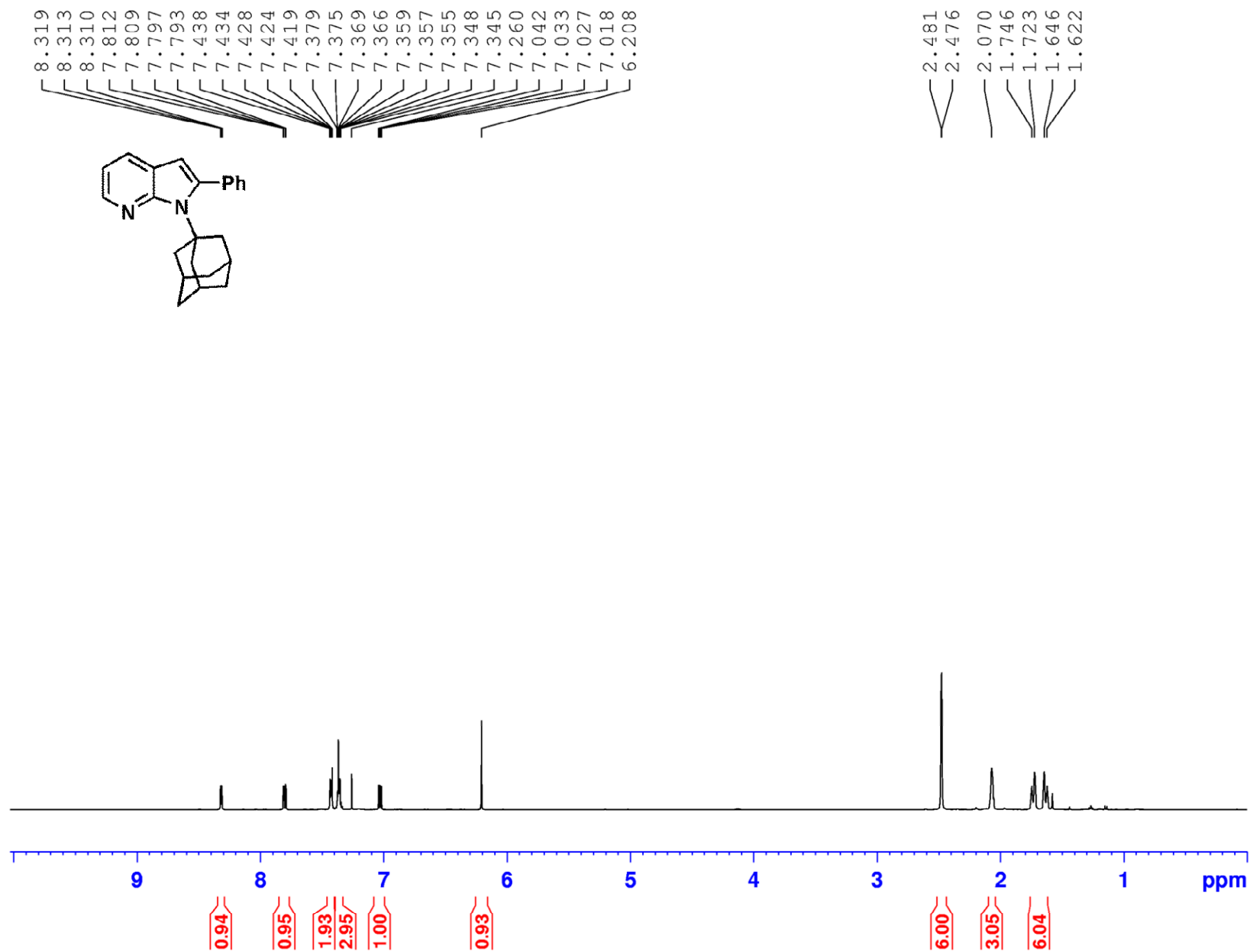
^1H NMR of **26**, 4-(2,6-Dimethyl-phenyl)-5-phenyl-4*H*-thieno[3,2-*b*]pyrrole (CDCl₃, 500 MHz, 300 K)



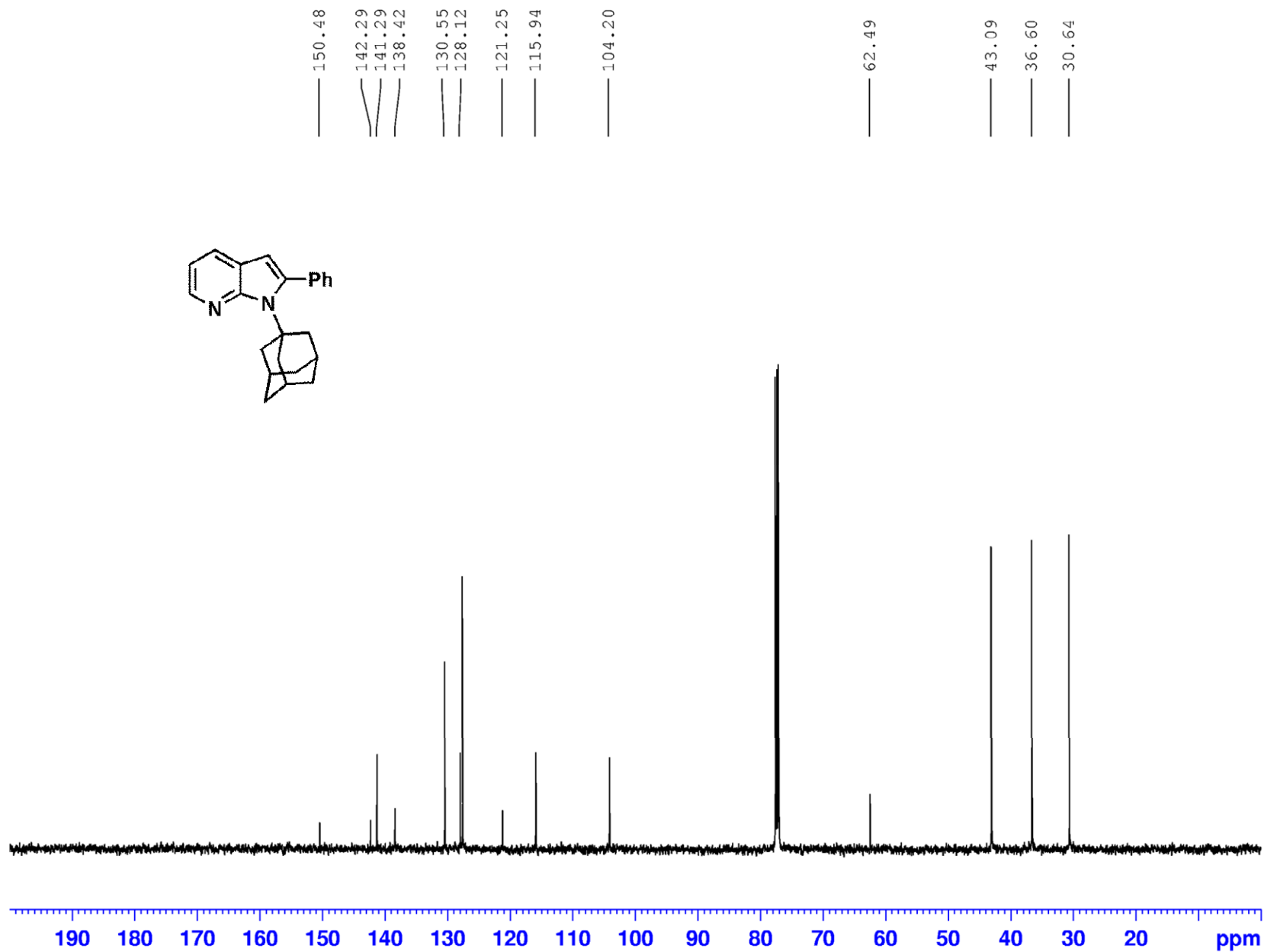
$^{13}\text{C}\{^1\text{H}\}$ NMR of **26**, 4-(2,6-Dimethyl-phenyl)-5-phenyl-4*H*-thieno[3,2-*b*]pyrrole (CDCl₃, 125.8 MHz, 300 K)



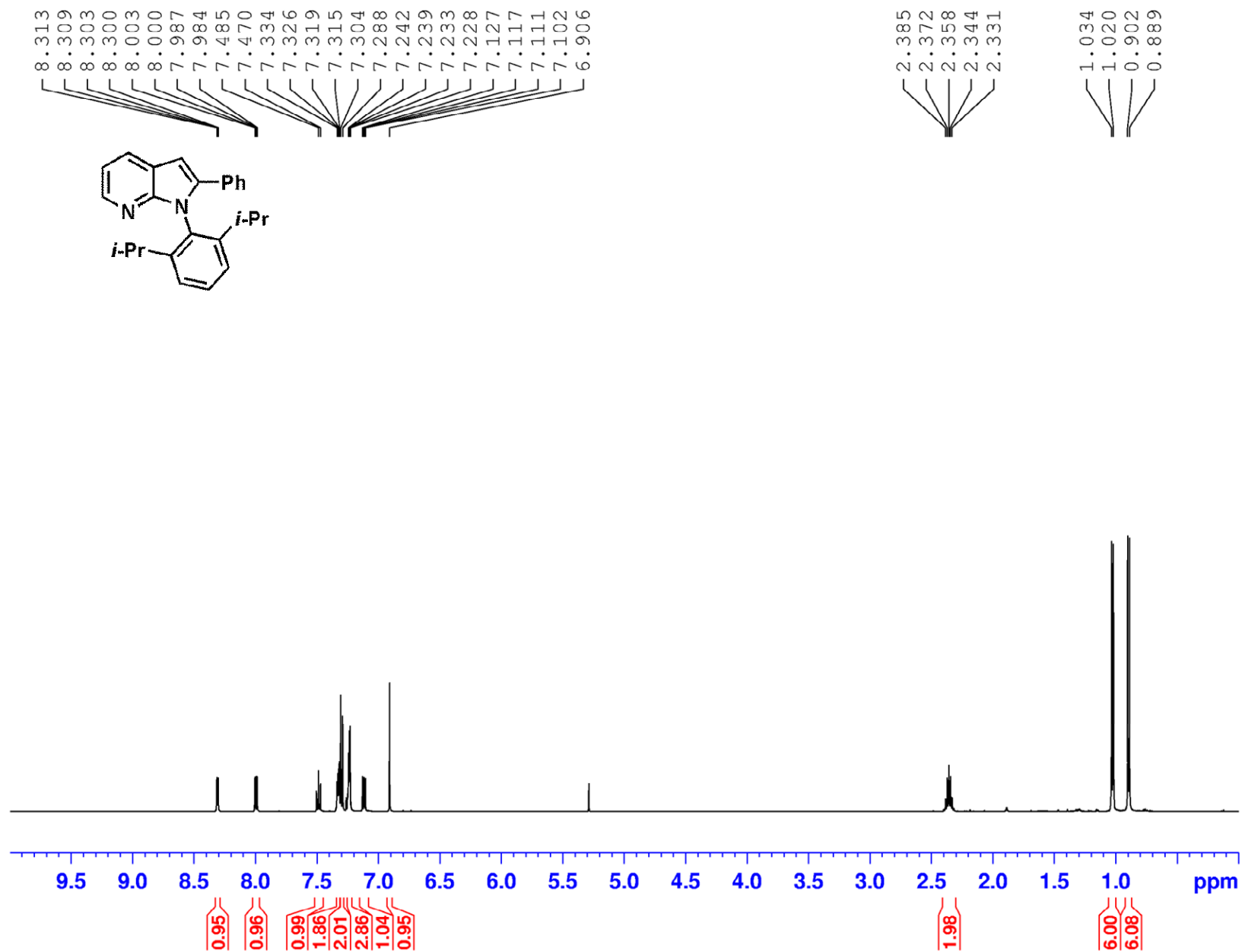
^1H NMR of **27**, 1-Adamantan-1-yl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (CDCl_3 , 500 MHz, 300 K)



$^{13}\text{C}\{^1\text{H}\}$ NMR of **27**, 1-Adamantan-1-yl-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (CDCl_3 , 125.8 MHz, 300 K)



^1H NMR of **28**, 1-(2,6-Diisopropyl-phenyl)-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (CDCl_3 , 500 MHz, 300 K)



$^{13}\text{C}\{^1\text{H}\}$ NMR of **28**, 1-(2,6-Diisopropyl-phenyl)-2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (CDCl₃, 125.8 MHz, 300 K)

