Electronic Supplementary Information

Uranyl Nitrate as a Recyclable Homogeneous Photocatalyst for Selective Cross-Coupling of *N*-Substituted Amines and Indoles

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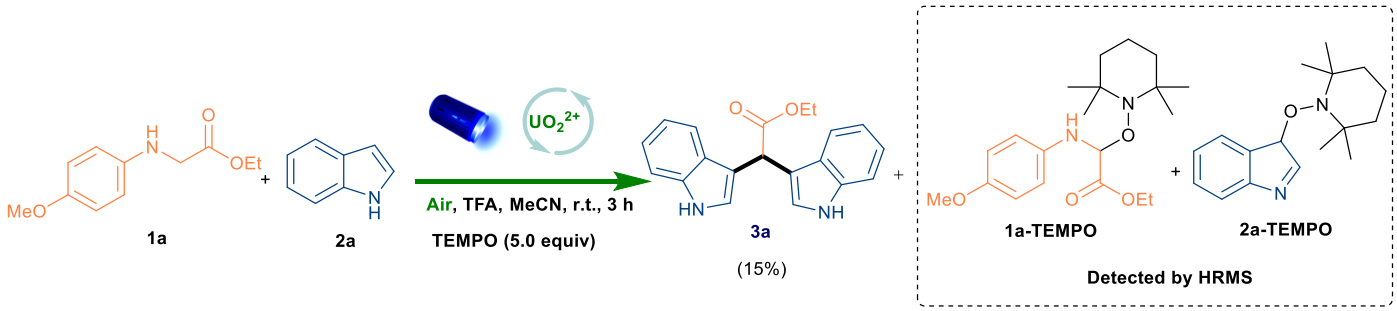
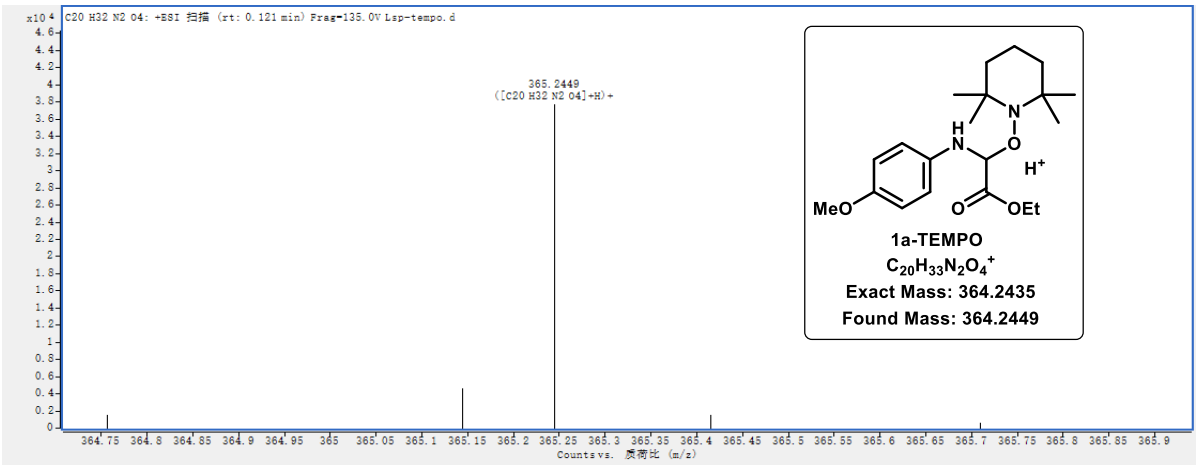
I Mechanistic Study

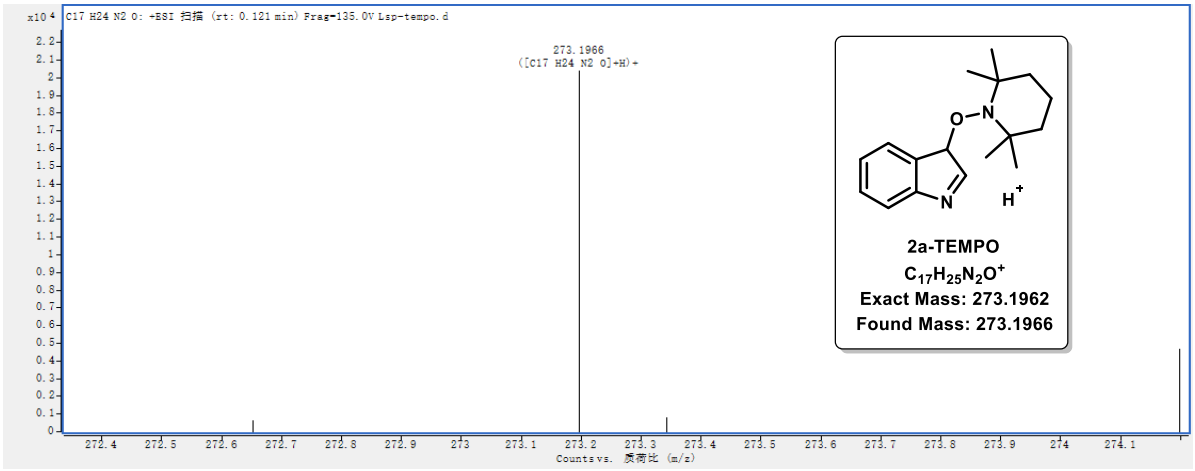
1. Radical Quenching Experiment

For the cross-coupling reaction of secondary anilines and indoles:

The reaction was conducted under standard conditions with 5 equiv 2,2,6,6-tetramethyl-1-piperinedinyloxy (TEMPO).



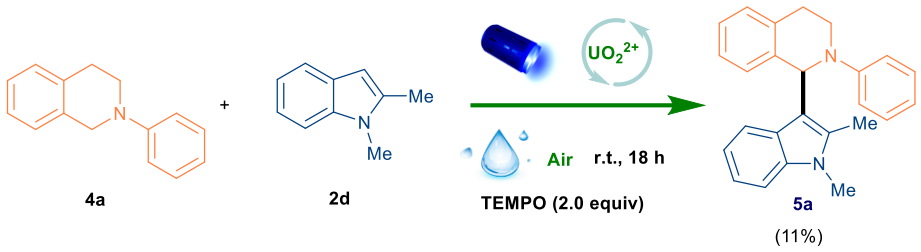




Scheme S1. Radical quenching experiment of **3a**.

For the cross-coupling reaction of tetrahydroisoquinolines and indoles:

The reaction was conducted under standard conditions with 2.0 equiv 2,2,6,6-tetramethyl-1-piperinedinyloxy (TEMPO).



Scheme S2. Radical quenching experiment of **5a**.

2. Ultraviolet-Visible Absorption Experiments

Ultraviolet-visible absorption experiments were performed using a Hitachi U-2910 spectrophotometer. In each experiment, the varying samples were combined in MeCN in screw-top 1.0 cm quartz cuvettes. The concentration of each component was 4×10^{-3} M. Uranyl cation was approved to serve as photosensor at 420 nm.

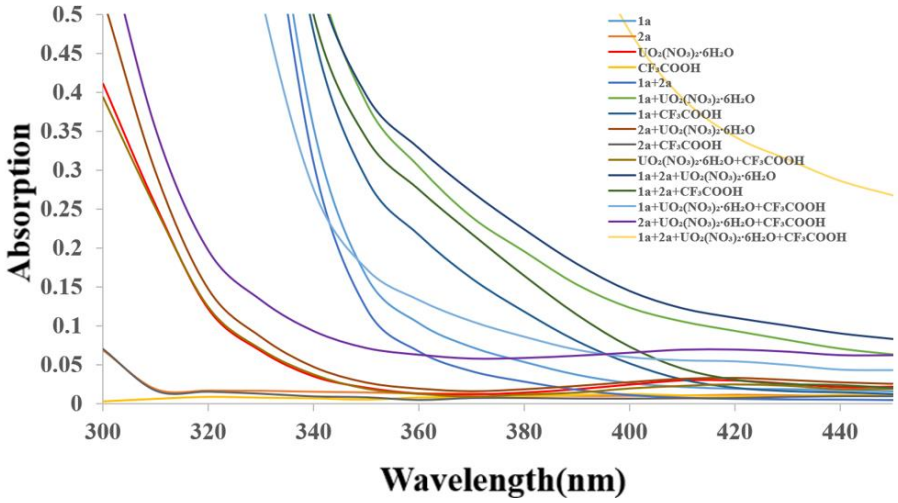


Figure S1. UV-Vis experiments of $UO_2(NO_3)_2 \cdot 6H_2O$, trifluoroacetic acid, ethyl (4-methoxyphenyl)glycinate (**1a**) and 1*H*-indole (**2a**).

Ultraviolet-visible absorption experiments were performed using a Hitachi U-2910 spectrophotometer. In each experiment, the varying samples were combined in the mixture solvent H_2O/MeCN (v/v 1:1) in

screw-top 1.0 cm quartz cuvettes. The concentration of each component was 4×10^{-3} M. Uranyl cation was approved to serve as photosensor at 416 nm.

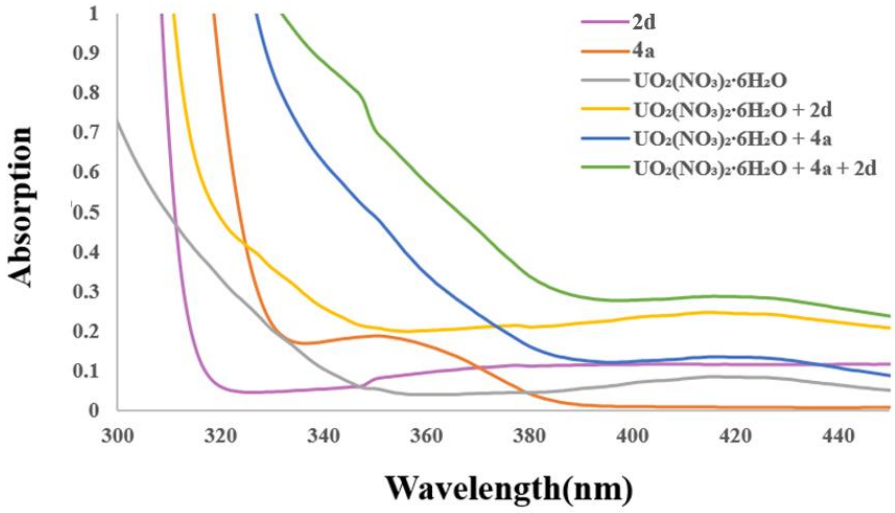


Figure S2. UV-Vis experiments of $UO_2(NO_3)_2 \cdot 6H_2O$, *N*-phenyl-tetrahydroisoquinoline (**4a**) and 1,2-dimethyl-1*H*-indole (**2d**).

3. Stern-Volmer Fluorescence Quenching Experiments with $UO_2(NO_3)_2 \cdot 6H_2O$

Fluorescence quenching studies were performed using a Hitachi F-2700 Fluorescence Spectrophotometers. In each experiment, the photoredox catalyst and varying concentrations of quencher were combined in MeCN in screw-top 1.0 cm quartz cuvettes. For the emission quenching of $UO_2(NO_3)_2 \cdot 6H_2O$, the photoredox catalyst concentration was 4×10^{-3} M and the solution was irradiated at 420 nm.

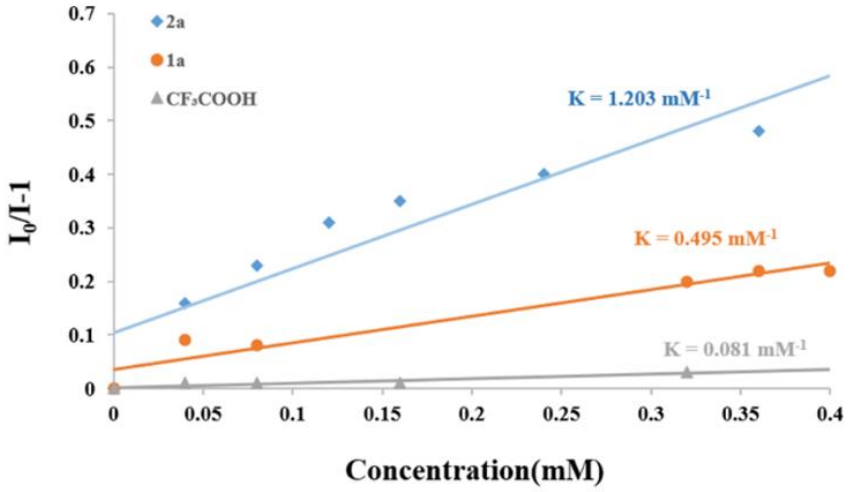


Figure S3. Stern-Volmer plots of fluorescence quenching experiments.

Fluorescence quenching studies were performed using a Hitachi F-2700 Fluorescence Spectrophotometers. In each experiment, the photoredox catalyst and varying concentrations of quencher were combined in the mixture solvent H_2O/MeCN (v/v 1:1) in screw-top 1.0 cm quartz cuvettes. For the emission quenching of $UO_2(NO_3)_2 \cdot 6H_2O$, the photocatalyst concentration was 4×10^{-3} M and the solution was irradiated at 416 nm.

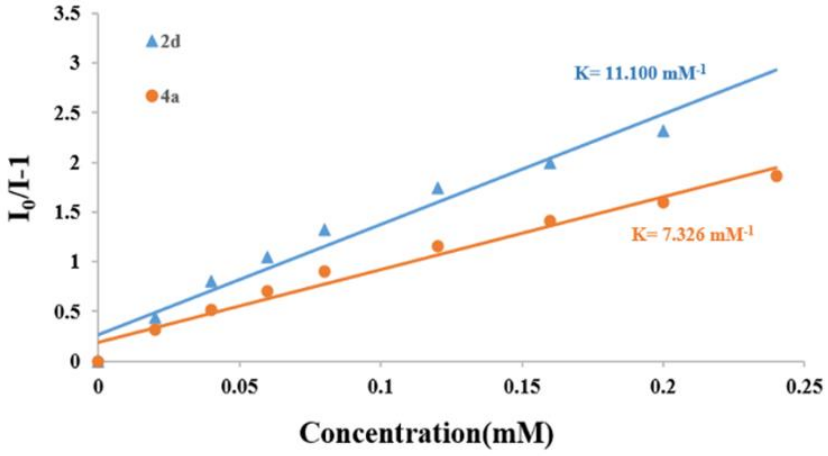
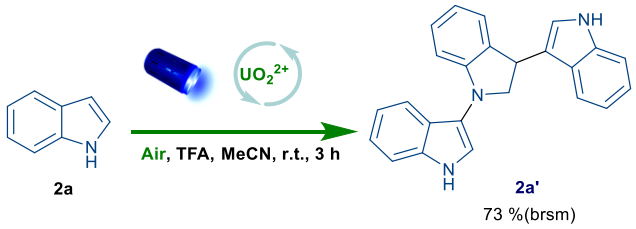


Figure S4. Stern-Volmer plots of fluorescence quenching experiments.

4. Control Experiments

Homo-Coupling Reaction of 1*H*-indole (2a)

To a stirring solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (1.0 mg, 0.002 mmol) in 1.0 mL MeCN were added trifluoroacetic acid (11.4 mg, 0.1 mmol) and 1*H*-indole **2a** (12.3 mg, 0.105mmol). The solution was irradiated by blue LEDs (456 nm 40W) with cooling fan to keep the reaction temperature near 25 °C under air for 3 h. The mixture was concentrated in vacuo. Dichloromethane (2.0 mL) and water (1.0 mL) were then added. The mixture was extracted with dichloromethane (2.0 mL). The combined organic phases were purified by column chromatography on silica gel to give the desired product dimer product **2a′** (2.4 mg, 73% (brsm)). **2a′**: ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.92 (s, 2 H), 7.48–7.46 (m, 2 H), 7.33–7.31 (m, 2 H), 7.15–7.11 (m, 2 H), 7.02–7.01 (m, 2 H), 6.99–6.94 (m, 4 H), 6.64-6.61 (m, 1 H), 6.57–6.55 (m, 1 H), 4.93–4.71 (m, 1 H), 3.43 (d, *J* = 7.4 Hz, 2 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 136.72, 130.49, 127.07, 126.99, 122.00, 121.95, 119.80, 119.78, 119.29, 115.85, 111.17, 37.23, 34.63; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{20}N_3^+$ 350.1652, found 350.1657.

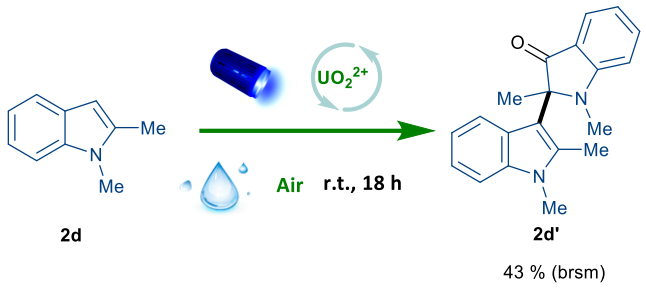


Scheme S3. Homo-coupling reaction of 1*H*-indole.

Homo-Coupling Reaction of 1,2-Dimethyl-1*H*-indole (2d)

To a stirring solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (2.0 mg, 0.004 mmol) in 1.0 mL H_2O was added 1,2-dimethyl-1*H*-indole **2d** (7.3 mg, 0.05 mmol). The solution was irradiated by blue LEDs (456 nm 40W) with cooling fan to keep the reaction temperature near 25 °C for 18 h. The mixture was extracted with EtOAc (3 × 2.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give the desired product dimer product **2d′** (2.2 mg, 43% (brsm)). **2d′**: ^{1}H NMR (500 MHz, Dimethyl sulfoxide-d_6): δ = 7.60–7.57 (m, 1 H), 7.52–7.48 (m, 1 H), 7.42–7.36 (m, 1 H), 7.18 (d, *J* = 8.1 Hz, 1 H), 7.06–7.02 (m, 1 H), 6.99 (d, *J* =

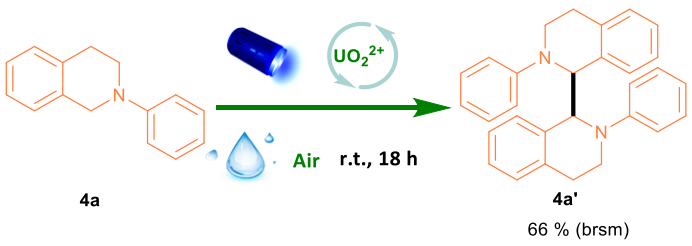
8.4 Hz, 1 H), 6.87–6.83 (m, 1 H), 6.76–6.73 (m, 1 H), 3.65 (s, 3 H), 2.81 (s, 3 H), 2.29 (s, 3 H), 1.75 (s, 3 H); ^{13}C NMR (126 MHz, Dimethyl sulfoxide-d_6): δ = 202.6, 158.7, 137.9, 136.2, 135.9, 126.5, 124.4, 120.3, 119.1, 118.8, 117.5, 116.6, 109.5, 108.8, 106.0, 70.4, 29.3, 27.6, 21.6, 11.4; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{20}H_{20}N_2O^+$ 305.1648, found 305.1656.



Scheme S4. Homo-coupling reaction of 1,2-dimethyl-1*H*-indole.

Homo-Coupling Reaction of *N*-Phenyl-tetrahydroisoquinoline (4a)

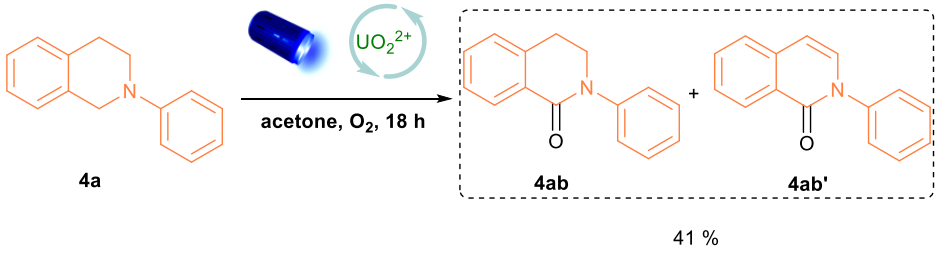
To a stirring solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (2.0 mg, 0.004 mmol) in 1.0 mL H_2O was added *N*-phenyl-tetrahydroisoquinoline **4a** (20.9 mg, 0.1 mmol). The solution was irradiated by blue LEDs (456 nm) with cooling fan to keep the reaction temperature near 25 °C for 18 h. The mixture was extracted with EtOAc (3 × 2.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give the desired product dimer product **4a′** (8.6 mg, 66% (brsm)). **4a′**: ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.30–7.28 (m, 1 H), 7.22–7.15 (m, 5 H), 7.10–7.02 (m, 4 H), 6.98–6.96 (m, 3 H), 6.88–6.84 (m, 3 H), 6.78–6.71 (m, 2 H), 5.33 (d, *J* = 13.5 Hz, 2 H), 3.58–3.19 (m, 4 H), 2.91–2.50 (m, 4 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 149.76, 149.65, 136.68, 136.16, 135.80, 129.57, 129.42, 129.40, 128.30, 127.82, 127.77, 127.28, 127.13, 125.90, 125.52, 117.40, 117.24, 113.98, 113.02, 64.55, 63.28, 44.37, 43.13, 27.45, 27.30; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{30}H_{29}N_2^+$ 417.2325, found 417.2326.



Scheme S5. Homo-coupling reaction of *N*-phenyltetrahydroisoquinoline.

Reaction of *N*-Phenyl-tetrahydroisoquinoline (4a) with excess O_2

To a stirring solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (2.0 mg, 0.004 mmol) in 1.0 mL acetone was added *N*-phenyl-tetrahydroisoquinoline **4a** (20.9 mg, 0.1 mmol). The solution was irradiated by blue LEDs (456 nm) with cooling fan to keep the reaction temperature near 25 °C for 18 h in an atmosphere of O_2. The mixture was extracted with EtOAc (3 × 2.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give the mixed products **4ab** and **4ab′** (9.1 mg, 41%). **4ab**: ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.17 (d, J = 7.8 Hz,1H), 7.46-7.48 (m, 1H), 7.37–7.46 (m, 5H), 7.24–7.27 (m, 2H), 3.99–4.01(m, 2H), 3.14–3.16 (m, 2H) ; ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 164.3, 143.3, 138.4, 132.2, 129.9, 129.0, 128.9, 127.3, 127.1, 126.4, 125.5, 49.5, 28.8; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{14}NO^+$ 224.1070, found 224.1076. **4ab′**: ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.49–8.47 (m, 1H), 7.70–7.67 (m, 1H), 7.57–7.54 (m, 1H), 7.54–7.48 (m, 3H), 7.46–7.39 (m, 3H), 7.19 (d, J = 7.4 Hz, 1H), 6.57 (d, J = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 162.1, 141.4, 137.1, 132.6, 132.2, 129.3, 128.3, 128.1, 127.2, 126.9, 126.6, 126.0, 106.2; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{15}H_{11}NNaO^+$ 244.0733, found 244.0736.



Scheme S6. Reaction of *N*-Phenyl-tetrahydroisoquinoline with excess O_2

II Experimental Procedures and Spectroscopic Data of Compounds

1. General Information

Acetonitrile was purchased in anhydrous form and used without further purification. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Adamas-beta®. Reactions were monitored by thin layer chromatography (TLC) carried out on Millipore Sigma glass TLC plates (silica gel 60 coated with F_{254}, 250 μm) using UV light for visualization and aqueous ammonium cerium nitrate/ammonium molybdate or basic aqueous potassium permanganate as developing agent. SiliaFlash® P60 silica gel (particle size: 40–63 μm, pore size: 60 Å) was used for flash column chromatography. NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer. The spectra were calibrated by using residual undeuterated solvents (for ^{1}H NMR) and deuterated solvents (for ^{13}C NMR) as internal references: undeuterated chloroform (δ_H = 7.26 ppm) and $CDCl_3$ (δ_C = 77.16 ppm); undeuterated DMSO (δ_H = 2.50 ppm) and DMSO-d_6 (δ_C = 39.52 ppm); undeuterated methanol (δ_H = 3.31 ppm) and methanol-d_4 (δ_C = 49.00 ppm). The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quint = quintet, br = broad. Melting points (m.p.) are uncorrected and were recorded on an SGW X-4 apparatus. High-resolution mass spectra (HRMS) were recorded on an Agilent MSD-Trap-XCT or Q-Tof micro mass spectrometer. Ultraviolet-visible absorption experiments were performed using a Hitachi U-2910 spectrophotometer. Fluorescence quenching studies were performed using a Hitachi F-2700 Fluorescence Spectrophotometers.

2. Typical Procedure for the Preparation of 4-Methoxyanilines

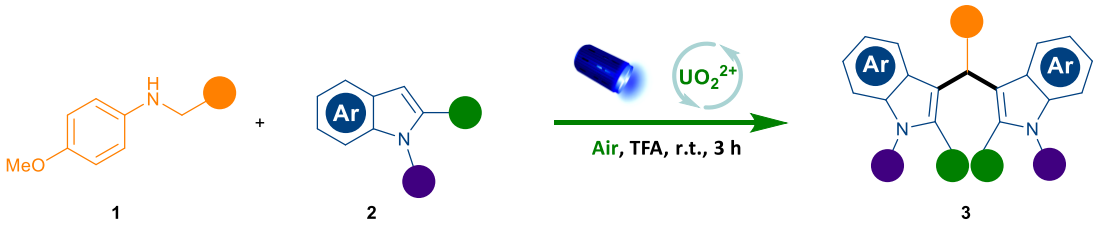
The substrates **1a-1z** were synthesized according to literature procedures.[1] A typical procedure is described as following for the synthesis of **1a**: To a solution of the aromatic amine (1.5 equiv) and the benzyl bromine (1.0 equiv) in CH_3CN (30 mL), was added K_2CO_3 (2.0 equiv). The suspension was stirred for 24 h at 24 ˚C. After the reaction was complete, the reaction mixture was filtered by Celite and washed with EtOAc. The combined organic layers were concentrated under vacuum. The residue was purified

directly by flash silica-gel chromatography to provide the desired product **1a** with 56% yield. Compounds **1a**–**1z** were also synthesized according to the similar method.

3. Typical Procedure for the Preparation of *N*-Aryl-tetrahydroisoquinolines

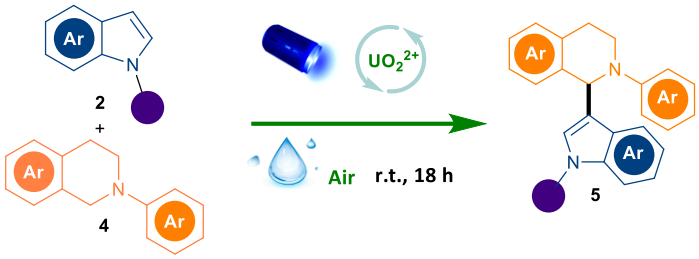
The substrates **4a-4j** were synthesized according to literature procedures.[2] A typical procedure is described as following for the synthesis of **4a**: Copper (I) iodide (0.2 g, 1.0 mmol) and potassium phosphate (4.3 g, 20.0 mmol) were added to a Schlenk tube. The tube was evacuated and back filled with nitrogen. 2-propanol (10.0 mL), ethylene glycol (1.1 mL, 20.0 mmol), 1,2,3,4-tetrahydroisoquinoline (2.0 g, 15.0 mmol) and iodobenzene (1.1 mL, 10.0 mmol) were added successively via a micro-syringe at room temperature. The reaction mixture was heated at 85–90 °C for 24 h and then allowed to cool to room temperature. Diethyl ether (20.0 mL) and water (20.0 mL) were then added. The aqueous layer was extracted by diethyl ether (3 × 2.0 mL). The combined organic phases was washed with brine and dried over magnesium sulfate. The solvent was removed via rotary evaporation, and the residue was subjected to a short plug of silica gel for purification using EtOAc/ Hexane (1:30 → 1:20) as eluent to give the desired product **4a** with 93% yield. Compounds **4b**–**4j** were also synthesized according to the similar method.

4. General Procedures



To a stirring solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (1.0 mg, 0.002 mmol) in 1.0 mL MeCN were added trifluoroacetic acid (11.4 mg, 0.1 mmol), 4-methoxyanilines (0.05 mmol) and indole derivatives (0.1 mmol). The solution was irradiated by blue LEDs (456 nm 40 W) with cooling fan to keep the reaction temperature near 25 °C under air for 3 h. The mixture was concentrated in vacuo. Dichloromethane (2.0 mL) and water (1.0 mL) were then added. The mixture was extracted with dichloromethane (2.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The water phase was

recovered. The crude product was purified by column chromatography on silica gel to give the desired products.



To a stirring solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (2.0 mg, 0.004 mmol) in 1.0 mL H_2O were added *N*-aryl-tetrahydroisoquinoline derivatives (0.1 mmol, **4b**, **4c** need to be dispersed into water by 50 μL MeCN) and indole derivatives (0.05 mmol). The solution was irradiated by blue LEDs (456 nm 40 W) with cooling fan to keep the reaction temperature near 25 °C for 18 h. The mixture was extracted with dichloromethane (3 × 2.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The water phase was recovered. The crude product was purified by column chromatography on silica gel to give the desired products.

5. Recovery of the Catalyst and Recyclability Test

For the cross-coupling reaction of secondary anilines and indoles:

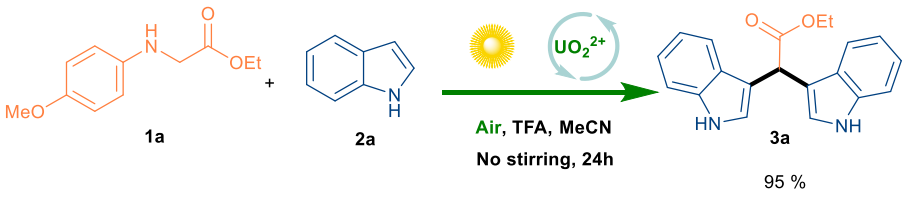
To a stirring solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (1.0 mg, 0.002 mmol) in 1.0 mL MeCN were added trifluoroacetic acid (11.4 mg, 0.1 mmol), ethyl (4-methoxyphenyl)glycinate **1a** (10.5 mg, 0.05 mmol) and 1*H*-indole **2a** (12.3 mg, 0.105mmol). The solution was irradiated by blue LEDs (456 nm 40W) with cooling fan to keep the reaction temperature near 25 °C under air for 3 h. The mixture was concentrated in vacuo. Dichloromethane (2.0 mL) and water (1.0 mL) were then added. The mixture was extracted with dichloromethane (2.0 mL). The combined organic phases were purified by column chromatography on silica gel to give the desired product dimer product **3a**. The recovered water phase was dried by lyophilization then the residue used for the next catalytic cycle. The catalytic activity diminished after 4th cycle, the yield was still more than 75% (Figure 3).

For the cross-coupling reaction of tetrahydroisoquinolines and indoles:

To a stirring solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (2.0 mg, 0.004 mmol) in 1.0 mL H_2O were added *N*-phenyl-tetrahydroisoquinoline **4a** (20.9 mg, 0.1 mmol) and 1,2-dimethyl-1*H*-indole **2d** (7.3 mg, 0.05mmol). The solution was irradiated by blue LEDs (456 nm) with cooling fan to keep the reaction temperature near 25 °C for 18 h. The mixture was extracted with dichloromethane (3 × 2.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give the desired product dimer product **5a**. The recovered water phase was used for the next catalytic cycle. The catalytic activity diminished after 4th cycle, the yield was still more than 73% (Figure 3).

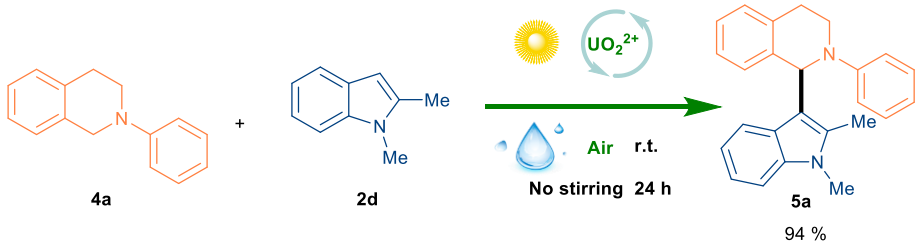
6. Photocatalyzed "Window Ledge" Reactions

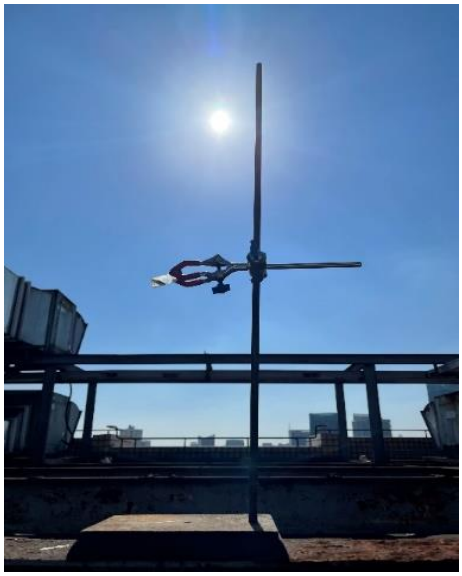
To a solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (1.0 mg, 0.002 mmol) in 1.0 mL MeCN were added trifluoroacetic acid (11.4 mg, 0.1 mmol), ethyl (4-methoxyphenyl)glycinate (10.5 mg, 0.05 mmol) and 1*H*-indole (11.7 mg, 0.1 mmol). The solution was irradiated by sunlight under air for 24 h. The mixture was concentrated in vacuo. Dichloromethane (2.0 mL) and water (1.0 mL) were then added. The mixture was extracted with dichloromethane (3 × 2.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The water phase was recovered. The crude product was purified by column chromatography on silica gel to give the desired products **3a** with 95% yield.



Scheme S7. The "Window Ledge" reaction of **3a**.

To a solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (2.0 mg, 0.004 mmol) in 1.0 mL H_2O were added 2-phenyl-1,2,3,4-tetrahydroisoquinoline (11.4 mg, 0.1 mmol) and 1,2-dimethyl-1*H*-indole (7.3 mg, 0.05 mmol). The solution was irradiated by sunlight under air for 24 h. The mixture was extracted with dichloromethane (3 × 2.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The water phase was recovered. The crude product was purified by column chromatography on silica gel to give the desired products **5a** with 94% yield.

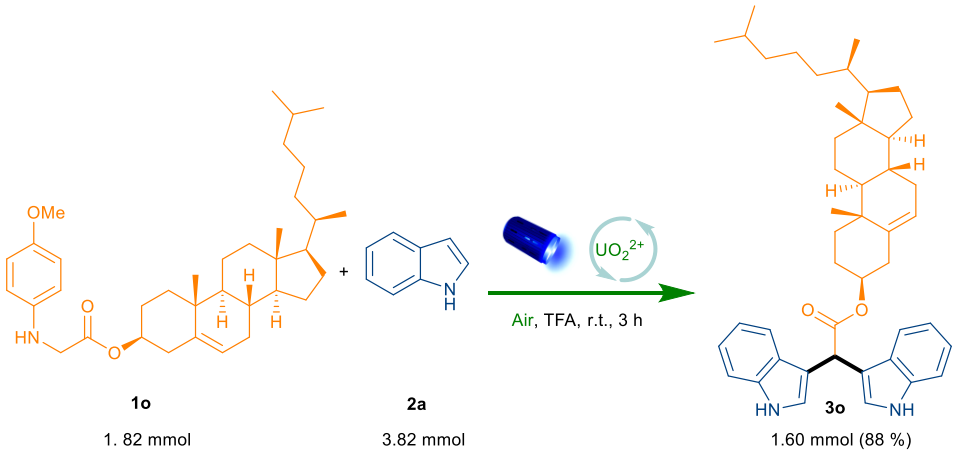




Scheme S8. The "Window Ledge" reaction of **5a**.

7. Gram-scale Synthesis of 3o and 5a.

To a stirring solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (36.4 mg, 0.073 mmol) in 37 mL MeCN were added trifluoroacetic acid (415.1 mg, 3.64 mmol), cholesteryl ester **1o** (1g, 1.82 mmol) and 1*H*-indole **2a** (446.9 mg, 3.82 mmol). The solution was irradiated by blue LEDs (456 nm 40W) with cooling fan to keep the reaction temperature near 25 °C under air for 3 h. The mixture was concentrated in vacuo. Dichloromethane (70.0 mL) and water (35.0 mL) were then added. The mixture was extracted with dichloromethane (3 × 70.0 mL). The water phase was recovered. The combined organic phases were purified by column chromatography on silica gel to give the desired product dimer product **3o** with 88% yield.



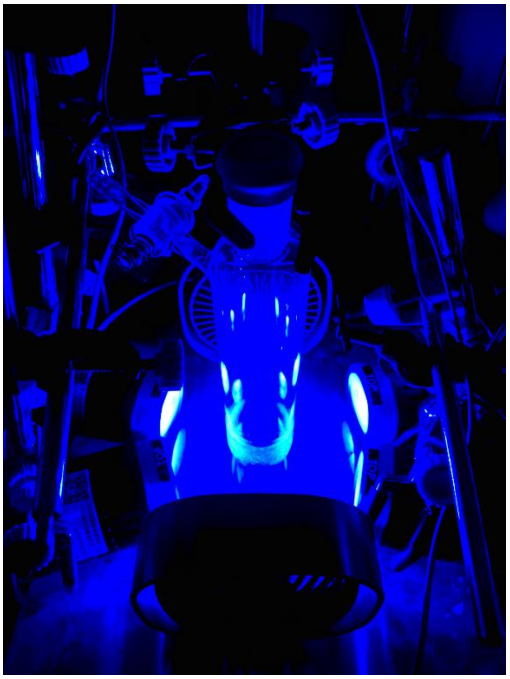
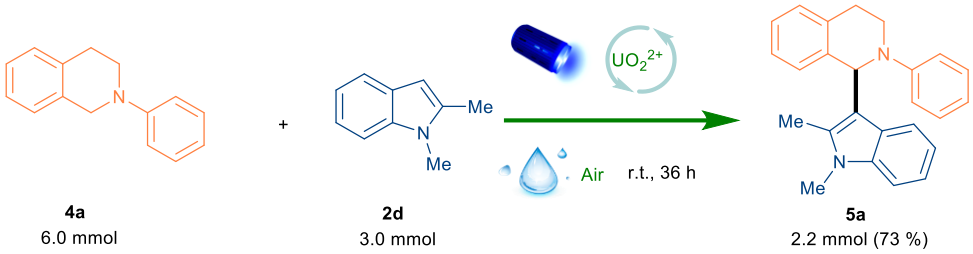


Figure S5. Gram-scale synthesis of **3o**.

To a stirring solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (120.0 mg, 0.24 mmol) in 60.0 mL H_2O were added *N*-phenyl-tetrahydroisoquinoline **4a** (1.25 g, 6.0 mmol) and 1,2-dimethyl-1*H*-indole **2d** (438 mg, 3.0 mmol). The solution was irradiated by blue LEDs (456 nm 40W) with cooling fan to keep the reaction temperature near 25 °C for 36 h. The mixture was extracted with dichloromethane (3 × 100.0 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The water phase was recovered. The crude product was purified by column chromatography on silica gel to give the desired product dimer product **5a** with 73% yield.



4a
6.0 mmol

2d
3.0 mmol

5a
2.2 mmol (73 %)

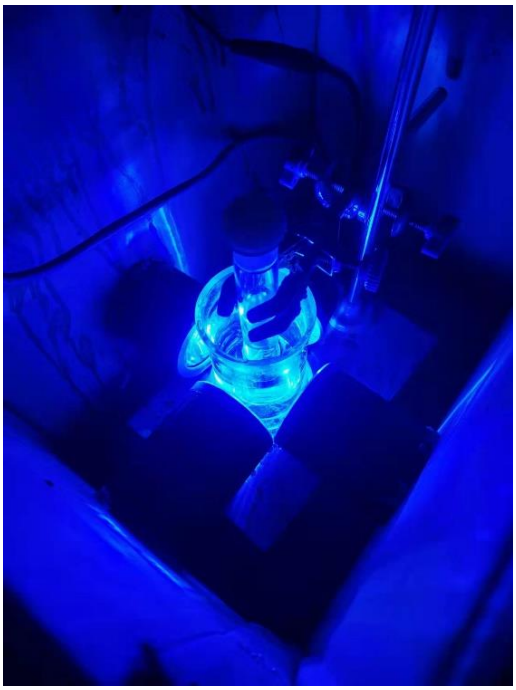
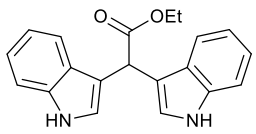


Figure S6. Gram-scale synthesis of **5a**.

8. Spectroscopic Data of Compounds

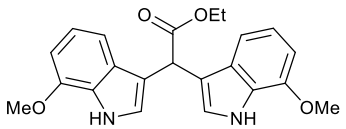
Ethyl 2,2-di(1*H*-indol-3-yl)acetate (3a)



3a

Following the general procedure, was obtained as a red powder (15.3 mg, 96%), m.p. 57～59 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.02 (s, 2 H), 7.65 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.19 (t, *J* = 7.1 Hz, 2 H), 7.12–7.05 (m, 4 H), 5.51 (s, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 1.27 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.6, 136.5, 126.8, 123.5, 122.3, 119.7, 119.5, 113.9, 111.3, 61.2, 40.8, 14.4; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{18}N_2NaO_2^+$ 341.1260, found 341.1275.

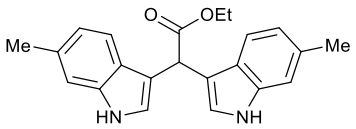
Ethyl 2,2-bis(7-methoxy-1*H*-indol-3-yl)acetate (3b)



3b

Following the general procedure, was obtained as a red powder (18.5 mg, 98%), m.p. 131～133 ℃; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.02 (s, 2 H), 7.65 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.19 (t, *J* = 7.1 Hz, 2 H), 7.12–7.05 (m, 2 H), 5.51 (s, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 3.95 (s, 6 H),1.27 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.5, 146.2, 128.2, 127.0, 123.0, 120.1, 114.4, 112.3, 102.1, 61.1, 55.4, 41.1, 14.4; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{23}N_2O_4^+$ 379.1640, found 379.1653.

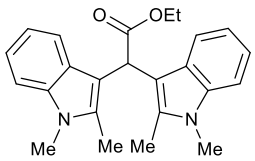
Ethyl 2,2-bis(6-methyl-1*H*-indol-3-yl)acetate (3c)



3c

Following the general procedure, was obtained as a red powder (16.9 mg, 98%), m.p. 128～130 ℃; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.88 (s, 2 H), 7.51 (d, *J* = 8.1 Hz, 2 H), 7.11 (s, 2 H), 6.99 (d, *J* = 2.3 Hz, 2 H), 6.93 (d, *J* = 9.1 Hz, 2 H), 5.45 (s, 1 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 2.45 (s, 6 H), 1.26 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.6, 136.9, 132.0, 124.7, 122.8, 121.4, 119.2, 113.7, 111.3, 61.2, 40.9, 21.8, 14.4; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{22}H_{23}N_2O_2^+$ 347.1754, found 347.1739.

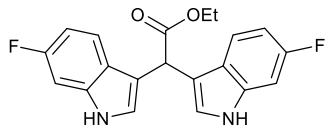
Ethyl 2,2-bis(1,2-dimethyl-1*H*-indol-3-yl)acetate (3d)



3d

Following the general procedure, was obtained as a red powder (18.2 mg, 97%), m.p. 144～146 ℃; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.42 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.2 Hz, 2 H), 7.14–7.11 (m, 2 H), 7.10–6.97 (m, 2 H), 5.53 (s, 1 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 3.64 (s, 6 H), 2.26 (s, 6 H), 1.25 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 174.0, 136.6, 134.2, 127.4, 120.5, 119.1, 118.9, 108.7, 108.5, 61.1, 40.7, 29.6, 14.4, 10.9; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{27}N_2O_2^+$ 375.2067, found 375.2050.

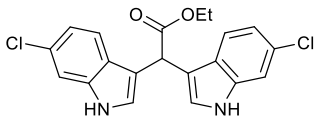
Ethyl 2,2-bis(6-fluoro-1*H*-indol-3-yl)acetate (3e)



3e

Following the general procedure, was obtained as a red powder (16.6 mg, 94%), m.p. 65～67 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.11 (s, 2 H), 7.50 (dd, *J* = 8.7, 5.3 Hz, 2 H), 7.03 (d, *J* = 2.4 Hz, 2 H), 6.99 (dd, *J* = 9.5, 2.2 Hz, 2 H), 6.91–6.80 (m, 2 H), 5.42 (s, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.4, 160.1 (d, *J* = 238.0 Hz), 136.4 (d, *J* = 12.4 Hz), 123.7 (d, *J* = 3.5 Hz), 123.3, 120.2 (d, *J* = 10.1 Hz), 113.7, 108.6 (d, *J* = 24.4 Hz), 97.7 (d, *J* = 26.1 Hz), 61.4, 40.9, 14.3; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{20}H_{17}F_2N_2O_2^+$ 355.1253, found 355.1293.

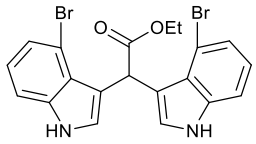
Ethyl 2,2-bis(6-chloro-1*H*-indol-3-yl)acetate (3f)



3f

Following the general procedure, was obtained as a red powder (18.4 mg, 95%), m.p. 68～70 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.13 (s, 2 H), 7.48 (d, *J* = 8.5 Hz, 2 H), 7.29 (d, *J* = 1.5 Hz, 2 H), 7.04 (dd, *J* = 8.7, 1.9 Hz, 2 H), 7.01 (d, *J* = 1.9 Hz, 2 H), 5.41 (s, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 1.26 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.3, 136.8, 128.3, 125.2, 124.1, 120.5, 120.3, 113.6, 111.4, 61.5, 40.7, 29.8, 14.4; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{20}H_{17}Cl_2N_2O_2^+$ 387.0662, found 387.0667.

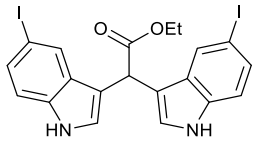
Ethyl 2,2-bis(4-bromo-1*H*-indol-3-yl)acetate (3g)



3g

Following the general procedure, was obtained as a red powder (17.6 mg, 74%), m.p. 63～65 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.24 (s, 2 H), 7.23 (dd, *J* = 7.6, 4.9 Hz, 4 H), 6.97 (t, *J* = 7.9 Hz, 2 H), 6.82 (s, 1 H), 6.76 (d, *J* = 2.3 Hz, 2 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 174.9, 138.0, 125.3, 124.7, 124.3, 123.1, 115.7, 114.3, 110.8, 61.4, 40.9, 14.4; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{16}Br_2N_2NaO_2^+$ 496.9471, found 496.9475.

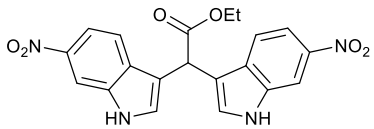
Ethyl 2,2-bis(5-iodo-1*H*-indol-3-yl)acetate (3h)



3h

Following the general procedure, was obtained as a red powder (26.8 mg, 94%), m.p. 74～76 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.16 (s, 2 H), 7.95 (s, 2 H), 7.42 (d, *J* = 10.1 Hz, 2 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 6.98 (s, 2 H), 5.34 (s, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 1.30 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.2, 135.6, 130.7, 129.1, 128.3, 124.3, 113.5, 112.7, 83.3, 61.6, 40.6, 14.4; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{16}I_2N_2NaO_2^+$ 592.9193, found 592.9209.

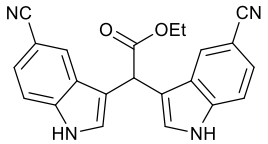
Ethyl 2,2-bis(6-nitro-1*H*-indol-3-yl)acetate (3i)



3i

Following the general procedure, was obtained as a red powder (12.8 mg, 63%), m.p. 95～97 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.76 (s, 2 H), 8.34 (s, 2 H), 7.98 (d, *J* = 9.3 Hz, 2 H), 7.62 (d, *J* = 8.9 Hz, 2 H), 7.45 (s, 2 H), 5.51 (s, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 172.4, 143.8, 135.0, 131.1, 129.1, 119.4, 115.5, 114.3, 108.5, 61.9, 40.5, 14.4; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{16}N_4NaO_6^+$ 431.0962, found 431.0968.

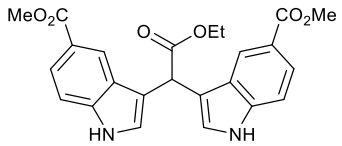
Ethyl 2,2-bis(5-cyano-1*H*-indol-3-yl)acetate (3j)



3j

Following the general procedure, was obtained as a red powder (9.8 mg, 53%), m.p. 133～135 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.70 (s, 2 H), 7.92 (s, 2 H), 7.42–7.41 (m, 4 H), 7.33 (d, *J* = 2.3 Hz, 2 H), 5.44 (s, 1 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 172.31, 138.31, 126.36, 125.54, 125.40, 125.39, 120.78, 113.91, 112.52, 103.01, 61.82, 40.85, 29.83, 14.33; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{22}H_{16}N_4NaO_2^+$ 391.1165, found 391.1175.

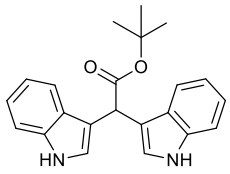
Dimethyl 3,3'-(2-ethoxy-2-oxoethane-1,1-diyl)bis(1*H*-indole-5-carboxylate) (3k)



3k

Following the general procedure, was obtained as a red powder (20.4 mg, 94%), m.p. 208～210 ℃; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.62 (s, 2 H), 8.41 (s, 2 H), 7.86 (dd, *J* = 8.6, 1.6 Hz, 2 H), 7.29 (d, *J* = 8.6 Hz, 2 H), 7.11 (d, *J* = 1.8 Hz, 2 H), 5.55 (s, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 3.88 (s, 6 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.4, 168.4, 139.2, 126.3, 124.9, 123.7, 122.4, 121.8, 114.7, 111.2, 61.6, 52.0, 40.6, 14.3; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{24}H_{22}N_2NaO_6^+$ 457.1370, found 457.1392.

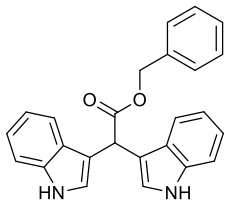
***tert*-Butyl 2,2-di(1*H*-indol-3-yl)acetate (3l)**



3l

Following the general procedure, was obtained as a red powder (16.1 mg, 93%), m.p. 69～71 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.02 (s, 2 H), 7.64 (d, *J* = 7.9 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.18 (t, *J* = 7.1 Hz, 2 H), 7.09 (t, *J* = 7.9 Hz, 2 H), 7.04 (d, *J* = 1.9 Hz, 2 H), 5.41 (s, 1 H), 1.46 (s, 9 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 172.9, 136.5, 126.9, 123.3, 122.1, 119.6, 119.5, 114.3, 111.3, 81.2, 41.8, 28.2; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{22}H_{22}N_2NaO_2^+$ 369.1573, found 369.1576.

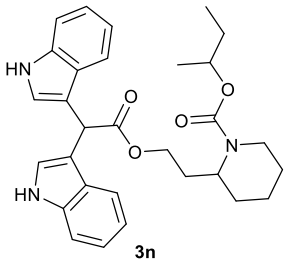
Benzyl 2,2-di(1*H*-indol-3-yl)acetate (3m)



3m

Following the general procedure, was obtained as a colorless crystal (17.4 mg, 92%); ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.02 (s, 2 H), 7.59 (d, *J* = 7.9 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.32–7.25 (m, 5 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.11–6.98 (m, 4 H), 5.57 (s, 1 H), 5.20 (s, 2 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.3, 136.5, 136.0, 128.6, 128.4, 128.3, 126.8, 123.5, 122.3, 119.8, 119.5, 113.7, 111.3, 67.0, 40.8; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{25}H_{20}N_2NaO_2^+$ 403.1417, found 403.1416; CCDC 2220117 contains the supplementary crystallographic data of **3m** [m.p.: 167–168 °C (Hexane/EtOAc, 3:1)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

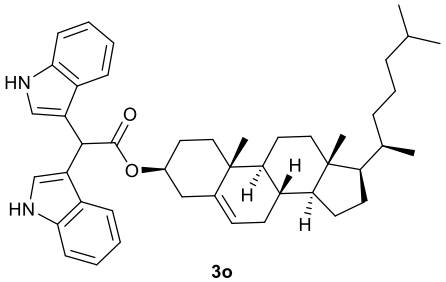
***sec*-Butyl 2-(2-(2,2-di(1*H*-indol-3-yl)acetoxy)ethyl)piperidine-1-carboxylate (3n)**



3n

Following the general procedure, was obtained as a red powder (23.3 mg, 93%), m.p. 86～88 ℃; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.16 (s, 2 H), 7.62 (dd, *J* = 7.8, 5.2 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.17 (t, *J* = 7.6 Hz, 2 H), 7.12–7.02 (m, 4 H), 5.50 (s, 1 H), 4.73 (q, *J* = 6.2 Hz, 1 H), 4.37 (s, 1 H), 4.19–4.10 (m, 2 H), 4.00 (s, 1 H), 2.74 (t, *J* = 12.7 Hz, 1 H), 2.05 (s, 1 H), 1.92–1.83 (m, 1 H), 1.77–1.68 (m, 1 H), 1.61–1.37 (m, 5 H), 1.17 (d, *J* = 6.2 Hz, 3 H), 0.85 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.59, 155.73, 155.71, 136.49, 136.47, 126.80, 126.78, 123.60, 122.19, 119.64, 119.39, 119.37, 113.69, 113.59, 111.37, 111.36, 73.23, 73.18, 62.99, 48.19, 40.74, 29.19, 29.16, 19.91, 19.86, 19.05, 9.85, 9.81; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{30}H_{35}N_3NaO_4^+$ 524.2520, found 524.2532.

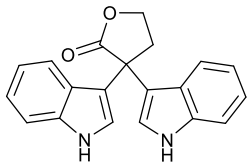
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2,2-di(1*H*-indol-3-yl)acetate (3o)



3o

Following the general procedure, was obtained as a white powder (29.9 mg, 91%), m.p. 202～204 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.01 (s, 2 H), 7.65 (d, *J* = 7.9 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.13–7.06 (m, 2 H), 7.06–7.01 (m, 2 H), 5.48 (s, 1 H), 5.33 (dd, *J* = 5.0, 2.0 Hz, 1 H), 4.75–4.68 (m, 1 H), 2.34 (d, *J* = 8.1 Hz, 2 H), 1.98 (ddt, *J* = 32.3, 17.3, 4.4 Hz, 2 H), 1.84 (ddt, *J* = 16.9, 9.7, 3.5 Hz, 3 H), 1.65–1.22 (m, 13 H), 1.18–1.03 (m, 8 H), 1.00 (s, 3 H), 0.92 (d, *J* = 6.5 Hz, 3 H), 0.88 (dd, *J* = 6.6, 2.3 Hz, 6 H), 0.68 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 173.02, 139.77, 136.48, 126.84, 123.48, 122.79, 122.20, 119.61, 119.55, 113.91, 111.34, 74.91, 56.81, 56.27, 50.12, 42.44, 41.05, 39.86, 39.66, 38.16, 37.09, 36.72, 36.32, 35.93, 32.03, 31.98, 28.37, 28.15, 27.87, 24.42, 23.97, 22.96, 22.71, 21.15, 19.46, 18.85, 11.99; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{45}H_{58}N_2NaO_2^+$ 681.4390, found 681.4401.

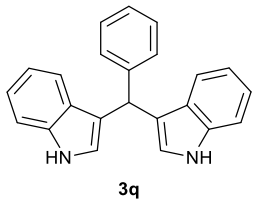
3,3-di(1*H*-indol-3-yl)dihydrofuran-2(3*H*)-one (3p)



3p

Following the general procedure, was obtained as a red powder (11.2 mg, 71%), m.p. 163～165 ℃; ^{1}H NMR (500 MHz, Dimethyl sulfoxide-d_6) : δ = 11.05 (s, 2 H), 7.36 (t, *J* = 7.9 Hz, 4 H), 7.30 (d, *J* = 2.6 Hz, 2 H), 7.02 (t, *J* = 8.1 Hz, 2 H), 6.84 (t, *J* = 7.0 Hz, 2 H), 4.44 (t, *J* = 6.6 Hz, 2 H), 3.07 (t, *J* = 6.7 Hz, 2 H); ^{13}C NMR (126 MHz, Dimethyl sulfoxide-d_6): δ = 177.1, 137.0, 125.4, 123.4, 121.0, 120.1, 118.3, 113.6, 111.6, 65.8, 45.9, 36.3; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{16}N_2NaO_2^+$ 339.1104, found 339.1118.

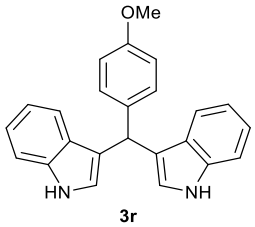
Turbomycin B (3q)



3q

Following the general procedure, was obtained as a red powder (8.7 mg, 54%), m.p. 124～126 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.92 (s, 2 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 7.37–7.34 (m, 4 H), 7.28 (t, *J* = 7.6 Hz, 2 H), 7.19 (dt, *J* = 20.5, 7.2 Hz, 3 H), 7.00 (t, *J* = 7.5 Hz, 2 H), 6.67 (dd, *J* = 2.5, 1.0 Hz, 2 H), 5.89 (s, 1 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 144.1, 136.8, 128.9, 128.4, 127.2, 126.3, 123.7, 122.1, 120.1, 119.9, 119.4, 111.1, 40.3; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{23}H_{19}N_2^+$ 323.1543, found 323.1563.

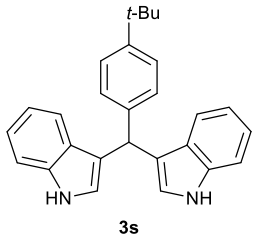
3,3'-((4-Methoxyphenyl)methylene)bis(1*H*-indole) (3r)



3r

Following the general procedure, was obtained as a red powder (10.3 mg, 59%), m.p. 187～189 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.90 (s, 2 H), 7.39 (d, *J* = 7.9 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.29–7.22 (m, 2 H), 7.17 (t, *J* = 7.6 Hz, 2 H), 7.00 (t, *J* = 7.9 Hz, 2 H), 6.82 (d, *J* = 8.7 Hz, 2 H), 6.67–6.63 (m, 2 H), 5.84 (s, 1 H), 3.78 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 158.0, 136.9, 136.4, 129.7, 127.2, 123.6, 122.0, 120.2, 120.1, 119.3, 113.7, 111.1, 55.4, 39.5; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{21}N_2O^+$ 353.1649, found 353.1654.

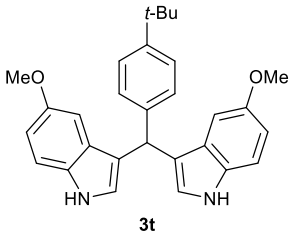
3,3'-((4-(*tert*-Butyl)phenyl)methylene)bis(1*H*-indole) (3s)



3s

Following the general procedure, was obtained as a red powder (11.9 mg, 63%), m.p. 126～128 ℃; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.92 (s, 2 H), 7.41 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.27–7.27 (m, 3 H), 7.16 (t, *J* = 8.1 Hz, 2 H), 7.00 (t, *J* = 7.9 Hz, 2 H), 6.70 (d, *J* = 3.0 Hz, 2 H), 5.86 (s, 1 H), 1.29 (s, 9 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 148.86, 140.95, 136.84, 128.36, 127.31, 125.18, 123.66, 122.00, 120.18, 120.15, 119.28, 111.10, 39.79, 34.51, 31.59; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{27}H_{27}N_2^+$ 379.2169, found 379.2154.

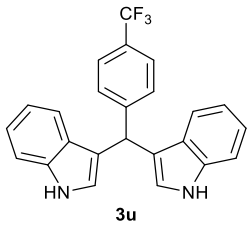
3,3'-((4-(*tert*-Butyl)phenyl)methylene)bis(5-methoxy-1*H*-indole) (3t)



3t

Following the general procedure, was obtained as a red powder (14.4 mg, 66%), m.p. 188～190 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.82 (s, 2 H), 7.28 (d, *J* = 3.4 Hz, 4 H), 7.25–7.23 (m, 2 H), 6.84–6.78 (m, 4 H), 6.72–6.69 (m, 2 H), 5.74 (s, 1 H), 3.68 (s, 6 H), 1.30 (s, 9 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 153.8, 148.9, 140.9, 132.0, 128.4, 127.7, 125.2, 124.5, 119.7, 112.0, 111.8, 102.2, 56.0, 39.9, 34.5, 31.6; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{29}H_{31}N_2O_2^+$ 439.2380, found 439.2380.

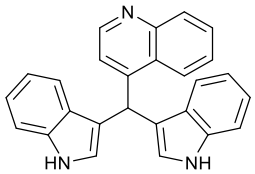
3,3'-((4-(Trifluoromethyl)phenyl)methylene)bis(1*H*-indole) (3u)



3u

Following the general procedure, was obtained as a red powder (8.0 mg, 41%), m.p. 135～137 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.97 (s, 2 H), 7.53 (d, *J* = 8.2 Hz, 2 H), 7.46 (d, *J* = 8.1 Hz, 2 H), 7.37 (t, *J* = 7.1 Hz, 4 H), 7.19 (t, *J* = 8.1 Hz, 2 H), 7.02 (t, *J* = 7.5 Hz, 2 H), 6.66 (d, *J* = 1.5 Hz, 2 H), 5.95 (s, 1 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 148.3, 136.8, 129.2, 128.7, 128.5, 127.0, 125.4 (q, *J* = 3.6 Hz), 123.8, 122.3, 119.9, 119.6, 118.9, 111.3, 40.2; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{18}F_3N_2^+$ 391.1417, found 391.1428.

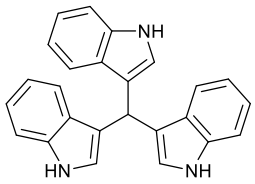
Arsindoline A (3v)



3v

Following the general procedure, was obtained as a red powder (13.8 mg, 74%), m.p. 125～127 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.75 (d, *J* = 4.5 Hz, 1 H), 8.16 (t, *J* = 8.1 Hz, 2 H), 8.06 (s, 2 H), 7.68 (t, *J* = 8.3 Hz, 1 H), 7.49–7.42 (m, 1 H), 7.38 (t, *J* = 7.3 Hz, 4 H), 7.24–7.14 (m, 3 H), 7.03 (t, *J* = 7.9 Hz, 2 H), 6.66 (s, 1 H), 6.59 (d, *J* = 1.8 Hz, 2 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 150.4, 136.9, 130.0, 129.2, 127.5, 126.9, 126.7, 124.4, 124.3, 122.4, 121.1, 119.7, 119.6, 117.8, 111.4, 35.7; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{26}H_{20}N_3^+$ 374.1652, found 374.1658.

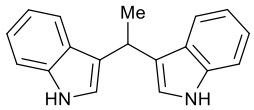
Turbomycin A (3w)



3w

Following the general procedure, was obtained as a red powder (11.7 mg, 65%), m.p. 168～170 °C; ^{1}H NMR (500 MHz, Acetone-d_6): δ = 9.92 (s, 3 H), 7.47 (d, *J* = 7.9 Hz, 3 H), 7.37 (d, *J* = 8.1 Hz, 3 H), 7.05-6.87 (m, 3 H), 6.93 (d, *J* = 1.3 Hz, 3 H), 6.88 (m, 3 H), 6.18 (s, 1 H); ^{13}C NMR (126 MHz, Acetone-d_6): δ = 138.1, 128.3, 124.2, 121.8, 120.4, 120.0, 119.1, 112.1, 32.2; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{20}N_3^+$ 362.1652, found 362.1665.

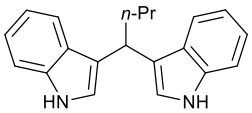
Vibrindole A (3x)



3x

Following the general procedure, was obtained as a red powder (2.2 mg, 17%), m.p. 89～91 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.91 (s, 2 H), 7.57 (d, *J* = 7.9 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.16 (t, *J* = 8.1 Hz, 2 H), 7.04 (t, *J* = 7.5 Hz, 2 H), 6.94 (d, *J* = 2.2 Hz, 2 H), 4.68 (q, *J* = 7.1 Hz, 1 H), 1.81 (d, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 136.81, 127.07, 121.93, 121.88, 121.31, 119.89, 119.17, 111.18, 28.33, 21.87; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{18}H_{16}N_2Na^+$ 283.1205, found 283.1211.

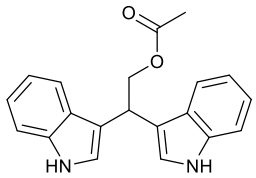
ST-1385 (3y)



3y

Following the general procedure, was obtained as a red powder (4.6 mg, 32%), m.p. 95～97 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.91 (s, 2 H), 7.60 (d, *J* = 7.9 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.14 (t, *J* = 7.6 Hz, 2 H), 7.06–6.95 (m, 4 H), 4.50 (t, *J* = 7.5 Hz, 1 H), 2.20 (q, *J* = 7.5 Hz, 2 H), 1.48–1.38 (m, 2 H), 0.95 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 136.7, 127.4, 121.9, 121.5, 120.8, 119.8, 119.1, 111.2, 77.4, 77.2, 76.9, 38.2, 33.8, 21.6, 14.4; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{20}H_{21}N_2^+$ 289.1699, found 289.1716.

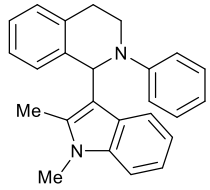
Streptindole (3z)



3z

Following the general procedure, was obtained as a red powder (2.4 mg, 15%), m.p. 96～98 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.00 (s, 2 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.18 (t, *J* = 7.6 Hz, 2 H), 7.07 (t, *J* = 7.9 Hz, 2 H), 7.02 (d, *J* = 2.0 Hz, 2 H), 4.95 (d, *J* = 7.1 Hz, 1 H), 4.74 (d, *J* = 7.1 Hz, 2 H), 1.99 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 171.4, 136.6, 127.2, 122.3, 122.2, 119.7, 119.5, 116.5, 111.3, 67.5, 33.7, 21.3; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{18}N_2NaO_2^+$ 341.1260, found 341.1265.

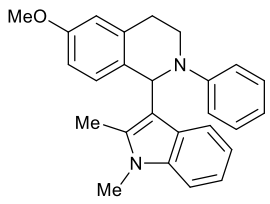
1-(1,2-Dimethyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5a)



5a

Following the general procedure, was obtained as a colorless crystal (16.8 mg, 96%), m.p. 113～115 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.22–7.18 (m, 5 H), 7.10–7.03 (m, 5 H), 6.89–6.83 (m, 3 H), 6.02 (s, 1 H), 3.74–3.61 (m, 2 H), 3.60 (s, 3 H), 3.13–2.99 (m, 2 H), 2.13 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 151.1, 138.3, 136.6, 135.4, 135.3, 128.9, 128.8, 128.4, 127.9, 126.3, 126.2, 120.4, 120.2, 119.6, 119.2, 119.2, 112.9, 108.6, 57.2, 46.1, 29.5, 27.9, 10.7; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{25}N_2^+$ 353.2012, found 353.2015; CCDC 2124830 contains the supplementary crystallographic data of **5a** [m.p.: 113–115 °C (Hexane/EtOAc, 10:1)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

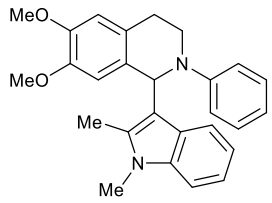
1-(1,2-Dimethyl-1*H*-indol-3-yl)-6-methoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**5b**)



5b

Following the general procedure, was obtained as light yellow powder (12.8 mg, 67%), m.p. 135～137 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.22–7.14 (m, 3 H), 7.09–7.06 (m, 1 H), 7.03–6.93 (m, 4 H), 6.91–6.87 (m, 1 H), 6.84–6.81 (m, 1 H), 6.72 (d, *J* = 2.7 Hz, 1 H), 6.66 (dd, *J* = 8.5, 2.7 Hz, 1 H), 5.96 (s, 1 H), 3.80 (s, 3 H), 3.72–3.60 (m, 2 H), 3.59 (s, 3 H), 3.13–2.89 (m, 2 H), 2.12 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 157.99, 151.07, 136.65, 136.56, 135.27, 130.51, 129.42, 128.91, 127.91, 120.34, 120.15, 119.50, 119.26, 119.20, 113.20, 113.04, 112.62, 108.56, 56.68, 55.34, 45.84, 29.52, 28.08, 10.70; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{26}H_{27}N_2O^+$ 383.2118, found 383.2126.

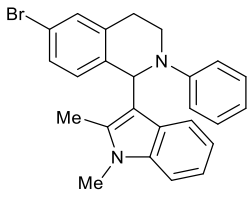
1-(1,2-Dimethyl-1*H*-indol-3-yl)-6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5c)



5c

Following the general procedure, was obtained as a light yellow powder (16.7 mg, 81%), m.p. 156～158 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.23–7.16 (m, 3 H), 7.10–7.01 (m, 3 H), 6.92–6.78 (m, 3 H), 6.65 (s, 1 H), 6.59 (s, 1 H), 5.98 (s, 1 H), 3.89 (s, 3 H), 3.68 (s, 3 H), 3.65–3.62 (m, 2 H), 3.61 (s, 3 H), 2.99 (dt, *J* = 16.2, 8.0 Hz, 1 H), 2.75 (dt, *J* = 16.2, 3.7 Hz, 1 H), 2.10 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 150.81, 147.81, 147.70, 136.50, 135.37, 129.75, 129.05, 128.07, 127.57, 120.39, 119.85, 119.32, 119.22, 118.98, 112.75, 111.35, 111.11, 108.53, 56.42, 56.04, 55.98, 44.92, 29.54, 26.46, 10.72, 10.72; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{27}H_{29}N_2O_2^+$ 413.2224, found 413.2230.

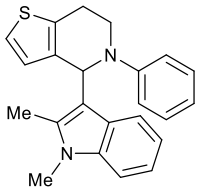
6-Bromo-1-(1,2-dimethyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5d)



5d

Following the general procedure, was obtained as a light yellow powder (18.1 mg, 84%), m.p. 107～109 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.35 (s, 1 H), 7.22–7.13 (m, 4 H), 7.08 (t, *J* = 7.0 Hz, 1 H), 6.99–6.82 (m, 6 H), 5.82 (s, 1 H), 3.66–3.61 (m, 1 H), 3.58 (s, 3 H), 3.57–3.53 (m, 1 H), 3.08–2.88 (m, 2 H), 2.09 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 151.0, 137.8, 137.6, 136.6, 135.5, 131.5, 130.2, 129.3, 128.9, 127.7, 120.9, 120.5, 120.1, 120.0, 119.4, 119.1, 112.2, 108.7, 57.3, 46.2, 29.6, 28.0, 10.7; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{24}BrN_2^+$ 431.1117, found 431.1115.

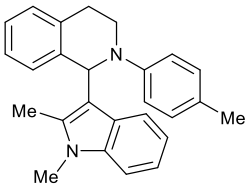
4-(1,2-Dimethyl-1*H*-indol-3-yl)-5-phenyl-4,5,6,7-tetrahydrothieno[3,2-c]pyridine (5e)



5e

Following the general procedure, was obtained as a light yellow powder (13.6. mg, 76%), m.p. 110～112 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.18 (dd, *J* = 15.6, 7.7 Hz, 3 H), 7.09 (t, *J* = 7.5 Hz, 1 H), 7.05–6.96 (m, 4 H), 6.93 (t, *J* = 7.4 Hz, 1 H), 6.87 (t, *J* = 7.2 Hz, 1 H), 6.63 (d, *J* = 5.1 Hz, 1 H), 5.92 (s, 1 H), 3.79–3.60 (m, 2 H), 3.58 (s, 3 H), 3.14–2.88 (m, 2 H), 2.11 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 151.1, 137.1, 136.6, 135.2, 134.2, 128.9, 127.8, 126.9, 122.4, 120.9, 120.5, 120.4, 119.3, 119.0, 111.5, 108.6, 55.6, 47.3, 29.5, 24.5, 10.5; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{23}H_{23}N_2S^+$ 359.1732, found 359.1737.

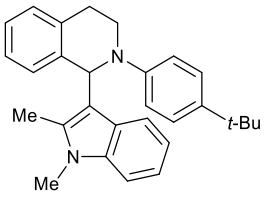
1-(1,2-Dimethyl-1*H*-indol-3-yl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (5f)



5f

Following the general procedure, was obtained as a white powder (14.4mg, 79%), m.p. 123～125 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.16 (dt, *J* = 14.8, 7.6 Hz, 3 H), 7.09–6.99 (m, 3 H), 6.95 (t, *J* = 7.7 Hz, 3 H), 6.93–6.83 (m, 3 H), 5.89 (s, 1 H), 3.67-3.62 (m, 2 H), 3.58 (s, 3 H), 3.56–3.52 (m, 1 H), 3.13–2.83 (m, 1 H), 2.23 (s, 3 H), 2.10 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 149.03, 138.54, 136.59, 135.42, 135.37, 130.01, 129.43, 128.72, 128.43, 127.93, 120.31, 119.26, 119.15, 113.03, 108.53, 57.64, 47.08, 29.55, 28.09, 20.71, 10.67; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{26}H_{27}N_2^+$ 367.2169, found 367.2174.

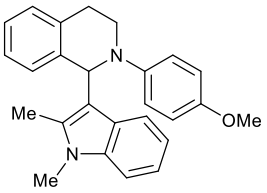
2-(4-(*tert*-Butyl)phenyl)-1-(1,2-dimethyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5g)



5g

Following the general procedure, was obtained as a light yellow powder (15.7 mg, 77%), m.p. 122～124 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.22–7.15 (m, 5 H), 7.09–7.02 (m, 3 H), 6.96–6.83 (m, 4 H), 5.94 (s, 1 H), 3.72–3.63 (m, 1 H), 3.59 (s, 3 H), 3.58–3.54 (m, 1 H), 3.15–3.03 (m, 1 H), 2.97 (dt, *J* = 16.3, 4.4 Hz, 1 H), 2.09 (s, 3 H), 1.26 (s, 9 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 148.59, 142.96, 138.53, 136.57, 135.55, 135.43, 128.76, 128.45, 127.96, 126.28, 126.15, 125.67, 120.30, 119.30, 119.22, 119.17, 113.02, 108.53, 57.57, 46.01, 34.10, 31.62, 29.53, 27.82, 10.68; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{29}H_{33}N_2^+$ 409.2638, found 409.2637.

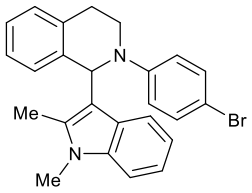
1-(1,2-Dimethyl-1*H*-indol-3-yl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (5h)



5h

Following the general procedure, was obtained as a white powder (13.9 mg, 73%), m.p. 130～132 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.22–7.13 (m, 3 H), 7.11–7.04 (m, 4 H), 6.89 (dt, *J* = 14.7, 7.5 Hz, 2 H), 6.66 (dd, *J* = 8.2, 1.6 Hz, 1 H), 6.54 (s, 1 H), 6.38 (dd, *J* = 8.1, 1.9 Hz, 1 H), 6.01 (s, 1 H), 3.71–3.66 (m, 1 H), 3.65 (s, 3 H), 3.64–3.61 (m, 1 H), 3.60 (s, 3 H), 3.13–3.03 (m, 1 H), 2.96 (dt, *J* = 16.4, 4.4 Hz, 1 H), 2.14 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 160.4, 152.3, 138.2, 136.6, 135.5, 135.3, 129.6, 128.8, 128.4, 127.9, 126.4, 126.2, 120.4, 119.3, 119.1, 113.0, 111.7, 108.6, 105.2, 105.1, 57.0, 55.2, 45.8, 29.5, 27.7, 10.8; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{26}H_{27}N_2O^+$ 383.2118, found 383.2118.

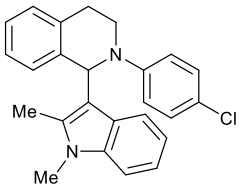
2-(4-Bromophenyl)-1-(1,2-dimethyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5i)



5i

Following the general procedure, was obtained as a light yellow powder (16.8 mg, 96%), m.p. 115～117 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.25–7.15 (m, 6 H), 7.11–7.01 (m, 4 H), 6.94–6.86 (m, 5 H), 5.93 (s, 1 H), 3.67–3.64 (m, 1 H), 3.60 (s, 1 H), 3.58–3.54 (m, 1 H), 3.09–3.01 (m, 1 H), 2.13 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 150.1, 138.0, 136.6, 135.3, 135.2, 131.7, 128.7, 128.4, 127.7, 126.5, 126.3, 121.2, 120.5, 119.3, 119.0, 112.6, 112.5, 108.7, 57.2, 46.4, 29.6, 28.0, 10.8; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{24}BrN_2^+$ 431.1117, found 431.1112.

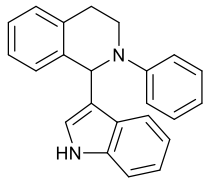
2-(4-Chlorophenyl)-1-(1,2-dimethyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5j)



5j

Following the general procedure, was obtained as a light yellow powder (16.2 mg, 84%), m.p. 112～114 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.20–7.17 (m, 3 H), 7.10–7.01 (m, 5 H), 6.95–6.86 (m, 4 H), 5.90 (s, 1 H), 3.66–3.61(m, 1 H), 3.59 (s, 3 H), 3.57–3.53 (m, 1 H), 3.07–3.01 (m, 2 H), 2.11 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 149.8, 138.0, 136.6, 135.3, 135.2, 128.8, 128.7, 128.4, 127.7, 126.5, 126.3, 125.3, 121.1, 120.5, 119.3, 119.1, 112.6, 108.7, 57.5, 46.7, 29.6, 28.1, 10.8; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{24}ClN2^+$ 387.1623, found 387.1625.

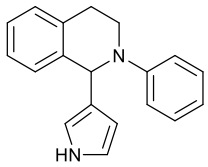
1-(1*H*-Indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5k)



5k

Following the general procedure, was obtained as a white powder (5.3 mg, 33%), m.p. 167～169 °C; ^{1}H NMR (500 MHz, Dimethyl sulfoxide-d_6): δ = 10.88 (s, 1 H), 7.48 (d, *J* = 7.9 Hz, 1 H), 7.41–7.28 (m, 2 H), 7.26–7.12 (m, 5 H), 7.08–6.96 (m, 3 H), 6.92–6.89 (m, 1 H), 6.79 (d, *J* = 2.5 Hz, 1 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 6.24 (s, 1 H), 3.59-3.57 (m, 2 H), 3.04-2.98 (m, 1 H), 2.93-2.87 (m, 1 H); ^{13}C NMR (126 MHz, Dimethyl sulfoxide-d_6): δ = 149.1, 137.9, 136.5, 134.9, 129.0, 128.4, 127.7, 126.4, 125.9, 125.6, 124.3, 121.0, 119.2, 118.5, 117.4, 117.0, 114.5, 111.5, 55.4, 26.5; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{23}H_{21}N_2^+$ 325.1699, found 325.1704

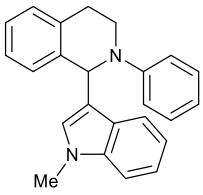
2-Phenyl-1-(1*H*-pyrrol-3-yl)-1,2,3,4-tetrahydroisoquinoline (5l)



5l

Following the general procedure, was obtained as a colorless oil (6.1 mg, 45%); ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 8.12 (s, 1 H), 7.33–7.14 (m, 6 H), 6.99 (d, *J* = 8.1 Hz, 2 H), 6.83 (t, *J* = 7.2 Hz, 1 H), 6.66 (q, *J* = 2.3 Hz, 1 H), 6.08 (q, *J* = 2.9 Hz, 1 H), 5.90 (s, 1 H), 5.70 (d, *J* = 3.4 Hz, 1 H), 3.61–3.56 (m, 1 H), 3.51–3.47 (m, 1 H), 3.03–2.97 (m, 1 H), 2.79–2.74 (m, 1 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 150.0, 136.0, 135.5, 133.6, 129.6, 128.9, 127.9, 127.3, 126.1, 118.9, 117.2, 115.7, 108.4, 107.7, 57.7, 43.0, 27.2; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{19}H_{19}N_2^+$ 275.1619, found 275.1614.

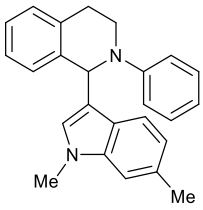
1-(1-Methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5m)



5m

Following the general procedure, was obtained as a white powder (11.1 mg, 66%), m.p. 126～128 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.55 (d, *J* = 8.0 Hz, 1 H), 7.31–7.28 (m, 1 H), 7.27–7.13 (m, 7 H), 7.02 (dd, *J* = 8.0, 5.4 Hz, 3 H), 6.77 (t, *J* = 7.3 Hz, 1 H), 6.51 (s, 1 H), 6.18 (s, 1 H), 3.66 (s, 3 H), 3.65–3.58 (m, 2 H), 3.07 (dt, *J* = 15.9, 8.0 Hz, 1 H), 2.82 (d, *J* = 16.1 Hz, 1 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 149.9, 137.8, 137.5, 135.7, 129.3, 128.9, 128.2, 127.0, 126.8, 125.8, 121.8, 120.3, 119.3, 118.1, 117.8, 115.8, 109.3, 56.7, 42.3, 32.9, 26.8; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{24}H_{23}N_2^+$ 339.1856, found 339.1848.

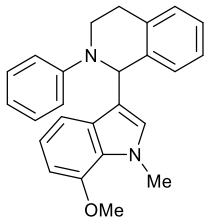
1-(1,6-Dimethyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5n)



5n

Following the general procedure, was obtained as a white powder (13.9 mg, 79%), m.p. 120～122 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.41 (d, *J* = 8.1 Hz, 1 H), 7.31–7.28 (m, 1 H), 7.26–7.22 (m, 2 H), 7.20–7.13 (m, 3 H), 7.06–6.99 (m, 3 H), 6.86 (dd, *J* = 8.2, 1.5 Hz, 1 H), 6.77 (t, *J* = 7.3 Hz, 1 H), 6.43 (s, 1 H), 6.15 (s, 1 H), 3.69–3.58 (m, 5 H), 3.07 (ddd, *J* = 15.6, 9.3, 5.9 Hz, 1 H), 2.82 (dt, *J* = 16.1, 4.6 Hz, 1 H), 2.46 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 149.94, 137.90, 137.85, 135.68, 131.62, 129.32, 128.89, 128.34, 128.14, 126.72, 125.80, 124.87, 120.99, 119.96, 118.00, 117.61, 115.72, 109.28, 56.80, 42.31, 32.76, 26.83, 21.95; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{25}N_2^+$ 353.2012, found 353.2017.

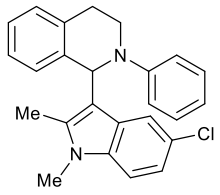
1-(7-Methoxy-1-methyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5o)



5o

Following the general procedure, was obtained as a light yellow powder (14.0 mg, 76%), m.p. 131～133 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.27 (d, *J* = 8.5 Hz, 1 H), 7.25–7.21 (m, 2 H), 7.19–7.11 (m, 4 H), 7.02 (d, *J* = 8.1 Hz, 2 H), 6.90 (t, *J* = 7.9 Hz, 1 H), 6.75 (d, *J* = 7.6 Hz, 1 H), 6.58 (d, *J* = 7.7 Hz, 1 H), 6.36 (s, 1 H), 6.12 (s, 1 H), 3.91 (s, 3 H), 3.89 (s, 3 H), 3.64 (q, *J* = 7.2, 5.6 Hz, 2 H), 3.06 (dt, *J* = 15.8, 7.7 Hz, 1 H), 2.80 (d, *J* = 16.3 Hz, 1 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 149.88, 147.84, 137.78, 135.66, 130.02, 129.32, 129.29, 128.92, 128.20, 127.15, 126.70, 125.80, 119.76, 118.02, 117.80, 115.75, 113.03, 102.62, 56.58, 55.52, 42.28, 36.61, 26.69; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{25}N_2O^+$ 369.1961, found 369.1957.

1-(5-Chloro-1,2-dimethyl-1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (5p)



5p

Following the general procedure, was obtained as a light yellow powder (8.9 mg, 46%), m.p. 105～107 °C; ^{1}H NMR (500 MHz, Chloroform-*d*): δ = 7.21–7.12 (m, 4 H), 7.08 (d, *J* = 8.7 Hz, 2 H), 6.99 (td, *J* = 6.0, 5.5, 2.7 Hz, 4 H), 6.88–6.82 (m, 2 H), 5.89 (s, 1 H), 3.70–3.58 (m, 2 H), 3.56 (s, 3 H), 3.05 (s, 2 H), 2.11 (s, 3 H); ^{13}C NMR (126 MHz, Chloroform-*d*): δ = 151.16, 135.02, 128.92, 128.85, 128.76, 128.22, 126.56, 126.30, 124.88, 120.77, 120.71, 120.59, 120.10, 119.12, 118.68, 109.74, 109.52, 99.45, 57.28, 46.95, 29.74, 28.14, 10.80; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{24}ClN_2^+$ 387.1623, found 387.1629.

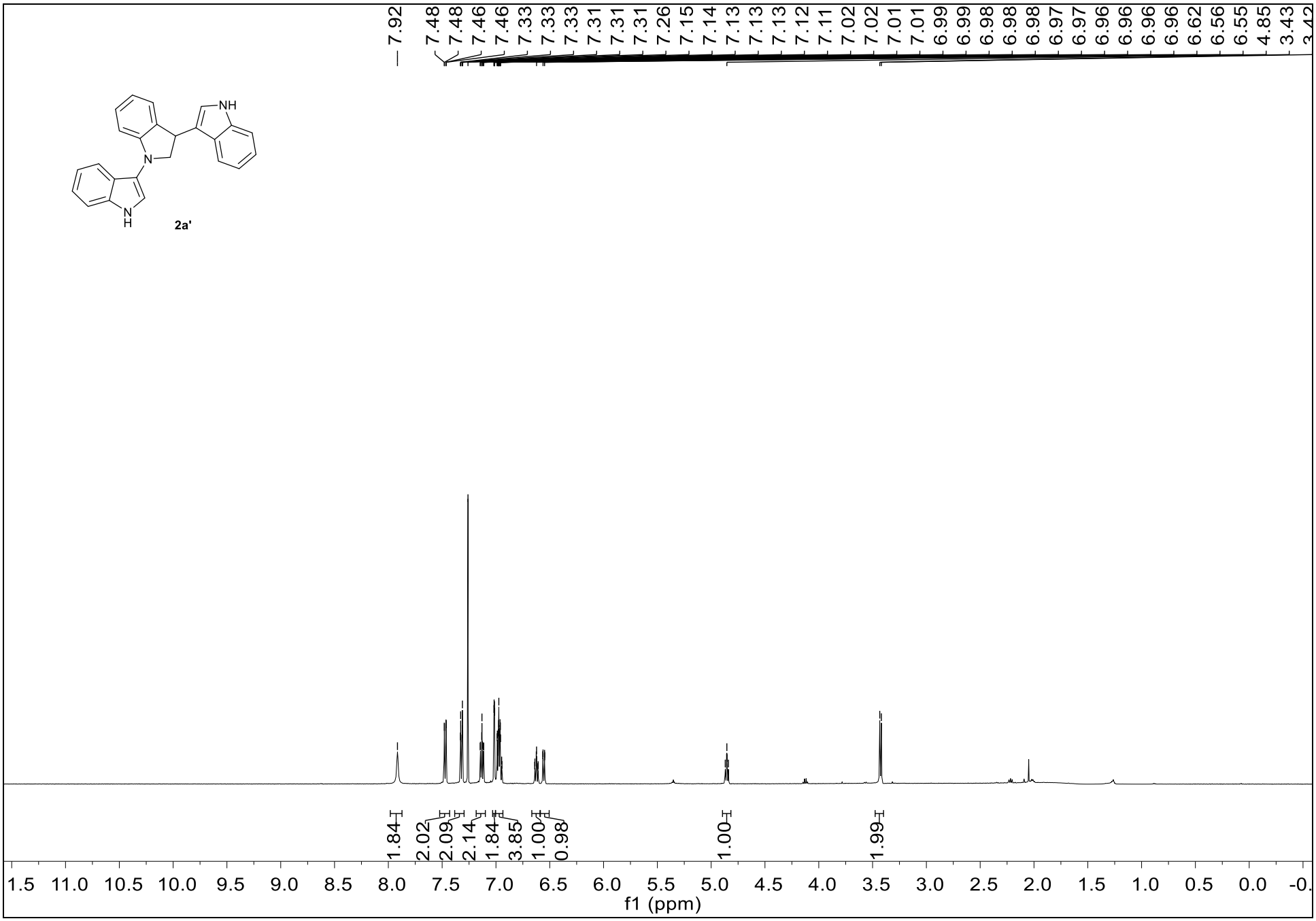
III References

1. L. Leng and J. M. Ready, *ACS Catal*., 2020, **10**, 13196-13201.

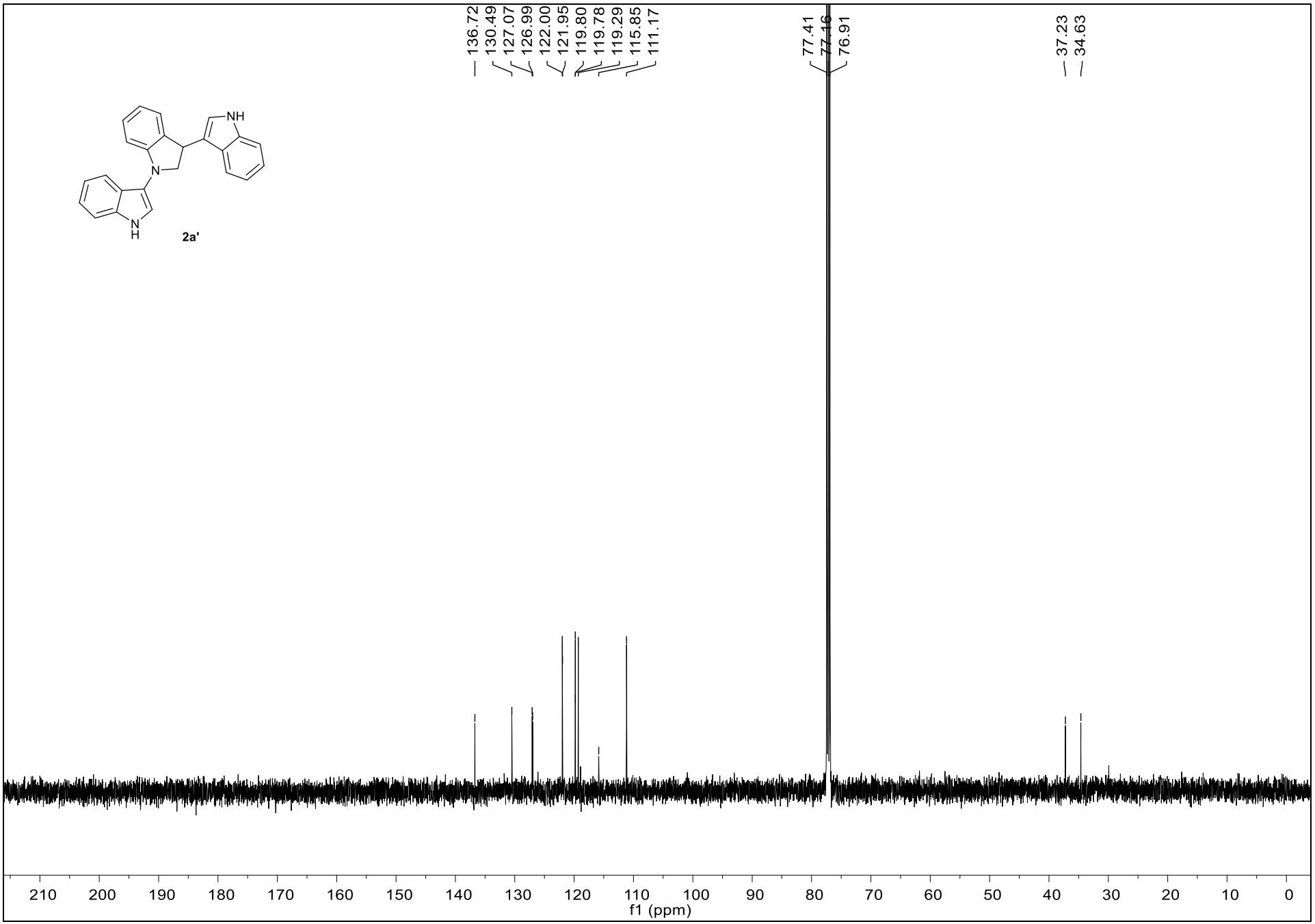
2. J. Zhang, B. Tiwari, C. Xing, X. Chen and Y. R. Chi, *Angew. Chem. Int. Ed.*, 2012, **51**, 3649-3652.

IV NMR Spectra

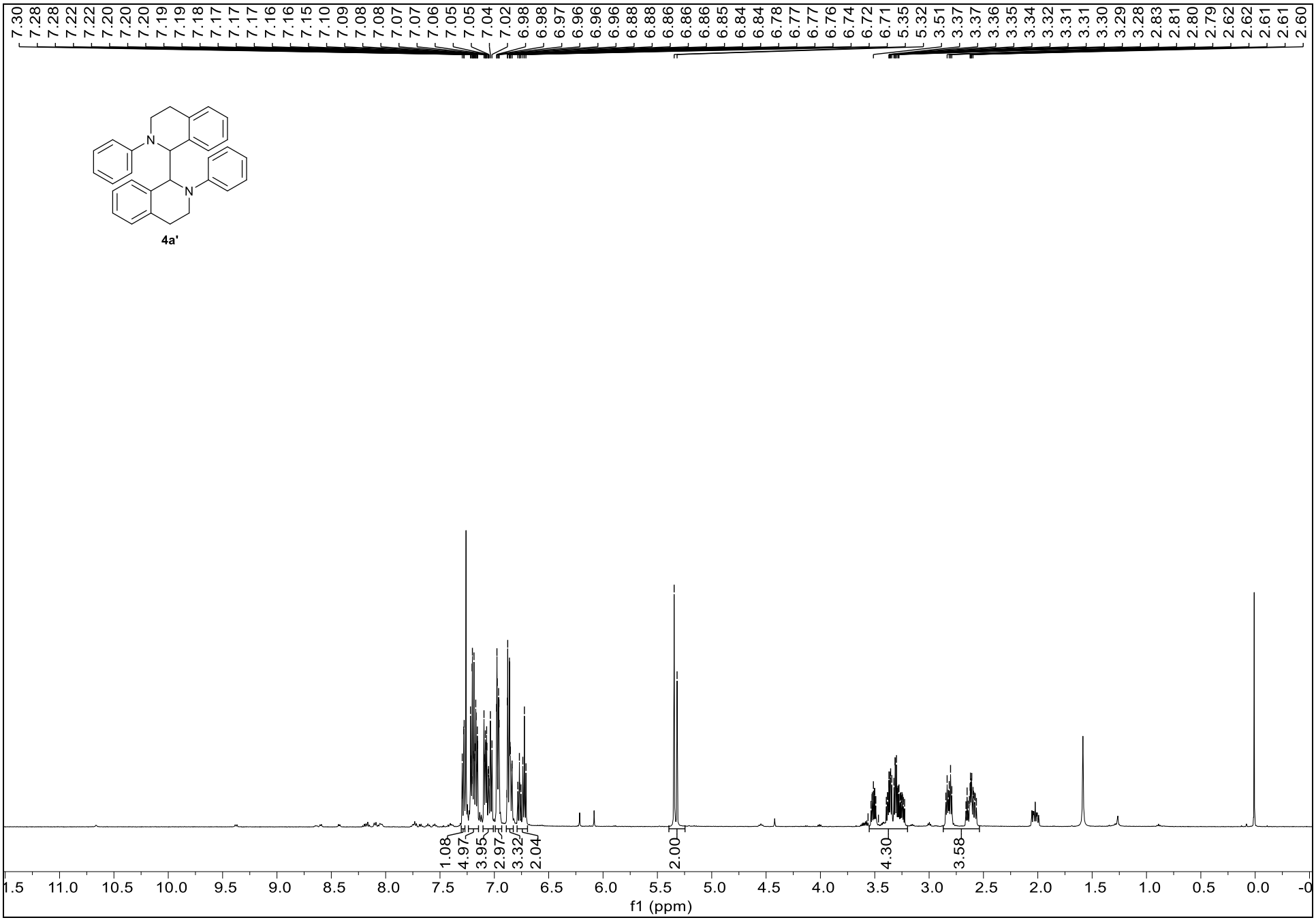
^{1}H NMR Spectrum of 2a′ (500 MHz, $CDCl_3$)



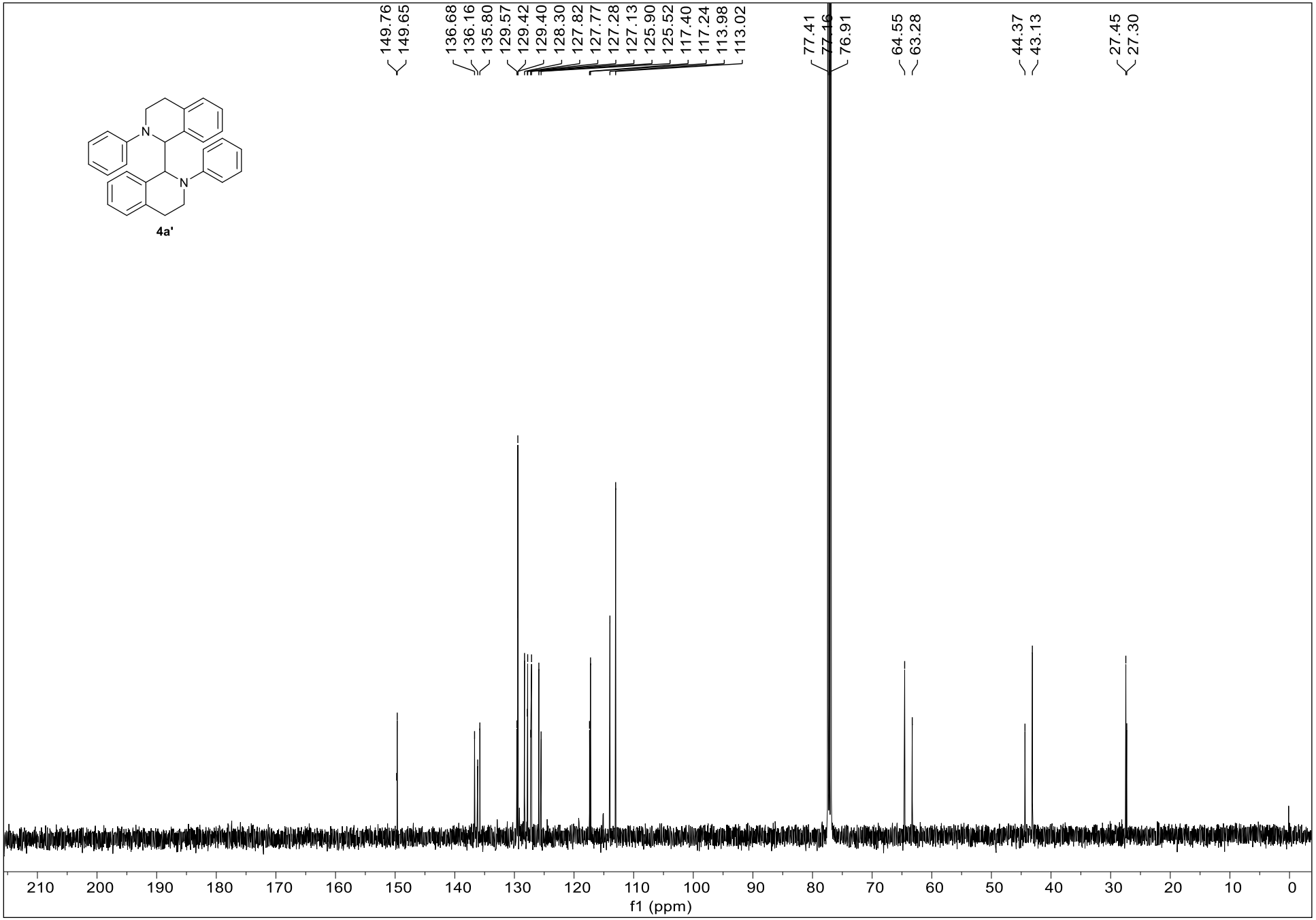
^{13}C NMR Spectrum of 2a′ (126 MHz, $CDCl_3$)



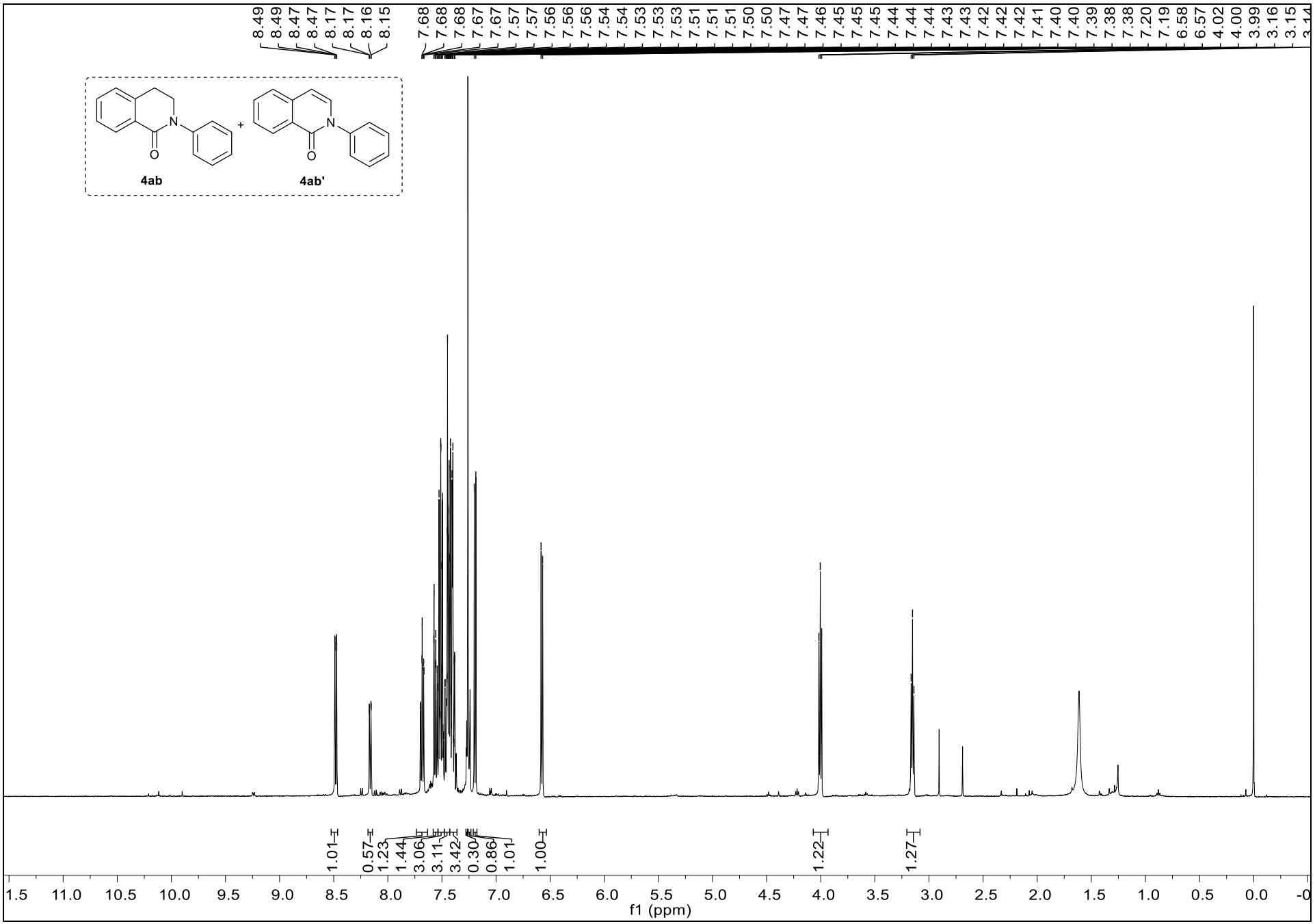
^{1}H NMR Spectrum of 4a′ (500 MHz, $CDCl_3$)



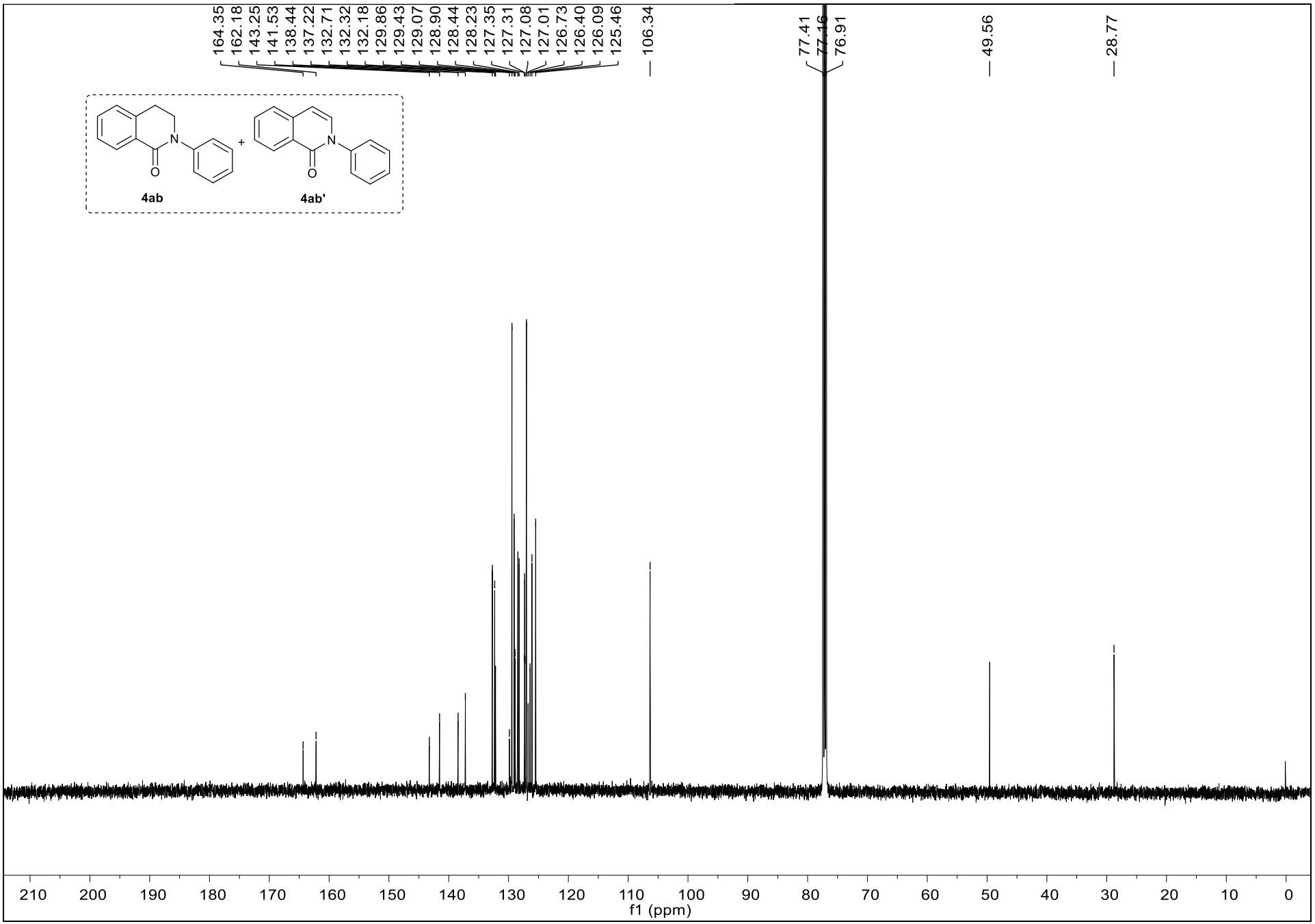
^{13}C NMR Spectrum of 4a′ (126 MHz, $CDCl_3$)



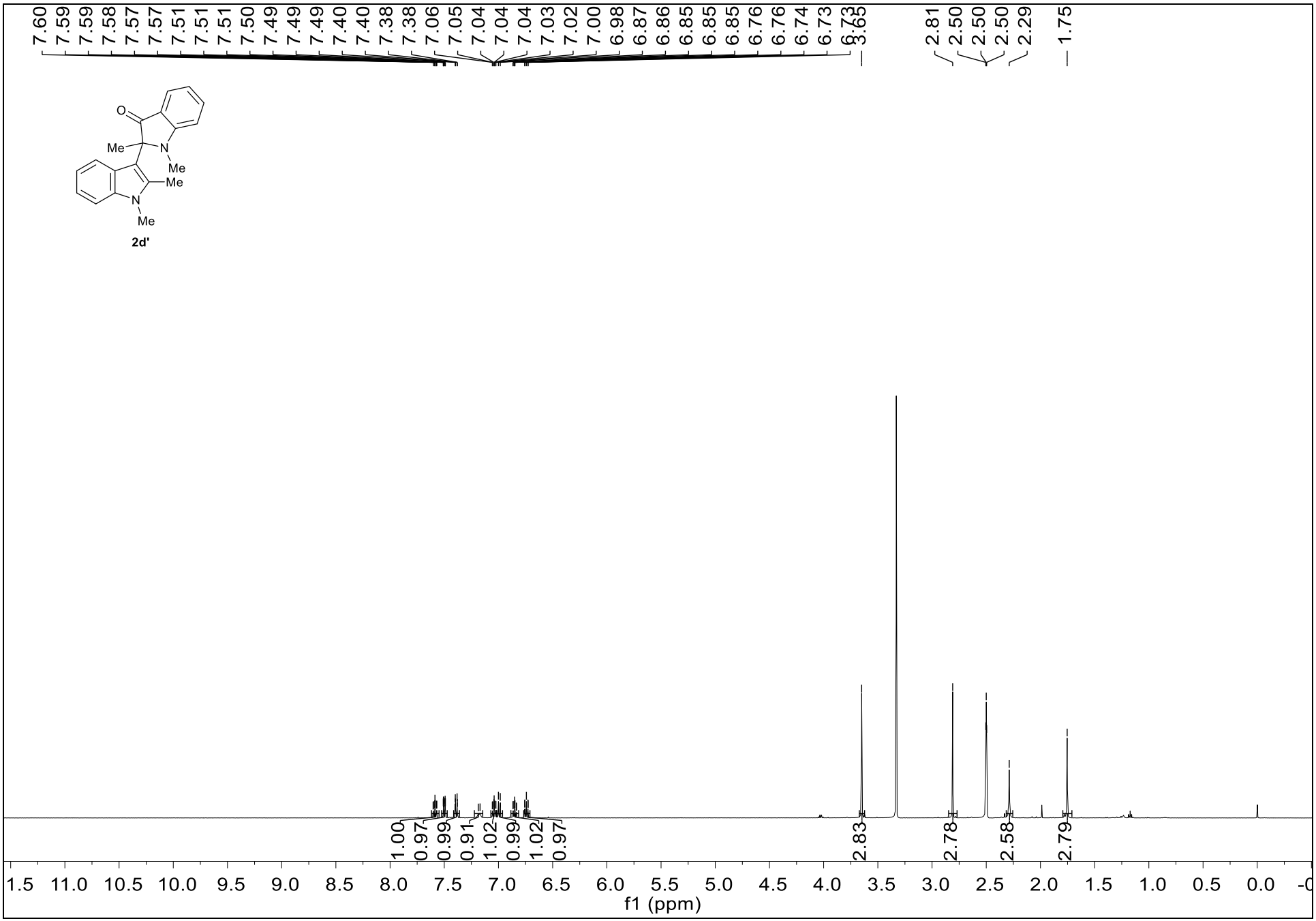
^{1}H NMR Spectrum of 4ab and 4ab′ (500 MHz, $CDCl_3$)



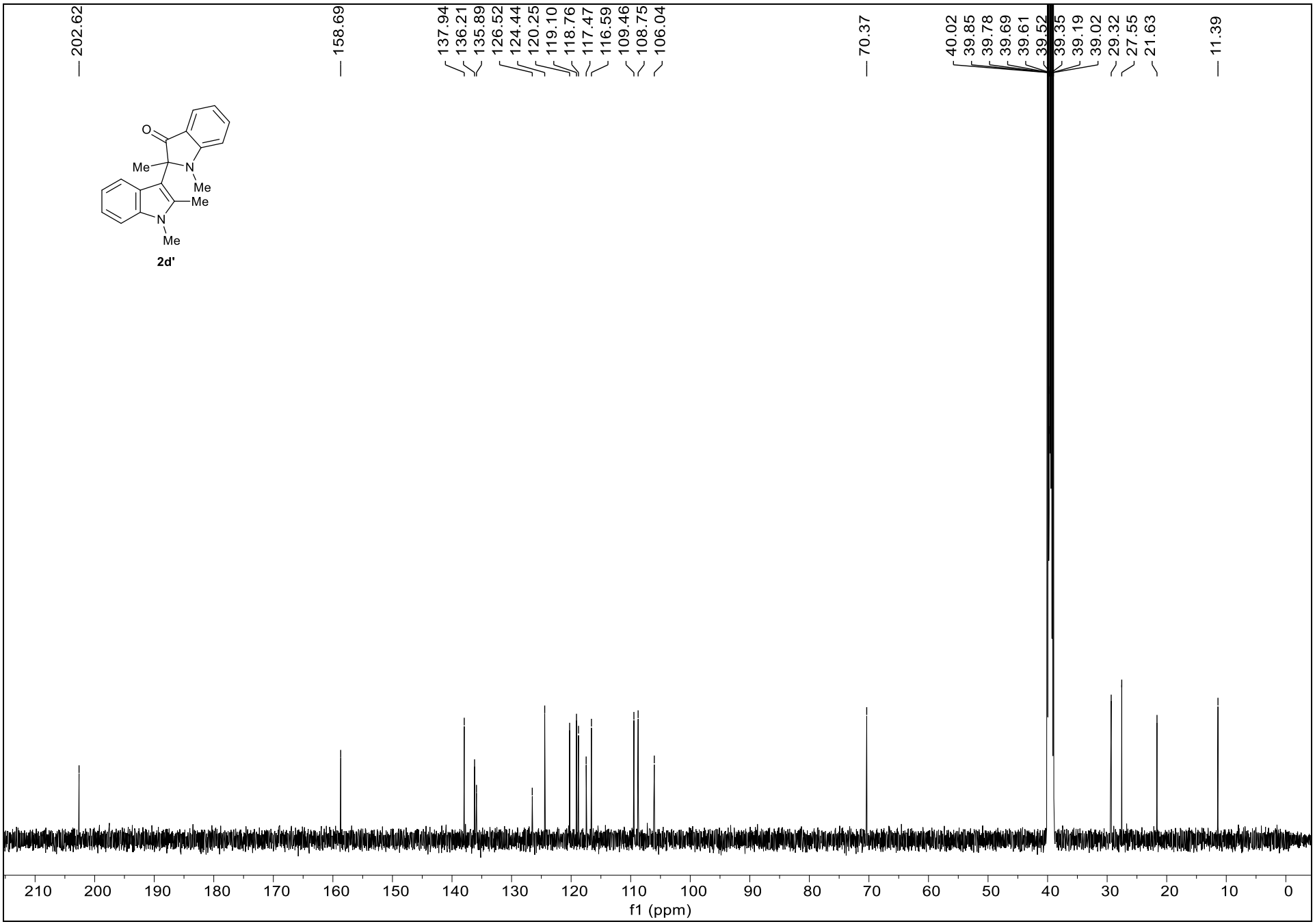
^{13}C NMR Spectrum of 4ab and 4ab′ (126 MHz, $CDCl_3$)



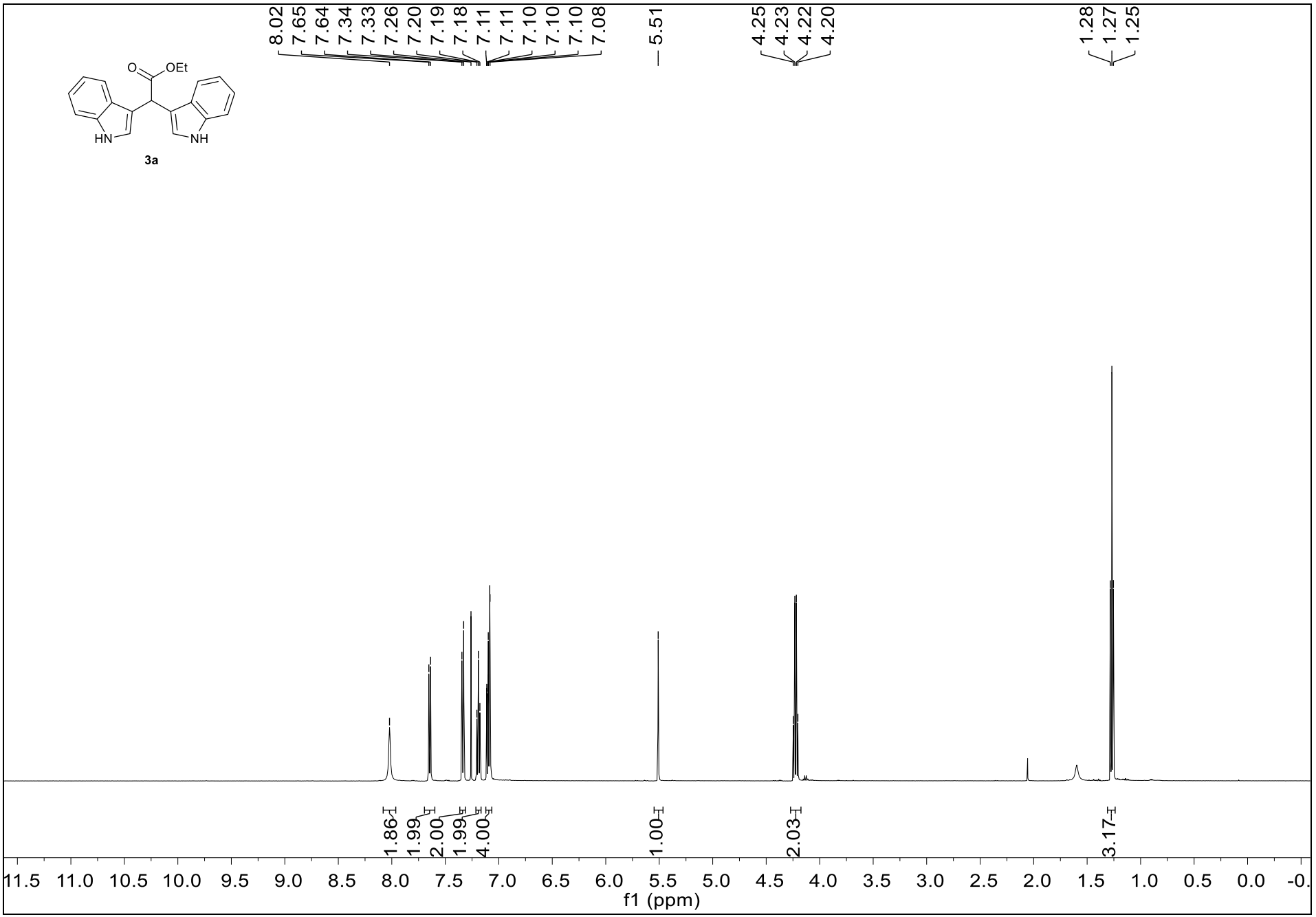
^{1}H NMR Spectrum of 2d′ (500 MHz, DMSO)



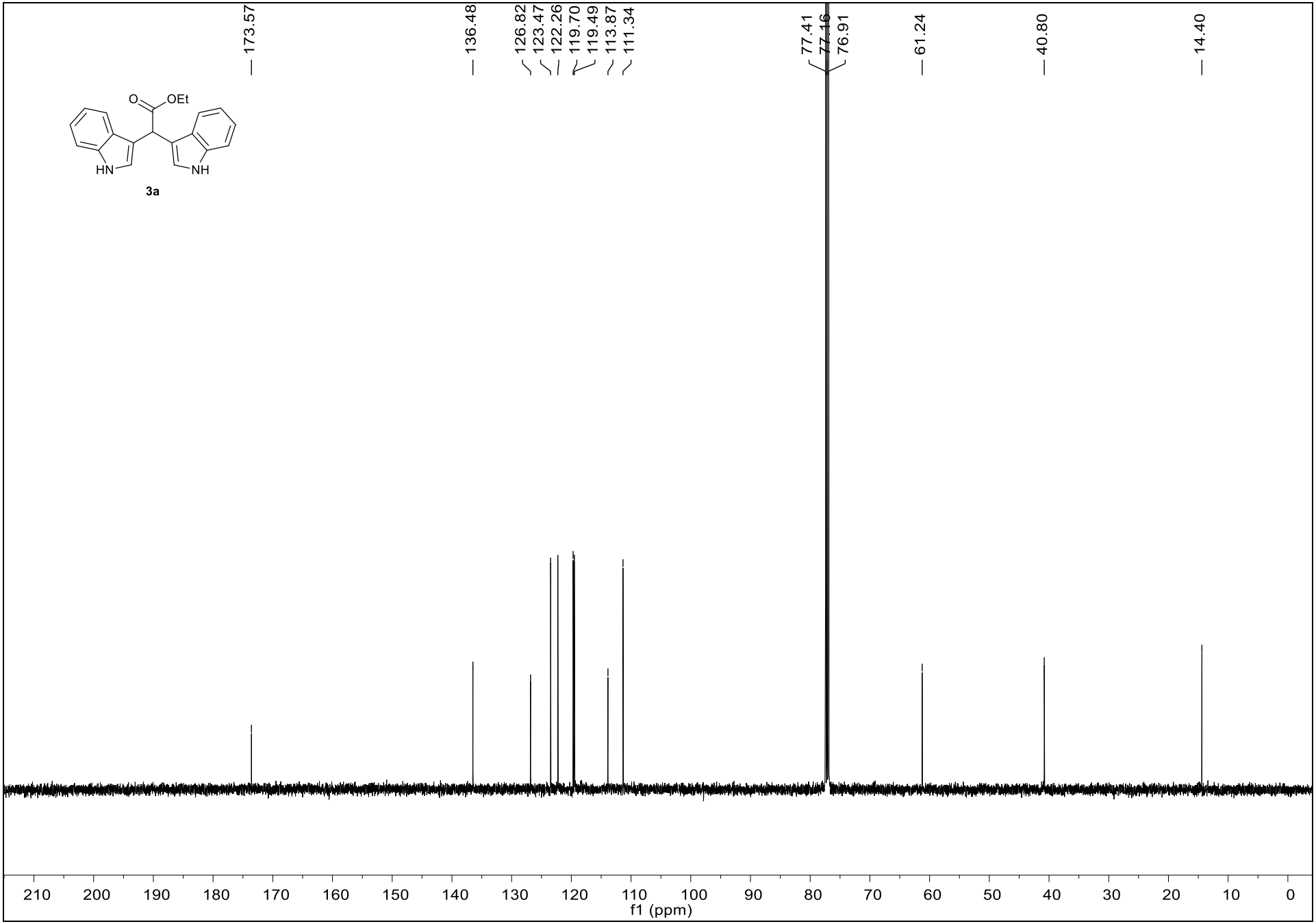
^{13}C NMR Spectrum of 2d′ (126 MHz, DMSO)



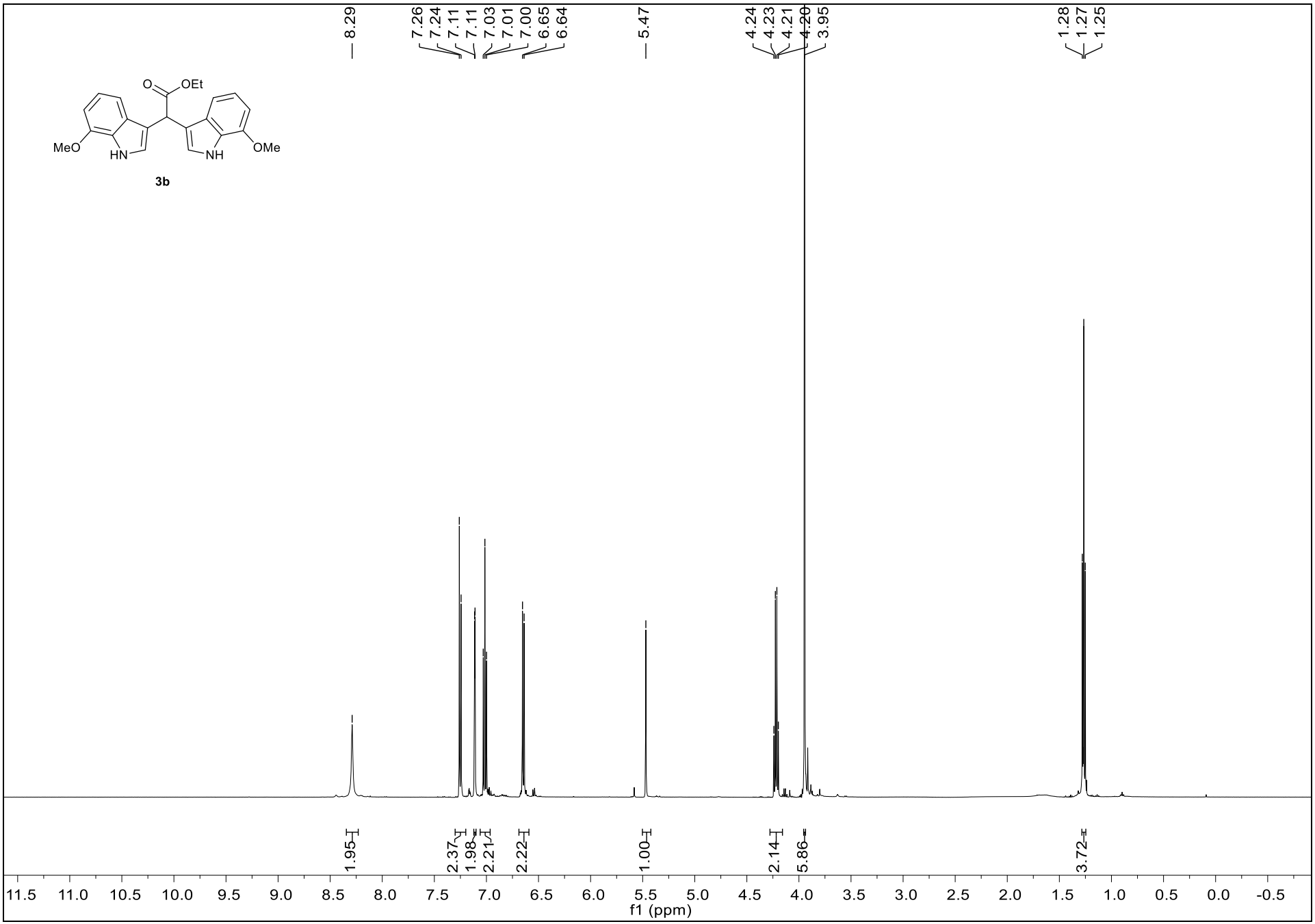
^{1}H NMR Spectrum of 3a (500 MHz, $CDCl_3$)



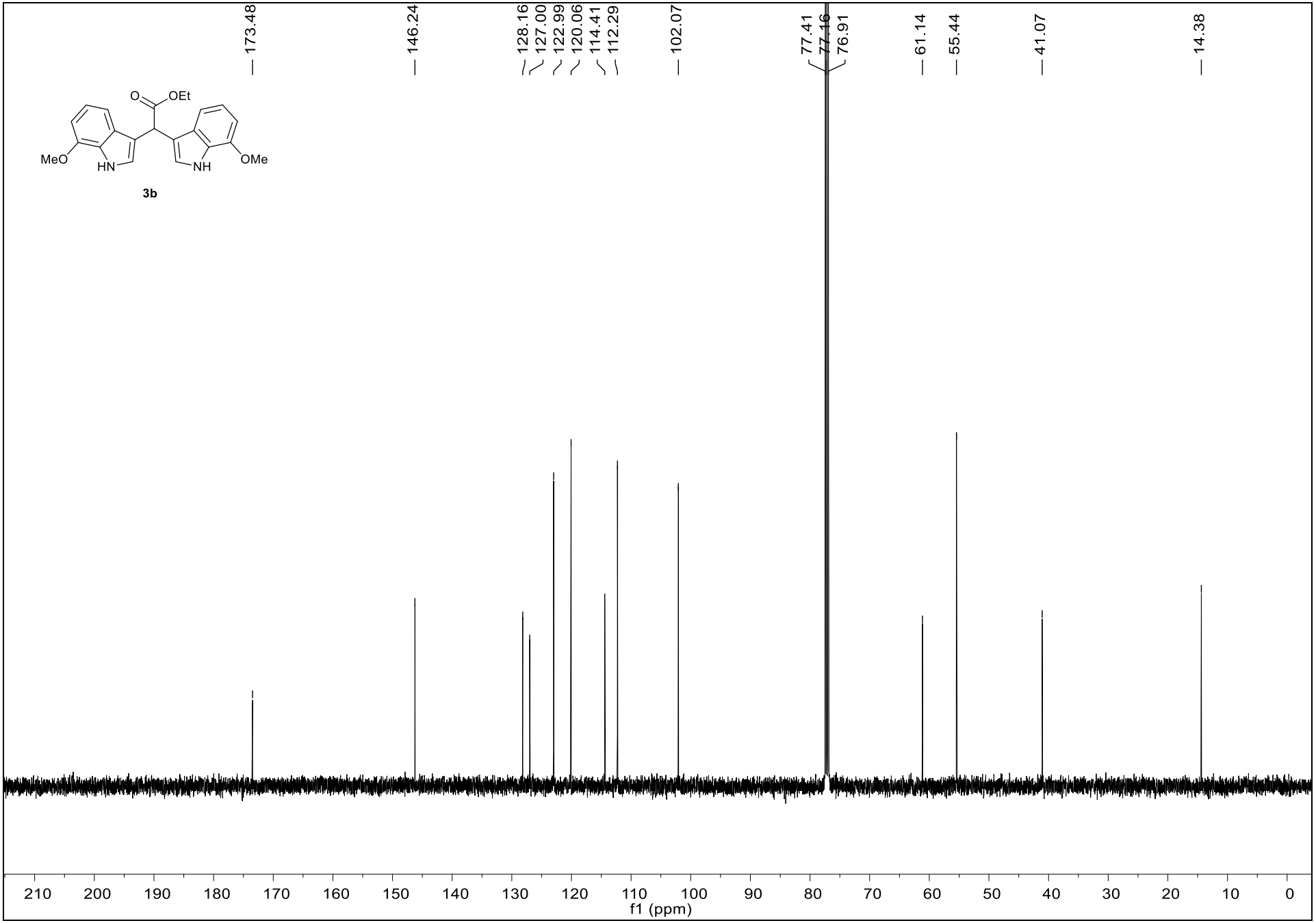
^{13}C NMR Spectrum of 3a (126 MHz, $CDCl_3$)



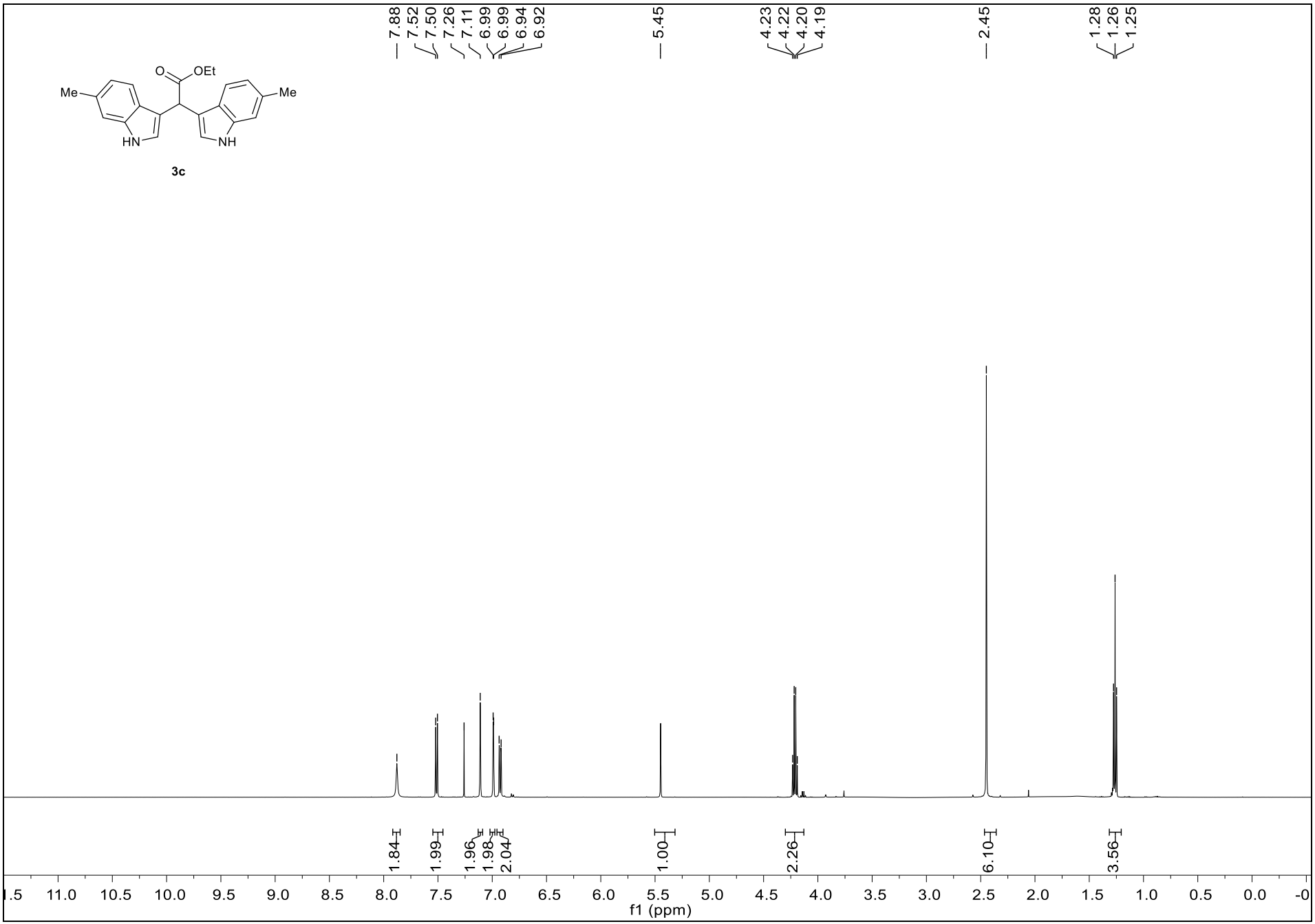
^{1}H NMR Spectrum of 3b (500 MHz, $CDCl_3$)



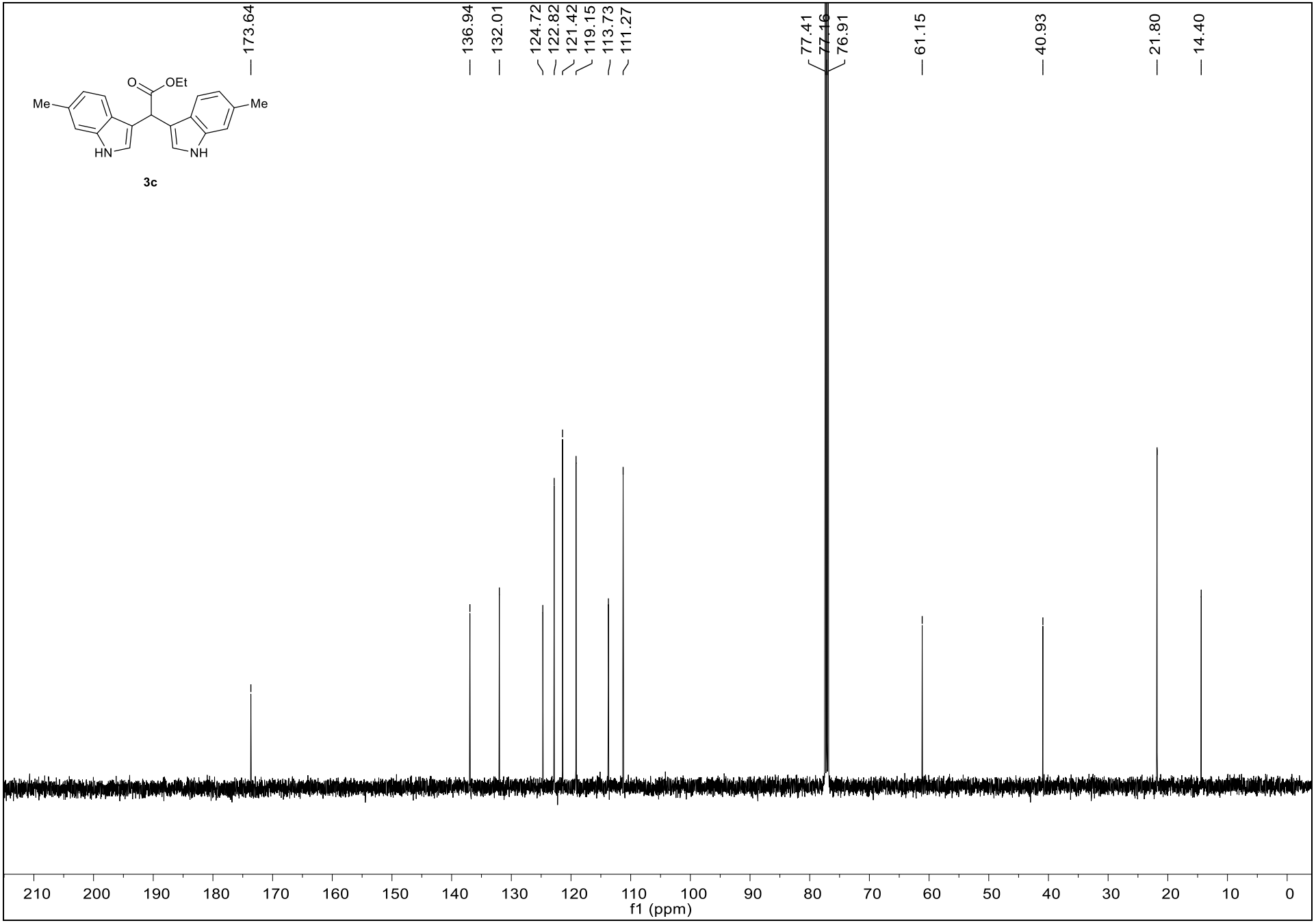
^{13}C NMR Spectrum of 3b (126 MHz, $CDCl_3$)



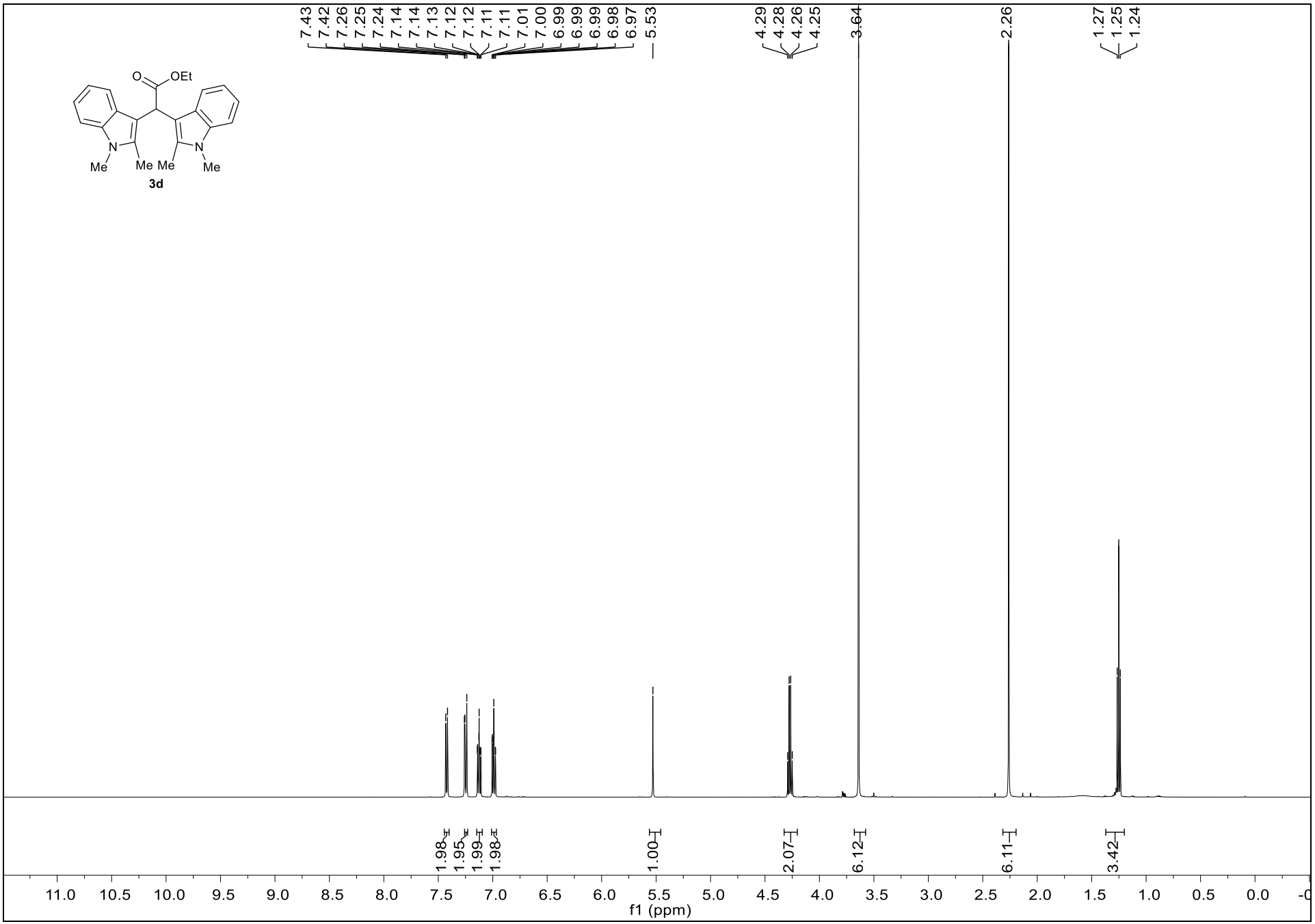
^{1}H NMR Spectrum of 3c (500 MHz, $CDCl_3$)



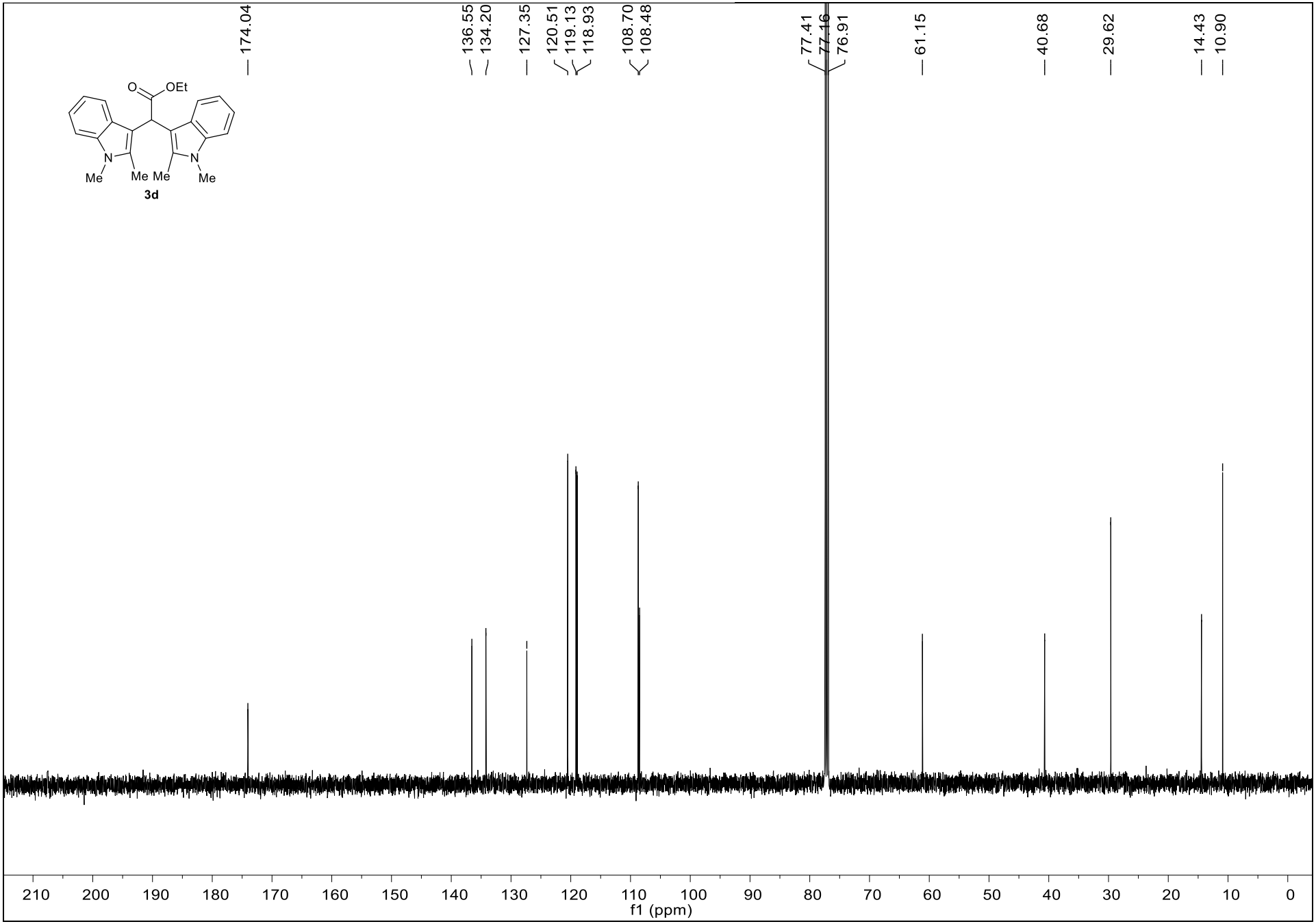
^{13}C NMR Spectrum of 3c (126 MHz, $CDCl_3$)



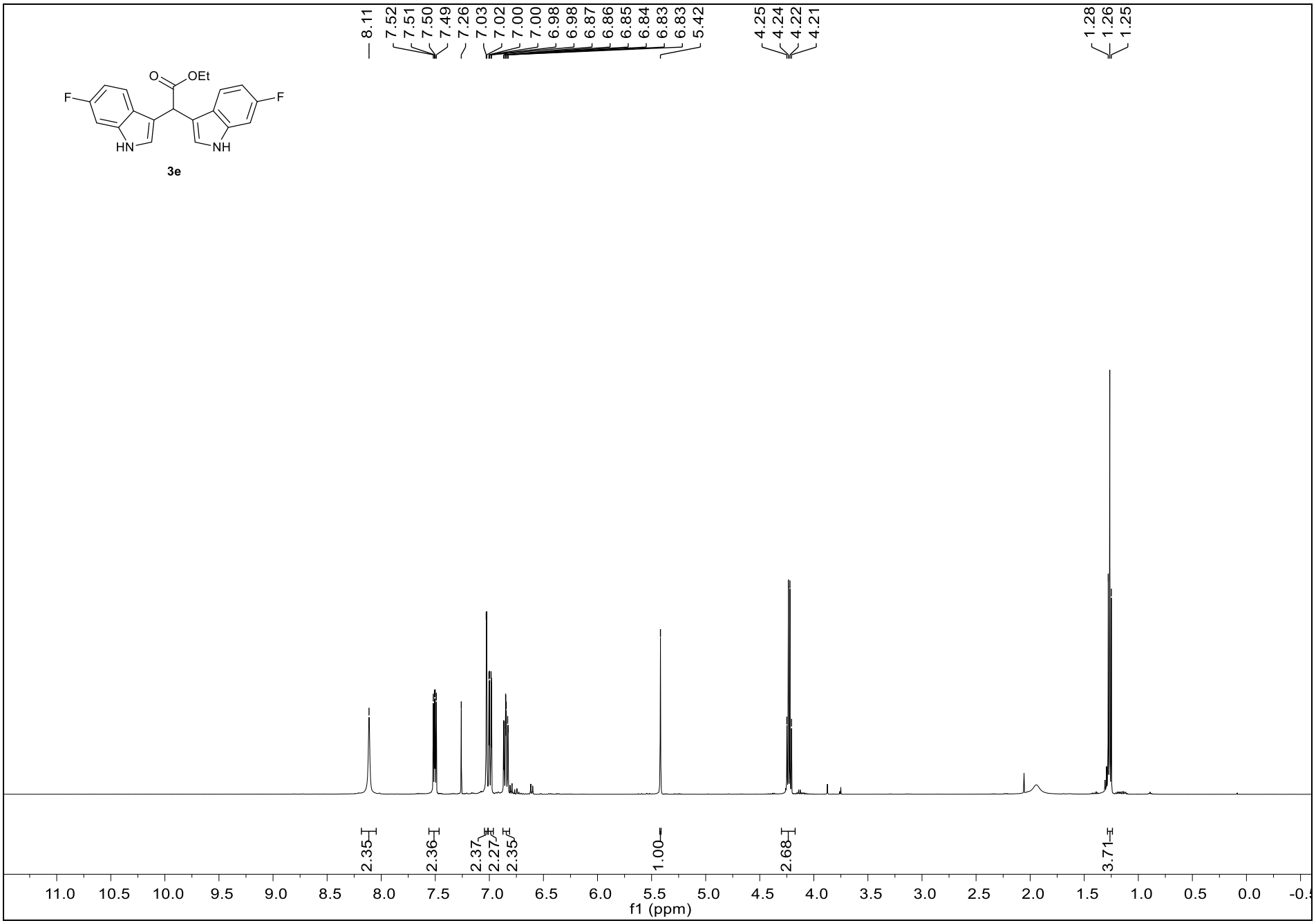
^{1}H NMR Spectrum of 3d (500 MHz, $CDCl_3$)



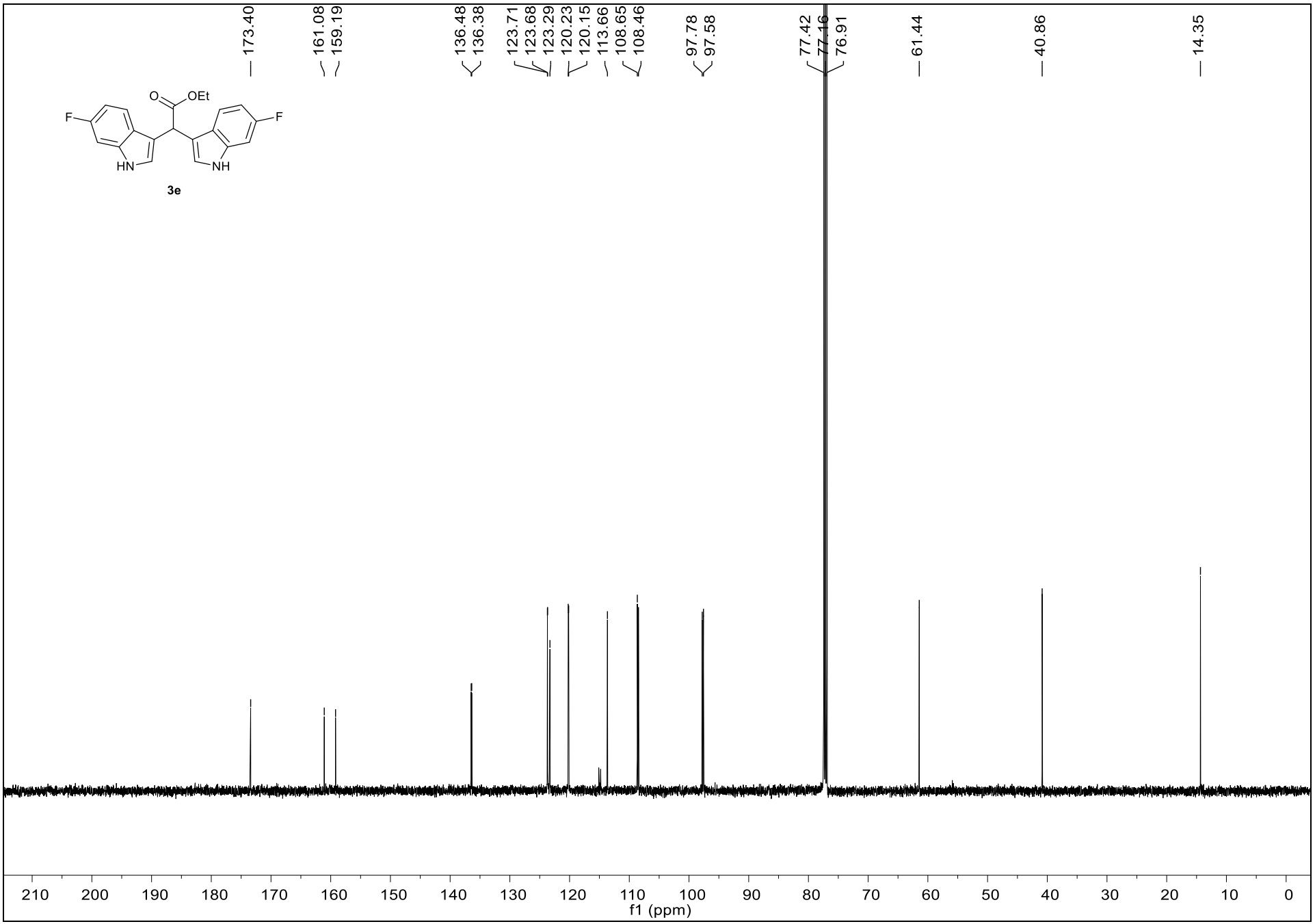
^{13}C NMR Spectrum of 3d (126 MHz, $CDCl_3$)



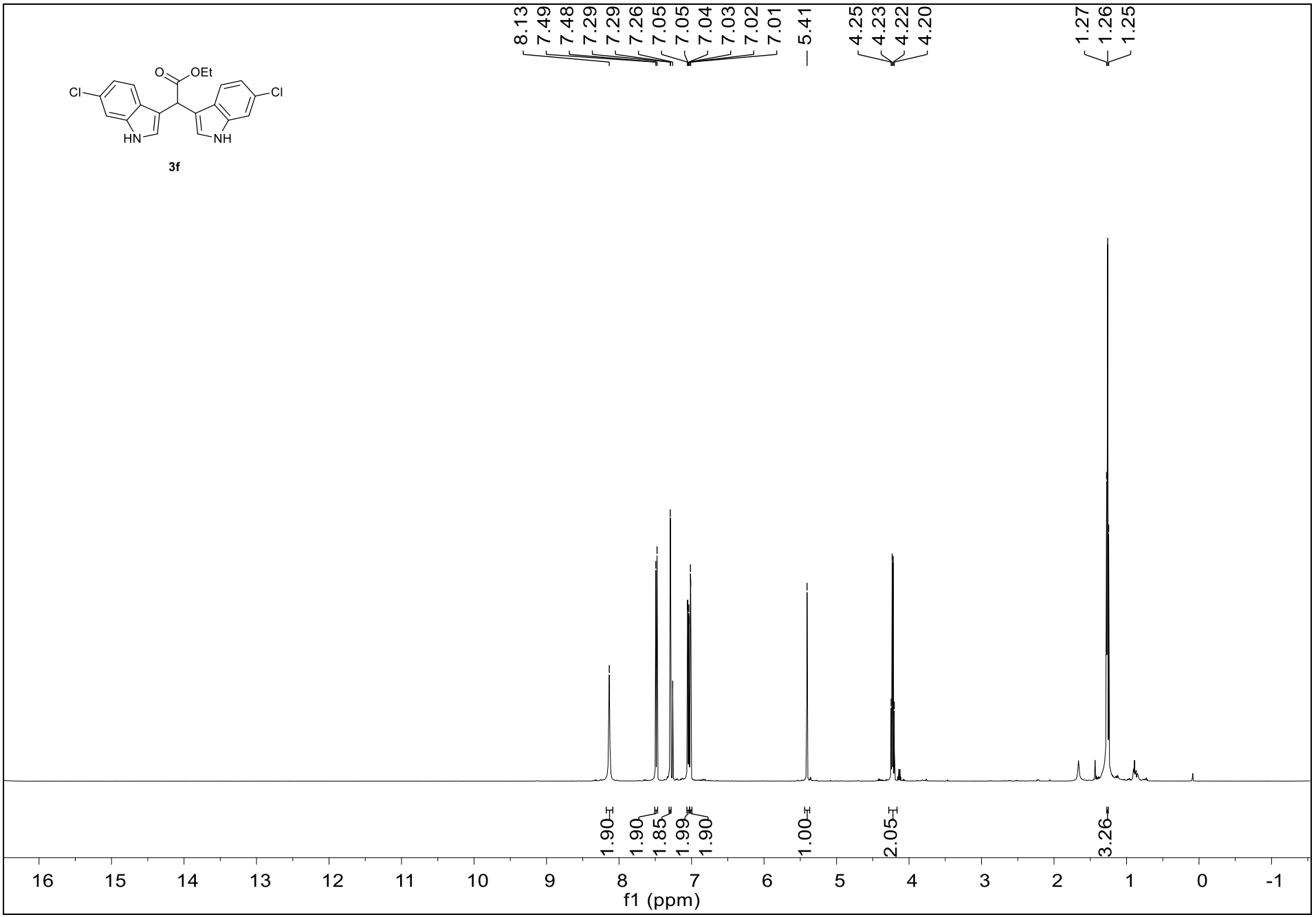
^{1}H NMR Spectrum of 3e (500 MHz, $CDCl_3$)



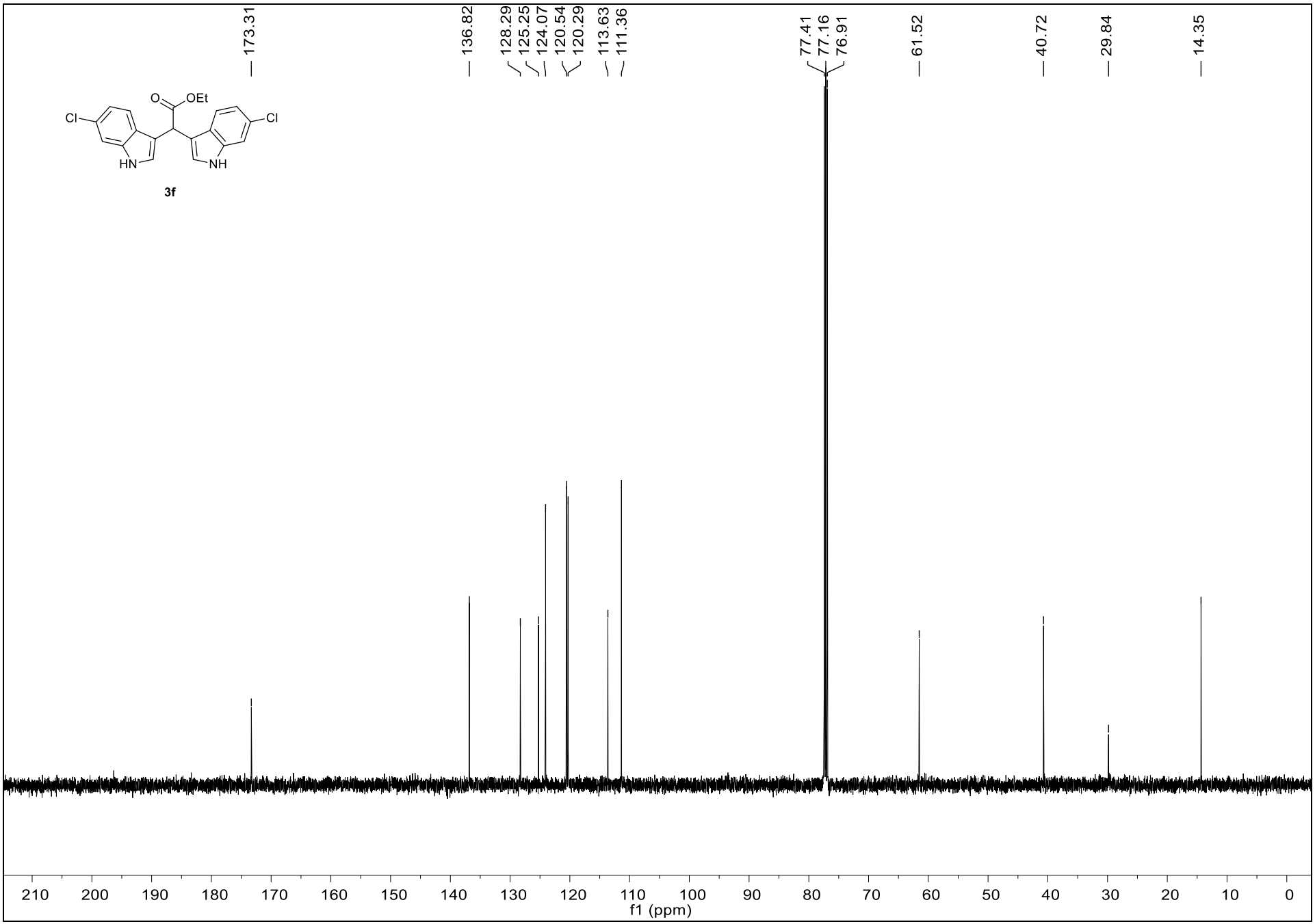
^{13}C NMR Spectrum of 3e (126 MHz, $CDCl_3$)



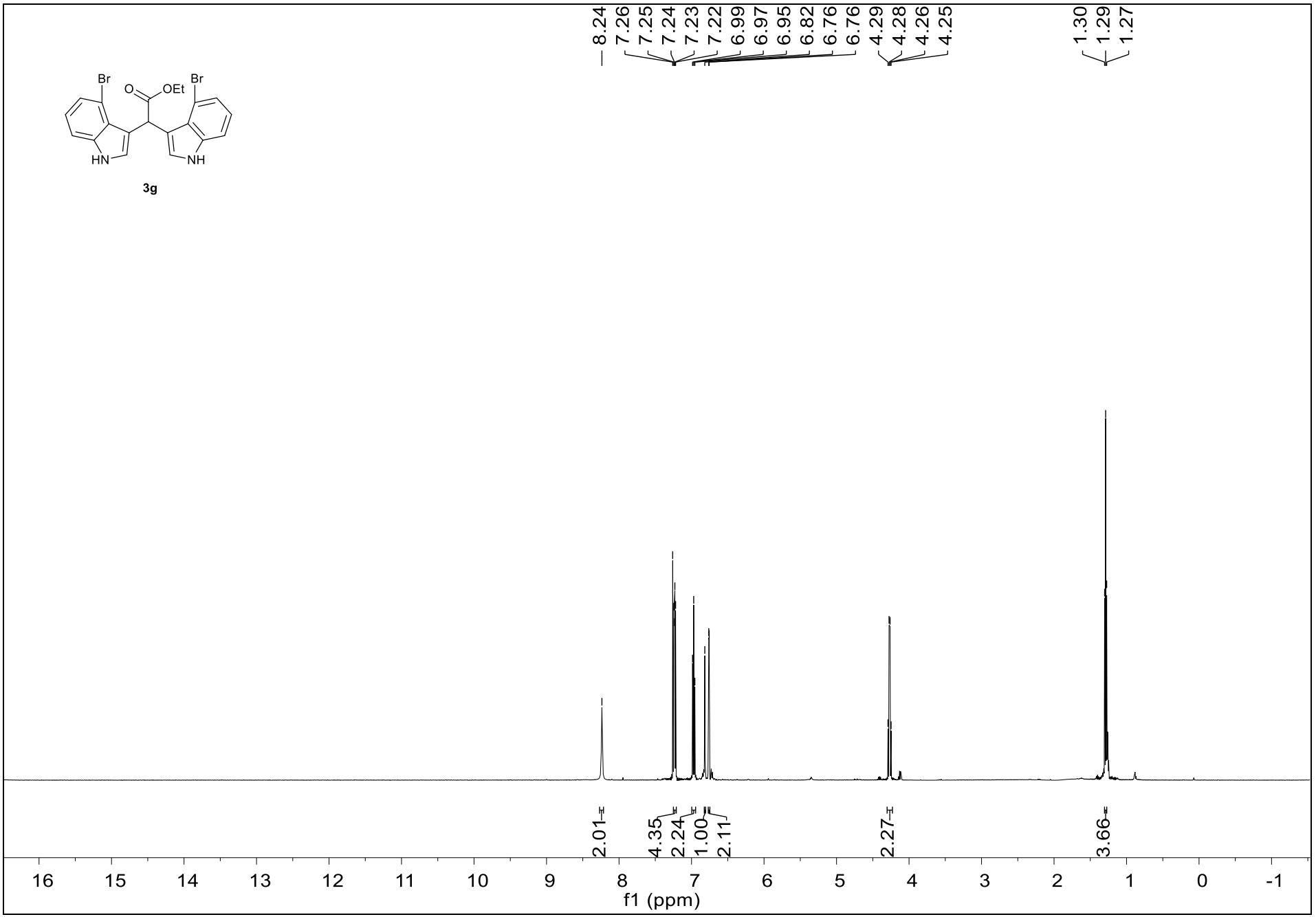
^{1}H NMR Spectrum of 3f (500 MHz, $CDCl_3$)



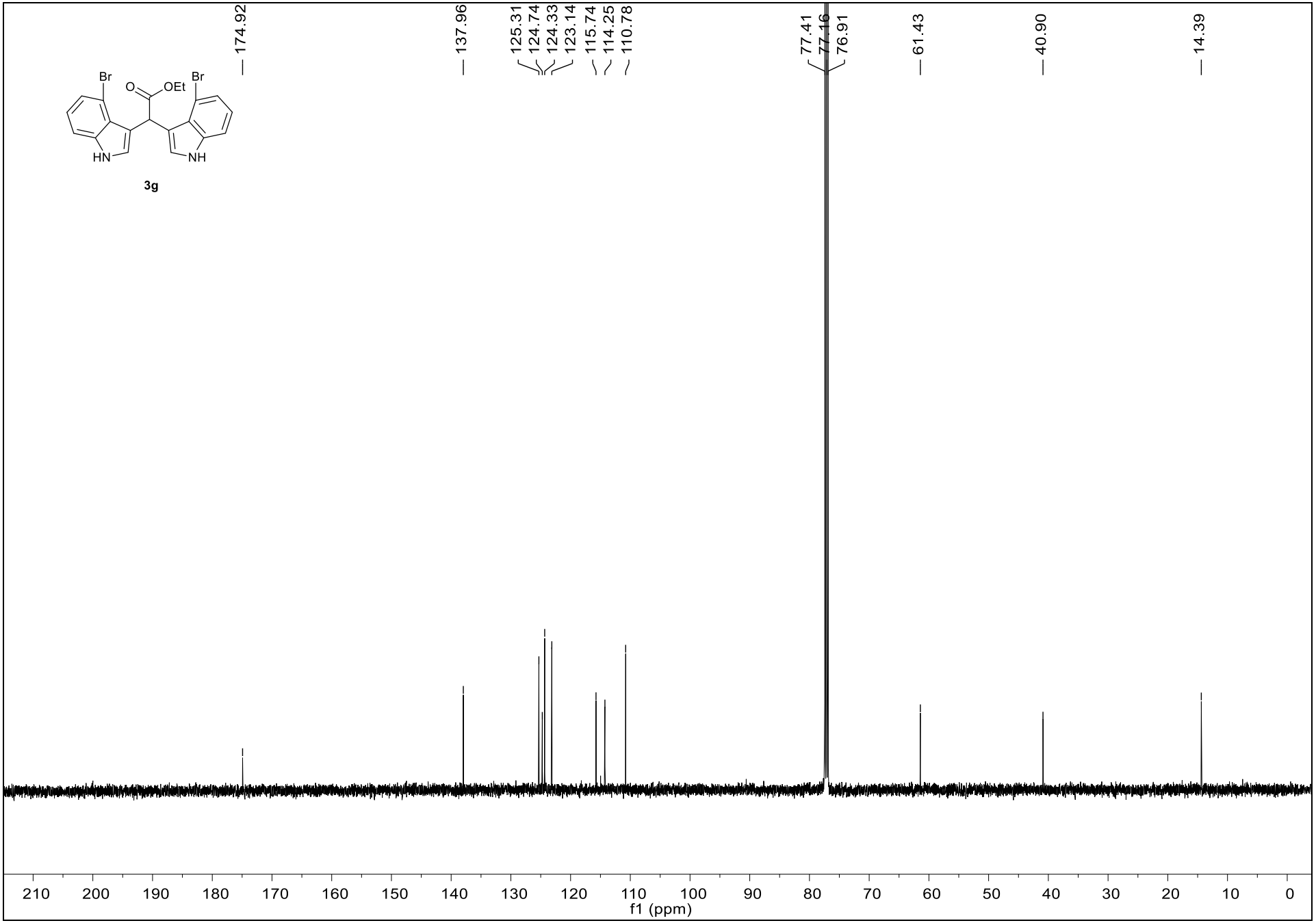
^{13}C NMR Spectrum of 3f (126 MHz, $CDCl_3$)



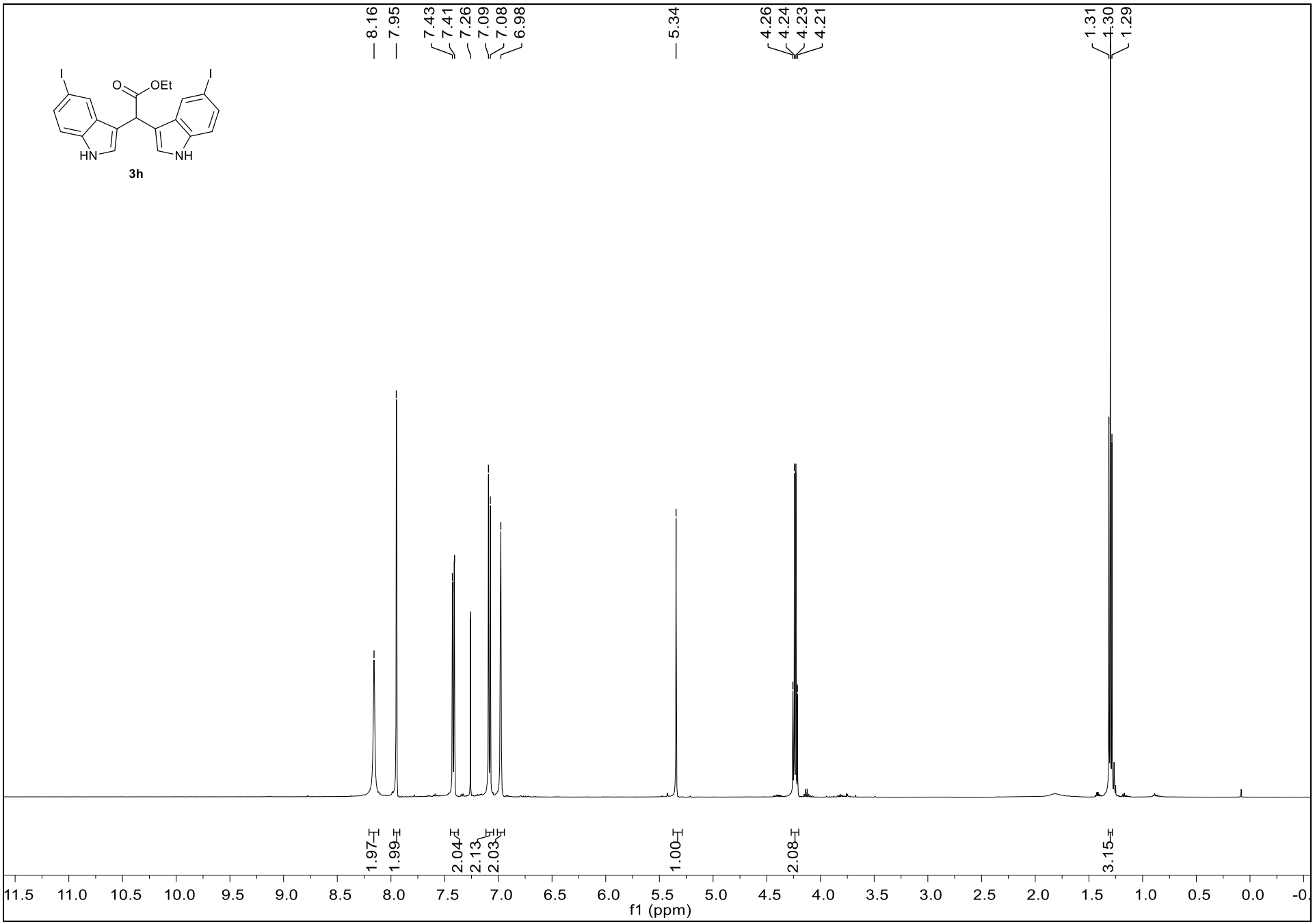
^{1}H NMR Spectrum of 3g (500 MHz, $CDCl_3$)



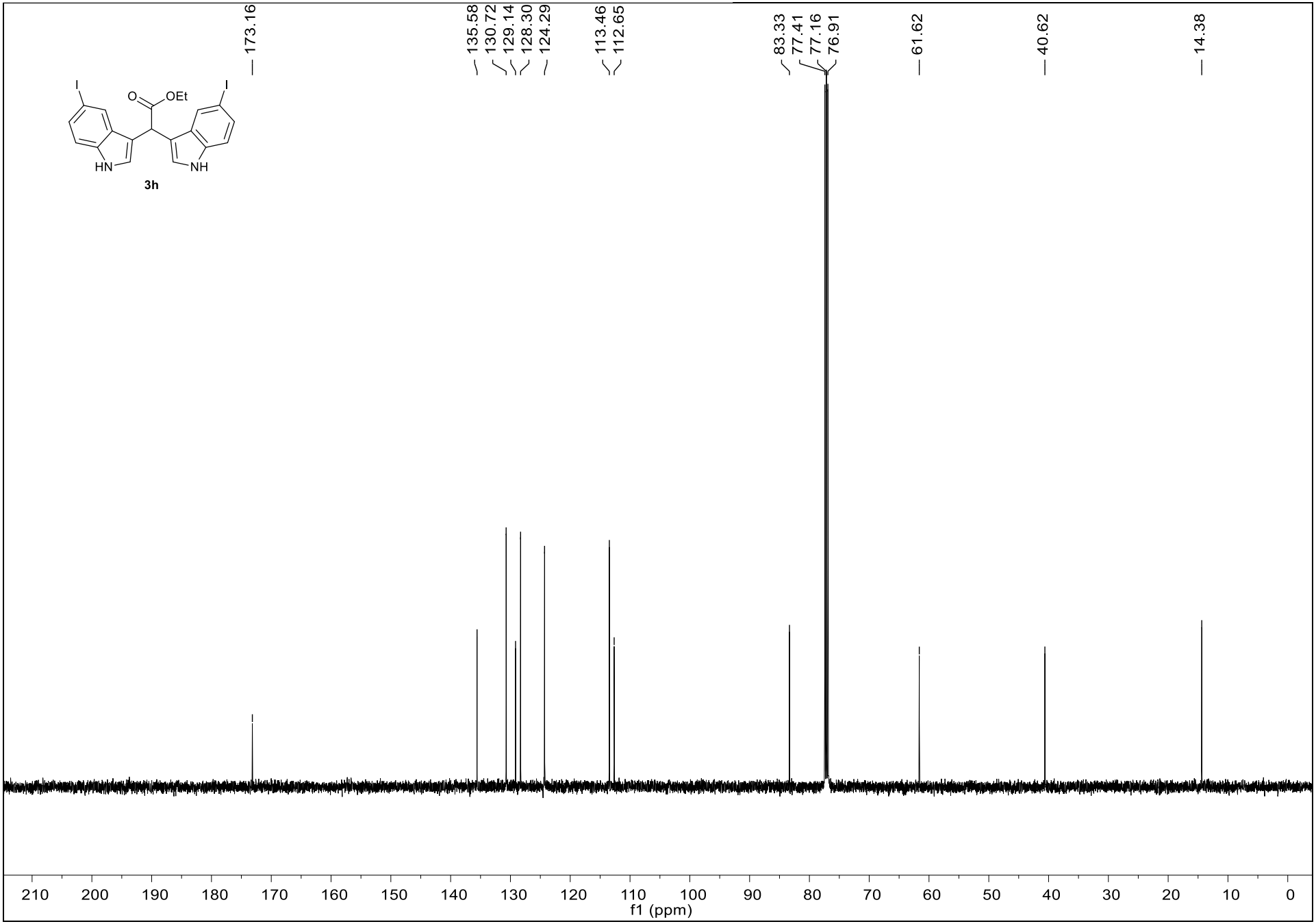
^{13}C NMR Spectrum of 3g (126 MHz, $CDCl_3$)

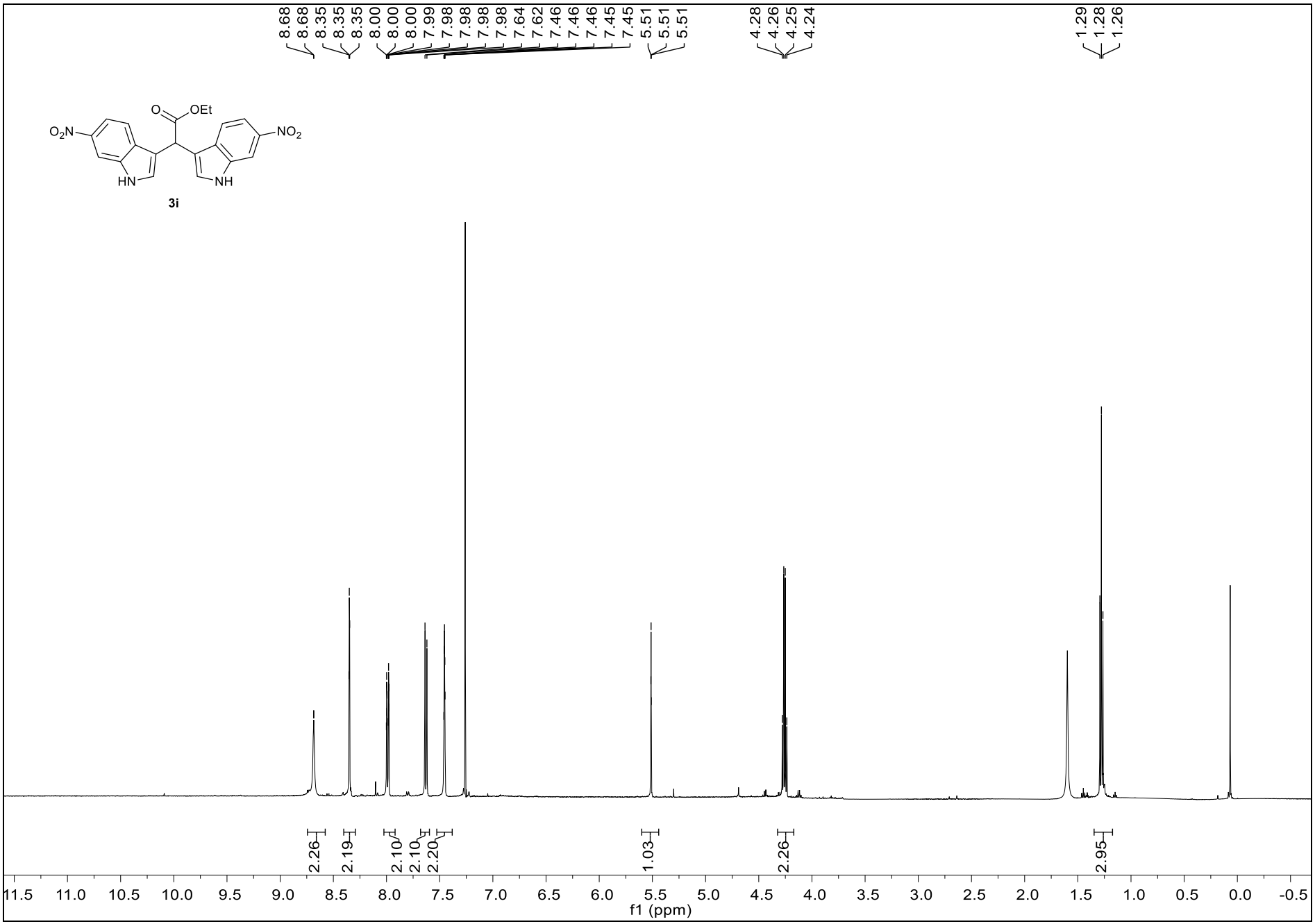


^{1}H NMR Spectrum of 3h (500 MHz, $CDCl_3$)

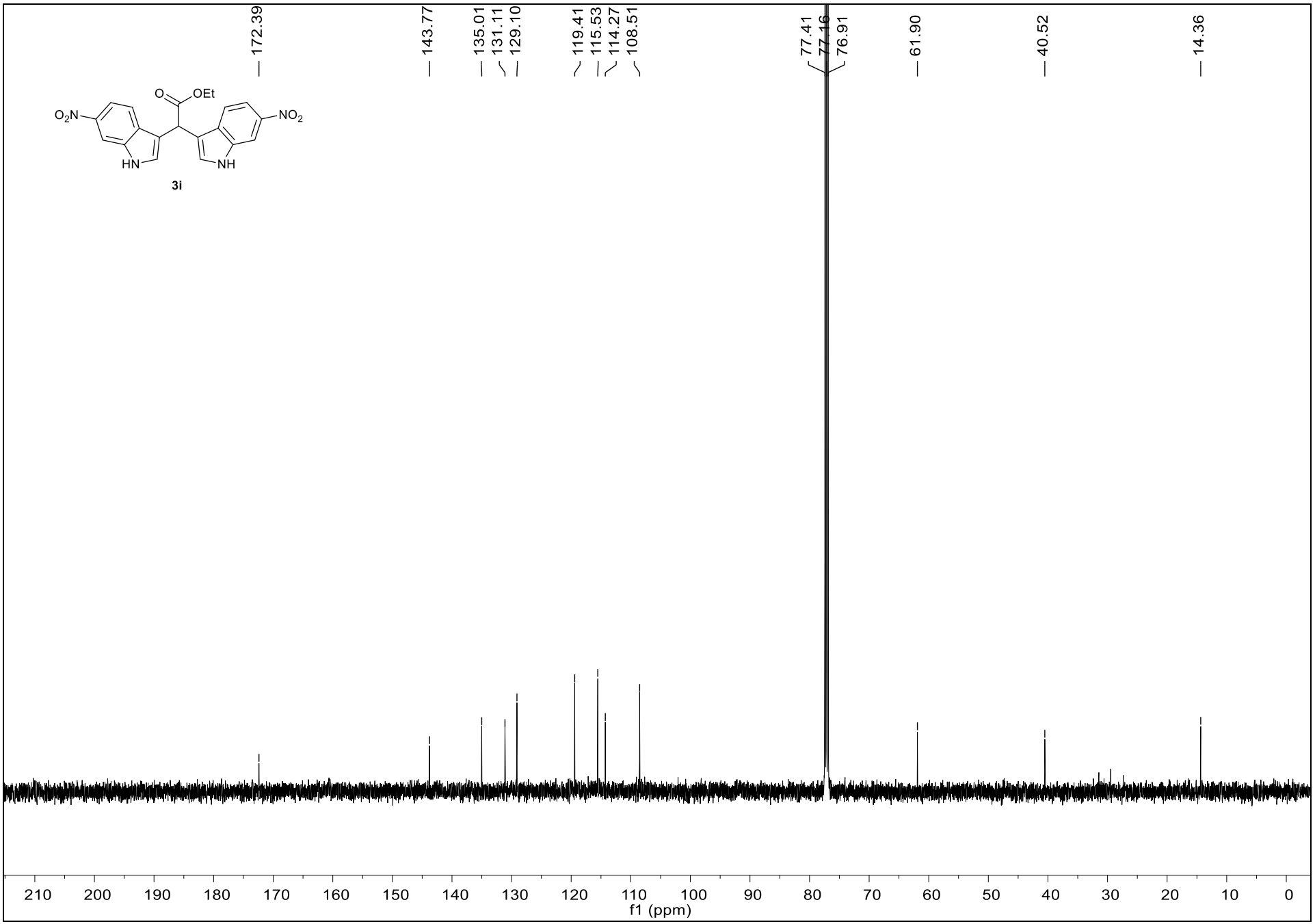


^{1}H NMR Spectrum of 3i (500 MHz, $CDCl_3$)

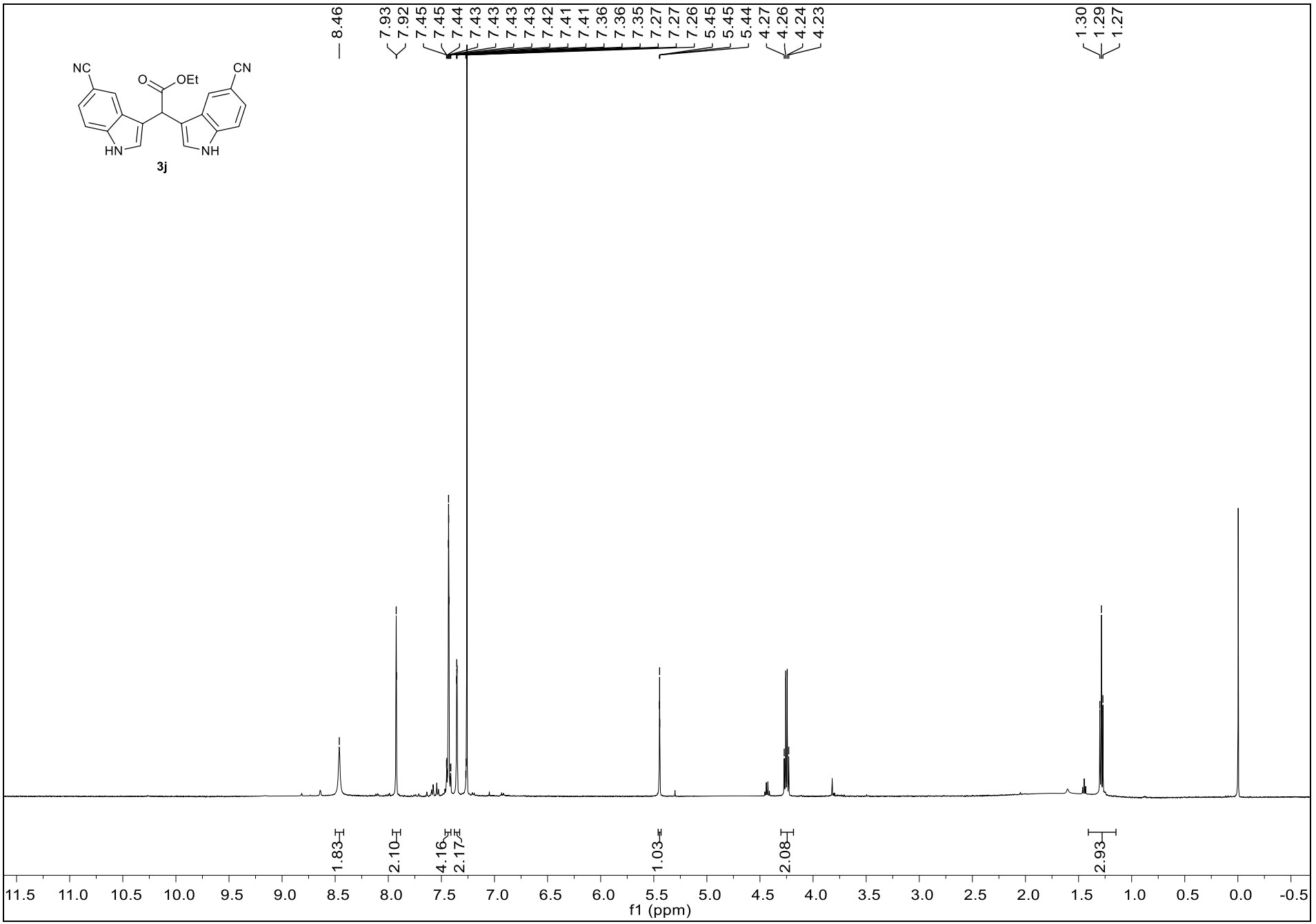



8.68
8.68
8.35
8.35
8.35
8.00
8.00
8.00
7.99
7.98
7.98
7.98
7.98
7.64
7.62
7.46
7.46
7.46
7.45
7.45
5.51
5.51
5.51
4.28
4.26
4.25
4.24
1.29
1.28
1.26
O
OEt
O2N
NO2
HN
NH
3i
2.26
2.19
2.10
2.10
2.20
1.03
2.26
2.95
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

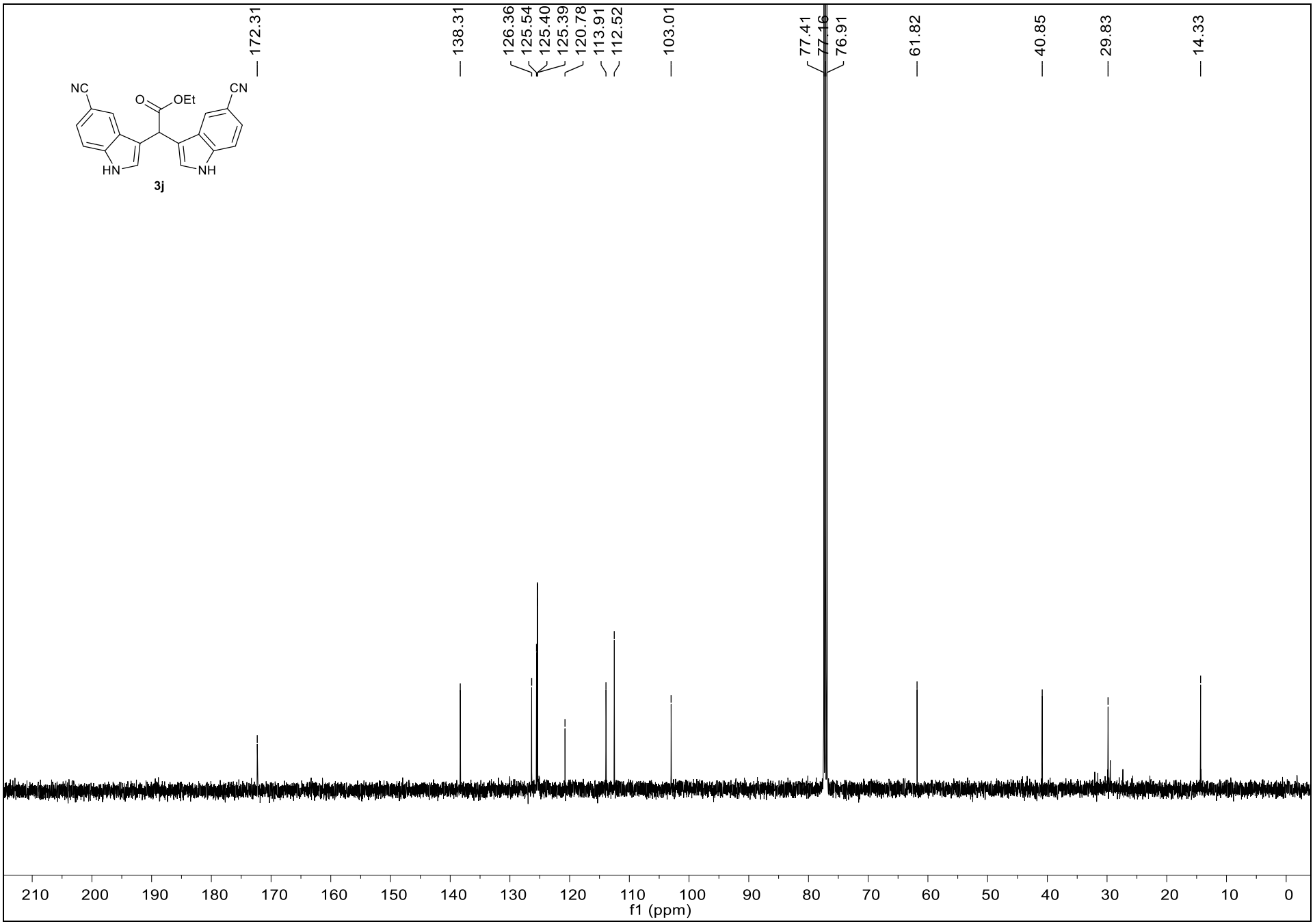
^{13}C NMR Spectrum of 3i (126 MHz, $CDCl_3$)



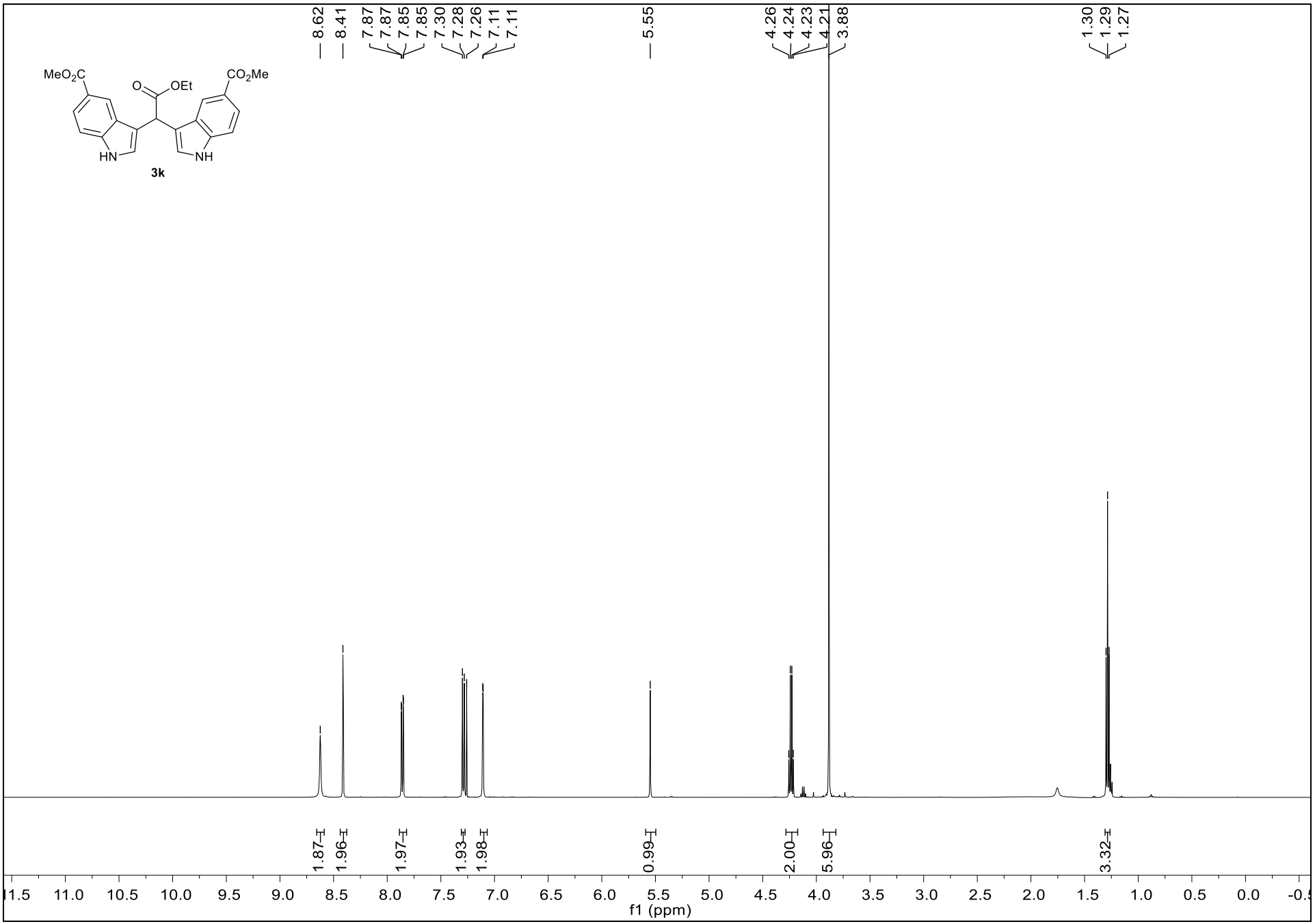
^{1}H NMR Spectrum of 3j (500 MHz, $CDCl_3$)



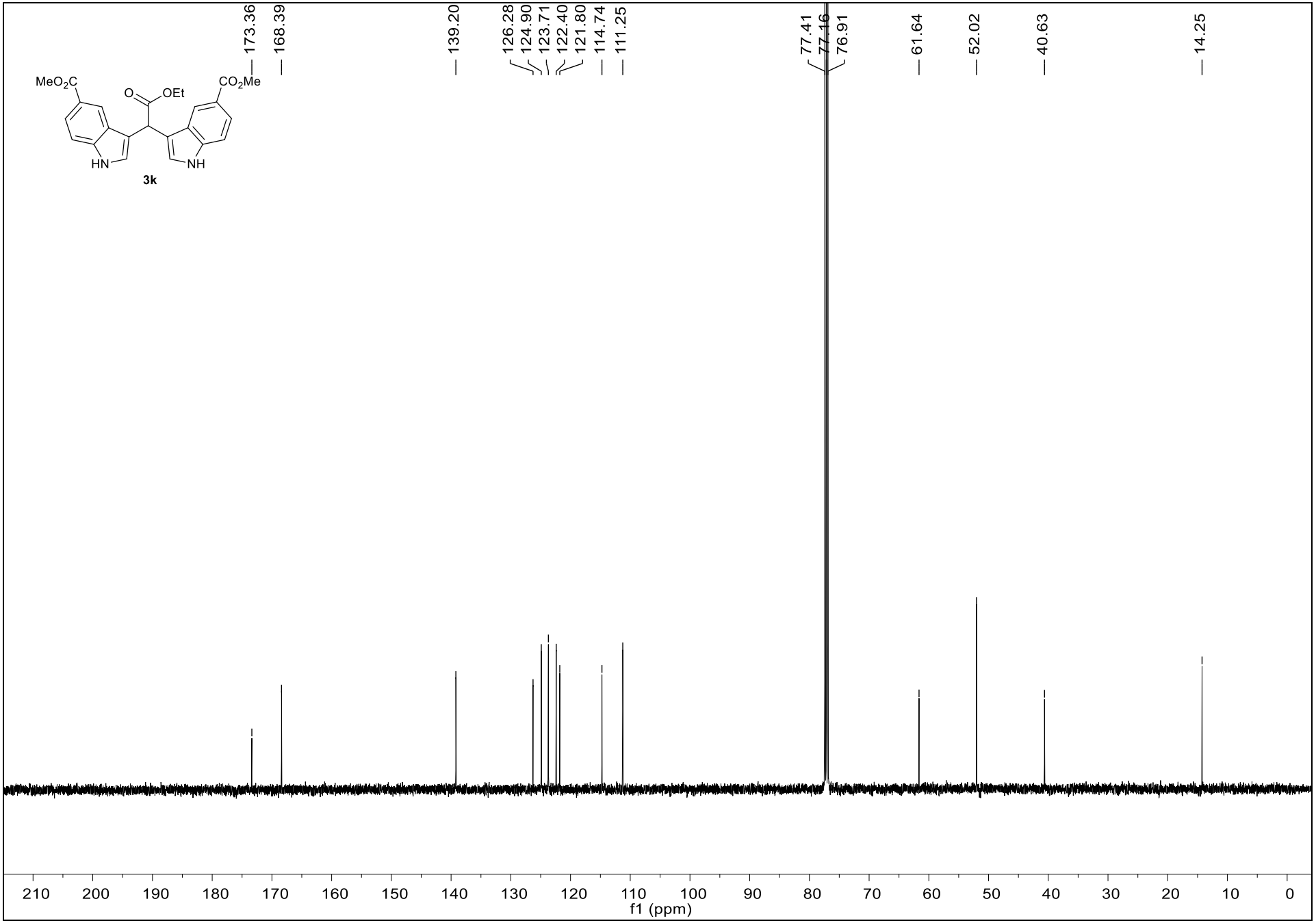
^{13}C NMR Spectrum of 3j (126 MHz, $CDCl_3$)



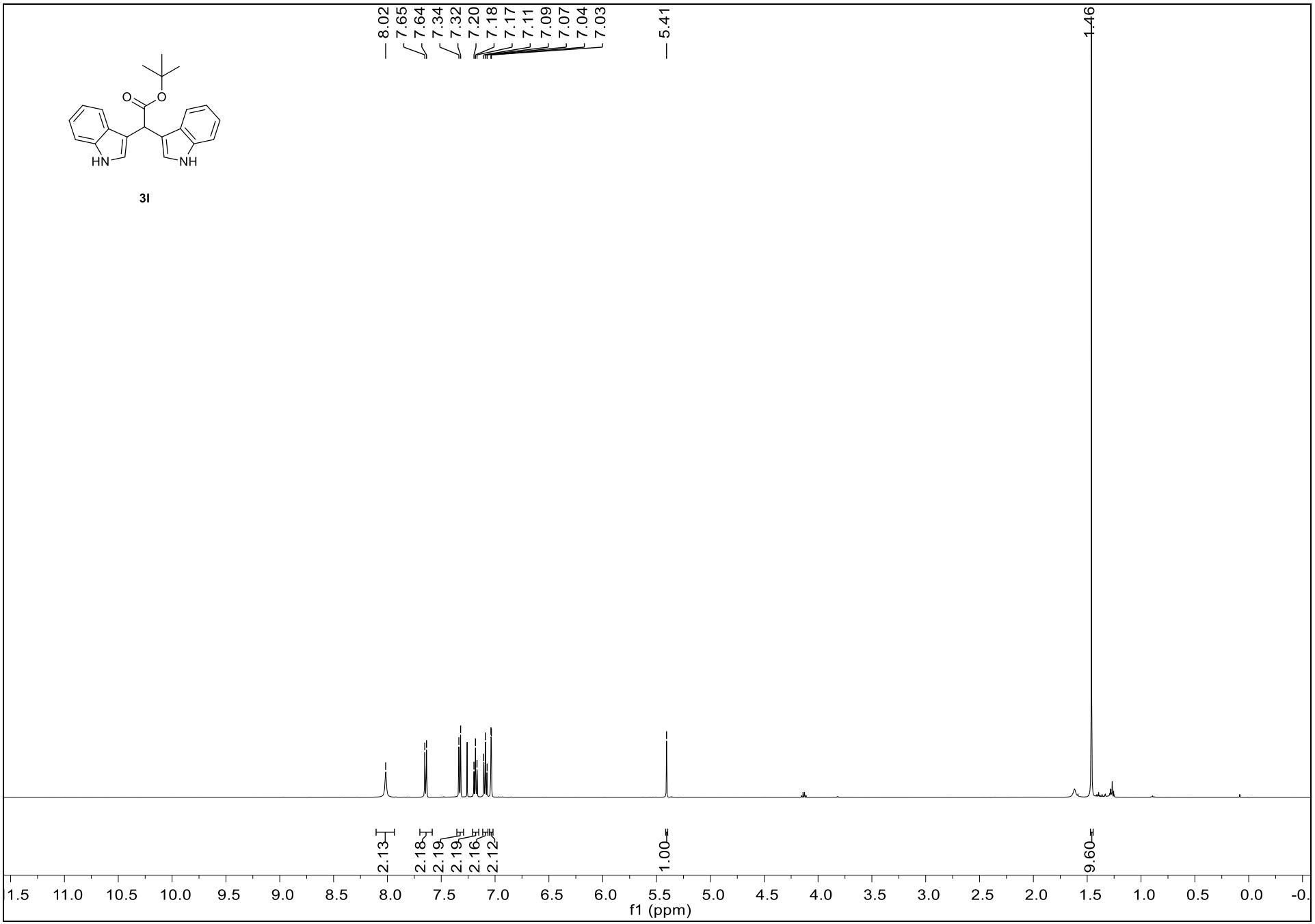
^{1}H NMR Spectrum of 3k (500 MHz, $CDCl_3$)



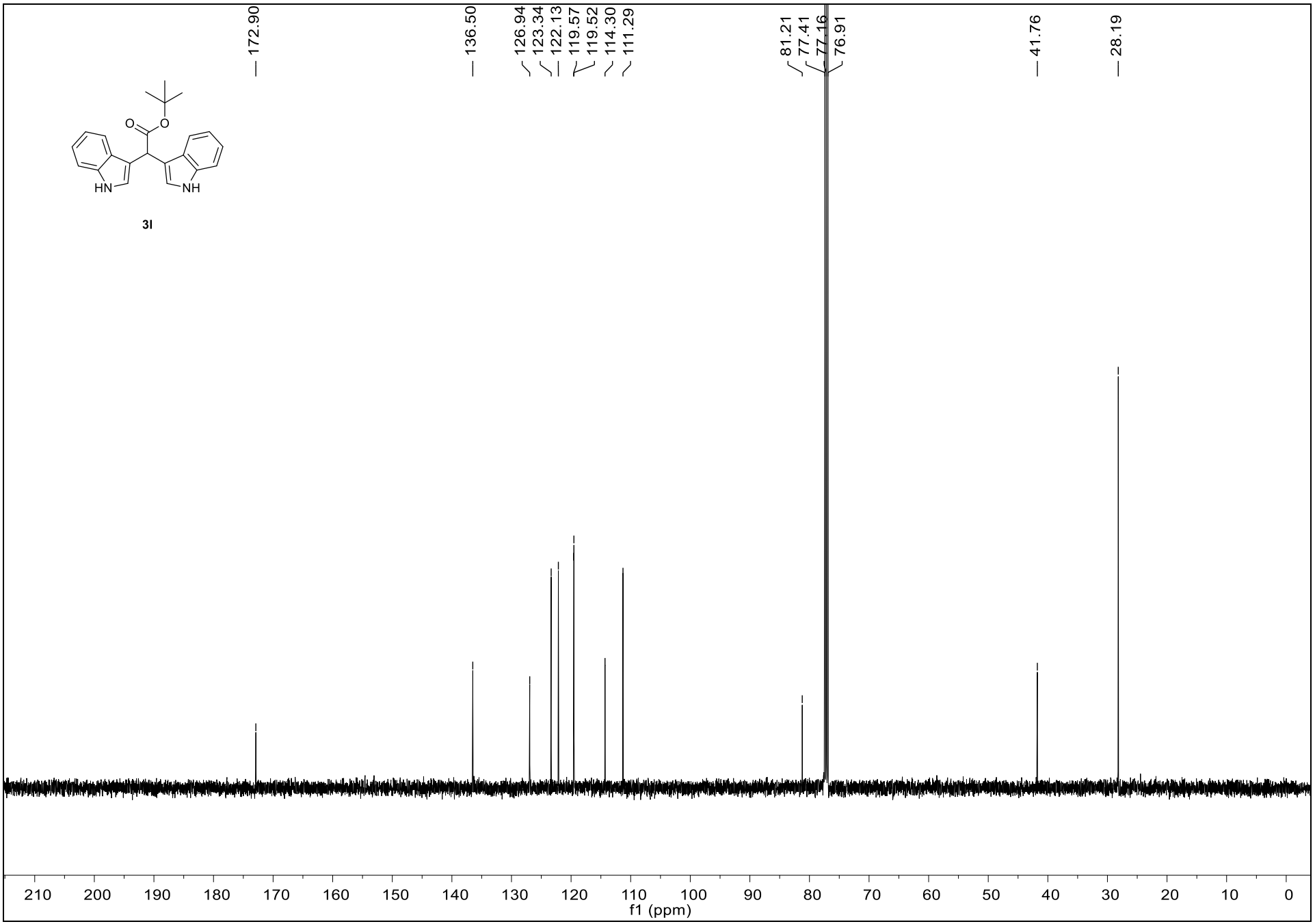
^{13}C NMR Spectrum of 3k (126 MHz, $CDCl_3$)



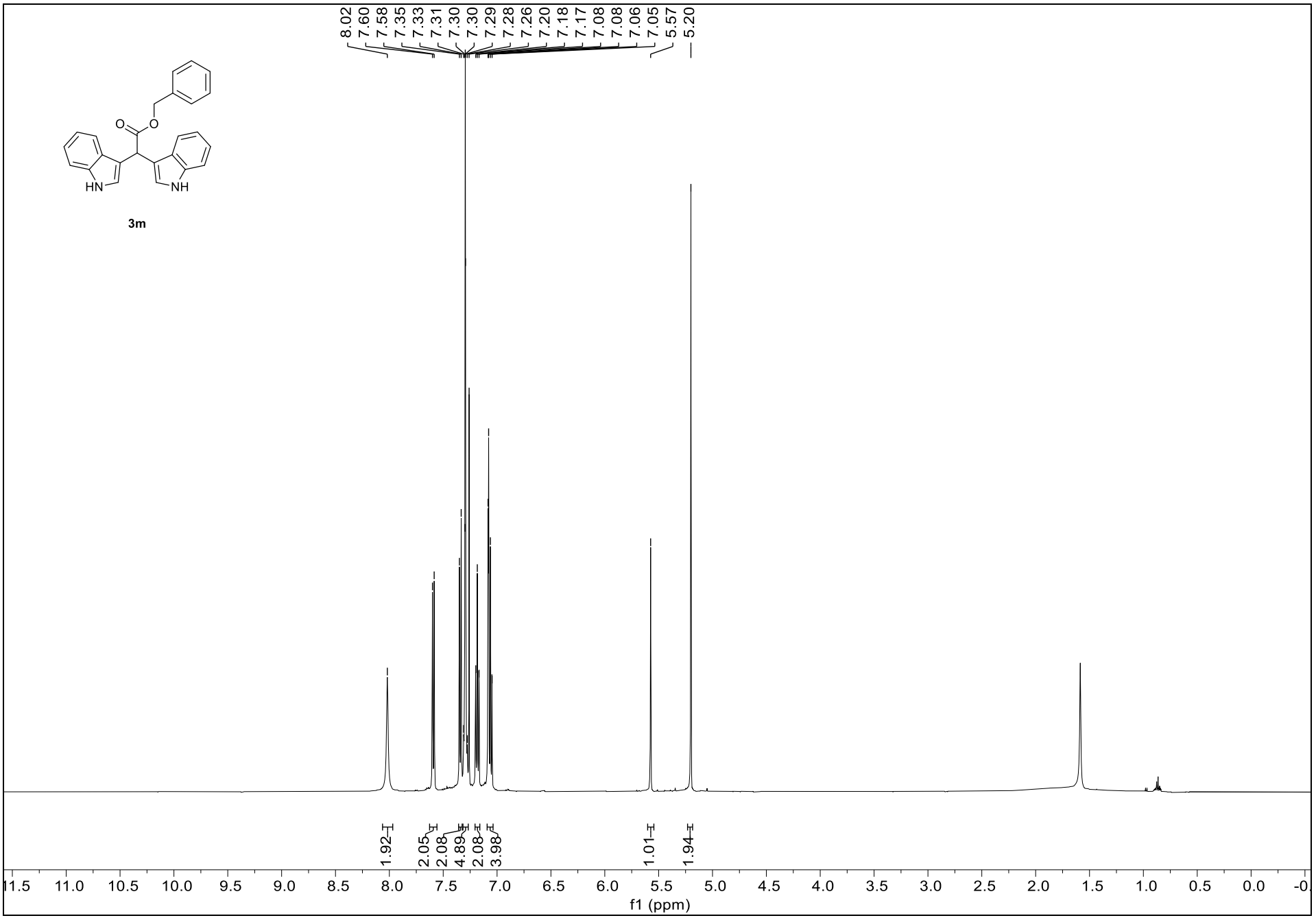
^{1}H NMR Spectrum of 3l (500 MHz, $CDCl_3$)



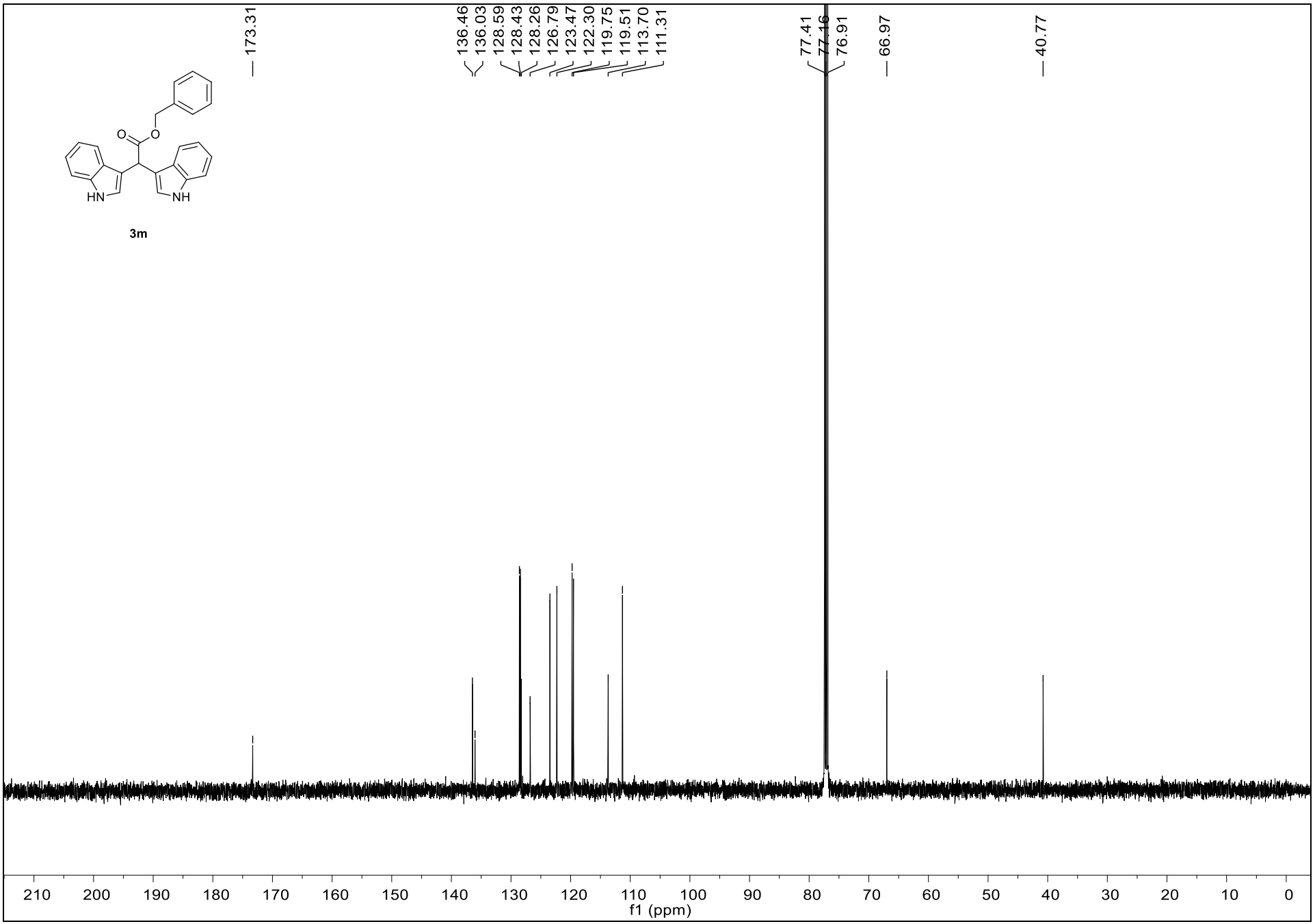
^{13}C NMR Spectrum of 3l (126 MHz, $CDCl_3$)



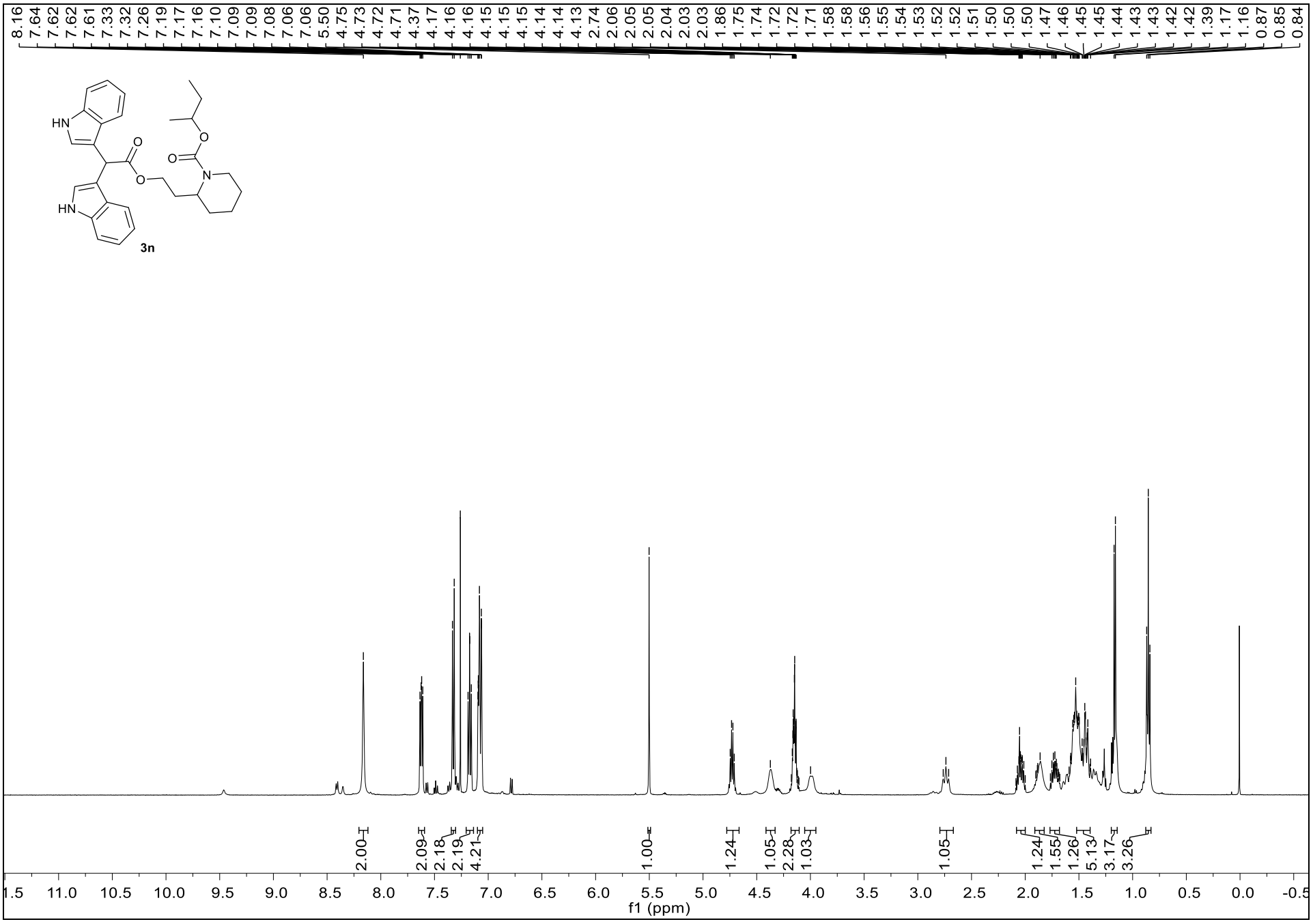
^{1}H NMR Spectrum of 3m (500 MHz, $CDCl_3$)



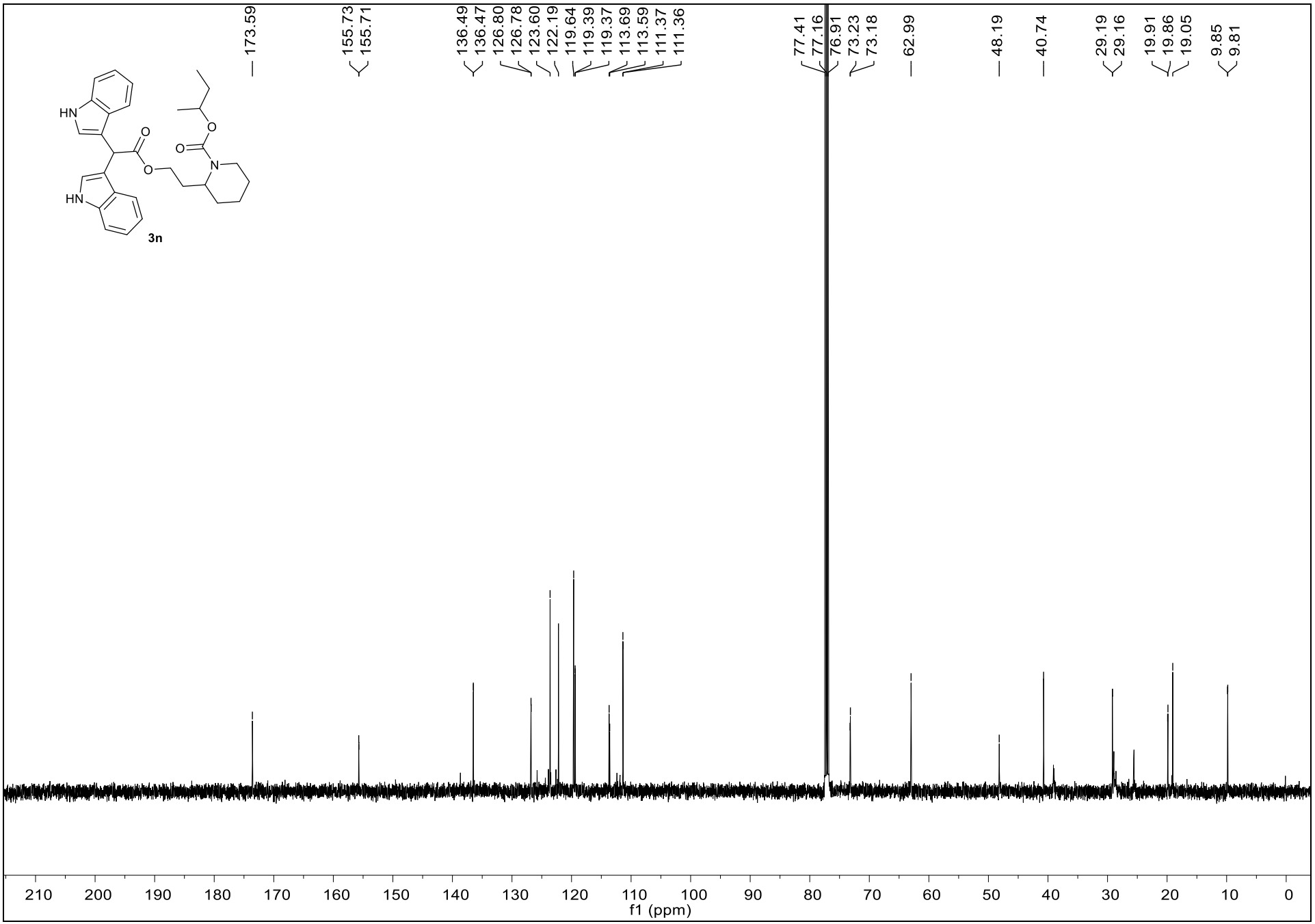
^{13}C NMR Spectrum of 3m (126 MHz, $CDCl_3$)



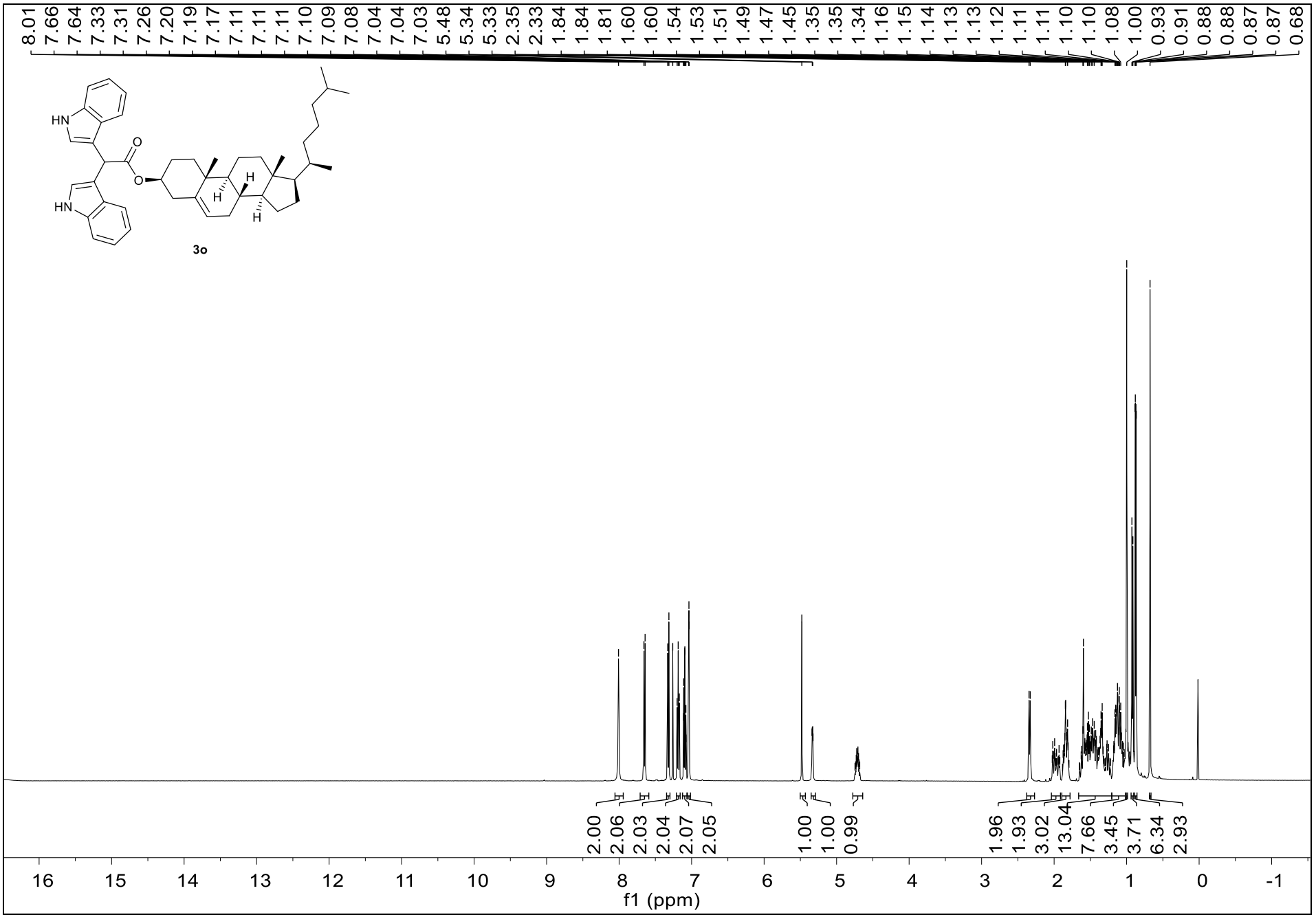
^{1}H NMR Spectrum of 3n (500 MHz, $CDCl_3$)



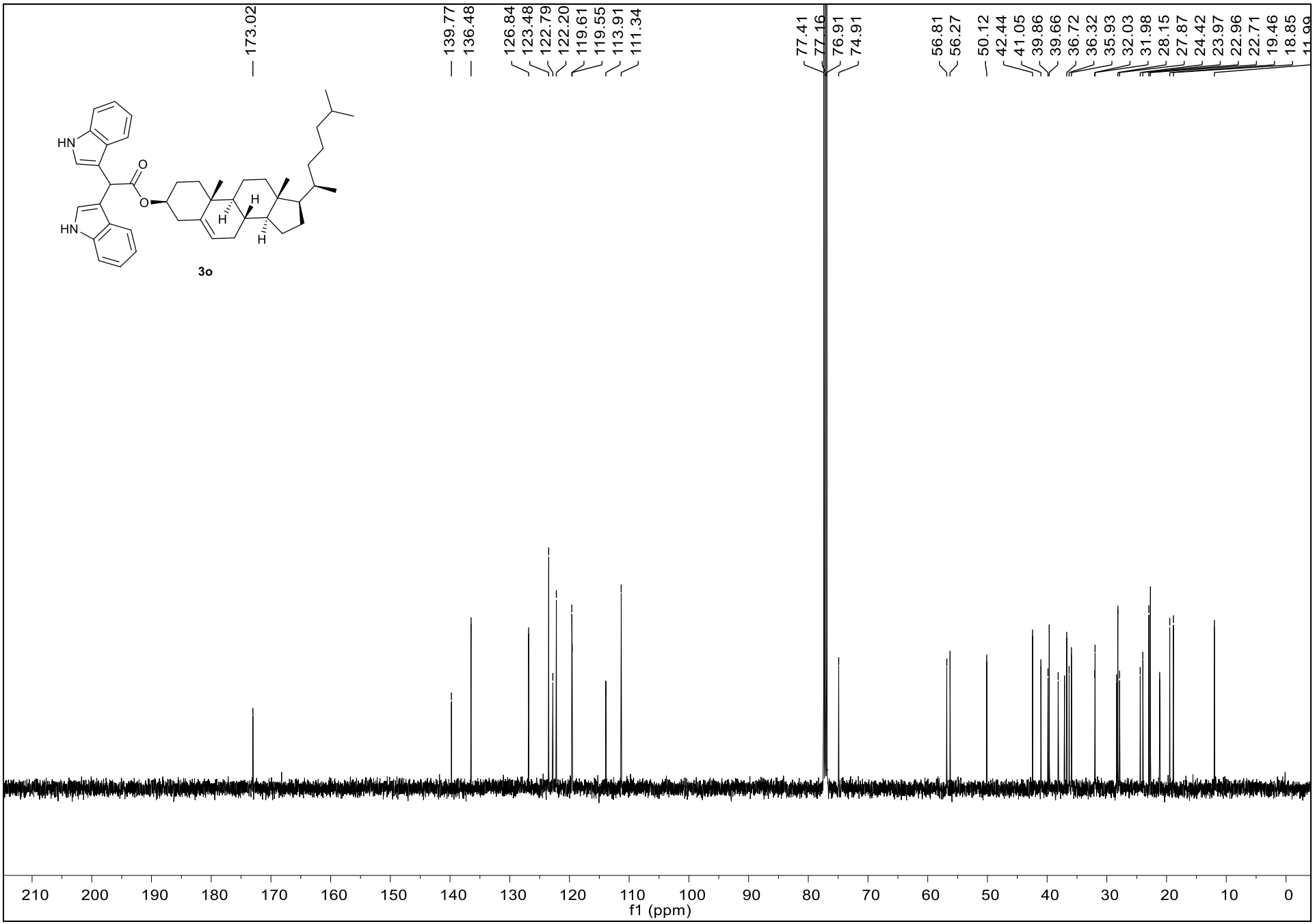
^{13}C NMR Spectrum of 3n (126 MHz, $CDCl_3$)



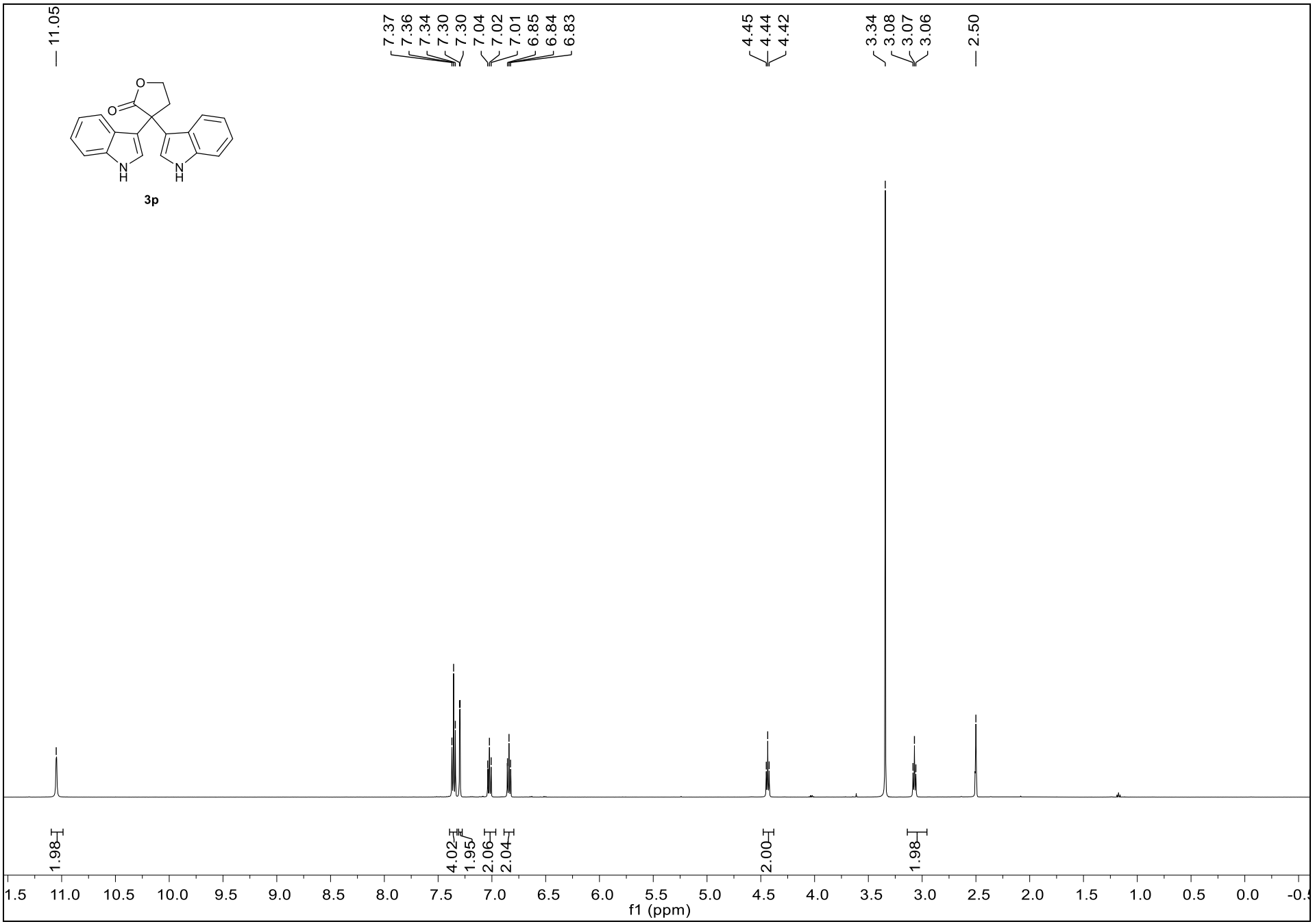
^{1}H NMR Spectrum of 3o (500 MHz, $CDCl_3$)



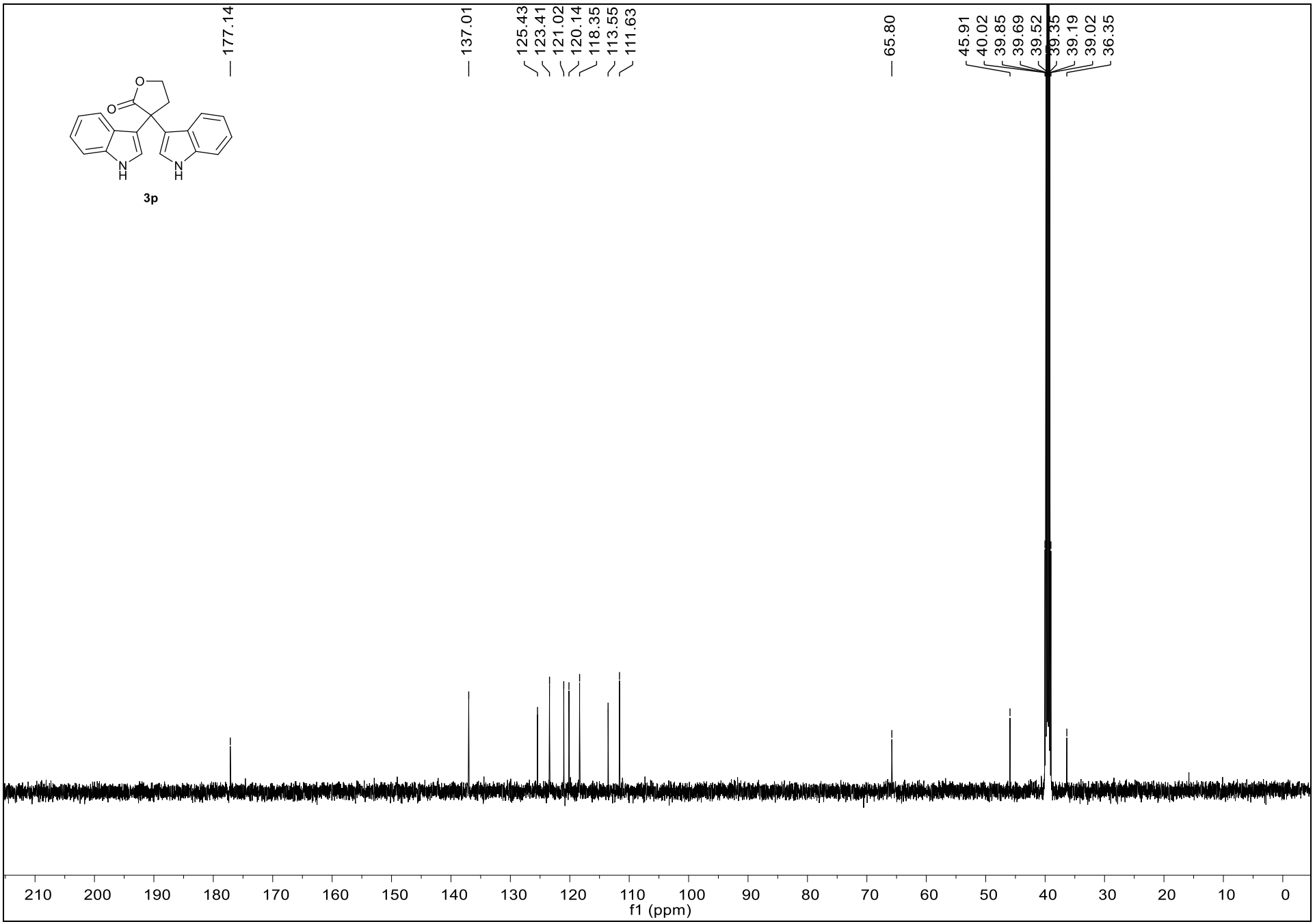
^{13}C NMR Spectrum of 3o (126 MHz, $CDCl_3$)



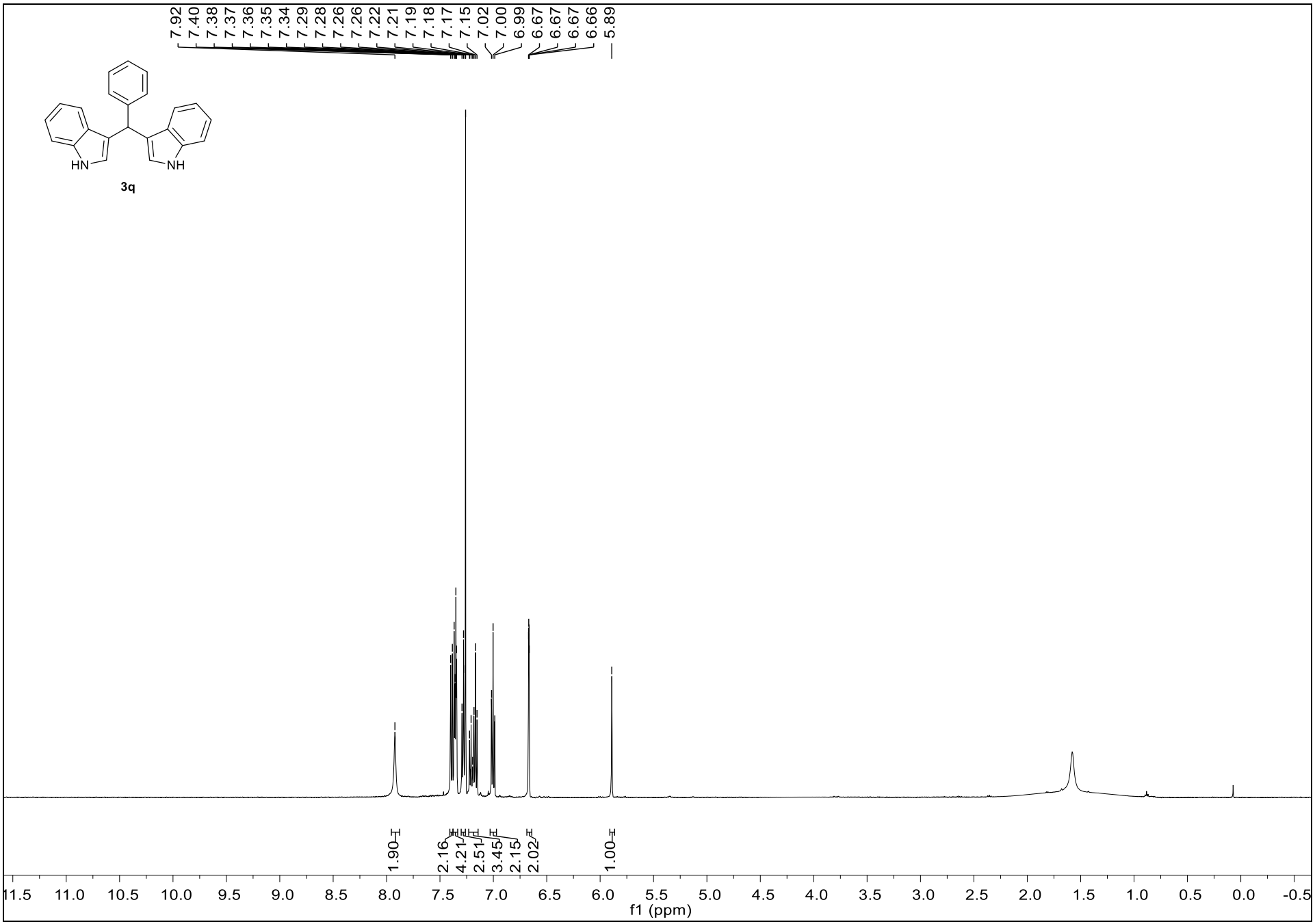
^{1}H NMR Spectrum of 3p (500 MHz, DMSO)



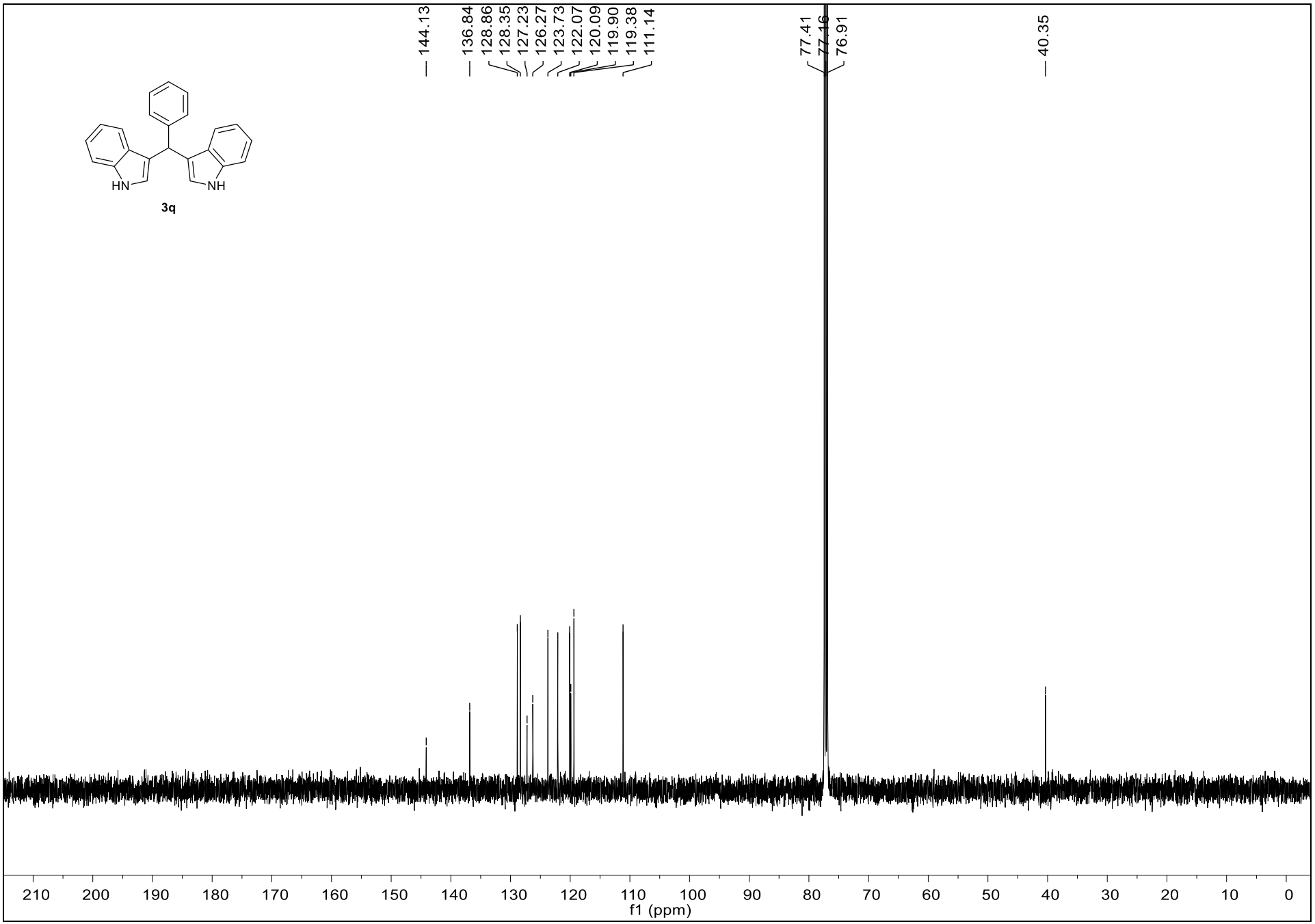
^{13}C NMR Spectrum of 3p (126 MHz, DMSO)



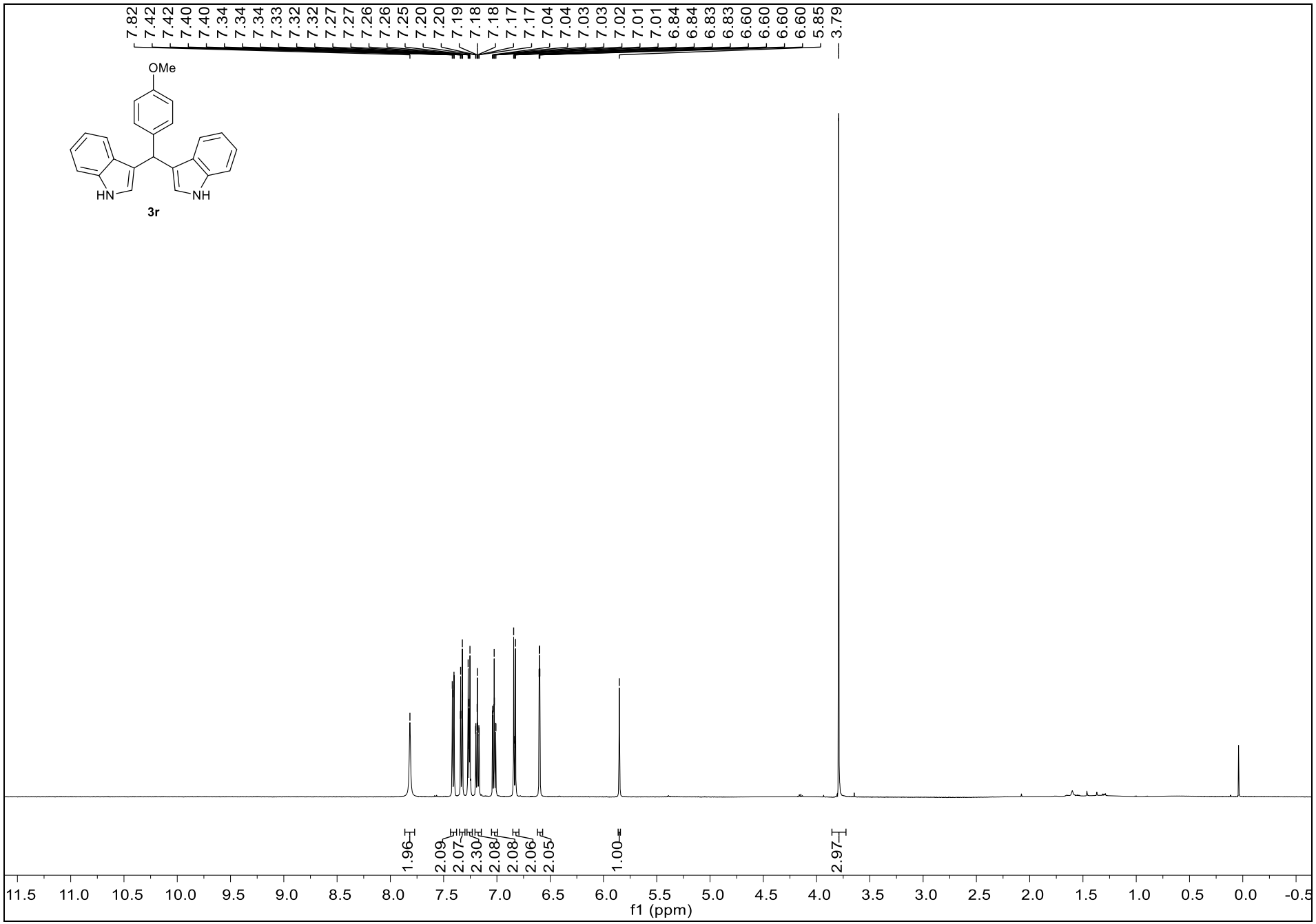
^{1}H NMR Spectrum of 3q (500 MHz, $CDCl_3$)



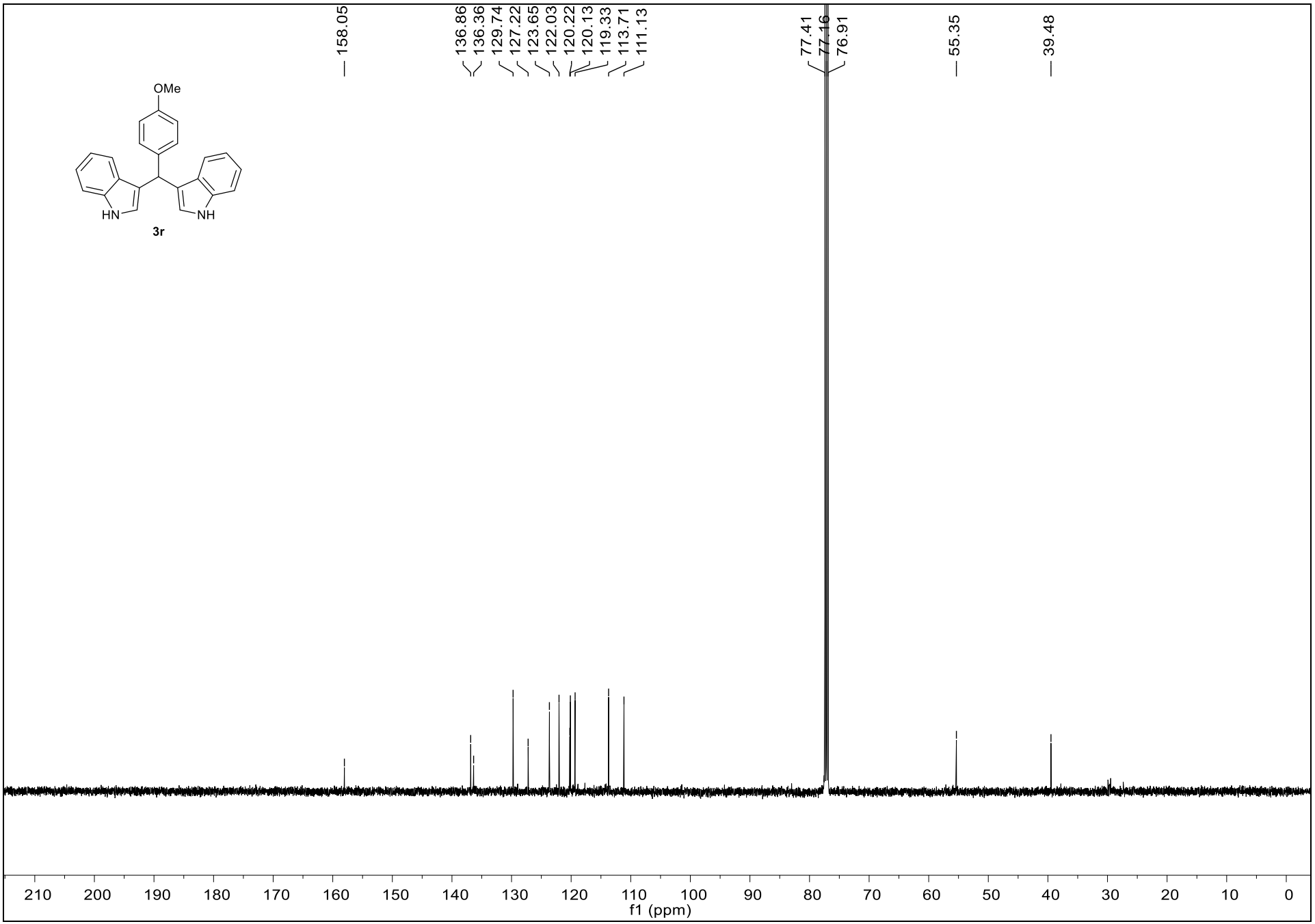
^{13}C NMR Spectrum of 3q (126 MHz, $CDCl_3$)



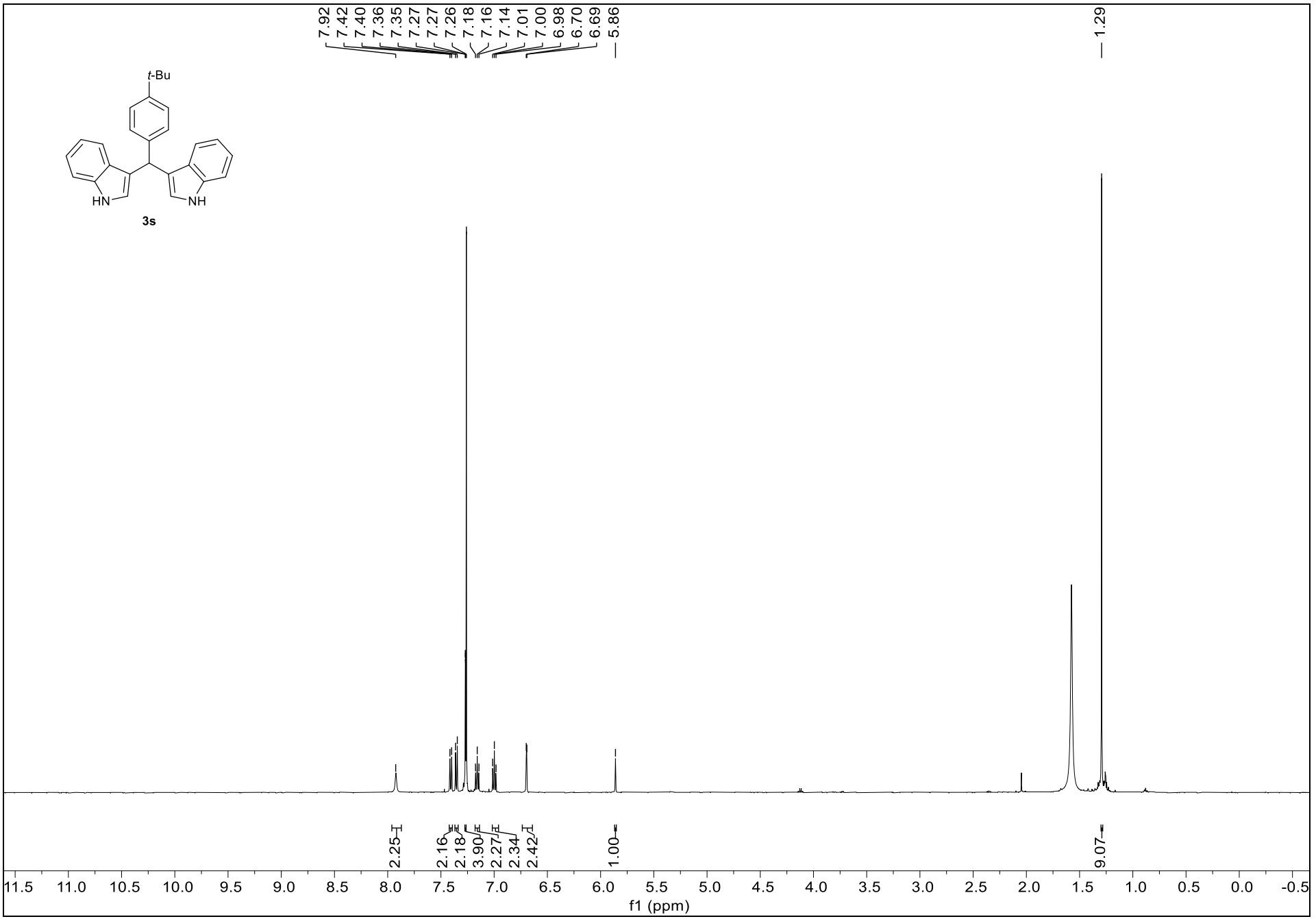
^{1}H NMR Spectrum of 3r (500 MHz, $CDCl_3$)



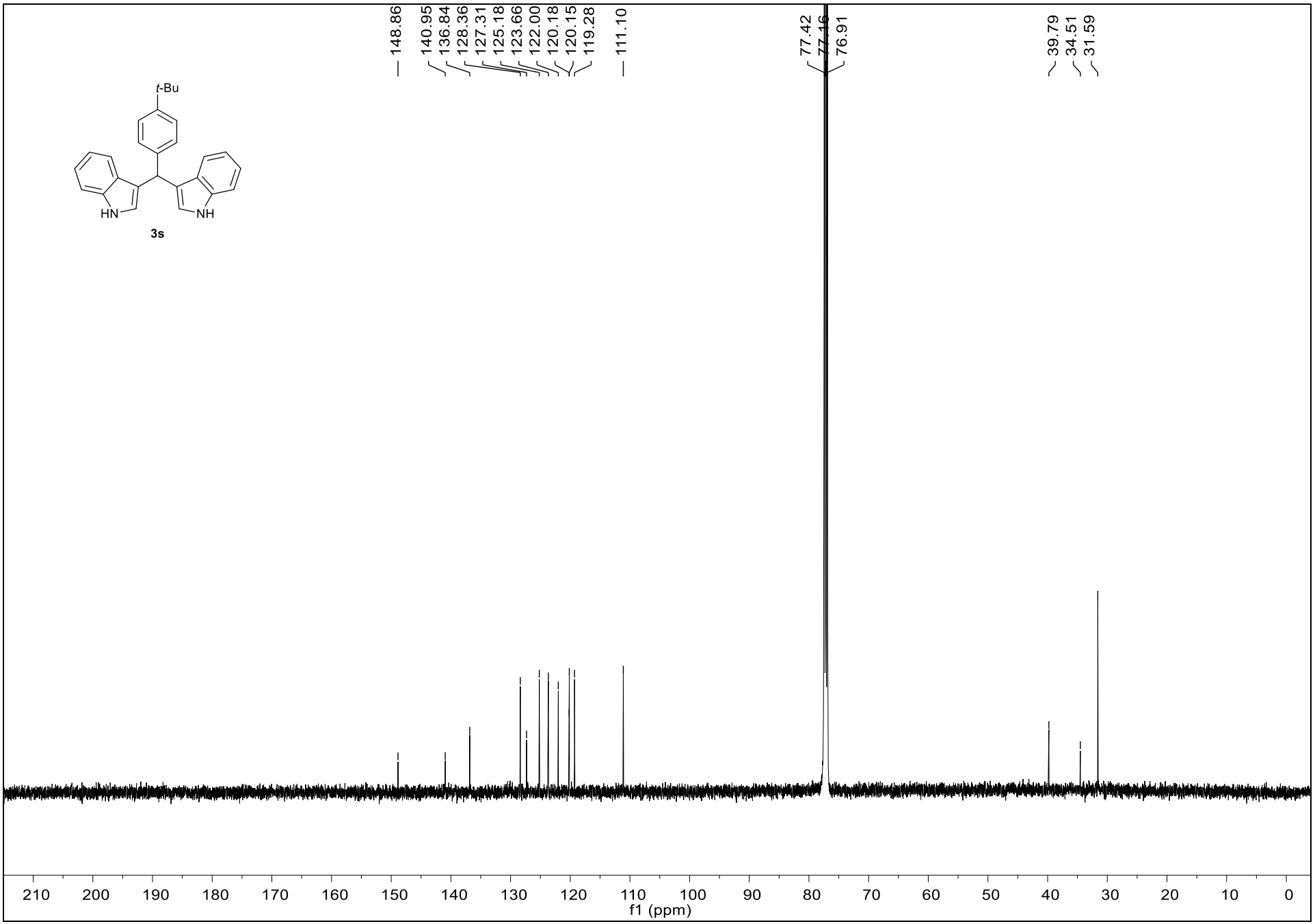
^{13}C NMR Spectrum of 3r (126 MHz, $CDCl_3$)



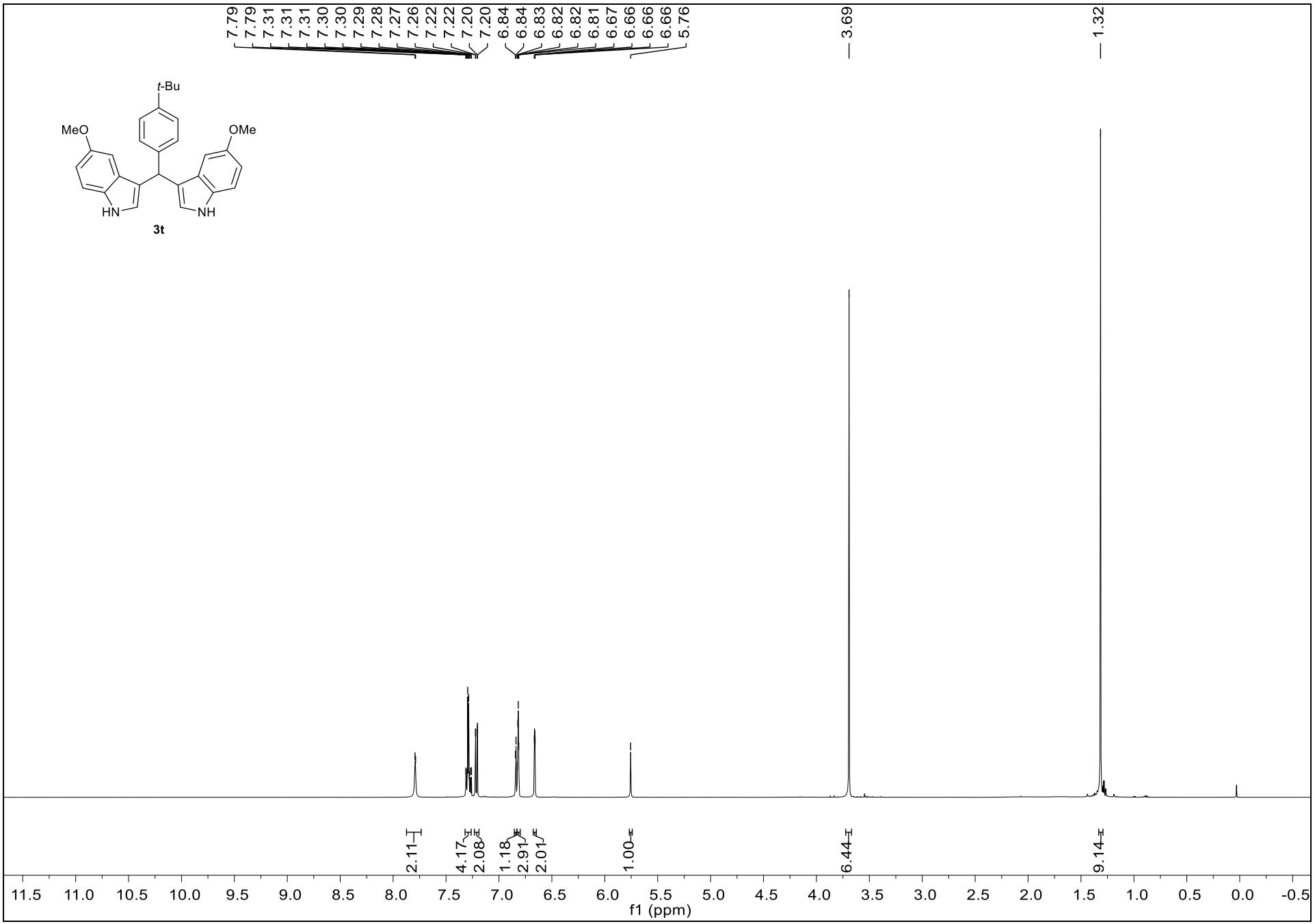
^{1}H NMR Spectrum of 3s (500 MHz, $CDCl_3$)



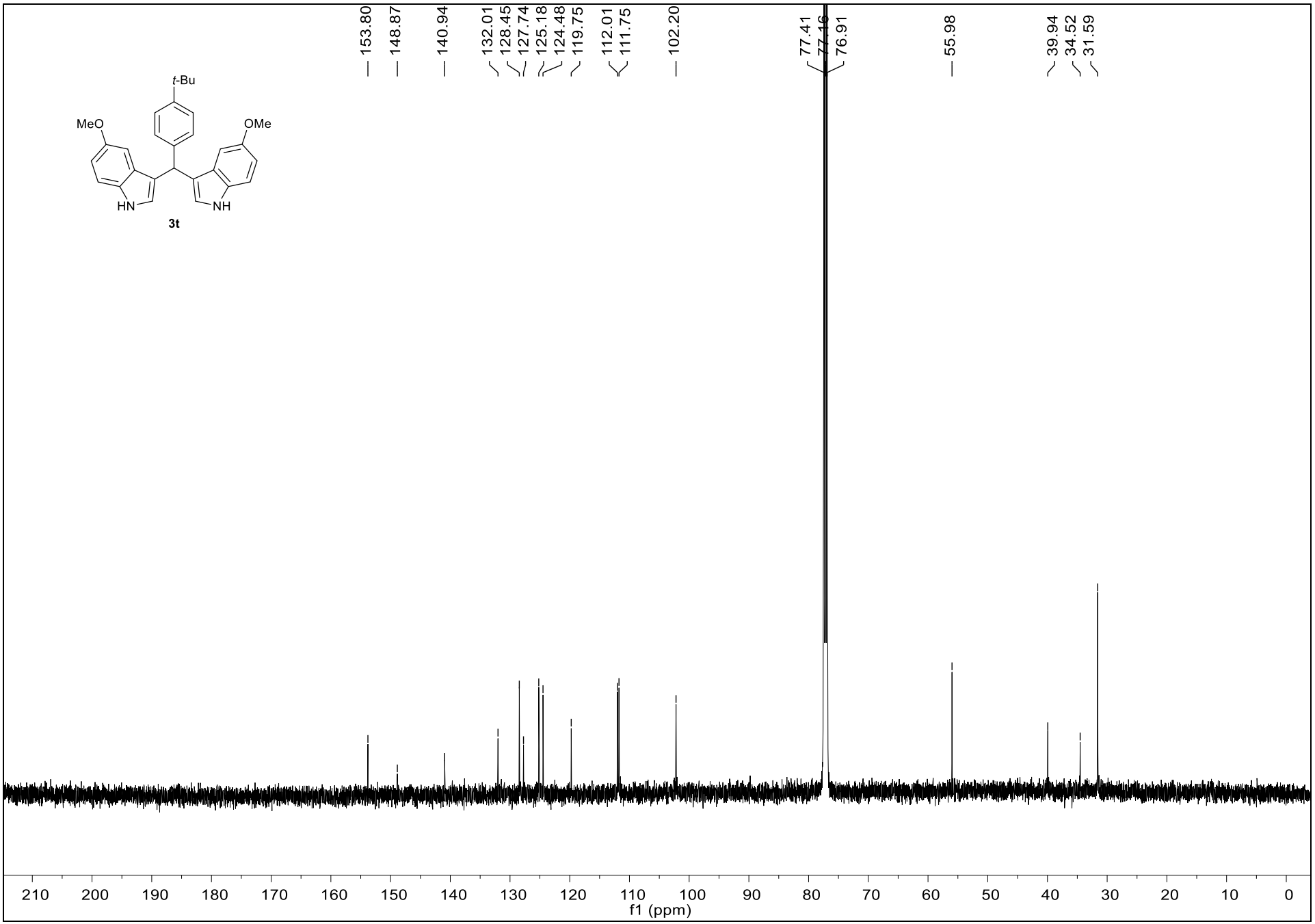
^{13}C NMR Spectrum of 3s (126 MHz, $CDCl_3$)



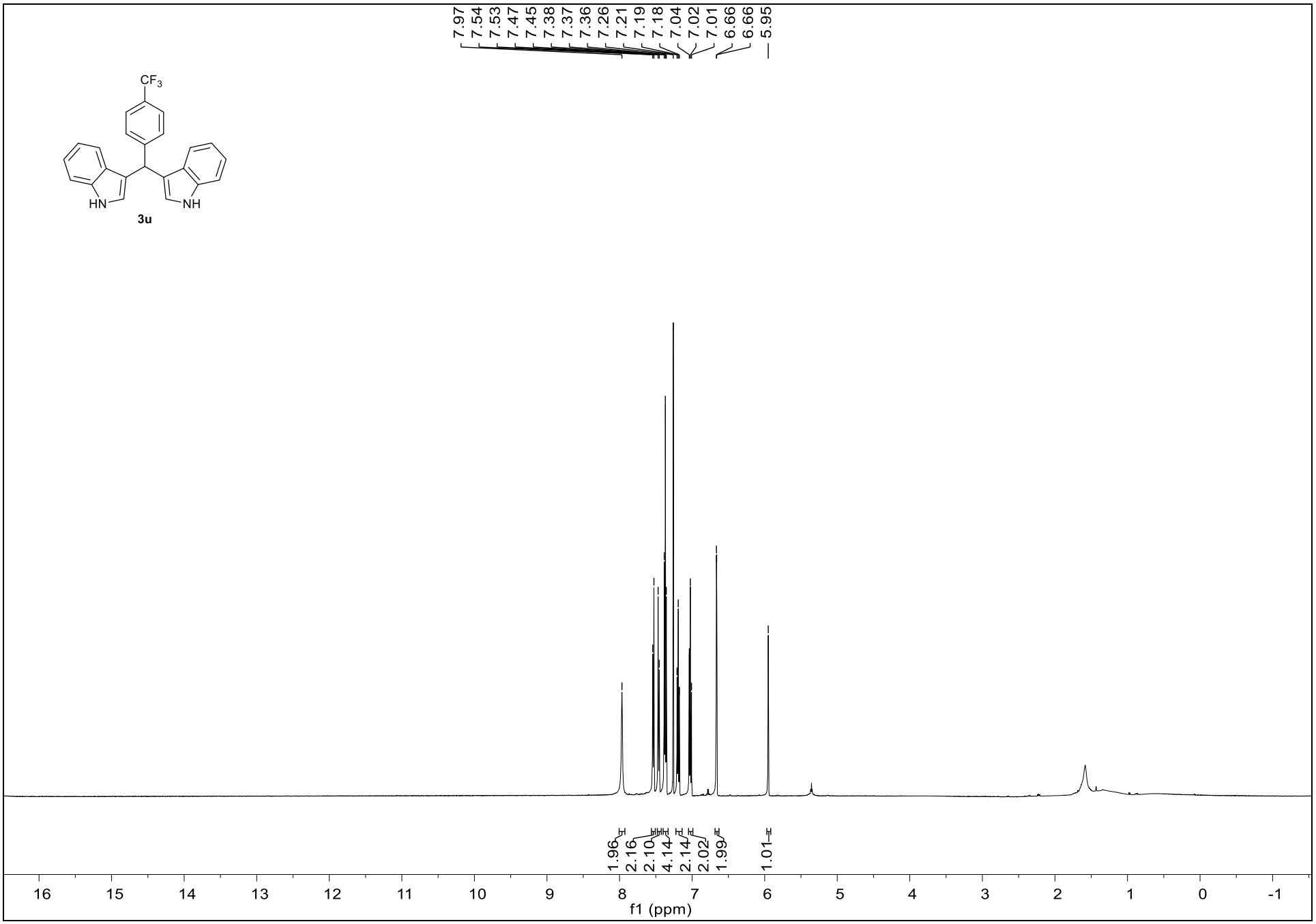
^{1}H NMR Spectrum of 3t (500 MHz, $CDCl_3$)



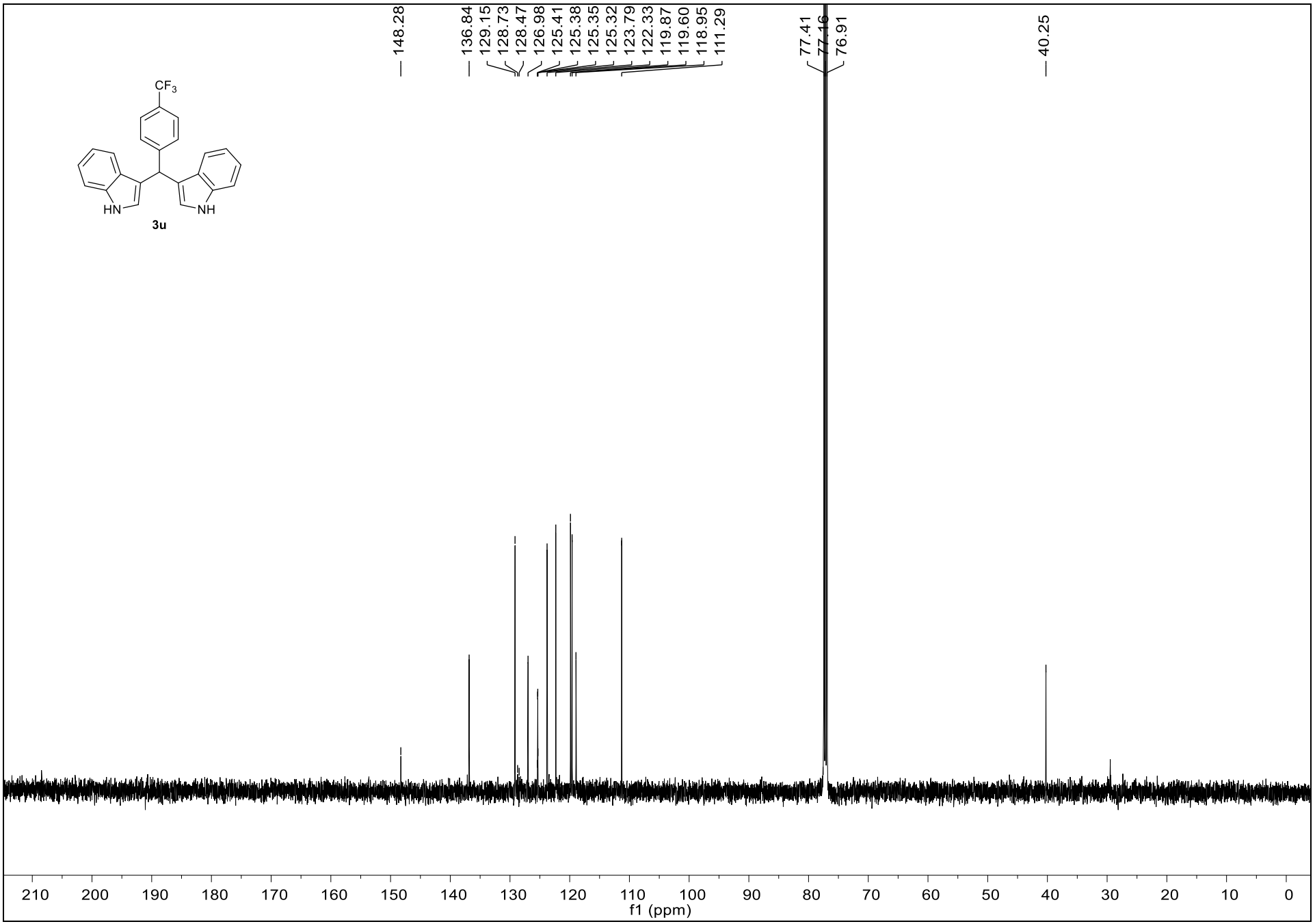
^{13}C NMR Spectrum of 3t (126 MHz, $CDCl_3$)



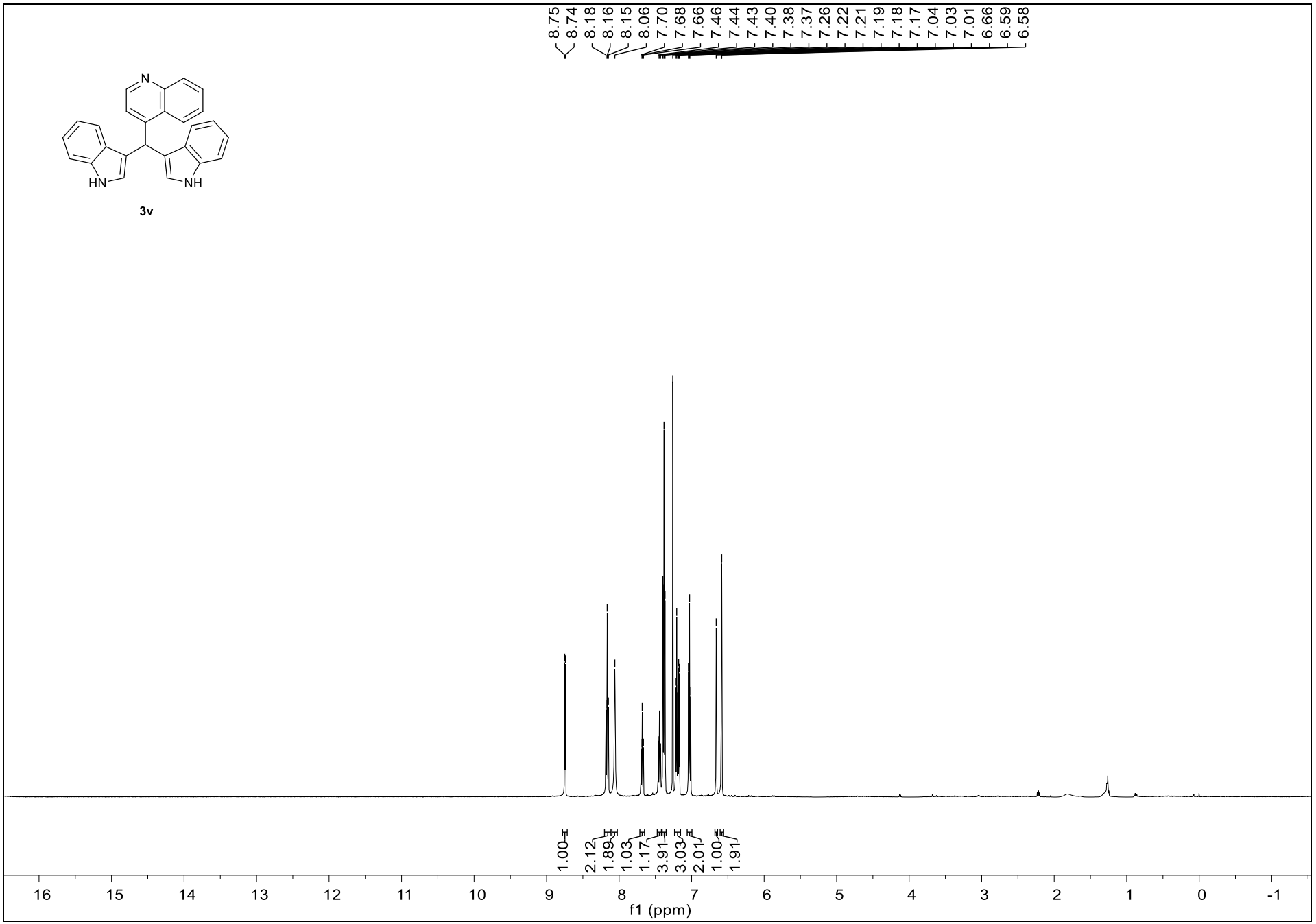
^{1}H NMR Spectrum of 3u (500 MHz, $CDCl_3$)



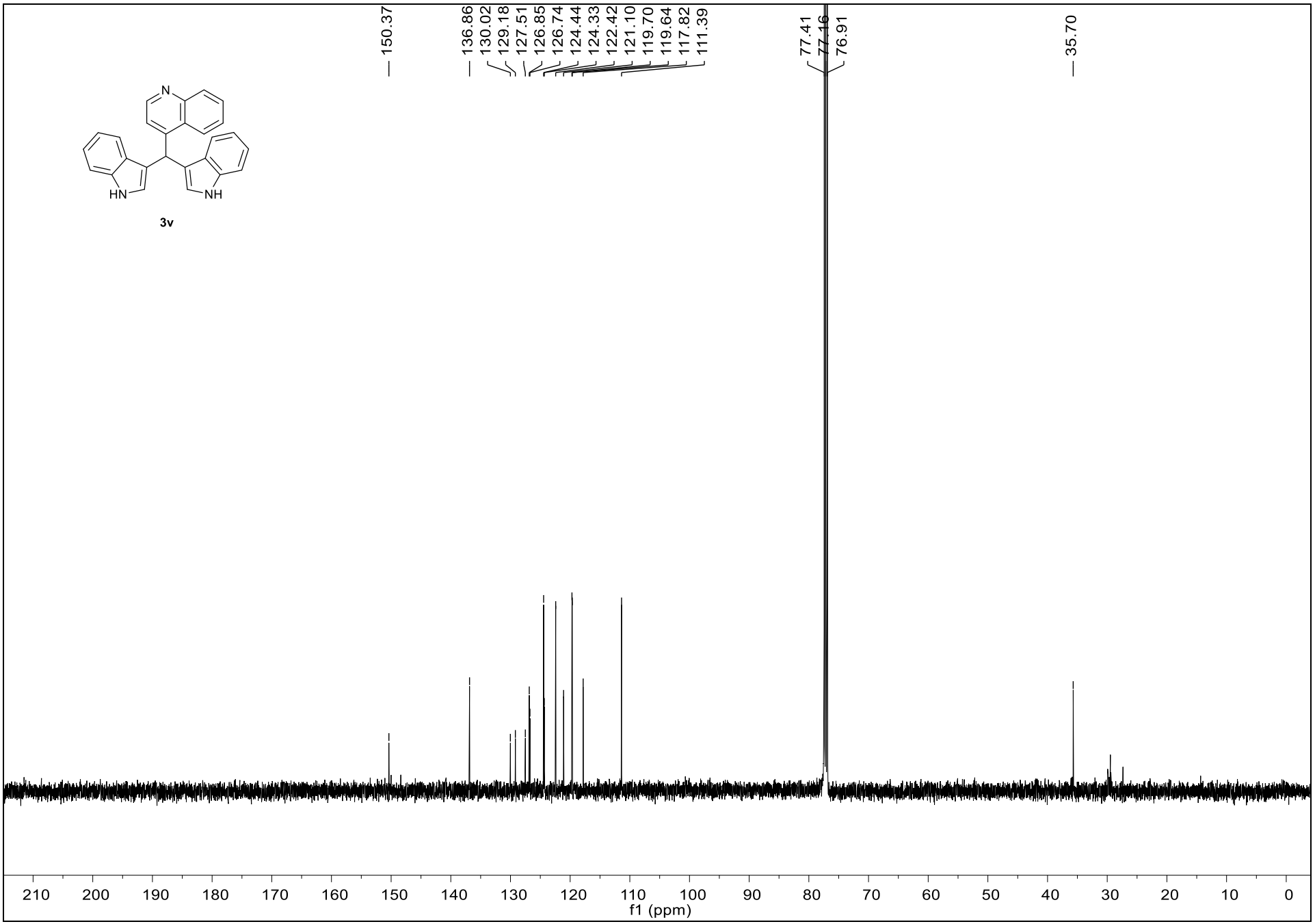
^{13}C NMR Spectrum of 3u (126 MHz, $CDCl_3$)



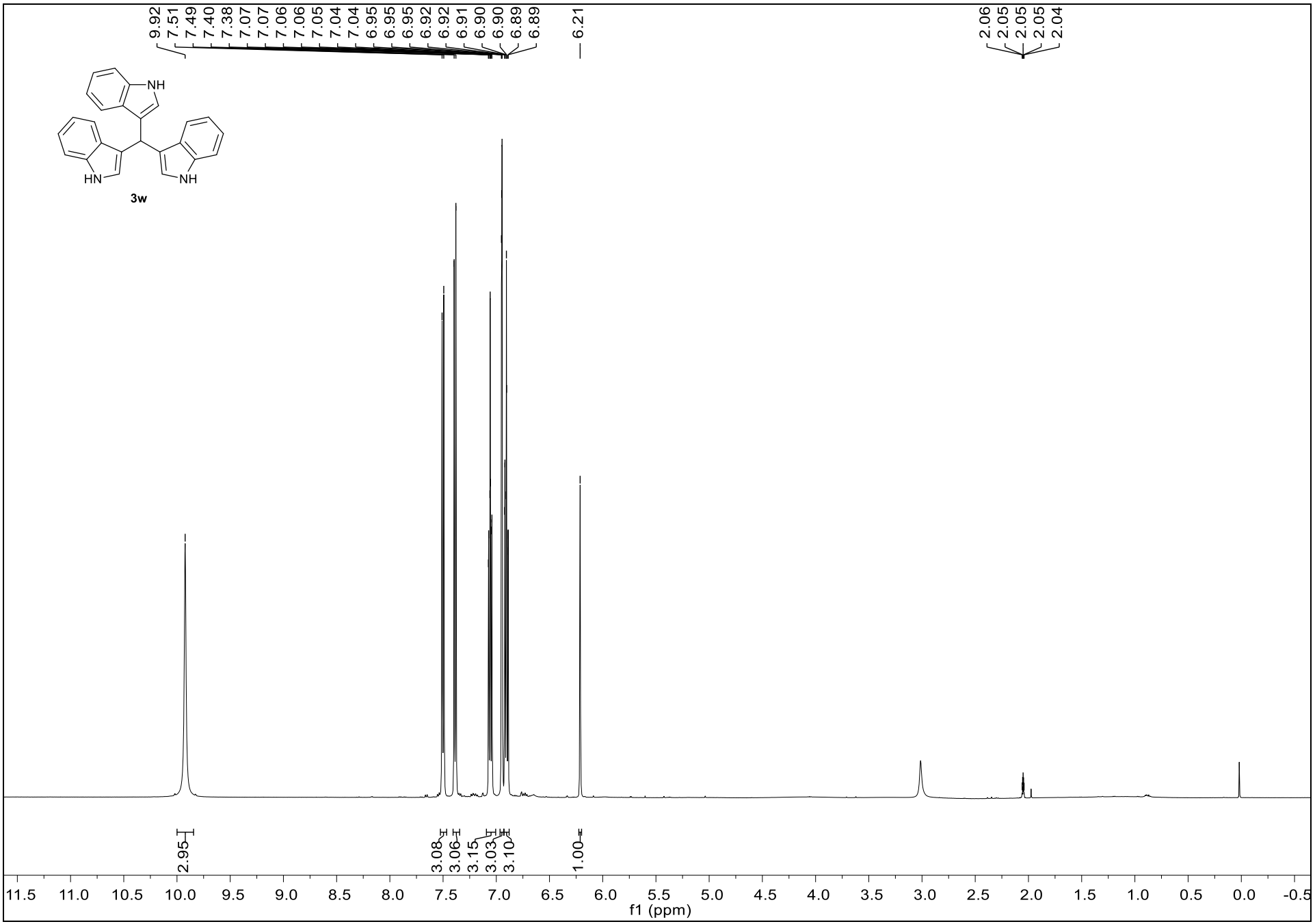
^{1}H NMR Spectrum of 3v (500 MHz, $CDCl_3$)



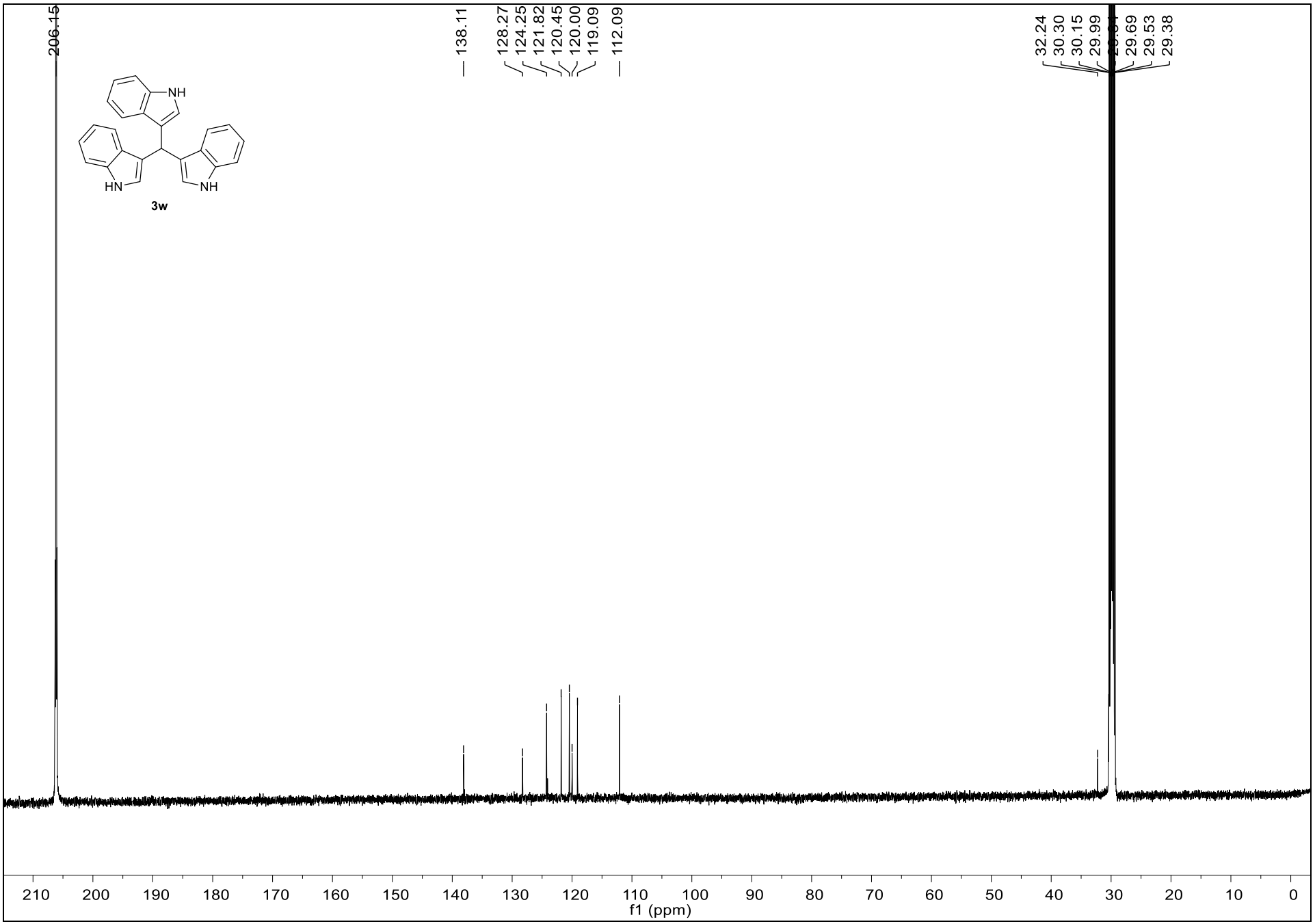
^{13}C NMR Spectrum of 3v (126 MHz, $CDCl_3$)



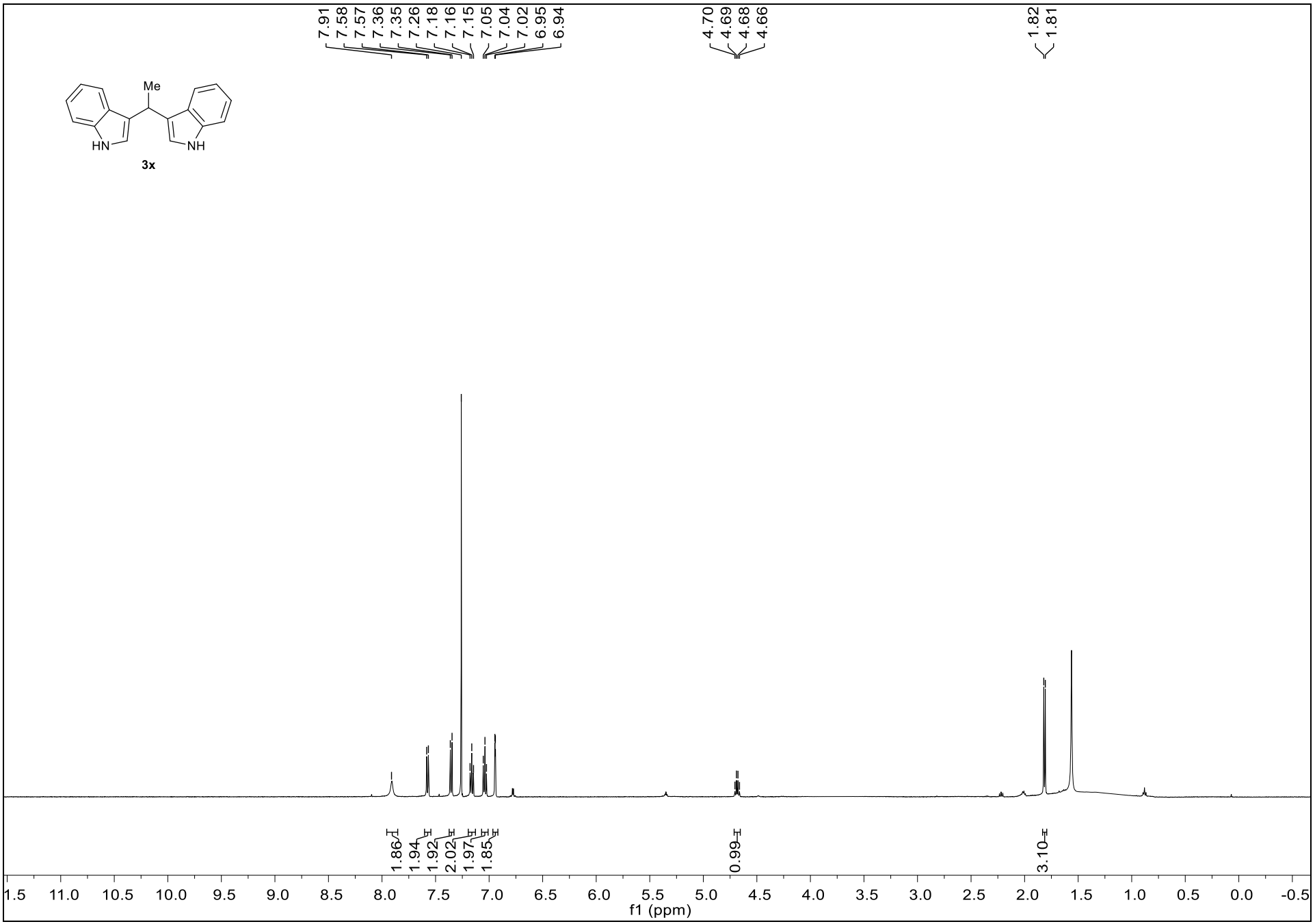
^{1}H NMR Spectrum of 3w (500 MHz, Acetone-d_6)



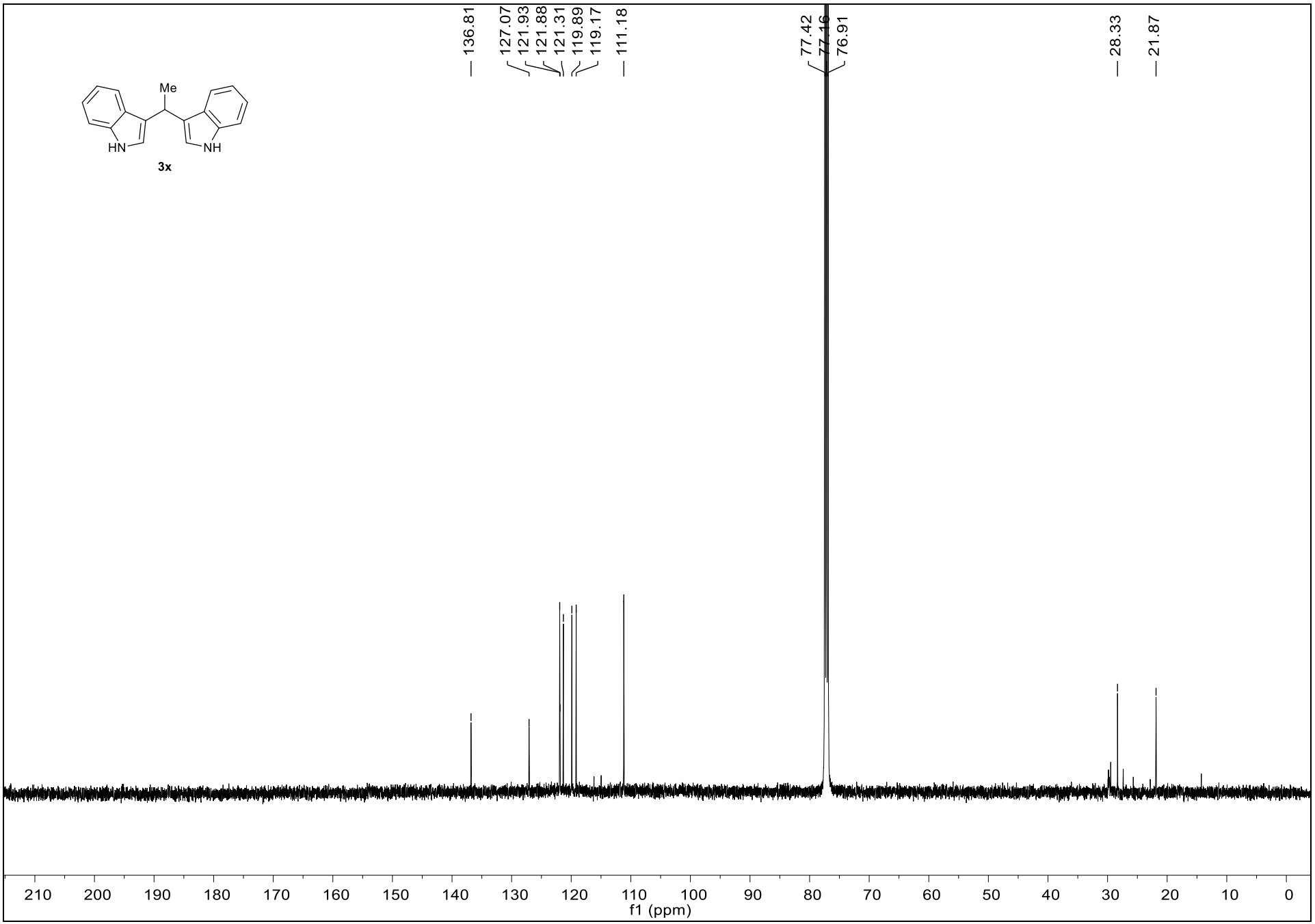
^{13}C NMR Spectrum of 3w (126 MHz, Acetone-d_6)



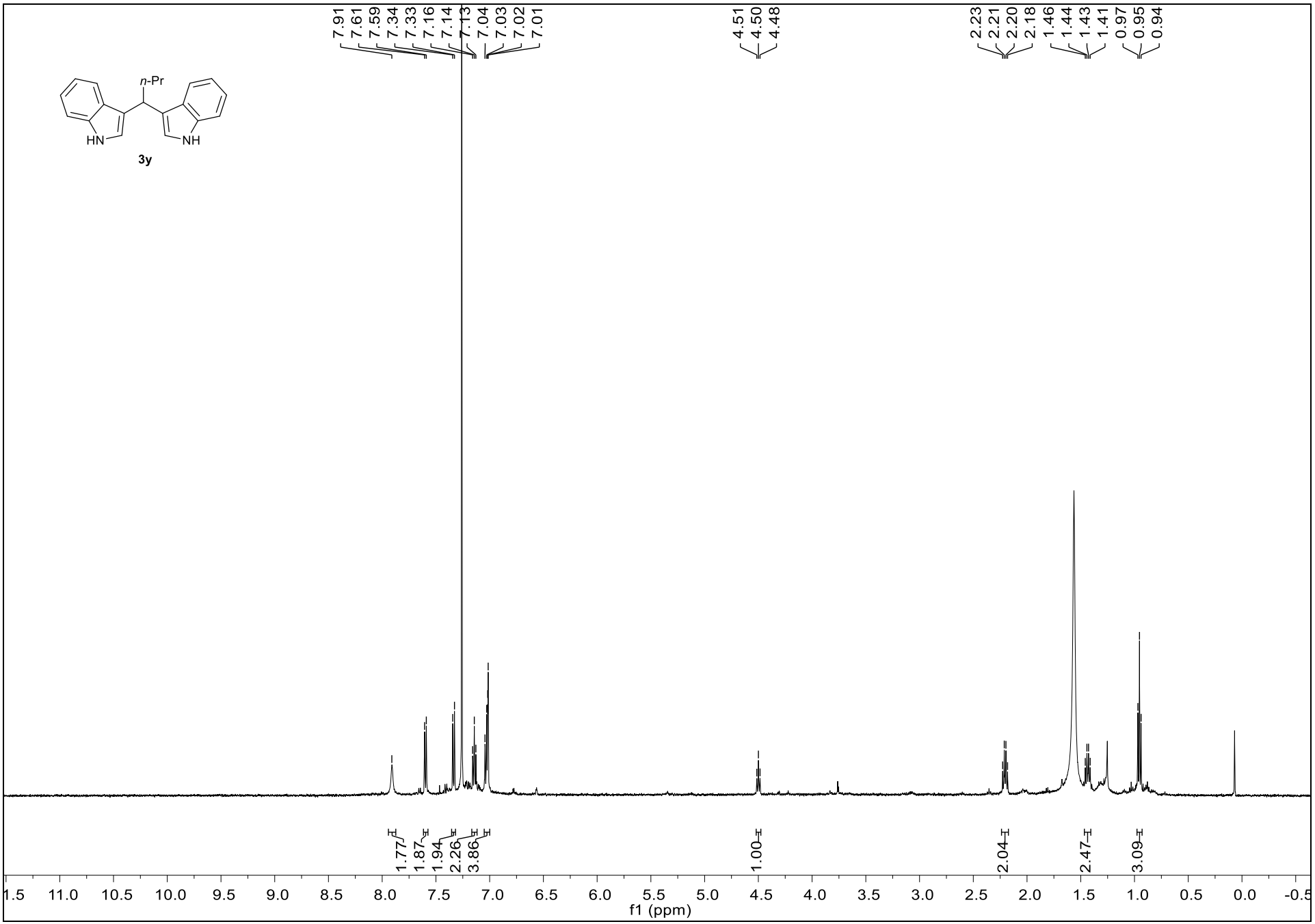
^{1}H NMR Spectrum of 3x (500 MHz, $CDCl_3$)



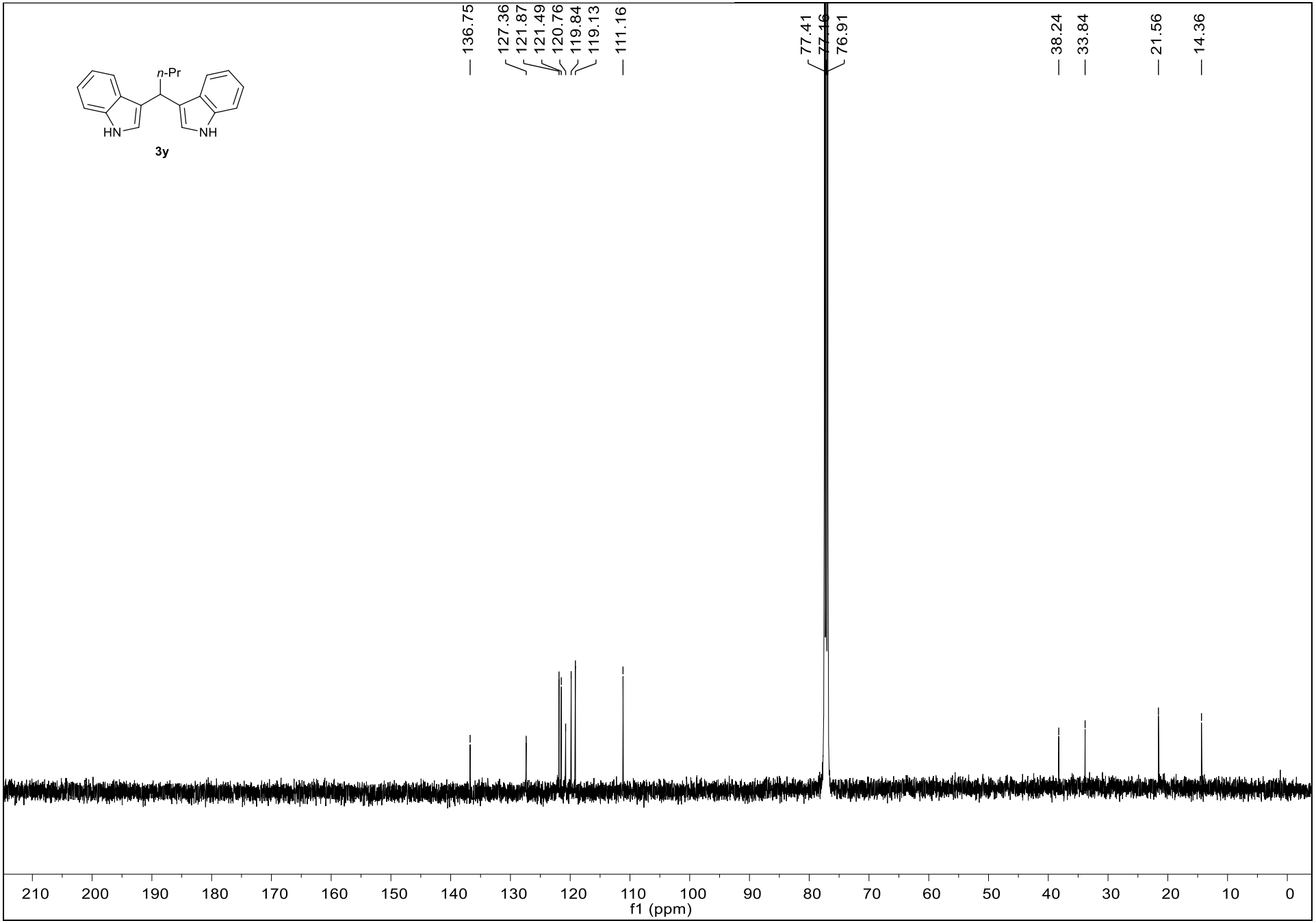
^{13}C NMR Spectrum of 3x (126 MHz, $CDCl_3$)



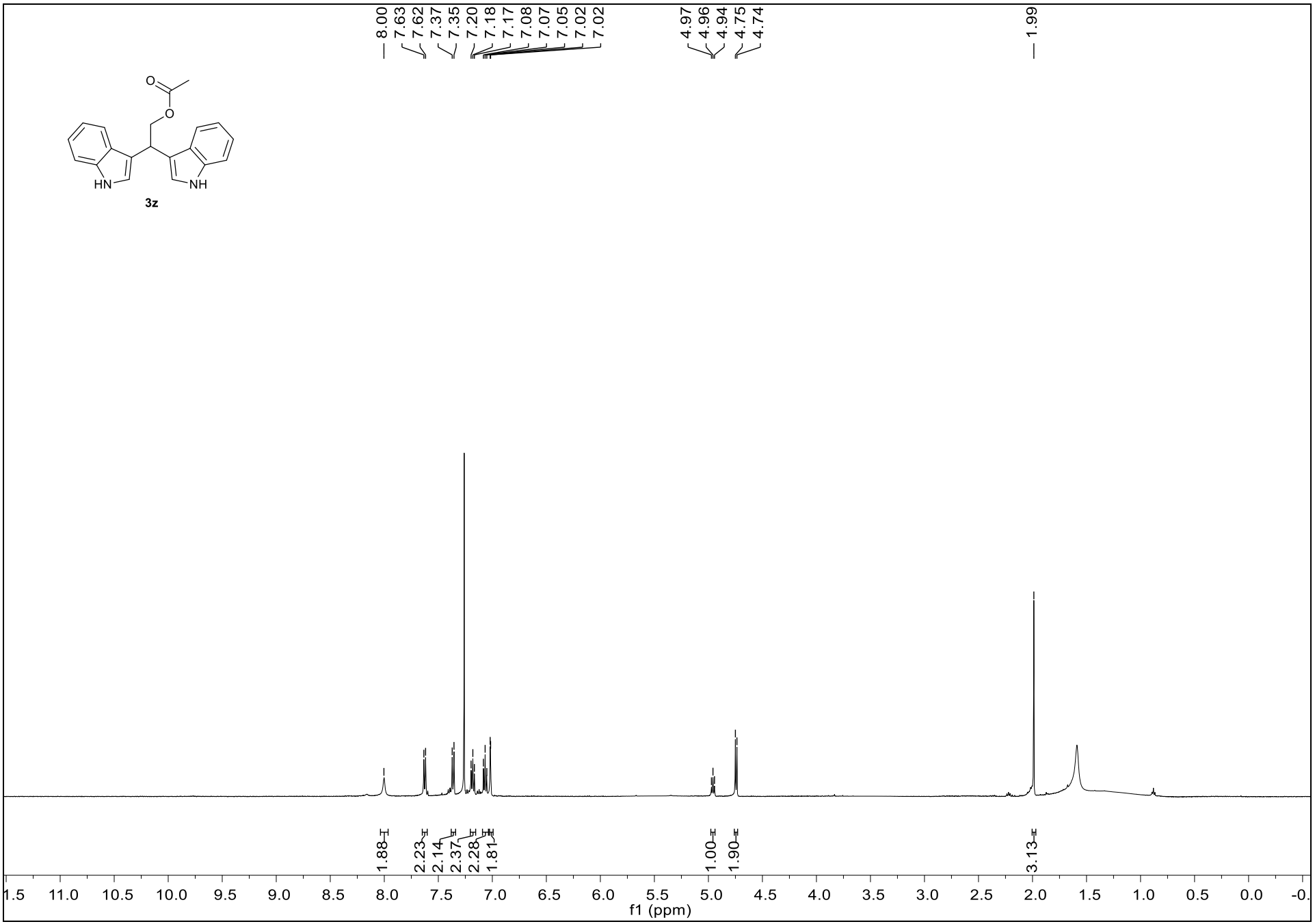
^{1}H NMR Spectrum of 3y (500 MHz, $CDCl_3$)



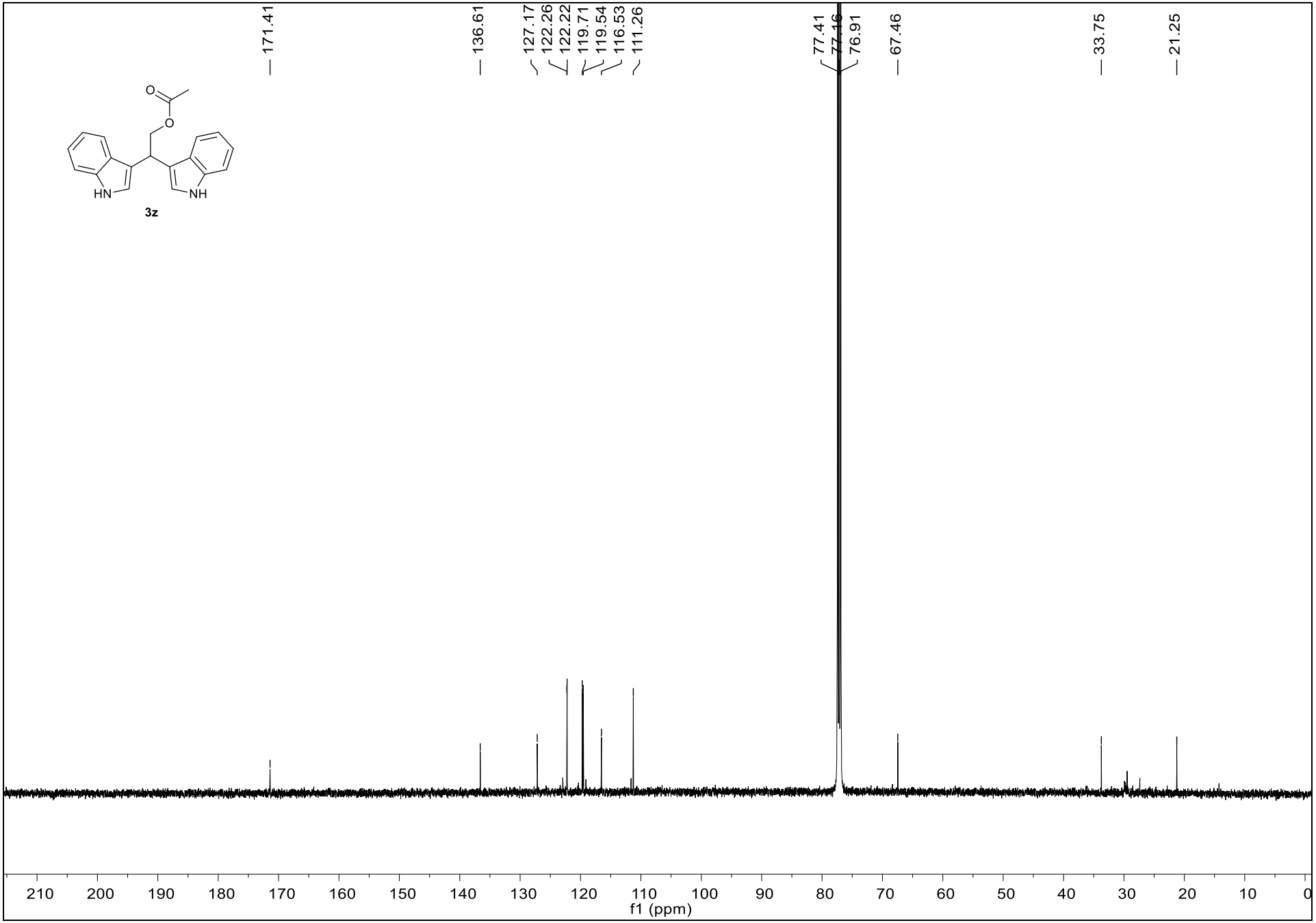
^{13}C NMR Spectrum of 3y (126 MHz, $CDCl_3$)



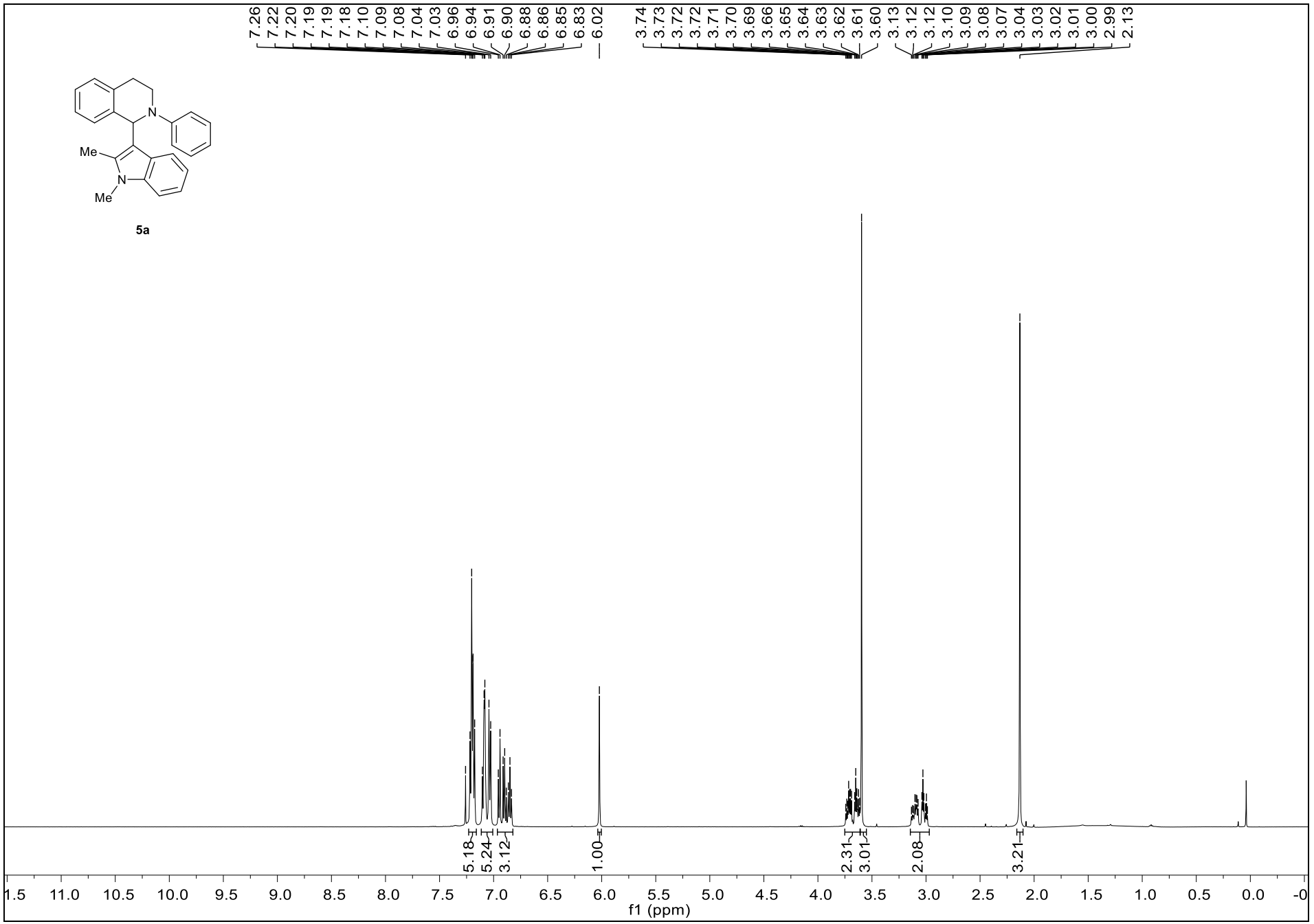
^{1}H NMR Spectrum of 3z (500 MHz, $CDCl_3$)



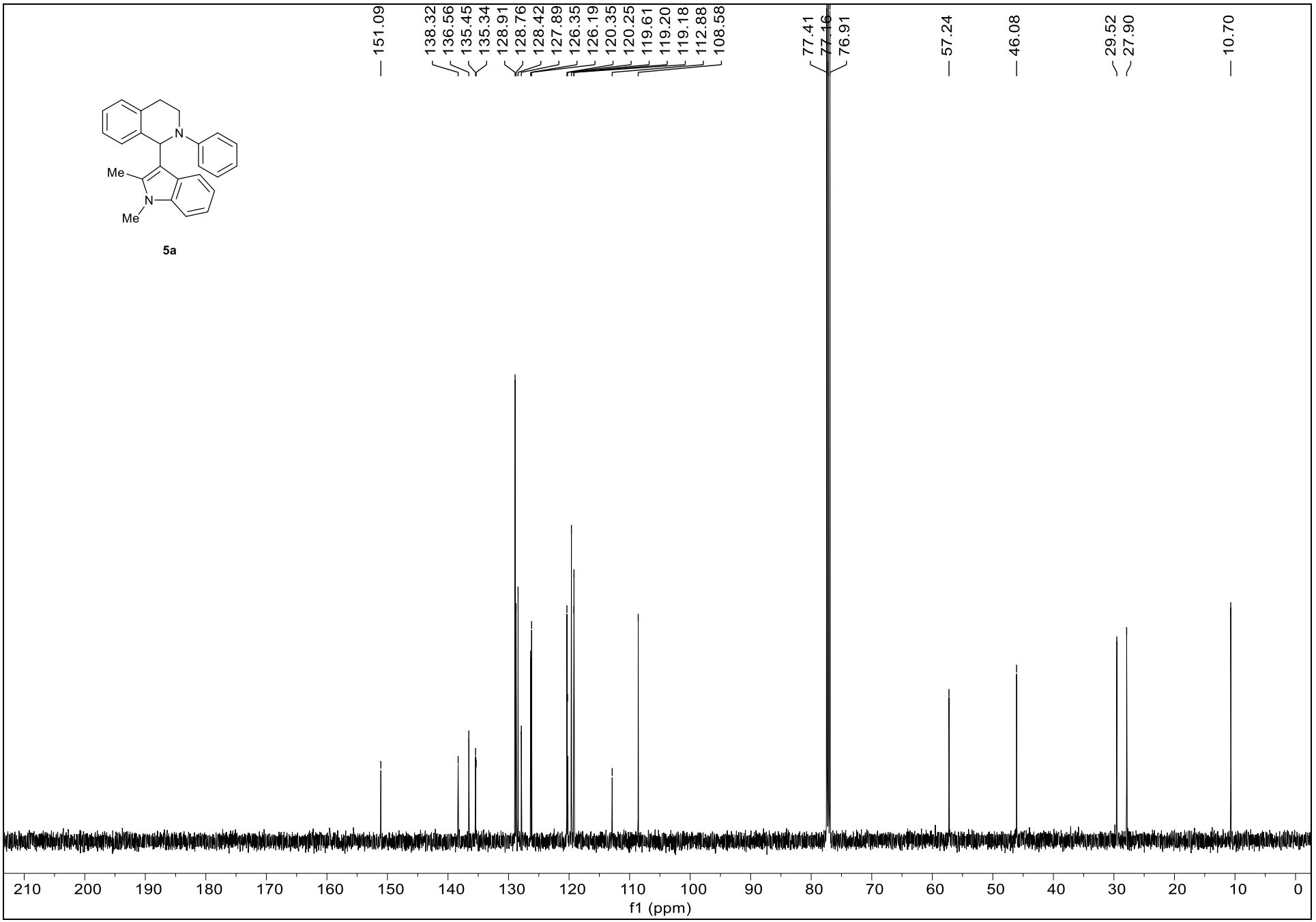
^{13}C NMR Spectrum of 3z (126 MHz, $CDCl_3$)



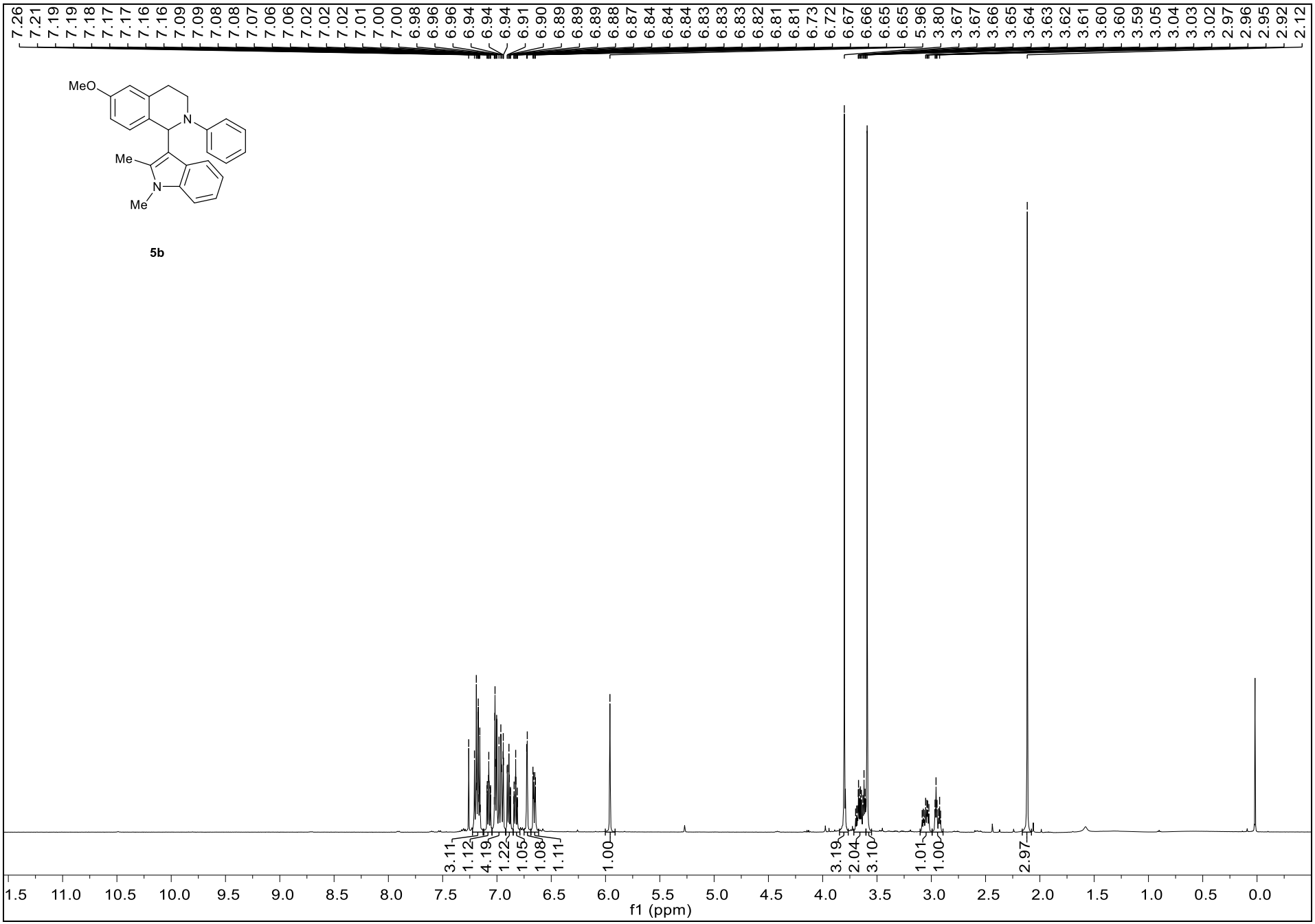
^{1}H NMR Spectrum of 5a (500 MHz, $CDCl_3$)



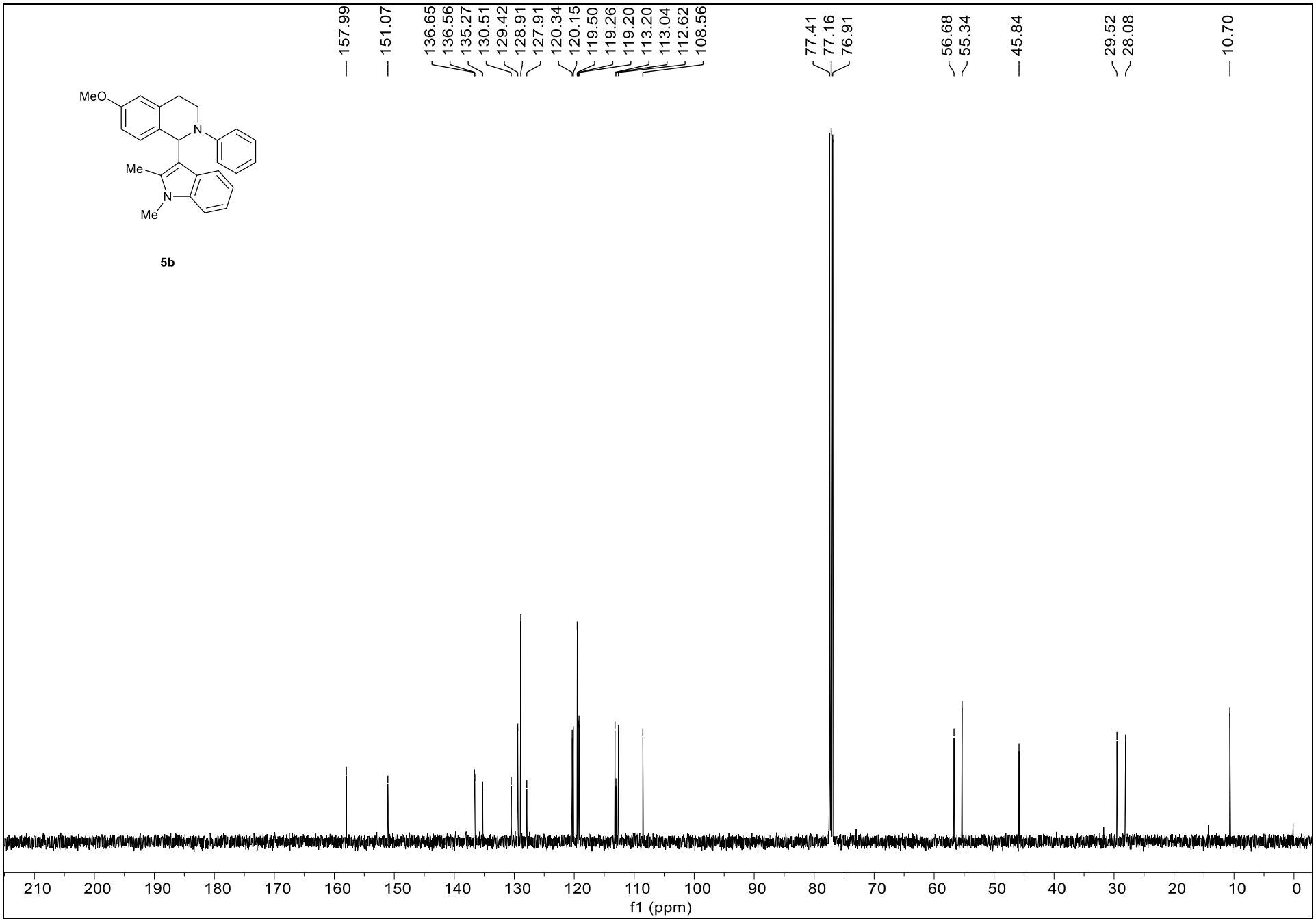
^{13}C NMR Spectrum of 5a (126 MHz, $CDCl_3$)



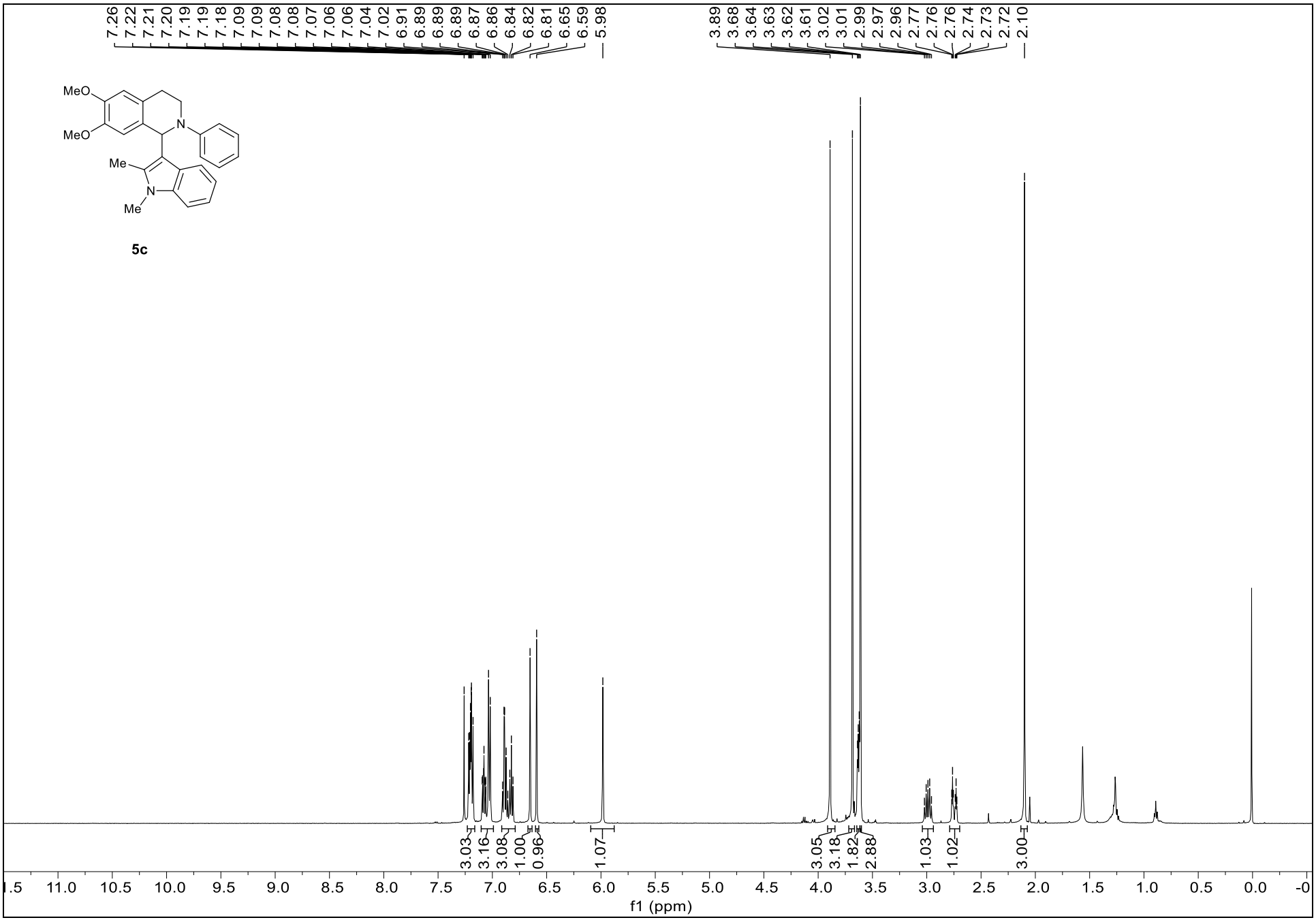
^{1}H NMR Spectrum of 5b (500 MHz, $CDCl_3$)



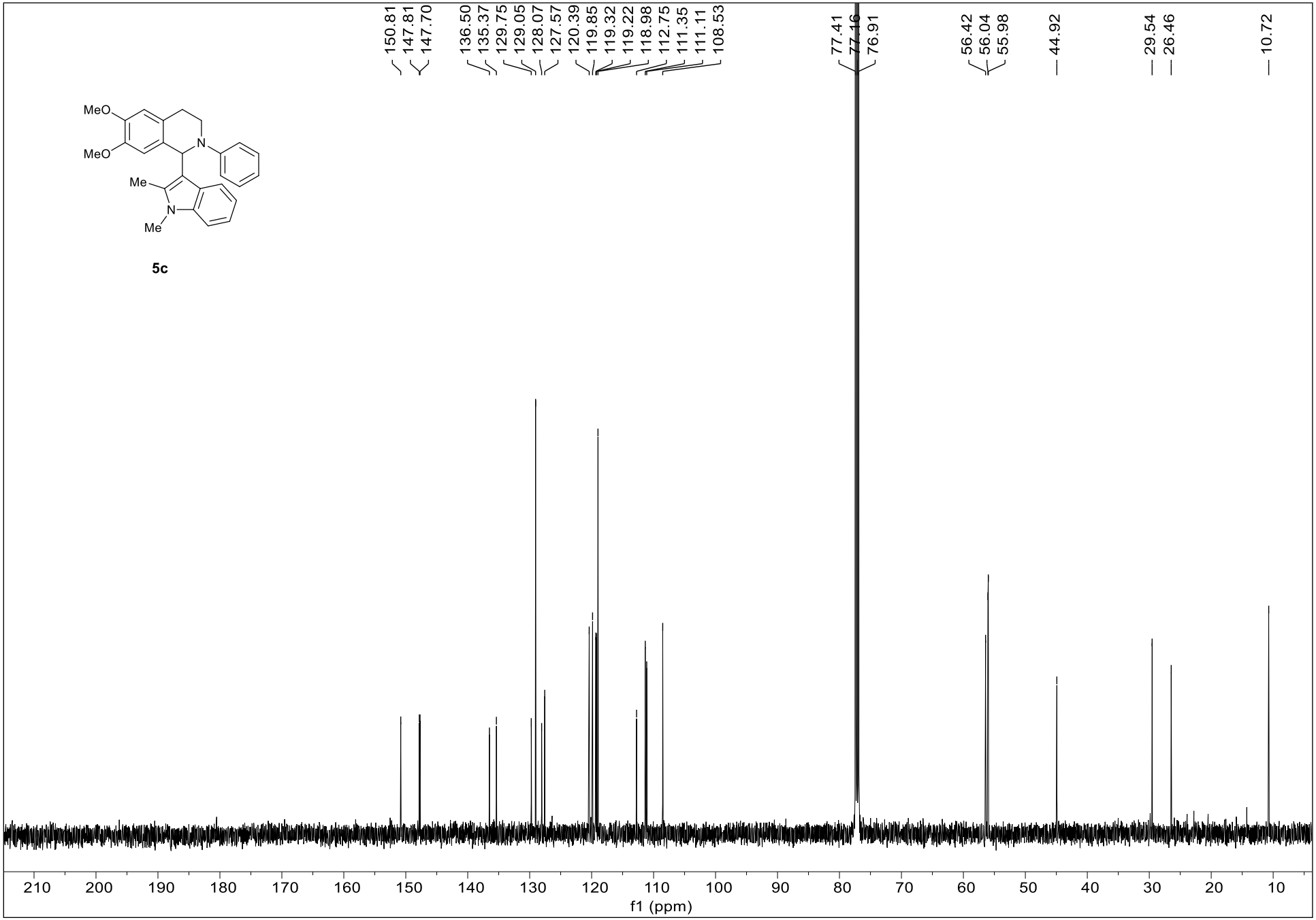
^{13}C NMR Spectrum of 5b (126 MHz, $CDCl_3$)



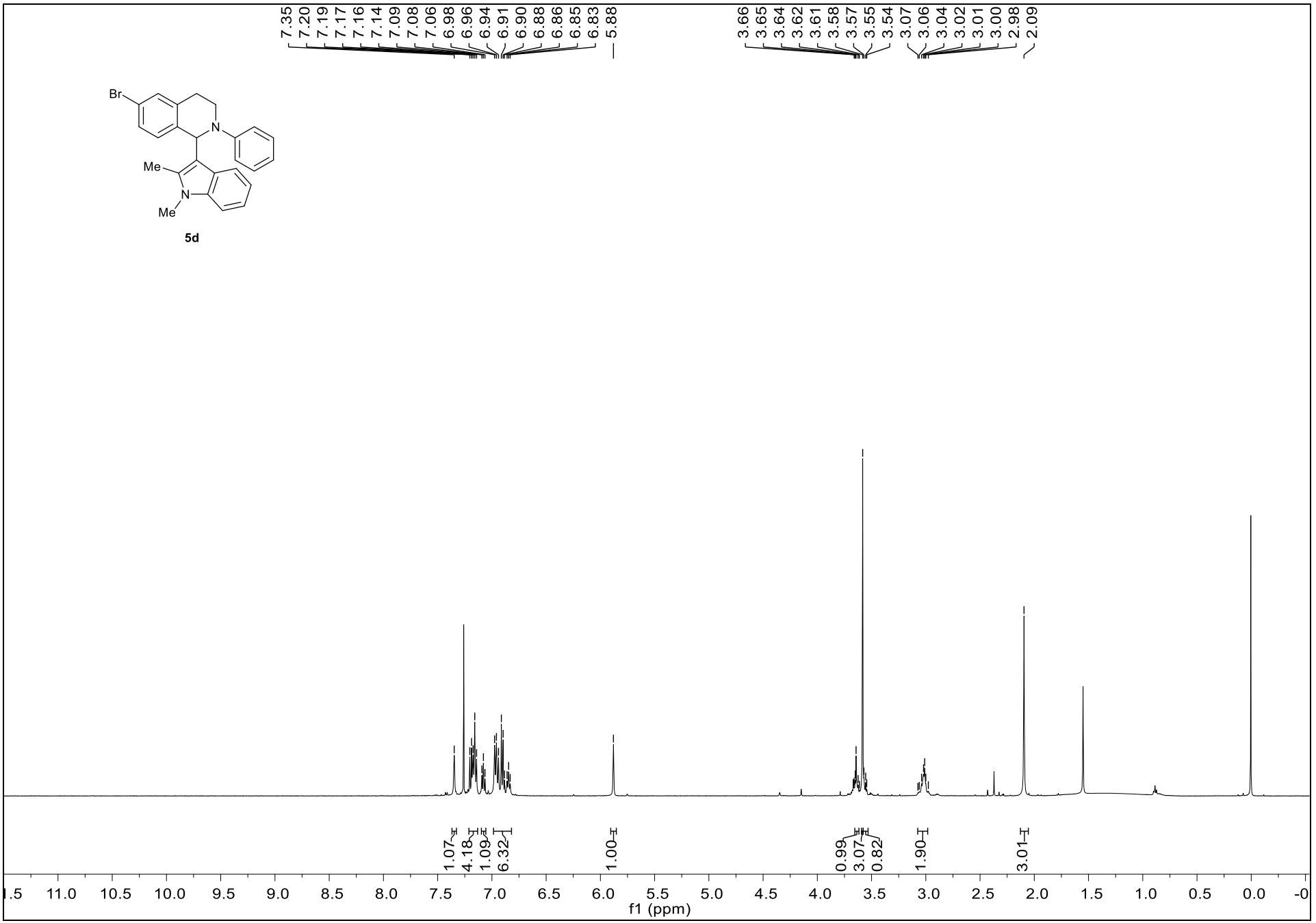
^{1}H NMR Spectrum of 5c (500 MHz, $CDCl_3$)



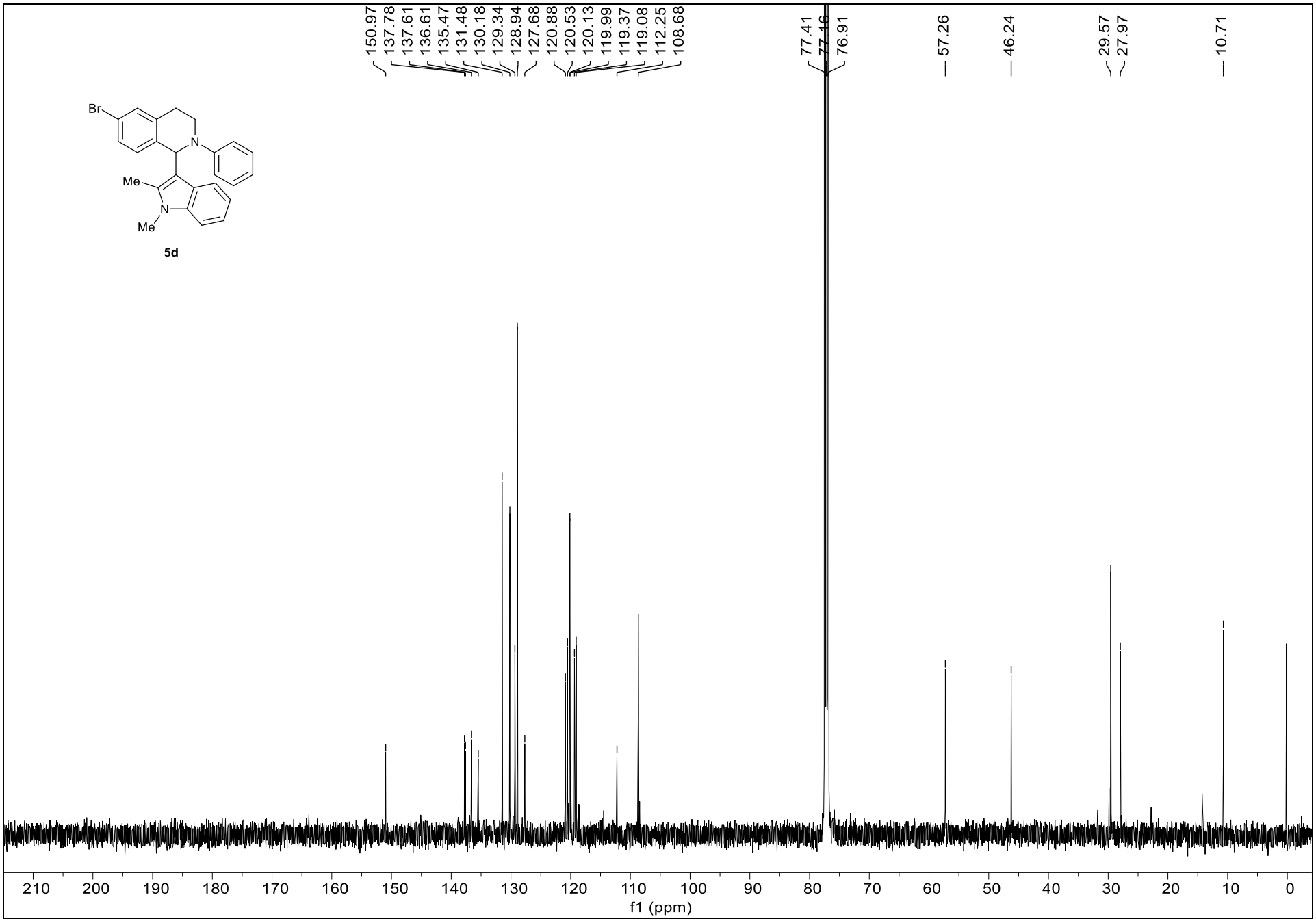
^{13}C NMR Spectrum of 5c (126 MHz, $CDCl_3$)



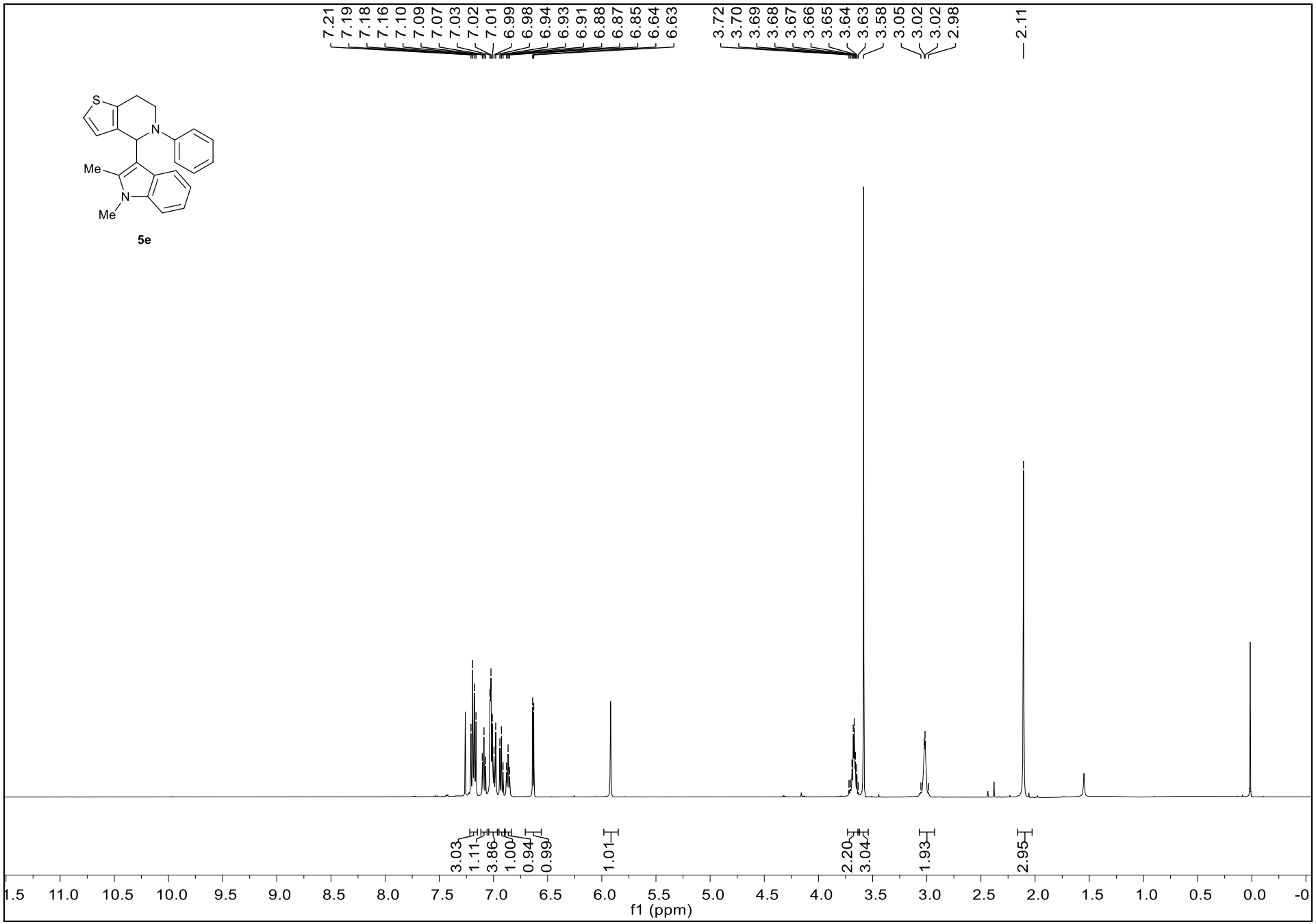
^{1}H NMR Spectrum of 5d (500 MHz, $CDCl_3$)



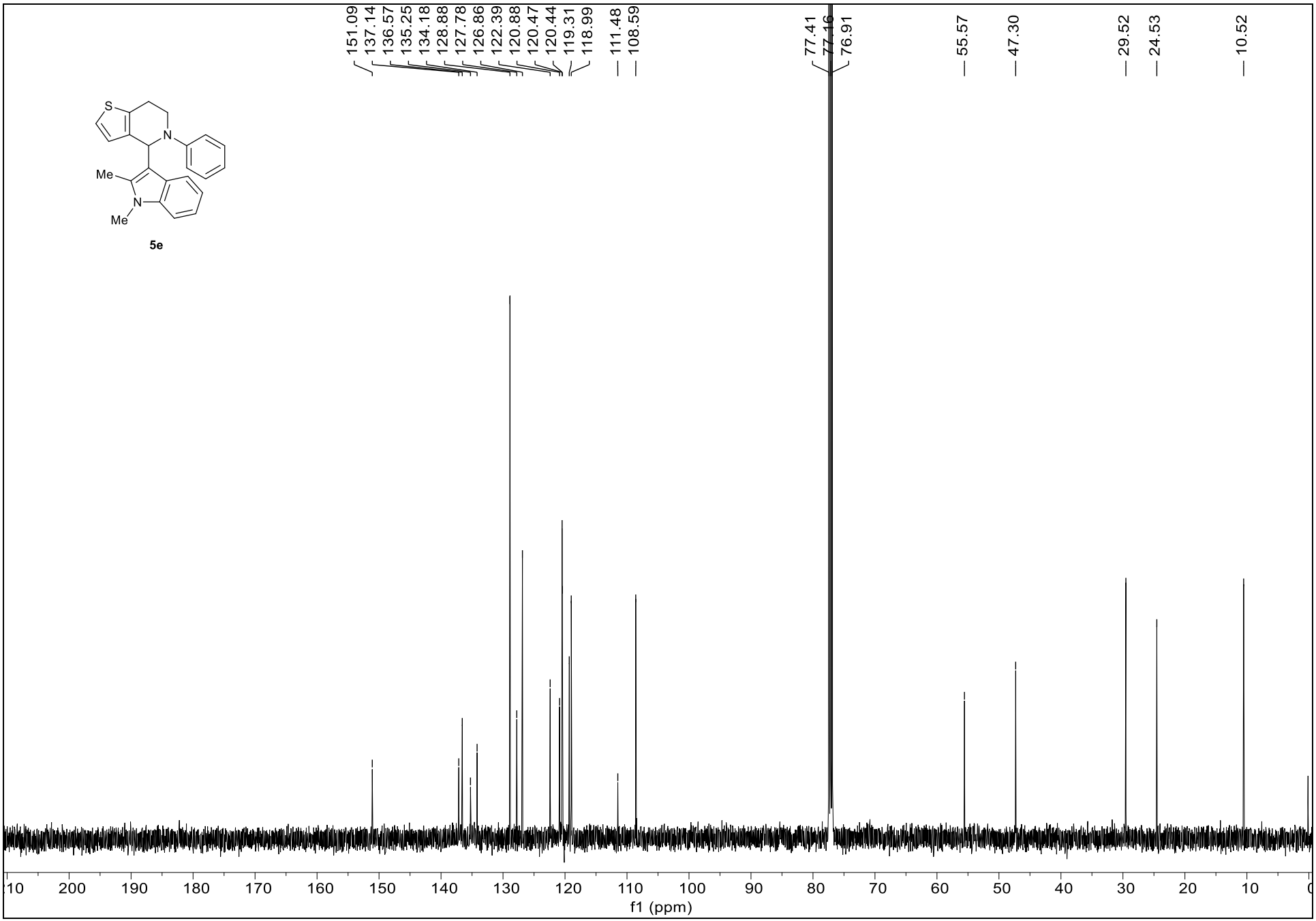
^{13}C NMR Spectrum of 5d (126 MHz, $CDCl_3$)



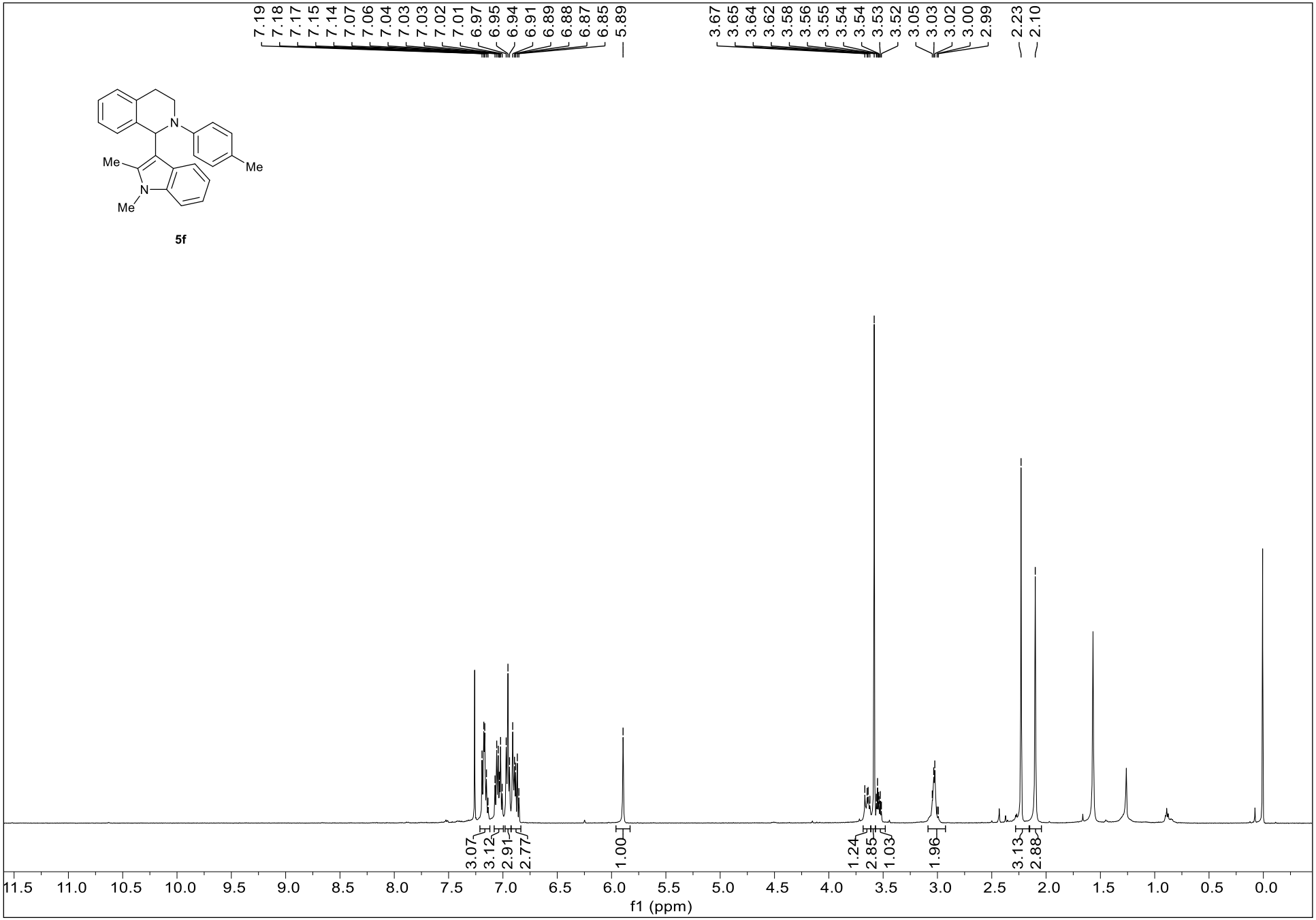
^{1}H NMR Spectrum of 5e (500 MHz, $CDCl_3$)



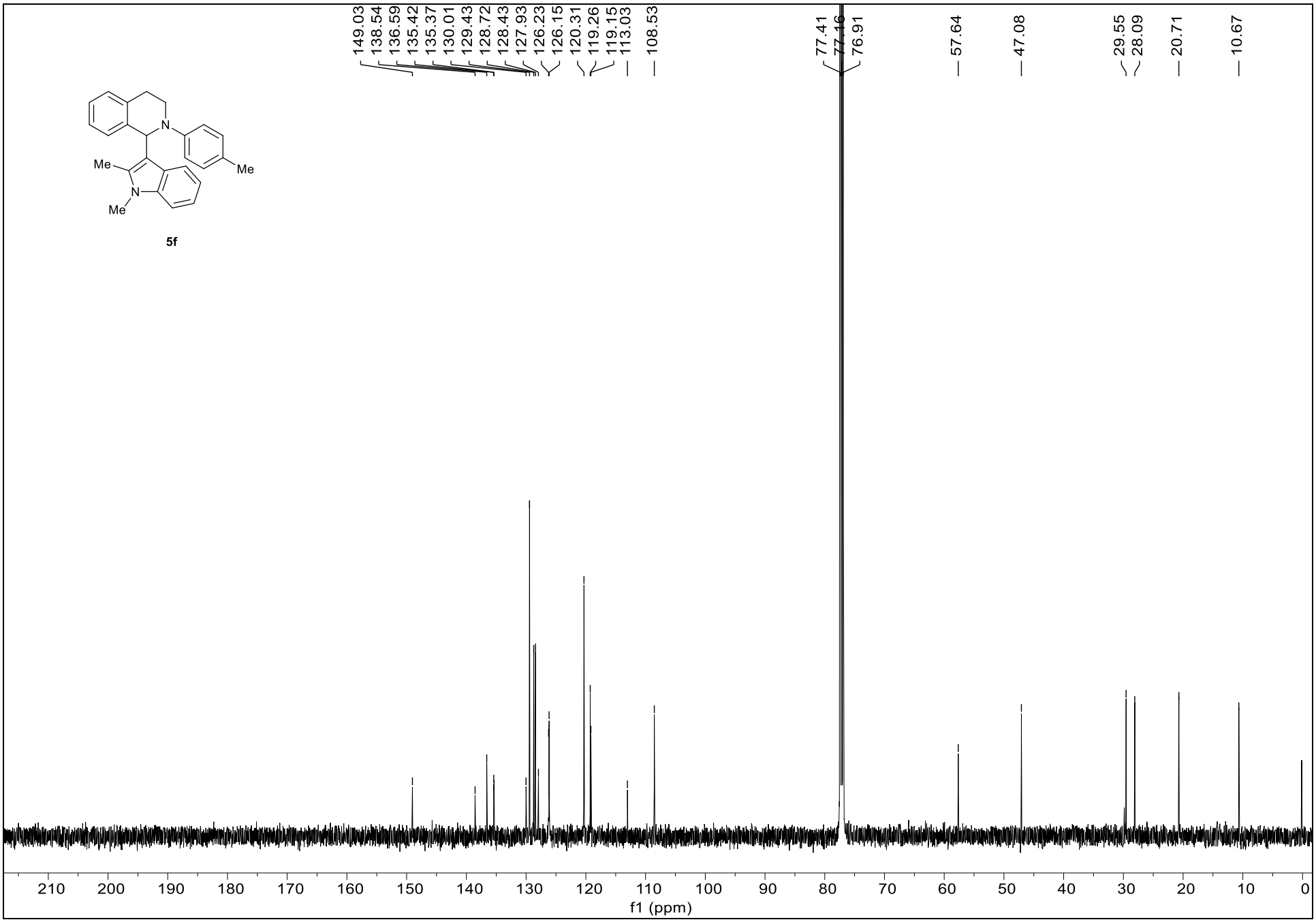
^{13}C NMR Spectrum of 5e (126 MHz, $CDCl_3$)



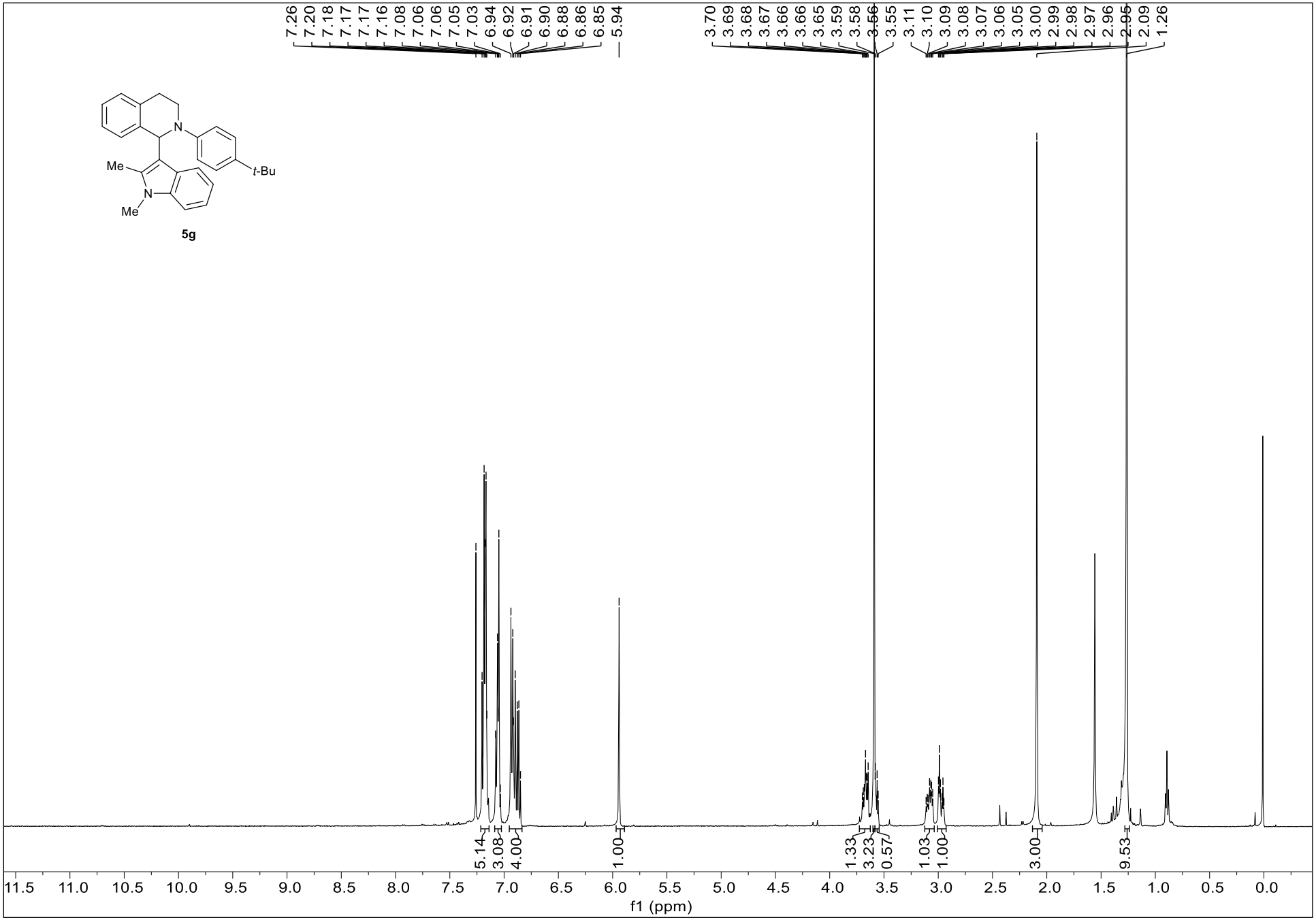
^{1}H NMR Spectrum of 5f (500 MHz, $CDCl_3$)



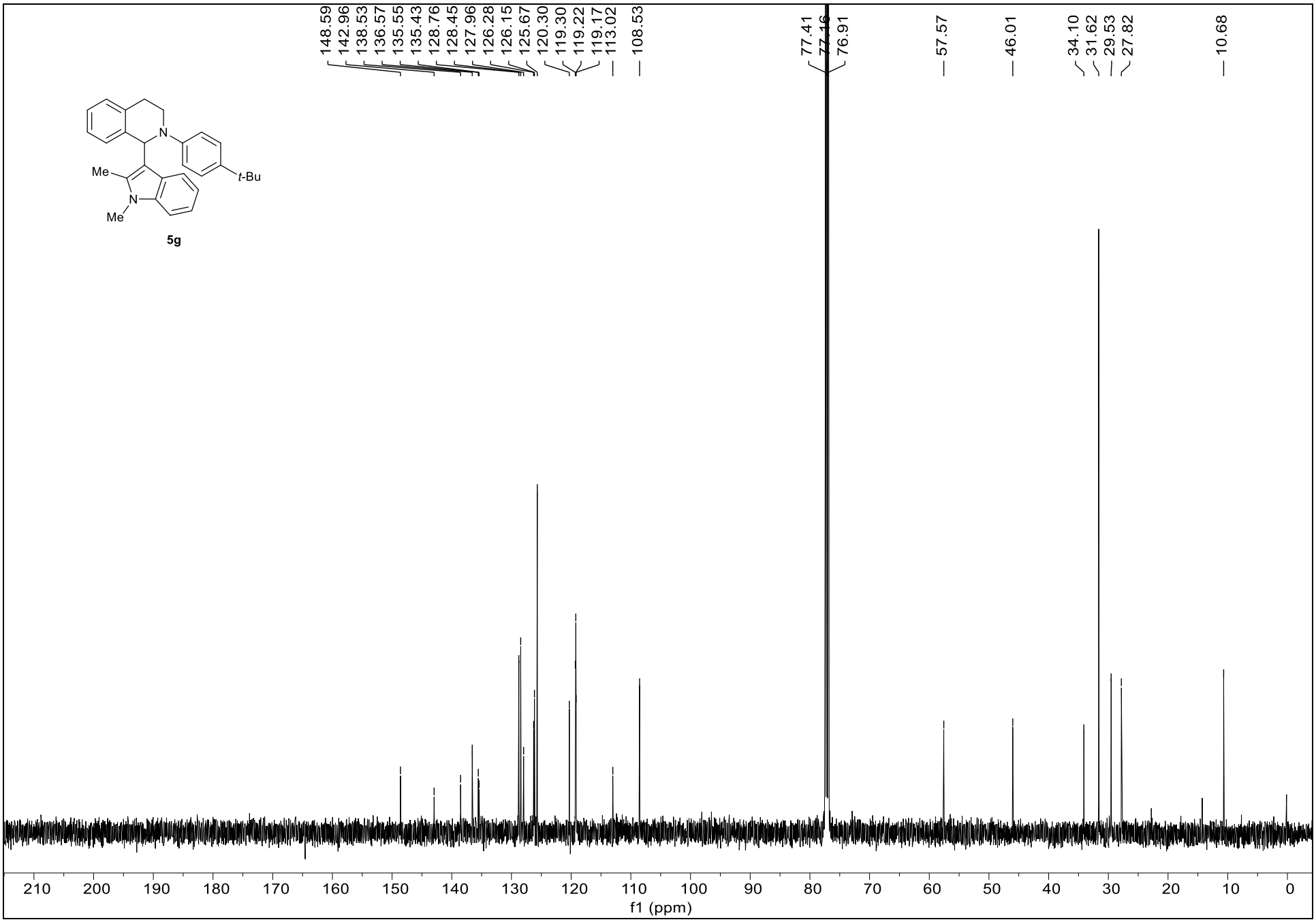
^{13}C NMR Spectrum of 5f (126 MHz, $CDCl_3$)



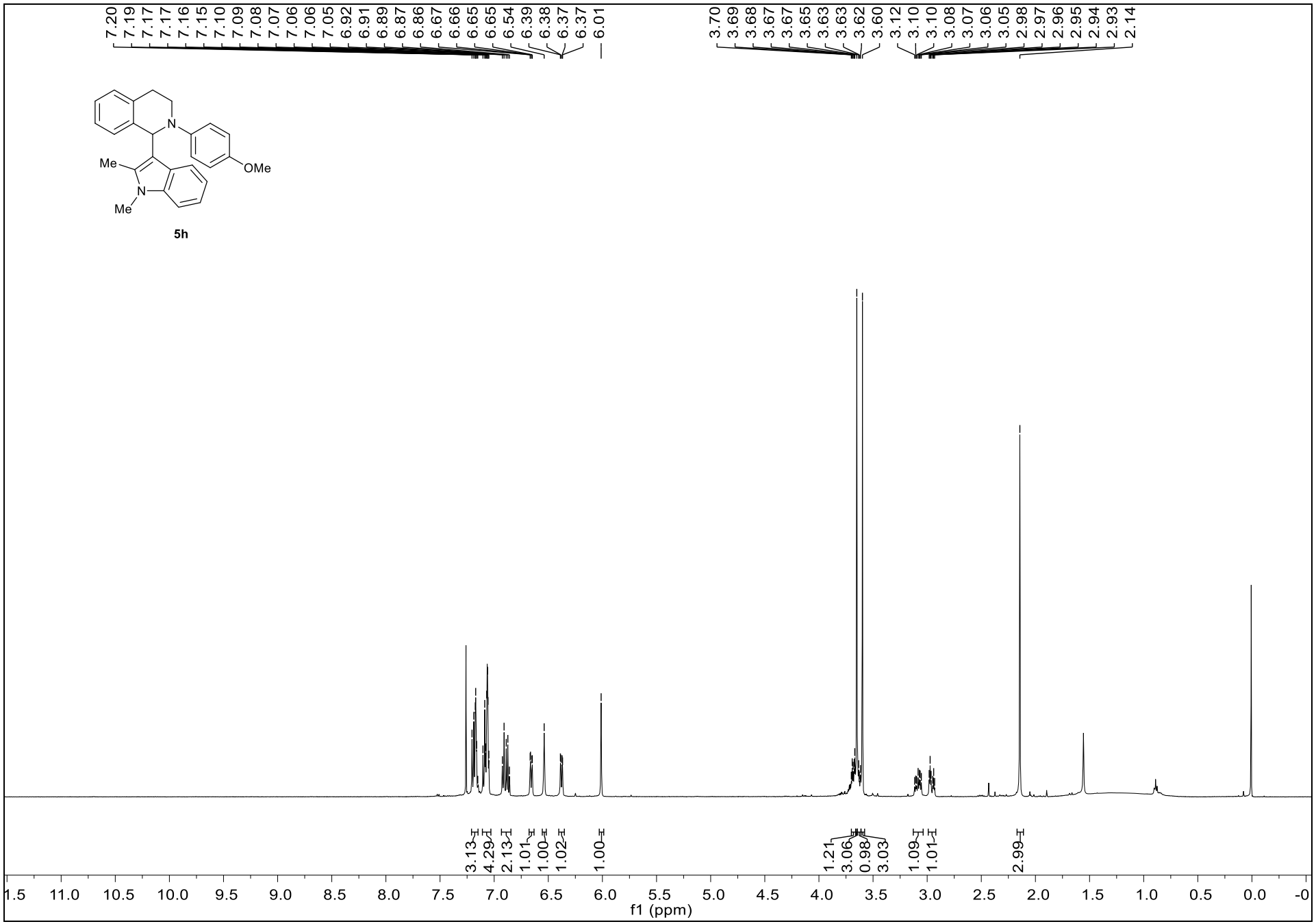
^{1}H NMR Spectrum of 5g (500 MHz, $CDCl_3$)



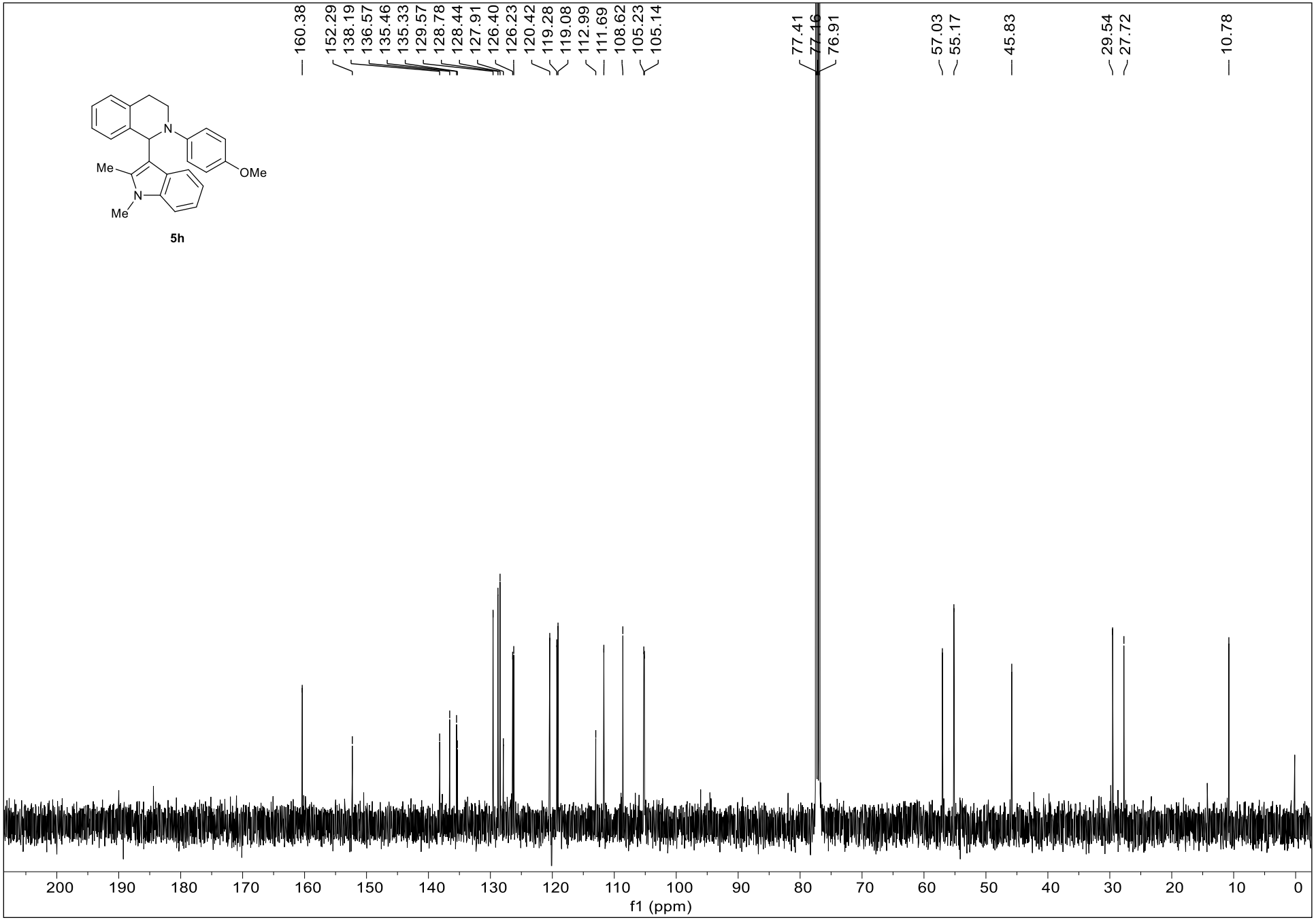
^{13}C NMR Spectrum of 5g (126 MHz, $CDCl_3$)



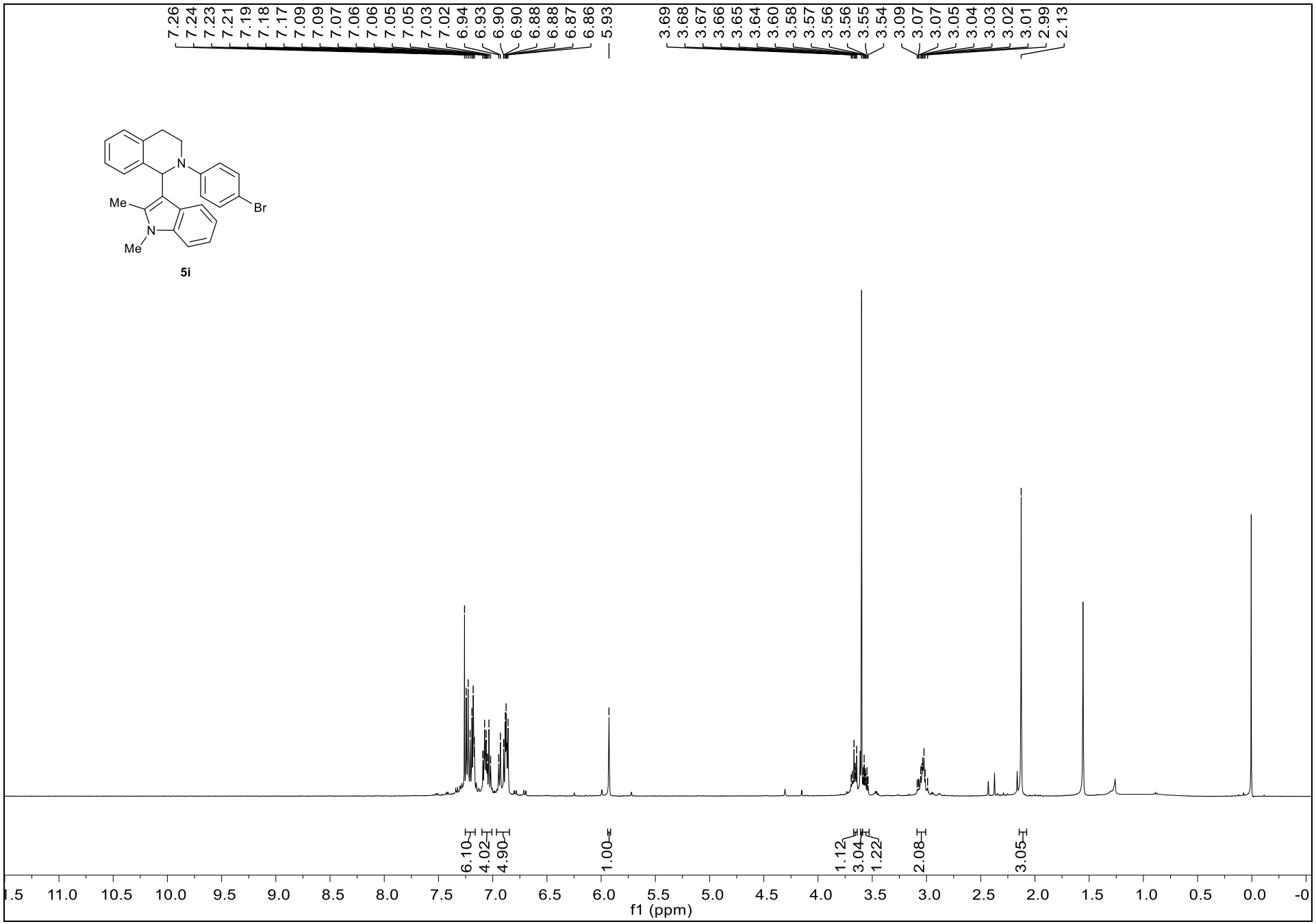
^{1}H NMR Spectrum of 5h (500 MHz, $CDCl_3$)



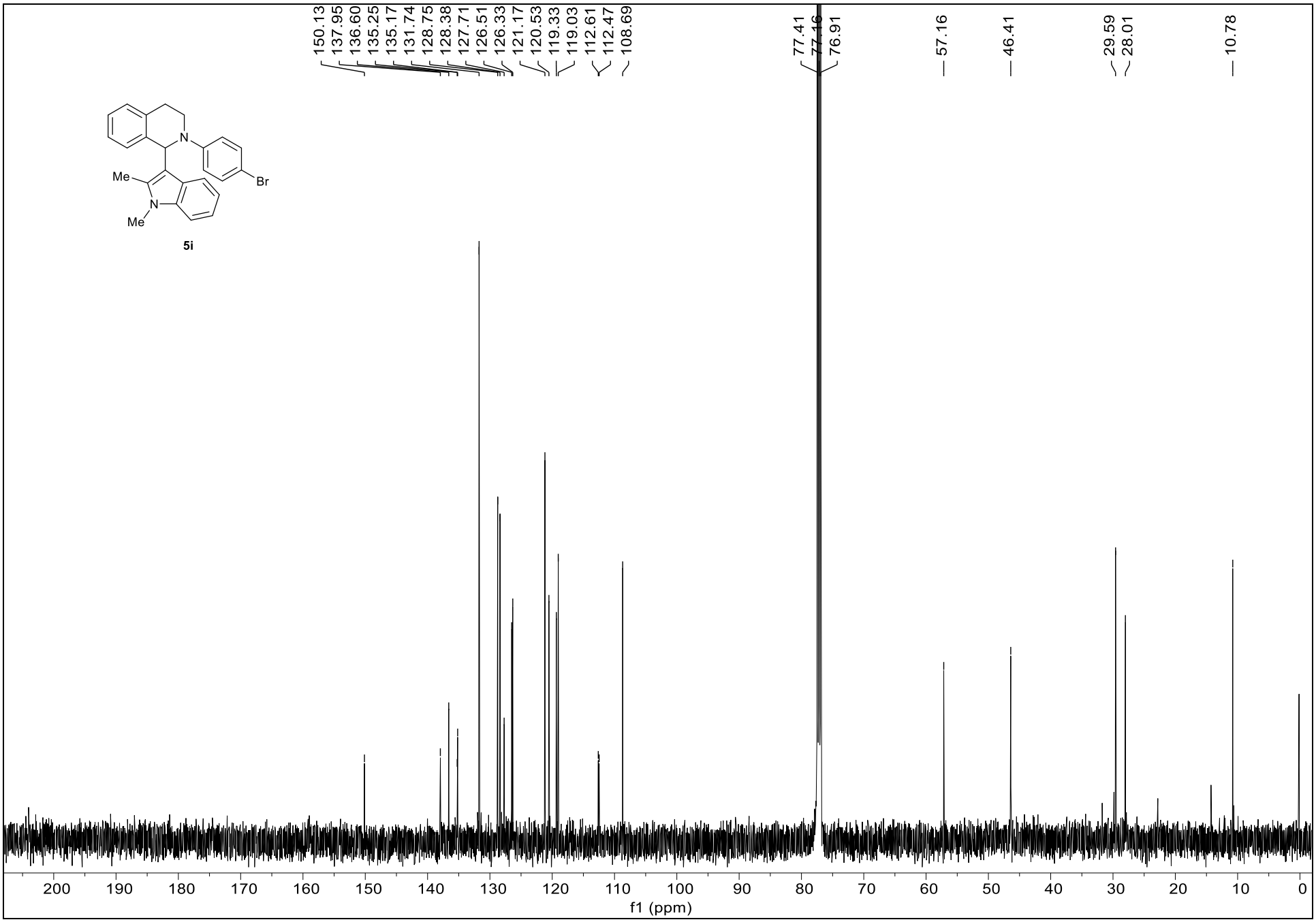
^{13}C NMR Spectrum of 5h (126 MHz, $CDCl_3$)



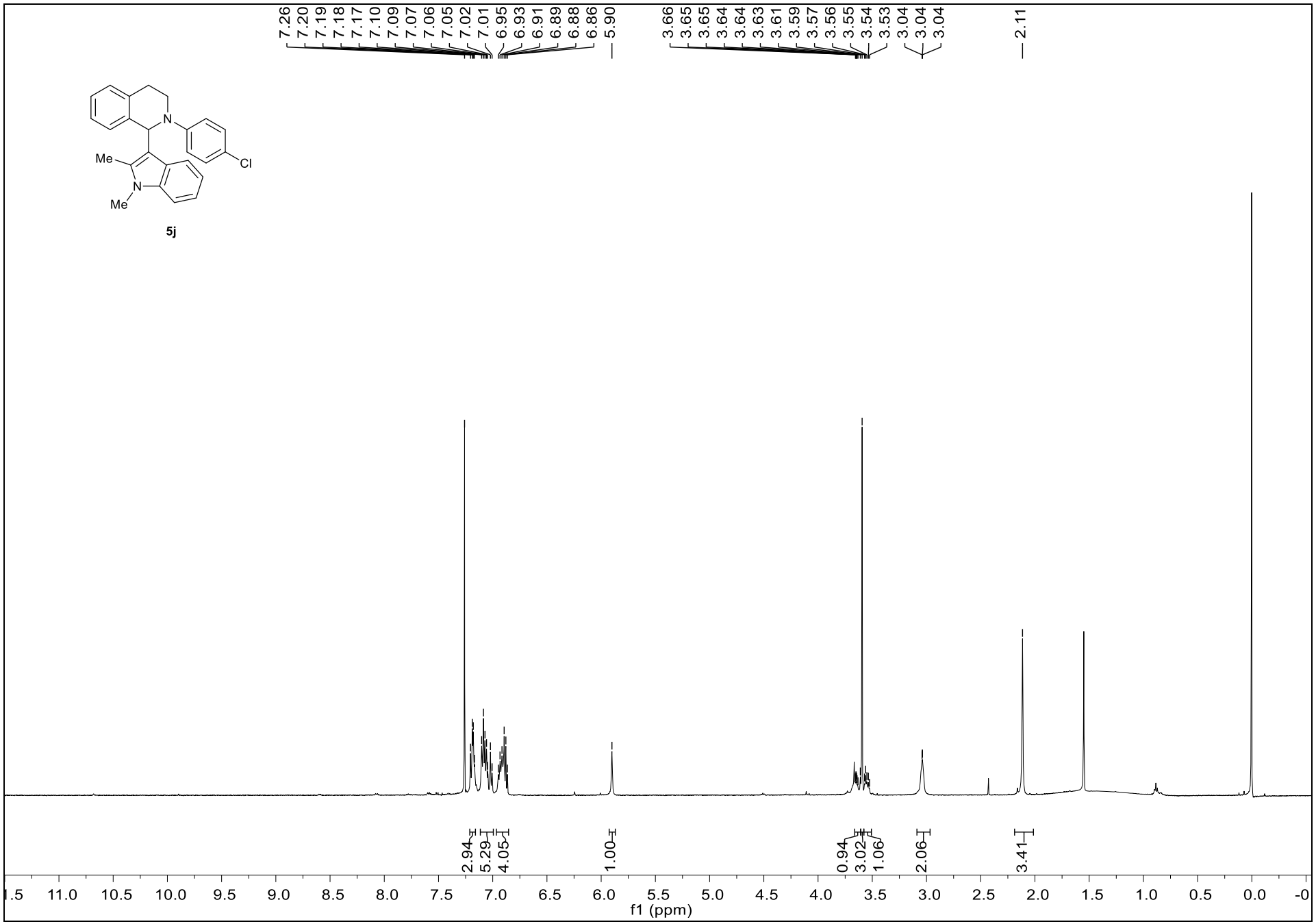
^{1}H NMR Spectrum of 5i (500 MHz, $CDCl_3$)



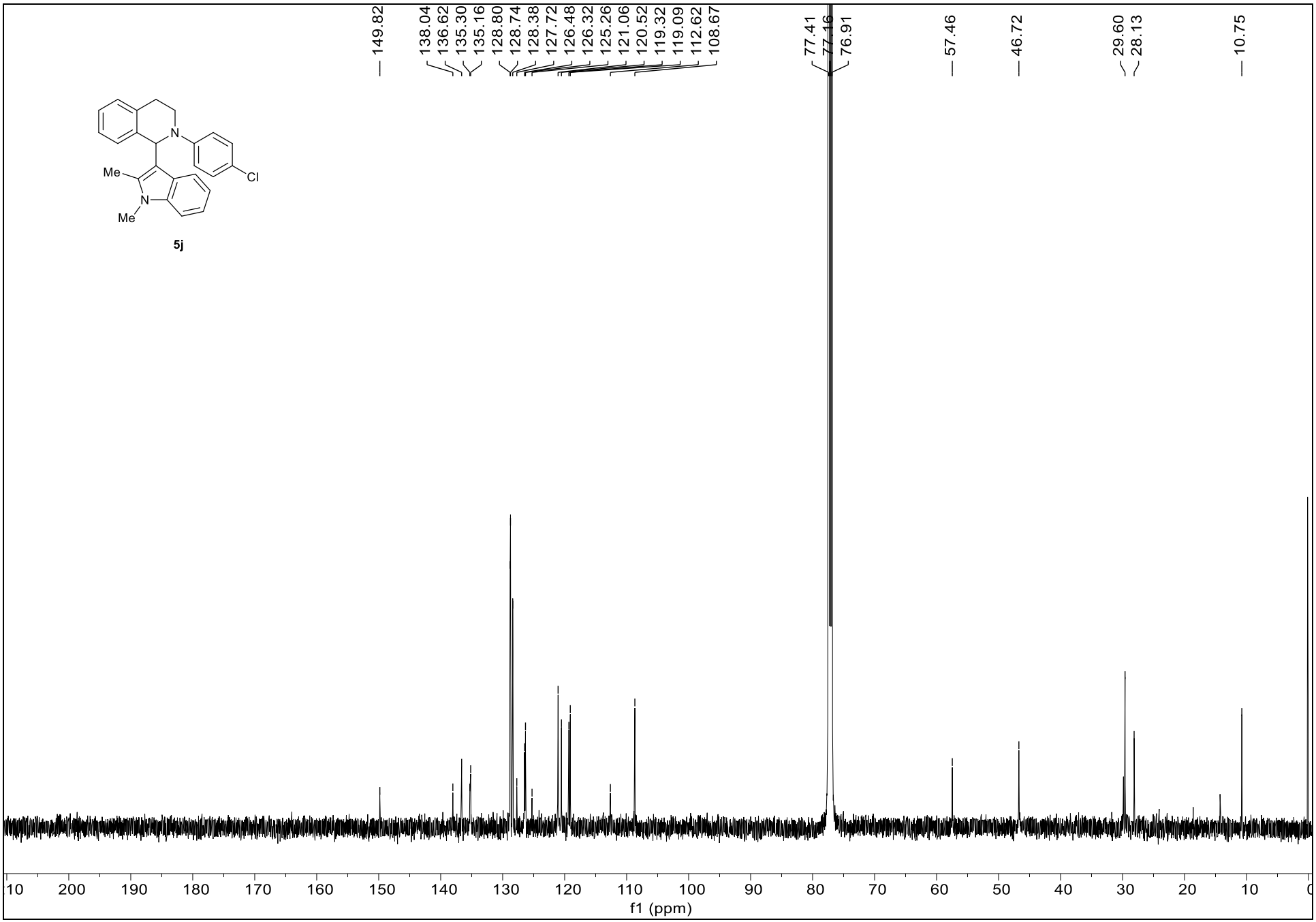
^{13}C NMR Spectrum of 5i (126 MHz, $CDCl_3$)



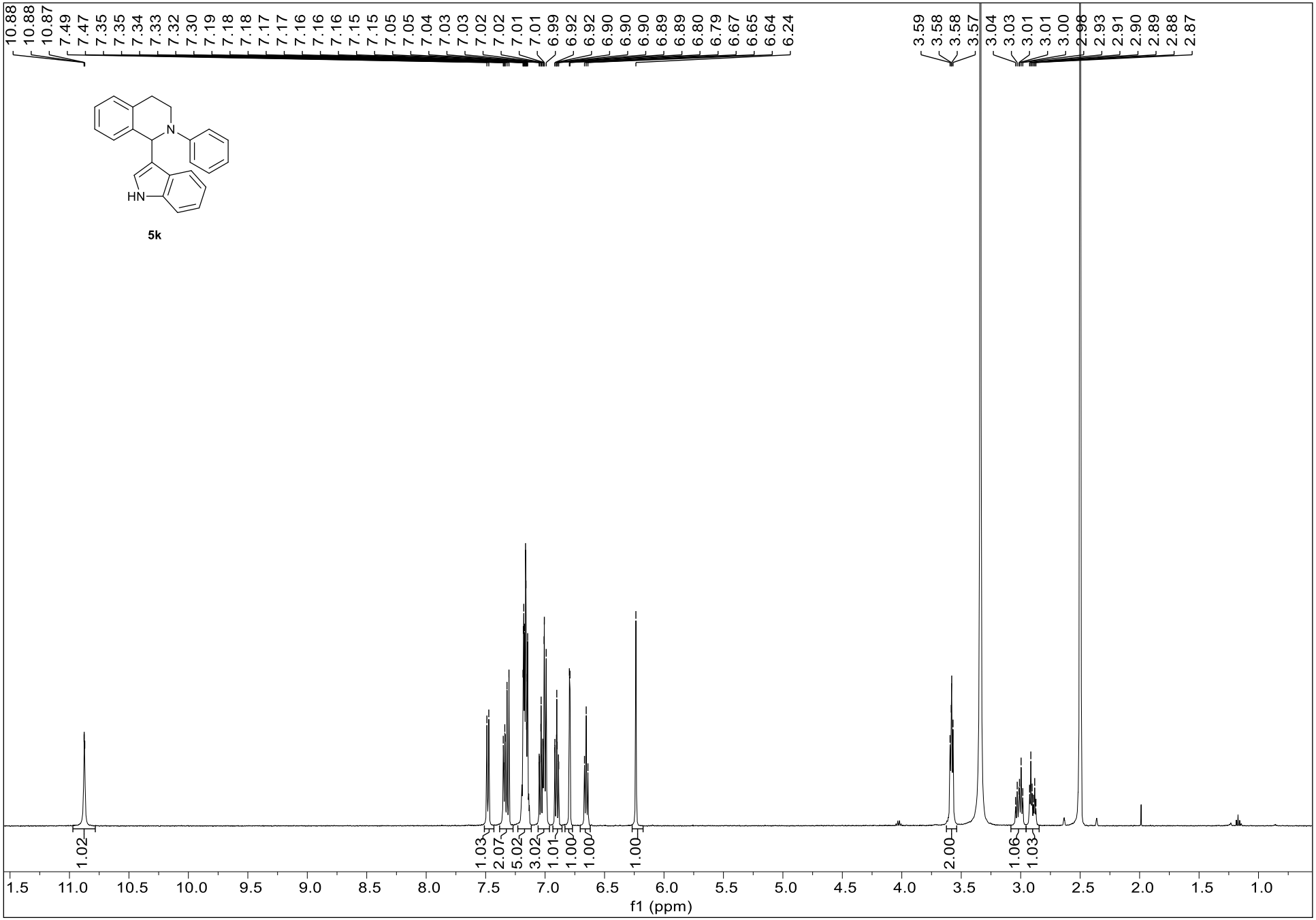
^{1}H NMR Spectrum of 5j (500 MHz, $CDCl_3$)



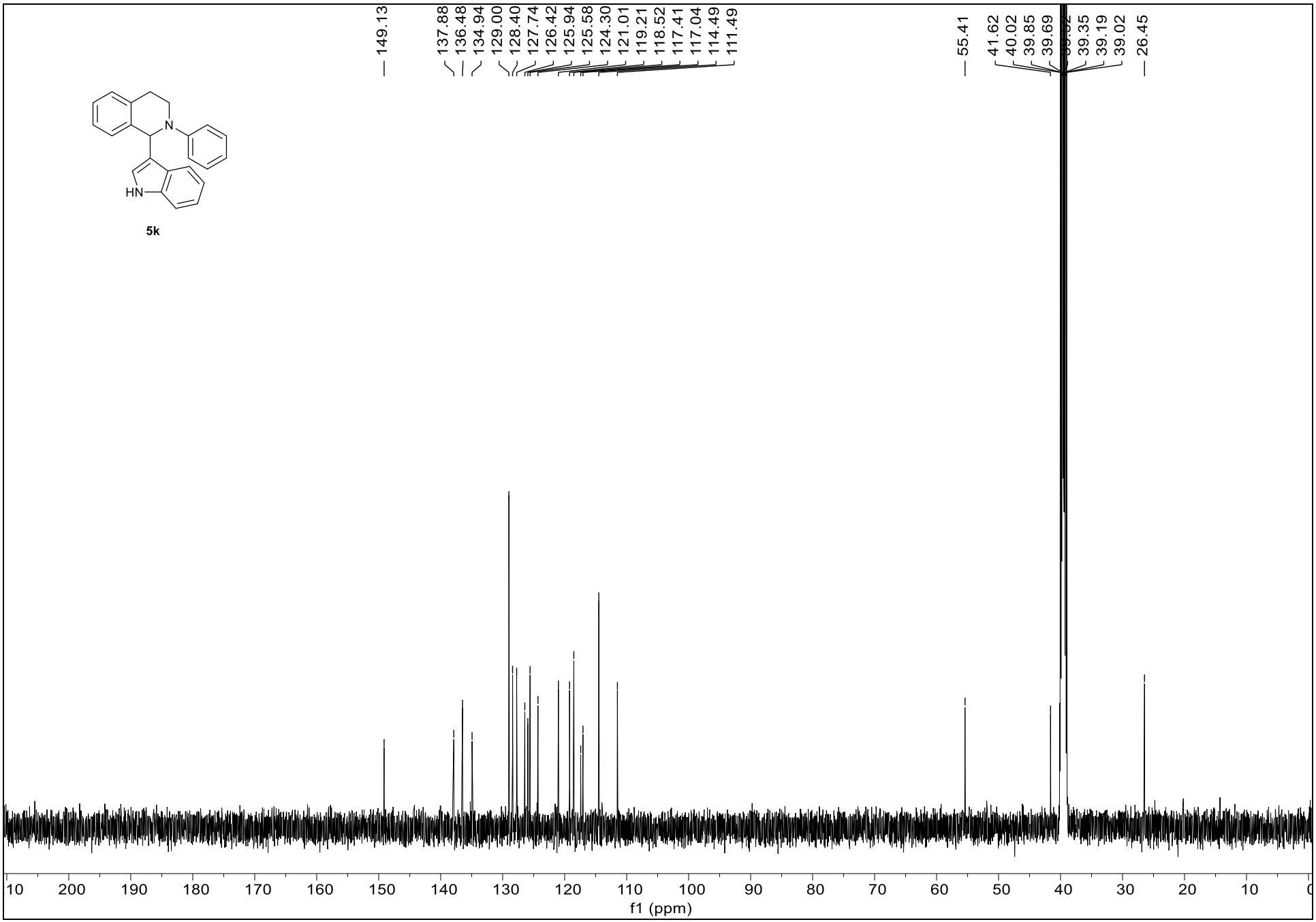
^{13}C NMR Spectrum of 5j (126 MHz, $CDCl_3$)



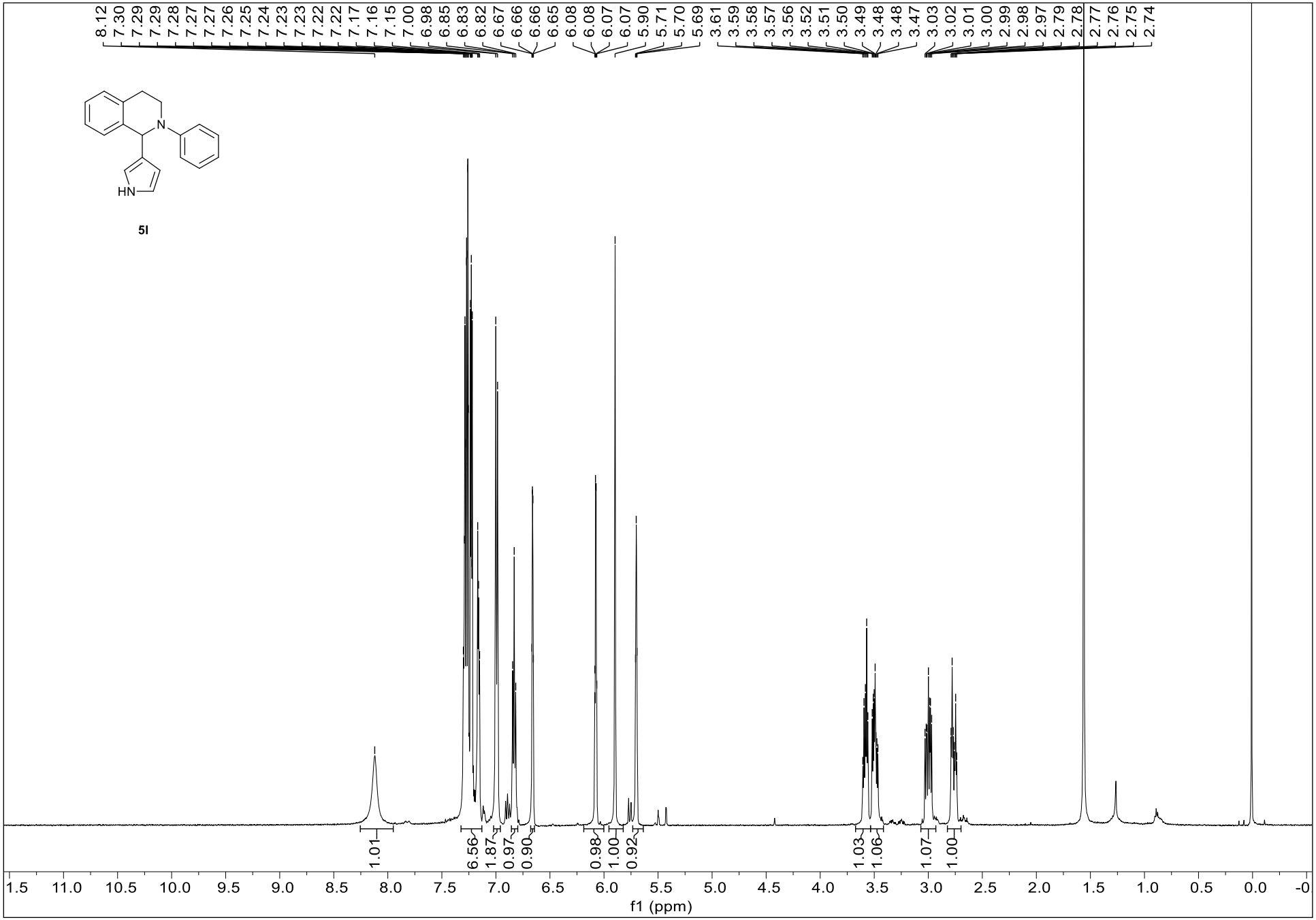
^{1}H NMR Spectrum of 5k (500 MHz, DMSO)



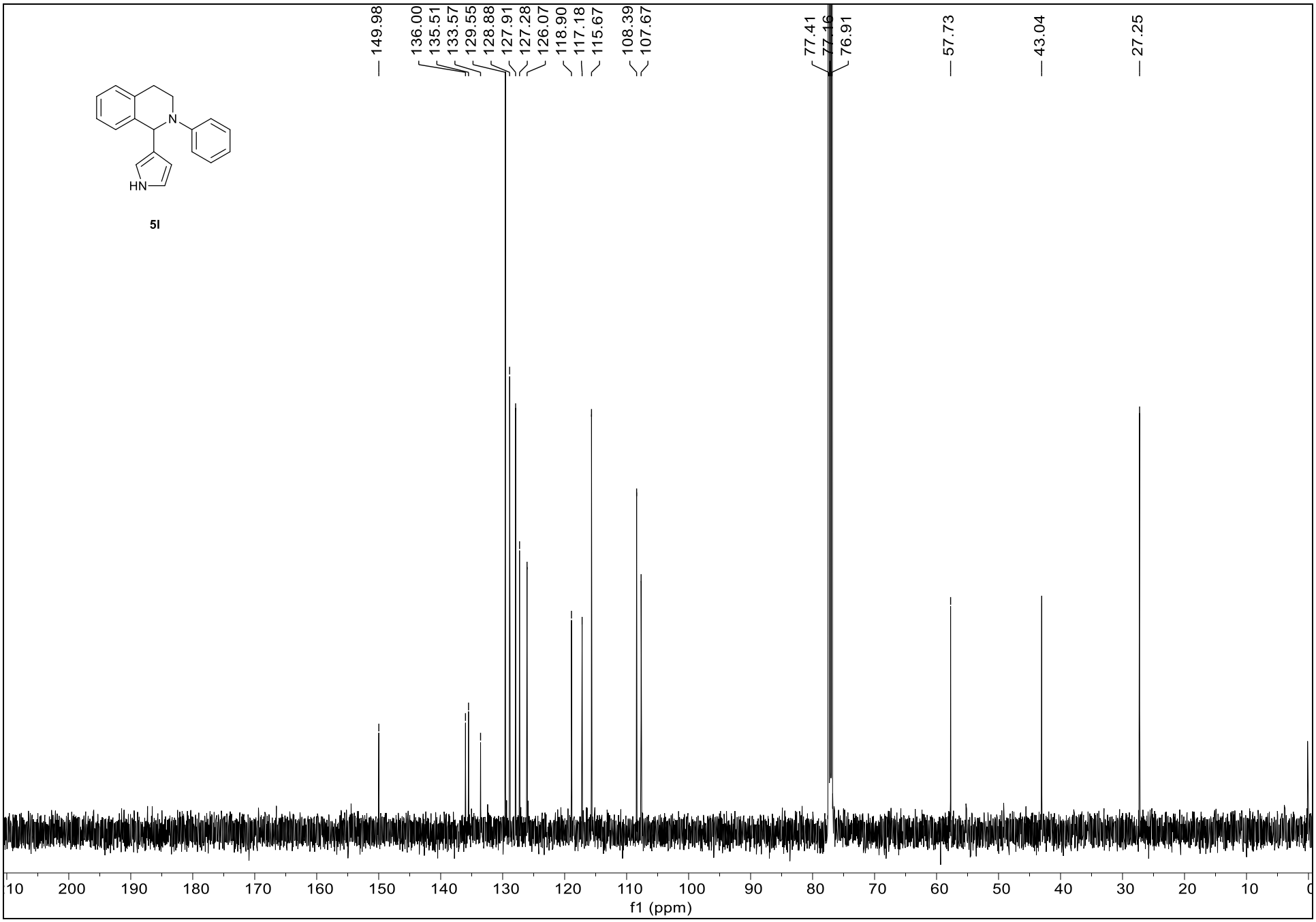
^{13}C NMR Spectrum of 5k (126 MHz, DMSO)



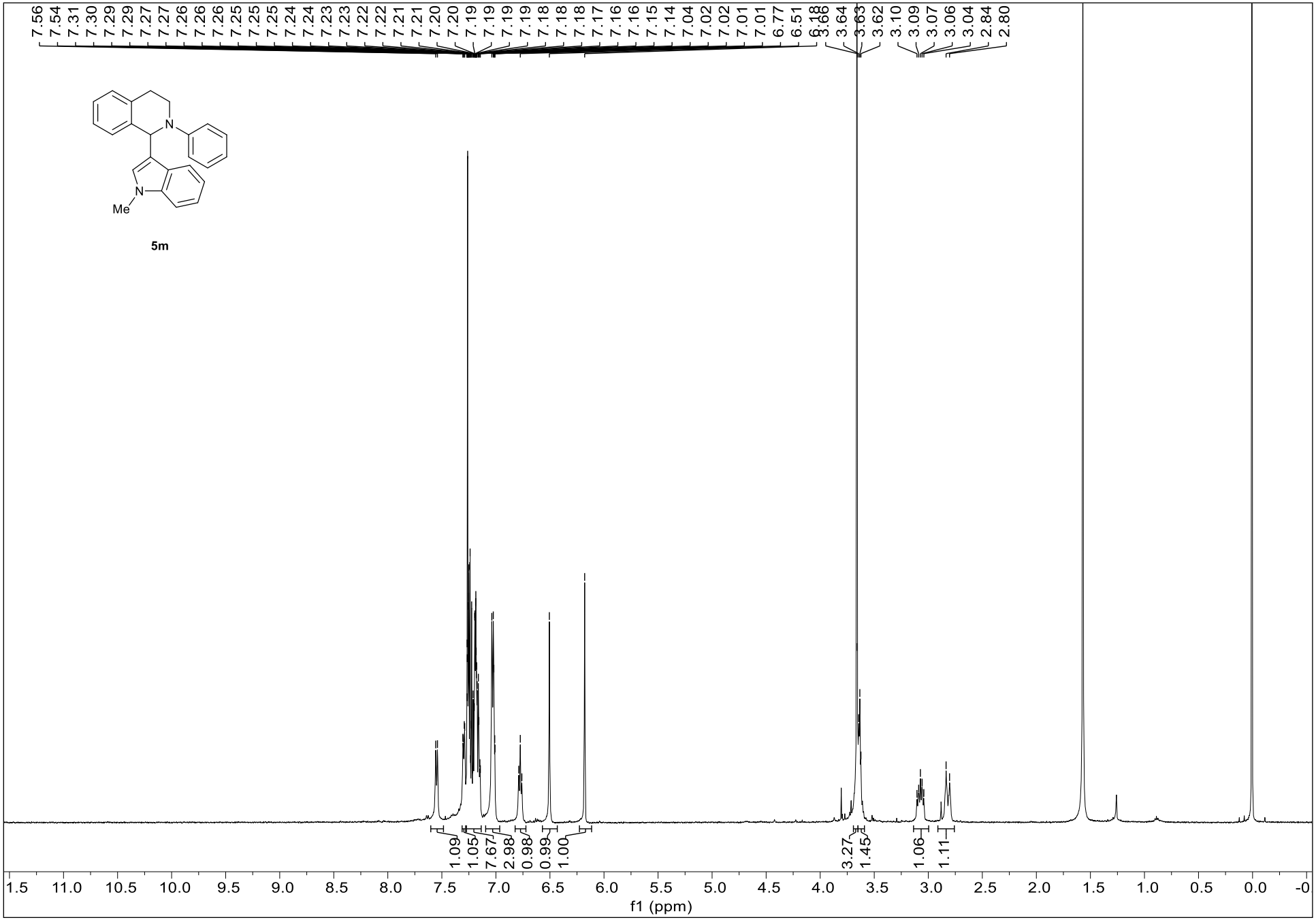
^{1}H NMR Spectrum of 5l (500 MHz, $CDCl_3$)



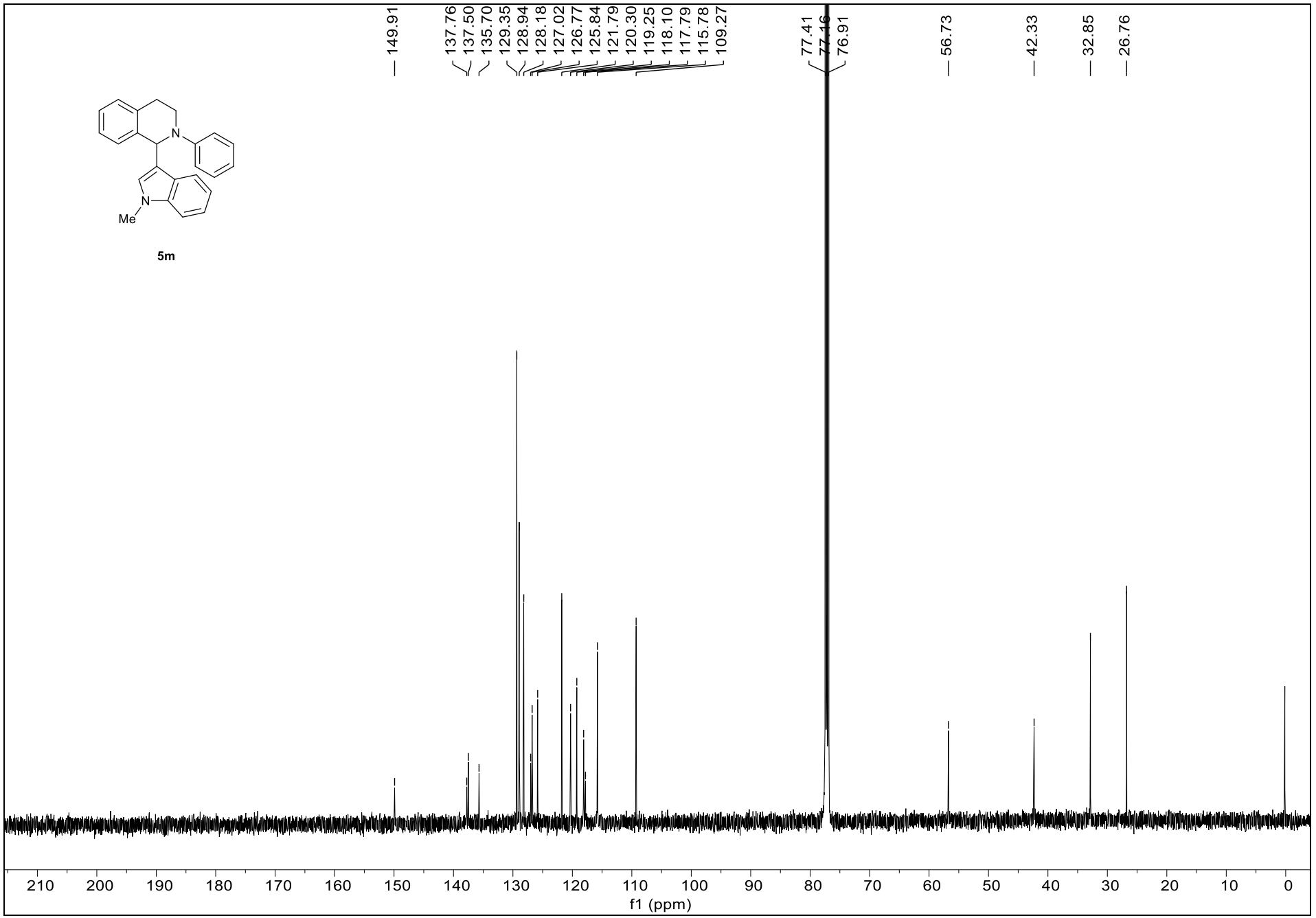
^{13}C NMR Spectrum of 5l (126 MHz, $CDCl_3$)



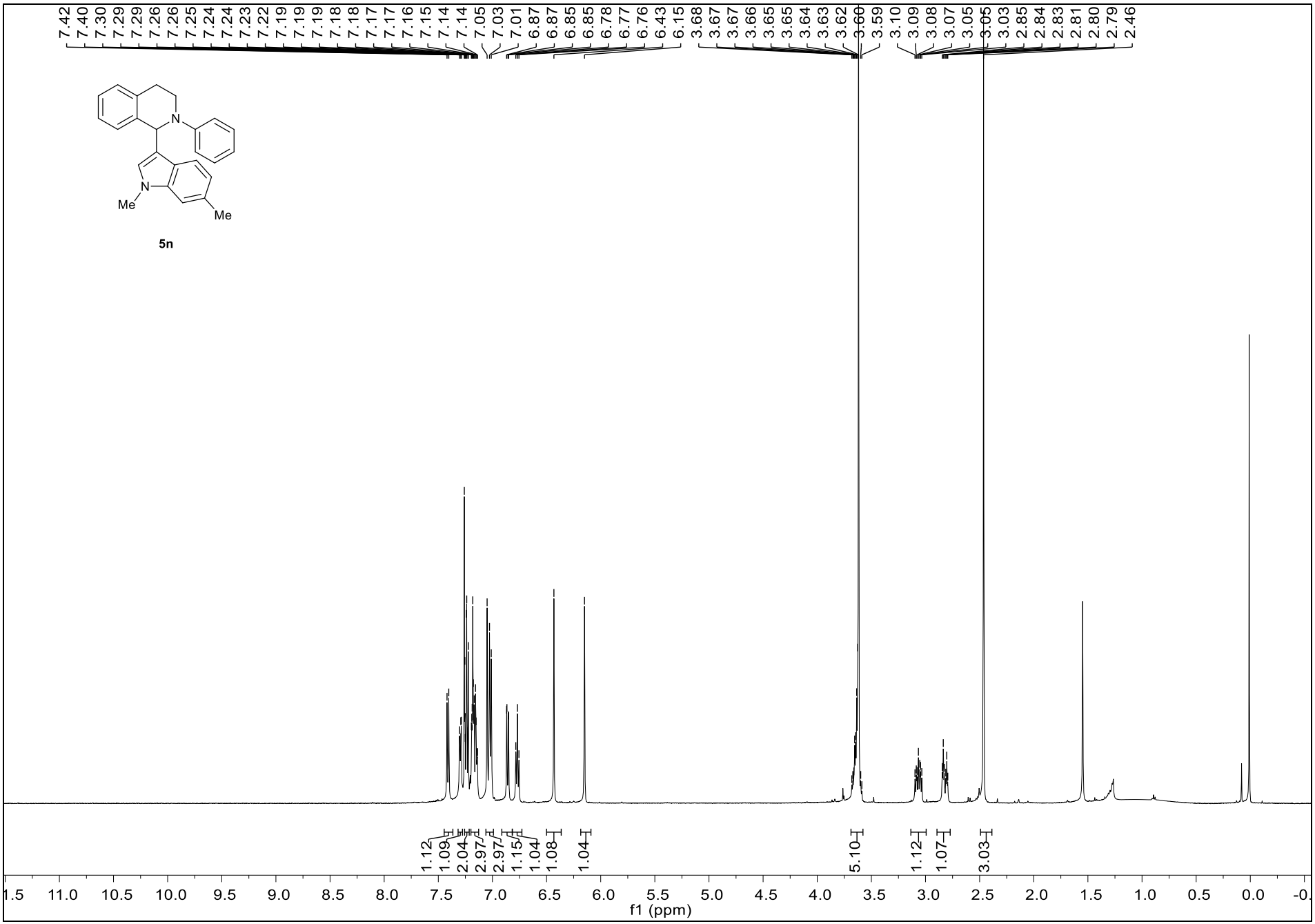
^{1}H NMR Spectrum of 5m (500 MHz, $CDCl_3$)



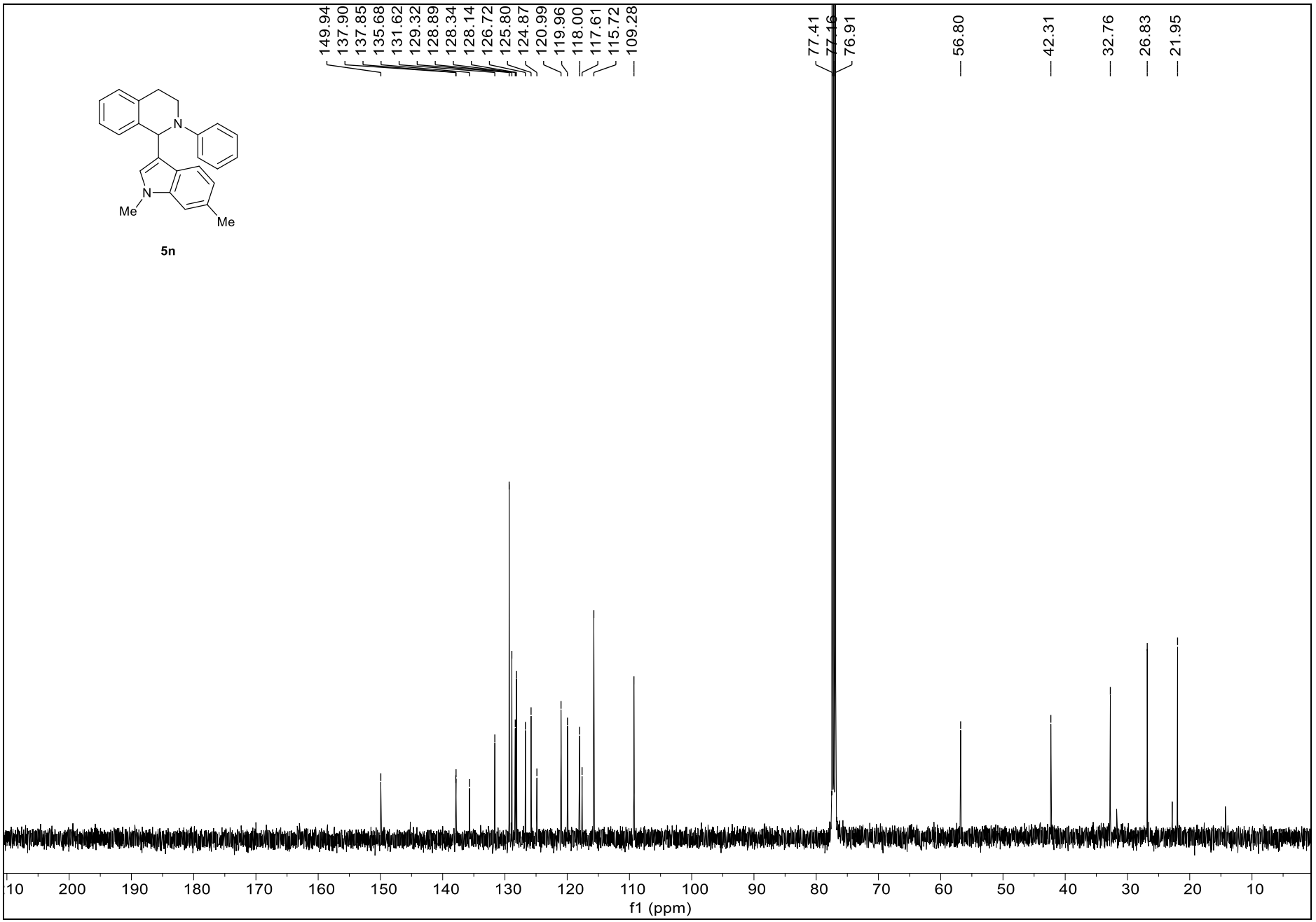
^{13}C NMR Spectrum of 5m (126 MHz, $CDCl_3$)



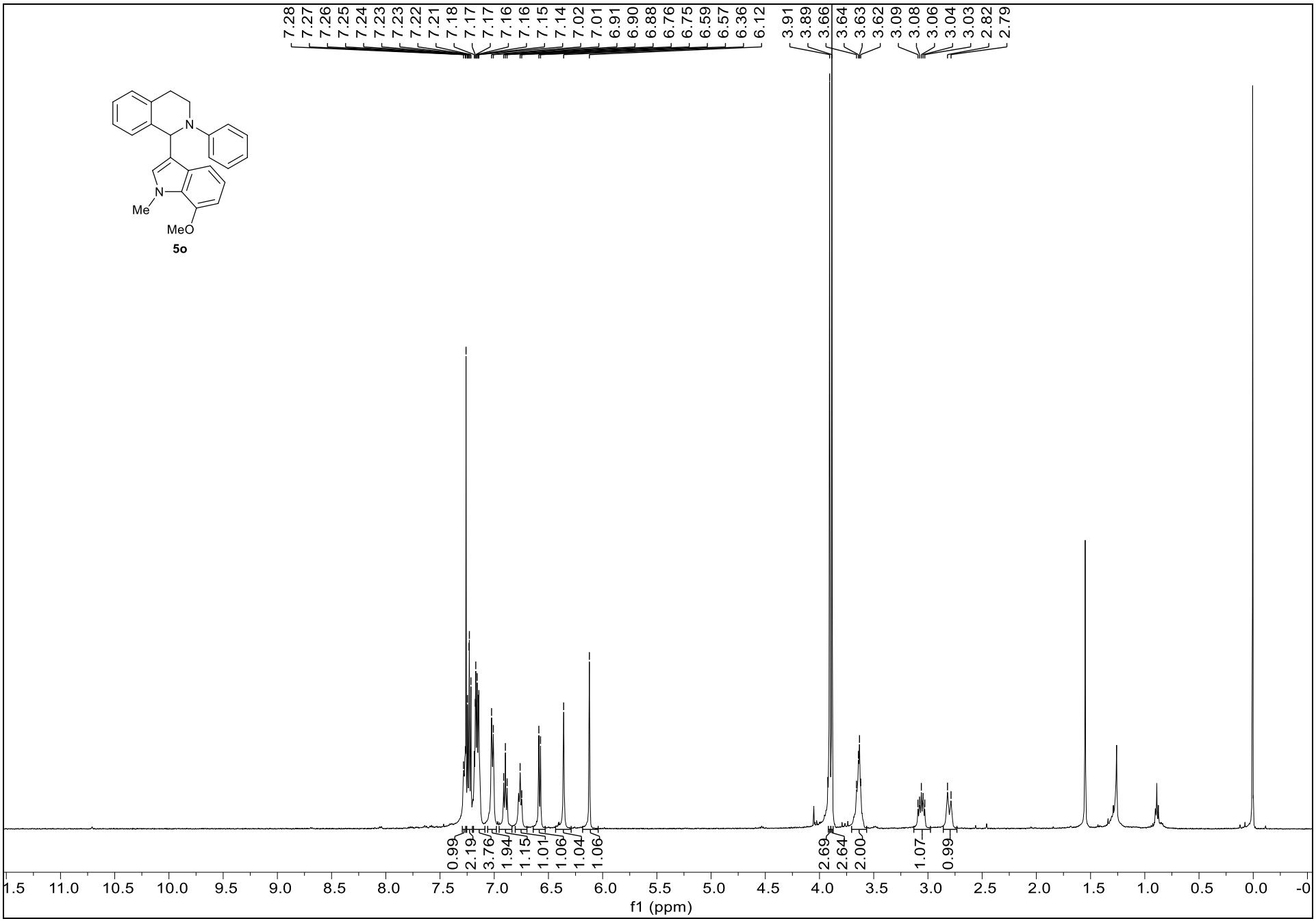
^{1}H NMR Spectrum of 5n (500 MHz, $CDCl_3$)



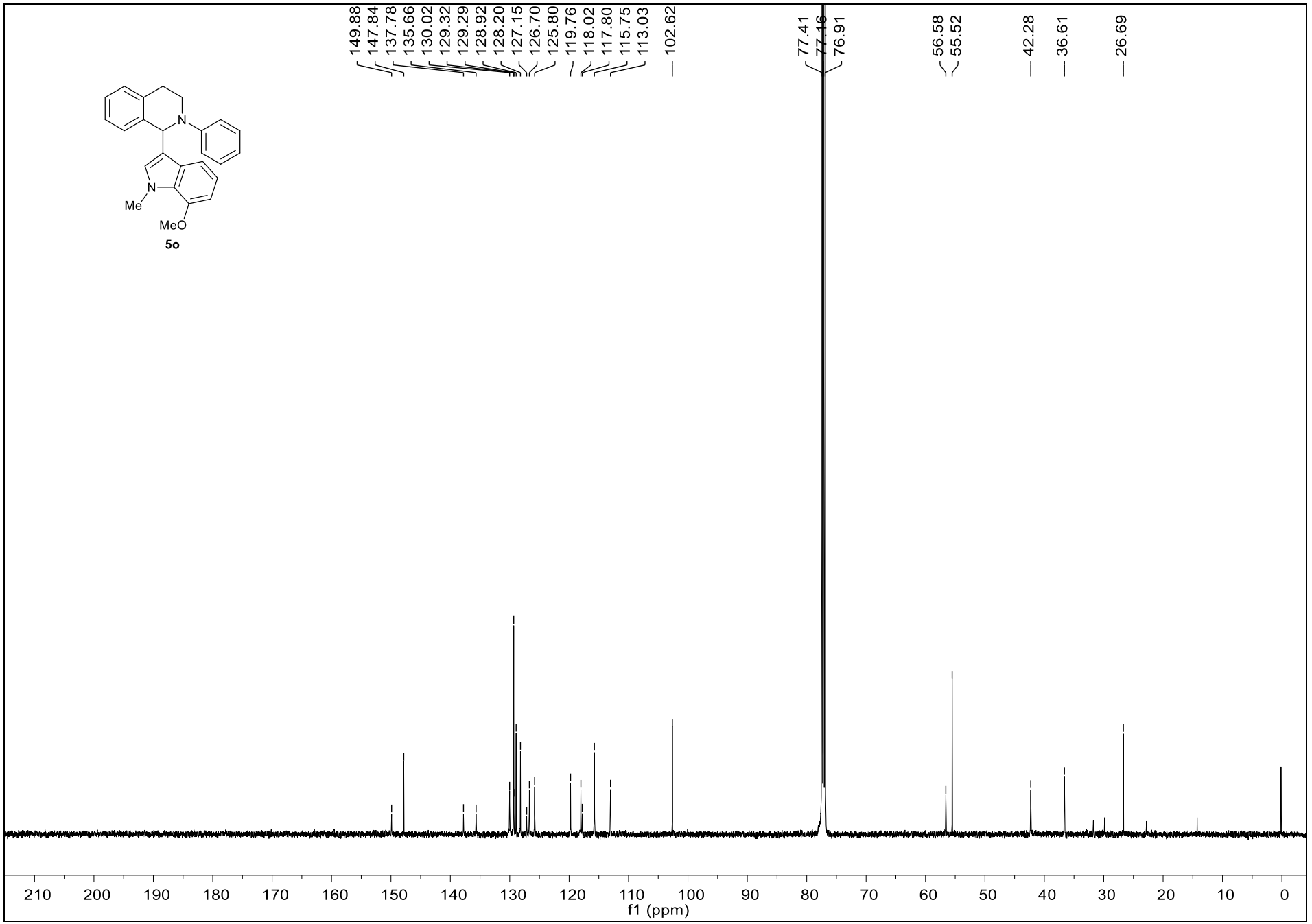
^{13}C NMR Spectrum of 5n (126 MHz, $CDCl_3$)



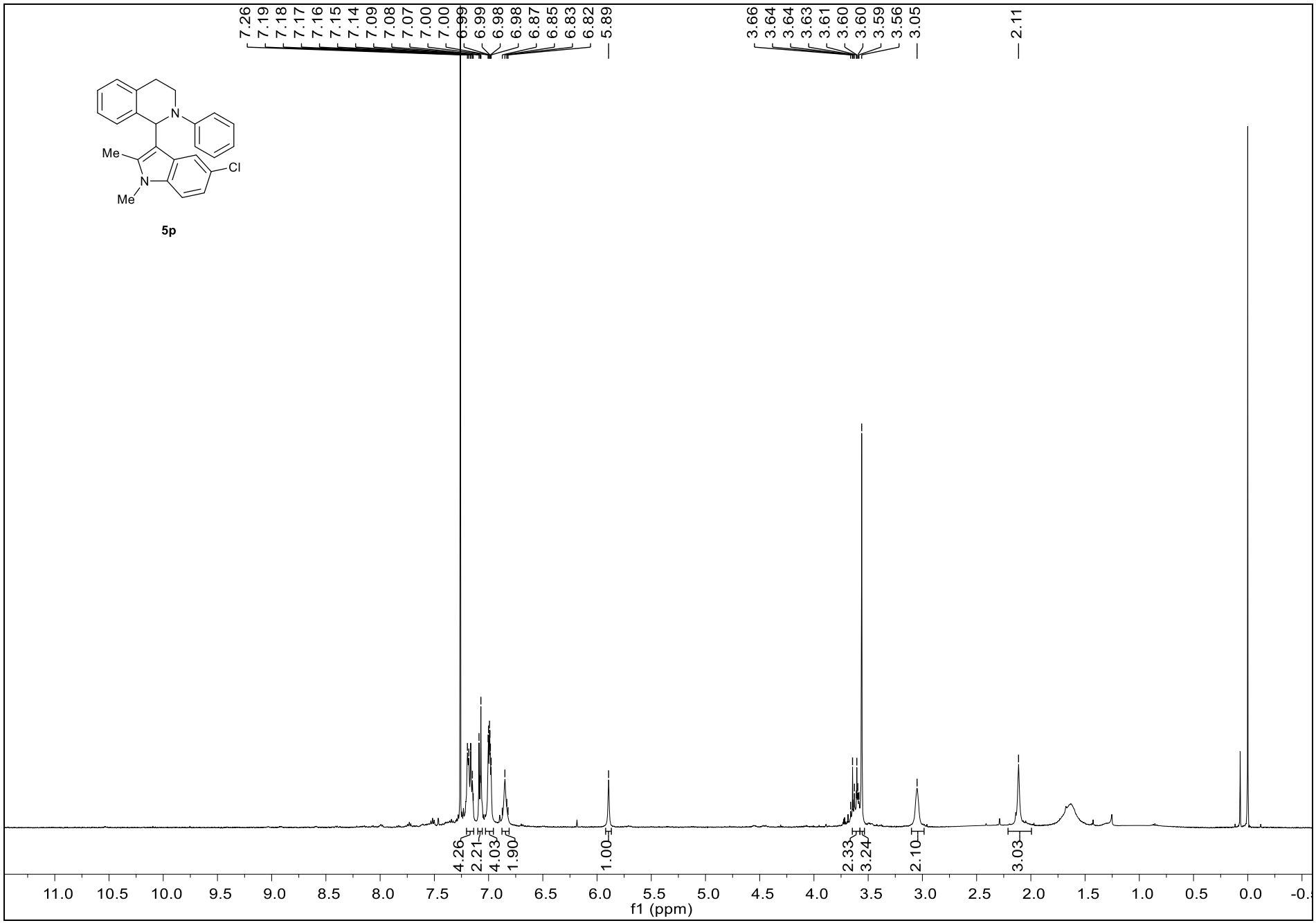
^{1}H NMR Spectrum of 5o (500 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 5o (126 MHz, $CDCl_3$)



^{1}H NMR Spectrum of 5p (500 MHz, $CDCl_3$)



^{13}C NMR Spectrum of 5p (126 MHz, $CDCl_3$)