

Supporting Information

Borane-catalysed C2-selective Indole Reductive Functionalisation

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S1 General Experimental Information

Reaction Setup: All reactions were carried out in oven (185 °C) dried glassware, which had been cleaned using base (KOH in propan-2-ol) and acid (HCl in H₂O) baths. All air- and moisture sensitive reactions were carried out using an argon atmosphere glovebox or a Schleck line (nitrogen). All reported reaction temperatures corresponded to external bath temperatures. Room temperature was approximately 20 °C. "Brine" refers to a saturated solution of sodium chloride in H₂O.

NMR Spectroscopy: ¹H, ¹³C, ¹¹B and ¹⁹F NMR Spectrum were recorded on Bruker Avance III 400 and 500 MHz; Bruker AVI 400 MHz; Bruker Avance I 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm). ¹H NMR Spectrum were referenced to the residual proteosolvent peak (CHCl₃: 7.26 ppm, CH₂Cl₂: 5.32 ppm, THF: 1.73 ppm). ¹³C NMR spectra were referenced to the solvent peak (CDCl₃: 77.00 ppm). Multiplicities are shown as s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext. (sextet), sept. (septet), non. (nonet), ap. (apparent). Coupling constants, *J*, are reported in Hertz, rounded to the nearest 0.1 Hz and as observed. Integration of peaks is provided with the assignments indicated where appropriate.

Infrared Spectroscopy: Infra-red (IR) Spectrum were recorded on a Perkin-Elmer Spectrum One FT-IR, or Shimadzu IRAffinity-1 spectrometer (serial no. A213749) spectrometer. Peaks are reported in cm⁻¹ with indicated relative intensities: s (strong, 0-33% T), m (medium, 34-66% T), w (weak, 67-100% T), and br (broad).

Chromatography: Column chromatography was carried out on a Teledyne ISCO CombiFlash NextGen 300+ using RediSep R_f normal phase silica flash columns (12, 25, 40, or 80 g; 20-40 microns). Substrates were purified using 40/60 petroleum ether and EtOAc on a gradient of 100:0 to 0:100 with flow rates of 10-110 mL min⁻¹ depending on the size of column and ΔR_f.

Mass Spectrometry: Mass spectrometry (MS) was performed by the University of Edinburgh, School of Chemistry, Mass Spectrometry Laboratory. High resolution mass spectra were recorded on a VG autospec, or Thermo/Finnigan MAT 900, mass spectrometer. Electron Impact (EI⁺) spectra were performed at 70 eV using methane as the carrier gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Chemical Ionization (CI⁺) spectra were performed with methane reagent gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Electrospray Ionization (ESI⁺) spectra were performed using a time-of-flight (TOF) mass analyzer. Data are reported in the form of *m/z* (intensity relative to the base peak = 100).

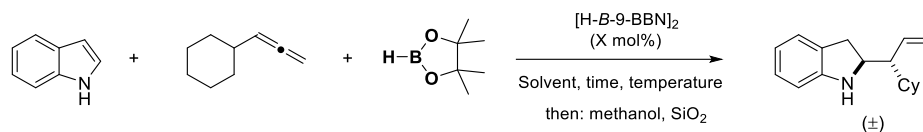
Melting Points: Melting points were determined using a Stuart Scientific SMP10, or Griffin Gallankamp and are uncorrected.

Chemicals: All reagents were purchased from Sigma Aldrich, Acros Organics or Alfa Aesar, or were synthesised in the laboratory.

Solvents: All solvents for air- and moisture sensitive techniques were obtained from an anhydrous solvent system (Innovative Technology). Reaction solvents tetrahydrofuran (THF) (Fisher, HPLC grade), ether (Et₂O) (Fisher, BHT stabilized ACS grade), and dichloromethane (CH₂Cl₂) (Fisher, unstabilised HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Toluene (ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Solvents for filtration, transfers, chromatography, and recrystallization were dichloromethane (CH₂Cl₂) (ACS grade), ether (Et₂O) (Fisher, BHT stabilised ACS grade), ethyl acetate (EtOAc) (Fisher, ACS grade), *n*-hexane (Optima), methanol (MeOH) (ACS grade), pentane (ACS grade), and petroleum ether (40–60°C, ACS grade).

Diastereoselectivity: Diastereoselectivity was determined from ¹H NMR of the crude reaction mixture.

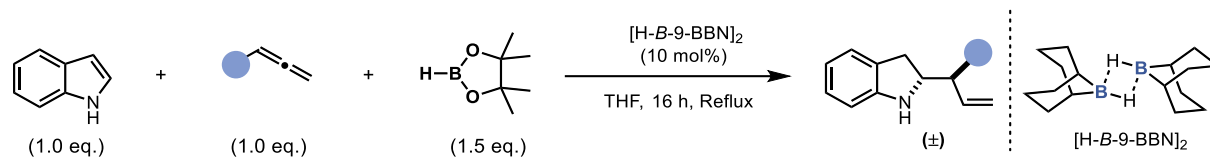
S2 Optimisation of Reaction Conditions



Entry	Allene (eq.)	HBpin (eq.)	Solvent	Catalyst (%)	Temp.	Conc. (Indole, M)	Time (h)	Yield (%)	d.r.
1	1	2	THF	10	reflux	0.5	16	64	>95:5
2	1	2	Hexane	10	reflux	0.5	16	Trace	-
3	1	2	CH ₂ Cl ₂	10	reflux	0.5	16	Trace	-
4	1	2	DME	10	reflux	0.5	16	Trace	-
5	1	2	Toluene	10	reflux	0.5	16	Trace	-
6	1	2	THF	10	reflux	0.5	16	54	>95:5
7	1	2	THF	10	reflux	1	16	Trace	-
8	1	2	THF	10	reflux	2	16	Trace	-
9	1	2	THF	10	reflux	neat	16	Trace	-
10	1	1	THF	10	reflux	0.5	66	62	>95:5
11	1	1	THF	5	reflux	0.5	66	39	>95:5
12	1	1.5	THF	10	reflux	0.5	16	81	>95:5
13	1.5	1.5	THF	10	reflux	0.5	16	80	>95:5
14	2	1.5	THF	10	reflux	0.5	16	65	>95:5
15	1	1.5	THF	5	reflux	0.5	22	55	>95:5
15	1	1.5	THF	5	reflux	0.5	42	59	>20:1
16	1	1.5	Hexane	5	reflux	0.5	16	18	>95:5
17	1	1.5	Toluene	5	reflux	0.5	16	24	>95:5
18	1	1.5	CH ₂ Cl ₂	5	reflux	0.5	16	17	>95:5

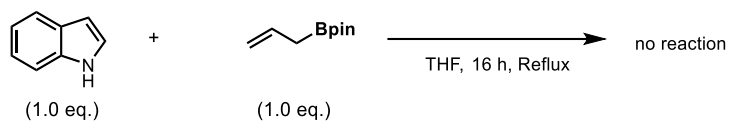
Table S1 Optimisation of reaction conditions, Yields calculated by ¹H NMR with respect to 1,3,5-trimethoxybenzene internal standard. Diastereoselectivity calculated from analysis of the crude reaction mixture.

S3 General procedure A



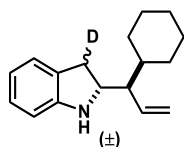
In an argon filled vial indole (1.0 eq.), 9-borobicyclo(3.3.1)nonane [H-B-9-BBN]₂ (10 mol%), allene (1.0 eq.) and HBpin (1.5 eq.) were reacted in THF (0.5 M) at reflux for 16 hours. The reactions were quenched with silica (SiO₂, 0.1 g) and the diastereoselectivity was determined by analysis of the crude reaction mixture by ¹H NMR spectroscopy. The product was purified by flash column chromatography.

S4 Mechanistic Studies



In an argon filled vial indole (0.5 mmol, 0.059 g), and allylboronic acid pinacol ester (0.5 mmol, 83 mg), were reacted in THF (0.5 M) at reflux for 16 hours. The reactions were quenched with silica (SiO_2 , 0.1 g), the crude reaction mixture was analysed by ^1H NMR spectroscopy which showed the presence of no product and the recovery of both starting materials.

3-Deutero-2-(1-cyclohexylallyl)indoline



According to general procedure A cyclohexylallene (72 μL , 0.5 mmol), D-N-indole (60 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol), [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO_2) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO_2 , 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (69 mg, 0.29 mmol, 57%)

¹H NMR (500 MHz, CDCl_3) 7.08 (d, $J = 7.2$ Hz, 1H), 7.01 (td, $J = 7.5, 1.1$ Hz, 1H), 6.68 (td, $J = 7.3, 1.0$ Hz, 1H), 6.59 (d, $J = 7.7$ Hz, 1H), 5.73 (dt, $J = 17.2, 10.1$ Hz, 1H), 5.19 (dd, $J = 10.3, 2.3$ Hz, 1H), 5.09 (dd, $J = 17.2, 2.3$ Hz, 1H), 3.98 – 3.93 (m, 1H), 3.87 (s, 1H), 3.08 (dd, $J = 16.1, 8.8$ Hz, 0.5H), 2.85 (dd, $J = 16.2, 9.0$ Hz, 0.5H), 2.02 (td, $J = 9.0, 4.6$ Hz, 1H), 1.82 – 1.45 (m, 5H), 1.37 – 1.10 (m, 5H), 1.04 (qd, $J = 12.3, 3.3$ Hz, 1H).

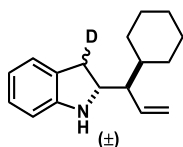
²H NMR (77 MHz, CHCl_3) 3.06 (m), 2.84 (m).

¹³C NMR (126 MHz, CDCl_3) 150.9 (t, $J = 3.2$ Hz), 137.7, 128.8, (dd, $J = 8.7$ Hz, 6.1 Hz), 127.2, 124.6 (dd, $J = 4.0$ Hz, 1.4 Hz), 118.2, 118.1 (d, $J = 14.4$ Hz), 60.0 (dd, $J = 14.2, 6.8$ Hz), 55.6 (d, $J = 6.5$ Hz), 38.8, 34.2, 33.8 (td, $J = 20.0, 6.1$ Hz), 32.2, 28.5 (d, $J = 2.0$ Hz), 26.7 (t, $J = 5.9$ Hz).

IR ν_{max} (neat) 3380 (w), 3071 (w), 2922 (s), 2851 (m), 1636 (w), 1607 (m), 1484 (m), 1245 (m).

HRMS (EI⁺) m/z : Calcd for $\text{C}_{17}\text{H}_{22}\text{ND}$ 242.1888; Found 242.1897.

3-Deutero-2-(1-cyclohexylallyl)indoline



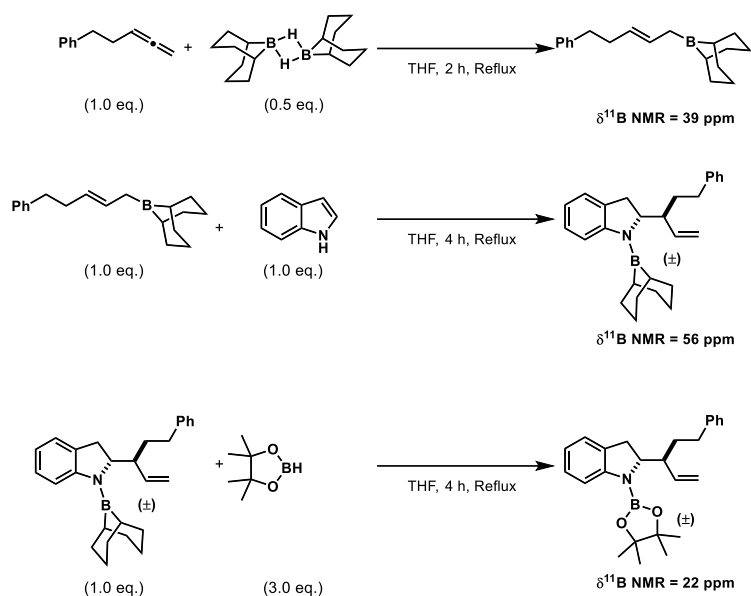
According to general procedure A, cyclohexylallene (72 μ L, 0.5 mmol), 3-D-indole (60 mg, 0.5 mmol), HBpin (109 μ L, 0.6 mmol), [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (82 mg, 0.34 mmol, 68%)

¹H NMR (500 MHz, CDCl₃) 7.08 (d, J = 7.2 Hz, 1H), 7.01 (td, J = 7.5, 1.1 Hz, 1H), 6.68 (td, J = 7.3, 1.0 Hz, 1H), 6.59 (d, J = 7.7 Hz, 1H), 5.73 (dt, J = 17.2, 10.1 Hz, 1H), 5.19 (dd, J = 10.3, 2.3 Hz, 1H), 5.09 (dd, J = 17.2, 2.3 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.87 (s, 1H), 3.08 (dd, J = 16.1, 8.8 Hz, 0.5H), 2.85 (dd, J = 16.2, 9.0 Hz, 0.5H), 2.02 (td, J = 9.0, 4.6 Hz, 1H), 1.82 – 1.45 (m, 5H), 1.37 – 1.10 (m, 5H), 1.04 (qd, J = 12.3, 3.3 Hz, 1H).

²H NMR (77 MHz, CHCl₃) 3.06 (m), 2.84 (m).

¹³C NMR (126 MHz, CDCl₃) 150.9 (t, J = 3.2 Hz), 137.7, 128.8, (dd, J = 8.7 Hz, 6.1 Hz), 127.2, 124.6 (dd, J = 4.0 Hz, 1.4 Hz), 118.2, 118.1 (d, J = 14.4 Hz), 60.0 (dd, J = 14.2, 6.8 Hz), 55.6 (d, J = 6.5 Hz), 38.8, 34.2, 33.8 (td, J = 20.0, 6.1 Hz), 32.2, 28.5 (d, J = 2.0 Hz), 26.7 (t, J = 5.9 Hz).

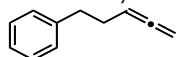
Stepwise experiments



In an argon filled vial penta-3,4-dienyl-benzene (0.1 mmol, 14 μL) and 9-borabicyclo(3.3.1)nonane (0.05 mmol, 12 mg) were reacted in THF (0.5 mL) at reflux for 2 hours, the crude reaction mixture was then subject to ^{11}B NMR spectroscopy (s, 39 ppm). To the crude mixture was then added indole (0.1 mmol, 12 mg) and heated to reflux for 4 hours and subject to ^{11}B NMR spectroscopy (s, 56 ppm). To the crude reaction mixture was then added HBpin (0.3 mmol, 43 μL) and heated to reflux for 4 hours and subject to ^{11}B NMR spectroscopy (s, 22 ppm), liberation of 9-borabicyclo(3.3.1)nonane was not observed, likely due to reaction with the alkene functionality of the substrate resulting in an ^{11}B NMR resonance (s, 78 ppm).

S5 Synthesis of allenes

Penta-3,4-dienyl-benzene



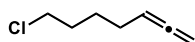
According to the procedure of Chanthamath,^[1] to a stirred solution of paraformaldehyde (1.88 g, 72.5 mmol) and CuI (2.4 g, 12.5 mmol), in dioxane (150 mL) was added but-3-ynylbenzene (3.5 mL, 25 mmol) and dicyclohexylamine (9 mL, 45 mmol). The resulting mixture was refluxed under an inert atmosphere for 16 hours. Upon cooling to room temperature, the crude reaction mixture was filtered. To the filtrate was added HCl (2 M) till the pH = 2 when the mixture was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (20 mL) and dried (Na₂SO₄). The crude product was concentrated under reduced pressure and purified by flash column chromatography (CombiFlash Isco NextGen300+, 24 g SiO₂, 50 mm Ø, petroleum ether/ diethyl ether 4:1) to give the allene as a colourless oil (3.08 g, 21.4 mmol, 85%).

¹H NMR (600 MHz, CDCl₃) δ 7.30 (td, *J* = 7.2, 1.5 Hz, 2H), 7.23 – 7.17 (m, 3H), 5.16 (*app* p, *J* = 6.7 Hz, 1H), 4.69 (m, 2H), 2.78 – 2.68 (m, 2H), 2.37 – 2.28 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) 208.5, 141.6, 128.4, 128.2, 125.8, 89.3, 75.0, 35.3, 29.9.

The data are in accordance with those previously reported.^[1]

7-Chlorohepta-1,2-diene



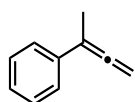
According to the procedure of Chanthamath,^[1] to a stirred solution of paraformaldehyde (1.88 g, 72.5 mmol) and CuI (2.4 g, 12.5 mmol), in dioxane (150 mL) was added 6-chloro-1-hexyne (3 mL, 25 mmol) and dicyclohexylamine (9 mL, 45 mmol). The resulting mixture was refluxed under an inert atmosphere for 16 hours. Upon cooling to room temperature, the crude reaction mixture was filtered. To the filtrate was added HCl (2 M) till the pH = 2 when the mixture was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (20 mL) and dried (Na₂SO₄). The crude product was purified by distillation (52 °C, 1 atm), then flash column chromatography (CombiFlash Isco NextGen300+, 24 g SiO₂, 50 mm Ø, petroleum ether/ diethyl ether 20:1) to give the allene as a colourless oil (0.91 g, 7.0 mmol, 28%).

¹H NMR (400 MHz, CDCl₃) δ 5.09 (p, *J* = 6.7 Hz, 1H), 4.68 (dt, *J* = 6.6, 3.2 Hz, 2H), 3.55 (t, *J* = 6.7 Hz, 2H), 2.11 – 1.95 (m, 2H), 1.87 – 1.74 (m, 2H), 1.66 – 1.45 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) 208.4, 89.2, 74.8, 44.7, 31.8, 27.3, 26.1.

The data are in accordance with those previously reported.^[2]

1-methyl-1-phenylallene



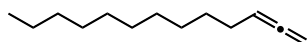
To a solution of α -methyl styrene (5.7 mL, 44 mmol), bromoform (9.7 mL, 110 mmol) and *N*-benzyl-*N,N,N*-triethylammonium bromide (1.2 g, 4.4 mmol) in dichloromethane (50 mL) was added NaOH (50 mol%, 50 mL) dropwise. After addition the mixture was heated to reflux overnight. Upon cooling, water (50 mL) was added to the crude reaction mixture and then extracted with dichloromethane (3 x 50 mL), the combined organic extracts were dried (MgSO₄) and concentrated. The crude product, a brown oil (15.04 g), was used in the next step without further purification. To a solution of crude (2,2-dibromo-1-methylcyclopropyl)-benzene (7.5 g, 26 mmol) in THF (50 mL) was added EtMgBr (9 mL, 3M, 27 mmol) dropwise at 0 °C. After stirring for 16 hours the reaction mixture was quenched with HCl (2 M, 20 mL), diluted with diethyl ether (100 mL), and washed with water (3 x 20 mL). The organic layers were concentrated, dried (MgSO₄) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 24 g SiO₂, 50 mm Ø, petroleum ether) to give the allene (3.3 g, 25.4 mmol, 99%) as a colourless oil.

¹H NMR (400 MHz, CDCl₃) 7.44 – 7.40 (m, 2H), 7.33 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.24 – 7.17 (m, 1H), 5.03 (q, *J* = 3.2 Hz, 2H), 2.11 (t, *J* = 3.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) 209.4, 137.2, 128.8, 127.0, 126.1, 100.2, 77.3, 17.1.

Data were in accordance with those previously recorded.^[3]

Trideca-1,2-diene



To a solution of dodec-1-ene (9.6 mL, 44 mmol), bromoform (9.7 mL, 110 mmol) and *N*-benzyl-*N,N,N*-triethylammonium bromide (1.2 g, 4.4 mmol) in dichloromethane (50 mL) was added NaOH (50 mol%, 50 mL) dropwise. After addition the mixture was heated to reflux overnight. Upon cooling water (50 mL) was added to the crude reaction mixture and then extracted with dichloromethane (3 x 50 mL), the combined organic extracts were dried (MgSO₄) and concentrated. The crude product, a brown oil (7.5 g), was used in the next step without further purification. To a solution of crude 1,1-dibrom-2-decylcyclopropan (5.5 g, 16 mmol) in THF (50 mL) was added EtMgBr (6 mL, 3M, 18 mmol) dropwise at 0 °C. After stirring for 16 hours the reaction mixture was quenched with HCl (2 M, 20 mL), diluted with diethyl ether (100 mL), and washed with water (3 x 20 mL). The organic layers were concentrated, dried (MgSO₄) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 24 g SiO₂, 50 mm Ø, petroleum ether) to give the allene (2.7 g, 15.0 mmol, 94%) as a colourless oil.

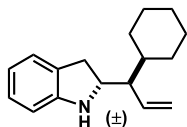
¹H NMR (400 MHz, CDCl₃) 5.12 (p, *J* = 6.8 Hz, 1H), 4.67 (dt, *J* = 6.6, 3.2 Hz, 2H), 2.09 – 1.95 (m, 2H), 1.40 – 1.24 (m, 13H), 0.95 – 0.82 (m, 6H).

¹³C NMR (126 MHz, CDCl₃) 208.5, 90.1, 74.5, 31.9, 29.6, 29.6, 29.5, 29.4, 29.2, 29.1, 28.3, 22.7, 14.1.

Data were in accordance with those previously recorded.^[4]

S6 Substrate Scope

2-(1-Cyclohexylallyl)indoline **3a**



According to general procedure A, cyclohexylallene (72 μL , 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a yellow oil (98 mg, 0.41 mmol, 82% yield, >95:5 *d.r.*).

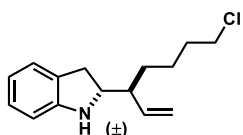
¹H NMR (500 MHz, CDCl₃) 7.08 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.68 (td, *J* = 7.4, 1.0 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 5.75 (app. dt, *J* = 17.1, 10.1 Hz, 1H), 5.19 (dt, *J* = 10.2, 1.7 Hz, 1H), 5.09 (dd, *J* = 17.2, 1.8 Hz, 1H), 3.96 (q, *J* = 8.5 Hz, 1H), 3.88 (s, 1H), 3.08 (dd, *J* = 15.4, 8.5 Hz, 1H), 2.85 (dd, *J* = 15.4, 8.8 Hz, 1H), 2.03 (td, *J* = 9.0, 4.6 Hz, 1H), 1.85 – 1.66 (m, 4H), 1.57 – 1.50 (m, 1H), 1.37 – 1.09 (m, 5H), 1.05 (td, *J* = 12.3, 3.2 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) 151.2, 138.0, 129.2, 127.6, 124.9, 118.6, 118.5, 109.3, 60.5, 56.0, 39.1, 34.5, 32.6, 28.9, 27.1, 27.1, 27.1.

IR ν_{max} (neat) 3380 (w), 3072 (w), 3052 (w), 3031 (w), 2921 (m), 2849 (m), 1534 (w), 1608 (m), 1484 (m), 1245 (m).

HRMS (EI⁺) *m/z*: Calcd for C₁₇H₂₃N 241.1825; Found 241.1838.

2-(1-(4-Chlorobutyl)allyl)indoline **3b**



According to general procedure A, 7-chlorohepta-1,2-diene (65 mg, 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μ L, 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (57 mg, 0.23 mmol, 46% yield, >95:5 *d.r.*)

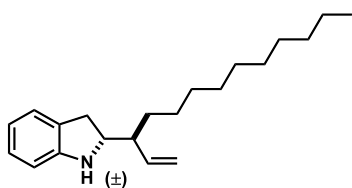
¹H NMR (600 MHz, CDCl₃) 7.08 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.01 (td, *J* = 7.6, 1.1 Hz, 1H), 6.68 (td, *J* = 7.4, 1.0 Hz, 1H), 6.61 – 6.54 (m, 1H), 5.61 (ddd, *J* = 17.1, 10.2, 9.3 Hz, 1H), 5.17 (dd, *J* = 10.3, 2.1 Hz, 1H), 5.12 (ddd, *J* = 17.1, 2.1, 0.7 Hz, 1H), 3.96 (br s, 1H), 3.69 (q, *J* = 8.4 Hz, 1H), 3.10 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.83 (ddt, *J* = 15.5, 8.5, 1.1 Hz, 1H) 2.16 – 2.10 (m, 1H), 1.36 – 1.30 (m, 6H), 0.93 – 0.86 (m, 6H).

¹³C NMR (151 MHz, CDCl₃) 150.7, 139.7, 128.5, 127.3, 124.6, 118.3, 117.8, 108.8, 62.9, 50.1, 44.9, 34.1, 32.6, 30.5, 24.6.

IR ν_{max} (neat) 3393 (w), 2955 (s), 2922 (s), 2852 (m), 1609 (m), 1485 (m), 1465 (m).

HRMS (EI⁺) *m/z*: Calcd for C₁₅H₂₀ClN 249.1279; Found 249.1274.

2-(1-Decylallyl)indoline **3c**



According to general procedure A, trideca-1,2-diene (99 μ L, 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μ L, 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (93 mg, 0.31 mmol, 62% yield, >95:5 *d.r.*)

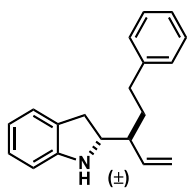
¹H NMR (600 MHz, CDCl₃) 7.10 – 7.05 (m, 1H), 7.01 (qd, *J* = 8.4, 8.0, 1.2 Hz, 1H), 6.71 – 6.65 (m, 1H), 6.62 – 6.56 (m, 1H), 5.62 (ddd, *J* = 17.1, 10.3, 9.4 Hz, 1H), 5.18 (dd, *J* = 10.3, 2.1 Hz, 1H), 5.12 (dd, *J* = 17.1, 2.0 Hz, 1H), 4.03 – 3.90 (m, 1H), 3.69 (q, *J* = 8.4 Hz, 1H), 3.10 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.83 (dd, *J* = 15.5, 8.4 Hz, 1H), 2.19 – 2.07 (m, 1H), 1.42 – 1.10 (m, 18H), 0.91 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) 150.8, 140.3, 128.7, 127.2, 124.6, 118.2, 117.3, 108.8, 63.0, 50.2, 34.1, 31.9, 31.3, 29.7, 28.4, 27.2, 22.7, 14.1.

HRMS (EI⁺) *m/z*: Calcd for C₂₁H₃₃N 299.2608; Found 299.2606.

IR ν_{\max} (neat) 3386 (w), 2937 (w), 2861 (w), 1609 (m).

2-(1-(2-Phenylethyl)allyl)indoline **3d**



According to general procedure A, penta-3,4-dienyl-benzene (99 μ L, 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μ L, 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (68 mg, 0.26 mmol, 53% yield, >95:5 *d.r.*)

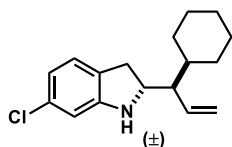
¹H NMR (600 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 7.06 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.01 (td, *J* = 7.7, 1.2 Hz, 1H), 6.69 (td, *J* = 7.3, 1.0 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 5.70 (ddd, *J* = 17.1, 10.3, 9.3 Hz, 1H), 5.27 (dd, *J* = 10.3, 2.0 Hz, 1H), 5.24 – 5.14 (m, 1H), 4.08 (br s, 1H), 3.84 – 3.70 (m, 1H), 3.09 (dd, *J* = 15.6, 8.7 Hz, 1H), 2.87 – 2.71 (m, 2H), 2.54 (ddd, *J* = 13.9, 10.0, 6.9 Hz, 1H), 2.29 – 2.16 (m, 1H), 1.88 (dddd, *J* = 13.4, 10.2, 7.0, 3.2 Hz, 1H), 1.62 (dtd, *J* = 13.4, 10.3, 4.9 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) 150.7, 142.3, 139.7, 128.6, 128.4, 128.4, 127.3, 125.8, 124.6, 118.4, 118.1, 108.8, 63.0, 49.8, 34.1, 33.5, 33.2.

HRMS (EI⁺) *m/z*: Calcd for C₁₉H₂₁N 263.1669; Found 263.1665.

IR ν_{\max} (neat) 3380 (w), 3026 (w), 2920 (w), 1609 (m).

6-Chloro-2-(1-cyclohexylallyl)indoline, **3e**



According to general procedure A, cyclohexylallene (72 μL , 0.5 mmol), 6-chloroindole (76 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (106 mg, 0.39 mmol, 77% yield, >95:5 *d.r.*)

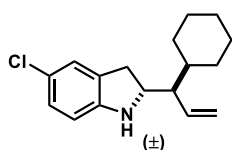
¹H NMR (500 MHz, CDCl₃) 6.94 (d, *J* = 7.8 Hz, 1H), 6.62 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.53 (d, *J* = 1.9 Hz, 1H), 5.70 (app. dt, *J* = 17.1, 10.1 Hz, 1H), 5.25 – 5.17 (m, 1H), 5.08 (dd, *J* = 17.1, 2.2, 1H), 3.98 (q, *J* = 8.5 Hz, 1H), 3.81 (s, 1H), 3.04 (ddt, *J* = 15.5, 8.6, 0.7 Hz, 1H), 2.80 (ddd, *J* = 15.7, 8.5, 1.2 Hz, 1H), 1.99 (ddd, *J* = 9.7, 8.1, 4.7 Hz, 1H), 1.85 – 1.58 (m, 5H), 1.54 – 1.44 (m, 1H), 1.33 – 1.10 (m, 4H), 1.03 (qd, *J* = 12.4, 3.4 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) 152.4, 137.7, 133.1, 127.6, 125.5, 118.8, 118.2, 109.2, 60.8, 56.0, 39.0, 33.9, 32.5, 28.9, 27.0, 27.0, 27.0.

IR ν_{max} (neat) 3402 (w), 2922 (m), 2851 (m), 1607 (m), 1483 (s).

HRMS (EI⁺) *m/z*: Calcd for C₁₇H₂₂NCl 275.1435; Found 275.1443.

5-Chloro-2-(1-cyclohexylallyl)indoline **3f**



According to general procedure A, cyclohexylallene (72 μL , 0.5 mmol), 5-chloroindole (93 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-*B*-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (114 mg, 0.42 mmol, 83% yield, >95:5 *d.r.*).

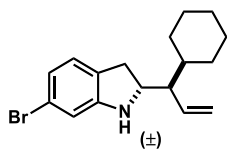
¹H NMR (500 MHz, CDCl₃) 7.04 – 7.00 (m, 1H), 6.95 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.48 (d, *J* = 8.3 Hz, 1H), 5.70 (app. dt, *J* = 17.1, 10.0 Hz, 1H), 5.20 (dd, *J* = 10.2, 2.2 Hz, 1H), 5.08 (ddd, *J* = 17.1, 2.3, 0.7 Hz, 1H), 3.98 (q, *J* = 8.5 Hz, 1H), 3.83 (d, *J* = 36.8 Hz, 1H), 3.06 (dd, *J* = 15.7, 8.6 Hz, 1H), 2.89 – 2.78 (m, 1H), 2.00 (ddd, *J* = 9.8, 8.1, 4.7 Hz, 1H), 1.82 – 1.65 (m, 4H), 1.60 (ddt, *J* = 13.1, 4.0, 2.1 Hz, 1H), 1.49 (tdt, *J* = 11.7, 4.8, 3.3 Hz, 1H), 1.36 – 1.10 (m, 4H), 1.03 (qd, *J* = 12.4, 3.4 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) 149.3, 137.2, 130.7, 126.8, 124.6, 122.5, 118.2, 109.3, 60.3, 55.4, 38.6, 34.0, 32.0, 28.4, 26.5, 26.5, 26.5.

IR ν_{max} (neat) 3387 (w), 2921 (m), 2850 (m), 1634 (w), 1599 (w), 1478 (m), 1247 (m).

HRMS (EI⁺) *m/z*: Calcd for C₁₇H₂₂NCl 275.1435; Found 275.1447.

6-Bromo-2-(1-cyclohexylallyl)indoline **3g**



According to general procedure A, cyclohexylallene (72 μL , 0.5 mmol), 6-bromoindole (76 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (93 mg, 0.29 mmol, 58% yield, >95:5 *d.r.*).

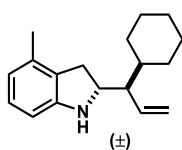
¹H NMR (500 MHz, CDCl₃) 6.87 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.74 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.66 (d, *J* = 1.8 Hz, 1H), 5.67 (dt, *J* = 17.1, 10.0 Hz, 1H), 5.18 (dd, *J* = 10.2, 2.2 Hz, 1H), 5.06 (dd, *J* = 17.1, 2.2 Hz, 1H), 3.95 (q, *J* = 8.4 Hz, 1H), 3.90 (s, 1H), 3.00 (ddd, *J* = 15.6, 8.7, 1.1 Hz, 1H), 2.76 (ddd, *J* = 15.6, 8.4, 1.2 Hz, 1H), 1.96 (ddd, *J* = 9.9, 8.2, 4.8 Hz, 1H), 1.80 – 1.63 (m, 3H), 1.57 (dtd, *J* = 13.0, 4.6, 4.0, 2.3 Hz, 1H), 1.47 (tdt, *J* = 11.6, 4.8, 3.3 Hz, 1H), 1.35 – 1.04 (m, 5H), 1.04 – 0.88 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) 152.7, 137.6, 128.2, 126.0, 121.1, 121.0, 118.8, 112.0, 60.7, 55.9, 39.0, 33.9, 32.5, 28.9, 26.7, 26.6 (2 C).

IR ν_{max} (neat) 3393 (w), 2922 (m), 2849 (m), 1636 (w), 1603 (m), 1481 (m).

HRMS (EI⁺) *m/z*: Calcd for C₁₇H₂₂NBr 319.0930; Found 319.0921.

4-Methyl-(1-cyclohexylallyl)indoline **3h**



According to general procedure A, cyclohexylallene (73 μL , 0.5 mmol), 4-methylindole (66 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a yellow oil (82 mg, 0.32 mmol, 64% yield, >95:5 *d.r.*)

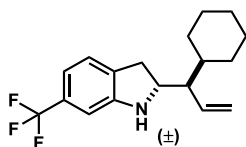
¹H NMR (600 MHz, CDCl₃) 6.91 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 7.7 Hz, 1H), 5.72 (app. dt, *J* = 17.1, 10.0 Hz, 1H), 5.18 (dd, *J* = 10.3, 2.3 Hz, 1H), 5.08 (dd, *J* = 17.1, 2.3 Hz, 1H), 3.96 (q, *J* = 8.6 Hz, 1H), 3.85 (s, 1H), 3.01 (dd, *J* = 15.5, 8.8 Hz, 1H), 2.74 (dd, *J* = 15.5, 8.8 Hz, 1H), 2.21 (s, 3H), 2.02 (ddd, *J* = 9.8, 8.1, 4.7 Hz, 3H), 1.82 – 1.65 (m, 2H), 1.65 – 1.48 (m, 2H), 1.38 – 0.97 (m, 5H).

¹³C NMR (126 MHz, CDCl₃) 151.0, 138.1, 134.5, 127.9, 127.6, 119.8, 118.4, 106.7, 60.1, 56.2, 39.1, 33.3, 32.6, 28.9, 27.1, 27.1, 27.1, 19.1.

IR ν_{max} (neat) 3379 (w) 2920 (s), 2851 (s), 1636 (w), 1600 (s), 1468 (s), 1255 (s).

HRMS (EI⁺) *m/z*: Calcd for C₁₈H₂₅N 255.1982; Found 255.1989.

6-Trifluoromethyl-2-(1-cyclohexylallyl)indoline **3i**



According to general procedure A, cyclohexylallene (72 μL , 0.5 mmol), 6-(trifluoromethyl)indole (93 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-*B*-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (100 mg, 0.33 mmol, 65% yield, isolated as single diastereomer).

¹H NMR (500 MHz, CDCl₃) 7.11 (d, *J* = 7.6 Hz, 1H), 6.91 (dq, *J* = 7.6, 0.9 Hz, 1H), 6.75 (d, *J* = 1.5 Hz, 1H), 5.71 (app. dt, *J* = 17.1, 10.0 Hz, 1H), 5.21 (dd, *J* = 10.3, 2.2 Hz, 1H), 5.10 (dd, *J* = 17.1, 2.1 Hz, 1H), 4.03 (m, 2H), 3.12 (ddt, *J* = 16.0, 8.7, 1.2 Hz, 1H), 2.89 (ddt, *J* = 16.1, 8.6, 1.4 Hz, 1H), 2.01 (ddd, *J* = 9.9, 8.1, 4.8 Hz, 1H), 1.83 – 1.66 (m, 3H), 1.61 (ddt, *J* = 12.9, 3.6, 1.8 Hz, 1H), 1.51 (tdt, *J* = 11.6, 4.8, 3.4 Hz, 1H), 1.38 – 1.09 (m, 5H), 1.05 (qd, *J* = 12.5, 3.4 Hz, 1H).

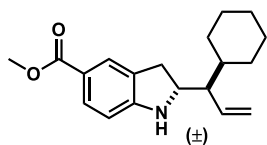
¹³C NMR (126 MHz, CDCl₃) 151.1, 137.2, 132.7, 130.0 (q, *J* = 31.5 Hz), 126.5 (q, *J* = 272.0 Hz), 124.5, 118.5, 115.1 (q, *J* = 4.2 Hz), 104.8 (q, *J* = 3.7 Hz), 60.1, 55.6, 38.7, 33.9, 32.1, 28.6, 26.6, 26.6, 26.6.

¹⁹F NMR (471 MHz, CDCl₃) -62.31 (s).

IR ν_{max} (neat) 3403 (w), 2925 (m), 2852 (m), 1620 (w), 1451 (m), 1318 (s), 1115 (s).

HRMS (EI⁺) *m/z*: Calcd for C₁₈H₂₂NF₃ 309.1699; Found 309.1699.

5-Methoxycarbonyl-(1-cyclohexylallyl)indoline **3j**



According to general procedure A, cyclohexylallene (73 μL , 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (76 mg, 0.25 mmol, 51% yield, >95:5 *d.r.*).

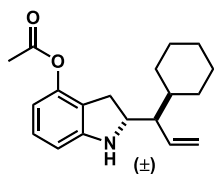
¹H NMR (600 MHz, CDCl₃) δ 7.78 – 7.74 (m, 1H), 7.72 (d, *J* = 1.4 Hz, 1H), 6.49 (d, *J* = 8.2 Hz, 1H), 5.69 (app. dt, *J* = 17.1, 10.1 Hz, 1H), 5.20 (dd, *J* = 10.3, 2.2 Hz, 1H), 5.09 (ddd, *J* = 17.1, 2.2, 0.7 Hz, 1H), 4.27 (s, 1H), 4.05 (q, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.11 (ddd, *J* = 15.6, 9.0, 1.1 Hz, 1H), 2.87 (ddt, *J* = 15.6, 8.3, 0.9 Hz, 1H), 2.00 (ddd, *J* = 9.8, 8.2, 4.8 Hz, 1H), 1.81 – 1.75 (m, 2H), 1.71 (dddd, *J* = 14.2, 10.7, 3.4, 1.7 Hz, 2H), 1.54 – 1.46 (m, 1H), 1.34 – 1.24 (m, 2H), 1.18 – 1.10 (m, 2H), 1.04 (qd, *J* = 12.5, 3.4 Hz, 1H), 0.97 – 0.87 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) 167.8, 155.4, 137.4, 131.1, 128.6, 126.5, 119.6, 118.9, 107.3, 60.4, 56.1, 51.9, 38.9, 33.7, 32.5, 28.9, 27.0, 27.0, 26.9.

IR ν_{max} (neat) 3374 (w), 1924 (m), 2851 (m), 1691 (m), 1610 (m), 1267 (s).

HRMS (EI⁺) *m/z*: Calcd for C₁₉H₂₅O₂N 299.1880; Found 299.1874.

4-Acetoxy-(1-cyclohexylallyl)indoline **3k**



According to general procedure A, cyclohexylallene (73 μL , 0.5 mmol), 4-methylindole (88 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a colourless microcrystalline solid (91 mg, 0.30 mmol, 61% yield, >95:5 *d.r.*).

¹H NMR (600 MHz, CDCl₃) 7.02 – 6.94 (m, 1H), 6.42 (dd, *J* = 7.8, 0.8 Hz, 1H), 6.36 (dd, *J* = 8.1, 0.8 Hz, 1H), 5.69 (app. dt, *J* = 17.1, 10.1 Hz, 1H), 5.18 (dd, *J* = 10.3, 2.3 Hz, 1H), 5.07 (ddd, *J* = 17.1, 2.2, 0.7 Hz, 1H), 3.98 (q, *J* = 8.7 Hz, 1H), 3.94 (s, 1H), 2.94 (dd, *J* = 15.6, 8.7 Hz, 1H), 2.70 (ddd, *J* = 15.6, 8.9, 0.9 Hz, 1H), 2.29 (s, 3H), 2.06 – 1.95 (m, 1H), 1.79 – 1.63 (m, 3H), 1.61 – 1.42 (m, 2H), 1.42 – 0.85 (m, 6H).

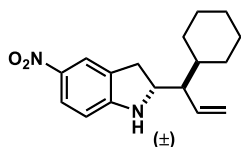
¹³C NMR (126 MHz, CDCl₃) 168.8, 152.9, 147.4, 137.4, 128.5, 120.5, 118.4, 111.1, 106.4, 60.1, 55.7, 38.6, 32.2, 31.6, 28.4, 26.6, 26.6, 26.6, 21.0.

IR ν_{max} (neat) 3360 (s), 2922 (s), 2852 (m), 1731 (s), 1615 (m), 1473 (m), 1215 (s).

HRMS (EI⁺) *m/z*: Calcd for C₁₉H₂₅O₂N 299.1880; Found 299.1893.

m.p. 118 – 119 °C (Ethyl acetate).

4-Nitro-2-(1-cyclohexylallyl)indoline **31**



According to general procedure A, cyclohexylallene (72 μL , 0.5 mmol), 5-nitroindole (81 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a yellow microcrystalline solid (82 mg, 0.29 mmol, 57% yield, >95:5 *d.r.*).

¹H NMR (500 MHz, CDCl₃) 8.00 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.92 (d, *J* = 1.9 Hz, 1H), 6.43 (d, *J* = 8.7 Hz, 1H), 5.68 (app. dt, *J* = 17.1, 10.1 Hz, 1H), 5.24 (dd, *J* = 10.3, 2.1 Hz, 1H), 5.12 (dd, *J* = 17.0, 2.1, 1H), 4.60 (s, 1H), 4.16 (dtd, *J* = 9.2, 8.0, 1.3 Hz, 1H), 3.24 – 3.14 (m, 1H), 2.92 (ddt, *J* = 16.2, 8.0, 1H), 2.00 (ddd, *J* = 9.8, 8.1, 4.9 Hz, 1H), 1.82 – 1.66 (m, 4H), 1.66 – 1.55 (m, 1H), 1.55 – 1.43 (m, 1H), 1.37 – 1.10 (m, 4H), 1.05 (qd, *J* = 12.5, 3.4 Hz, 1H).

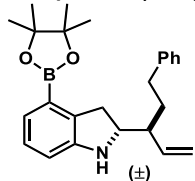
¹³C NMR (126 MHz, CDCl₃) 156.4, 138.7, 136.4, 128.5, 126.1, 120.9, 119.0, 105.6, 60.0, 55.8, 38.3, 32.9, 31.9, 28.5, 26.4, 26.4, 26.4.

IR ν_{max} (neat) 3310 (m), 2921 (m), 2851 (w), 1636 (w), 1612 (s), 1518 (m), 1449 (m), 1301 (s), 1239 (s).

HRMS (EI⁺) *m/z*: Calcd for C₁₇H₂₂O₂N₂ 286.1676; Found 286.1674.

m.p. 118 – 119 °C (Ethyl acetate).

4-Bpin-2-(1-cyclohexylallyl)indoline **3m**



According to general procedure A, penta-3,4-dienyl-benzene (99 μ L, 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μ L, 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (76 mg, 0.20 mmol, 39% yield, >95:5 *d.r.*)

¹H NMR (600 MHz, CDCl₃) δ 7.38 – 7.27 (m, 2H), 7.31 – 7.20 (m, 2H), 7.24 – 7.13 (m, 1H), 7.08 – 7.00 (m, 1H), 6.69 (dd, *J* = 7.7, 1.1 Hz, 1H), 5.74 (ddd, *J* = 17.1, 10.3, 9.3 Hz, 1H), 5.29 (dd, *J* = 10.3, 2.1 Hz, 1H), 5.26 – 5.15 (m, 1H), 3.96 (s, 1H), 3.74 (td, *J* = 8.8, 7.8 Hz, 1H), 3.37 (dd, *J* = 16.7, 8.7 Hz, 1H), 2.96 (ddd, *J* = 16.8, 8.9, 0.9 Hz, 1H), 2.80 (ddd, *J* = 13.8, 10.4, 4.8 Hz, 1H), 2.57 (ddd, *J* = 13.9, 10.3, 6.8 Hz, 1H), 2.31 – 2.18 (m, 1H), 2.10 – 1.90 (m, 1H), 1.72 – 1.53 (m, 2H), 1.37 (s, 12H), 1.03 – 0.87 (m, 2H).

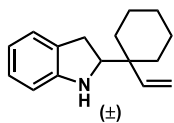
¹¹B NMR (128 MHz, CDCl₃) 30.9 (s).

¹³C NMR (151 MHz, CDCl₃) 150.1, 142.5, 140.0, 136.1, 128.5, 128.4, 126.5, 125.8, 125.1, 117.9, 111.4, 83.4, 62.9, 50.0, 40.9, 35.1, 33.6, 33.2, 25.0, 23.9, 20.8, 17.5, 17.3, 14.7.

HRMS (EI⁺) *m/z*: Calcd for C₂₅H₃₂BNO₂ 389.2521; Found 389.2525.

IR ν_{\max} (neat) 3400 (w), 2978 (w), 2931 (w), 1604 (m), 1579 (m), 1370 (s), 1351 (s).

1-Ethenyl-1-(2-indoliny)cyclohexane **3n**



According to general procedure A, vinylidenecyclohexane (63 μ L, 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μ L, 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (56 mg, 0.25 mmol, 50% yield).

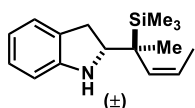
¹H NMR (600 MHz, CDCl₃) 7.04 (dq, J = 7.3, 1.4 Hz, 1H), 6.99 (ddt, J = 7.6, 6.6, 1.1 Hz, 1H), 6.65 (td, J = 7.4, 1.0 Hz, 1H), 6.57 (dd, J = 7.8, 1.0 Hz, 1H), 5.70 (dd, J = 18.0, 11.1 Hz, 1H), 5.29 (dd, J = 11.1, 1.5 Hz, 1H), 5.11 (dd, J = 17.9, 1.5 Hz, 1H), 3.88 – 3.84 (m, 1H), 3.74 (t, J = 9.5 Hz, 1H), 2.91 (dt, J = 9.5, 1.2 Hz, 2H), 1.78 – 1.37 (m, 8H), 1.37 – 1.19 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) 151.2, 143.1, 129.0, 127.1, 124.5, 118.1, 115.9, 108.6, 68.2, 43.5, 33.3, 30.8, 30.7, 26.6, 22.2, 21.9.

IR ν_{\max} (neat) 3376 (w), 3076 (w), 2925 (m), 2852 (m), 1636 (w), 1609 (m), 1485 (m), 1249 (m).

HRMS (EI⁺) m/z : Calcd for C₁₆H₂₁N 227.1669; Found 227.1668.

2-(1-Trimethylsilyl-1-methyl-propenyl)indoline **3o**



According to general procedure A, 2-(trimethylsilyl)-2,3-pentadiene (70 mg, 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μ L, 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (73 mg, 0.28 mmol, 56% yield, >95:5 *d.r.*).

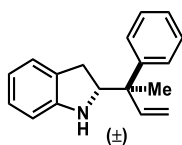
¹H NMR (600 MHz, CDCl₃) 7.09 – 7.05 (m, 1H), 7.03 – 6.97 (m, 1H), 6.65 (td, *J* = 7.4, 1.0 Hz, 1H), 6.58 (dd, *J* = 7.8, 0.9 Hz, 1H), 5.49 (dq, *J* = 12.4, 7.2 Hz, 1H), 5.40 (dq, *J* = 12.4, 1.7 Hz, 1H), 4.20 (dd, *J* = 10.0, 9.0 Hz, 1H), 3.84 (s, 1H), 2.98 – 2.83 (m, 2H), 1.80 (dd, *J* = 7.2, 1.6 Hz, 3H), 1.28 (s, 3H), 0.11 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) 151.5, 134.5, 129.3, 127.6, 124.9, 123.5, 118.3, 108.8, 66.5, 36.2, 32.5, 16.9, 15.3, -2.1.

IR ν_{\max} (neat) 3393 (w), 2951 (w), 1609 (m), 1485 (m), 1463 (m), 1246 (s).

HRMS (EI⁺) *m/z*: Calcd for C₁₆H₂₅NSi 259.1751; Found 259.1763.

2-(1-Phenyl-1-methylallyl)indoline **3p**



According to general procedure A, 1-methyl-1-phenylallene (67 μL , 0.5 mmol), indole (59 mg, 0.5 mmol), HBpin (109 μL , 0.6 mmol) and [H-B-9-BBN]₂ (12 mg, 0.050 mmol) were reacted in THF (1 mL) at reflux for 16 hours. The crude reaction mixture was quenched (SiO₂) and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm \varnothing , petroleum ether/ diethyl ether 10:1) to give the *indoline* as a brown oil (66 mg, 0.26 mmol, 53% yield, >95:5 *d.r.*).

¹H NMR (600 MHz, CDCl₃) 7.48 – 7.42 (m, 2H), 7.42 – 7.37 (m, 2H), 7.30 – 7.26 (m, 2H), 7.03 (ddt, *J* = 7.4, 1.8, 1.2 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.66 (td, *J* = 7.4, 1.0 Hz, 1H), 6.50 (dq, *J* = 7.7, 0.6 Hz, 1H), 6.35 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.36 (dd, *J* = 10.9, 1.4 Hz, 1H), 5.36 – 5.21 (m, 1H), 4.49 (t, *J* = 9.2 Hz, 1H), 3.94 – 3.59 (m, 1H), 3.00 (ddq, *J* = 16.0, 9.3, 0.8 Hz, 1H), 2.89 (ddt, *J* = 16.0, 9.0, 1.1 Hz, 1H), 1.41 (s, 3H).

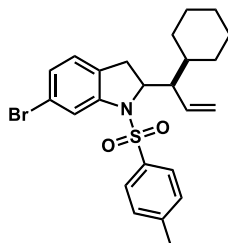
¹³C NMR (126 MHz, CDCl₃) 150.9, 146.1, 142.4, 128.5, 128.4, 127.1, 126.7, 126.2, 124.4, 117.9, 114.7, 108.1, 66.5, 48.3, 31.8, 21.6.

IR ν_{max} (neat) 3413 (w), 2972 (w), 1609 (m), 1484 (m).

HRMS (EI⁺) *m/z*: Calcd for C₁₈H₁₉N 249.1512; Found 249.1506.

S7 Derivatisation of indoline products

6-Bromo-2-(1-Cyclohexylallyl)-*N*-tosylindoline **4a**



Tosylchloride (95 mg, 0.5 mmol) and 6-bromo-2-(1-cyclohexylallyl)indoline **3p** (100 mg, 0.31 mmol) were reacted in dichloromethane (1 mL) and pyridine (0.1 mL). The reaction was stirred at room temperature for 2 hours. The crude reaction mixture was washed with brine, dried (Na_2SO_4), concentrated and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO_2 , 50 mm \varnothing , petroleum ether/ diethyl ether 5:1) to give the *indoline* as a colourless oil (116 mg, 0.25 mmol, 81%).

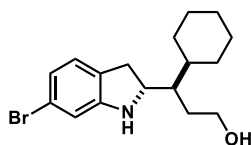
$^1\text{H NMR}$ (500 MHz, CDCl_3) 7.80 (d, $J = 1.8$ Hz, 1H), 7.46 (d, $J = 8.3$ Hz, 2H), 7.19 – 7.13 (m, 3H), 6.85 – 6.77 (m, 1H), 5.51 (dt, $J = 17.0, 9.9$ Hz, 1H), 4.92 – 4.74 (m, 2H), 4.47 (ddd, $J = 8.8, 4.8, 1.8$ Hz, 1H), 2.50 (ddd, $J = 16.0, 8.7, 1.4$ Hz, 1H), 2.38 (s, 4H), 1.93 (d, $J = 12.5$ Hz, 1H), 1.81 – 1.65 (m, 5H), 1.44 – 0.79 (m, 6H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) 143.9, 136.0, 135.0, 133.6, 129.5, 128.4, 127.1, 125.7, 122.0, 120.6, 117.1, 63.3, 57.1, 36.8, 33.5, 32.3, 30.3, 26.6, 26.4, 21.6.

IR ν_{max} (neat) 3454 (m), 3004 (w), 2978 (w), 2957 (w), 1611 (m).

HRMS (ESI⁺) m/z : Calcd for $^+\text{NaC}_{24}\text{H}_{28}\text{BrNO}_2\text{S}$ 496.0922; Found 496.0917.

6-Bromo-2-(1-Cyclohexylpropan-3-ol)indoline **4b**



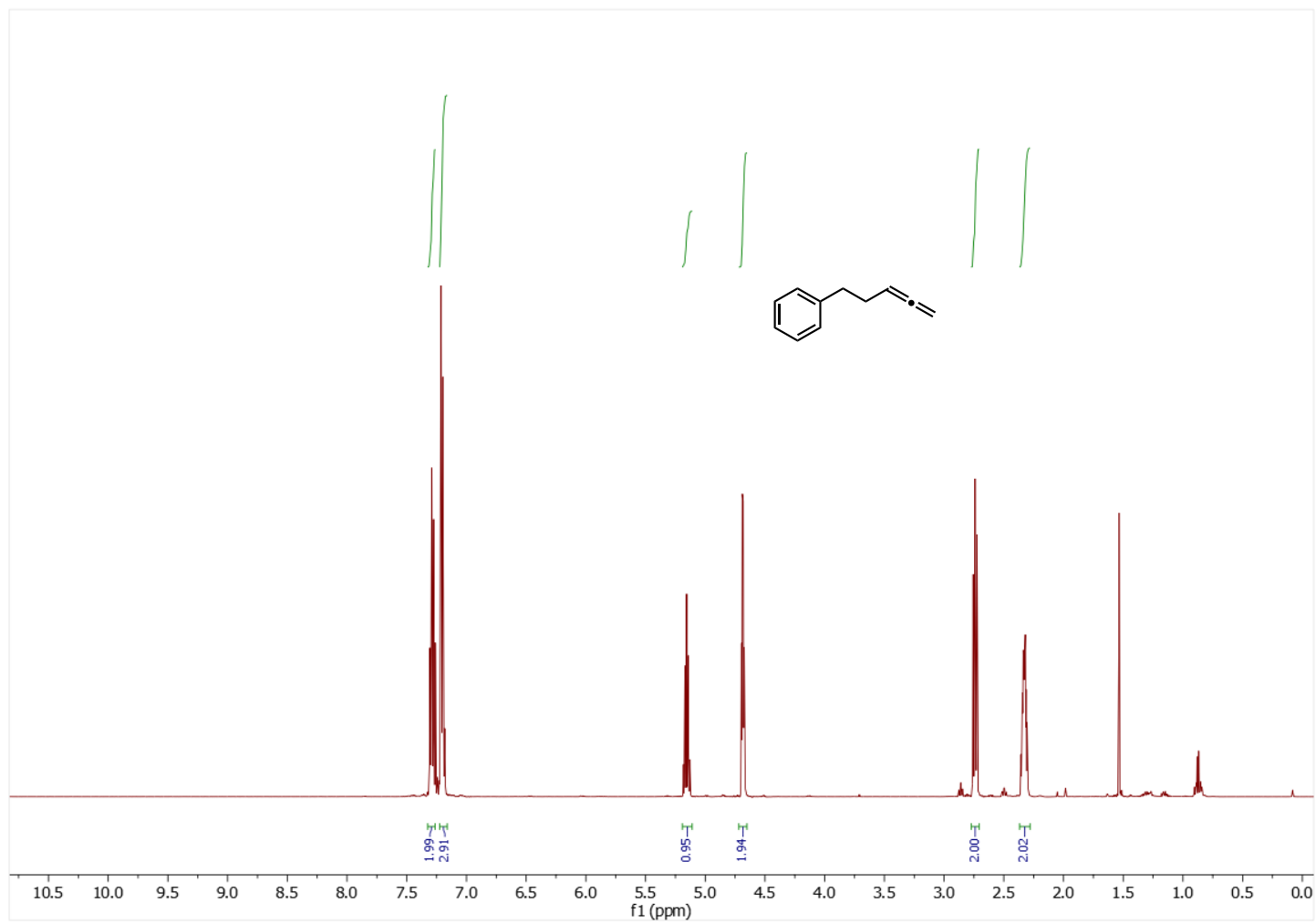
[H-B-9-BBN]₂ (37 mg, 0.15 mmol) and 6-bromo-2-(1-cyclohexylallyl)indoline **3p** (80 mg, 0.25 mmol) were reacted in THF (1 mL) at room temperature for 1 hour. To the reaction mixture was rapidly added a premixed solution of H₂O₂ (0.33 mL) and NaOH (0.66 mL, 2M), this mixture was left to stir for 45 minutes. The reaction was quenched with diethyl ether (5 mL), the aqueous layer was extracted with diethyl ether (2 x 3 mL). The combined organic extracts were dried (Na₂SO₄), concentrated and purified by flash column chromatography (CombiFlash Isco NextGen300+, 12 g SiO₂, 50 mm Ø, petroleum ether/diethyl ether 5:1) to give the *alcohol* as a pale-yellow oil (73 mg, 0.22 mmol, 87%).

¹H NMR (400 MHz, CDCl₃) 6.91 (dt, *J* = 7.8, 1.1 Hz, 1H), 6.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.74 (d, *J* = 1.7 Hz, 1H), 4.02 (ddd, *J* = 10.0, 8.8, 6.4 Hz, 1H), 3.91 – 3.72 (m, 1H), 3.65 (ddd, *J* = 10.6, 7.8, 6.0 Hz, 1H), 3.07 (dd, *J* = 15.8, 8.9 Hz, 1H), 2.75 (ddd, *J* = 15.7, 10.1, 1.3 Hz, 1H), 1.95 – 1.38 (m, 9H), 1.38 – 1.03 (m, 7H).

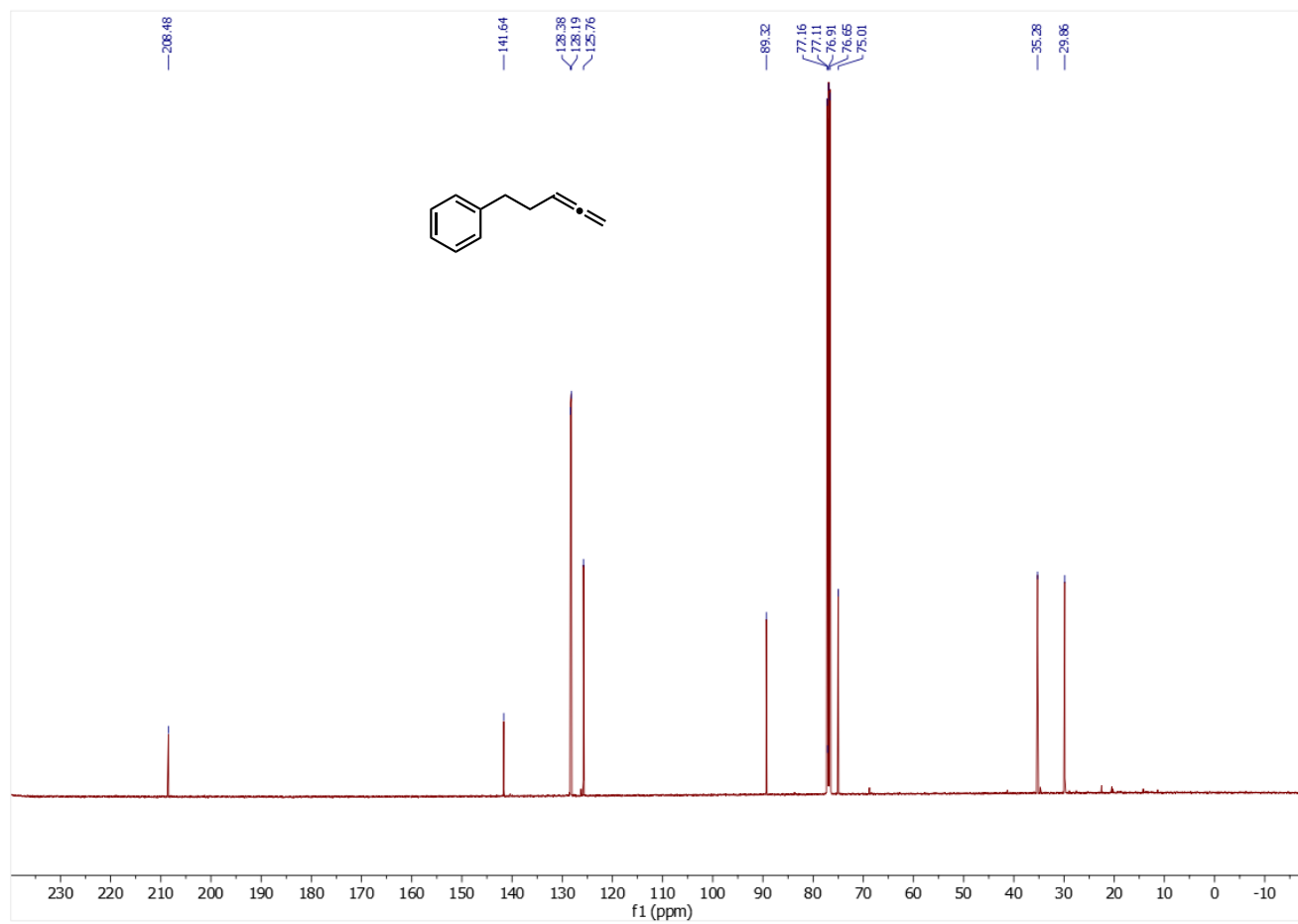
¹³C NMR (126 MHz, CDCl₃) 152.5, 128.2, 125.6, 121.5, 120.6, 112.6, 62.5, 62.1, 46.9, 40.1, 35.1, 31.2, 30.9, 29.2, 26.8, 26.7, 26.6.

IR ν_{\max} 3541 (br), 3245 (m), 3004 (w), 2934 (w), 1576 (w).

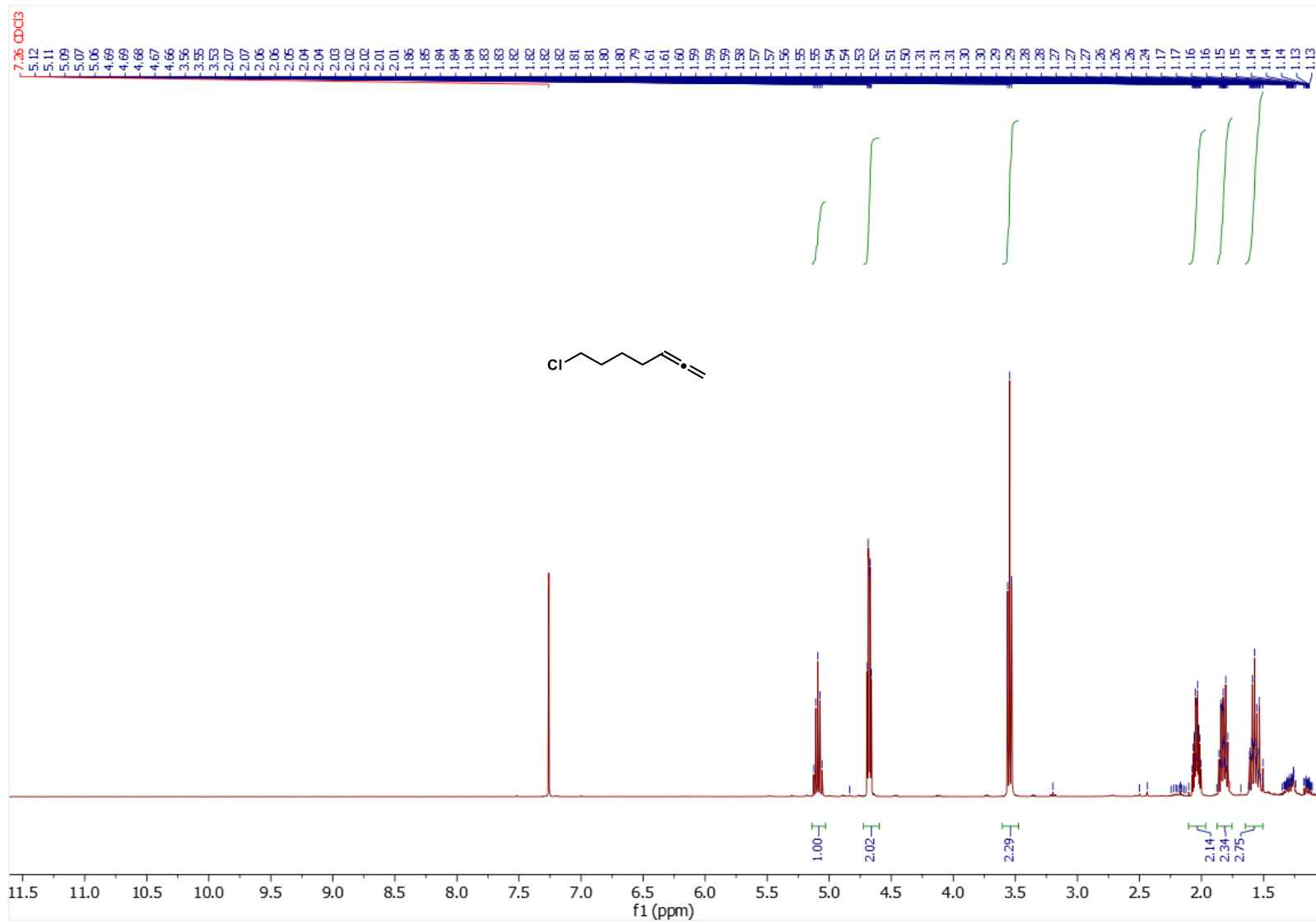
S8 NMR Spectra



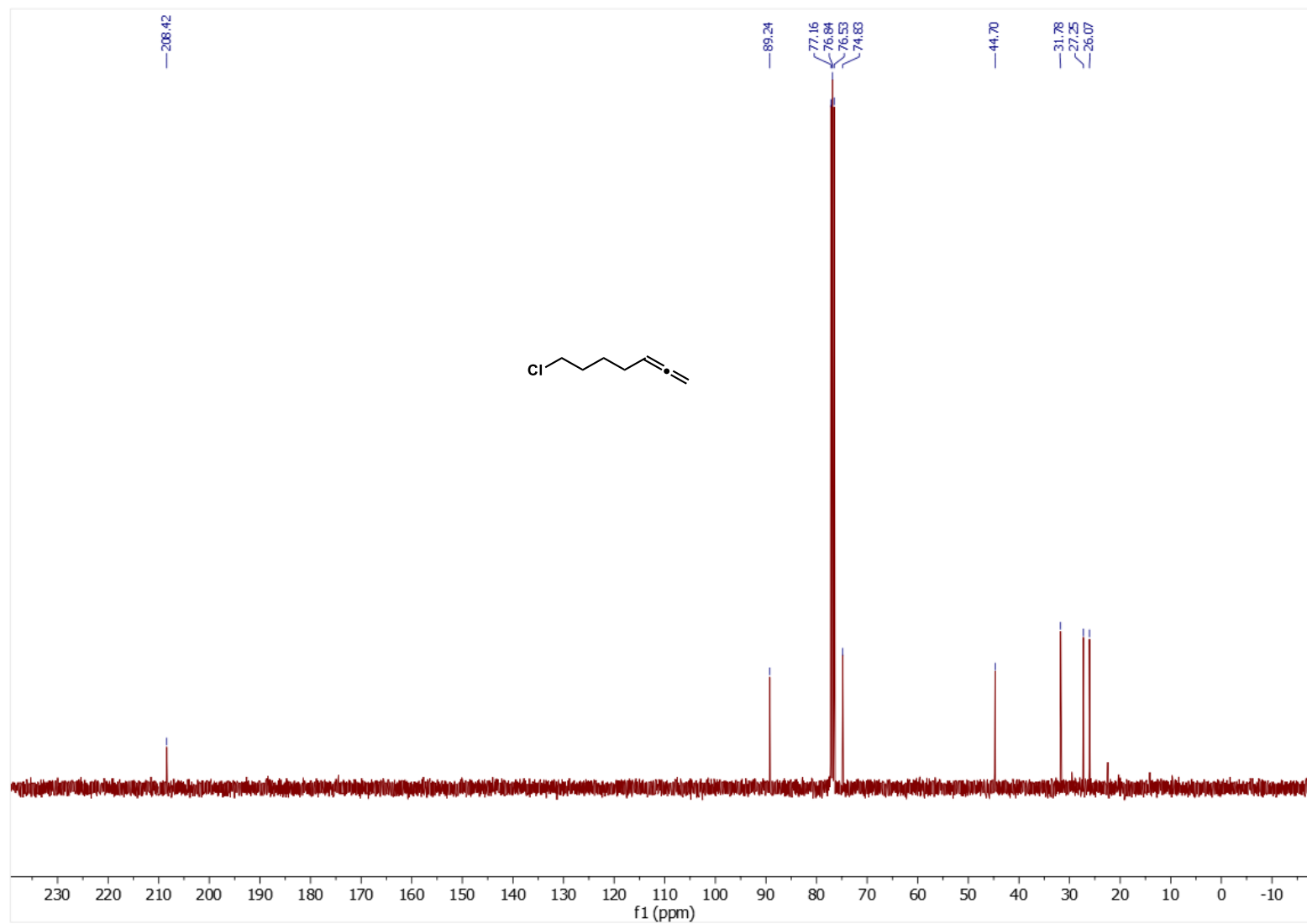
^1H NMR (600 MHz, CDCl_3) spectrum of penta-3,4-dienyl-benzene



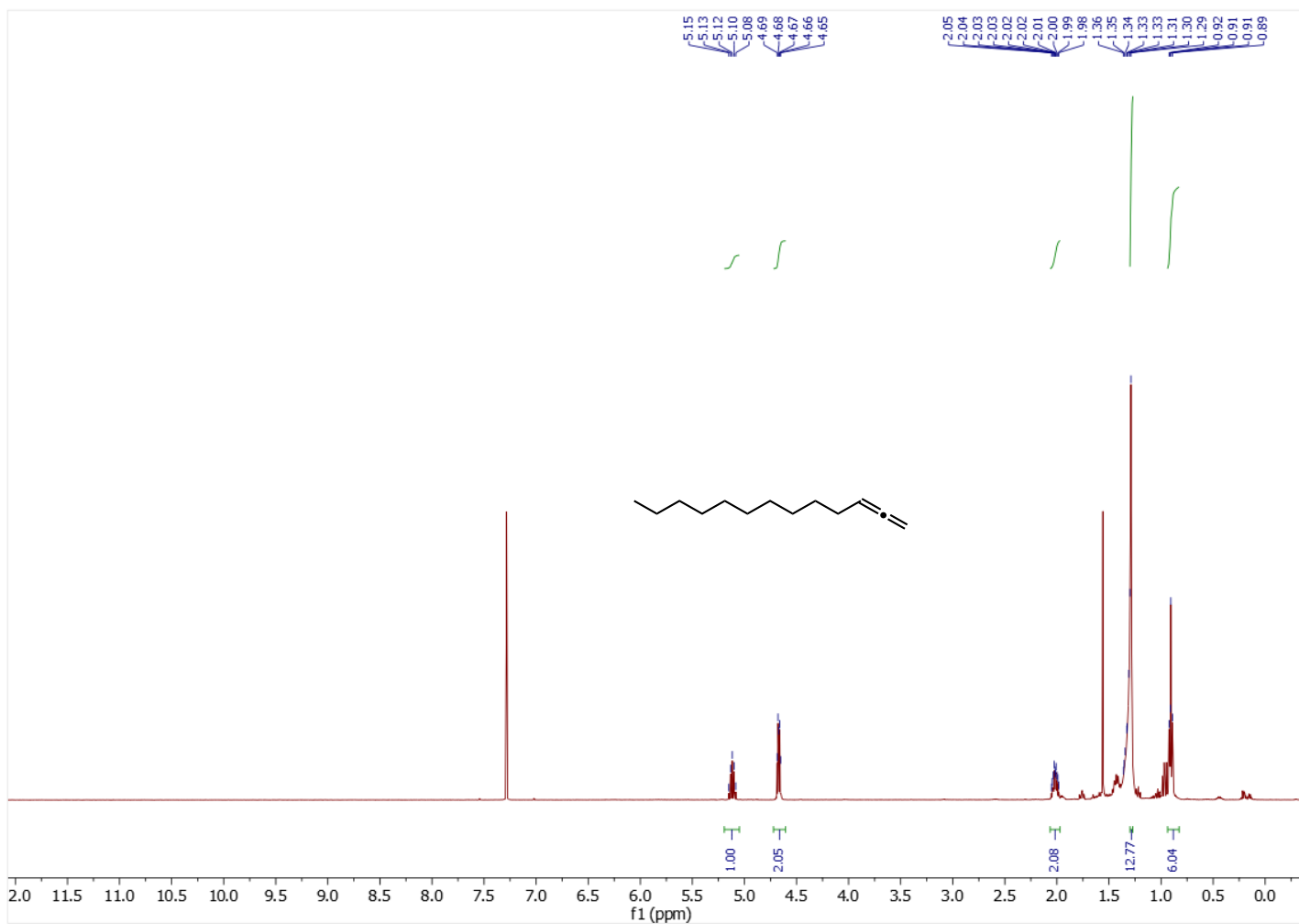
¹³C NMR (126 MHz, CDCl₃) spectrum of penta-3,4-dienyl-benzene



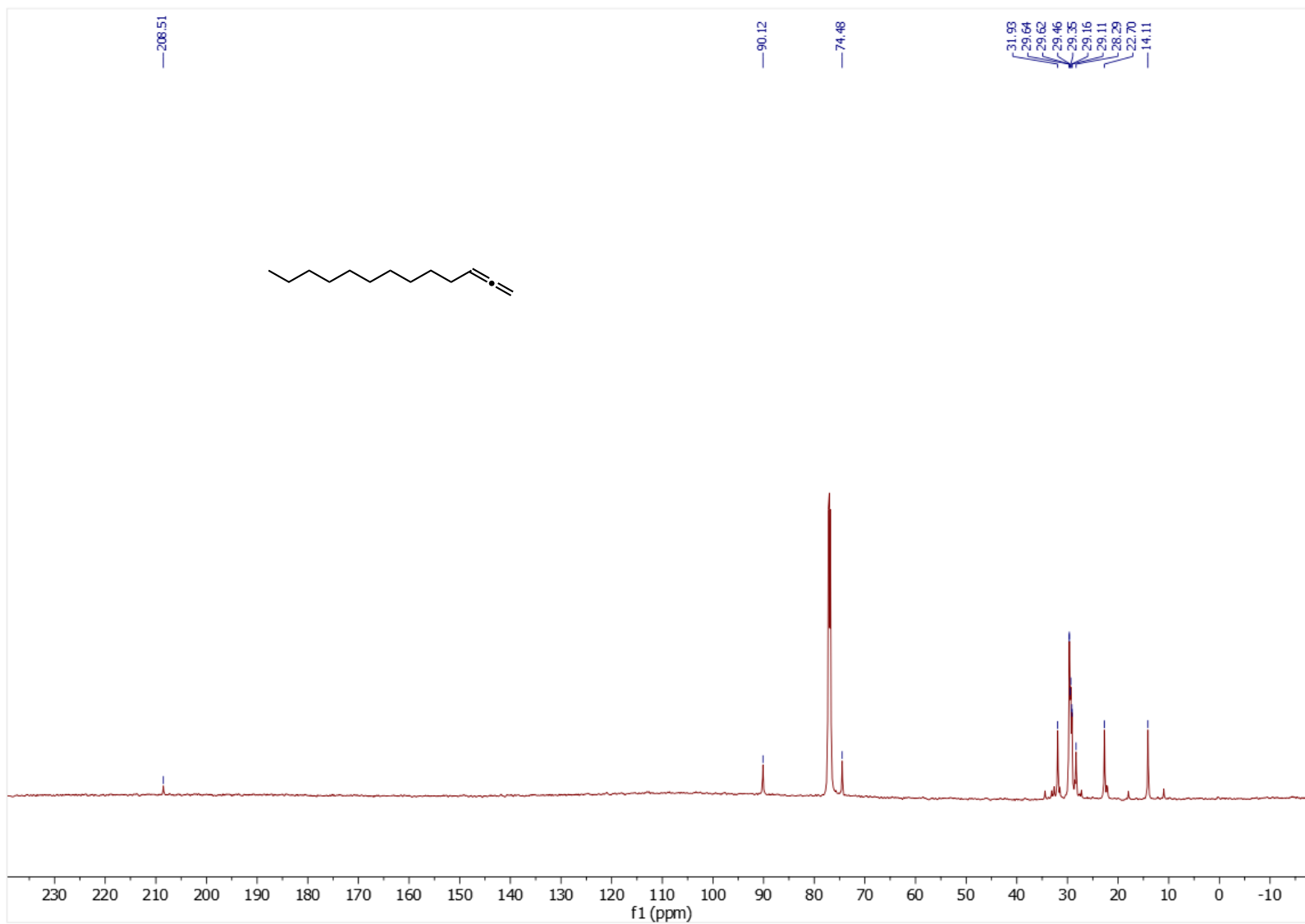
¹H NMR (400 MHz, CDCl₃) spectrum of 7-chlorohepta-1,2-diene



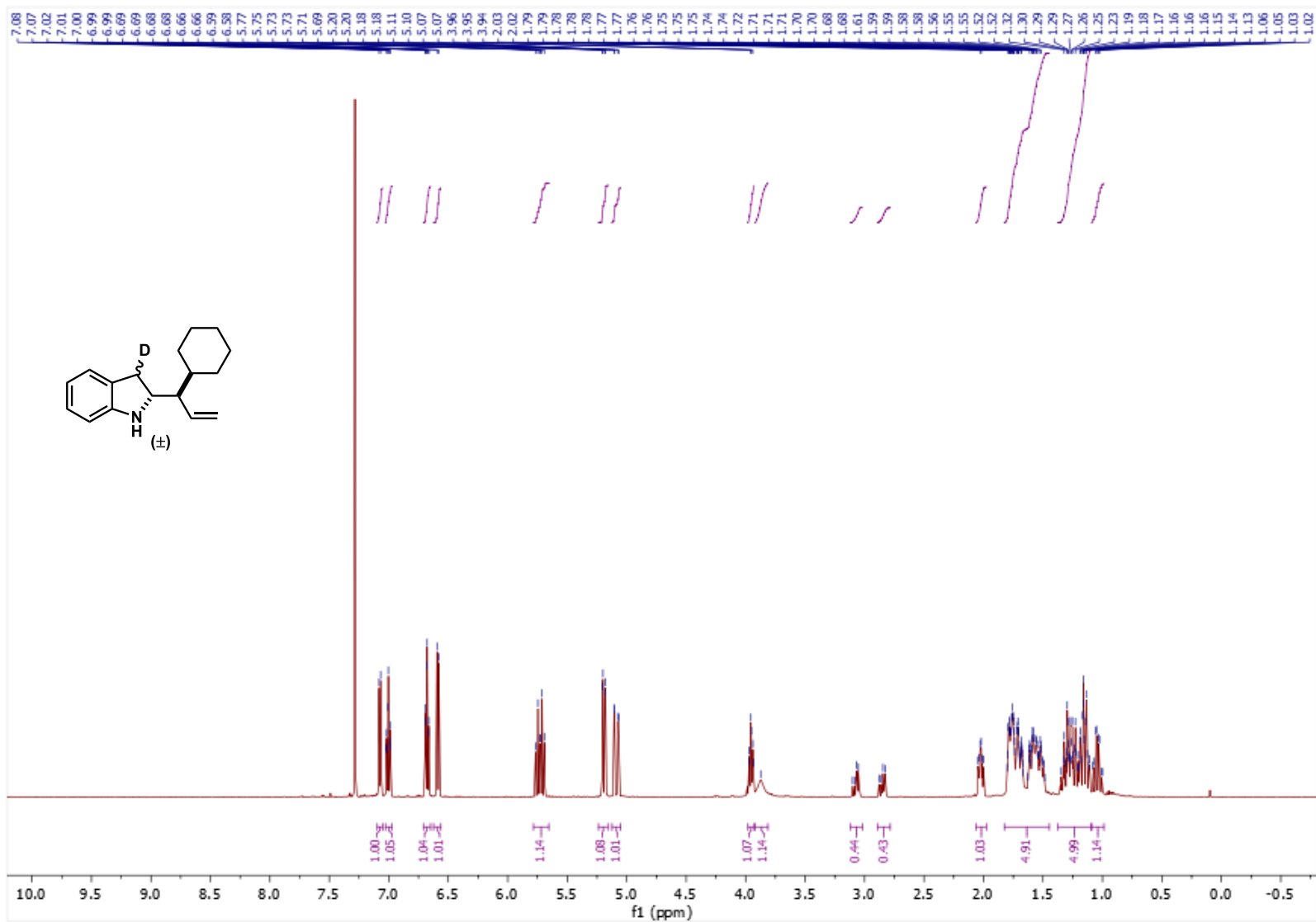
¹³C NMR (126 MHz, CDCl₃) spectrum of 7-chlorohepta-1,2-diene



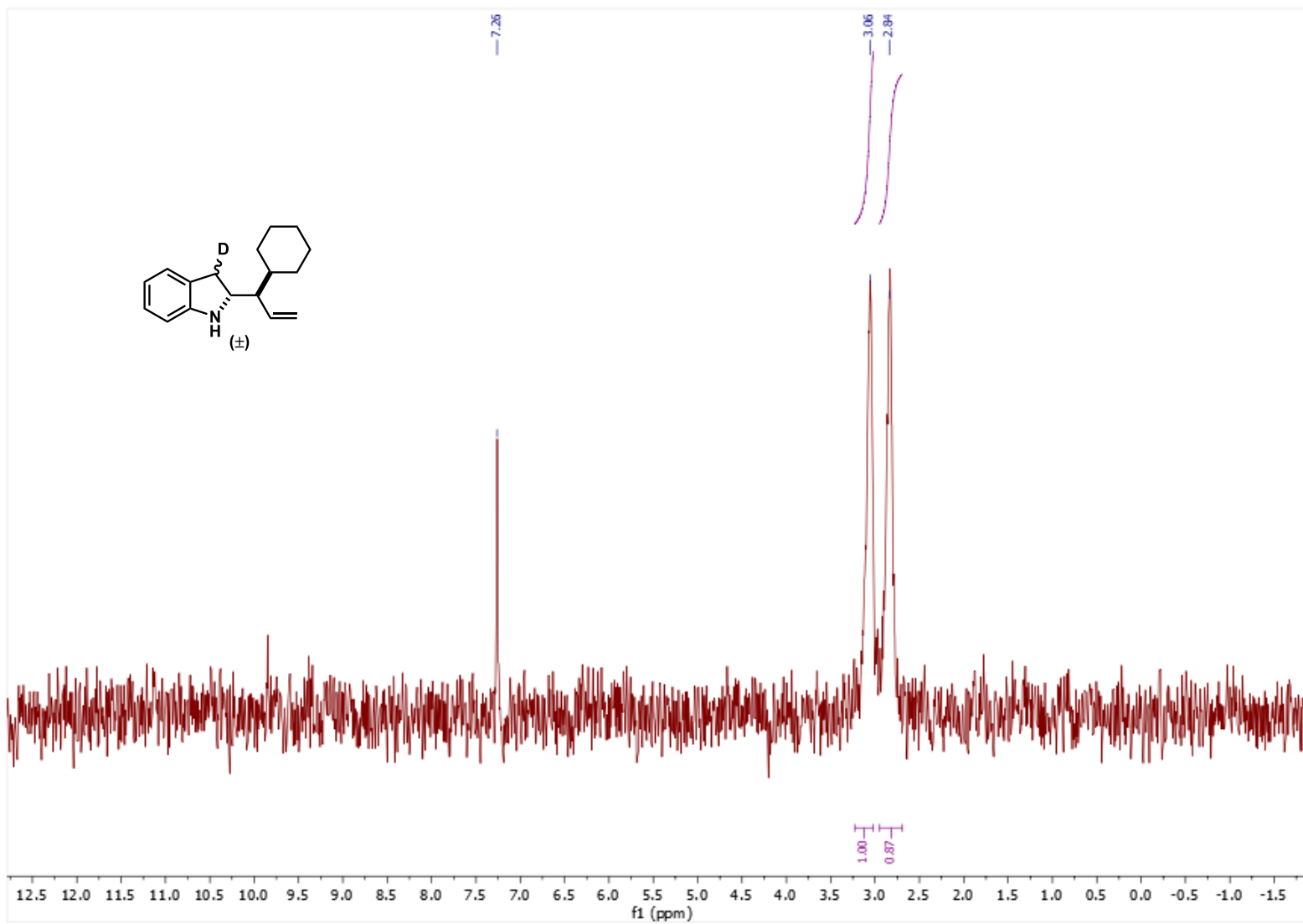
¹H NMR (400 MHz, CDCl₃) spectrum of trideca-1,2-diene



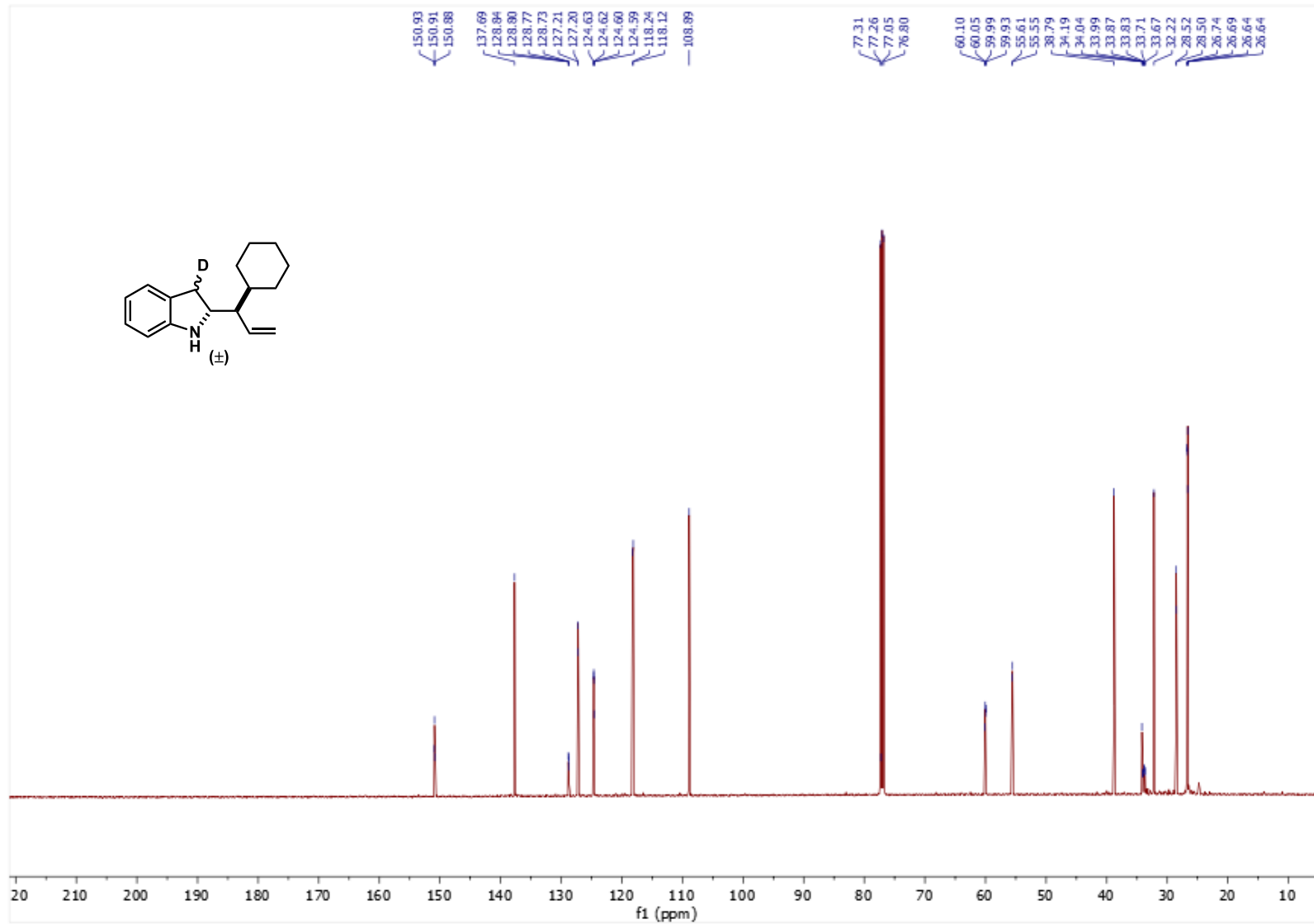
¹³C NMR (126 MHz, CDCl₃) spectrum of trideca-1,2-diene



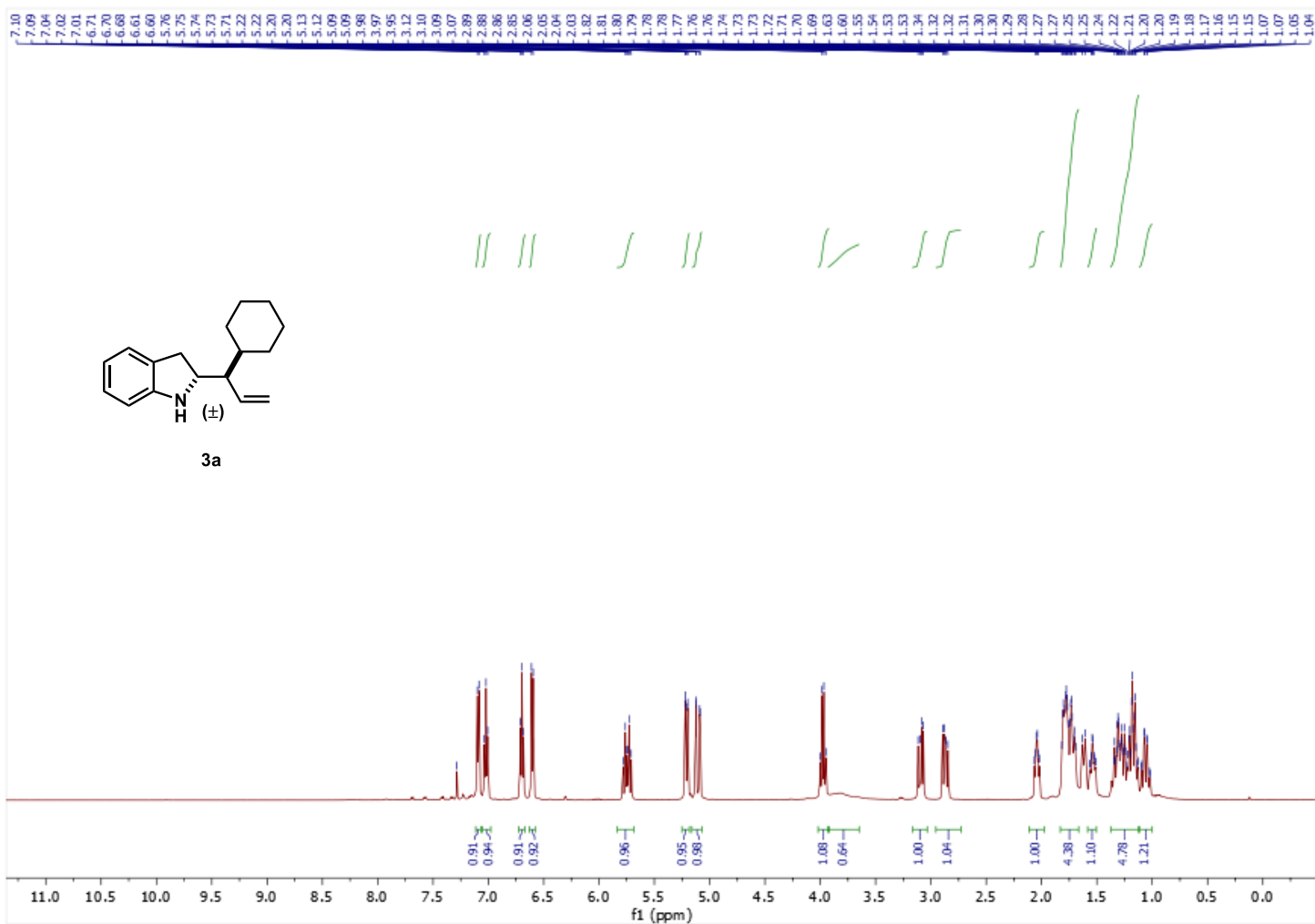
¹H NMR (500 MHz, CDCl₃) spectrum of 3-deutero-2-(1-cyclohexylallyl)indoline



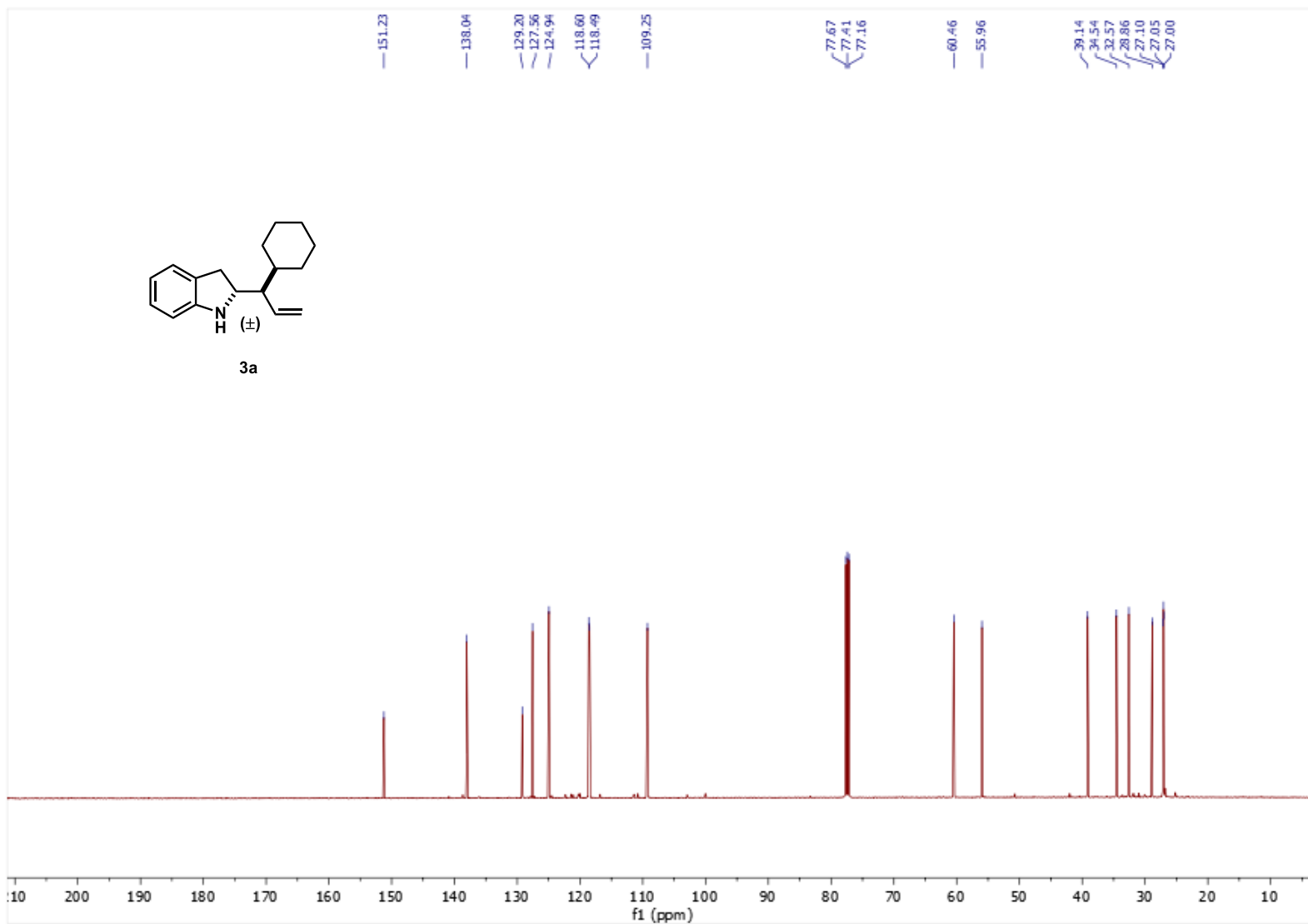
^2H NMR (77 MHz, CDCl_3) spectrum of 3-deutero-2-(1-cyclohexylallyl)indoline



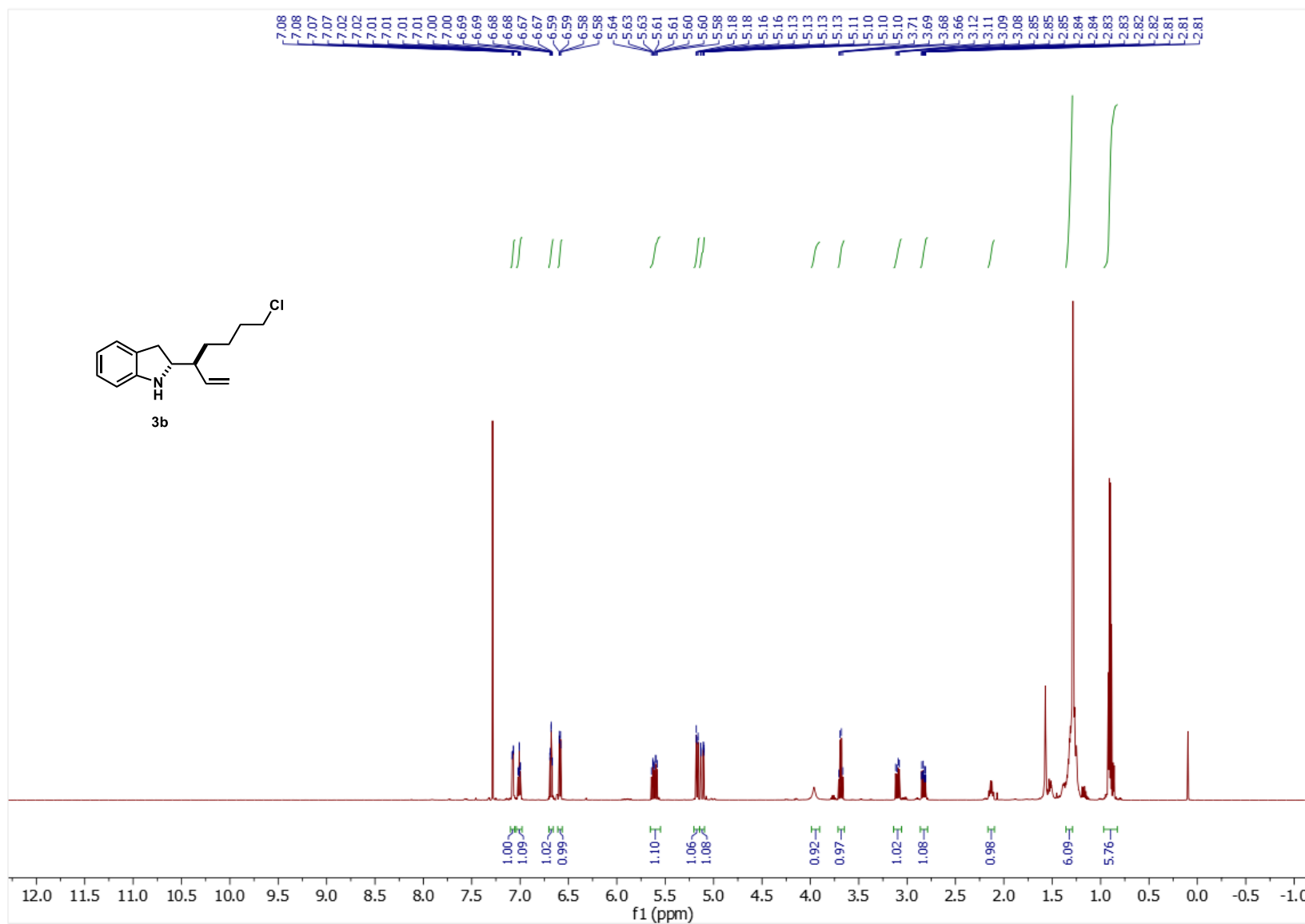
^{13}C NMR (126 MHz, CDCl_3) spectrum of 3-deutero-2-(1-cyclohexylallyl)indoline



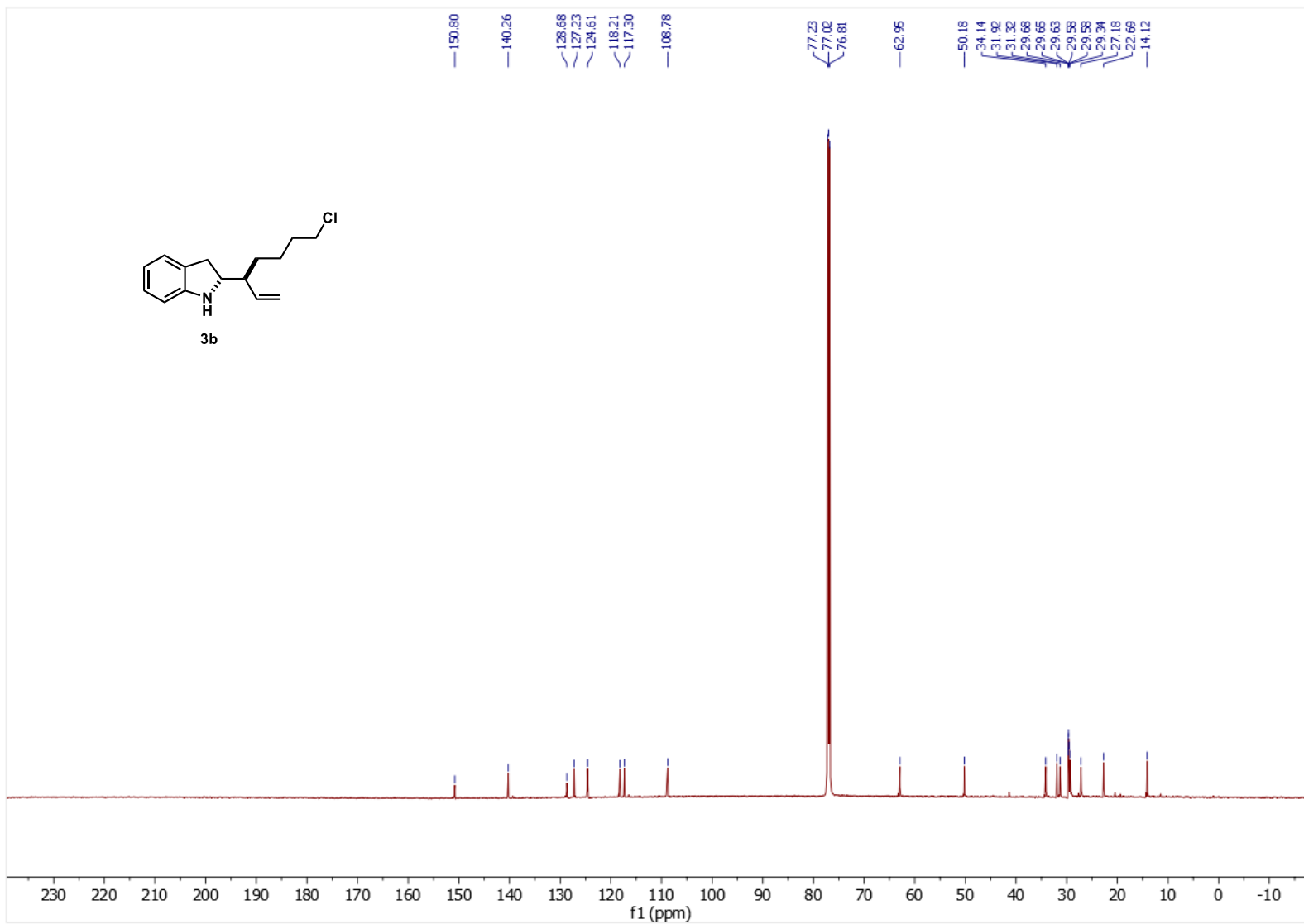
¹H NMR (500 MHz, CDCl₃) spectrum of 2-(1-cyclohexylallyl)indoline **3a**



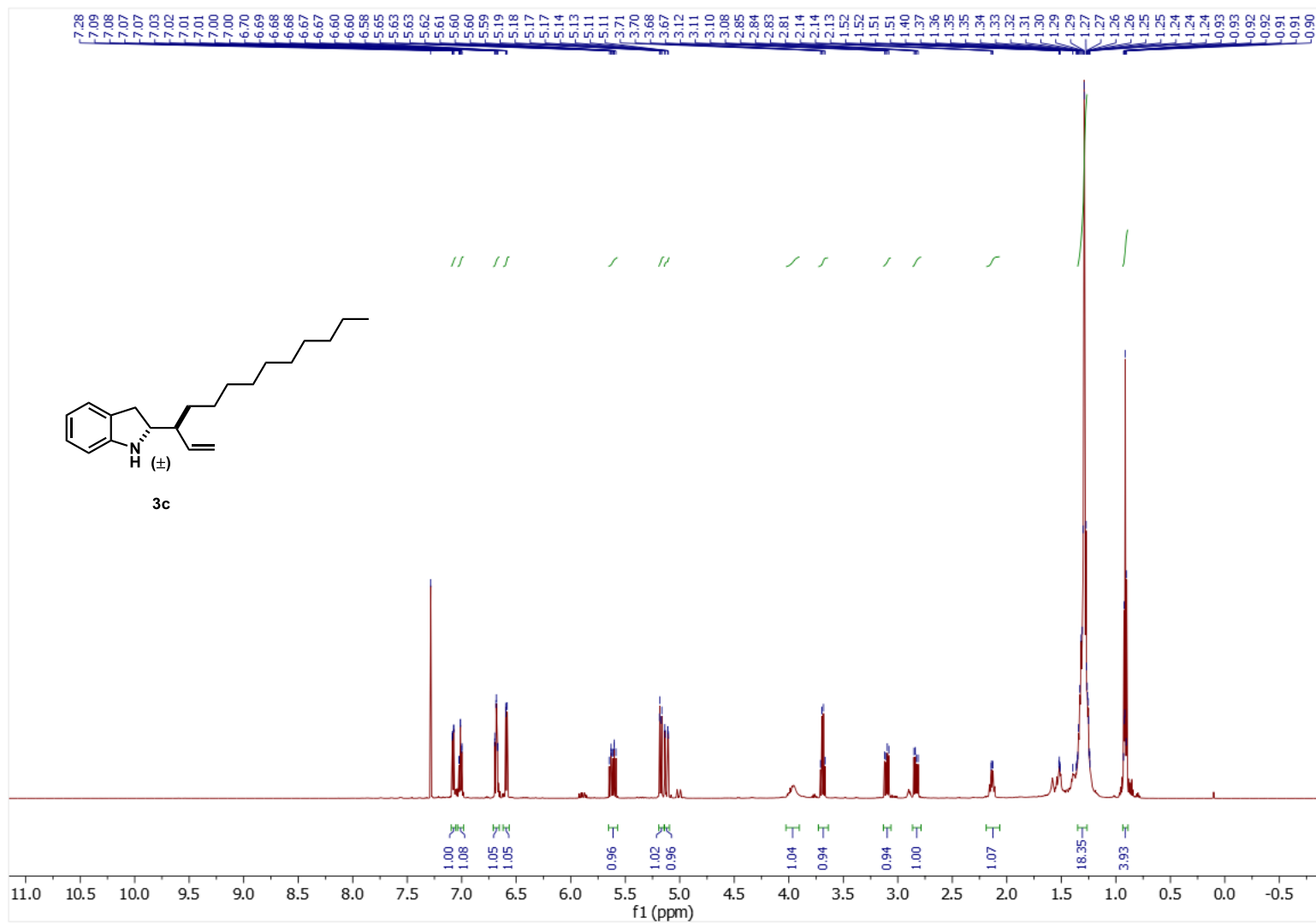
¹³C NMR (126 MHz, CDCl₃) spectrum of 2-(1-cyclohexylallyl)indoline **3a**



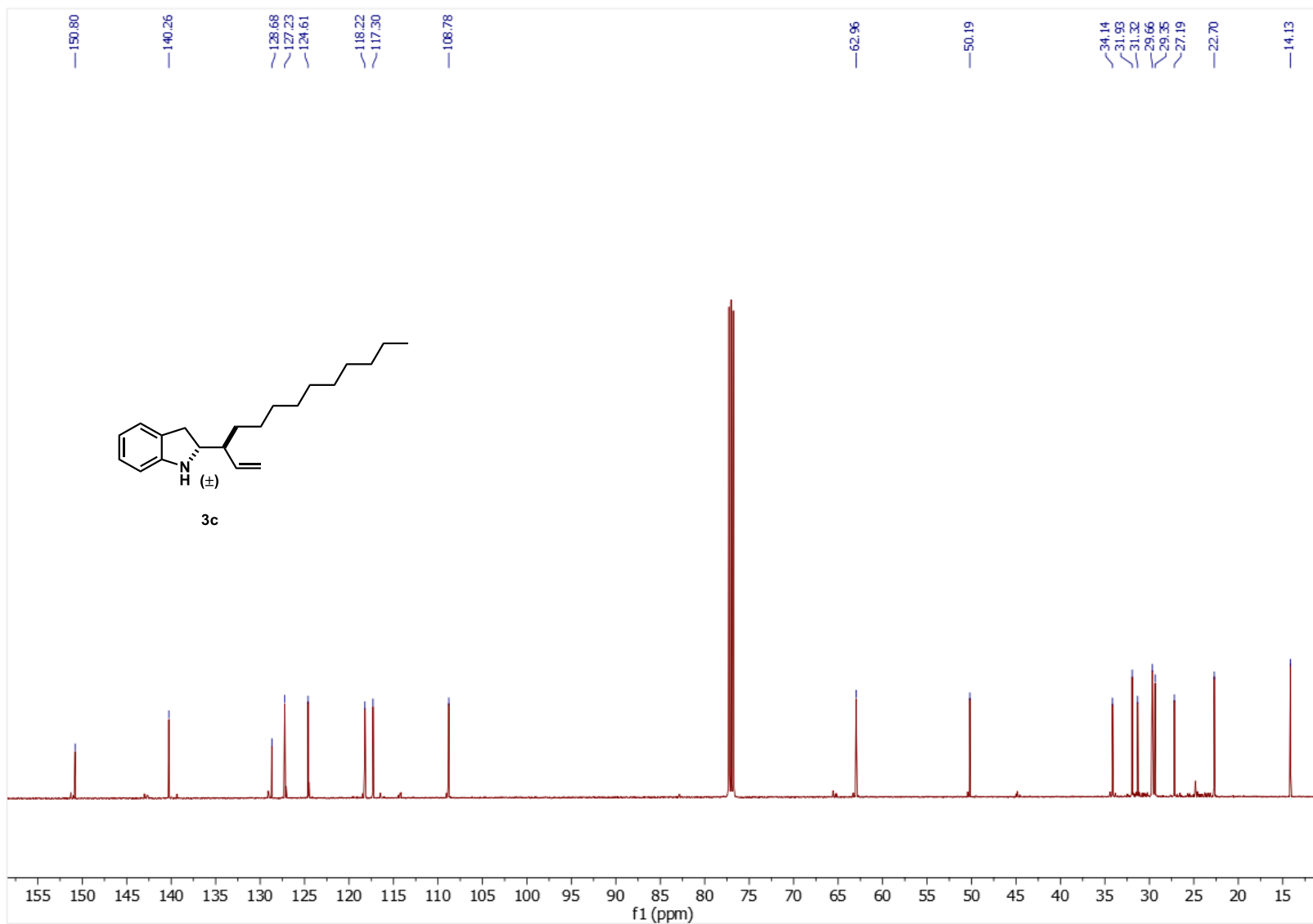
¹H NMR (600 MHz, CDCl₃) spectrum of 2-(1-(4-chlorobutyl)allyl)indoline **3b**



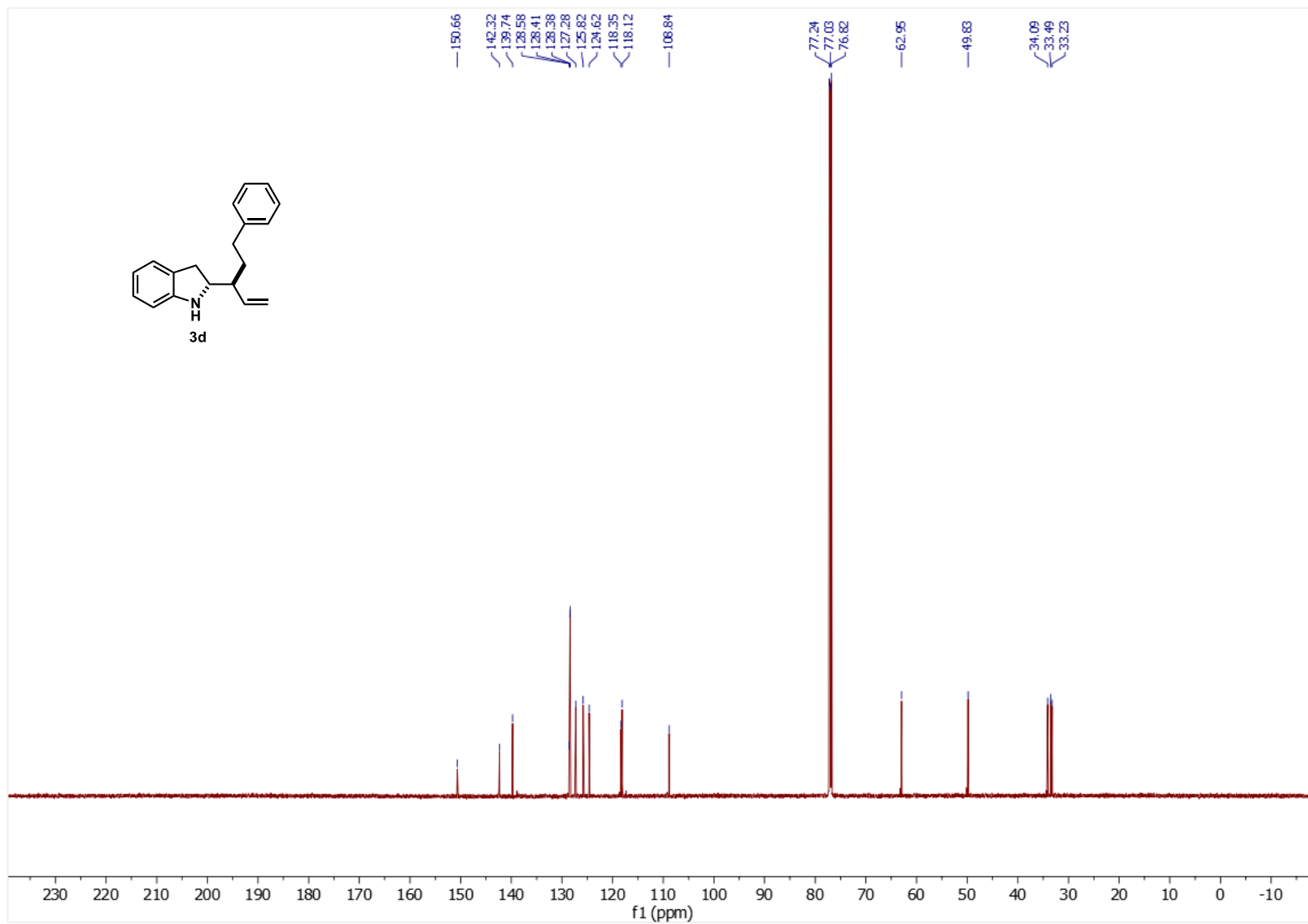
¹³C NMR (151 MHz, CDCl₃) spectrum of 2-(1-(4-chlorobutyl)allyl)indoline **3b**



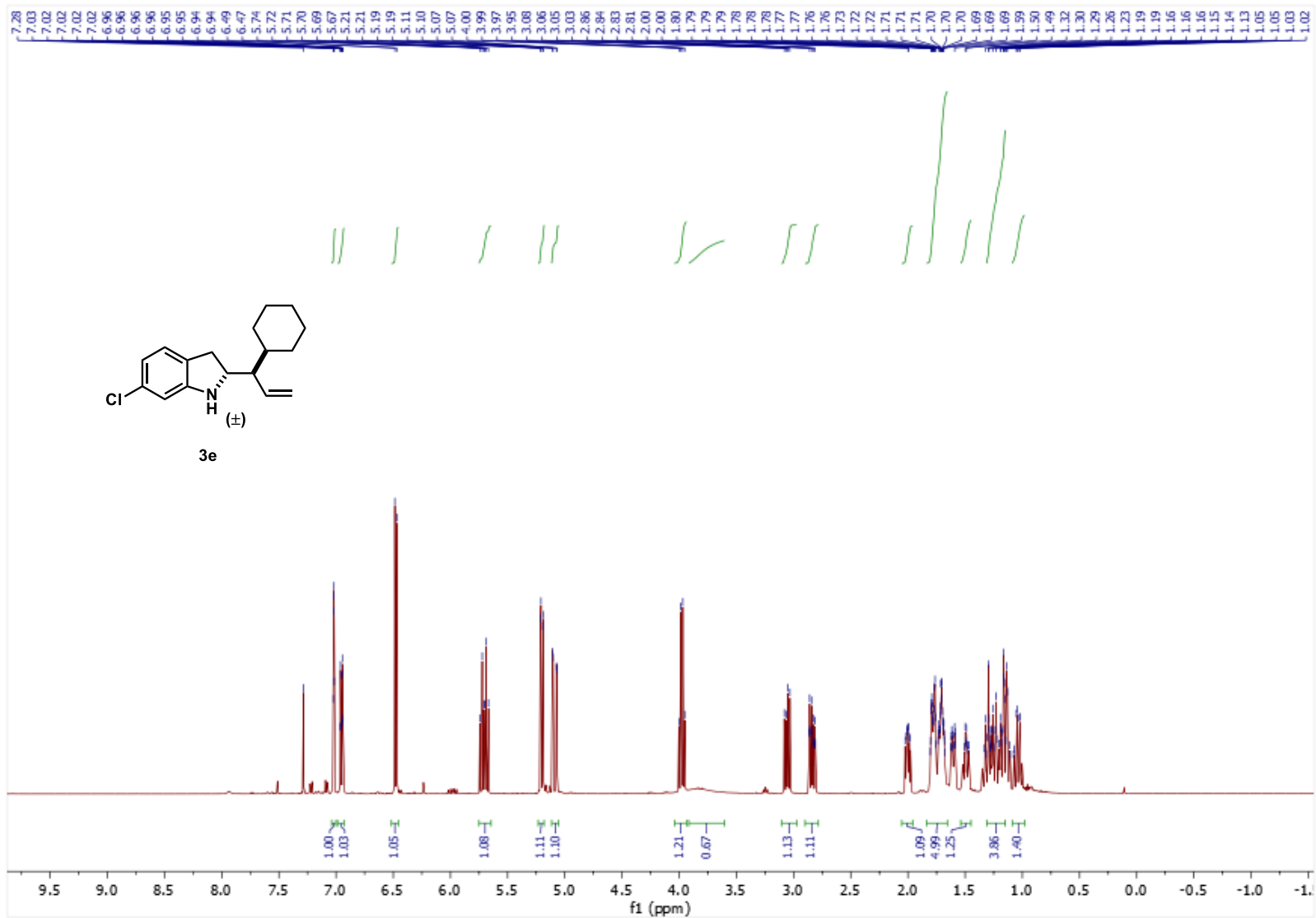
¹H NMR (500 MHz, CDCl₃) spectrum of 2-(1-decylallyl)indoline **3c**



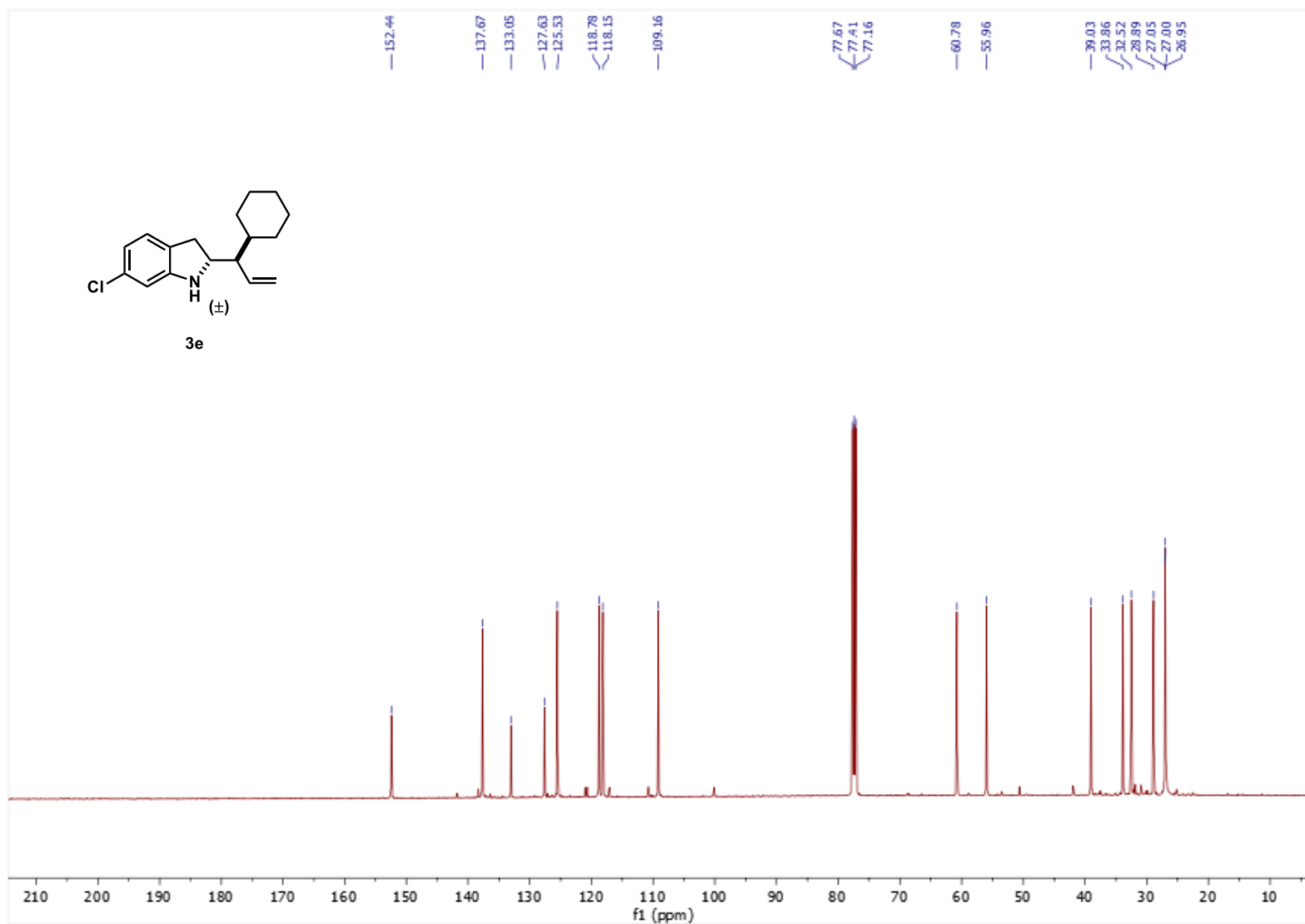
¹³C NMR (126 MHz, CDCl₃) spectrum of 2-(1-decylallyl)indoline **3c**



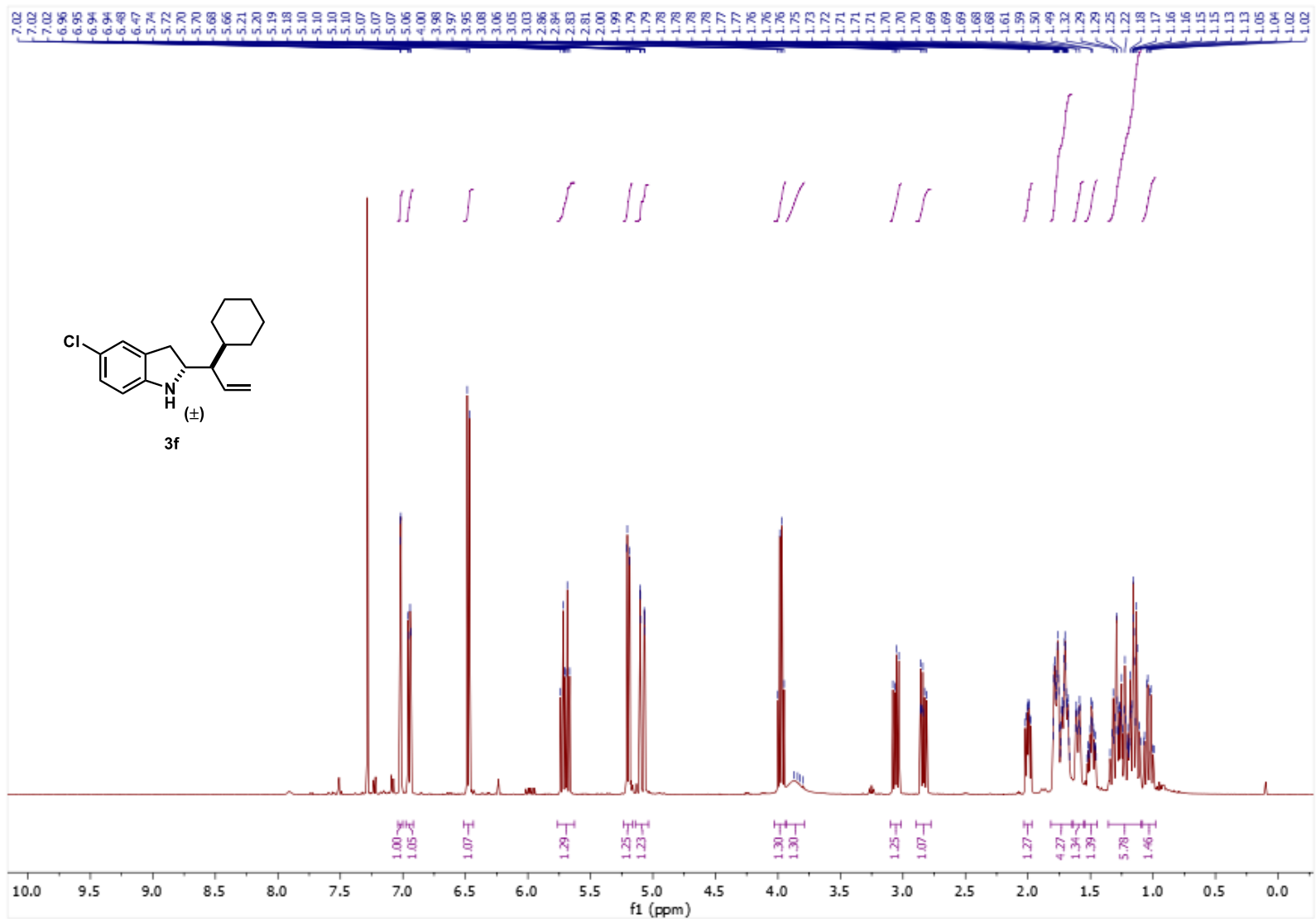
¹³C NMR (151 MHz, CDCl₃) spectrum of 2-(1-(2-phenylethyl)allyl)indoline **3d**



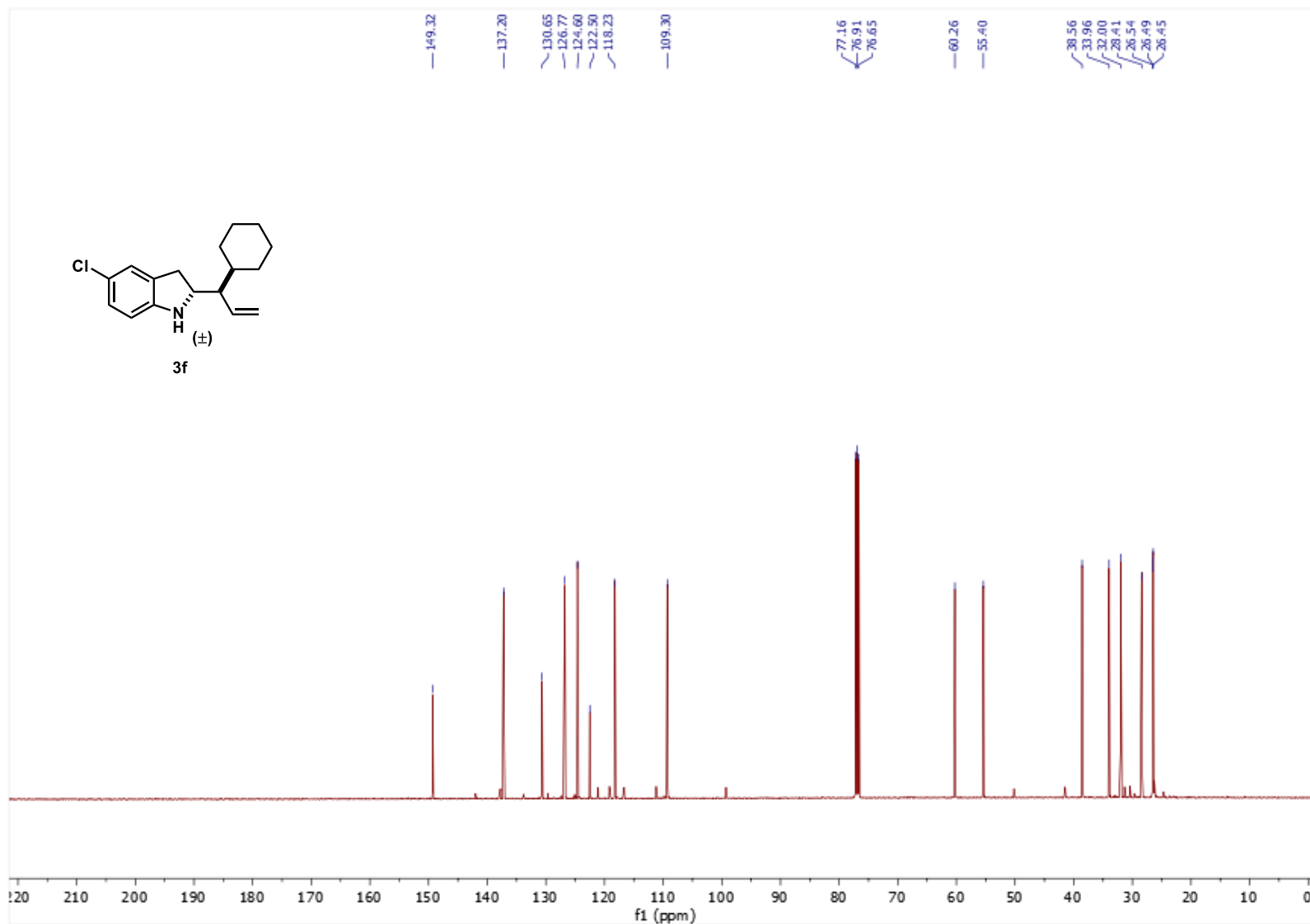
$^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of 6-chloro-2-(1-cyclohexylallyl)indoline **3e**



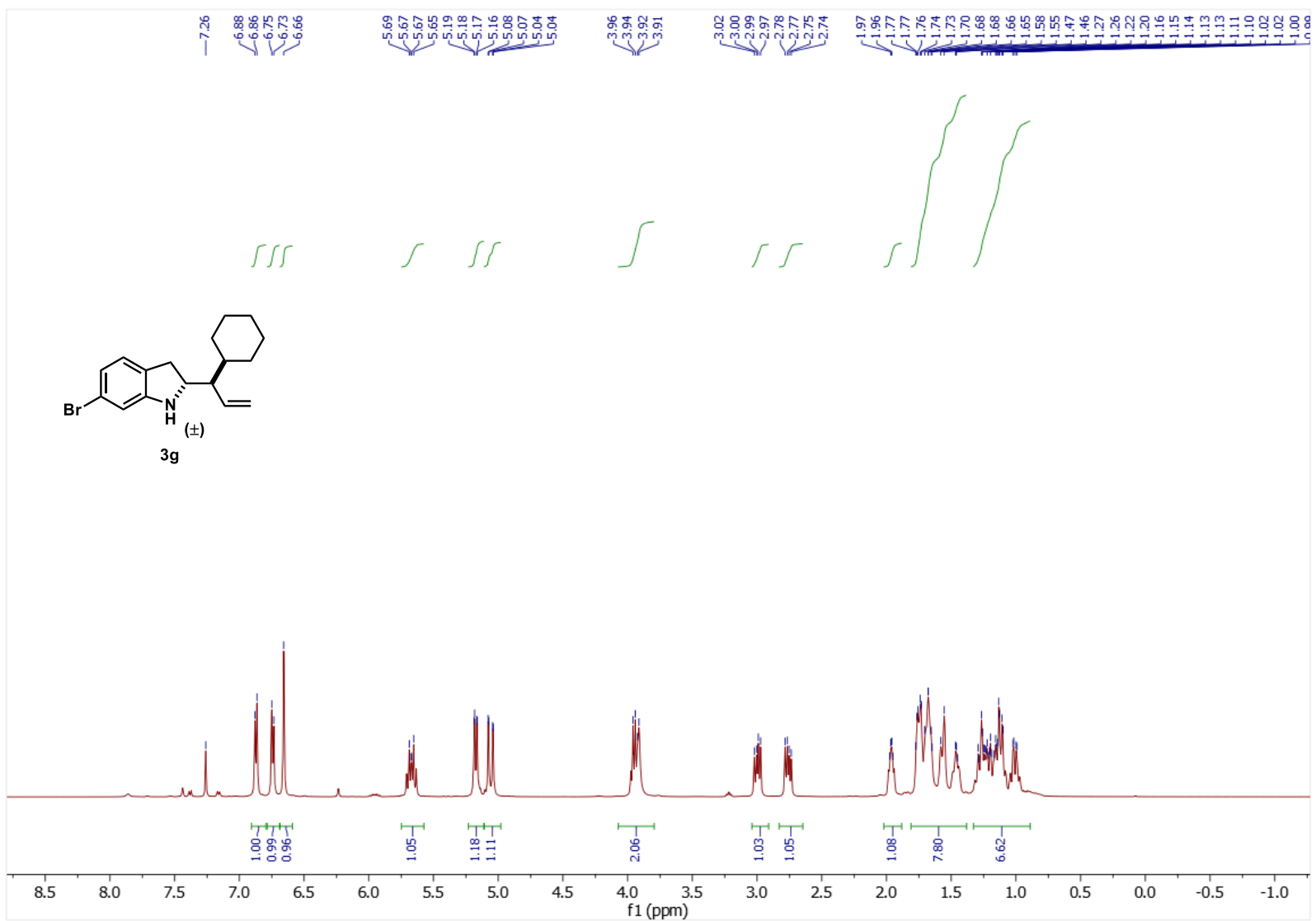
¹³C NMR (126 MHz, CDCl₃) spectrum of 6-chloro-2-(1-cyclohexylallyl)indoline **3e**



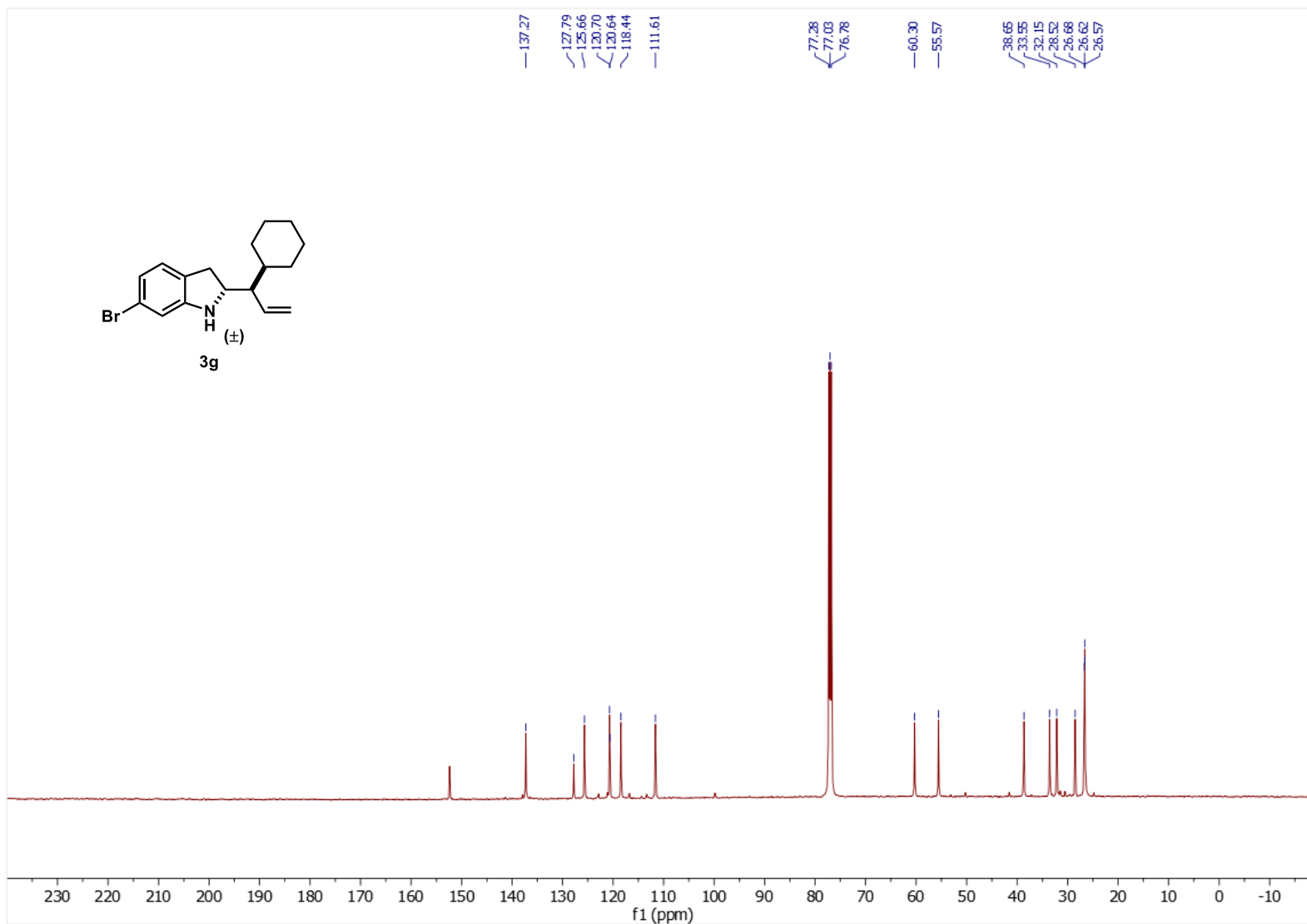
¹H NMR (500 MHz, CDCl₃) spectrum of 5-chloro-2-(1-cyclohexylallyl)indoline **3f**



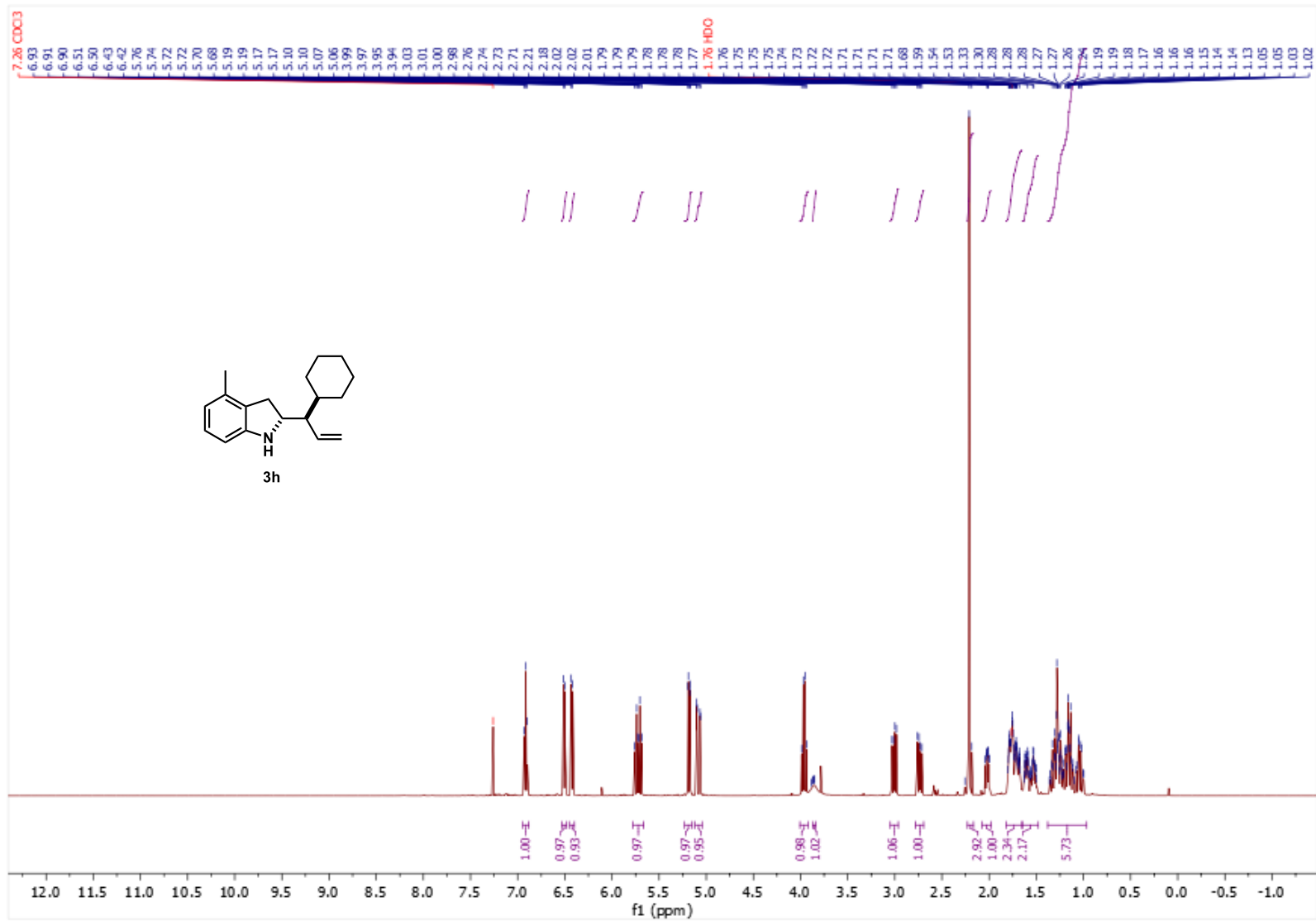
¹³C NMR (126 MHz, CDCl₃) spectrum of 5-chloro-2-(1-cyclohexylallyl)indoline **3f**



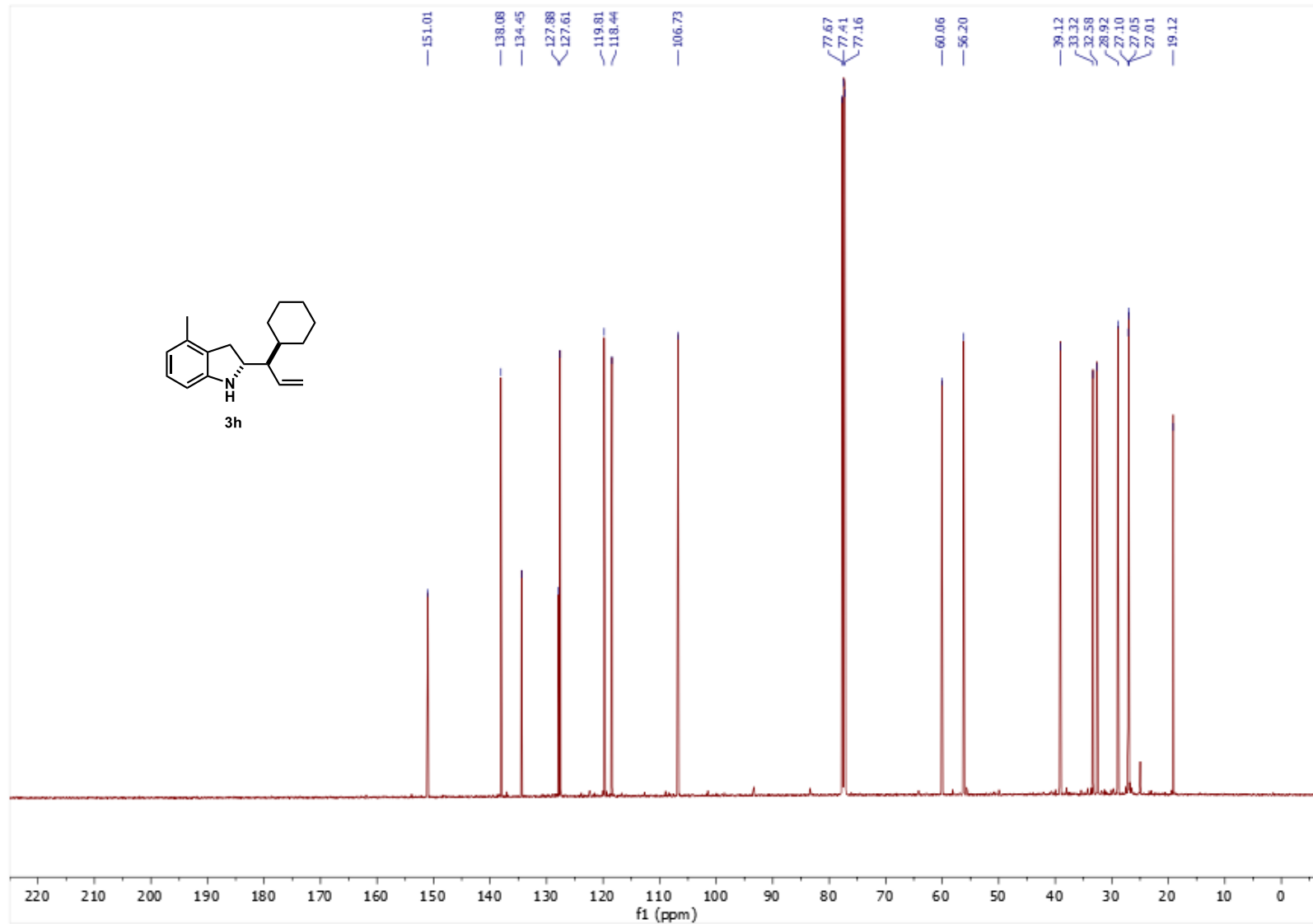
$^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of 6-bromo-2-(1-cyclohexylallyl)indoline **3g**



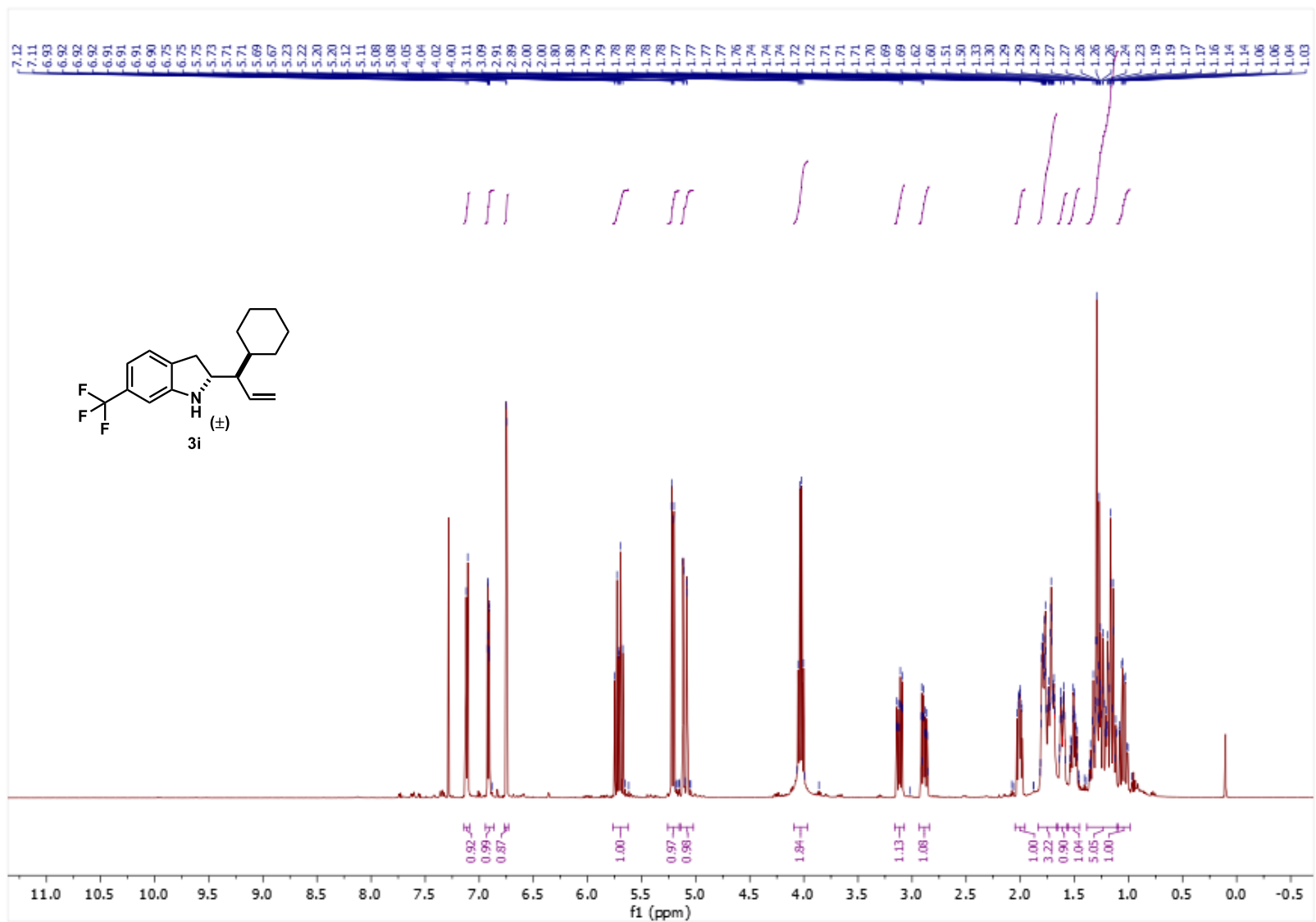
¹³C NMR (126 MHz, CDCl₃) spectrum of 6-bromo-2-(1-cyclohexylallyl)indoline **3g**



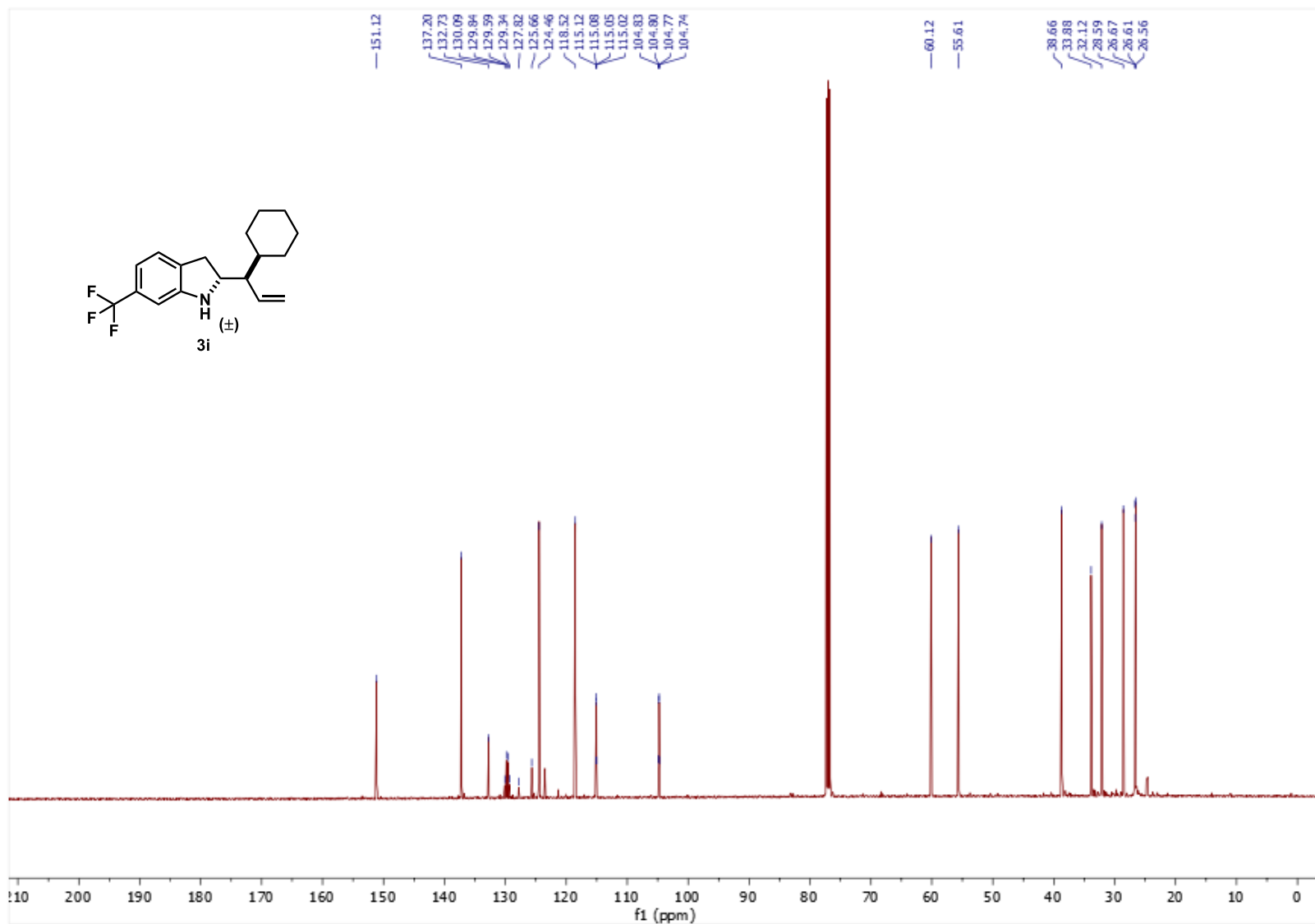
¹H NMR (600 MHz, CDCl₃) spectrum of 4-methyl-(1-cyclohexylallyl)indoline **3h**



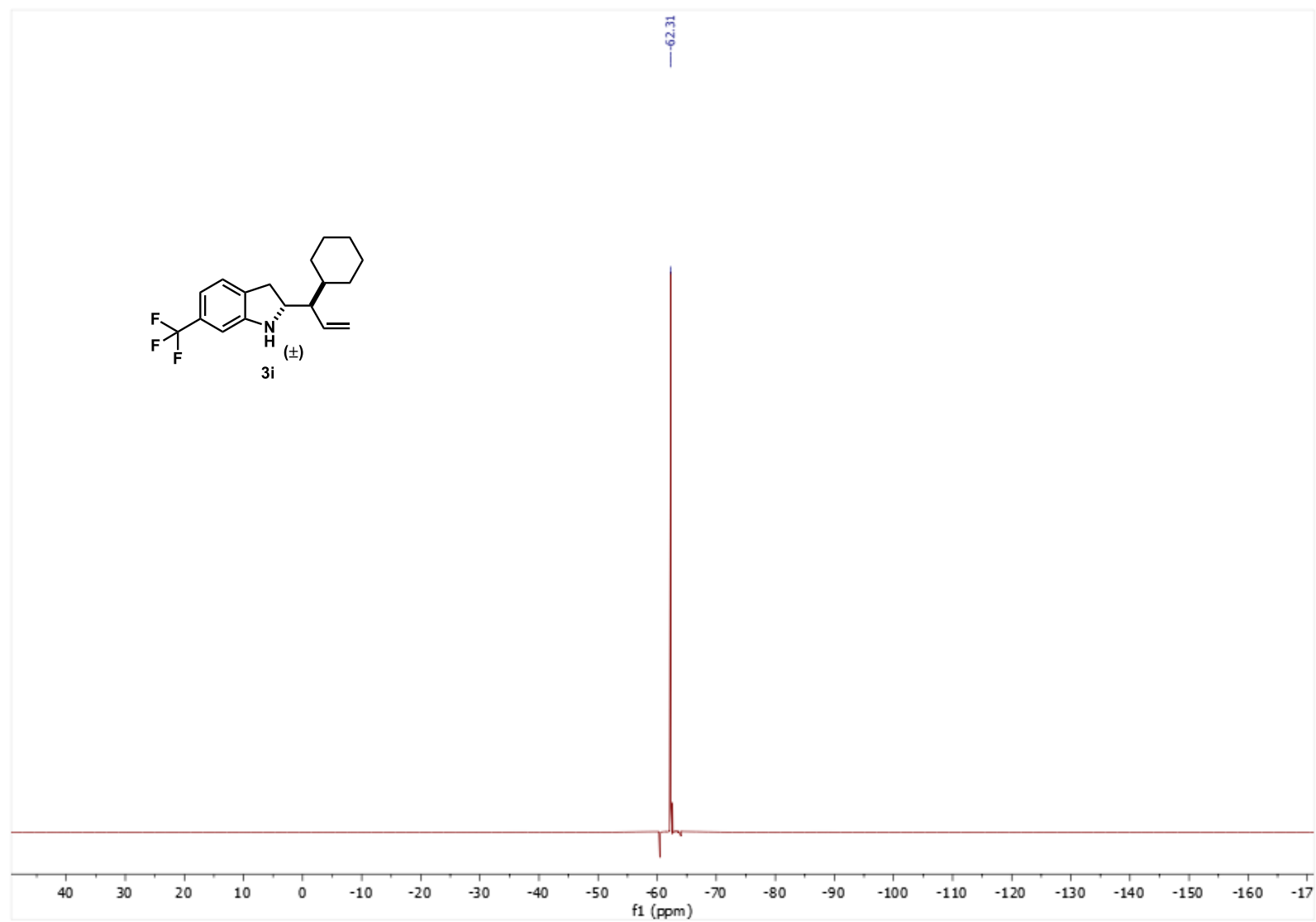
^{13}C NMR (151 MHz, CDCl_3) spectrum of 4-methyl-(1-cyclohexylallyl)indoline **3h**



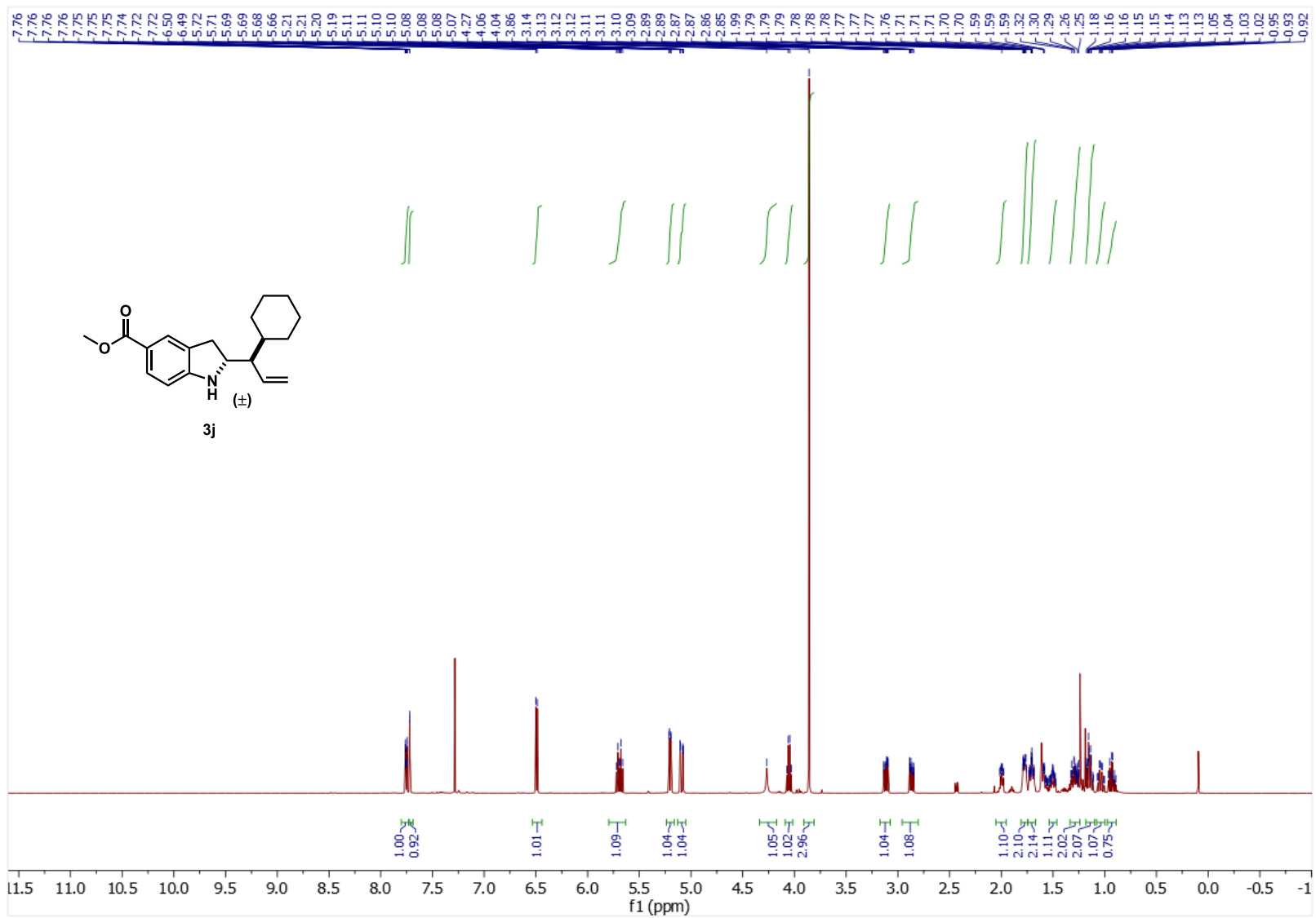
¹H NMR (500 MHz, CDCl₃) spectrum of 6-(trifluoromethyl)-2-(1-cyclohexylallyl)indoline **3i**



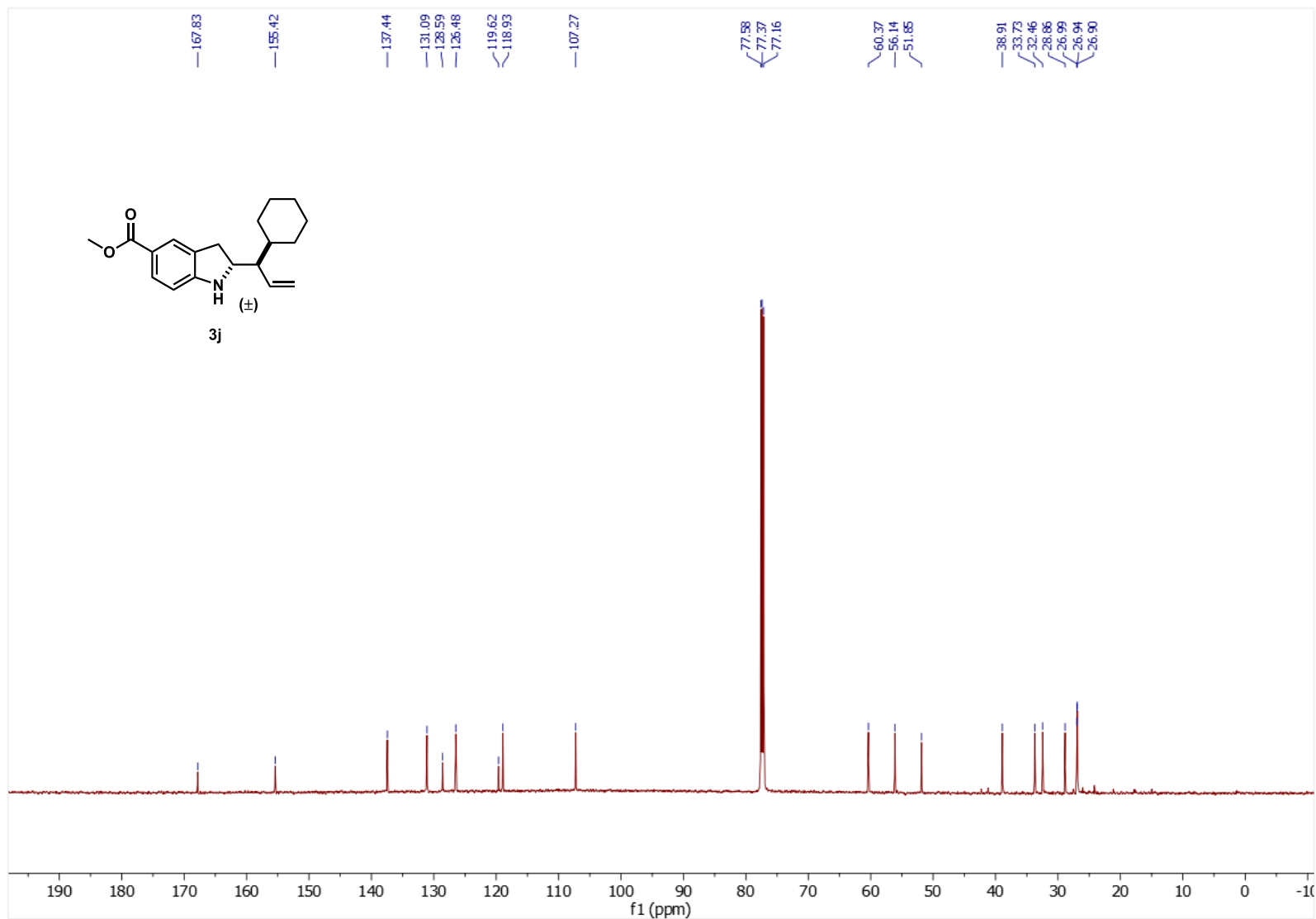
^{13}C NMR (126 MHz, CDCl_3) Spectra of 6-Trifluoromethyl-2-(1-cyclohexylallyl)indoline **3i**



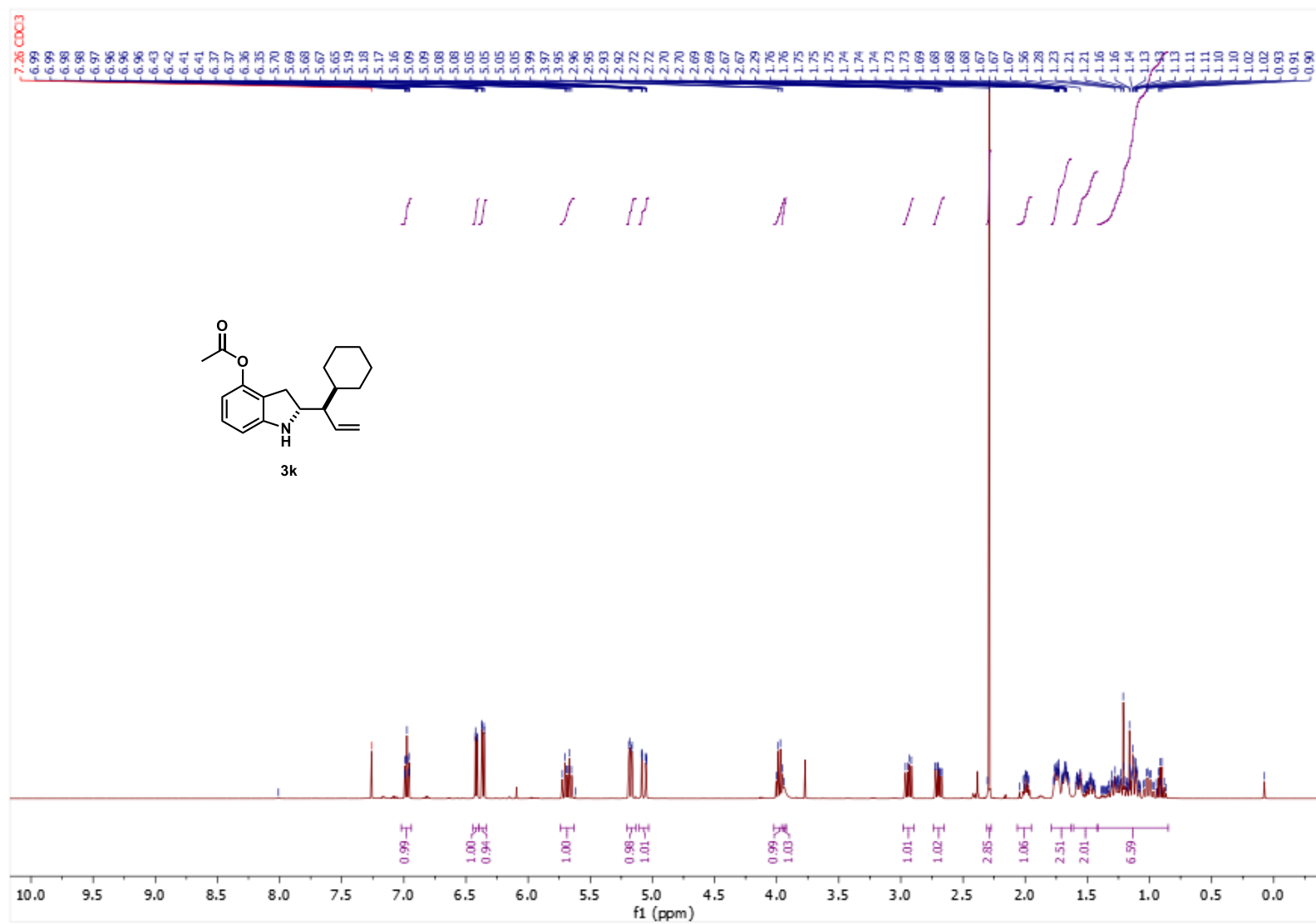
^{19}F NMR (471 MHz, CDCl_3) spectrum of 6-trifluoromethyl-2-(1-cyclohexylallyl)indoline **3i**



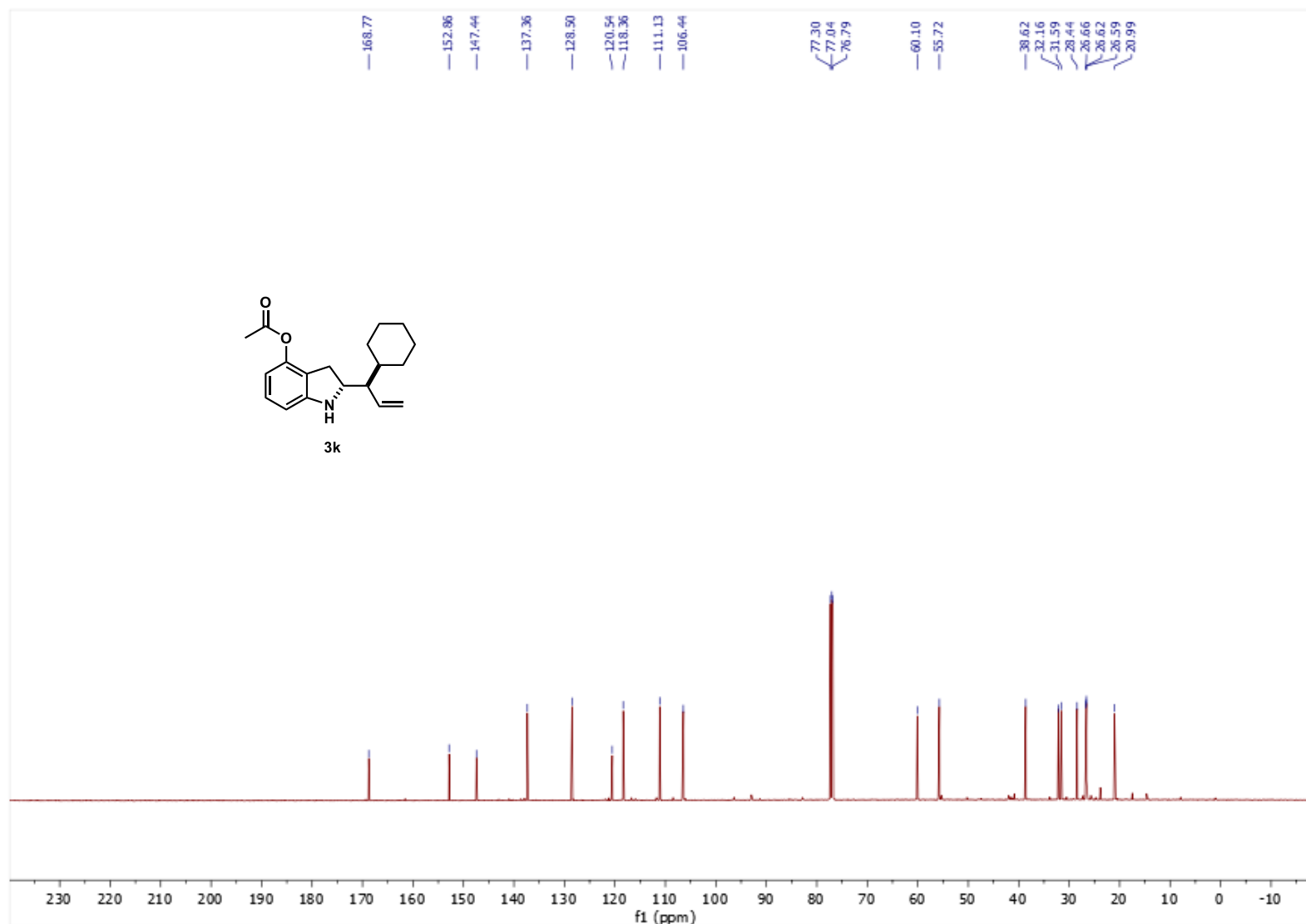
$^1\text{H NMR}$ (600 MHz, CDCl_3) spectrum of 5-methoxycarbonyl-(1-cyclohexylallyl)indoline **3j**



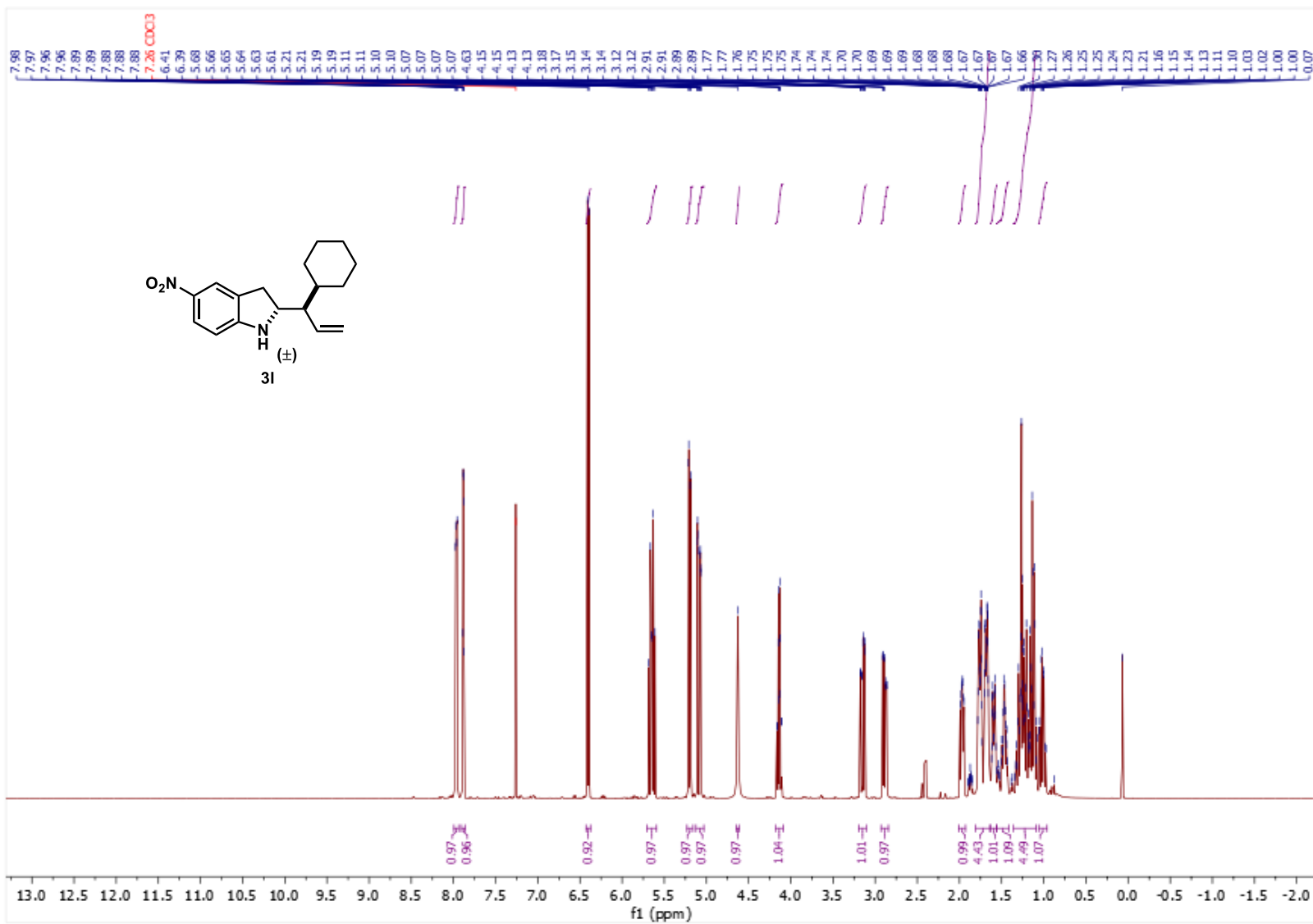
¹³C NMR (151 MHz, CDCl₃) spectrum of 5-methoxycarbonyl-(1-cyclohexylallyl)indoline **3j**



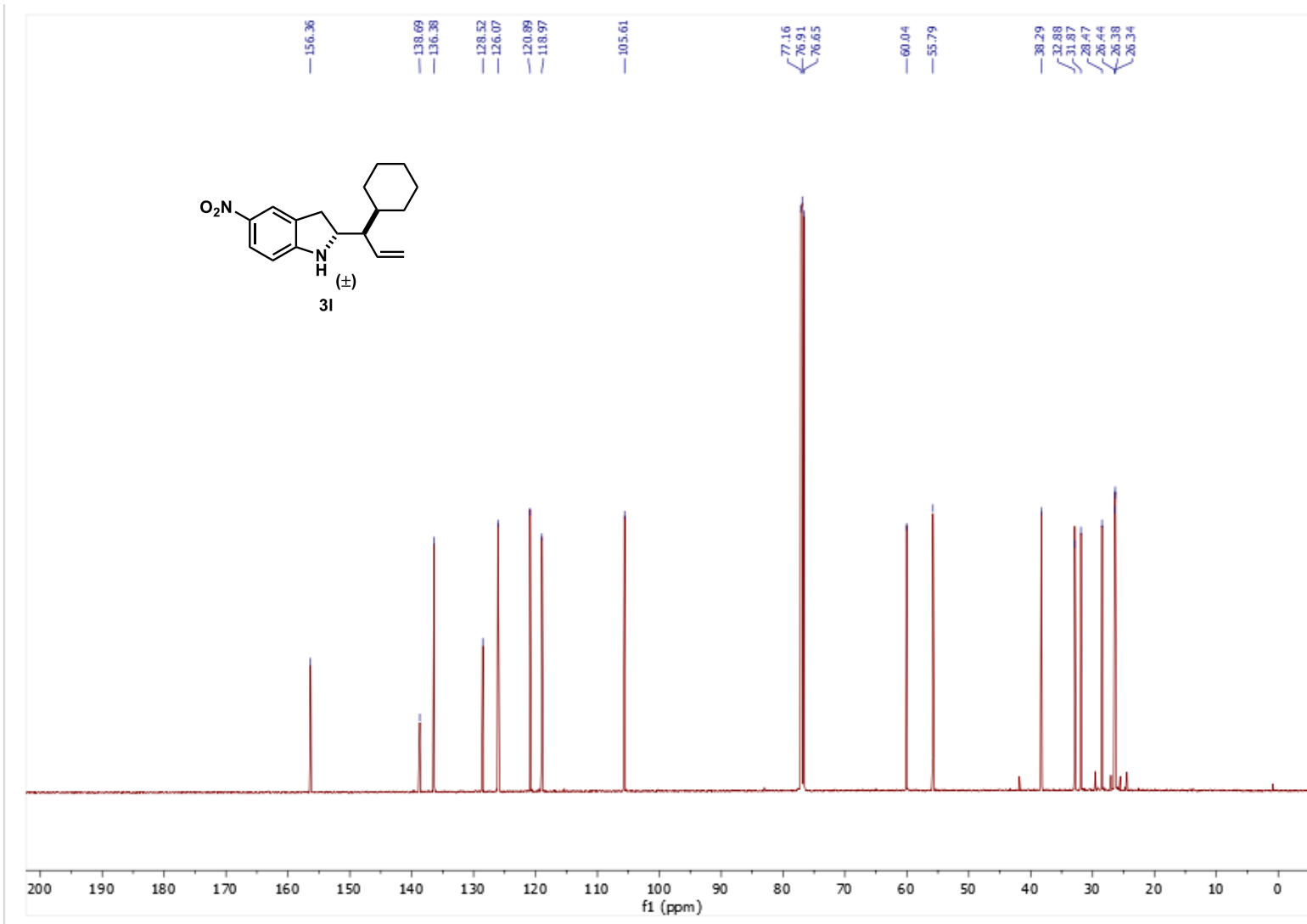
¹H NMR (600 MHz, CDCl₃) spectrum of 4-acetoxy-(1-cyclohexylallyl)indoline **3k**



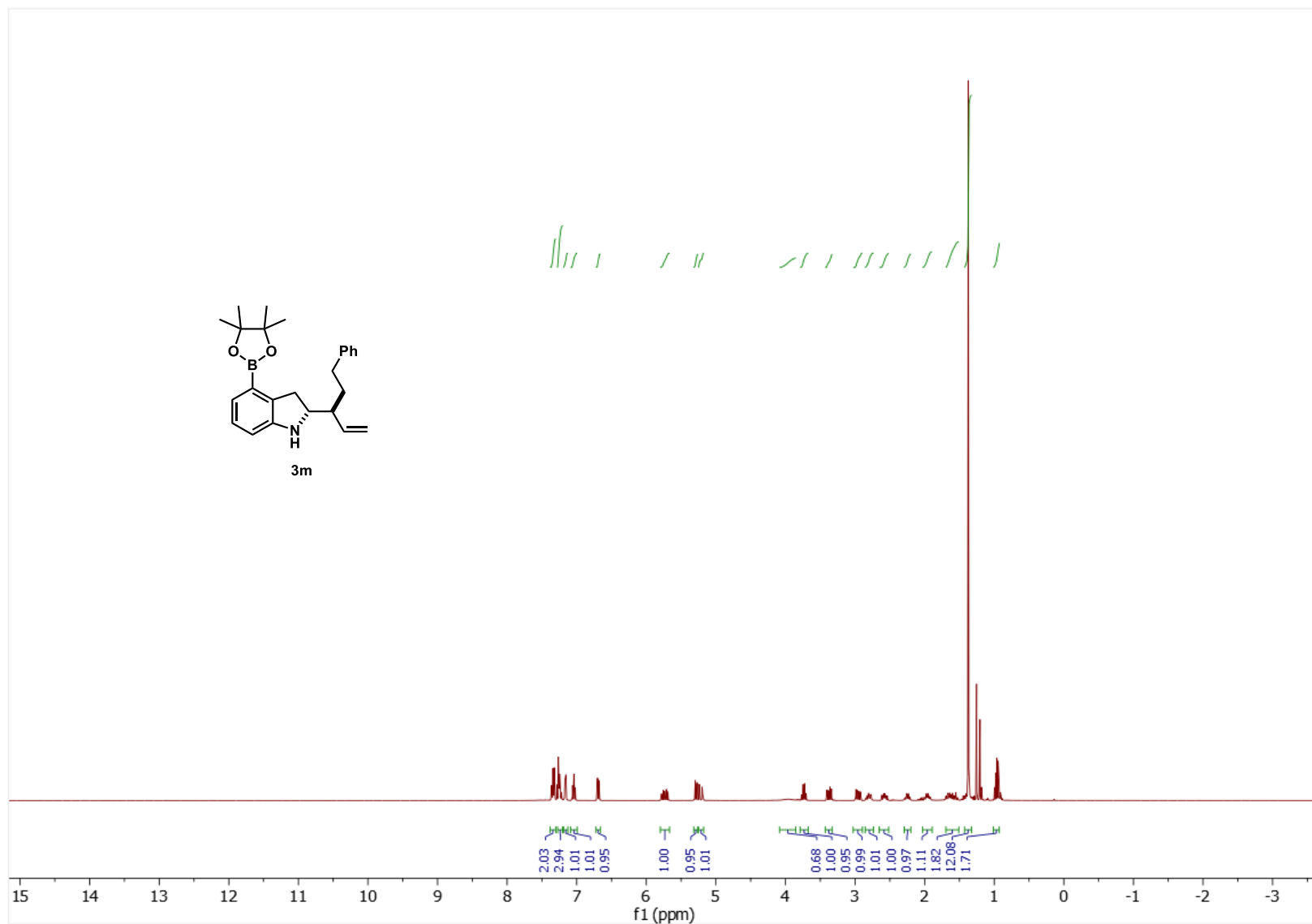
¹³C NMR (151 MHz, CDCl₃) spectrum of 4-acetoxy-(1-cyclohexylallyl)indoline **3k**



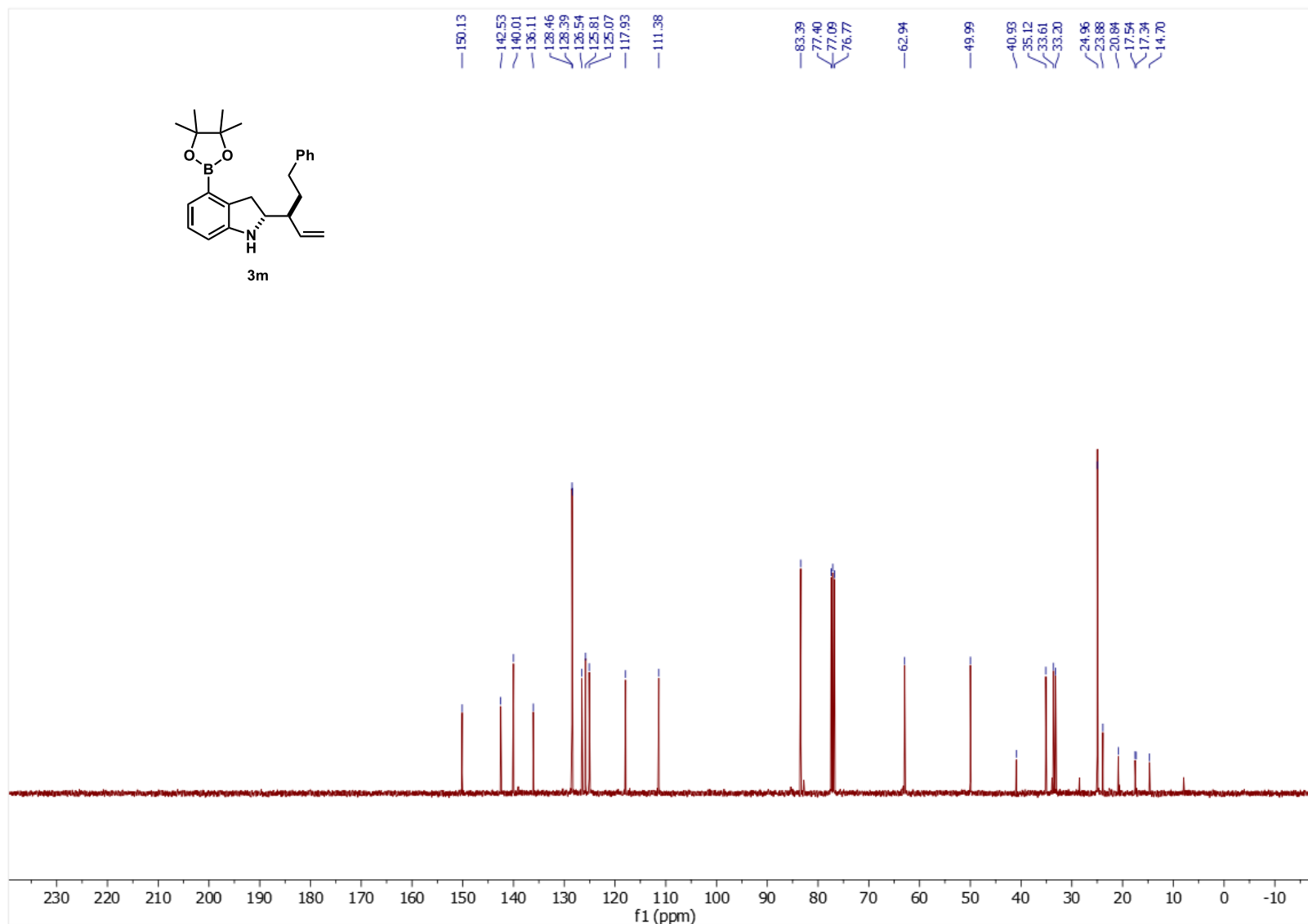
¹H NMR (500 MHz, CDCl₃) spectrum of 4-nitro-2-(1-cyclohexylallyl)indoline 3I



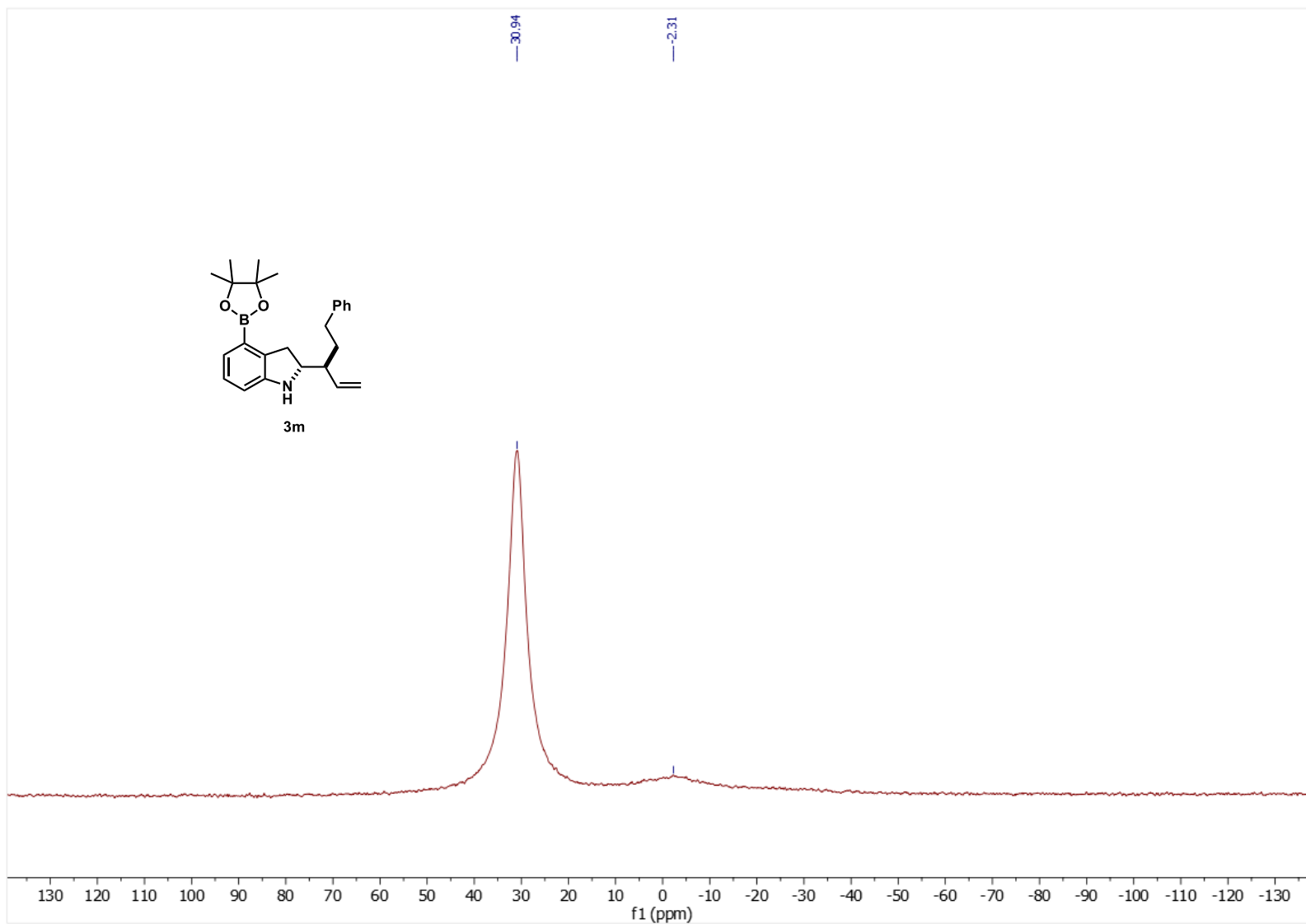
¹³C NMR (126 MHz, CDCl₃) spectrum of 4-nitro-2-(1-cyclohexylallyl)indoline **3I**



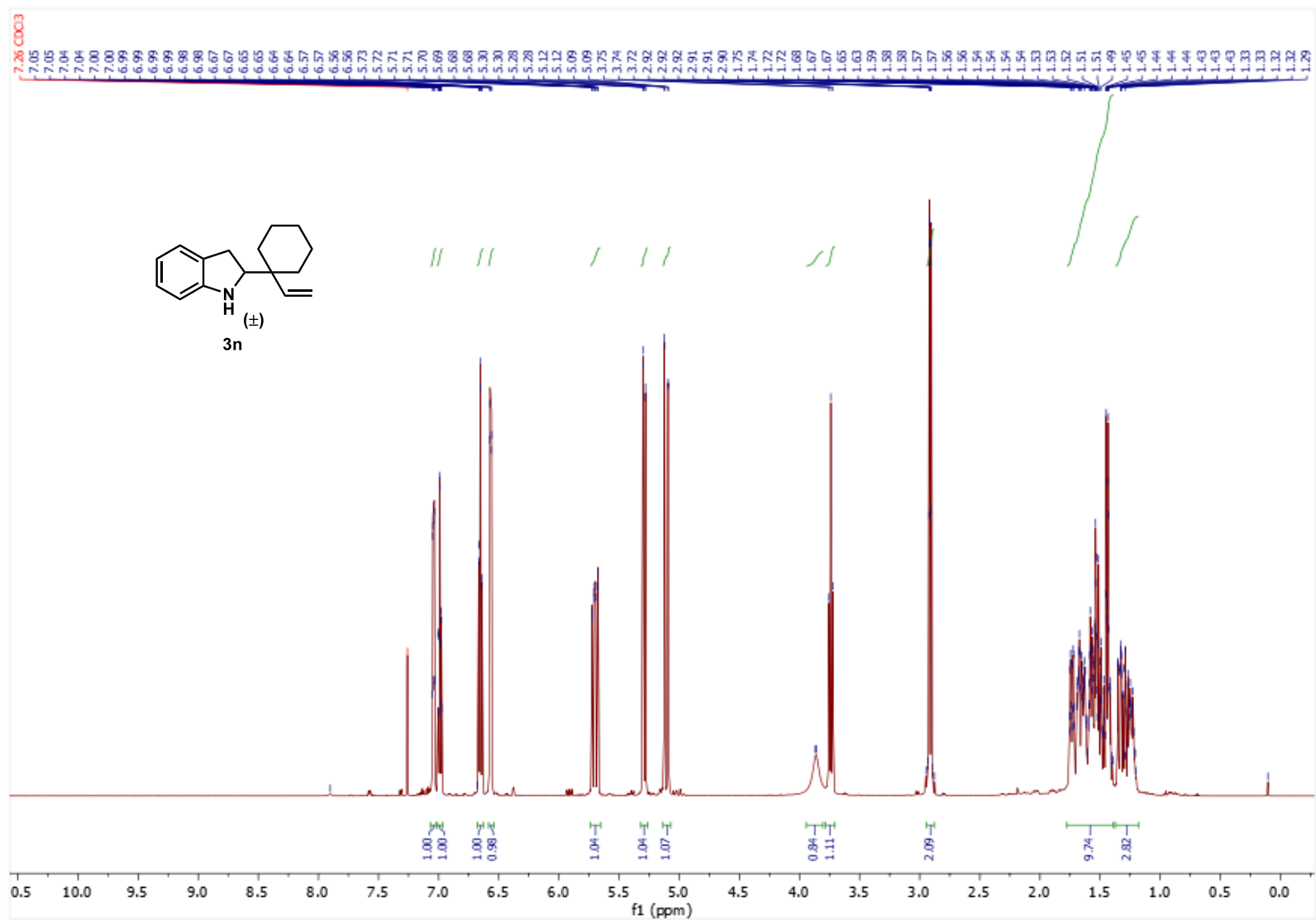
$^1\text{H NMR}$ (600 MHz, CDCl_3) spectrum of 4-Bpin-2-(1-cyclohexylallyl)indoline **3m**



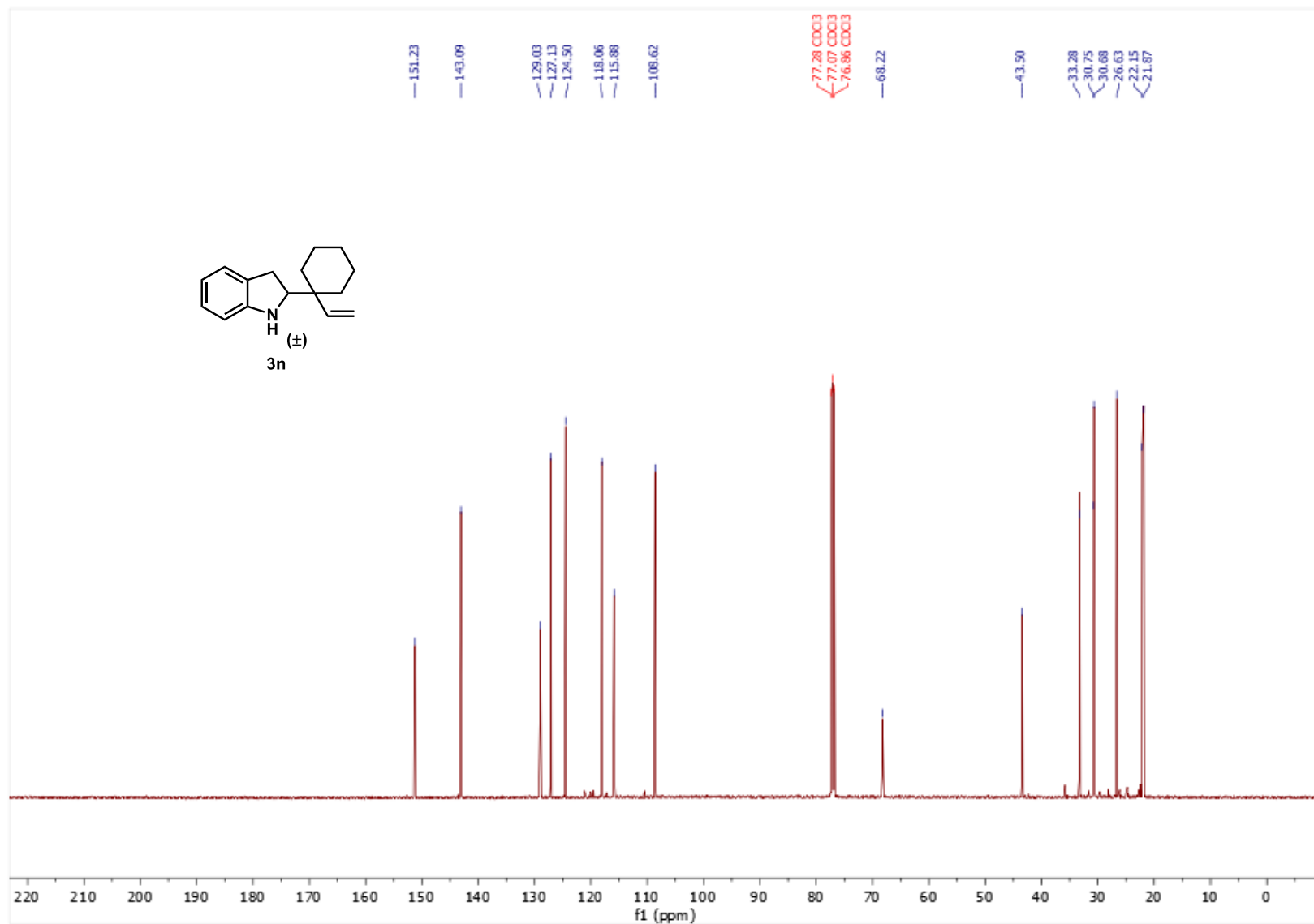
^{13}C NMR (151 MHz, CDCl_3) spectrum of 4-Bpin-2-(1-cyclohexylallyl)indoline **3m**



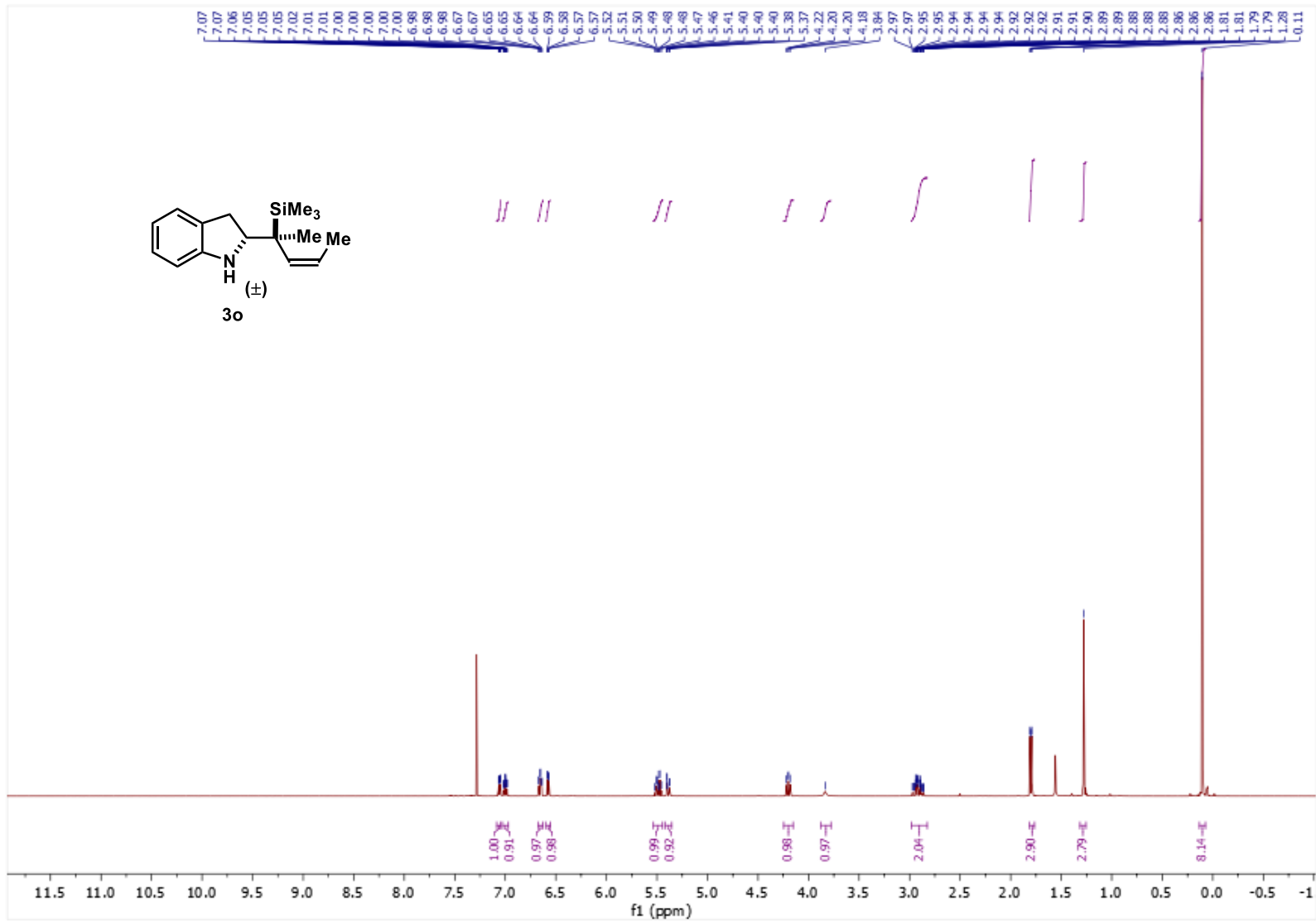
^{11}B NMR (128 MHz, CDCl_3) spectrum of 4-Bpin-2-(1-cyclohexylallyl)indoline **3m**



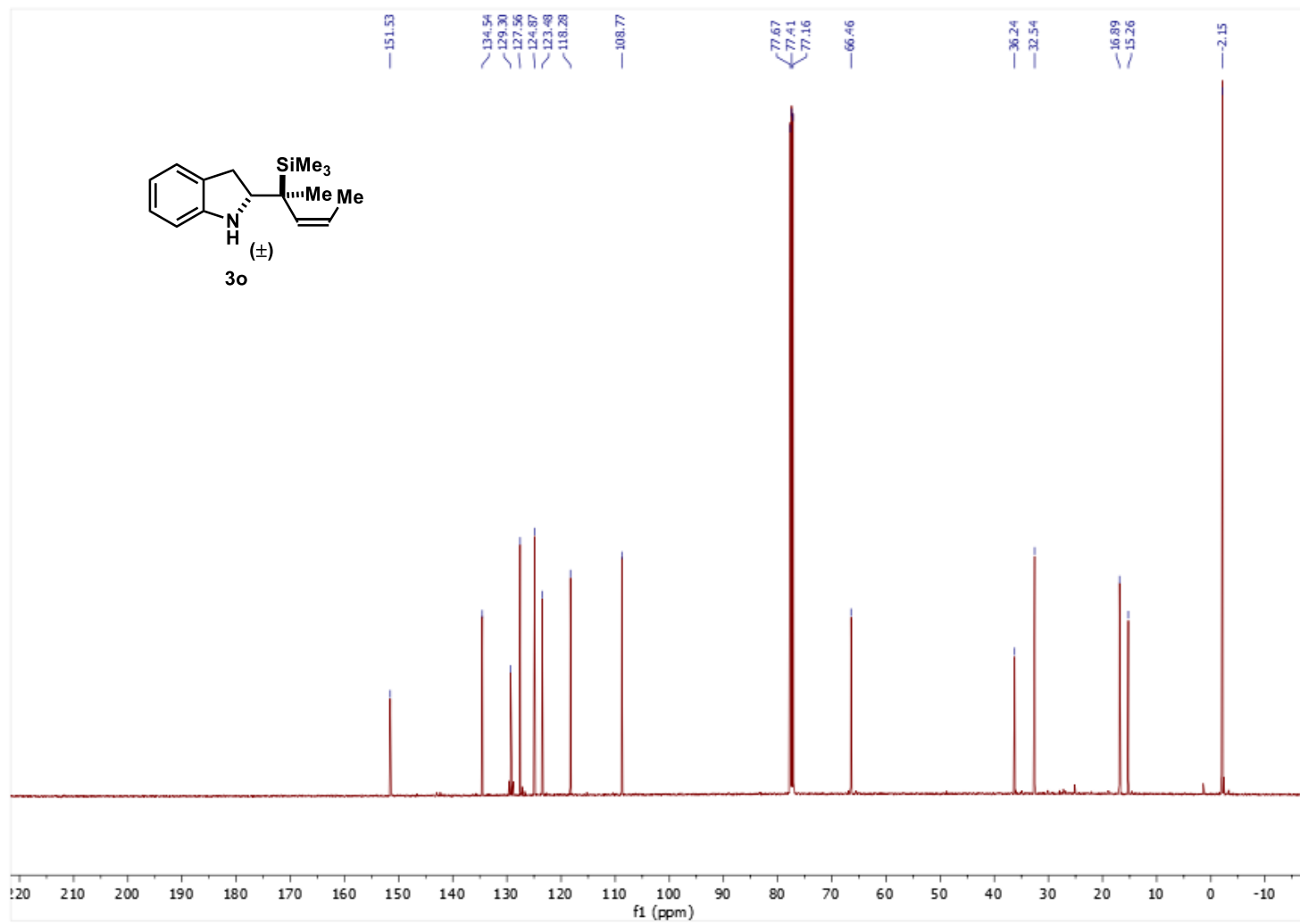
$^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of 1-ethenyl-1-(2-indolyl)cyclohexane **3n**



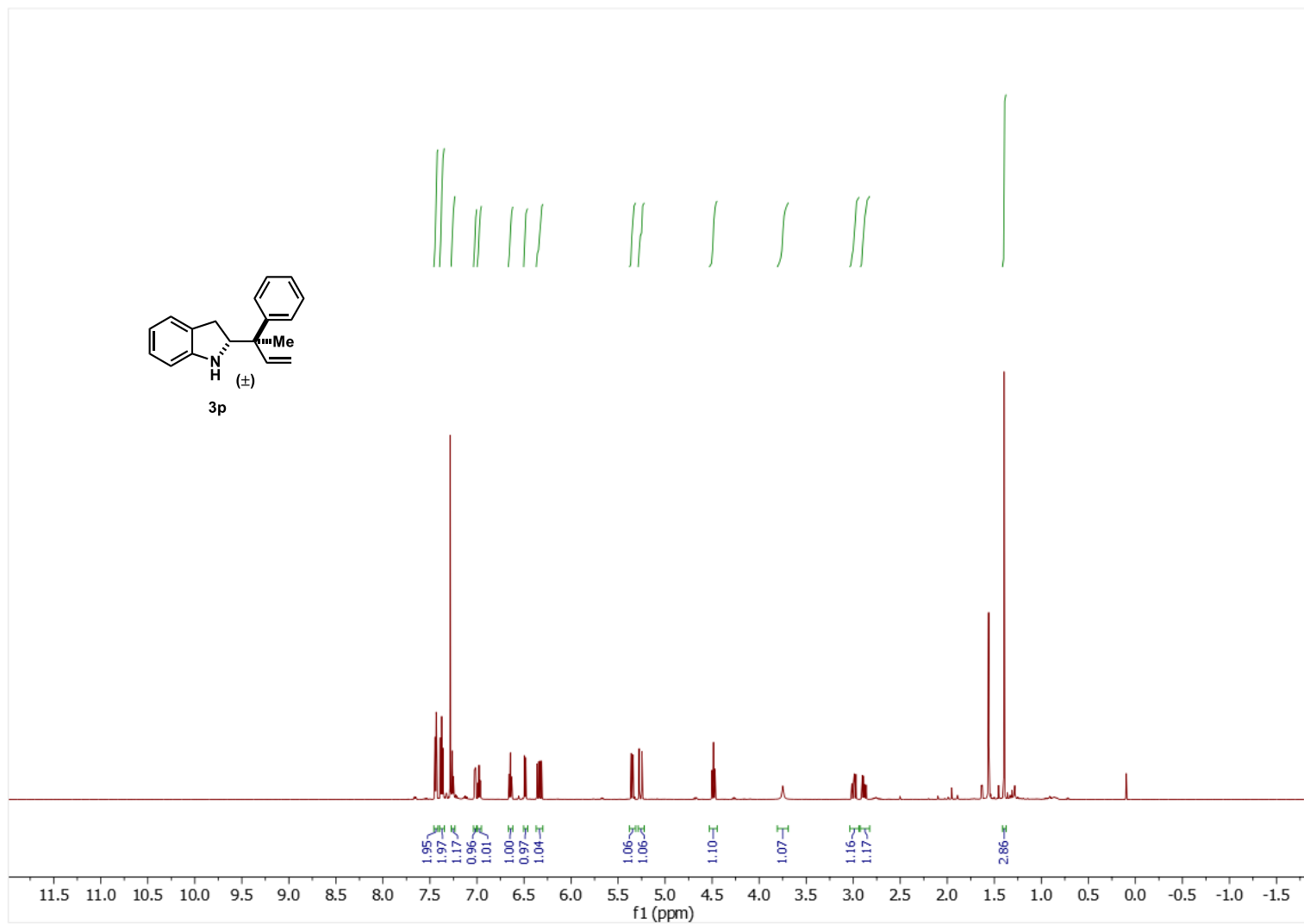
¹³C NMR (126 MHz, CDCl₃) spectrum of 1-ethenyl-1-(2-indolyl)cyclohexane **3n**



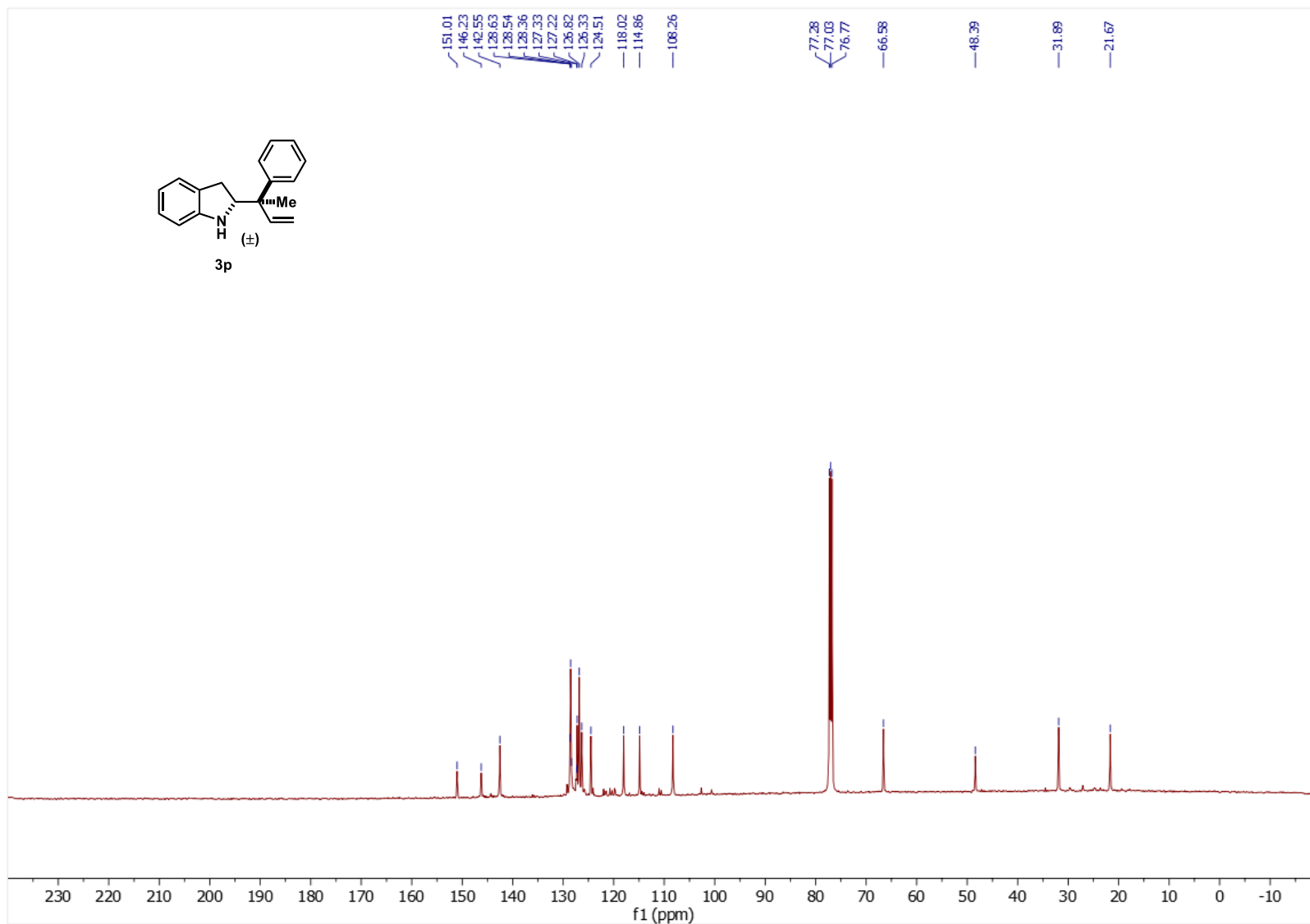
$^1\text{H NMR}$ (500 MHz, CDCl_3) spectrum of 2-(1-trimethylsilyl-1-methyl-propenyl)indoline **3o**



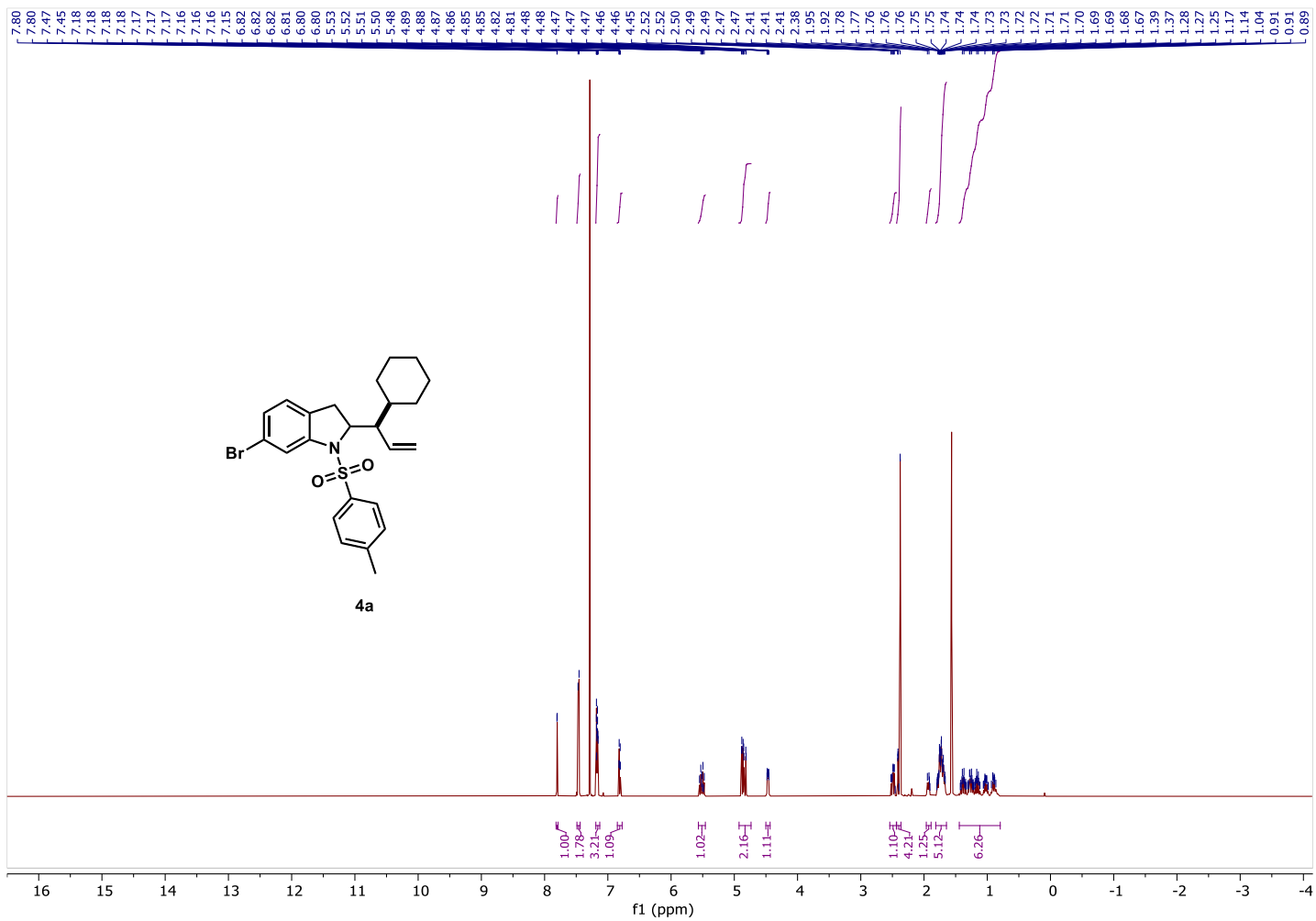
¹³C NMR (126 MHz, CDCl₃) spectrum of 2-(1-trimethylsilyl-1-methyl-propenyl)indoline **3o**



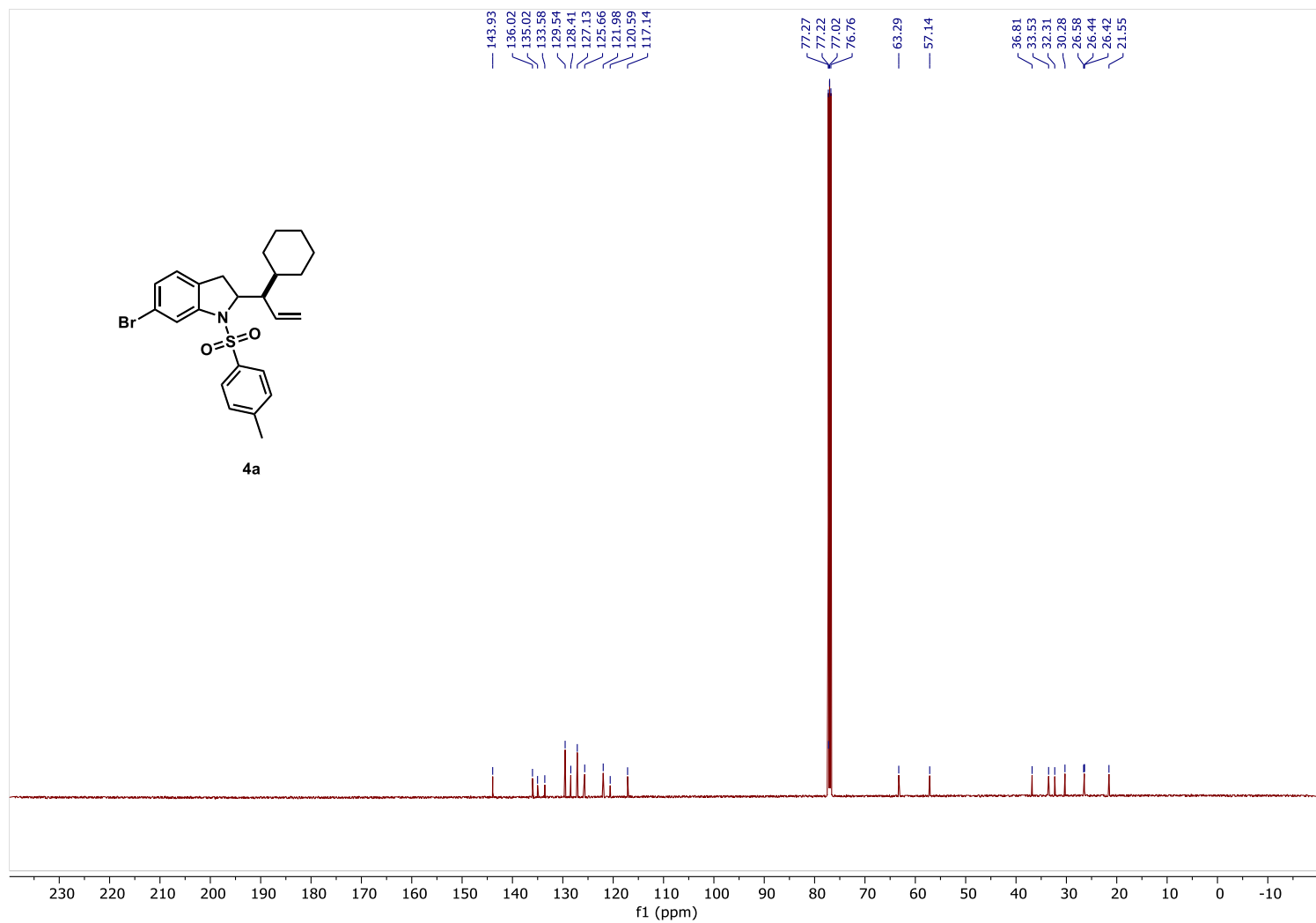
¹H NMR (500 MHz, CDCl₃) spectrum of 2-(1-phenyl-1-methylallyl)indoline **3p**



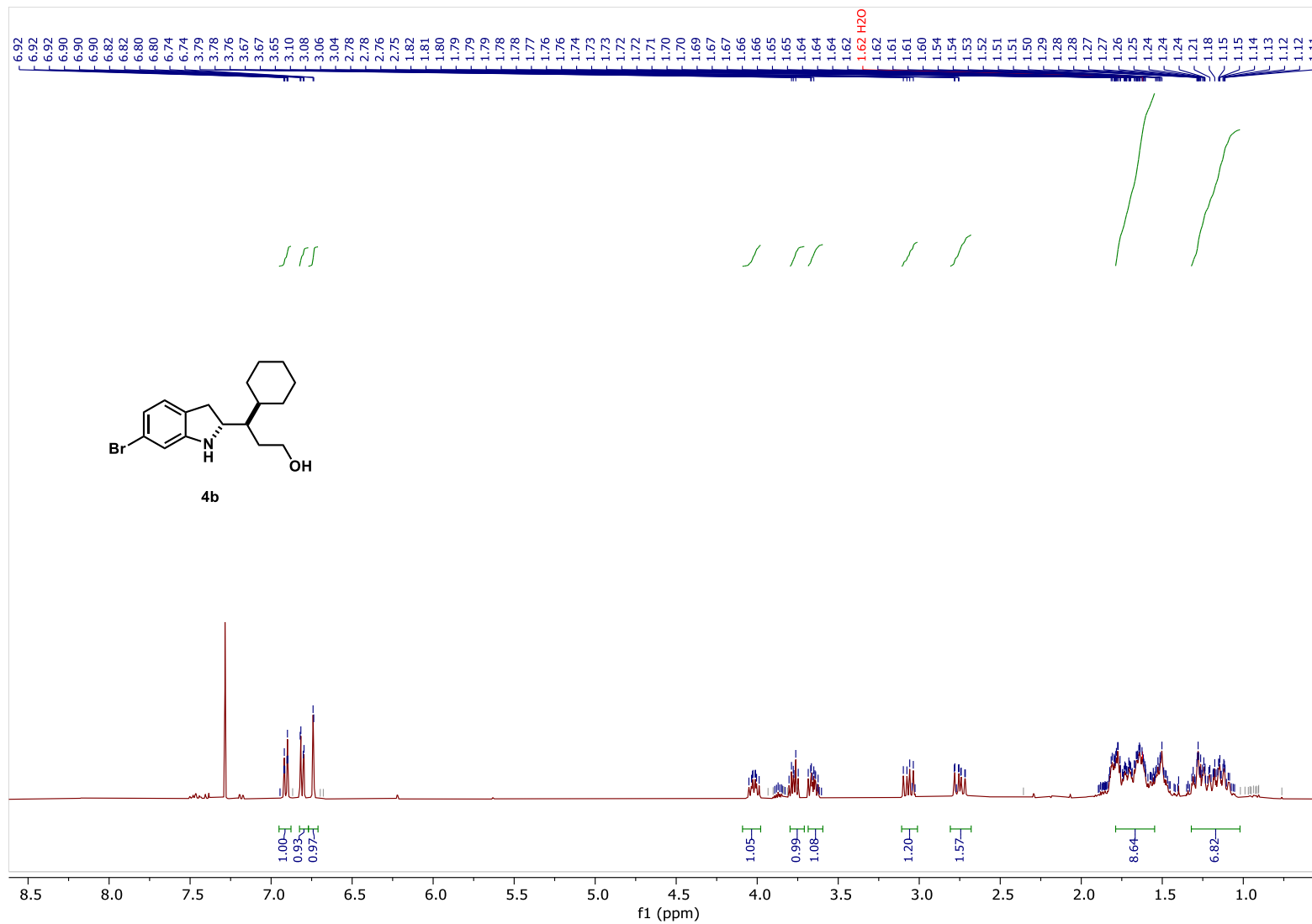
^{13}C NMR (126 MHz, CDCl_3) spectrum of 2-(1-phenyl-1-methylallyl)indoline **3p**



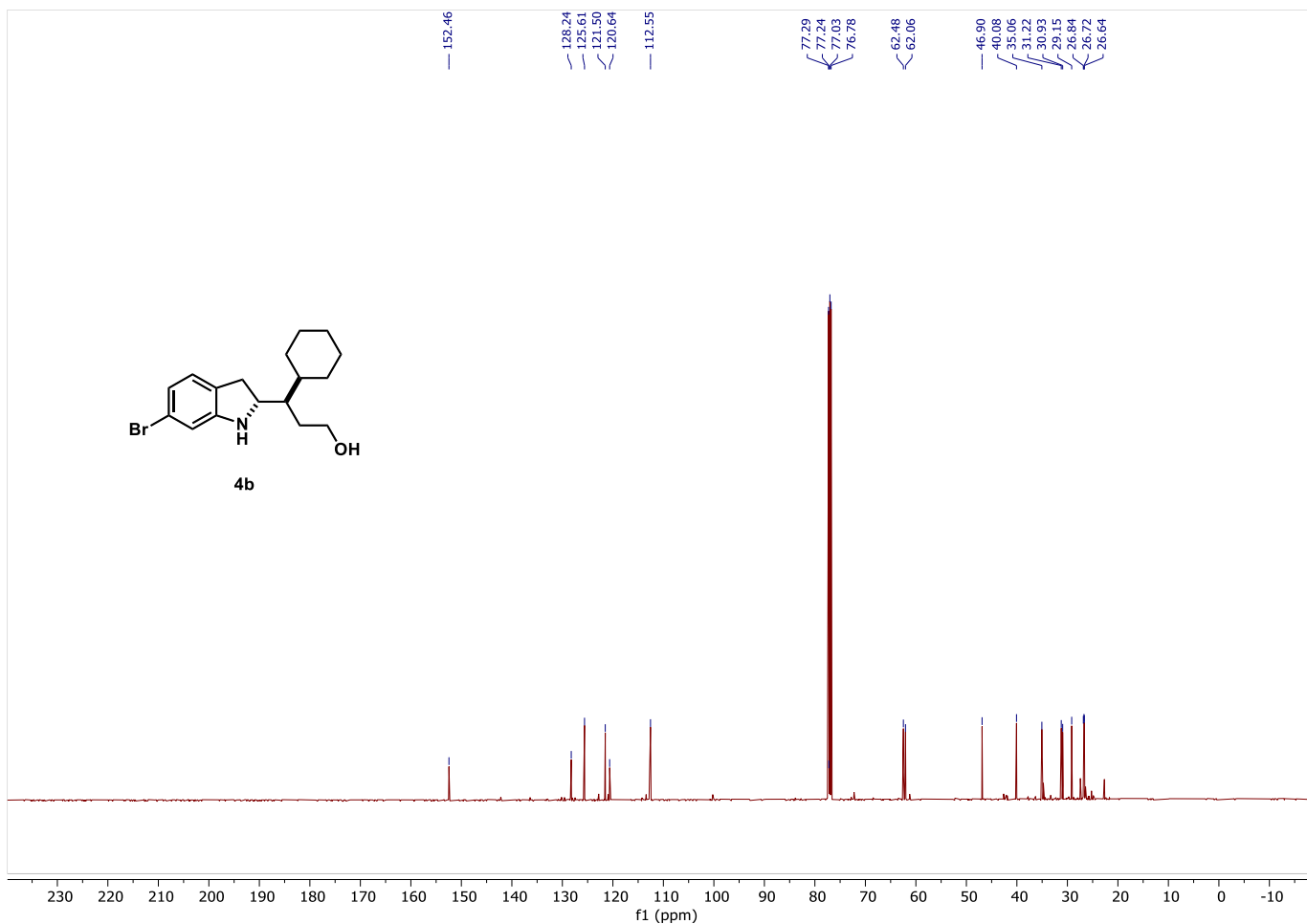
1H NMR (500 MHz, CDCl₃) spectrum of 6-bromo-2-(1-Cyclohexylallyl)-N-tosylindoline **4a**



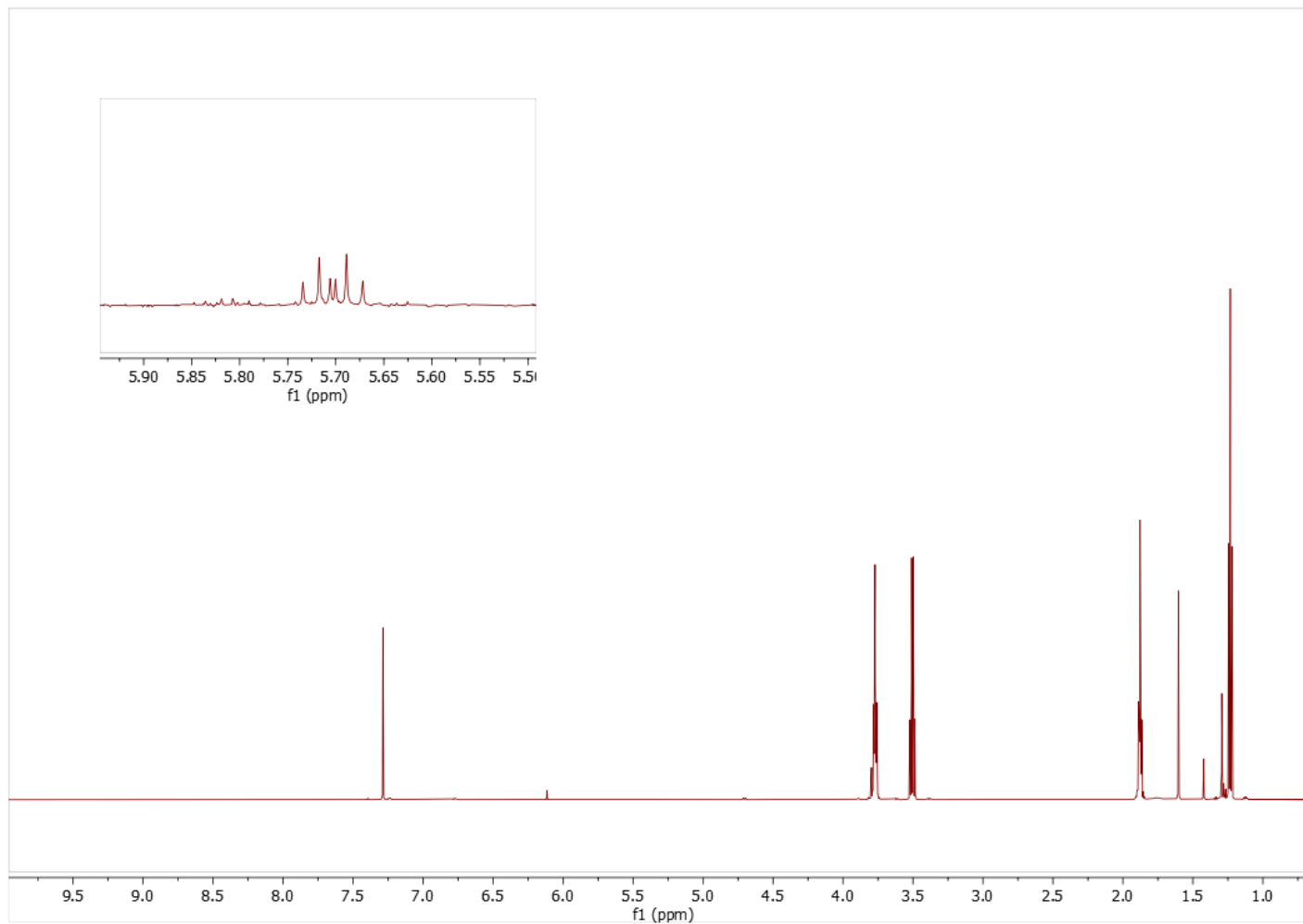
¹³C NMR (126 MHz, CDCl₃) spectrum of 6-bromo-2-(1-cyclohexylallyl)-N-tosylindoline **4a**



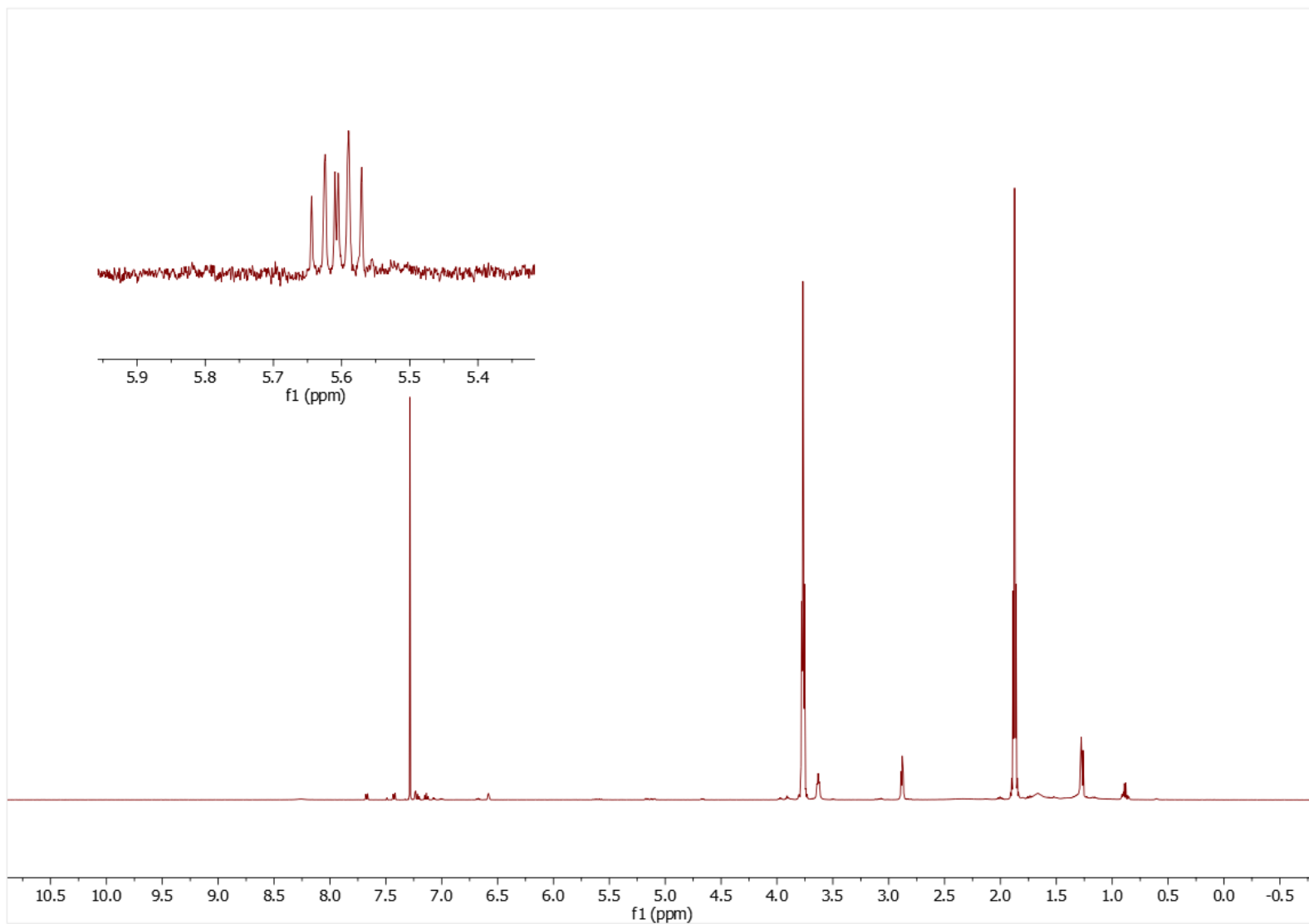
1H NMR (400 MHz, CDCl₃) spectrum of 6-bromo-2-(1-Cyclohexylpropan-3-ol)indoline **4b**



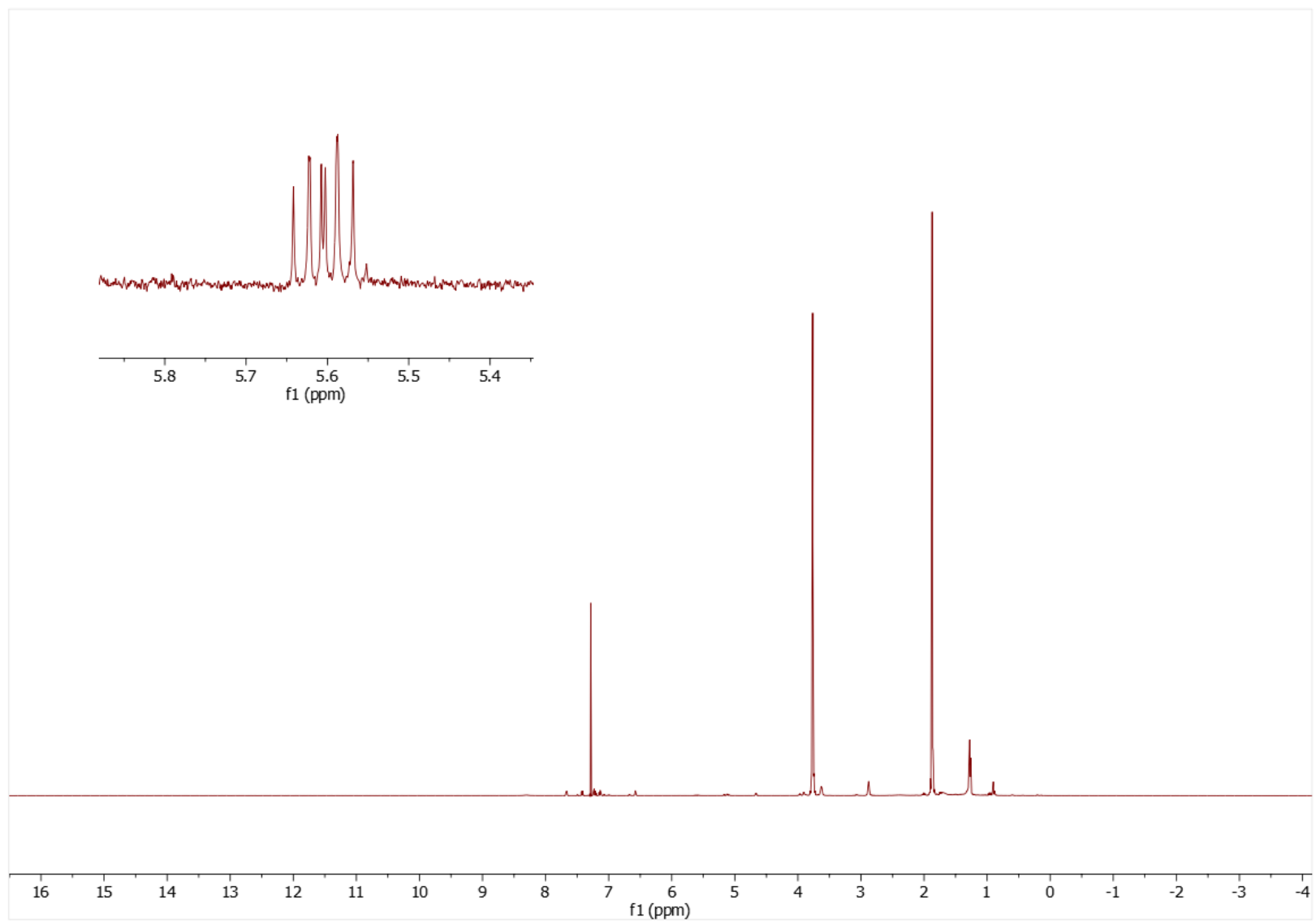
¹³C NMR (126 MHz, CDCl₃) spectrum of 6-bromo-2-(1-cyclohexylpropan-3-ol)indoline **4b**



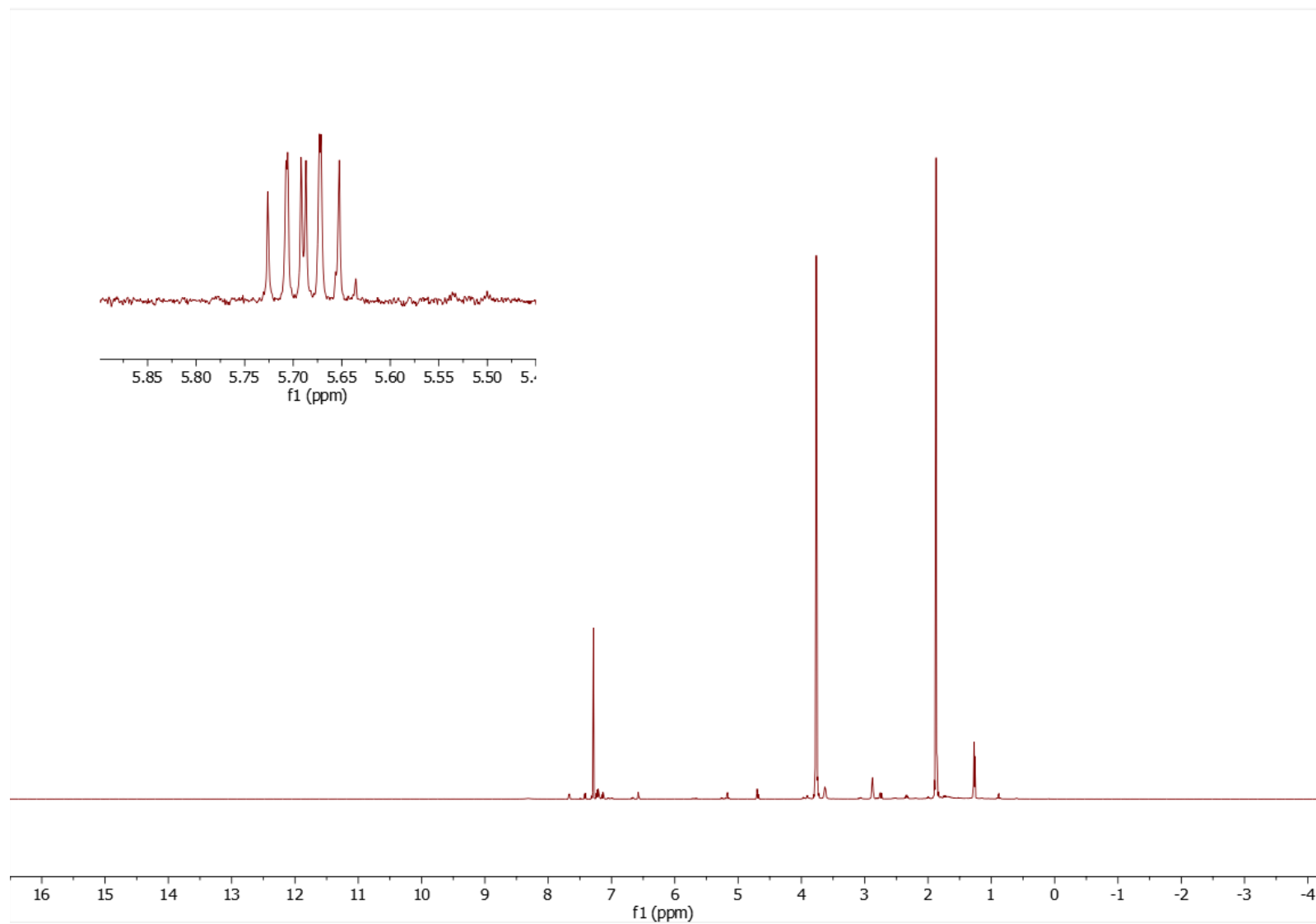
¹H NMR (400 MHz, CDCl₃) spectrum of the crude reaction mixture for **3a >95:5 *d.r.***



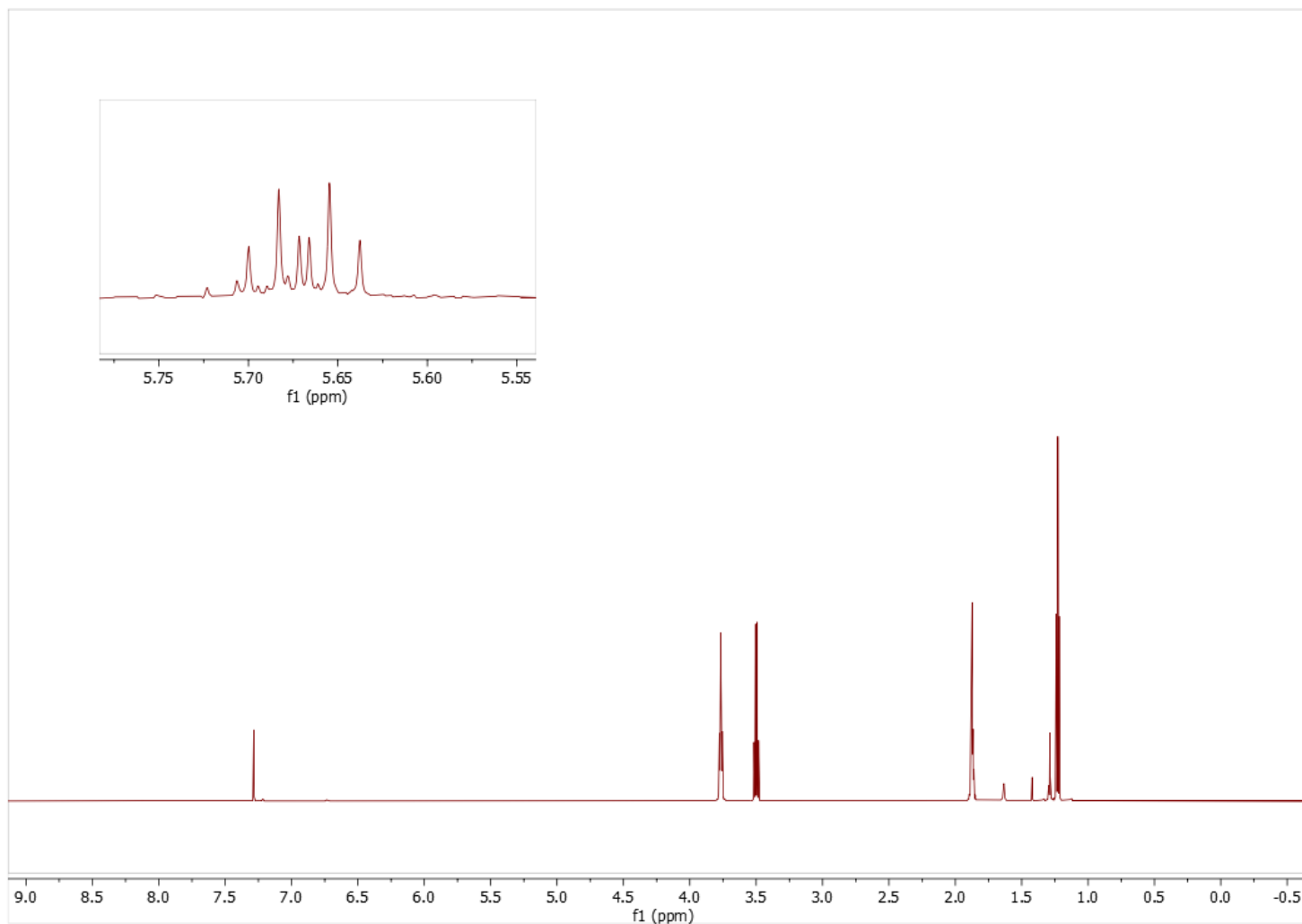
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3b** >95:5 *d.r.*



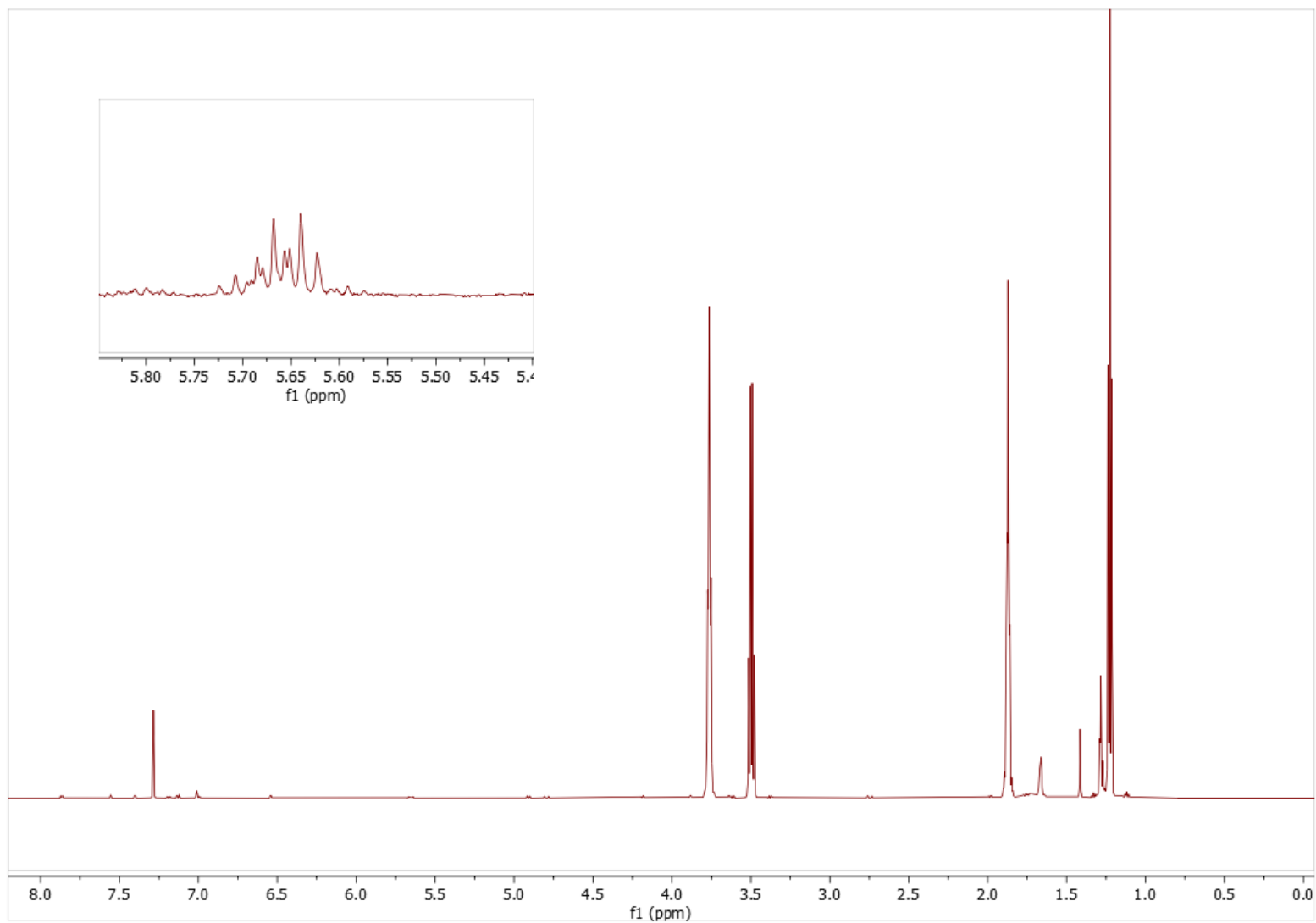
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3c** >95:5 *d.r.*



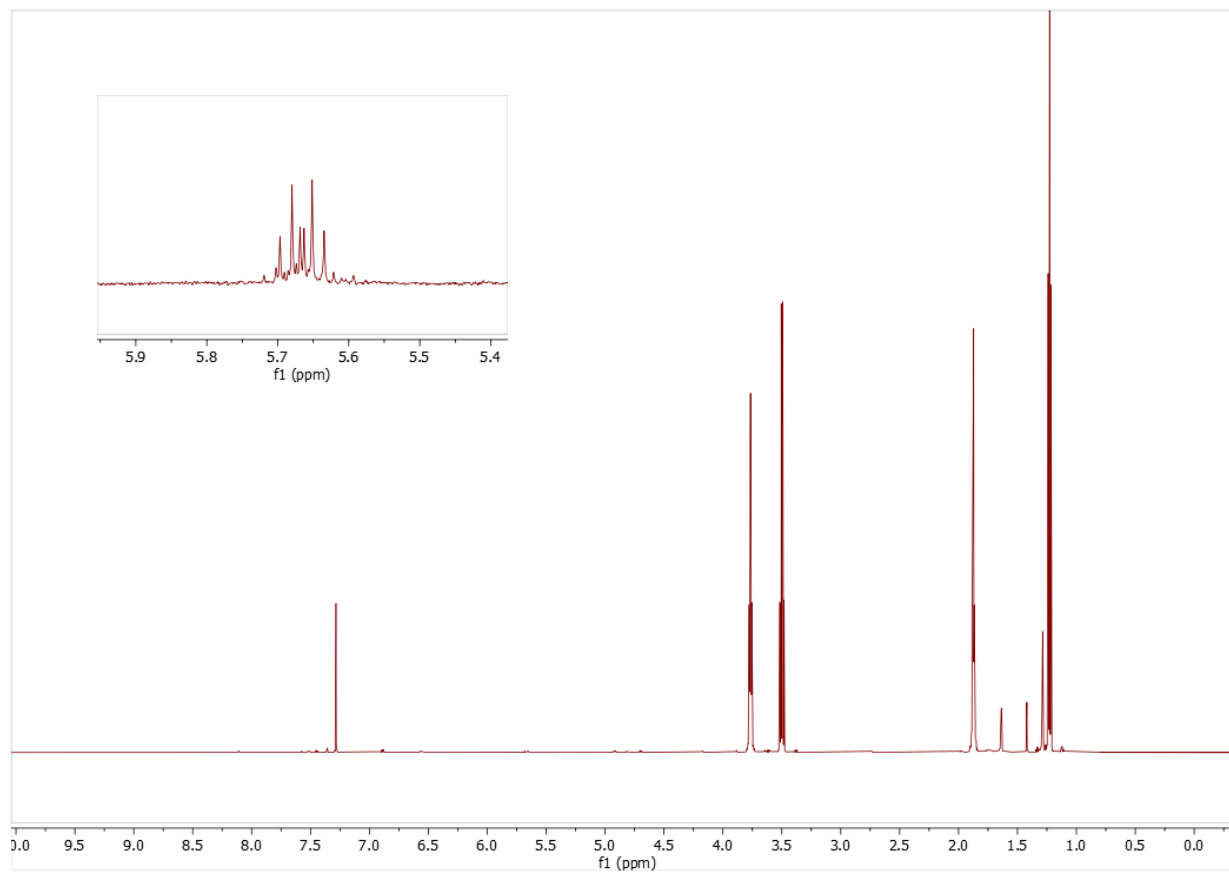
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3d** >95:5 *d.r.*



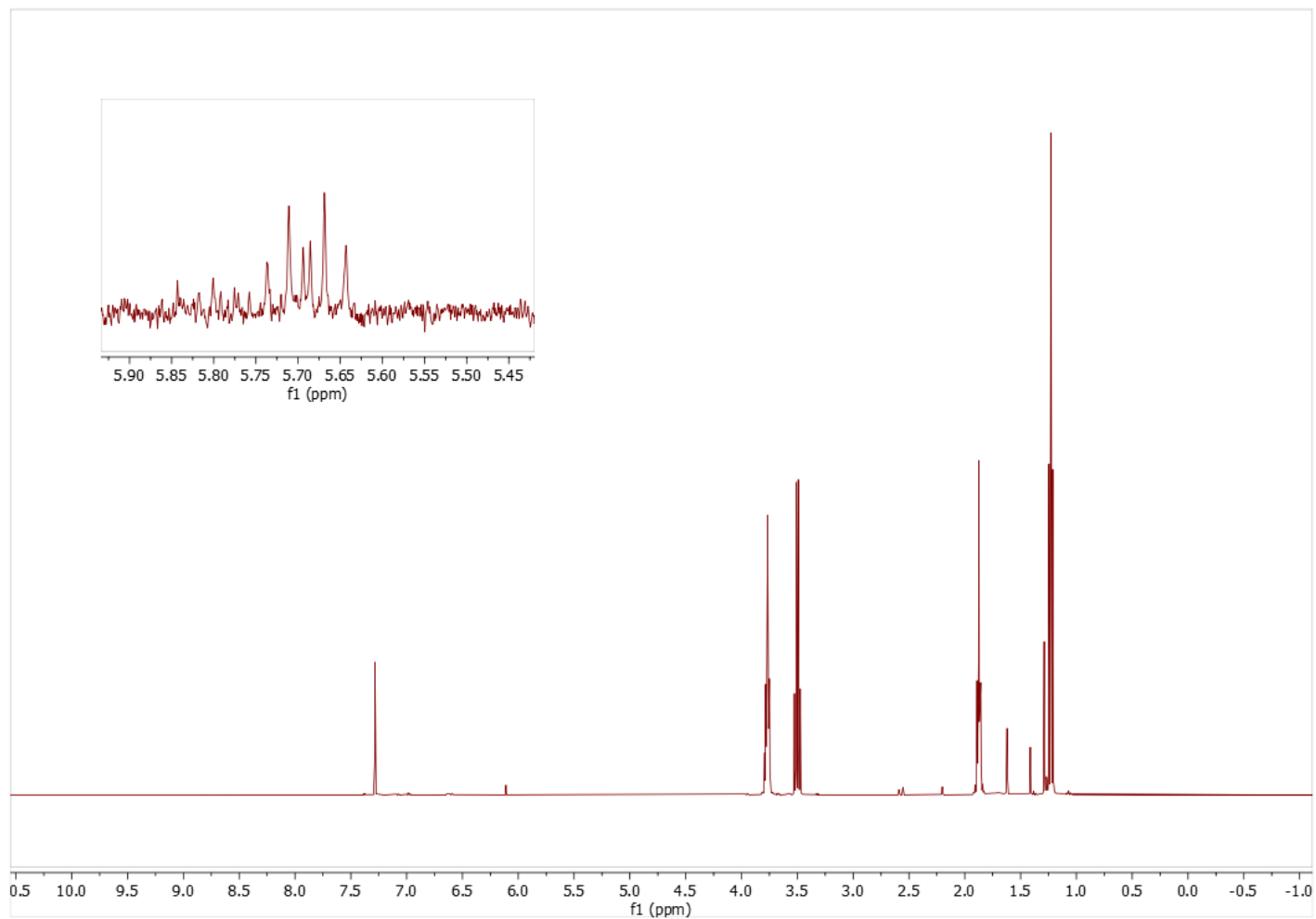
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3e** >95:5 *d.r.*



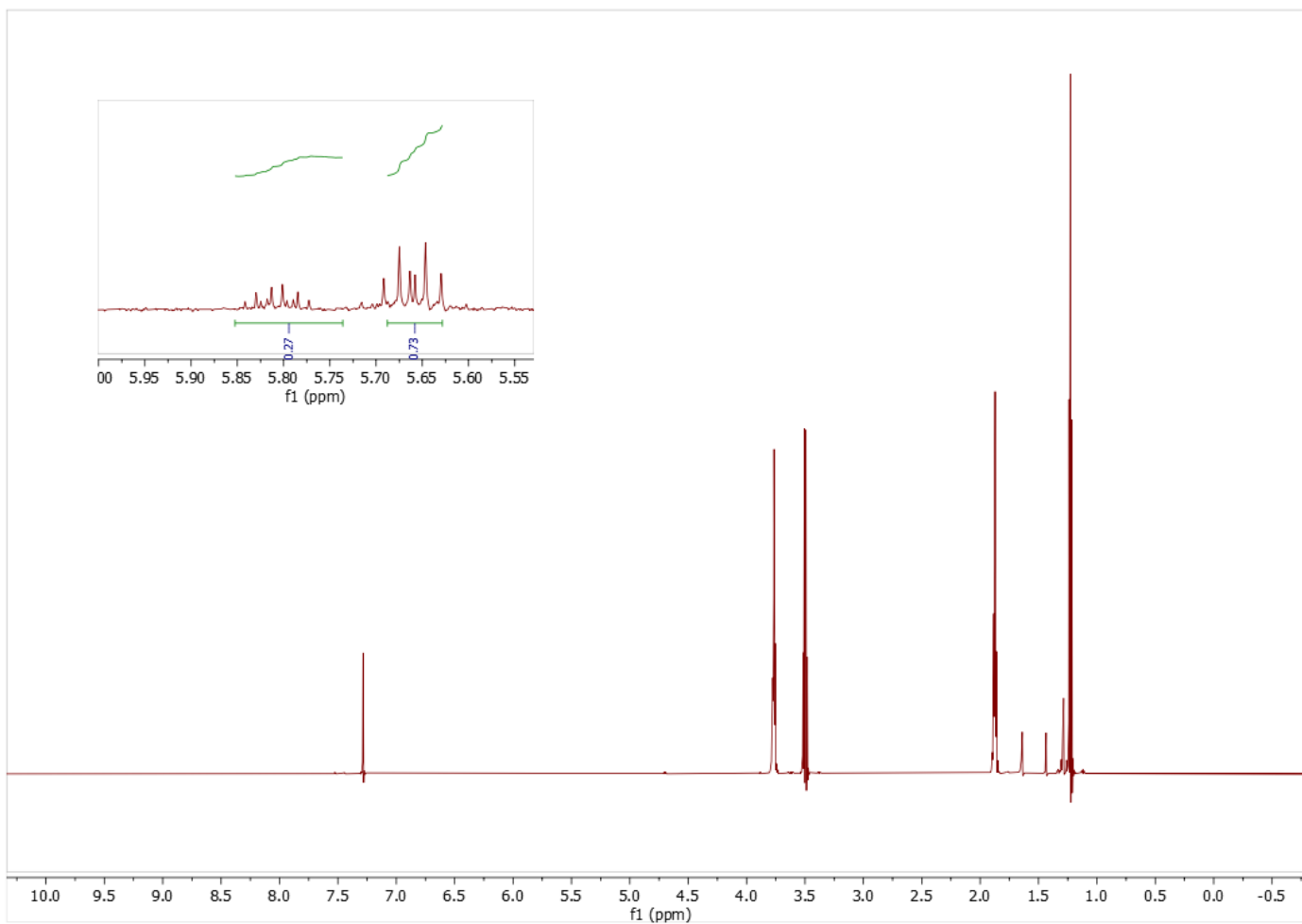
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3f** >95:5 *d.r.*



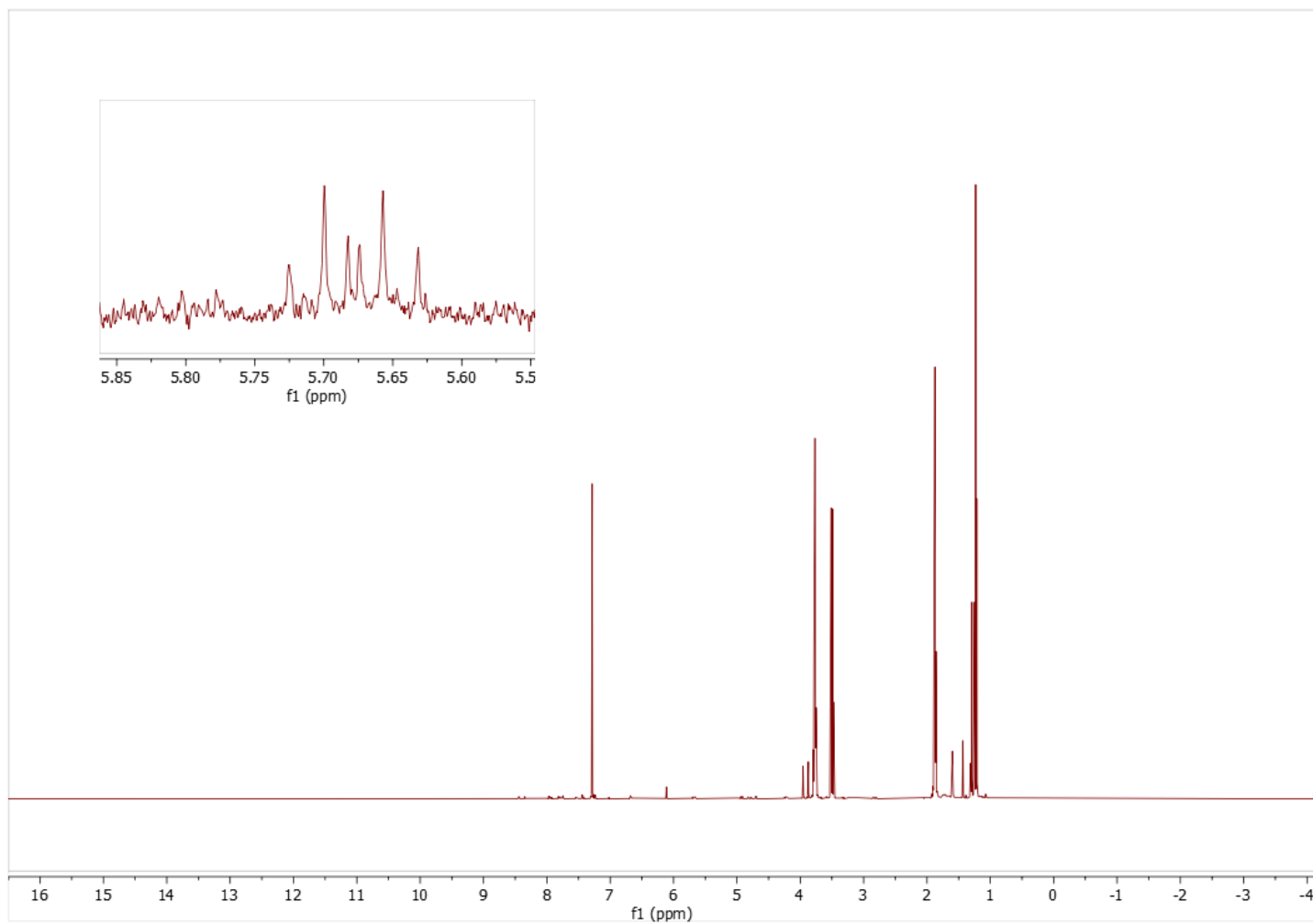
¹H NMR (400 MHz, CDCl₃) spectrum of the crude reaction mixture for **3g** >95:5 *d.r.*



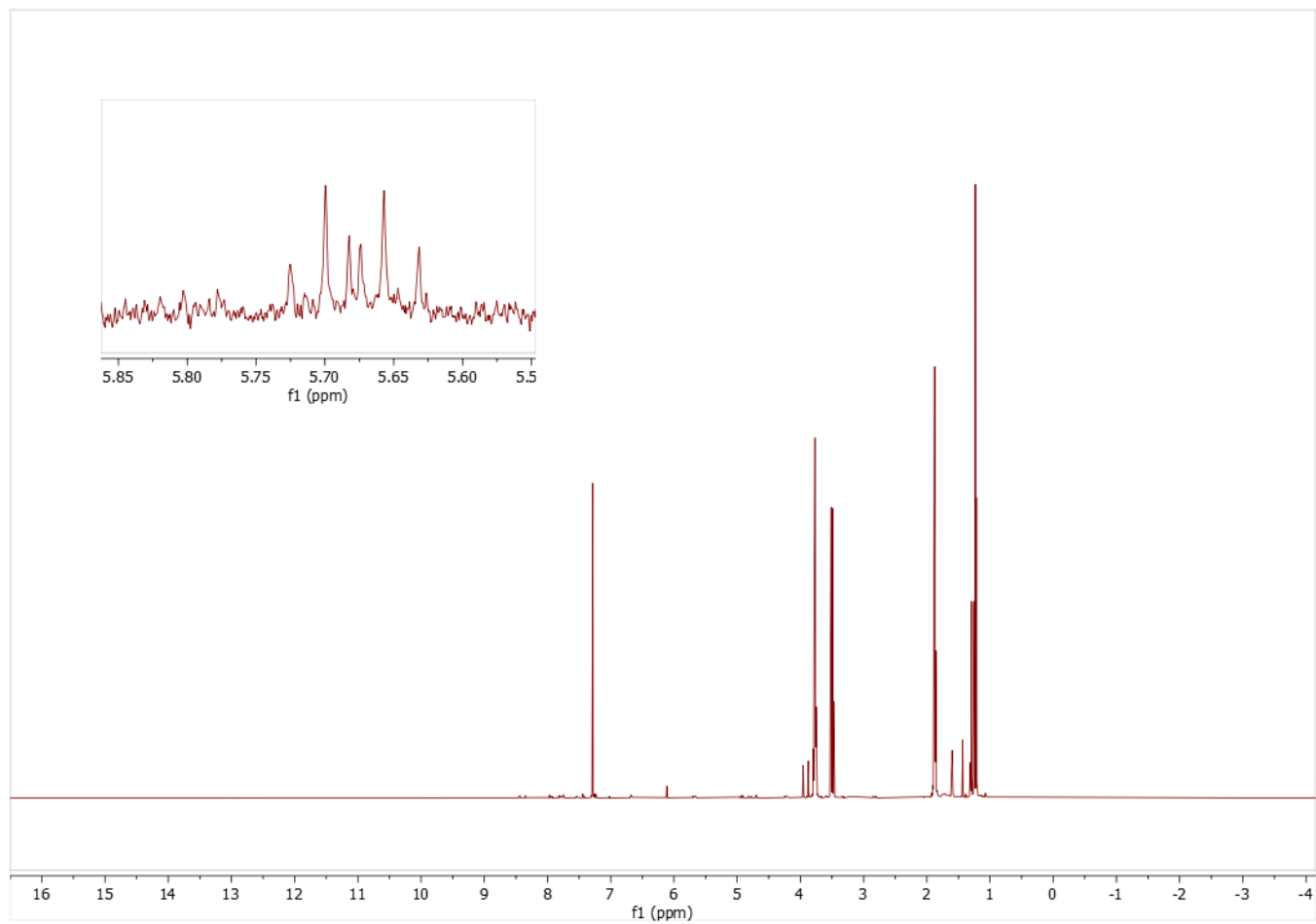
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3h** >95:5 *d.r.*



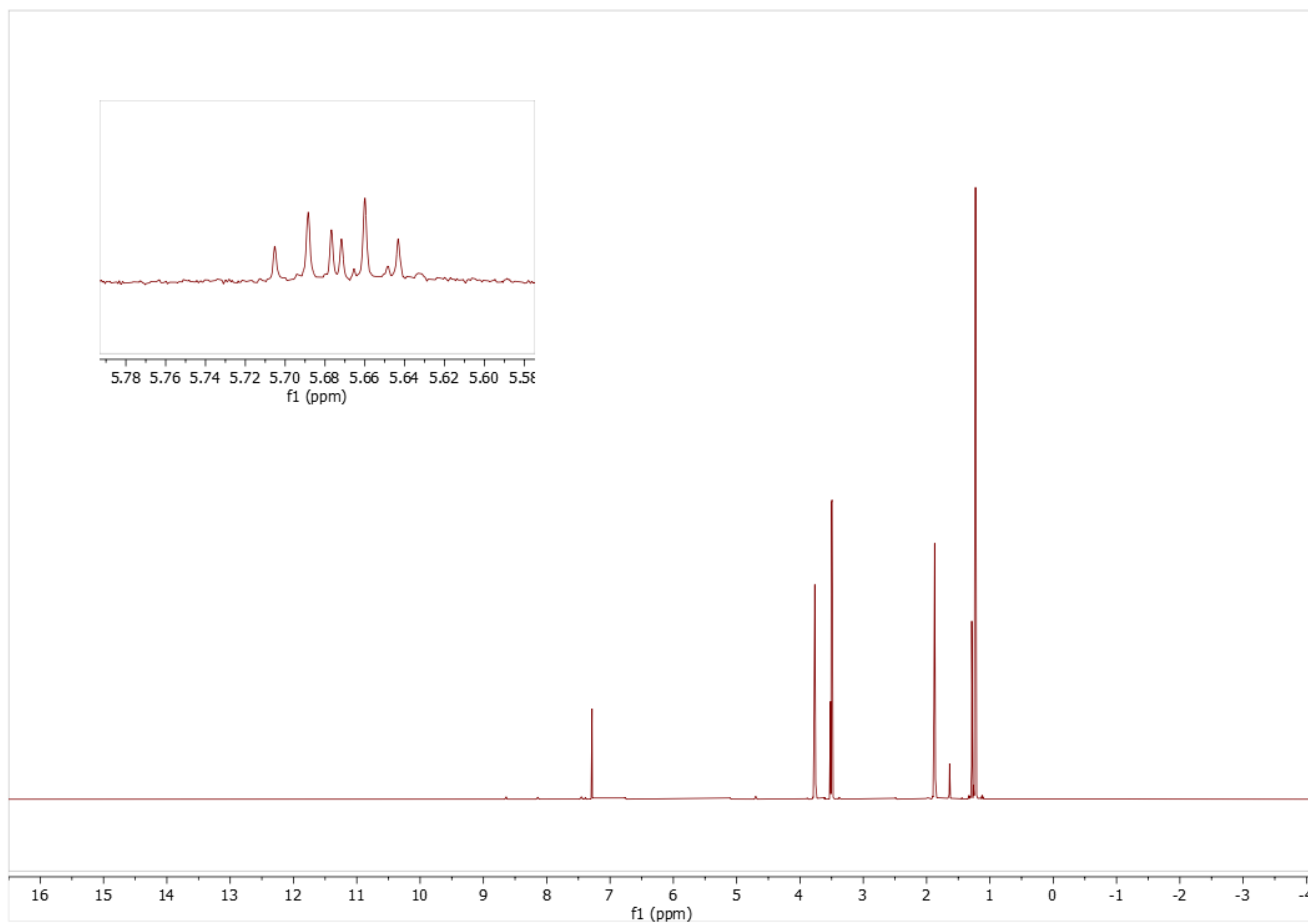
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3i** >73:27 *d.r.*



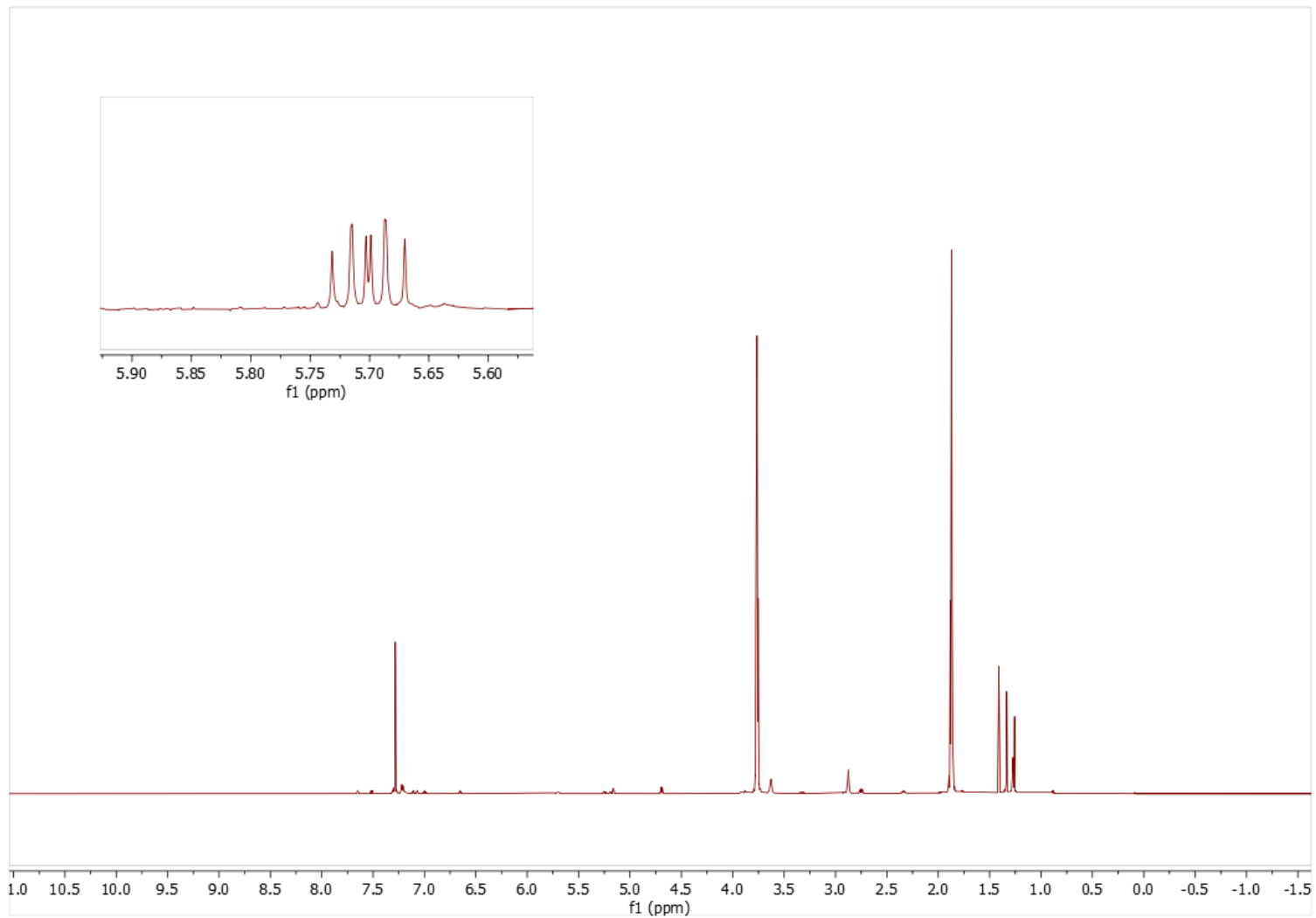
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3j** >95:5 *d.r.*



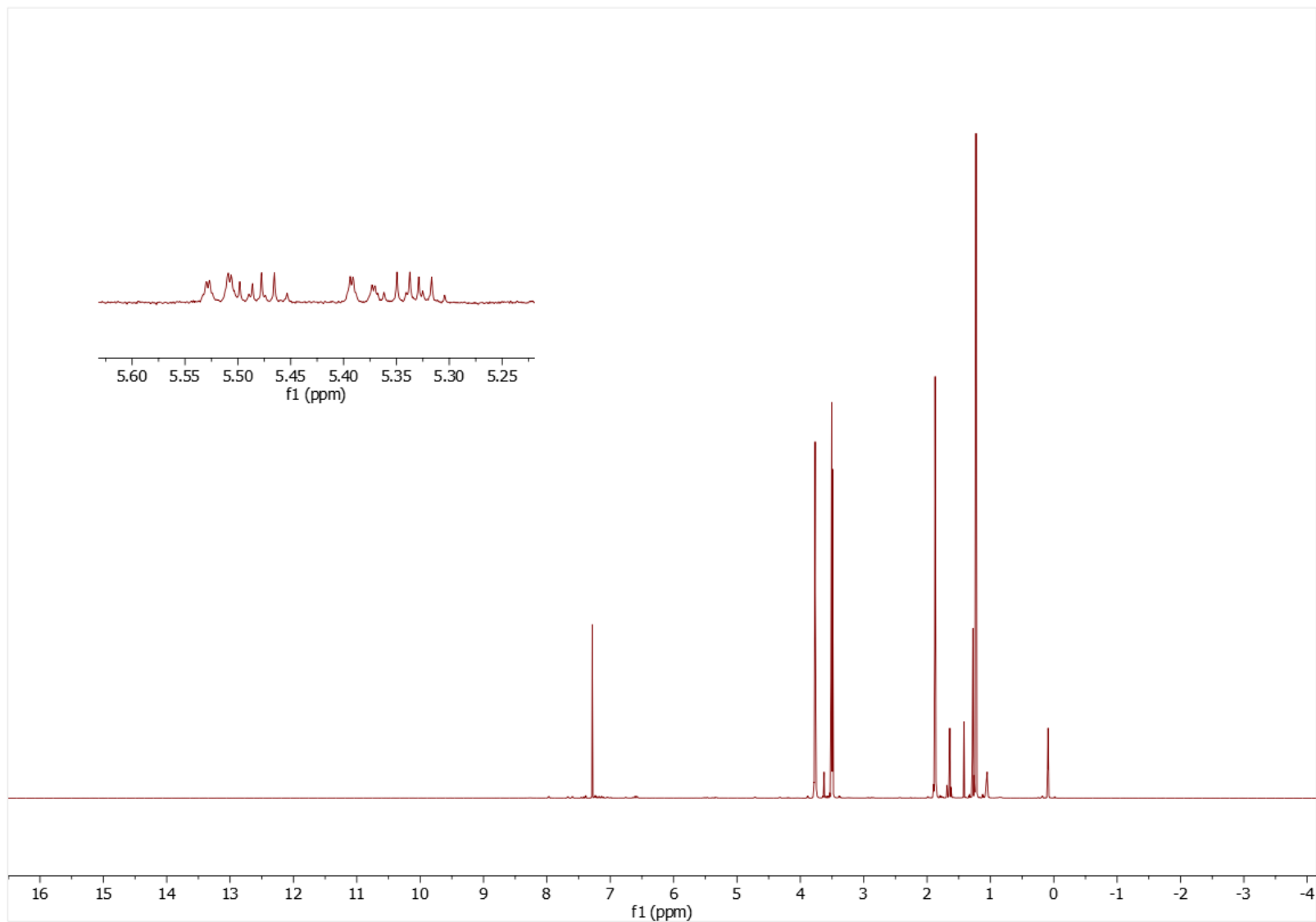
^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3k** >95:5 *d.r.*



^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3I** >95:5 *d.r.*



^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3m** >95:5 *d.r.*



^1H NMR (400 MHz, CDCl_3) spectrum of the crude reaction mixture for **3o** >95:5 *d.r.*

S9 Crystallographic data of 3I

Submitted by: Kieran Nicholson

$R_1=4.54\%$

Solved by: Gary S Nichol

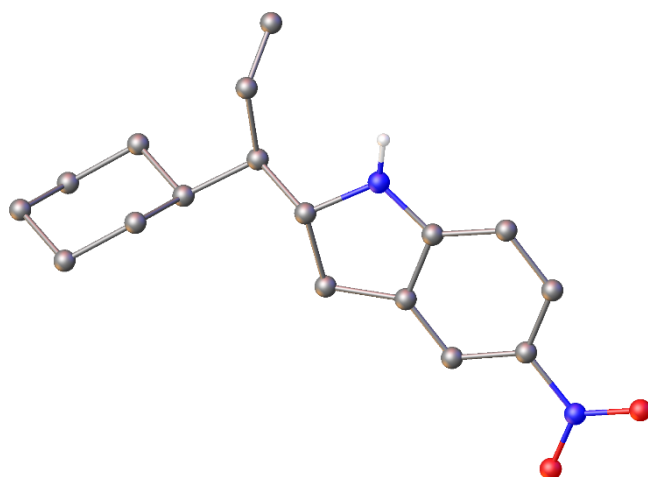


THE UNIVERSITY of EDINBURGH
Crystal Structure Service

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Crystallography Service Manager
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Compound KN06-174 was provided as orange crystals suitable for single crystal X-ray diffraction, yielding structure 3I.

Crystal Data and Experimental



Experimental. Single translucent dark orange block crystals of **3I** recrystallised from a mixture of petrol and ethyl acetate by slow evaporation. A suitable crystal with dimensions $0.37 \times 0.33 \times 0.26 \text{ mm}^3$ was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady $T = 120.01(10) \text{ K}$ during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2 .

Crystal Data. $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$, $M_r = 286.36$, monoclinic, $P2_1/n$ (No. 14), $a = 8.5689(2) \text{ \AA}$, $b = 14.0796(4) \text{ \AA}$, $c = 12.6116(3) \text{ \AA}$, $\beta = 91.050(2)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 1521.29(7) \text{ \AA}^3$, $T = 120.01(10) \text{ K}$, $Z = 4$, $Z' = 1$, $\mu(\text{Mo K}\alpha) = 0.082$, 33550 reflections measured, 4012 unique ($R_{\text{int}} = 0.0393$) which were used in all calculations. The final wR_2 was 0.1114 (all data) and R_1 was 0.0454 ($I \geq 2 \sigma(I)$).

Compound	3I
Formula	$\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$
$D_{\text{calc.}} / \text{g cm}^{-3}$	1.250
μ / mm^{-1}	0.082
Formula Weight	286.36
Colour	translucent dark orange
Shape	block
Size/ mm^3	$0.37 \times 0.33 \times 0.26$
T / K	120.01(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
$a / \text{ \AA}$	8.5689(2)
$b / \text{ \AA}$	14.0796(4)
$c / \text{ \AA}$	12.6116(3)
$\alpha / ^\circ$	90
$\beta / ^\circ$	91.050(2)
$\gamma / ^\circ$	90
$V / \text{ \AA}^3$	1521.29(7)
Z	4
Z'	1
Wavelength/ \AA	0.71073
Radiation type	Mo $\text{K}\alpha$
$\theta_{\text{min}} / ^\circ$	3.314
$\theta_{\text{max}} / ^\circ$	29.697
Measured Refl's.	33550
Indep't Refl's	4012
Refl's $I \geq 2 \sigma(I)$	3412
R_{int}	0.0393
Parameters	278
Restraints	0
Largest Peak	0.291
Deepest Hole	-0.239
GooF	1.058
wR_2 (all data)	0.1114
wR_2	0.1063
R_1 (all data)	0.0549
R_1	0.0454

Structure Quality Indicators

Reflections:	d min (Mo) 2 θ =59.4° 0.72	I/ σ (I) 39.3	Rint 3.93%	CAP 52.6° 93% to 59.4° 99.7
Refinement:	Shift -0.001	Max Peak 0.3	Min Peak -0.2	Goof 1.058

A translucent dark orange block-shaped crystal with dimensions $0.37 \times 0.33 \times 0.26 \text{ mm}^3$ was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at $T = 120.01(10) \text{ K}$.

Data were measured using ω scans using Mo K_{α} radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.41.99a, 2021). The maximum resolution that was achieved was $\Theta = 29.697^{\circ}$ (0.72 \AA).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.41.99a, 2021). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.41.99a, 2021) on 12906 reflections, 38% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.41.99a, 2021). The final completeness is 99.60 % out to 29.697° in Θ . A multi-scan absorption correction was performed using CrysAlisPro 1.171.41.99a (Rigaku Oxford Diffraction, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this material is 0.082 mm^{-1} at this wavelength ($\lambda = 0.71073 \text{ \AA}$) and the minimum and maximum transmissions are 0.897 and 1.000.

The structure was solved and the space group $P2_1/n$ (# 14) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: H atoms were identified from a difference map and freely refined.

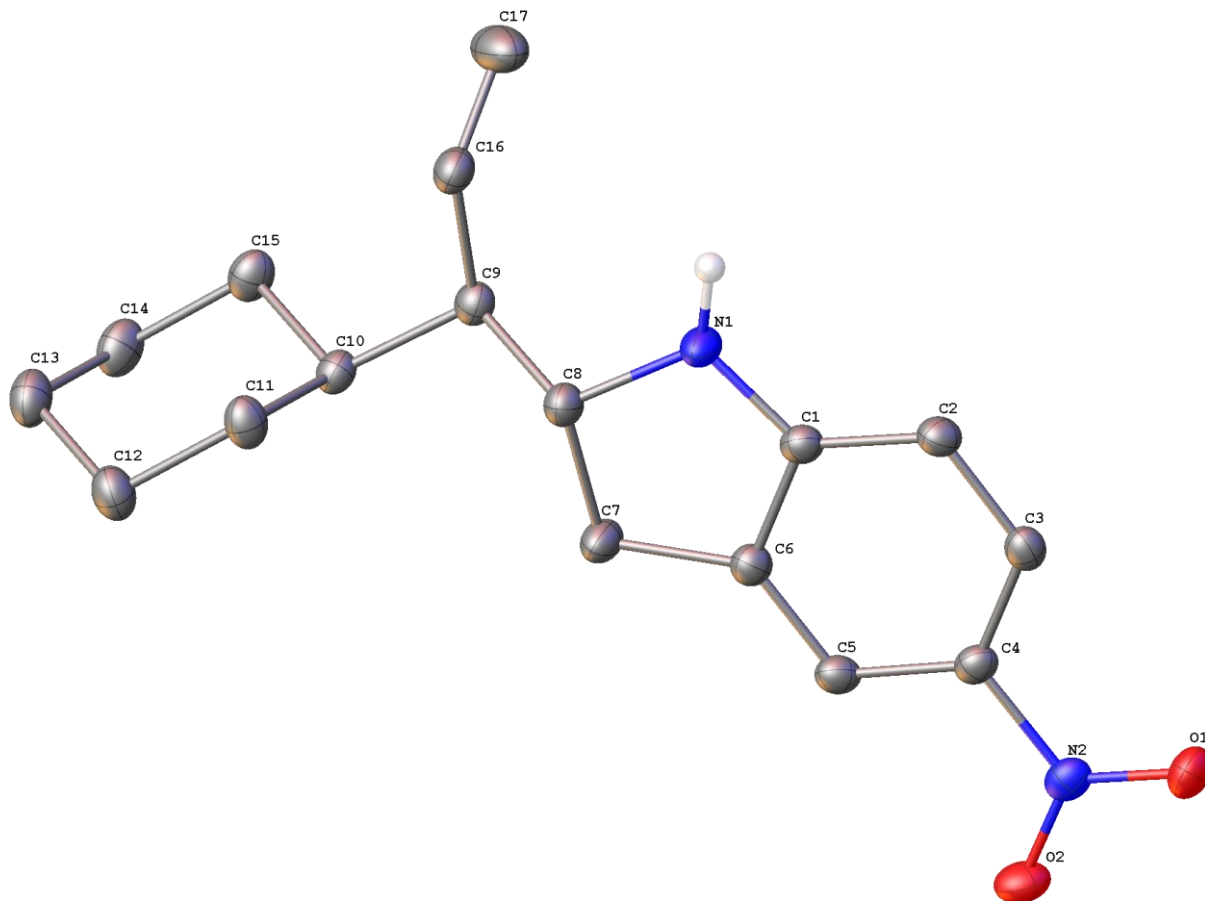
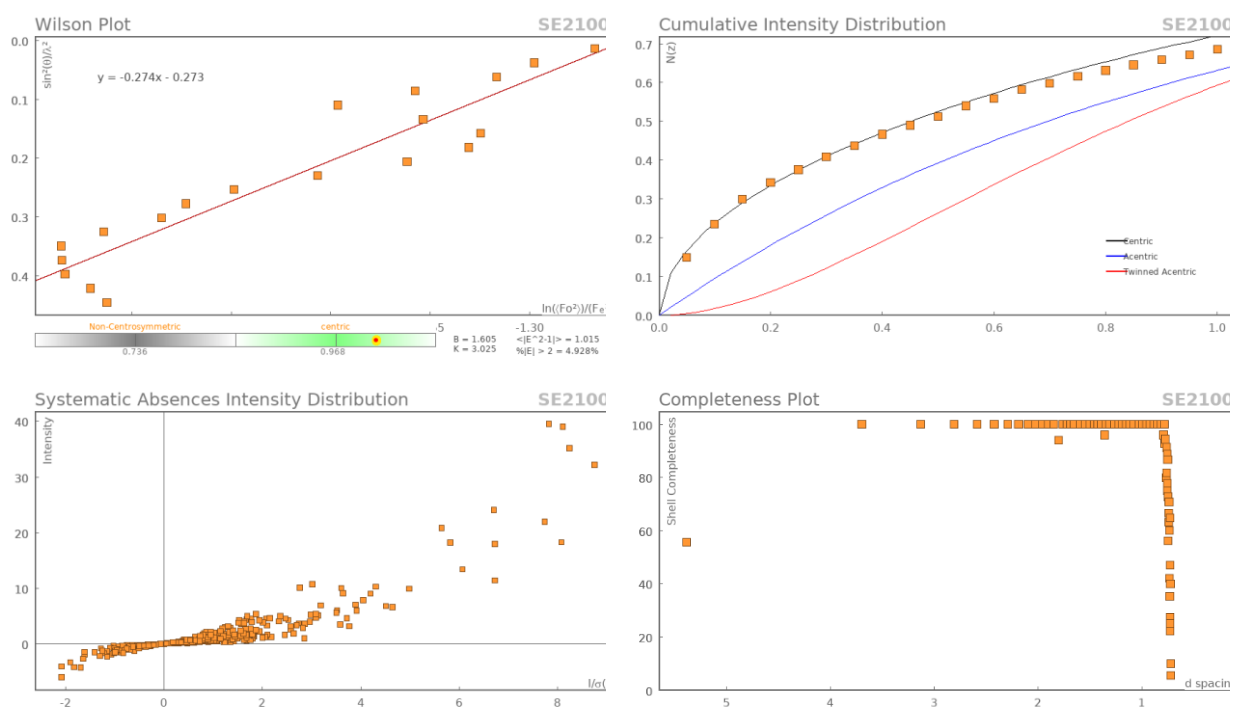
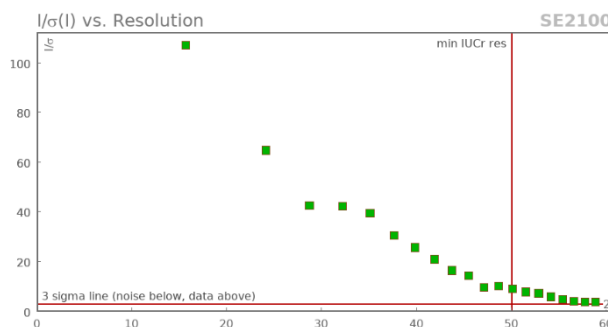


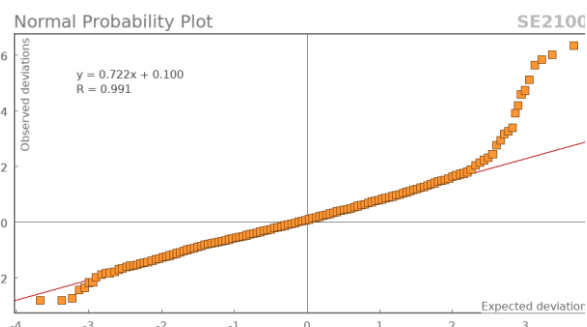
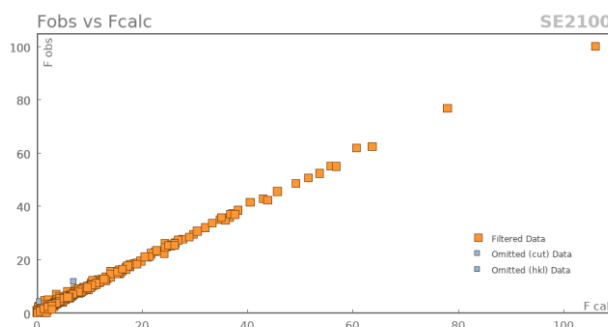
Figure 1: The molecular structure of **3I**. Displacement ellipsoids are at the 50% probability level and C-bound H atoms are not shown.

Data Plots: Diffraction Data





Data Plots: Refinement and Data



Reflection Statistics

Total reflections (after filtering)	34399	Unique reflections	4012
Completeness	0.933	Mean I/σ	24.86
hkl_{\max} collected	(11, 19, 16)	hkl_{\min} collected	(-11, -19, -17)
hkl_{\max} used	(11, 19, 17)	hkl_{\min} used	(-11, 0, 0)
Lim d_{\max} collected	100.0	Lim d_{\min} collected	0.36
d_{\max} used	6.15	d_{\min} used	0.72
Friedel pairs	6588	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0393
R_{sigma}	0.0255	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	20
Multiplicity	(4248, 4765, 2781, 1321, 621, 229, 132, 85, 69, 29)	Maximum multiplicity	25
Removed systematic absences	829	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3l**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
O1	1005.2(12)	6101.6(7)	8511.2(7)	27.2(2)
O2	640.1(11)	6794.4(6)	6989.5(7)	25.9(2)
N1	3444.1(13)	3061.3(8)	5329.8(8)	21.5(2)
N2	1091.0(12)	6111.4(7)	7529.9(8)	19.8(2)
C1	2948.5(14)	3754.6(8)	5983.6(9)	18.0(2)
C2	2859.6(15)	3744.6(9)	7092.5(10)	19.8(3)
C3	2249.4(14)	4529.8(9)	7589.6(9)	19.4(2)
C4	1728.7(14)	5303.3(8)	6995.2(9)	17.9(2)
C5	1842.6(14)	5329.5(9)	5885.3(9)	19.0(2)
C6	2471.1(14)	4559.3(9)	5391.2(9)	18.6(2)
C7	2698.5(17)	4350.5(9)	4231.4(10)	23.0(3)
C8	3665.1(15)	3417.8(9)	4242.0(9)	19.7(3)
C9	3158.3(14)	2694.7(9)	3396.8(9)	18.7(2)
C10	3282.2(14)	3119.5(9)	2268.0(9)	18.2(2)

Atom	x	y	z	U_{eq}
C11	4924.0(15)	3450.6(10)	1986.4(10)	22.9(3)
C12	4957.9(17)	3894.5(10)	880.5(10)	26.3(3)
C13	4307.5(16)	3211.7(11)	44.7(10)	26.6(3)
C14	2670.9(16)	2882.0(11)	321.6(10)	26.0(3)
C15	2658.3(15)	2428.8(10)	1422.0(10)	23.1(3)
C16	4064.5(16)	1788.0(9)	3531.6(10)	21.9(3)
C17	3466(2)	965.2(11)	3776.5(13)	36.2(4)

Table 2: Anisotropic Displacement Parameters ($\times 10^4$) for **3I**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \dots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	34.4(5)	26.6(5)	20.7(4)	-6.8(4)	3.4(4)	1.0(4)
O2	29.8(5)	17.9(4)	29.9(5)	-2.3(4)	-2.9(4)	4.8(4)
N1	30.5(6)	17.4(5)	16.5(5)	0.7(4)	0.5(4)	6.5(4)
N2	18.7(5)	18.1(5)	22.6(5)	-4.3(4)	-1.0(4)	-2.2(4)
C1	19.5(6)	15.4(5)	19.2(6)	-0.7(4)	-0.1(4)	-0.6(4)
C2	24.4(6)	17.0(6)	18.0(5)	1.3(4)	-0.8(4)	0.2(5)
C3	22.1(6)	20.0(6)	16.0(5)	-0.8(4)	0.5(4)	-3.7(5)
C4	17.9(6)	15.7(6)	19.9(6)	-3.1(4)	0.1(4)	-1.7(4)
C5	22.3(6)	15.5(6)	19.1(6)	0.3(4)	-2.1(4)	-1.0(5)
C6	20.8(6)	18.4(6)	16.4(5)	0.0(4)	-0.7(4)	-1.1(5)
C7	33.0(7)	19.6(6)	16.4(6)	-0.6(5)	0.8(5)	5.4(5)
C8	23.1(6)	19.7(6)	16.2(5)	-0.4(4)	0.9(4)	0.6(5)
C9	18.4(6)	19.9(6)	17.8(5)	-1.5(4)	1.6(4)	0.0(5)
C10	18.6(6)	19.7(6)	16.4(5)	-2.1(4)	0.3(4)	1.4(5)
C11	22.4(6)	28.3(7)	18.0(6)	-0.3(5)	-0.5(5)	-4.3(5)
C12	28.2(7)	30.7(7)	20.1(6)	2.7(5)	2.7(5)	-2.7(6)
C13	28.3(7)	34.3(8)	17.2(6)	-0.8(5)	1.2(5)	4.5(6)
C14	25.4(6)	33.2(7)	19.1(6)	-5.3(5)	-4.3(5)	4.1(6)
C15	21.4(6)	27.0(7)	20.7(6)	-5.2(5)	-0.9(5)	-2.2(5)
C16	24.5(6)	22.5(6)	18.7(6)	-1.9(5)	2.4(5)	3.2(5)
C17	41.3(9)	24.3(7)	43.4(9)	4.3(6)	14.1(7)	4.0(7)

Table 3: Bond Lengths in Å for **3I**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N2	1.2411(14)	C7	C8	1.5526(17)
O2	N2	1.2365(14)	C8	C9	1.5311(17)
N1	C1	1.3512(16)	C9	C10	1.5496(16)
N1	C8	1.4762(15)	C9	C16	1.5022(17)
N2	C4	1.4357(15)	C10	C11	1.5300(17)
C1	C2	1.4020(16)	C10	C15	1.5325(17)
C1	C6	1.4135(17)	C11	C12	1.5291(18)
C2	C3	1.3787(17)	C12	C13	1.5246(19)
C3	C4	1.3910(17)	C13	C14	1.524(2)
C4	C5	1.4055(16)	C14	C15	1.5278(18)
C5	C6	1.3663(17)	C16	C17	1.306(2)
C6	C7	1.5081(16)			

Table 4: Bond Angles in ° for **3I**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C8	111.63(10)	O2	N2	O1	122.32(10)
O1	N2	C4	119.31(10)				

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	N2	C4	118.37(10)	N1	C8	C9	112.42(9)
N1	C1	C2	128.67(11)	C9	C8	C7	114.33(10)
N1	C1	C6	110.34(10)	C8	C9	C10	111.08(10)
C2	C1	C6	120.98(11)	C16	C9	C8	110.30(10)
C3	C2	C1	118.26(11)	C16	C9	C10	112.83(10)
C2	C3	C4	120.22(11)	C11	C10	C9	114.18(10)
C3	C4	N2	119.23(11)	C11	C10	C15	110.02(10)
C3	C4	C5	121.99(11)	C15	C10	C9	111.45(10)
C5	C4	N2	118.75(11)	C12	C11	C10	111.66(11)
C6	C5	C4	117.94(11)	C13	C12	C11	111.11(12)
C1	C6	C7	108.37(10)	C14	C13	C12	111.10(11)
C5	C6	C1	120.52(11)	C13	C14	C15	110.93(11)
C5	C6	C7	131.00(11)	C14	C15	C10	111.05(11)
C6	C7	C8	103.59(10)	C17	C16	C9	125.17(13)
N1	C8	C7	102.59(10)				

Table 5: Torsion Angles in ° for **3l**.

Atom	Atom	Atom	Atom	Angle/°
O1	N2	C4	C3	-0.56(17)
O1	N2	C4	C5	-178.99(11)
O2	N2	C4	C3	179.69(11)
O2	N2	C4	C5	1.26(16)
N1	C1	C2	C3	-177.38(12)
N1	C1	C6	C5	176.34(11)
N1	C1	C6	C7	-0.27(15)
N1	C8	C9	C10	175.52(10)
N1	C8	C9	C16	-58.62(13)
N2	C4	C5	C6	179.16(11)
C1	N1	C8	C7	-18.61(14)
C1	N1	C8	C9	-141.90(11)
C1	C2	C3	C4	0.50(18)
C1	C6	C7	C8	-10.93(14)
C2	C1	C6	C5	-3.10(19)
C2	C1	C6	C7	-179.70(12)
C2	C3	C4	N2	179.72(11)
C2	C3	C4	C5	-1.91(19)
C3	C4	C5	C6	0.78(18)
C4	C5	C6	C1	1.68(18)
C4	C5	C6	C7	177.41(12)
C5	C6	C7	C8	172.95(13)
C6	C1	C2	C3	1.95(18)
C6	C7	C8	N1	16.96(13)
C6	C7	C8	C9	138.96(11)
C7	C8	C9	C10	59.07(14)
C7	C8	C9	C16	-175.07(10)
C8	N1	C1	C2	-168.14(12)

Atom	Atom	Atom	Atom	Angle/°
C8	N1	C1	C6	12.48(15)
C8	C9	C10	C11	58.99(14)
C8	C9	C10	C15	-175.59(10)
C8	C9	C16	C17	115.73(15)
C9	C10	C11	C12	-177.94(11)
C9	C10	C15	C14	175.71(10)
C10	C9	C16	C17	-119.40(15)
C10	C11	C12	C13	-55.53(15)
C11	C10	C15	C14	-56.59(14)
C11	C12	C13	C14	55.25(16)
C12	C13	C14	C15	-56.20(16)
C13	C14	C15	C10	57.15(15)
C15	C10	C11	C12	55.88(15)
C16	C9	C10	C11	-65.46(14)
C16	C9	C10	C15	59.97(14)

Table 6: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **3I**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} .

Atom	x	y	z	U_{eq}
H1	3852(19)	2531(13)	5548(12)	28(4)
H2	3247(18)	3207(12)	7495(12)	26(4)
H3	2189(18)	4551(11)	8344(12)	24(4)
H5	1448(18)	5868(11)	5509(12)	23(4)
H7A	1670(20)	4256(12)	3871(13)	32(4)
H7B	3214(19)	4855(12)	3840(13)	30(4)
H8	4804(18)	3559(11)	4174(11)	21(4)
H9	2071(17)	2569(10)	3524(11)	19(4)
H10	2572(16)	3686(10)	2248(10)	14(3)
H11A	5342(19)	3900(12)	2516(13)	30(4)
H11B	5656(19)	2921(12)	2012(12)	29(4)
H12A	4313(18)	4506(12)	868(12)	24(4)
H12B	6030(20)	4089(12)	722(13)	34(4)
H13A	4997(19)	2650(12)	1(12)	25(4)
H13B	4310(20)	3530(13)	-678(14)	39(5)
H14A	2300(20)	2402(12)	-215(13)	34(4)
H14B	1989(19)	3434(12)	315(12)	29(4)
H15A	3320(20)	1832(13)	1431(13)	34(4)
H15B	1590(20)	2217(12)	1624(13)	33(4)
H16	5173(19)	1835(11)	3459(12)	28(4)
H17A	4090(20)	377(14)	3878(15)	47(5)
H17B	2370(20)	915(14)	3859(15)	48(5)

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