Supporting Information:

Manganese Catalyzed *α*-Olefination of Nitriles with Secondary Alcohols

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1. General Information

All experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. Toluene was refluxed over sodium/benzophenone and followed by distillation under argon atmosphere and stored over sodium. Metal complexes and other chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (230-400 mesh). ^1H NMR (400 or 500 MHz), $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent and chemical shift values (δ) are reported in parts per million relatives to the residual signals of this solvent [δ 7.26 for ^1H (chloroform-d), δ 77.2 for $^{13}C\{^1H\}$ (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer).

2. Experimental Section

2.1 General procedure for the synthesis of Mn-PNP complex

In a three necked round-bottom flask (100 mL) under an argon atmosphere, Mn $(CO)_5Br$ (1.0 eq.) was suspended in toluene. Then, PNP ligand (1.05 eq.) was added at room temperature. The resultant mixture was stirred for 10-15 minutes. Followed by stirring, the reaction mixture was kept at 100°C for 16 h. After the completion of 16 h, the mixture was cooled down to room temperature and removal of solvent under reduced pressure resulted in the formation of yellow solid. Further washing of this solid with n-octane (3×10 mL) and drying under high vacuum provide the corresponding manganese complex in 90% yield. The complex was characterized using ^{1}H and ^{31}P NMR spectroscopy and the data obtained was well correlated with the literature reported once (*Angew. Chem. Int. Ed*. **2016**, *55*, 14967–14971).

2.2 General procedure for α-olefination of nitriles with secondary alcohols

To an oven dried 15 mL screw cap pressure tube, nitrile (0.5 mmol, 1 eq.), secondary alcohol (1.0 mmol, 2 eq.), [Mn]-1 catalyst (3 mol%), KO^{t}Bu (0.15 mmol, 30 mol %) and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120°C for 12 h. Then, the reaction was quenched with water (4 mL) and extracted with dichloromethane (3x5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

3. Kinetic experiments

3.1. Monitoring the kinetics of the reaction

To an oven dried 15 mL screw cap pressure tube, **1a** (1.0 mmol, 1 eq.), **2a** (2.0 mmol, 2 eq.), **[Mn]-1** catalyst (0.03 mmol, 3 mol%), KO^{t}Bu (0.3 mmol, 30 mol %), mesitylene (1.0 mmol, 1 eq.) as an internal standard, and toluene (2.5 mL) were added under a gentle stream of argon to make up the total volume of the reaction mixture to 3 mL. The reaction mixture was kept for stirring at 120°C. At regular intervals (1 h, 2 h, 4 h, 6 h, 8 h, 10 h, 12 h) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with methanol and subjected to gas chromatographic analysis. The concentration of the products was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (M) *vs* time (hours) plot (**Figure S1**). The data represented was taken from the average of two independent set of experiments.

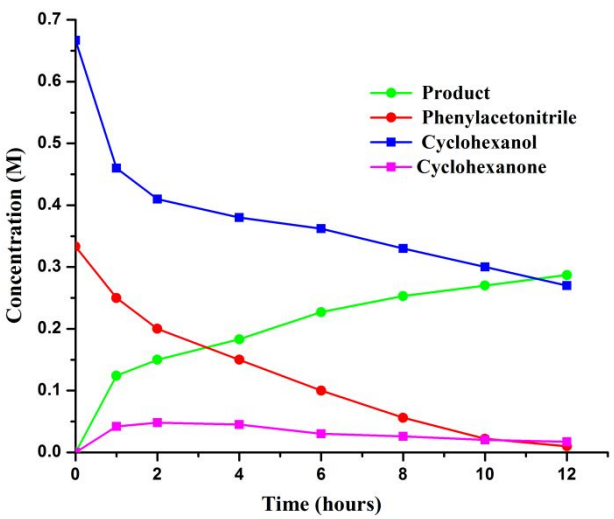


Figure S1. Kinetic profile of Mn(I)-catalyzed α-olefination reaction of nitriles with cyclohexanol.

3.2. Rate-order determination

The initial rate method was used to determine the rate order of the α-olefination reaction with respect to various components of the reaction. The data of the concentration (M) *vs* time (min.) plot was fitted to linear using origin pro 8. The slope of the linear fitted curve represents the reaction rate. The order of the reaction was determined by plotting log(rate) *vs* log(conc.) of that particular component.

3.2.1. Rate order determination with respect to phenylacetonitrile (1a)

To determine the order of the α-olefination reaction on **1a**, the initial rates at different initial concentrations of **1a** were recorded. The final data was obtained by averaging the results of two independent runs for each experiment.

To an oven dried 15 mL screw cap pressure tube, **2a** (2.0 mmol, 2 eq.), **[Mn]-1** catalyst (0.03 mmol, 3 mol%), KO^{t}Bu (0.3 mmol, 30 mol %), mesitylene (1.0 mmol, 1 eq.) as an internal standard, specific amount of **1a** and toluene were added under a gentle stream of argon to make up the total volume of the reaction mixture to 3 mL. The reaction mixture was kept for stirring at 120°C. At regular intervals (5 min, 10 min, 15 min, 20 min, 25 min, 30 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with methanol and subjected to gas chromatographic analysis. The concentration of the products was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (M) *vs* time (min.) plot (**Figure S2. (A)**). The data represented was taken from the average of two independent set of experiments.

The rate of reaction at different initial concentration of **1a** was given in (**Table S1**) and used to plot the log(rate) *vs* log(conc.) plot (**Figure S2. (B)**) to determine the order of reaction with respect to phenylacetonitrile.

Table S1. Rate of α-olefination reaction at different initial concentration of (**1a**).

Experiment	Initial concentration of 1a (M)	Initial rate (Set 1) [M/min]× 10^{-3}	Initial rate (Set II) [M/min]× 10^{-3}	Average Initial rate [M/min]× 10^{-3}
1	0.17	0.41	0.43	0.42
2	0.33	0.68	0.75	0.72
3	0.50	1.38	1.22	1.29
4	0.67	1.46	1.48	1.47
5	0.83	2.20	1.86	1.99

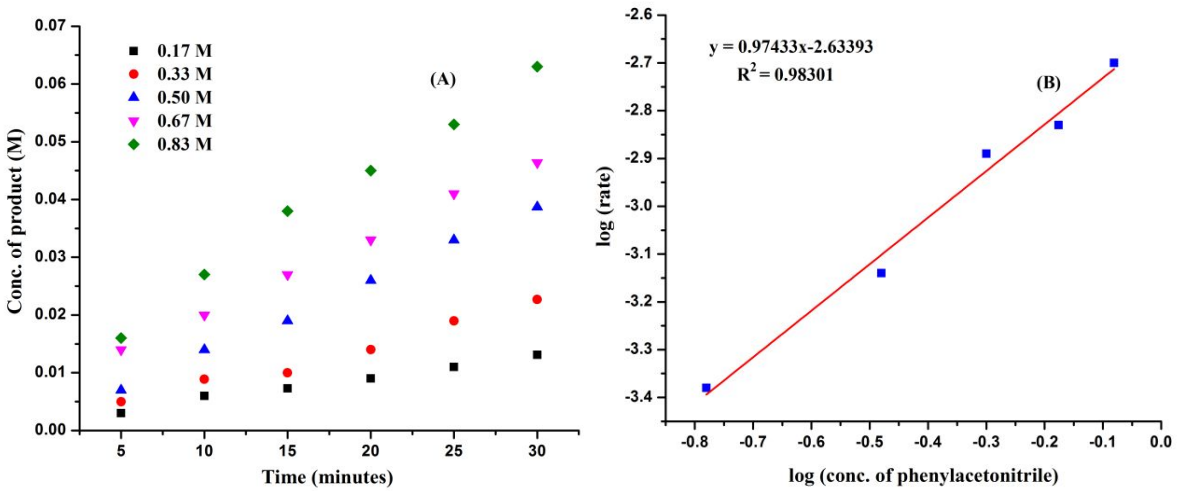


Figure S2. (A) Concentration versus time plot at various concentrations of (**1a**). **(B)** log(rate) versus log(conc.) graph of (**1a**).

3.2.2. Rate order determination with respect to cyclohexanol (2a)

To determine the order of the α-olefination reaction on **2a**, the initial rates at different initial concentrations of **2a** were recorded. The final data was obtained by averaging the results of two independent runs for each experiment.

To an oven dried 15 mL screw cap pressure tube, **1a** (0.5 mmol, 1 eq.), **[Mn]-1** catalyst (0.015 mmol, 3 mol%), KO^{t}Bu (0.15 mmol, 30 mol %), mesitylene (0.5 mmol, 1 eq.) as an internal standard, specific amount of **2a** and toluene were added under a gentle stream of argon to make up the total volume of the reaction mixture to 2 mL. The reaction mixture was kept for stirring at 120°C. At regular intervals (5 min, 10 min, 15 min, 20 min, 25 min, 30 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with methanol and subjected to gas chromatographic analysis. The concentration of the products was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (M) *vs* time (min.) plot (**Figure S3. (A)**). The data represented was taken from the average of two independent set of experiments. The rate of reaction at different initial concentration of **2a** was used to plot the log(rate) *vs* log(conc.) plot (**Figure S3. (B)**) to determine the order of reaction with respect to cyclohexanol.

Table S2. Rate of α-olefination reaction at different initial concentration of (**2a**).

Experiment	Initial concentration of 2a (M)	Initial rate (Set 1) [M/min]× 10^{-3}	Initial rate (Set II) [M/min]× 10^{-3}	Average Initial rate [M/min]× 10^{-3}
1	0.13	0.18	0.22	0.20
2	0.25	0.42	0.47	0.45
3	0.38	0.72	0.91	0.81
4	0.50	0.99	0.97	0.98
5	0.63	1.23	1.27	1.26

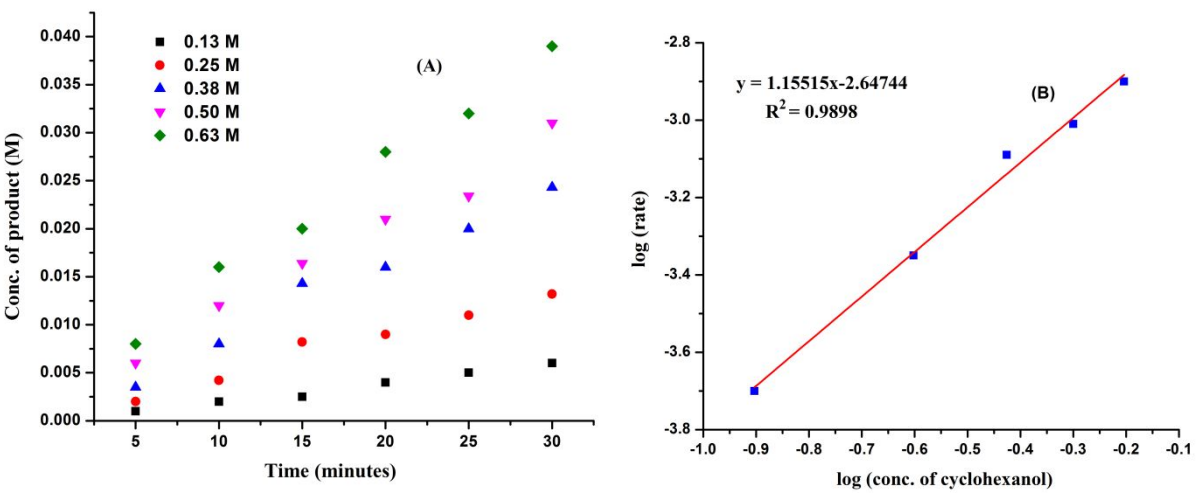


Figure S3. (A) Concentration versus time plot at various concentrations of (**2a**). **(B)** log(rate) versus log(conc.) graph of (**2a**).

3.2.3. Rate order determination with respect to catalyst

To determine the order of the α-olefination reaction with respect to catalyst, the initial rates at different initial concentrations of catalyst were recorded. The final data was obtained by averaging the results of two independent runs for each experiment.

To an oven dried 15 mL screw cap pressure tube, **1a** (1.0 mmol, 1 eq.), cyclohexanol (2.0 mmol, 2 eq.), **[Mn]-1** catalyst (0.03 mmol, 3 mol%), KO^{t}Bu (0.3 mmol, 30 mol %), mesitylene (1.0 mmol, 1 eq.) as an internal standard, specific amount of catalyst and toluene (2.5 mL) were added under a gentle stream of argon to make up the total volume of the reaction mixture to 3 mL. The reaction mixture was kept for stirring at 120°C. At regular intervals (5 min, 10 min, 15 min, 20 min, 25 min, 30 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with methanol and subjected to gas chromatographic analysis. The concentration of the products was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (M) *vs* time (min.) plot (**Figure S4. (A)**). The data represented was taken from the average of two independent set of experiments. The rate of reaction at different initial concentration of catalyst was given in (Table S3) and used to plot the log(rate) *vs* log(conc.) plot (**Figure S4. (B)**) to determine the order of reaction with respect to catalyst.

Table S3. Rate of α-olefination reaction at different initial concentration of catalyst.

Experiment	Initial concentration of catalyst (M)	Initial rate (Set 1) [M/min]× 10^{-3}	Initial rate (Set II) [M/min]× 10^{-3}	Average Initial rate [M/min]× 10^{-3}
1	0.003	0.35	0.42	0.39
2	0.010	0.78	0.80	0.79
3	0.017	1.05	1.10	1.10
4	0.020	1.36	1.33	1.35
5	0.027	1.74	1.81	1.77

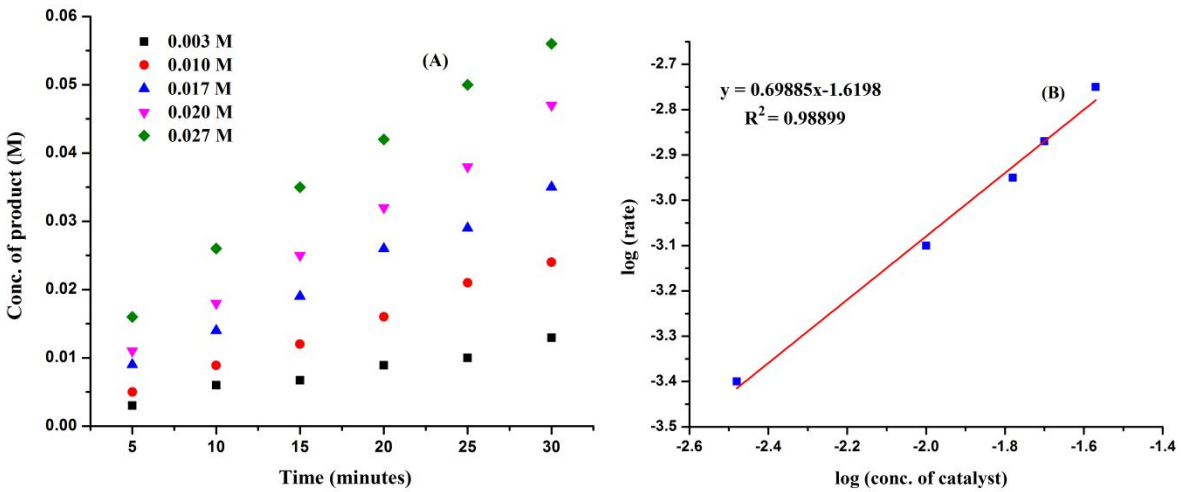
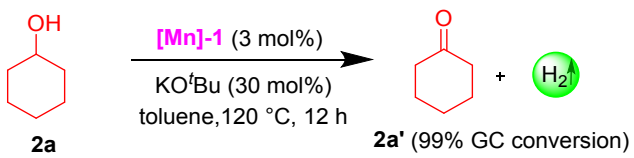


Figure S4. (A) Concentration versus time plot at various concentrations of catalyst. **(B)** log(rate) versus log(conc.) graph of catalyst.

4. Mechanistic studies

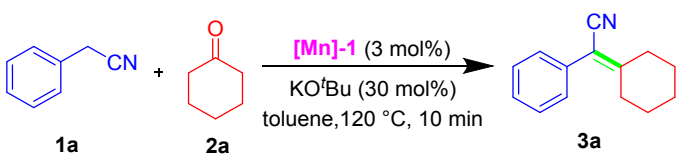
4.1. Dehydrogenation of cyclohexanol to cyclohexanone (2a')



To an oven dried 15 mL screw cap pressure tube, cyclohexanol (1.0 mmol, 2 eq.), **[Mn]-1** catalyst (3 mol%), KO^{t}Bu (0.15 mmol, 30 mol %), mesitylene as an internal standard and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120°C for 12 h. Then the reaction mixture was used for GC and GC-MS analysis which indicates 100% conversion of cyclohexanol to cyclohexanone.

Later the reaction was also performed in absence of catalyst and also in absence of base for 12 h. GC analysis indicated that there is no product formation in absence of catalyst while trace of product formation was detected in absence of base. To confirm the GC results, ^{1}H NMR of crude mixture was taken which also showed the same result.

4.2. α-Olefination reaction of 1a with cyclohexanone under different set of conditions

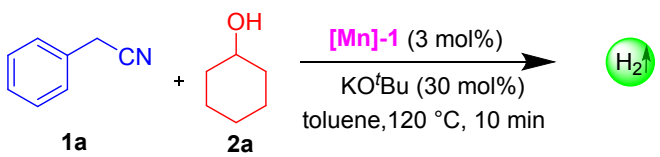


To an oven dried 15 mL screw cap pressure tube, nitrile (0.5 mmol, 1 eq.), cyclohexanone (1.0 mmol, 2 eq.), [Mn]-1 catalyst (3 mol%), KO^{t}Bu (0.15 mmol, 30 mol %) and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 120°C

for 10 min. Then, the reaction was quenched with water (4 mL) and extracted with dichloromethane (3x5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

Later the reaction was also performed in absence of base and also in absence of catalyst for 10 min. GC analysis indicated that there is no product formation in absence of base while significant product formation was detected in absence of catalyst. To confirm the GC result ^1H NMR of crude mixture was taken which also showed the same result.

4.3. H_2 detection experiment



Procedure: The molecular hydrogen detection experiment was performed in a J-Young NMR tube using the standard reaction condition. After 10 min of reaction, we have analyzed the gas phase of reaction using gas chromatography and molecular hydrogen was identified (**Figure S5**).

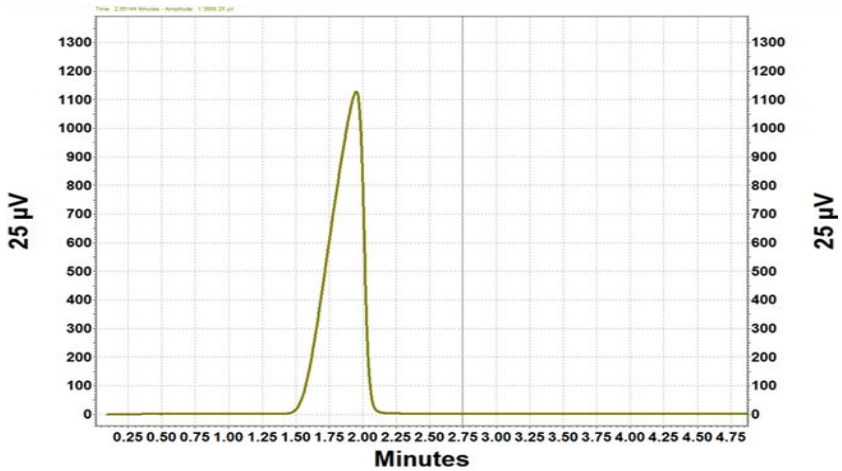


Figure S5. Molecular hydrogen identification using gas phase GC analysis.

4.4. Deuterium labelling experiment

To an oven dried 15 mL screw cap pressure tube, cyclohexanol (2.0 mmol, 1 eq.), Ru-MACHO catalyst (1 mol %), KO^{t}Bu (1.0 mmol, 50 mol %) and D_2O (2 mL) were added under a gentle stream of argon. The reaction mixture was kept for stirring at 80°C for 16 h. Then, the reaction was quenched with water (4 mL) and extracted with dichloromethane (3x5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to provide the corresponding deuterated cyclohexanol product. The deuterium incorporation percentage was calculated using ^{1}H NMR (**Figure S6, S7**). After the NMR analysis the product was used further for α-olefination reaction.

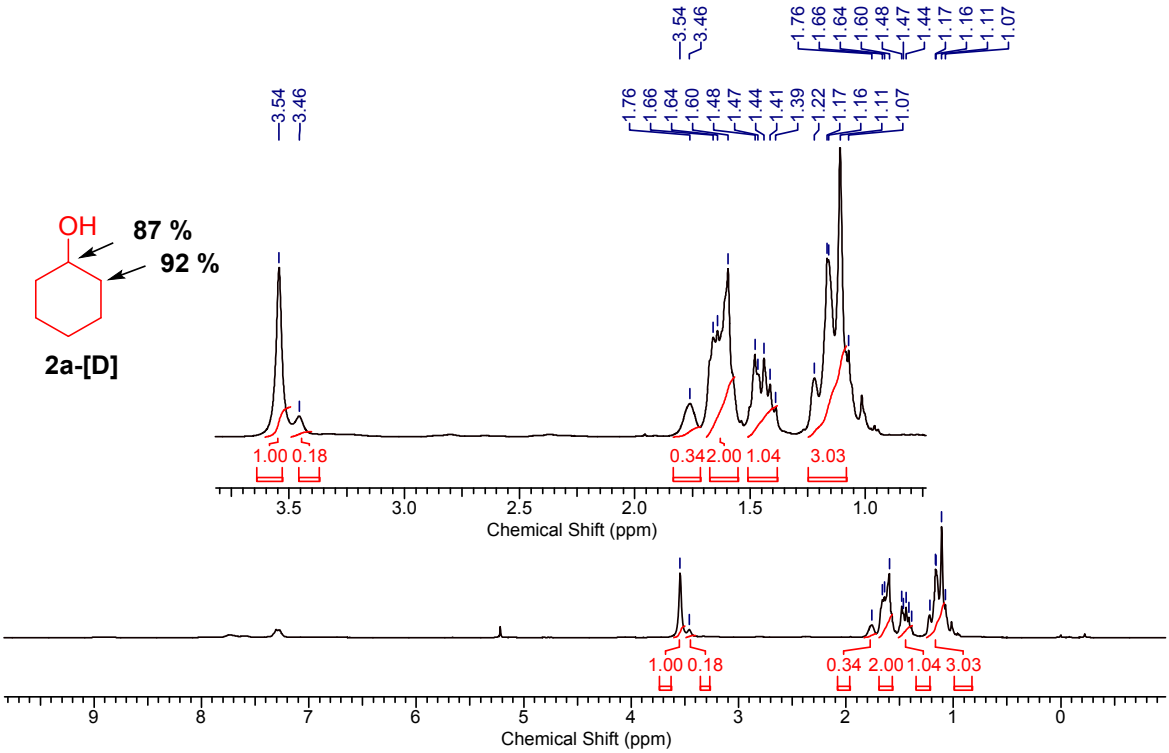


Figure S6. ^{1}H NMR of deuterated cyclohexanol (**2a**)

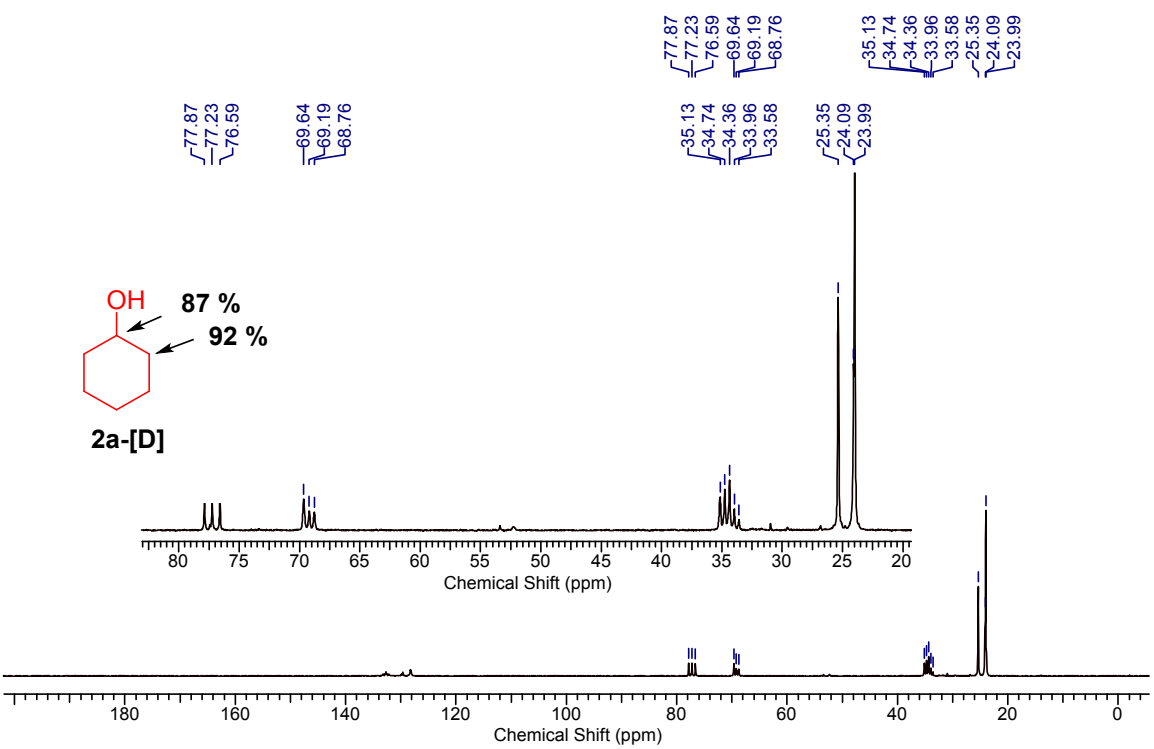


Figure S7. ^{13}C NMR of deuterated cyclohexanol (**2a**)

4.5. Reaction with deuterium labelled alcohol

To an oven dried 15 mL screw cap pressure tube, nitrile (0.5 mmol, 1 eq.), cyclohexanol (1.0 mmol, 2 eq.), or deuterated cyclohexanol, **[Mn]-1** catalyst (3 mol%), KO^{t}Bu (0.15 mmol, 30 mol %), mesitylene (1.0 mmol, 1 eq.) as an internal standard and toluene were added under a gentle stream of argon to make up the total volume of the reaction mixture to 1 mL. The reaction mixture was kept for stirring at 120°C. At regular intervals (2 min, 4 min, 6 min, 8 min, 10 min) the reaction mixture was cooled to ambient temperature and an aliquot of mixture was taken in a GC vial. The GC sample was diluted with methanol and subjected to gas chromatographic analysis. The concentration of the products was determined with respect to mesitylene internal standard. The data was used to draw the concentration of the product (**M**) *vs* time (min.) plot (**Figure S8**). The data represented was taken from the average of two independent set of experiments. The product was further purified by column chromatography, and ^{1}H NMR spectra of product was taken (**Figure S9).**

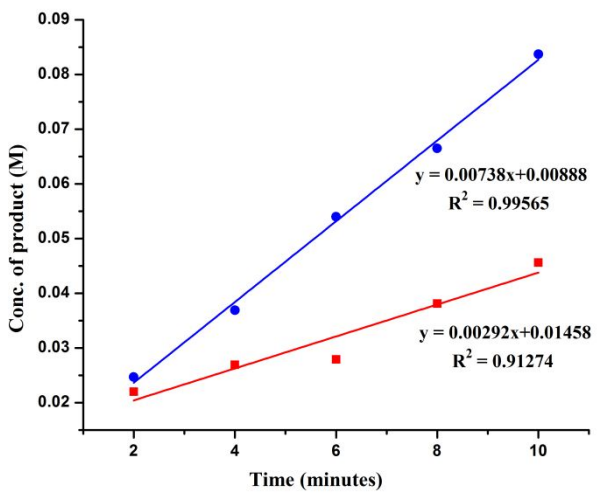


Figure S8. Time dependent formation of product **3a** using deuterium and normal cyclohexanol.

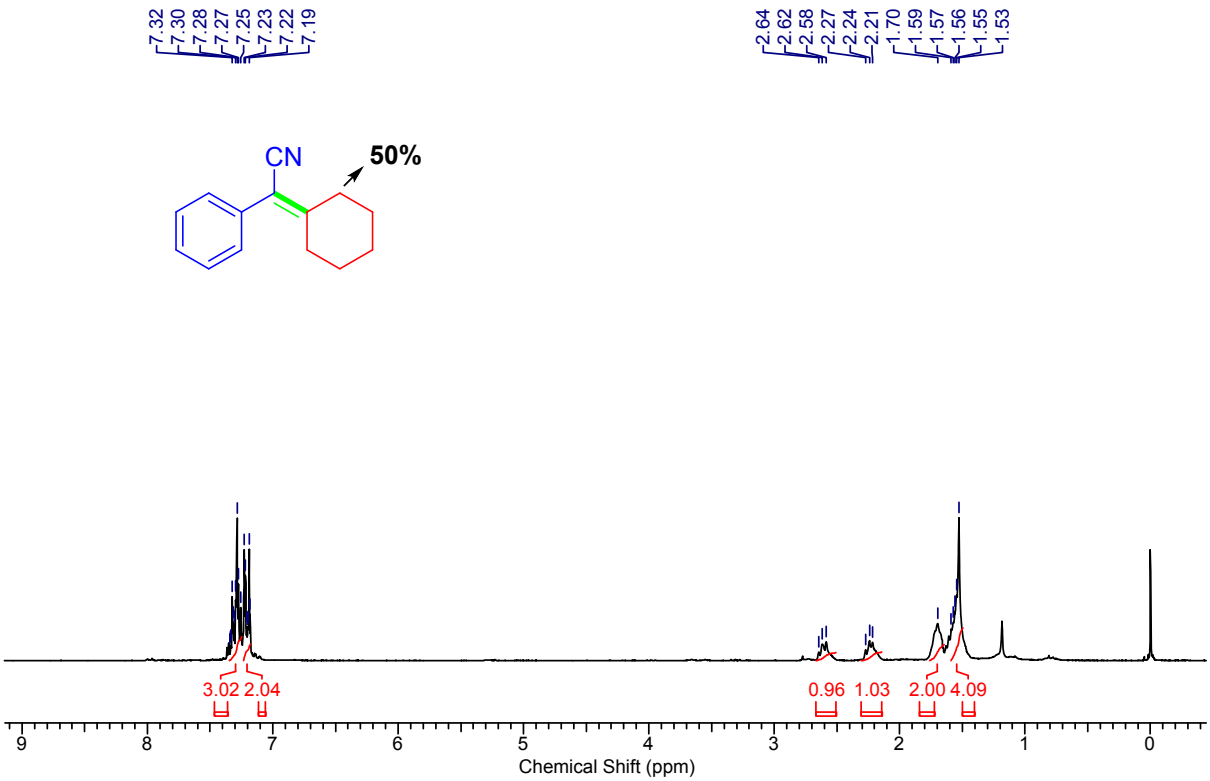
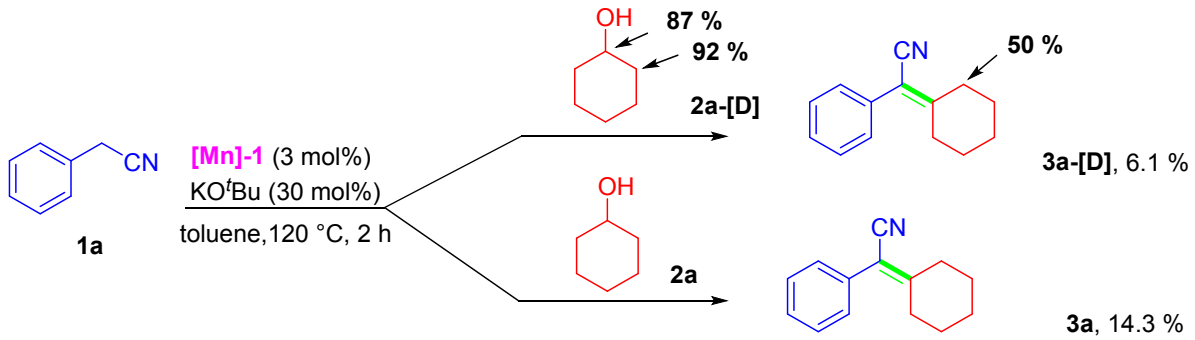


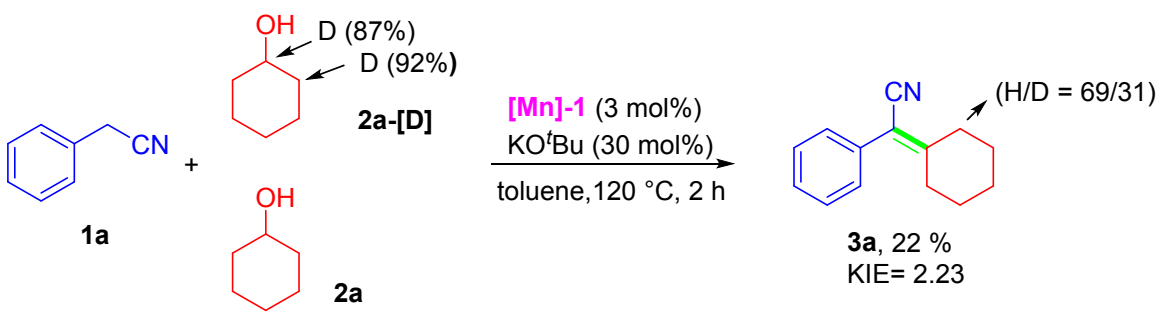
Figure S9. ^{1}H NMR of product 3a-D.

4.6. Competitive KIE experiments

Parallel reactions: To an oven dried 15 mL screw cap pressure tubes (two separate tubes), nitrile (0.256 mmol cyclohexanol (0.512 mmol) or cyclohexanol-D (0.512 mmol), **[Mn]-1** (3 mol%) and KOtBu (30 mol%) and toluene (1 mL) were added under a gentle stream of argon. Both the reaction mixture was kept for stirring at 120°C for 2 h. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.



Competition reaction: To an oven dried 15 mL screw cap pressure tube, nitrile (0.256 mmol), cyclohexanol (**2a**, 0.512 mmol), cyclohexanol-D (**2a-[D]**, 0.512 mmol), **[Mn]-1** (3 mol%), KOtBu (30 mol%), and toluene (1 mL) were added under a gentle stream of argon. The reaction mixture was kept stirring at 120 °C for 2 h. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system. The NMR spectrum of the product is shown in **Figure 10**.



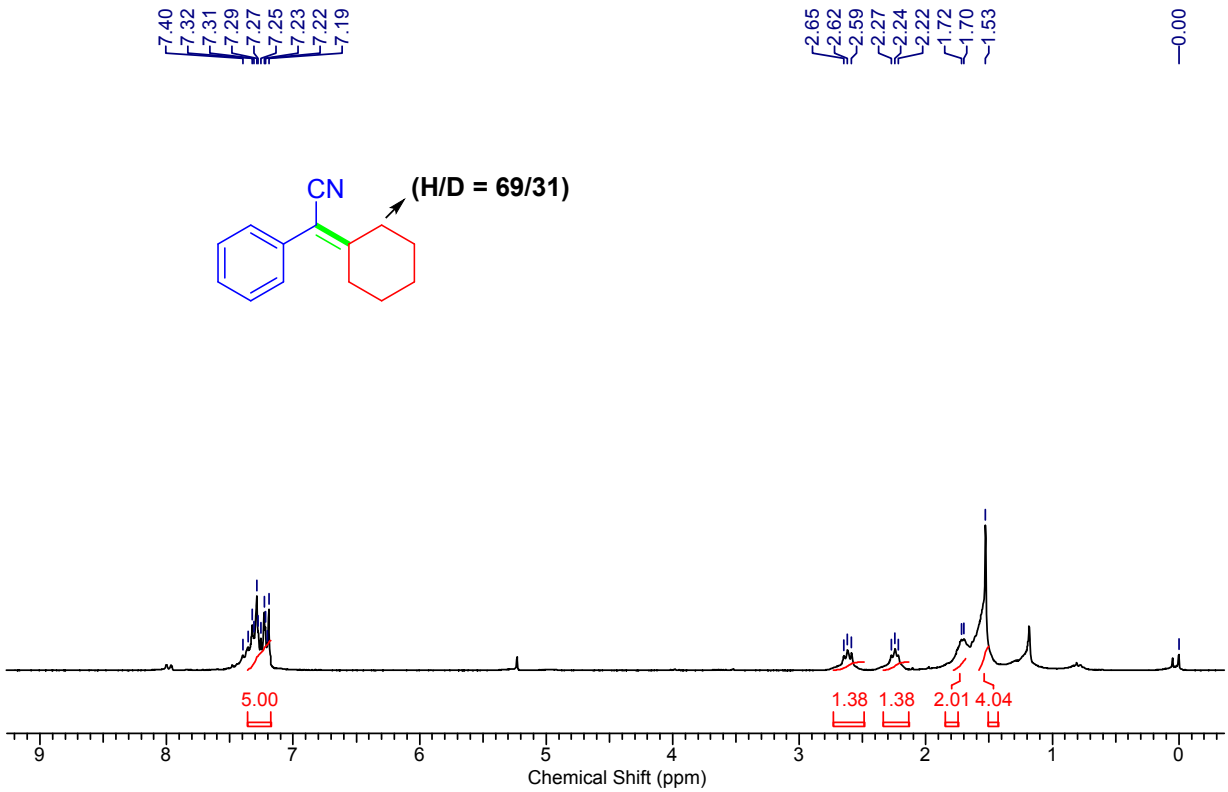
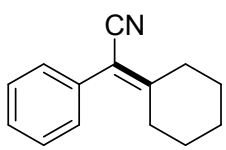


Figure S10. ^{1}H NMR of product **3a**.

5. Characterization data

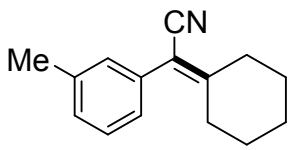
2-cyclohexylidene-2-phenylacetonitrile **(3a)**



Colorless liquid, 85% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$):δ ppm 7.26 - 7.39 (m, 5 H, ArC*H*), 2.68 (t, *J* = 6.3 Hz,2 H, CH_2), 2.31 (t, *J* = 6.3 Hz, 2 H, CH_2), 1.70 - 1.78 (m, 2H, CH_2), 1.60 - 1.65 (m, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$):δ ppm 161.9 (Olefinic-*C*), 133.9 (quat-*C*), 129.3 (Ar*C*H), 128.7 (Ar*C*H), 128.2 (Ar*C*H), 118.7 (*C*N), 107.8 (Olefinic-*C*), 35.4 (*C*H_2),

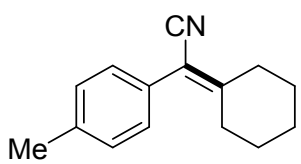
31.3 (*C*H_2), 28.2 (*C*H_2), 27.9 (*C*H_2), 25.9 (*C*H_2). HRMS (ESI) m/z calcd for $C_{14}H_{16}N$ $(M+H)^+$: 198.1277, found: 198.1280.

2-cyclohexylidene-2-(m-tolyl)acetonitrile **(3b)**



Colorless liquid, 72% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 7.07 - 7.30 (m, 4 H, ArC*H*), 2.67 (t, *J*= 6.3 Hz, 2 H, C*H*$_2$), 2.36 (s, 3 H, C*H*$_3$), 2.31 (t, *J* = 6.3 Hz, 2 H, C*H*$_2$), 1.74.-.1.80 (m, 2 H, C*H*$_2$), 1.57 - 1.67 (m, 4 H, C*H*$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 161.7 (Olefinic-*C*), 138.4 (quat-*C*), 133.8 (quat-*C*), 129.8 (Ar*C*H), 128.9 (Ar*C*H), 128.5 (Ar*C*H), 126.4 (Ar*C*H), 118.8 (*C*N), 107.8 (Olefinic-*C*), 35.4 (*C*H_2), 31.3 (*C*H_2), 28.2 (*C*H_2), 27.9 (*C*H_2), 25.9 (*C*H_2), 21.4 (*C*H_3). HRMS (ESI) m/z calcd for $C_{15}H_{18}N$ $(M+H)^+$: 212.1434, found: 212.1438.

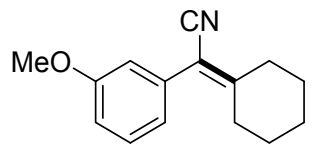
2-cyclohexylidene-2-(p-tolyl)acetonitrile **(3c)**



Colorless liquid, 75% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 7.16 - 7.17 (m, 4 H, ArC*H*), 2.67 (t, *J* = 6.2 Hz, 2 H, C*H*$_2$), 2.36 (s, 3 H, C*H*$_3$), 2.28- 2.34(m, 2 H, C*H*$_2$), 1.71-1.77 (m, 2 H, C*H*$_2$), 1.59 - 1.63 (m, 4 H, C*H*$_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 161.6 (Olefinic-

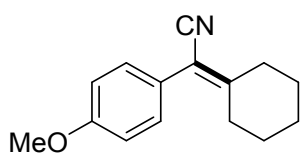
C), 133.9 (quat-*C*), 129.3 (quat-*C*), 128.7 (Ar*C*H), 128.2 (Ar*C*H), 118.7 (*C*N), 107.9 (Olefinic-*C*), 36.0 (*C*H_2), 35.8 (*C*H_2), 34.7 (*C*H_2), 32.0 (*C*H_2), 30.6 (*C*H_2), 21.4 (*C*H_3). HRMS (ESI) m/z calcd for $C_{15}H_{18}N$ $(M+H)^+$: 212.1434, found: 212.1438.

2-cyclohexylidene-2-(3-methoxyphenyl)acetonitrile **(3d)**



Colorless liquid, 81% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.25 - 7.33 (m, 1 H, ArC*H*), 6.83 – 6.90 (m, 2 H, ArC*H*), 6.80 – 6.83 (m, 1 H, ArC*H*), 3.81 (s, 3 H, OCH_3), 2.67 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.32 (t, *J* = 6.2 Hz, 2 H, CH_2), 1.75-1.78 (m, 2 H, CH_2), 1.60 - 1.67 (m, 4 H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 162.0 (Olefinic-*C*), 159.7 (quat-*C*), 135.1 (quat-*C*), 129.7 (Ar*C*H), 121.6 (Ar*C*H), 118.6 (*C*N), 114.8 (Ar*C*H), 113.8 (Ar*C*H), 107.6 (Olefinic-*C*), 55.3 (O*C*H_3), 35.3 (*C*H_2), 31.4 (*C*H_2), 28.1 (*C*H_2), 27.9 (*C*H_2), 25.9 (*C*H_2). HRMS (ESI) m/z calcd for $C_{15}H_{18}NO$ $(M+H)^+$: 228.1383, found: 228.1383.

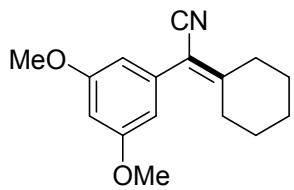
2-cyclohexylidene-2-(4-methoxyphenyl)acetonitrile (**3e**)



Colorless liquid, 84% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 7.16 - 7.24 (m, 2 H, ArC*H*), 6.88 – 6.94 (m, 2 H, ArC*H*), 3.81 (s, 3 H, OCH_3), 2.66 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.31

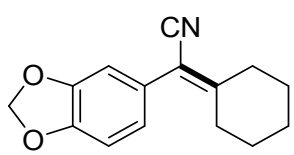
(t, J = 6.2 Hz, 2 H, CH_2), 1.74-1.79 (m, 2 H, CH_2), 1.59 - 1.66 (m, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 161.0 (Olefinic-*C*), 159.4 (quat-*C*), 130.5 (Ar*C*H), 126.2 (quat-*C*), 118.9 (*C*N), 114.0 (Ar*C*H), 107.3 (Olefinic-*C*), 55.3 (O*C*H_3), 35.3 (*C*H_2), 31.2 (*C*H_2), 28.1 (*C*H_2), 27.9 (*C*H_2), 25.9 (*C*H_2). HRMS (ESI) m/z calcd for $C_{15}H_{18}NO$ $(M+H)^+$: 228.1383, found: 228.1383.

2-cyclohexylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**3f**)



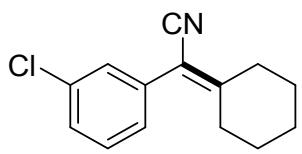
Colorless liquid, 88% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 6.40 - 6.44 (m, 3 H, ArC*H*), 3.79 (s, 6 H, OCH_3), 2.66 (t, J = 6.2 Hz, 2 H, CH_2), 2.33 (t, J = 6.2 Hz, 2 H, CH_2), 1.73-1.77 (m, 2 H, CH_2), 1.60 - 1.62 (m, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 162.3 (Olefinic-*C*), 160.9 (quat-*C*), 135.7 (quat-*C*), 118.5 (*C*N), 107.6 (Ar*C*H), 107.4 (Olefinic-*C*), 100.3 (Ar*C*H), 55.4 (O*C*H_3), 35.3 (*C*H_2), 31.5 (*C*H_2), 28.1 (*C*H_2), 28.0 (*C*H_2), 25.9 (*C*H_2). HRMS (ESI) m/z calcd for $C_{16}H_{20}NO_2$ $(M+H)^+$: 258.1489, found: 258.1488.

2-(benzo[d][1,3]dioxol-5-yl)-2-cyclohexylideneacetonitrile (**3g**)



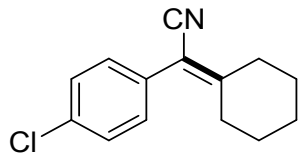
Colorless liquid, 70% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.81 (dd, *J* = 8.4 Hz 1 H, ArC*H*), 6.73 - 6.74 (m, 2 H, ArC*H*), 5.98 (s, 2 H, OCH_2), 2.65 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.30 (t, *J* = 5.8 Hz, 2 H, CH_2), 1.73-1.77 (m, 2 H, CH_2), 1.58 - 1.66 (m, 4 H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 161.6 (Olefinic-*C*), 147.8 (quat-*C*), 147.5 (quat-*C*), 127.5 (quat-*C*), 123.0 (Ar*C*H), 118.7 (*C*N), 109.6 (Ar*C*H), 108.4 (Ar*C*H), 107.3 (Olefinic-*C*), 101.4 (O*C*H_2), 35.3 (*C*H_2), 31.3 (*C*H_2), 28.1 (*C*H_2), 27.9 (*C*H_2), 25.9 (*C*H_2). HRMS (ESI) m/z calcd for $C_{15}H_{16}NO_2$ $(M+H)^+$: 242.1176, found: 242.1173.

2-(3-chlorophenyl)-2-cyclohexylideneacetonitrile (**3h**)



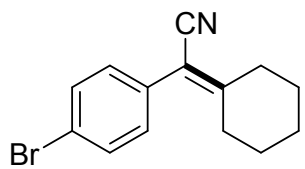
Colorless liquid, 65% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 7.28 - 7.34 (m, 3 H, ArC*H*), 7.14 - 7.21 (m, 1 H, ArC*H*), 2.68 (t, *J* = 6.1 Hz, 2 H, CH_2), 2.30 (t, *J* = 5.7 Hz, 2 H, CH_2), 1.76-1.79 (m, 2 H, CH_2), 1.61 - 1.64 (m, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 163.2 (Olefinic-*C*), 135.6 (quat-*C*), 134.6 (quat-*C*), 130.0 (Ar*C*H), 129.4 (Ar*C*H), 128.5 (Ar*C*H), 127.5 (Ar*C*H), 118.2 (*C*N), 106.6 (Olefinic-*C*), 35.4 (*C*H_2), 31.4 (*C*H_2), 28.1 (*C*H_2), 27.9 (*C*H_2), 25.8 (*C*H_2). HRMS (ESI) m/z calcd for $C_{14}H_{15}NCl$ $(M+H)^+$: 232.0884, found: 232.0886.

2-(4-chlorophenyl)-2-cyclohexylideneacetonitrile (**3i**)



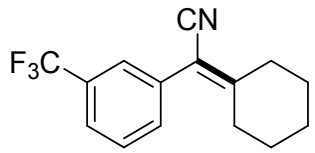
Colorless liquid, 68% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 7.33 - 7.40 (m, 2 H, ArC*H*), 7.18 - 7.25 (m, 2 H, ArC*H*), 2.68 (t, *J* = 6.1 Hz, 2 H, CH_2), 2.29 (t, *J* = 5.3 Hz, 2 H, CH_2), 1.76-1.79 (m, 2 H, CH_2), 1.60 - 1.63 (m, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δppm 162.7 (Olefinic-*C*), 134.3 (quat-*C*), 132.3 (quat-*C*), 130.6 (Ar*C*H), 128.9 (Ar*C*H), 118.3 (*C*N), 106.7 (Olefinic-*C*), 35.4 (*C*H_2), 31.3 (*C*H_2), 28.1 (*C*H_2), 27.9 (*C*H_2), 25.8 (*C*H_2). HRMS (ESI) m/z calcd for $C_{14}H_{15}NCl$ $(M+H)^+$: 232.0884, found: 232.0886.

2-(4-bromophenyl)-2-cyclohexylideneacetonitrile (**3j**)



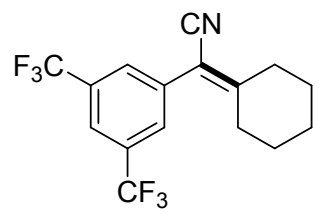
Colorless liquid, 60% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.45 (d, *J* =8.4 Hz, 2 H, ArC*H*), 7.08 (d, *J* =8.4 Hz, 2 H, ArC*H*), 2.60 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.22 (t, *J* = 6.1 Hz, 2 H, CH_2), 1.68-1.73 (quint, *J* = 5.9 Hz, 2 H, CH_2), 1.55 - 1.60 (m, 2 H, CH_2), 1.49 - 1.54 (quint, *J* = 5.7 Hz, 2 H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 162.7 (Olefinic-*C*), 132.8 (quat-*C*), 131.9 (Ar*C*H), 130.9 (Ar*C*H), 122.4 (quat-*C*), 118.2 (*C*N), 106.7 (Olefinic-*C*), 35.4 (*C*H_2), 31.3 (*C*H_2), 28.1 (*C*H_2), 27.9 (*C*H_2), 25.8 (*C*H_2). HRMS (ESI) m/z calcd for $C_{14}H_{15}NBr$ $(M+H)^+$: 276.0384, found: 276.0372.

2-cyclohexylidene-2-(3-(trifluoromethyl)phenyl)acetonitrile (**3k**)



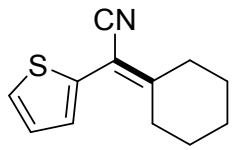
Colorless liquid, 52% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 7.45 – 7.63 (m, 4 H, ArC*H*), 2.71 (t, *J* = 6.0 Hz, 2 H, CH_2), 2.30 (t, *J* = 5.7 Hz, 2 H, CH_2), 1.78 - 1.81 (m, 2 H, CH_2), 1.62 - 1.64 (m, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 163.7 (Olefinic-*C*), 134.7 (quat-*C*), 132.7 (quat-*C*), 129.3 (Ar*C*H), 126.1 (Ar*C*H), 126.1 (*C*F_3), 125.2 (Ar*C*H), 125.1 (Ar*C*H), 118.1 (*C*N), 106.6 (Olefinic-*C*), 35.5 (*C*H_2), 31.4 (*C*H_2), 28.1 (*C*H_2), 27.9 (*C*H_2), 25.8 (*C*H_2). HRMS (ESI) m/z calcd for $C_{15}H_{15}NF_3$ $(M+H)^+$: 266.1151, found: 266.1149.

2-(3,5-bis(trifluoromethyl)phenyl)-2-cyclohexylideneacetonitrile (**3m**)



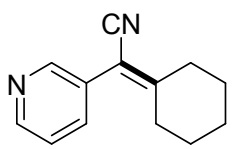
Colorless liquid, 50% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.87 (s, 1 H, ArC*H*), 7.74 (s, 2 H, ArC*H*), 2.74 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.30 (t, *J* = 6.1 Hz, 2 H, CH_2), 1.80 - 1.84 (m,2 H, CH_2), 1.64 - 1.69 (m, 4 H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 165.4 (Olefinic-*C*), 135.9 (quat-*C*), 132.5 (quat-*C*), 132.1 (quat-*C*), 129.5 (Ar*C*H), 124.3 (*C*F_3), 122.3 (Ar*C*H), 121.6 (*C*F_3), 117.4 (*C*N), 105.4 (Olefinic-*C*), 35.5 (*C*H_2), 31.5 (*C*H_2), 28.0 (*C*H_2), 27.9 (*C*H_2), 25.6 (*C*H_2). HRMS (ESI) m/z calcd for $C_{16}H_{13}NF_6$ $(M+Na)^+$: 356.0844, found: 356.0847.

2-cyclohexylidene-2-(3*H*-1λ^3-thiophen-2-yl)acetonitrile (**3o**)



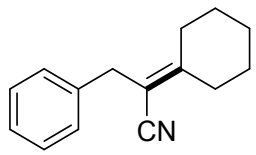
Colorless liquid, 47% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.33(d, 1 H, ArC*H*), 7.08 (m, 1 H, ArC*H*), 7.03 – 7.04 (m, 1 H, ArC*H*), 2.68 (t, *J* = 5.8 Hz, 2 H, CH_2), 2.30 (bs, 2 H, CH_2), 1.78 (bs, 2 H, CH_2), 1.65 (bs, 4 H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δppm 163.3 (Olefinic-*C*), 134.9 (quat-*C*), 128.7 (Ar*C*H), 127.1 (Ar*C*H), 126.6 (Ar*C*H), 117.9 (*C*N), 101.3 (Olefinic-*C*), 35.6 (*C*H_2), 31.8 (*C*H_2), 28.1 (*C*H_2), 27.8 (*C*H_2), 25.8 (*C*H_2). HRMS (ESI) m/z calcd for $C_{12}H_{15}NS$ $(M+H)^+$: 205.0841, found: 205.0842.

2-cyclohexylidene-2-(pyridin-3-yl)acetonitrile (**3p**)



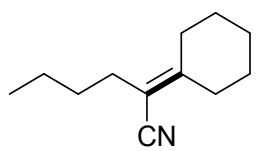
Colorless liquid, 64% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.58-8.60 (m, 1 H, ArC*H*), 8.53 –8.57 (m, 1 H, ArC*H*), 7.62 – 7.67 (m, 1 H, ArC*H*),), 7.32 – 7.39 (m, 1 H, ArC*H*), 2.72 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.32 (t, *J* = 6.0 Hz, 2 H, CH_2), 1.78 – 1.82 (m, 2 H, CH_2), 1.63 –1.66 (m, 4 H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δppm 164.5 (Olefinic-*C*), 150.1 (quat-*C*), 149.4 (Ar*C*H), 136.7 (Ar*C*H), 130.1 (Ar*C*H), 123.6 (Ar*C*H), 118.1 (*C*N), 104.5 (Olefinic-*C*), 35.6 (*C*H_2), 31.5 (*C*H_2), 28.2 (*C*H_2), 28.1 (*C*H_2), 25.8 (*C*H_2). HRMS (ESI) m/z calcd for $C_{13}H_{15}N_2$ $(M+H)^+$: 199.1230, found: 199.1234.

2-cyclohexylidene-3-phenylpropanenitrile (**3q**)



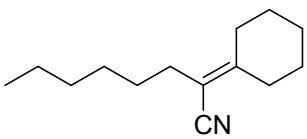
Colorless liquid, 45% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.23-7.26 (m, 2 H, ArC*H*), 7.13 –7.19 (m, 3 H, ArC*H*), 3.50 (s, 2 H, CH_2), 2.49 (t, *J* = 6.1 Hz 2 H, CH_2), 2.29 – 2.32 (m, 2 H, CH_2), 1.60 – 1.62 (m, 2 H, CH_2), 1.54 –1.56 (m,4 H, CH_2). ^{13}C NMR (100.16 MHz, $CDCl_3$): δppm 160.2 (Olefinic-*C*), 137.9 (quat-*C*), 128.8 (Ar*C*H), 128.3 (Ar*C*H), 126.9 (Ar*C*H), 119.3 (*C*N), 105.2 (Olefinic-*C*), 35.4 (*C*H_2), 30.7 (*C*H_2), 28.1 (*C*H_2), 27.7 (*C*H_2), 26.1 (*C*H_2). HRMS (ESI) m/z calcd for $C_{15}H_{18}N$ $(M+H)^+$: 212.1434, found: 212.1436.

2-cyclohexylidenehexanenitrile (**3r**)



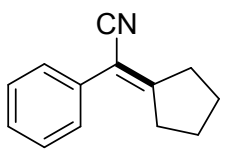
Colorless liquid, 35% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.41 –2.44 (m, 2 H, CH_2), 2.12 – 2.19 (m, 4 H, CH_2), 1.52 – 1.58 (m, 6 H, CH_2), 1.38 – 1.44 (m, 2 H, CH_2), 1.24 – 1.29 (m, 2 H, CH_2), 0.85 (t, *J* = 7.3 Hz, 3 H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δppm 159.0 (Olefinic-*C*), 119.5 (*C*N), 106.3 (Olefinic-*C*), 35.3 (*C*H_2), 30.9 (*C*H_2), 30.3 (*C*H_2), 29.0 (*C*H_2), 28.1 (*C*H_2), 27.8 (*C*H_2), 26.2 (*C*H_2), 22.1 (*C*H_2), 13.9 (*C*H_3). HRMS (ESI) m/z calcd for $C_{12}H_{20}N$ $(M+H)^+$: 178.1590, found: 178.1591.

2-cyclohexylideneoctanenitrile (**3s**)



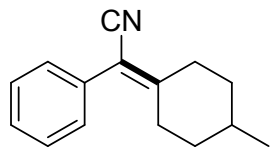
Colorless liquid, 40% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.41 – 2.44 (m, 2 H, C*H*$_2$), 2.12 – 2.20 (m, 4 H, C*H*$_2$), 1.52 – 1.58 (m, 6 H, C*H*$_2$), 1.22 – 1.24 (m, 8 H, C*H*$_2$), 1.24 – 1.29 (m, 2 H, C*H*$_2$), 0.80 – 0.82 (m, 3 H, C*H*$_3$). ^{13}C NMR (106.16 MHz, $CDCl_3$): δppm 158.9 (Olefinic-*C*), 119.5 (*C*N), 106.3 (Olefinic-*C*), 35.3 (*C*H$_2$), 31.6 (*C*H$_2$), 30.4 (*C*H$_2$), 29.3 (*C*H$_2$), 28.7 (*C*H$_2$), 28.6 (*C*H$_2$), 28.1 (*C*H$_2$), 27.8 (*C*H$_2$), 26.2 (*C*H$_2$) 22.6 (*C*H$_2$), 14.1 (*C*H$_3$). HRMS (ESI) m/z calcd for $C_{14}H_{24}N$ $(M+H)^+$: 206.1903, found: 206.1905.

2-cyclopentylidene-2-phenylacetonitrile (**4a**)



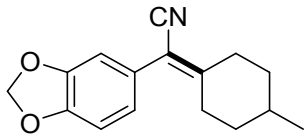
Pale yellow liquid, 60% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.37 – 7-43 (m, 4 H, ArC*H*), 7.29 - 7.32 (t, 1 H, *J* = 7.1 Hz, ArC*H*), 2.82 (t, *J* = 7.0 Hz, 2 H, C*H*$_2$), 2.59 (t, *J* = 6.9 Hz, 2 H, C*H*$_2$), 1.76 - 1.87 (m, 4 H, C*H*$_2$). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 166.9 (Olefinic-*C*), 134.3 (quat-*C*), 128.6 (Ar*C*H), 128.0 (Ar*C*H), 127.9 (Ar*C*H), 118.6 (*C*N), 107.1 (Olefinic-*C*), 35.9 (*C*H$_2$), 33.8 (*C*H$_2$), 27.0 (*C*H$_2$), 25.5 (*C*H$_2$). HRMS (ESI) m/z calcd for $C_{13}H_{14}N$ $(M+H)^+$: 184.1121, found: 184.1124.

2-(4-methylcyclohexylidene)-2-phenylacetonitrile (**4b**)



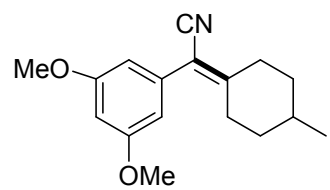
Colorless liquid, 70% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 7.25 – 7.43 (m, 5 H, ArC*H*), 3.03 –3.14 (m, 1 H, CH_2), 2.63 – 2.74 (m, 1 H, CH_2), 2.25 – 2.41 (m, 1 H, CH_2), 1.91 – 2.06 (m, 2 H, CH_2), 1.61 - 1.86 (m, 2 H, CH_2), 1.19 – 1.34 (m, 1 H, CH_2),1.00 – 1.16 (m, 1 H, CH_2), 0.94 (d, J = 6.4 Hz, 3 H, CH$_3$). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 161.7 (Olefinic-*C*), 138.4 (quat-*C*), 133.8 (Ar*C*H), 129.8 (Ar*C*H), 129.0 (Ar*C*H), 128.5 (Ar*C*H), 126.4 (Ar*C*H), 118.8 (*C*N), 107.8 (Olefinic-*C*), 35.4 (*C*H$_2$), 31.3 (*C*H$_2$), 28.2 (*C*H$_2$), 28.0, 25.9 (*C*H$_2$), 21.4 (*C*H$_3$). HRMS (ESI) m/z calcd for $C_{15}H_{18}N$ $(M+H)^+$: 212.1434, found: 212.1438.

2-(benzo[d][1,3]dioxol-5-yl)-2-(4-methylcyclohexylidene)acetonitrile (**4c**)



Pale yellow liquid, 75% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 6.71 – 6.85 (m, 3 H, ArC*H*), 5.99 (s, 2 H, OCH_2), 2.99 – 3.10 (m, 1 H, CH_2), 2.64 – 2.75 (m, 1 H, CH_2), 2.22 – 2.38 (m, 1 H, CH_2), 1.89 – 2.05 (m, 2 H, CH_2), 1.58 - 1.87 (m, 2 H, CH_2), 1.17 – 1.32 (m, 1 H, CH_2),0.98 – 1.13 (m, 1 H, CH_2), 0.94 (d, J = 6.4 Hz, 3 H, *C*H_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 161.3 (Olefinic-*C*), 147.8 (quat-*C*), 147.6(quat-*C*), 127.5 (quat-*C*), 123.1 (Ar*C*H), 118.7 (*C*N), 109.6 (Ar*C*H), 108.5 (Ar*C*H), 107.4 (Olefinic-*C*), 101.4 (O*C*H_2), 35.9 (*C*H_2), 35.8 (*C*H_2), 34.7 (*C*H_2), 32.0 (*C*H_2), 30.7 (*C*H_2), 21.4 (*C*H_3). HRMS (ESI) m/z calcd for $C_{16}H_{18}NO_2$ $(M+H)^+$: 256.1332, found: 256.1331.

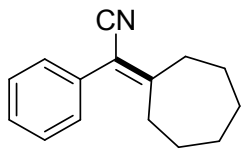
2-(3,5-dimethoxyphenyl)-2-(4-methylcyclohexylidene)acetonitrile (**4d**)



Colorless liquid, 85% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 6.40 – 6.44 (m, 3 H, ArC*H*), 3.79 (s, 6 H, OCH_3), 3.00 – 3.11 (m, 1 H, CH_2), 2.67 – 2.78 (m, 1 H, CH_2), 2.23 – 2.39 (m, 1 H, CH_2), 1.91 – 2.06 (m, 2 H, CH_2), 1.58 - 1.85 (m, 2 H, CH_2), 1.19 – 1.27 (m, 1 H, CH_2),0.99 – 1.15 (m, 1 H, CH_2), 0.94 (d, J = 6.4 Hz, 3 H, *C*H_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 162.0 (Olefinic-*C*), 160.9 (quat-*C*), 135.7 (quat-*C*), 118.5 (*C*N), 107.7 (Ar*C*H), 107.4

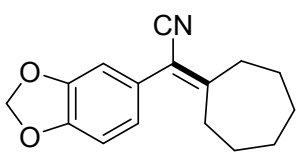
(Olefinic-*C*), 100.3 (Ar*C*H), 55.4 (O*C*H_3), 36.0 (*C*H_2), 35.9 (*C*H_2), 34.7 (*C*H_2), 32.0 (*C*H_2), 30.8 (*C*H_2), 21.4 (*C*H_3). HRMS (ESI) m/z calcd for $C_{17}H_{22}NO_2$ $(M+H)^+$: 272.1645, found: 272.1643.

2-cycloheptylidene-2-phenylacetonitrile (**4e**)



Colorless liquid, 88% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 7.25 – 7.39 (m, 5 H, ArC*H*), 2.80 (t, *J* = 5.9 Hz, 2 H, CH_2), 2.42 (t, *J* = 5.8 Hz, 2 H, CH_2), 1.74 - 1.80 (m, 2 H, CH_2), 1.56 - 1.66 (m, 6 H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 164.5 (Olefinic-*C*), 134.4 (quat-*C*), 129.1 (Ar*C*H), 128.7 (Ar*C*H), 128.2 (Ar*C*H), 118.8 (*C*N), 110.5 (Olefinic-*C*), 36.2 (*C*H_2), 32.9 (*C*H_2), 29.6 (*C*H_2), 28.8 (*C*H_2), 27.3 (*C*H_2), 27.0 (*C*H_2). HRMS (ESI) m/z calcd for $C_{15}H_{18}N$ $(M+H)^+$: 212.1434, found: 212.1436.

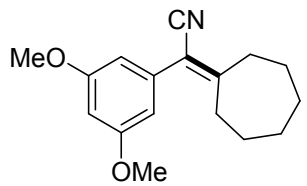
2-(benzo[*d*][1,3]dioxol-5-yl)-2-cycloheptylideneacetonitrile (**4f**)



Colorless liquid, 70% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 6.72 – 6.84 (m, 3 H, ArC*H*), 5.99 (s, 2 H, OCH_2), 2.77 (t, *J* = 5.9 Hz, 2 H, CH_2), 2.42 (t, *J* = 5.8 Hz, 2 H, CH_2), 1.73

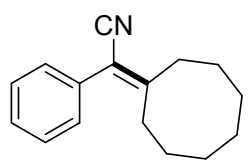
- 1.79 (m, 2 H, CH_2), 1.56 - 1.60 (m, 6 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 164.3 (Olefinic-*C*), 147.8 (quat-*C*), 147.5 (quat-*C*), 128.0 (quat-*C*), 122.9 (Ar*C*H), 118.8 (*C*N), 110.0 (Olefinic-*C*), 109.5 (Ar*C*H), 108.4(Ar*C*H), 101.4 (O*C*H_2), 36.0 (*C*H_2), 32.9 (*C*H_2), 29.6 (*C*H_2), 28.8 (*C*H_2), 27.3 (*C*H_2), 26.9 (*C*H_2). HRMS (ESI) m/z calcd for $C_{16}H_{18}NO_2$ $(M+H)^+$: 256.1332, found: 256.1331.

2-cycloheptylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**4g**)



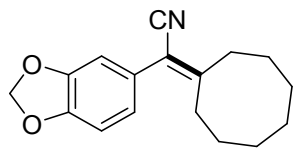
Colorless liquid, 80% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 6.41 – 6.46 (m, 3 H, Ar*CH*), 3.79 (s, 6 H, O*C*H_3), 2.78 (t, *J* = 5.9 Hz, 2 H, CH_2), 2.44 (t, *J* = 5.9 Hz, 2 H, CH_2), 1.77 - 1.80 (m, 2 H, CH_2), 1.56 - 1.67 (m, 6 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 164.8 (Olefinic-*C*), 160.9 (quat-*C*), 136.1 (quat-*C*), 118.6 (*C*N), 110.3 (Olefinic-*C*), 107.2 (Ar*C*H), 100.2(Ar*C*H), 55.4 (O*C*H_3), 36.1 (*C*H_2), 32.9 (*C*H_2), 29.6 (*C*H_2), 28.8 (*C*H_2), 27.2 (*C*H_2), 27.0 (*C*H_2). HRMS (ESI) m/z calcd for $C_{17}H_{22}NO_2$ $(M+H)^+$: 272.1644, found: 272.1642.

2-cyclooctylidene-2-phenylacetonitrile (**4h**)



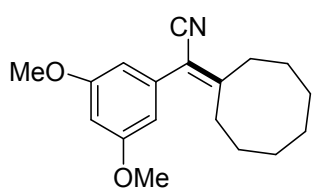
Colorless liquid, 70% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 7.26 – 7.40 (m, 5 H, ArC*H*), 2.70 (t, *J* = 6.2 Hz, 2 H, CH_2), 2.36 (t, *J* = 5.9 Hz, 2 H, CH_2), 1.96 - 1.98 (m, 2 H, CH_2), 1.49 - 1.66 (m, 8 H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 166.3 (Olefinic-*C*), 134.5 (quat-*C*), 129.1 (Ar*C*H), 128.8 (Ar*C*H), 128.2 (Ar*C*H), 119.0 (*C*N), 109.8 (Olefinic-*C*), 34.3 (*C*H_2), 32.8 (*C*H_2), 28.5 (*C*H_2), 27.7 (*C*H_2), 25.9 (*C*H_2), 25.5 (*C*H_2), 23.7(*C*H_2). HRMS (ESI) m/z calcd for $C_{16}H_{20}N$ $(M+H)^+$: 226.1590, found: 226.1590.

2-(benzo[*d*][1,3]dioxol-5-yl)-2-cyclooctylideneacetonitrile (**4i**)



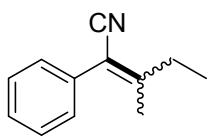
Colorless liquid, 65% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 6.71 – 6.85 (m, 3 H, ArC*H*), 6.00 (s, 2 H, OCH_2), 2.67 (t, *J* = 5.9 Hz, 2 H, CH_2), 2.34 (t, *J* = 5.8 Hz, 2 H, CH_2), 1.87 - 1.99 (m, 2 H, CH_2), 1.52 - 1.60 (m, 2 H, CH_2), 1.47 - 1.48 (m, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 166.1 (Olefinic-*C*), 147.9 (quat-*C*), 147.4 (quat-*C*), 128.1 (quat-*C*), 122.8 (Ar*C*H), 118.9 (*C*N), 109.4 (Ar*C*H), 109.3 (Olefinic-*C*), 108.6 (Ar*C*H), 101.4 (O*C*H_2), 34.2 (*C*H_2), 32.8 (*C*H_2), 28.4 (*C*H_2), 27.7 (*C*H_2), 25.9 (*C*H_2), 25.5 (*C*H_2), 23.7 (*C*H_2). HRMS (ESI) m/z calcd for $C_{17}H_{20}NO_2$ $(M+H)^+$: 270.1489, found: 270.1486.

2-cyclooctylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**4j)**



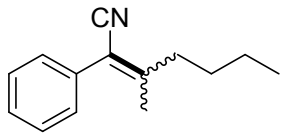
Colorless liquid, 70% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ ppm 6.41 – 6.42 (m, 3 H, ArC*H*), 3.80 (s, 6 H, OCH_3), 2.65 – 2.71 (m, 2 H, CH_2), 2.35 – 2.41 (m, 2 H, CH_2), 1.88 - 2.00 (m, 2 H, CH_2), 1.65 - 1.65 (m, 2 H, CH_2), 1.54 - 1.62 (m, 2 H, CH_2), 1.49 – 1.50 (m, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ ppm 166.6 (Olefinic-*C*), 160.9 (quat-*C*), 136.3 (quat-*C*), 118.8 (*C*N), 109.6 (Olefinic-*C*), 107.2 (Ar*C*H), 100.1 (Ar*C*H), 55.4 (O*C*H_3), 34.2 (*C*H_2), 32.9 (*C*H_2), 28.5 (*C*H_2), 27.7 (*C*H_2), 25.8 (*C*H_2), 25.5 (*C*H_2), 23.7 (*C*H_2). HRMS (ESI) m/z calcd for $C_{18}H_{24}NO_2$ $(M+H)^+$: 286.1802, found: 286.1797.

3-methyl-2-phenylpent-2-enenitrile (**4k**)



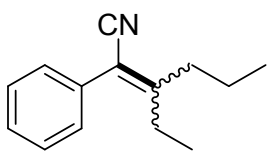
Pale yellow liquid, 55% isolated yield. Isomer ratio = 56:44 (Z/E) (according to ^{1}H NMR).^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.27 – 7.41 (m, 10 H, ArC*H*) – both isomers, 2.61 (q, *J* = 7.6 Hz, 2 H, CH_2) - major, 2.22 (q, *J* = 7.6 Hz, 2 H, CH_2) - minor, 2.23 (s, 3 H, CH_3) - minor, 1.90 (s, 3 H, CH_3) - major, 1.22 (t, *J* = 7.6 Hz, 3 H, CH_3) – major, 1.06 (t, *J* = 7.6 Hz, 3 H, CH_3) – minor.^{13}C NMR (100.6 MHz, $CDCl_3$): δ ppm 160.2, 160.0 (Olefinic-*C*), 134.3, 134.2 (quat-*C*), 129.2, 129.0 (Ar*C*H), 128.8, 128.7 (Ar*C*H), 128.4, 128.3 (Ar*C*H), 119.0, 118.7 (*C*N), 110.8, 110.3 (Olefinic-*C*), 31.9, 27.6(CH_3*C*H_2), 21.9, 19.2 (*C*H_3C=), 12.7, 12.5 (*C*H_3*C*H_2). HRMS (ESI) m/z calcd for $C_{12}H_{14}N$ $(M+H)^+$: 172.1121, found: 172.1123.

3-methyl-2-phenylhept-2-enenitrile (**4l**)



Colorless liquid, 50% isolated yield. Isomer ratio = 61:39 (Z/E) (according to ^{1}H NMR).^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.37 – 7.40 (m, 5 H, ArC*H*) – minor, 7.25 – 7.34 (m, 5 H, ArC*H*) – major, 2.58 (t, *J* = 7.6 Hz, 2 H, CH_2) - major, 2.22 (s, 3 H, CH_3) - minor, 2.19 (t, *J* = 7.7 Hz, 2 H, CH_2) - minor, 1.89 (s, 3 H, CH_3) - major, 1.59 (quint, *J* = 7.6 Hz, 2 H, CH_2) – major, 1.40 – 1.48 (m,4 H, CH_2) – both isomers, 1.19 – 1.27 (m, 2 H, CH_2) – minor, 0.98 (t, *J* = 7.4 Hz, 3 H, CH_3) – major, 0.82 (t, *J* = 7.4 Hz, 3 H, CH_3) – minor. ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 158.9, 158.8 (Olefinic-*C*), 134.3, 134.2 (quat-*C*), 129.2, 129.0 (Ar*C*H), 128.7, 128.6 (Ar*C*H), 128.3, 128.2 (Ar*C*H), 118.9, 118.8 (*C*N), 111.1, 110.9 (Olefinic-*C*), 38.4, 34.0(*C*H_3C=), 30.2, 29.9 (*C*H_2), 22.5(*C*H_2), 22.0, 19.5 (*C*H_2), 13.9, 13.7 (*C*H_3). HRMS (ESI) m/z calcd for $C_{14}H_{18}N$ $(M+H)^+$: 200.1434, found: 200.1438.

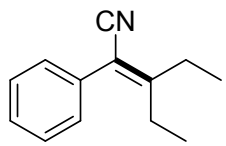
3-ethyl-2-phenylhex-2-enenitrile (**4m**)



Colorless liquid, 58% isolated yield. Isomer ratio = 53:47 (Z/E) (according to ^{1}H NMR).^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.30 – 7.40 (m, 5 H, ArC*H*) – major, 7.24 – 7.28 (m, 5 H, ArC*H*) – minor, 2.53 – 2.61 (m, 4 H, CH_2) – both isomers, 2.15 - 2.23 (m, 4 H, CH_2) - both

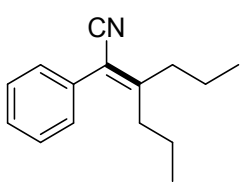
isomers, 1.58 –1.67 (m, 2 H, CH_2) - major, 1.40 - 1.49 (m, 2 H, CH_2) - minor, 1.20 (t, J = 7.6 Hz, 2 H, CH_2) – minor, 1.04 (t, J = 7.6 Hz, 2 H, CH_2) – major, 1.01 (t, J = 7.6 Hz, 2 H, CH_2) – major, 0.82 (t, J = 7.6 Hz, 3 H, CH_3) – minor. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ ppm 164.4, 164.1 (Olefinic-*C*), 134.3 (quat-*C*), 129.2, 129.1 (Ar*C*H), 128.8, 128.3 (Ar*C*H), 119.0, 118.8 (*C*N), 111.0, 110.7 (Olefinic-*C*), 36.9, 33.5 (*C*H_2), 28.2, 25.0 (CH_3*C*H_2C=), 21.7, 21.3 (*C*H_2), 14.1, 14.0 (*C*H_3), 13.0, 12.7 (*C*H_3CH_2). HRMS (ESI) m/z calcd for $C_{14}H_{18}N$ $(M+H)^+$: 200.1434, found: 200.1438.

3-ethyl-2-phenylpent-2-enenitrile (**4n**)



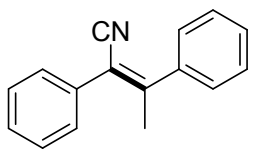
Colorless liquid, 62% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.26 – 7.40 (m, 5 H, Ar*C*H), 2.61 (q, J = 7.7 Hz, 2 H, CH_2), 2.24 (q, J = 7.7 Hz, 2 H, CH_2), 1.21 (t, J = 7.7 Hz, 3 H, CH_3), 1.03 (t, J = 7.7 Hz, 3 H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 165.5 (Olefinic-*C*), 134.2 (quat-*C*), 129.0 (Ar*C*H), 128.7 (Ar*C*H), 128.3 (Ar*C*H), 118.7 (*C*N), 110.3(Olefinic-*C*), 28.3 (*C*H_2), 24.6 (*C*H_2), 12.9 (*C*H_3), 12.5 (*C*H_3). HRMS (ESI) m/z calcd for $C_{13}H_{16}N$ $(M+H)^+$: 186.1199, found: 186.1328.

2-phenyl-3-propylhex-2-enenitrile (**4o**)



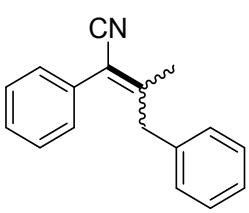
Colorless liquid, 50% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.24 – 7.39 (m, 5 H, ArC*H*), 2.56 (t, *J* = 7.7 Hz, 2 H, CH_2), 2.17 (t, *J* = 7.9 Hz, 2 H, CH_2), 1.54 – 1.73 (m, 2 H, CH_2), 1.35– 1.50 (m, 2 H, CH_2),1.04 (t, *J* = 7.2 Hz, 3 H, CH_3),0.82 (t, *J* = 7.2 Hz, 3 H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 162.8 (Olefinic-*C*), 134.4 (quat-*C*), 129.1 (Ar*C*H), 128.7 (Ar*C*H), 128.2 (Ar*C*H), 118.9 (*C*N), 111.4 (Olefinic-*C*), 37.2 (*C*H_2), 33.7 (*C*H_2), 21.7 (*C*H_2), 21.3 (*C*H_2), 14.0 (*C*H_3), 13.9 (*C*H_3). HRMS (ESI) m/z calcd for $C_{15}H_{20}N$ $(M+H)^+$: 214.1590, found: 214.1595.

(Z)-2,3-diphenylbut-2-enenitrile (**4p**)



Colorless liquid, 20% isolated yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.84 – 7.87 (m, 2 H, ArC*H*), 7.35 – 7.50 (m, 3 H, ArC*H*), 7.19 – 7.25 (m, 5 H, ArC*H*) 2.50 (s, 3 H, CH_3). ^{13}C NMR (100.16 MHz, $CDCl_3$): δ ppm 155.1 (Olefinic-*C*), 139.2, (quat-*C*), 133.0 (quat-*C*), 129.5 (Ar*C*H), 128.6 (Ar*C*H), 128.1 (Ar*C*H), 126.9 (Ar*C*H), 119.1 (*C*N), 112.0 (Olefinic-*C*), 21.9 (*C*H_3). HRMS (ESI) m/z calcd for $C_{16}H_{14}N$ $(M+H)^+$: 220.1121, found: 220.1122.

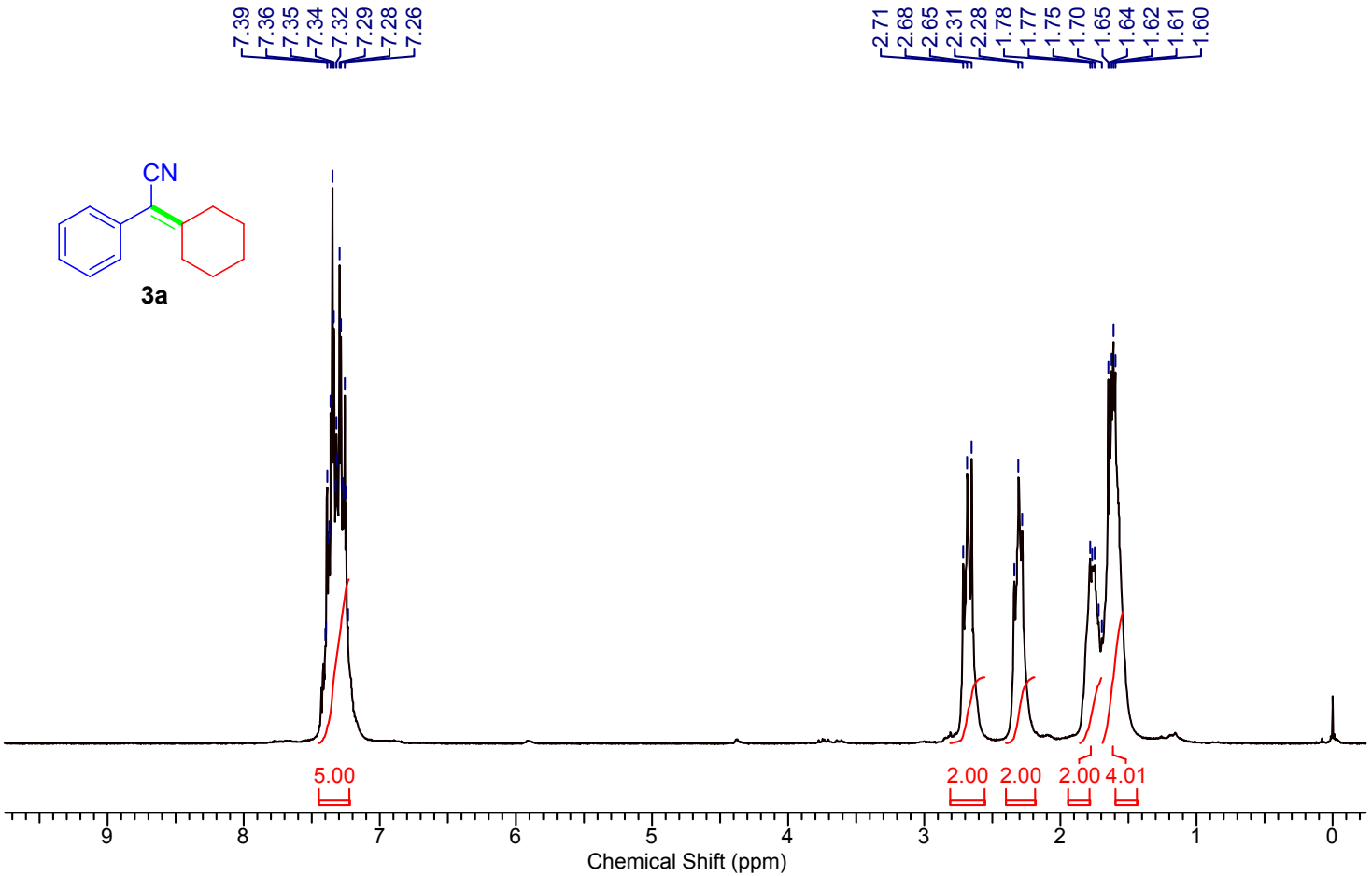
3-methyl-2,4-diphenylbut-2-enenitrile (**4q**)



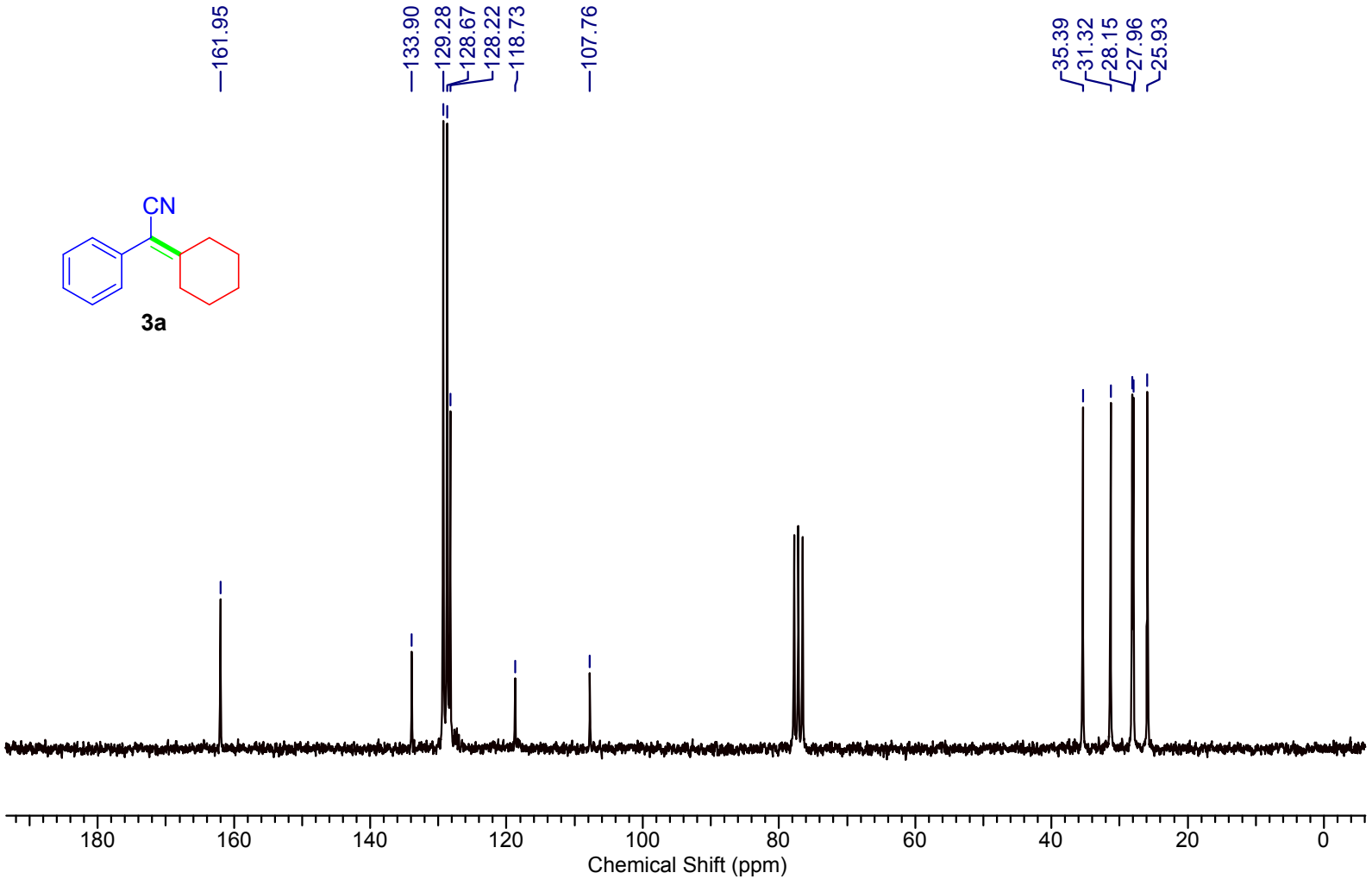
Colorless liquid, 60% isolated yield. Isomer ratio = 61:39 (Z/E) (according to ^{1}H NMR).^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.25 – 7.39 (m, 20 H, ArC*H*) – both isomers, 3.90 (s, 2 H, CH_2) - major, 3.57 (s, 2 H, CH_2) - minor, 2.14 (s, 3 H, CH_3),1.80 (s, 3 H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ ppm 156.7, 156.1 (Olefinic-*C*), 137.4, (quat-*C*), 133.9, 133.8 (quat-*C*), 129.2, 129.0 (Ar*C*H), 129.0, 128.9 (Ar*C*H), 128.8, 128.7 (Ar*C*H), 128.6, 128.5 (Ar*C*H), 127.3, 127.1 (Ar*C*H), 126.9, 126.5 (Ar*C*H),119.1, 118.7 (*C*N), 112.7, 111.8 (Olefinic-*C*), 44.6, 40.1 (*C*H_2), 22.3, 19.4 (*C*H_3). HRMS (ESI) m/z calcd for $C_{17}H_{16}N$ $(M+H)^+$: 234.1277, found: 234.1275.

6. NMR spectra:

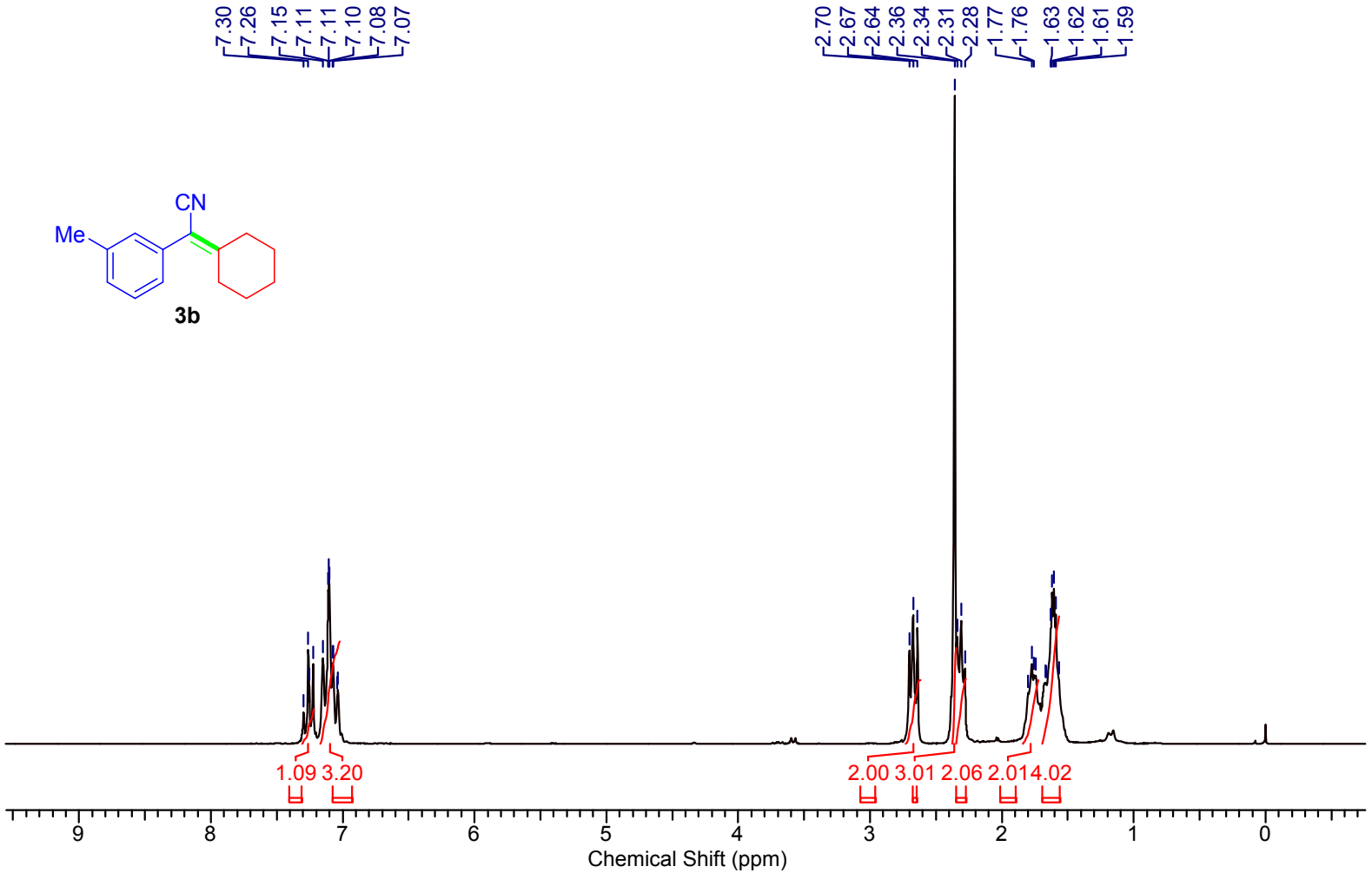
^{1}H NMR spectrum of 2-cyclohexylidene-2-phenylacetonitrile(**3a**)



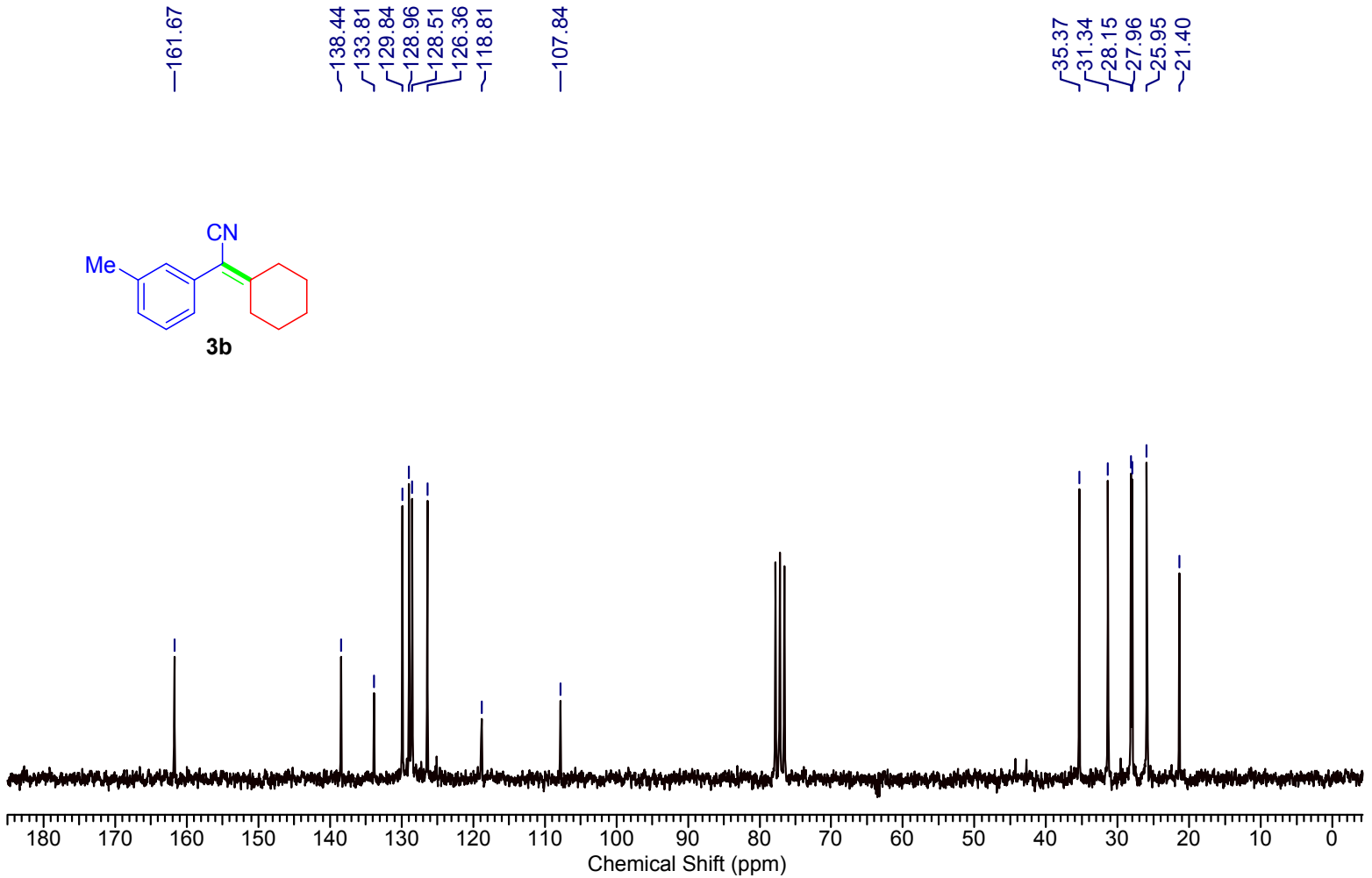
^{13}C NMR spectrum of 2-cyclohexylidene-2-phenylacetonitrile(**3a**)



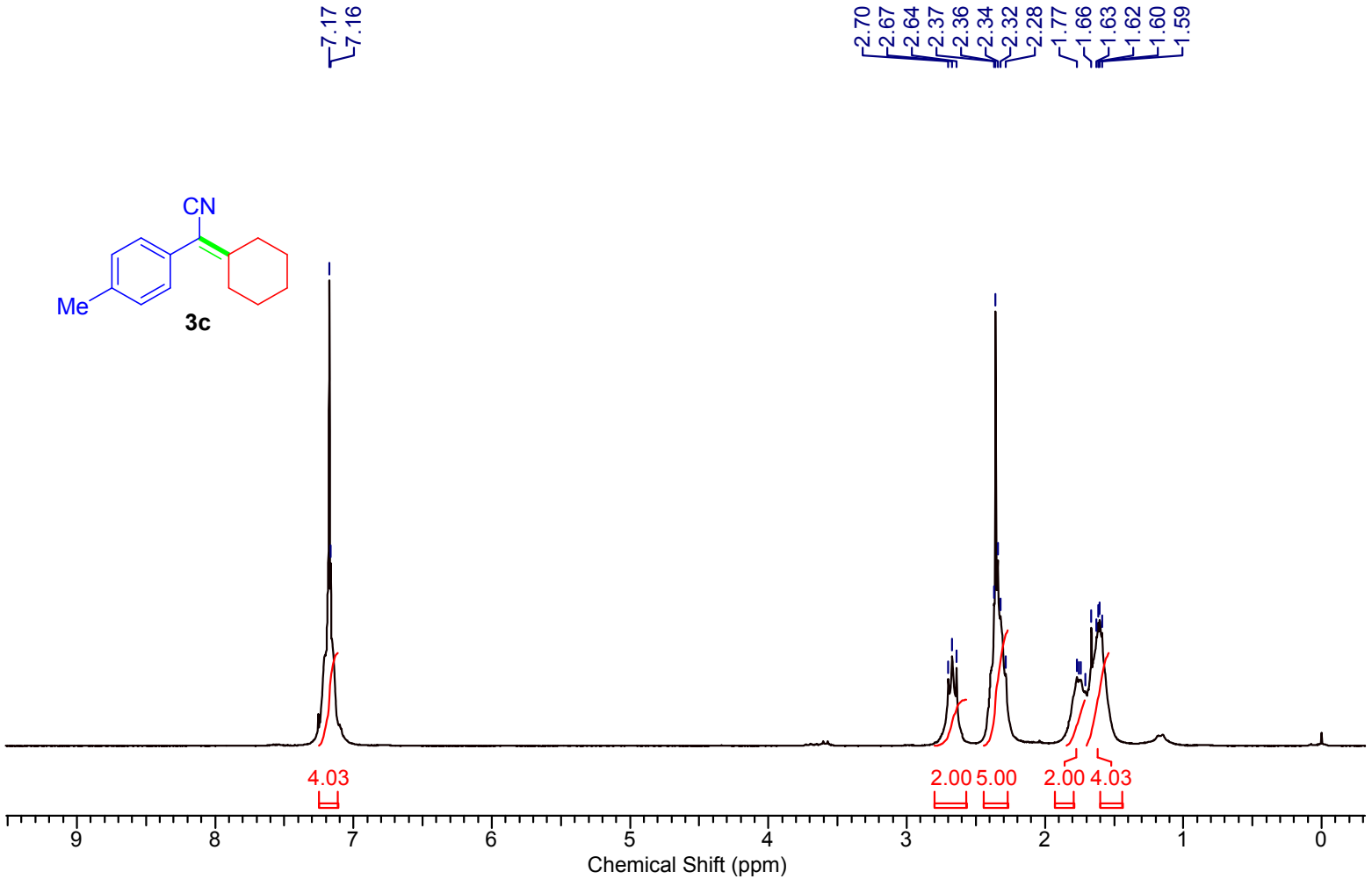
^{1}H NMR spectrum of 2-cyclohexylidene-2-(m-tolyl)acetonitrile (**3b**)



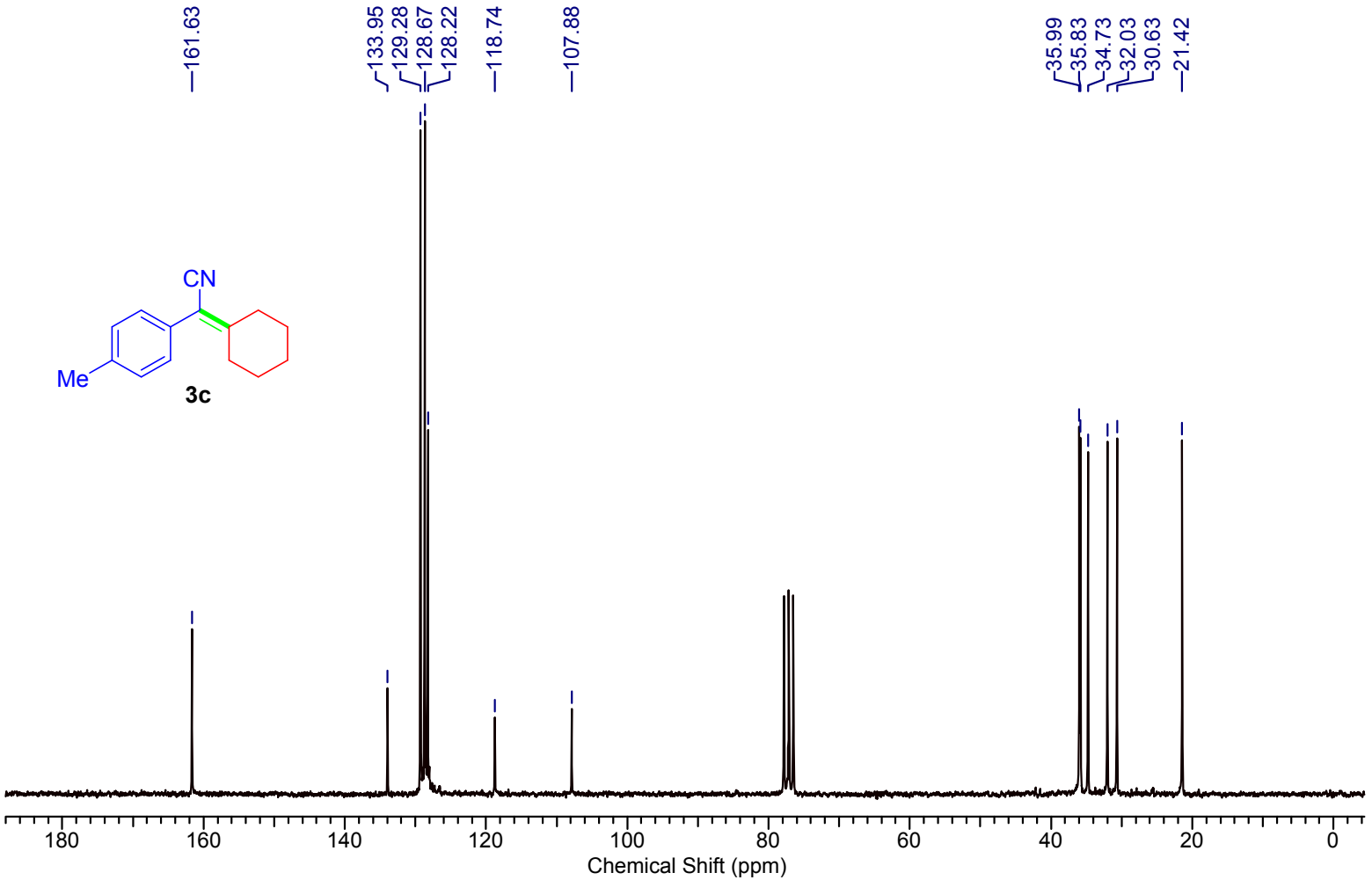
^{13}CNMR spectrum of 2-cyclohexylidene-2-(m-tolyl)acetonitrile (**3b**)



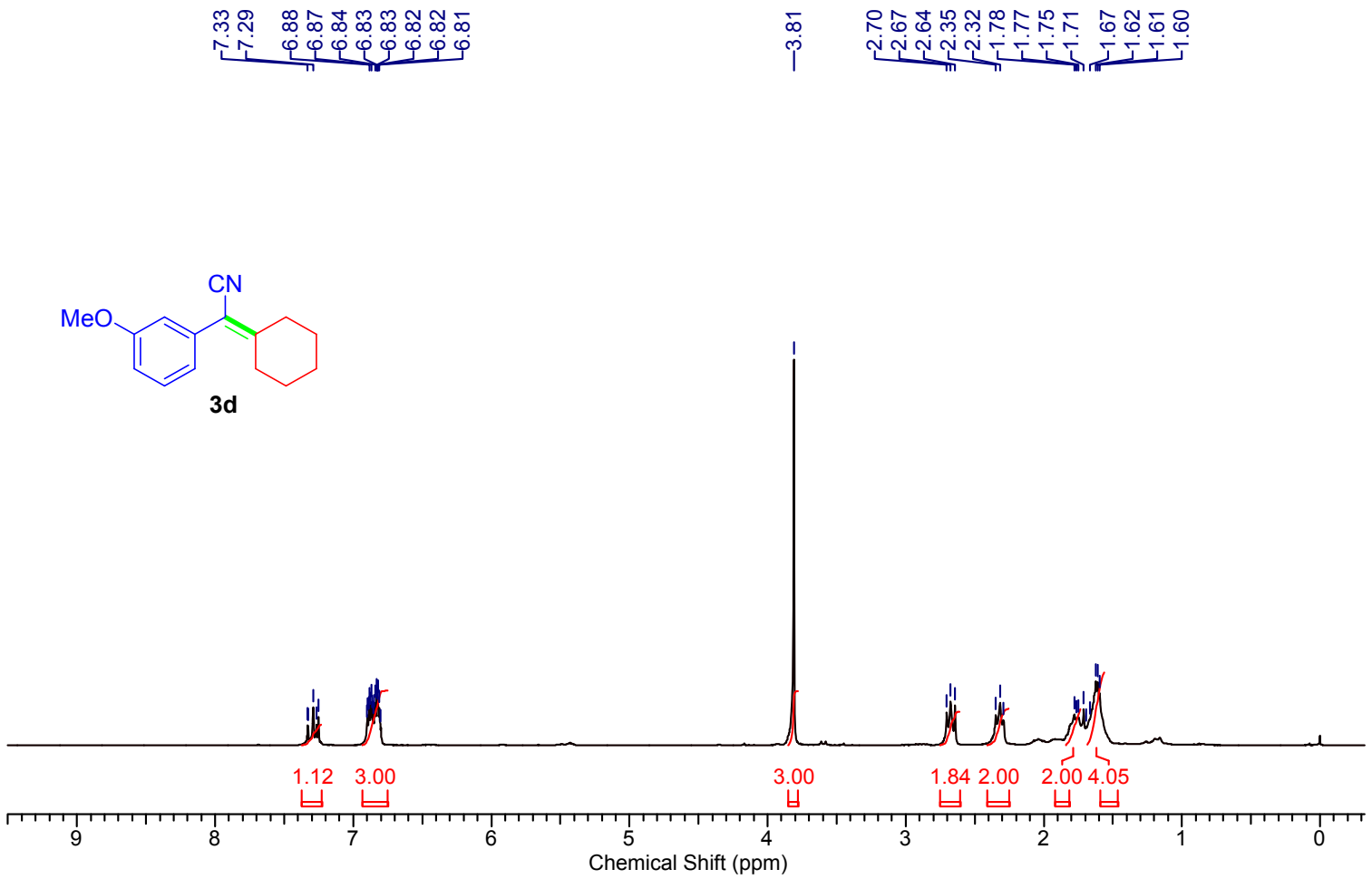
^{1}H NMR spectrum of 2-cyclohexylidene-2-(p-tolyl)acetonitrile (**3c**)



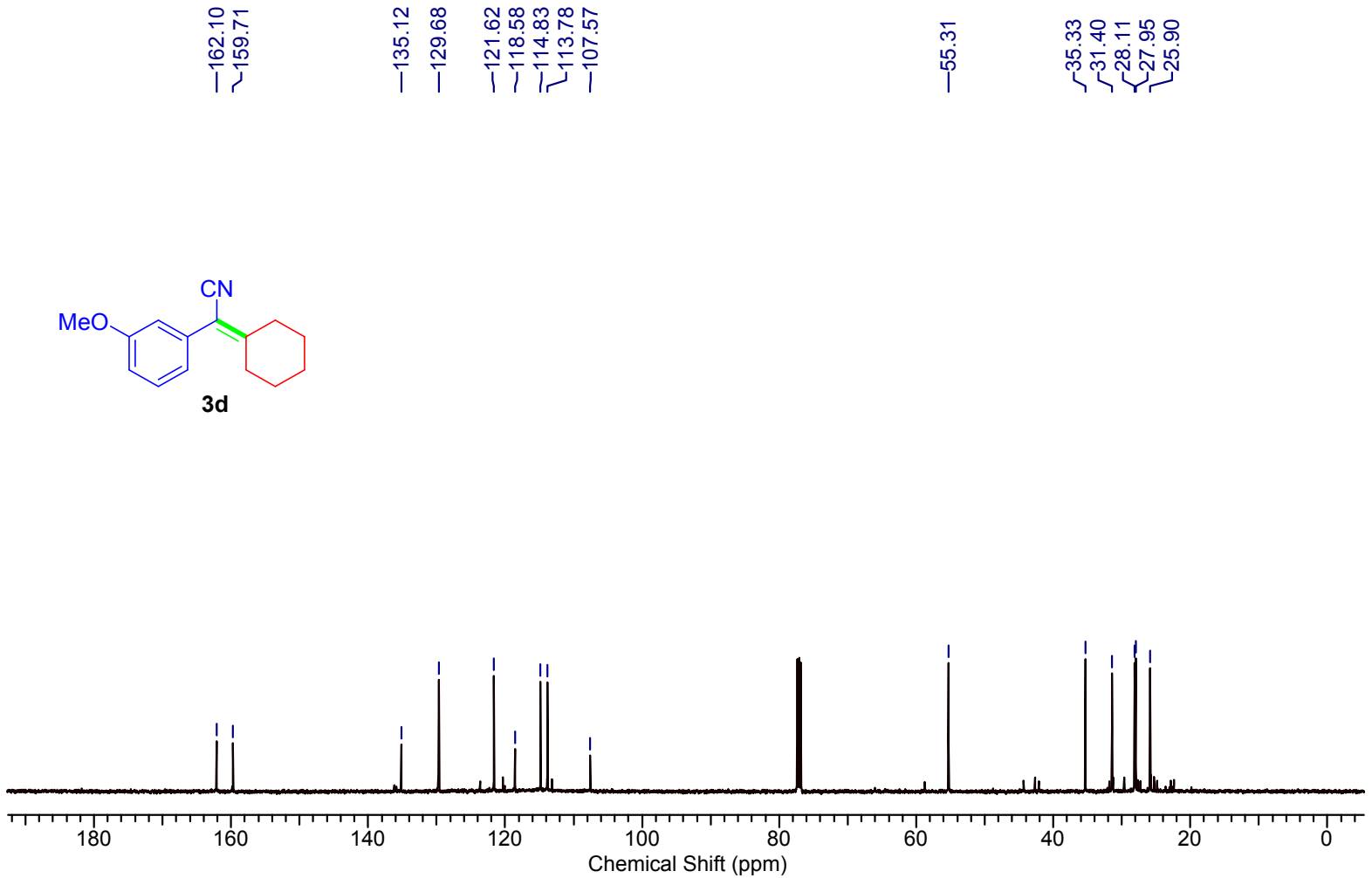
^{13}C NMR spectrum of 2-cyclohexylidene-2-(p-tolyl)acetonitrile (**3c**)



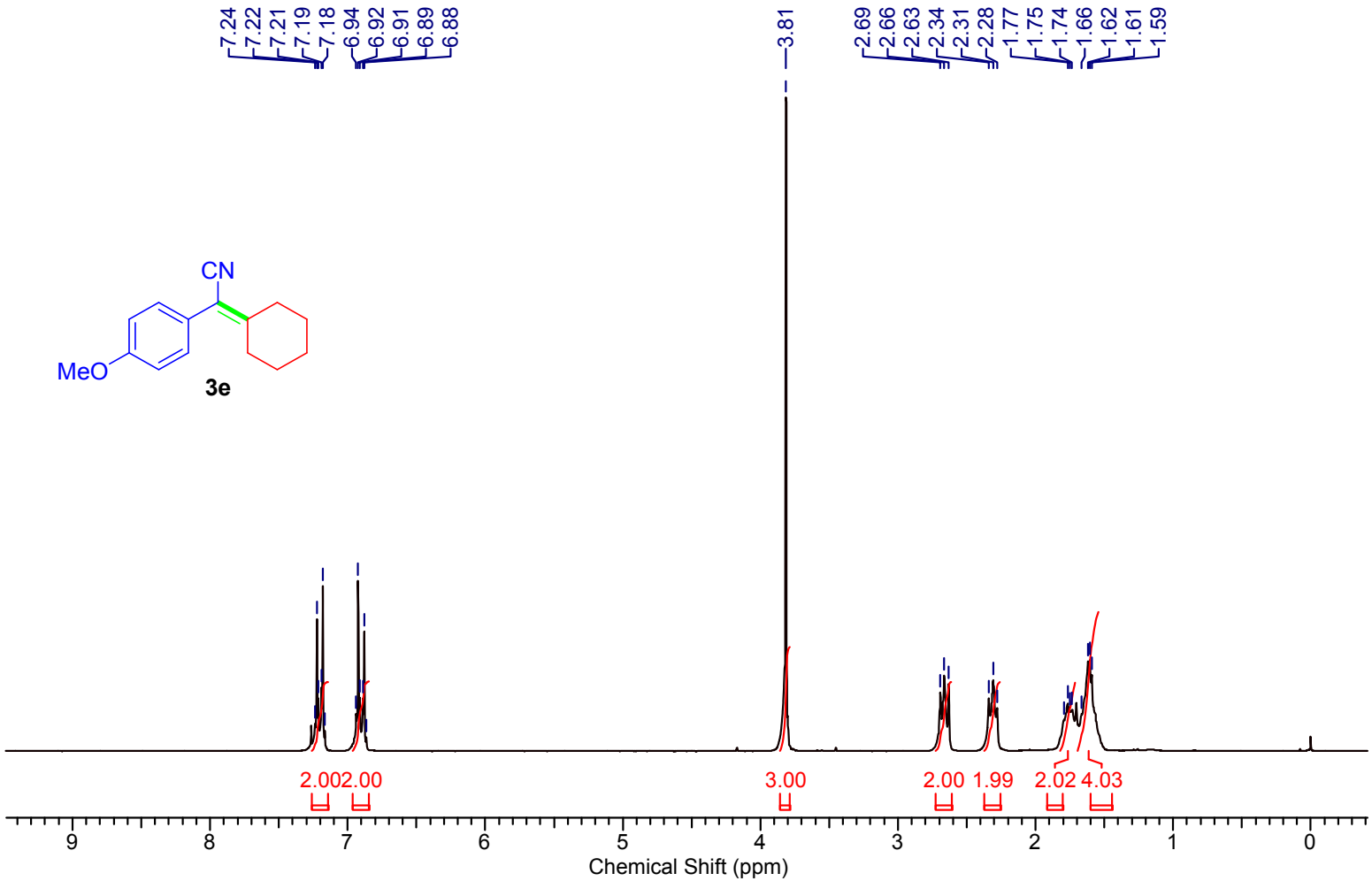
^{1}H NMR spectrum of 2-cyclohexylidene-2-(3-methoxyphenyl)acetonitrile (**3d**)



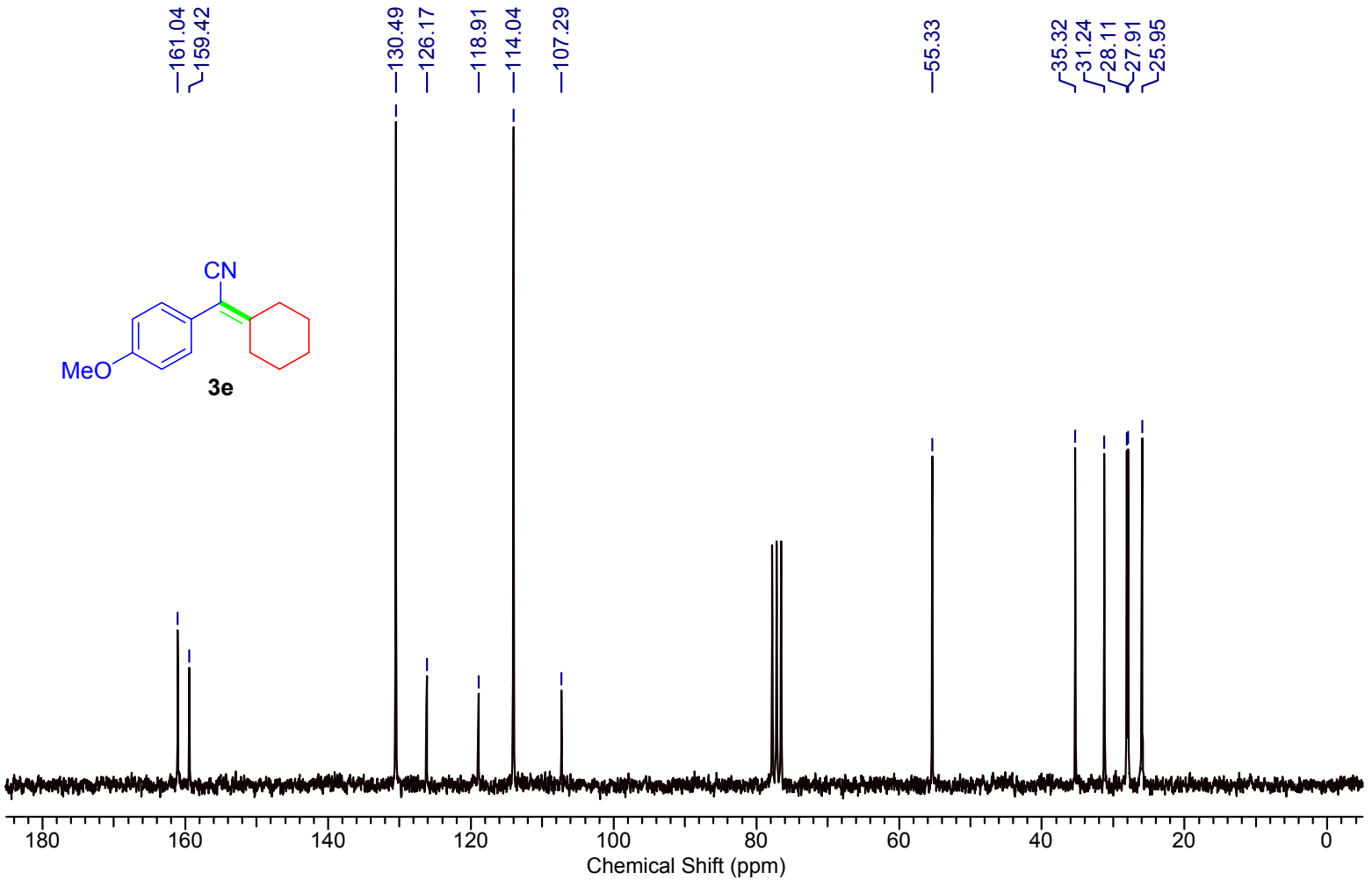
^{13}C NMR spectrum of 2-cyclohexylidene-2-(3-methoxyphenyl)acetonitrile (**3d**)



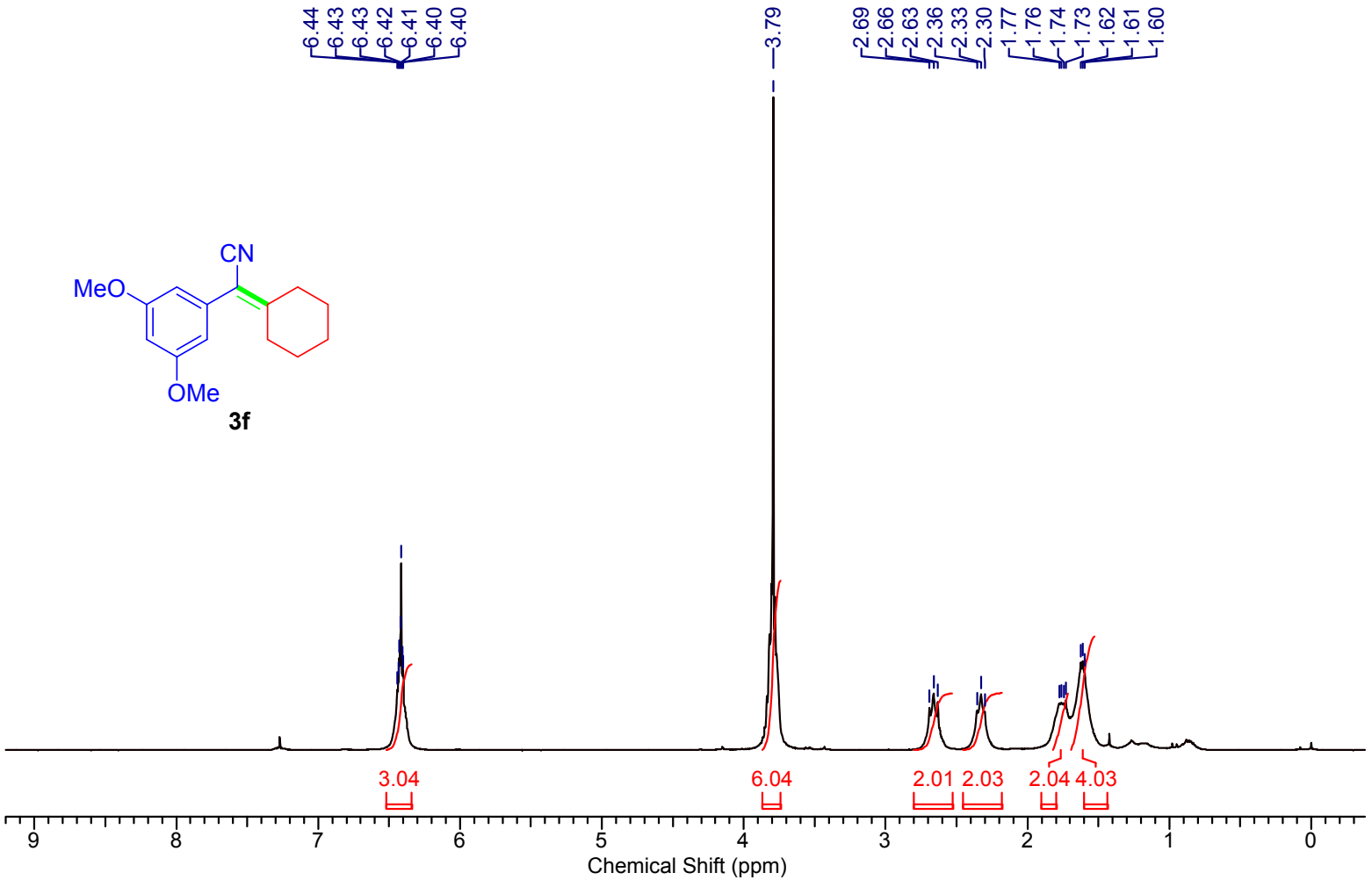
^{1}H NMR spectrum of 2-cyclohexylidene-2-(4-methoxyphenyl)acetonitrile (**3e**)



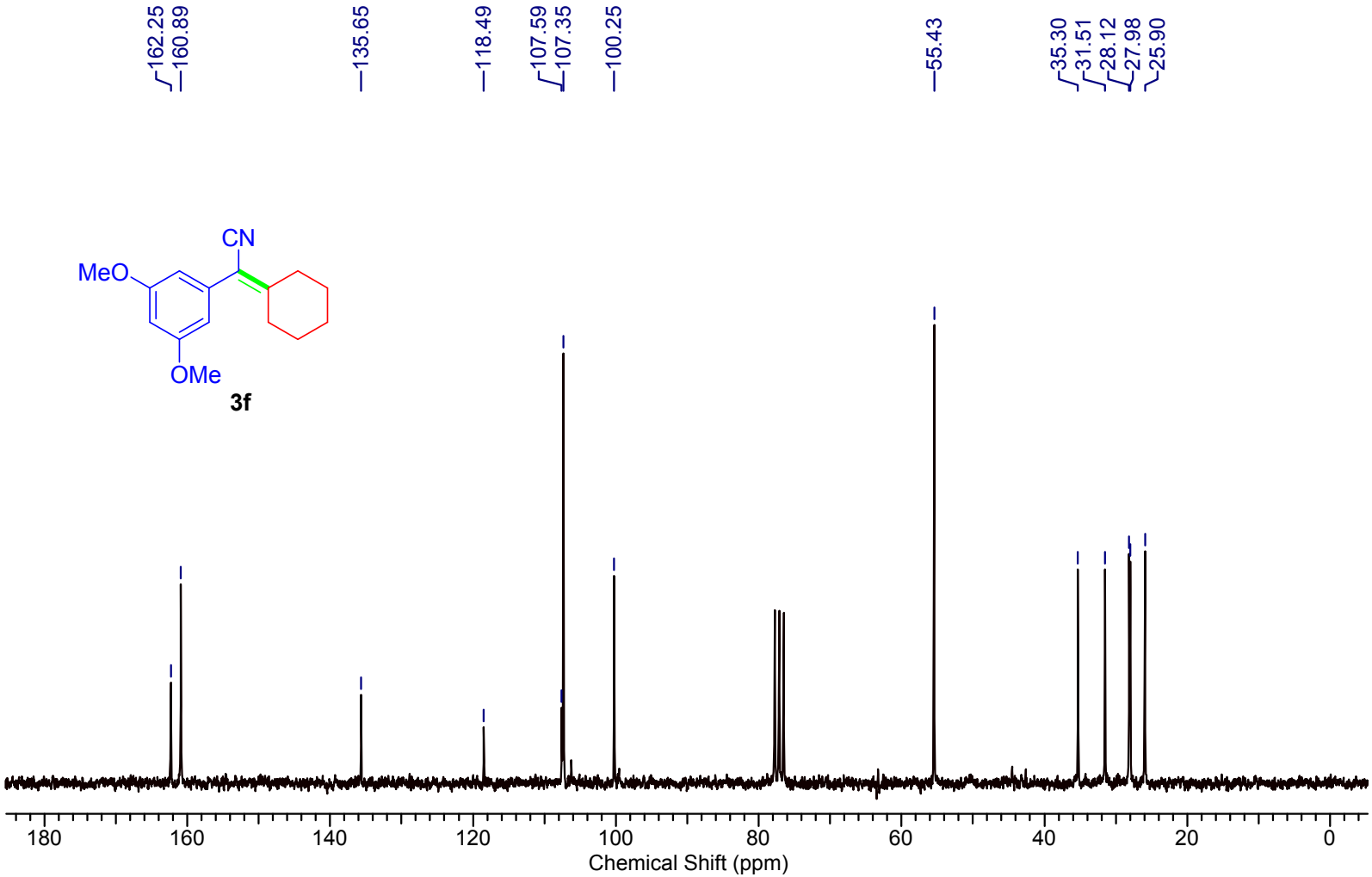
^{13}C NMR spectrum of 2-cyclohexylidene-2-(4-methoxyphenyl)acetonitrile (**3e**)



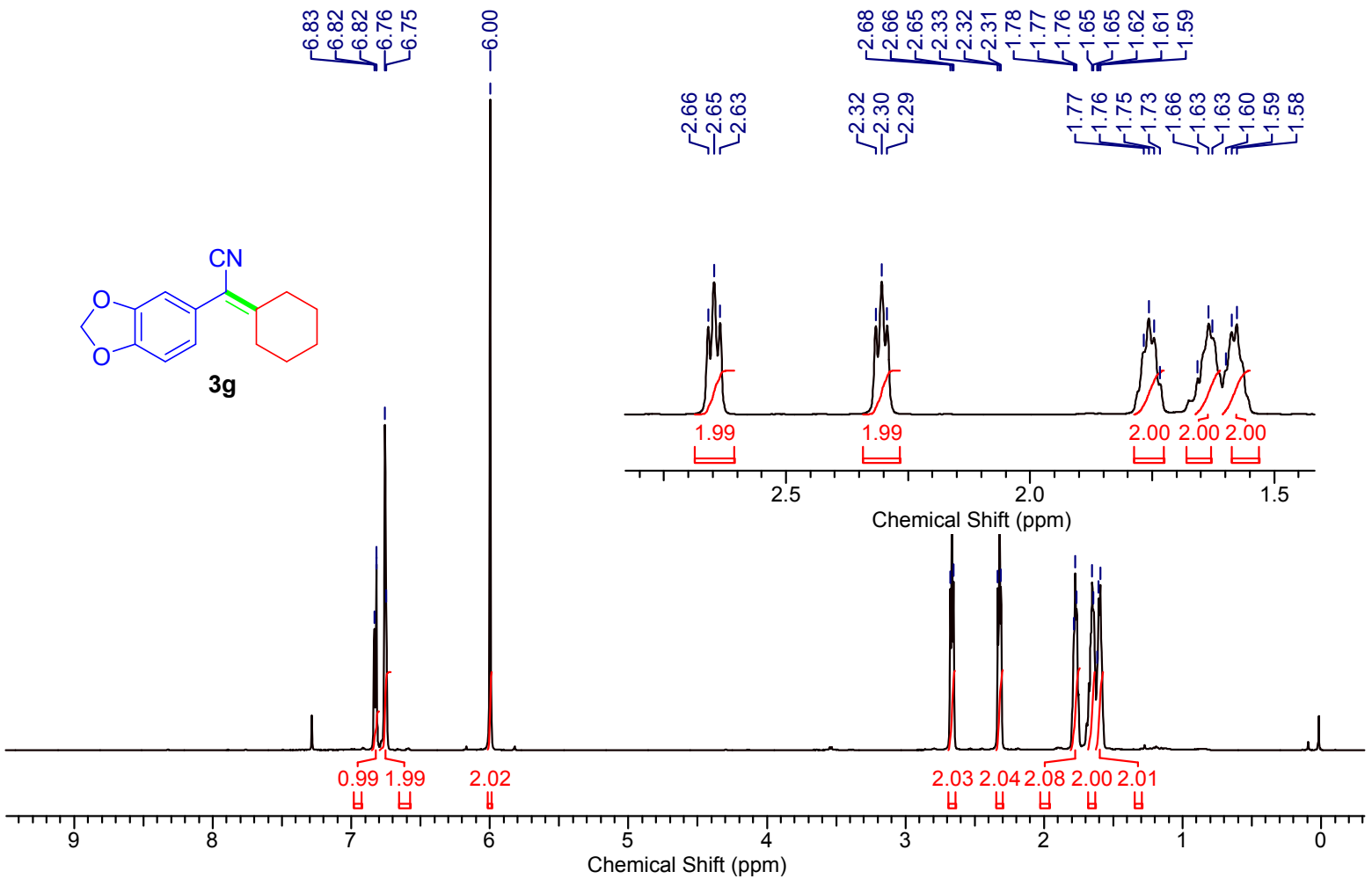
^{1}H NMR spectrum of 2-cyclohexylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**3f**)



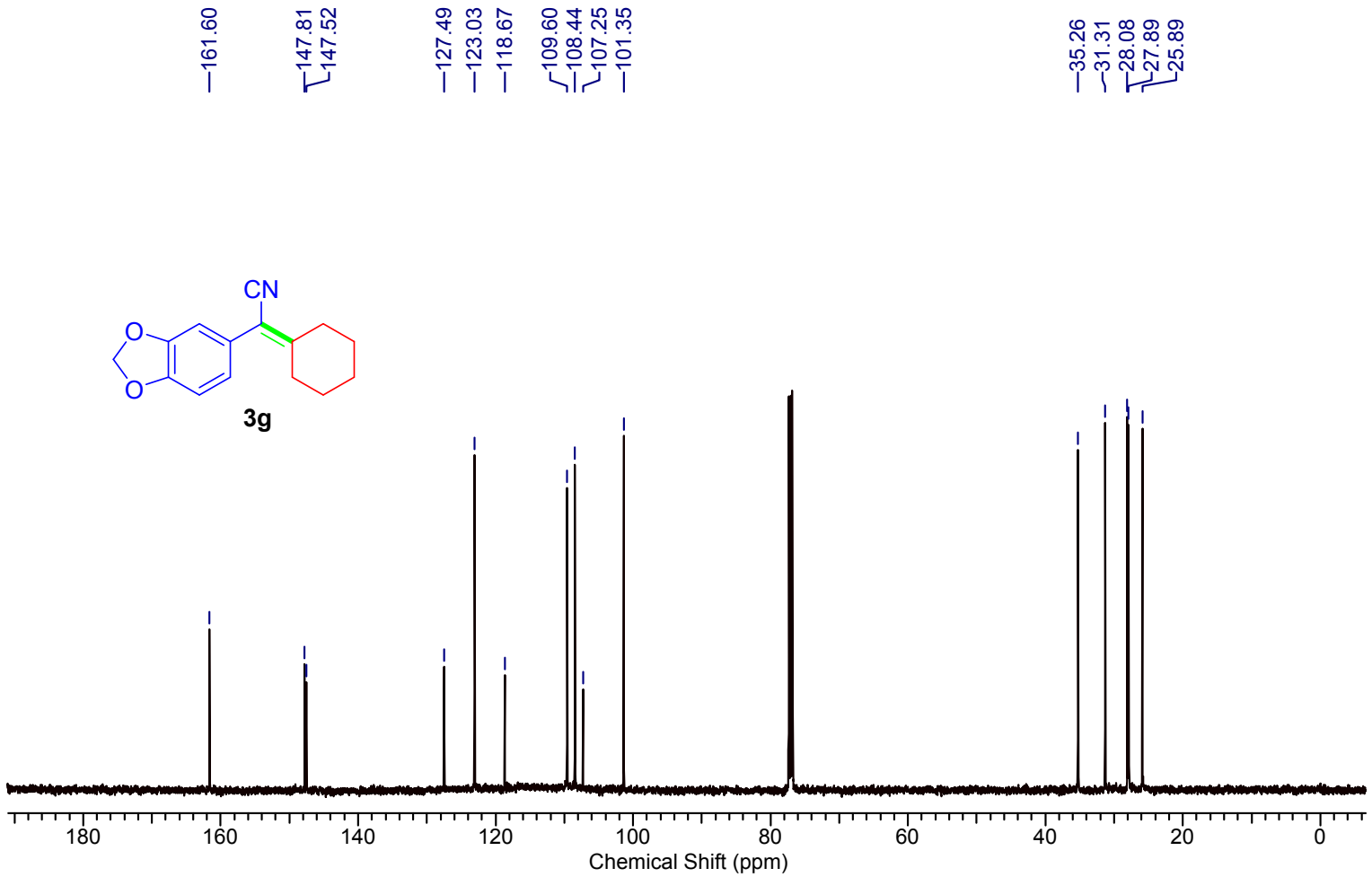
^{13}C NMR spectrum of 2-cyclohexylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**3f**)



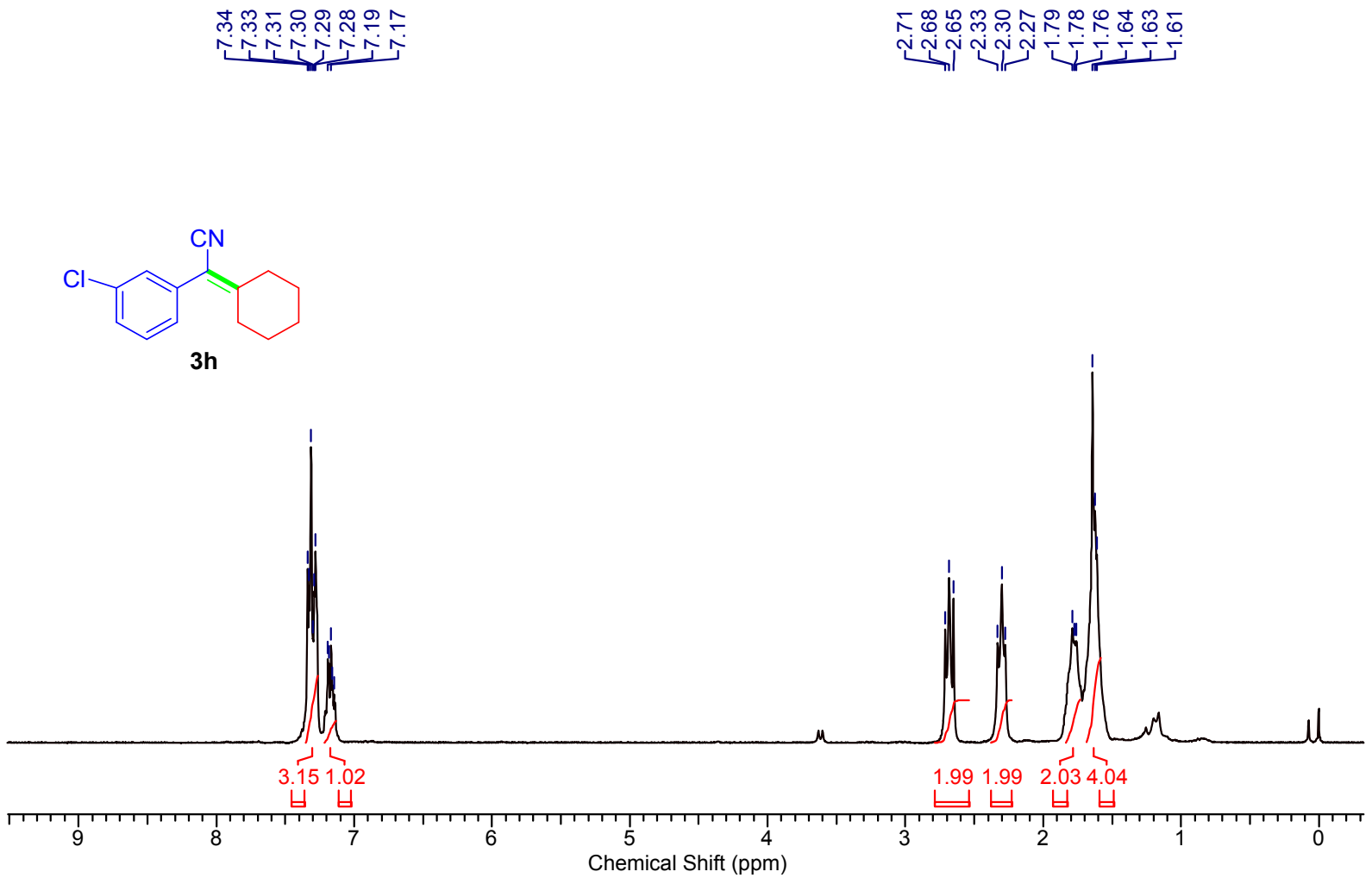
^{1}H NMR spectrum of 2-(benzo[d][1,3]dioxol-5-yl)-2-cyclohexylideneacetonitrile (**3g**)



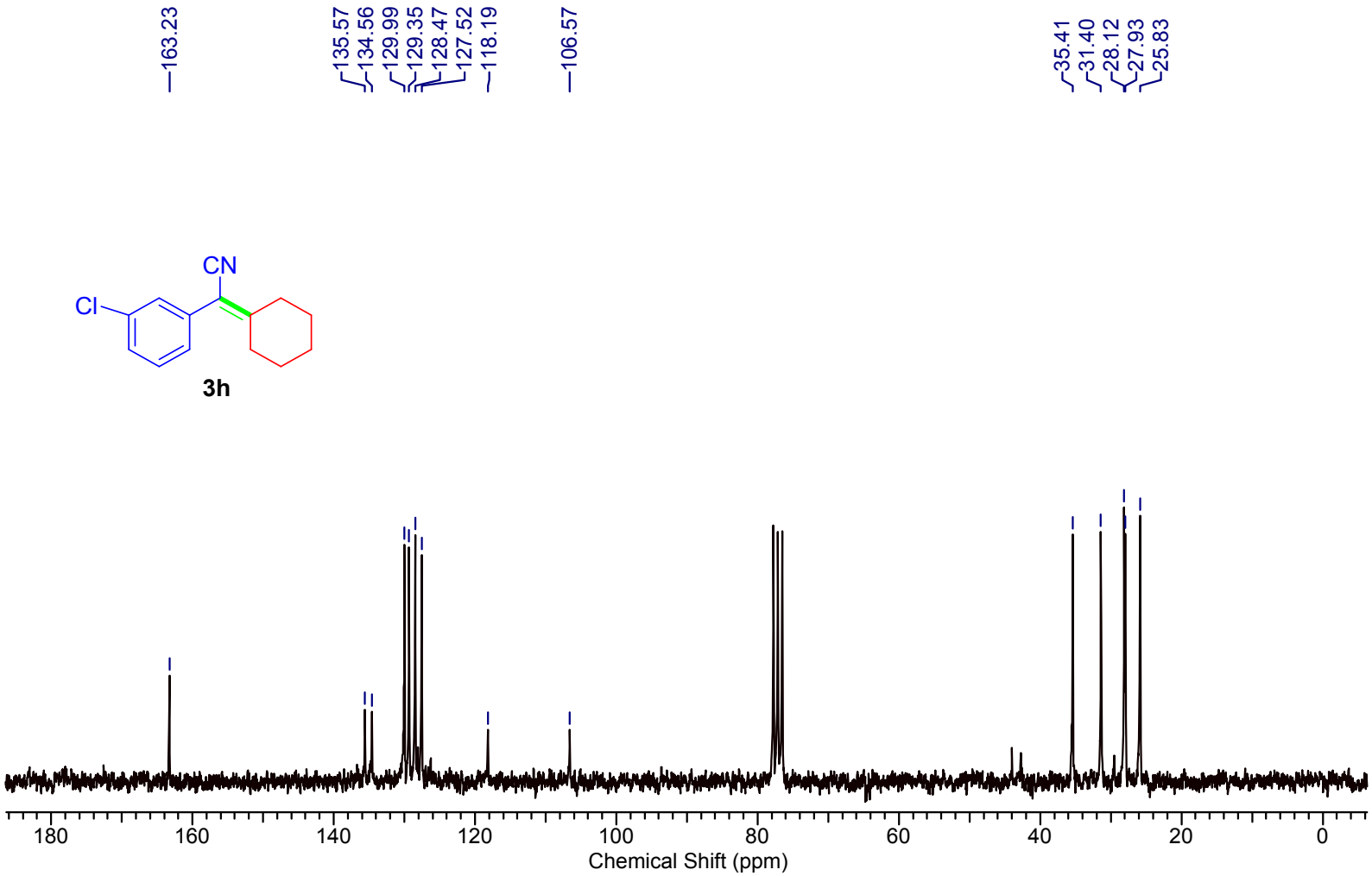
^{13}C NMR spectrum of 2-(benzo[d][1,3]dioxol-5-yl)-2-cyclohexylideneacetonitrile (**3g**)



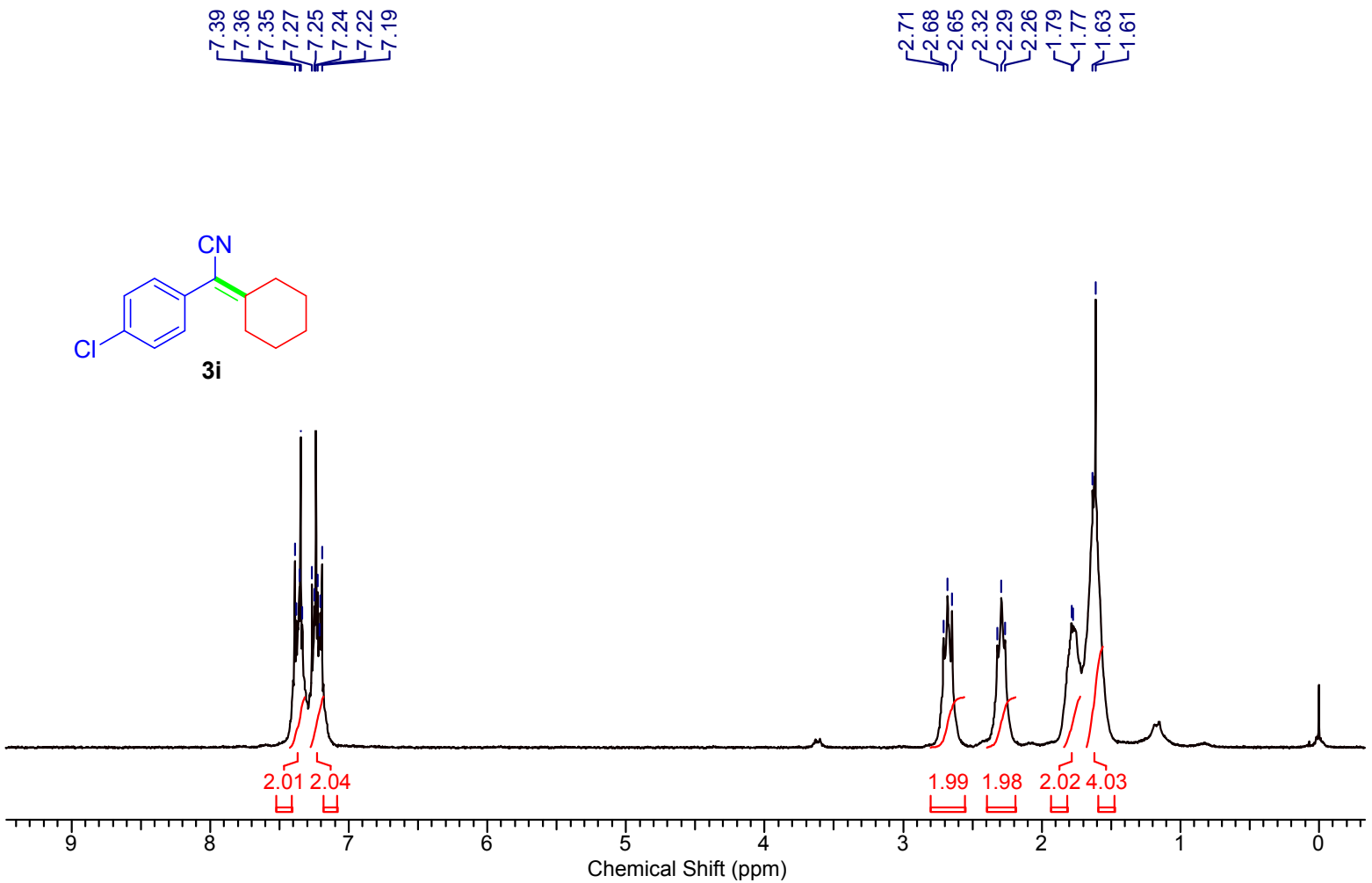
^{1}H NMR spectrum of 2-(3-chlorophenyl)-2-cyclohexylideneacetonitrile (**3h**)



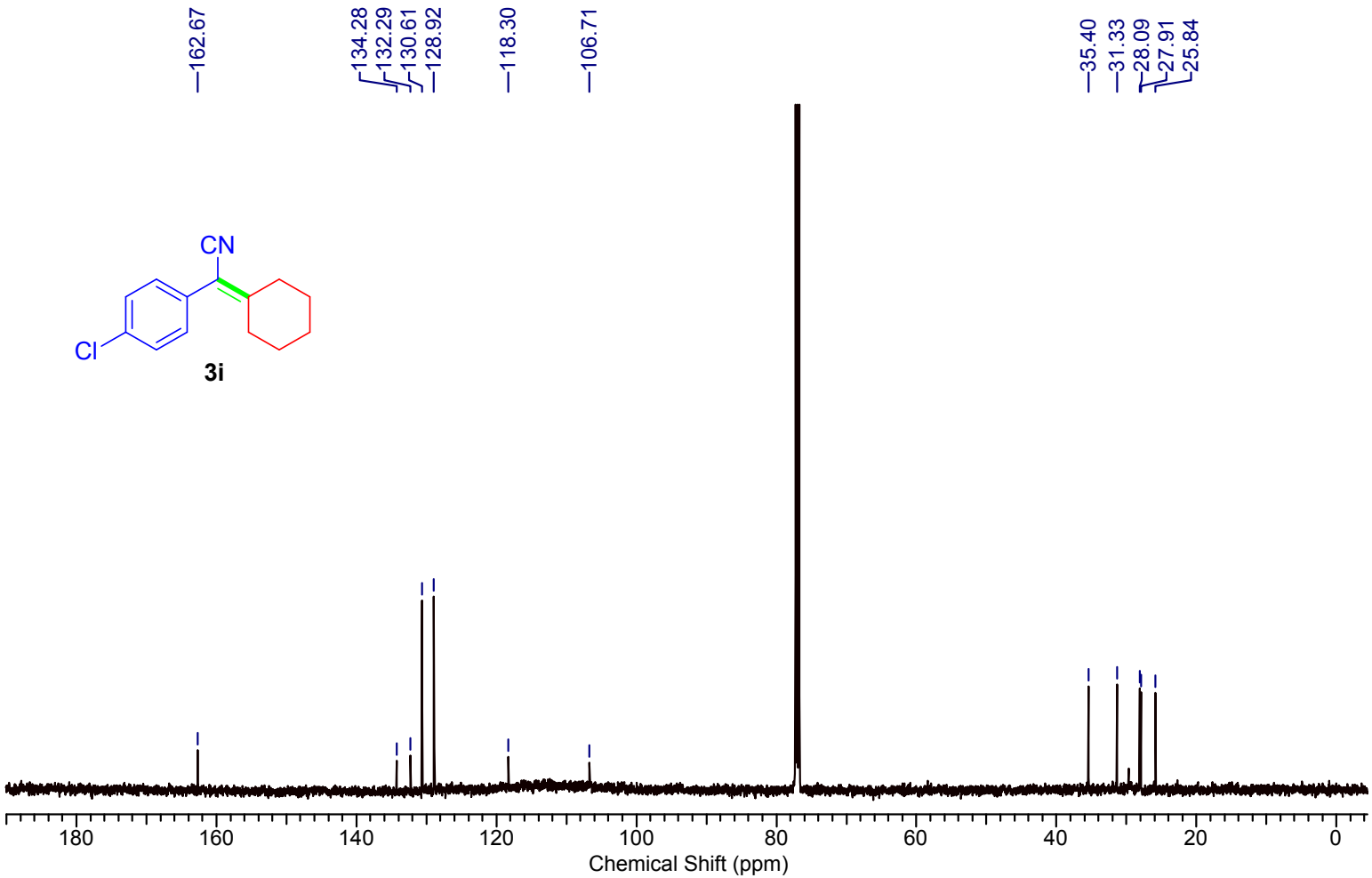
^{13}C NMR spectrum of 2-(3-chlorophenyl)-2-cyclohexylideneacetonitrile (**3h**)



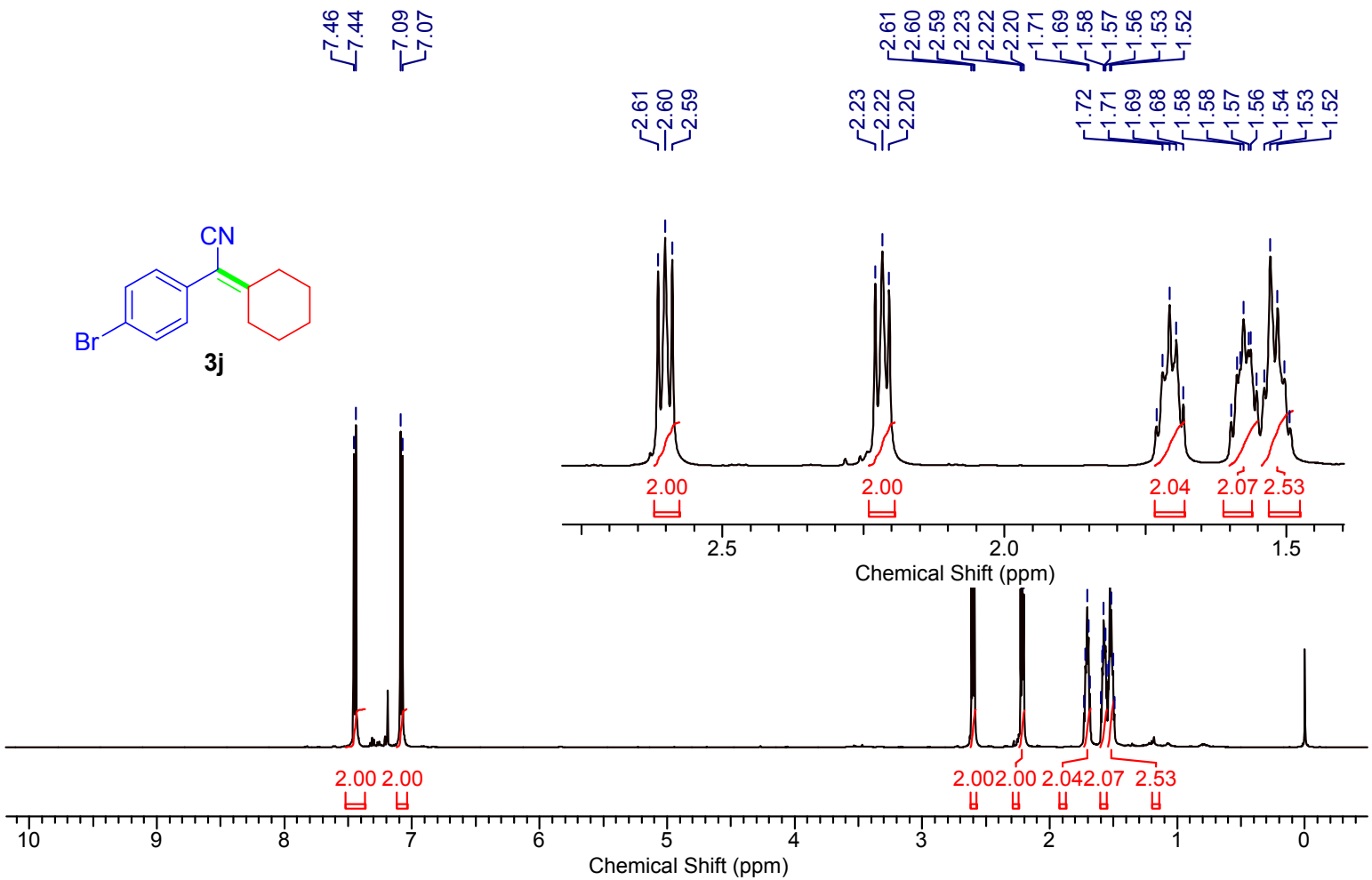
^{1}H NMR spectrum of 2-(4-chlorophenyl)-2-cyclohexylideneacetonitrile (**3i**)



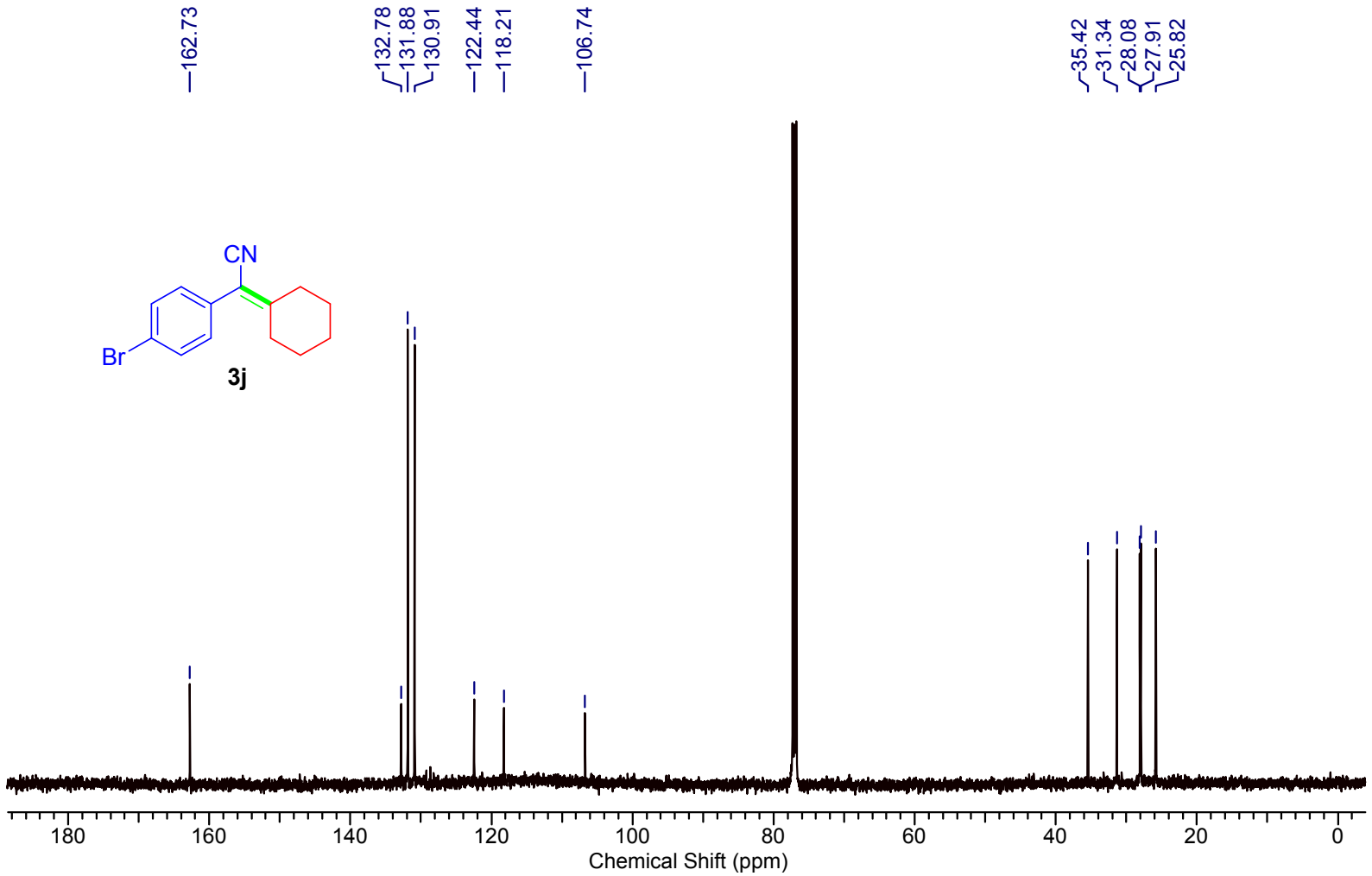
^{13}C NMR spectrum of 2-(4-chlorophenyl)-2-cyclohexylideneacetonitrile (**3i**)



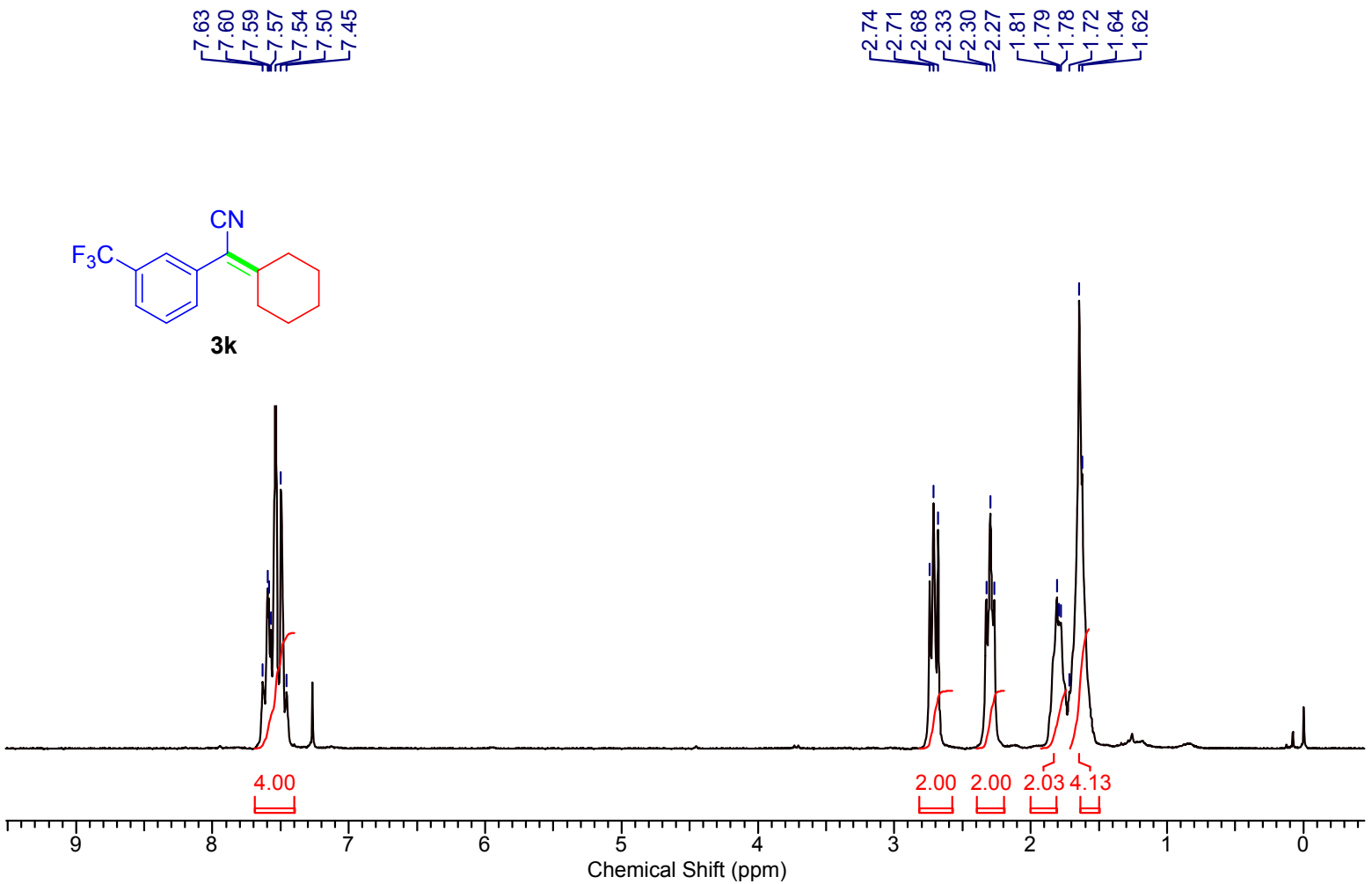
^{1}H NMR spectrum of 2-(4-bromophenyl)-2-cyclohexylideneacetonitrile (**3j**)



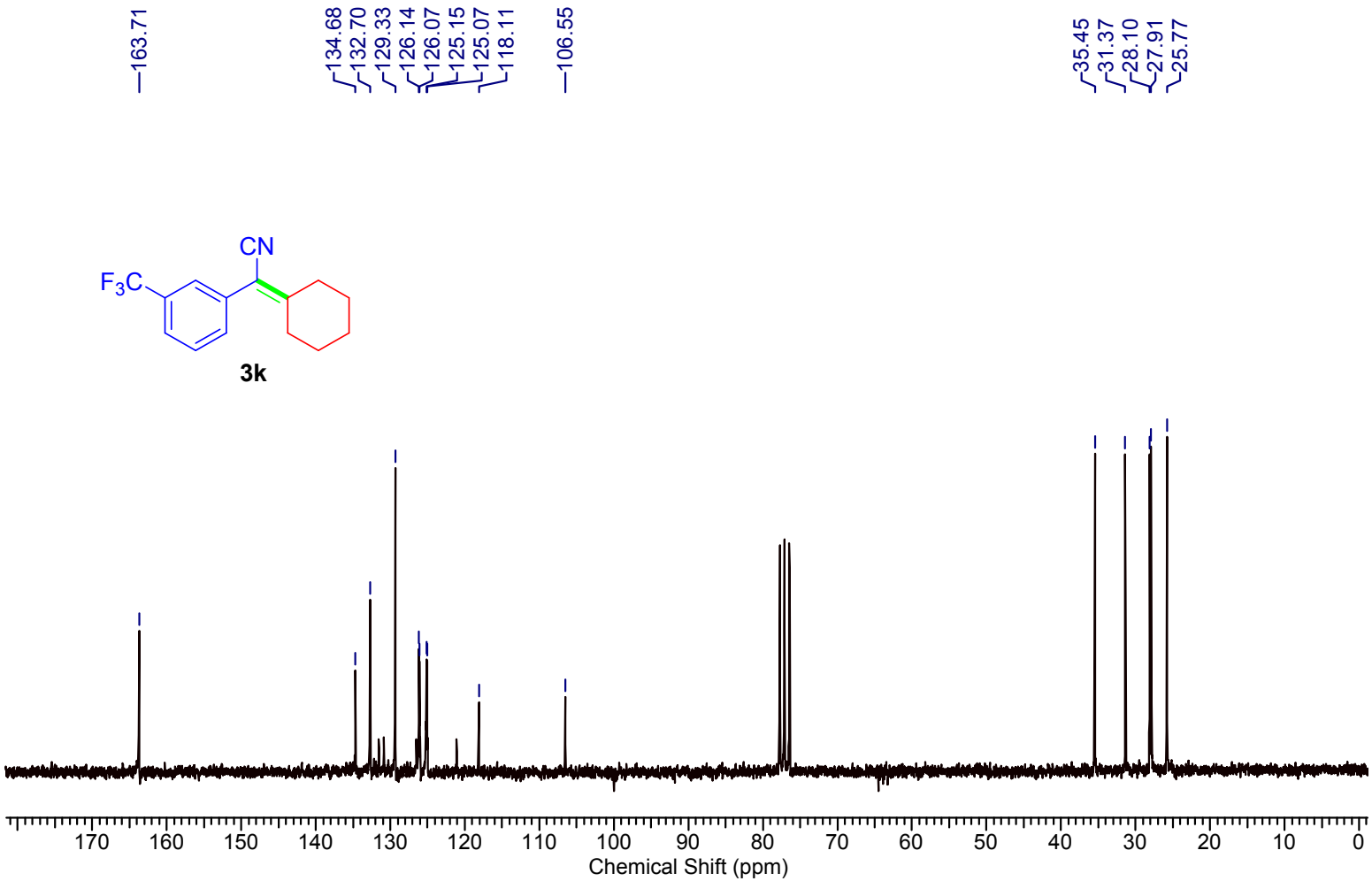
^{13}C NMR spectrum of 2-(4-bromophenyl)-2-cyclohexylideneacetonitrile (**3j**)



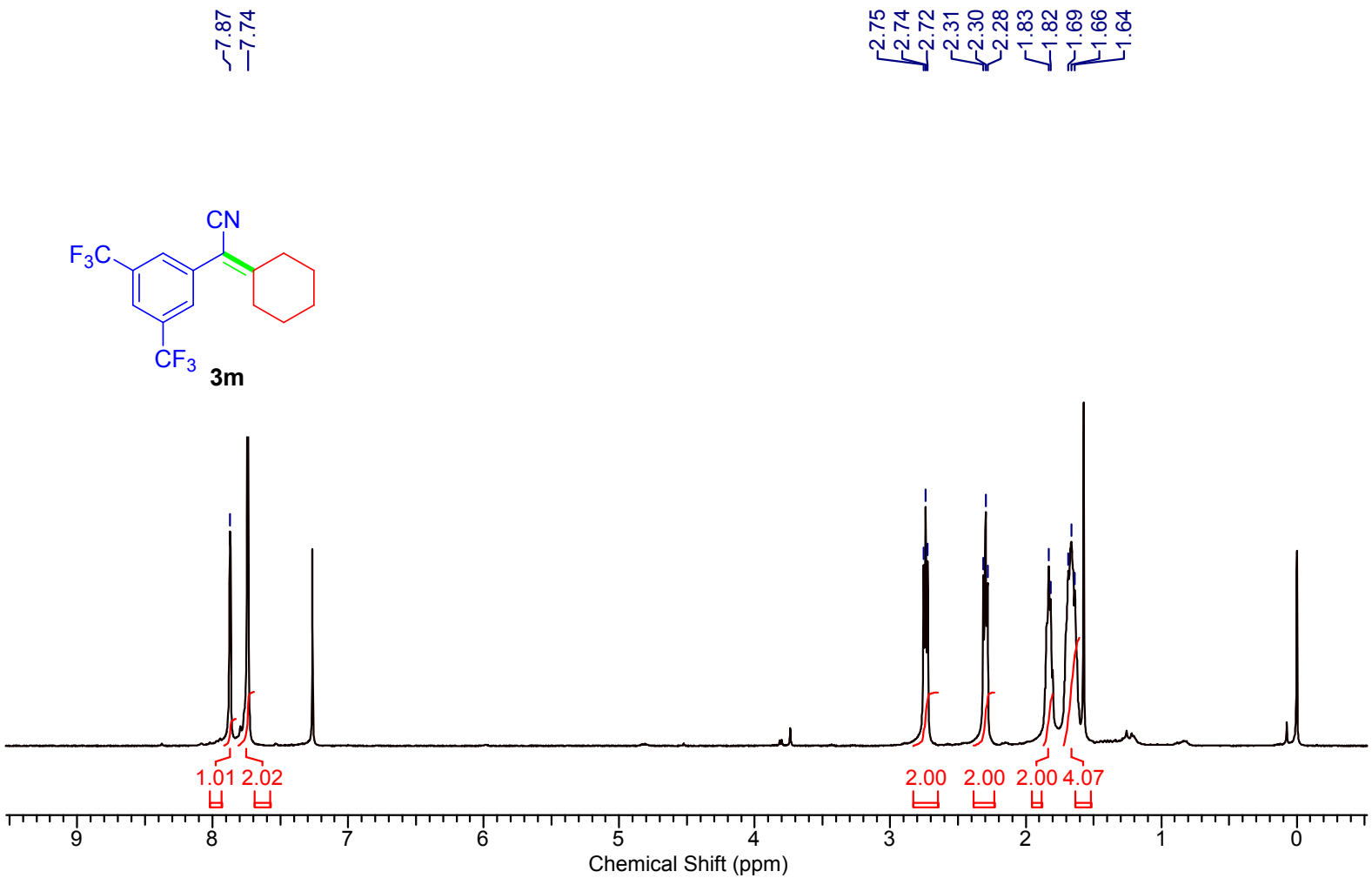
^{1}H NMR spectrum of 2-cyclohexylidene-2-(3-(trifluoromethyl)phenyl)acetonitrile (**3k**)



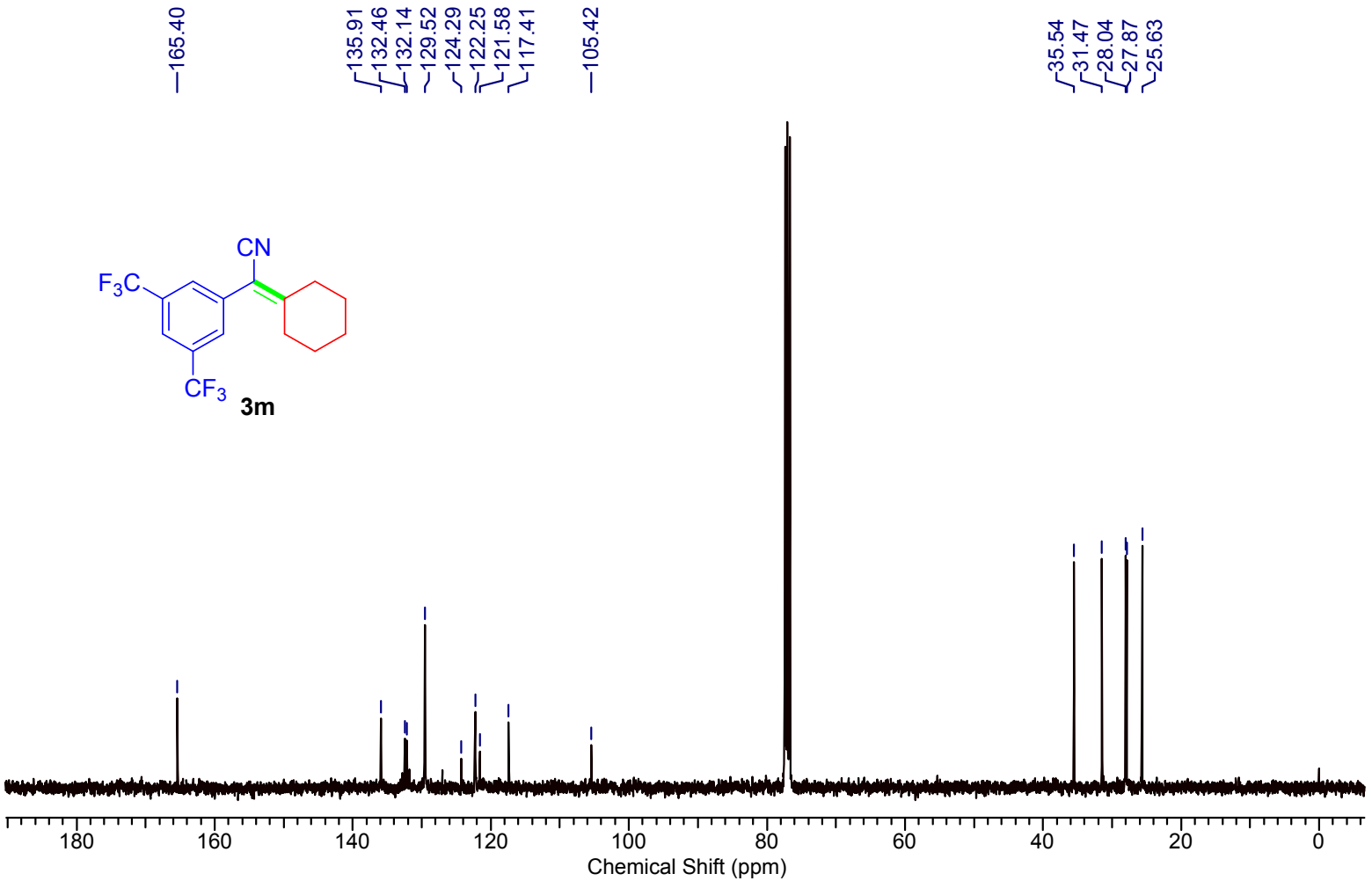
^{13}C NMR spectrum of 2-cyclohexylidene-2-(3-(trifluoromethyl)phenyl)acetonitrile (**3k**)



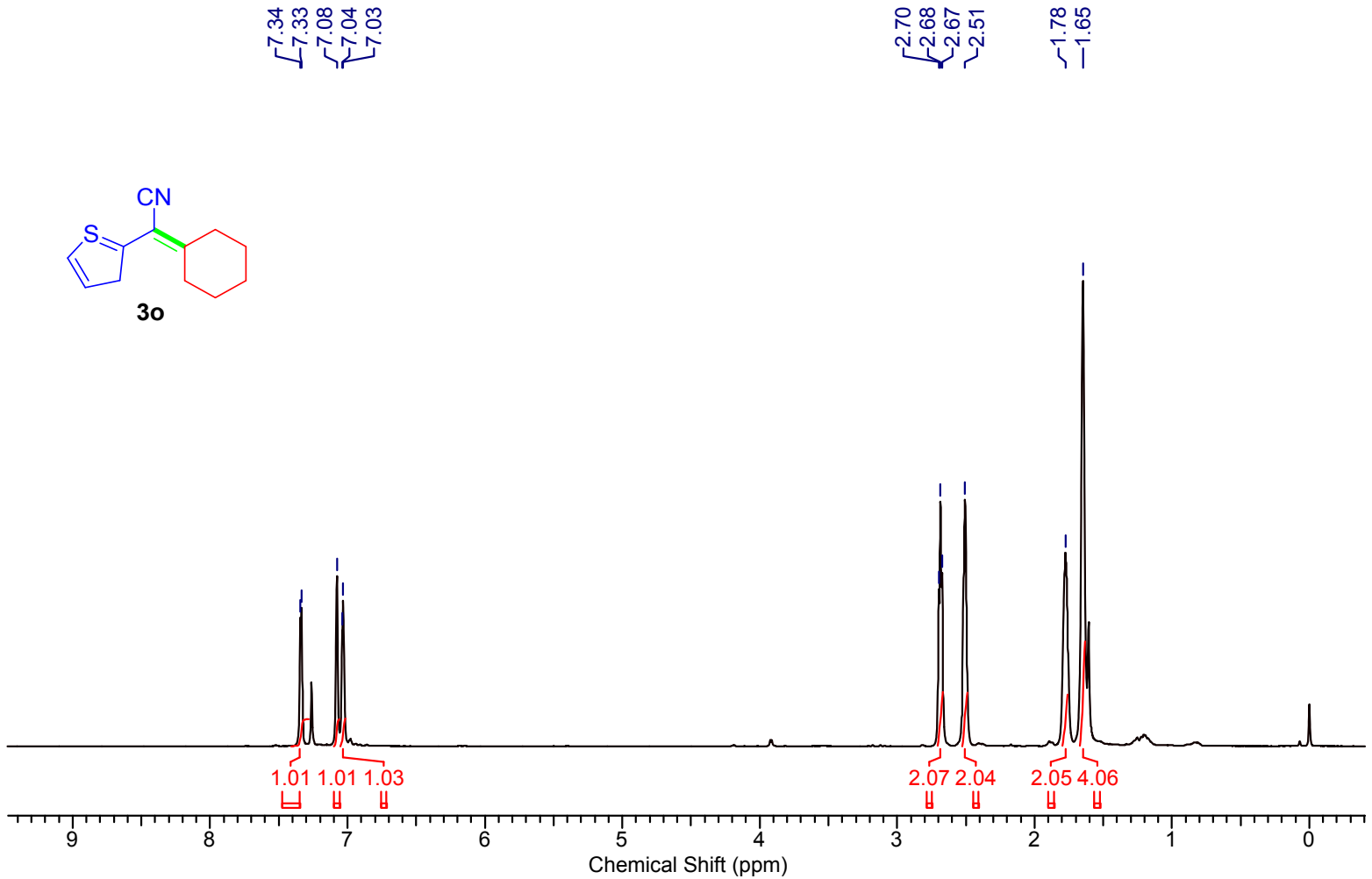
^{1}H NMR spectrum of 2-(3,5-bis(trifluoromethyl)phenyl)-2-cyclohexylideneacetonitrile (**3m**)



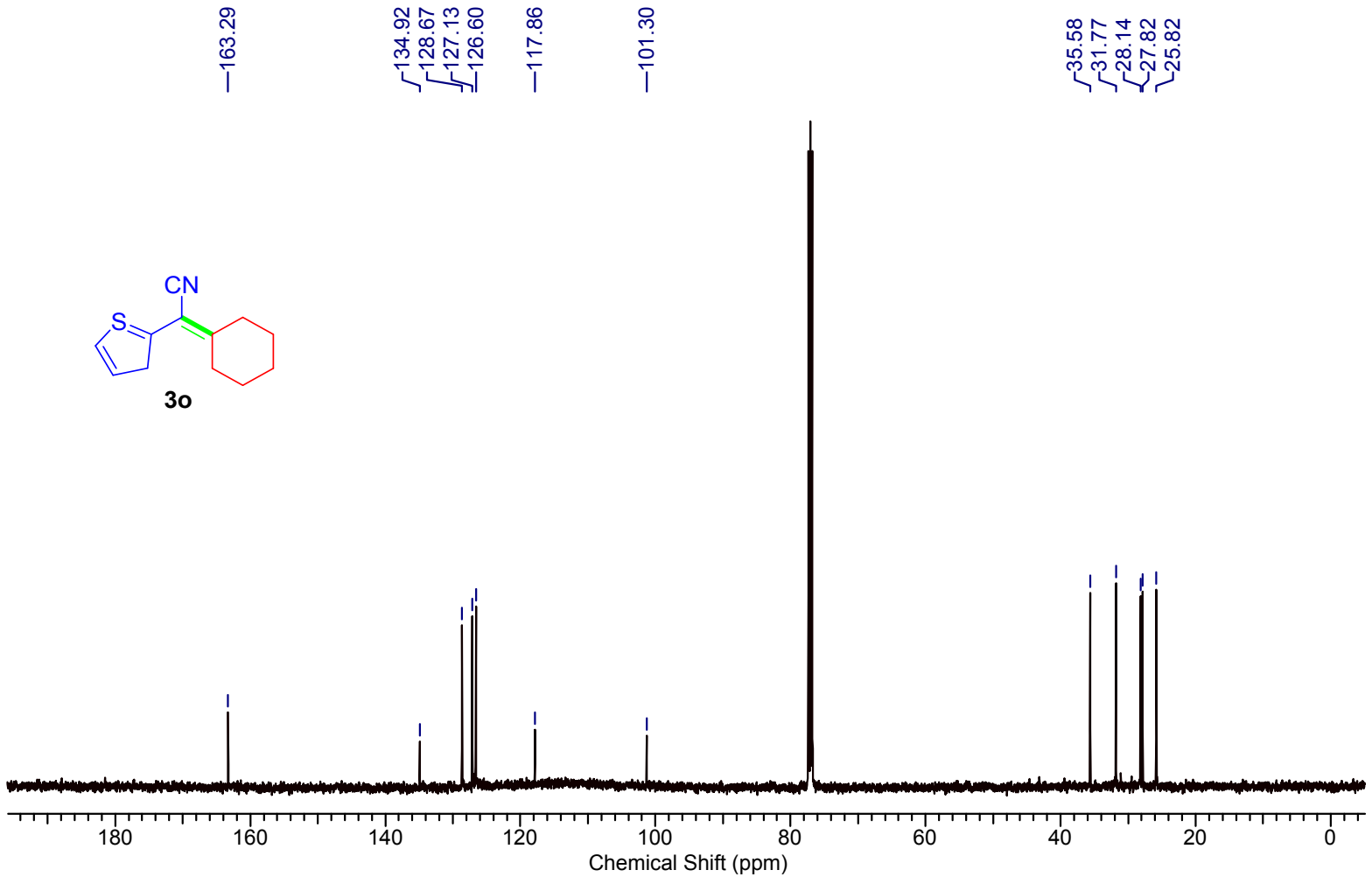
^{13}C NMR spectrum of 2-(3,5-bis(trifluoromethyl)phenyl)-2-cyclohexylideneacetonitrile (**3m**)



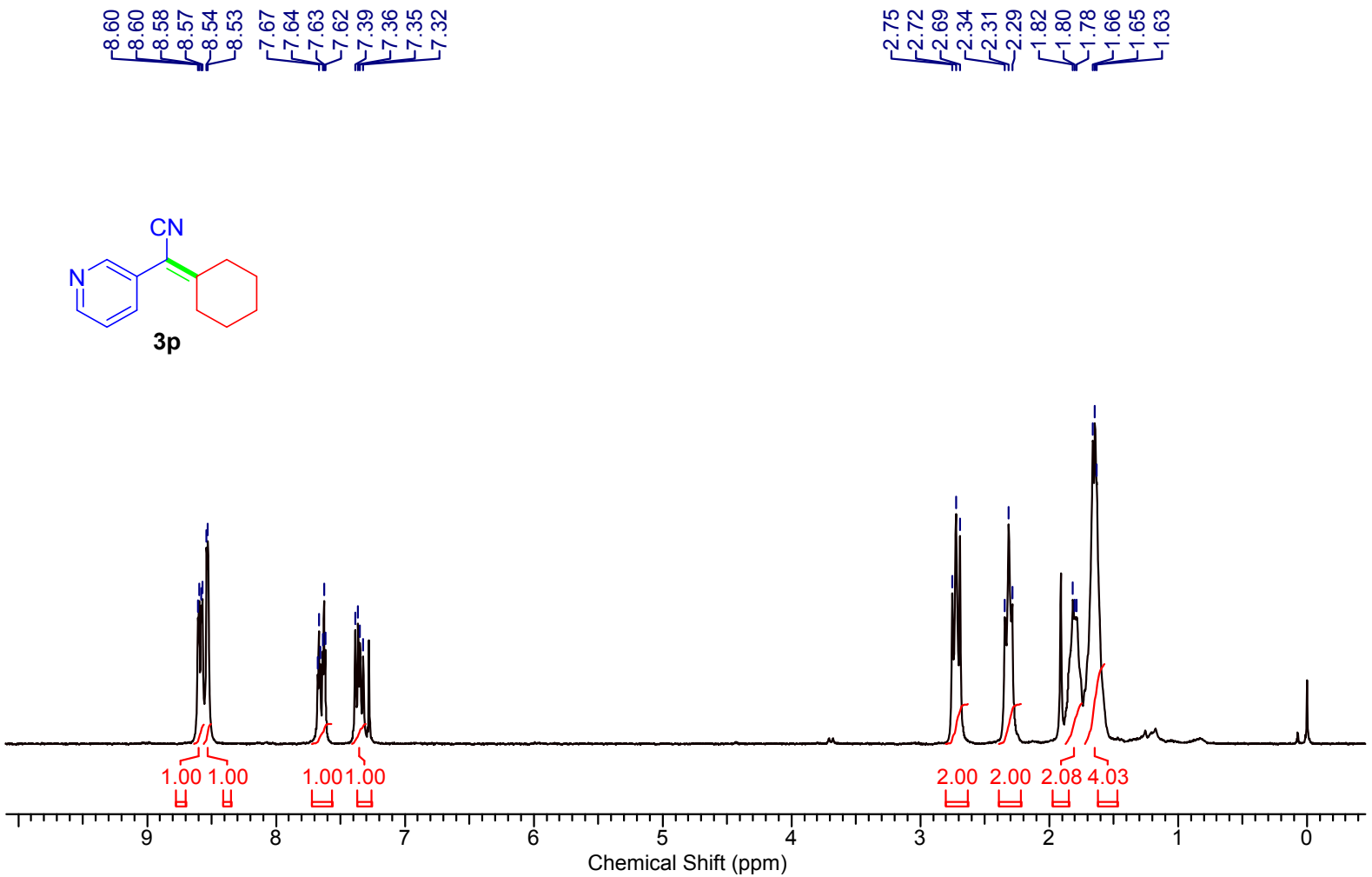
^{1}H NMR spectrum of 2-cyclohexylidene-2-(3*H*-1λ^{3}-thiophen-2-yl)acetonitrile (**3o)**



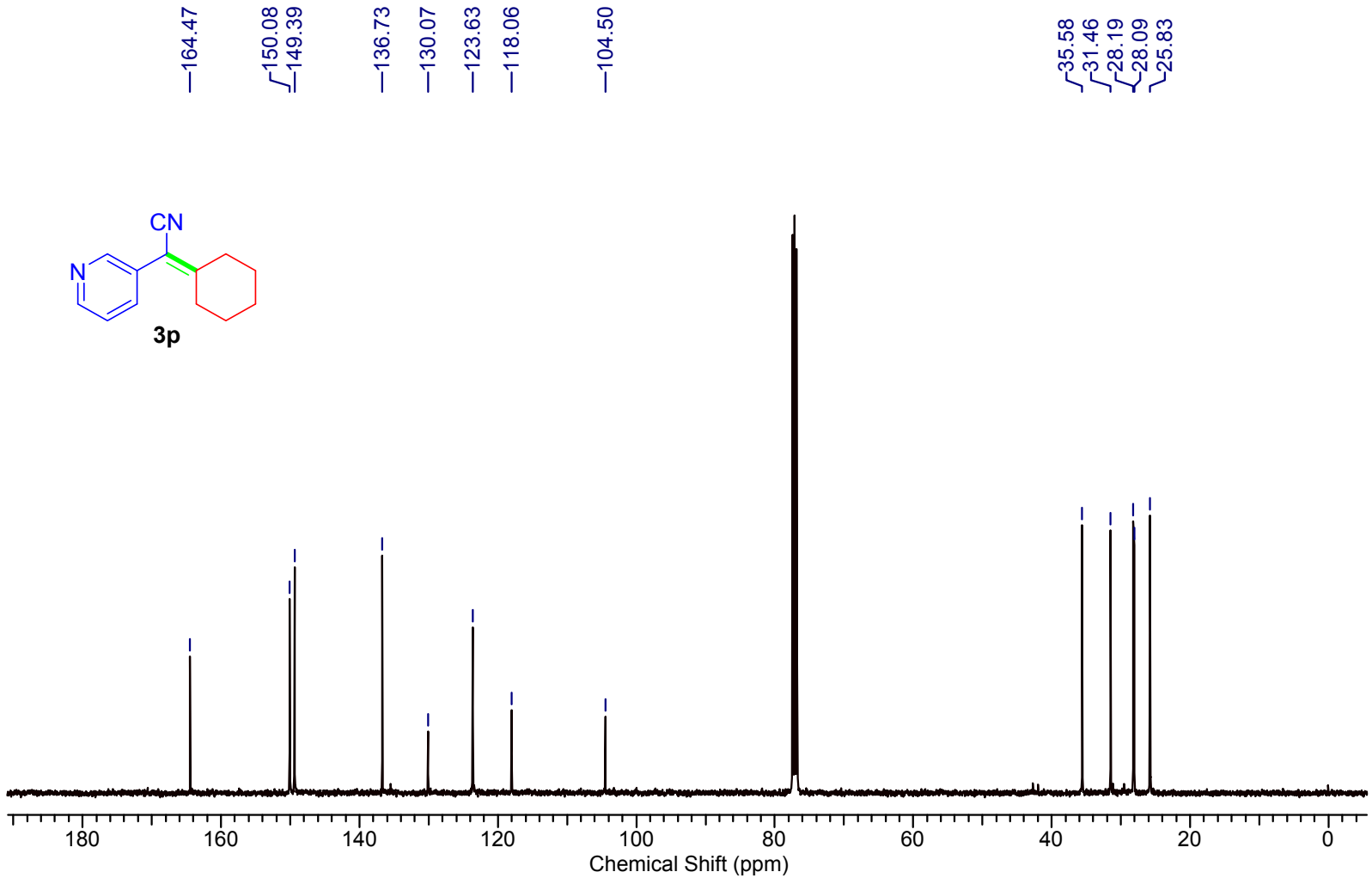
^{13}C NMR spectrum of 2-cyclohexylidene-2-(3*H*-1λ^{3}-thiophen-2-yl)acetonitrile (**3o**)



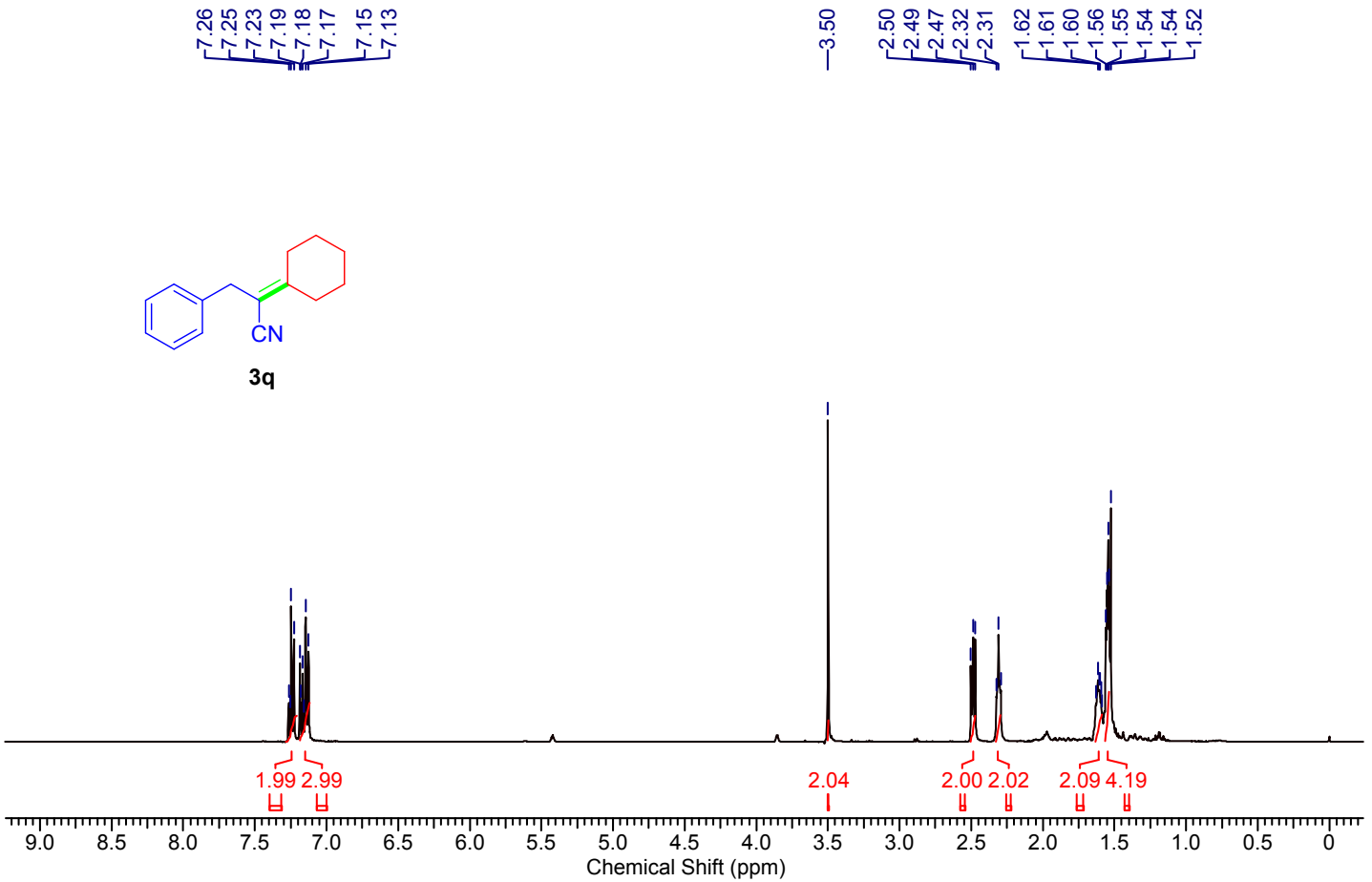
^{1}H NMR spectrum of 2-cyclohexylidene-2-(pyridin-3-yl)acetonitrile (**3p**)



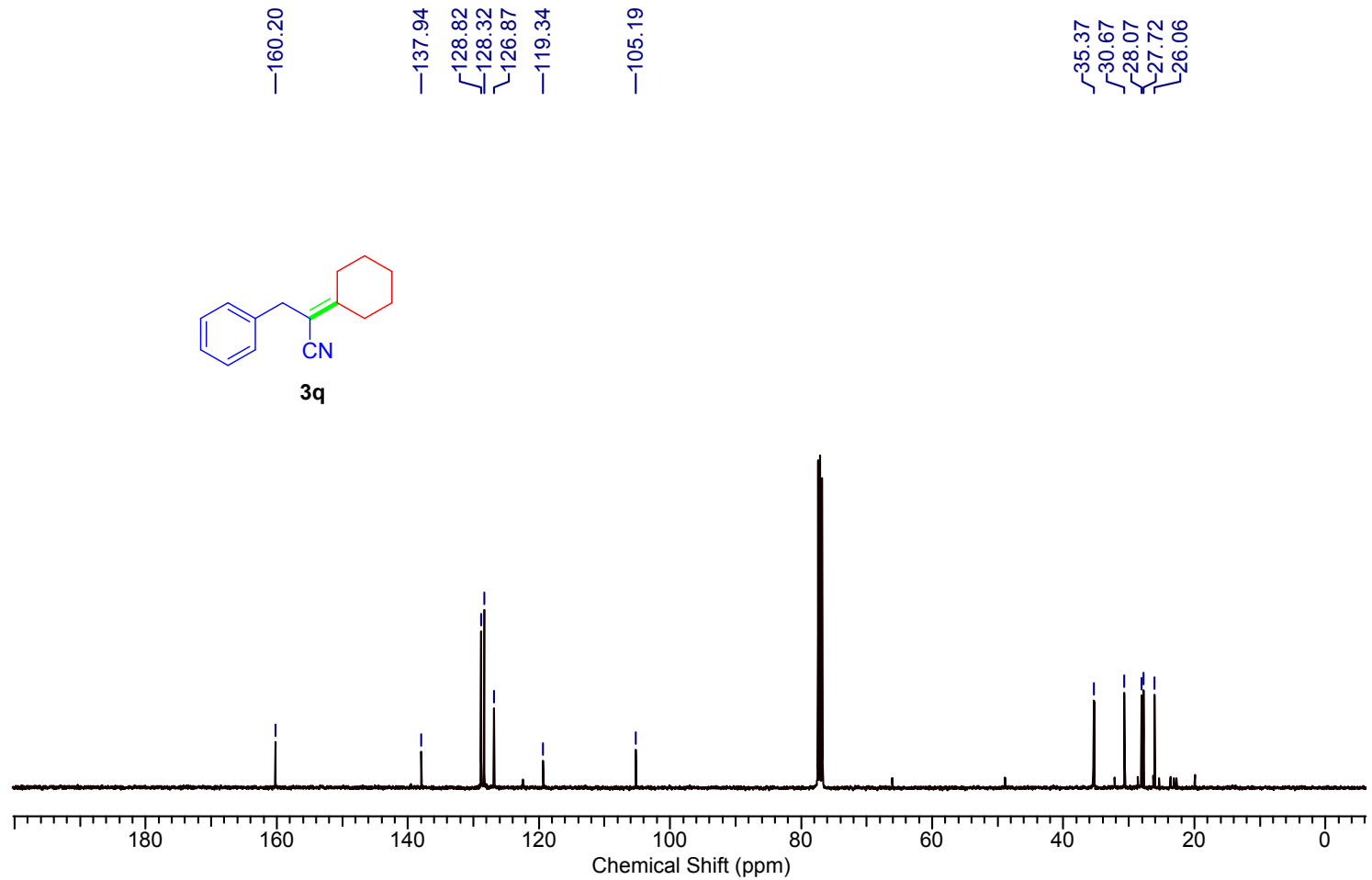
^{13}C NMR spectrum of 2-cyclohexylidene-2-(pyridin-3-yl)acetonitrile (**3p**)



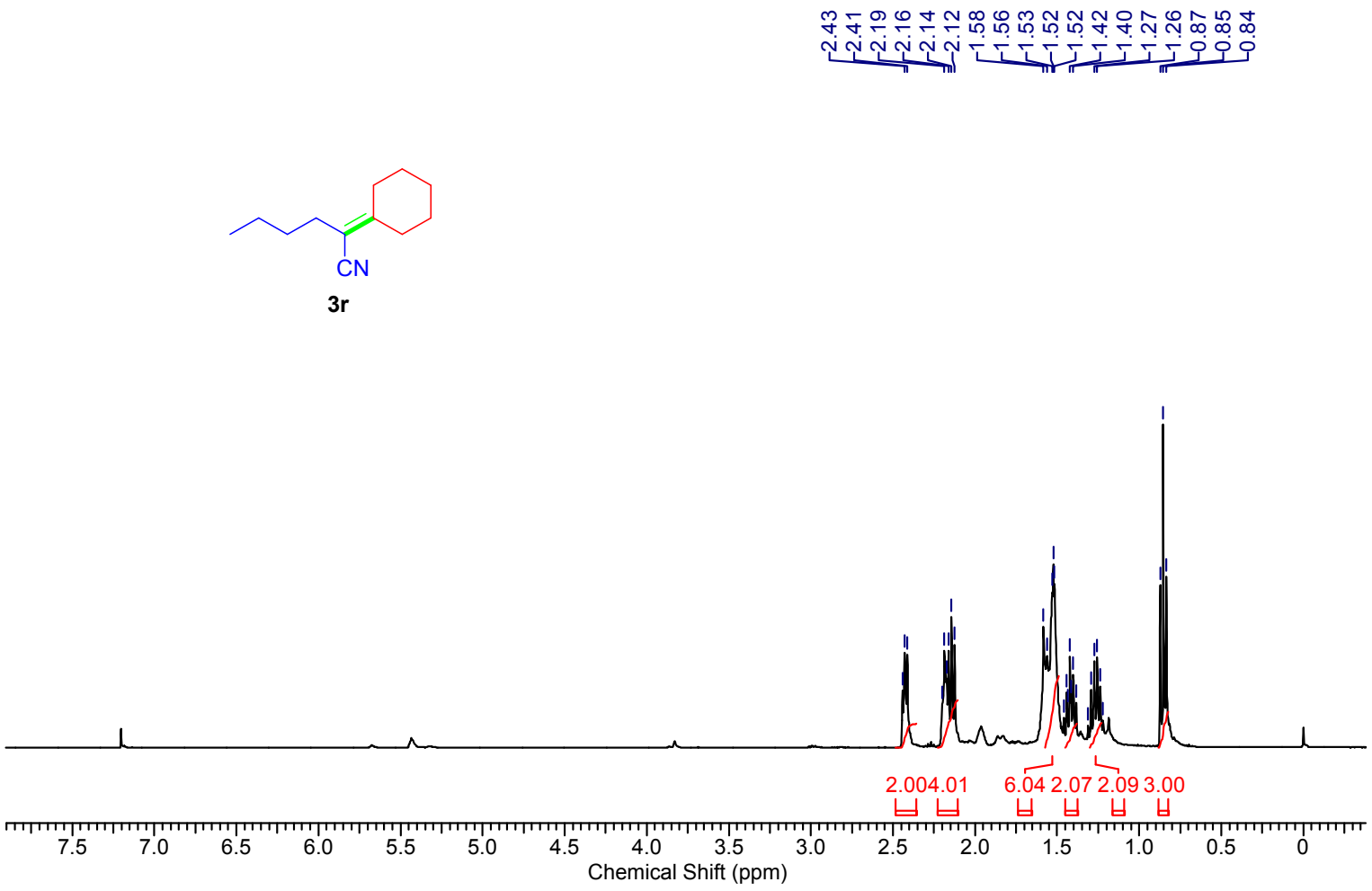
^{1}H NMR spectrum of 2-cyclohexylidene-3-phenylpropanenitrile (**3q**)



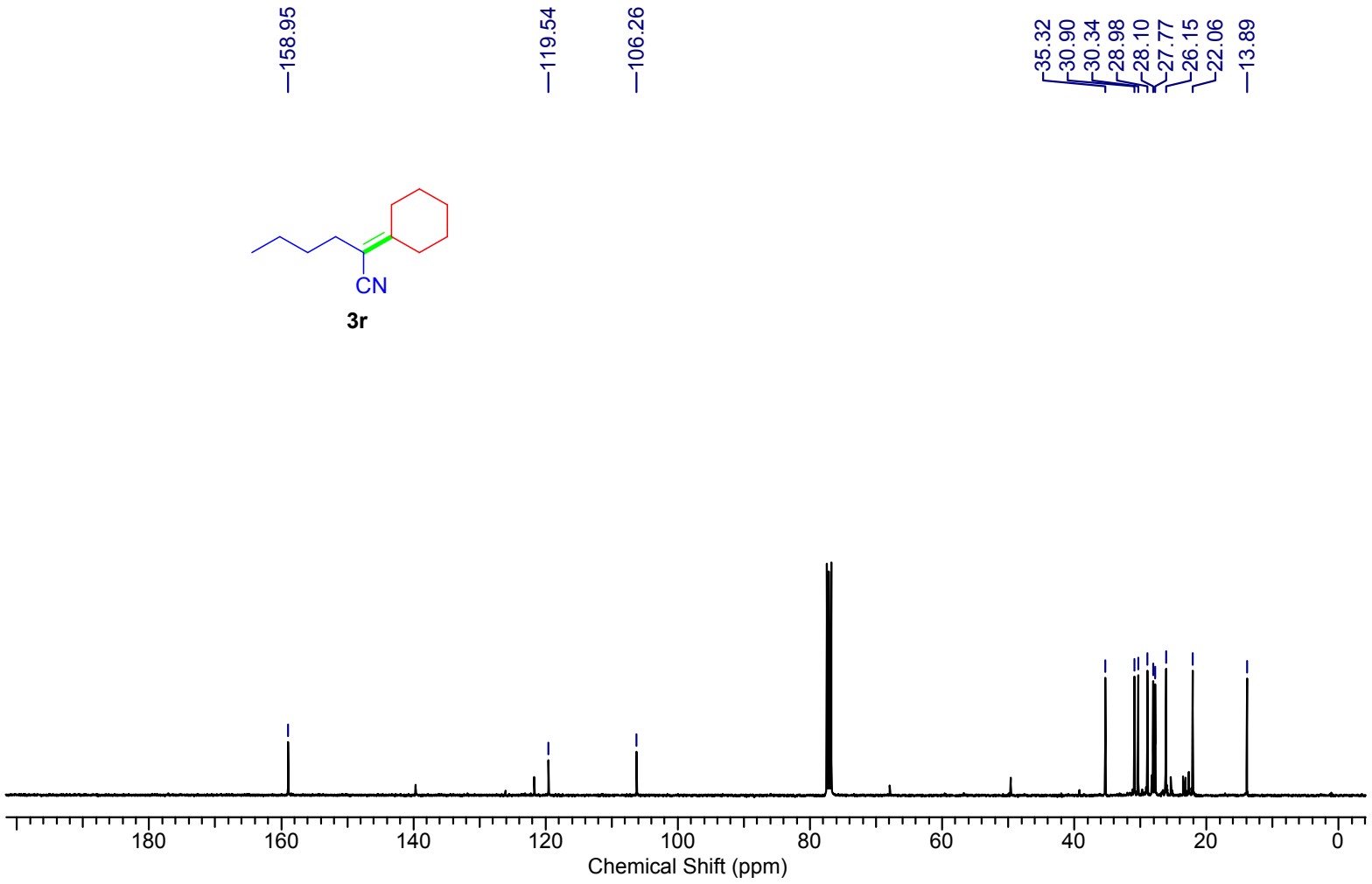
^{13}C NMR spectrum of 2-cyclohexylidene-3-phenylpropanenitrile (**3q**)



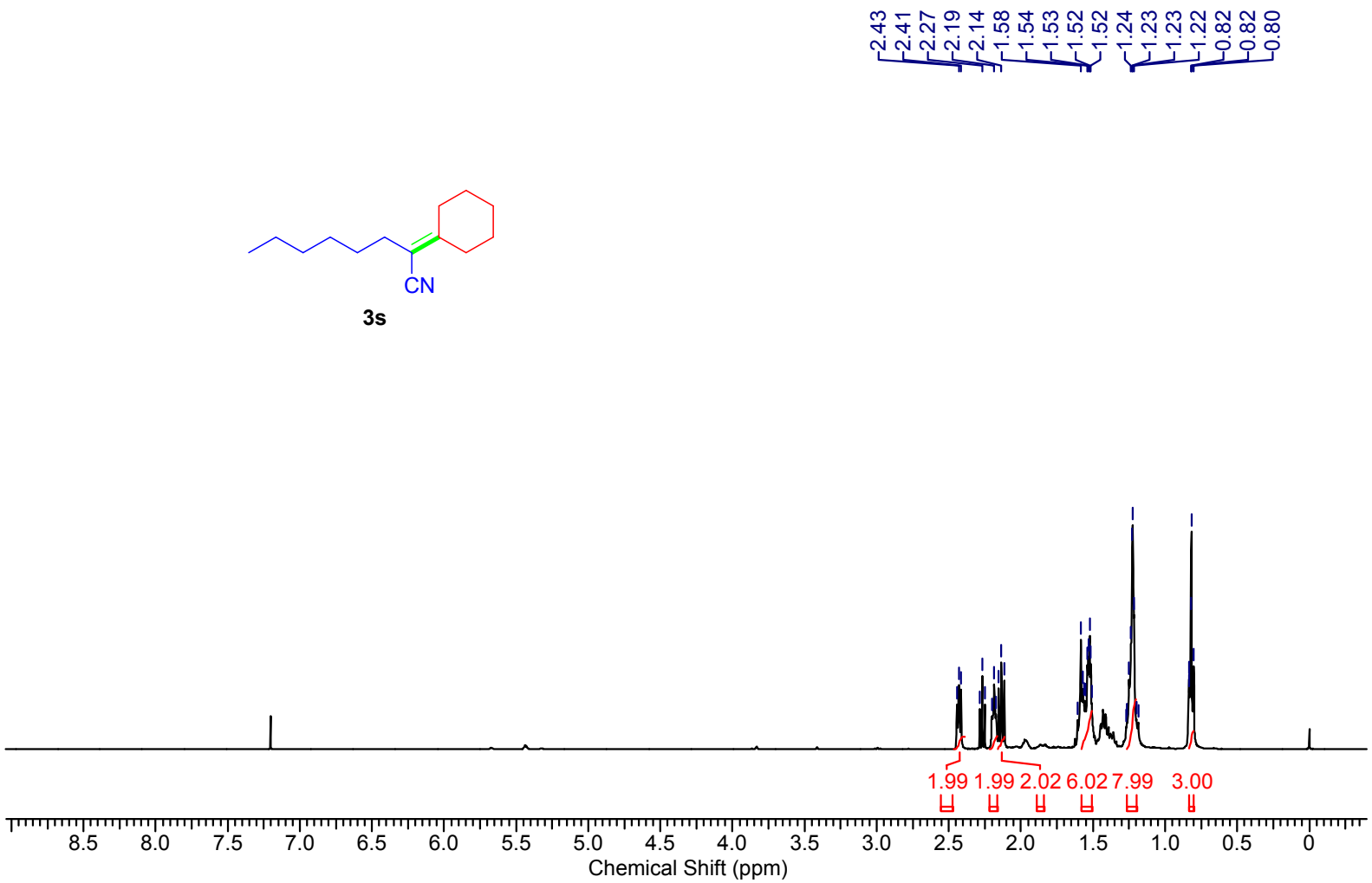
^{1}H NMR spectrum of 2-cyclohexylidenehexanenitrile (**3r**)



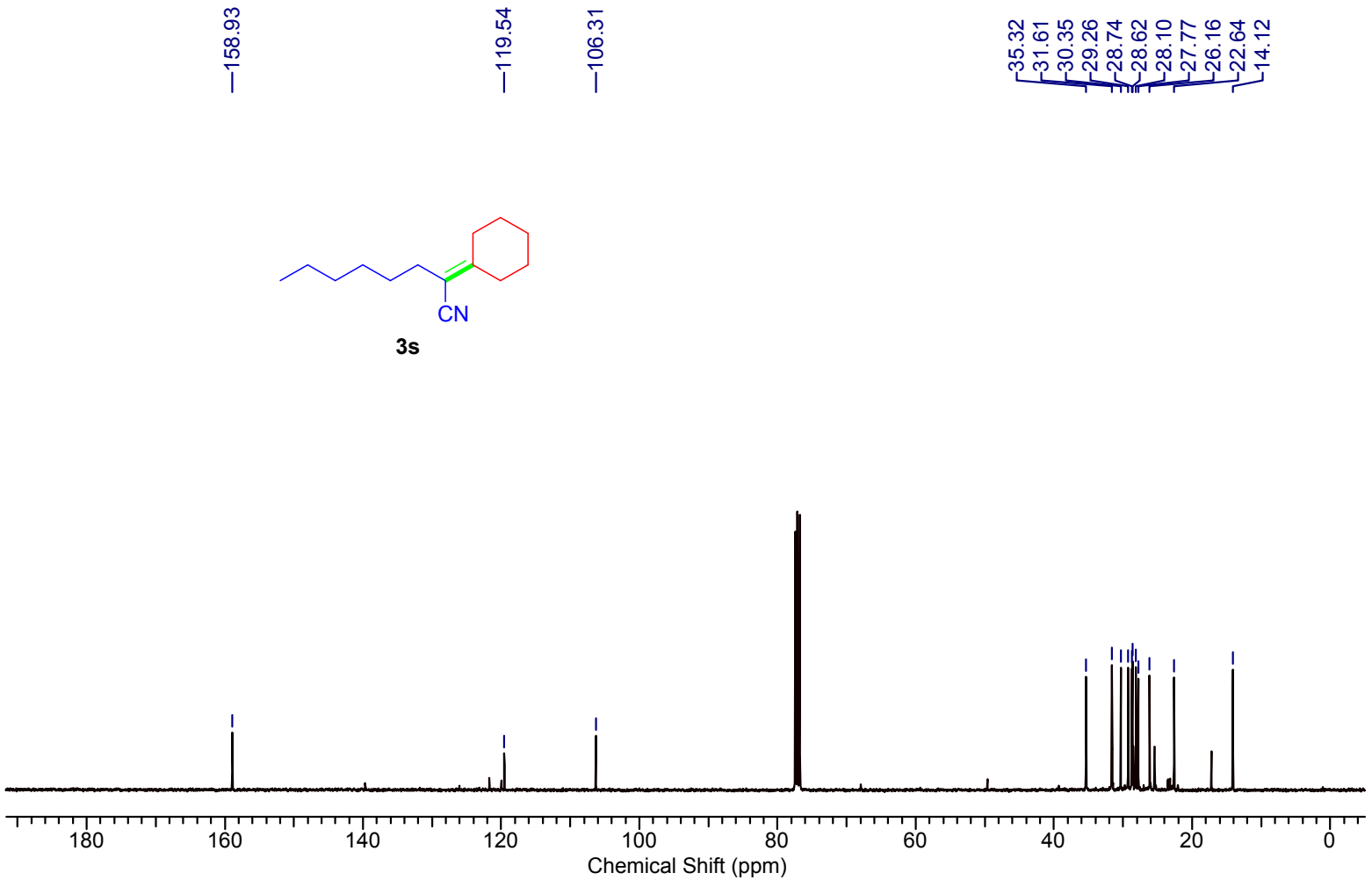
^{13}C NMR spectrum of 2-cyclohexylidenehexanenitrile (**3r**)



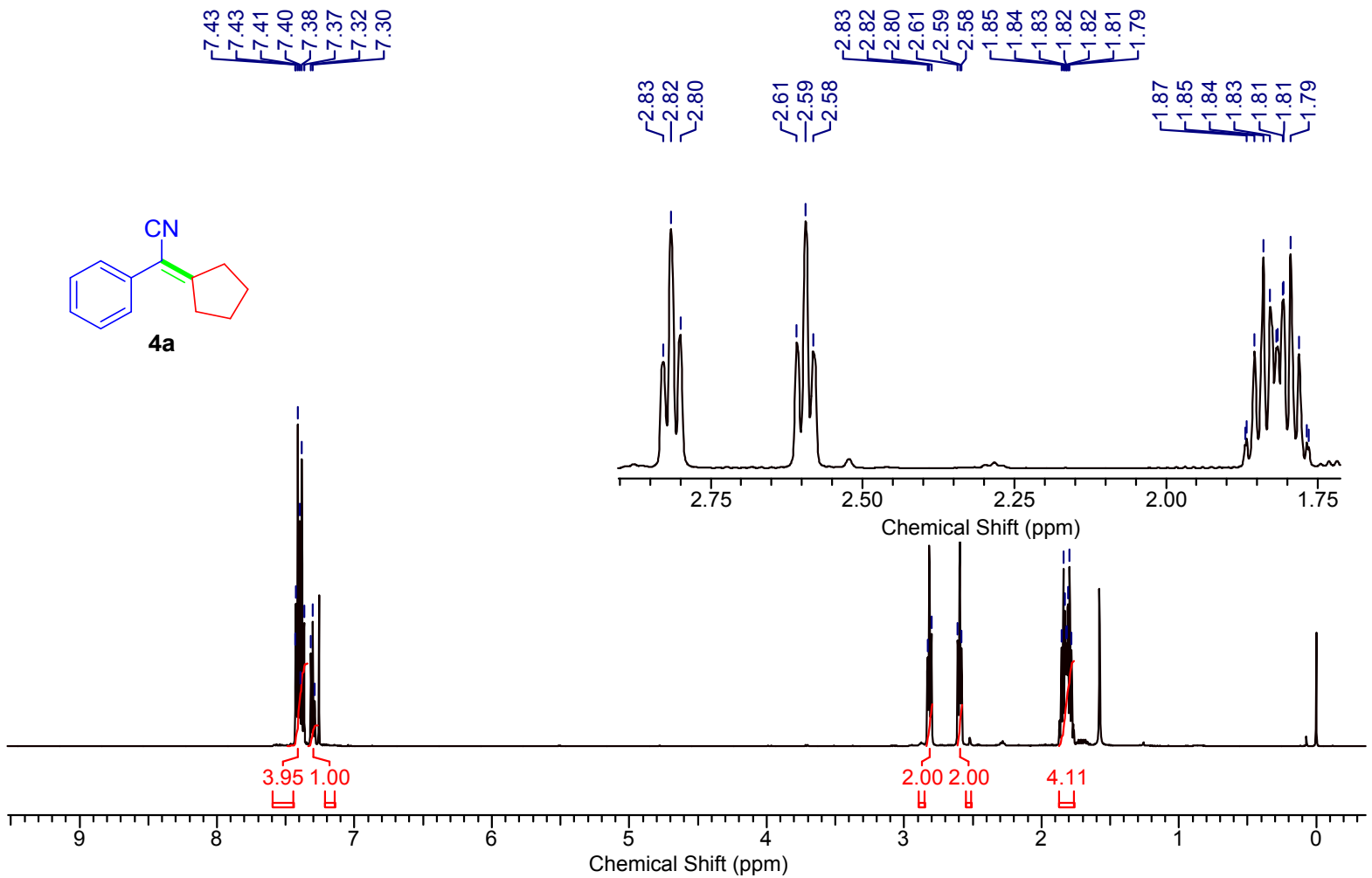
^{1}H NMR spectrum of 2-cyclohexylideneoctanenitrile (**3s**)



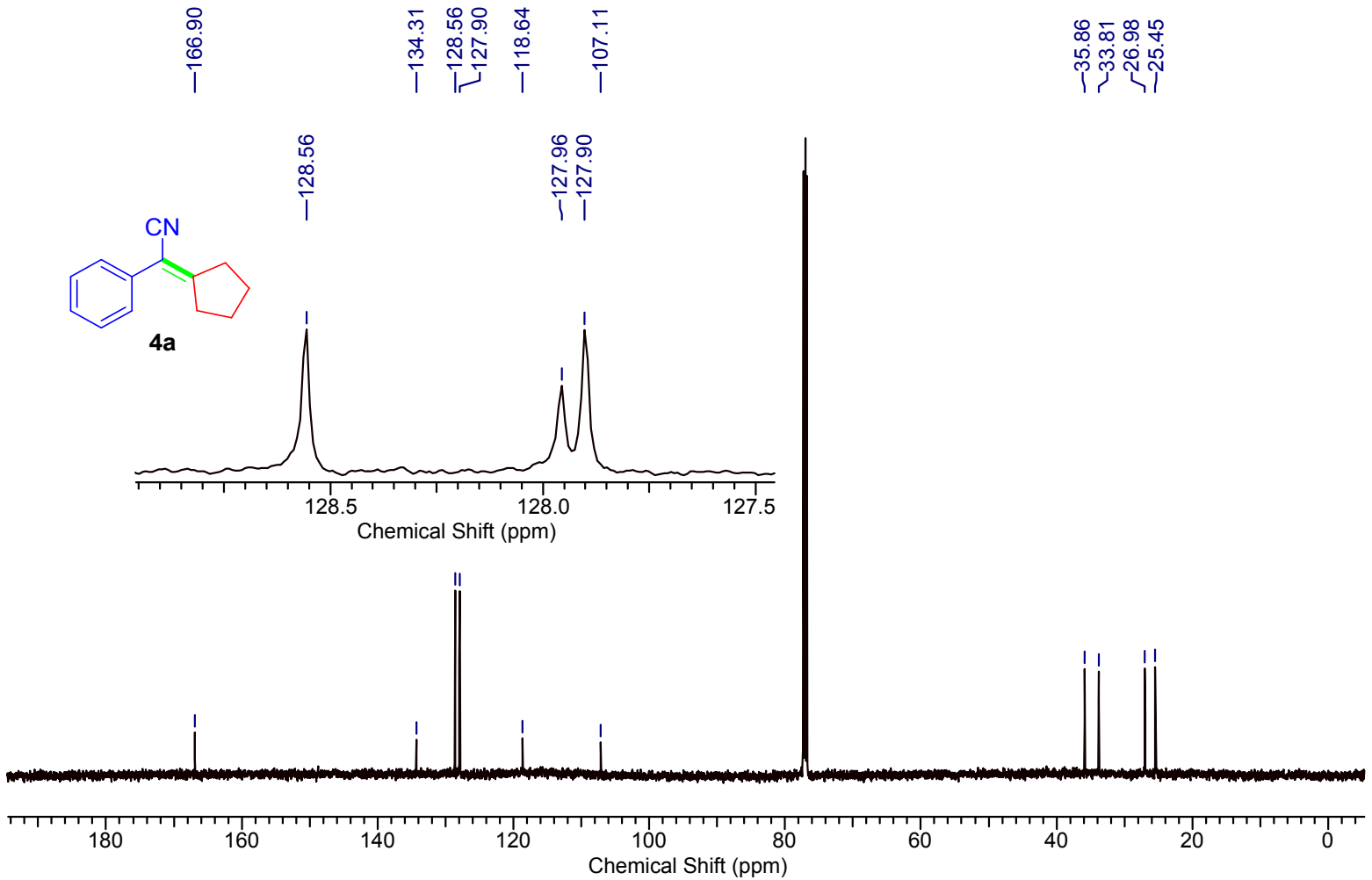
^{13}C NMR spectrum of 2-cyclohexylideneoctanenitrile (**3s**)



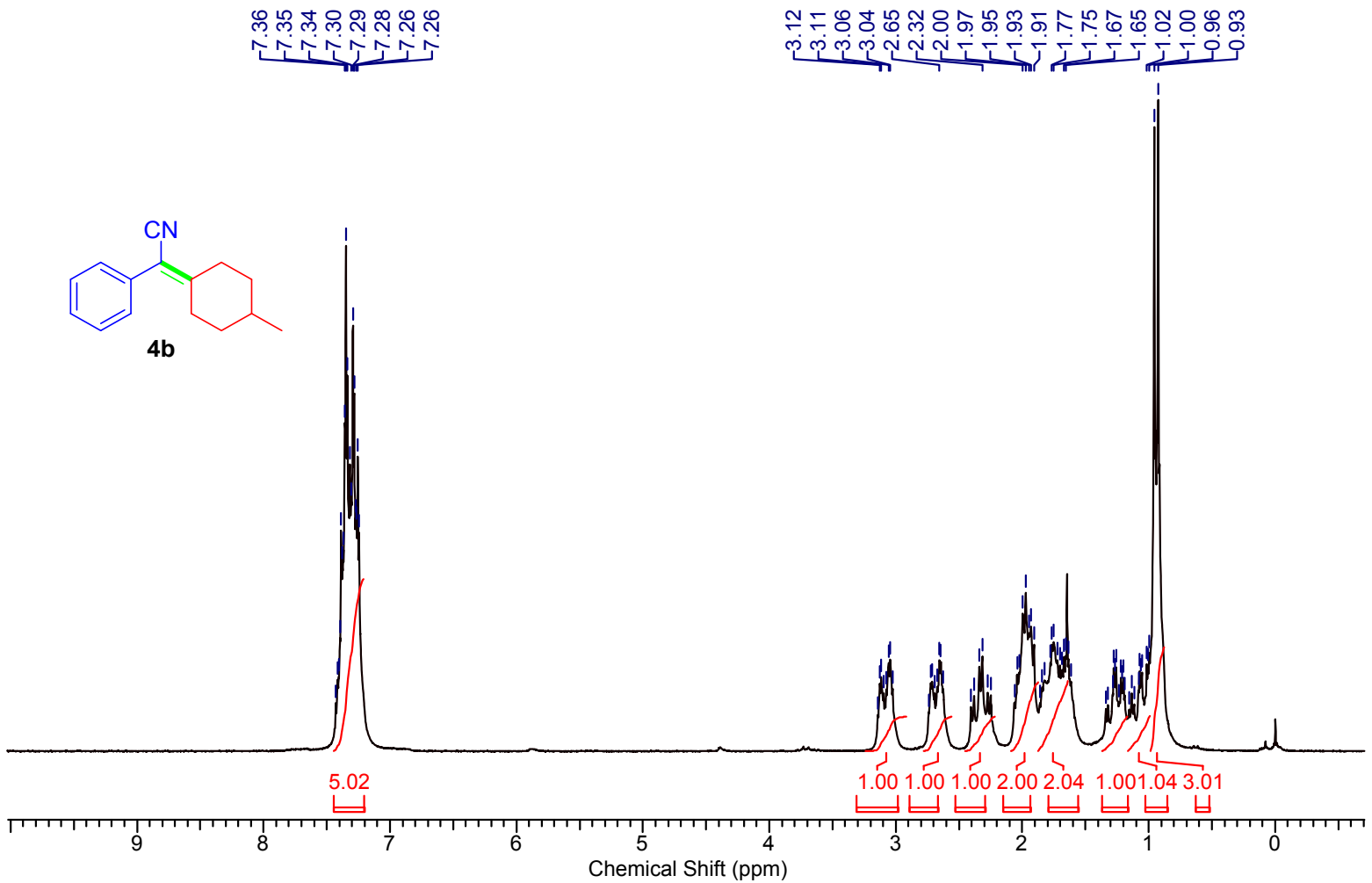
^{1}H NMR spectrum of 2-cyclopentylidene-2-phenylacetonitrile (**4a**)



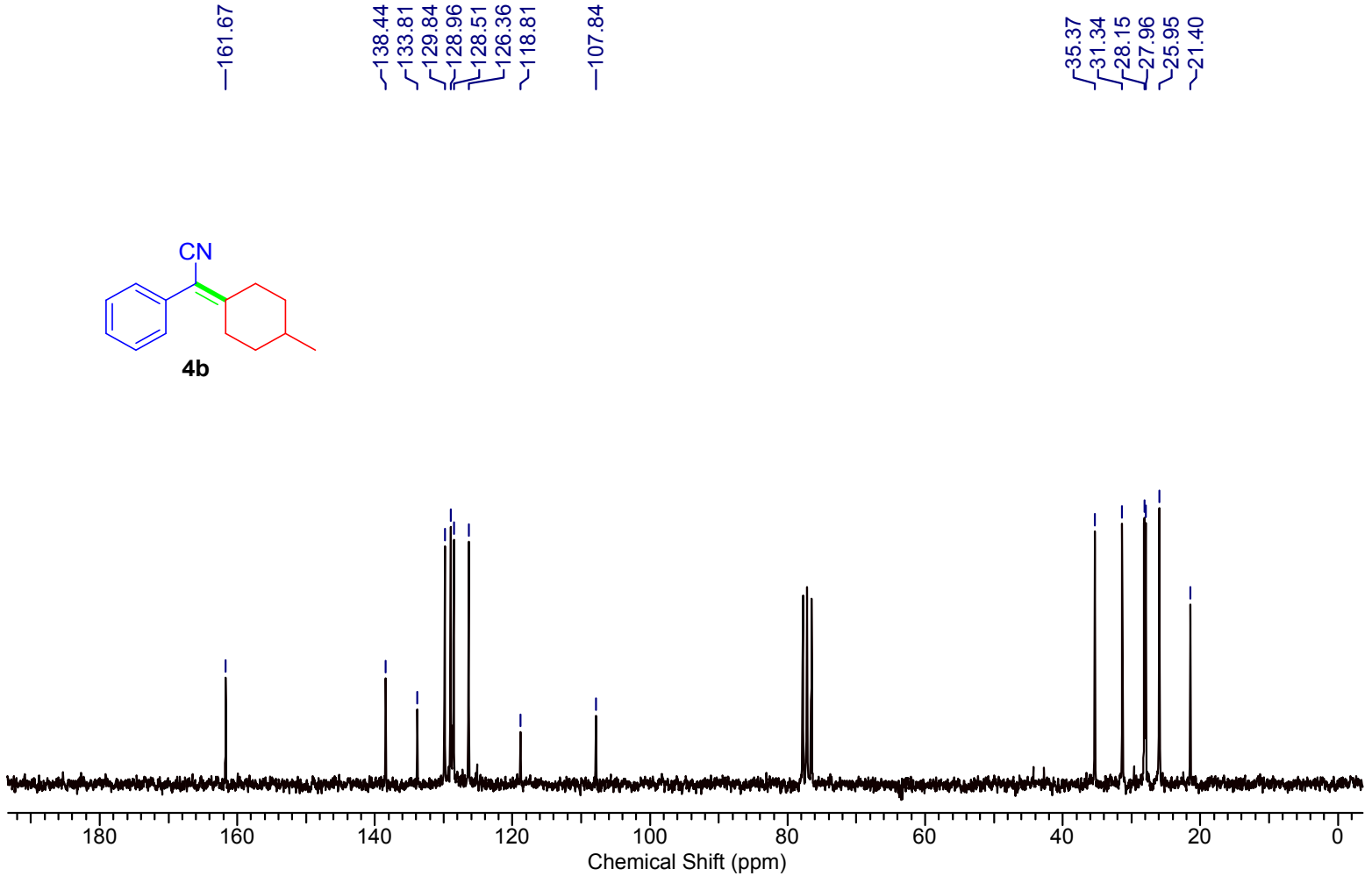
^{13}C NMR spectrum of 2-cyclopentylidene-2-phenylacetonitrile (**4a**)



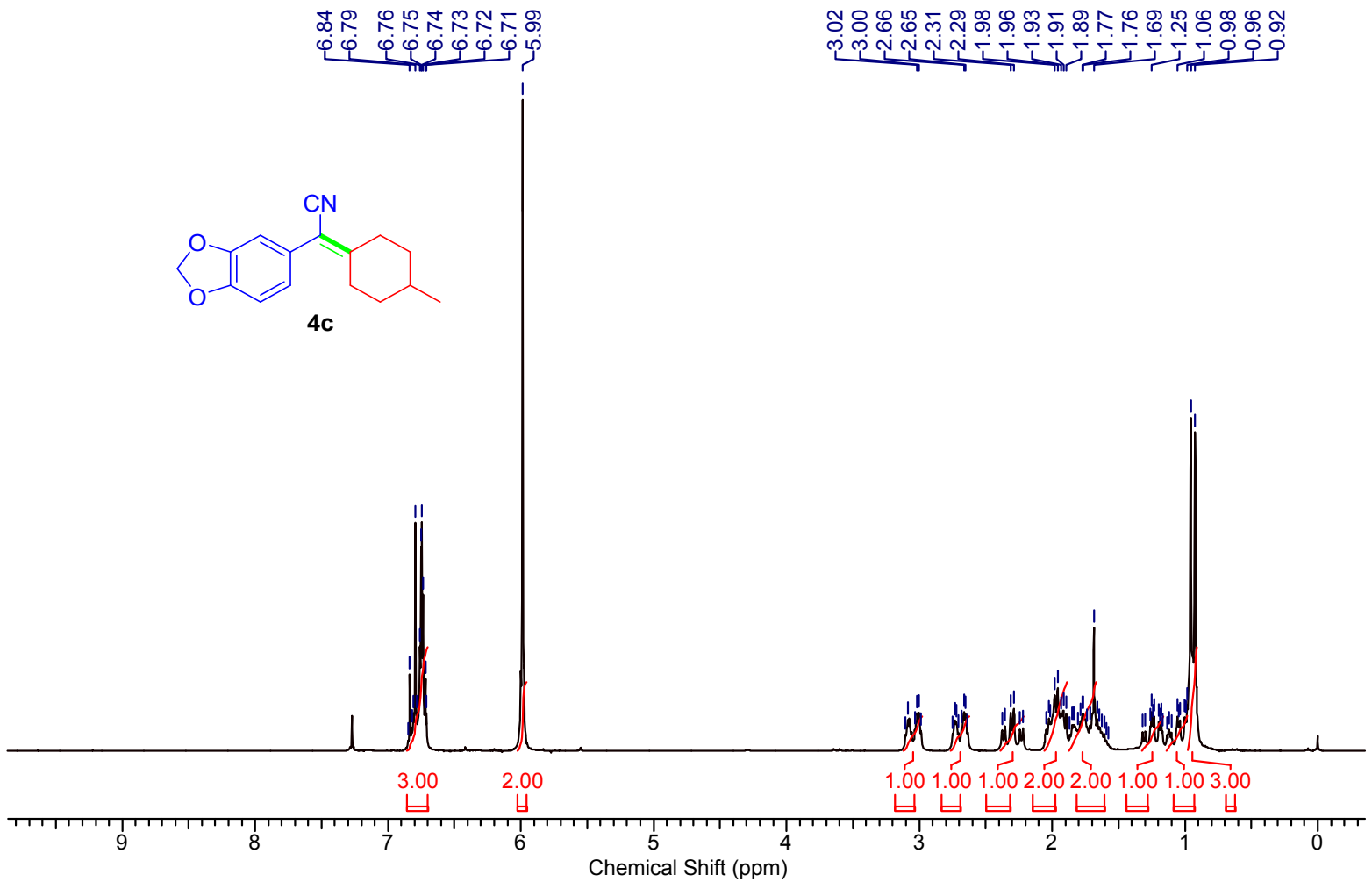
^{1}H NMR spectrum of 2-(4-methylcyclohexylidene)-2-phenylacetonitrile (**4b**)



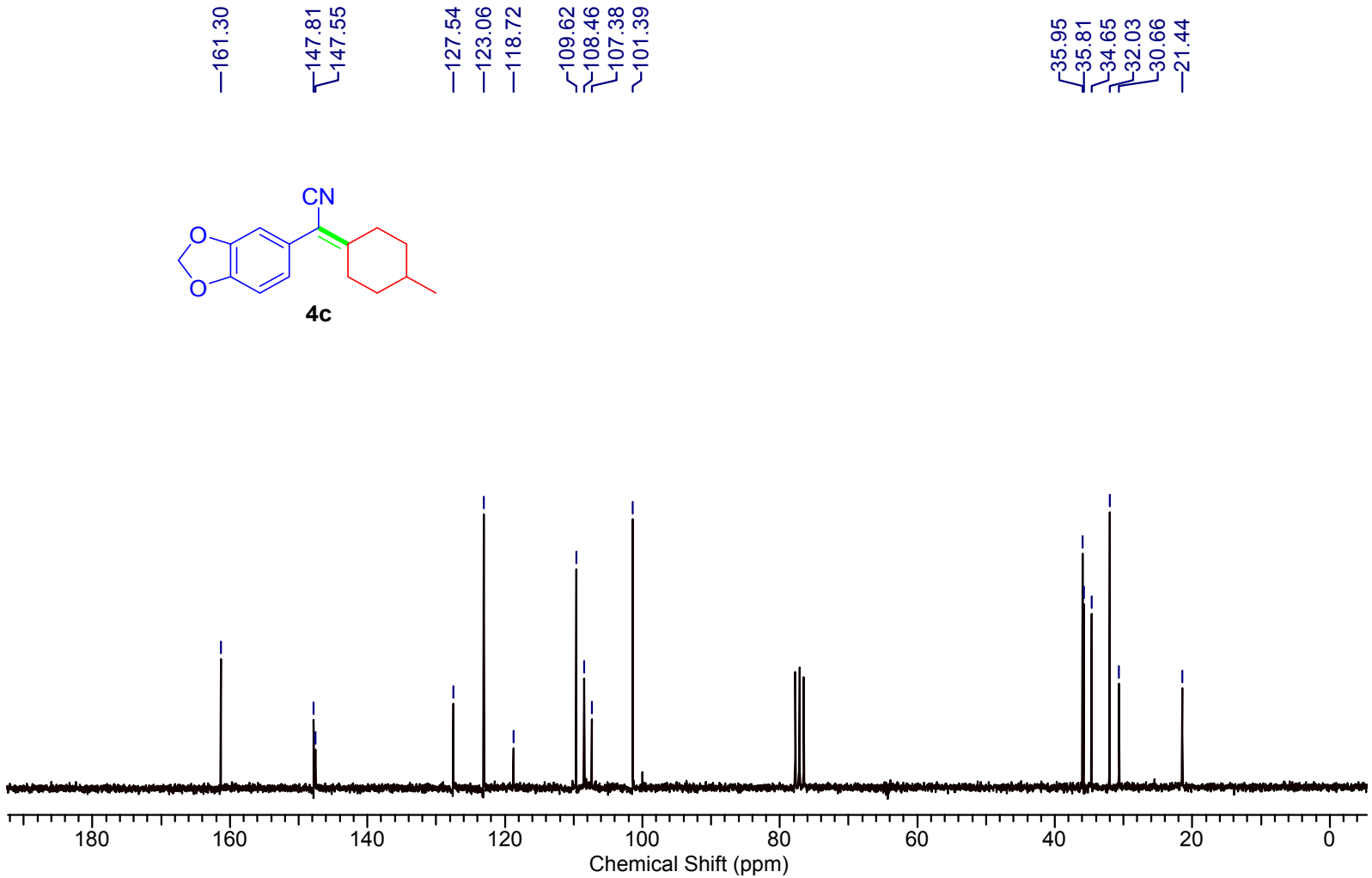
^{13}C NMR spectrum of 2-(4-methylcyclohexylidene)-2-phenylacetonitrile (**4b**)



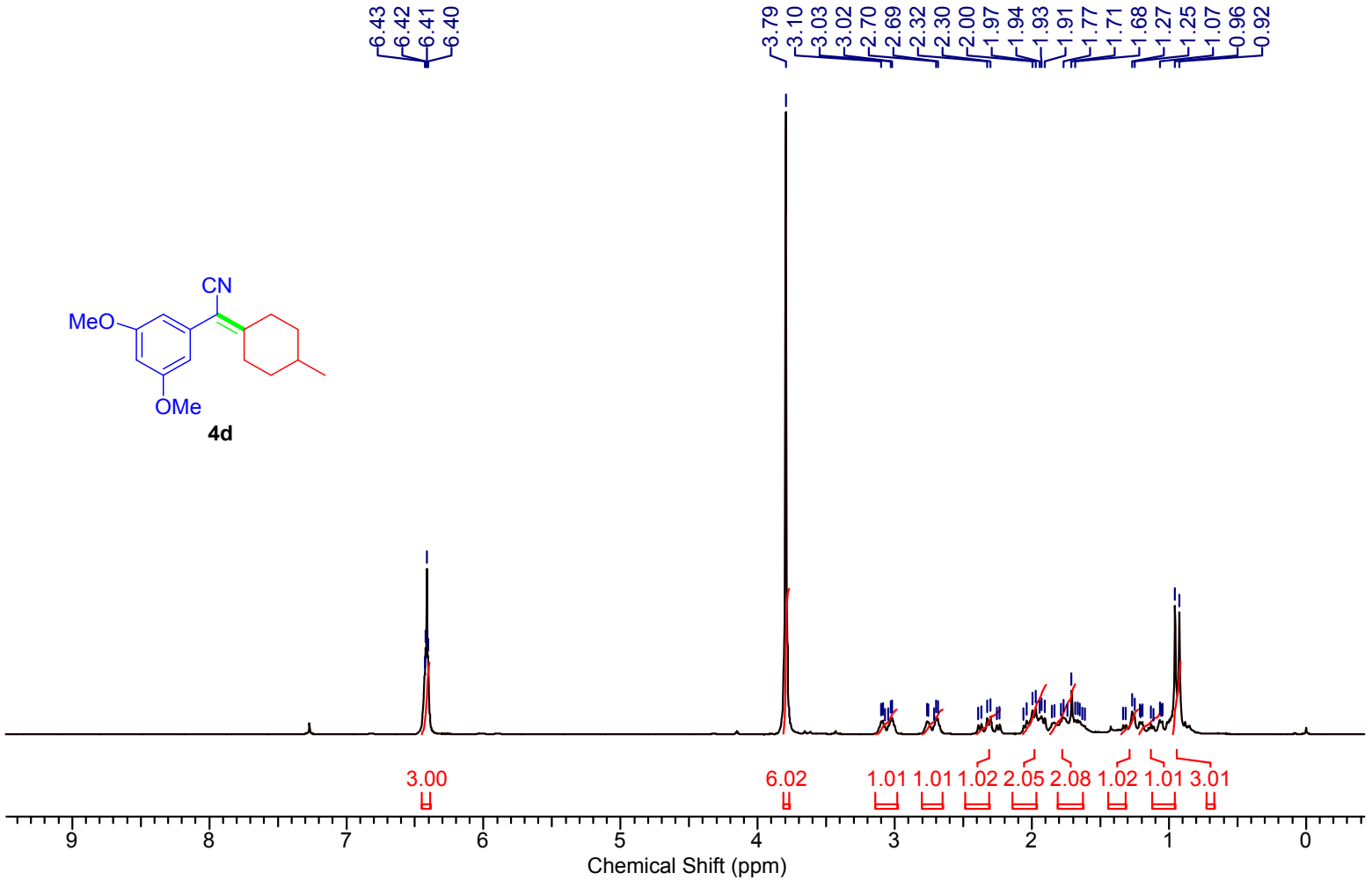
^{1}H NMR spectrum of 2-(benzo[d][1,3]dioxol-5-yl)-2-(4-methylcyclohexylidene)acetonitrile (**4c**)



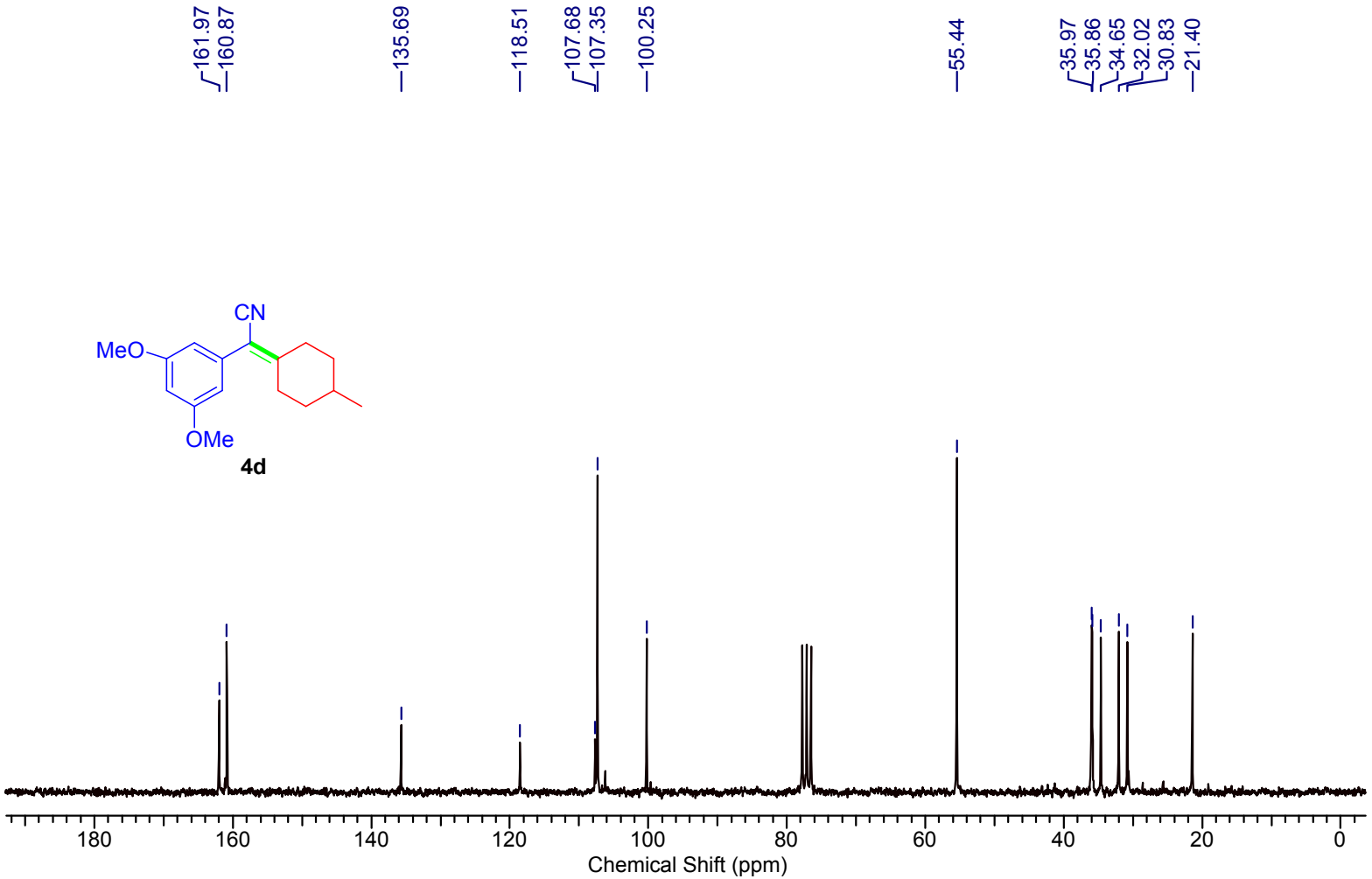
^{13}C NMR spectrum of 2-(benzo[d][1,3]dioxol-5-yl)-2-(4-methylcyclohexylidene)acetonitrile (**4c**)



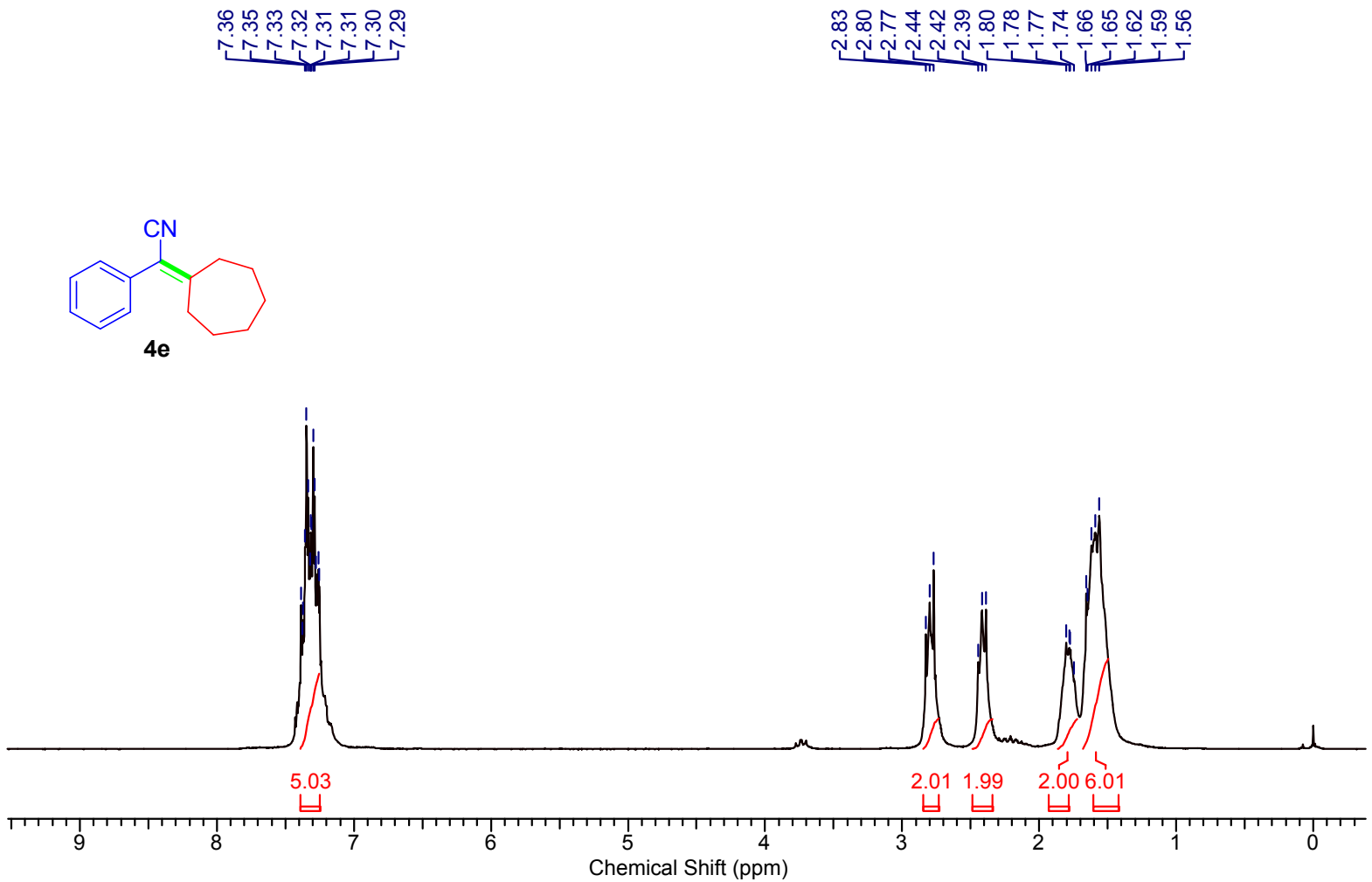
^{1}H NMR spectrum of 2-(3,5-dimethoxyphenyl)-2-(4-methylcyclohexylidene)acetonitrile (**4d**)



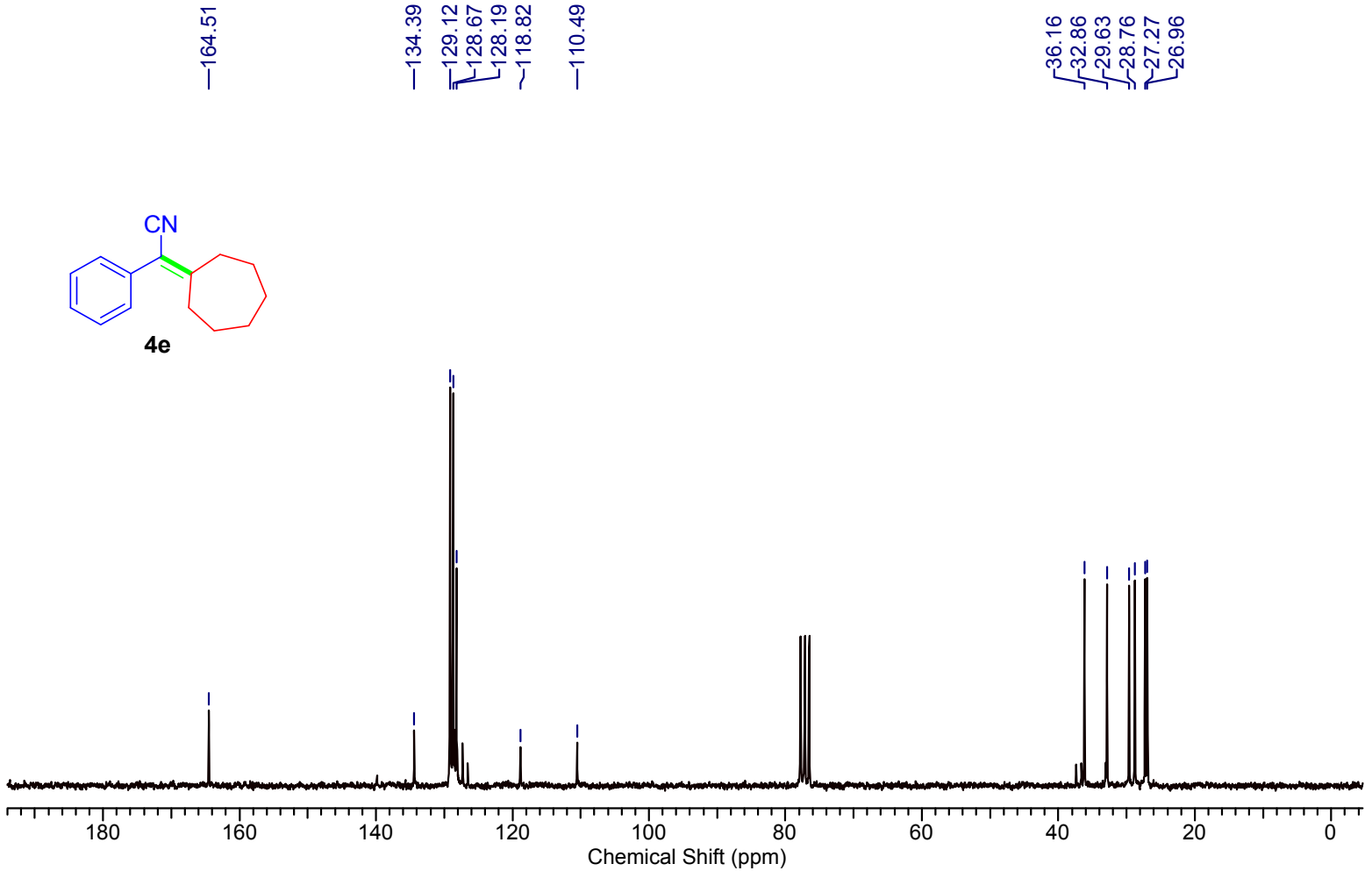
^{13}C NMR spectrum of 2-(3,5-dimethoxyphenyl)-2-(4-methylcyclohexylidene)acetonitrile (**4d**)



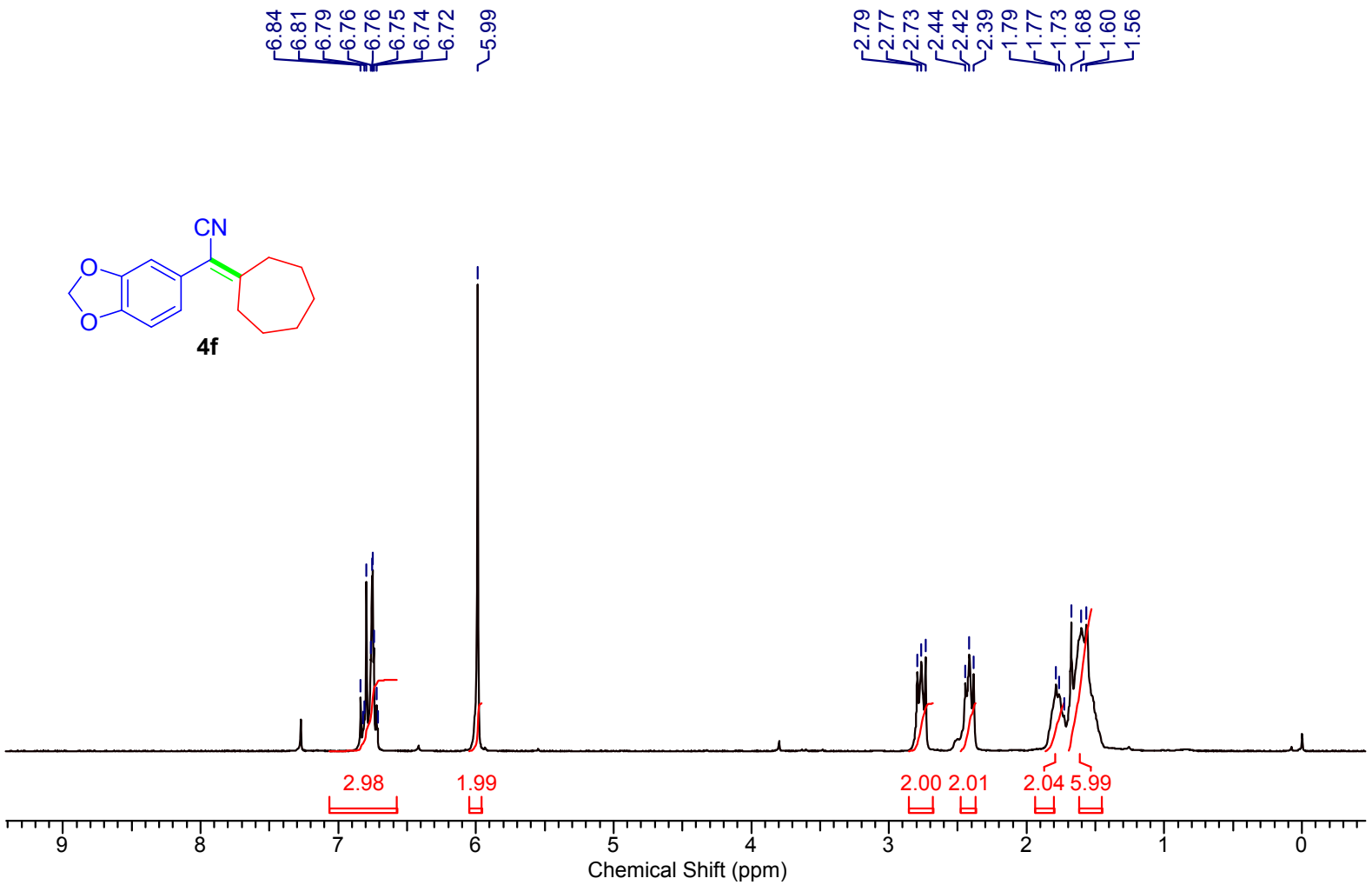
^{1}H NMR spectrum of 2-cycloheptylidene-2-phenylacetonitrile (**4e**)



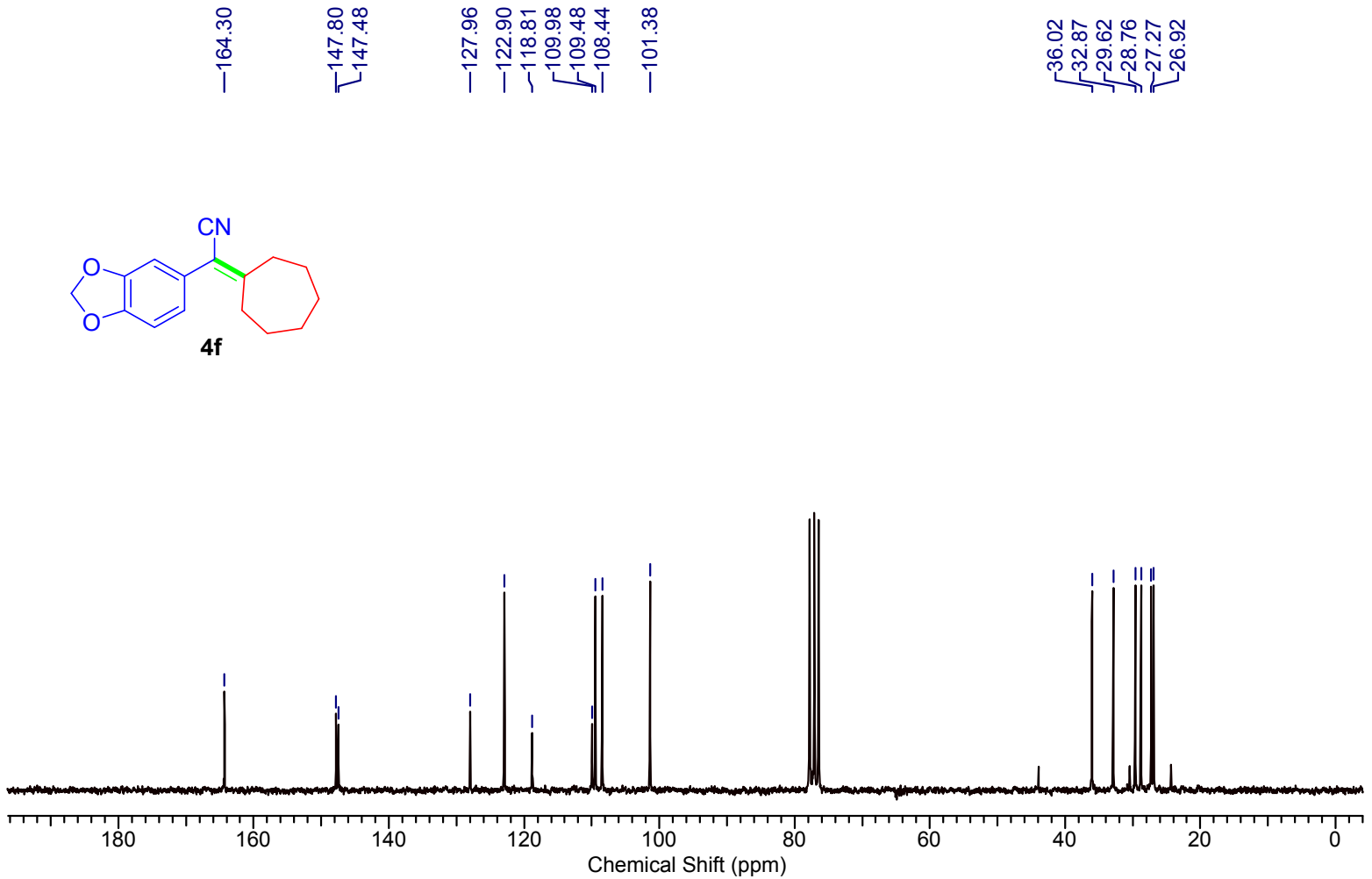
^{13}C NMR spectrum of 2-cycloheptylidene-2-phenylacetonitrile (**4e**)



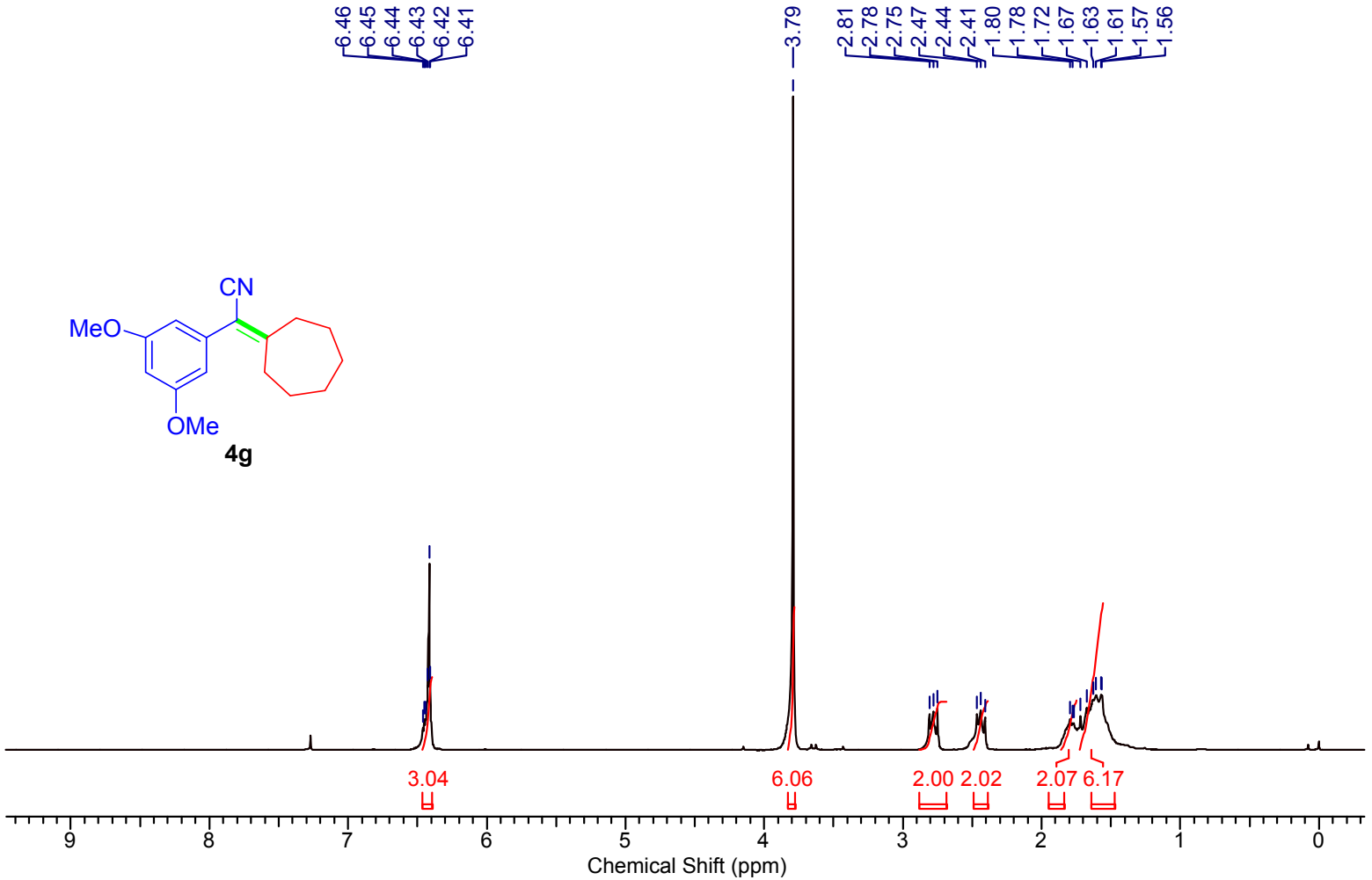
^{1}H NMR spectrum of 2-(benzo[*d*][1,3]dioxol-5-yl)-2-cycloheptylideneacetonitrile (**4f**)



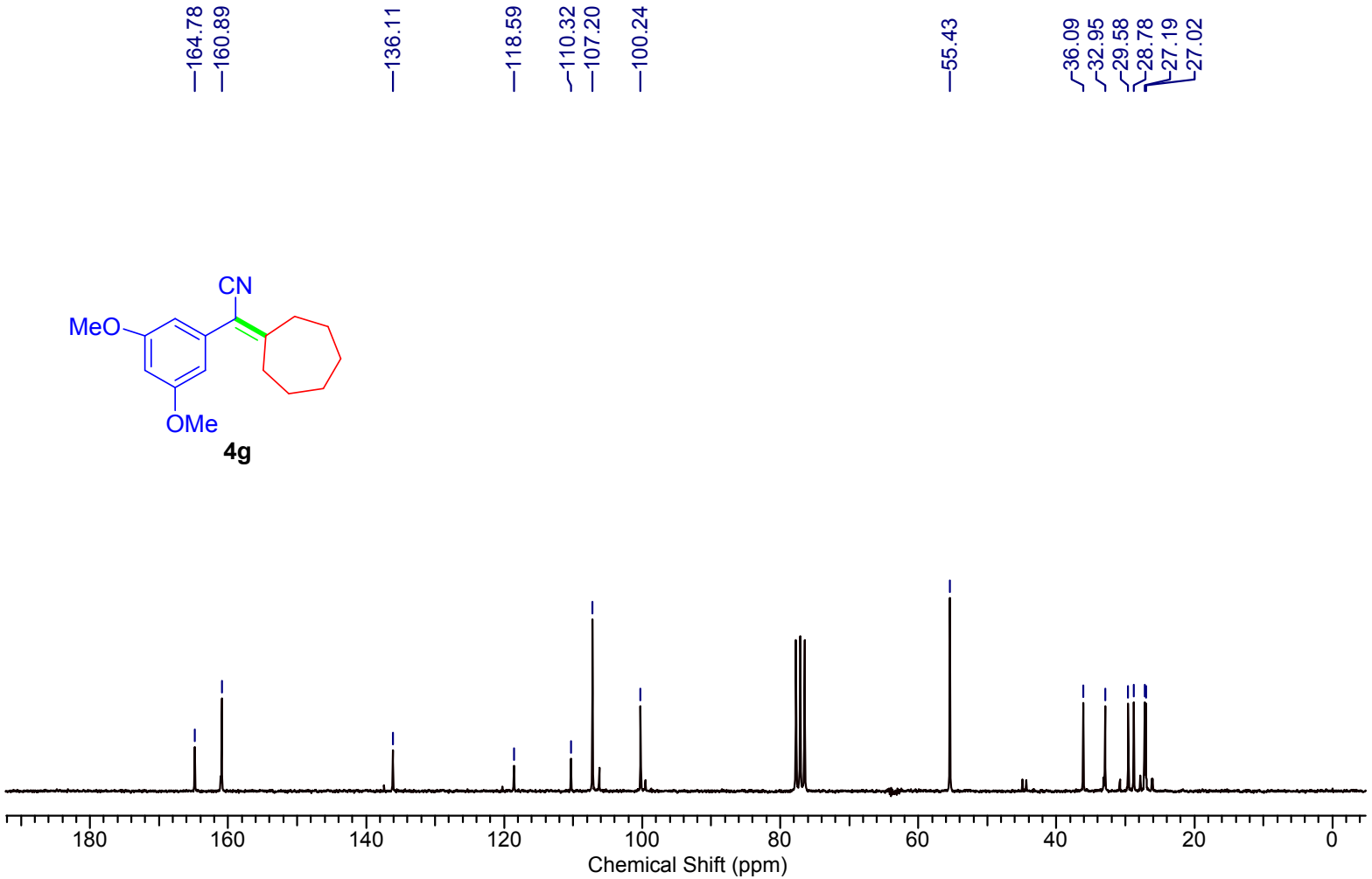
^{13}C NMR spectrum of 2-(benzo[d][1,3]dioxol-5-yl)-2-cycloheptylideneacetonitrile (**4f**)



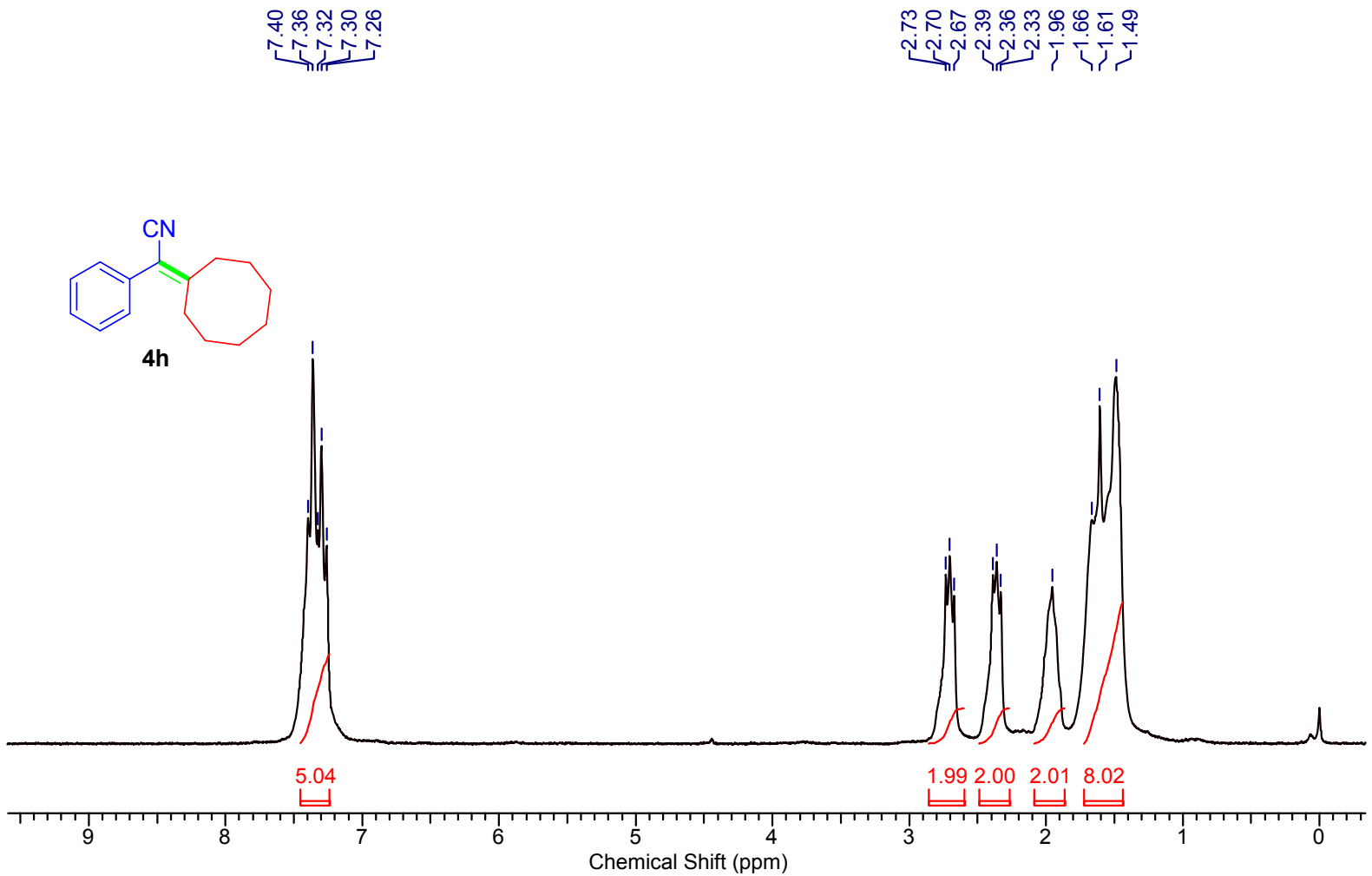
^{1}H NMR spectrum of 2-cycloheptylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**4g**)



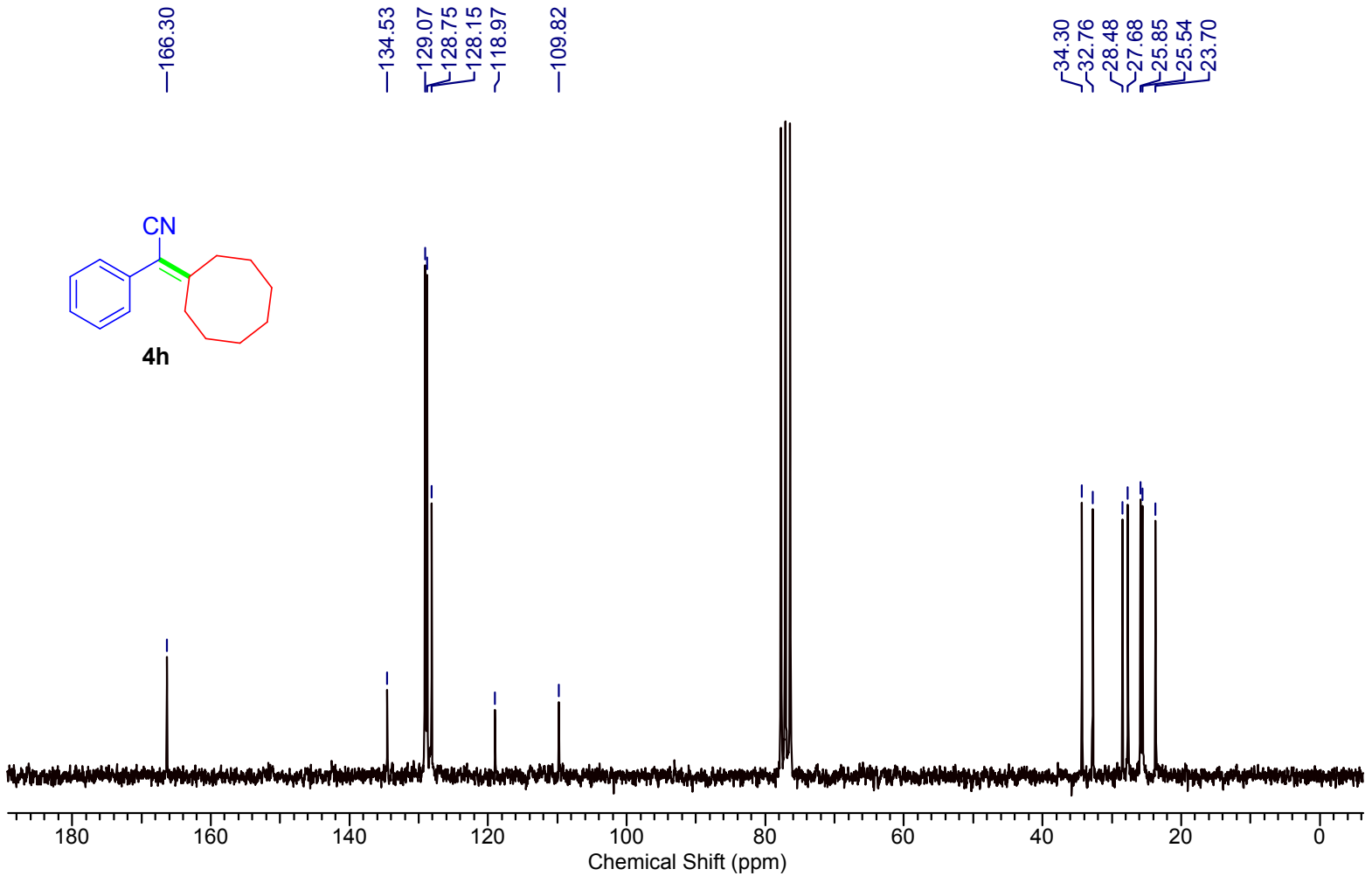
^{13}C NMR spectrum of 2-cycloheptylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**4g**)



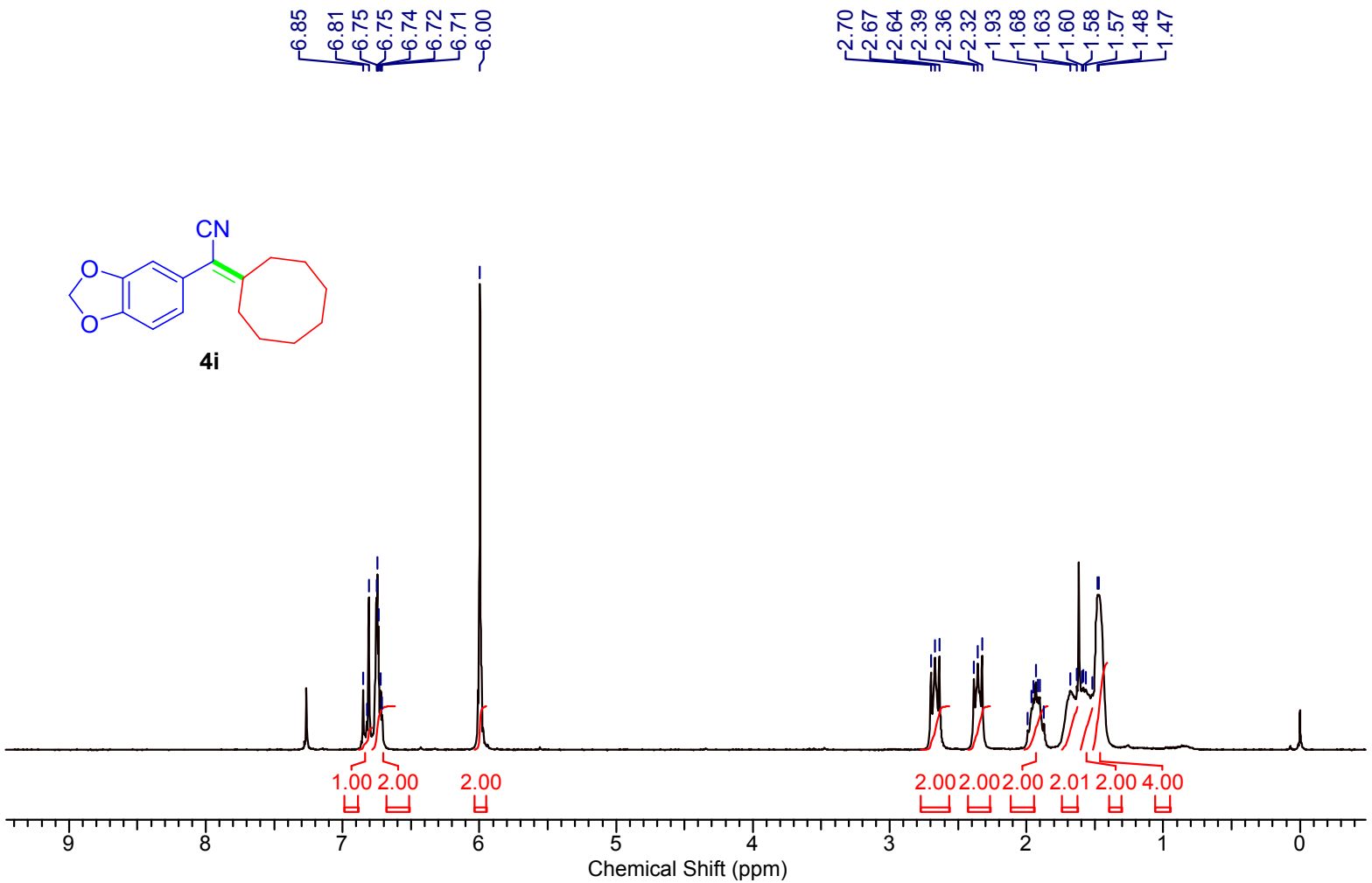
^{1}H NMR spectrum of 2-cyclooctylidene-2-phenylacetonitrile (**4h**)



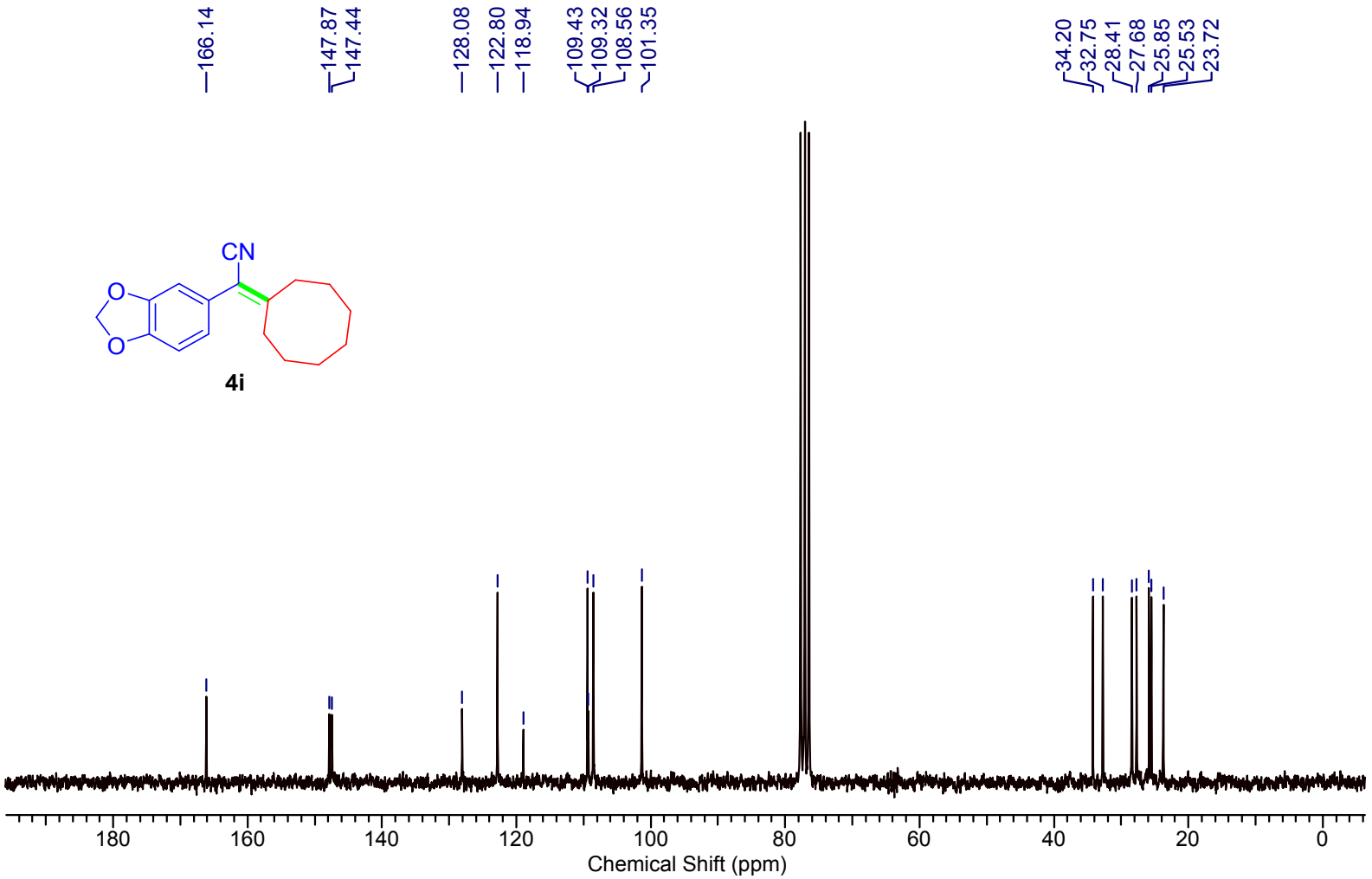
^{13}C NMR spectrum of 2-cyclooctylidene-2-phenylacetonitrile (**4h**)



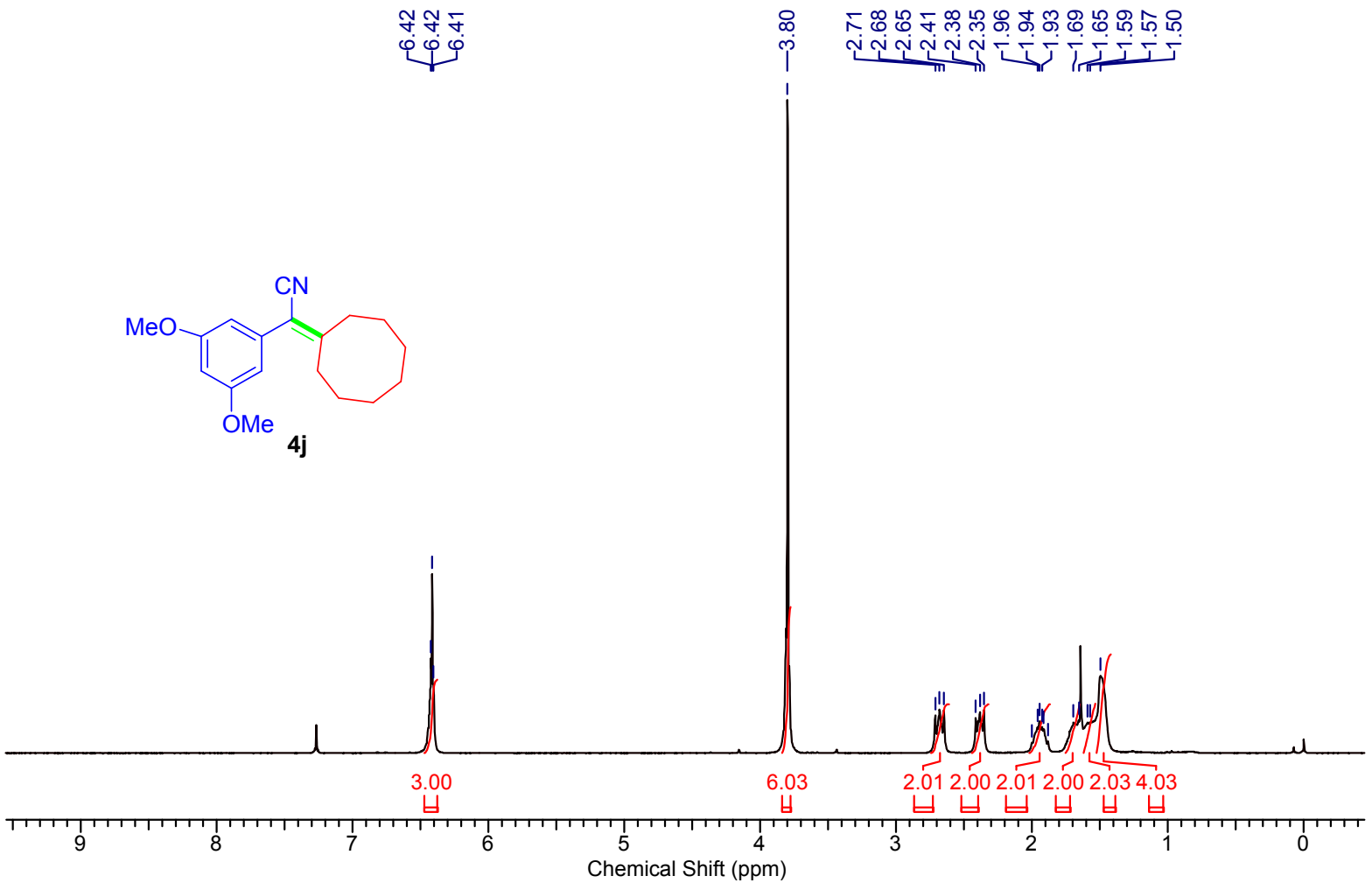
^{1}H NMR spectrum of 2-(benzo[*d*][1,3]dioxol-5-yl)-2-cyclooctylideneacetonitrile (**4i**)



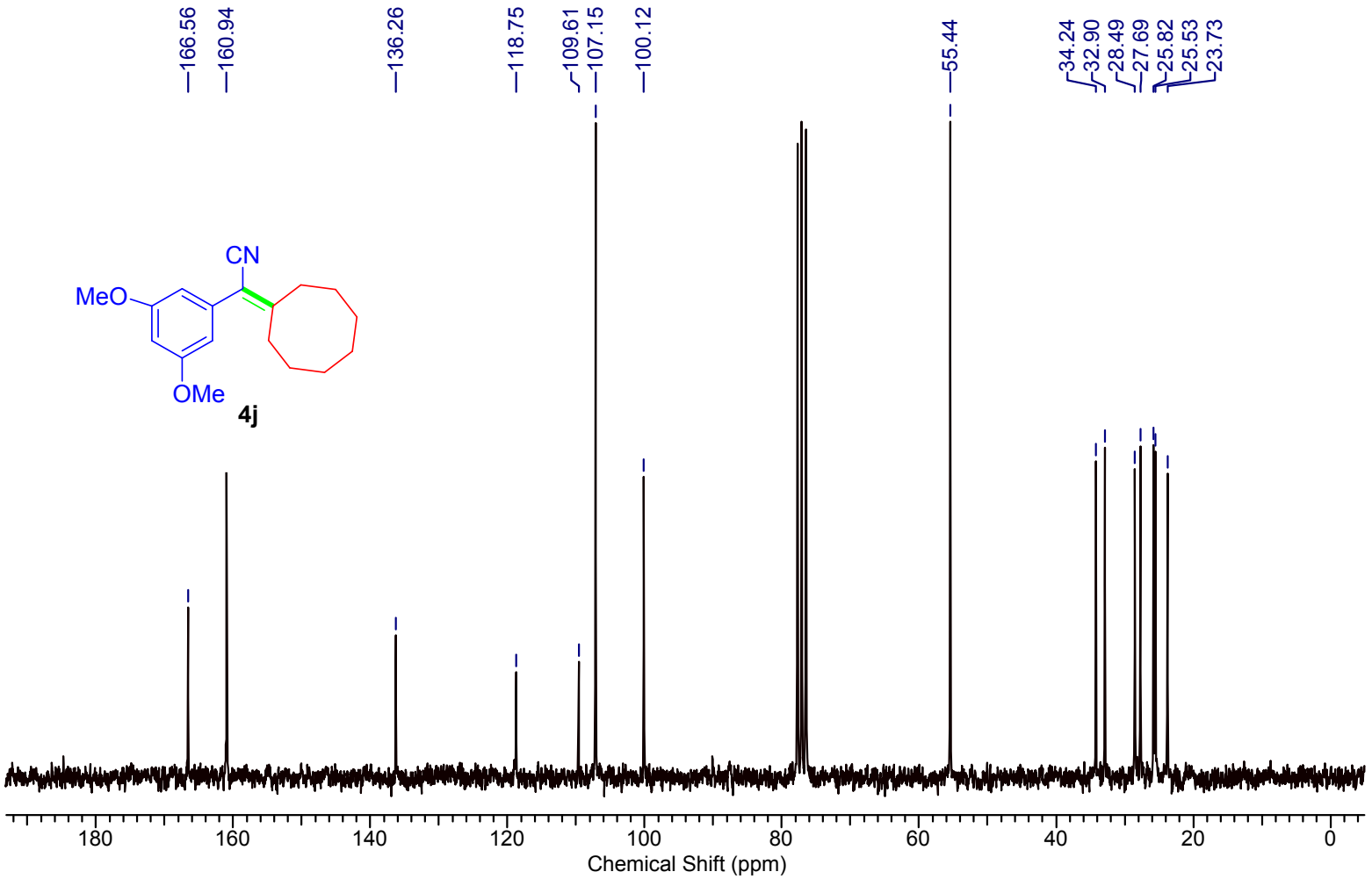
^{13}C NMR spectrum of 2-(benzo[*d*][1,3]dioxol-5-yl)-2-cyclooctylideneacetonitrile (**4i**)



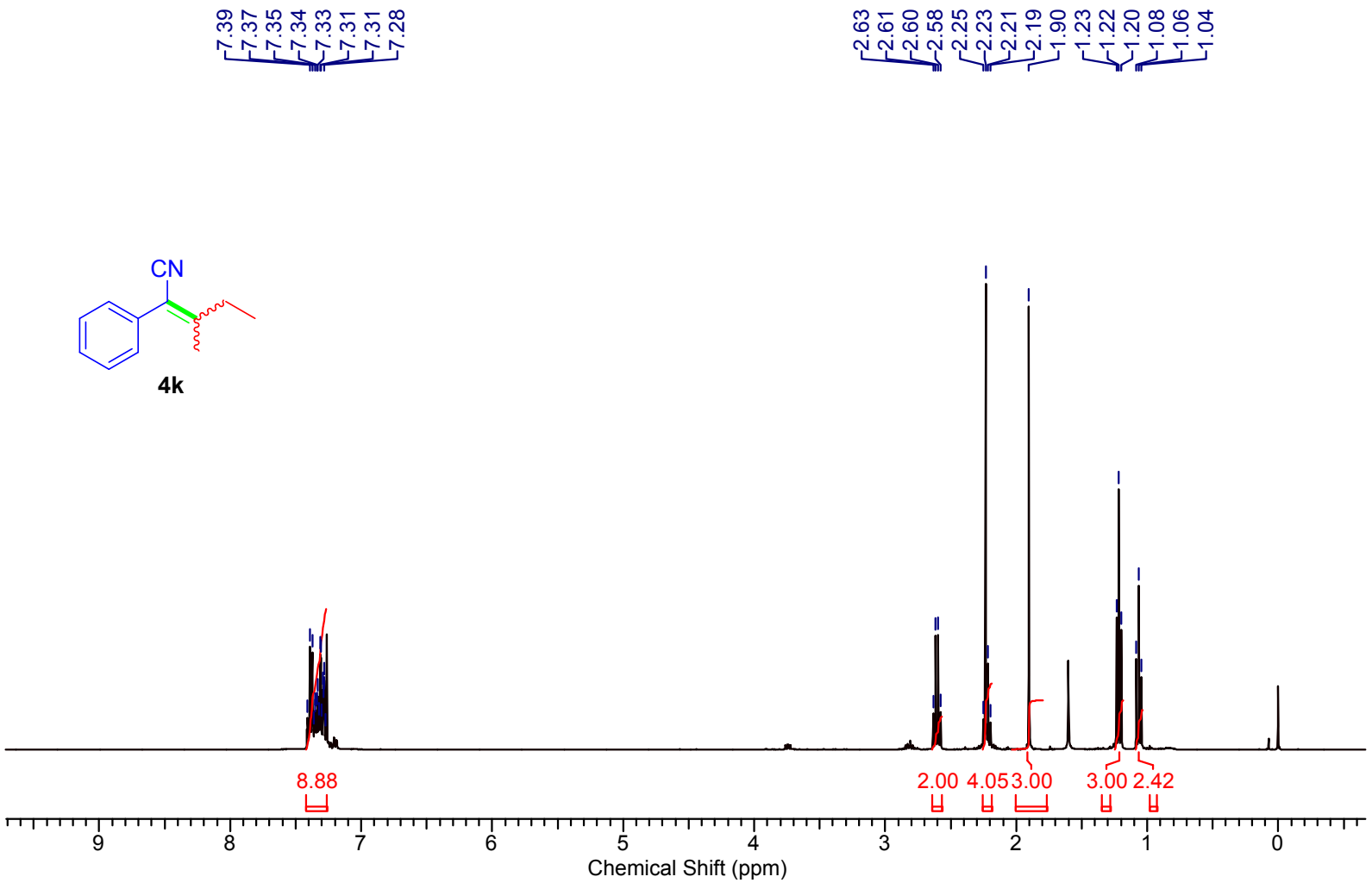
^{1}H NMR spectrum of 2-cyclooctylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**4j**)



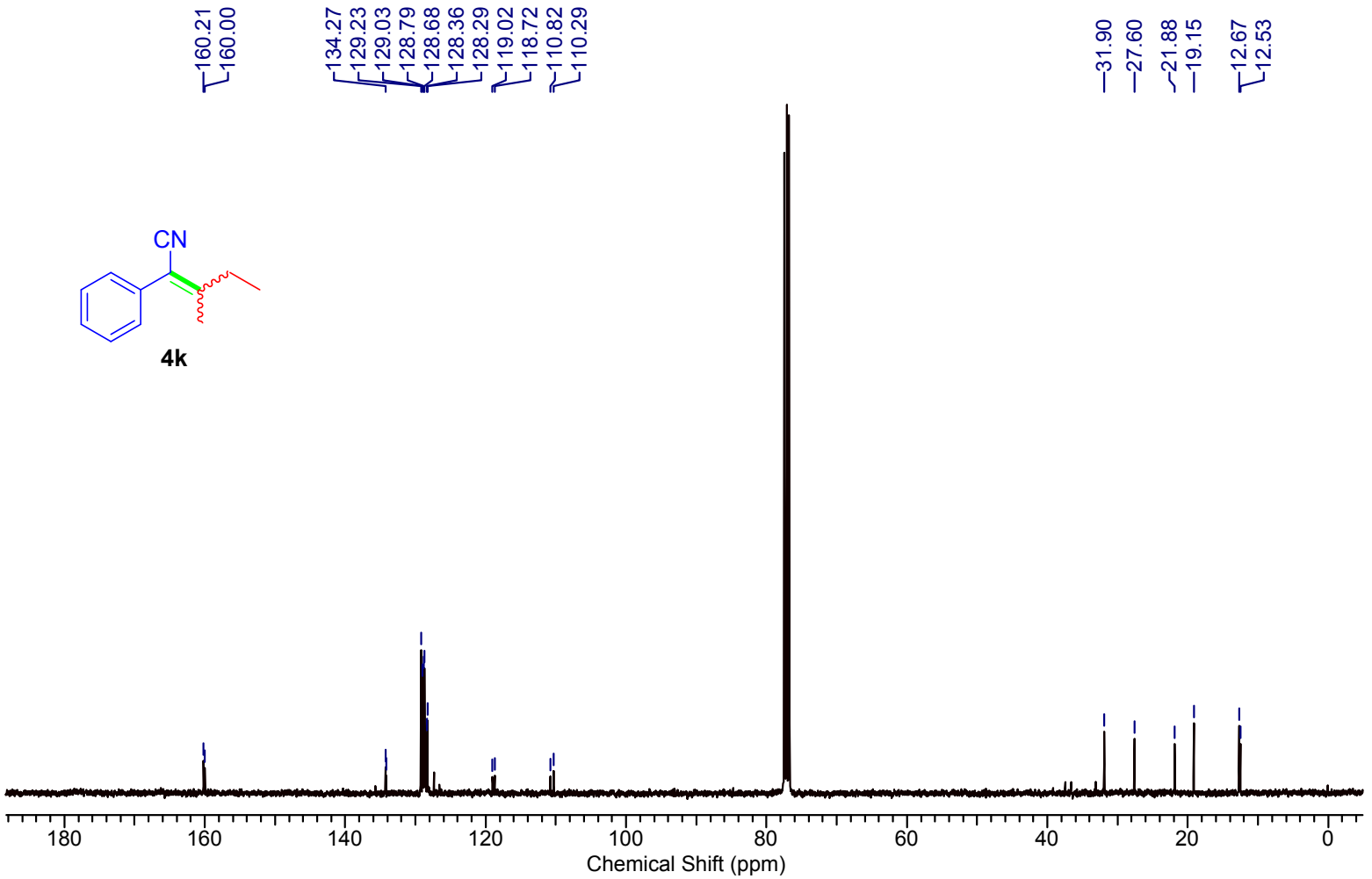
^{13}C NMR spectrum of 2-cyclooctylidene-2-(3,5-dimethoxyphenyl)acetonitrile (**4j)**



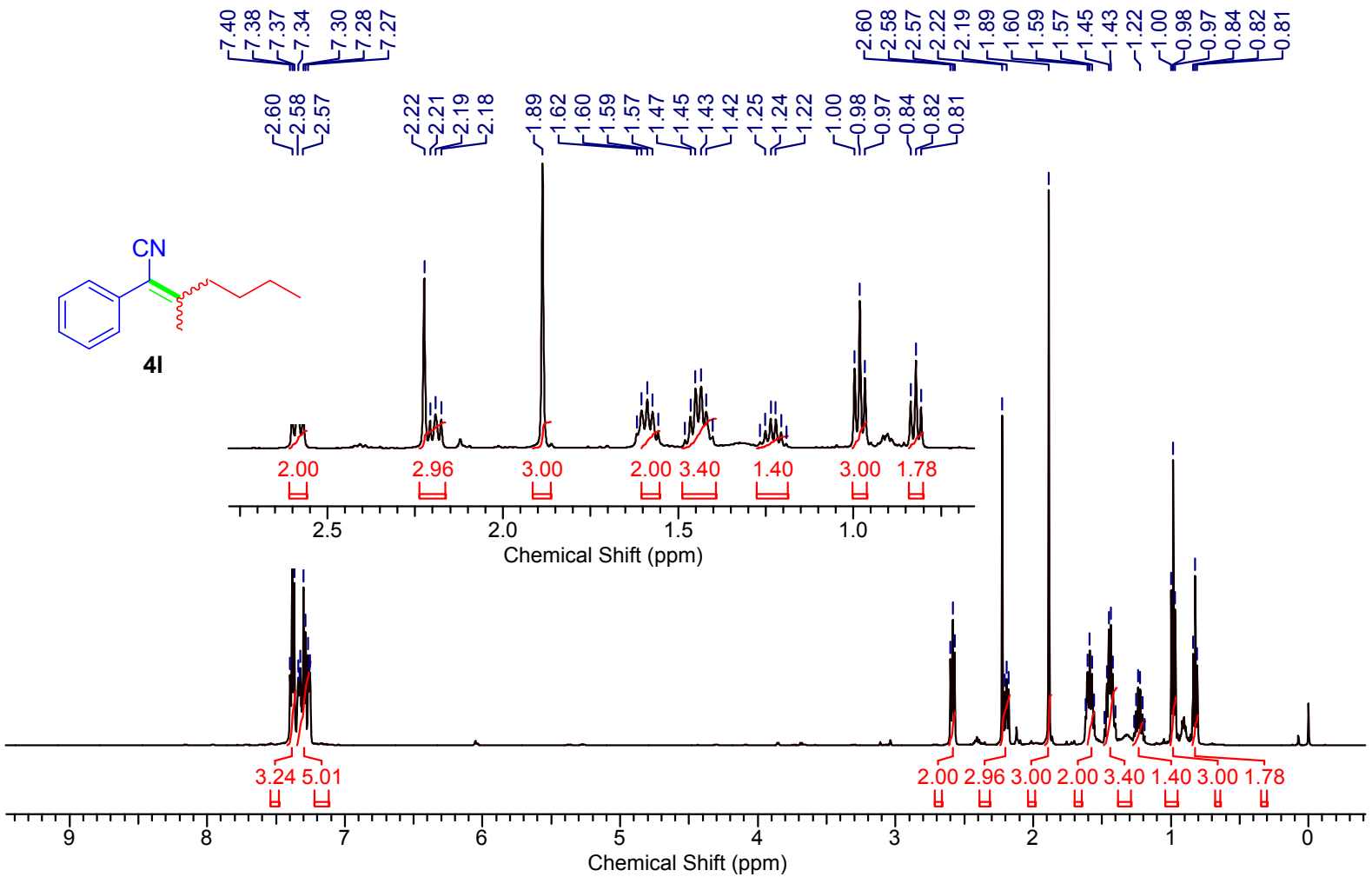
^{1}H NMR spectrum of 3-methyl-2-phenylpent-2-enenitrile (**4k**)



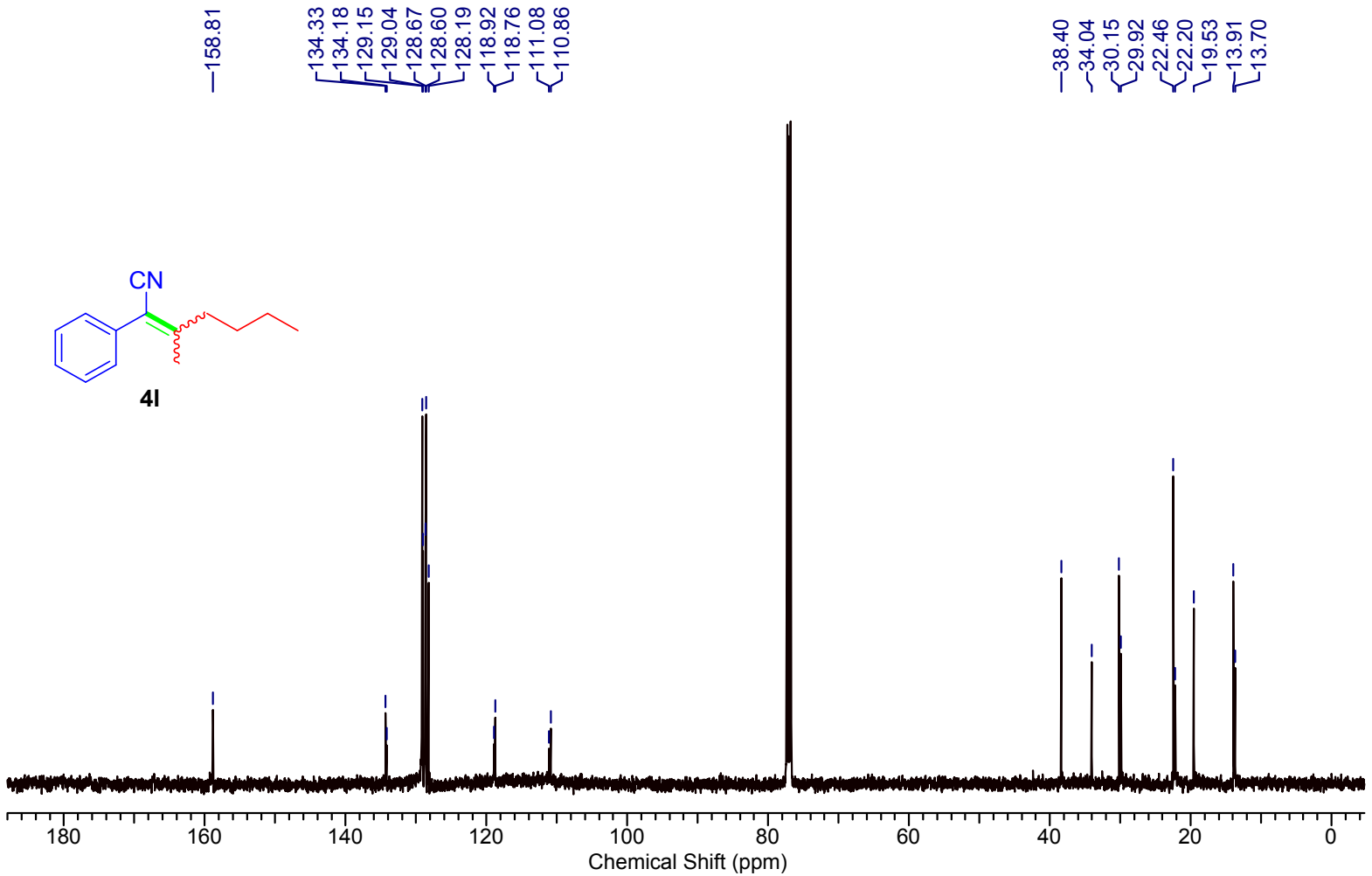
^{13}C NMR spectrum of 3-methyl-2-phenylpent-2-enenitrile (**4k**)



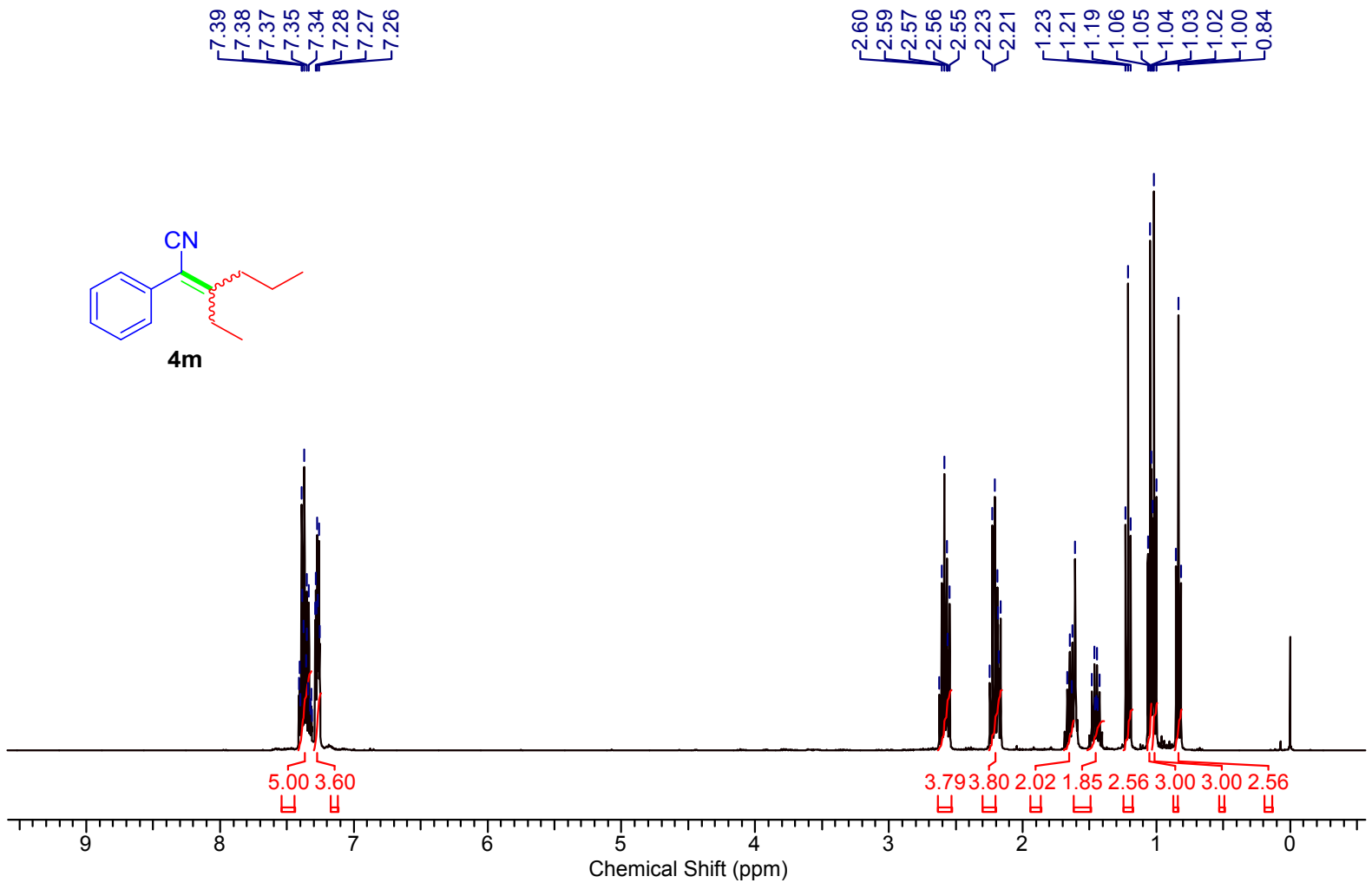
^{1}H NMR spectrum of 3-methyl-2-phenylhept-2-enenitrile (**4l**)



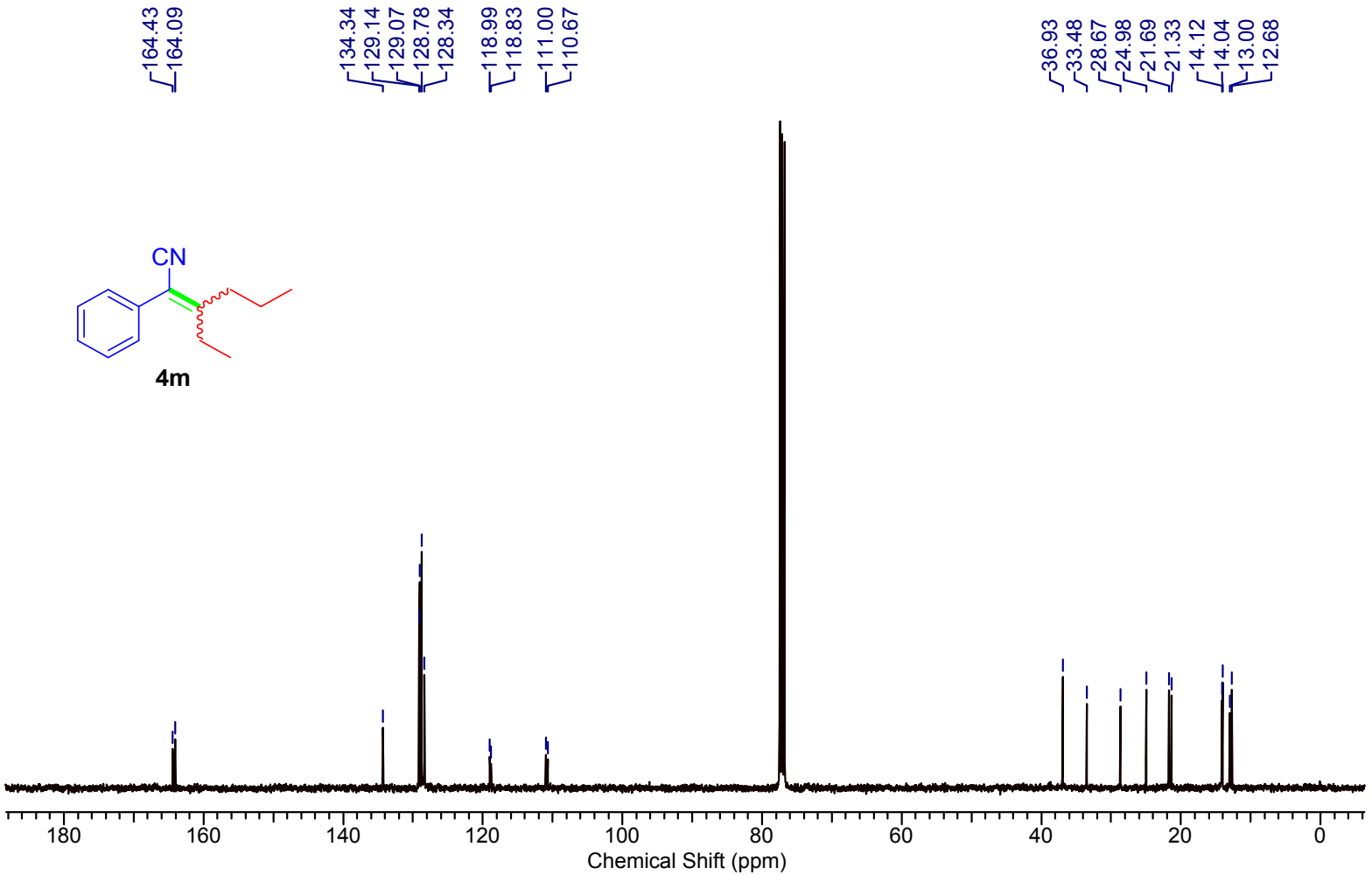
^{13}C NMR spectrum of 3-methyl-2-phenylhept-2-enenitrile (**4l**)



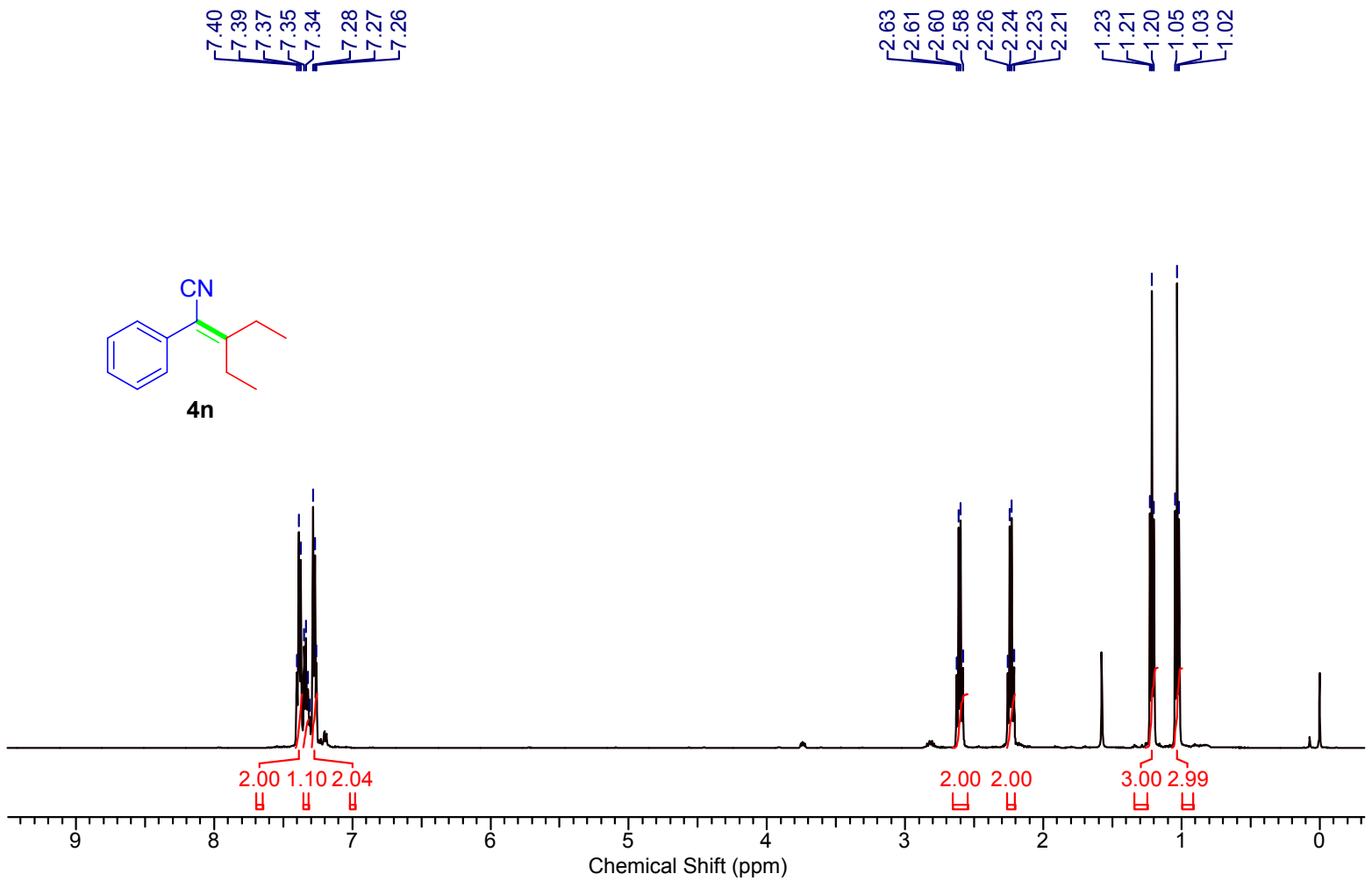
^{1}H NMR spectrum of 3-ethyl-2-phenylhex-2-enenitrile (**4m**)



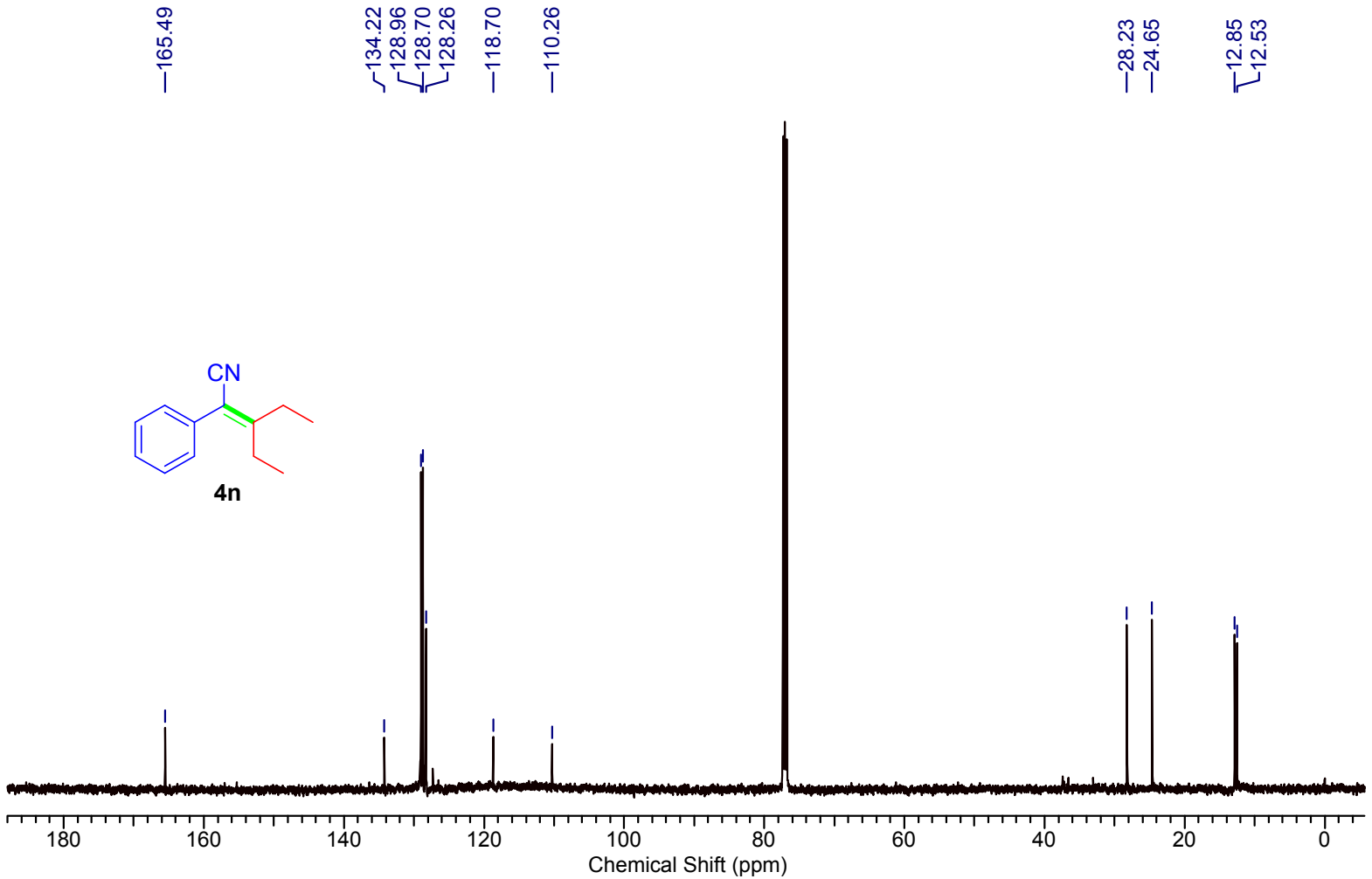
^{13}C NMR spectrum of 3-ethyl-2-phenylhex-2-enenitrile (**4m**)



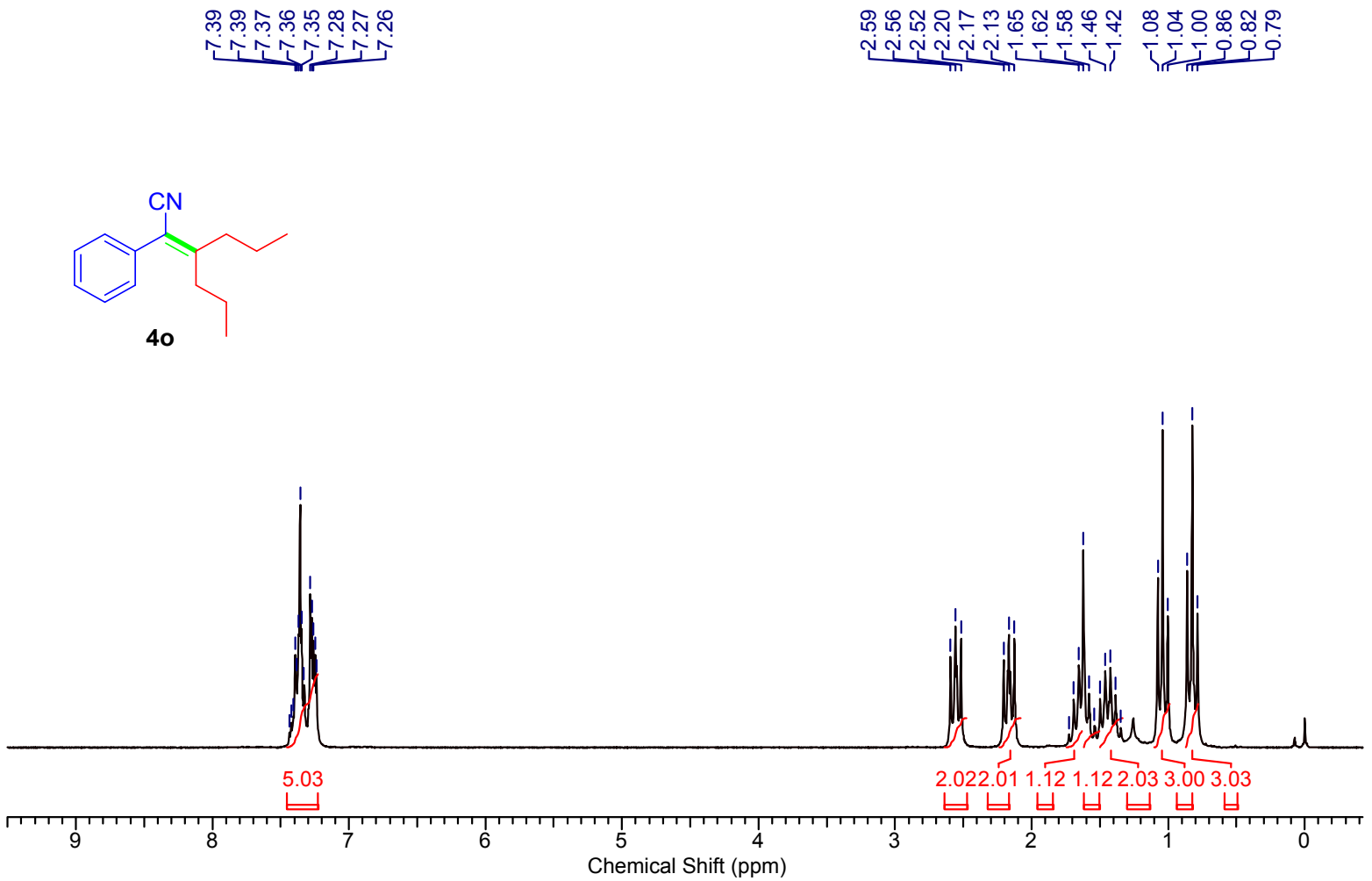
^{1}H NMR spectrum of 3-ethyl-2-phenylpent-2-enenitrile (**4n**)



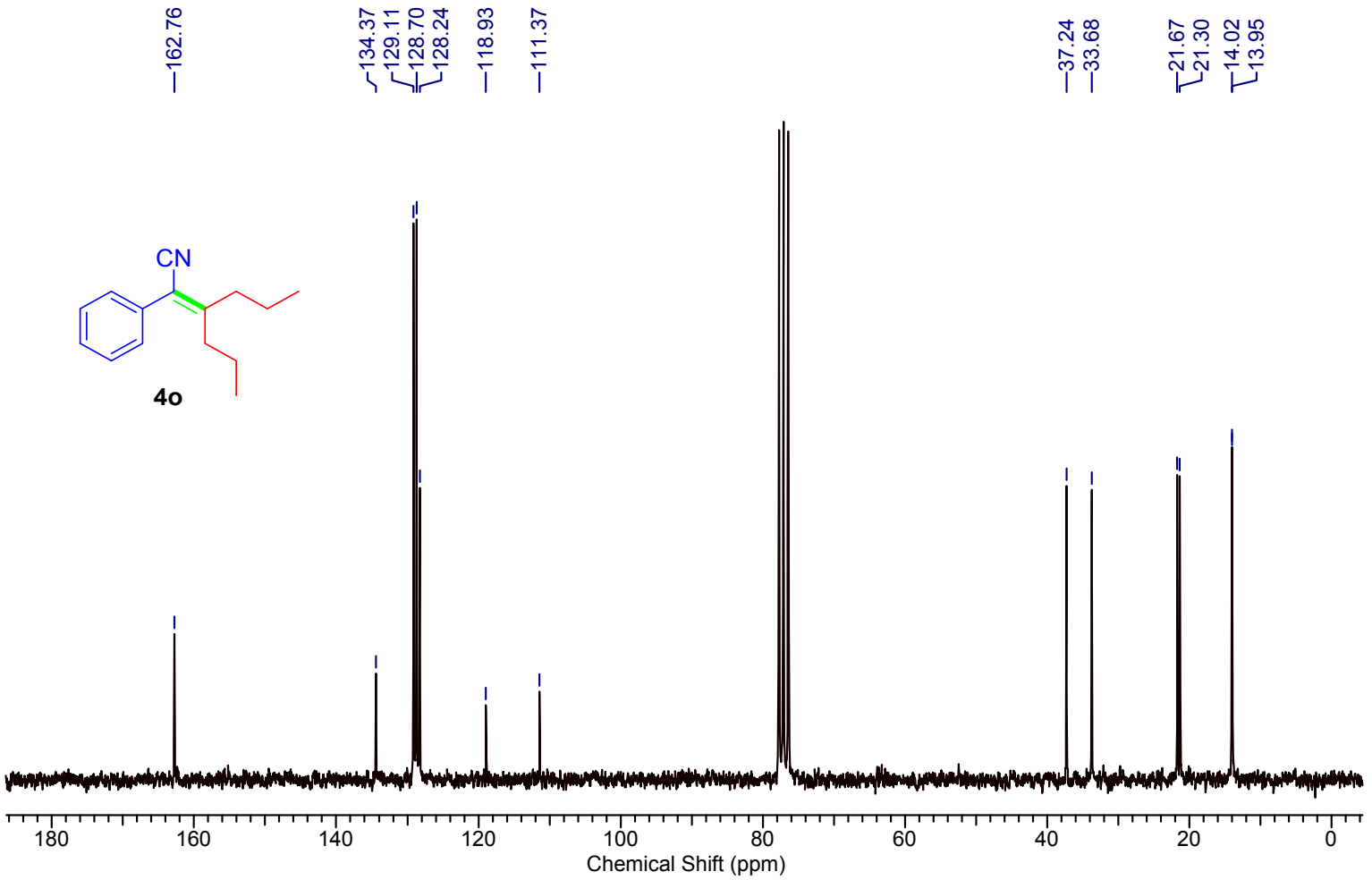
^{13}C NMR spectrum of 3-ethyl-2-phenylpent-2-enenitrile (**4n**)



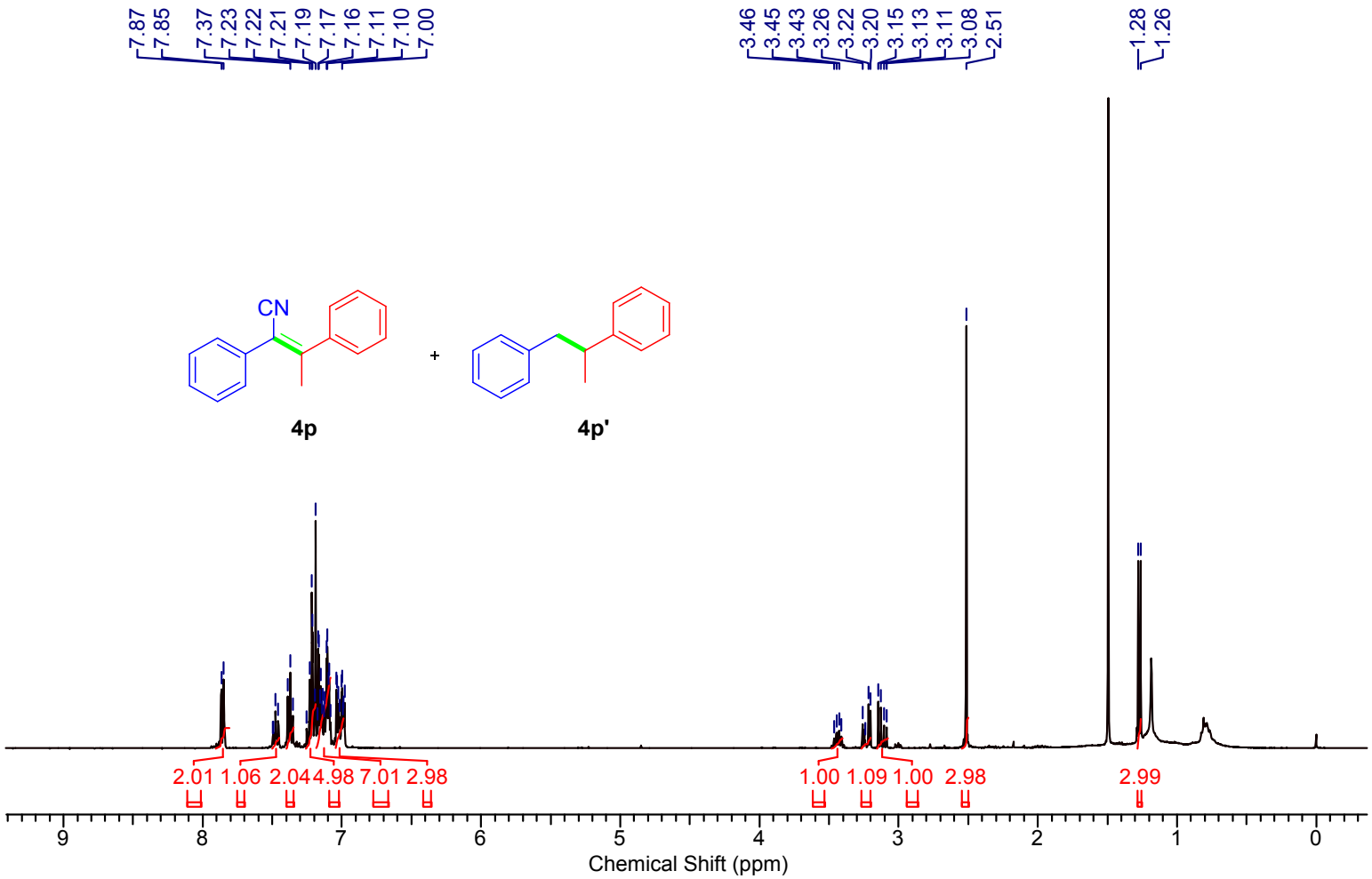
^{1}H NMR spectrum of2-phenyl-3-propylhex-2-enenitrile (**4o**)



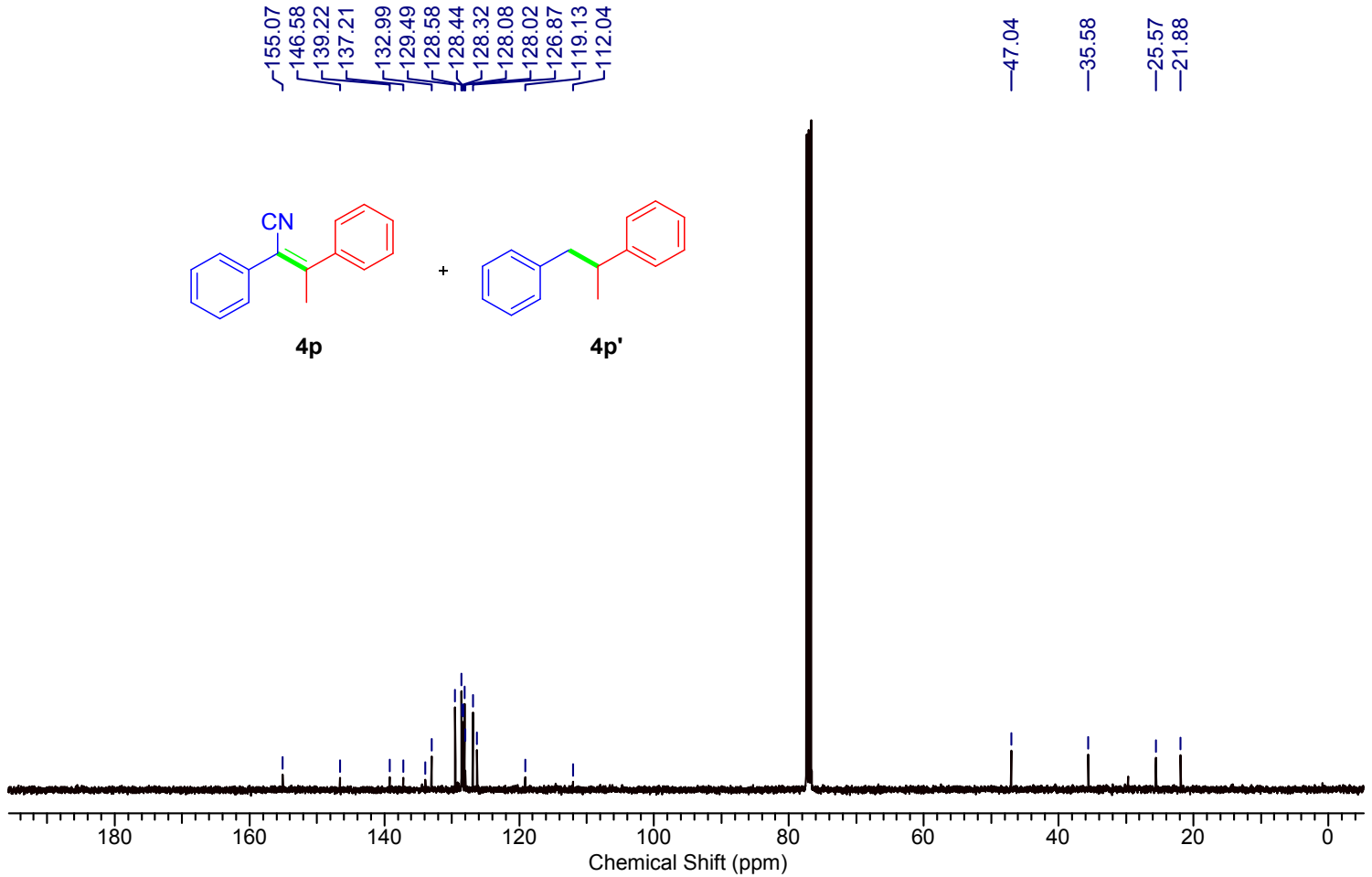
^{13}C NMR spectrum of 2-phenyl-3-propylhex-2-enenitrile (**4o**)



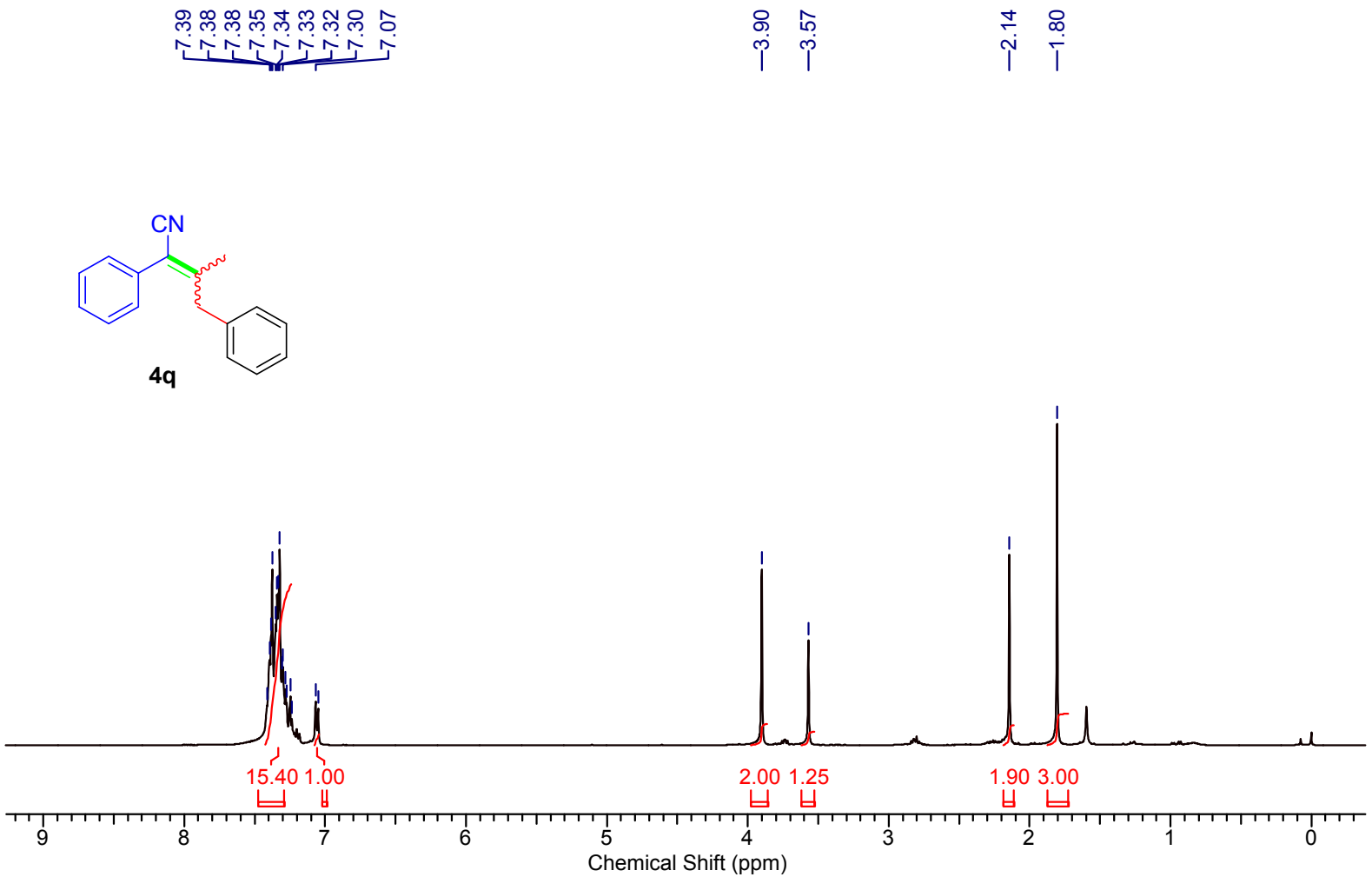
^{1}H NMR spectrum of (Z)-2,3-diphenylbut-2-enenitrile (**4p**)



^{13}C NMR spectrum of (Z)-2,3-diphenylbut-2-enenitrile (**4p**)



^{1}H NMR spectrum of 3-methyl-2,4-diphenylbut-2-enenitrile (**4q**)



^{13}C NMR spectrum of 3-methyl-2,4-diphenylbut-2-enenitrile (**4q**)