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Transient [3,3] Cope rearrangement of 3,3-dicyano-1,5-dienes: computational analysis and 2-step synthesis of arylcycloheptanes

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Abstract: A simple and modular route to arylcycloheptene scaffolds is reported. The two-step route from Knoevenagel adducts and allylic electrophiles is made possible through the design of a Cope rearrangement that utilizes a “traceless” activating group to promote an otherwise thermodynamically unfavorable transformation. Experimentally, the [3,3] rearrangement occurrs transiently at room temperature with a computed barrier of 19.5 kcal/mol, which ultimately allows for three-component bis-allylation. Ring-closing metathesis delivers the arylcycloheptane and removes the activating group. This report describes the design and optimization of the methodology, scope and mechanistic studies, and computational analysis.

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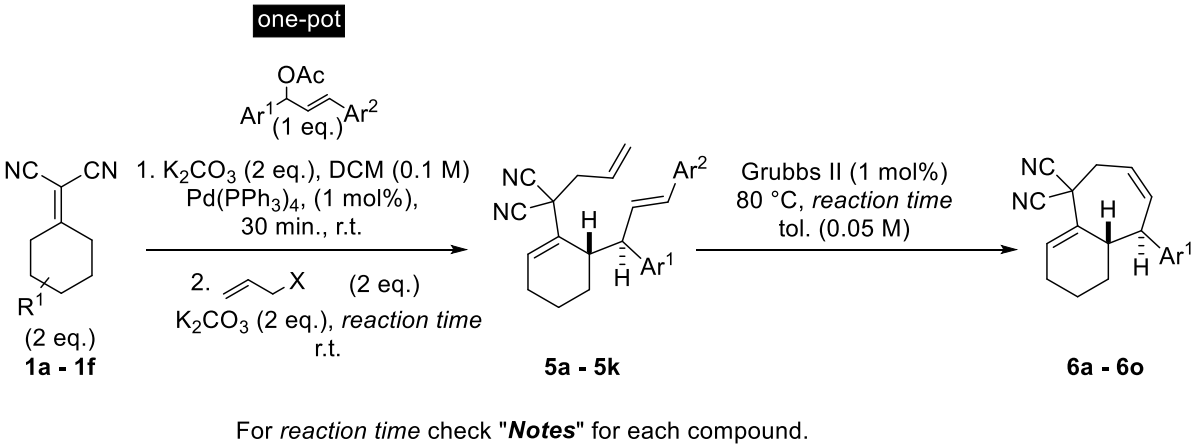
1. General Experimental Details

All commercial materials were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded in either chloroform-d, acetone-d6 or dimethyl sulfoxide-d6 using a 600MHz, 500 MHz or 300 MHz spectrometer. All ^{13}C NMR spectra were recorded with complete proton decoupling. HRMS data were recorded on Agilent Time of Flight 6200 spectrometer. LRMS were recorded on a Finnigan LCQ-DUO mass spectrometer or on a Finnigan 2001 Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Reaction progress was monitored by thin-layer chromatography (TLC) and visualized by UV light, phosphomolybdic acid stain, and $KMnO_4$ stain. All reactions were carried out using anhydrous solvents obtained dried by passing through activated alumina columns. According to the reported synthetic processes, chalcones were easily synthesized in nearly quantitative yields by NaOH-mediated aldol condensation of acetophenones and arylaldehydes in ethanol. Without further purification, the chalcone derivatives was treated with 1.0 equiv. of $NaBH_4$ in in the co-solvent of THF and MeOH (v/v: 1/1) at 0 °C for 10 min., followed by acetylation of the resulting the allylic alcohols in an excellent yield. Synthesis of **2a-2g**, **7a** are known and the spectroscopic data were consistent with those reported in the literature. [1-2] Allyl tert-butyl carbonate (**4a**) was prepared from prop-2-en-1-ol according to the previously reported procedure.[3] All spectroscopic data for these three electrophiles were consistent with those reported in the literature. The allylated malononitrile (**11a**) was synthesized using the know procedure in the literature [4] and all the analytical data were identical to the cited reference. The Knoevenagel adducts (**1a**-**1i**) synthesized according to the previously reported procedures and the spectroscopic data were consistent with those reported in the literature. [3,5-7] All other synthetic protocols are outlined below.

2. General procedure A and B: Pd-catalyzed diallylation of Knoevenagel adducts (one-pot) and Ring Closing Metathesis



Pd-catalyzed diallylation of Knoevenagel adducts (one-pot) and Ring Closing Metathesis

General procedure A: Pd-catalyzed diallylation of Knoevenagel adducts (one-pot):

All reactions were performed under nitrogen atmosphere in flame-dried round bottom flasks. Chalcone derivatives were added at room temperature to a solution of tetrakis(triphenylphosphine)palladium(0) (1 mol%), the Knoevenagel adduct (1 equiv.) and K_2CO_3

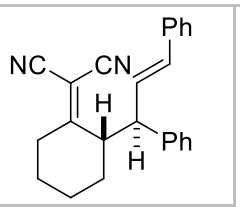
(2 equiv.) in DCM (0.1 M). The mixture was stirred at r.t. for 30 minutes. Then, 2 equiv. of the Allyl tert-butyl carbonate or allyl bromide was added via syringe. After completion, DCM was removed in vacuo, and the resulting residue was purified by flash column chromatography on silica gel. and the crude products were purified by column chromatography (hexanes – ethyl acetate).

General procedure A1: All reactions were performed under nitrogen atmosphere in flame-dried round bottom flasks. Chalcone derivatives were added at room temperature to a solution of tetrakis(triphenylphosphine)palladium(0) (1 mol%), the Knoevenagel adduct (1 equiv.) and K_2CO_3 (2 equiv.) in DCM (0.1 M). The mixture was stirred at r.t. for 30 minutes. After completion, DCM was removed in vacuo, and the resulting residue was purified by flash column chromatography on silica gel. and the crude products were purified by column chromatography (hexanes – ethyl acetate).

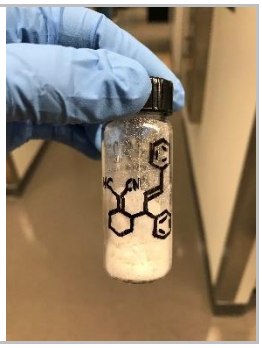
General procedure B: Ring Closing Metathesis:

All reactions were performed under nitrogen atmosphere in flame-dried round bottom flasks. The γ,α-diallylated Knoevenagel adduct **5a – 5k** was taken in anhydrous degassed toluene (0.05 M). Then, Grubbs Catalyst 2nd generation (1 mol%) was added to it and the solution was stirred at 80 °C for the time shown for each compound. After completion of the reaction, it was cooled to room temperature and passed through a short silica gel bed and washed with ethyl acetate. Then the solution was evaporated under reduced pressure. The residue was then purified by silica gel chromatography (EtOAc/hexane) to afford the final product. Note: Stereochemistry of the final products was assigned based on **6n** and those reported in the previous work.[6]

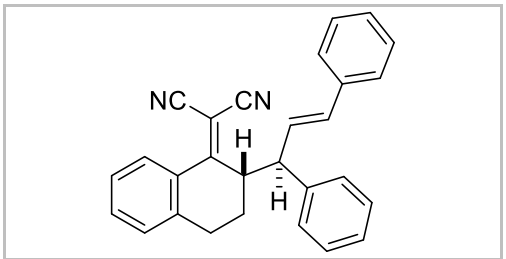
3. ^{1}H & ^{13}C NMR Spectral Data



(E)-2-(2-(1,3-diphenylallyl) cyclohexylidene) malononitrile (3a)



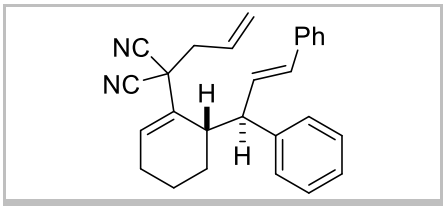
Prepared by general procedure **A1** with the following notes:
Note: *reaction time: 30 min.*
Isolated: 5 g
Yield: 50% (>20:1 dr)
Physical state: white solid
TLC: R_f =0.59 (20% EtOAc in hexanes); Purified using recrystallization (ethanol)
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (dt, *J* = 12.9, 5.5 Hz, 7H), 7.27 – 7.22 (m, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.28 (dd, *J* = 15.6, 9.4 Hz, 1H), 3.82 – 3.74 (m, 1H), 3.53 (dd, *J* = 11.2, 4.3 Hz, 1H), 3.03 (d, *J* = 14.3 Hz, 1H), 2.50 (td, *J* = 13.8, 5.5 Hz, 1H), 2.19 (d, *J* = 12.9 Hz, 1H), 1.86 – 1.74 (m, 1H), 1.71 (d, *J* = 14.0 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.48 (ddd, *J* = 18.7, 9.5, 4.5 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 186.7, 140.8, 136.2, 131.3, 129.3, 129.2, 128.7, 127.9, 127.7, 127.4, 126.4, 112.0, 111.5, 84.3, 51.3, 48.3, 31.5, 29.2, 28.1, 19.7.



(E)-2-(2-(1,3-diphenylallyl)-3,4-dihydro naphthalen-1(2H)-ylidene)malononitrile (3b)

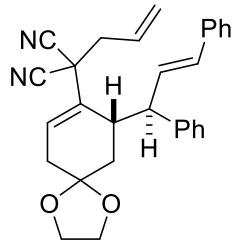
Prepared by general procedure **A1** with the following notes:
Note: *reaction time: 30 min.*
Isolated: 0.7 g

Yield: 75% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.53 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.29 (m, 12H), 6.37 (dd, *J* = 15.6, 9.6 Hz, 1H), 5.99 (d, *J* = 15.6 Hz, 1H), 3.83 (dt, *J* = 11.1, 3.4 Hz, 1H), 3.35 (t, *J* = 10.3 Hz, 1H), 3.07 (ddd, *J* = 17.8, 11.1, 6.4 Hz, 1H), 2.91 (dd, *J* = 18.1, 6.4 Hz, 1H), 2.07 – 1.99 (m, 1H), 1.92 – 1.84 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 176.8, 140.6, 139.9, 136.4, 133.7, 131.4, 129.9, 129.7, 129.2, 128.7, 128.7, 127.8, 127.6, 127.4, 126.9, 113.7, 113.7, 80.8, 60.4, 51.4, 47.3, 24.8, 24.6, 21.1, 14.2.



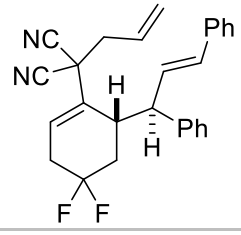
(E)-2-allyl-2-(6-(1,3-diphenylallyl)cyclo hex-1-en-1-yl)malononitrile (5a)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 156 mg
Yield: 60% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.52 (20% EtOAc in hexanes); Purified using 8% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.41 – 7.28 (m, 7H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.69 (dd, *J* = 15.7, 9.6 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.21 (t, *J* = 3.9 Hz, 1H), 5.93 – 5.77 (m, 1H), 5.34 (t, *J* = 10.8 Hz, 1H), 5.22 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.58 (t, *J* = 9.8 Hz, 1H), 3.03 (d, *J* = 9.5 Hz, 1H), 2.88 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.76 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.27 (tdd, *J* = 12.9, 8.6, 4.6 Hz, 1H), 1.91 – 1.79 (m, 1H), 1.65 – 1.57 (m, 2H), 1.41 (ddd, *J* = 14.0, 9.0, 4.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 142.6, 136.7, 133.4, 132.8, 131.5, 131.1, 129.0, 128.5, 127.8, 127.5, 126.8, 126.5, 123.1, 115.5, 115.2, 54.0, 47.0, 43.2, 42.0, 25.5, 24.5, 15.3



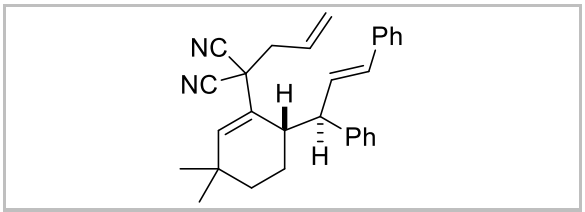
(E)-2-allyl-2-(9-(1,3-diphenylallyl)-1,4-dioxaspiro[4.5]dec-7-en-8-yl)malononitrile (5d)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 1 h.*
Isolated: 124 mg
Yield: 59% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.23 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 7.42 – 7.30 (m, 8H), 7.25 – 7.18 (m, 2H), 6.61 (dd, *J* = 15.7, 9.8 Hz, 1H), 6.40 (dd, *J* = 18.6, 15.8 Hz, 1H), 6.28 – 6.19 (m, 1H), 5.83 (ddt, *J* = 17.3, 10.1, 7.2 Hz, 1H), 5.34 (d, *J* = 10.2 Hz, 1H), 5.23 (d, *J* = 16.9 Hz, 1H), 4.08 – 3.98 (m, 2H), 3.89 – 3.76 (m, 4H), 3.18 – 3.09 (m, 1H), 2.76 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.65 (dd, *J* = 9.8, 4.4 Hz, 2H), 1.87 (dd, *J* = 14.0, 2.5 Hz, 1H), 1.70 – 1.65 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 142.7, 136.8, 133.8, 132.9, 131.4, 129.3, 129.1, 128.8, 128.7, 128.5, 128.4, 128.2, 127.5, 126.7, 126.5, 126.4, 123.4, 115.3, 114.9, 112.0, 111.4, 108.2, 106.6, 64.6, 63.9, 60.4, 52.3, 51.6, 48.0, 46.7, 43.5, 37.3, 36.1, 35.9, 35.5, 29.2, 21.1, 14.3.



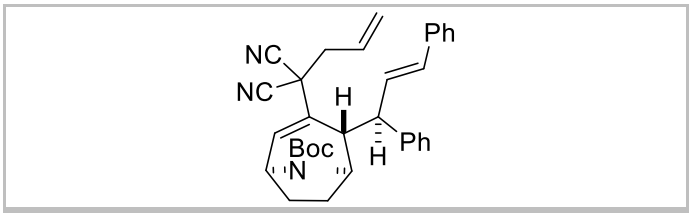
(E)-2-allyl-2-(6-(1,3-diphenylallyl)-4,4-difluorocyclohex-1-en-1-yl)malononitrile (5c)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 1 h.*
Isolated: 178 mg
Yield: 78% (>20:1 dr)
Physical state: yellow oil
TLC: R_f =0.48 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.44 – 7.37 (m, 6H), 7.29 (dt, *J* = 9.9, 5.9 Hz, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.62 (ddd, *J* = 15.7, 9.6, 1.0 Hz, 1H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.21 – 6.15 (m, 1H), 5.82 (ddt, *J* = 17.4, 10.1, 7.3 Hz, 1H), 5.36 (d, *J* = 9.7 Hz, 1H), 5.23 (dd, *J* = 16.9, 1.1 Hz, 1H), 3.74 (t, *J* = 10.0 Hz, 1H), 3.21 (dd, *J* = 11.4, 4.6 Hz, 1H), 2.93 – 2.72 (m, 4H), 2.21 (tdd, *J* = 15.1, 6.9, 2.1 Hz, 1H), 1.99 – 1.84 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 141.4, 136.3, 134.7, 132.1, 131.6, 129.1, 128.6, 128.2, 127.8, 127.2, 126.5, 125.0, 123.8, 123.1, 121.1, 114.9, 114.5, 52.1, 52.1, 46.8, 42.8, 35.9, 35.0.



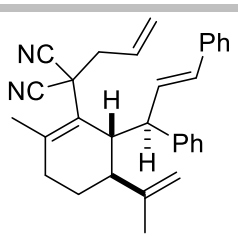
(E)-2-allyl-2-(6-(1,3-diphenylallyl)-3,3-dimethylcyclohex-1-en-1-yl)malononitrile (5d)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 1 h.*
Isolated: 176 mg
Yield: 66% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.65 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.43 (d, *J* = 7.4 Hz, 4H), 7.38 – 7.35 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.15 (m, 2H), 6.66 (dd, *J* = 15.7, 9.5 Hz, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 5.86 – 5.75 (m, 2H), 5.32 (d, *J* = 10.1 Hz, 1H), 5.21 (dd, *J* = 16.9, 1.1 Hz, 1H), 3.55 (t, *J* = 9.5 Hz, 1H), 2.91 – 2.84 (m, 2H), 2.73 (dd, *J* = 13.6, 7.3 Hz, 1H), 1.64 (tt, *J* = 13.6, 6.8 Hz, 1H), 1.50 (dt, *J* = 7.4, 3.5 Hz, 2H), 1.35 (dt, *J* = 13.9, 3.0 Hz, 1H), 1.16 (s, 3H), 0.99 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 142.7, 141.7, 136.8, 132.7, 131.4, 131.3, 129.0, 128.9, 128.6, 128.0, 127.6, 126.9, 126.7, 123.2, 115.6, 115.4, 54.3, 47.7, 42.6, 42.2, 33.4, 31.0, 30.5, 29.6, 23.9.



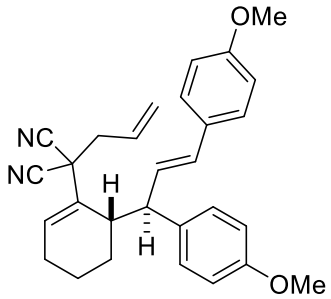
tert-butyl (1S,5R)-3-(1,1-dicyanobut-3-en-1-yl)-4-((E)-1,3-diphenylallyl)-8-azabicyclo[3.2.1]oct-2-ene-8-carboxylate (5e)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 48 mg
Yield: 26% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.5 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.58 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 3H), 7.32 – 7.28 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.70 (s, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.30 (t, *J* = 8.0 Hz, 1H), 5.83 (td, *J* = 17.1, 7.2 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 16.7 Hz, 1H), 4.80 (s, 1H), 4.35 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 3.86 (t, *J* = 9.6 Hz, 1H), 2.86 (dd, *J* = 13.9, 7.5 Hz, 2H), 2.74 – 2.64 (m, 1H), 2.04 – 1.90 (m, 1H), 1.90 – 1.82 (m, 1H), 1.82 – 1.72 (m, 1H), 1.53 (s, 7H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 142.5, 136.6, 134.5, 132.2, 132.0, 128.9, 128.7, 128.6, 127.7, 126.9, 126.5, 123.3, 115.5, 114.8, 60.4, 54.5, 45.8, 42.1, 29.3, 28.4, 21.1, 14.2.



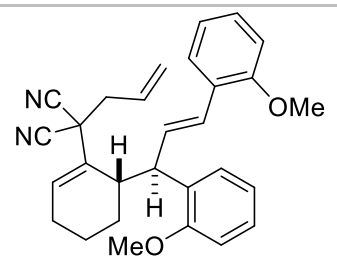
2-allyl-2-((5S)-6-((E)-1,3-diphenylallyl)-2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)malononitrile (5f)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 30 min.*
Isolated: 60 mg
Yield: 45% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.62 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 7.45 – 7.38 (m, 7H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 6.9 Hz, 1H), 6.70 – 6.59 (m, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.03 – 5.89 (m, 1H), 5.37 (d, *J* = 10.1 Hz, 1H), 5.26 (d, *J* = 16.9 Hz, 1H), 4.82 (d, *J* = 14.8 Hz, 1H), 4.54 (s, 1H), 3.49 (t, *J* = 9.7 Hz, 1H), 3.36 (d, *J* = 10.2 Hz, 1H), 2.85 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.68 (dd, *J* = 13.9, 6.7 Hz, 1H), 2.37 (dd, *J* = 18.6, 9.9 Hz, 1H), 2.28 – 2.14 (m, 2H), 2.02 (d, *J* = 15.1 Hz, 4H), 1.68 (s, 4H), 1.52 (dd, *J* = 38.1, 9.2 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 147.6, 142.4, 138.2, 136.9, 132.5, 131.5, 129.4, 129.1, 128.7, 128.5, 126.9, 126.5, 122.8, 115.3, 114.7, 110.6, 55.3, 47.3, 43.3, 42.4, 40.9, 30.0, 22.3, 21.7, 19.8.



(E)-2-allyl-2-(6-(1,3-bis(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile (5g)

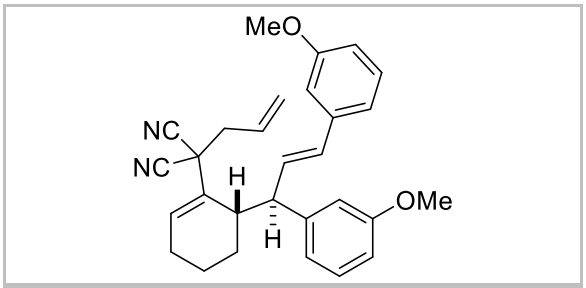
Prepared by general procedure **A** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 62 mg
Yield: 45% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.34 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.46 (dd, *J* = 15.7, 9.5 Hz, 1H), 6.32 (d, *J* = 15.7 Hz, 1H), 6.15 (t, *J* = 3.9 Hz, 1H), 5.82 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 5.20 (dd, *J* = 16.9, 1.1 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.46 (t, *J* = 9.7 Hz, 1H), 2.92 (d, *J* = 9.8 Hz, 1H), 2.85 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.73 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.38 (ddd, *J* = 19.7, 7.7, 3.1 Hz, 1H), 2.22 (tdd, *J* = 13.3, 8.8, 4.4 Hz, 1H), 1.85 – 1.72 (m, 1H), 1.64 – 1.52 (m, 2H), 1.36 (tt, *J* = 13.4, 4.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1, 158.4, 135.0, 133.6, 131.4, 131.0, 130.2, 129.8, 129.1, 128.7, 127.7, 123.1, 115.5, 115.4, 114.4, 114.0, 55.4, 55.3, 53.2, 47.1, 43.3, 42.2, 29.8, 25.6, 24.5, 15.4.



(E)-2-allyl-2-(6-(1,3-bis(2-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile (5h)

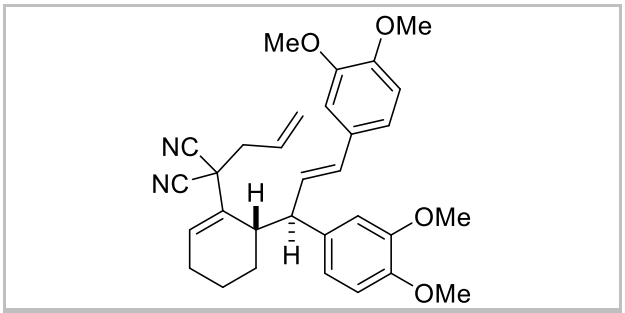
Prepared by general procedure **A** with the following notes:
Note: *reaction time: 1 h.*
Isolated: 120 mg
Yield: 85% (>20:1 dr)

Physical state: colorless oil
TLC: R_f =0.40 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.19 (dt, *J* = 16.5, 4.1 Hz, 2H), 6.96 (q, *J* = 7.7 Hz, 1H), 6.90 (dd, *J* = 15.7, 7.9 Hz, 2H), 6.86 – 6.81 (m, 1H), 6.82 – 6.75 (m, 2H), 6.14 (t, *J* = 3.9 Hz, 1H), 5.89 – 5.78 (m, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 5.15 (d, *J* = 16.9 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.21 (d, *J* = 9.7 Hz, 1H), 2.90 (dd, *J* = 13.7, 7.6 Hz, 1H), 2.70 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.22 (tdd, *J* = 13.5, 8.8, 4.5 Hz, 1H), 2.01 – 1.84 (m, 1H), 1.63 – 1.46 (m, 2H), 1.44 – 1.30 (m, 1H), 1.31 – 1.24 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 157.1, 156.6, 134.0, 132.7, 131.3, 129.4, 128.8, 128.3, 127.5, 126.8, 125.9, 125.8, 122.7, 121.1, 120.7, 115.9, 115.2, 111.1, 110.9, 55.5, 55.5, 46.5, 43.5, 41.1, 26.2, 24.6, 15.5



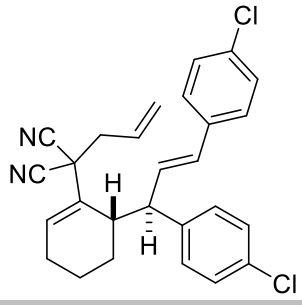
(E)-2-allyl-2-(6-(1,3-bis(3-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile (5i)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 83 mg
Yield: 60% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.43 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 6.4 Hz, 2H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.82 – 6.73 (m, 2H), 6.63 (dd, *J* = 15.7, 9.6 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.17 (t, *J* = 3.8 Hz, 1H), 5.82 (dq, *J* = 10.0, 7.2 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 16.9 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.50 (t, *J* = 9.8 Hz, 1H), 2.40 (ddd, *J* = 19.6, 7.5, 2.4 Hz, 1H), 2.29 – 2.19 (m, 1H), 1.85 – 1.75 (m, 1H), 1.66 – 1.55 (m, 2H), 1.37 (tt, *J* = 12.1, 3.4 Hz, 1H), 1.32 – 1.16 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 160.1, 159.8, 144.2, 138.2, 133.4, 133.0, 131.7, 131.1, 130.0, 129.5, 129.0, 123.2, 120.1, 119.4, 115.6, 115.3, 113.9, 113.8, 111.8, 111.3, 55.3, 55.3, 54.1, 47.1, 43.2, 42.0, 29.8, 25.7, 24.5, 15.4.
HRMS (ESI) m/z: $[M + H]^+$ Calcd $C_{29}H_{31}NO_2$ for 439.2380; Found 439.2399.



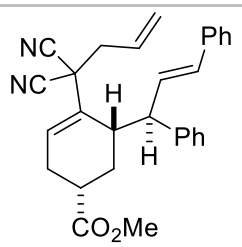
(E)-2-allyl-2-(6-(1,3-bis(3,4-dimethoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile (5j)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2h.*
Isolated: 70 mg
Yield: 50% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.60 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 6.85 (d, *J* = 8.2 Hz, 1H), 6.76 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.71 (d, *J* = 1.8 Hz, 1H), 6.48 (t, *J* = 3.7 Hz, 1H), 5.94 (dd, *J* = 11.3, 4.0 Hz, 1H), 5.76 – 5.68 (m, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.46 – 3.35 (m, 2H), 2.91 – 2.76 (m, 2H), 2.33 (dt, *J* = 19.2, 5.0 Hz, 1H), 2.28 – 2.13 (m, 1H), 1.82 – 1.68 (m, 1H), 1.69 – 1.53 (m, 2H), 1.47 – 1.35 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 149.3, 148.2, 140.3, 134.8, 133.3, 132.4, 120.5, 119.5, 116.0, 115.9, 111.3, 111.1, 56.0, 55.9, 52.0, 41.7, 37.6, 34.6, 29.7, 25.7, 25.5, 15.8.



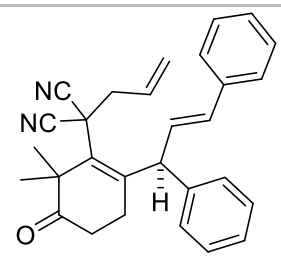
(E)-2-allyl-2-(6-(1,3-bis(4-chlorophenyl)allyl)cyclohex-1-en-1-yl)malononitrile (5k)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 58 mg
Yield: 42% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.54 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.36 (dd, *J* = 8.6, 2.2 Hz, 4H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.57 (dd, *J* = 15.7, 9.5 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.20 (t, *J* = 3.9 Hz, 1H), 5.83 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.37 (d, *J* = 10.1 Hz, 1H), 5.27 (d, *J* = 16.9 Hz, 1H), 3.52 (t, *J* = 9.8 Hz, 1H), 2.93 (d, *J* = 10.0 Hz, 1H), 2.85 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.76 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.43 (ddd, *J* = 19.5, 7.8, 2.8 Hz, 1H), 2.26 (tdd, *J* = 13.1, 8.8, 4.4 Hz, 1H), 1.87 – 1.72 (m, 1H), 1.67 – 1.53 (m, 2H), 1.44 – 1.35 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 140.8, 135.0, 133.2, 133.0, 132.8, 132.6, 131.6, 130.2, 129.2, 129.0, 128.7, 128.7, 127.7, 123.3, 115.2, 115.2, 53.4, 47.4, 43.0, 41.9, 29.7, 25.4, 24.4, 15.2.
HRMS (ESI) m/z**:** $[M + NH_4]^+$ Calcd $C_{27}H_{28}Cl_2N_3$ for 464.1655; Found 464.1647.



methyl (1R)-4-(1,1-dicyanobut-3-en-1-yl)-5-((E)-1,3-diphenylallyl)cyclohex-3-ene-1-carboxylate (5l)

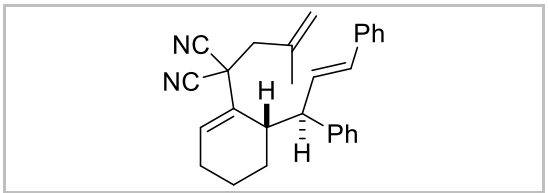
Prepared by general procedure **A** with the following notes:
Note: *reaction time: 1 h.*
Isolated: 73 mg
Yield: 41% (2.5:1 dr) (Shown spectra are an isolated diastereomer with >20:1 dr)
Physical state: colorless oil
TLC: R_f =0.33 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.36 (m, 4H), 7.32 – 7.27 (m, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.67 (dd, *J* = 15.7, 9.4 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.21 (t, *J* = 3.9 Hz, 1H), 5.81 (ddt, *J* = 17.4, 10.1, 7.3 Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.22 (dd, *J* = 16.9, 1.1 Hz, 1H), 4.12 – 4.05 (m, 2H), 3.54 (t, *J* = 9.3 Hz, 1H), 3.04 (d, *J* = 7.4 Hz, 1H), 2.87 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.82 – 2.73 (m, 2H), 2.58 (ddd, *J* = 19.4, 7.5, 3.7 Hz, 1H), 2.46 (ddd, *J* = 13.8, 9.3, 3.8 Hz, 1H), 1.90 (ddd, *J* = 13.3, 3.7, 2.3 Hz, 1H), 1.53 (td, *J* = 13.3, 4.5 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 175.1, 141.8, 136.6, 133.1, 131.9, 131.7, 130.5, 129.2, 128.7, 128.6, 127.9, 127.2, 126.6, 123.5, 115.3, 115.2, 60.9, 54.1, 47.1, 42.8, 42.1, 33.4, 28.7, 27.3, 14.2.



(E)-2-allyl-2-(2-(1,3-diphenylallyl)-6,6-dimethyl-5-oxocyclohex-1-en-1-yl)malononitrile (5m)

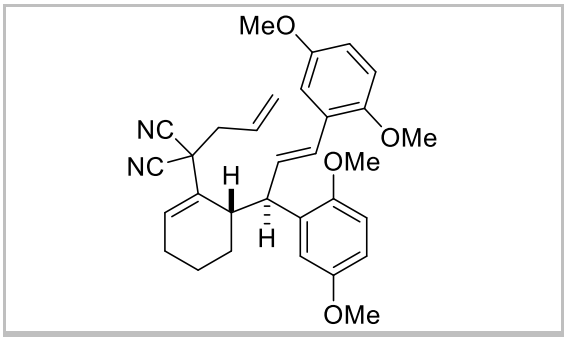
Prepared by general procedure **A** with the following notes:
Note: *reaction time: 1 h.*

Isolated: 23 mg
Yield: 57% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.27 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ δ 7.43 (d, *J* = 7.4 Hz, 2H), 7.37 (s, 3H), 7.29 (t, *J* = 6.2 Hz, 4H), 6.67 (d, *J* = 16.1 Hz, 1H), 6.39 (dd, *J* = 15.9, 7.4 Hz, 1H), 6.03 (td, *J* = 17.3, 7.3 Hz, 1H), 5.47 (d, *J* = 9.9 Hz, 1H), 5.38 (d, *J* = 16.8 Hz, 1H), 5.27 (d, *J* = 7.4 Hz, 1H), 3.10 (dd, *J* = 14.3, 7.5 Hz, 1H), 2.94 (dd, *J* = 14.3, 7.0 Hz, 1H), 2.63 – 2.51 (m, 2H), 2.50 – 2.42 (m, 1H), 2.30 – 2.20 (m, 1H), 1.72 (s, 3H), 1.64 (s, 3H), 0.89 (t, *J* = 7.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 209.7, 141.7, 139.5, 136.4, 134.8, 132.9, 129.1, 129.0, 128.8, 128.4, 128.0, 127.6, 127.1, 126.6, 123.8, 116.2, 115.9, 50.5, 49.4, 44.5, 38.9, 35.2, 27.8, 25.1, 23.7, 14.4.



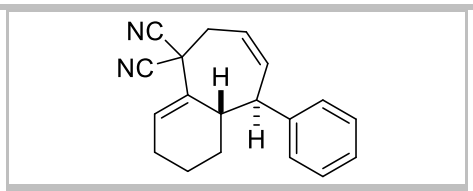
(E)-2-(6-(1,3-diphenylallyl)cyclohex-1-en-1-yl)-2-(2-methylallyl)malononitrile (5n)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 62 mg
Yield: 55% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.44 (20% EtOAc in hexanes); Purified using 4% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.36 (m, 4H), 7.30 (dd, *J* = 12.9, 4.8 Hz, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.69 (dd, *J* = 15.7, 9.6 Hz, 1H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.22 (t, *J* = 3.9 Hz, 1H), 5.10 (s, 1H), 4.96 (s, 1H), 3.57 (t, *J* = 9.8 Hz, 1H), 3.09 (d, *J* = 9.9 Hz, 1H), 2.82 (d, *J* = 13.9 Hz, 1H), 2.70 (d, *J* = 13.9 Hz, 1H), 2.43 (ddd, *J* = 19.7, 8.0, 2.5 Hz, 1H), 2.27 (dtd, *J* = 13.1, 8.7, 4.4 Hz, 1H), 1.86 (s, 3H), 1.63 (ddd, *J* = 24.5, 8.4, 3.4 Hz, 2H), 1.41 (ddd, *J* = 18.1, 8.9, 4.3 Hz, 1H), 1.30 (d, *J* = 7.0 Hz, 1H).21
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 142.6, 137.5, 136.7, 134.0, 132.8, 131.7, 131.1, 129.0, 128.5, 127.8, 127.5, 126.8, 126.5, 118.9, 115.8, 115.7, 54.0, 49.7, 42.5, 41.9, 25.8, 24.5, 23.2, 15.3, 1.1.



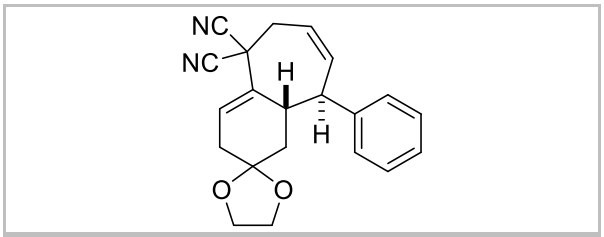
(E)-2-allyl-2-(6-(1,3-bis(2,5-dimethoxyphenyl)allyl) cyclohex-1-en-1-yl)malononitrile (5o)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 305 mg
Yield: 86% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.25 (20% EtOAc in hexanes); Purified using 86% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.19 (d, *J* = 2.8 Hz, 1H), 7.01 (d, *J* = 2.9 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 6.80 – 6.72 (m, 5H), 6.15 (t, *J* = 3.9 Hz, 1H), 5.85 (ddt, *J* = 17.2, 10.1, 7.3 Hz, 1H), 5.32 (d, *J* = 10.1 Hz, 1H), 5.19 (dd, *J* = 16.9, 0.9 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.19 (d, *J* = 9.7 Hz, 1H), 2.89 (dd, *J* = 13.7, 7.5 Hz, 1H), 2.73 (dd, *J* = 13.7, 7.0 Hz, 1H), 2.41 (ddd, *J* = 10.4, 8.0, 2.8 Hz, 1H), 2.23 (tdd, *J* = 12.9, 8.6, 4.5 Hz, 1H), 2.01 – 1.89 (m, 1H), 1.64 – 1.54 (m, 2H), 1.38 (tt, *J* = 12.5, 3.9 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 153.9, 153.7, 151.5, 151.1, 133.9, 132.8, 132.4, 131.4, 129.3, 126.7, 125.7, 122.8, 115.9, 115.2, 115.1, 114.1, 112.5, 112.3, 111.5, 111.4, 56.3, 56.2, 55.7, 55.7, 48.6, 46.6, 43.4, 41.2, 26.2, 24.6, 15.5.



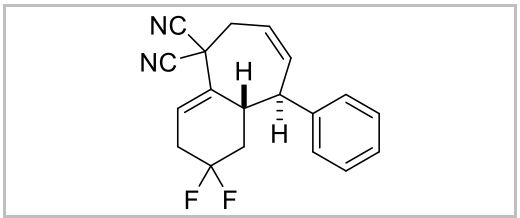
9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6a)

Prepared from **5a** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 1 g
Yield: 92% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.63 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.38 – 7.29 (m, 3H), 7.25 – 7.20 (m, 2H), 6.57 (t, *J* = 3.6 Hz, 1H), 5.98 (ddd, *J* = 11.3, 5.5, 2.0 Hz, 1H), 5.74 – 5.65 (m, 1H), 3.88 (t, *J* = 5.2 Hz, 1H), 3.35 (ddt, *J* = 8.7, 4.3, 2.0 Hz, 1H), 3.17 (s, 1H), 2.94 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.88 – 1.79 (m, 1H), 1.75 – 1.62 (m, 2H), 1.22 – 1.11 (m, 1H), 0.62 – 0.46 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 140.3, 137.6, 136.4, 129.4, 129.3, 128.5, 127.2, 120.4, 116.7, 116.5, 52.2, 40.9, 36.9, 35.4, 27.5, 25.1, 17.4.
HRMS (DART) m/z**:** $[M + NH_4]^+$ Calcd for $C_{19}H_{22}N_3$ 292.1808; Found 292.1812.



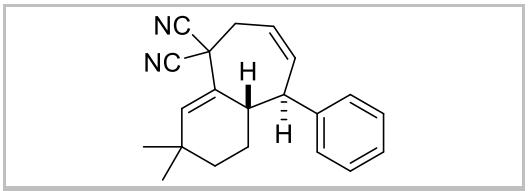
9-phenyl-3,6,9,9a-tetrahydrospiro[benzo[7]annulene-2,2'-[1,3]dioxolane]-5,5(1H)-dicarbonitrile (6b)

Prepared from **5b** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 20 mg
Yield: 42% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.40 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.34 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.19 (m, 3H), 6.43 (t, *J* = 3.9 Hz, 1H), 5.87 (dd, *J* = 11.3, 4.4 Hz, 1H), 5.72 – 5.65 (m, 1H), 4.05 (dd, *J* = 11.1, 2.1 Hz, 1H), 3.99 – 3.86 (m, 3H), 3.79 – 3.70 (m, 1H), 3.35 (dd, *J* = 15.2, 5.9 Hz, 1H), 3.18 – 3.10 (m, 1H), 2.85 (dd, *J* = 15.2, 7.3 Hz, 1H), 2.58 – 2.45 (m, 2H), 1.63 (qd, *J* = 13.9, 4.6 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 143.0, 140.6, 131.9, 131.0, 128.8, 128.6, 127.0, 119.4, 115.8, 115.7, 106.7, 64.9, 64.1, 50.6, 41.6, 39.4, 37.2, 34.8, 34.7.
HRMS (ESI) m/z**:** $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2O_2Na$ 355.1417; Found 355.1425.



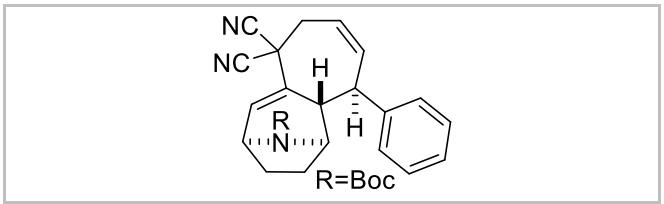
2,2-difluoro-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6c)

Prepared from **5c** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 17 mg
Yield: 76% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.51 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.38 (dd, *J* = 10.3, 4.6 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 6.43 – 6.38 (m, 1H), 5.93 – 5.86 (m, 1H), 5.79 – 5.71 (m, 1H), 3.76 – 3.69 (m, 1H), 3.37 (ddt, *J* = 15.2, 5.9, 1.6 Hz, 1H), 3.22 – 3.14 (m, 1H), 2.95 – 2.83 (m, 2H), 2.82 – 2.67 (m, 1H), 2.09 – 1.96 (m, 1H), 1.91 – 1.75 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 141.7, 139.8, 132.5, 129.1, 128.6, 128.4, 128.4, 127.5, 123.7, 121.7, 119.8, 115.3, 115.3, 50.8, 50.8, 41.4, 39.1, 39.0, 36.0, 35.8, 35.6, 34.7, 33.8, 33.5.
HRMS (DART) m/z**:** $[M + H]^+$ Calcd for $C_{19}H_{16}F_2N_2$ 311.1354; Found 311.1367.



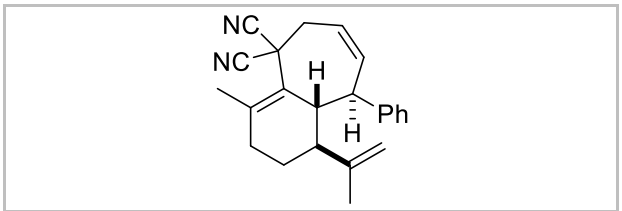
3,3-dimethyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6d)

Prepared from **5d** by general procedure **B** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 73 mg
Yield: 56% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.77 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.35 (dd, *J* = 9.3, 5.6 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 7.1 Hz, 2H), 6.16 (s, 1H), 5.95 – 5.89 (m, 1H), 5.75 – 5.68 (m, 1H), 3.45 – 3.36 (m, 2H), 2.84 – 2.77 (m, 2H), 1.69 – 1.58 (m, 1H), 1.56 – 1.46 (m, 1H), 1.45 – 1.36 (m, 2H), 1.15 (s, 3H), 1.03 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 142.8, 142.5, 140.2, 130.6, 129.0, 128.3, 127.3, 119.8, 116.1, 115.9, 52.2, 41.8, 37.9, 34.8, 33.3, 30.9, 30.3, 28.2, 23.6.
HRMS (DART/ESI) m/z**:** $[M + Na]^+$ Calcd for $C_{21}H_{22}N_2Na$ 325.1675; Found 325.1669.



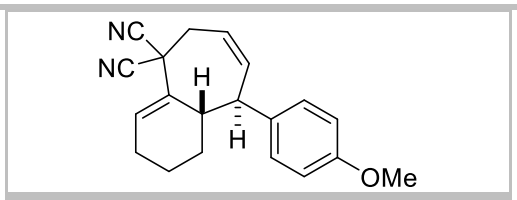
tert-butyl (1S,4R)-6,6-dicyano-10-phenyl-1,2,3,4,6,7,10,10a-octahydro-1,4-epiminoheptalene-11-carboxylate (6e)

Prepared from **5e** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 10 mg
Yield: 41% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.64 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
All spectroscopic data for this compound was consistent with the reported in the literature.[6]



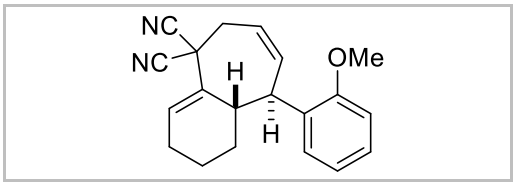
4-methyl-9-phenyl-1-(prop-1-en-2-yl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6f)

Prepared from **5f** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 32 mg
Yield: 73% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.76 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (dd, *J* = 9.4, 5.2 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 2H), 5.88 – 5.80 (m, 1H), 5.79 – 5.71 (m, 1H), 4.82 (s, 1H), 4.62 (s, 1H), 3.76 – 3.66 (m, 1H), 3.56 (d, *J* = 11.5 Hz, 1H), 3.29 (d, *J* = 11.5 Hz, 1H), 2.90 (dd, *J* = 15.0, 8.8 Hz, 1H), 2.15 (dd, *J* = 18.4, 6.3 Hz, 1H), 2.10 (s, 3H), 2.09 – 2.02 (m, 1H), 2.00 (s, 1H), 1.93 – 1.84 (m, 1H), 1.71 (d, *J* = 15.8 Hz, 1H), 1.57 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 145.1, 142.8, 142.1, 138.4, 129.0, 127.9, 127.3, 122.0, 119.1, 115.8, 115.4, 110.3, 55.1, 40.4, 39.9, 38.9, 33.0, 30.1, 22.3, 21.5, 18.6.
HRMS (ESI) m/z**:** $[M + Na]^+$ Calcd for $C_{23}H_{24}N_2Na$ 351.1832; Found 351.1820.



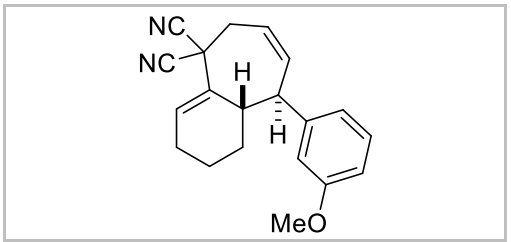
9-(4-methoxyphenyl)-1,2,3,6,9,9a-hexahydro -5H-benzo[7]annulene-5,5-dicarbonitrile (6g)

Prepared from **5g** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 27 mg
Yield: 73% (>20:1dr)
Physical state: colorless oil
TLC: R_f =0.53 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.45 (t, *J* = 3.7 Hz, 1H), 5.89 (dd, *J* = 11.1, 4.3 Hz, 1H), 5.72 – 5.65 (m, 1H), 3.81 (s, 3H), 3.43 – 3.36 (m, 2H), 2.80 (dd, *J* = 14.9, 7.6 Hz, 2H), 2.31 (dt, *J* = 19.1, 5.2 Hz, 1H), 2.18 (dt, *J* = 17.5, 9.0 Hz, 1H), 1.78 – 1.67 (m, 1H), 1.64 – 1.53 (m, 2H), 1.42 – 1.34 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 158.8, 140.4, 134.4, 133.6, 132.4, 129.3, 119.4, 116.2, 116.1, 114.3, 55.4, 51.7, 41.7, 37.8, 34.3, 29.8, 25.6, 25.6, 15.7
HRMS (ESI) m/z**:** $[M + Na]^+$ Calcd for $C_{20}H_{20}N_2ONa$ 327.1468; Found 327.1464.



9-(2-methoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6h)

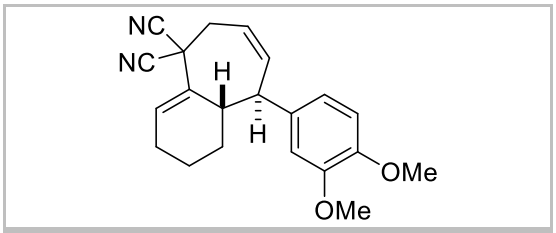
Prepared from **5h** by general procedure **B** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 53 mg
Yield: 78% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.75 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.31 – 7.25 (m, 1H), 7.19 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.48 (t, *J* = 3.7 Hz, 1H), 5.86 (dd, *J* = 11.1, 4.9 Hz, 1H), 5.73 – 5.65 (m, 1H), 3.90 (dd, *J* = 10.6, 4.5 Hz, 1H), 3.86 (s, 3H), 3.47 (dd, *J* = 14.7, 6.1 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.79 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.33 (dt, *J* = 19.2, 5.3 Hz, 1H), 2.26 – 2.14 (m, 1H), 1.87 – 1.75 (m, 1H), 1.65 – 1.53 (m, 1H), 1.47 (dd, *J* = 13.5, 2.4 Hz, 1H), 1.42 – 1.35 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 157.2, 139.7, 133.2, 132.8, 130.2, 129.7, 128.3, 121.0, 119.3, 116.3, 116.1, 111.0, 55.4, 46.7, 41.8, 36.2, 34.3, 29.7, 25.9, 25.6, 15.8.
HRMS (DART/ESI) m/z**:** $[M + Na]^+$ Calcd for $C_{20}H_{20}N_2ONa$ 327.1468; Found 327.1479.



9-(3-methoxyphenyl)-1,2,3,6,9,9a-hexahydro -5H-benzo[7]annulene-5,5-dicarbonitrile (6i)

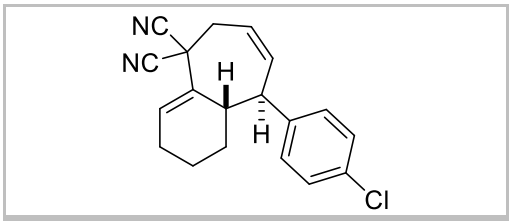
Prepared from **5i** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 38 mg
Yield: 74% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.50 (% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.27 (t, *J* = 7.9 Hz, 1H), 6.84 – 6.78 (m, 2H), 6.75 – 6.74 (m, 1H), 6.46 (t, *J* = 3.7 Hz, 1H), 5.91 (dd, *J* = 11.2, 4.0 Hz, 1H), 5.74 – 5.67 (m, 1H), 3.82 (s, 3H), 3.41 (ddd, *J* = 21.1, 12.9, 5.3 Hz, 2H), 2.87 (dd, *J* = 8.6, 2.1 Hz, 1H), 2.80 (dd, *J* = 14.9, 7.5 Hz, 1H), 2.31 (dt, *J* = 19.0, 5.1 Hz, 1H), 2.25 – 2.14 (m, 1H), 1.78 – 1.67 (m, 1H), 1.65 – 1.53 (m, 2H), 1.43 – 1.35 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 160.0, 143.9, 139.9, 133.5, 132.3, 129.9, 120.6, 119.7, 116.1, 115.9, 114.5, 111.8, 55.3, 52.4, 41.7, 37.4, 34.3, 25.6, 25.5, 15.7.

HRMS (DART) m/z**:** $[M + H]^+$ Calcd for $C_{20}H_{21}N_2O$ 305.1648; Found 305.1639.



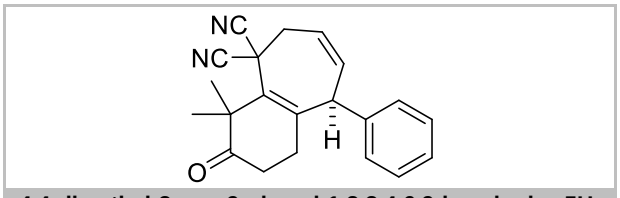
9-(3,4-dimethoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6j)

Prepared from **5j** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 26 mg
Yield: 60% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.20 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 6.85 (d, *J* = 8.2 Hz, 1H), 6.76 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.71 (d, *J* = 1.8 Hz, 1H), 6.48 (t, *J* = 3.7 Hz, 1H), 5.94 (dd, *J* = 11.3, 4.0 Hz, 1H), 5.76 – 5.68 (m, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.46 – 3.35 (m, 2H), 2.91 – 2.76 (m, 2H), 2.33 (dt, *J* = 19.2, 5.0 Hz, 1H), 2.28 – 2.13 (m, 1H), 1.82 – 1.68 (m, 1H), 1.69 – 1.53 (m, 2H), 1.47 – 1.35 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 149.3, 148.2, 140.3, 134.8, 133.3, 132.4, 120.5, 119.5, 116.0, 115.9, 111.3, 111.1, 56.0, 55.9, 52.0, 41.7, 37.6, 34.6, 29.7, 25.7, 25.5, 15.8.
HRMS (ESI) m/z**:** $[M + Na]^+$ Calcd for $C_{21}H_{22}N_2O_2Na$ 357.1573; Found 357.1575.



9-(4-chlorophenyl)-1,2,3,6,9,9a-hexahydro -5H-benzo[7]annulene-5,5-dicarbonitrile (6k)

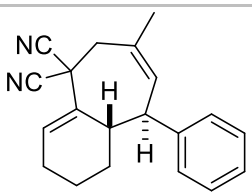
Prepared from **5k** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 28 mg
Yield: 75% (>20:1 dr)
Physical state: oil
TLC: R_f =0.56 (% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.34 – 7.30 (m, 2H), 7.16 – 7.12 (m, 2H), 5.86 (ddd, *J* = 11.3, 4.7, 1.1 Hz, 1H), 5.76 – 5.70 (m, 1H), 3.45 (dd, *J* = 10.8, 4.7 Hz, 1H), 3.40 – 3.34 (m, 1H), 2.85 – 2.78 (m, 2H), 2.32 (dt, *J* = 19.1, 4.7 Hz, 1H), 2.25 – 2.15 (m, 1H), 1.75 – 1.58 (m, 2H), 1.53 – 1.47 (m, 1H), 1.39 (tt, *J* = 13.5, 4.0 Hz, 1H), 1.24 – 1.17 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 140.9, 139.6, 133.8, 133.1, 132.2, 129.7, 129.2, 120.4, 116.1, 115.9, 51.8, 41.7, 37.6, 34.5, 29.8, 25.7, 25.5, 15.8.
HRMS (DART) m/z**:** $[M + H]^+$ Calcd for $C_{19}H_{18}ClN_2$ 309.1153; Found 309.1157.



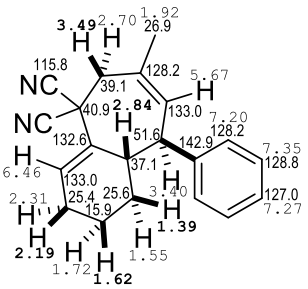
4,4-dimethyl-3-oxo-9-phenyl-1,2,3,4,6,9-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6m)

Prepared from **3c** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 13 mg
Yield: 78% (>20:1 dr)
Physical state: yellow oil
TLC: R_f =0.33 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 13.1, 5.9 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 2H), 6.40 (ddd, *J* = 9.9, 7.1, 1.7 Hz, 1H), 5.96 – 5.87 (m, 1H), 4.51 (d, *J* = 7.0 Hz, 1H), 3.26 (dd, *J* = 15.4, 5.8 Hz, 1H), 2.93 (dd, *J* = 15.1, 7.0 Hz, 1H), 2.60 – 2.51 (m, 2H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.76 (s, 3H), 1.65 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 210.7, 143.2, 140.2, 138.0, 131.3, 129.1, 127.8, 127.3, 124.1, 116.4, 115.3, 51.4, 50.1, 37.4, 35.9, 35.3, 32.9, 25.1, 24.3.
HRMS (DART/ESI) m/z**:** $[M + NH_4]^+$ Calcd for $C_{21}H_{24}N_3O$ 334.1914; Found 334.1909.

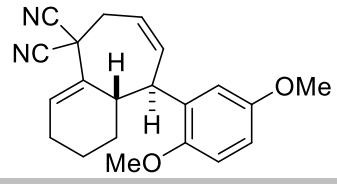


7-methyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6n)



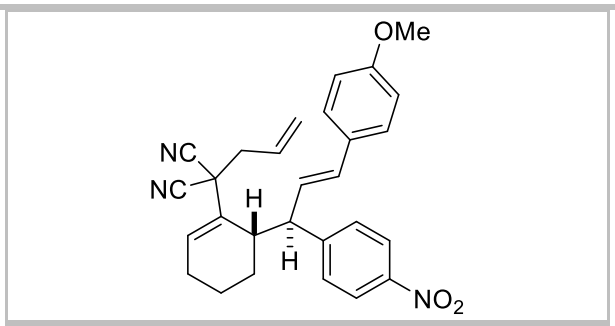
Structural assignments of 7-methyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile

Prepared from **5n** by general procedure **B** with the following notes:
Note: *reaction time: overnight*
Isolated: 20 mg
Yield: 54% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.52 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.35 (t, *J* = 7.3 Hz, 2 H), 7.27 (t, *J* = 7.3 Hz, 1 H), 7.20 (d, *J* = 8.3 Hz, 2 H), 6.46 (dd, *J* = 4.5, 3.1 Hz, 1 H), 5.67 (d, *J* = 5.5 Hz, 1 H), 3.49 (d, *J* = 14.6 Hz, 1 H), 3.40 (dd, *J* = 10.4, 5.1 Hz, 1 H), 2.84 (ddt, *J* = 10.9, 4.5, 2.2 Hz, 1 H), 2.70 (d, *J* = 14.8 Hz, 1 H), 2.31 (dt, *J* = 19.3, 5.3 Hz, 1 H), 2.19 (dtdd, *J* = 18.8, 8.3, 3.1, 2.0 Hz, 1 H), 1.92 (s, 3 H), 1.72 (qdd, *J* = 12.7, 6.2, 2.8 Hz, 1 H), 1.62 (tdd, *J* = 13.7, 4.7, 3.4 Hz, 1 H), 1.55 (m, 1 H), 1.39 (dq, *J* = 13.4, 3.0 Hz, 1 H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 142.9, 133.0, 133.0, 132.6, 128.8, 128.2, 127.0, 115.8, 51.6, 40.9, 39.1, 37.1, 26.9, 25.6, 25.4, 15.9.
HRMS (ESI) m/z**:** $[M + Na]^+$ Calcd for $C_{22}H_{24}N_2Na$ 339.1832; Found 339.1824.
Stereochemistry: Structural assignments were made using additional information from gHMBC, HSQC, and NOESY experiments.



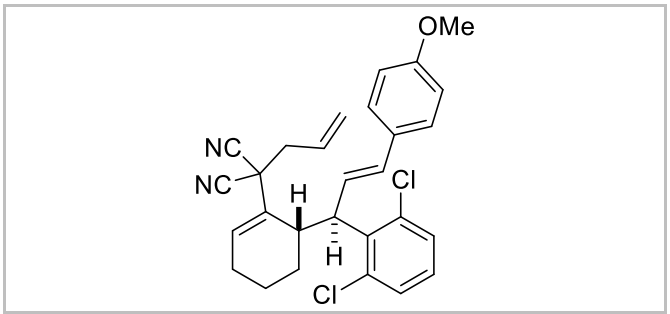
9-(2,5-dimethoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6o)

Prepared from **5o** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 45 mg
Yield: 84% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.42 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 6.80 (ddd, *J* = 17.4, 16.4, 7.4 Hz, 3H), 6.47 (s, 1H), 5.84 (dd, *J* = 11.0, 4.7 Hz, 1H), 5.76 – 5.65 (m, 1H), 3.85 (d, *J* = 6.2 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.45 (dd, *J* = 14.7, 6.0 Hz, 1H), 3.05 (d, *J* = 9.9 Hz, 1H), 2.78 (dd, *J* = 14.8, 7.5 Hz, 1H), 2.32 (d, *J* = 19.2 Hz, 1H), 2.18 (dd, *J* = 19.1, 8.9 Hz, 1H), 1.81 (dd, *J* = 10.2, 3.4 Hz, 1H), 1.59 (s, 1H), 1.49 (d, *J* = 13.5 Hz, 1H), 1.39 (t, *J* = 13.7 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 153.8, 151.6, 139.5, 133.4, 132.7, 131.5, 127.8, 123.7, 119.4, 116.3, 116.0, 113.6, 112.3, 111.9, 111.8, 56.4, 56.0, 55.7, 41.7, 36.2, 34.2, 25.9, 25.6, 15.8.
HRMS (ESI) m/z**:** $[M + NH_4]^+$ Calcd for $C_{21}H_{26}N_3O_2$ 352.2020; Found 352.2016.



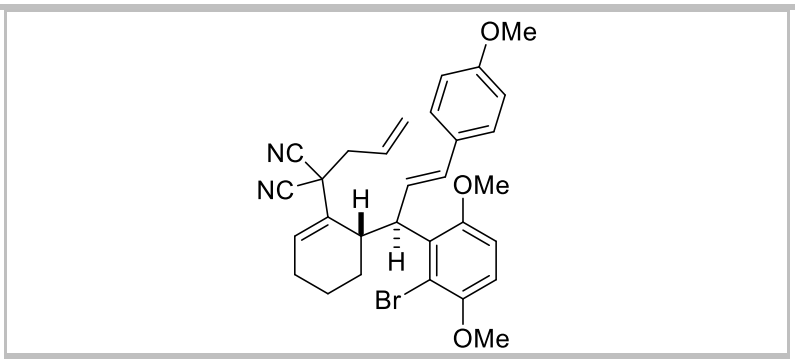
(E)-2-allyl-2-(6-(3-(4-methoxyphenyl)-1-(4-nitrophenyl) allyl)cyclohex-1-en-1-yl)malononitrile (9a)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 1 h.*
Isolated: 71 mg
Yield: 51% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.19 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.49 – 6.36 (m, 2H), 6.23 (t, *J* = 3.9 Hz, 1H), 5.83 (ddt, *J* = 17.3, 10.1, 7.2 Hz, 1H), 5.36 (d, *J* = 10.1 Hz, 1H), 5.24 (dd, *J* = 16.9, 1.0 Hz, 1H), 3.80 (s, 3H), 3.69 – 3.64 (m, 1H), 3.03 (d, *J* = 10.0 Hz, 1H), 2.88 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.76 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.44 (ddd, *J* = 19.8, 7.0, 3.3 Hz, 1H), 2.28 (tdd, *J* = 13.2, 8.8, 4.3 Hz, 1H), 1.86 – 1.73 (m, 1H), 1.70 – 1.58 (m, 1H), 1.56 – 1.39 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 159.5, 150.5, 146.8, 132.8, 132.0, 131.9, 129.0, 128.7, 128.5, 128.4, 127.8, 124.3, 123.3, 115.4, 115.2, 114.0, 55.2, 54.0, 47.1, 43.0, 41.8, 29.7, 25.5, 24.4, 15.2.



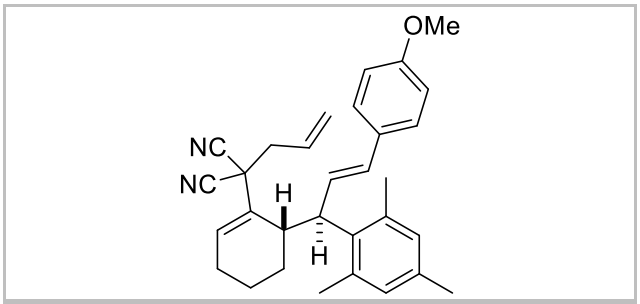
(E)-2-allyl-2-(6-(1-(2,6-dichlorophenyl)-3-(4-methoxyphenyl) allyl)cyclohex-1-en-1-yl)malononitrile (9b)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 90 mg
Yield: 66% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.55 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 7.7 Hz, 2H), 6.55 (dd, *J* = 27.6, 15.0 Hz, 1H), 6.21 (d, *J* = 3.4 Hz, 1H), 5.93 – 5.78 (m, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 5.18 (d, *J* = 16.9 Hz, 1H), 4.42 (t, *J* = 10.3 Hz, 1H), 3.98 (d, *J* = 10.6 Hz, 1H), 3.81 (s, 3H), 2.92 (dt, *J* = 18.5, 9.2 Hz, 1H), 2.75 (dd, *J* = 13.6, 7.0 Hz, 1H), 2.50 (dd, *J* = 19.4, 5.2 Hz, 1H), 2.29 (ddd, *J* = 18.9, 13.3, 8.6 Hz, 1H), 1.90 – 1.76 (m, 1H), 1.59 – 1.42 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 159.3, 137.0, 135.9, 135.3, 134.5, 132.6, 132.0, 130.2, 129.3, 129.1, 129.1, 128.2, 128.0, 125.7, 123.0, 115.4, 115.3, 114.0, 55.2, 51.5, 46.9, 43.3, 38.1, 26.7, 24.4, 15.6.



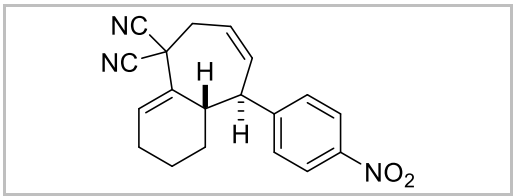
(E)-2-allyl-2-(6-(1-(2-bromo-3,6-dimethoxyphenyl)-3-(4-methoxyphenyl) allyl)cyclohex-1-en-1-yl)malononitrile (9c)

Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 40 mg
Yield: 62% (>4.4:1 dr)
Physical state: colorless oil
TLC: R_f =0.27 (20% EtOAc in hexanes); Purified using 20% EtOAc in hexane
^{1}H NMR (300 MHz, $CDCl_3$) *major diastereomer*: δ 7.33 (dd, *J* = 14.5, 8.5 Hz, 2H), 6.86 – 6.72 (m, 4H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.22 – 6.10 (m, 1H), 5.29 (dd, *J* = 16.6, 10.5 Hz, 1H), 5.11 (d, *J* = 17.3 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 2.90 (dd, *J* = 13.5, 8.0 Hz, 1H), 2.79 – 2.63 (m, 1H), 2.45 (dd, *J* = 20.0, 8.4 Hz, 1H), 2.32 – 2.10 (m, 1H), 1.73 – 1.34 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 152.4, 150.5, 135.2, 131.6, 131.3, 127.7, 122.7, 113.8, 110.4, 110.1, 60.4, 56.8, 55.9, 55.2, 53.5, 46.6, 38.5, 24.4, 16.1, 14.2.



(E)-2-allyl-2-(6-(1-mesityl-3-(4-methoxyphenyl)allyl)cyclo hex-1-en-1-yl)malononitrile (9d)

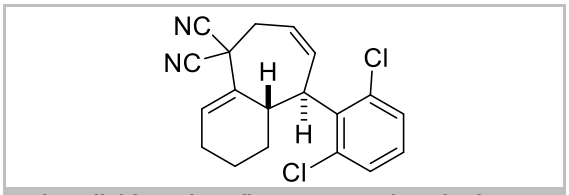
Prepared by general procedure **A** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 78 mg
Yield: 60% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.68 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer*: δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 13.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.51 (dd, *J* = 15.6, 9.7 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.18 (t, *J* = 4.0 Hz, 1H), 5.84 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.22 (dd, *J* = 16.9, 1.1 Hz, 1H), 3.81 (s, 3H), 3.50 (d, *J* = 11.1 Hz, 1H), 2.91 (dd, *J* = 13.6, 7.4 Hz, 1H), 2.77 (dd, *J* = 13.6, 7.1 Hz, 1H), 2.61 (s, 3H), 2.52 – 2.44 (m, 1H), 2.39 (s, 3H), 2.35 – 2.29 (m, 1H), 2.28 (s, 3H), 2.26 (d, *J* = 9.0 Hz, 1H), 1.66 – 1.52 (m, 3H), 1.48 – 1.38 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.0, 136.7, 136.2, 135.7, 135.6, 134.6, 131.4, 131.0, 130.6, 129.9, 129.6, 129.1, 127.9, 127.8, 123.0, 115.5, 115.5, 113.8, 55.2, 50.8, 47.4, 43.4, 39.0, 29.7, 26.0, 24.4, 22.1, 21.1, 20.7, 15.8.



9-(4-nitrophenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (10a)

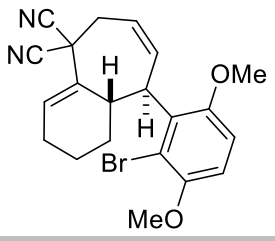
Prepared from **9a** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 27 mg

Yield: 59% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.30 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 8.27 – 8.19 (m, 2H), 7.43 – 7.38 (m, 2H), 6.53 (t, *J* = 3.7 Hz, 1H), 5.84 (tdd, *J* = 11.3, 9.6, 3.0 Hz, 2H), 3.64 (dd, *J* = 10.9, 3.9 Hz, 1H), 3.40 (dd, *J* = 15.2, 5.8 Hz, 1H), 2.96 – 2.82 (m, 2H), 2.41 – 2.32 (m, 1H), 2.30 – 2.18 (m, 1H), 1.80 – 1.62 (m, 2H), 1.52 – 1.40 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 149.8, 147.1, 138.2, 134.0, 131.7, 129.1, 124.2, 121.5, 115.7, 115.5, 52.0, 41.6, 37.4, 34.6, 25.7, 25.4, 15.7.
HRMS (DART) m/z**:** $[M + H]^+$ Calcd for $C_{19}H_{18}N_3O_2$ 320.1394; Found 320.1406.



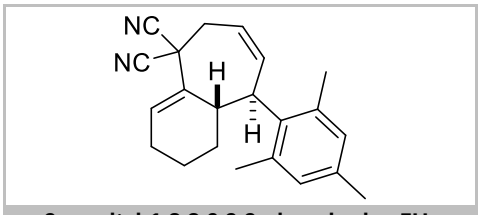
9-(2,6-dichlorophenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (10b)

Prepared from **9b** by general procedure **B** with the following notes:
Note: *reaction time: 4 h.*
Isolated: 10 mg
Yield: 50% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.62 (20% EtOAc in hexanes); Purified using 5% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.42 – 7.33 (m, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.54 (t, *J* = 3.6 Hz, 1H), 5.93 (dd, *J* = 11.2, 4.2 Hz, 1H), 5.83 (dd, *J* = 13.6, 9.0 Hz, 1H), 4.48 (d, *J* = 10.6 Hz, 1H), 3.58 (d, *J* = 10.1 Hz, 1H), 3.36 (dd, *J* = 15.0, 6.9 Hz, 1H), 2.83 (dd, *J* = 14.8, 6.4 Hz, 1H), 2.33 (d, *J* = 18.8 Hz, 1H), 2.27 – 2.14 (m, 1H), 1.79 – 1.68 (m, 1H), 1.58 – 1.45 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 137.6, 136.8, 133.4, 132.6, 130.2, 128.8, 128.8, 121.9, 115.9, 47.9, 42.3, 36.2, 34.8, 29.7, 26.6, 25.6, 16.8.
HRMS (DART) m/z**:** $[M + H]^+$ Calcd for $C_{19}H_{16}Cl_2N_2$ 343.0763; Found 343.0774.



9-(2-bromo-3,6-dimethoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (10c)

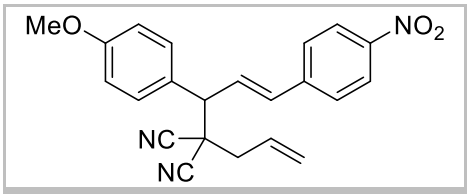
Prepared from **9c** by general procedure **B** with the following notes:
Note: *reaction time: 3 h.*
Isolated: 17 mg
Yield: 61% (>4.4:1 dr) [one of the diastereomers was isolated and the dr was >11:1 dr]
Physical state: colorless oil
TLC: R_f =0.32 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 6.85 (q, *J* = 8.9 Hz, 2H), 6.51 – 6.49 (m, 1H), 5.77 (dd, *J* = 11.0, 4.6 Hz, 1H), 5.73 – 5.67 (m, 1H), 4.35 (d, *J* = 6.1 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.48 (dd, *J* = 13.8, 6.8 Hz, 2H), 2.77 (dd, *J* = 14.5, 6.9 Hz, 1H), 2.36 – 2.29 (m, 1H), 2.24 – 2.11 (m, 1H), 1.94 – 1.84 (m, 1H), 1.46 – 1.33 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 152.9, 150.4, 137.8, 133.2, 133.1, 131.1, 120.2, 116.6, 116.3, 116.1, 110.7, 110.6, 56.8, 56.1, 50.2, 42.0, 34.8, 34.2, 26.4, 25.6, 16.9.
HRMS (DART) m/z**:** $[M +H]^+$ Calcd for $C_{21}H_{22}BrN_2O_2$ 413.0859; Found 413.0875.



9-mesityl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (10d)

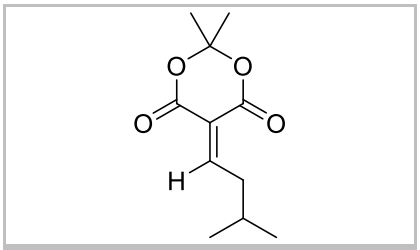
Prepared from **9d** by general procedure **B** with the following notes:

Note: *reaction time: 3 h.*
Isolated: 20 mg
Yield: 77% (>20:1 dr)
Physical state: colorless oil
TLC: R_f =0.74 (20% EtOAc in hexanes); Purified using 2% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 6.87 (d, *J* = 6.0 Hz, 2H), 6.50 (t, *J* = 3.8 Hz, 1H), 5.98 (dd, *J* = 11.2, 3.1 Hz, 1H), 5.83 – 5.74 (m, 1H), 3.91 (d, *J* = 11.0 Hz, 1H), 3.24 (dd, *J* = 15.1, 6.9 Hz, 1H), 3.15 (d, *J* = 10.5 Hz, 1H), 2.82 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.27 (d, *J* = 10.2 Hz, 3H), 1.59 (s, 1H), 1.51 – 1.36 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 141.3, 136.4, 136.1, 136.1, 135.9, 134.4, 131.1, 129.5, 121.3, 115.8, 115.5, 46.2, 42.6, 37.2, 36.3, 30.9, 29.7, 26.5, 25.6, 21.5, 21.0, 20.7, 17.6
HRMS (ESI) m/z**:** $[M + Na]^+$ Calcd for $C_{22}H_{24}N_2Na$ 339.1832; Found 339.1824.



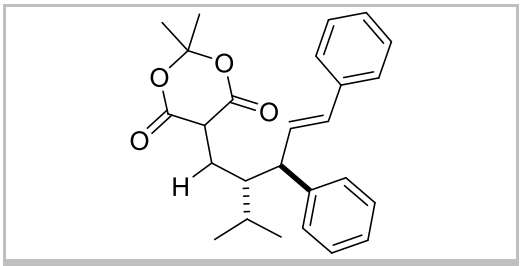
(E)-2-allyl-2-(1-(4-methoxyphenyl)-3-(4-nitrophenyl)allyl)malononitrile (11b)

Prepared by general procedure **A1** with the following notes:
Note: *reaction time: 2 h.*
Isolated: 50 mg
Yield: 60% (>20:1 rr)
Physical state: colorless oil
TLC: R_f =0.20 (20% EtOAc in hexanes); Purified using 20% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.42 (t, *J* = 9.2 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 6.7 Hz, 2H), 6.01 – 5.89 (m, 1H), 5.43 (dt, *J* = 17.8, 3.5 Hz, 2H), 3.89 – 3.86 (m, 1H), 3.85 (s, 3H), 2.67 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.57 (dd, *J* = 14.0, 7.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 160.2, 147.5, 141.9, 134.0, 129.8, 128.8, 128.5, 127.4, 126.9, 124.1, 123.5, 114.9, 55.4, 54.1, 43.7, 40.4, 29.7.



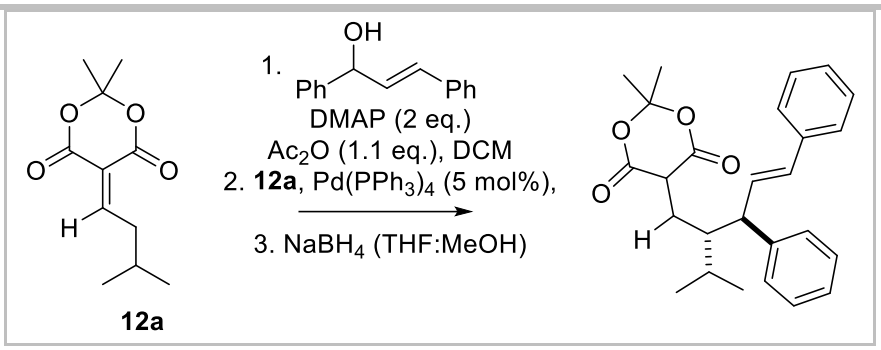
2,2-dimethyl-5-(3-methylbutylidene) -1,3-dioxane-4,6-dione (12a)

Prepared by reported procedure[17] and the NMR spectra were consistent with those reported in the literature.[17]
Isolated: 33 g
Yield: 67%
Physical state: colorless oil
TLC: R_f =0.44 (20% EtOAc in hexanes)

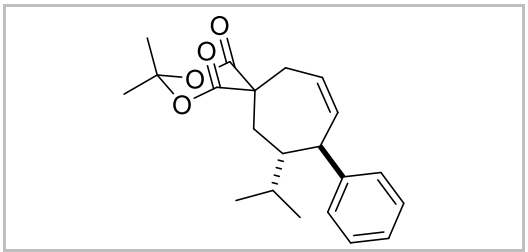


(E)-5-(2-isopropyl-3,5-diphenylpent-4-en-1-yl) -2,2-dimethyl-1,3-dioxane-4,6-dione (12b)

Prepared by following procedure:

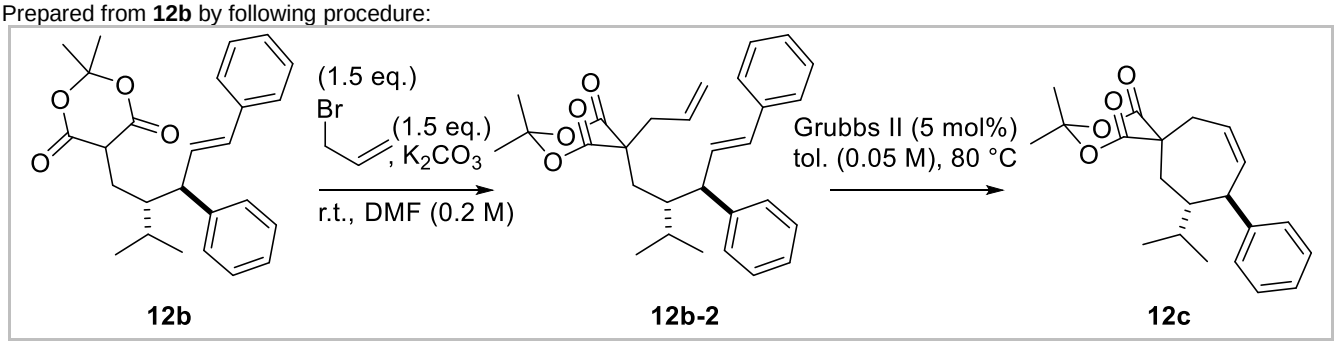


Note: *reaction time: 1. 5 min. 2. 30 min. 3. 10 min.*
Isolated: 100 mg
Yield: 52% (>20:1)
Physical state: colorless oil
TLC: R_f =0.45 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane
^{1}H NMR (500 MHz, $CDCl_3$) *major diastereomer***:** δ 7.35 (dd, *J* = 14.0, 7.0 Hz, 4H), 7.32 – 7.27 (m, 4H), 7.22 (dt, *J* = 18.8, 7.3 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.42 (dd, *J* = 15.8, 9.7 Hz, 1H), 3.85 (dd, *J* = 8.9, 2.7 Hz, 1H), 3.56 (t, *J* = 9.2 Hz, 1H), 2.37 – 2.25 (m, 2H), 2.15 (dd, *J* = 12.6, 9.0 Hz, 1H), 1.68 (dtd, *J* = 13.8, 6.9, 3.1 Hz, 1H), 1.62 (s, 3H), 1.28 (s, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$)**:** δ 165.7, 165.6, 143.7, 136.9, 133.1, 130.7, 128.9, 128.7, 127.7, 127.5, 126.5, 126.2, 104.6, 54.4, 46.5, 45.2, 29.1, 28.6, 25.3, 24.8, 21.4, 16.3.



(E)-5-(2-isopropyl-3,5-diphenylpent-4-en-1-yl) -2,2-dimethyl-1,3-dioxane-4,6-dione (12c)

Prepared from **12b** by following procedure:



Note: *reaction time: First step: 1 h.; Second step: 3 h.*
Isolated: *First step: 100 mg; Second step: 28 mg*
Yield: First step: 93% (>20:1 dr); Second step: 80% (>20:1 dr)
Physical state: *First step:* colorless oil*, Second step:* colorless oil
TLC: *First step:* R_f =0.48 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane; Second step: R_f =0.41 (20% EtOAc in hexanes); Purified using 10% EtOAc in hexane.
^{1}H NMR (600 MHz, $CDCl_3$) **12b-2** *major diastereomer***:** δ 7.39 (d, *J* = 7.5 Hz, 2H), 7.31 (ddd, *J* = 18.8, 13.0, 5.5 Hz, 6H), 7.21 (dd, *J* = 16.1, 7.4 Hz, 2H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.32 (dd, *J* = 15.7, 9.3 Hz, 1H), 5.74 – 5.64 (m, 1H), 5.24 (d, *J* = 16.8 Hz, 1H), 5.19 (d, *J* = 10.2 Hz, 1H), 3.41 (t, *J* = 9.0 Hz, 1H), 2.81 (dd, *J* = 13.0, 7.4 Hz, 1H), 2.71 (dd, *J* = 13.0, 7.6 Hz, 1H), 2.36 – 2.30 (m, 1H), 2.22 (dd, *J* = 14.6, 3.6 Hz, 1H), 2.15 (dd, *J* = 14.6, 5.3 Hz, 1H), 1.76 (dtd, *J* = 13.9, 7.0, 2.2 Hz, 1H), 1.63 (s, 3H), 1.43 (s, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) **12b-2:** δ 169.45 (s), 168.94 (s), 144.16 (s), 137.23 (s), 132.98 (s), 131.51 (s), 131.02 (s), 128.71 (s), 128.43 (s), 127.97 (s), 127.25 (s), 126.42 (s), 126.38 (s), 121.48 (s), 105.65 (s), 54.39 (s), 52.75 (s), 43.39 (s), 41.30 (s), 38.61 (s), 30.53 (s), 29.38 (s), 28.53 (s), 19.85 (s), 18.54 (s).

^{1}H NMR (600 MHz, $CDCl_3$) **12c** *major diastereomer***:** δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (dd, *J* = 16.6, 7.5 Hz, 3H), 5.72 (ddd, *J* = 10.8, 5.3, 1.7 Hz, 1H), 5.69 – 5.64 (m, 1H), 3.54 – 3.46 (m, 1H), 3.39 (dd, *J* = 11.5, 5.2 Hz, 1H), 2.70 – 2.64 (m, 1H), 2.40 (dd, *J* = 14.9, 8.6 Hz, 1H), 2.16 (dd, *J* = 14.2, 8.9 Hz, 1H), 2.04 (d, *J* = 14.2 Hz, 1H), 1.82 (s, 3H), 1.77 (s, 3H), 1.65 – 1.56 (m, 1H), 0.78 (dd, *J* = 6.8, 3.3 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) **12c:** δ 170.8, 170.1, 143.4, 135.0, 128.6, 128.4, 126.7, 121.1, 104.9, 53.3, 53.0, 41.5, 34.4, 30.6, 29.4, 28.9, 27.7, 21.1, 14.9.
m/z (ESI–MS) 12c: 365.1 $[M+Na]^+$

4. Computational Methods

Conformational searches of the starting material and product were performed using the Schrödinger MacroModel[8] software package to identify low-energy conformers for quantum mechanical calculations; reported quantum mechanical energies and geometries are for the lowest energy conformer. All quantum mechanical calculations were performed using the Gaussian 09[9] software package. Structures were optimized at the M06-2X[3]/6-31+G(d) level of theory using the CPCM[11-13] solvent model for dichloromethane; frequency calculations were used to confirm the presence of local minima (no imaginary frequencies) and transition states (one imaginary frequency) and to calculate free energies at 298 K. To obtain more accurate energetics, single-point energy calculations were performed on the optimized structures at the M06-2X[10]/6-311++G(2d,2p) level of theory using Grimme's D3 dispersion correction[14-15] and the CPCM[11-13] solvent model for dichloromethane. Partial charges were computed at this level of theory using natural bond orbital (NBO) analysis,[16] and hydrogen atom charges were summed into the neighboring heavy atom.

5. Optimized Quantum Mechanical Energies and Geometries

Structure	**Single-Point Energy** (Hartree) M06-2X/6-311++G(2d,2p) CPCM dichloromethane solvent D3 dispersion correction	**Enthalpy Correction** (Hartree) M06-2X/6-31+G(d) CPCM dichloromethane solvent	**Gibbs Free Energy Correction** (Hartree) M06-2X/6-31+G(d) CPCM dichloromethane solvent
Starting Material	-1037.13337591	0.423517	0.343704
Transition State	-1037.10414202	0.421206	0.345621
Product	-1037.14820643	0.424433	0.344843

SUPPORTING INFORMATION

Starting Material Geometries

0 1

C	-0.420056	2.664409	1.250945
C	0.236517	2.171056	0.196394
C	-0.096867	2.550167	-1.229027
C	-0.952715	3.816900	-1.284209
C	-2.113137	3.709610	-0.296446
C	-1.580257	3.616611	1.133479
C	1.375555	1.151907	0.354090
C	2.621717	1.730212	-0.198728
C	1.631812	0.834208	1.772994
C	1.041610	-0.191205	-0.425163
C	-0.280242	-0.722637	0.058744
C	-1.296838	-0.987305	-0.769059
C	-2.621433	-1.513298	-0.392117
C	-3.644684	-1.505261	-1.350105
C	-4.920508	-1.974240	-1.041118
C	-5.191985	-2.466122	0.234511
C	-4.177705	-2.489141	1.195324
C	-2.905006	-2.020164	0.885848
C	2.181144	-1.194179	-0.341792
C	2.308546	-2.082804	0.731997
C	3.373755	-2.980696	0.782918
C	4.322229	-3.004943	-0.239539
C	4.198656	-2.128240	-1.316664
C	3.133303	-1.230615	-1.365953
N	1.808372	0.563332	2.881942
N	3.569622	2.196096	-0.667506
H	-0.125024	2.380862	2.259388
H	-0.641245	1.723203	-1.707166
H	0.825867	2.689868	-1.807017
H	-1.318537	3.965958	-2.304855
H	-0.334205	4.687245	-1.028419
H	-2.698276	2.808861	-0.527417
H	-2.787400	4.566643	-0.390783
H	-2.370605	3.299533	1.823596
H	-1.254140	4.606657	1.483051
H	0.938500	0.108134	-1.473830
H	-0.383889	-0.879694	1.132670
H	-1.163264	-0.791586	-1.834385
H	-3.436249	-1.122675	-2.346568
H	-5.699894	-1.956203	-1.797183
H	-6.183528	-2.835115	0.479118
H	-4.378755	-2.880365	2.188343
H	-2.126192	-2.061284	1.642071
H	1.575759	-2.083265	1.534114
H	3.458793	-3.664740	1.621995
H	5.149495	-3.707209	-0.199366
H	4.927557	-2.143998	-2.121408
H	3.038812	-0.552205	-2.210952

Transition State Geometries

0 1

C	-2.824717	2.634666	-0.491721
C	-2.748596	1.705463	0.718872
C	-1.358747	1.181845	0.954005
C	-0.230753	1.838351	0.519414
C	-0.327517	2.978508	-0.470072
C	-1.695764	3.663087	-0.439974
C	1.063680	1.326158	0.837774
C	1.220683	0.409447	1.925332
C	2.240542	2.053139	0.476970
N	3.195586	2.625901	0.148969
N	1.317662	-0.359287	2.789472
C	-1.154522	-0.557744	-0.776582
C	-2.416571	-1.245153	-0.483031
C	0.098258	-1.057400	-0.461790
C	1.257655	-0.369537	-0.824235
C	2.621425	-0.871143	-0.642439
C	3.661194	-0.285219	-1.383496
C	4.972718	-0.731099	-1.246685
C	5.267391	-1.766189	-0.359441
C	4.243535	-2.352958	0.388714
C	2.932024	-1.911975	0.250753
C	-2.562900	-2.095166	0.625319
C	-3.777681	-2.724498	0.874864
C	-4.867917	-2.513268	0.025976
C	-4.736626	-1.664167	-1.072279
C	-3.521123	-1.030006	-1.320461
H	-1.252827	0.409787	1.714511
H	-1.208529	0.220959	-1.536565
H	-3.799590	3.131942	-0.518821
H	-2.741044	2.048091	-1.417377
H	-3.449442	0.868077	0.620741
H	-3.059698	2.250003	1.623231
H	-0.134221	2.581789	-1.480493
H	0.466390	3.707609	-0.276419
H	-1.768490	4.364275	-1.277195
H	-1.785346	4.251018	0.482862
H	0.174362	-1.946763	0.159675
H	1.151962	0.425848	-1.561887
H	3.432008	0.524256	-2.071850
H	5.763493	-0.269721	-1.830353
H	6.289743	-2.115355	-0.249432
H	4.469595	-3.156367	1.083301
H	2.151324	-2.372077	0.848413
H	-1.730045	-2.245575	1.307977
H	-3.879479	-3.374427	1.738752
H	-5.815906	-3.003368	0.226186
H	-5.580489	-1.491506	-1.733406
H	-3.420517	-0.365631	-2.175669

Product Geometries

0 1

C	-2.948449	2.105163	-1.396539
C	-2.840815	1.573936	0.032905
C	-1.437876	1.022154	0.359379
C	-0.396384	2.055469	0.014895
C	-0.478984	2.662026	-1.354013
C	-1.896810	3.185408	-1.646351
C	0.575936	2.404577	0.895550
C	0.695399	1.782265	2.187098
C	1.584609	3.381255	0.583065
N	2.398811	4.167109	0.338020
N	0.799985	1.266027	3.218545
C	-1.121494	-0.318277	-0.385292
C	-2.154893	-1.373746	-0.031325
C	0.274651	-0.775050	-0.049979
C	1.262777	-0.880807	-0.945507
C	2.655863	-1.265727	-0.648761
C	3.473156	-1.731413	-1.688044
C	4.790233	-2.117824	-1.445607
C	5.316237	-2.034434	-0.156865
C	4.517534	-1.554929	0.884018
C	3.202314	-1.169687	0.640693
C	-2.301175	-1.827765	1.285280
C	-3.256496	-2.791529	1.601687
C	-4.081509	-3.316282	0.605037
C	-3.942090	-2.871556	-0.708501
C	-2.983681	-1.906434	-1.022047
H	-1.391640	0.808560	1.433297
H	-1.175004	-0.144575	-1.466505
H	-3.950805	2.514707	-1.559029
H	-2.822486	1.288682	-2.120045
H	-3.578775	0.786539	0.218547
H	-3.059783	2.388947	0.734607
H	-0.234648	1.871039	-2.078811
H	0.265259	3.451944	-1.481464
H	-1.933715	3.539034	-2.681004
H	-2.097660	4.049428	-1.000253
H	0.462015	-1.005607	1.000511
H	1.042211	-0.681526	-1.995744
H	3.066752	-1.796787	-2.694686
H	5.405124	-2.481529	-2.263708
H	6.343229	-2.330393	0.035202
H	4.924881	-1.470641	1.887348
H	2.602537	-0.774495	1.456809
H	-1.666900	-1.429240	2.074887
H	-3.356689	-3.133653	2.627658
H	-4.826325	-4.066812	0.852319
H	-4.578307	-3.273675	-1.491622
H	-2.879174	-1.562665	-2.048933

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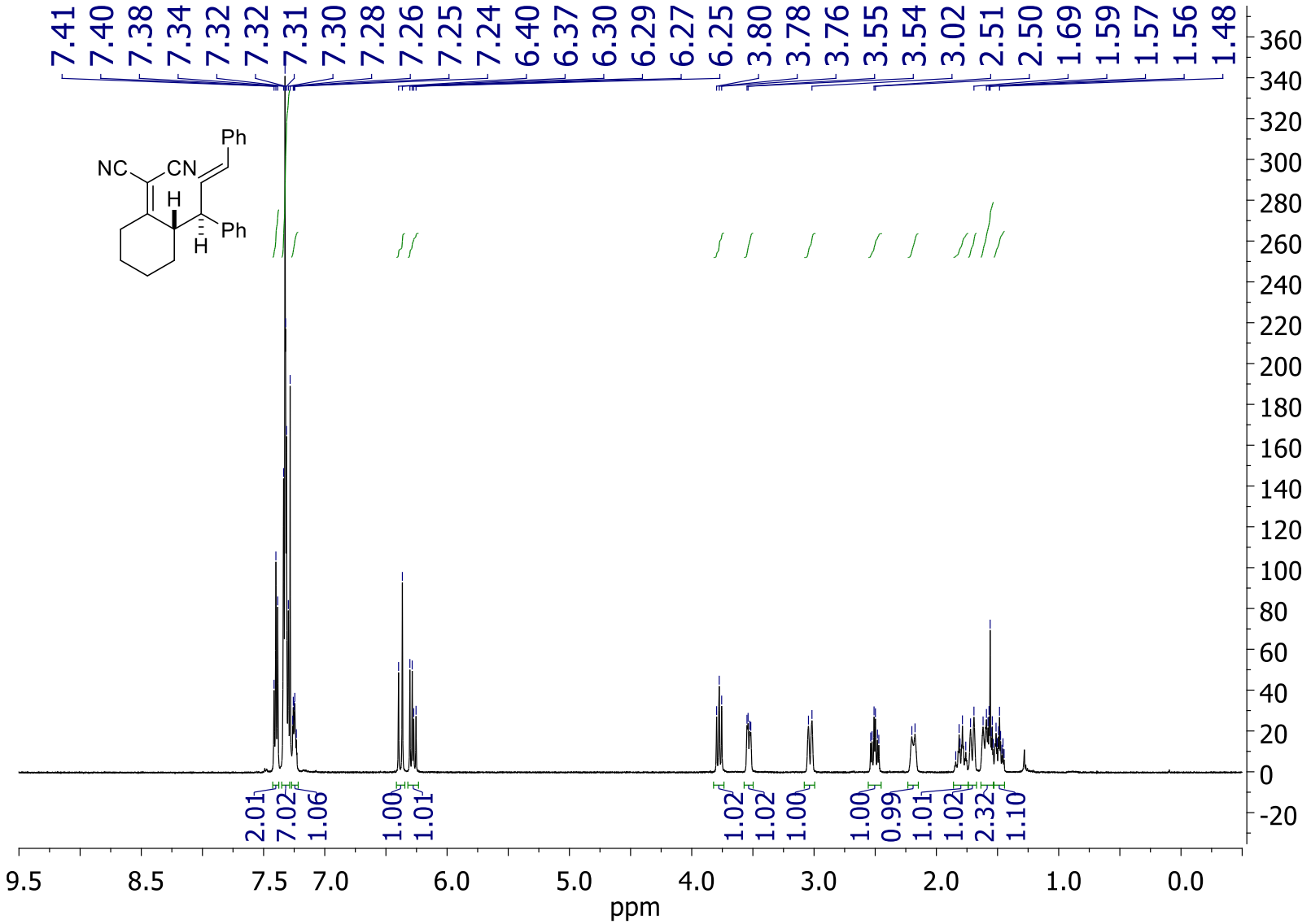
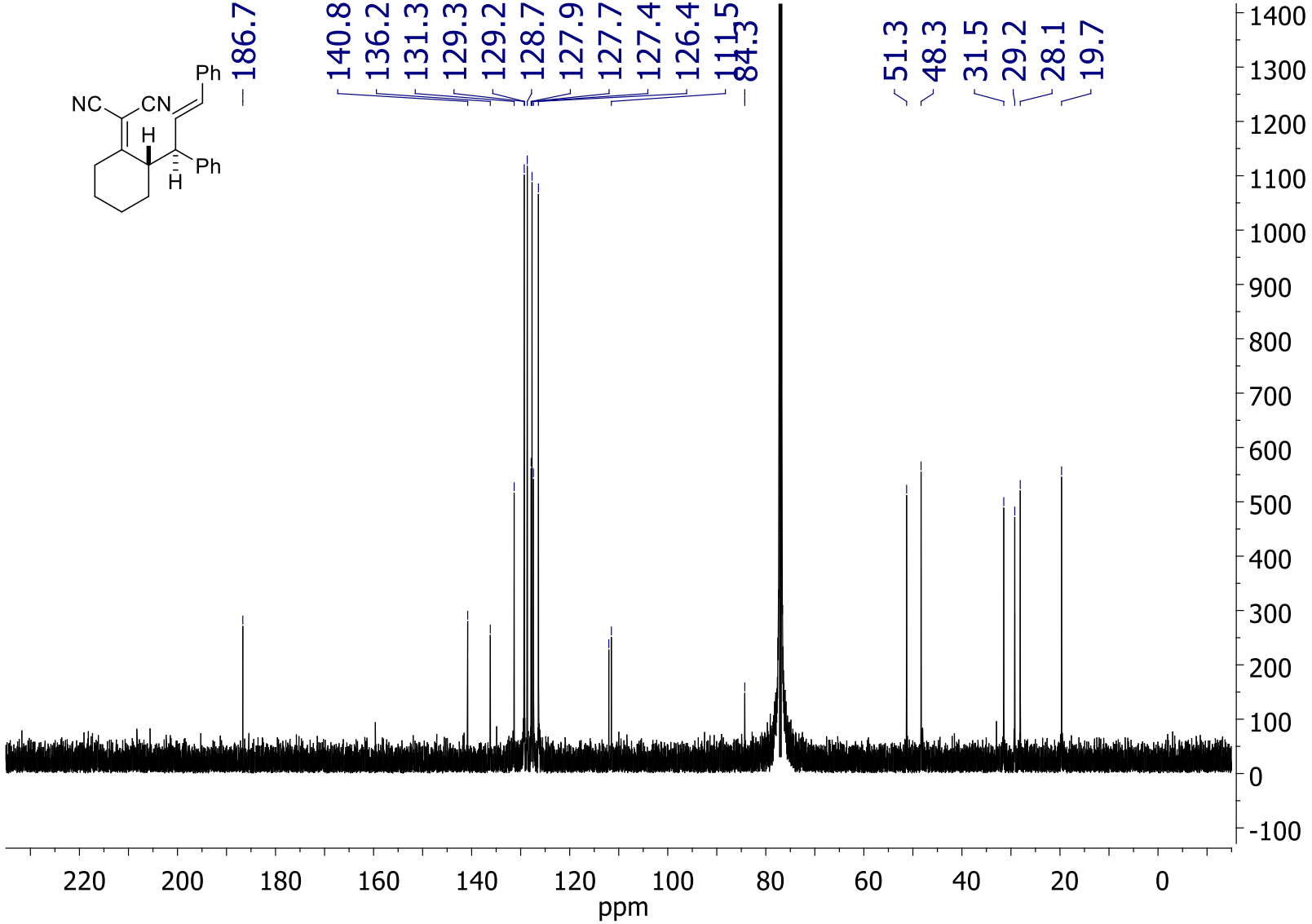
7. NMR Reprints

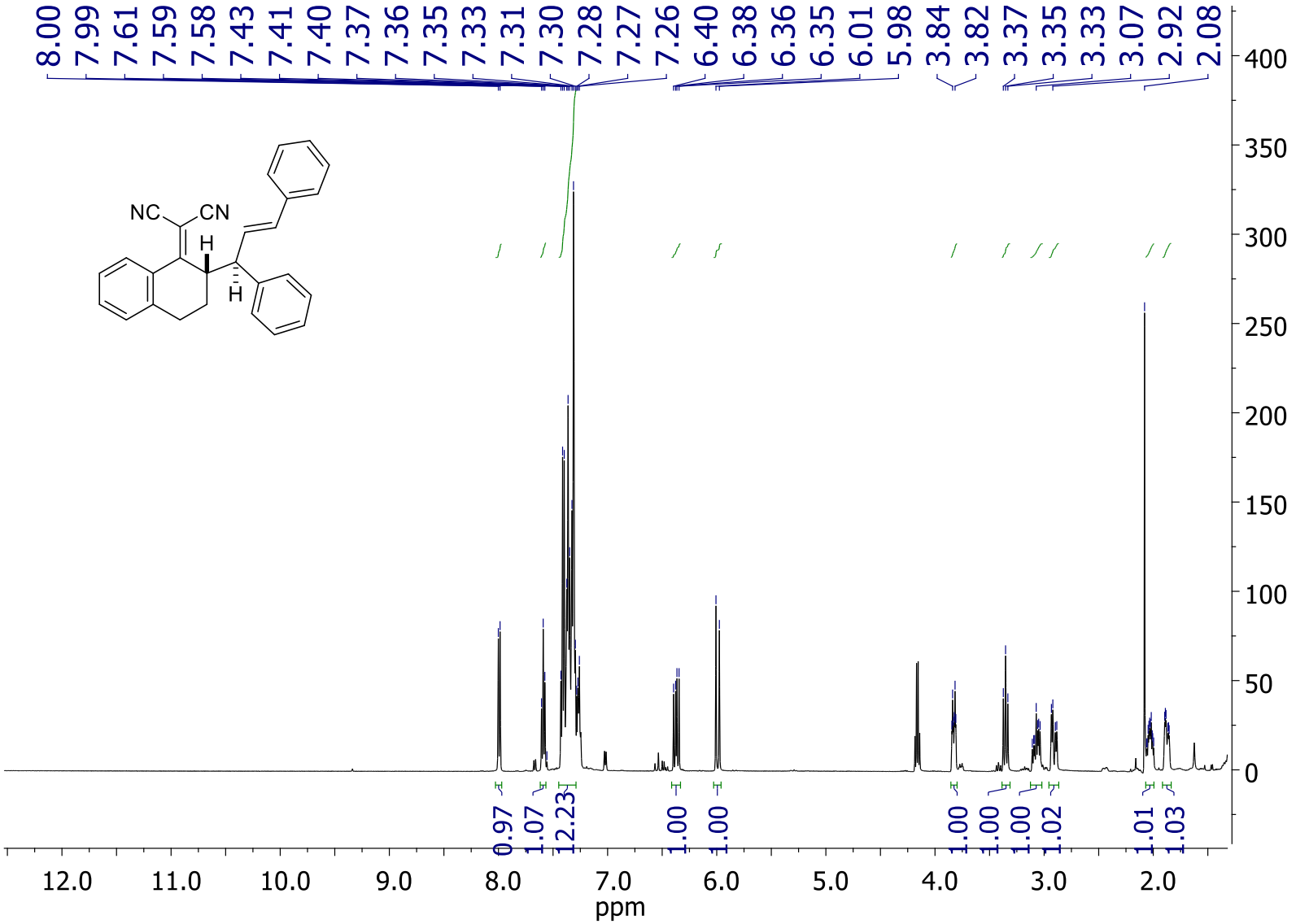
^{1}H NMR spectrum of (E)-2-(2-(1,3-diphenylallyl)cyclohexylidene)malononitrile $CDCl_3$ (3a)



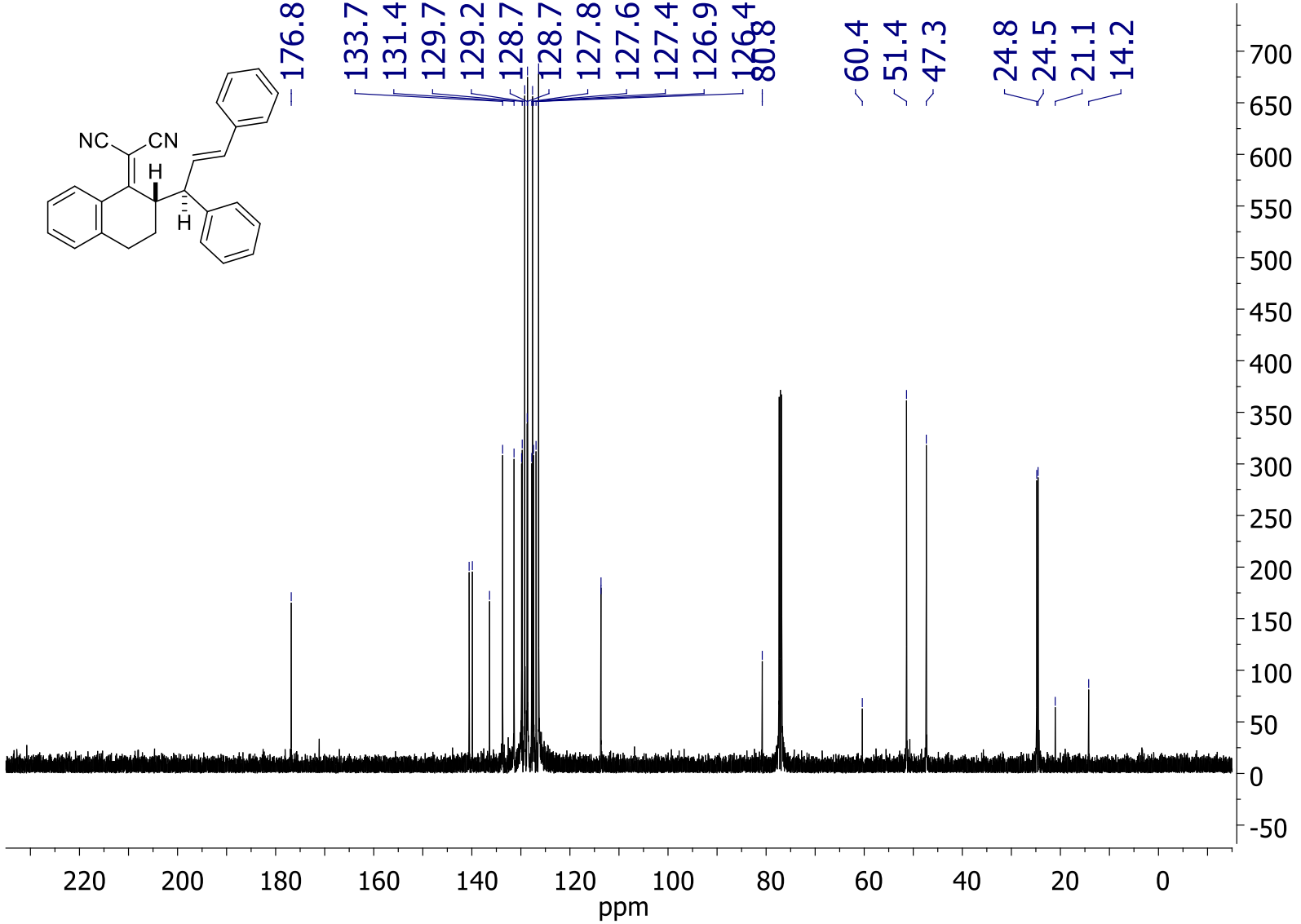
^{13}C NMR spectrum of (E)-2-(2-(1,3-diphenylallyl)cyclohexylidene)malononitrile $CDCl_3$ (3a)



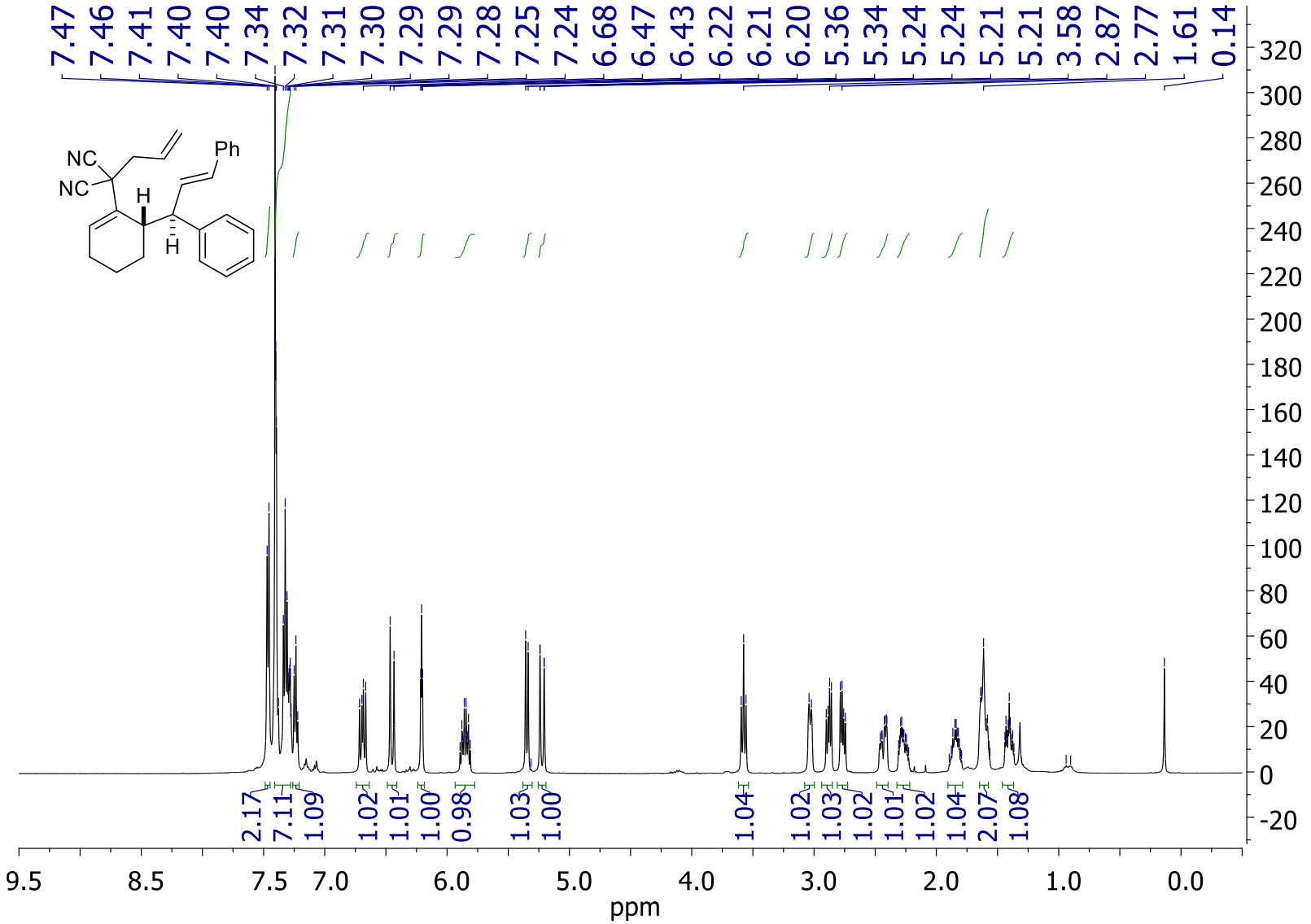
^{1}H NMR spectrum of (E)-2-(2-(1,3-diphenylallyl)cyclohexylidene)malononitrile $CDCl_3$ (3b)



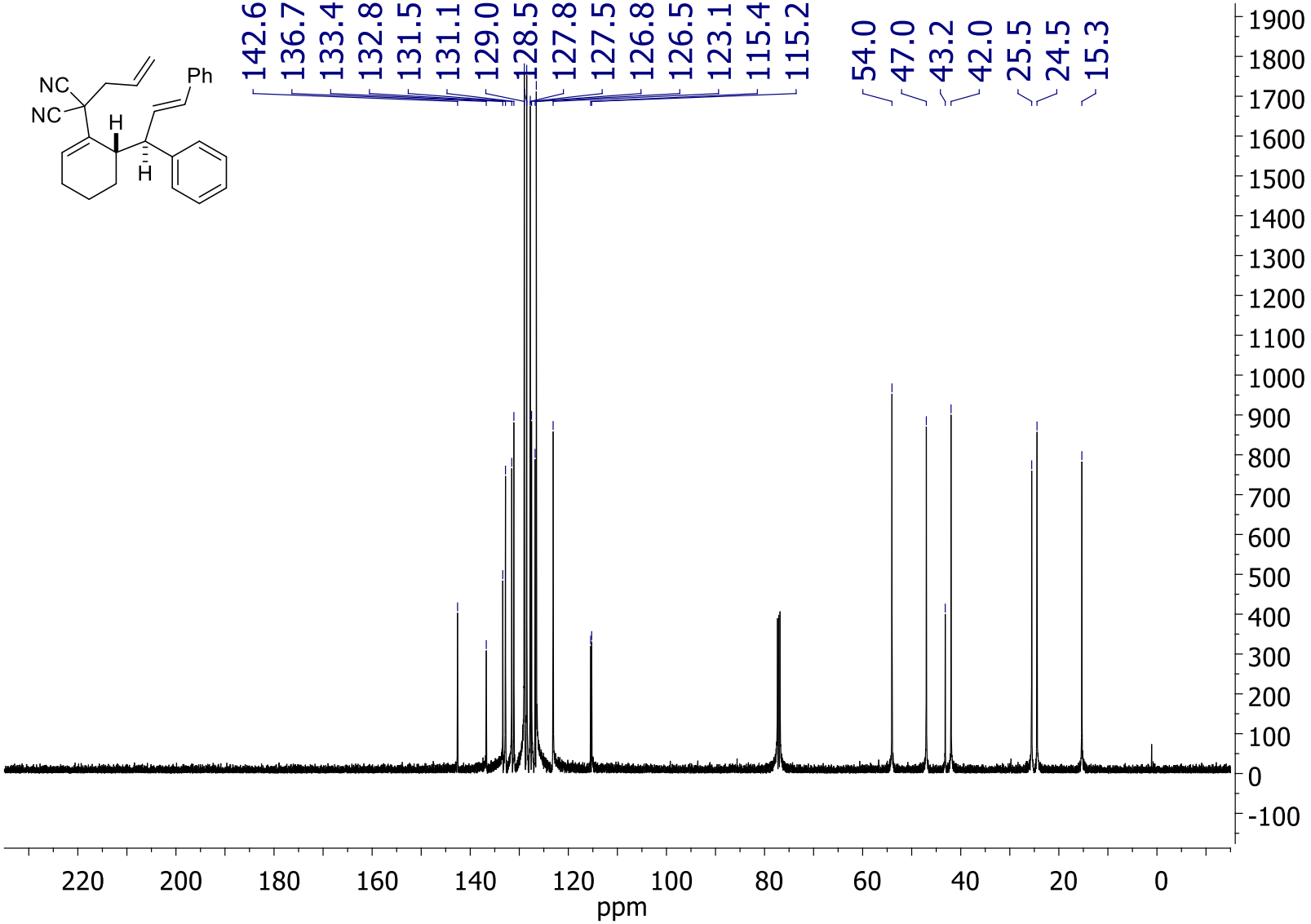
^{13}C NMR spectrum of (E)-2-(2-(1,3-diphenylallyl)cyclohexylidene)malononitrile $CDCl_3$ (3b)



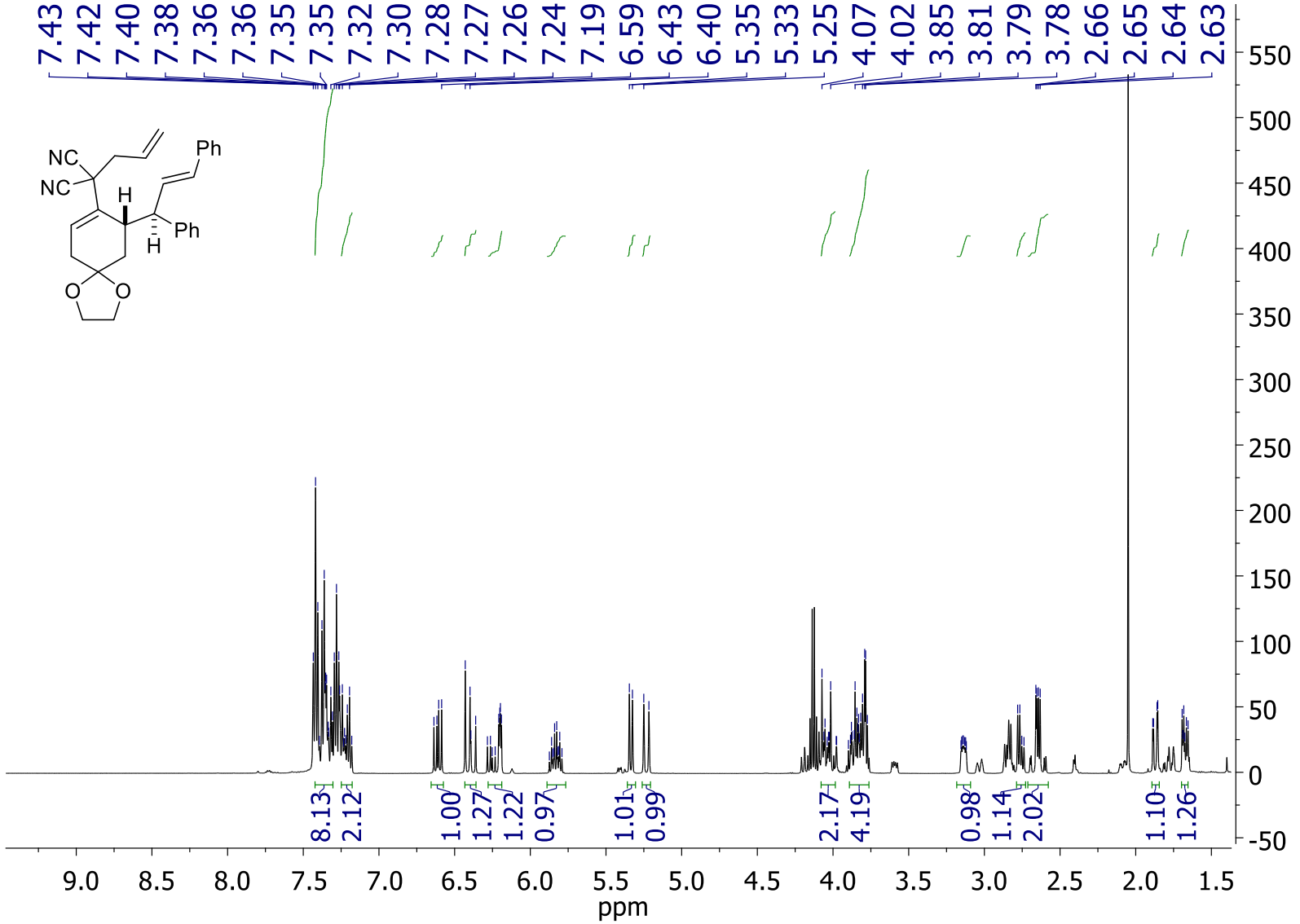
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-diphenylallyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5a)



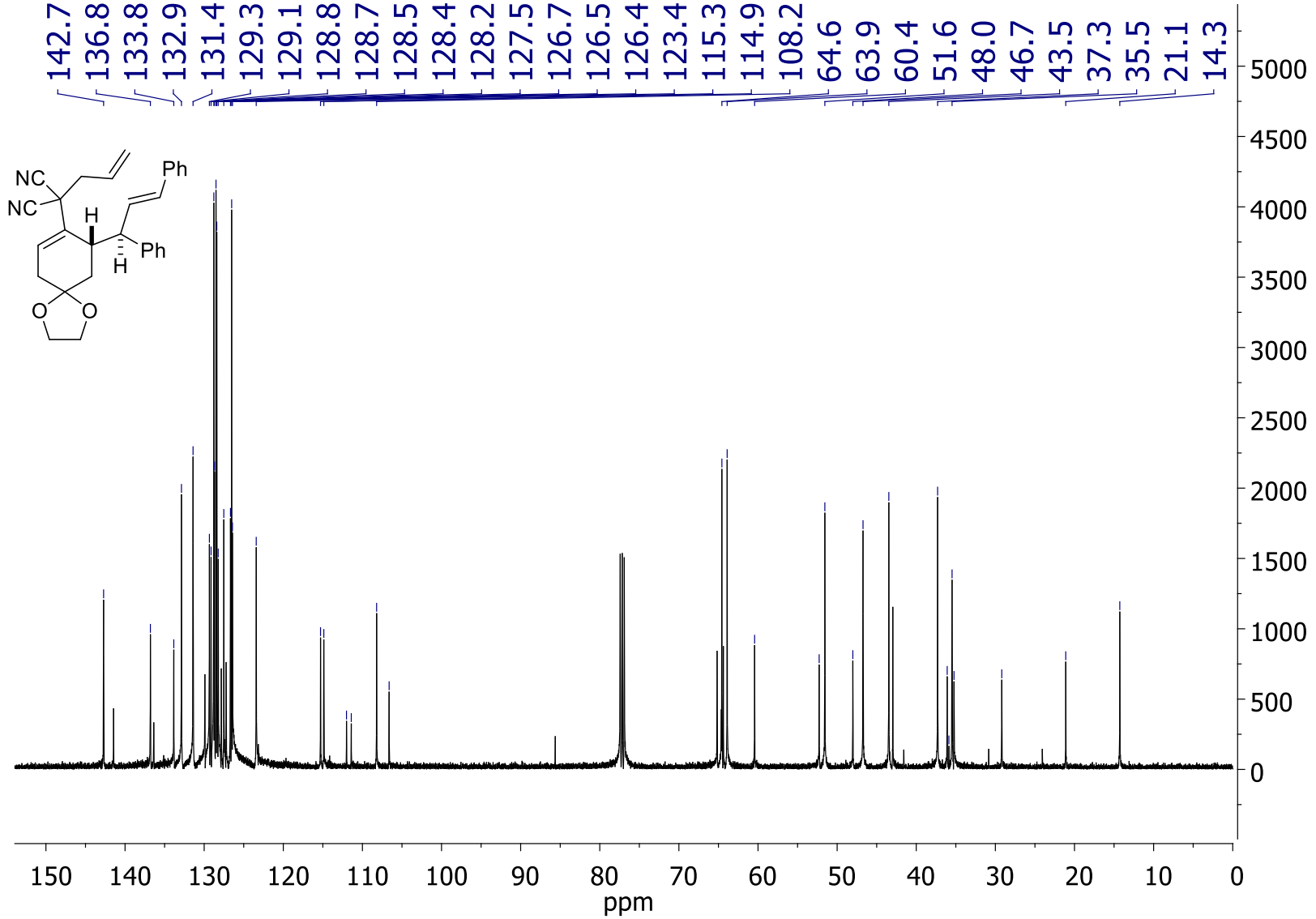
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-diphenylallyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5a)



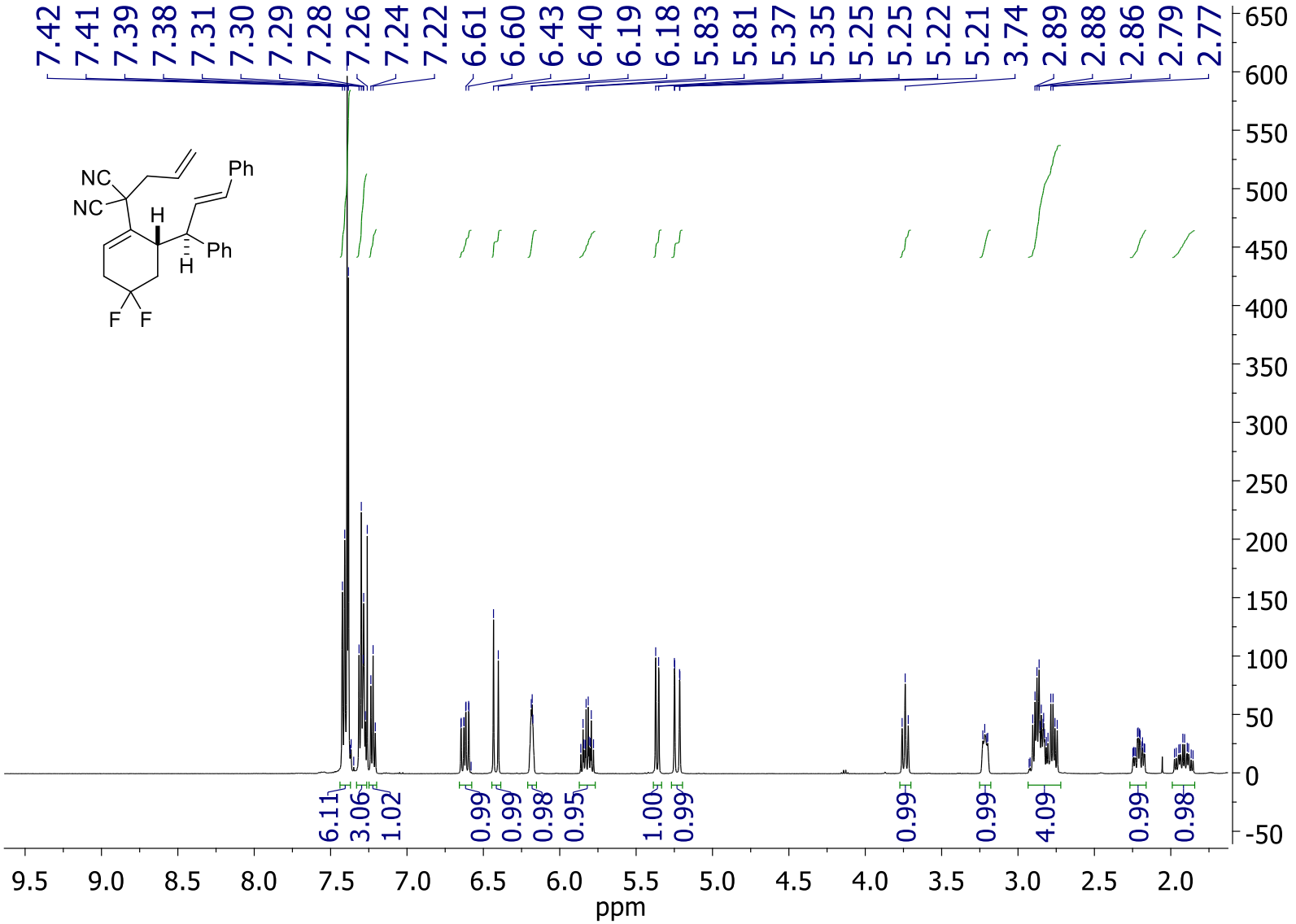
^{1}H NMR spectrum of (E)-2-allyl-2-(9-(1,3-diphenylallyl)-1,4-dioxaspiro[4.5]dec-7-en-8-yl)malononitrile $CDCl_3$ (5b)



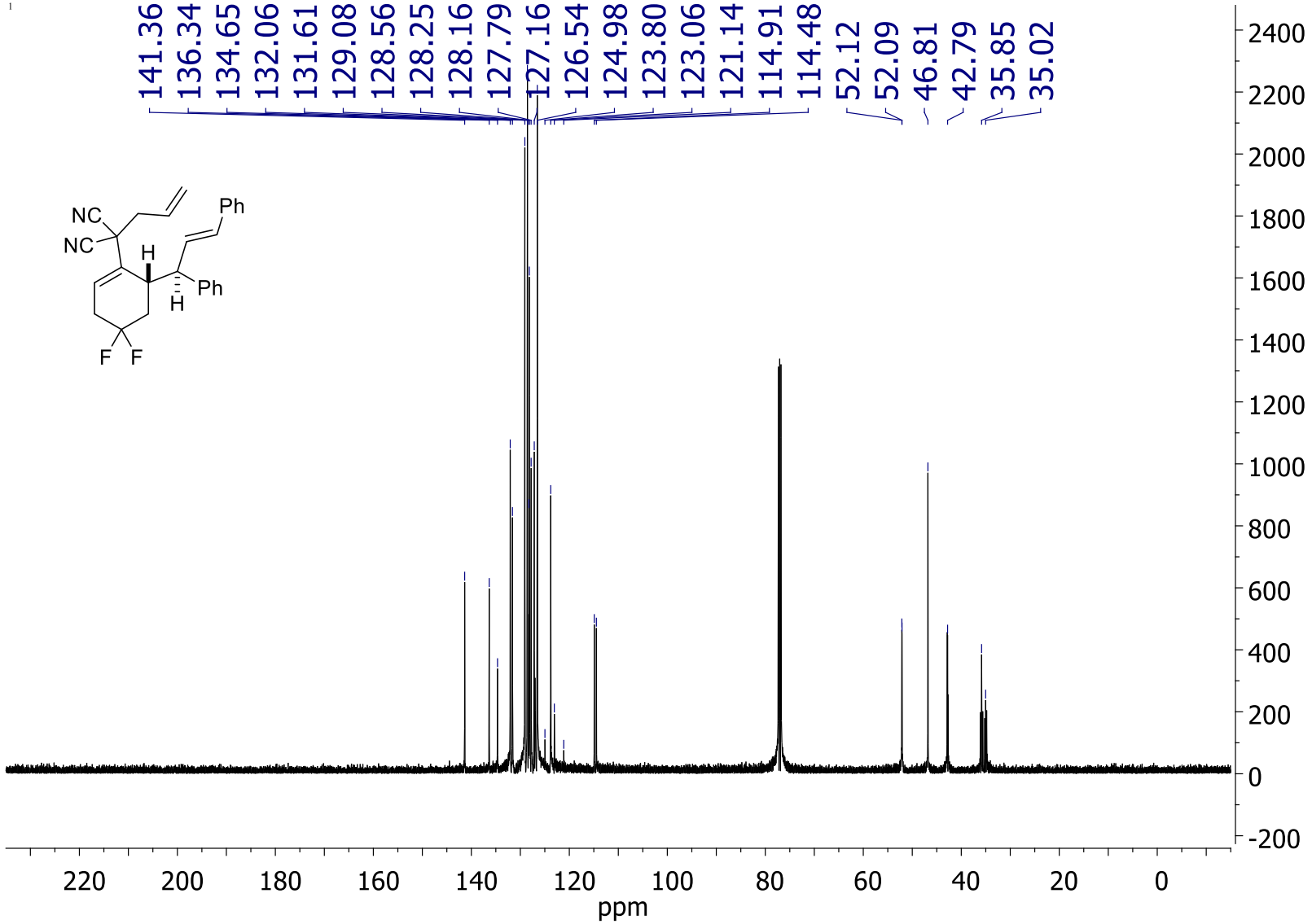
^{13}C NMR spectrum of (E)-2-allyl-2-(9-(1,3-diphenylallyl)-1,4-dioxaspiro[4.5]dec-7-en-8-yl)malononitrile $CDCl_3$ (5b)



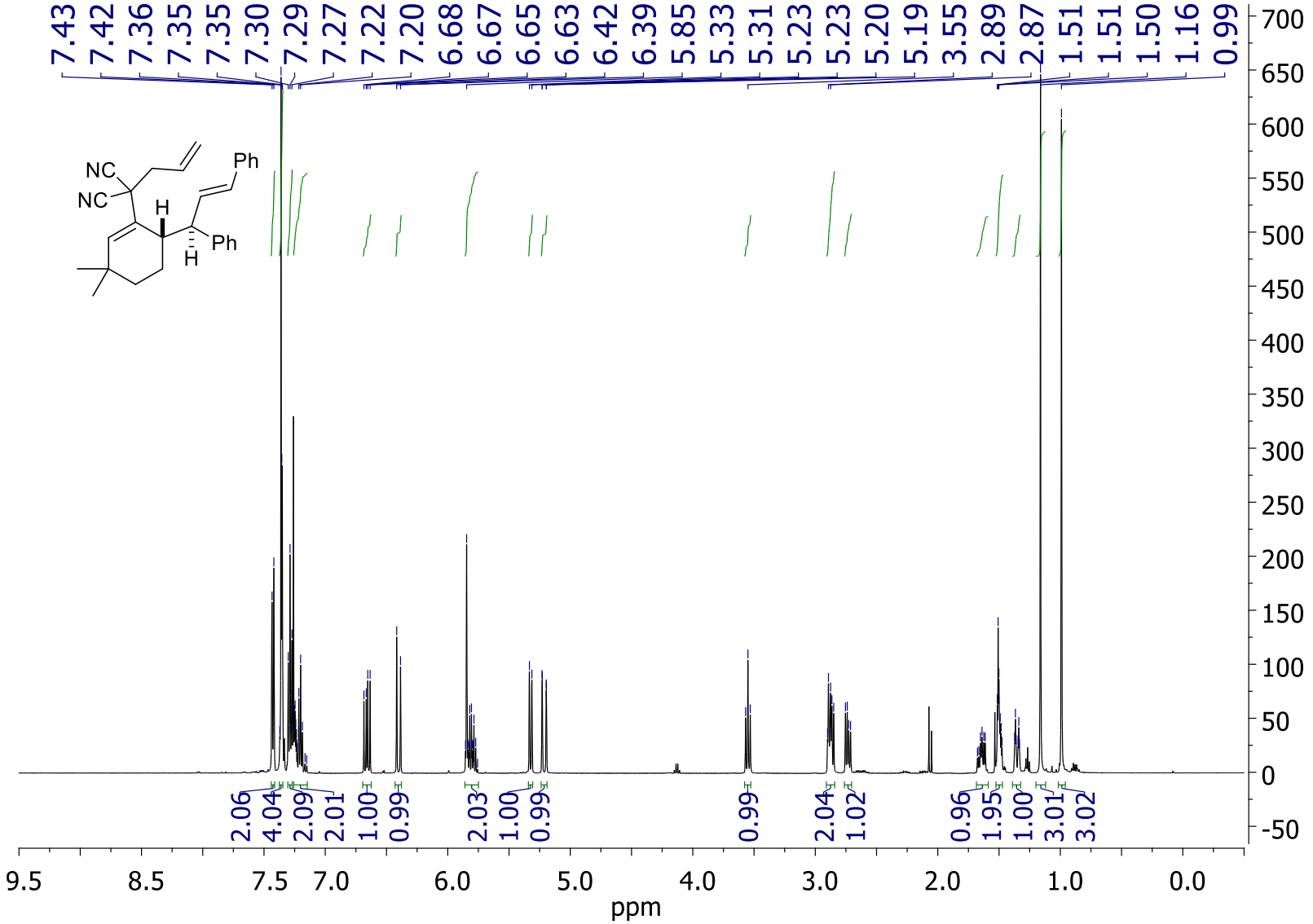
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-diphenylallyl)-4,4-difluorocyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5c)



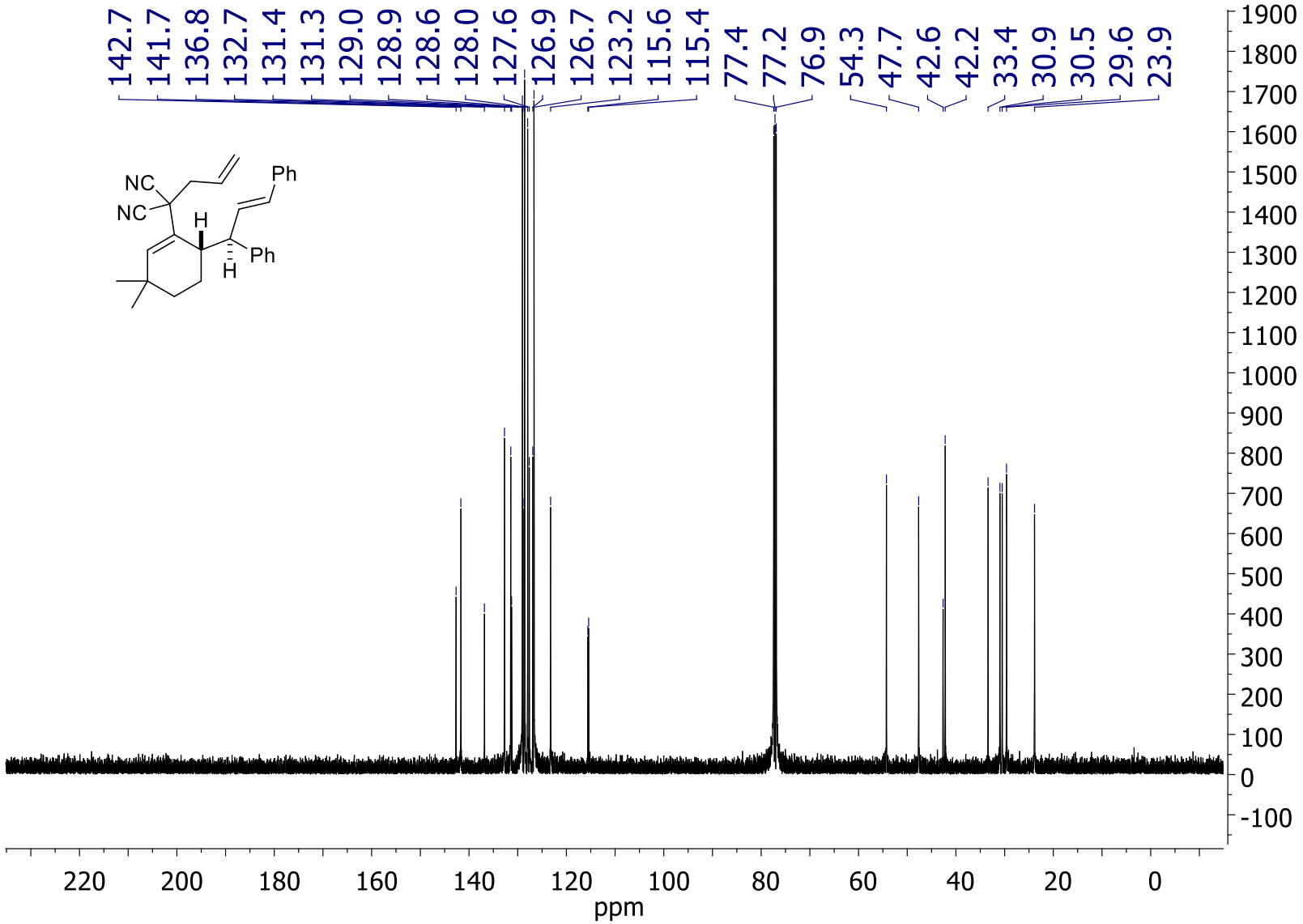
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-diphenylallyl)-4,4-difluorocyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5c)



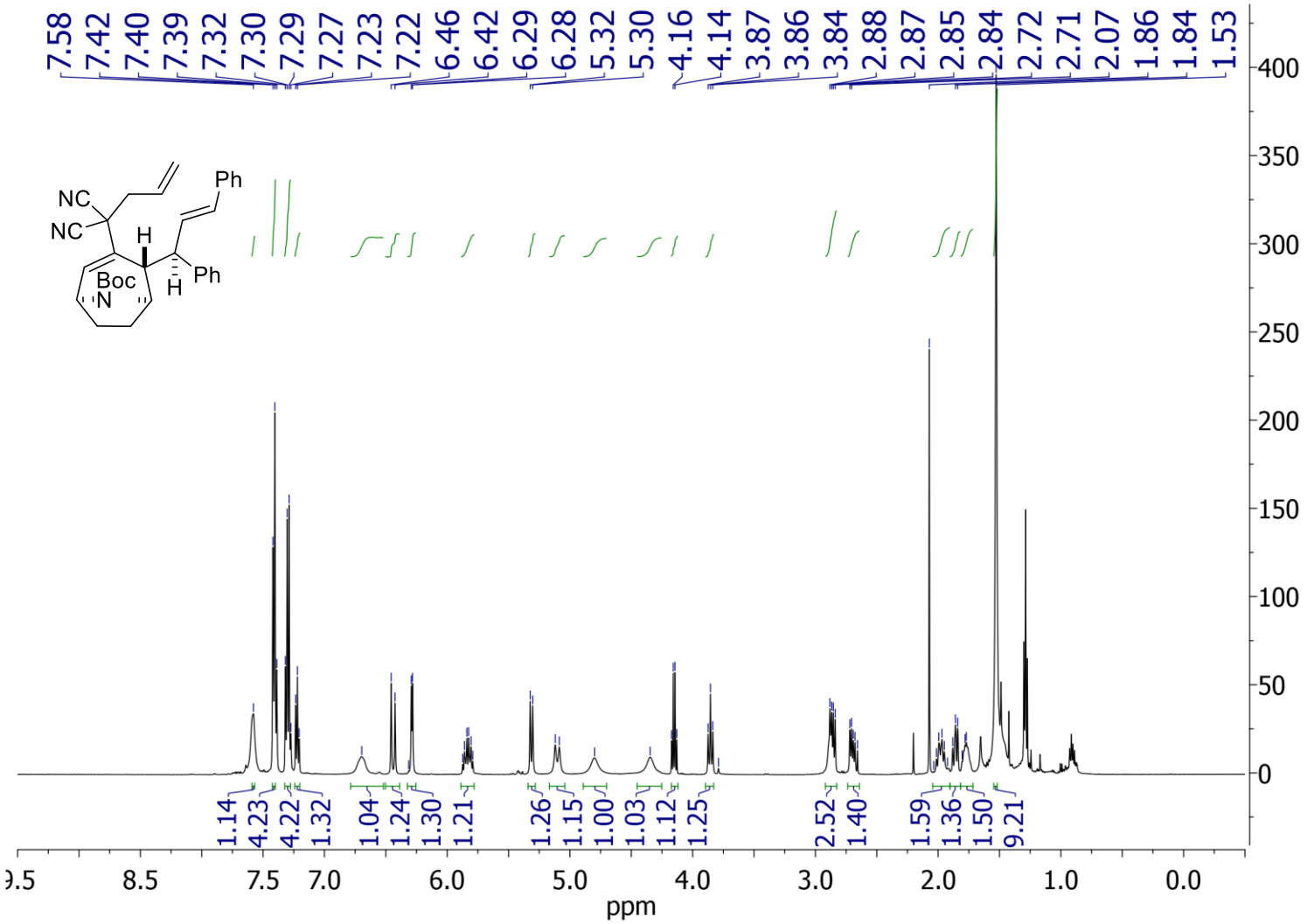
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-diphenylallyl)-3,3-dimethylcyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5d)



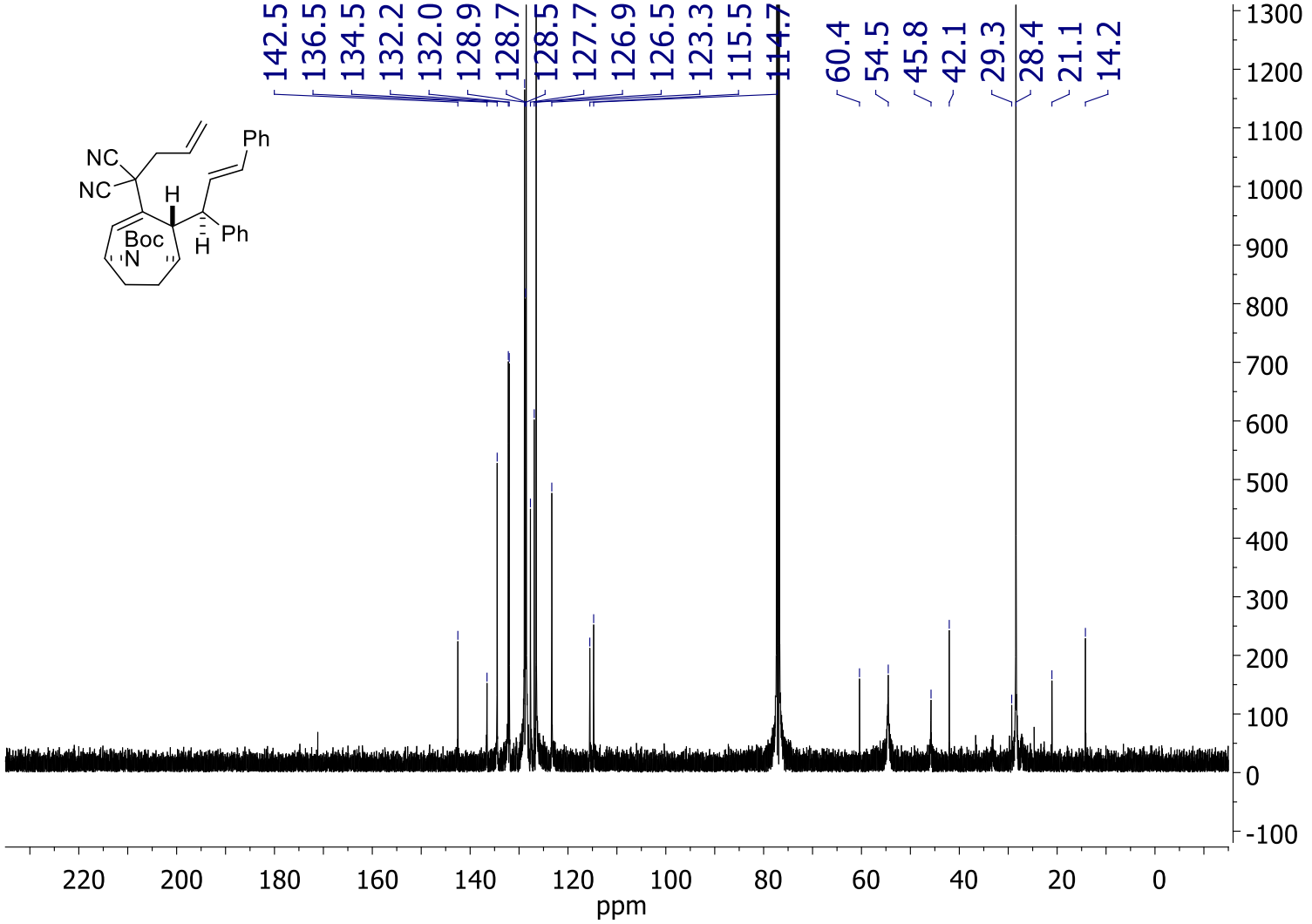
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-diphenylallyl)-3,3-dimethylcyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5d)



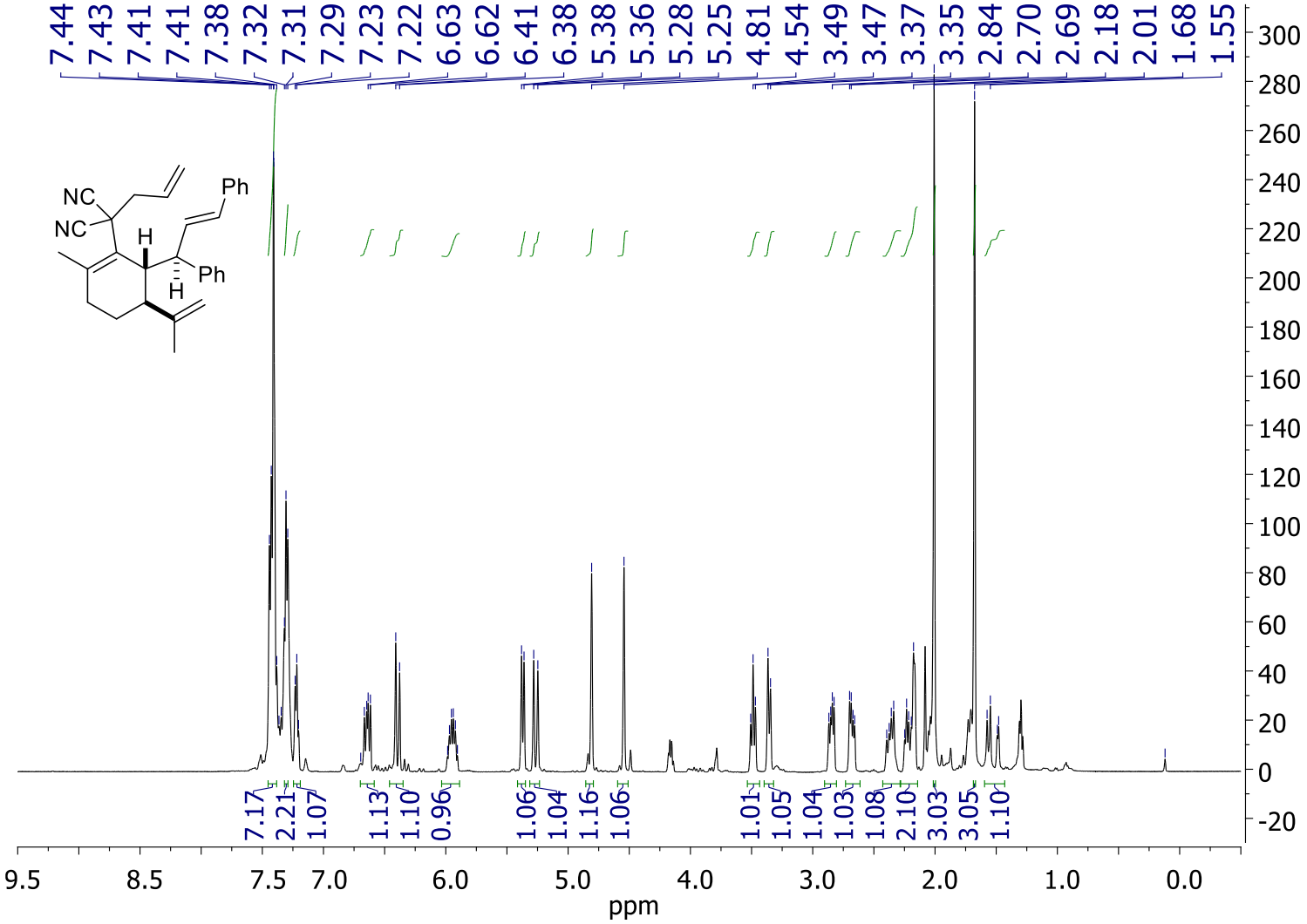
^{1}H NMR spectrum of tert-butyl (1S,5R)-3-(1,1-dicyanobut-3-en-1-yl)-4-((E)-1,3-diphenylallyl)-8-azabicyclo[3.2.1]oct-2-ene-8-carboxylate $CDCl_3$ (5e)



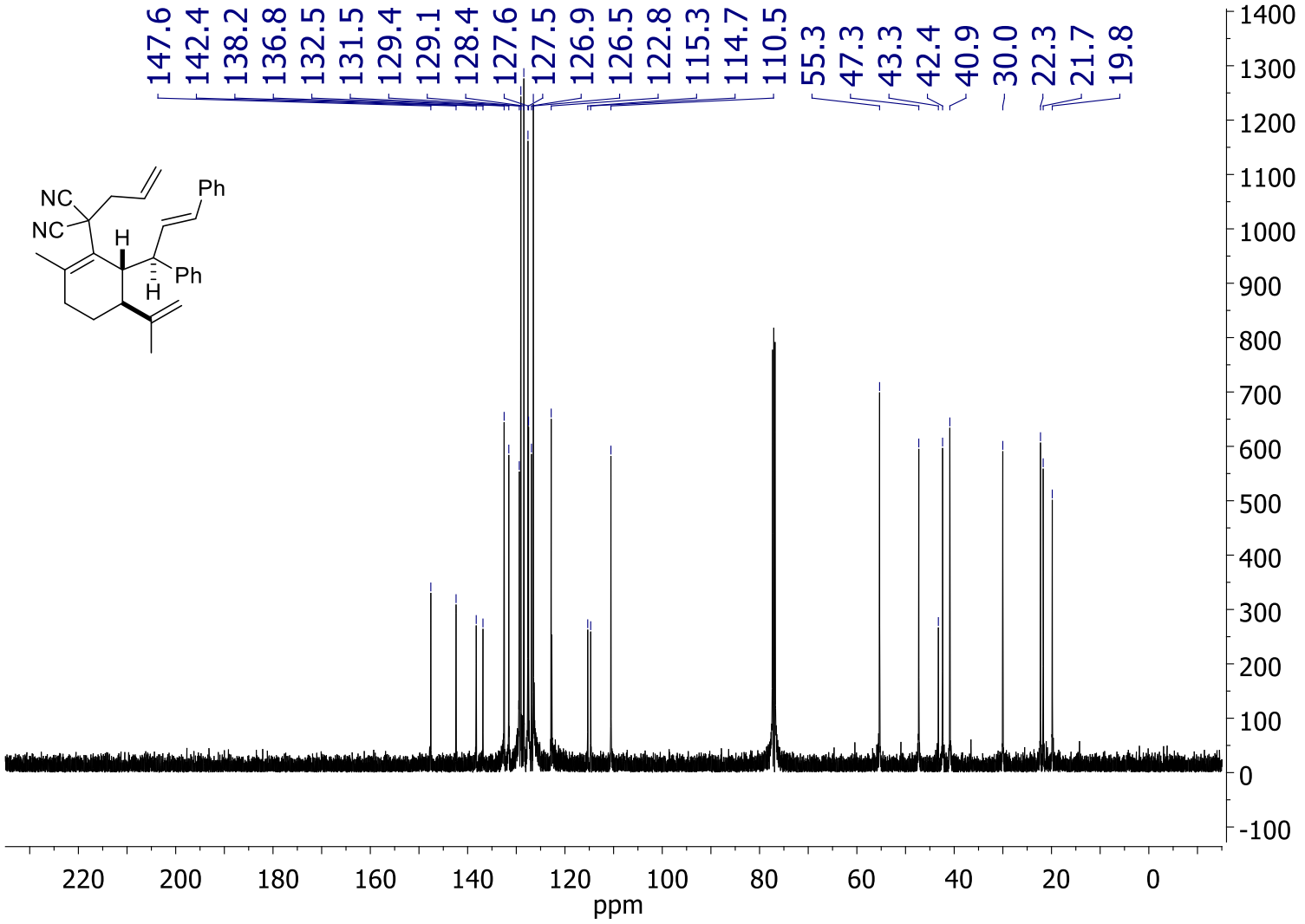
^{13}C NMR spectrum of tert-butyl (1S,5R)-3-(1,1-dicyanobut-3-en-1-yl)-4-((E)-1,3-diphenylallyl)-8-azabicyclo[3.2.1]oct-2-ene-8-carboxylate $CDCl_3$ (5e)



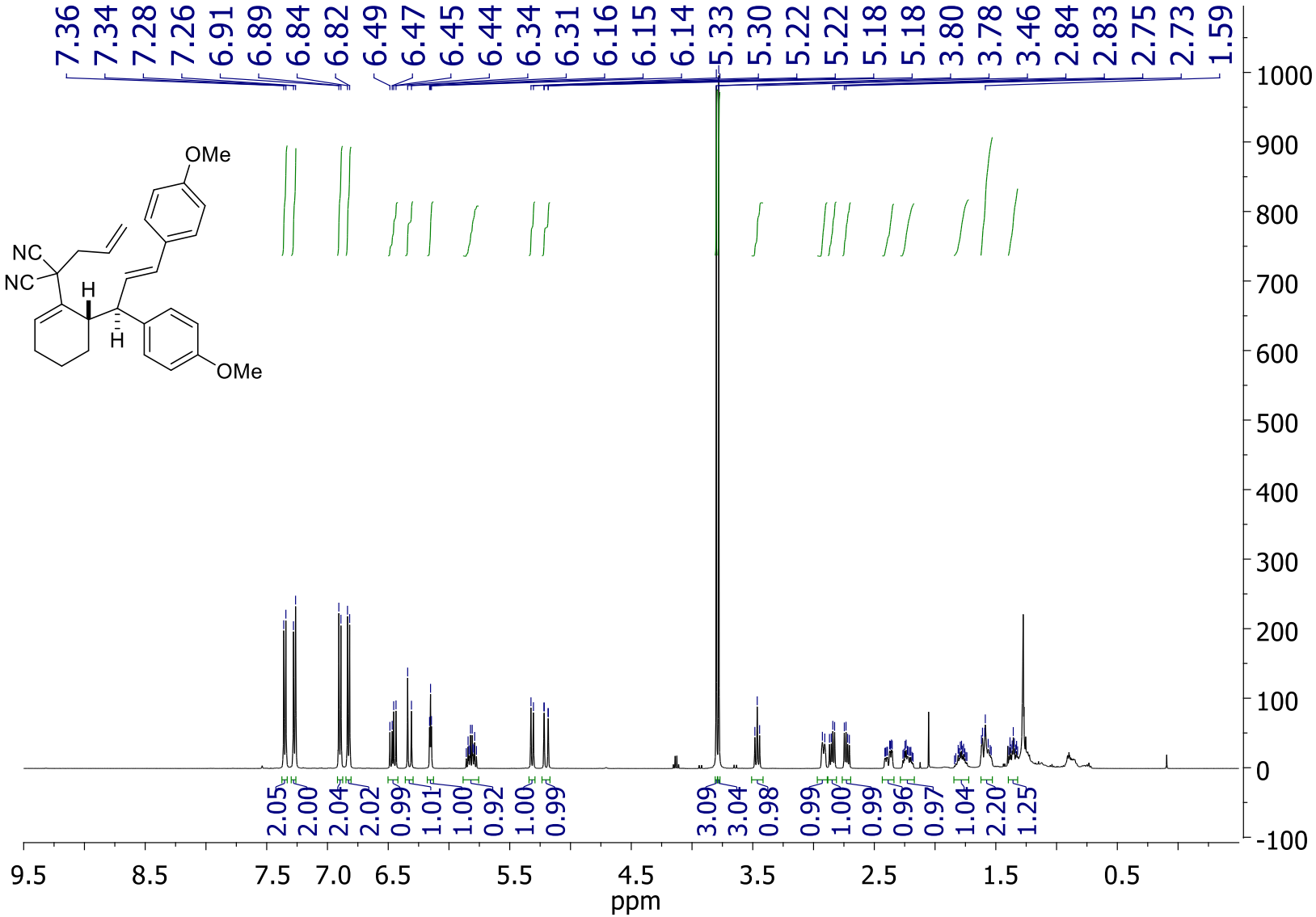
^{1}H NMR spectrum of 2-allyl-2-((5S)-6-((E)-1,3-diphenylallyl)-2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5f)



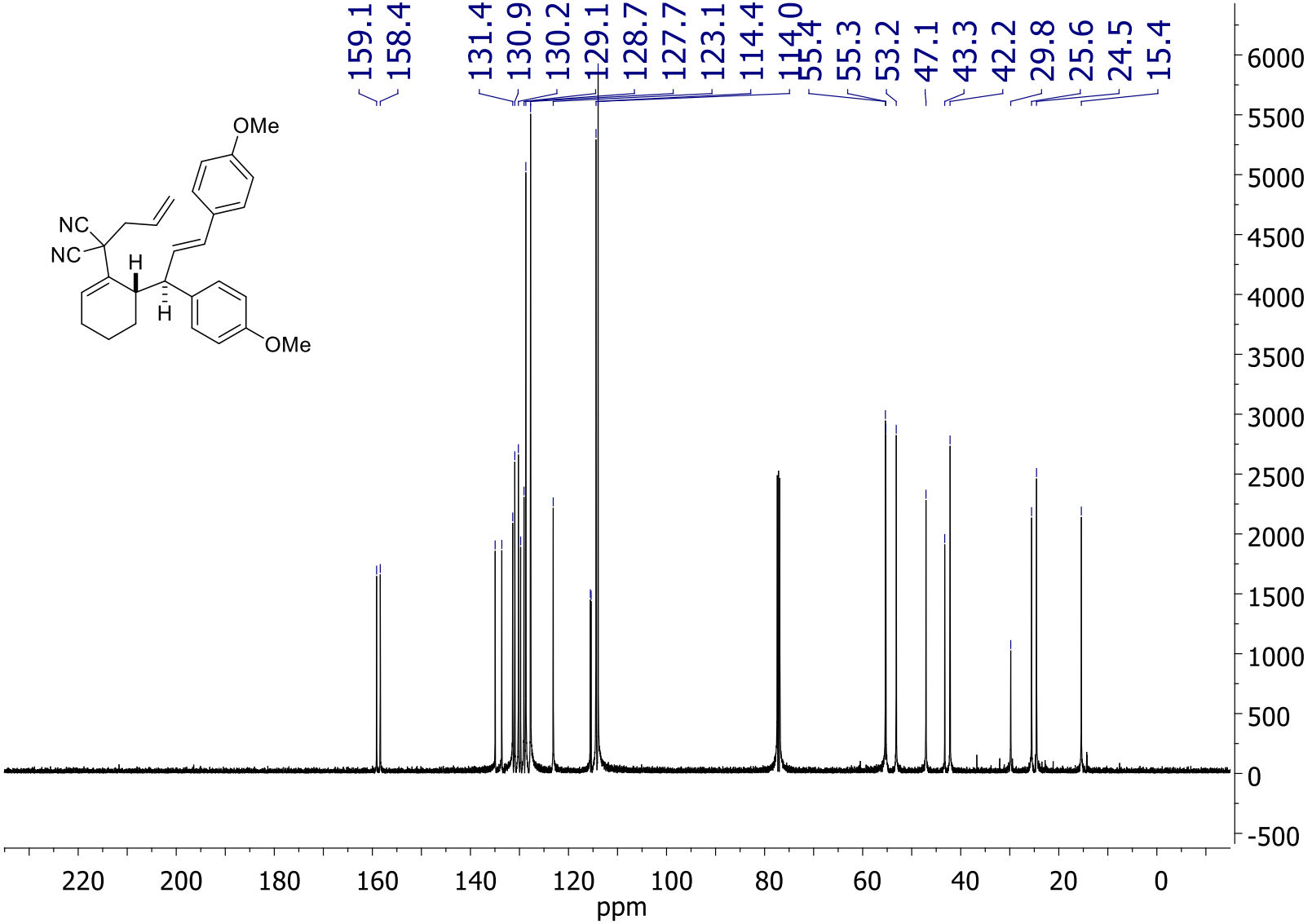
^{13}C NMR spectrum of 2-allyl-2-((5S)-6-((E)-1,3-diphenylallyl)-2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5f)



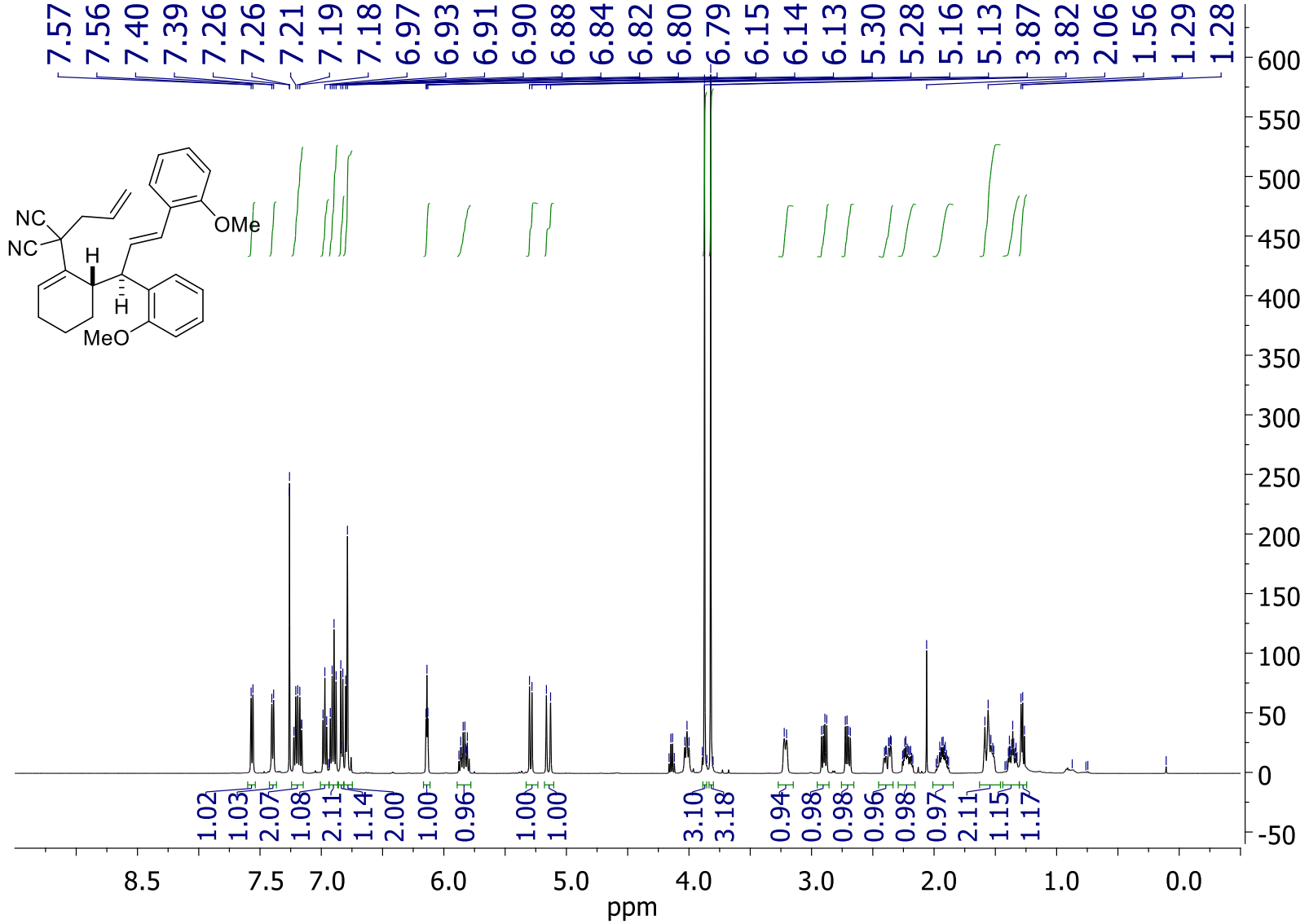
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5g)



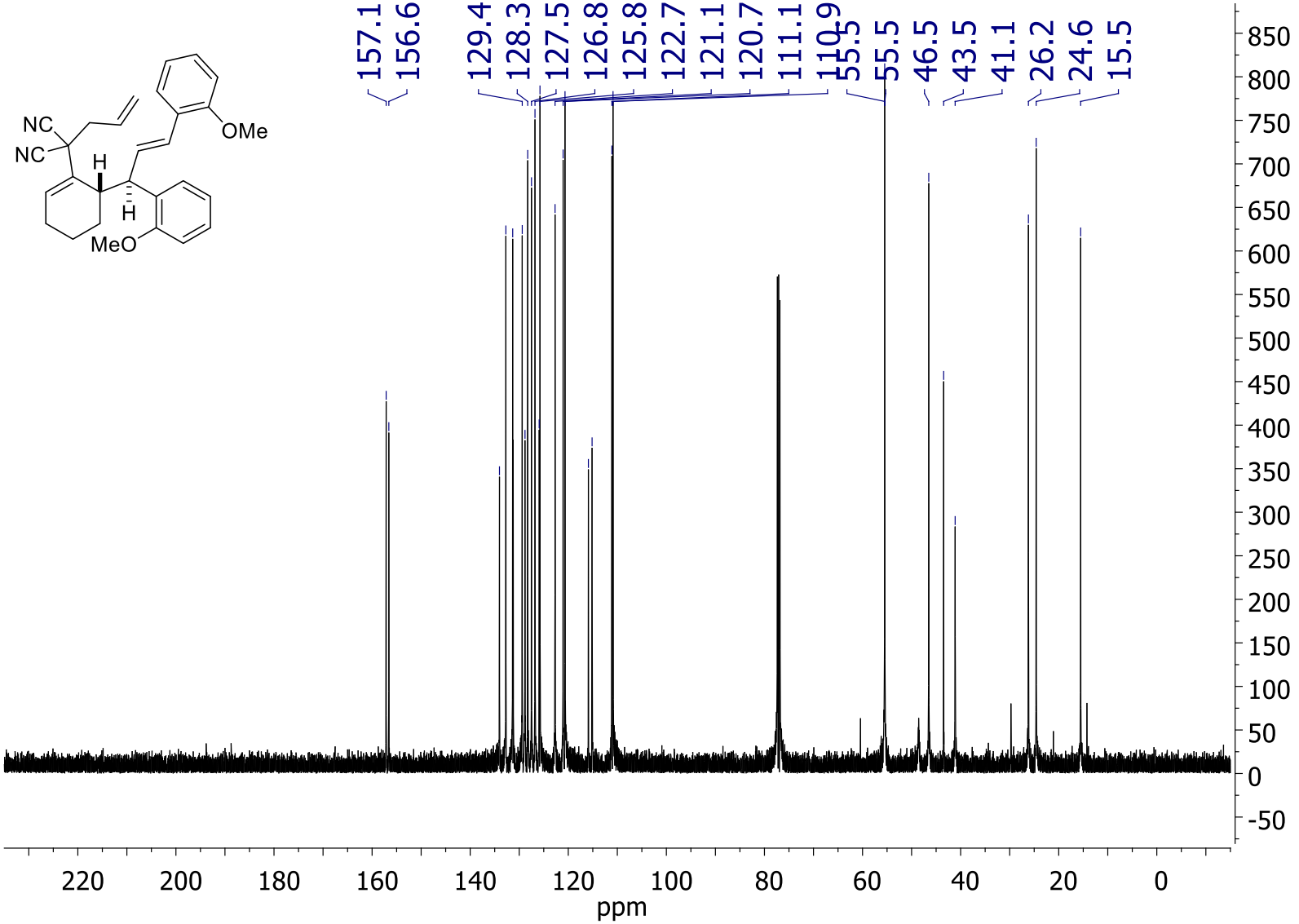
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5g)



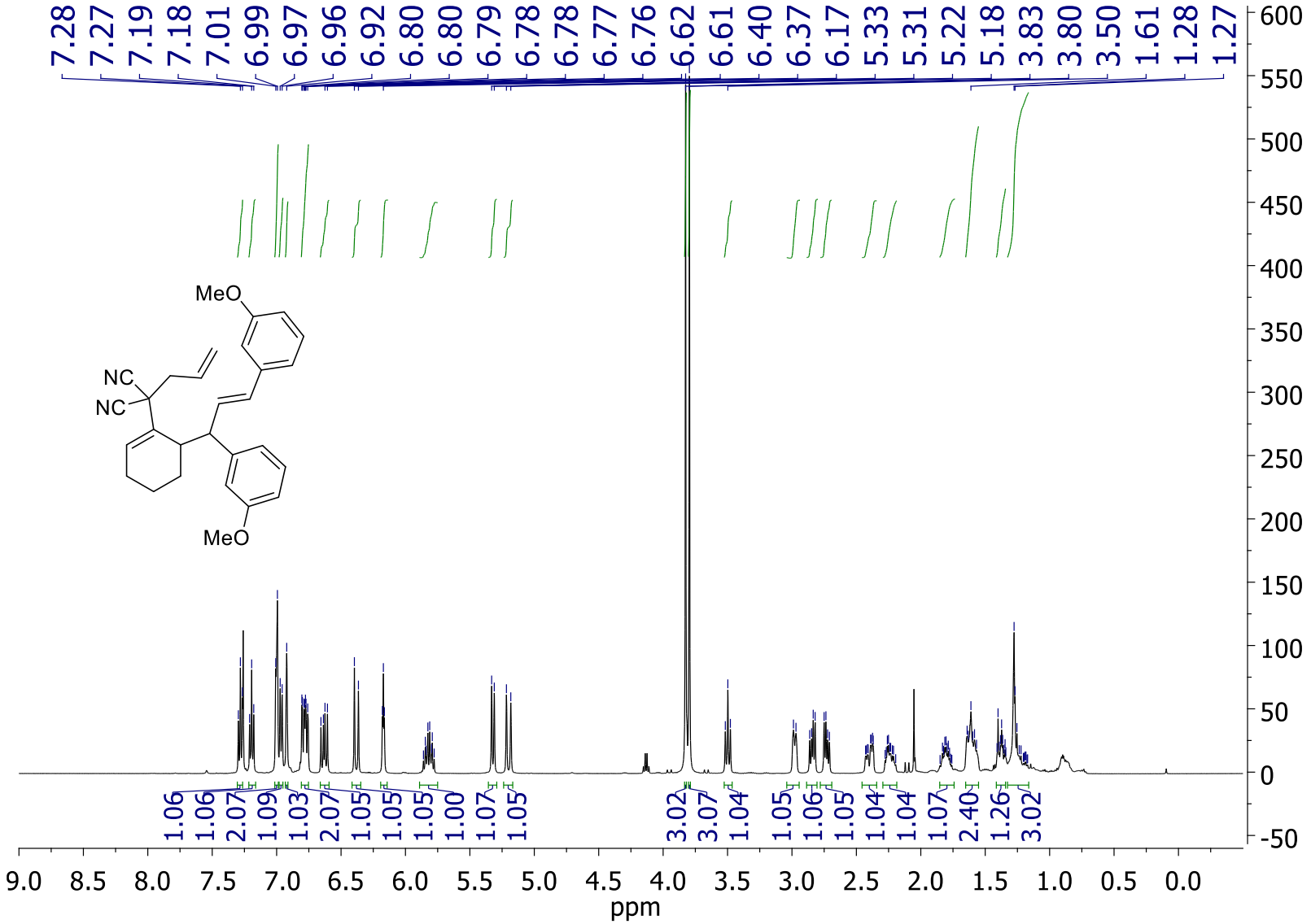
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(2-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5h)



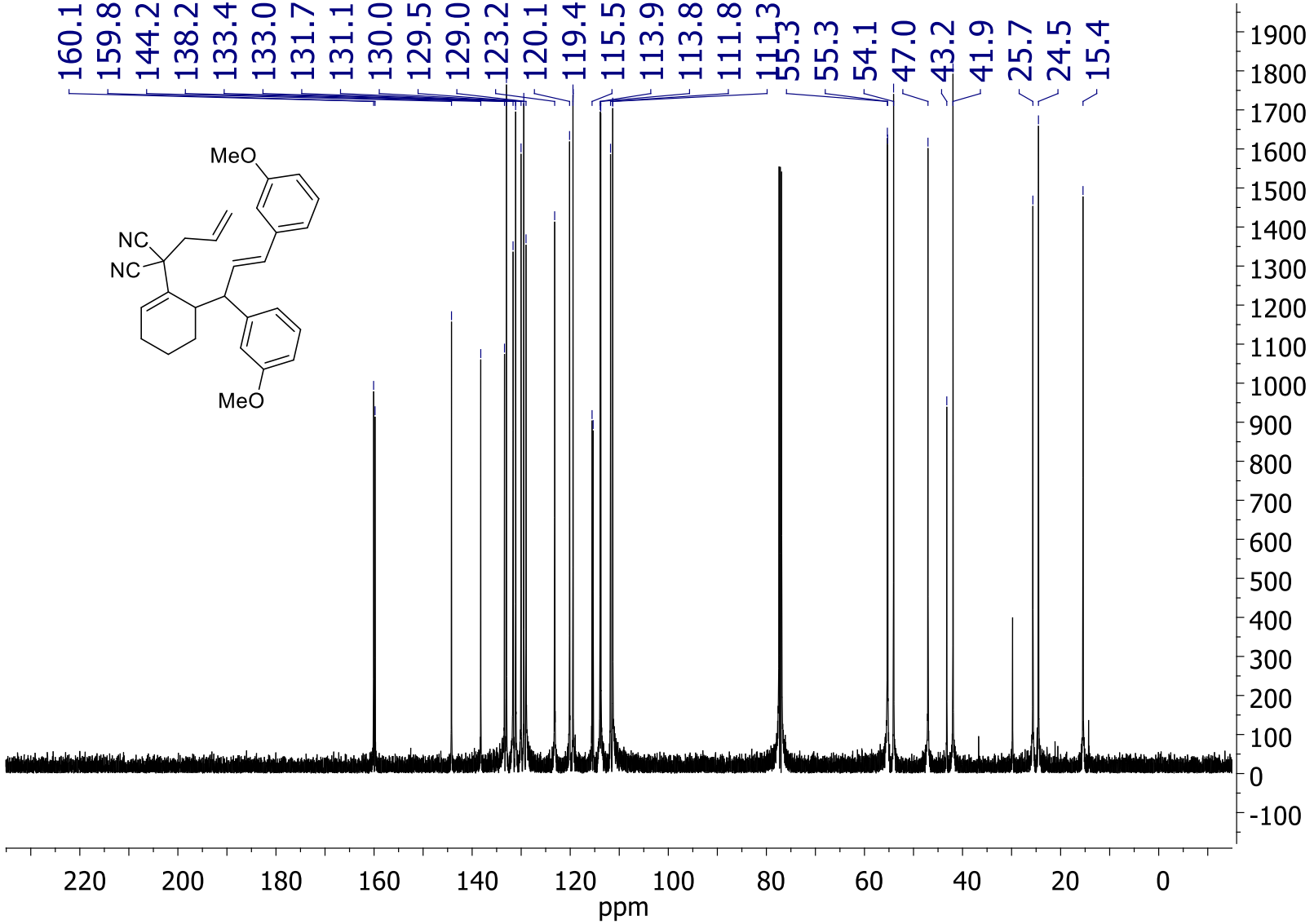
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(2-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5h)



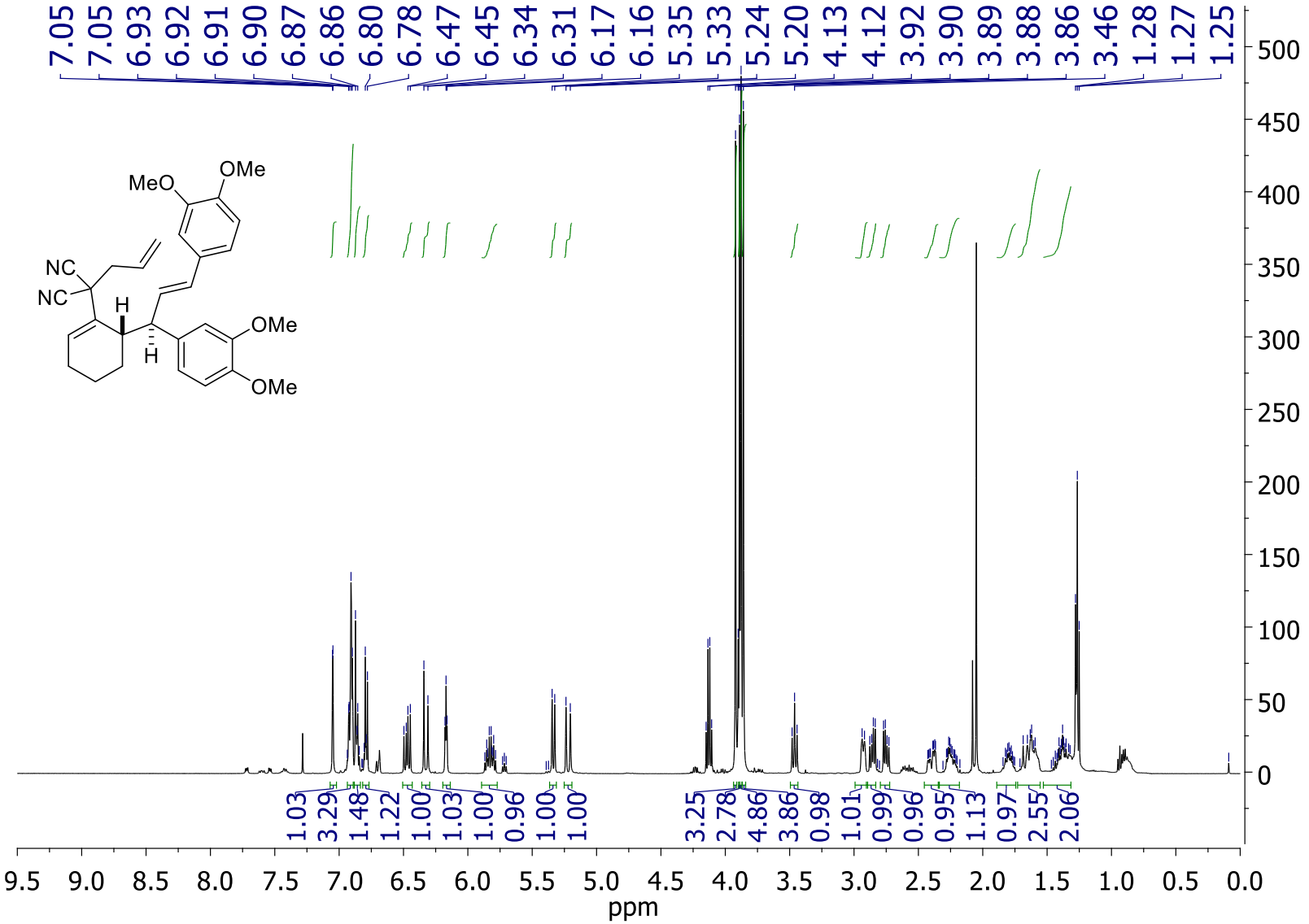
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(3-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5i)



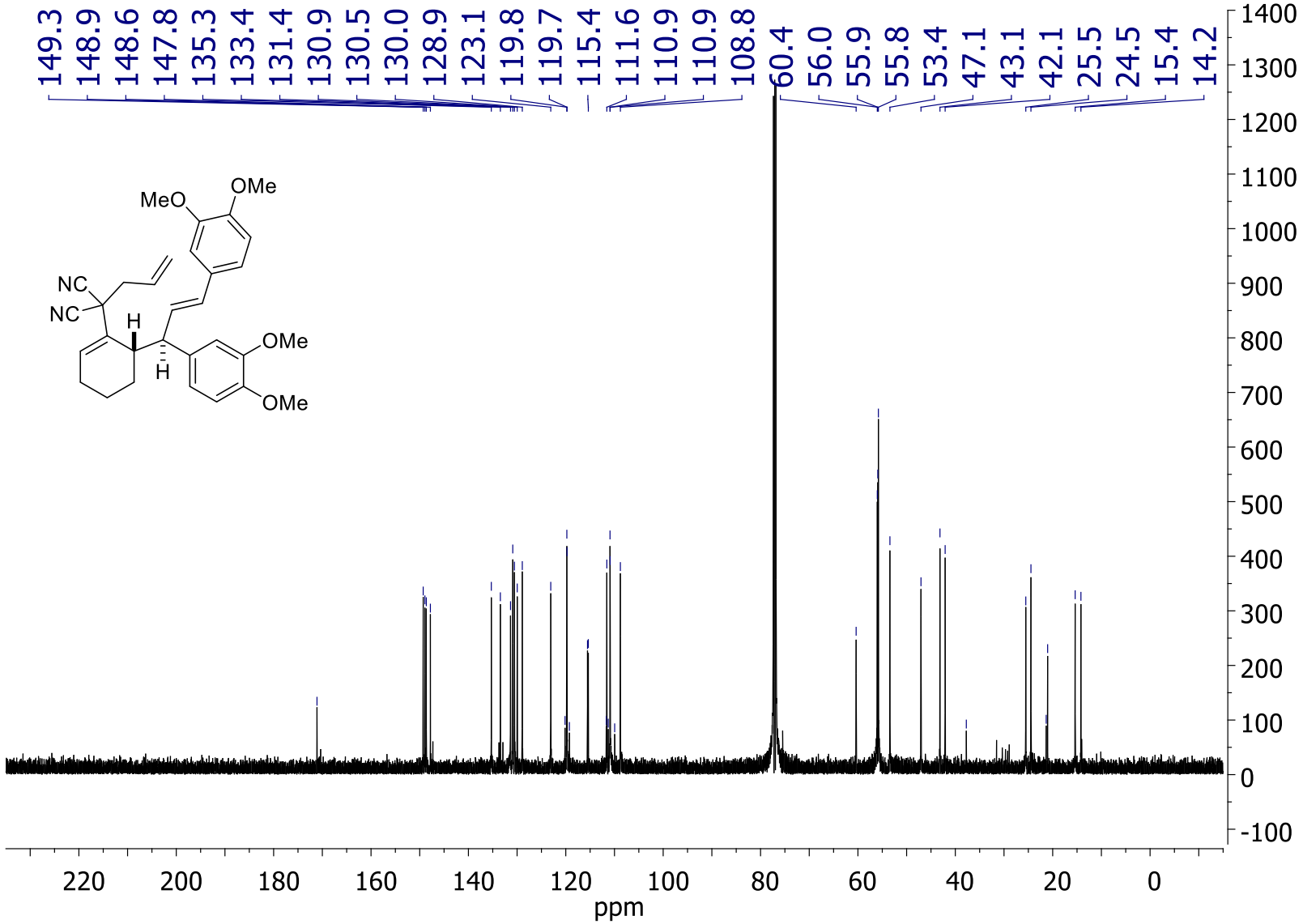
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(3-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5i)



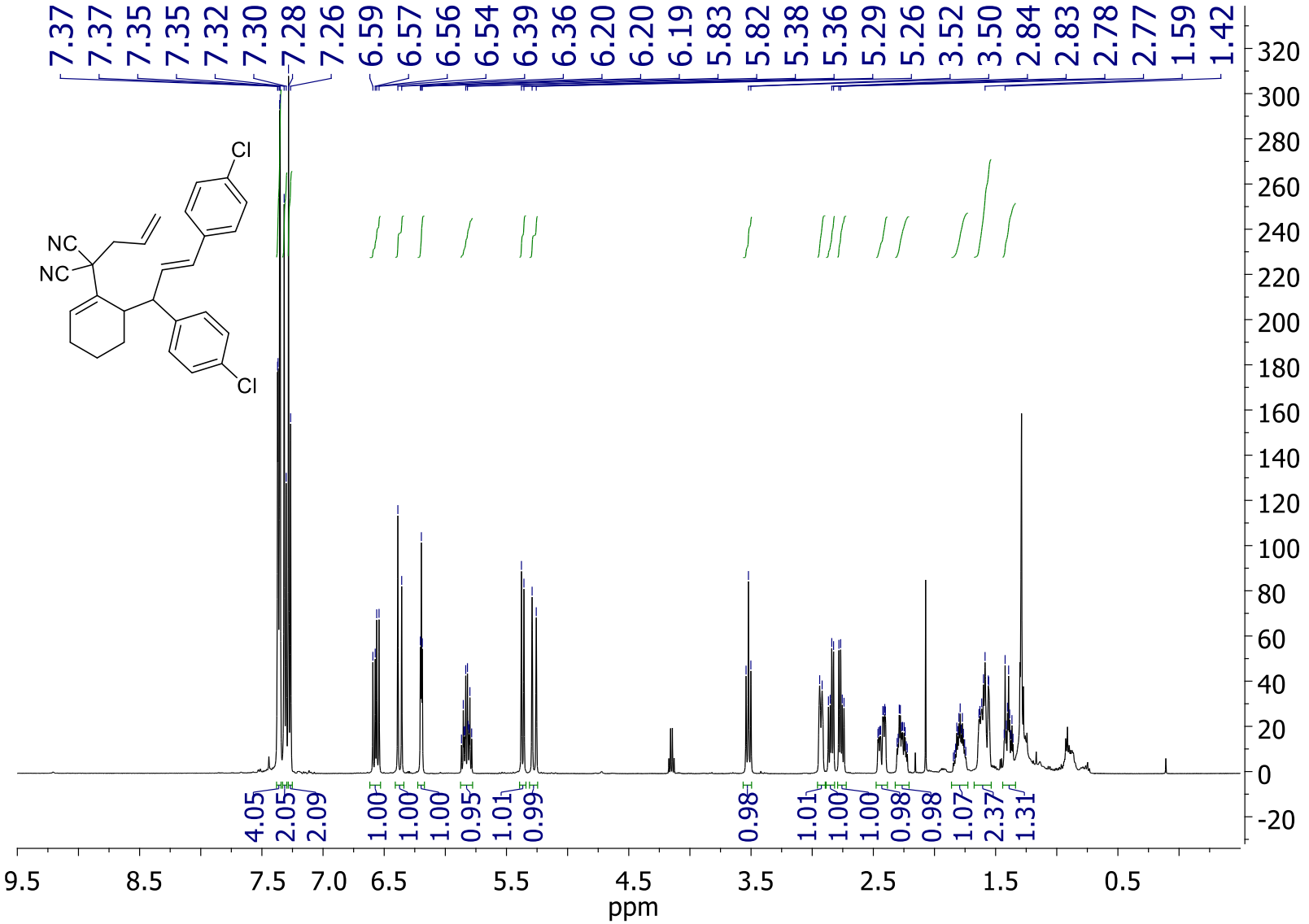
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(3,4-dimethoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5j)



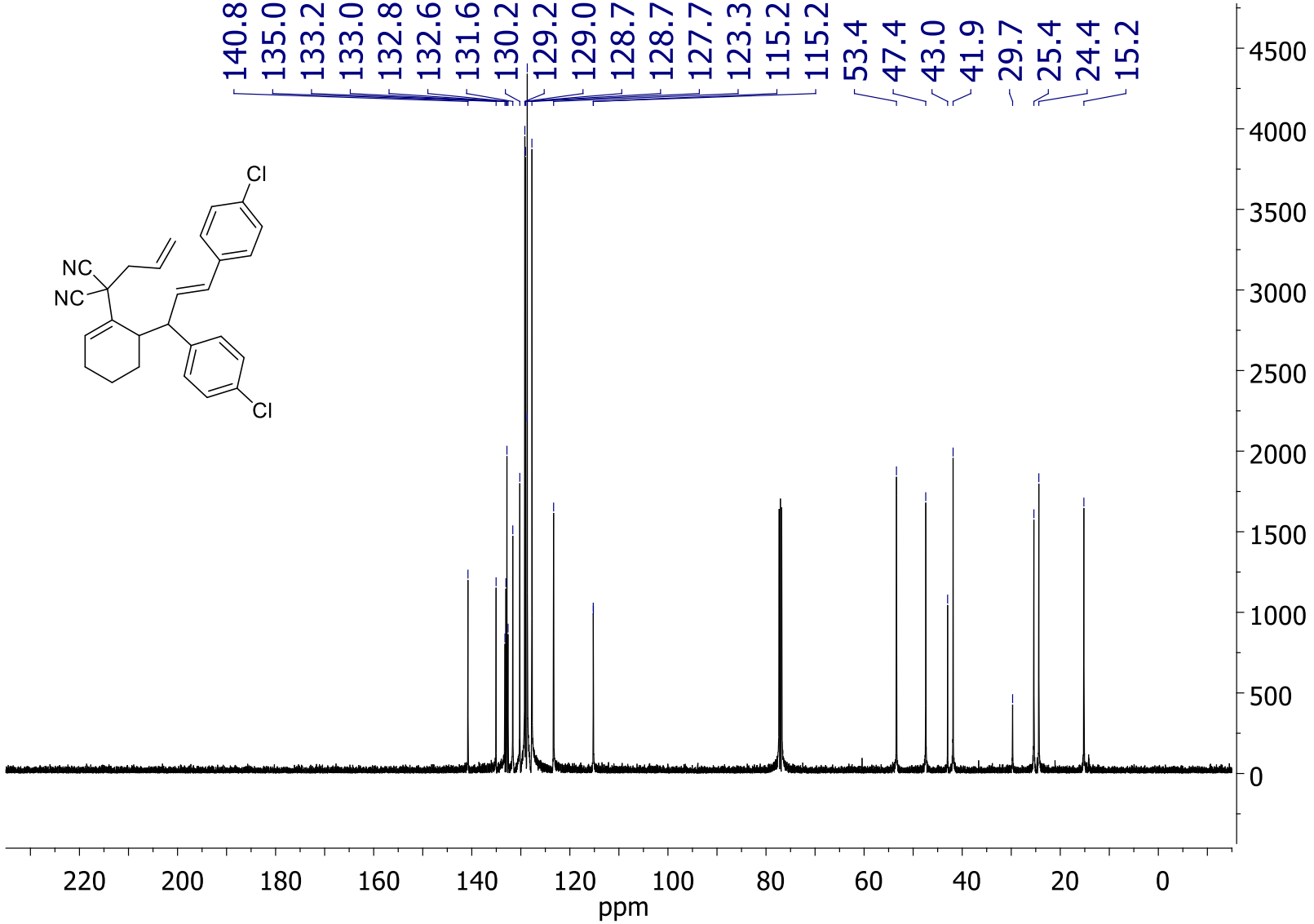
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(3,4-dimethoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5j)



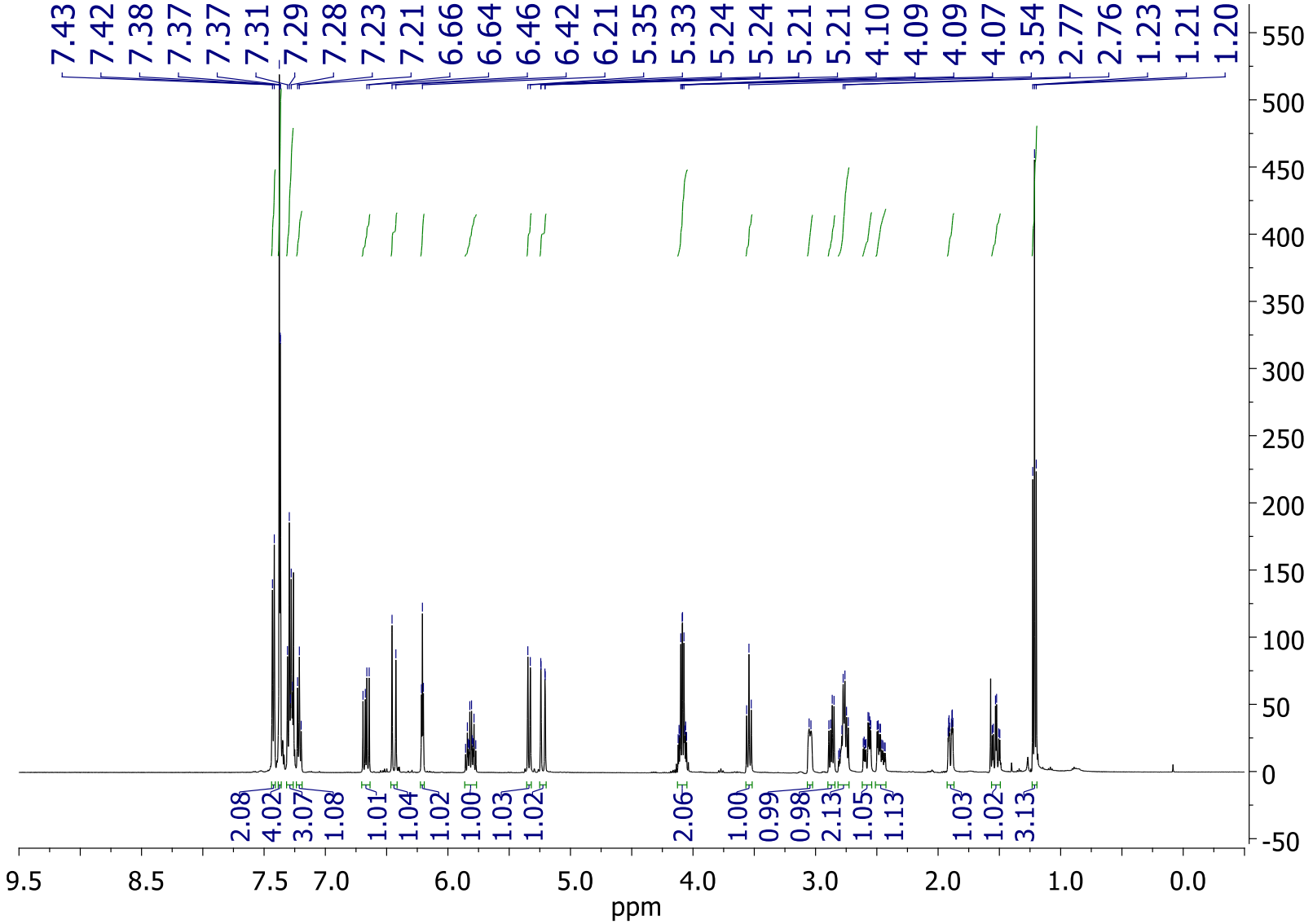
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(4-chlorophenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5k)



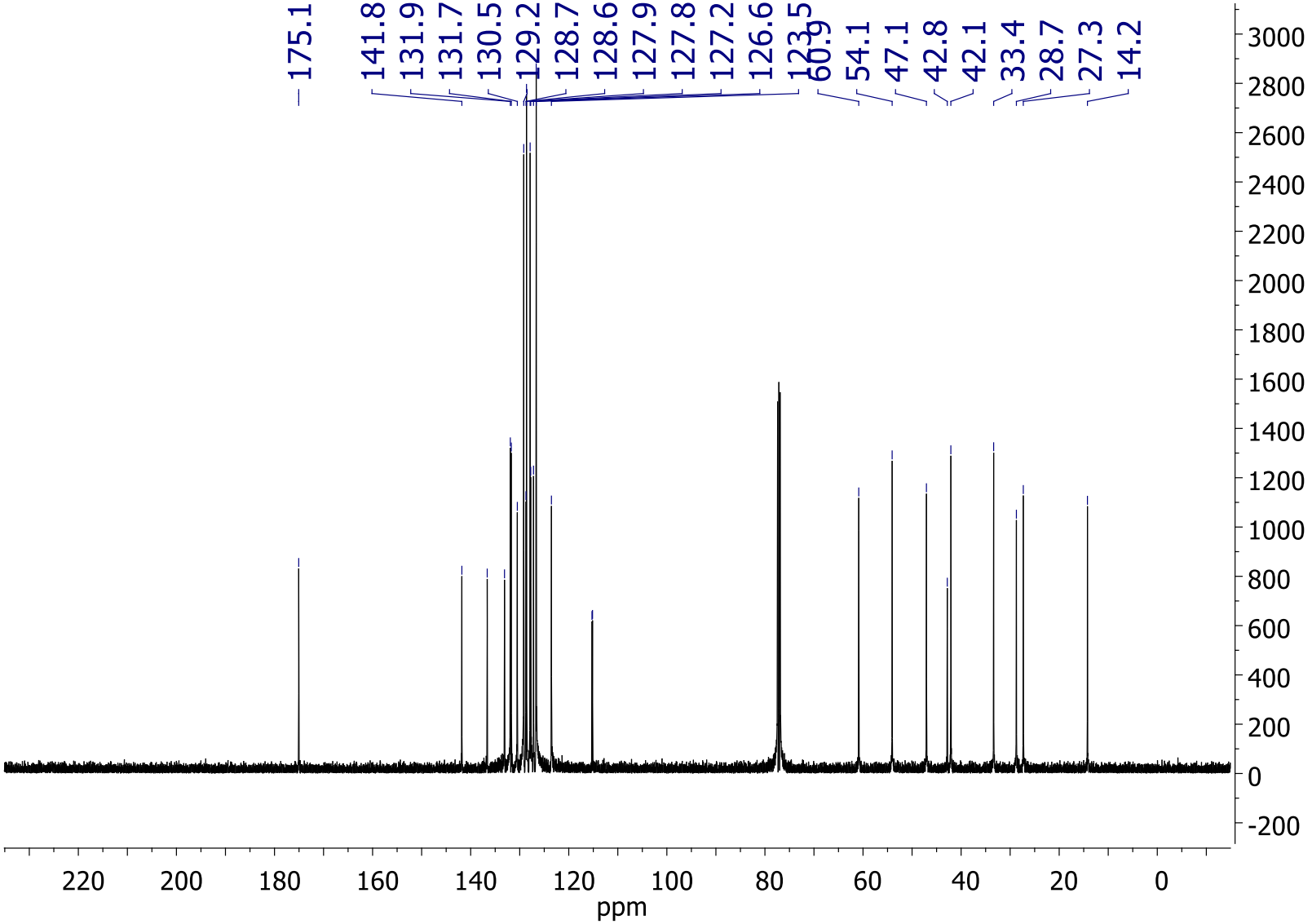
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(4-chlorophenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5k)



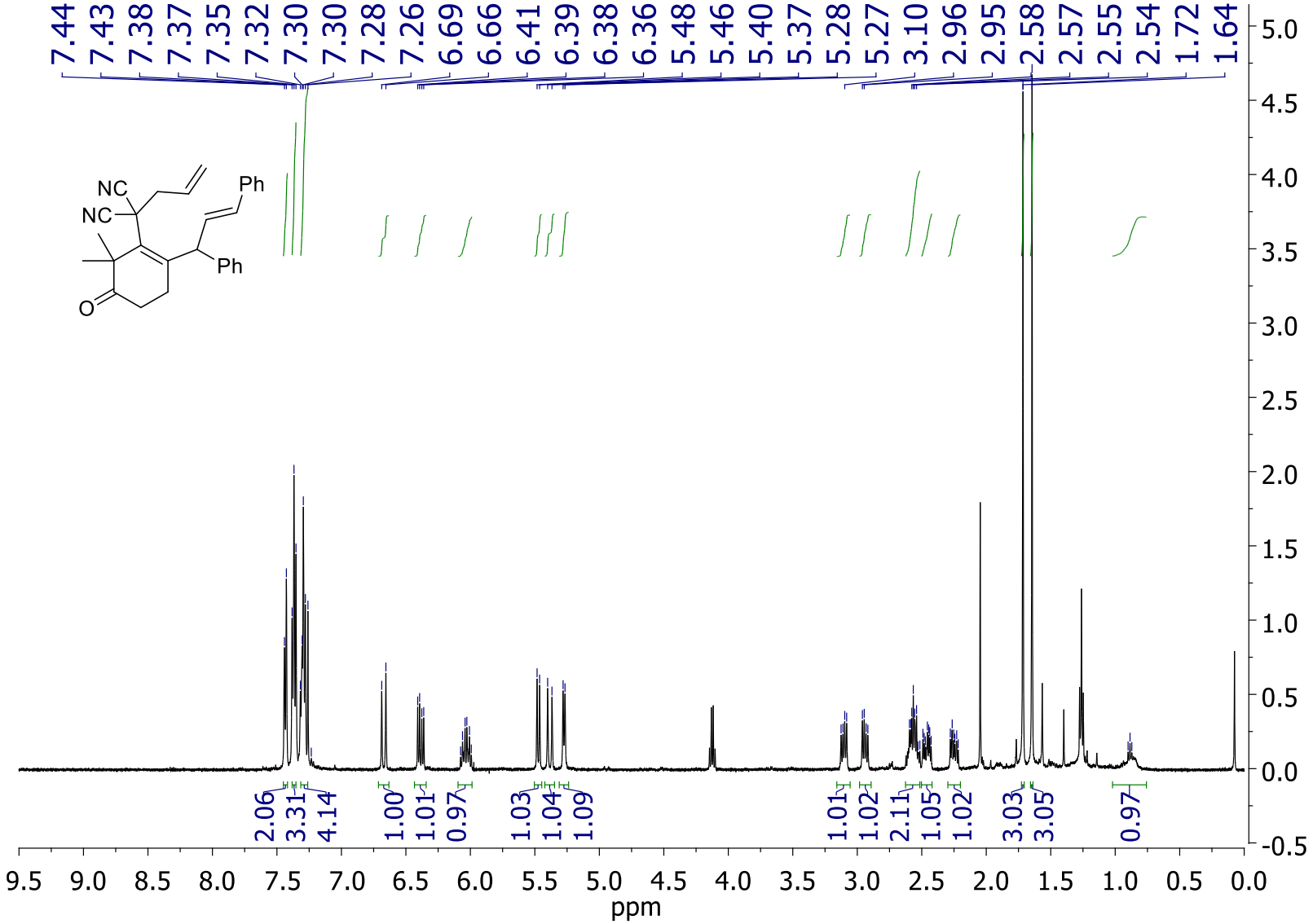
^{1}H NMR spectrum of methyl (1R)-4-(1,1-dicyanobut-3-en-1-yl)-5-((E)-1,3-diphenylallyl)cyclohex-3-ene-1-carboxylate $CDCl_3$ (5l)



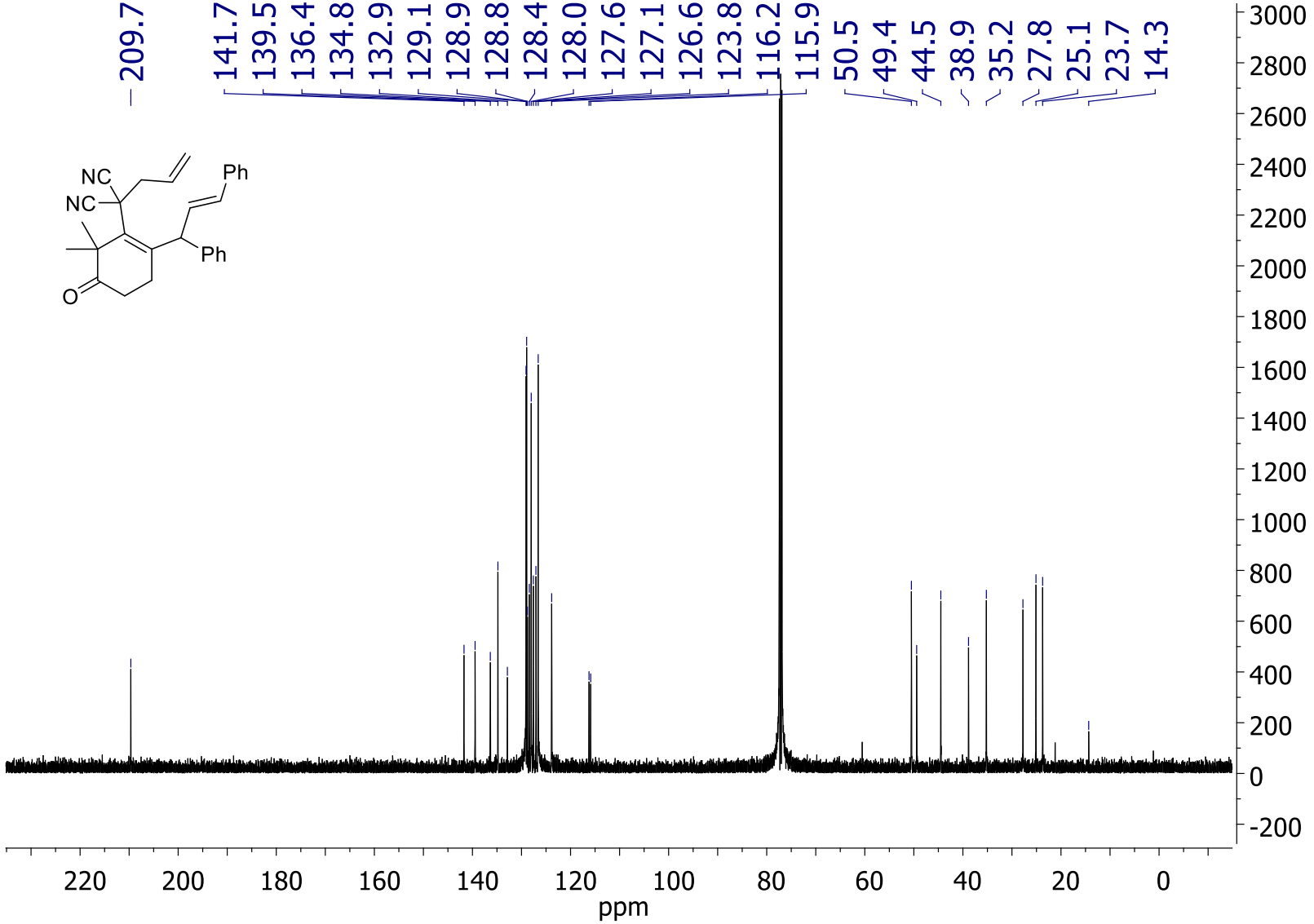
^{13}C NMR spectrum of methyl (1R)-4-(1,1-dicyanobut-3-en-1-yl)-5-((E)-1,3-diphenylallyl)cyclohex-3-ene-1-carboxylate $CDCl_3$ (5l)



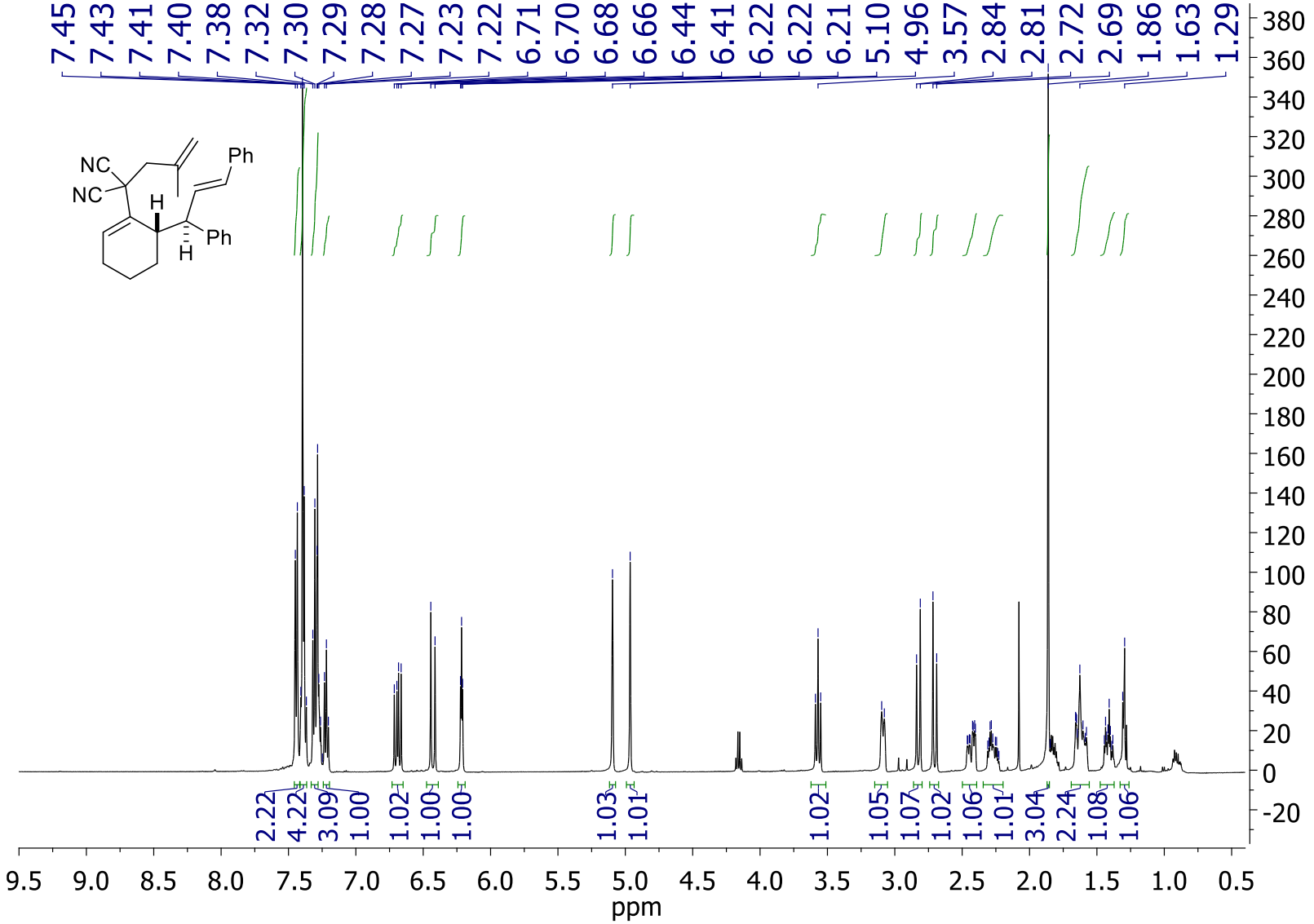
^{1}H NMR spectrum of (E)-2-allyl-2-(2-(1,3-diphenylallyl)-6,6-dimethyl-5-oxocyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5m)



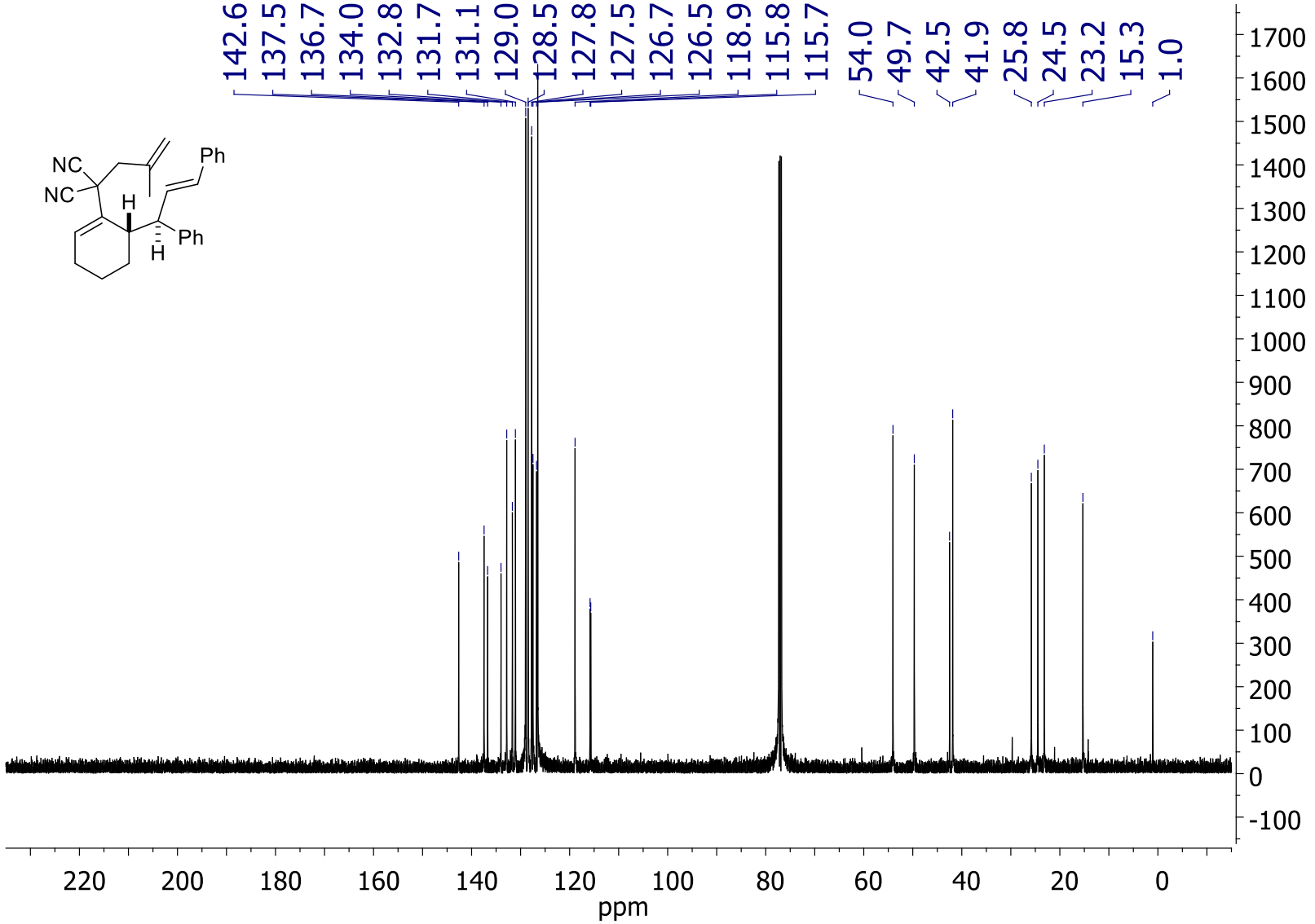
^{13}C NMR spectrum of (E)-2-allyl-2-(2-(1,3-diphenylallyl)-6,6-dimethyl-5-oxocyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5m)



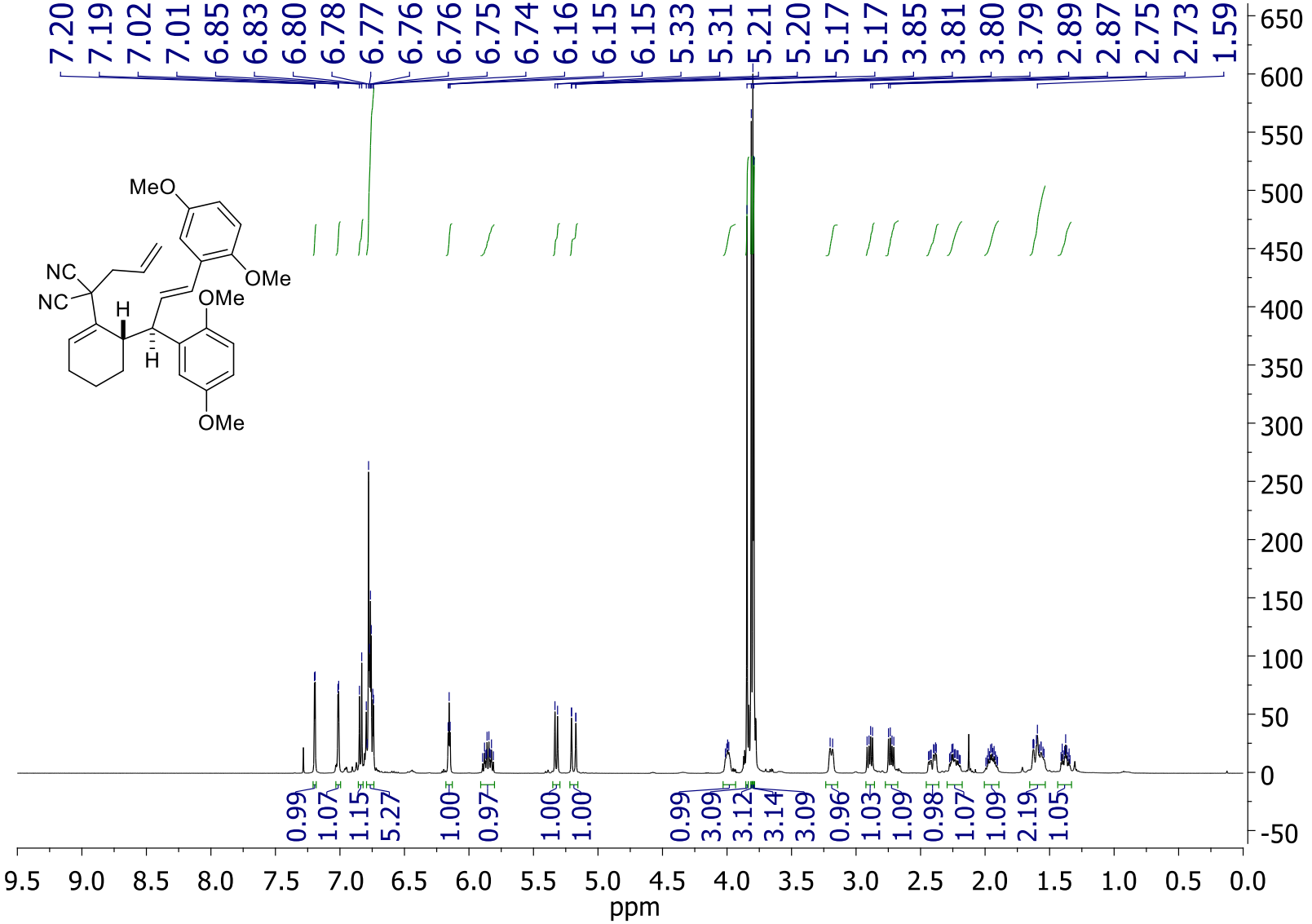
^{1}H NMR spectrum of (E)-2-(6-(1,3-diphenylallyl)cyclohex-1-en-1-yl)-2-(2-methylallyl)malononitrile $CDCl_3$ (5n)



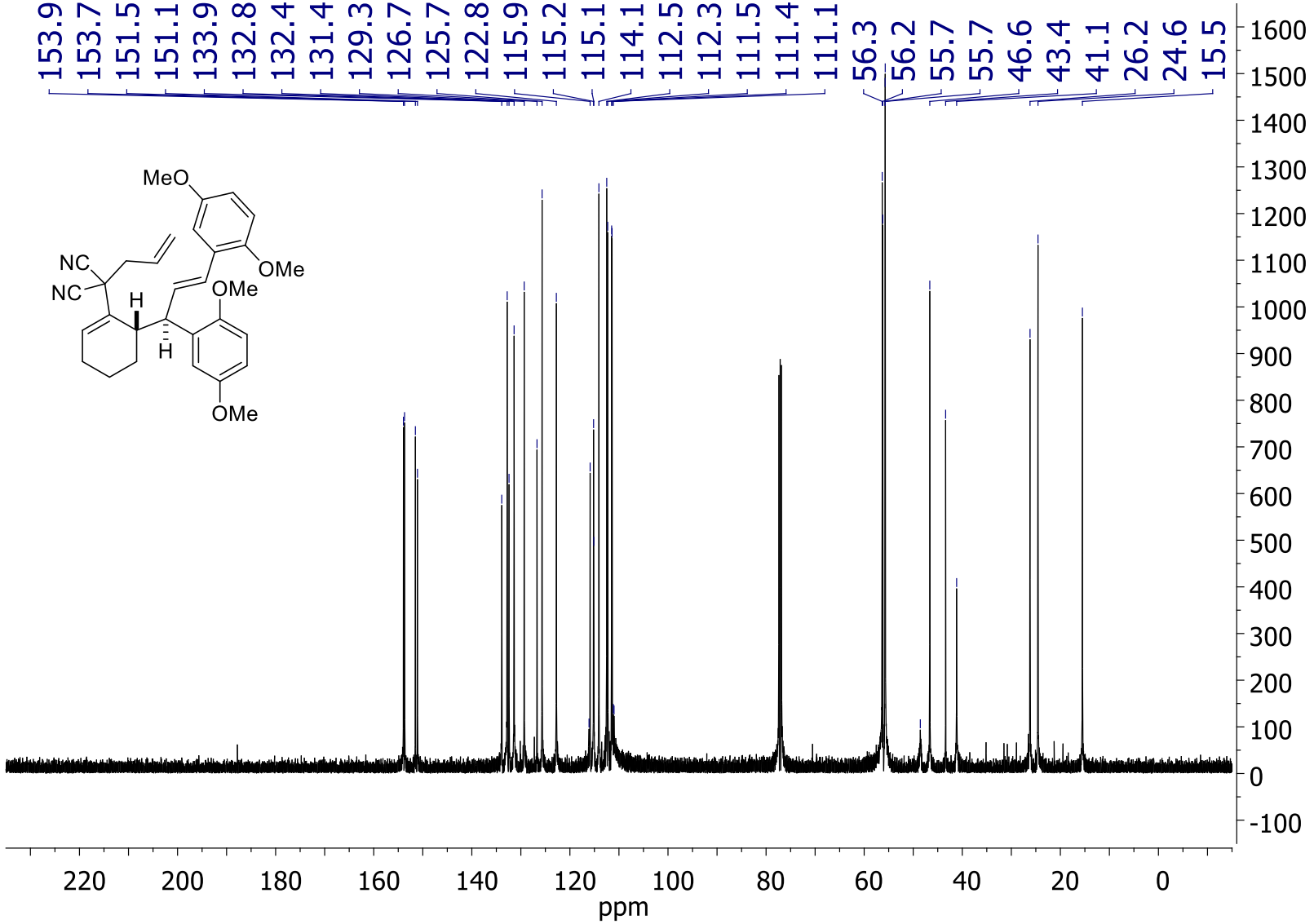
^{13}C NMR spectrum of (E)-2-(6-(1,3-diphenylallyl)cyclohex-1-en-1-yl)-2-(2-methylallyl)malononitrile $CDCl_3$ (5n)



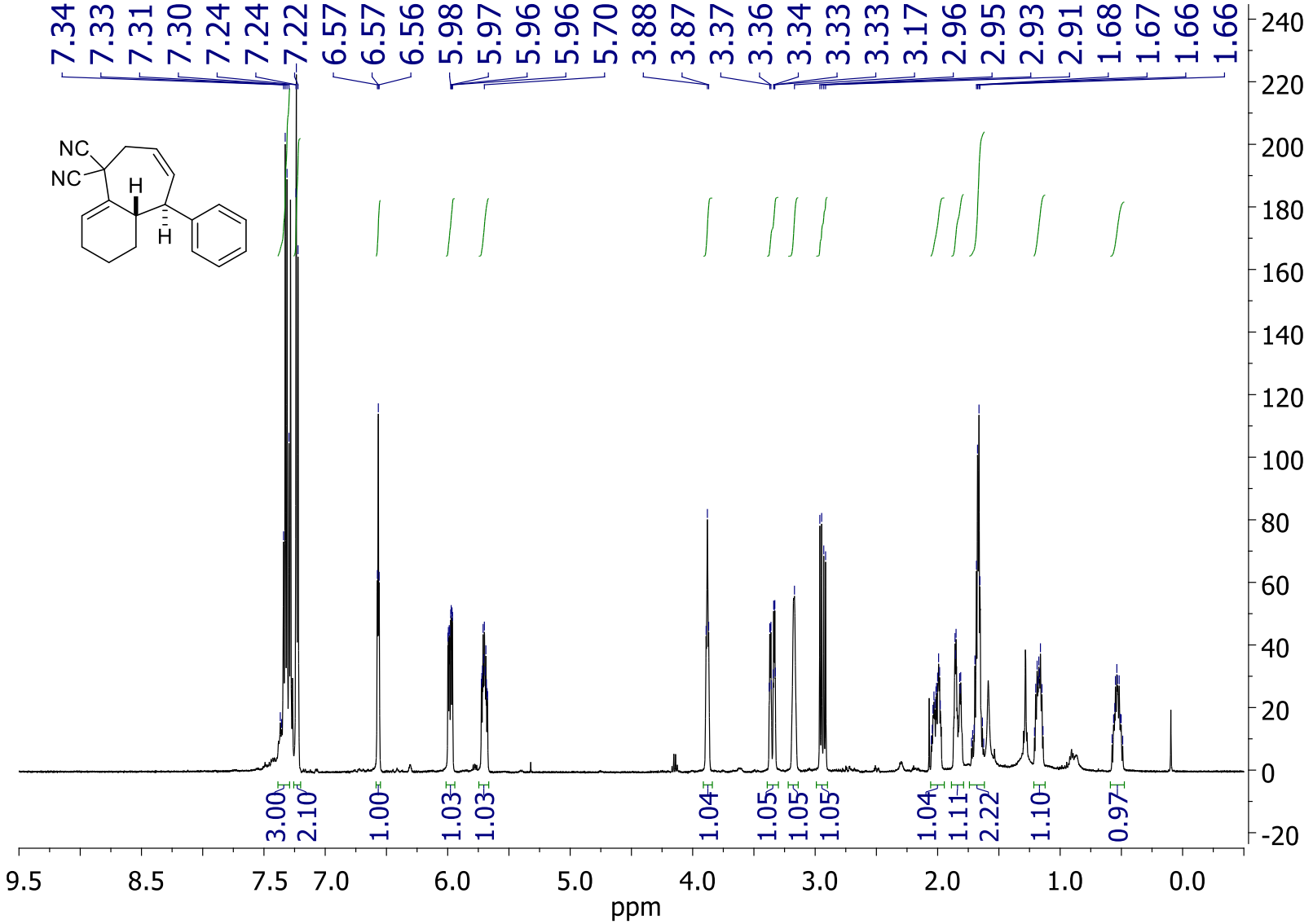
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(2,5-dimethoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5o)



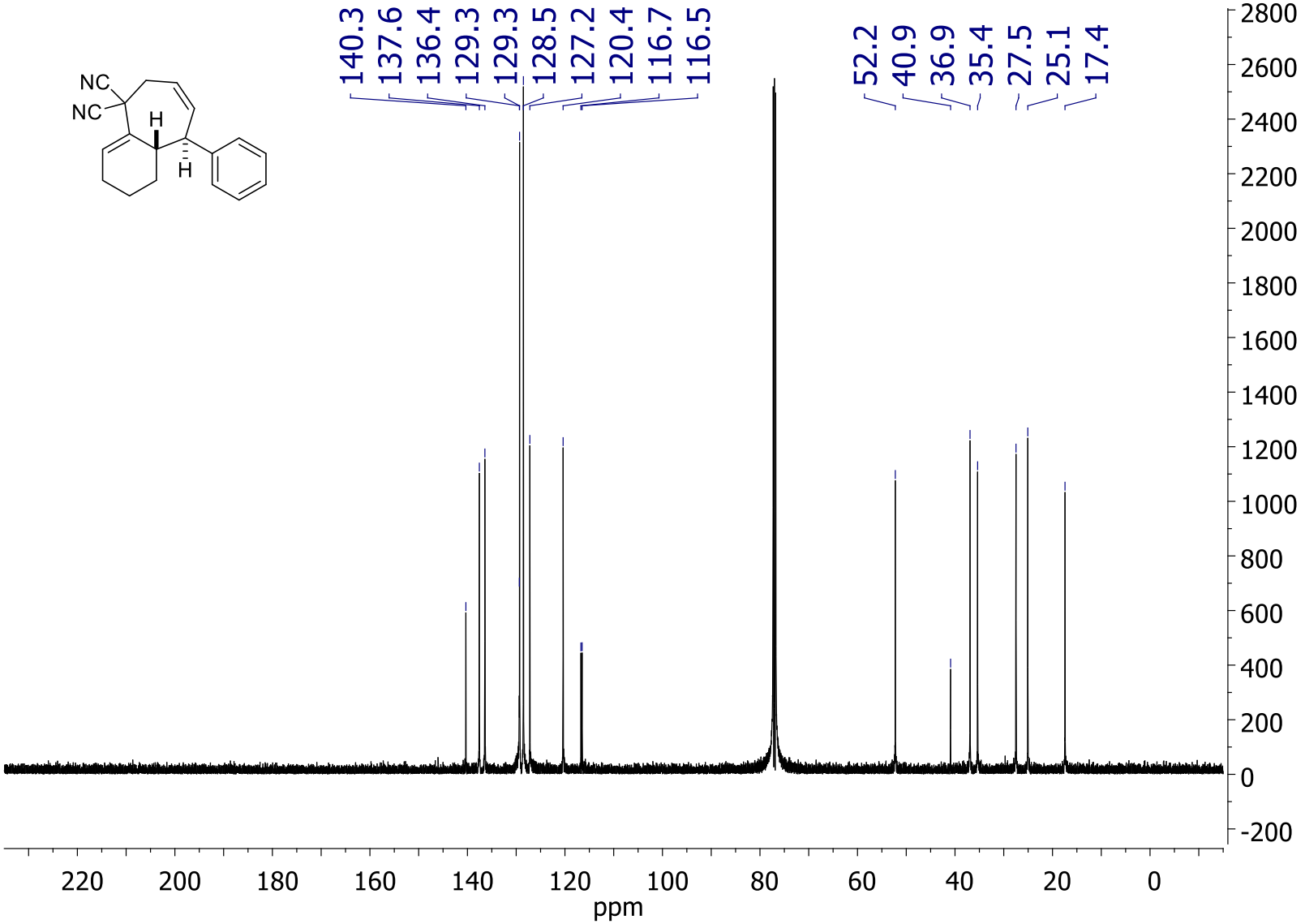
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1,3-bis(2,5-dimethoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (5o)



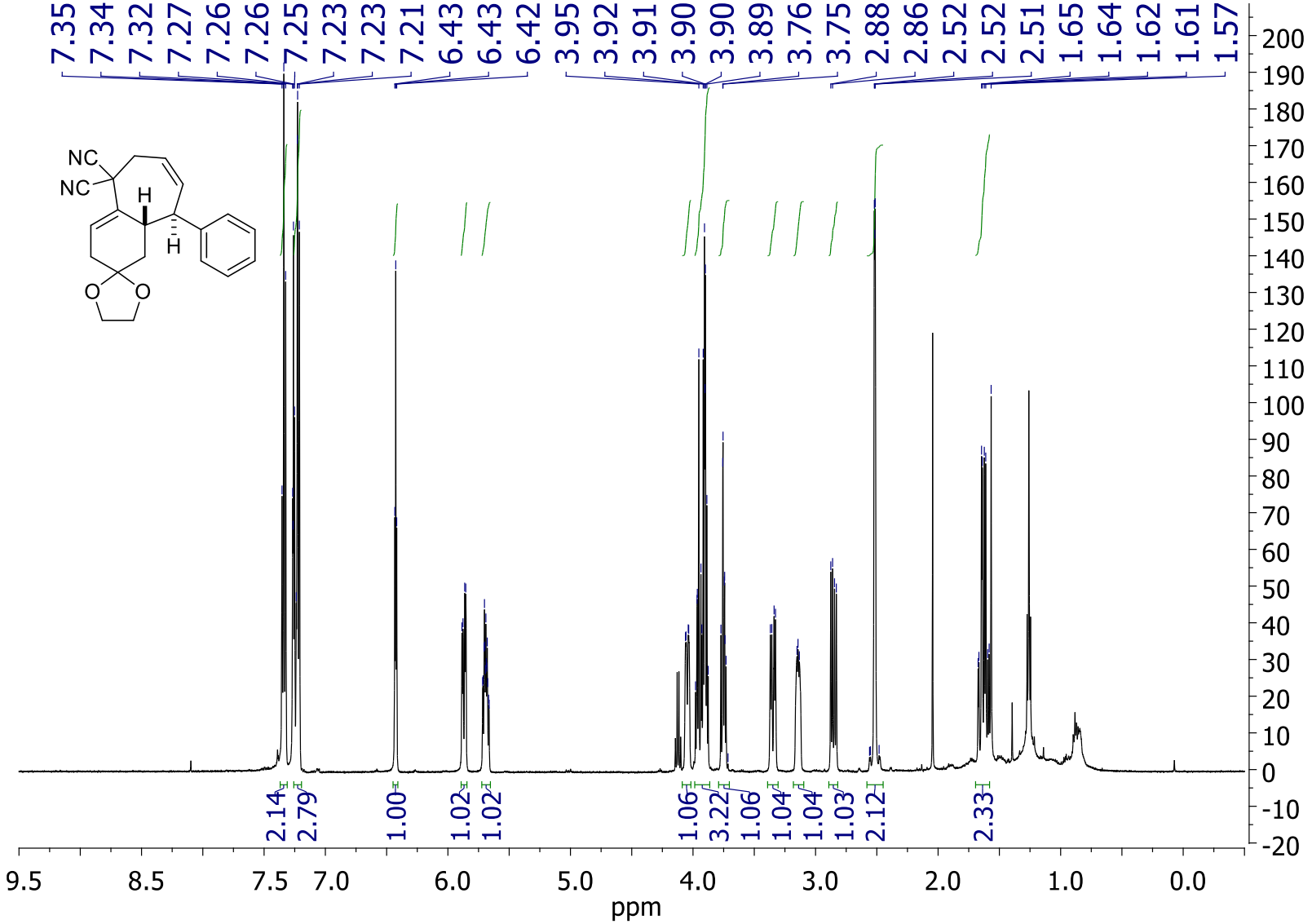
^{1}H NMR spectrum of 9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6a)



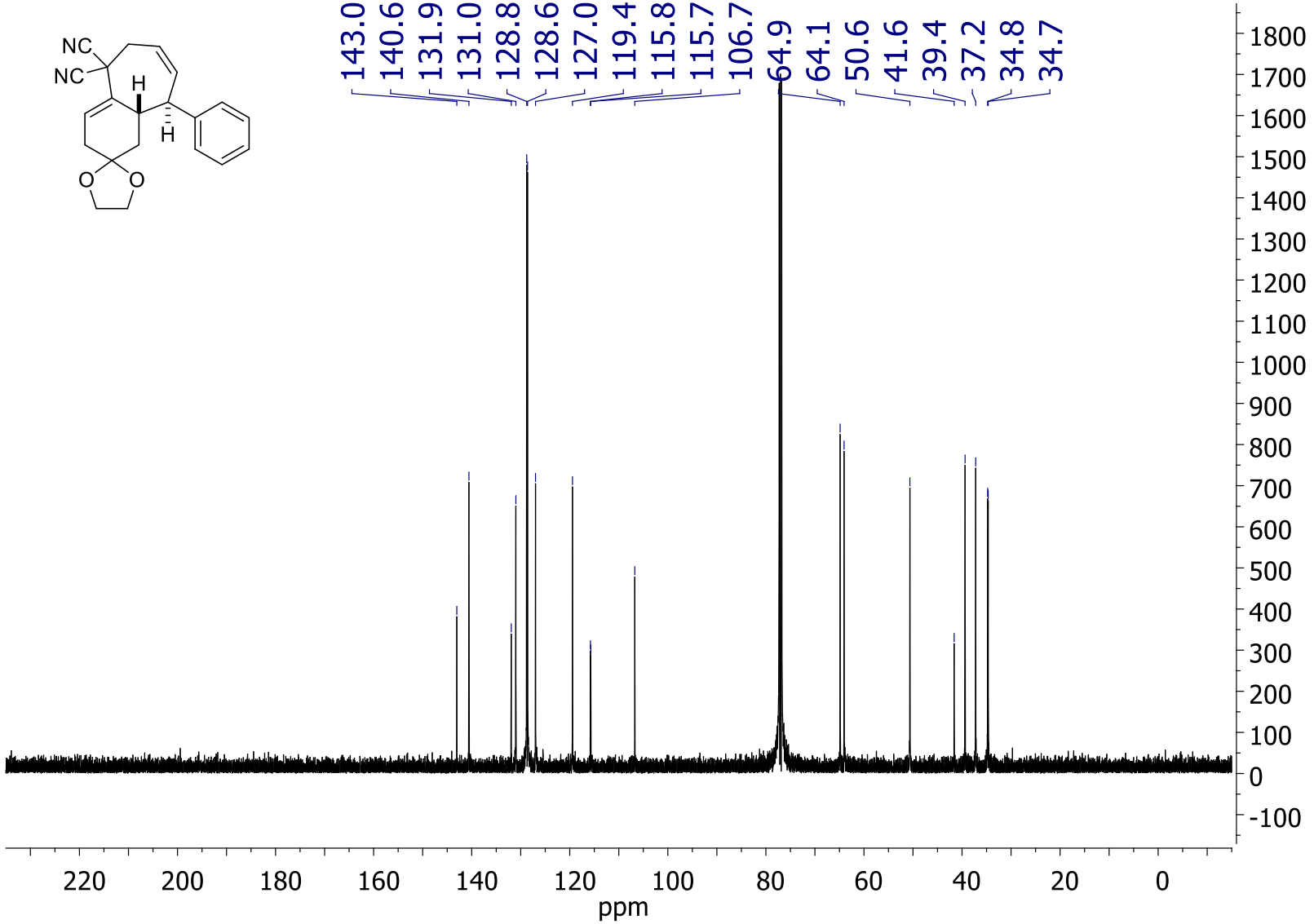
^{13}C NMR spectrum of 9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6a)



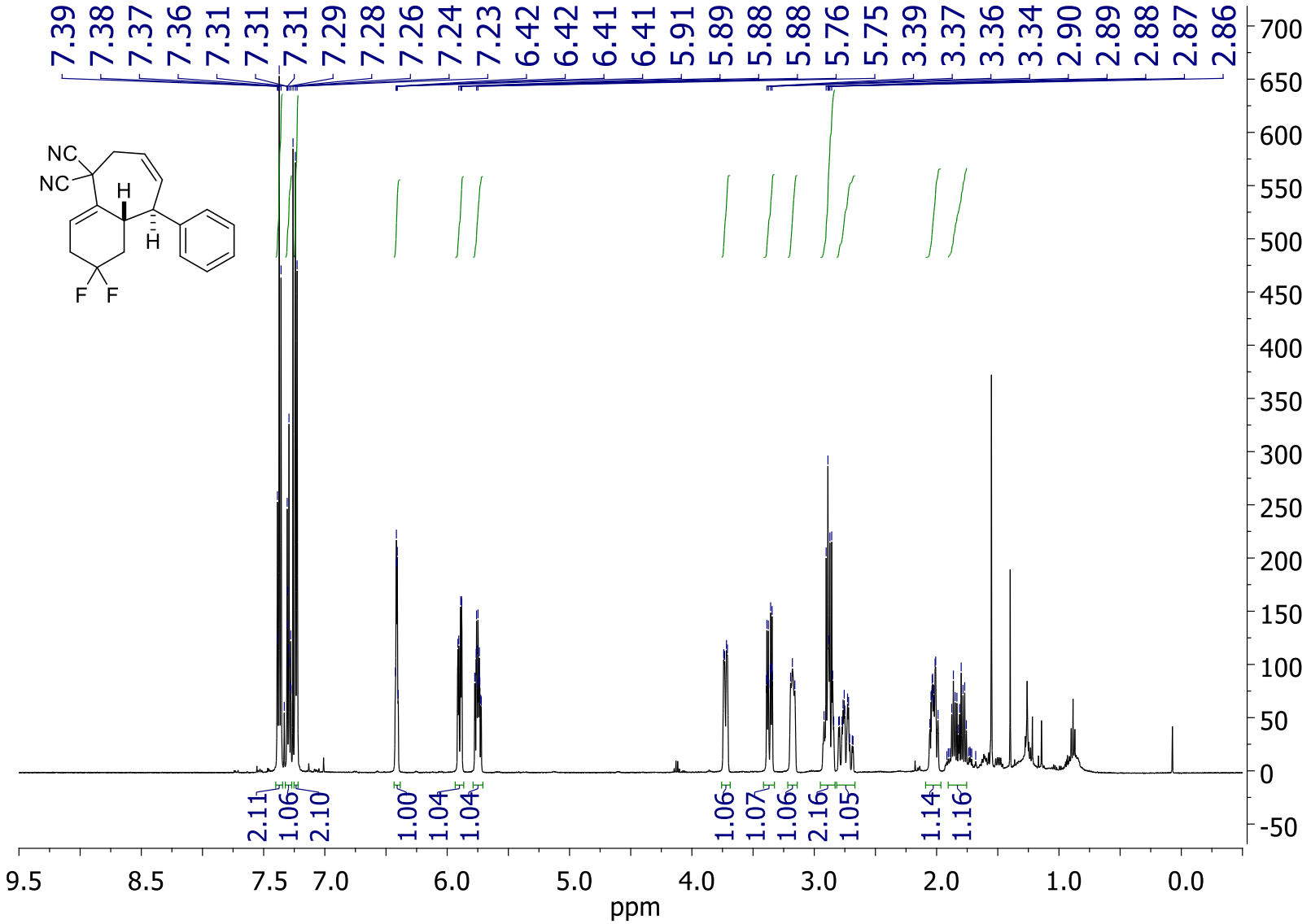
^{1}H NMR spectrum of 9-phenyl-3,6,9,9a-tetrahydrospiro[benzo[7]annulene-2,2'-[1,3]dioxolane]-5,5(1H)-dicarbonitrile $CDCl_3$ (6b)



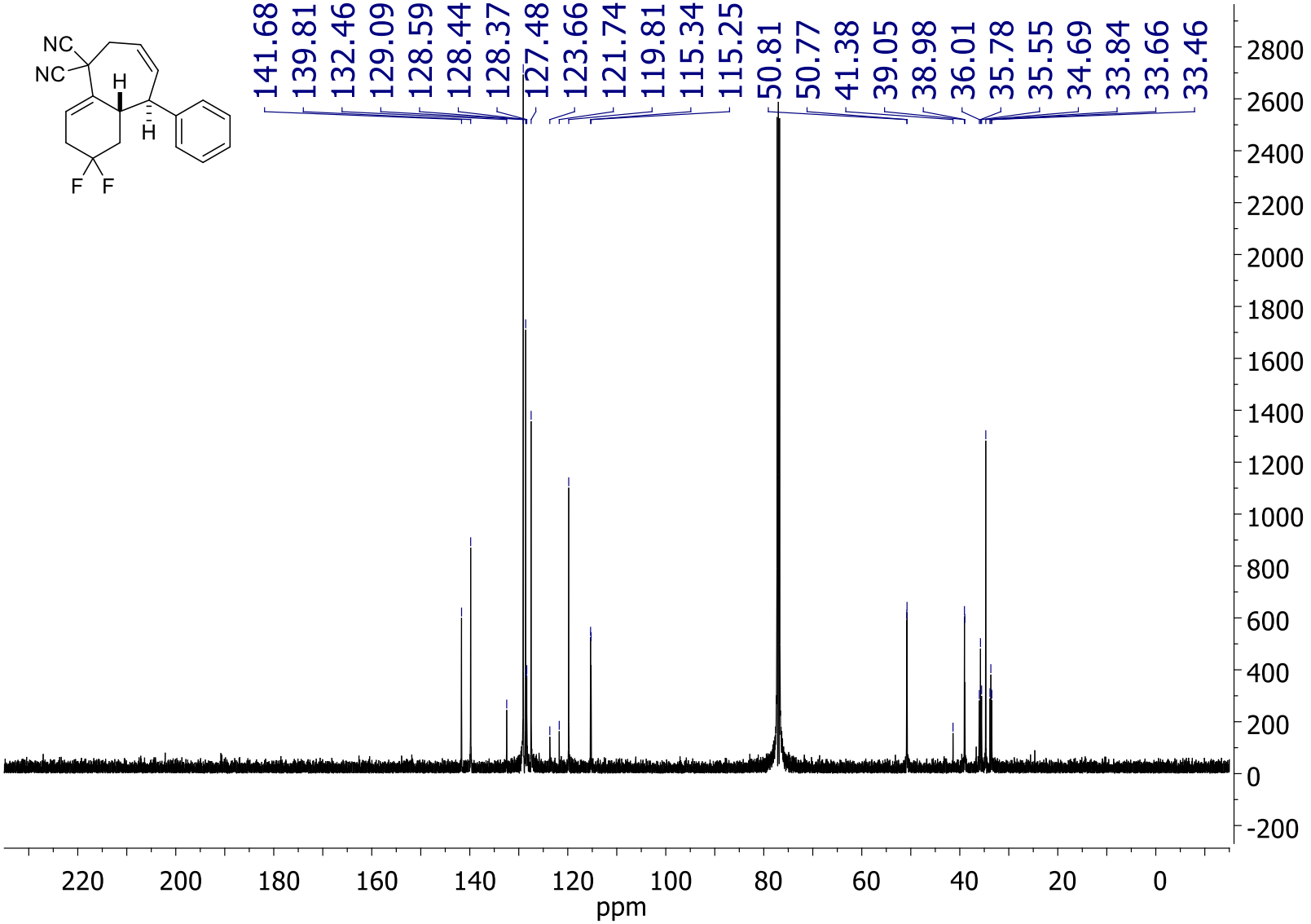
^{13}C NMR spectrum of 9-phenyl-3,6,9,9a-tetrahydrospiro[benzo[7]annulene-2,2'-[1,3]dioxolane]-5,5(1H)-dicarbonitrile $CDCl_3$ (6b)



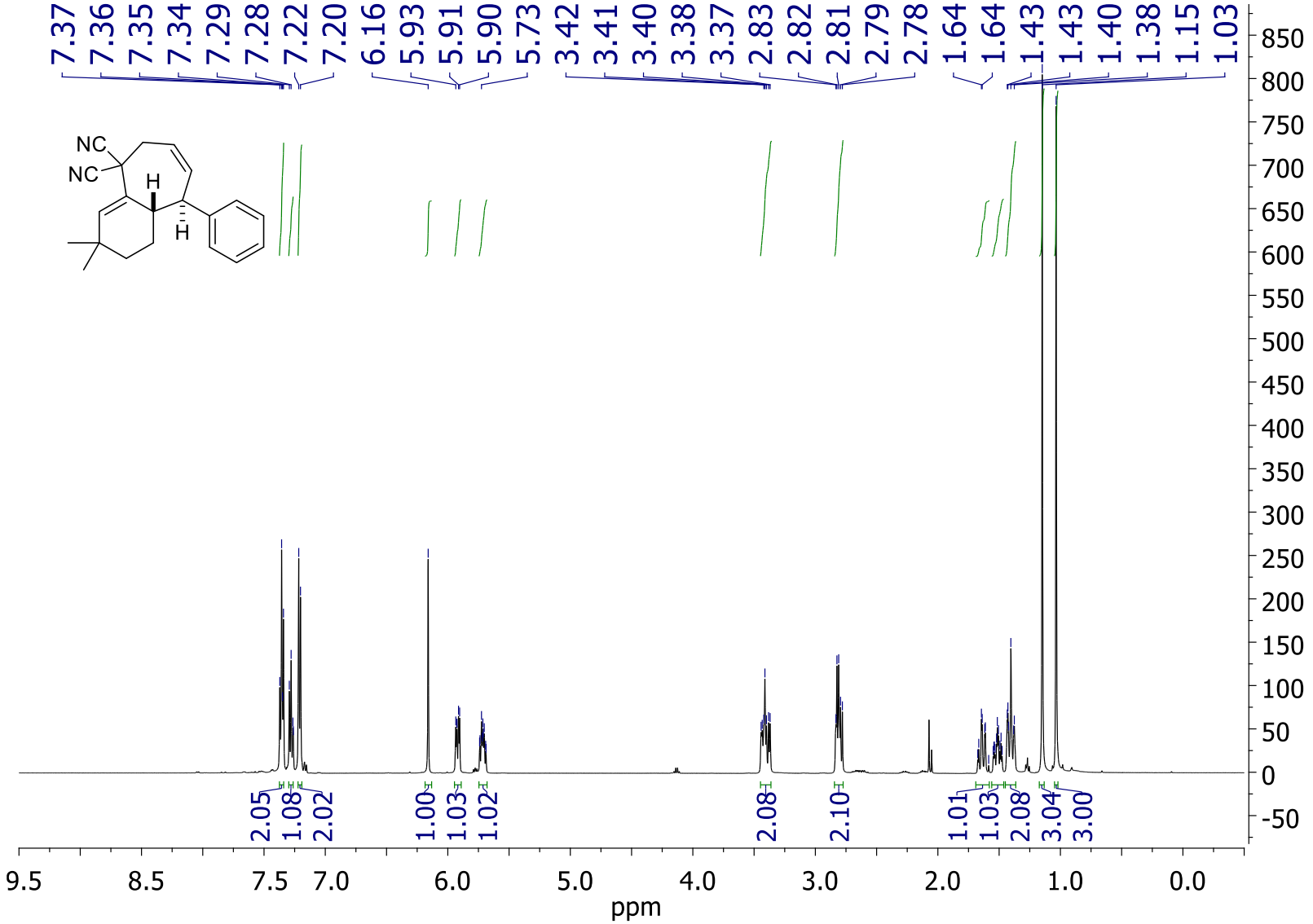
^{1}H NMR spectrum of 2,2-difluoro-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6c)



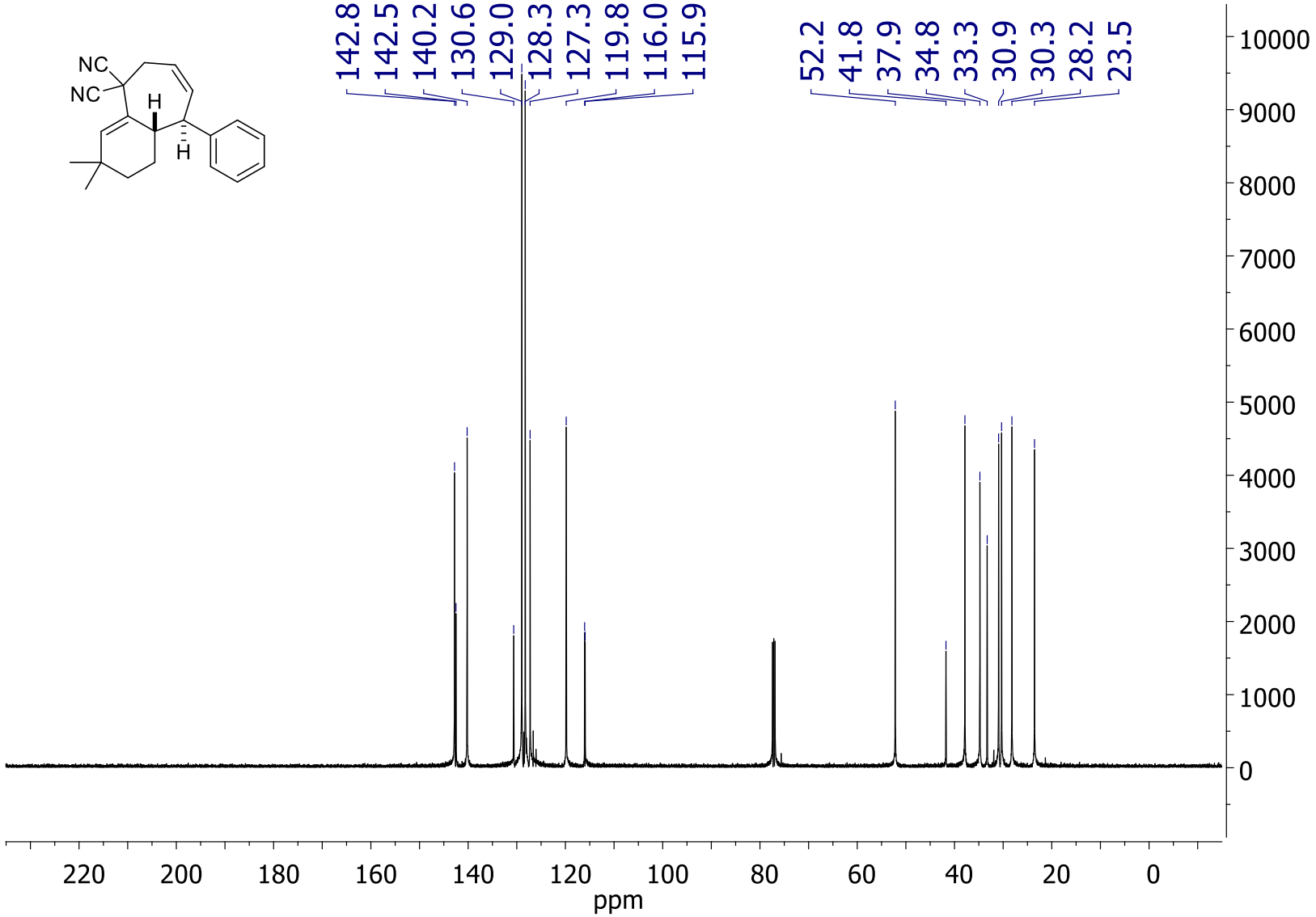
^{13}C NMR spectrum of 2,2-difluoro-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6c)



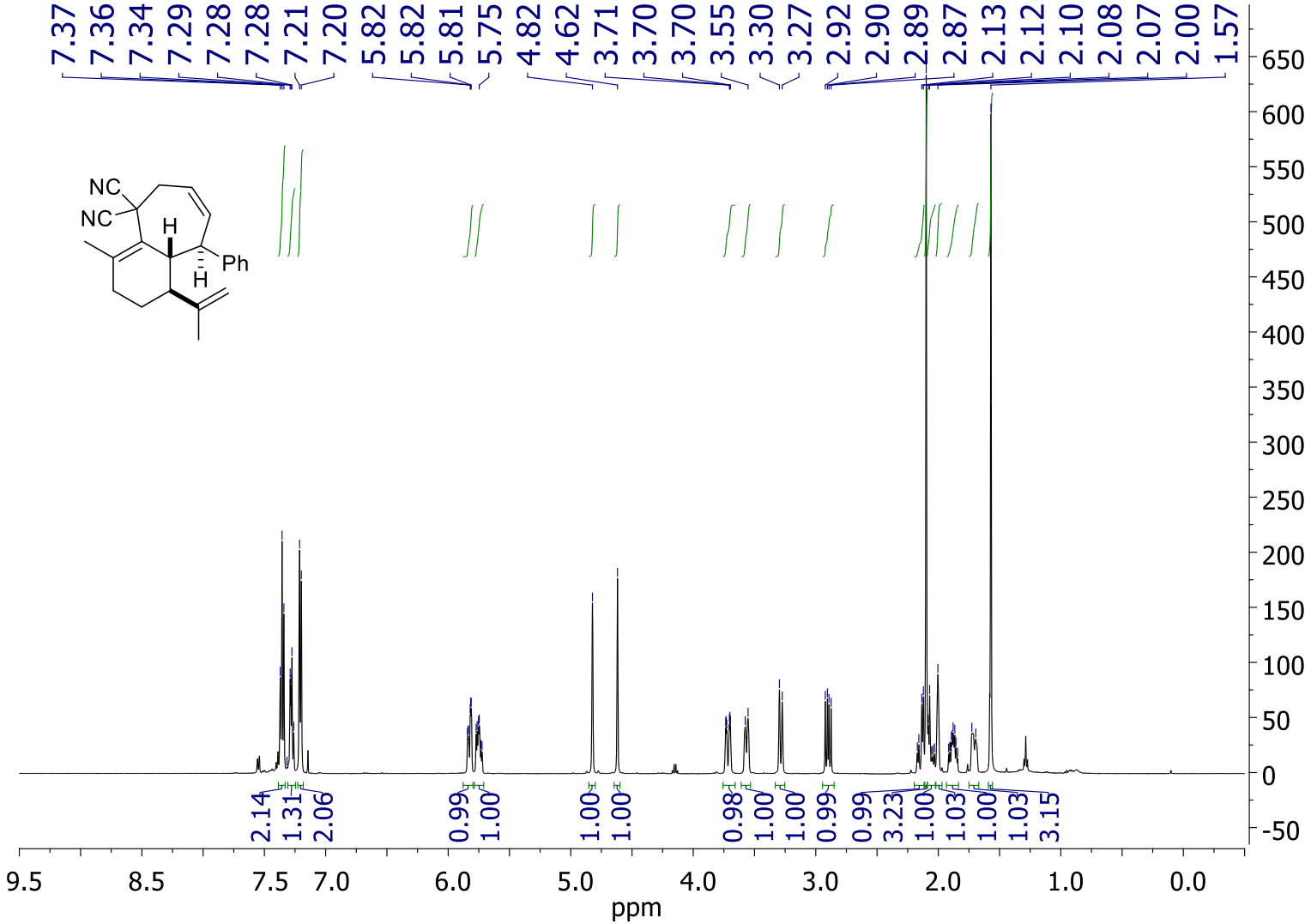
^{1}H NMR spectrum of 3,3-dimethyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6d)



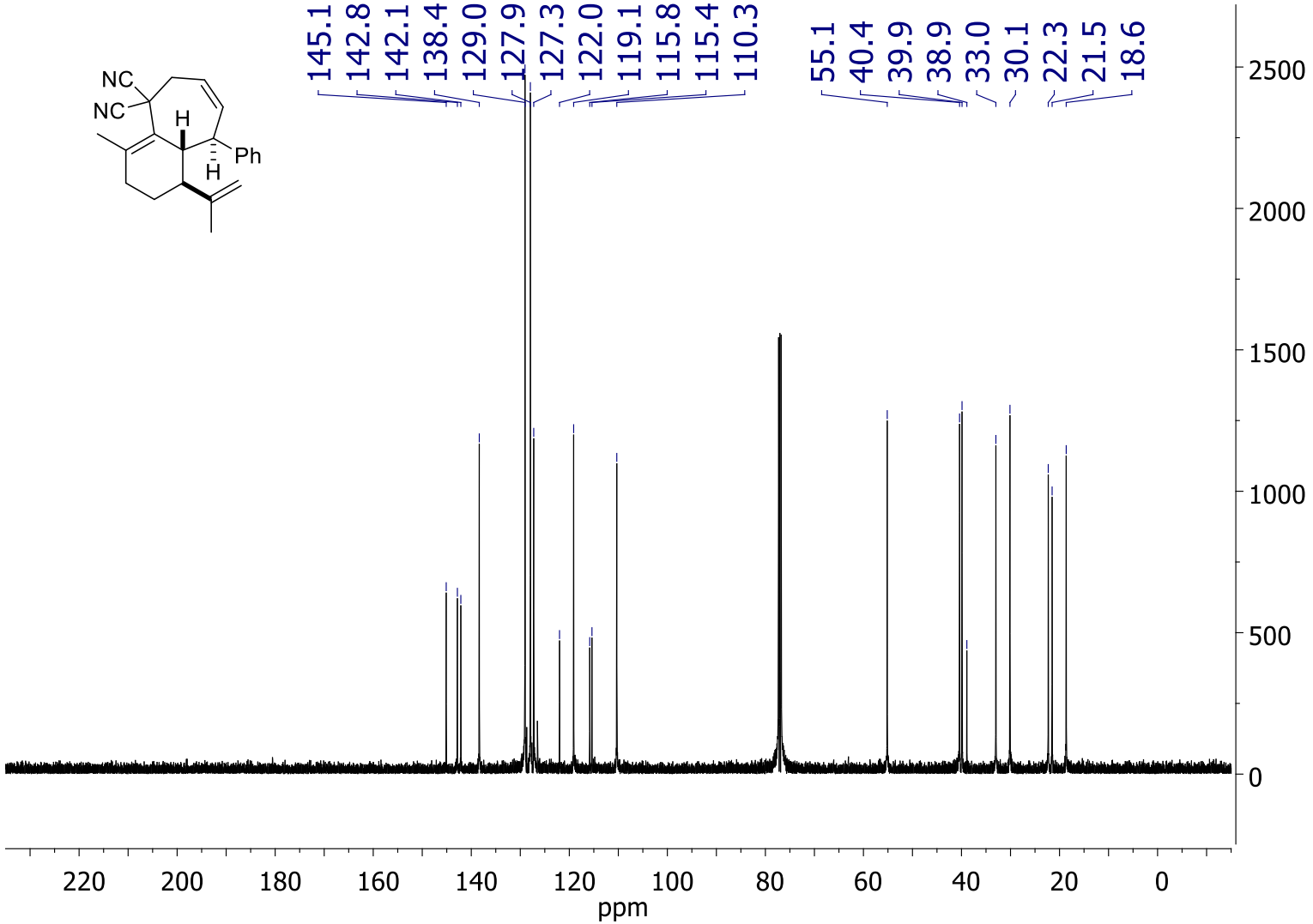
^{13}C NMR spectrum of 3,3-dimethyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6d)



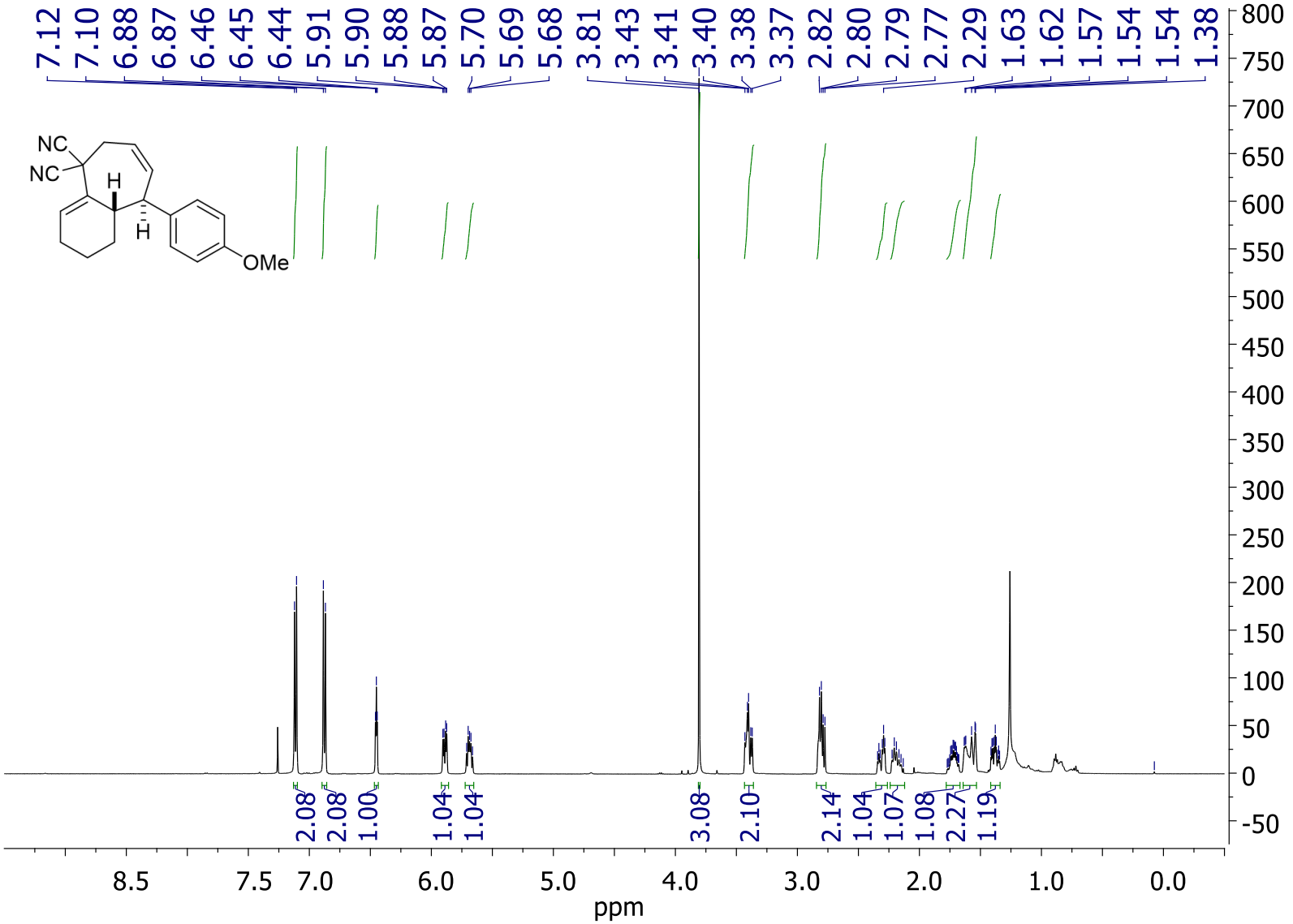
^{1}H NMR spectrum of 4-methyl-9-phenyl-1-(prop-1-en-2-yl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6f)



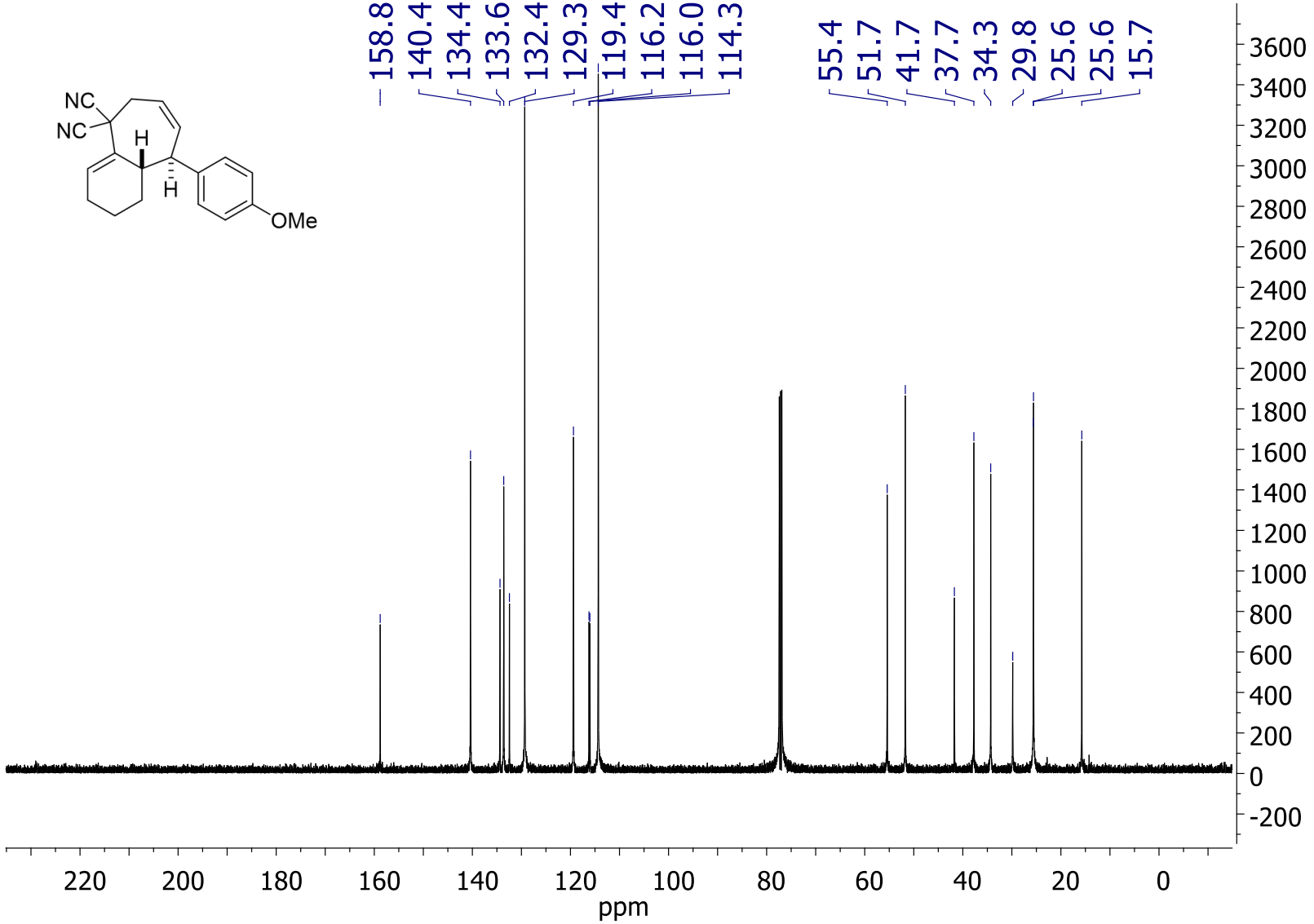
^{13}C NMR spectrum of 4-methyl-9-phenyl-1-(prop-1-en-2-yl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6f)



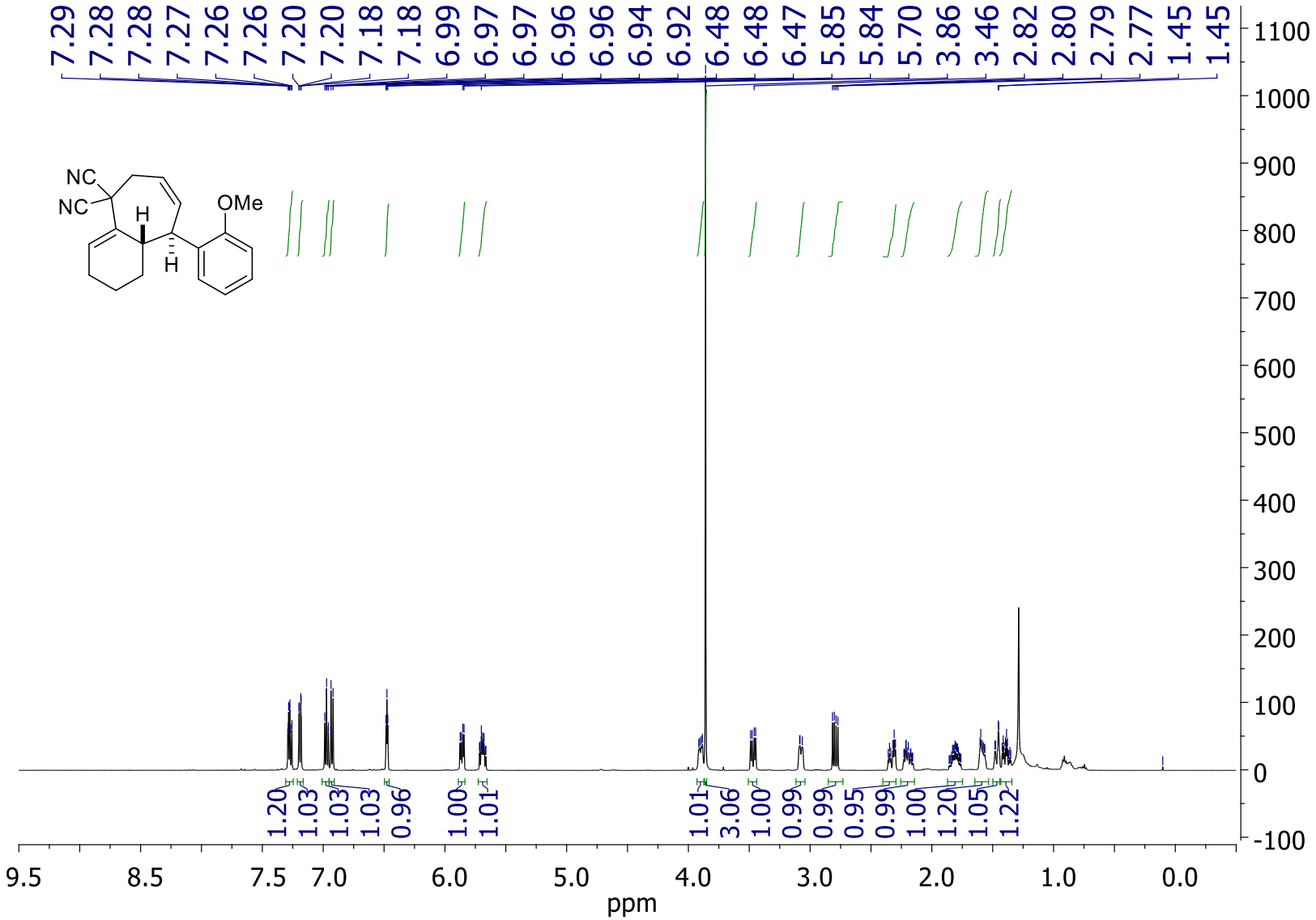
^{1}H NMR spectrum of 9-(4-methoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6g)



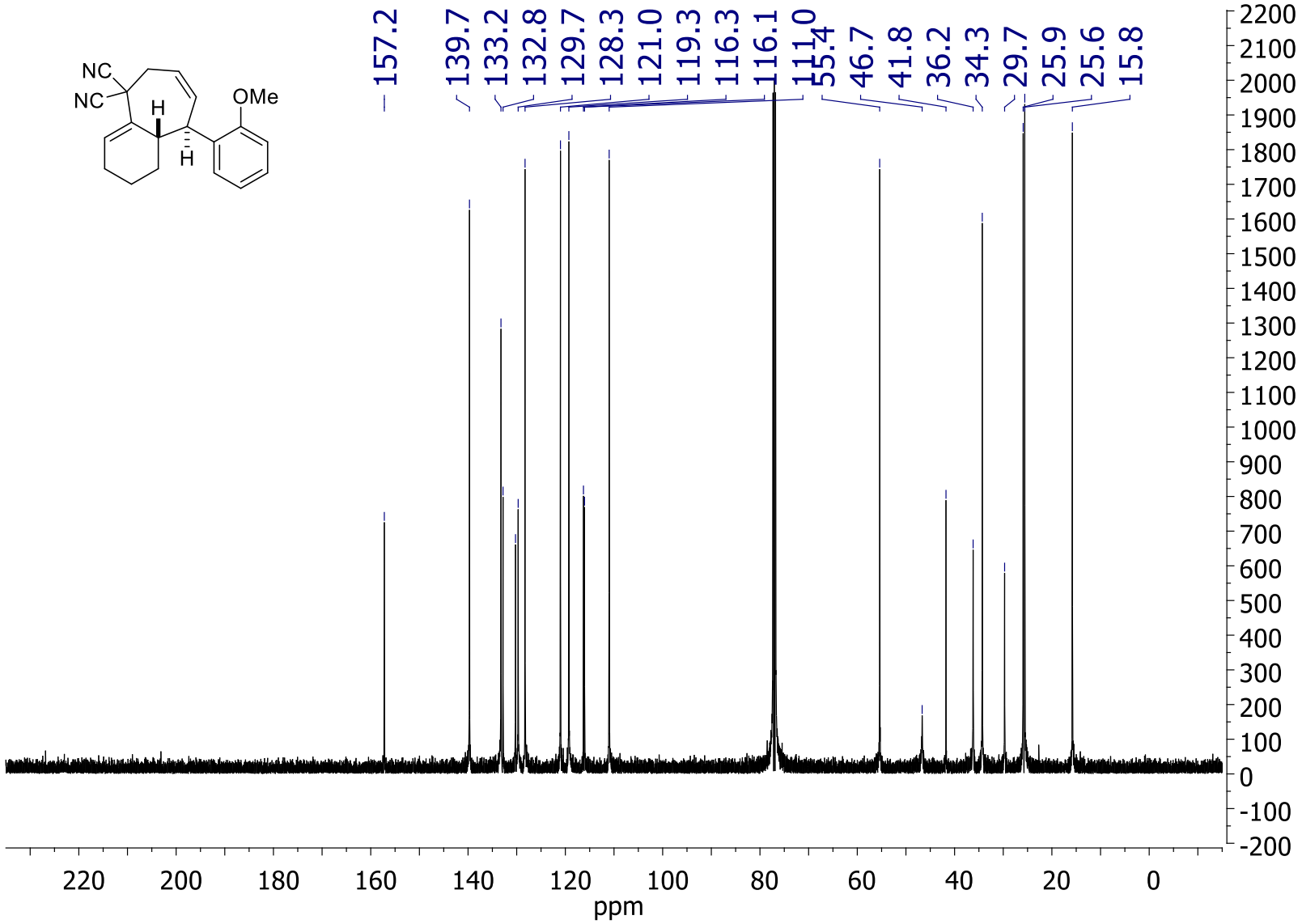
^{13}C NMR spectrum of 9-(4-methoxyphenyl)-1,2,3,6,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6g)



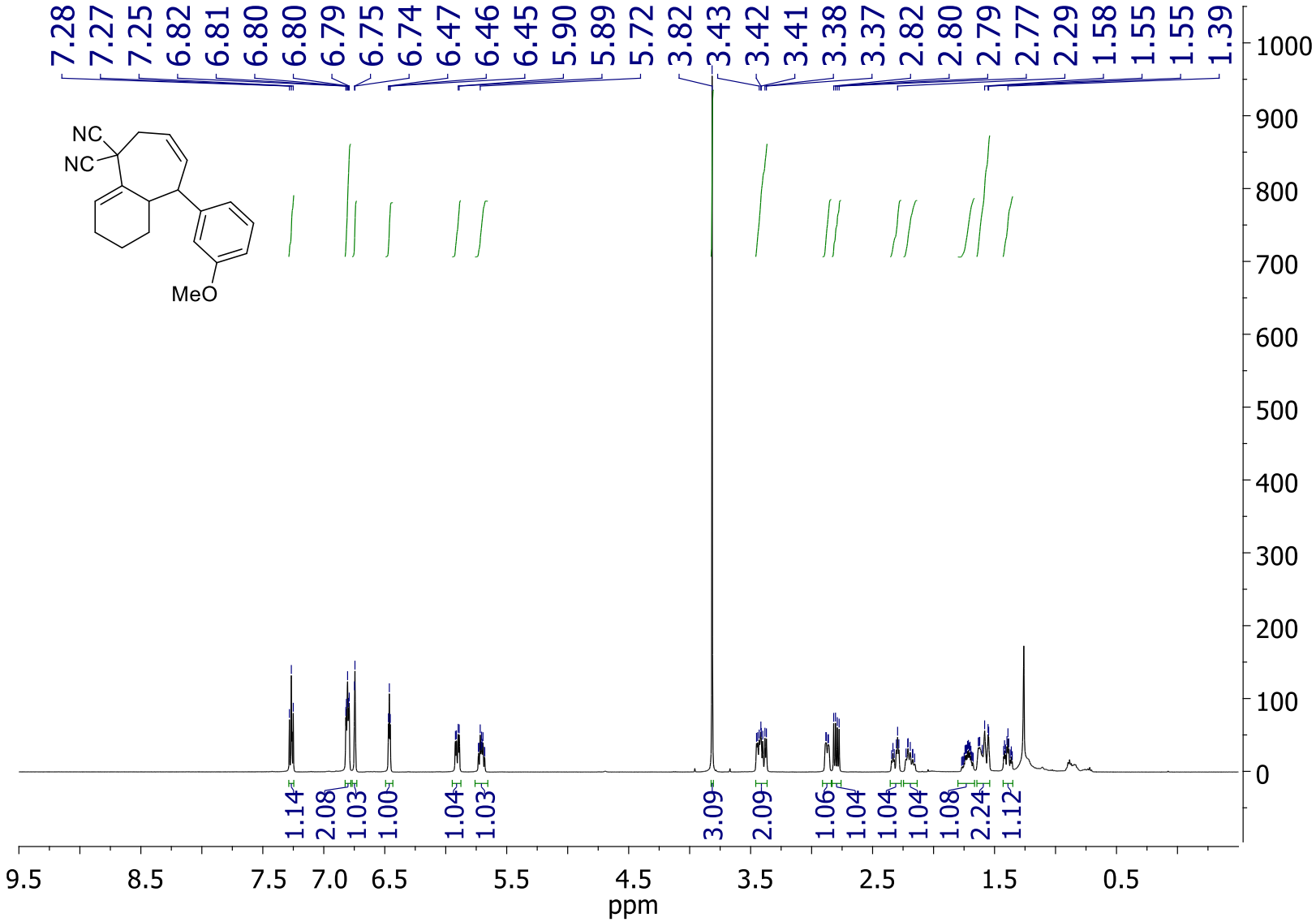
^{1}H NMR spectrum of 9-(2-methoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6h)



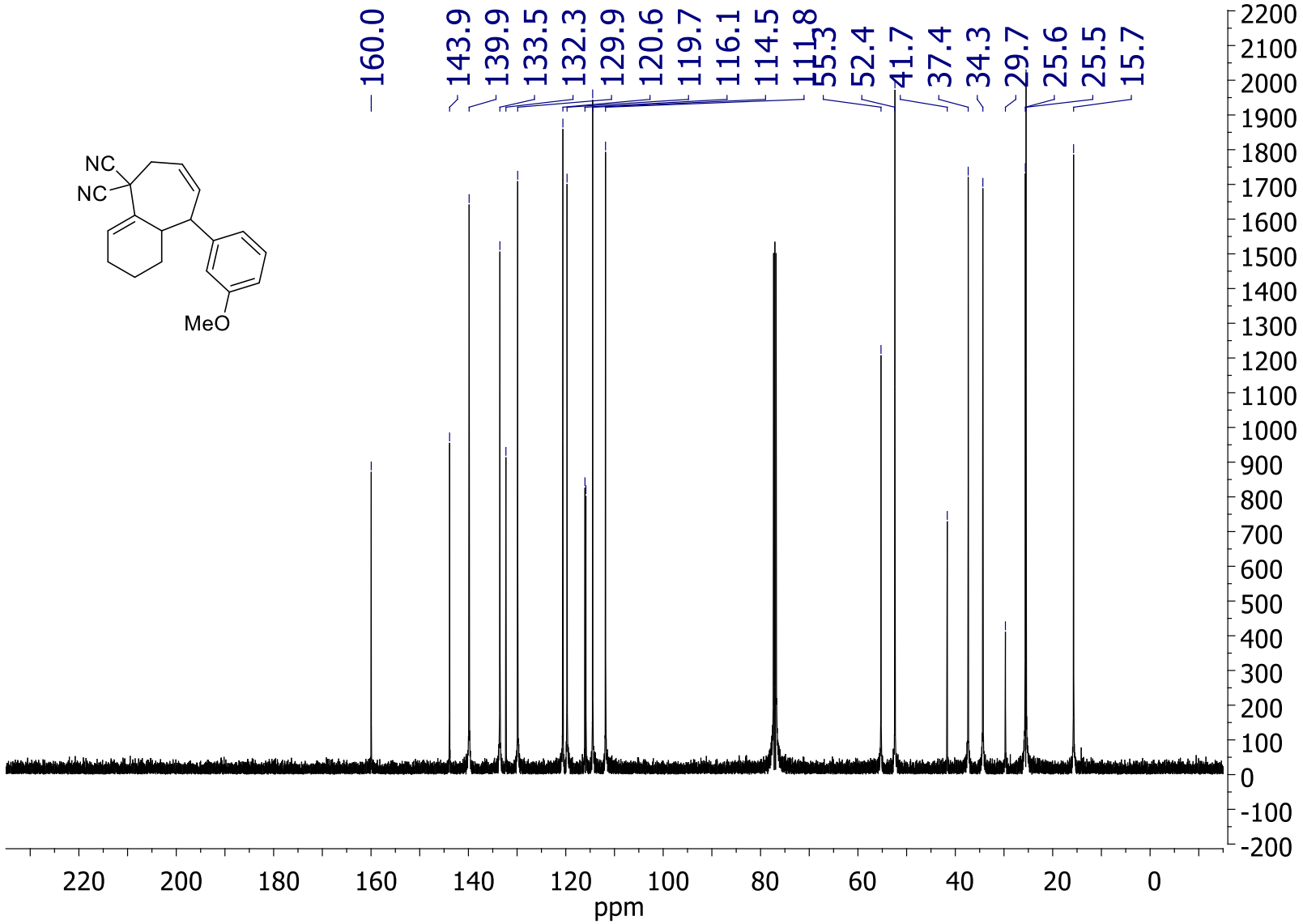
^{13}C NMR spectrum of 9-(2-methoxyphenyl)-1,2,3,6,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6h)



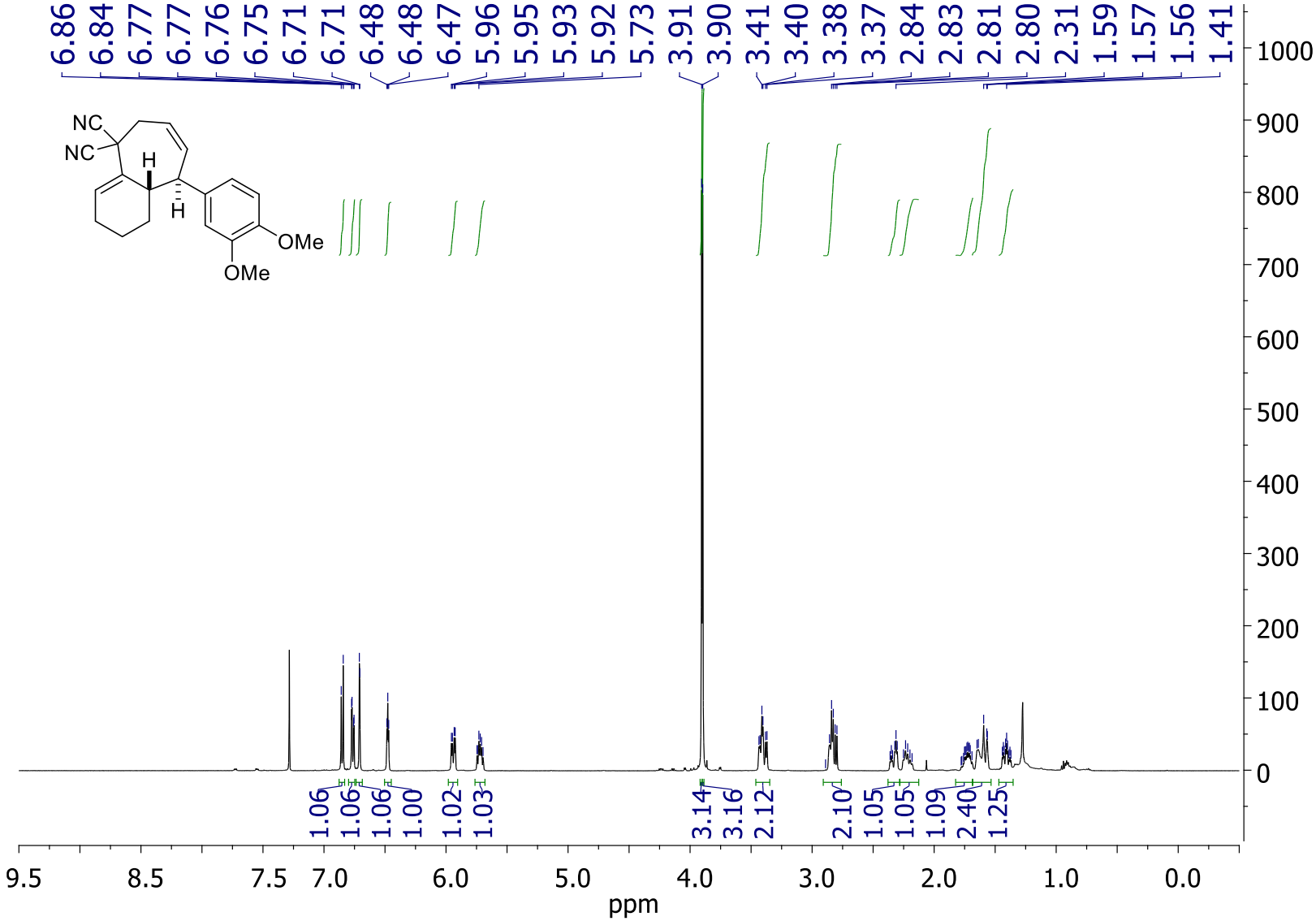
^{1}H NMR spectrum of 9-(3-methoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6i)



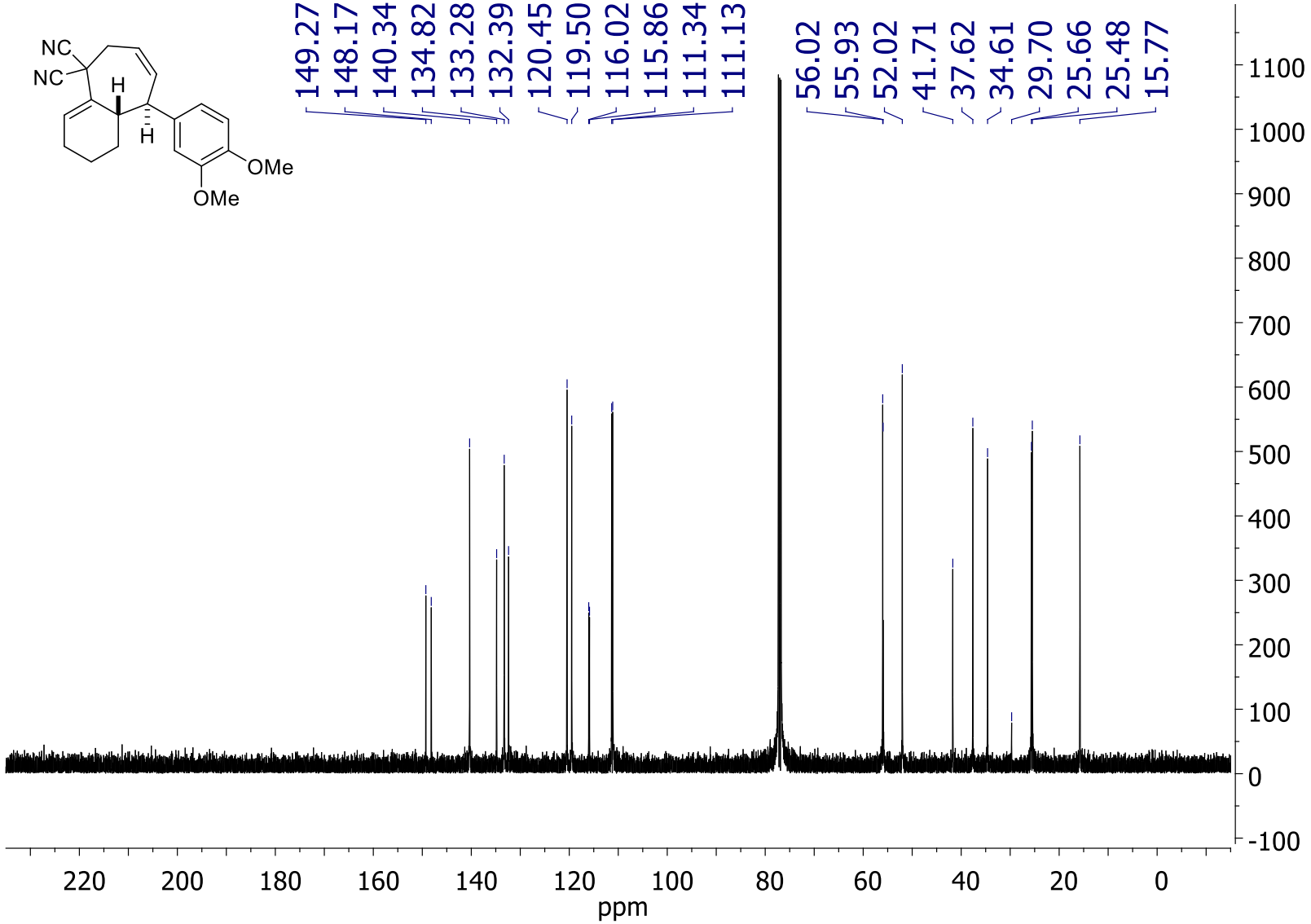
^{13}C NMR spectrum of 9-(3-methoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6i)



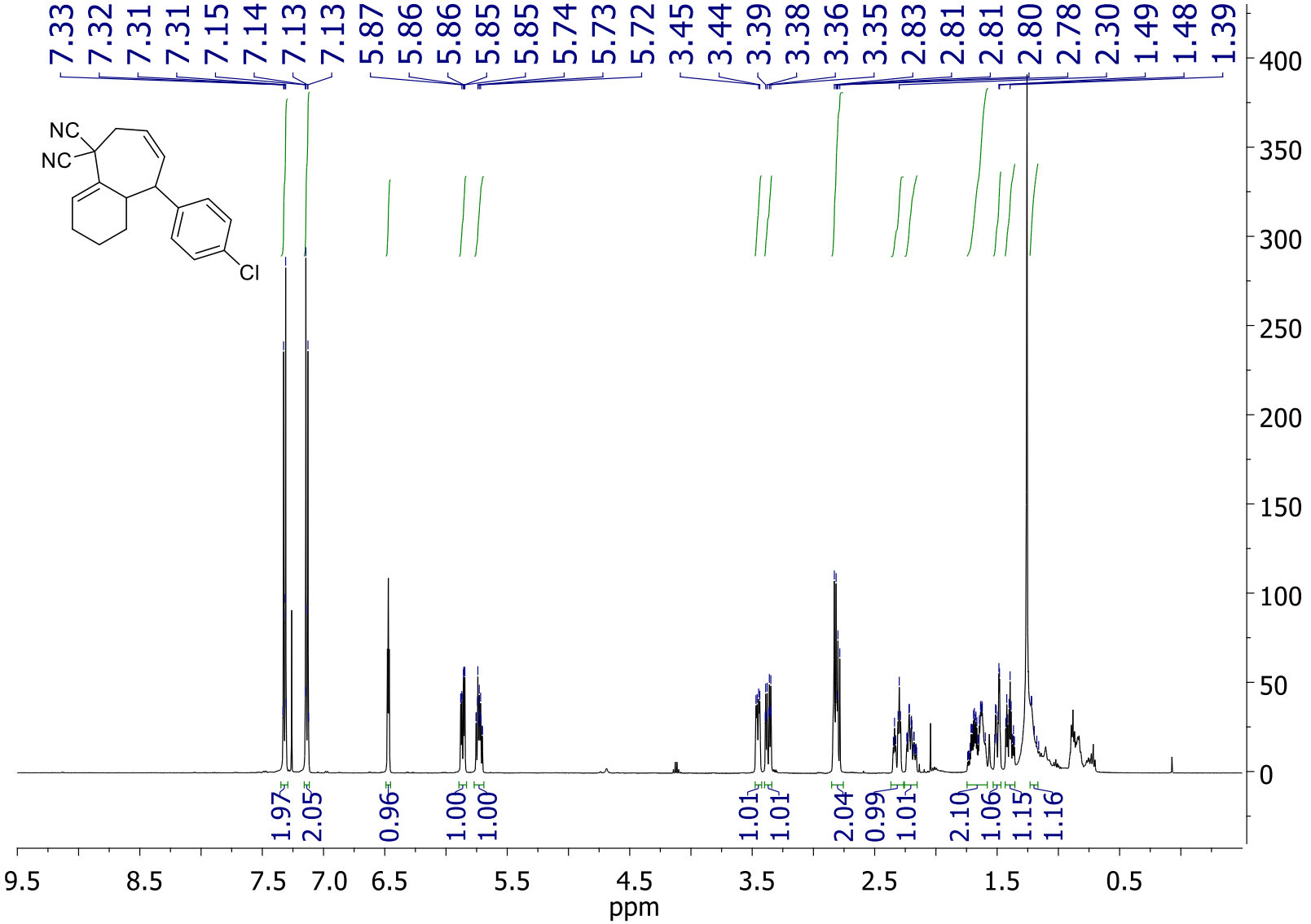
^{1}H NMR spectrum of 9-(3,4-dimethoxyphenyl)-1,2,3,6,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6j)



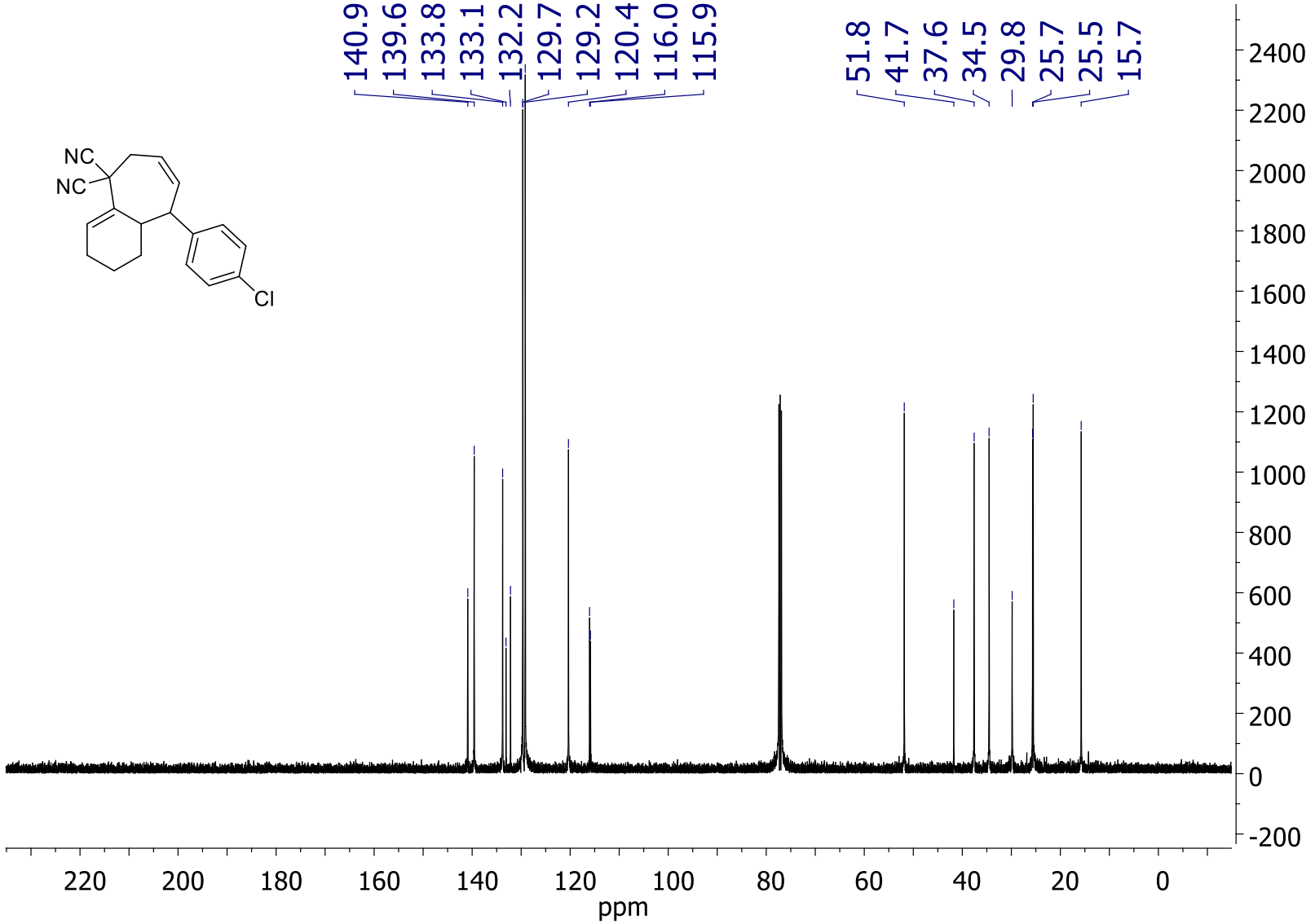
^{13}C NMR spectrum of 9-(3,4-dimethoxyphenyl)-1,2,3,6,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6j)



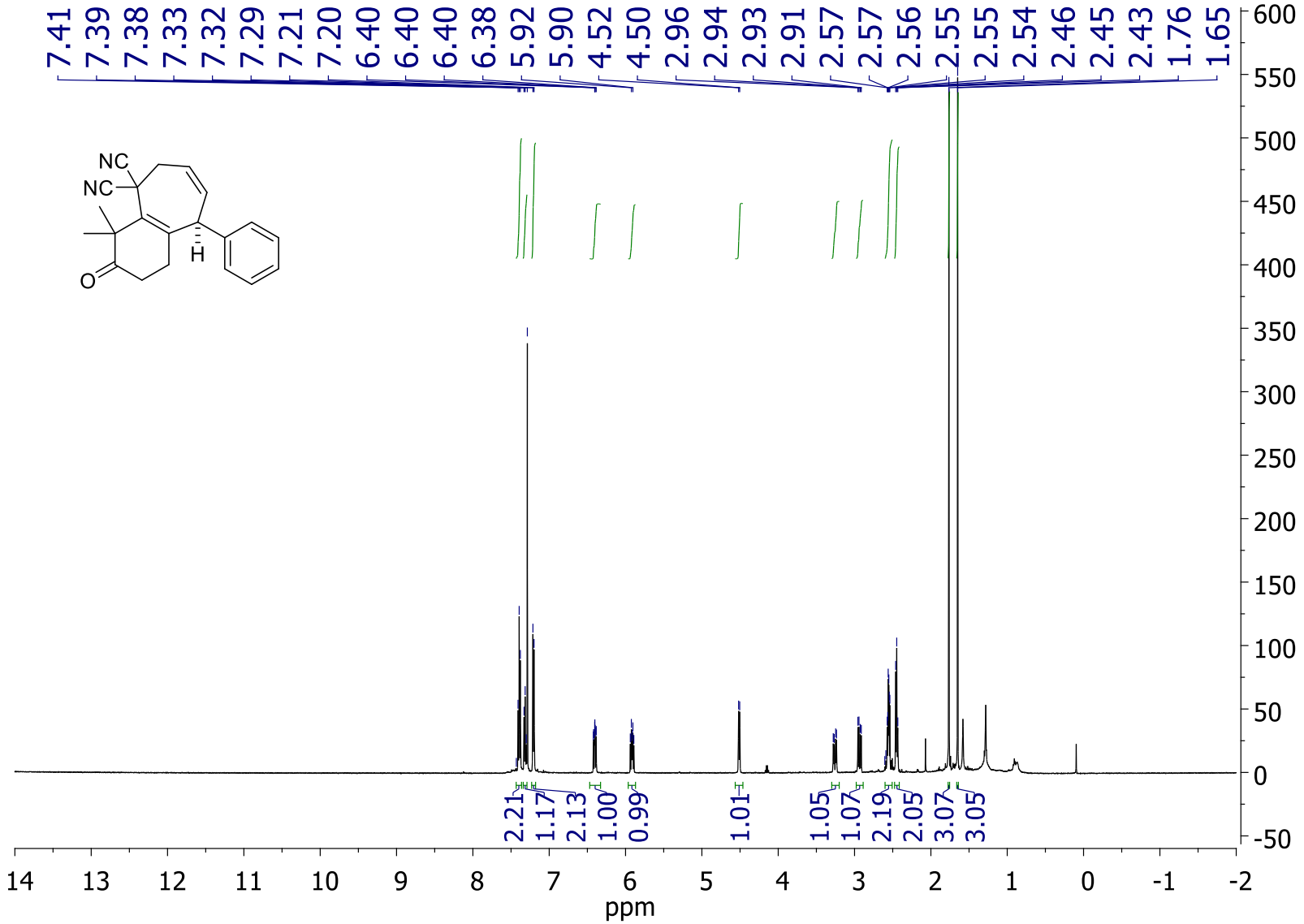
^{1}H NMR spectrum of 9-(4-chlorophenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6k)



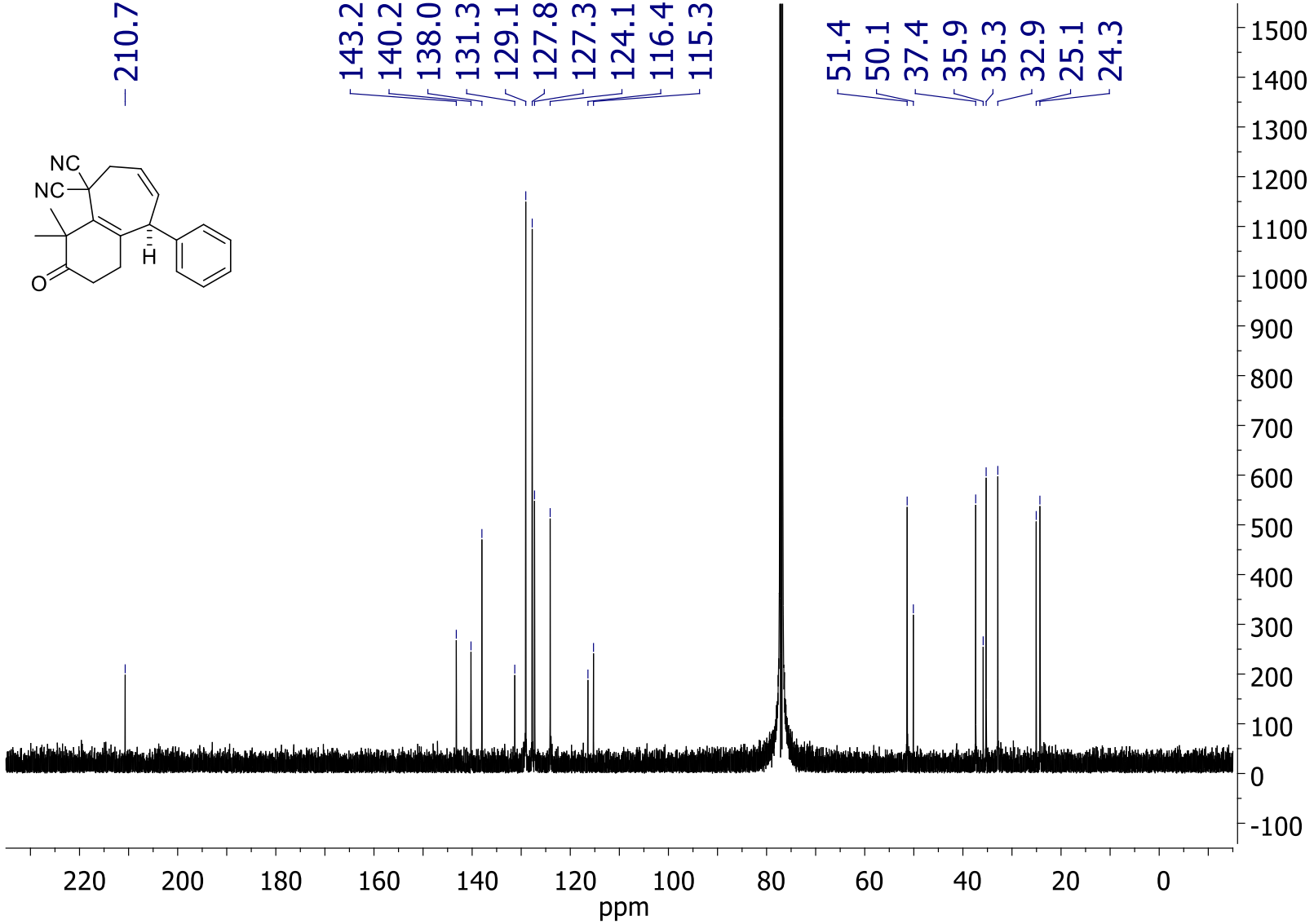
^{13}C NMR spectrum of 9-(4-chlorophenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6k)



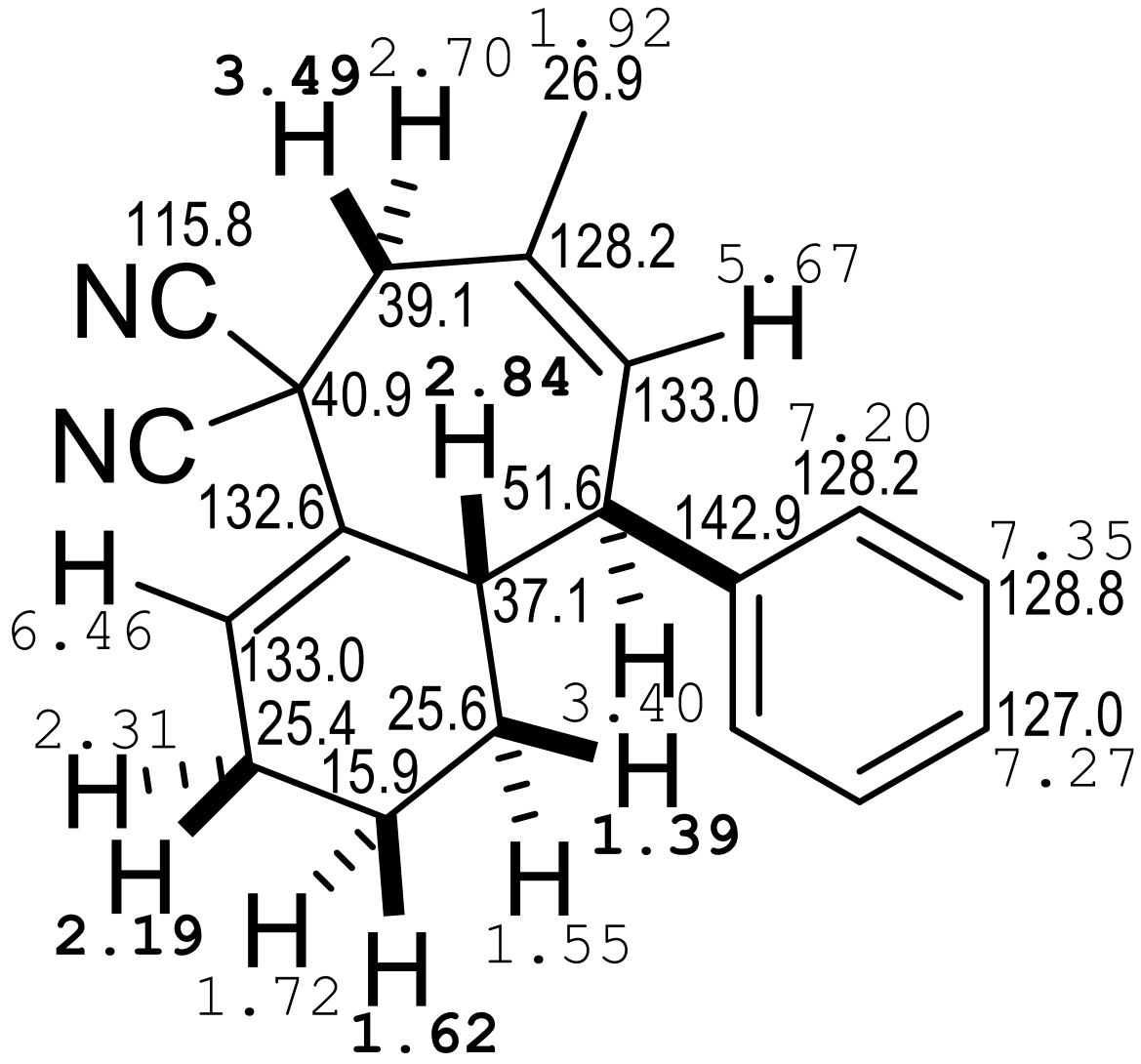
^{1}H NMR spectrum of 4,4-dimethyl-3-oxo-9-phenyl-1,2,3,4,6,9-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6m)



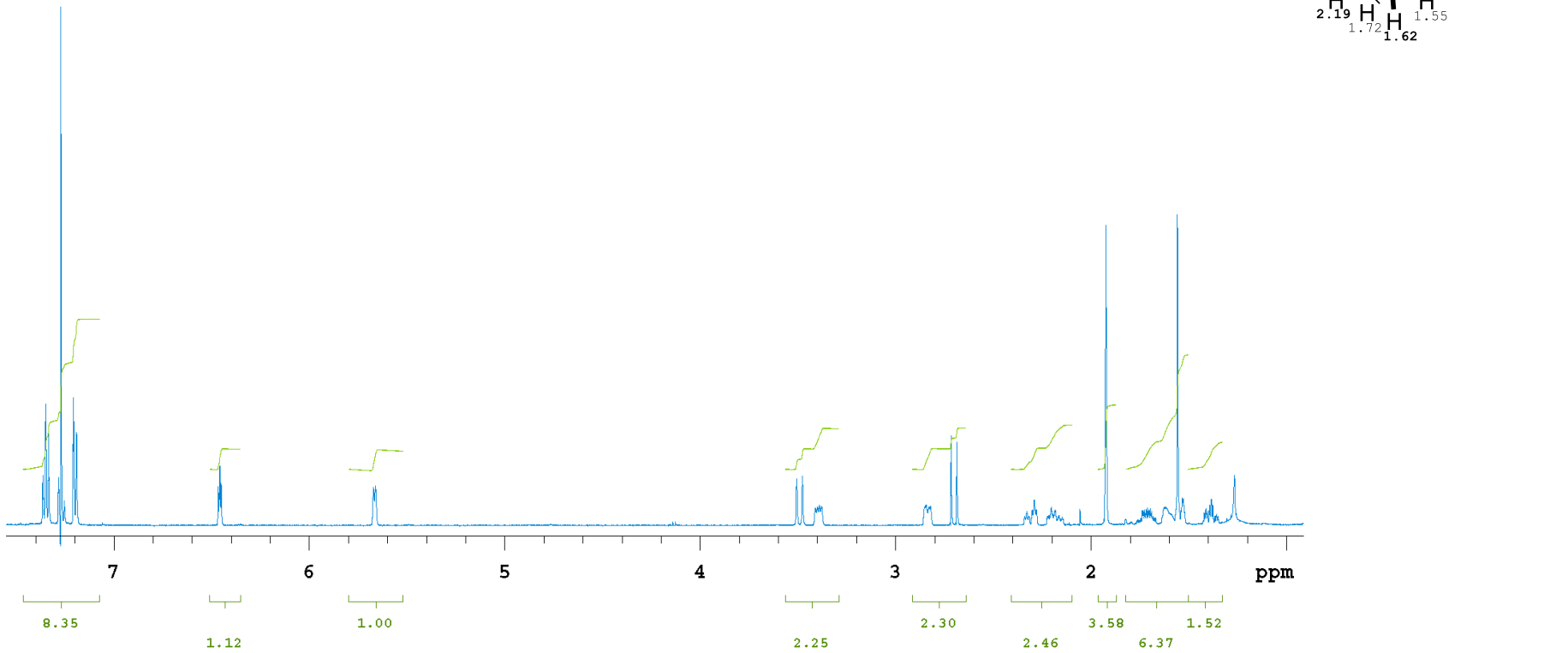
^{13}C NMR spectrum of 4,4-dimethyl-3-oxo-9-phenyl-1,2,3,4,6,9-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6m)



Characterization of 7-methyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile (6n)

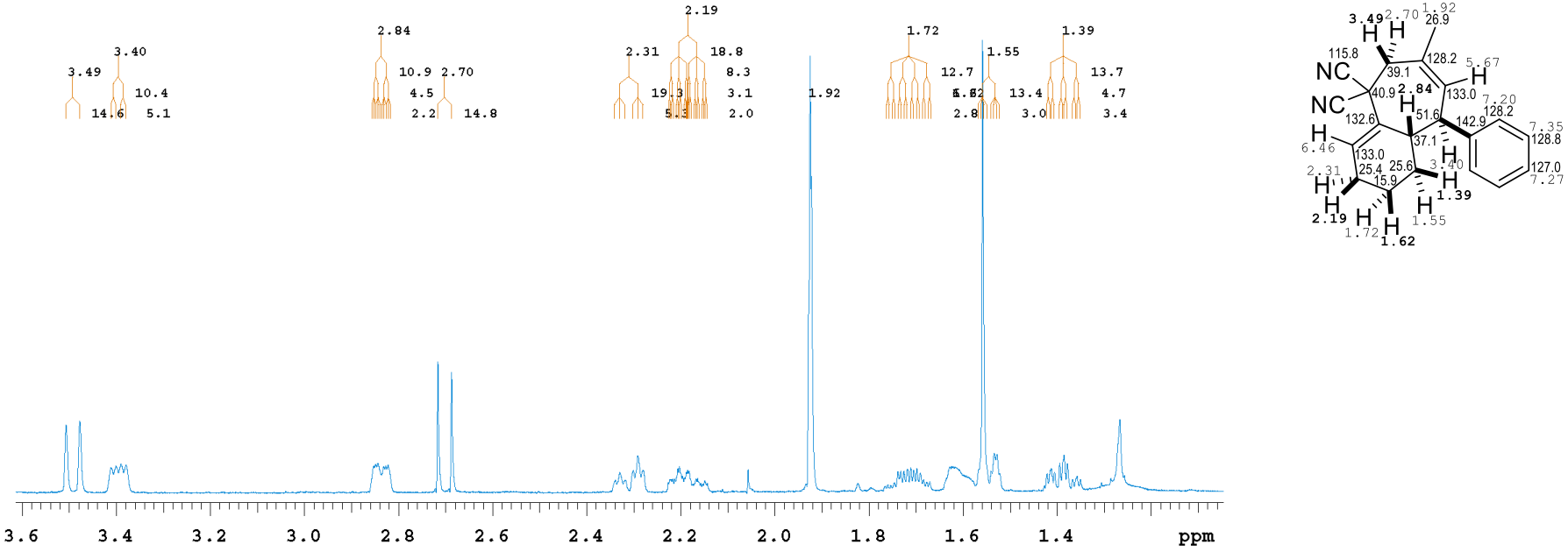


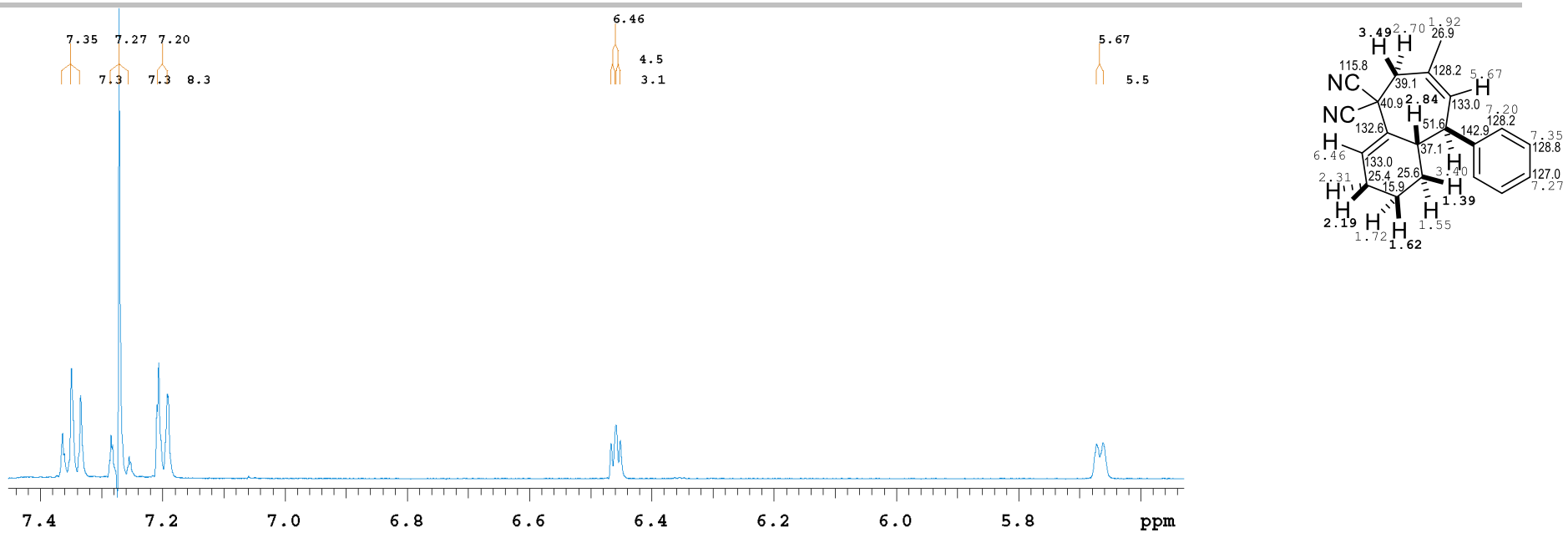
^{1}H NMR spectrum of 7-methyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6n)



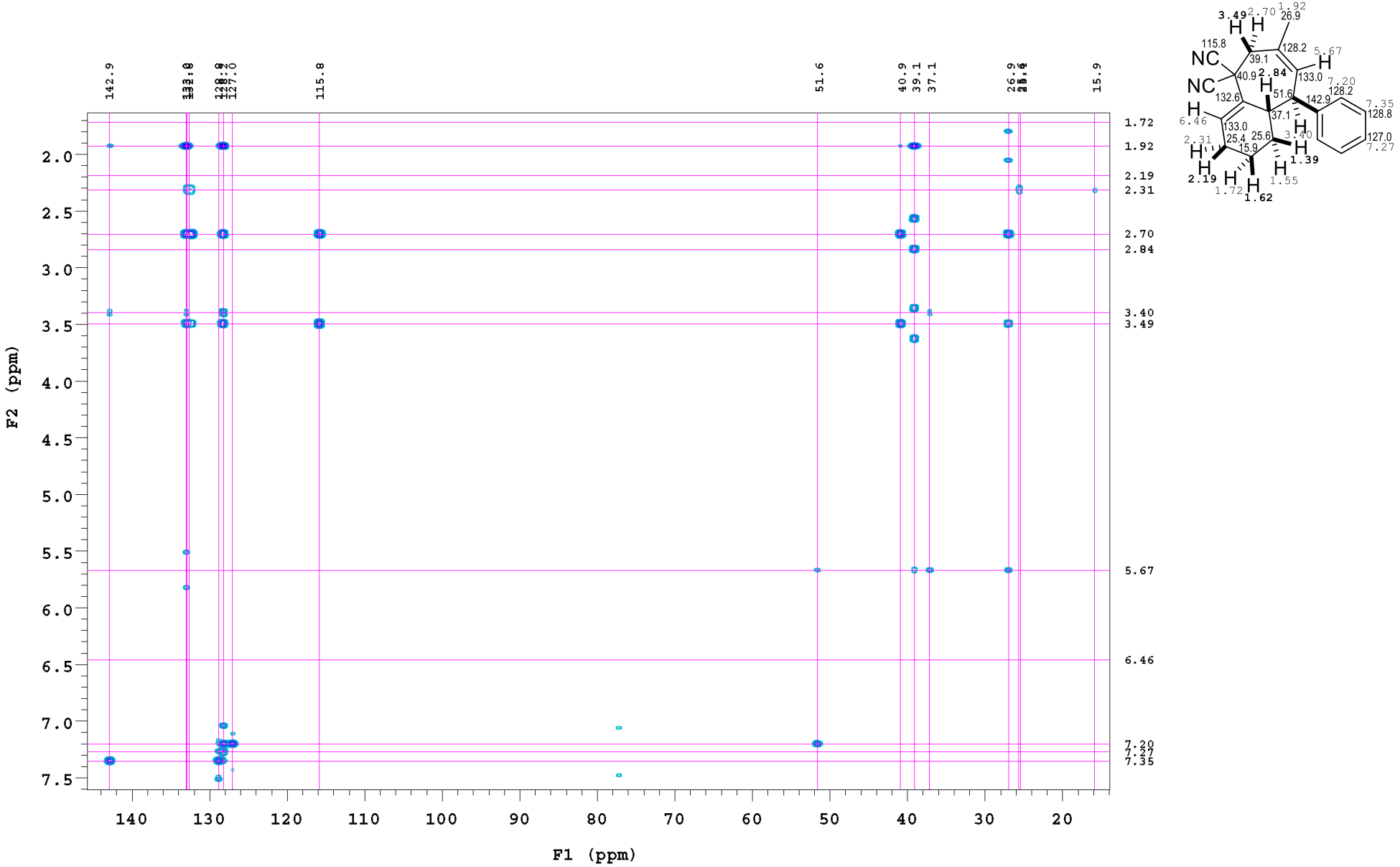
SUPPORTING INFORMATION

Expansions for ^{1}H NMR spectrum of 7-methyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6n)



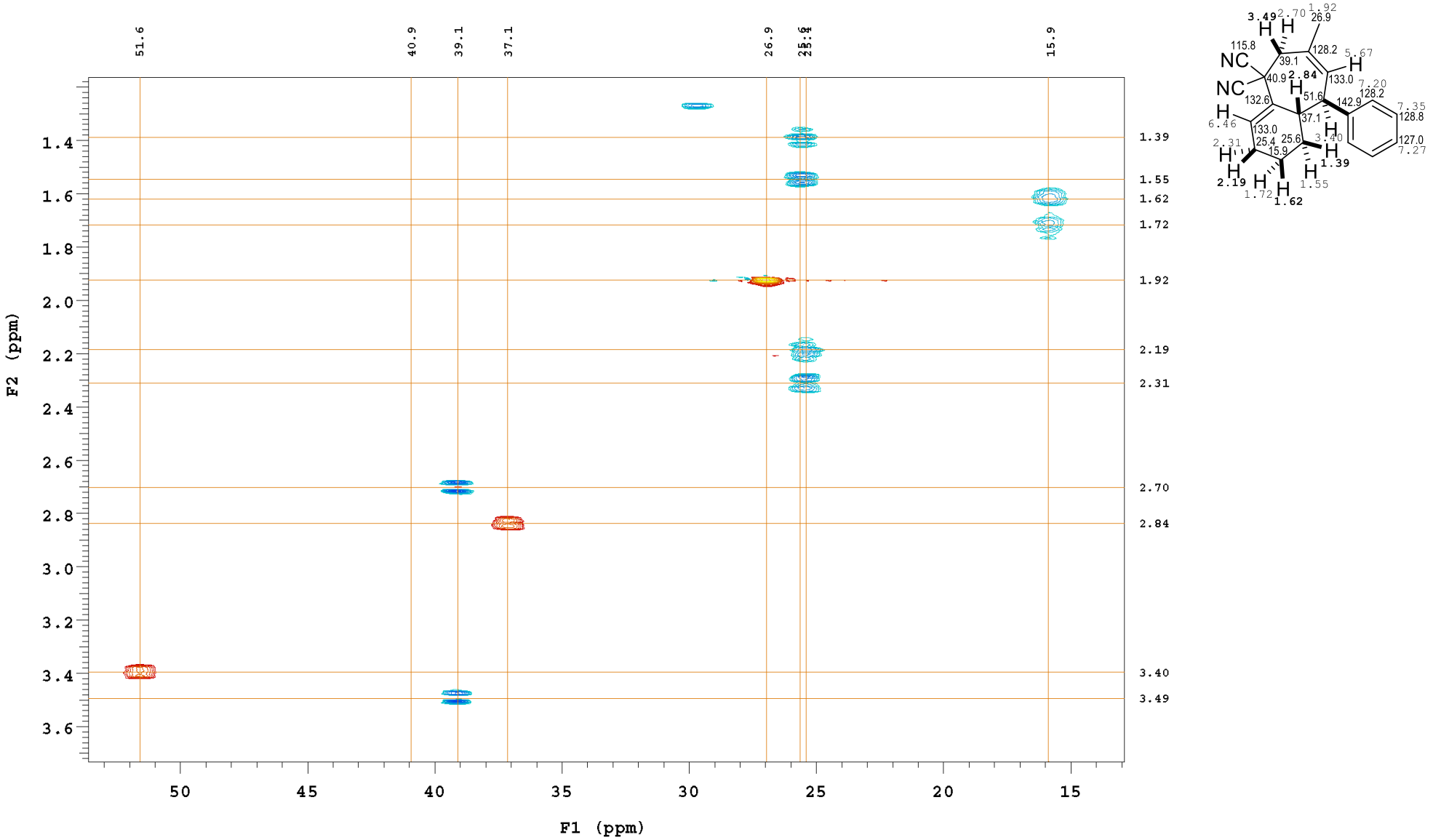


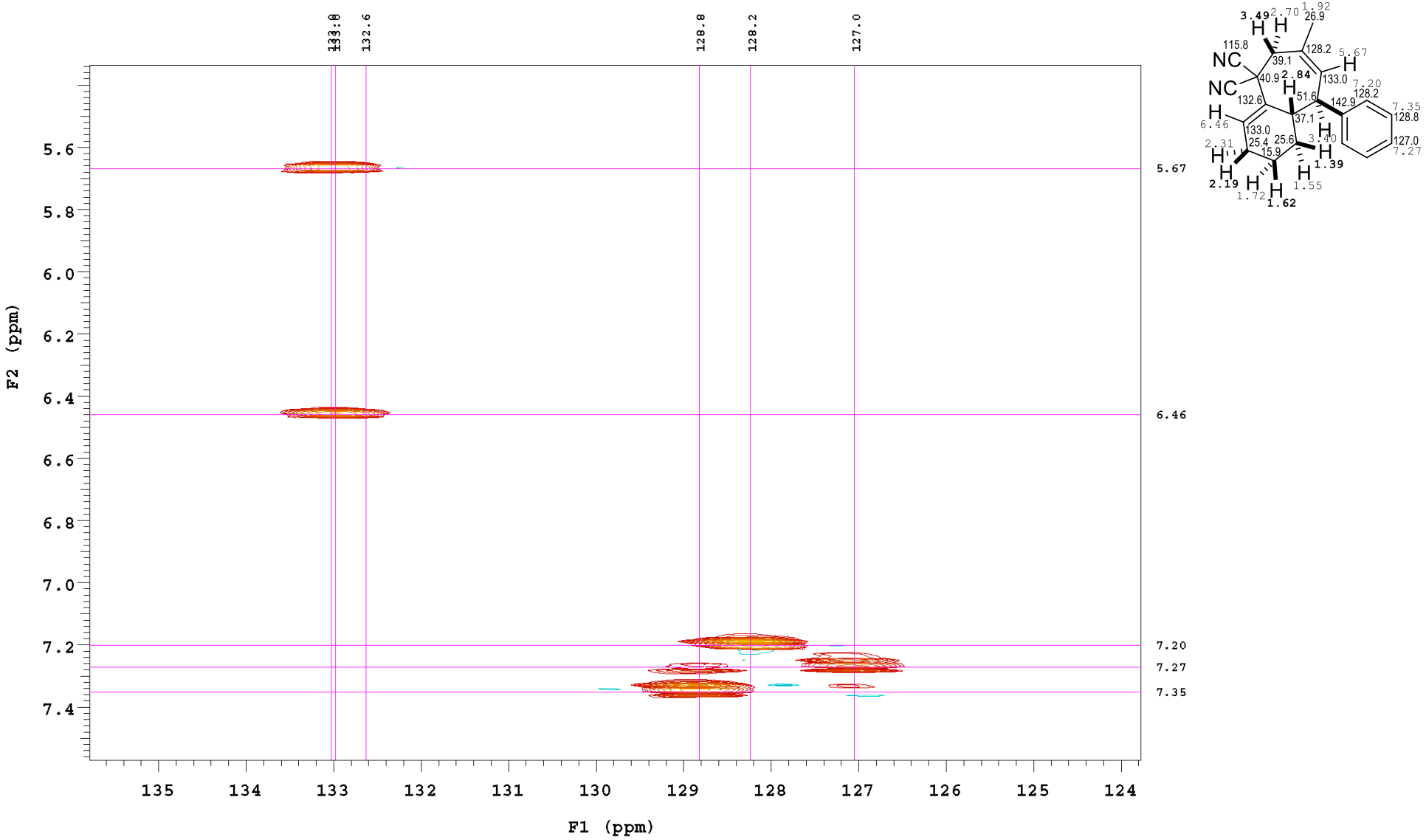
gHMBC spectrum of 7-methyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6n)


142.9
115.8
51.6
40.9
39.1
37.1
26.9
15.9
1.72
1.92
2.19
2.31
2.70
2.84
3.40
3.49
5.67
6.46
7.20
7.27
7.35
F2 (ppm)
F1 (ppm)
3.49
2.70
1.92
26.9
115.8
NC
39.1
128.2
5.67
H
40.9
2.84
133.0
7.20
NC
132.6
51.6
142.9
128.2
7.35
H
6.46
37.1
128.8
133.0
25.4
25.6
3.40
127.0
2.31
15.9
7.27
1.39
2.19
1.55
1.72
1.62

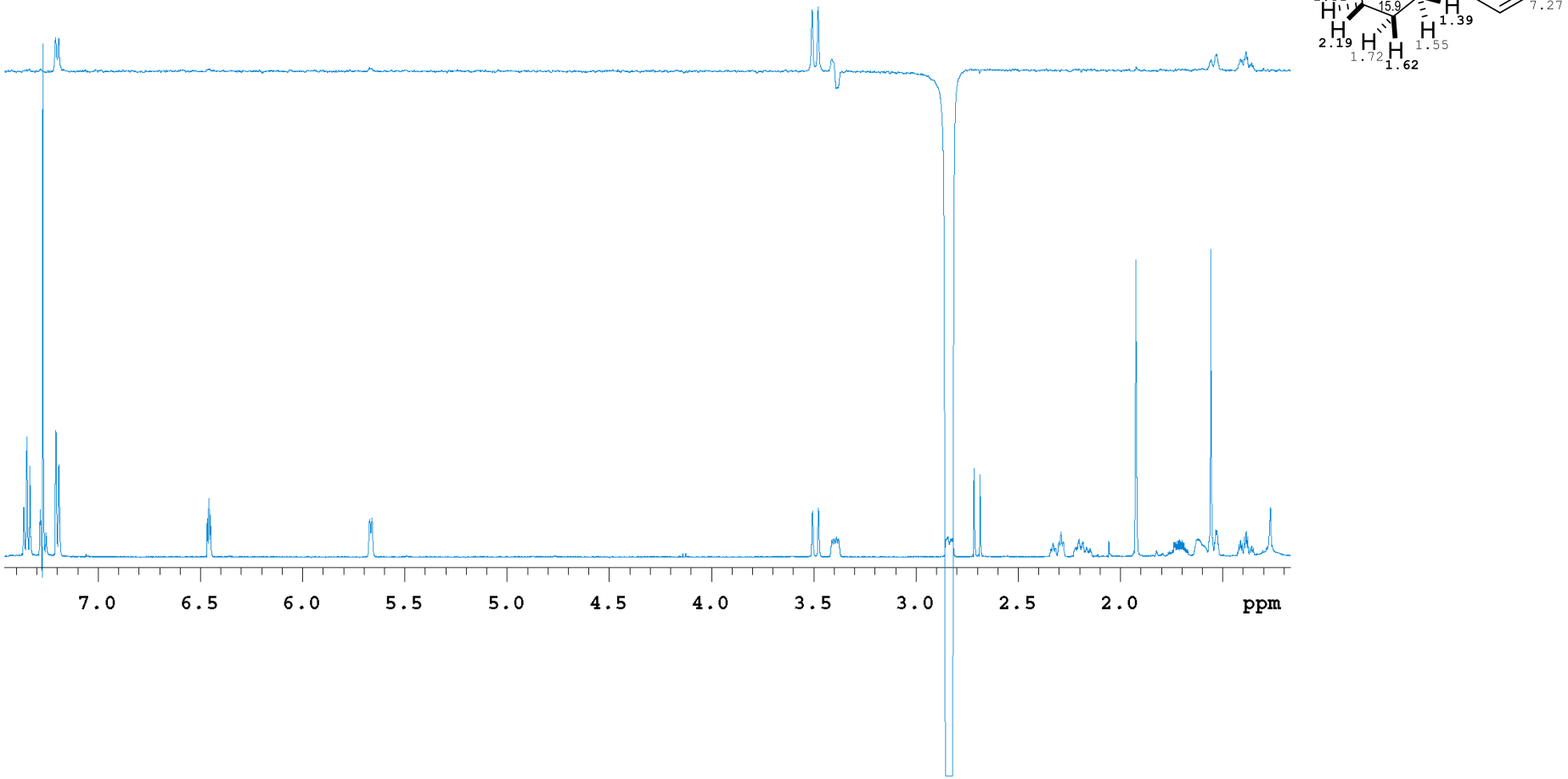
SUPPORTING INFORMATION

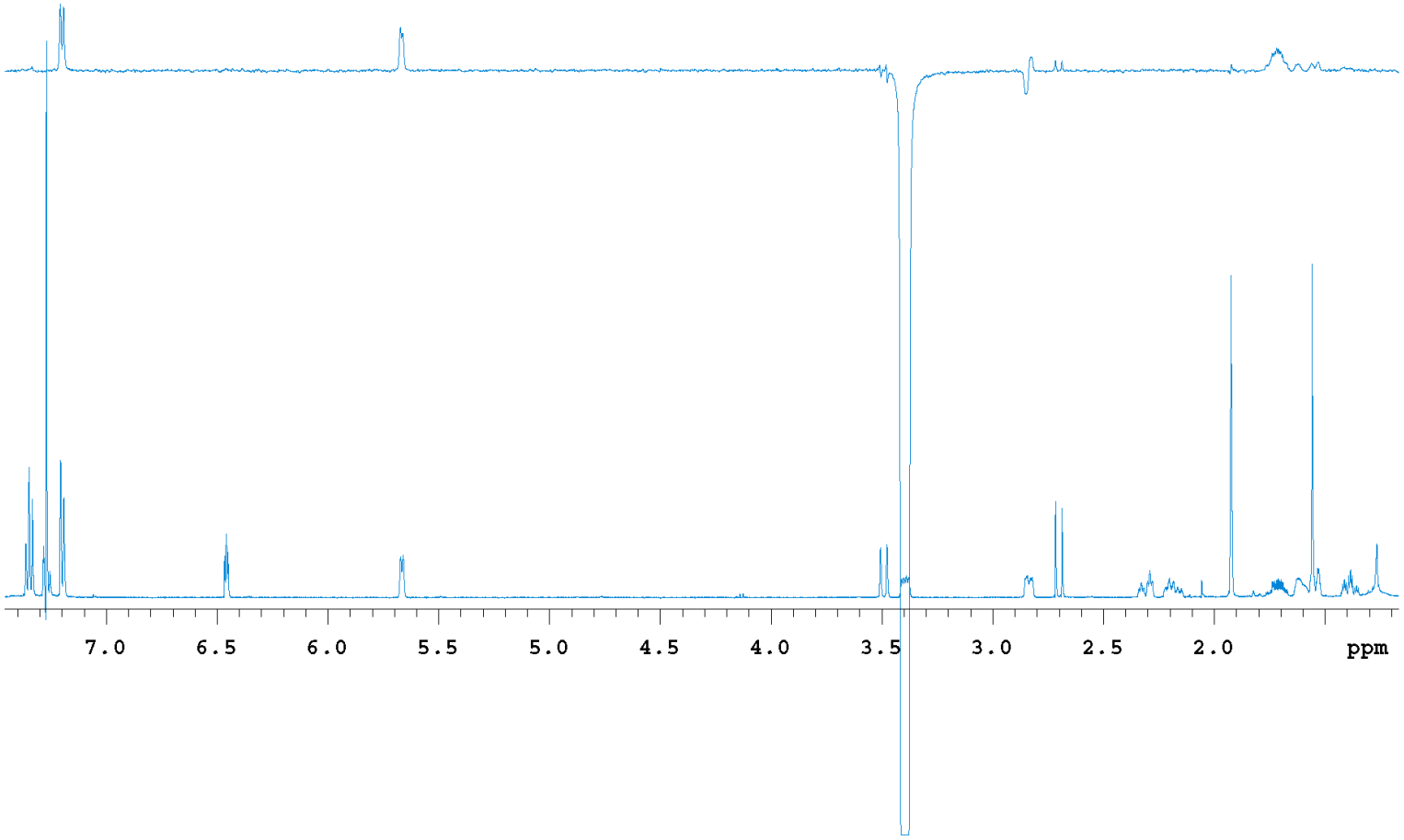
HSQC spectrum of 7-methyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6n)

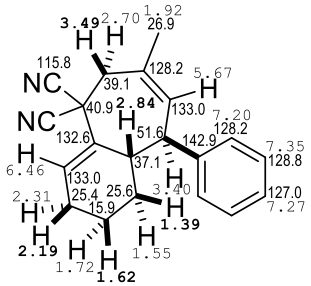



133.0
132.6
128.8
128.2
127.0
F2 (ppm)
F1 (ppm)
5.67
6.46
7.20
7.27
7.35
3.49
2.70
1.92
26.9
115.8
NC
39.1
128.2
5.67
40.9
2.84
133.0
7.20
NC
132.6
51.6
142.9
128.2
7.35
6.46
37.1
128.8
133.0
25.4
25.6
3.40
127.0
2.31
15.9
7.27
1.39
2.19
1.72
1.55
1.62

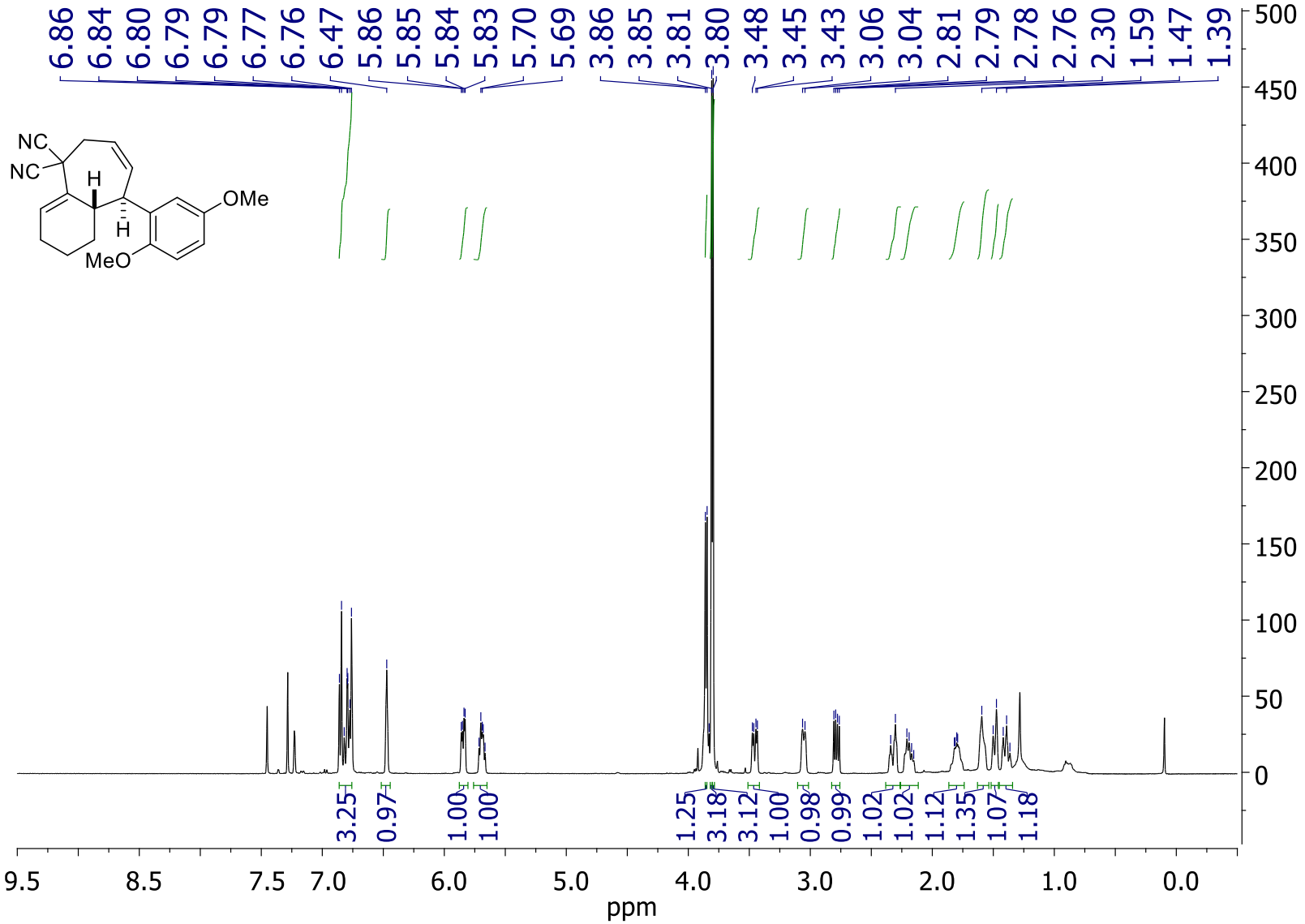
NOESY spectrum 7-methyl-9-phenyl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6n)



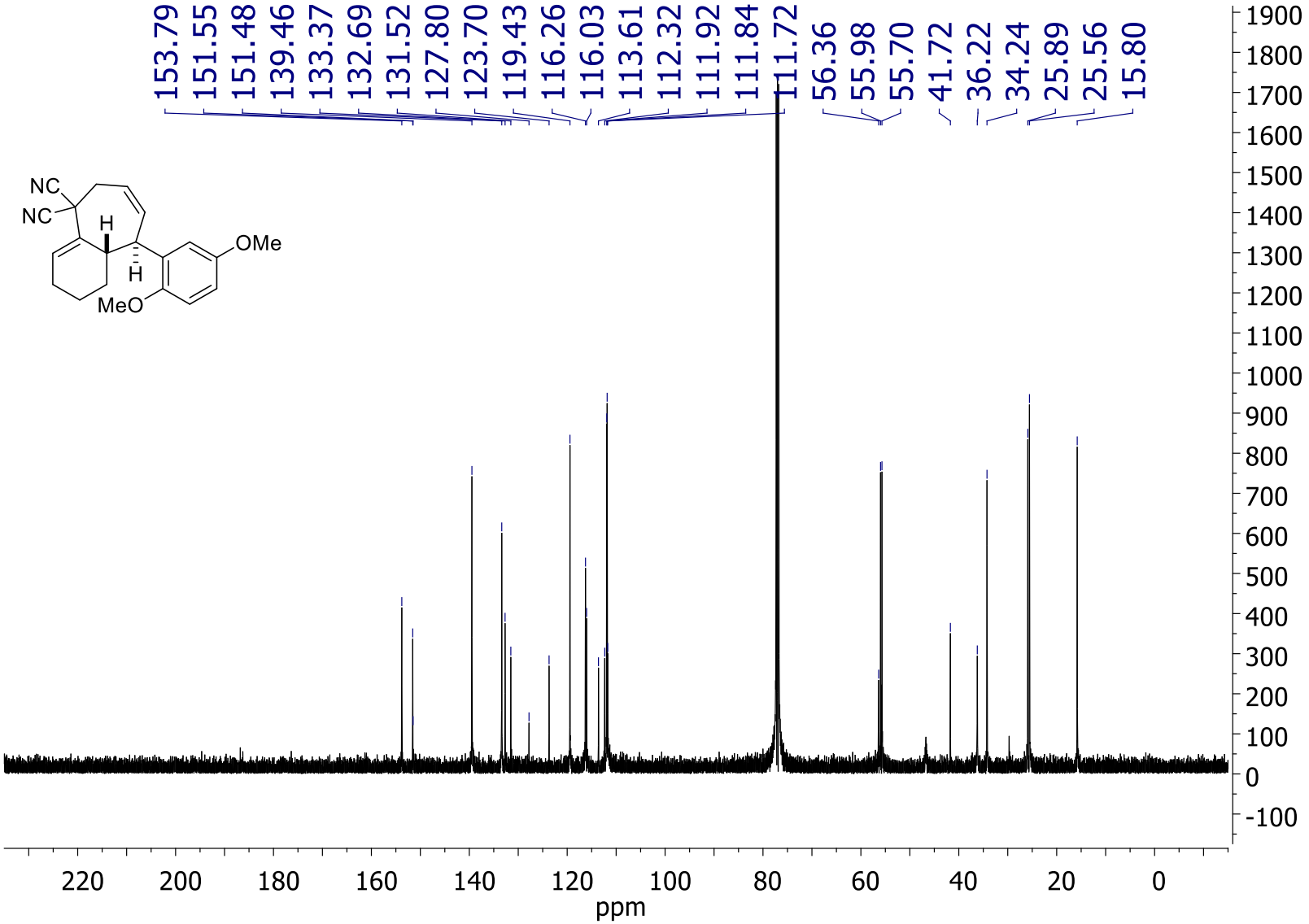

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm


3.49
2.70
1.92
26.9
115.8
128.2
5.67
NC
39.1
H
40.9
2.84
133.0
7.20
NC
132.6
51.6
142.9
128.2
7.35
H
6.46
37.1
128.8
133.0
25.4
25.6
3.40
127.0
2.31
15.9
7.27
H
1.39
2.19
H
H
1.55
1.72
H
1.62

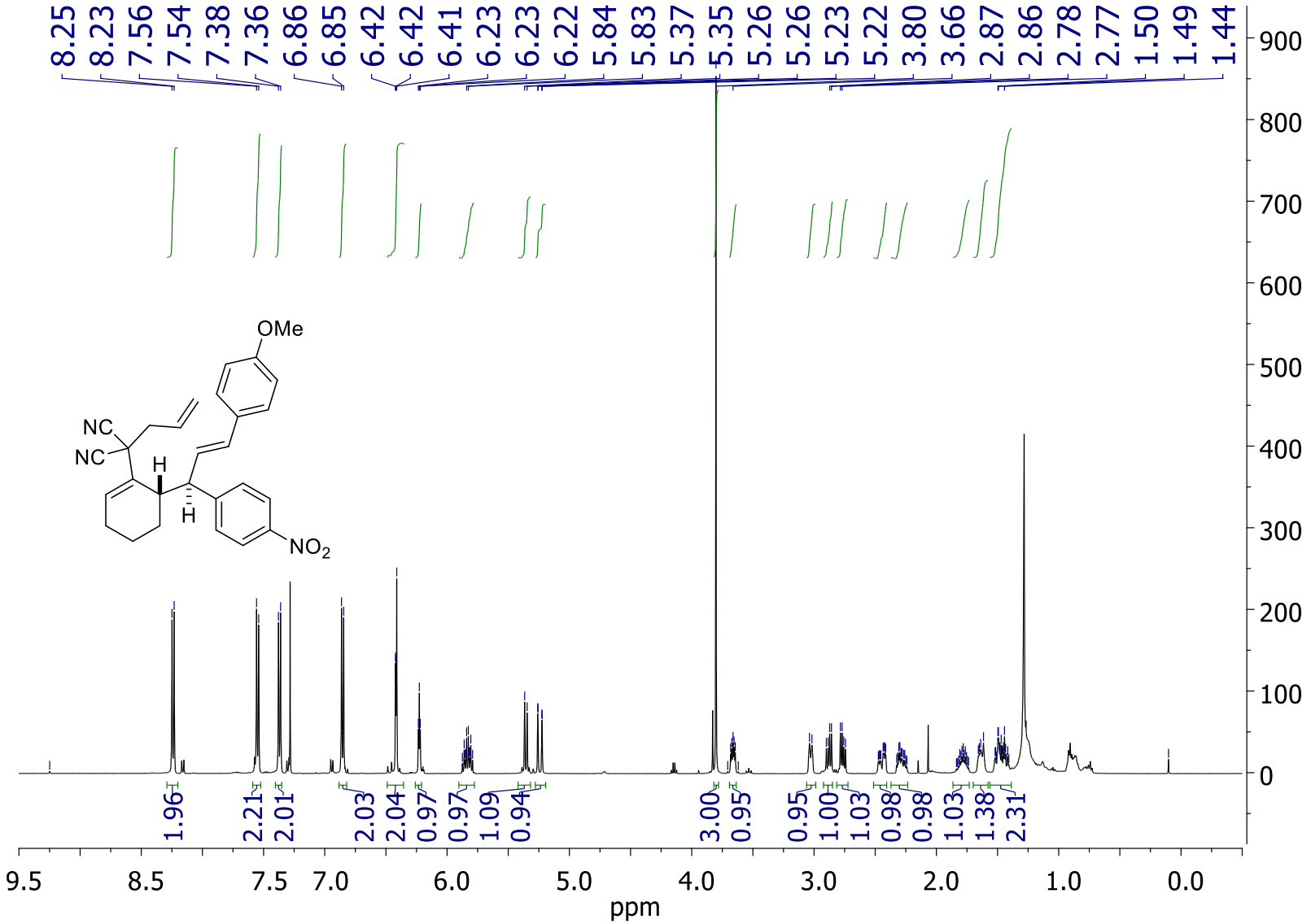
^{1}H NMR spectrum of 9-(2,5-dimethoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6o)



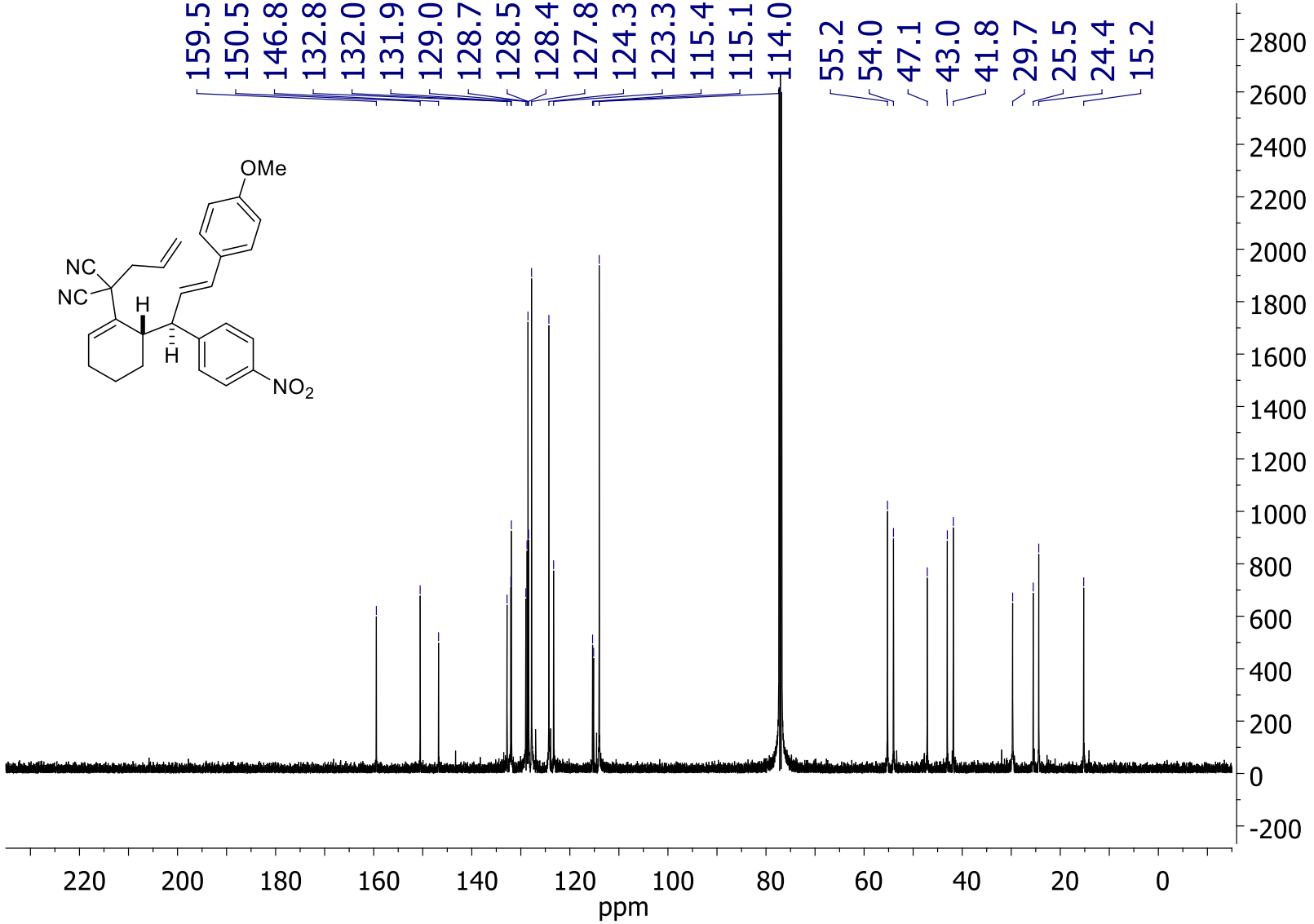
^{13}C NMR spectrum of 9-(2,5-dimethoxyphenyl)-1,2,3,6,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (6o)



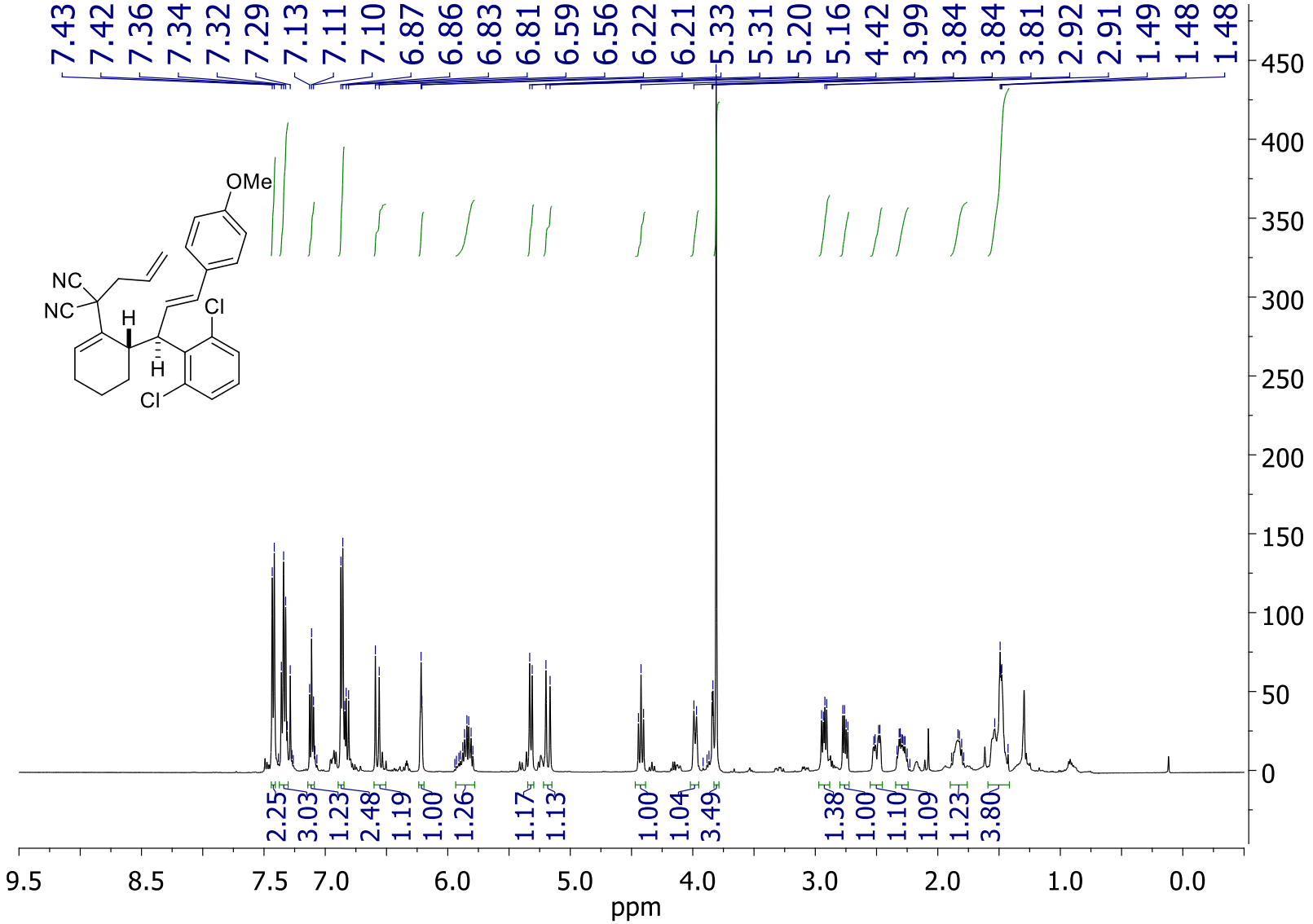
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(3-(4-methoxyphenyl)-1-(4-nitrophenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (9a)



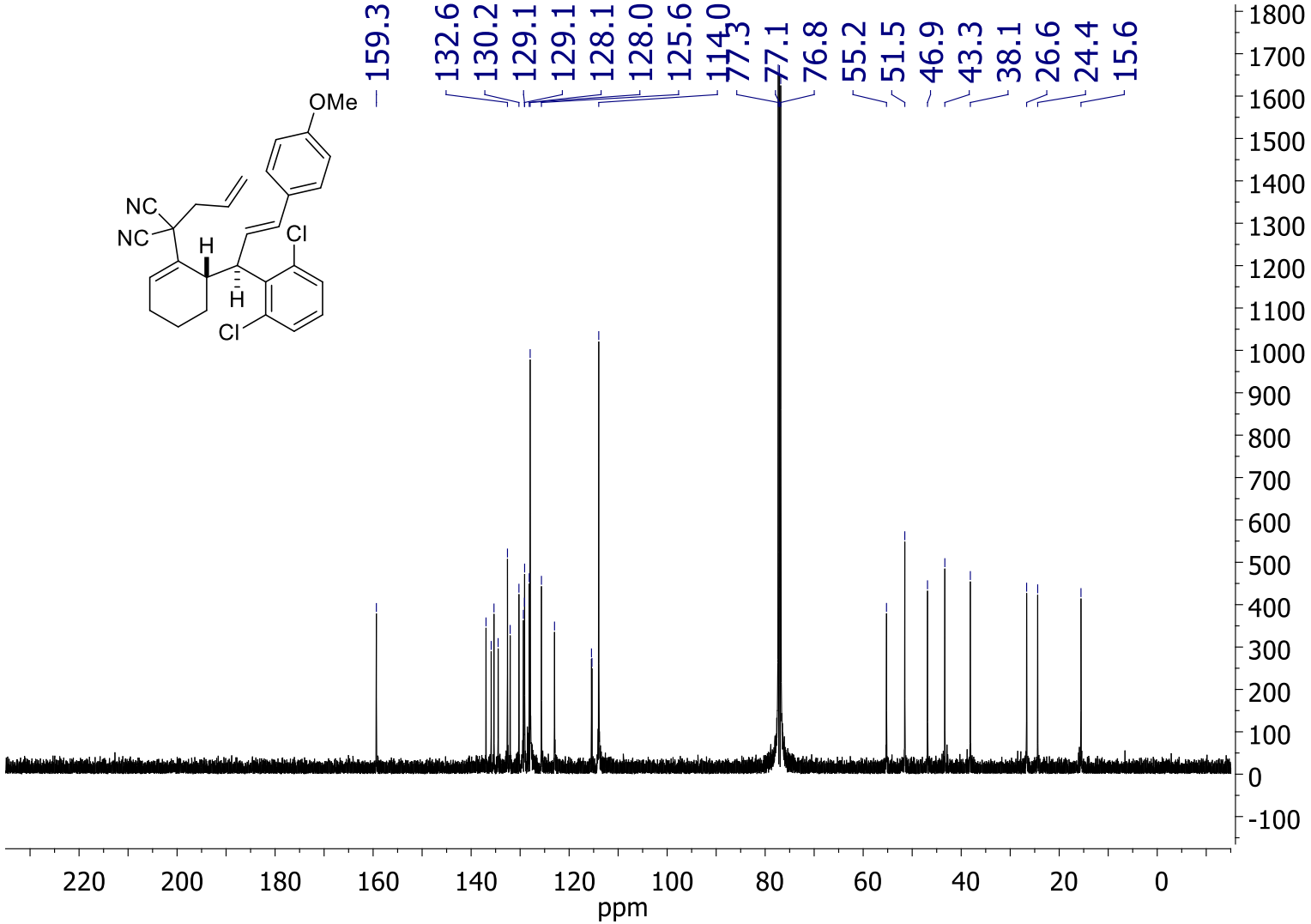
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(3-(4-methoxyphenyl)-1-(4-nitrophenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (9a)



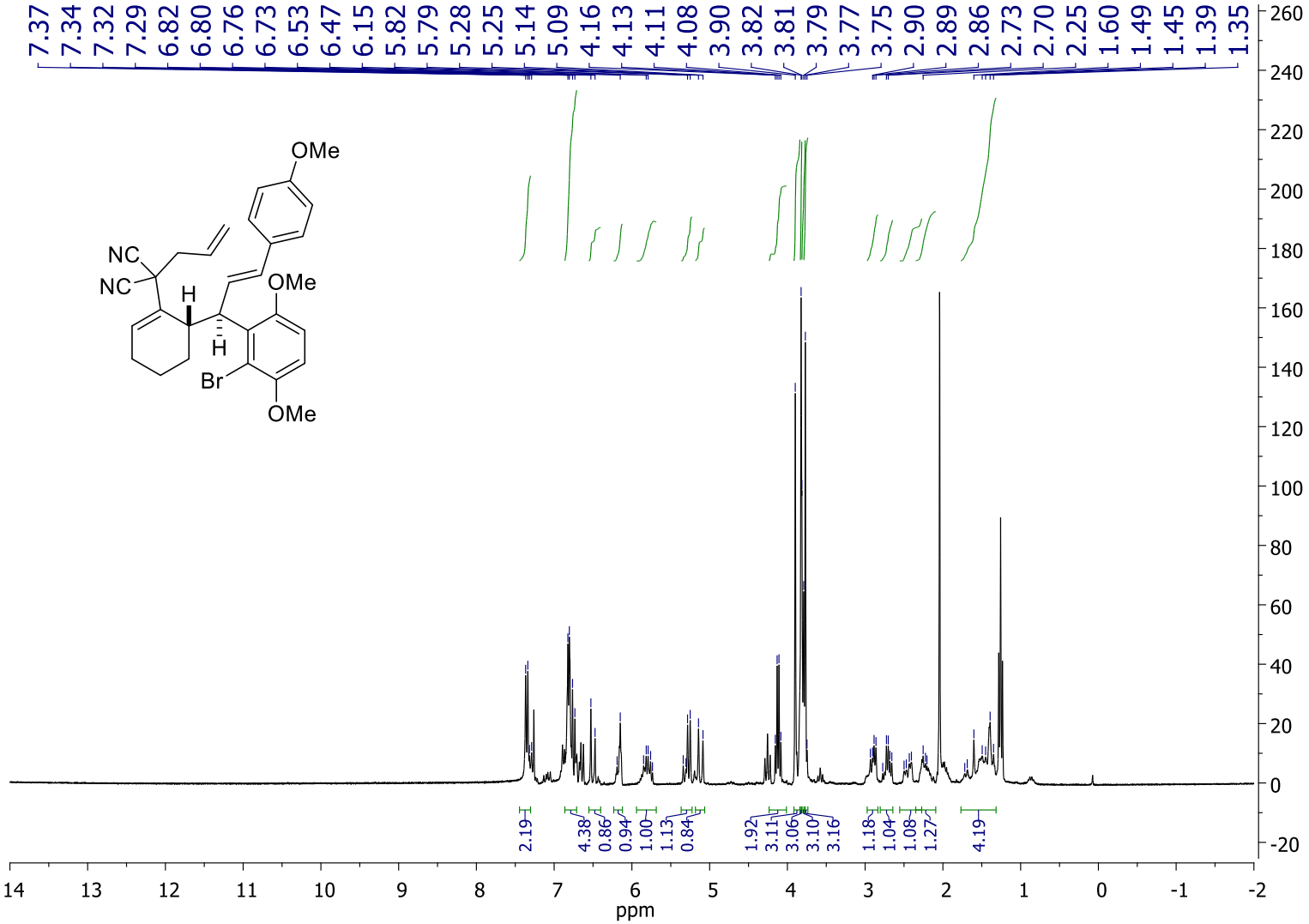
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1-(2,6-dichlorophenyl)-3-(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (9b)



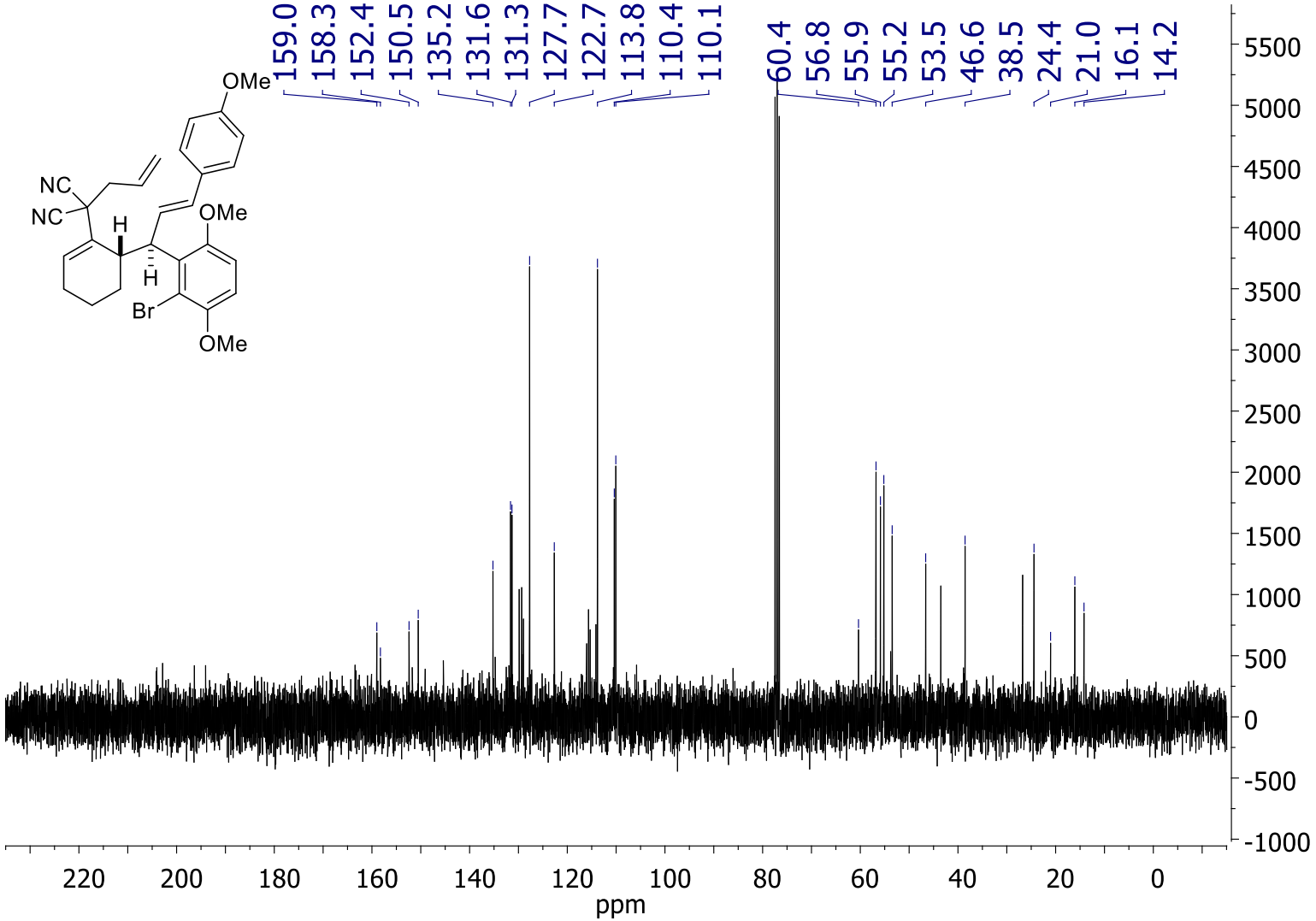
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1-(2,6-dichlorophenyl)-3-(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (9b)



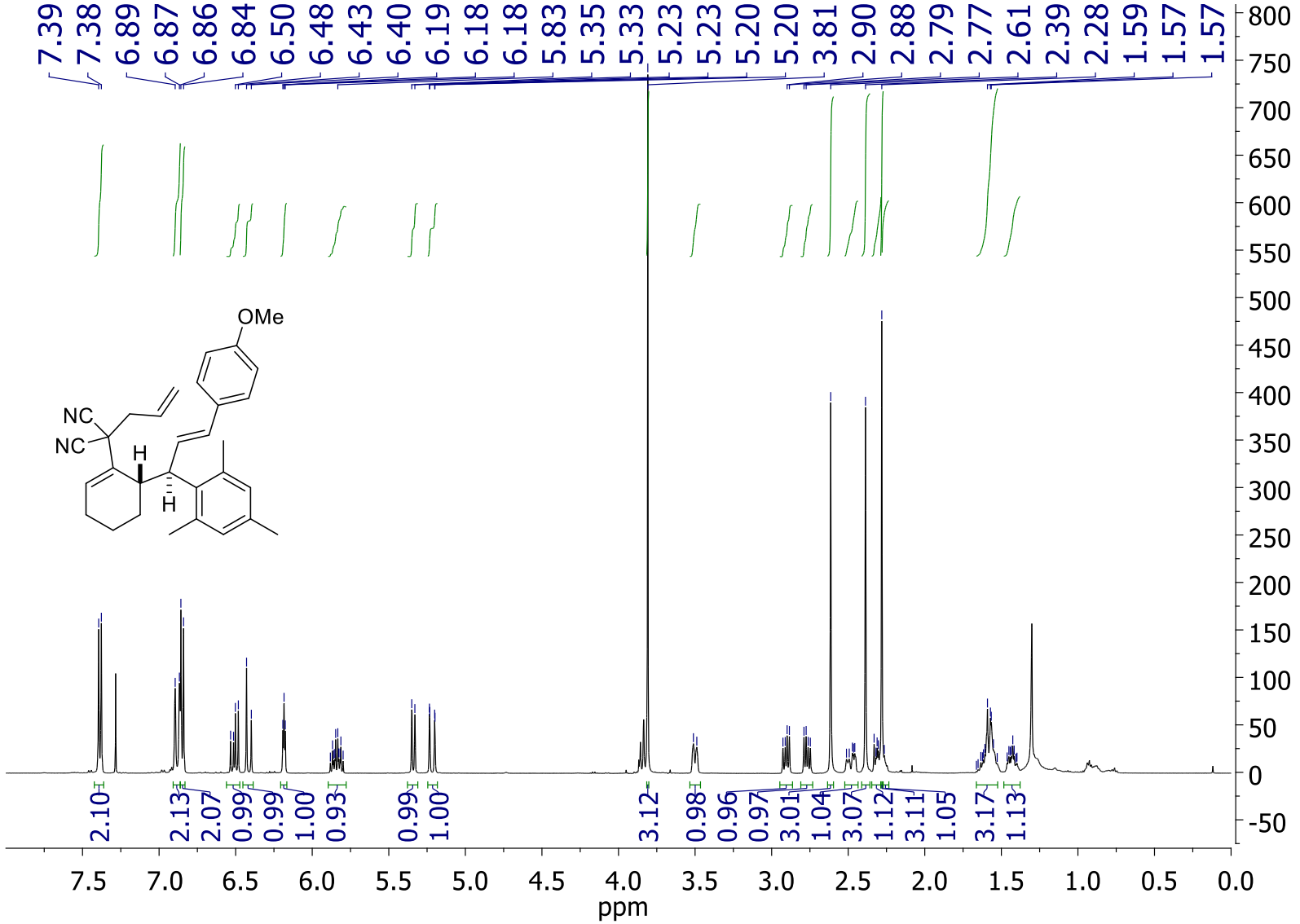
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1-(2-bromo-3,6-dimethoxyphenyl)-3-(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (#9c)



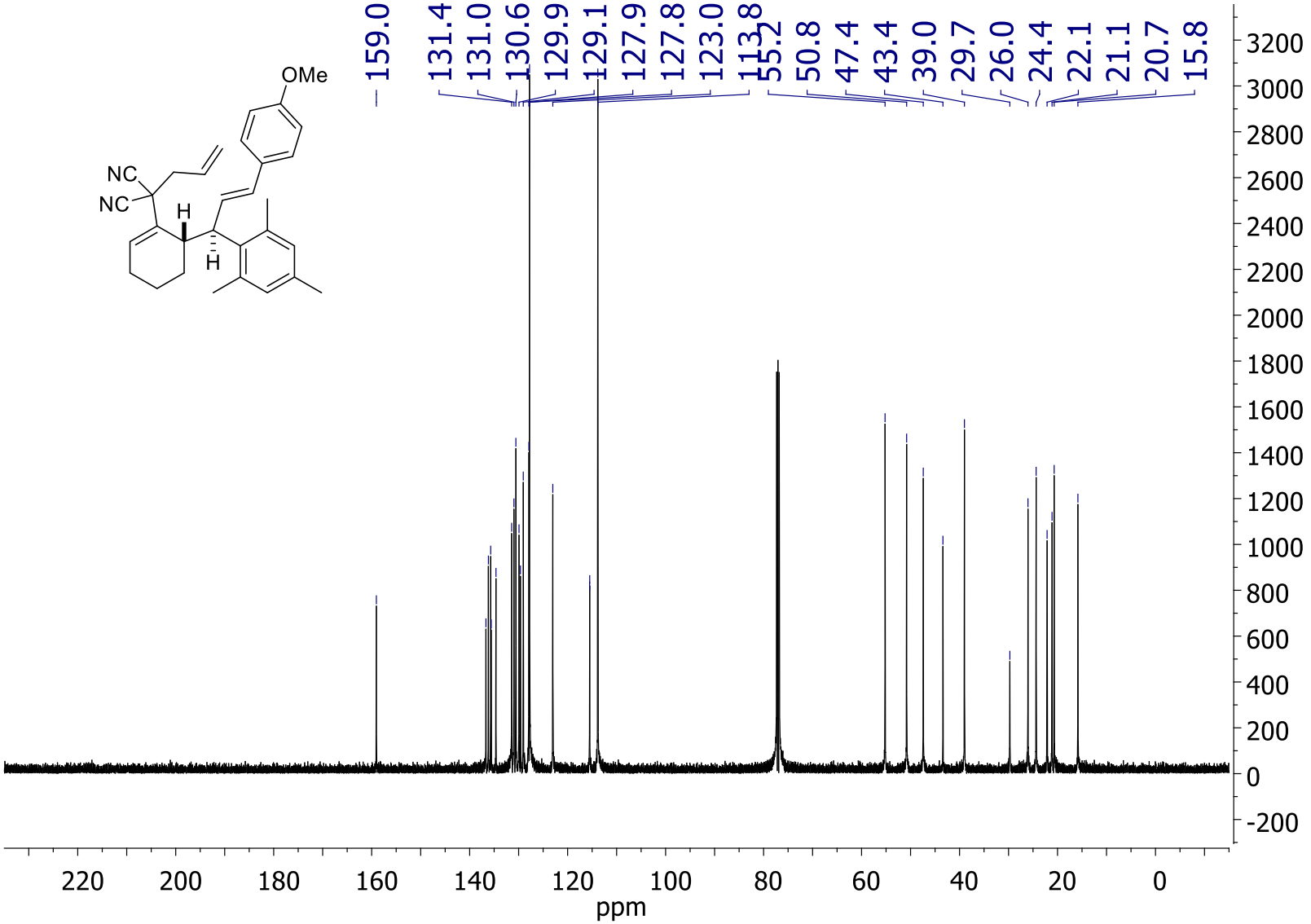
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1-(2-bromo-3,6-dimethoxyphenyl)-3-(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (#9c)



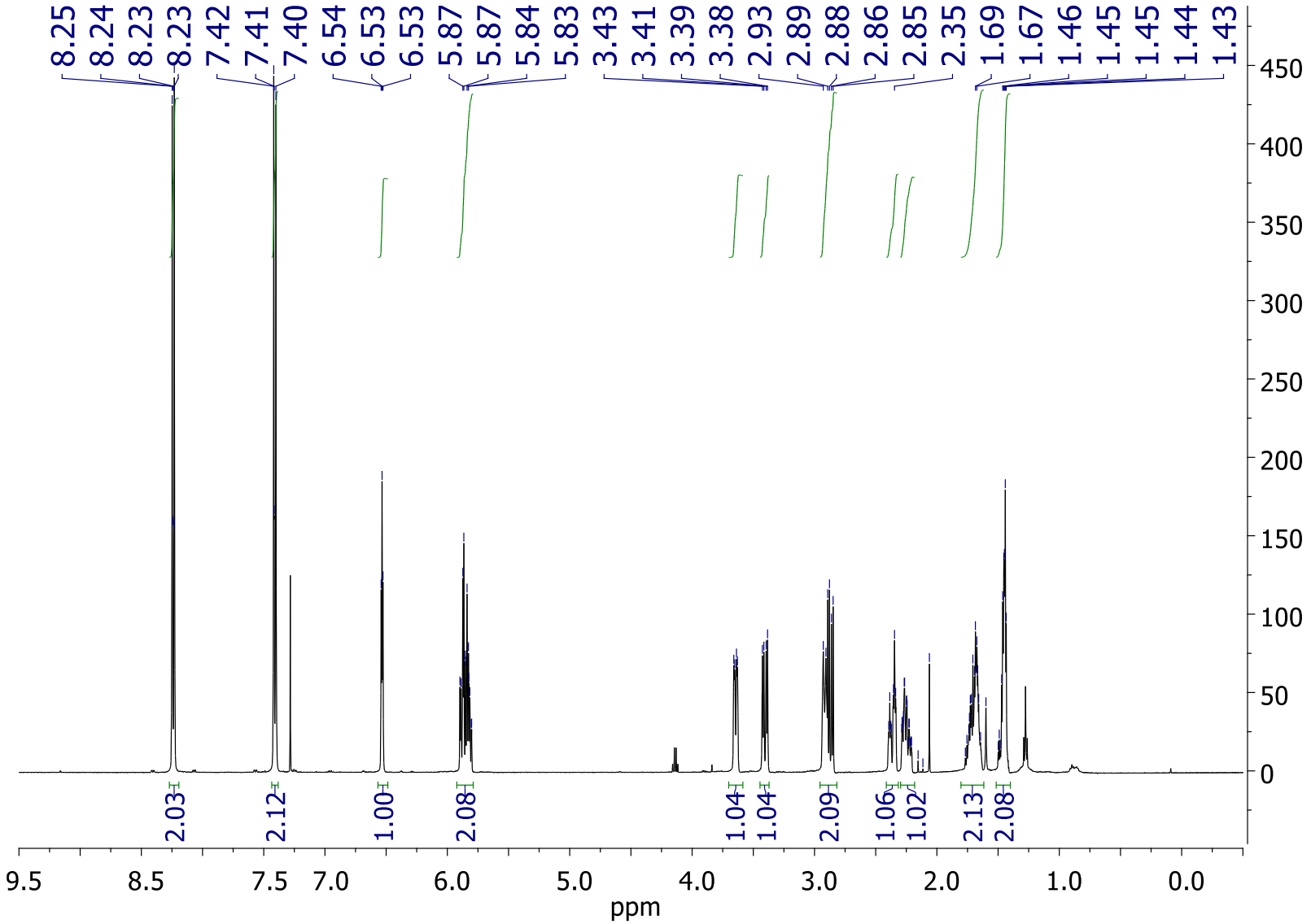
^{1}H NMR spectrum of (E)-2-allyl-2-(6-(1-mesityl-3-(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (9d)



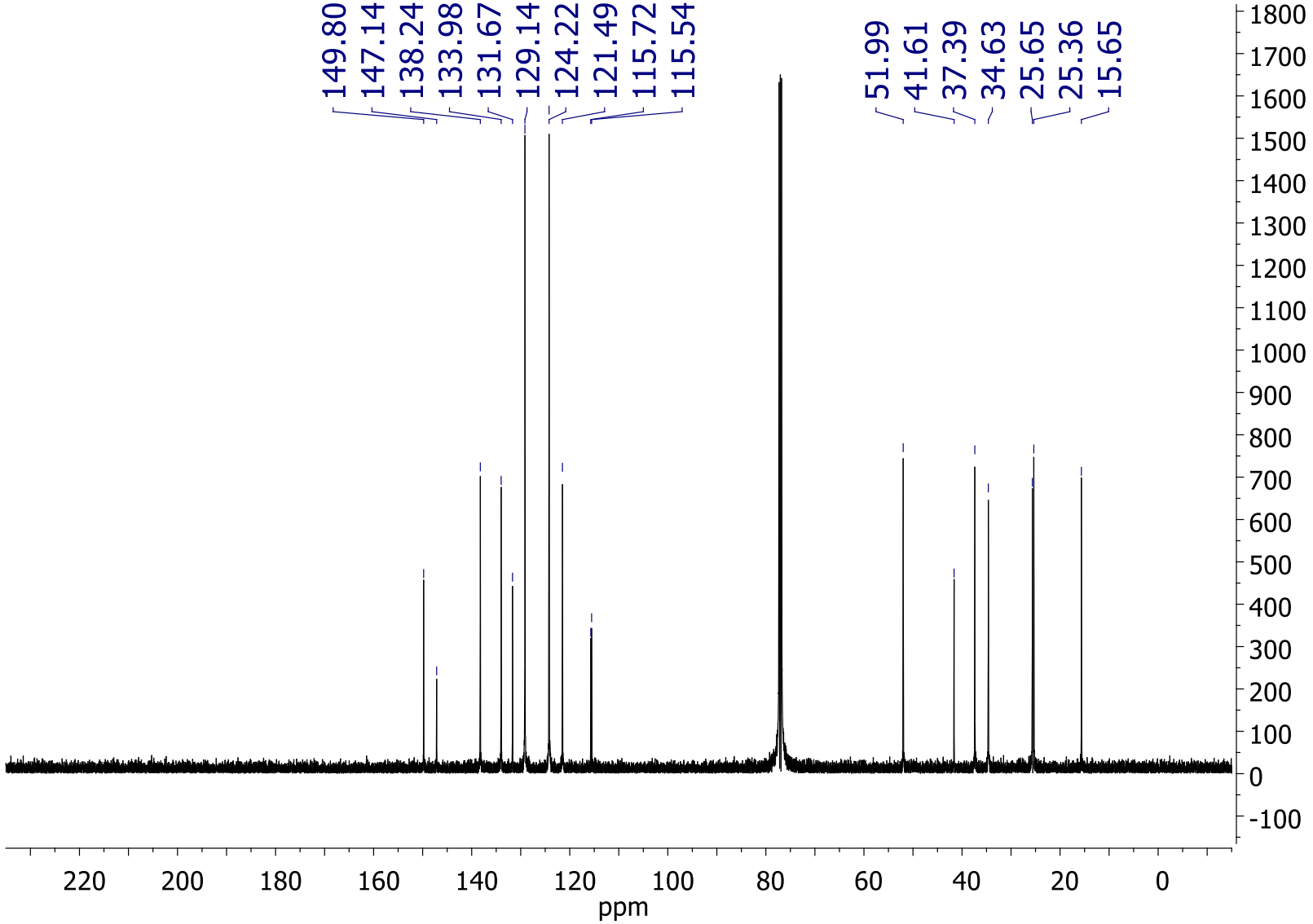
^{13}C NMR spectrum of (E)-2-allyl-2-(6-(1-mesityl-3-(4-methoxyphenyl)allyl)cyclohex-1-en-1-yl)malononitrile $CDCl_3$ (9d)



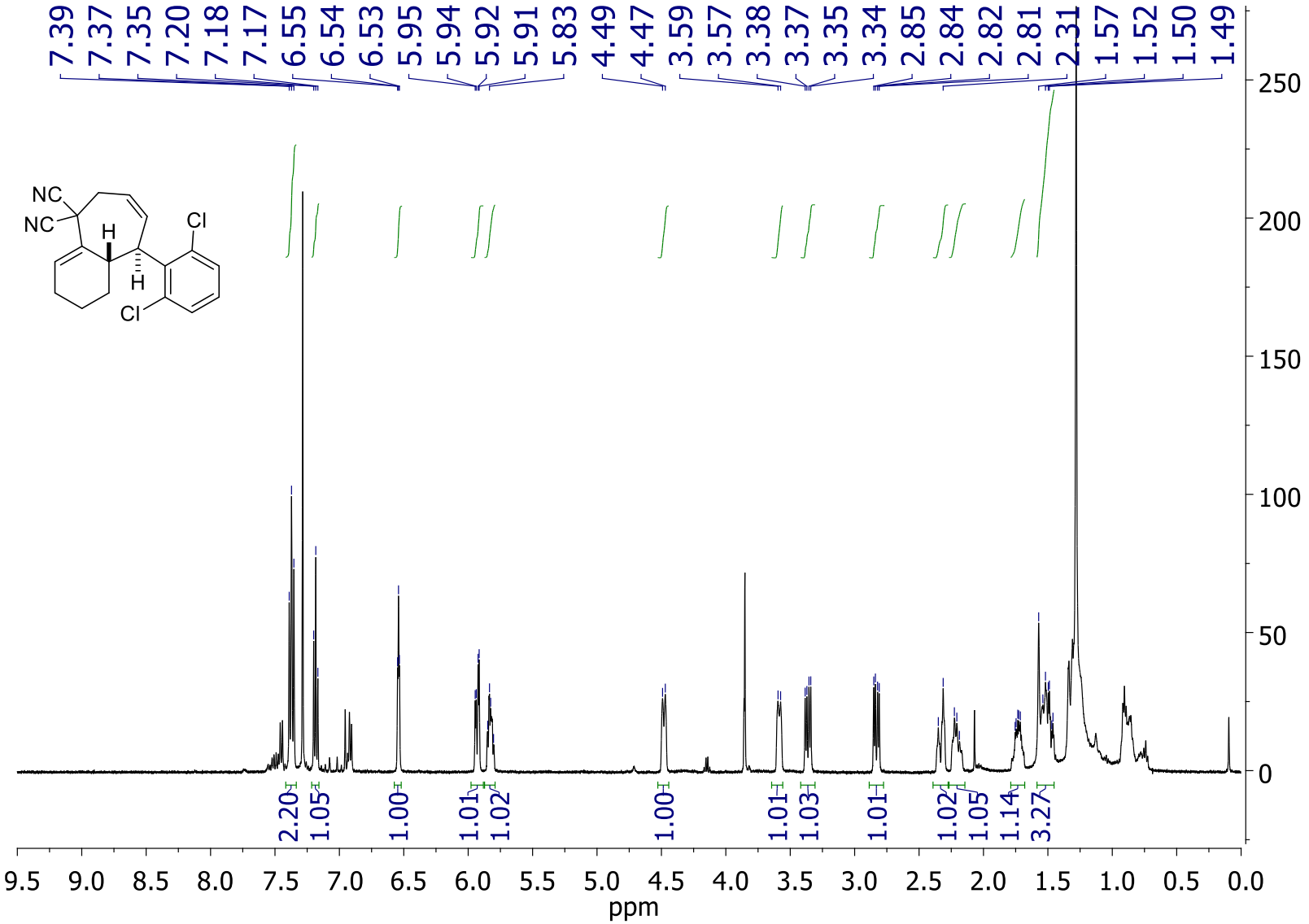
^{1}H NMR spectrum of 9-(4-nitrophenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (10a)



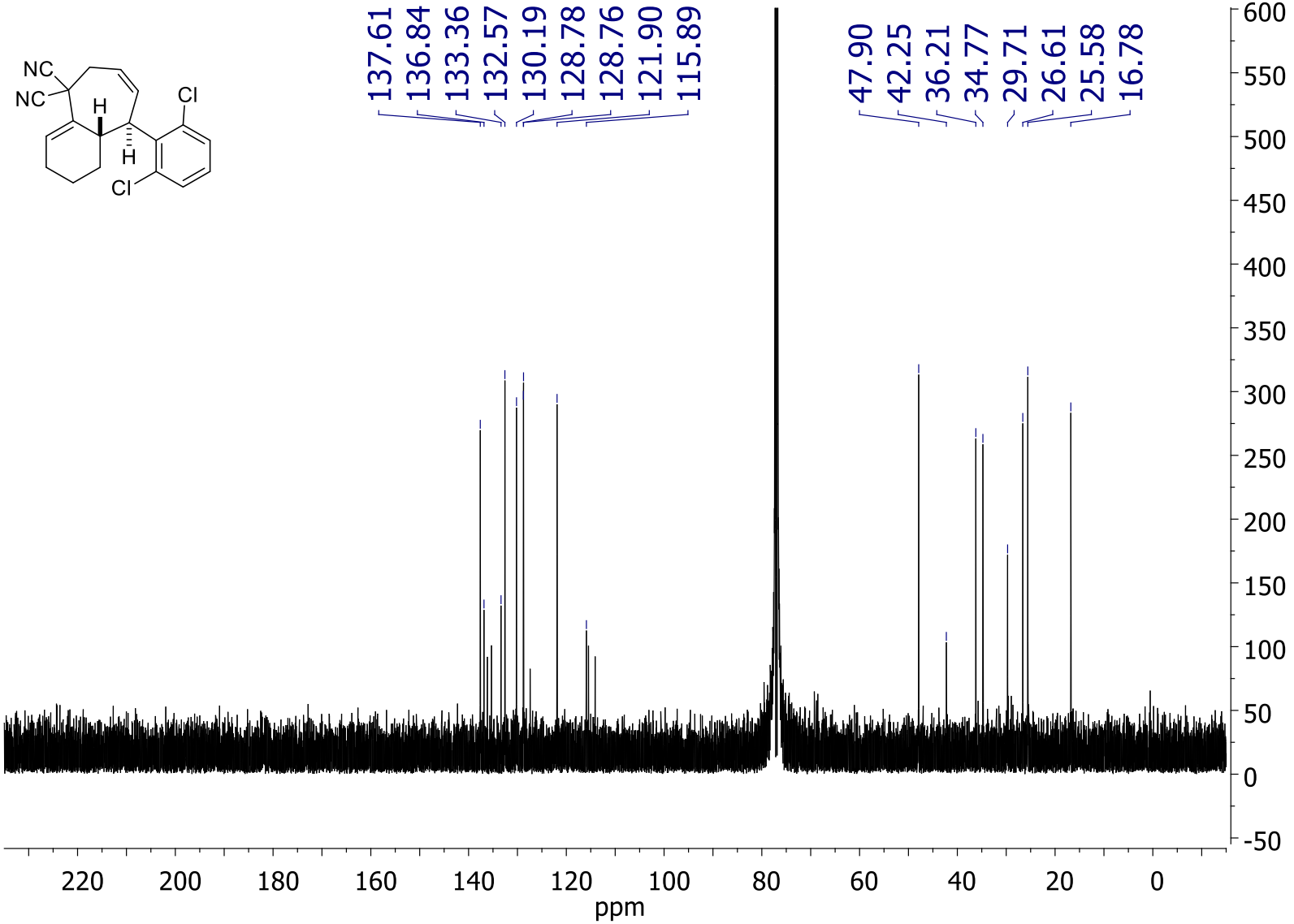
^{13}C NMR spectrum of 9-(4-nitrophenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (10a)



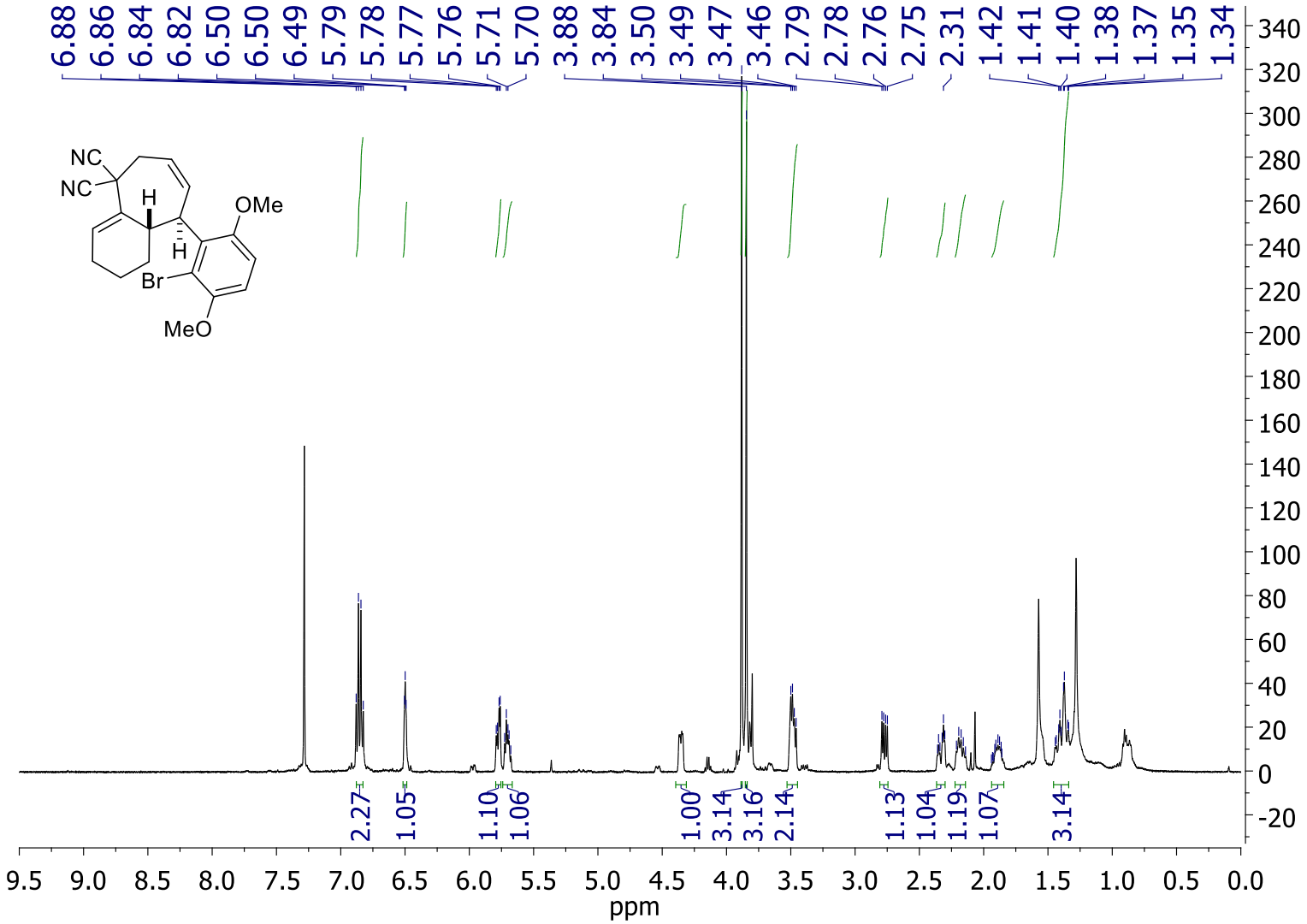
^{1}H NMR spectrum of 9-(2,6-dichlorophenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (10b)



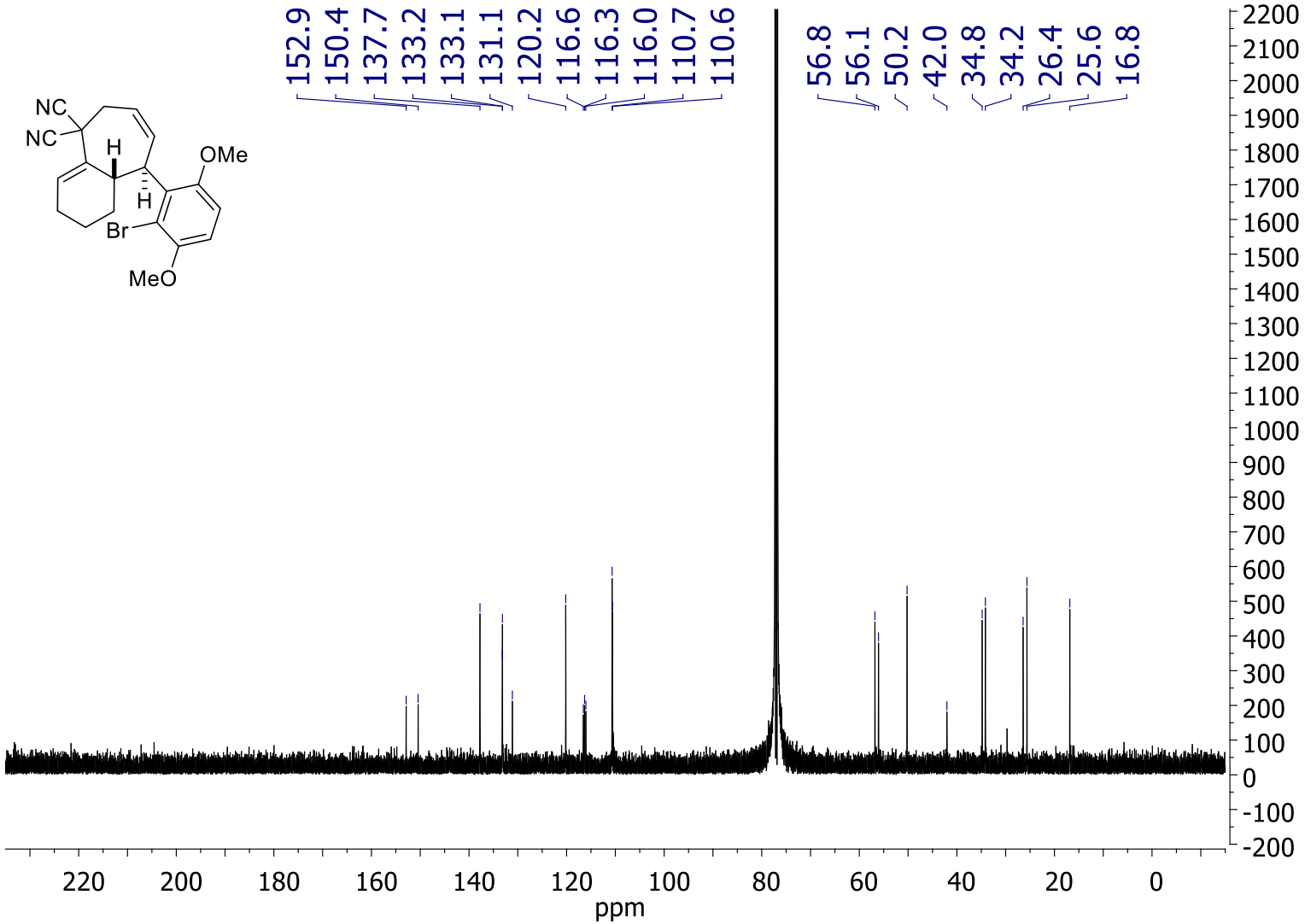
^{13}C NMR spectrum of 9-(2,6-dichlorophenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (10b)



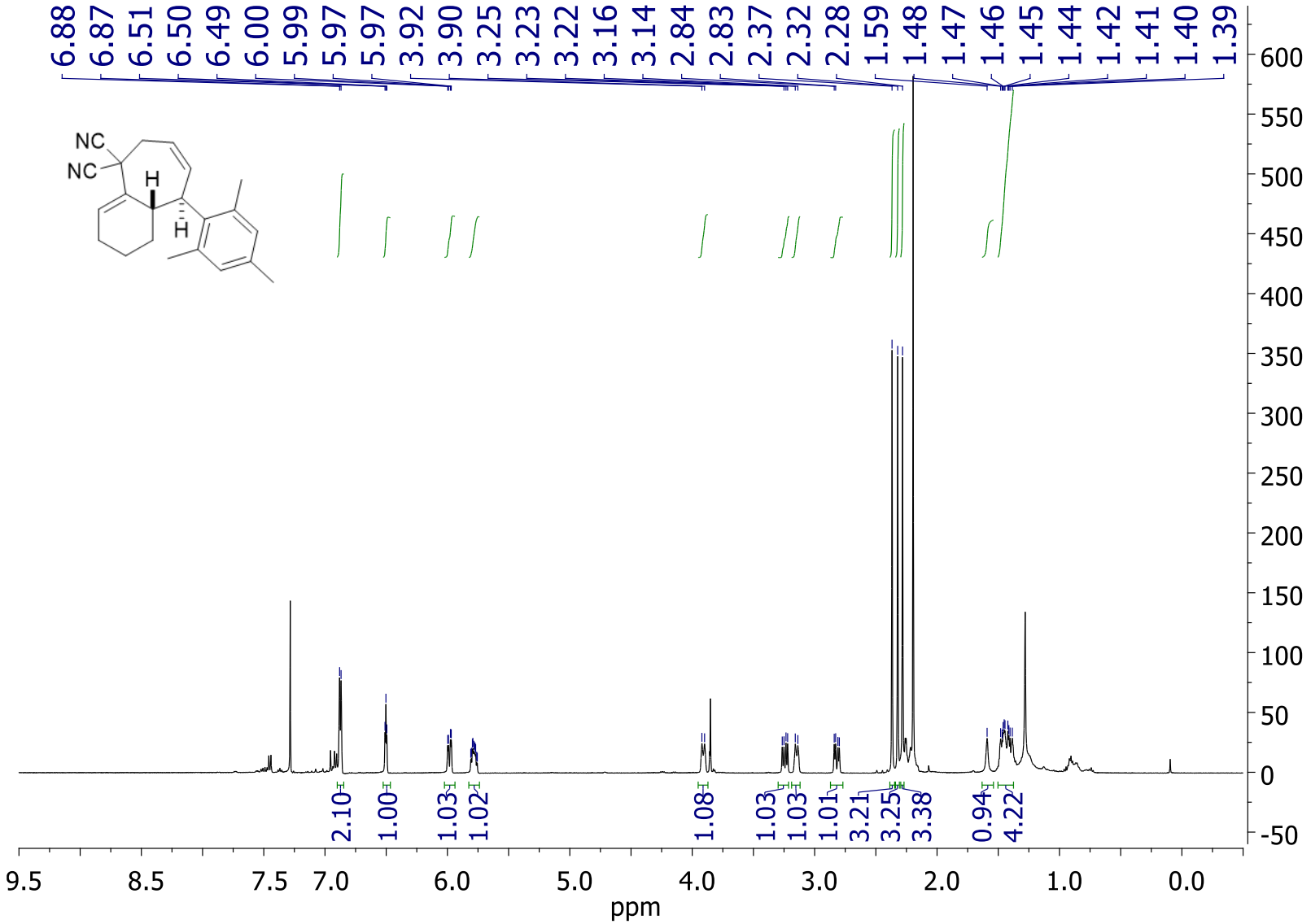
^{1}H NMR spectrum of 9-(2-bromo-3,6-dimethoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (10c)



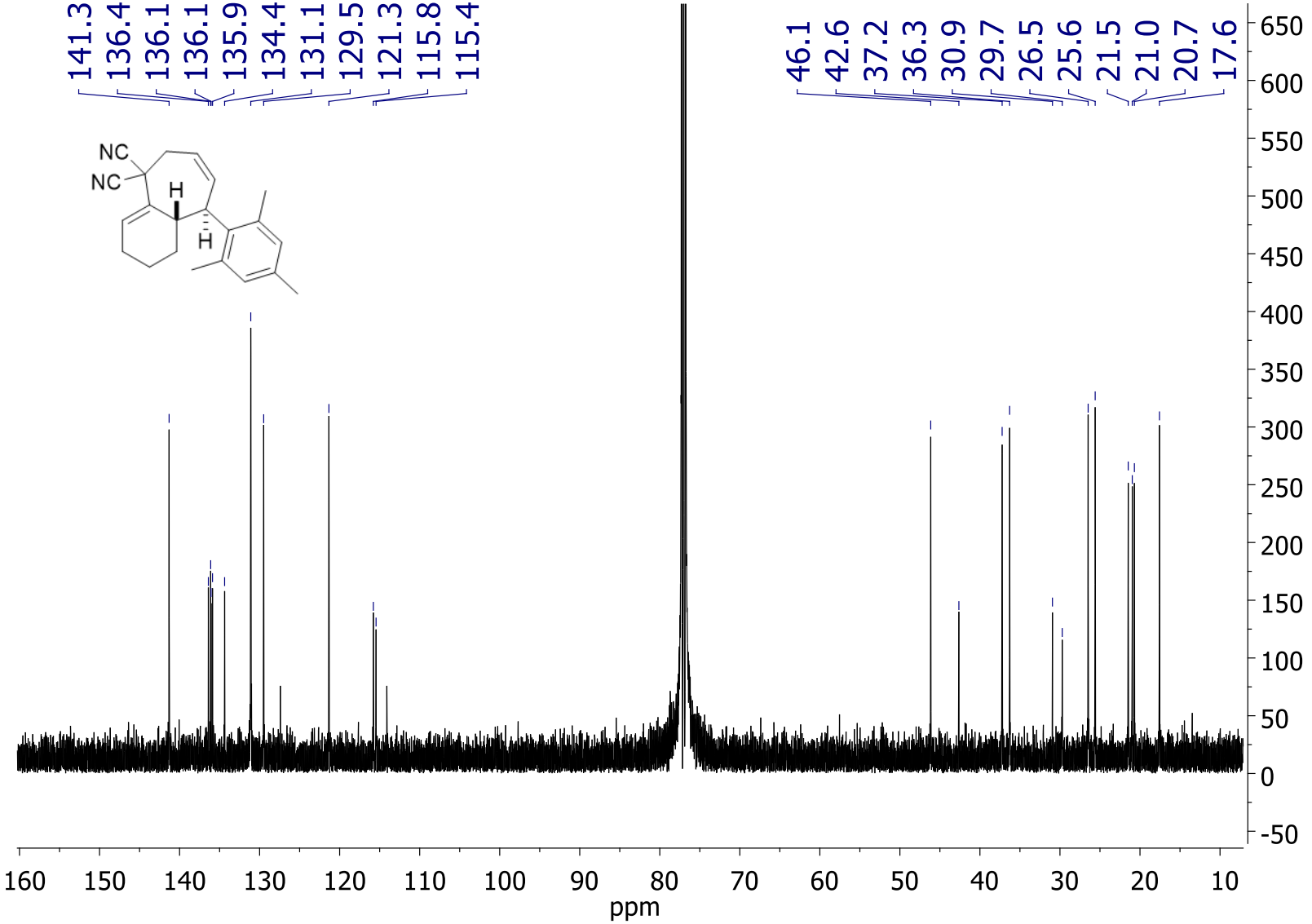
^{13}C NMR spectrum of 9-(2-bromo-3,6-dimethoxyphenyl)-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (10c)



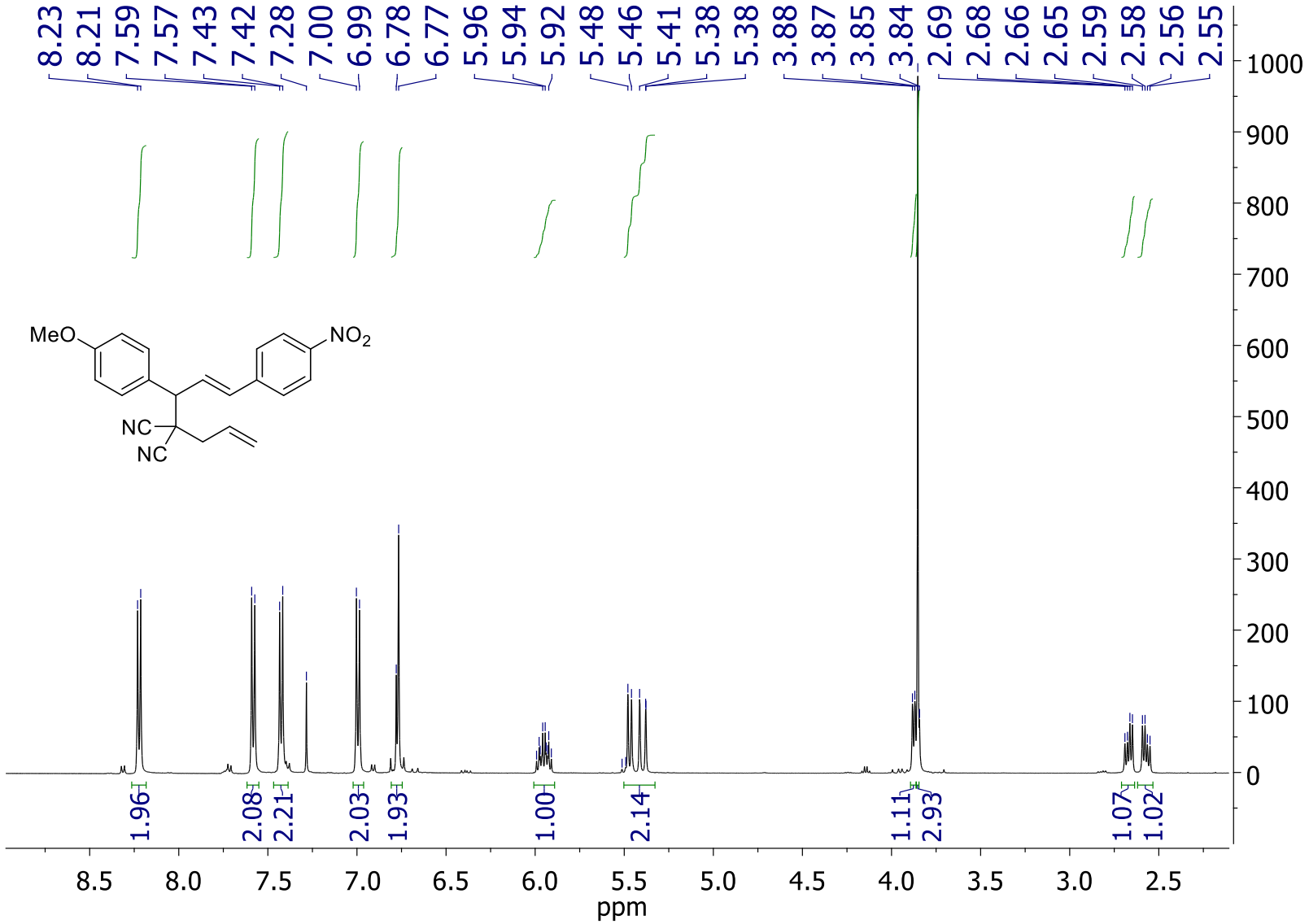
^{1}H NMR spectrum of 9-mesityl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (10d)



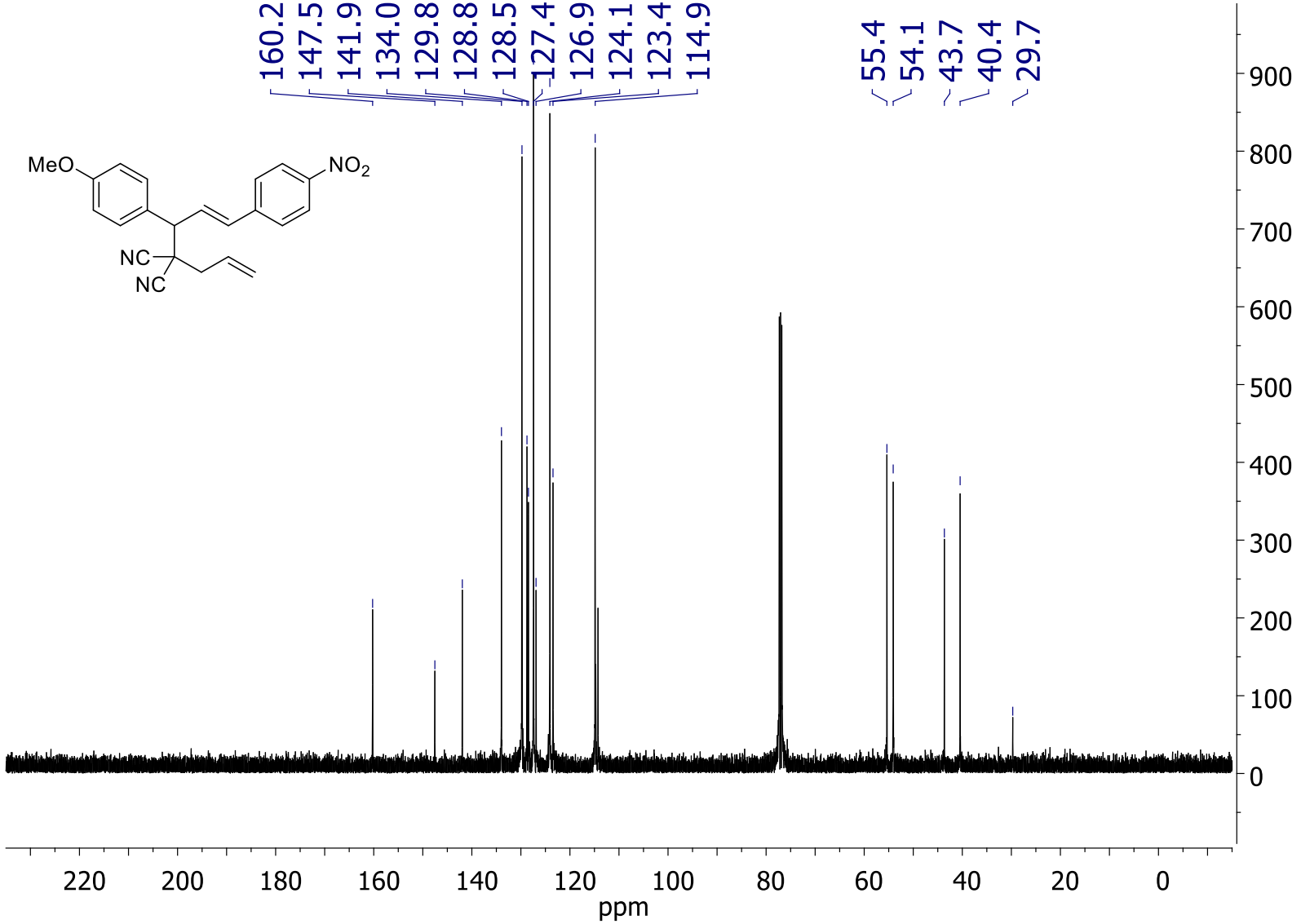
^{13}C NMR spectrum of 9-mesityl-1,2,3,6,9,9a-hexahydro-5H-benzo[7]annulene-5,5-dicarbonitrile $CDCl_3$ (10d)



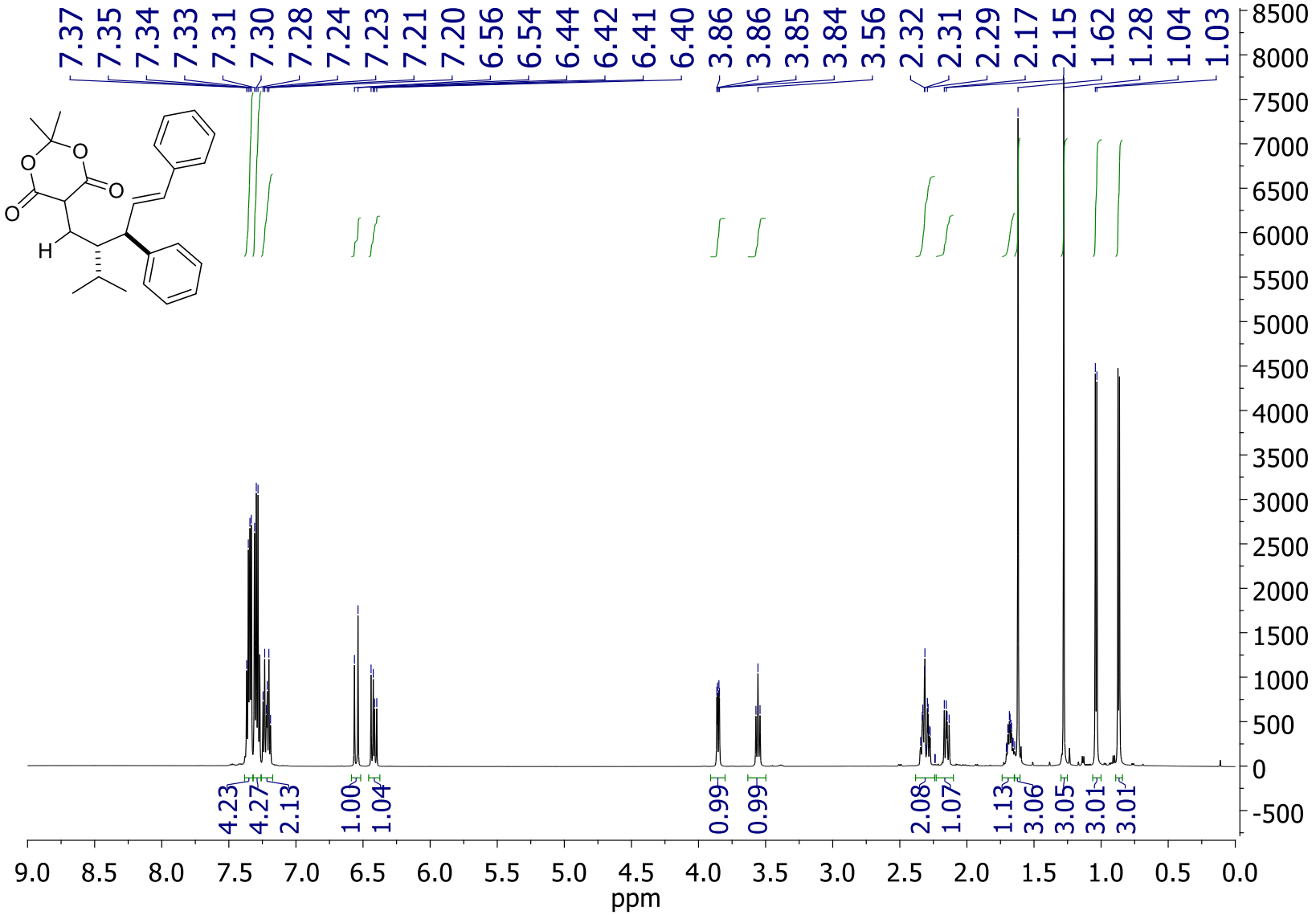
^{1}H NMR spectrum of (E)-2-allyl-2-(1-(4-methoxyphenyl)-3-(4-nitrophenyl)allyl)malononitrile $CDCl_3$ (11b)



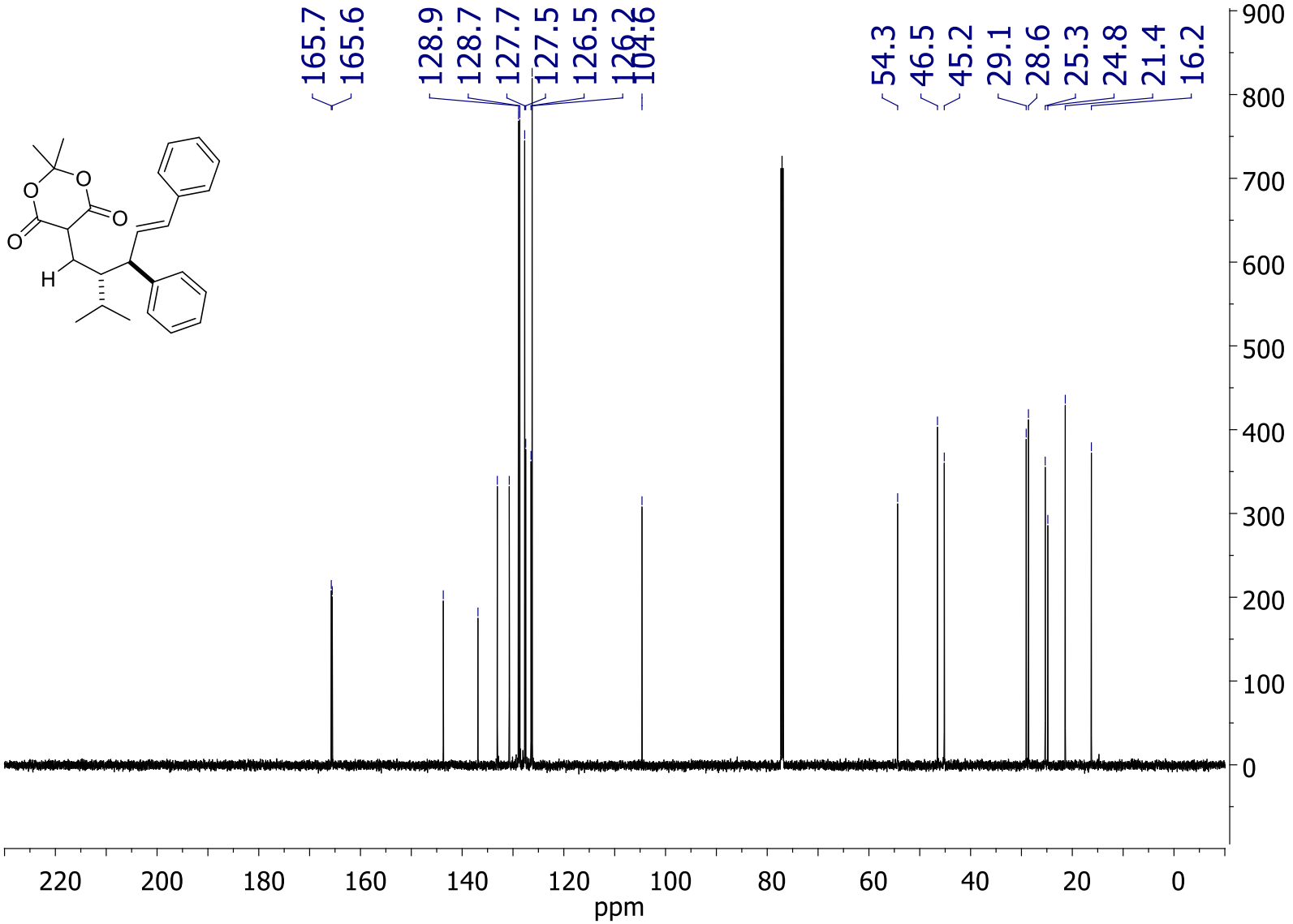
^{13}C NMR spectrum of (E)-2-allyl-2-(1-(4-methoxyphenyl)-3-(4-nitrophenyl)allyl)malononitrile $CDCl_3$ (11b)



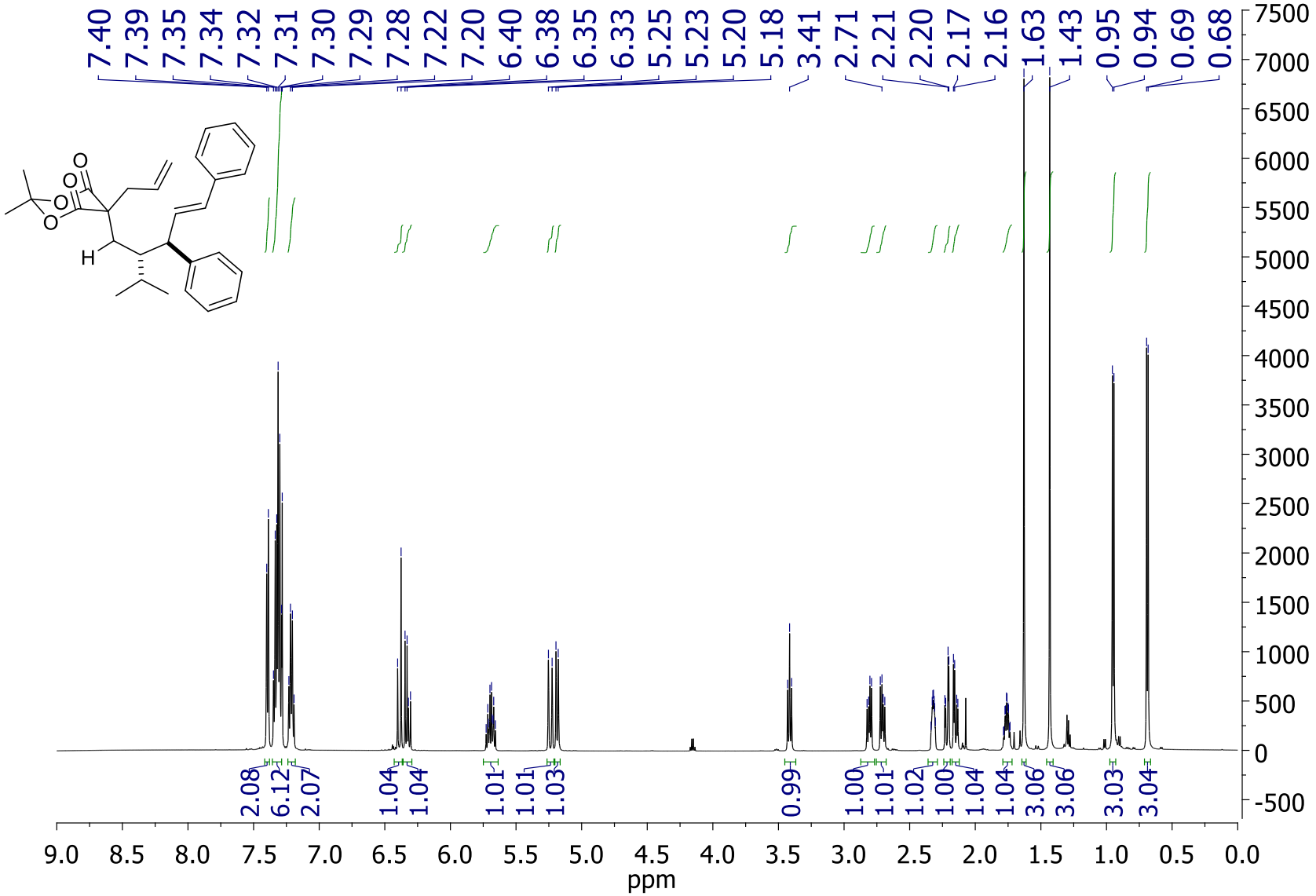
^{1}H NMR spectrum of (E)-5-(2-isopropyl-3,5-diphenylpent-4-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione $CDCl_3$ (12b)



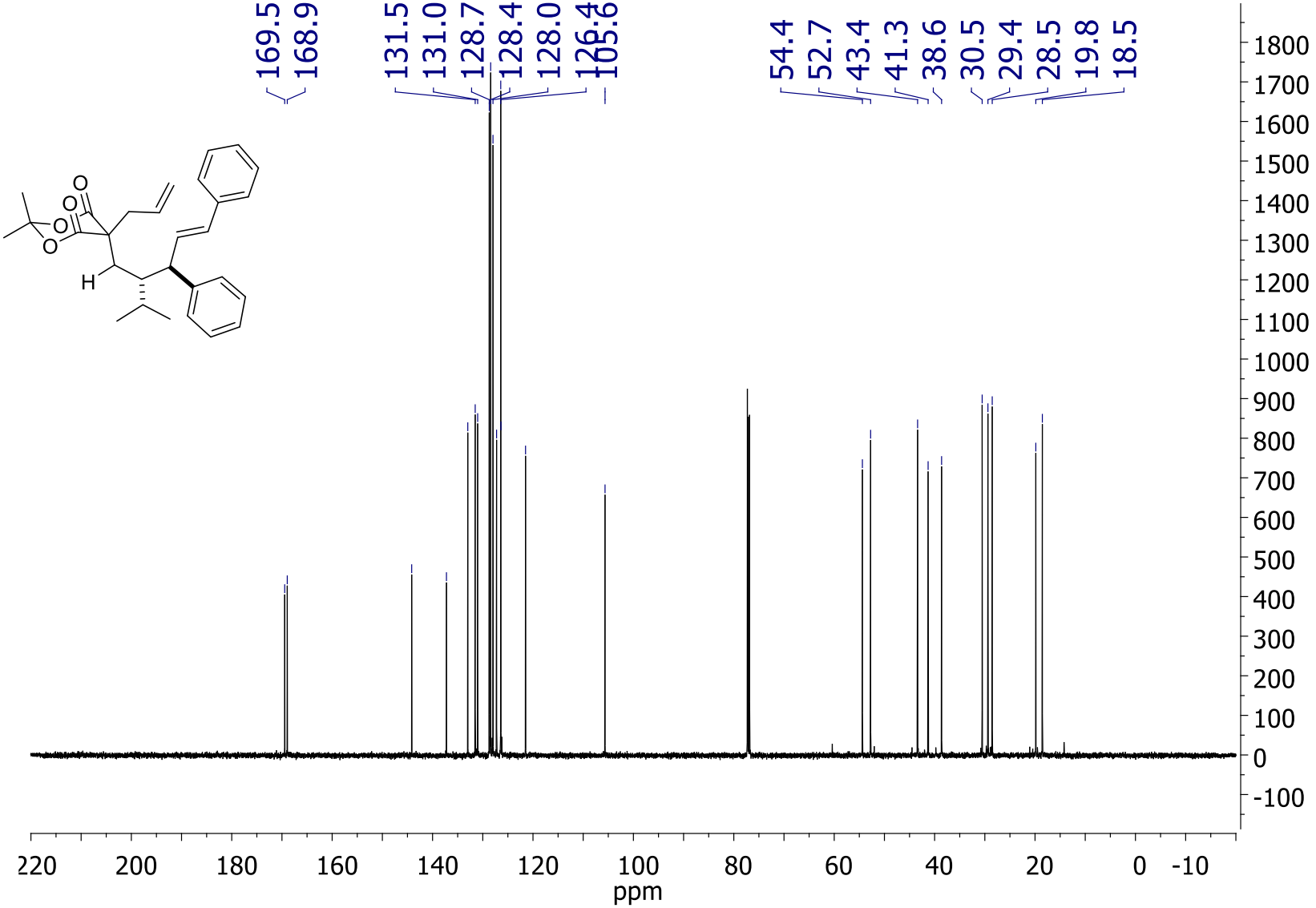
^{13}C NMR spectrum of (E)-5-(2-isopropyl-3,5-diphenylpent-4-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione $CDCl_3$ (12b)



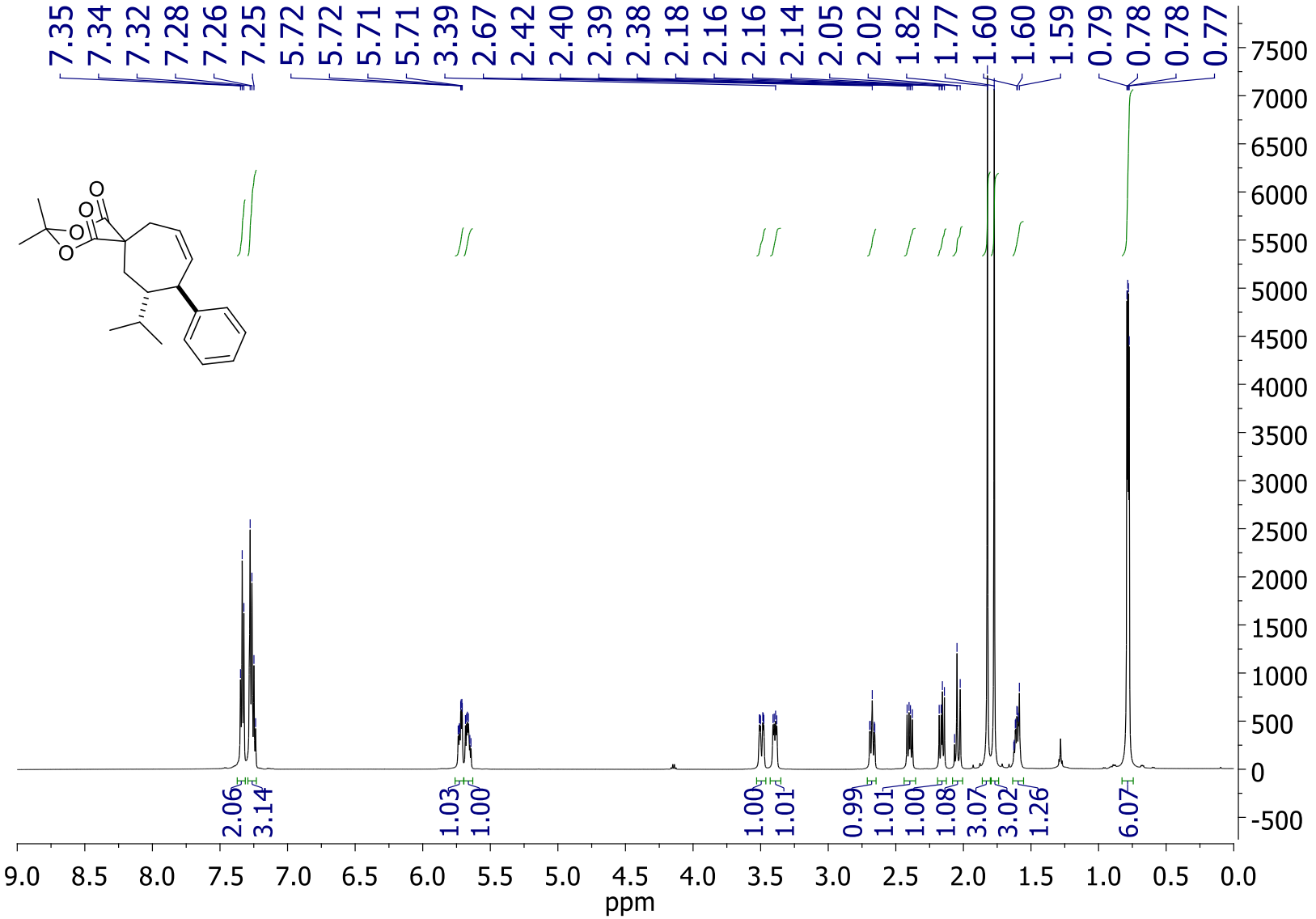
^{1}H NMR spectrum of (E)-5-allyl-5-(2-isopropyl-3,5-diphenylpent-4-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione $CDCl_3$ (12b-2)



^{13}C NMR spectrum of (E)-5-allyl-5-(2-isopropyl-3,5-diphenylpent-4-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione $CDCl_3$ (12b-2)



^{1}H NMR spectrum of (E)-5-(2-isopropyl-3,5-diphenylpent-4-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione $CDCl_3$ (12c)



^{13}C NMR spectrum of (E)-5-(2-isopropyl-3,5-diphenylpent-4-en-1-yl)-2,2-dimethyl-1,3-dioxane-4,6-dione $CDCl_3$ (12c)