Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for:

Visible light-mediated intermolecular [2+2] photocycloaddition of 1-aryl-2-nitroethenes and olefins: Reaction scope and mechanistic studies

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Table of Contents

1. General Information

All preparations and manipulations of air and moisture sensitive compounds were carried out in flame dried glassware under an argon atmosphere using standard *Schlenk* techniques. Reactions at 0 °C were performed using an ice water cooling bath, reactions at −78 °C were performed using a dry ice/*iso*-propanol cooling bath. Tetrahydrofuran and dichloromethane were obtained water and oxygen free by a *Braun* MB SPS purification system using argon as inert gas and MB-Kol-M (3 Å molecular sieves) and MB-Kol-A (activated Al_2O_3) columns to remove residual water. Other dry solvents [acetonitrile (MeCN), methanol (MeOH), dimethylsulfoxide (DMSO); ≥ 99.8 % puritiy] were purchased from *Acros Organics*, *Sigma Aldrich* or *Fluka* and were used without further purification. Solvents for photochemical reactions were degassed in a continuous argon flow for 15 minutes, during which the previously flame-dried flask was placed inside an ultrasonic bath. Molecular sieves (3 or 4 Å) was added and the solvent was stored in a *Schlenk* flask under an argon atmosphere. Ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), pentane (P), cyclohexane (cHex), methanol (MeOH), toluene (Tol) and diethyl ether (Et_2O) for column chromatography, thin layer chromatography or aqueous work-ups were distilled prior to use. Unless stated otherwise, all chemicals were purchased from commercial sources and used without further purification. Argon (4.8) and hydrogen (5.0) were obtained from *Westfalen* AG and were used without further purification.

2. Analytical Methods and Equipment

Irradiation experiments were performed in a *Rayonet* RPR-100 photochemical reactor (Southern New England Ultra Violet Company, Branford, CT, USA) or similarly designed replicas equipped with fluorescence lamps with λ_{max} = 419 nm (16 lamps, cool white, 8 W, *Osram*).[1] Duran glass phototubes were used for irradiation experiments. Irradiation experiments at lower temperatures were performed with a *Huber* high-performance cryostate. Irradiation experiments with light emitting diodes (LEDs) were performed in *Schlenk* tubes (Ø = 1.0 cm). High power LEDs with λ_{max} = 424 nm (*Roithner* Lasertechnik, 350 mA, UF ~ 3.4 V) or λ_{max} = 382 nm (*Avonec*, 700 mA, UF ~ 3.8 V), which were mounted on a passive heat sink, were used as the light source. The light was transmitted into the reaction via a Quarz glass rod (Ø = 0.8 cm). Flash Column Chromatography was performed with silica 60 (*Merck*, 230-400 mesh) as the stationary phase. The eluent mixtures and the diameter of the column are indicated at each experiment individually. Thin Layer Chromatography (TLC) was performed on silica coated glass plates (*Merck*, silica 60, F_{254}) with detection by UV light (λ = 254 nm) and/or by staining with a potassium permanganate solution [$KMnO_4$; potassium

permanganate (3.00 g), potassium carbonate (20.0 g) and aqueous sodium hydroxide solution (5 wt-%, 5.00 mL) in water (300 mL)] or with a cerium ammonium molybdate solution [CAM; cerium sulfate tetrahydrate (1.00 g), ammonium molybdate (25.0 g) and concentrated sulfuric acid (25.0 mL) in water (250 mL)] followed by heat treatment. Infrared (IR) Spectra were recorded on a *Perkin Elmer* Frontier IR FTR spectrometer by ATR technique. The signals are given in $\tilde{\nu}$ [cm^{-1}] and the signal intensity is assigned using the following abbreviations: br (broad), vs (very strong), s (strong), m (medium), w (weak). Nuclear Magnetic Resonance (NMR) Spectra were recorded at room temperature either on a *Bruker* AVHD 300, AVHD 400, AVHD 500 or an AV 500 cryo. ^{1}H NMR spectra were referenced to the residual proton signal of $CDCl_3$ (δ = 7.26 ppm) or C_6D_6 (δ = 7.16 ppm). ^{13}C NMR spectra were referenced to the ^{13}C-D triplet of $CDCl_3$ (δ = 77.16 ppm) or to the ^{13}C-D triplet of C_6D_6 (δ = 128.06 ppm). Apparent multiplets which occur as a result of coupling constant equality between magnetically nonequivalent protons are marked as virtual (*virt*.). The following abbreviations for single multiplicities were used: br broad, s singlet, d doublet, t triplet, q quartet, quint quintet, sext sextet, sept septet. Assignment and multiplicity of the ^{13}C NMR signals were determined by two-dimensional NMR experiments (COSY, HSQC, HMBC). Melting Points were determined using a *Kofler* melting point apparatus ("Thermopan", *Reichert*), with a range quoted to the nearest whole number. Mass Spectrometry (MS) was measured on an *Agilent* system [mass detection: *Agilent* 5973 Network Mass Selective Detector (EI, 70 eV)], which was coupled to a GC [*Agilent* 6890, column: HP-5MS (Dimethylpolysiloxane, 30 m), carrier gas: Helium]. High Resolution Mass Spectrometry (HRMS) was measured on a *Thermo Scientific* LTQ FT Ultra (ESI) or a *Thermo Scientific* DFS HRMS spectrometer (EI). UV/Vis Spectroscopy was measured on a *Perkin Elmer* Lambda 35 UV/Vis spectrometer. Spectra were recorded using a *Hellma* precision cell made of quartz SUPRASIL® with a pathway of d = 1 mm. Solvents and concentrations are given for each spectrum. Luminescence Spectroscopy was measured on a *Horiba Scientific* Fluoromax-4 spectrofluorometer. The samples were prepared in a *Hellma* precicion cell (Quarz SUPRASIL® (exc.: 4mm/emi.: 10 mm).

Data sheet LED (λ_{max} = 382 nm):

Lehrstuhl OC 1 - TUM

200 nm 250 nm 300 nm 350 nm 400 nm 450 nm 500 nm 550 nm 600 nm 650 nm

Datasheet LED033 Av-380-3W

Basic Information

Type	High-Power-LED
Description	Avonec 370-380 nm / 3 W
Manufacturer / Supplier	n/a / Avonec
Order number / Date of purch.	n/a / 07/2016
Internal lot / serial number	2016-07 / LED033

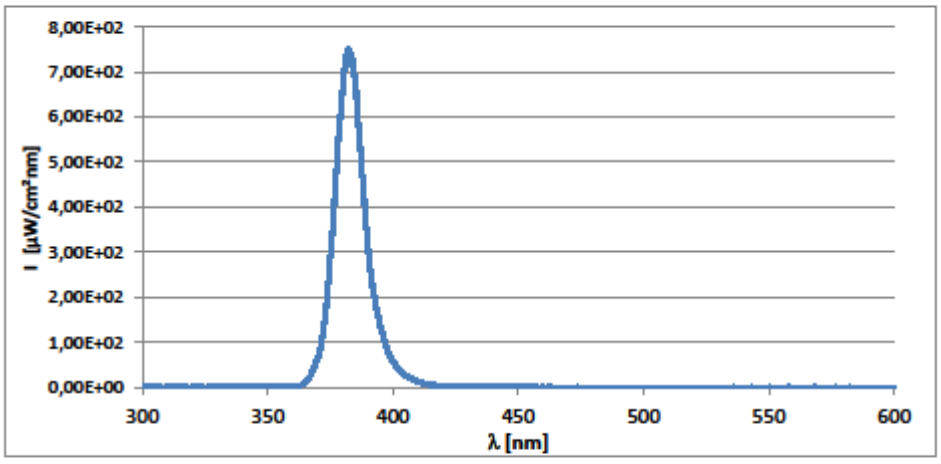
Specification Manufacturer

Type / size	single emitter / ca. 1 x 1 mm
Mechanical specification	
Electrical specification	700 mA, UF 3.8 V
Wavelength (range, typ.)	380-390 nm, typ. n/a
Spectral width (FWHM)	n/a
Datasheet	n/a

Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 700 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	382 nm
Measured spectral width	13 nm
Integral Reference intensity	11360 µW/cm² (350-425 nm @ 20 mm distance, 4 mmcosine corr.)

Spectrum



Data sheet LED (λ_{max} = 424 nm):

Lehrstuhl OC 1 - TUM

200 nm 250 nm 300 nm 350 nm 400 nm 450 nm 500 nm 550 nm 600 nm 650 nm

Datasheet LED011 H2A1-H420

Basic Information

Type	High-Power-LED
Description	H2A1-H420
Manufacturer / Supplier	n/a / Roithner-Lasertechnik, Wien
Order number / Date of purch.	H2A1-H420 / 2014/04
Internal lot / serial number	H2A1-H420_2014/04 / LED011

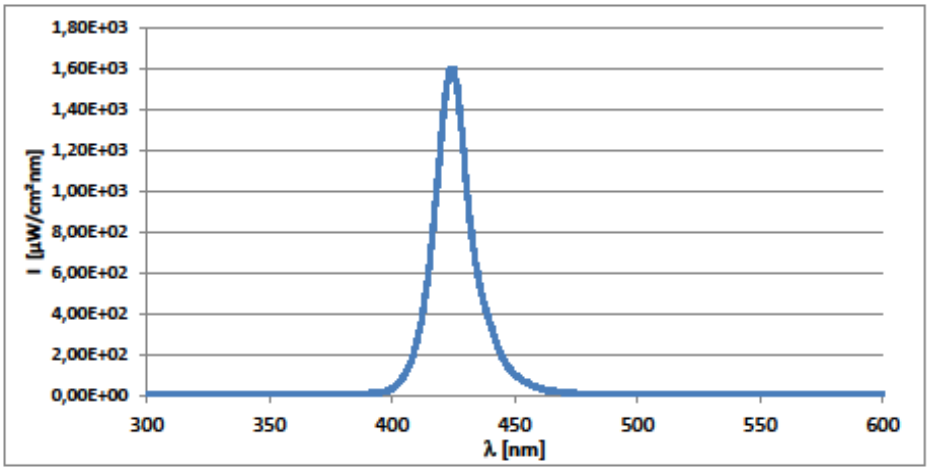
Specification Manufacturer

Type	single emitter, InGaN
Mechanical specification	hexagonal mount
Electrical specification	<500 mA, UF~3,4 V. abs. max. 500 mA
Wavelength (range, typ.)	420 nm
Spectral width (FWHM)	20 nm
Datasheet	h2a1-h420.pdf

Characterization

Description of measurement	Measured with Ocean-optics USB4000 spectrometer using a calibrated setup (cosine corrector/fibre). The distance between the emitting surface and the surface of the cosine corrector was 20 mm. The LED was operated at 350 mA on a passive heat-sink at approx. 20 °C
Measured wavelength	424 nm
Measured spectral width	17 nm
Integral Reference intensity	3,44 mW/mm² (350 mA, 390-490 nm @ 20 mm distance, 4 mm cc) 4,62 mW/mm² (500 mA, 390-490 nm @ 20 mm distance, 4 mm cc)

Spectrum



3. Synthesis of nitroethenes 1b-1o

trans-β-Nitrostyrene (**1a**) was purchased from Sigma Aldrich (99% purity). The syntheses and analytical data for nitroethenes **1b-1e** have already been published in a communication.[2]

General Procedure 1 (GP 1) for the synthesis of nitroethenes:

Based on a literature-known procedure,[3] a solution of the aromatic aldehyde (1.00 equiv), nitromethane (3.00 – 35.0 equiv) and NH_4OAc (1.00 – 2.50 equiv) in glacial acetic acid (the concentration is indicated in every experiment individually) was heated at reflux. The progress of the reaction was monitored via TLC. When full conversion was reached, the reaction solution was cooled to room temperature and poured onto ice water. The reaction mixture was partitioned between water and either dichloromethate or ethyl acetate (the solvent used is indicated at each experiment individually). The aqueous layer was extracted twice with the respective solvent (the volumen are indicated at each experiment individually). The combined organic layers were washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated *in vacou*. If not noted otherwise, the crude product was purified by column chromatography.

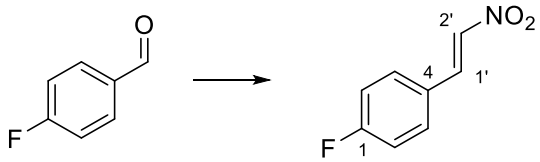
General Procedure 2 (GP 2) for the synthesis of nitroethenes:

Based on a literature-known procedure,[4] a solution of the aromatic aldehyde (1.00 equiv) and NH_4OAc (0.50 equiv) in nitromethane (c = 0.5 M) was heated at reflux. The reaction progress was monitored via TLC. When full conversion was reached, water was added, and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with saturated aqueous NaCl solution, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by recrystallization from ethanol.

General Procedure 3 (GP 3) for the synthesis of nitroethenes:

Based on a literature-known procedure,[5] nitromethane (1.00 equiv) was added to a solution of the aromatic aldehyde (1.00 equiv) in methanol (c = 2 M). NaOH (1.05 equiv; c = 3.5 M solution in water) was added slowly over 30 minutes at 0 °C. The solution was stirred for 30 minutes at 0 °C, warmed to room temperature and was held at that temperature for 30 minutes. The reaction solution was added to a vigorously stirred aqueous hydrochloric acid solution (c = 5 M), which resulted in the formation of a precipitate. The solution was stored at 4 °C overnight, filtered and the precipitate was washed with cold water. The crude product was purified by column chromatography.

(*E*)-1-Fluoro-4-(2‘-nitrovinyl)benzene (1f)



1f
$C_8H_6FNO_4$
MW = 167.14 g/mol

Following **GP 2**, a solution of 4-fluorobenzaldehyde (500 mg, 4.03 mmol, 1.00 equiv) and NH_4OAc (341 mg, 4.43 mmol, 1.10 equiv) in nitromethane (29 mL) was heated at reflux for 16 hours. The work-up was performed with dichloromethane (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 25 cm, P/Et_2O = 19/1) to yield **1f** (375 mg, 2.24 mmol, 57%) as a pale-yellow coloured powder.

TLC: R_f = 0.35 (P/Et_2O = 9/1) [UV, $KMnO_4$].

mp: 98 °C.

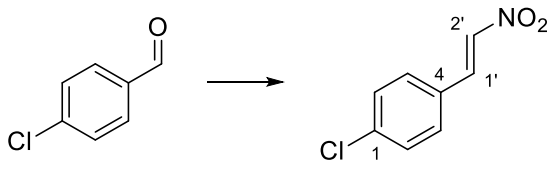
UV-Vis: ε_{315} = 12720 (c = 1 mM, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.98 (d, ^3J = 13.8 Hz, 1H, H-1’), 7.58–7.55 (m, 2H, H-2, H-6), 7.53 (d, ^3J = 13.8 Hz, 1H, H-2‘), 7.19–7.10 (m, 2H, H-3, H-5).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 165.1 (d, $^1J_{CF}$ = 254.8 Hz, C-1), 137.9 (d, C-1‘), 137.0 (d, C-2‘), 131.4 (d, $^3J_{CF}$ = 8.9 Hz, C-3, C-5), 126.5 (d, $^4J_{CF}$ = 3.5 Hz, C-4), 116.9 (d, $^2J_{CF}$ = 22.2 Hz, C-2, C-6).

The analytical data match those reported in the literature.[6]

(*E*)-1-Chloro-4-(2‘-nitrovinyl)benzene (1g)



1g
$C_8H_6ClNO_4$
MW = 183.59 g/mol

Following **GP 3**, nitromethane (190 µL, 217 mg, 3.56 mmol, 1.00 equiv) and NaOH (1.1 mL, c = 3.4 M) were added in sequence to a solution of freshly distilled 4-chlorobenzaldehyde (500 mg, 3.56 mmol, 1.00 equiv) in methanol (1.8 mL). The crude product was purified by column chromatography (3 × 20 cm, P/Et_2O = 19/1) to yield **1g** (260 mg, 1.42 mmol, 40%) as yellow coloured needles.

TLC: R_f = 0.42 (P/Et_2O = 9/1) [UV].

mp: 109 °C.

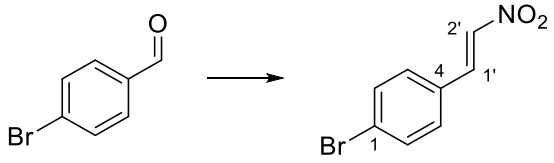
UV-Vis: ε_{319} = 14400 (*c* = 1 mM, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.96 (d, ^3J = 13.7 Hz, 1H, H-1‘), 7.56 (d, ^3J =13.7 Hz, 1H, H-2‘), 7.51–7.47 (m, 2H, H-2, H-6), 7.46–7.42 (m, 2H, H-3, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): 138.5 (s, C-1), 137.8 (d, C-1’), 137.6 (s, C-4), 130.4 (d, 2C, C-2, C-6), 129.9 (d, 2C, C-3, C-5), 128.7 (d, C-2’).

The analytical data match those reported in the literature.[7]

(*E*)-1-Bromo-4-(2‘-nitrovinyl)benzene (1h)



1h
$C_8H_6BrNO_2$
MW = 228.05 g/mol

Following **GP 1**, a solution of 4-bromobenzaldehyde (1.00 g, 5.40 mmol, 1.00 equiv), nitromethane (10.1 mL, 11.5 g, 189 mmol, 35.0 equiv) and NH_4OAc (500 mg, 6.49 mmol, 1.20 equiv) in glacial acetic acid (20 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (4 × 5 cm, cHex/EtOAc = 5/1) to yield **1h** (1.11 g, 4.85 mmol, 90%) as a yellow coloured crystalline solid.

TLC: R_f = 0.81 (cHex/EtOAc = 2/1) [UV, $KMnO_4$].

mp: 141 °C.

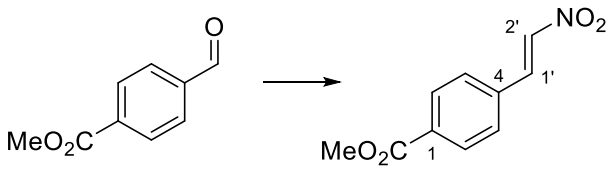
UV-Vis: ε_{322} = 20680 (c = 1 mM, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.95 (d, ^3J = 13.7 Hz, 1H, H-1’), 7.61–7.59 (m, 2H, H-2, H-6), 7.57 (d, ^3J = 13.7 Hz, 1H, H-2’), 7.43–7.40 (m, 2H, H-3, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 137.9 (d, C-1’), 137.6 (d, C-2’), 132.9 (d, 2C, C-2, C-6), 130.5 (d, 2C, C-3, C-5), 129.1 (s, C-1), 126.9 (s, C-4).

The analytical data match those reported in the literature.[7]

Methyl (*E*)-4-(2'-nitrovinyl)benzoate (1i)



1i
$C_{10}H_9NO_4$
MW = 207.19 g/mol

Following **GP 1**, a solution of methyl 4-formylbenzoate (500 mg, 3.05 mmol, 1.00 equiv), NH_4OAc (141 mg, 1.83 mmol, 0.60 equiv) and nitromethane (197 µL, 223 mg, 3.65 mmol, 1.20 equiv) in glacial acetic acid (2.5 mL) was heated at reflux for six hours. The work-up was performed with ethyl acetate (2 × 10 mL) as the solvent. The crude product was purified by column chromatography (3 × 20 cm, CH_2Cl_2) to yield **1i** (508 mg, 2.45 mmol, 80%) as a pale yellow coloured crystalline solid.

TLC: R_f = 0.40 (CH_2Cl_2) [UV].

mp: 145 °C.

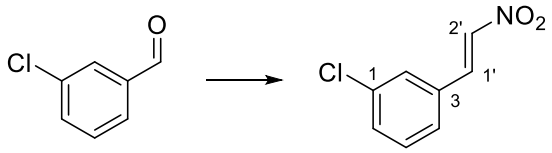
UV-Vis: ε_{311} = 20190 (*c* = 1 mM, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.13–8.10 (m, 2H, H-2, H-6), 8.02 (d, ^3J = 13.7 Hz, 1H, H-1'), 7.64–7.60 (m, 3H, H-2', H-3, H-5), 3.95 (s, 3H, CO_2CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 168.6 (s, *C*O_2Me), 138.8 (d, C-2'), 137.7 (d, C-1'), 134.3 (s, C-1), 133.2 (s, C-4), 130.6 (d, 2C, C-2, C-6), 129.1 (d, 2C, C-3, C-5), 52.7 (q, ArCO_2*C*H_3).

The analytical data match those reported in the literature.[7]

(*E*)-1-Chloro-3-(2‘-nitrovinyl)benzene (1j)



1j
$C_8H_6ClNO_2$
MW = 183.59 g/mol

Following **GP 1**, a solution of freshly distilled 3-chlorobenzaldehyde (1.00 g, 21.3 mmol, 1.00 equiv), nitromethane (3.43 mL, 3.91 g, 64.0 mmol, 3.00 equiv) and NH_4OAc (4.11 g, 53.4 mmol, 2.50 equiv) in glacial acetic acid (10 mL) was heated at reflux for six hours. The work-up was performed with dichloromethane (2 × 30 mL) as the solvent. The crude product was purified by column chromatography (6 × 12 cm, cHex/EtOAc = 20/1) to yield **1j** (2.80 g, 15.3 mmol, 71%) as a yellow coloured solid.

TLC: R_f = 0.22 (cHex/EtOAc = 9/1) [UV, $KMnO_4$].

mp: 62 °C.

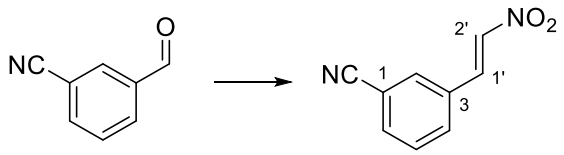
UV-Vis: ε_{302} = 15690 (*c* = 1 mM, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.94 (d, ^3J = 13.7 Hz, 1H, H-1’), 7.56 (d, ^3J = 13.7 Hz, 1H, H-2’), 7.56−7.54 (m, 1H, H-2), 7.49−7.40 (m, 3H, H-3, H-4, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.3 (d, C-2’), 137.6 (d, C-1’), 135.6 (s, C-3), 132.1 (d, C-4) 131.9 (s, C-1), 130.8 (d, C-5), 128.9 (d, C-2), 127.4 (d, C-6).

The analytical data match those reported in the literature.[8]

(*E*)-3-(2'-Nitrovinyl)benzonitrile (1k)



1k
$C_9H_6N_2O_2$
MW = 174.16 g/mol

Following **GP 1**, a solution of freshly distilled 3-formylbenzonitrile (1.00 g, 7.63 mmol, 1.00 equiv), nitromethane (1.22 mL, 1.40 g, 22.9 mmol, 3.00 equiv) and NH_4OAc (1.47 g, 19.1 mmol, 2.50 equiv) in glacial acetic acid (4 mL) was heated at reflux for six hours. The work-up was performed with dichloromethane (2 × 10 mL) as the solvent. The crude product was purified by column chromatography (5 × 15 cm, cHex/EtOAc = 20/1) to yield **1k** (720 mg, 4.13 mmol, 54%) as a beige coloured crystalline solid.

TLC: R_f = 0.59 (cHex/EtOAc = 9/1) [UV, $KMnO_4$].

mp: 123 °C.

UV-Vis: ε_{293} = 16300 (*c* = 1 mM, CH_2Cl_2).

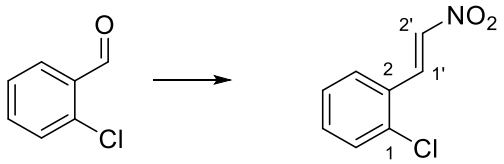
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.00 (d, ^3J = 13.7 Hz, 1H, H-1'), 7.86 (t, ^4J = 1.7 Hz, 1H, H-2), 7.81 (dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 2H, H-4, H-6), 7.63 (t, ^3J = 7.7 Hz, 1H, H-5), 7.62 (d, ^3J = 13.7 Hz, 1H, H-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.1 (d, C-1'), 136.4 (d, C-2'), 134.9 (d, C-4)*, 132.8 (d, C-6)*, 132.4 (d, C-2), 131.6 (s, C-1), 130.5 (d, C-5), 117.6 (s, C_{ar}*C*N), 114.2 (s, C-3).

*The assignments are interconvertible.

The analytical data match those reported in the literature.[9]

(*E*)-1-Chloro-2-(2‘-nitrovinyl)benzene (1l)



1l
$C_8H_6ClNO_2$
MW = 183.59 g/mol

Following **GP 1**, a solution of freshly distilled 2-chlorobenzaldehyde (2.42 mL, 1.00 g, 21.3 mmol, 1.00 equiv), nitromethane (3.43 mL, 3.91 g, 64.0 mmol, 3.00 equiv) and NH_4OAc (4.11 g, 53.4 mmol, 2.50 equiv) in glacial acetic acid (10 mL) was heated at reflux for six hours. The work-up was performed with dichloromethane (2 × 30 mL) as the solvent. The crude product was purified by column chromatography (6 × 12 cm, cHex/EtOAc = 20/1) to yield **1l** (1.51 g, 822 mmol, 38%) as an orange coloured crystalline solid.

TLC: R_f = 0.21 (cHex/EtOAc = 9/1) [UV, $KMnO_4$].

mp: 48 °C.

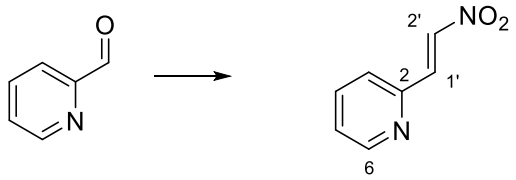
UV-Vis: ε_{305} = 14240 (c = 1 mM, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): 8.41 (d, ^3J = 13.8 Hz, 1H, H-1’), 7.59 (d, ^3J = 13.8 Hz, 1H, H-2), 7.61–7.57 (m, 1H, H-3), 7.53–7.48 (m, 1H, H-6), 7.46–7.39 (m, 1H, H-4), 7.37–7.31 (m, 1H, H-5).

^{13}C NMR (101 MHz, $CDCl_3$): 139.0 (d, C-1’), 136.2 (s, C-2), 135.2 (d, C-1’), 133.0 (d, C-4), 130.9 (d, C-6), 128.8 (d, C-3), 128.7 (s, C-1), 127.6 (d, C-5).

The analytical data match those reported in the literature.[8]

(*E*)-2-(2'-Nitrovinyl)pyridine (1m)



1m
$C_7H_6N_2O_2$
MW = 150.14 g/mol

Following **GP 1**, a solution of picolinaldehyde (877 µL, 1.00 g, 9.34 mmol, 1.00 equiv), NH_4OAc (863 mg, 11.2 mmol, 1.20 equiv) and nitromethane (10.0 mL, 11.4 g, 187 mmol, 20.0 equiv) in glacial acetic acid (20 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (4 × 15 cm, CH_2Cl_2/MeOH = 99/1 → 95/5) to yield **1m** (300 mg, 1.99 mmol, 21%) as a brown coloured crystalline solid.

TLC: R_f = 0.21 (CH_2Cl_2/MeOH = 99/1) [UV, $KMnO_4$].

mp: 118 °C.

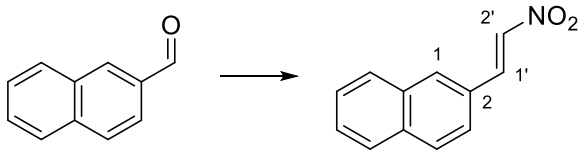
UV-Vis: ε_{304} = 15580 (*c* = 1 mM, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.80 (d, ^3J = 2.3 Hz, 1H, H-3), 8.72 (dd, ^3J = 4.9 Hz, ^4J = 1.6 Hz, 1H, H-6), 8.01 (d, ^3J = 13.8 Hz, 1H, H-1'), 7.87 (*virt*. dt, ^3J = 8.0 Hz, $^3J \cong {}^4J$ = 1.9 Hz, 1H, H-4), 7.63 (d, ^3J = 13.8 Hz, 1H, H-2'), 7.42 (ddd, ^3J = 8.0, 4.9 Hz, 1H, H-5).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 152.7 (d, C-6), 150.4 (d, C-3), 138.4 (d, C-2'), 135.4 (d, C-1'), 135.2 (d, C-4), 126.3 (s, C-2) 124.1 (d, C-5).

The analytical data match those reported in the literature.[6]

(*E*)-2-(2'-Nitrovinyl)naphthalene (1n)



1n
$C_{12}H_9NO_2$
MW = 199.21 g/mol

Following **GP 1**, a solution of 2-naphthaldehyde (1.00 g, 6.40 mmol, 1.00 equiv), NH_4OAc (592 mg, 7.68 mmol, 1.20 equiv) and nitromethane (12.0 mL, 13.7 mg, 224 mmol, 35.0 equiv) in glacial acetic acid (20 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 12 cm, CH_2Cl_2) to yield **1n** (1.10 g, 5.52 mmol, 86%) as a dark yellow coloured crystalline solid.

TLC: R_f = 0.81 (CH_2Cl_2) [UV].

mp: 117 °C.

UV-Vis: ε_{330} = 21770 (c = 1 mM, CH_2Cl_2).

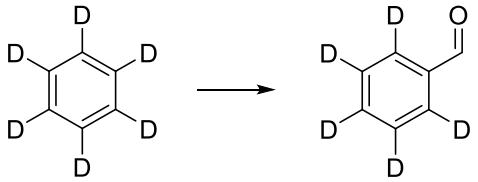
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.17 (d, ^3J = 13.7 Hz, 1H, C-1'), 8.03 (br. s, 1H, H-1), 7.92–7.84 (m, 3H, H_{ar})*, 7.71 (d, ^3J = 13.7 Hz, 1H, C-2'), 7.62–7.54 (m, 3H, H_{ar})*.

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.4 (d, C-1'), 137.3 (d, C-2'), 135.1 (s, C-8a), 133.3 (s, C-4a), 132.4 (d, C-1), 129.5 (d, $C_{ar}H$)*, 128.9 (d, $C_{ar}H$)*, 128.5 (d, $C_{ar}H$)*, 128.1 (d, $C_{ar}H$)*, 127.7 (s, C-2), 127.4 (d, $C_{ar}H$)*, 123.5 (d, $C_{ar}H$)*.

* The exact assignment of these signals was not possible.

The analytical data match those reported in the literature.[7]

Benzaldehyde-2,3,4,5,6-*d*$_5$



C_7HD_5O
MW = 111.15 g/mol

According to a literature known procedure:[10] A solution of benzene-d_6 (1.05 mL, 1.00 g, 11.9 mmol, 1.00 equiv) in dichloromethane (20 mL) was cooled to 0 °C. $TiCl_4$ (2.65 mL, 4.51 g, 23.8 mmol, 2.00 equiv; 1 M solution in CH_2Cl_2) was added slowly. The yellow coloured solution was stirred for five minutes, and freshly distilled dichloromethylmethylether (1.08 mL, 1.37 g, 11.9 mmol, 1.00 equiv) was added dropwise. The reaction solution was stirred for 20 minutes at 0 °C, warmed to room temperature and was stirred at this temperature for further 60 minutes. The reaction mixture was poured onto ice water (50 mL) and was subsequently partitioned between water and dichloromethane (50 mL). The aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined organic layers were washed consecutively with saturated aqueous $NaHCO_3$ solution (150 mL) and saturated aqueous NaCl solution (150 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* (note: due to the volatility of the product, the vacuum should not deceed 200 mbar!). The crude product was purified by column chromatography (4 × 15 cm, P/Et_2O = 5/1) to yield benzaldehyde-2,3,4,5,6-d_5 (660 mg, 5.94 mmol, 50%) as a colorless liquid.

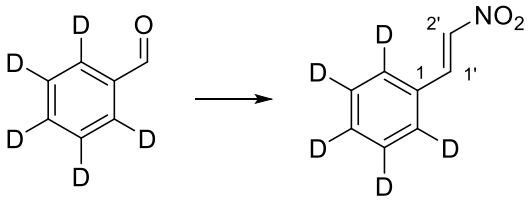
TLC: R_f = 0.54 (P/Et_2O = 2/1) [UV, $KMnO_4$].

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 10.0 (s, 1H, ArCHO).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 171.9 (d, CHO).

The analytical data match those reported in the literature.[10]

(*E*)-1-(2‘-Nitrovinyl)benzene-2,3,4,5,6-*d*$_5$ (1a-*d*$_5$)



1a-*d*$_5$
$C_8H_2D_5NO_2$
MW = 154.18 g/mol

Following **GP 1**, a solution of benzaldehyde-2,3,4,5,6-*d*$_5$ (200 mg, 1.80 mmol, 1.00 equiv), NH_4OAc (166 mg, 2.16 mmol, 1.20 equiv) and nitromethane (3.37 mL, 3.84 g, 63.0 mmol, 35.0 equiv) in glacial acetic acid (5 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 15 cm, P/Et_2O = 5/1) to yield **1a-*d*$_5$** (115 mg, 74.6 mmol, 42%) as yellow coloured needles.

TLC: R_f = 0.56 (P/Et_2O = 20/1) [UV, $KMnO_4$].

mp: 56 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3109 (w), 1629 (m, $R_2C{=}CR_2$), 1506 (s, C-NO_2), 1490 (s), 1331 (s, C-NO_2), 1241 (m), 1160 (m), 973 (s), 960 (s), 845 (s).

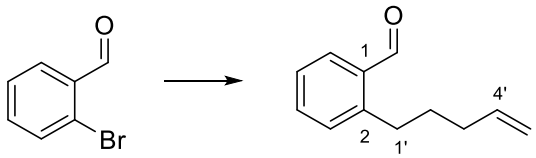
MS (EI, 70 eV): *m/z (%)* = 154 (86) $[M]^+$, 108 (96) $[M\text{-}NO_2]^+$, 96 (100) $[C_7H_2D_5]^+$, 81 (67) $[C_6D_5]^+$.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 8.04 (d, ^3J = 13.7 Hz, 1H, H-1’), 7.61 (d, ^3J =13.7 Hz, 1H, H-2’).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.1 (d, C-1’), 137.3 (d, C-2’), 131.8 (t, $^1J_{CD}$ = 24.4 Hz, C_{ar}D-4), 130.1 (s, C-1), 129.0 (t, 2C, $^1J_{CD}$ = 24.7 Hz, C_{ar}D-3, C_{ar}D-5)*, 128.9 (t, 2C, $^1J_{CD}$ = 24.3 Hz, C_{ar}D-2, C_{ar}D-6)*.

* The assignment is interconvertible.

2-(Pent-4‘-en-1‘-yl)benzaldehyde



$C_{12}H_{14}O$
MW = 174.24 g/mol

According to a modified literature known procedure:[11] The *Grignard* reagent was prepared freshly from activated magnesia (310 mg, 12.8 mmol, 0.95 equiv) and 5-bromopent-1-ene (1.50 mL, 2.00 g, 13.4 mmol, 1.00 equiv) in tetrahydrofuran (13.5 mL). A solution of $ZnCl_2$ (1.77 g, 13.0 mmol, 2.00 equiv) in tetrahydrofuran (12 mL) was added slowly to the stirred solution of the *Grignard* reagent and the reaction solution was stirred at room temperature for 30 minutes. In parallel, 2-(bromomethyl) benzaldehyde (1.20 g, 6.49 mmol, 1.00 equiv) was added to a stirred solution of $Pd_2(dba)_3$ (297 mg, 324 µmol, 0.05 equiv) and RuPhos (453 mg, 971 µmol, 0.10 equiv) in tetrahydrofuran (10 mL). The solution of the aldehyde was added dropwise to the solution of the *Grignard* reagent, resulting in an exothermic reaction. The reaction solution was stirred at room temperature overnight. Saturated aqueous NH_4Cl solution (30 mL) was added to quench the reaction and the reaction mixture was partitioned between the aqueous and the organic layer. The aqueous layer was extracted with diethyl ether (3 × 30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (5 × 10 cm, P/Et_2O = 19/1) to yield 2-(Pent-4‘-en-1‘-yl)benzaldehyde (482 mg, 2.77 mmol, 43%) as a pale-yellow coloured oil.

TLC: R_f = 0.44 (P/Et_2O = 9/1) [UV, $KMnO_4$].

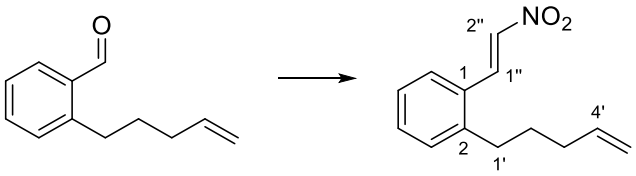
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 10.3 (s, 1H, ArC*H*O), 7.83 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, H_{ar})*, 7.50 (td, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, H_{ar})*, 7.37 (td, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1H, H_{ar})*, 7.28 (dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1H, H_{ar})*, 5.84 (ddt, ^3J = 17.0 Hz, 10.2 Hz, 6.7 Hz, 1H, H-4’), 5.04 (*virt*. dq, ^3J = 17.0 Hz, $^2J \cong {}^4J$ = 1.7 Hz, 1H, C*H*H-5’), 5.00 (ddt, ^2J = 2.3 Hz, ^3J = 10.2 Hz, ^4J = 1.3 Hz, 1H, CH*H*-5’), 3.10–3.00 (m, 2H, CH_2-1’), 2.21-2.09 (m, 2H, CH_2-3’), 1.78–1.67 (m, 2H, CH_2-2’).

^{13}C NMR (75 MHz, $CDCl_3$): δ [ppm] = 192.5 (d, CHO), 145.7 (s, C-1), 138.8 (d, C-4’), 133.0 (d, $C_{ar}H$)*, 131.4 (d, $C_{ar}H$)*, 128.2 (s, C-2), 126.6 (d, $C_{ar}H$)*, 126.1 (d, $C_{ar}H$)*, 114.8 (t, C-5’), 32.0 (t, C-3’), 31.0 (t, C-1’), 26.0 (t, C-2’).

* The exact assignment of these signals was not possible.

The analytical data match those reported in the literature.[12]

(*E*)-1-(2‘‘-Nitrovinyl)-2-(pent-4‘-en-1‘-yl)benzene (1o)



1a **1o**

$C_{13}H_{15}NO_2$

MW = 217.17 g/mol

Following **GP 1**, a solution of 2-(pent-4-en-1-yl)benzaldehyde (200 mg, 1.15 mmol, 1.00 equiv), NH_4OAc (84.1 mg, 1.09 mmol, 0.95 equiv) and nitromethane (2.34 mL, 2.66 g, 43.6 mmol, 38.0 equiv) in glacial acetic acid (5 mL) was heated at reflux for five hours. The work-up was performed with ethyl acetate (2 × 50 mL) as the solvent. The crude product was purified by column chromatography (3 × 15 cm, P/E = 19/1) to yield **1o** (157 mg, 7.23 mmol, 63%) as a yellow coloured oil.

TLC: R_f = 0.64 (P/E = 9/1) [UV, $KMnO_4$].

UV-Vis: ε_{323} = 18850 (*c* = 1 mM, CH_2Cl_2).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3072 (w, C_{ar}-H), 2935 (w, C-H), 2869 (w, C-H), 1629 (m, -CH=CH-Ar), 1510 (s, C-NO_2), 1482 (m), 1336 (vs, C-NO_2), 991 (w), 962 [s, (*E*)-CH=CH-R], 912 (m, R-CH-CH_2), 839 (m, C_{ar}-H), 760 (m, C_{ar}-H).

MS (EI, 70 eV): *m/z (%)* = 171 (43) $[C_{13}H_{15}]^+$, 129 (100) $[C_{10}H_9]^+$, 115 (84) $[C_9H_7]^+$, 91 (13) $[C_7H_7]^+$.

HRMS (ESI): calcd for $C_{13}H_{16}NO_2^+$ $[M+H]^+$: 218.1176; found: 218.1176.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 8.33 (d, ^3J = 13.5 Hz, 1H, H-1‘‘), 7.55–7.48 (m, 2H, H-2, H_{ar}*), 7.43−7.40 (m, 1H, H_{ar})*, 7.29−7.25 (m, 2H, H_{ar})*, 5.83 (ddt, ^3J = 16.9 Hz, 10.2 Hz, 6.6 Hz, 1H, H-4’), 5.09–5.00 (m, 2H, CH_2-5’), 2.83–2.76 (m, 2H, CH_2-1’), 2.14 (*virt*. q, $^3J \cong {}^3J$ = 7.0 Hz, 2H, CH_2-3’), 1.75–1.65 (m, 2H, CH_2-2’).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 143.9 (s, C-1), 138.0 (d, C-2’’), 137.9 (d, C-4’), 136.7 (d, C-1’’), 132.1 (d, $C_{ar}H$)*, 130.8 (d, $C_{ar}H$)*, 128.5 (s, C-2), 127.4 (d, $C_{ar}H$)*, 127.0 (d, $C_{ar}H$)*, 115.6 (t, C-5’), 32.8 (t, C-3’), 31.0 (t, C-1’), 25.7 (t, C-2’).

* The exact assignment of these signals was not possible.

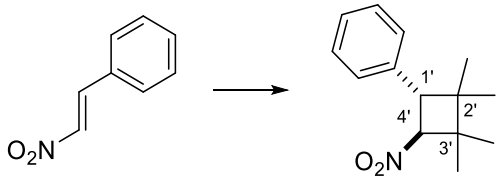
4. [2+2] photocycloaddition of nitroethenes 1a-1o to 2,3-dimethyl-2-butene

The analytical data for nitrocyclobutanes **2a-2e** have already been published in a communication.[2]

General Procedure 4 (GP 4) for the [2+2] photocycloaddition of nitroethenes with 2,3-dimethlybut-2-ene

A solution of the nitroethene (1.00 equiv) and 2,3-dimethyl-2-butene (10.0 equiv) in dichloromethane (c = 20 mM) was irradiated with visible light (the wavelength λ [nm] of the light source is indicated for each reaction individually) at room temperature or at −78 °C. The progress of the reaction was monitored by TLC. After full conversion was reached, irradiation was stopped, and the solvent was removed *in vacuo*. In some cases, the reaction was stopped when the TLC did not indicate any further consumption of the starting material over a period of two to three hours. The crude product was dry loaded onto CELITE® and purified by column chromatography.

(2‘,2‘,3‘,3‘-Tetramethyl-4‘-nitrocyclobutyl)benzene (2a)



1a **2a**

$C_{14}H_{19}NO_2$

MW = 233.31 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1a** (29.8 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (234 µL, 166 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for twelve hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 20/1) to yield **2a** (26.9 mg, 1.16 mmol, 59%) as a yellow coloured oil.

Conditions B: Following **GP 4**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for twelve hours at room temperature. The crude

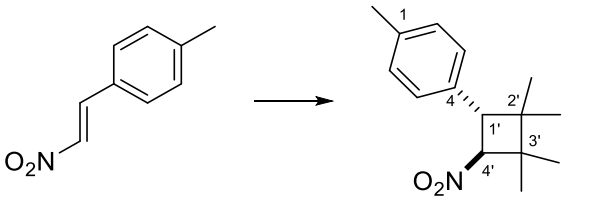
product was purified by column chromatography (2 × 10 cm, P/Et_2O = 20/1) to yield **2a** (12.2 mg, 52.3 μmol, 53%) as a yellow coloured oil.

Conditions C: Following **GP 4**, a solution of nitroethene **1a** (14.9 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for twelve hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 20/1) to yield **2a** (13.0 mg, 55.7 μmol, 56%) as a yellow coloured oil.

Reaction at λ = 382 nm (LED): Following **GP 4**, a solution of nitroethene **1a** (14.9 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 382 nm (LED) for three hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 20/1) to yield **2a** (13.2 mg, 56.6 μmol, 57%) as a yellow coloured oil.

The analytical data match those reported in the literature.[12]

1-Methyl-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2b)



1b **2b**

$C_{15}H_{21}NO_2$

MW = 247.33 g/mol

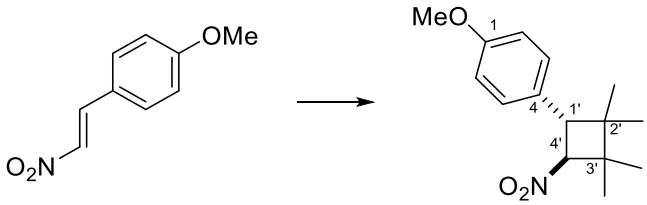
Conditions A: Following **GP 4**, a solution of nitroethene **1b** (32.6 mg, 200 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 μL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for three hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 20/1) to yield **2b** (26.9 mg, 1.09 mmol, 54%) as a pale-yellow coloured oil.

Conditions B: Following **GP 4**, a solution of nitroethene **1b** (16.3 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for three hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 20/1) to yield **2b** (16.7 mg, 67.5 μmol, 68%) as a pale-yellow coloured oil.

Conditions C: Following **GP 4**, a solution of nitroethene **1b** (16.3 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for three hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 20/1) to yield **2b** (16.5 mg, 66.7 µmol, 67%) as a pale-yellow coloured oil.

The analytical data match those reported in the literature.[12]

1-Methoxy-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2c)



1c **2c**

$C_{15}H_{21}NO_3$

MW = 263.34 g/mol

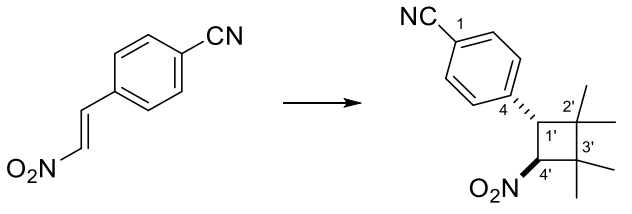
Conditions A: Following **GP 4**, a solution of nitroethene **1c** (35.8 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for four hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 9/1) to yield **2c** (27.3 mg, 1.04 mmol, 52%) as a yellow coloured oil.

Conditions B: Following **GP 4**, a solution of nitroethene **1c** (17.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for three hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1) to yield **2c** (14.3 mg, 54.3 µmol, 58%) as a yellow coloured oil.

Conditions C: Following **GP 4**, a solution of nitroethene **1c** (17.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for three hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1) to yield **2c** (20.3 mg, 77.1 µmol, 77%) as a yellow coloured oil.

The analytical data match those reported in the literature.[12]

4-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)benzonitrile (2d)



1d **2d**

$C_{15}H_{18}N_2O_2$

MW = 258.32 g/mol

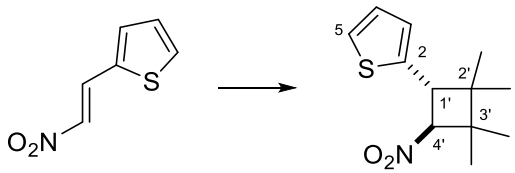
Conditions A: Following **GP 4**, a solution of nitroethene **1d** (34.8 mg, 200 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 μL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for five hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1) to yield **2d** (15.7 mg, 60.8 mmol, 31%) and the side product (2.64 mg, 10.2 μmol, 5%) each as a colorless solid.

Conditions B: Following **GP 4**, a solution of nitroethene **1d** (17.4 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for four hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1) to yield **2d** (6.70 mg, 25.9 μmol, 26%) and the side product (0.9 mg, 3.48 μmol, 3%) each as a colorless solid.

Conditions C: Following **GP 4**, a solution of nitroethene **1d** (17.4 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for four hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1) to yield **2d** (11.4 mg, 43.9 μmol, 44%) as colorless solid. The side product was only observed in traces.

The analytical data match those reported in the literature.[12]

2-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)thiophene (2e)



1e **2e**

$C_{12}H_{17}NO_2S$
MW = 239.33 g/mol

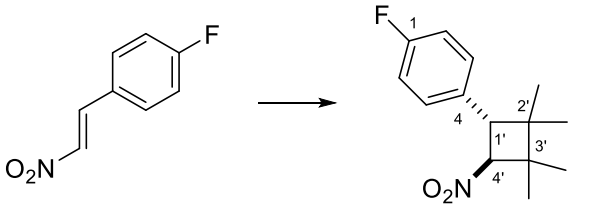
Conditions A: Following **GP 4**, a solution of nitroethene **1e** (31.0 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for two hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield **2e** (23.8 mg, 99.4 mmol, 50%) as a yellow coloured oil.

Conditions B: Following **GP 4**, a solution of nitroethene **1e** (15.5 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for two hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2e** (12.1 mg, 50.6 µmol, 51%) as a yellow coloured oil.

Conditions C: Following **GP 4**, a solution of nitroethene **1e** (15.5 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for two hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2e** (20.5 mg, 85.7 µmol, 86%) as a yellow coloured oil.

The analytical data match those reported in the literature.[12]

1-Fluoro-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2f)



1f **2f**

$C_{14}H_{18}FNO_2$
MW = 251.30 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1f** (33.4 mg, 200 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 μL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for four hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield **2f** (22.2 mg, 88.3 μmol, 44%) as a colorless solid.

Conditions B: Following **GP 4**, a solution of nitroethene **1f** (16.7 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for four hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield **2f** (10.5 mg, 41.8 μmol, 42%) as a colorless solid.

Conditions C: Following **GP 4**, a solution of nitroethene **1f** (16.7 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for four hours at −78 °C. The crude product was purified by column chromatography (2 × 20 cm, P/Et_2O = 15/1) to yield **2f** (12.6 mg, 50.1 μmol, 50%) as a colorless solid

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, C_{ar}-H), 2967 (m, C_{ar}-H), 2871 (w), 1538 (vs, C-NO_2), 1510 (s), 1460 (m, C_{sp3}-H), 1371 (s, C-NO_2), 1226 (s, C_{ar}-F), 1151 (m), 1135 (m), 844 (s, C_{ar}-H), 761 (s, C_{ar}-H).

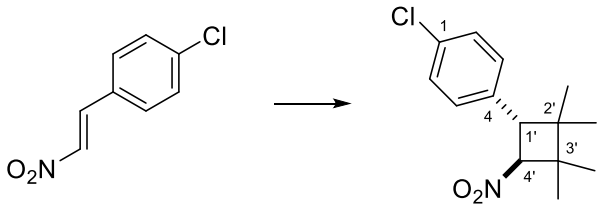
MS (EI): *m/z (%)* = 205 (45) $[M\text{-}NO_2]^+$, 163 (100) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 106 (54) $[C_7H_6F]^+$.

HRMS (EI, 70 eV): calcd for $C_{14}H_{18}FNO_2^+$ $[M]^+$: 251.1316; found: 251.1316.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.09–7.00 (m, 4H, H_{ar}), 4.85 (d, ^{3}J = 10.1 Hz, 1H, H-4'), 3.92 (d, ^{3}J = 10.1 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-2'), 1.16 (s, 3H, CH_3-3'), 1.14 (s, 3H, CH_3-2'), 0.70 (s, 3H, CH_3-3').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 162.1 (d, $^{1}J_{CF}$ = 254.4 Hz, C-1), 132.2 (s, C-4), 128.5 (d, $^{3}J_{CF}$ = 7.9 Hz, C-3, C-5), 115.6 (d, $^{2}J_{CF}$ = 21.4 Hz, C-2, C-6), 85.2 (d, C-4'), 48.9 (d, C-1'), 45.0 (s, C-3'), 39.3 (s, C-2'), 24.2 [q, (C-3')*C*H_3], 22.8 [q, (C-2')*C*H_3], 21.4 [q, (C-3')*C*H_3], 19.4 [q, (C-2')*C*H_3].

1-Chloro-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2g)



1g **2g**

$C_{14}H_{18}ClNO_2$

MW = 267.70 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1g** (36.7 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for four hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield **2g** (26.5 mg, 99.0 µmol, 49%) as a pale-yellow coloured solid.

Conditions B: Following **GP 4**, a solution of nitroethene **1g** (18.3 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for four hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2g** (11.5 mg, 43.0 µmol, 43%) as a pale-yellow coloured solid.

Conditions C: Following **GP 4**, a solution of nitroethene **1g** (18.3 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for four hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2g** (14.4 mg, 53.8 µmol, 54%) as a pale-yellow coloured solid.

TLC: R_f = 0.54 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3073 (w, C_{ar}-H), 2972 (m, C_{ar}-H), 2958 (w), 1539 (vs, C-NO_2), 1494 (m, C_{sp3}-H), 1370 (s, C-NO_2), 1153 (m), 1135 (m), 1089 (m. C_{ar}-Cl), 877 (m, C_{ar}-H), 839 (s, C_{ar}-H), 767 (s, C_{ar}-H).

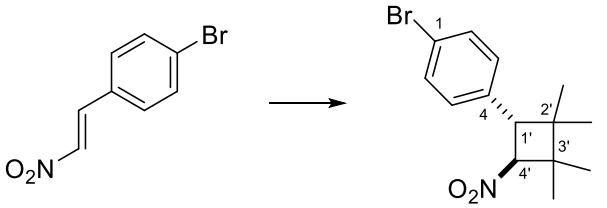
MS (EI): *m/z (%)* = 221 (29) $[M\text{-}NO_2]^+$, 179 (100) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 125 (64) $[C_7H_6Cl]^+$.

HRMS (EI, 70 eV): calcd for $C_{14}H_{18}ClNO_2^+$ $[M]^+$: 267.1021; found: 267.1021.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.33–7.29 (m, 2H, H-2, H-6), 7.06–7.02 (m, 2H, H-3, H-5), 4.85 (d, ^3J = 10.0 Hz, 1H, H-4'), 3.92 (d, ^3J = 10.0 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-2'), 1.17 (s, 3H, CH_3-3'), 1.15 (s, 3H, CH_3-2'), 0.70 (s, 3H, CH_3-3').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 134.9 (s, C-4), 133.0 (s, C-1), 128.9 (d, 2C, C-2, C-6), 128.4 (d, 2C, C-3, C-5), 84.9 (d, C-4'), 49.0 (d, C-1'), 45.1 (s, C-3'), 39.4 (s, C-2'), 24.3 [q, (C-3')*C*H_3], 22.8 [q, (C-2')*C*H_3], 21.5 [q, (C-3')*C*H_3], 19.5 [q, (C-2')*C*H_3].

1-Bromo-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2h)



1h **2h**

$C_{14}H_{18}BrNO_2$

MW = 312.21 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1h** (22.8 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 419 nm (fluorescent lamps) for six hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2h** (17.6 mg, 56.4 μmol, 56%) as a yellow coloured oil.

Conditions B: Following **GP 4**, a solution of nitroethene **1h** (22.8 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2h** (18.0 mg, 56.0 μmol, 58%) as a yellow coloured oil.

Conditions C: Following **GP 4**, a solution of nitroethene **1h** (22.8 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2h** (17.0 mg, 54.5 µmol, 55%) as a yellow coloured oil.

TLC: R_f = 0.43 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2962 (w, C_{ar}-H), 2925 (w, C-H), 1552 (w, C-NO_2), 1464 (w, C_{sp3}-H), 1376 (w, C-NO_2), 1259 (m), 1072 (m, C_{ar}-Br), 1010 (s), 861 (s, C_{ar}-H), 797 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 265 (20) $[M\text{-}NO_2]^+$, 168 (100) $[M\text{-}NO_2\text{-}Br]^+$, 143 (56) $[M\text{-}NO_2\text{-}Br\text{-}C_3H_6]^+$.

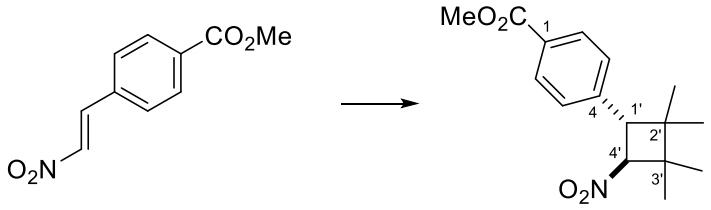
HRMS (ESI): calcd for $C_{14}H_{19}{}^{79}BrNO_2^+$ $[M+H]^+$: 312.0594; found: 312.0593.

calcd for $C_{14}H_{19}{}^{81}BrNO_2^+$ $[M+H]^+$: 314.0573; found: 314.0573.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.48–7.44 (m, 2H, H-2, H-6), 7.00–6.96 (m, 2H, H-3, H-5), 4.85 (d, ^3J = 10.1 Hz, 1H, H-4'), 3.90 (d, ^3J = 10.1 Hz, 1H, H-1'), 1.23 (s, 3H, CH_3-3'), 1.17 (s, 3H, CH_3-2'), 1.14 (s, 3H, CH_3-3'), 0.70 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 135.5 (s, C-1), 131.8 (d, 2C, C-2, C-6), 128.7 (d, 2C, C-3,C-5), 121.1 (s, C-4), 84.8 (d, C-4'), 49.1 (d, C-1'), 45.1 (s, C-3'), 39.4 (s, C-2'), 24.3 [q, (C-3')*C*H_3], 22.8 [q, (C-2')*C*H_3], 21.5 [q, (C-3')*C*H_3], 19.5 [q, (C-2')*C*H_3].

Methyl 4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzoate (2i)



1i **2i**

$C_{16}H_{21}NO_4$

MW = 291.34 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1i** (41.4 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for five hours at room temperature.

The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1) to yield **2i** (16.8 mg, 57.7 mmol, 32%) and the side product (1.18 mg, 4.05 µmol, 2%) as a mixture (colorless solid).

Conditions B: Following **GP 4**, a solution of nitroethene **1i** (20.7 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for five hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1) to yield **2i** (6.45 mg, 22.1 µmol, 22%) and the side product (0.65 mg, 2.23 µmol, 2%) as a mixture (colorless solid).

Conditions C: Following **GP 4**, a solution of nitroethene **1i** (20.7 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for four hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1) to yield **2i** (9.47 mg, 32.5 µmol, 33%) and the side product (1.23 mg, 4.22 µmol, 4%) as a mixture (colorless solid).

TLC: R_f = 0.64 (P/Et_2O = 1/1) [UV, $KMnO_4$].

mp: 112 °C.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954 (m, C_{ar}-H), 1717 (vs, C=O), 1541 (s, C-NO_2), 1433 (m, C_{sp3}-H), 1371 (s, C-NO_2), 1277 (s, O=C-OCH_3), 1181 (m), 1151 (m), 1138 (m), 1110 (s, O=C-OCH_3), 1017 (s), 860 (m, C_{ar}-H), 756 (s, C_{ar}-H).

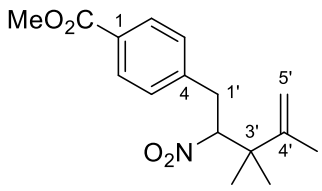
MS (EI): *m/z (%)* = 245 (92) $[M\text{-}NO_2]^+$, 203 (39) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 171 (51), 159 (34), 84 (100) $[C_6H_{12}]^+$, 69 (35).

HRMS (ESI): calcd for $C_{16}H_{22}NO_4^+$ $[M+H]^+$ 292.1543; found: 292.1544.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.00 (d, ^3J = 7.3 Hz, 2H, H-2, H-6), 7.18 (d, ^3J = 7.3 Hz, 2H, H-3, H-5), 4.92 (d, ^3J = 9.9 Hz, 1H, H-4'), 4.01 (d, ^3J = 9.9 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-3'), 1.20 (s, 3H, CH_3-2'), 1.16 (s, 3H, CH_3-3'), 0.69 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 167.0 (s, CH_3CO_2Ar), 141.8 (s, C-1), 130.0 (d, 2C, C-2, C-6), 129.1 (s, C-4), 127.0 (d, 2C, C-3, C-5), 84.6 (d, C-4'), 53.2 (q, CH_3CO_2Ar) 49.5 (d, C-1'), 45.1 (s, C-2'), 39.7 (s, C-3'), 24.3 [q, (C-3')CH_3], 22.7 [q, (C-2')CH_3], 21.5 [q, (C-2')CH_3], 19.5 [q, (C-3')CH_3].

Methyl 4-(4'-methyl-2'-nitropent-4'-en-1'-yl)benzoate



$C_{16}H_{21}NO_4$
MW = 291.34 g/mol

TLC: R_f = 0.70 (P/Et_2O = 1/1) [UV, $KMnO_4$].

MS (EI): *m/z (%)* = 245 (21) $[M\text{-}NO_2]^+$, 229 (41) $[C_{15}H_{17}O_2]^+$, 149 (100) $[C_9H_9O_2]^+$, 121 (33) $[C_7H_5O_2]^+$, 83 (54), 55 (24).

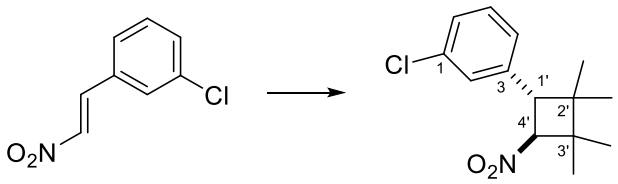
HRMS (ESI): calcd for $C_{16}H_{22}NO_4^+$ $[M+H]^+$ 292.1543; found: 292.1543.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3096 (w, C_{ar}-H), 2922 (m, C=CH_2), 2854 (m, C-H), 1721 (s, C=O), 1549 (s, C-NO_2), 1436 (m, C_{sp3}-H), 1367 (m, C-NO_2), 1278 (s, O=C-OCH_3), 1182 (m), 1109 (m, O=C-OCH_3), 759 (m, C_{ar}-H).

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.95 (d, ^3J = 7.1 Hz, 2H, H-2, H-6), 7.18 (d, ^3J = 7.1 Hz, 2H, H-3, H-5), 5.01 (d, ^4J = 1.1 Hz, 2H, C=CH_2), 4.80 (*virt*. d, $^3J \cong {}^3J$ = 11.9 Hz, 1H, H-2'), 3.33 (*virt*. t, $^2J \cong {}^3J$ = 13.2 Hz, 1H, C*H*H-1'), 2.96 (d, ^2J = 14.8 Hz, 1H, CH*H*-1'), 1.87 [s, 3H, (C-4')CH_3], 1.29 [s, 3H, (C-3')CH_3], 1.23 [s, 3H, (C-3')CH_3].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 166.9 (s, CH_3CO_2Ar), 147.6 (s, C-4'), 142.1 (s, C-4), 130.3 (d, 2C, C-3, C-5), 129.4 (s, $C_{ar}CO_2CH_3$), 128.8 (d, 2C, C-2, C-6), 114.2 (t, C=CH_2), 96.1 (d, C-2'), 52.3 (q, CH_3CO_2Ar), 43.1 (s, C-3'), 34.9 (t, C-1'), 24.7 [q, (C-3')CH_3], 21.7 [q, (C-3')CH_3], 19.7 [q, (C-4')CH_3].

1-Chloro-3-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2j)



1j **2j**

$C_{14}H_{18}ClNO_2$
MW = 267.75 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1j** (36.7 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield **2j** (20.4 mg, 76.2 µmol, 38%) as a colorless oil. Starting material was recovered as *trans*-isomer *trans*-**1j** (9.60 mg, 52.3 µmol, 26%).

Conditions B: Following **GP 4**, a solution of nitroethene **1j** (18.4 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2j** (10.3 mg, 38.5 µmol, 38%) as a colorless oil. Starting material was recovered as *trans*-isomer *trans*-**1j** (5.00 mg, 27.2 µmol, 27%).

Conditions C: Following **GP 4**, a solution of nitroethene **1j** (18.4 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2j** (6.90 mg, 25.8 µmol, 26%) as a colorless oil. Starting material was recovered as *trans*-isomer *trans*-**1j** (3.90 mg, 21.2 µmol, 21%).

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3066 (w, C_{ar}-H), 2967 (m, C_{ar}-H), 1598 (m), 1538 (vs, C-NO_2), 1371 (s, C-NO_2), 1151 (m), 1138 (m), 1081 (m. C_{ar}-Cl), 877 (m, C_{ar}-H), 8147 (m, C_{ar}-H), 772 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 221 (32) $[M\text{-}NO_2]^+$, 179 (100) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 125 (32) $[C_7H_6Cl]^+$.

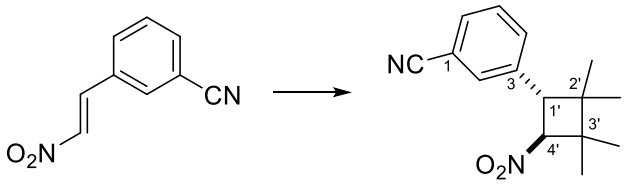
HRMS (ESI): calcd for $C_{14}H_{19}ClNO_2^+$ $[M+H]^+$: 268.1099; found: 268.1098.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.29–7.22 (m, 2H, H_{ar})*, 7.09−7.08 (m, 1H, H_{ar})*, 6.99 (dtd, ^3J = 7.1 Hz, ^4J = 1.8 Hz, 0.8 Hz, 1H, H_{ar})*, 4.86 (d, ^3J = 10.0 Hz, 1H, H-4'), 3.93 (d, ^3J = 10.0 Hz, 1H, H-1'), 1.24 (s, 3H, CH_3-3'), 1.18 (s, 3H, CH_3-2'), 1.14 (s, 3H, CH_3-3'), 0.72 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.6 (s, C-3), 134.7 (s, C-1), 129.9 (d, $C_{ar}H$)*, 127.3 (d, $C_{ar}H$)*, 127.2 (d, $C_{ar}H$)*, 125.2 (d, $C_{ar}H$)*, 84.7 (d, C-4'), 49.2 (d, C-1'), 45.0 (s, C-3'), 39.5 (s, C-2'), 24.3 [q, (C-2')*C*H_3], 22.7 [q, (C-3')*C*H_3], 21.5 [q, (C-2')*C*H_3], 19.4 [q, (C-3')*C*H_3].

* The exact assignment of these signals was not possible.

3-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)benzonitrile (2k)



1k **2k**

$C_{15}H_{18}N_2O_2$

MW = 258.32 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1k** (34.8 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) were irradiated at λ = 419 nm (fluorescent lamps) for six hours at room temperature. The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield **2k** (18.2 mg, 70.5 µmol, 35%) and the side product **6** (2.32 mg, 8.99 µmol, 11%) as a mixture (colorless liquid).

Conditions B: Following **GP 4**, a solution of nitroethene **1k** (17.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2k** (8.84 mg, 34.2 µmol, 33%) and the side product **6** (>1.00 mg, 3.81 µmol, 13%) as a mixture (colorless liquid).

Conditions C: Following **GP 4**, a solution of nitroethene **1k** (17.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane

(5 mL) was irradiated at λ = 424 nm (LED) for six hours at −78 °C. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2k** (5.12 mg, 19.8 µmol, 20%) and the side product **6** (1.00 mg, 3.87 µmol, 16%) as a mixture (colorless liquid).

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, C_{ar}-H), 2960 (m, C_{ar}-H), 2231 (m, -C≡N), 1533 (vs, C-NO_2), 1372 (s, C-NO_2), 1151 (w), 1136 (w), 793 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 212 (32) $[M\text{-}NO_2]^+$, 170 (100) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 116 (20) $[C_8H_6N]^+$.

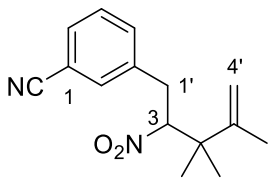
HRMS (ESI): calcd for $C_{15}H_{19}N_2O_2^+$ $[M+H]^+$: 259.1440; found: 259.1442.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.59–7.55 (m, 1H, H_{ar})*, 7.46 (td, ^3J = 7.7 Hz, ^4J = 0.6 Hz, 1H, H_{ar})*, 7.41−7.39 (m, 1H, H_{ar})*, 7.36−7.33 (m, 1H, H_{ar})*, 4.87 (d, ^3J = 10.0 Hz, 1H, H-4'), 3.97 (d, ^3J = 10.0 Hz, 1H, H-1'), 1.25 (s, 3H, CH_3-3'), 1.20 (s, 3H, CH_3-2'), 1.16 (s, 3H, CH_3-3'), 0.71 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.2 (s, C-3), 131.5 (d, C_{ar}H)*, 130.9 (d, C_{ar}H)*, 130.6 (d, C_{ar}H)*, 129.6 (d, C_{ar}H)*, 118.7 (s, C_{ar}*C*N), 113.0 (s, C-1), 84.4 (d, C-4'), 49.1 (d, C-'1), 45.2 (s, C-3'), 39.6 (s, C-2'), 24.3 [q, (C-2')*C*H_3], 22.7 [q, (C-3')*C*H_3], 21.5[q, (C-2')*C*H_3], 19.4 [q, (C-3')*C*H_3].

* The exact assignment of these signals was not possible.

3-(3',3',4'-Trimethyl-2'-nitropent-4'-en-1'-yl)-benzonitrile (6)



6
$C_{15}H_{18}N_2O_2$
MW = 258.32 g/mol

TLC: R_f = 0.23 (P/Et_2O = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2923 (m, C_{ar}-H), 2231 (w), 1549 (vs, C-NO_2), 1365 (m, C-NO_2), 1148 (m), 905 (m), 798 (m, C_{ar}-H), 691 (m, C_{ar}-H).

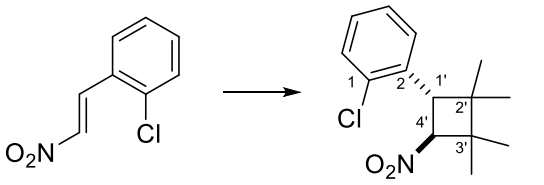
MS (EI): *m/z (%)* = 196 (15) $[M\text{-}NO_2]^+$, 170 (58) $[C_{12}H_{12}N]^+$, 116 (100) $[C_8H_6N]^+$.

HRMS (ESI): calcd for $C_{15}H_{19}N_2O_2^+$ $[M+H]^+$: 259.1441; found: 259.1439.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.54 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, H-4)*, 7.41–7.38 (m, 2H, H-2, H-5), 7.35 (d, ^3J = 8.0 Hz, 1H, H-6)*, 5.04 (s, 1H, C*H*H-5'), 5.00 (s, 1H, CH*H*-5'), 4.76 (dd, ^3J = 12.0 Hz, 2.2 Hz, 1H, H-2'), 3.32 (dd, ^2J = 15.0, ^3J = 11.9 Hz, 1H, C*H*H-1'), 2.94 (dd, ^2J = 15.0, ^3J = 2.2 Hz, 1H, CH*H*-1'), 1.87 (d, ^4J = 1.4 Hz, 3H, CH_3-4'), 1.29 (s, 3H, CH_3-3'), 1.23 (s, 3H, CH_3-3').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 147.3 (s, C-4'), 138.3 (s, C-3), 133.3 (d, C-6)*, 132.4 (d, C-2), 131.2 (d, C-4)*, 129.9 (d, C-5), 118.6 (s, CN), 114.5 (t, C-5'), 113.2 (s, C-1), 96.0 (d, C-2'), 43.0 (s, C-3'), 34.4 (t, C-1'), 24.7 [q, (C-3')*C*H_3], 21.6 [q, (C-3')*C*H_3], 19.6 [q, (C-4')*C*H_3].

1-Chloro-2-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2l)



1l **2l**
$C_{14}H_{18}ClNO_2$
MW = 267.75 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1l** (36.7 mg, 200 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (237 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 19/1) to yield **2l** (15.2 mg, 56.8 µmol, 28%, 46% *brsm*) as a colorless oil. Starting material **1l** was recovered as mixture of isomers (13.5 mg, 73.5 µmol, 39%, *cis*/*trans* = 70/30).

Conditions B: Following **GP 4**, a solution of nitroethene **1l** (18.4 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at room temperature (at that point, no

further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2l** (4.96 mg, 18.5 μmol, 19%, 30% *brsm*) as a colorless oil. Starting material **1l** was recovered as mixture of isomers (6.74 mg, 36.7 μmol, 37%, *cis*/*trans* = 92/8).

Conditions C: Following **GP 4**, a solution of nitroethene **2l** (18.4 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **2l** (7.46 mg, 27.9 μmol, 28%, 49% *brsm*) as a colorless oil. Starting material was recovered as *cis*-isomer *cis*-**1l** (7.94 mg, 43.2 μmol, 43%).

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3061 (w, C_{ar}-H), 2973 (m, C_{ar}-H), 2960 (w), 1541 (vs, C-NO_2), 1372 (s, C-NO_2), 1153 (m), 1135 (m), 1033 (m. C_{ar}-Cl), 876 (m, C_{ar}-H), 807 (m, C_{ar}-H), 754 (vs, C_{ar}-H).

MS (EI): *m/z (%)* = 221 (32) $[M\text{-}NO_2]^+$, 179 (100) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 125 (28) $[C_7H_6Cl]^+$.

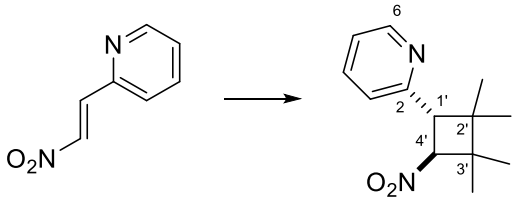
HRMS (ESI): calcd for $C_{14}H_{19}ClNO_2^+$ $[M+H]^+$: 268.1099; found: 268.1094.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.41 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, H-6), 7.28–7.18 (m, 2H, H-5, H-4), 7.16 (dd, ^3J = 7.5 Hz, ^4J = 1.9 Hz, 1H, H-3), 4.99 (d, ^3J = 10.2 Hz, 1H, H-4'), 4.43 (d, ^3J = 10.2 Hz, 1H, H-1'), 1.26 (s, 3H, CH_3-2'), 1.24 (s, 3H, CH_3-3'), 1.19 (s, 3H, CH_3-3'), 0.73 (s, 3H, CH_3-2').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 134.7 (s, C-2), 134.1 (s, C-1), 130.3 (d, C-6), 128.4 (d, C-5)*, 128.1 (d, C-3), 126.8 (d, C-4)*, 84.4 (d, C-4'), 46.8 (d, C-1'), 44.5 (s, C-2'), 40.5 (s, C-3'), 24.9 [q, (C-3')*C*H_3], 22.7 [q, (C-2')*C*H_3], 21.8 [q, (C-2')*C*H_3], 19.4 [q, (C-3')*C*H_3].

* The assignment is interconvertible.

2-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)pyridine (2m)



1m **2m**

$C_{13}H_{18}N_2O_2$
MW = 234.29 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1m** (15.0 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, CH_2Cl_2/MeOH = 40/1) to yield **2m** (13.7 mg, 58.5 μmol, 58%) as a yellow coloured oil.

Conditions B: Following **GP 4**, a solution of nitroethene **1m** (15.0 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, CH_2Cl_2/MeOH = 40/1) to yield **2m** (13.4 mg, 57.2 μmol, 57%) as a yellow coloured oil.

Conditions C: Following **GP 4**, a solution of nitroethene **1m** (15.0 mg, 100 μmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 μL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 24 hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, CH_2Cl_2/MeOH = 40/1) to yield **2m** (15.5 mg, 66.2 μmol, 66%) as a yellow coloured oil.

TLC: R_f = 0.25 (CH_2Cl_2/MeOH = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3445 (br), 3008 (w, C_{ar}-H), 2930 (w, C-H), 1597 (w, C-NO_2), 1448 (m, C_{sp3}-H), 1386 (m, C-NO_2), 1225 (m), 1052 (s), 1025 (s), 992 (s, C_{ar}-H), 760 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 188 (100) $[M\text{-}NO_2]^+$, 146 (72) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 132 (40) $[C_9H_{10}N]^+$.

HRMS (ESI): calcd for $C_{13}H_{19}N_2O_2^+$ $[M+H]^+$: 235.1441; found: 235.1441.

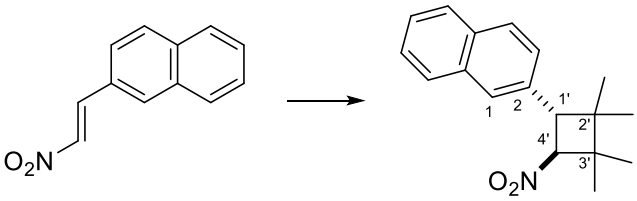
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] 8.59–8.37 (m, 2H, H-5, H-6), 7.43 (dt, ^3J = 7.9 Hz, ^4J = 2.0 Hz, 1H, H-3), 7.31–7.27 (m, 1H, H-4), 4.90 (d, ^3J = 10.0 Hz, 1H, H-4'), 3.96 (d,

^{3}J = 10.0 Hz, 1H, H-1'), 1.25 (s, 3H, CH_3-2'), 1.19 (s, 3H, CH_3-3'), 1.16 (s, 3H, CH_3-2'), 0.73 (s, 3H, CH_3-3').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 148.7 (d, C-6)*, 148.6 (d, C-5)*, 134.5 (d, C-3), 131.9 (s, C-2), 123.4 (d, C-4), 84.2 (d, C-4'), 47.4 (d, C-1'), 45.3 (s, C-3'), 39.4 (s, C-2'), 24.2 [q, (C-2')*C*H_3], 22.7 [q, (C-3')*C*H_3], 21.6 [q, (C-2')*C*H_3], 19.3 [q, (C-3')*C*H_3].

* The assignment is interconvertible.

2-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)napthalene (2n)



1n **2n**

$C_{18}H_{21}NO_2$

MW = 283.37 g/mol

Conditions A: Following **GP 4**, a solution of nitroethene **1n** (19.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 419 nm (fluorescent lamps) for three hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield **2n** (12.9 mg, 45.5 µmol, 46%) as a yellow coloured oil.

Conditions B: Following **GP 4**, a solution of nitroethene **1n** (19.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for three hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield **2n** (12.6 mg, 44.7 µmol, 44%) as a yellow coloured oil.

Conditions C: Following **GP 4**, a solution of nitroethene **1n** (19.9 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (119 µL, 84.2 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for three hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield **2n** (22.4 mg, 79.1 µmol, 79%) as a yellow coloured oil.

TLC: R_f = 0.56 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2954 (m, C_{ar}-H), 1537 (s, C-NO_2), 1459 (m, C_{sp3}-H), 1367 (m, C-NO_2), 1139 (w), 858 (m, C_{ar}-H), 810 (m, C_{ar}-H), 755 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 237 (28) $[M\text{-}NO_2]^+$, 181 (100) $[M\text{-}NO_2\text{-}C_4H_8]^+$, 127 (10) $[C_{10}H_7]^+$.

HRMS (ESI): calcd for $C_{18}H_{22}NO_2^+$ $[M+H]^+$: 284.1645; found: 284.1646.

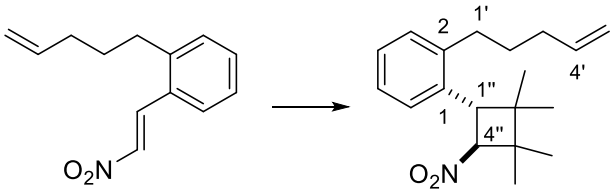
^{1}H NMR (500 MHz, $CDCl_3$): 7.85–7.79 (m, 3H, H_{ar})*, 7.54–7.52 (br. s, 1H, H_{ar})*, 7.51–7.43 (m, 2H, H_{ar})*, 7.26–7.23 (m, 1H, H_{ar})*, 5.06 (d, ^3J = 10.1 Hz, 1H, H-4'), 4.14 (d, ^3J = 10.1 Hz, 1H, H-1'), 1.28 (s, 3H, CH_3-2'), 1.26 (s, 3H, CH_3-3'), 1.20 (s, 3H, CH_3-2'), 0.73 (s, 3H, CH_3-3').

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 134.2 (s, C-2), 133.5 (s, C-10)*, 132.6 (s, C-5)*, 128.4 (d, C_{ar}H)**, 127.8 (d, C_{ar}H)**, 126.5 (d, C_{ar}H)**, 125.9 (d, C_{ar}H)**, 125.7 (d, C_{ar}H)**, 125.1 (d, C_{ar}H)**, 85.0 (d, C-4'), 49.6 (d, C-1'), 45.1 (s, C-3'), 39.5 (s, C-2'), 24.4 [q, (C-2')*C*H_3], 22.8 [q, (C-3')*C*H_3], 21.6 [q, (C-2')*C*H_3], 19.5 [q, (C-3')*C*H_3].

* The assignment is interconvertible.

** The exact assignment of these signals was not possible.

1-(Pent-4'-en-1'-yl)-2-(2'',2'',3'',3''-tetramethyl-4''-nitrocyclobutyl)-benzene (2o)



1o **2o**

$C_{19}H_{27}NO_2$

MW = 301.43 g/mol

Following **GP 4**, a solution of nitroethene **1o** (21.7 mg, 100 µmol, 1.00 equiv) and 2,3-dimethyl-2-butene (356 µL, 252 mg, 3.00 mmol, 30.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 18 hours at room temperature. The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 4/1) to yield **2o** (13.8 mg, 45.8 µmol, 46%) as a yellow coloured oil.

TLC: R_f = 0.68 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3066 (w, C_{ar}-H), 2931 (w, C-H), 2870 (w, C-H), 1542 (vs, C-NO_2), 1460 (m), 1371 (s, C-NO_2), 993 (w), 912 (m, R-CH-CH_2), 751 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 301 (2) $[M]^+$, 255 (20) $[M\text{-}NO_2]^+$, 199 (49) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 143 (100) $[C_{11}H_{11}]^+$

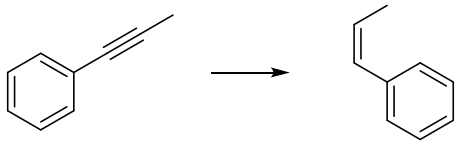
HRMS (ESI): calcd for $C_{19}H_{28}NO_2^+$ $[M+H]^+$: 302.2115; found: 302.2115.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.15−7.09 (m, 3H, H-3, H-4, H-5), 7.07–7.03 (m, 1H, H-6), 5.83 (ddt, ^3J = 17.0 Hz, 10.2 Hz, 6.7 Hz, 1H, H-4'), 5.02 (*virt*. dq, ^3J = 17.2 Hz, $^2J \cong {}^4J$ = 1.7 Hz, 1H, C*H*H-5'), 4.98–4.92 (m, 2H, CH*H*-5', H-4''), 4.15 (d, ^3J = 10.2 Hz, 1H, H-1''), 2.76 (ddd, ^2J = 14.0 Hz, ^3J = 10.5 Hz, 5.3 Hz, 1H, C*H*H-1'), 2.46 (ddd, ^2J = 14.0 Hz, ^3J = 10.6 Hz, 6.0 Hz, 1H, CH*H*-1'), 2.19–2.03 (m, 2H, H-3'), 1.82–1.72 (m, 1H, C*H*H-2'), 1.70–1.58 (m, 1H, CH*H*-2'), 1.18 (s, 3H, CH_3-3''), 1.10 (s, 3H, CH_3-3''), 1.09 (s, 3H, CH_3-2''), 0.67 (s, 3H, CH_3-2'').

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 141.7 (s, C-1), 138.6 (d, C-4'), 133.2 (s, C-2), 129.8 (d, C-6), 127.1 (d, C-5)*, 127.0 (d, C-3), 125.9 (d, C-4)*, 115.3 (t, C-5'), 85.3 (d, C-4''), 45.6 (d, C-1''), 44.4 (s, C-2''), 40.1 (s, C-3''), 33.8 (t, C-3'), 32.4 (t, C-1'), 30.6 (t, C-2'), 24.6 [q, (C-2')*C*H_3], 22.8 [q, (C-3')*C*H_3], 21.8 [q, (C-2')*C*H_3], 19.4 [q, (C-3')*C*H_3].

5. Synthesis of olefins

cis-*β*-Methylstyrene (*cis*-14)



***cis*-14**
C_9H_{10}
MW = 118.18 g/mol

According to a literature known procedure:[13] Prop-1-yn-1-ylbenzene (900 µL, 835 mg, 7.19 mmol, 1.00 equiv) and *Lindlar's* catalyst (500 mg) were suspended in 250 mL of freshly distilled cyclohexane. The flask was alternately evacuated and flushed with H_2-gas for four cycles to establish a saturated H_2-atomosphere inside the flask. The flask was charged with H_2 (p = 1 atm) and the suspension was stirred at room temperature. The reaction progress was monitored via TLC. After ten minutes, the suspension was filtered over a plug of CELITE® and the filtrate was concentrated *in vacuo* (note: due to the volatility of the product, the vacuum should not deceed 150 mbar!). The crude product was purified by column chromatography (5 × 15 cm, P) to yield ***cis*-14** (380 mg, 3.22 mmol, 45%) as a colorless liquid.

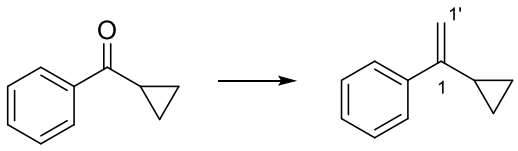
TLC: R_f = 0.62 (P) [UV, $KMnO_4$].

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.39–7.28 (m, 4H, H_{Ph}), 7.26−7.20 (m, 1H, H_{Ph}), 6.45 (d, ^3J = 11.6 Hz, 1H, PhC*H*), 5.80 (dq, ^3J = 11.6, 7.2 Hz, 1H, PhCH=C*H*CH_3), 1.91 (d, ^3J = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 137.8 (s, C_{Ph}), 130.0 (d, C_{Ph}H), 128.9 (d, 2C, C_{Ph}H), 128.3 (d, 2C, C_{Ph}H), 126.9 (d, ArCH), 126.5 (d, ArCH=*C*HCH_3), 14.8 (q, CH_3).

The analytical data match those reported in the literature.[13]

(1-Cyclopropylvinyl)benzene



$C_{11}H_{12}$
MW = 144.22 g/mol

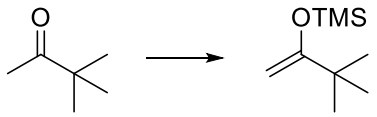
According to a literature known procedure:[14] NaH (547 mg, 27.4 mmol, 2.00 equiv; 60 wt-% in mineral oil) was washed with pentane (4 × 10 mL). The flask was deoxygenated by alternately evacuating and flushing with argon for three cycles. The white powder was dissolved in dimethylsulfoxide (12 mL) and heated to 85 °C, until the evolution of gas ceased. Methyltriphenylphosphonium bromide (9.77 g, 27.4 mmol, 2.00 equiv) was dissolved in warm dimethylsulfoxide (13 mL). The NaH-Suspension was cooled to 0 °C, and the solution of the *Wittig* salt was added quickly to avoid freezing of the solvent. The yellow coloured reaction suspension was stirred at room temperature for ten minutes. Subsequently, a solution of cyclopropyl(phenyl)methanone (1.89 mL, 2.00 g, 13.7 mmol, 1.00 equiv) in dimethylsulfoxide (10 mL) was added, and the resulting orange coloured suspension was stirred for one hour at room temperature. Water (50 mL) was added, and the reaction mixture was partitioned between water and pentane (200 ml). The aqueous layer was extracted with large excess of pentane (2 × 200 mL). The combined organic layers were washed with saturated aqueous NaCl solution (700 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* (note: due to the volatility of the product, the vacuum should not deceed 500 mbar!). The crude product was taken up in pentane (50 mL) and filtered over silica. The silica plug was washed carefully with pentane (50 mL) and the filtrate was again concentrated *in vacuo* (> 500 mbar) to yield (1-cyclopropylvinyl)-benzene (880 mg, 770 mmol, 47%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 7.64–7.56 (m, 2H, H_{Ph}), 7.39–7.27 (m, 3H, H_{Ph}), 5.28 (d, ^2J = 1.1 Hz, 1H, C*H*H-1') 4.94 (*virt*. t, $^4J \cong {}^2J$ = 1.2 Hz, 1H, CH*H*-1'), 1.66 [ttd, ^3J = 8.3 Hz, 5.4 Hz, ^4J = 1.3 Hz, 1H, C*H*$(CH_2)_2$], 0.97–0.79 [m, 2H, CH(CH_2)$_2$], 0.66–0.52 [m, 2H, CH(CH_2)$_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 149.5 (s, *C*=CH_2), 141.8 (s, C_{Ph}), 128.3 (d, 2C, C_{Ph}H), 127.6 (d, C_{Ph}H), 126.3 (d, 2C, C_{Ph}H), 109.2 (t, C=*C*H_2), 15.8 [d, *C*H$(CH_2)_2$], 6.82 [t, 2C, CH(*C*H_2)$_2$].

The analytical data match those reported in the literature.[15]

[(3,3-Dimethylbut-1-en-2-yl)oxy]trimethylsilane



$C_9H_{20}OSi$
MW = 172.34 g/mol

According to a literature known procedure:[16] TMSCl (1.51 mL, 1.30 g, 12.0 mmol, 1.20 equiv) was added dropwise over a period of ten minutes to a solution of pinacolone (1.25 mL, 1.00 g, 9.98 mmol, 1.00 equiv) and dry triethylamine (1.66 mL, 1.21 g, 12.0 mmol, 1.20 equiv) in acetonitrile (20 mL). Subsequently, a solution of NaI (1.95 g, 13.0 mmol, 1.30 equiv) in acetonitrile (20 mL) was added. The suspension was stirred for four hours at room temperature and the reaction was quenched by the addition of cold water (50 mL) and cold pentane (40 mL). The resulting three layers were separated, and the aqueous layer was extracted with pentane (3 × 50 mL). The combined organic layers (acetonitrile and pentane) were washed with water, until a neutral pH was reached. The organic layer was washed with saturated aqueous NaCl solution (250 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by distillation over a *Vigreux* column (Ø = 1.5 cm, h = 10 cm) to yield [(3,3-dimethylbut-1-en-2-yl)oxy]trimethylsilane (800 mg, 4.64 mmol, 47%) as a colorless liquid.

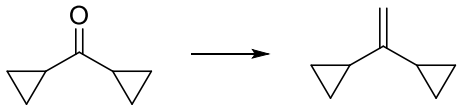
bp: 138–145 °C [p = 1013 mbar].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 4.08 (d, ^2J = 1.3 Hz, 1H, C*H*H), 3.93 (d, ^2J = 1.3 Hz, 1H, CH*H*), 1.05 [s, 9H, $Si(CH_3)_3$], 0.21 [s, 9H, $C(CH_3)_3$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 167.4 (s, C-2), 85.9 (t, CH_2), 36.6 [s, *C*$(CH_3)_3$], 28.2 [q, C(*C*$H_3)_3$], 0.32 [q, OSi$(CH_3)_3$].

The analytical data match those reported in the literature.[16]

1,1,-Dicyclopropylethylene



C_8H_{12}
MW = 108.18 g/mol

According to a literature known procedure:[14] NaH (1.65 g, 41.3 mmol, 0.91 equiv; 60 wt-% in mineral oil) were washed with pentane (4 × 10 mL). The flask was deoxygenated by alternately evacuating and flushing with argon for three cycles. The white powder was dissolved in dimethylsulfoxide (25 mL) and heated to 85 °C, until the evolution of gas ceased. Methyltriphenylphosphonium bromide (14.2 g, 41.3 mmol, 0.91 equiv) was dissolved in warm dimethylsulfoxide (25 mL). The NaH-suspension was cooled to 0 °C, and the solution of the *Wittig* salt was added quickly to avoid freezing of the solvent. The yellow coloured reaction suspension was stirred at room temperature for ten minutes. Subsequently, a solution of dicyclopropylmethanone (5.15 mL, 5.00 g, 45.4 mmol, 1.00 equiv) in dimethylsulfoxide (50 mL) was added, and the resulting orange coloured suspension was stirred for one hour at room temperature. The product was distilled directly from the reaction mixture (T = 120 °C, p = 120 – 60 mbar) and subsequently filtered over silica to remove the residual dimethylsulfoxide, yielding 1,1-dicyclopropylethylene (3.81 g, 776 mmol, 78%) as a colorless liquid.

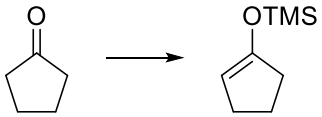
bp: ~ 125 °C [p = 120 – 60 mbar].

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] = 4.58 (t, ^4J = 0.6 Hz, 2H, CH_2), 1.30 [tt, ^3J = 8.2, 5.2 Hz, 2H, C*H*(CH_2)$_2$], 0.66–0.57 [m, 4H, CH(C*H*$_2$)$_2$], 0.56–0.49 [m, 4H, CH(C*H*$_2$)$_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 152.1 (s, CH_2=*C*), 104.5 (t, *C*H_2=C), 15.3 [d, 2C, *C*H(CH_2)$_2$], 5.81 [t, 4C, CH(*C*H_2)$_2$].

The analytical data match those reported in the literature.[17]

(Cyclopent-1-en-1-yloxy)trimethylsilane



$C_8H_{16}OSi$
MW = 156.30 g/mol

According to a literature known procedure:[18] Cyclopentanone (1.05 mL, 1.00 g, 11.9 mmol, 1.00 equiv) and triethylamine (2.07 mL, 1.50 g, 14.9 mmol, 1.15 equiv) were added to a solution of NaI (2.23 g, 14.9 mmol, 1.25 equiv) in acetonitrile (18 mL). TMSCl (1.74 mL, 1.49 g, 13.7 mmol, 1.15 equiv) was added dropwise over a period of 30 minutes. The suspension was stirred for two hours at room temperature. The reaction mixture was partitioned between acetonitrile and pentane (20 mL). The acetonitrile layer was extracted with pentane (3 × 20 mL). The combined pentane layers were washed with water, until a neutral pH was reached. Subsequently, the pentane layer was washed with saturated aqueous NaCl solution (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by *Kugelrohr* distillation to yield (cyclopent-1-en-1-yloxy)trimethylsilane (1.53 g, 9.79 mmol, 82%) as a colorless liquid.

bp: 50 °C [p = 10 mbar].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 4.66–4.58 (m, 1H, $CH_2C\mathit{H}$=C), 2.28–2.24 (m, 4H, CH_2), 1.91–1.76 (m, 2H, CH_2), 0.20 [s, 9H, $OSi(CH_3)_3$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 155.2 (s, C-1), 102.3 (d, C-2), 33.7 (t, CH_2), 28.9 (t, CH_2), 21.5 (t, CH_2), 0.19 [q, $OSi(CH_3)_3$].

The analytical data match those reported in the literature.[18]

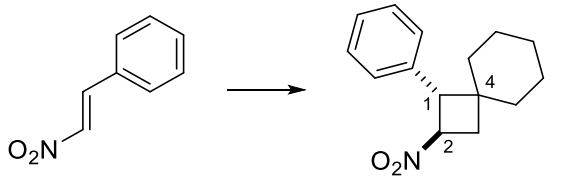
6. [2+2] photocycloaddition of nitroethene 1a to different olefins

The analytical data for nitrocyclobutanes **3a** and **3b** have already been published in a communication.[2]

General Procedure 5 (GP 5) for the [2+2] photocycloaddition of *trans*-β-nitrostyrene 1a with different olefins

A solution of *trans*-β-nitrostyrene **1a** (1.00 equiv) and the olefin (10.0 equiv) in dichloromethane (c = 20 mM) was irradiated with visible light (the wavelength λ [nm] of the light source is indicated for each reaction individually) at room temperature or at −78 °C. The progress of the reaction was monitored by TLC. After full conversion was reached, irradiation was stopped, and the solvent was removed *in vacuo*. In some cases, the reaction was stopped when the TLC did not indicate any further consumption of the starting material over a period of two to three hours. The crude product was dry loaded onto CELITE® and purified by column chromatography.

2-Nitro-1-phenylspiro[3.5]nonane (3a)



1a **3a**

$C_{15}H_{19}NO_2$

MW = 245.32 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (29.8 mg, 200 μmol, 1.00 equiv) and methylenecyclohexane (240 μL, 192 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 14 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 19/1) to yield **3a** (24.7 mg, 1.01 mmol, 51%) as a colorless oil. Starting material was recovered as *trans*-isomer *trans*-**1a** (6.00 mg, 40.2 μmol, 20%).

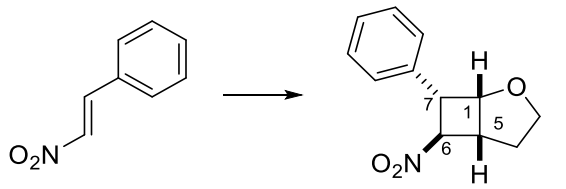
Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 μmol, 1.00 equiv) and methylenecyclohexane (136 μL, 96.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane

(5 mL) was irradiated at λ = 424 nm (LED) for 14 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield **3a** (11.8 mg, 48.1 µmol, 48%) as a colorless oil. Starting material **1a** was recovered as mixture of isomers (1.65 mg, 11.1 µmol, 11%, *cis*/*trans* = 12/88).

Conditions C: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and methylenecyclohexane (136 µL, 96.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 14 hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 19/1) to yield **3a** (15.0 mg, 61.9 µmol, 61%, 98% *brsm*) as a colorless oil. Starting material **1a** was recovered as mixture of isomers (6.64 mg, 42.9 µmol, 43%, *cis*/*trans* = 12:88).

The analytical data match those reported in the literature.[2]

6-Nitro-7-phenyl-2-oxabicyclo[3.2.0]heptane (3b)



1a **3b**

$C_{12}H_{13}NO_3$

MW = 219.24 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (29.8 mg, 200 µmol, 1.00 equiv) and 2,3-dihydrofurane (152 µL, 140 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for six hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 9/1 → 4/1) to yield **3b** (15.7 mg, 71.6 µmol, 36%) as a yellow coloured oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (2.30 mg, 15.2 µmol, 8%).

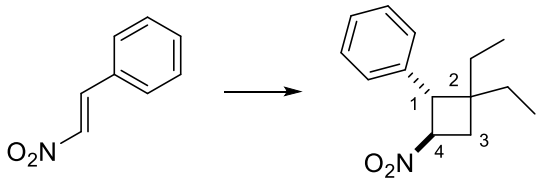
Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dihydrofurane (75.5 µL, 70.0 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at room temperature (at that point, no further

conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 9/1 → 4/1) to yield **3b** (8.10 mg, 36.9 µmol, 37%) as a yellow coloured oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (2.00 mg, 13.4 µmol, 13%).

Conditions C: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dihydrofurane (75.5 µL, 70.0 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for six hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 12 cm, P/Et_2O = 9/1 → 4/1) to yield the product **3b** (6.00 mg, 27.4 µmol, 27%) as yellow coloured oil. Starting material **1a** was recovered as a mixture of isomers (6.60 mg, 44.3 µmol, 44%, *cis*/*trans* = 64:36).

The analytical data match those reported in the literature.[2]

(2,2-Diethyl-4-nitrocyclobutyl)-benzene (3c)



1a **3c**

$C_{14}H_{19}NO_2$

MW = 233.31 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (29.8 mg, 200 µmol, 1.00 equiv) and 1,1-diethylethylene (244 µL, 168 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 14 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 30/1) to yield **3c** (20.7 mg, 88.7 mmol, 44%) as a yellow coloured oil. Starting material **1a** was recovered as a mixture of isomers (4.70 mg, 31.5 µmol, 16%, *cis*/*trans* = 44:56).

Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and 1,1-diethylethylene (122 µL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 14 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography

(2 × 15 cm, P/Et_2O = 30/1) to yield **3c** (5.80 mg, 24.9 μmol, 25%) as as a yellow coloured oil. Starting material **1a** was recovered as a mixture of isomers (9.50 mg, 63.7 μmol, 63%, *cis*/*trans* = 44:56).

Conditions C: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 μmol, 1.00 equiv) and 1,1-diethylethylene (122 μL, 84.1 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 14 hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 30/1) to yield **3c** (7.50 mg, 32.2 μmol, 32%) as as a yellow coloured oil. Starting material **1a** was recovered as a mixture of isomers (5.70 mg, 38.2 μmol, 38%, *cis*/*trans* = 36:64).

TLC: R_f = 0.45 (P/Et_2O = 19/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063 (w, C_{ar}-H), 3030 (w, C_{ar}-H), 2965 (w, C-H), 1542 (vs, C-NO_2), 1455 (m, C_{sp3}-H), 1366 (m, C-NO_2), 784 (m, C_{ar}-H).

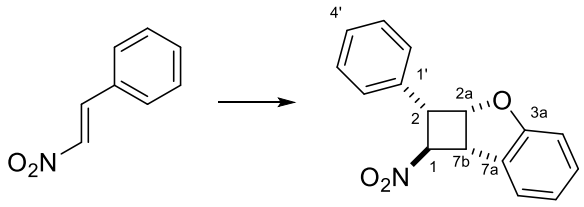
MS (EI): *m/z (%)* = 187 (4) $[M\text{-}NO_2]^+$, 157 (12) $[M\text{-}NO_2\text{-}C_2H_6]^+$, 117 (100) $[C_9H_9]^+$.

HRMS (ESI): calcd for $C_{14}H_{20}NO_2^+$ $[M+H]^+$: 234.1488; found: 234.1489.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.34 (t, ^3J = 7.5 Hz, 2H, *meta*-H_{ar}), 7.29–7.24 (m, 1H, *para*-H_{ar}), 7.23–7.20 (m, 2H, *ortho*-H_{ar}), 5.27 (*virt*. q, $^3J \cong {}^3J$ = 8.7 Hz, 1H, H-4'), 3.98 (d, ^3J = 9.1 Hz, 1H, H-1'), 2.40 (dd, ^2J = 11.9 Hz, ^3J = 8.5 Hz, 1H, C*H*H-3), 2.30 (dd, ^2J = 11.9 Hz, ^3J = 8.6 Hz, 1H, CH*H*-3), 1.76 (dq, ^2J = 14.8 Hz, ^3J = 7.5 Hz, 1H, C*H*HCH_3), 1.64 (dq, ^2J = 14.8 Hz, ^3J = 7.5 Hz, 1H, CH*H*CH_3), 1.30–1.19 (m, 2H, CH_2CH_3), 0.96 (t, ^3J = 7.5 Hz, 3H, CH_2CH_3), 0.60 (t, ^3J = 7.4 Hz, 3H, CH_2CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 136.6 (s, C_{ar}), 128.6 (d, 2C, *meta*-C_{ar}H), 127.5 (d, 2C, *ortho*-C_{ar}H), 127.2 (d, *para*-C_{ar}H), 76.6 (d, C-4'), 53.8 (d, C-1'), 41.8 (s, C-2'), 33.7 (t, C-3'), 31.7 (t, CH_2CH_3), 26.4 (t, CH_2CH_3), 8.62 (q, CH_2CH_3), 7.98 (q, CH_2CH_3).

1-Nitro-2-phenyl-1,2,2a,7b-tetrahydrocyclobuta[b]benzofuran (3d)



1a **3d**

$C_{16}H_{13}NO_2$

MW = 267.28 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and benzofurane (108 µL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 36 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield **3d** (12.5 mg, 46.7 mmol, 47%) as a yellow coloured oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (2.0 mg, 13.4 µmol, 13%).

Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and benzofurane (108 µL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) were irradiated at λ = 424 nm (LED) for 36 hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield **3d** (12.8 mg, 47.9 µmol, 48%) as a yellow coloured oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (5.40 mg, 36.2 µmol, 36%).

Conditions C: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and benzofurane (108 µL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) were irradiated at λ = 424 nm (LED) for 36 hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield **3d** (8.60 mg, 32.2 µmol, 32%) as a yellow coloured oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (6.70 mg, 44.9 µmol, 45%).

TLC: R_f = 0.53 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3062 (w, C_{ar}-H), 3032 (w, C_{ar}-H), 2923 (w, C-H), 1543 (vs, C-NO_2), 1474 (m), 1368 (m, C-NO_2), 1218 (m), 1095 (s, C-O-C), 1051 (m), 1019 (s), 814 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 221 (12) $[M\text{-}NO_2]^+$, 118 (100) $[C_8H_6O]^+$, 90 (8).

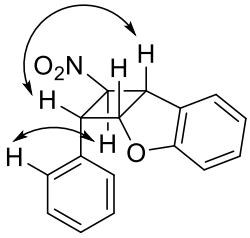
HRMS (ESI): calcd for $C_{16}H_{14}NO_3^+$ $[M+H]^+$: 268.0968; found: 268.0970.

^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 6.98−6.96 (m 3H, *meta*-H_{ar}, *para*-H_{ar}), 6.84 (t, ^3J = 7.5 Hz, 1H, H-5), 6.79 (d, ^3J = 7.5 Hz, 1H, H-4), 6.61–6.56 (m, 2H, *ortho*-H_{ar}), 6.45 (t, ^3J = 7.5 Hz, 1H, H-6), 6.29 (d, ^3J = 7.5 Hz, 1H, H-7), 5.13 (dd, ^3J = 7.4 Hz, 4.2 Hz, 1H, H-2a), 4.97 (ddd, ^3J = 9.4 Hz, 4.2 Hz, ^4J = 1.5 Hz, 1H, H-1), 3.72 (*virt*. t, $^3J \cong {}^3J$ = 9.3 Hz, 1H, H-2), 3.50 (*virt*. t, $^3J \cong {}^3J$ = 8.4 Hz, 1H, H-7b).

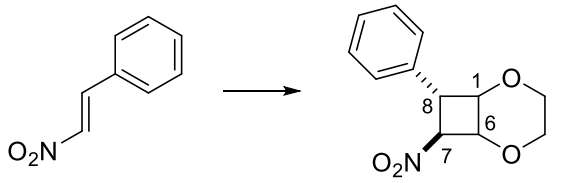
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 160.9 (s, C-3a), 135.4 (s, C-2'), 129.6 (d, C-5), 128.6 (d, *meta*-$C_{ar}H$/*para*-$C_{ar}H$)*, 128.3 (d, C-7), 127.9 (d, *meta*-$C_{ar}H$/*para*-$C_{ar}H$)*, 127.6 (d, 2C, *ortho*-$C_{ar}H$)*, 124.9 (s, C-7a), 121.6 (d, C-6), 111.5 (d, C-4), 85.6 (d, C-1), 80.6 (d, C-2a), 45.6 (d, C-2), 44.6 (d, C-7b).

* The exact assignment of these signals was not possible due to the large overlap with the signal of the solvent C_6D_6.

significant NOE contacts:



7-Nitro-8-phenyl-2,5-dioxabicyclo[4.2.0]octane (3e)



1a **3e**

$C_{12}H_{13}NO_4$

MW = 235.24 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (29.8 mg, 200 µmol, 1.00 equiv) and 2,3-dihydro-1,4-dioxine (159 µL, 172 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for twelve hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1 → 4/1) to yield **3e** (34.0 mg, 145 µmol, 72%, d.r. = 52:19:29) as an orange coloured oil. Starting material **1a** was recovered as a mixture of isomers (4.50 mg, 30.2 µmol, 15%, *cis*/*trans* = 55:45).

Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dihydro-1,4-dioxine (80.0 µL, 86 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for twelve hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1 → 4/1) to yield **3e** (12.7 mg, 54.0 µmol, 54%, d.r. = 58:19:23) as an orange coloured oil. Starting material **1a** was recovered as a mixture of isomers (5.00 mg, 33.5 µmol, 34%, *cis*/*trans* = 55/45).

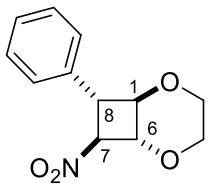
Conditions C: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and 2,3-dihydro-1,4-dioxine (80.0 µL, 86 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for twelve hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 9/1 → 4/1) to yield **3e** (6.1 mg, 25.9 µmol, 26%, d.r. = 58:19:23) as an orange coloured oil. Starting material **1a** was recovered as a mixture of isomers (5.90 mg, 39.6 µmol, 39%, *cis*/*trans* = 54/46).

TLC: R_f = 0.06 (P/Et_2O = 4/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3031 (w, C_{ar}-H), 2923 (w, C_{ar}-H), 1545 (s, C-NO_2), 1375 (m, C-NO_2), 1132 (m, C-O-C), 1043 (m), 874 (m, C_{ar}-H), 751 (m, C_{ar}-H).

HRMS (ESI): calcd for $C_{12}H_{14}NO_4^+$ $[M+H]^+$: 236.0917; found.: 236.0918.

3e:



3e

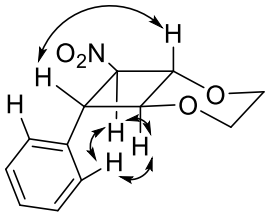
MS (EI): *m/z (%)* = 235 (16) $[M]^+$, 189 (52) $[M\text{-}NO_2]^+$, 117 (72) $[C_9H_9]^+$, 91 (100) $[C_7H_7]^+$.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.02–6.93 (m, 5H, H_{ar}), 4.26 (*virt*. t, $^3J \cong {}^3J$ = 7.8 Hz, 1H, H-7), 3.81 (*virt*. t, $^3J \cong {}^3J$ = 8.6 Hz, 1H, H-6), 3.56 (dd, ^3J = 9.8 Hz, 7.3 Hz, 1H, H-8), 3.40–3.28 (m, 2H, C*H*H-3, C*H*H-4), 3.19–3.15 (m, 2H, CH*H*-3, CH*H*-4), 2.99 (d, ^3J = 9.8 Hz, 1H, H-1).

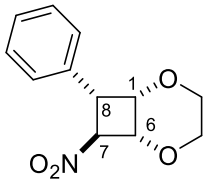
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 136.5 (s, C_{ar}), 129.0 (d, 2C, *ortho*-C_{ar}H)*, 127.9 (d, 2C, *meta*-C_{ar}H)*, 126.9 (d, *para*-C_{ar}H), 82.3 (d, C-7), 77.9 (d, C-6), 75.2 (d, C-1), 68.3 (t, C-3), 68.1 (t, C-4), 51.2 (d, C-8).

* The assignments are interconvertible.

significant NOE contacts:



3e':



3e'

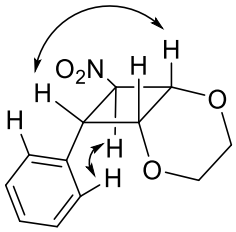
MS (EI): *m/z (%)* = 189 (20) $[M\text{-}NO_2]^+$, 117 (40) $[C_9H_9]^+$, 86 (100) $[C_4H_6O_2]^+$.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.13–7.04 (m, 5H, H_{ar}), 5.53 (dd, ^3J = 9.4 Hz, 7.1 Hz, 1H, H-7), 4.11 (dd, ^3J = 7.1 Hz, 4.8 Hz, 1H, H-6), 3.71 (*virt*. t, $^3J \cong {}^3J$ = 5.0 Hz, 1H, H-1), 3.25–3.20 (m, 2H, H-8, C*H*H-4), 2.97–2.93 (m, 1H, CH*H*-4), 2.92−2.88 (m, 1H, C*H*H-3), 2.83 (dd, ^2J = 12.0 Hz, ^4J = 2.8 Hz, 1H, CH*H*-3).

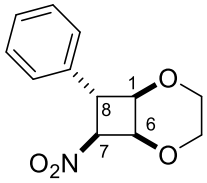
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 134.2 (s, C_{ar}), 128.6 (d, 2C, *ortho*-C_{ar}H)*, 128.0 (d, 2C, *meta*-C_{ar}H)*, 127.5 (d, *para*-C_{ar}H), 82.5 (d, C-7), 69.9 (d, C-6), 69.3 (d, C-1), 63.3 (t, C-3), 61.4 (t, C-4), 43.3 (d, C-8).

* The assignments are interconvertible.

significant NOE contacts:



3e'':



3e"

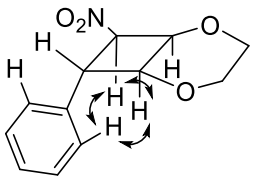
MS (EI): *m/z (%)* = 189 (40) $[M\text{-}NO_2]^+$, 145 (12) $[C_{10}H_9O]^+$, 117 (88) $[C_9H_9]^+$, 86 (100) $[C_4H_6O_2]^+$.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.12–6.98 (m, 5H, H_{ar}), 4.95 (*virt*. t, $^3J \cong {}^3J$ = 9.0 Hz, 1H, H-8), 4.09–4.05 (m, 1H, H-6), 3.73 (dd, ^3J = 9.0 Hz, 5.0 Hz, 1H, H-7), 3.46 (dd, ^3J = 9.0 Hz, 4.2 Hz, 1H, H-1), 3.44–3.36 (m, 1H, C*H*H-3), 3.05–2.97 (m, 2H, CH_2-4), 2.93 (dt, ^2J =11.8 Hz, ^4J = 1.6 Hz, 1H, CH*H*-3).

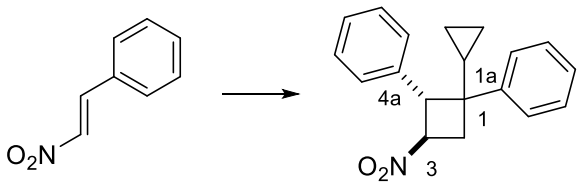
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 138.8 (s, C_{ar}), 128.9 (d, 2C, *ortho*-C_{ar}H)*, 127.4 (d, *para*-C_{ar}H), 126.7 (d, 2C, *meta*-C_{ar}H)*, 77.0 (d, C-7), 71.4 (d, C-6), 66.9 (d, C-1), 63.6 (t, C-4), 60.2 (t, C-3), 45.2 (d, C-8).

* The assignments are interconvertible.

significant NOE contacts:



(1-Cyclopropyl-3-nitrocyclobutane-1,2-diyl)dibenzene (3f)



1a **3f**

$C_{19}H_{19}NO_2$

MW = 293.37 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and (1-cyclopropylvinyl) benzene (144 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 16 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield **3f** (25.6 mg, 86.6 µmol, 88%, d.r. = 67:33) as a pale-yellow coloured oil.

Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and (1-cyclopropylvinyl) benzene (144 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 16 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield **3f** (22.4 mg, 76.4 µmol, 76%, d.r. = 56:44) as a pale-yellow coloured oil.

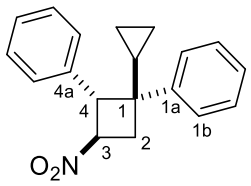
Conditions C: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and (1-cyclopropylvinyl) benzene (144 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 16 hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 20/1) to yield **3f** (11.1 mg, 37.8 µmol, 37%, d.r. = 88:12) as a pale-yellow coloured oil. Starting material was recovered as *trans*-isomer *trans*-**1a** (2.41 mg, 16.2 µmol, 16%).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3028 (w, C_{ar}-H), 1542 (s, C-NO_2), 1496 (m), 1368 (m, C-NO_2), 1028 (m), 824 (w, C_{ar}-H), 770 (m, C_{ar}-H).

MS (EI): *m/z (%)* = 247 (4) $[M\text{-}NO_2]^+$, 205 (32) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 117 (100) $[C_9H_9]^+$.

HRMS (ESI): calcd for $C_{19}H_{20}NO_2^+$ $[M+H]^+$: 294.1488; found: 294.1488.

3f:



3f

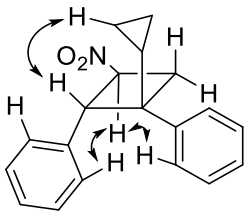
TLC: R_f = 0.69 (P/Et_2O = 9/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.17−7.13 (m, 6H, H_{ar})*, 7.00−6.98 (m, 2H, H_{ar})*, 6.83–6.77 (m, 2H, H_{ar})*, 5.13 (*virt*. q, $^3J \cong {}^3J$ = 9.0 Hz, 1H, H-3‘), 4.07 (d, ^3J = 9.5 Hz, 1H, H-4‘), 3.01 (dd, ^2J = 12.3 Hz, ^3J = 8.1 Hz, 1H, C*H*H-2‘), 2.60 (dd, ^2J = 12.4 Hz, ^3J = 9.2 Hz, 1H, CH*H*-2‘), 1.43 [tt, ^3J = 8.3 Hz, 5.6 Hz, 1H, C*H*(CH_2)$_2$], 0.77–0.66 [m, 2H, CH(CH_2)$_2$], 0.57 [*virt*. tt, $^2J \cong {}^3J$ = 8.6 Hz, ^3J = 5.5 Hz, 1H, CH(CH_2)$_2$], 0.44 [*virt*. dq, ^2J = 9.0 Hz, $^3J \cong {}^3J$ = 5.5 Hz, 1H, CH(CH_2)$_2$].

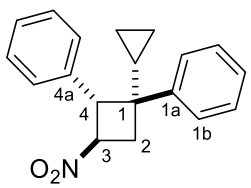
^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 141.1 (s, C-1a), 136.2 (s, C-4a), 128.4 (d, 2C, C_{ar}H)*, 128.3 (d, 2C, C_{ar}H)*, 128.0 (d, 2C, C_{ar}H)*, 127.8 (d, C_{ar}H)*, 127.5 (d, C_{ar}H)*, 126.8 (d, 2C, C_{ar}H)*, 76.9 (d, C-3’), 55.1 (d, C-4’), 47.3 (s, C-1’), 32.1 (t, C-2’), 22.58 [d, *C*H(CH_2)$_2$], 3.21 [t, CH(*C*H_2)$_2$], 2.11 [t, CH(*C*H_2)$_2$].

* The exact assignment of these signals was not possible.

significant NOE contacts:



3f’:



3f'

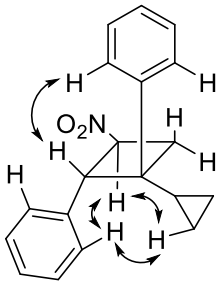
TLC: R_f = 0.58 (P/Et_2O = 9/1) [UV, $KMnO_4$].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.51–7.45 (m, 2H, H_{ar})*, 7.43−7.40 (m, 2H, H_{ar})*, 7.38−7.34 (m, 3H, H_{ar})*, 7.28−7.24 (m, 3H, H_{ar})*, 5.38 (*virt*. q, $^3J \cong {}^3J$ = 8.9 Hz, 1H, H-3‘), 4.43 (d, ^3J = 9.3 Hz, 1H, H-4‘), 2.91 (dd, ^2J = 12.1 Hz, ^3J = 8.9 Hz, 1H, C*H*H-2‘), 2.41 (dd, ^2J = 12.1 Hz, ^3J = 8.1 Hz, 1H, CH*H*-2‘), 0.87 [tt, ^3J = 8.3 Hz, 5.7 Hz, 1H, C*H*$(CH_2)_2$], 0.67–0.61 [m, 1H, CH(C*H*$_2)_2$], 0.48 [*virt*. dq, ^2J = 10.3 Hz, $^3J \cong {}^3J$ = 5.3 Hz, 1H, CH(C*H*$_2)_2$], 0.42 [*virt*. tt, $^2J \cong {}^3J$ = 8.9 Hz, ^3J = 5.1 Hz, 1H, C*H*$(CH_2)_2$], 0.09 [virt. dq, ^2J = 9.3 Hz, $^3J \cong {}^3J$ = 5.7 Hz, 1H, C*H*$(CH_2)_2$].

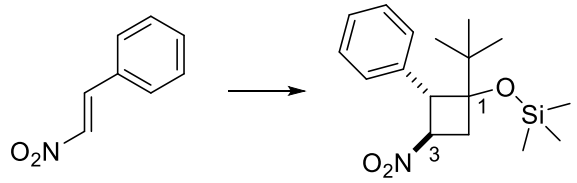
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 148.3 (s. C_{ar}-1a), 136.2 (s, C_{ar}-4a), 128.7 (d, 2C, C_{ar}H)*, 128.7 (d, 2C, C_{ar}H)*, 128.5 (d, 2C, C_{ar}H)*, 127.8 (d, C_{ar}H)*, 126.6 (d, C_{ar}H)*, 125.6 (d, 2C, C_{ar}H)*, 77.8 (d. C-3’), 57.6 (d, C-4’), 45.4 (s, C-1’), 31.9 (t, C-2’), 16.5 [d, *C*H$(CH_2)_2$], 4.36 [t, CH(*C*H$_2)_2$], 1.82 [t, CH(*C*H$_2)_2$].

* The exact assignment of these signals is not possible.

significant NOE contacts:



[1-(*tert*-Butyl)-3-nitro-2-phenylcyclobutoxy]trimethylsilane (3g)



1a **3g**

$C_{17}H_{27}NO_3Si$

MW = 321.49 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (29.8 mg, 200 µmol, 1.00 equiv) and [(3,3-dimethylbut-1-en-2-yl)oxy]trimethylsilane (431 µL, 344 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 24 hours at

room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield **3g** (22.2 mg, 69.0 μmol, 34%, d.r. = 77:23) as a yellow coloured oil.

Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 μmol, 1.00 equiv) and [(3,3-dimethylbut-1-en-2-yl)oxy]trimethylsilane (216 μL, 172 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield **3g** (12.3 mg, 38.3 μmol, 38%, d.r. = 77:23) as a yellow coloured oil.

Conditions C: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 μmol, 1.00 equiv) and [(3,3-dimethylbut-1-en-2-yl)oxy]trimethylsilane (216 μL, 172 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 16 hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield **3g** (11.8 mg, 36.7 μmol, 37%, d.r. = 77:23) as a yellow coloured oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (7.20 mg, 48.3 μmol, 48%).

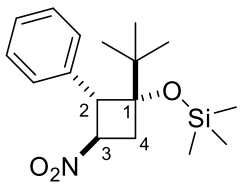
TLC: R_f = 0.70 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063 (w, C_{ar}-H), 3031 (w, C_{ar}-H), 2958 (w, C-H), 1546 (s, C-NO_2), 1480 (m, C_{sp3}-H), 1395 (w), 1368 (m, C-NO_2), 1252 [s, O-Si-C(CH_3)], 1146 (s), 1029 (m), 870 (m, C_{ar}-H), 833 [vs, O-Si-C(CH_3)].

MS (EI): *m/z (%)* = 275 (17) $[M\text{-}NO_2]^+$, 219 (18) $[M\text{-}NO_2\text{-}C(CH_3)_3]^+$, 117 (100) $[C_9H_9]^+$, 73 (36) $[Si(CH_3)_3]^+$.

HRMS (ESI): calcd for $C_{17}H_{28}NO_3Si^+$ $[M+H]^+$: 322.1833; found: 322.1833.

3g:

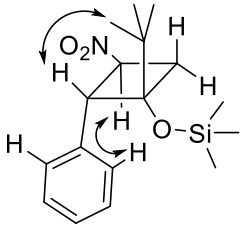


3g

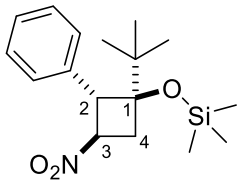
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.33−7.31 (m, 5H, H_{ar}), 5.13 (*virt*. q, $^{3}J \cong {}^{3}J$ = 8.5 Hz, 1H, H-3), 4.24 (d, ^{3}J = 8.6 Hz, 1H, H-2), 2.93 (dd, ^{2}J = 13.2 Hz, ^{3}J = 8.2 Hz, 1H, C*H*H-4), 2.50 (dd, ^{2}J = 13.2 Hz, ^{3}J = 8.6 Hz, 1H, CH*H*-4), 0.97 [s, 9H, $C(CH_3)_3$], 0.12 [s, 9H, $OSi(CH_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 136.4 (s, C_{ar}), 129.0 (d, 2C, *ortho*-C_{ar}H), 128.1 (d, 2C, *meta*-C_{ar}H), 127.3 (d, *para*-C_{ar}H), 83.3 (s, C-1), 78.2 (d, C-3), 52.2 (d, C-2), 37.9 [s, *C*$(CH_3)_3$], 34.3 (t, C-4), 25.8 [q, 3C, C(*C*$H_3)_3$], 2.6 [q, 3C, OSi(*C*$H_3)_3$].

significant NOE contacts:



3g':

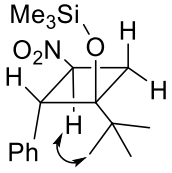


3g'

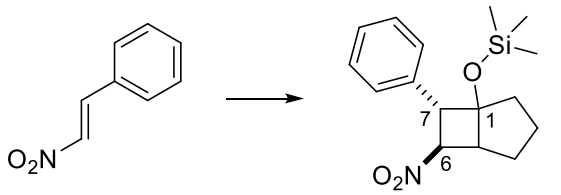
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.35–7.29 (m, 5H, H_{ar}), 5.23 (*virt*. q, $^{3}J \cong {}^{3}J$ = 8.6 Hz, 1H, H-3), 4.24 (d, ^{3}J = 8.6 Hz, 1H, H-2), 2.93 (ddd, ^{2}J = 13.3 Hz, ^{3}J = 8.3 Hz, ^{4}J = 0.9 Hz, 1H, C*H*H-4), 2.50 (dd, ^{2}J = 13.3 Hz, ^{3}J = 8.6 Hz, 1H, CH*H*-4), 0.97 [s, 9H, $C(CH_3)_3$], 0.12 [s, 9H, $OSi(CH_3)_3$].

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 135.9 (s, C_{ar}), 128.4 (d, 2C, *meta*-C_{ar}H), 127.8 (d, 2C, *ortho*-C_{ar}H), 127.3 (d, *para*-C_{ar}H), 80.1 (s, C-1), 73.3 (d, C-3), 61.2 (d, C-2), 38.4 [s, *C*$(CH_3)_3$], 36.8 (t, C-4), 25.2 [q, 3C, C(*C*$H_3)_3$], 2.18 [q, 3C, $OSi(CH_3)_3$].

significant NOE contacts:



Trimethyl[(6-nitro-7-phenylbicyclo[3.2.0]heptan-1-yl)oxy]silane (3h)



1a **3h**

$C_{16}H_{23}NO_3Si$

MW = 305.45 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (29.8 mg, 200 µmol, 1.00 equiv) and (cyclopent-1-en-1-yloxy) trimethylsilane (312 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 18 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield **3h** (20.7 mg, 67.8 µmol, 35%, d.r. = 59:41) as a colorless oil.

Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and (cyclopent-1-en-1-yloxy) trimethylsilane (156 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 24 hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield **3h** (9.8 mg, 32.1 µmol, 32%, d.r. = 59:41) as a colorless oil.

Conditions C: Following general procedure **5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and (cyclopent-1-en-1-yloxy) trimethylsilane (156 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for 24 hours at −78 °C. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield **3h** (11.7 mg, 38.3 µmol, *38*%, d.r. = 61:39) as a colorless oil.

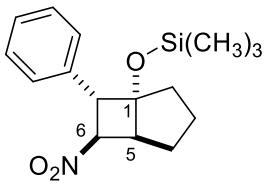
TLC: R_f = 0.70 (P/Et_2O = 9/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3004 (w, C_{ar}-H), 2926 (w, C-H), 1542 (s, C-NO_2), 1497 (m), 1364 (m, C-NO_2), 1264 [w, O-Si-C(CH_3)], 1045 (m), 1018 (m), 891 (m, C_{ar}-H), 822 [m, O-Si-C(CH_3)], 758 (s, C_{ar}-H).

MS (EI): *m/z (%)* = 259 (88) $[M\text{-}NO_2]^+$, 169 (60) $[M\text{-}NO_2\text{-}OSi(CH_3)_3]^+$, 91 (28) $[C_9H_9]^+$, 73 (100) $[Si(CH_3)_3]^+$.

HRMS (ESI): calcd for $C_{16}H_{24}NO_3Si^+$ $[M+H]^+$: 306.1522; found: 306.1522.

3h:



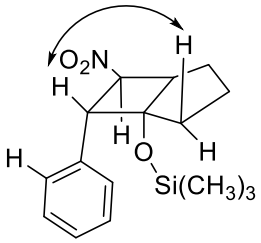
3h

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.38−7.32 (m, 2H, *meta*-H_{ar}), 7.29−7.25 (m, 3H, *ortho*-H_{ar}, *para*-H_{ar}), 5.35 (dd, ^{3}J = 10.1 Hz, 8.8 Hz, 1H, H-6), 4.06 (d, ^{3}J = 8.8 Hz, 1H, H-7), 3.09 (*virt*. t, $^{3}J \cong {}^{3}J$ = 9.2 Hz, 1H, H-5), 2.00−1.91 (m, 4H, CH_2-3, C*H*H-2, C*H*H-4), 1.89−1.77 (m, 1H, CH*H*-2), 1.62−1.44 (m, 1H, CHH-4), −0.14 [s, 9H, $OSi(CH_3)_3$].

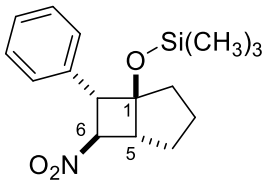
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 136.5 (s, C_{ar}), 129.5 (d, 2C, *ortho*-$C_{ar}H$), 128.8/128.5 (d, 2C *meta*-$C_{ar}H$)*, 127.5/127.3 (d, *para*-$C_{ar}H$)*, 83.5 (s, C-1), 81.0 (d, C-6), 51.9 (d, C-7), 49.9 (d, C-5), 40.1 (t, CH_2-2), 26.1 (t, CH_2-4), 25.9 (t, CH_2-3), 1.64 [q, 3C, $OSi(CH_3)_3$].

* The exact assignment of these ^{13}C-signals was not possible.

significant NOE contacts:



3h':



3h'

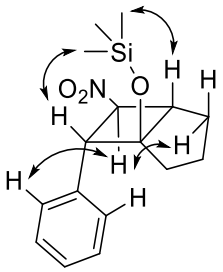
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.38–7.32 (m, 2H, *meta*-H_{ar}), 7.29−7.25 (m, 1H, *para*-H_{ar}), 7.24−7.21 (m, 2H, *ortho*-H_{ar}), 4.59 (dd, ^{3}J = 8.3 Hz, 5.4 Hz, 1H, H-6), 4.40 (d, ^{3}J = 8.3 Hz, 1H, H-7), 3.30 (*virt*. t, $^{3}J \cong {}^{3}J$ = 6.2 Hz, 1H, H-5), 2.00−1.91 (m, 1H, C*H*H-4), 1.89−1.77 (m,

2H, CH*H*-4, C*H*H-2), 1.71−1.66 (m, 1H, C*H*H-3), 1.62−1.44 (m, 2H, CH*H*-2, CH*H*-3), 0.22 [s, 9H, OSi(CH_3)$_3$].

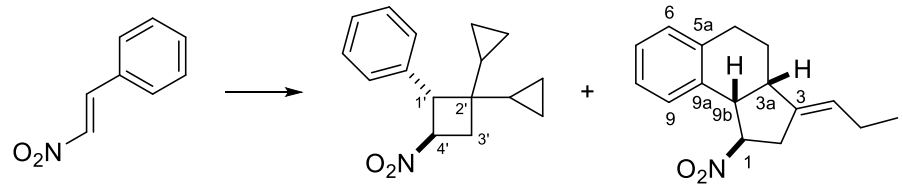
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 136.3 (s, C_{ar}), 128.8/128.5 (d, *meta*-C_{ar}H)*, 127.5/127.3 (d, *para*-C_{ar}H)*, 126.7 (d, *ortho*-C_{ar}H), 84.3 (s, C-1), 79.2 (d, C-6), 56.3 (d, C-7), 52.7 (d, C-5), 35.8 (d, CH_2-3), 30.0 (d, CH_2-4), 24.9 (d, CH_2-2), 2.03 [q, 3C, OSi(CH_3)$_3$].

* The exact assignment of these ^{13}C-signals was not possible.

significant NOE contacts:



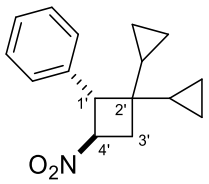
(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)benzene (3i)



1a | **3i** $C_{16}H_{19}NO_2$ MW = 257.33 g/mol | **7** $C_{16}H_{19}NO_2$ MW = 257.33 g/mol

Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 μmol, 1.00 equiv) and ethene-1,1-diyldicyclopropane (109 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 419 nm (fluorescent lamps) for twelve hours at room temperature. The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 40/1) to yield **3i** (18.0 mg, 69.9 μmol, 70%) and the side product **7** (2.20 mg, 8.55 μmol, 9%) both as a yellow coloured liquid.

3i:



3i

TLC: R_f = 0.58 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, $C_{cyclopropane}$-H), 3004 (w, C_{ar}-H), 1542 (s, C-NO_2), 1449 (w), 1369 (m, C-NO_2), 1017 (s), 822 (w, C_{ar}-H), 758 (s, C_{ar}-H).

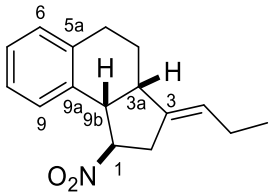
MS (EI): *m/z (%)* = 211 (4) $[M\text{-}NO_2]^+$, 169 (16) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 117 (100) $[C_9H_9]^+$.

HRMS (ESI): calcd for $C_{16}H_{20}NO_2^+$ $[M+H]^+$: 258.1448; found: 258.1449.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.44–7.20 (m, 5H, H_{ar}), 5.20 (*virt*. q, $^3J \cong {}^3J$ = 8.7 Hz, 1H, H-4'), 3.97 (d, ^3J = 9.2 Hz, 1H, H-1'), 2.06 (dd, ^2J = 12.2 Hz, ^3J = 8.7 Hz, 1H, C*H*H-3'), 1.71 (dd, ^3J = 12.2 Hz, ^3J = 8.3 Hz, 1H, CH*H*-3'), 1.09 [tt, ^3J = 8.4 Hz, 5.5 Hz, 1H, C*H*$(CH_2)_2$], 0.60-0.25 [m, 6H, C*H*$(CH_2)_2$, CH(C*H*$_2)_2$], 0.20–0.13 [m, 1H, CH(C*H*$_2)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 136.4 (s, C_{ar}), 128.5 (d, 2C, *meta*-C_{ar}H), 127.7 (d, 2C, *ortho*-C_{ar}H), 127.2 (d, *para*-C_{ar}H), 76.6 (d, C-4'), 55.5 (d, C-1'), 41.7 (s, C-2'), 27.8 (t, C-3'), 20.2 [d, *C*H$(CH_2)_2$], 14.6 [d, *C*H$(CH_2)_2$], 1.93 [t, CH(*C*H$_2)_2$], 1.74 [t, CH(*C*H$_2)_2$], 0.90 [t, CH(*C*H$_2)_2$], 0.72 [t, CH(*C*H$_2)_2$].

1-Nitro-3-propylidene-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[a]naphthalene (7)



7

TLC: R_f = 0.69 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}]: 3419 (br), 2928 (w, CR_3-H), 1722 (w), 1547 (s, C-NO_2), 1367 (m, C-NO_2), 1023 (m), 856 (m, C_{ar}-H), 791 (m, R_2C=CHR).

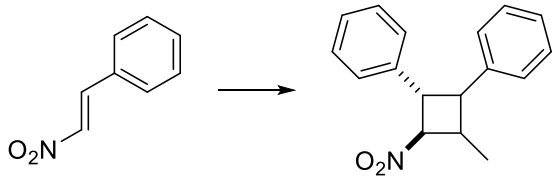
MS (EI): *m/z (%)* = 181 (100) $[M\text{-}NO_2\text{-}C_2H_4]^+$, 167 (40) $[C_{13}H_{11}]^+$, 128 (16) $[C_{10}H_8]^+$.

HRMS (ESI): calcd for $C_{16}H_{20}NO_2^+$ $[M+H]^+$: 258.1448; found: 258.1449.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.17–7.05 (m, 4H, H_{ar}), 5.45 (ttd, ^3J = 7.1 Hz, ^4J = 2.5 Hz, 1.6 Hz, 1H, C=C*H*CH_2CH_3), 4.90 (*virt*. q, $^3J \cong {}^3J$ = 7.3 Hz, 1H, H-1), 3.90 (*virt*. t, $^3J \cong {}^3J$ = 7.5 Hz, 1H, H-9b), 3.07–2.94 (m, 2H, H-3a, C*H*H-2), 2.90 (dddd, ^2J = 17.3 Hz, ^3J = 7.9 Hz, ^4J = 2.7 Hz, 1.4 Hz, 1H, CH*H*-2), 2.80–2.75 (m, 1H, C*H*H-5), 2.73–2.68 (m, 1H, CH*H*-5), 2.07-1.98 (m, 2H, C=CHCH_2CH_3), 1.84 (ddt, ^2J = 13.8 Hz, ^3J = 6.2 Hz, 4.7 Hz, 1H, C*H*H-4), 1.67 (dtd, ^2J = 13.8 Hz, ^3J = 9.5 Hz, 4.8 Hz, 1H, CH*H*-4), 1.00 (t, ^3J = 7.5 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 138.7 (s, C-3), 137.1 (s, C-5a), 134.4 (s, C-9a), 129.3 (d, C-6), 128.6 (d, C-9), 127.2 (d, C-8), 126.6 (d, C-7), 125.9 (d, *C*=CHCH_2CH_3), 92.2 (d, C-1), 47.7 (d, C-9b), 42.0 (d, C-3a), 34.6 (t, C-2), 27.8 (t. C-5), 27.3 (t, C-4), 22.8 (t, C=CH*C*H_2CH_3), 14.1 (q, CH_3).

(3'-Methyl-4'-nitrocyclobutane)-1,2-diyl-dibenzene (3j)



1a **3j**

$C_{17}H_{17}NO_2$

MW = 267.33 g/mol

Conditions A: Following **GP 5**, a solution of nitroethene **1a** (29.8 mg, 200 µmol, 1.00 equiv) and ***trans*-14** (259 µL, 236 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for twelve hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield **3j** (28.1 mg, 1.05 mmol, 53%, d.r. = 46:54) as a colorless oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (6.60 mg, 42.3 µmol, 22%).

Conditions B: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 µmol, 1.00 equiv) and ***trans*-14** (130 µL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was

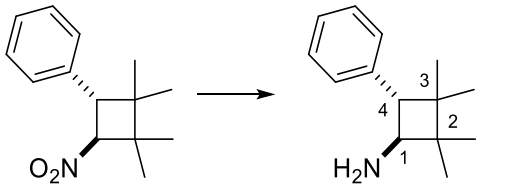
irradiated at λ = 424 nm (LED) for twelve hours at room temperature (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 50/1) to yield **3j** (14.6 mg, 54.6 μmol, 53%, d.r. = 49:51) as a colorless oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (3.03 mg, 20.3 μmol, 20%).

Conditions C: Following **GP 5**, a solution of nitroethene **1a** (14.9 mg, 100 μmol, 1.00 equiv) and ***trans*-14** (130 μL, 118 mg, 1.00 mmol, 10.0 equiv) in dichloromethane (5 mL) was irradiated at λ = 424 nm (LED) for twelve hours at −78 °C (at that point, no further conversion was observed). The crude product was purified by column chromatography (2 × 10 cm, P/Et_2O = 50/1) to yield **3j** (10.7 mg, 40.0 μmol, 40%, d.r. = 64:36) as a colorless oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (2.80 mg, 18.8 μmol, 19%).

Procedure for the [2+2] photocycloaddition reaction of *trans*-β-nitrostyrene with *cis*-β-methylstyrene: Following **GP 5**, a solution of nitroethene **1a** (29.8 mg, 200 μmol, 1.00 equiv) and ***cis*-14** (260 μL, 236 mg, 2.00 mmol, 10.0 equiv) in dichloromethane (10 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 15 hours at room temperature (at this point, no further conversion was observed). The crude product was purified by column chromatography (2 × 15 cm, P/Et_2O = 50/1) to yield **3j** (45.8 mg, 1.12 mmol, 56%, d.r. = 77:23) as a colorless oil. Starting material was recovered as *cis*-isomer *cis*-**1a** (6.80 mg, 45.6 μmol, 23%) was recovered. The olefin was recovered exclusively as ***cis*-14**.

The analytical data match those reported in the literature.[2]

2,2,3,3-Tetramethyl-4-phenylcyclobutan-1-amine (4)



2a **4**

$C_{14}H_{21}N$

MW = 203.33 g/mol

According to a literature known procedure:[19] Zn powder (350 mg, 5.36 mmol, 25.0 equiv) was added in small portions to a stirred solution of nitrocyclobutane **2a** (50.0 mg, 214 μmol, 1.00 equiv) in a mixture of water/acetic acid (2 mL; 1/1 v/v). The suspension was stirred for

four hours at room temperature. Aqueous NaOH solution (c = 5 M) was added until pH = 7 was reached. The cloudy solution was extracted with dichloromethane (2 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl solution (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield **4** (33.6 mg, 165 µmol, 77%) as a colorless oil.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3060 (w, C_{Ph}-H), 2959 (m, C_{Ph}-H), 2866 (w), 2604 (w), 1566 (br s, C-NH_2), 1458 (s), 1449 (s), 1358 (m),1337 (s), 1270 (m), 1132 (m), 885 (m), 810 (m, C_{Ph}-H).

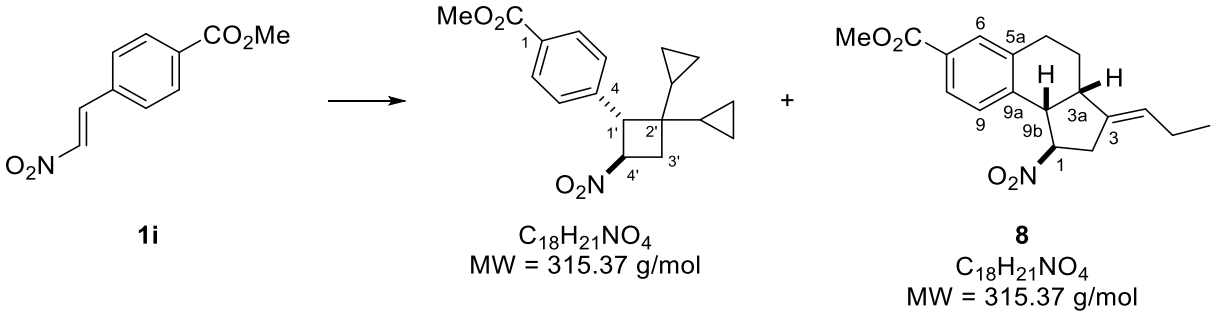
MS (EI, 70 eV): *m/z (%)* = 132 (5) $[M\text{-}C_4H_9N]^+$, 119 (100) $[M\text{-}C_4H_9N\text{-}CH_3]^+$, 91 (13) $[C_7H_7]^+$, 71 (31) $[C_4H_9]^+$, 56 (11).

HRMS (ESI): calcd for $C_{14}H_{22}N^+$ $[M+H]^+$: 204.1741; found: 204.1748.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.29–7.21 (m, 2H, *meta*-H_{ar}), 7.19–7.08 (m, 3H, *ortho*-H_{ar}, *para*-H_{ar}), 3.37 (d, ^3J = 9.9 Hz, 1H, H-1), 2.86 (d, ^3J = 9.9 Hz, 1H, H-4), 1.51 (br. s., 2H, NH_2), 1.03 [s, 3H, CH_3-2], 1.01 [s, 3H, CH_3-3], 0.93 [s, 3H, CH_3-2], 0.59 [s, 3H, CH_3-3].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 139.6 (s, C_{ar}), 128.3 (d, 2C, *meta*-$C_{ar}H$), 127.7 (d, 2C, *ortho*-$C_{ar}H$), 126.1 (d, *para*-$C_{ar}H$), 56.8 (d, C-4), 55.5 (d, C-1), 41.7 (s, C-2), 39.6 (s, C-3), 24.2 [q, (C-3)CH_3], 22.6 [q, (C-2)CH_3], 21.1 [q, (C-3)CH_3], 18.7 [q, (C-2)CH_3].

Methyl (E)-1-nitro-3-propylidene-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthalene-7-carboxylate (8)



1i

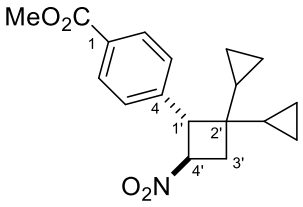
$C_{18}H_{21}NO_4$
MW = 315.37 g/mol

8
$C_{18}H_{21}NO_4$
MW = 315.37 g/mol

Following **GP 5**, a solution of nitroethene **1i** (248 mg, 1.20 mmol, 1.00 equiv) and 1,1-dicyclopropylethylene (1.29 g, 12.0 mmol, 10.0 equiv) in dichloromethane (60 mL) were irradiated at λ = 419 nm (fluorescent lamps) for 16 hours at room temperature. The crude product was purified by column chromatography (4 × 20 cm, P/Et_2O = 40/1) to yield

(2',2'-dicyclopropyl-4'-nitrocyclobutyl)-benzene (213 mg, 6.75 mmol, 57%) and **8** (16.0 mg, 50.7 µmol, 5%) both as a colorless solid.

(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)benzene



TLC: R_f = 0.48 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, $C_{cyclopropane}$-H), 3003 (w, C_{ar}-H), 2845 (w, O-CH_3), 1717 (vs, C=O), 1543 (s, C-NO_2), 1369 (m, C-NO_2), 1277 (vs, O=C-OCH_3), 1107 (s, O=C-OCH_3), 1018 (m), 803 (w, C_{ar}-H).

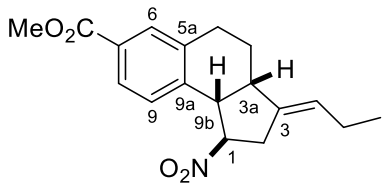
MS (EI): *m/z (%)* = 269 (12) $[M\text{-}NO_2]^+$, 227 (16) $[M\text{-}NO_2\text{-}C_3H_6]^+$, 175 (100) $[C_{11}H_{11}O_2]^+$, 149 (55) $[C_9H_9O_2]^+$, 115 (66), 91 (46) $[C_7H_7]^+$.

HRMS (ESI): calcd for $C_{18}H_{22}NO_4^+$ $[M+H]^+$: 316.1543; found: 316.1544.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.02 (d, ^3J = 8.3 Hz, 2H, H-2, H-6), 7.38 (d, ^3J = 8.3 Hz, 2H, H-3, H-5), 5.21 (*virt*. q, $^3J \cong {}^3J$ = 8.7 Hz, 1H, H-4'), 4.02 (d, ^3J = 9.2 Hz, 1H, H-1'), 3.91 (s, 3H, CO_2CH_3), 2.08 (dd, ^2J = 12.3 Hz, ^3J = 8.6 Hz, 1H, C*H*H-3'), 1.73 (dd, ^2J = 12.3 Hz, ^3J = 8.3 Hz, 1H, CH*H*-3'), 1.15–1.02 [m, 1H, C*H*$(CH_2)_2$], 0.62–0.25 [m, 8H, C*H*$(CH_2)_2$, CH(C*H*$_2)_2$], 0.19−0.13 (m, 1H, CH(C*H*$_2)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 166.9 (*C*O_2CH_3), 141.7 (s, C-4), 129.8 (d, 2C, C-2, C-6), 127.6 (d, 2C, C-3, C-5), 76.1 (d, C-4'), 55.6 (d, C-1'), 52.3 (q, CO_2*C*H_3), 42.1 (s, C-2'), 27.8 (t, C-3'), 20.0 [d, *C*H$(CH_2)_2$], 14.6 [d, *C*H$(CH_2)_2$], 1.87 [t, CH(*C*$H_2)_2$], 1.75 [t, CH(*C*$H_2)_2$], 0.98 [t, CH(*C*$H_2)_2$], 0.75 [t, CH(*C*$H_2)_2$].

8:



8

TLC: R_f = 0.53 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3423 (br), 2955 (w, CR_3-H), 1720 (s, C=O), 1550 (s, C-NO_2), 1437 (m, R_2C-H_2), 1368 (m, C-NO_2), 1284 (s, O=C-OCH_3), 1105 (m, O=C-OCH_3), 762 (s, C_{ar}-H).

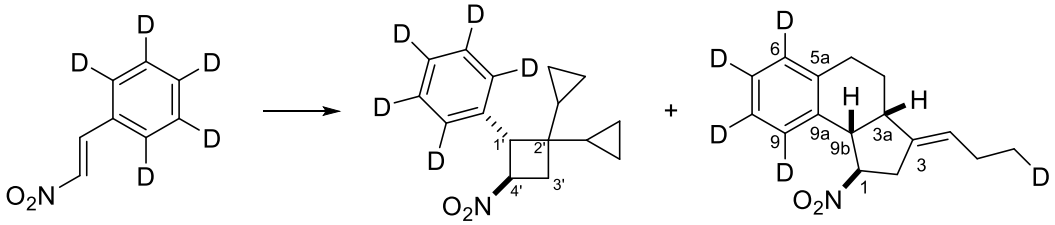
MS (EI): *m/z (%)* = 284 (19) $[M\text{-}OCH_3]^+$, 253 (54), 149 (100) $[C_9H_9O_2]^+$, 115 (49), 91 (63) $[C_7H_7]^+$.

HRMS (ESI): calcd for $C_{18}H_{22}NO_2^+$ $[M+H]^+$: 316.1543; found: 316.1545.

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.80–7.77 (m, 2H, H-6, H-8), 7.14 (d, ^3J = 8.6 Hz, 1H, H-9), 5.46 (*virt*. tq, ^3J = 6.9 Hz, $^4J \cong {}^4J$ = 2.4 Hz, 1H, C=C*H*CH_2CH_3), 4.88 (*virt*. q, $^3J \cong {}^3J$ = 7.3 Hz, 1H, H-1), 3.96–3.91 (m, 1H, H-9b), 3.90 (s, 3H, CO_2CH_3), 3.11–2.95 (m, 2H, H-3a, C*H*H-2), 2.95–2.80 (m, 2H, CH*H*-2, C*H*H-5), 2.78–2.66 (m, 1H, CH*H*-5), 2.08–1.96 (m, 2H, C=CHCH_2CH_3), 1.91–1.81 (m, 1H, C*H*H-4), 1.68 (dtd, ^2J = 13.9 Hz, ^3J = 9.3 Hz, 4.8 Hz, 1H, CH*H*-4), 1.00 (t, ^3J = 7.5 Hz, 3H, C=CHCH_2CH_3).

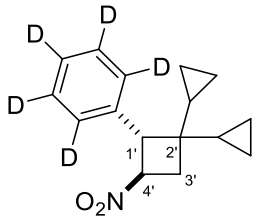
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 138.7 (s, C-3), 137.1 (s, C-5a), 134.4 (s, C-9a), 129.3 (d, C-6), 128.6 (d, C-9), 127.2 (d, C-8), 126.6 (d, C-7), 125.9 (d, *C*=$CHCH_2CH_3$), 92.2 (d, C-1), 52.3 (q, CO_2CH_3) 47.7 (d, C-9b), 42.0 (d, C-3a), 34.6 (t, C-2), 27.8 (t. C-5), 27.3 (t, C-4), 22.8 (t, C=CH*C*H_2CH_3), 14.1 (q, C=$CHCH_2CH_3$).

(*E*)-1-Nitro-3-(propylidene-3-*d*)-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[a]naphthalene-6,7,8,9-*d*$_4$ (7-*d*$_5$)



Following **GP 5**, a solution of nitroethene **1a-*d*$_5$** (62.0 mg, 402 µmol, 1.00 equiv) and ethene-1,1-diyldicyclopropane (435 mg, 4.02 mmol, 10.0 equiv) in dichloromethane (20 mL) was irradiated at λ = 419 nm (fluorescent lamps) for 14 hours at room temperature. The crude product was purified by column chromatography (3 × 20 cm, P/Et$_2$O = 40/1) to yield 1-(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)-benzene-2,3,4,5,6-*d*$_5$ (64.0 mg, 244 µmol, 61%) and the side product **7-*d*$_5$** (11.5 mg, 43.8 µmol, 11%) both as a yellow coloured oil.

1-(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)-benzene-2,3,4,5,6-*d*$_5$



TLC: R_f = 0.60 (P/Et$_2$O = 19/1) [UV, KMnO$_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3079 (w, C$_{cyclopropyl}$-H), 3003 (w, C$_{ar}$-H), 2275 (w), 1542 (s, C NO$_2$), 1369 (m, C-NO$_2$), 1018 (m), 824 (w, C$_{ar}$-H), 696 (w, CH).

MS (EI): *m/z (%)* = 216 (8) [M-NO$_2$]$^+$, 173 (10), 133 (15) [C$_{10}$H$_5$D$_5$]$^+$, 122 (100) [C$_9$H$_4$D$_5$]$^+$, 96 (15) [C$_7$H$_2$D$_5$]$^+$, 79 (20).

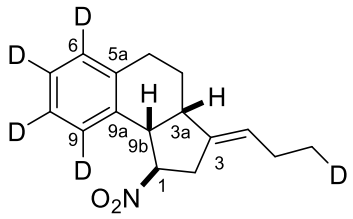
HRMS (ESI): calcd for C$_{16}$H$_{15}$D$_5$NO$_2^+$ [M+H]$^+$: 263.1802; found: 263.1803.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.20 (*virt*. q, $^3J \cong {}^3J$ = 8.7 Hz, 1H, H-4'), 3.97 (d, ^3J = 9.2 Hz, 1H, H-1'), 2.06 (dd, ^2J = 12.2 Hz, ^3J = 8.7 Hz, 1H, C*H*H-3'), 1.71 (dd, ^3J = 12.2 Hz, ^3J = 8.3 Hz, 1H, CH*H*-3'), 1.09 [tt, ^3J = 8.3 Hz, 5.5 Hz, 1H, C*H*$(CH_2)_2$], 0.56–0.26 [m, 8H, C*H*$(CH_2)_2$, CH(C*H*$_2)_2$], 0.20–0.12 [m, 1H, CH(C*H*$_2)_2$].

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 136.2 (s, C_{ar}), 76.6 (d, C-4'), 55.4 (d, C-1'), 41.7 (s, C-2'), 27.8 (t, C-3'), 20.2 [d, *C*H$(CH_2)_2$], 14.6 [d, *C*H$(CH_2)_2$], 1.93 [t, CH(*C*H$_2)_2$], 1.73 [t, CH(*C*H$_2)_2$], 0.90 [t, CH(*C*H$_2)_2$], 0.73 [t, CH(*C*H$_2)_2$].

The aromatic ^{13}C-signals of carbons connected to deuterium-atoms were not visible in the ^{13}C-spectrum.

7-*d*$_5$:



7-*d*$_5$

TLC: R_f = 0.70 (P/Et_2O = 19/1) [UV, $KMnO_4$].

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3418 (br), 2928 (w, CR_3-H), 1711 (w), 1547 (s, C-NO_2), 1368 (m, C-NO_2), 1261 (w), 1024 (m), 858 (m, C_{ar}-H), 803 (w), 752 (m, R_2C=CHR).

MS (EI): *m/z (%)* = 215 (65) $[M\text{-}NO_2]^+$, 185 (100) $[M\text{-}NO_2\text{-}C_2H_4]^+$, 171 (36), 132 (20) $[C_{10}H_4D_4]^+$, 95 (6) $[C_7H_3D_4]^+$.

HRMS (ESI): calcd for $C_{16}H_{15}D_5NO_2^+$ $[M+H]^+$: 263.1802; found: 263.1804.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.45 (tq, ^3J = 7.1 Hz, ^4J = 2.4 Hz, 1H, C=C*H*CH_2CH_3), 4.90 (*virt*. q, $^3J \cong {}^3J$ = 7.4 Hz, 1H, H-1), 3.90 (*virt*. t, $^3J \cong {}^3J$ = 7.6 Hz, 1H, H-9b), 3.08–2.94 (m, 2H, H-3a, C*H*H-2), 2.90 (dd, ^2J = 17.3 Hz, ^3J = 7.8 Hz, 1H, CH*H*-2), 2.81–2.75 (m, 1H, C*H*H-5), 2.69 (ddd, ^2J = 16.4 Hz, ^3J = 9.1 Hz, 4.8 Hz, 1H, CH*H*-5), 2.05−1.98 (m, 2H, C=CHC*H*$_2CH_3$), 1.89–1.79 (m, 1H, C*H*H-4), 1.67 (dtd, ^2J = 14.0 Hz, ^3J = 9.4 Hz, 4.8 Hz, 1H, CH*H*-4), 0.98 (tt, ^3J = 7.6 Hz, ^2J = 2.1 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 138.8 (s, C-3), 137.0 (s, C-5a), 134.4 (s, C-9a), 126.0 (d, *C*=CHCH$_2$CH$_2$D), 92.2 (d, C-1), 47.6 (d, C-9b), 42.1 (d, C-3a), 34.6 (t, C-2), 27.7 (t. C-5), 27.3 (t, C-4), 22.8 (t, C=CH*C*H$_2$CH$_2$D), 14.1 (t, $^1J_{CD}$ = 19.4 Hz C=CHCH$_2$*C*H$_2$D).

The aromatic ^{13}C-signals of carbons connected to deuterium-atoms were not visible in the ^{13}C-spectrum.

7. UV Vis Spectra of Nitroethenes 1a-1o

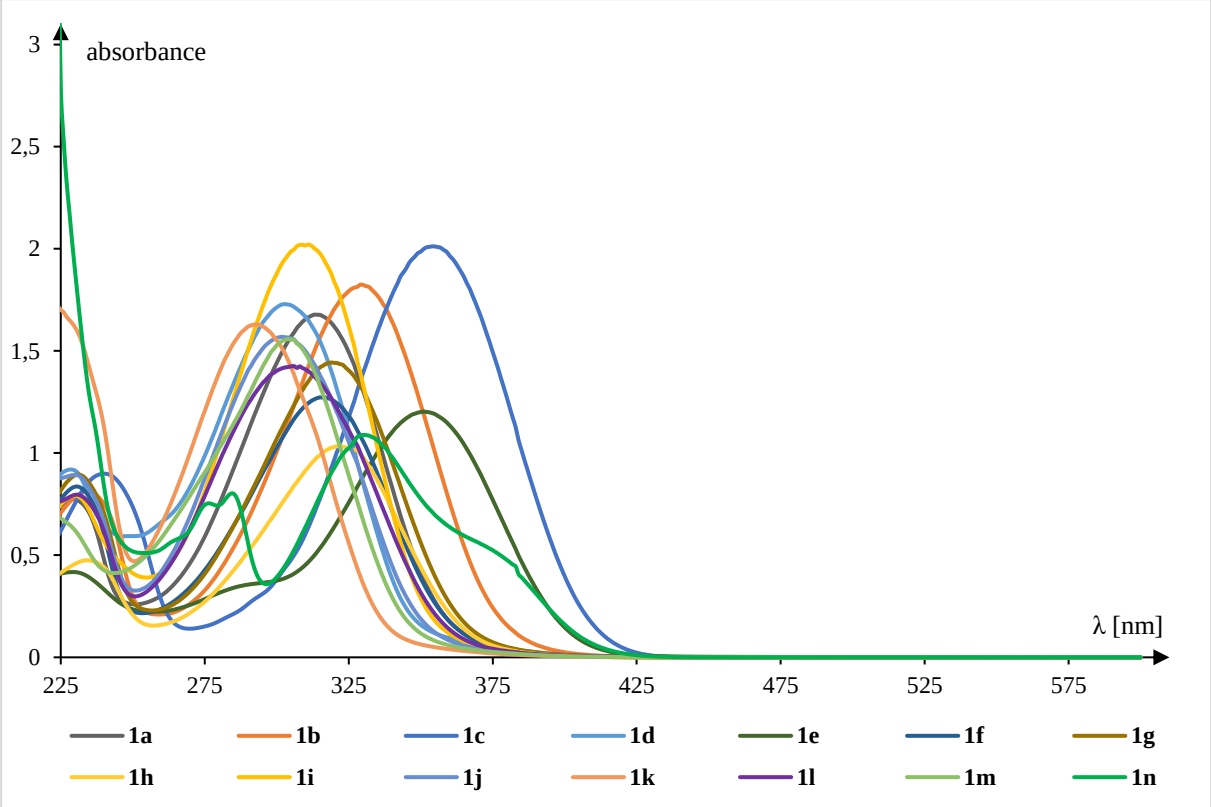


Figure S1. UV-Vis spectra of nitroethenes **1a-1n** (c = 1 mM, CH_2Cl_2).

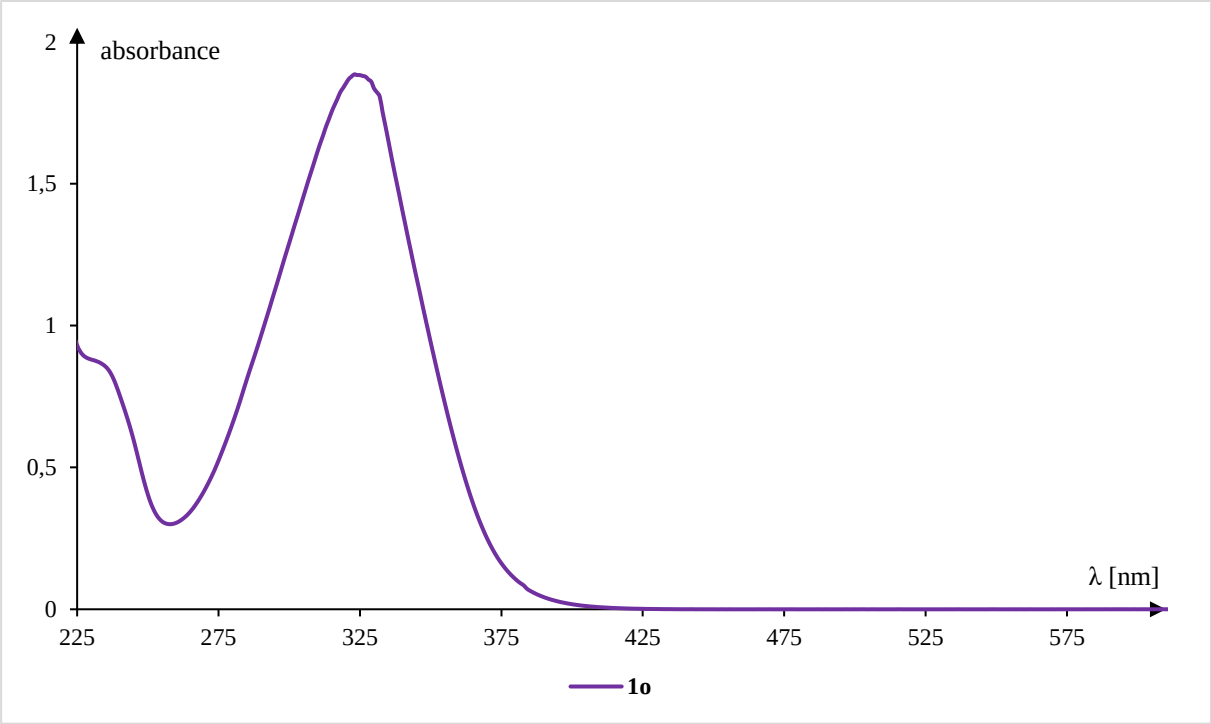


Figure S2. UV-Vis spectrum of nitroethene **1o** (c = 1 mM, CH_2Cl_2).

8. Luminescence Spectroscopy and Determination of E_T of Nitroethene 1a

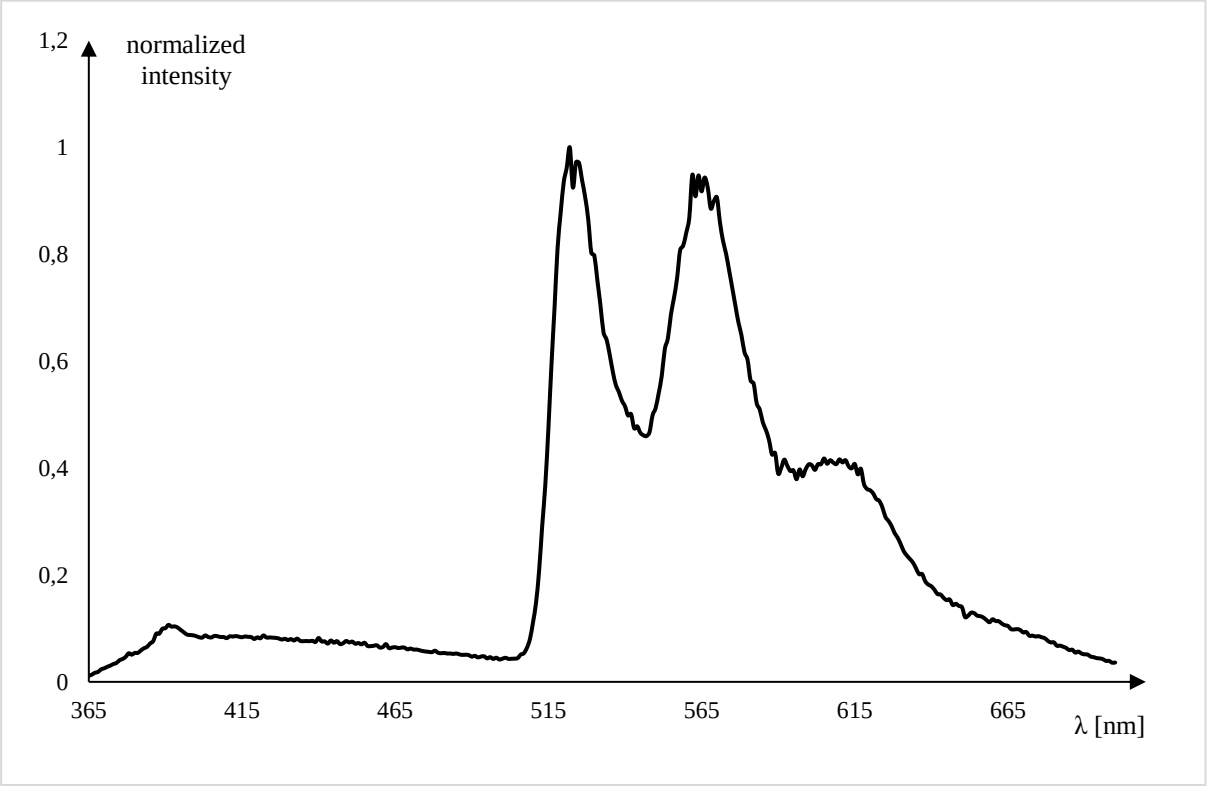


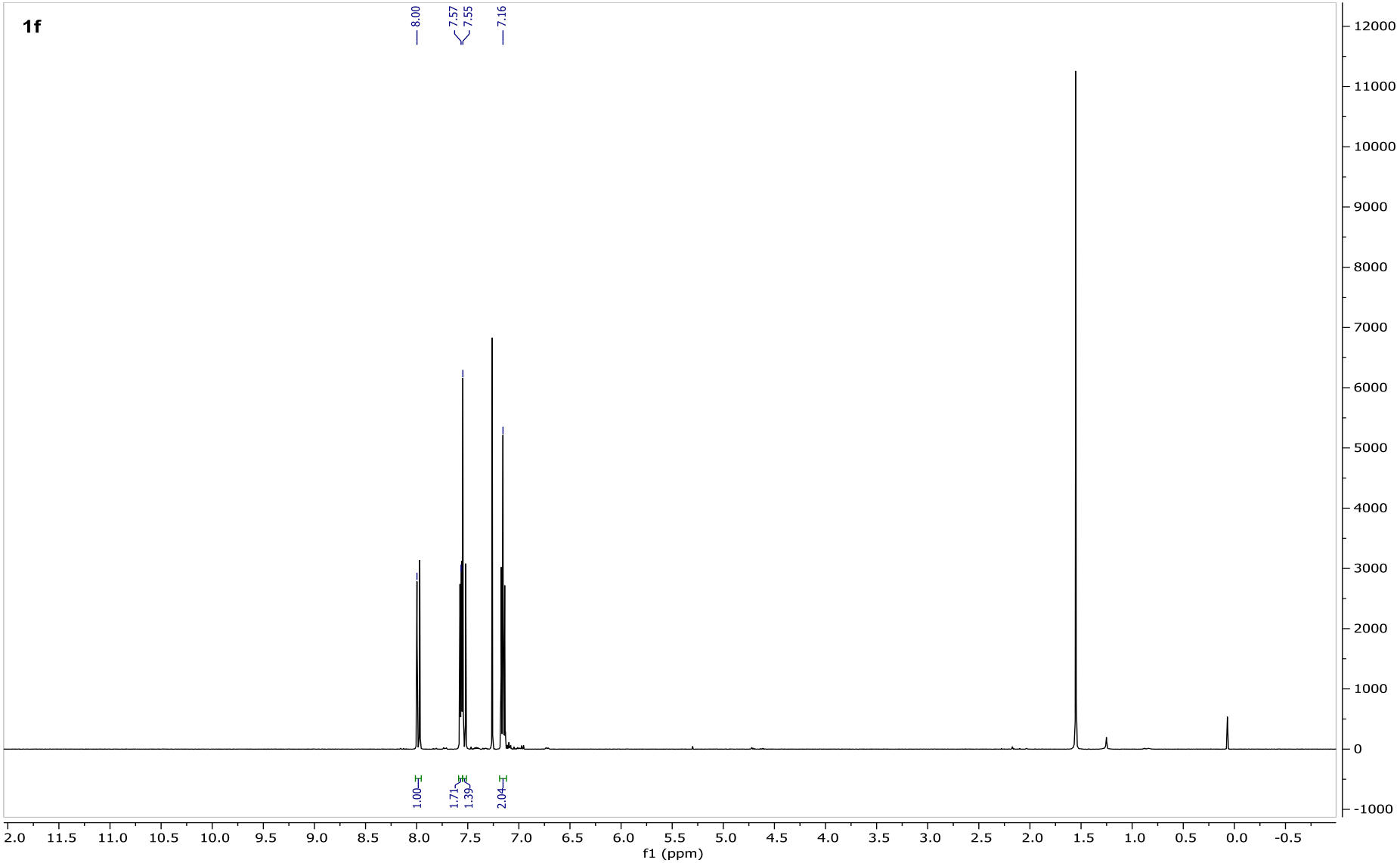
Figure S3. Phosphorescence spectrum of nitroethene **1a** (*c* = 300 μM, EtOH, 77 K) (Excitation at λ = 350 nm, pulsed, flash delay 50 μs).

The triplet energy E_T has been calculated from the emission maximum $\lambda_{max}(0,0)$ = 523 nm, which corresponds to E_T = 229 kJ/mol (in EtOH). This is in accordance with findings in the literature, with a measured emission of λ = 524 nm (E_T = 228 kJ/mol) in ethanol as the solvent.[20]

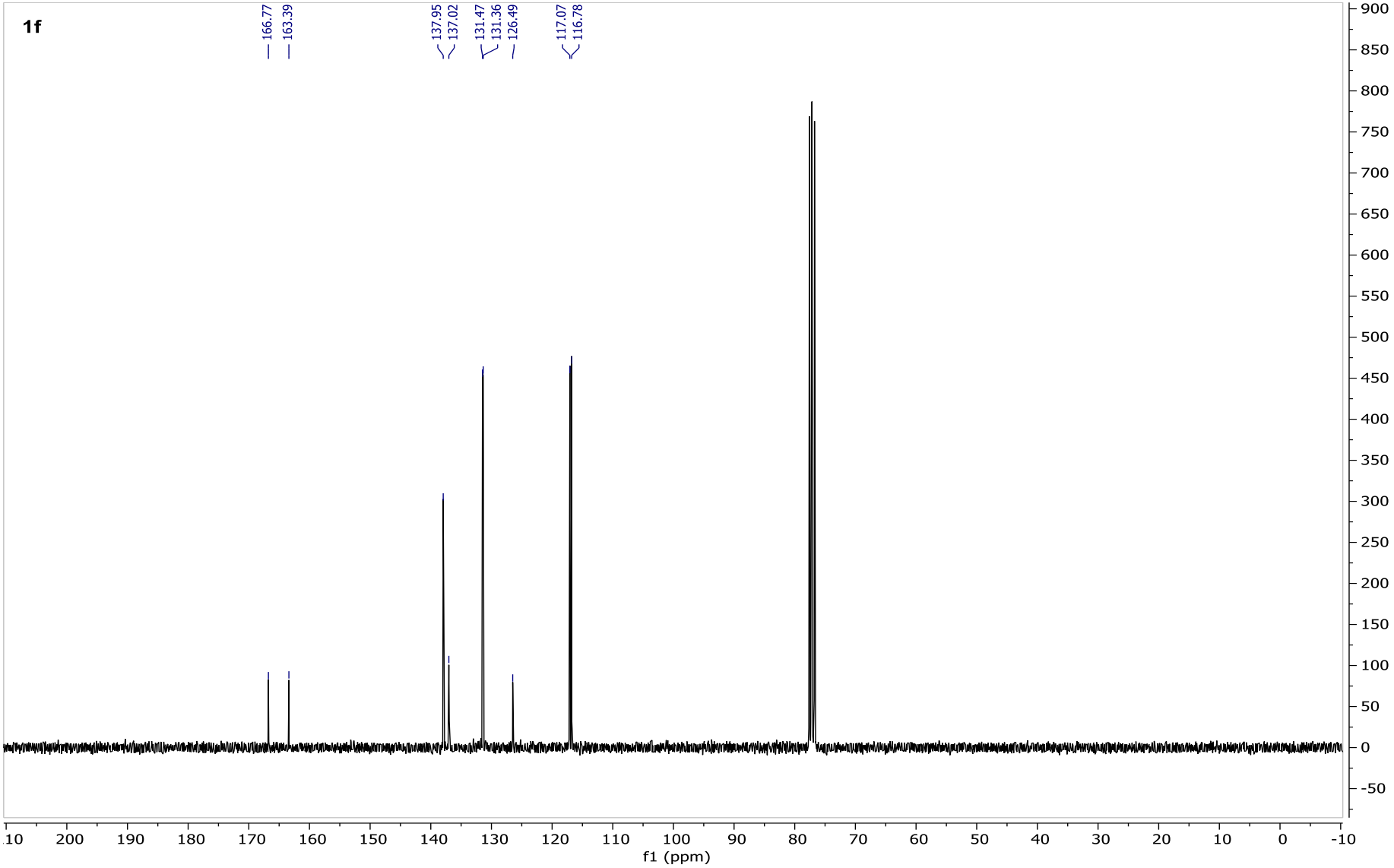
9. NMR Spectra

The NMR-Spectra of nitroethenes **1b**-**1e** and nitrocyclobutanes **2a**-**2e** as well as **3a**, **3b** and **3j** have already been published elsewhere and are therefore not included in this supporting information.[synlett]

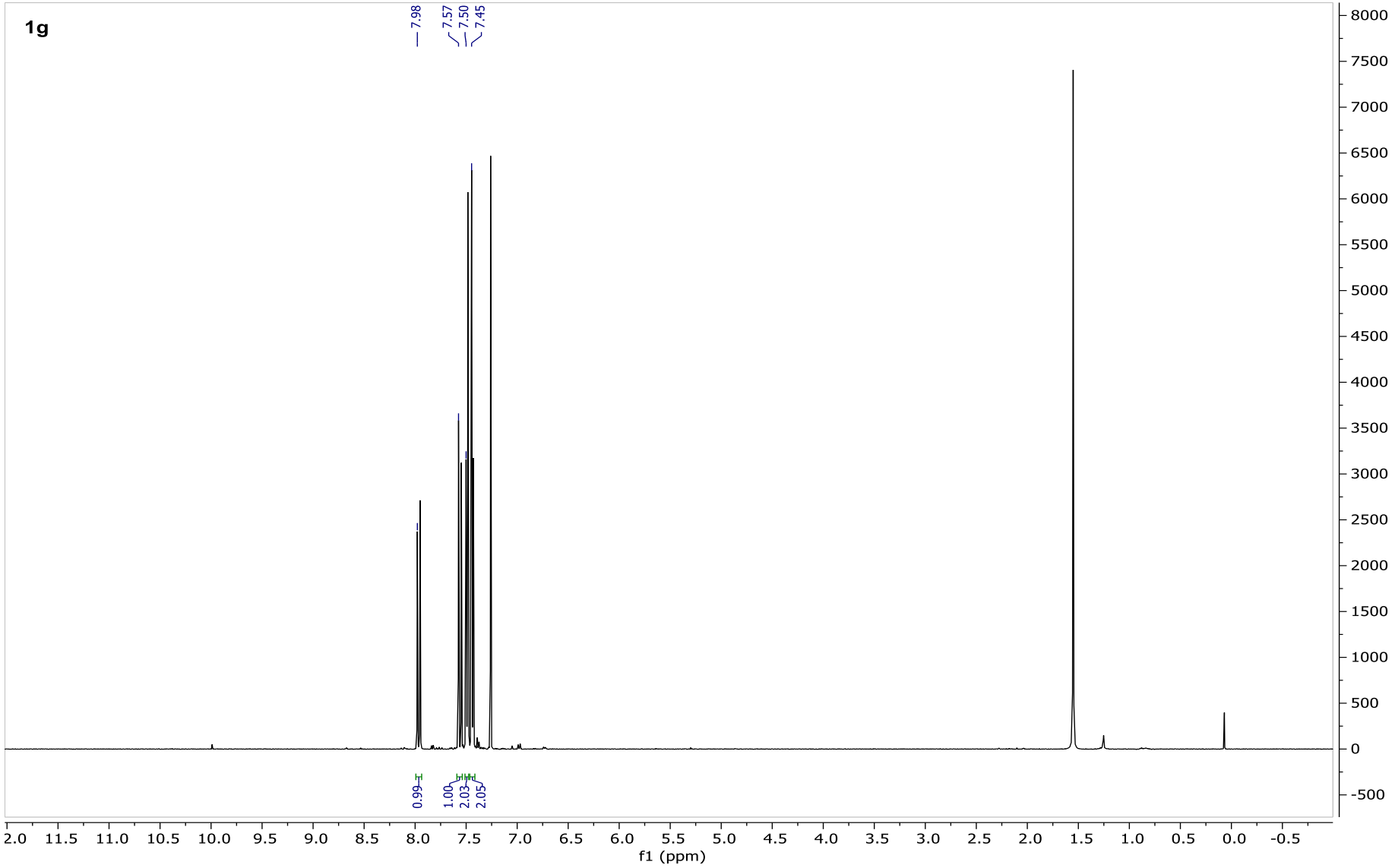
(*E*)-1-Fluoro-4-(2‘-nitrovinyl)benzene (1f): ^{1}H NMR (500 MHz, $CDCl_3$):



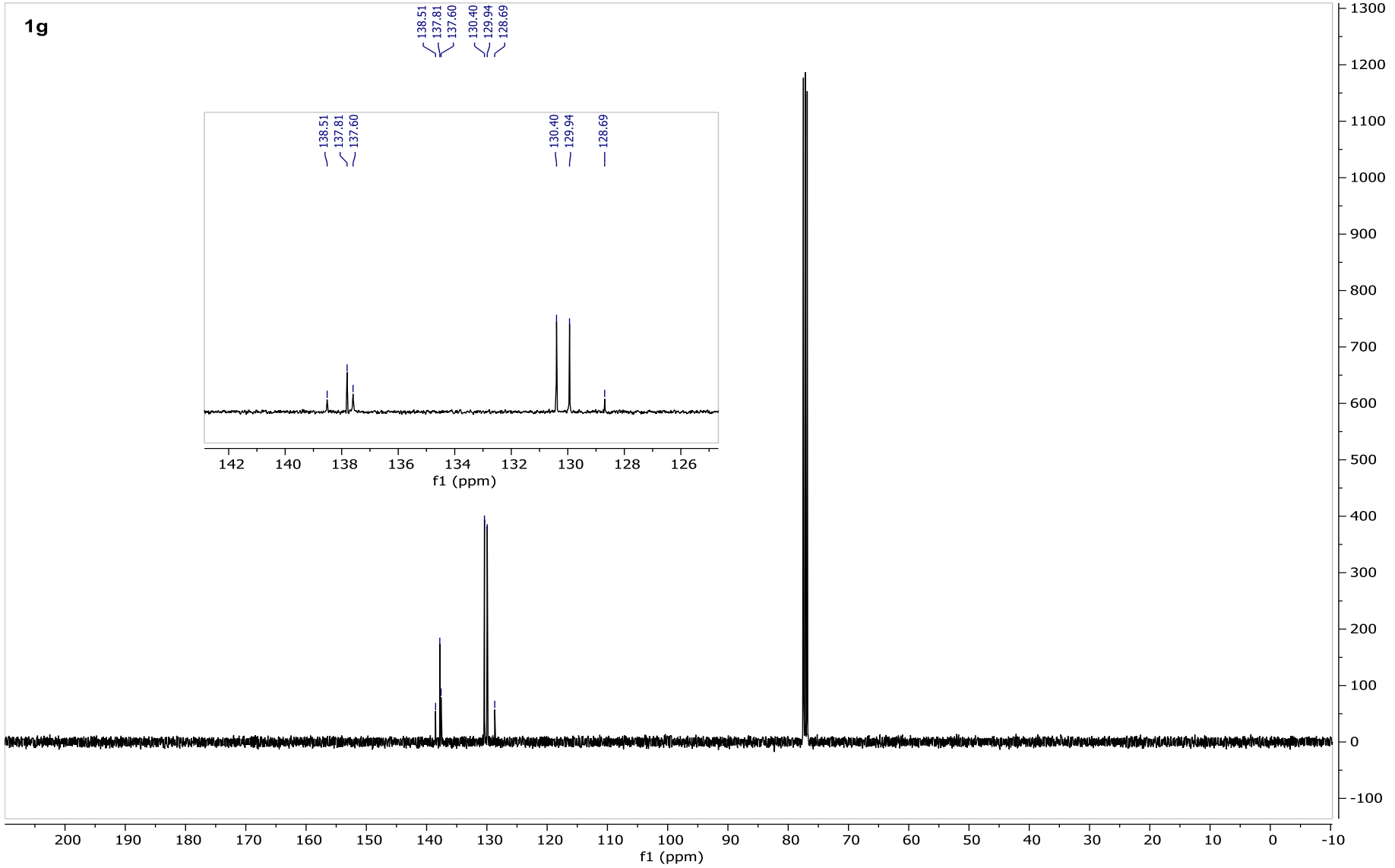
^{13}C NMR (75 MHz, $CDCl_3$):



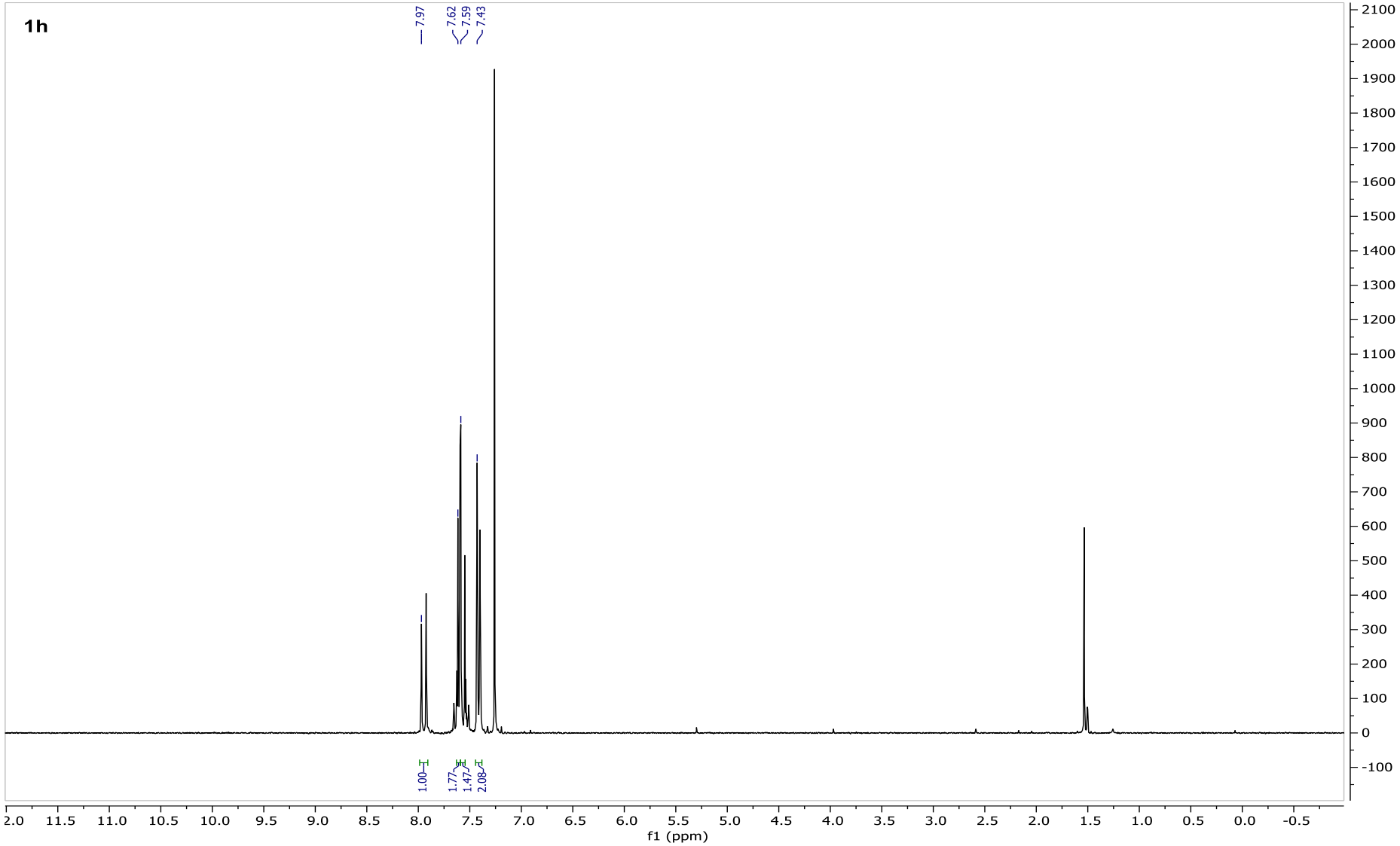
(*E*)-1-Chloro-4-(2‘-nitrovinyl)benzene (1g): ^{1}H NMR (500 MHz, $CDCl_3$):



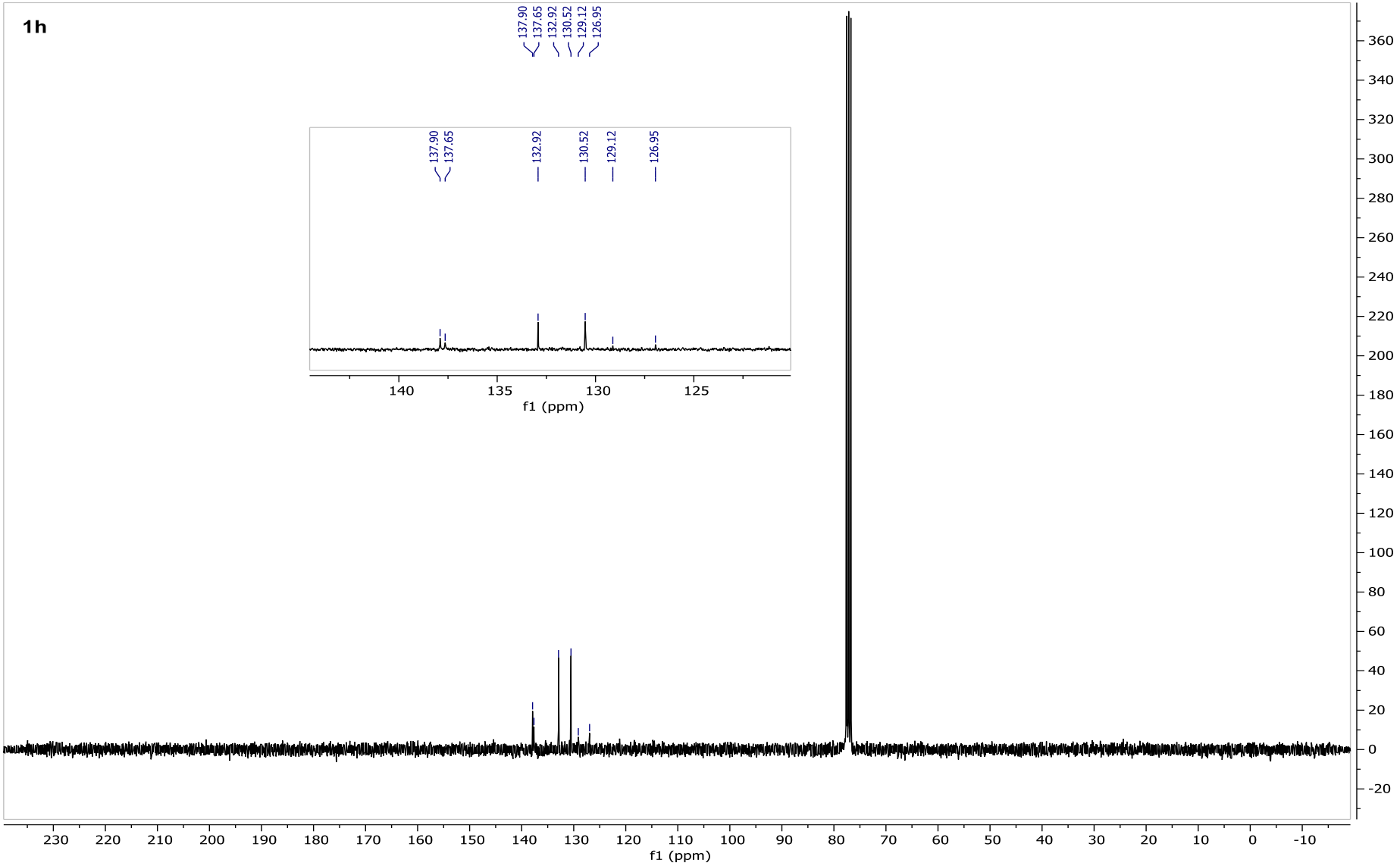
^{13}C NMR (101 MHz, $CDCl_3$):



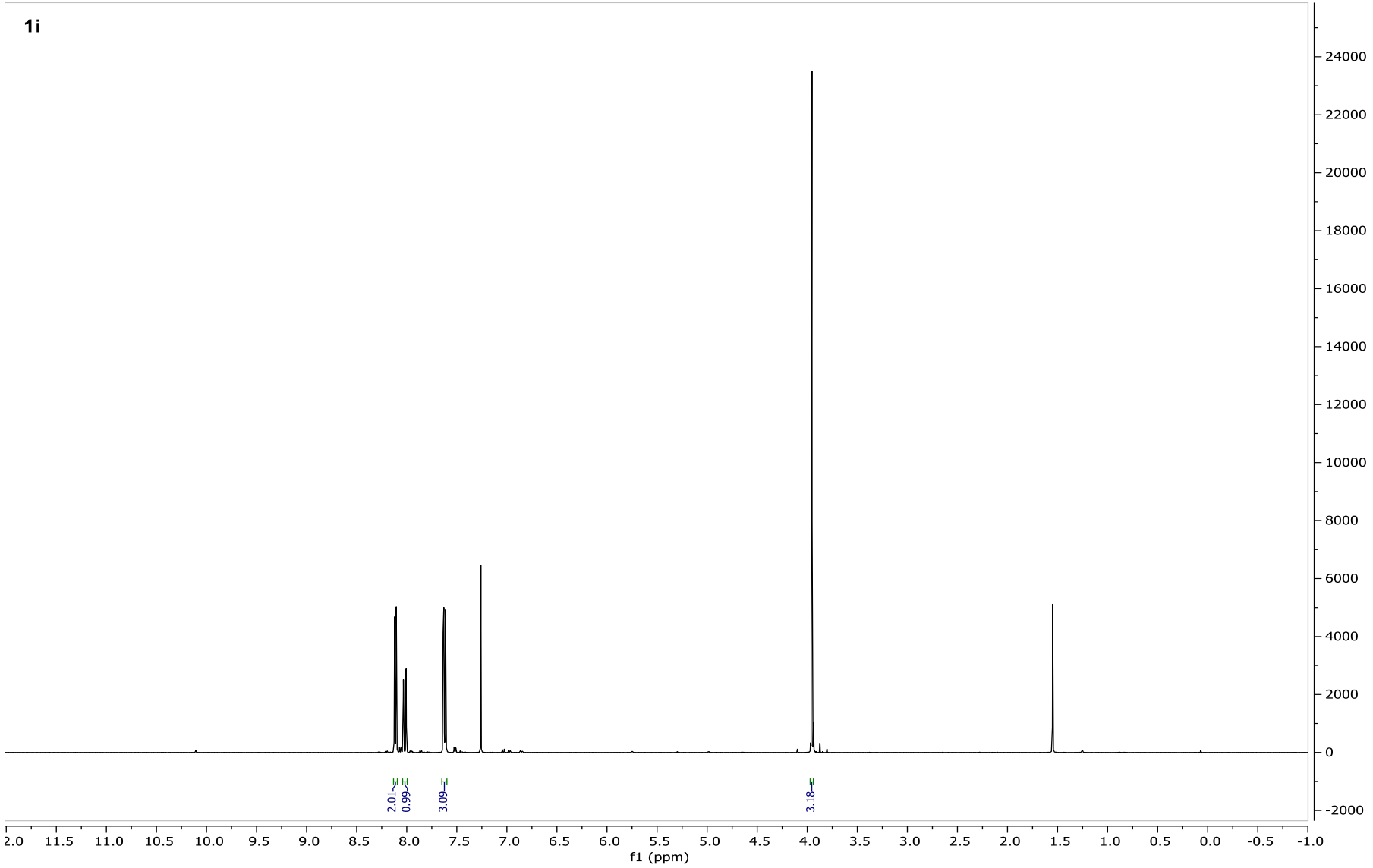
(*E*)-1-Bromo-4-(2‘-nitrovinyl)benzene (1h): ^{1}H NMR (500 MHz, $CDCl_3$):



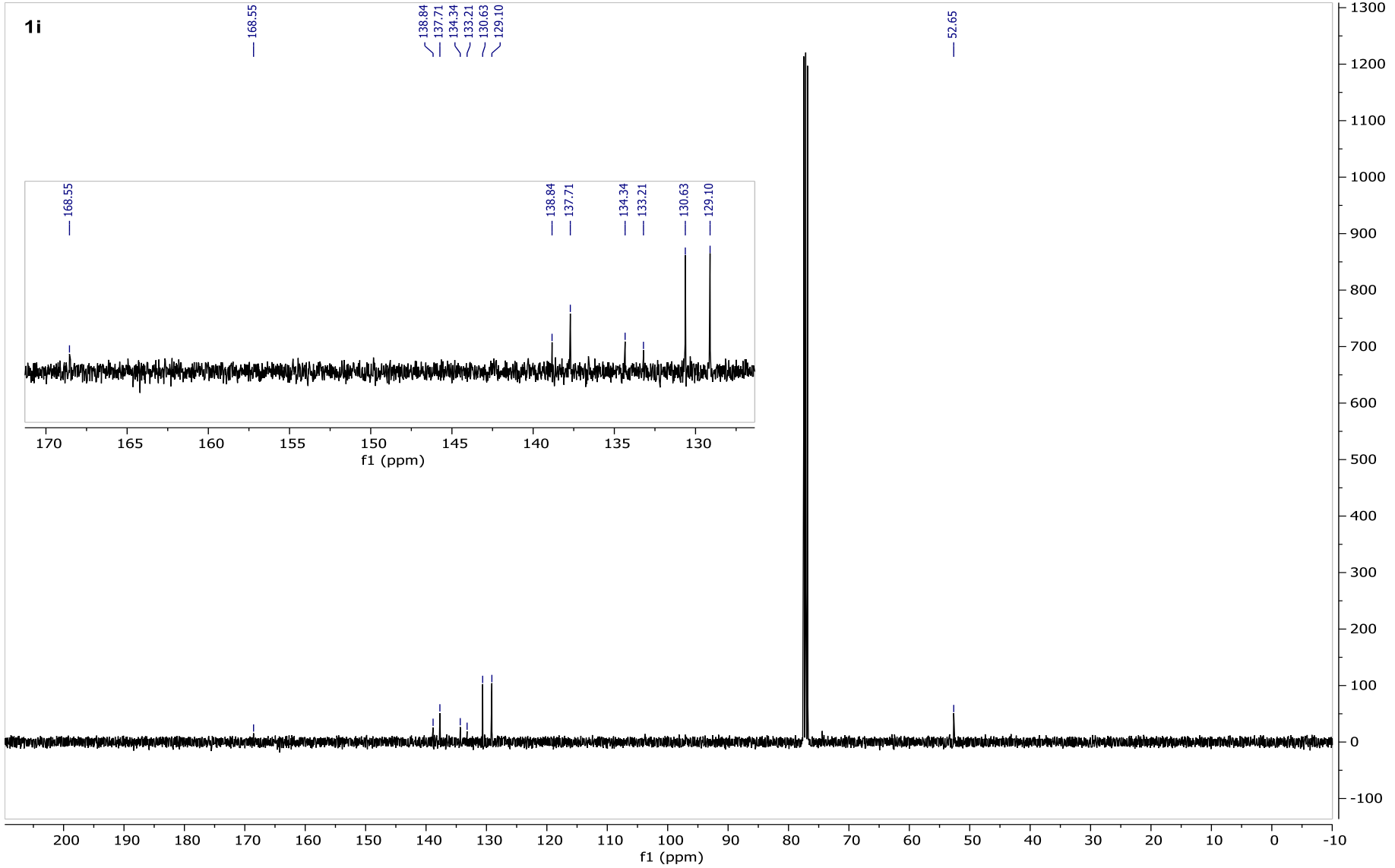
^{13}C NMR (101 MHz, $CDCl_3$):



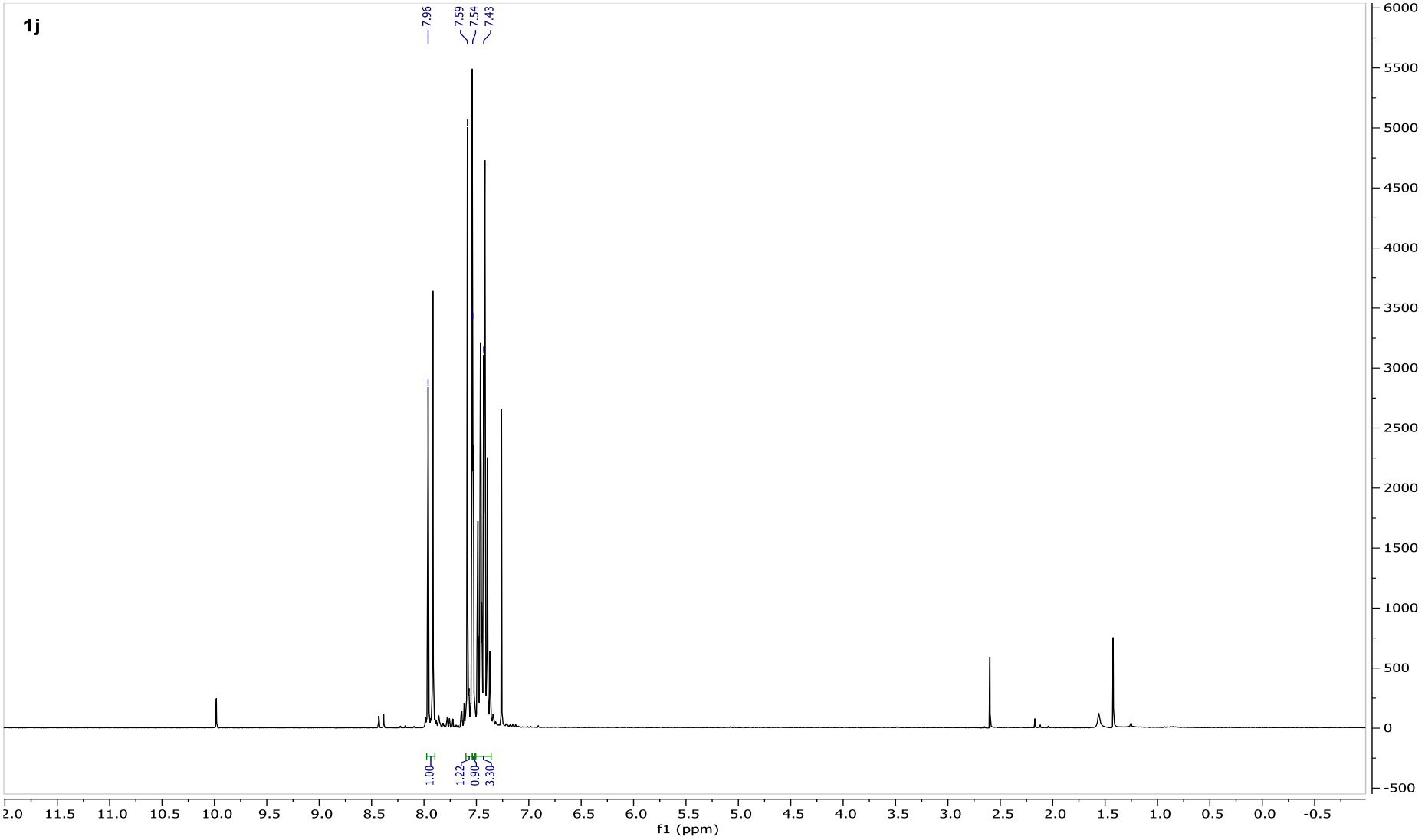
Methyl (*E*)-4-(2'-nitrovinyl)benzoate (1i): ^{1}H NMR (500 MHz, $CDCl_3$):



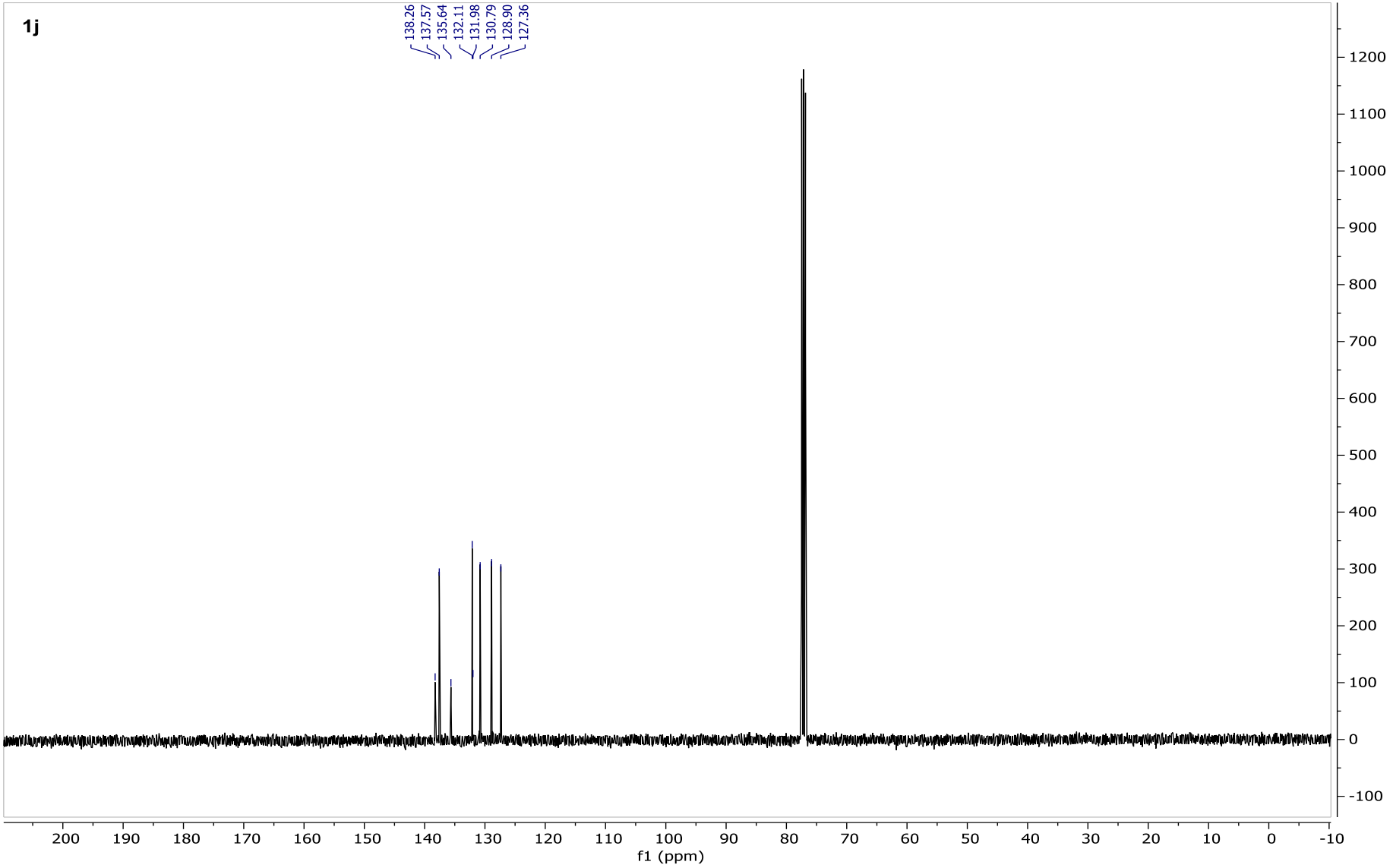
^{13}C NMR (101 MHz, $CDCl_3$):



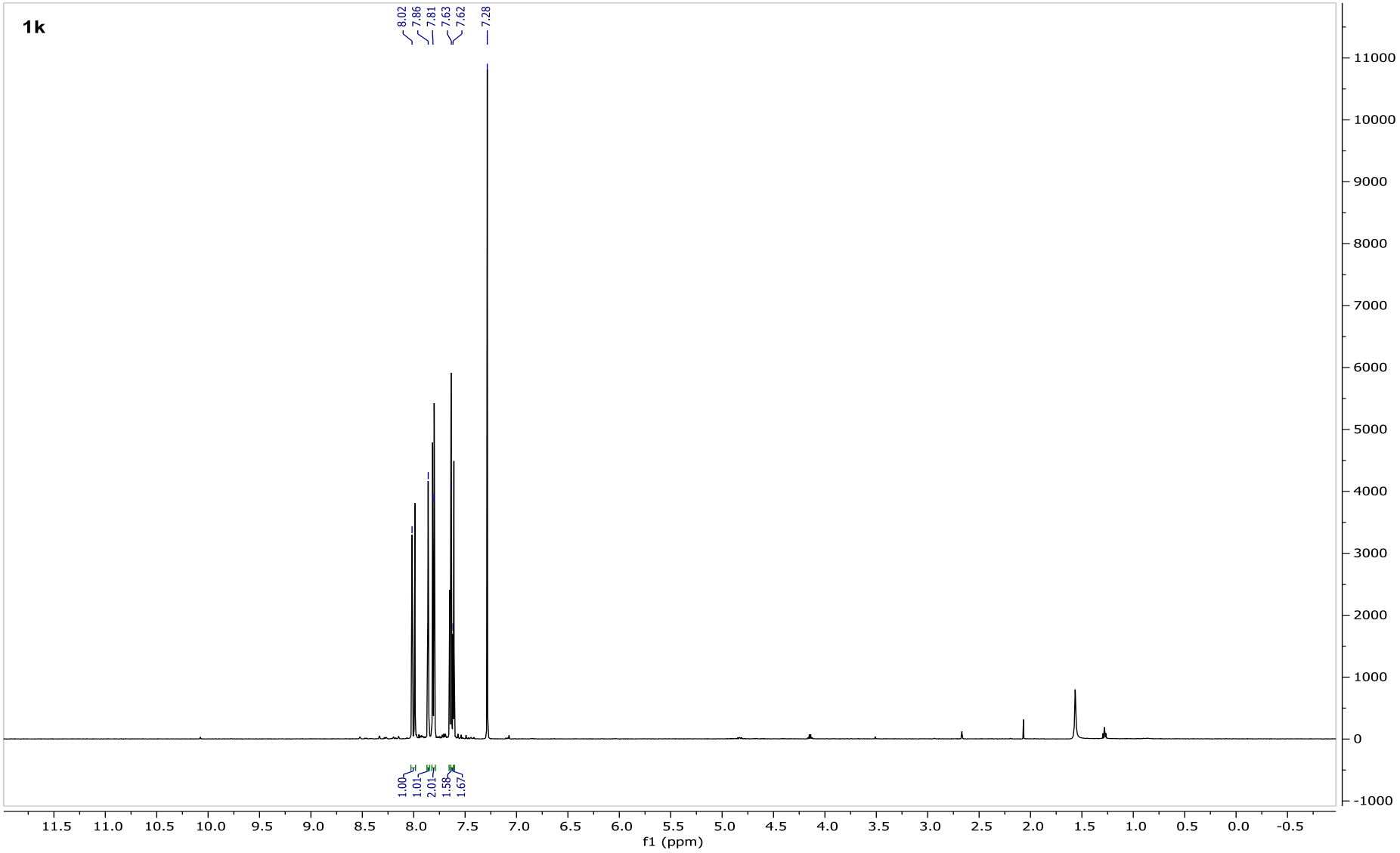
(*E*)-1-Chloro-3-(2‘-nitrovinyl)benzene (1j); ^{1}H NMR (500 MHz, $CDCl_3$):



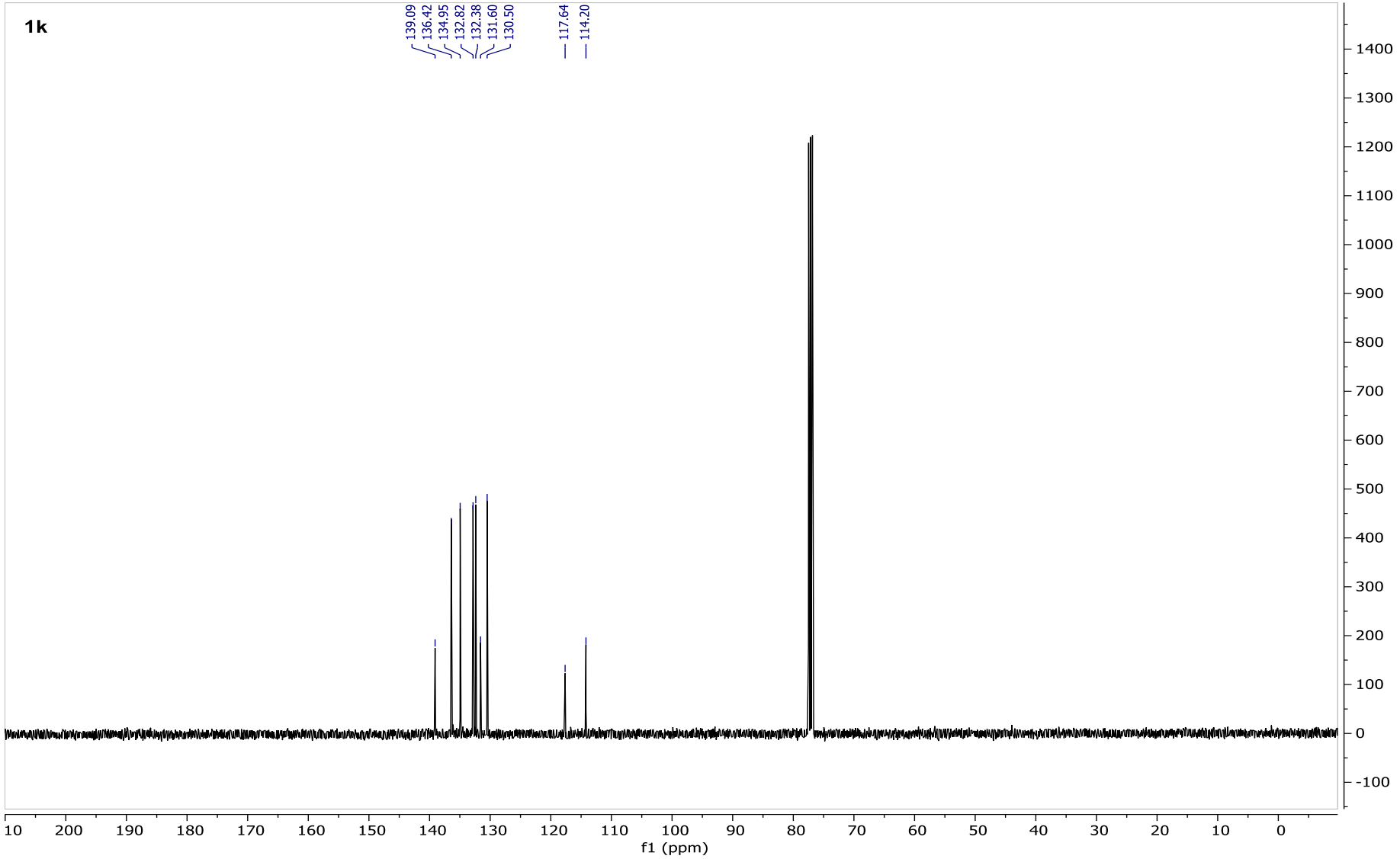
^{13}C NMR (101 MHz, $CDCl_3$):



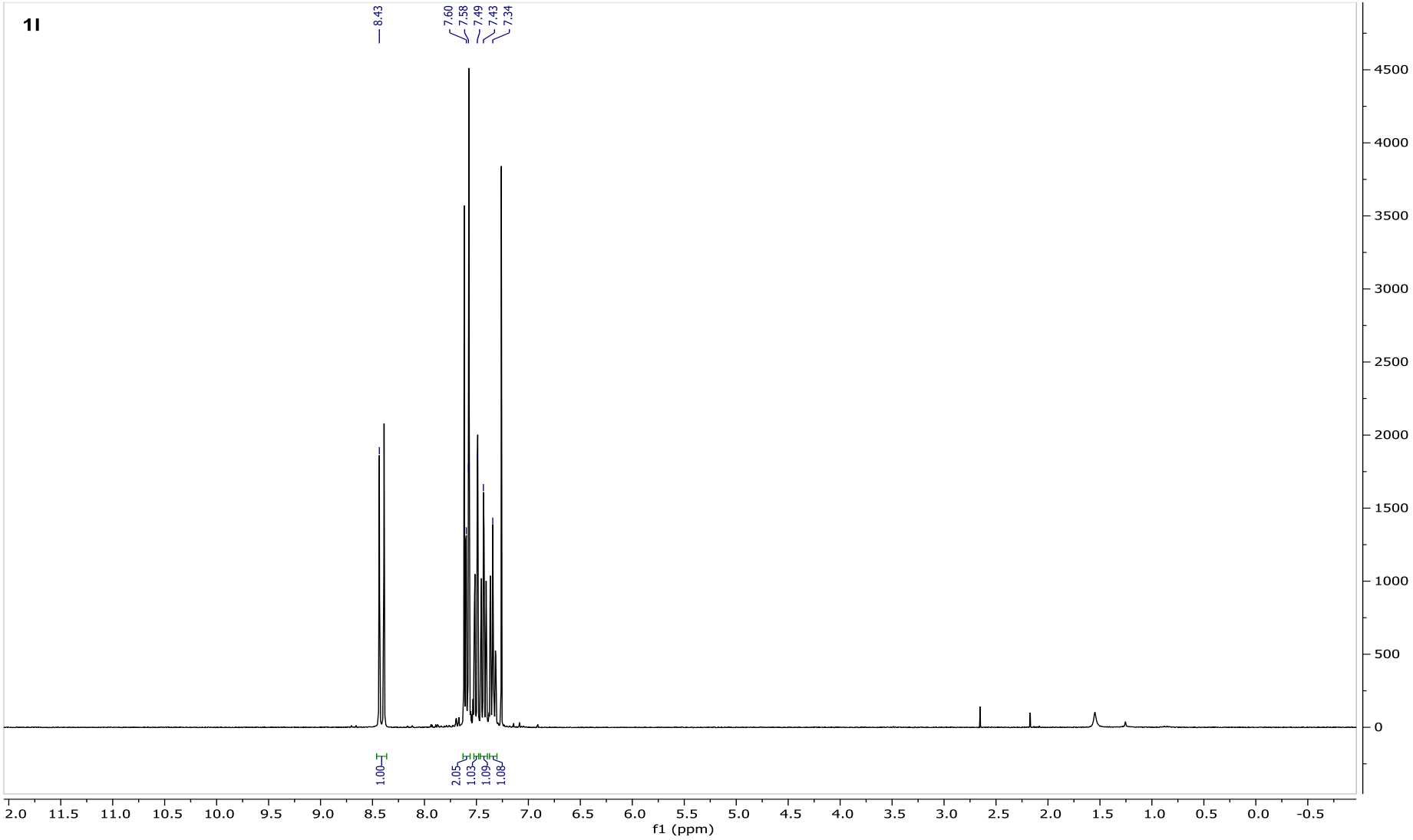
(*E*)-3-(2'-Nitrovinyl)benzonitrile (1k): ^{1}H NMR (500 MHz, $CDCl_3$):



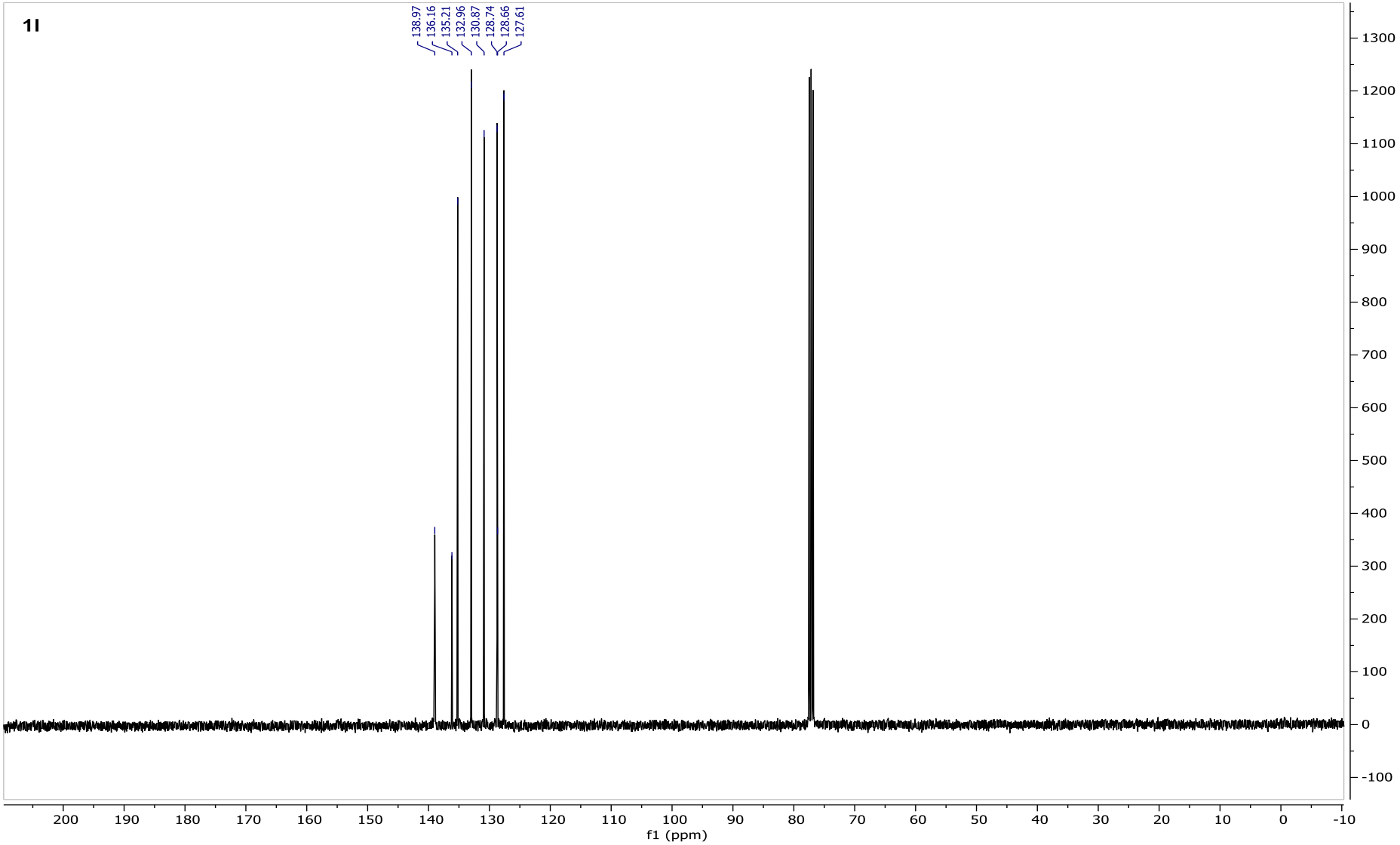
^{13}C NMR (101 MHz, $CDCl_3$):



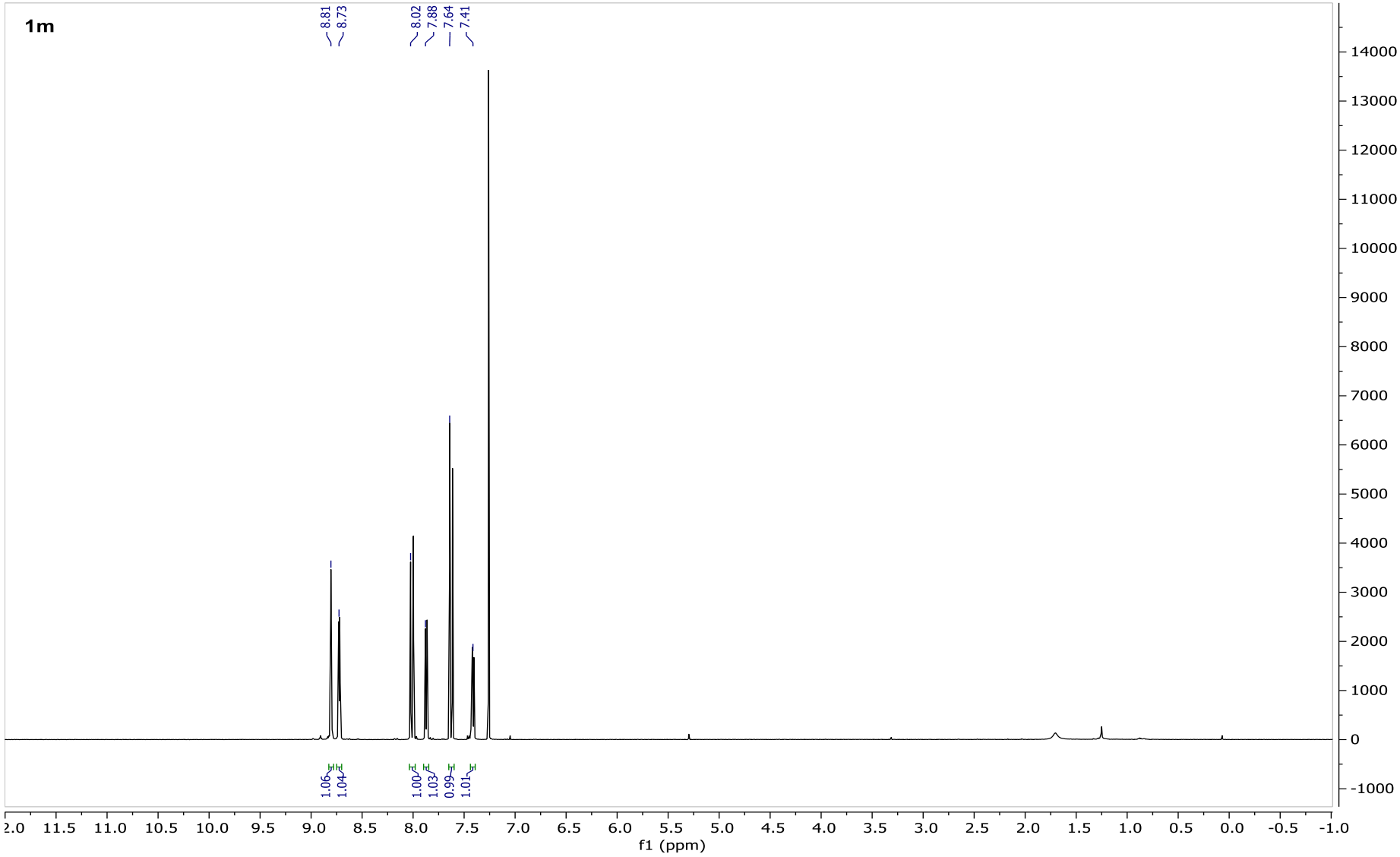
(*E*)-1-Chloro-2-(2‘-nitrovinyl)benzene (1l): ^{1}H NMR (300 MHz, $CDCl_3$):



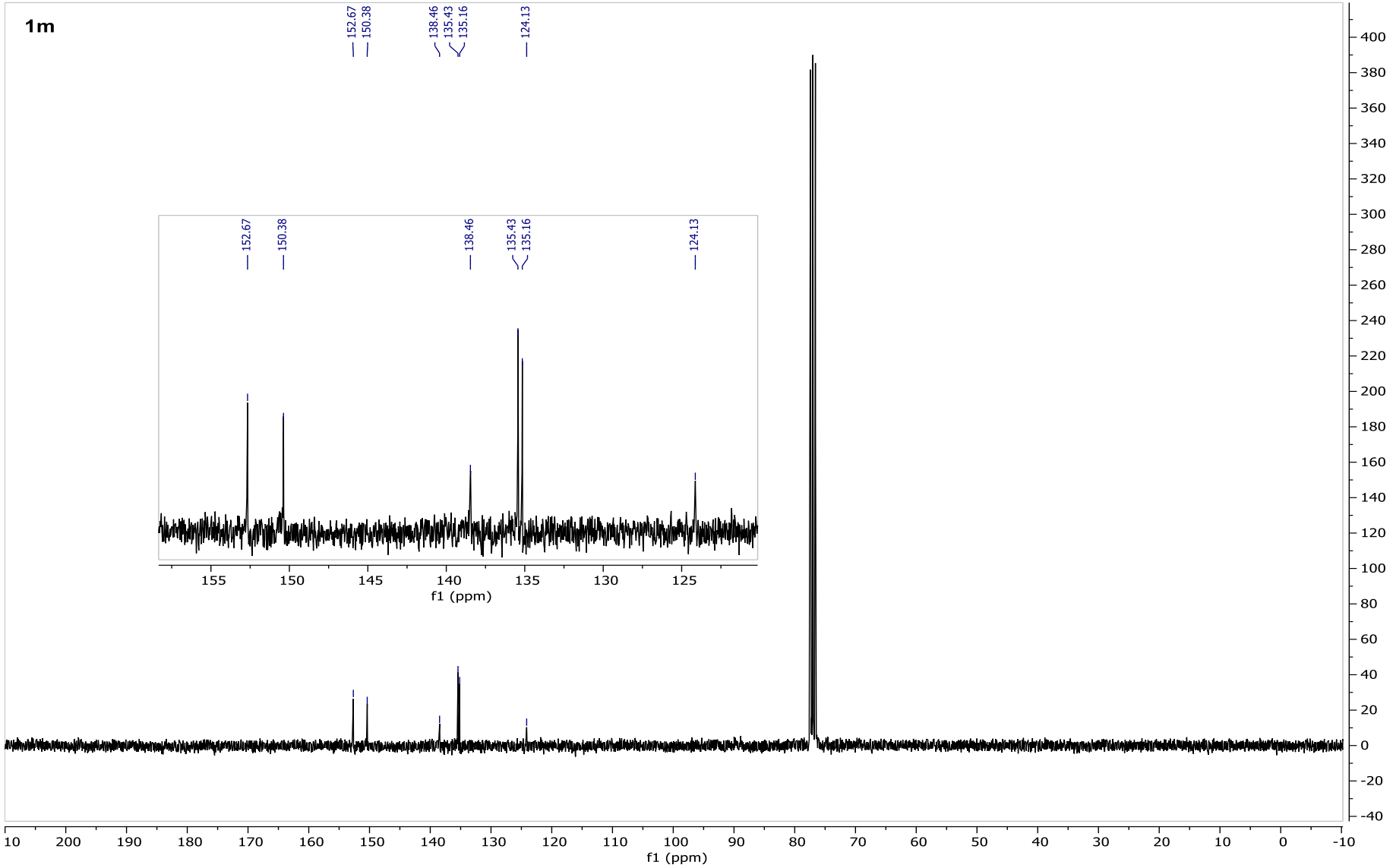
^{13}C NMR (101 MHz, $CDCl_3$):



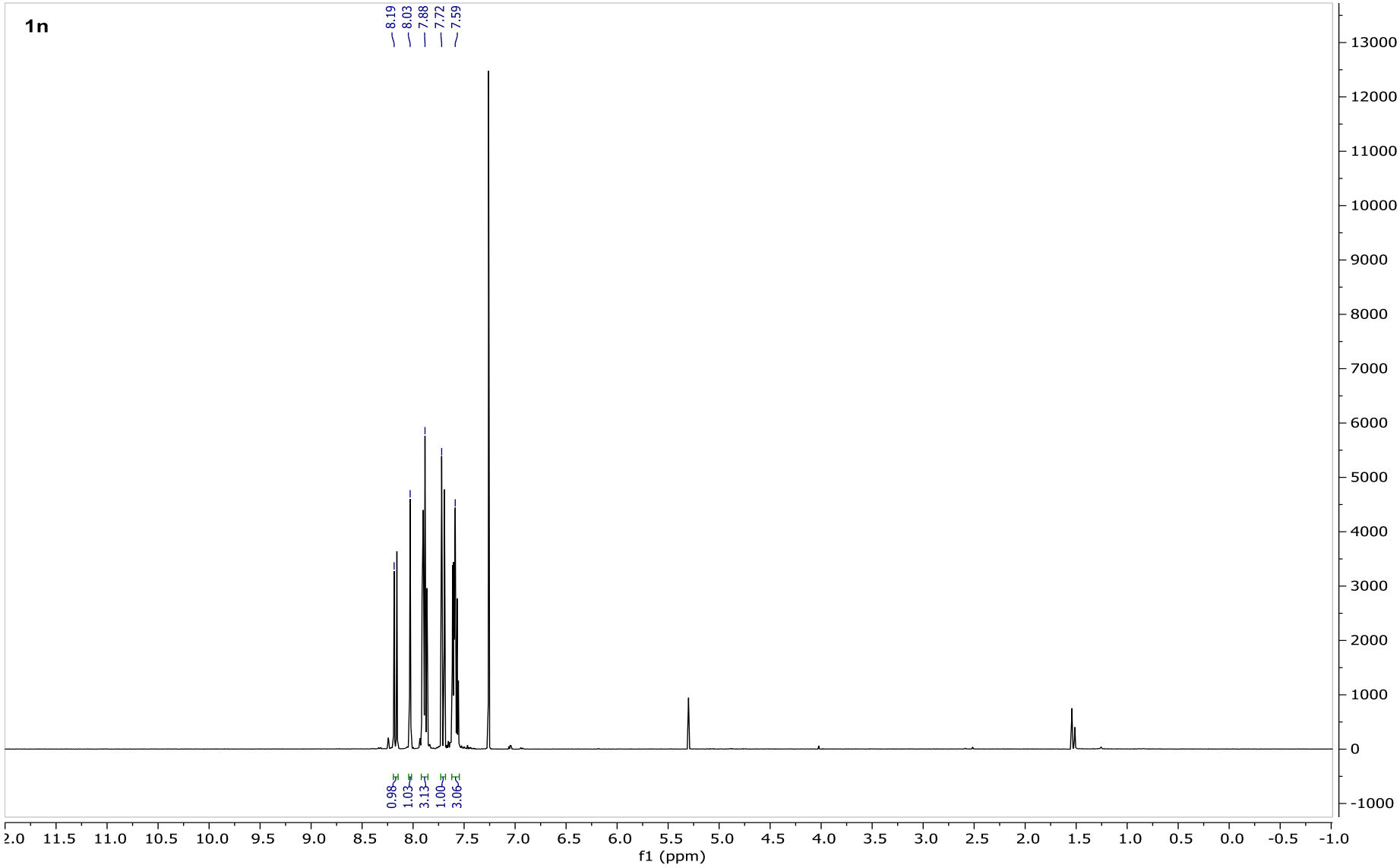
(*E*)-2-(2'-Nitrovinyl)pyridine (1m): ^{1}H NMR (500 MHz, $CDCl_3$):



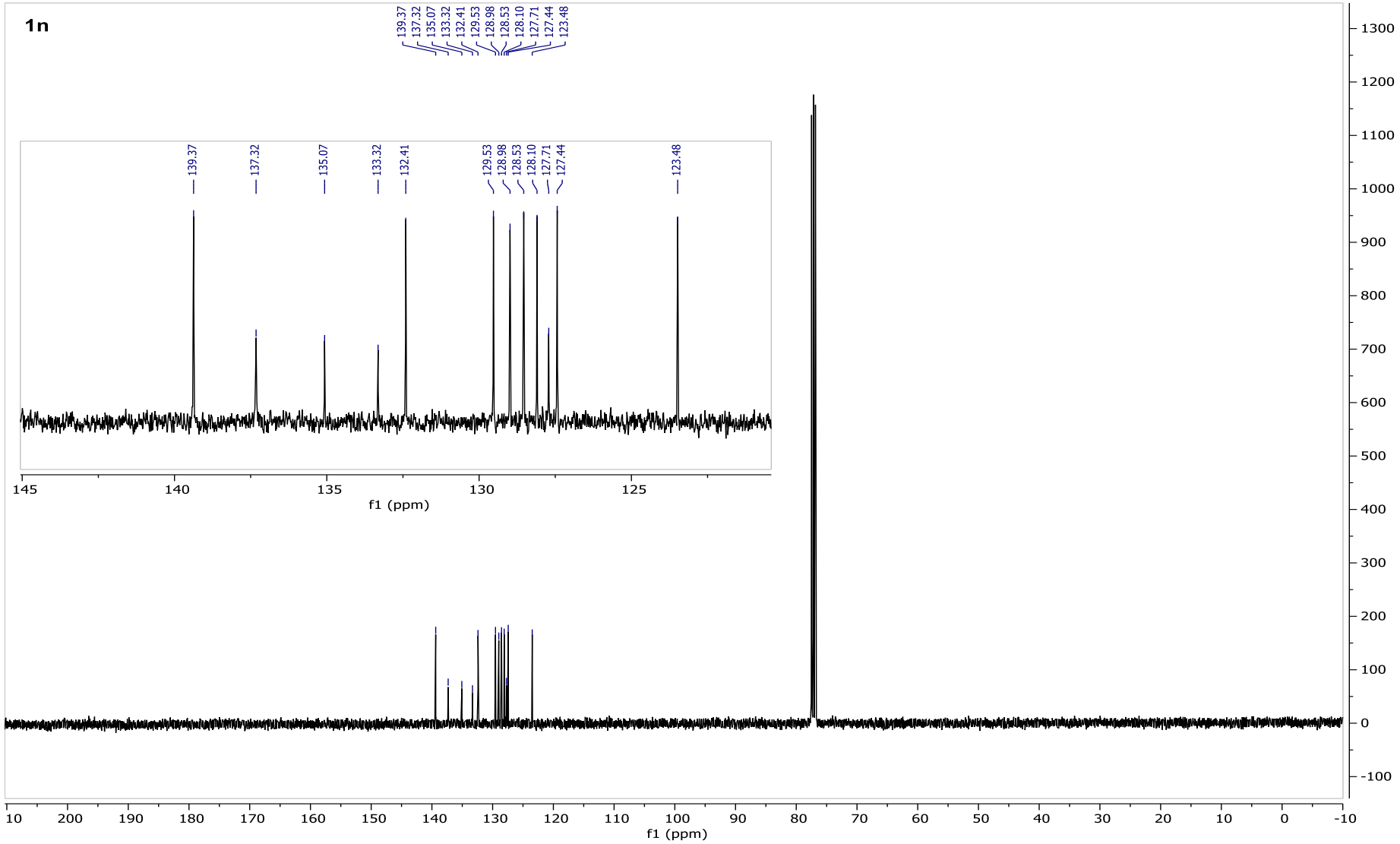
^{13}C NMR (75 MHz, $CDCl_3$):



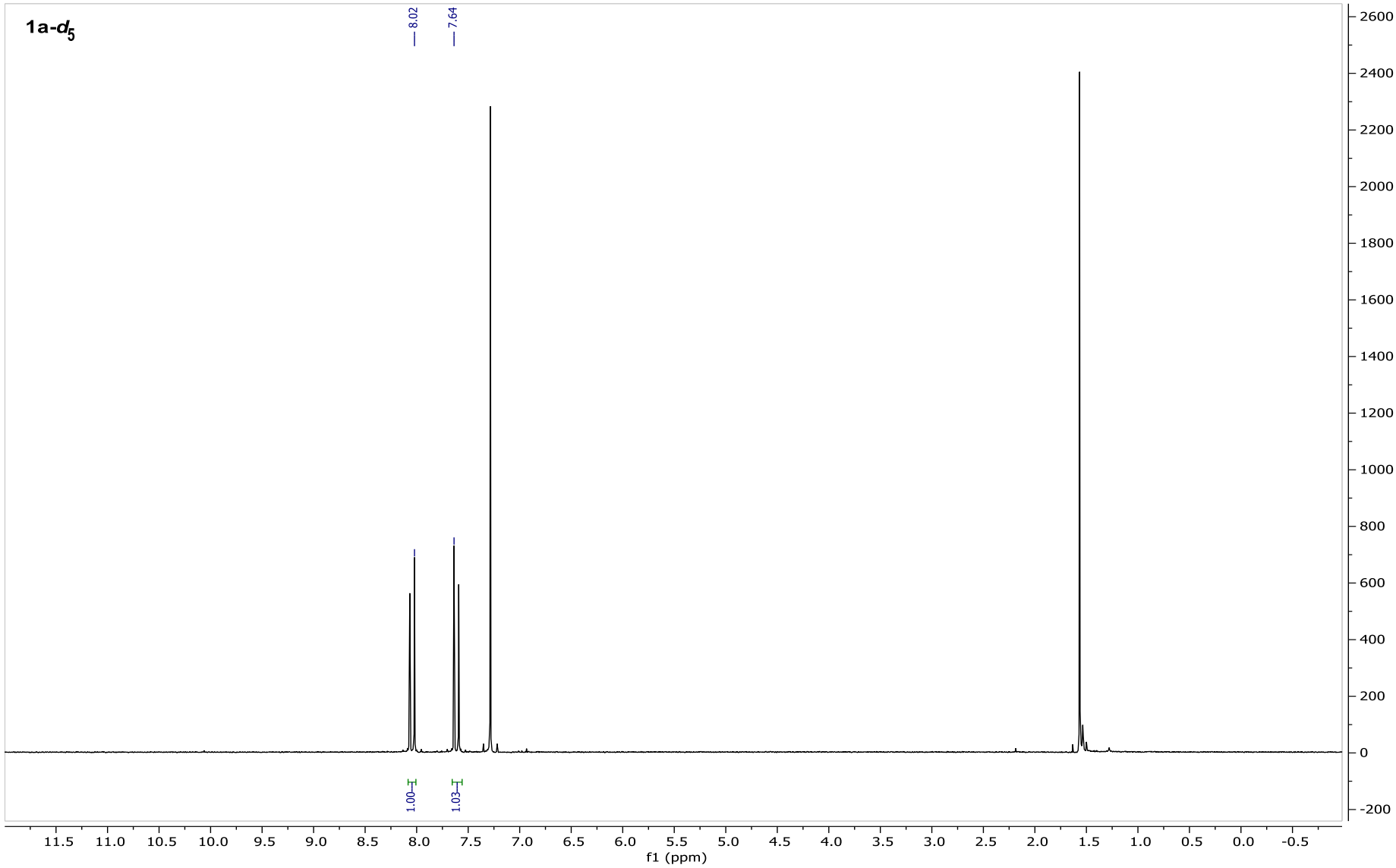
(*E*)-2-(2'-Nitrovinyl)naphthalene (1n): ^{1}H NMR (500 MHz, $CDCl_3$):



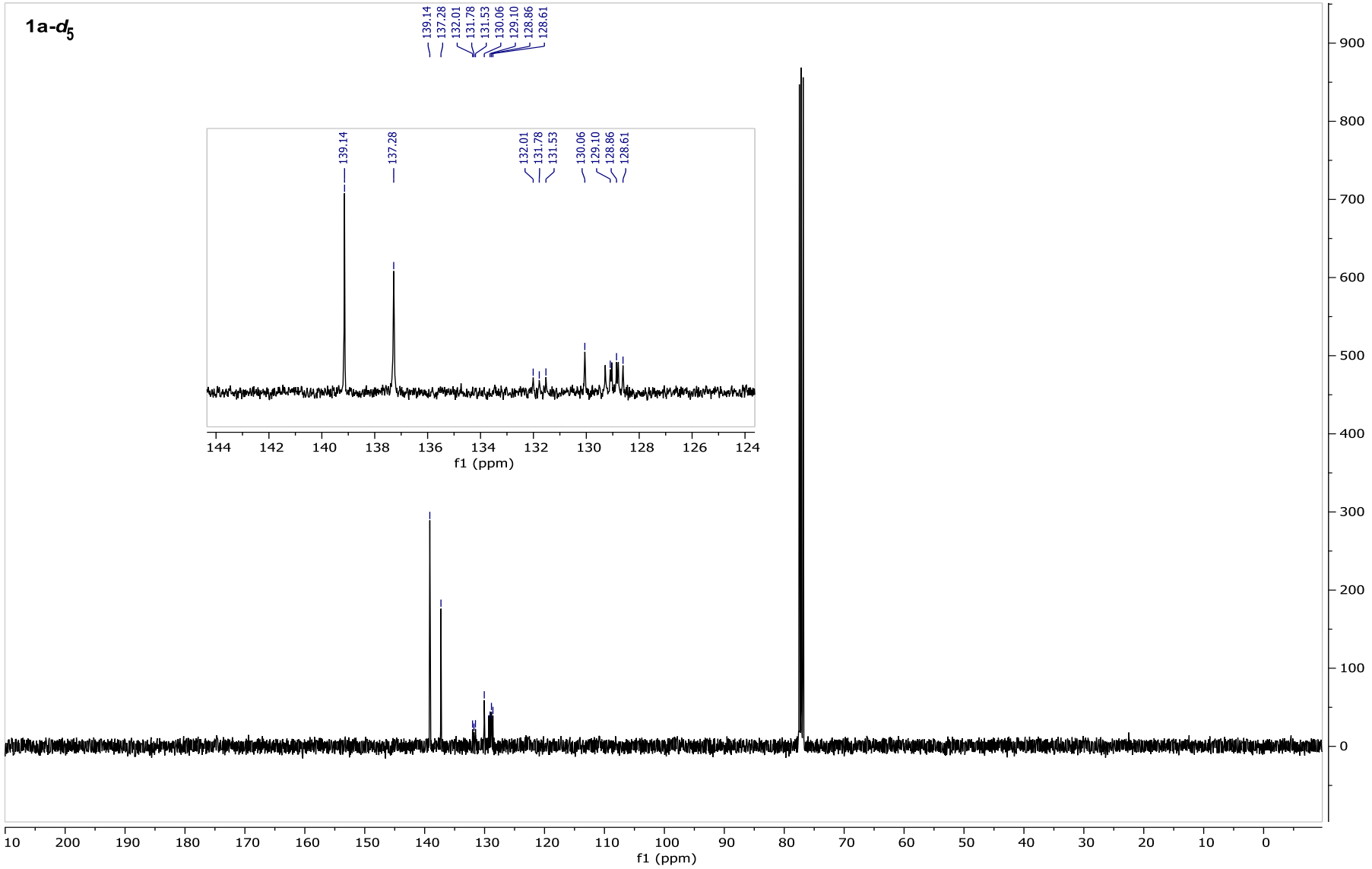
^{13}C NMR (101 MHz, $CDCl_3$):



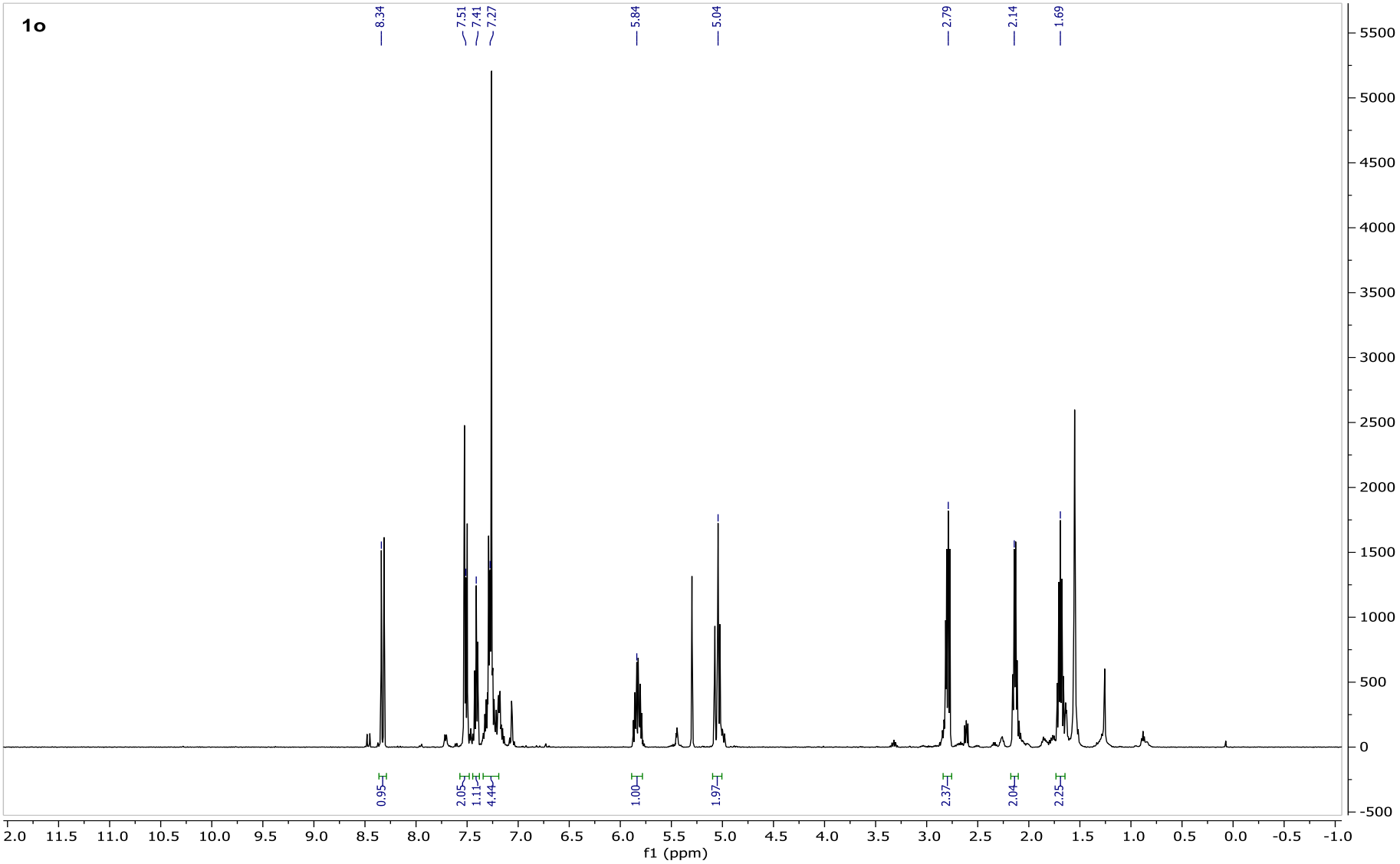
(*E*)-1-(2‘-Nitrovinyl)benzene-2,3,4,5,6-d_5 (1a-d_5): **^{1}H NMR** (300 MHz, $CDCl_3$):



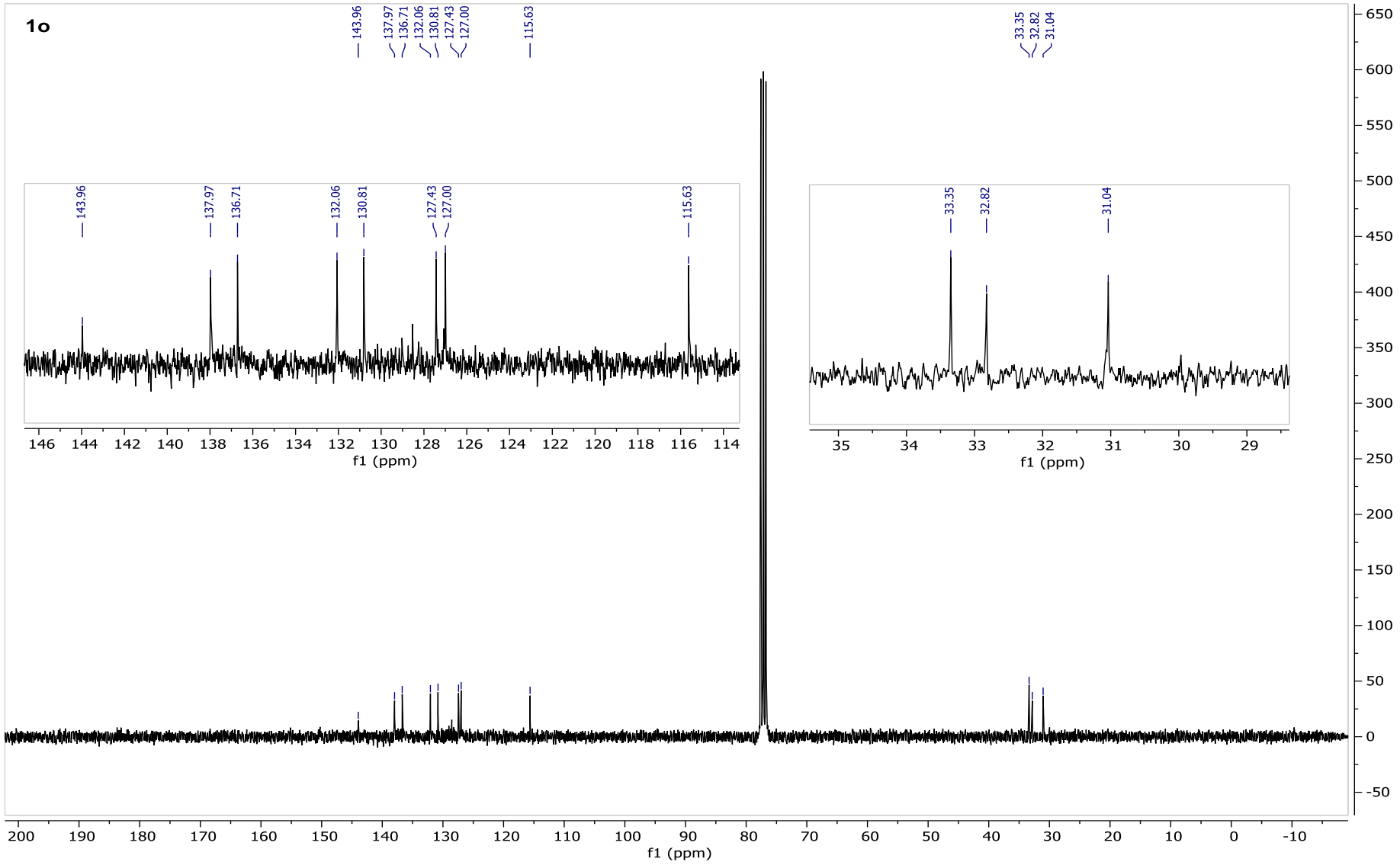
^{13}C NMR (101 MHz, $CDCl_3$):



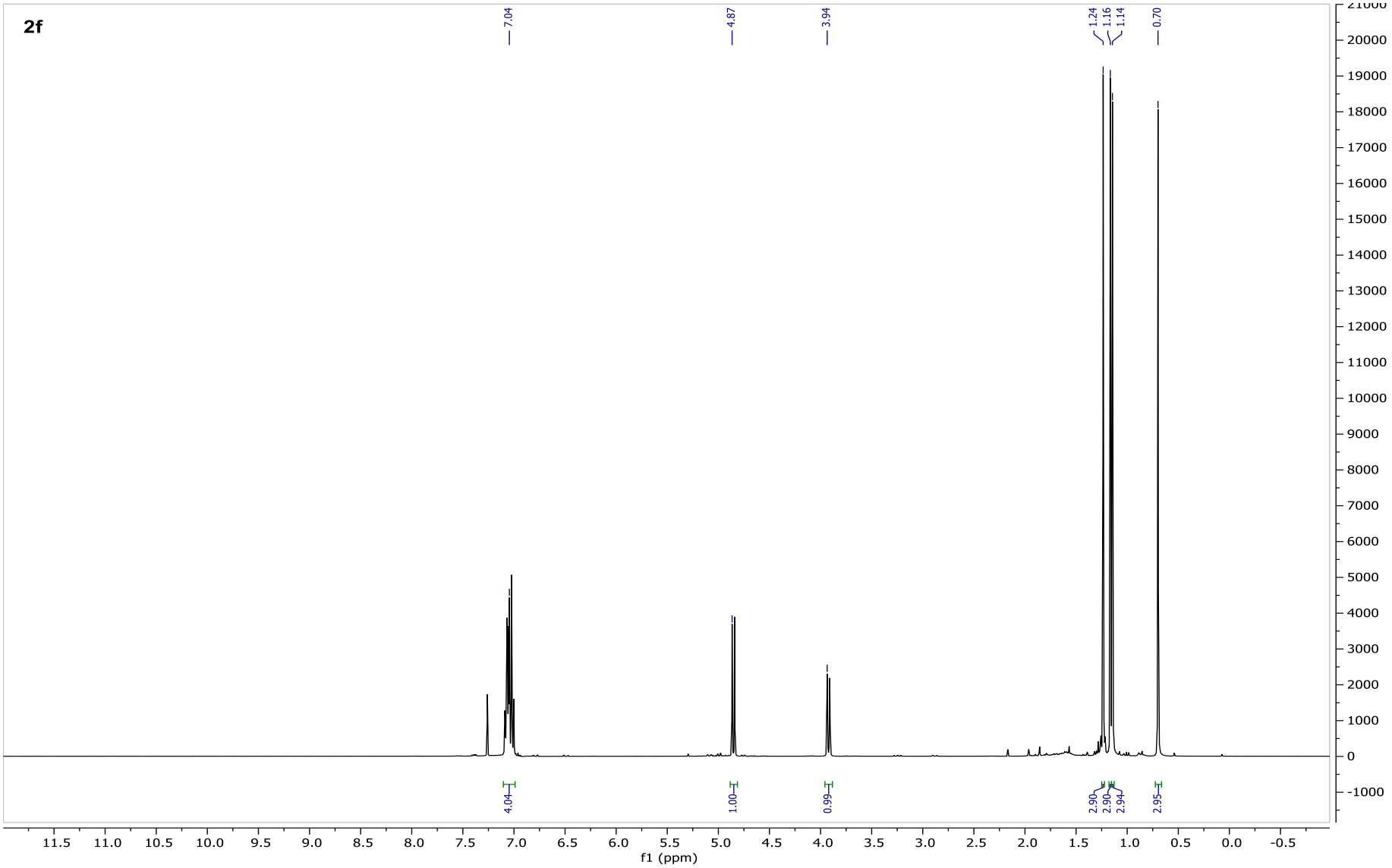
(*E*)-1-(2‘‘-Nitrovinyl)-2-(pent-4‘-en-1‘-yl)benzene (1o): ^{1}H NMR (300 MHz, $CDCl_3$):



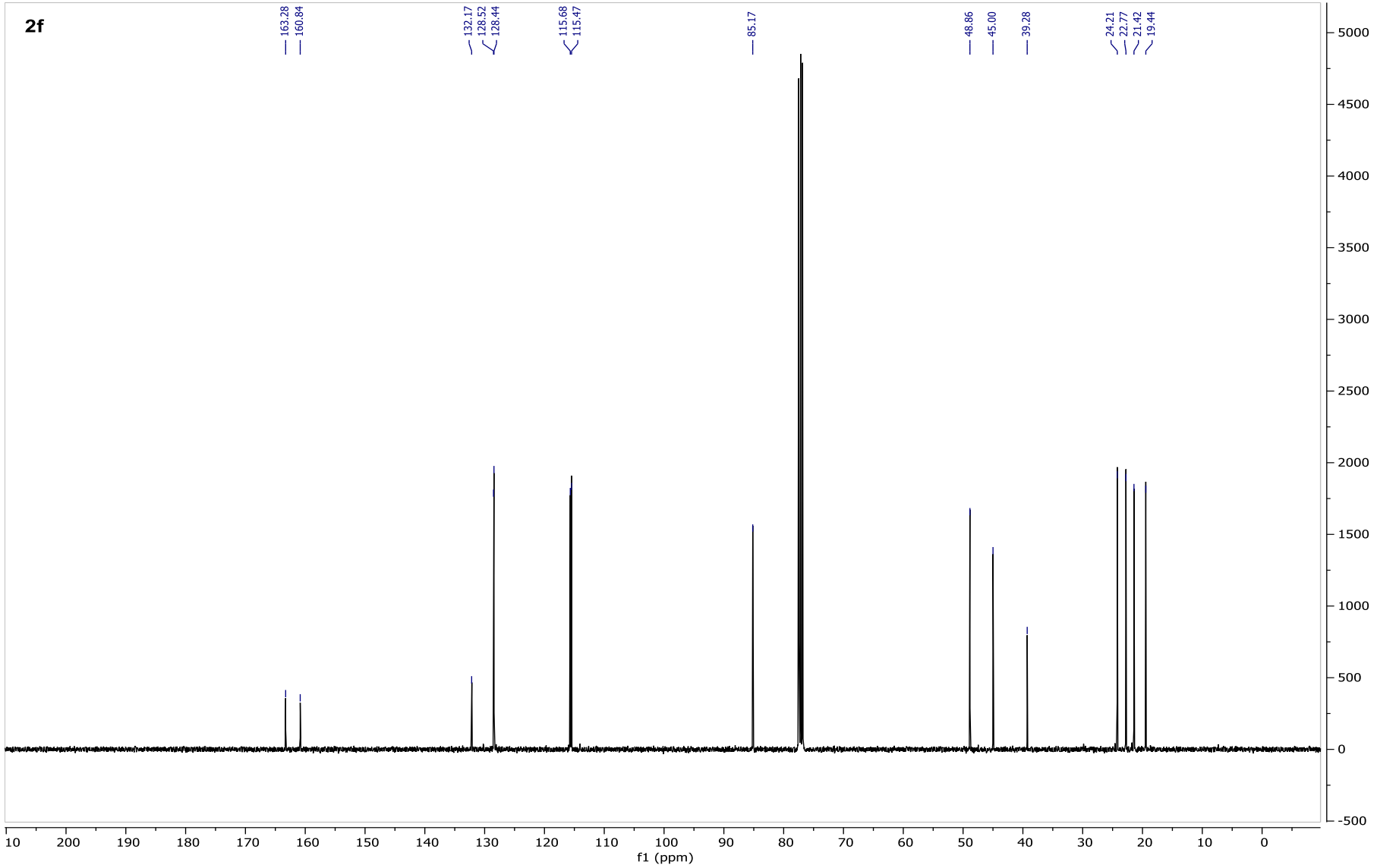
^{13}C NMR (75* MHz, $CDCl_3$):



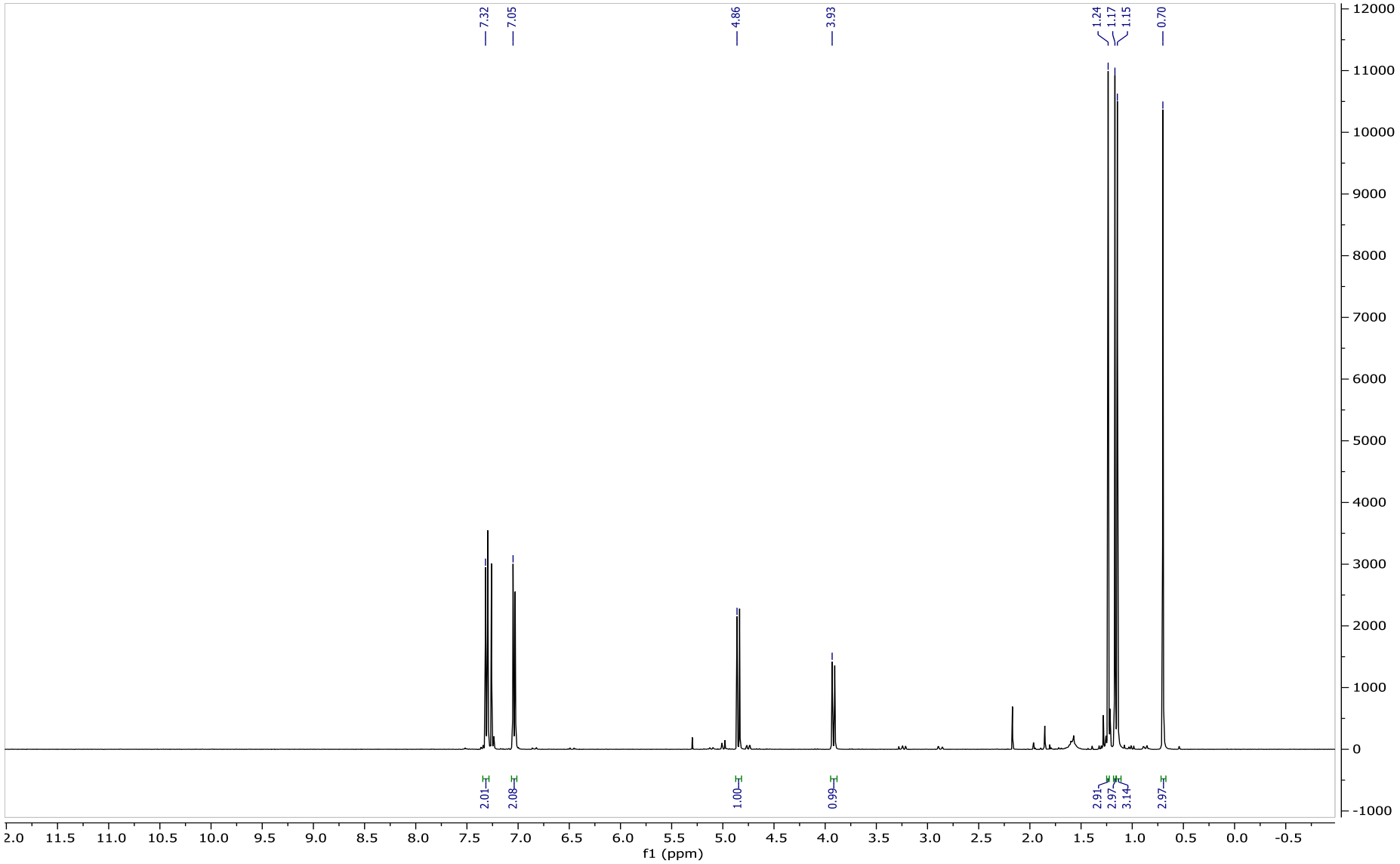
1-Fluoro-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2f): **^{1}H NMR** (400 MHz, $CDCl_3$):



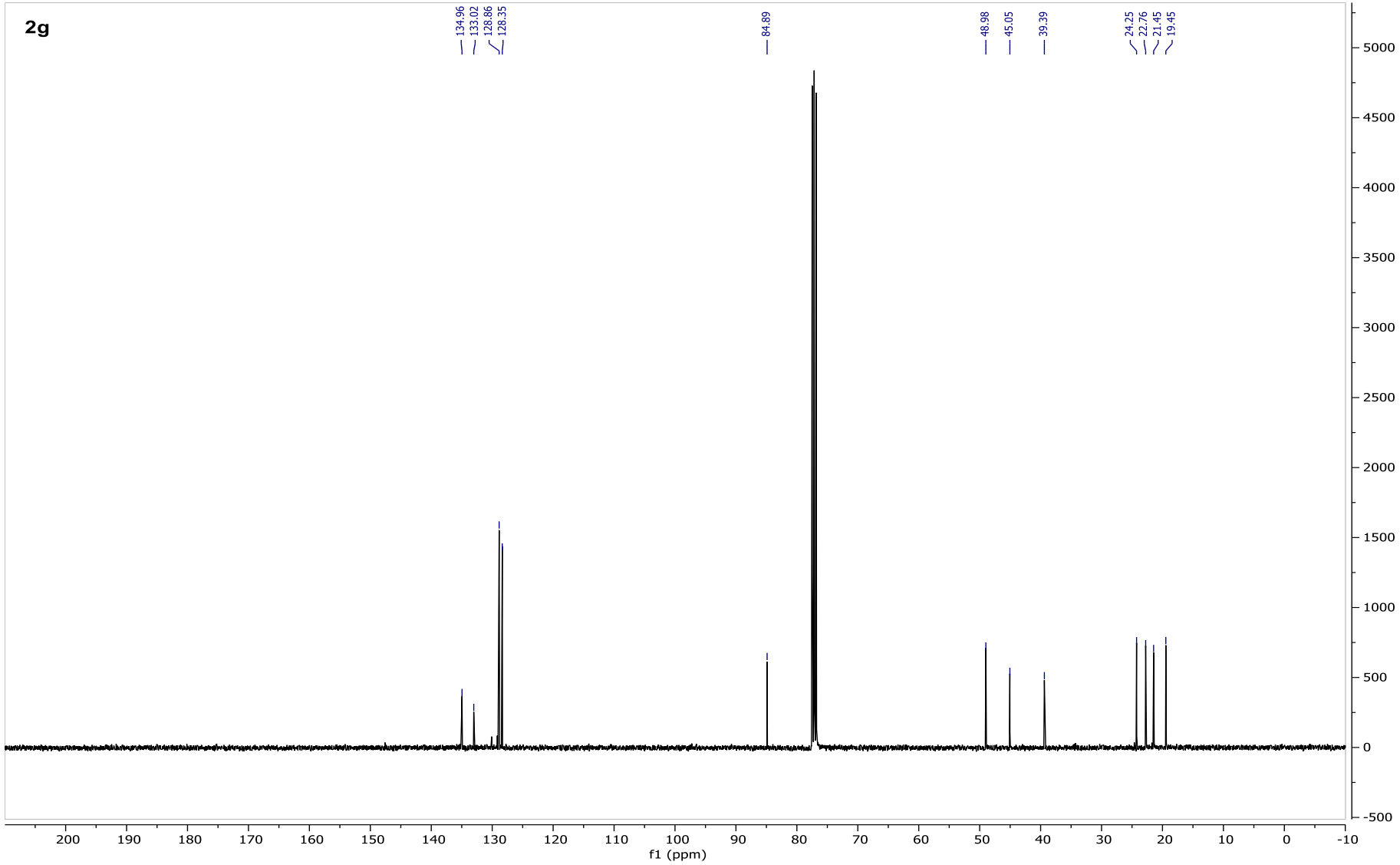
^{13}C NMR (101 MHz, $CDCl_3$):



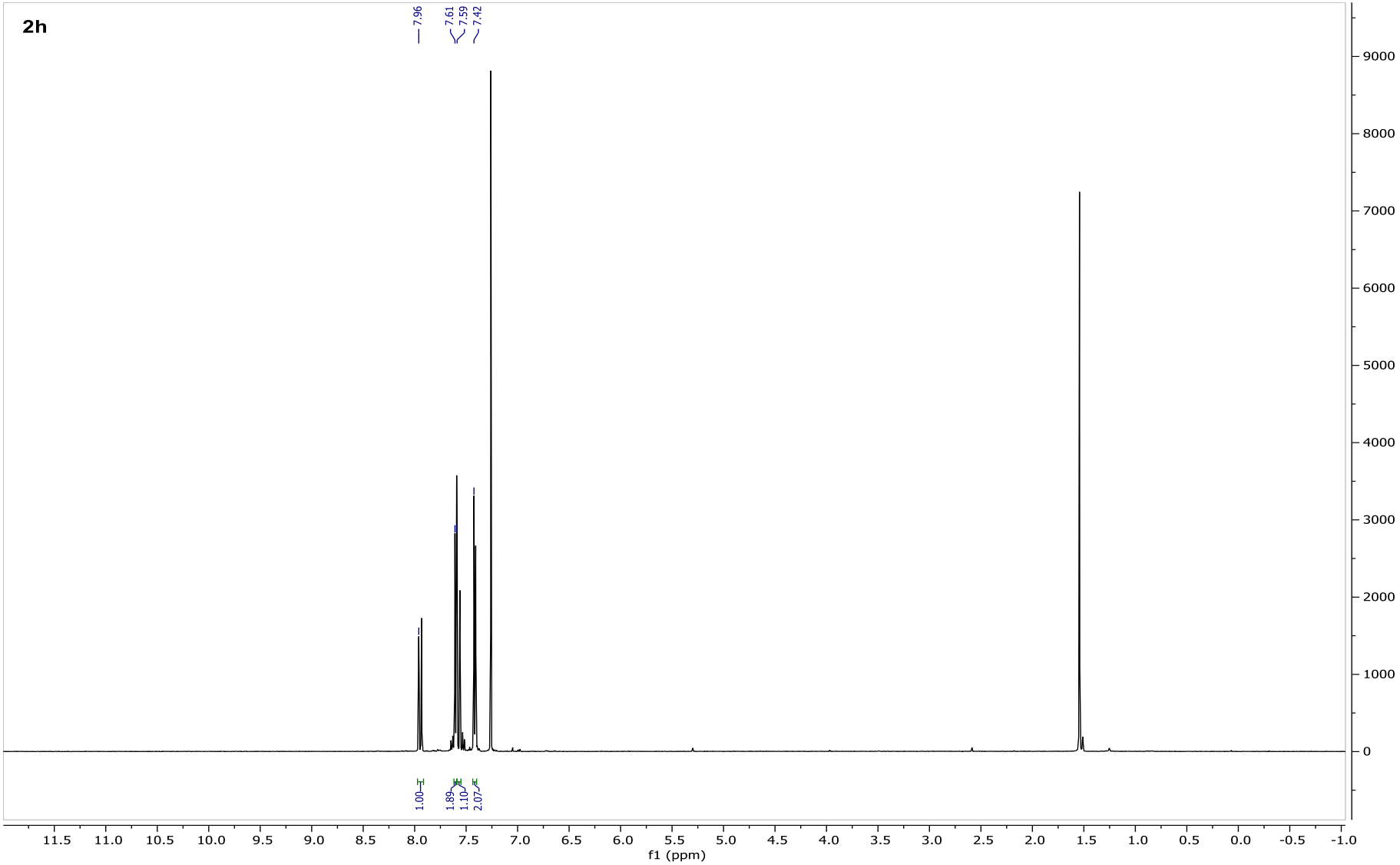
1-Chloro-4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2g): **^{1}H NMR** (400 MHz, $CDCl_3$):



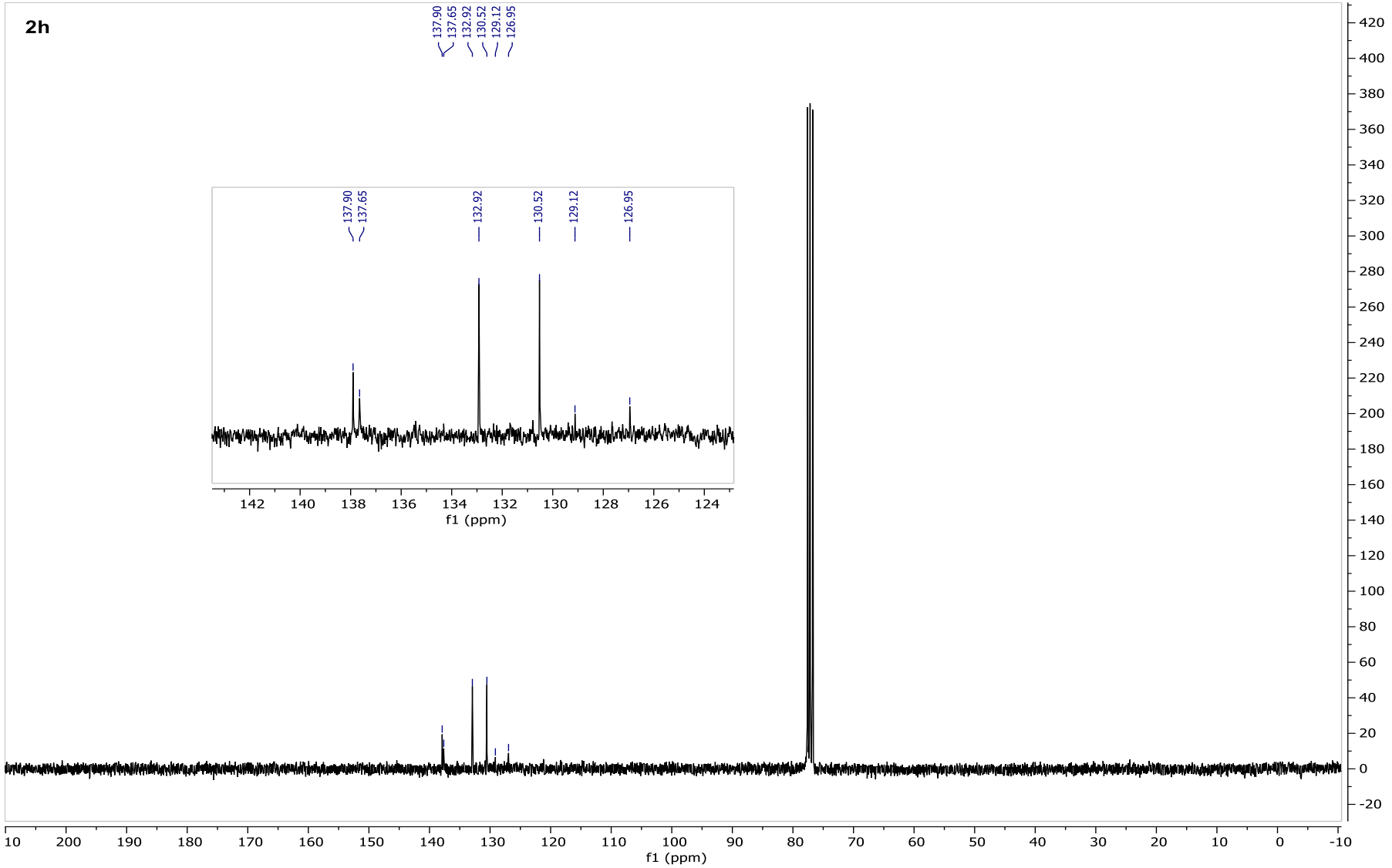
^{13}C NMR (101 MHz, $CDCl_3$):



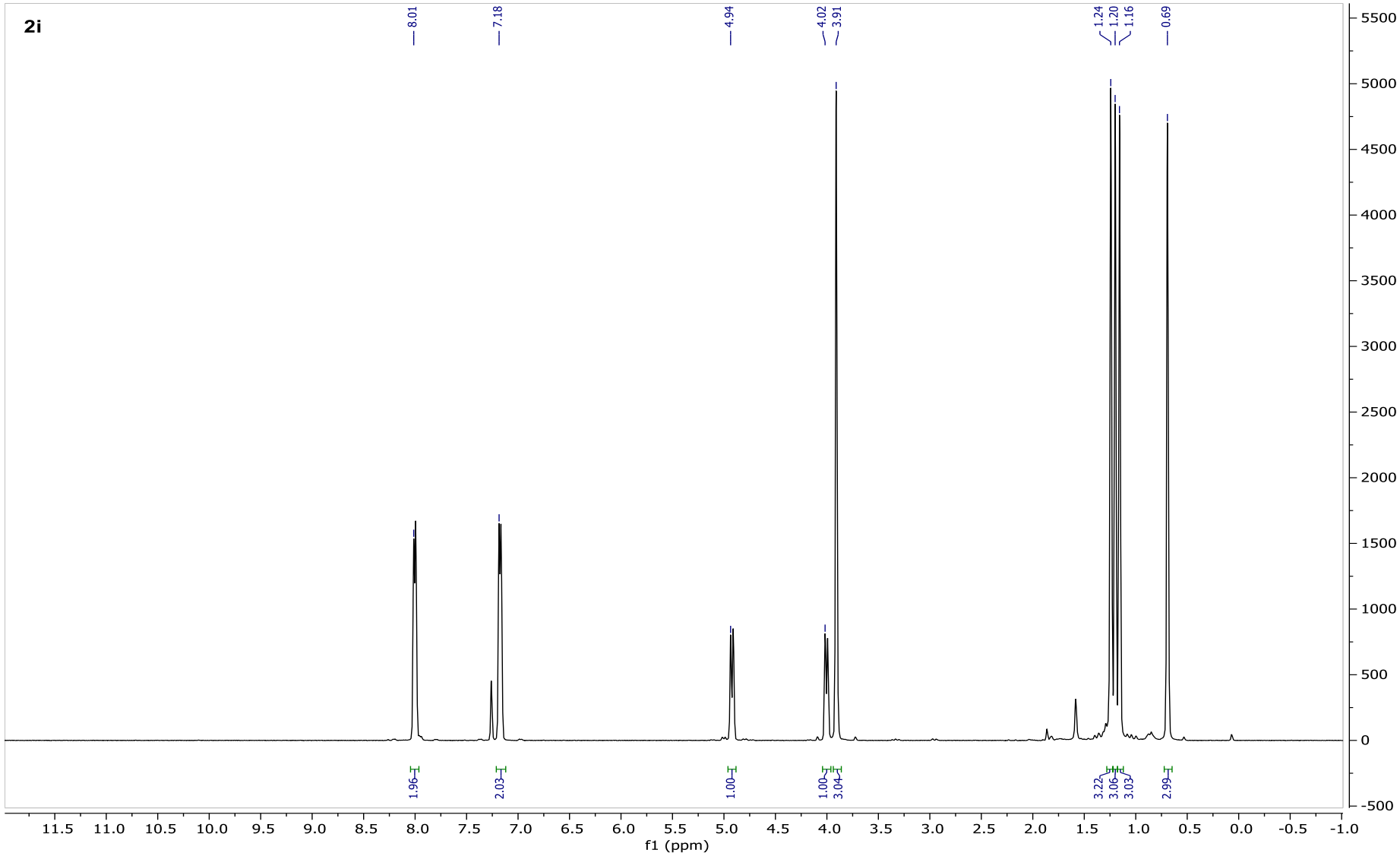
1-Bromo-4-(2‘,2‘,3‘,3‘-tetramethyl-4’-nitrocyclobutyl)benzene (2h): ^{1}H NMR (500 MHz, $CDCl_3$):



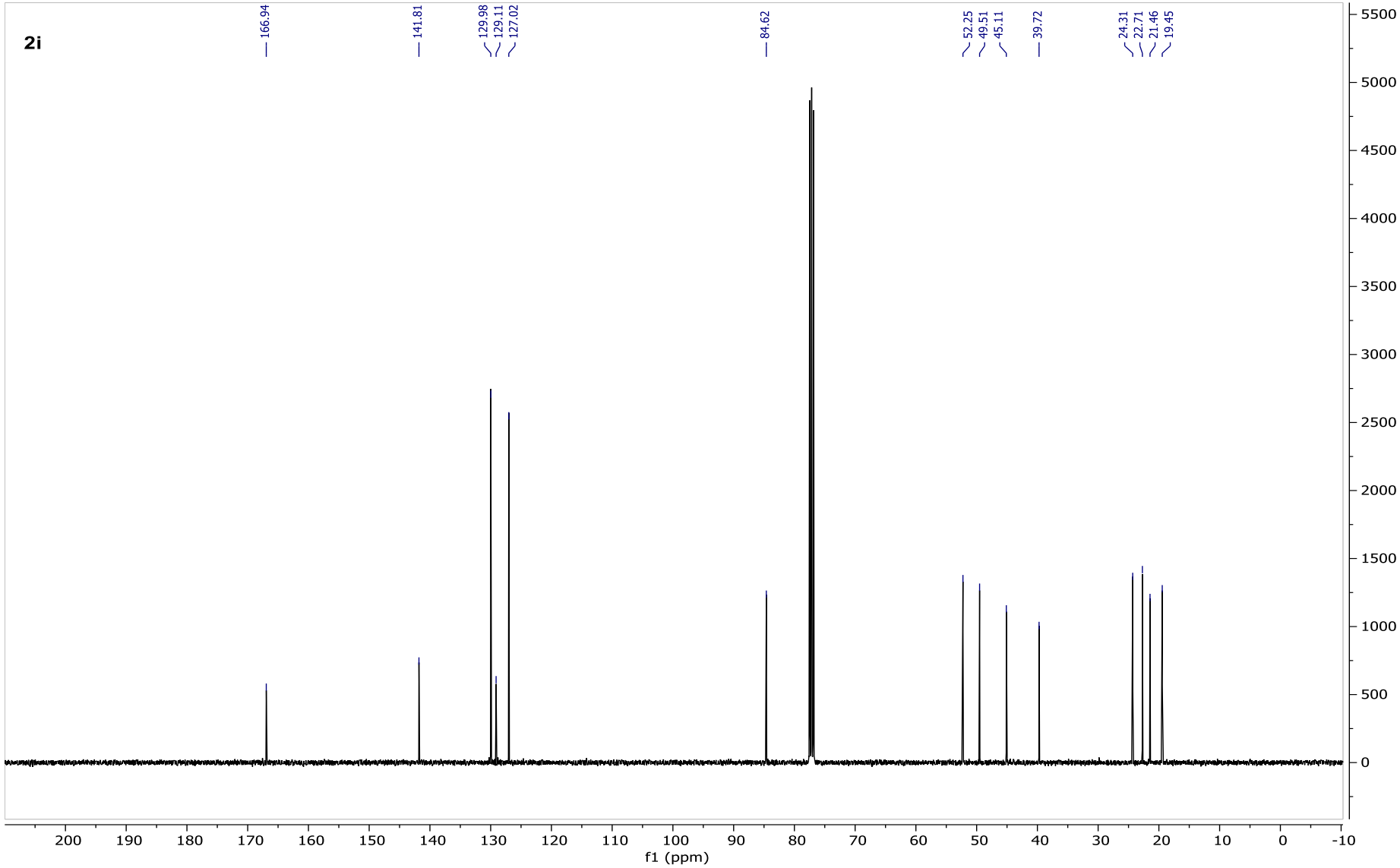
^{13}C NMR (101 MHz, $CDCl_3$):



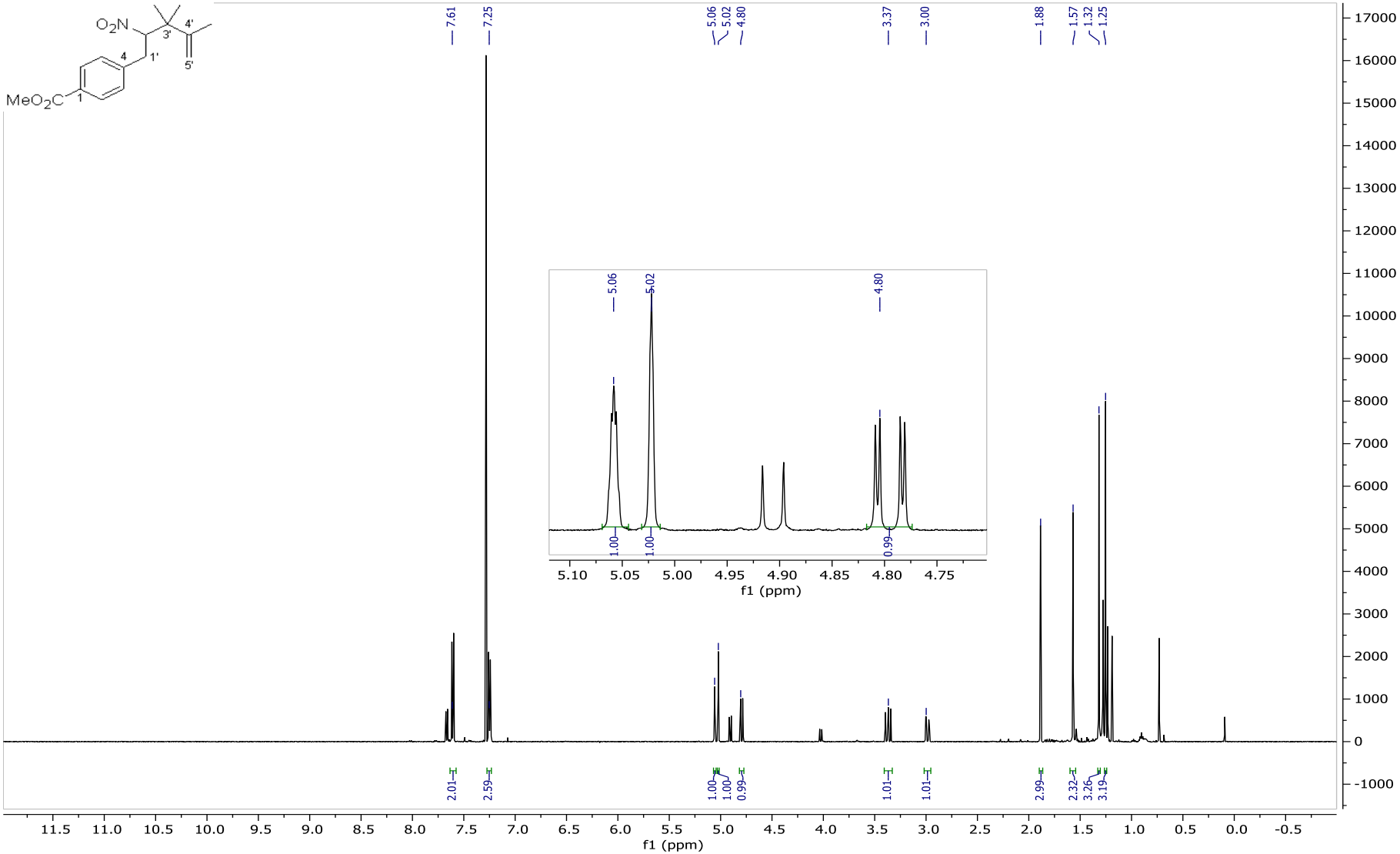
Methyl 4-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzoate (2i): **^{1}H NMR** (400 MHz, $CDCl_3$):



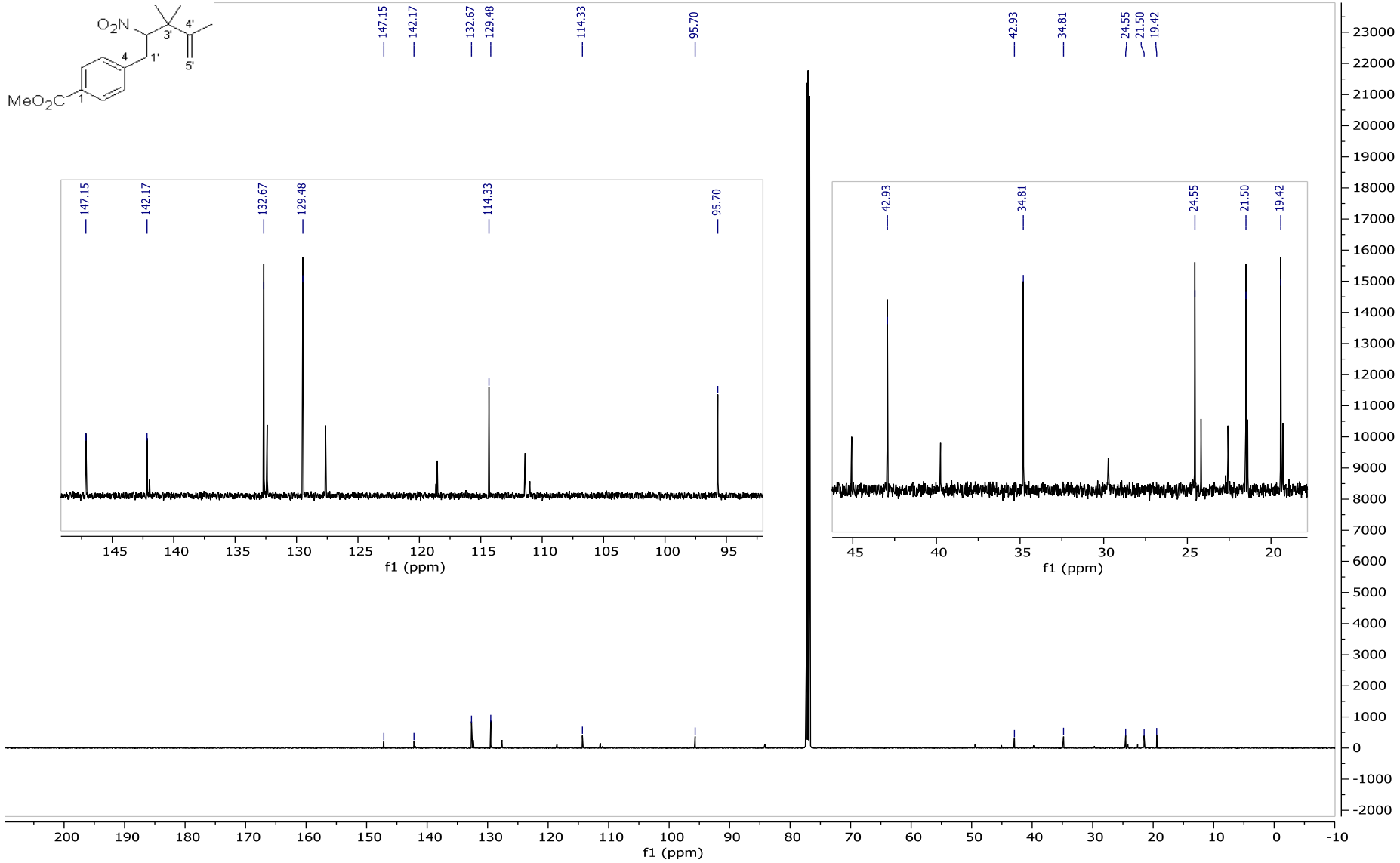
^{13}C NMR (101 MHz, $CDCl_3$):



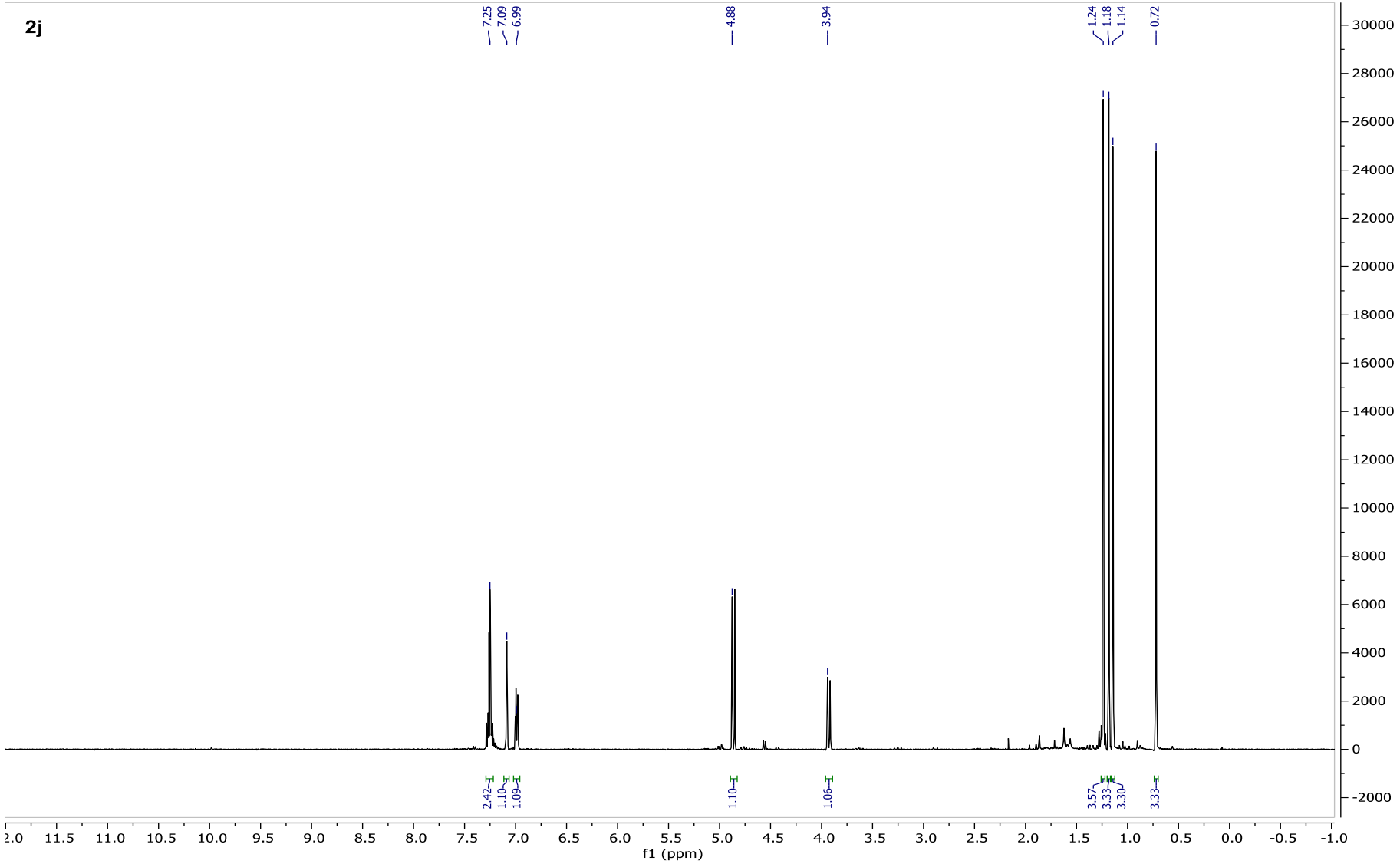
Methyl 4-(4'-methyl-2'-nitropent-4'-en-1'-yl)benzoate: ^{1}H NMR (500 MHz, $CDCl_3$):



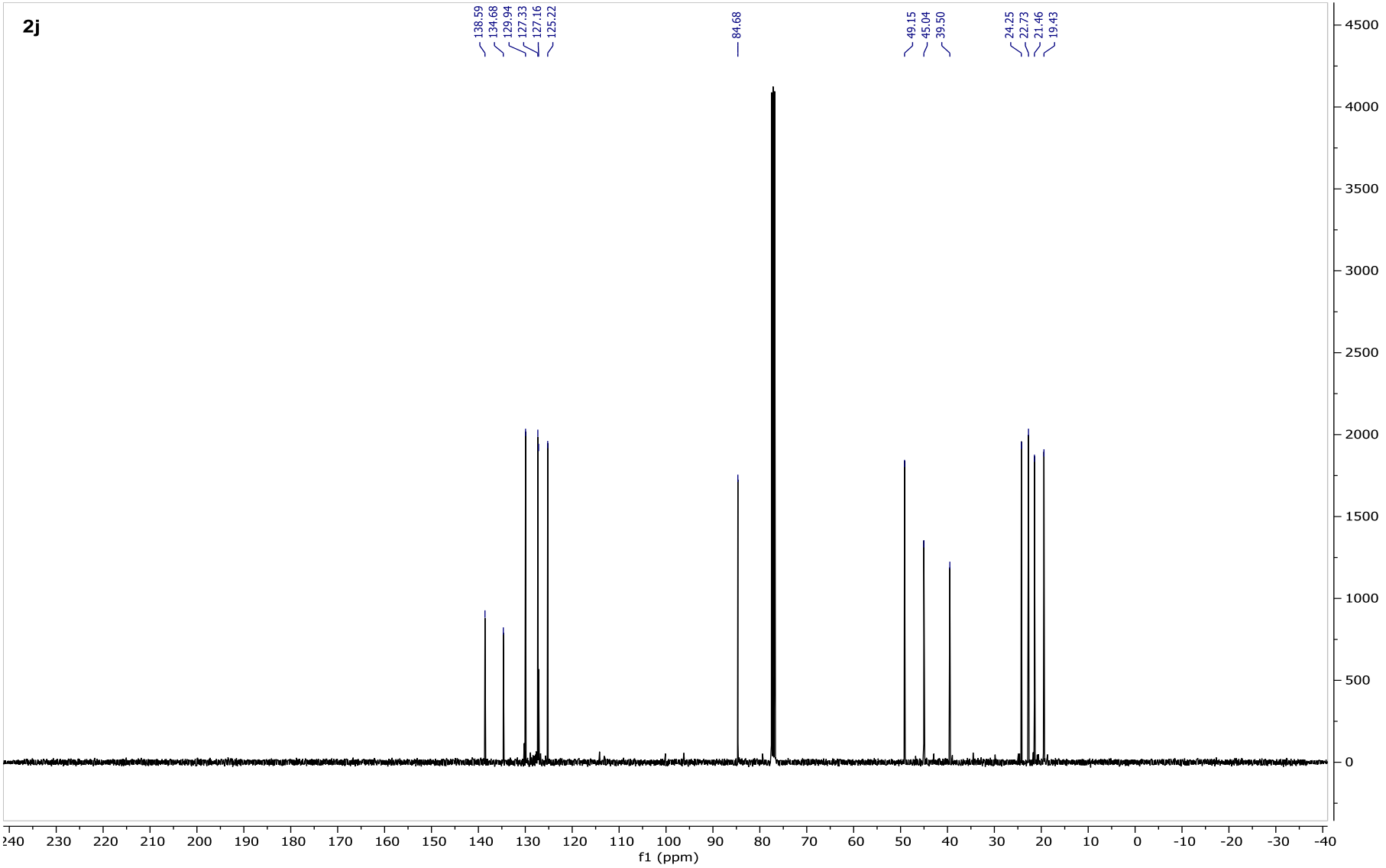
^{13}C NMR (101 MHz, $CDCl_3$):



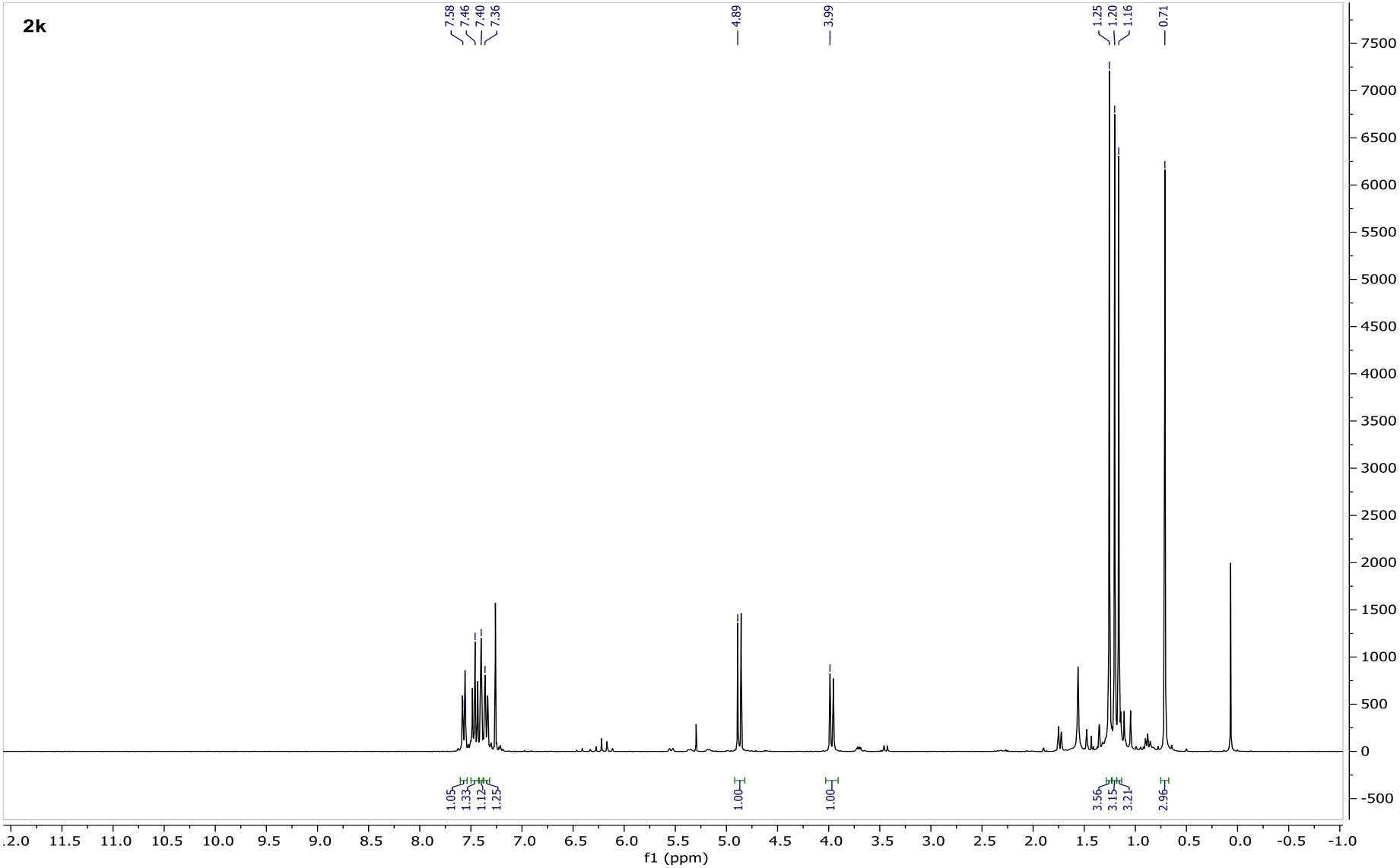
1-Chloro-3-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2j): ^{1}H NMR (400 MHz, $CDCl_3$):



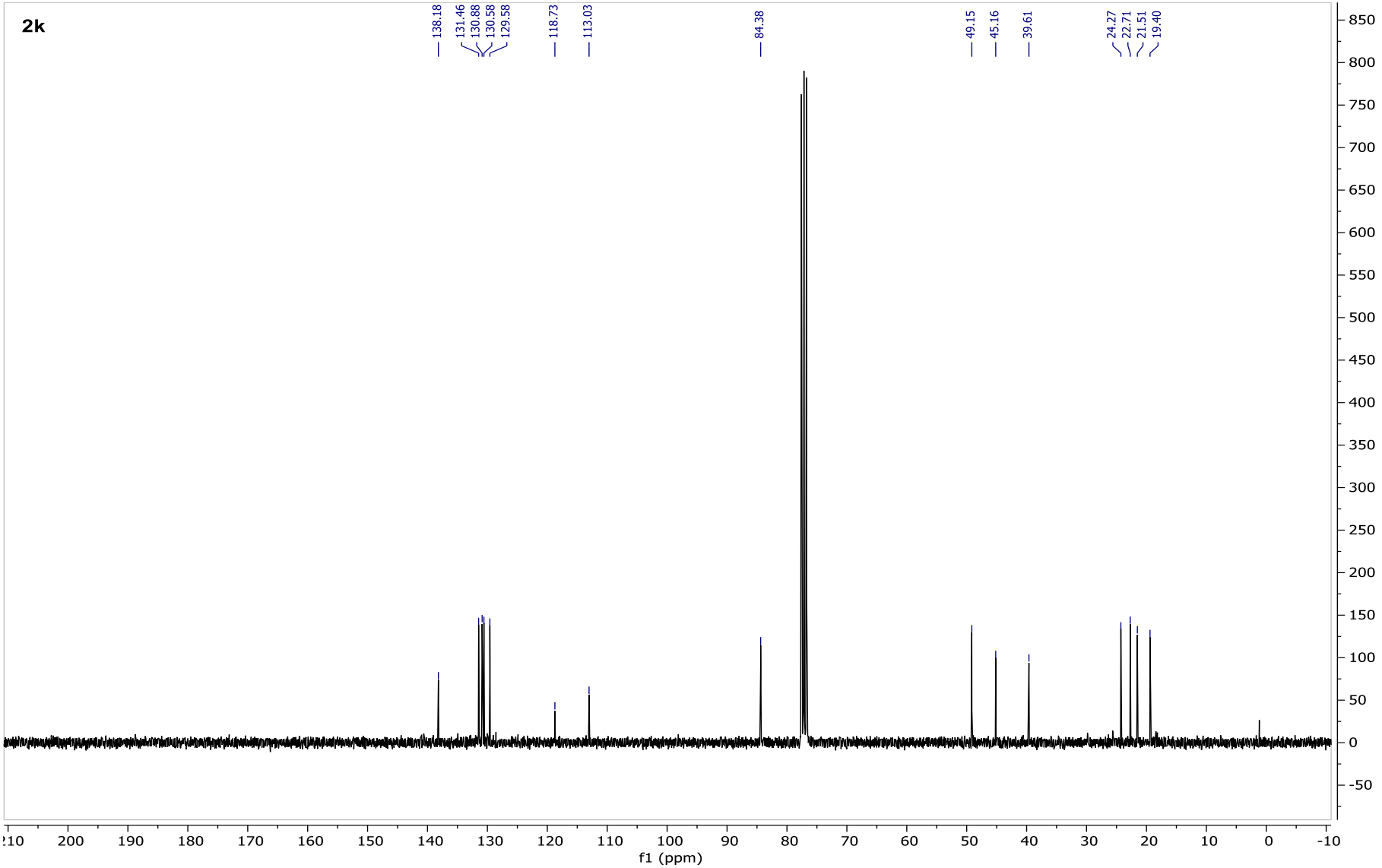
^{13}C NMR (101 MHz, $CDCl_3$):



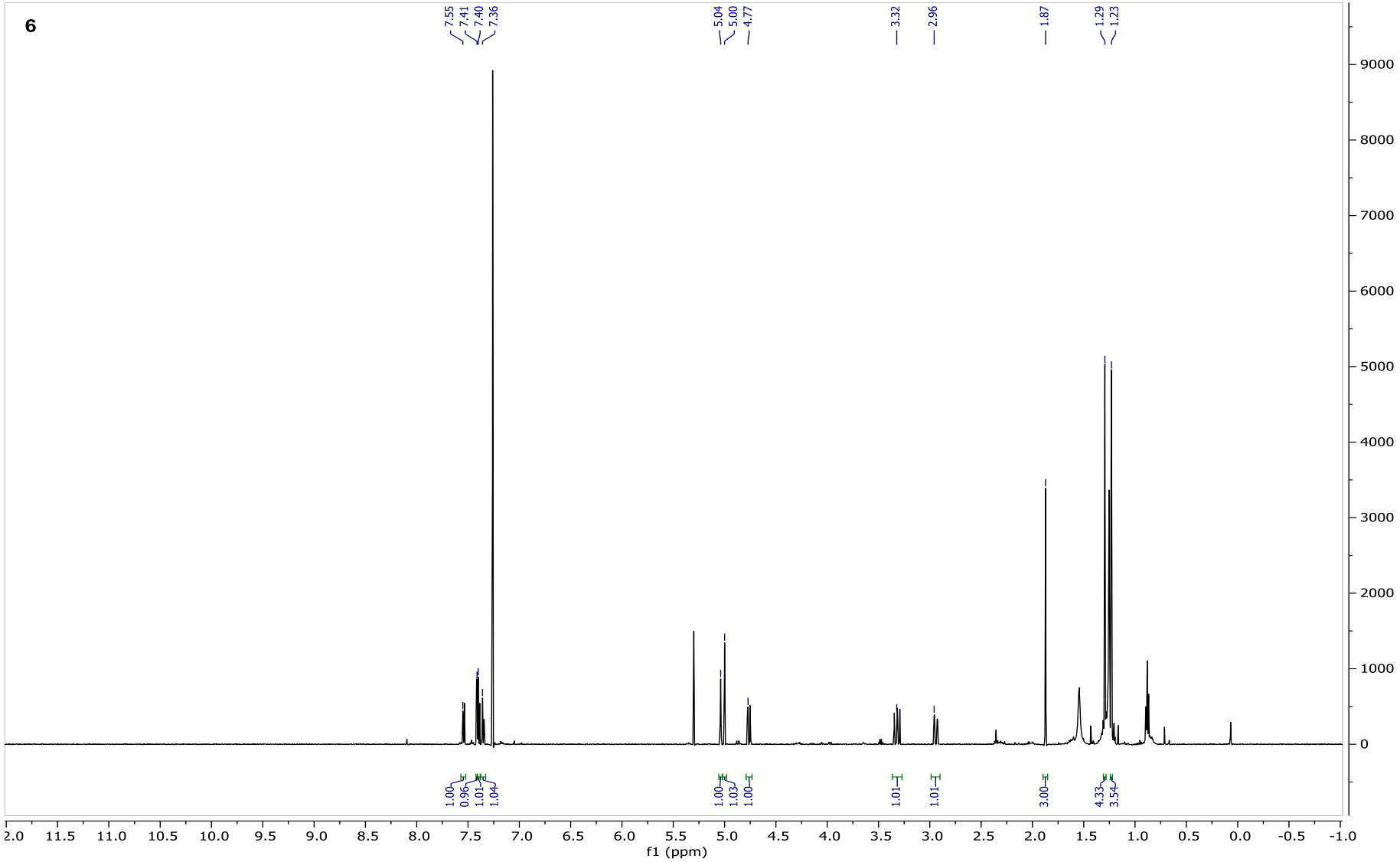
3-(2',2',3',3'-Tetramethyl-4'-nitrocyclobutyl)benzonitrile (2k): ^{1}H NMR (300 MHz, $CDCl_3$):



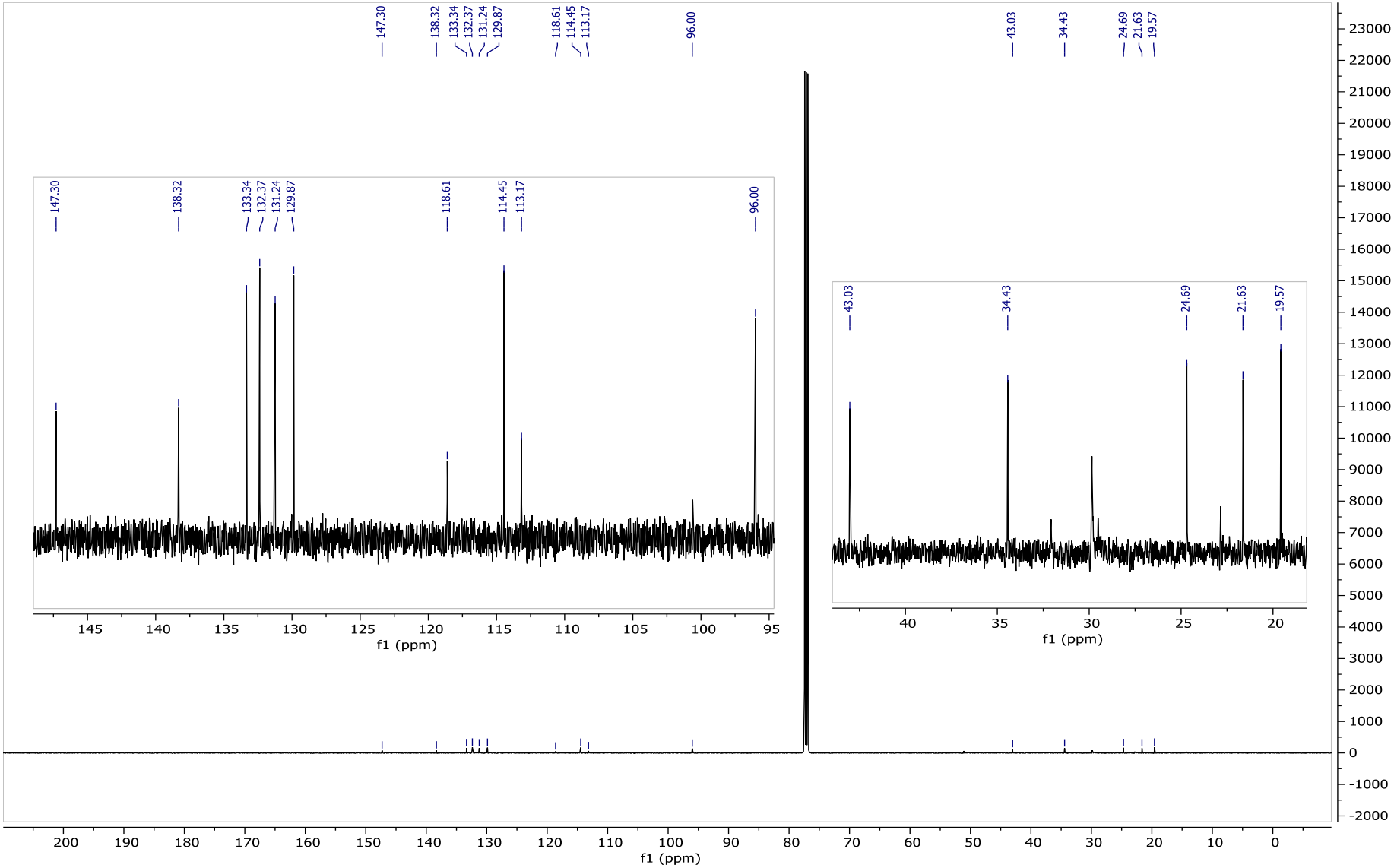
^{13}C NMR (75 MHz, $CDCl_3$):



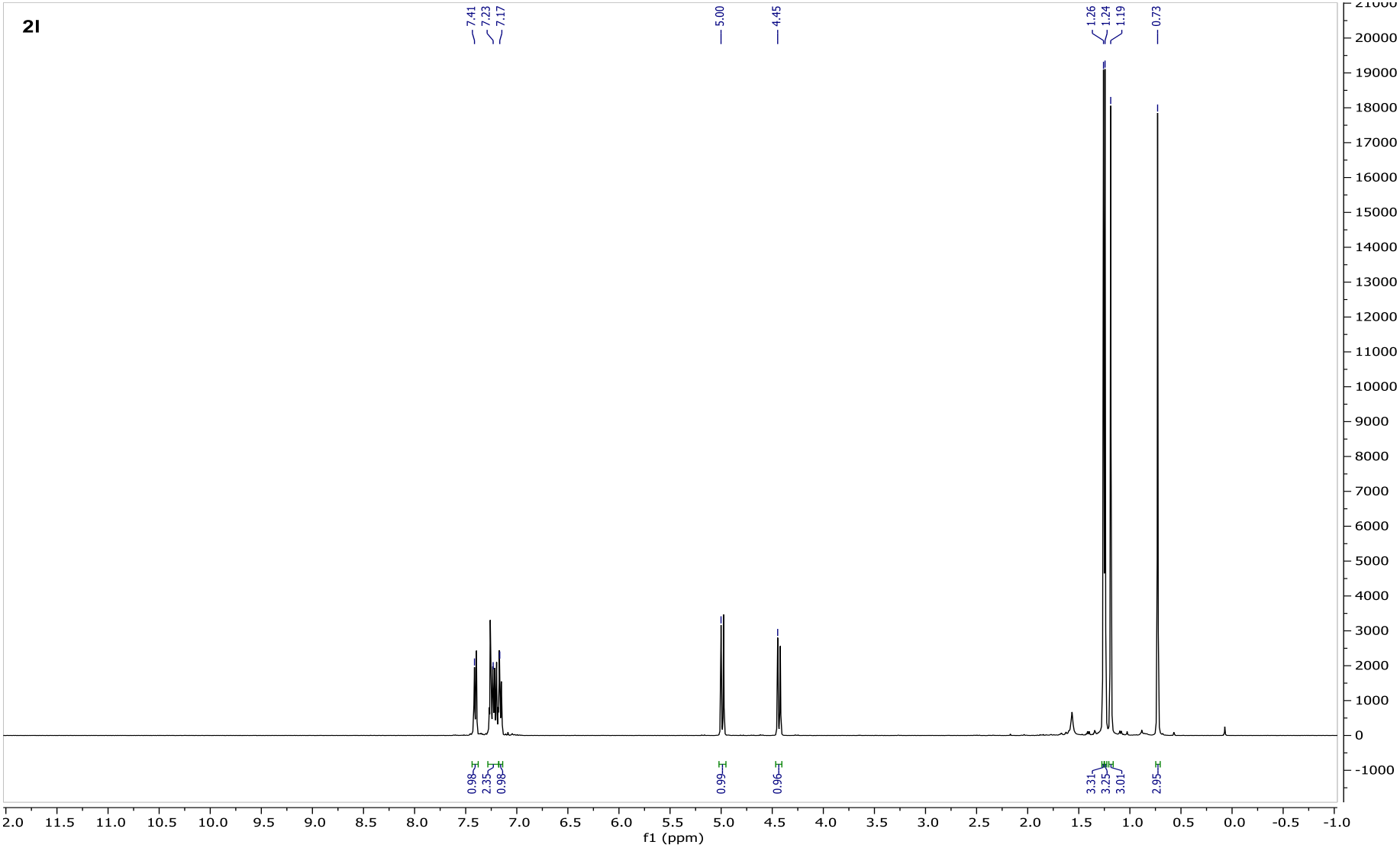
3-(3',3',4'-trimethyl-2'-nitropent-4'-en-1'-yl)-benzonitrile (6): ^{1}H NMR (500 MHz, $CDCl_3$):



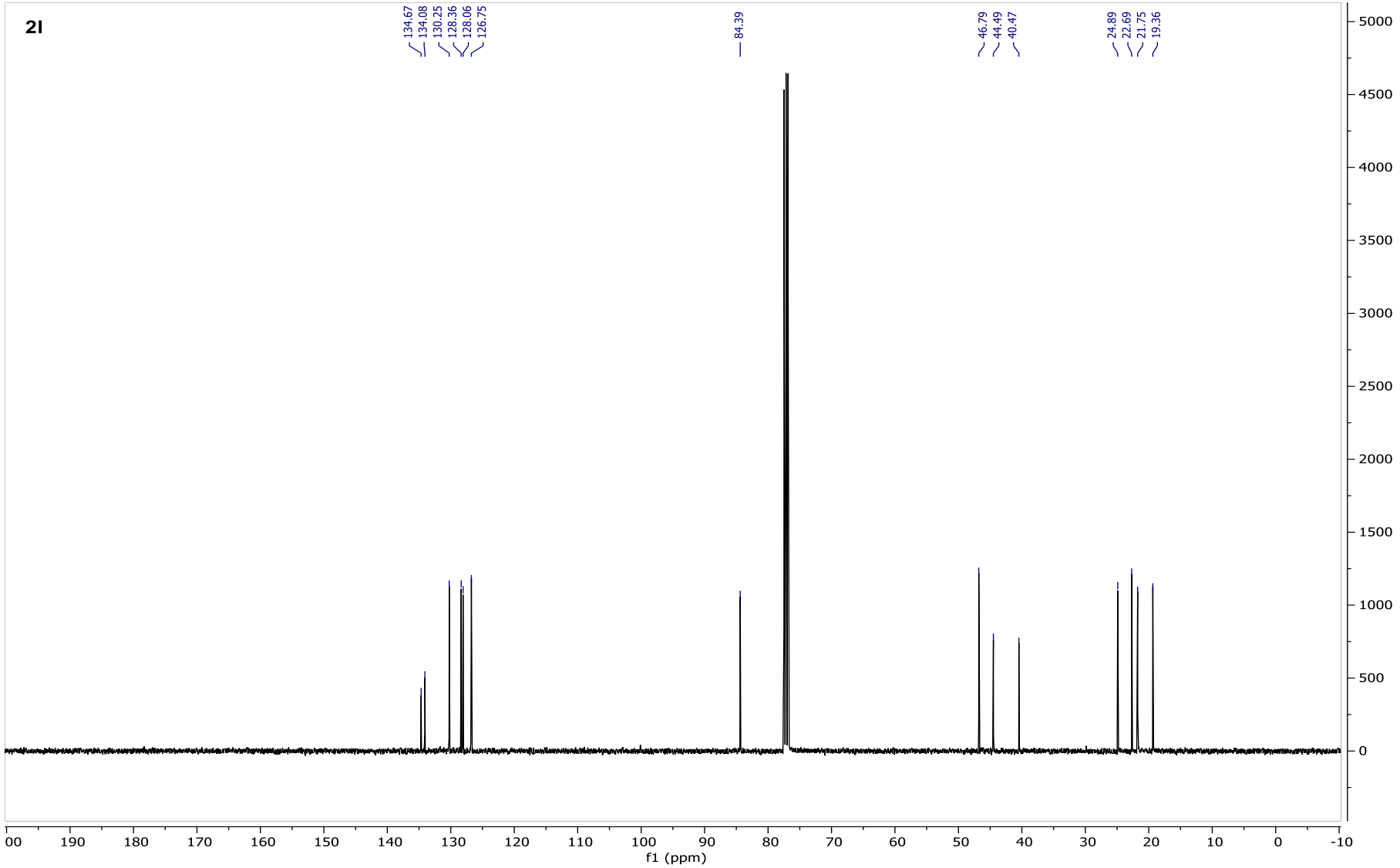
^{13}C NMR (126 MHz, $CDCl_3$):



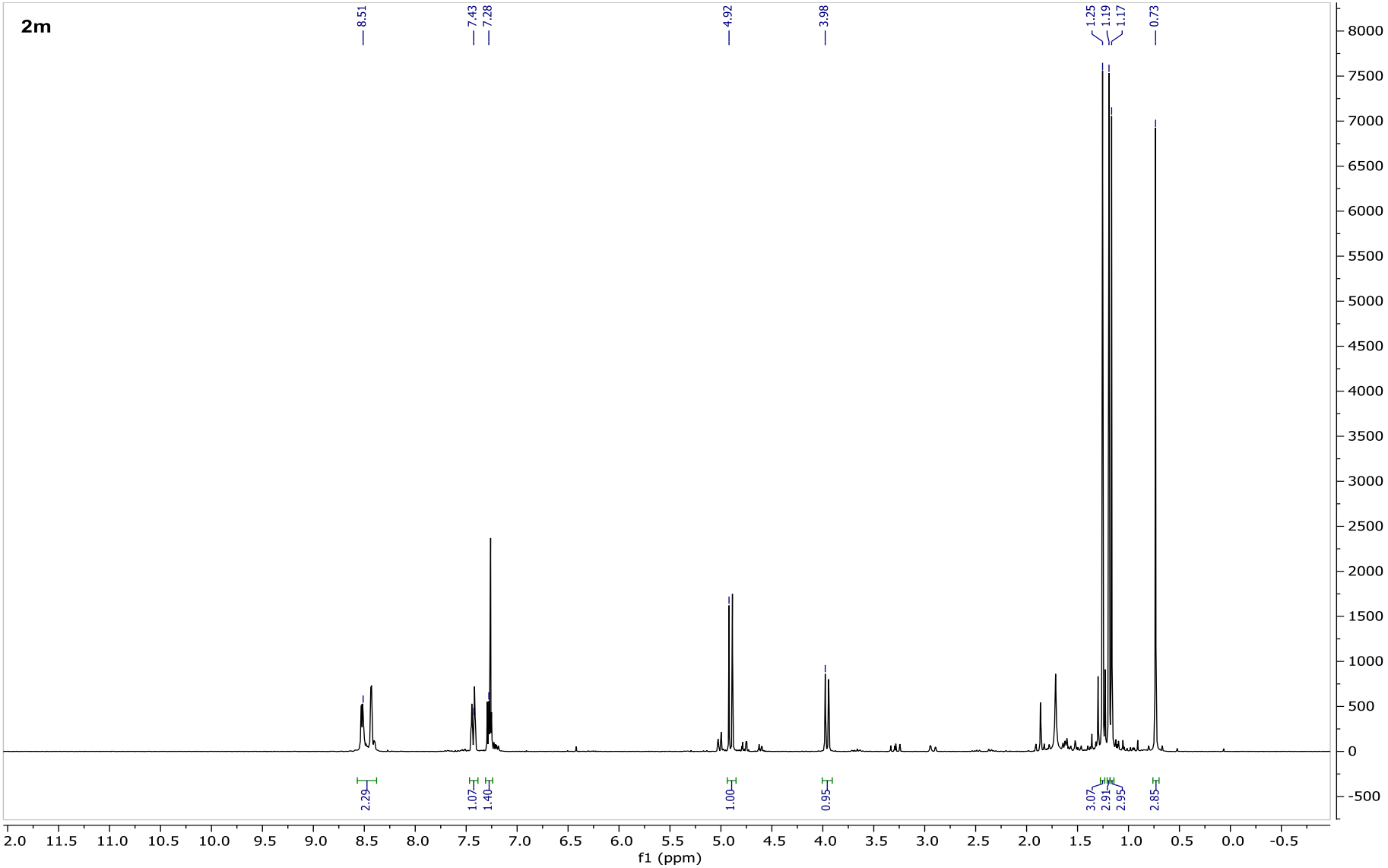
1-Chloro-2-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)benzene (2l): ^{1}H NMR (400 MHz, $CDCl_3$):



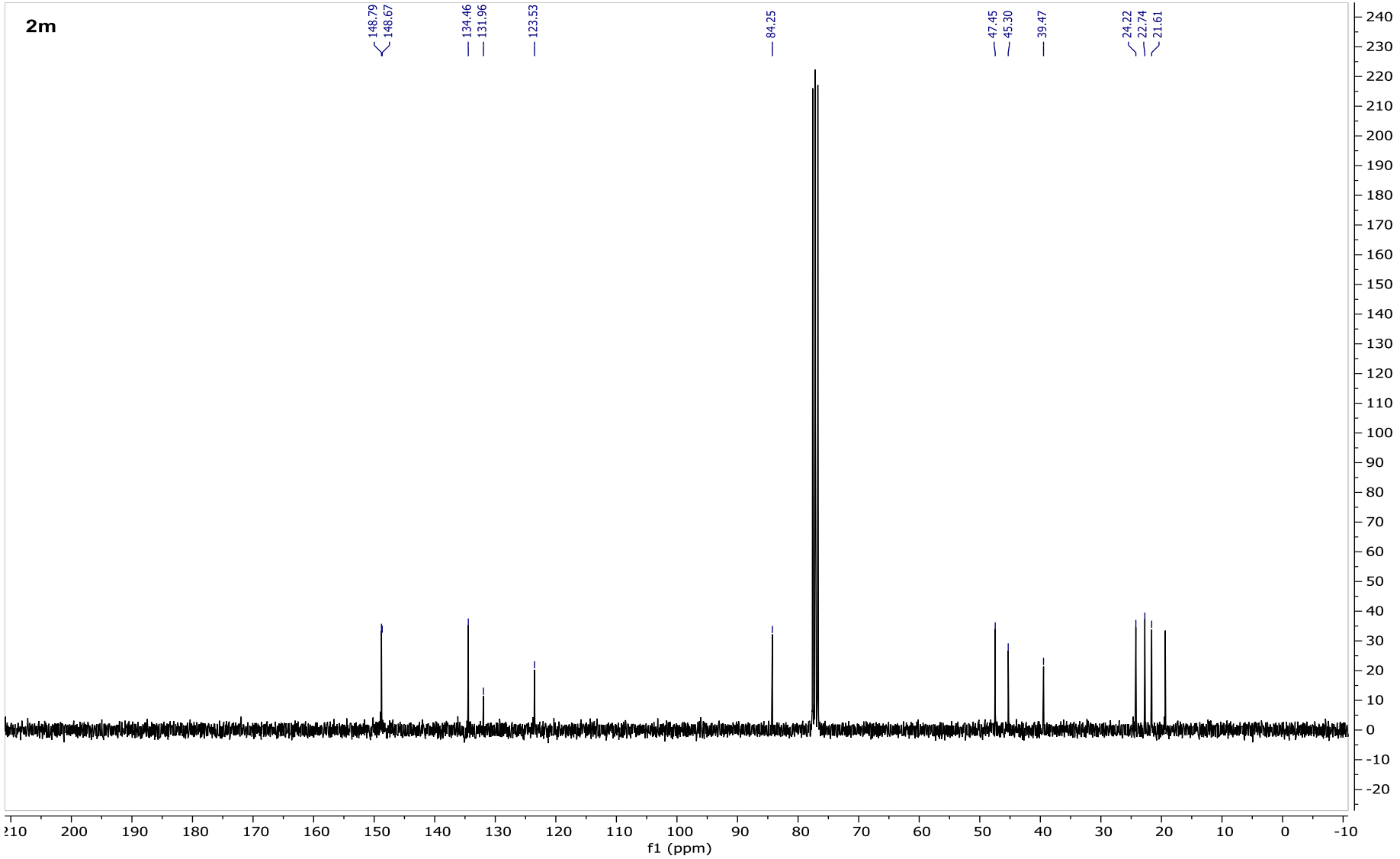
^{13}C NMR (101 MHz, $CDCl_3$):



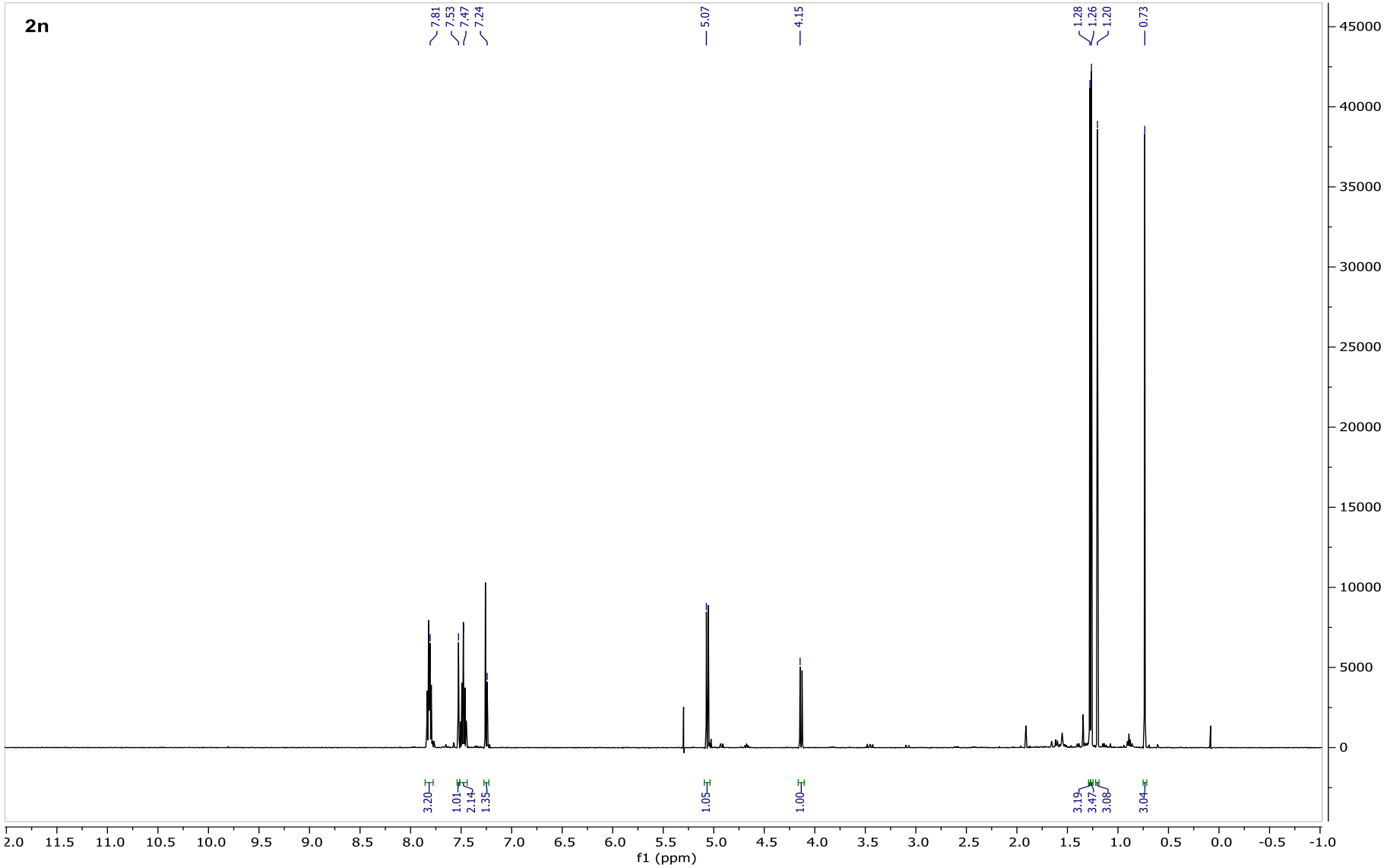
2-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)pyridine (2m): ^{1}H NMR (300 MHz, $CDCl_3$):



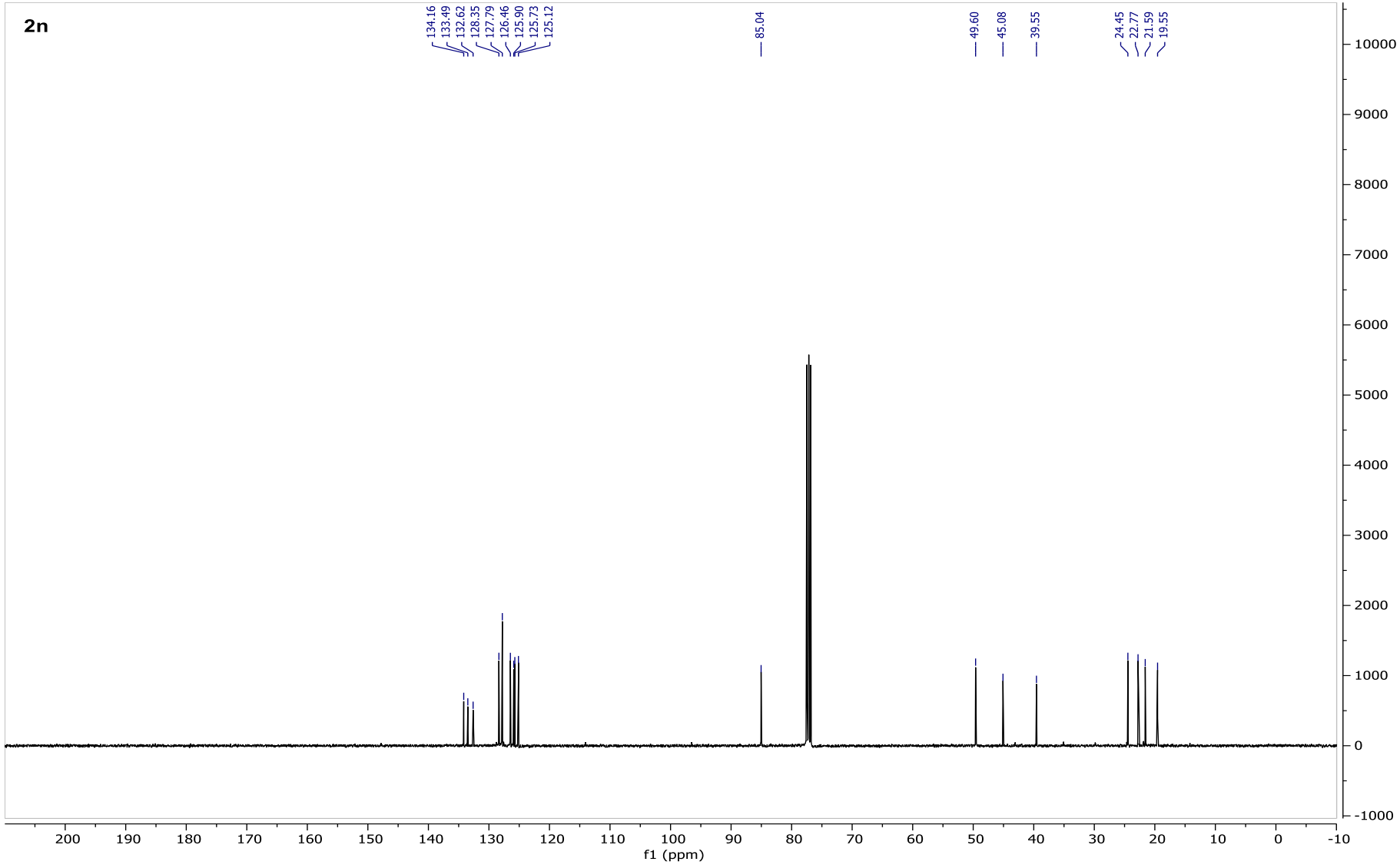
^{13}C NMR (75 MHz, $CDCl_3$):



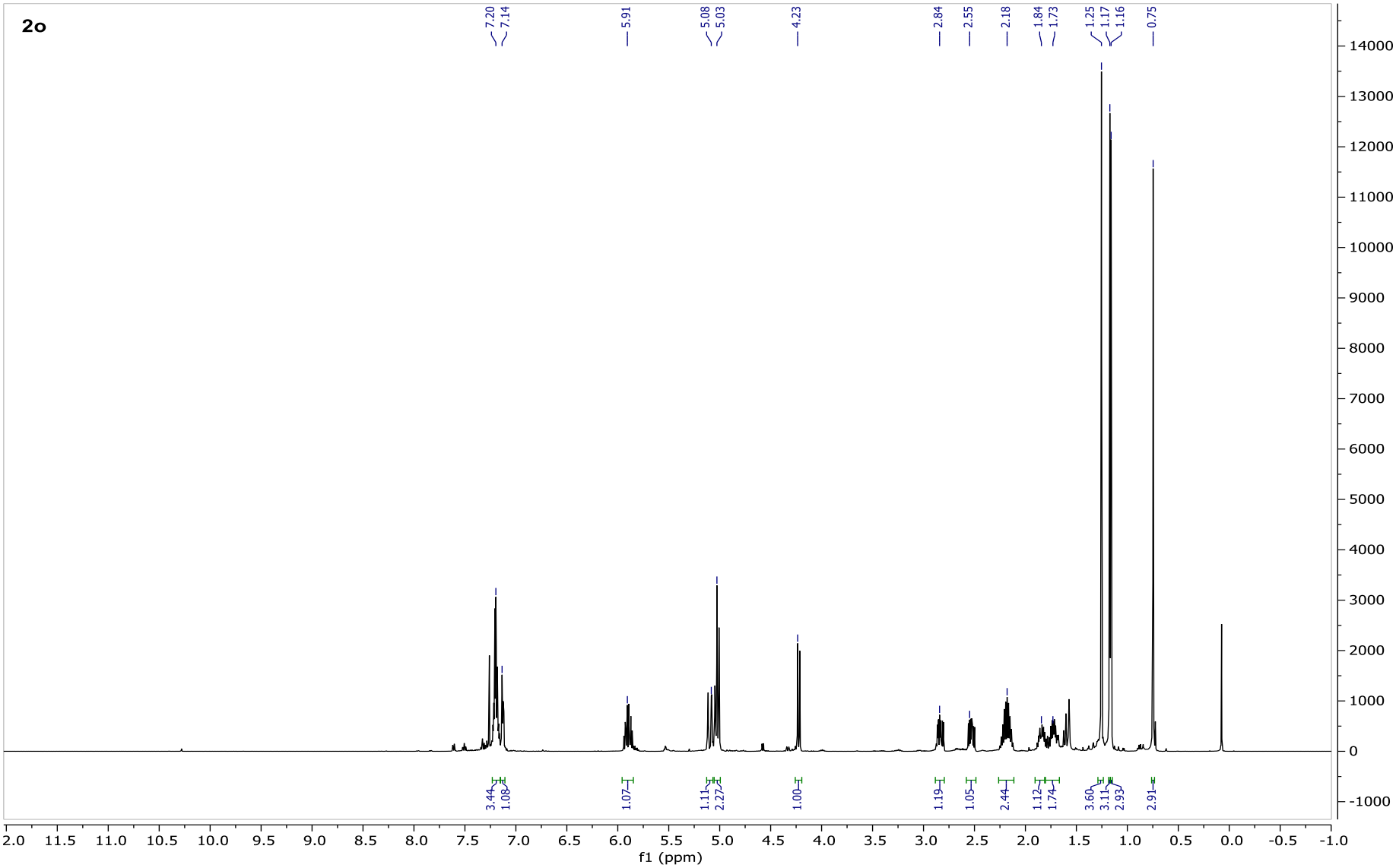
2-(2',2',3',3'-tetramethyl-4'-nitrocyclobutyl)napthalene (2n): ^{1}H NMR (500 MHz, $CDCl_3$):



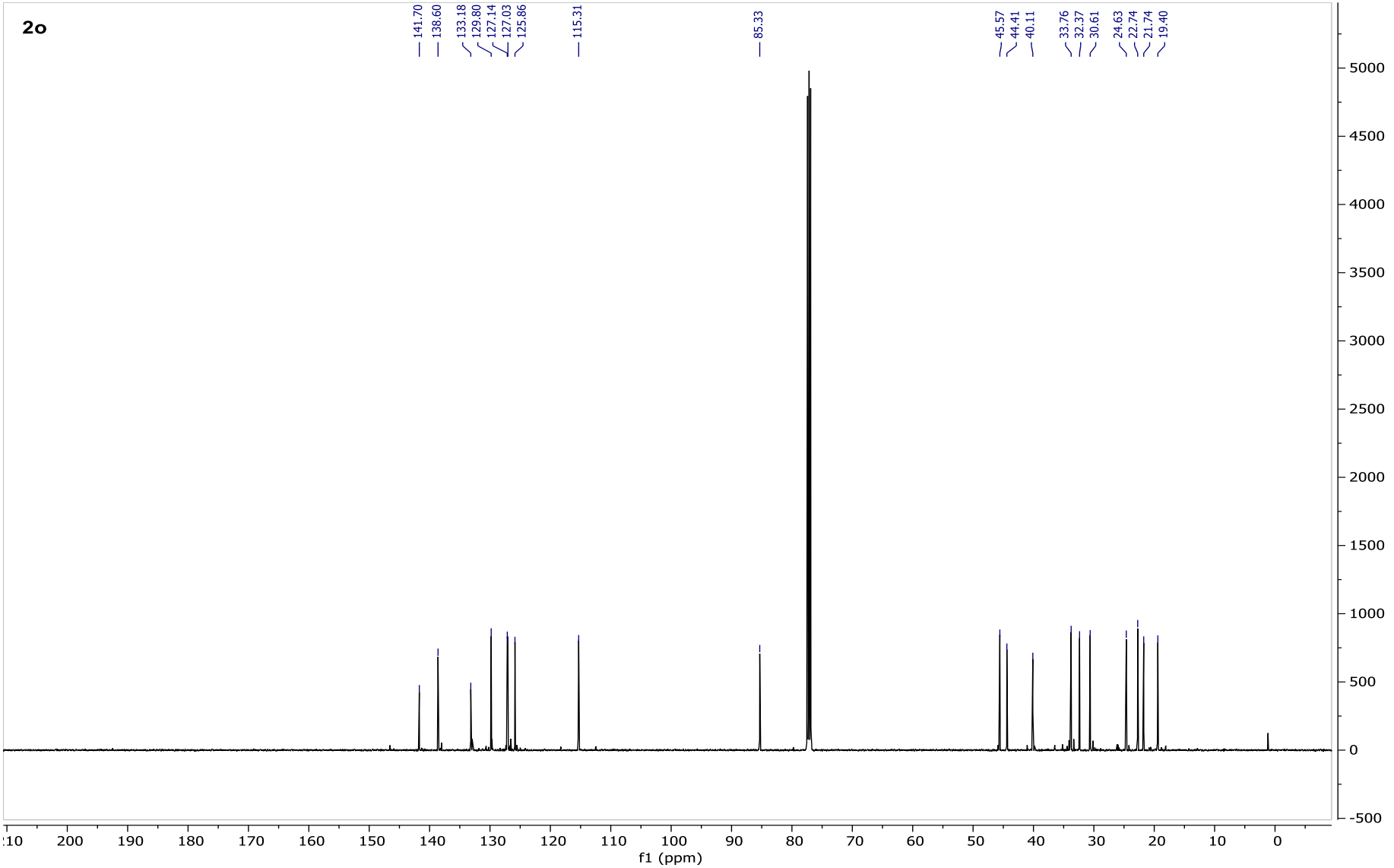
^{13}C NMR (101 MHz, $CDCl_3$):



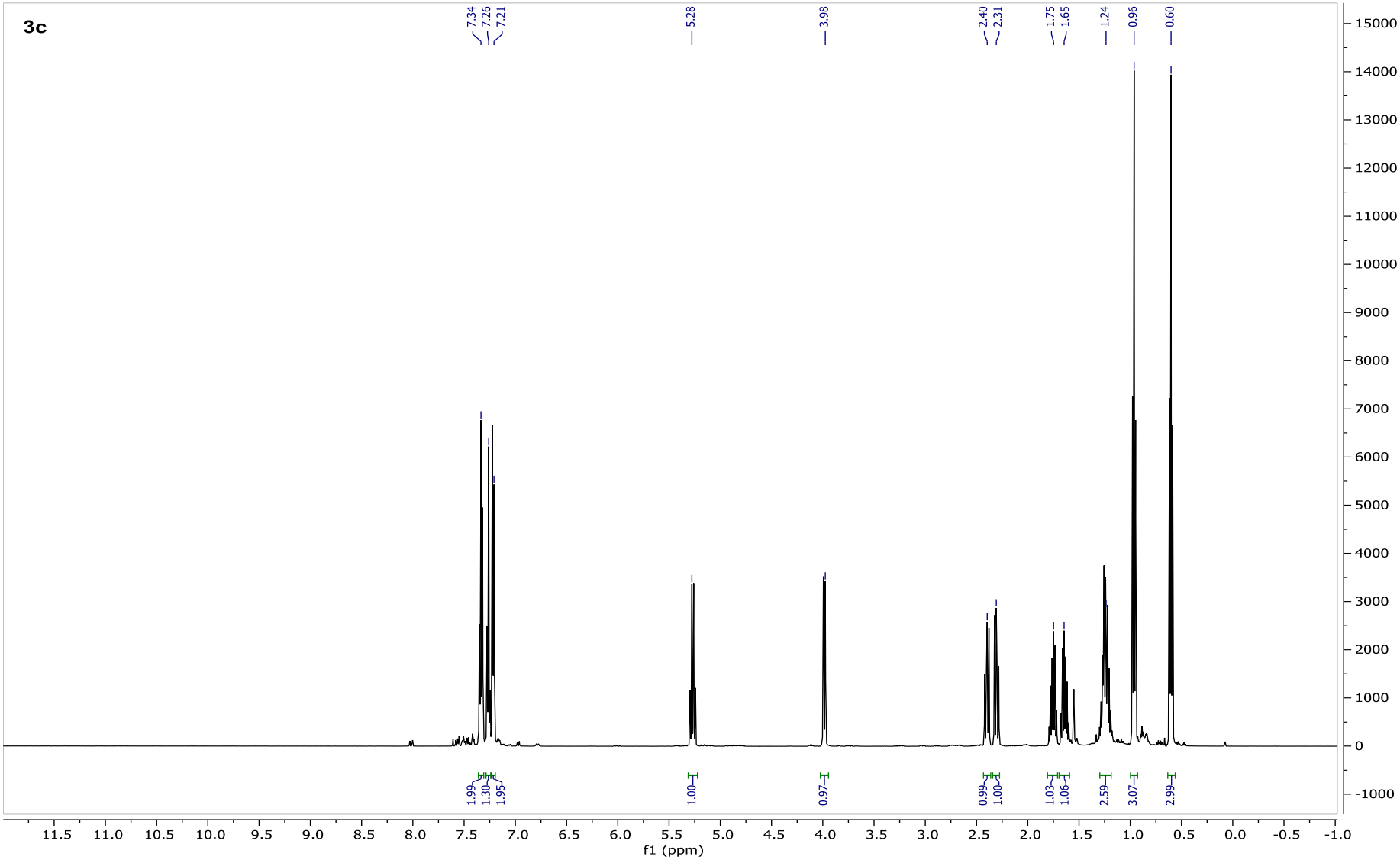
1-(pent-4’-en-1’-yl)-2-(2’’,2’’,3’’,3’’-tetramethyl-4’’-nitrocyclobutyl)-benzene (2o): ^{1}H NMR (500 MHz, $CDCl_3$):



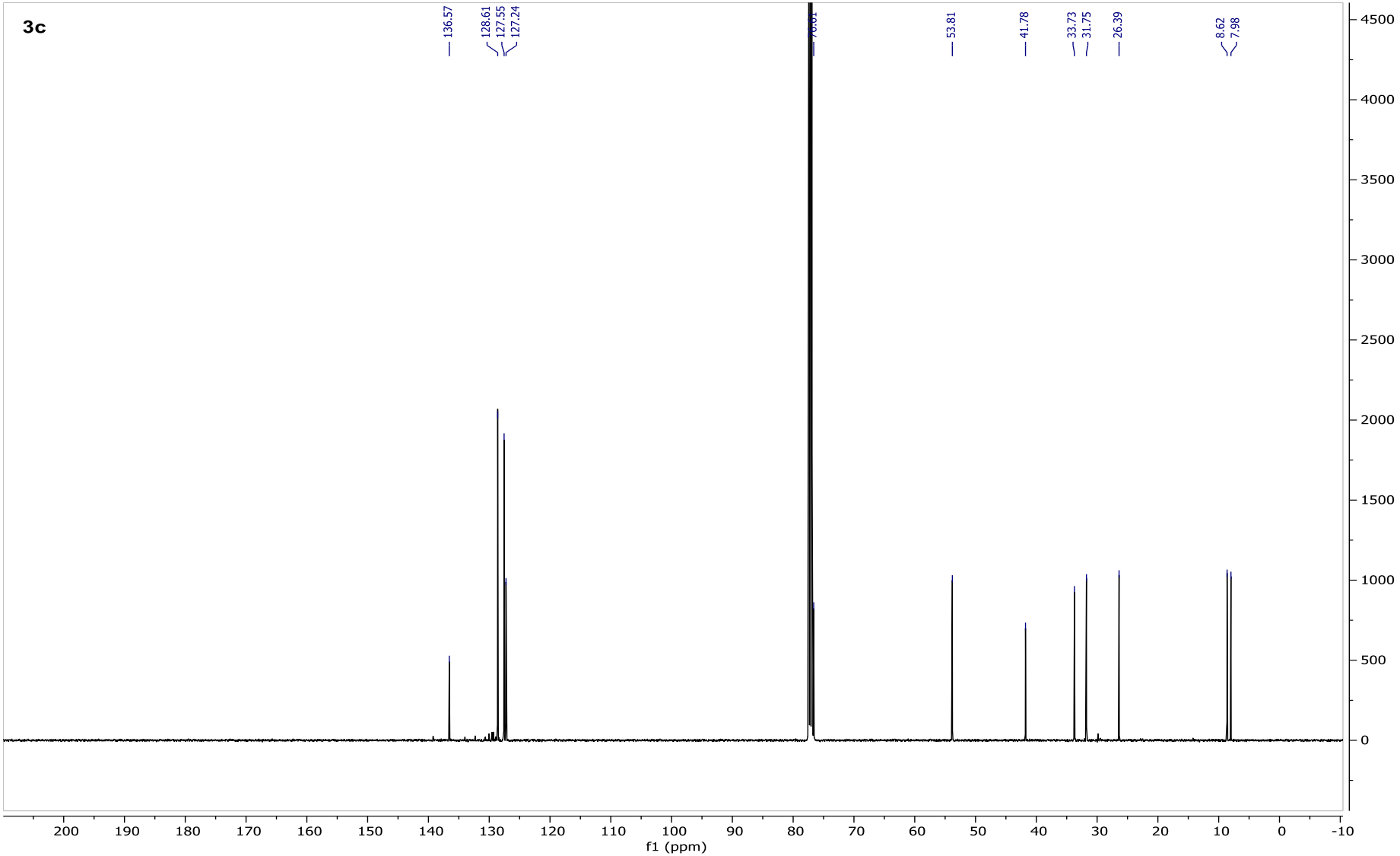
^{13}C NMR (126 MHz, $CDCl_3$):



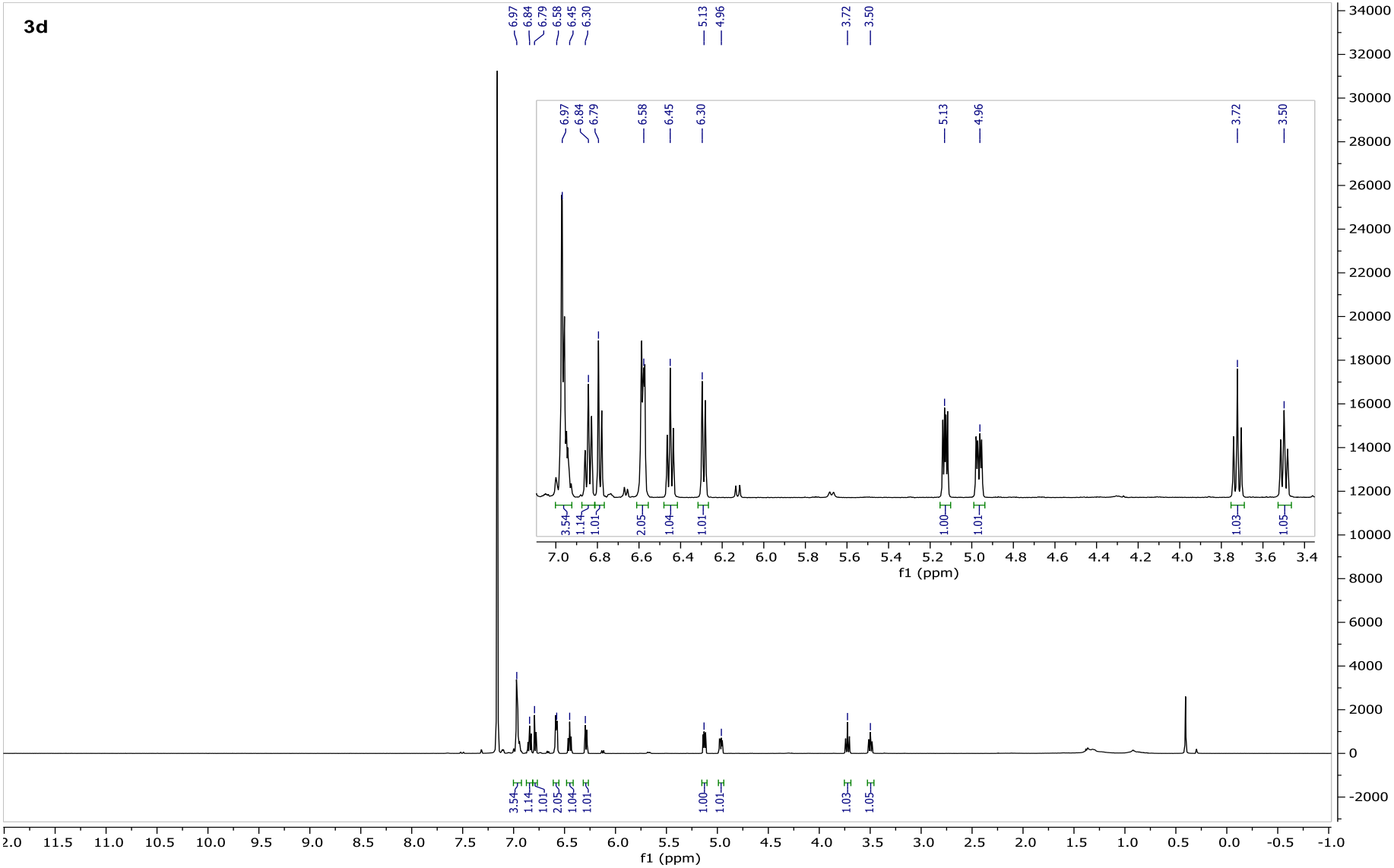
(2',2'-Diethyl-4'-nitrocyclobutyl)benzene (3c): ^{1}H NMR (500 MHz, $CDCl_3$):



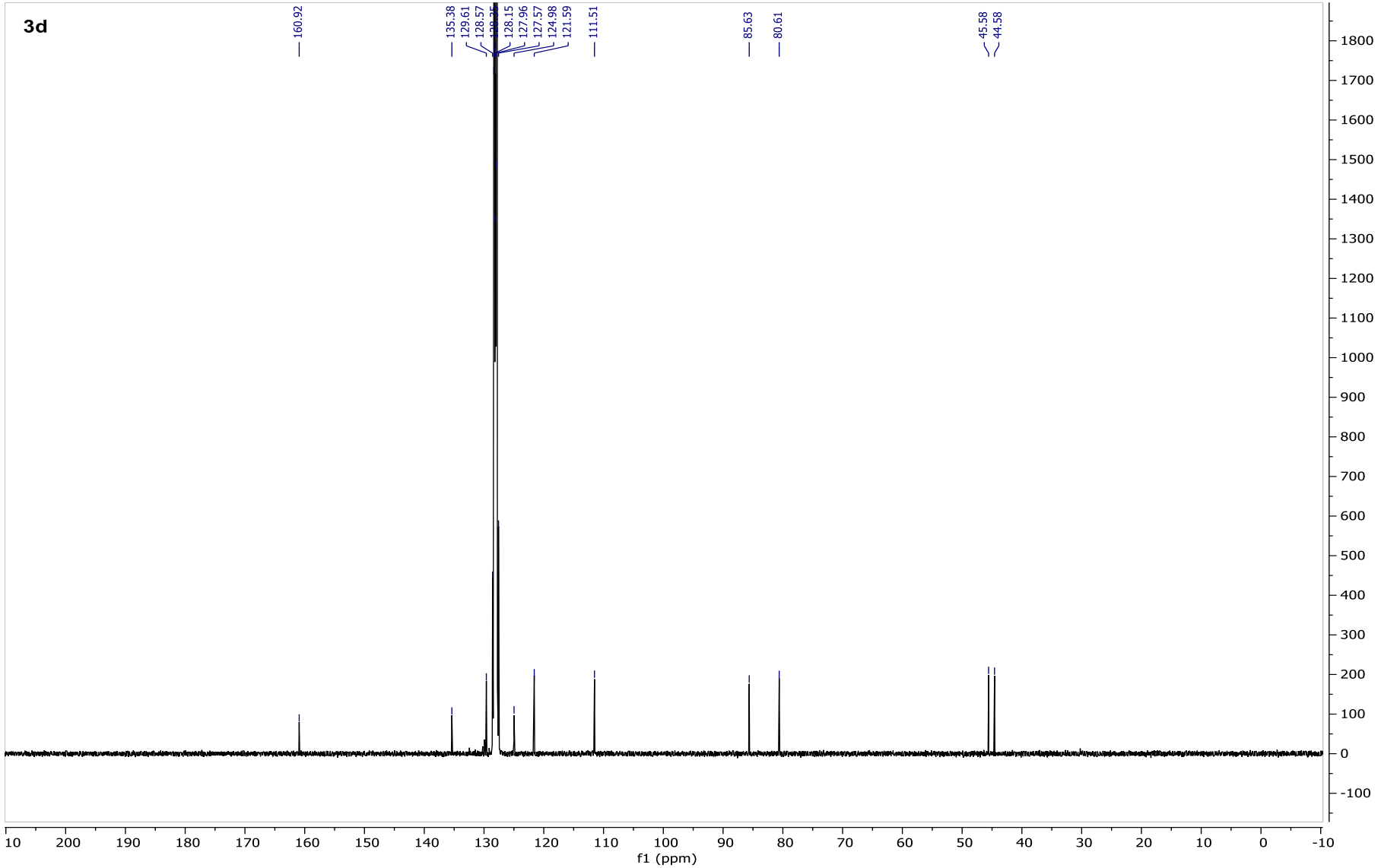
^{13}C NMR (126 MHz, $CDCl_3$):



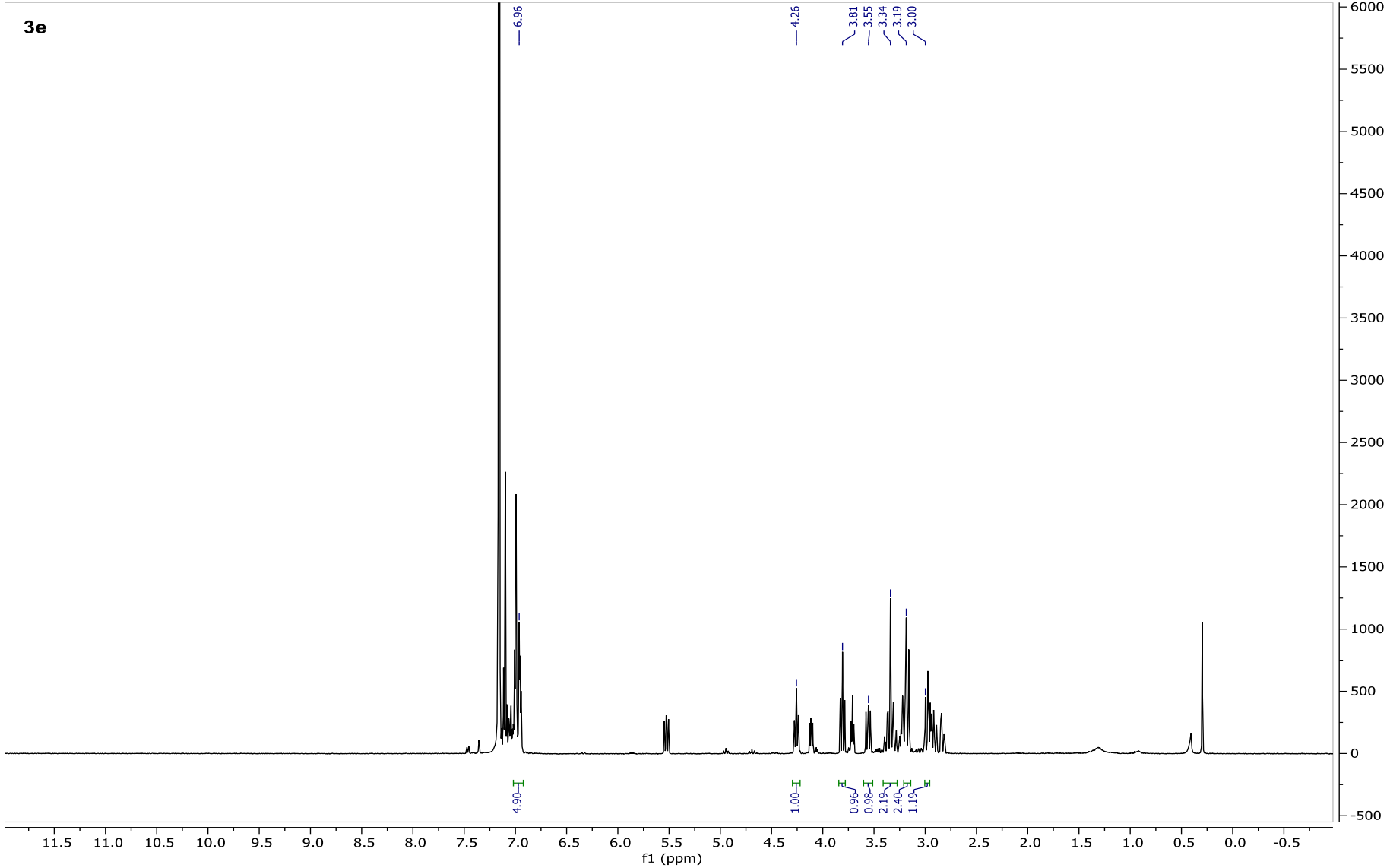
1-Nitro-2-phenyl-1,2,2a,7b-tetrahydrocyclobuta[b]benzofuran (3d): ^{1}H NMR (500 MHz, C_6D_6):



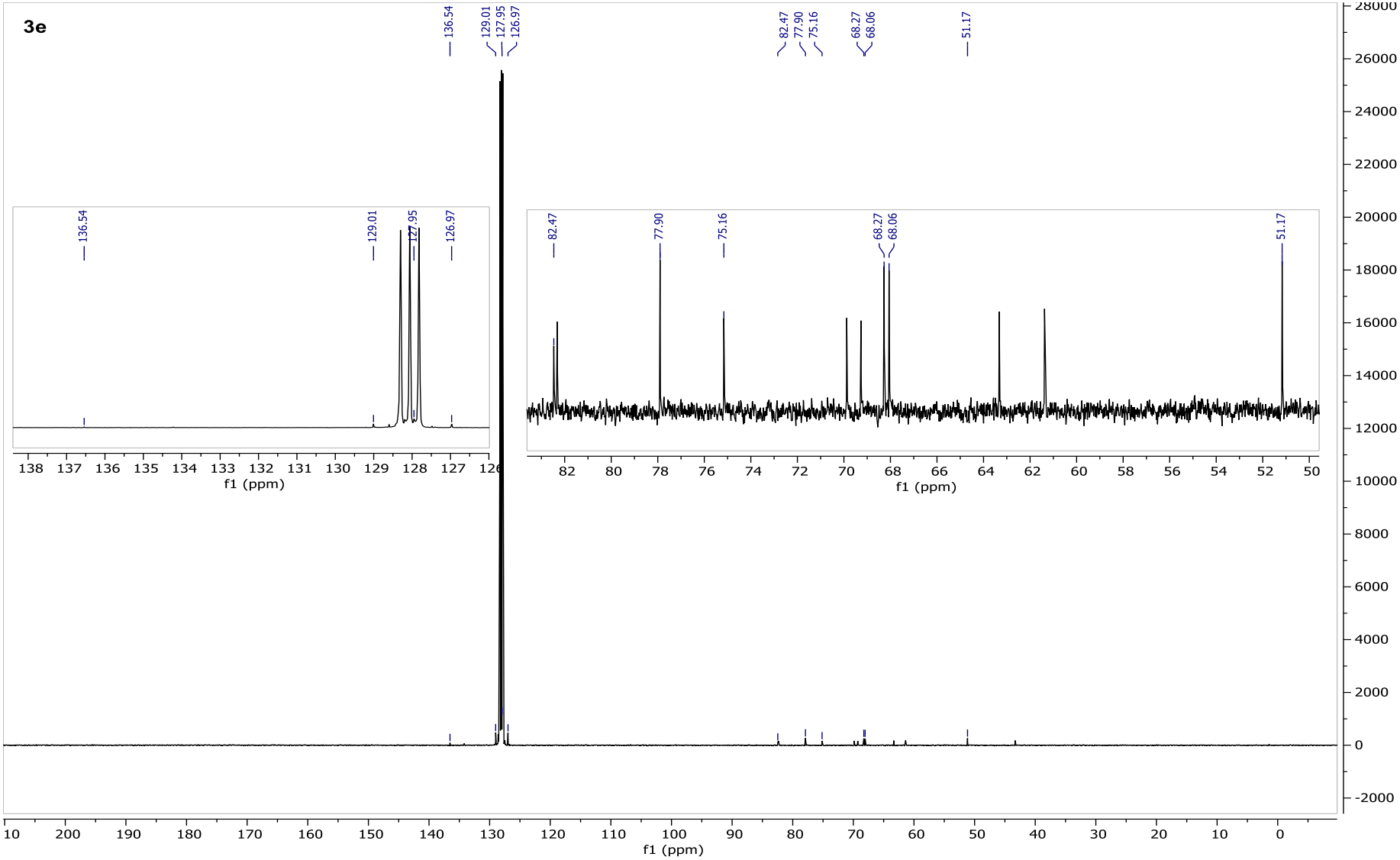
^{13}C NMR (101 MHz, C_6D_6):



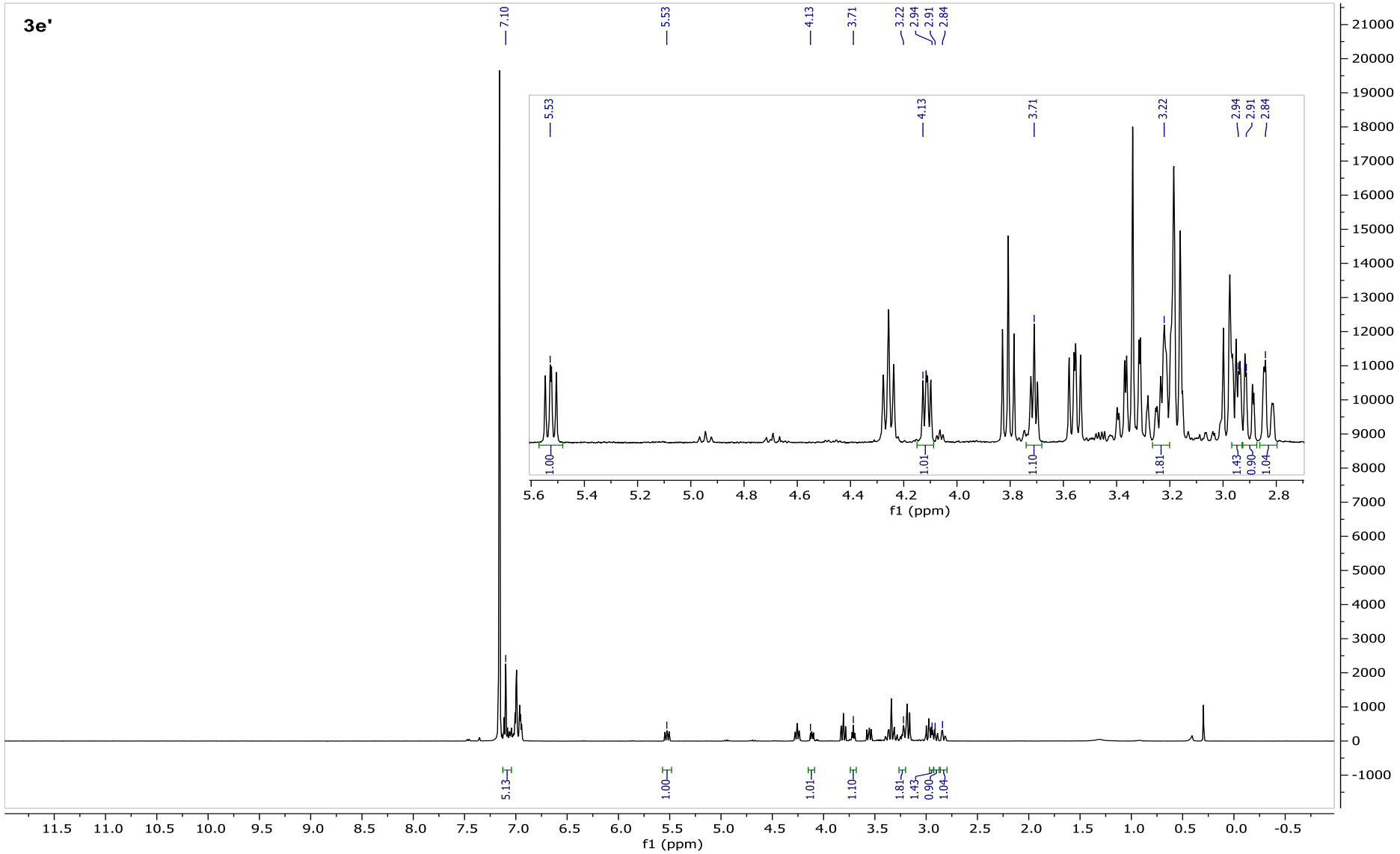
7-Nitro-8-phenyl-2,5-dioxabicyclo[4.2.0]octane (3e): ^{1}H NMR (400 MHz, C_6D_6):



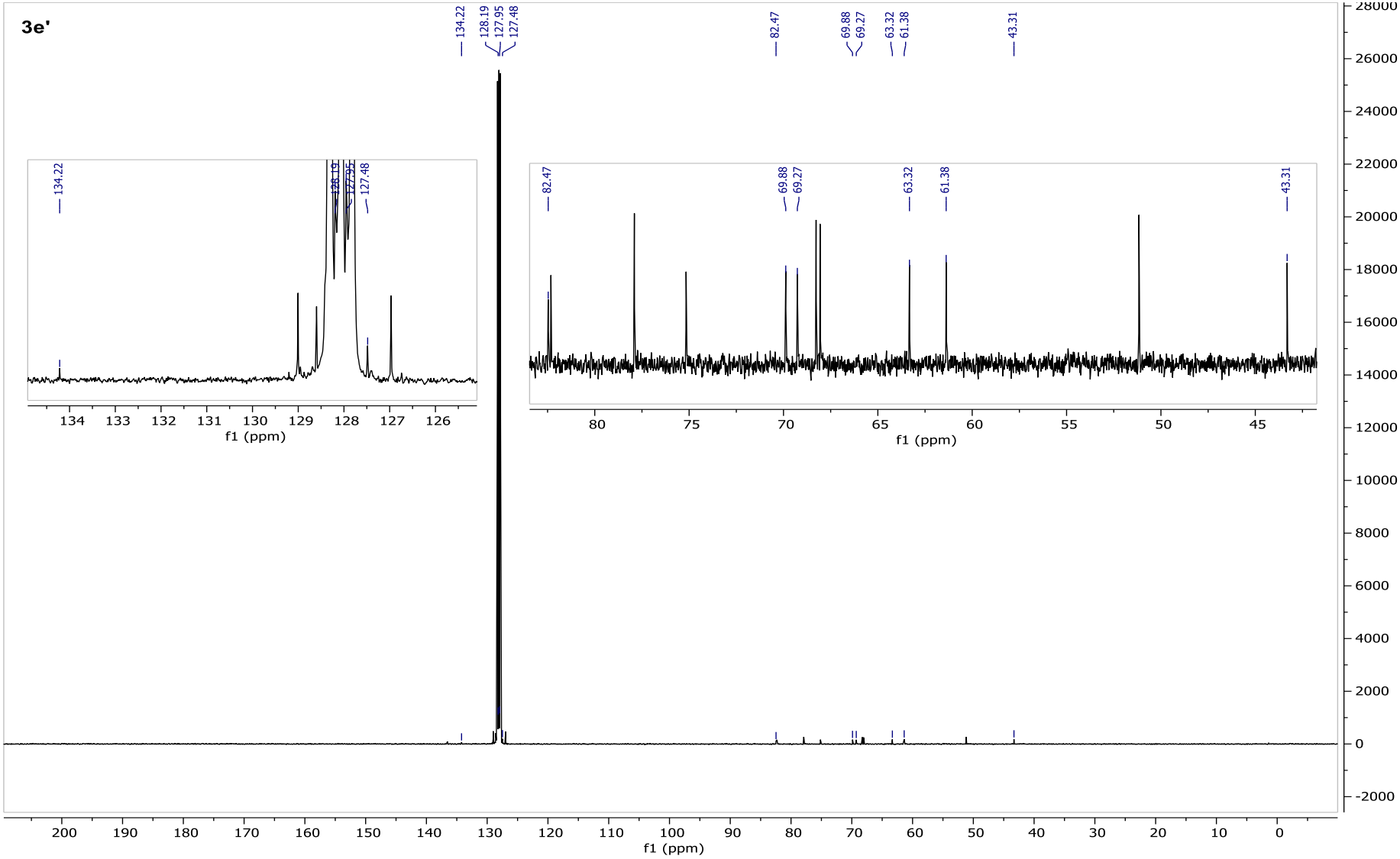
^{13}C NMR (101 MHz, C_6D_6):



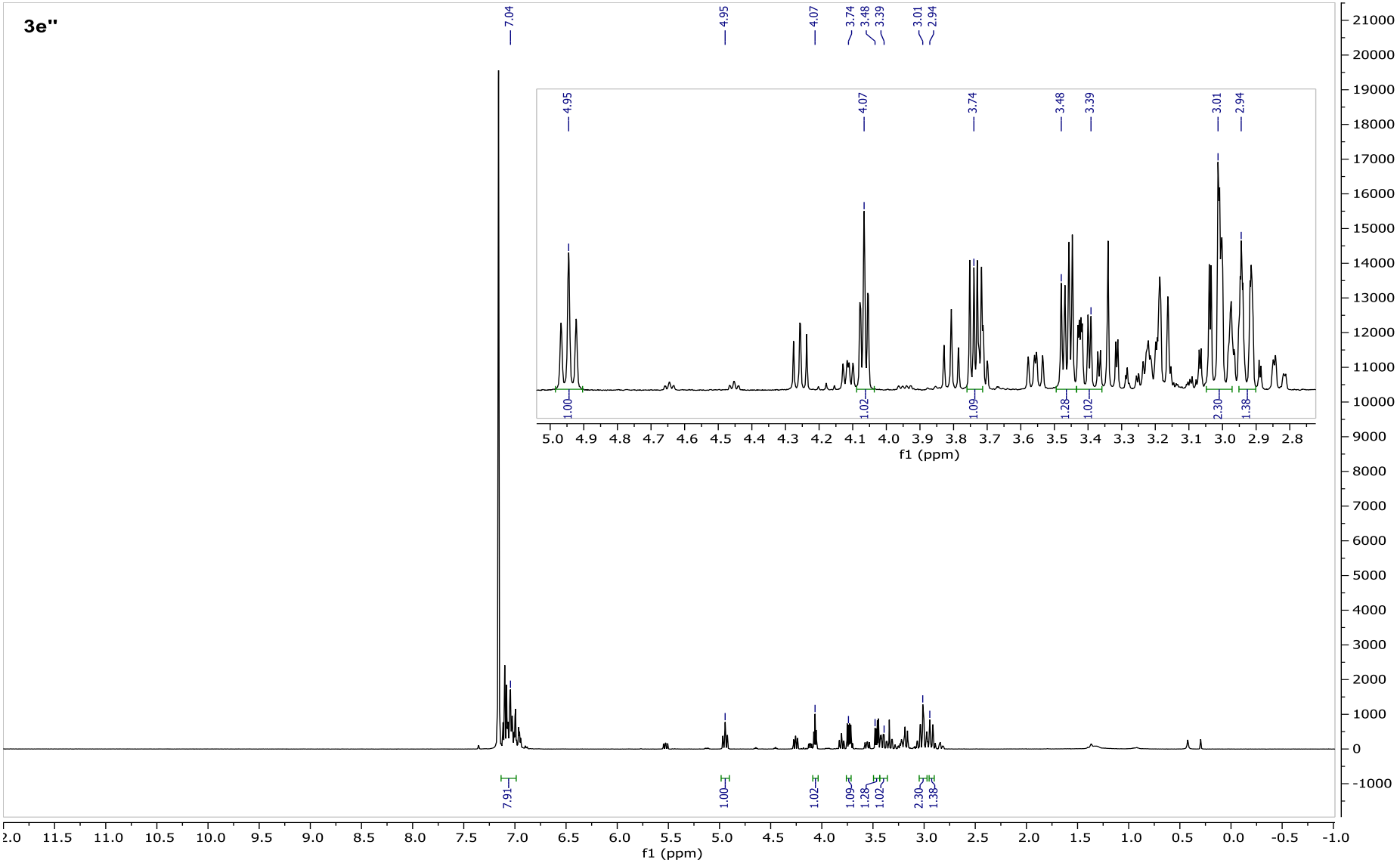
3e': ^{1}H NMR (400 MHz, C_6D_6):



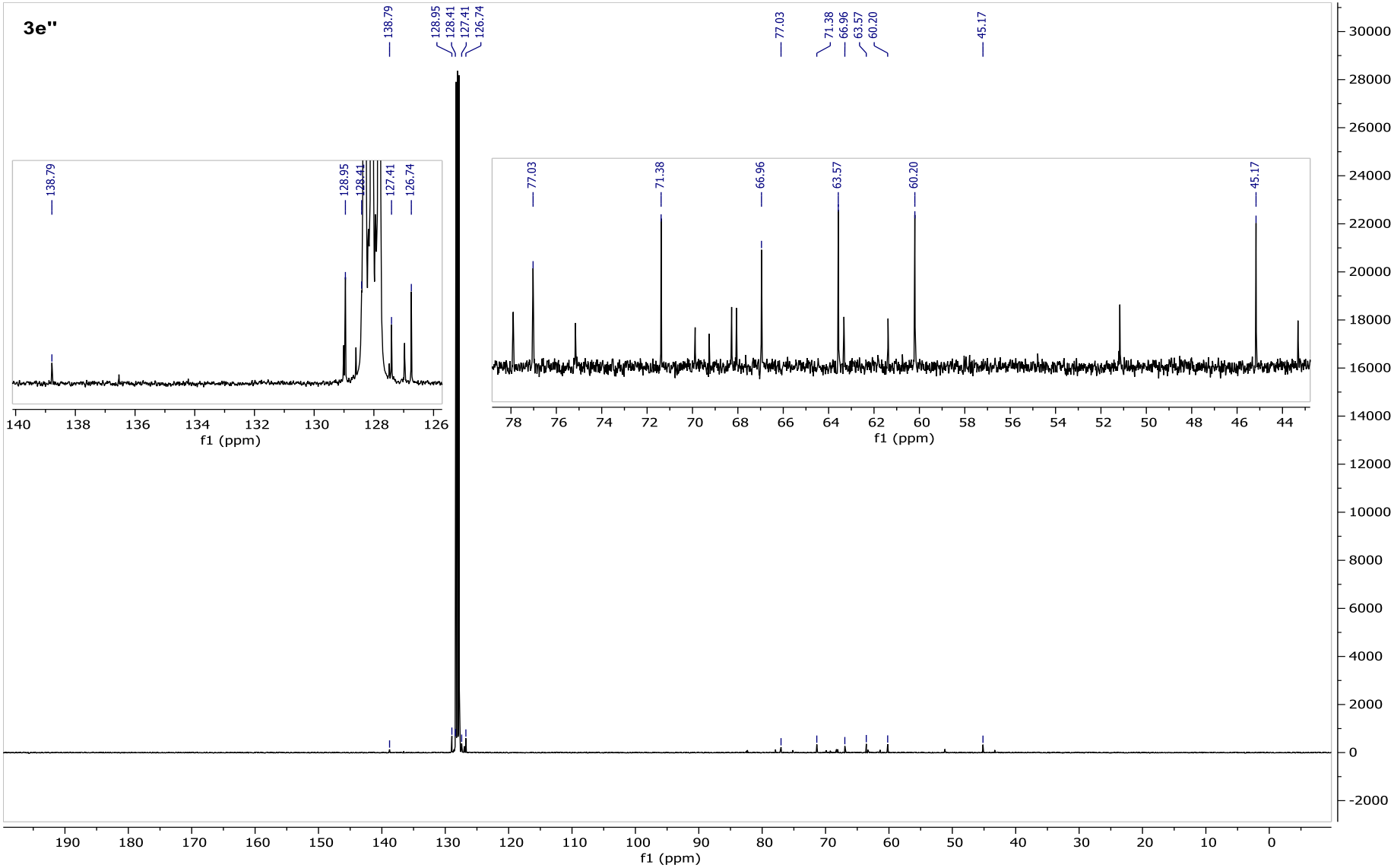
^{13}C NMR (101 MHz, C_6D_6):



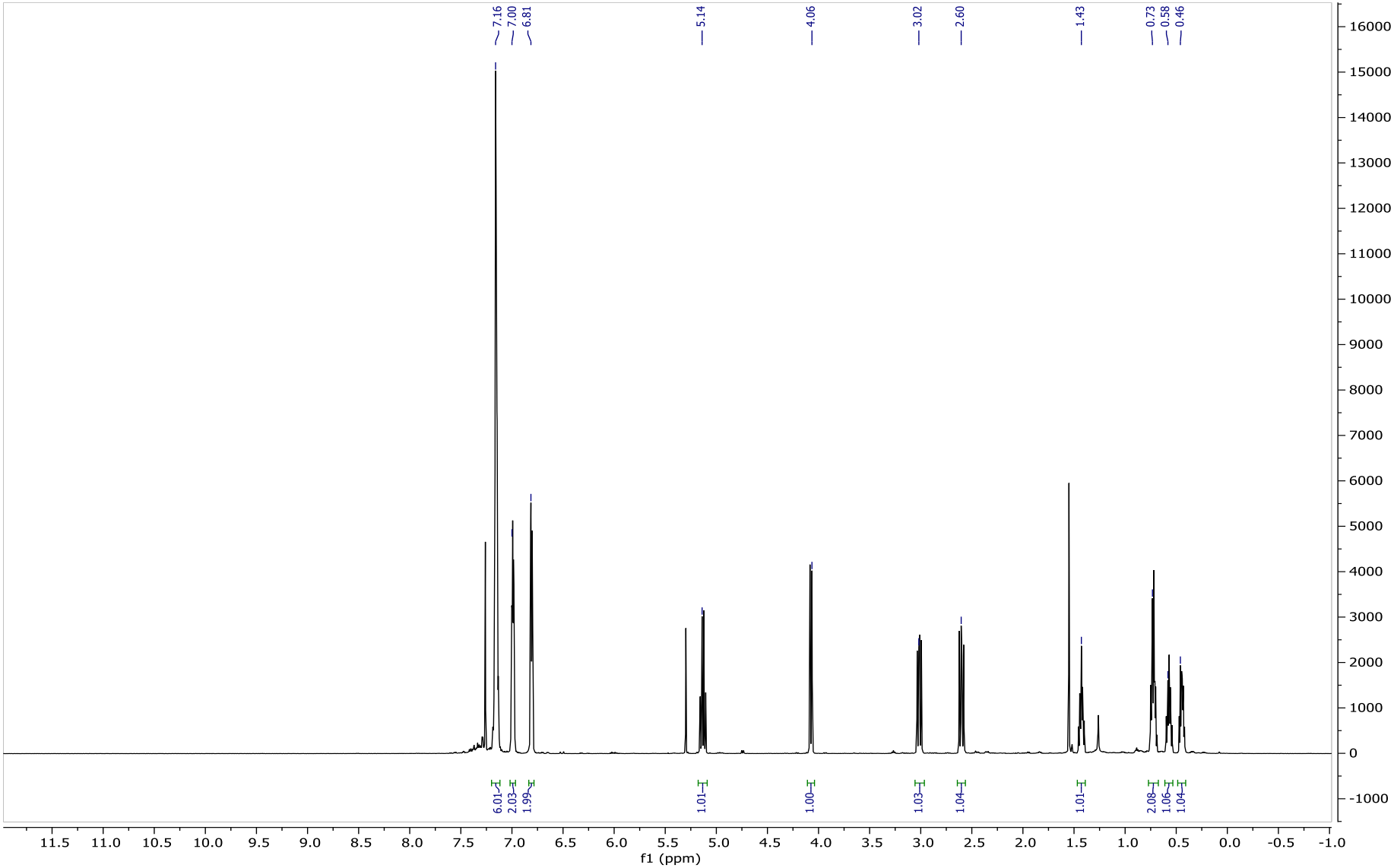
3e'': ^{1}H NMR (400 MHz, C_6D_6):



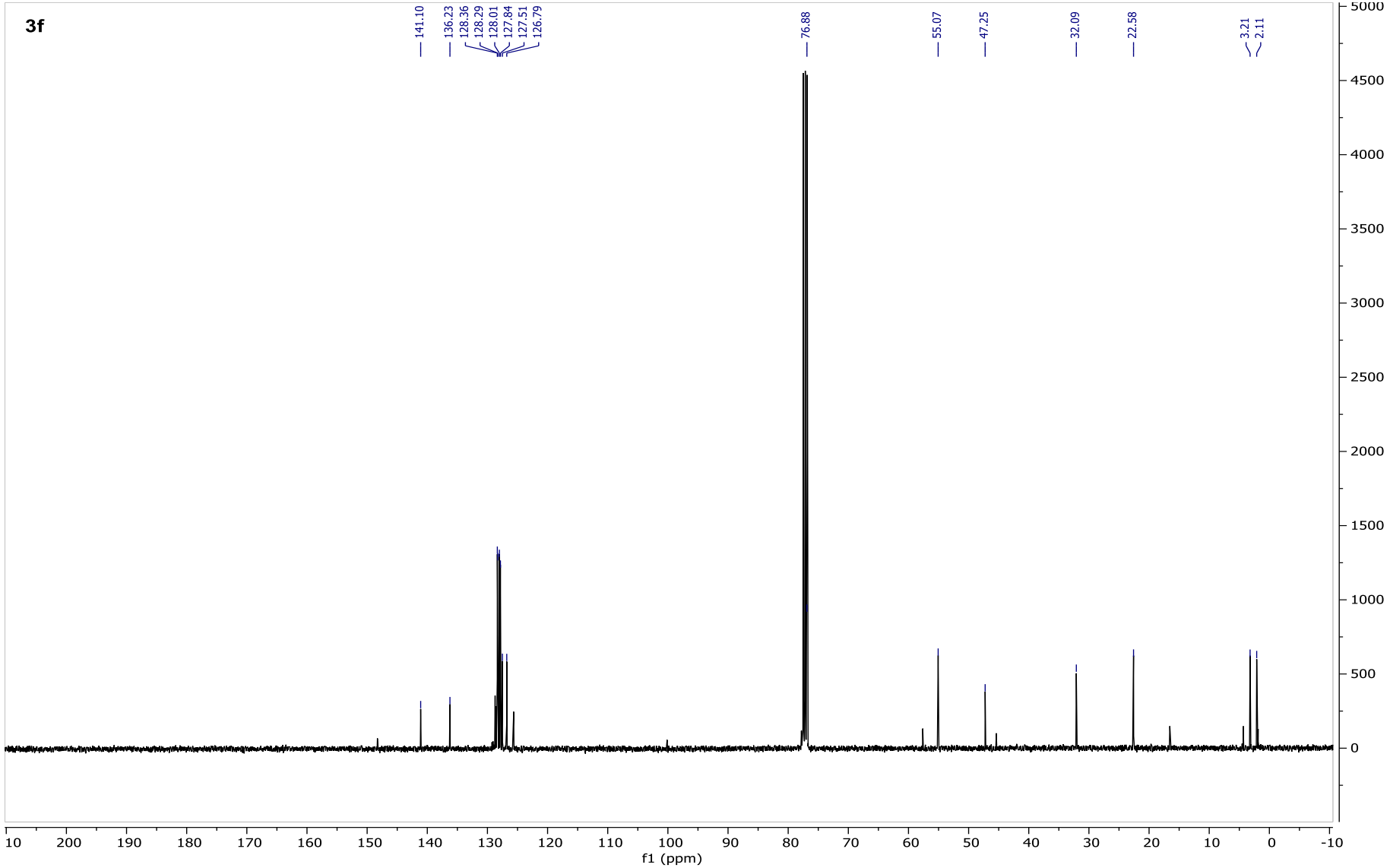
^{13}C NMR (101 MHz, C_6D_6):



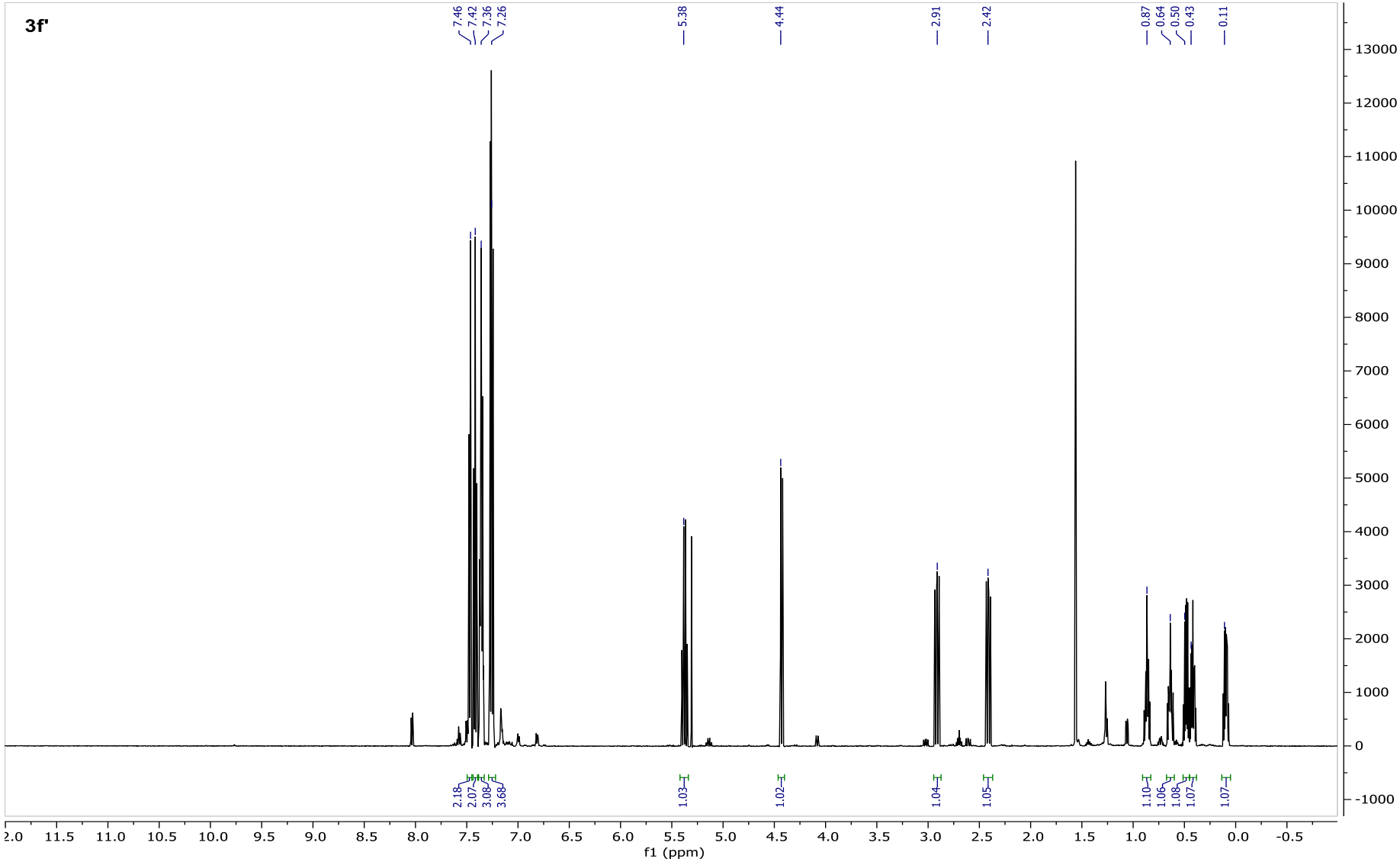
(1'-Cyclopropyl-3'-nitrocyclobutane-1',2'-diyl)dibenzene (3f): ^{1}H NMR (500 MHz, $CDCl_3$):



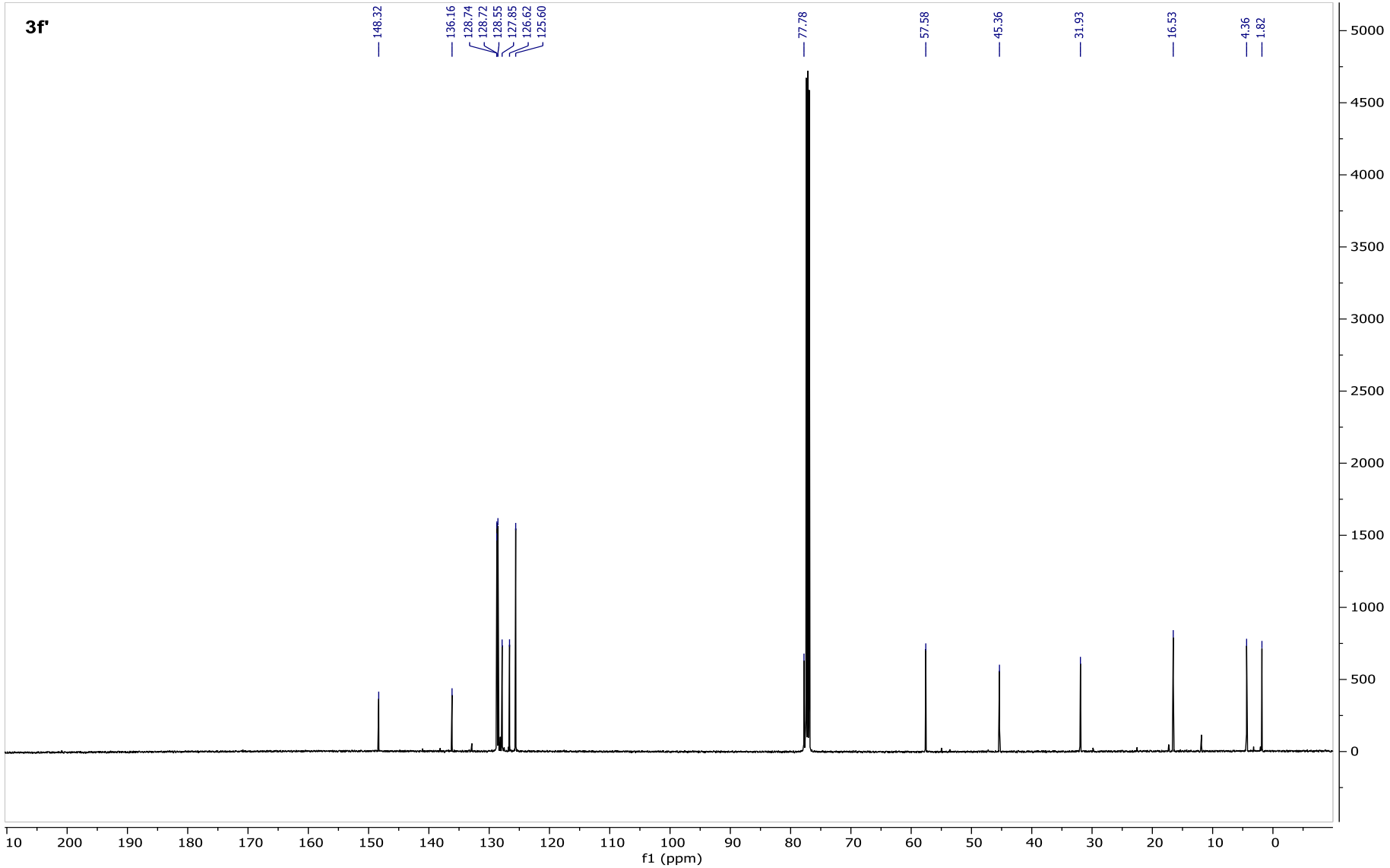
^{13}C NMR (101 MHz, $CDCl_3$):



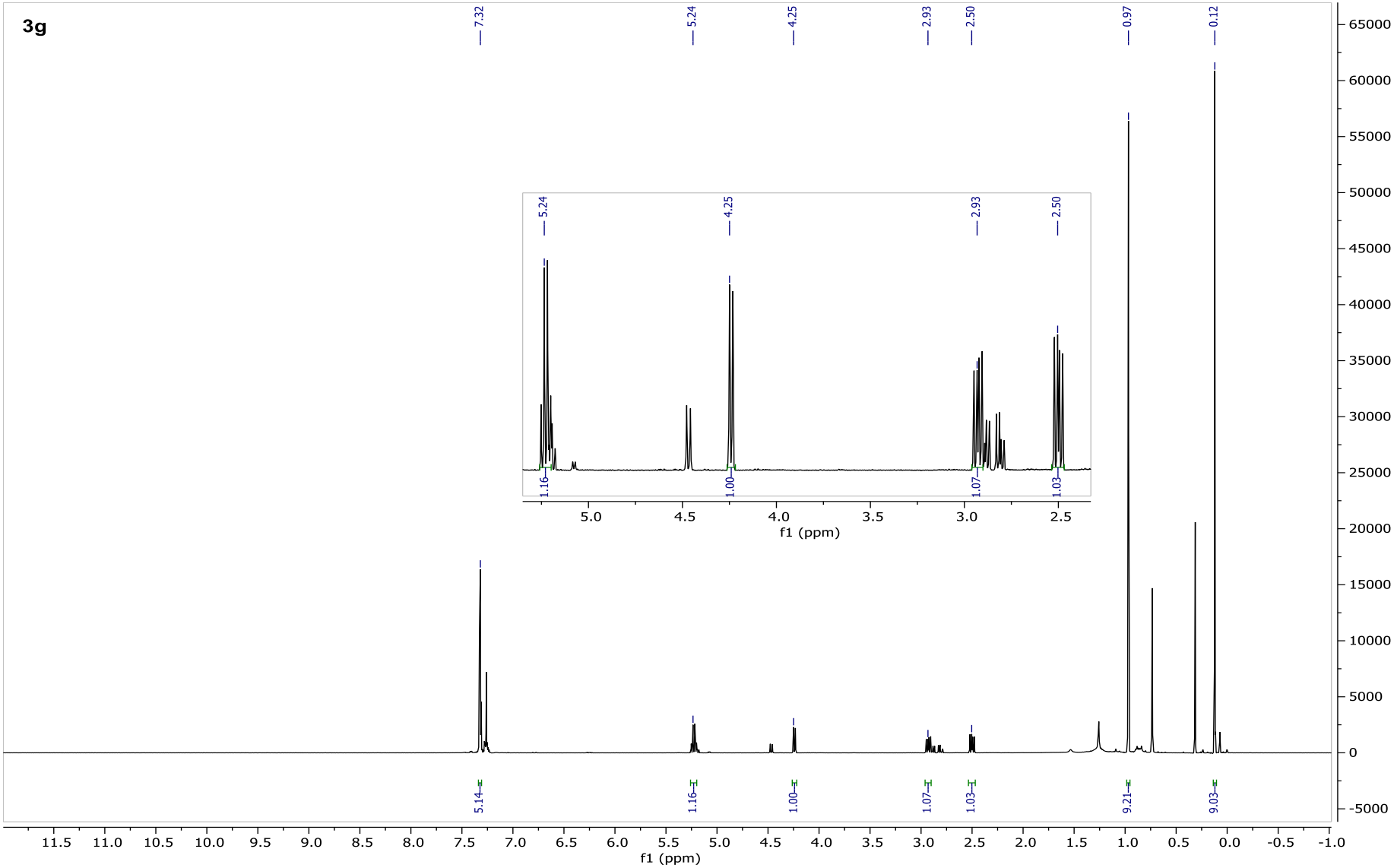
3f': ^{1}H NMR (500 MHz, $CDCl_3$):



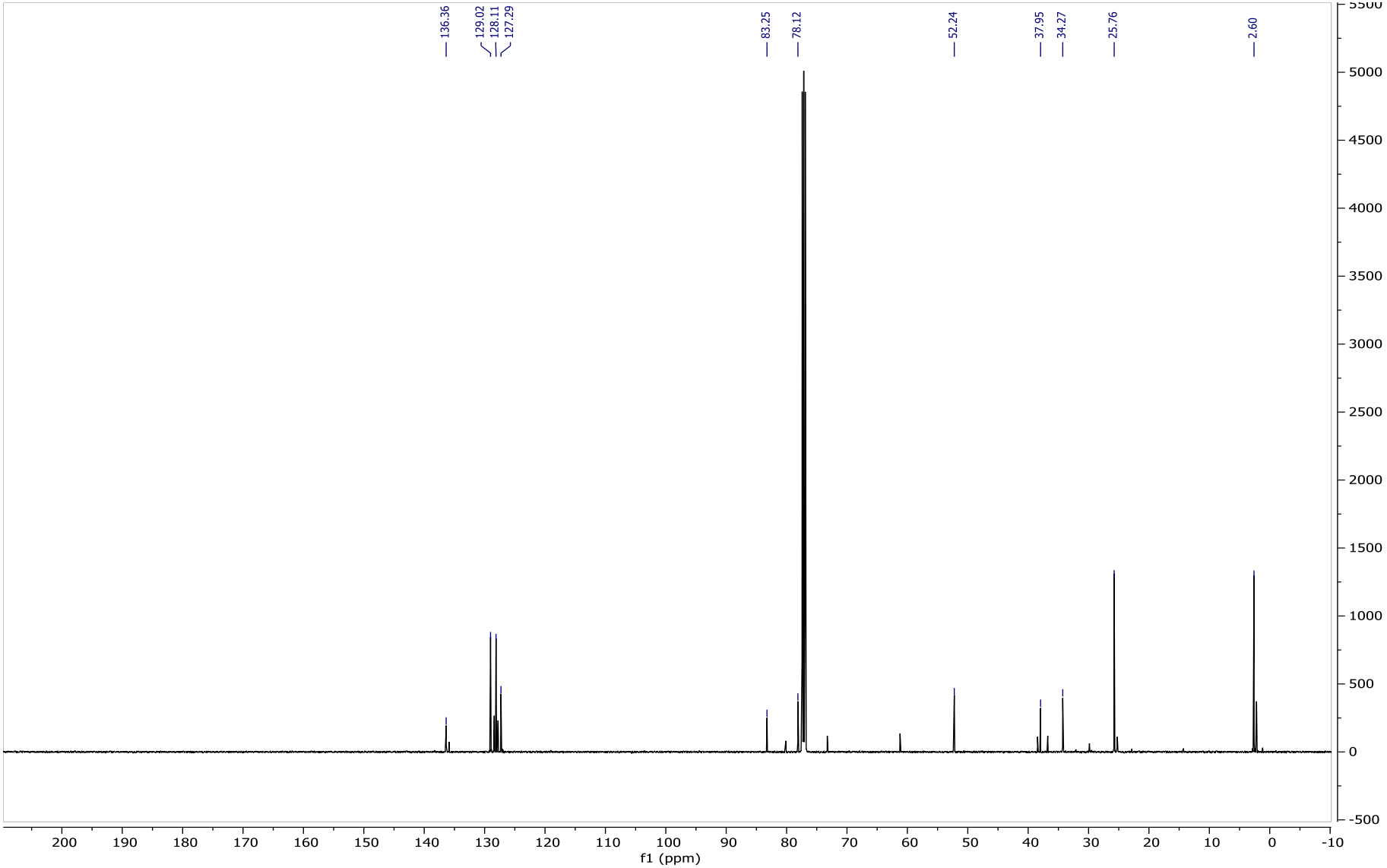
^{13}C NMR (126 MHz, $CDCl_3$):



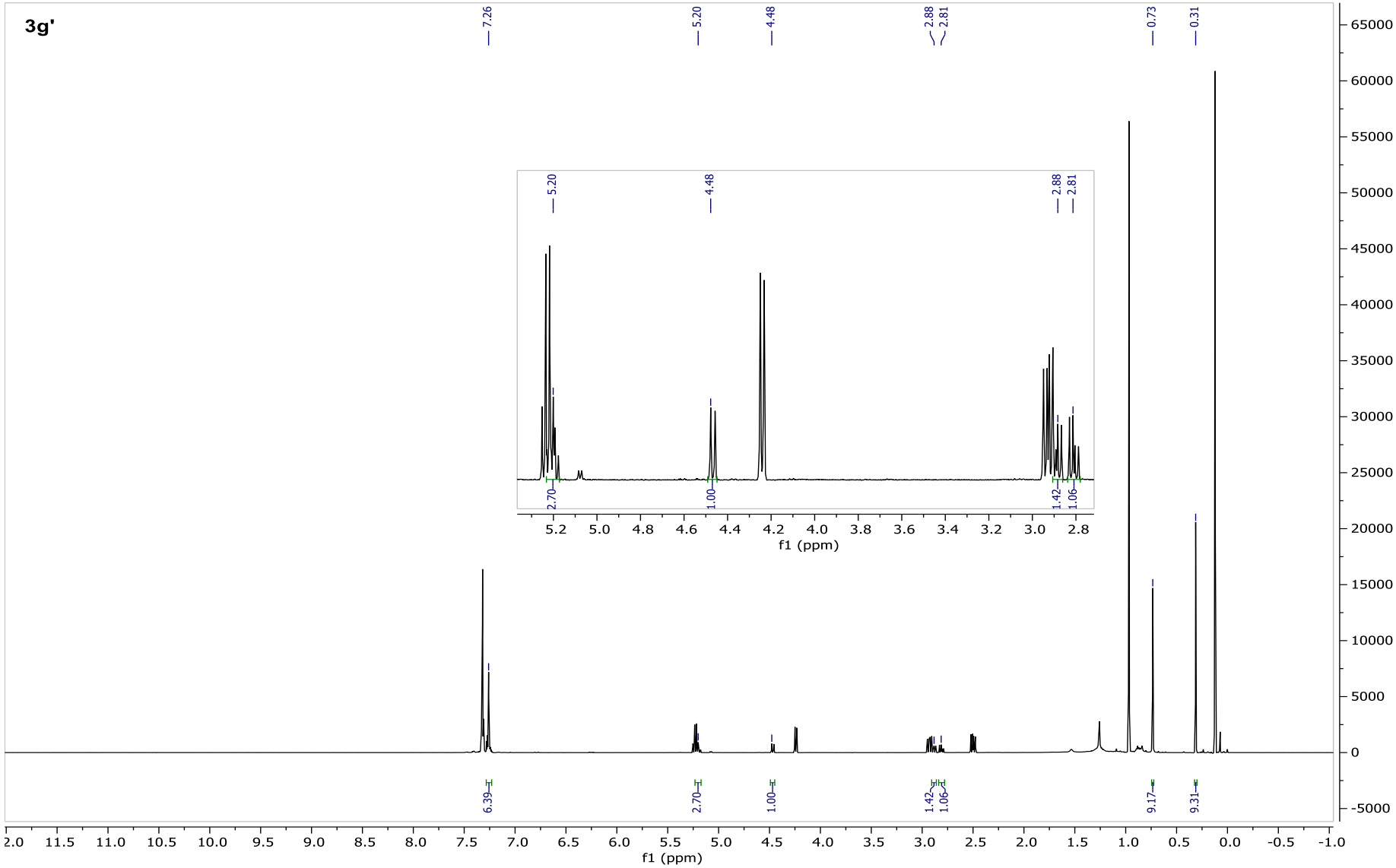
[1-(*tert*-Butyl)-3-nitro-2-phenylcyclobutoxy]trimethylsilane (3g): ^{1}H NMR (500 MHz, $CDCl_3$):



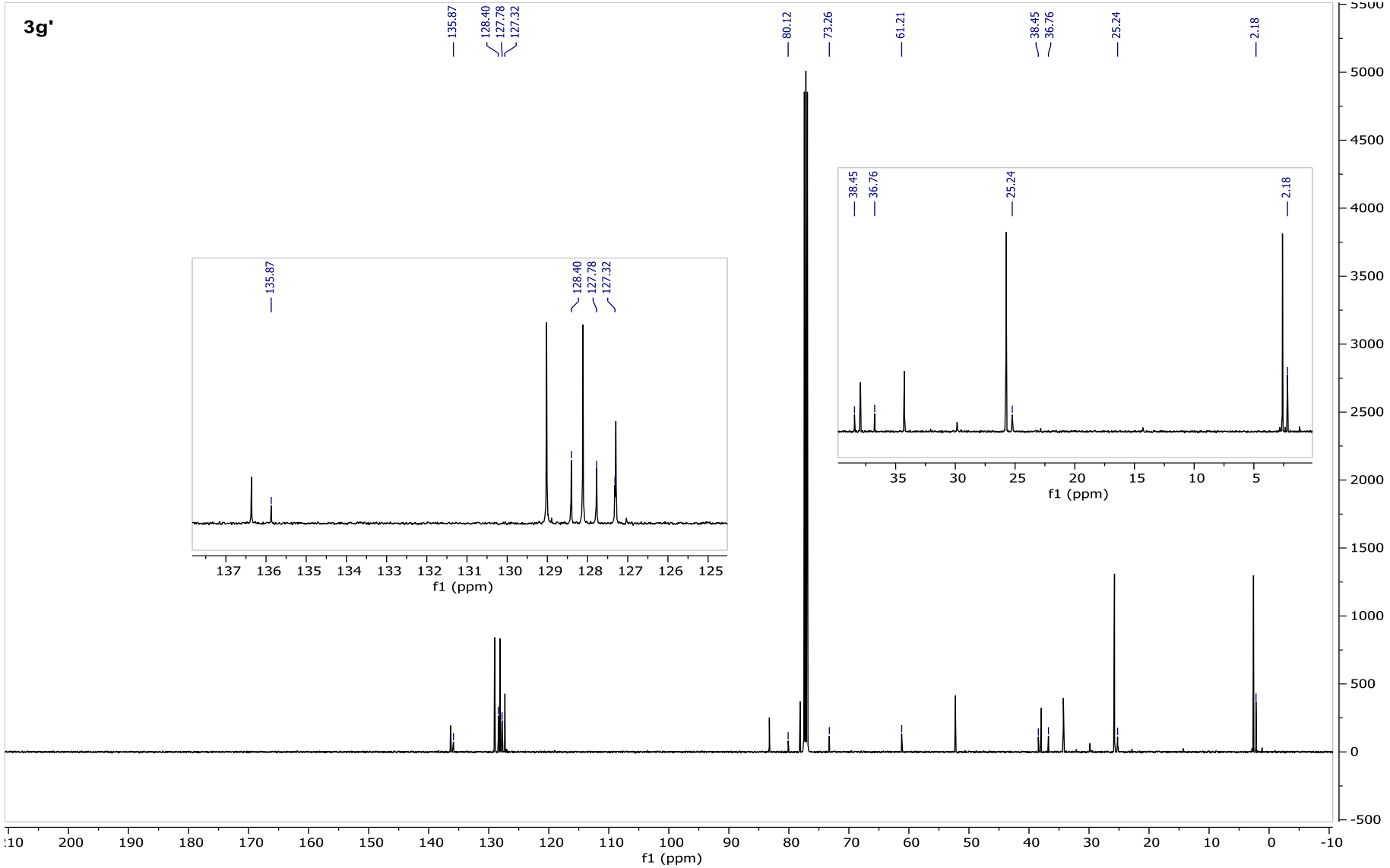
^{13}C NMR (126 MHz, $CDCl_3$):



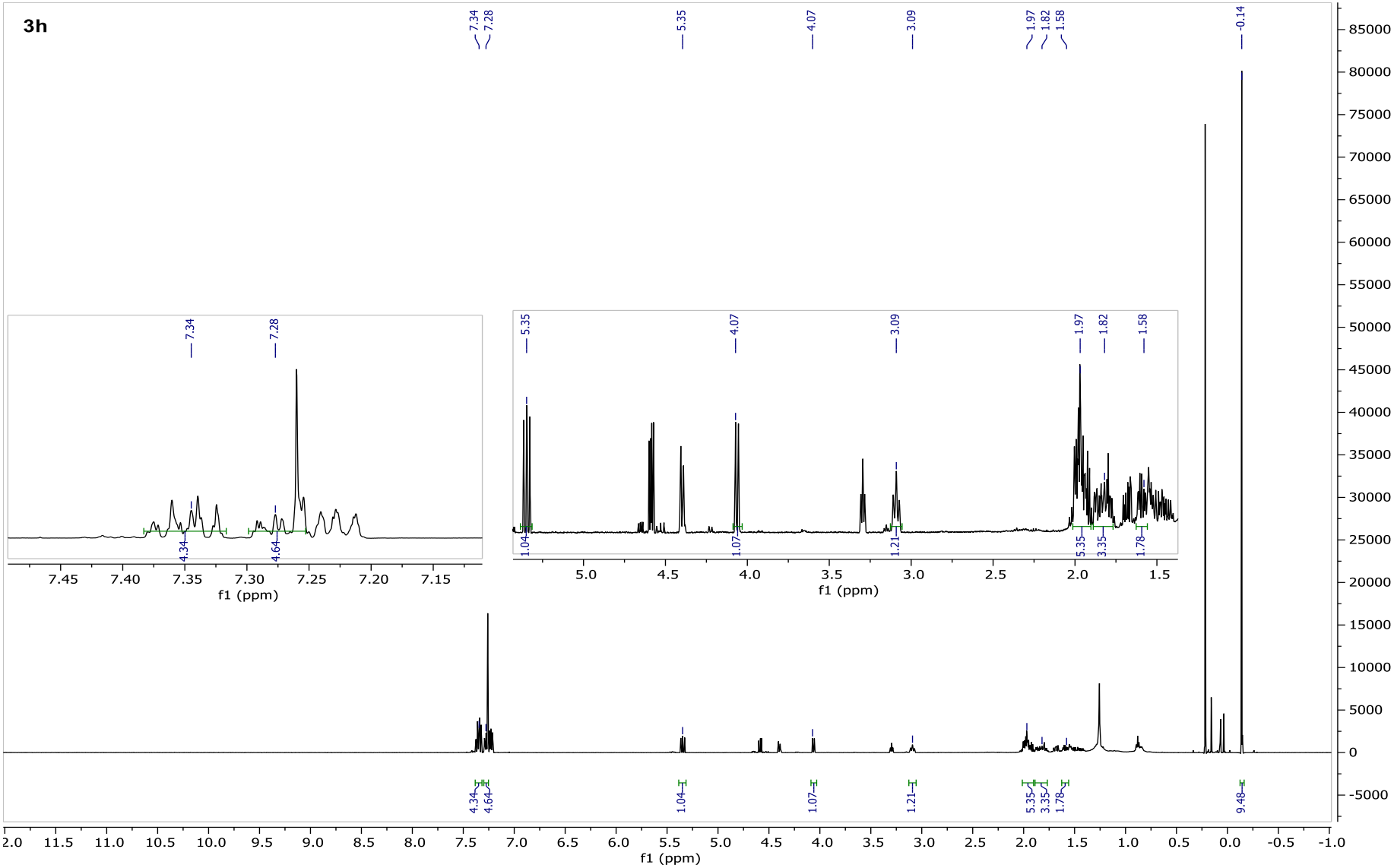
3g': ^{1}H NMR (500 MHz, $CDCl_3$):



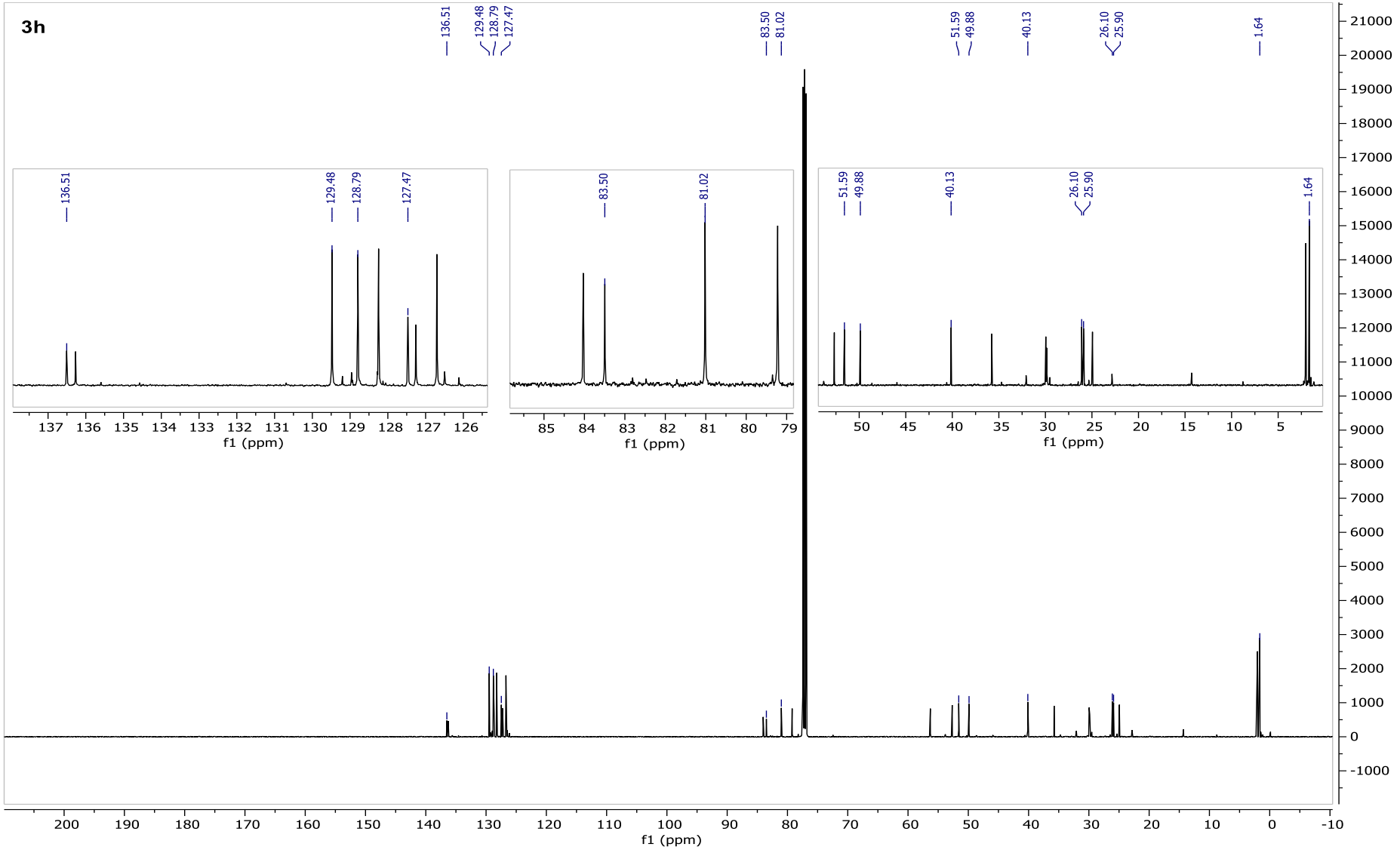
^{13}C NMR (126 MHz, $CDCl_3$):



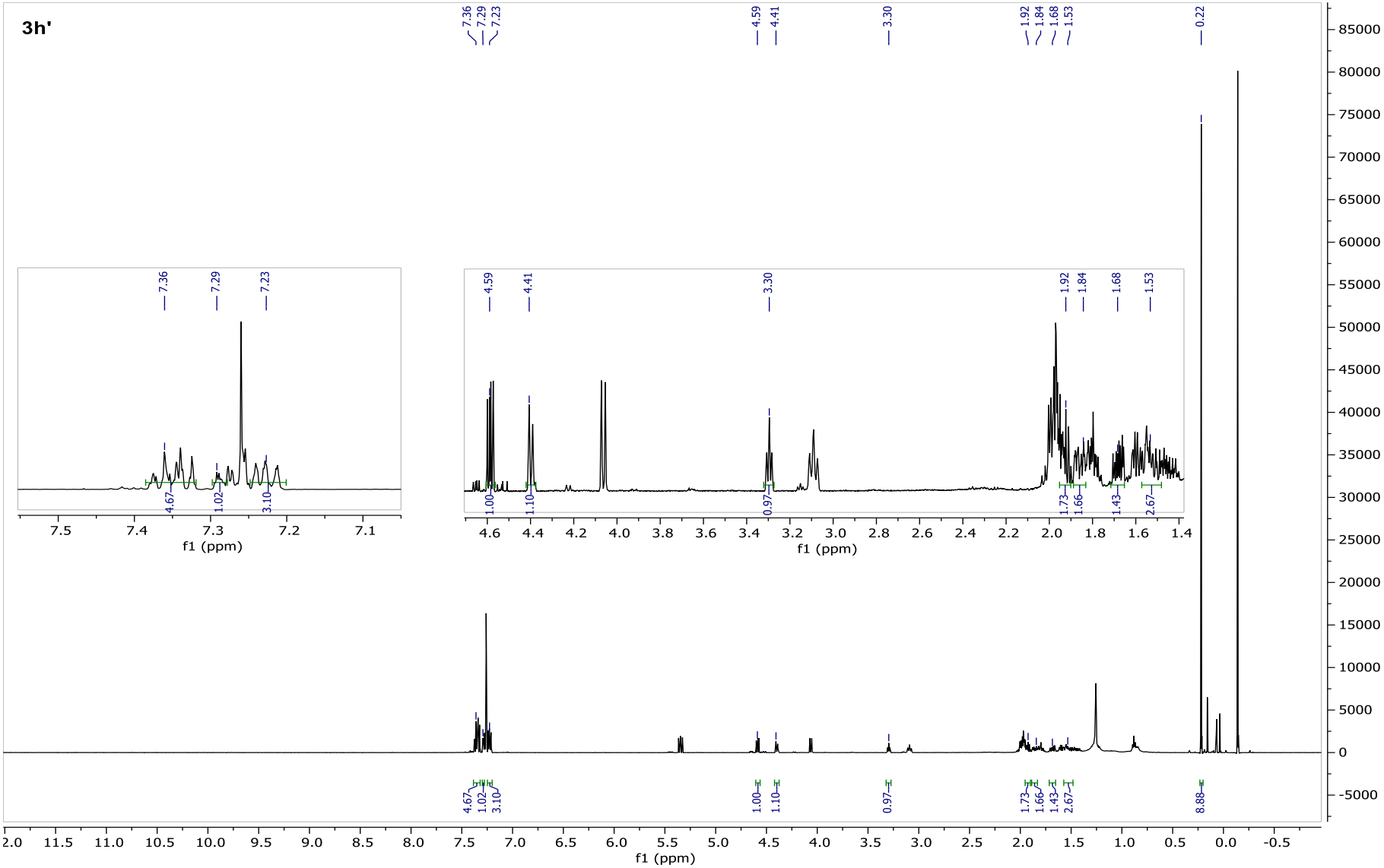
Trimethyl[(6-nitro-7-phenylbicyclo[3.2.0]heptan-1-yl)oxy]silane (3h): ^{1}H NMR (500 MHz, $CDCl_3$):



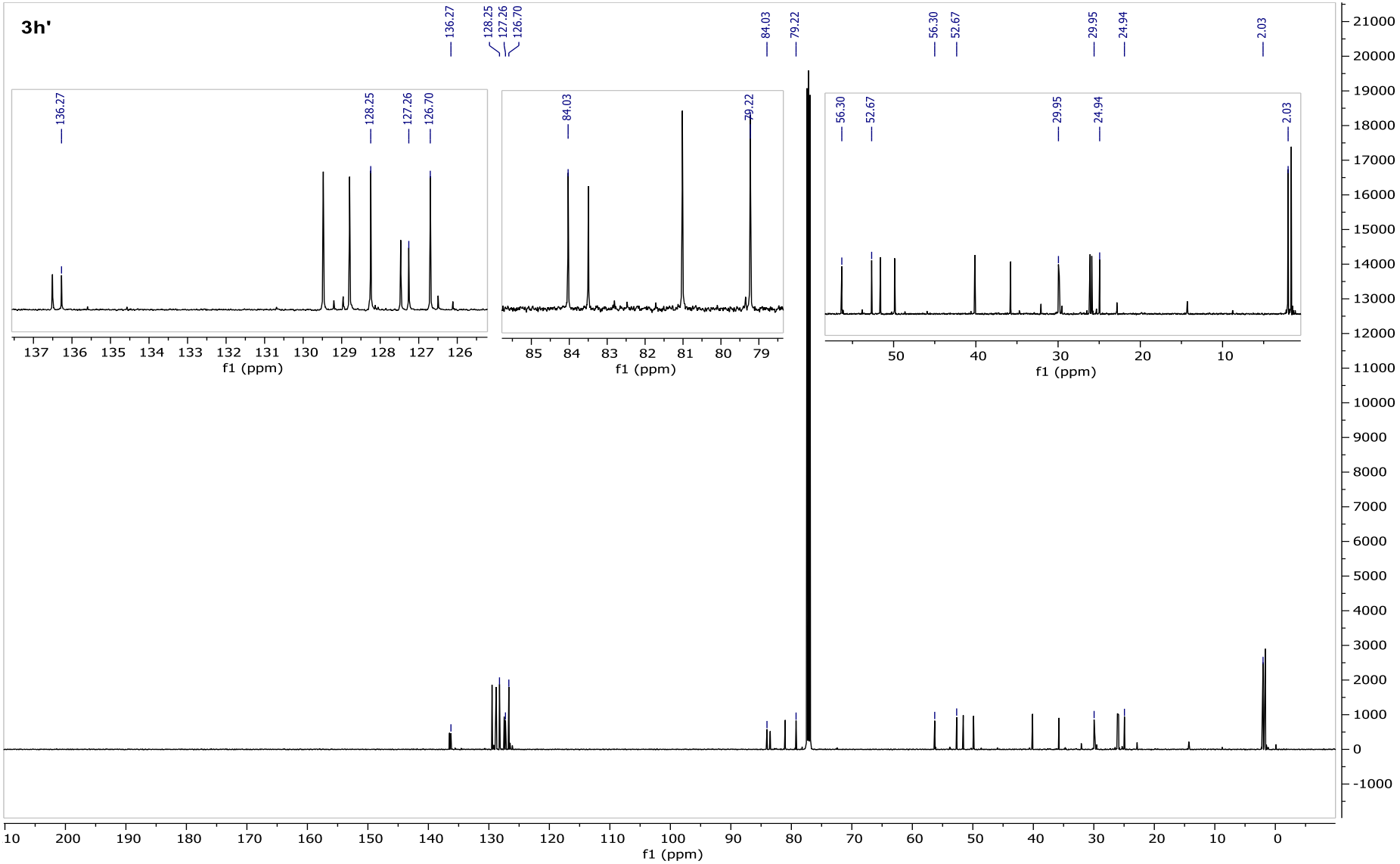
^{13}C NMR (126 MHz, $CDCl_3$):



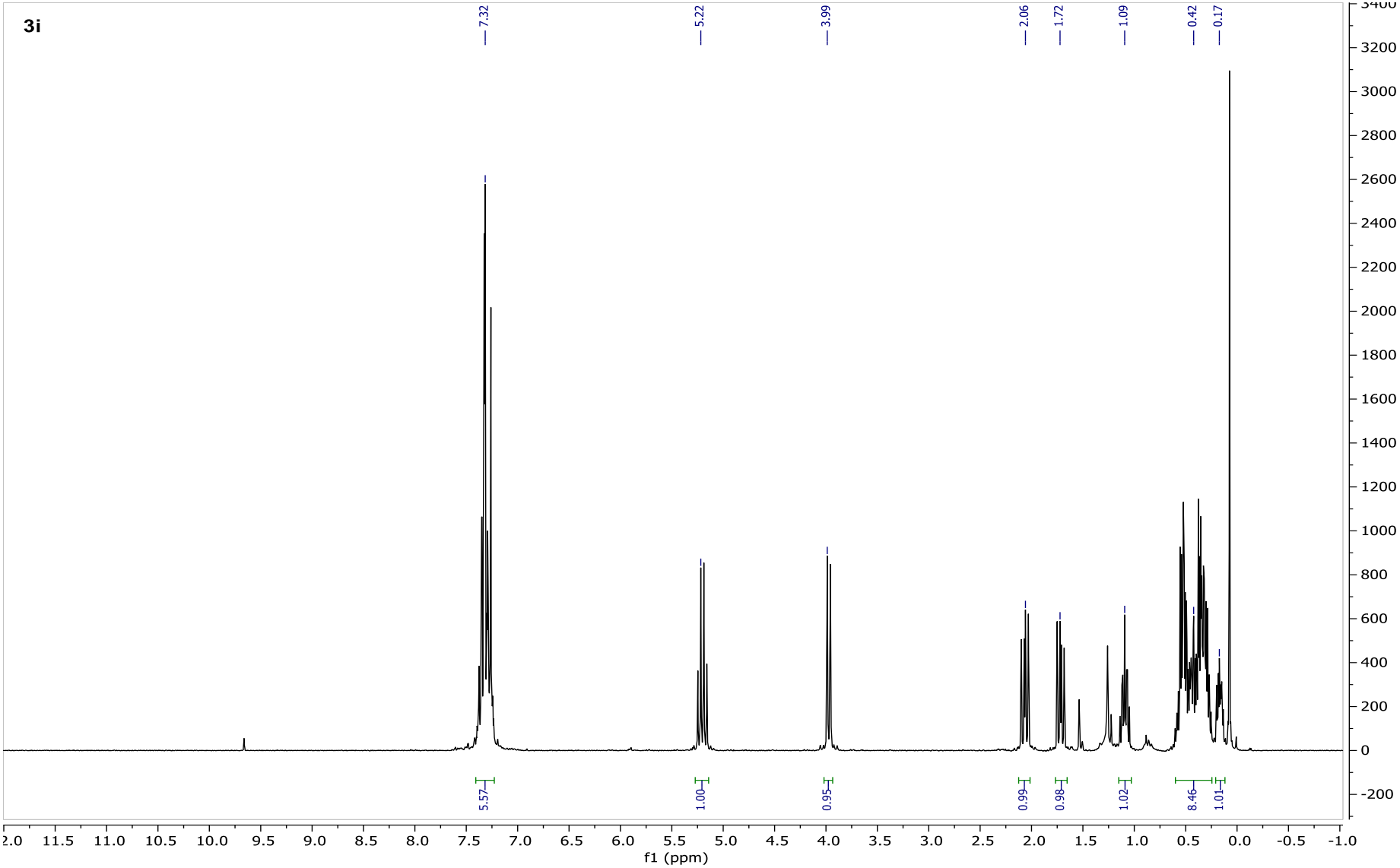
3h': ^{1}H NMR (500 MHz, $CDCl_3$):



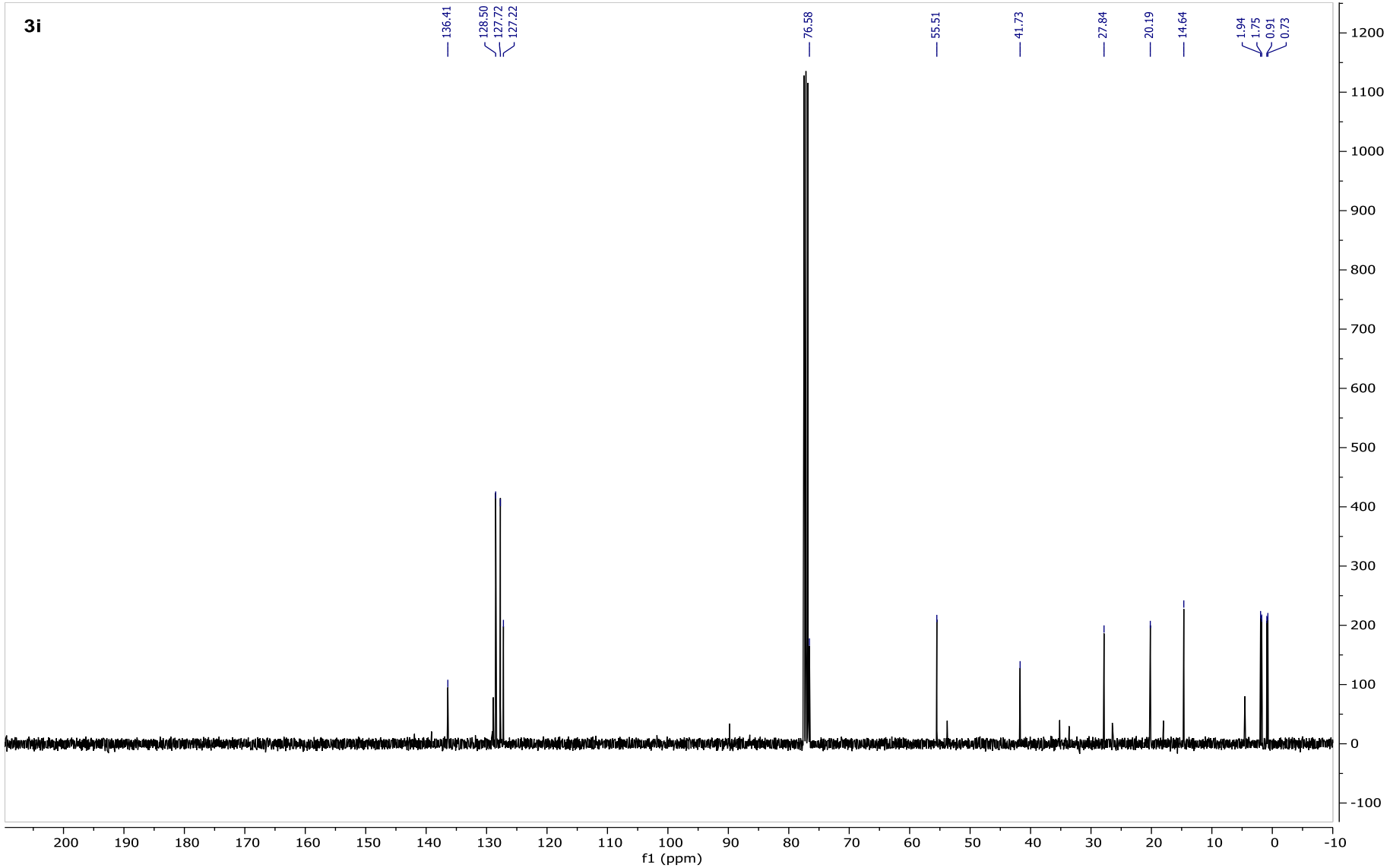
^{13}C NMR (126 MHz, $CDCl_3$):



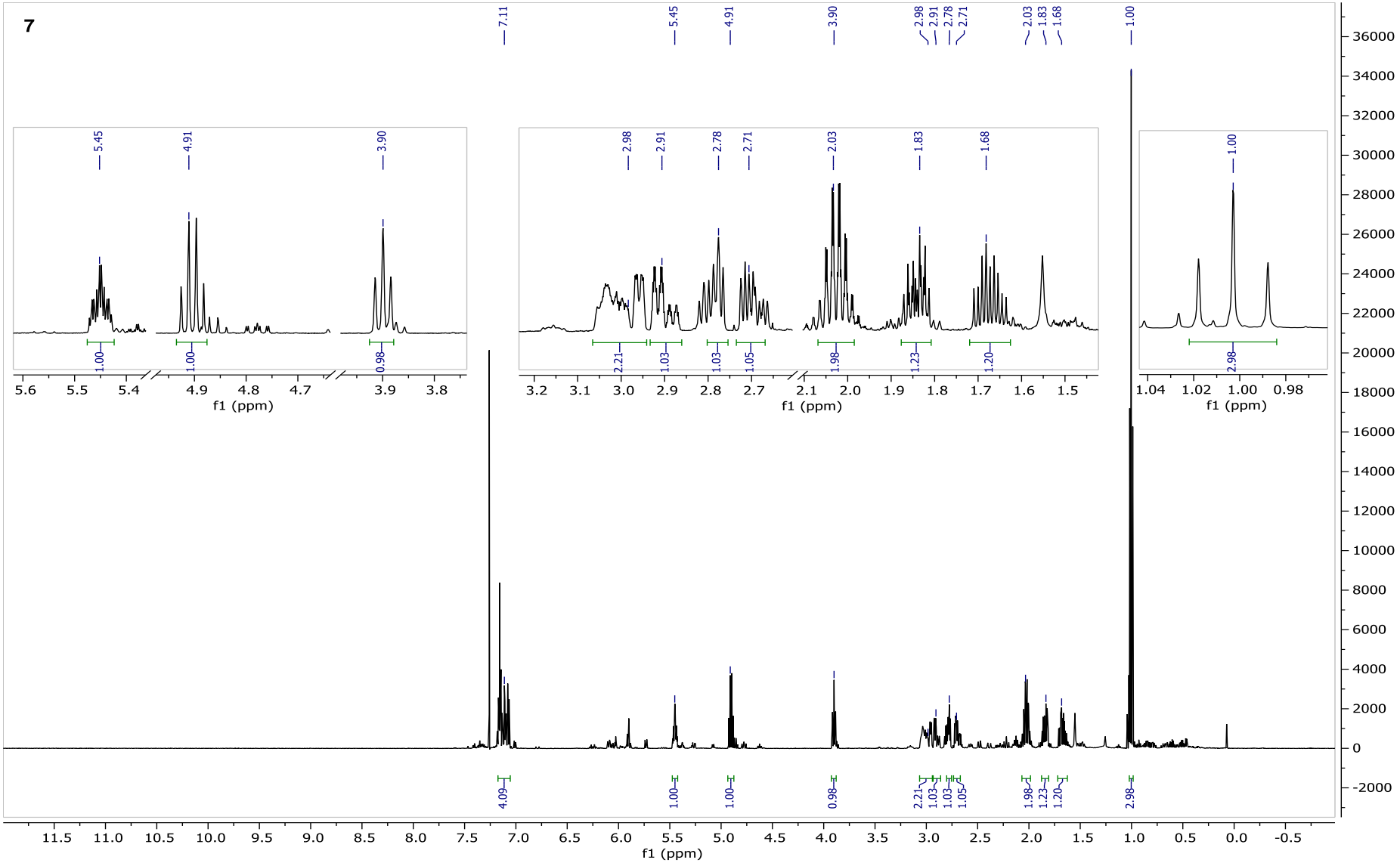
(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)benzene (3i): ^{1}H NMR (400 MHz, $CDCl_3$):



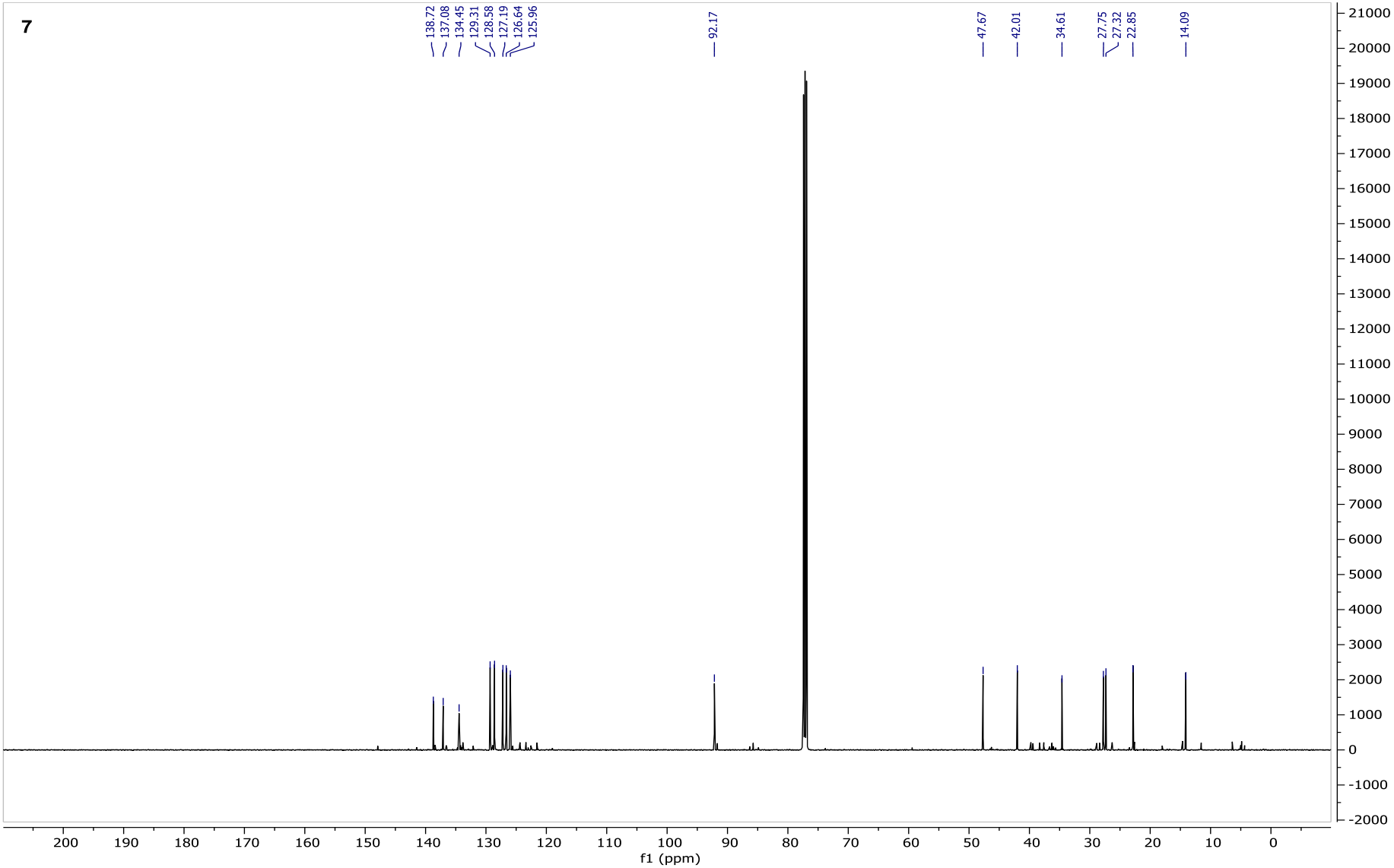
^{13}C NMR (101 MHz, $CDCl_3$):



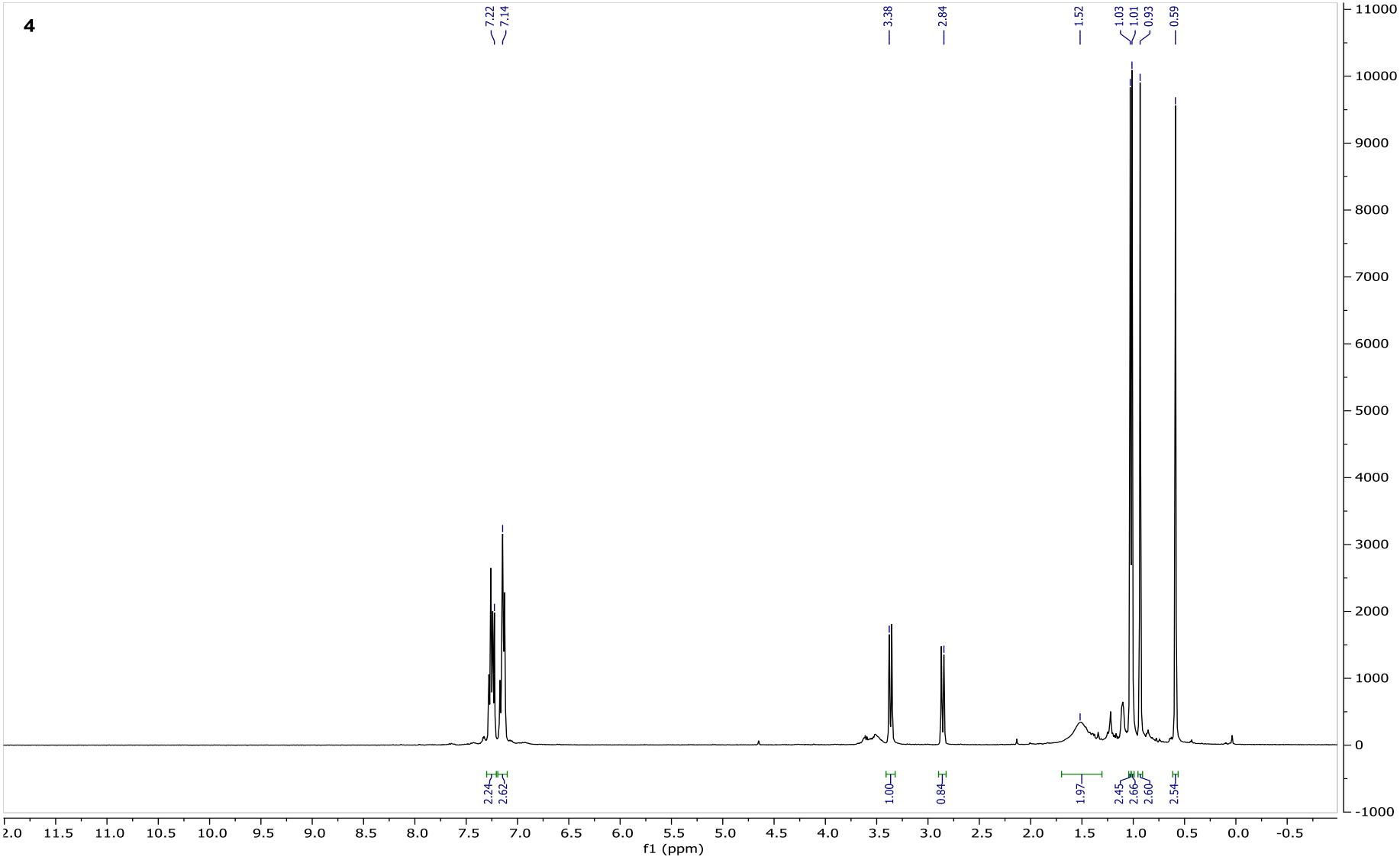
1-Nitro-3-propylidene-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[a]naphthalene (7): ^{1}H NMR (500 MHz, $CDCl_3$):



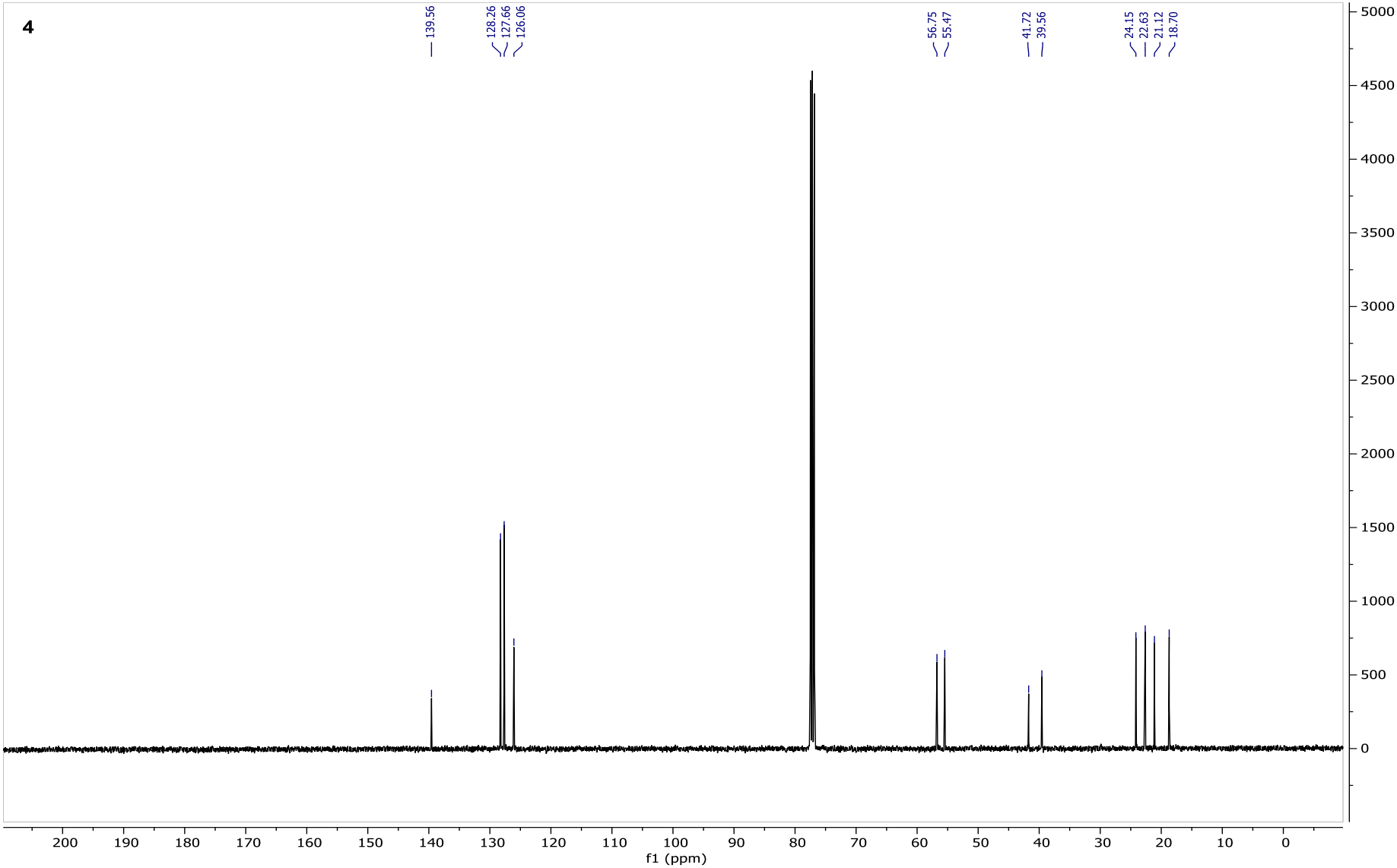
^{13}C NMR (126 MHz, $CDCl_3$):



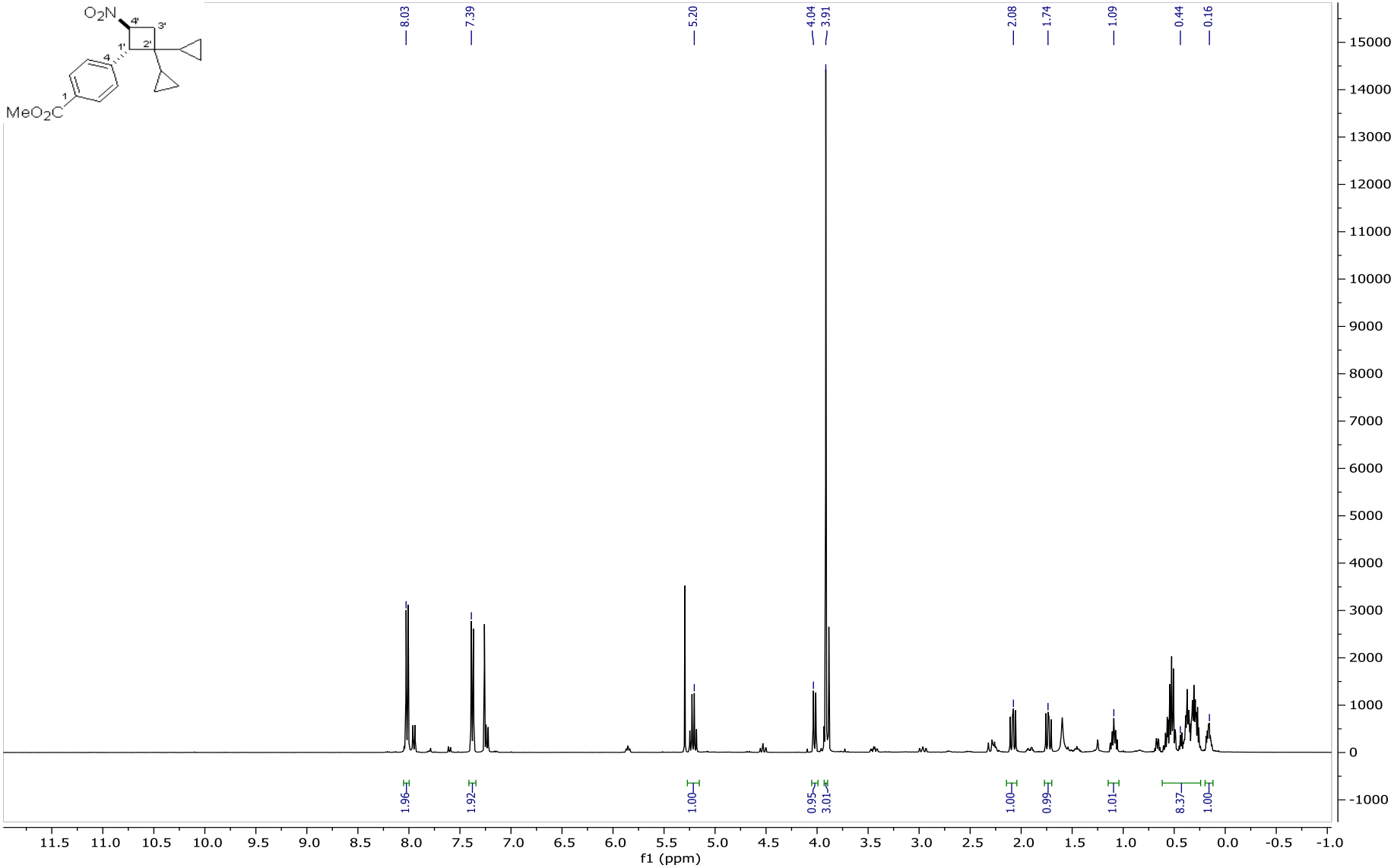
2,2,3,3-Tetramethyl-4-phenylcyclobutan-1-amine (4): ^{1}H NMR (400 MHz, $CDCl_3$):



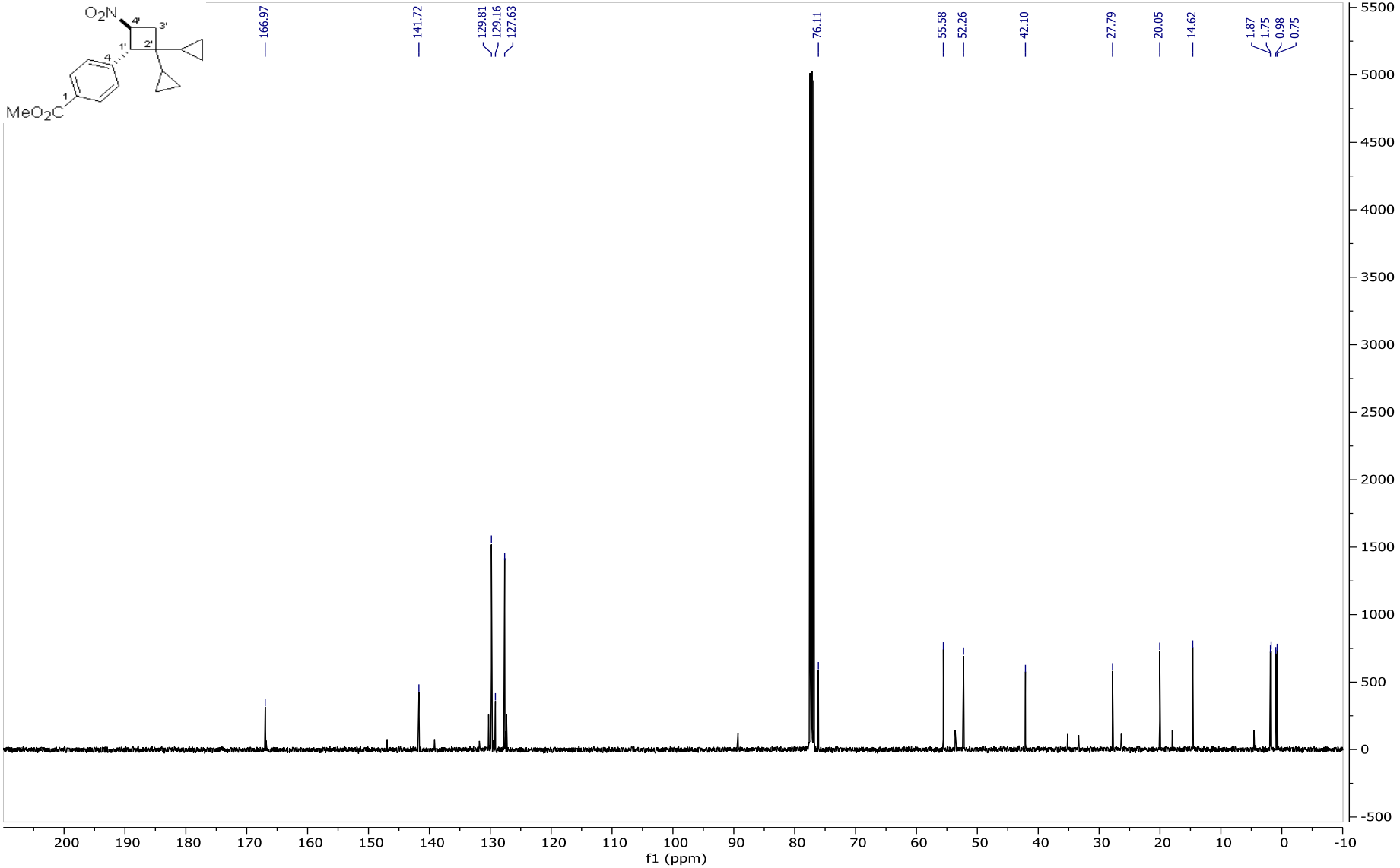
^{13}C NMR (101 MHz, $CDCl_3$):



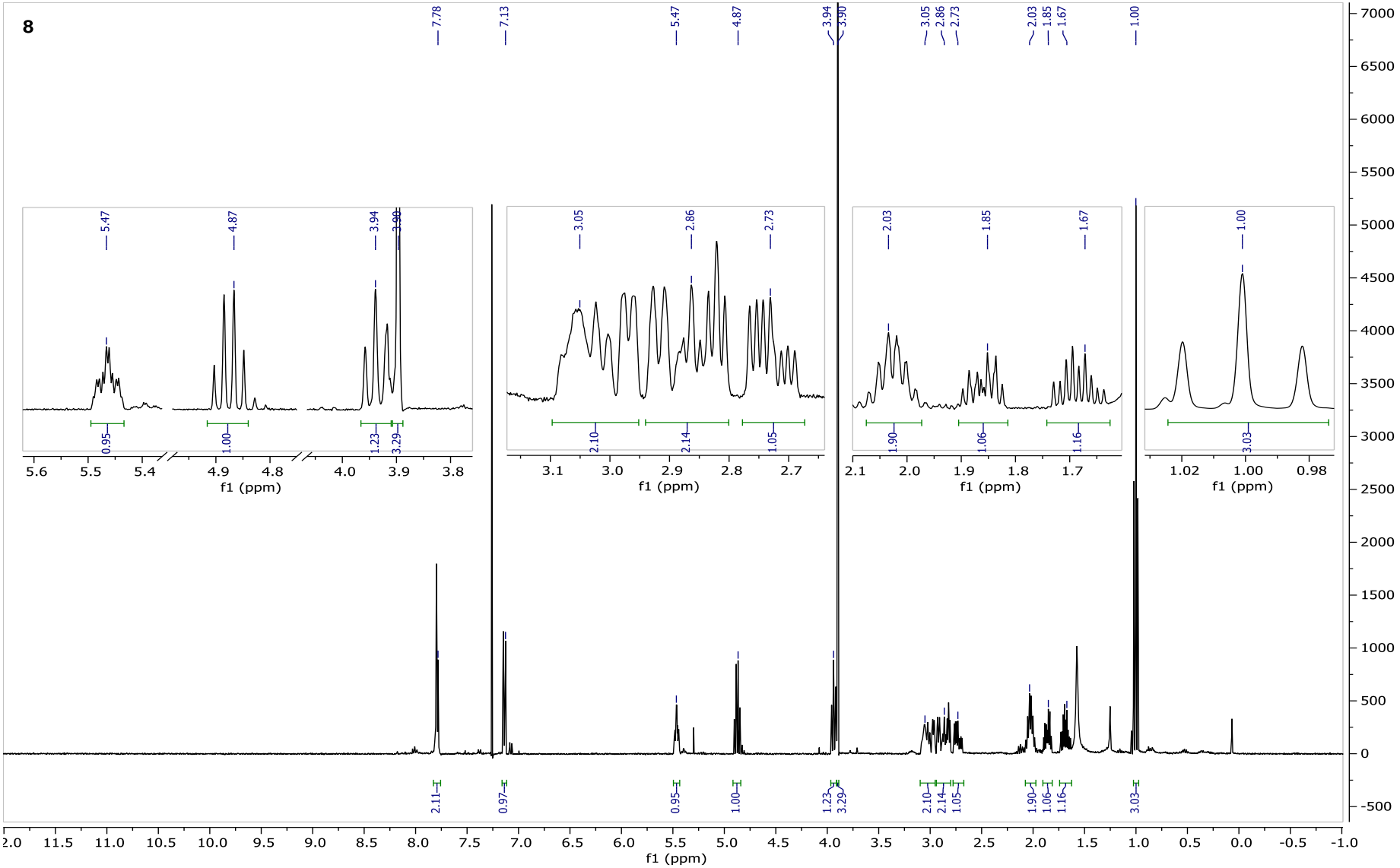
(2',2'-dicyclopropyl-4'-nitrocyclobutyl)benzene: ^{1}H NMR (400 MHz, $CDCl_3$):



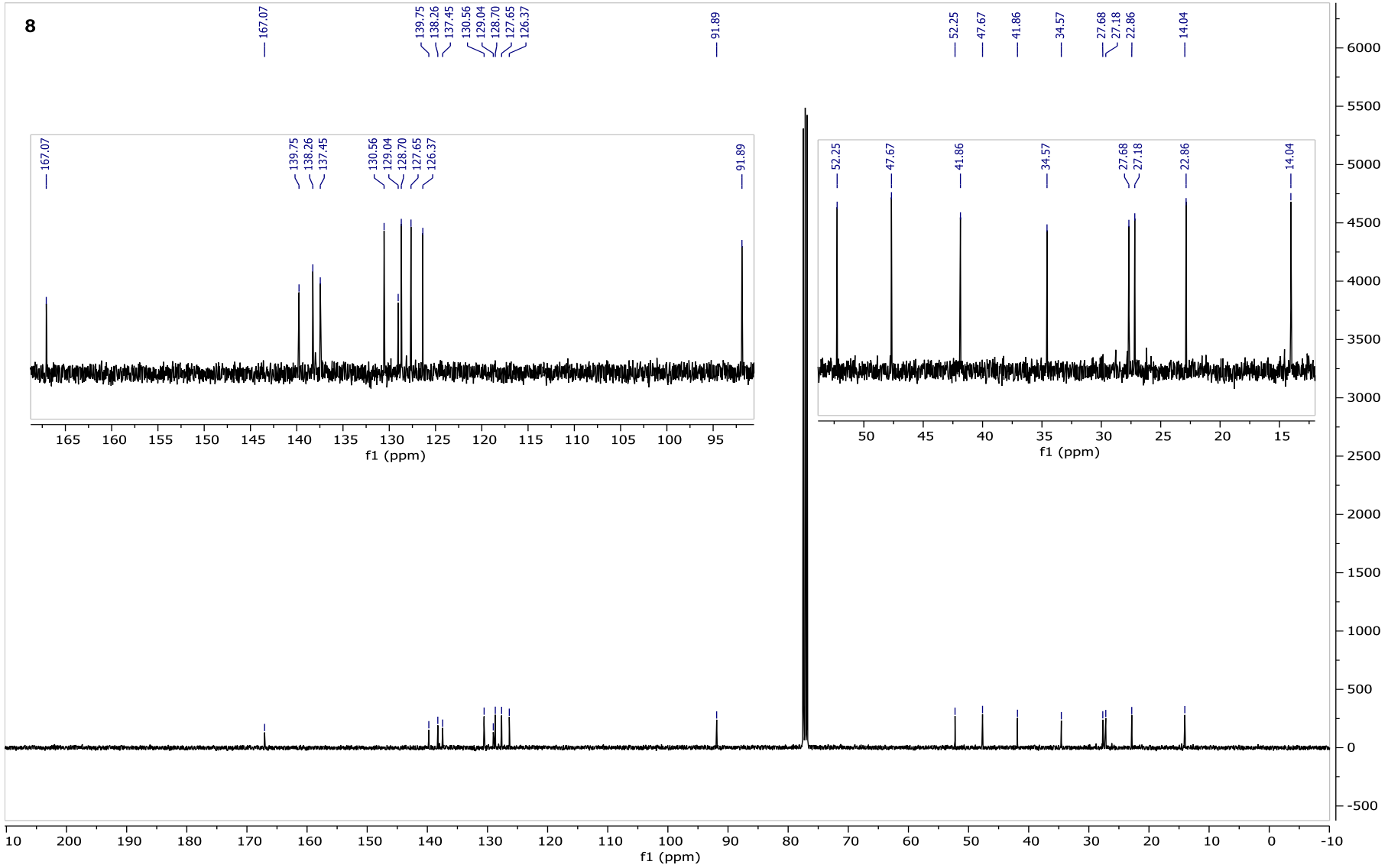
^{13}C NMR (101 MHz, $CDCl_3$):



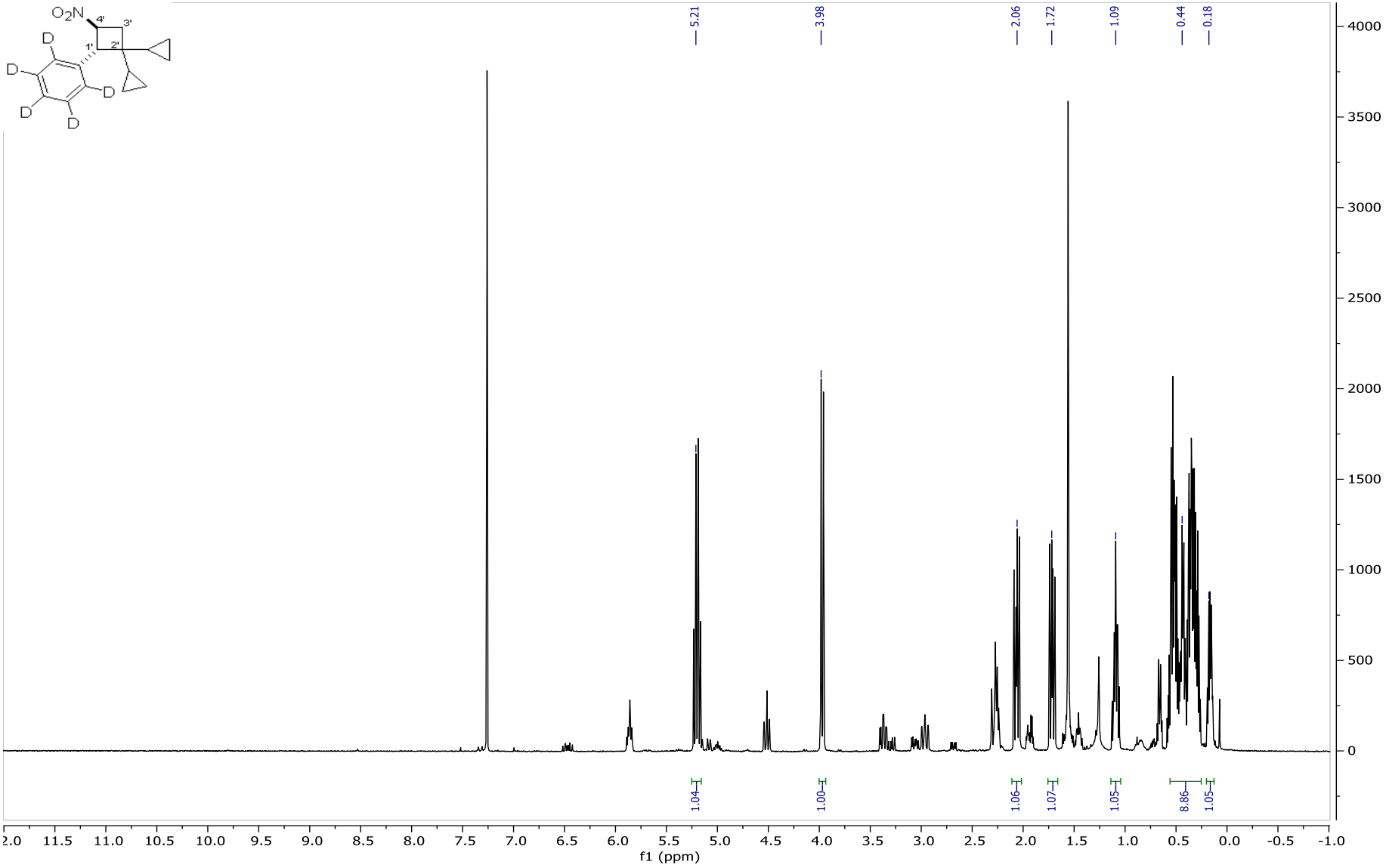
Methyl (E)-1-nitro-3-propylidene-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[a]naphthalene-7-carboxylate (8): ^{1}H NMR (500 MHz, $CDCl_3$):



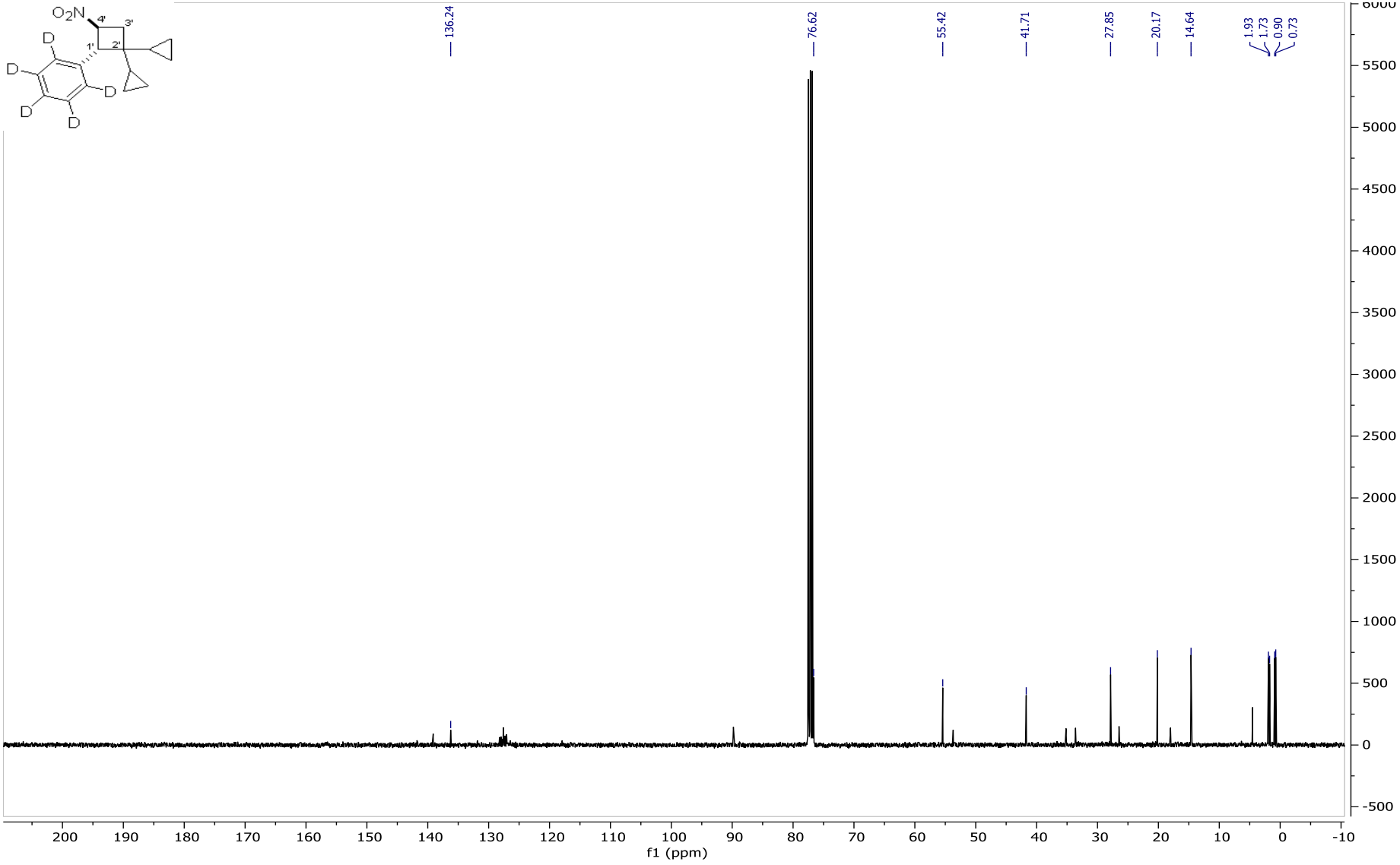
^{13}C NMR (126 MHz, $CDCl_3$):



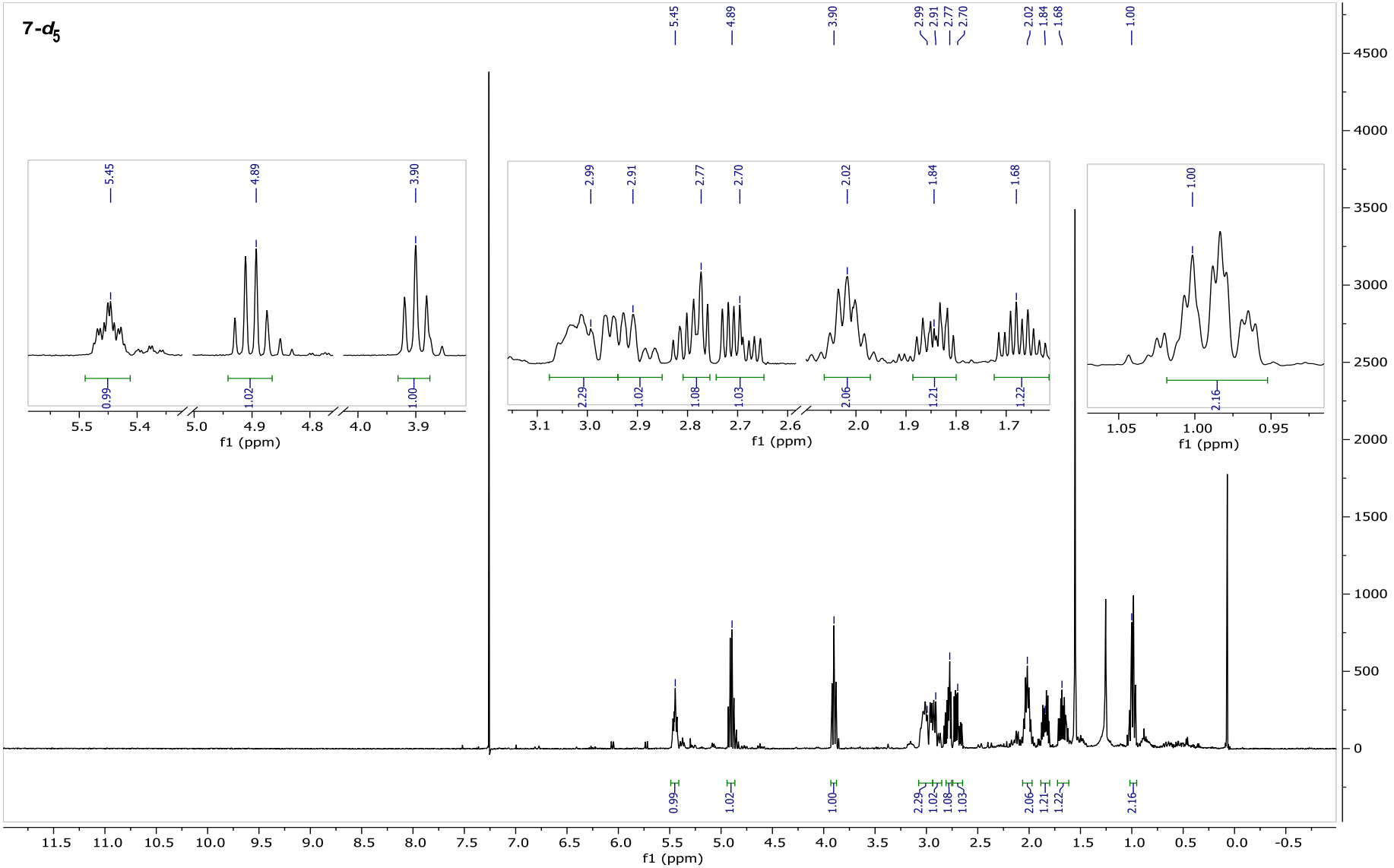
1-(2',2'-Dicyclopropyl-4'-nitrocyclobutyl)-benzene-2,3,4,5,6-*d*$_5$: ^{1}H NMR (400 MHz, $CDCl_3$):



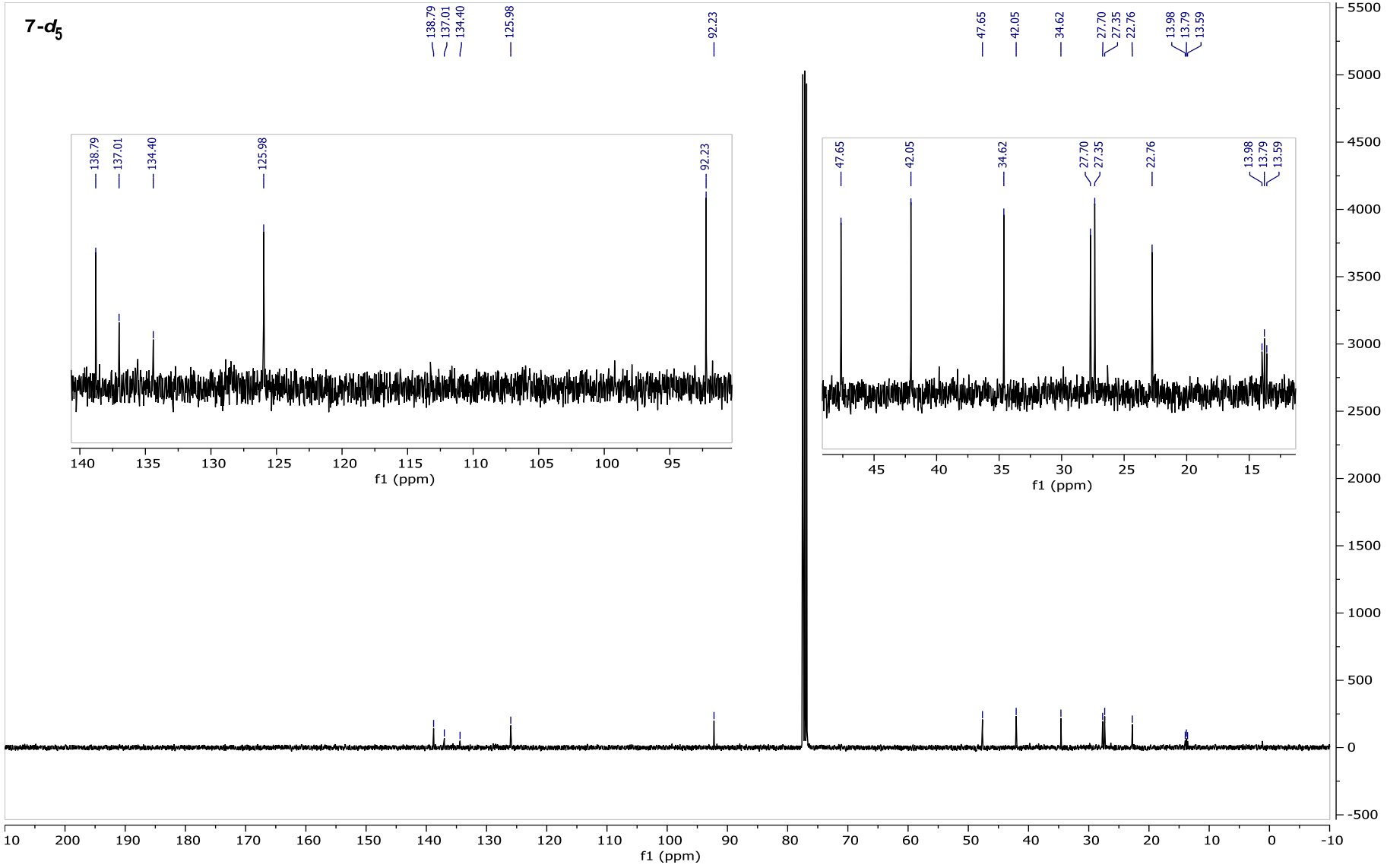
^{13}C NMR (101 MHz, $CDCl_3$):



(*E*)-1-nitro-3-(propylidene-3-*d*)-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[a]naphthalene-6,7,8,9-d_4 (7-d_5): ^{1}H NMR (400 MHz, $CDCl_3$):



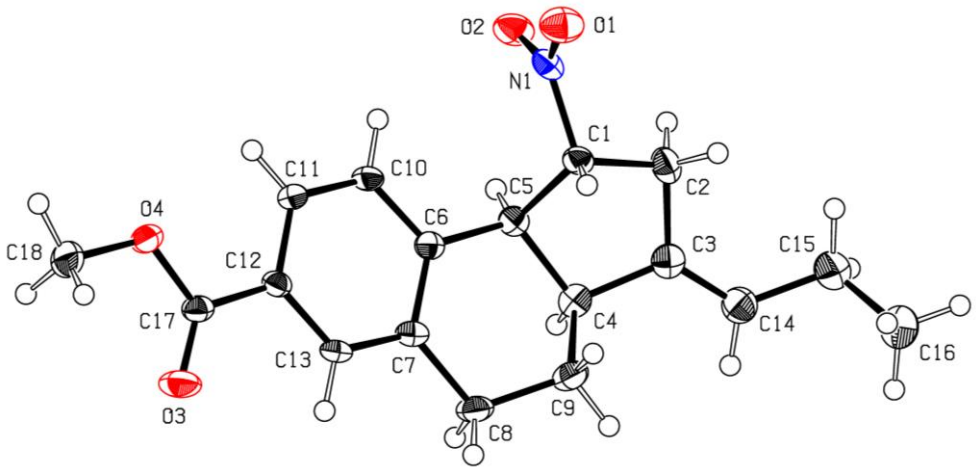
^{13}C NMR (101 MHz, $CDCl_3$):



10. X-ray Crystallographic Details

Data were collected on a single crystal x-ray diffractometer equipped with a CMOS detector (Bruker APEX III, κ-CMOS), a TXS rotating anode with MoK_α radiation (λ = 0.71073 Å) and a Helios optic using the APEX3 software package.[21] Measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on top of a kapton micro sampler and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.[22] Absorption correction, including odd and even ordered spherical harmonics was performed using SADABS.[22] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved using SHELXT with the aid of successive difference Fourier maps, and were refined against all data using SHELXL-2014 in conjunction with SHELXLE.[23-25] Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 Å and $U_{iso(H)} = 1.5 \cdot U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, other C–H distances of 1.00 Å, all with $U_{iso(H)} = 1.2 \cdot U_{eq(C)}$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2-F_c^2)^2$ with the SHELXL weighting scheme.[23] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[26] Images of the crystal structures were generated with Mercury and PLATON.[27,28] CCDC 1915359 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Compound 8 (CCDC 1915359)



Diffractometer operator C. Jandl
scanspeed 60 s per frame
dx 40 mm
1364 frames measured in 9 data sets
phi-scans with delta_phi = 0.5
omega-scans with delta_omega = 0.5

Crystal data

$C_{18}H_{21}NO_4$

M_r = 315.36	D_x = 1.287 Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: ? K
Hall symbol: -P 2yn	Mo Kα radiation, λ = 0.71073 Å
a = 17.209 (3) Å	Cell parameters from 6968 reflections
b = 5.0340 (8) Å	θ = 2.5–25.6°
c = 19.434 (3) Å	μ = 0.09 mm^{-1}
β = 104.812 (5)°	*T* = 100 K
V = 1627.6 (5) Å^3	Needle, colourless
Z = 4	0.81 × 0.10 × 0.08 mm
F(000) = 672	

Data collection

Bruker Photon CMOS diffractometer	2946 independent reflections

Radiation source: TXS rotating anode

Helios optic monochromator

Detector resolution: 16 pixels mm^{-1}

phi– and ω–rotation scans

Absorption correction: multi-scan SADABS 2016/2, Bruker

T_{min} = 0.593, T_{max} = 0.745

32123 measured reflections

2185 reflections with I > 2σ(I)

R_{int} = 0.097

θ_{max} = 25.3°, θ_{min} = 2.5°

h = −20 20

k = −6 5

l = −23 23

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.051

$wR(F^2)$ = 0.126

S = 1.03

2946 reflections

210 parameters

0 restraints

0 constraints

Primary atom site location: intrinsic phasing

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$W = 1/[\Sigma^2(FO^2) + (0.0548P)^2 + 1.1721P]$
WHERE $P = (FO^2 + 2FC^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.27 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.24 e $Å^{-3}$

Extinction correction: none

Extinction coefficient: -

11. Determination of Quantum Yield

The quantum yield of the [2+2] photocycloaddition reaction was determined for substrate **1a** with 2,3-dimethyl-2-butene. The initial rate was determined by measuring the yield of product **2a** using calibrated GC.

Setup

A 380 nm LED[1], operated at constant current (700 mA) was imaged by a pair of best-form quartz lenses into the cuvette (resulting image size: 8.0 mm x 8.0 mm²). The cuvette holder is equipped with a magnetic stir bar drive (2mag, cuvetteMixdrive1). The intensity of (residual) light passing through the cuvette was measured using a calibrated setup consisting of a cosine-corrector, a 600 µm fiber and an Ocean Optics USB4000 spectrometer.[29,30]

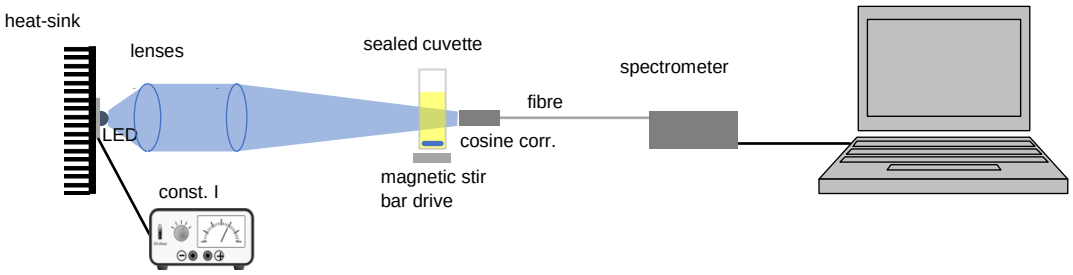


Figure S4: Setup used for the determination of the quantum yield.

Using this setup, the light-intensity available for a photochemical reaction can be determined with the above mentioned spectrometer to be 357±5 W/m² (23 mW integral power at the sample) after thermal equilibration of the LED (30 minutes), which corresponds (380 nm) to $7.26 \cdot 10^{-8}$ Einstein·s^{-1}. This value was verified using a chemical actinometer.

All operations described below where conducted in a "black box" under red-light conditions using the phenyl glyoxylate actinometer.[31,32]

A degassed solution of phenylglyoxylic acid in 3:1 acetonitrile:water (V=3 mL, c=25 mM) was transferred under inert gas conditions (Ar) into the cuvette used for the quantum yield determination (10x10 mm; see below). As described in detail earlier,[29] the most reliable way to determine both, the intensity of residual light not being absorbed by the actinometer solution as well as the remaining phenylglyoxylate is using the fibre coupled USB4000 spectrometer,

[1] A 380 nm LED was chosen to maximise the overlap integral of substrate **1a** and the light source. The precision in the quantification of absorbed photons was too low for the 424 nm LED used in the preparative examples. For the combination of **1a** and 2,3-dimethyl-2-butene, the yield of a preparative experiment (cf. page SI-23) was determined to be (near) identical in comparison with the outcome using the 424 nm LED.

the cosine corrector of which is placed behind the sample cuvette. From these spectrophotometrically determined conversion values and the respective time resolved optical densities (ranging from 0.55 at t=0 min to 0.34 at 14 min.), the photon flux is calculated in a nonlinear fitting (least square fit) to be $4.36 \cdot 10^{16}$ s^{-1} or $7.24 \cdot 10^{-8}$ Einstein s^{-1} using a reference quantum yield of 0.735.

Taking the uncertainties of the reference quantum yield and the variance of the spectrophotometrically determined conversion of the decarboxylation into account, an error of ±5% can be estimated.

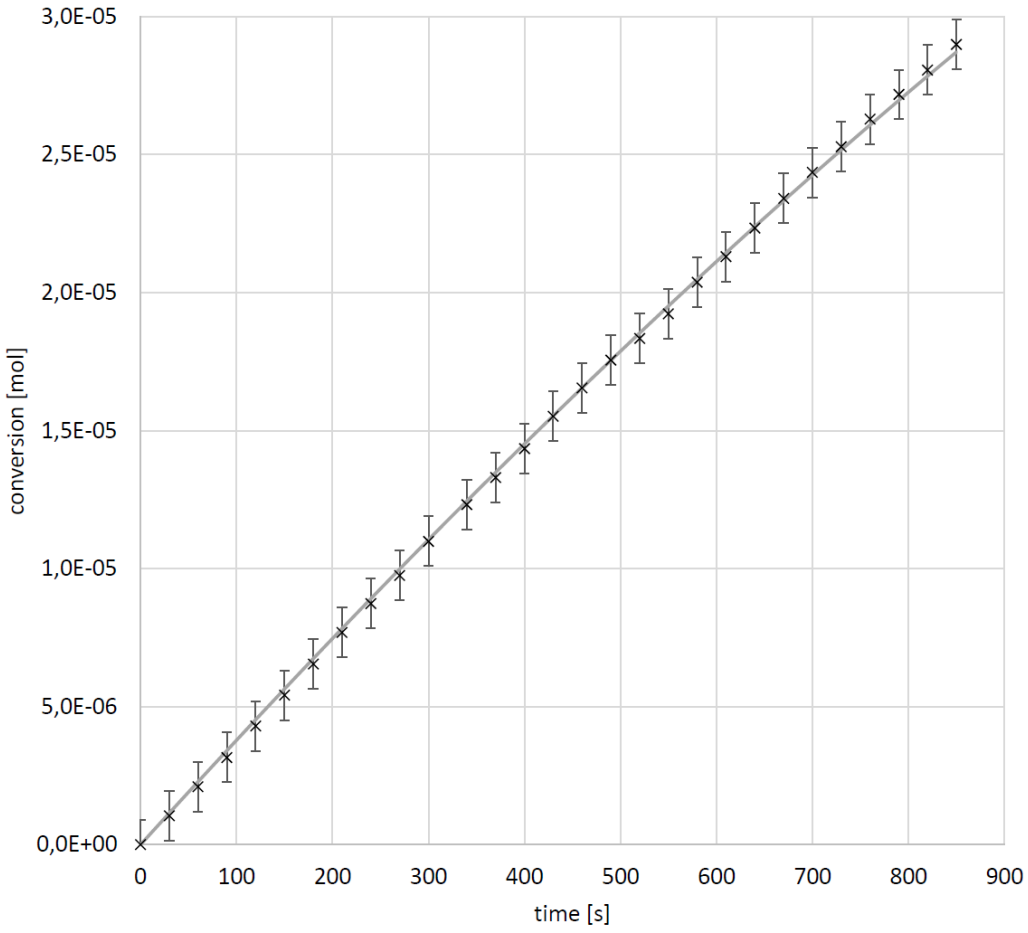


Figure S5: Conversion of the Norrish-type-I decarboxylation of phenylglyoxylic acid at 380 nm.

The photocycloaddition reaction was conducted in a sealed cuvette (quartz, 10x10 mm) using 3 mL of a 20.2 mmol/L sample of **1a** and 2,3-dimethyl-2-butene prepared as described on page SI-22 (according to **GP 4**). The sample was irradiated for 60 min, during which the optical density was again monitored continuously using the fibre-coupled spectrometer. After 60

minutes, the GC yield of **2a** was determined as 16.0% (30% conversion), with dodecane as internal standard (τ_R (trans-**1a**) = 11.7 min, τ_R (cis-**1a**) = 10.9 min, τ_R (**2a**) = 14.09 [60 °C (3 min), 300 °C (15 °C/min), 300 °C (5 min)], HP-5). This procedure was repeated to verify the obtained values giving 15.8% yield at 30% conversion. The measured absorbance at 380 nm is very high throughout the reaction ranging from A_{380nm}(t=0 min.)=0.995 (OD = 2.3) to A_{380nm}(t=60 min.)=0.997 (OD = 2.15). The integration over the wavelength region of the LED-emission was performed in time increments of 30 seconds and used in the calculation of the quantum yield. Due to the very high optical density throughout the reaction, the difference between the calculation given below, which is based on average values and an incremental evaluation of the quantum yield (calculated quantum yield 0.0372) is marginal.

$$\Phi = \frac{\dot{n}(\mathbf{2a})}{I_0 \cdot \bar{\beta}} = \frac{2.678 \cdot 10^{-9} mol/s}{7.24 \cdot 10^{-8} mol/s \cdot 0.996} = 0.0371$$

From the uncertainty of the photon flux and the uncertainty of the yield (and in turn the conversion rate) an error of ±0.002 can be given which allows to give a quantum yield of φ=0.037±0,002.

12. References

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