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Supporting Information

Organophotocatalytic [2+2] Cycloaddition of Electron-Deficient Styrenes

Maxim Golfmann, Louis Glagow, Antonios Giakoumidakis, Christopher Golz, and Johannes C. L. Walker*

Table of Contents

1 General Information

Reagents and Solvents

Standard solvents and reagents were obtained from *ABCR, Acros, Alfa Aesar, BLD, Merck, Sigma-Aldrich* or *Tokyo Chemical Industry* (TCI). CH_2Cl_2, THF, and PhMe were obtained from a MBraun Solvent Purification System, stored over activated 3Å molecular sieves and sparged with argon prior to use. MeCN (ExtraDry over molecular sieves, AcroSeal^{TM}) was purchased from *Acros*. HPLC grade Acetone, $CHCl_3$, and EtOH were used as received. Brine refers to a saturated solution of NaCl in deionized H_2O. Styrene (**1b**) was filtered through a short plug of basic alumina and K_2CO_3 prior to use.

Reactions

Reactions were performed using standard Schlenk techniques. Glassware for reactions was dried under vacuum using a heat gun. All reactions were stirred with magnetic followers. All stated temperatures refer to external bath temperatures.

Chromatography

Flash column chromatography was performed on *Sigma Aldrich* silica gel (40–63 µm, 230–400 mesh, product number 717185) according to the method reported by W. C. Still and co-workers.[1] Technical grade solvents were distilled prior to use. TLC analyses were performed on MilliporeSigma silica gel 60 F254 aluminium backed plates with layer thickness of 200 µm (product number EM1.05554.0001). Product spots were visualised under UV light (λ_{max} = 254 nm) and/or by staining with $KMnO_4$, vanillin, or phosphomolybdic acid solution.

Nuclear Magnetic Resonance (NMR) Spectroscopy

All spectra were recorded in $CDCl_3$ or $CHCl_3$ on *Bruker* Avance III 300 MHz, Avance III HD 300 MHz, Avance III 400, Avance III HD 400 MHz or Avance Neo 400 MHz instruments with the deuterated solvent acting as internal deuterium lock. ^{1}H NMR spectra were recorded at 300 or 400 MHz, ^{2}H NMR at 77 MHz, ^{13}C NMR spectra at 101 MHz with broadband proton decoupling, ^{19}F NMR spectra at 377 MHz without proton decoupling as stated, and ^{31}P NMR spectra at 121 MHz. The residual protic solvent signal acted as an internal reference for ^{1}H NMR and the deuterated solvent carbon signal acted as an internal reference for ^{2}H NMR and ^{13}C NMR ($CHCl_3$: ^{1}H NMR = 7.26 ppm, $CDCl_3$: ^{13}C NMR = 77.16 ppm; ^{2}H NMR = 7.26 Hz). ^{19}F and ^{31}P chemical shifts are given in ppm relative to $CFCl_3$ and H_3PO_4, respectively (external standard). Chemical shifts are reported to 0.01 ppm for ^{1}H NMR and ^{2}H NMR spectra and to 0.1 ppm for ^{13}C NMR and ^{19}F spectra. Peaks that are within 0.01 ppm for ^{1}H NMR or 0.1 ppm for ^{13}C NMR but are still distinguishable are reported to 0.001 ppm and 0.01 ppm, respectively. Coupling constants are quoted to the nearest 0.1 Hz for ^{1}H NMR and ^{13}C NMR. The multiplicity of a signal is reported as follows: s–singlet, d–doublet, t–triplet, q–quartet, quint.–quintet, sext.-sextet, sept.-septet, m–multiplet, br.–broad, app.–apparent, or combinations thereof. Structural assignments were made with the aid of COSY, HSQC, and HMBC experiments.

Infrared Spectroscopy

Fourier-transform infrared (FTIR) spectra were recorded from neat samples on a *Jasco* FT/IR-4100 spectrometer equipped with an ATR unit. Selected absorption maxima are given in wavenumbers (cm^{-1}).

UV/Vis Spectroscopy
UV/Vis spectra were recorded on a *Jasco* V-650 Spectrophotometer.

Mass Spectrometry
High resolution mass spectra (HRMS) were obtained from the *Analytical Facility* at the *Institut für organische and biomolekulare Chemie, Georg-August-Universität Göttingen*.

Melting Points
Melting points (M.P.) were obtained from recrystallized samples using a *Büchi* melting point determination apparatus instrument and are uncorrected. The solvent used for recrystallisation is quoted in parentheses.

X-Ray Crystallography
Data collection was done on two dual source equipped *Bruker D8 Venture* four-circle-diffractometer from *Bruker AXS GmbH*; used X-ray sources: microfocus *IμS* 3.0 Ag/Mo from *Incoatec GmbH* with mirror optics *HELIOS* and single-hole collimator from *Bruker AXS GmbH*; used detector: *Photon III HE* (Ag/Mo) from *Bruker AXS GmbH*.
Used programs: *APEX3 Suite* (v2019.11-0) for data collection and therein integrated programs *SAINT V8.40A* (Integration) und *SADABS 2016/2* (Absorption correction) from *Bruker AXS GmbH*; structure solution was done with *SHELXT*, refinement with *SHELXL-2018/3*,[2] *OLEX2* and *FinalCif* were used for data finalization.[3]
Special Utilities: *SMZ1270* stereomicroscope from *Nikon Metrology GmbH* was used for sample preparation; crystals were mounted on *MicroMounts* or *MicroLoops* from *MiTeGen* in *NVH oil*; crystals were cooled to given temperature with *Cryostream 800* from *Oxford Cryosystems*.

High Pressure Liquid Chromatography
HPLC analyses were performed using a Shimadzu Nexera-i LC2040C 3D or Interchim PuriFlash 4.250. Specific conditions such as column type used, eluent mixtures, flow rates and temperatures are stated for each compound. System control and chromatogram analysis were carried out with Intersoft (Interchim) or LabSolutions (Shimadzu) software.

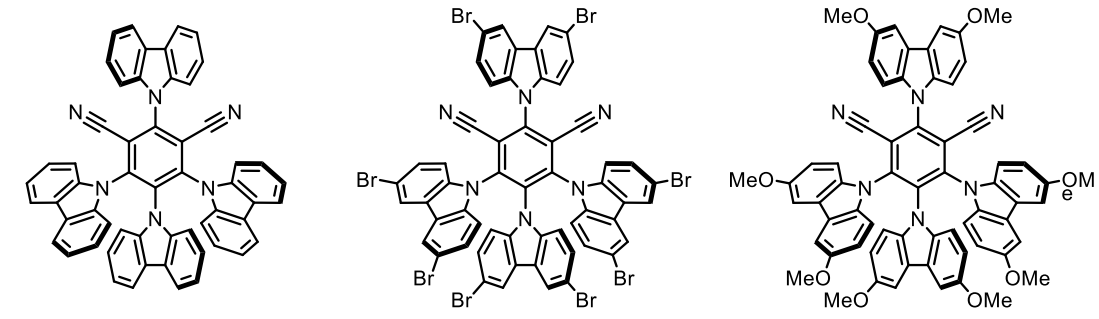
Photochemical Experiments
Photochemical experiments were conducted in a photoreactor of in-house design. The reaction chamber was surround by 700 blue LEDs (456 nm) (revoART, 102 mW output/LED, 5 m LEDs total, product number: X105-0700). Schlenk tubes were placed in a circular stand at a distance of approximately 5 cm from the LEDs. The photoreactor was cooled internally by a fan installed in the top of the reactor. The complete reactor setup was placed on top a standard magnetic stirrer.

Compound Naming
Compound names were generated by the computer program *ChemDraw* according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC).

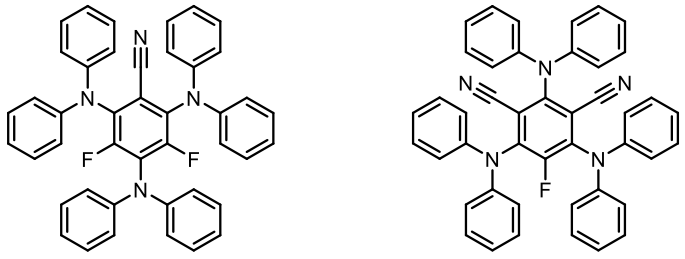
2 Reaction optimisation

Catalysts used in optimisation

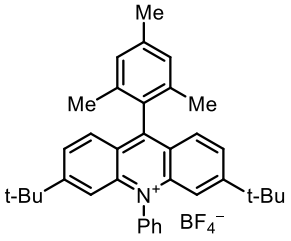
4CzIPN (*see below*), 4-BrCzIPN,[4] 4-MeOCzIPN,[5] 3DPA2FBN,[5] and 3DPAFIPN[5] were prepared using literature procedures. Rose Bengal (*Fisher Scientfic*), Fluorescein (*BLD Pharmatech*), [*t*BuMesAcr][BF_4] (*BLD Pharmatech*), and [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6 (*Sigma Aldrich*) were purchased from the indicated supplier and used as received.



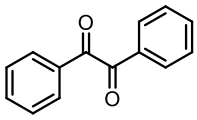
4CzIPN **4-BrCzIPN** **4-MeOCzIPN**



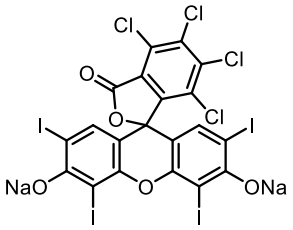
3DPA2FBN **3DPAFIPN**



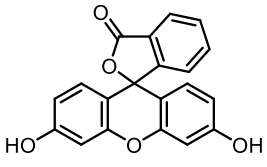
[*t*BuMesAcr][BF_4]



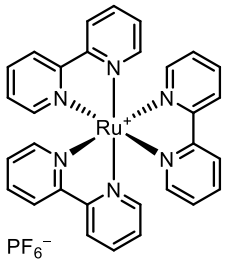
Benzil



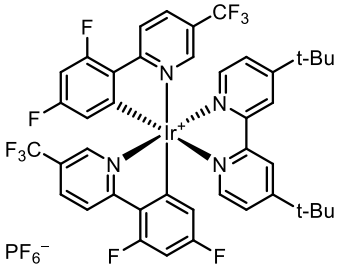
Rose Bengal



Fluorescein



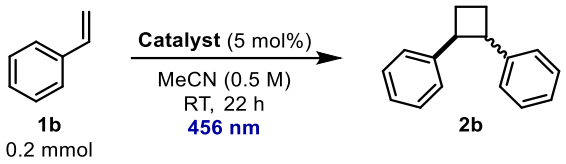
[Ru(bpy)$_3$]PF_6



[Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6

Figure S1. Catalysts used in reaction optimisation.

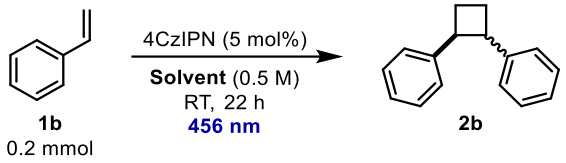
Table S1. Catalyst Optimisation



Entry	Catalyst	dr (*trans*:*cis*)[a]	Yield (%)[b]
1	**4CzIPN**	**2:1**	**10**
2	4-BrCzIPN	6:1	9
3	4-MeOCzIPN	1:3	>5
4	3DPA2FBN	n.d.	>5
5	3DPAFIPN	n.d.	>5
6	[*t*BuMesAcr][BF_4]	1:2	11[c]
7	Benzil	8.3:1	>5
8	Rose Bengal	n.d.	>5
9	Fluorescein	n.d.	>5
10	$Ru(bpy)_3PF_6$	n.d.	>5

[a] Diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard. [c] Numerous other side-reactions.

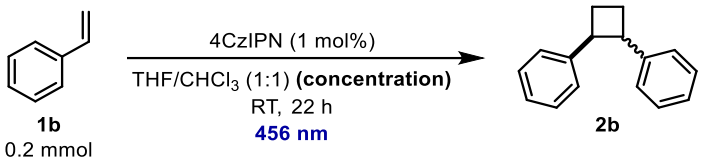
Table S2. Solvent Optimisation



Entry	Solvent	dr (*trans*:*cis*)[a]	Yield (%)[b]
1	MeCN	2:1	10
2	DMSO	4:1	8
3	DMF	2.8:1	10
4	CH_2Cl_2	6:1	17
5	$CHCl_3$	3.6:1	26
6	THF	3.7:1	31
7	PhMe	4.8:1	11
8	Acetone	5.1:1	15
9	NMP	4.6:1	4
10	EtOH	3.3:1	9
11	**THF/$CHCl_3$ (1:1)**	3.5:1	36

[a] Diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard.

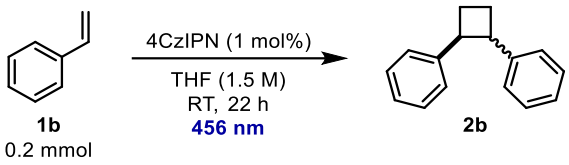
Table S3. Concentration Optimisation



Entry	Solvent	dr (*trans*:*cis*)[a]	Yield (%)[b]
1	1 M	3.4:1	37
2	1.5 M	3.7:1	75
3	neat	4.5:1	67
4	**1.5 M (only THF)**	**3.6:1**	**83**
5	1.5 M (only $CHCl_3$)	3.7:1	58

[a] Diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard.

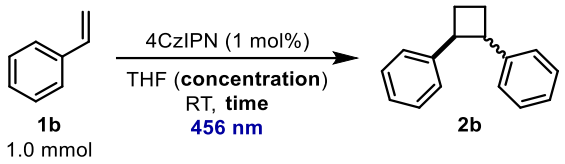
Table S4. Control Experiments



Entry	Deviation to standard conditions	dr (*trans*:*cis*)[a]	Yield (%)[b]
1	**None**	**3.6:1**	**83**
2	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1 mol%)	3.3:1	41
3	DMF	1.6:1	6
4	HPLC grade THF	3.3:1	71
5	Under Air	3.2:1	23
6	Argon sparged THF	3.5:1	63
7	No 4CzIPN	n.d	<5
8	Reaction in dark	n.d	<5

[a] Diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard.

Table S5. Reoptimisation of 1.00 mmol Scale Reaction

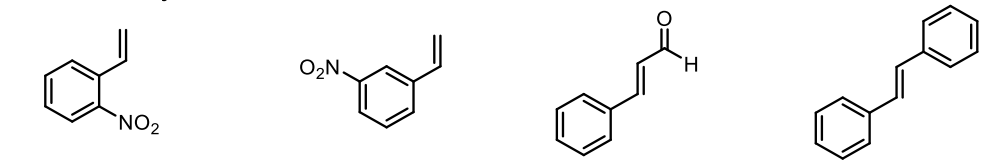


Entry	Concentration (M)	Time (h)	Conversion[a]
1	1.5	22	30
2	1.5	72	87
3	0.5	22	32
4	4	22	71
5	**4**	**48**	**Quant (56)[b]**

[a] Conversion was determined by ^{1}H NMR spectroscopy relative to unreacted styrene (**1b**). [b] Isolated yield.

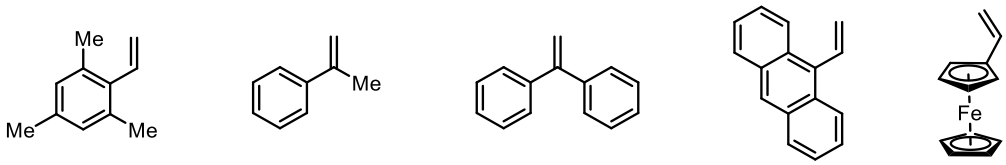
3 Unsuccessful styrenes

Low or other reactivity



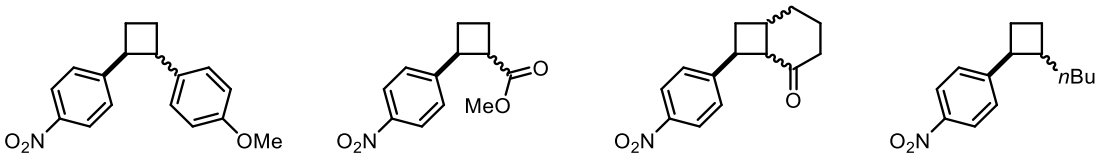
1w *ca. 10% conversion* | **S1** *low conversion* | **S2** *E/Z isomerisation* | **S3** *E/Z isomerisation*

No reactivity



1x | **1y** | **1z** | **S4** | **S5**

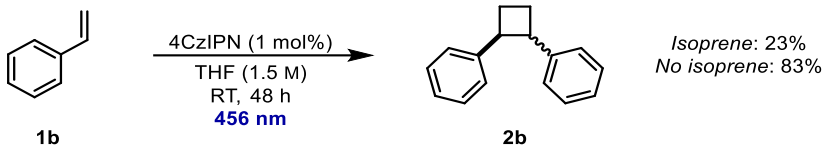
Heterodimerisation



inseparable mixture of homo- and heterodimers | *only styrene homodimer observed* | *only styrene homodimer observed* | *only styrene homodimer observed*

Figure S2. Overview of less successful styrenes and attempts at heterodimerisation.

4 Triplet quenching control experiment



Scheme S1. Triplet quenching control experiment.

Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard.

5 UV/Vis Spectroscopy

The appearance of a new band at around 325 nm can be seen at concentrations >2M (see Figures S3–5). Although a definitive assignment of this band is not possible at the moment, it is possible that its appearance is related to a π-stacking interaction between styrene units at high concentrations. It has been proposed that this interaction enables more facile excitation of styrene in energy transfer reactions (see Ref. 16b, main manuscript), which would be consistent with the much improved reactivity at higher concentrations observed in this investigation.

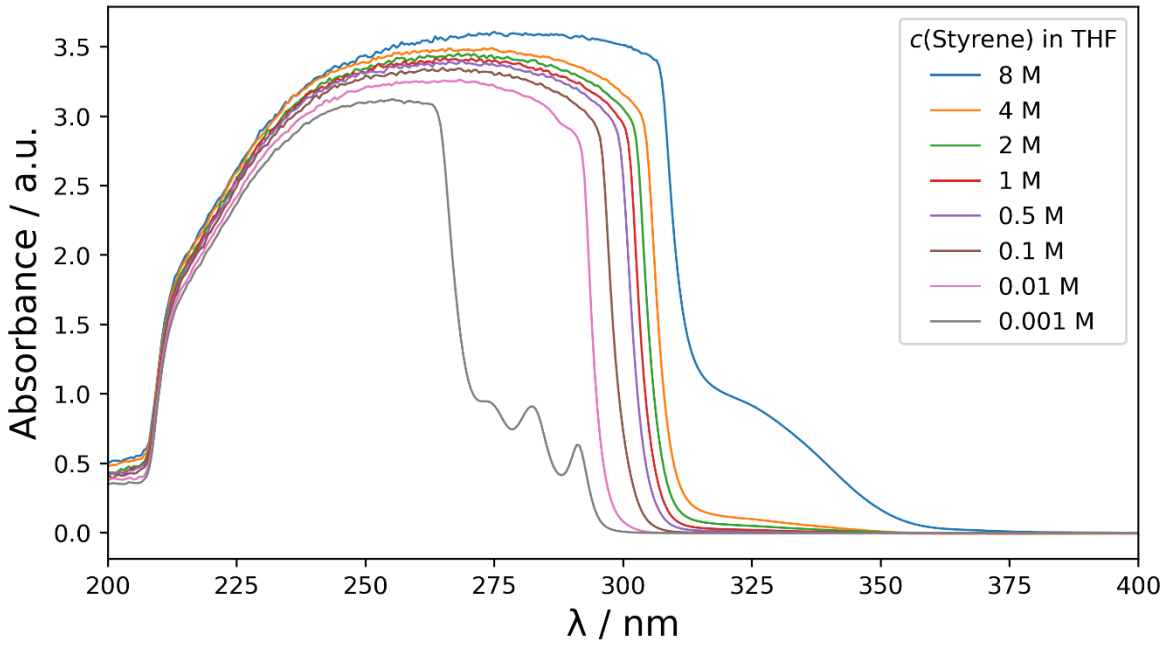


Figure S3. UV/Vis Spectra of Styrene (**1b**) in THF at the indicated concentrations.

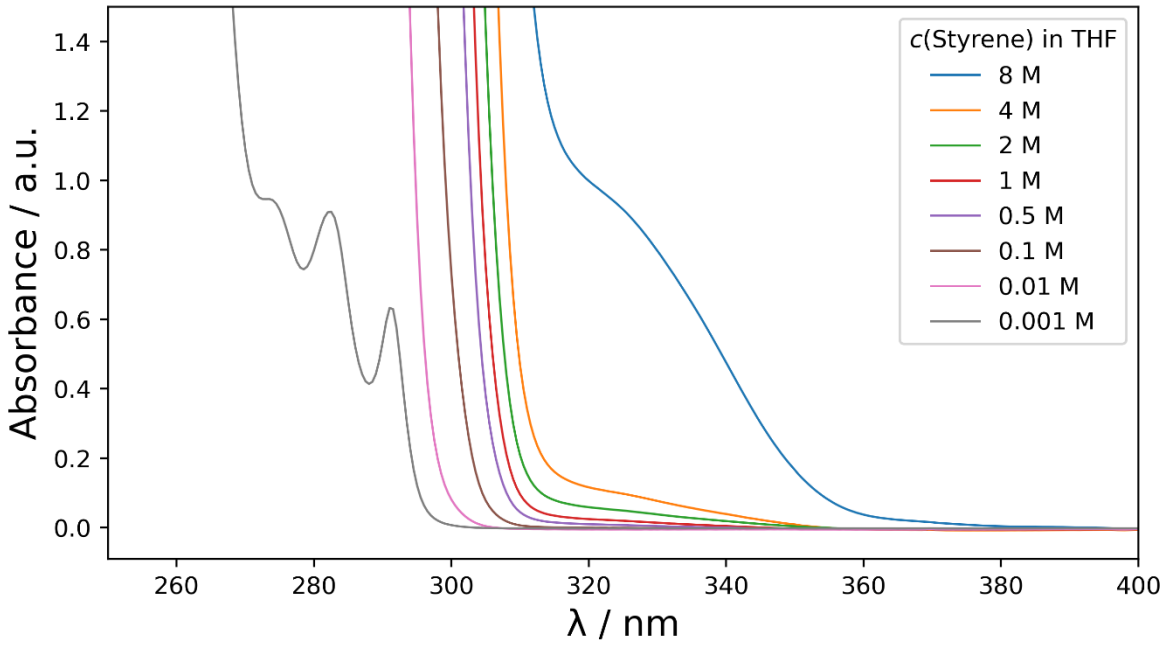


Figure S4. Magnified UV/Vis Spectra of Styrene (**1b**) in THF at the indicated concentrations.

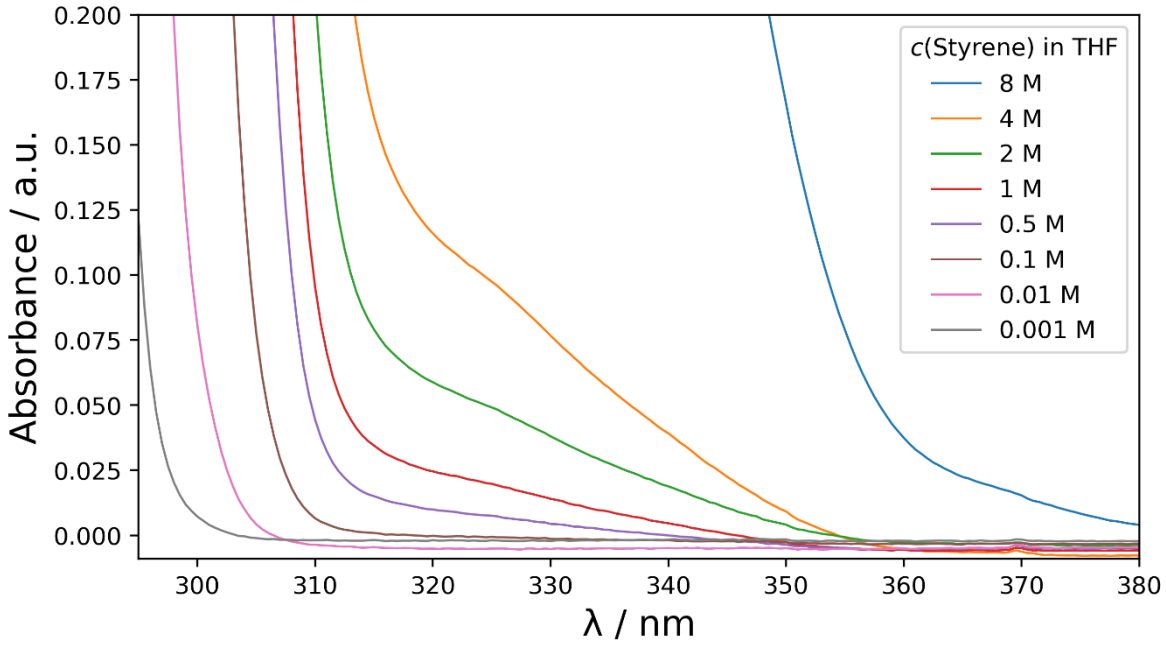


Figure S5. Magnified UV/Vis Spectra of Styrene (**1b**) in THF at the indicated concentrations.

6 Synthesis of starting materials

General Procedures

General Procedure 1 (GP1): Wittig reaction with DBU.
To a refluxing solution of the corresponding Wittig salt (2 equiv) in CH_2Cl_2 (0.2 M with respect to Wittig salt) was added DBU (2.2 equiv). After 30 min, a solution of the corresponding aldehyde (1.0 equiv) in CH_2Cl_2 (0.33 M with respect to aldehyde) was added to the reaction mixture and stirred for further 2 hours at 40 °C. The reaction mixture was washed with water (3×), and the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2) to afford the title compound.

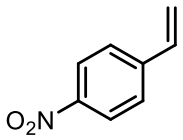
General Procedure 2 (GP2): Wittig reaction with KO*t*Bu.

The corresponding Wittig salt (1.2 equiv) was suspended in THF (0.5 M with respect to aldehyde). KO*t*Bu (1.2 equiv) was added portionwise and the reaction was stirred at room temperature for 0.5 h. The corresponding aldehyde (1 equiv) was added as a single portion and the reaction was then stirred overnight at room temperature. The reaction mixture was diluted with water and CH_2Cl_2 (each double volume of THF) and the layers were separated. The organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2) to afford the title compound.

General Procedure 3 (GP3): Grignard reaction.

A two-neck round bottomed flask was equipped with a condenser with magnesium shavings (1.2 equiv). The complete apparatus was dried with a heat gun (3×) under vacuum and once cool, evacuated and backfilled with argon (3×), THF (0.5 M with respect to 4-chlorostyrene) and an iodine crystal or 0.1 mL of 1,2-dibromoethane as indicated was added. 4-Chlorostyrene (1 equiv) was added dropwise and the reaction mixture was heated to reflux (90 °C oil bad temperature). The resulting black reaction was stirred for 1 hour at this temperature. The solution was then cooled to 0 °C, the corresponding electrophile was added dropwise. The reaction was allowed to stirred at room temperature for 2.5 hours or overnight as indicated. The reaction was quenched with either HCl (1 M, aq.) or NH_4Cl (sat., aq.) (volume of THF) as indicated. The reaction mixture was extracted with EtOAc (volume of THF, 3×). The combined organic phases were washed sequentially with water and brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction mixture was then purified by flash column chromatography (SiO_2) to afford the title compound.

1-Nitro-4-vinylbenzene (1a)



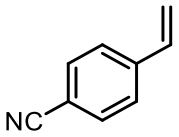
1a
Chemical Formula: $C_8H_7NO_2$
Molecular Weight: 149.15

(4-Nitrophenyl)methyltriphenylphosphonium bromide (8.00 g, 16.7 mmol, 1.0 equiv) was suspended in paraformaldehyde (37%, aq., 62 mL) and H_2O (33.5 mL). NaOH (5 M, aq., 25.1 mL, 125 mmol) was added dropwise and the reaction was stirred at room temperature for 1 h. The reaction mixture was extracted with EtOAc (3×120 mL) and the combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude reaction mixture was purified by flash column chromatography (SiO_2, 19:1 pentane:EtOAc) afforded the title compound as a yellow oil (2.00 g, 13.4 mmol, 80%).

Data were consistent with that reported.[6]

R_f = 0.5 (19:1 pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.19 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 8.9 Hz, 2H), 6.78 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.93 (d, *J* = 17.6 Hz, 1H), 5.50 (d, *J* = 11.0 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 147.3, 144.0, 135.1, 127.0 (2C), 124.1 (2C), 118.7.

4-Vinylbenzonitrile (1c)



1c
Chemical Formula: C_9H_7N
Molecular Weight: 129.16

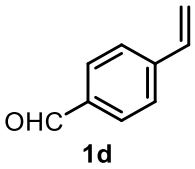
Prepared according to **GP2** using 4-cyanobenzaldehyde (1.31 g, 10.0 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol, 1.2 equiv) and KO*t*Bu (1.35 g, 12.0 mmol, 1.2 equiv) in dry THF (25 mL). Purification by flash column chromatography (SiO_2, 19:1 Pentane:EtOAc) afforded the title compound as a colourless oil (823 mg, 6.38 mmol, 63%).

Data were consistent with that reported.[7]

R_f = 0.33 (19:1 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.64–7.57 (m, 2H), 7.51–7.44 (m, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.87 (d, *J* = 17.6 Hz, 1H), 5.45 (d, *J* = 10.9 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 142.0, 135.5, 132.5 (2C), 126.9 (2C), 119.0, 117.9, 111.3.

4-Vinylbenzaldehyde (1d)



1d

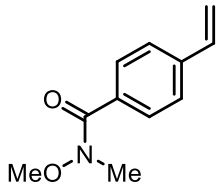
Chemical Formula: C_9H_8O
Molecular Weight: 132.16

Prepared according to **GP3** using magnesium (316 mg, 13.0 mmol, 1.2 equiv), 4-chlorostyrene (1.50 g, 10.8 mmol, 1.0 equiv) in THF (21.6 mL), and *N,N*-dimethylformamide (3.95 g, 54.1 mmol, 5.0 equiv) as electrophile. Purification by flash column chromatography (SiO_2, 95:5 Pentane) afforded the title compound as a colourless liquid (1.22 g, 9.23 mmol, 85%).

Data were consistent with that reported.[6]

***R*$_f$** = 0.29 (95:5 Pentane:EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 9.99 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.91 (d, *J* = 17.6 Hz, 1H), 5.44 (d, *J* = 10.9 Hz, 1H).
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 192.2, 143.9, 136.3, 136.1, 130.5 (2C), 127.2 (2C), 117.9.

***N*-Methoxy-*N*-methyl-4-vinylbenzamide (1e)**



1e

Chemical Formula: $C_{11}H_{13}NO_2$
Molecular Weight: 191.23

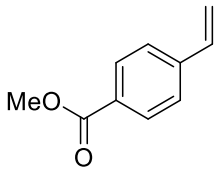
Thionyl chloride (3.21 g, 27.0 mmol, 2.0 eq) was added to a solution of 4-vinylbenzoic acid (**S6**) (2.00 g, 13.5 mmol, 1.0 equiv) in CH_2Cl_2 (27.0 mL, 0.5 M with respect to 4-vinylbenzoic acid). The flask was sealed with a greased glass stopper, secured tightly with with a HWS-fork clamp and was allowed to stir at 55 °C oil bath temperature overnight (Warning: vessel has to be pressure resistant!). The reaction mixture was allowed to cool to room temperature and subsequently all volatiles were removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (27.1 mL) and *N,O*-dimethylhydroxylamine hydrochloride (1.98 g, 20.2 mmol, 1.50 equiv) added. Pyridine (3.20 g, 40.5 mmol, 3.00 eq) was added dropwise at 0 °C and the reaction mixture stirred for 2.5 hours at 0 °C. HCl (1 M, aq., 100 mL) was added to the reaction mixture and the layers were separated. The aqueous phase was extracted with EtOAc

(3×100 mL). The combined organic phases were washed with HCl (1 M, aq., 100 mL), brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2,7:3 *n*-pentane/EtOAc) to afforded the title compound as a colourless liquid (1.73 g, 9.05 mmol, 67%).

Data were consistent with that reported.[8]

***R*$_f$** = 0.25 (7:3 Pentane:EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.66 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.82 (d, *J* = 17.6 Hz, 1H), 5.33 (d, *J* = 10.9 Hz, 1H), 3.55 (s, 3H), 3.36 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 169.7, 139.9, 136.3, 133.3, 128.8 (2C), 125.9 (2C), 115.7, 61.2, 33.9.

Methyl 4-vinylbenzoate (1f)



1f

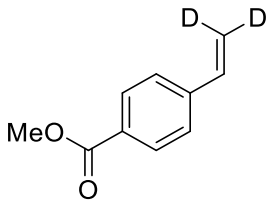
Chemical Formula: $C_{10}H_{10}O_2$
Molecular Weight: 162.19

Methyltriphenylphosphonium bromide (2.67 g, 5.00 mmol, 1.5 equiv) was suspended in dry THF (25 mL). KO*t*Bu (673 mg, 6.00 mmol, 1.2 equiv) was added portionwise and the reaction was stirred at room temperature for 0.5 h. Methyl 4-formylbenzoate (1.20 g, 10.0 mmol, 1.0 equiv) was added at 0°C as a single portion and the reaction was then stirred overnight at room temperature. The reaction mixture was diluted with NH_4Cl (sat., aq., 10 mL), the layers were separated and the aqueous phase extracted with Et_2O (3×30 mL). The organic phase was washed with H_2O (50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting solid was extracted with pentane (5×10 mL) The crude reaction mixture was purified by flash column chromatography (SiO_2, 95:5 Pentane:EtOAc) to afford the title compound (688 mg, 4.24 mmol, 84%).

Data were consistent with that reported.[6]

***R*$_f$** = (95:5 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.00 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (d, *J* = 17.6 Hz, 1H), 5.38 (d, *J* = 10.9 Hz, 1H), 3.92 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 167.0, 142.1, 136.2, 130.0 (2C), 129.4, 126.3 (2C), 116.6, 52.2.

Methyl 4-(vinyl-2,2-d_2)benzoate(2f-d_2)



1f-d_2

Chemical Formula: $C_{10}H_8D_2O_2$
Molecular Weight: 164.20

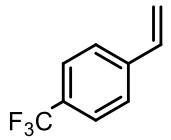
(Methyl)triphenylphosphonium iodide-d_3 (**S8**) (2.16 g, 5.31 mmol, 1.2 equiv) was suspended in dry THF (22 mL). KO*t*Bu (596 mg, 5.31 mmol, 1.2 equiv) was added portionwise and the reaction was stirred at room temperature for 0.5 h. 4-(Trifluoromethyl)benzaldehyde (1.74 g, 10.0 mmol, 1.0 equiv) was added at 0°C as a single portion and the reaction was then stirred overnight at room temperature. The reaction mixture was diluted with NH_4Cl (sat., aq., 20 mL), the layers were separated and the aqueous phase extracted with EtOAc (2×20 mL). The organic phase was washed with H_2O (20 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2, 95:5 Pentane:EtOAc) to afford the title compound (542 mg, 3.30 mmol, 74%).

Incorporation of ^2H was estimated by ^1H NMR spectroscopy to be around 84%.

Data were consistent with that reported.[9]

***R*$_f$** = (95:5 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.06–7.96 (m, 2H), 7.51–7.41 (m, 2H), 6.80–6.69 (m, 1H), 5.86 (dd, *J* = 17.7, 4.6 Hz, 0.16H), 5.38 (dd, *J* = 11.0, 4.6 Hz, 0.16H), 3.91 (s, 3H).
^{2}H NMR (77 MHz, $CDCl_3$) δ/ppm = 5.90, 5.42.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 167.0, 142.1, 136.1, 136.0, 130.0 (2C), 129.4, 126.3 (2C), 52.2.
IR (ATR): ν = 3039, 3002, 2949, 2850, 1711, 1438, 1275, 1180, 1107, 938, 773, 742, 704 cm^{-1}.

1-(trifluoromethyl)-4-vinylbenzene (1j)



1j

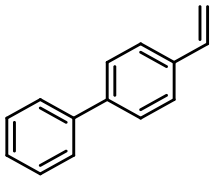
Chemical Formula: $C_9H_7F_3$
Molecular Weight: 172.15

Methyltriphenylphosphonium bromide (5.34 g, 15.0 mmol, 1.5 equiv) was suspended in dry THF (50 mL). KO*t*Bu (1.35 g, 12.0 mmol, 1.2 equiv) was added portionwise and the reaction was stirred at room temperature for 0.5 h. 4-(Trifluoromethyl)benzaldehyde (1.74 g, 10.0 mmol, 1.0 equiv) was added at 0 °C as a single portion and the reaction was then stirred overnight at room temperature. The reaction mixture was diluted with NH_4Cl (sat., aq., 20 mL), the layers were separated and the aqueous phase extracted with Et_2O (3×60 mL). The organic phase was washed with H_2O (60 mL), brine (60 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2, Pentane) to afford the title compound (1.04 g, 6.04 mmol, 60%).

Data were consistent with that reported.[10]

***R*$_f$** = 0.33 (19:1 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.58 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.85 (d, *J* = 17.6 Hz, 1H), 5.39 (d, *J* = 10.9 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 141.1 (d, *J* = 1.6 Hz), 135.8, 129.8 (q, *J* = 32.3 Hz), 126.5 (2C), 125.6 (q, *J* = 3.8 Hz, 2C), 123.0, 116.6.
^{19}F NMR (282 MHz, $CDCl_3$)): δ/ppm = –62.6.

4-Vinylbiphenyl (1m)



1m

Chemical Formula: $C_{14}H_{12}$
Molecular Weight: 180.25

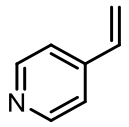
Prepared according to **GP2** using 4-phenylbenzaldehyde (1.82 g, 10.0 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol, 1.2 equiv) and KO*t*Bu (1.35 g, 12.0 mmol, 1.2 equiv) in dry THF (25 mL). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as an off white solid (1.30 g, 7.21 mmol, 72%).

Data were consistent with that reported.[11]

***R*$_f$** = 0.3 (Pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.64–7.54 (m, 4H), 7.52–7.41 (m, 4H), 7.37–7.32 (m, 1H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.80 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 140.9, 140.7, 136.7, 136.6, 128.9 (2C), 127.5, 127.4 (2C), 127.1 (2C), 126.8 (2C), 114.0.

4-Vinylpyridine (1n)



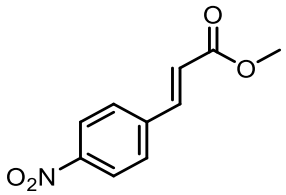
1n
Chemical Formula: C_7H_7N
Molecular Weight: 105.14

Prepared according to **GP2** using 4-pyridinecarboxaldehyde (1.07 g, 10.0 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol, 1.2 equiv) and KO*t*Bu (1.35 g, 12.0 mmol, 1.2 equiv) in dry THF (25 mL). Purification by flash column chromatography (SiO_2, 6:4 Pentane:EtOAc) afforded the title compound as a yellowish oil (334 mg, 3.18 mmol, 31%).

Data were consistent with that reported.[12]

R_f = 0.26 (6:4 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.55 (d, *J* = 5.5 Hz, 2H), 7.29–7.23 (m, 2H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.96 (d, *J* = 17.6 Hz, 1H), 5.48 (d, *J* = 10.9 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 150.3 (2C), 144.8, 134.9, 120.9 (2C), 118.8.

(*E*)-methyl 4-nitrocinnamate (1o)



1o
Chemical Formula: $C_{10}H_9NO_4$
Molecular Weight: 207.19

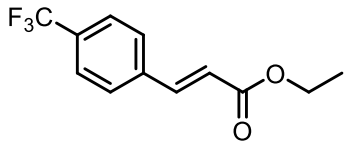
NaOH (1.2 M, aq., 58 mL, 2 equiv) was added to a solution of (2-methoxy-2-oxoethyl) triphenylphosphonium bromide (**S7**) (14.5 g, 34.9 mmol, 1 equiv) in CH_2Cl_2 (87 mL, 0.4 M) in a separatory funnel and shaken. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (60 mL) and the combined organic phases dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure to afford methyl (triphenylphosphoranylidene)acetate as a white solid, which was used directly without further purification.
A round bottom flask was charged with methyl (triphenylphosphoranylidene)acetate (6.64 g, 19.8 mmol, 2 equiv), 4-nitrobenzaldehyde (1.50 g, 9.93 mmol, 1 equiv) and CH_2Cl_2 (25 mL,

0.4 M) and stirred for 24 hours at ambient temperature. The reaction was concentrated *in vacuo* and the crude reaction mixture was purified by flash column chromatography (SiO_2, 8:2 Pentane:EtOAc) to afford the title compound as a light-yellow solid (1.58 g, 9.93 mmol, 76%).

Data were consistent with that reported.[13]

***R*$_f$** = 0.51 (8:2 Pentane:EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 8.25 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 16.0, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 166.6, 148.7, 142.1, 140.6, 128.8 (2C), 124.3 (2C), 122.2, 55.2.

Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (1p)



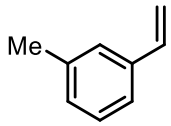
1p
Chemical Formula: $C_{12}H_{11}F_3O_2$
Molecular Weight: 244,21

Trimethyl silyl chloride (1.29 mL, 10.2 mmol, 2.2 equiv) was added to a solution of (*E*)-3-(4-(trifluoromethyl)phenyl)acrylic acid (1.00 g, 4.63 mmol, 1.0 equiv) in ethanol (23.1 mL) under air. The reaction mixture was stirred at room temperature for 19 h. The solution was concentrated *in vacuo.* The resulting crystalline solid was dissolved in ethyl acetate (60 mL), washed with $NaHCO_3$ (sat., aq., 50 mL), washed with H_2O (50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to afford the title compound as a colourless solid (1.10 g, 4.51 mmol, 97%), which was used without further purification.

Data were consistent with that reported.[14]

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.74–7.58 (m, 5H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 166.6, 142.9, 138.0, 131.9, 129.8, 128.3 (2C), 126.0 (2C), 121.0, 61.0, 14.4.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ/ppm = 62.9.

1-methyl-3-vinylbenzene (1s)



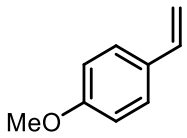
1s
Chemical Formula: C_9H_{10}
Molecular Weight: 118.18

Methyltriphenylphosphonium bromide (5.34 g, 15.0 mmol, 1.5 equiv) was suspended in dry THF (50 mL). KO*t*Bu (1.35 g, 12.0 mmol, 1.2 equiv) was added portionwise and the reaction was stirred at room temperature for 0.5 h. 3-Methylbenzaldehyde (1.20 g, 10.0 mmol, 1.0 equiv) was added at 0°C as a single portion and the reaction was then stirred overnight at room temperature. The reaction mixture was diluted with NH_4Cl (sat., aq., 20 mL), the layers were separated and the aqueous phase extracted with Et_2O (3×60 mL). The organic phase was washed with H_2O (60 mL), brine (60 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography (SiO_2, Pentane) to afford the title compound (890 mg, 7.53 mmol, 75%).

Data were consistent with that reported.[6]

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.22 (d, *J* = 5.1 Hz, 3H), 7.11–7.04 (m, 1H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 11.0 Hz, 1H), 2.35 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 138.2, 137.7, 137.1, 128.7, 128.6, 127.1, 123.5, 113.7, 21.5.

4-Methoxystyrene (1t)



1t
Chemical Formula: $C_9H_{10}O$
Molecular Weight: 134.18

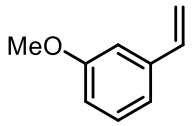
Prepared according to **GP2** using 4-methoxybenzaldehyde (1.36 g, 10.0 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol, 1.2 equiv) and KO*t*Bu (1.35 g, 12.0 mmol, 1.2 equiv) in dry THF (25 mL). Purification by flash column chromatography (SiO_2, 98:2 Pentane:EtOAc) afforded the title compound as a colourless oil (1.09 g, 8.12 mmol, 81%).

Data were consistent with that reported.[7]

R_f = 0.4 (98:2 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.35 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.61 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.9 Hz, 1H), 3.81 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 159.5, 136.4, 130.6, 127.5 (2C), 114.0 (2C), 111.7, 55.4

3-Methoxystyrene (1u)



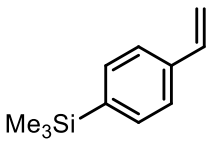
1u
Chemical Formula: $C_9H_{10}O$
Molecular Weight: 134.18

Prepared according to **GP2** using 3-methoxybenzaldehyde (1.50 g, 11.0 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (4.72 g, 13.2 mmol, 1.2 equiv) and KO*t*Bu (1.48 g, 13.2 mmol, 1.2 equiv) in dry THF (25 mL). Purification by flash column chromatography (SiO_2, 98:2 Pentane:EtOAc) afforded the title compound as a colourless oil (723 mg, 5.39 mmol, 48%).

Data were consistent with that reported.[15]

***R*$_f$** = 0.43 (98:2 Pentane:EtOAc).
^1H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.23 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 2.1 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.28 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.83 (s, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 160.0, 139.2, 136.9, 129.6, 119.1, 114.3, 113.6, 117.7, 55.4.

4-Trimethylsilylstyrene (1v)



1v
Chemical Formula: $C_{11}H_{16}Si$
Molecular Weight: 176.33

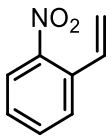
Prepared according to **GP3** using magnesium (316 mg, 13.0 mmol, 1.2 equiv), 4-chlorostyrene (1.50 g, 10.8 mmol, 1.0 equiv) in THF (21.6 mL), and trimethylsilylchloride (1.41 g, 13.0 mmol, 1.20 equiv) as electrophile. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless liquid (1.06 g, 10.8 mmol, 55%).

Data were consistent with that reported.[16]

***R*$_f$** = 0.6 (Pentane:EtOAc).
^1H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.50 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.26 (dd, *J* = 10.9, 1.0 Hz, 1H), 0.27 (s, 9H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 140.3, 138.1, 137.0, 133.7 (2C), 125.7 (2C), 114.2, –1.0 (3C).
$^{29}Si\{^1H\}$ NMR (60 MHz, $CDCl_3$): δ/ppm = –4.15.

2-Nitrostyrene (1w)



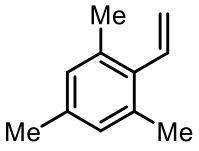
1w
Chemical Formula: $C_8H_7NO_2$
Molecular Weight: 149.15

Prepared according to **GP2** using 2-nitrobenzaldehyde (2.00 g, 13.2 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (6.12 g, 17.2 mmol, 1.3 equiv) and KO*t*Bu (2.23 g, 19.9 mmol, 1.5 equiv) in dry THF (40 mL). Purification by flash column chromatography (SiO_2, 98:2 Pentane:EtOAc) afforded the title compound as a light yellow oil (1.04 g, 5.09 mmol, 55%).

Data were consistent with that reported.[17]

***R*$_f$** = 0.42 (98:2 Pentane:EtOAc).
^1H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.93 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.64–7.55 (m, 2H), 7.44–7.38 (m, 1H), 7.18 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.75 (dd, *J* = 17.3, 0.9 Hz, 1H), 5.49 (dd, *J* = 11.0, 0.9 Hz, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 148.0, 135.5, 133.2, 132.6, 128.6, 128.5, 124.6, 119.1.

2,4,6-Trimethylstyrene (1x)



1x
Chemical Formula: $C_{11}H_{14}$
Molecular Weight: 146.23

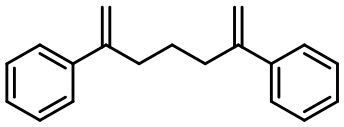
Prepared according to **GP2** using 2,4,6-trimethylbenzaldehyde (1.48 g, 10.0 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (4.29 g, 12.0 mmol, 1.2 equiv) and KO*t*Bu (1.35 g, 12.0 mmol, 1.2 equiv) in dry THF (25 mL). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless oil (1.10 g, 7.55 mmol, 75%).

Data were consistent with that reported.[7]

***R*$_f$** = 0.5 (Pentane).

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 6.89 (s, 2H), 6.70 (dd, *J* = 17.9, 11.5 Hz, 1H), 5.53 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.27 (dd, *J* = 17.9, 2.1 Hz, 1H), 2.31 (s, 6H), 2.30 (s, 3H).
^{13}C{^{1}H} NMR (101MHz, $CDCl_3$): δ/ppm = 136.3, 135.8, 135.2, 134.9, 128.6 (2C), 119.2 (2C), 21.1, 20.9 (2C).

Hepta-1,6-diene-2,6-diylbenzene (3a)



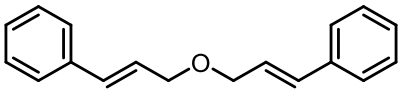
3a
Chemical Formula: $C_{19}H_{20}$
Molecular Weight: 248.37

A solution of methyl triphenylphosphonium bromide (6.43 g, 18.0 mmol, 3.6 equiv) and KO*t*Bu (1.68 g, 15.0 mmol, 3.6 equiv) in dry THF (20 mL) was stirred for 30 min. The solution was cooled to 0 °C and 1,5-diphenylpentane-1,5-dione (1.26 g, 5.00 mmol, 1.0 equiv) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 120 h. The mixture was diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo.* Purification by flash column chromatography (SiO_2, 49:1 Pentane:EtOAc) afforded the title compound as a colourless oil (344 mg, 1.38 mmol, 27%).

Data were consistent with that reported.[18]

***R*$_f$** = 0.25 (49:1 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.41–7.18 (m, 10H), 5.27 (d, *J* = 1.5 Hz, 2H), 5.05 (q, *J* = 1.4 Hz, 2H), 2.54 (td, *J* = 7.5, 1.2 Hz, 4H), 1.62 (tt, *J* = 8.8, 6.8 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.4 (2C), 141.3 (2C), 128.4 (4C), 127.4 (2C), 126.3 (4C), 112.6 (2C), 34.9 (2C), 26.7.
IR (ATR): ν = 3080, 3054, 3023, 2937, 2864, 1625, 1600, 1574, 1494, 1443, 1301, 1074, 1027, 891, 775, 699, 536 cm^{-1}.
GC-MS (EI): calculated for $C_{19}H_{20}^{+}$ $[M]^{+}$: 248.2; found: 248.1.

((1*E*,1'*E*)-Oxybis(prop-1-ene-3,1-diyl))dibenzene (3b)



3b
Chemical Formula: $C_{18}H_{18}O$
Molecular Weight: 250.34

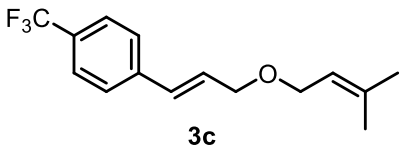
NaH (60% suspension in mineral oil, 167 mg, 4.18 mmol, 1.85 equiv) was added to a solution of (*E*)-3-phenylprop-2-en-1-ol (303 mg, 2.26 mmol, 1.00 equiv) in dry THF (6.7 mL). The suspension was stirred for 40 min, was then cooled to 0 °C and (*E*)-(3-bromoprop-1-en-1-yl)benzene) (494 mg, 2.51 mmol, 1.11 equiv) was added. The reaction mixture was allowed

to warm to ambient temperature and stirred for 25 h. The mixture was quenched with NH_4Cl (sat., aq., 3 mL) and extracted with Et_2O (2×10 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo.* Purification by flash column chromatography (SiO_2, 55:2 Pentane:EtOAc) afforded the title compound as a colourless oil (351 mg, 1.40 mmol, 61%).

Data were consistent with that reported.[19]

***R*$_f$** = 0.45 (55:2 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.45–7.19 (m, 10H), 6.65 (dt, *J* = 15.9, 1.5 Hz, 2H), 6.34 (dt, *J* = 15.9, 6.0 Hz, 2H), 4.22 (dd, *J* = 6.0, 1.4 Hz, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 136.9 (2C), 132.8 (2C), 128.7 (4C), 127.8 (2C), 126.7 (4C), 126.2 (2C), 70.9 (2C).

(*E*)-1-(3-((4-Methylpent-3-en-1-yl)oxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene (3c)



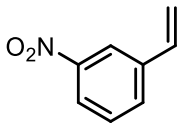
3c
Chemical Formula: $C_{15}H_{17}F_3O$
Molecular Weight: 270.30

NaH (60% suspension in mineral oil, 101 mg, 2.53 mmol, 1.71 equiv) was added to dry THF (4.5 mL). The suspension was stirred for 5 min. (*E*)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol (**S10**) (300 mg, 1.48 mmol, 1.00 equiv) was added and the suspension was stirred for 30 min before being cooled to 0 °C. 1-Bromo-3-methylbut-2-ene (246 mg, 1.65 mmol, 1.12 equiv) was added dropwise and the reaction mixture was then allowed to warm to room temperature and stirred for 19 h. The reaction was quenched by addition of NH_4Cl (sat., aq., 1 mL). The aqueous phase was separated and extracted with Et_2O (2×4 mL). The combined organic phases were washed with brine (10 mL), and dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography (SiO_2, 97:3 Pentane:EtOAc) afforded the title compound as a pale yellow liquid (188 mg, 0.700 mmol, 47%).

Data were consistent with that reported.[20]

***R*$_f$** = 0.2 (97:3 Pentane:EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.56 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.40 (dt, *J* = 16.0, 5.6 Hz, 1H), 5.40 (t, J = 6.8 Hz, 1H), 4.15 (d, *J* = 5.7 Hz, 2H), 4.03 (d, *J* = 7.0 Hz, 2H), 1.77 (s, 3H), 1.70 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 140.5, 137.6, 130.6, 129.4, 126.7 (2C), 125.7 (2C), 121.0, 70.3, 67.1, 26.0, 18.2. Signals corresponding to 2 carbon atoms could not be resolved.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ/ppm = 62.5.
IR (ATR): ν = 2973, 2917, 2854, 1615, 1448, 1416, 1378, 1362, 1322, 1163, 1118, 1065, 1015, 967, 855, 787, 724, 682, 650, 596 cm^{-1}.
GC-MS (EI): calculated for $C_{15}H_{17}F_3O^+$ $[M]^+$: 270.1; found: 270.1.

3-Nitrostyrene (S1)



S1

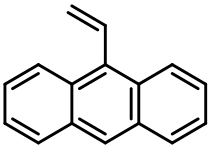
Chemical Formula: $C_8H_7NO_2$
Molecular Weight: 149.15

Prepared according to **GP1** using 3-nitrobenzaldehyde (2.00 g, 13.2 mmol, 1.0 equiv) in CH_2Cl_2 (40 mL), methyltriphenylphosphonium bromide (9.46 g, 26.5 mmol, 2.0 equiv) and DBU (4.43 g, 29.1 mmol, 2.2 equiv) in CH_2Cl_2 (130 mL). Purification by flash column chromatography (SiO_2, 95:5 Pentane:EtOAc) afforded the title compound as a light yellow oil (1.54 g, 10.3 mmol, 78%).

Data were consistent with that reported.[7]

R_f = 0.42 (95:5 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.28–8.21 (m, 1H), 8.10 (dd, *J* = 8.5, 1.7 Hz, 1H) 7.70 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.90 (d, *J* = 17.6 Hz, 1H), 5.44 (d, *J* = 10.9 Hz, 1H)
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.8, 139.4, 134.9, 132.2, 129.6, 122.6, 121.0, 117.2.

9-Vinylanthracene (S4)



S4

Chemical Formula: $C_{16}H_{12}$
Molecular Weight: 204.27

Prepared according to **GP2** using 9-anthracenecarboxaldehyde (1.88 g, 9.10 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (3.90 g, 10.9 mmol, 1.2 equiv) and KO*t*Bu (1.23 g, 10.9 mmol, 1.2 equiv) in dry THF (21 mL). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a yellow solid (1.04 g, 5.09 mmol, 55%).

Data were consistent with that reported.[21]

R_f = 0.3 (Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = δ 8.39 (s, 1H), 8.35–8.30 (m, 2H), 8.03–7.98 (m, 2H), 7.53–7.44 (m, 5H), 6.02 (dd, *J* = 11.5, 2.1 Hz, 1H), 5.63 (dd, *J* = 17.9, 2.1 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 133.8, 133.7, 131.6 (2C), 129.4 (2C), 128.7 (2C), 126.5, 126.1 (2C), 125.5 (2C), 125.3 (2C), 123.1.

Vinylferrocene (S5)

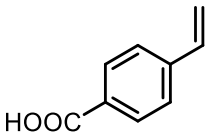
S5
Chemical Formula: $C_{12}H_{12}Fe$
Molecular Weight: 212.07

Prepared according to **GP2** using ferrocenecarboxaldehyde (2.50 g, 11.7 mmol, 1.0 equiv), methyltriphenylphosphonium bromide (5.01 g, 14.0 mmol, 1.2 equiv) and KO*t*Bu (1.57 g, 14.0 mmol, 1.2 equiv) in dry THF (27 mL). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a brown-red solid (1.81 g, 8.53 mmol, 73%).

Data were consistent with that reported.[22]

R_f = 0.36 (Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 6.45 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.34 (dd, *J* = 17.5, 1.6 Hz, 1H), 5.02 (dd, *J* = 10.7, 1.6 Hz, 1H), 4.35 (t, *J* = 1.9 Hz, 2H), 4.21 (t, *J* = 1.9 Hz, 2H), 4.10 (s, 5H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 134.8, 111.2, 83.7, 69.4 (5C), 68.8 (2C), 66.8 (2C).

4-Vinylbenzoic acid (S6)



S6
Chemical Formula: $C_9H_8O_2$
Molecular Weight: 148.16

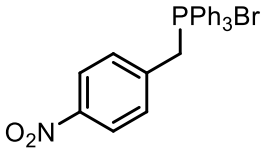
A two neck round bottom flask equipped was equipped with a condenser with an inlet to a vacuum manifold and charged with magnesium shavings (2.10 g, 86.6 mmol, 1.2 equiv). After flame drying (3×) under vacuum and three evacuation and argon backfilling cycles, tetrahydrofuran (120 mL, 0.6 M with respect to 4-chlorostyrene) alongside an iodine crystal or 0.1 mL of 1,2-dibromoethane was added. Then, 4-chlorostyrene (10.0 g 72.2 mmol, 1.0 equiv) was added dropwise and the mixture was heated to 90 °C oil bad temperature, which resulted in a black suspension. The reaction was allowed to further stir for 1 hour at this temperature. Subsequently, the solution was cooled to 0 °C with an ice bath. An excess of CO_2 was generated in an Erlenmeyer flask by sublimation of dry ice and was transferred to the reaction flask *via* cannula for 2.5 h. The reaction mixture was diluted with HCl (1 M, aq., 120 mL) and extracted with EtOAc (3×120 mL) The combined organic phases were washed with NaOH (1 M, aq., 3×120 mL). To the collected aqueous phases was added an excess of HCl (conc., aq.) solution until no more solid separated out of solution. The solid was filtered and

dissolved in EtOAc. After drying over anhydrous $MgSO_4$, filtration and concentration *in vacuo*, the title compound was afforded as a white solid (9.23 g, 62.3 mmol, 86%).

Data were consistent with that reported.[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 8.08 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 6.78 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.90 (d, *J* = 17.6 Hz, 1H), 5.42 (d, *J* = 10.9 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ/ppm = 171.7, 143.0, 136.1, 130.7 (2C), 128.5, 126.4 (2C), 117.1.

(4-Nitrobenzyl)triphenylphosphonium bromide (S7)



S7

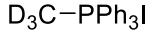
Chemical Formula: $C_{25}H_{21}BrNO_2P$
Molecular Weight: 478.33

A round bottom flask was charged with 4-nitrobenzyl bromide (10.0 g, 46.3 mmol, 1 equiv), triphenylphosphine (12.1 g, 46.3 mmol, 1 equiv) and toluene (164 mL, 0.28 mM). The solution was stirred at reflux for 12 h. The reaction was cooled to room temperature and concentrated *in vacuo*. The title compound was obtained as a light-yellow solid (21.8 g, 45.6 mmol, 98 %) and was used directly without further purification.

Data were consistent with that reported.[23]

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.90–7.72 (m, 11H), 7.66–7.57 (m, 6H), 7.48–7.42 (m, 2H), 5.95 (d, *J* = 15.6 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 147.6 (d, *J* = 4.4 Hz), 135.8 (d, J = 8.7 Hz), 135.3 (d, *J* = 3.0 Hz, 3C), 134.6 (d, *J* = 9.9 Hz, 6C), 133.0 (d, *J* = 5.3 Hz, 2C), 130.4 (d, *J* = 12.9 Hz, 6C), 123.5 (d, *J* = 3.3 Hz, 3C), 117.5 (d, *J* = 86.1 Hz, 2C), 30.2 (d, *J* = 46.9 Hz).
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ/ppm = 21.2.

(Methyl)triphenylphosphonium iodide-d_3 (S8)



S8

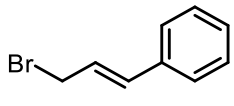
Chemical Formula: $C_{19}H_{15}D_3IP$
Molecular Weight: 407.25

CD_3I (1.00 g, 6.90 mmol, 1.2 equiv) was added to a suspension of PPh_3 (1.51 g, 5.75 mmol, 1.0 equiv.) in anhydrous THF (11.5 mL). The reaction mixture was stirred at room temperature for 30 min and afterwards refluxed for 1.5 h. The solid was filtered off and washed with small portions of Et_2O (60 mL in total). After drying, the title compound was obtained as a white solid (2.16 g, 5.30 mmol, 92%).

Data were consistent with that reported.[24]

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.90–7.61 (m, 15H).
^{2}H NMR (77 MHz, $CDCl_3$) δ/ppm = 3.24.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 135.4 (d, *J* = 3.1 Hz, 3C), 133.6 (6C), 133.5 (6C), 130.7 (d, *J* = 12.9 Hz, 3C), 119.1 (d, *J* = 88.8 Hz).
^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ/ppm = 21.5.

(*E*)-(3-Bromoprop-1-en-1-yl)benzene (S9)



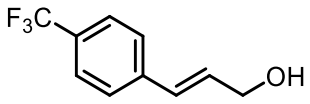
S9
Chemical Formula: C_9H_9Br
Molecular Weight: 197.08

HBr (48%, aq., 51 mL) was added to (*E*)-3-phenylprop-2-en-1-ol (3.00 g, 22.4 mmol, 1.0 equiv) at 0 °C. The suspension was allowed to warm to ambient temperature and stirred for 18 h before being quenched with Na_2CO_3 (sat., aq.). The reaction mixture was extracted with EtOAc (2×50 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The resulting brown solid (3.53 g, 17.9 mmol, 80%) was used without further purification.

Data were consistent with that reported.[25]

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.47–7.19 (m, 5H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.40 (dt, *J* = 15.5, 7.8, 1H), 4.17 (d, *J* = 7.7 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 136.0, 134.7, 128.8 (2C), 128.5, 126.9 (2C), 125.4, 33.4.

(*E*)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol (S10)



S10
Chemical Formula: $C_{10}H_9F_3O$
Molecular Weight: 202.18

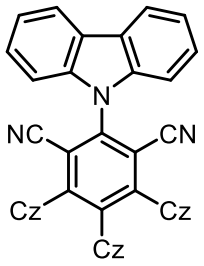
A solution of Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (**1p**) (1.02 g, 4.19 mmol, 1.0 equiv) in CH_2Cl_2 (19.5 mL) was cooled to –78 °C. DIBAL-H (8.31 mL, 1 M in hexanes, 8.31 mmol, 1.98 equiv) was added dropwise and the yellow solution was stirred for 1.5 h. The reaction was quenched by addition of NaOH (1 M, aq., 28 mL). The mixture was allowed to warm to room temperature and stirred for 1 h. The aqueous phase was separated and extracted with CH_2Cl_2 (55 mL). The combined organic phases were washed with brine (185 mL), dried over

anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to afford the title compound as a colourless solid (0.671 g, 3.32 mmol, 79%), which was used without further purification.

Data were consistent with that reported.[26]

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.57 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 6.67 (dt, *J* = 16.0, 1.7 Hz, 1H), 6.46 (dt, *J* = 15.9, 5.4 Hz, 1H), 4.37 (dd, *J* = 5.3, 1.7 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 140.3, 131.4, 129.8, 129.5, 126.7 (2C), 125.7 (2C), 123.0, 63.5.
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): –62.5.

2,4,5,6-Tetrakis(9H-carbazol-9-yl) isophthalonitrile (4CzIPN)



Chemical Formula: $C_{56}H_{32}N_6$
Molecular Weight: 788.89

A solution of carbazole (2.21 g, 13.2 mmol, 4.4 equiv) in dry THF (27 mL) was cooled to 0 °C. NaHMDS (2 M in THF, 6.30 mL, 12.6 mmol, 4.2 equiv) was added and the solution was stirred for 5 min. The cooling bath was removed and the reaction mixture allowed to warm to room temperature and stirred for 30 min. Tetrafluoroisophthalonitrile (600 mg, 3.00 mmol, 1.0 equiv) was added and the reaction mixture stirred at 65°C for 72 h. The reaction mixture was cooled to room temperature and filtered through a fritted glass filter funnel. The brown solid was washed with Et_2O until a bright yellow solid remained, which was extracted with $CHCl_3$. After concentration of the $CHCl_3$ filtrate *in vacuo*, the title compound was obtained as a bright yellow powder (1.95 g, 2.47 mmol, 82%).

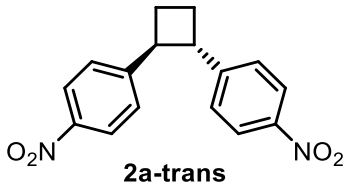
Data were consistent with that reported.[27]

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.28–8.18 (m, 2H), 7.78–7.60 (m, 8H), 7.49 (ddd, *J* = 8.0, 6.2, 2.0 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.27–7.16 (m, 5H), 7.14–7.03 (m, 7H), 6.90–6.77 (m, 4H), 6.64 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ/ppm = 145.4 (2C), 144.8, 140.1 (2C), 138.3 (2C), 137.1 (2C), 134.9, 127.1 (2C), 125.9 (4C), 125.1 (2C), 124.9 (2C), 124.7 (2C), 124.0 (2C), 122.5 (2C), 122.1 (4C), 121.5 (2C), 121.1 (2C), 120.6 (4C), 119.8 (2C), 116.5 (2C), 111.7 (2C), 110.1 (4C), 109.61 (2C), 109.55 (2C).

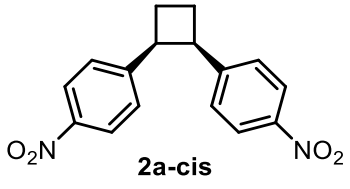
7 Synthesis of Cyclobutanes

General Procedure 4 (GP4): 2+2 Cycloaddition.
A 10 mL Schlenk tube was charged with alkene (1 equiv), 4CzIPN (0.5–1 mol%) and anhydrous THF (4 M with respect to the alkene) and the reaction mixture was subsequently deoxygenated by three freeze-pump-thaw cycles. The reaction mixture was irradiated with 456 nm LEDs for 48 h (or as indicated). See general information for details of the experimental setup. The reaction was concentrated *in vacuo* and directly purified by flash column chromatopraphy (SiO_2) to afford the title compound(s).

1,2-bis(4-Nitrophenyl)cyclobutane (2a)



2a-trans
Chemical Formula: $C_{16}H_{14}N_2O_4$
Molecular Weight: 298.30



2a-cis
Chemical Formula: $C_{16}H_{14}N_2O_4$
Molecular Weight: 298.30

Prepared according to **GP4**: 4-vinylnitrobenzene (**1a**) (149 mg, 1.00 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 9:1 Pentane:EtOAc) afforded the title compound as a mixture of diastereomers as a yellow solid (89.0 mg, 0.298 mmol, 59%).

A sufficient quantity of **2a-trans** could be isolated by flash column chromatography for analytical purposes. A pure sample of **2a-cis** could be obtained by recrystallization from CH_2Cl_2 for analytical purposes.

2a-trans

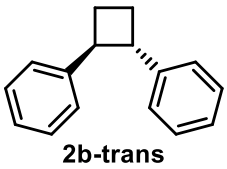
R_f = 0.18 (9:1 Pentane:EtOAc).
M.P. = 78–79 °C (CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 8.18 (d, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 8.2 Hz, 4H), 3.75–3.62 (m, 2H), 2.52–2.39 (m, 2H), 2.32–2.15 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 151.0 (2C), 146.9 (2C), 127.5 (4C), 124.1 (4C), 47.8 (2C), 25.9 (2C).
IR (ATR): ν = 3107, 3077, 3006, 2975, 2947, 2912, 1599, 1506, 1339, 1327, 851, 694 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{16}H_{14}N_2O_4Na^+$ $[M+Na]^+$: 321.0846; found: 321.0848.

2a-cis

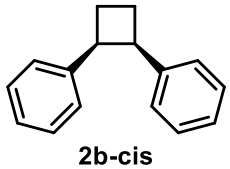
R_f = 0.10 (9:1 Pentane:EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.97 (d, *J* = 7.1 Hz, 4H), 7.10 (d, *J* = 7.0 Hz, 4H), 4.26–4.16 (m, 2H), 2.71–2.58 (m, 2H), 2.58–2.45 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.7 (2C), 146.4 (2C), 128.5 (4C), 123.5 (4C), 45.2 (2C), 24.2 (2C).

IR (ATR): ν = 2991, 2962, 2919, 1605, 1597, 1520, 1342, 1108, 851, 706, 698 cm^{-1}.
HRMS (ESI^+) calculated for $C_{16}H_{14}N_2O_4Na^+$ $[M+Na]^+$: 321.0846; found: 321.0850.

1,2-Diphenylcyclobutane (2b)



2b-trans
Chemical Formula: $C_{16}H_{16}$
Molecular Weight: 208.30



2b-cis
Chemical Formula: $C_{16}H_{16}$
Molecular Weight: 208.30

Prepared according to **GP4**: Styrene (**1b**) (108 mg, 1.04 mmol, 1 equiv), 4CzIPN (4 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 3.8:1 (trans:cis) mixture of diastereomers as colourless liquid (62.0 mg, 0.290 mmol, 56%).

NMR signals for **2b-cis** were extracted from spectra containing both diastereomers. Purification by HPLC (80:20 MeCN/H_2O, isocratic for 20 min; 1.0 mL/min, 295 K (prep 21.0 mL/min, 295K)) afforded **2b-trans** as a colourless oil for analytical purposes.

Data were consistent with that reported.[28]

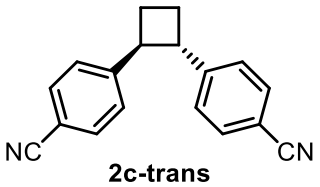
2b-trans

R_f = 0.20 (Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.35–7.16 (m, 10H), 3.70–3.51 (m, 2H), 2.42–2.26 (m, 2H), 2.23–2.06 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 144.7 (2C), 128.4 (4C), 126.8 (4C), 126.2 (2C), 48.0 (2C), 26.1 (2C).
IR (ATR): ν = 3081, 3059, 3025, 2972, 2939, 2908, 2866, 1394, 749, 696 cm^{-1}.

2b-cis

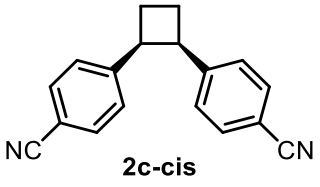
R_f = 0.20 (Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.12–7.06 (m, 4H), 7.05–6.99 (m, 2H), 6.97–6.92 (m, 4H), 4.08–3.98 (m, 2H), 2.54–2.42 (m, 4H)
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 141.6 (2C), 128.1 (4C), 127.8 (4C), 125.7 (2C), 45.4 (2C), 24.3 (2C).

4,4'-(Cyclobutane-1,2-diyl)dibenzonitrile (2c)



2c-trans

Chemical Formula: $C_{18}H_{14}N_2$
Molecular Weight: 258.32



2c-cis

Chemical Formula: $C_{18}H_{14}N_2$
Molecular Weight: 258.32

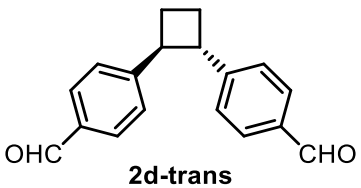
Prepared according to **GP4**: 4-Vinylbenzonitrile (**1c**) (131 mg, 1.00 mmol, 1 equiv), 4CzIPN (4 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 40 h. Purification by flash column chromatography (SiO_2, 9:1 Pentane/EtOAc) afforded **2c-trans** (72.1 mg, 0.279, 55%) and **2c-cis** as viscous yellow oils (25.6 mg, 99.0 µmol, 19%).

2c-trans

R_f = 0.22 (9:1 Pentane/EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.60 (dd, *J* = 8.3 Hz, 4H), 7.29 (dd, *J* = 8.3 Hz, 4H), 3.65-3.57 (m, 2H), 2.45 2.34 (m, 2H), 2.25 2.14 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 149.0 (2C), 132.5 (4C), 127.4 (4C), 119.0 (2C), 110.5 (2C), 47.8 (2C), 25.8 (2C).
IR (ATR): ν = 2973, 2943, 2868, 2225, 1605, 1504, 829, 555 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{18}H_{14}N_2Na^+$ $[M+Na]^+$: 281.1049; found: 281.1045.

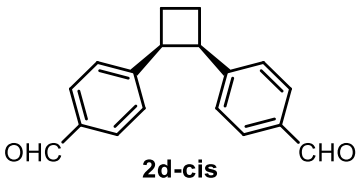
2c-cis
R_f = 0.09 (9:1 Pentane/EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.39 (d, *J* = 8.4 Hz, 4H), 7.01 (d, *J* = 8.4 Hz, 4H), 4.20–4.06 (m, 2H), 2.62–2.50 (m, 2H), 2.50–2.37 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 146.5 (2C), 131.9 (4C), 128.5 (4C), 118.9 (2C), 110.0 (2C), 45.3 (2C), 23.9 (2C).
IR (ATR): ν = 2980, 29478, 2880, 2226, 1606, 841, 748, 567, 556 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{18}H_{14}N_2Na^+$ $[M+Na]^+$: 281.1040; found: 281.1057.

4,4'-(Cyclobutane-1,2-diyl)dibenzaldehyde (2d)



2d-trans

Chemical Formula: $C_{18}H_{16}O_2$
Molecular Weight: 264.32



2d-cis

Chemical Formula: $C_{18}H_{16}O_2$
Molecular Weight: 264.32

Prepared according to **GP4**: 4-Vinylbenzaldehyde (**1d**) (131 mg, 0.987 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 1:4 Pentane:CH_2Cl_2) afforded the title

compounds **2d-trans** as a colourless liquid (90.0 mg, 0.341 mmol, 68%) and **2d-cis** as a colourless liquid (24.0 mg, 91.0 µmol, 18%).

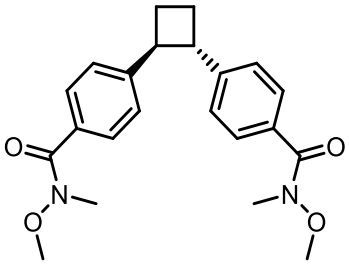
2d-trans

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 9.98 (s, 2H), 7.83 (d, *J* = 8.1 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 3.77–3.57 (m, 2H), 2.48–2.34 (m, 2H), 2.31–2.14 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 192.0 (2C), 151.1 (2C), 135.1(2C), 130.2(4C), 127.4(4C), 48.1(2C), 25.9(2C).
IR (ATR): ν = 3024, 2977, 2943, 2863, 2826, 2731, 1693, 1603, 1207, 1167, 826, 751 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{18}H_{17}O_2^+$ $[M+H]^+$: 265.1223; found: 265.1222.

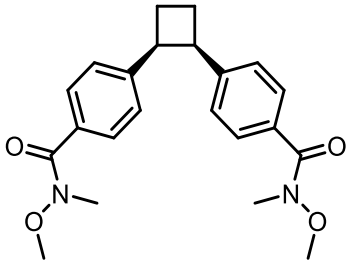
2d-cis

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 9.85 (s, 2H), 7.60 (d, *J* = 8.1 Hz, 4H), 7.10 (d, *J* = 8.0 Hz, 4H), 4.25–4.09 (m, 2H), 2.67–2.42 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 192.0 (2C), 148.5 (2C), 134.5 (2C), 129.6 (4C), 128.5 (4C), 45.7 (2C), 24.1 (2C).
IR (ATR): ν = 2947, 2828, 2733, 1693, 1604, 1572, 1211, 1168, 831, 743 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{18}H_{17}O_2^+$ $[M+H]^+$: 265.1223; found: 265.1225.

4,4'-(Cyclobutane-1,2-diyl)bis(N-methoxy-N-methylbenzamide) (2e)



2e-trans
Chemical Formula: $C_{22}H_{26}N_2O_4$
Molecular Weight: 382.46



2e-cis
Chemical Formula: $C_{22}H_{26}N_2O_4$
Molecular Weight: 382.46

Prepared according to **GP4**: 4-Vinylbenzonitrile (**1e**) (129 mg, 1.00 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 1:1 Pentane/EtOAc) afforded the title compound as a mixture of diastereomers as a yellow oil (123 mg, 0.322 mmol, 64%).

A sufficient quantity of **2e-trans** and **2e-cis** could be isolated by flash column chromatography for analytical purposes.

4e-trans

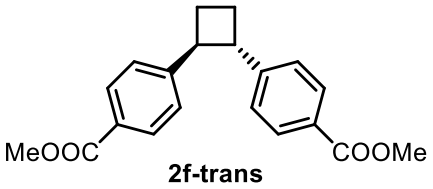
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.61 (d, *J* = 8.3 Hz, 4H), 7.25 (d, *J* = 8.3 Hz, 4H), 3.67–3.58 (m, 2H), 3.57 (s, 6H), 3.35 (6H), 2.47–2.33 (m, 2H), 2.28–2.11 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 170.3 (2C), 147.4 (2C), 132.4 (2C), 128.9 (4C), 126.7 (4C), 61.5 (2C), 48.3 (2C), 34.3 (2C), 26.2 (2C).
IR (ATR): ν = 2966, 2935, 2872, 2821, 1632, 1608, 1372, 976, 839, 754, 699, 568 cm^{-1}.
HRMS (ESI^+) calculated for $C_{22}H_{27}N_2O_4^+$ $[M+H]^+$: 383.1965; found: 383.1955.

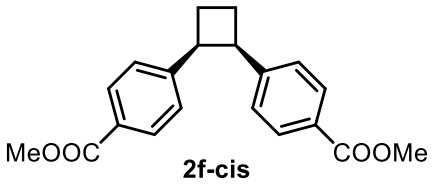
4e-cis

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.39 (d, *J* = 8.3 Hz, 4H), 6.95 (d, *J* = 8.3 Hz, 4H), 4.13 – 4.01 (m, 2H), 3.41 (s, 6H), 3.26 (s, 6H), 2.57–2.42 (m, 4H).
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 169.8 (2C), 144.2 (2C), 131.4 (2C), 127.9 (4C), 127.6 (4C), 61.0 (2C), 45.4 (2C), 33.9 (2C) 23.8 (2C).
IR (ATR): ν = 2969, 2936, 2360, 2341, 1636, 1611, 1417, 1376, 977, 848, 707 cm^{-1}.
HRMS (ESI^+) calculated for $C_{22}H_{27}N_2O_4^+$ $[M+H]^+$: 383.1965; found: 383.1963.

Dimethyl 4,4'-(cyclobutane-1,2-diyl)dibenzoate (2f)



2f-trans
Chemical Formula: $C_{20}H_{20}O_4$
Molecular Weight: 324.38



2f-cis
Chemical Formula: $C_{20}H_{20}O_4$
Molecular Weight: 324.38

Prepared according to **GP4**: Methyl 4-vinylbenzoate (**1f**) (162 mg, 1.00 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 10% → 15% EtOAc/Pentane) afforded the title compound as a mixture of diastereomers as a white solid (129 mg, 0.398 mmol, 79%).

A sufficient quantity of **2f-trans** could be isolated by flash column chromatography for analytical purposes. NMR signals for **2f-cis** were extracted from spectra containing both diastereomers.

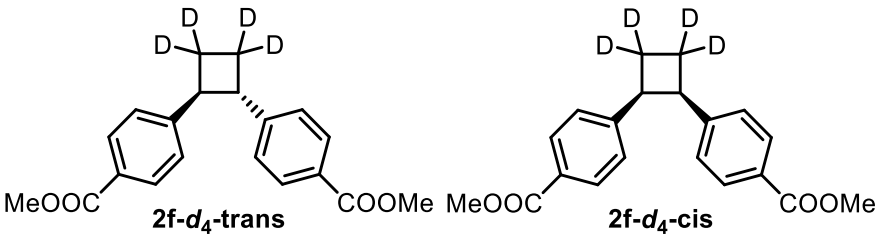
4f-trans

R_f = 0.23 (10% EtOAc/Pentane).
M.P. = 74–75 °C (CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.97 (d, *J* = 8.4 Hz, 4H), 7.27 (d, *J* = 8.4 Hz, 4H), 3.90 (s, 6H), 3.69–3.58 (m, 2H), 2.46–2.30 (m, 2H), 2.27–2.13 (m, 2H).
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ/ppm = 167.2 (2C), 149.4 (2C), 129.9 (4C), 128.4 (2C), 126.7 (4C), 52.2 (2C), 48.0 (2C), 25.8 (2C).
IR (ATR): ν = 2985, 2947, 1714, 1607, 1607, 1438, 1282, 1102, 746, 702 cm^{-1}.
HRMS (ESI^+) calculated for $C_{20}H_{21}O_4^+$ $[M+H]^+$: 325.1434; found: 325.1428.

4f-cis

R_f = 0.15 (10% EtOAc/Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.75 (d, *J* = 7.7 Hz, 4H), 6.99 (d, *J* = 7.8 Hz, 4H), 4.16–4.07 (m, 2H), 3.84 (s, 6H), 2.61–2.44 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 167.2 (2C), 146.8 (2C), 129.2 (4C), 128.4 (2C), 127.8 (4C), 52.0 (2C), 45.4 (2C), 24.2 (2C).
HRMS (ESI$^+$) calculated for $C_{20}H_{21}O_4^+$ [M+H]$^+$: 325.1434; found: 325.1433.

Dimethyl 4,4'-(cyclobutane-1,2-diyl-3,3,4,4-*d*$_4$)dibenzoate (2f-*d*$_4$)



Chemical Formula: $C_{20}H_{16}D_4O_4$
Molecular Weight: 328.40

Chemical Formula: $C_{20}H_{16}D_4O_4$
Molecular Weight: 328.40

Prepared according to **GP4**: Methyl 4-(vinyl-2,2-*d*$_2$)benzoate (**1f-d$_4$**) (162 mg, 1.00 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 10% EtOAc/Pentane) afforded the title compound as a mixture of diastereomers as a white solid (137 mg, 0.417 mmol, 83%).

A sufficient quantity of **2f-*d*$_4$-trans** could be isolated by flash column chromatography as a white solid for analytical purposes. NMR signals for **2f-*d*$_4$-cis** were extracted from spectra containing both diastereomers.

2f-*d*$_4$-trans

Incorporation of ^{2}H was estimated by ^{1}H NMR spectroscopy to be around 82%.

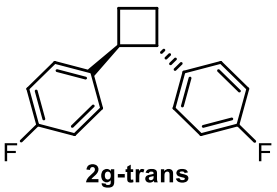
R_f = 0.23 (10% EtOAc/Pentane).
M.P. = 75–76 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.97 (d, *J* = 8.3 Hz, 4H), 7.27 (d, *J* = 8.2 Hz, 4H), 3.90 (s, 6H), 3.61 (s, 2H), 2.40–2.32 (m, 0.36 H), 2.23–2.09 (m, 0.36 H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 167.2 (2C), 149.5 (2C), 129.9 (4C), 128.4 (2C), 126.7 (4C), 52.2 (2C), 47.8 (2C), 25.3 (2C).
^{2}H NMR (77 MHz, $CDCl_3$): δ/ppm = 2.36, 2.18.
IR (ATR): ν = 3032, 2957, 2928, 2852, 1713, 1435, 1272, 1178, 1104, 765, 704 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{20}H_{17}O_4D_4^+$ [M+H]$^+$: 329.1685; found: 329.1680.

2f-*d*$_4$-cis

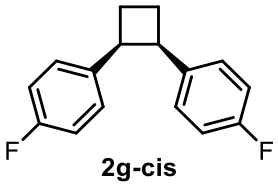
Incorporation of ^{2}H was estimated by ^{1}H NMR spectroscopy to be around 91%.

R_f = 0.15 (10% EtOAc/Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.75 (d, *J* = 8.1 Hz, 4H), 6.99 (d, *J* = 8.1 Hz, 4H), 4.16–4.07 (m, 2H), 3.84 (s, 6H), 2.61–2.44 (m, 0.34H).
^{2}H NMR (77 MHz, $CDCl_3$): δ/ppm = 2.49.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 167.1 (2C), 149.4 (2C), 129.2 (4C), 127.8 (2C), 126.7 (4C), 52.0 (2C), 45.38–44.91 (m, 2C), 23.91–22.76 (m, 2C).
HRMS (ESI$^+$) calculated for $C_{20}H_{16}O_4D_4Na^+$ $[M+Na]^+$: 351.1505; found: 351.1505.

1,2-Bis(4-fluorophenyl)cyclobutane (2g)



2g-trans
Chemical Formula: $C_{16}H_{14}F_2$
Molecular Weight: 244.28



2g-cis
Chemical Formula: $C_{16}H_{14}F_2$
Molecular Weight: 244.28

Prepared according to **GP4**: 4-Fluorostyrene (**1g**) (131 mg, 1.07 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 3.2:1 (trans:cis) mixture of diastereomers as a yellow liquid (77 mg, 0.32 mmol, 58%).

NMR signals for **2g-trans** and **2g-cis** were extracted from spectra containing both diastereomers.

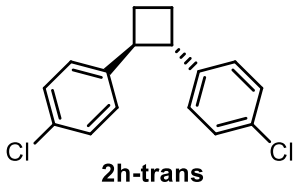
2g-trans

R_f = 0.3 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.22–7.12 (m, 4H), 7.03–6.93 (m, 4H), 3.54–3.39 (m, 2H), 2.31–2.21 (m, 2H), 2.16–1.98 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 161.6 (d, *J* = 244.1 Hz, 2H), 140.0 (d, *J* = 3.1 Hz, 2H), 128.18 (d, *J* = 7.9 Hz, 4C), 115.2 (d, *J* = 21.1 Hz, 4C), 47.8 (2C), 26.1 (2C).
^{19}F NMR (282 MHz, $CDCl_3$) δ/ppm = –117.1.
GC-MS (EI) calculated for $C_{16}H_{14}F_2^+$ $[M]^+$: 244.1; found: 244.1.

2g-cis

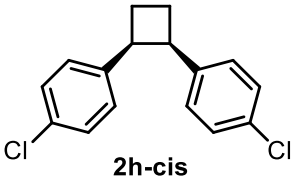
R_f = 0.3 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 6.89–6.74 (m, 8H), 4.01–3.93 (m, 2H), 2.52–2.34 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 161.2 (d, *J* = 243.5 Hz, 2H), 137.0 (d, *J* = 2.8 Hz, 2C), 128.3 (d, *J* = 7.9 Hz, 4C), 114.7 (d, *J* = 21.1 Hz, 4C), 44.6 (2C), 24.3 (2C).
^{19}F NMR (282 MHz, $CDCl_3$) δ/ppm = –117.6.
GC-MS (EI) calculated for $C_{16}H_{14}F_2^+$ $[M]^+$: 244.1; found: 244.1.

1,2-Bis(4-chlorophenyl)cyclobutane (2h)



2h-trans

Chemical Formula: $C_{16}H_{14}Cl_2$
Molecular Weight: 277.19



2h-cis

Chemical Formula: $C_{16}H_{14}Cl_2$
Molecular Weight: 277.19

Prepared according to **GP4**: 4-Chlorostyrene (**1h**) (137 mg, 0.99 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 4.1:1 (trans:cis) mixture of diastereomers as a colourless liquid (92 mg, 0.33 mmol, 67%).

Purification by HPLC (70:30 MeCN/H_2O, Gradient to 100:0 in 30 min; 1.0 mL/min, 295 K (prep 21.0 mL/min, 295K)) afforded **2h-trans** and **2h-cis** as colourless liquids for analytical purposes.

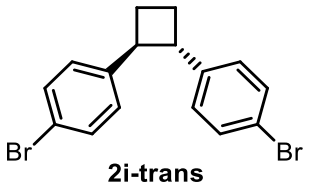
2h-trans

R_f = 0.34 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.33–7.22 (m, 4H), 7.20–7.08 (m, 4H), 3.58–3.40 (m, 2H), 2.42–2.21 (m, 2H), 2.25–2.02 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 142.7 (2C), 132.1 (2C), 128.6 (4C), 128.1 (4C), 47.7 (2C), 25.9 (2C).
IR (ATR): ν = 2973, 2943, 2869, 1490, 1090, 1012, 1012, 819, 521, 505 cm^{-1}.
GC-MS (EI) calculated for $C_{16}H_{14}Cl_2^+$ $[M]^+$: 276.0; found: 276.0.

2h-cis

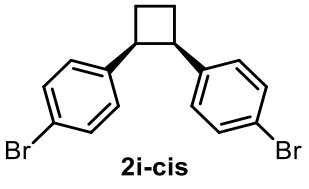
R_f = 0.34 (Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.08 (d, *J* = 8.2 Hz, 4H), 6.85 (d, *J* = 8.2 Hz, 4H), 4.01–3.90 (m, 2H), 2.54–2.43 (m, 2H), 2.40–2.23 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 139.8 (2C), 131.6 (2C), 129.3 (4C), 128.1 (4C), 44.7 (2C), 24.3 (2C).
GC-MS (EI) calculated for $C_{16}H_{14}Cl_2^+$ $[M]^+$: 276.0; found: 276.0.

1,2-Bis(4-Bromophenyl)cyclobutane (2i)



2i-trans

Chemical Formula: $C_{16}H_{14}Br_2$
Molecular Weight: 366.10



2i-cis

Chemical Formula: $C_{16}H_{14}Br_2$
Molecular Weight: 366.10

Prepared according to **GP4**: 4-Bromostyrene (**1i**) (183 mg, 1.00 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 5.4:1 (trans:cis) mixture of diastereomers as a colourless liquid (61 mg, 0.17 mmol, 33%).

NMR signals for **2i-trans** and **2i-cis** were extracted from spectra containing both diastereomers.

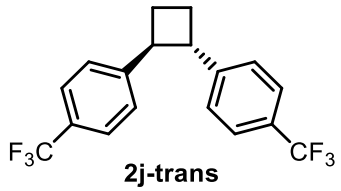
2i-trans

R_f = 0.36 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.41 (d, *J* = 8.3 Hz, 4H), 7.07 (d, *J* = 8.2 Hz, 4H), 3.51–3.37 (m, 2H), 2.41–2.21 (m, 2H), 2.17–1.99 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 143.2 (2C), 131.6 (4C), 128.5 (4C), 120.2 (2C), 47.7 (2C), 25.8 (2C).
HRMS (ESI^+) calculated for $C_{16}H_{14}Br_2Na^+$ $[M+Na]^+$: 364.9334; found: 364.9316.

2i-cis

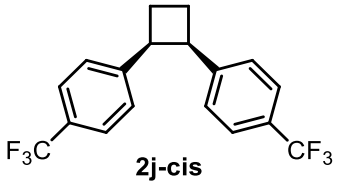
R_f = 0.36 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.23 (d, *J* = 8.4 Hz, 4H), 6.79 (d, *J* = 8.3 Hz, 4H), 4.03–3.90 (m, 2H), 2.48 (q, *J* = 5.5 Hz, 2H), 2.37–2.19 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 140.3 (2C), 131.1 (4C), 129.7 (4C), 119.7 (2C), 44.7 (2C), 24.3 (2C).
HRMS (ESI^+) calculated for $C_{16}H_{15}Br_2^+$ $[M+H]^+$: 364.9334; found: 364.9316.

1,2-Bis(4-(trifluoromethyl)phenyl)cyclobutane (2j)



2j-trans

Chemical Formula: $C_{18}H_{14}F_6$
Molecular Weight: 344.30



2j-cis

Chemical Formula: $C_{18}H_{14}F_6$
Molecular Weight: 344.30

Prepared according to **GP4**: 4-(Trifluoromethyl)styrene (**1j**) (178 mg, 1.03 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 2.9:1 (trans:cis) mixture of diastereomers as an off-white solid (89 mg, 0.26 mmol, 50%).

NMR signals for **2j-trans** and **2j-cis** were extracted from spectra containing both diastereomers.

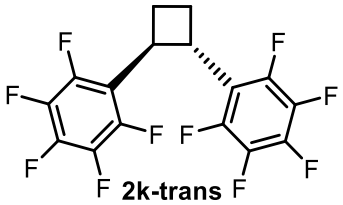
2k-trans

R_f = 0.39, 0.29 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.56 (d, *J* = 8.1 Hz, 4H), 7.32 (d, *J* = 8.1 Hz, 4H), 3.69 – 3.55 (m, 2H), 2.44 – 2.30 (m, 2H), 2.26 – 2.10 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.0 (d, *J* = 1.4 Hz, 2C), 128.8 (q, *J* = 32.3 Hz, 2C), 127.0 (4C)z, 125.6 (q, *J* = 3.7 Hz, 4C), 123.1 (2C), 47.8 (2C), 25.9 (2C).
^{19}F NMR (282 MHz, $CDCl_3$): δ/ppm = 62.4.
GC-MS (EI) calculated for $C_{18}H_{14}F_6^+$ $[M]^+$: 344.1; found: 344.0.

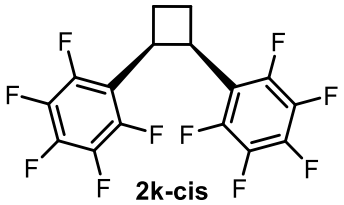
2k-cis

R_f = 0.39, 0.29 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 1H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 4H), 7.03 (d, *J* = 8.1 Hz, 4H), 4.17 – 4.06 (m, 2H), 2.61 – 2.49 (m, 2H), 2.43 – 2.31 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 145.3 (d, *J* = 1.5 Hz, 2C), 128.2 (4C), 124.9 (q, *J* = 3.8 Hz, 4C), 123.0 (2C), 120.3 (2C), 45.1 (2C), 24.3 (2C).
^{19}F NMR (282 MHz, $CDCl_3$): δ/ppm =–62.4.
GC-MS (EI) calculated for $C_{18}H_{14}F_6^+$ $[M]^+$: 344.1; found: 344.0.

1,2,3,4,5-Pentafluoro-6-(2-(2,3,5,6-tetrafluorophenyl)cyclobutyl)benzene (2k)



Chemical Formula: $C_{16}H_6F_{10}$
Molecular Weight: 388.21



Chemical Formula: $C_{16}H_6F_{10}$
Molecular Weight: 388.21

Prepared according to **GP4**: 1,2,3,4,5-Pentafluoro-6-vinylbenzene (**1k**) (199 mg, 1.02 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 3.2:1 (trans:cis) mixture of diastereomers as a colourless liquid (81.0 mg, 0.208 mmol, 41%).

NMR signals for **2k-trans** and **2k-cis** were extracted from spectra containing both diastereomers.

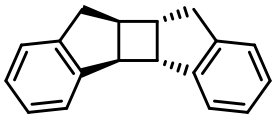
2k-trans

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 4.31–4.14 (m, 2H), 2.55–2.37 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 36.2, 26.1–26.0 (m) (further signals in the aromatic region could be seen, however no assignment of peaks was possible, due to the low sensitivity of the fluorinated carbon atoms).
^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm = -143.19 (dd, *J* = 22.3, 7.8 Hz), -156.63 (t, *J* = 20.9 Hz), -162.57 (td, *J* = 22.2, 7.9 Hz).
GC-MS (EI) calculated for $C_{16}H_6F_{10}^+$ $[M]^+$: 388.0; found: 388.1.

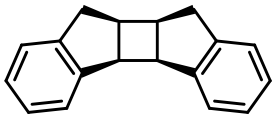
2k-cis

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 4.51–4.41 (m, 2H), 2.97–2.85 (m, 2H), 2.71–2.59 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 35.7, 24.3 – 24.1 (m) (further signals in the aromatic region could be seen, however no assignment of peaks was possible, due to the low sensitivity of the fluorinated carbon atoms).
^{19}F NMR (376 MHz, $CDCl_3$): δ/ppm = -141.98 – -142.15 (m), -155.87 (t, *J* = 21.1 Hz), -162.28 (td, *J* = 22.7, 7.9 Hz).
GC-MS (EI) calculated for $C_{16}H_6F_{10}^+$ $[M]^+$: 388.0; found: 388.0.

4b,4c,9,9a,9b,10-Hexahydrocyclobuta[1,2-a:4,3-a']diindene (2l)



2l-trans
Chemical Formula: $C_{18}H_{16}$
Molecular Weight: 232.33



2l-cis
Chemical Formula: $C_{18}H_{16}$
Molecular Weight: 232.33

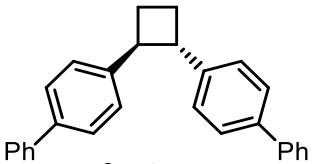
Prepared according to **GP4**: Indene (**1l**) (119 mg, 1.03 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2,Pentane) afforded the title compound as a 5.9:1 (trans:cis) mixture of diastereomers as a white solid (106 mg, 0.456 mmol, 88%).

Data were consistent with that reported.[29]

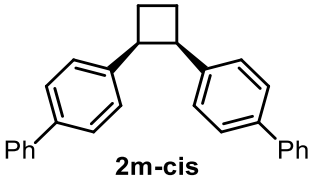
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.42 (d, *J* = 6.8 Hz, 2H), 7.34–7.20 (m, 6H), 3.71 (d, *J* = 5.5 Hz, 2H), 3.20 (dd, *J* = 16.5, 7.2 Hz, 2H), 2.95 (d, *J* = 16.5 Hz, 2H), 2.77 (dt, *J* = 7.2, 3.8 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 146.7 (2C), 144.1 (2C), 127.0 (2C), 126.9 (2C), 125.6 (2C), 125.3 (2C), 54.1 (2C), 43.3 (2C), 39.6 (2C).

Full characterisation of **2l-cis** was not possible due to small quantities of material and difficulties resolving peaks in the NMR spectra.

1,2-Di([1,1'-biphenyl]-4-yl)cyclobutane (2m)



2m-trans
Chemical Formula: $C_{28}H_{24}$
Molecular Weight: 360.50



2m-cis
Chemical Formula: $C_{28}H_{24}$
Molecular Weight: 360.50

Prepared according to **GP4**: 4-Phenylstyrene (**1m**) (180 mg, 1.00 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 99:1 Pentane:EtOAc) afforded the title compound as a 10.6:1 (trans:cis) mixture of diastereomers as a white solid (144 mg, 0.400 mmol, 79%).

Purification by HPLC (70:30 MeCN/H_2O, Gradient to 100:0 in 30 min; 1.0 mL/min, 295 K (prep 21.0 mL/min, 295K)) afforded **2m-trans** and **2m-cis** as white solids for analytical purposes.

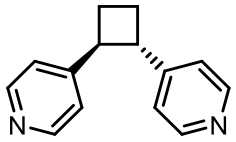
2m-trans

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.71–7.62 (m, 8H), 7.55–7.48 (m, 4H), 7.45–7.39 (m, 6H), 3.80–3.70 (m, 2H), 2.52–2.41 (m, 2H), 2.35–2.23 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 143.7 (2C), 141.2 (2C), 139.2 (2C), 128.9 (4C), 127.21 (8C), 127.18 (2C), 127.12 (4C), 47.9 (2C), 26.2 (2C).
IR (ATR): ν = 3077, 3051, 3026, 2967, 2939, 2902, 2868, 1486, 832, 760, 693 cm^{-1}.
HRMS (ESI^+) calculated for $C_{28}H_{24}Na^+$ $[M+Na]^+$: 383.1770; found: 383.178.

2m-cis

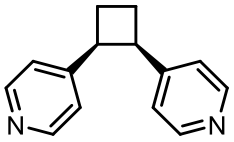
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.53–7.48 (m, 4H), 7.40–7.34 (m, 8H), 7.31–7.27 (m, 2H), 7.08–7.03 (m, 4H), 4.16–4.05 (m, 2H), 2.60–2.46 (m, 4H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ/ppm = 141.1 (2C), 140.9 (2C), 138.4 (2C), 128.7 (4C), 128.5 (4C), 127.01 (2C), 127.00 (4C), 126.5 (4C), 45.2 (2C), 24.6 (2C).
IR (ATR): ν = 3078, 3054, 3027, 2970, 2940, 2868, 1486, 838, 763, 738, 696 cm^{-1}.
HRMS (ESI^+) calculated for $C_{28}H_{24}Na^+$ $[M+Na]^+$: 383.1770; found: 383.1762.

1,2-Di(pyridin-4-yl)cyclobutane (2n)



2n-trans

Chemical Formula: $C_{14}H_{14}N_2$
Molecular Weight: 210.28



2n-cis

Chemical Formula: $C_{14}H_{14}N_2$
Molecular Weight: 210.28

Prepared according to **GP4**: 4-Vinylpyridine (**1n**) (112 mg, 1.07 mmol, 1 equiv), 4CzIPN (7.9 mg, 10.0 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h Purification by flash column chromatography (SiO_2, EtOAc → 95:5 CH_2Cl_2:MeOH) afforded the title compound as a mixture of diastereomers as a yellow liquid (70 mg, 0.33 mmol, 62%).

A sufficient quantity of **2n-trans** could be isolated by flash column chromatography for analytical purposes as a yellow solid. NMR signals for **2n-cis** were extracted from spectra containing both diastereomers.

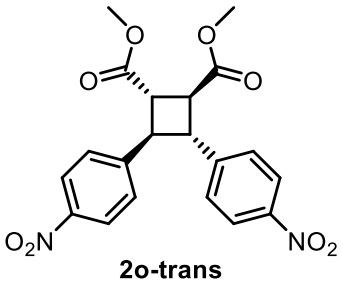
2n-trans

***R*$_f$** = 0.24 (95:5 CH_2Cl_2:MeOH).
M.P. = 42–44 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.53 (d, *J* = 5.4 Hz, 4H), 7.12 (d, *J* = 6.1 Hz, 4H), 3.67–3.48 (m, 2H), 2.48–2.31 (m, 2H), 2.26–2.04 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 152.4 (2C), 150.0 (4C), 122.0 (4C), 46.5 (2C), 25.4 (2C).
IR (ATR): ν = 3067, 3024, 2990, 2973, 2947, 2912, 2867, 1594, 1411, 827, 814, 644, 555, 528 cm^{-1}.
HRMS (ESI^+) calculated for $C_{14}H_{15}N_2^+$ $[M+H]^+$: 211.1230; found: 211.1237.

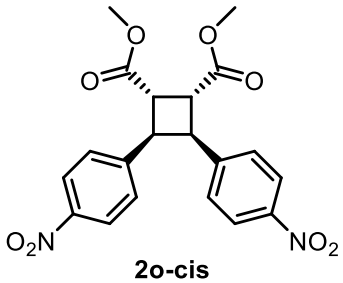
2n-cis

R_f = 0.13 (95:5 CH_2Cl_2:MeOH).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.33 (s, 4H), 6.85 (d, *J* = 5.7 Hz, 4H), 4.16–3.98 (m, 2H), 2.66–2.36 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 149.8 (2C), 149.5 (4C), 123.1 (4C), 44.3 (2C), 23.6 (2C).
IR (ATR): ν = 3068, 3025, 2980, 2949, 2876, 1598, 1415, 829, 828, 537 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{14}H_{15}N_2^+$ [M+H]$^+$: 211.1230; found: 211.1229.

Dimethyl 3,4-bis(4-nitrophenyl)cyclobutane-1,2-dicarboxylate (2o)



2o-trans
Chemical Formula: $C_{20}H_{18}N_2O_8$
Molecular Weight: 414.37



2o-cis
Chemical Formula: $C_{20}H_{18}N_2O_8$
Molecular Weight: 414.37

Prepared according to **GP4**: Methyl (*E*)-3-(4-nitrophenyl)acrylate (**1o**) (207 mg, 1.00 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.5 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 7:3 Pentane/EtOAc) afforded the title compound **2o-trans** as a yellow oil (177 mg, 282 mmol, 56%) and **2o-cis** as a yellow oil (77.0 mg, 0.186 mmol, 37%).

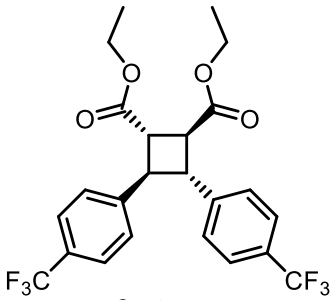
2o-trans

R_f = 0.13 (7:3 pentane:EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 8.22 (d, *J* = 8.8 Hz, 4H), 7.45 (d, *J* = 8.8 Hz, 4H), 3.86–3.82 (m, 2H), 3.78 (s, 6H), 3.58–3.52 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 172.1 (2C), 147.5 (2C), 147.4 (2C), 127.8 (4C), 124.4 (4C), 52.8 (2C), 46.8 (2C), 44.4 (2C).
IR (ATR): ν = 3112, 3080, 3000, 2952, 2848, 1730, 1514, 1346, 855, 729, 704 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{20}H_{19}N_2O_8^+$ [M+H]$^+$: 437.0955; found: 437.0953.

2o-cis

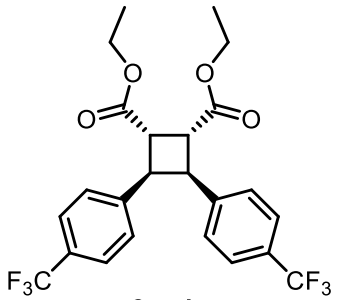
R_f = 0.13 (9:1 pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): 8.01 (d, *J* = 8.8 Hz, 4H), 7.10 (d, *J* = 8.7 Hz, 4H), 4.61–4.55 (m, 2H), 3.91–3.86 (m, 2H), 3.79 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 172.0 (2C), 147.0 (2C), 145.5 (2C), 128.6 (4C), 123.8 (4C), 52.7 (2C), 44.9 (2C), 43.2 (2C).
IR (ATR): ν = 3112, 3080, 3005, 3953, 2851, 2851, 1727, 1515, 1342, 851, 827, 748, 695 cm^{-1}.
HRMS (ESI$^+$) calculated for $C_{20}H_{19}N_2O_8^+$ [M+H]$^+$: 437.10; found: 437.20.

Diethyl 3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (2p)



2p-trans

Chemical Formula: $C_{24}H_{22}F_6O_4$
Molecular Weight: 488.43



2p-cis

Chemical Formula: $C_{24}H_{22}F_6O_4$
Molecular Weight: 488.43

Prepared according to **GP4**: ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (**1p**) (245 mg, 1.00 mmol, 1 equiv), 4CzIPN (7.9 mg, 10.0 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 9:1 Pentane/EtOAc) afforded the title compounds **2p-trans** as an off white solid (161 mg, 0.330 mmol, 65%) and **2p-cis** as a yellow oil (65.0 mg, 0.133 mmol, 26%).

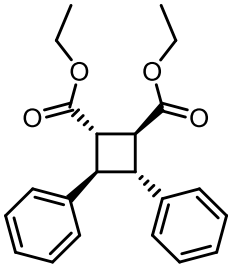
2p-trans

R_f = 0.36 (9:1 pentane:EtOAc).
M.P. = 75–76 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.60 (d, *J* = 8.2 Hz, 4H), 7.40 (d, *J* = 8.1 Hz, 4H), 4.22 (q, *J* = 7.1 Hz, 4H), 3.85–3.76 (m, 2H), 3.54–3.41 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 172.1 (2C), 144.7 (2C), 129.7 (d, *J* = 32.6 Hz, 2C), 127.31 (4C), 125.9 (q, *J* = 3.8 Hz, 4C), 122.8 (2C, corroborated by HMBC), 61.5 (2C), 46.7 (2C), 44.8 (2C), 14.4 (2C).
^{19}F NMR (282 MHz, $CDCl_3$): δ/ppm = –62.56.
IR (ATR): ν = 3001, 2969, 2953, 2933, 2907, 2880, 1717, 1321, 1162, 1114, 1066, 1013, 831 cm^{-1}.
HRMS (ESI^+) calculated for $C_{24}H_{23}O_4F_6^+$ $[M+H]^+$: 511.1314; found: 511.1312.

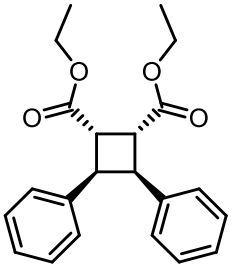
2p-cis

R_f = 0.18 (9:1 pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.39 (d, *J* = 8.1 Hz, 4H), 7.03 (d, *J* = 8.0 Hz, 4H), 4.51–4.45 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 4H), 3.85–3.79 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 6H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ/ppm = 171.9 (2C), 142.2 (2C), 128.1 (4C), 125.3 (q, *J* = 3.9 Hz, 4C), 122.3 (2C, corroborated by HMBC), 61.5 (2C), 44.7 (2C), 43.5 (2C), 14.3 (2C). One signal corresponding to two carbon atoms could not be resolved.
^{19}F NMR (282 MHz, $CDCl_3$): δ/ppm = –62.61.
IR (ATR): ν = 2985, 2939, 2907, 2873, 1730, 1322, 1161, 1110, 1066, 1016, 831 cm^{-1}.
HRMS (ESI^+) calculated for $C_{24}H_{23}O_4F_6^+$ $[M+H]^+$: 511.1314; found: 511.1308.

Diethyl 3,4-diphenylcyclobutane-1,2-dicarboxylate (2q)



2q-trans
Chemical Formula: $C_{22}H_{24}O_4$
Molecular Weight: 352.43



2q-cis
Chemical Formula: $C_{22}H_{24}O_4$
Molecular Weight: 352.43

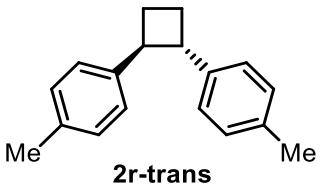
Prepared according to **GP4**: (*E*)-Ethyl cinnamate (**1q**) (178 mg, 1.01 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, 9:1 Pentane/EtOAc) afforded **2q-trans** as a single diastereomer as a colourless liquid (141 mg, 0.400 mmol, 78%).

2q-trans

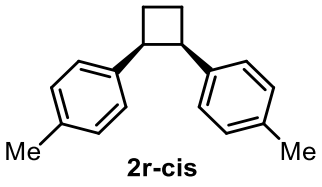
R_f = 0.39 (9:1 pentane:EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.27 (d, *J* = 6.7 Hz, 6H), 7.22–7.17 (m, 4H), 4.15 (q, *J* = 7.0 Hz, 4H), 3.75–3.67 (m, 2H), 3.43–3.37 (m, 2H), 1.22 (td, *J* = 7.1, 1.3 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 172.7 (2C), 141.3 (2C), 128.7 (4C), 127.2 (2C), 127.0 (4C), 61.1 (2C), 47.1 (2C), 45.0 (2C), 14.4 (2C).
IR (ATR): ν = 3088, 3061, 3029, 2980, 2936, 2904, 2872, 1723, 1199, 1156, 1031, 751, 696 cm^{-1}.
HRMS (ESI^+) calculated for $C_{22}H_{25}O_4^+$ $[M+H]^+$: 353.1747; found: 353.1746.

Full characterisation of **2q-cis** was not possible due to small quantities of material and difficulties resolving peaks in the NMR spectra.

1,2-Di-*p*-tolylcyclobutane (2r)



2r-trans
Chemical Formula: $C_{18}H_{20}$
Molecular Weight: 236.36



2r-cis
Chemical Formula: $C_{18}H_{20}$
Molecular Weight: 236.36

Prepared according to **GP4**: 4-Methylstyrene (**1r**) (117 mg, 1.00 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 6.5:1 (trans:cis) mixture of diastereomers as a colourless liquid (62 mg, 0.26 mmol, 52%).

Purification by HPLC (70:30 MeCN/H_2O, Gradient to 100:0 in 30 min; 1.0 mL/min, 295 K (prep 21.0 mL/min, 295K)) afforded **2r-trans** and **2r-cis** as colourless liquids for analytical purposes.

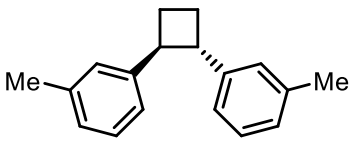
2r-trans

R_f = 0.24 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.19 – 7.09 (m, 8H), 3.59–3.45 (m, 2H), 2.35–2.26 (m, 8H), 2.15–2.04 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 141.8 (2C), 135.6 (2C), 129.1 (4C), 126.7 (4C), 47.9 (2C), 26.1 (2C), 21.2 (2C).
IR (ATR): ν = 3047, 3018, 2970, 2939, 2919, 2865, 1514, 810, 534, 513 cm^{-1}.
HRMS (ESI^+) calculated for $C_{18}H_{20}Na^+$ $[M+Na]^+$: 259.1457; found: 259.1447.

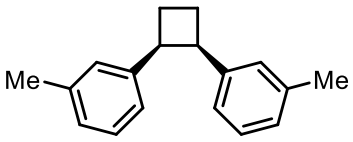
2r-cis

R_f = 0.24 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 6.91 (d, *J* = 8.2 Hz, 4H), 6.84 (d, *J* = 8.2 Hz, 4H), 3.99–3.92 (m, 2H), 2.48–2.36 (m, 4H), 2.21 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 138.8 (2C), 134.9 (2C), 128.5 (4C), 128.0 (4C), 45.0 (2C), 24.8 (2C), 21.1 (2C).
IR (ATR): ν = 3021, 2971, 2942, 2921, 2867, 1682, 1605, 1514, 819 cm^{-1}.
HRMS (ESI^+) calculated for $C_{18}H_{20}Na^+$ $[M+Na]^+$: 259.1457; found: 259.1454.

1,2-Di-*m*-tolylcyclobutane (2s)



2s-trans
Chemical Formula: $C_{18}H_{20}$
Molecular Weight: 236.36



2s-cis
Chemical Formula: $C_{18}H_{20}$
Molecular Weight: 236.36

Prepared according to **GP4**: 3-Methylstyrene (**1s**) (118 mg, 1.00 mmol, 1 equiv), 4CzIPN (3.9 mg, 5.0 µmol, 0.5 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 4.4:1 (trans:cis) mixture of diastereomers as a colourless liquid (64 mg, 0.27 mmol, 54%).

Purification by HPLC (70:30 MeCN/H_2O, Gradient to 100:0 in 30 min; 1.0 mL/min, 295 K (prep 21.0 mL/min, 295K)) afforded **2s-trans** and **2s-cis** as colourless liquids for analytical purposes.

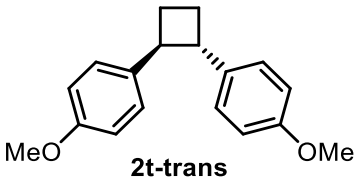
2s-trans

R_f = 0.44 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.22 (t, *J* = 7.6 Hz, 2H), 7.12–7.01 (m, 6H), 3.65–3.53 (m, 2H), 2.42–2.28 (m, 8H), 2.23–2.07 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 144.8 (2C), 138.0 (2C), 128.3 (2C), 127.5 (2C), 126.9 (2C), 123.8 (2C), 47.7 (2C), 26.2 (2C), 21.6 (2C).
IR (ATR): ν = 3018, 2961, 2939, 2918, 2863, 1605, 1488, 779, 753, 697 cm^{-1}.
HRMS (ESI^+) calculated for $C_{18}H_{20}Na^+$ $[M+Na]^+$: 259.1457; found: 259.1450.

2*s*-cis

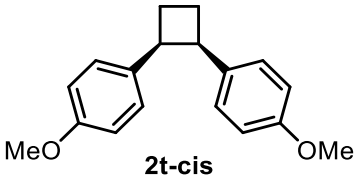
R_f = 0.44 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 6.97 (t, *J* = 7.5 Hz, 2H), 6.82 (d, *J* = 7.5 Hz, 2H), 6.77–6.70 (m, 4H), 4.00–3.91 (m, 2H), 2.48–2.35 (m, 4H), 2.18 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 141.6 (2C), 137.1 (2C), 129.0 (2C), 127.6 (2C), 126.3 (2C), 125.1 (2C), 45.3 (2C), 24.5 (2C), 21.5 (2C).
IR (ATR): ν = 3021, 2972, 2942, 2920, 2862, 1606, 789, 701, 669 cm^{-1}.
HRMS (ESI^+) calculated for $C_{18}H_{20}Na^+$ $[M+Na]^+$: 259.1457; found: 259.1445.

1,2-Bis(4-methoxyphenyl)cyclobutane (2t)



2t-trans

Chemical Formula: $C_{18}H_{20}O_2$
Molecular Weight: 268.36



2t-cis

Chemical Formula: $C_{18}H_{20}O_2$
Molecular Weight: 268.36

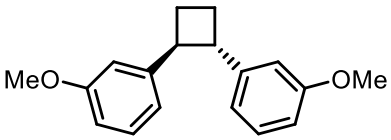
Prepared according to **GP4**: 1-methoxy-4-vinylbenzene(**1t**) (134 mg, 1.00 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 144 h. Purification by flash column chromatography (SiO_2, 95:5 Pentane:EtOAc) afforded the title compound **2t-trans** as a single diastereomer as colourless liquid (60.0 mg, 0.224 mmol, 44%).

Data were consistent with that reported.[30]

2t-trans

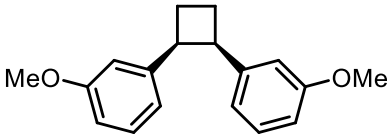
R_f = 0.34 (95:5 Pentane:EtOAc).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.15 (d, *J* = 8.6 Hz, 4H), 6.84 (d, *J* = 8.5 Hz, 4H), 3.79 (s, 6H), 3.44 (q, *J* = 8.2 Hz, 2H), 2.33–2.21 (m, 2H), 2.12–2.02 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 158.1 (2C), 136.9 (2C), 127.7 (4C), 113.8 (4C), 55.3 (2C), 47.9 (2C), 26.1 (2C).
HRMS (ESI^+) calculated for $C_{18}H_{21}O_2^+$ $[M+H]^+$: 291.1356; found: 291.1368.

1,2-Bis(3-methoxyphenyl)cyclobutane (2u)



2u-trans

Chemical Formula: $C_{18}H_{20}O_2$
Molecular Weight: 268.36



2u-cis

Chemical Formula: $C_{18}H_{20}O_2$
Molecular Weight: 268.36

Prepared according to **GP4**: 1-Methoxy-3-vinylbenzene (**1u**) (136 mg, 1.01 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 48 h. Purification by flash column chromatography (SiO_2,) afforded the title compound as a 2.8:1 (trans:cis) mixture of diastereomers as a colourless liquid (61.8 mg, 0.231 mmol, 45%).

NMR signals for **2u-trans** and **2u-cis** were extracted from spectra containing both diastereomers.

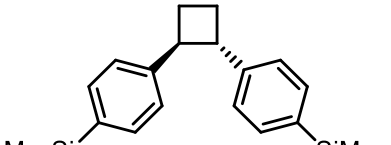
2u-trans

R_f = 0.38 (96:4 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.21 (t, *J* = 7.8 Hz, 2H), 6.86–6.71 (m, 6H), 3.78 (s, 6H), 3.54 (q, *J* = 8.2, 7.6 Hz, 2H), 2.37–2.25 (m, 2H), 2.20–2.06 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 159.8 (2C), 146.4 (2C), 129.4 (2C), 119.2 (2C), 112.6 (2C), 111.4 (2C), 55.3 (2C), 48.0 (2C), 26.0 (2C).
HRMS (ESI^+) calculated for $C_{18}H_{21}O_2^+$ $[M+H]^+$: 269.1536; found: 269.1545.

2u-cis

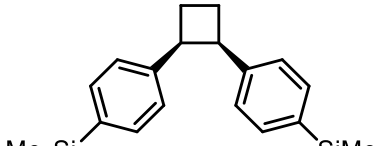
R_f = 0.38 (96:4 Pentane:EtoAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.03 (t, *J* = 7.9 Hz, 2H), 6.63–6.56 (m, 4H), 6.47 (t, *J* = 2.1 Hz, 2H), 4.03–3.95 (m, 2H), 3.62 (s, 6H), 2.49–2.39 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 159.3 (2C), 143.3 (2C), 128.7 (2C), 120.6 (2C), 113.7 (2C), 111.5 (2C), 55.2 (2C), 45.4 (2C), 24.5 (2C).
HRMS (ESI^+) calculated for $C_{18}H_{21}O_2^+$ $[M+H]^+$: 269.1536; found: 269.1545.

1,2-Bis(4-(trimethylsilyl)phenyl)cyclobutane (2v)



2v-trans

Chemical Formula: $C_{22}H_{32}Si_2$
Molecular Weight: 352.67



2v-cis

Chemical Formula: $C_{22}H_{32}Si_2$
Molecular Weight: 352.67

Prepared according to **GP4**: Trimethyl(4-vinylphenyl)silane (**1v**) (185 mg, 1.05 mmol, 1 equiv), 4CzIPN (7.9 mg, 10 µmol, 1 mol%) in anhydrous THF (0.25 mL). The reaction was irradiated for 144 h. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a 3.6:1 (trans:cis) mixture of diastereomers as a colourless liquid (47.0 mg, 0.133 mmol, 26%).

NMR signals for **2v-trans** and **2v-cis** were extracted from spectra containing both diastereomers.

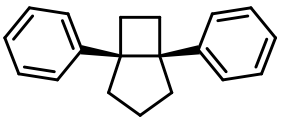
2v-trans

R_f = 0.34 (Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.45 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 4H), 3.66–3.55 (m, 2H), 2.39–2.28 (m, 2H), 2.20–2.09 (m, 2H), 0.25 (s, 18H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 145.3 (2C), 137.9 (2C), 133.5 (4C), 126.2 (4C), 47.7 (2C), 26.1 (2C), –0.9 (6C).
^{29}Si NMR-INEPT (79 MHz, $CDCl_3$): δ/ppm = –4.4.
HRMS (ESI^+) calculated for $C_{22}H_{32}Si_2Na^+$ $[M+Na]^+$: 375.1935; found: 375.1932.

2v-cis

R_f = 0.34 (Pentane).
^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.22 (d, *J* = 7.1 Hz, 4H), 6.90 (d, *J* = 7.9 Hz, 4H), 4.06–3.96 (m, 2H), 2.50–2.41 (m, 4H), 0.17 (s, 18H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 142.3 (2C), 137.1 (2C), 132.8 (4C), 127.5 (4C), 45.4 (2C), 24.3 (2C), –1.0 (6C).
^{29}Si NMR-INEPT (79 MHz, CDCl3): δ/ppm = –4.7.
HRMS (ESI^+) calculated for $C_{22}H_{32}Si_2Na^+$ $[M+Na]^+$: 375.1935; found: 375.1932.

1,5-Diphenylbicyclo[3.2.0]heptane (4a)



4a
Chemical Formula: $C_{19}H_{20}$
Molecular Weight: 248.37

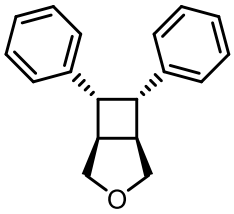
Prepared according to **GP4**: Hepta-1,6-diene-2,6-diylbenzene (**3a**) (79.6 mg, 0.320 mmol, 1.00 equiv), 4CzIPN (2.4 mg, 3.0 µmol, 0.9 mol%) in anhydrous THF (0.075 mL) and 48 h of illumination. Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless solid (76.6 mg, 0.308 mmol, 96%).

Data were consistent with that reported.[20]

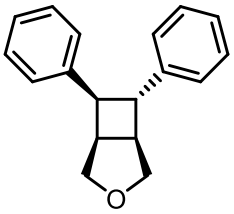
R_f = 0.3 (Pentane).
M.P. = 68–70 °C (CH_2Cl_2)

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.12–6.85 (m, 10H), 2.53–2.41 (m, 2H), 2.32–1.96 (m, 8H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 147.2 (2C), 127.5 (4C), 127.3 (4C), 125.1 (2C), 57.0 (2C), 42.7 (2C), 29.9 (2C), 25.0.
IR (ATR): ν = 3084, 3059, 3023, 2951, 2926, 2852, 2360, 2342, 1601, 1543, 1497, 1449, 758, 697 cm^{-1}.
GC-MS (EI) calculated for $C_{19}H_{20}^+$ $[M]^+$: 248.2; found: 248.1.

6,7-Diphenyl-3-oxabicyclo[3.2.0]heptane (4b)



4b-trans
Chemical Formula: $C_{18}H_{18}O$
Molecular Weight: 250.34



4b-cis
Chemical Formula: $C_{18}H_{18}O$
Molecular Weight: 250.34

Prepared according to **GP4**: ((1*E*,1'*E*)-Oxybis(prop-1-ene-3,1-diyl))dibenzene (**3b**) (79.9 mg, 0.320 mmol, 1.0 equiv), 4CzIPN (2.9 mg, 3.6 µmol, 1.1 mol%) in anhydrous THF (0.075 mL) and 48 h of illumination. Purification by flash column chromatography (SiO_2, 95:5 Pentane:EtOAc) afforded the title compound as a 1.4:1 (trans:cis) mixture of diastereomers as a white solid (50 mg, 0.20 mmol, 62%).

Data were consistent with that reported.[29]

R_f = 0.19 (19:1 Pentane:EtOAc).

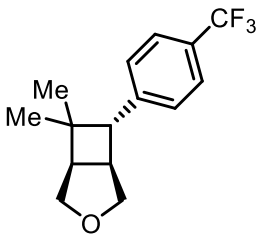
4b-trans

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.12–6.88 (m, 10H), 4.11 (d, *J* = 9.4 Hz, 2H), 3.77–3.69 (m, 4H), 3.36–3.28 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 140.9 (2C), 128.2 (4C), 127.8 (4C), 125.7 (2C), 74.2 (2C), 47.4 (2C), 42.3 (2C).

4b-cis

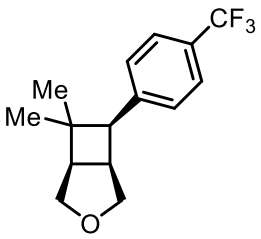
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.41–7.16 (m, 10H), 4.04 (d, *J* = 9.2 Hz, 1H), 3.89–3.77 (m, 2H), 3.68–3.63 (m, 1H), 3.58–3.44 (m, 2H), 3.28–3.20 (m, 1H), 3.17–3.08 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ/ppm = 140.5, 128.62 (2C), 128.58 (2C), 127.9 (2C), 126.6 (2C), 126.5, 126.4, 73.1, 68.6, 46.08, 46.06, 45.7, 44.3, 40.9.

6,6-Dimethyl-7-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.2.0]heptane (4c)



4c-trans

Chemical Formula: $C_{15}H_{17}F_3O$
Molecular Weight: 270.30



4c-cis

Chemical Formula: $C_{15}H_{17}F_3O$
Molecular Weight: 270.30

Prepared according to **GP4**: (*E*)-1-(3-((4-Methylpent-3-en-1-yl)oxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene (**3c**) (81.0 mg, 0.300 mmol, 1.0 equiv), 4CzIPN (2.4 mg, 3.0 µmol, 1.0 mol%) in anhydrous THF (0.075 mL) and 90 h of illumination. Purification by flash column chromatography (SiO_2, 19:1 Pentane:EtOAc) afforded the title compound as a >10:1 (trans:cis) mixture of diastereomers as a white solid (31.1 mg, 0.120 mmol, 38%).

Data were consistent with that reported.[20]

R_f = 0.2 (19:1 Pentane:EtOAc).

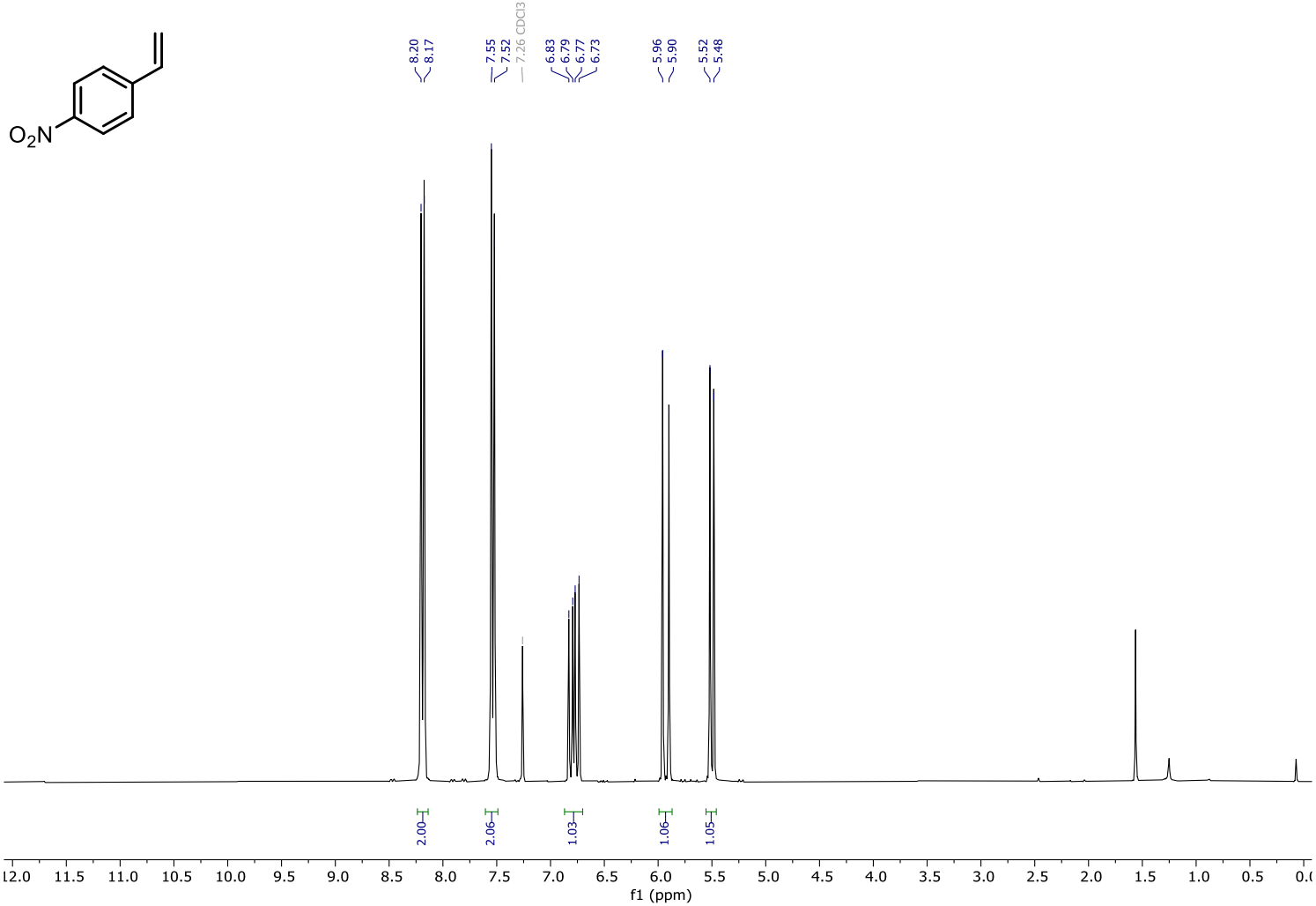
4c-trans

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.56 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 4.18 (d, *J* = 10.1 Hz, 1H), 3.79 (d, *J* = 9.0 Hz, 1H), 3.58–3.40 (m, 2H), 3.35–3.22 (m, 1H), 3.04 (d, *J* = 7.3 Hz, 1H), 2.43 (t, *J* = 7.4 Hz, 1H), 1.13 (s, 3H), 0.74 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 144.9 (d, *J* = 1.1 Hz), 128.0 (2C), 125.1 (q, *J* = 3.7 Hz, 2C), 72.1, 69.2, 51.9, 46.8, 38.1, 37.7, 26.4, 24.4. Signals corresponding to 2 carbon atoms could not be resolved.
^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ/ppm = 62.3.

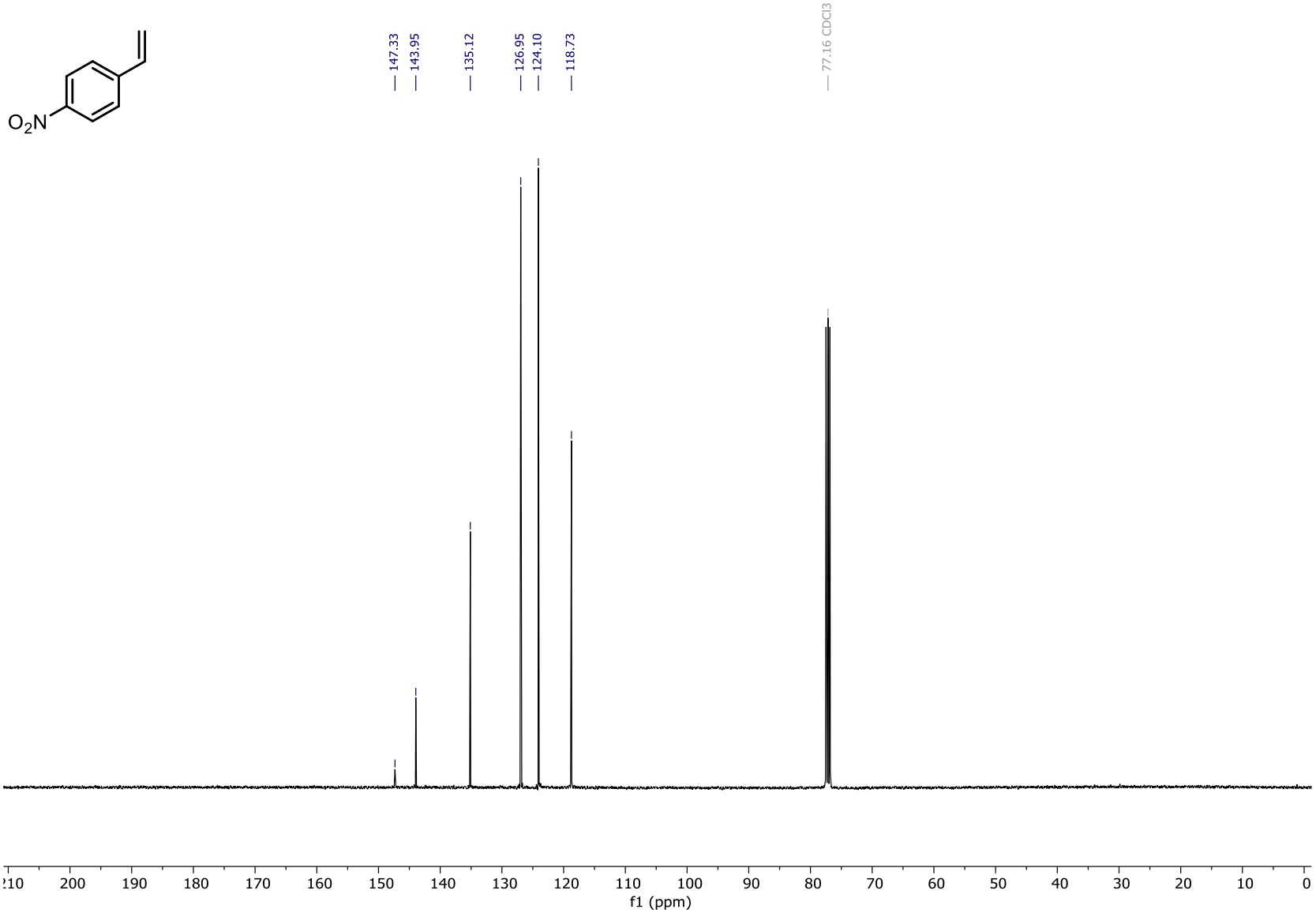
Full characterisation of **4c-cis** was not possible due to small quantities of material and difficulties resolving peaks in the NMR spectra.

8 NMR Spectra
8.1 Starting Materials

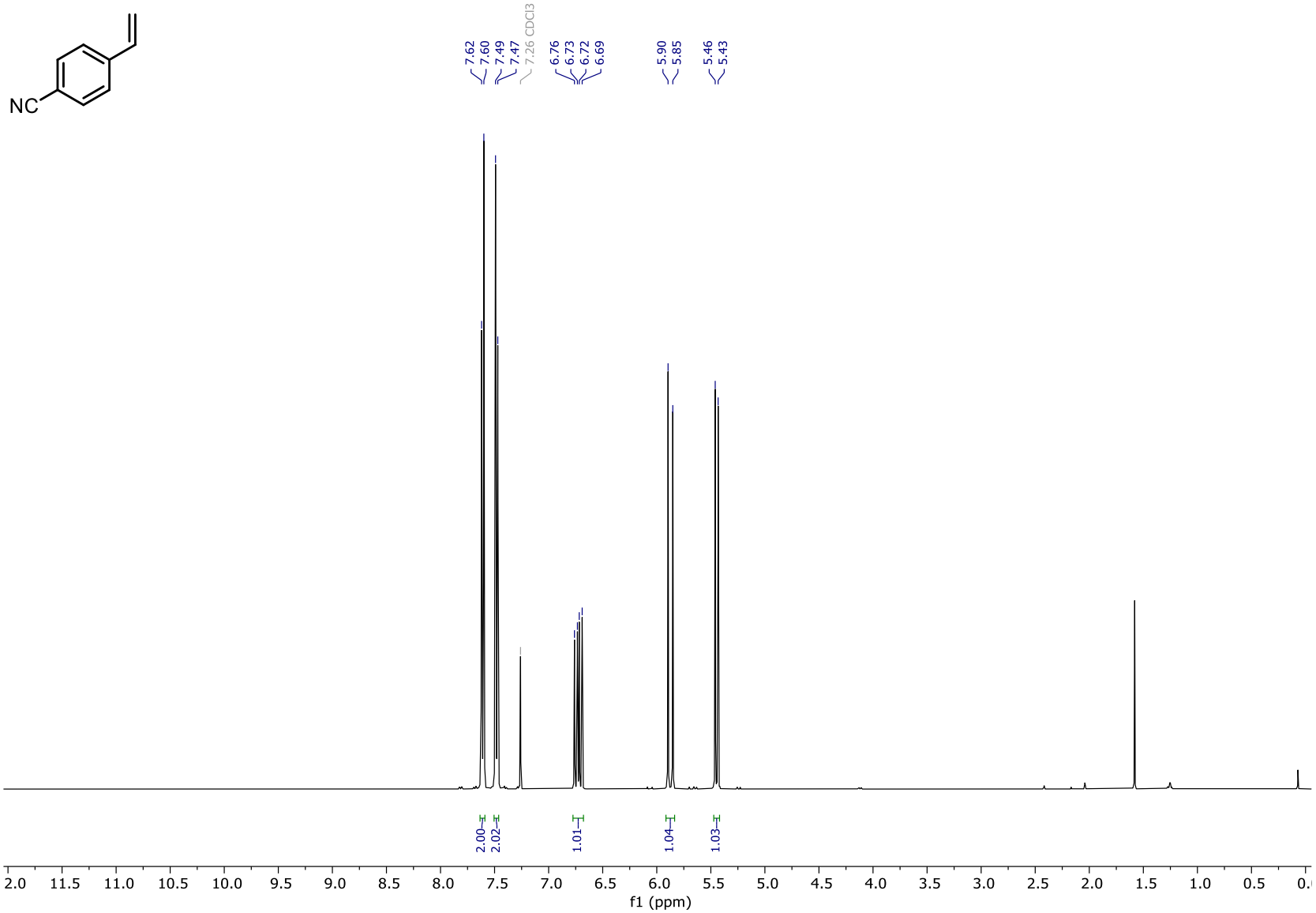
1-Nitro-4-vinylbenzene (1a): ^{1}H NMR (300 MHz, $CDCl_3$)



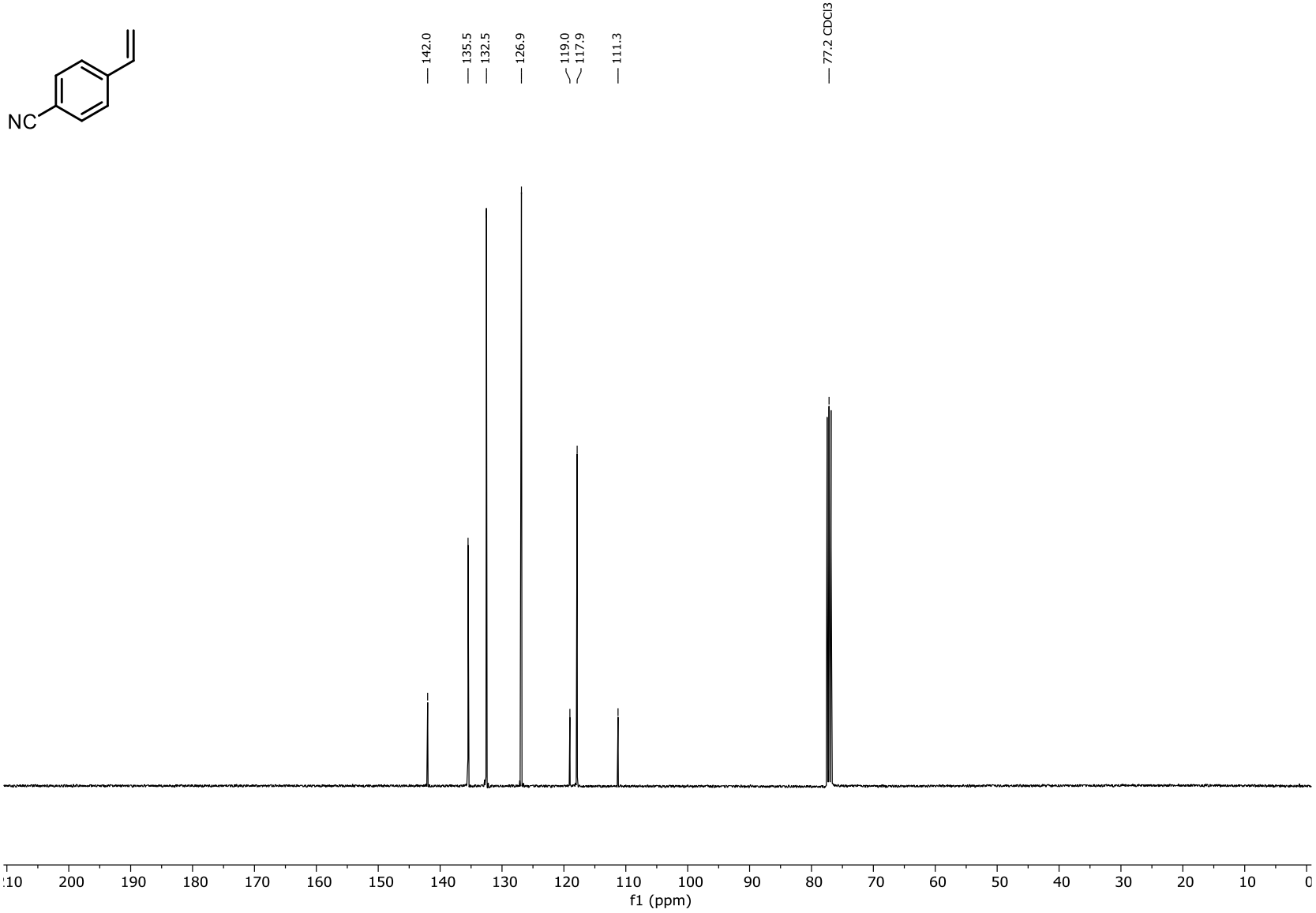
1-Nitro-4-vinylbenzene (1a): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



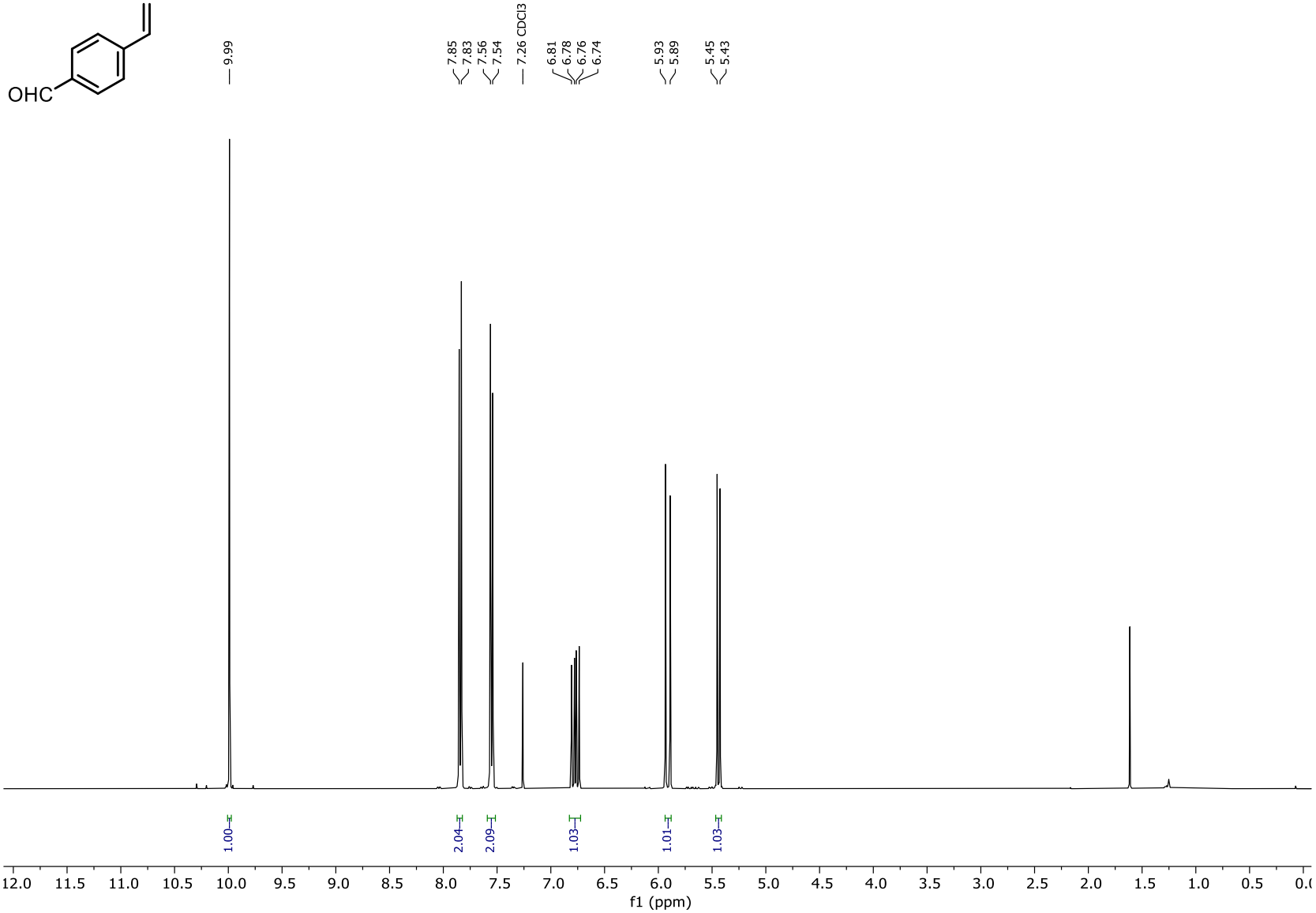
4-Vinylbenzonitrile (1c): ^{1}H NMR (300 MHz, $CDCl_3$)



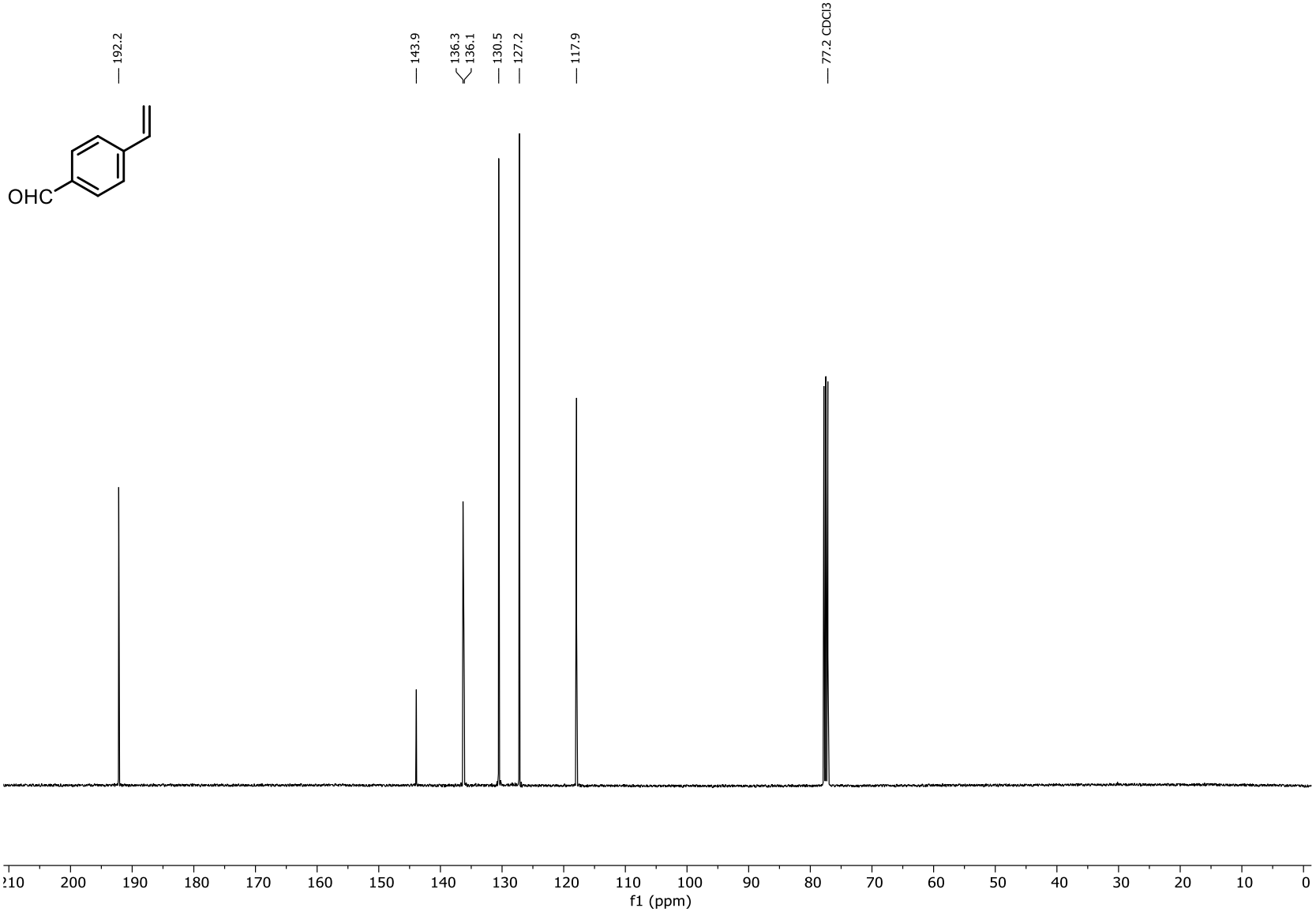
4-Vinylbenzonitrile (1c): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



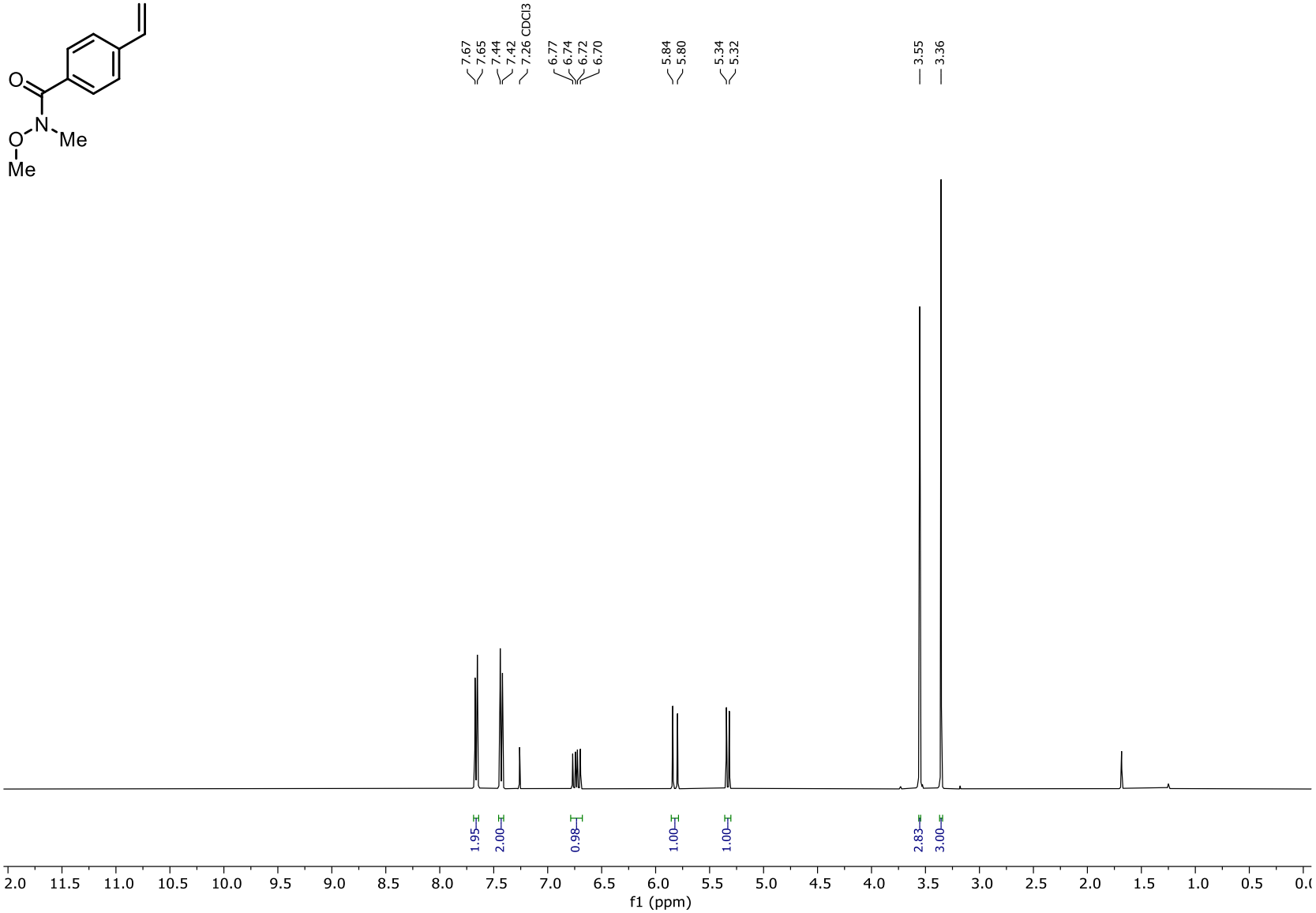
4-Vinylbenzaldehyde (1d): ^{1}H NMR (300 MHz, $CDCl_3$)



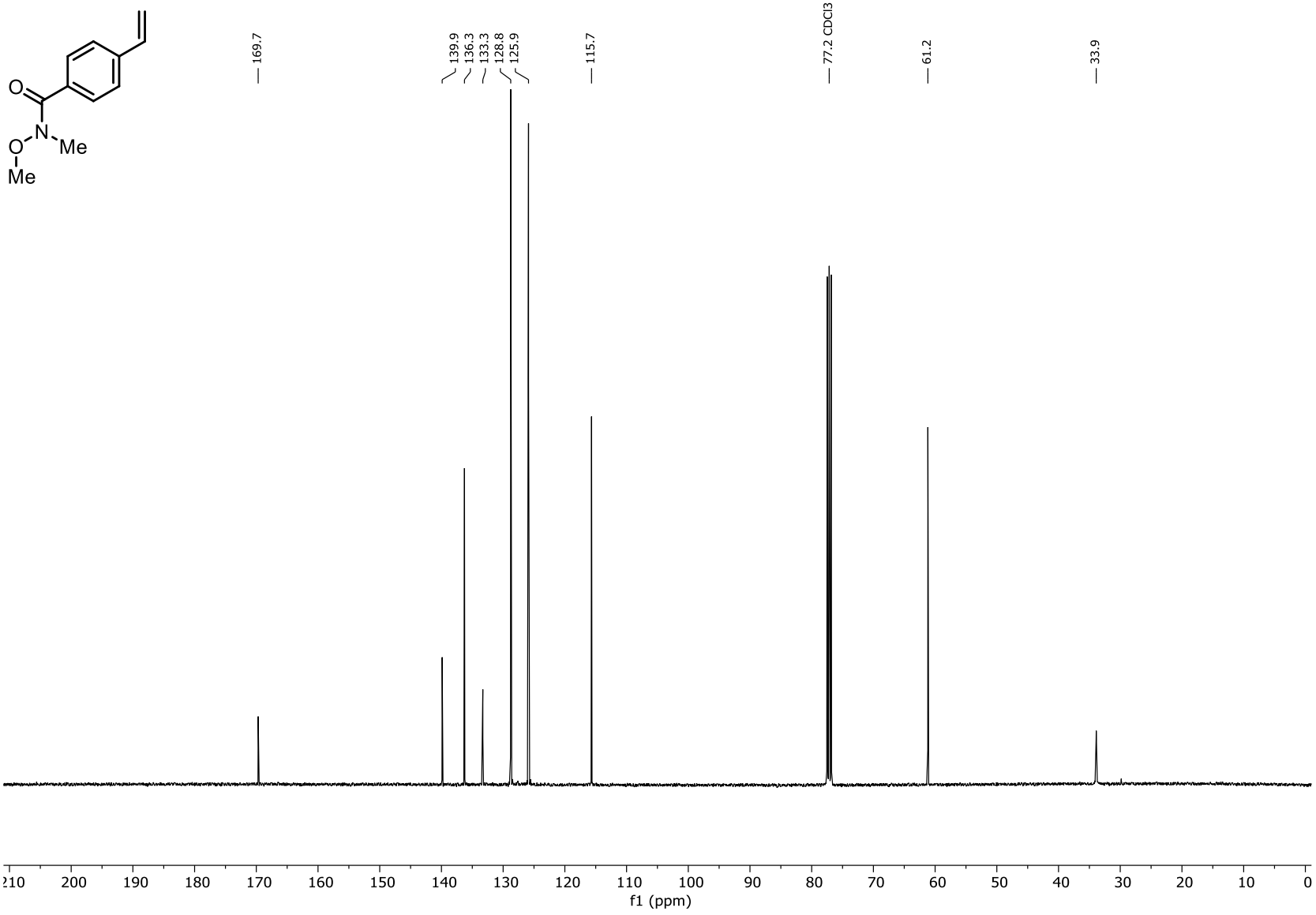
4-Vinylbenzaldehyde (1d): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



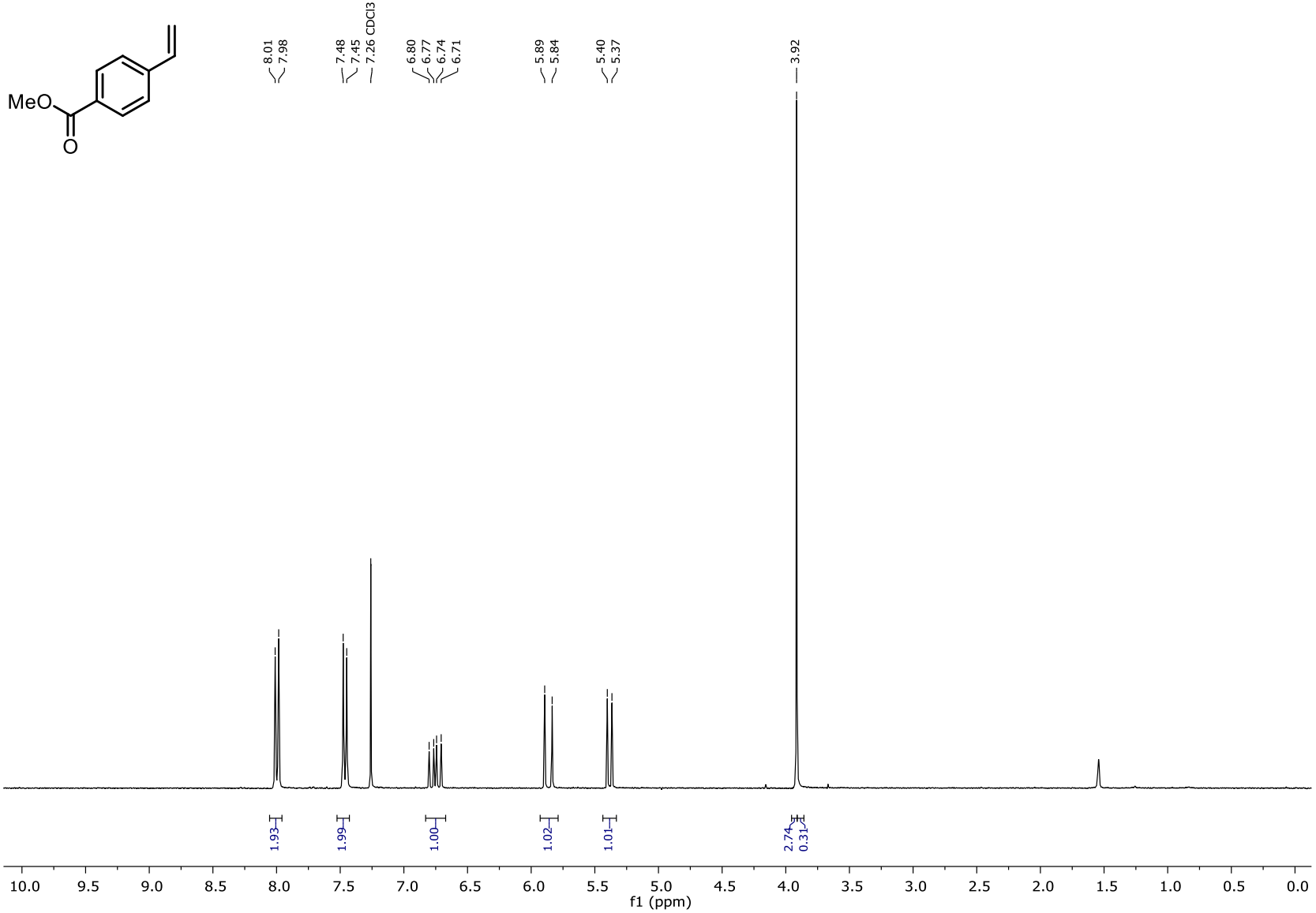
_N_-Methoxy-_N_-methyl-4-vinylbenzamide (1e): ^{1}H NMR (300 MHz, $CDCl_3$)



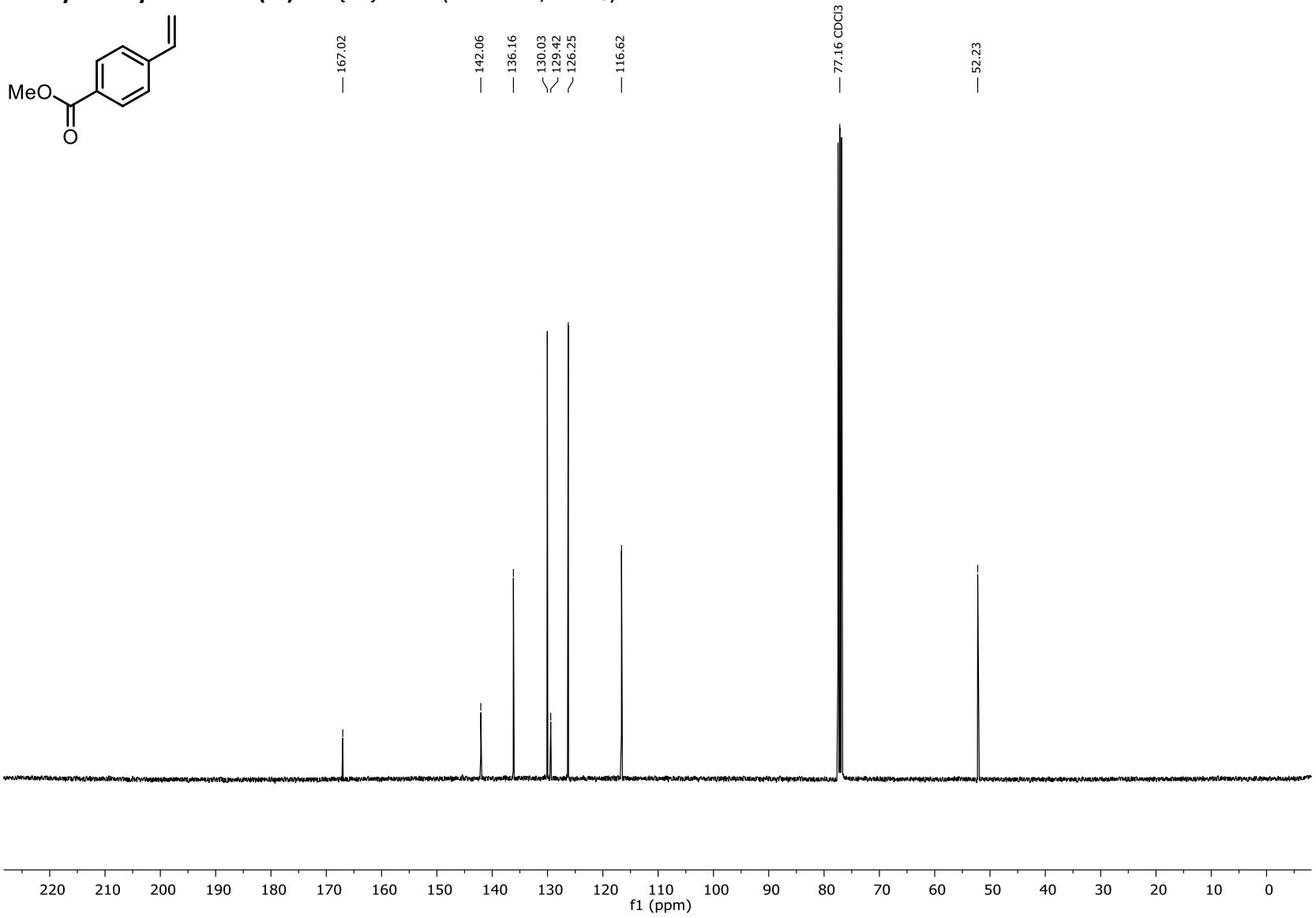
_N_-Methoxy-_N_-methyl-4-vinylbenzamide (1e): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



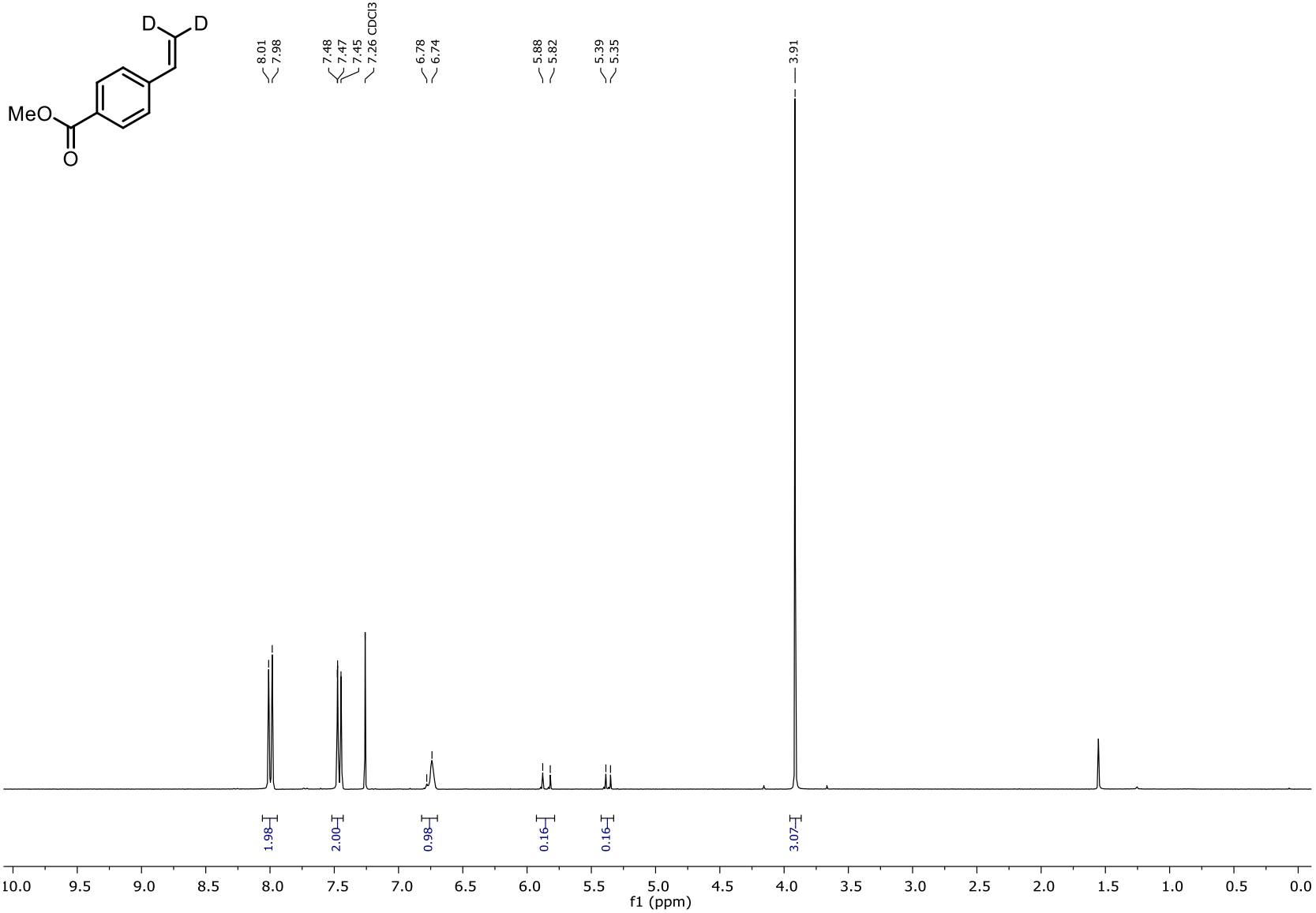
Methyl 4-vinylbenzoate (1f): ^{1}H NMR (300 MHz, $CDCl_3$)



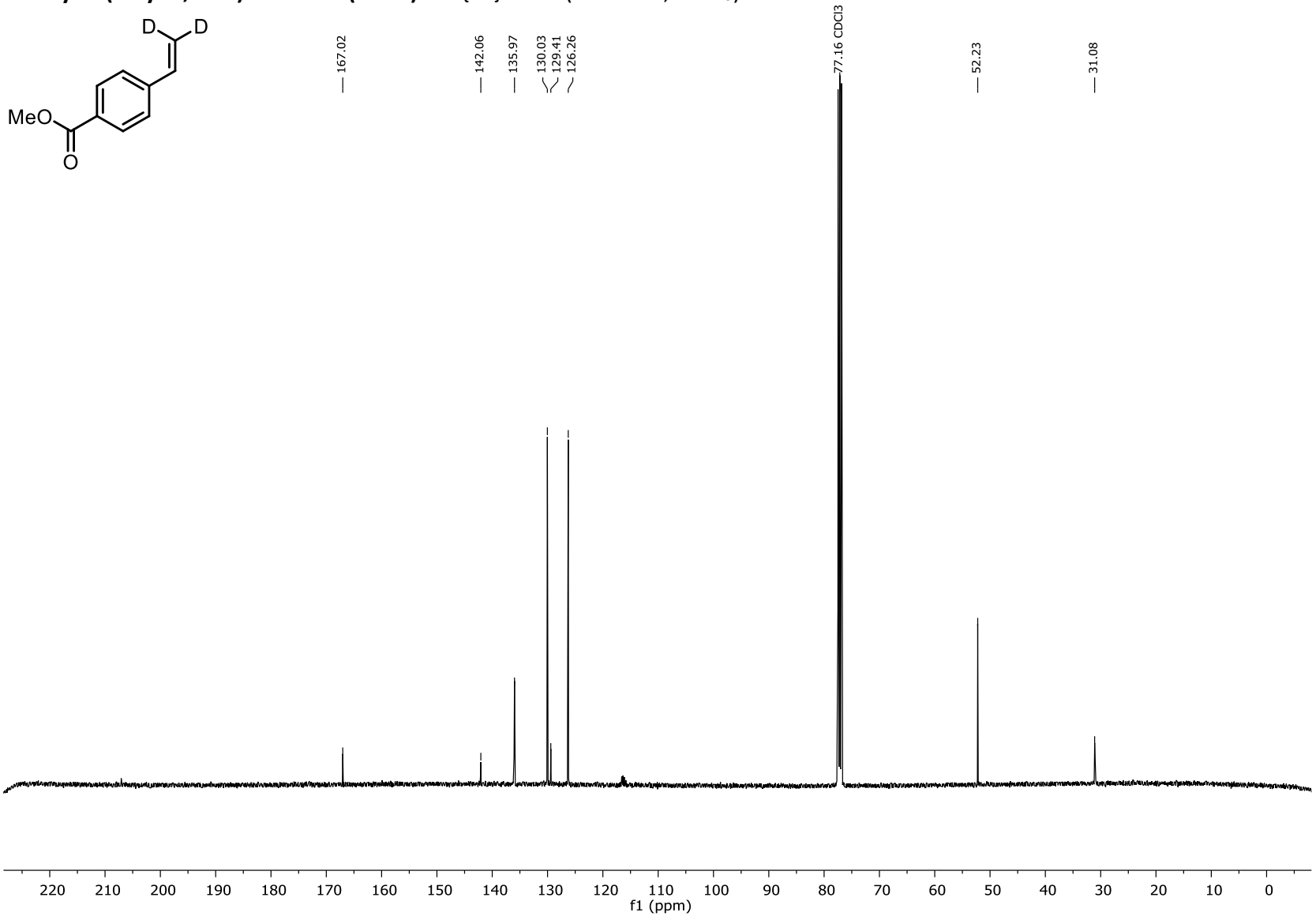
Methyl 4-vinylbenzoate (1f): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



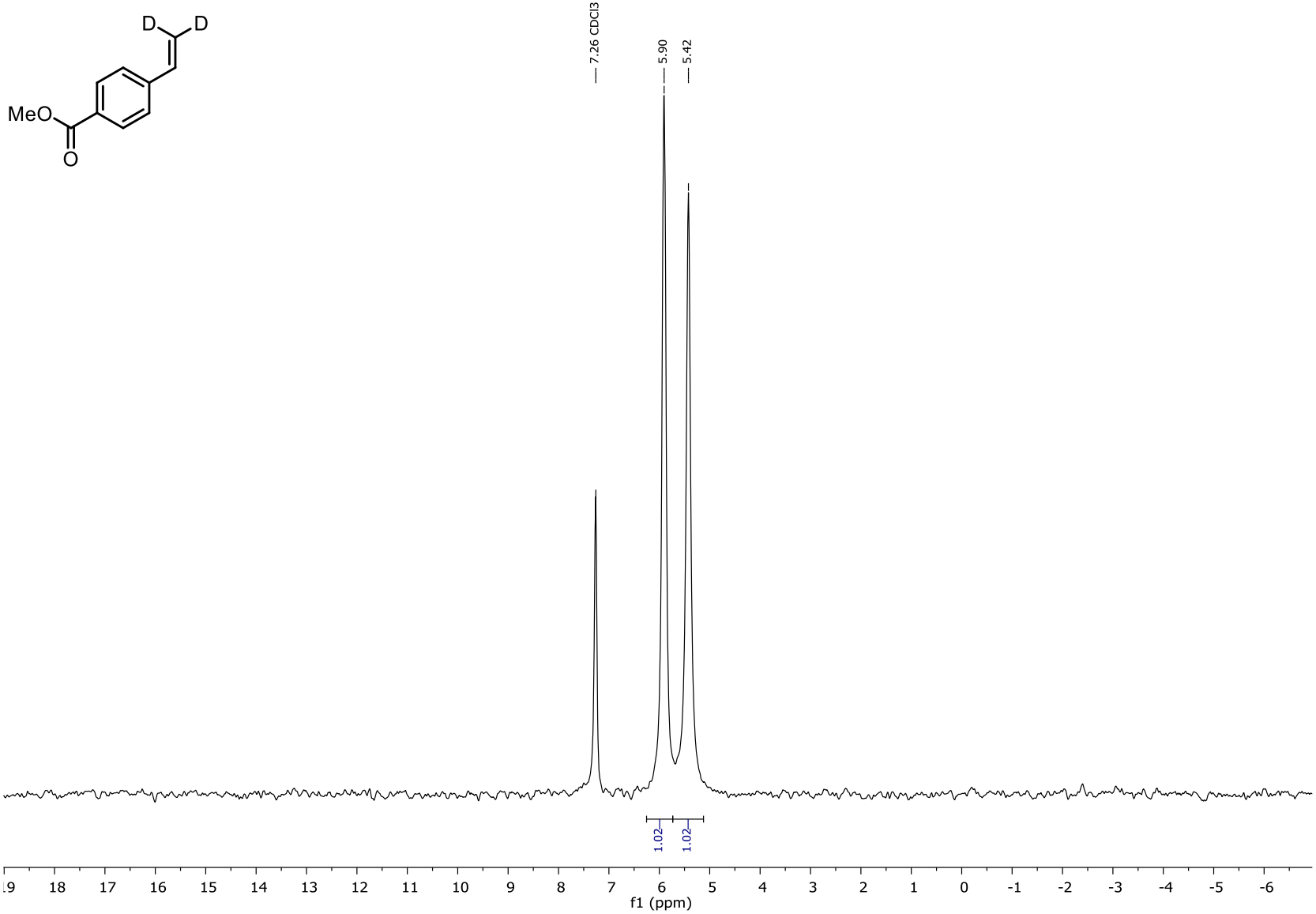
Methyl 4-(vinyl-2,2-d2)benzoate (1f-*d2*): ^{1}H NMR (300 MHz, $CDCl_3$)



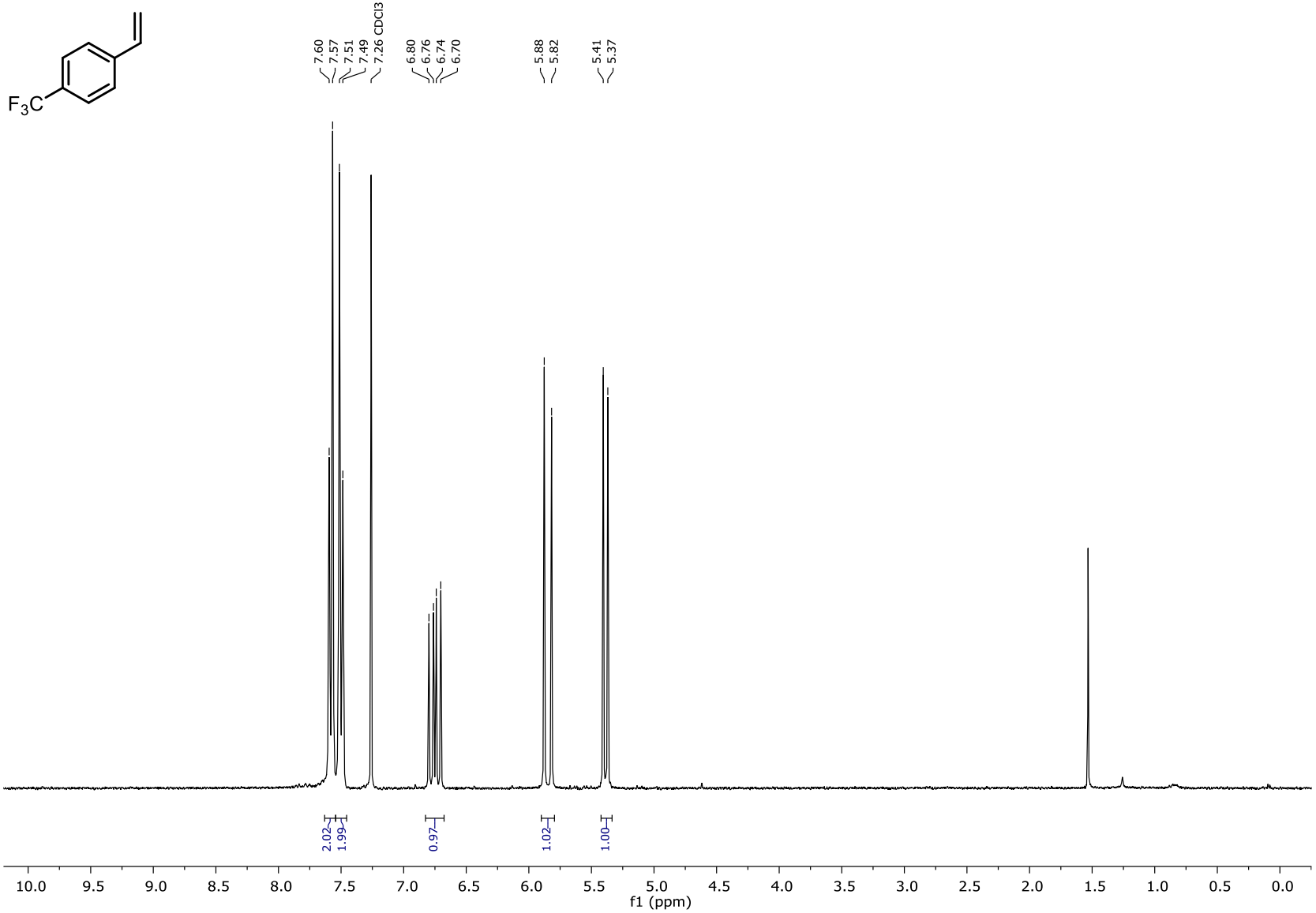
Methyl 4-(vinyl-2,2-d2)benzoate (1f-*d2*): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



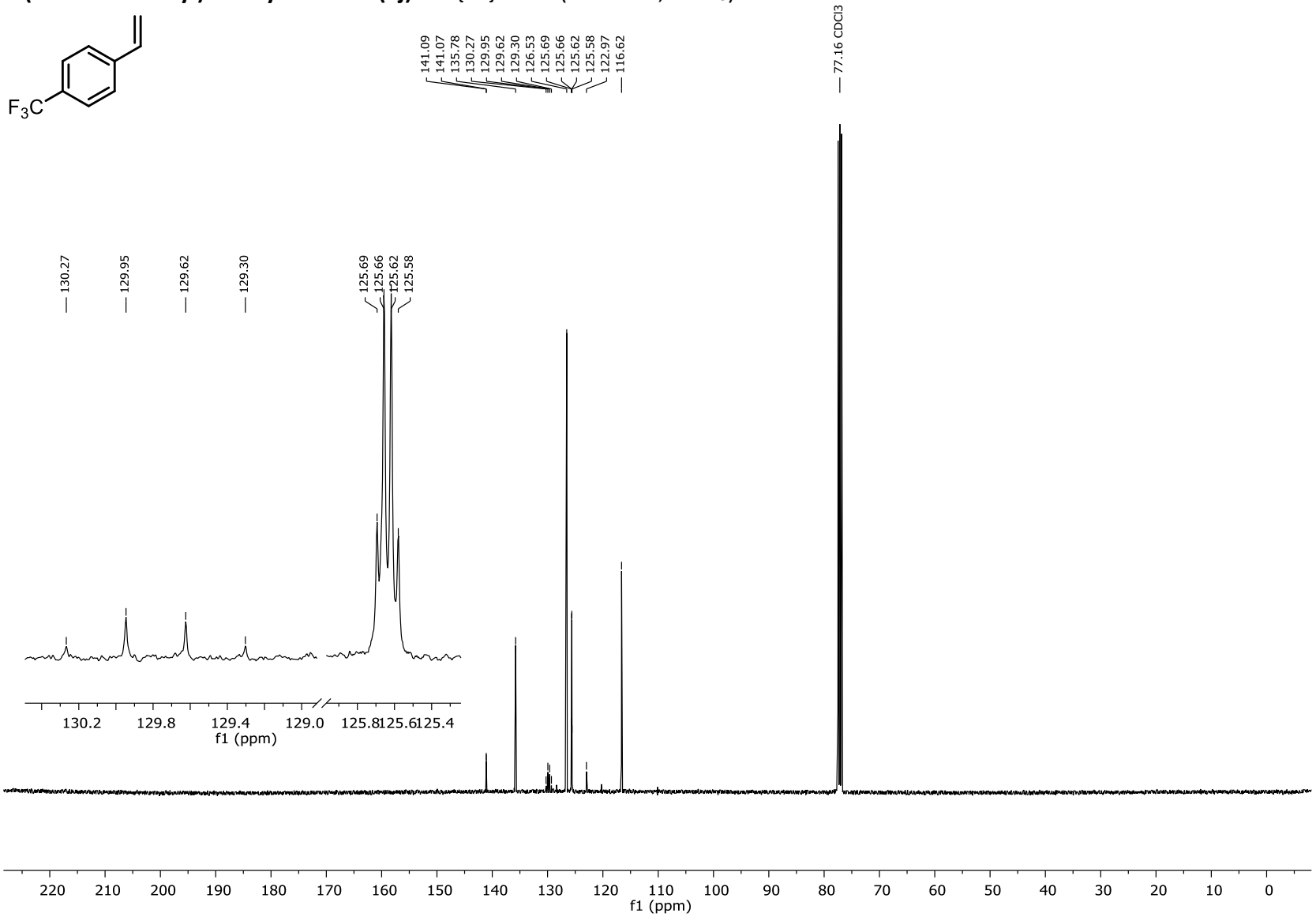
Methyl 4-(vinyl-2,2-d2)benzoate (1f-*d2*): ^{2}H NMR (77 MHz, CDCl3)



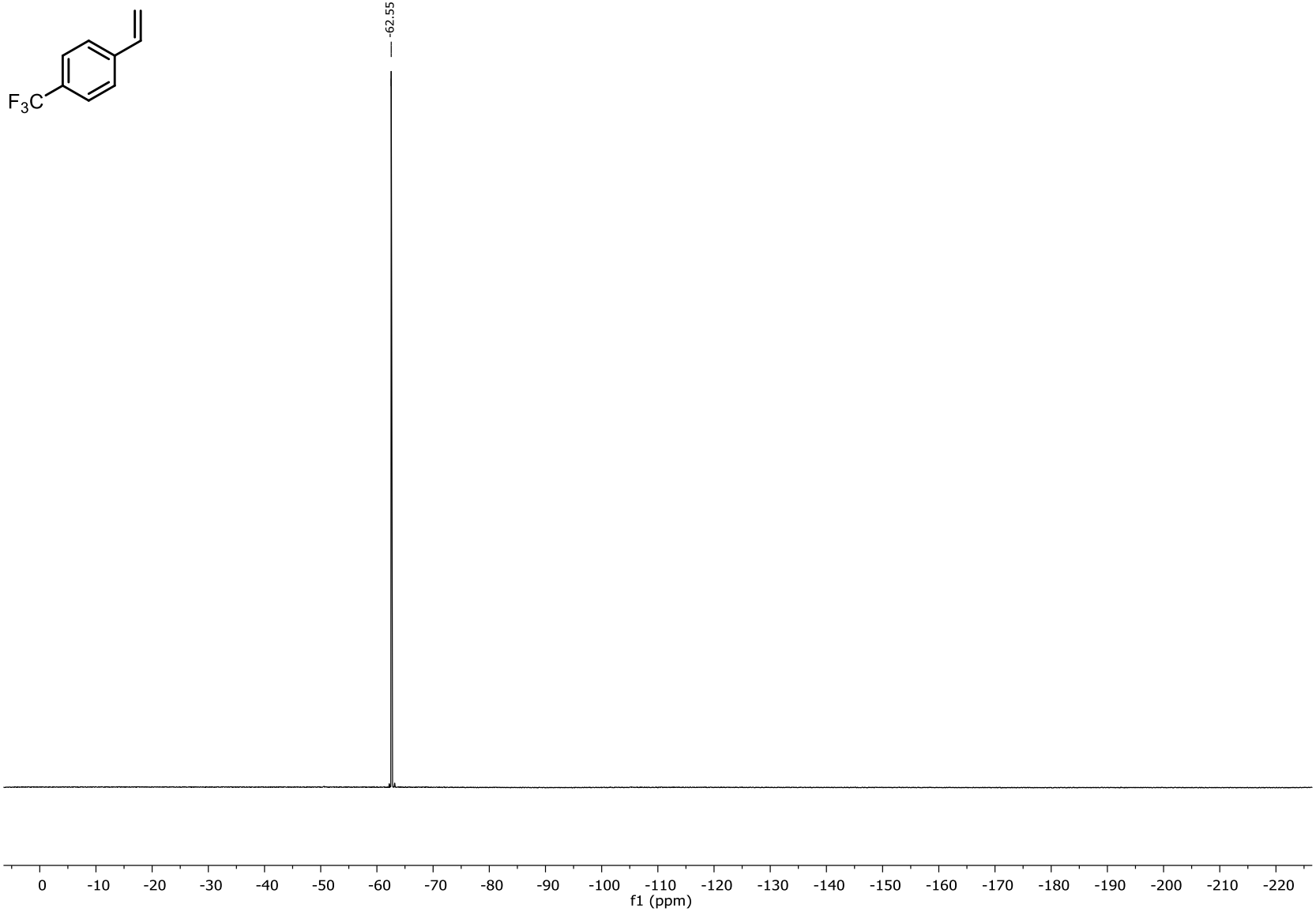
1-(Trifluoromethyl)-4-vinylbenzene (1j): : ^{1}H NMR (300 MHz, $CDCl_3$)



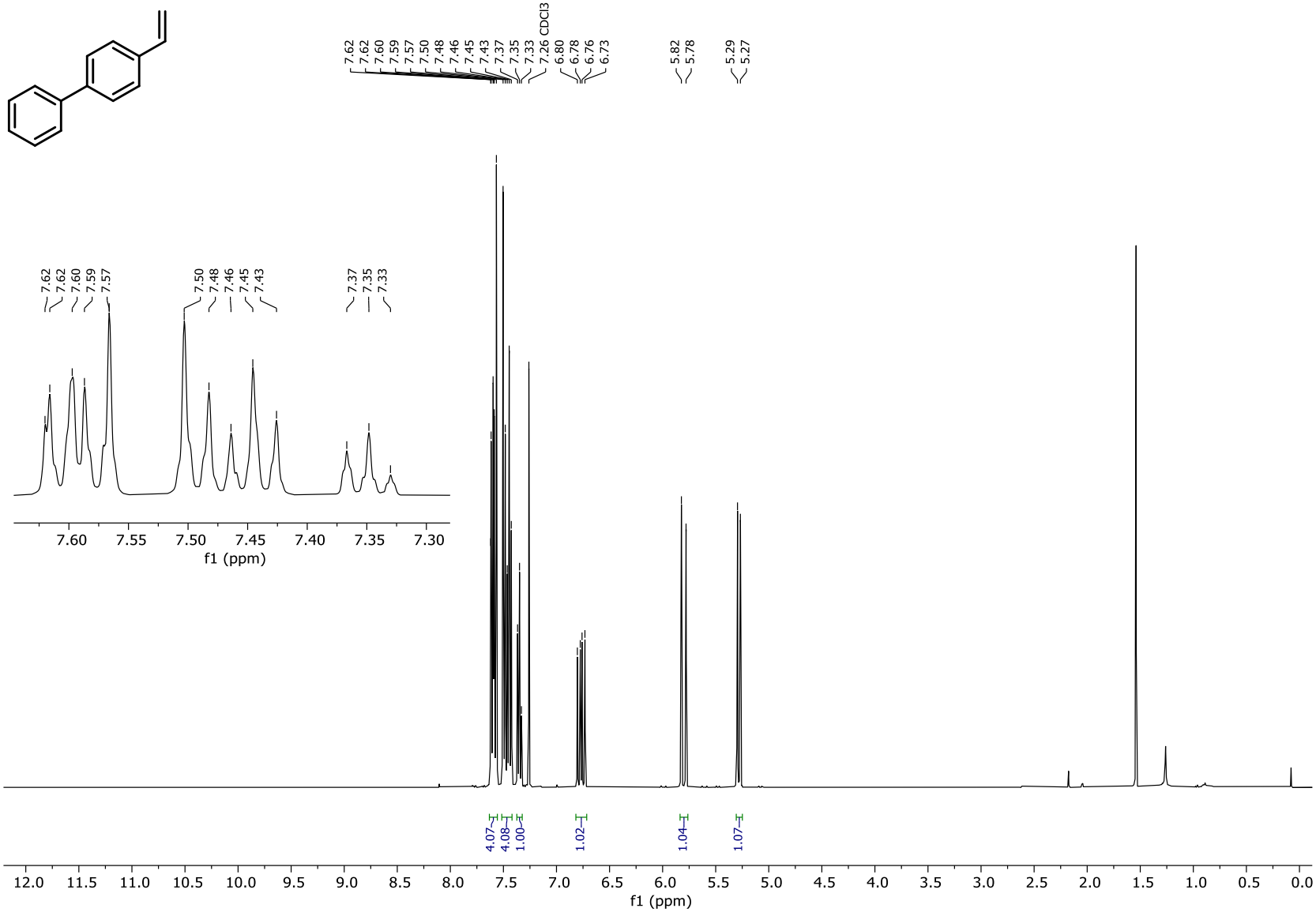
1-(Trifluoromethyl)-4-vinylbenzene (1j): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



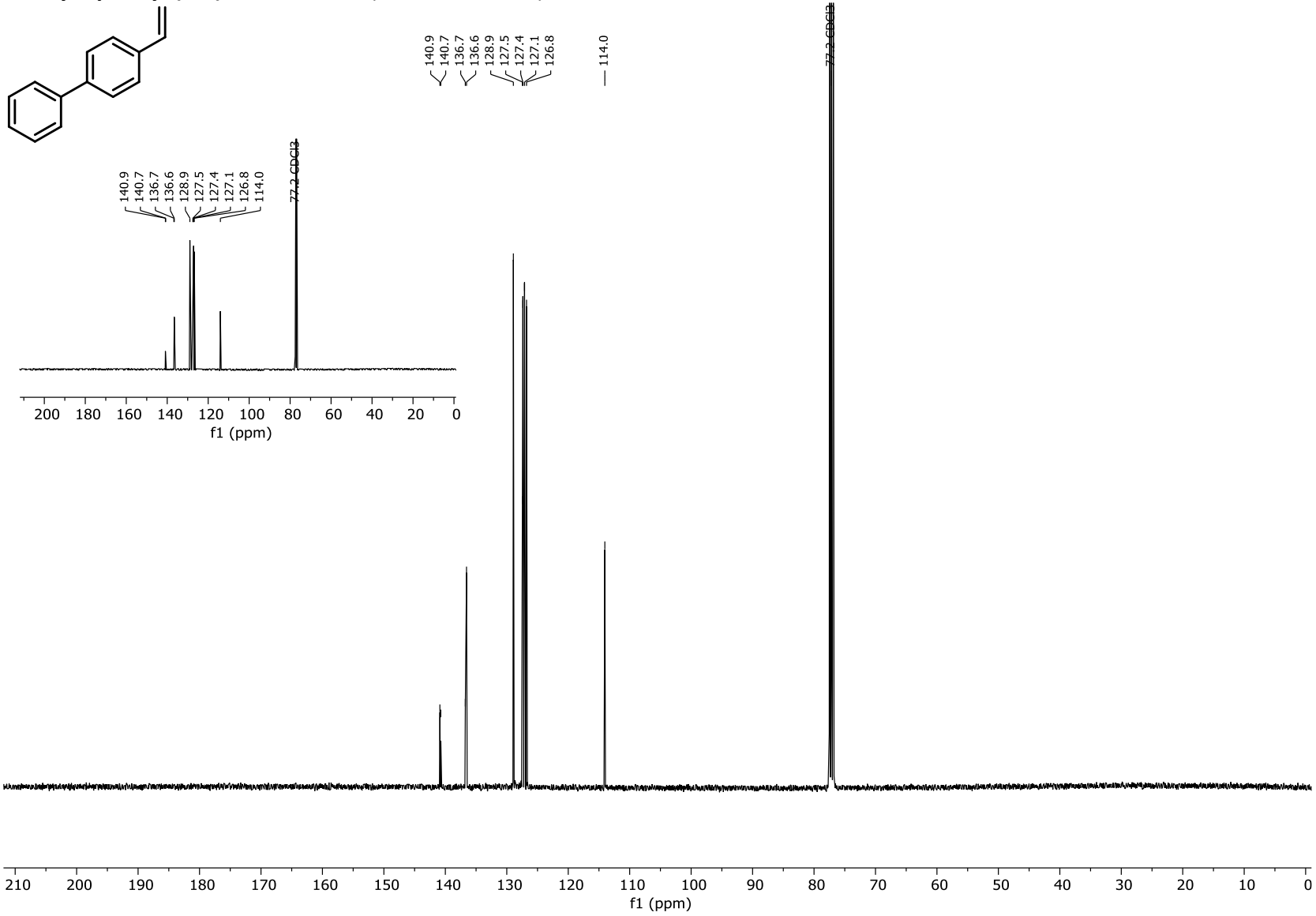
1-(Trifluoromethyl)-4-vinylbenzene (1j): ^{19}F NMR (282 MHz, CDCl3)



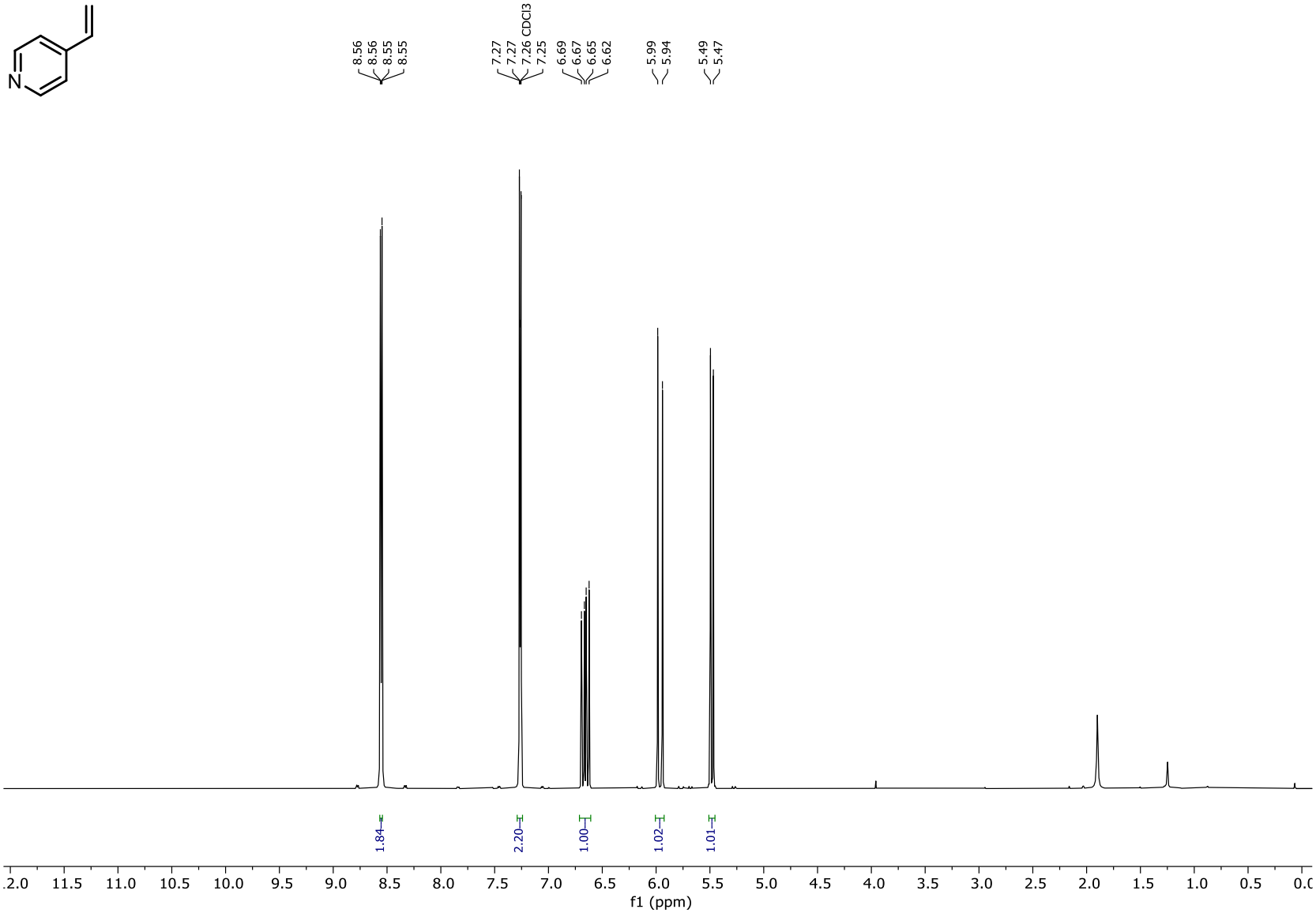
4-Vinylbiphenyl (1m): ^{1}H NMR (300 MHz, $CDCl_3$)



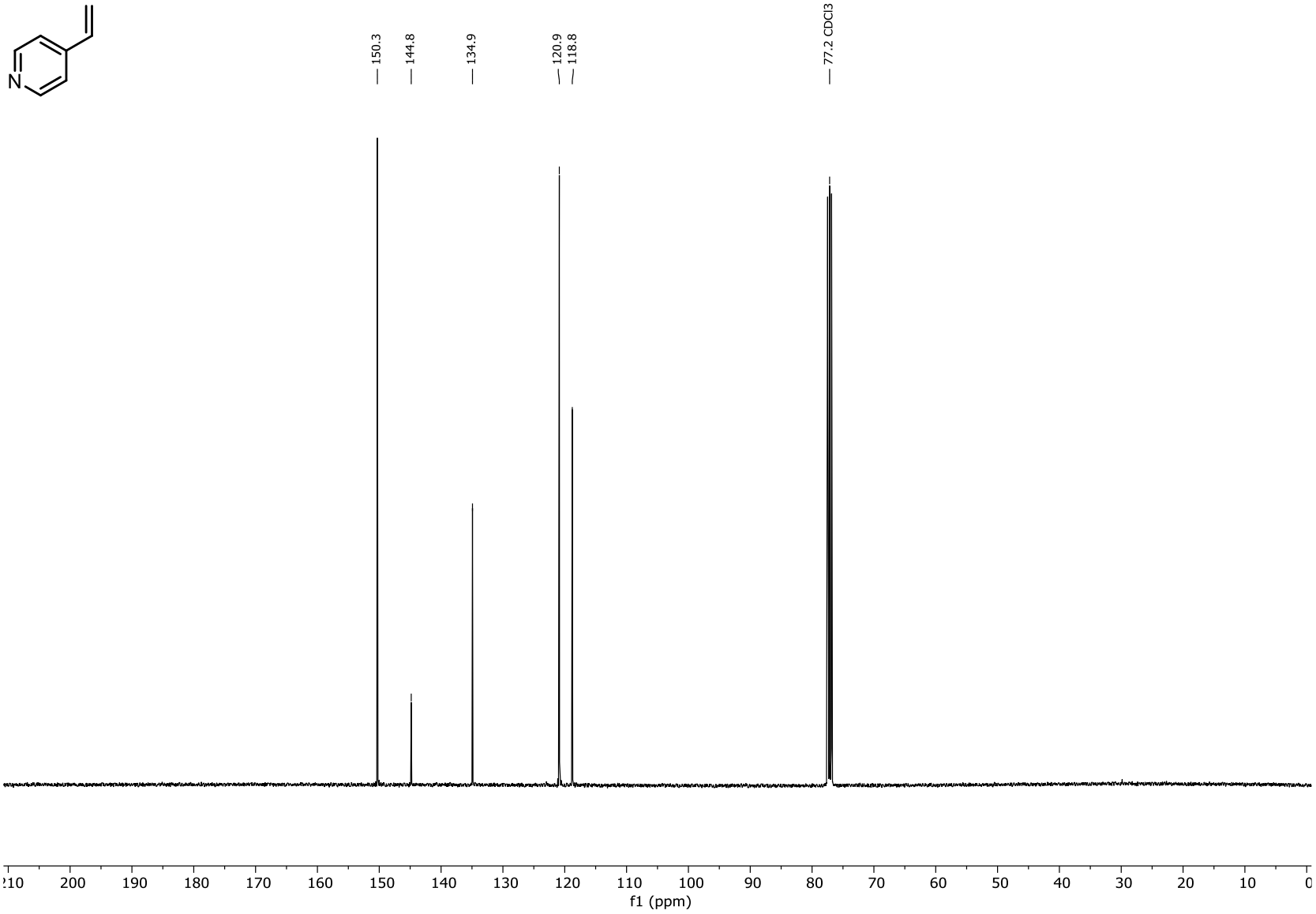
4-Vinylbiphenyl (1m): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



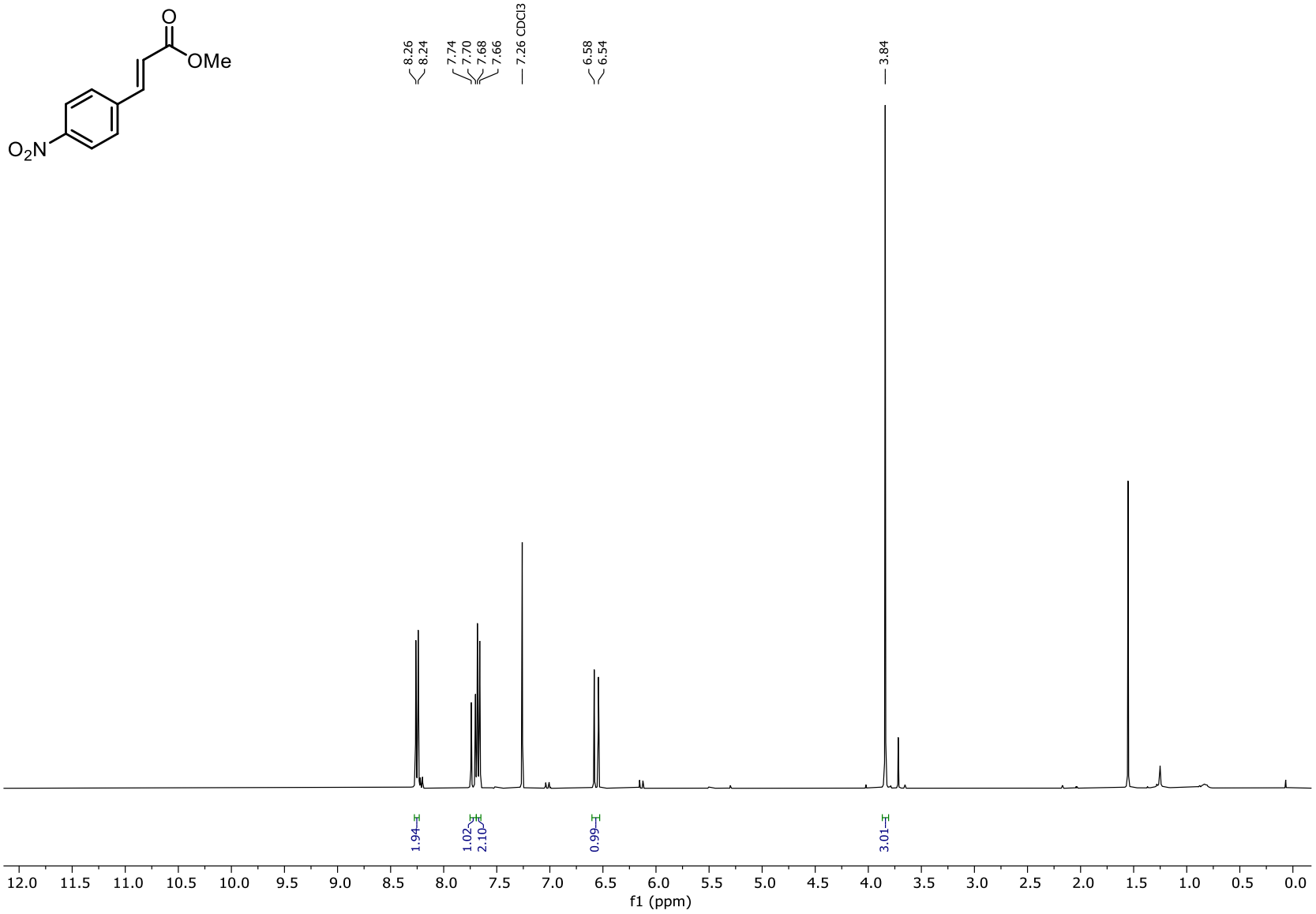
4-Vinylpyridine (1n): ^{1}H NMR (300 MHz, $CDCl_3$)



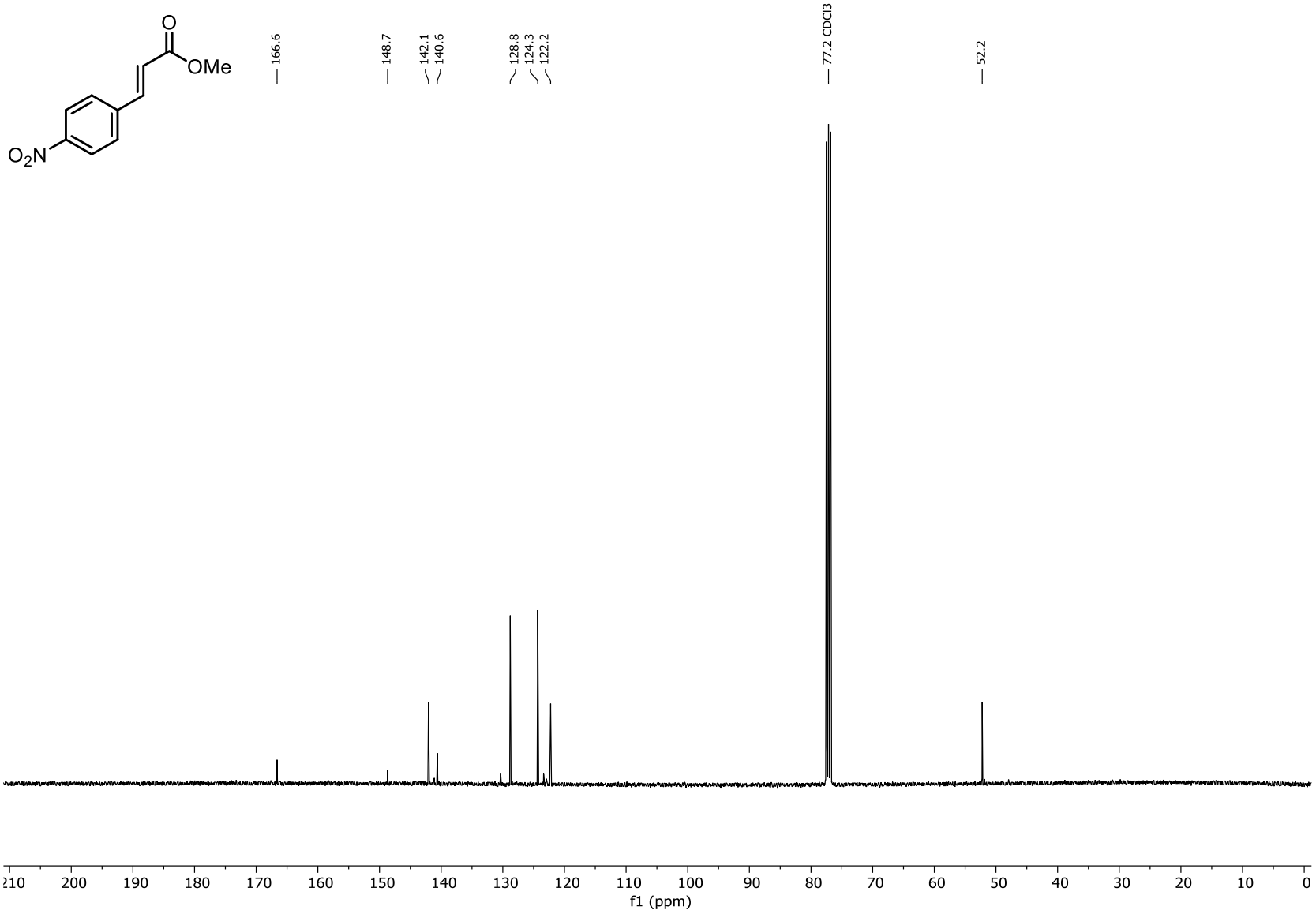
4-Vinylpyridine (1n): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



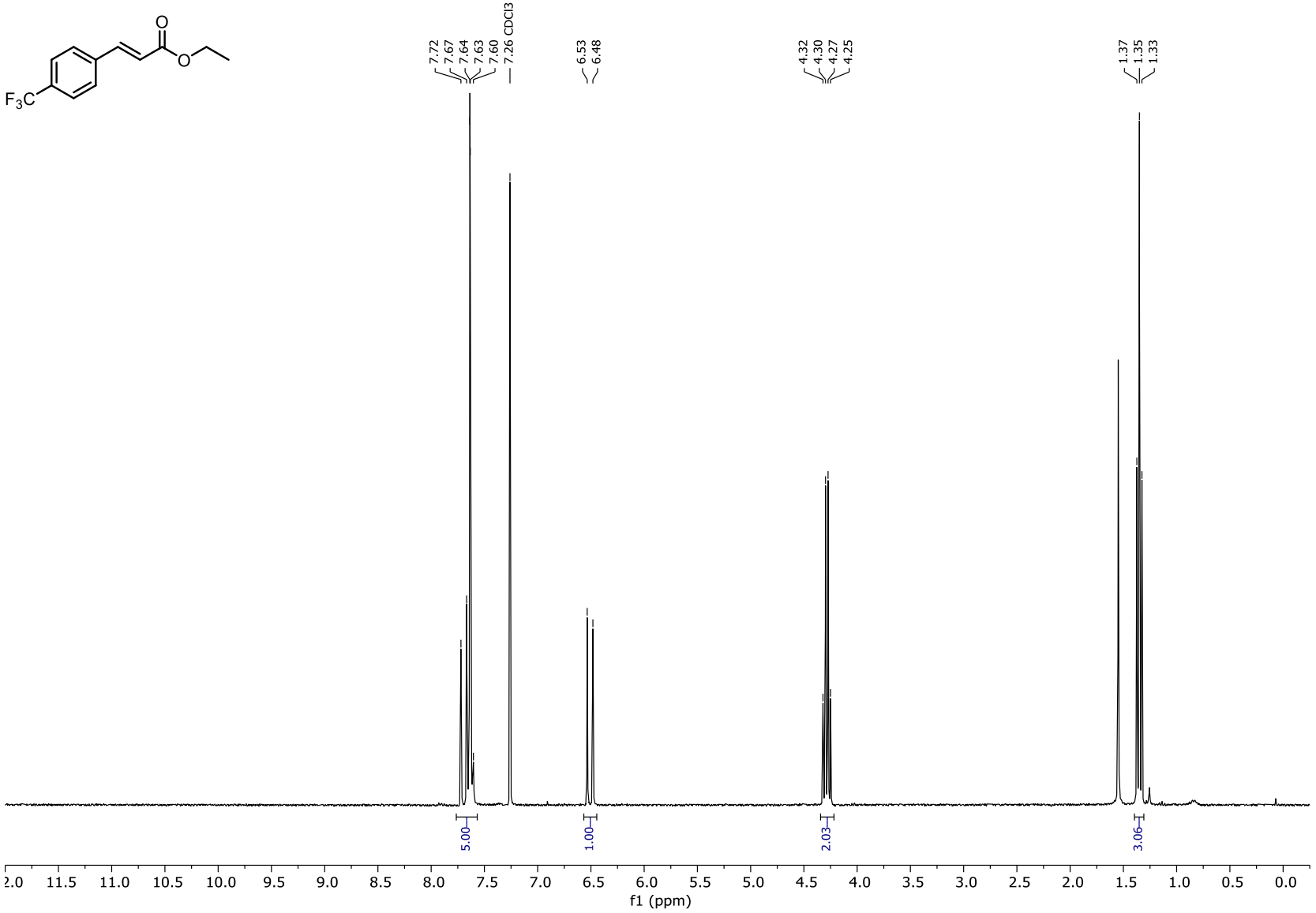
(*E*)-Methyl 4-nitrocinnamate (1o): ^{1}H NMR (300 MHz, $CDCl_3$)



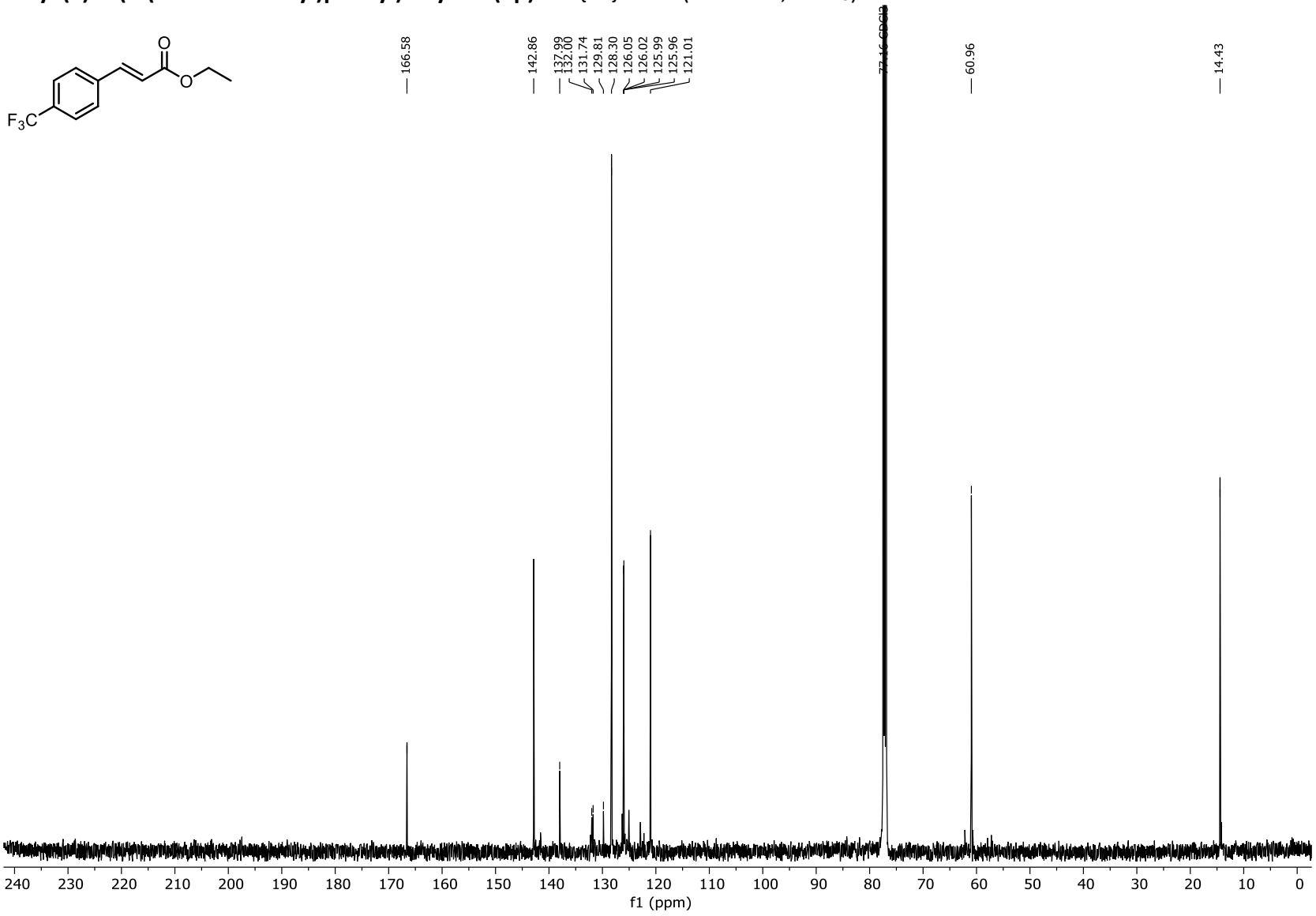
(*E*)-Methyl 4-nitrocinnamate (1o): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



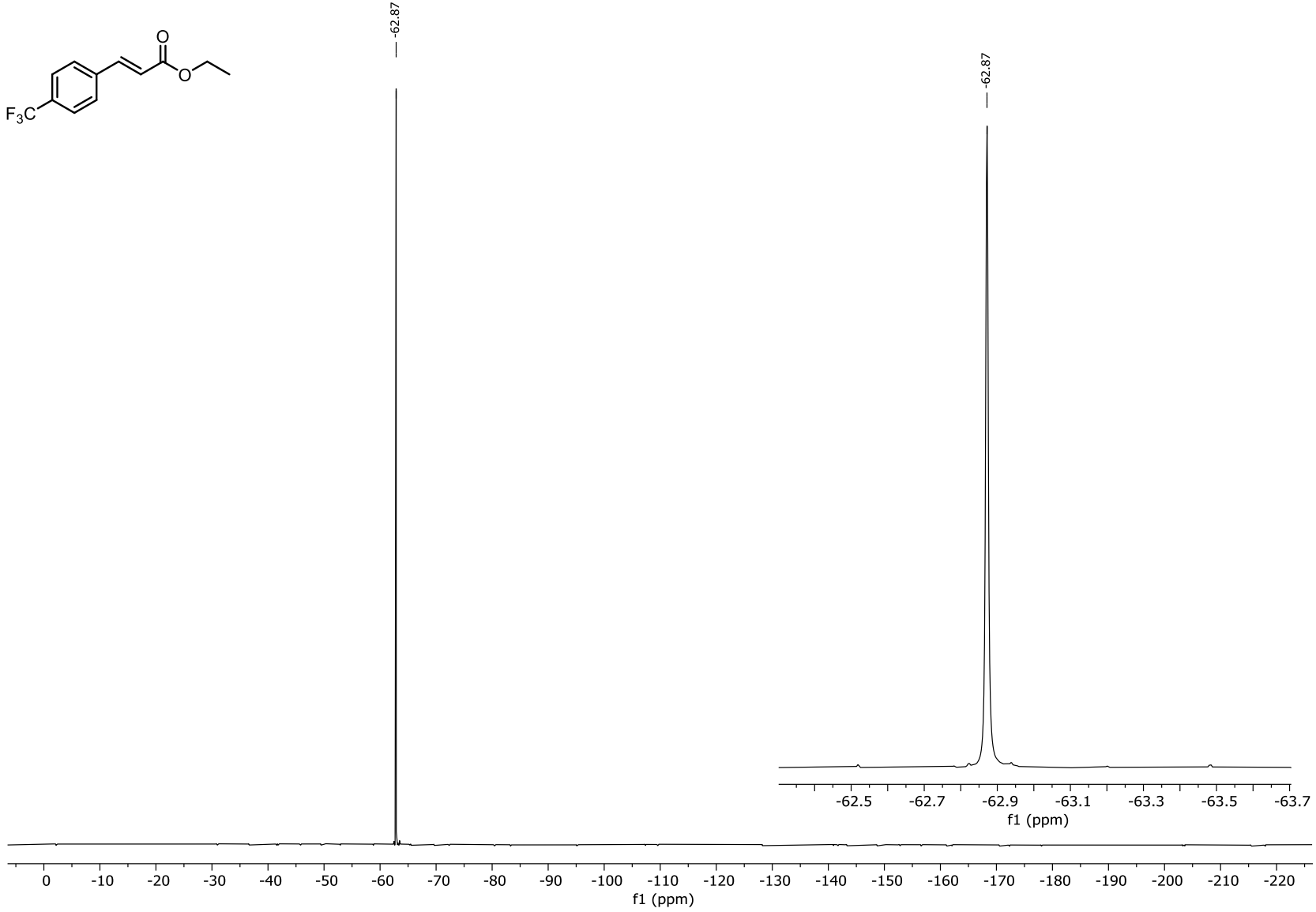
Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (1p): ^{1}H NMR (300 MHz, $CDCl_3$)



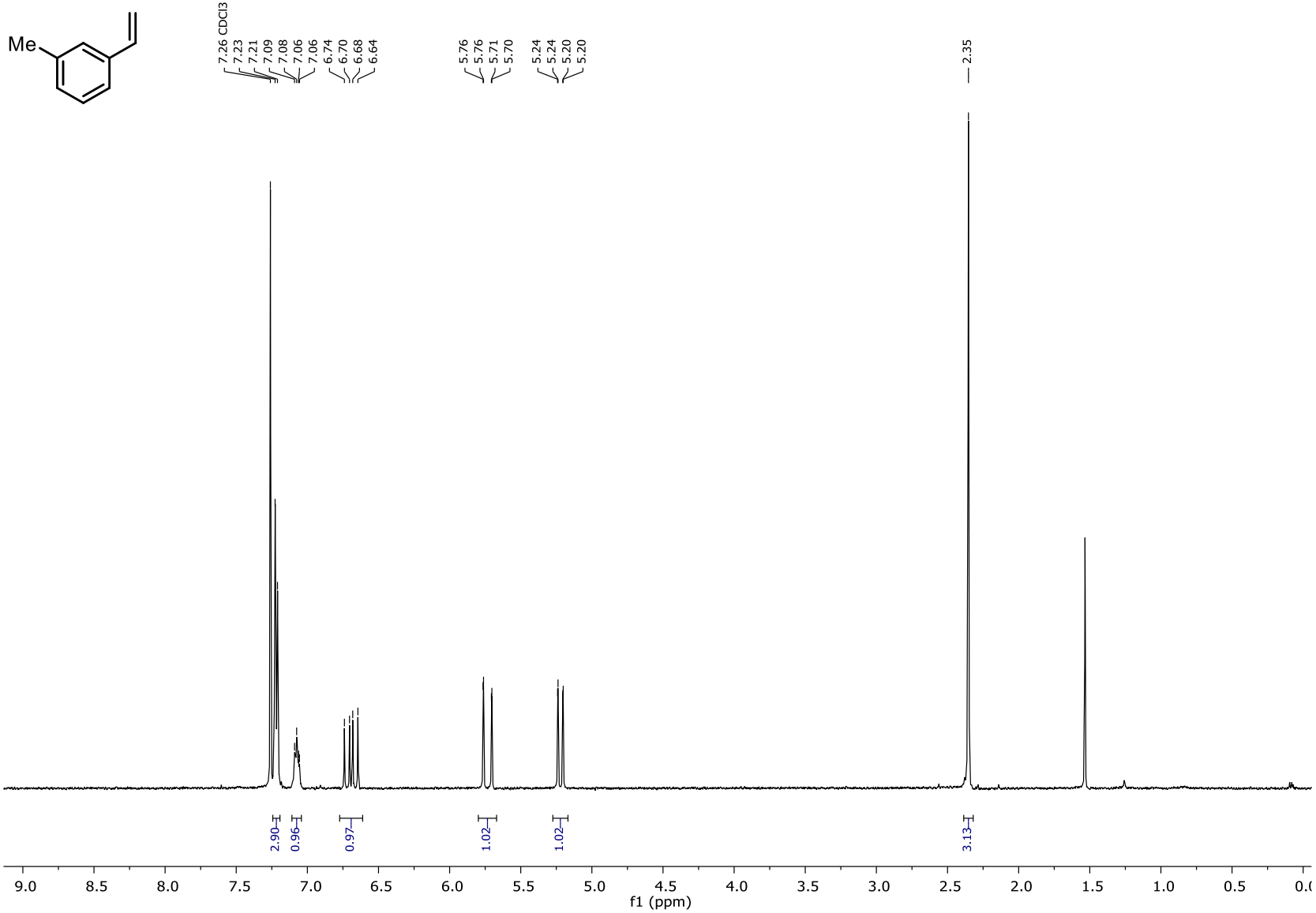
Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (1p): $^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$)



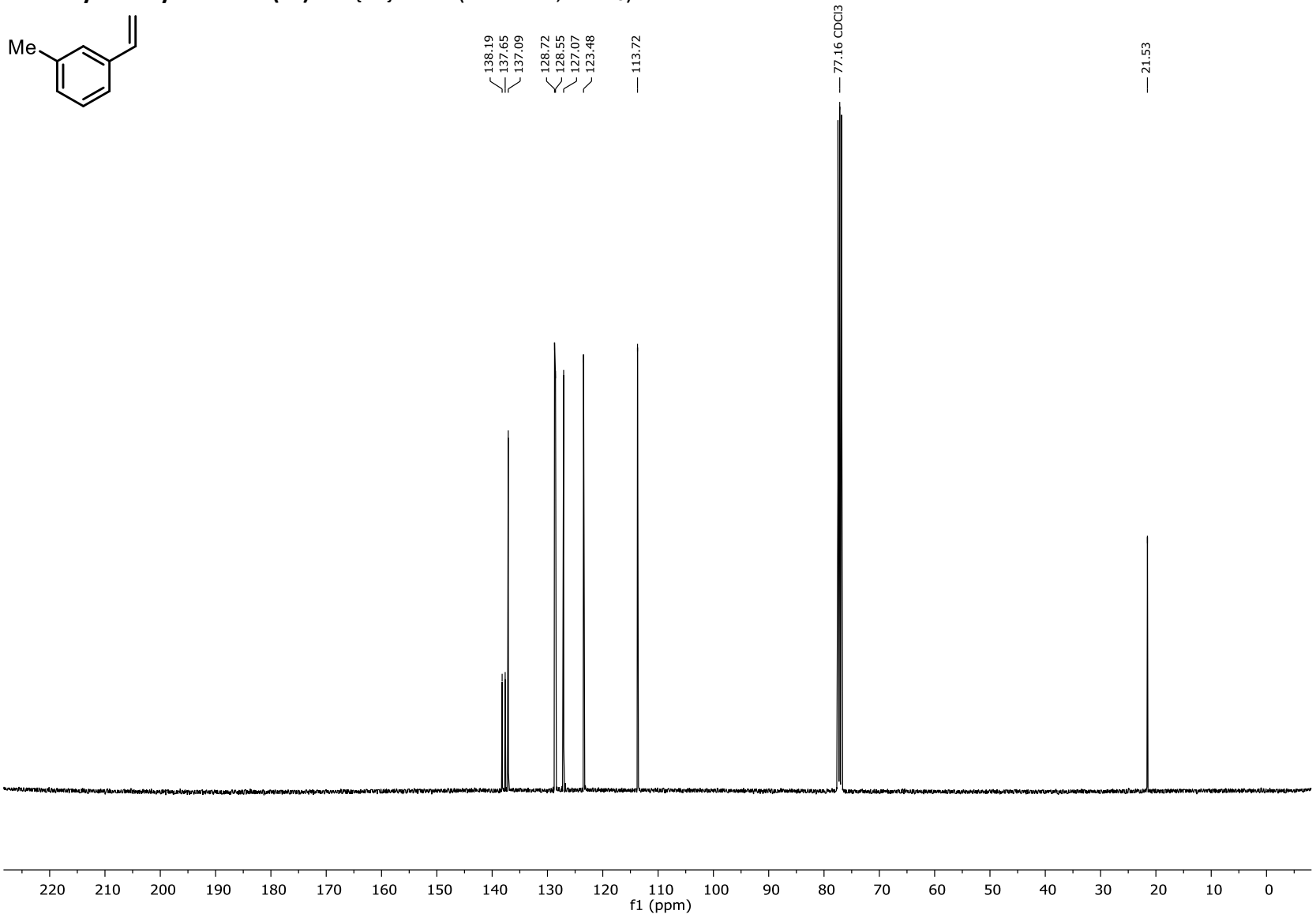
Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)acrylate (1p): $^{19}F\{^{1}H\}$ NMR (500 MHz, $CDCl_3$)



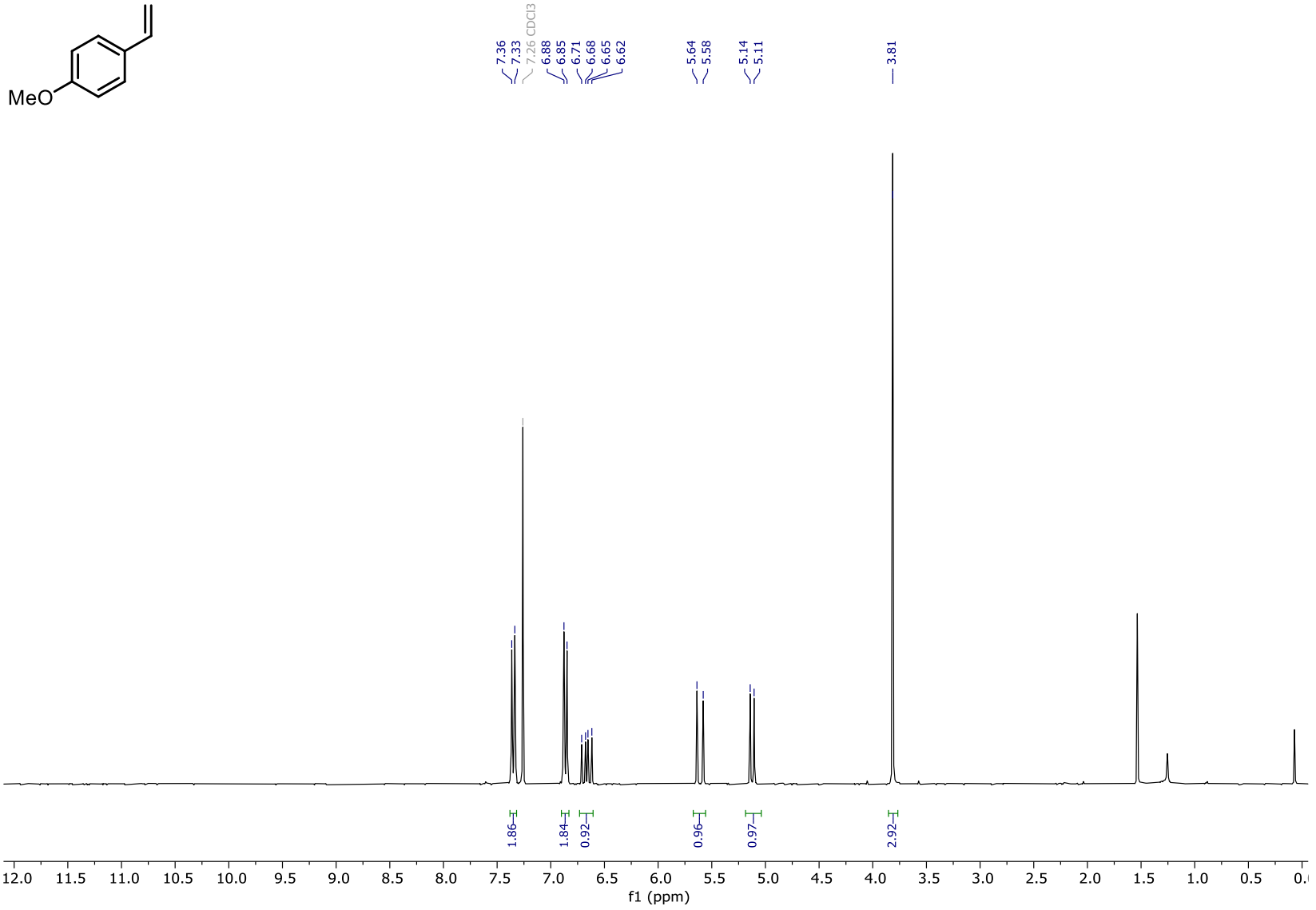
1-Methyl-3-vinylbenzene (1s): ^{1}H NMR (300 MHz, $CDCl_3$)



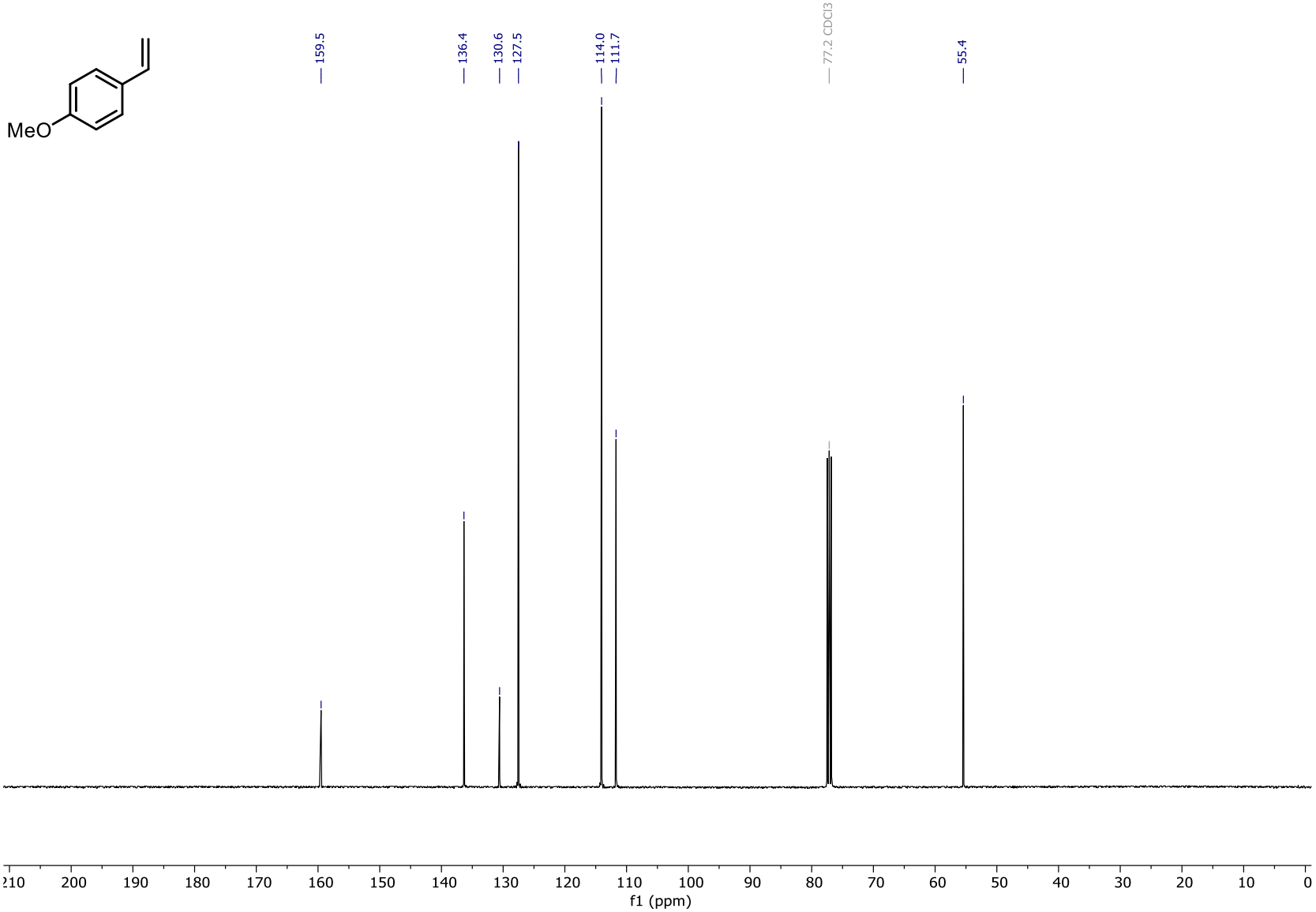
1-Methyl-3-vinylbenzene (1s): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



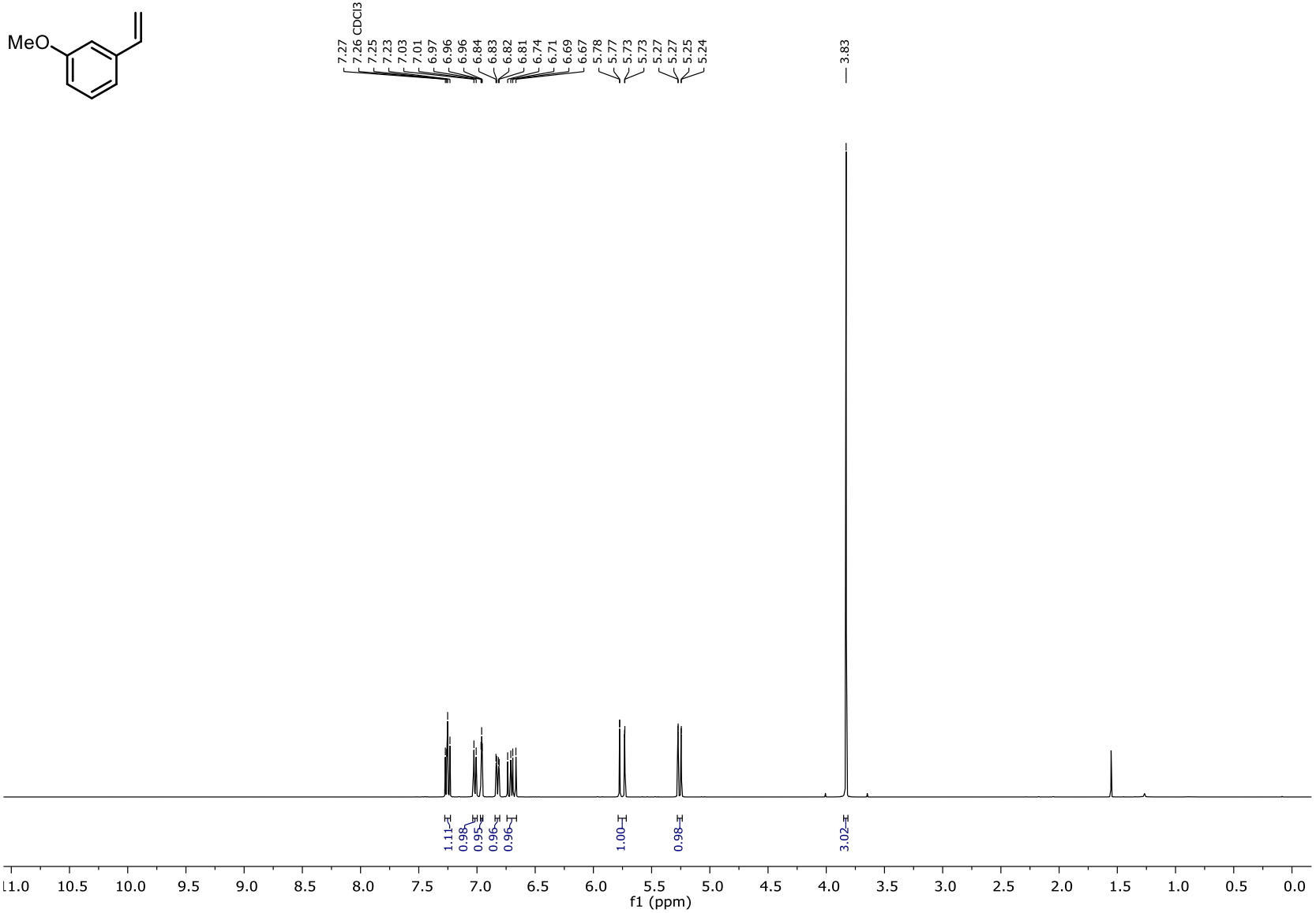
4-Methoxystyrene (1t): ^{1}H NMR (300 MHz, $CDCl_3$)



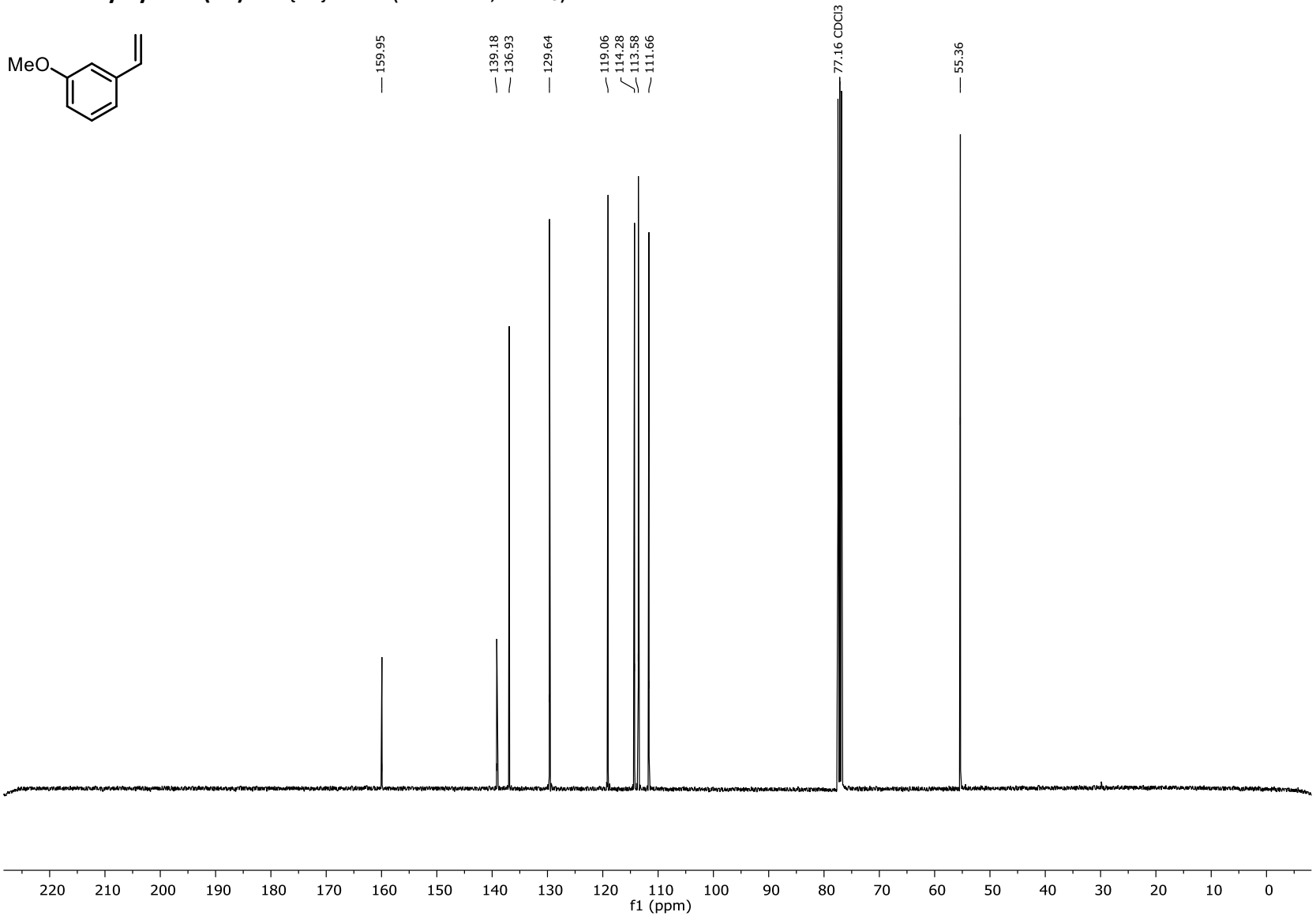
4-Methoxystyrene (1t): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



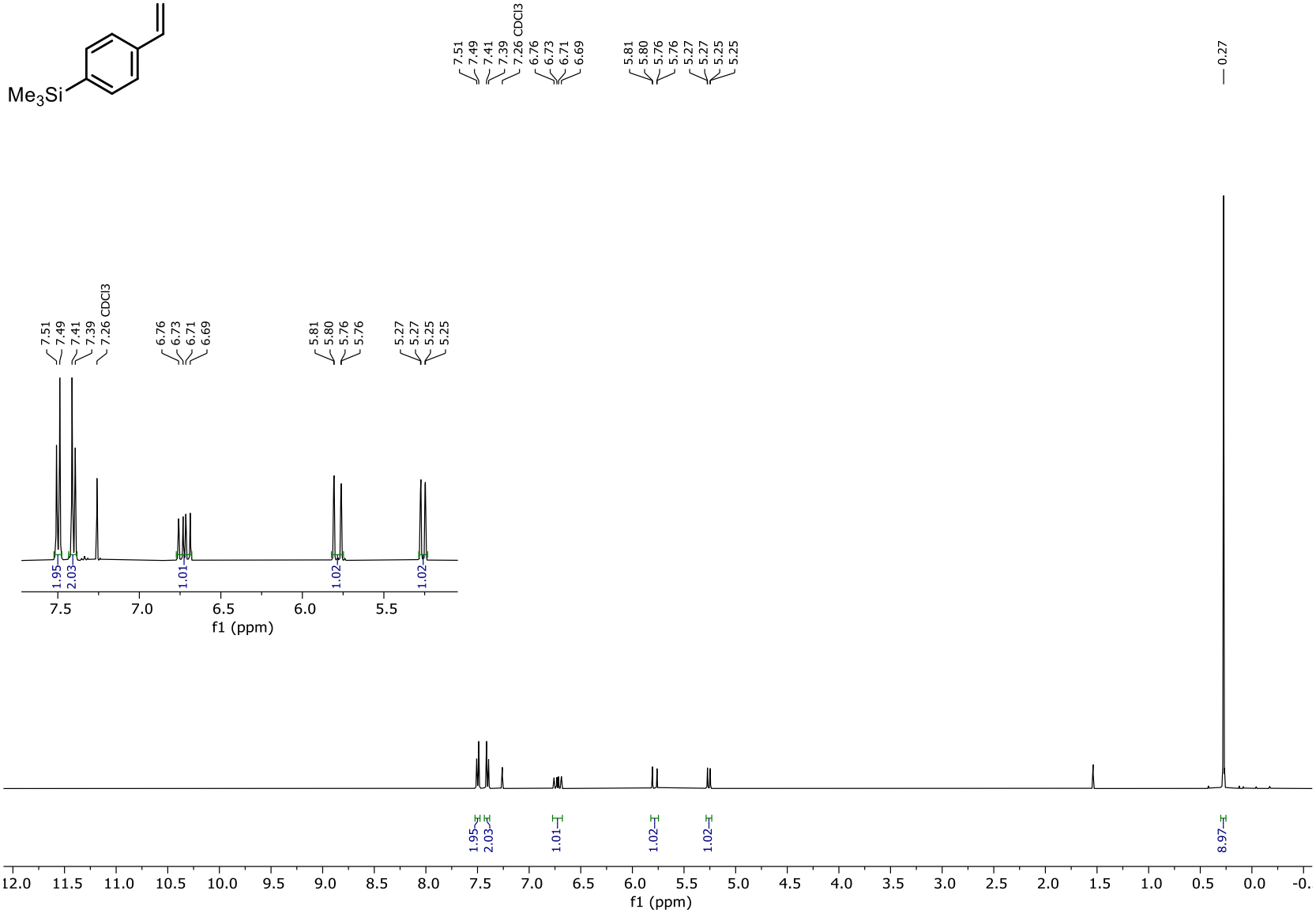
3-Methoxystyrene (1u): 1H NMR (300 MHz, $CDCl_3$)



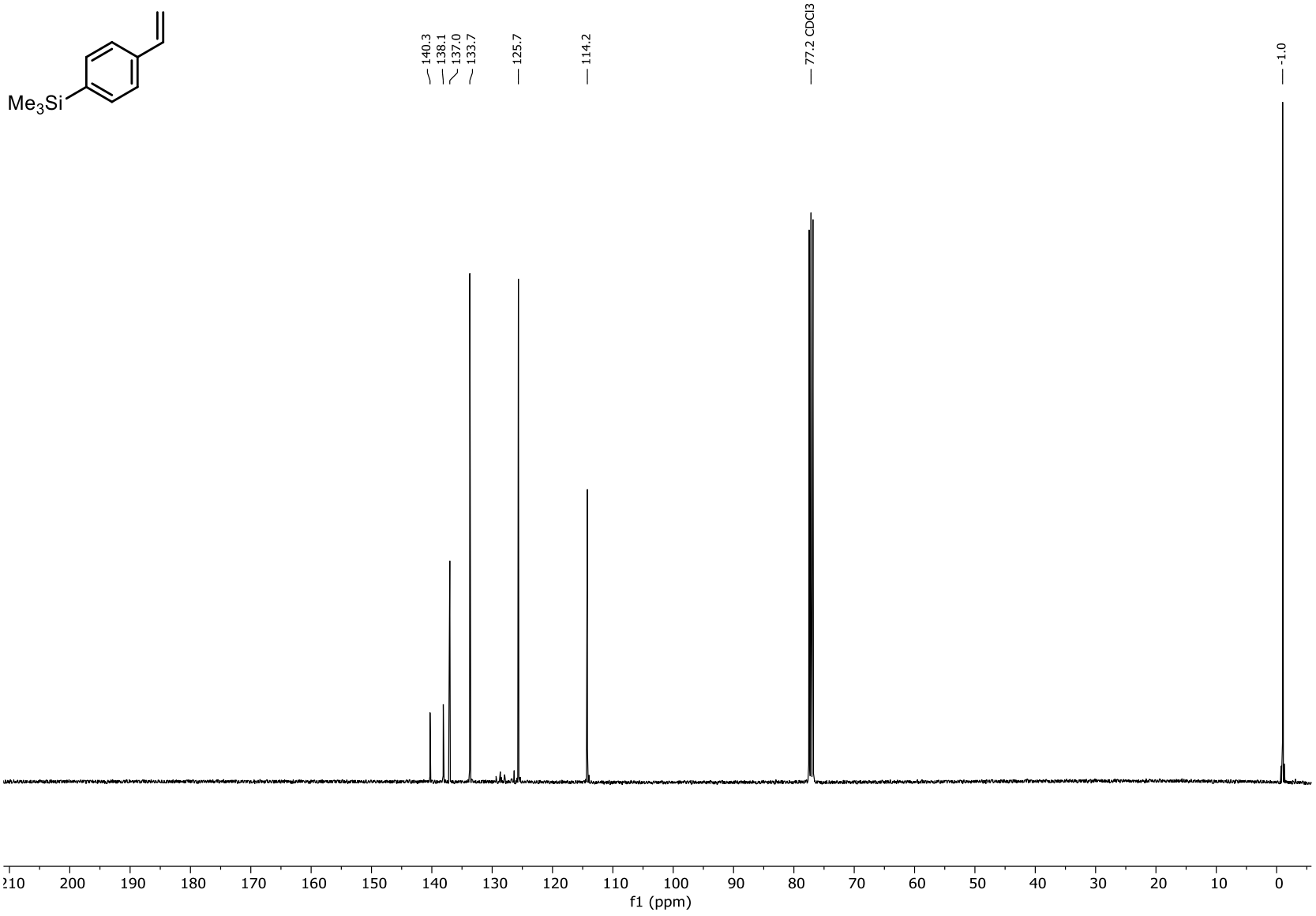
3-Methoxystyrene (1u): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



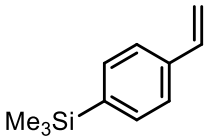
4-Trimethylsilylstyrene (1v): ^{1}H NMR (400 MHz, $CDCl_3$)



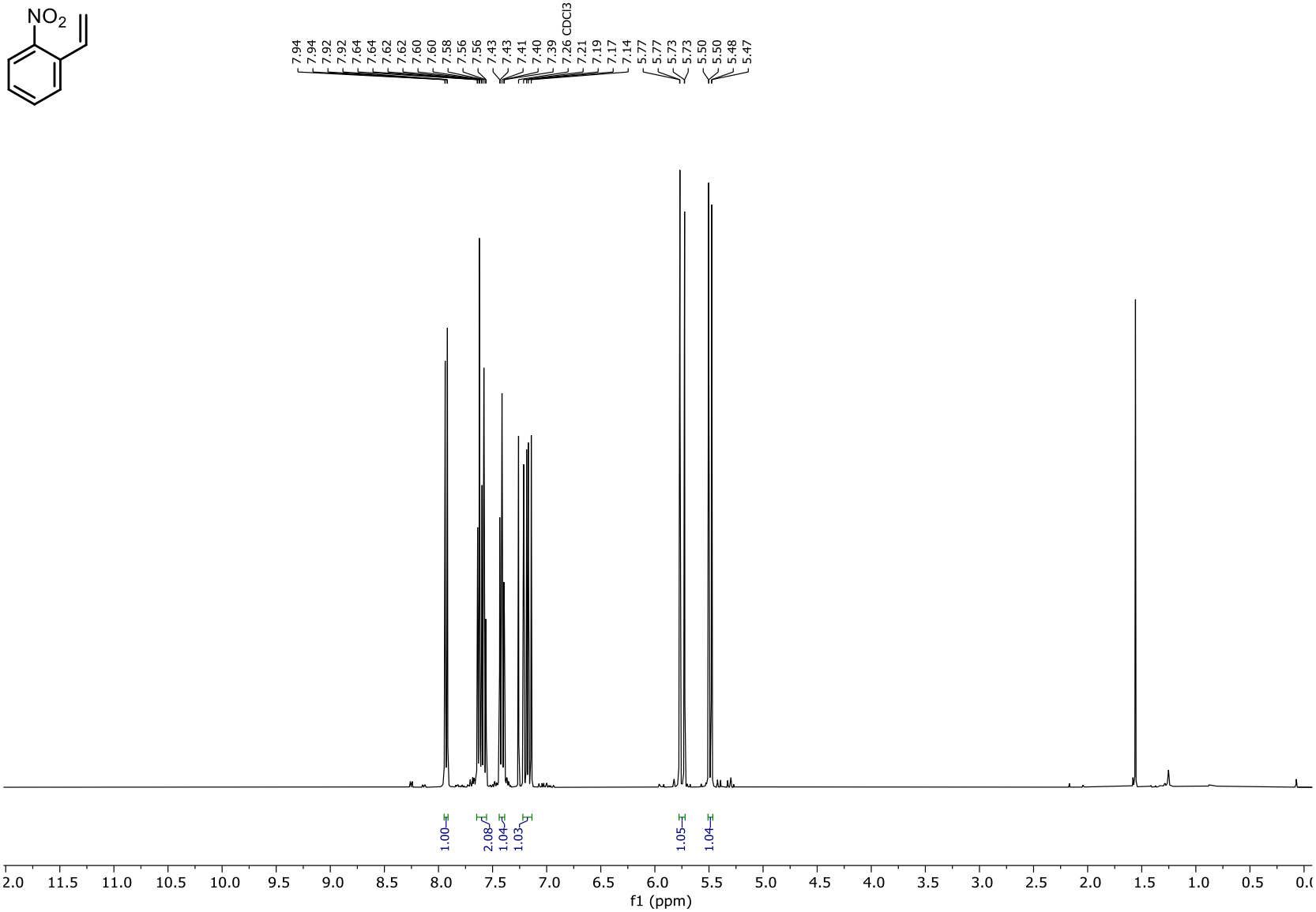
4-Trimethylsilylstyrene (1v): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



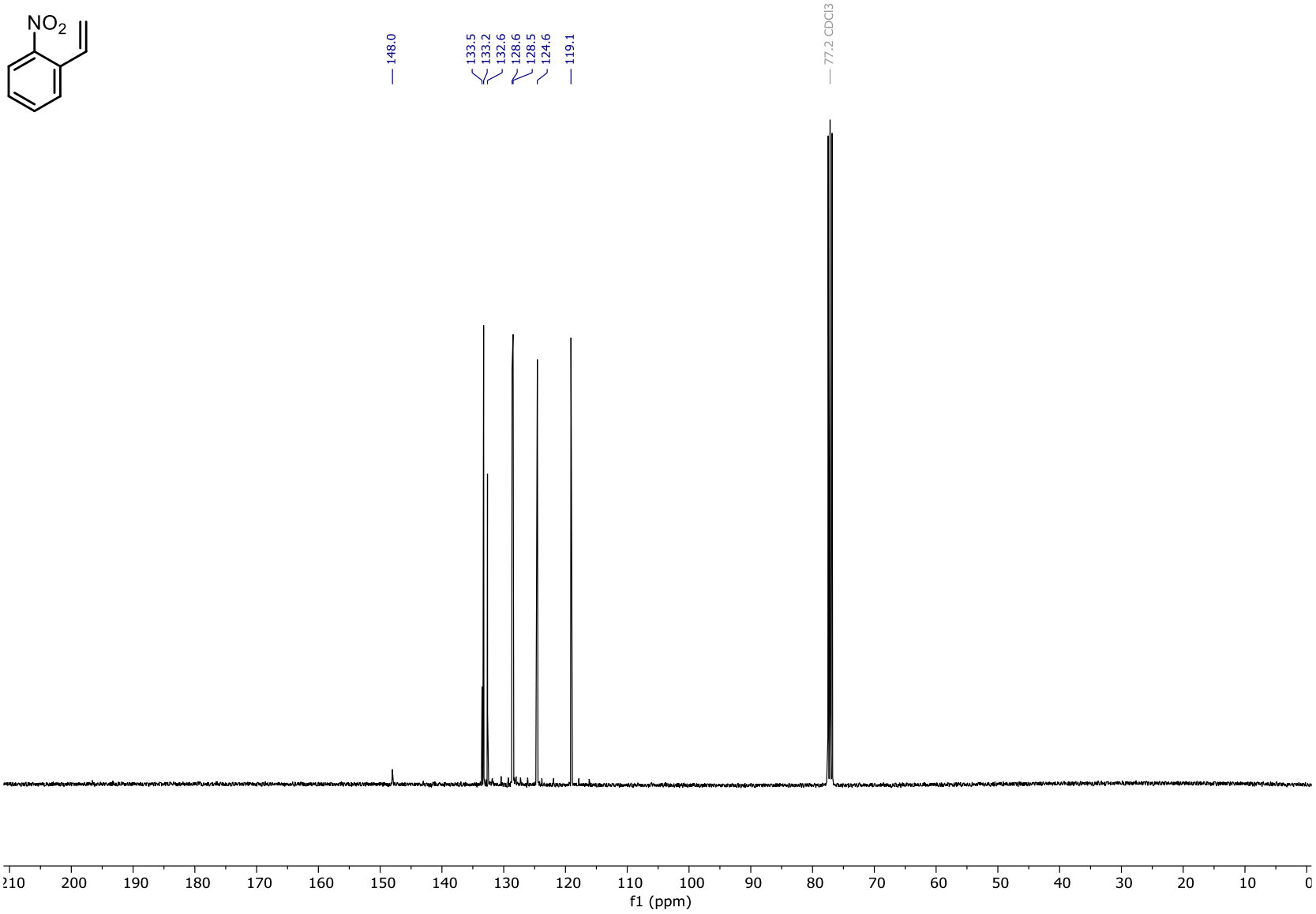
4-Trimethylsilylstyrene (1v): ^{29}Si NMR (60 MHz, $CDCl_3$)



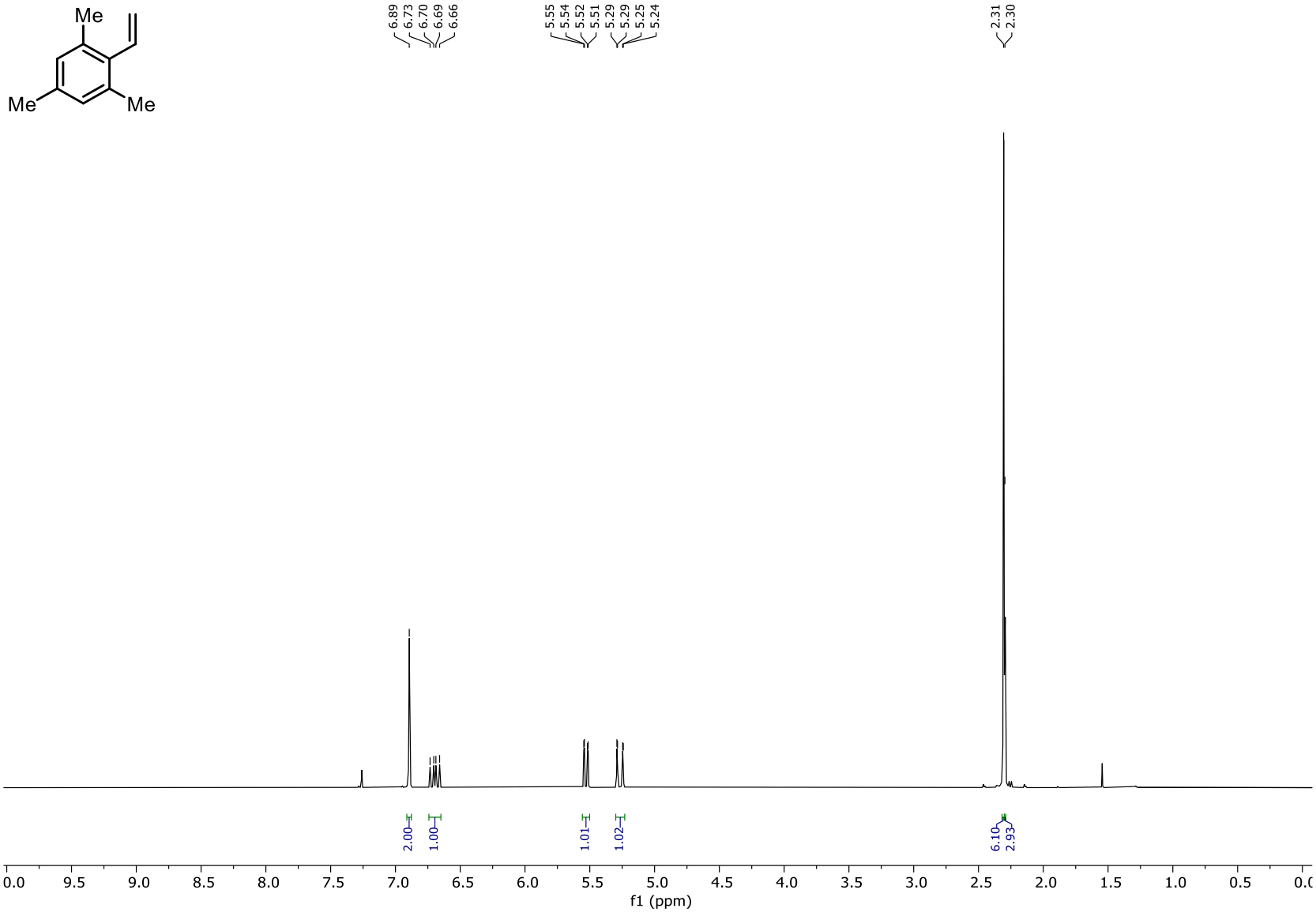
2-Nitrostyrene (1w): ^{1}H NMR (400 MHz, $CDCl_3$)



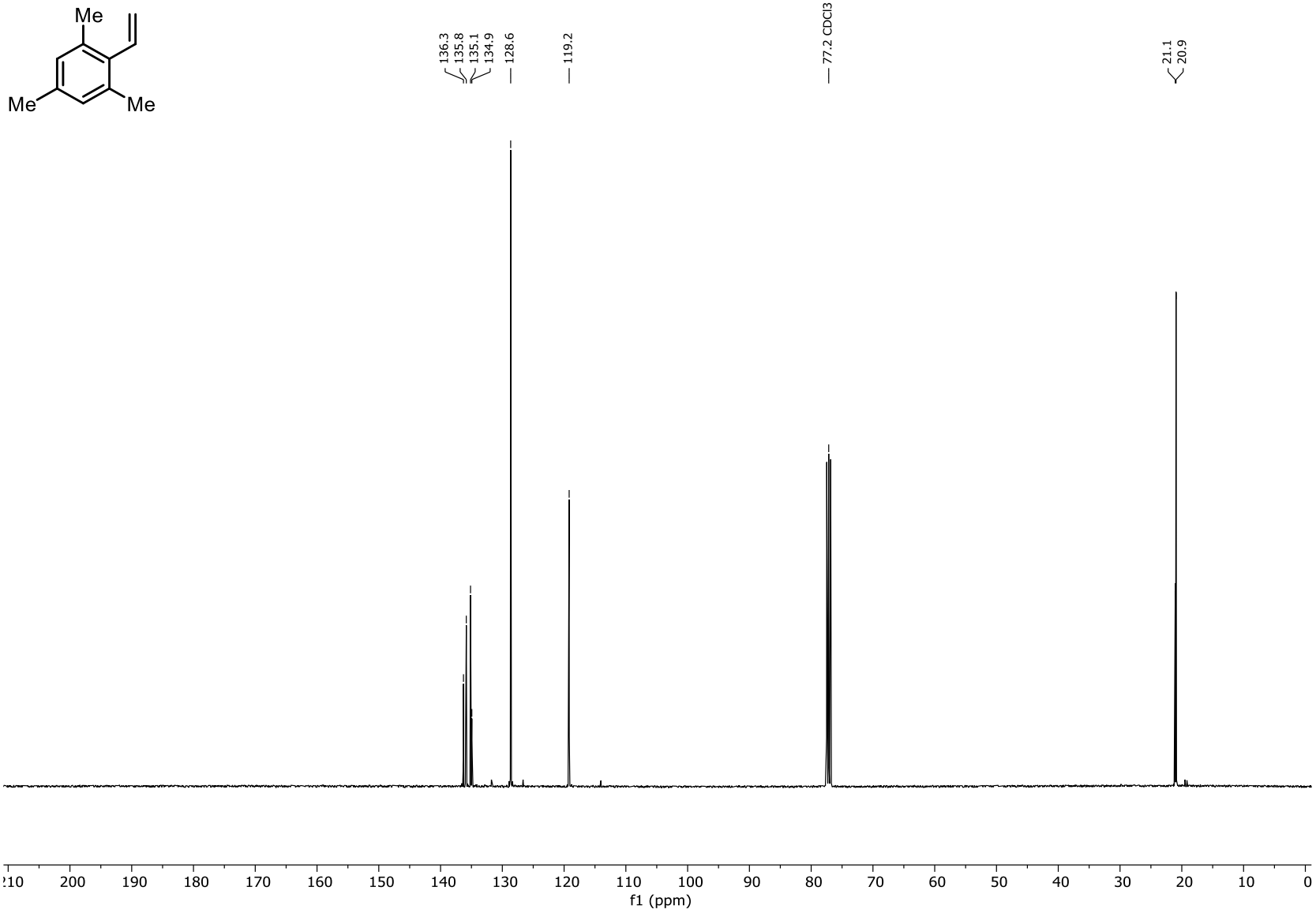
2-Nitrostyrene (1w): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



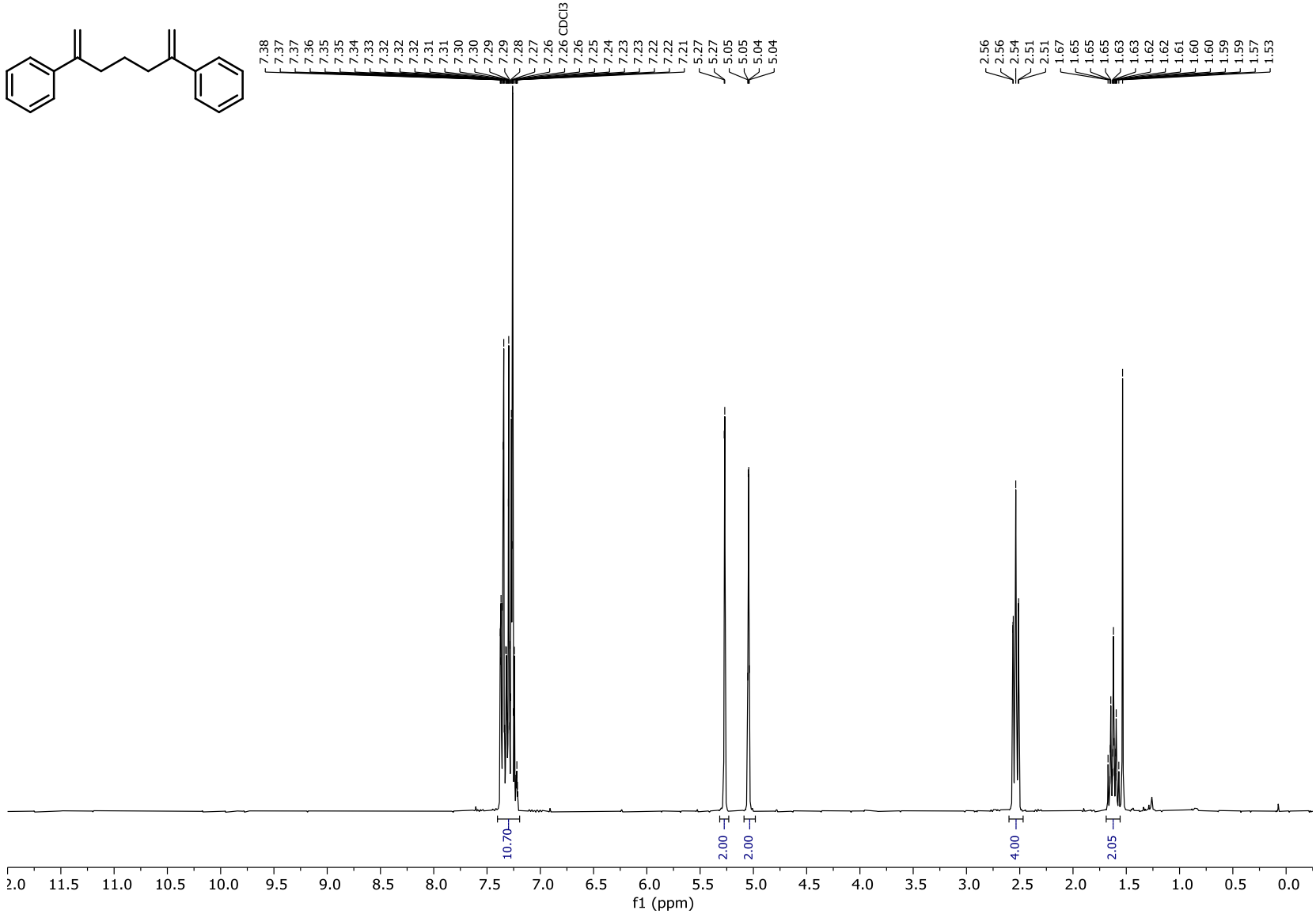
2,4,6-Trimethylstyrene (1x): ^{1}H NMR (400 MHz, $CDCl_3$)



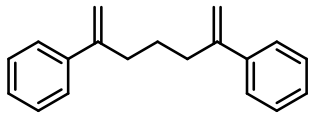
2,4,6-Trimethylstyrene (1x): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



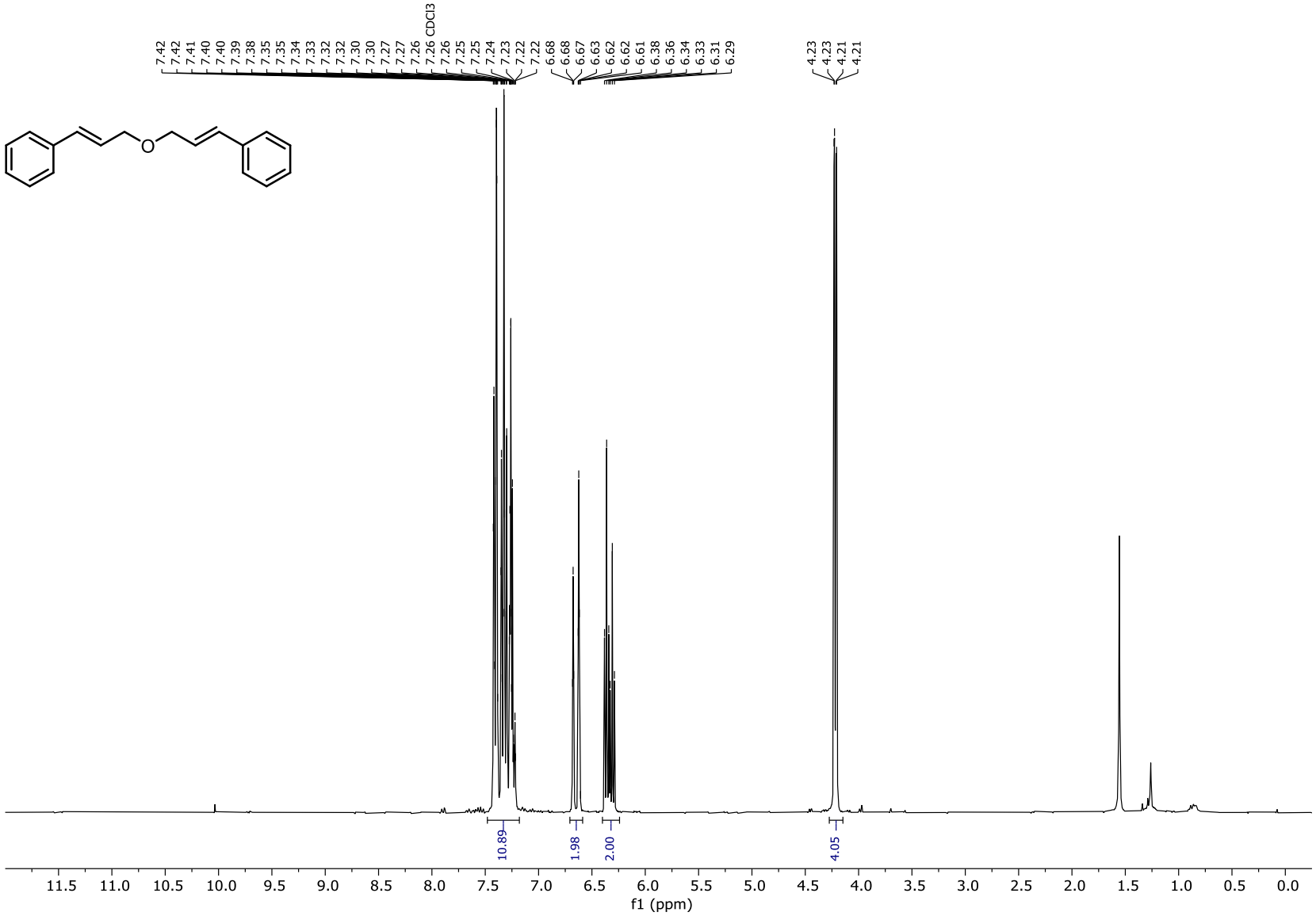
Hepta-1,6-diene-2,6-diylbenzene (3a): ^{1}H NMR (300 MHz, $CDCl_3$)



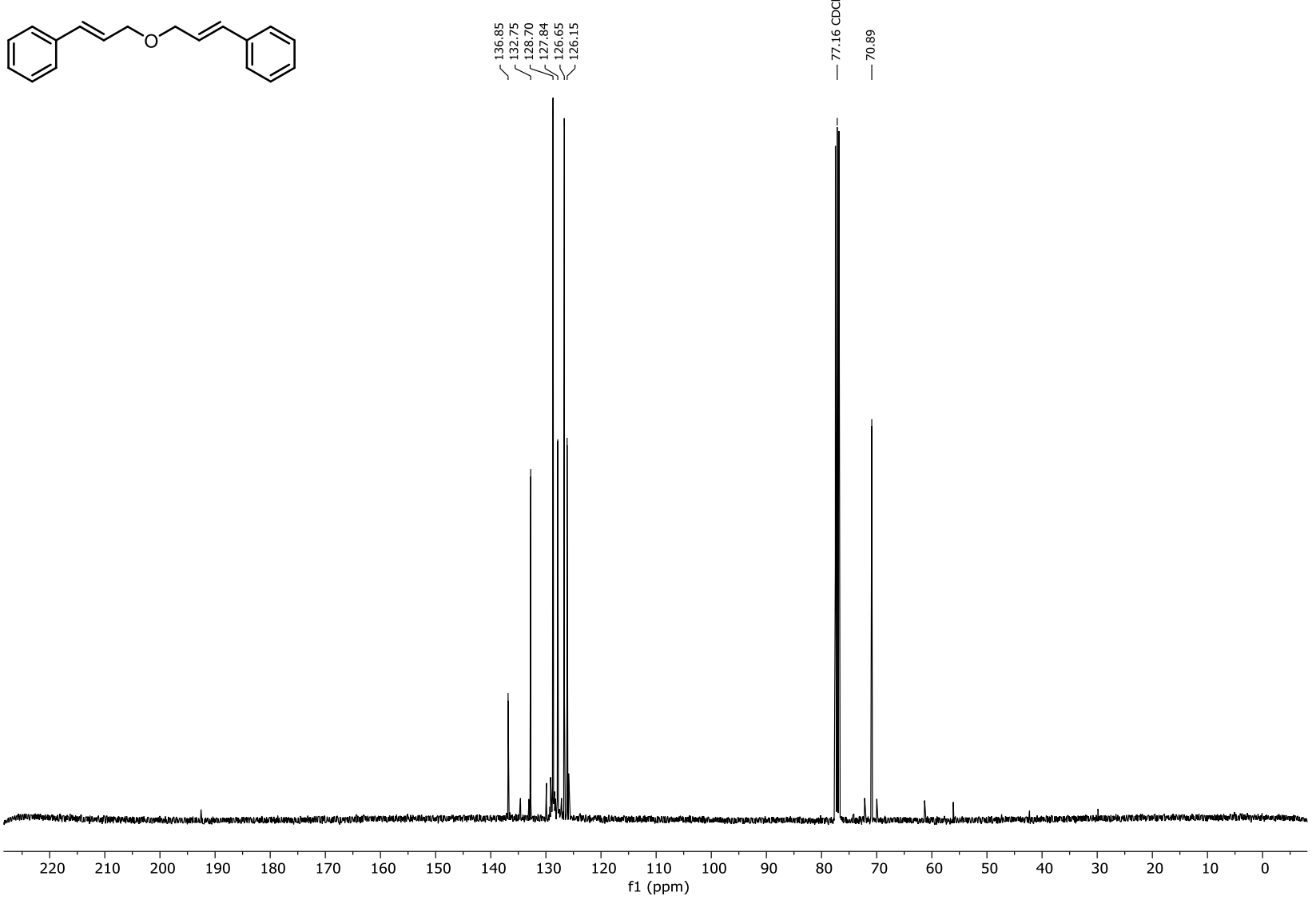
Hepta-1,6-diene-2,6-diylbenzene (3a): $^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$)



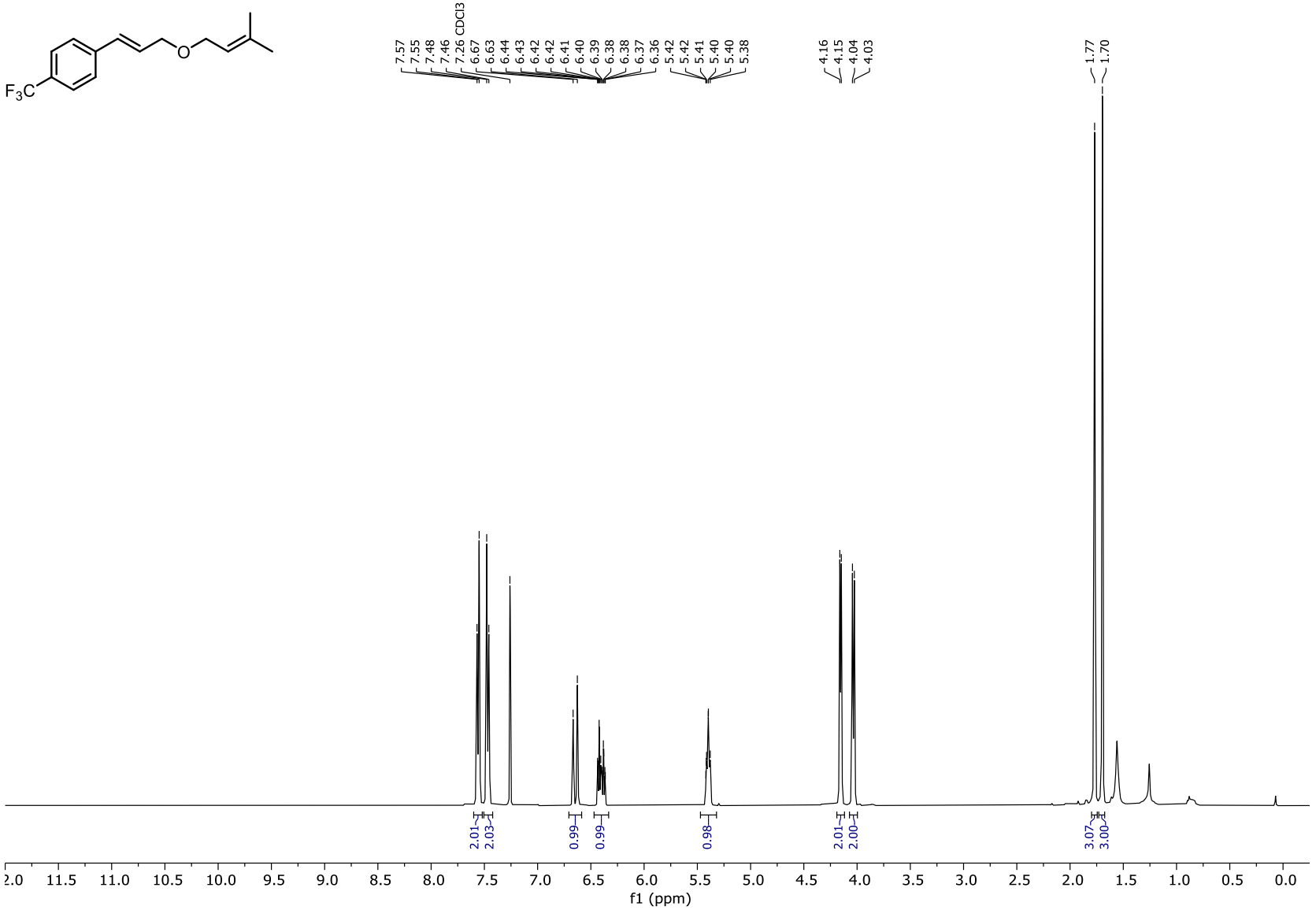
((1E,1'E)-oxybis(prop-1-ene-3,1-diyl))dibenzene (3b): ^{1}H NMR (300 MHz, $CDCl_3$)



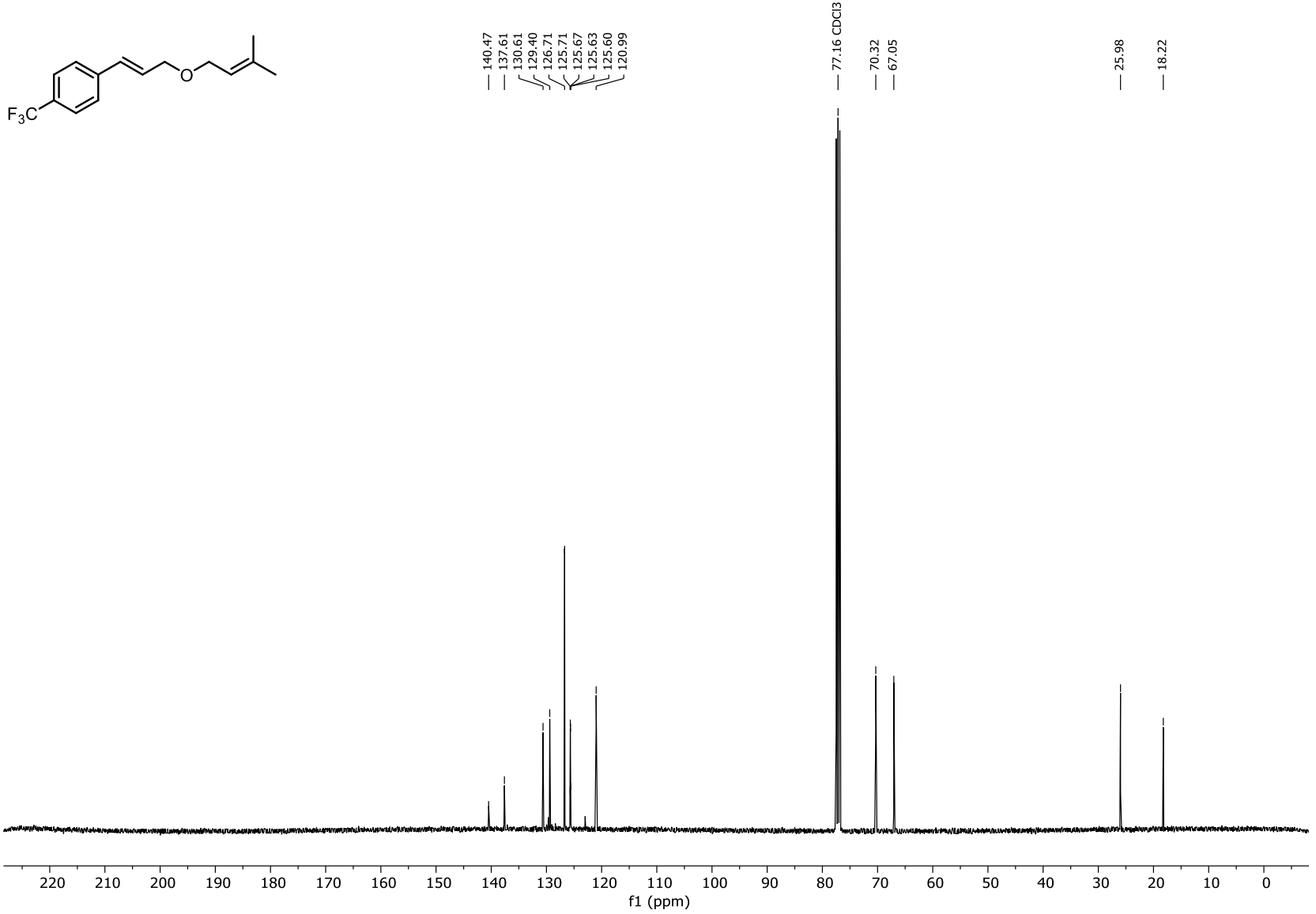
((1E,1'E)-oxybis(prop-1-ene-3,1-diyl))dibenzene (3b): $^{13}C\{^{1}H\}$ NMR (400 MHz, $CDCl_3$)



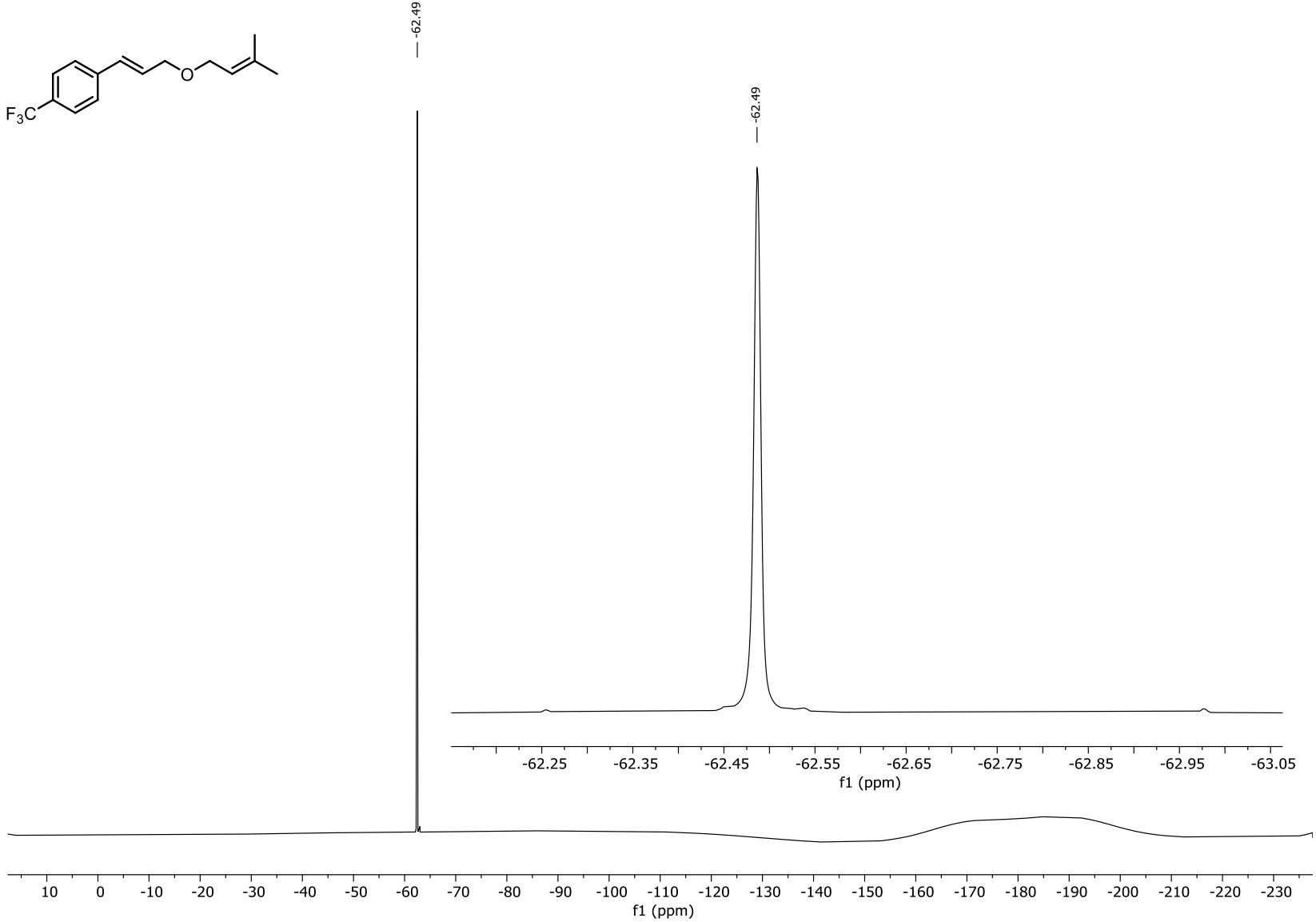
(*E*)-1-(3-((4-methylpent-3-en-1-yl)oxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene (3c): ^{1}H NMR (400 MHz, $CDCl_3$)



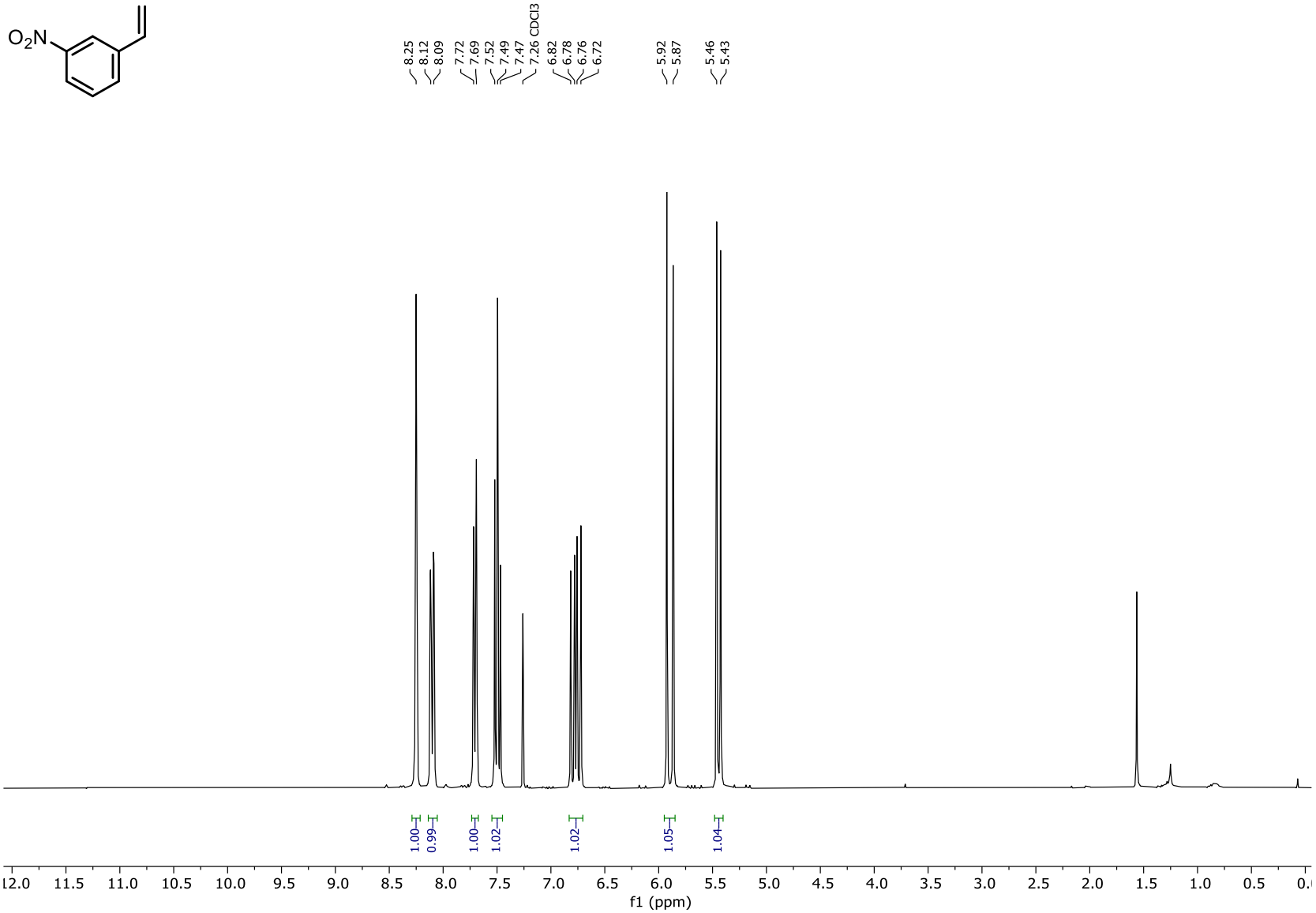
(*E*)-1-(3-((4-methylpent-3-en-1-yl)oxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene (3c): $^{13}C\{^{1}H\}$ NMR (400 MHz, $CDCl_3$)



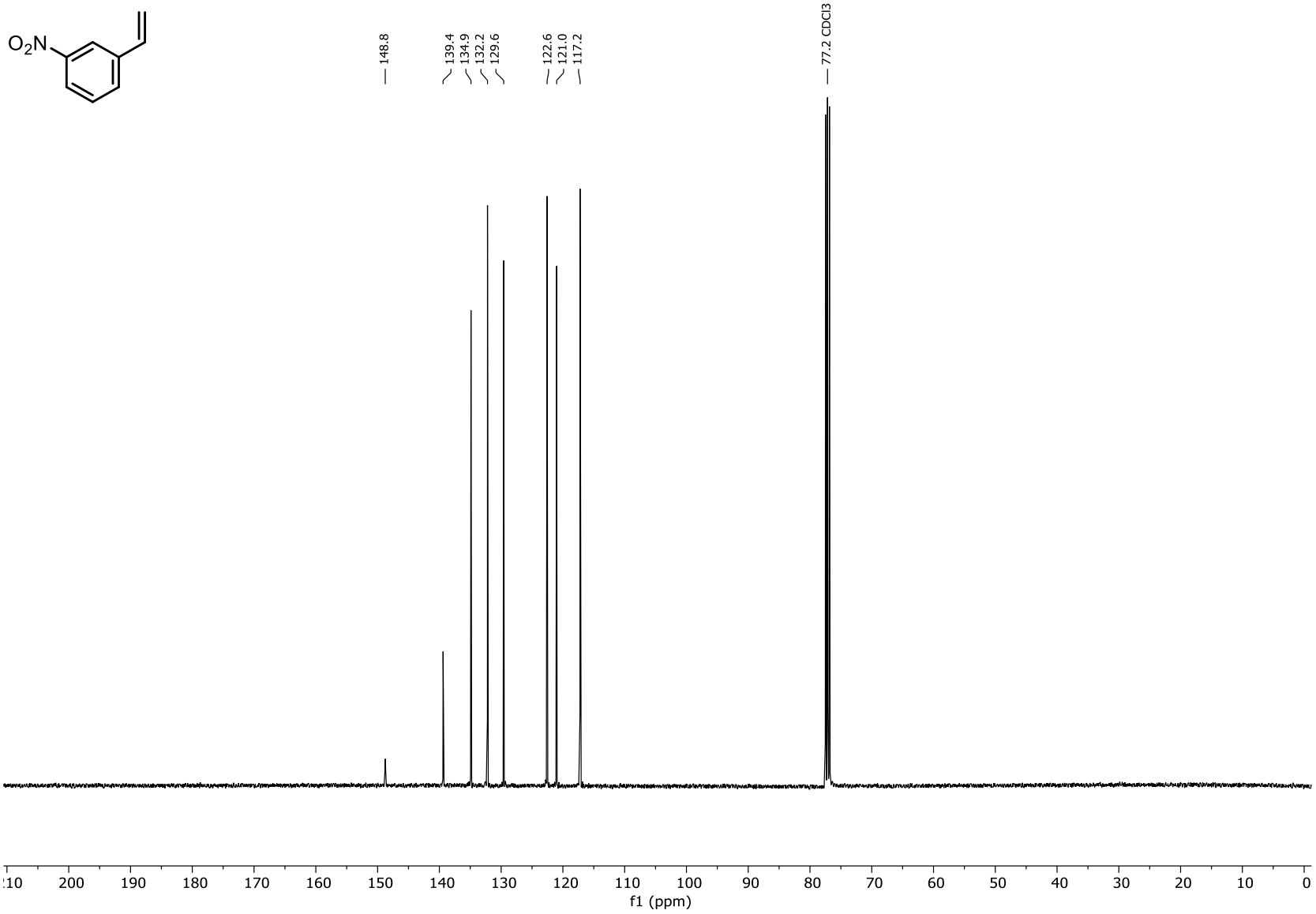
(*E*)-1-(3-((4-methylpent-3-en-1-yl)oxy)prop-1-en-1-yl)-4-(trifluoromethyl)benzene (3c): $^{19}F\{^{1}H\}$ NMR (400 MHz, $CDCl_3$)



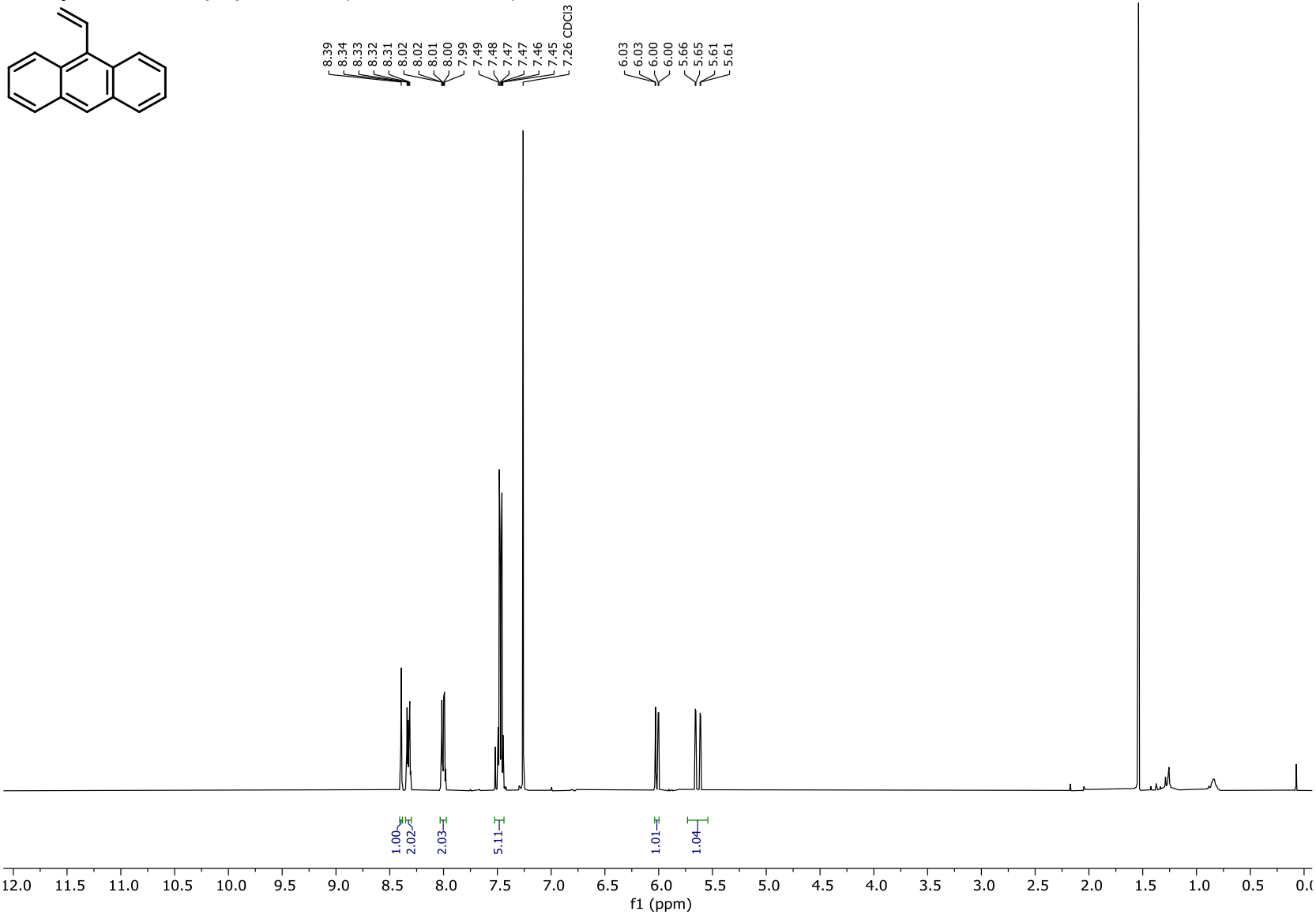
3-Nitrostyrene (S1): ^{1}H NMR (300 MHz, $CDCl_3$)



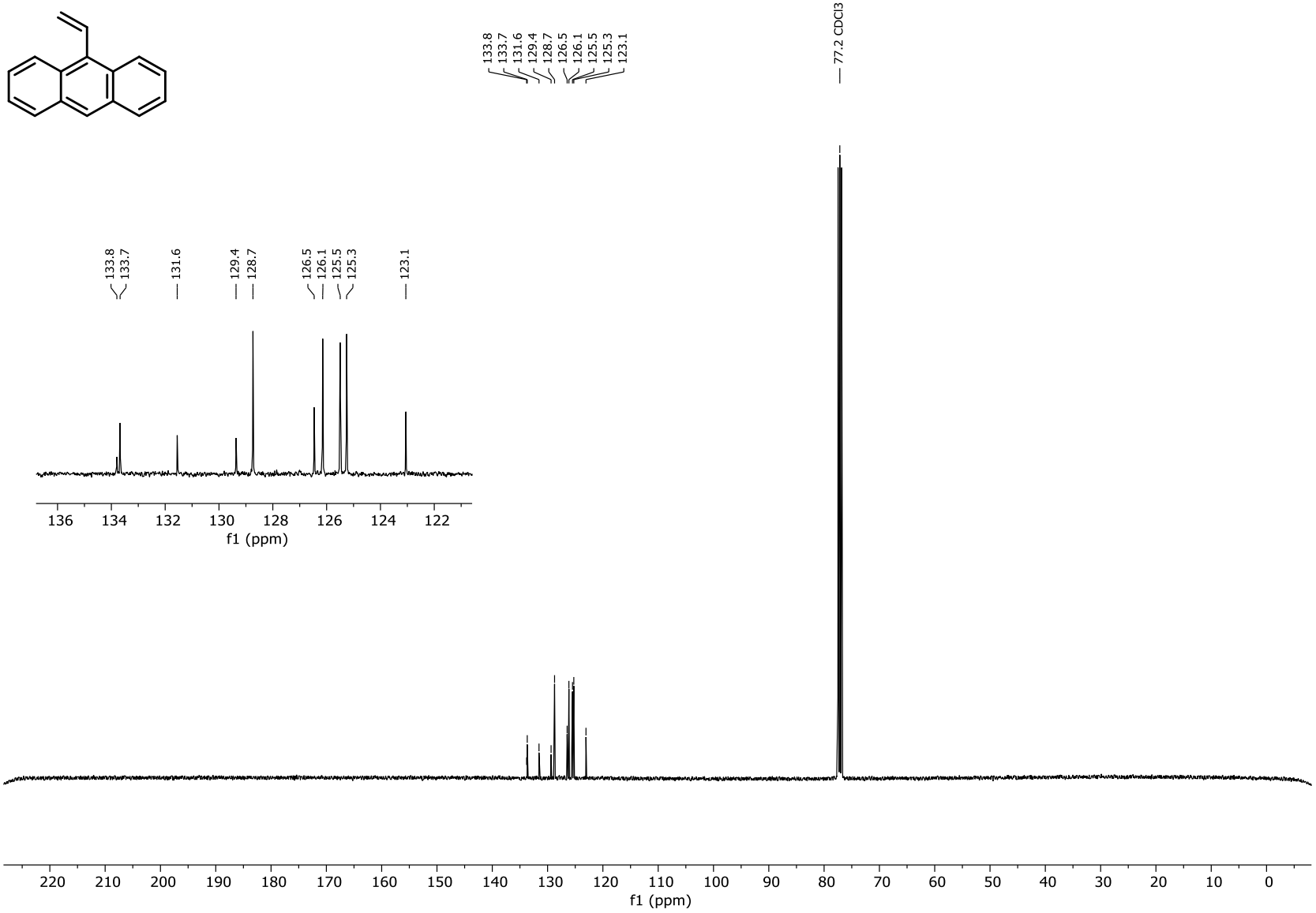
3-Nitrostyrene (S1): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



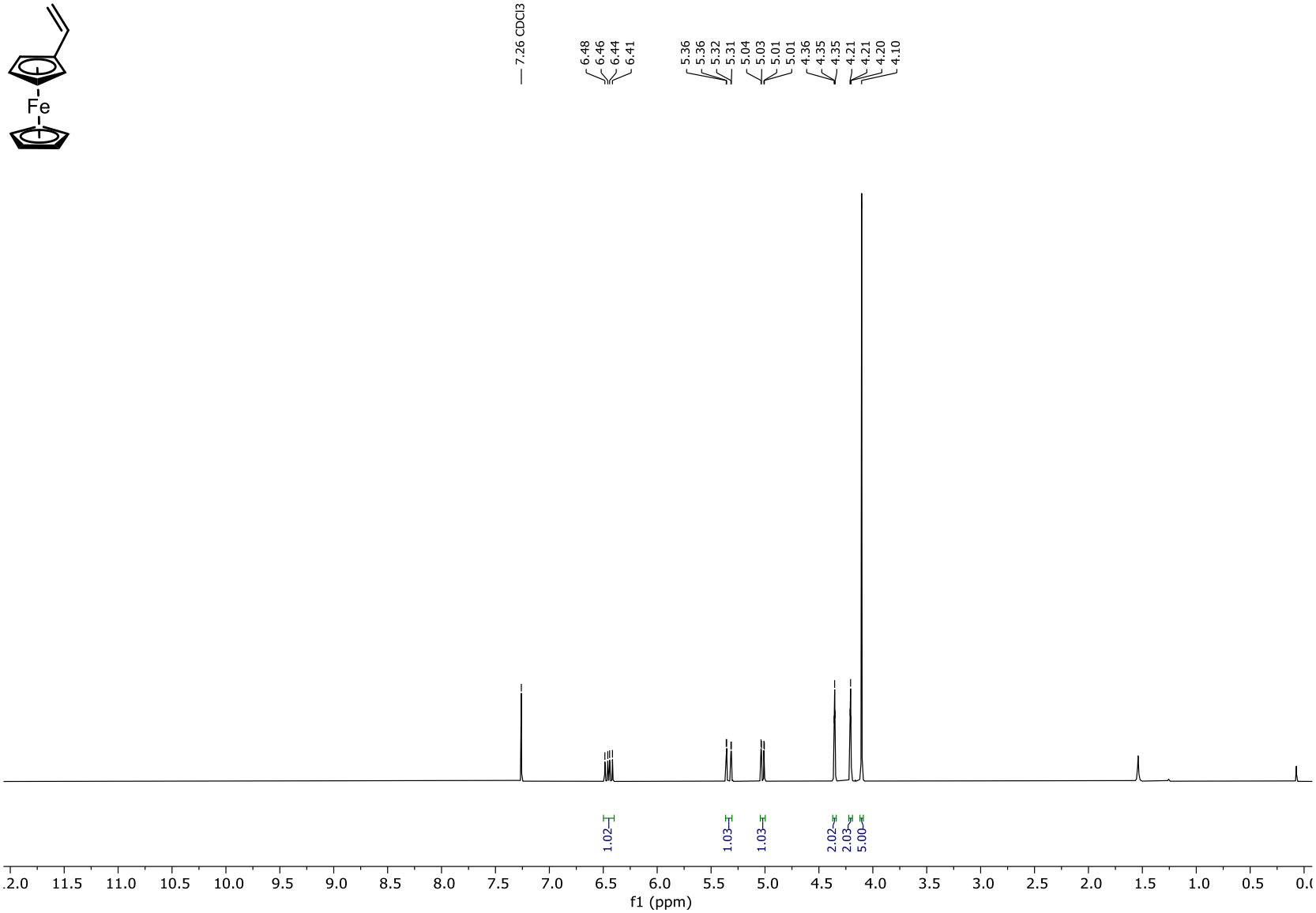
9-Vinylanthracene (S4): ^{1}H NMR (400 MHz, $CDCl_3$)



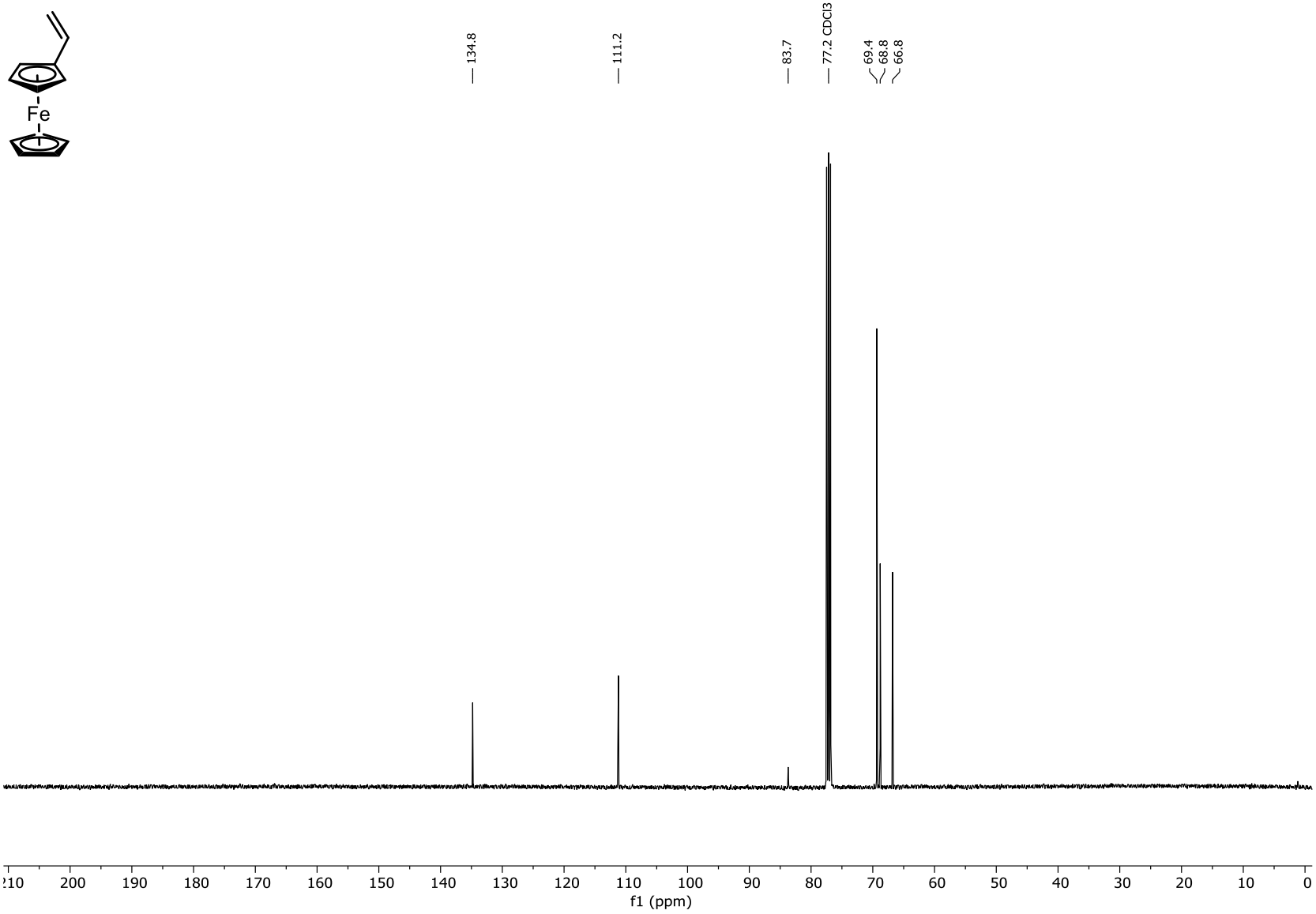
9-Vinylanthracene (S4): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



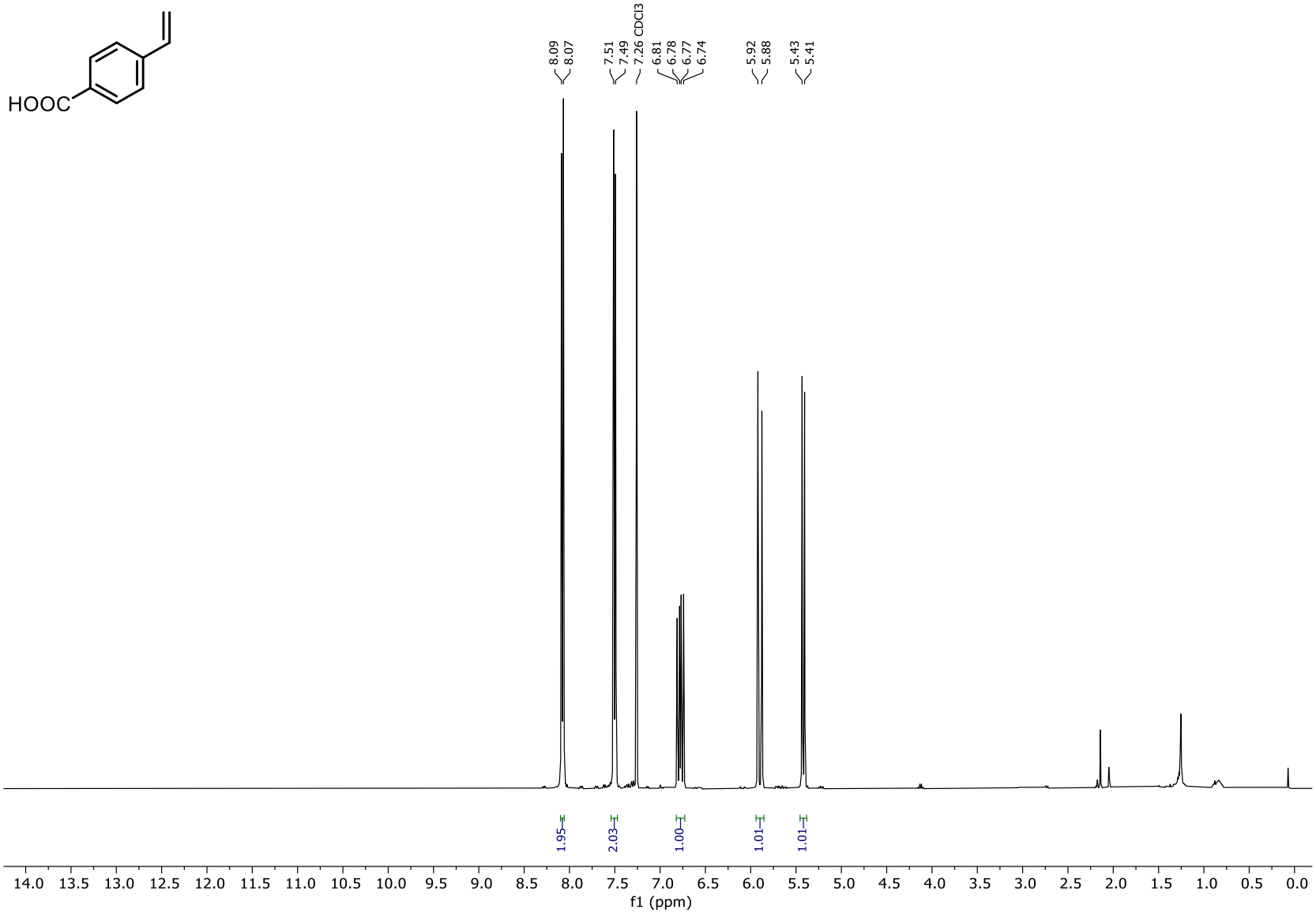
Vinylferrocene (S5): ^{1}H NMR (400 MHz, $CDCl_3$)



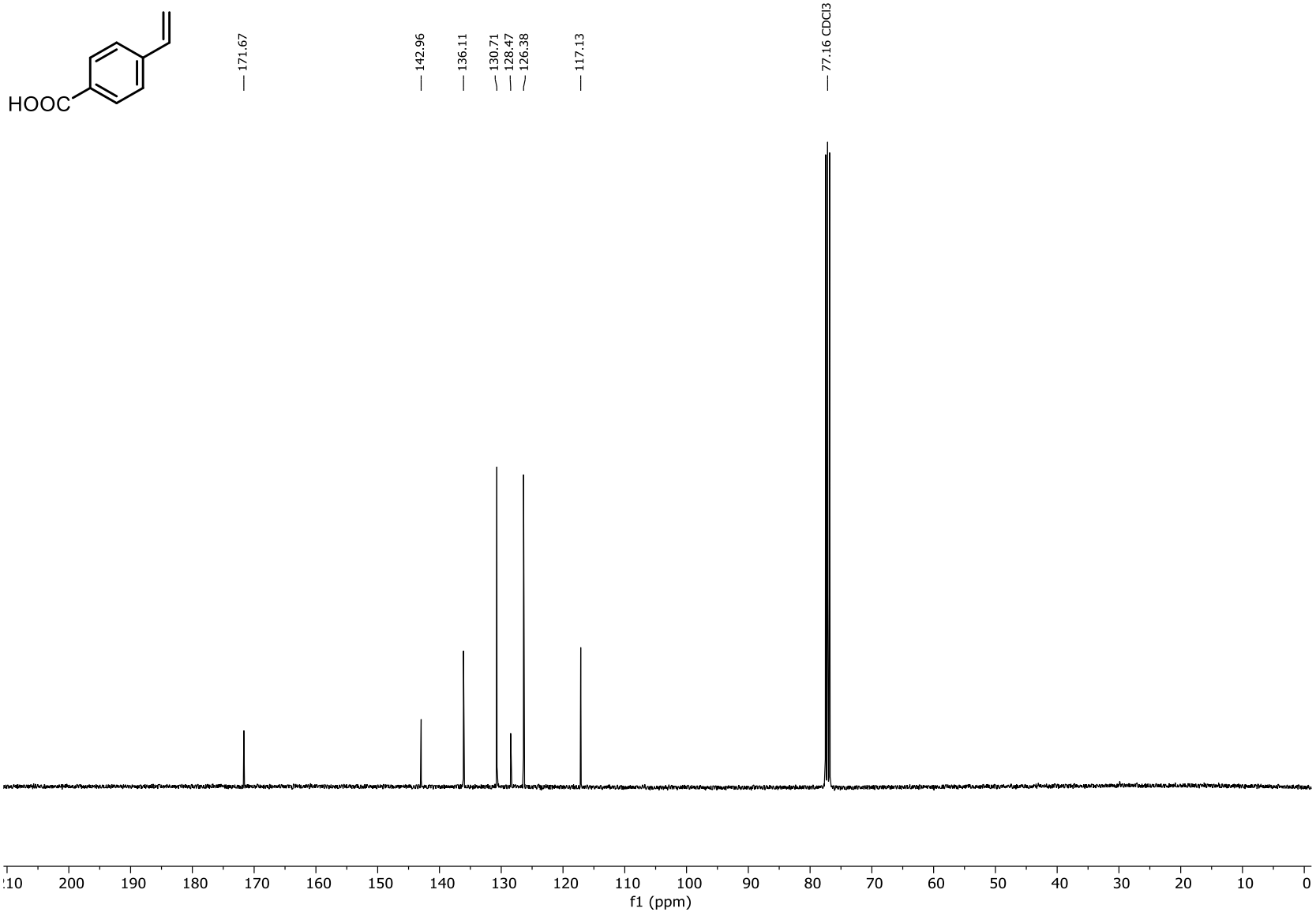
Vinylferrocene (S5): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



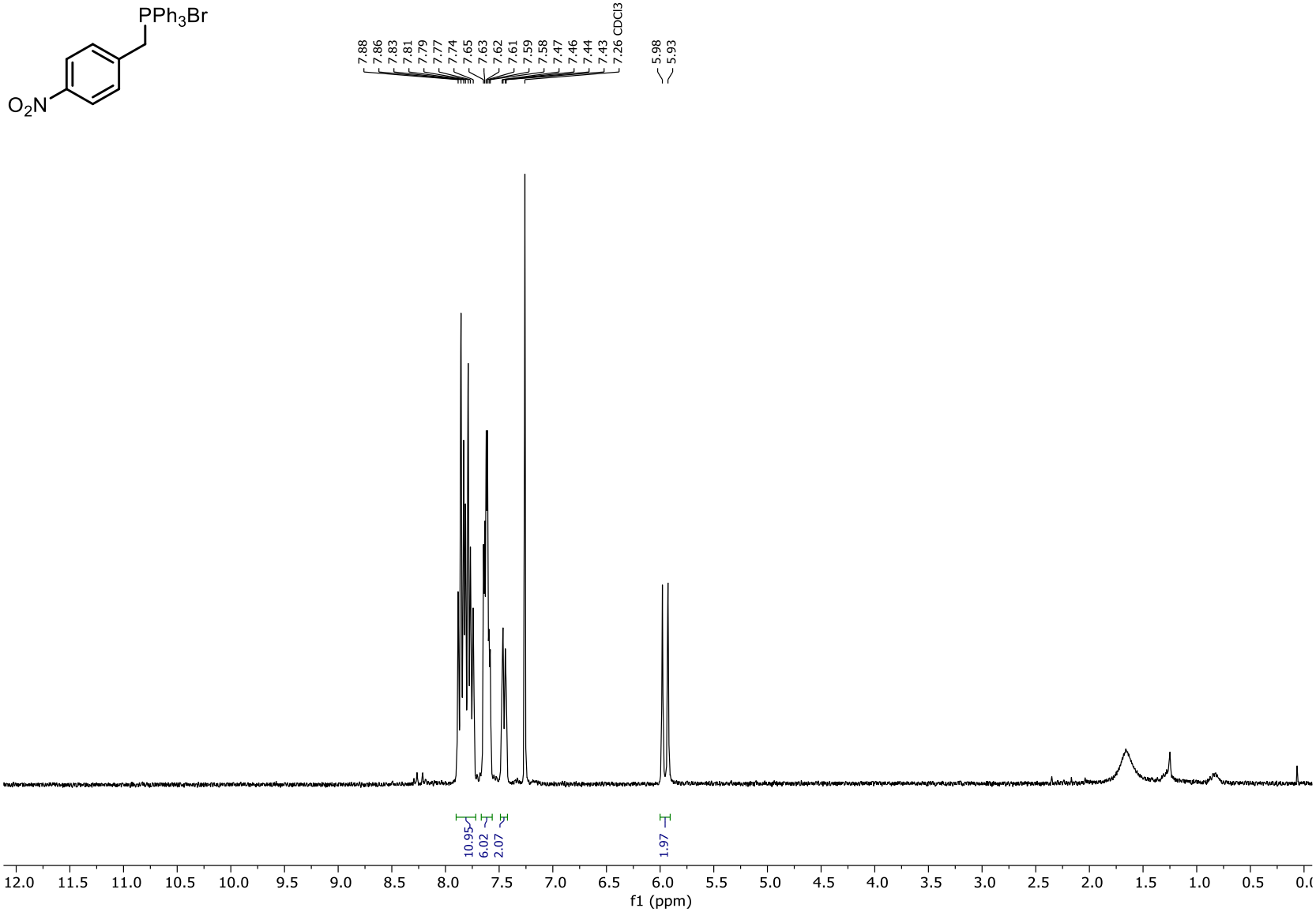
4-Vinylbenzoic acid (S6): ^{1}H NMR (400 MHz, $CDCl_3$)



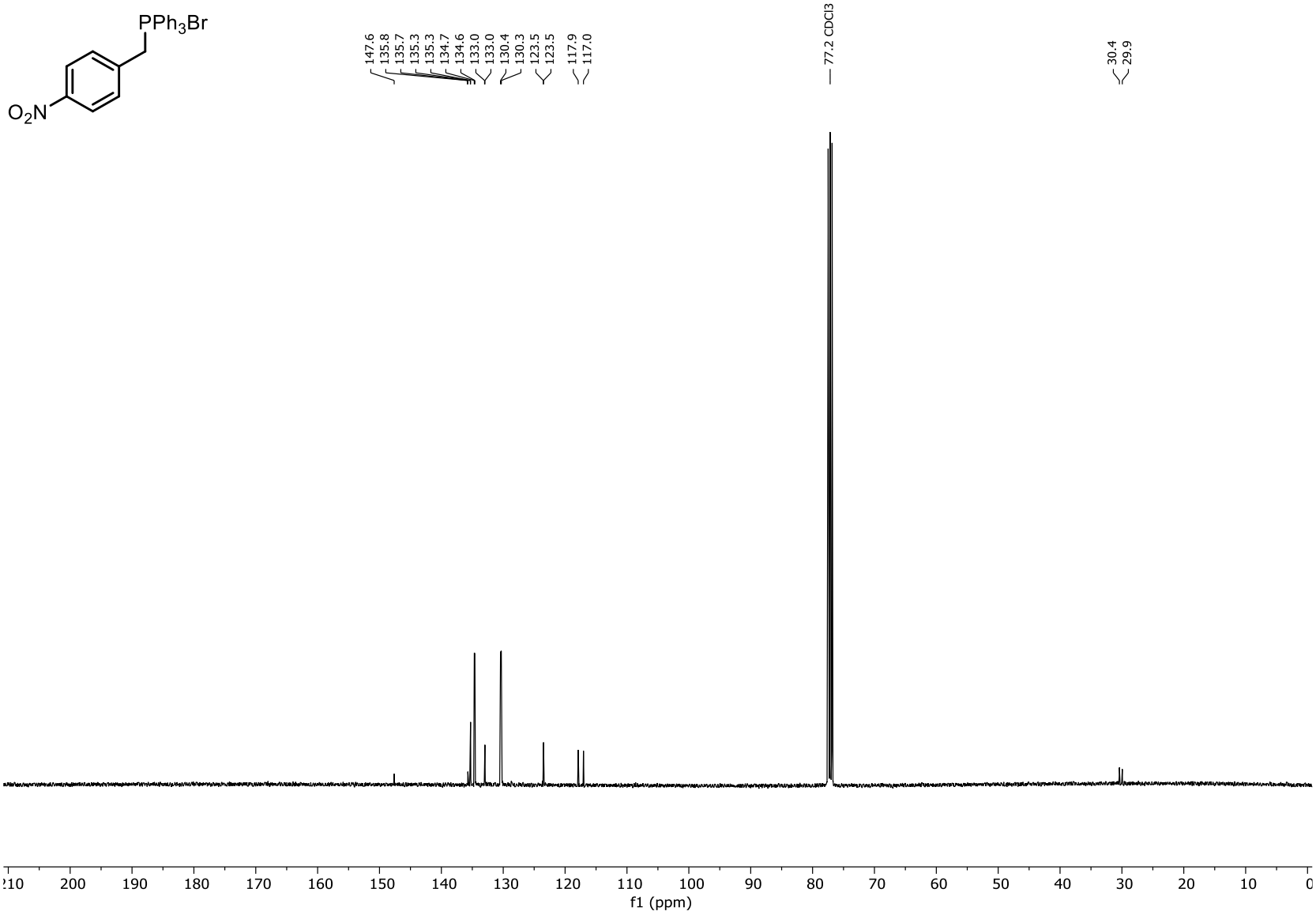
4-Vinylbenzoic acid (S6): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



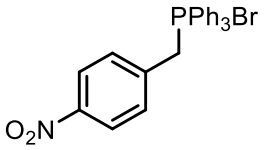
(4-Nitrobenzyl)triphenylphosphonium bromide (S7): ^{1}H NMR (300 MHz, $CDCl_3$)



(4-Nitrobenzyl)triphenylphosphonium bromide (S7): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

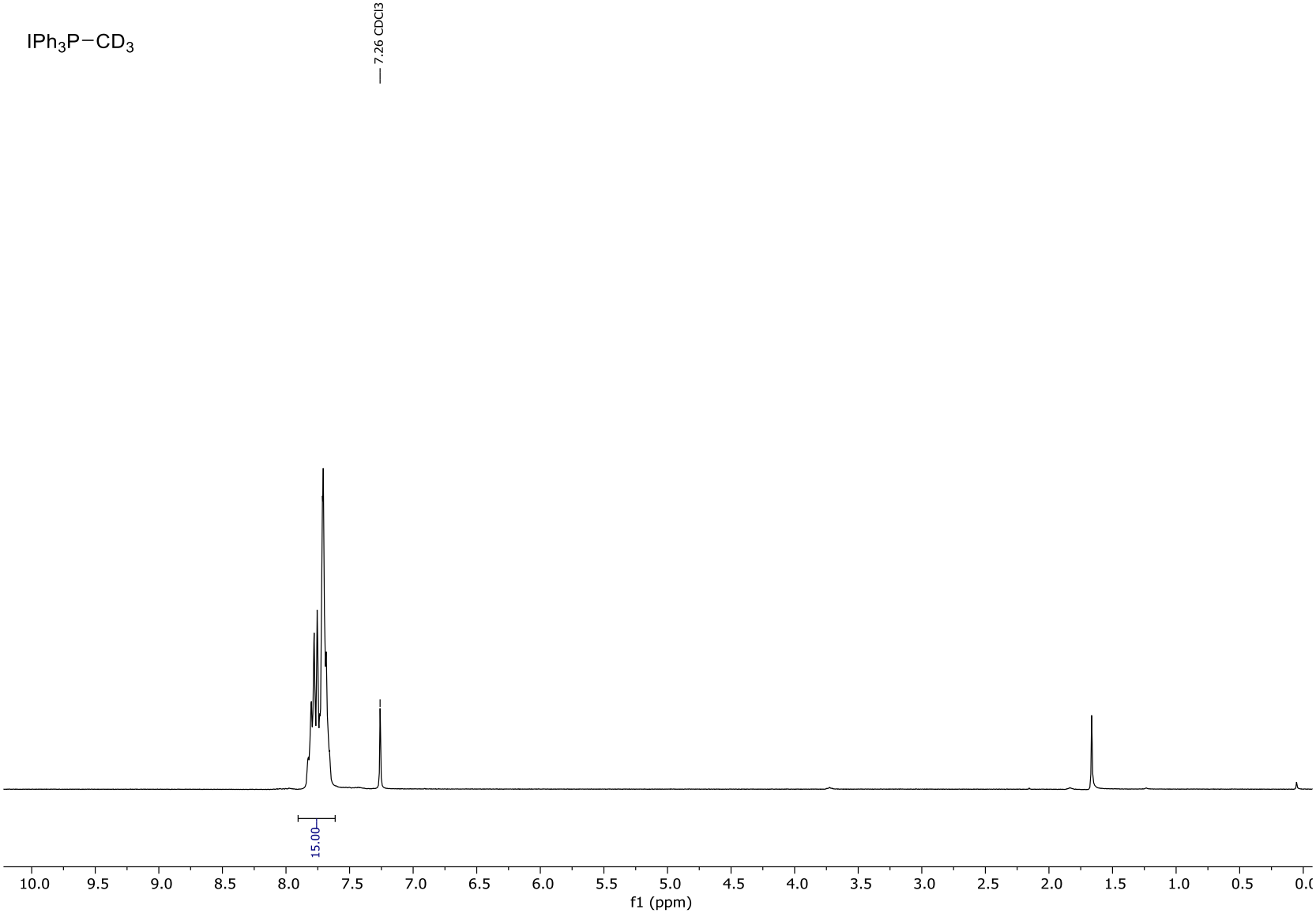


(4-Nitrobenzyl)triphenylphosphonium bromide (S7): ^{31}P NMR (121 MHz, $CDCl_3$)

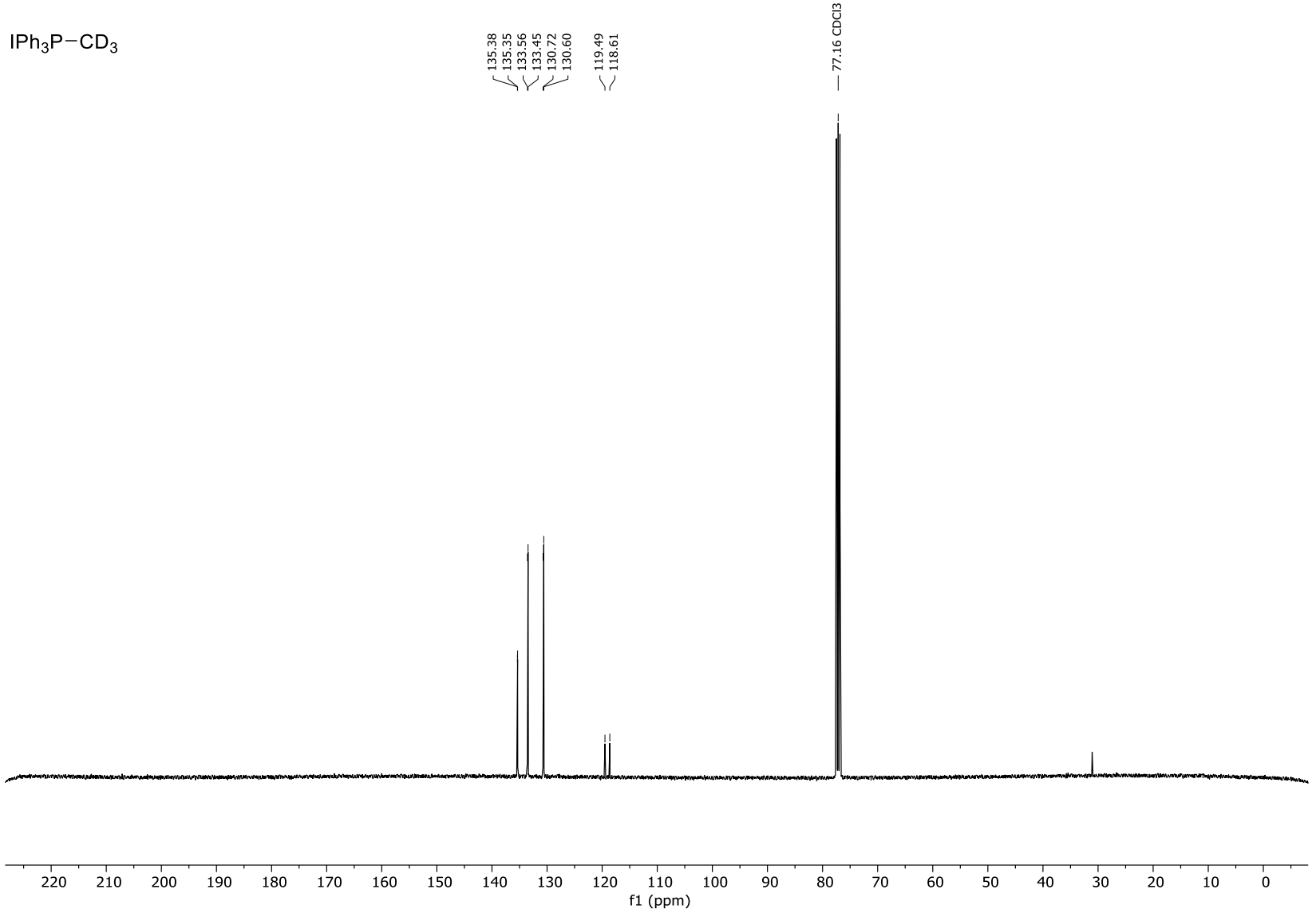


(Methyl)triphenylphosphonium iodide-d_3 (S8): ^{1}H NMR (300 MHz, $CDCl_3$)

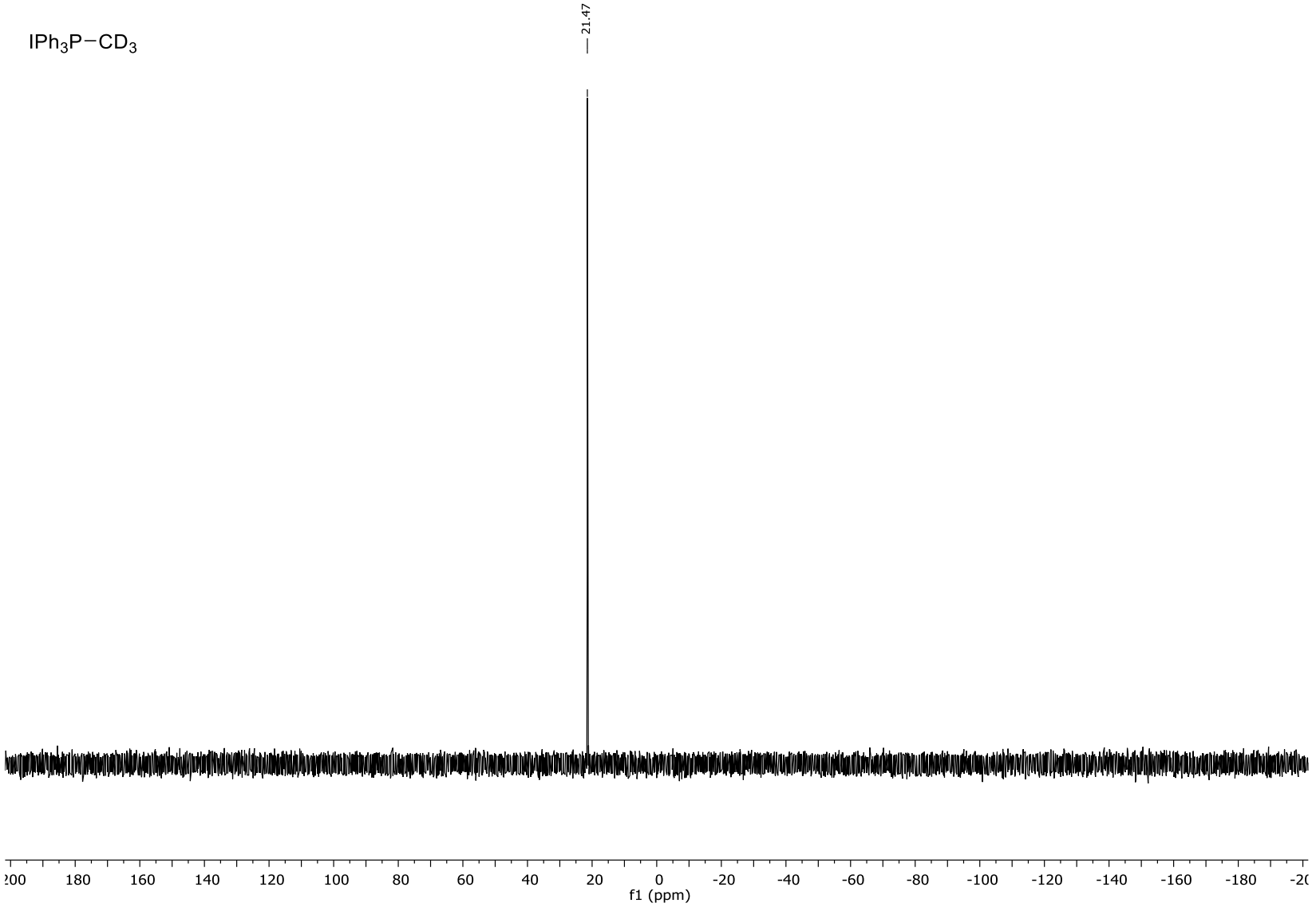
IPh_3P-CD_3



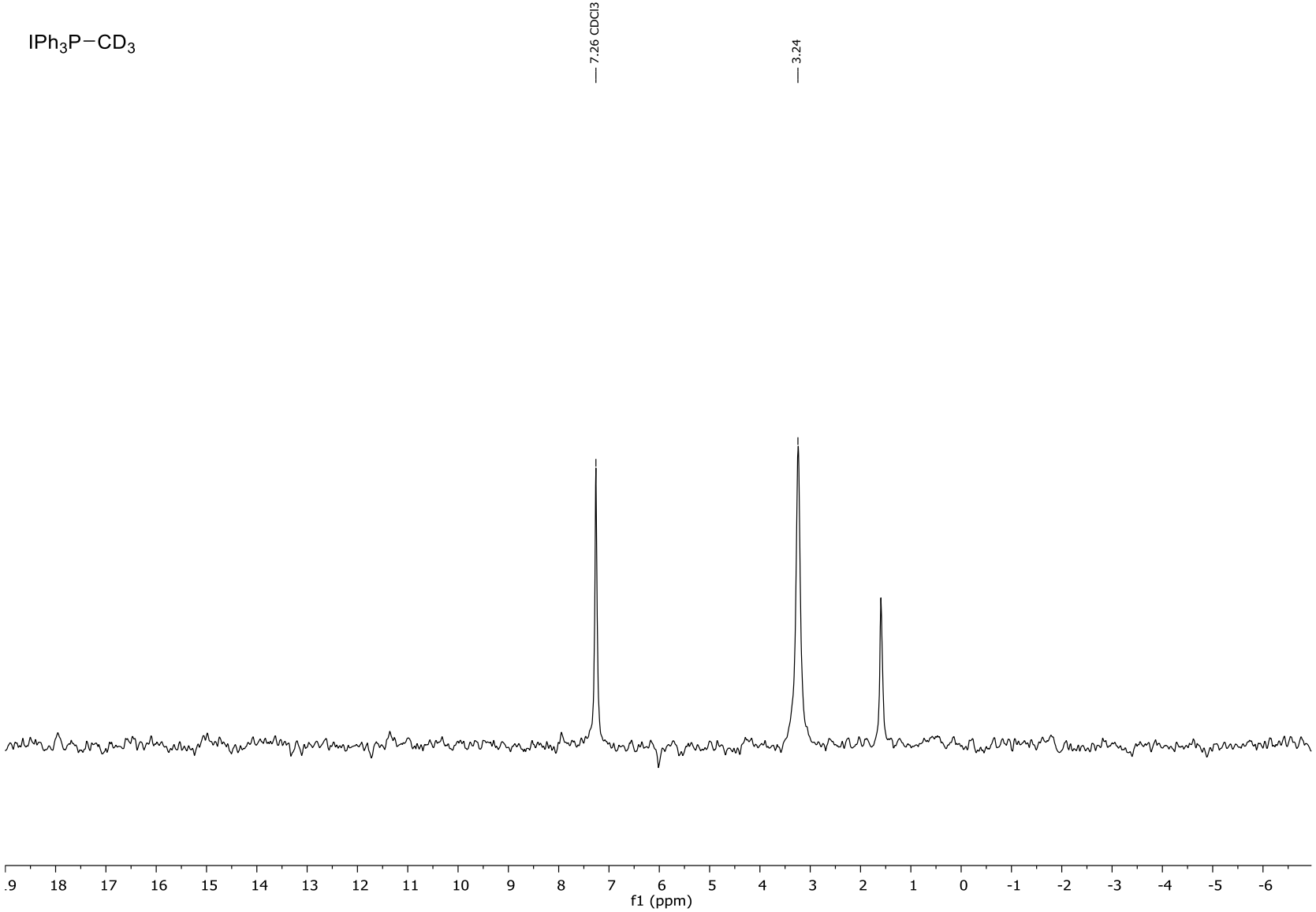
(Methyl)triphenylphosphonium iodide-d_3 (S8): $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$)



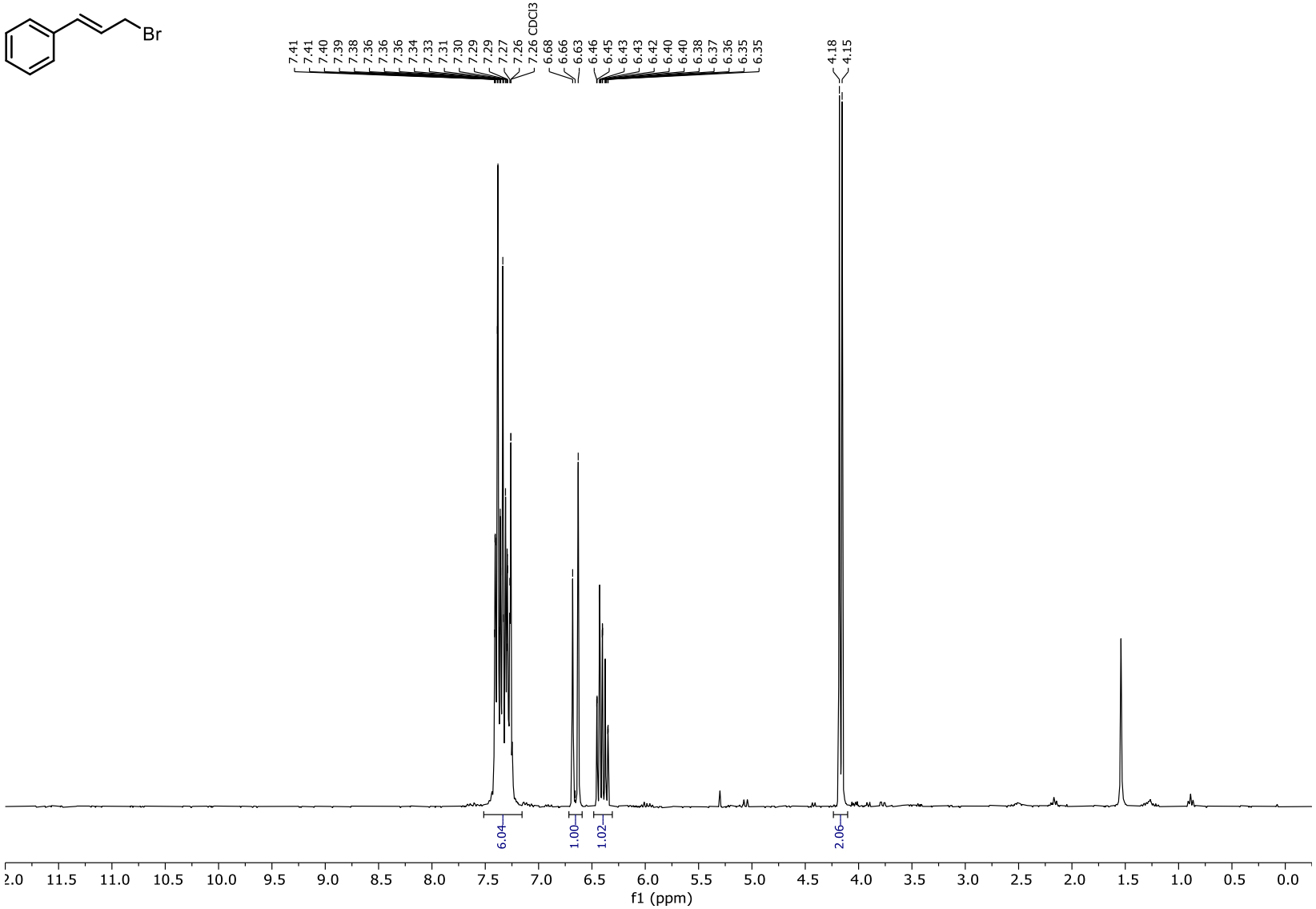
(Methyl)triphenylphosphonium iodide-d_3 (S8): ^{31}P NMR (121 MHz, $CDCl_3$)



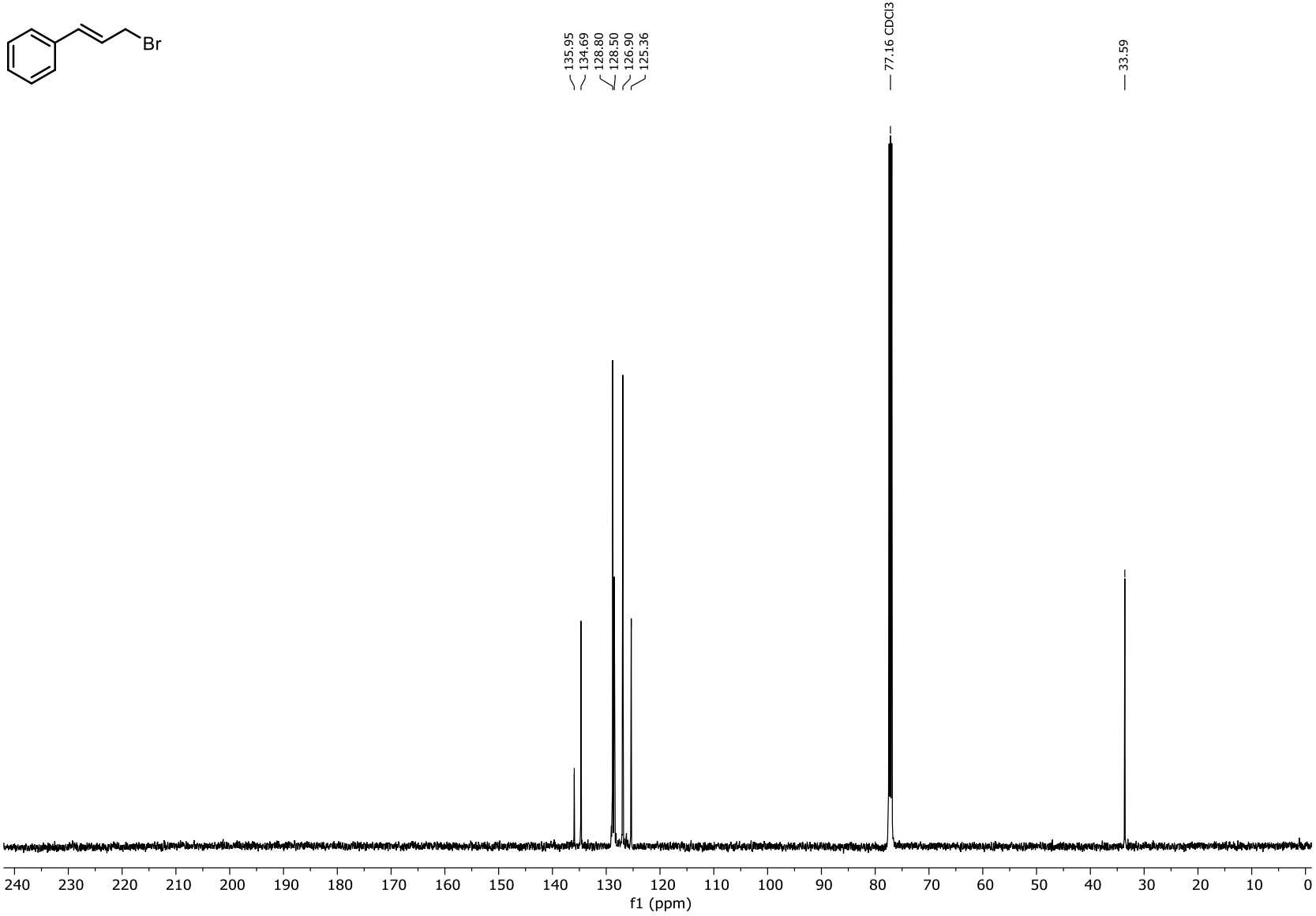
(Methyl)triphenylphosphonium iodide-d_3 (S8): ^{2}H NMR (77 MHz, $CDCl_3$)



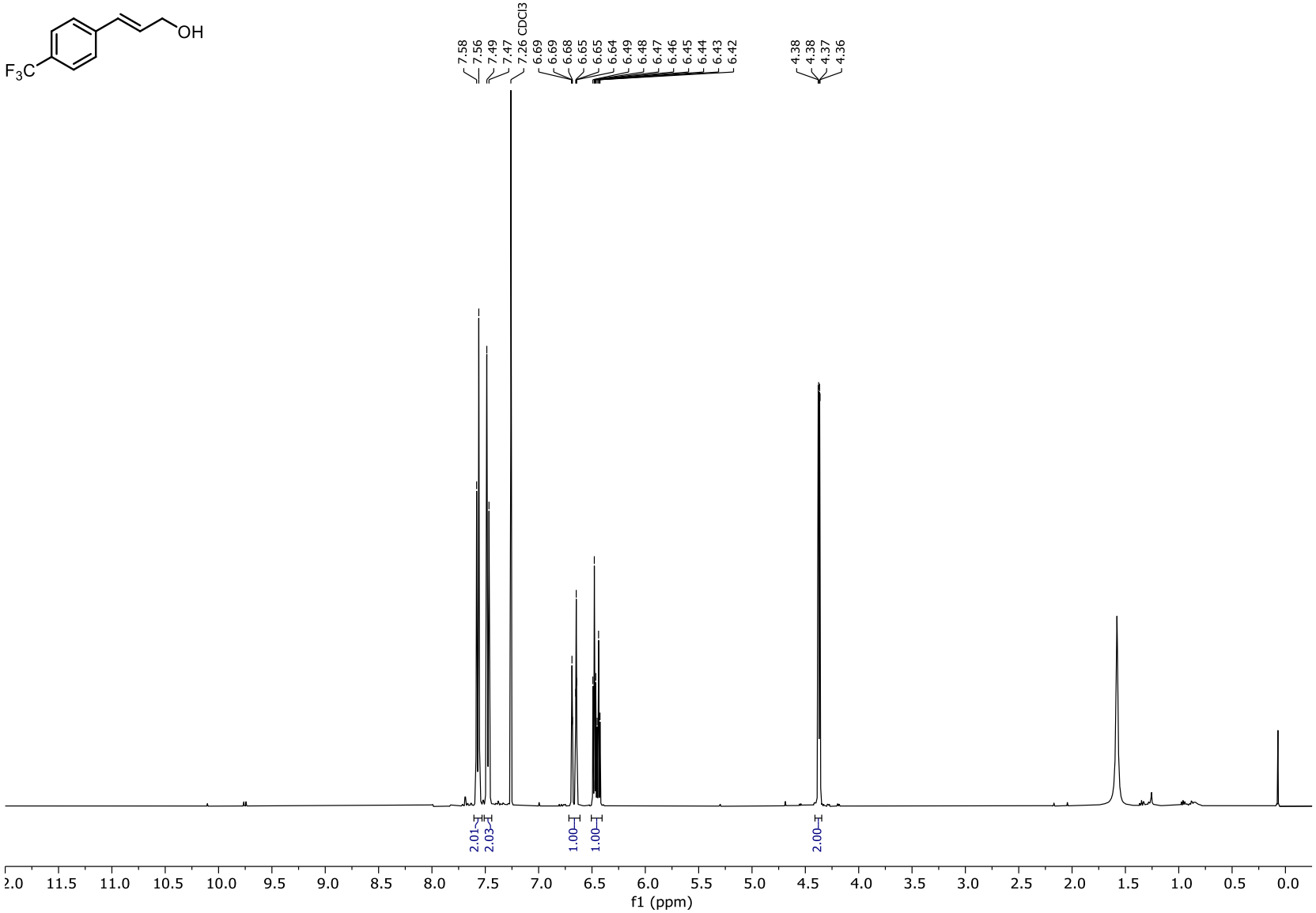
(*E*)-(3-bromoprop-1-en-1-yl)benzene (S9): ^{1}H NMR (300 MHz, $CDCl_3$)



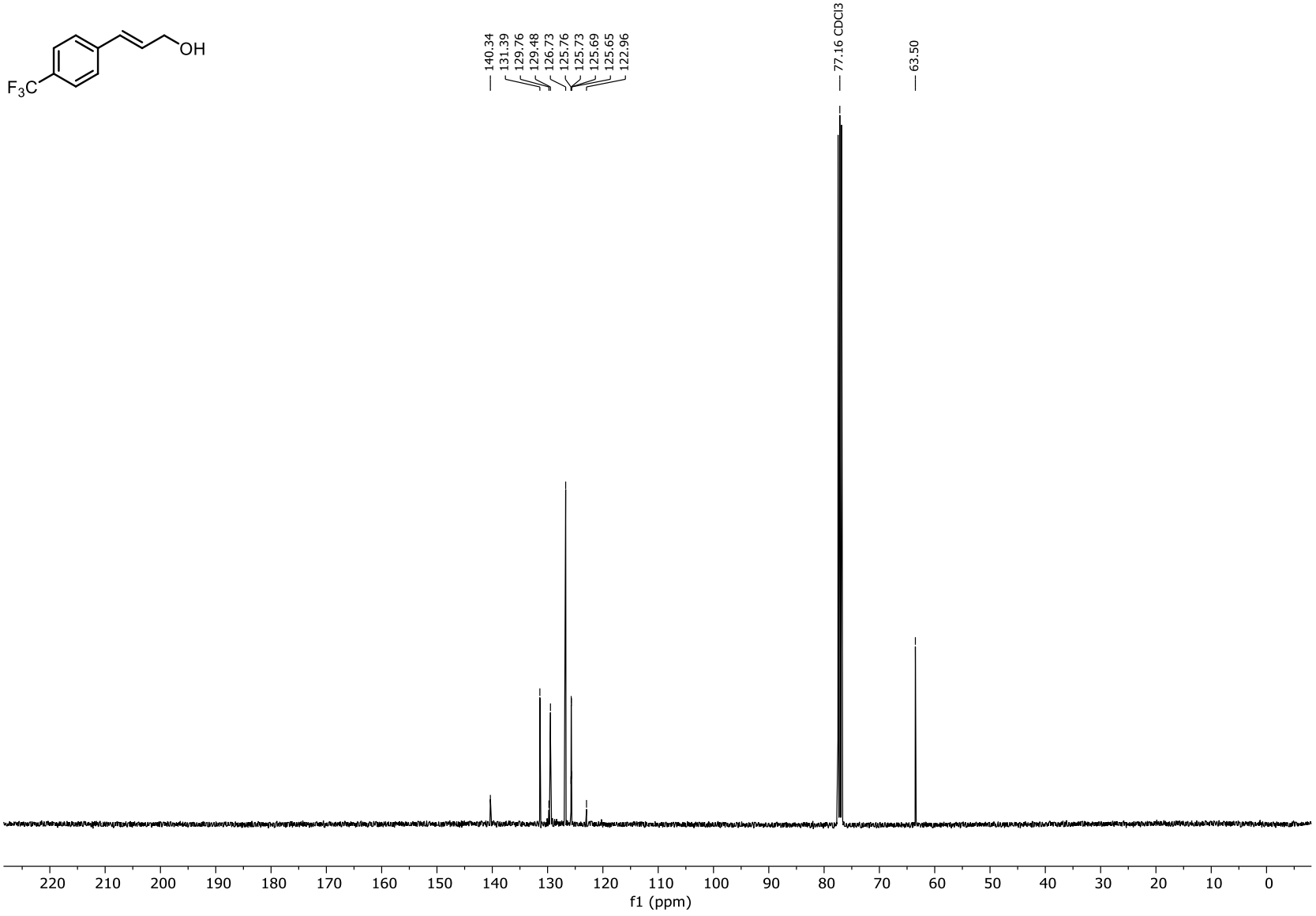
(*E*)-(3-bromoprop-1-en-1-yl)benzene (S9): $^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$)



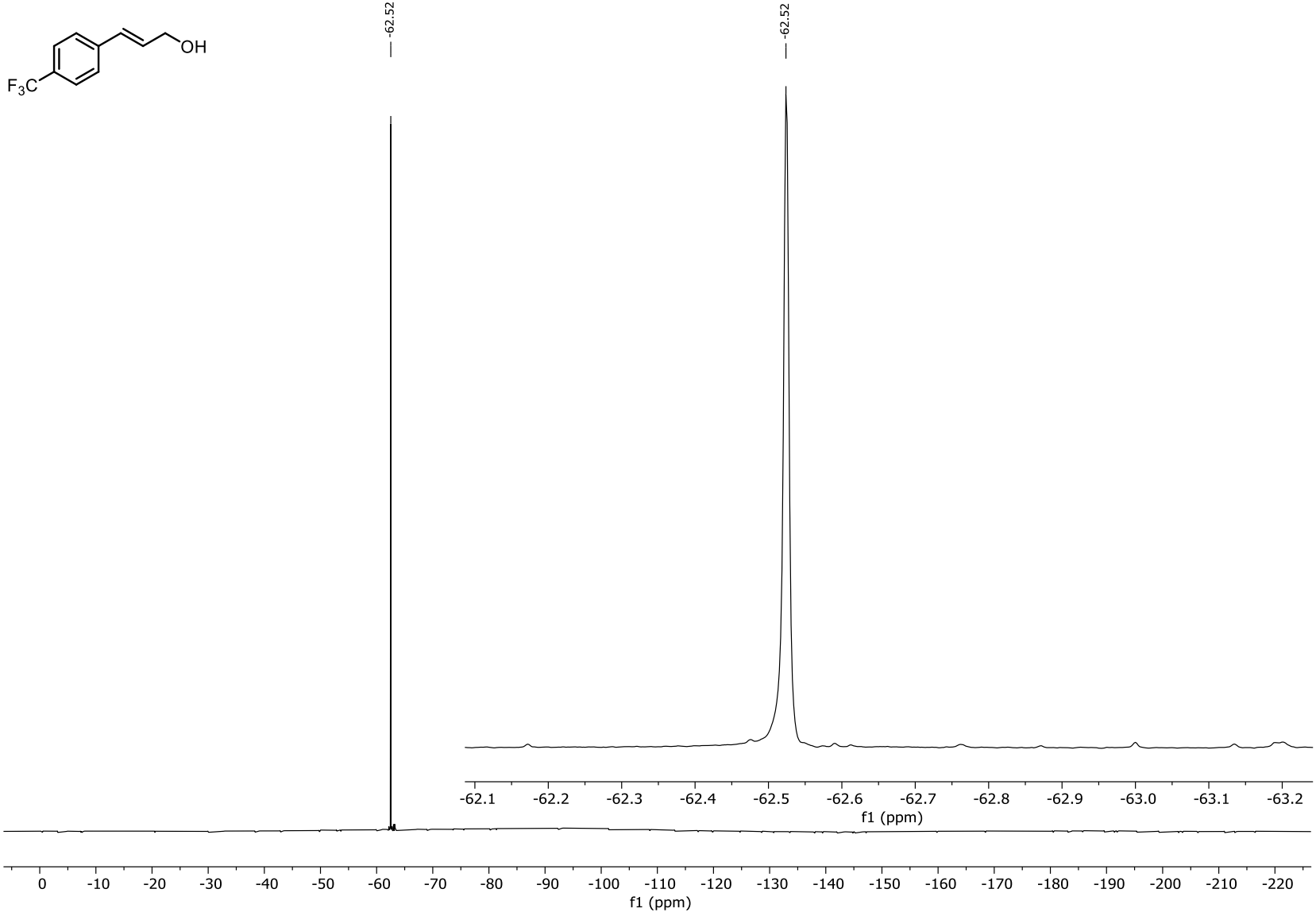
(*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (S10): ^{1}H NMR (400 MHz, $CDCl_3$)



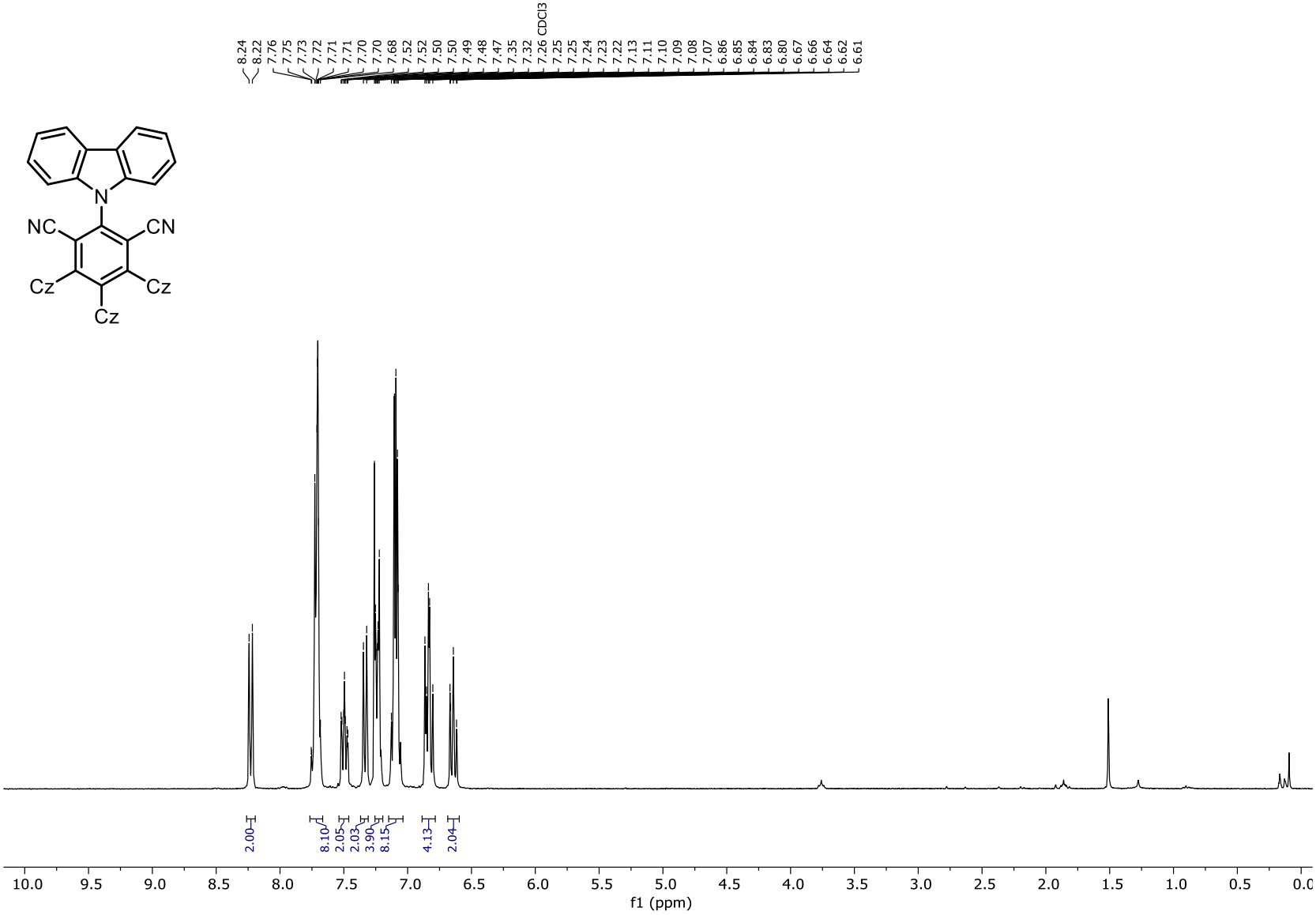
(*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (S10): $^{13}C\{^{1}H\}$ NMR (400 MHz, $CDCl_3$)



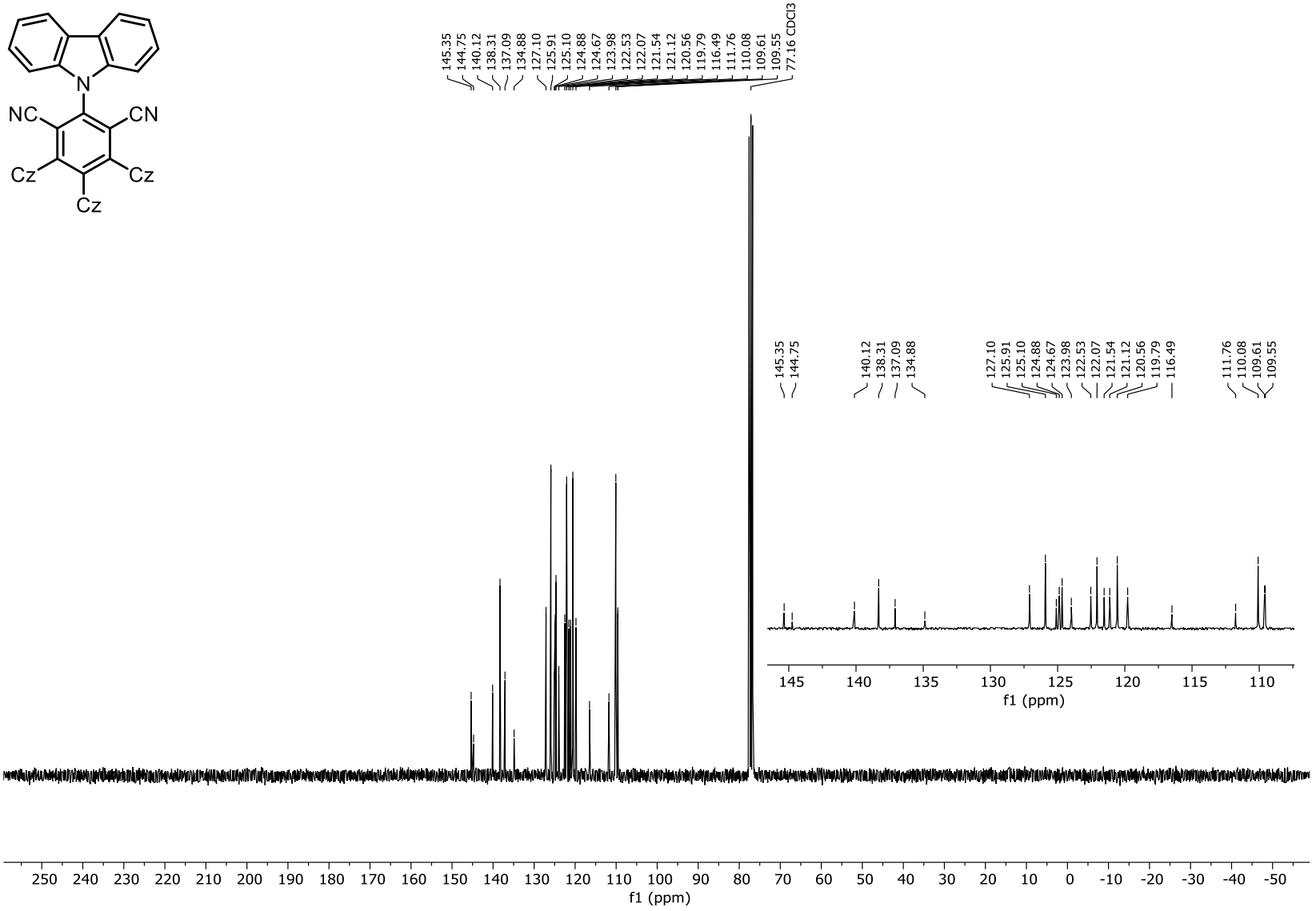
(*E*)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol (S10): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



4CzIPN: ^{1}H NMR (300 MHz, $CDCl_3$)

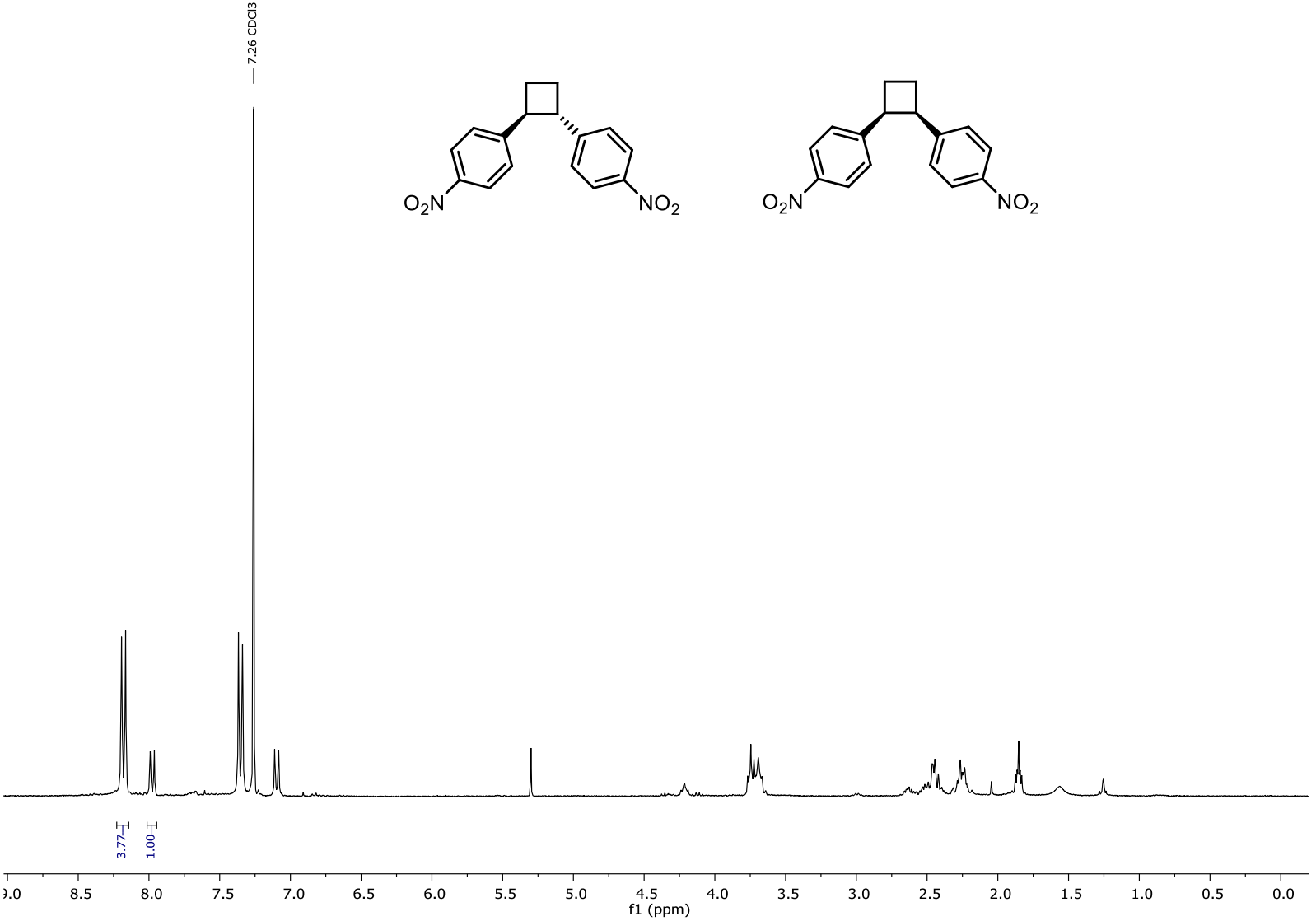


4CzIPN: $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

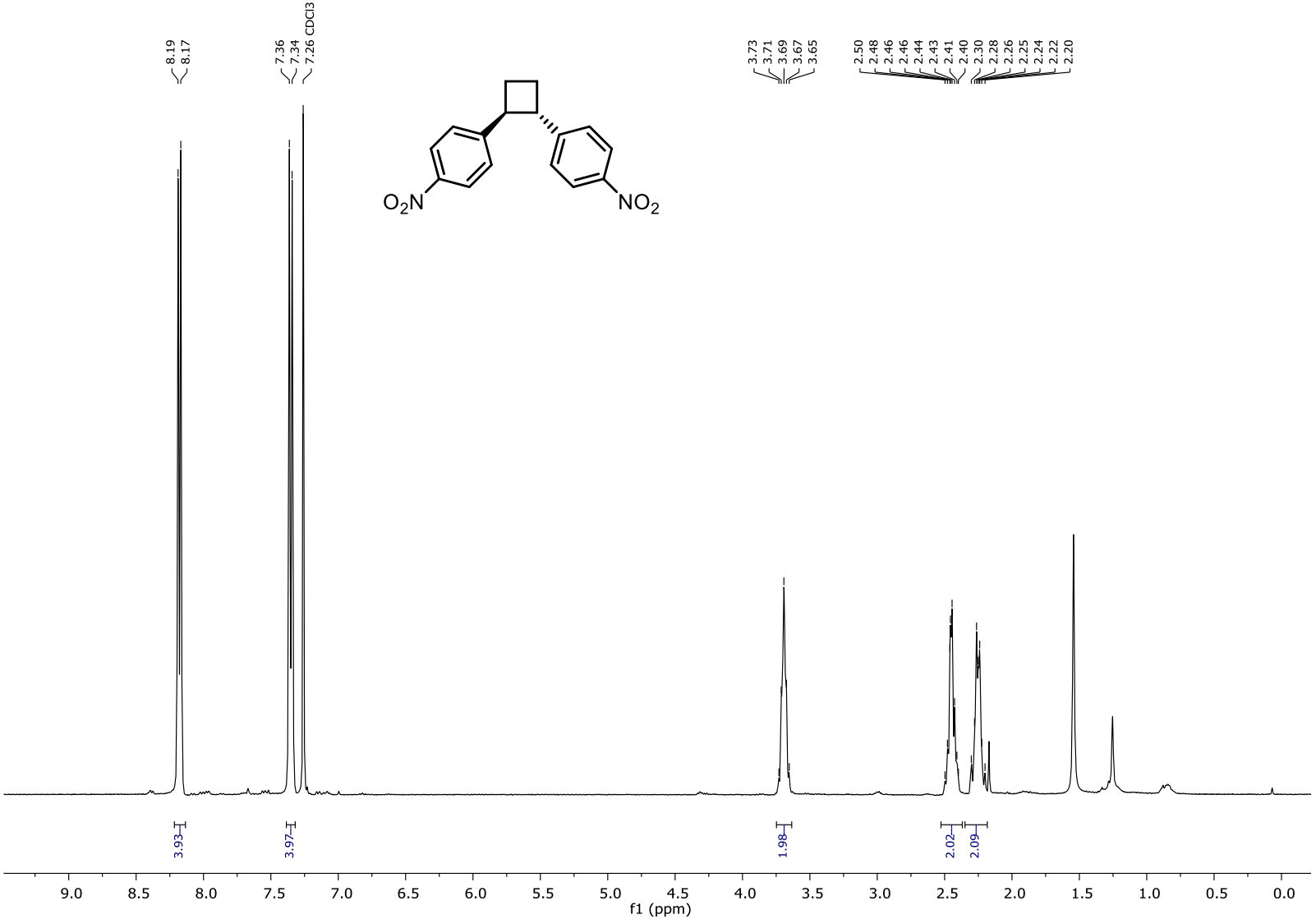


8.2 Cyclobutanes

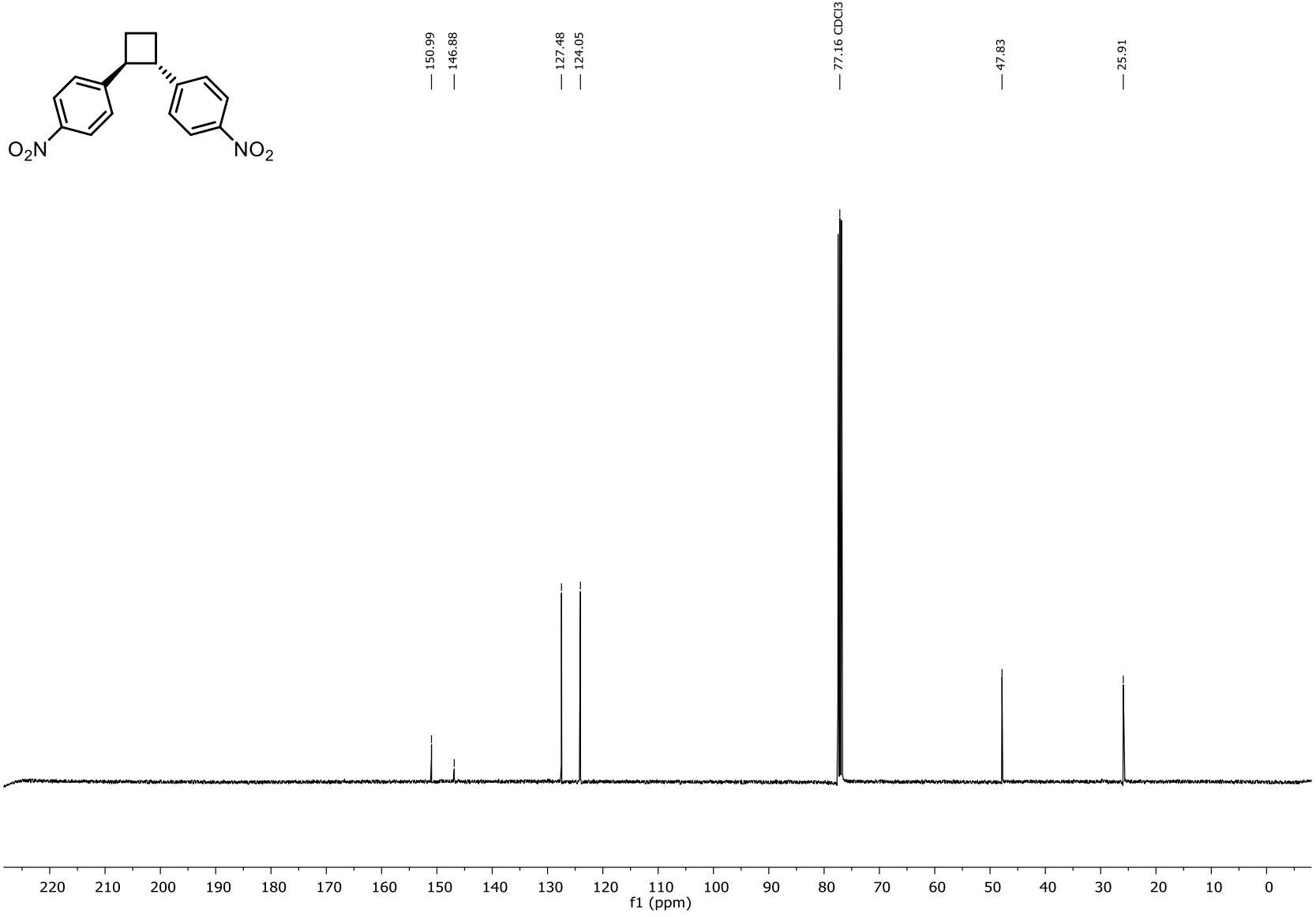
1,2-bis(4-nitrophenyl)cyclobutane (2a-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



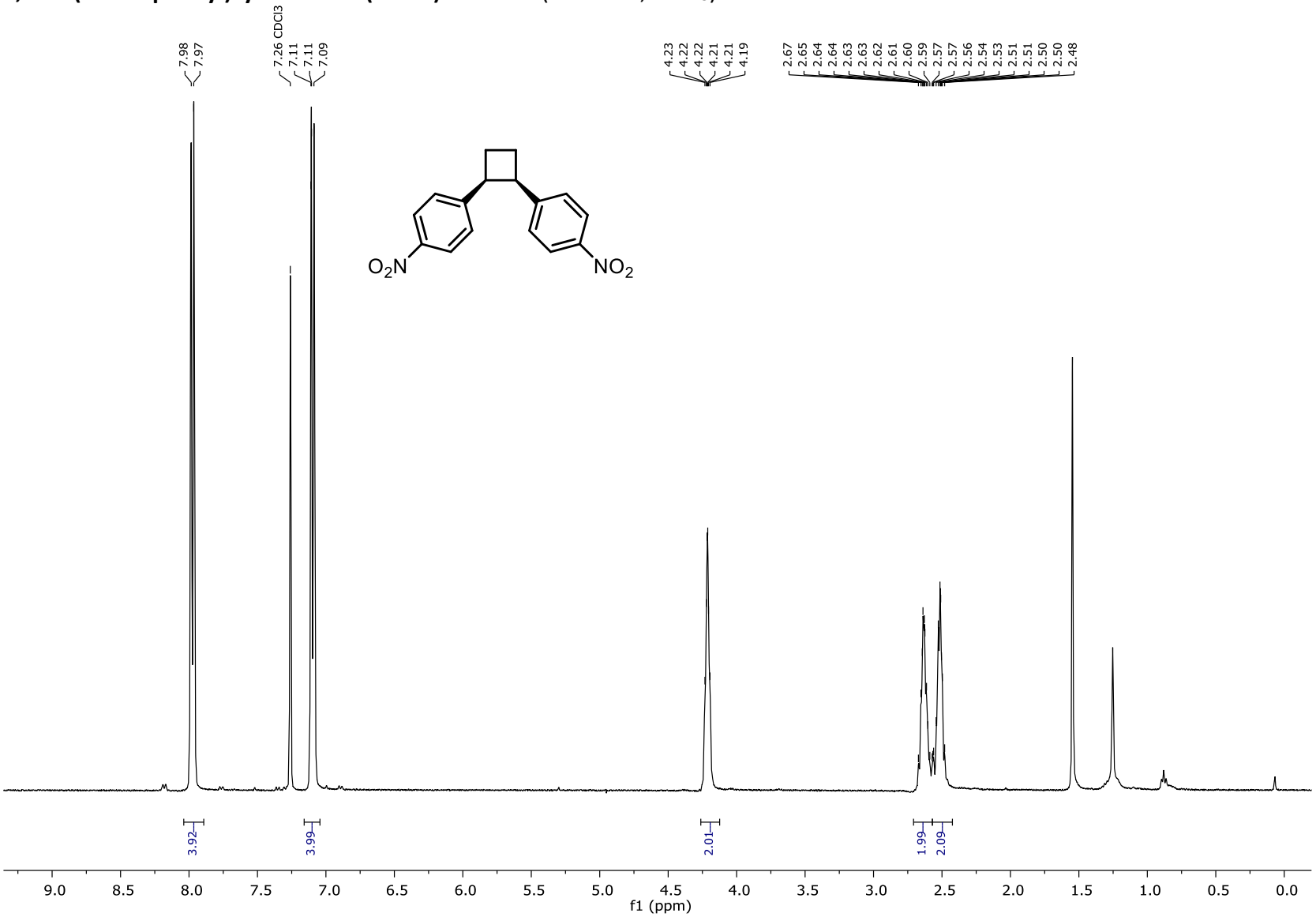
1,2-bis(4-nitrophenyl)cyclobutane (2a-trans): ^{1}H NMR (400 MHz, $CDCl_3$)



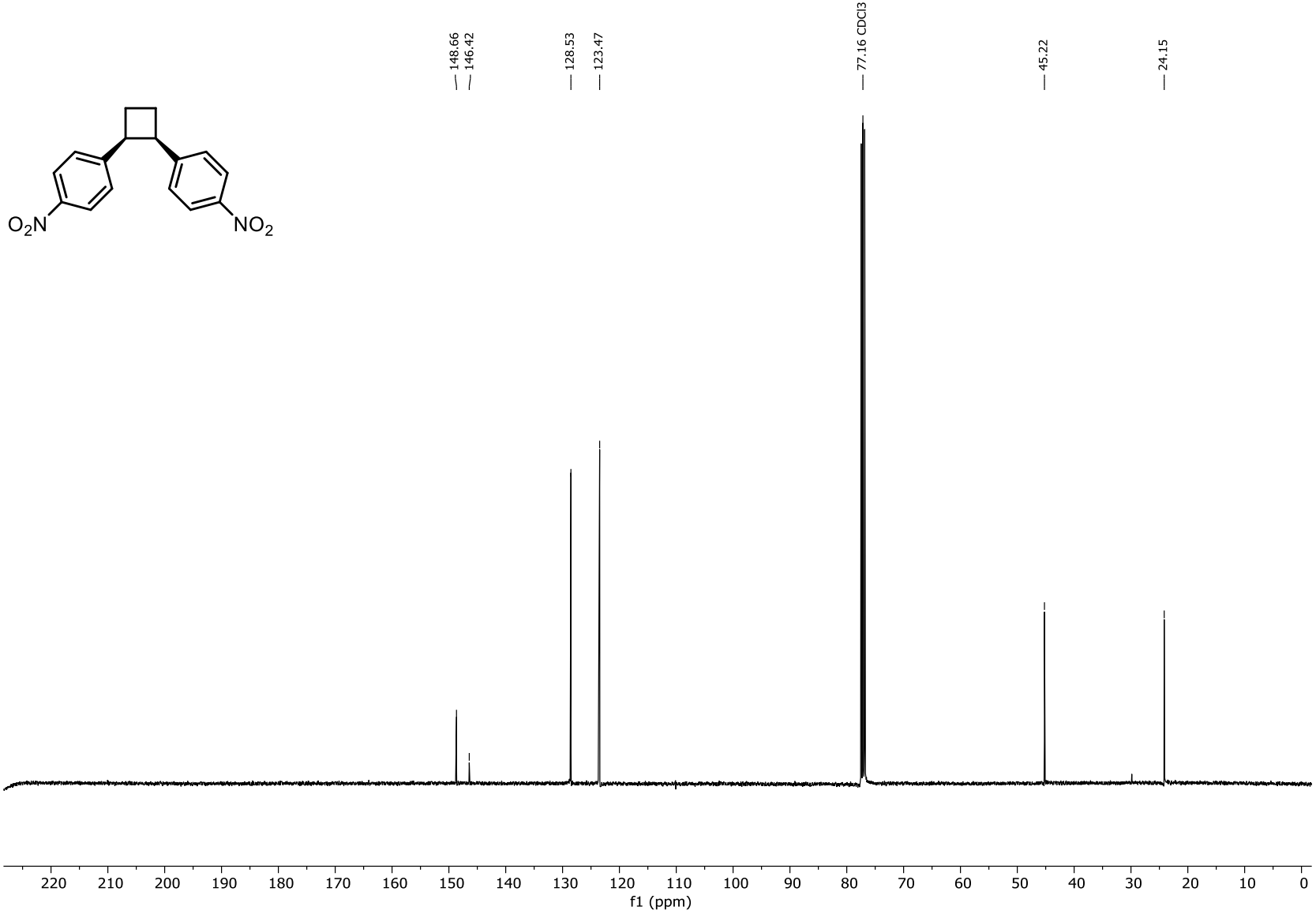
1,2-bis(4-nitrophenyl)cyclobutane (2a-trans): 13C{^{1}H} NMR (400 MHz, $CDCl_3$)



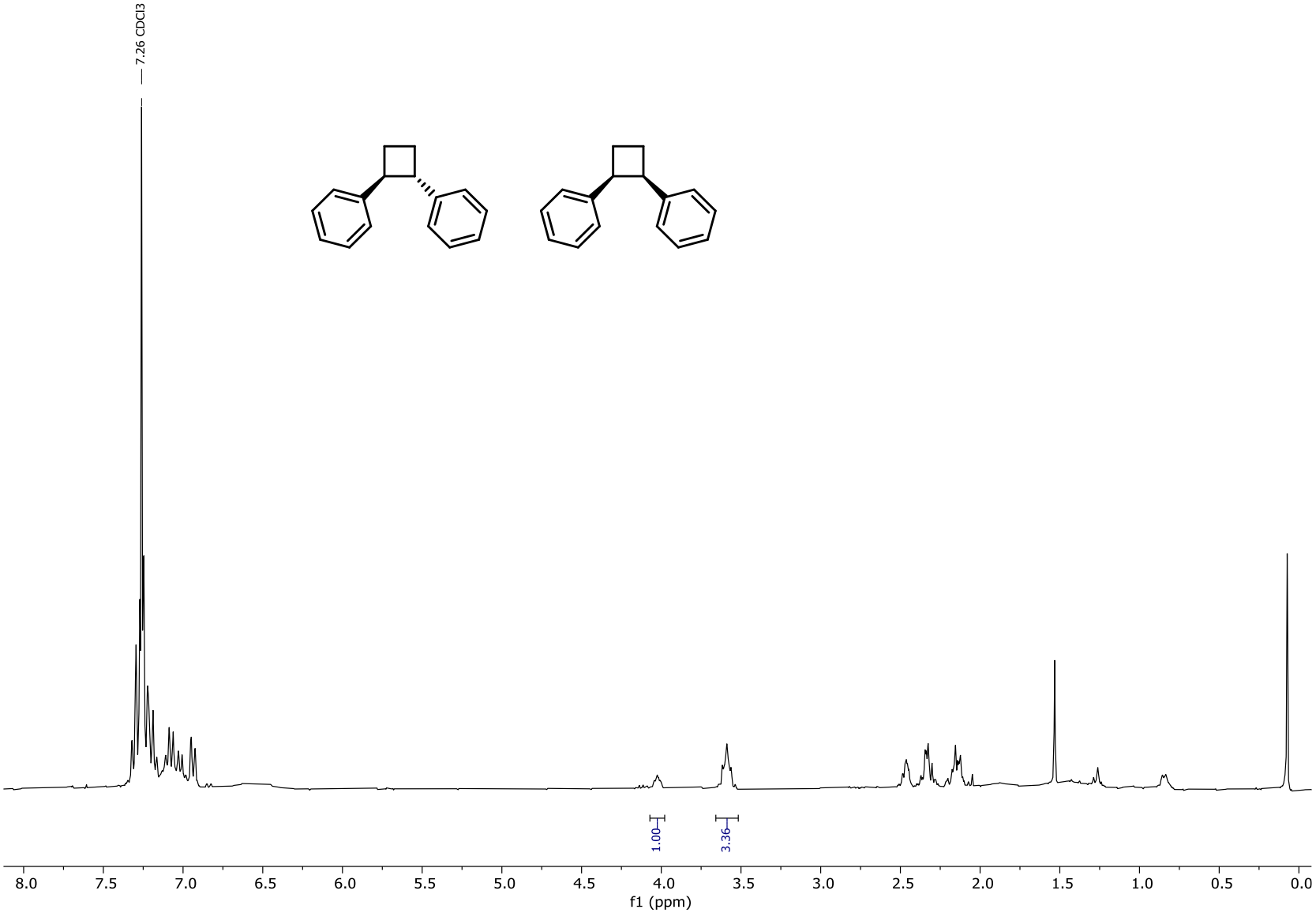
1,2-bis(4-nitrophenyl)cyclobutane (2a-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



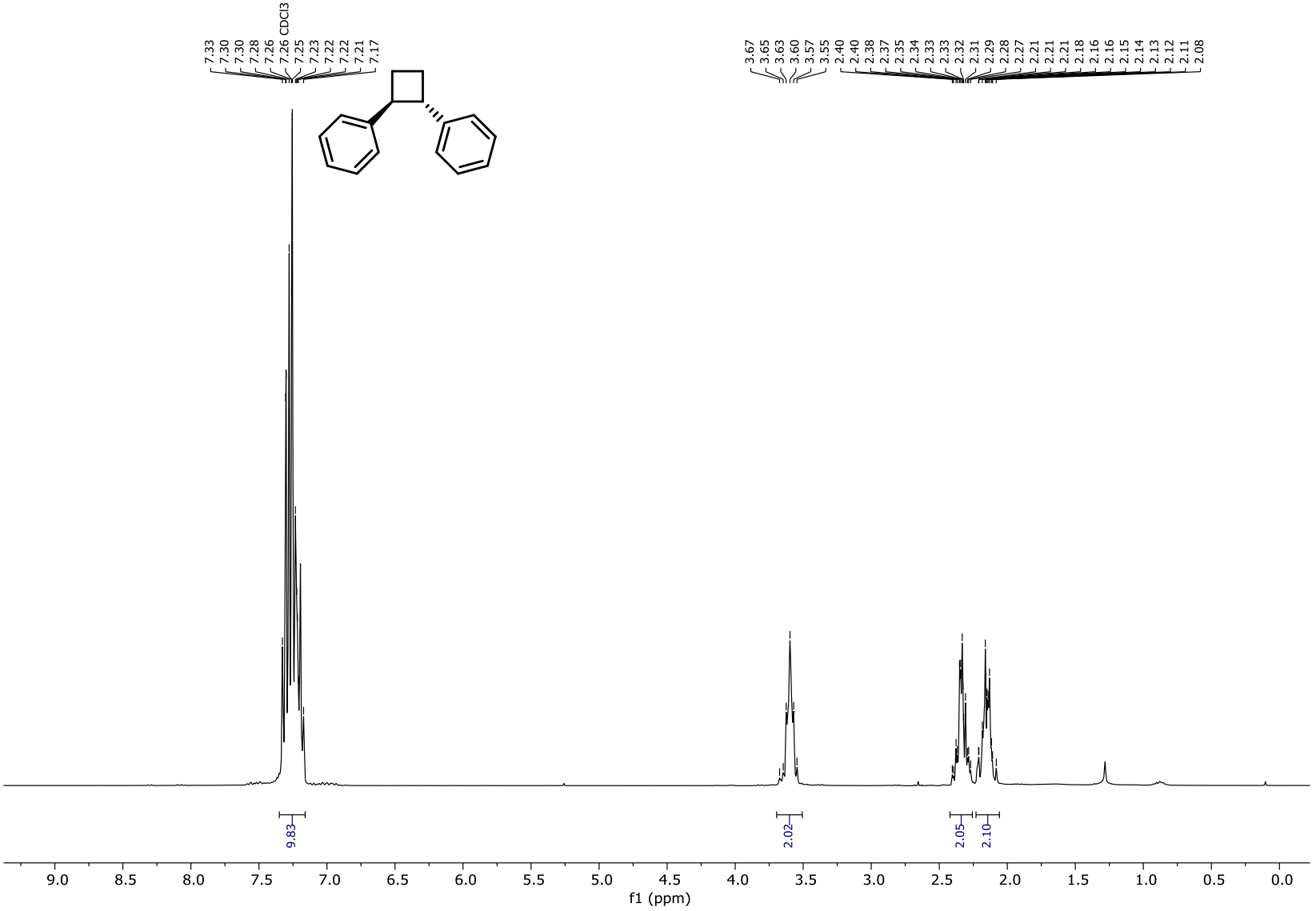
1,2-bis(4-nitrophenyl)cyclobutane (2a-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



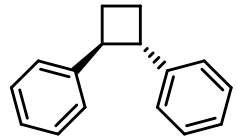
1,2-diphenylcyclobutane (2b-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



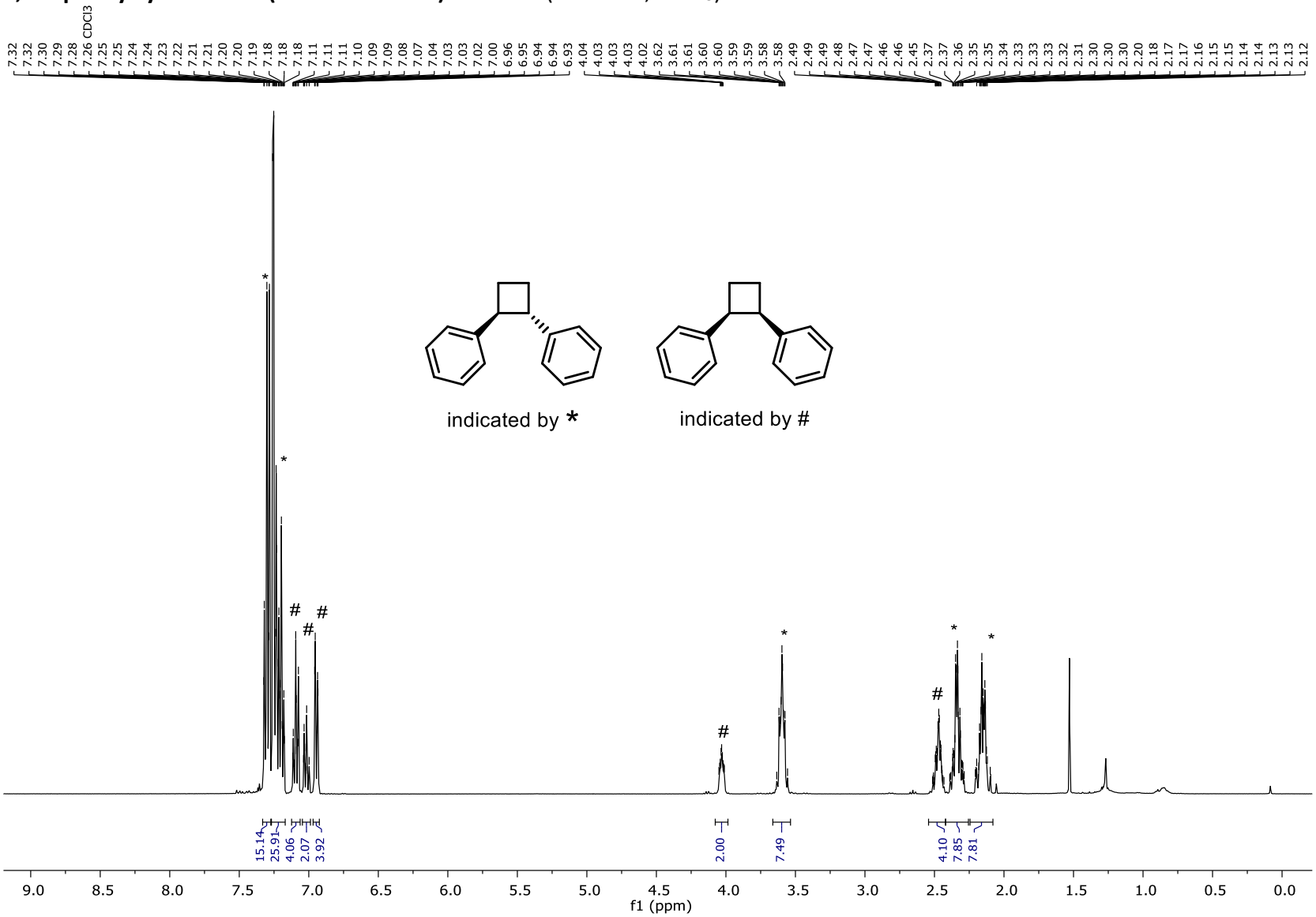
1,2-diphenylcyclobutane (2b-trans): ^{1}H NMR (300 MHz, $CDCl_3$)



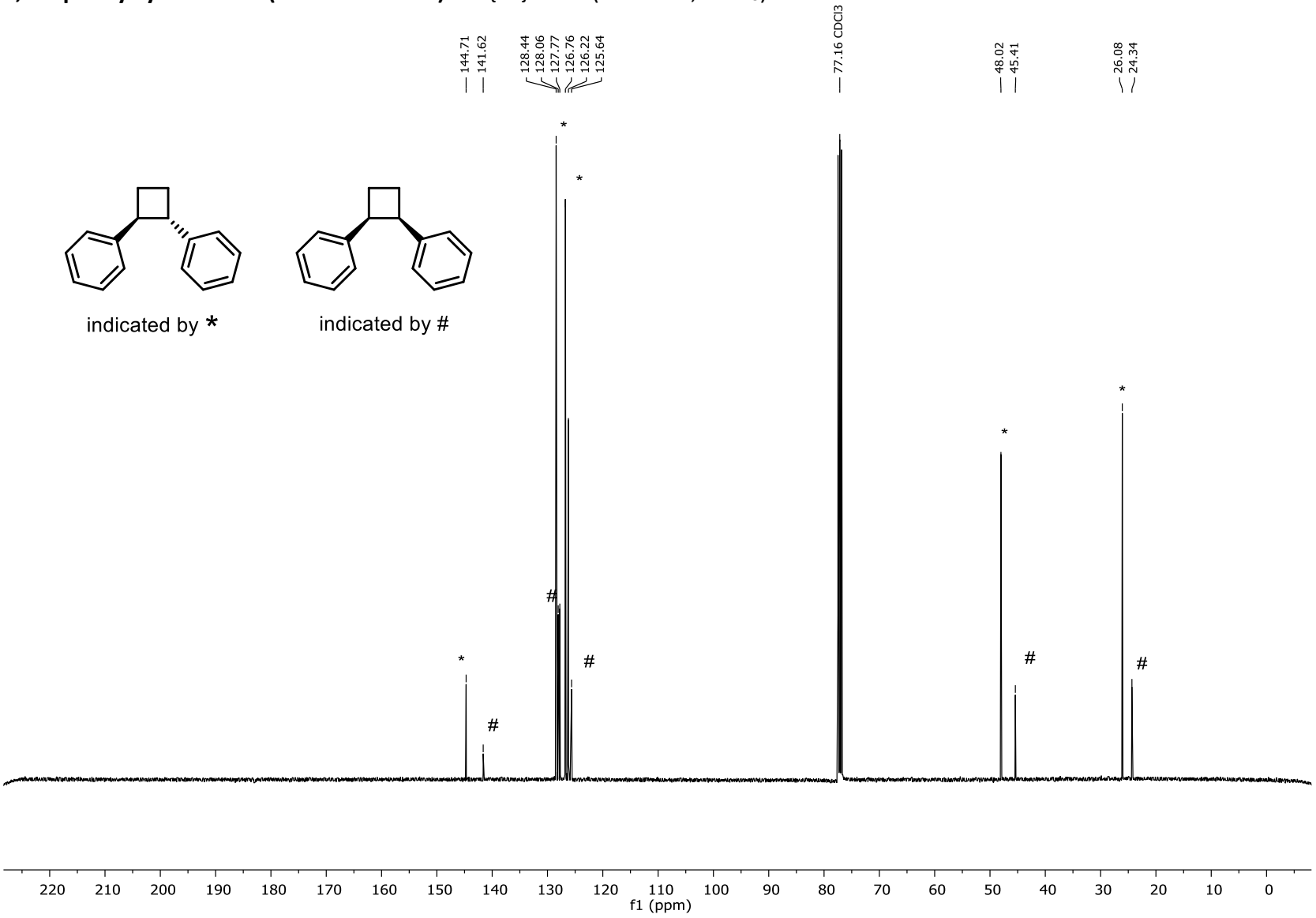
1,2-diphenylcyclobutane (2b-trans): $^{13}C\{^{1}H\}$ NMR (400 MHz, $CDCl_3$)



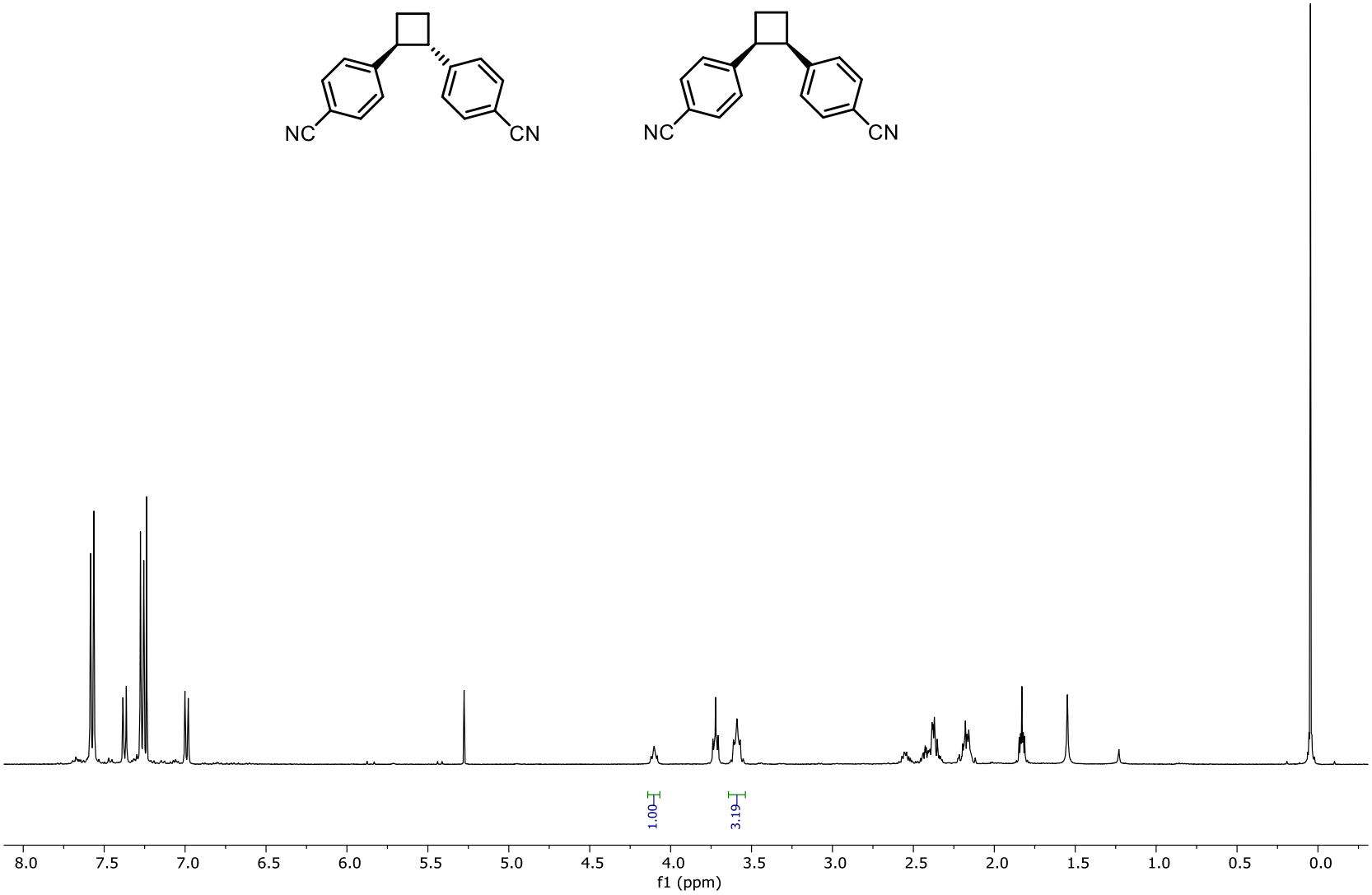
1,2-diphenylcyclobutane (2b-trans+2b-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



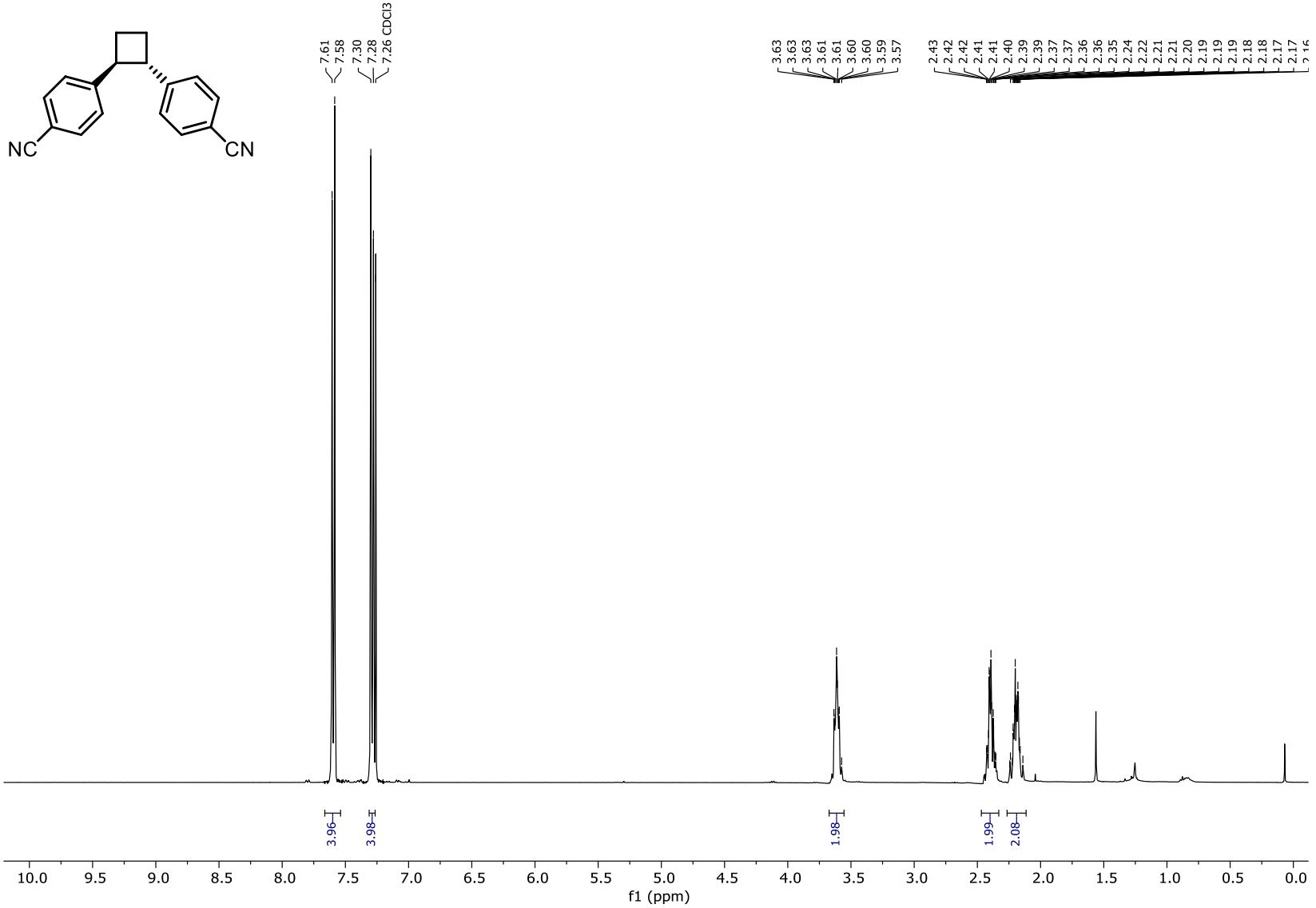
1,2-diphenylcyclobutane (2b-trans+2b-cis): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



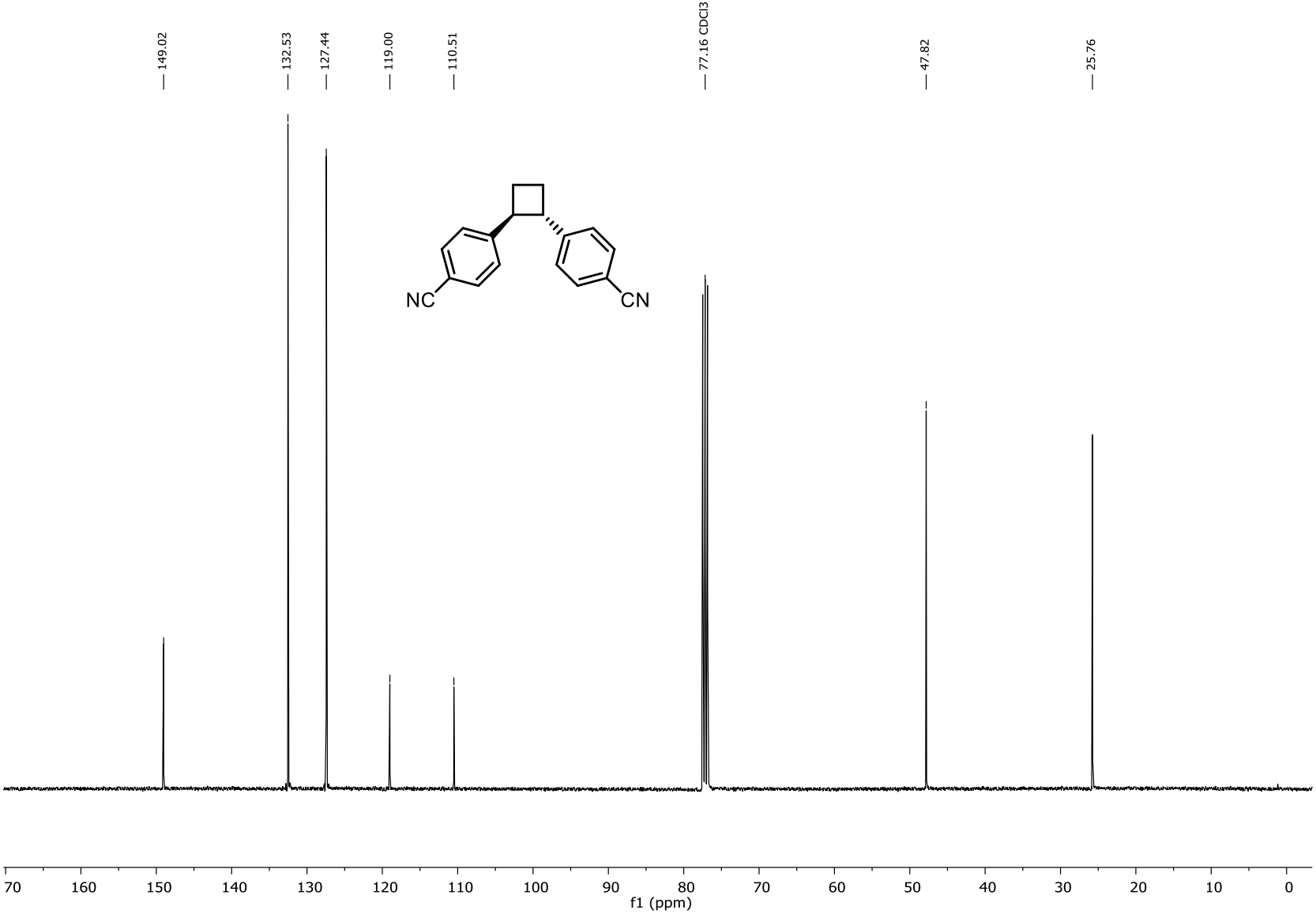
4,4'-(cyclobutane-1,2-diyl)dibenzonitrile (2c-crude): ^{1}H NMR (400 MHz, $CDCl_3$)



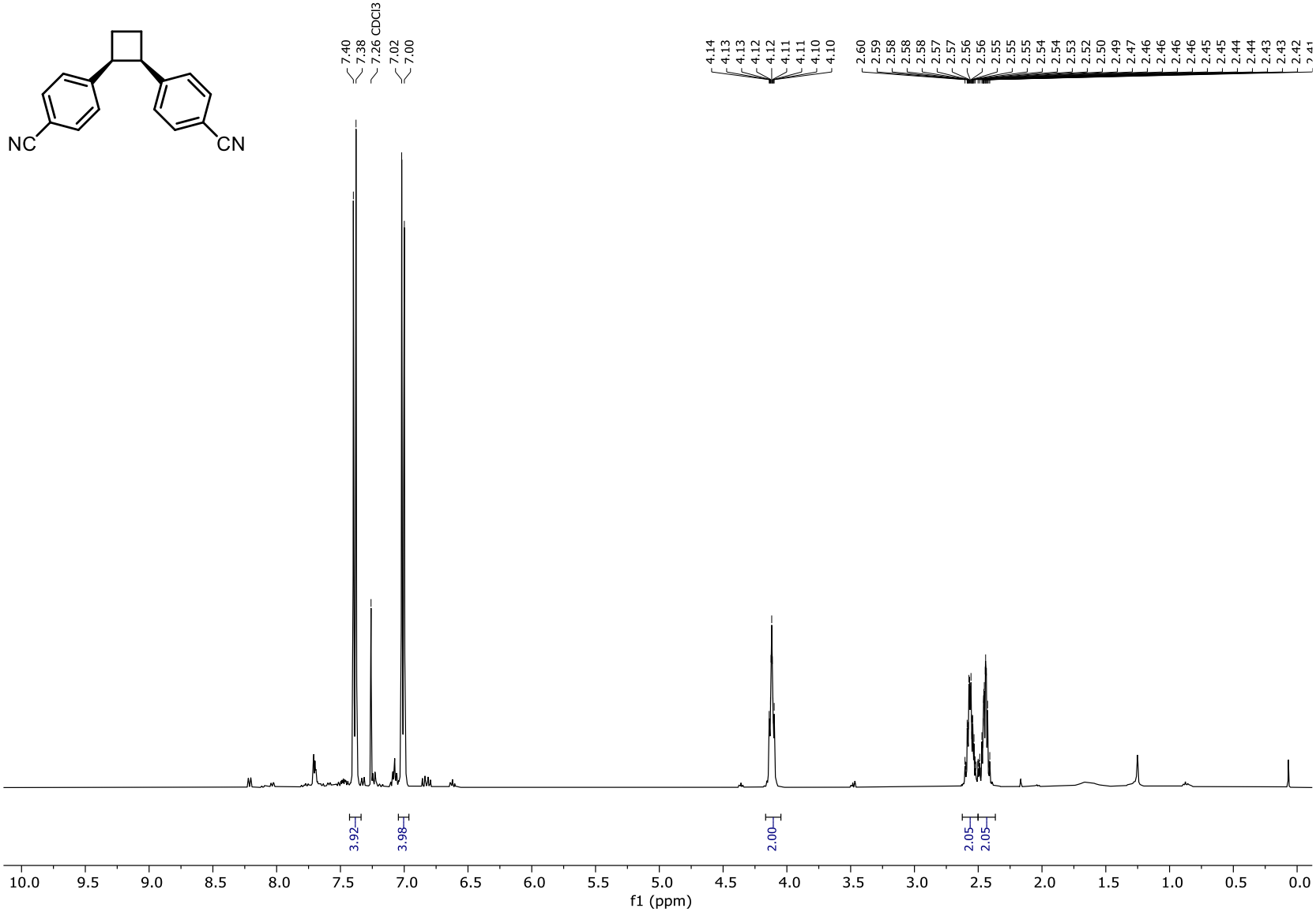
4,4'-(cyclobutane-1,2-diyl)dibenzonitrile (2c-trans): ^{1}H NMR (400 MHz, $CDCl_3$)



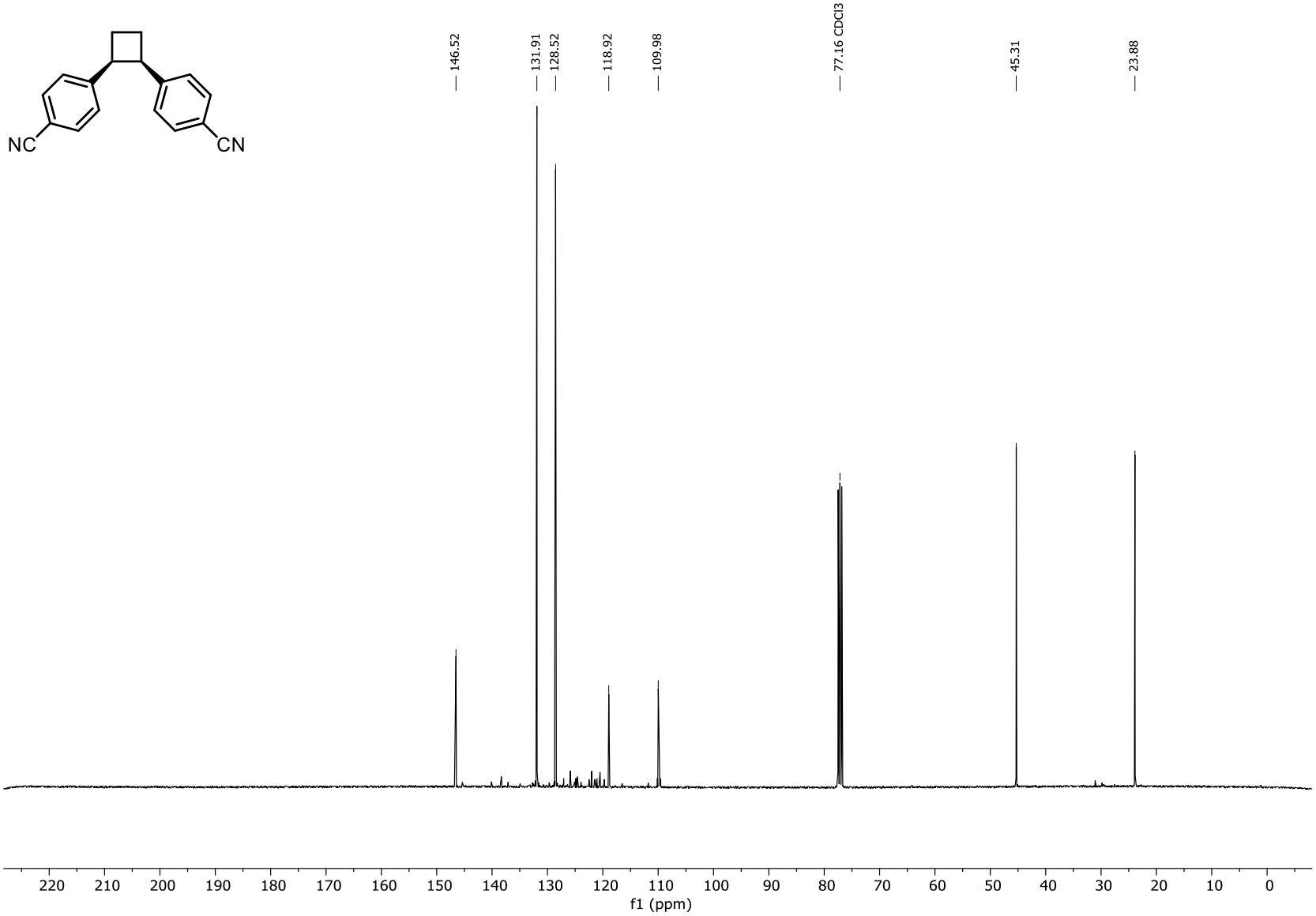
4,4'-(cyclobutane-1,2-diyl)dibenzonitrile (2c-trans): 13C{^{1}H} NMR (400 MHz, $CDCl_3$)



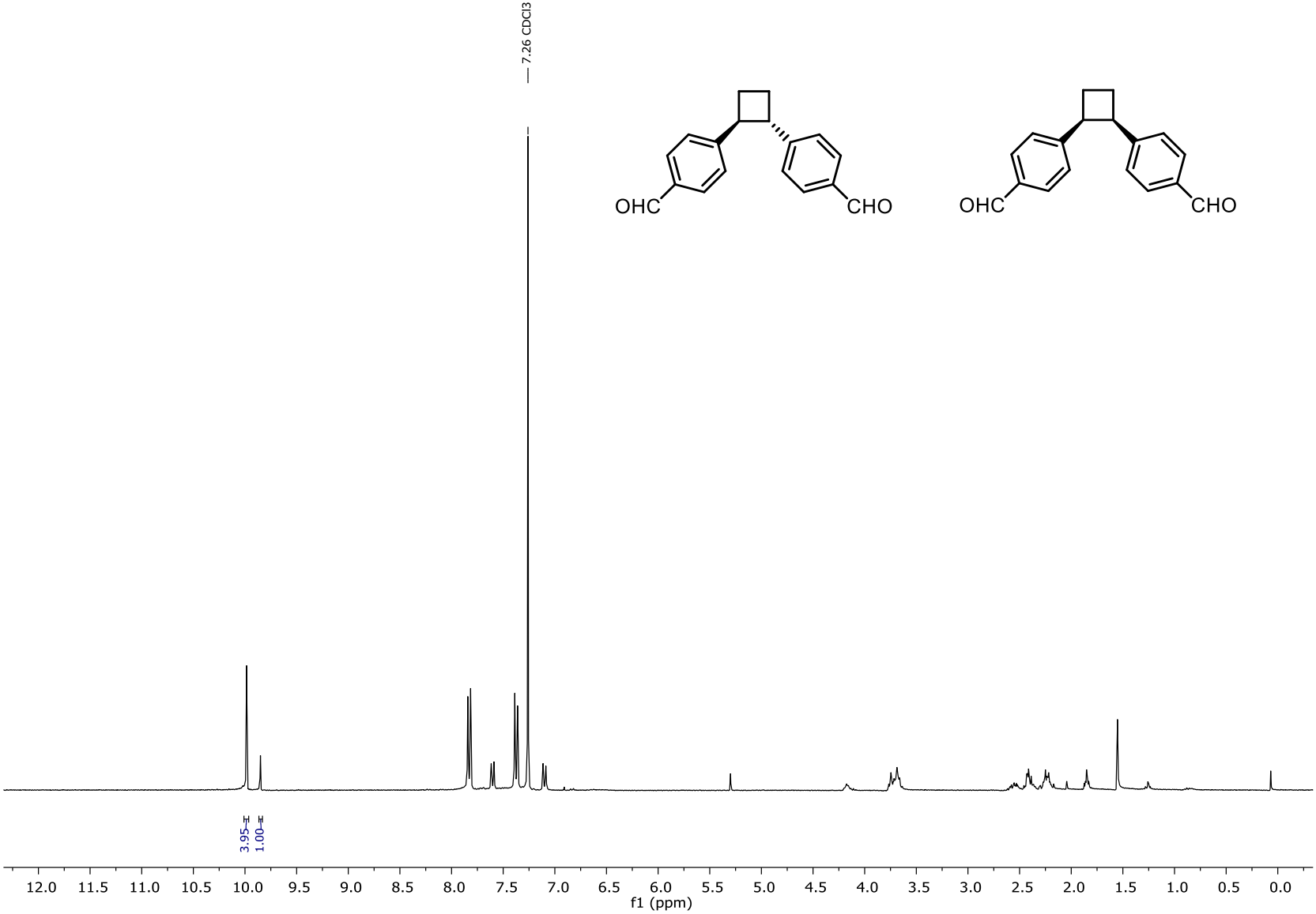
4,4'-(cyclobutane-1,2-diyl)dibenzonitrile (2c-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



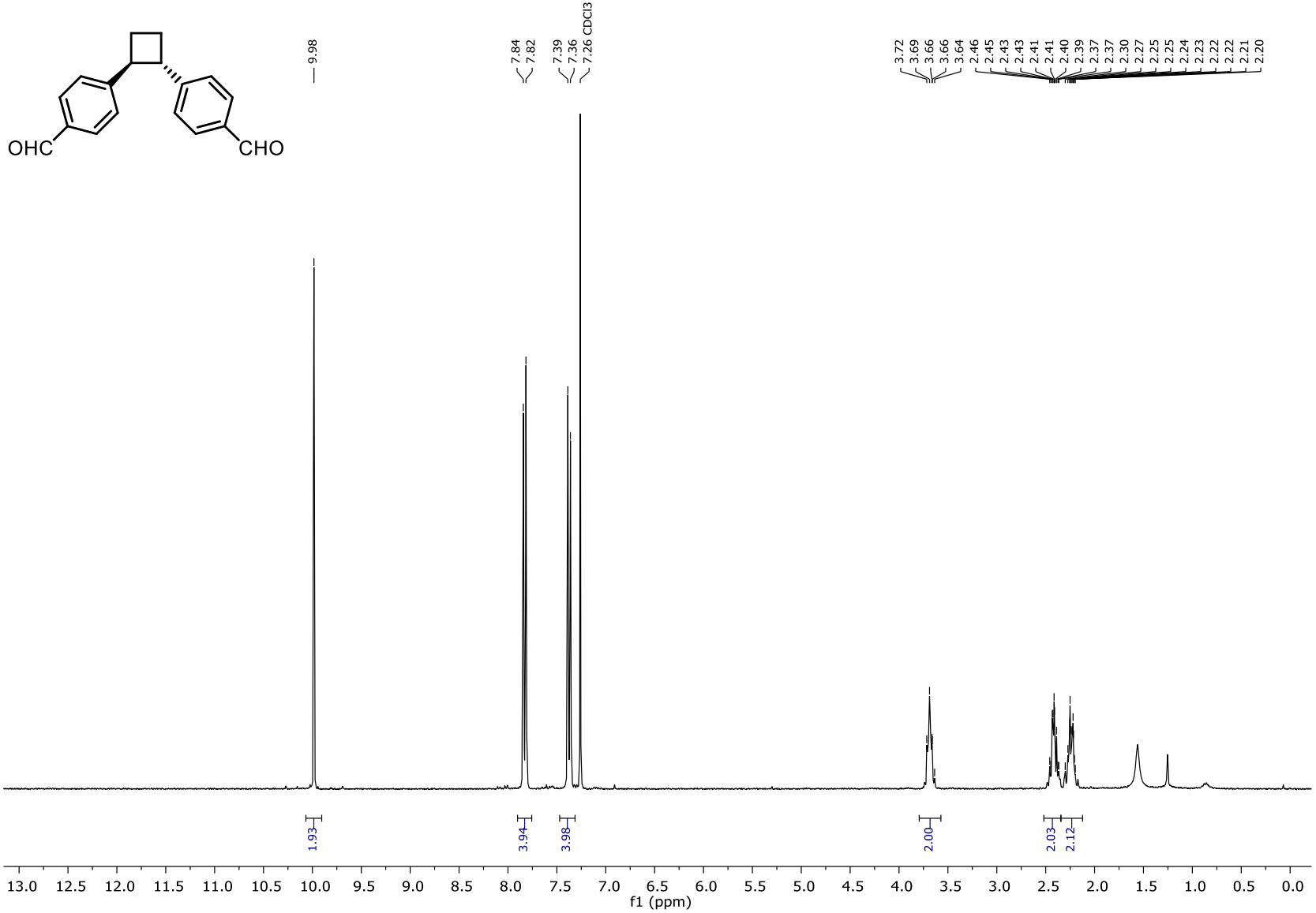
4,4'-(cyclobutane-1,2-diyl)dibenzonitrile (2c-cis): 13C{^{1}H} NMR (400 MHz, $CDCl_3$)



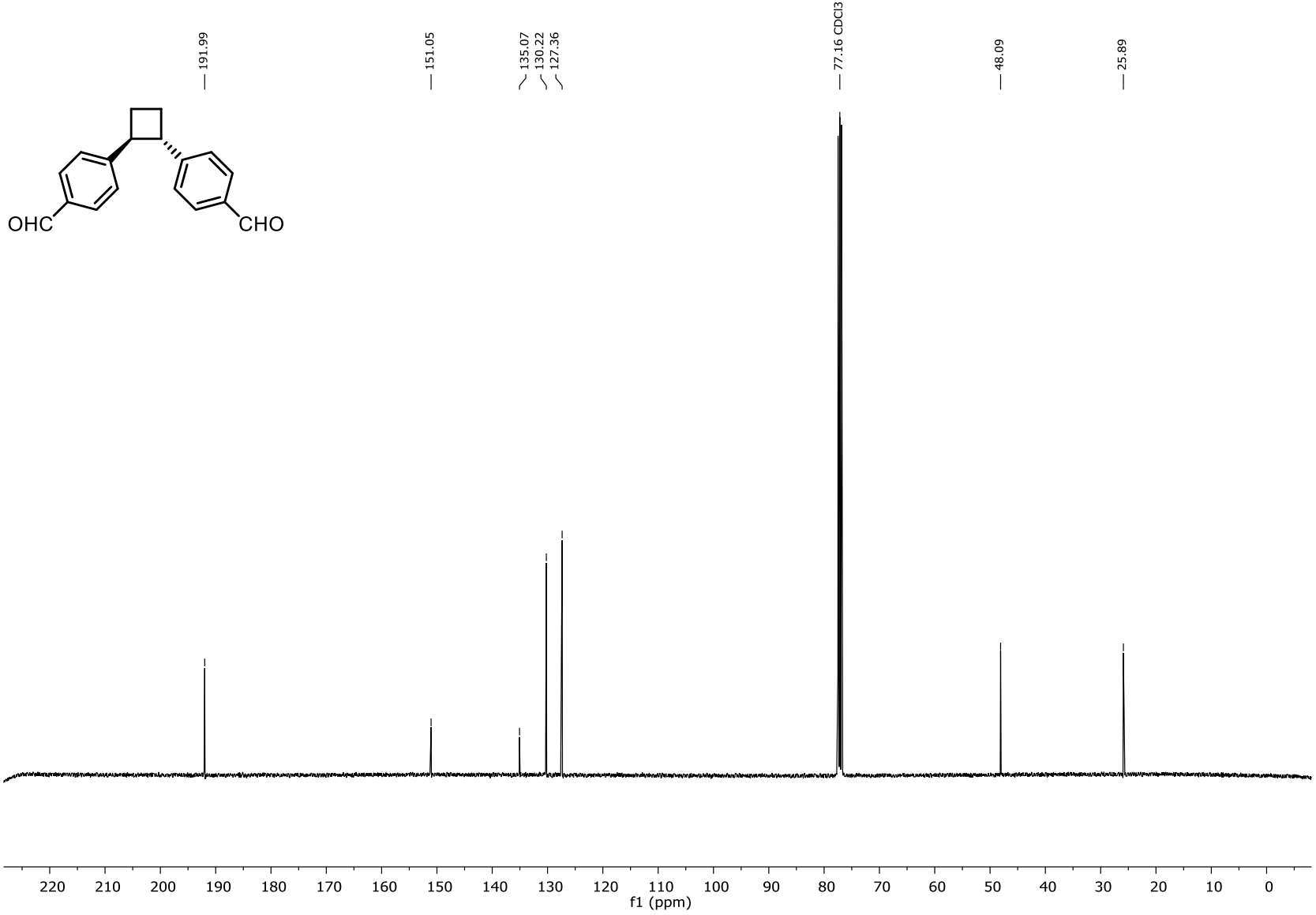
4,4'-(cyclobutane-1,2-diyl)dibenzaldehyde (2d-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



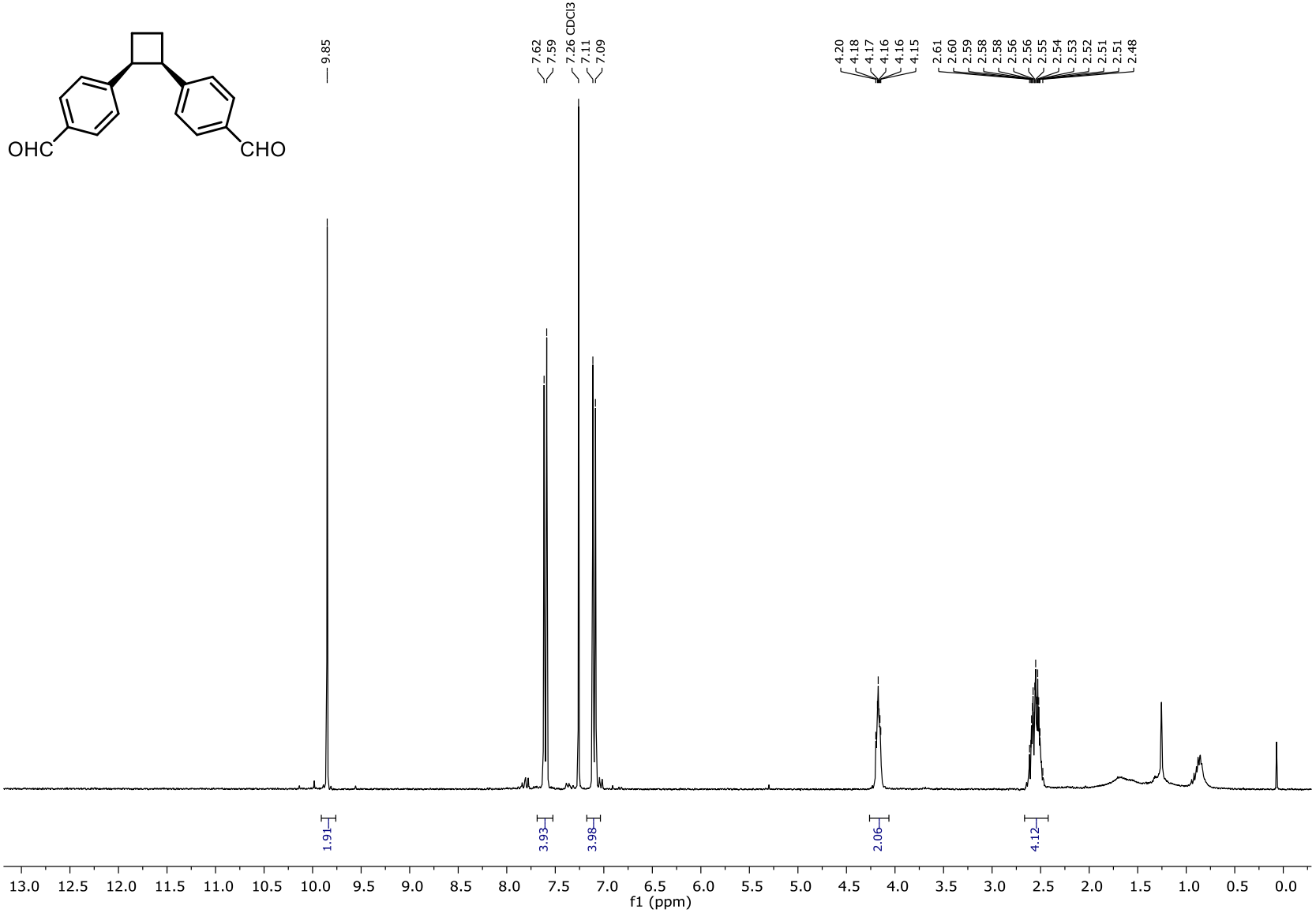
4,4'-(cyclobutane-1,2-diyl)dibenzaldehyde (2d-trans): ^{1}H NMR (300 MHz, $CDCl_3$)



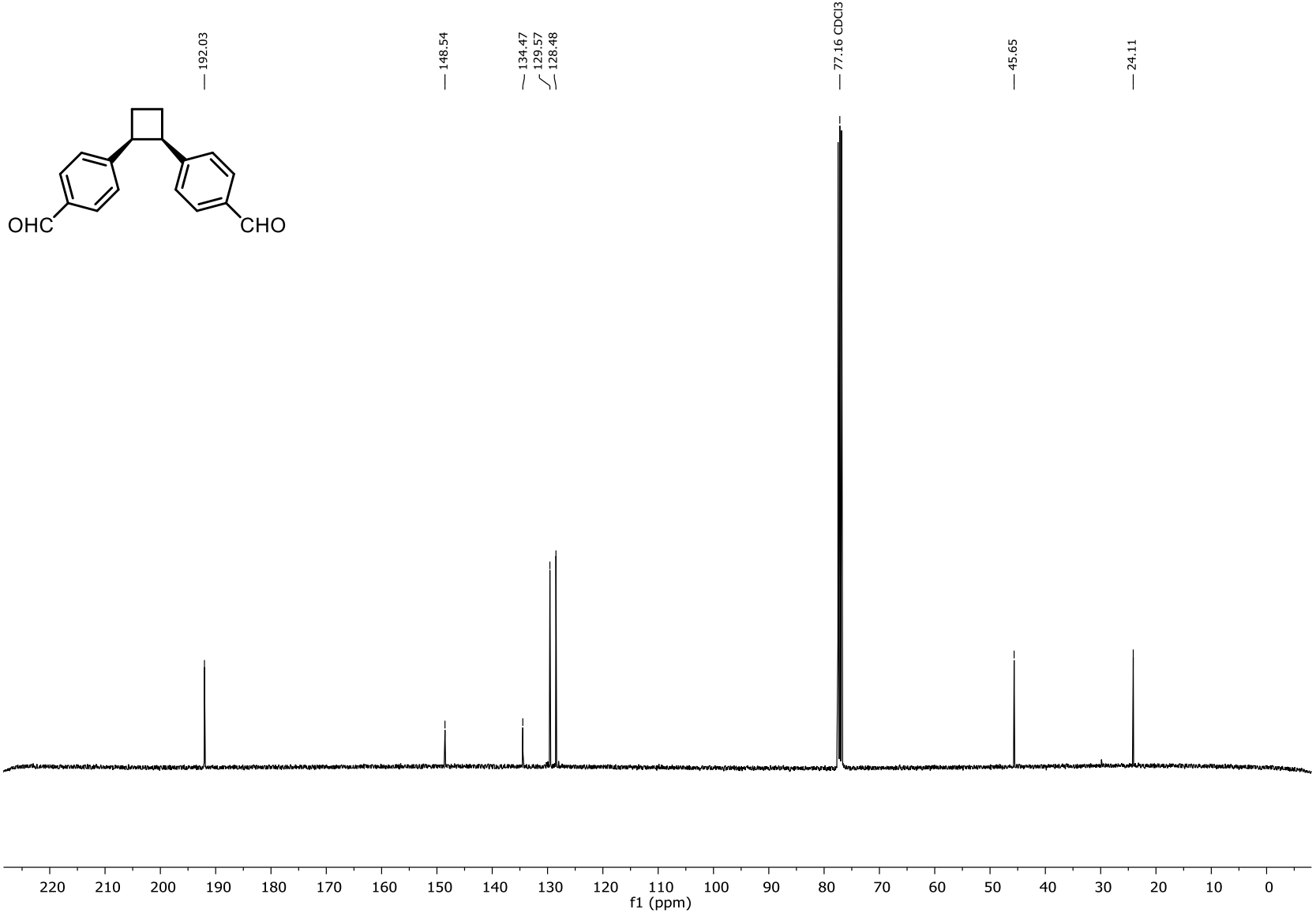
4,4'-(cyclobutane-1,2-diyl)dibenzaldehyde (2d-trans): 13C{^{1}H} NMR (400 MHz, $CDCl_3$)



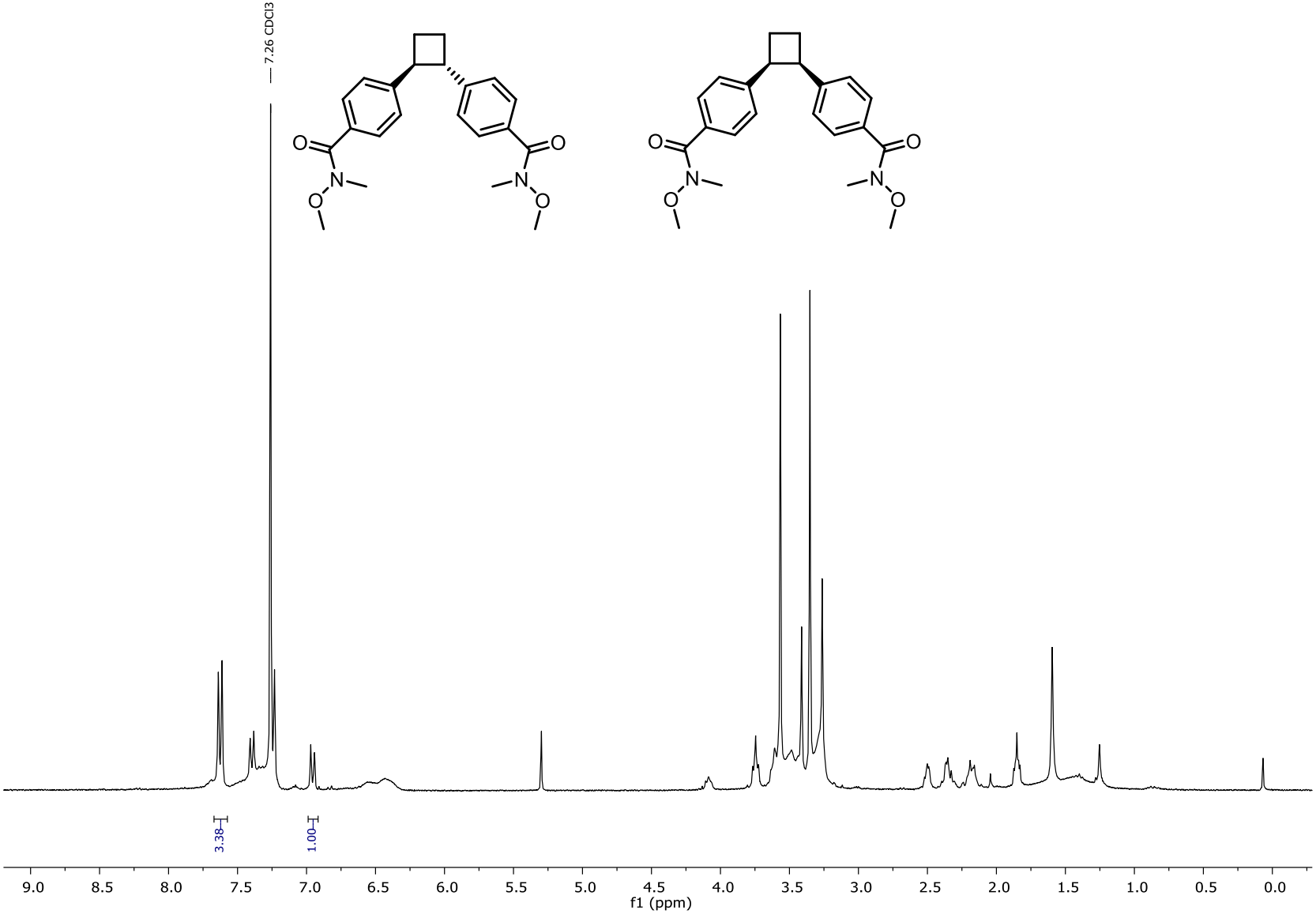
4,4'-(cyclobutane-1,2-diyl)dibenzaldehyde (2d-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



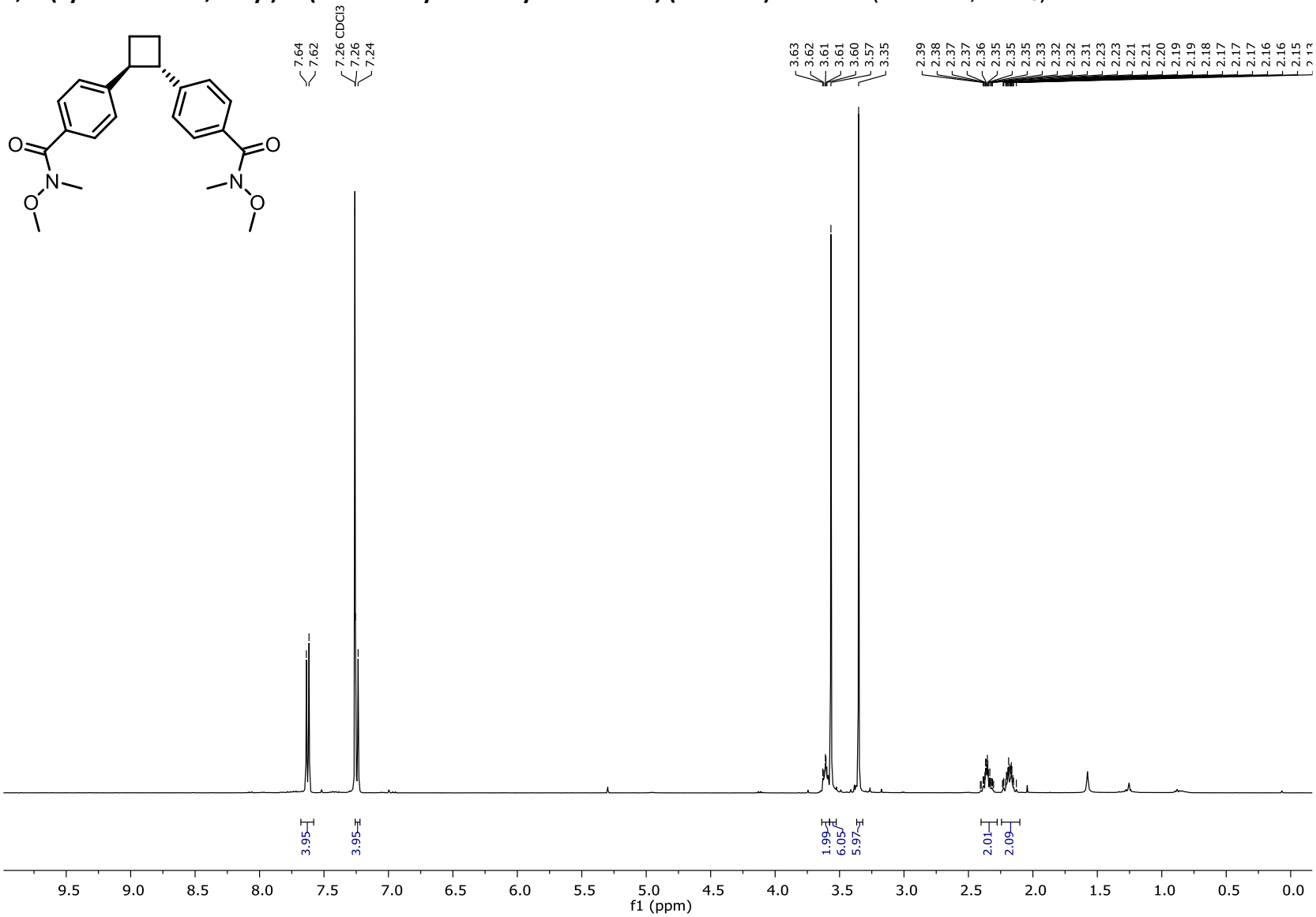
4,4'-(cyclobutane-1,2-diyl)dibenzaldehyde (2d-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



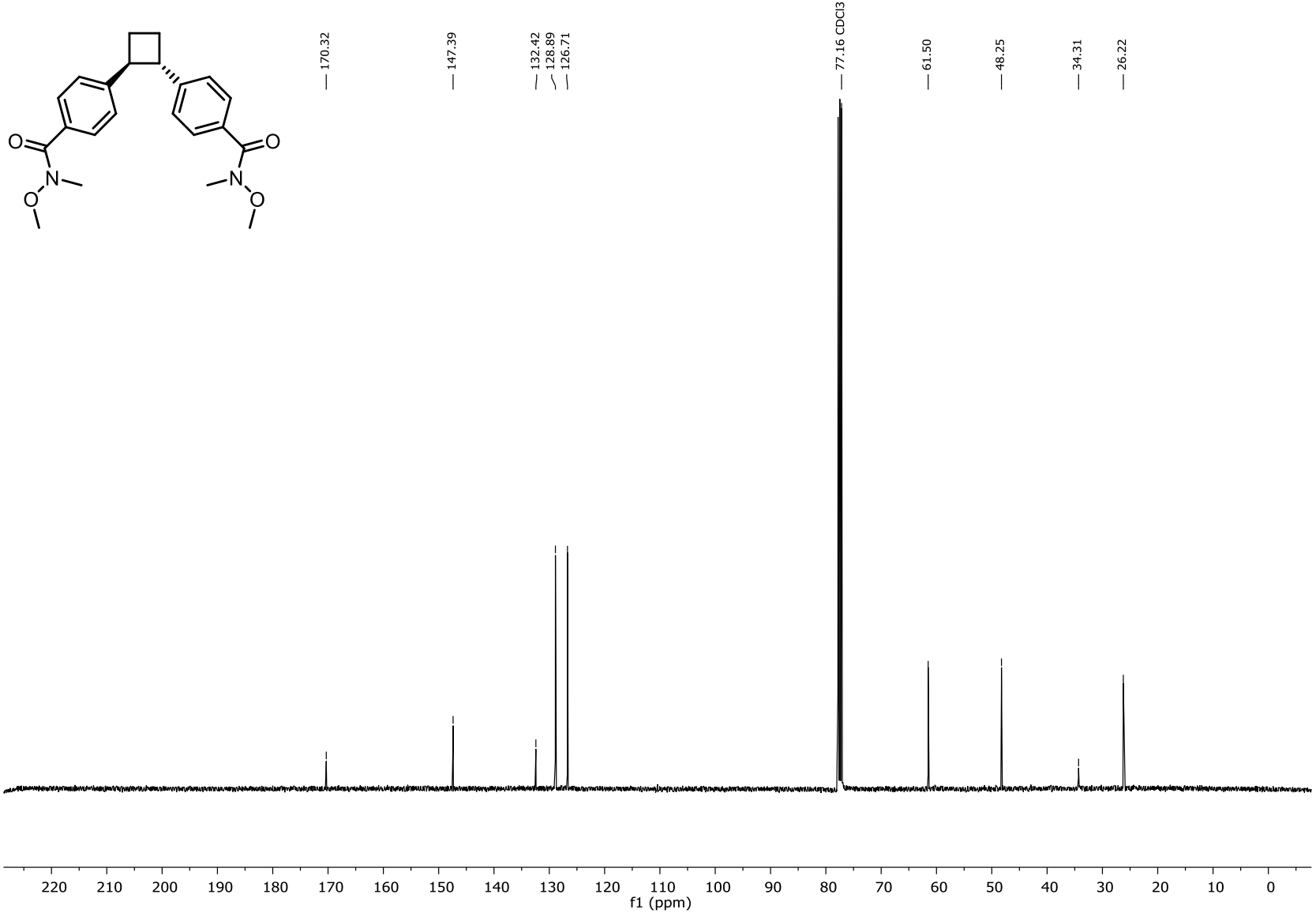
4,4'-(cyclobutane-1,2-diyl)bis(N-methoxy-N-methylbenzamide) (2e-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



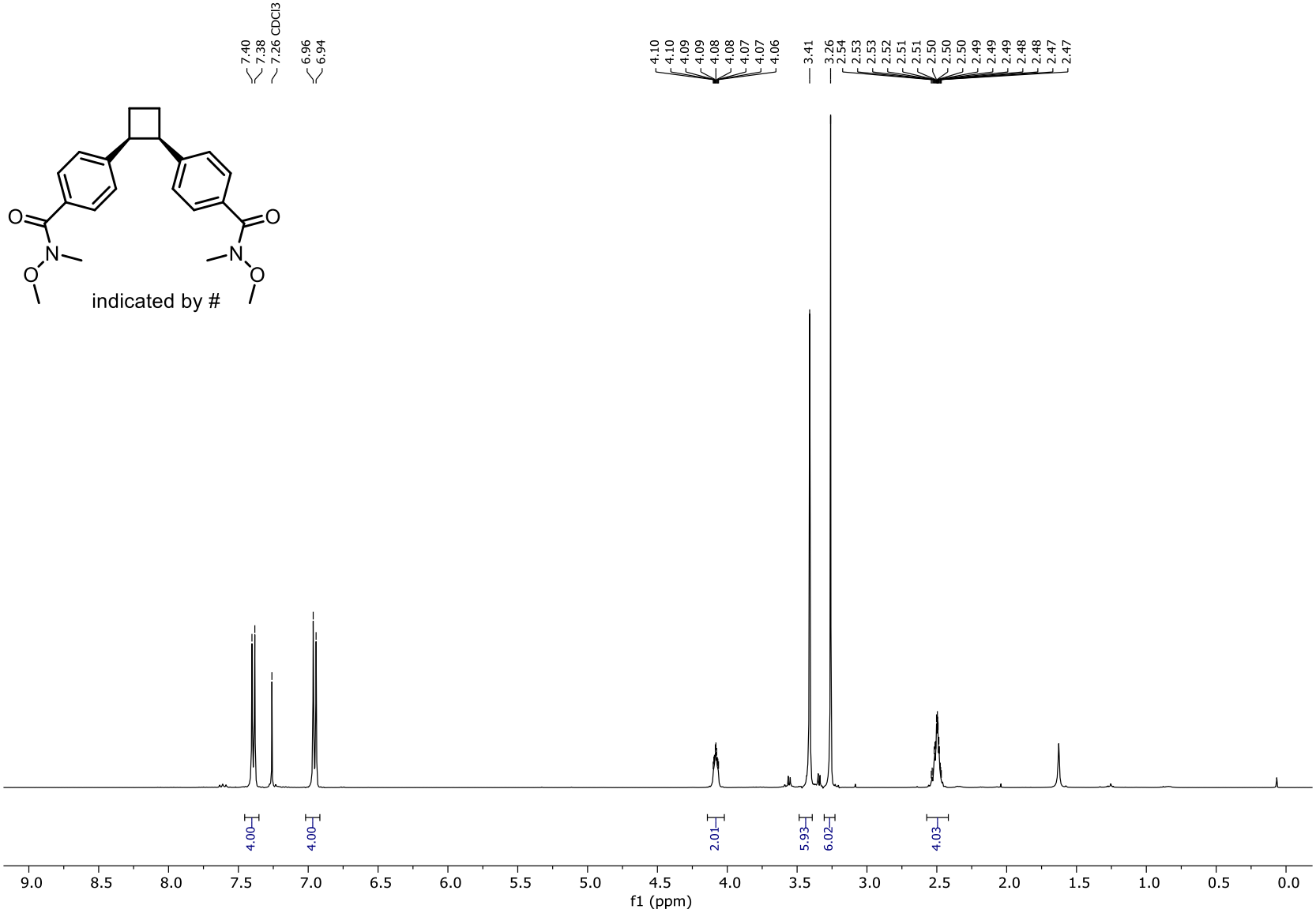
4,4'-(cyclobutane-1,2-diyl)bis(N-methoxy-N-methylbenzamide) (2e-trans): ^{1}H NMR (400 MHz, $CDCl_3$)



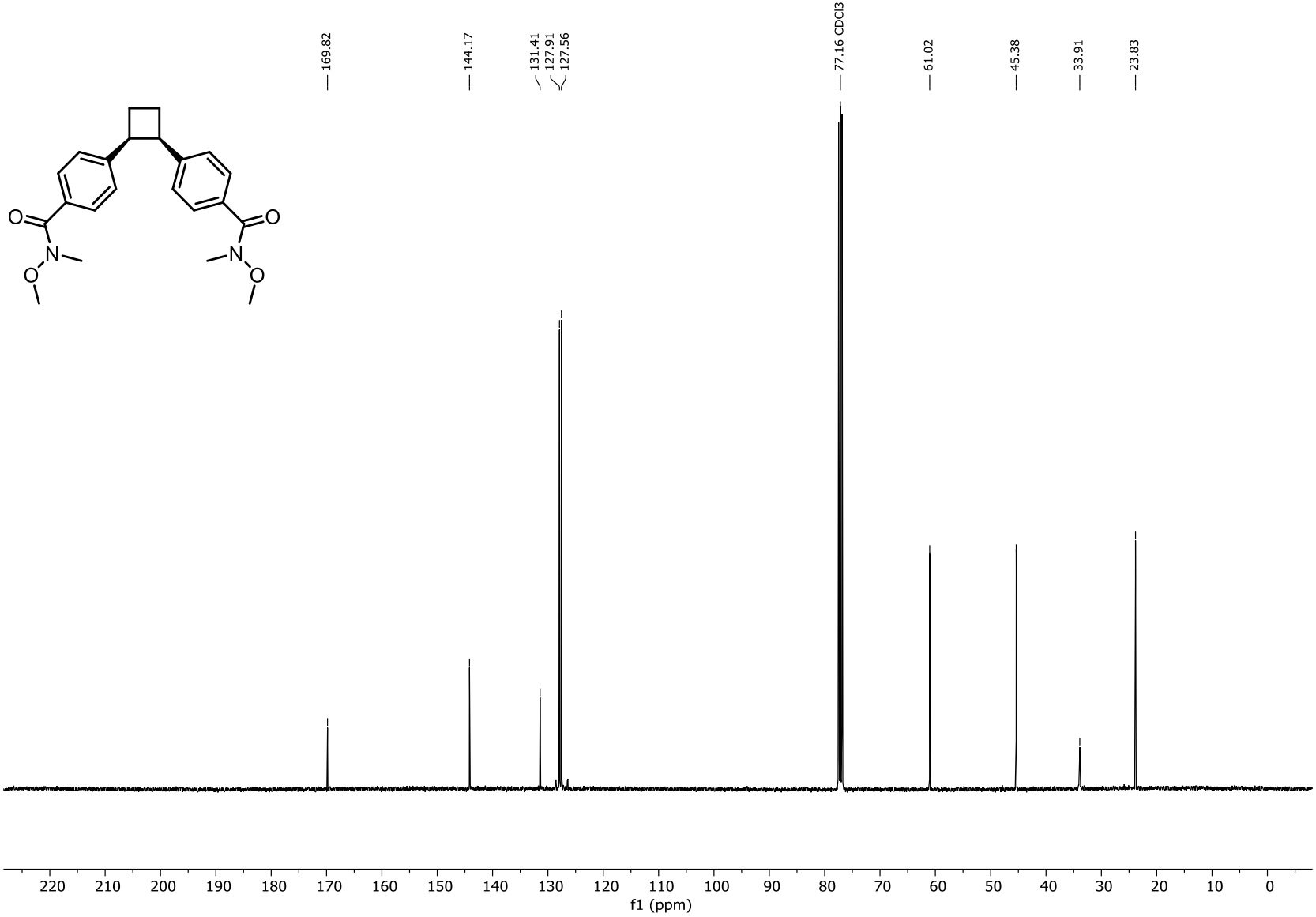
4,4'-(cyclobutane-1,2-diyl)bis(N-methoxy-N-methylbenzamide) (2e-trans): 13C{^{1}H} NMR (400 MHz, $CDCl_3$)



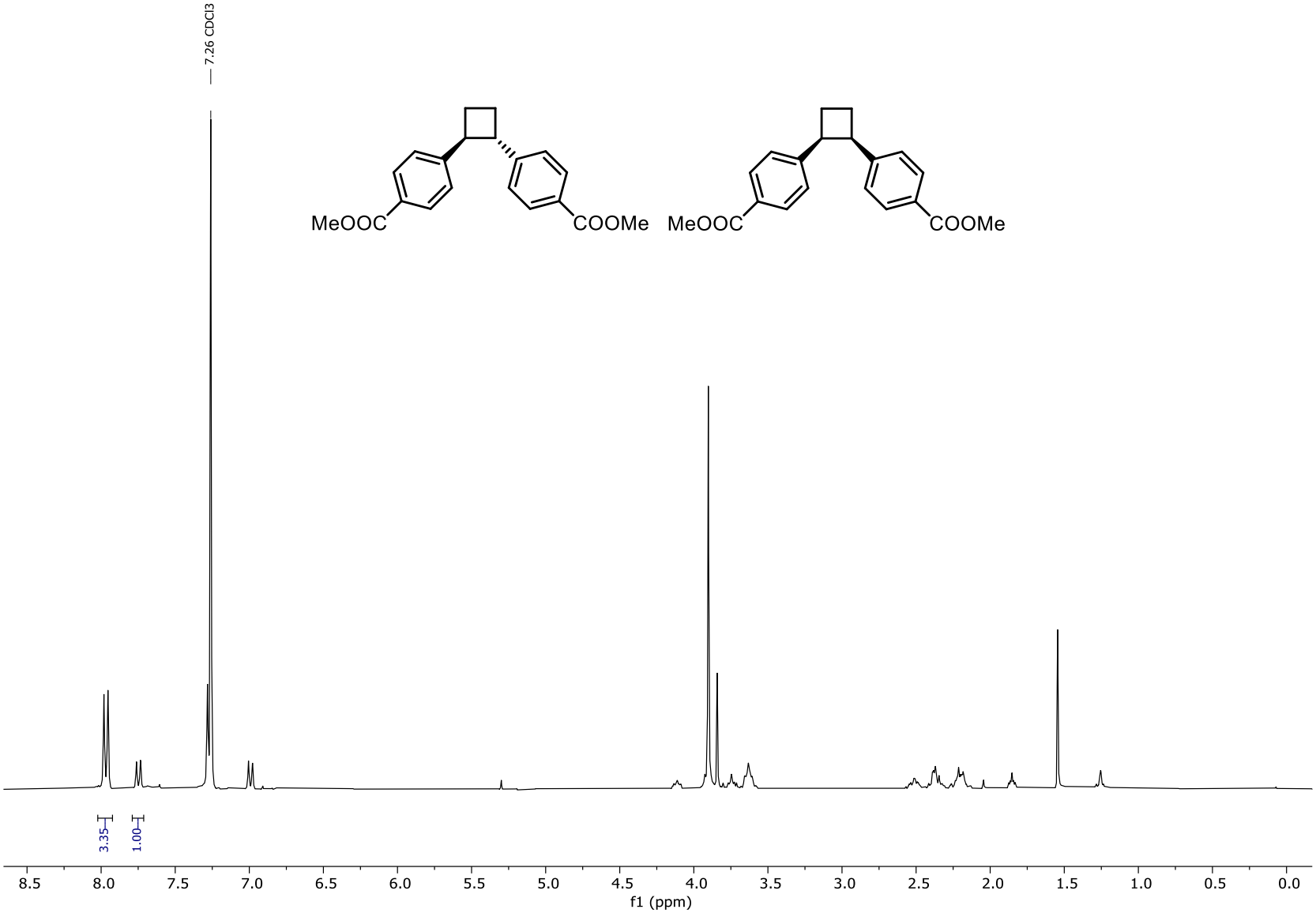
4,4'-(cyclobutane-1,2-diyl)bis(N-methoxy-N-methylbenzamide) (2e-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



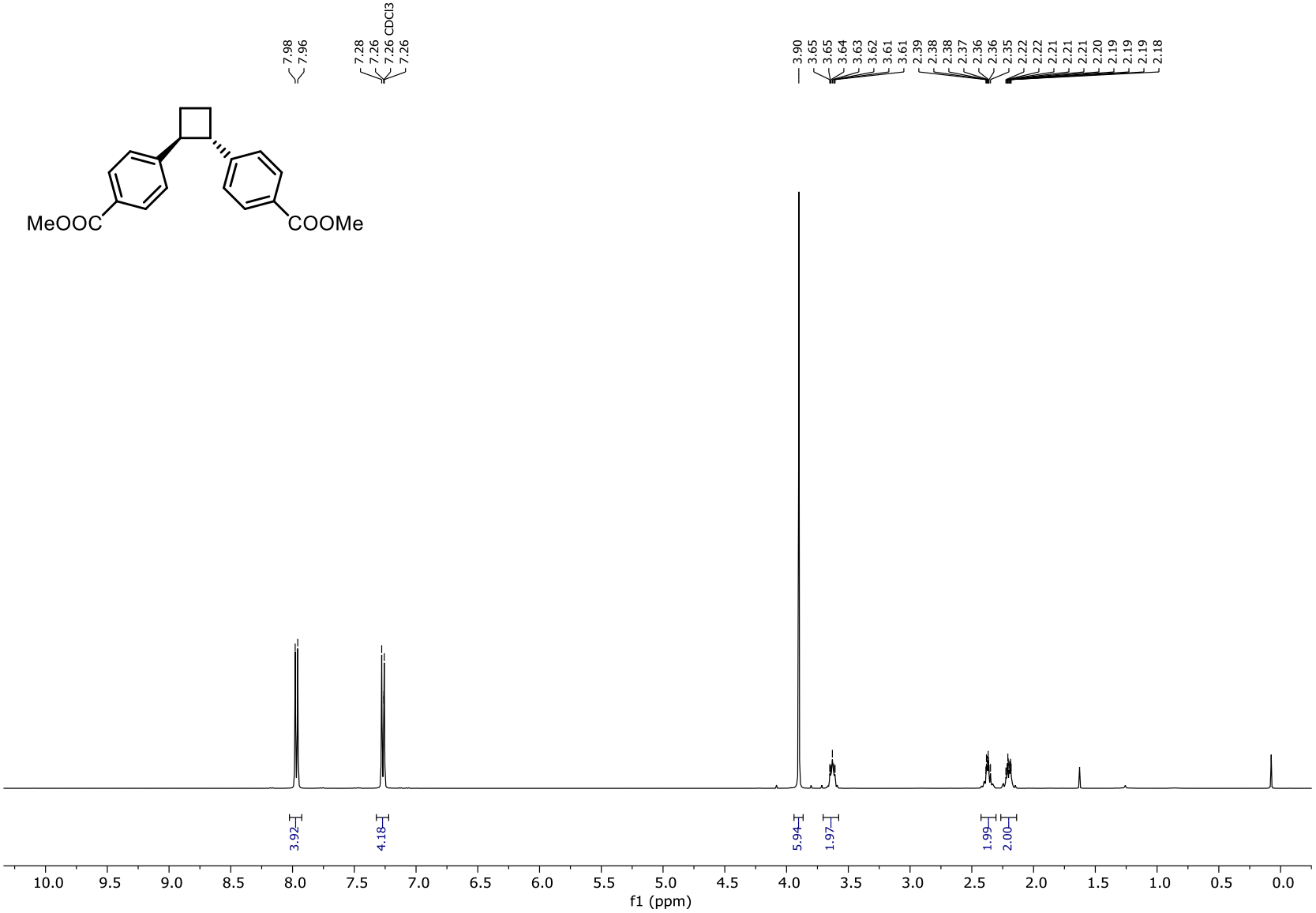
4,4'-(cyclobutane-1,2-diyl)bis(N-methoxy-N-methylbenzamide) (2e-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



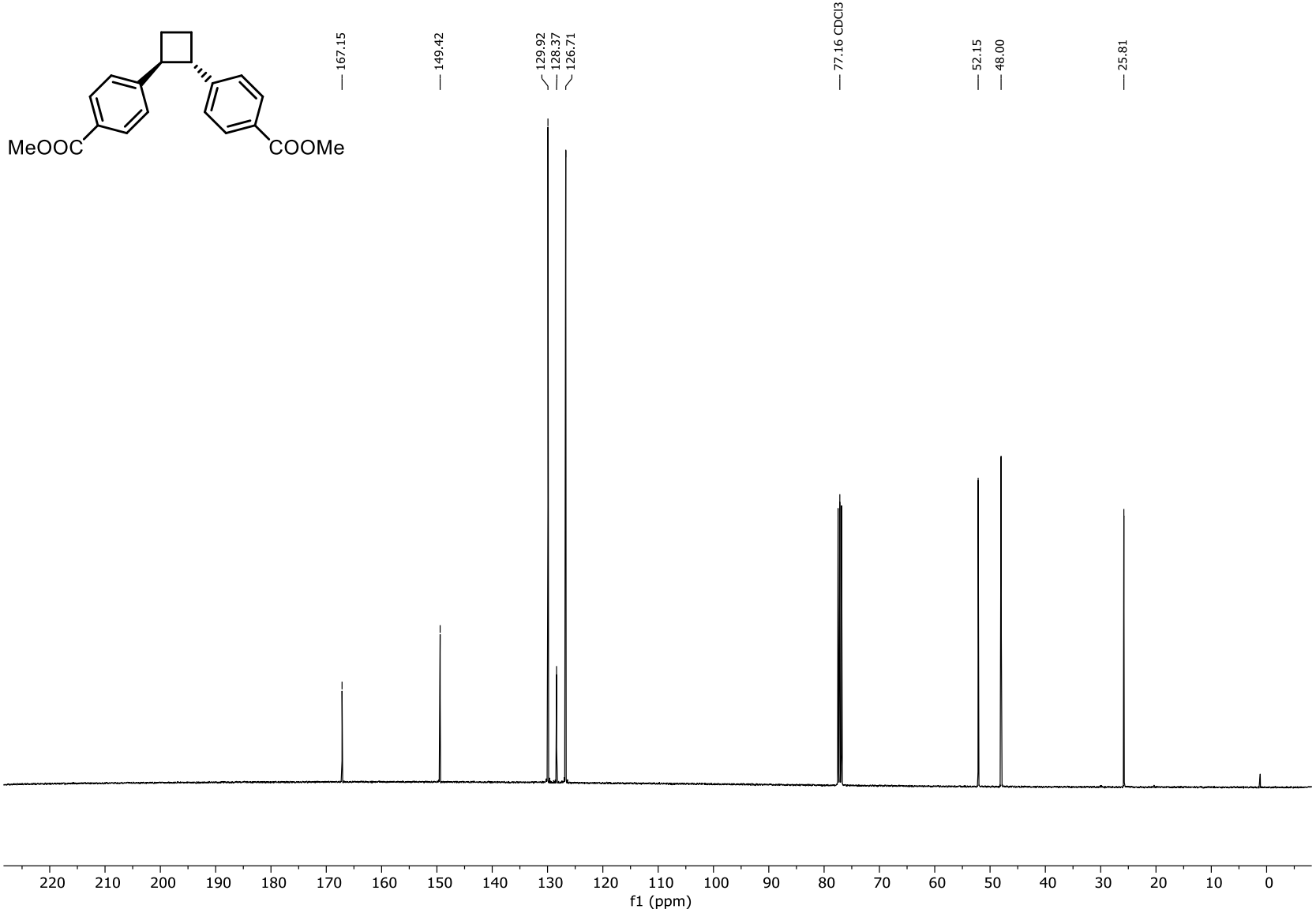
Dimethyl 4,4'-(cyclobutane-1,2-diyl)dibenzoate (2f-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



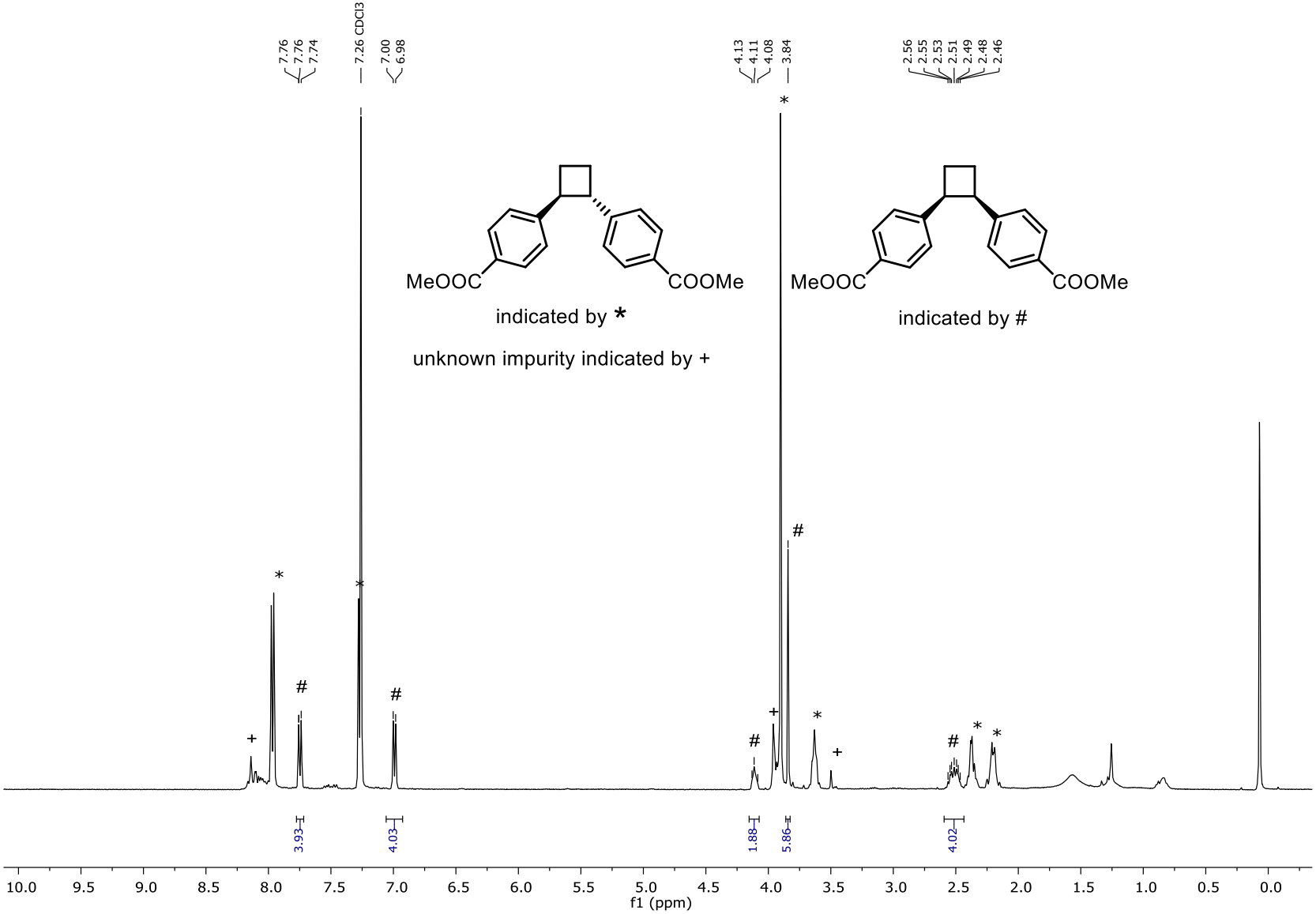
Dimethyl 4,4'-(cyclobutane-1,2-diyl)dibenzoate (2f-trans): ^{1}H NMR (400 MHz, $CDCl_3$)



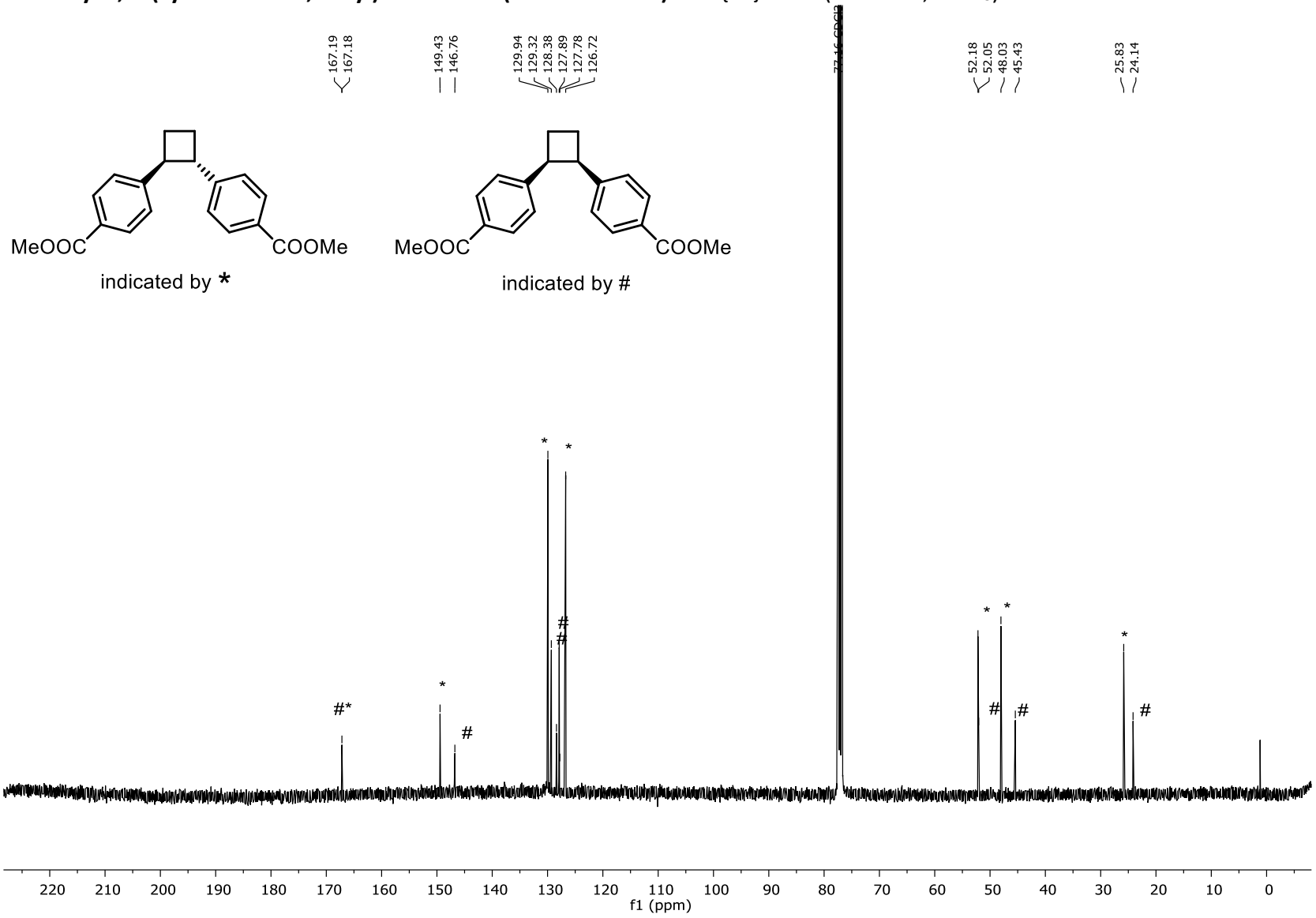
Dimethyl 4,4'-(cyclobutane-1,2-diyl)dibenzoate (2f-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



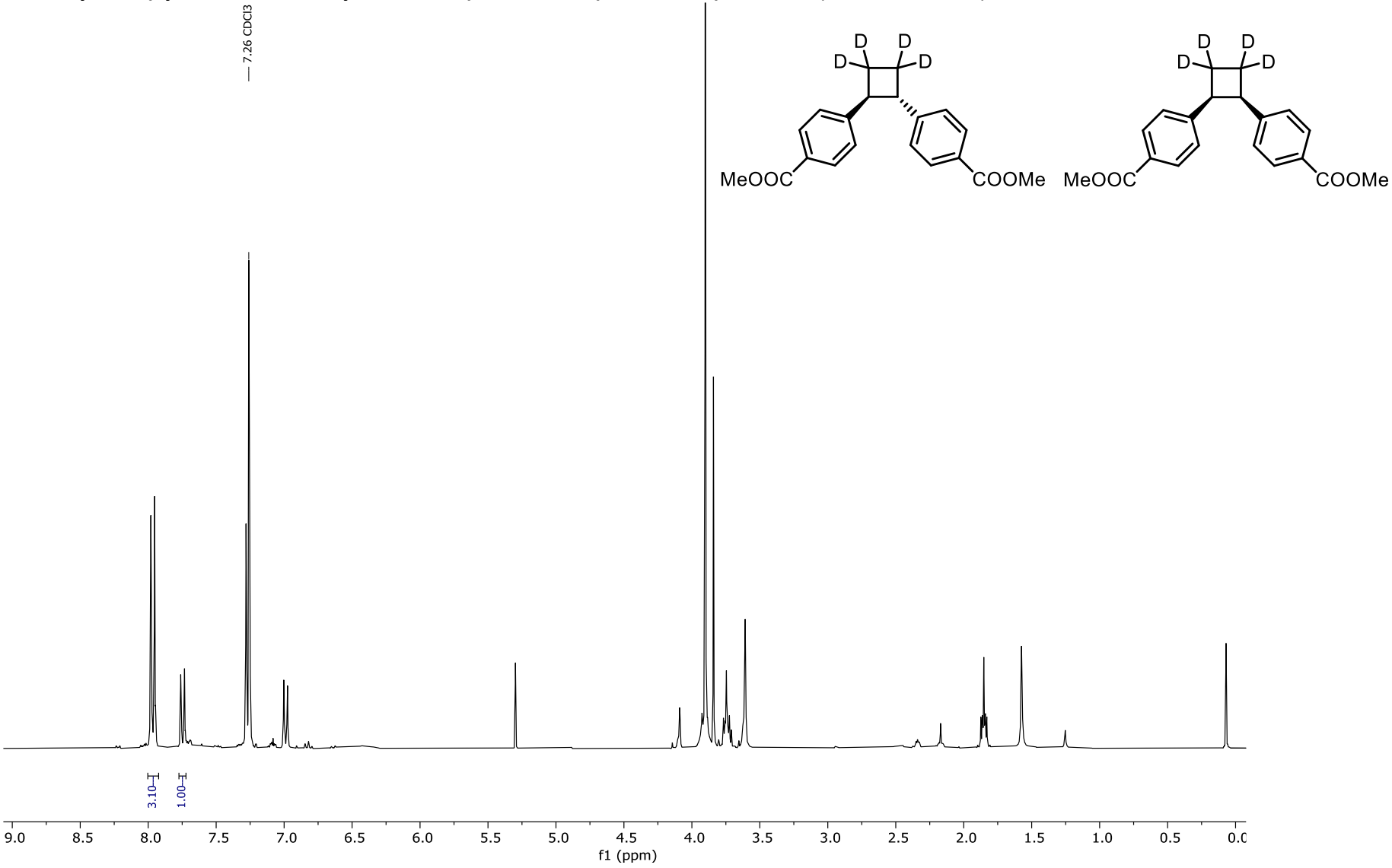
Dimethyl 4,4'-(cyclobutane-1,2-diyl)dibenzoate (2f-cis+2f-trans): ^{1}H NMR (400 MHz, $CDCl_3$)



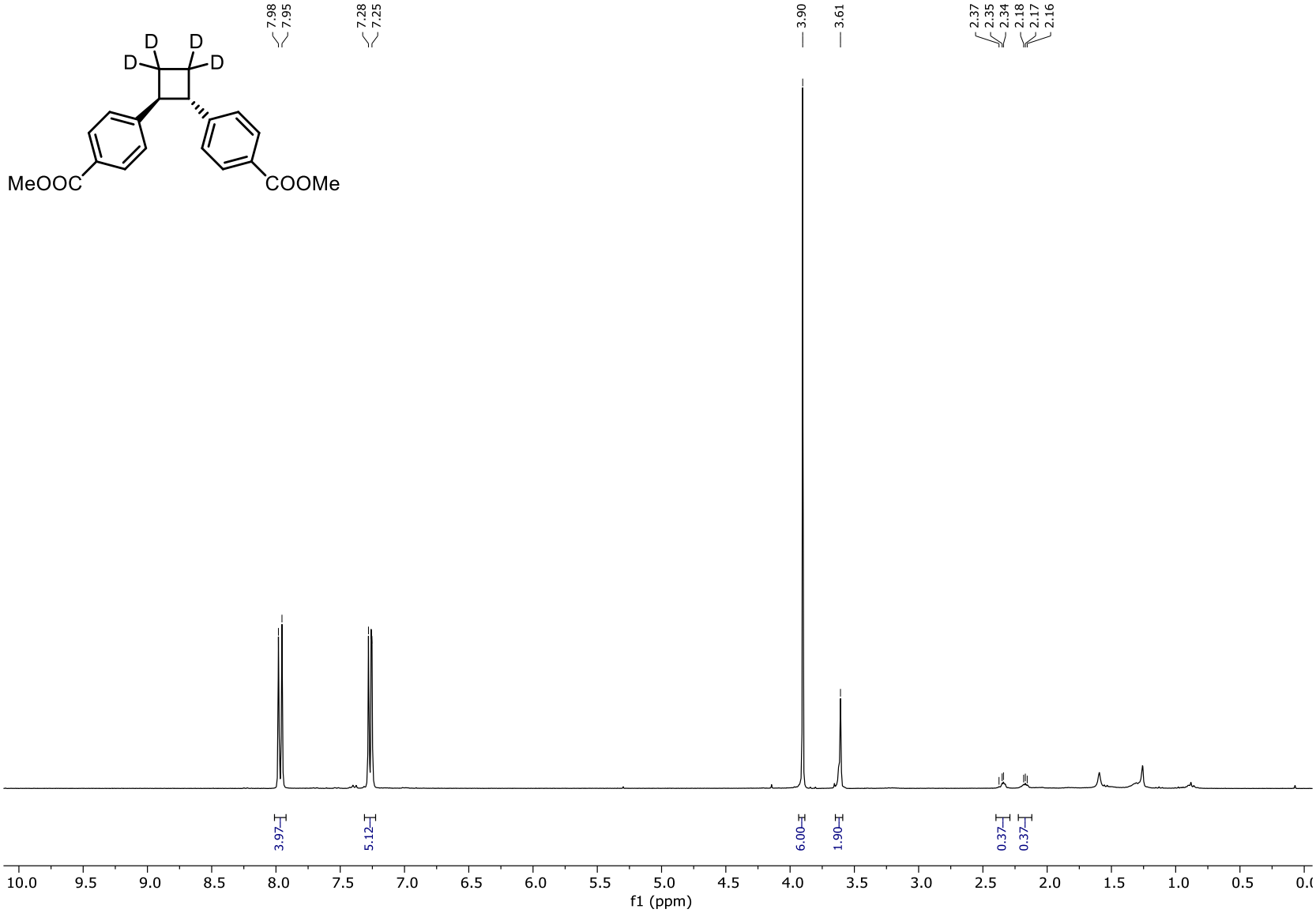
Dimethyl 4,4'-(cyclobutane-1,2-diyl)dibenzoate (2f-cis+2f-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



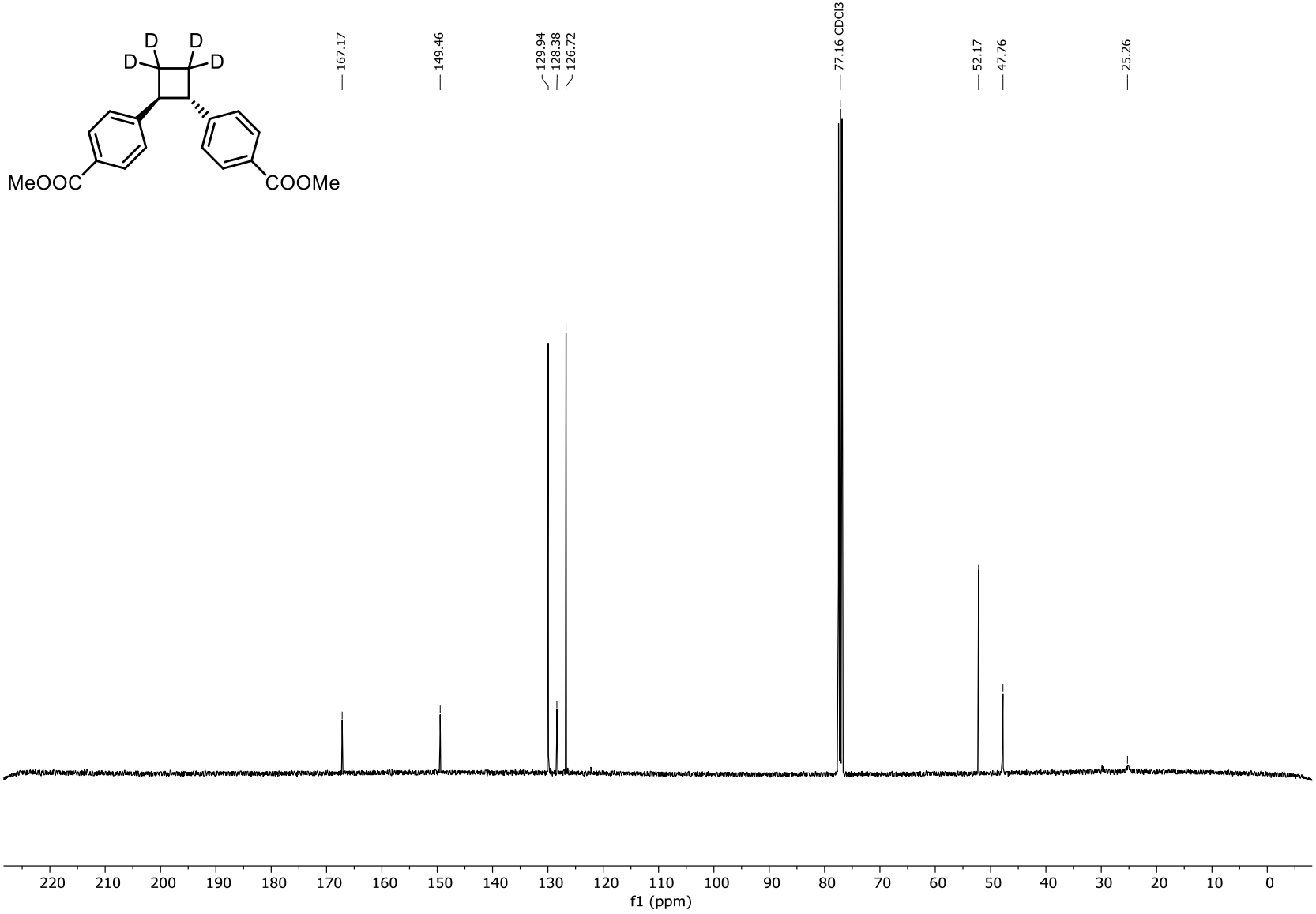
Dimethyl 4,4'-(cyclobutane-1,2-diyl-3,3,4,4-*d*4)dibenzoate (2f-d_4-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



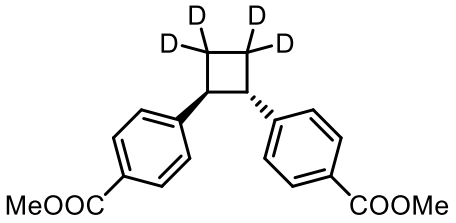
Dimethyl 4,4'-(cyclobutane-1,2-diyl-3,3,4,4-*d*4)dibenzoate (2f-d_4-trans): ^{1}H NMR (300 MHz, $CDCl_3$)



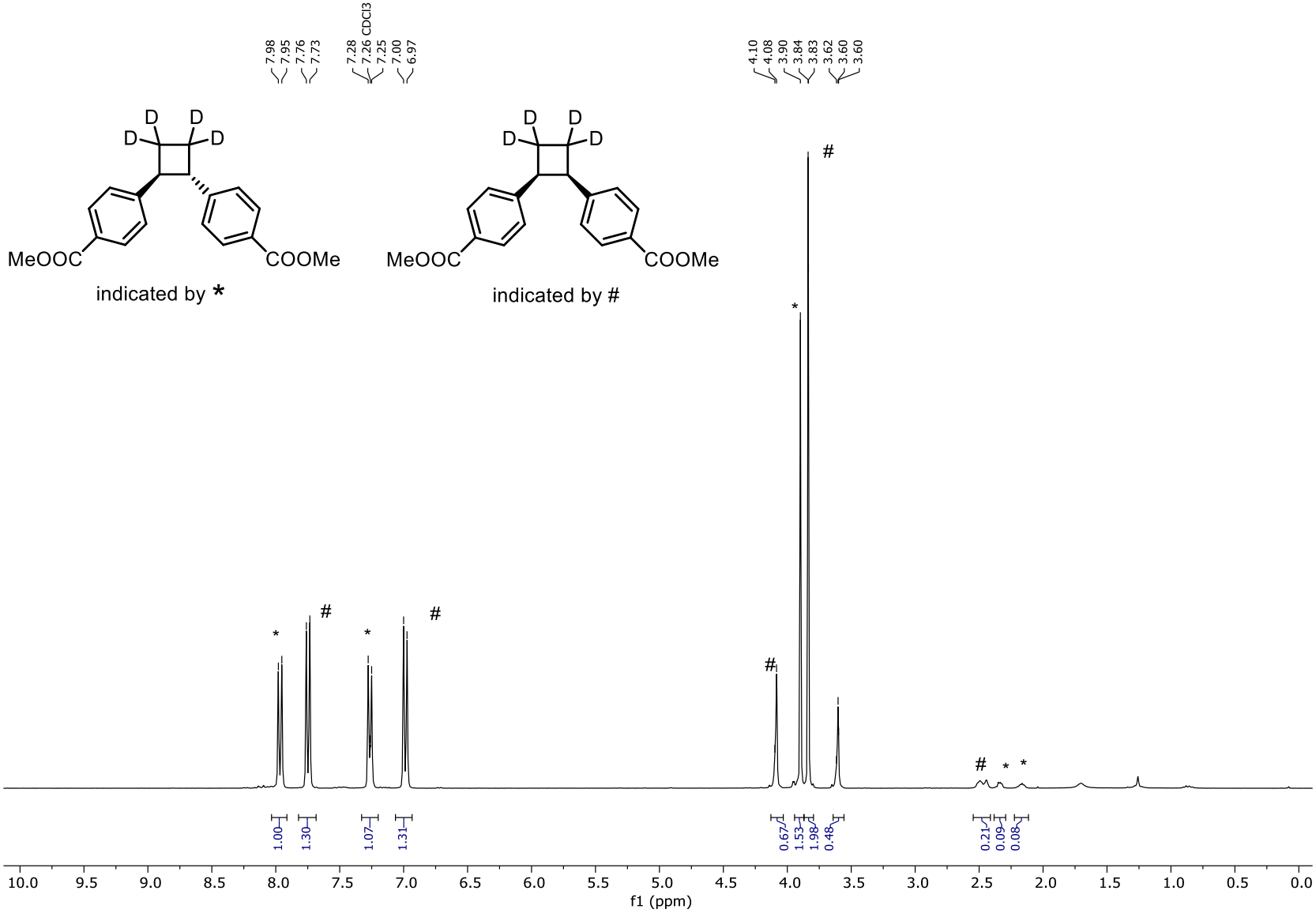
Dimethyl 4,4'-(cyclobutane-1,2-diyl-3,3,4,4-*d*4)dibenzoate (2f-d_4-trans): 13C{^{1}H} NMR (400 MHz, $CDCl_3$)



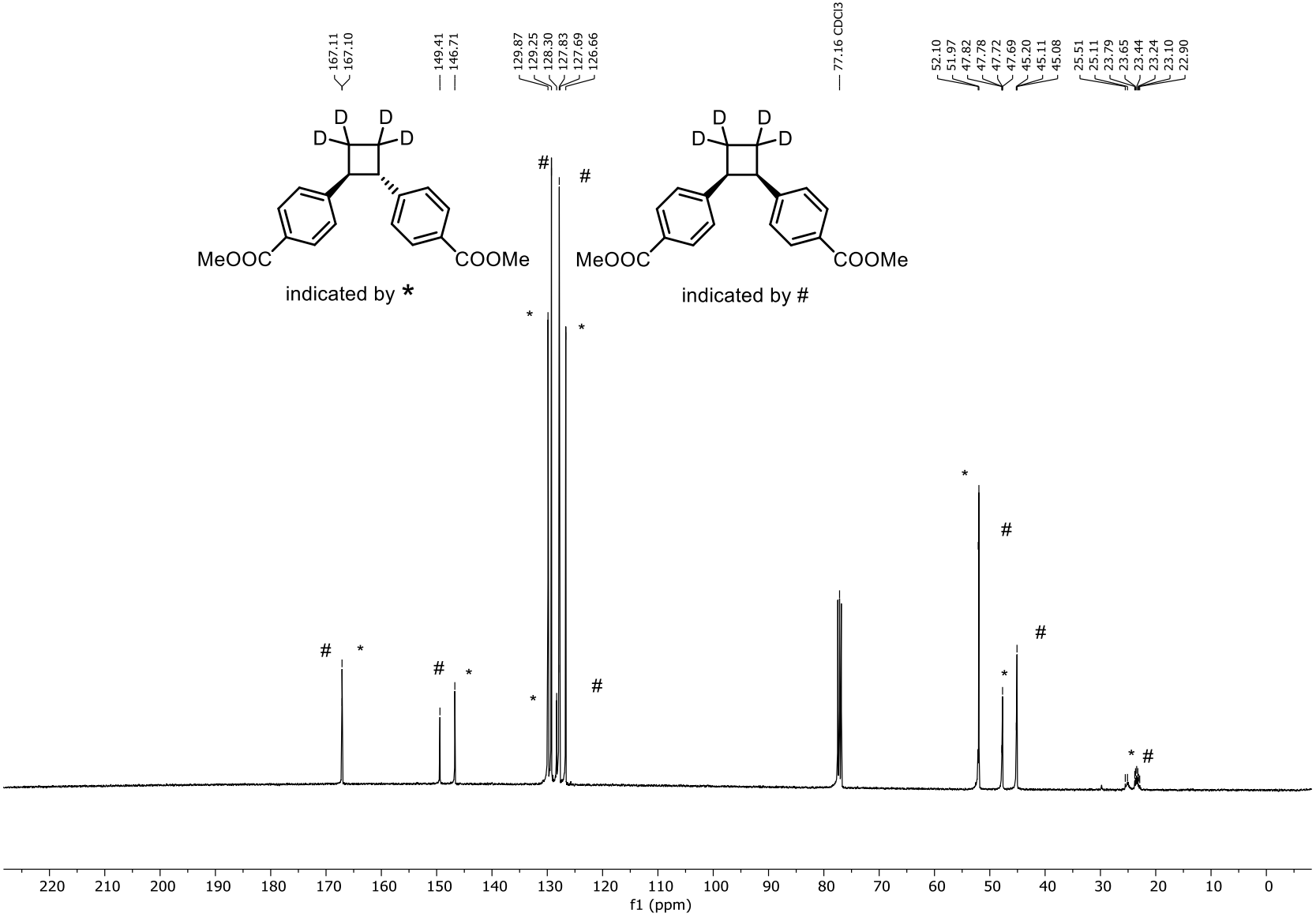
Dimethyl 4,4'-(cyclobutane-1,2-diyl-3,3,4,4-*d*4)dibenzoate (2f-d_4-trans): ^{2}H NMR (77 MHz, CDCl3) δ



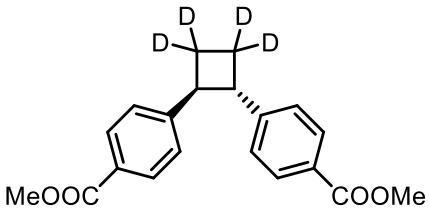
Dimethyl 4,4'-(cyclobutane-1,2-diyl-3,3,4,4-*d*4)dibenzoate (2f-d_4-cis+2f-d_4-trans): ^{1}H NMR (400 MHz, $CDCl_3$)



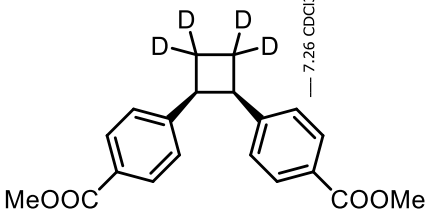
Dimethyl 4,4'-(cyclobutane-1,2-diyl-3,3,4,4-*d*4)dibenzoate (2f-d_4-cis+2f-d_4-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



Dimethyl 4,4'-(cyclobutane-1,2-diyl-3,3,4,4-*d*4)dibenzoate (2f-d_4-cis+2f-d_4-trans): ^{2}H NMR (77 MHz, CDCl3)

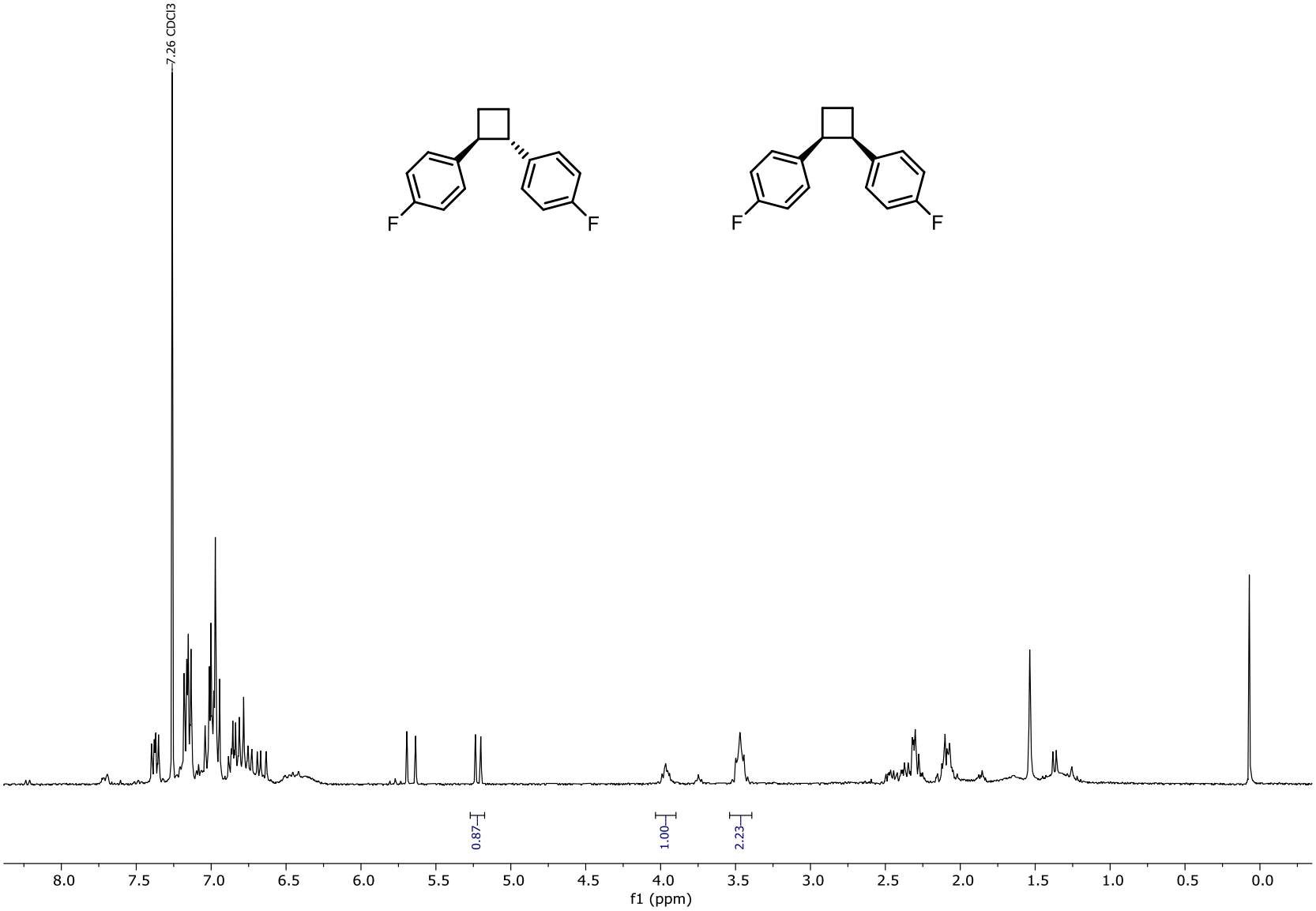


indicated by *

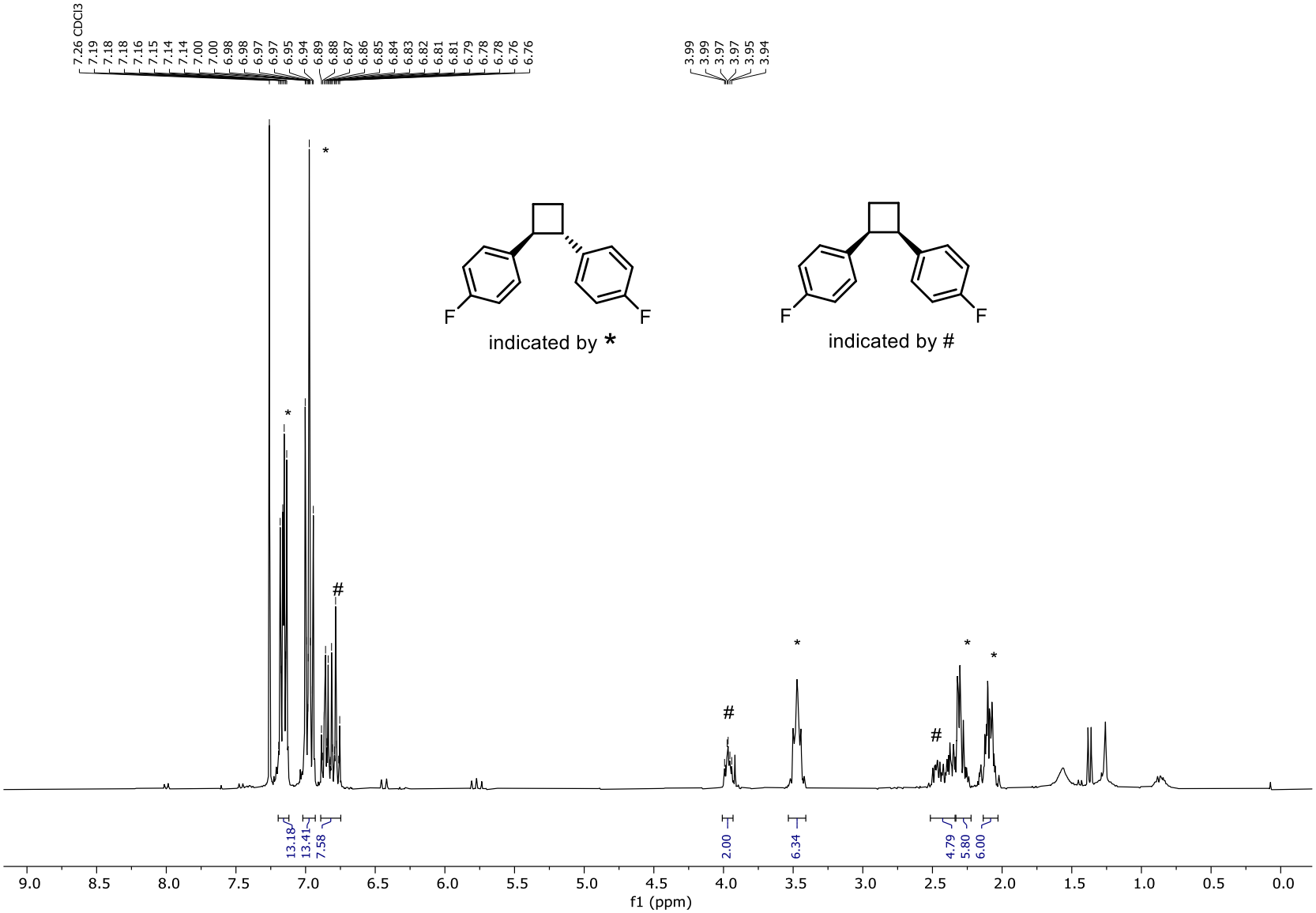


indicated by #

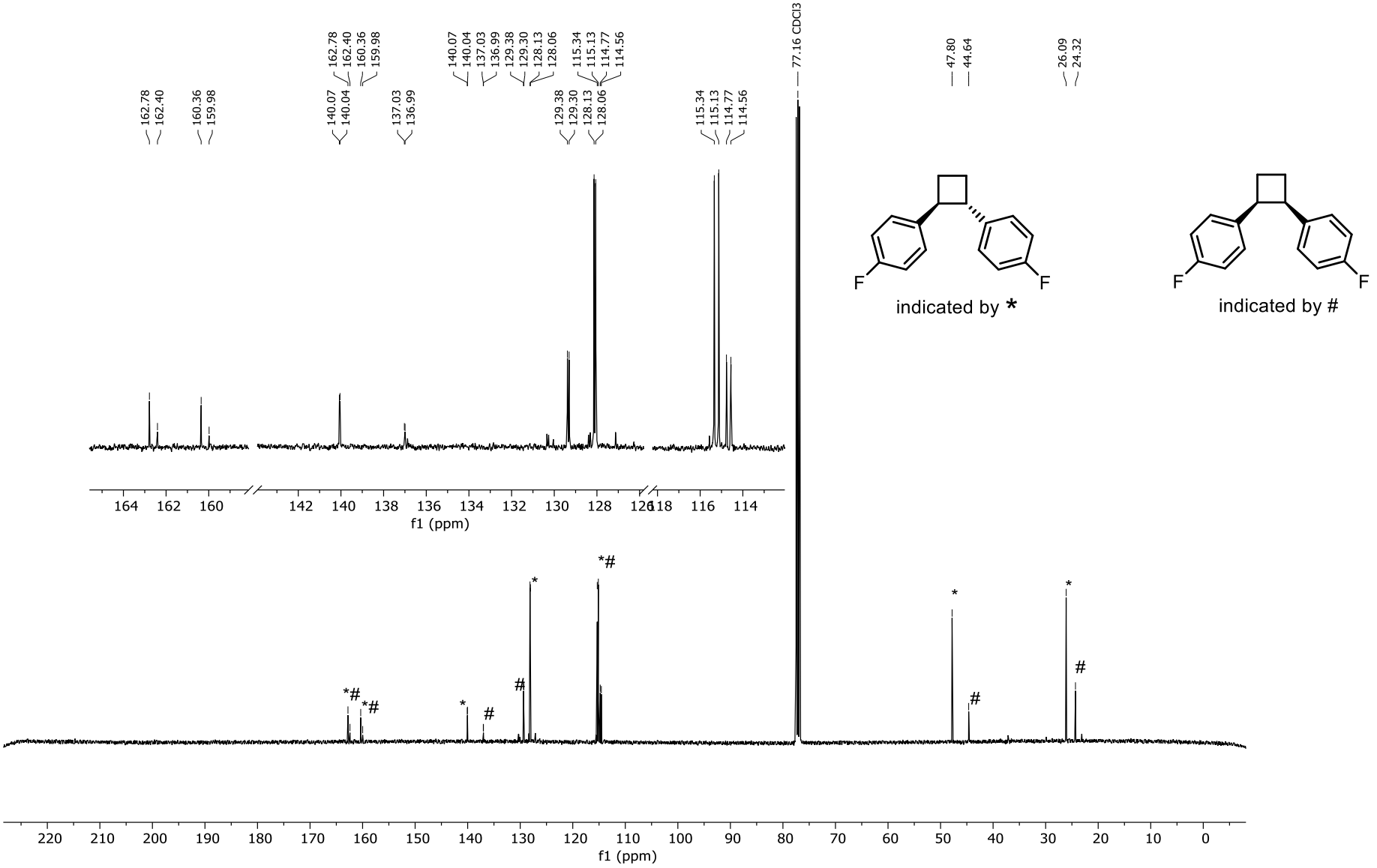
1,2-bis(4-fluorophenyl)cyclobutane (2g-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



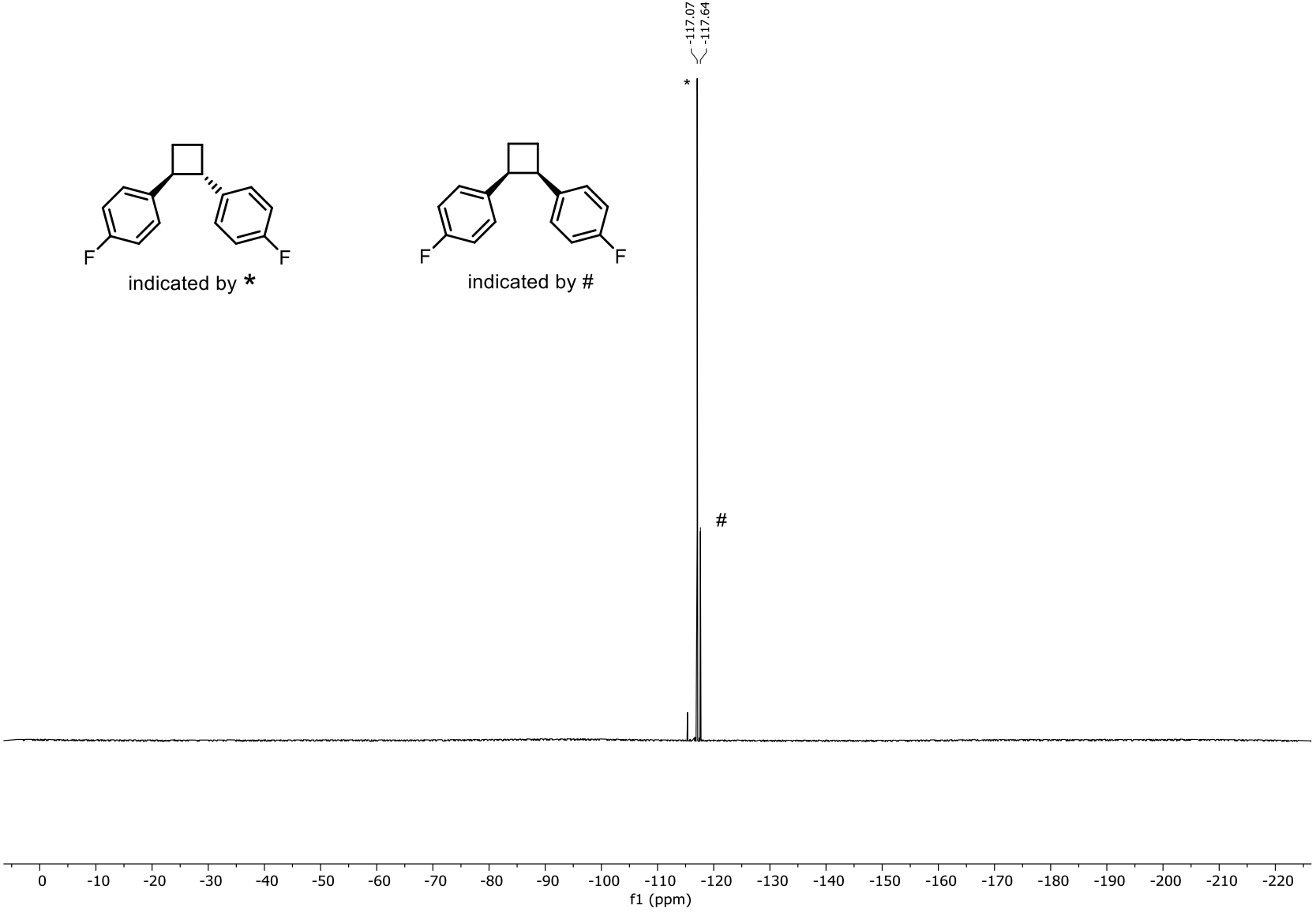
1,2-bis(4-fluorophenyl)cyclobutane (2g-trans+2g-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



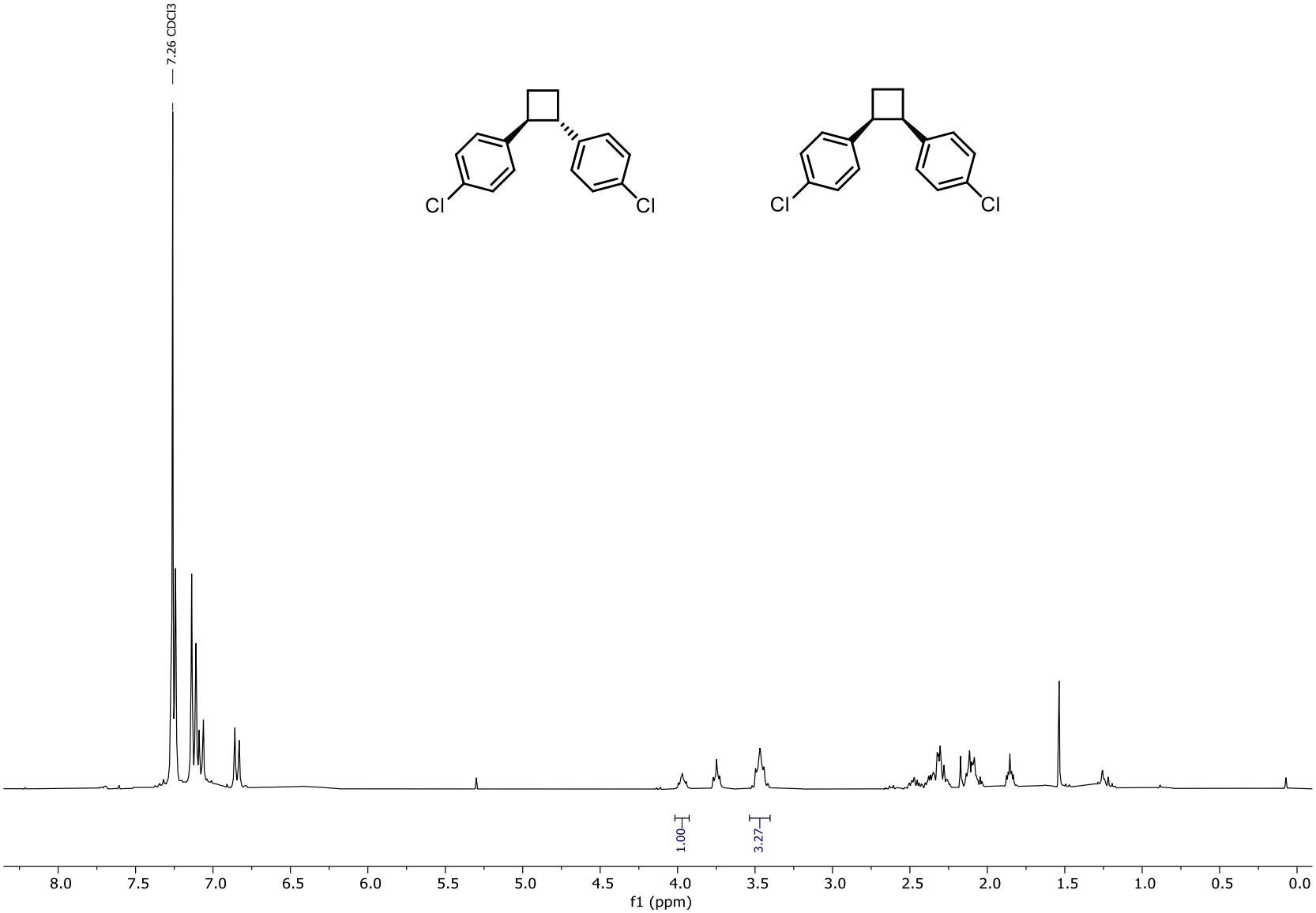
1,2-bis(4-fluorophenyl)cyclobutane (2g-trans+2g-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



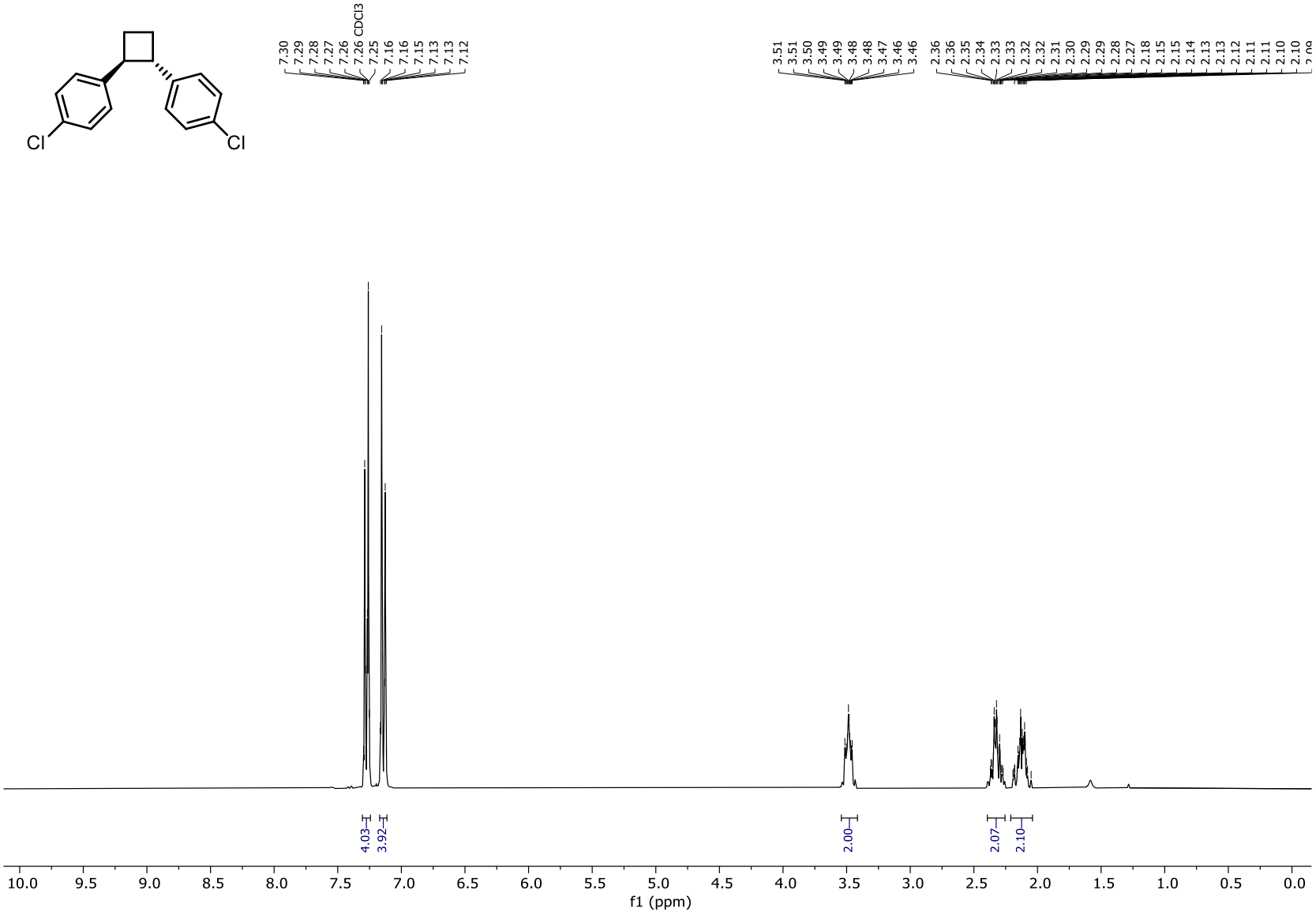
1,2-bis(4-fluorophenyl)cyclobutane (2g-trans+2g-cis): 19F{^{1}H} NMR (282 MHz, $CDCl_3$)



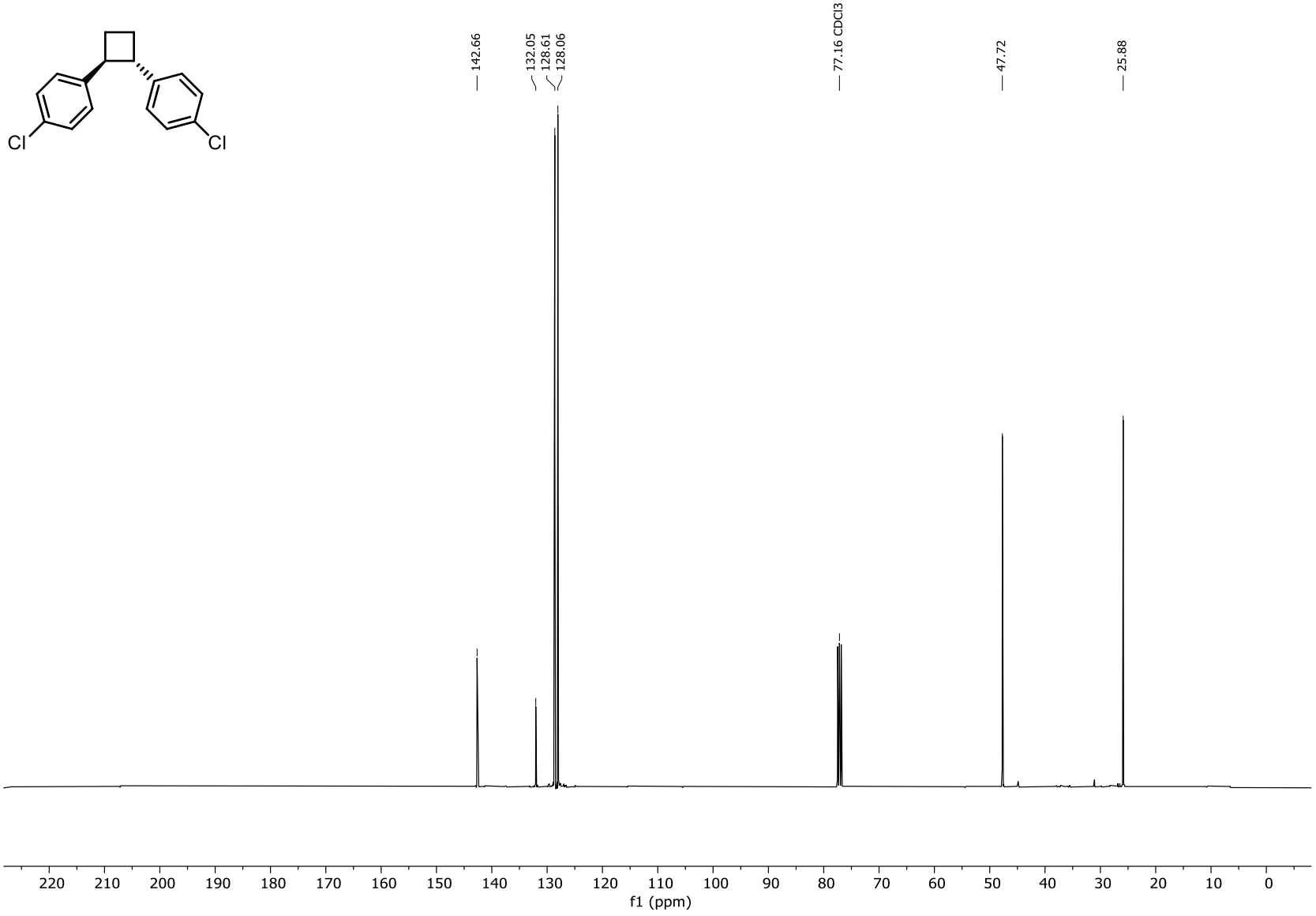
1,2-bis(4-chlorophenyl)cyclobutane (2h-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



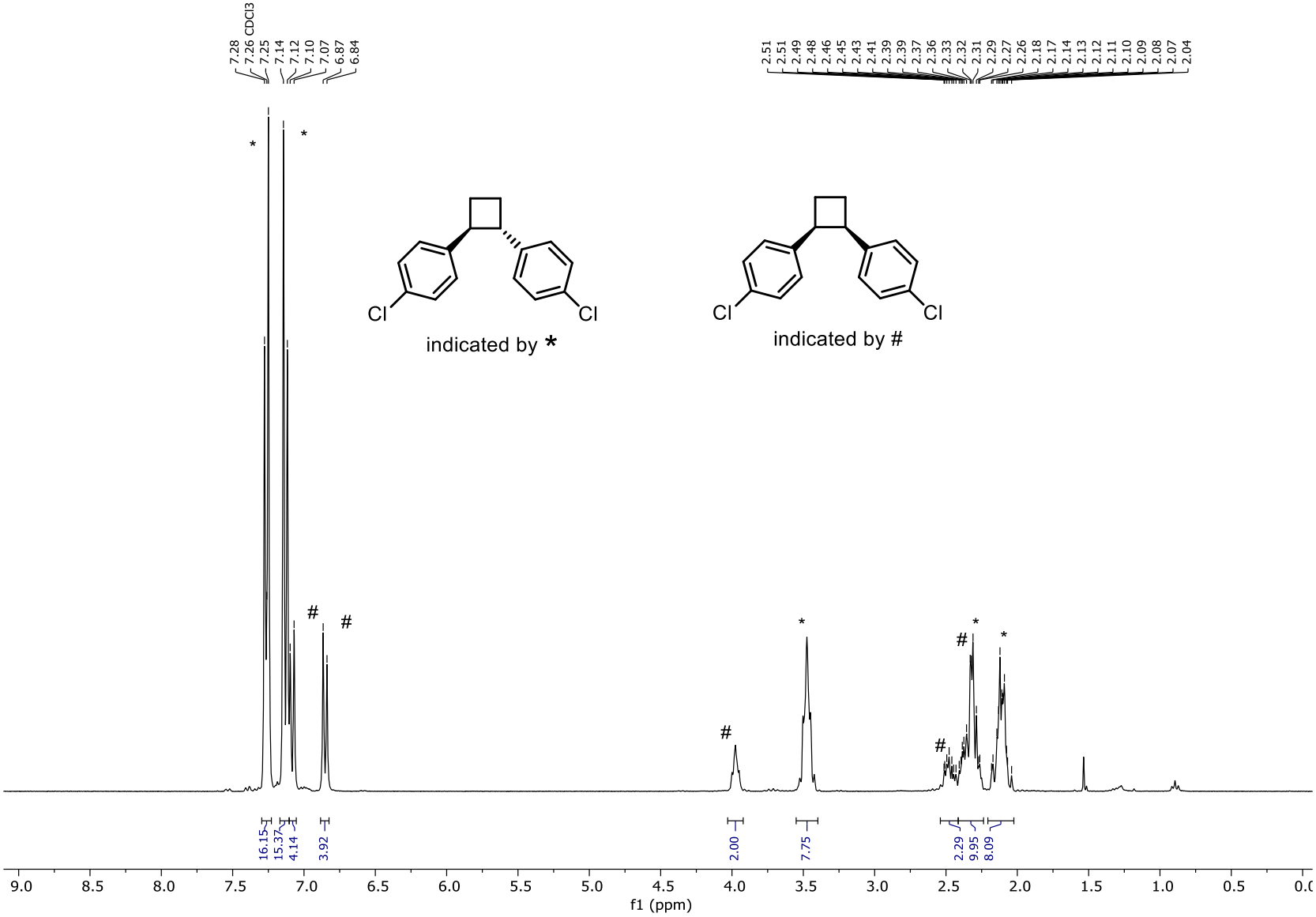
1,2-bis(4-chlorophenyl)cyclobutane (2h-trans): ^{1}H NMR (300 MHz, $CDCl_3$)



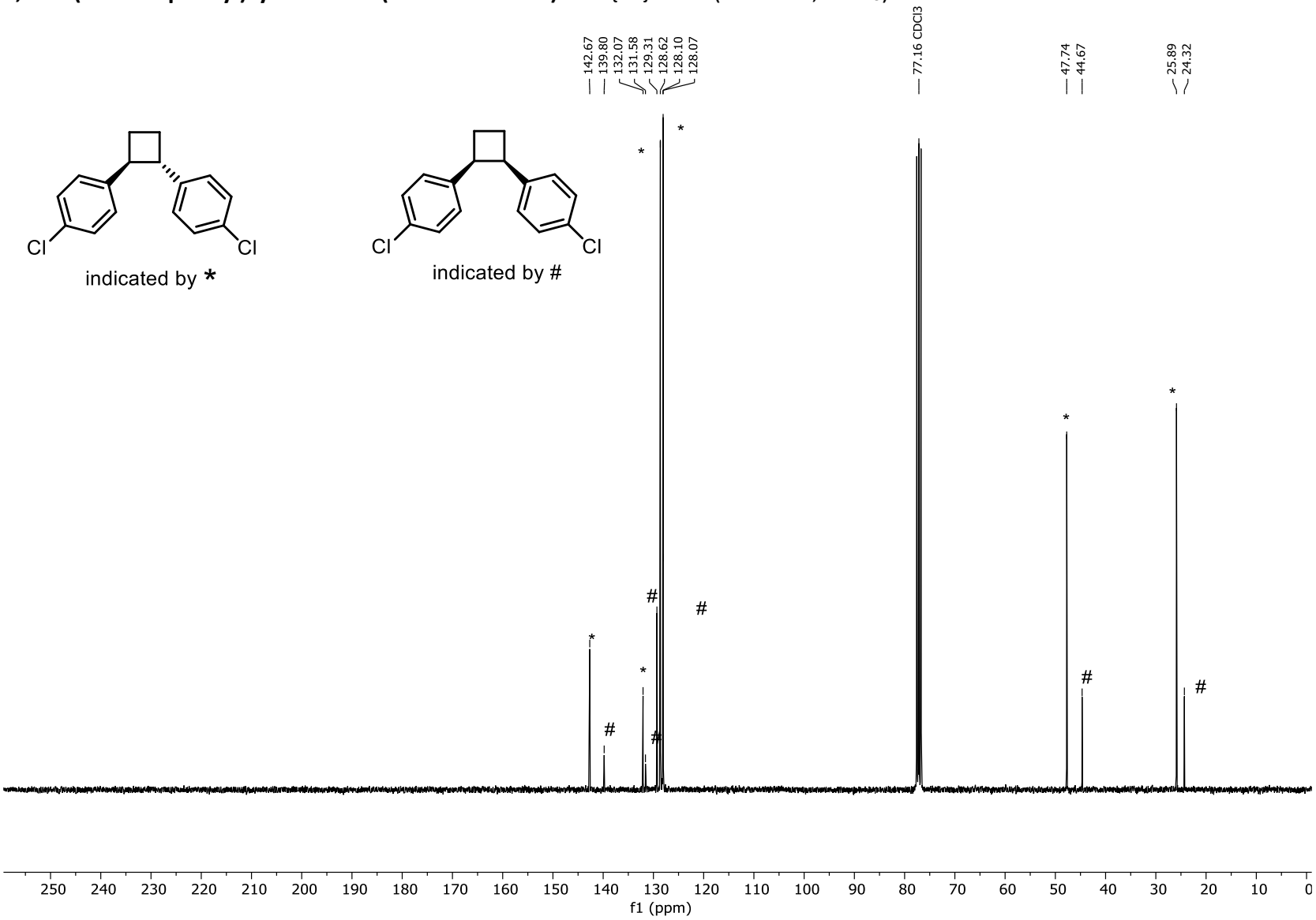
1,2-bis(4-chlorophenyl)cyclobutane (2h-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



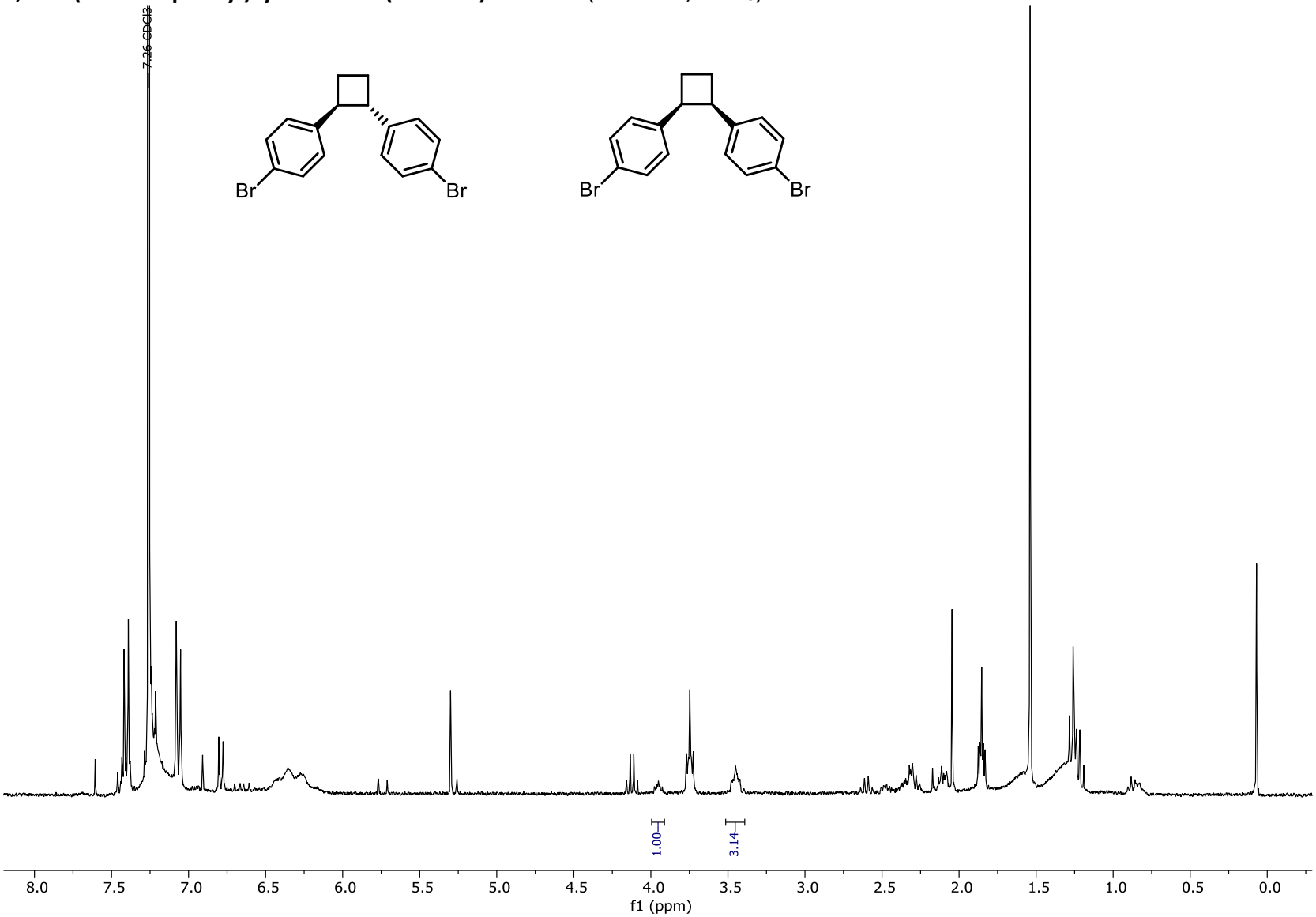
1,2-bis(4-chlorophenyl)cyclobutane (2h-trans+2h-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



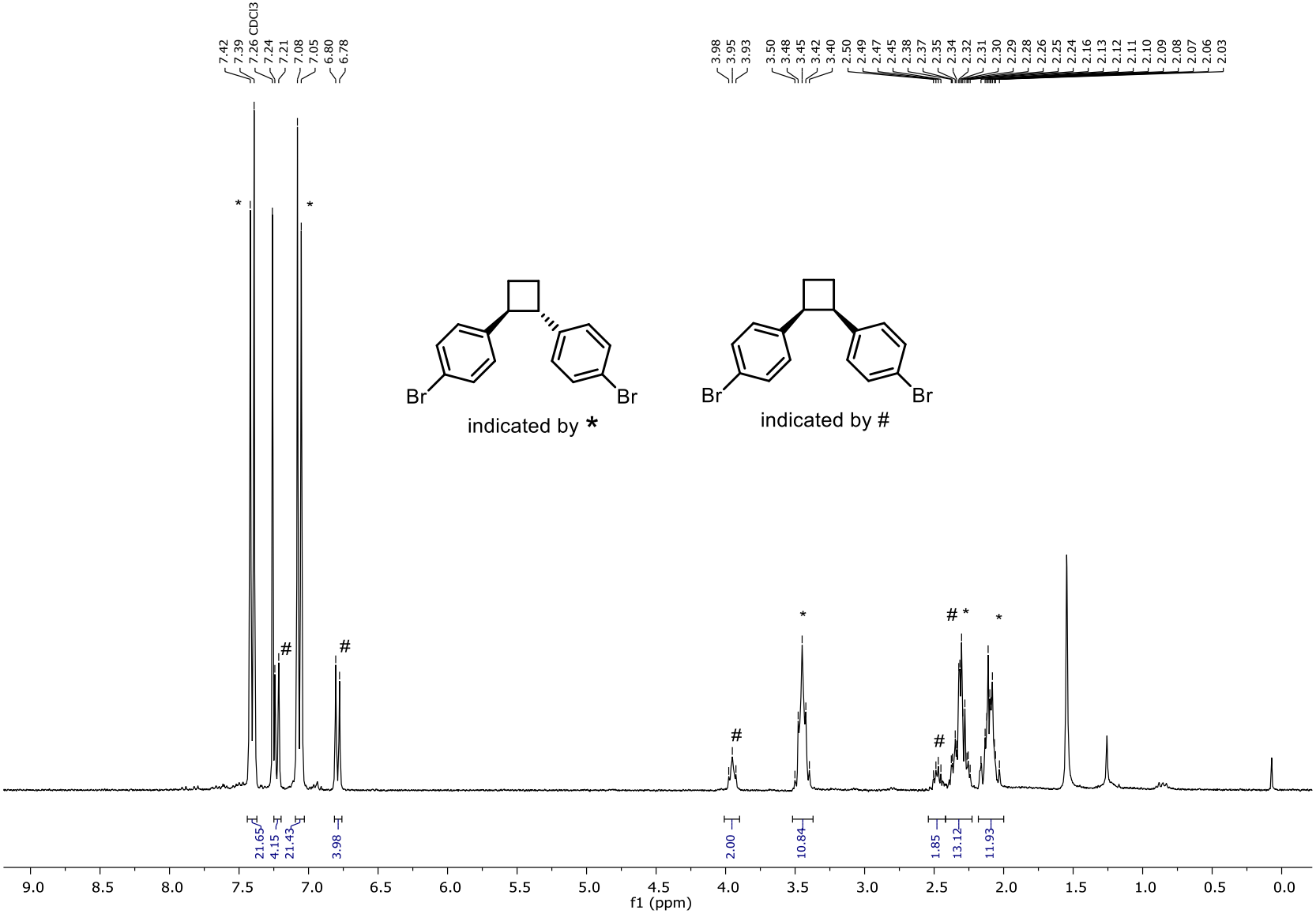
1,2-bis(4-chlorophenyl)cyclobutane (2h-trans+2h-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



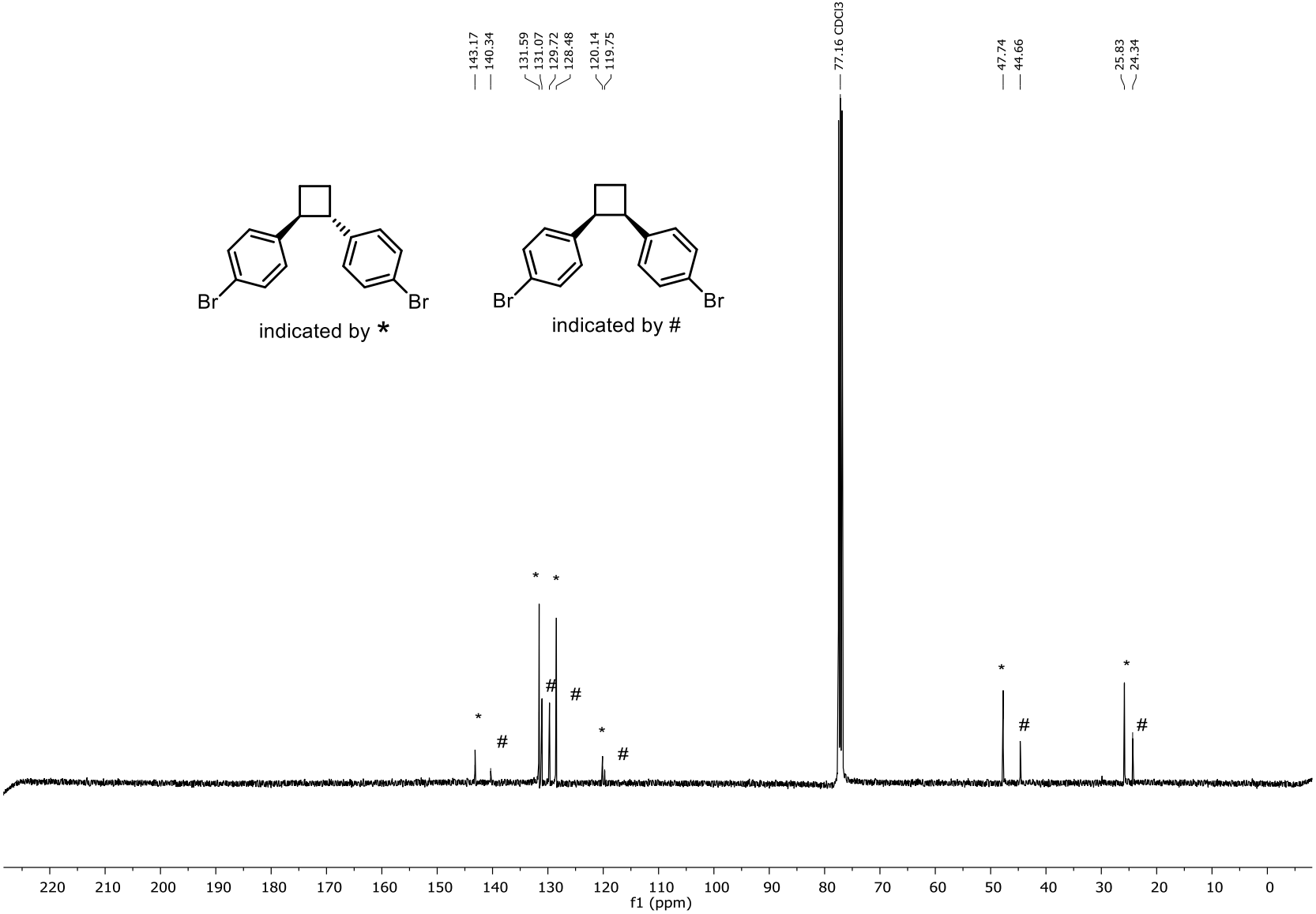
1,2-bis(4-bromophenyl)cyclobutane (2i-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



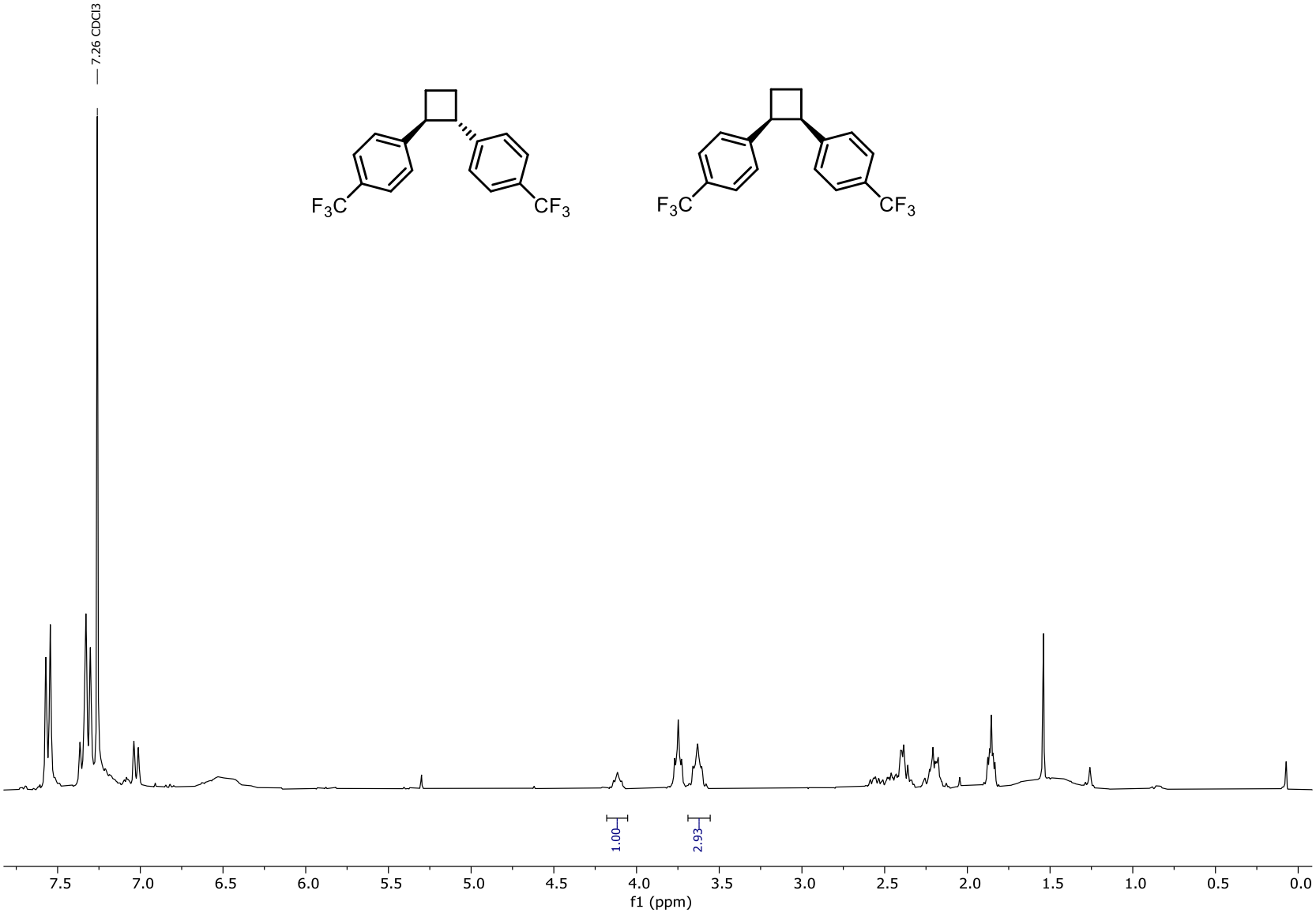
1,2-bis(4-bromophenyl)cyclobutane (2i-trans+2i-cis): ^{1}H NMR (301 MHz, $CDCl_3$)



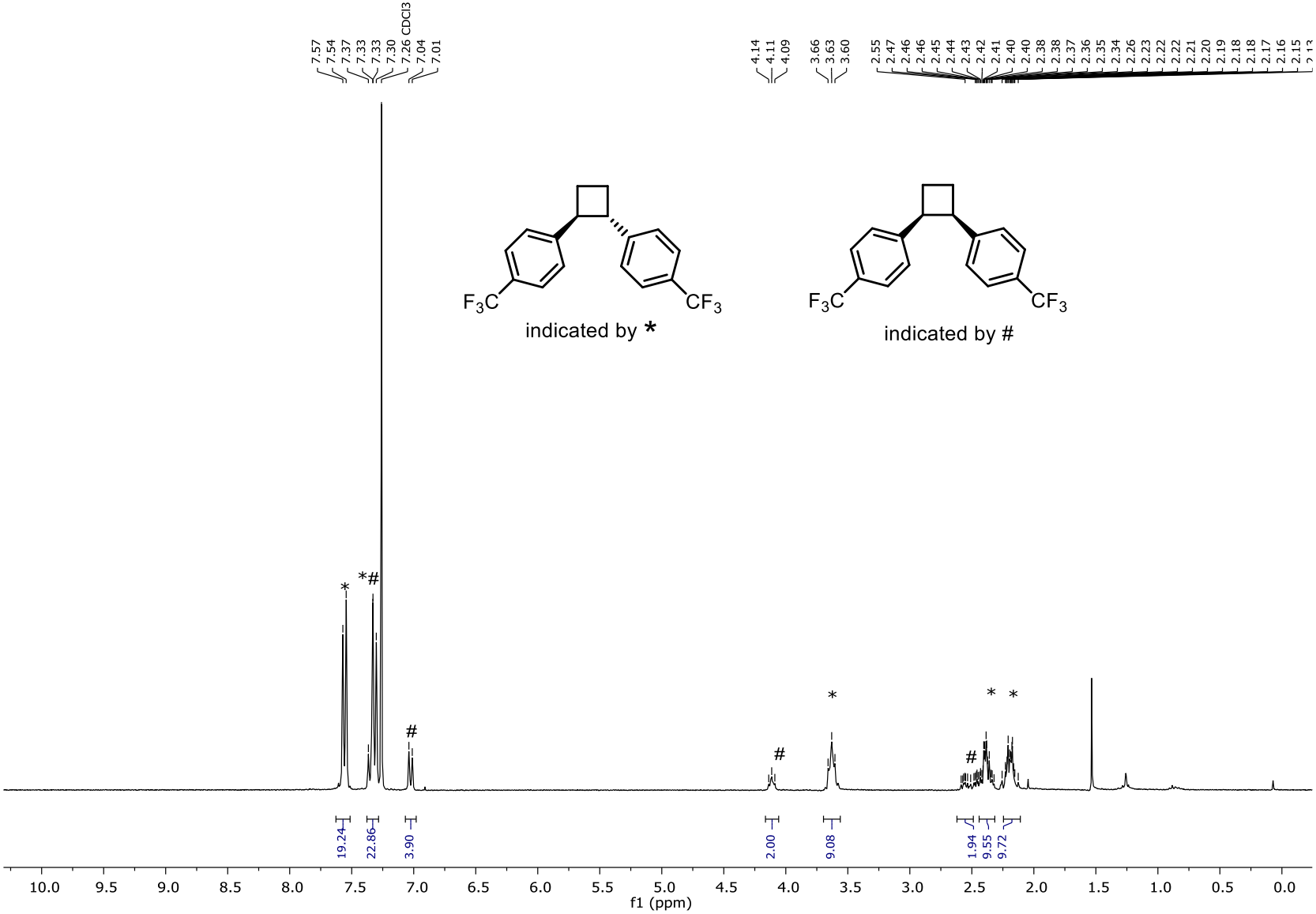
1,2-bis(4-bromophenyl)cyclobutane (2i-trans+2i-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



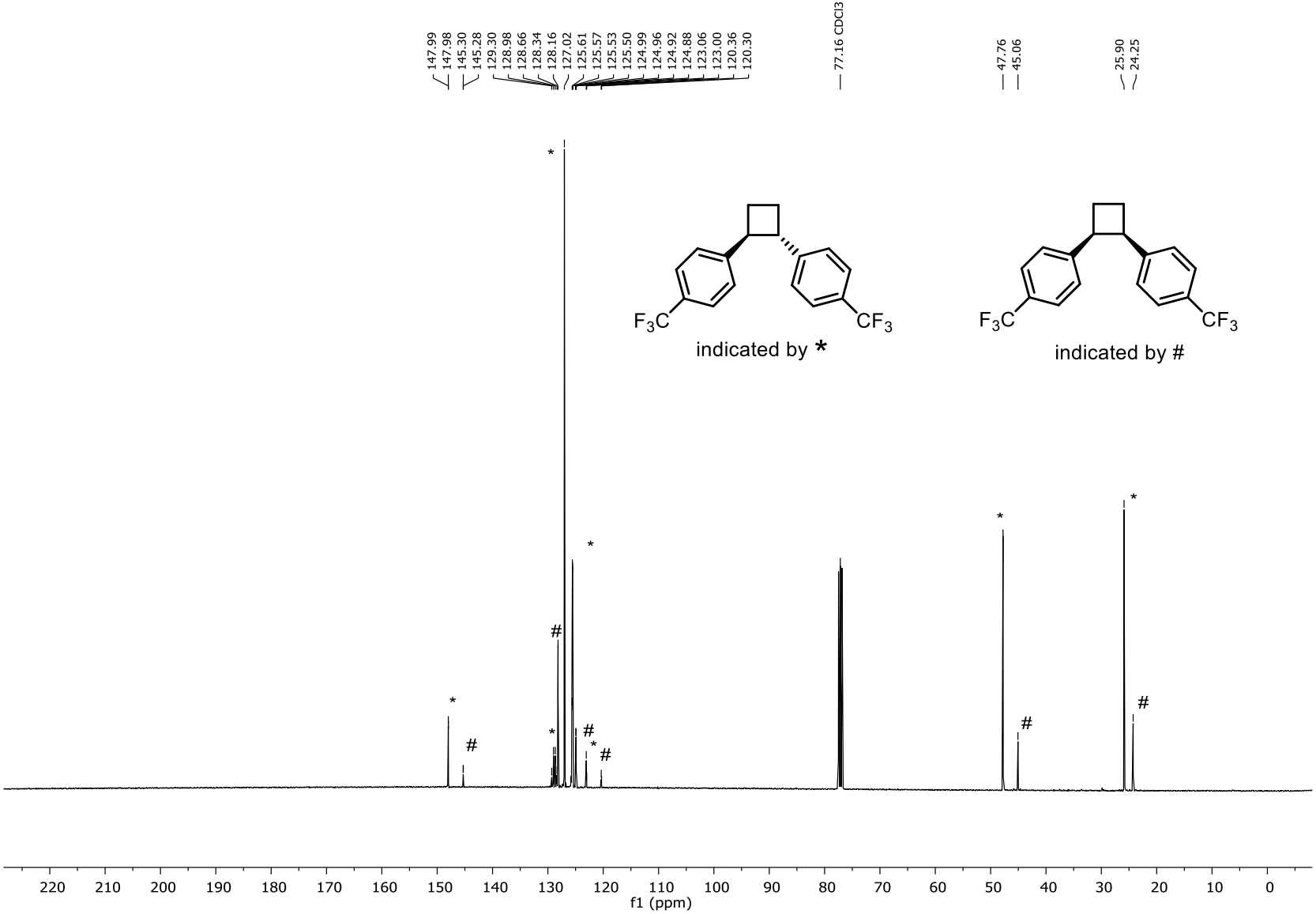
1,2-bis(4-(trifluoromethyl)phenyl)cyclobutane (2j-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



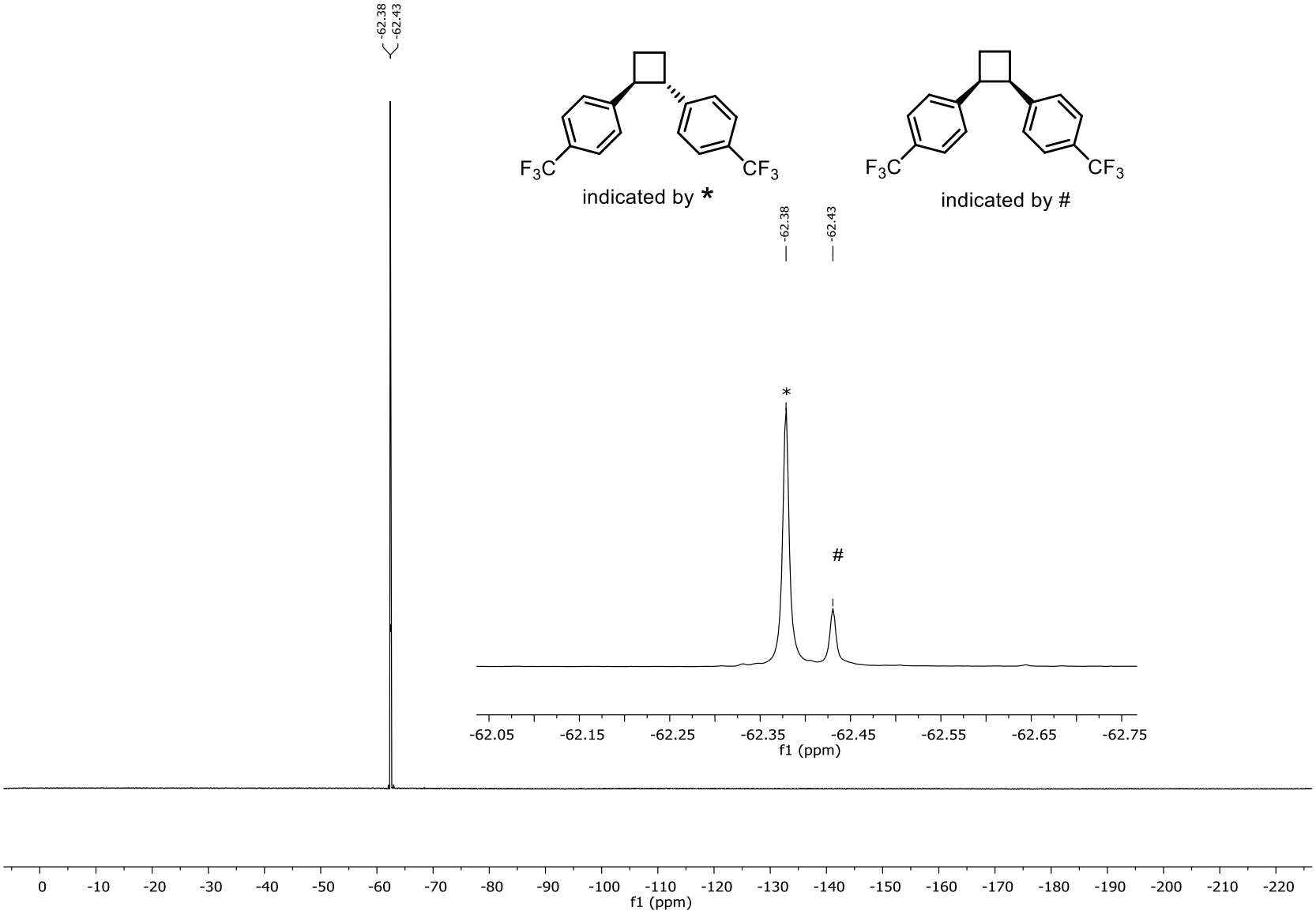
1,2-bis(4-(trifluoromethyl)phenyl)cyclobutane (2j-trans+2j-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



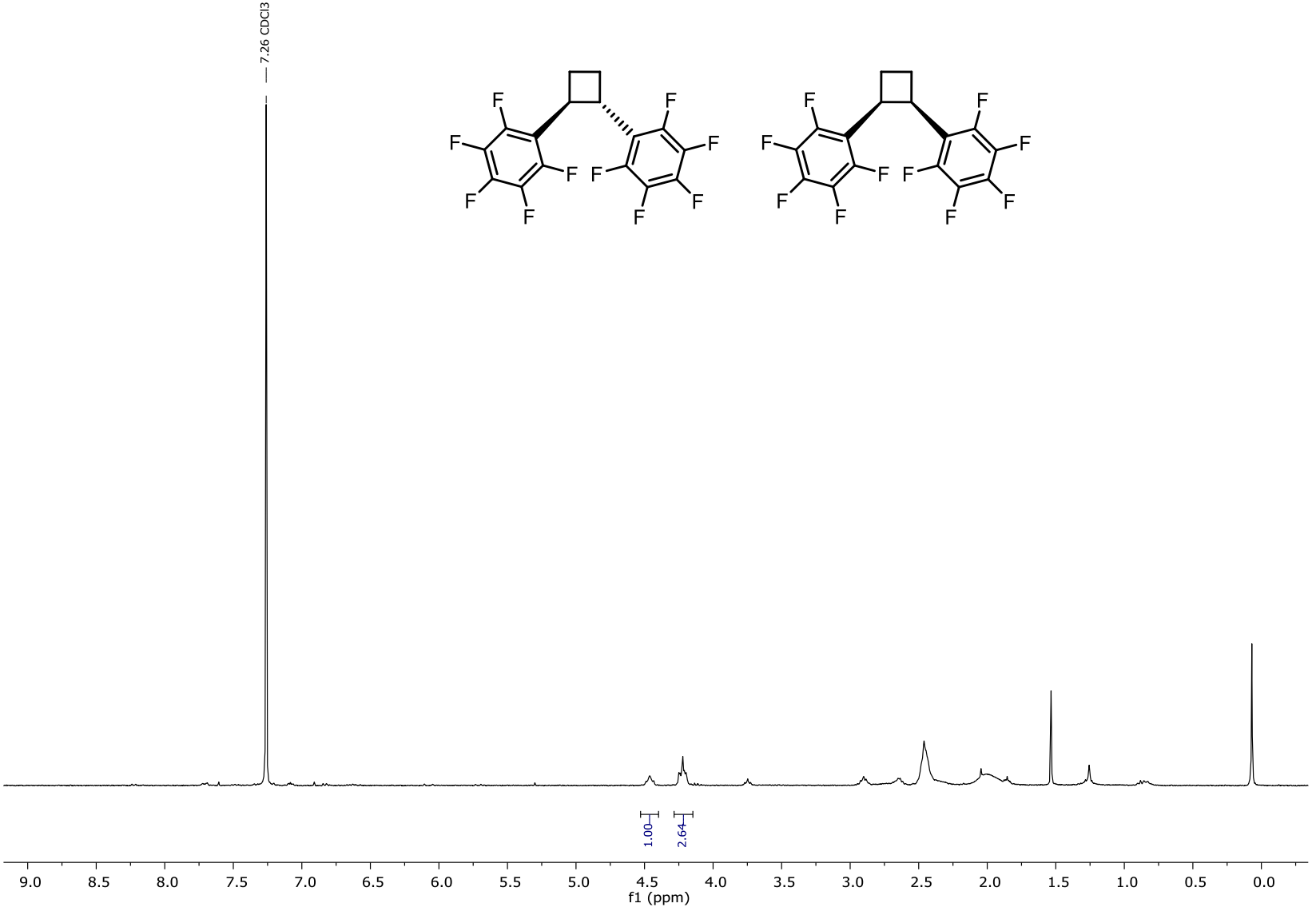
1,2-bis(4-(trifluoromethyl)phenyl)cyclobutane (2j-trans+2j-cis): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



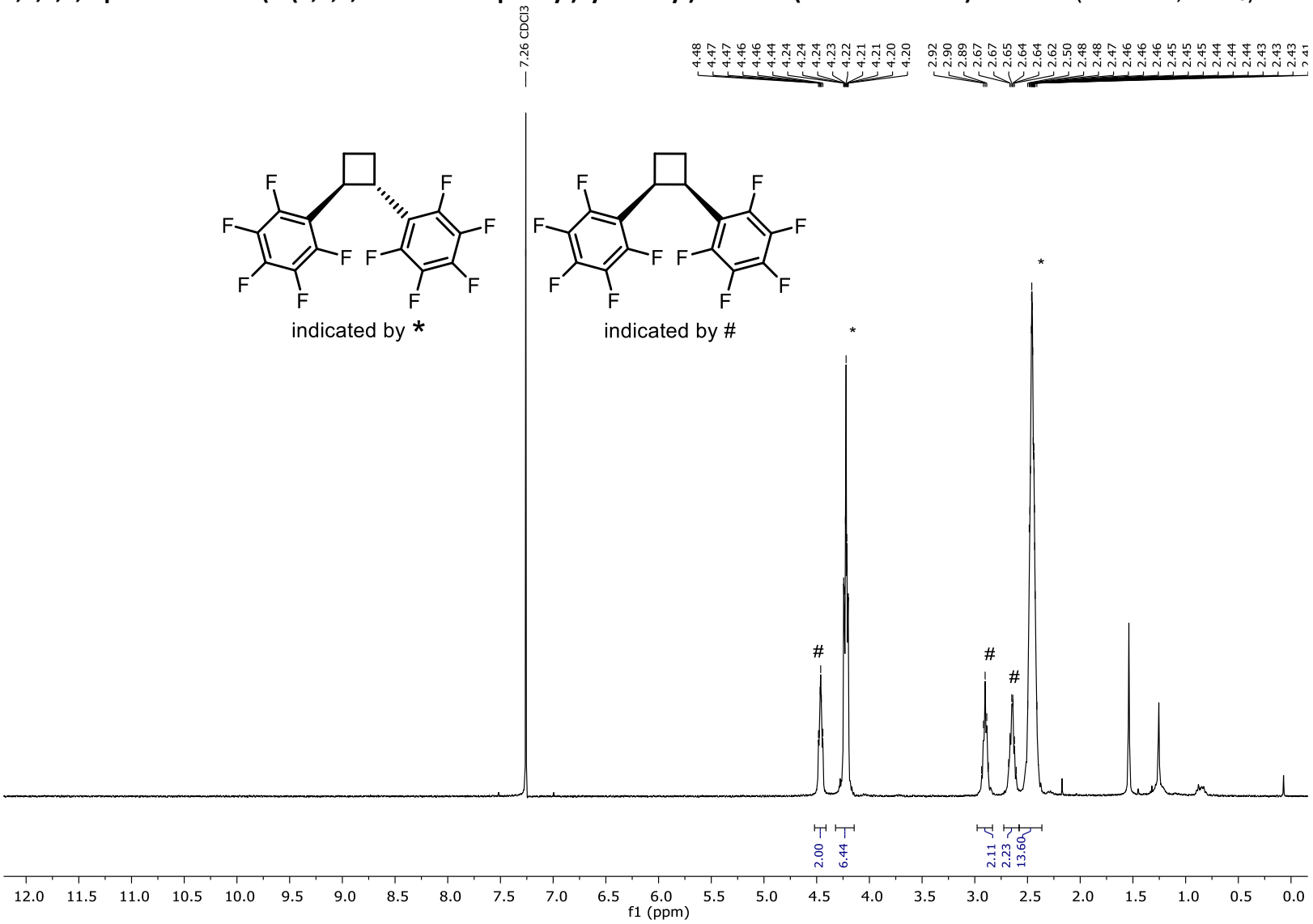
1,2-bis(4-(trifluoromethyl)phenyl)cyclobutane (2j-trans+2j-cis): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



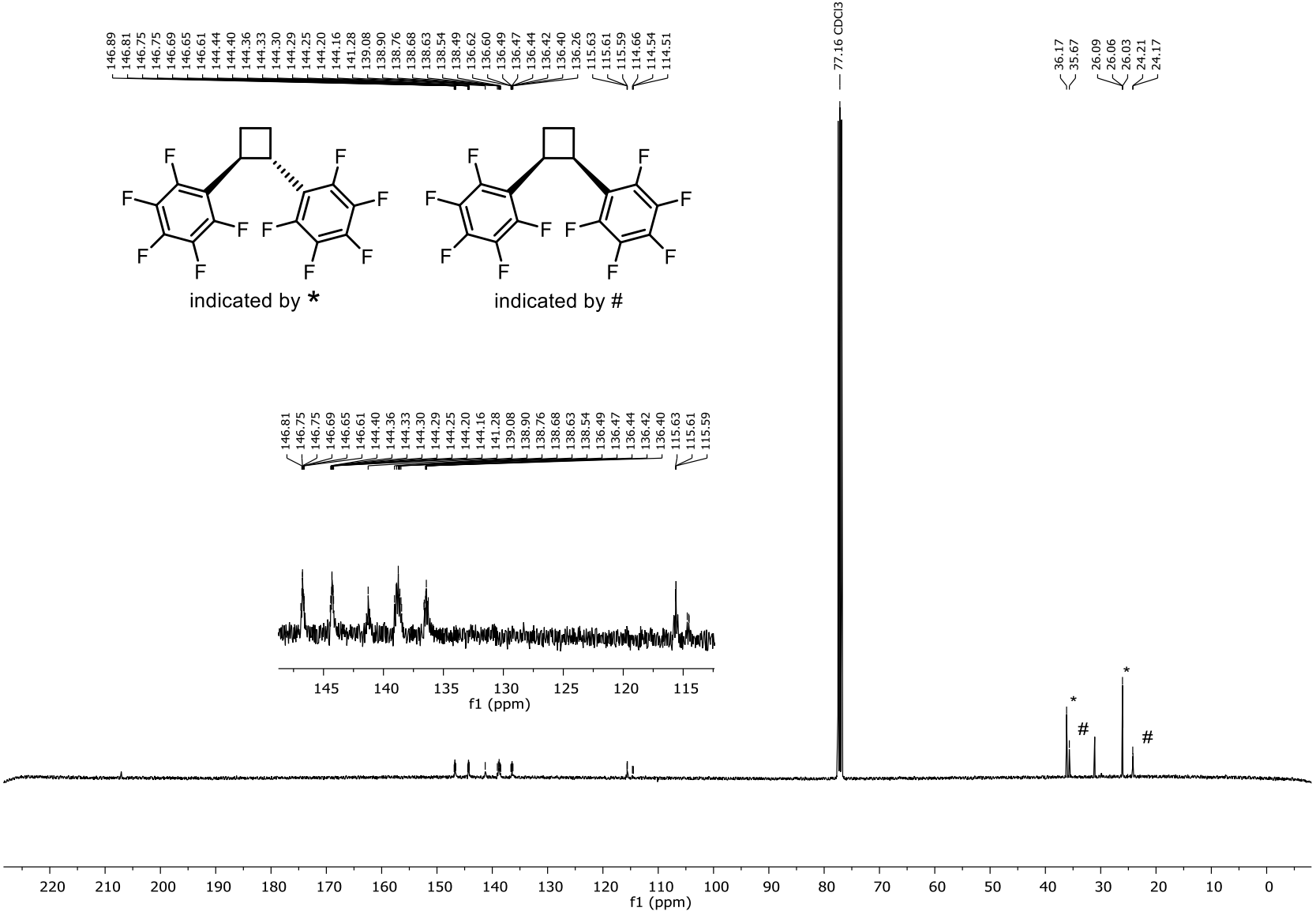
1,2,3,4,5-pentafluoro-6-(2-(2,3,5,6-tetrafluorophenyl)cyclobutyl)benzene (2k-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



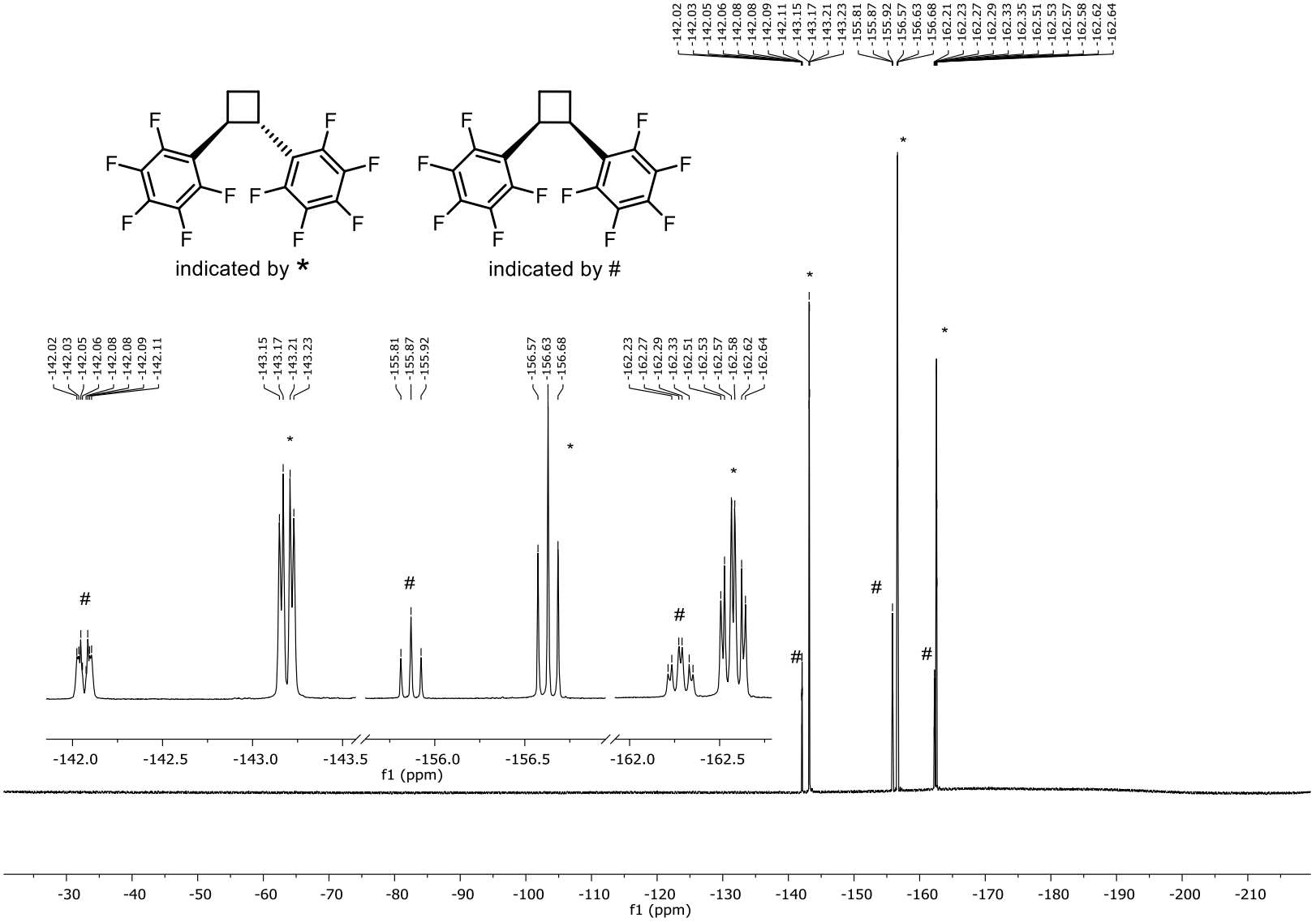
1,2,3,4,5-pentafluoro-6-(2-(2,3,5,6-tetrafluorophenyl)cyclobutyl)benzene (2k-trans+2k-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



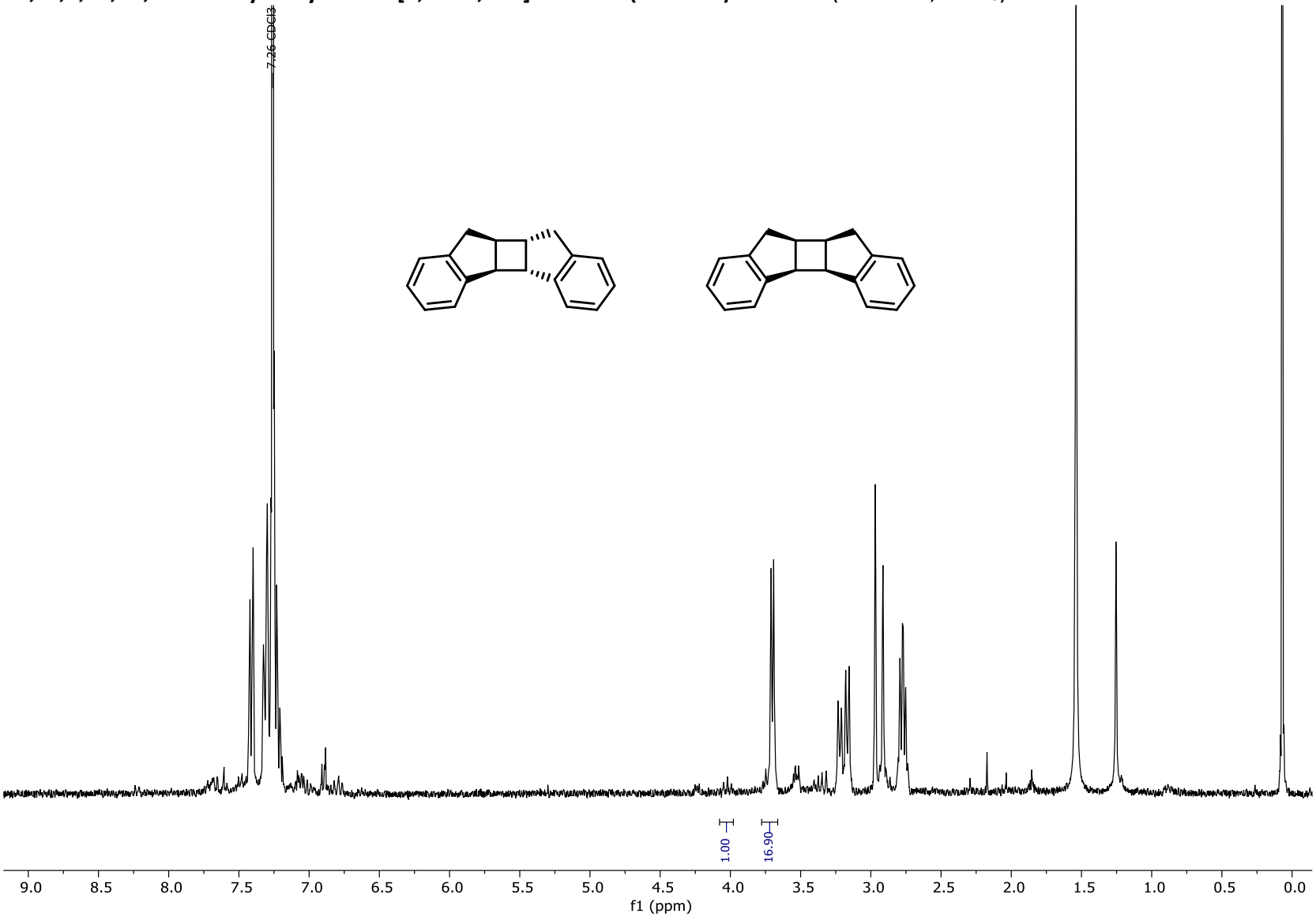
1,2,3,4,5-pentafluoro-6-(2-(2,3,5,6-tetrafluorophenyl)cyclobutyl)benzene (2k-trans+2k-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



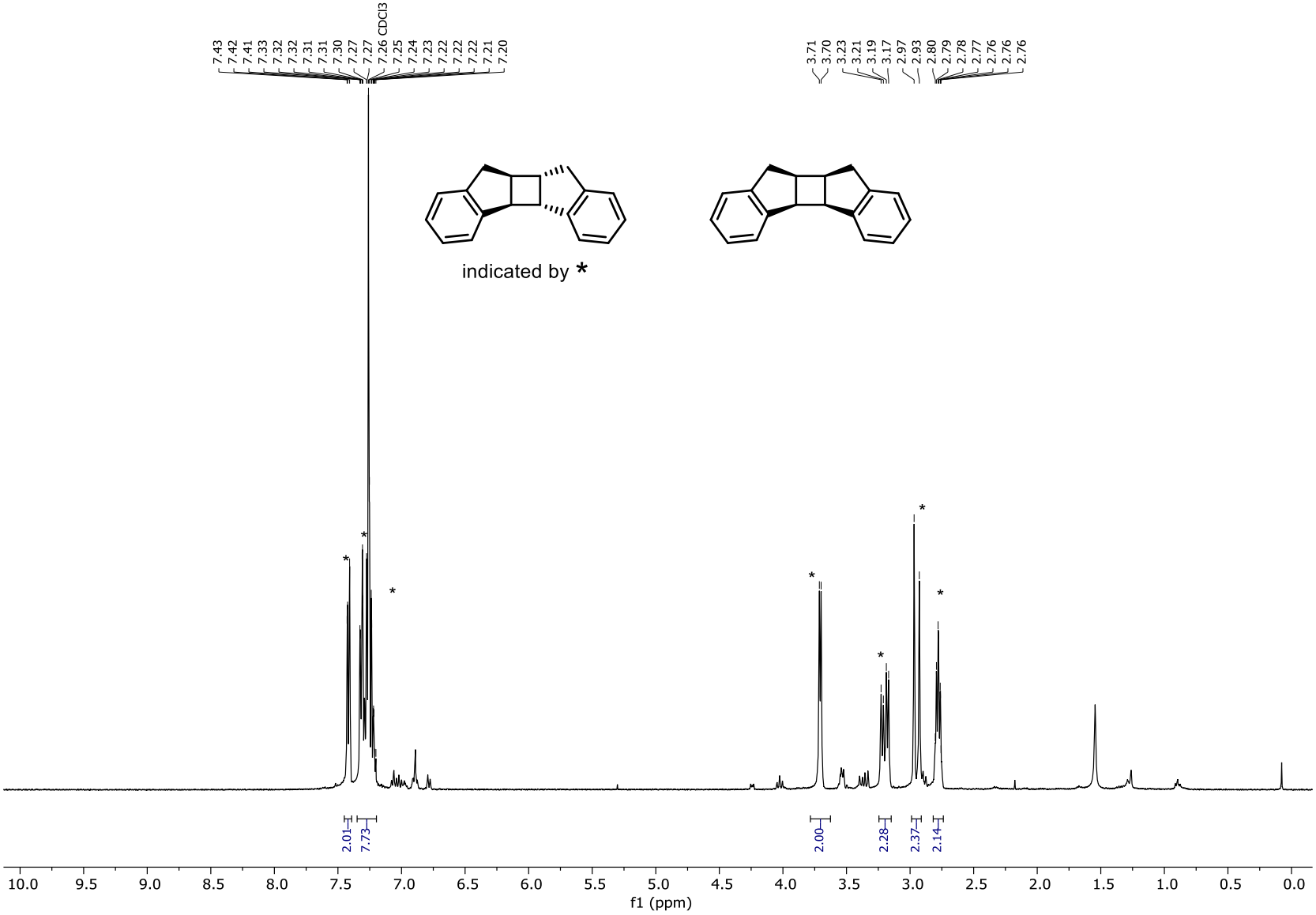
1,2,3,4,5-pentafluoro-6-(2-(2,3,5,6-tetrafluorophenyl)cyclobutyl)benzene (2k-trans+2k-cis): ^{19}F NMR (376 MHz, CDCl3)



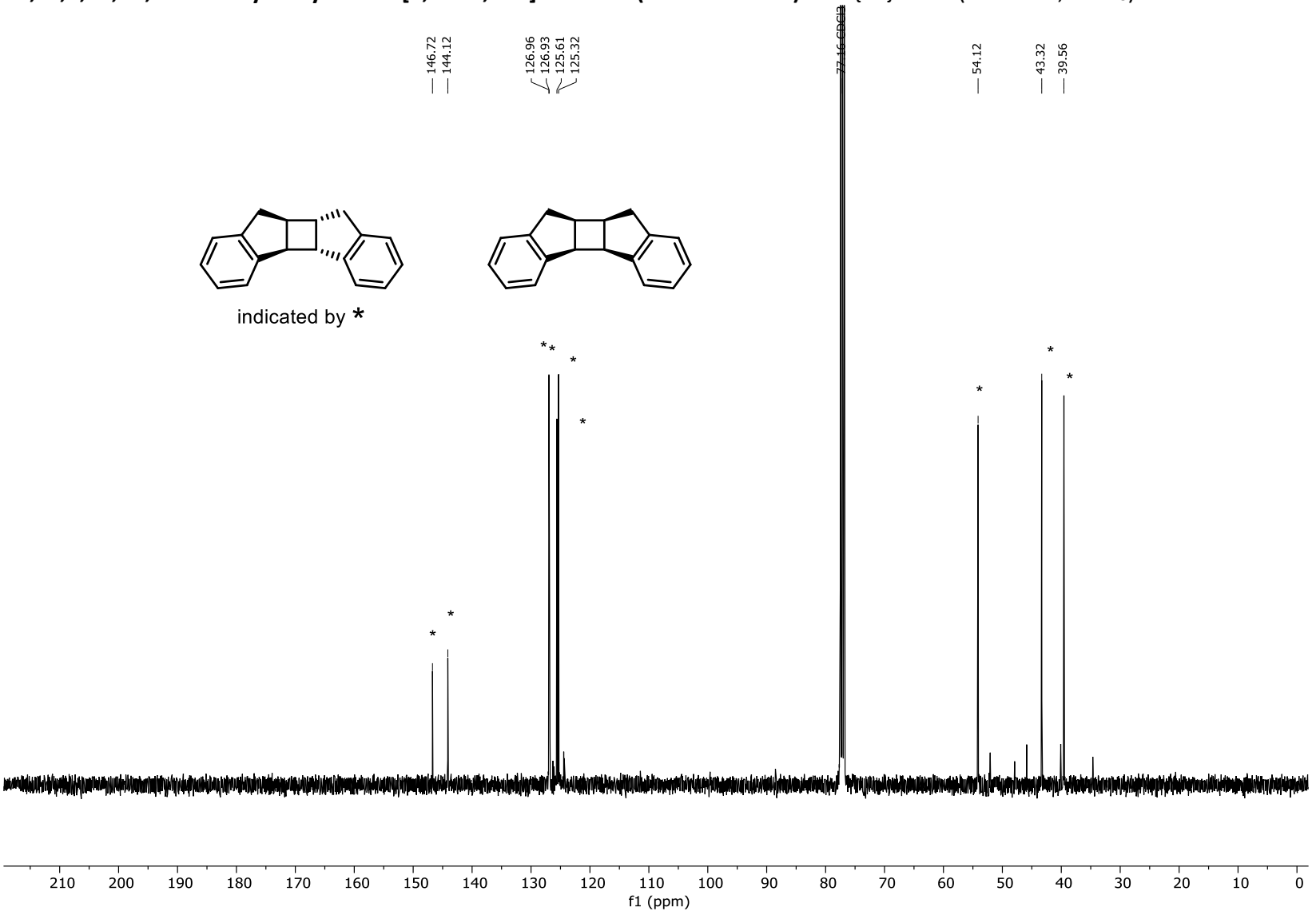
4b,4c,9,9a,9b,10-hexahydrocyclobuta[1,2-a:4,3-a']diindene (2l-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



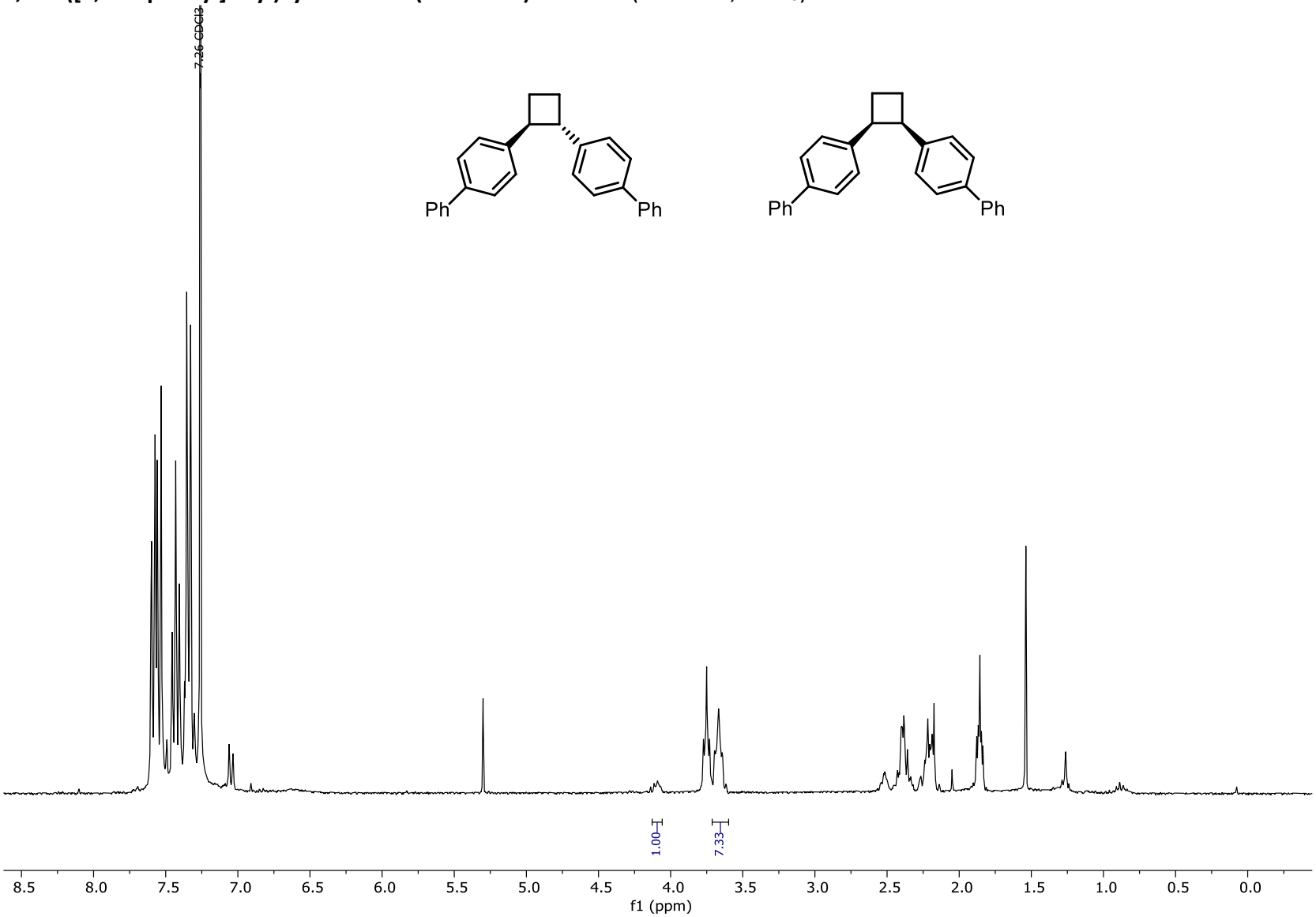
4b,4c,9,9a,9b,10-hexahydrocyclobuta[1,2-a:4,3-a']diindene (2l-trans+2l-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



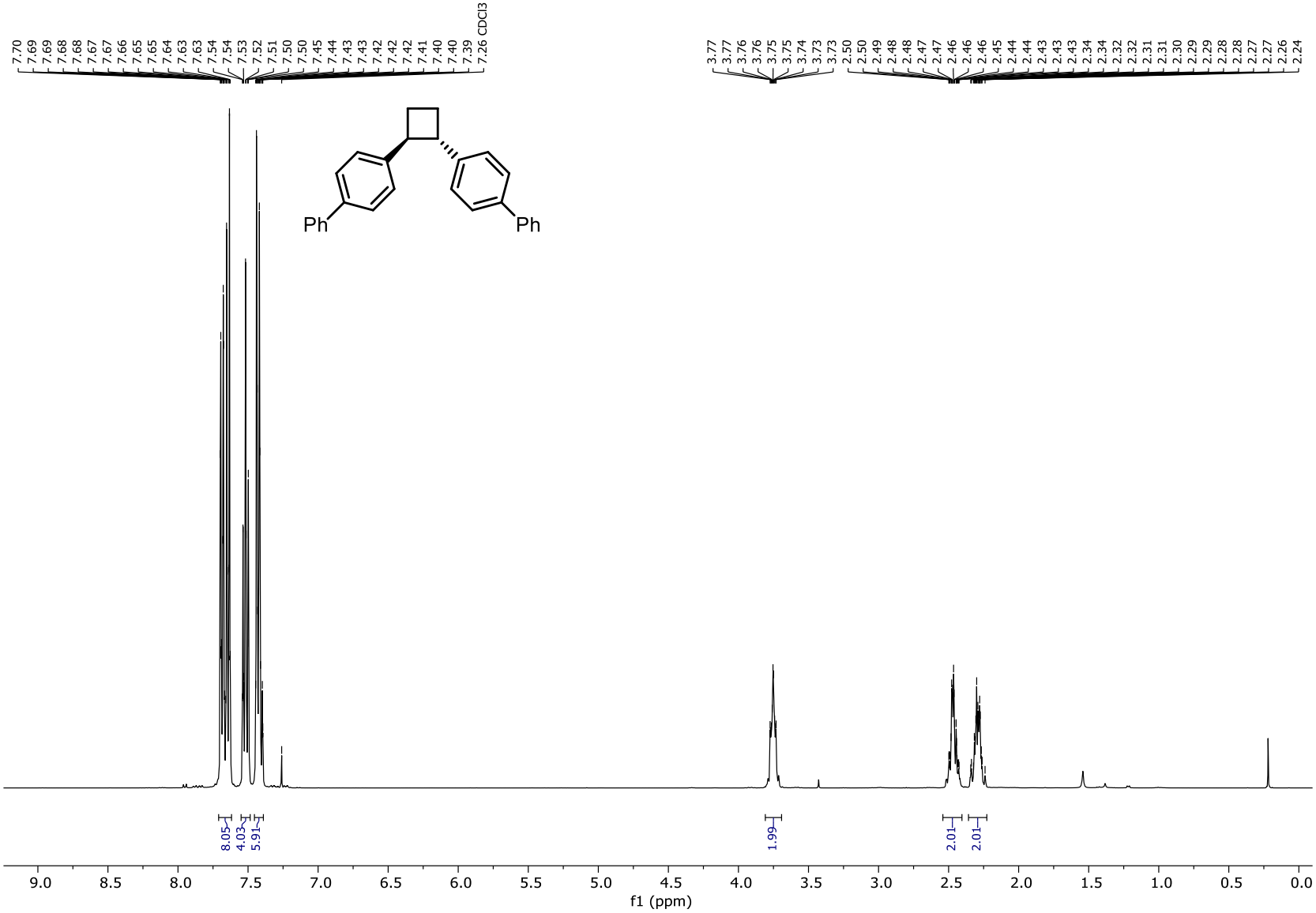
4b,4c,9,9a,9b,10-hexahydrocyclobuta[1,2-a:4,3-a']diindene (2l-trans+2l-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



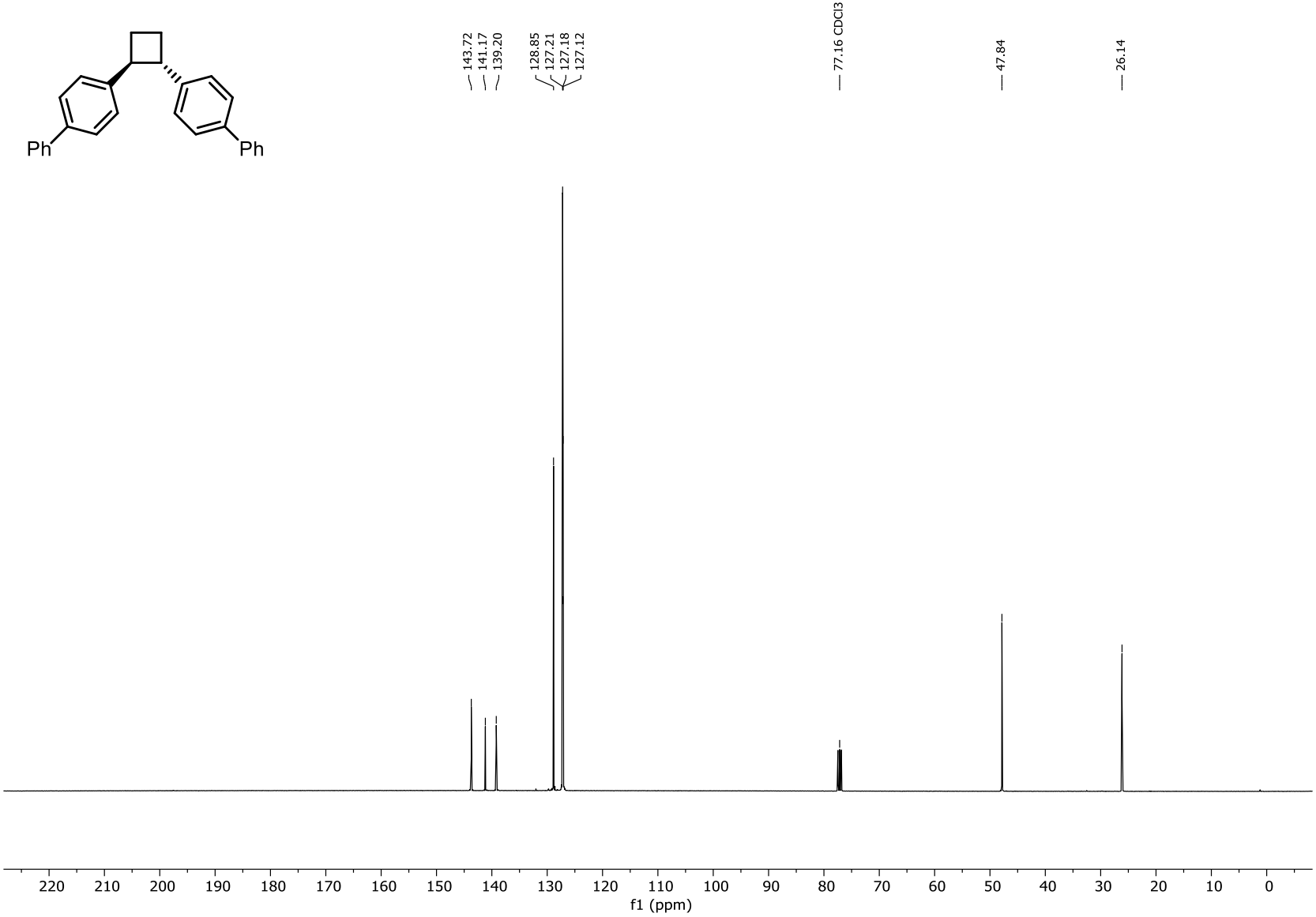
1,2-Di([1,1'-biphenyl]-4-yl)cyclobutane (2m-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



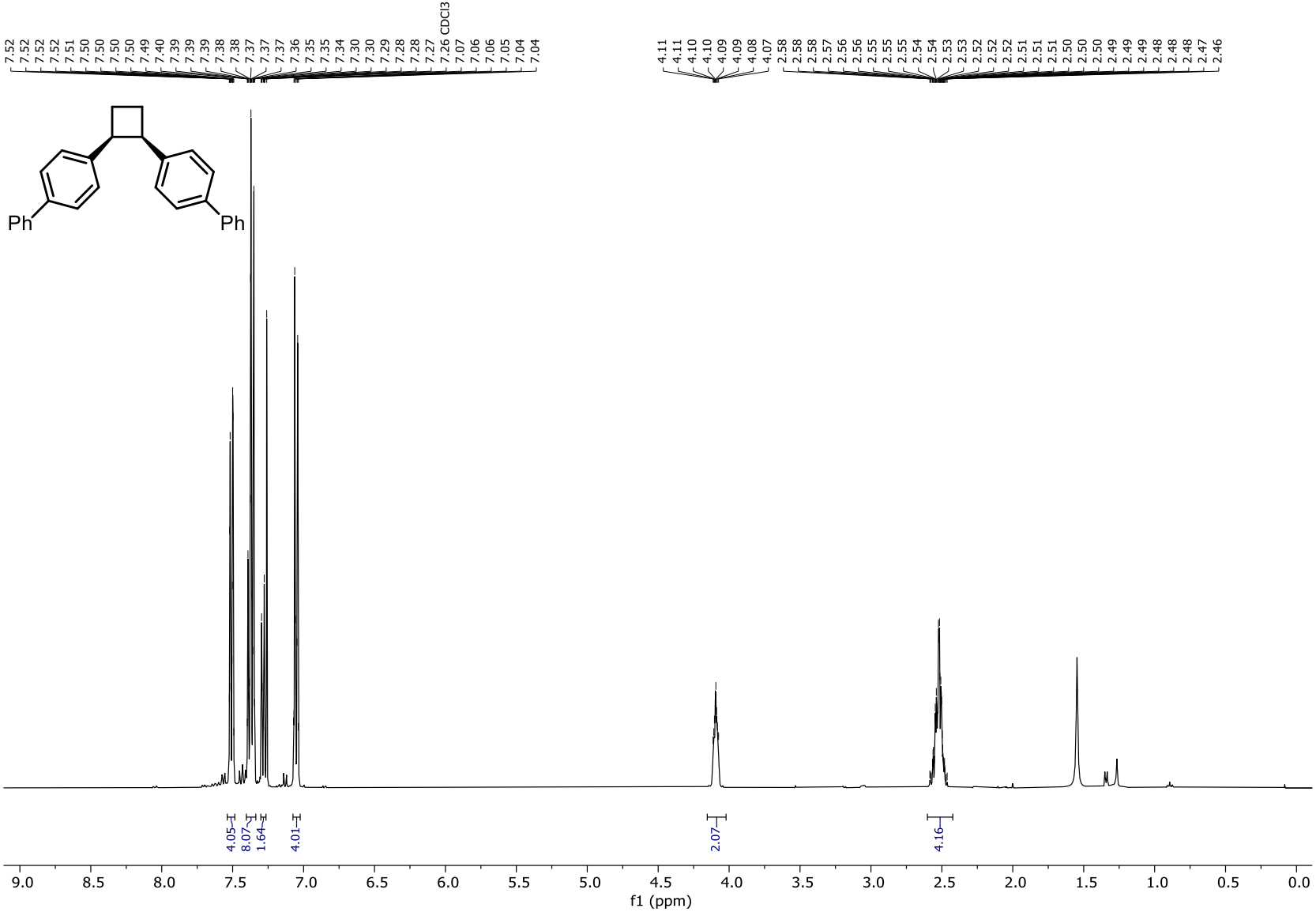
1,2-Di([1,1'-biphenyl]-4-yl)cyclobutane (2m-trans): ^{1}H NMR (400 MHz, $CDCl_3$)



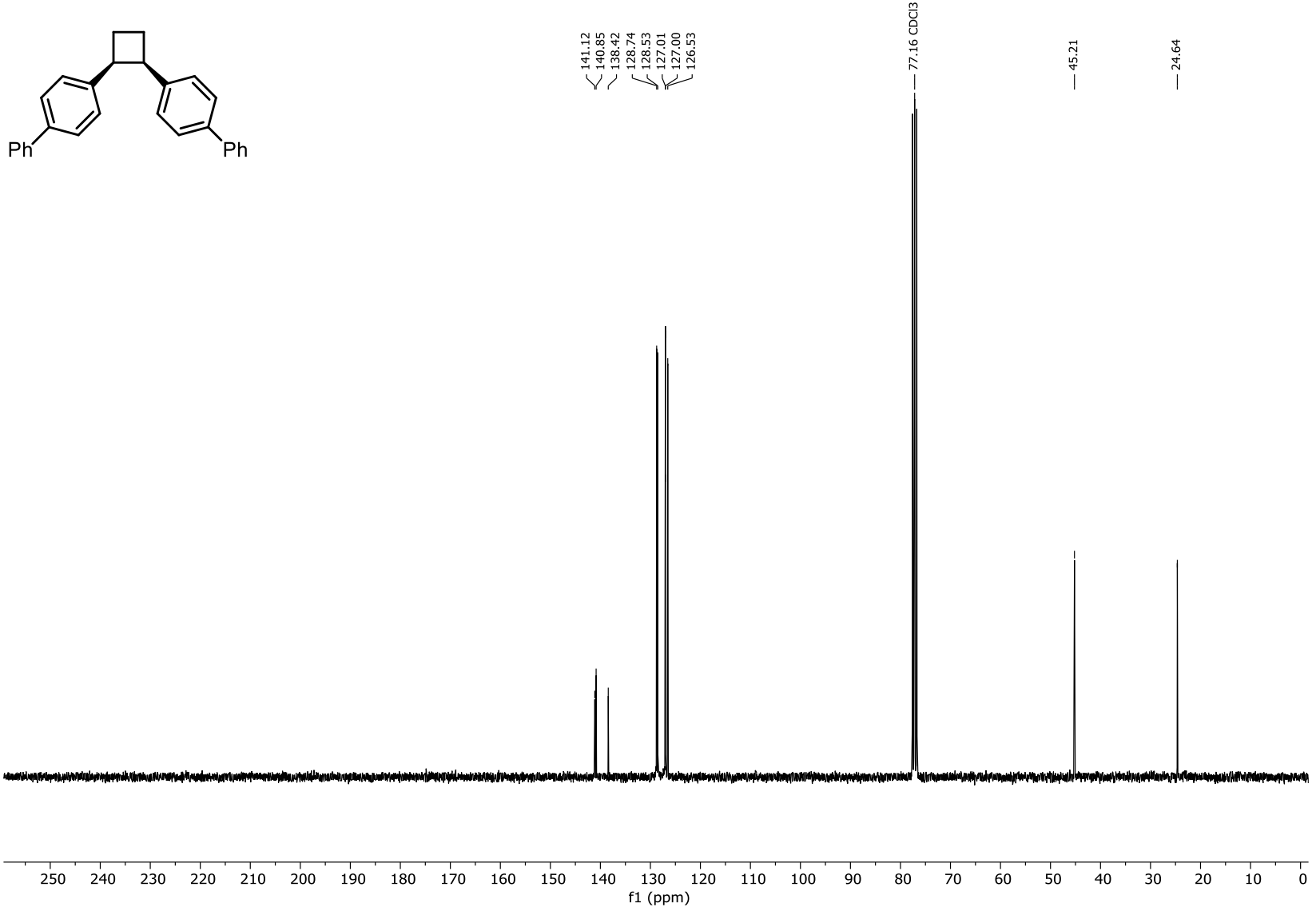
1,2-Di([1,1'-biphenyl]-4-yl)cyclobutane (2m-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



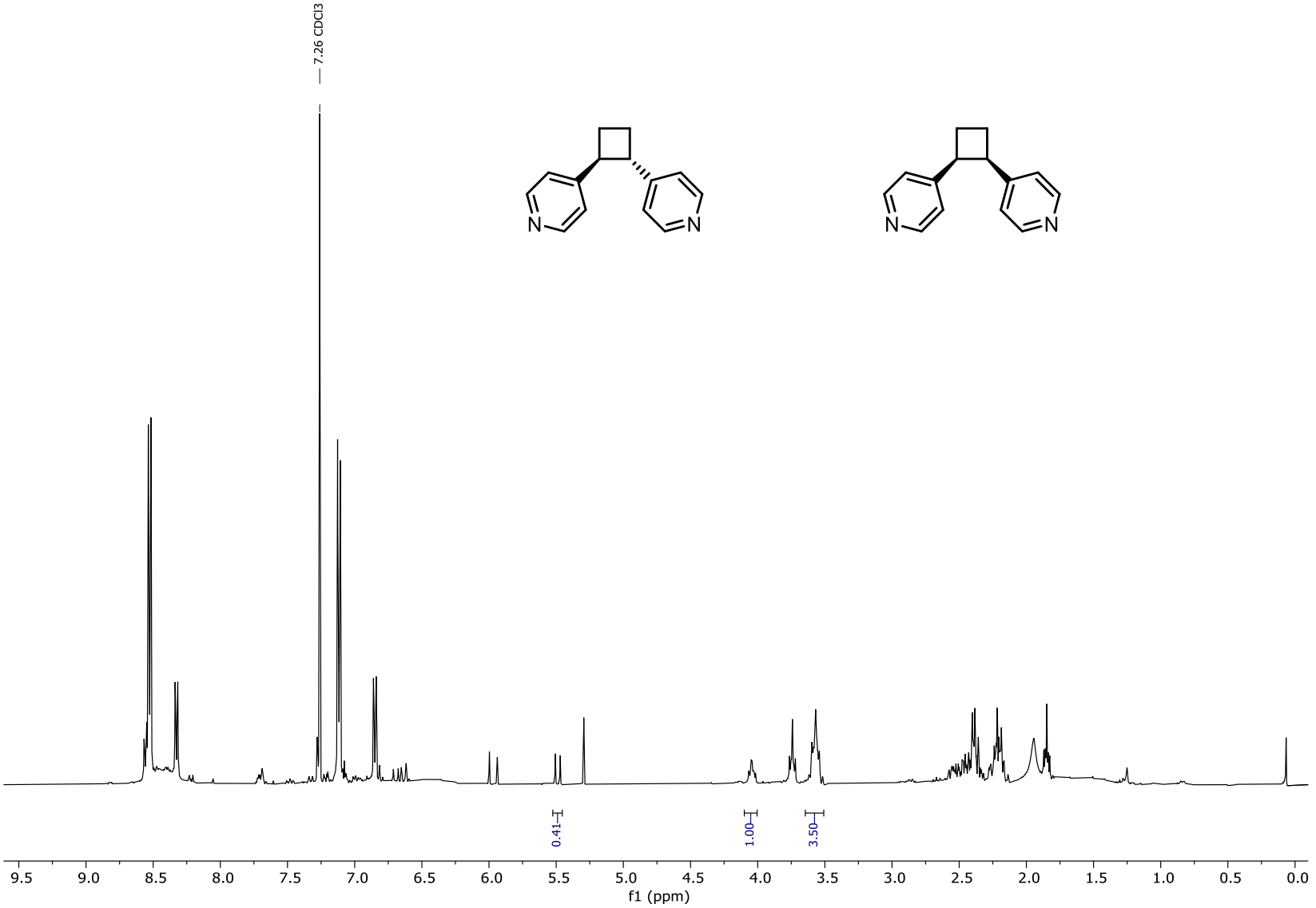
1,2-Di([1,1'-biphenyl]-4-yl)cyclobutane (2m-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



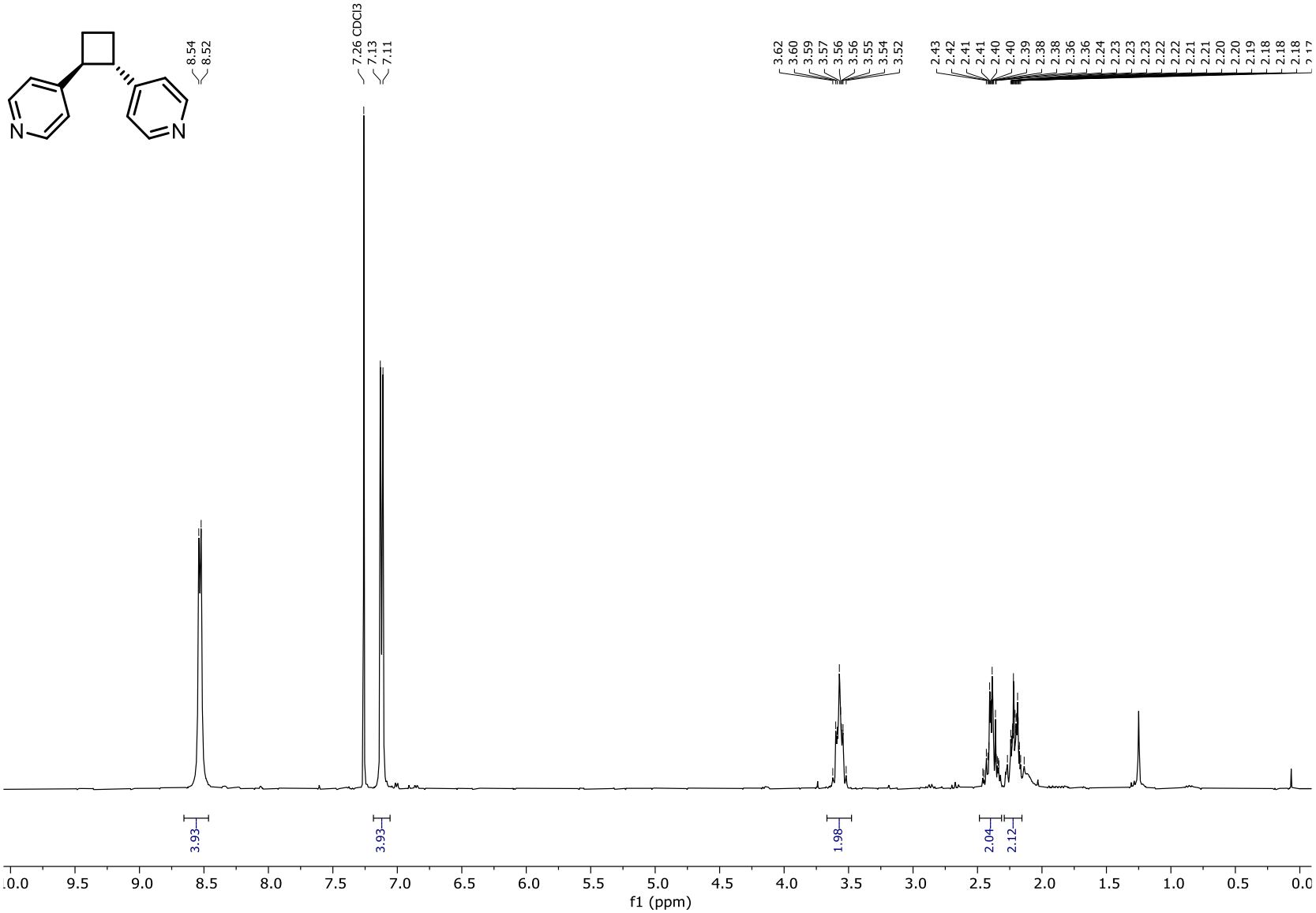
1,2-Di([1,1'-biphenyl]-4-yl)cyclobutane (2m-cis): 13C{^{1}H} NMR (75 MHz, $CDCl_3$)



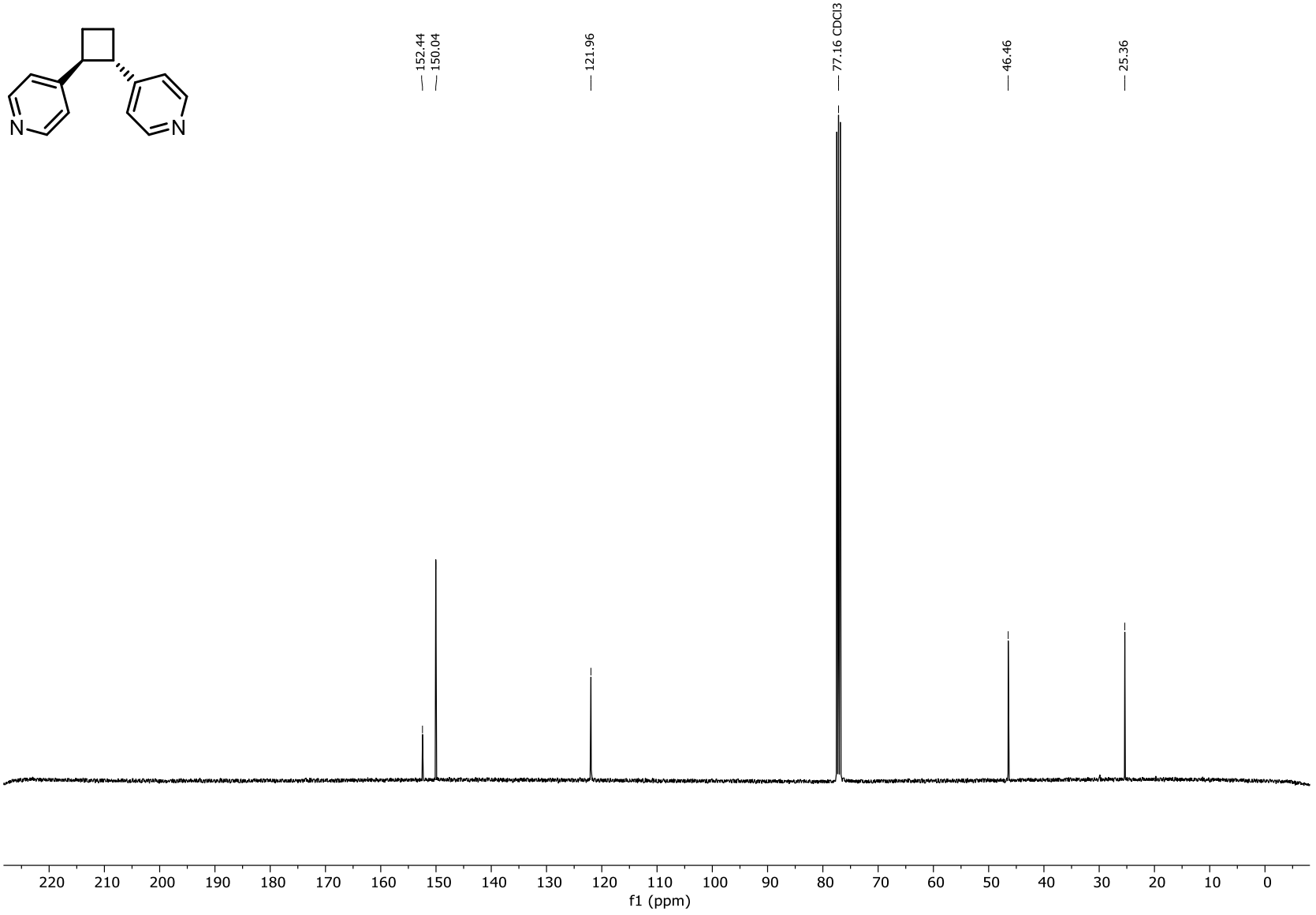
1,2-di(pyridin-4-yl)cyclobutane (2n-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



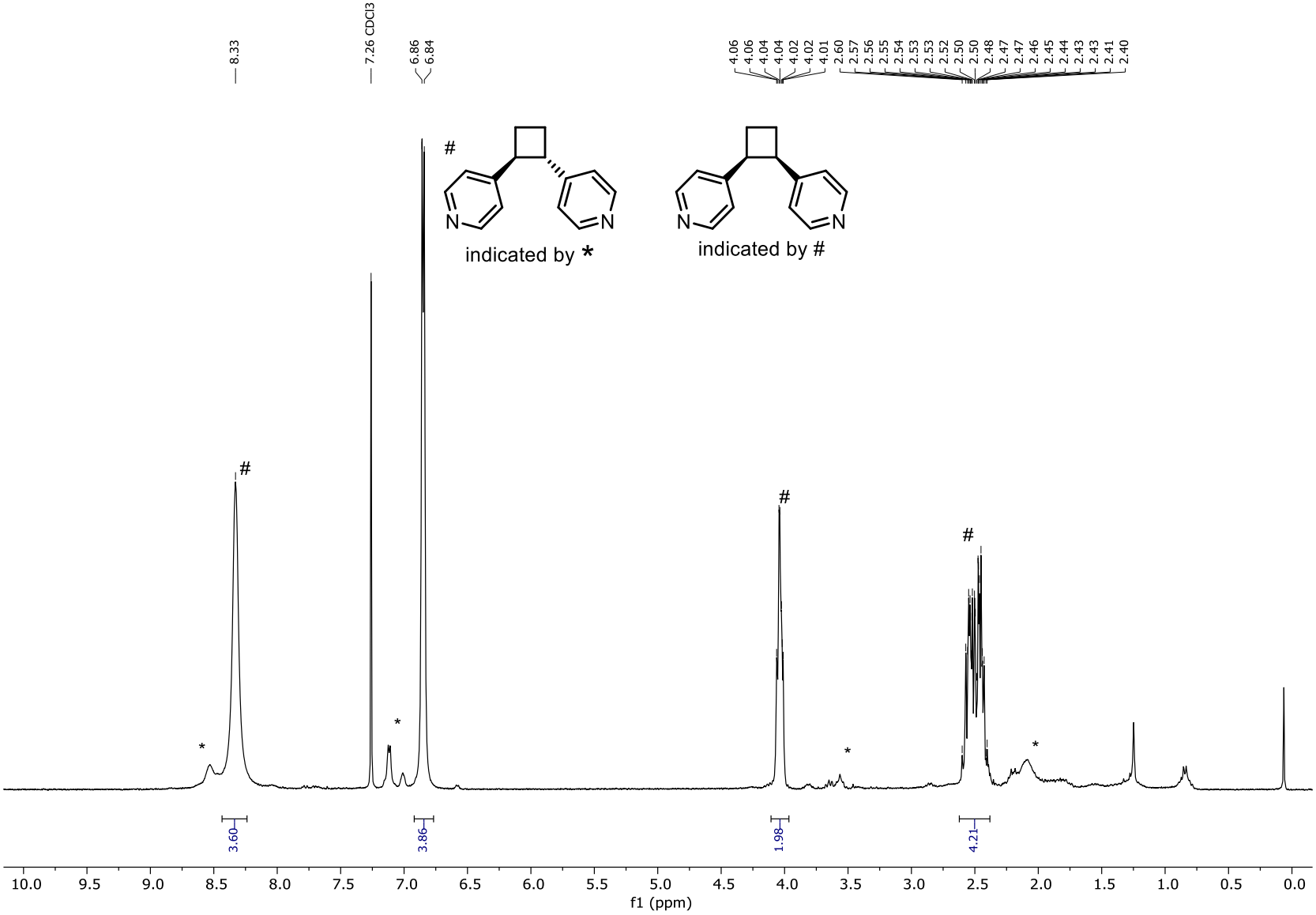
1,2-di(pyridin-4-yl)cyclobutane (2n-trans): ^{1}H NMR (300 MHz, $CDCl_3$)



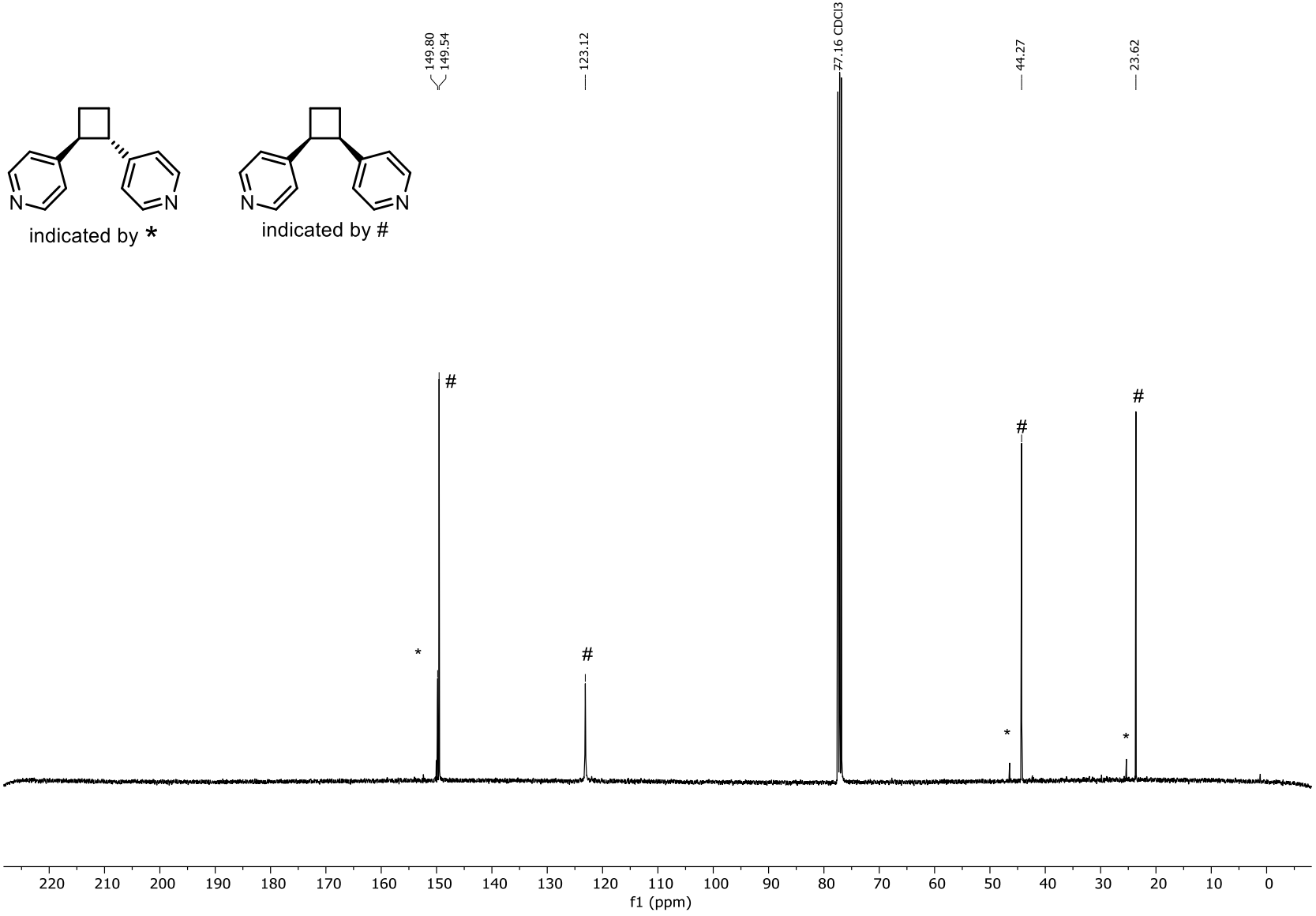
1,2-di(pyridin-4-yl)cyclobutane (2n-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



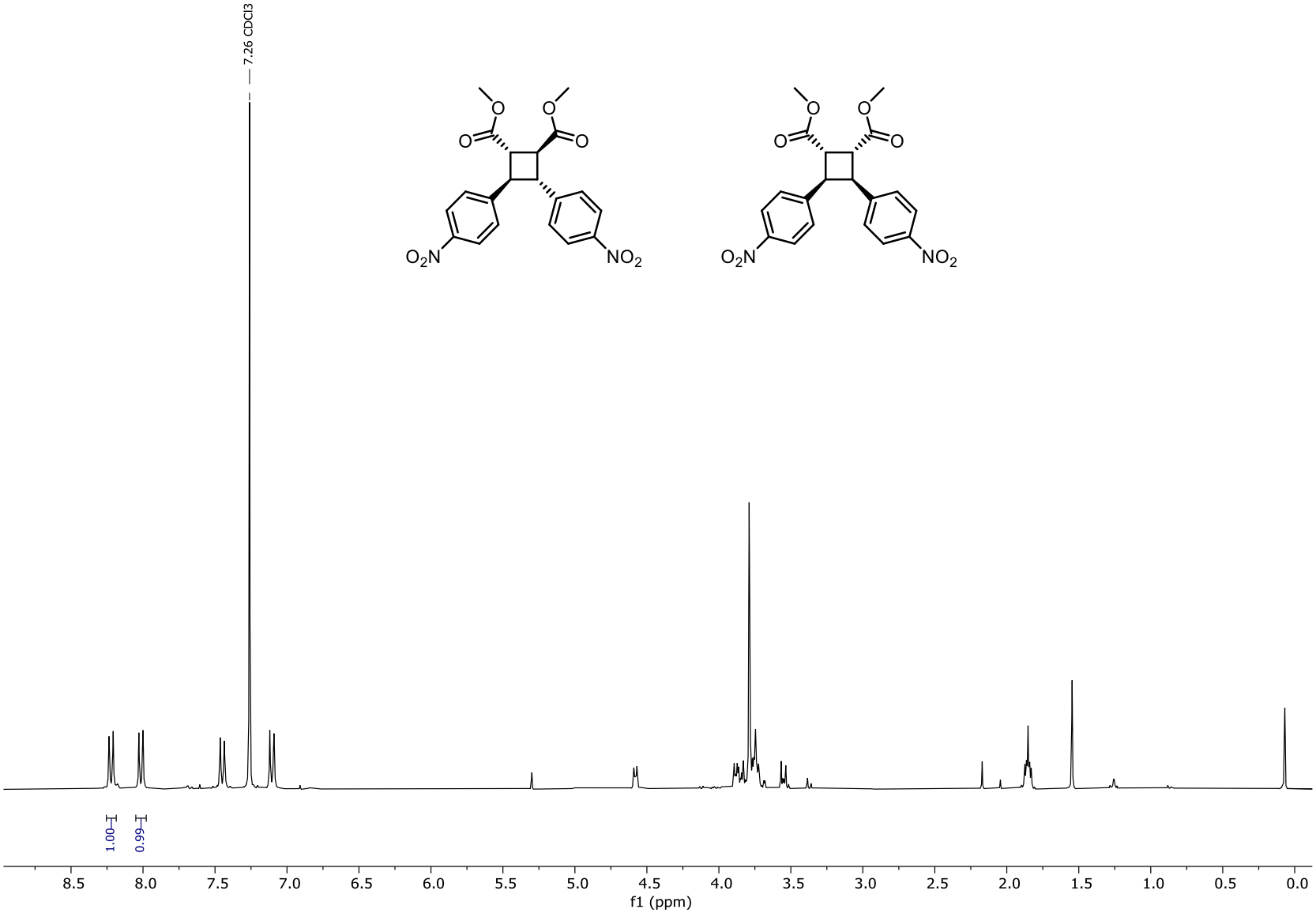
1,2-di(pyridin-4-yl)cyclobutane (2n-cis+2n-trans): ^{1}H NMR (300 MHz, $CDCl_3$)



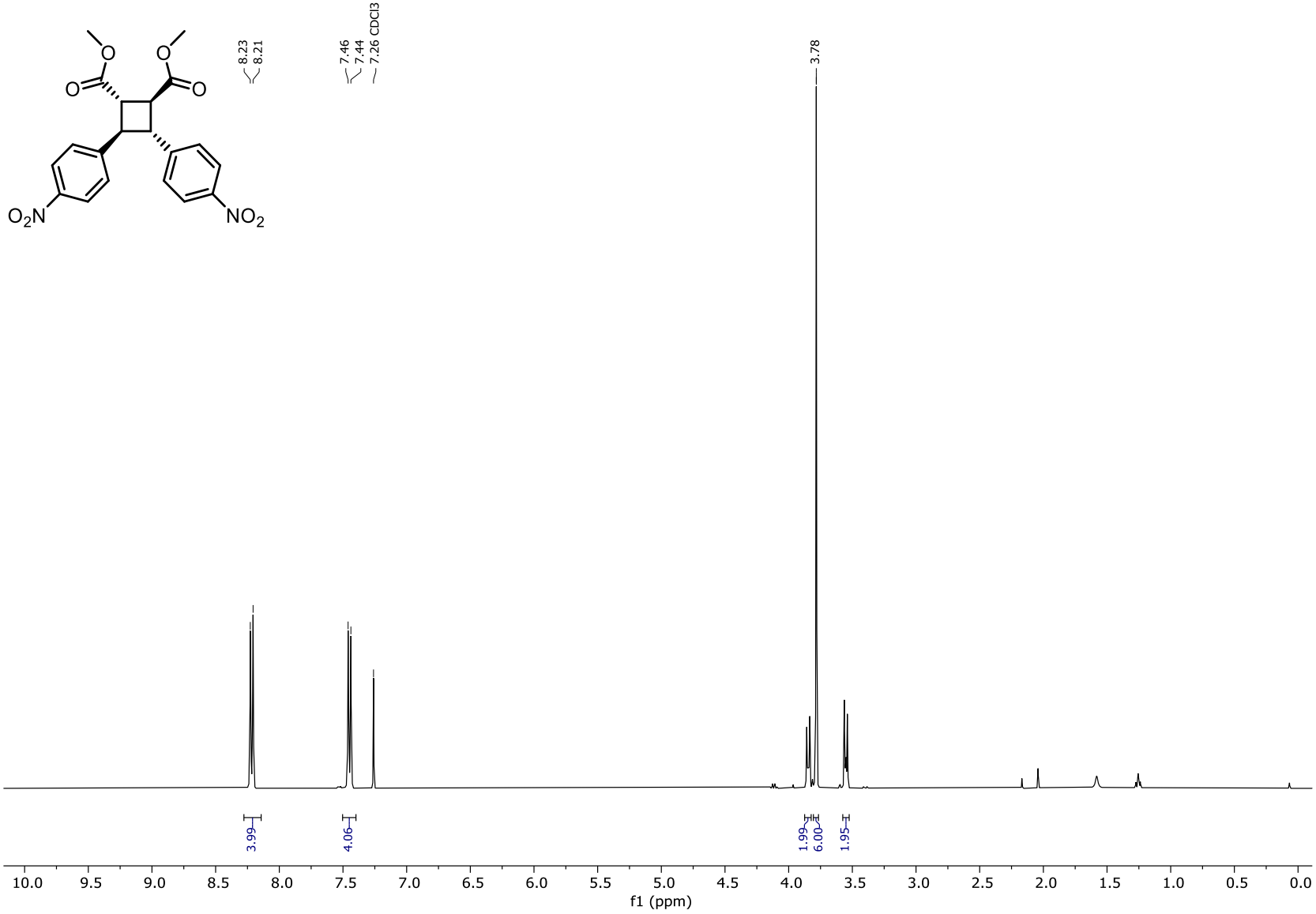
1,2-di(pyridin-4-yl)cyclobutane (2n-cis+2n-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



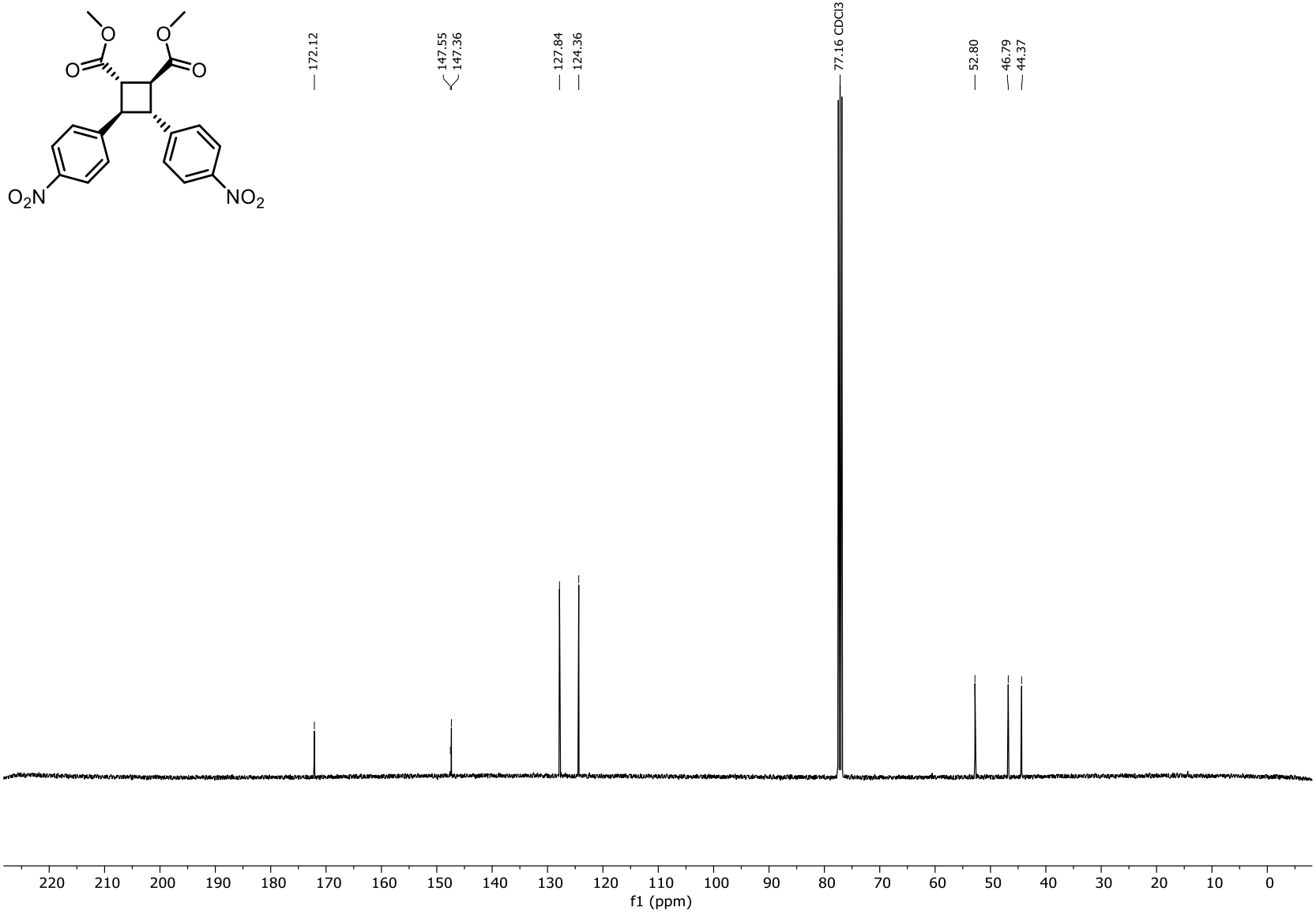
dimethyl 3,4-bis(4-nitrophenyl)cyclobutane-1,2-dicarboxylate (2o-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



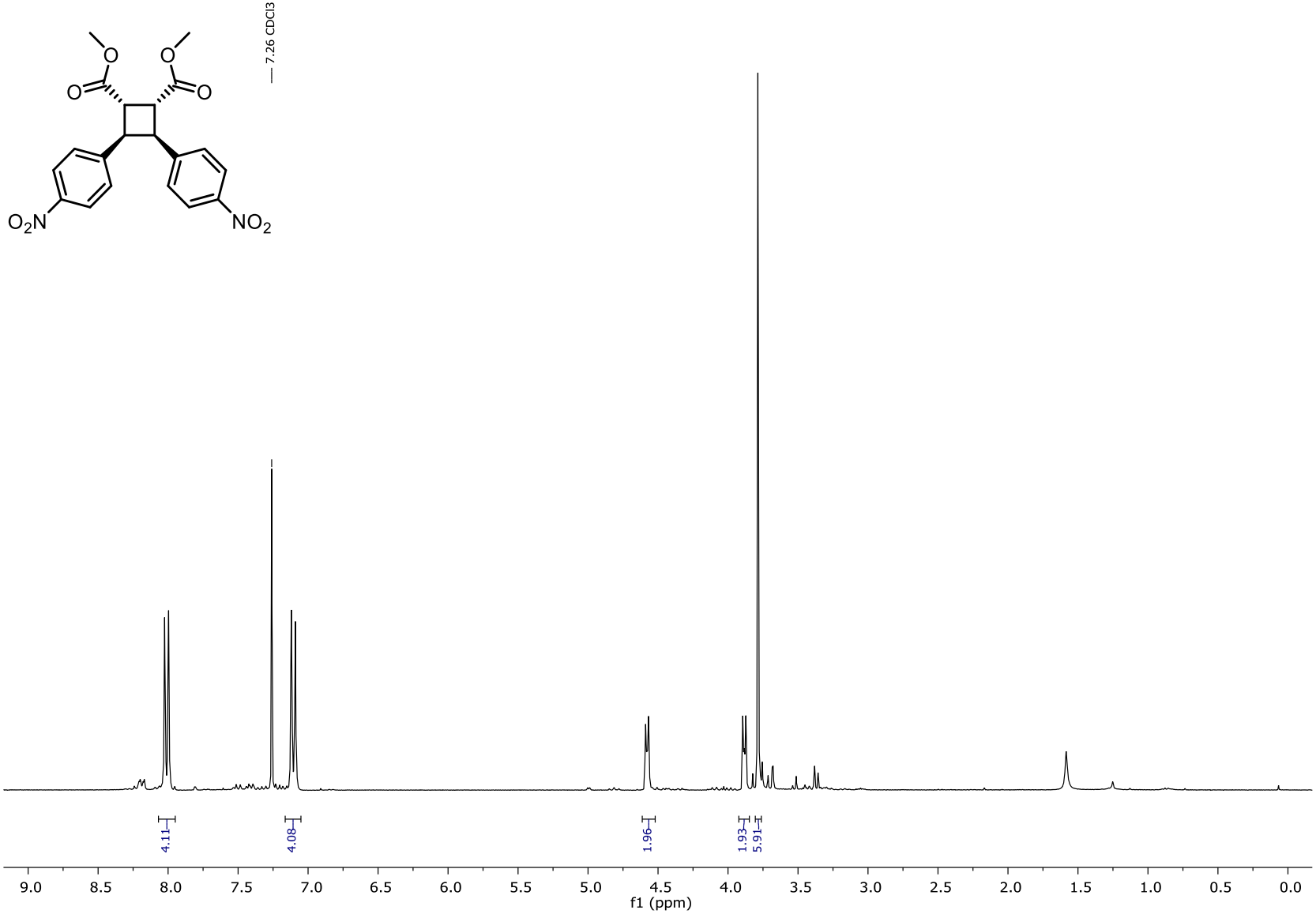
dimethyl 3,4-bis(4-nitrophenyl)cyclobutane-1,2-dicarboxylate (2o-trans): ^{1}H NMR (400 MHz, $CDCl_3$)



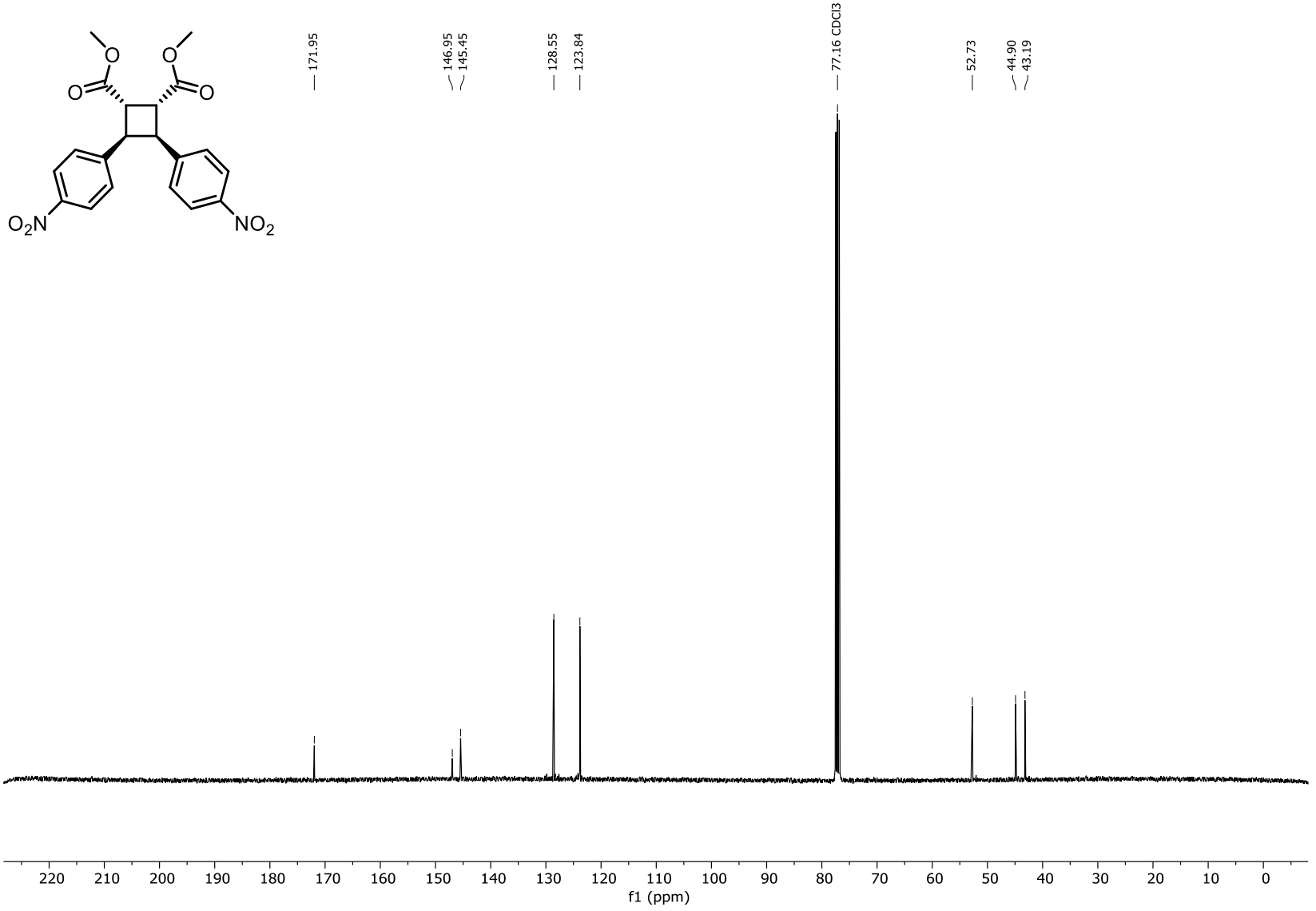
dimethyl 3,4-bis(4-nitrophenyl)cyclobutane-1,2-dicarboxylate (2o-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



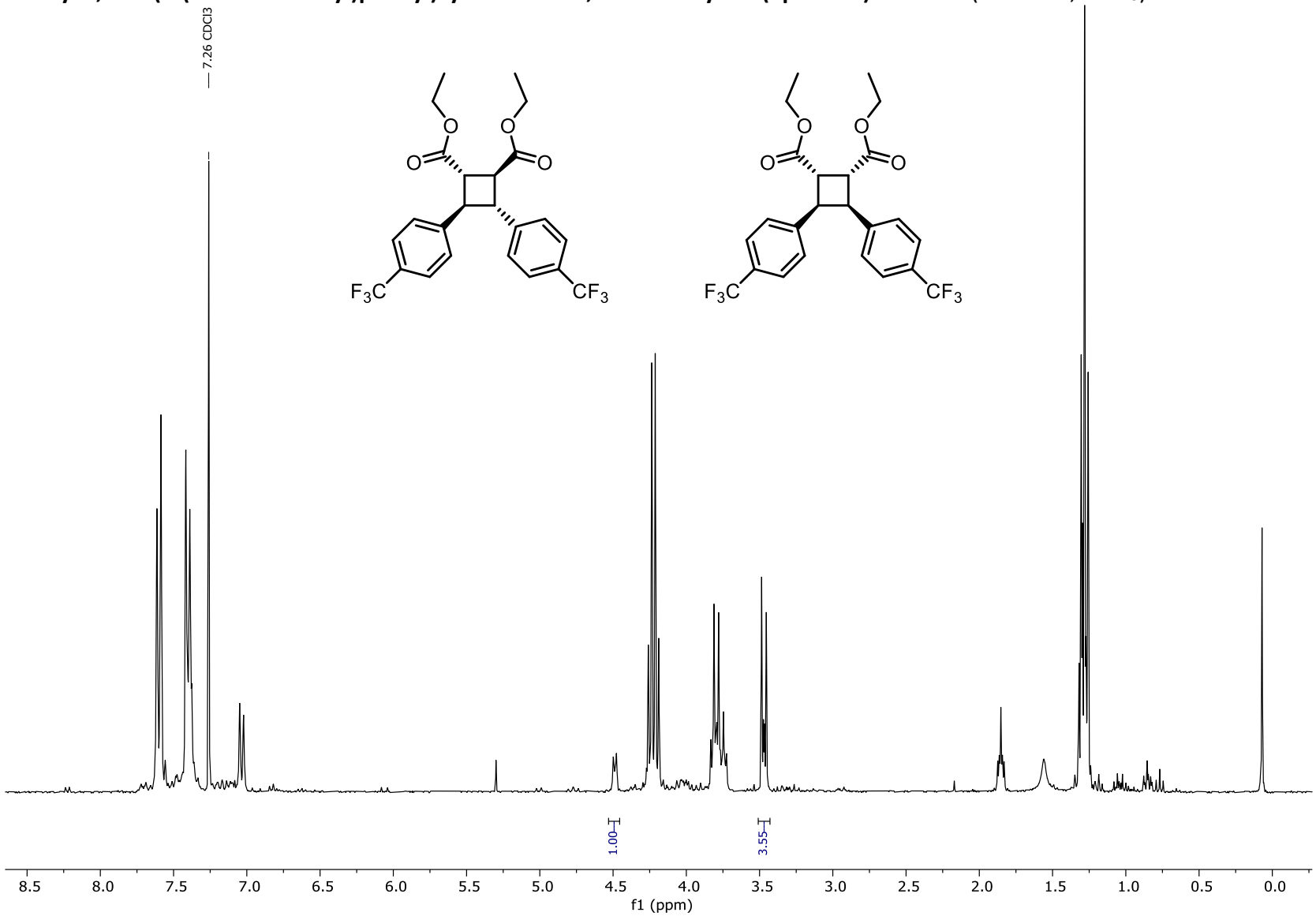
Dimethyl 3,4-bis(4-nitrophenyl)cyclobutane-1,2-dicarboxylate (2o-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



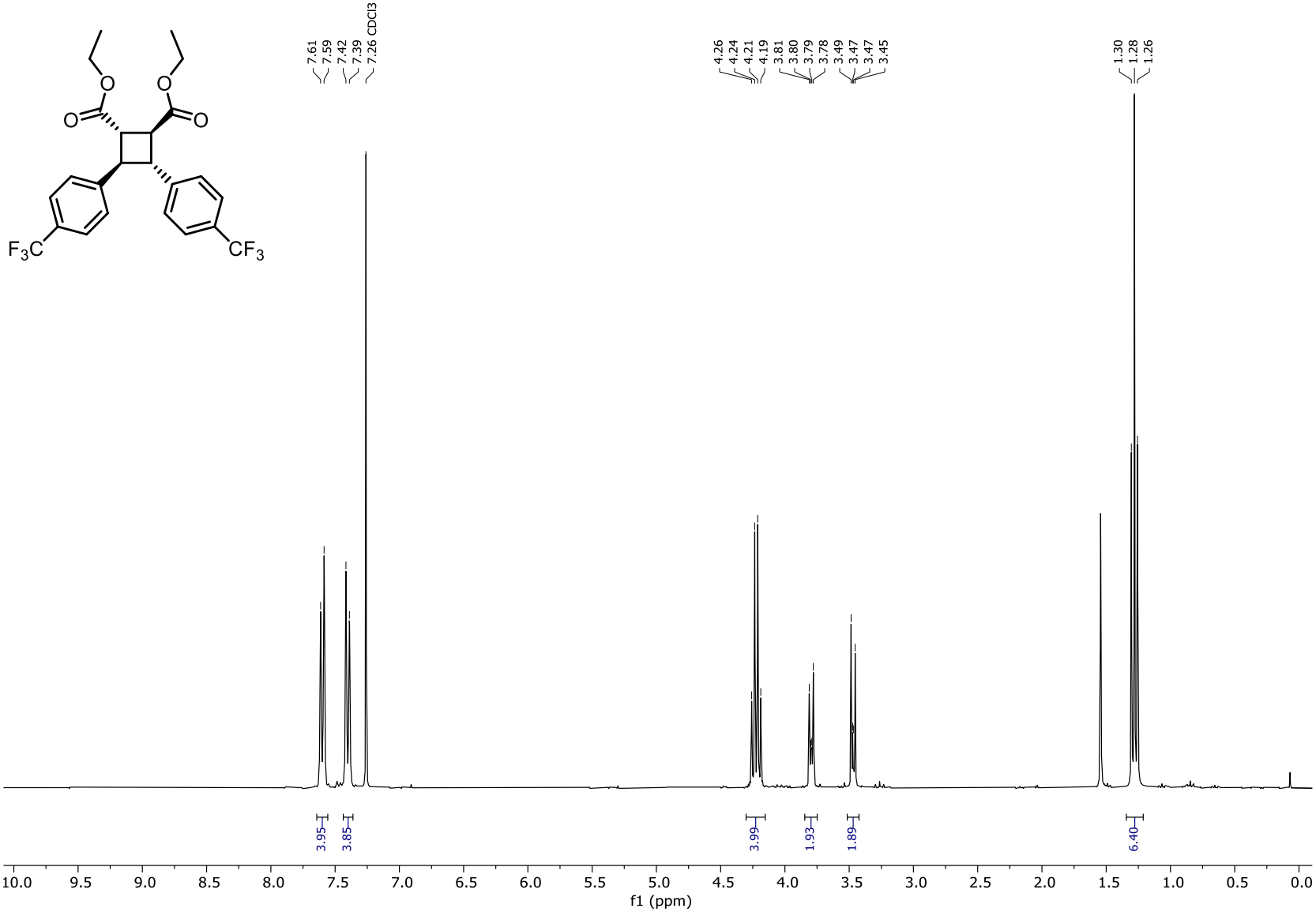
Dimethyl 3,4-bis(4-nitrophenyl)cyclobutane-1,2-dicarboxylate (2o-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



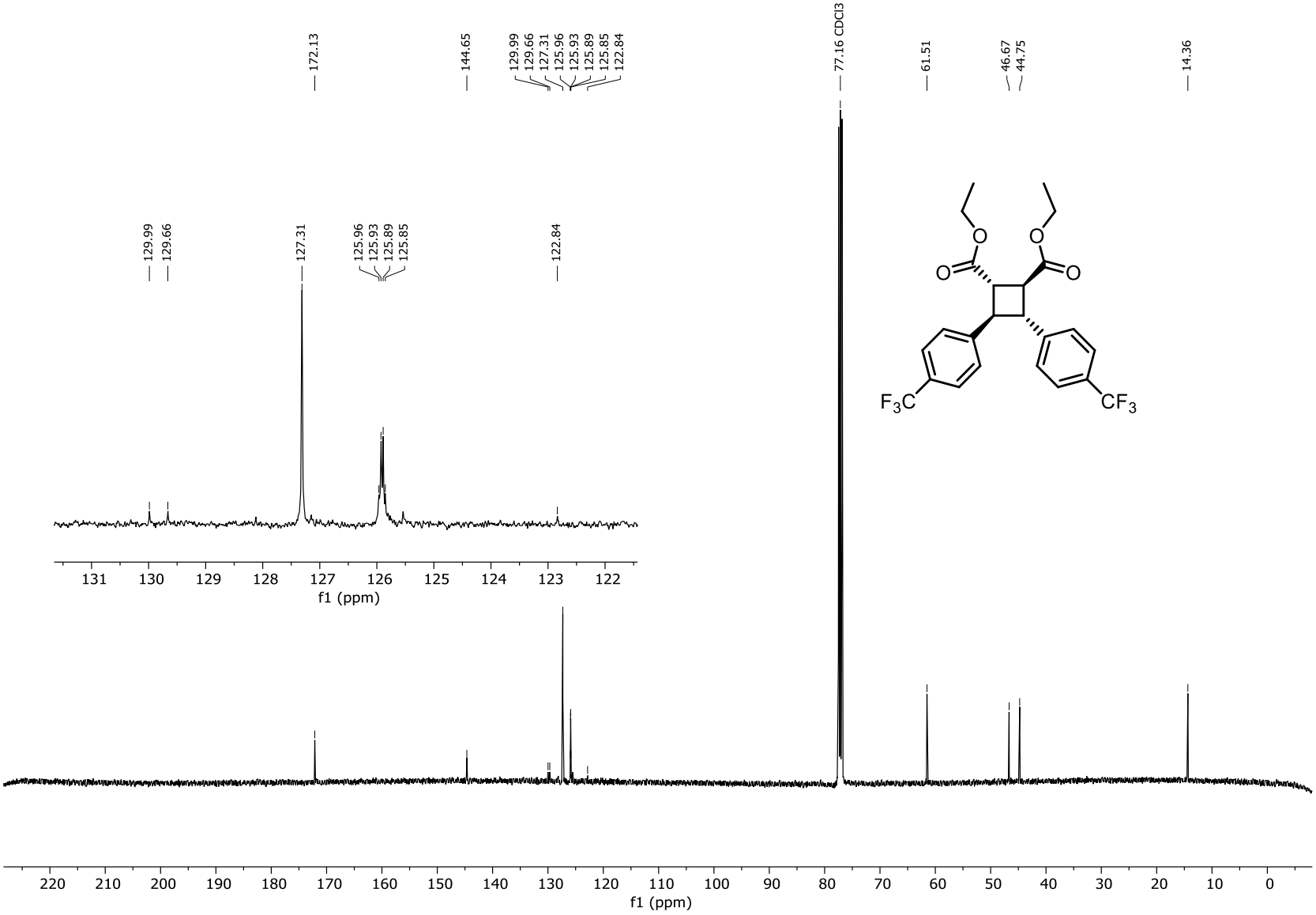
diethyl 3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (2p-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



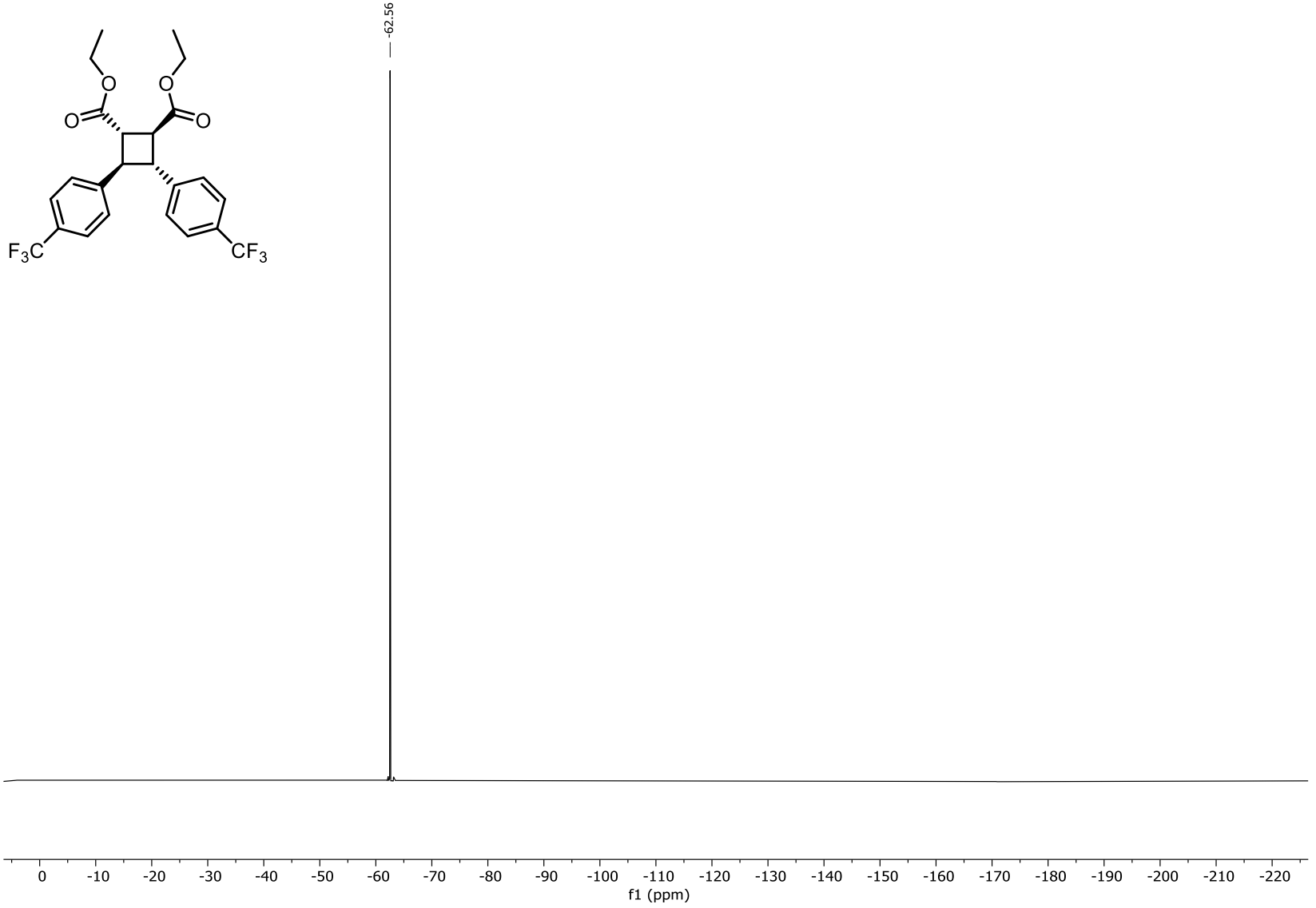
diethyl 3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (2p-trans): ^{1}H NMR (300 MHz, $CDCl_3$)



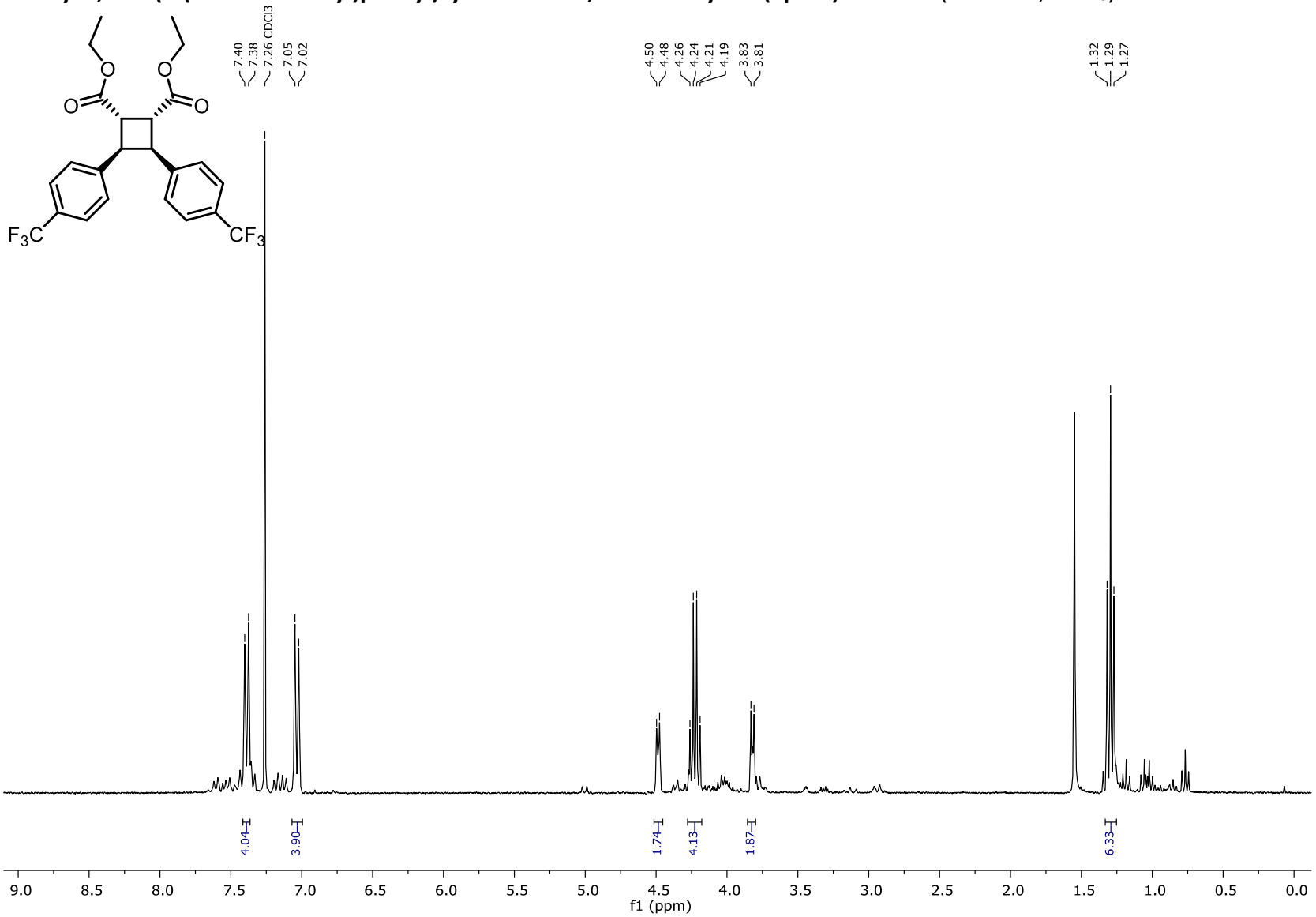
Diethyl 3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (2p-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



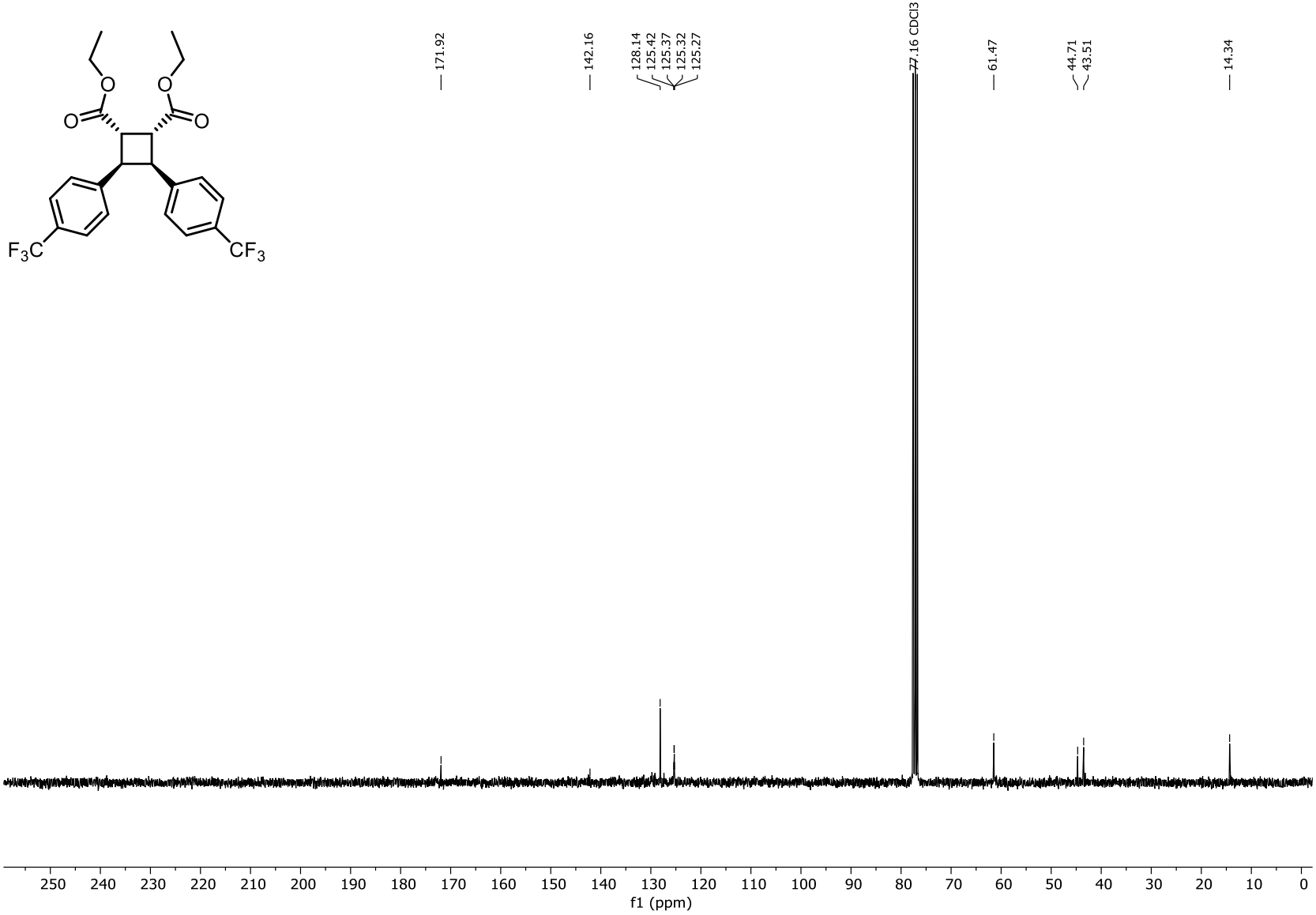
Diethyl 3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (2p-trans): ^{19}F NMR (282 MHz, CDCl3) δ -62.56.



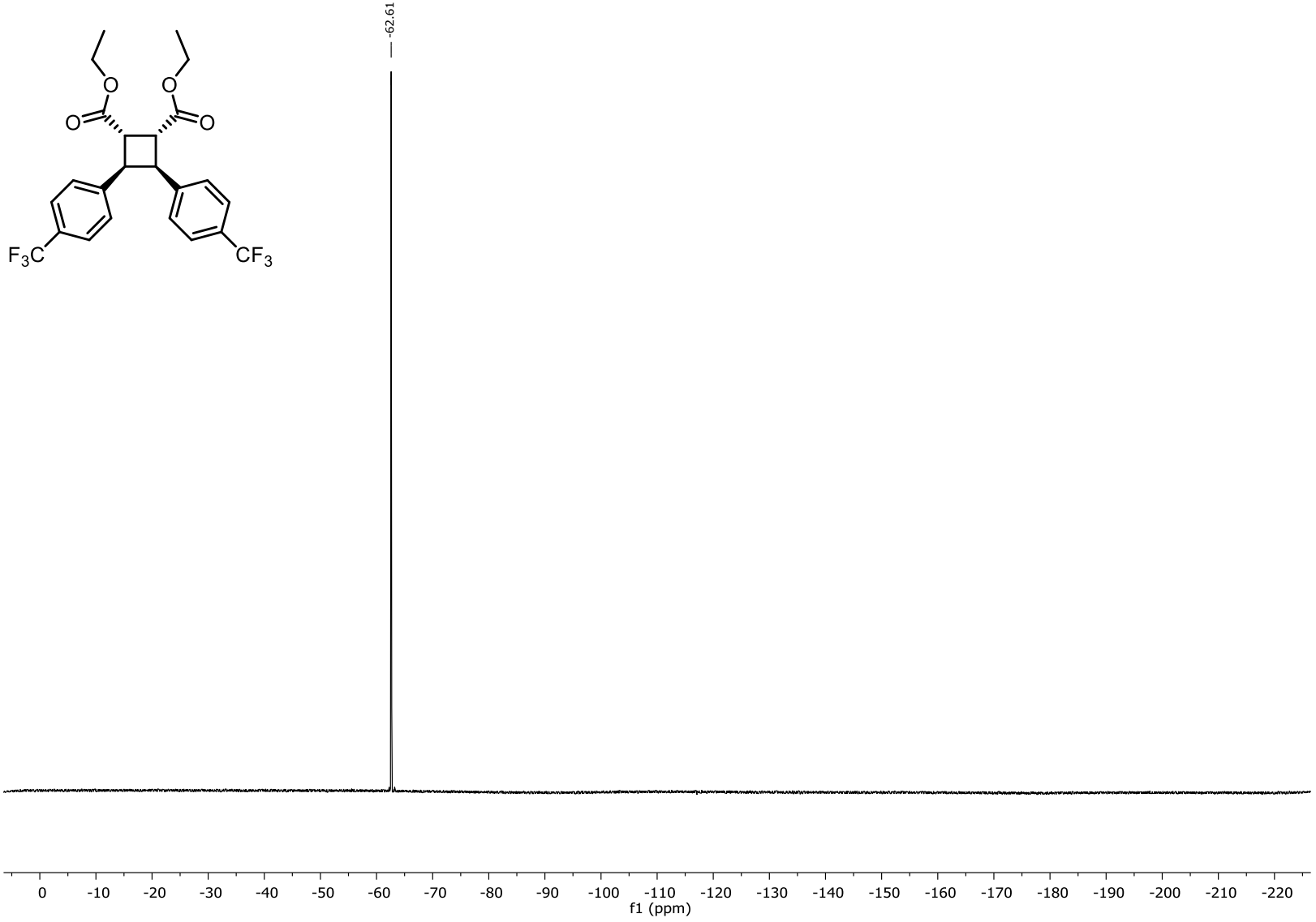
Diethyl 3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (2p-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



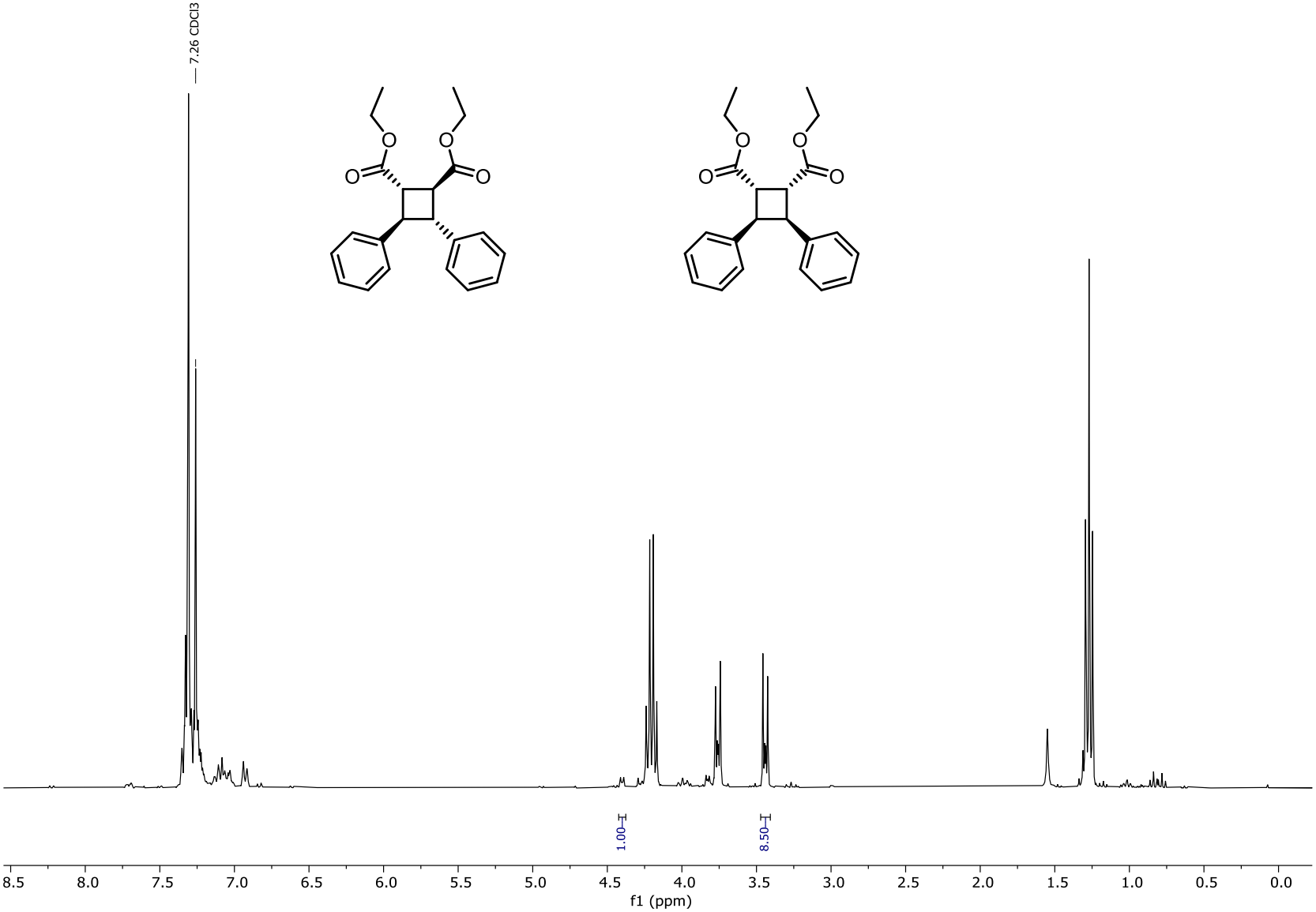
Diethyl 3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (2p-cis): 13C{^{1}H} NMR (75 MHz, $CDCl_3$)



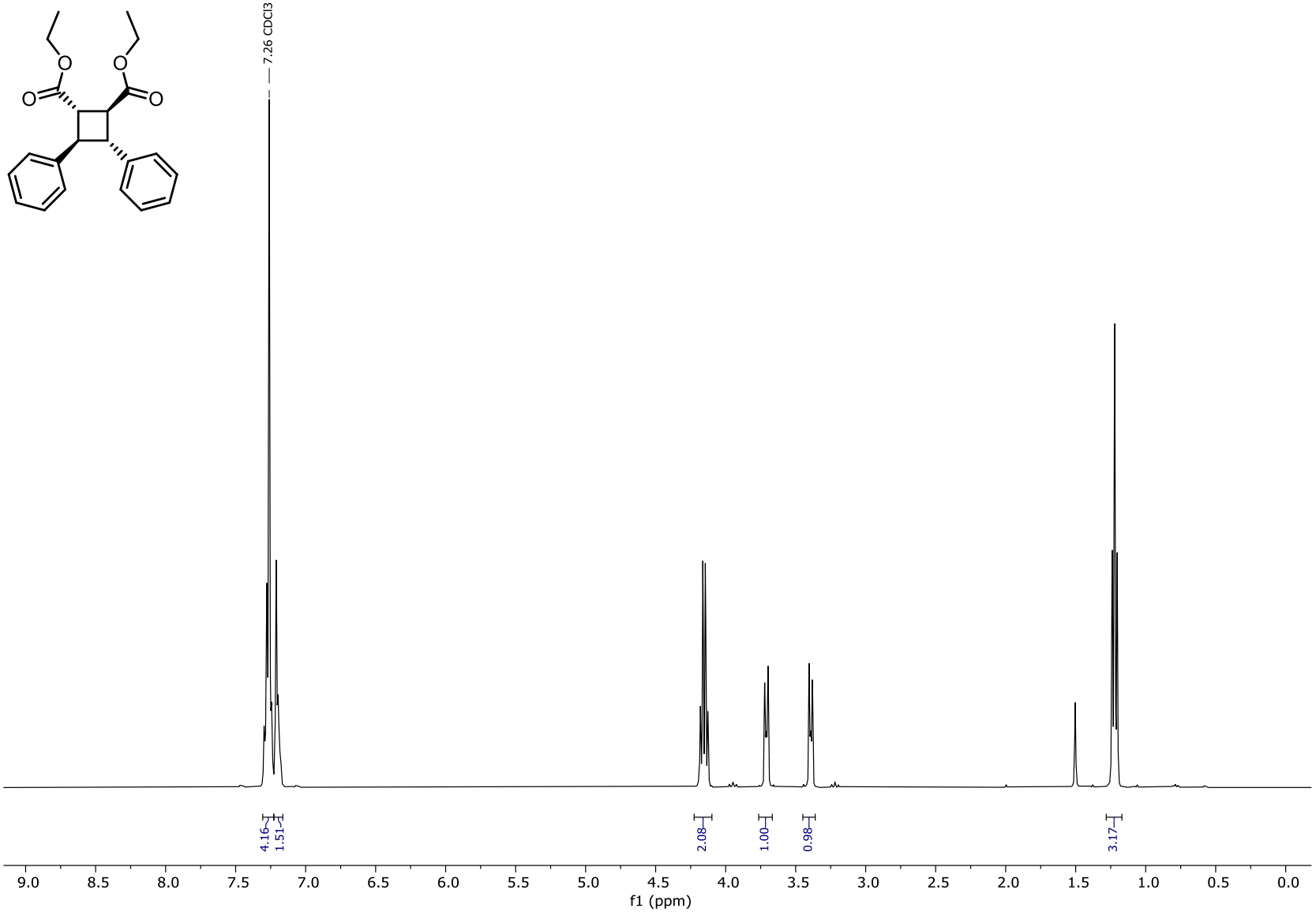
Diethyl 3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (2p-cis): ^{19}F NMR (282 MHz, $CDCl_3$)**.**



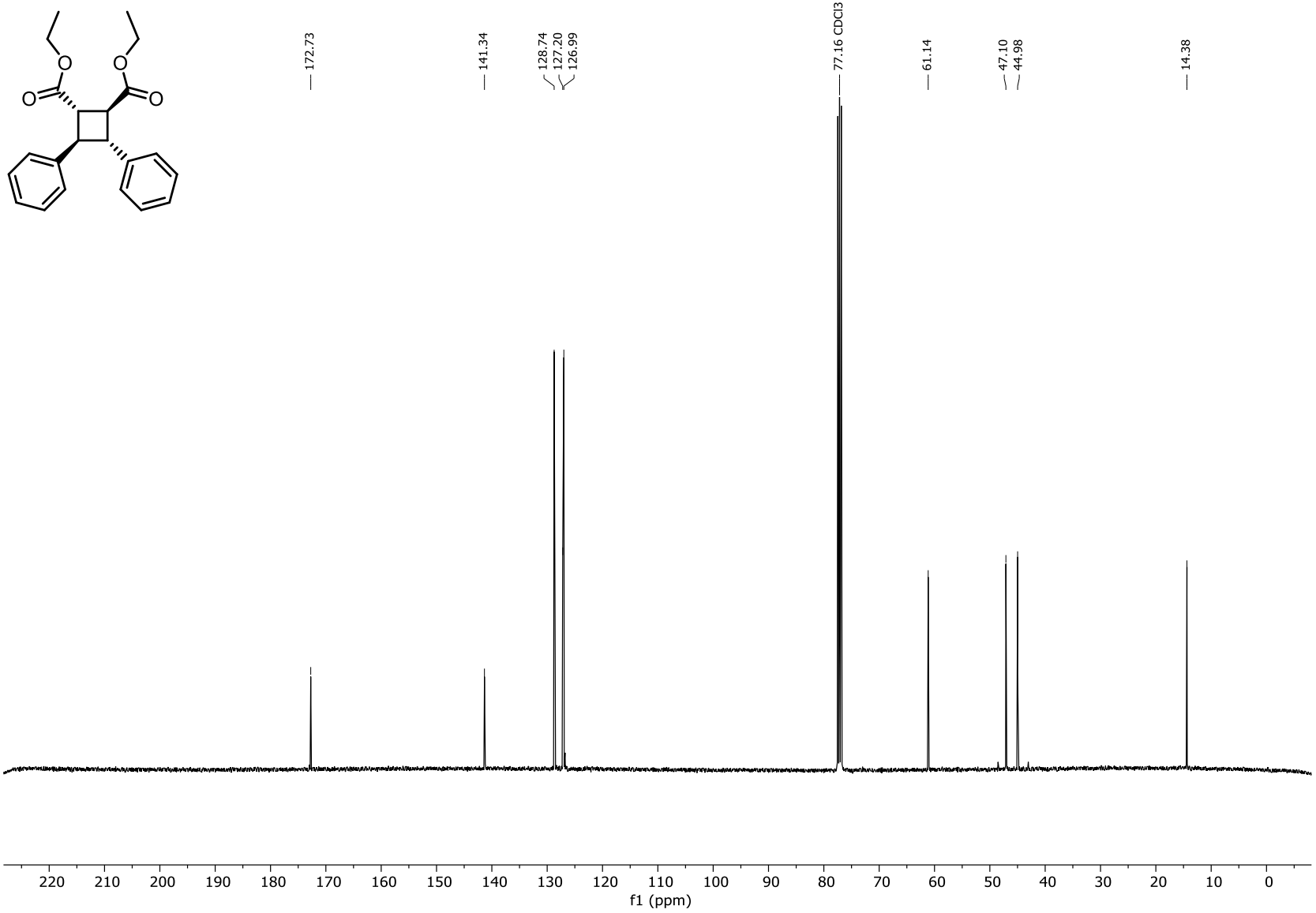
Diethyl 3,4-diphenylcyclobutane-1,2-dicarboxylate (2q-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



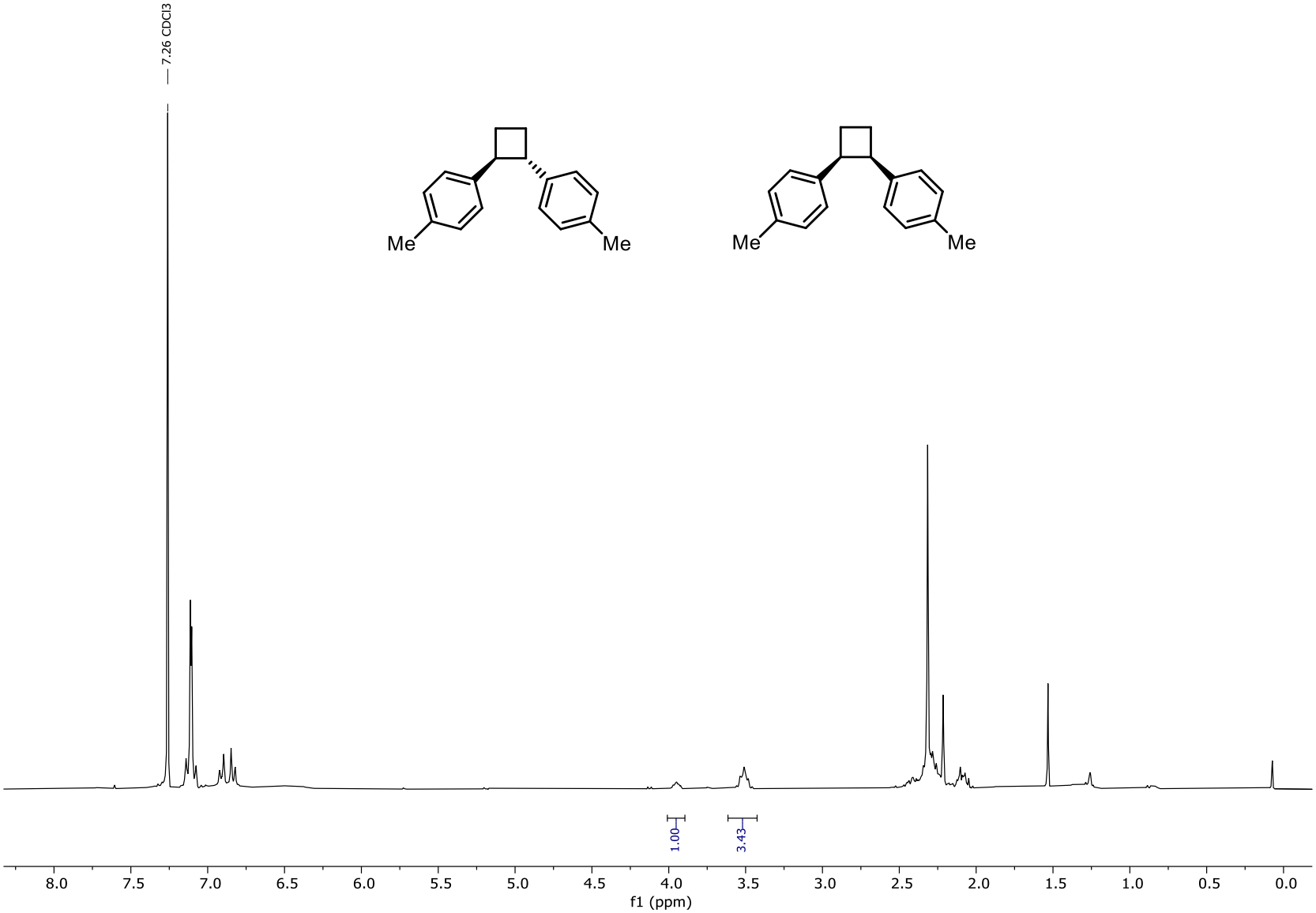
Diethyl 3,4-diphenylcyclobutane-1,2-dicarboxylate (2q-trans): ^{1}H NMR (101 MHz, $CDCl_3$)



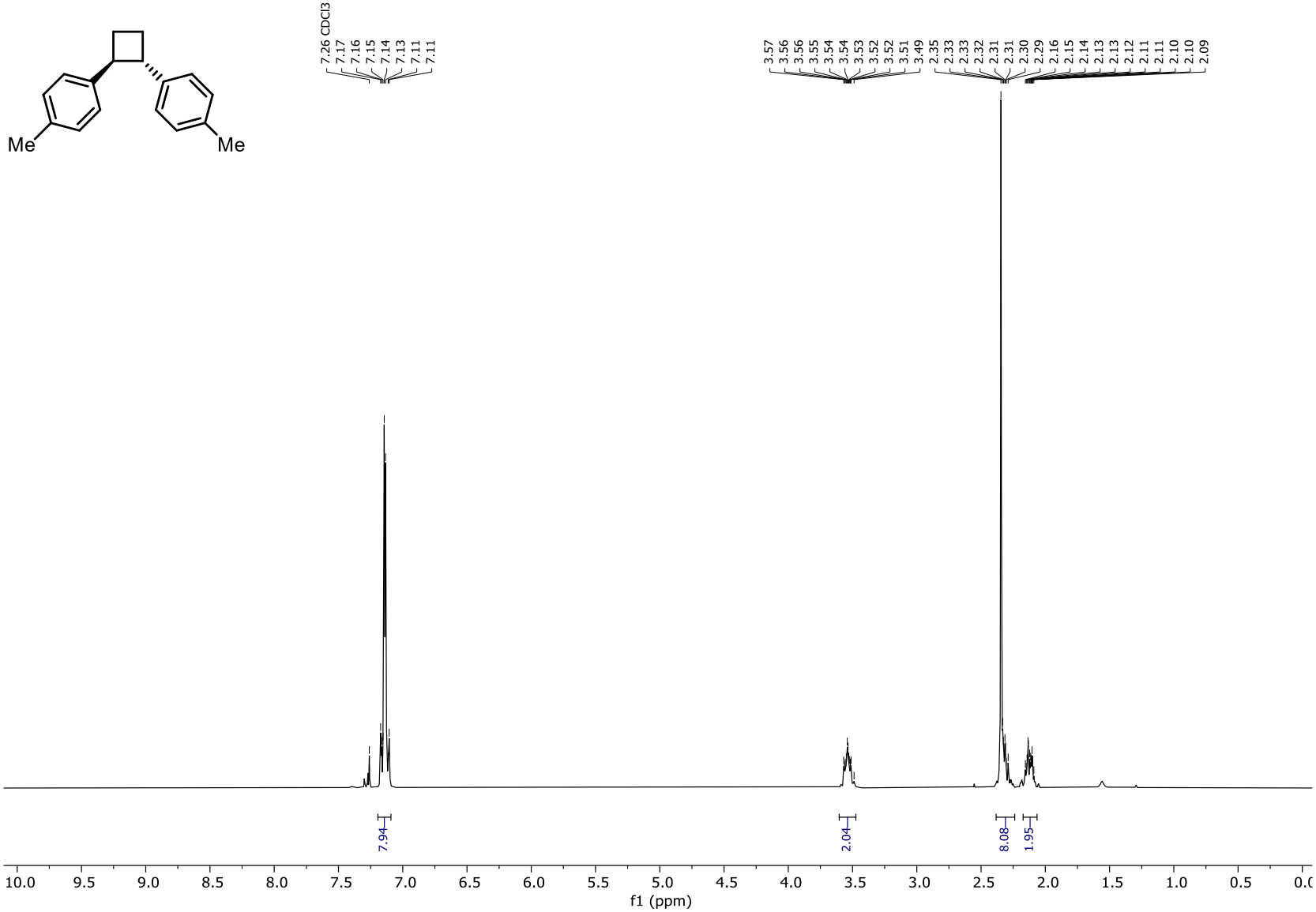
Diethyl 3,4-diphenylcyclobutane-1,2-dicarboxylate (2q-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



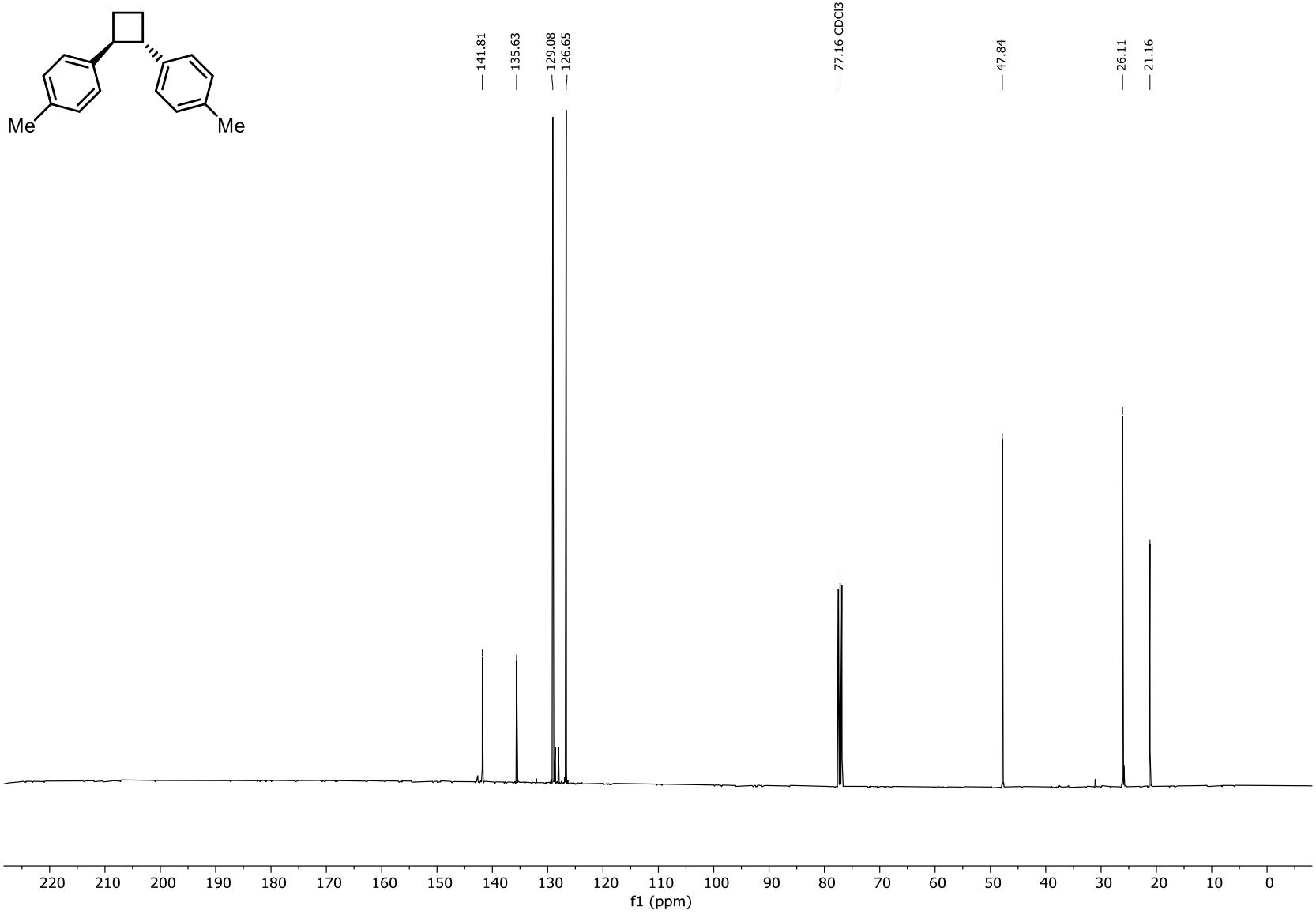
1,2-Di-p-tolylcyclobutane (2r-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



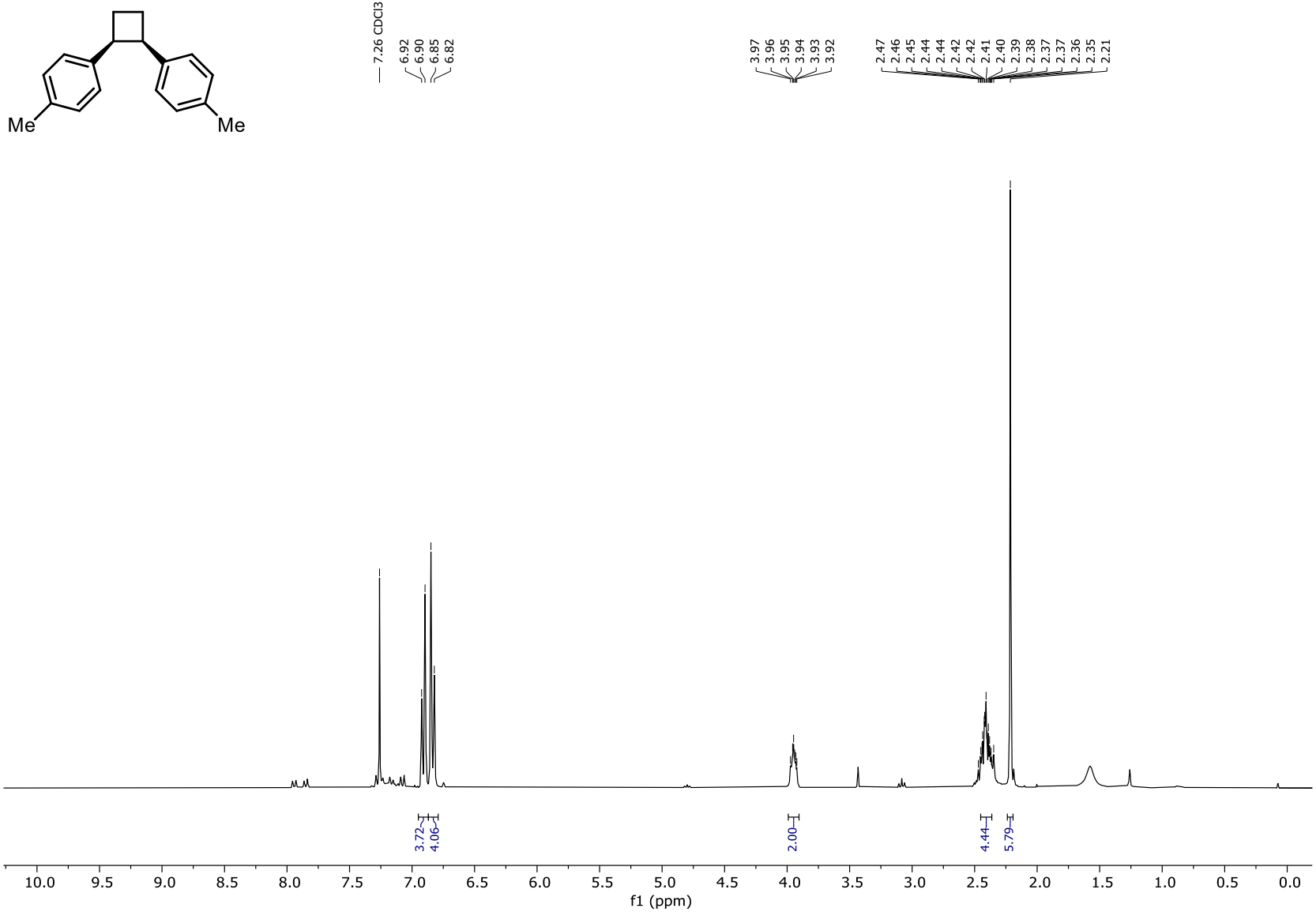
1,2-Di-p-tolylcyclobutane (2r-trans): ^{1}H NMR (300 MHz, $CDCl_3$)



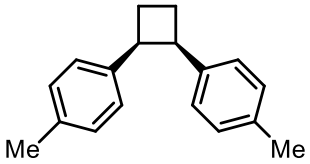
1,2-Di-p-tolylcyclobutane (2r-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



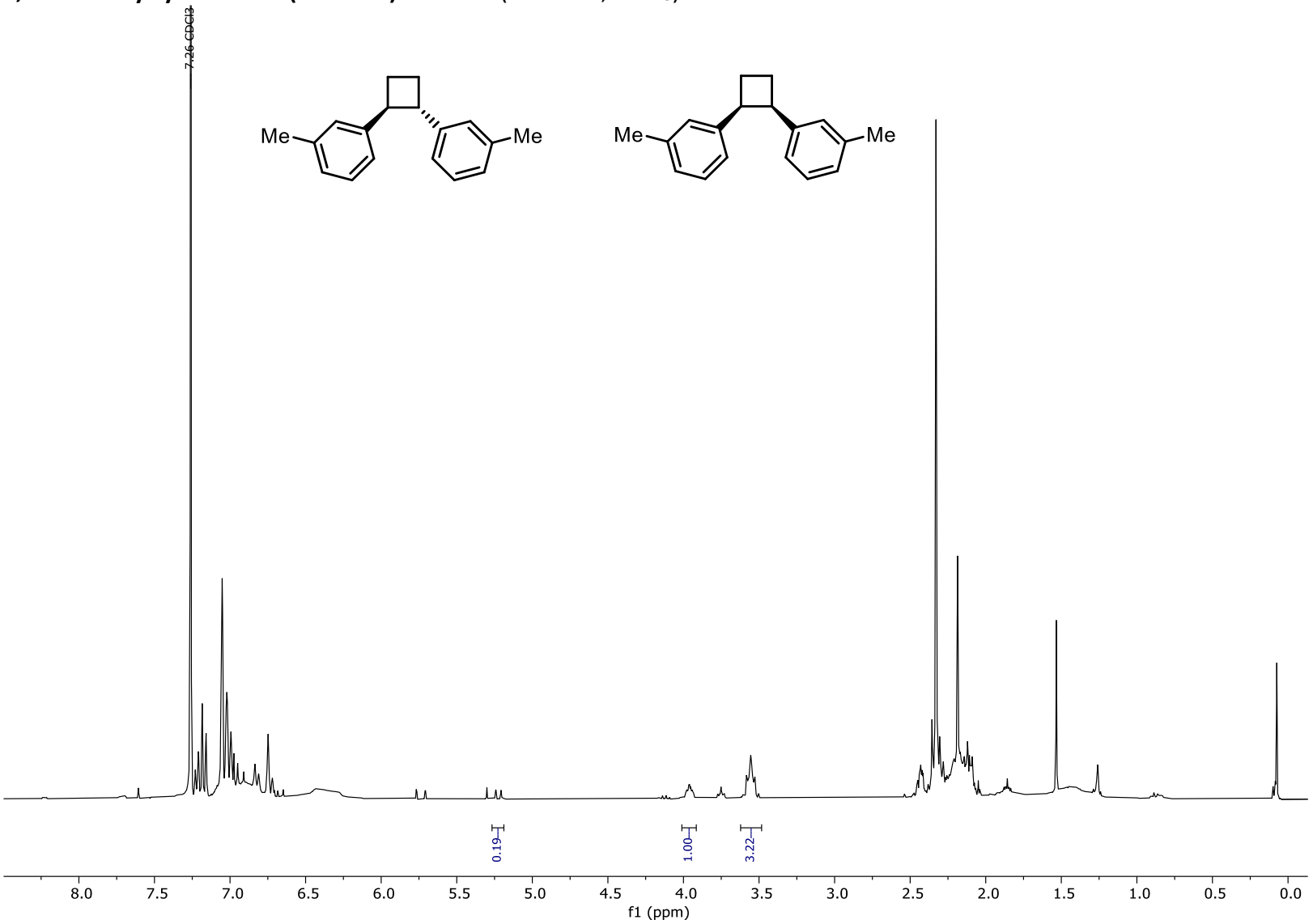
1,2-Di-p-tolylcyclobutane (2r-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



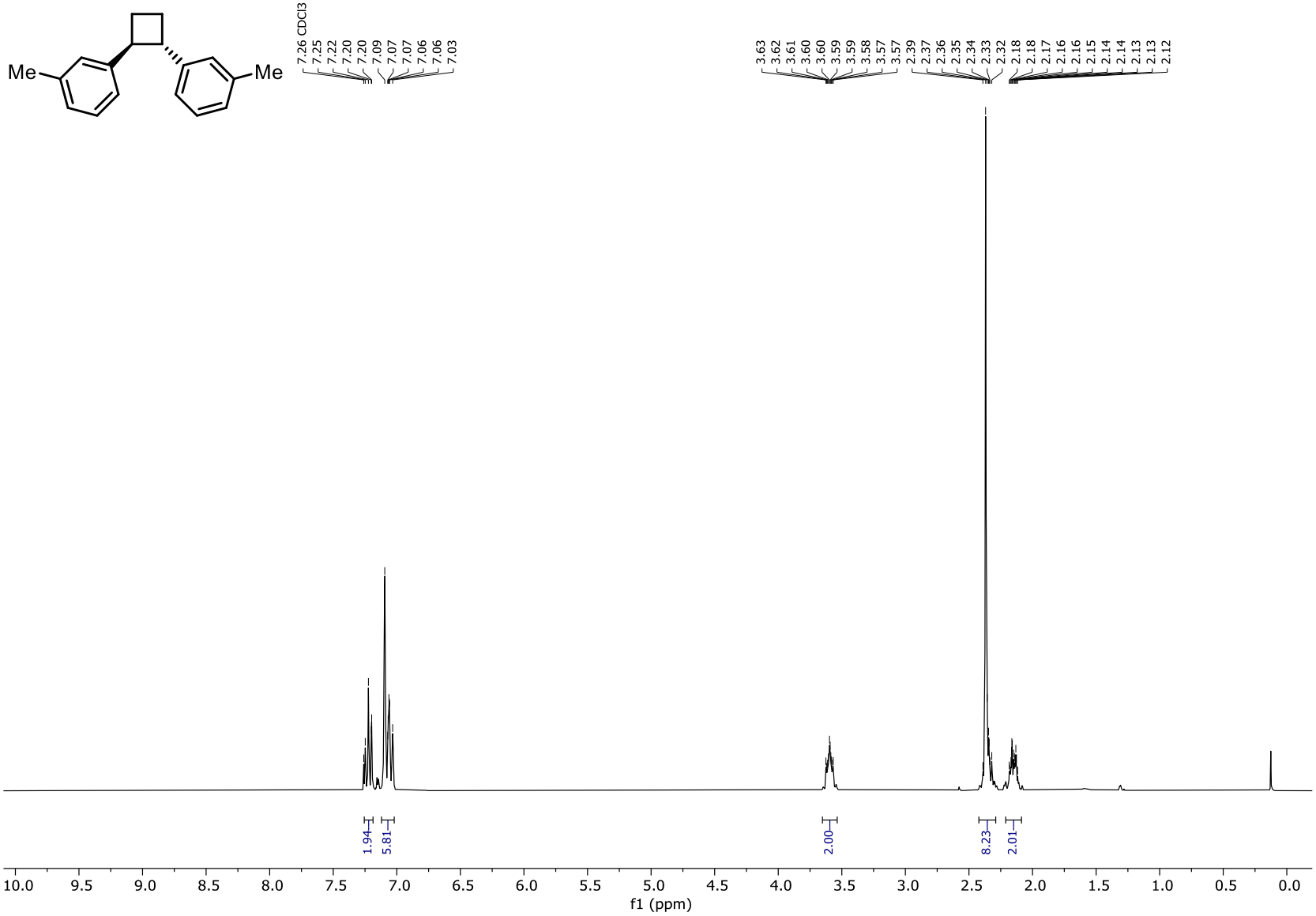
1,2-Di-p-tolylcyclobutane (2r-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



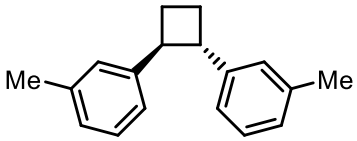
1,2-Di-m-tolylcyclobutane (2s-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



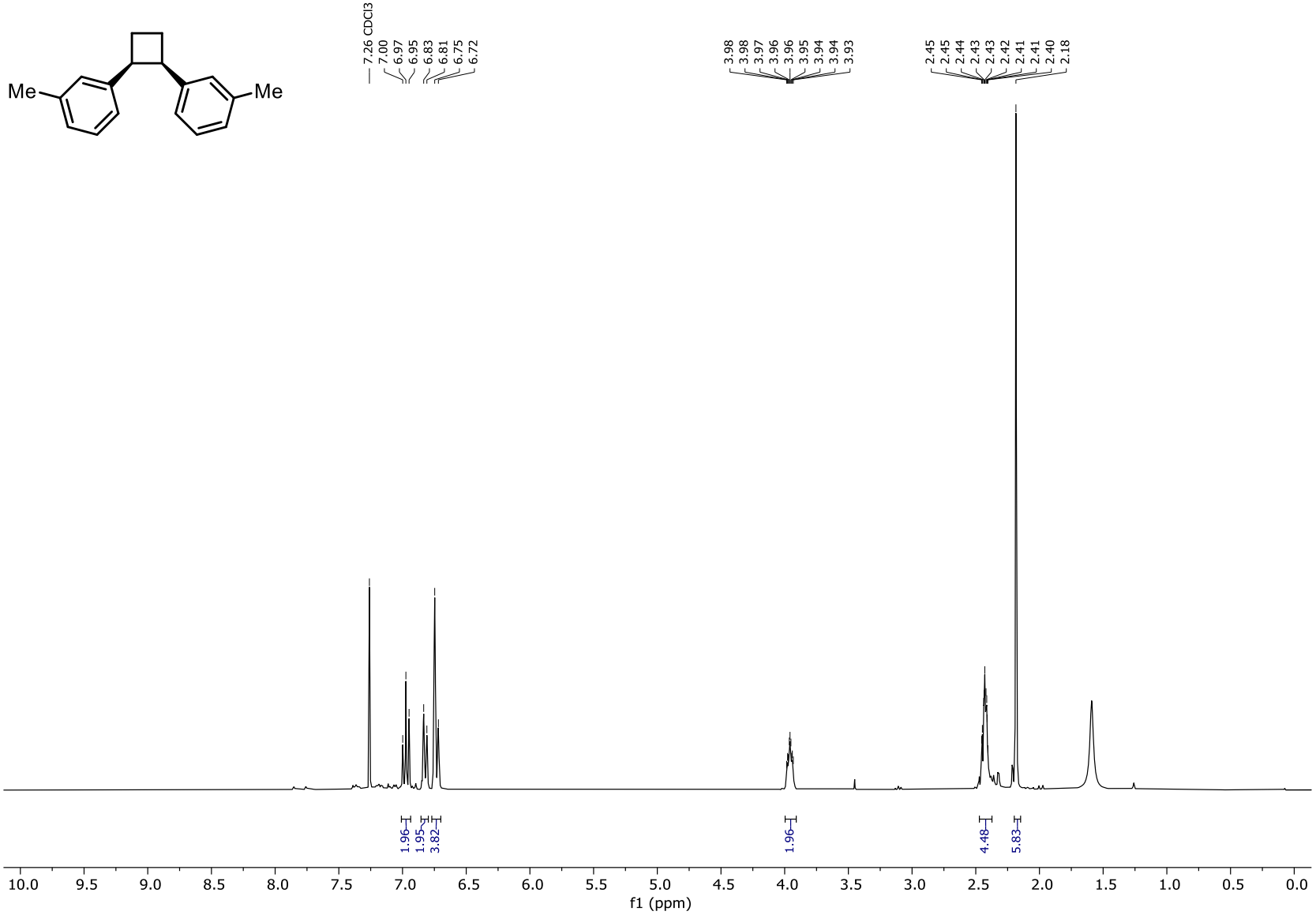
1,2-Di-m-tolylcyclobutane (2s -trans): ^{1}H NMR (300 MHz, $CDCl_3$)



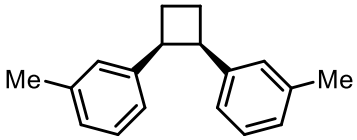
1,2-Di-m-tolylcyclobutane (2s-trans): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



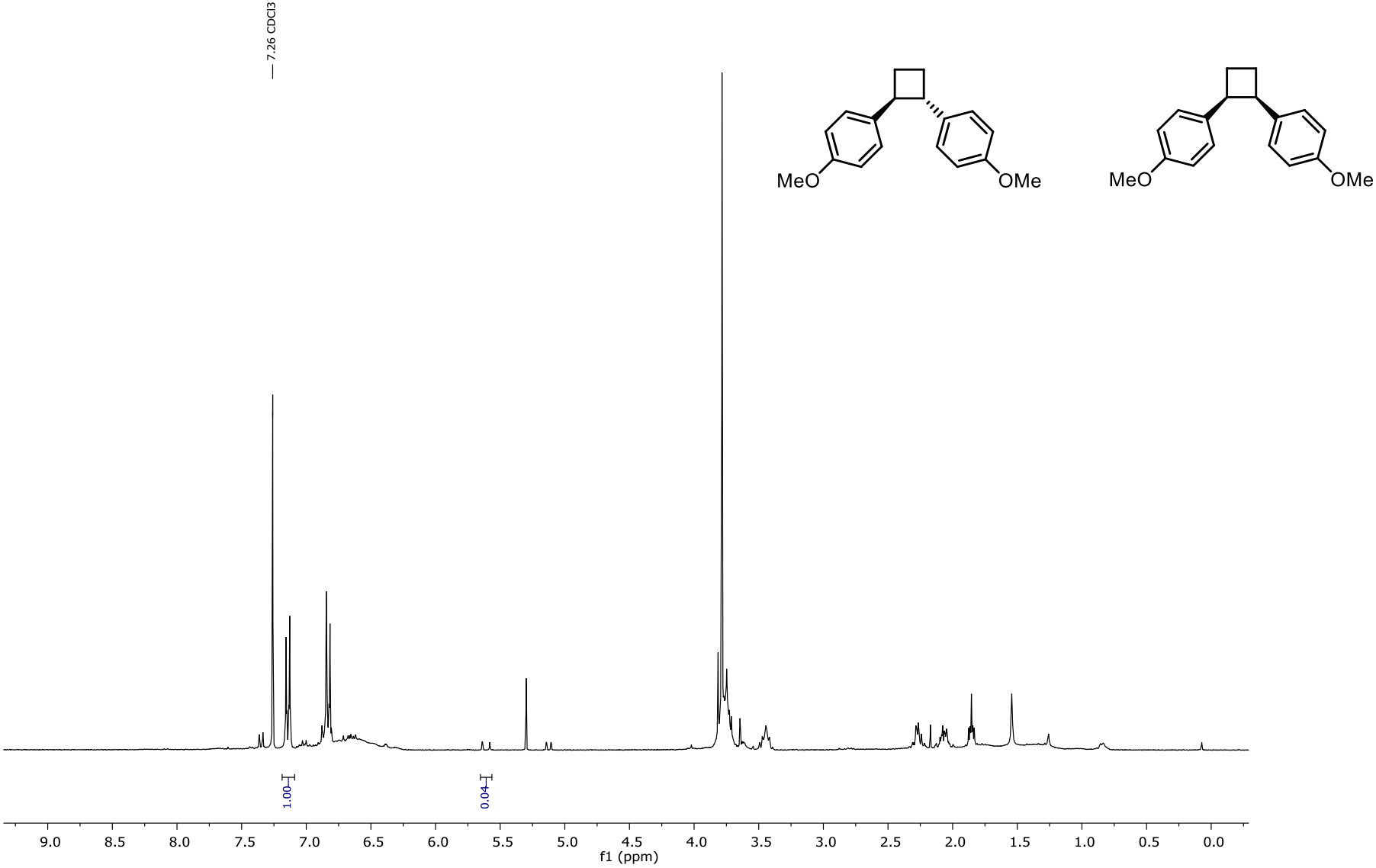
1,2-Di-m-tolylcyclobutane (2s-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



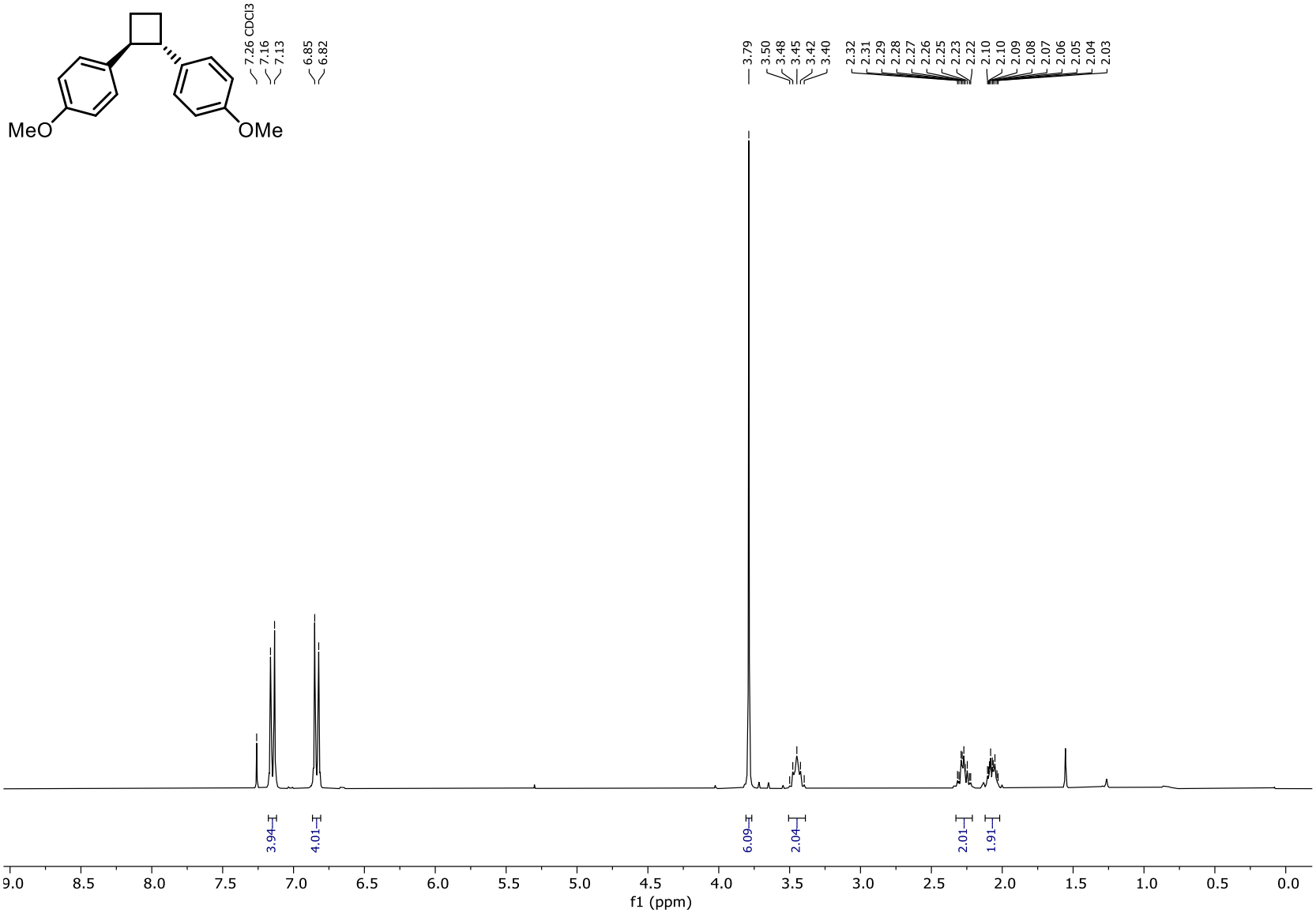
1,2-Di-m-tolylcyclobutane (2s-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



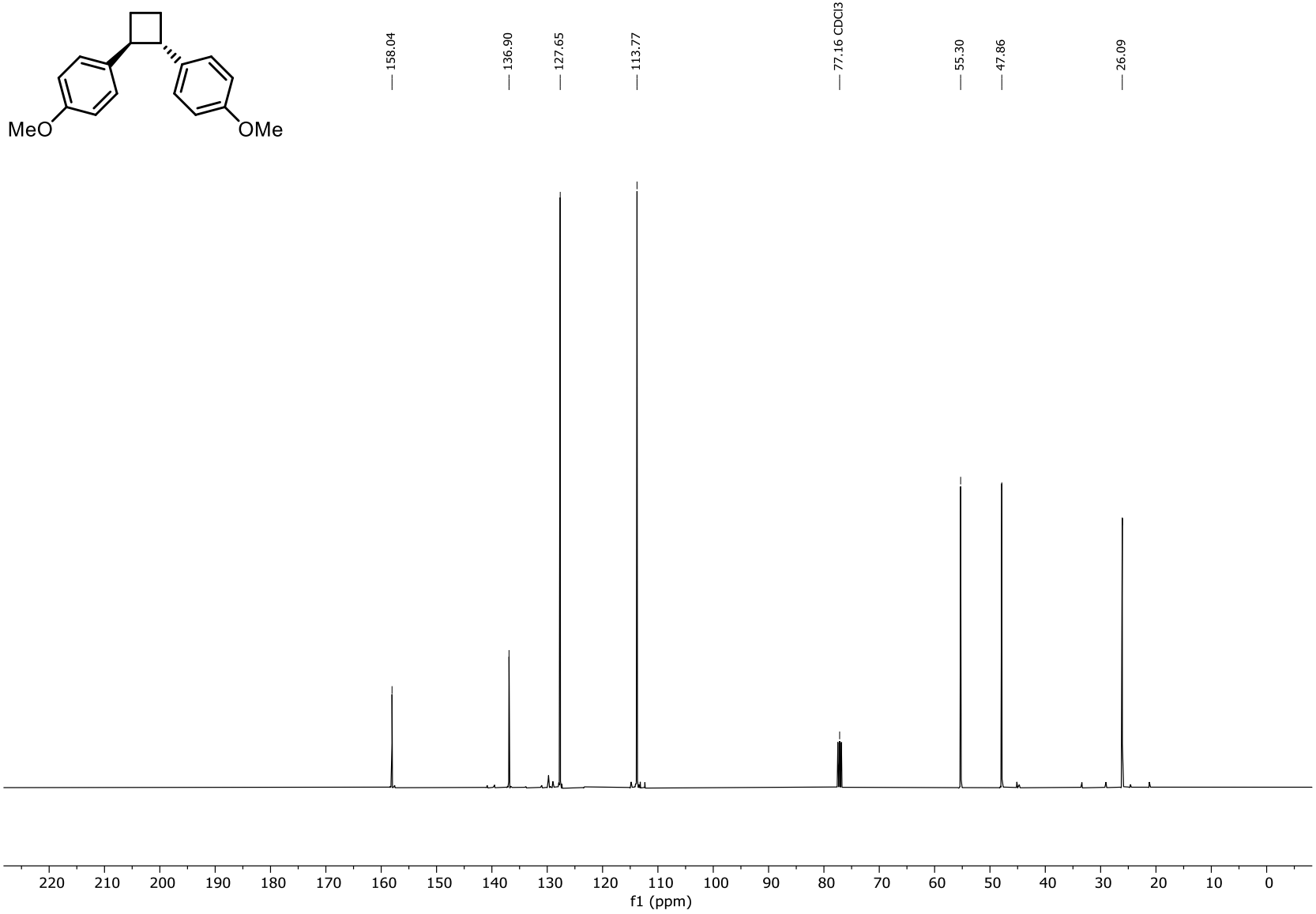
1,2-bis(4-Methoxyphenyl)cyclobutane (2t-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



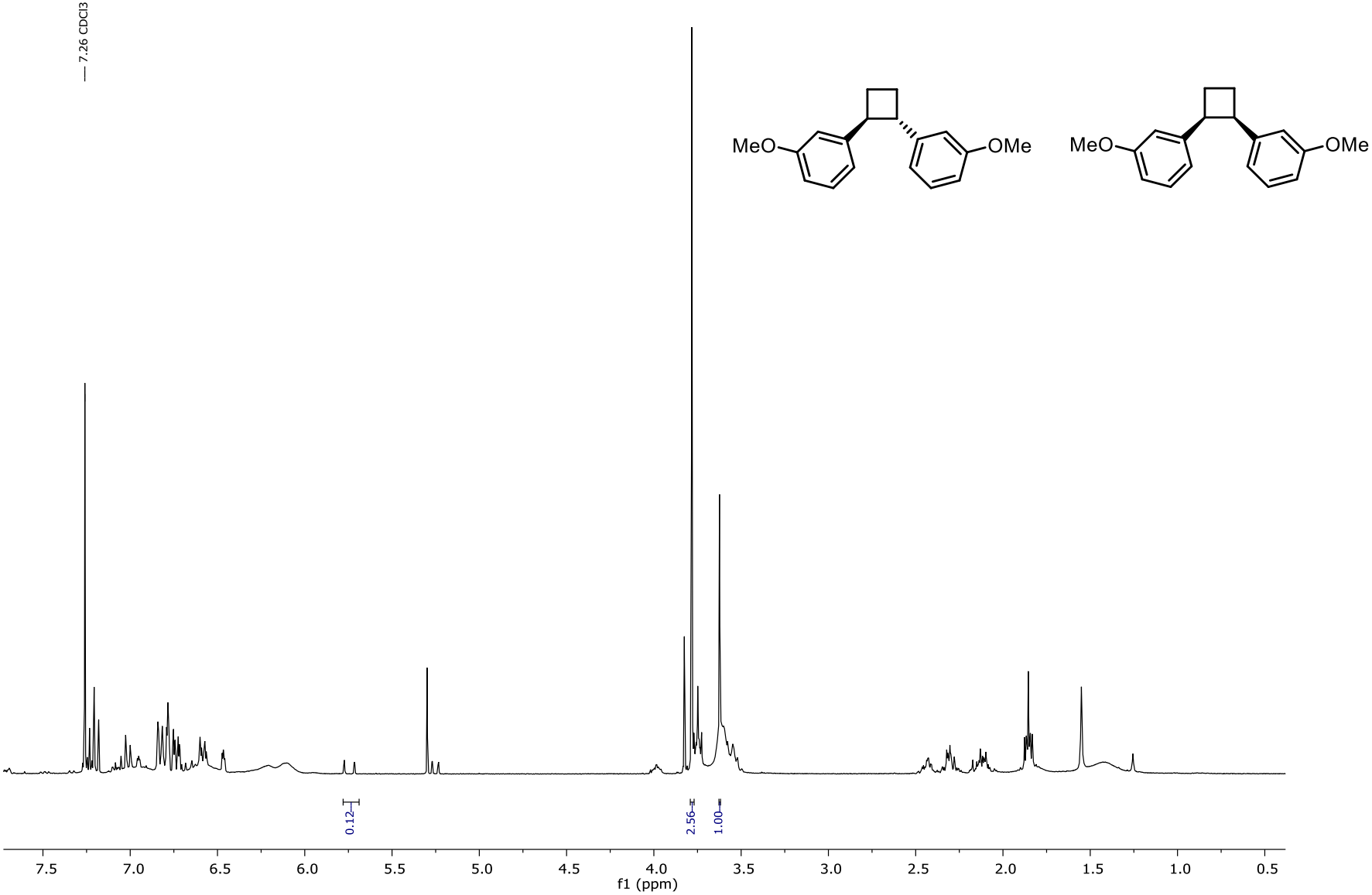
1,2-bis(4-Methoxyphenyl)cyclobutane (2t-trans+2t-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



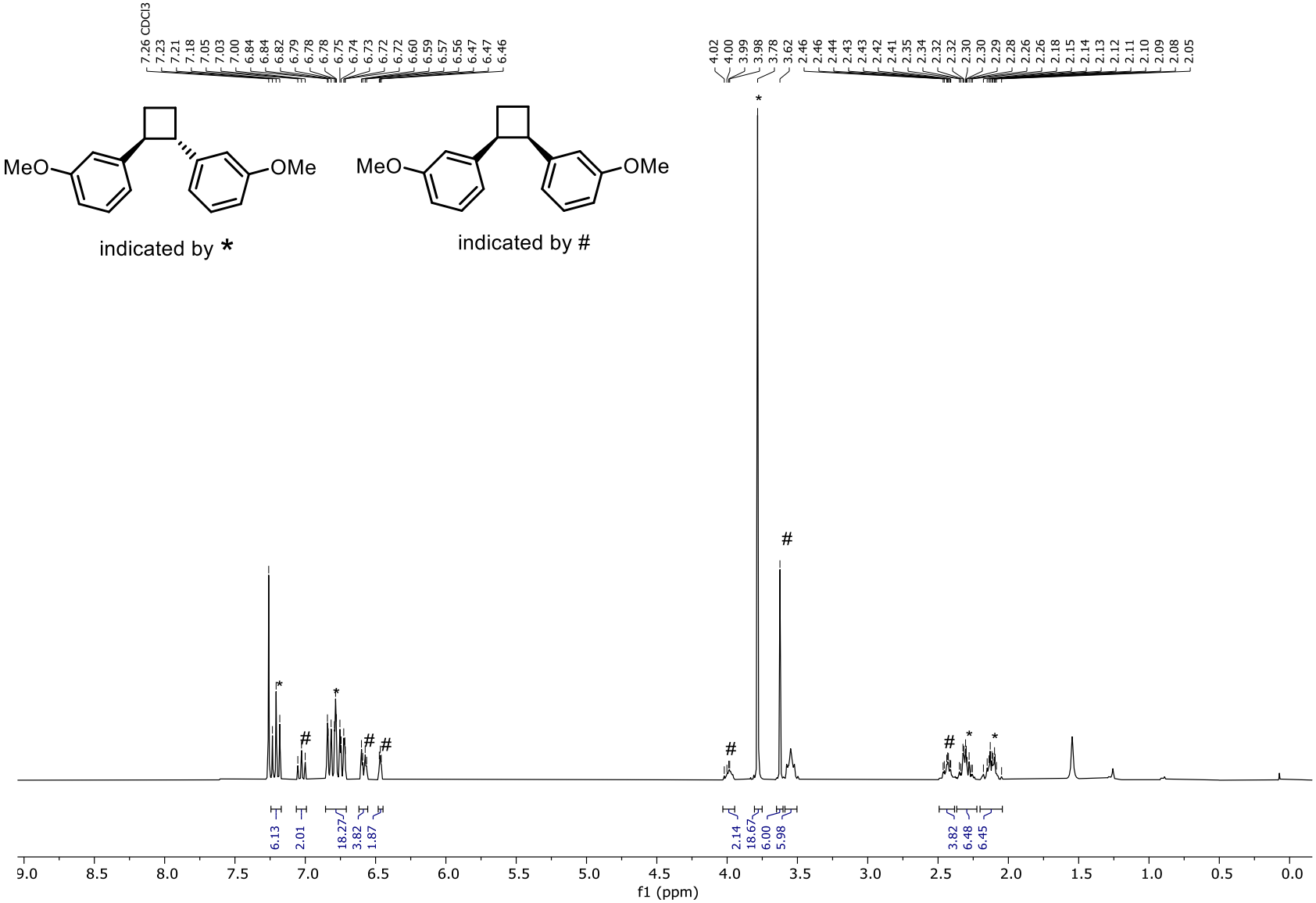
1,2-bis(4-Methoxyphenyl)cyclobutane (2t-trans+2t-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



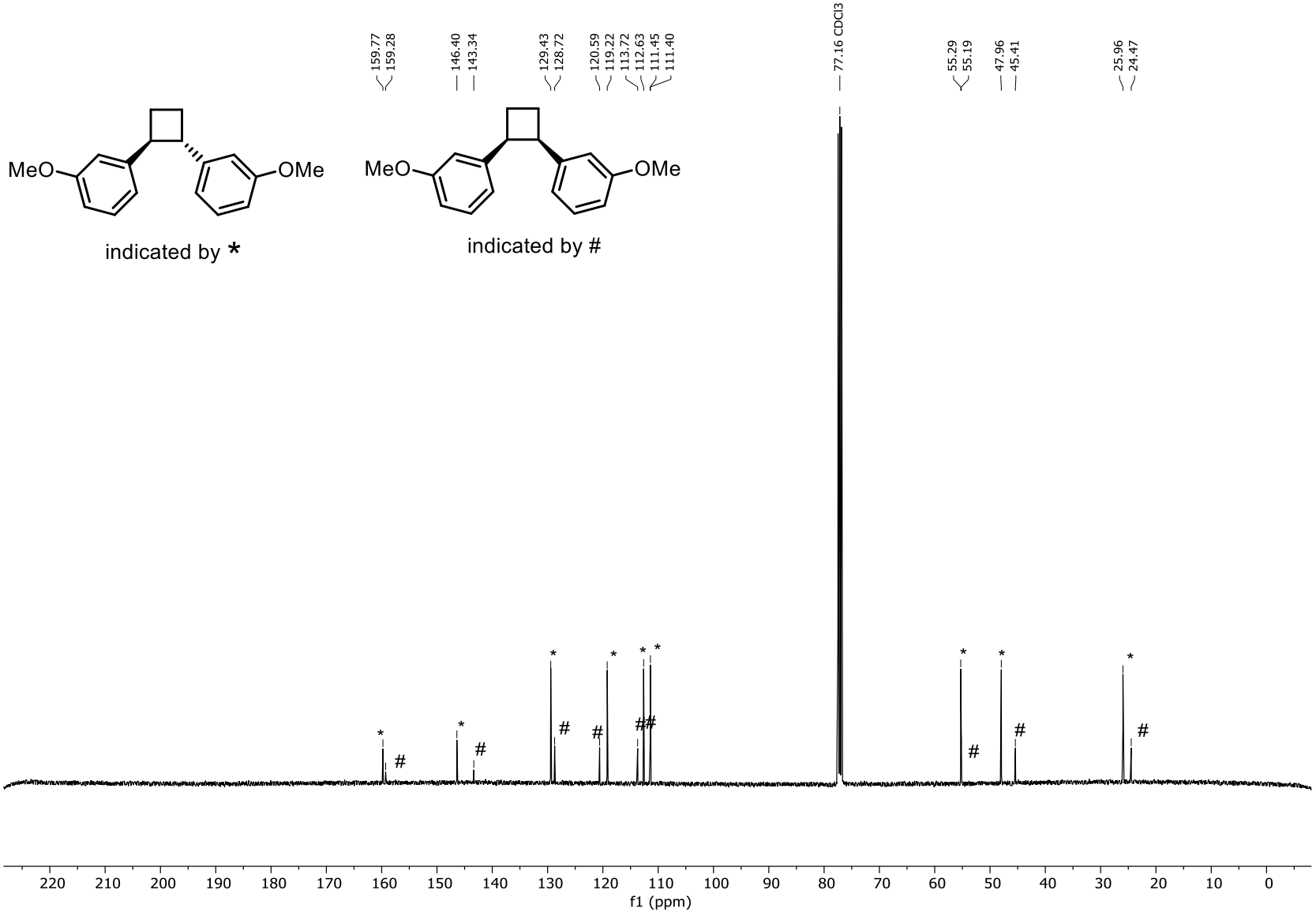
1,2-bis(3-Methoxyphenyl)cyclobutane (2u-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



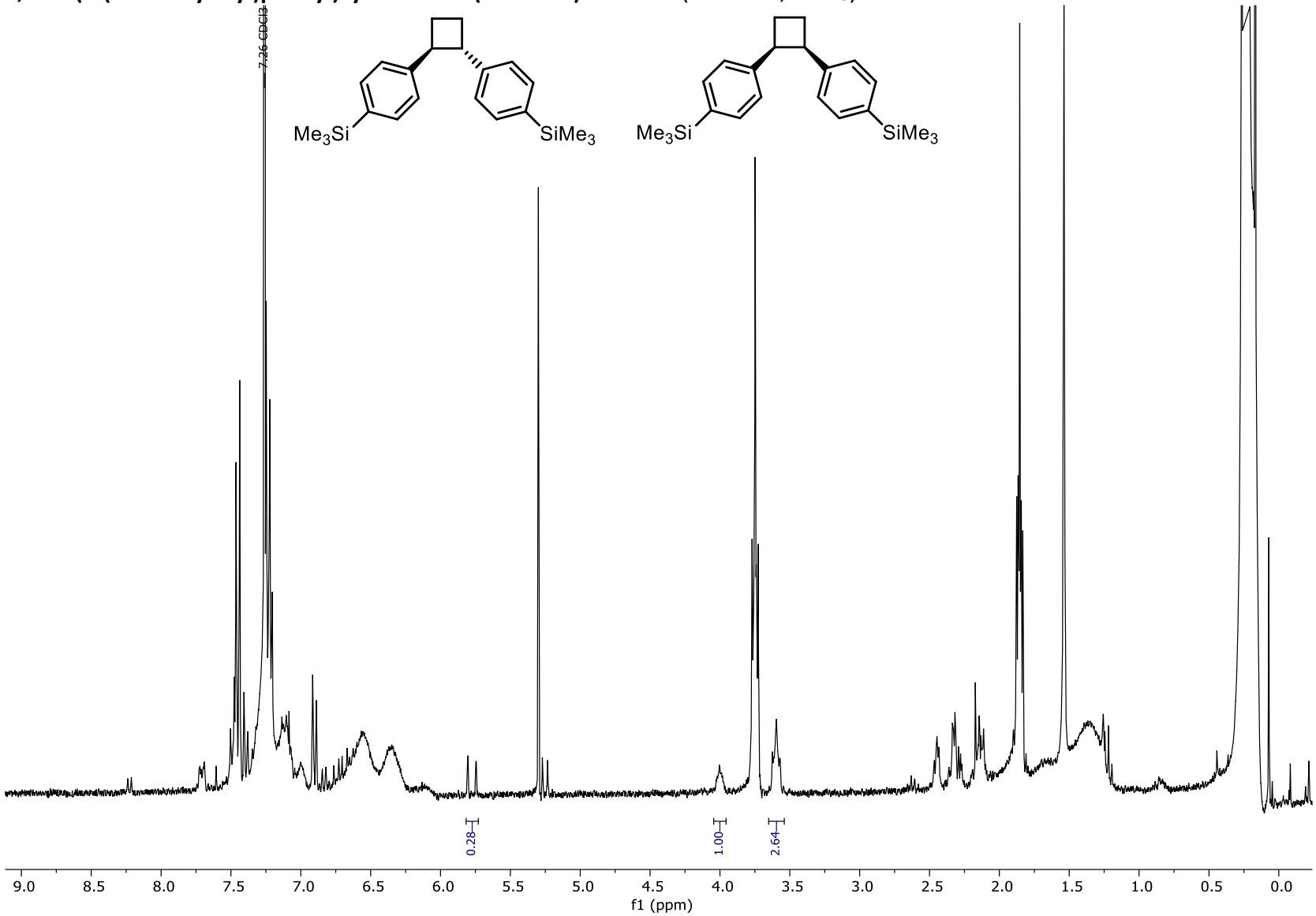
1,2-bis(3-Methoxyphenyl)cyclobutane (2u-trans+2u-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



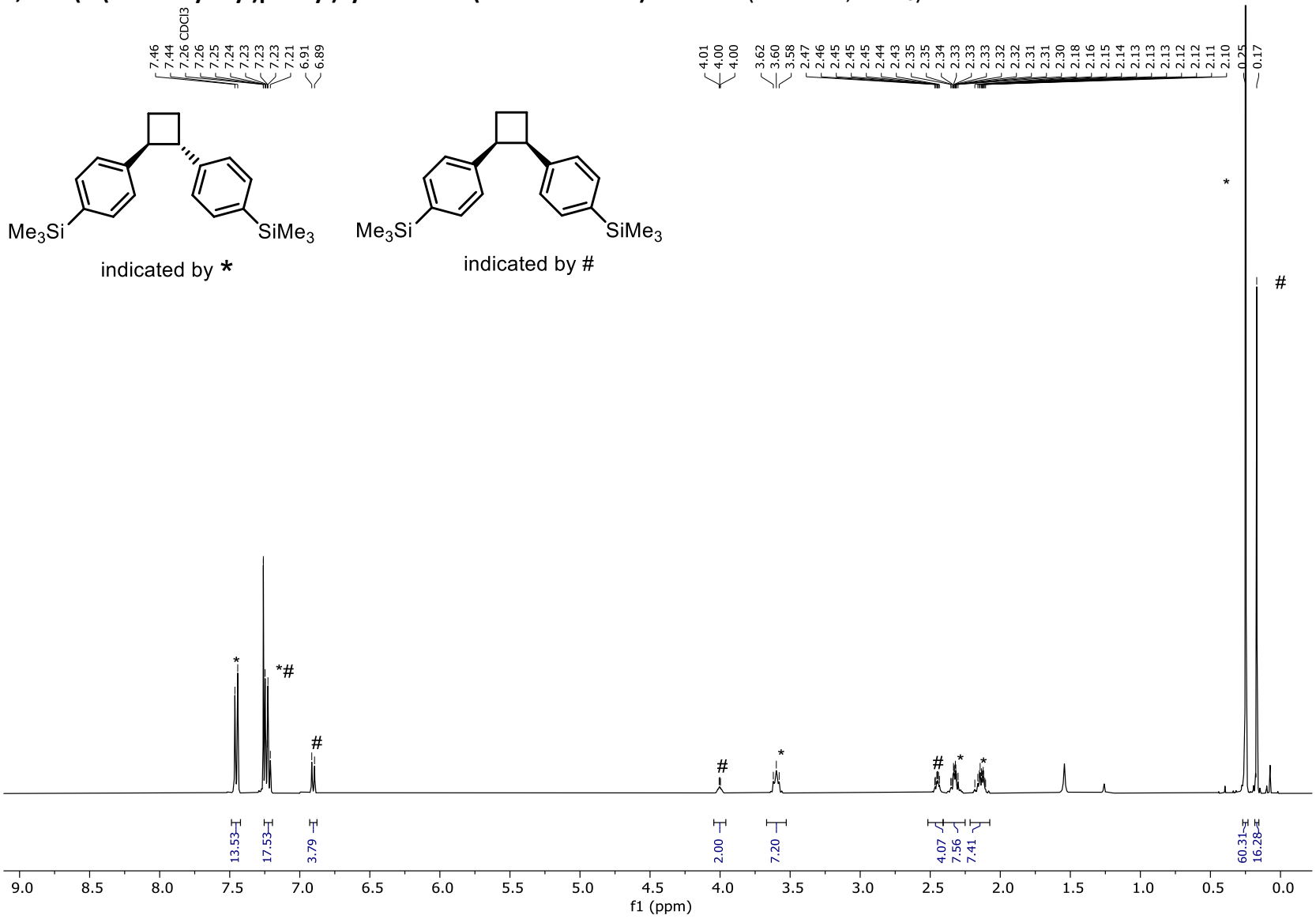
1,2-bis(3-Methoxyphenyl)cyclobutane (2u-trans+2u-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



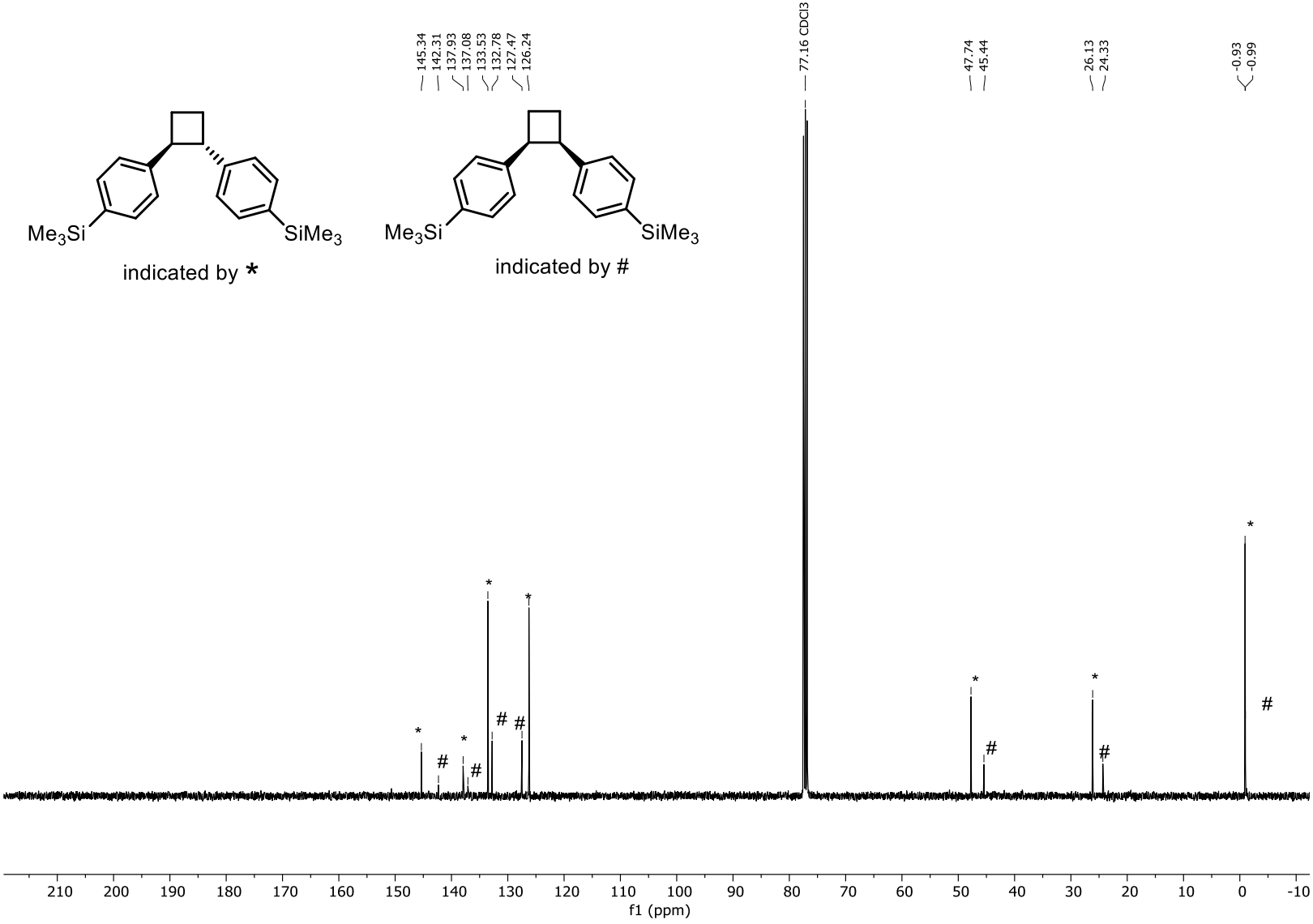
1,2-bis(4-(Trimethylsilyl)phenyl)cyclobutane (2v-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



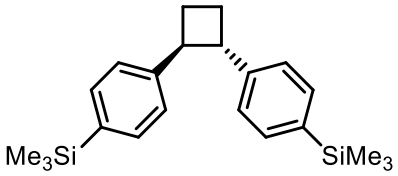
1,2-bis(4-(Trimethylsilyl)phenyl)cyclobutane (2v-trans+2v-cis): ^{1}H NMR (400 MHz, $CDCl_3$)



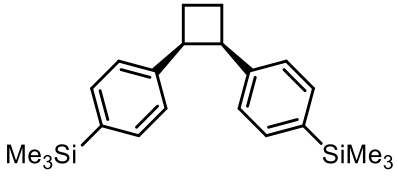
1,2-bis(4-(Trimethylsilyl)phenyl)cyclobutane (2v-trans+2v-cis): 13C{^{1}H} NMR (101 MHz, $CDCl_3$)



1,2-bis(4-(Trimethylsilyl)phenyl)cyclobutane (2v-trans+2v-cis): ^{29}Si NMR (79 MHz, $CDCl_3$)

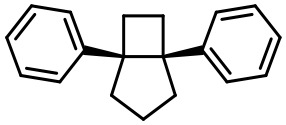


indicated by *

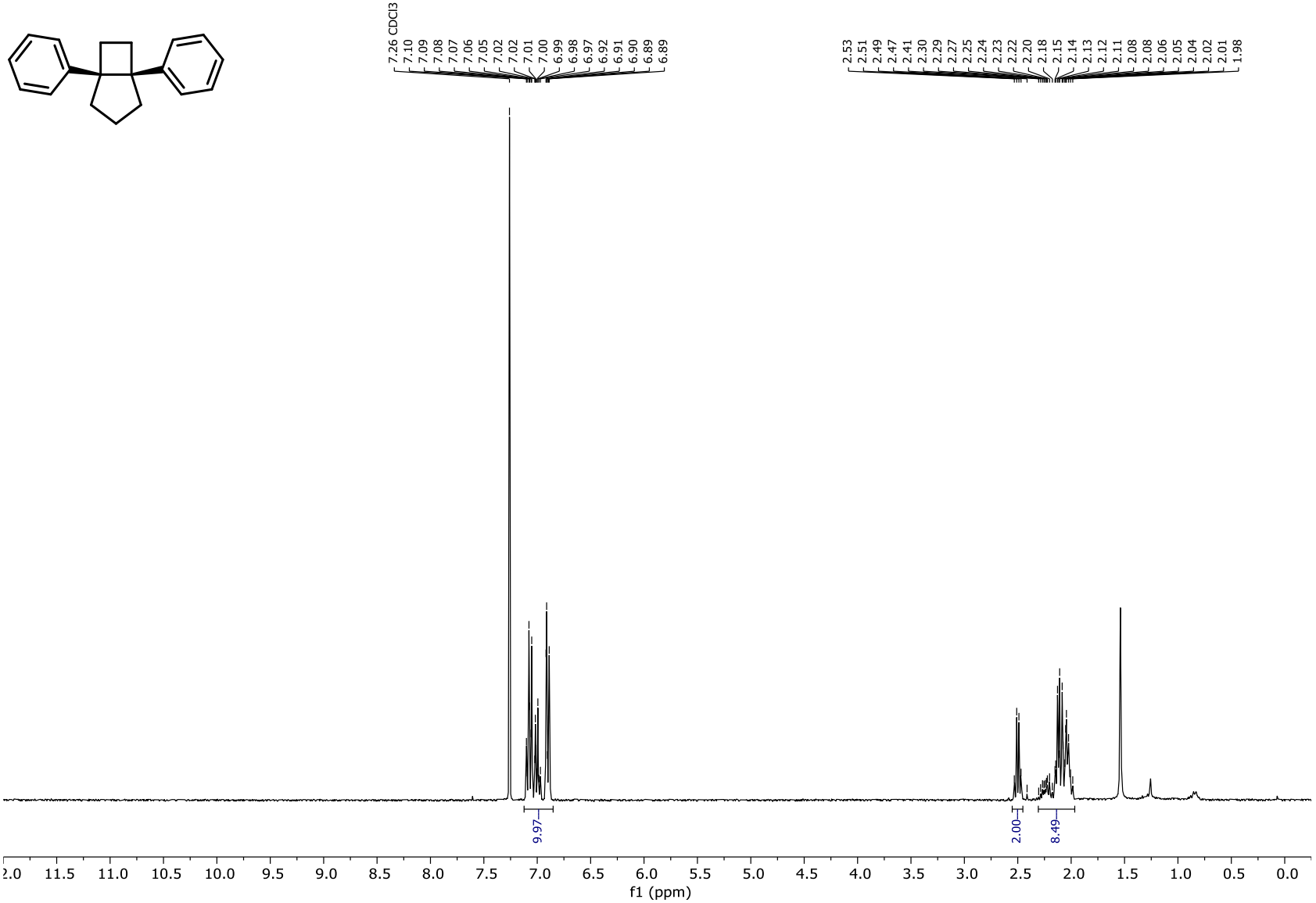


indicated by #

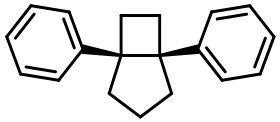
1,5-diphenylbicyclo[3.2.0]heptane (4a-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



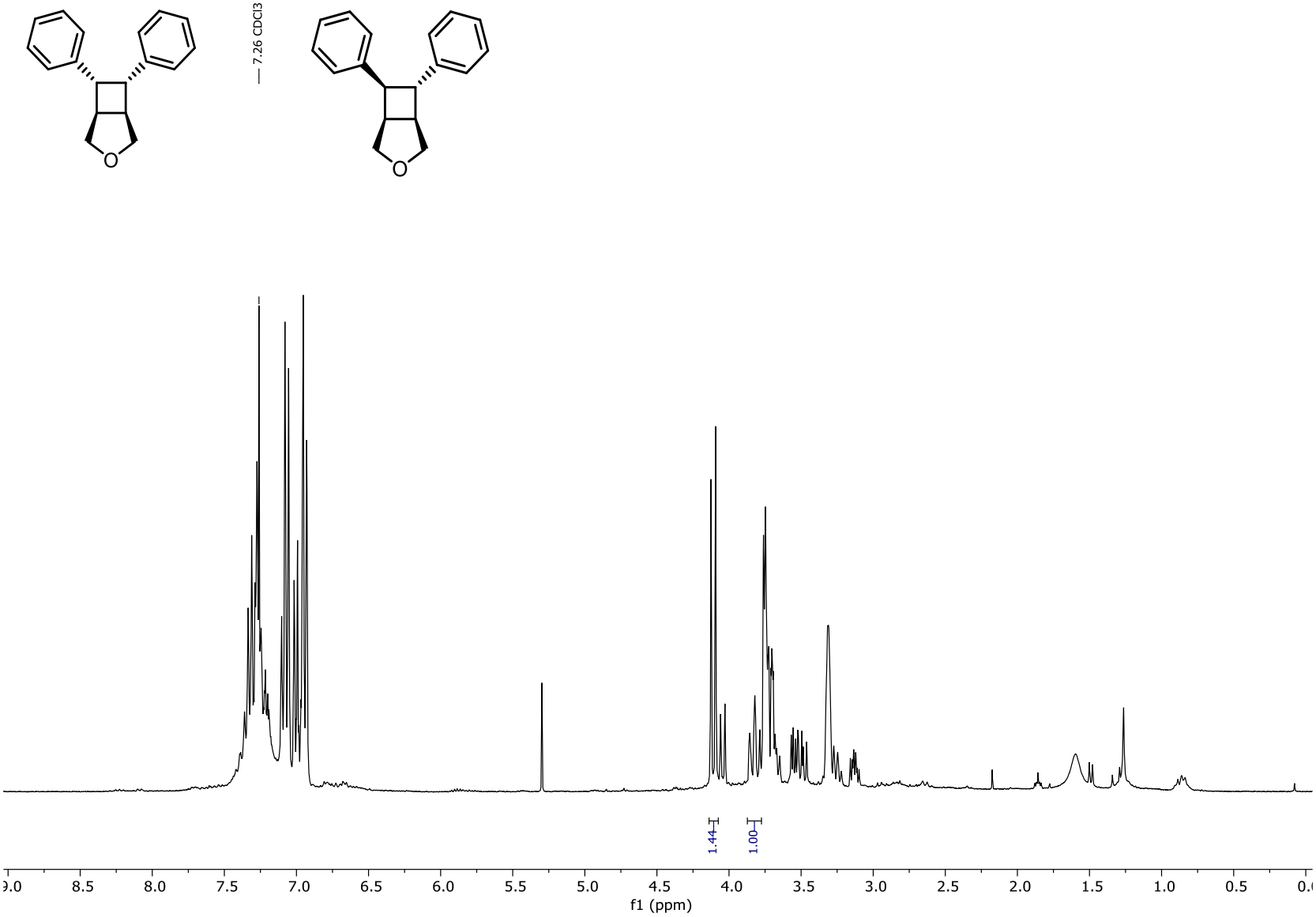
1,5-diphenylbicyclo[3.2.0]heptane (4a): ^{1}H NMR (300 MHz, $CDCl_3$)



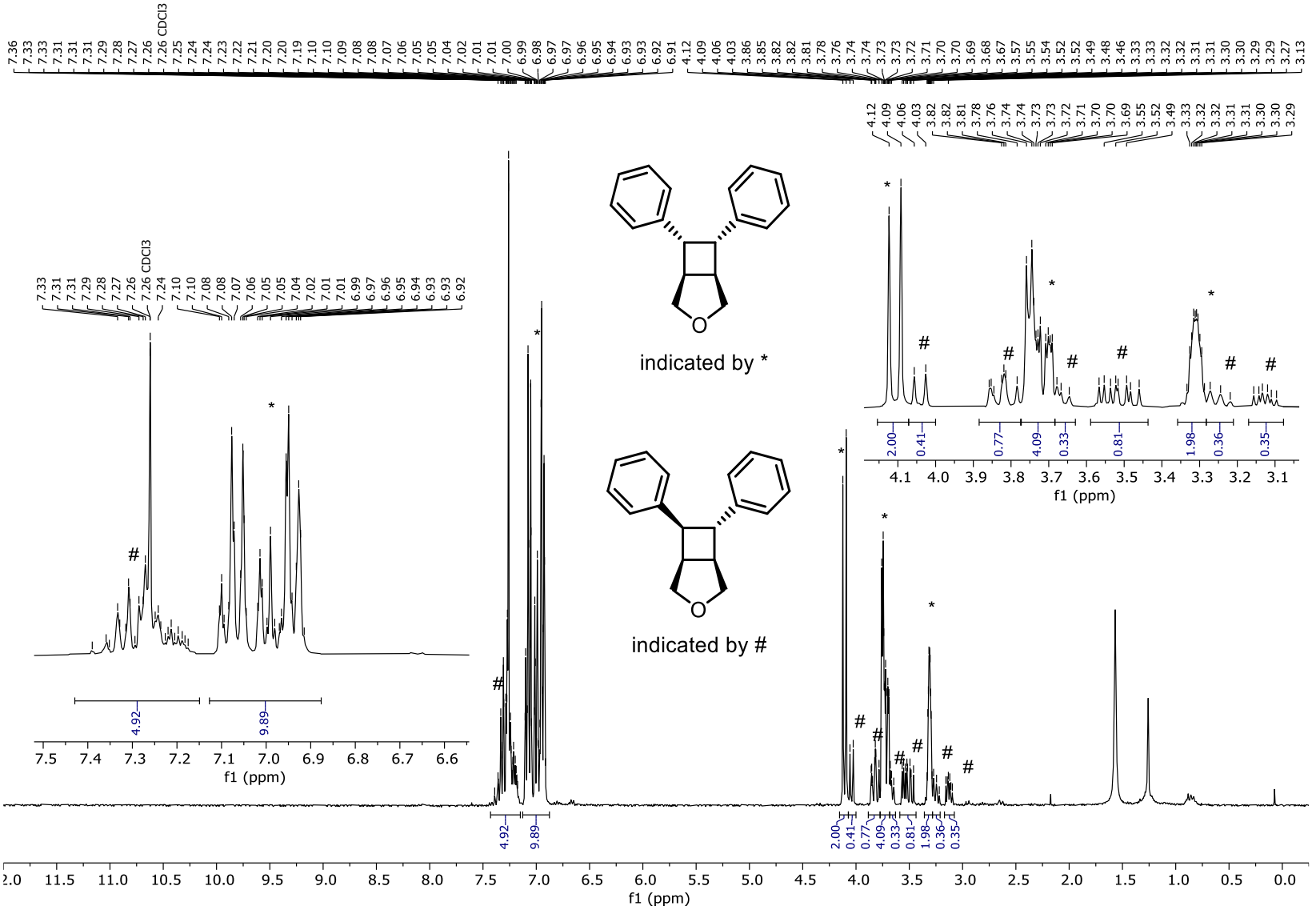
6,7-Diphenyl-3-bicyclo[3.2.0]heptane (4a): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



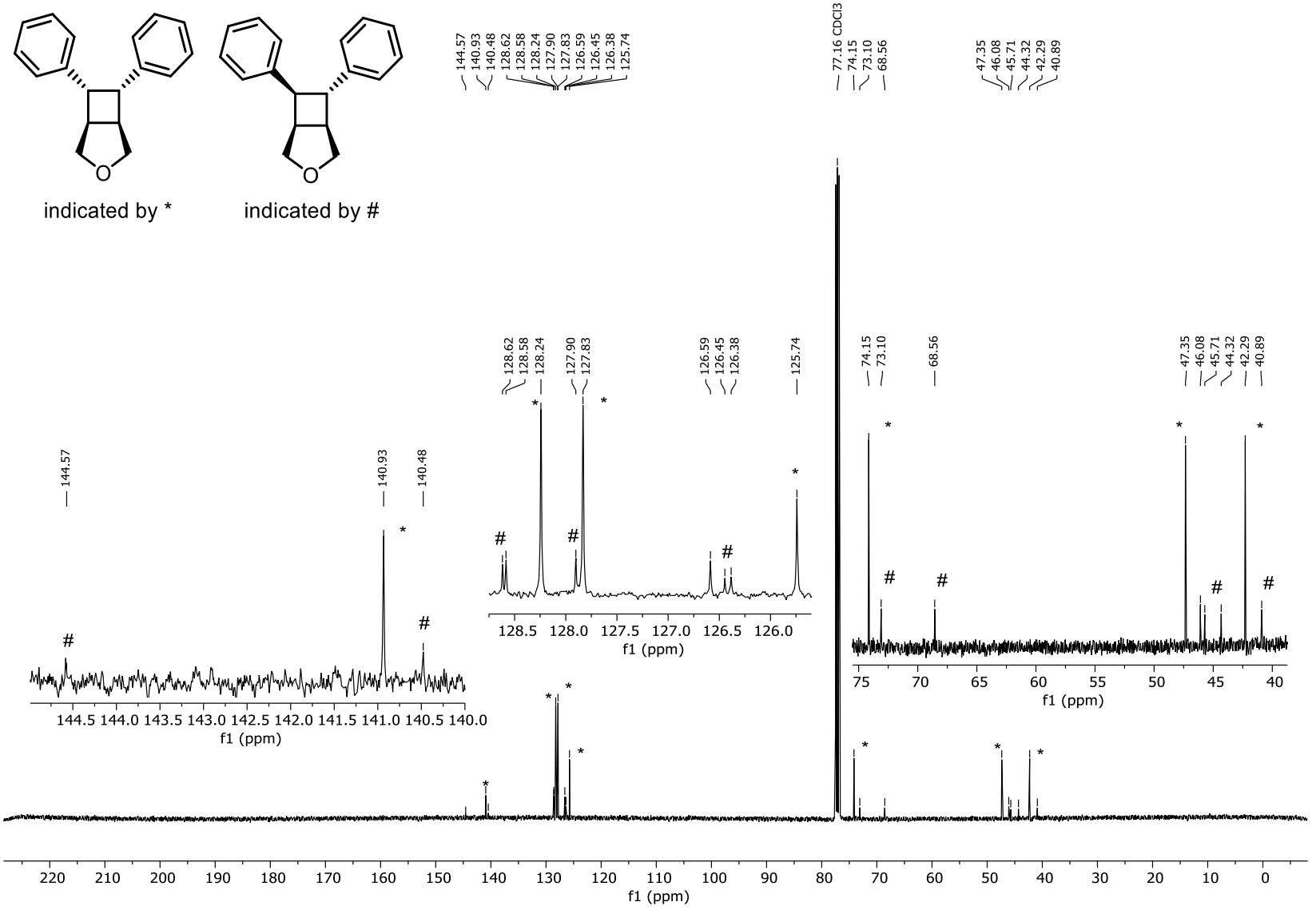
6,7-Diphenyl-3-oxabicyclo[3.2.0]heptane (4b-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



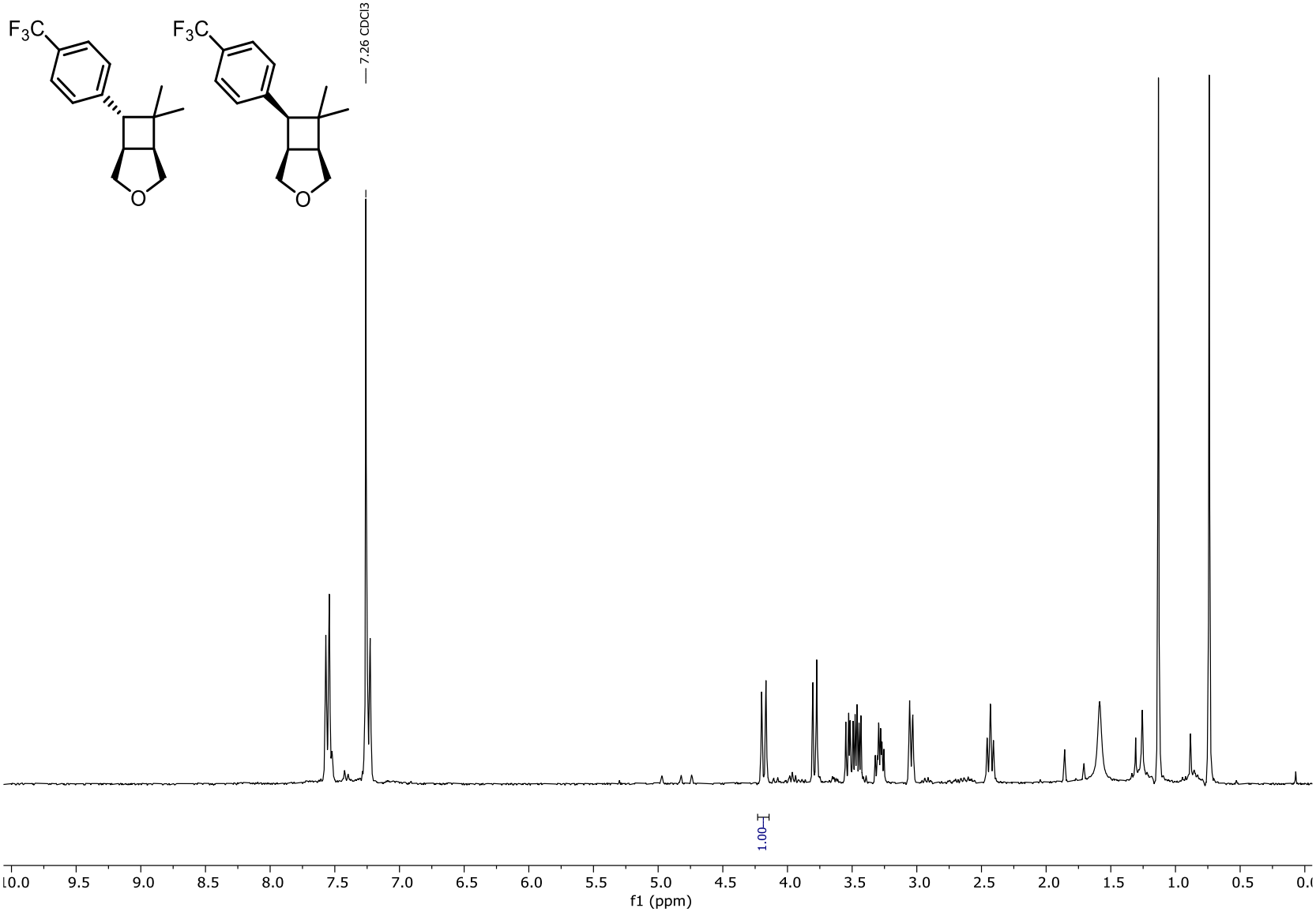
6,7-Diphenyl-3-oxabicyclo[3.2.0]heptane (4b-trans+4b-cis): ^{1}H NMR (300 MHz, $CDCl_3$)



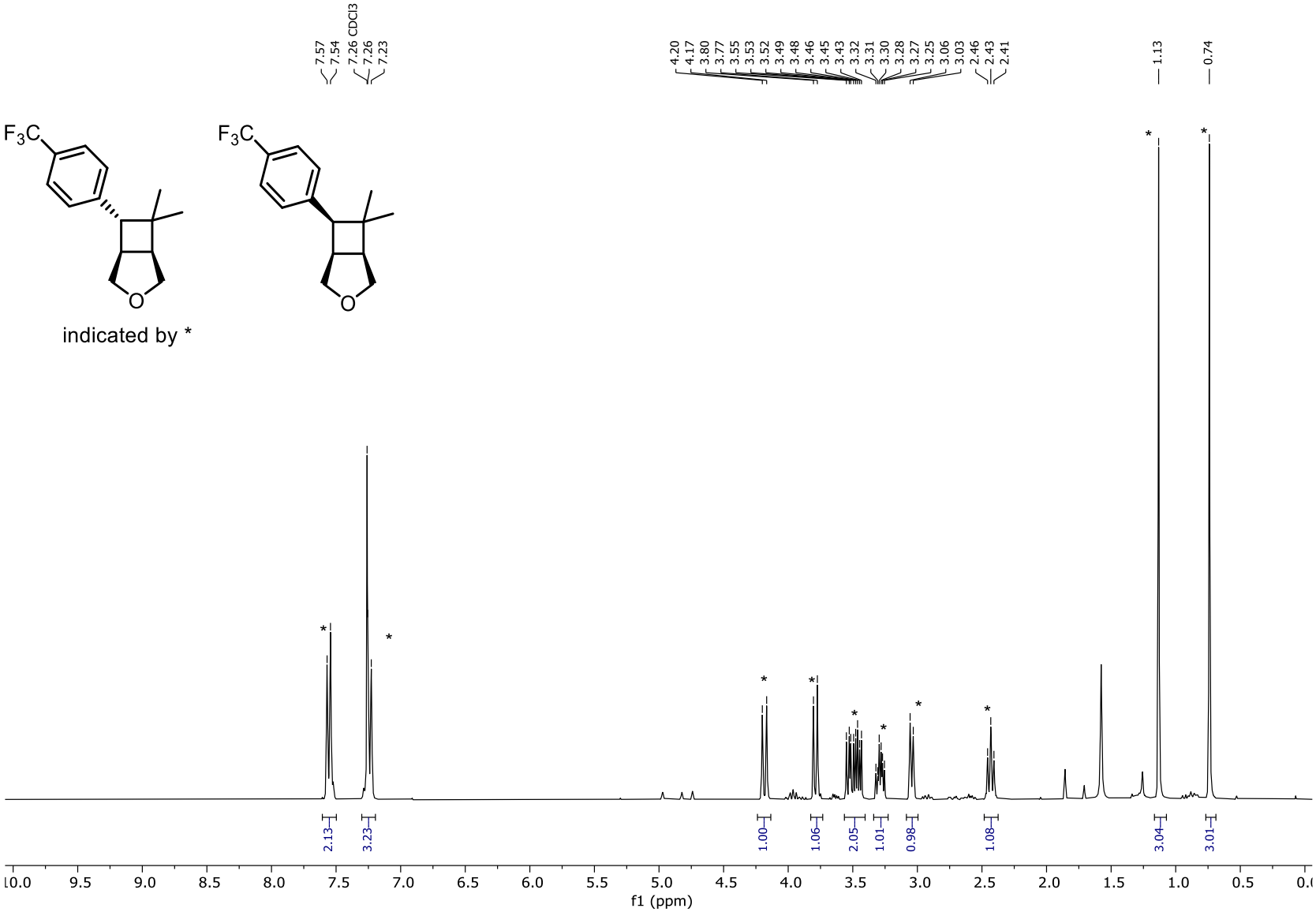
6,7-Diphenyl-3-oxabicyclo[3.2.0]heptane (4b-trans+4b-cis): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



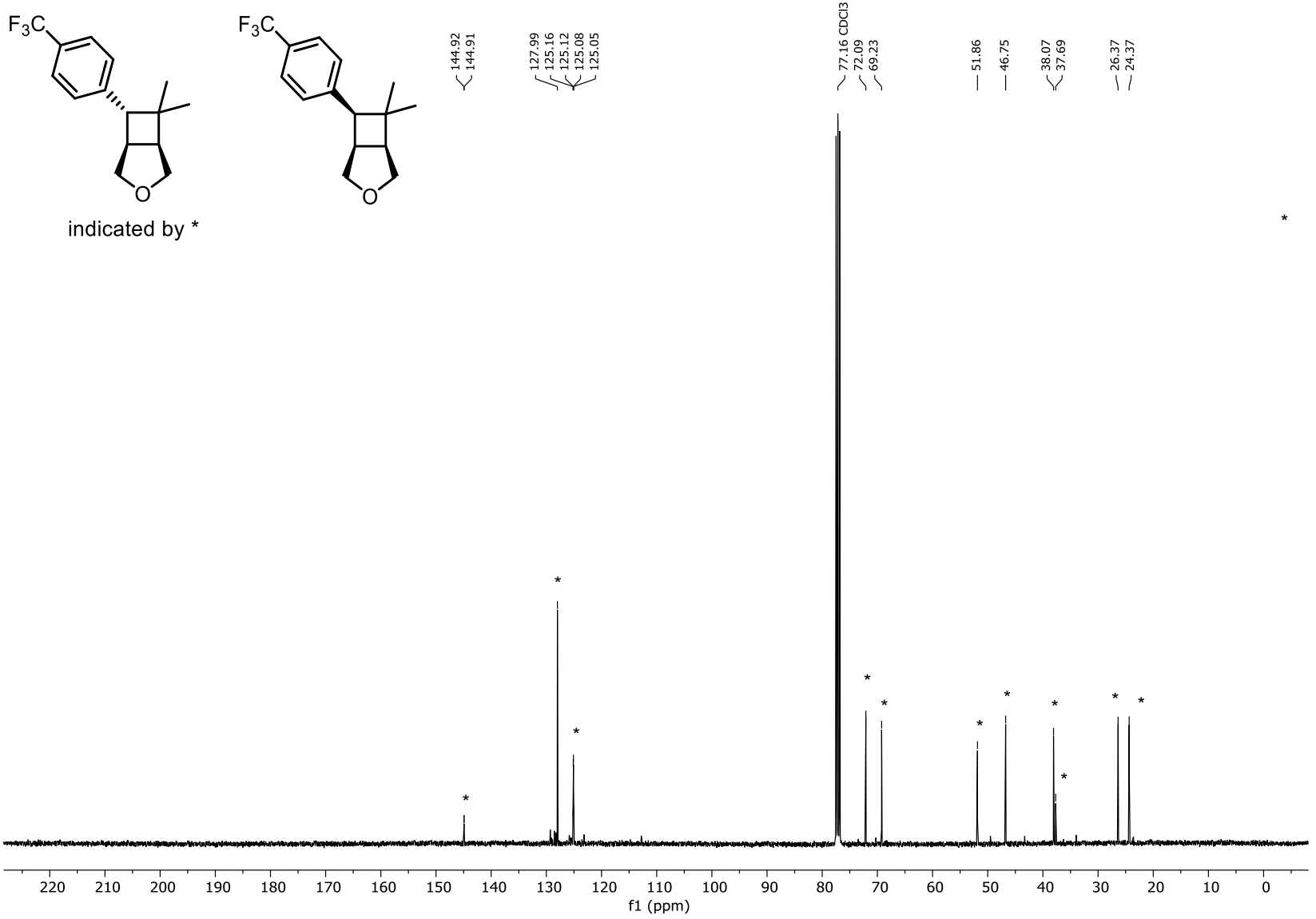
6,6-Dimethyl-7-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.2.0]heptane (4c-crude): ^{1}H NMR (300 MHz, $CDCl_3$)



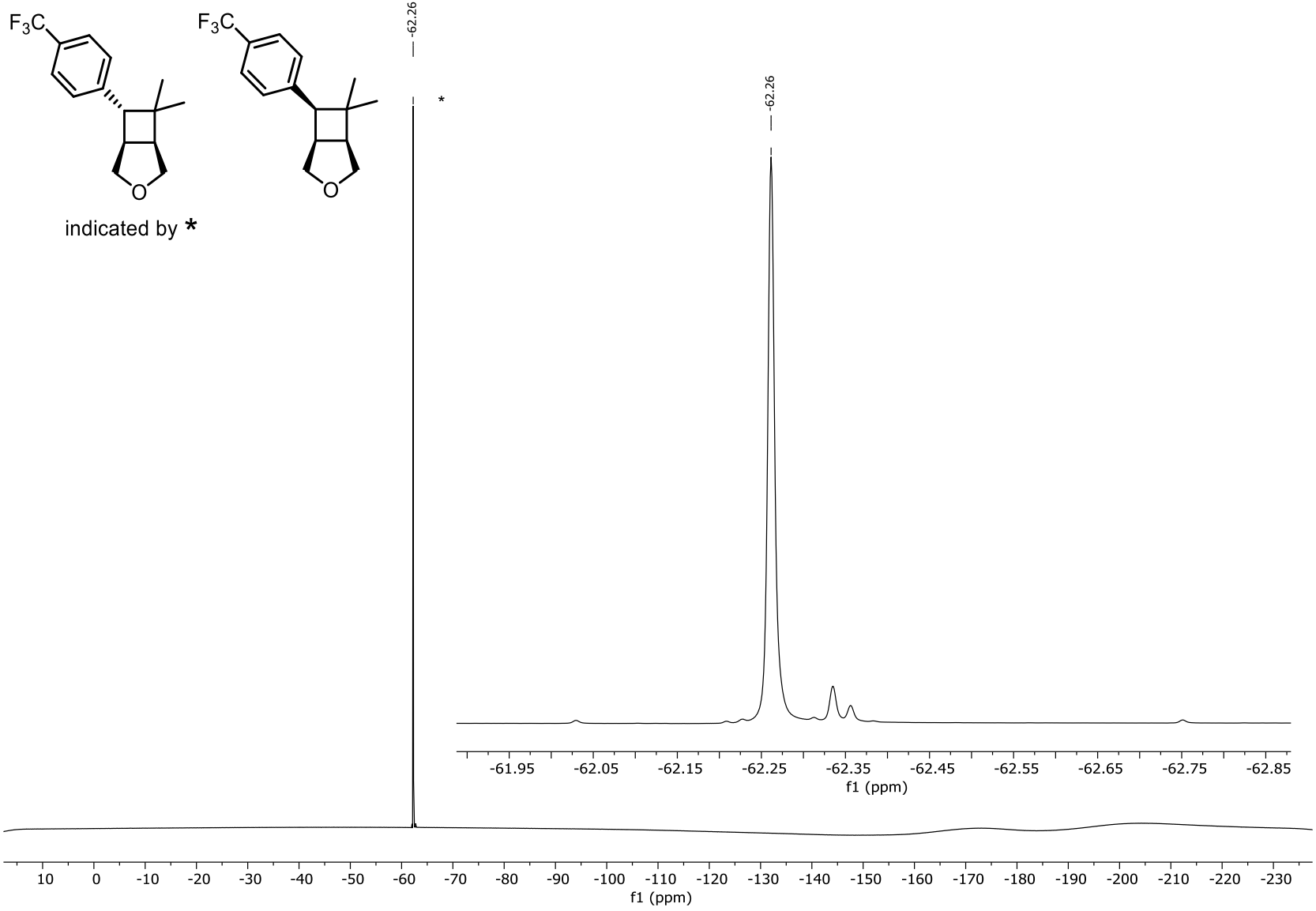
6,6-Dimethyl-7-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.2.0]heptane (4c): ^{1}H NMR (300 MHz, $CDCl_3$)



6,6-Dimethyl-7-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.2.0]heptane (4c): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



6,6-Dimethyl-7-(4-(trifluoromethyl)phenyl)-3-oxabicyclo[3.2.0]heptane (4c): $^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$)



9 Crystallographic Supplement

Refinement table and details for *syn*-1,2-bis(4-nitrophenyl)cyclobutene (**2a-*cis***)

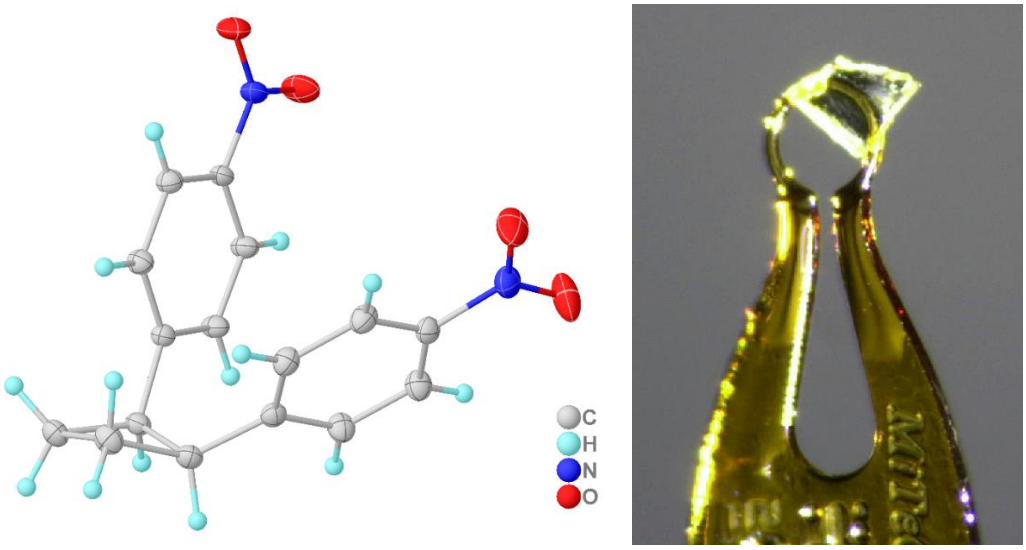


Figure S6. Molecular structure of **2a-*cis*** in the solid state and picture of used crystal.

Crystals of **2a-*cis*** were obtained from dichloromethane by evaporation. Ellipsoids drawn at 50% probability level.

Table S6. Crystal data and structure refinement.

CCDC number	2180881	**2Θ range [°]**	4.96 to 67.57 (0.64 Å)
Empirical formula	$C_{16}H_{14}N_2O_4$		
Formula weight	298.29	**Index ranges**	-11 ≤ h ≤ 11 -12 ≤ k ≤ 11 -18 ≤ l ≤ 18
Temperature [K]	100		
Crystal system	triclinic		
Space group (number)	$P\bar{1}$ (2)	**Reflections collected**	50229
***a* [Å]**	7.1562(10)	**Independent reflections**	5481 R_{int} = 0.0261 R_{sigma} = 0.0144
***b* [Å]**	8.2256(10)		
***c* [Å]**	11.8066(16)		
α [°]	92.200(6)	**Completeness to Θ = 25.242°**	99.9 %
β [°]	98.186(4)		
γ [°]	92.324(4)	**Data / Restraints / Parameters**	5481/0/223
Volume [Å^3]	686.65(16)		
Z	2	**Goodness-of-fit on F^2**	1.058
ρ_{calc} [gcm^{-3}]	1.443		
μ [mm^{-1}]	0.105	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0498 wR_2 = 0.1375
***F*(000)**	312		
Crystal size [mm^3]	0.204×0.17×0.116	**Final *R* indexes [all data]**	R_1 = 0.0554 wR_2 = 0.1428
Crystal colour	colorless		
Crystal shape	block	**Largest peak/hole [eÅ^{-3}]**	0.77/-0.32
Radiation	MoK_α (λ=0.71073 Å)		

Refinement table and details for *anti*-1,2-bis(4-nitrophenyl)cyclobutene (**2a-*trans***)

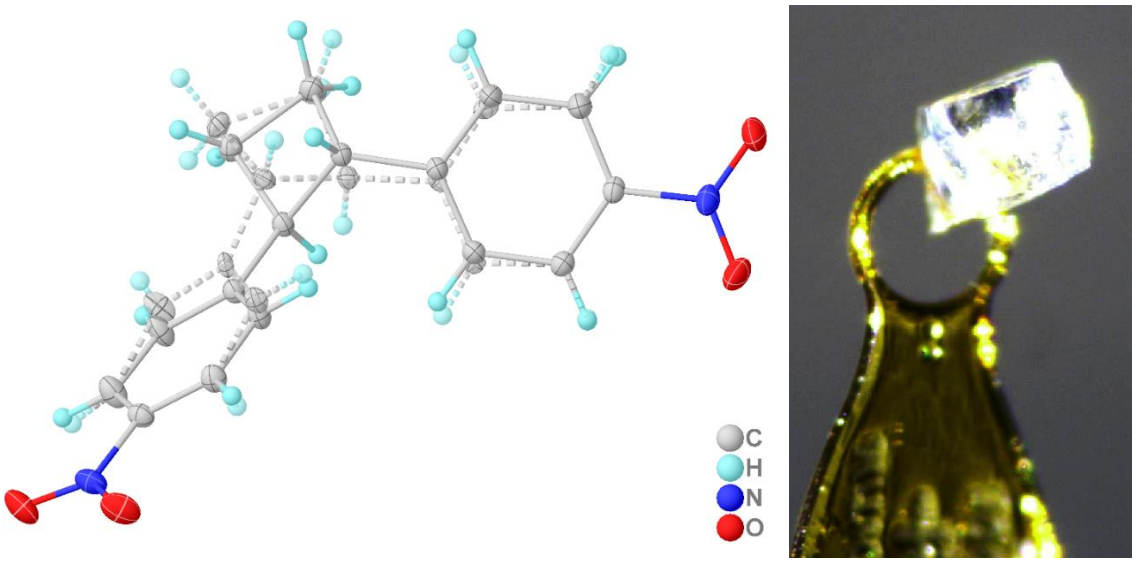


Figure S7. Molecular structure of **2a-*trans*** in the solid state and picture of used crystal.

Crystals of **2a-*trans*** were obtained from dichloromethane by evaporation. Ellipsoids drawn at 50% probability level; minor part of disorder drawn translucent with stippled bonds; the asymmetric unit consists of half of the C2-symmetric molecule, the second half is generated by symmetry operation 1-X,Y,3/2-Z.

Table S7. Crystal data and structure refinement.

CCDC number	2180882	**2Θ range [°]**	5.47 to 72.68 (0.60 Å)
Empirical formula	$C_{16}H_{14}N_2O_4$		
Formula weight	298.29	**Index ranges**	-17 ≤ h ≤ 17 -19 ≤ k ≤ 19 -20 ≤ l ≤ 20
Temperature [K]	100		
Crystal system	monoclinic		
Space group (number)	$C2/c$ (15)	**Reflections collected**	47838
***a* [Å]**	10.3245(7)	**Independent reflections**	3416 R_{int} = 0.0187 R_{sigma} = 0.0081
***b* [Å]**	11.6312(8)		
***c* [Å]**	12.5817(6)		
α [°]	90	**Completeness to Θ = 25.242°**	100.0 %
β [°]	110.206(2)		
γ [°]	90	**Data / Restraints / Parameters**	3416/18/146
Volume [Å^3]	1417.91(15)		
Z	4	**Goodness-of-fit on *F*^{2}**	1.041
ρ_{calc} **[gcm^{-3}]**	1.397		
μ **[mm^{-1}]**	0.102	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0355 wR_2 = 0.1099
***F*(000)**	624		
Crystal size [mm^3]	0.349×0.277×0.27	**Final *R* indexes [all data]**	R_1 = 0.0367 wR_2 = 0.1110
Crystal colour	colorless		
Crystal shape	block	**Largest peak/hole [eÅ^{-3}]**	0.49/-0.19
Radiation	MoK_α (λ=0.71073 Å)		

Refinement table and details for *cis-transoid-cis*-Cyclobuta(1,2-*a*;4,3-*a*')di-indene (**2l-*trans***)

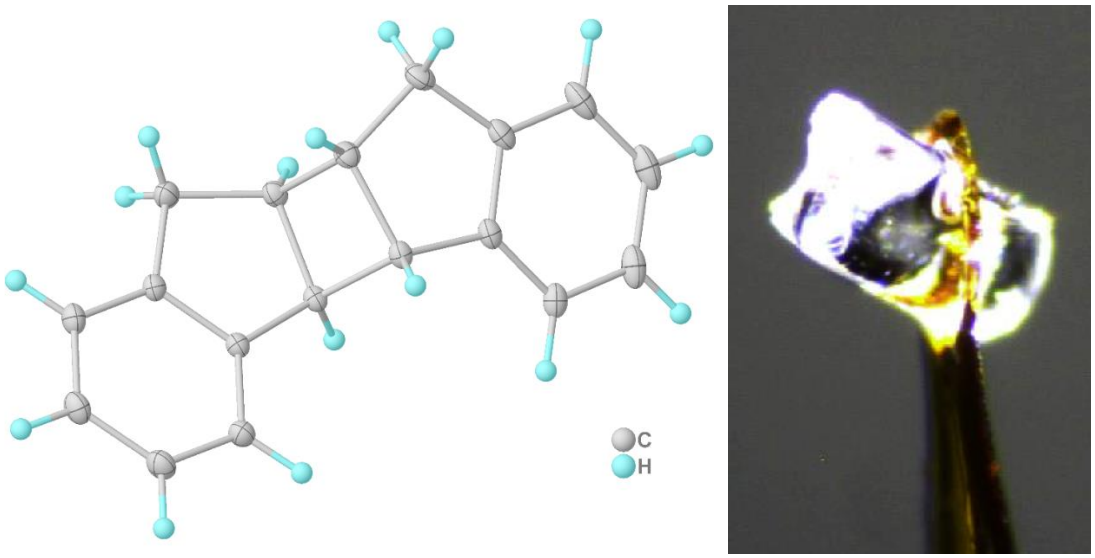


Figure S8. Molecular structure of **2l-*trans*** in the solid state and picture of used crystal.

Crystals of **2l-*trans*** were obtained from dichloromethane solution by cooling down in a fridge. Ellipsoids drawn at 50% probability level. This compound is already present in the CCDC as KERGAP,[31] however, the data obtained in this study is of higher resolution and was therefore also deposited.

Table S8. Crystal data and structure refinement.

CCDC number	2183059	**2θ range [°]**	5.21 to 95.62 (0.48 Å)
Empirical formula	$C_{18}H_{16}$		
Formula weight	232.31	**Index ranges**	−25 ≤ h ≤ 25 −28 ≤ k ≤ 28 −30 ≤ l ≤ 30
Temperature [K]	100		
Crystal system	orthorhombic		
Space group (number)	$Pbca$ (61)	**Reflections collected**	191722
***a* [Å]**	12.3957(13)	**Independent reflections**	11922 R_{int} = 0.0316 R_{sigma} = 0.0117
***b* [Å]**	13.8050(16)		
***c* [Å]**	14.7027(12)		
α [°]	90	**Completeness to θ = 25.242°**	99.8 %
β [°]	90		
γ [°]	90	**Data / Restraints / Parameters**	11922/0/211
Volume [Å^3]	2516.0(4)		
Z	8	**Goodness-of-fit on F^2**	1.075
ρ_{calc} **[gcm^{-3}]**	1.227		
μ **[mm^{-1}]**	0.069	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0369 wR_2 = 0.1110
***F*(000)**	992		
Crystal size [mm^3]	0.492×0.252×0.222	**Final *R* indexes [all data]**	R_1 = 0.0436 wR_2 = 0.1161
Crystal colour	colorless		
Crystal shape	block	**Largest peak/hole [eÅ^{-3}]**	0.58/-0.21
Radiation	MoK_α (λ=0.71073 Å)		

Refinement table and details for *trans-transoid-trans*-diethyl-3,4-bis(4-(trifluoromethyl)phenyl)cyclobutane-1,2-dicarboxylate (**2p-*trans***)

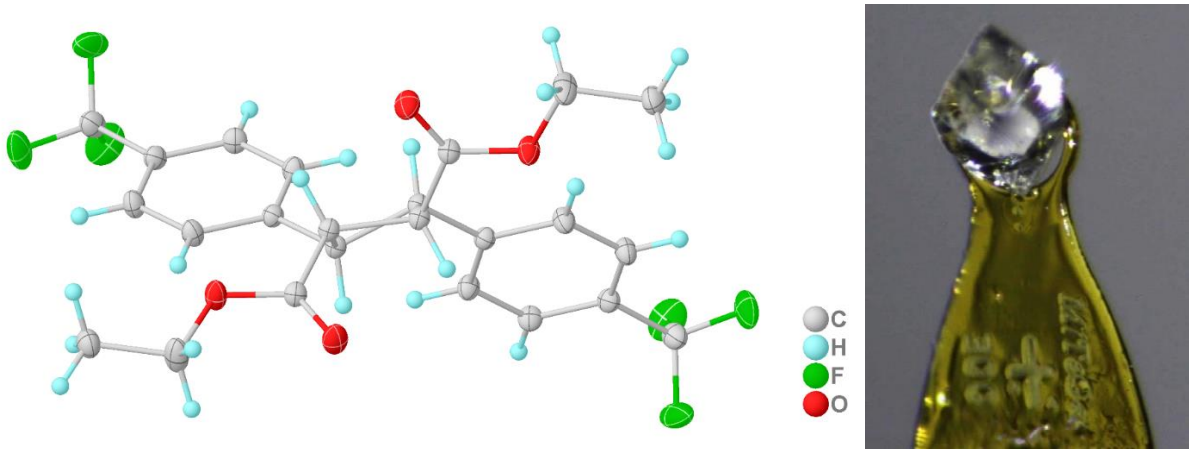


Figure S9. Molecular structure of **2p-*trans*** in the solid state and picture of used crystal.

Crystals of **2p-*trans*** were obtained from ethyl acetate by evaporation. Ellipsoids drawn at 50% probability level; the asymmetric unit consists of half of the C2-symmetric molecule, the second half is generated by symmetry operation 1-X,Y,1/2-Z.

Table S9. Crystal data and structure refinement.

CCDC number	2189564	**2θ range [°]**	5.69 to 65.25 (0.66 Å)
Empirical formula	$C_{24}H_{22}F_6O_4$		
Formula weight	488.41	**Index ranges**	−38 ≤ h ≤ 37 −10 ≤ k ≤ 11 −16 ≤ l ≤ 17
Temperature [K]	100.00		
Crystal system	monoclinic		
Space group (number)	$C2/c$ (15)	**Reflections collected**	40906
***a* [Å]**	25.779(2)	**Independent reflections**	3840 R_{int} = 0.0238 R_{sigma} = 0.0117
***b* [Å]**	7.4486(7)		
***c* [Å]**	11.4443(11)		
α [°]	90	**Completeness to θ = 25.242°**	99.9 %
β [°]	93.721(3)		
γ [°]	90	**Data / Restraints / Parameters**	3840/0/155
Volume [Å^3]	2192.9(3)		
Z	4	**Goodness-of-fit on F^2**	1.020
ρ_{calc} [gcm^{-3}]	1.479		
μ [mm^{-1}]	0.133	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0375 wR_2 = 0.1032
***F*(000)**	1008		
Crystal size [mm^3]	0.402×0.358×0.198	**Final *R* indexes [all data]**	R_1 = 0.0400 wR_2 = 0.1057
Crystal colour	colourless		
Crystal shape	block	**Largest peak/hole [eÅ^{-3}]**	0.45/-0.38
Radiation	MoK_α (λ=0.71073 Å)		

Refinement table and details for 1.6. cis-transoid-cis-Diethyl-3,4-bis(4-nitrophenyl)cyclobutane-1,2-dicarboxylate (**2o-*cis***)

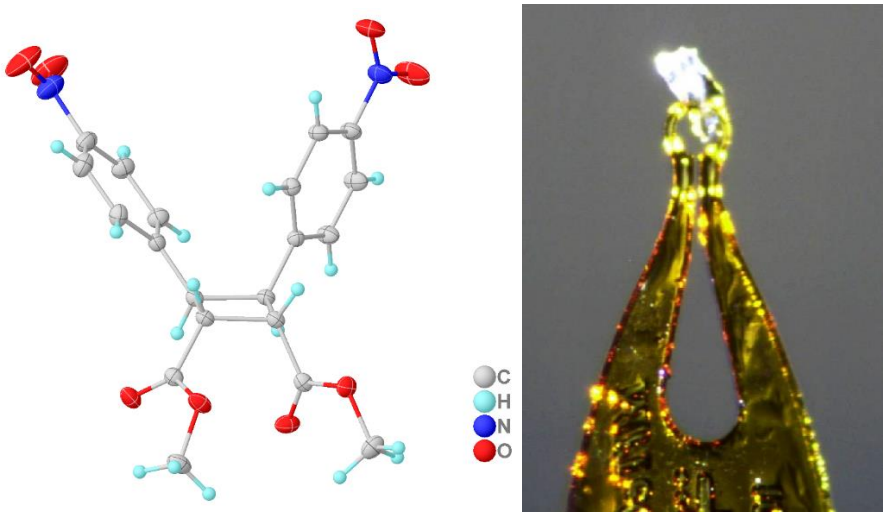


Figure S10. Molecular structure of **2o-*cis*** in the solid state and picture of used crystal.

Crystals of **2o-*cis*** were obtained from ethyl acetate by evaporation. Ellipsoids drawn at 50% probability level.

Table S10. Crystal data and structure refinement.

CCDC number	2189565	**2θ range [°]**	4.32 to 61.05 (0.70 Å)
Empirical formula	$C_{20}H_{18}N_2O_8$		
Formula weight	414.36	**Index ranges**	−24 ≤ h ≤ 16 −33 ≤ k ≤ 34 −14 ≤ l ≤ 14
Temperature [K]	100.00		
Crystal system	monoclinic		
Space group (number)	$C2/c$ (15)	**Reflections collected**	39708
***a* [Å]**	16.8641(17)	**Independent reflections**	5801 R_{int} = 0.0402 R_{sigma} = 0.0288
***b* [Å]**	24.249(4)		
***c* [Å]**	10.4378(18)		
α [°]	90	**Completeness to θ = 25.242°**	99.9 %
β [°]	116.424(4)		
γ [°]	90	**Data / Restraints / Parameters**	5801/0/274
Volume [Å^3]	3822.4(10)		
Z	8	**Goodness-of-fit on *F*^{2}**	1.079
ρ_{calc} [gcm^{-3}]	1.440		
μ [mm^{-1}]	0.113	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0456 wR_2 = 0.1058
***F*(000)**	1728		
Crystal size [mm^3]	0.272×0.144×0.059	**Final *R* indexes [all data]**	R_1 = 0.0670 wR_2 = 0.1234
Crystal colour	colourless		
Crystal shape	plate	**Largest peak/hole [eÅ^{-3}]**	0.37/-0.27
Radiation	MoK_α (λ=0.71073 Å)		
		Extinction coefficient	0.0032(3)

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