Supporting Information

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.

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, ^{13}C NMR spectra at 101 MHz with broadband proton decoupling, ^{19}F NMR spectra at 377 MHz with broadband proton decoupling as stated, ^{11}B NMR spectra at 161 MHz with broadband proton decoupling, ^{29}Si NMR spectra at 99 MHz with broadband proton decoupling as stated. 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 ^{13}C NMR ($CHCl_3$: ^{1}H NMR = 7.26 ppm, $CDCl_3$: ^{13}C NMR = 77.16 ppm). ^{19}F, ^{11}B, and ^{29}Si chemical shifts are given in ppm relative to $CFCl_3$, $BF_3{\cdot}OEt_2$, and Me_4Si (external standards). Chemical shifts are reported to 0.01 ppm for ^{1}H, ^{19}F, ^{11}B, and ^{29}Si NMR spectra and to 0.1 ppm for ^{13}C NMR. 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 (if not noted otherwise) 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*; for sensitive samples the *X-TEMP 2 System* was used for picking of crystals[4]; crystals were cooled to given temperature with *Cryostream 800* from *Oxford Cryosystems*.
Refinement with non-spherical structure factors was carried out with NoSpherA2 as implemented in OLEX2 using olex.refine.[5] The wavefunction for calculation of non-spherical atomic form factors was done at B3LYP/def2-TZVP level of theory and reiterated during refinement until converged.

Identifier	CCDC number	Identifier	CCDC number
2a	2262000	**2r**	2289325
2g	2262001	**2s**	2289324
2n	2289323	**2ab**	2261999

Cyclic Voltammetry
Cyclic voltammetry measurements were performed with a Gamry 1010 T using Gamry Framework Software. A standard three electrodes setup was used with a glassy carbon working electrode (ALS 013714, ZL722, 6×3 mm), a platinum disc counter electrode (ALS 002422, AE077, 6×3 mm) and an SCE reference electrode (ALS 013693, RE-2BP Calomel reference electrode).

Specific Rotation
Specific rotation measurements were performed on a *Jasco* P-2000 polarimeter equipped with a Na/Hg lamp (λ = 589 nm) using a 1.00 dm quartz sample cell at the stated temperature and concentration. The specific rotation is given in degree (°) as the mean value over five measurements.

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,6 2CzPN,7 and 3DPA2FBN8 were prepared using literature procedures. $[Ru(bpy)_3]Cl_2$ and $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (*Sigma Aldrich* and *TCI*) were purchased from the indicated supplier and used as received.

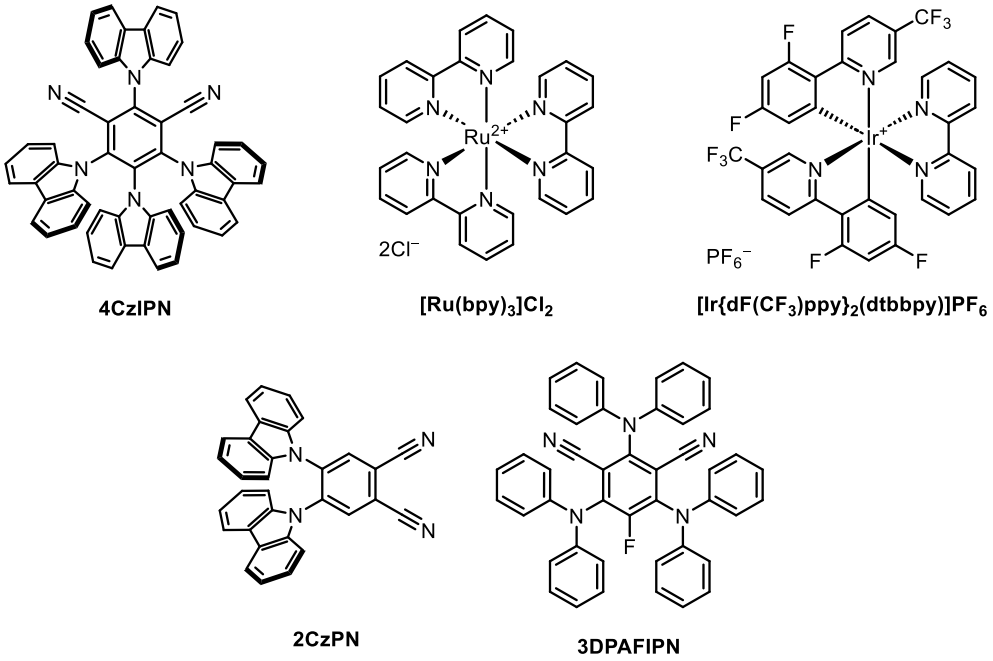
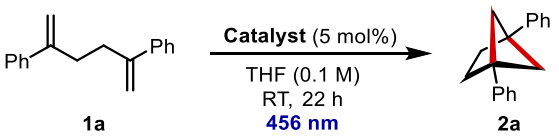


Figure S1. Catalysts used in reaction optimisation.

Table S1. Initial catalyst screening

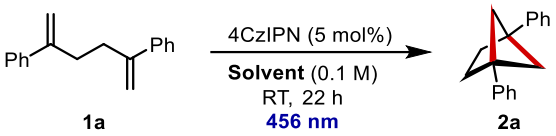


Entry	Catalyst	Conversion (%)[a]	Yield (%)[b]
1	$[Ru(bpy)_3]Cl_2$	<5	n.d.
2	4CzIPN	14	n.d.
3	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$	**>95**	**n.d.**
4	2CzPN	13	n.d.
5	3DPAFIPN	<5	n.d.

Reactions performed with 10 mg of diene **1a**. [a] Conversion estimated by ^{1}H NMR spectroscopy relative to unreacted diene **1a**. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard. n.d = not determined.

We initially elected to continue optimisation with 4CzIPN as the lower yield for this catalyst would allow us to better assess the impact of other variables and due to the lower cost of the catalyst.

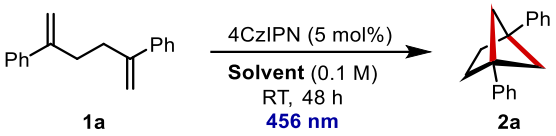
Table S2. Solvent screening with a reaction time of 22 hours



Entry	Solvent	Conversion (%)[a]	Yield (%)[b]
1	THF	14	n.d.
2	DMSO	4	n.d.
3	$CHCl_3$	7	n.d.
4	CH_2Cl_2	15	n.d.
5	MeCN	18	n.d.

Reactions performed with 10 mg of diene **1a**. [a] Conversion estimated by ^{1}H NMR spectroscopy relative to unreacted diene **1a**. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard. n.d = not determined.

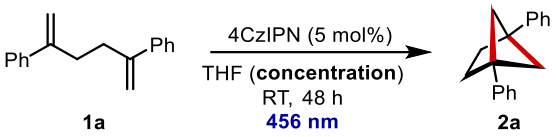
Table S3. Solvent screening with a reaction time of 48 hours



Entry	Solvent	Conversion (%)[a]	Yield (%)[b]
1	**THF**	**83**	**55**
2	$CHCl_3$	9	8
3	CH_2Cl_2	23	18
4	MeCN	35	22

Reactions performed with 10 mg of diene **1a**. [a] Conversion estimated by ^{1}H NMR spectroscopy relative to unreacted diene **1a**. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard.

Table S4. Solvent concentration optimisation (reactions performed with 50 mg of **1a**)

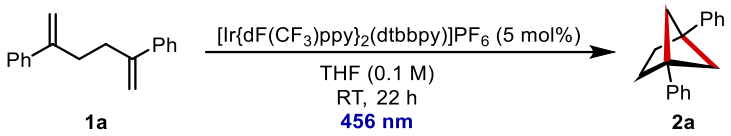


Entry	Concentration (M)	Conversion (%)[a]	Yield (%)[b]
1	**0.1**	**25**	**19**
2	0.5	16	11
3	1.0	9	9

Reactions performed with 50 mg of diene **1a**. [a] Conversion estimated by ^{1}H NMR spectroscopy relative to unreacted diene **1a**. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard.

From these experiments (Table S4, Entry 1 vs. Table S3, Entry 1) it is also clear that the performance of 4CzIPN decreases at higher reaction scales. In contrast, $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ demonstrates excellent reactivity, even on 1.00 mmol scale (see Table S5).

Table S5. Control experiments

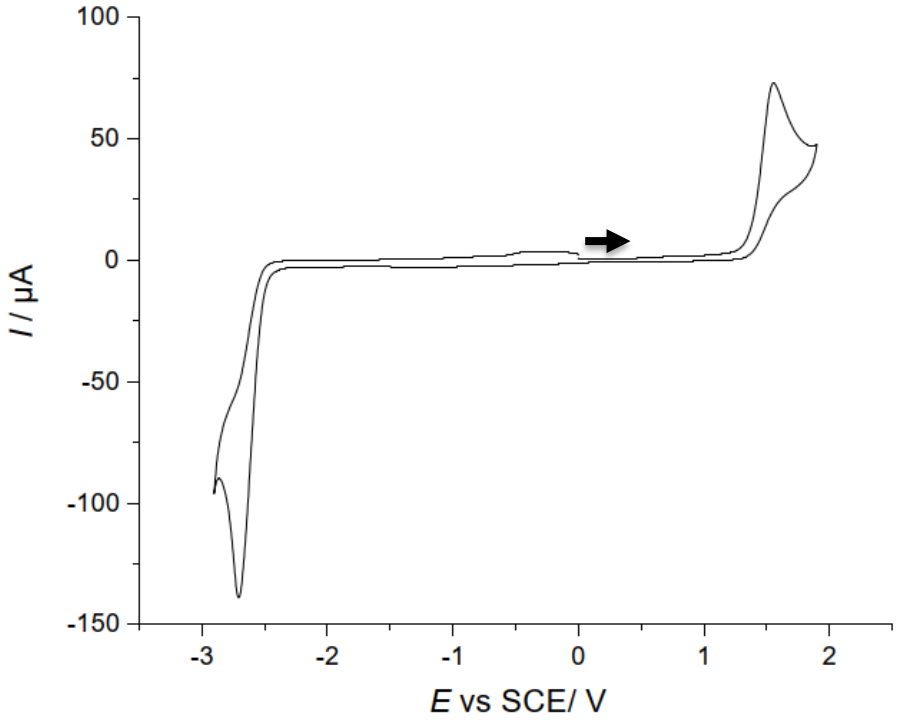


1a 2a

Entry	Deviation from standard conditions	Conversion (%)[a]	Yield (%)[b]
1	none	>95	94[c]
2	1 mol% [Ir], 10 mg **1a**	27	n.d.
3	1 mol% [Ir], 10 mg **1a**, 0.5 M	63	54[d]
4	1 mol% [Ir], 10 mg **1a**, 0.05 M	26	27[d]
5	No photocatalyst	<5	n.d.
6	Reaction in the dark	<5	n.d.
7	1.00 eq. isoprene	n.d.	46
8	1.00 mmol **1a**, 66 h	n.d.	91

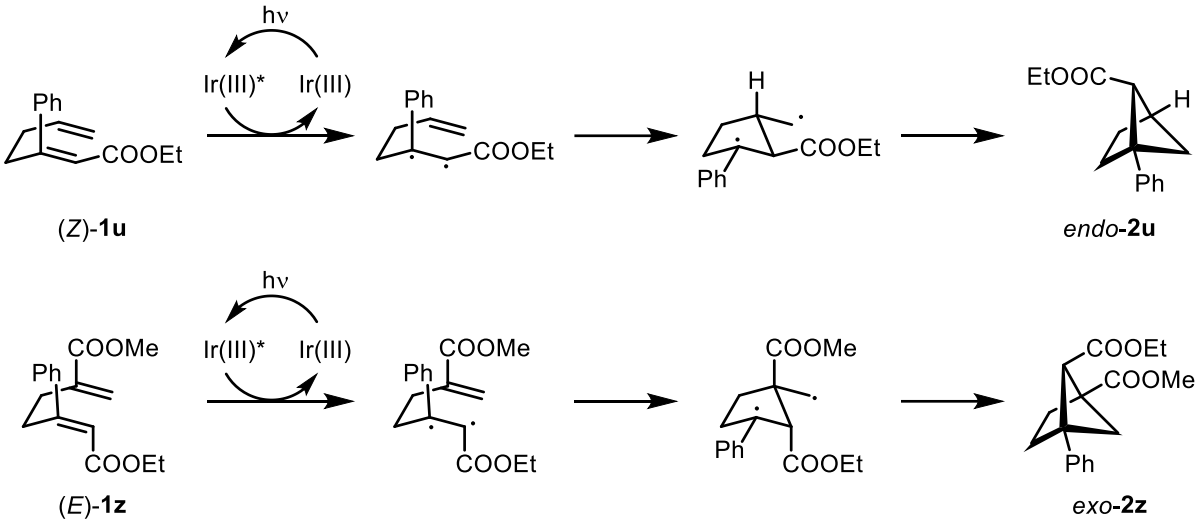
Reactions performed with 42 mg of diene **1a**. [a] Conversion estimated by ^{1}H NMR spectroscopy relative to unreacted diene **1a**. [b] Yield estimated from the ^{1}H NMR of the reaction mixture relative to 1,3,5-trimethoxybenzene as internal standard. [c] isolated yield. [d] Yield estimated from the ^{1}H NMR of the reaction mixture relative to CH_2Br_2 as internal standard.

3 Cyclic Voltammetry



Cyclic voltammogram of diene **1a**,*v* = 100 mV/s, NBu_4PF_6 (0.2 M) MeCN.

4 Proposed transition states for [2+2] crossed cycloadditions to BCHs 2u and 2z

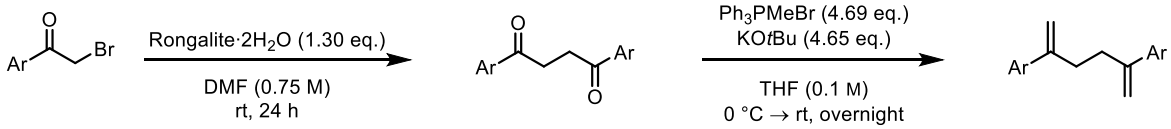


Scheme S1. Proposed transition states for [2+2] crossed cycloadditions to BCHs 2u and 2z.

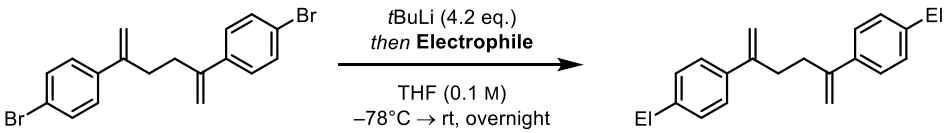
5 Overview of synthetic strategies to dienes 1

Many of the dienes **1** were prepared by similar synthetic routes. The main approaches that were used are summarized below.

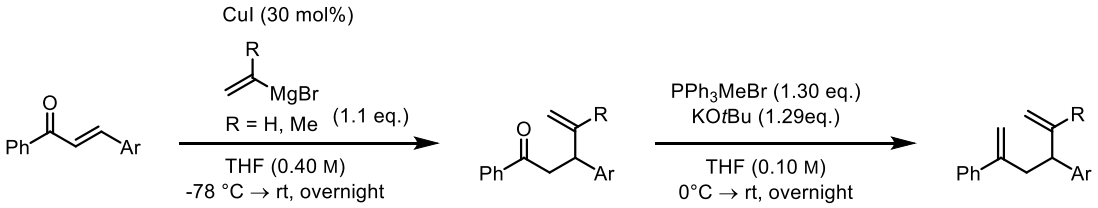
1) Rongalite + Wittig Approach: *Used for dienes* **1a**, **1c**, **1f**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n, 1ab**
Reference: W. F. Jarvis, M. D. Hoey, A. L. Finocchio D. C. Dittmer, *J. Org. Chem*., 1988, **53**, 5750–5756.



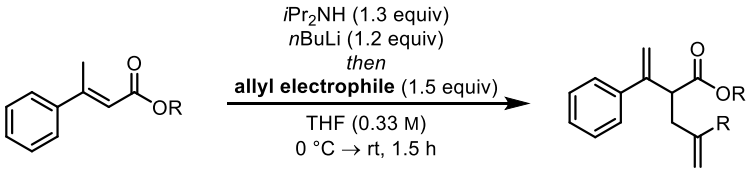
2) Lithiation Approach: *Used for dienes* **1d**, **1e**, **1g**, **1h**



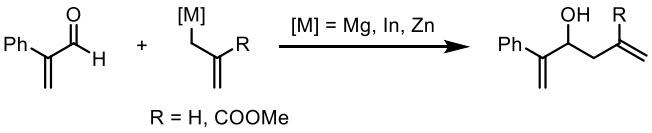
3) Conjugate addition + Wittig: *Used for dienes* **1s**, **1t**, **1x**



4) Enolate allylation: *Used for dienes* **(+)-1r, 1v, 1z**



5) 1,2-addition of allyl nucleophiles: *Used for dienes* **1q, 1w, 1aa**



Scheme S2. Overview of synthetic strategies to dienes **1**.

6. Synthesis procedures

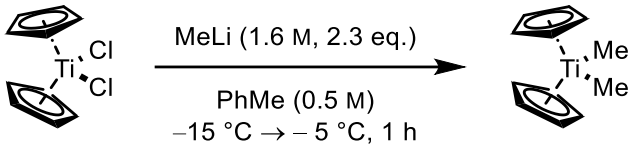
6.1 General Procedures

General Procedure 1 (GP1): [2+2] Cycloaddition

A 10 mL Schlenk tube was charged with the given diene (0.200 mmol, 1.00 eq.), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (11.2 mg, 10.0 µmol, 5 mol%), and THF (2 mL, 0.1 M) and subsequently deoxygenated by three freeze-pump-thaw cycles (30 minutes each). The reaction was irradiated with 456 nm LEDs for 22 hours (or as indicated) at room temperature under strong stirring. The reaction was concentrated *in vacuo* and directly purified by flash column chromatography (SiO_2) to afford the title compound(s).

6.2 Synthesis of dienes 1a–z

Petatis reagent

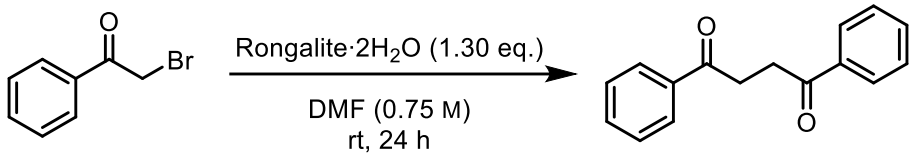


A suspension of titanocene dichloride (498 mg, 2.00 mmol, 1.00 eq.) in PhMe (4 mL, 0.5 M) was cooled to −15 °C. MeLi (1.6 M in Et_2O, 2.9 mL, 4.6 mmol, 2.3 eq.) was added dropwise over five minutes and the reaction was stirred for one hour at −5 °C. The solution was warmed to 0 °C and ice cold NH_4Cl (6%, aq., 1.3 mL) was added dropwise over two minutes. The reaction was diluted with PhMe (5 mL), washed with water (1 mL) and brine (1 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to approximately one third of its initial volume to afford the title compound as an orange solution (0.57 M in PhMe). The concentration of the solution was determined by ^{1}H NMR spectroscopy using PhMe as internal standard.

Data were consistent with that reported in literature.[9]

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 6.05 (s, 10H), −0.11 (s, 6H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 113.2 (10 C), 45.7 (2C).

1,4-Diphenylbutane-1,4-dione (S1)



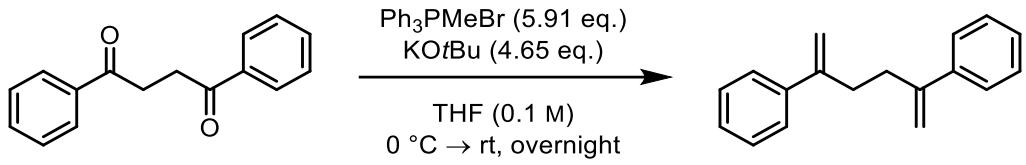
S1
$C_{16}H_{14}O_2$
M = 238.29 g/mol

DMF (20 mL, 0.75 M) was added to a flask charged with 2-bromacetophenone (3.00 g, 15.1 mmol, 1.00 eq.) and Rongalite·$2H_2O$ (3.02 g, 19.6 mmol, 1.30 eq.) and the suspension was stirred for 24 hours at room temperature. The reaction mixture was poured into ice cold water (50 mL) and the precipitated solid was filtered off and redissolved in CH_2Cl_2 (50 mL). After washing with NaOH (1 M, aq., 50 mL) and brine (50 mL) the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to afford the title compound as colourless solid (1.47 g, 6.17 mmol, 81%).

Data were consistent with that reported in literature.[10]

M.P. = 141−142 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.06–8.04 (m, 4H), 7.61–7.56 (m, 2H), 7.51–7.46 (m, 4H), 3.47 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 198.8 (2C), 136.9 (2C), 133.3 (2C), 128.8 (4C), 128.3 (4C), 32.7 (2C).

Hexa-1,5-diene-2,5-diyldibenzene (1a)



S1 **1a**

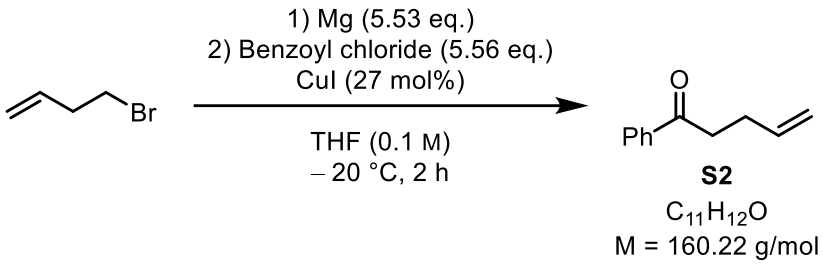
$C_{18}H_{18}$

M = 234.34 g/mol

THF (13 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (2.11 g, 5.91 mmol, 4.69 eq.) and KO*t*Bu (658 mg, 5.86 mmol, 4.65 eq.). The suspension was stirred for one hour at room temperature and then cooled down to 0 °C. Diketone **S1** (300 mg, 1.26 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq. 10 mL) and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as white solid (274 mg, 1.17 mmol, 93%).

***R**f* = 0.55 (Pentane).
M.P. = 43−45 °C (Pentane)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.41−7.29 (m, 10H), 5.28 (d, *J* = 1.38 Hz, 2H), 5.05 (s, 2H), 2.65 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.2 (2C), 141.3 (2C), 128.4 (4C), 127.5 (2C), 126.3 (4C), 112.7 (2C), 34.4 (2C).
IR (ATR): ν_{max} = 1623, 1574, 1493, 1443, 1409, 1324, 1309, 1071, 1027, 891, 775, 699, 549, 504 cm^{-1}.
GCMS (EI): calculated for $C_{18}H_{18}^+$ $[M]^+$: 234.1; found: 234.1.

1-Phenylpent-4-en-1-one (S2)

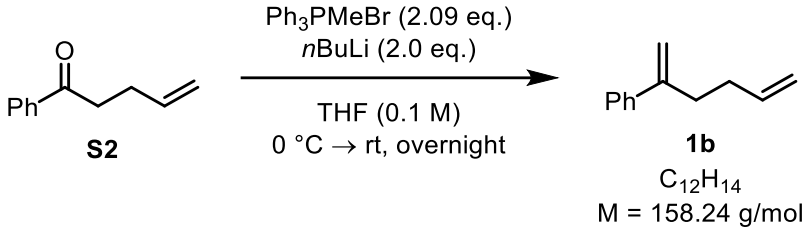


THF (2 mL, 8 M) was added to a flask charged with magnesium turnings (397 mg, 16.3 mmol, 5.53 eq.) and a grain of iodine. A solution of 4-bromo-1-butene (398 mg, 2.95 mmol, 1.00 eq.) in THF (18 mL, 0.2 M) was added dropwise over 10 minutes and the suspension was stirred for one hour at room temperature. In a second flask, THF (17 mL, 1 M) was cooled to −20 °C and benzoyl chloride (1.9 mL, 16 mmol, 5.6 eq.) and CuI (152 mg, 0.798 mmol, 27.1 mol%) were added and the mixture was stirred for 10 minutes. The Grignard reagent solute
ion was added dropwise over one hour at −20 °C and the reaction mixture was then stirred for a further two hours at −20 °C. HCl (1 M, aq., 20 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with $NaHCO_3$ (sat., aq., 20 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 99:1 Pentane:EtOAc) to afford the title compound as a pale green oil (2.11 g, 13.2 mmol, 78%).

Data were consistent with that reported in literature.[11]

***R*$_f$** = 0.32 (99:1 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.98−7.96 (m, 2H), 7.61−7.54 (m, 1H), 7.49−7.44 (m, 2H), 5.98−5.84 (m, 1H), 5.13−4.99 (m, 2H), 3.11−3.06 (m, 2H), 2.54−2.47 (m, 2H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 199.6 (1C), 137.4 (1C), 137.1 (1C), 133.2 (1C), 128.7 (2C), 128.2 (2C), 115.4 (1C), 37.9 (1C), 28.3 (1C).

Hexa-1,5-dien-2-ylbenzene (1b)



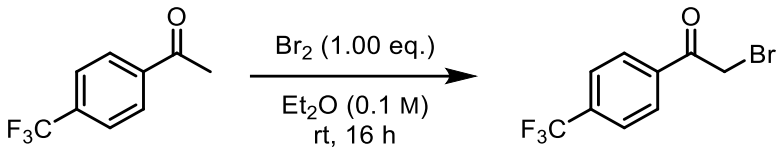
At room temperature *n*BuLi (2.5 M in hexane, 1.5 mL, 3.8 mmol, 2.0 eq.) was added slowly to a solution of Ph_3PMeBr (1.41 g, 3.95 mmol, 2.09 eq.) in THF (18 mL, 0.1 M). After stirring for one hour, the solution was cooled to 0 °C and ketone **S2** (303 mg, 1.89 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. NH_4Cl (sat., aq., 15 mL) was added and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic phases were washed with brine (10 mL) and concentrated under reduced pressure (850 mbar, 40 °C water bath). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless oil (225 mg, 1.42 mmol, 75%).

CAUTION: Product proved to be volatile at low pressures.

Data were consistent with that reported in literature.[12]

R_f = 0.38 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.42−7.27 (m, 5H), 5.91−5.78 (m, 1H), 5.29 (s, 1H), 5.08−4.96 (m, 3H), 2.63−2.58 (m, 2H), 2.26−2.18 (m, 2H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.0 (1C), 141.3 (1C), 138.2 (1C), 128.3 (2C), 127.4 (1C), 126.2 (2C), 114.7 (1C), 112.5 (1C), 34.8 (1C), 32.5 (1C).

2-Bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (S3)



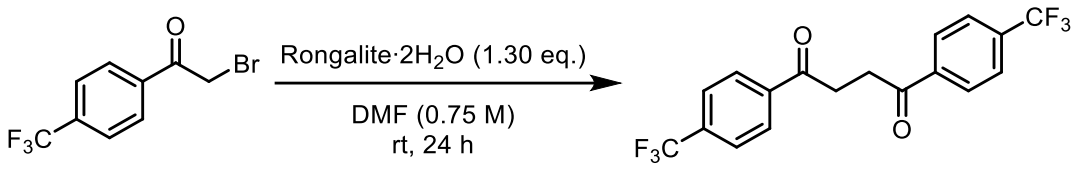
S3
$C_9H_6BrF_3O$
M = 267.05 g/mol

4-Trifluoromethyl acetophenone (3.76 g, 20.0 mmol, 1.00 eq.) was dissolved in Et_2O (30 mL, 0.1 M). Bromine (1.0 mL, 20 mmol, 1.0 eq.) was added dropwise over two minutes at room temperature and the reaction mixture was stirred for 12 hours. The reaction was diluted with water (20 mL) and the aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic phases were washed with $NaHCO_3$ (sat., aq., 30 mL), $Na_2S_2O_3$ (sat., aq., 30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. After purification by recrystallization from a hot mixture of $CHCl_3$ and pentane (3:1) the title compound was obtained as colourless crystals (2.37 g, 8.87 mmol, 44%).

Data were consistent with that reported in literature.[13]

M.P. = 47−49 °C (3:1 $CHCl_3$:Pentane)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.12–8.09 (m, 2H), 7.79–7.76 (m, 2H), 4.45 (s, 2H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 190.6, 136.8, 135.5, 129.5 (2C), 126.0 (q, *J* = 3.6 Hz,2C), 124.9, 30.4.
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ/ppm = 63.28.
IR (ATR): ν_{max} = 3063, 3024, 2997, 2947, 1694, 1509, 1413, 1326, 1314, 1277, 1164, 1111, 1066, 1013, 992, 825, 706, 647, 595 cm^{-1}.
GCMS (EI): calculated for $C_9H_6BrF_3O^+$ $[M]^+$: 266.0; found: 265.9.

1,4-Bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (S4)



S3 **S4**

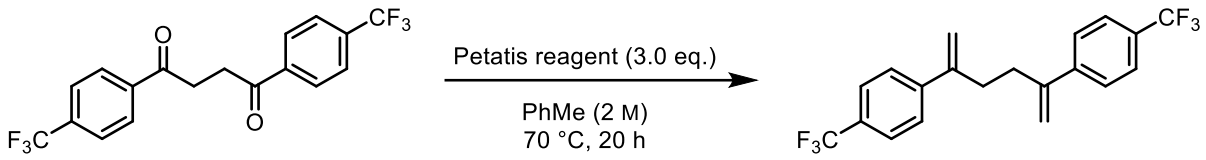
$C_{18}H_{12}F_6O_2$

M = 374.28 g/mol

DMF (10 mL, 0.75 M) was added to a flask charged with acetophenone **S3** (2.00 g, 7.49 mmol, 1.00 eq.) and Rongalite·$2H_2O$ (1.50 g, 9.74 mmol, 1.30 eq.) and the suspension was stirred for 24 hours. at room temperature. After addition of water (26 mL), the precipitate was filtered off and redissolved in CH_2Cl_2 (26 mL). The organic phase was washed with NaOH (1 M, aq., 26 mL) and brine (26 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford the title compound as pale yellow crystals (1.07 g, 2.87 mmol, 76%).

M.P. = 130−133 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.16–8.13 (m, 4H), 7.78–7.75 (m, 4H), 3.50 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 197.6 (2C), 139.4 (2C), 134.6 (2C), 128.6 (8C), 125.9 (q, *J* = 3.6 Hz, 2C), 32.9 (2C).
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ/ppm = 63.13.
IR (ATR): ν_{max} = 2942, 2912, 1682, 1582, 1509, 1408, 1315, 1170, 1129, 1107, 1064, 1004, 866, 851, 792, 731, 600, 520 cm^{-1}.
HRMS (ESI): calculated for $C_{18}H_{12}O_2F_6Na^+$ $[M+Na]^+$: 397.0634; found: 397.0635.

4,4'-(Hexa-1,5-diene-2,5-diyl)bis((trifluoromethyl)benzene) (1C)



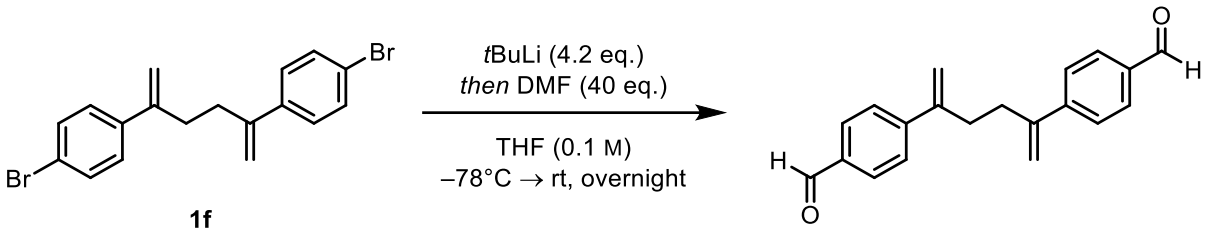
S4 **1c**

$C_{20}H_{16}F_6$
M = 370.34 g/mol

To a flask charged with diketone **S4** (108 mg, 0.300 mmol, 1.00 eq.) Petatis reagent (0.57 M in PhMe, 1.6 mL, 9.1 mmol, 3.0 eq.) was added and the solution was stirred for 20 h at 70 °C. The reaction mixture was diluted with pentane (5 mL), filtered over Celite®, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a colourless solid (38 mg, 0.103 mmol, 34%).

***R*$_f$** = 0.36 (Pentane).
M.P. = 58−59 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.49–7.56 (m, 4H), 7.46–7.43 (m, 4H), 5.33 (s, 2H), 5.12 (s, 2H), 2.65 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 146.8 (2C), 144.7 (2C), 128.6 (2C), 126.6 (8C), 125.9 (q, *J* = 125.5 Hz, 2C), 125.4 (2C), 115.0 (2C), 34.0 (2C).
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ/ppm = 62.51.
IR (ATR): ν_{max} = 2923, 1615, 1402, 1335, 1169, 1137, 1121, 1094, 1068, 1013, 914, 907, 850, 680, 601 cm^{-1}.
GCMS (EI): calculated for $C_{20}H_{16}F_6^+$ $[M]^+$: 370.1; found: 370.0.

4,4'-(Hexa-1,5-diene-2,5-diyl)dibenzaldehyde (1d)



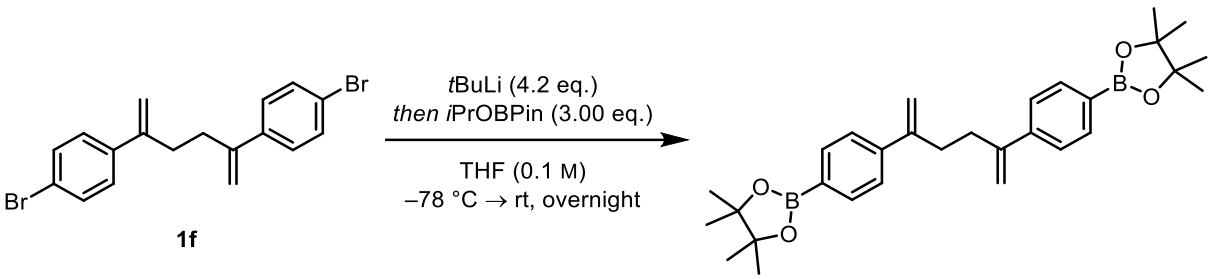
1d
$C_{20}H_{18}O_2$
M = 290.36 g/mol

A solution of diene **1f** (300 mg, 0.765 mmol, 1.00 eq.) in THF (7 mL, 0.1 M) was cooled to −78 °C. Under stirring, *t*BuLi (1.6 M in Pentane, 2.0 mL, 3.2 mmol, 4.2 eq.) was added dropwise over 15 minutes. After stirring for one hour at −78 °C, dry DMF (2.4 mL, 31 mmol, 40 eq.) was added dropwise over 30 minutes. The suspension was allowed to warm to room temperature overnight. The reaction was neutralised by dropwise addition of NH_4Cl (sat., aq., 7 mL), diluted with water (20 mL), and the aqueous phase was extracted with Et_2O (3 × 15 mL). The combined organic phases were washed with HCl (1 M, aq., 10 mL), water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 6:1 Pentane:EtOAc) to afford the title compound as a white powder (118 mg, 0.407 mmol, 53%).

Data were consistent with that reported in literature.[14]

***R*$_f$** = 0.38 (6:1 Pentane:EtOAc).
M.P. = 90−91 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 10.0 (s, 2H), 7.86−7.83 (m, 4H), 7.53−7.50 (m, 4H), 5.41 (s, 2H), 5.16 (s, 2H), 2.68 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 191.9 (2C), 174.2 (2C), 174.0 (2C), 135.6 (2C), 130.0 (4C), 126.8 (4C), 115.8 (2C), 34.0 (2C).
IR (ATR): ν_{max} = 2927, 2826, 2734, 1693, 1602, 1562, 1386, 1306, 1213, 1166, 1084, 911, 837, 744, 715, 575, 504 cm^{-1}.
HRMS (ESI): calculated for $C_{20}H_{18}O_2Na^+$ $[M+Na]^+$: 313.1199; found: 313.1201.

2,2'-(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1e)

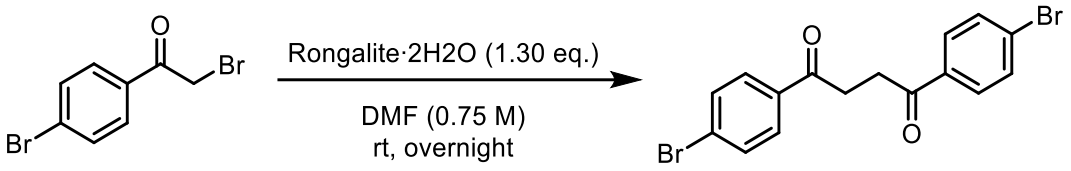


1e
$C_{30}H_{40}B_2O_4$
M = 486.27 g/mol

A solution of diene **1f** (400 mg, 1.02 mmol, 1.00 eq.) in THF (10 mL, 0.1 M) was cooled to −78 °C. Under stirring, *t*BuLi (1.6 M in Pentane, 2.7 mL, 4.3 mmol, 4.2 eq.) was added dropwise over 15 minutes and the reaction was stirred for one hour at −78 °C. In a second flask, a solution of isopropylpinacolylborate (570 mg, 3.06 mmol, 3.00 eq.) in THF (3 mL, 1 M) was cooled to −78 °C. The suspension of lithiated **1f** was added dropwise over 30 minutes to the borate solution. The reaction was allowed to warm to room temperature and was stirred overnight. The reaction was neutralised by dropwise addition of NH_4Cl (sat., aq., 10 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic phases were washed with Brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 20:1 Pentane:EtOAc) to afford the title compound as white solid (115 mg, 0.236 mmol, 23%).

***R*$_f$** = 0.26 (20:1 Pentane:EtOAc).
M.P. = 127−130 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.79–7.76 (m, 4H), 7.40–7.37 (m, 4H), 5.31–5.30 (m, 2H), 5.04 (m, 2H), 2.63 (s, 4H), 1.35 (s, 24H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.1 (2C), 144.0 (2C), 135.0 (4C), 127.9 (2C), 125.7 (4C), 113.5 (2C), 83.9 (4C), 34.3 (2C), 25.0 (8C).
^{11}B NMR (161 MHz, $CDCl_3$): δ/ppm = 30.96.
IR (ATR): ν_{max} = 3901, 3851, 3838, 3750, 3734, 3647, 3081, 2979, 2361, 1610, 1545, 1516, 1399, 1361, 1323, 1268, 1146, 1099, 1018, 961, 897, 860, 660 cm^{-1}.
HRMS (ESI): calculated for $C_{30}H_{40}B_2O_4Na^+$ $[M+Na]^+$: 509.3042; found: 509.3041.

1,4-Bis(4-bromophenyl)butane-1,4-dione (S5)



S5
$C_{16}H_{12}Br_2O_2$
M = 396.08 g/mol

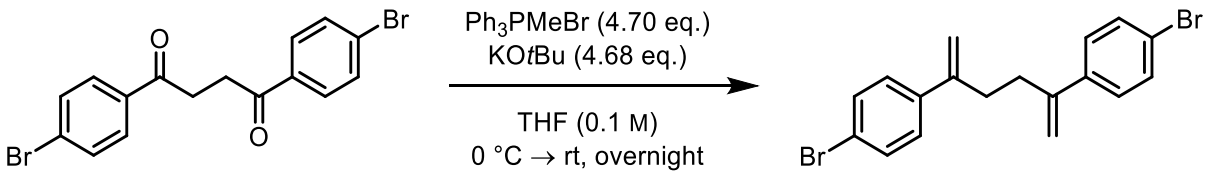
DMF (30 mL, 0.75 M) was added to a flask charged with 4-bromophenacyl bromide (6.00 g, 21.6 mmol, 1.00 eq.) and Rongalite·$2H_2O$ (3.31 g, 28.1 mmol, 1.30 eq.) at room temperature. The suspension was stirred overnight and poured in ice water (120 mL). The participate was filtered off and redissolved in $CHCl_3$ (120 mL). The organic phase was washed with NaOH (1 M, aq., 100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. After recrystallization from a hot mixture of $CHCl_3$ and Pentane (4:1, 85 mL) the title compound was obtained as colourless crystals (2.81 g, 7.09 mmol, 66%).

CAUTION: the obtained product is only soluble in $CHCl_3$.

Data were consistent with that reported in literature.[10]

M.P. = 115−117 °C (4:1 $CHCl_3$:Pentane)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.92−7.84 (m, 4H), 7.66−7.60 (m, 4H), 3.41 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 197.7 (2C), 135.5 (2C), 132.1 (4C), 129.8 (4C), 128.6 (2C), 32.6 (2C).

4,4'-(Hexa-1,5-diene-2,5-diyl)bis(bromobenzene) (1f)



S5 **1f**

$C_{18}H_{16}Br_2$

M = 392.13 g/mol

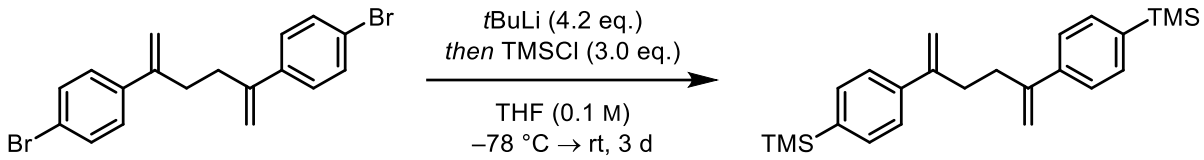
THF (30 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (10.2 g, 28.5 mmol, 4.70 eq.) and KO*t*Bu (3.13 g, 27.9 mmol, 4.60 eq.). After stirring for one hour at room temperature, the suspension was cooled to 0 °C. Diketone **S10** (2.40 g, 6.06 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. NH_4Cl (sat., aq. 30 mL) was added slowly and the reaction mixture was diluted with water (20 mL). The aqueous phase was extracted with EtOAc (3 × 20 mL) and the combined organic phases were washed with brine (20 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 99:1 Pentane:EtOAc) to afford the title compound as a white solid (2.24 g, 5.71 mmol, 94%).

CAUTION: the purification needs to be carried out fast, since the product starts to crystallise on the column.

Data were consistent with that reported in literature.[15]

***R*$_f$** = 0.51 (99:1 Pentane:EtOAc).
M.P. = 80−81 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.46−7.43 (m, 4H), 7.24−7.21 (m, 4H), 5.26 (s, 2H), 5.03 (s, 2H), 2.58 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 146.9 (2C), 140.0 (2C), 131.6 (4C), 128.0 (4C), 121.5 (2C), 113.6 (2C), 34.1 (2C).
IR (ATR): ν_{max} = 3103, 2920, 2843, 1623, 1484, 1388, 1323, 1118, 1092, 1069, 1004, 899, 835, 757, 733, 503 cm^{-1}.
GCMS (EI): calculated for $C_{18}H_{16}Br_2^+$ $[M]^+$: 390.0; found: 389.9.

(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(trimethylsilane) (1g)



1f **1g**

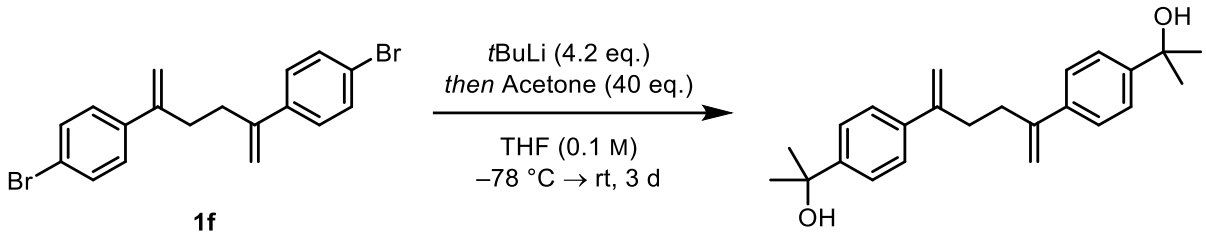
$C_{24}H_{34}Si_2$

M = 378.71 g/mol

A solution of diene **1f** (400 mg, 1.02 mmol, 1.00 eq.) in THF (10 mL, 0.1 M) was cooled to −78 °C. Under stirring, *t*BuLi (1.6 M in Pentane, 2.7 mL, 4.3 mmol, 4.2 eq.) was added dropwise over 15 minutes. After stirring for one hour at −78 °C, TMSCl (freshly distilled from CaH_2, 0.39 mL, 3.1 mmol, 3.0 eq.) was added dropwise over one minute. The reaction was allowed to warm to room temperature and was stirred for three days. The reaction was neutralised by dropwise addition of NH_4Cl (sat., aq., 10 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic phases were washed with Brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as colourless crystals (281 mg, 0.743 mmol, 73%).

***R**f* = 0.26 (Pentane).
M.P. = 57−59 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.50–7.47 (m, 4H), 7.39–7.36 (m, 4H), 5.31 (s, 2H), 5.06 (s, 2H), 2.65 (s, 4H), −0.27 (s, 18H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.1 (2C), 141.6 (2C), 139.6 (2C), 133.5 (4C), 125.6 (4C), 112.8 (2C), 34.3 (2C), -0.96 (6C).
^{29}Si NMR (99 MHz, $CDCl_3$): δ/ppm = –4.25.
IR (ATR): ν_{max} = 3065, 3015, 2954, 2896, 1627, 1597, 1389, 1246, 1125, 1115, 1086, 905, 898, 839, 824, 764, 752, 734, 694, 660, 637, 624, 515 cm^{-1}.
HRMS (ESI): calculated for $C_{24}H_{34}Si_2Na^+$ $[M+Na]^+$: 401.2091; found: 401.2101.

2,2'-(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(propan-2-ol) (1h)



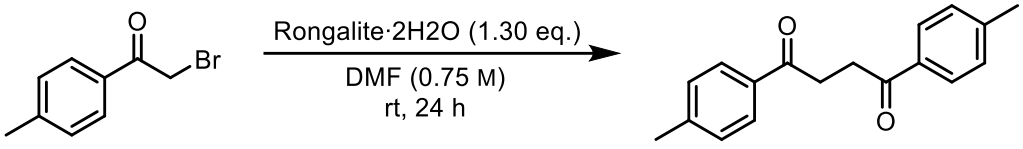
1f

1h
$C_{24}H_{30}O_2$
M = 350.50 g/mol

A solution of diene **1f** (400 mg, 1.02 mmol, 1.00 eq.) in THF (10 mL, 0.1 M) was cooled to −78 °C. Under stirring, *t*BuLi (1.6 M in Pentane, 2.7 mL, 4.3 mmol, 4.2 eq.) was added dropwise over 15 minutes. After stirring for one hour at −78 °C, dry acetone (3.0 mL, 40 mmol, 40 eq.) was added dropwise over one minute. The reaction was allowed to warm to room temperature and stirred for three days. The reaction was neutralised by dropwise addition of NH_4Cl (sat., aq., 5 mL) and diluted with water (20 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic phases were washed with brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. After recrystallization from a mixture of hot $CHCl_3$ and pentane (4:1), the participate was filtered off and washed with ice cold Pentane (3 × 1 mL) to afford the title compound as white solid (144 mg, 0.411 mmol, 40%).

M.P. = 104−105 °C (4:1 $CHCl_3$:Pentane)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.46–7.43 (m, 4H), 7.38–7.35 (m, 4H), 5.29 (s, 2H), 5.05 (s, 2H), 2.65 (s, 4H), 1.60 (s, 12H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.4 (2C), 147.7 (2C), 139.6 (2C), 126.1 (4C), 124.5 (4C), 112.5 (2C), 72.6 (2C), 34.4 (2C), 31.9 (4C).
IR (ATR): ν_{max} = 3348, 3089, 3030, 2973, 2929, 1909, 1797, 1626, 1507, 1457, 1361, 1255, 1168, 1139, 1124, 1096, 1013, 955, 900, 864, 843, 755, 689, 555 cm^{-1}.
HRMS (ESI): calculated for $C_{24}H_{30}O_2Na^+$ $[M+Na]^+$: 373.2138; found: 373.2138.

1,4-Di-*p*-tolylbutane-1,4-dione (S6)

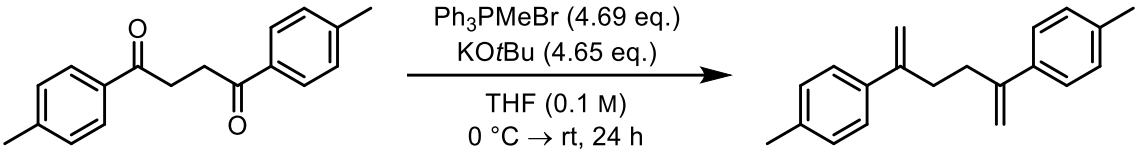


S6
$C_{18}H_{18}O_2$
M = 266.34 g/mol

DMF (6.7 mL, 0.75 M) was added to a flask charged with 4-methylphenacyl bromide (1.00 g, 4.69 mmol, 1.00 eq.) and Rongalite·$2H_2O$ (940 mg, 6.10 mmol, 1.30 eq.) and the suspension was stirred for 24 hours at room temperature. The reaction mixture was poured into ice cold water (17 mL) and the precipitated solid was filtered off and redissolved in CH_2Cl_2 (17 mL). The organic phase was washed with NaOH (1 M, aq., 17 mL) and brine (17 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford the title compound as colourless solid (334 mg, 1.25 mmol, 53%).

M.P. = 150–152 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.31, 4H), 7.28 (d, *J* = 8.31, 4H), 3.43 (s, 4H), 2.42 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 198.6 (2C), 144.0 (2C), 134.5 (2C), 129.4 (4C), 128.4 (4C), 32.7 (2C), 21.8 (2C).
IR (ATR): ν_{max} = 2916, 1672, 1593, 1405, 1323, 1142, 1010, 777 cm^{-1}.
GCMS (ESI): m/z calculated for $C_{18}H_{18}O_2Na^+$ $[M+Na]^+$: 289.1204; found: 289.1199.

4,4'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1i)



S6 **1i**

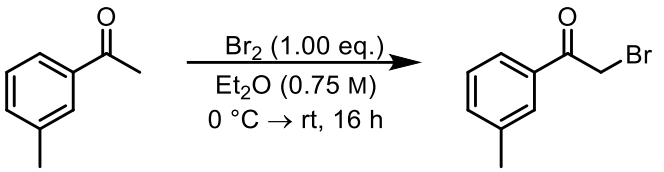
$C_{20}H_{22}$

M = 262.40 g/mol

THF (11 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (1.89 g, 5.28 mmol, 4.69 eq.) and KO*t*Bu (588 mg, 5.24 mmol, 4.65 eq.). The suspension was stirred for one hour at room temperature and then cooled down to 0 °C. Diketone **S6** (300 mg, 1.13 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq., 10 mL) and the aqueous phase was extracted with EtOAc (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a colourless solid (229 mg, 0.87 mmol, 77%).

***R*$_f$** = 0.35 (Pentane).
M.P. = 69–71 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.30–7.26 (m, 6H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 2H), 5.00 (s, 2H), 2.62 (s, 4H), 2.35 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 148.0 (2C), 138.3 (2C), 137.3 (2C), 129.1 (4C), 126.2 (4C), 111.9 (2C), 34.5 (2C), 21.4 (2C).
IR (ATR): ν_{max} = 3083, 2946, 2912, 1815, 1623, 1509, 902, 821 cm^{-1}.
GCMS (EI): m/z calculated for $C_{20}H_{22}^+$ $[M]^+$: 262.1; found: 262.0.

2-Bromo-1-(*m*-tolyl)ethan-1-one (S7)

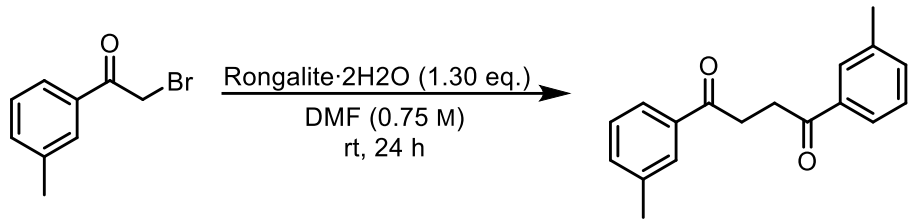


S7
C_9H_9BrO
M = 213.07 g/mol

To a solution of 1-(*m*-tolyl)ethan-1-one (2.01 g, 15.0 mmol, 1.00 eq.) in Et_2O (20 mL, 0.75 M) was added bromine (0.77 mL, 15 mmol, 1.0 eq.) at 0 °C. The mixture was washed with $NaHCO_3$ (sat., aq.) and the aqueous phase was extracted with Et_2O (3×5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 98:2 Pentane:Et_2O) to obtain the title compound as a colourless oil (1.19 g, 5.58 mmol, 37%).

R_f = 0.26 (98:2 Pentane:Et_2O).
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80–7.77 (m, 2H), 7.44–7.35 (m, 2H), 4.45 (s, 2H), 2.43 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 191.6 (1C), 138.9 (1C), 134.9 (1C), 134.2 (1C), 129.5 (1C), 128.9 (1C), 126.3 (1C), 31.2 (1C), 21.5 (1C).
IR (ATR): ν_{max} = 2942, 1674, 1583, 1430, 1279, 1154, 781, 680 cm^{-1}.
GCMS (ESI): m/z calculated for $C_9H_9BrONa^+$ $[M+Na]^+$: 234.9831; found: 234.9829.

1,4-Di-*m*-tolylbutane-1,4-dione (S8)



S7 **S8**

$C_{18}H_{18}O_2$

M = 266.34 g/mol

DMF (6.0 mL, 0.75 M) was added to a flask charged with ketone **S7** (0.96 g, 4.5 mmol, 1.0 eq.) and Rongalite·$2H_2O$ (906 mg, 5.88 mmol, 1.30 eq.) and the suspension was stirred for 24 hours at room temperature. The reaction mixture was poured into ice cold water (15 mL) and the precipitated solid was filtered off and redissolved in CH_2Cl_2 (15 mL). The organic phase was washed with NaOH (1 M, aq., 15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford the title compound as a colourless solid (434 mg, 1.63 mmol, 72%).

M.P. = 119–121 °C (CH_2Cl_2)

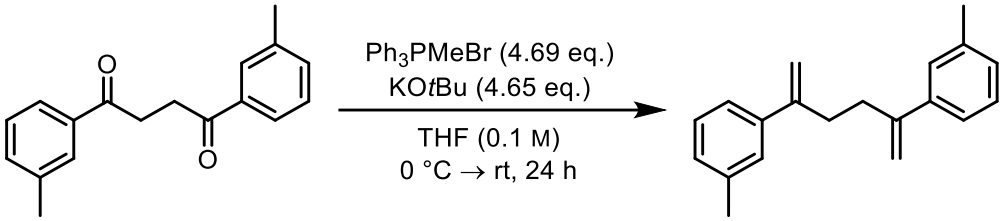
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.85–7.83 (m, 4H), 7.39–7.36 (m, 4H), 3.45 (s, 4H), 2.43 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 199.1 (2C), 138.5 (2C), 137.0 (2C), 134.0 (2C), 128.8 (2C), 128.6 (2C), 125.5 (2C), 32.9 (2C), 21.5 (2C).

IR (ATR): ν_{max} = 2916, 1672, 1593, 1408, 1305, 1142, 1043, 766 cm^{-1}.

GCMS (ESI): m/z calculated for $C_{18}H_{18}O_2Na^+$ $[M+Na]^+$: 289.1204; found: 289.1202.

3,3'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1j)

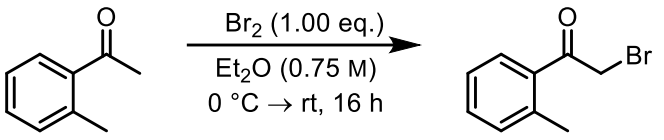


S8 **1j**
$C_{20}H_{22}$
M = 262.40 g/mol

THF (11 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (1.89 g, 5.28 mmol, 4.69 eq.) and KO*t*Bu (588 mg, 5.24 mmol, 4.65 eq.). The suspension was stirred for one hour at room temperature and then cooled down to 0 °C. Diketone **S8** (300 mg, 1.13 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq., 10 mL) and the aqueous phase was extracted with EtOAc (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a colourless oil (227 mg, 0.87 mmol, 77%).

R_f = 0.38 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.23–7.18 (m, 6H), 7.11–7.08 (m, 2H), 5.27 (s, 2H), 5.05 (s, 2H), 2.64 (s, 4H), 2.36 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 148.4 (2C), 141.3 (2C), 137.9 (2C), 128.31 (2C), 128.27 (2C), 127.1 (2C), 123.4 (2C), 112.5 (2C), 34.5 (2C), 21.7 (2C).
IR (ATR): ν_{max} = 3079, 3031, 2939, 2916, 2858, 1623, 1597, 1483, 1450, 891, 788 cm^{-1}.
GCMS (EI): m/z calculated for $C_{20}H_{22}^+$ $[M]^+$: 262.1; found: 262.1.

2-Bromo-1-(o-tolyl)ethan-1-one (S9)

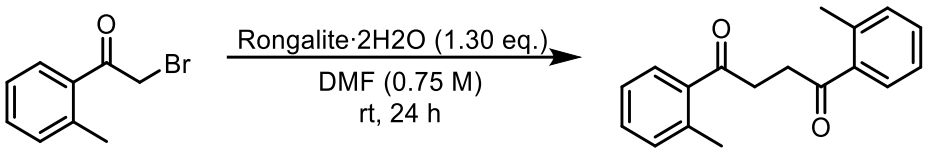


S9
C_9H_9BrO
M = 213.07 g/mol

To a solution of 1-(*o*-tolyl)ethan-1-one (2.01 g, 15.0 mmol, 1.00 eq.) in Et_2O (20 mL, 0.75 M) was added bromine (0.77 mL, 15 mmol, 1.0 eq.) at 0 °C. The mixture was washed with $NaHCO_3$ (sat., aq.) and the aqueous phase was extracted with Et_2O (3×5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 98:2 Pentane:Et_2O) to obtain the title compound as colourless oil (1.20 g, 5.63 mmol, 37%).

R_f = 0.37 (98:2 Pentane:Et_2O).
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.69–7.66 (m, 1H), 7.46–7.41 (m, 1H), 7.31–7.29 (m, 2H), 4.42 (s, 2H), 2.53 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 194.3 (1C), 139.9 (1C), 134.6 (1C), 132.49 (1C), 132.46 (1C), 129.1 (1C), 125.9 (1C), 33.9 (1C), 21.6 (1C).
IR (ATR): ν_{max} = 2968, 2928, 1674, 1453, 1257, 1184, 980, 732, 614 cm^{-1}.
GCMS (EI): m/z calculated for $C_9H_9BrO^+$ $[M]^+$: 211.9831; found: 211.9830.

1,4-Di-o-tolylbutane-1,4-dione (S10)



S9 **S10**

$C_{18}H_{18}O_2$

M = 266.34 g/mol

DMF (6.7 mL, 0.75 M) was added to a flask charged with ketone **S9** (1.00 g, 4.69 mmol, 1.00 eq.) and Rongalite·$2H_2O$ (940 mg, 6.10 mmol, 1.30 eq.) and the suspension was stirred for 24 hours at room temperature. The reaction mixture was poured into ice cold water (15 mL) and the precipitated solid was filtered off and redissolved in CH_2Cl_2 (15 mL). The organic phase was washed with NaOH (1 M, aq., 15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford the title compound as a colourless solid (323 mg, 1.22 mmol, 51%).

M.P. = 62–64 °C (CH_2Cl_2)

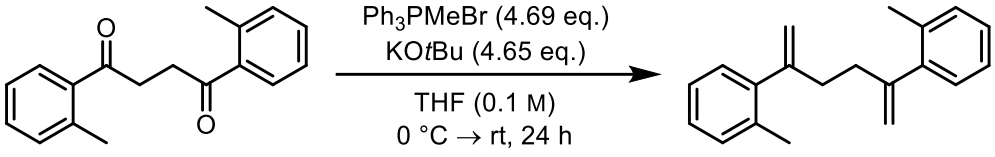
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.80 (d, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H) 7.30–7.24 (m, 4H), 3.34 (s, 4H), 2.50 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 202.8 (2C), 138.2 (2C), 138.0 (2C), 132.0 (2C), 131.4 (2C), 128.7 (2C), 125.8 (2C), 35.8 (2C), 21.4 (2C).

IR (ATR): ν_{max} = 2916, 1674, 1564, 1412, 1176, 988, 747 cm^{-1}.

GCMS (ESI): m/z calculated for $C_{18}H_{18}O_2Na^+$ $[M+Na]^+$: 289.1204; found: 289.1199.

2,2'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1k)



S10 **1k**

$C_{20}H_{22}$

M = 262.40 g/mol

THF (11 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (1.89 g, 5.28 mmol, 4.69 eq.) and KO*t*Bu (588 mg, 5.24 mmol, 4.65 eq.). The suspension was stirred for one hour at room temperature and then cooled down to 0 °C. Diketone **S10** (300 mg, 1.13 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq., 10 mL) and the aqueous phase was extracted with EtOAc (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a colourless oil (188 mg, 0.715 mmol, 63%).

R_f = 0.32 (Pentane).

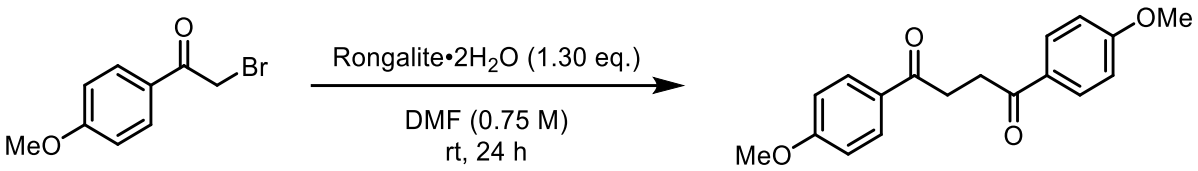
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.17–7.10 (m, 6H), 7.06–7.03 (m, 2H), 5.19 (s, 2H), 4.88 (s, 2H), 2.45 (s, 4H), 2.25 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 149.7 (2C), 143.0 (2C), 135.0 (2C), 130.2 (2C), 128.5 (2C), 126.9 (2C), 125.2 (2C), 114.1 (2C), 35.9 (2C), 20.0 (2C).

IR (ATR): ν_{max} = 3068, 3017, 2920, 1630, 1486, 895, 762, 729 cm^{-1}.

GCMS (EI): m/z calculated for $C_{20}H_{22}^+$ $[M]^+$: 262.1; found: 262.0.

1,4-Bis(4-methoxyphenyl)butane-1,4-dione (S11)



S11
$C_{18}H_{18}O_4$
M = 298.34 g/mol

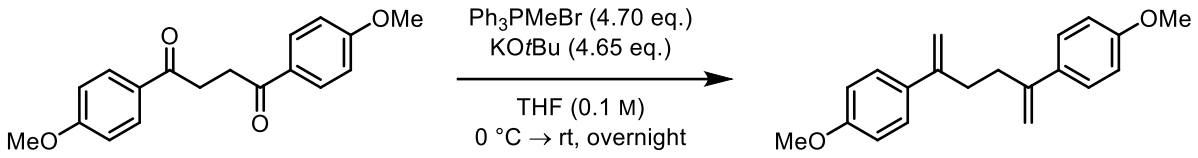
DMF (6.0 mL, 0.75 M) was added to a flask charged with 4-methoxyphenacyl bromide (1.00 g, 4.37 mmol, 1.00 eq.) and Rongalite dihydrate·$2H_2O$ (875 mg, 5.68 mmol, 1.30 eq.) and the suspension was stirred for 24 h at room temperature. After addition of ice cold water (16 mL), the participate was filtered of and redissolved in CH_2Cl_2 (16 mL). The organic phase was washed with NaOH (1 M, aq., 16 mL) and brine (16 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. After recrystallization from CH_2Cl_2, the title compound was obtained as colourless crystals (536 mg, 1.80 mmol, 82%).

CAUTION: Product proved to be unstable in solution.

Data were consistent with that reported in literature.[10]

M.P. = 145−149 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.04–8.01 (m, 4H), 6.96–6.93 (m, 4H), 3.88 (s, 6H), 3.40 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 197.6 (2C), 163.7 (2C), 130.5 (4C), 130.1 (2C), 113.9 (4C), 55.6 (2C), 32.5 (2C).

4,4'-(Hexa-1,5-diene-2,5-diyl)bis(methoxybenzene) (1l)



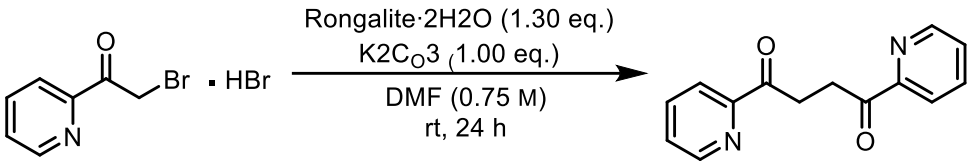
S11 **1l**

$C_{20}H_{22}O_2$
M = 294.39 g/mol

THF (8 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (1.34 g, 3.76 mmol, 4.70 eq.) and KO*t*Bu (417 mg, 3.72 mmol, 4.65 eq.). The suspension was stirred for one hour at room temperature and then cooled down to 0 °C. Diketone **S11** (239 mg, 0.800 mmol, 1.00 eq.) was added in one portion, the reaction was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq., 10 mL) and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 19:1 Pentane:EtOAc) to afford the title compound as colourless crystals (202 mg, 0.685 mmol, 85%).

***R**f* = 0.32 (19:1 Pentane:EtOAc).
M.P. = 128−132 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.45–7.32 (m, 4H), 6.88–6.85 (m, 4H), 5.21 (s, 2H), 4.96 (s, 2H), 3.82 (s, 6H), 2.61 (s, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 159.2 (2C), 147.5 (2C), 133.7 (2C), 127.4 (4C), 113.8 (4C), 111.1 (2C), 55.4 (2C), 34.6 (2C).
IR (ATR): ν_{max} = 3098, 2957, 2919, 2839, 1621, 1603, 1574, 1509, 1469, 1440, 1403, 1324, 1295, 1265, 1249, 1196, 1182, 1156, 1125, 1092, 1027, 1009, 960, 886, 839, 826, 817, 804, 795, 745, 693, 683, 636, 546, 519 cm^{-1}.
HRMS (EI): calculated for $C_{20}H_{23}O_2^+$ $[M+H]^+$: 295.1693; found: 295.1692.

1,4-Di(pyridin-2-yl)butane-1,4-dione (S12)

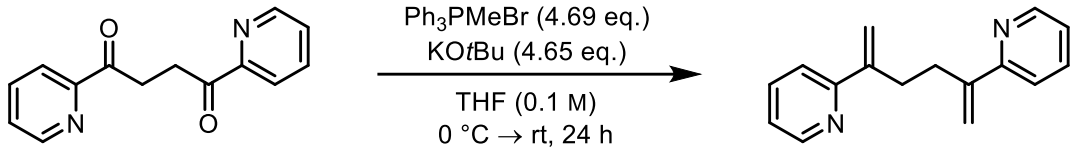


S12
$C_{14}H_{12}N_2O_2$
M = 240.26 g/mol

DMF (9.5 mL, 0.75 M) was added to a flask charged with 2-(Bromoacetyl)pyridine hydrobromide (2.00 g, 7.12 mmol, 1.00 eq.), Rongalite·$2H_2O$ (1.43 g, 9.25 mmol, 1.30 eq.) and K_2CO_3 (984 g, 7.12 mmol, 1.00 eq.) and the suspension was stirred for 24 hours at room temperature. The reaction mixture was poured into ice cold water (25 mL) and the precipitated solid was filtered off and redissolved in CH_2Cl_2 (25 mL). The organic phase was washed with NaOH (1 M, aq., 25 mL) and brine (25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to afford the title compound as a colourless solid (285 mg, 1.19 mmol, 33%).

M.P. = 134–136 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.71 (d, *J* = 4.6 Hz, 2H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.83 (dt, *J* = 7.6, 1.3 Hz, 2H), 7.48 (dd, *J* = 7.6, 4.8 Hz, 2H), 3.70 (s, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 200.6 (2C), 153.5 (2C), 149.1 (2C), 137.0 (2C), 127.3 (2C), 122.0 (2C), 32.2 (2C).
IR (ATR): ν_{max} = 3368, 2924, 2366, 1686, 1583, 1323, 995, 751 cm^{-1}.
GCMS (ESI): m/z calculated for $C_{14}H_{12}N_2O_2Na^+$ $[M+Na]^+$: 263.0796; found: 263.0791.

2,2'-(Hexa-1,5-diene-2,5-diyl)dipyridine (1m)



S12 **1m**

$C_{16}H_{16}N_2$

M = 236.32 g/mol

THF (10 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (1.74 g, 4.88 mmol, 4.69 eq.) and KO*t*Bu (543 mg, 4.84 mmol, 4.65 eq.). The suspension was stirred for one hour at room temperature and then cooled down to 0 °C. Diketone **S12** (250 mg, 1.04 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq., 10 mL) and the aqueous phase was extracted with EtOAc (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a yellow oil (139 mg, 0.592 mmol, 56%).

R_f = 0.17 (Pentane)

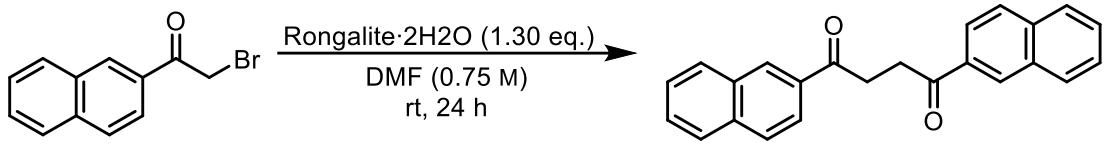
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.59 (d, *J* = 4.6 Hz, 2H), 7.63 (dt, *J* = 7.8 Hz 1.4 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.16 (dd, *J* = 4.9 Hz, 2.3 Hz, 2H), 5.77 (s, 2H), 5.27 (s, 2H), 2.85 (s, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 158.5 (2C), 149.1 (2C), 147.8 (2C), 136.4 (2C), 122.2 (2C), 120.6 (2C), 115.5 (2C), 32.9 (2C).

IR (ATR): ν_{max} = 3079, 3049, 2998, 2924, 1583, 1561, 1464, 1430, 902, 799, 740 cm^{-1}.

GCMS (ESI): m/z calculated for $C_{16}H_{16}N_2Na^+$ $[M+Na]^+$: 259.1211; found: 259.1206.

1,4-Di(naphthalen-2-yl)butane-1,4-dione (S13)

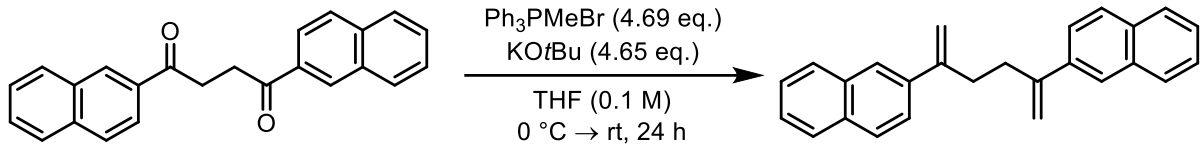


S13
$C_{24}H_{18}O_2$
M = 338.41 g/mol

DMF (5.4 mL, 0.75 M) was added to a flask charged with 2-(Bromoacetyl)naphthalene (1.00 g, 4.01 mmol, 1.00 eq.) and Rongalite·$2H_2O$ (804 mg, 5.22 mmol, 1.30 eq.) and the suspension was stirred for 24 hours at room temperature. The reaction mixture was poured into ice cold water (13 mL) and the precipitated solid was filtered and washed with NaOH (1 M, aq., 2×13 mL) and Et_2O (2×13 mL) to afford the title compound as colourless solid (407 mg, 1.20 mmol, 59%).

M.P. = 210–212 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.62 (s, 2H), 8.12 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.91 (t, *J* = 8.7 Hz, 4H), 7.64–7.55 (m, 4H), 3.68 (s, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 198.9 (2C), 135.8 (2C), 134.3 (2C), 132.7 (2C), 130.1 (2C), 129.8 (2C), 128.6 (4C), 128.0 (2C), 126.9 (2C), 124.1 (2C), 33.0 (2C).
IR (ATR): ν_{max} = 3053, 2912, 1674, 1619, 1468, 1297, 1120, 788 cm^{-1}.
GCMS (ESI): m/z calculated for $C_{24}H_{18}O_2Na^+$ $[M+Na]^+$: 361.1204; found: 361.1199.

2,2'-(Hexa-1,5-diene-2,5-diyl)dinaphthalene (1n)



S13 **1n**

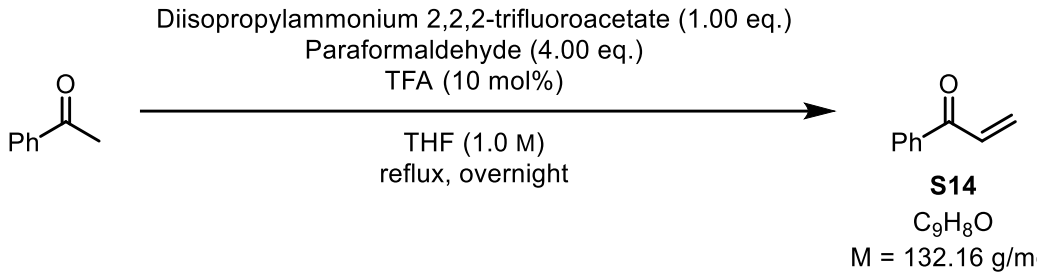
$C_{26}H_{22}$

M = 334.46 g/mol

THF (8.9 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (1.49 g, 4.16 mmol, 4.69 eq.) and KO*t*Bu (463 mg, 4.12 mmol, 4.65 eq.). The suspension was stirred for one hour at room temperature and then cooled down to 0 °C. Diketone **S13** (300 mg, 0.89 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq., 10 mL) and the aqueous phase was extracted with EtOAc (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a colourless solid (225 mg, 0.674 mmol, 76%).

R_f = 0.17 (Pentane).
M.P. = 41–43 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84–7.43 (m, 14H), 5.44 (s, 2H), 5.17 (s, 2H), 2.82 (s, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 148.0 (2C), 138.4 (2C), 133.5 (2C), 133 (2C), 128.3 (2C), 128.0 (2C), 127.7 (2C), 126.3 (2C), 126.0 (2C), 124.9 (4C), 113.4 (2C), 34.7 (2C).
IR (ATR): ν_{max} = 3049, 2950, 2928, 2359, 1619, 1590, 1128, 888, 862, 744 cm^{-1}.
GCMS (EI): m/z calculated for $C_{26}H_{22}^+$ $[M]^+$: 334.1; found: 334.1.

1-Phenylprop-2-en-1-one (S14):

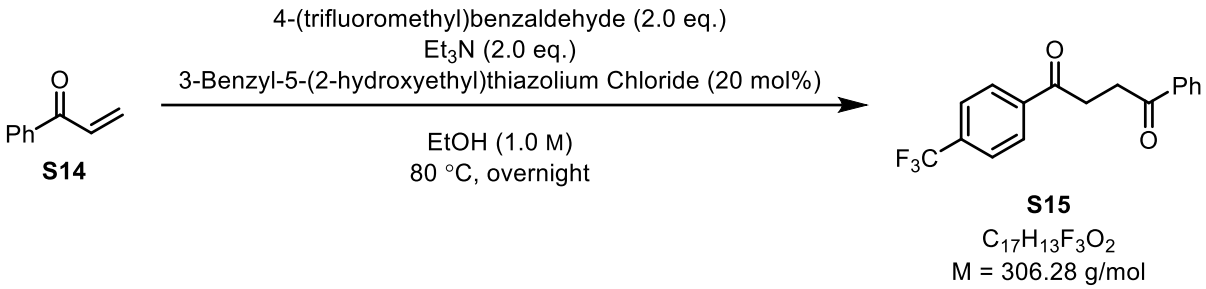


Trifluoroacetic acid (0.32 mL, 4.2 mmol, 10 mol%) was added to a suspension of diisopropylammonium 2,2,2-trifluoroacetate (8.96 g, 41.6 mmol, 1.00 eq.), acetophenone (4.9 mL, 42 mmol, 1.00 eq.) and paraformaldehyde (2.50 g, 83.3 mmol, 2.00 eq.) in THF (42 mL, 0.10 M). The reaction mixture was refluxed (T = 90 °C) for 2 h and cooled down to room temperature. Paraformaldehyde (2.50 g, 83.3 mmol, 2.00 eq.) was added in one portion and the reaction was refluxed overnight. After concentration *in vacuo*, the residue was redissolved in Et_2O (50 mL). The organic phase was washed with HCl (1 M, aq. 10 mL), NaOH (1 M, aq. 10 mL), brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by column chromatography (SiO_2, 95:5 Pentane:EtOAc) to afford the title compound as a pale yellow oil (686 mg, 5.19 mmol, 12%).[16]

Data were consistent with that reported in literature.[17]

R_f = 0.32 (95:5 Pentane:EtOAc)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.97−7.93 (m, 2H), 7.61−7.55 (m, 1H), 7.49 (ddt, *J* = 8.3, 6.7, 1.3 Hz, 2H), 7.16 (dd, *J* = 17.2, 10.6 Hz, 1H), 6.44 (dd, *J* = 17.2, 1.7 Hz, 1H), 5.94 (dd, *J* = 10.6, 1.7 Hz, 1H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm): 191.2 (1C), 137.4 (1C), 133.1 (2C), 132.5 (1C), 130.3 (2C), 128.8 (1C), 128.8 (1C).

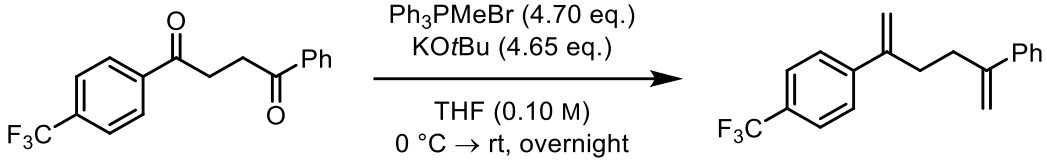
1-Phenyl-4-(4-(trifluoromethyl)phenyl)butane-1,4-dione (S15):



3-Benzyl-5-(2-hydroxyethyl)thiazolium chloride (108 mg, 0.400 mmol, 20 mol%), 4-(trifluoromethyl)benzaldehyde (696 mg, 4.00 mmol, 2 eq.) and Et_3N (0.560 mL, 4.00 mmol, 2 eq.) were sequentially added to a solution of phenyl vinyl ketone (264 mg, 2.00 mmol, 1 eq.) in EtOH (2.00 mL, 1.0 M) and the reaction was then stirred at 80 °C overnight. The reaction was cooled to room temperature and H_2O (5 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 9:1 Pentane:Et_2O) to afford the title compound as a colourless oil (539 mg, 1.75 mmol, 87%).

R_f = 0.2 (90:10 Pentane:Et_2O)
^{1}H NMR (400 MHz, $CDCl_3$): 8.18−8.11 (m, 2H), 8.06−8.01 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.61−7.56 (m, 1H), 7.52−7.46 (m, 2H), 3.52−3.43 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 198.5 (1C), 198.0 (1C), 139.6 (1C), 136.7 (1C), 134.7 (d, *J* = 32.6 Hz, 1C), 133.4 (1C), 128.8 (2C), 128.6 (2C), 128.3 (2C), 125.8 (q, *J* = 3.7 Hz, 2C), 122.4 (1C), 32.9 (1C), 32.7 (1C).
^{19}F{^{1}H} (282 MHz, $CDCl_3$): –63.10.
IR (ATR): ν_{max} = 2919, 1673, 1320, 1311, 1169, 1155, 1112, 1005, 751, 732, 689 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{17}H_{14}O_2F_3^+$ $[M+H]^+$: 307.0940; found: 30943.

1-(5-Phenylhexa-1,5-dien-2-yl)-4-(trifluoromethyl)benzene (1o):



S15 **1o**

$C_{19}H_{17}F_3$

M = 302.34 g/mol

THF (10 mL, 0.1 M) was added to a flask charged with Ph_3PMeBr (1.68 g, 4.70 mmol, 4.70 eq.) and KO*t*Bu (521 mg, 4.65 mmol, 4.65 eq.). The suspension was stirred for one hour at room temperature and then cooled down to 0 °C. Diketone **S15** (306 mg, 1.00 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq., 10 mL) and the aqueous phase was extracted with EtOAc (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a colourless solid (159 mg, 0.526 mmol, 52%).

M.P. = 31−32 °C

***R*f** = 0.27 (80:20 Pentane)

^{1}H NMR (300 MHz, $CDCl_3$): 7.57 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.39−7.26 (m, 5H), 5.30 (d, *J* = 17.2 Hz, 2H), 5.08 (d, *J* = 32.2 Hz, 2H), 2.65 (s, 4H).

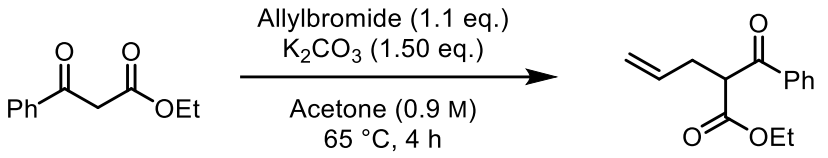
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 147.9 (1C), 147.1 (1C), 144.9 (d, *J* = 1.5 Hz, 1C), 141.1 (1C), 129.5 (q, *J* = 32.2 Hz, 1C), 128.5 (2C), 127.6 (1C), 126.6 (2C), 126.3 (2C), 125.4 (q, *J* = 3.8 Hz, 2C), 123.3 (1C), 114.8 (1C), 113.0 (1C), 34.3 (1C), 34.2 (1C).

^{19}F{^{1}H} (282 MHz, $CDCl_3$): –62.47.

IR (ATR): ν_{max} = 3085, 2941, 1324, 1166, 1120, 1066, 901, 847, 777, 703 cm^{-1}.

GCMS (EI): m/z calculated for $C_{19}H_{17}F_3$ $[M]^+$: 302.1277; found: 302.1274.

Ethyl 2-benzoylpent-4-enoate (S16)



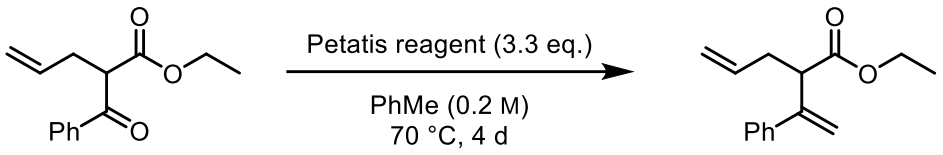
S16
$C_{14}H_{16}O_3$
M = 232.28 g/mol

Under air, allyl bromide (filtered over K_2CO_3, 1.4 mL, 16 mmol, 1.1 eq.) was added to a flask charged with ethyl benzoylacetate (3.1 mL, 15 mmol, 1.0 eq.) and K_2CO_3 (3.11 g, 22.5 mmol, 1.50 eq.). Acetone (17 mL, 0.9 M) was added and the suspension was stirred for 4 hours at 65 °C. The reaction was cooled to room temperature, filtered over Celite®, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 10:1 Pentane:EtOAc) to afford the title compound as a pale yellow oil (3.60 g, 15.5 mmol, 96%).

Data were consistent with that reported in literature.[18]

***R**f* = 0.35 (10:1 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.01–7.98 (m, 2H), 7.61–7.56 (m, 1H), 7.50–7.45 (m, 2H), 5.89–5.75 (m, 1H), 5.15–5.02 (m, 2H), 4.39 (t, *J* = 7.26 Hz, 1H), 4.14 (dq, *J* = 7.17, 2.02 Hz, 2H), 2.78–2.73 (m, 2H), 1.17 (t, *J* = 7.17 Hz, 3H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 194.7 (1C), 169.5 (1C), 136.3 (1C), 134.6 (1C), 133.7 (1C), 128.9 (2C), 128.8 (2C), 117.5 (1C), 61.6 (1C), 54.1 (1C), 33.1 (1C), 14.1 (1C).

Ethyl 2-(1-phenylvinyl)pent-4-enoate (1p)



S16 **1p**

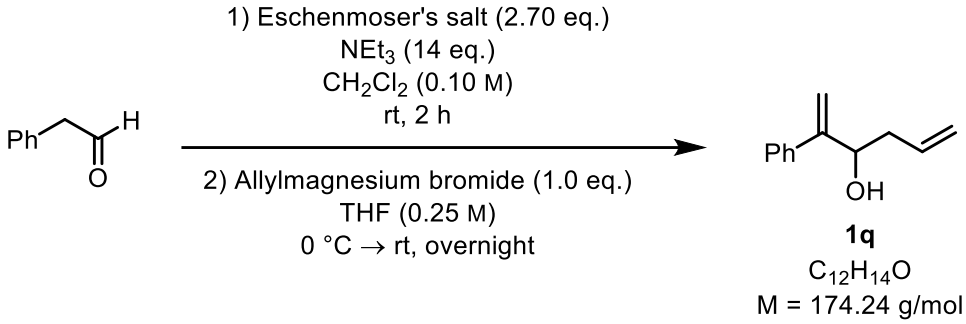
$C_{15}H_{18}O_2$

M = 230.31 g/mol

At room temperature, Petatis reagent (0.71 M in PhMe, 7.0 mL, 5.0 mmol, 3.3 eq.) was added to ketone **S16** (357 mg, 1.54 mmol, 1.00 eq.) and stirred at 70 °C for four days. NH_4Cl (aq., sat., 15 mL) was added, the reaction mixture was diluted with EtOAc (15 mL) and the aqueous phase extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 92:8, Pentane:EtOAc) to afford the title compound as a yellow oil (57.7 mg, 0.251 mmol, 16%).

R_f = 0.46 (92:8, Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.41–7.28 (m, 5H), 5.85–5.72 (m, 1H), 5.41 (s, 1H), 5.29 (s, 1H), 5.10–5.00 (m, 2H), 4.14 (q, *J* = 7.13 Hz, 2H), 3.61 (dd, *J* = 8.94, 6.16 Hz, 1H), 2.71–2.61 (m, 1H), 2.48–2.39 (m, 1H), 1.20 (t, *J* = 7.13 Hz, 3H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 173.4 (1C), 146.6 (1C), 141.4 (1C), 135.6 (1C), 128.5 (2C), 127.8 (1C), 126.7 (2C), 116.9 (1C), 115.0 (1C), 60.9 (1C), 50.3 (1C), 36.3 (1C), 14.3 (1C).
IR (ATR): ν_{max} = 3083, 2980, 2931, 1732, 1642, 1496, 1444, 1370, 1335, 1298, 1275, 1261, 1246, 1222, 1176, 1161, 1120, 1097, 1073, 1028, 999, 908, 777, 701 cm^{-1}.
HRMS (ESI): calculated for $C_{15}H_{18}O_2Na^+$ [M+Na]+: 253.1199; found: 253.1203.

2-Phenylhexa-1,5-dien-3-ol (1q):

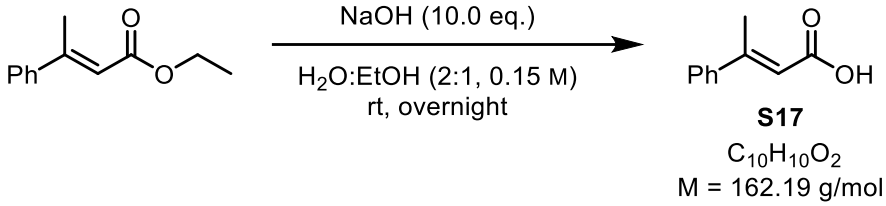


1q
$C_{12}H_{14}O$
M = 174.24 g/mol

Step 1: To a suspension of Eschenmoser's salt (2.50g, 13.5 mmol, 2.70 eq.) in CH_2Cl_2 (50 mL, 0.10 M) 2-phenylacetaldehyde (0.58 mL, 5.0 mmol, 1.0 eq.) and NEt_3 (9.7 mL, 70 mmol, 14 eq.) were added. The solution was stirred for 2 h at room temperature, washed with $NaHCO_3$ (2 × 20 mL) and brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure (the water bath temperature was kept at 0 °C to reduce polymerisation).
Step 2: The pale yellow residue was redissolved in THF (5 mL, 1.0 M) and added dropwise to a solution of allylmagnesium bromide (1.0 M in Et_2O, 5.0 mL, 5.0 mmol, 1.0 eq.) in THF (20 mL, 0.25 M) over 5 minutes at 0 °C. The reaction was allowed to warm to room temperature overnight. After quenching with NH_4Cl (sat., aq., 10 mL), the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by column chromatography (SiO_2, 90:10 Pentane:EtOAc) to affor the title compound as a pale yellow oil (261 mg, 1.50 mmol, 29%).

R_f = 0.29 (90:10 Pentane:EtOAc)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.40−7.27 (m, 5H), 5.88−5.74 (m, 1H), 5.35 (d, *J* = 17.3 Hz, 2H), 5.15−5.09 (m, 2H), 4.70 (dt, *J* = 8.3, 4.2 Hz, 1H), 2.45−2.37 (m, 1H), 2.23 (dt, *J* = 14.3, 7.6 Hz, 1H), 1.93 (d, *J* = 4.3 Hz, 1H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm): 151.2 (1C), 140.1 (1C), 134.4 (1C), 128.5 (2C), 127.8 (1C), 127.1 (2C), 118.5 (1C), 112.9 (1C), 72.5 (1C), 40.6 (1C).
IR (ATR): ν_{max} = 3385, 3058, 1493, 1053, 908, 777, 699 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{12}H_{14}ONa^+$ $[M+Na]^+$: 197.0937; found: 197.0937.

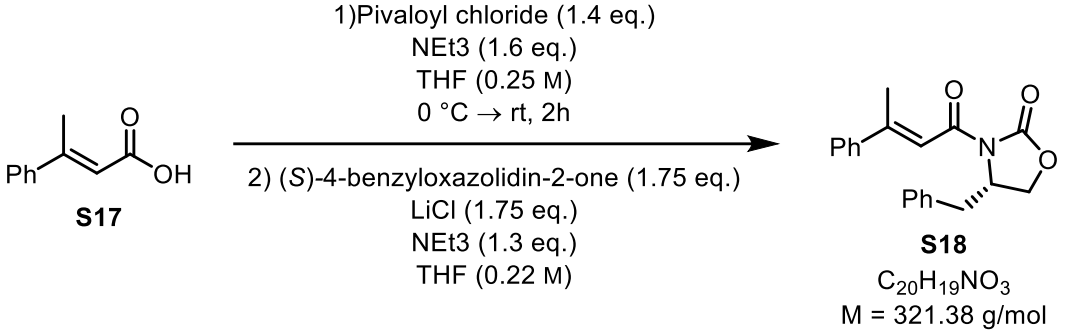
(*E*)-3-phenylbut-2-enoic acid (S17):



NaOH (2.2 M, aq., 19 mL, 42 mmol, 10 eq.) was added to a solution of 3-phenylbut-2-enoate (800 mg, 4.21 mmol, 1.00 eq.) in EtOH (9 mL, 0.5 M) at room temperature. The reaction was stirred overnight, volatiles were removed *in vacuo* and H_2O (15 mL) was added. [19] The aqueous phase was washed with EtOAc (2 × 5 mL) and acidified using HCl (1 M, aq.). After extraction of the aqueous phase with EtOAc (3× 25 mL), the combined organic phases were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The title compound was obtained as colorless solid (649 mg, 4.01 mmol, 95%) and was used without further purification.

M.P. = 85−88 °C
^{1}H NMR (300 MHz, $CDCl_3$): 7.50−7.48 (m, 2H), 7.39 (dd, *J* = 5.1, 1.8 Hz, 3H), 6.18 (m, 1H), 2.61 (d, *J* = 1.3 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 171.0 (1C), 158.6 (1C), 142.2 (1C), 129.5 (1C), 128.7 (2C), 126.6 (2C), 116.3 (1C), 18.4 (1C).
IR (ATR): ν_{max} = 3061, 2921, 1677, 1622, 1450, 910, 867 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{10}H_9O_2^-$ $[M-H]^-$: 161.0608; found: 161.0608.

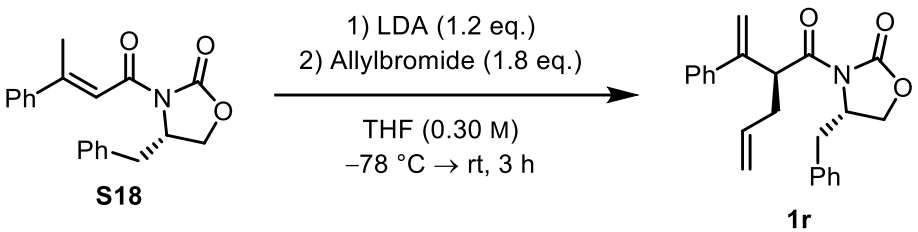
(*S,E*)-4-benzyl-3-(3-phenylbut-2-enoyl)oxazolidin-2-one (S18):



Step 1: At 0 °C NEt_3 (0.40 mL, 2.9 mmol, 1.6 eq.) and pivaloyl chloride (0.31 mL, 2.5 mmol, 1.4 eq.) were added dropwise over one minute to a suspension of (*E*)-3-phenylbut-2-enoic acid (292 mg, 1.80 mmol, 1.00 eq.) in THF (7.2 mL, 0.25 M) and the reaction mixture was stirred for 2 hours at 0 °C.
Step 2: At 0 °C NEt_3 (0.32 mL, 2.3 mmol, 1.3 eq.) was added to a suspension of (*S*)-4-benzyloxazolidin-2-one (558 mg, 3.15 mmol, 1.75 eq.) and LiCl (134 mg, 3.15 mmol, 1.75 eq.) in THF (0.9 mL, 2 M). after stirring for one hour at 0 °C the anhydride suspension was added dropwise over 20 minutes and was allowed to warm to room temperature overnight. NH_4Cl (sat., aq., 10 mL) and water (4 mL) were added and the aqueous phase was extracted with EtOAc (3× 25 mL). The combined organic phases were washed with brine (3 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by column chromatography (SiO_2, 80:20 Pentane:EtOAc) to afford the title compound as a colourless solid (578 mg, 1.80 mmol, quant.).

M.P. = 82−84 **°C**
R_f = 0.29 (80:20 Pentane:EtOAc)
^{1}H NMR (300 MHz, $CDCl_3$): 7.61−7.58 (m, 2H), 7.44−7.23 (m, 9H), 4.83−4.75 (m, 1H), 4.26−4.16 (m, 2H), 3.41 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.83 (dd, *J* = 13.3, 9.6 Hz, 1H), 2.62 (d, *J* = 1.3 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 165.4 (1C), 157.2 (1C), 153.7 (1C), 142.4 (1C), 135.7 (1C), 129.6 (2C), 129.5 (1C), 129.1 (2C), 128.7 (2C), 127.4 (1C), 126.8 (2C), 116.9 (1C), 66.2 (1C), 55.5 (1C), 38.2 (1C), 19.0 (1C).
IR (ATR): ν_{max} = 3024, 1772, 1675, 1387, 1208, 700 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{20}H_{20}NO_3^+$ $[M+H]^+$: 322.1438; found: 322.1438.

(*S*)-4-Benzyl-3-((*S*)-2-(1-phenylvinyl)pent-4-enoyl)oxazolidin-2-one (1r):



At 0 °C *n*BuLi (2.5 M in hexanes, 0.58 mL, 1.4 mmol, 1.2 eq.) was added to a solution of diisopropylamine (0.22 mL, 1.6 mmol, 1.3 eq.) in THF (4.0 mL, 0.30 M). After stirring for 30 minutes at 0 °C the reaction mixture was cooled down to −78 °C, alkene **S18** (386 mg, 1.20 mmol, 1.00 eq.) was added in one portion and the reaction was stirred for further 30 minutes. Allyl bromide (0.19 mL, 2.2 mmol, 1.8 eq., freshly filtered over K_2CO_3) was added dropwise over one minute, the cooling bath was removed and the reaction was stirred for 3 hours at room temperature. NH_4Cl (sat., aq., 5 mL) and H_2O (5 mL) were added and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with HCl (1 M, aq., 3 mL), brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by column chromatography (SiO_2, 90:10, Pentane:EtOAc) to afford the title compound as a yellow oil (144 mg, 0.400 mmol, 33%).

R_f = 0.40 (85:15 Pentane:EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$): 7.50−7.47 (m, 2H), 7.36−7.31 (m, 4H), 7.30−7.27 (m, 2H), 7.24−7.21 (m, 2H), 5.86 (dddd, *J* = 17.4, 10.3, 7.4, 6.0 Hz, 1H), 5.35 (s, 1H), 5.20−5.14 (m, 2H), 5.11 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.05 (dq, *J* = 10.2, 1.3 Hz, 1H), 4.64 (dddd, *J* = 9.9, 7.6, 3.3, 2.5 Hz, 1H), 4.13 (dd, *J* = 9.1, 2.5 Hz, 1H), 4.08 (ddd, *J* = 9.0, 7.7, 0.8 Hz, 1H), 3.32 (dd, *J* = 13.3, 3.3 Hz, 1H), 2.76 (dd, *J* = 13.4, 9.7 Hz, 1H), 2.71 (dddt, *J* = 14.4, 9.7, 7.4, 1.2 Hz, 1H), 2.44 (dddt, *J* = 14.5, 5.9, 4.4, 1.5 Hz, 1H).

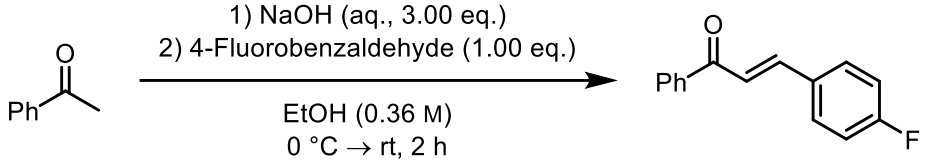
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 173.3 (1C), 153.2 (1C), 147.2 (1C), 140.7 (1C), 135.7 (1C), 135.4 (1C), 129.6 (2C), 129.1 (2C), 128.6 (2C), 128.0 (1C), 127.5 (1C), 127.0 (2C), 117.1 (1C), 114.0 (1C), 66.1 (1C), 56.0 (1C), 48.2 (1C), 38.2 (1C), 36.0 (1C).

IR (ATR): ν_{max} = 3063, 2980, 1775, 1697, 1384, 1350, 1252, 1226, 1206, 1200, 910, 701 cm^{-1}.

HRMS (ESI): m/z calculated for $C_{23}H_{24}NO_3^+$ $[M+H]^+$: 362.1751; found: 362.1749.

$[\alpha]_D^{21}$**:** +201.8080° (*c* = 0.25 g/dL, CH_2Cl_2).

(*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (S19):

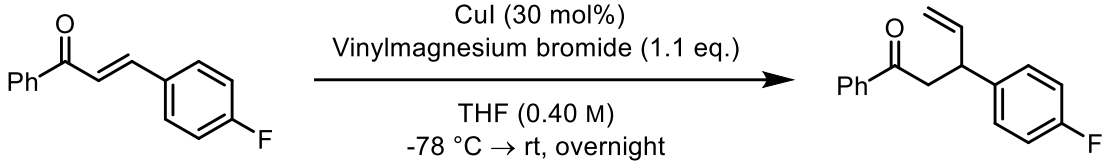


S19
$C_{15}H_{11}FO$
M = 226.25 g/mol

A solution of acetophenone (0.97 mL, 8.3 mmol, 1.0 eq.) in ethanol (23 mL, 0.36 M) was cooled down to 0 °C. NaOH (2.5 M, aq., 10 mL, 25 mmol, 3.0 eq.) was added dropwise over 20 minutes. The reaction was warmed to room temperature and stirred for one hour. 4-Fluorobenzaldehyde (0.89 mL, 8.3 mmol, 1.00 eq.) was then added dropwise over five minutes. After completion of the reaction (reaction control via TLC), ice cold water (10 mL) was added. The participate was filtered of, washed with ice cold Pentane (3 × 3 mL) and dried under reduced pressure to obtain the title compound as white solid (1.64 g, 7.25 mmol, 86%).

M.P. = 82–84 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.03–8.00 (m, 2H), 7.78 (d, *J* = 15.8, 1H), 7.76–7.57 (m, 3H), 7.54–7.44 (m, 3H), 7.12(t, *J* = 8.66 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 190.5 (1C), 165.5–163.0 (d, *J* = 251.8 Hz, 1C), 143.7 (1C), 138.3 (1C), 133.1 (1C), 131.3 (1C), 130.5 (d, *J* = 8.7 Hz, 2C), 128.8 (2C), 128.6 (2C), 122.0 (d, *J* = 2.5 Hz, 1C), 116.3 (d, *J* = 21.8 Hz, 2C).
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm): -109.07.
IR (ATR): ν_{max} = 3057, 1659, 1600, 1587, 1211, 1156, 980, 825, 686, 503 cm^{-1}.
HRMS(ESI): m/z calculated for $C_{15}H_{11}FONa^+$ $[M+Na]^+$: 249.0686; found: 249.0684.

3-(4-Fluorophenyl)-1-phenylpent-4-en-1-one (S20):



S19 **S20**

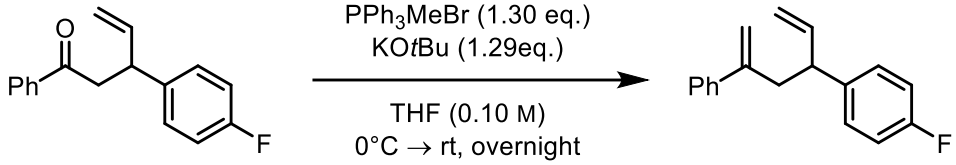
$C_{17}H_{15}FO$

M = 254.30 g/mol

THF (5 mL, 0.4 M) was added to a flask charged with chalcone **S19** (453 mg, 2.00 mmol, 1.00 eq.) and CuI (114 mg, 0.600 mmol, 30.0 mol%). The suspension was stirred for 15 minutes at room temperature before being cooled to –78 °C. Vinyl magnesium bromide (0.1 M in THF, 22 mL, 2.2 mmol, 1.1 eq.) was added dropwise over two hours and the suspension was allowed to warm to room temperature overnight. NH_4Cl (sat., aq., 10 mL) was added and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with NH_4Cl (sat., aq., 10 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by column chromatography (SiO_2, CH_2Cl_2:Pentane 1:1) to afford the title compound as a white solid (209 mg, 0.852 mmol, 41%).

***R*f** = 0.40 (CH_2Cl_2:Pentane 1:1)
M.P. = 31–37 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.97–7.87 (m, 2H), 7.58–7.53 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.45 (m, 2H), 6.98 (t, *J* = 8.8 Hz, 2H), 6.03 (ddd, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.10–4.99 (m, 2H), 4.13 (q, *J* = 7.0 Hz, 1H), 3.46–3.30 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 198.2 (1C), 161.7 (d, *J* = 244.5 Hz, 1C), 140.7 (1C), 138.9 (d, *J* = 3.3 Hz, 1C), 137.2 (1C), 133.3 (1C), 129.4 (d, *J* = 8.0 Hz, 2C), 128.8 (2C), 128.2 (2C), 115.5 (d, *J* = 21.4 Hz, 2C), 115.0 (1C), 44.2(1C), 43.8 (1C).
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm): –116.59.
IR (ATR): ν_{max} = 3046, 3058, 2899, 2362, 1685, 1508, 1221, 833, 689 cm^{-1}.
GCMS (EI): m/z calculated for $C_{17}H_{15}FO^+$ $[M]^+$ 254.1101:; found: 254.1101.

1-Fluoro-4-(5-phenylhexa-1,5-dien-3-yl)benzene (1s):



S20 **1s**

$C_{18}H_{17}F$

M =252.33 g/mol

THF (4.5 mL, 0.10 M) was added to a flask charged with Ph_3PMeBr (209 mg, 0.585 mmol, 1.30 eq.) and KO*t*Bu (65.1 mg, 0.580 mmol, 1.29 eq.) and the suspension was stirred for one hour at room temperature. The reaction was cooled down to 0 °C, ketone **S20** (114 mg, 0.450 mmol, 1.00 eq.) was added in one portion, and the reaction was allowed to warm to room temperature overnight. NH_4Cl (sat., aq., 10 mL) was added and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by column chromatography (SiO_2, Pentane) to afford the title compound as a colorless oil (84.5 mg, 0.332 mmol, 73%).

***R*f** = 0.26 (Pentane)

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.37–7.27 (m, 5H), 7.05 (dd, *J* = 8.4, 5.9 Hz, 2H), 6.95 (t, *J* = 8.8 Hz, 2H), 5.95 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.19 (d, *J* = 1.6 Hz, 1H), 5.03 (d, *J* = 10.3 Hz, 1H), 4.94–4.88 (m, 2H), 3.38 (q, *J* = 7.4 Hz, 1H), 2.99–2.80 (m, 2H).

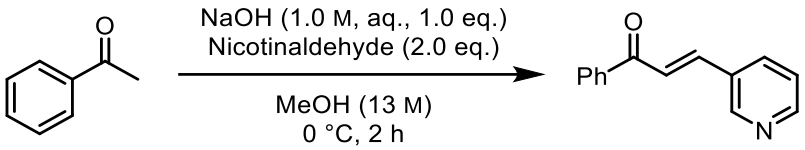
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 162.7–160.3 (d, *J* = 243.8 Hz, 1C), 146.2 (1C), 141.4 (1C), 14.1 (1C), 139.4 (d, *J* = 3.3 Hz, 1C), 129.3 (d, *J* = 8.0 Hz, 2C), 128.5 (2C), 127.6 (1C), 126.5 (2C), 115.3–115.1 (d, *J* = 21.1 Hz, 2C), 115.0 (1C), 114.7 (1C), 47.0 (1C), 42.0 (1C).

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm): -117.11.

IR (ATR): ν_{max} = 3081, 2928, 1634, 1603, 1508, 1222, 914, 900, 777, 534 cm^{-1}.

GCMS (EI): m/z calculated for $C_{18}H_{17}F^+$ $[M]^+$: 252.1309; found: 252.1308.

(*E*)-1-phenyl-3-(pyridin-3-yl)prop-2-en-1-one (S21):

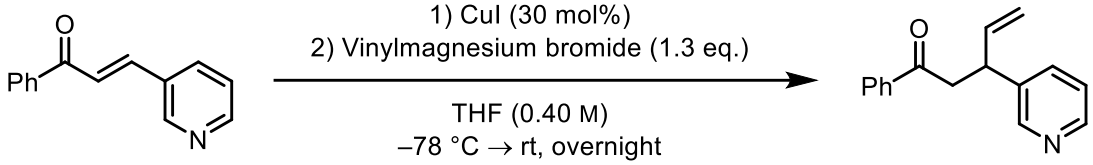


S21
$C_{14}H_{11}NO$
M = 209.25 g/mol

A solution of NaOH (1.0 M, aq., 13 mL, 13 mmol, 1.0 eq.) and MeOH (1.0 mL, 13 M) was cooled to 0 °C and nictotinaldehyde (2.4 mL, 26 mmol, 2.0 eq.) was added in one portion. Subsequently, acetophenone (1.5 mL, 13 mmol, 1.0 eq.) was added dropwise over 5 minutes. After two hours, ice cold water (20 mL) was added under strong stirring. The precipitate was filtered, washed with ice cold water (3 × 3 mL) and dried *in vacuo*. After recrystallisation from hot ethanol (approx. 5 mL), the title compound was obtained as pale yellow crystals (2.44 g, 12.8 mmol, 98%).

M.P. = 97–98 °C (EtOH)
^{1}H NMR (300 MHz, DMSO-*d*6): δ (ppm): 9.03 (d, *J* = 2.4 Hz, 1H), 8.63–8.61 (m, 1H), 8.39–8.35 (m, 1H), 8.19–8.16 (m, 2H), 8.09 (d, *J* = 15.7 Hz, 1H), 7.78 (d, *J* = 15.8 Hz, 1H), 7.71–7.66 (m, 1H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.50 (dd, *J* = 8.2, 4.5 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*6): δ (ppm): 189.0 (1C), 151.0 (1C), 150.4 (1C), 140.6 (1C), 137.3 (1C), 135.1 (1C), 133.4 (1C), 130.5 (1C), 128.8 (2C), 128.6 (2C), 123.9 (1C), 123.9 (1C).
IR (ATR): ν_{max} = 3061, 3039, 1659, 1307, 1219, 1013, 766, 680, 573 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{14}H_{12}NO^+$ $[M+H]^+$: 210.0913; found: 210.0914.

1-Phenyl-3-(pyridin-3-yl)pent-4-en-1-one (S22):



S21 **S22**

$C_{16}H_{15}NO$

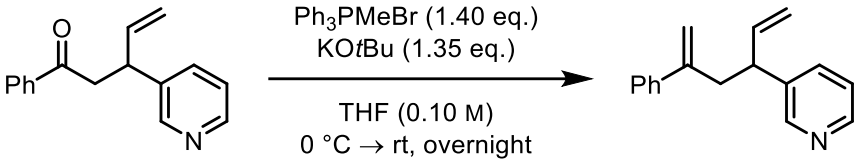
M = 237.30 g/mol

THF (5 mL, 0.4 M) was added to a flask charged with CuI (114 mg, 0.600 mmol, 30 mol%) and chalcone **S21** (419 mg, 2.00 mmol, 1.00 eq.). The suspension was stirred for 15 min. at room temperature and cooled to -78 °C. Vinylmagensium bromide (0.10 M in THF, 26 mL, 2.6 mmol, 1.3 eq.) was added dropwise over 2 h and the reaction was allowed to warm to room temperature overnight. NH_4Cl (sat., aq., 15 mL) and H_2O (10 mL) were added to the reaction mixture. The aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with NH_4Cl (sat., aq., 5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentratead *in vacuo*. After purification by column chromatography (SiO_2, Pentane:EtoAc 1:1), the title compound was obtained as a yellow oil (294 mg, 1.24 mmol, 61%).

Note: Not all aromatic proton and carbon resonances could be observed in the corresponding NMR spectra.

R_f = 0.30 (Pentane:EtoAc 1:1)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.94–7.91 (m, 2H), 7.68–7.30 (m, 6H), 6.10–5.99 (m, 1H), 5.12–5.03 (m, 2H), 4.23 (bs, 1H), 3.52–3.35 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 197.7 (1C), 139.9 (1C), 137.0 (1C), 135.3 (app., 1C), 133.4 (1C), 128.8 (2C), 128.7 (1C), 128.2 (2C), 126.2 (app., 1C), 115.9 (1C), 43.7 (1C), 42.4 (1C).
IR (ATR): ν_{max} = 3082, 2879, 1674, 1593, 1410, 1259, 1203, 916, 749, 684, 607 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{16}H_{16}NO^+$ $[M+H]^+$: 238.1226; found: 238.1232.

3-(5-Phenylhexa-1,5-dien-3-yl)pyridine (1t):



S22 **1t**

$C_{17}H_{17}N$

M = 235.33 g/mol

THF (4.5 mL, 0.10 M) was added to a flask charged with Ph_3PMeBr (225 mg, 0.630 mmol, 1.40 eq.) and KO*t*Bu (68.2 mg, 0.607 mmol, 1.35 eq.) and the suspension was stirred for one hour at room temperature. The reaction was cooled down to 0 °C, ketone **S22** (107 mg, 0.450 mmol, 1.00 eq.) was added in one portion and the reaction was allowed to warm to room temperature overnight. NH_4Cl (sat., aq., 5 mL) was added and the aqueous phase was extracted with EtOAC (3 × 10 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. After purification by column chromatography (SiO_2, Pentane:EtOAc, 7:3 → 3:2), the title compound was obtained as colorless oil (69.0 mg, 0.293 mmol, 65%).

R_f = 0.36 (Pentane:EtOAc 3:2)

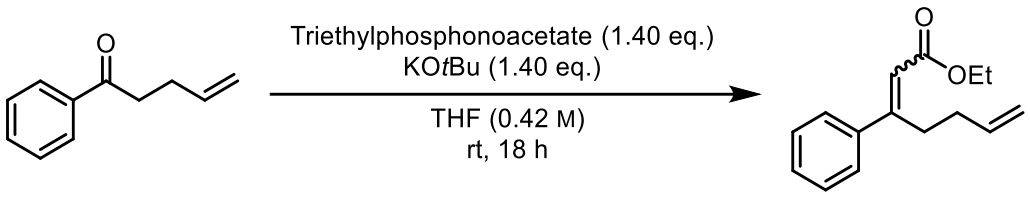
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.45–8.43 (m, 1H), 8.32 (d, *J* = 2.5 Hz, 1H), 7.44–7.40 (m, 1H), 7.34–7.28 (m, 5H), 7.22–7.18 (m, 1H), 6.03–5.92 (m, 1H), 5.19 (d, *J* = 1.6 Hz, 1H), 5.08 (d, *J* = 10.3 Hz, 1H), 4.96 (d, *J* = 17.1 Hz, 1H), 4.90 (d, *J* = 1.3 Hz, 1H), 3.42 (q, *J* = 6.9 Hz, 1H), 3.02 (dd, *J* = 14.8, 7.8 Hz, 1H), 2.85 (dd, *J* = 14.2, 8.2 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 149.8 (1C), 147.9 (1C), 145.9 (1C), 140.8 (1C), 140.4 (1C), 138.9 (1C), 135.4 (1C), 128.6 (2C), 127.7 (1C), 126.5 (2C), 123.4 (1C), 115.5 (1C), 115.4 (1C), 45.2 (1C), 41.7 (1C).

IR (ATR): ν_{max} = 3080, 3028, 2929, 1635, 1424, 913, 779, 715 cm^{-1}.

HRMS (ESI): m/z calculated for $C_{17}H_{17}NNa^+$ $[M+Na]^+$: 258.1253; found: 258.1255.

Ethyl 3-phenylhepta-2,6-dienoate (1u)



S2 **1u**

$C_{15}H_{18}O_2$

M = 230.31 g/mol

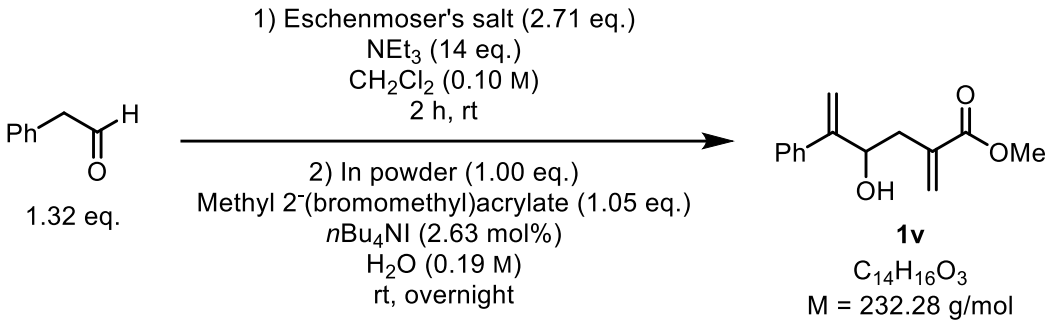
Triethyl phosphonoacetate (0.350 mL, 1.75 mmol, 1.40 eq.) was added to a solution of KO*t*Bu (196 mg, 1.75 mmol, 1.40 eq.) in THF (3.0 mL, 0.42 M) and stirred for 30 minutes. Ketone **S2** (200 mg, 1.25 mmol, 1.00 eq.) was added dropwise and the mixture was stirred at room temperature for 18 hours. The solvent was removed *in vacuo* and the residue was redissolved in H_2O (10 mL). The aqueous phase was extracted with EtOAc (3×15 mL) and the combined organic phases were washed with brine (10 mL) and H_2O (10 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 98:2 Pentane:EtOAc) to afford the title compound as an inseparable 98:2 (*E*:*Z*) mixture of geometric isomers and as a colourless oil (106 mg, 0.460 mmol, 36%).

R_f = 0.31 (98:2 Pentane:EtOAc)
IR (ATR): ν_{max} = 3075, 2979, 2935, 1723, 1700, 1638, 1220, 1154, 1035, 910, 696 cm^{-1}.
GCMS (EI): m/z calculated for $C_{15}H_{18}O_2Na^+$ $[M+Na]^+$: 253.1199; found: 253.1204.

Ethyl (*E*)-3-phenylhepta-2,6-dienoate:
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.49–7.30 (m, 3H), 7.17–7.14 (m, 2H), 5.89 (s, 1H), 5.84–5.71 (m, 1H), 5.04–5.00 (m, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.14 (m, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 166.0 (1C), 158.6 (1C), 139.9 (1C), 137.1 (1C), 127.9 (2C), 127.6 (1C), 127.1 (2C), 117.7 (1C), 115.5 (1C), 59.8 (1C), 39.6 (1C), 31.4 (1C), 13.9 (1C).

Ethyl (*Z*)-3-phenylhepta-2,6-dienoate:
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38–7.30 (m, 3H), 7.17–7.14 (m, 2H), 6.04 (s, 1H), 5.84–5.71 (m, 1H), 5.04–5.00 (m, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.20 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).

Methyl 4-hydroxy-2-methylene-5-phenylhex-5-enoate (1v):



Step 1: To a suspension of Eschenmoser's salt (1.90 g, 10.3 mmol, 2.71 eq.) in CH_2Cl_2 (50 mL, 0.10 M), 2-phenylacetaldehyde (601 mg, 5.00 mmol, 1.32 eq.) and NEt_3 (7.1 mL, 52 mmol, 14 eq.) were added. The solution was stirred for 2 h at room temperature and washed with $NaHCO_3$ (2 × 20 mL) and brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure (the water bath temperature was kept at 0 °C to reduce polymerisation).

Step 2: Water (20 mL, 0.19 M) was added to the pale yellow residue, followed by *n*Bu_4NI (36.9 mg, 0.100 mmol, 2.63 mol%), methyl 2-(bromomethyl)acrylate (680 mg, 3.80 mmol, 1.00 eq.) and In powder (459 mg, 4.00 mmol, 1.05 eq.). The reaction was stirred at room temperature overnight. The aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. After purification by column chromatography (SiO_2, 4:1 Pentane:EtOAc), the title compound was isolated as yellow oil (212 mg, 0.914 mmol, 18%).

R_f = 0.36 (Pentane:EtoAc 4:1)

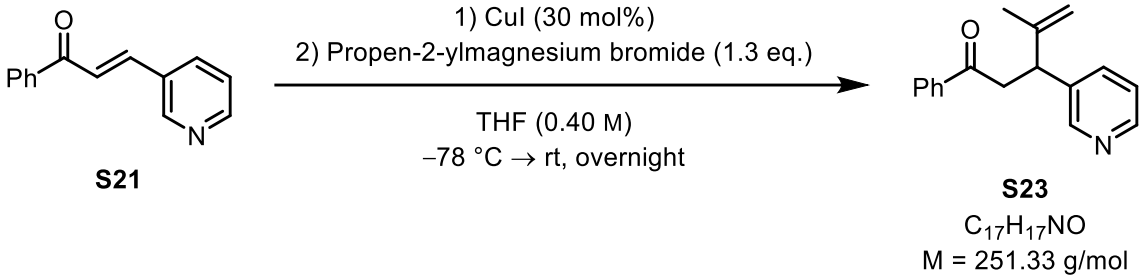
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.44–7.29 (m, 5H), 6.23 (d, *J* = 1.5 Hz, 1H), 5.55 (d, *J* = 1.2 Hz, 1H), 5.42 (t, *J* = 1.4 Hz, 1H), 5.36 (s, 1H), 4.87 (d, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 2.72 (ddd, *J* = 14.3, 3.4, 1.3 Hz, 1H), 2.39 (ddd, *J* = 14.3, 8.5, 1.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 168.6 (1C), 150.9 (1C), 139.8 (1C), 137.0 (1C), 128.6 (1C), 128.6 (2C), 127.9 (1C), 127.0 (2C), 112.9 (1C), 72.3 (1C), 52.3 (1C), 39.7 (1C).

IR (ATR): ν_{max} = 3464, 3058, 3030, 2951, 2360, 2342, 1715, 1440, 1204, 1146, 779, 669 cm^{-1}.

HRMS (ESI): m/z calculated for $C_{14}H_{16}O_3Na^+$ $[M+Na]^+$: 255.0992; found: 255.1003.

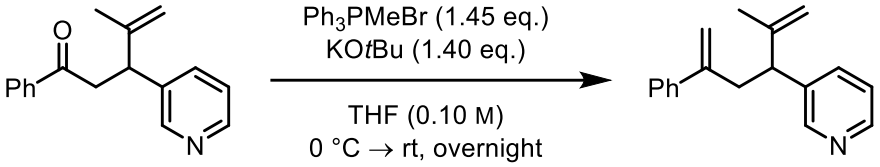
4-Methyl-1-phenyl-3-(pyridin-3-yl)pent-4-en-1-one (S23):



THF (5 mL, 0.4 M) was added to a flask charged with CuI (114 mg, 0.60 mmol, 30 mol%) and chalcone **S21** (419 mg, 2.00 mmol, 1.00 eq.). The suspension was stirred for 15 min. at room temperature and cooled to -78 °C. Propen-2-ylmagnesiumbromide (0.10 M in THF, 26 mL, 2.6 mmol, 1.3 eq.) was added dropwise over 2 h and the reaction was allowed to warm to room temperature overnight. NH_4Cl (sat., aq., 5 mL) and H_2O (15 mL) were added to the reaction mixture. The aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with $NaHCO_3$ (sat., aq., 10 mL) and brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane:EtOAc 1:1) to afford the title compound as a pale yellow solid (149 mg, 0.734 mmol, 36%).

***R*f** = 0.28 (Pentane:EtOAc 1:1)
M.P. = 54–56 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.51 (d, *J* = 25.4 Hz, 2H), 7.93–7.91 (m, 2H), 7.62–7.53 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.25–7.20 (m, 1H), 4.93 (d, *J* = 8.4 Hz, 2H), 4.08 (t, *J* = 7.0 Hz, 1H), 3.57 (dd, *J* = 17.1, 6.9 Hz, 1H), 3.38 (dd, *J* = 17.1, 6.9 Hz, 1H), 1.68 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 197.8 (1C), 149.7 (1C), 148.1 (1C), 146.2 (1C), 138.3 (1C), 137.0 (1C), 135.6 (1C), 133.4 (1C), 128.8 (2C), 128.1 (2C), 123.6 (1C), 111.4 (1C), 45.1 (1C), 42.8 (1C), 22.2 (1C).
IR (ATR): ν_{max} = 3084, 2969, 2918, 2360, 2340, 1685, 1448, 1206, 716, 690, 573 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{17}H_{18}NO^+$ $[M+H]^+$ 52.1383:; found: 252.1382.

3-(2-Methyl-5-phenylhexa-1,5-dien-3-yl)pyridine (1x):



S23 **1x**

$C_{18}H_{19}N$

M = 249.36 g/mol

THF (5.5 mL, 0.10 M) was added to a flask charged with Ph_3PMeBr (275 mg, 0.770 mmol, 1.45 eq.) and KO*t*Bu (83.3 mg, 0.742 mmol, 1.40 eq.) and the suspension was stirred for one hour at room temperature. The reaction was cooled down to 0 °C, ketone **S23** (133 mg, 0.530 mmol, 1.00 eq.) was added in one portion and the reaction was allowed to warm to room temperature overnight. NH_4Cl (sat., aq., 5 mL) and water (5 mL) were added and the aqueous phase was extracted with EtOAC (3 × 10 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered concentrated *in vacuo* before being purified by column chromatography (SiO_2, Pentane:EtOAc, 7:3) to afford the title compound as a pale orange oil (85.2 mg, 0.342 mmol, 64%).

R_f = 0.29 (Pentane:EtOAc 7:3)

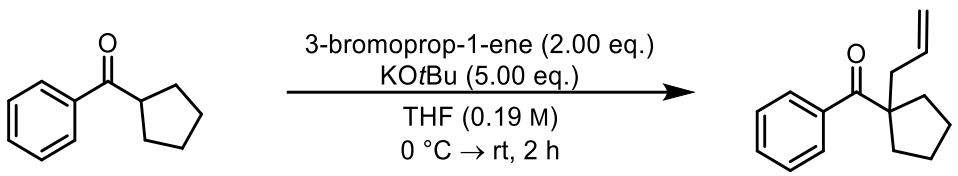
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.43 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.31 (d, *J* = 2.5 Hz, 1H), 7.44 (dt, *J* = 8.0, 2.1 Hz, 1H), 7.35–7.25 (m, 5H), 7.19 (dd, *J* = 8.0. 4.7 Hz, 1H), 5.14 (d, *J* = 1.6 Hz, 1H), 4.92 (s, 2H), 4.84 (s, 1H), 3.33 (dd, *J* = 9.1, 6.0 Hz, 1H), 3.17 (dd, *J* = 13.4, 6.8 Hz, 1H), 2.85 (dd, *J* = 14.2, 9.1 Hz, 1H), 1.57 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 150.0 (1C), 147.8 (1C), 146.5 (1C), 146.2 (1C), 140.9 (1C), 138.3 (1C), 135.4 (1C), 128.6 (2C), 127.7 (1C), 126.5 (2C), 123.3 (1C), 115.2 (1C), 111.6 (1C), 48.2 (1C), 39.5 (1C), 21.6 (1C).

IR (ATR): ν_{max} = 3081, 3027, 2940, 2362, 2340, 1646, 1422, 1026, 896, 778, 707, 562 cm^{-1}.

HRMS (ESI): m/z calculated for $C_{18}H_{20}N^+$ $[M+H]^+$: 250.1590; found: 250.1584.

(1-Allylcyclopentyl)(phenyl)methanone (S24)

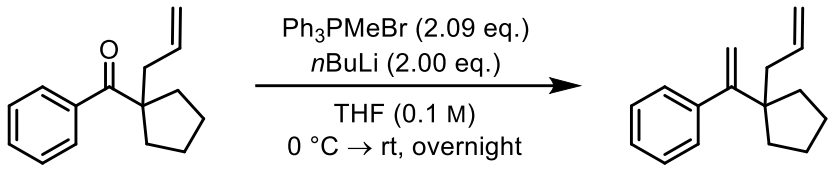


S24
$C_{15}H_{18}O$
M = 214.31 g/mol

Cyclopentyl(phenyl)methanone (500 mg, 2.87 mmol, 1.00 eq.) was added to a solution of KO*t*Bu (1.61 g, 14.4 mmol, 5.00 eq.) in THF (15.0 mL, 0.19 M) at 0 °C and stirred for 30 minutes. Vinyl bromide (694 mg, 5.74 mmol, 2.00 eq.) was then added dropwise, and the solution was warmed to room temperature. After 2 hours, HCl (1 M, aq.) was added until the pH < 0. The solvent was removed under reduced pressure and the residue was redissolved in EtOAc (137 mL), and the organic phase was washed with H_2O (34 mL) and brine (34 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 99:1 Pentane:EtOAc) to obtain the title compound as a colourless oil (289 mg, 1.35 mmol, 47%).

***R*$_f$** = 0.29 (99:1 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.85 (d, *J* = 7.8 Hz, 2H), 7.51–7.38 (m, 3H), 5.66–5.52 (m, 1H), 4.96–4.83 (m, 2H), 2.60 (d, *J* = 7.3 Hz, 2H), 2.37–2.28 (m, 2H), 1.82–1.71 (m, 2H), 1.71–1.59 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 205.7 (1C), 137.2 (1C), 134.4 (1C), 131.8 (1C), 129.0 (2C), 128.3 (2C), 117.8 (1C), 58.9 (1C), 44.4 (1C), 36.0 (2C), 25.7 (2C).
IR (ATR): ν_{max} = 3072, 2950, 2865, 1672, 1446, 1213, 914, 692 cm^{-1}.
GCMS (ESI): m/z calculated for $C_{15}H_{18}ONa^+$ $[M+Na]^+$: 237.1255; found: 237.1250.

(1-(1-Allylcyclopentyl)vinyl)benzene (1y)

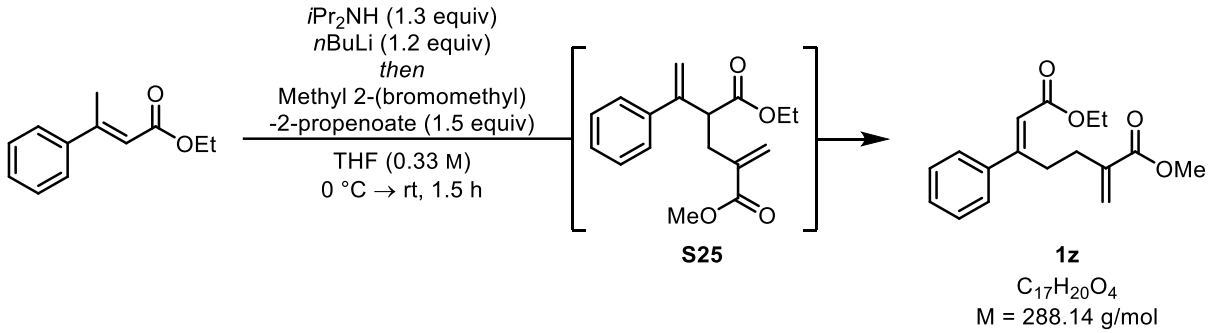


S24 **1y**
$C_{16}H_{20}$
M = 212.34 g/mol

At room temperature, *n*BuLi (2.5 M in Hexane, 0.750 mL, 1.87 mmol, 2.00 eq.) was added slowly to a suspension of Ph_3PMeBr (697 mg, 1.95 mmol, 2.09 eq.) in THF (9.3 mL, 0.10 M). After stirring for one hour, the solution was cooled to 0 °C and ketone **S24** (200 mg, 0.933 mmol, 1.00 eq.) was added in one portion. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched by slow addition of NH_4Cl (sat., aq., 10 mL) and the aqueous phase was extracted with EtOAc (3×15 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a colourless oil (159 mg, 0.750 mmol, 80%).

R_f = 0.65 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.31–7.20 (m, 5H), 5.89–5.75 (m, 1H), 5.11–4.97 (m, 4H), 2.17 (d, *J* = 7.1 Hz, 2H), 1.78–1.63 (m, 6H), 1.59–1.54 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 155.6 (1C), 143.9 (1C), 136.2 (1C), 128.6 (2C), 127.7 (2C), 126.6 (1C), 116.5 (1C), 114.5 (1C), 52.0 (1C), 41.4 (1C), 36.6 (2C), 23.3 (2C).
IR (ATR): ν_{max} = 3075, 2957, 2872, 2362, 1638, 1490, 902, 773, 700 cm^{-1}.
GCMS (EI): m/z calculated for $C_{16}H_{20}^+$ $[M]^+$: 212.1; found: 212.1.

1-Ethyl 7-methyl (*E*)-6-methylene-3-phenylhept-2-enedioate (1z)



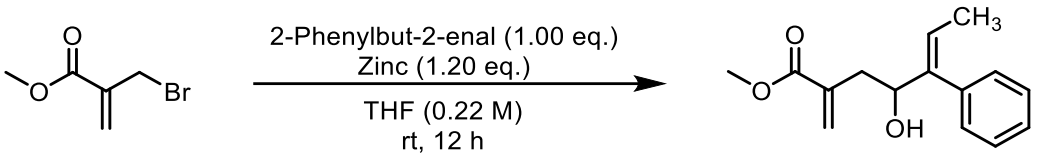
A solution of diisopropylamine (0.55 mL, 3.9 mmol, 1.3 eq.) in THF (9 mL, 0.3 M) was cooled to 0 °C. Under stirring, *n*BuLi (2.5 M in Hexanes, 1.44 mL, 3.60 mmol, 1.20 eq.) was added dropwise. After stirring at 0 °C for 30 minutes, ethyl (*E*)-3-phenylbut-2-enoate (0.55 mL, 3.0 mmol, 1.0 eq.) was added dropwise. After stirring at 0 °C for 1 hour, the reaction was cooled to –78 °C and methyl 2-(bromomethyl)-2-propenoate (0.54 mL, 4.5 mmol, 1.5 eq.) was added dropwise. The reaction was stirred for 15 minutes at –78 °C. The reaction was quenched by addition of HCl (1 M, aq., 6 mL) at –78 °C before being warmed to room temperature. The layers were separated and the aqueous layer was extracted with Et_2O (3×20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 95:5 Pentane:Et_2O) to afford an inseparable mixture of **1z** and **S25** as a colourless oil (503 mg, 1.74 mmol, 58%). **S25** rearranged to **1z** over time at room temperature.

1z and **S25** could be separated by preparative HPLC (MeOH-H_2O 70:30, Gradient to 100-0 in 30 min; 21.0 mL/min, 295 K)

Data for **1z**:

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm = 7.52–7.45 (m, 2H), 7.43–7.31 (m, 3H), 6.15 (d, *J* = 1.3 Hz, 1H), 6.09 (s, 1H), 5.58 (q, *J* = 1.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.33–3.25 (m, 2H), 2.50–2.41 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 167.6 (1C), 166.5 (1C), 159.1 (1C), 140.9 (1C), 139.7 (1C), 129.2 (1C), 128.7 (2C), 126.9 (2C), 125.7 (1C), 118.2 (1C), 60.0 (1C), 51.9 (1C), 31.3 (1C), 29.9 (1C), 14.5 (1C).
IR (ATR): ν_{max} = 2983, 2951, 1709, 1623, 1443, 1295, 1154, 1039, 770, 696 cm^{-1}.
HRMS (ESI): calculated for $C_{17}H_{21}O_4^+$ $[M+H]^+$: 289.1434; found: 289.436.

Methyl 4-hydroxy-2-methylene-5-phenylhept-5-enoate (1aa)

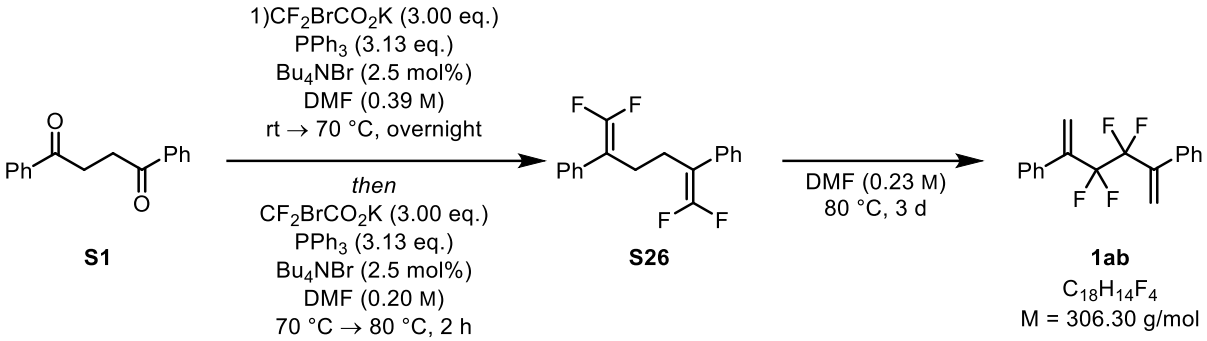


1aa
$C_{15}H_{18}O_3$
M = 246.31 g/mol

THF (9 mL, 0.2 M) was added to a mixture of 2-phenylbut-2-enal (292 mg, 2.00 mmol, 1.00 eq.), Methyl 2-(bromomethyl)-2-propenoate (356 mg, 2.00 mmol, 1.00 eq.), zinc (157 mg, 2.40 mmol, 1.20 eq.) and NH_4Cl (sat., aq., 3 mL). The suspension was stirred at room temperature overnight. The organic phase was separated, and the aqueous phase was extracted with EtOAc (3×10 mL). The combined organic phases were washed with NH_4Cl (sat., aq., 5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* before being purified by flash column chromatography (SiO_2, 75:25 Pentane:EtOAc) to afford the title compound as a colourless oil (446 mg, 1.81 mmol, 90%).

R_f = 0.19 (75:25 Pentane:EtOAc)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38–7.27 (m, 3H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.21 (s, 1H), 5.87 (q, *J* = 6.9 Hz, 1H), 5.56 (s, 1H), 4.52 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.74 (s, 3H), 2.57 (dd, *J* = 14.3, 3.7 Hz, 1H), 2.31 (dd, *J* = 14.3, 8.7 Hz, 1H), 2.20 (br. s, 1H), 1.57 (d, *J* = 6.9 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 168.5 (1C), 143.5 (1C), 138.2 (1C), 137.4 (1C), 129.5 (2C), 128.3 (2C), 128.1 (1C), 127.1 (1C), 123.1 (1C), 75.3 (1C), 52.2 (1C), 39.4 (1C), 14.4 (1C).
IR (ATR): ν_{max} = 3426, 2950, 2910, 2854, 2355, 1712, 1438, 1198, 1139, 702 cm^{-1}.
GCMS (ESI): m/z calculated for $C_{15}H_{18}O_3Na^+$ $[M+Na]^+$: 269.1154; found: 269.1148.

(3,3,4,4-tetrafluorohexa-1,5-diene-2,5-diyl)dibenzene (1ab):



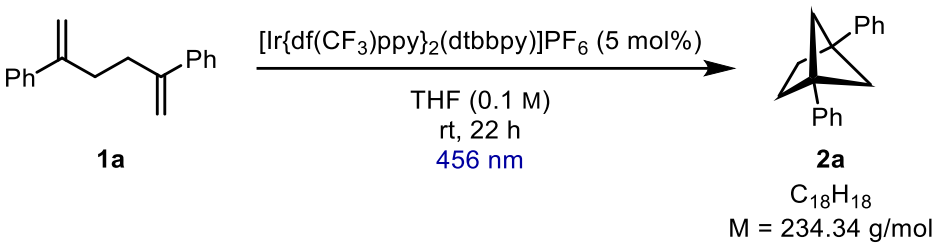
DMF (3.2 mL, 0.39 M) was added to a flask charged with ketone **S1** (300 mg, 1.26 mmol, 1.00 eq.), CF_2BrCO_2K (805 mg, 3.78 mmol, 3.00 eq.), PPh_3 (1.03 g, 3.94 mmol, 3.13 eq.) and *n*Bu_4NBr (10.1 mg, 31.5 µmol, 2.50 mol%). The reaction was heated slowly to 70 °C and stirred overnight. A suspension of CF_2BrCO_2K (805 mg, 3.78 mmol, 3.00 eq.), PPh_3 (1.03 g, 3.94 mmol, 3.13 eq.), *n*Bu_4NBr (10.1 mg, 31.5 µmol, 2.5 mol%) in DMF (3.2 mL, 1.18 M) was added dropwise over five minutes. After 30 minutes, the temperature was increased to 80 °C and the suspension was stirred for further 2 h. Water (60 mL) and EtOAc (20 mL) were added. The aqueous phase was extracted with EtOAc (3 × 15 mL) and the combined organic phases were washed with HCl (1 M, aq., 10 mL), LiCl (5 w%, aq., 10 mL), brine (5 mL), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, Pentane:EtOAc 95:5).

The resulting colourless solid was dissolved in DMF (1.5 mL, 0.23 M) and stirred for three days at 80 °C. Water (15 mL) was added and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic phases were washed with HCl (1 M, aq., 5 mL), LiCl (5 w%, aq., 5 mL), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the product was obtained as a low melting and inseparable mixture of the title compound with diene **S26** (97:3, 99.1 mg, 0.325 mmol, 25%)

R_f = 0.18 (Pentane)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.36–7.28 (m, 10H), 5.82 (s, 2H), 5.63 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 140.5 (2C), 136.5 (2C), 128.9 (4C), 128.4 (2C), 128.1 (4C), 124.1 (q, *J* = 5.2, 2C), 116.4 (2C).
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm): –107.84.
IR (ATR): ν_{max} = 3086, 3071, 3055, 3036, 3022, 1902, 1677, 1493,1445, 1393, 1228, 1165, 1088, 948, 695 cm^{-1}.
GCMS (EI): m/z calculated for $C_{18}H_{14}F_4^+$ $[M]^+$: 306.1026; found: 306.1024.

6.3 Synthesis of BCH 2a–ab.

1,4-Diphenylbicyclo[2.1.1]hexane (2a)



1a **2a**

$C_{18}H_{18}$

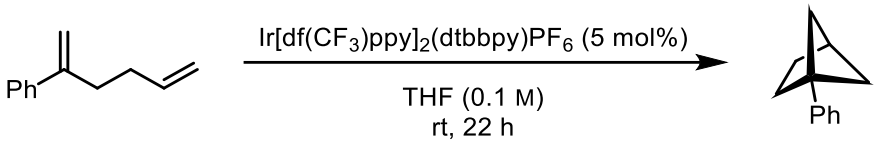
M = 234.34 g/mol

0.19 mmol scale:
Prepared according to **GP1** using diene **1a** (44.5 mg, 0.190 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (10.5 mg, 9.36 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as colourless crystals (41.9 mg, 0.179 mmol, 94%).

1.00 mmol scale:
A 10 mL Schlenk tube was charged with diene **1a** (234 mg, 1.00 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (56.1 mg, 50.0 µmol, 5 mol%), and THF (10 mL, 0.1 M) and subsequently deoxygenated by three freeze-pump-thaw cycles. The reaction was irradiated with 456 nm LEDS for 66 hours at room temperature under strong stirring. The reaction was concentrated *in vacuo* and directly purified by flash column chromatography (SiO_2, Pentane) to afford the title compound as a colourless solid (215 mg, 917 µmol, 91%).

R_f = 0.26 (Pentane).
M.P. = 70−72 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.37–7.30 (m, 8H), 7.24–7.19 (m, 2H), 2.09 (s, 4H), 2.02–1.98 (m, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 144.2 (2C), 128.4 (4C), 126.2 (2C), 126.1 (4C), 51.1 (2C), 47.7 (2C), 35.3 (2C).
IR (ATR): ν_{max} = 3059, 3028, 2946, 2926, 2863, 1602, 1494, 1446, 1354, 1320, 1193, 1171, 1073, 1027, 987, 895, 829, 755, 693, 668, 635, 545, 532 cm^{-1}.
GCMS (EI): calculated for $C_{18}H_{18}^+$ [M]+: 234.1; found: 234.1.

1-Phenylbicyclo[2.1.1]hexane (2b)



1b **2b**

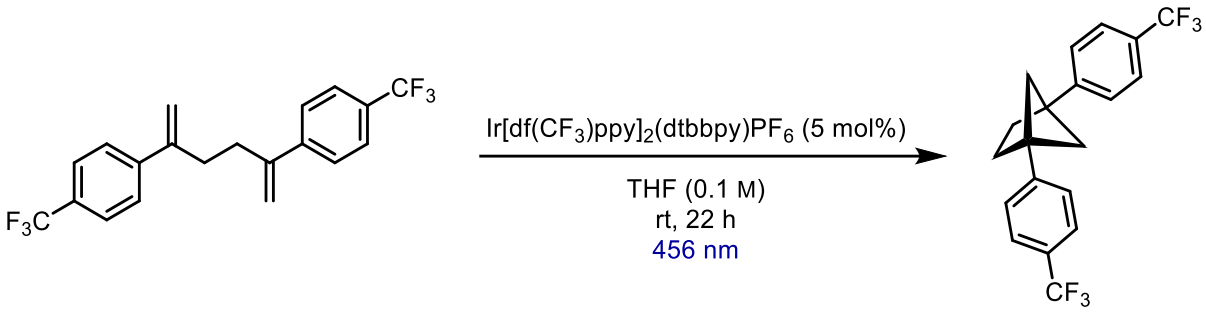
$C_{12}H_{14}$
M = 158.24 g/mol

Prepared according to **GP1** using diene **1b** (31.6 mg, 0.200 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless oil (27.4 mg, 0.173 mmol,86%).

CAUTION: product proved to be volatile at low pressures and solvent was removed at 35 °C, 300–350 mbar.

***R**$_f$* = 0.36 (Pentane).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.34–7.33 (m, 2H), 7.27–7.24 (m, 2H), 7.20–7.17 (m, 1H), 2.55–2.53 (m, 1H), 1.87–1.82 (m, 4H), 1.77 (bs, 2H), 1.46 (dd, *J* = 4.03, 1.98 Hz, 2H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 144.9 (1C), 128.2 (2C), 126.0 (2C), 126.0 (1C), 54.3 (1C), 43.4 (2C), 36.6 (1C), 33.5 (1C), 28.9 (1C).
IR (ATR): ν_{max} = 2963, 2869, 1604, 1498, 1446, 1335, 1283, 1202, 1068, 1021, 822, 753, 696, 538 cm^{-1}.
GCMS (EI): calculated for $C_{12}H_{14}^+$ $[M]^+$: 158.1; found: 158.1.

1,4-Bis(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (2c)



1c **2c**

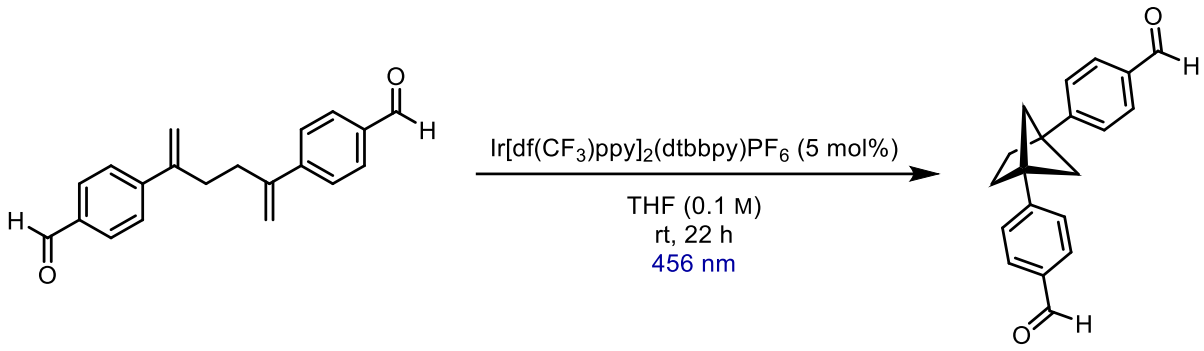
$C_{20}H_{16}F_6$

M = 370.34 g/mol

Prepared according to **GP1** using diene **1c** (66.7 mg, 0.190 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (10.2 mg, 9.00 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as colourless crystals (38.9 mg, 0.105 mmol, 58%).

***R**$_f$* = 0.30 (Pentane).
M.P. = 76−77 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.59 (d, *J* = 8.36 Hz, 4H), 7.39 (d, *J* = 8.26 Hz, 4H), 2.12 (s, 4H), 2.05–2.02 (m, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 147.7 (2C), 128.9 (4C), 128.5 (4C), 126.4 (2C), 125.5–125.3 (q, *J* = 3.8 Hz, 2C), 51.1 (2C), 47.6 (2C), 35.3 (2C).
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ/ppm = 62.36.
IR (ATR): ν_{max} = 2953, 2920, 2874, 1617, 1411, 1321, 1194, 1165, 1118, 1105, 1066, 1016, 990, 956, 862, 833, 697, 602, 518 cm^{-1}.
GCMS (EI): calculated for $C_{20}H_{16}F_6^+$ $[M]^+$: 370.1; found: 370 0.

4,4'-(Bicyclo[2.1.1]hexane-1,4-diyl)dibenzaldehyde (2d)

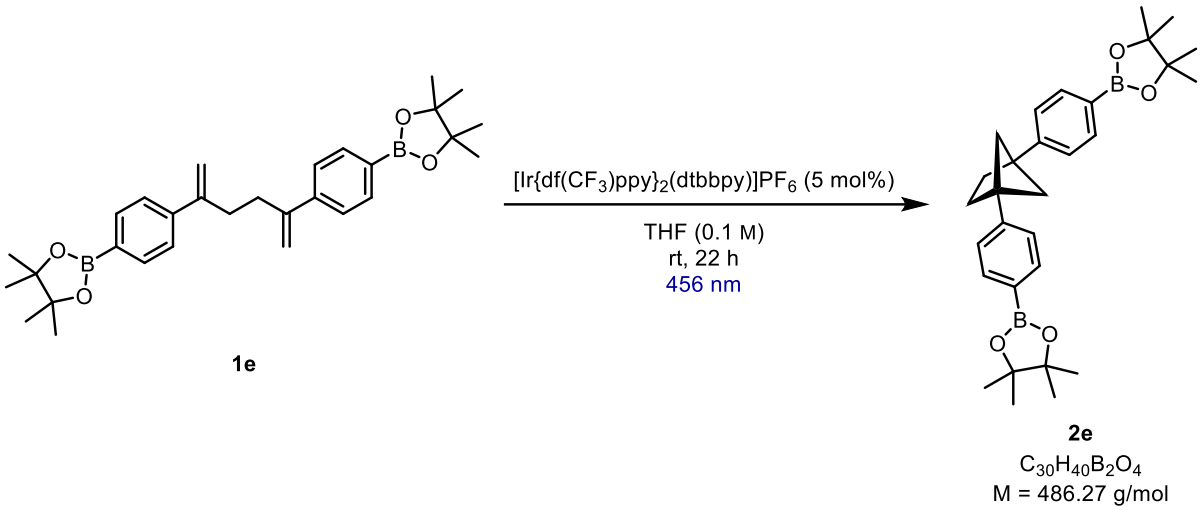


1d **2d**
$C_{20}H_{18}O_2$
M = 290.36 g/mol

Prepared according to **GP1** using diene **1d** (58.1 mg, 0.200 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 13:6 Pentane:EtOAc) afforded the title compound as a colourless solid (33.5 mg, 0.115 mmol, 57%).

***R*$_f$** = 0.30 (13:6 Pentane:EtOAc).
M.P. = 85−89 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 10.00 (s, 2H), 7.87–7.84 (m, 4H), 7.46–7.44 (m, 4H), 2.15 (s, 4H), 2.11–2.07 (m, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 192.1 (2C), 150.9 (2C), 134.9 (2C), 130.1 (4C), 126.7 (4C), 51.5 (2C), 47.7 (2C), 35.4 (2C).
IR (ATR): ν_{max} = 2965, 2945, 2917, 2869, 2737, 1692, 1601, 1567, 1394, 1303, 1255, 1210, 1161, 1100, 986, 813, 686, 542 cm^{-1}.
HRMS (ESI): calculated for $C_{20}H_{18}O_2Na^+$ [M+Na]$^+$: 313.1199; found: 313.1204.

1,4-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)bicyclo[2.1.1]hexane (2e)



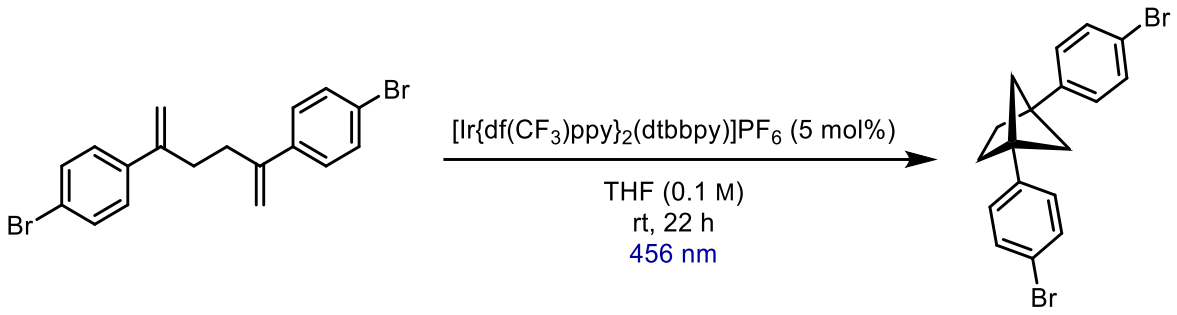
1e

2e
$C_{30}H_{40}B_2O_4$
M = 486.27 g/mol

Prepared according to **GP1** using diene **1e** (97.4 mg, 0.200 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 475:25:1 Pentane:EtOAc:CH_2Cl_2) afforded the title compound as a colourless solid (97.2 mg, 0.200 mmol, quant.).

M.P. = 205−207 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.79–7.77 (m, 4H), 7.31–7.29 (m, 4H), 2.08 (s, 4H), 2.00 (s, 4H), 1.34 (s, 24H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 147.5 (2C), 135.0 (4C), 128.4 (2C), 125.5 (4C), 83.8 (4C), 51.4 (2C), 47.6 (2C), 35.4 (2C), 25.0 (8C).
IR (ATR): ν_{max} = 2973, 2927, 2868, 1614, 1523, 1401, 1360, 1323, 1307, 1272, 1214, 1166, 1140, 1104, 1090, 1020, 997, 988, 961, 859, 827, 812, 746, 702, 676, 658, 639, 579, 534, 521 cm^{-1}.
HRMS (ESI): calculated for $C_{30}H_{40}B_2O_4Na^+$ $[M+Na]^+$: 507.3078; found: 507.3052.

1,4-Bis(4-bromophenyl)bicyclo[2.1.1]hexane (2f)



1f **2f**

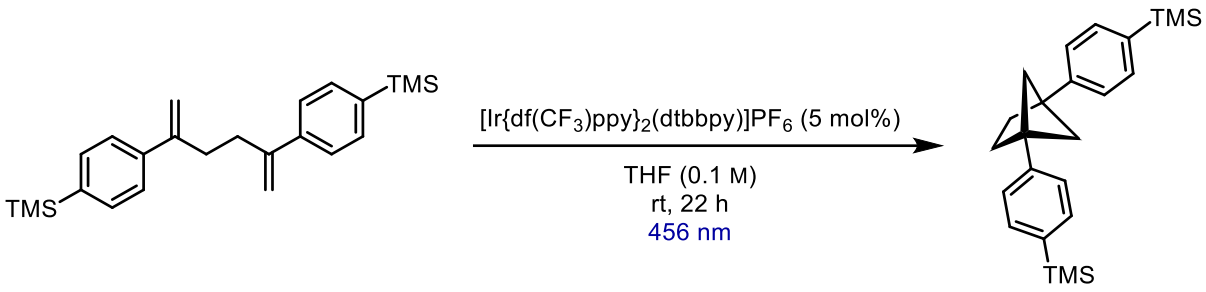
$C_{18}H_{16}Br_2$

M = 392.13 g/mol

Prepared according to **GP1** using diene **1f** (78.4 mg, 0.200 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.1 M). The title compound could not be isolated by flash column chromatography or recrystallization. The yield was estimated using 1,3,5-trimethoxybenzol as internal standard (50 µmol, 25%).

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.46–7.43 (m), 7.17–7.14 (m), 2.05 (s), 1.94 (s).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 142.8 (2C), 131.4 (4C), 127.8 (4C), 112.0 (2C), 50.6 (2C), 47.6 (2C), 35.1 (2C).

1,4-Bis(4-(trimethylsilyl)phenyl)bicyclo[2.1.1]hexane (2g)



1g **2g**

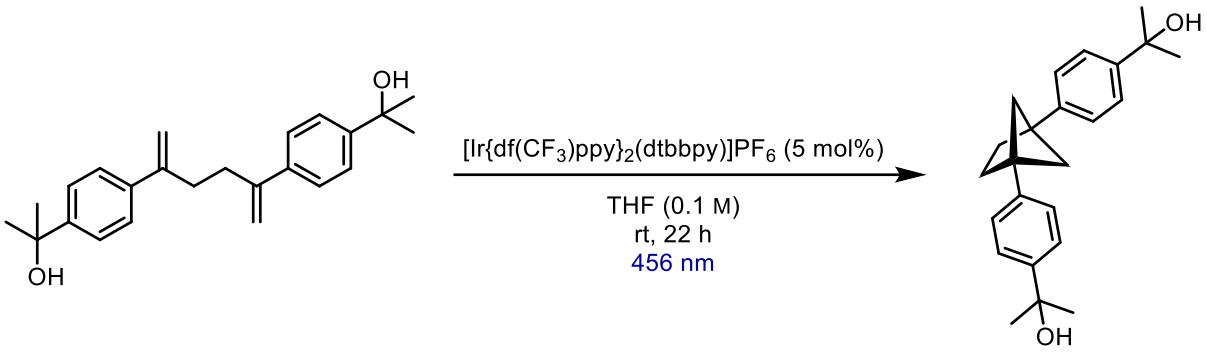
$C_{24}H_{34}Si_2$

M = 378.71 g/mol

Prepared according to **GP1** using diene **1g** (75.7 mg, 0.200 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as colourless crystals (57.6 mg, 0.152 mmol, 76%).

R_f = 0.23 (Pentane).
M.P. = 93−96°C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.52–7.49 (m, 4H), 7.32–7.29 (m, 4H), 2.08 (s, 4H), 1.99–1.97 (m, 4H), −0.27 (s, 18H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 144.8 (2C), 138.0 (2C), 133.5 (4C), 125.5 (4C), 51.1 (2C), 47.6 (2C), 35.2 (2C), -0.9 (6C).
^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$): δ/ppm = 4.32.
IR (ATR): ν_{max} = 3067, 3017, 2955, 2866, 1597, 1389, 1318, 1249, 1110, 1077, 983, 827, 809, 752, 736, 719, 692, 623, 530 cm^{-1}.
HRMS (ESI): calculated for $C_{24}H_{35}Si_2^+$ $[M+H]^+$: 379.2272; found: 379.2256.

2,2'-((Bicyclo[2.1.1]hexane-1,4-diyl)bis(4,1-phenylene))bis(propan-2-ol) (2h)



1h **2h**

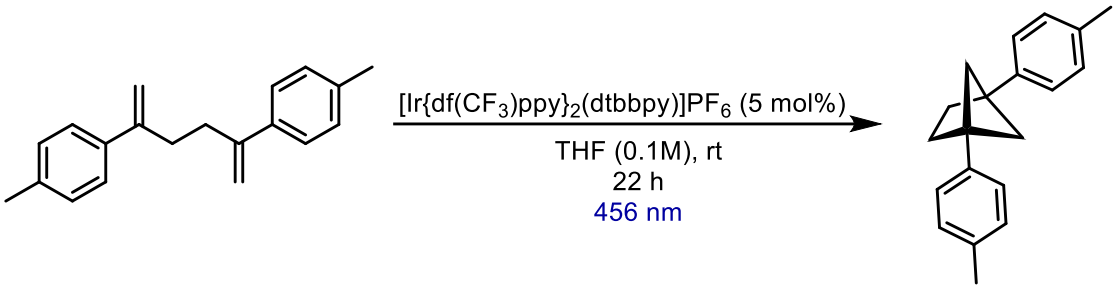
$C_{24}H_{30}O_2$

M = 350.50 g/mol

Prepared according to **GP1** using diene **1h** (70.1 mg, 0.200 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 13:6 Pentane:EtOAc) afforded the title compound as a colourless solid (59.7 mg, 0.170 mmol, 85%).

***R*$_f$** = 0.30 (13:6 Pentane:EtOAc).
M.P. = 115−117 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.48–7.45 (m, 4H), 7.30–7.27 (m, 4H), 2.08 (s, 4H), 2.01–1.96 (m, 4H), 1.71 (s, 2H), 1.59 (s, 12H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 147.1 (2C), 142.6 (2C), 126.0 (4C), 124.5 (4C), 72.6 (2C), 50.8 (2C), 47.9 (2C), 35.2 (2C), 31.9 (4C).
IR (ATR): ν_{max} = 3288, 2973, 2929, 2866, 1512, 1461, 1399, 1377, 1361, 1262, 1169, 1150, 1096, 987, 957, 864, 840, 833, 825, 816, 705, 593, 571 cm^{-1}.
HRMS (ESI): calculated for $C_{24}H_{30}O_2Na^+$ [M+Na]$^+$: 373.2138; found: 373.2147.

1,4-Di-*p*-tolylbicyclo[2.1.1]hexane (2i)



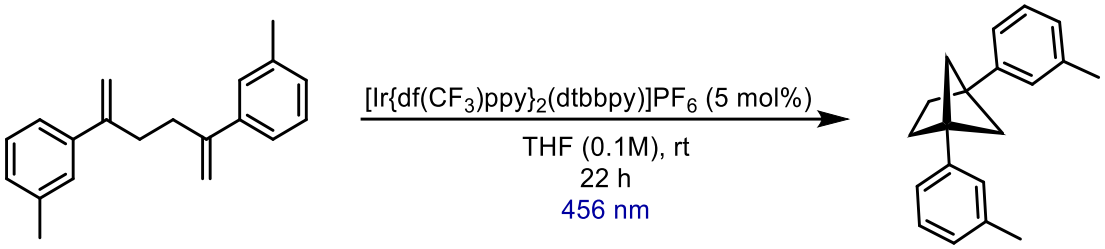
1i **2i**

$C_{20}H_{22}$
M = 262.40 g/mol

Prepared according to **GP1** using diene **1i** (49.9 mg, 0.190 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless solid (46.5 mg, 177 µmol, 93%).

***R*$_f$** = 0.30 (Pentane).
M.P. = 79–81 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.20 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 8.3 Hz, 4H), 2.34 (s, 6H), 2.05 (s, 4H), 1.97–1.92 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 141.2 (2C), 135.7 (2C), 129.0 (4C), 126.0 (4C), 50.7 (2C), 47.8 (2C), 35.2 (2C), 21.2 (2C).
IR (ATR): ν_{max} = 2961, 2865, 1889, 1645, 1512, 1446, 1317, 1106, 988, 807, 718, 540 cm^{-1}.
GC-MS (EI): m/z calculated for $C_{18}H_{18}^+$ [M]$^+$: 262.1; found: 262.1.

1,4-Di-*m*-tolylbicyclo[2.1.1]hexane (2j)



1j **2j**

$C_{20}H_{22}$

M = 262.40 g/mol

Prepared according to **GP1** using diene **1j** (49.9 mg, 0.190 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless oil (45.2 mg, 172 µmol, 90%).

***R*$_f$** = 0.33 (Pentane).

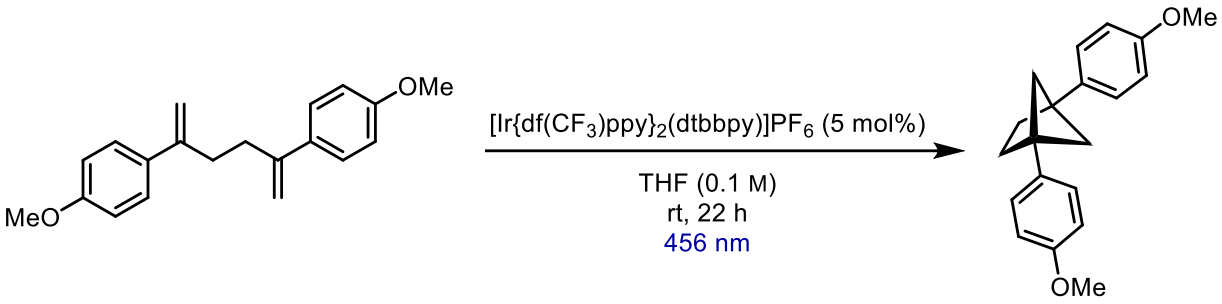
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.23–7.21 (m, 2H), 7.12–7.10 (m, 4H), 7.05–7.03 (m, 2H), 2.37 (s, 6H), 2.07 (s, 4H), 2.00–1.95 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 144.2 (2C), 137.9 (2C), 128.2 (2C), 126.9 (2C), 126.8 (2C), 123.1 (2C), 50.9 (2C), 47.7 (2C), 35.3 (2C), 21.6 (2C).

IR (ATR): ν_{max} = 3020, 2952, 2919, 2866, 1607, 1488, 1322, 778, 698 cm^{-1}.

GCMS (EI): m/z calculated for $C_{20}H_{22}^+$ $[M]^+$: 262.1; found: 262.0.

1,4-Bis(4-methoxyphenyl)bicyclo[2.1.1]hexane (2l)



1l **2l**

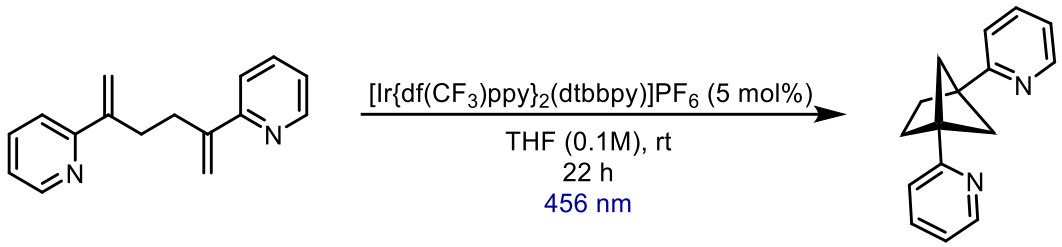
$C_{20}H_{22}O_2$

M = 294.39 g/mol

Prepared according to **GP1** using diene **1l** (58.9 mg, 0.200 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 19:1 Pentane:Et_2O) afforded the title compound as title compound as an inseparable mixture of diene **1l** and BCH **2l** (21 mg). A yield of 31% of BCH **2l** was determined by ^{1}H-NMR spectroscopy relative to diene **1l**.

***R*$_f$** = 0.34 (19:1 Pentane:Et_2O).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.24–7.21 (m, 4H), 6.89–6.86 (m, 4H), 3.81 (s, 6H), 2.04 (s, 4H), 1.95–1.89 (m, 4H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 158.1 (2C), 136.5 (2C), 127.2 (4C), 113.8 (4C), 55.5 (2C), 55.4 (2C), 48.1 (2C), 35.1 (2C).
HRMS (ESI^+): calculated for $C_{20}H_{22}O_3Na^+$ $[M+Na]^+$: 333.1461; found: 333.1467.

1,4-Di(pyridin-2-yl)bicyclo[2.1.1]hexane (2m)



1m **2m**

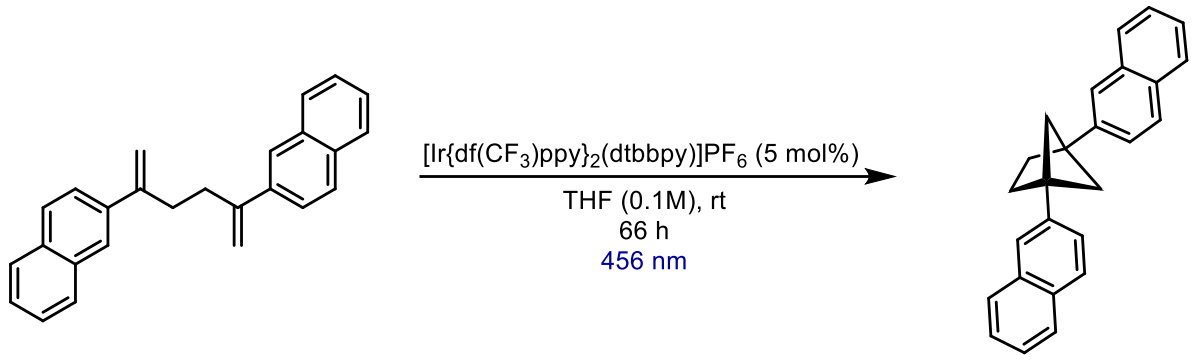
$C_{16}H_{16}N_2$

M = 236.32 g/mol

Prepared according to **GP1** using diene **1m** (44.9 mg, 0.190 mmol), [Ir{df(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, EtOAc) afforded the title compound as a yellow solid (43.1 mg, 182 µmol, 95%).

***R*$_f$** = 0.22 (EtOAc).
M.P. = 65–67 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.60 (dd, *J* = 4.9, 0.9 Hz, 2H), 7.68 (td, *J* = 7.7, 1.9 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.19–7.14 (m, 2H), 2.29–2.26 (m, 2H), 2.24 (s, 4H), 2.13 (dd, *J* = 4.0, 1.9 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) 162.6 (2C), 149.1 (2C), 136.6 (2C), 121.5 (2C), 120.9 (2C), 52.5 (2C), 46.9 (2C), 33.7 (2C).
IR (ATR): ν_{max} = 2979, 2954, 2868, 1601, 1583, 1561, 1472, 1430, 1327, 833, 777, 747, 551 cm^{-1}.
GCMS (EI): m/z calculated for $C_{16}H_{16}N_2^+$ $[M]^+$: 236.1; found: 236.0.

1,4-Di(naphthalen-2-yl)bicyclo[2.1.1]hexane (2n)

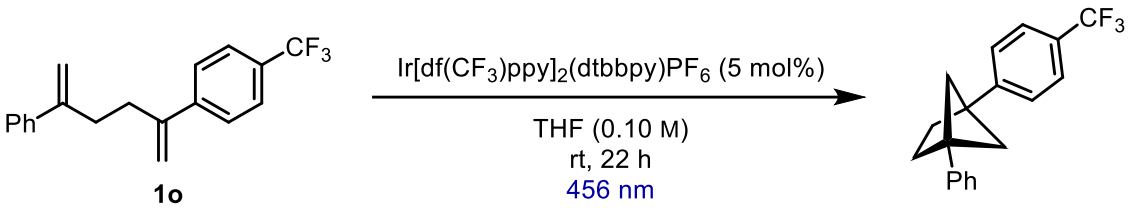


1n **2n**
$C_{26}H_{22}$
M = 334.46 g/mol

Prepared according to **GP1** using diene **1n** (63.6 mg, 0.190 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a yellow solid (42.0 mg, 125 µmol, 66%).

***R*f** = 0.26 (Pentane)
M.P. = 120–122 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84–7.81 (m, 6H), 7.74 (s, 2H), 7.52–7.41 (m, 6H), 2.23–2.16 (m, 8H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ (ppm) 141.5 (2C), 133.4 (2C), 132.1 (2C), 127.8 (2C), 127.6 (2C), 127.6 (2C), 126.0 (2C), 125.3 (2C), 124.7 (2C), 124.1 (2C), 51.3 (2C), 47.7 (2C), 35.3 (2C).
IR (ATR): ν_{max} = 3053, 2961, 2865, 1627, 1597, 1501, 1453, 1346, 1309, 891, 858, 813, 740 cm^{-1}.
GCMS (EI): m/z calculated for $C_{26}H_{22}^+$ $[M]^+$: 334.1721; found: 334.1716.

1-Phenyl-4-(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (2o):

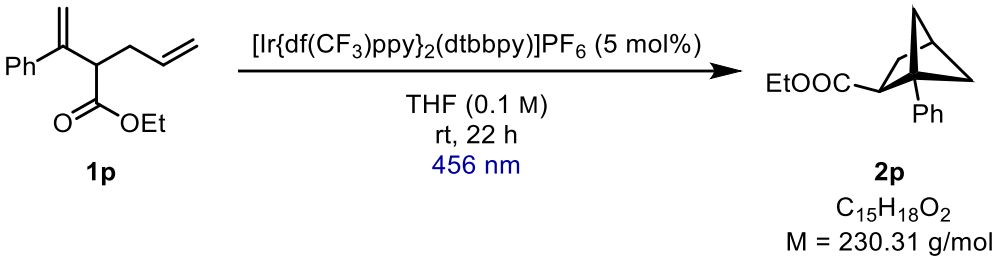


2o
$C_{19}H_{17}F_3$
M = 302.34 g/mol

Prepared according to **GP1** using diene **1o** (60.7 mg, 0.201 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (11.2 mg, 10.0 µmol, 5 mol%) and THF (2.0 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless oil (54.3 mg, 0.179 mmol, 89%).

***R*$_f$** = 0.35 (Pentane)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 8.1 Hz, 2H), 7.41–7.28 (m, 6H), 7.24–7.21 (m, 1H), 2.11 (s, 4H), 2.02 (s, 4H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 148.3 (1C), 143.7 (1C), 122.8 (1C), 128.4 (2C), 126.4 (2C), 126.1 (3C), 125.3 (q, *J* = 125.3 Hz, 2C), 122.7 (obtained from HMBC, 1C), 51.3 (1C), 50.9 (1C), 47.7 (2C), 35.4 (1C), 35.2 (1C).
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm): –62.31.
IR (ATR): ν_{max} = 2964, 2872, 1619, 1324, 1121, 837, 757, 698 cm^{-1}.
GCMS (EI): m/z calculated for $C_{19}H_{17}F_3^+$ $[M]^+$: 302.1277; found: 302.1275.

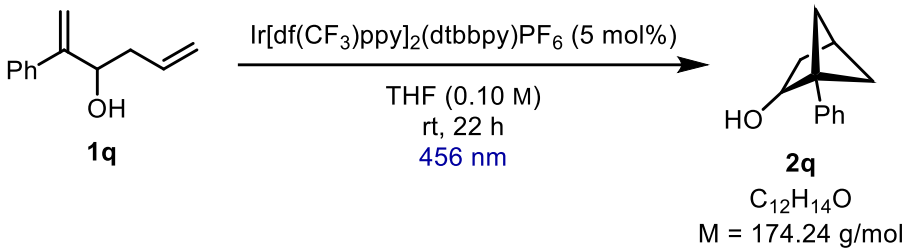
Ethyl 1-phenylbicyclo[2.1.1]hexane-2-carboxylate (2p)



Prepared according to **GP1** using diene **1p** (46.1 mg, 0.200 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 19:1 Pentane:EtOAc) afforded the title compound as a colourless oil (28.5 mg, 0.124 mmol, 62%).

R_f = 0.29 (19:1 Pentane:EtOAc).
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.32–7.34 (m, 2H), 7.27–7.10 (m, 3H), 3.91 (qq, *J* = 7.09, 3.66 Hz, 2H), 2.99 (ddd, *J* = 7.99, 5.01, 1.45 Hz, 1H), 2.53 (tt, *J* = 2.90, 1.47 Hz, 1H), 2.19–2.10 (m, 3H), 1.82–1.77 (m, 2H), 1.65 (dd, *J* = 9.80, 6.66 Hz, 1H), 0.94 (t, *J* = 7.14 Hz, 3H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 175.3 (1C), 142.3 (1C), 128.1 (2C), 126.4 (1C), 126.0 (2C), 60.0 (1C), 58.6 (1C), 48.8 (1C), 46.6 (1C), 38.0 (1C), 35.3 (1C), 34.1 (1C), 14.1 (1C).
IR (ATR): ν_{max} = 2976, 2961, 2874, 1727, 1447, 1373, 1348, 1288, 1266, 1234, 1181, 1149, 1120, 1114, 1097, 1082, 1054, 1041, 1023, 1012, 766, 698, 647, 544 cm^{-1}.
HRMS (ESI): calculated for $C_{15}H_{18}O_2Na^+$ $[M+Na]^+$: 253.1199; found: 253.1210.

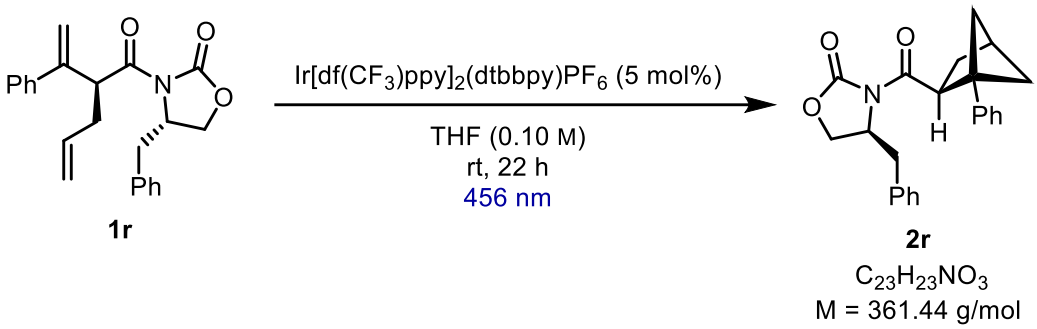
1-Phenylbicyclo[2.1.1]hexan-2-ol (2q):



Prepared according to **GP1** using diene **1q** (34.9 mg, 0.200 mmol), [Ir{df(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (11.2 mg, 10.0 µmol, 5 mol%) and THF (2.0 mL, 0.1 M). Purification by flash column chromatography (SiO$_2$, 80:20 Pentane:EtOAc) afforded the title compound as a colourless solid (34.4 mg, 0.197 mmol, 98%).

M.P. = 52–54 °C
***R*$_f$** = 0.32 (80:20Pentane:EtOAc)
^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.35–7.30 (m, 2H), 7.25–7.19 (m, 3H), 4.32 (d, *J* = 7.4 Hz, 1H), 2.47 (tt, *J* = 3.0, 1.5 Hz, 1H), 2.27 (dddd, *J* = 11.5, 7.3, 2.6, 1.5 Hz, 1H), 1.99 (dd, *J* = 9.5, 6.7 Hz, 1H), 1.85–1.76 (m, 2H), 1.61 (dd, *J* = 9.5, 6.9 Hz, 1H), 1.59–1.54 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): 141.9 (1C), 128.5 (2C), 126.6 (1C), 126.3 (2C), 76.1 (1C), 59.3 (1C), 43.9 (1C), 39.4 (1C), 37.6 (1C), 35.1 (1C).
IR (ATR): ν_{max} = 3274, 2972, 2357, 2330, 1092, 1040, 697 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{12}H_{14}ONa^+$ $[M+Na]^+$: 197.0937; found: 197.0940.

(*S*)-4-benzyl-3-((2*S*)-1-phenylbicyclo[2.1.1]hexane-2-carbonyl)oxazolidin-2-one (2r):



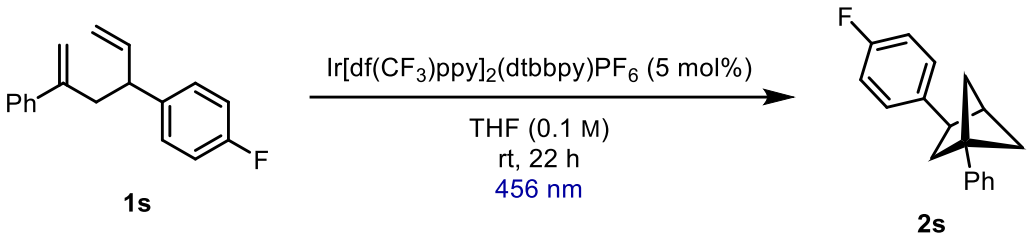
1r **2r**

$C_{23}H_{23}NO_3$
M = 361.44 g/mol

Prepared according to **GP1** using diene **1r** (72.3 mg, 0.200 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (11.2 mg, 10.0 µmol, 5 mol%) and THF (2.0 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 90:10 Pentane:EtOAc) afforded the title compound as a colourless oil (55.6 mg, 0.153 mmol, 76%).

M.P. = 105 °C (CH_2Cl_2)
***R*$_f$** = 0.25 (90:10 Pentane:EtOAc)
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33–7.28 (m,3H), 7.25–7.22 (m, 2H), 7.19–7.15 (m, 5H), 4.42 (ddd, *J* = 8.9, 4.4, 1.4 Hz, 1H), 4.35–4.29 (m, 1H), 3.90 (dd, *J* = 8.8, 1.9 Hz, 1H), 3.55 (t, *J* = 8.2 Hz, 1H), 3.25 (dd, *J* = 13.1, 3.4 Hz, 1H), 2.64 (dd, *J* = 13.4, 10.1 Hz, 1H), 2.59–2.58 (m, 1H), 2.31 (ddt, *J* = 11.2, 8.9, 2.1 Hz, 1H), 2.20 (dd, *J* = 9.5, 7.0 Hz, 1H), 2.17–2.12 (m, 1H), 1.86–1.78 (m, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 175.1 (1C), 155.3 (1C), 142.1 (1C), 135.7 (1C), 129.6 (2C), 129.0 (2C), 128.1 (2C), 127.4 (1C), 126.6 (1C), 126.1 (2C), 66.0 (1C), 59.3 (1C), 56.0 (1C), 46.9 (1C), 46.3 (1C), 38.6 (1C), 38.0 (1C), 35.5 (1C), 33.9 (1C).
IR (ATR): ν_{max} = 2978, 1779, 1696, 1348, 1288, 1207, 1196, 1081, 761, 750, 732, 700 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{23}H_{24}NO_3^+$ $[M+H]^+$: 362.1751; found: 362.1751.
$[\alpha]_D^{20}$**:** +136.8471° (*c* = 0.17 g/dL, CH_2Cl_2).

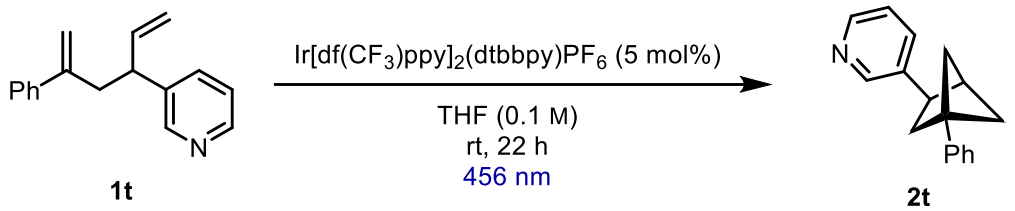
3-(4-Fluorophenyl)-1-phenylbicyclo[2.1.1]hexane (2s):



Prepared according to **GP1** using diene **1s** (50.5 mg, 0.200 mmol), [Ir{df(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.10 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless oil (45.4 mg, 0.178 mmol, 88%).

***R*$_f$** = 0.24 (Pentane)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.35–7.19 (m, 7H), 7.02 (t, *J* = 8.8 Hz, 2H), 3.52 (d, *J* = 14.4 Hz, 1H), 2.80 (d, *J* = 1.5 Hz, 1H), 2.47–2.39 (m, 1H), 2.02–1.96 (m, 2H), 1.80–1.75 (m, 1H), 1.72–1.65 (m, 2H)
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 161.2 (d, *J* = 243.4 Hz, 1C), 143.9 (1C), 141.0 (d, *J* = 3.2 Hz, 1C), 128.9 (d, *J* = 7.6 Hz, 2C), 128.3 (1C), 126.2 (2C), 125.9 (2C), 115.1 (d, *J* = 21.1 Hz, 2C), 54.4 (1C), 44.6 (1C), 44.5 (1C), 41.3 (1C), 40.8 (1C), 39.9 (1C).
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm): -118.04.
IR (ATR): ν_{max} = 3057, 2968, 2947 2870, 1604, 1508, 1221, 830, 562 cm^{-1}.
GC-MS (EI): calculated for $C_{18}H_{17}F^+$ $[M]^+$:252.1309; found:252.1310.

3-(4-Phenylbicyclo[2.1.1]hexan-2-yl)pyridine (2t):



1t **2t**

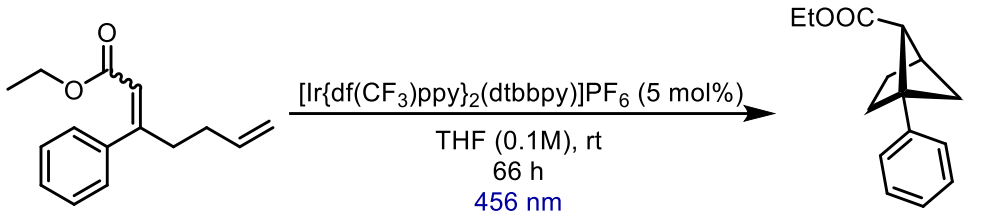
$C_{17}H_{17}N$

M = 235.33 g/mol

Prepared according to **GP1** using diene **1t** (47.1 mg, 0.200 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.10 M). Purification by flash column chromatography (SiO_2, Pentane:EtOAc 7:3) afforded the title compound as yellow oil (42.9 mg, 0.182 mmol, 91%).

***R*$_f$** = 0.21 (Pentane:EtOAc 7:3)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.59 (s, 1H), 8.45 (d, *J* = 3.9 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.34–7.27 (m, 2H), 7.25–7.18 (m, 4H), 3.57–3.53 (m, 1H), 2.87–2.85 (m, 1H), 2.49–2.43 (m, 1H), 2.06–1.99 (m, 2H), 1.83–1.78 (m, 1H), 1.73–1.64 (m, 2H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 149.6 (1C), 147.2 (1C), 143.5 (1C), 140.5 (1C), 135.1 (1C), 128.4 (2C), 126.4 (1C), 125.9 (2C), 123.3 (1C), 54.6 (1C), 44.5 (1C), 43.1 (1C), 40.7 (1C), 40.5 (1C), 39.9 (1C).
IR (ATR): ν_{max} = 3024, 2967, 2870, 1477, 1417, 1022, 755, 714, 697, 545 cm^{-1}.
HRMS (ESI): calculated for $C_{17}H_{18}N^+$ $[M+H]^+$: 236.1434; found: 236.1439.

Ethyl 1-phenylbicyclo[2.1.1]hexane-5-carboxylate (2u)



1t **2u**

$C_{15}H_{18}O_2$

M = 230.31 g/mol

Prepared according to **GP1** using diene **1u** (43.7 mg, 190 µmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 80:20 Pentane:EtOAc) afforded the title compound as a 10:1 (endo:exo) mixture of diastereomers and a colourless oil (42.0 mg, 182 µmol, 95%).

Data is consistent with that previously reported.[20]

Major (endo) diastereomer:

R_f = 1.00 (80:20 Pentane:EtOAc)

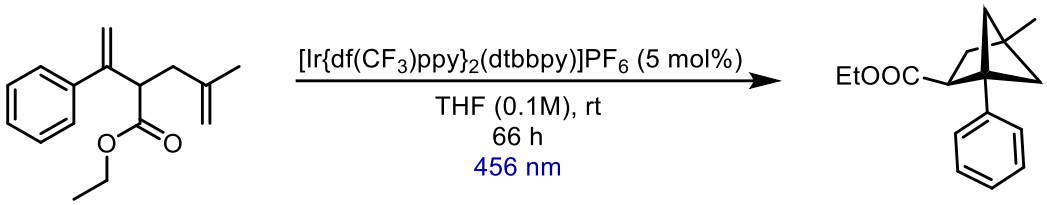
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 4.17–4.06 (m, 2H), 2.79 (s, 1H), 2.64 (m, 1H), 2.25–2.19 (m, 1H), 1.98–1.92 (m, 1H), 1.86–176 (m, 2H), 1.73–1.70 (m, 1H), 1.36 (d, *J* = 6.5 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 171.2 (1C), 142.2 (1C), 128.2 (2C), 126.8 (2C), 126.5 (1C), 59.9 (1C), 57.3 (1C), 53.1 (1C), 41.8 (1C), 39.9 (1C), 30.1 (1C), 26.7 (1C), 14.4 (1C).

IR (ATR): ν_{max} = 2976, 2880, 1723, 1446, 1372, 1213, 1194, 1054, 755, 696 cm^{-1}.

GCMS (EI): m/z calculated for $C_{15}H_{18}O_2Na^+$ $[M+Na]^+$: 253.1199; found: 253.1199.

Ethyl 4-methyl-1-phenylbicyclo[2.1.1]hexane-2-carboxylate (2v)



1v **2v**

$C_{16}H_{20}O_2$

M = 244.33 g/mol

Prepared according to **GP1** using diene **1v** (46.4 mg, 190 µmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 99:1 Pentane:EtOAc) afforded the title compound as a colourless oil (33.7 mg, 137 µmol, 72%).

***R*$_f$** = 0.21 (99:1 Pentane:EtOAc)

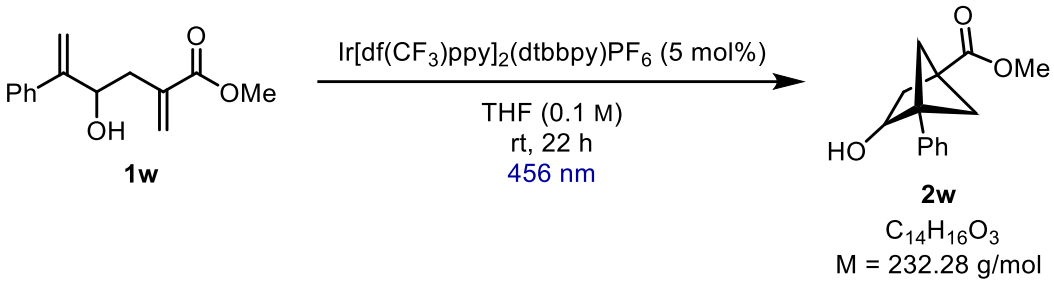
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.28–7.13 (m, 5H), 3.95–3.84 (m, 2H), 3.08–3.03 (m, 1H), 2.29–2.23 (m, 1H), 2.01–1.89 (m, 2H), 1.77–1.71 (m, 1H), 1.59–1.53 (m, 3H), 1.26 (m, 2H), 0.93 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 174.9 (1C), 142.1 (1C), 127.9 (2C), 126.2 (1C), 125.9 (2C), 59.8 (1C), 55.4 (1C), 51.0 (1C), 50.9 (1C), 43.4 (1C), 42.4 (1C), 39.4 (1C), 19.0 (1C), 13.9 (1C).

IR (ATR): ν_{max} = 2946, 2865, 1723, 1442, 1372, 1309, 1180, 1146, 1051, 766, 696 cm^{-1}.

GCMS (ESI): m/z calculated for $C_{16}H_{20}O_2Na^+$ [M+Na]$^+$: 267.1361; found: 267.1356.

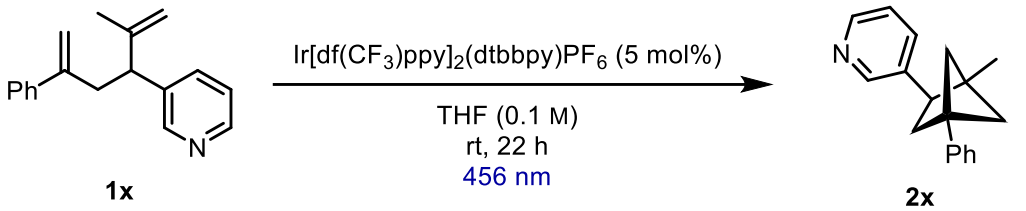
Methyl-3-hydroxy-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2w):



Prepared according to **GP1** using diene **1w** (46.5 mg, 0.200 mmol), [Ir{df(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.10 M). Purification by flash column chromatography (SiO_2, Pentane:EtOAC 4:1) afforded the title compound as colourless solid (28.7 mg, 0.124 mmol, 61%).

R$_f$ = 0.60 (Pentane:EtOAC 4:1)
M.P. = 140 – 141 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.37–7.28 (m, 3H), 7.24–7.18 (m, 2H), 4.38 (dt, *J* = 7.5, 2.0 Hz, 1H), 3.72 (s, 3H), 2.50 (ddd, *J* = 11.6, 7.4, 2.7 Hz, 1H), 2.38 (dd, *J* = 9.2, 6.6 Hz, 1H), 2.13–2.09 (m, 2H), 1.94 (dd, *J* = 9.2, 6.9 Hz, 1H), 1.87 (ddd, *J* = 11.6, 3.8, 2.3 Hz, 1H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 172.9 (1C), 140.1 (1C), 128.6 (2C), 127.0 (1C), 126.2 (2C), 75.8 (1C), 56.0 (1C), 51.7 (1C), 47.5 (1C), 45.8 (1C), 40.9 (1C), 40.3 (1C).
IR (ATR): ν_{max} = 3463, 2952, 1732, 1438, 1260, 1094, 1040, 758, 700 cm^{-1}.
HRMS (ESI): calculated for $C_{14}H_{16}O_3Na^+$ $[M+Na]^+$: 255.0992; found: 255.0997.

3-(1-methyl-4-phenylbicyclo[2.1.1]hexan-2-yl)pyridine (2x):



1x **2x**

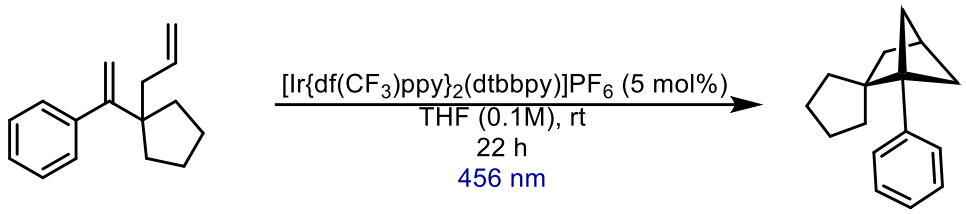
$C_{18}H_{19}N$

M = 249.36 g/mol

Prepared according to **GP1** using diene **1x** (49.9 mg, 0.200 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.10 M). Purification by flash column chromatography (SiO_2, CH_2Cl_2:EtOAC 9:1) afforded the title compound as pale yellow oil (44.2 mg, 0.177 mmol, 88%).

***R*$_f$** = 0.15 (CH_2Cl_2:EtOAC 9:1)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 8.61 (d, *J* = 2.4 Hz, 1H), 8.49 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.67 (dt, *J* = 8.0, 2.1 Hz, 1H), 7.38–7.20 (m, 6H), 3.23 (dd, *J* = 9.3, 1.8 Hz, 1H), 2.45 (ddd, *J* = 11.4, 4.5, 2.7 Hz, 1H), 2.25 (ddd, *J* = 11.4, 4.5 2.7 Hz, 1H), 2.10–2.04 (m, 1H), 1.87–1.79 (m, 2H), 1.53 (dt, *J* = 7.3, 2.1 Hz, 1H), 1.08 (s, 3H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 150.5 (1C), 147.6 (1C), 143.6 (1C), 138.5 (1C), 135.6 (1C), 128.4 (2C), 126.3 (1C), 126.1 (2C), 123.2 (1C), 51.4 (1C), 50.3 (1C), 49.7 (1C), 48.4 (1C), 43.0 (1C), 41.8 (1C), 18.1 (1C).
IR (ATR): ν_{max} = 3084, 2949, 2869, 2360, 2331, 1573, 1573, 1422, 1025, 757, 699, 546 cm^{-1}.
HRMS (ESI): calculated for $C_{18}H_{20}N^+$ $[M+H]^+$: 250.1590; found: 250.1590.

1-Phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclopentane] (2y)

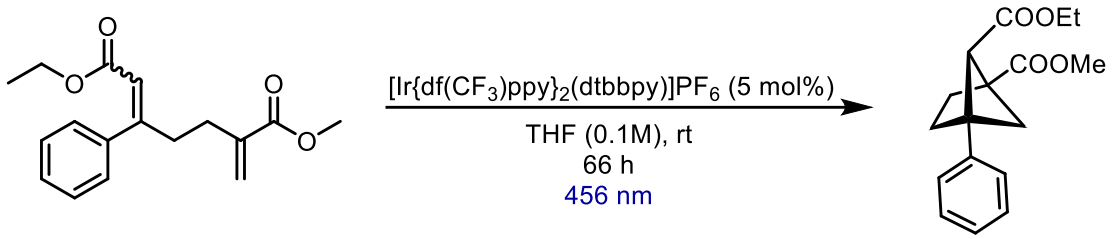


1y **2y**
$C_{16}H_{20}$
M = 212.34

Prepared according to **GP1** using diene **1y** (40.3 mg, 0.190 mmol), [Ir{df(CF_3)ppy}$_2$(dtbbpy)]PF_6 (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, Pentane) afforded the title compound as a colourless oil (39.0 mg, 183 µmol, 96%).

***R*$_f$** = 0.97 (Pentane)
M.P. = 31–33 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.30–7.25 (m, 2H), 7.20–7.16 (m, 1H), 7.12–7.09 (m, 2H), 2.48 (s, 1H), 1.89 (dd, *J* = 4.2, 2.1 Hz, 2H), 1.78–1.73 (m, 4H), 1.55–1.45 (m, 6H), 1.32–1.26 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4 (1C), 127.5 (2C), 127.3 (2C), 125.6 (1C), 59.8 (1C), 51.9 (1C), 46.4 (1C), 42.8 (2C), 35.2 (2C), 35.2 (1C), 24.4 (2C).
IR (ATR): ν_{max} = 3023, 2950, 2861, 1601, 1497, 1442, 1287, 1202, 769, 700 cm^{-1}.
GCMS (EI): m/z calculated for $C_{16}H_{20}^+$ $[M]^+$: 212.1565; found: 212.1558.

5-Ethyl 1-methyl-4-phenylbicyclo[2.1.1]hexane-1,5-dicarboxylate (2z)



1z **2z**

$C_{17}H_{20}O_4$

M = 288.34 g/mol

Prepared according to **GP1** using diene **1z** (55.0 mg, 0.190 mmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 95:5 Pentane:EtOAc) afforded the title compound as a colourless oil and an inseparable 2:1 (*exo*:*endo*) mixture of stereoisomers (35.1 mg, 121 µmol, 64%).

R_f = 0.20 (95:5 Pentane:EtOAc)

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): 174.0, 173.0, 172.1, 169.6, 140.7, 140.5, 128.4, 128.2, 127.0, 126.9, 126.7, 125.9, 60.3, 60.3, 55.3, 55.2, 55.0, 52.2, 51.9, 51.8, 49.4, 48.8, 47.9, 45.7, 40.9, 35.4, 31.0, 28.1, 14.3, 14.0.

IR (ATR): ν_{max} = 2987, 2954, 1726, 1434, 1346, 1257, 1180, 1098, 700 cm^{-1}.

GC-MS (ESI): m/z calculated for $C_{17}H_{20}O_4Na^+$ $[M+Na]^+$: 311.1259; found: 311.1254.

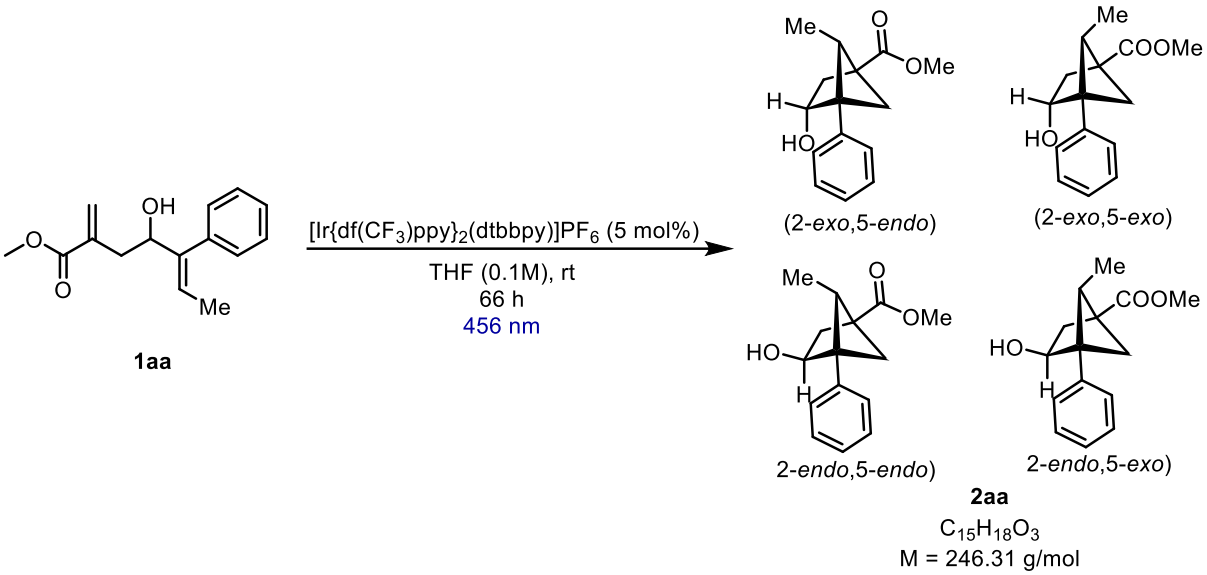
***exo*-2z**

^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38–7.13 (m, 5H), 3.92 (dq, *J* = 7.0, 2.9 Hz, 2H), 3.72 (s, 3H), 3.15–3.20 (m, 1H), 2.56 (dd, *J* = 9.5, 6.9 Hz, 1H), 2.38–2.26 (m, 2H), 2.21–1.93 (m, 3H), 0.94 (t, *J* = 7.2 Hz, 3H).

***endo*-2z**

^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38–7.13 (m, 5H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.99 (s, 1H), 2.38–2.26 (m, 2H), 2.21–1.93 (m, 3H), 1.75 (d, *J* = 6.2 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H).

Methyl-3-hydroxy-5-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa)



Prepared according to **GP1** using diene **1aa** (46.8 mg, 190 µmol), $[Ir\{df(CF_3)ppy\}_2(dtbbpy)]PF_6$ (10.7 mg, 9.50 µmol, 5 mol%), and THF (1.9 mL, 0.1 M). Purification by flash column chromatography (SiO_2, 80:20 Pentane:EtOAc) afforded the title compound as a colourless oil and an inseparable 1.7:1.7:1.4:1.0 (2-*endo*,5-*endo* : 2-*endo*,5-*exo* : 2-*exo*,5-*exo* : 2-*exo*,5-*endo*) mixture of stereoisomers (42.2 mg, 171 µmol, 90%).

The diastereomers could be separated by preparative HPLC (PVA-Sil, Hexane-IPA 99.5:0.5, isocratic; 1.0 mL/min, 295 K)

***R*f** = 0.46 (80:20 Pentane:EtOAc)
GCMS (ESI): m/z calculated for $C_{15}H_{18}O_3Na^+$ $[M+Na]^+$: 269.1154; found: 269.1148.

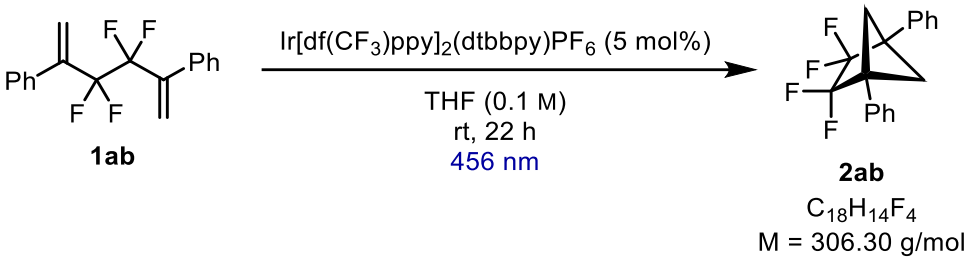
(2-*exo*,5-*exo*):
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38–7.33 (m, 2H), 7.28–7.22 (m, 1H), 7.11–7.08 (m, 2H), 4.38–4.35 (m, 1H), 3.71 (s, 3H), 2.54–2.48 (m, 2H), 2.33–2.26 (m, 2H), 1.83 (dd, *J* = 11.4, 2.3 Hz, 1H), 1.59 (d, *J* = 2.9 Hz, 1H), 0.97 (d, *J* = 6.5 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 172.6 (1C), 138.1 (1C), 128.7 (2C), 127.1 (2C), 127.0 (1C), 76.3 (1C), 58.8 (1C), 52.1 (1C), 51.6 (1C), 50.3 (1C), 42.1 (1C), 34.7 (1C), 9.5 (1C).
IR (ATR): ν_{max} = 3486, 2950, 2916, 1726, 1434, 1339, 1257, 1079, 700 cm^{-1}.

(2-*exo*,5-*endo*):
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.37–7.34 (m, 2H), 7.28–7.23 (m, 3H), 4.51 (d, *J* = 8.0 Hz, 1H), 2.54 (ddd, *J* = 12.0, 7.1, 2.8 Hz, 1H), 2.35 (dq, *J* = 6.8, 2.2 Hz, 1H), 2.27 (d, *J* = 6.7 Hz, 1H), 1.98–1.94 (m, 1H), 1.87 (dt, *J* = 12.0, 2.2 Hz, 2H), 1.47 (d, *J* = 3.3 Hz, 1H), 1.04 (d, *J* = 6.7 Hz, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 172.9 (1C), 139.7 (1C), 128.7 (2C), 127.1 (1C), 126.8 (2C), 73.9 (1C), 57.9 (1C), 52.9 (1C), 51.7 (1C), 50.1 (1C), 39.7 (1C), 37.6 (1C), 9.5 (1C).
IR (ATR): ν_{max} = 3452, 2950, 1726, 1434, 1349, 1257, 1228, 700 cm^{-1}.

(2-*endo*,5-*exo*):
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38–7.32 (m, 2H), 7.29–7.24 (m, 1H), 7.11–7.08 (m, 2H), 4.20 (dt, *J* = 7.7, 2.8 Hz, 1H), 2.85 (quint., *J* = 6.9 Hz, 1H), 2.59–2.42 (m, 2H), 1.94–1.82 (m, 2H), 1.75 (d, *J* = 3.2 Hz, 1H), 1.75 (d, *J* = 3.2 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 172.8 (1C), 138.9 (1C), 128.5 (2C), 126.9 (2C), 126.8 (1C), 76.4 (1C), 57.7 (1C), 51.6 (1C), 49.7 (1C), 46.9 (1C), 41.8 (1C), 39.5 (1C), 9.3 (1C).
IR (ATR): ν_{max} = 3445, 2950, 2355, 1726, 1434, 1257, 1091, 700 cm^{-1}.

(2-*endo*,5-*endo*):
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38–7.33 (m, 2H), 7.29–7.24 (m, 3H), 4.41–4.35 (m, 1H), 3.71 (s, 3H), 2.55–2.46 (m, 2H), 2.13 (dt, *J* = 12.1, 3.3 Hz, 1H), 1.86–1.82 (m, 1H), 1.77–1.72 (m, 2H), 1.37 (d, *J* = 6.7 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) 172.8 (1C), 140.3 (1C), 128.7 (2C), 127.0 (1C), 126.7 (2C), 76.6 (1C), 58.2 (1C), 51.7 (1C), 51.2 (1C), 49.1 (1C), 45.5 (1C), 37.2 (1C), 11.8 (1C).
IR (ATR): ν_{max} = 3438. 2950, 2359, 2337, 1726, 1434, 1257, 1087, 700 cm^{-1}.

2,2,3,3-tetrafluoro-1,4-diphenylbicyclo[2.1.1]hexane (2ab):

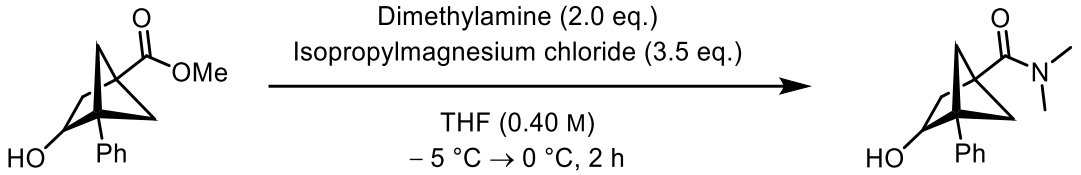


Prepared according to **GP1** using diene **1ab** (61.3 mg, 0.200 mmol), [Ir{df(CF$_3$)ppy}$_2$(dtbbpy)]PF$_6$ (11.2 mg, 9.36 µmol, 5 mol%), and THF (2 mL, 0.10 M). Purification by flash column chromatography (SiO_2, 95:5 Pentane:EtOAc) afforded the title compound as a colourless crystals (54.1 mg, 0.177 mmol, 88%).

R$_f$ = 0.54 (95:5 Pentane:EtOAc).
M.P. = 162 °C (CH_2Cl_2)
^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm = 7.44–7.36 (m, 5H), 7.34–7.28 (m, 5H), 2.73 (dd, *J* = 2.4 Hz, 2H), 2.41–2.28 (m, 2H)
^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ/ppm = 148.6 (2C), 133.7 (2C), 128.7 (4C), 128.4 (2C), 127.3 (4C), 53.3 (2C), 39.6 (2C)
^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ (ppm): -123.05.
IR (ATR): ν_{max} = 3031, 2962, 2932, 1779, 1448, 1331, 1287, 1140, 1066, 904, 767, 696, 573 cm^{-1}.
GC-MS (EI): calculated for $C_{18}H_{14}F_4^+$ $[M]^+$: 306.1026; found: 306.1026.

6.4 Synthesis of BCH 3, 4, 6, 8-10:

3-Hydroxy-N,N-dimethyl-4-phenylbicyclo[2.1.1]hexane-1-carboxamide (3):



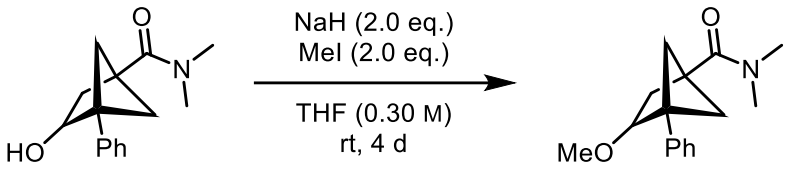
2w **3**

$C_{15}H_{19}NO_2$
M = 245.32 g/mol

A solution of BCH **2w** (20.0 mg, 86.1 µmol, 1.00 eq.) in THF (0.86, 0.40 M) was cooled to – 5 °C and dimethylamine (2.0 M in THF, 0.09 mL, 0.2 mmol, 2 eq.) was added. After dropwise addition of isopropylmagnesium chloride (2.0 M in THF, 0.15 mL, 3.5 eq.) over one minute, the reaction was allowed to warm to room temperature over 2 h.
The reaction was neutralised by addition of NH_4Cl (sat., aq., 1 mL) and the solution was further diluted with H_2O (1 mL) and CH_2Cl_2 (2 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 3 mL). The combined organic phases were washed with brine (1 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The title compound was obtained as colourless solid (20.2 mg, 82.3 µmol, 95%) and was used without further purification.

M.P. = 140 – 141 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.38–7.28 (m, 3H), 7.24–7.19 (m, 2H), 4.40 (dt, *J* = 7.4, 2.0 Hz, 1H), 3.04 (s, 3H), 2.96 (s, 3H), 2.52–2.44 (m, 2H), 2.11–2.04 (m, 3H), 1.86 (dt, *J* = 10.6, 2.7 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 172.8 (1C), 140.2 (1C), 128.7 (2C), 127.0 (1C), 126.4 (2C), 76.3 (1C), 54.0 (1C), 49.6 (1C), 46.6 (1C), 41.6 (1C), 41.4 (1C), 36.7 (only found in HSQC, 1C), 36.0 (only found in HSQC, 1C).
IR (ATR): ν_{max} = 3399, 2947, 2926, 1601, 1395, 1115, 1043, 764, 699, 516 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{15}H_{20}NO_2^+$ $[M+H]^+$: 246.1489; found: 246.1486.

3-Methoxy-N,N-dimethyl-4-phenylbicyclo[2.1.1]hexane-1-carboxamide (4):



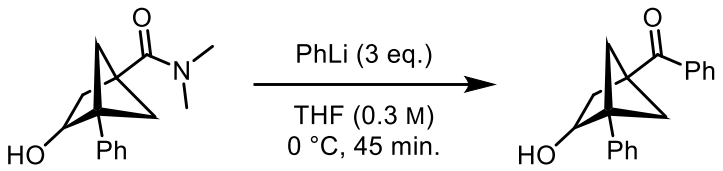
3 **4**

$C_{16}H_{21}NO_2$
M = 259.35 g/mol

A solution of BCH **3** (12.0 mg, 48.9 µmol, 1.00 eq.) in THF (0.16 mL, 0.30 M) was cooled down to 0 °C and NaH (60% dispersion in crude oil, 3.3 mg, 98 µmol, 2.0 eq.) was added in one portion. After 10 minutes, MeI (6.1 µL, 98 µmol, 2.0 eq.) was added, the reaction was allowed to warm to room temperature and stirred over 4 days.
The reaction was neutralised by addition of NH_4Cl (sat., aq., 2 mL) and diluted with CH_2Cl_2 (2 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 2 mL). The combined organic phases were washed with brine (1 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. After purification by column chromatography (SiO_2, 95:5 Pentane:EtOAc → EtOAc) the title compound was obtained as colourless solid (4.3 mg, 17 µmol, 33%). Due to the small amount of isolated product, the melting point could not be determined.

R_f = 0.21 (EtOAc)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.34–7.19 (m, 2H), 7.25–7.19 (m, 3H), 3.97 (dt, *J* = 7.0, 1.8 Hz, 1H), 3.18 (s, 3H), 3.03 (s, 3H), 2.95 (s, 3H), 2.50–2.43 (m, 1H), 2.40–2.34 (m, 1H), 2.10 (ddd, *J* = 6.7, 2.7, 1.5 Hz, 1H), 2.03–1.96 (m, 2H), 1.86 (dt, *J* = 11.3, 3.3 Hz, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 173.0 (1C), 141.1 (1C), 128.3 (2C), 126.6 (1C), 126.6 (2C), 84.7 (1C), 57.7 (1C), 53.2 (1C), 49.3 (1C), 46.9 (1C), 42.4 (1C), 40.0 (1C), 37.0 (1C), 36.1 (1C).
IR (ATR): ν_{max} = 2935, 2877, 2360, 1628, 1396, 1118, 1072, 763, 700, 573 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{16}H_{21}O_3NaCH_3OH^+$ $[M+Na+MeOH]^+$: 314.1727; found: 314.1726.

3-Hydroxy-4-phenylbicyclo[2.1.1]hexan-1-yl)(phenyl)methanone (6):



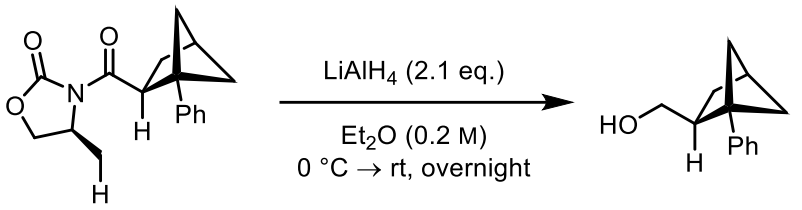
3 **6**

$C_{19}H_{18}O_2$
M = 278.35 g/mol

BCH **3** (7.2 mg, 29 µmol, 1.0 eq.) was dissolved in PhMe (1 mL), the solution was stirred for 5 minutes, concentrated *in vacuo* and dried for 45 minutes under fine vacuum. The residue was dissolved in THF (0.1 mL, 0.3 M), cooled to 0 °C and PhLi (1.9 M in dibutylether, 0.05 mL, 9 µmol, 3 eq.) was added dropwise over one minute.
After stirring for 45 minutes, the reaction was neutralised by addition of NH_4Cl (sat., aq., 1 mL) and diluted with H_2O (2 mL) and CH_2Cl_2 (2 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 2 mL). The combined organic phases were washed with brine (1 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. After purification by column chromatography (SiO_2, 85:15 Pentane:EtOAc) the title compound was obtained as pale yellow solid (6.4 mg, 23 µmol, 78%). Due to the small amount of isolated product, the melting point could not be determined.

R_f = 0.31 (85:15 Pentane:EtOAc)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 7.97–7.94 (m, 2H), 7.60–7.54 (m, 1H), 7.49–7.42 (m, 2H), 7.39–7.34 (m, 2H), 7.30–7.26 (m, 1H), 7.25–7.22 (m, 2H), 4.52– 4.49 (m, 1H), 2.80–2.72 (m, 1H), 2.62 (ddd, *J* = 11.6, 7.3, 2.7 Hz, 1H), 2.27–2.23 (m, 1H), 2.21–2.16 (m, 2H), 2.08 (dt, *J* = 11.7, 3.1 Hz, 1H), 1.89–1.76 (bs, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm): 201.3 (1C), 140.1 (1C), 136.3 (1C), 133.2 (1C), 128.8 (2C), 128.7 (2C), 128.7 (2C), 127.1 (1C), 126.4 (2C), 76.5 (1C), 55.1 (1C), 54.8 (1C), 46.4 (1C), 43.9 (1C), 42.3 (1C).
IR (ATR): ν_{max} = 3439, 2951, 2926, 1662, 1447, 1261, 1040, 875, 759, 699 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{19}H_{18}O_2Na^+$ $[M+Na]^+$: 301.1199; found: 301.1208.

(2*S*-Phenylbicyclo[2.1.1]hexan-2-yl)methanol (8):



2r **8**

$C_{13}H_{16}O$

M = 188.27 g/mol

At 0 °C $LiAlH_4$ (8.8 mg, 0.32 mmol, 2.1 eq.) was added to a solution of BCH **2r** (40.0 mg, 111 µmol, 1.00 eq.) in Et_2O (0.5 mL, 0.2 M). After 6 hours the ice bath was removed and the reaction was stirred overnight. The reaction was quenched by addition of water (1 mL) at 0 °C. The crude mixture was diluted NaOH (1 M, aq., 1 mL), water (2 mL) and Et_2O (5 mL). $MgSO_4$ was added, the suspension was stirred for 15 minutes at room temperature, filtered and the filter cake was washed with EtOAc (4 × 20 mL). The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, 85:15 Pentane:EtOAc) to obtain the title compound as pale yellow oil (26.5 mg, 29.2 µmol, 26%).

R_f = 0.33 (85:15 Pentane:EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.33–7.28 (m, 2H), 7.22–7.19 (m, 1H), 7.19–7.16 (m, 2H), 3.65 (dd, *J* = 11.1, 7.2 Hz, 1H), 3.50 (t, *J* = 9.1 Hz, 1H), 2.50 (tt, *J* = 2.9, 1.5 Hz, 1H), 2.41 (dtdd, *J* = 8.5, 7.0, 4.2, 1.5 Hz, 1H), 2.08 (dddd, *J* = 11.1, 8.8, 2.4, 1.6 Hz, 1H), 1.78–1.73 (m, 2H), 1.71–1.64 (m, 2H), 1.41 (dddd, *J* = 11.1, 4.1, 2.7, 1.4 Hz, 1H).

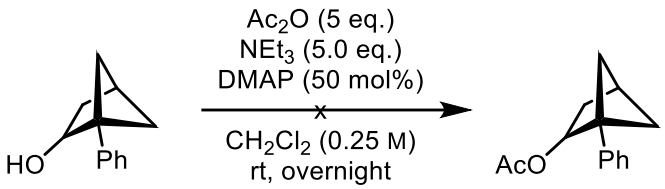
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 143.7 (1C), 128.7 (2C), 126.4 (1C), 125.7 (2C), 65.7 (1C), 56.3 (1C), 47.0 (1C), 46.7 (1C), 37.3 (1C), 35.7 (1C), 33.4 (1C).

IR (ATR): ν_{max} = 2960, 2872, 2360, 1745, 1501, 1044, 1038, 999, 991, 697, 565 cm^{-1}.

HRMS (ESI): m/z calculated for $C_{13}H_{16}ONa^+$ $[M+Na]^+$: 211.1093; found: 211.1096.

$[\alpha]_D^{23}$**:** +37.1853° (*c* = 0.14 g/dL, CH_2Cl_2).

1-Phenylbicyclo[2.1.1]hexan-2-yl acetate (9):



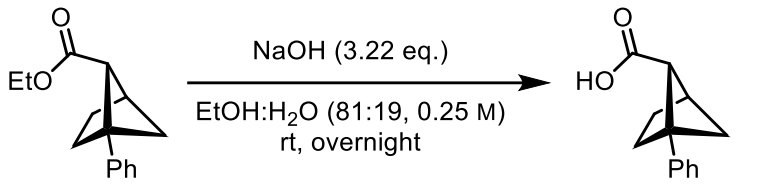
2q **9**

$C_{14}H_{16}O_2$
M = 216.28 g/mol

At 0 °C NEt_3 (0.10 mL, 0.746 mmol, 5.0 eq.) and Ac_2O (0.07 mL, 0.746 mmol, 5 eq.) were added to a solution of BCH **2q** (26.0 mg, 0.149 mmol, 1.00 eq.) and 4-Dimethylaminopyridine (9.1 mg, 75 µmol, 50 mol%) in CH_2Cl_2 (0.25 mL, 0.25 M). The reaction was allowed to warm to room temperature overnight, NH_4Cl (sat., aq., 3 mL) and water (5 mL) were added and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with Brine (3 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. After purification by column chromatography (SiO_2, 95:5 Pentane:EtOAc) the title compound was obtained as pale yellow oil (31 mg, 0.143 mmol, 96%).

R_f = 0.27 (95:5 Pentane:EtOAc)
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33–7.26 (m, 2H), 7.25–7.17 (m, 3H), 5.21 (dt, *J* = 7.3, 1.9 Hz, 1H), 2.53–2.48 (m, 1H), 2.47–2.37 (m, 1H), 2.02–1.88 (m, 5H), 1.83 (dt, *J* = 7.0, 3.4 Hz, 1H), 1.67–1.56 (m, 2H).
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 171.3(1C), 141.2 (1C), 128.2 (2C), 126.5 (1C), 126.4 (2C), 77.7 (1C), 57.5 (1C), 43.7 (1C), 39.2 (1C), 38.9 (1C), 35.0 (1C), 21.3 (1C).
IR (ATR): ν_{max} = 2975, 2949, 1731, 1373, 1286, 1241, 1210, 1075, 1039, 760, 699 cm^{-1}.
HRMS (ESI): m/z calculated for $C_{14}H_{16}O_2Na^+$ $[M+Na]^+$: 239.1043; found: 239.1042.

1-Phenylbicyclo[2.1.1]hexane-5-carboxylic acid (10):



2u **10**

$C_{13}H_{14}O_2$

M = 202.25 g/mol

Step 1: At 0 °C BCH **2u** (28.8 mg, 0.125 mmol, 1.00 eq.) in EtOH (0.85 mL. 0.15 M) was added to NaOH (2.5 M, aq., 0.15 mL). The reaction was warmed to room temperature and stirred overnight. NH_4Cl (sat., aq., 5 mL) and water (3 mL) were added and the aqueous phase was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic phases were washed with Brine (2 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure.

Step 2: The residue was redissolved in EtOH:H_2O (81:19, 0.25 M) and NaOH (16.1 mg, 0.403 mmol, 3.22 eq.) was added at 0 °C. The ice bath was removed and the reaction was stirred overnight. The crude reaction mixture was diluted with water (10 mL), washed with EtOAc (2 × 2 mL), acidified with HCl (1 M, aq.).and extracted with EtOAc (4 × 10 mL). The combined organic phases were washed with Brine (1 mL), dried over anhydrous Na_2SO_4, filtered and the solvent was removed under redouced pressure to obtain the title compound as pale brown oil (19.1 mg, 94.4 µmol, 75%). Data were consistent with that reported in literature.[21]

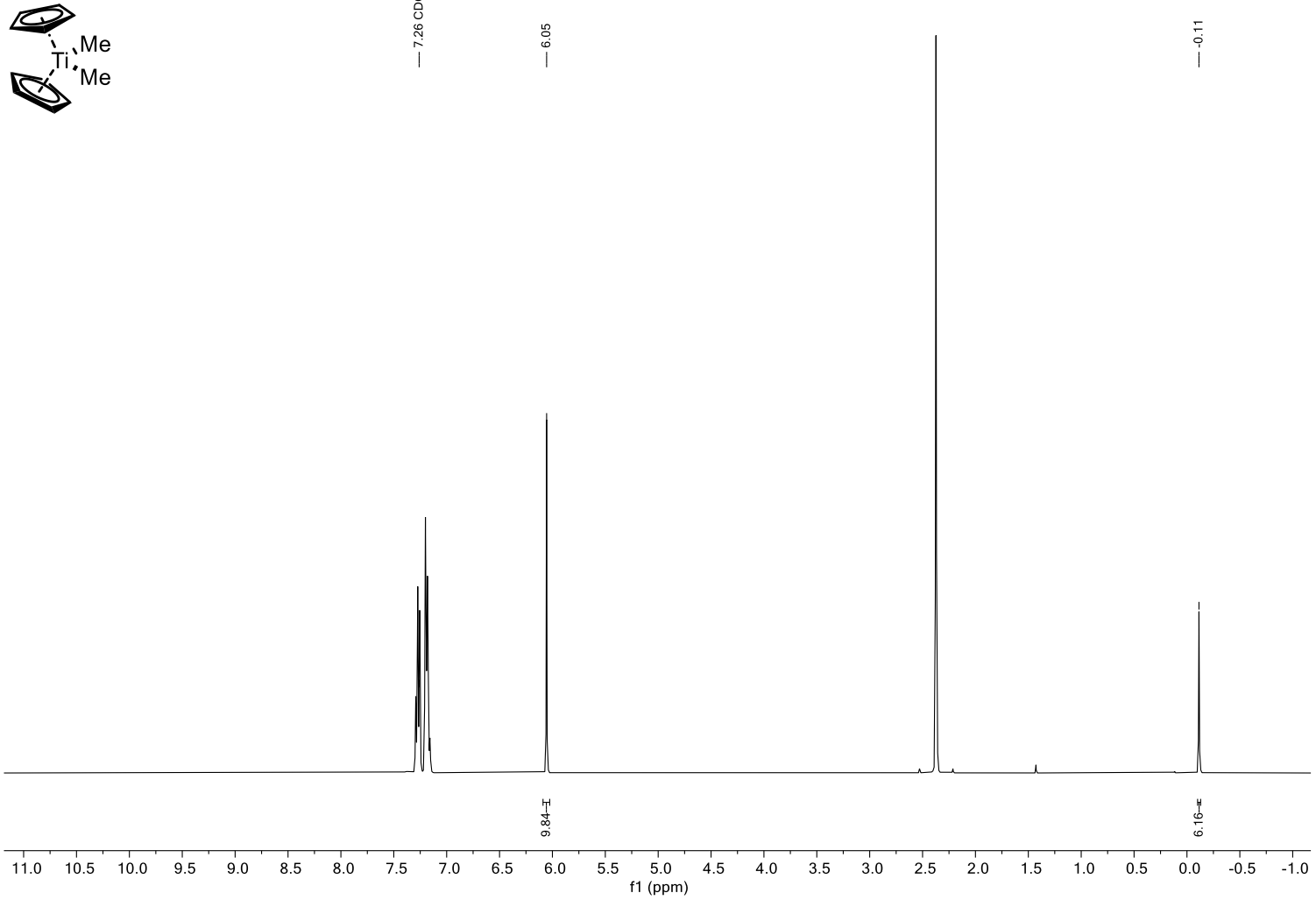
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.26–7.19 (m, 1H), 2.83 (s, 1H), 2.72 (s, 1H), 2.29–2.19 (m, 1H), 2.09–1.97 (m, 1H), 1.91–1.81 (m, 2H), 1.74 (dd, *J* = 6.5, 2.7 Hz, 1H), 1.38 (d, *J* = 6.5 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 177.0 (1C), 141.8 (1C), 128.3 (2C), 126.8 (2C), 126.1 (1C), 57.5 (1C), 52.7 (1C), 42.2 (1C), 40.1 (1C), 30.0 (1C), 26.7 (1C).

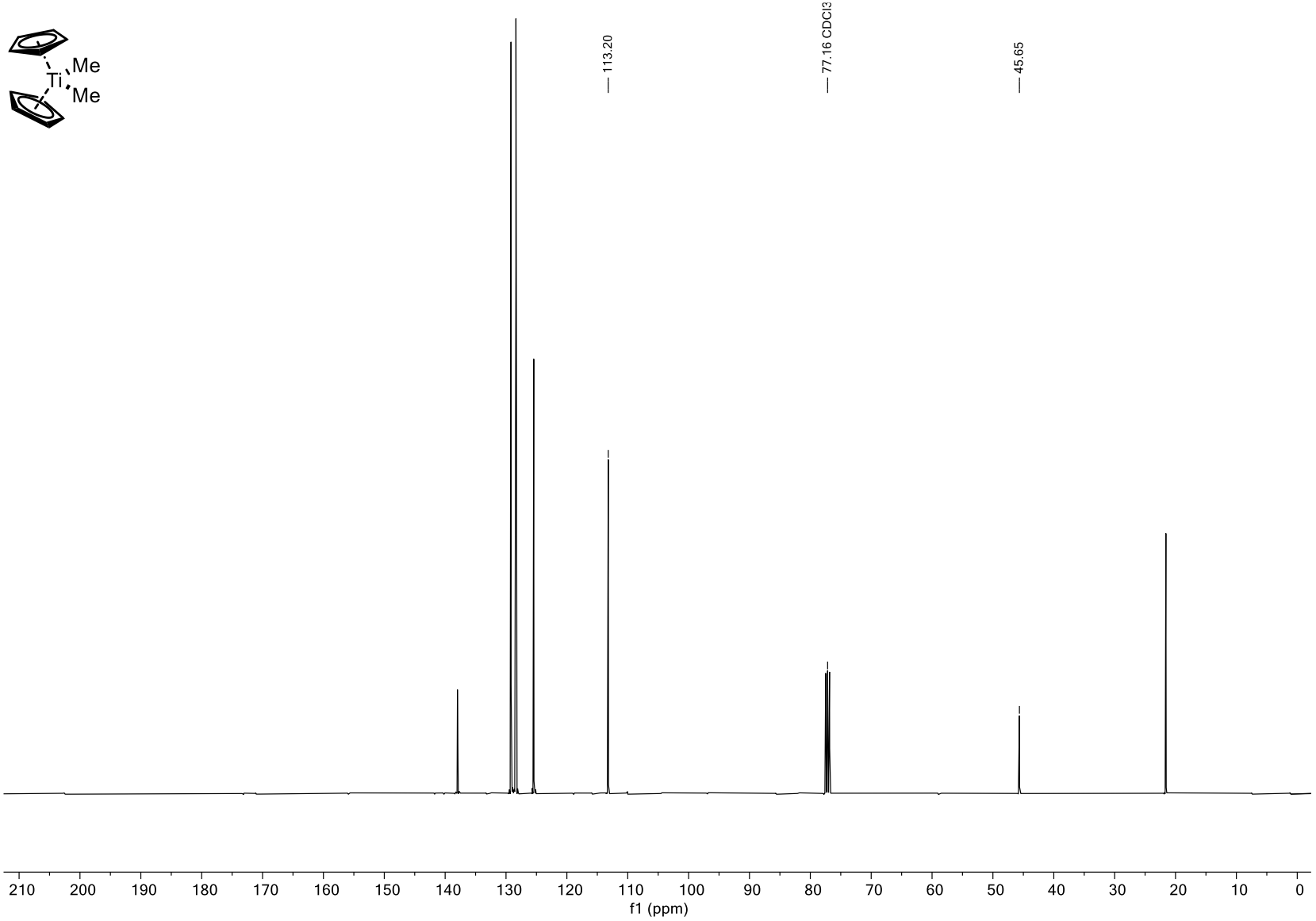
7 NMR Spectra

7.1 NMR Spectra of compounds towards dienes 1a–ab

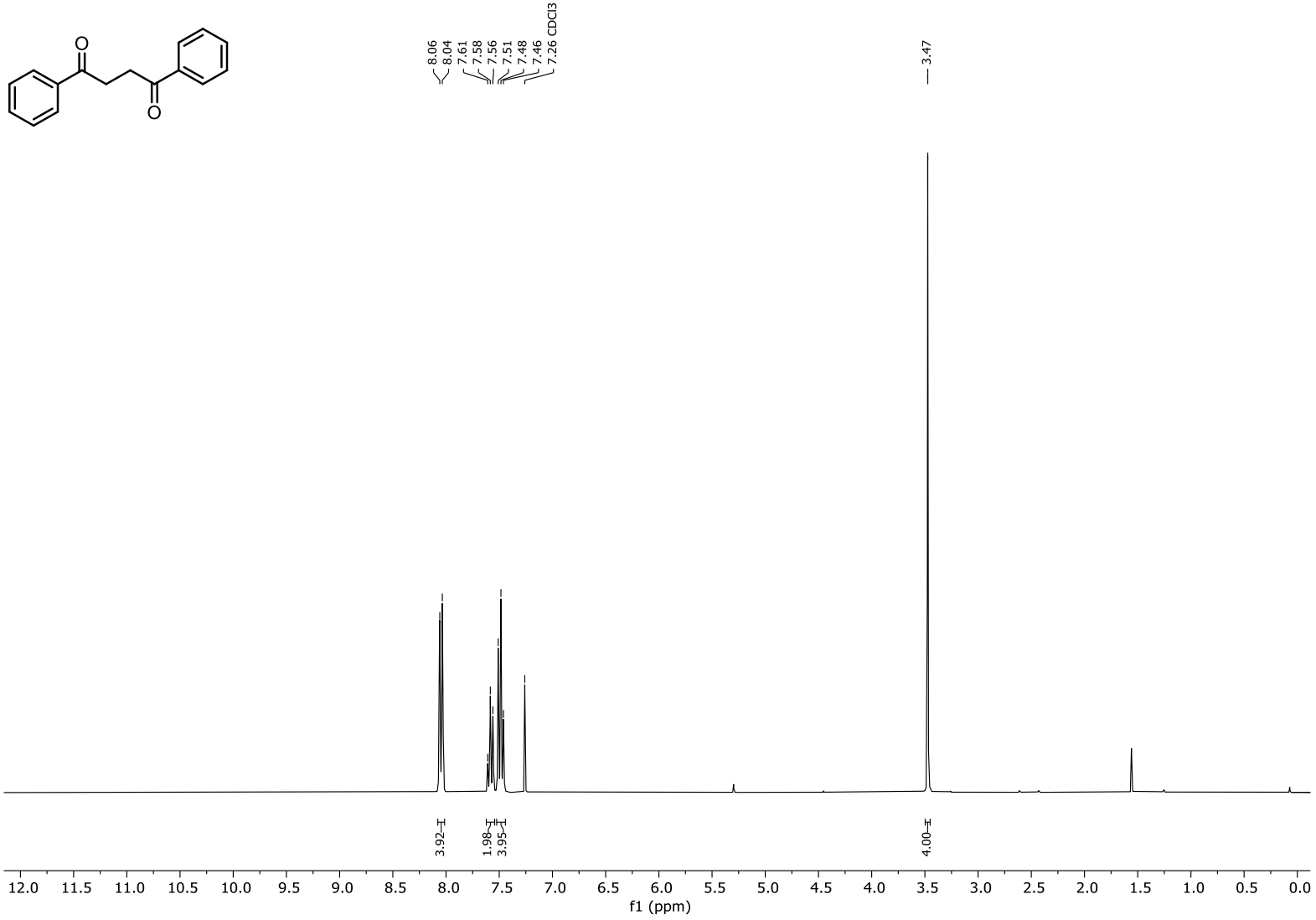
Petatis reagent: ^{1}H NMR (300 MHz, $CDCl_3$)



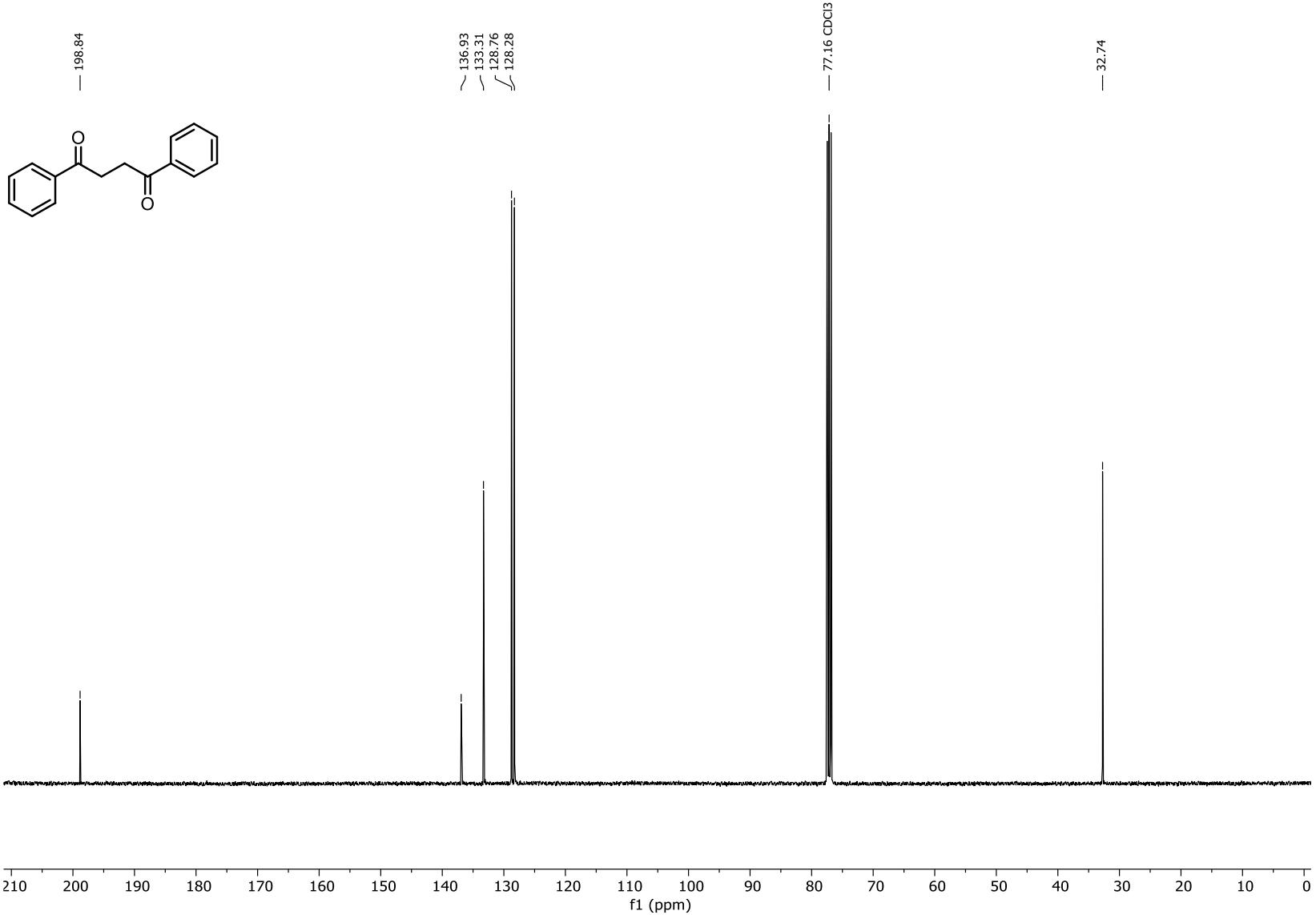
Petasis reagent: $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



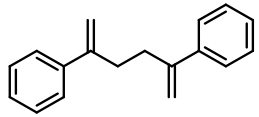
1,4-Diphenylbutane-1,4-dione (S1): ^{1}H NMR (300 MHz, $CDCl_3$)



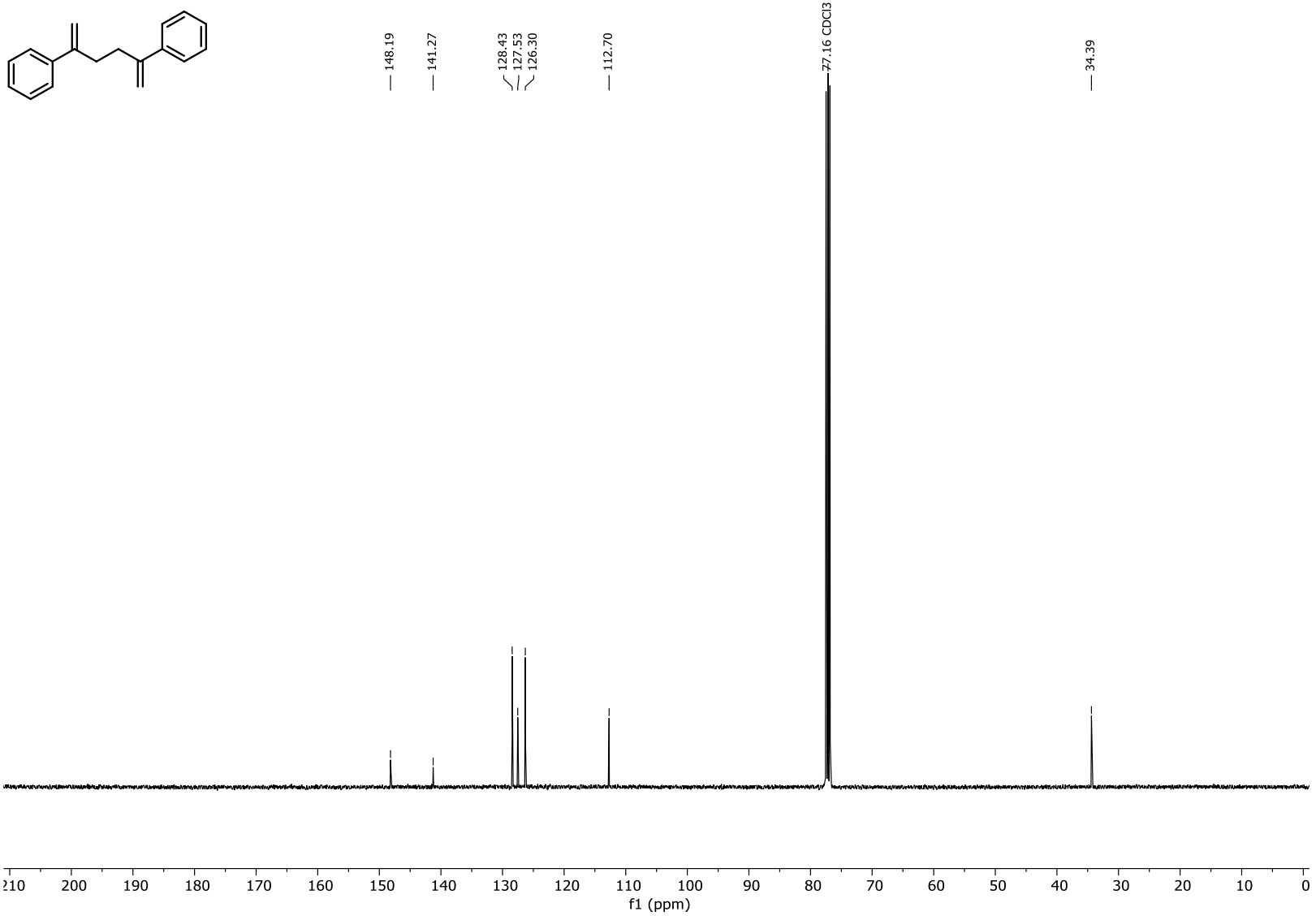
1,4-Diphenylbutane-1,4-dione (S1): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



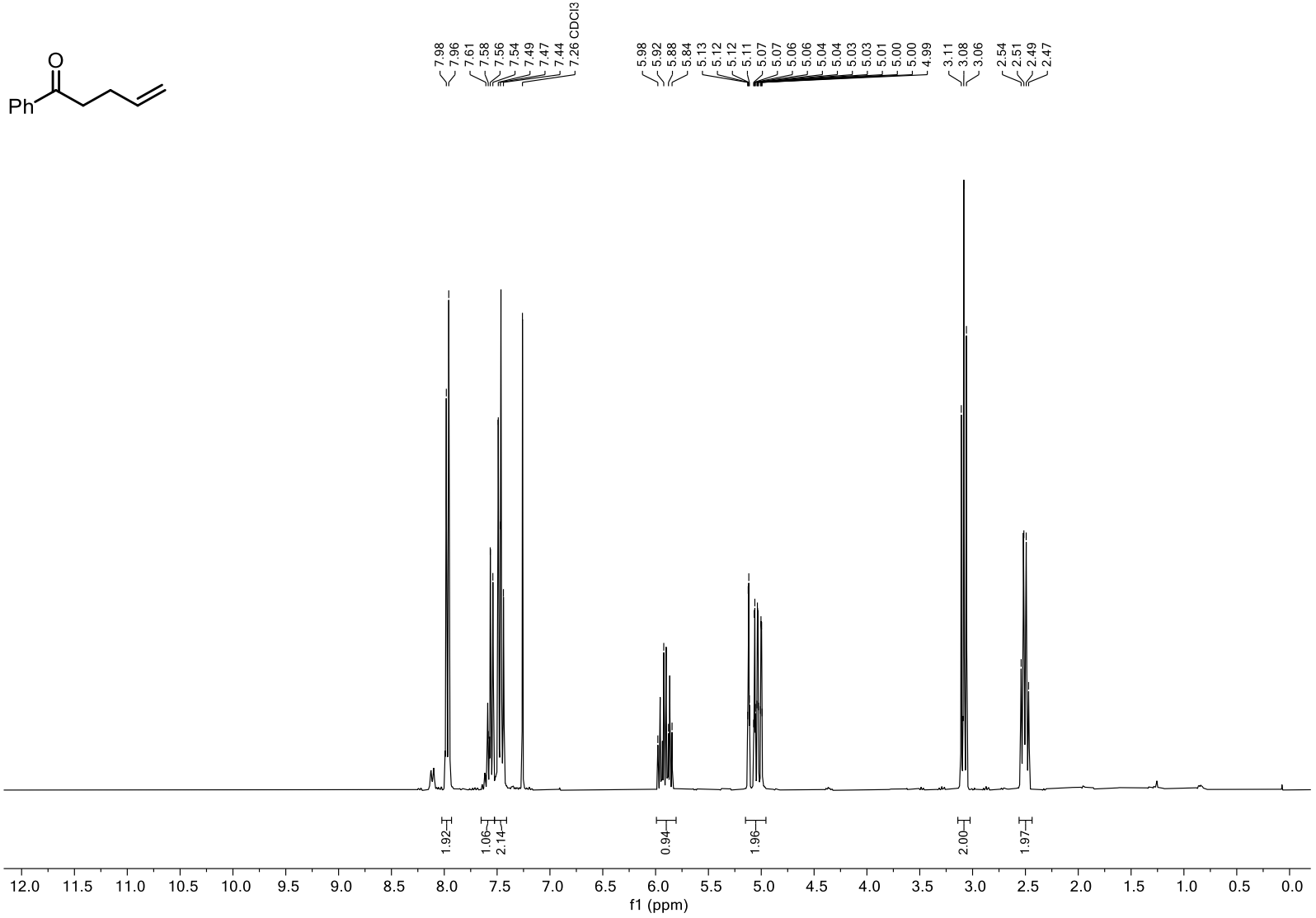
Hexa-1,5-diene-2,5-diyldibenzene (1a): ^{1}H NMR (300 MHz, $CDCl_3$)



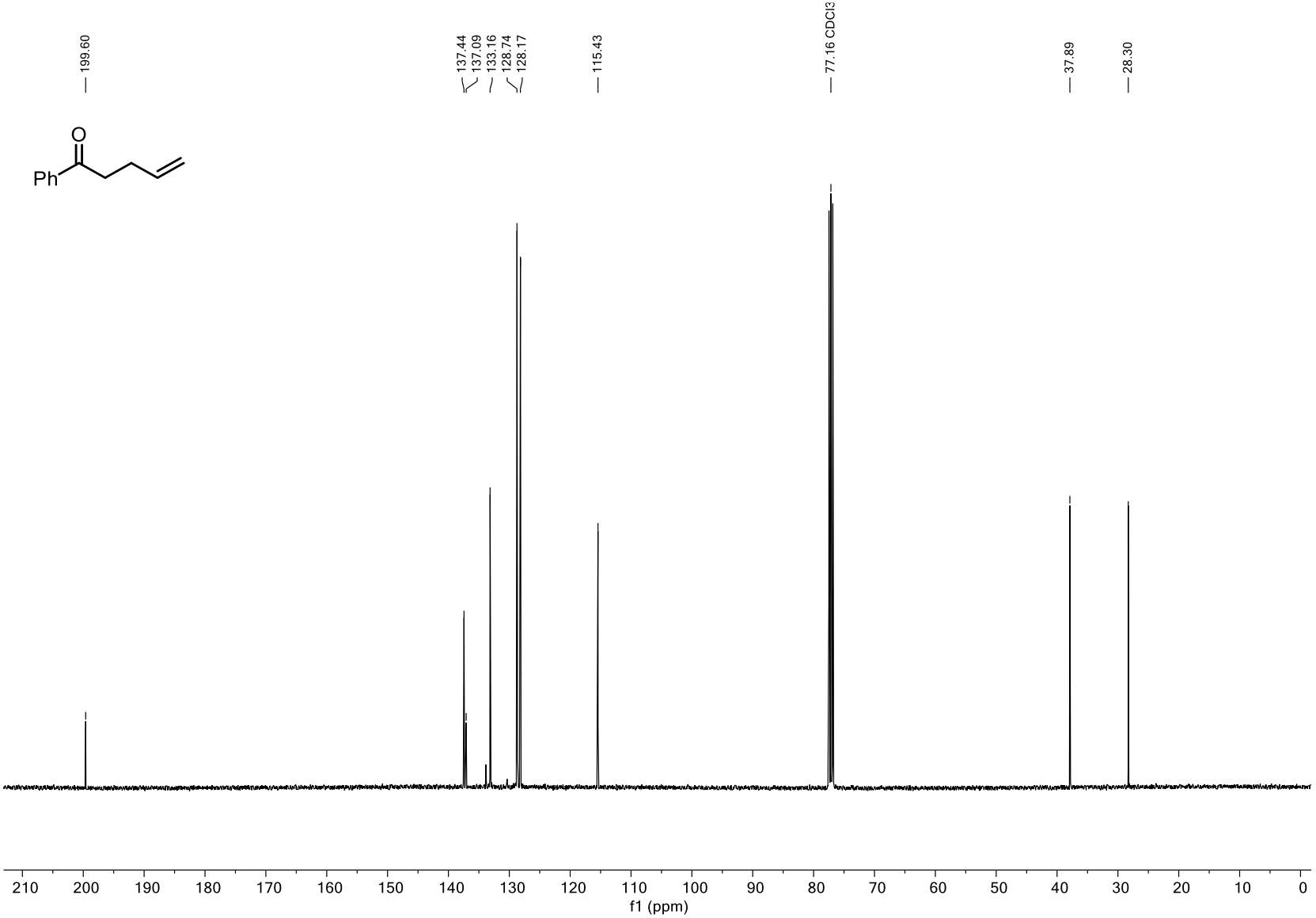
Hexa-1,5-diene-2,5-diyldibenzene (1a): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



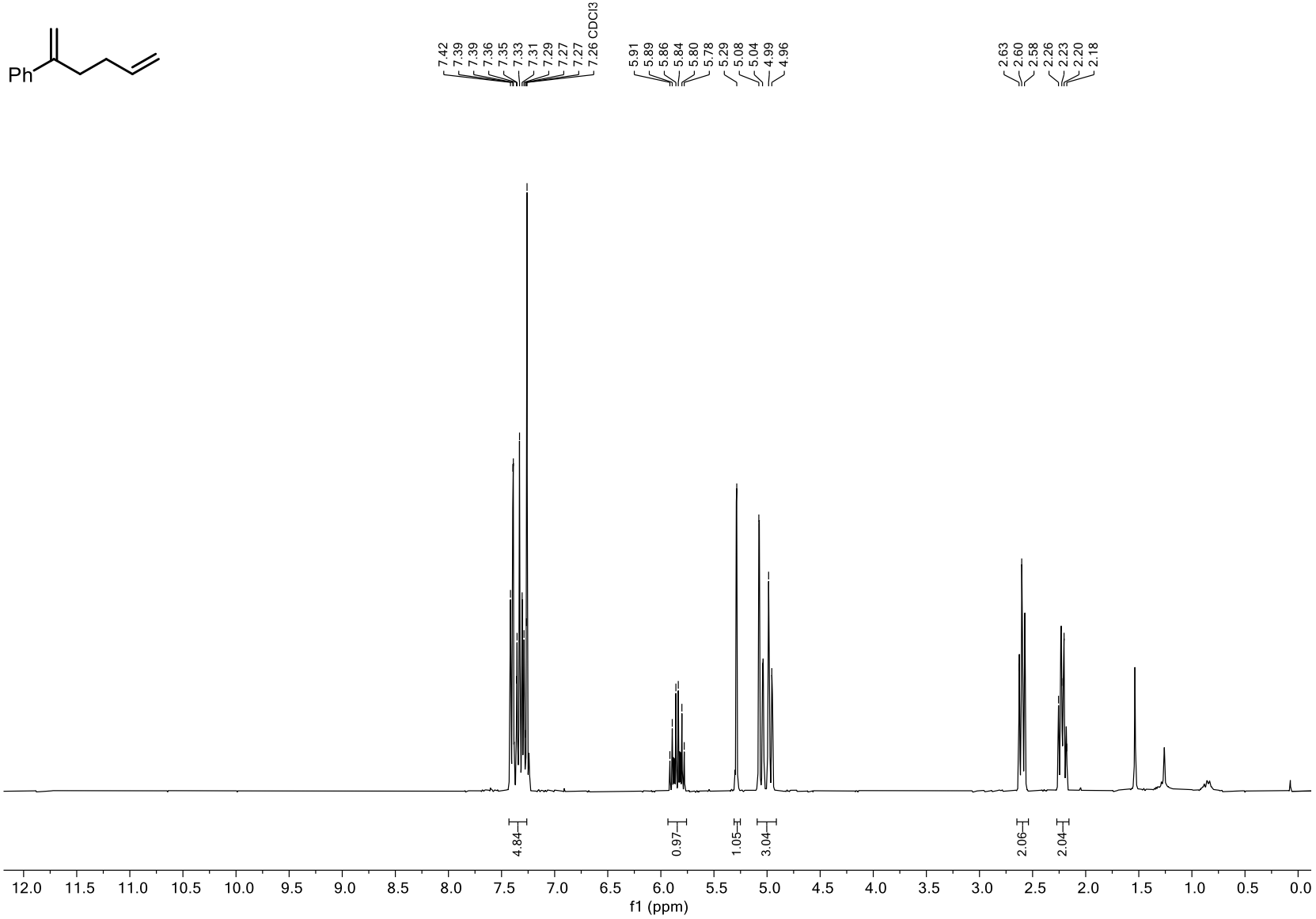
1-Phenylpent-4-en-1-one (S2): ^{1}H NMR (300 MHz, $CDCl_3$)



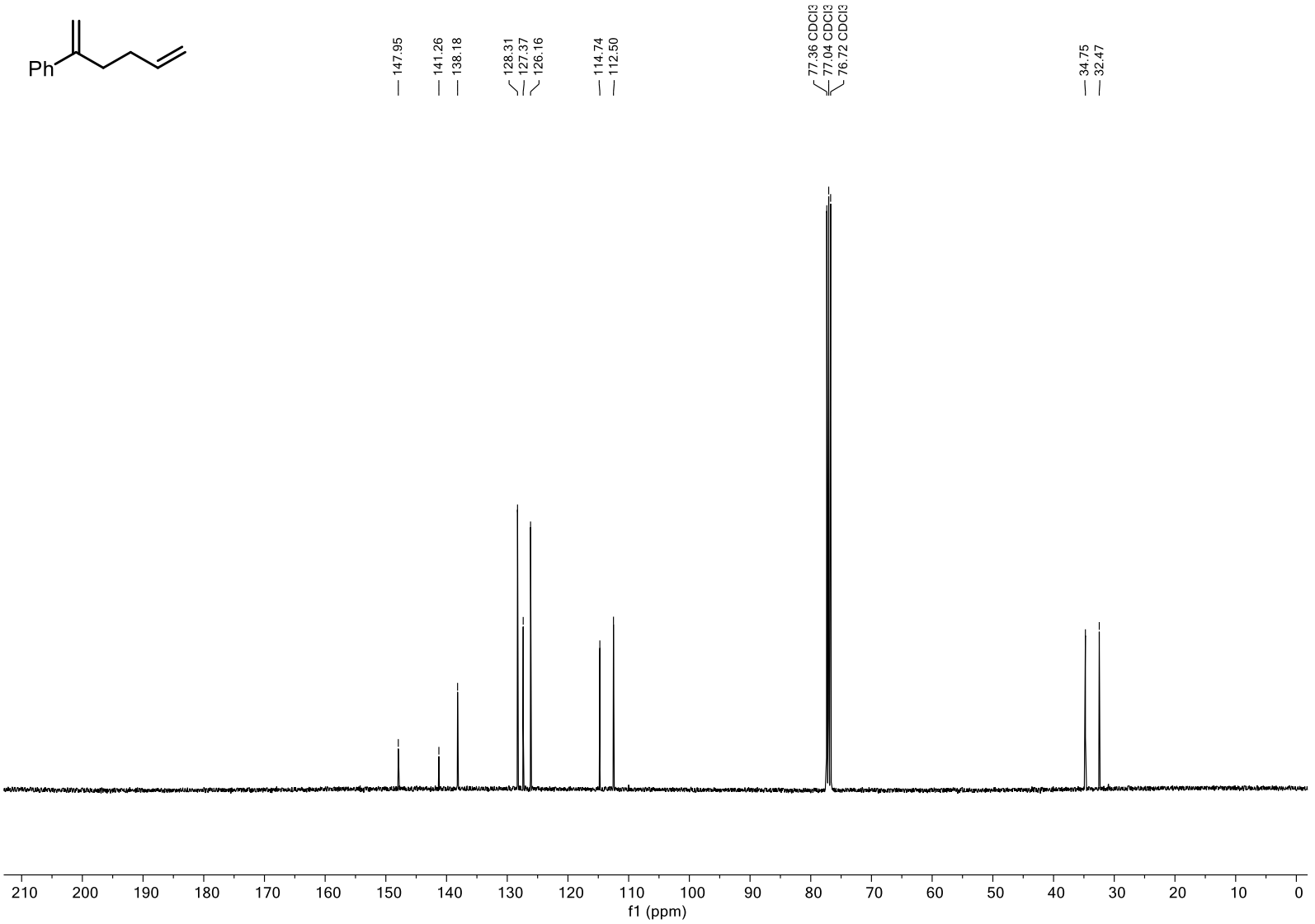
1-Phenylpent-4-en-1-one (S2): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



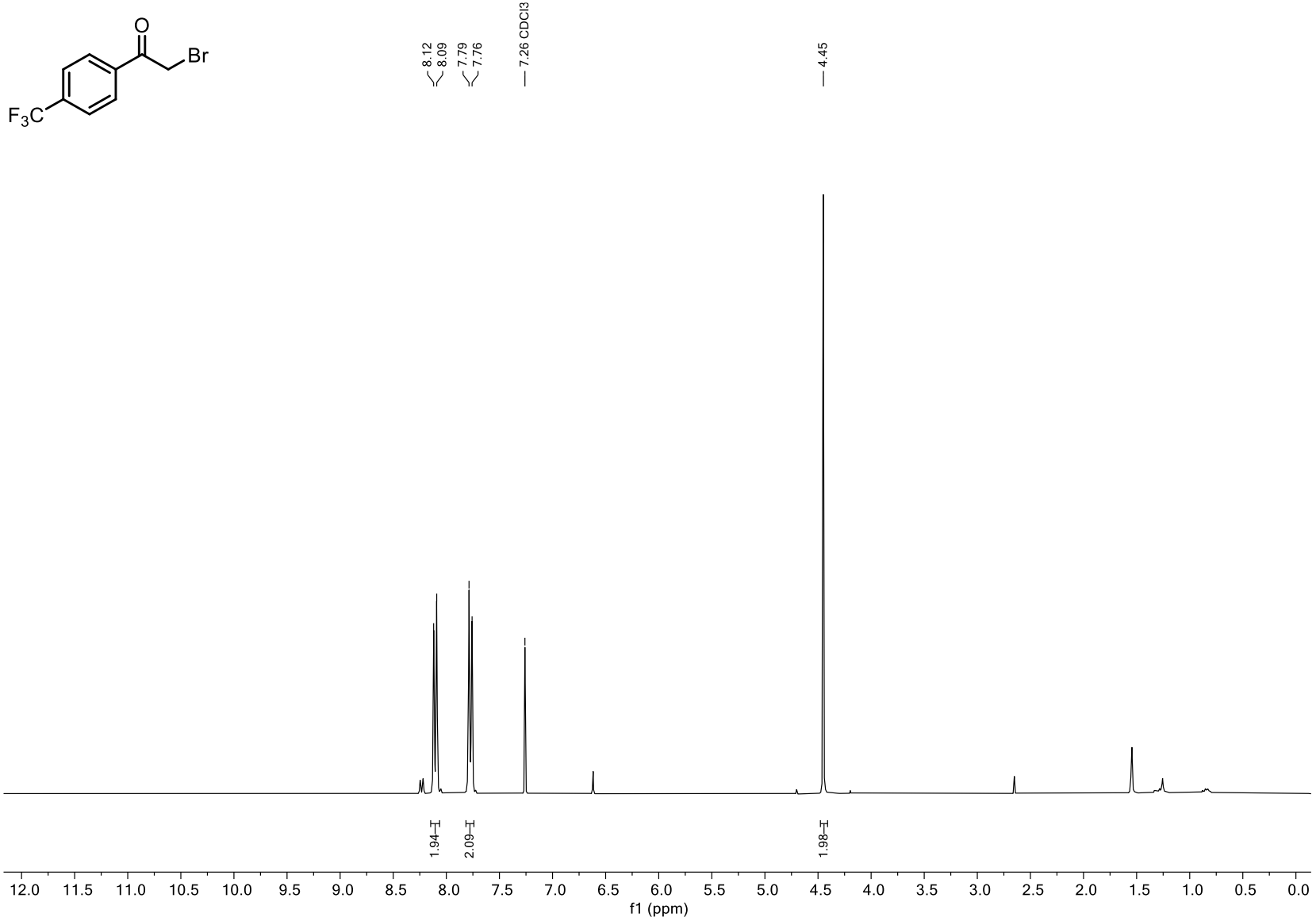
Hexa-1,5-dien-2-ylbenzene (1b): ^{1}H NMR (300 MHz, $CDCl_3$)



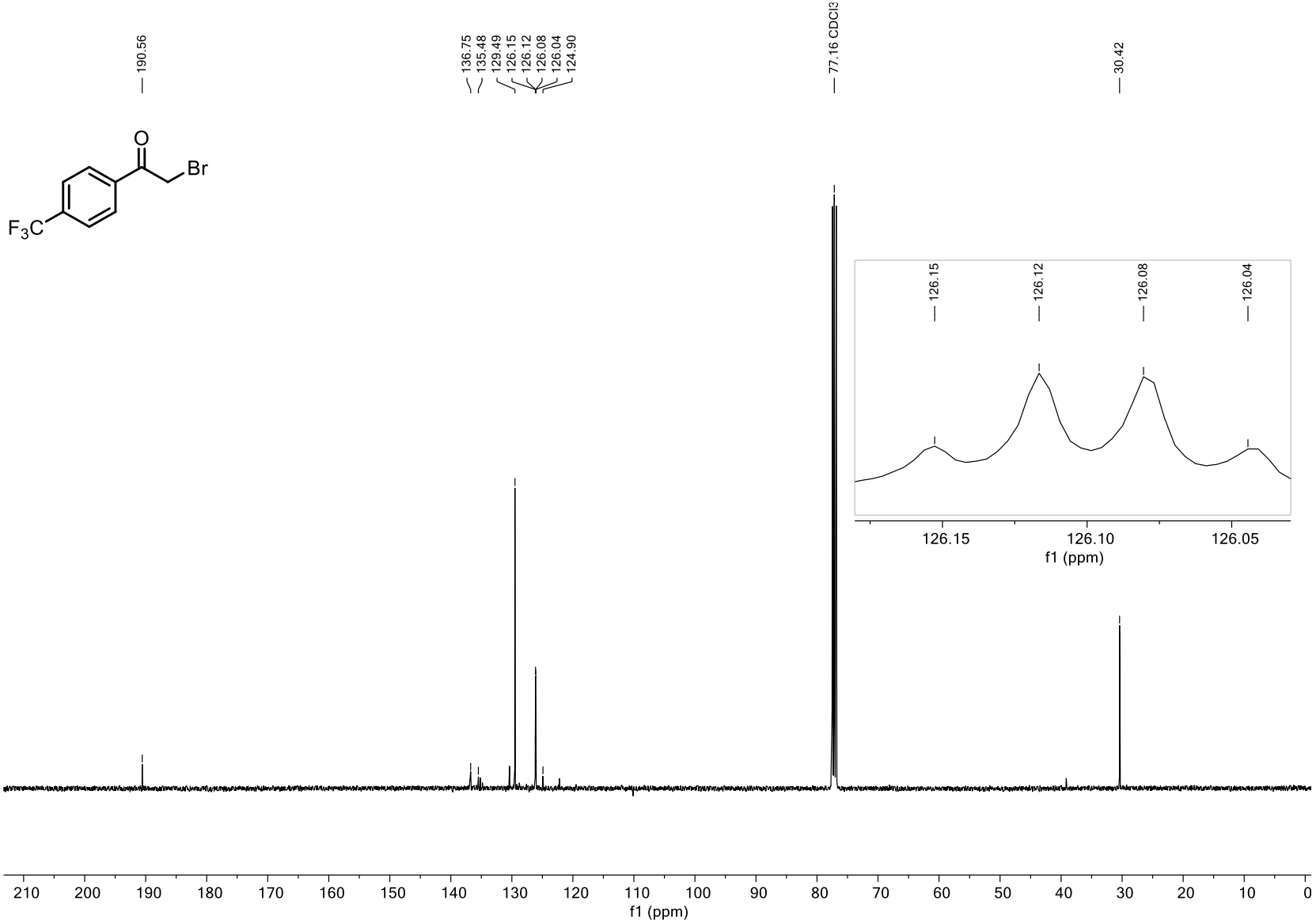
Hexa-1,5-dien-2-ylbenzene (1b): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



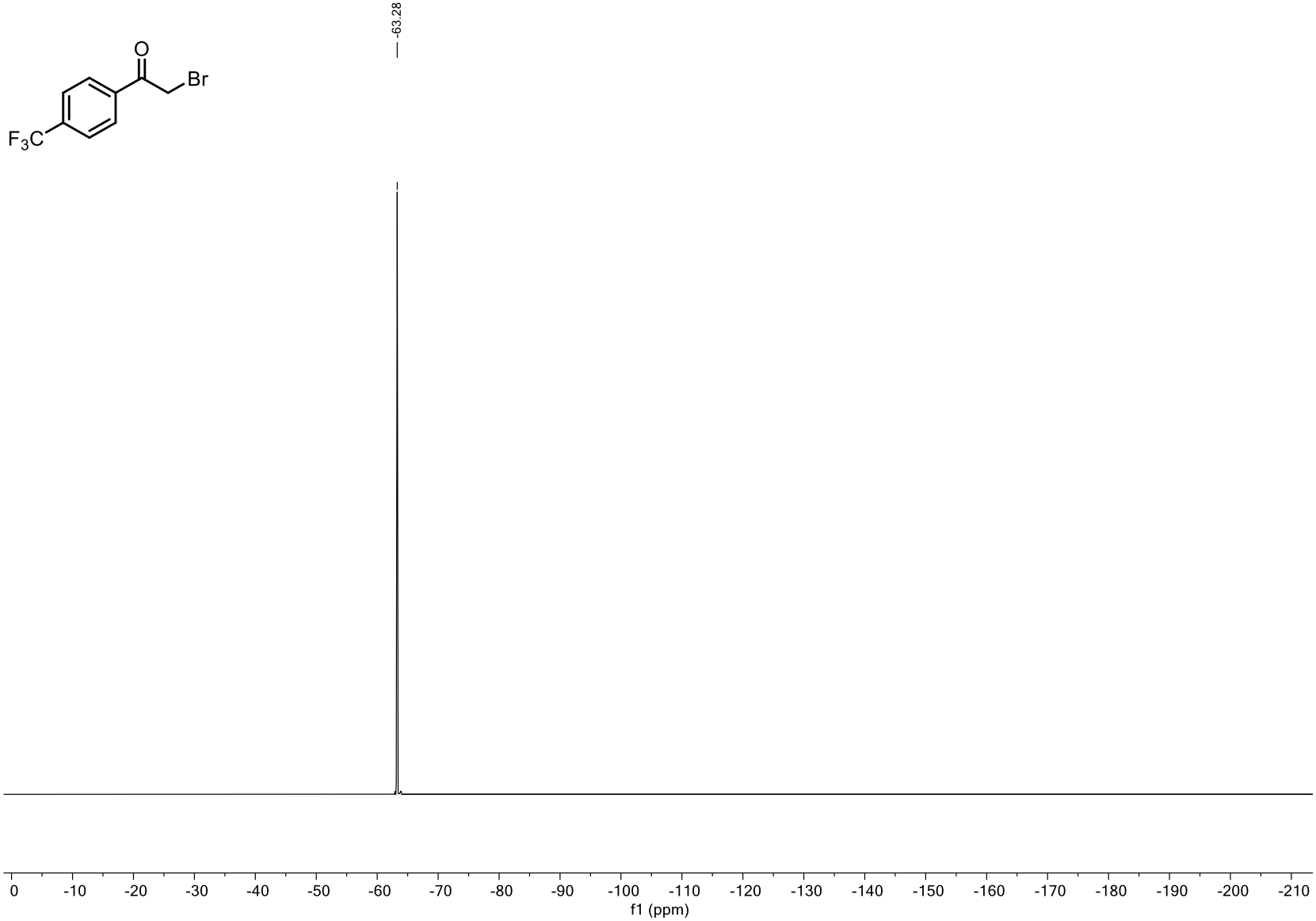
2-Bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (S3): ^{1}H NMR (300 MHz, $CDCl_3$)



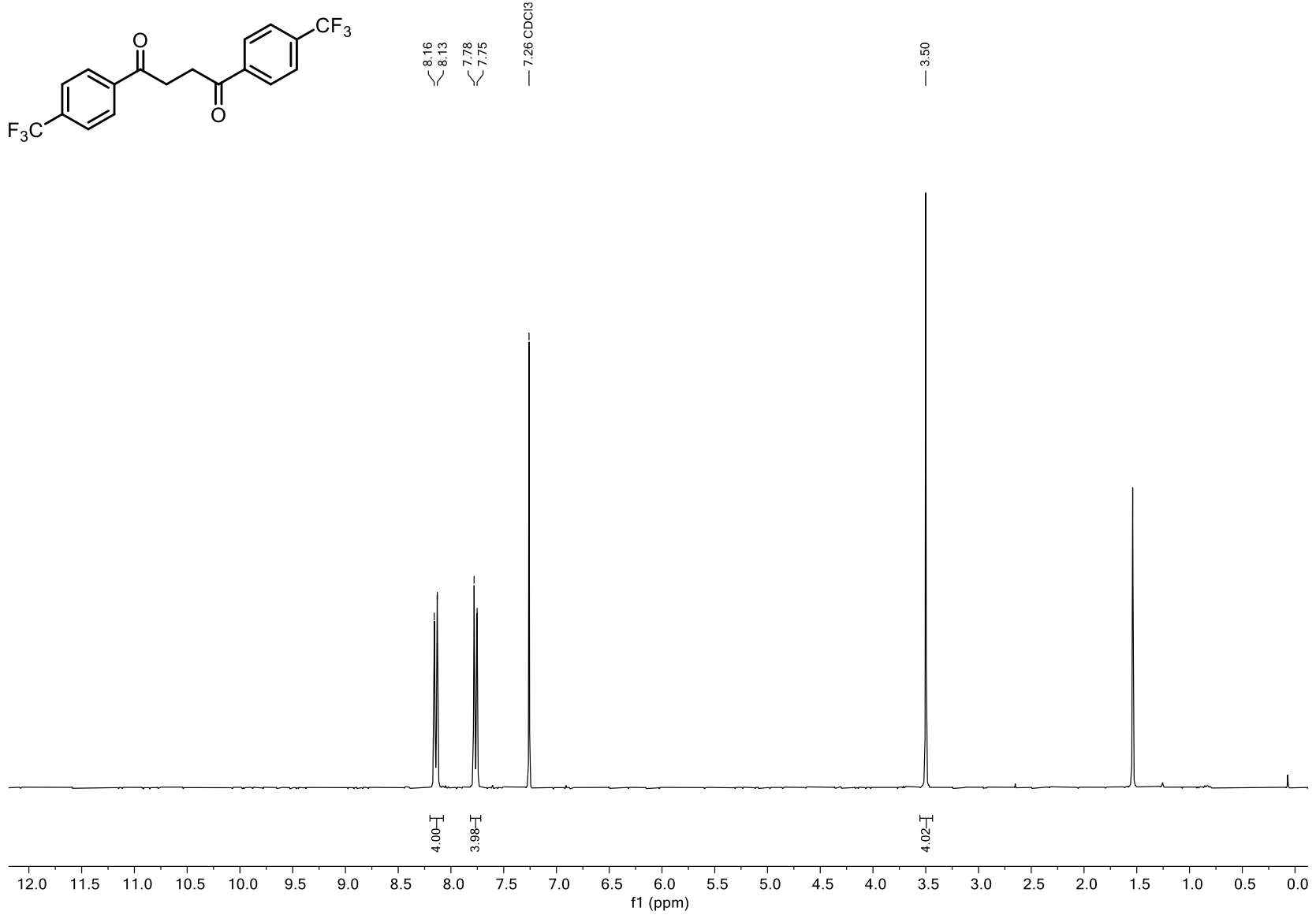
2-Bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (S3): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



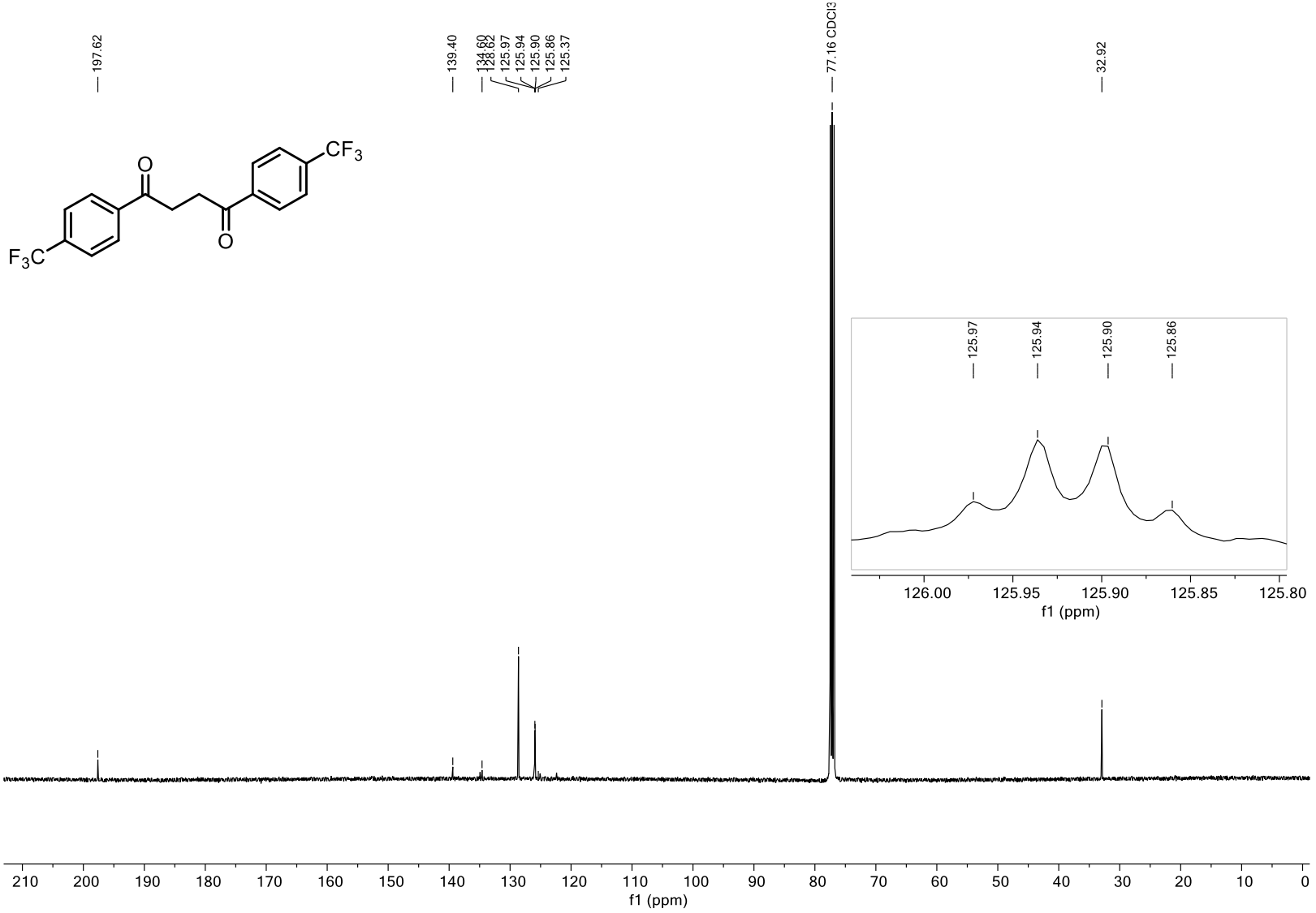
2-Bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (S3): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



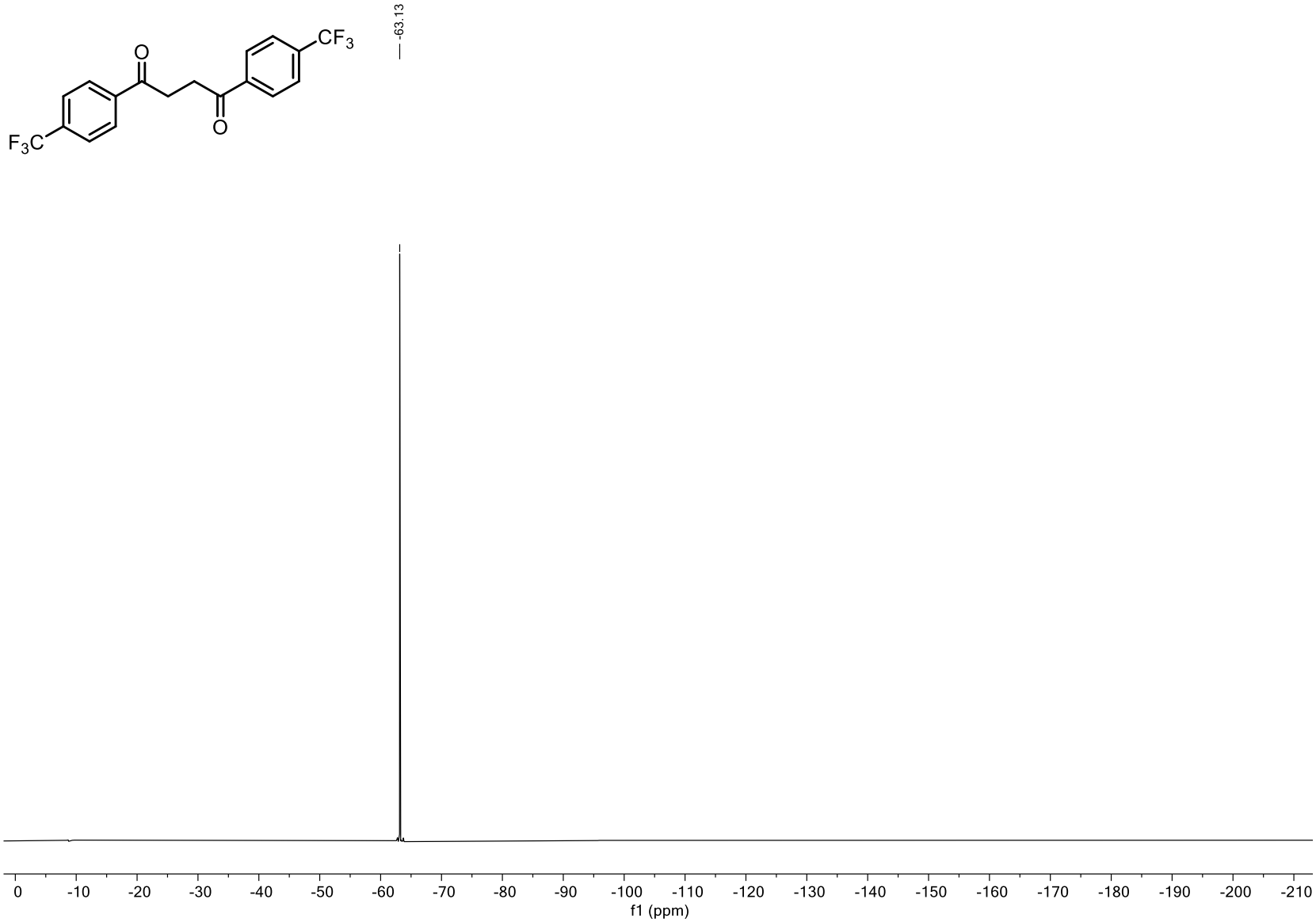
1,4-Bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (S4): ^{1}H NMR (300 MHz, $CDCl_3$)



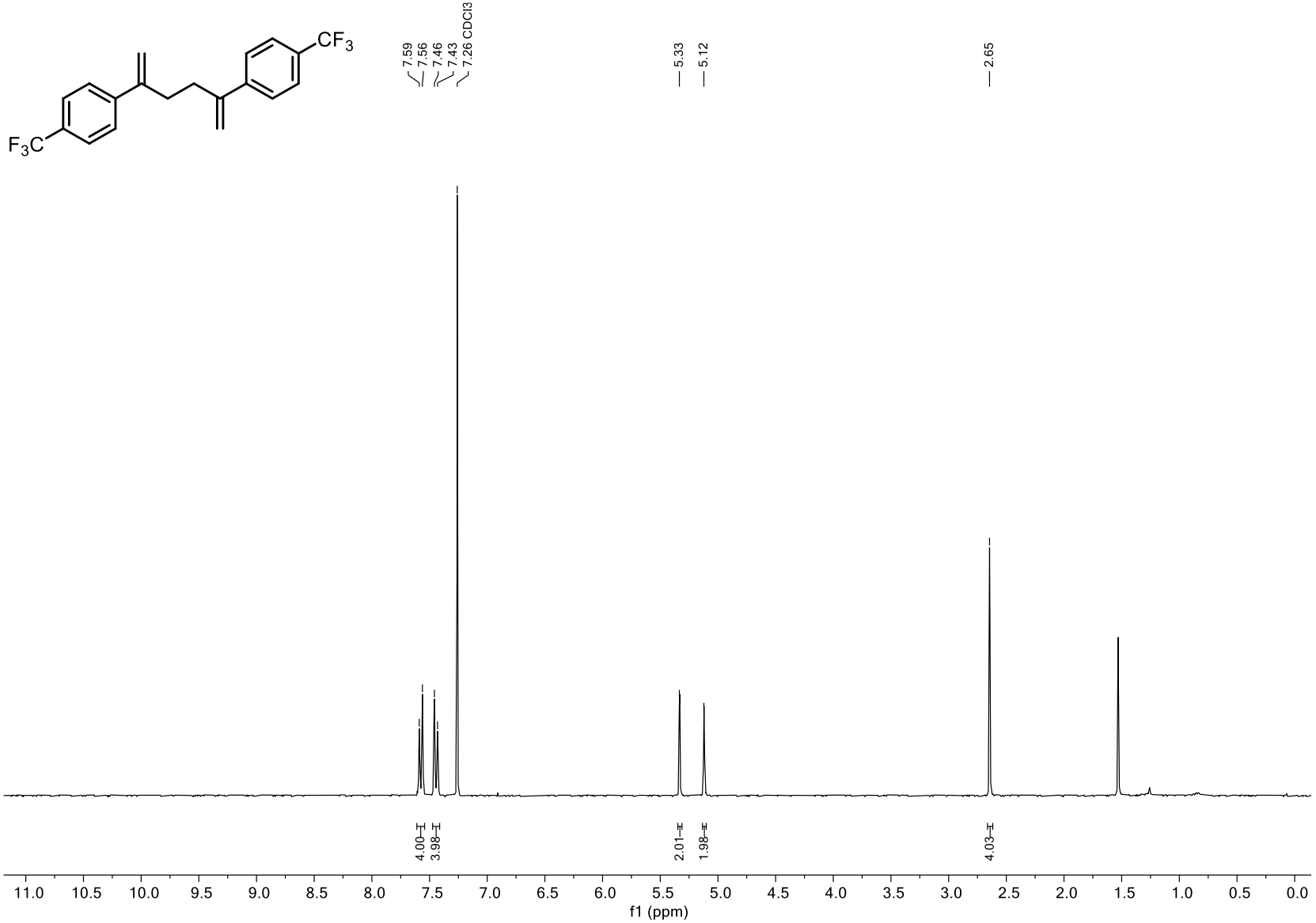
1,4-Bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (S4): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



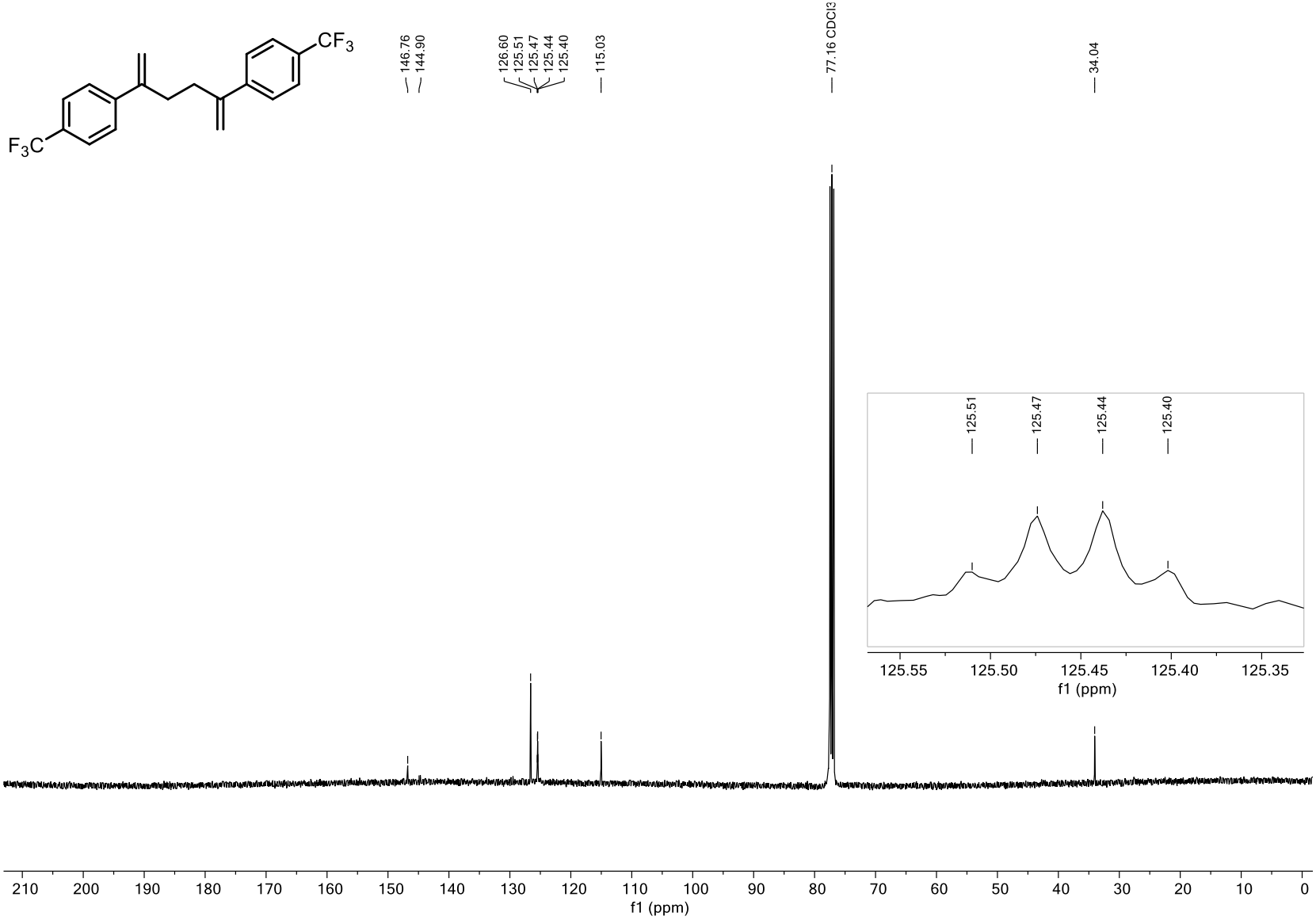
1,4-Bis(4-(trifluoromethyl)phenyl)butane-1,4-dione (S4): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



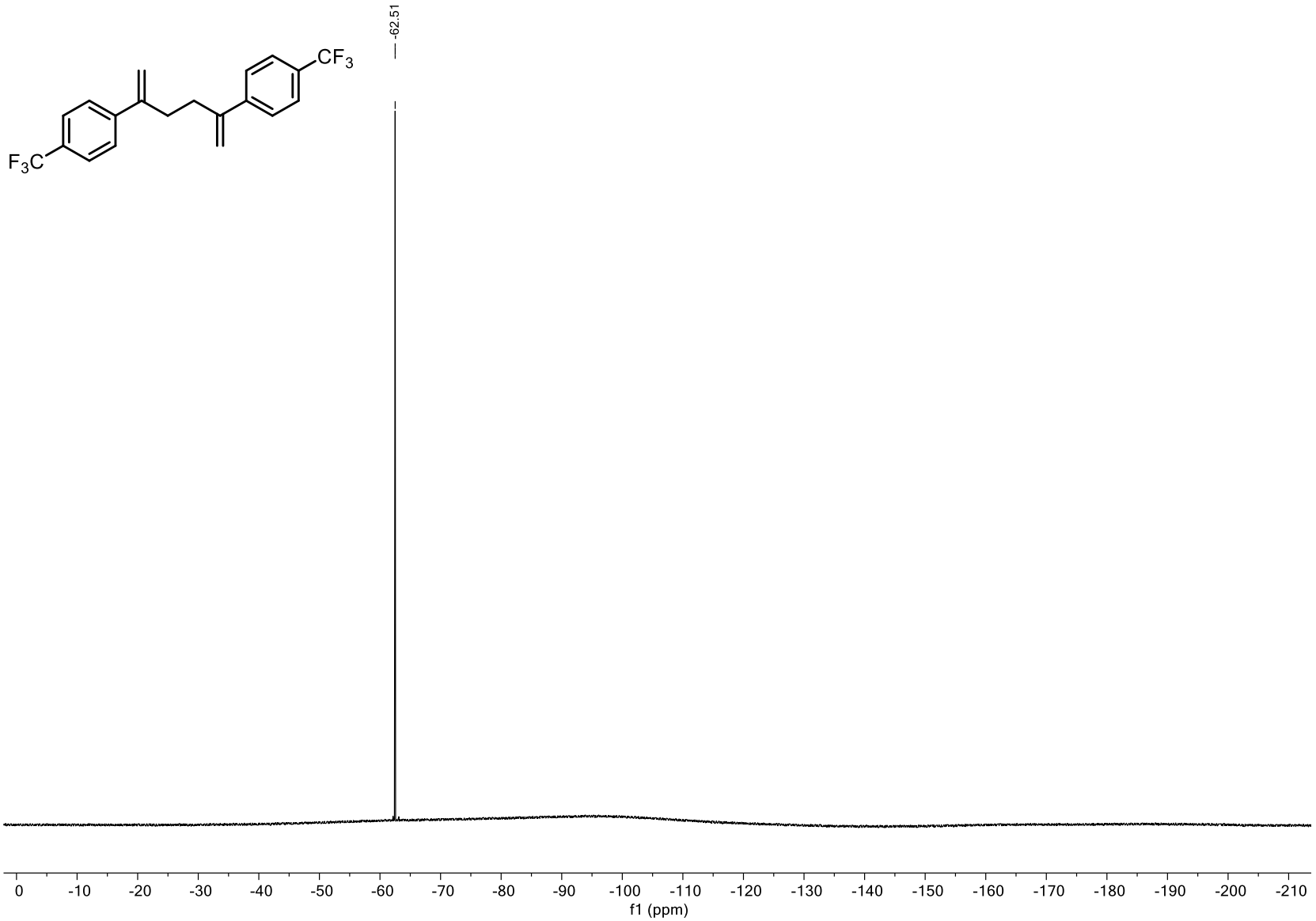
4,4'-(Hexa-1,5-diene-2,5-diyl)bis((trifluoromethyl)benzene) (1c): ^{1}H NMR (300 MHz, $CDCl_3$)



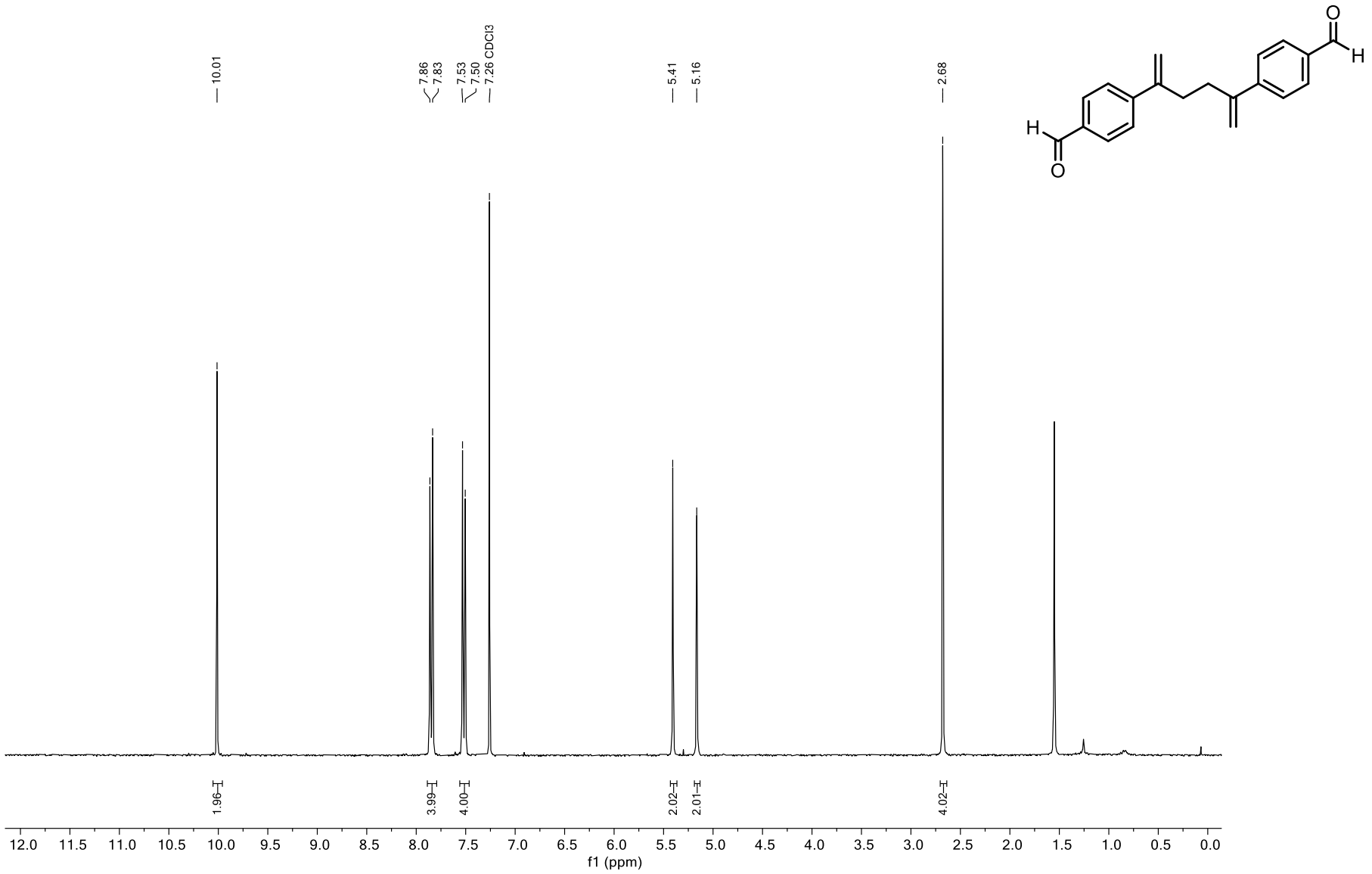
4,4'-(Hexa-1,5-diene-2,5-diyl)bis((trifluoromethyl)benzene) (1c): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



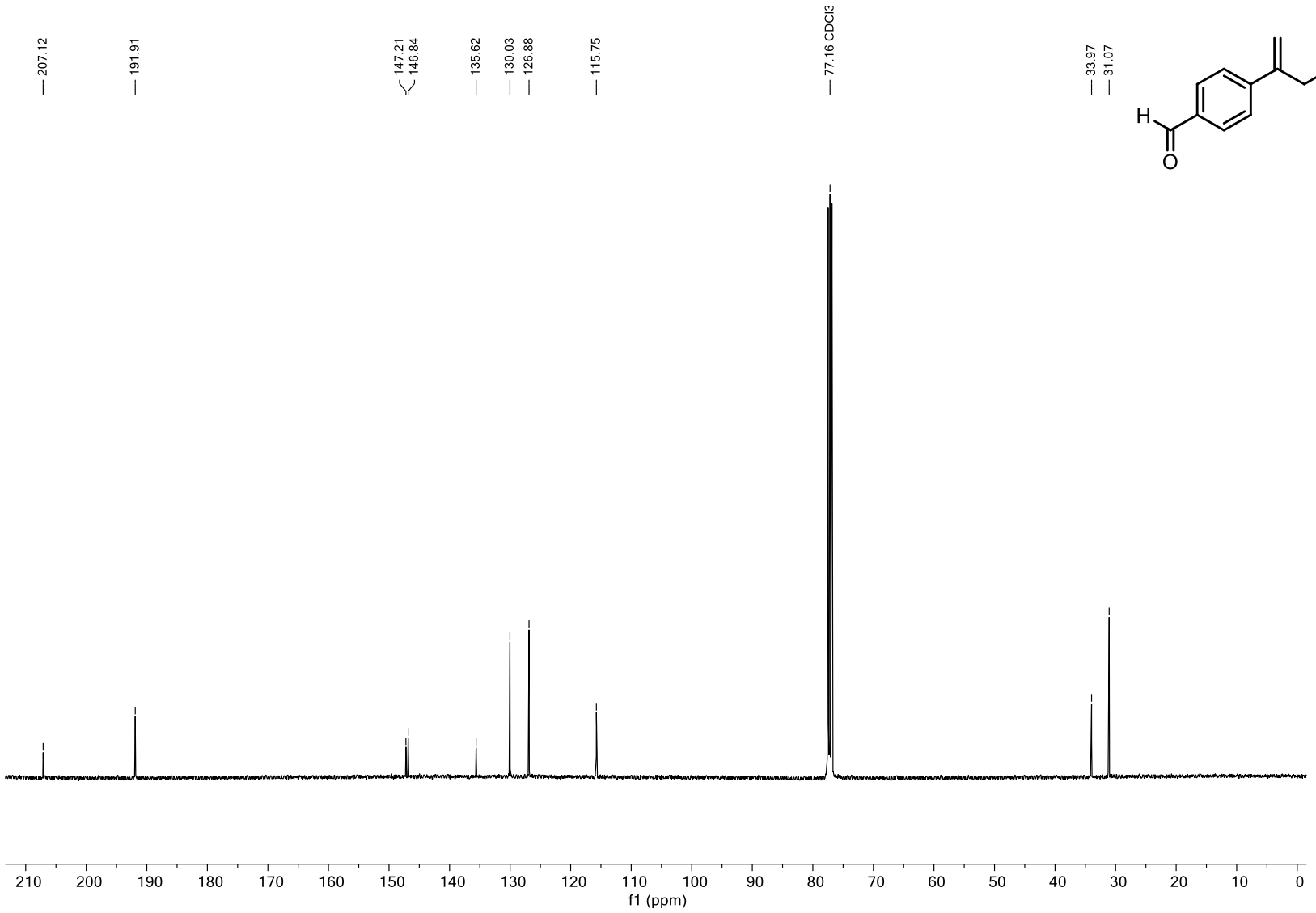
4,4'-(Hexa-1,5-diene-2,5-diyl)bis((trifluoromethyl)benzene) (1c): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



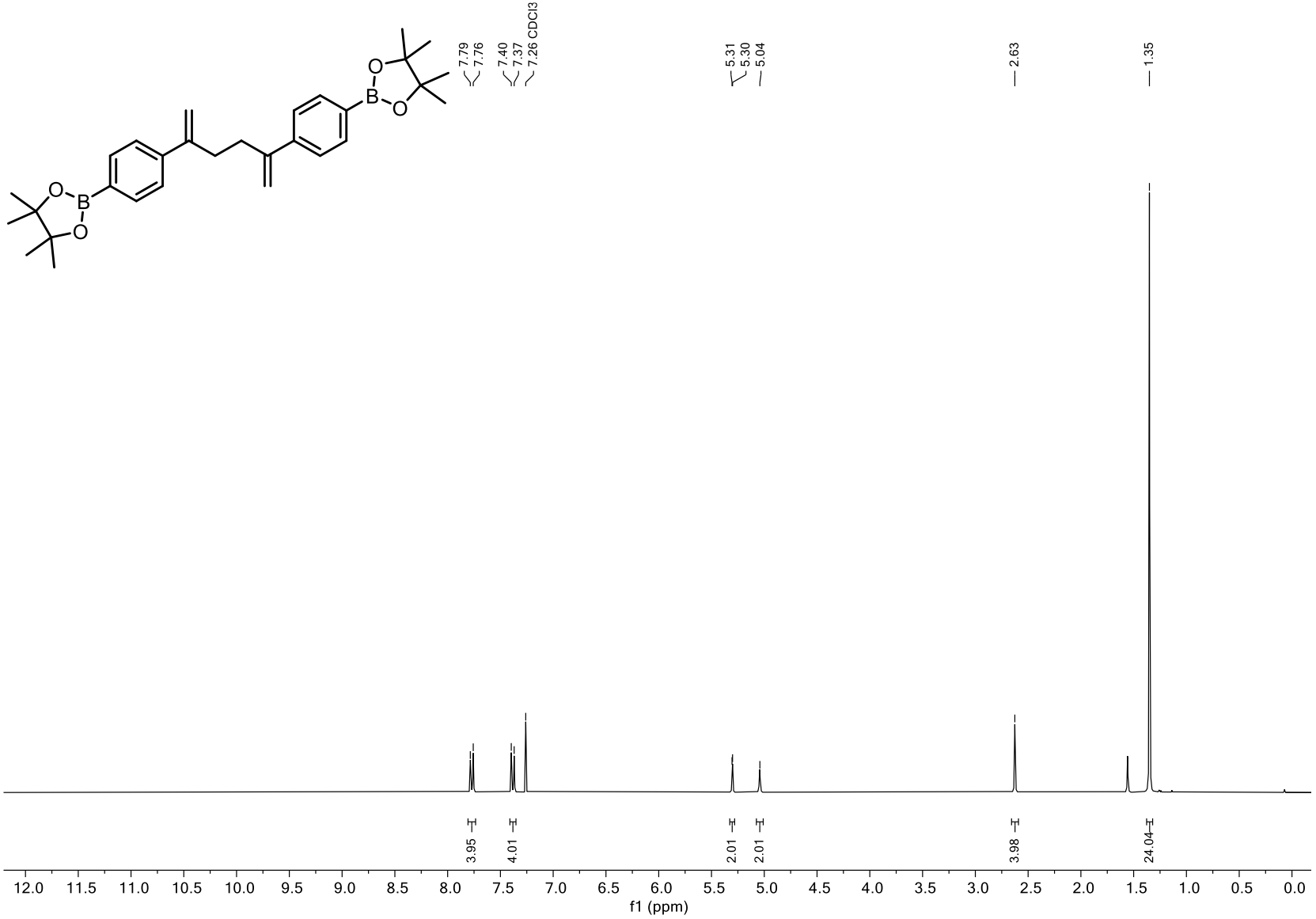
4,4'-(Hexa-1,5-diene-2,5-diyl)dibenzaldehyde (1d): ^{1}H NMR (300 MHz, $CDCl_3$)



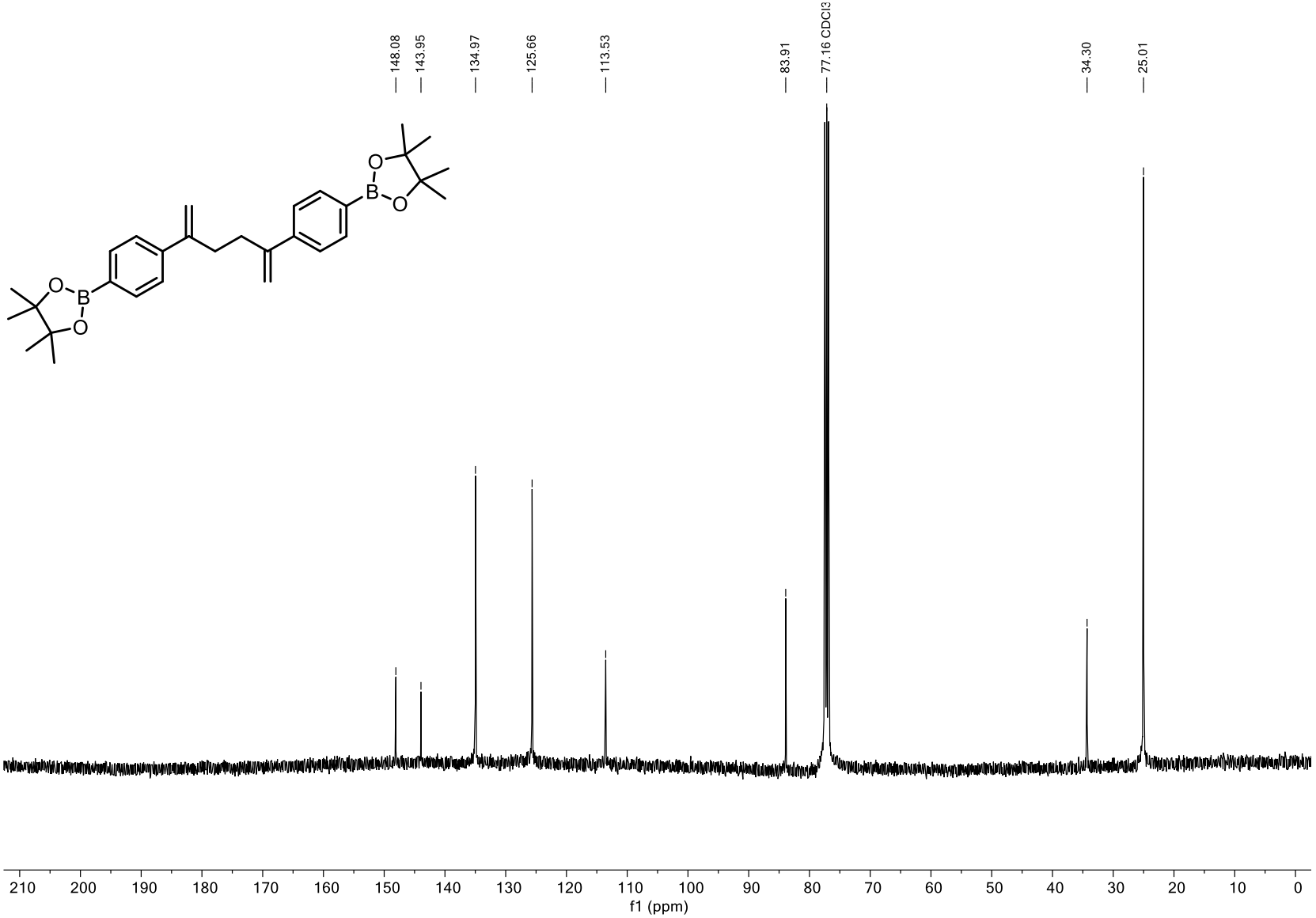
4,4'-(Hexa-1,5-diene-2,5-diyl)dibenzaldehyde (1d): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



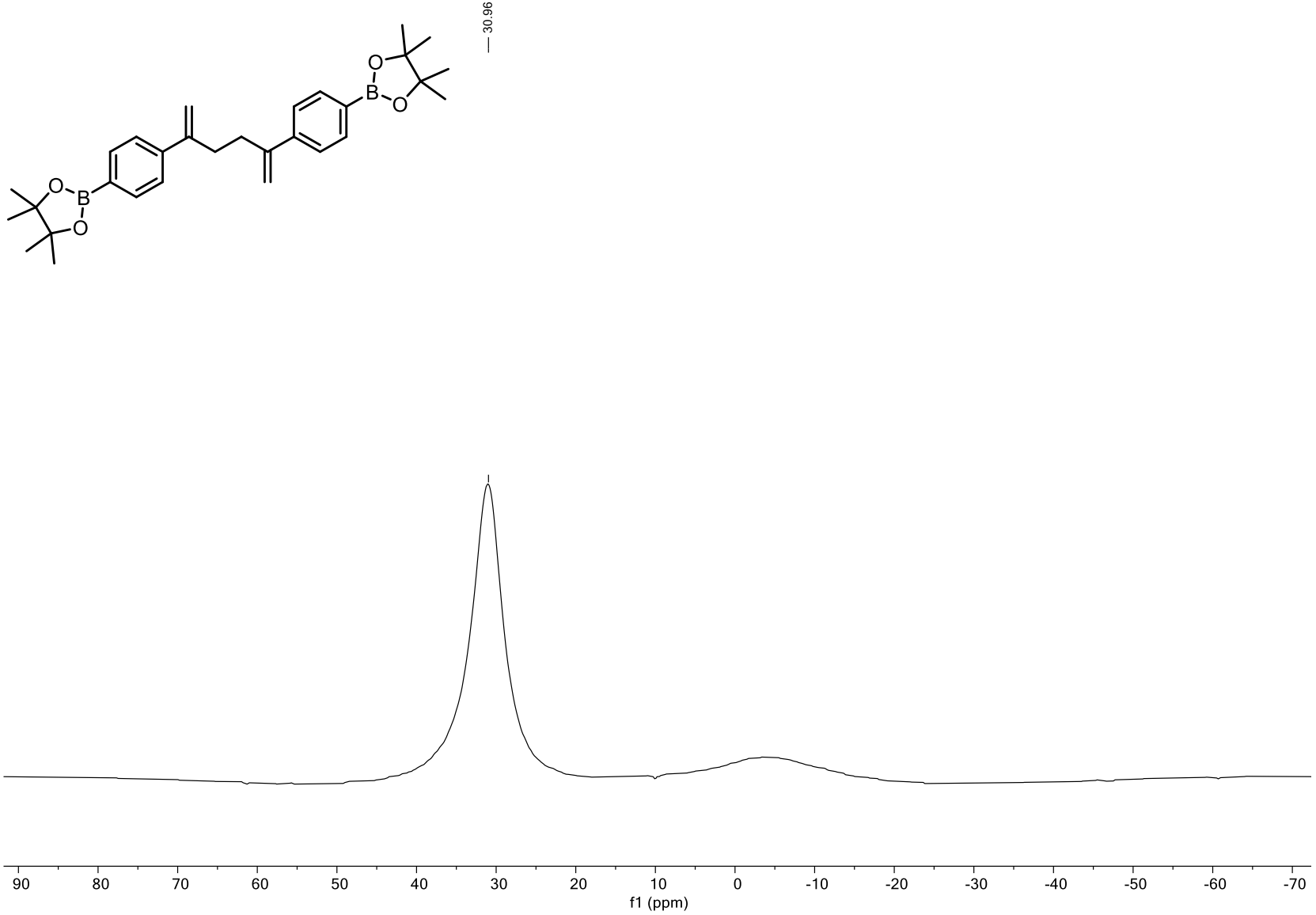
2,2'-(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1e): ^{1}H NMR (300 MHz, $CDCl_3$)



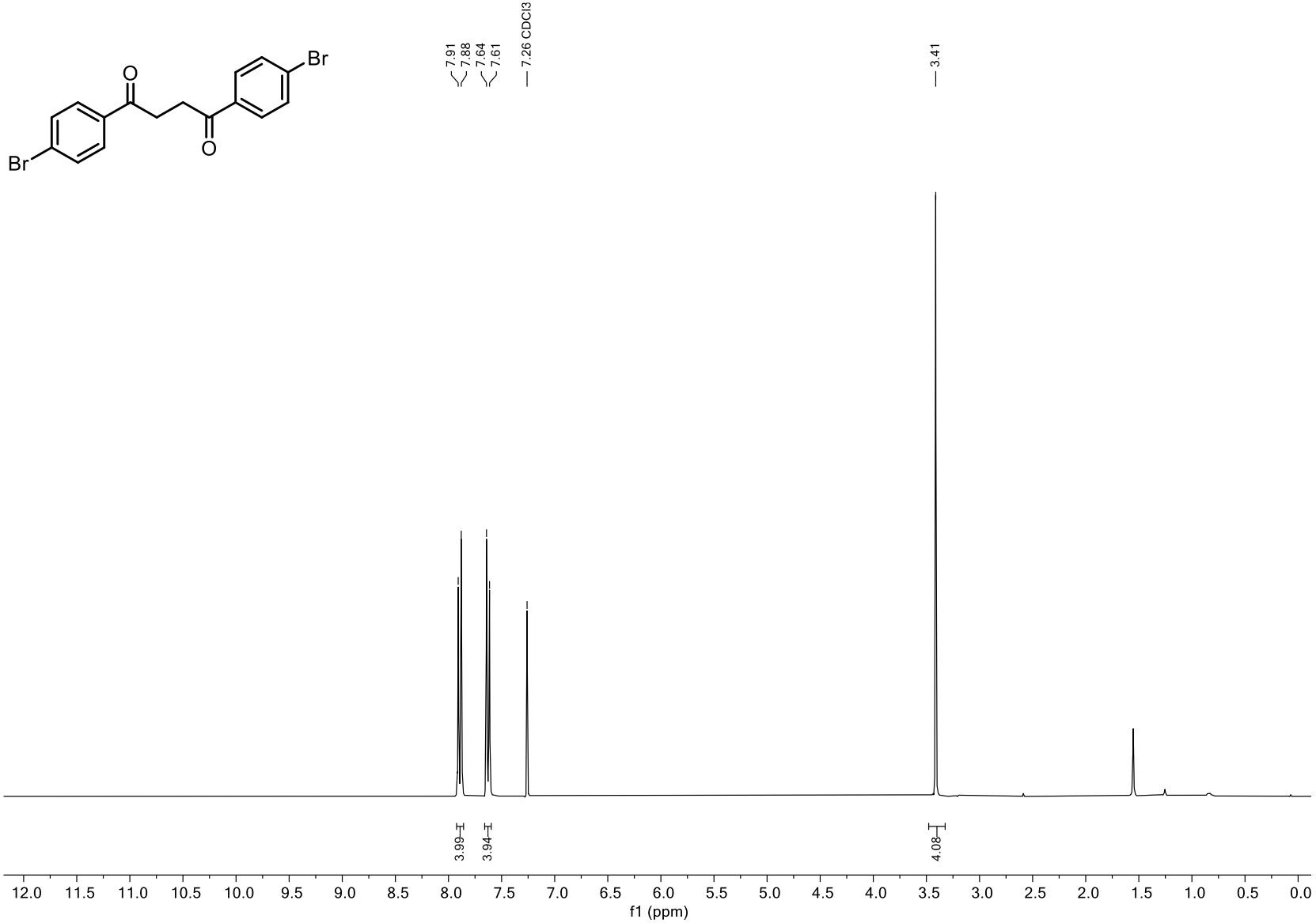
2,2'-(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1e): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



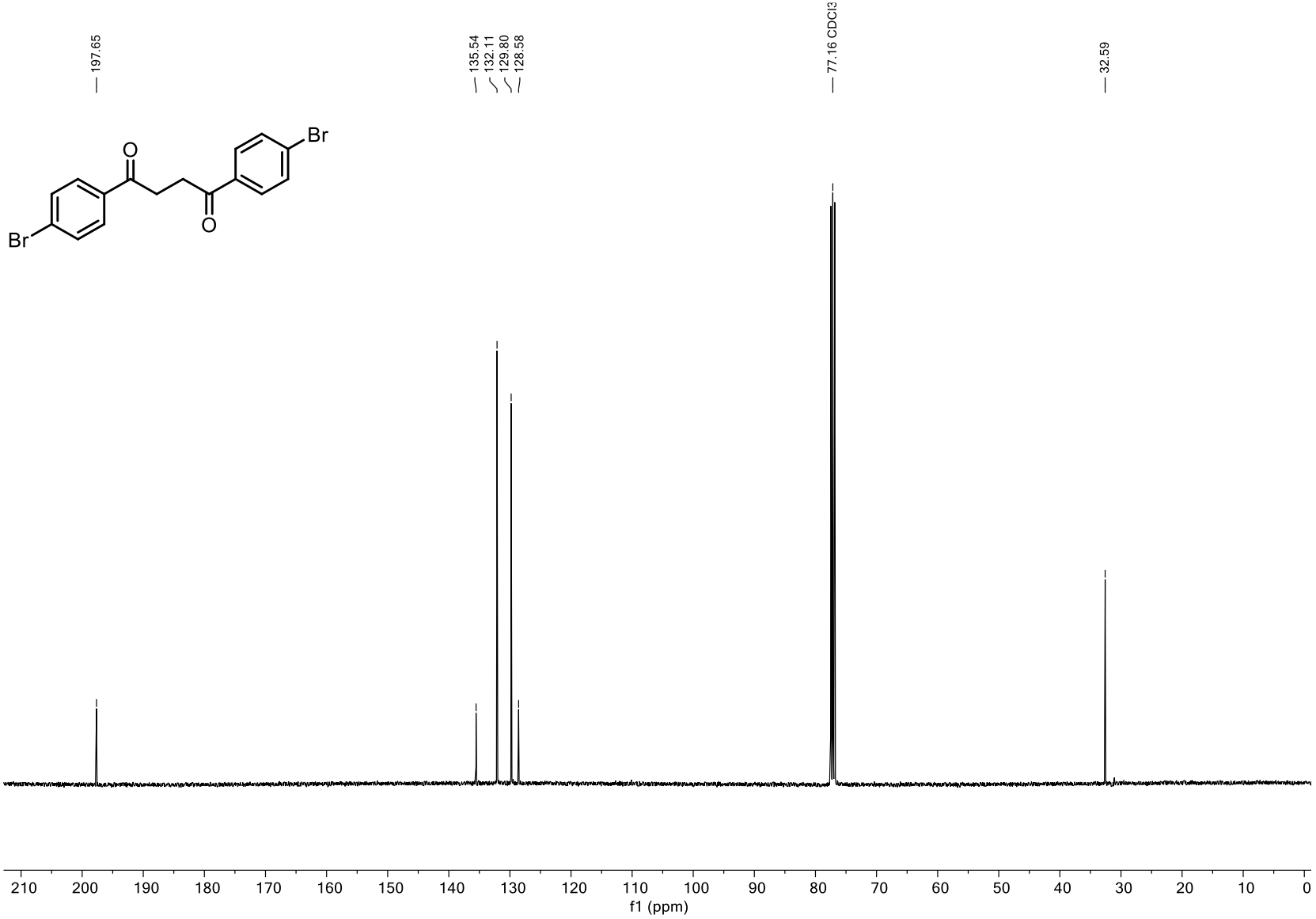
2,2'-(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1e): ^{11}B NMR (161 MHz, $CDCl_3$)



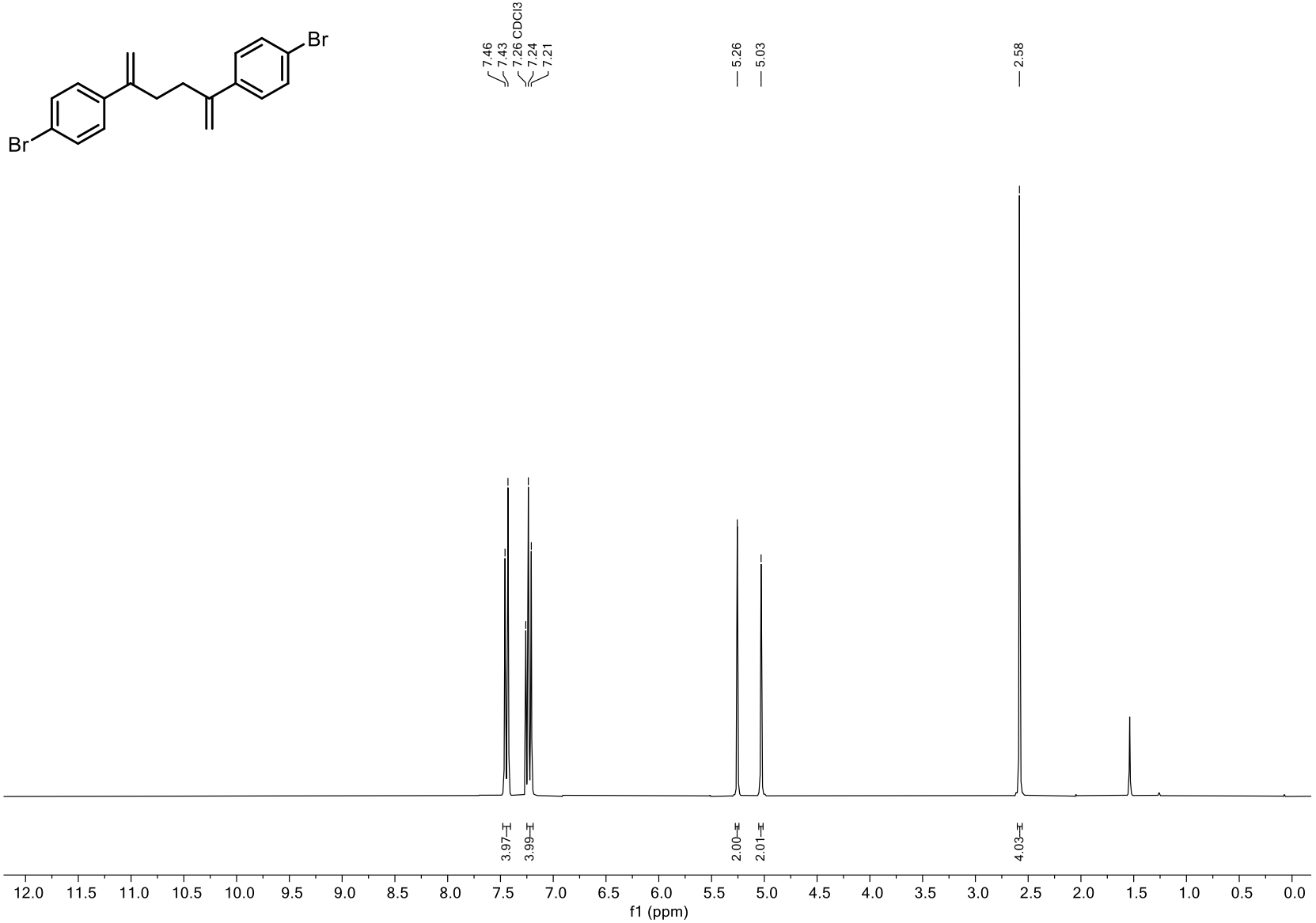
1,4-Bis(4-bromophenyl)butane-1,4-dione (S5): ^{1}H NMR (300 MHz, $CDCl_3$)



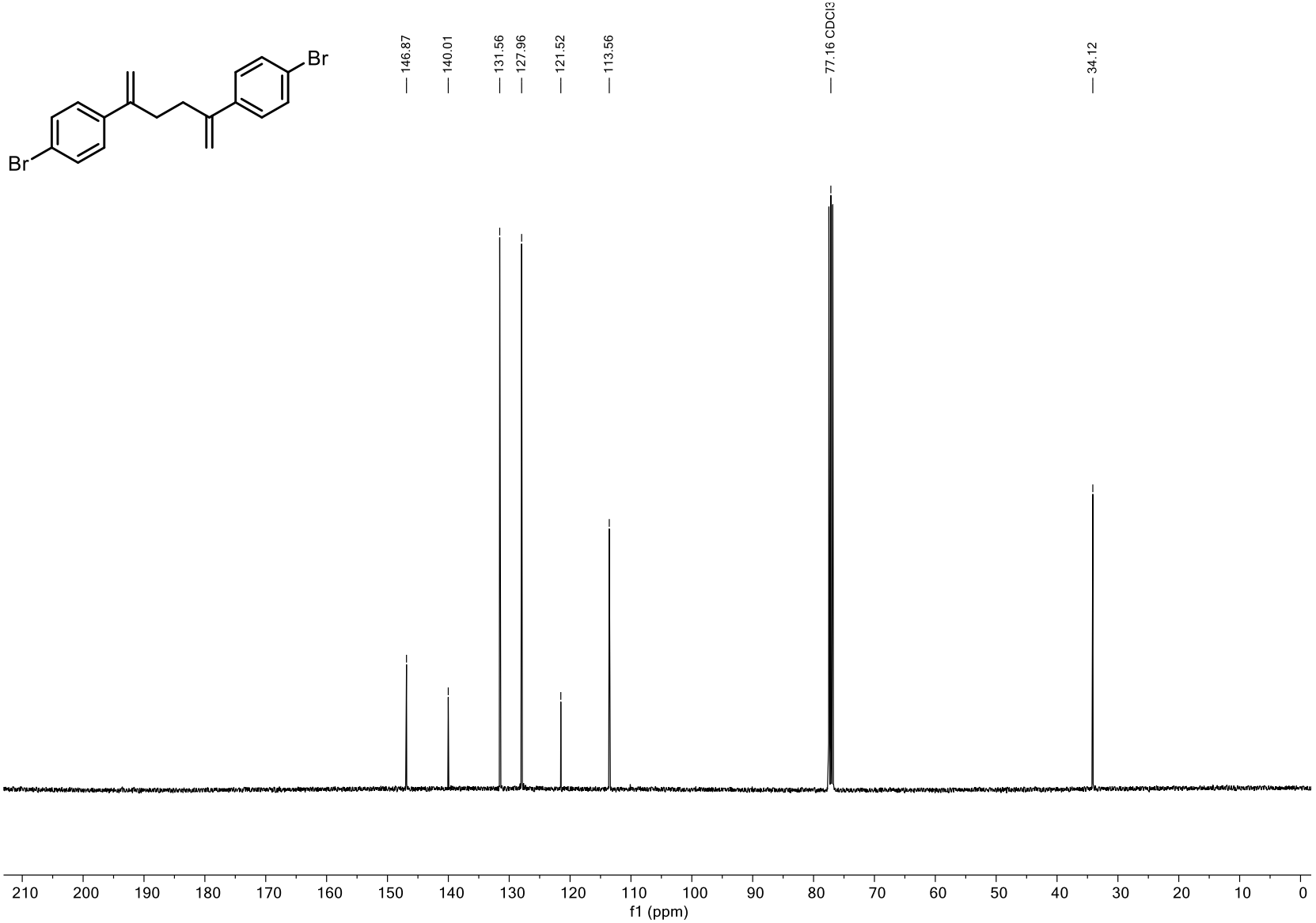
1,4-Bis(4-bromophenyl)butane-1,4-dione (S5): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



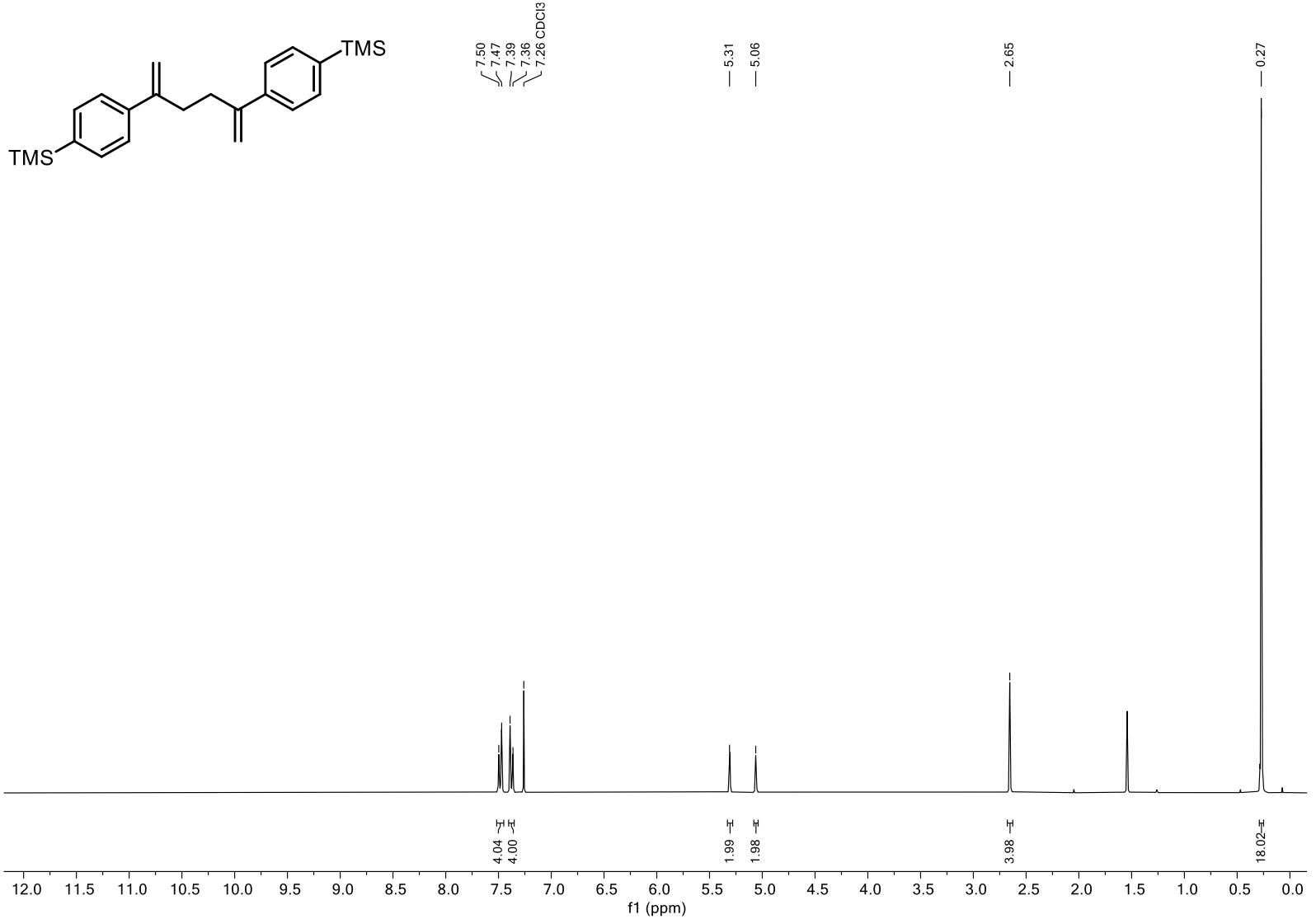
4,4'-(Hexa-1,5-diene-2,5-diyl)bis(bromobenzene) (1f): ^{1}H NMR (300 MHz, $CDCl_3$)



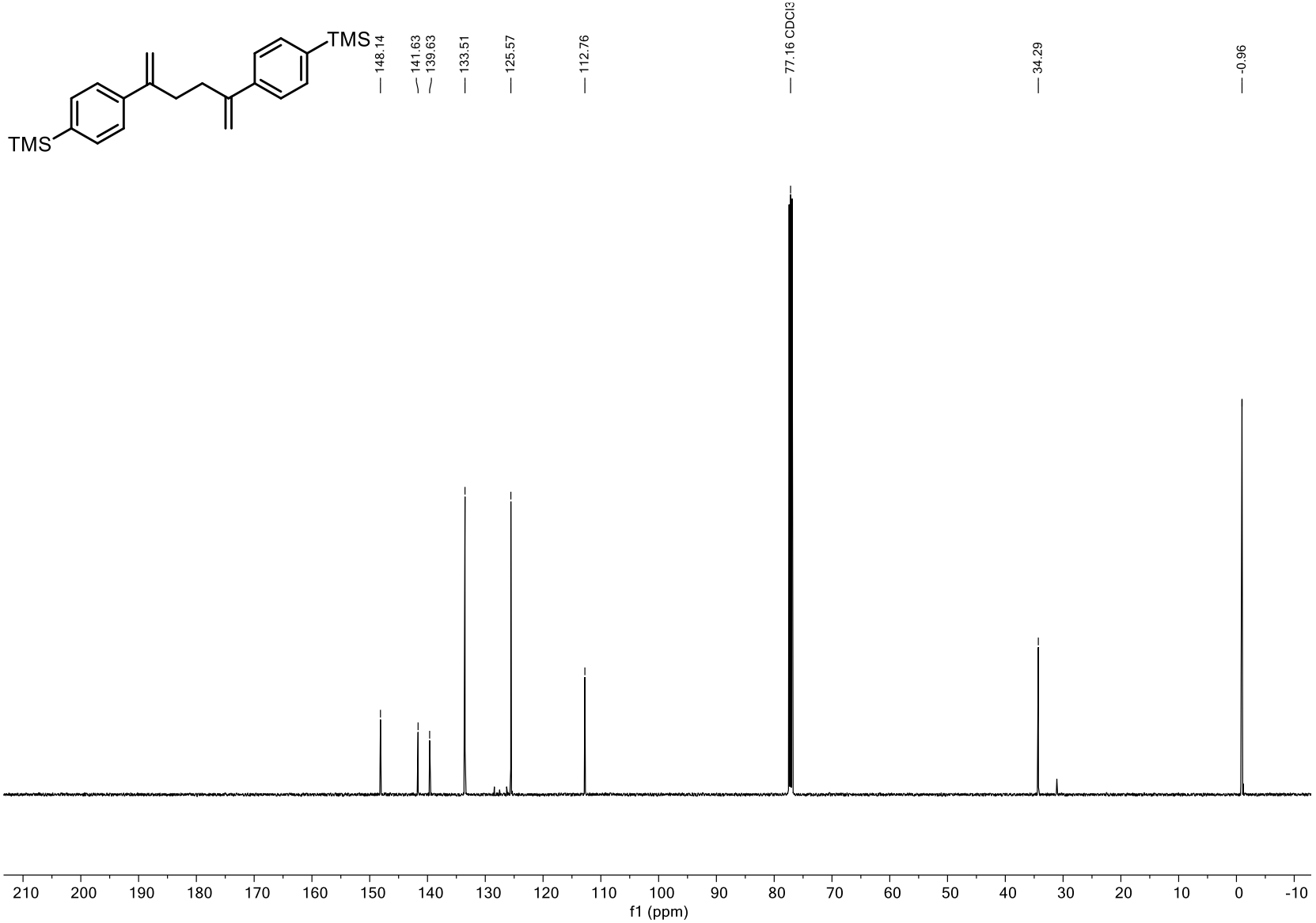
4,4'-(Hexa-1,5-diene-2,5-diyl)bis(bromobenzene) (1f): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



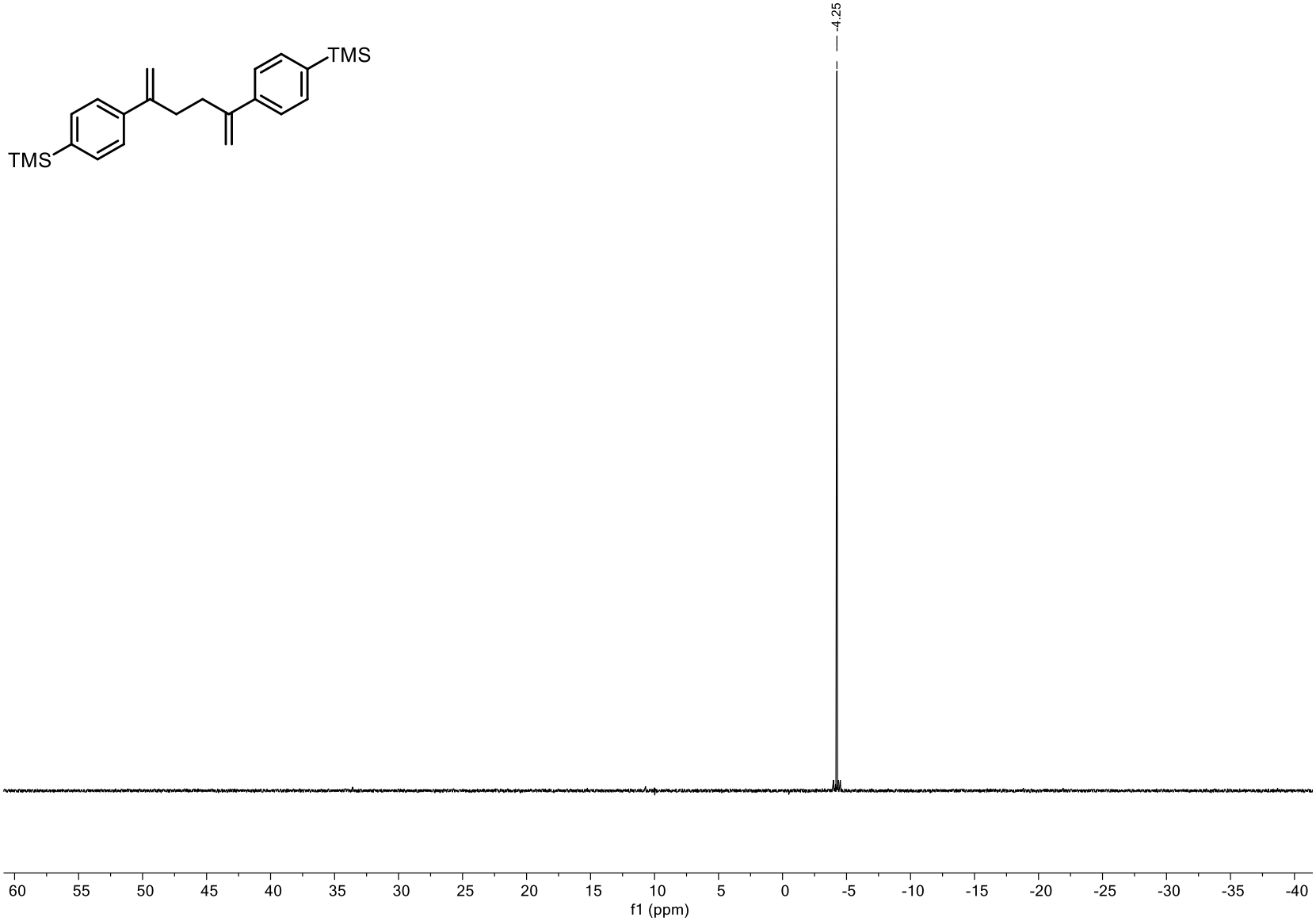
(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(trimethylsilane) (1g): ^{1}H NMR (300 MHz, $CDCl_3$)



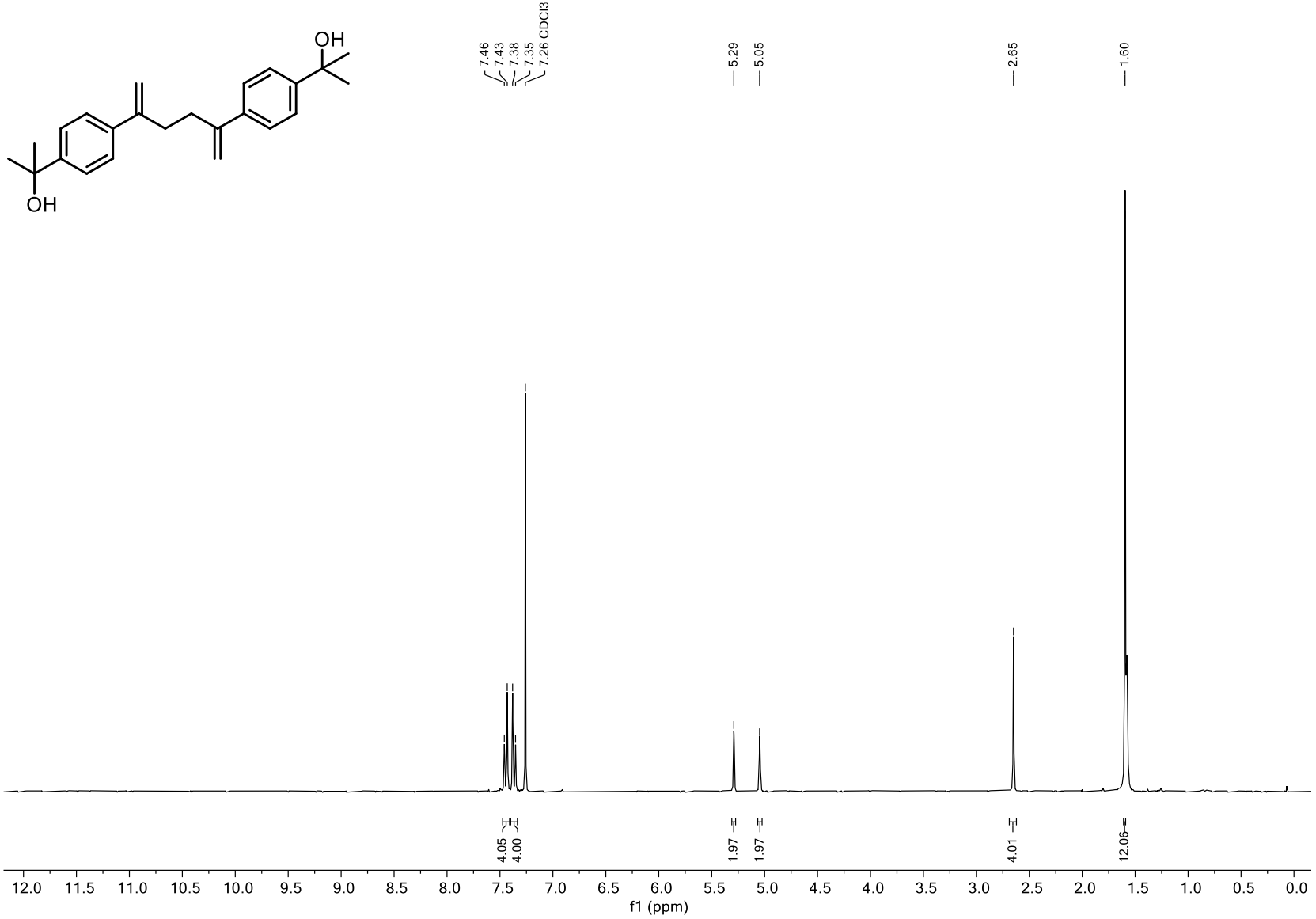
(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(trimethylsilane) (1g): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



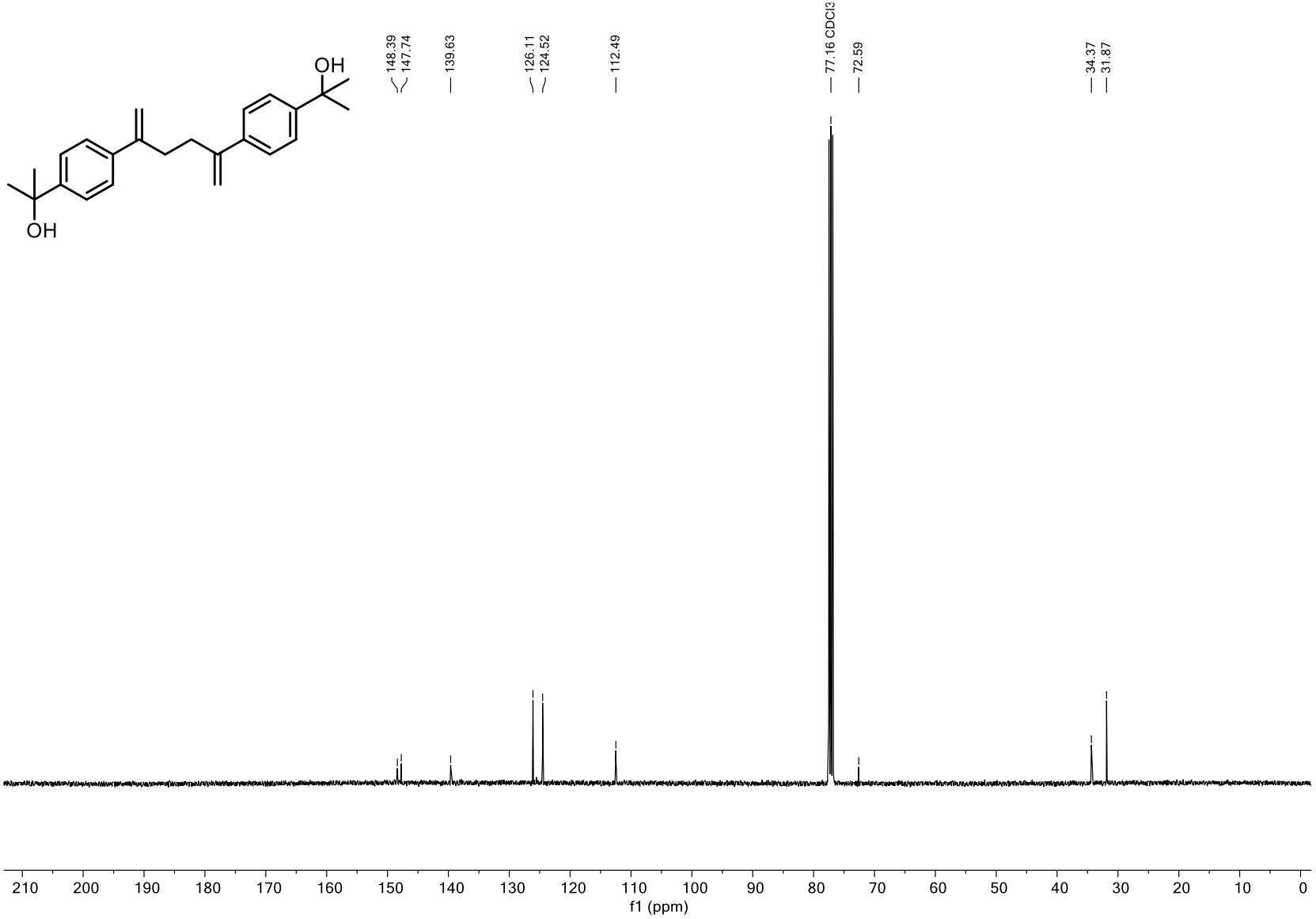
(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(trimethylsilane) (1g): $^{29}Si\{^{1}H\}$ NMR (99 MHz, $CDCl_3$)



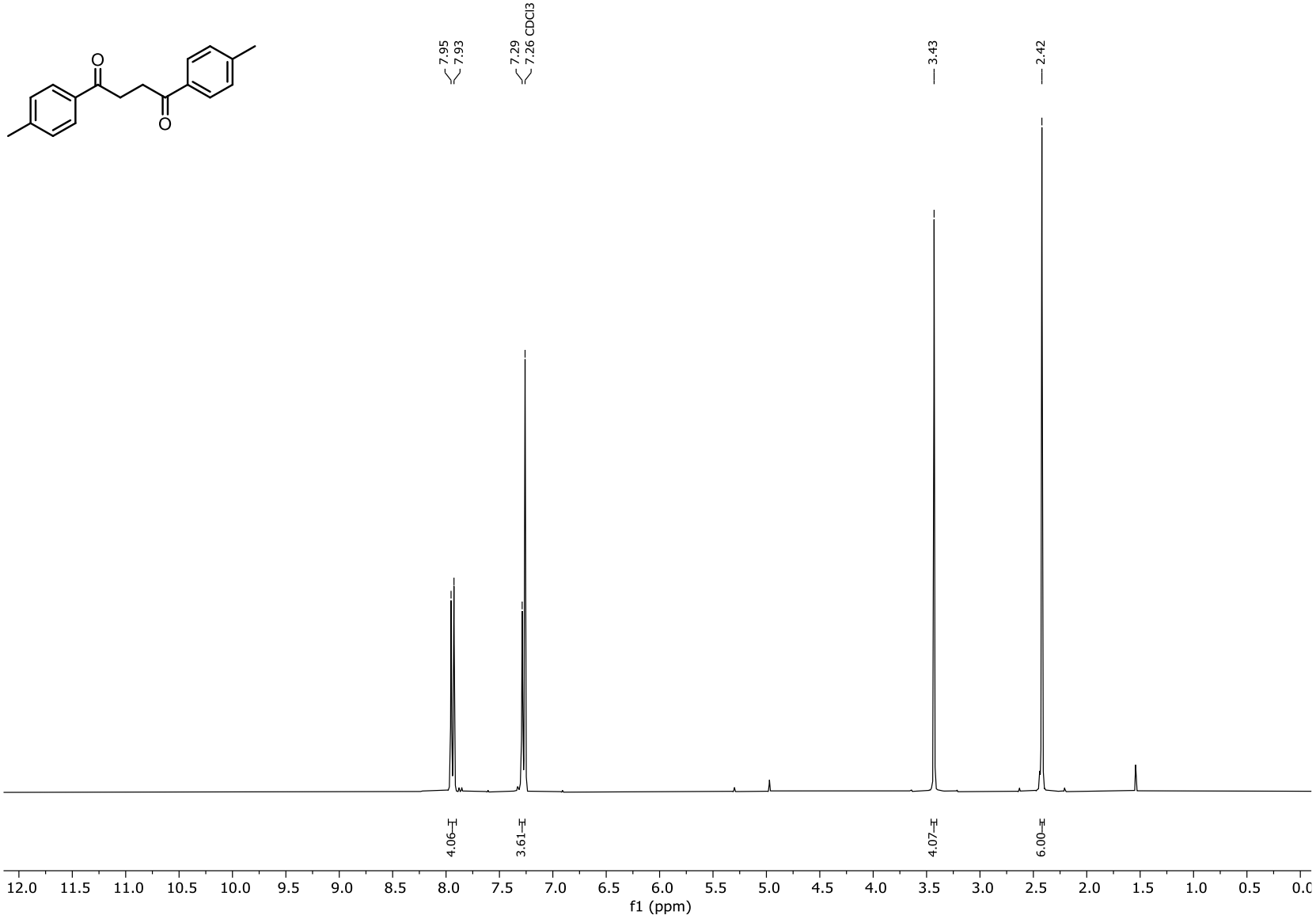
2,2'-(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(propan-2-ol) (1h): ^{1}H NMR (300 MHz, $CDCl_3$)



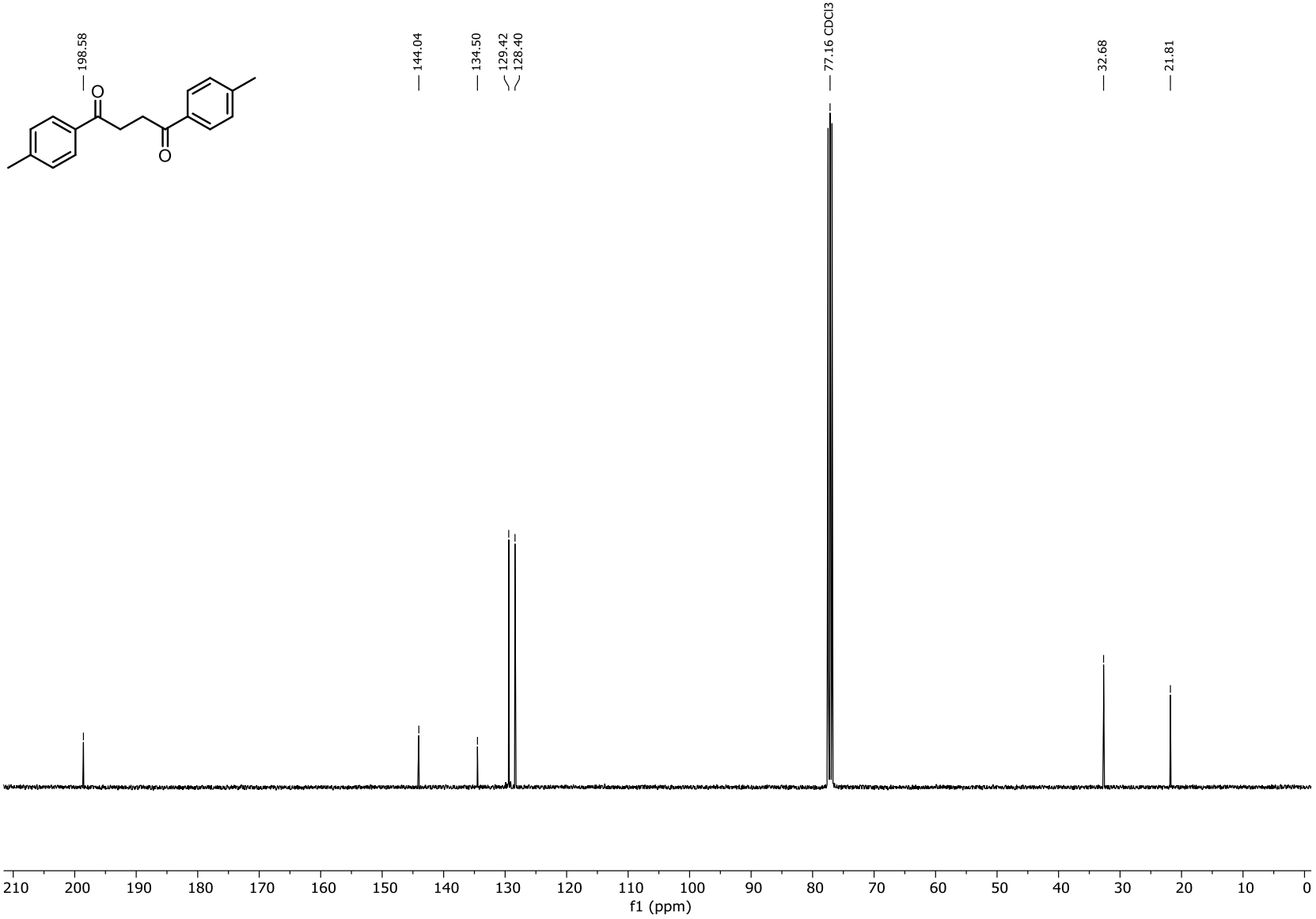
2,2'-(Hexa-1,5-diene-2,5-diylbis(4,1-phenylene))bis(propan-2-ol) (1h): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



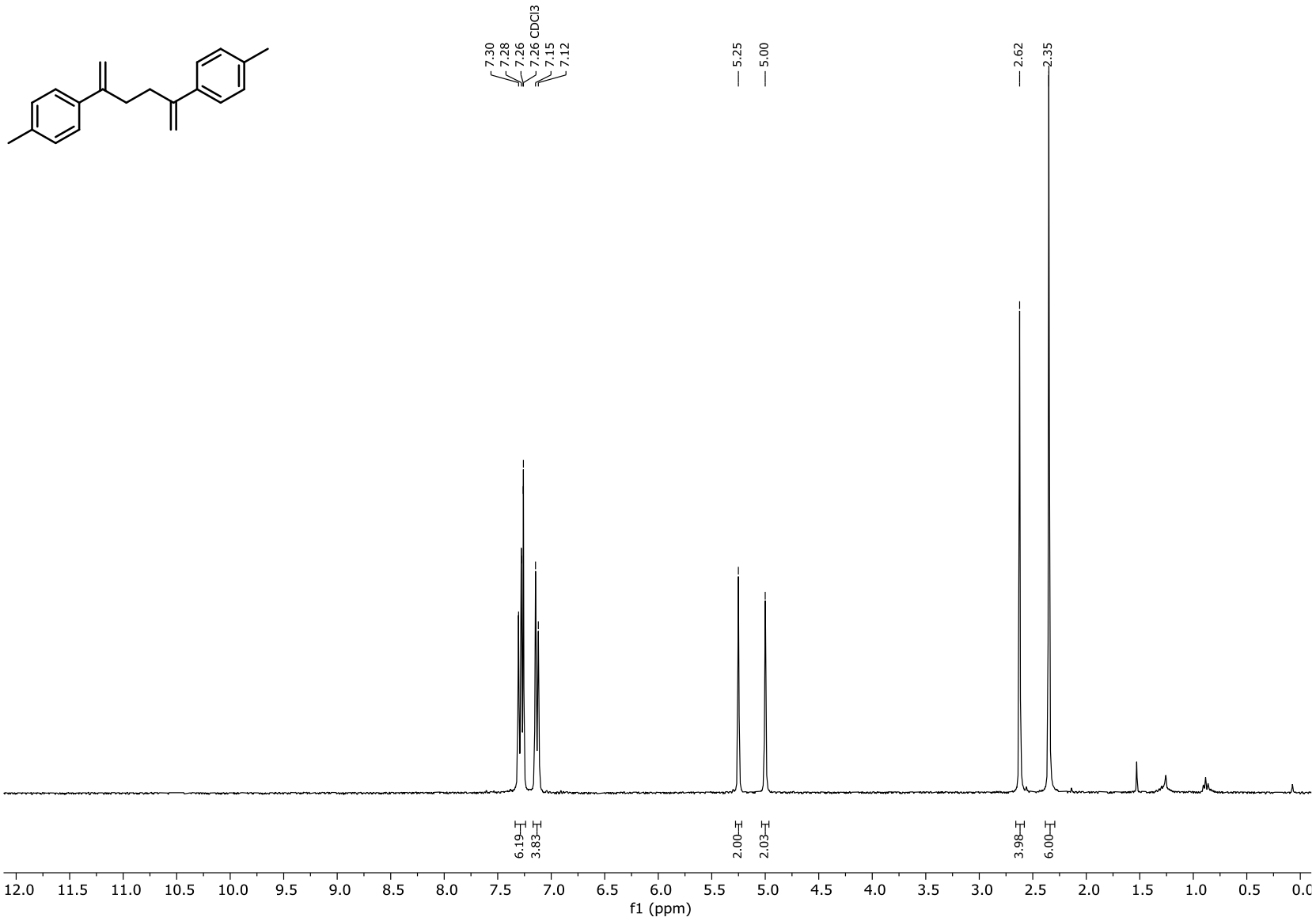
1,4-Di-*p*-tolylbutane-1,4-dione (S6): ^{1}H NMR (300 MHz, $CDCl_3$)



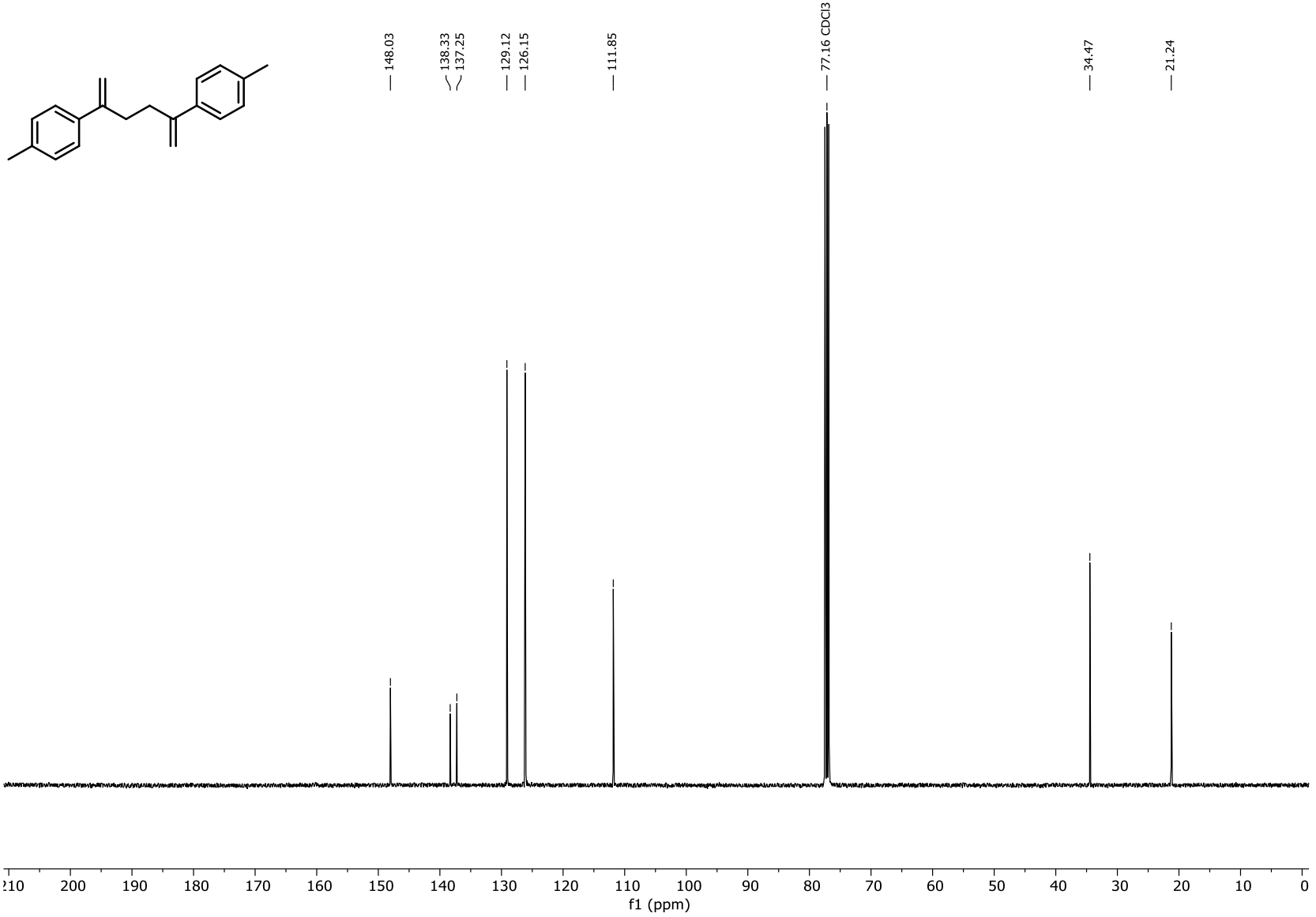
1,4-Di-*p*-tolylbutane-1,4-dione (S6): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



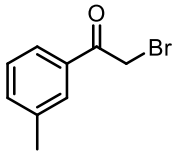
4,4'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1i): ^{1}H NMR (300 MHz, $CDCl_3$)



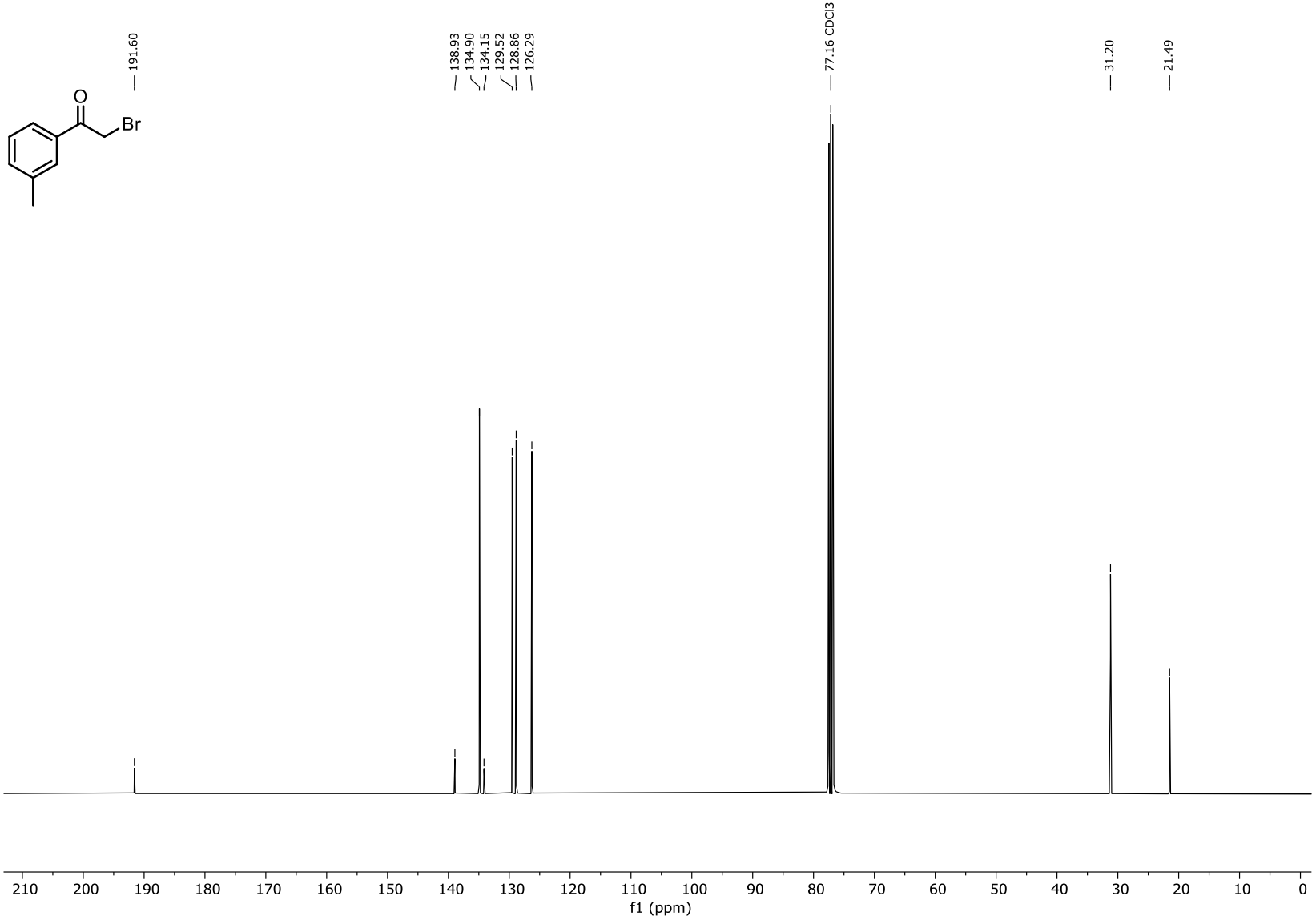
4,4'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1i): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



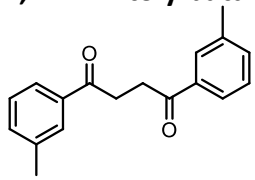
2-Bromo-1-(*m*-tolyl)ethan-1-one (S7): ^{1}H NMR (300 MHz, $CDCl_3$)



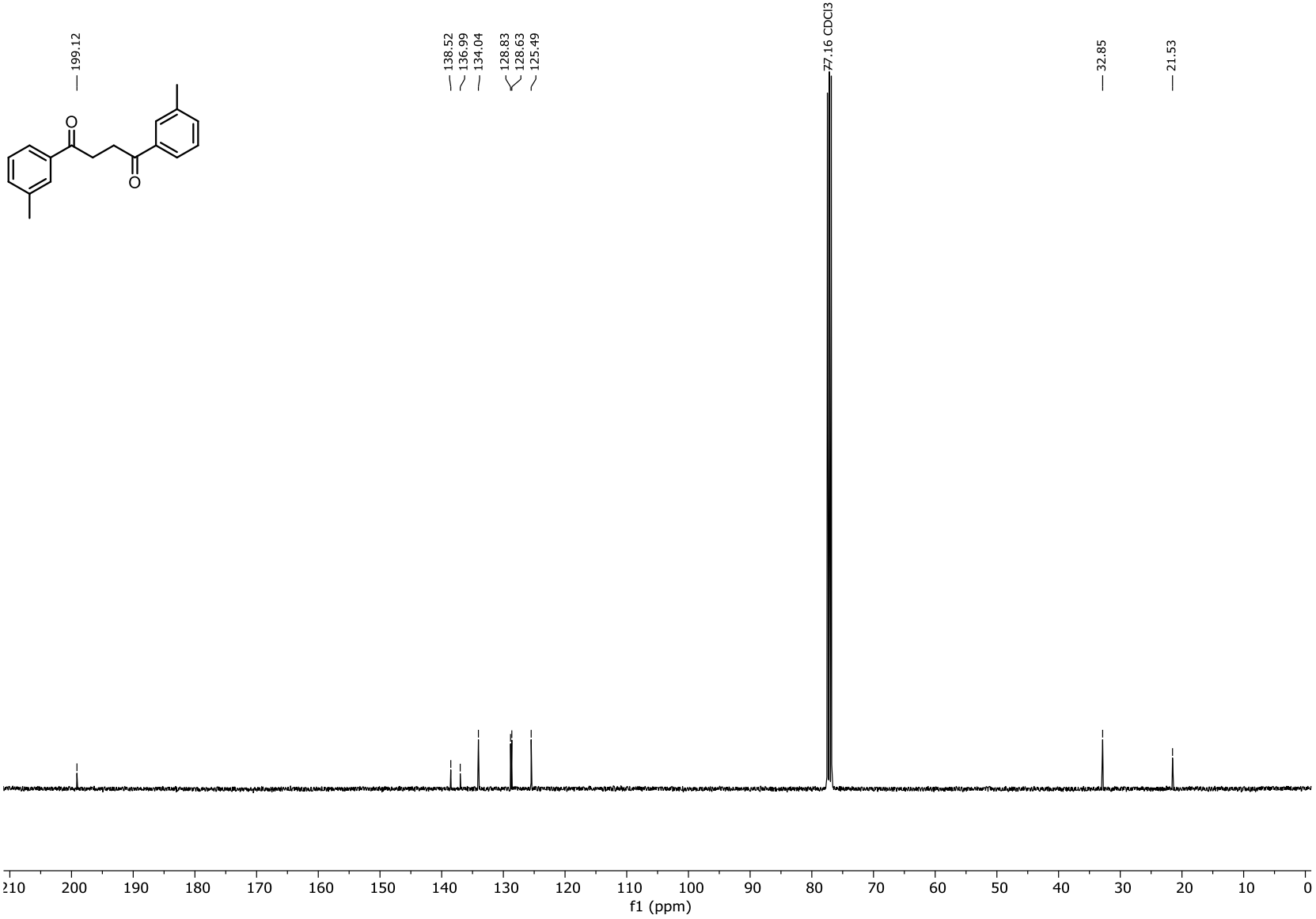
2-Bromo-1-(*m*-tolyl)ethan-1-one (S7): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



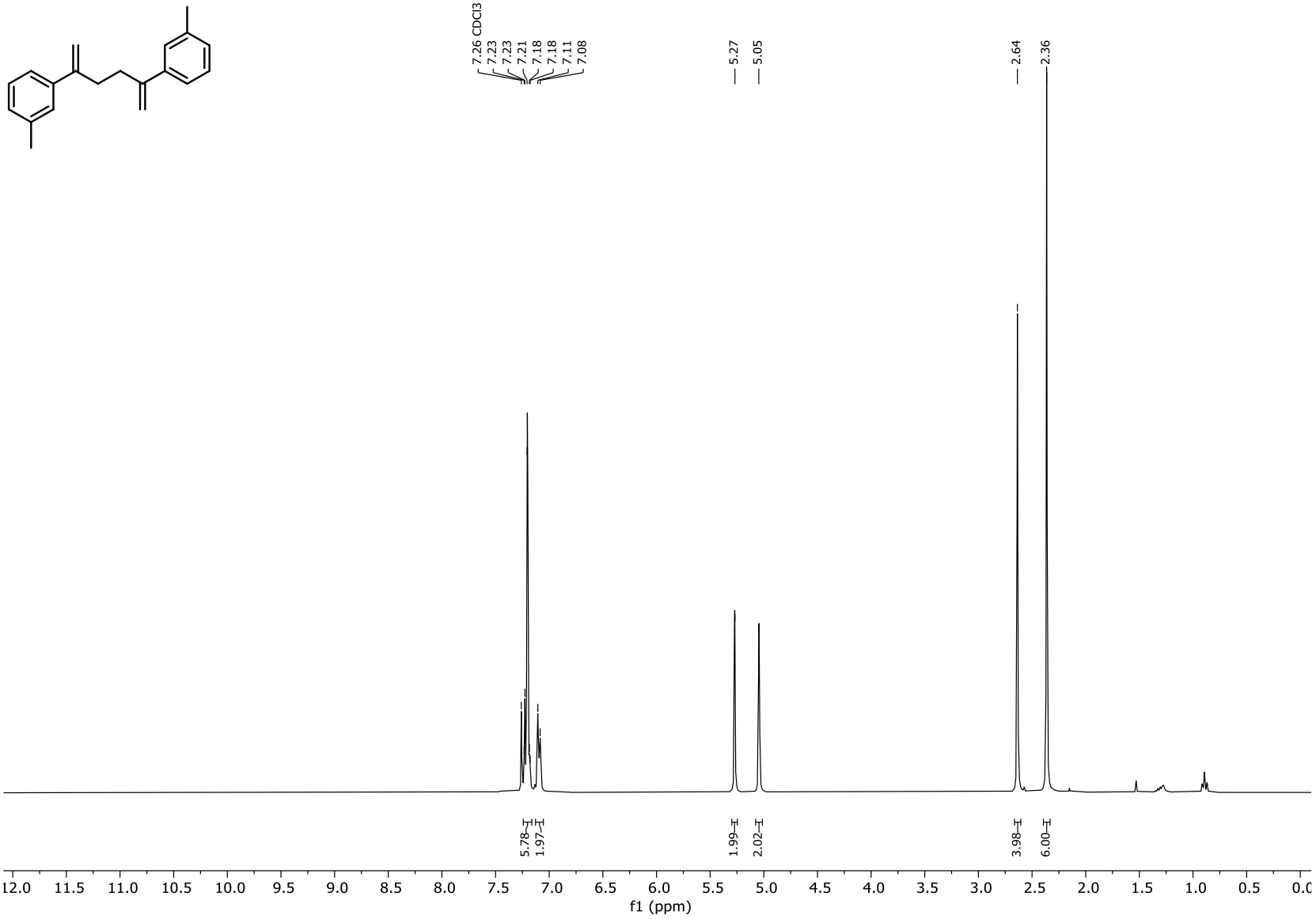
1,4-Di-*m*-tolylbutane-1,4-dione (S8): ^{1}H NMR (300 MHz, $CDCl_3$)



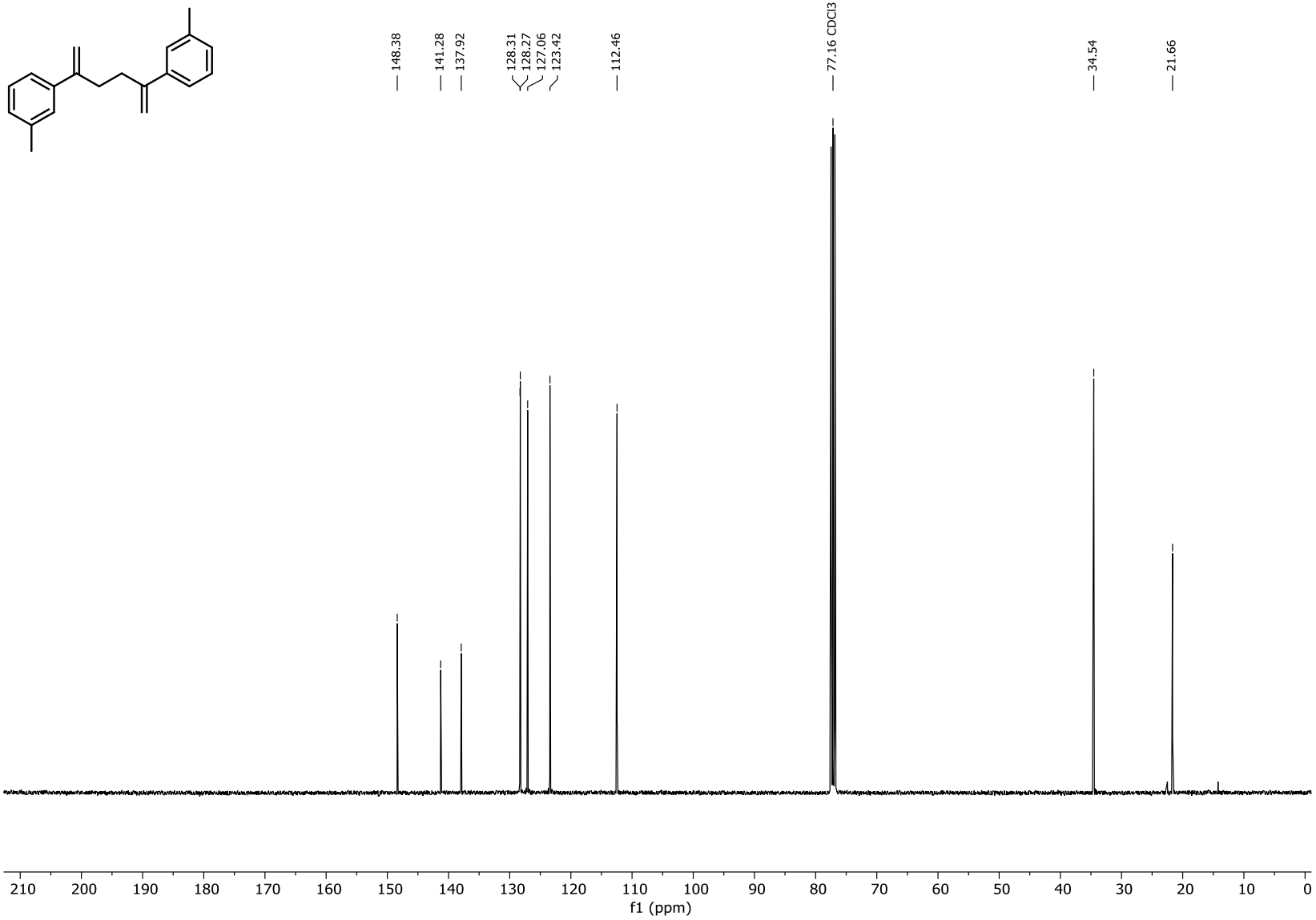
1,4-Di-*m*-tolylbutane-1,4-dione (S8): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



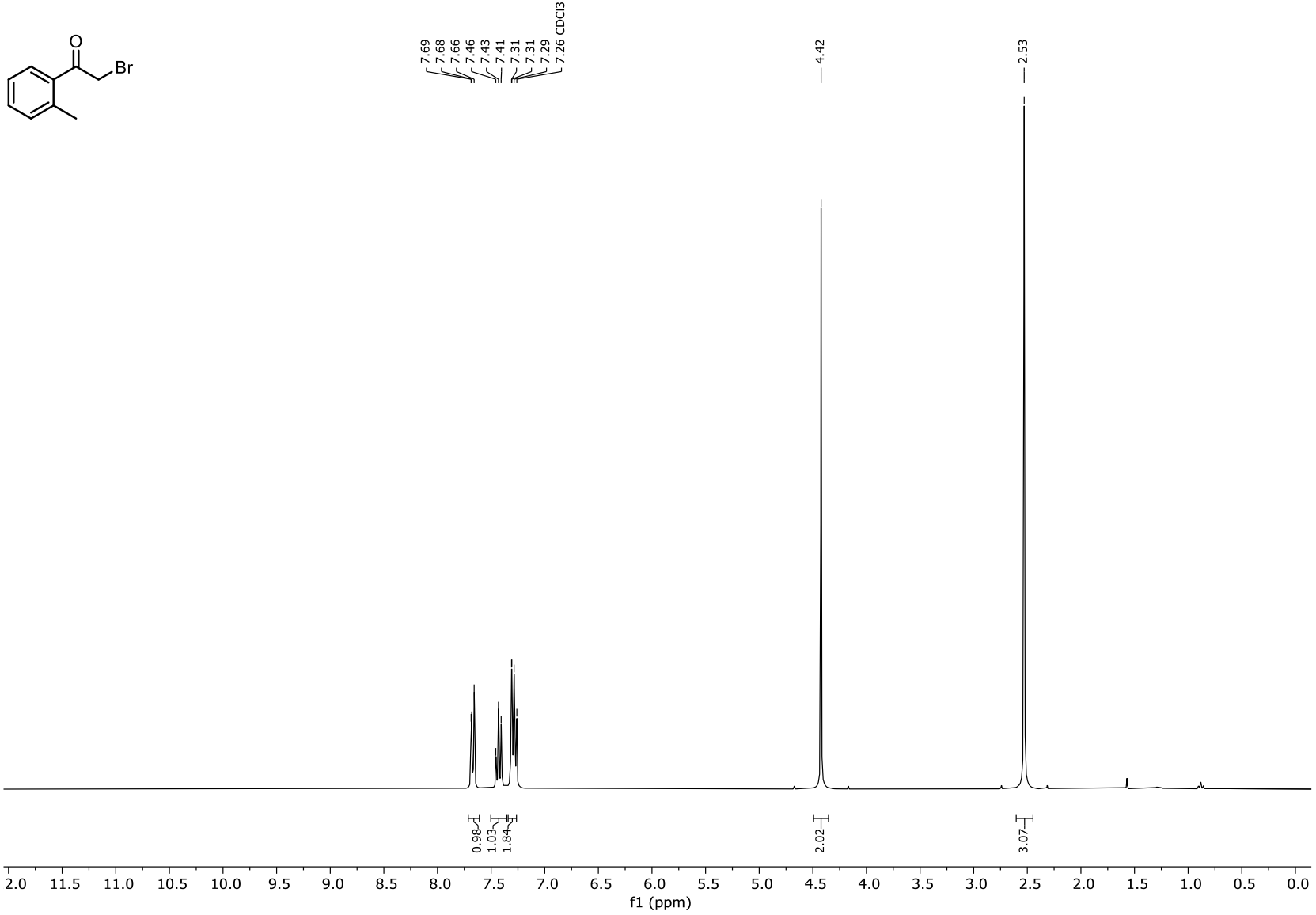
3,3'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1j): ^{1}H NMR (300 MHz, $CDCl_3$)



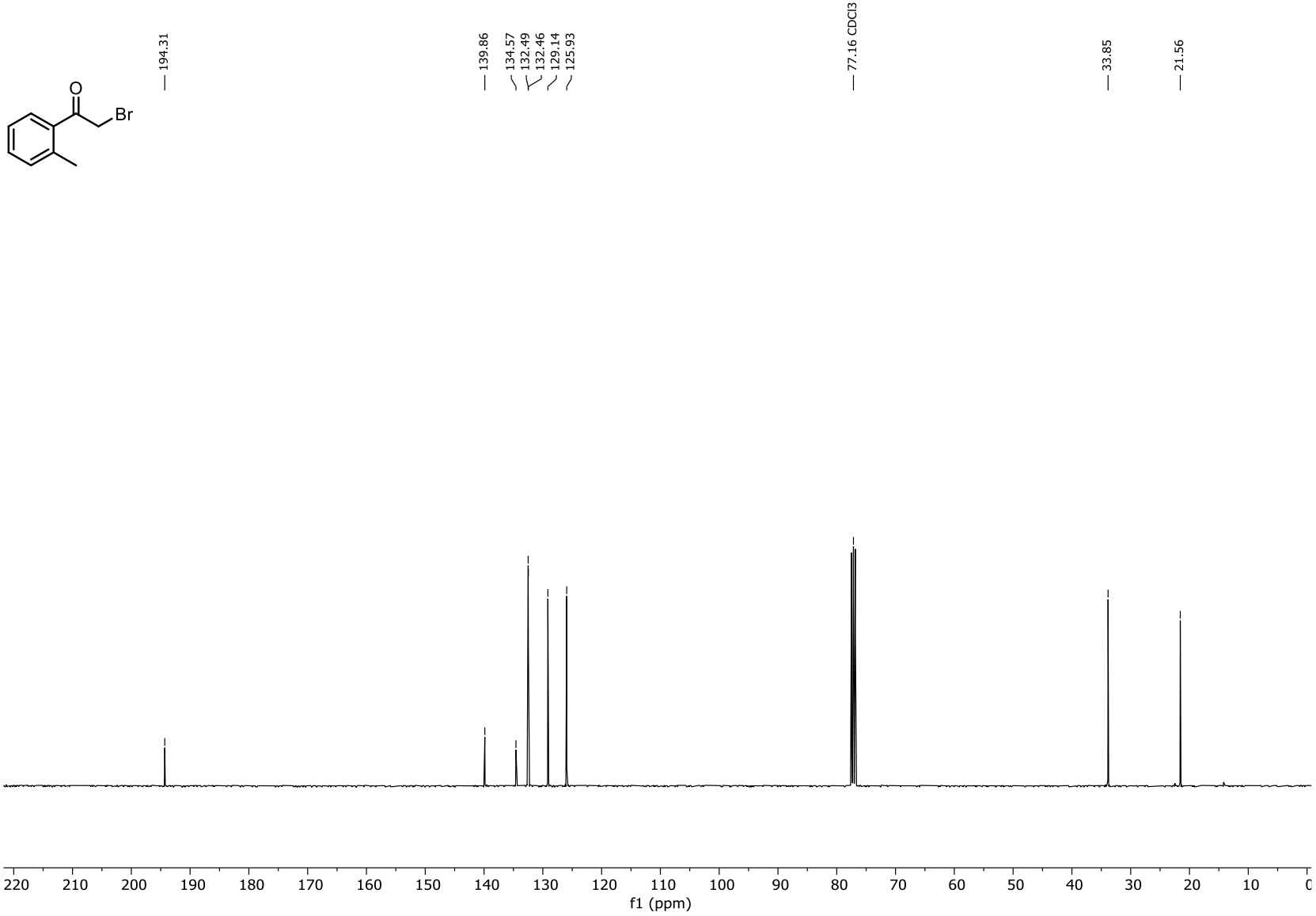
3,3'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1j): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



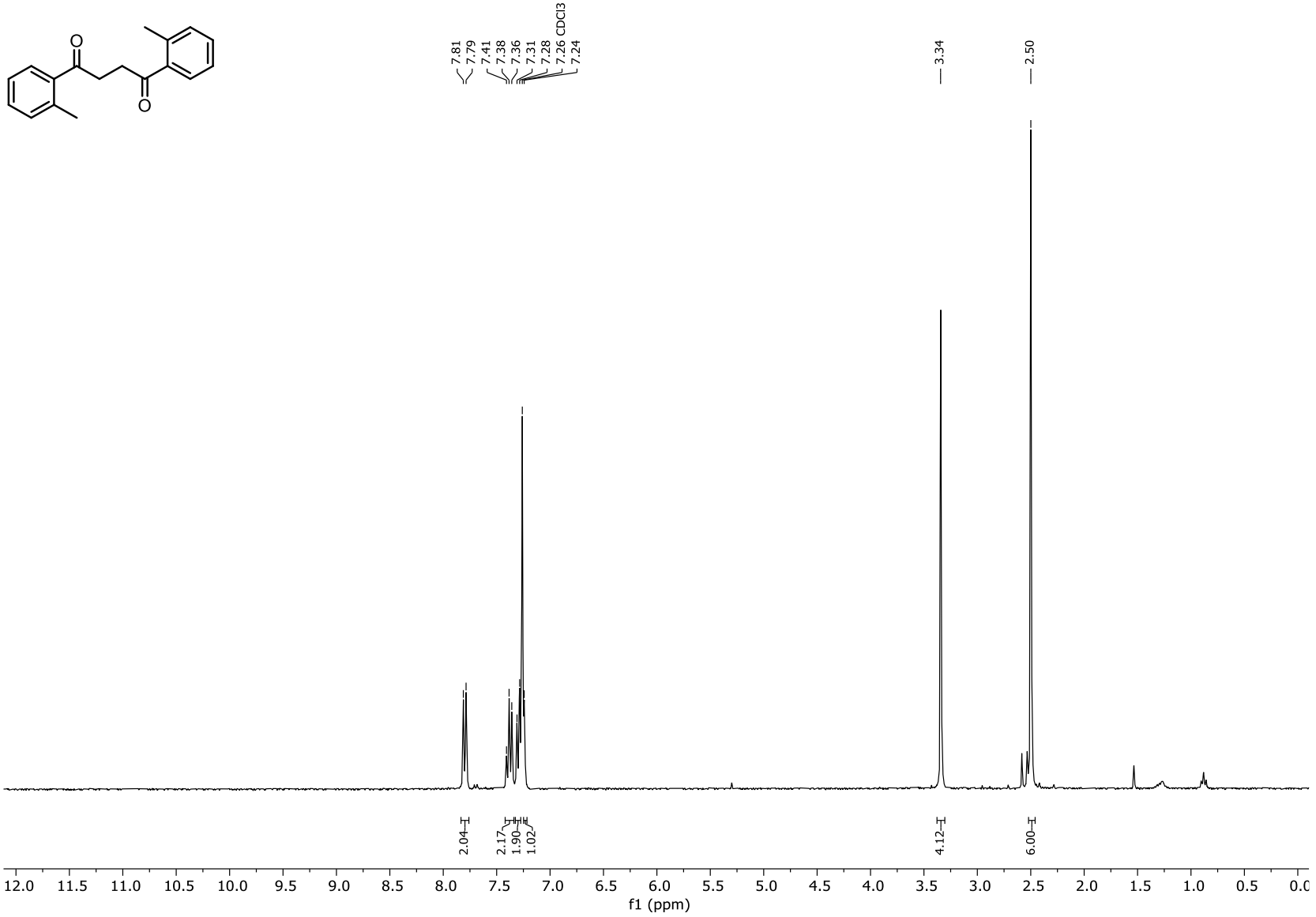
2-Bromo-1-(o-tolyl)ethan-1-one (S9): ^{1}H NMR (300 MHz, $CDCl_3$)



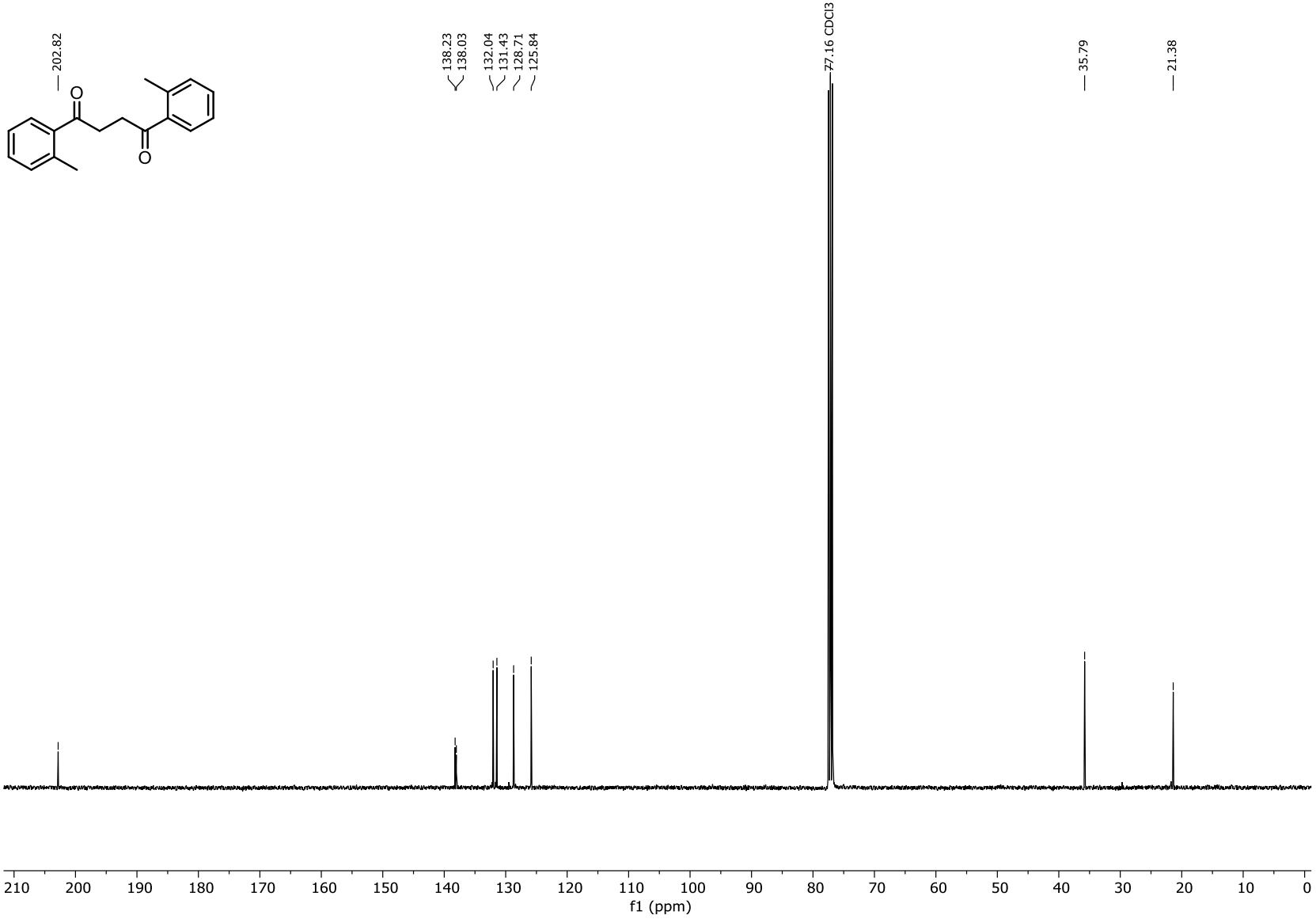
2-Bromo-1-(*o*-tolyl)ethan-1-one (S9): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



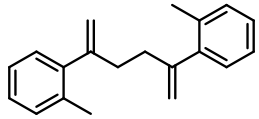
1,4-Di-o-tolylbutane-1,4-dione (S10): ^{1}H NMR (300 MHz, $CDCl_3$)



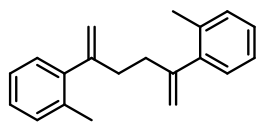
1,4-Di-*o*-tolylbutane-1,4-dione (S10): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



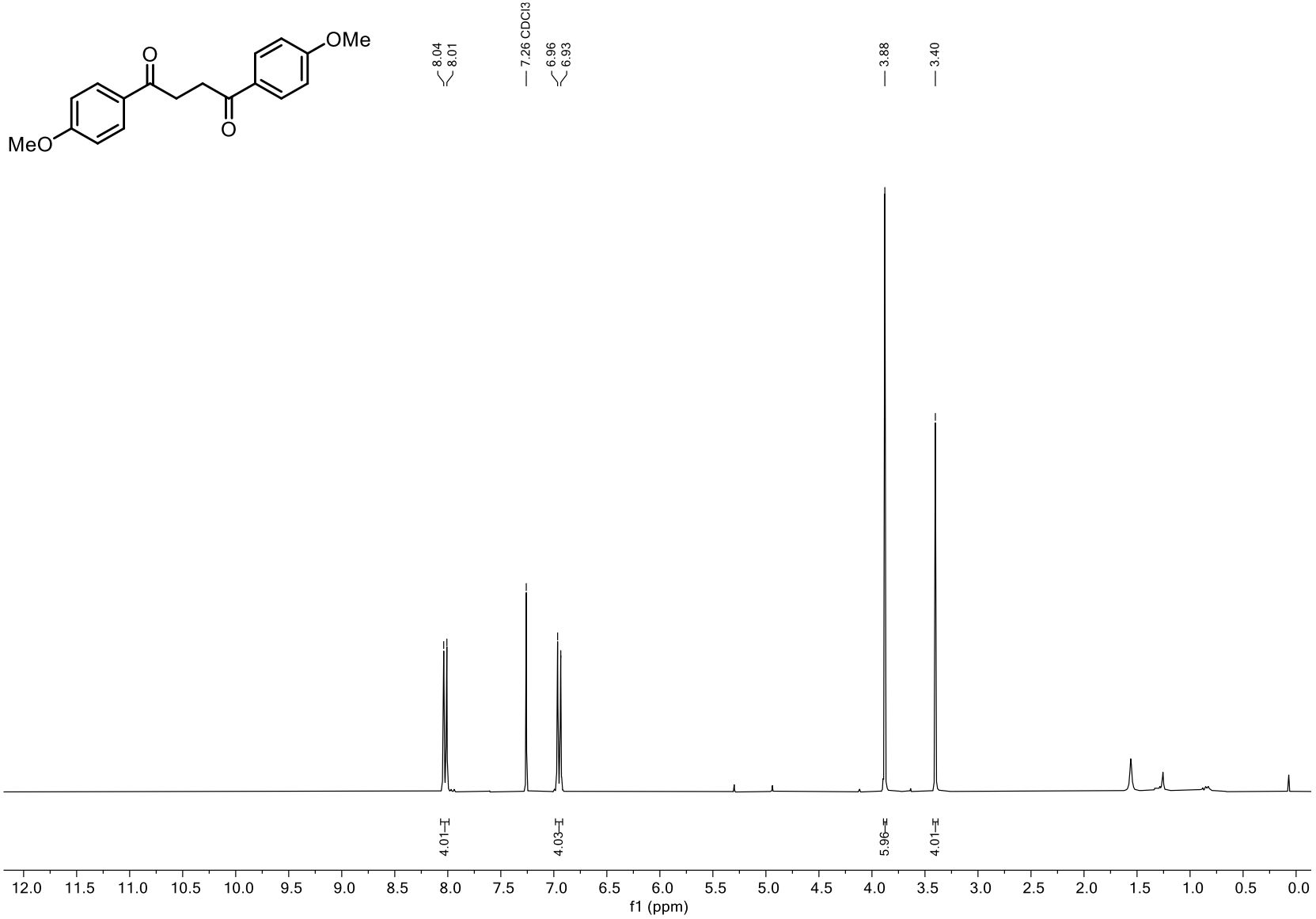
2,2'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1k): ^{1}H NMR (300 MHz, $CDCl_3$)



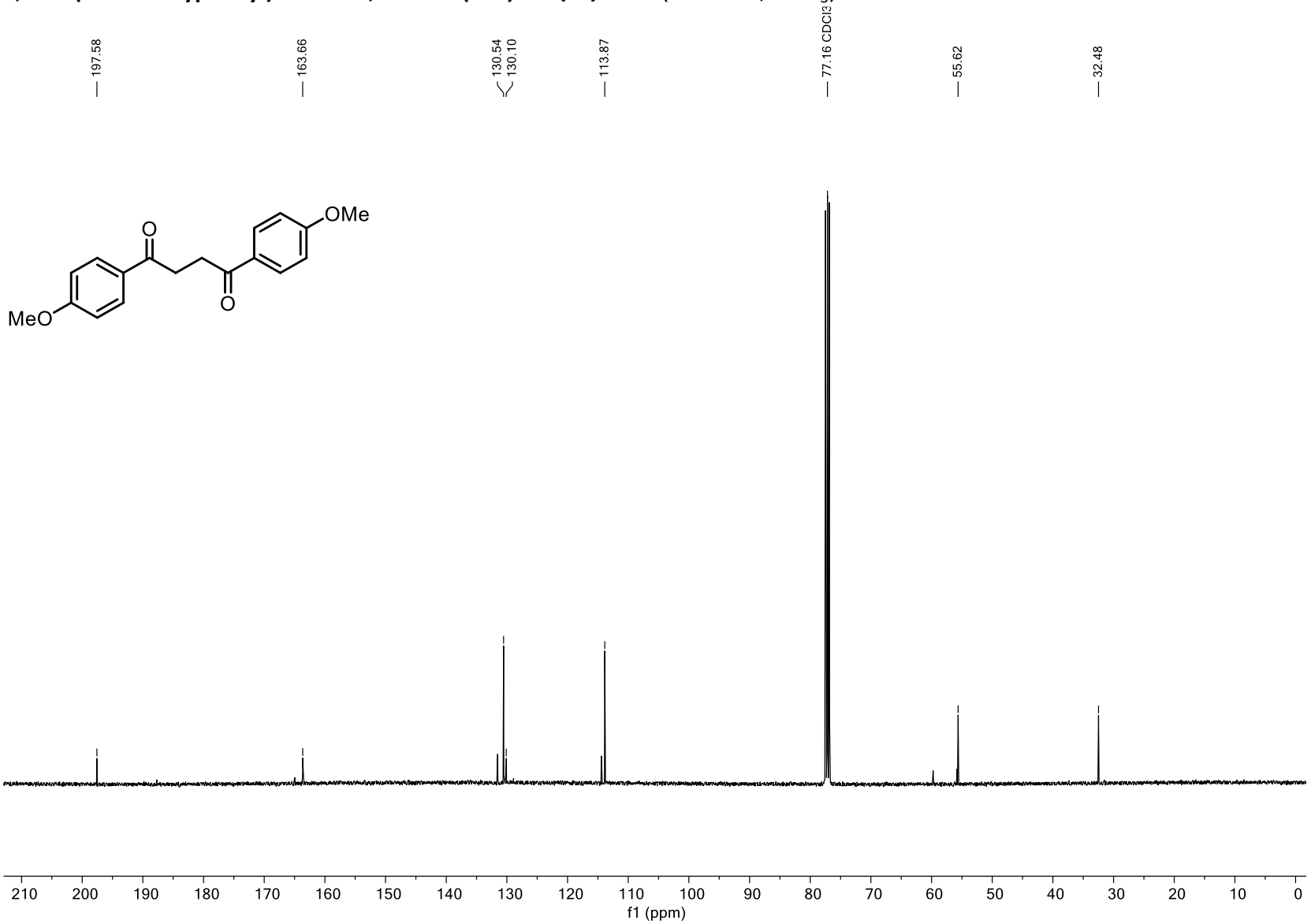
2,2'-(Hexa-1,5-diene-2,5-diyl)bis(methylbenzene) (1k): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



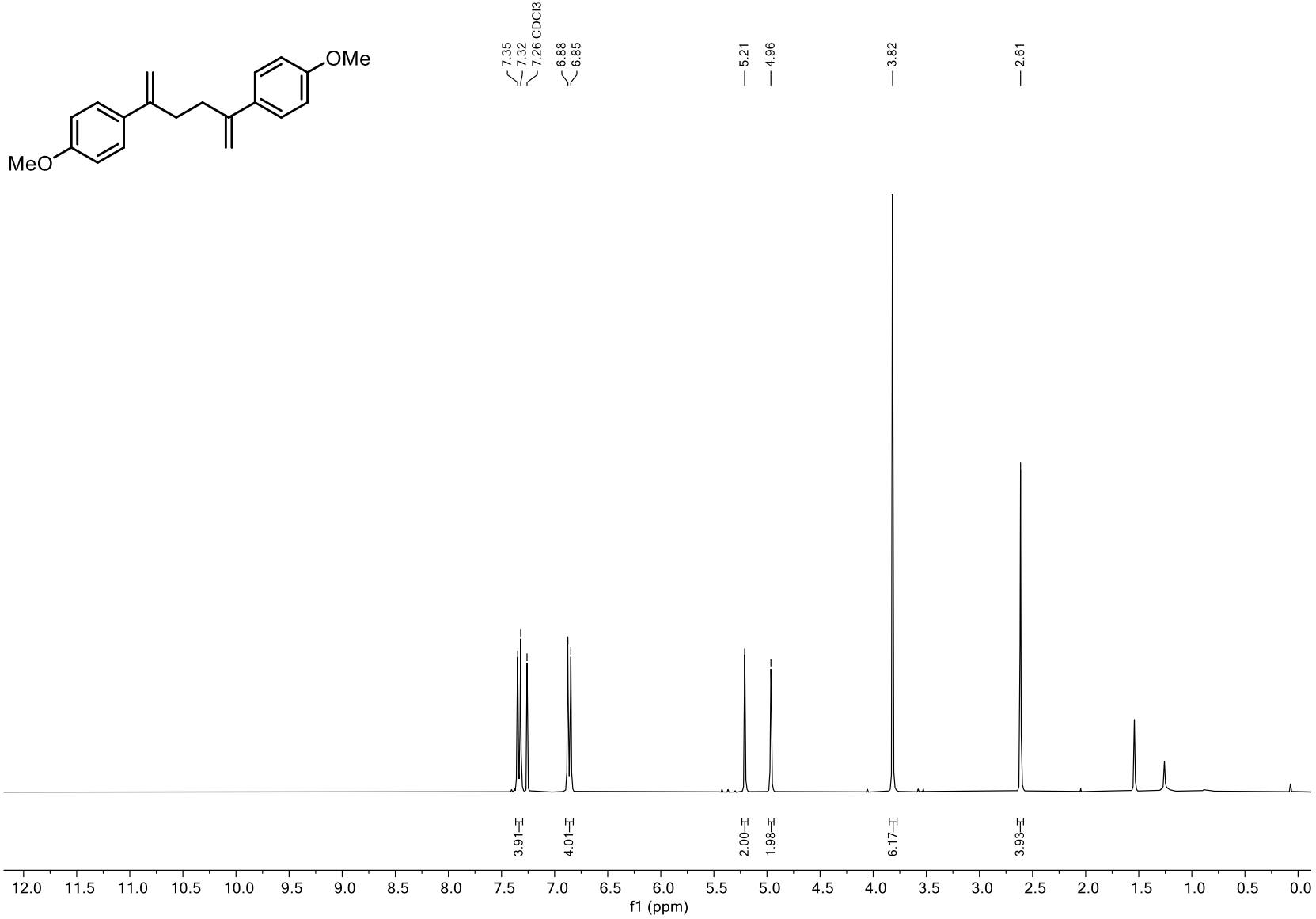
1,4-Bis(4-methoxyphenyl)butane-1,4-dione (S11): ^{1}H NMR (300 MHz, $CDCl_3$)



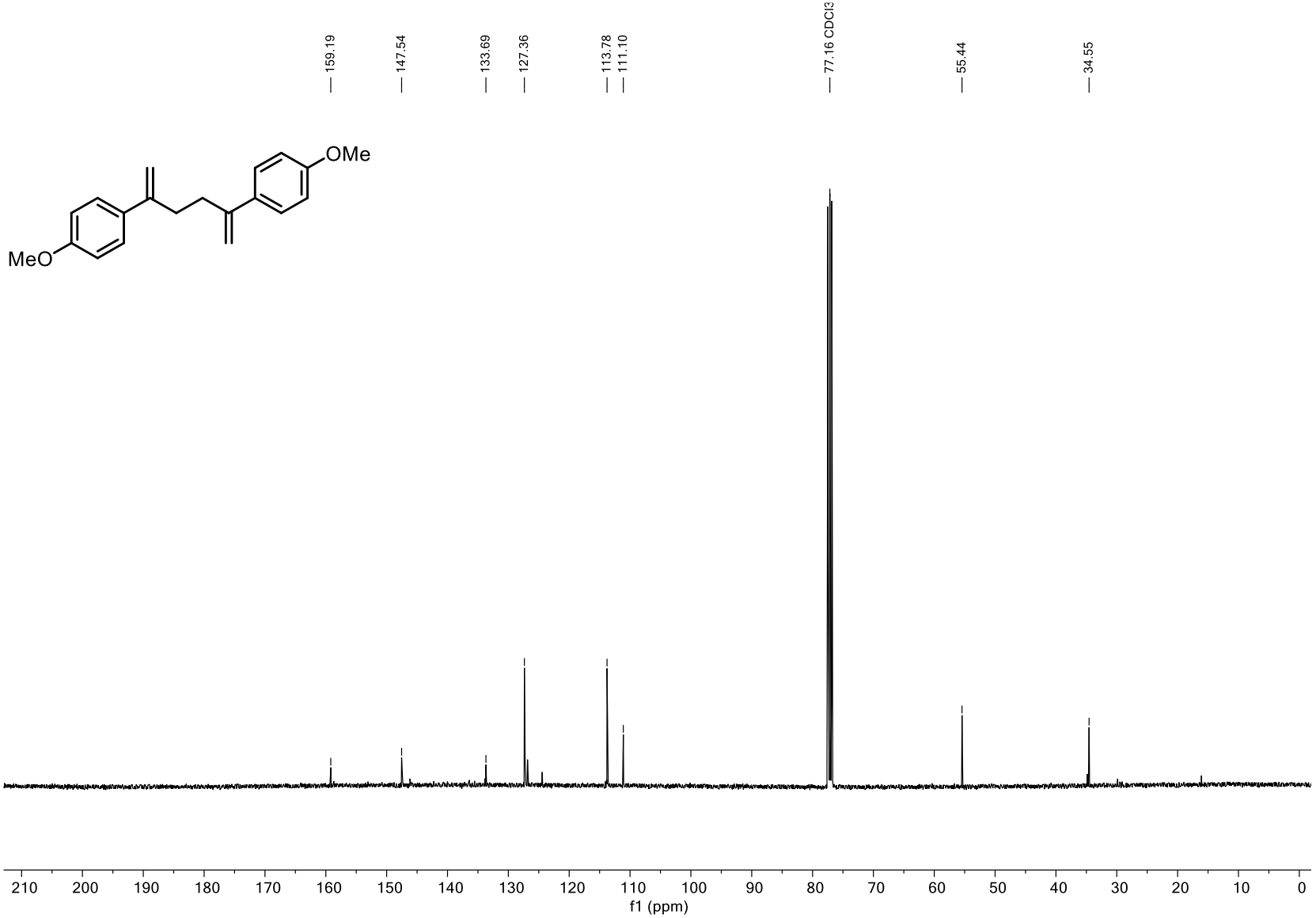
1,4-Bis(4-methoxyphenyl)butane-1,4-dione (S11): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



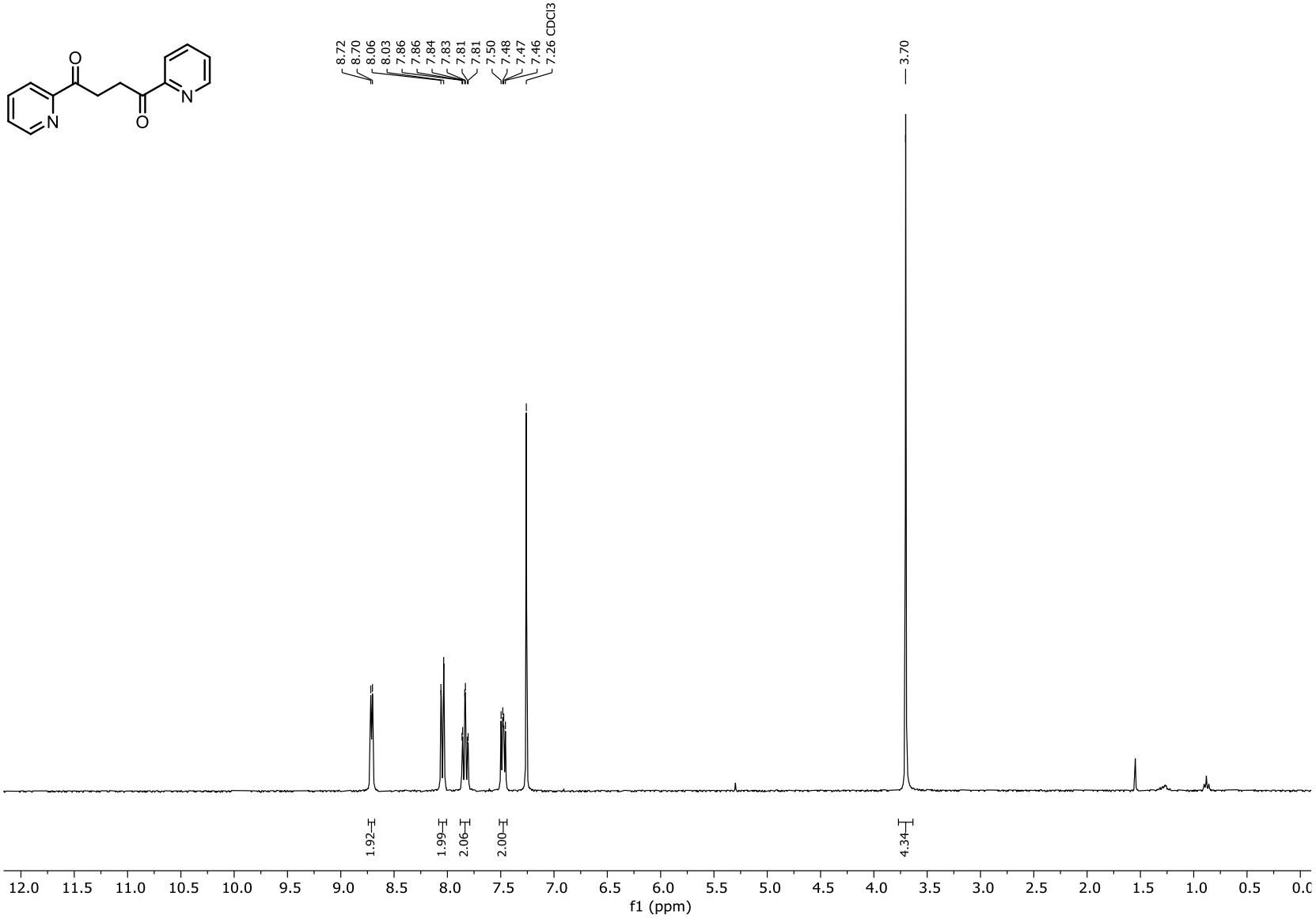
4,4'-(Hexa-1,5-diene-2,5-diyl)bis(methoxybenzene) (1l): ^{1}H NMR (300 MHz, $CDCl_3$)



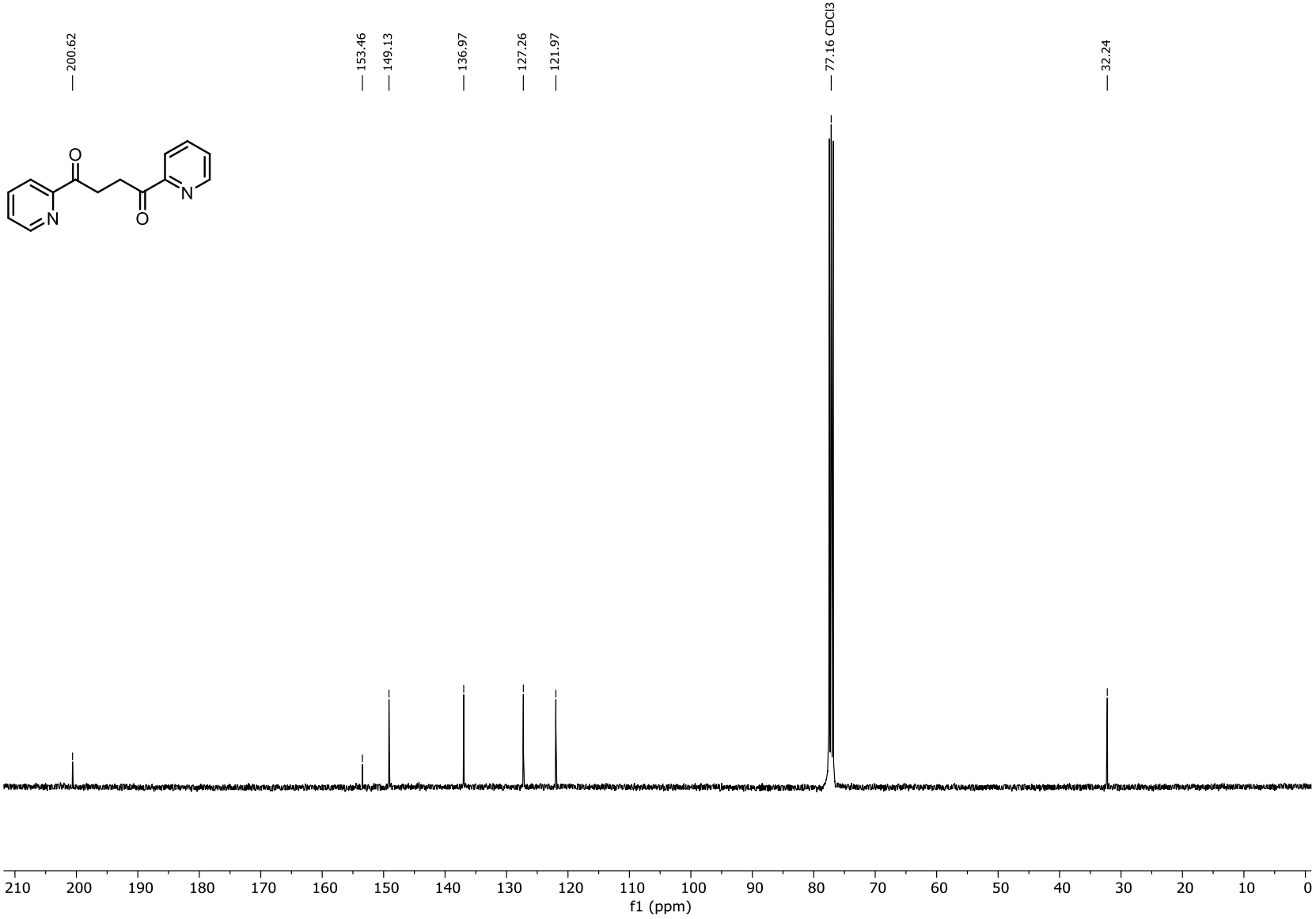
4,4'-(Hexa-1,5-diene-2,5-diyl)bis(methoxybenzene) (1l): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



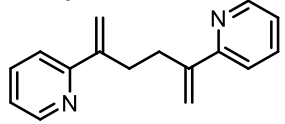
1,4-Di(pyridin-2-yl)butane-1,4-dione (S12): ^{1}H NMR (300 MHz, $CDCl_3$)



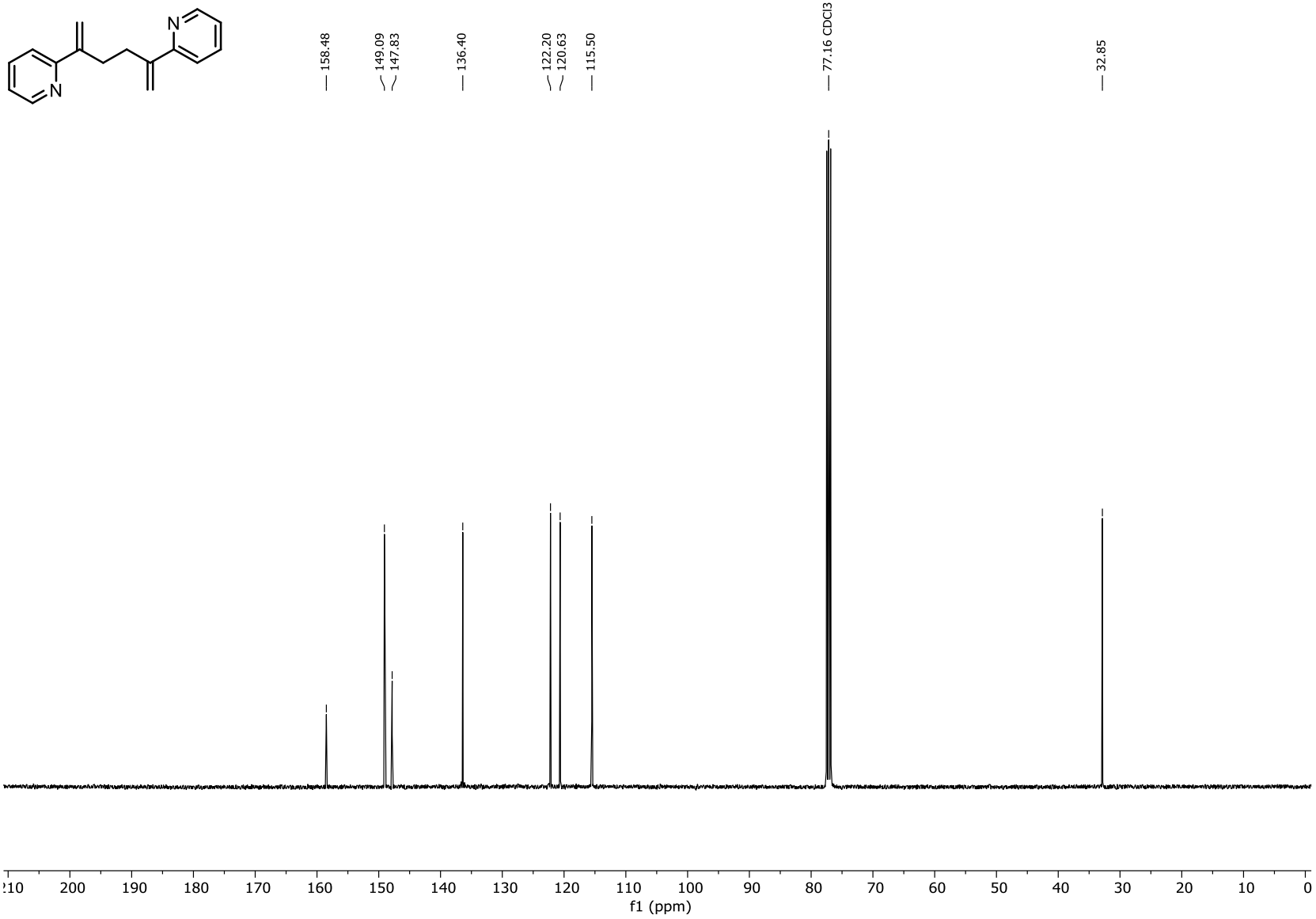
1,4-Di(pyridin-2-yl)butane-1,4-dione (S12): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



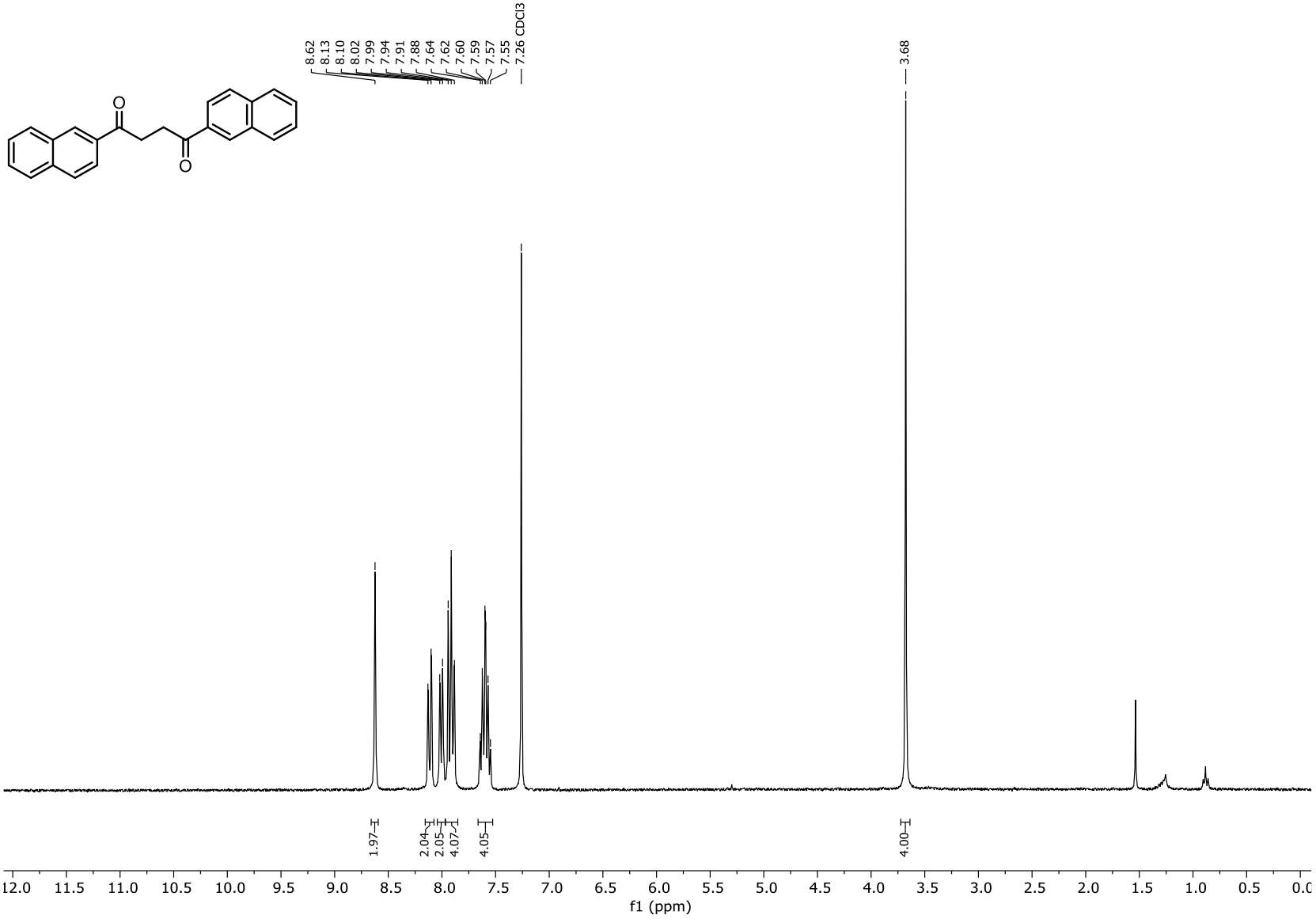
2,2'-(Hexa-1,5-diene-2,5-diyl)dipyridine (1m): ^{1}H NMR (300 MHz, $CDCl_3$)



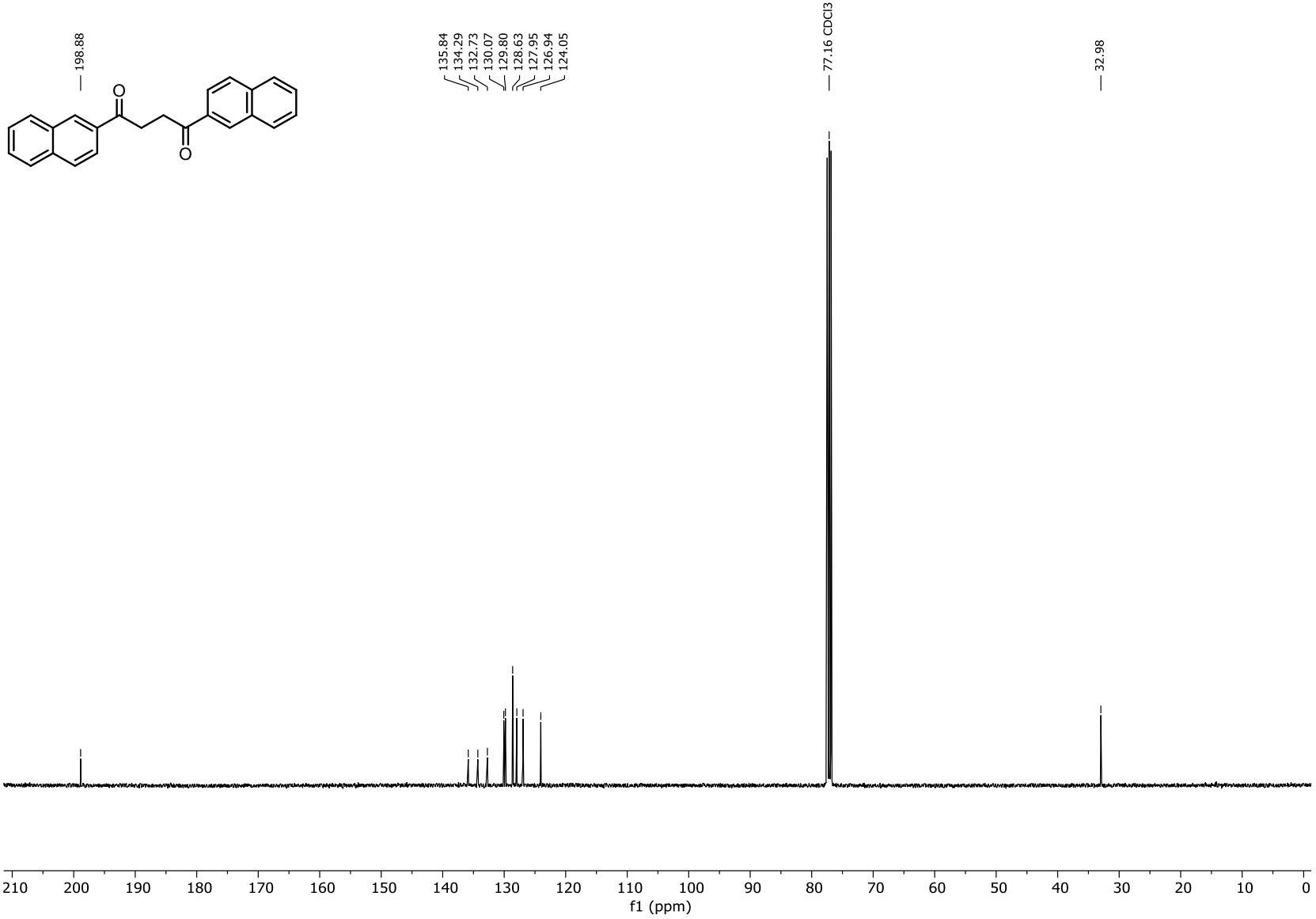
2,2'-(Hexa-1,5-diene-2,5-diyl)dipyridine (1m): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



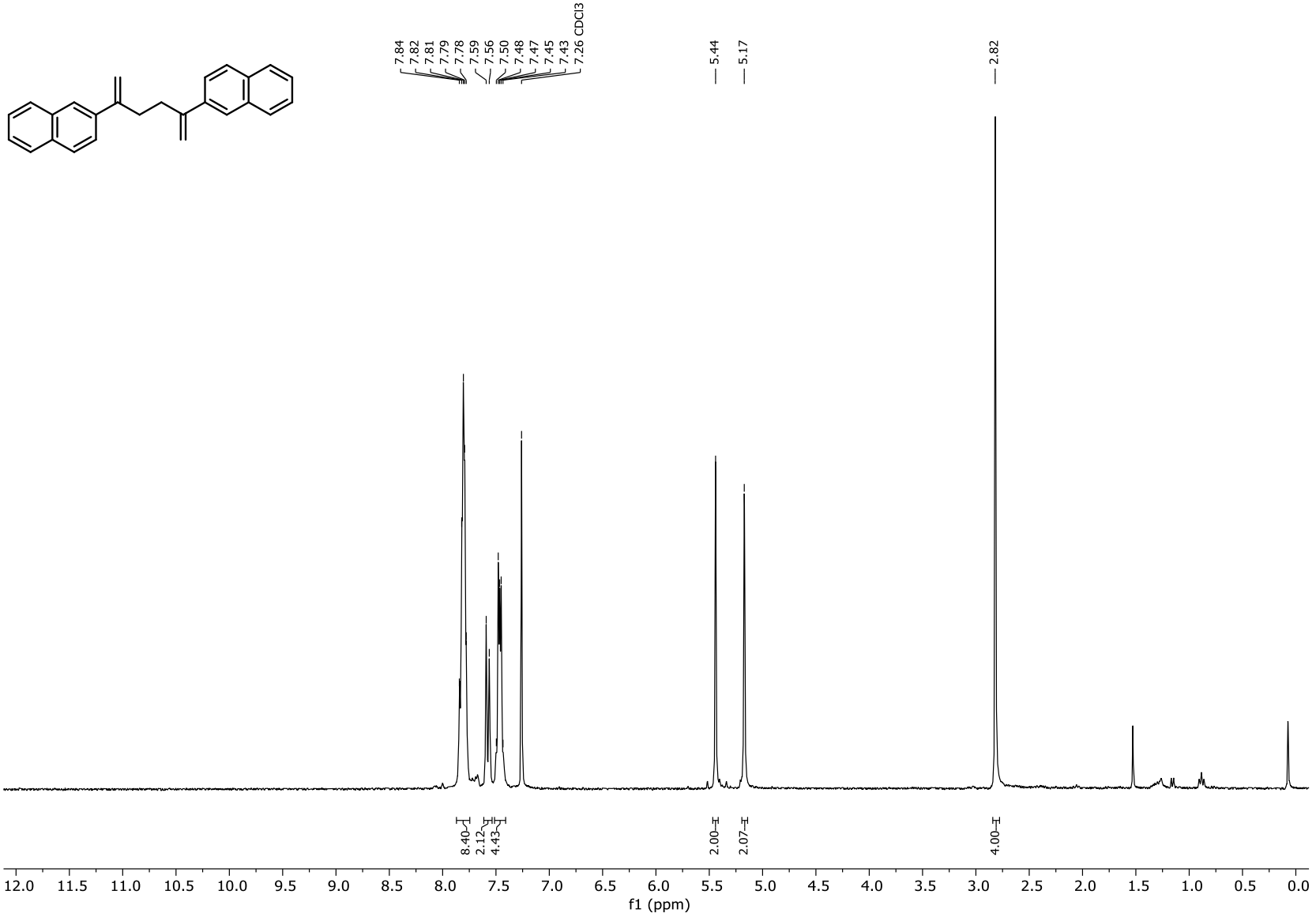
1,4-Di(naphthalen-2-yl)butane-1,4-dione (S13): ^{1}H NMR (300 MHz, $CDCl_3$)



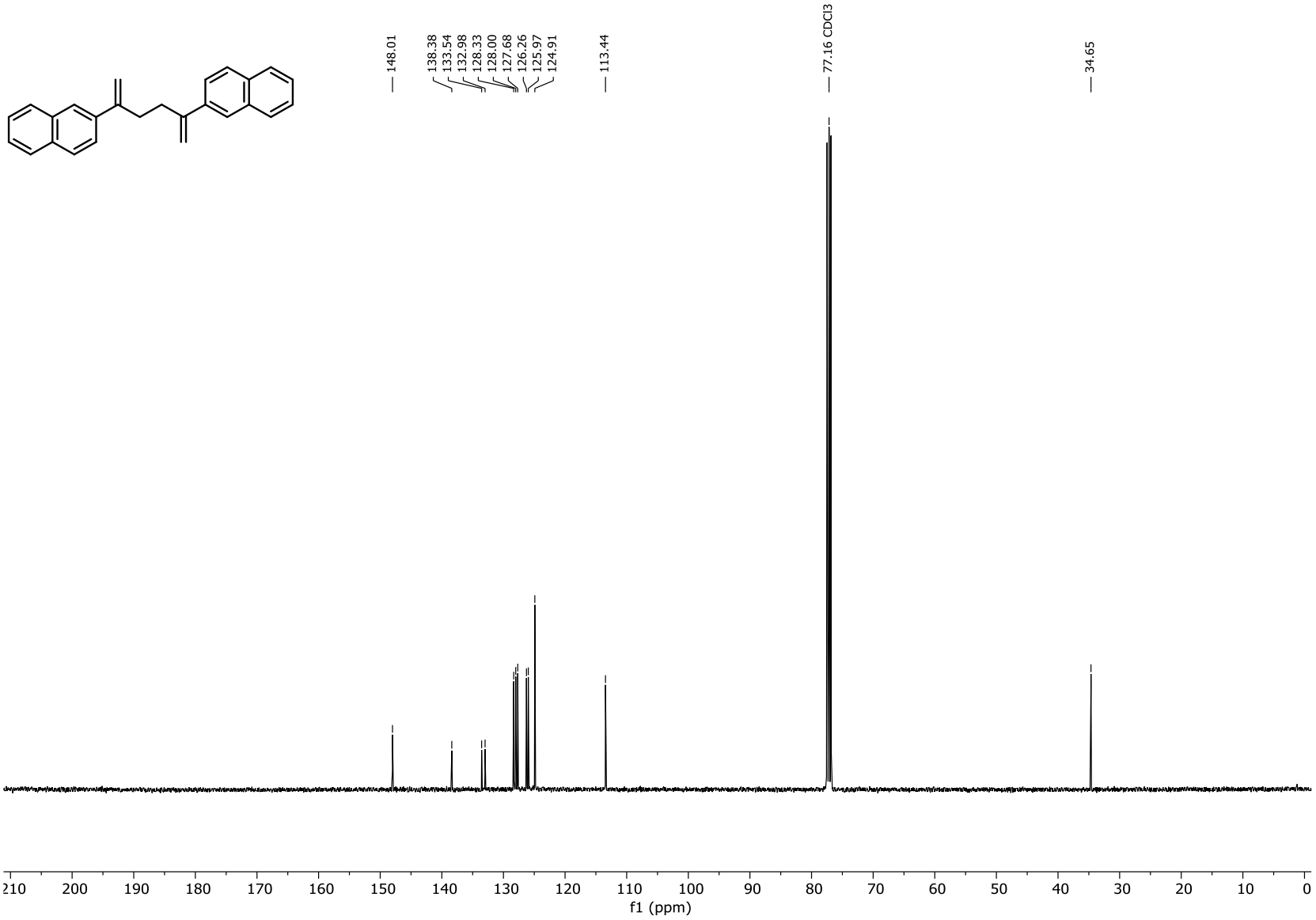
1,4-Di(naphthalen-2-yl)butane-1,4-dione (S13): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



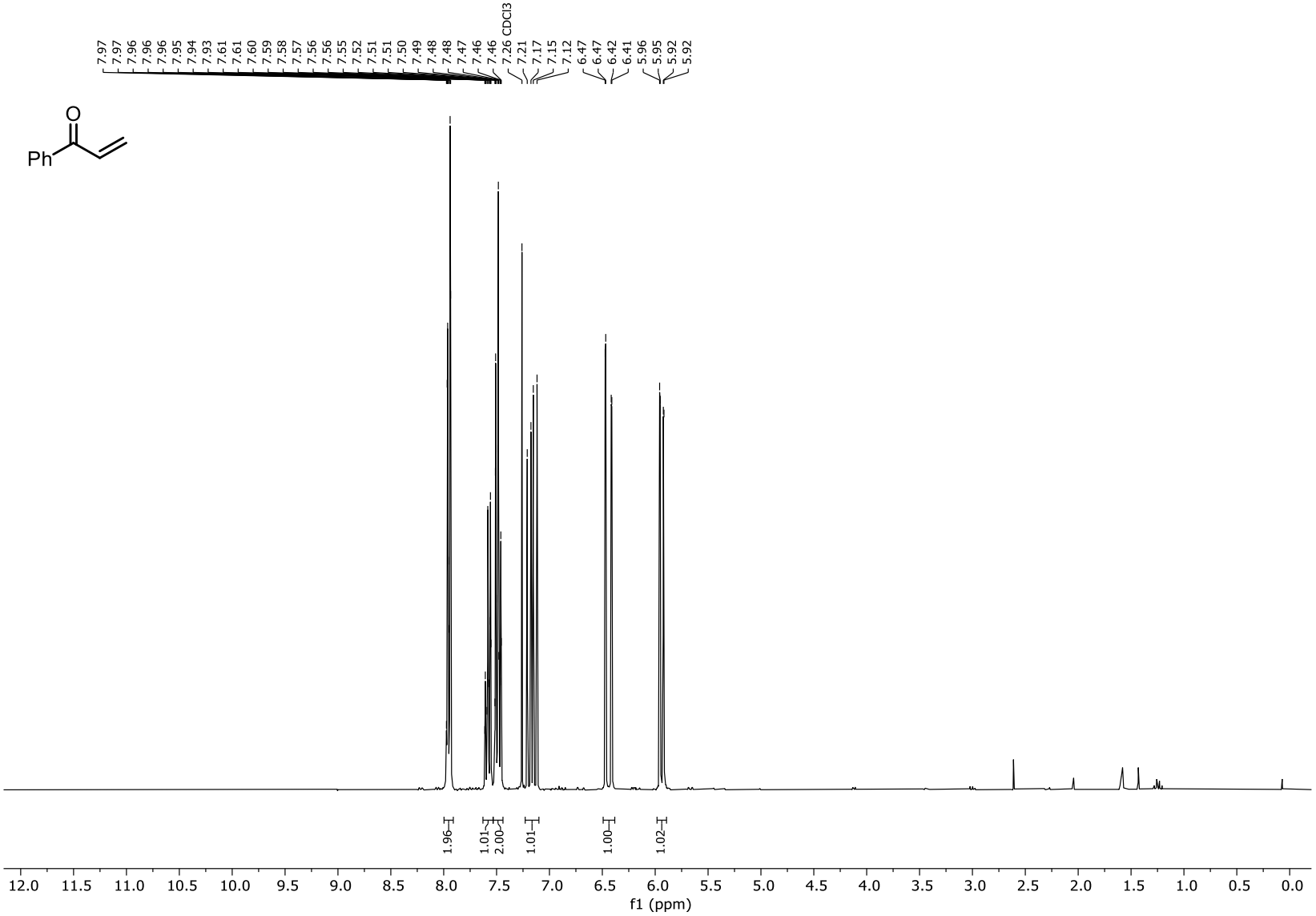
2,2'-(Hexa-1,5-diene-2,5-diyl)dinaphthalene (1n): ^{1}H NMR (300 MHz, $CDCl_3$)



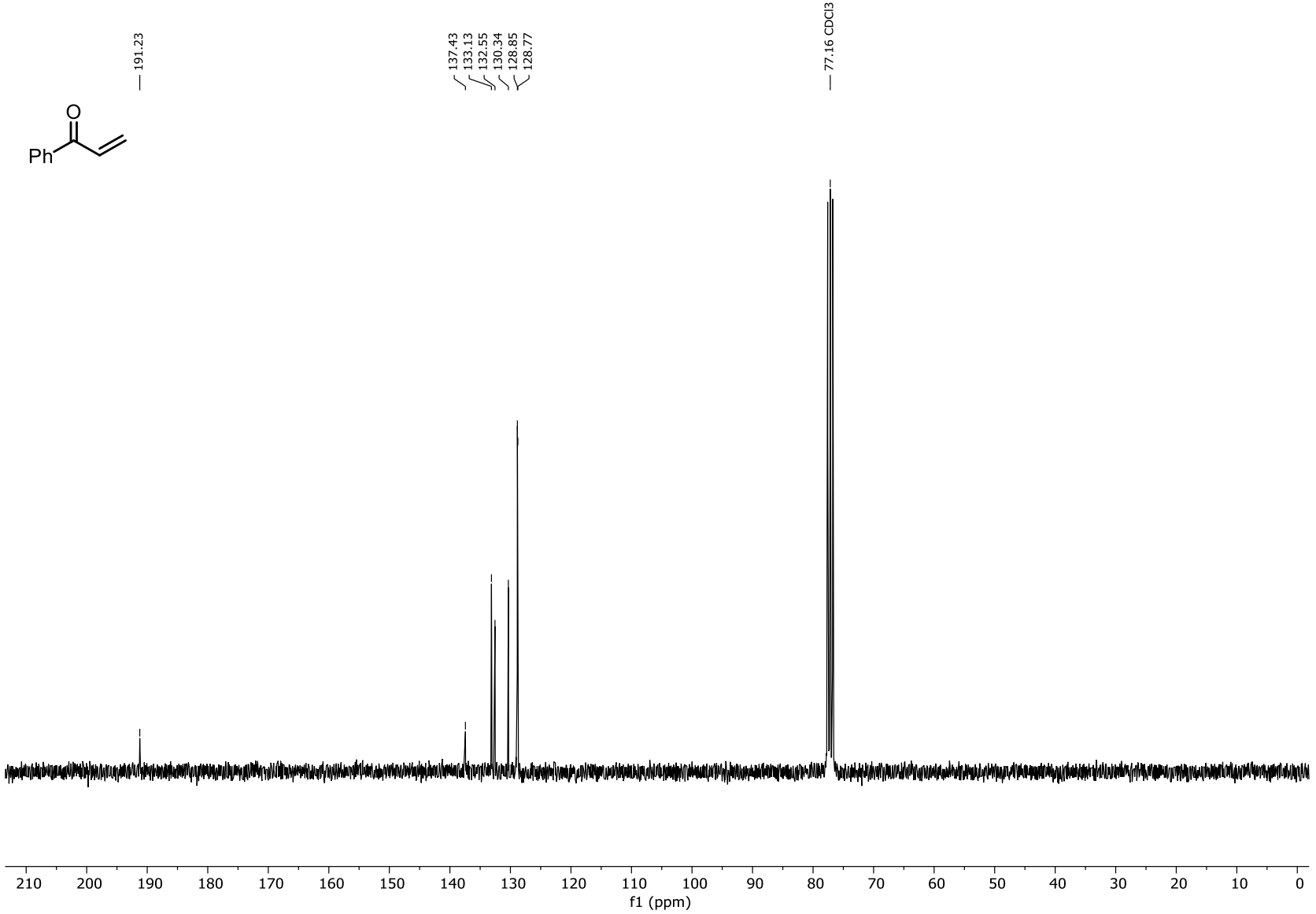
2,2'-(Hexa-1,5-diene-2,5-diyl)dinaphthalene (1n): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



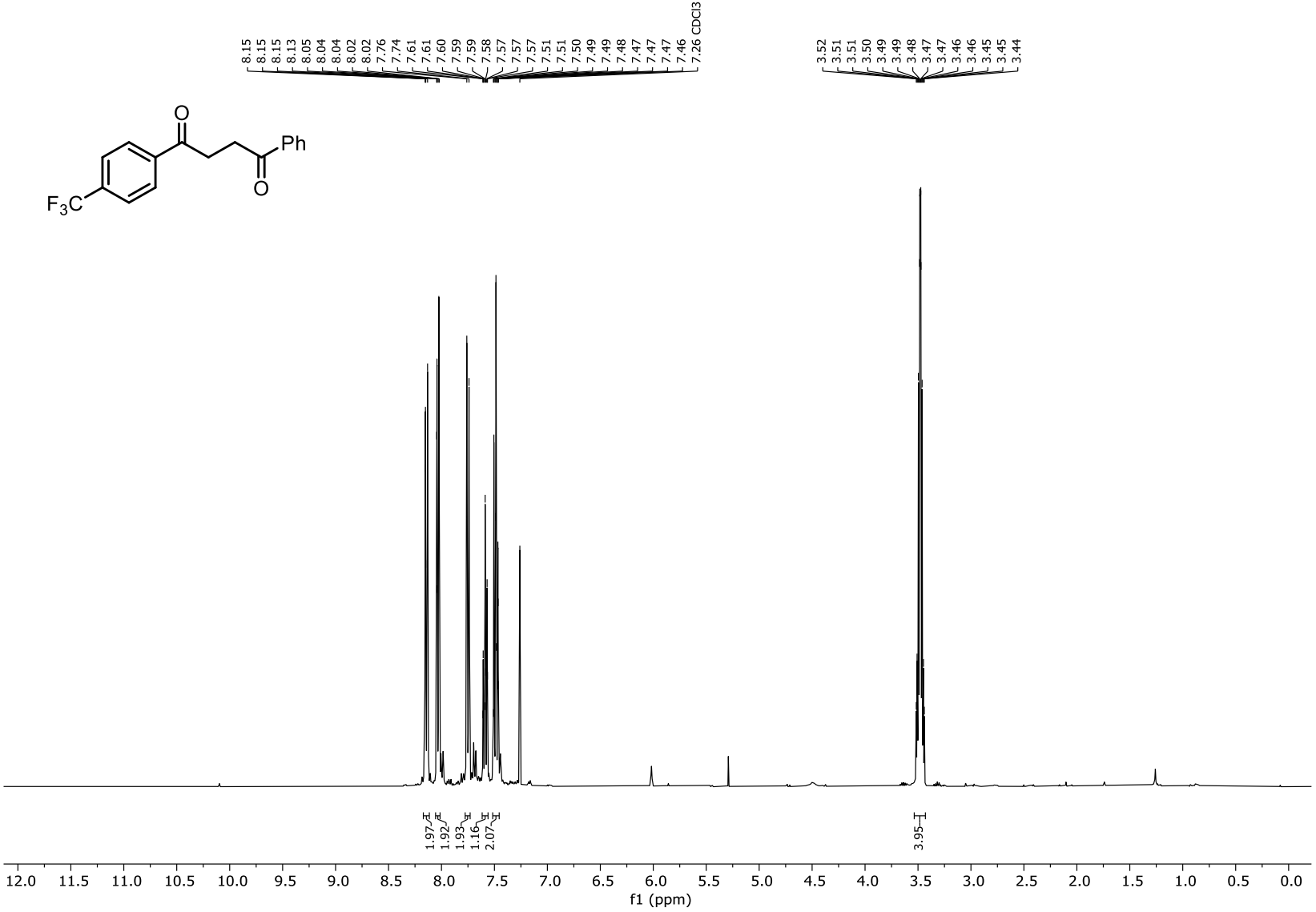
1-Phenylprop-2-en-1-one (S14): ^{1}H NMR (300 MHz, $CDCl_3$)



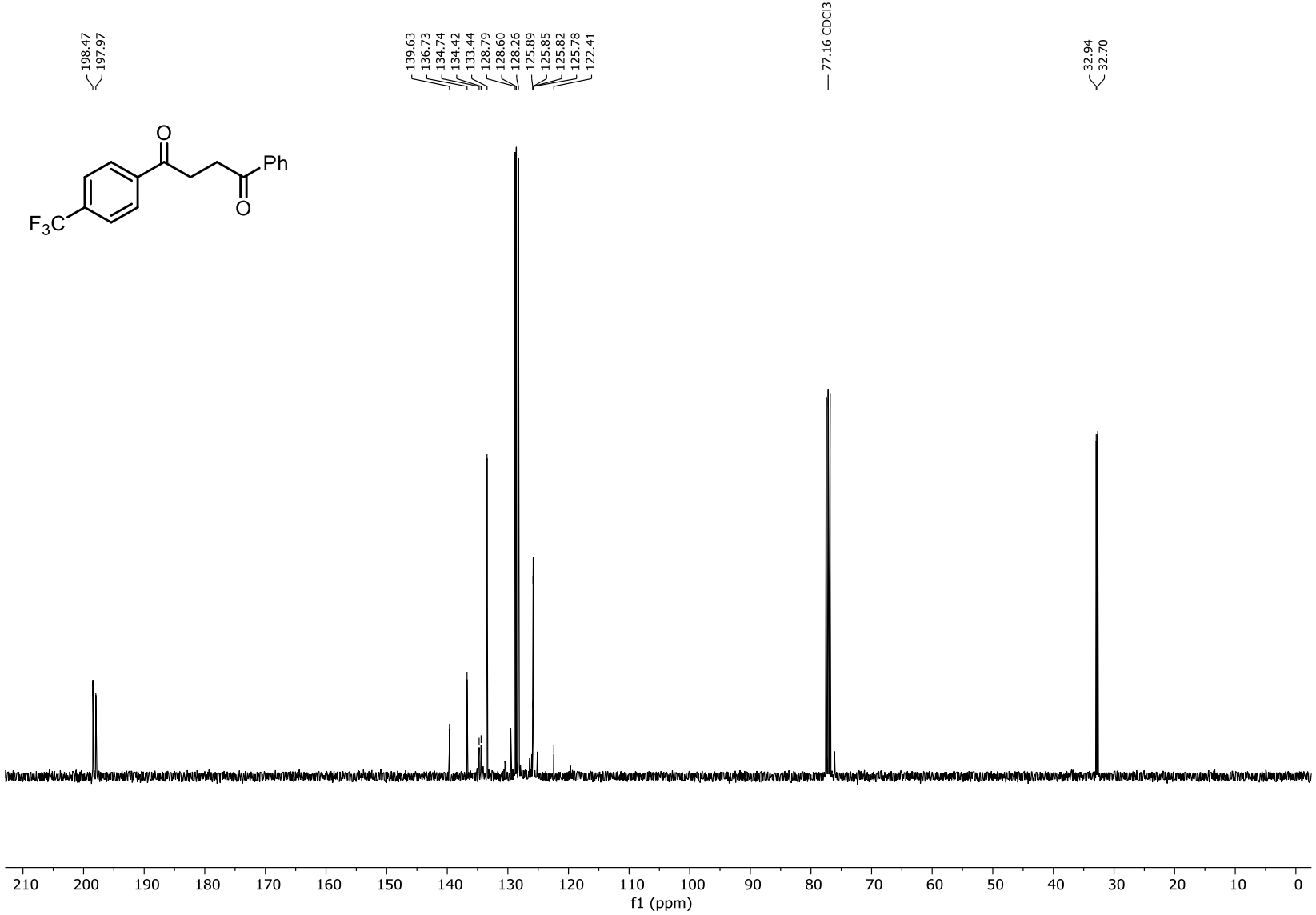
1-Phenylprop-2-en-1-one (S14): $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



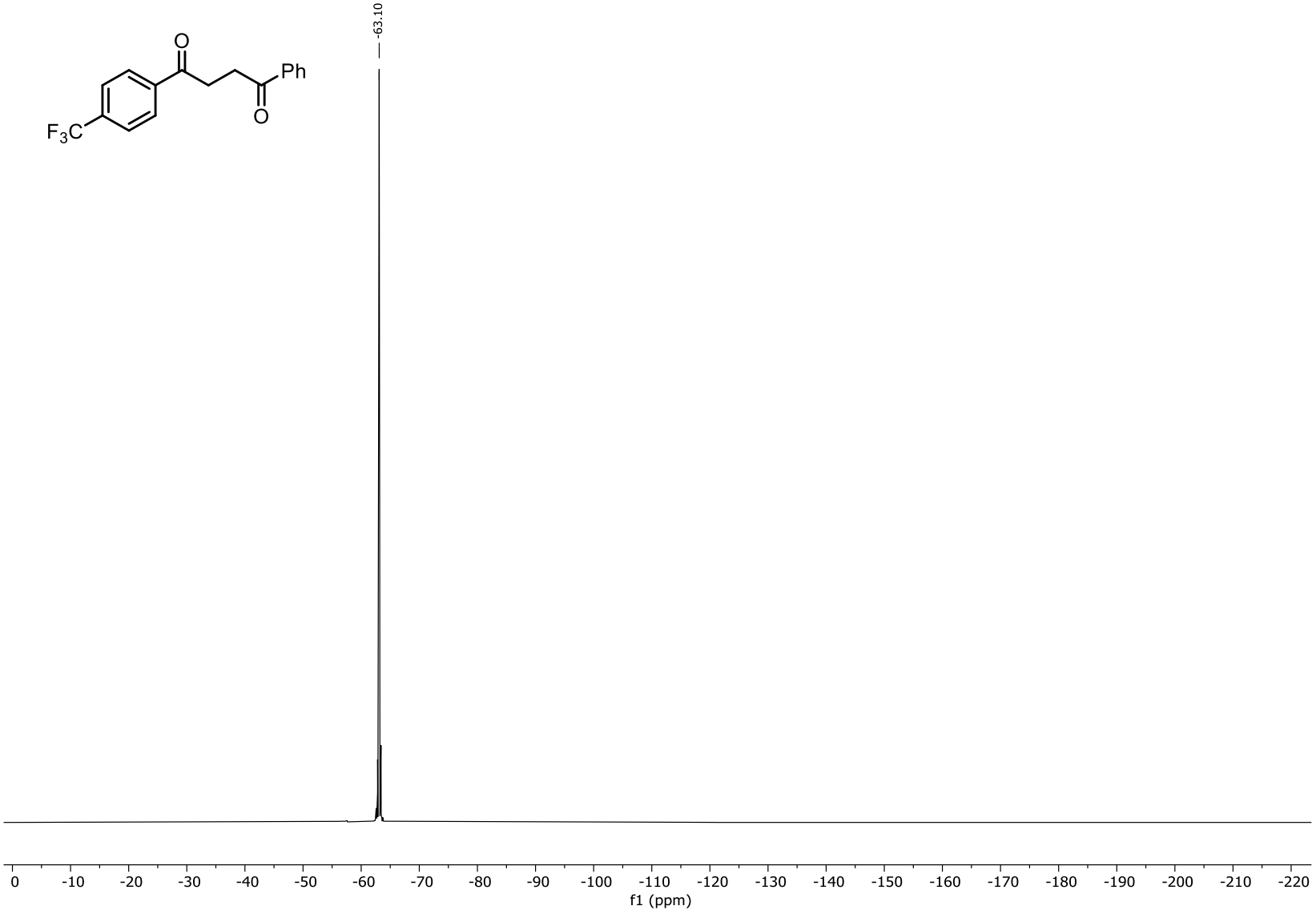
1-Phenyl-4-(4-(trifluoromethyl)phenyl)butane-1,4-dione (S15): ^{1}H NMR (400 MHz, $CDCl_3$)



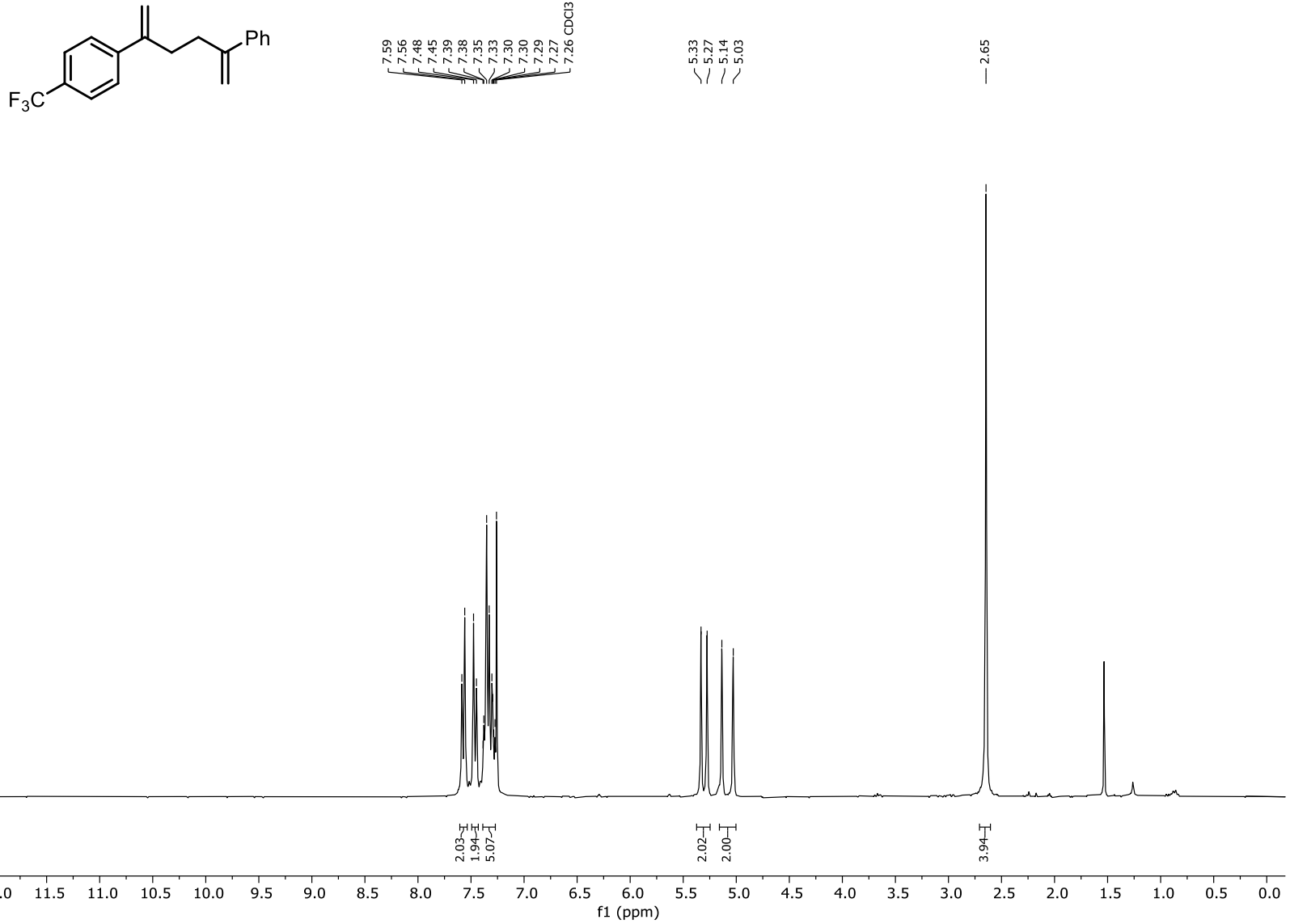
1-Phenyl-4-(4-(trifluoromethyl)phenyl)butane-1,4-dione (S15): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



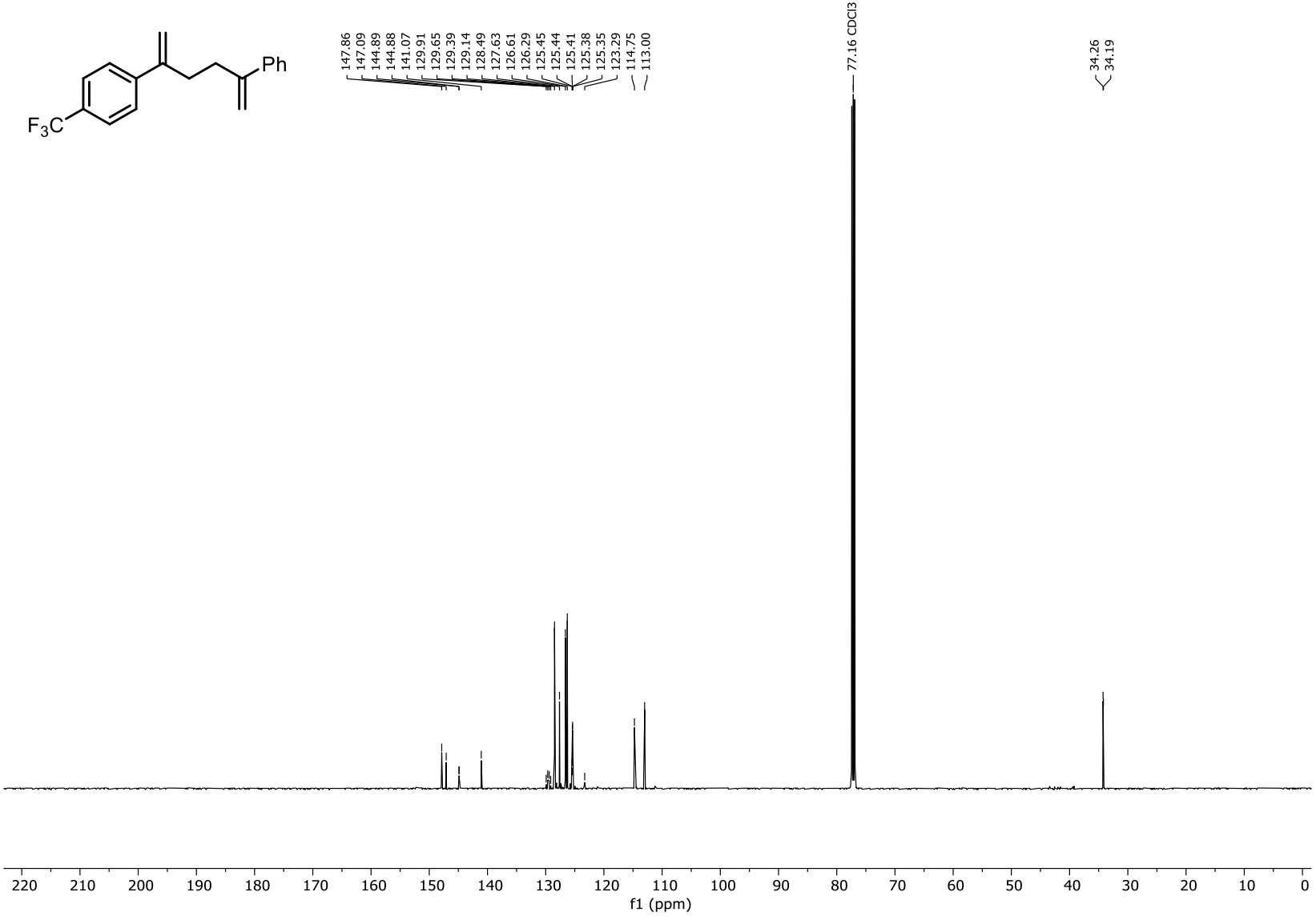
1-Phenyl-4-(4-(trifluoromethyl)phenyl)butane-1,4-dione (S15): $^{19}F\{^{1}H\}$ (282 MHz, $CDCl_3$)



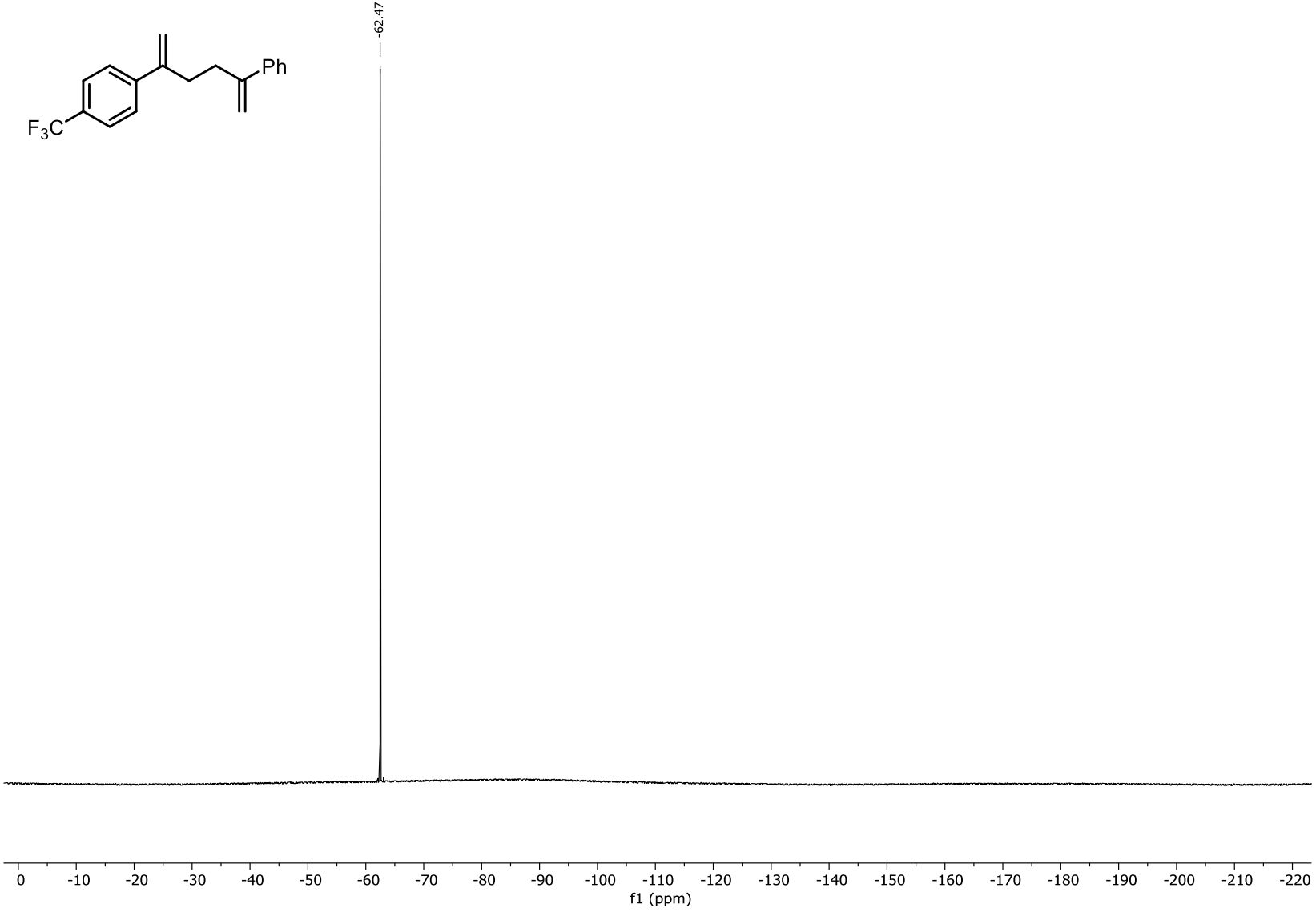
1-(5-Phenylhexa-1,5-dien-2-yl)-4-(trifluoromethyl)benzene (1o): ^{1}H NMR (300 MHz, $CDCl_3$)



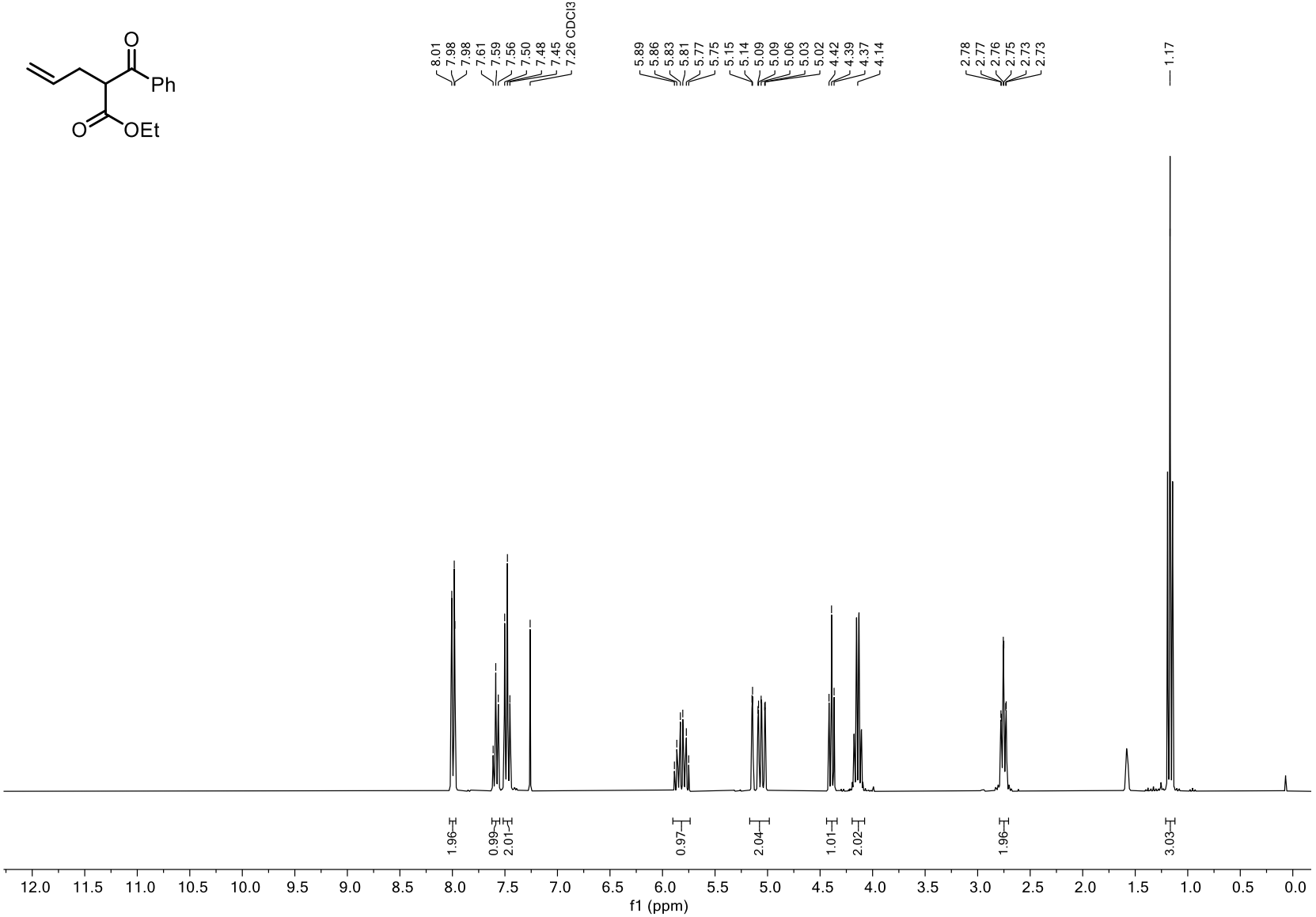
1-(5-Phenylhexa-1,5-dien-2-yl)-4-(trifluoromethyl)benzene (1o): $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



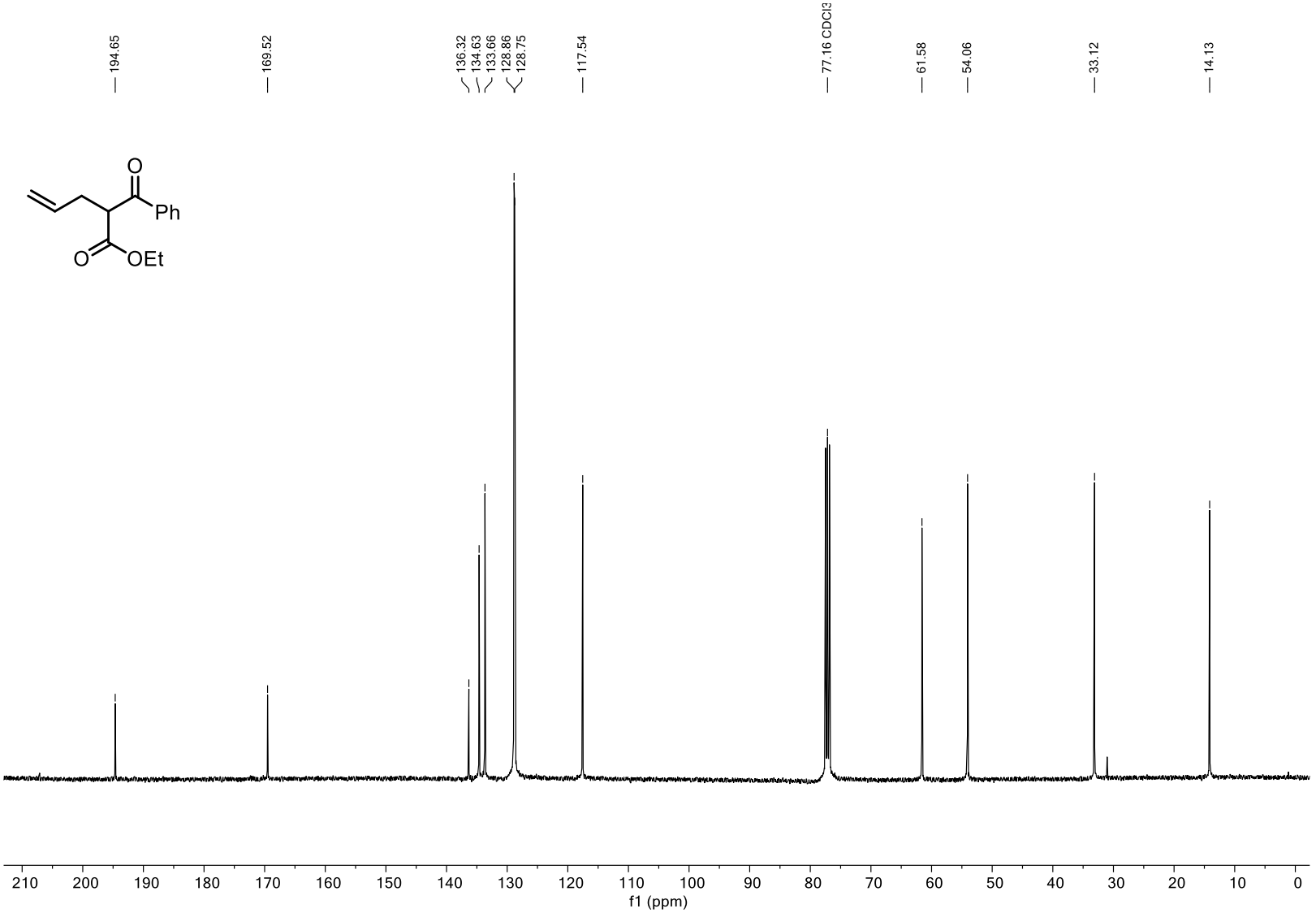
1-(5-Phenylhexa-1,5-dien-2-yl)-4-(trifluoromethyl)benzene (1o): $^{19}F\{^{1}H\}$ (282 MHz, $CDCl_3$)



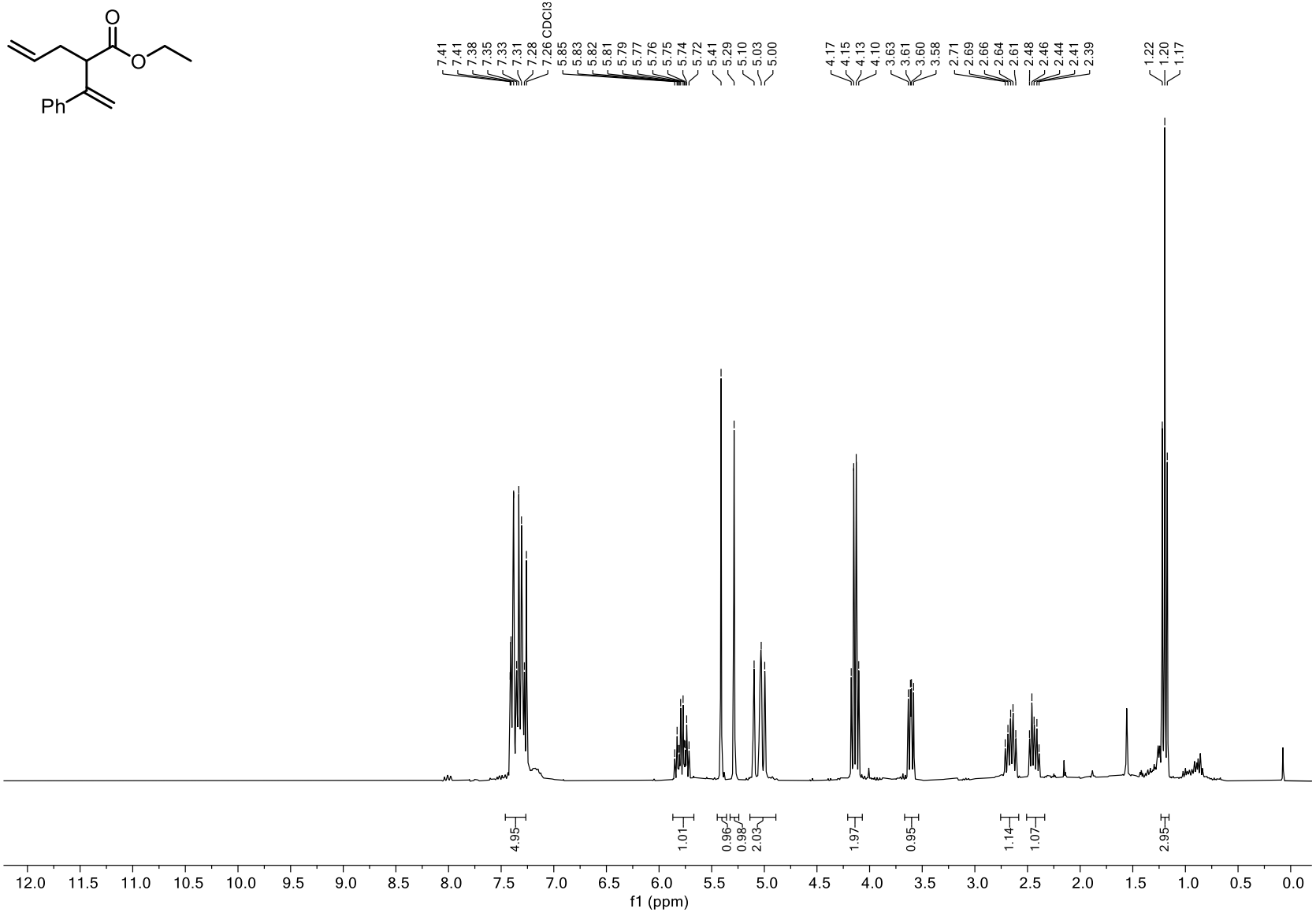
Ethyl 2-benzoylpent-4-enoate (S16): ^{1}H NMR (300 MHz, $CDCl_3$)



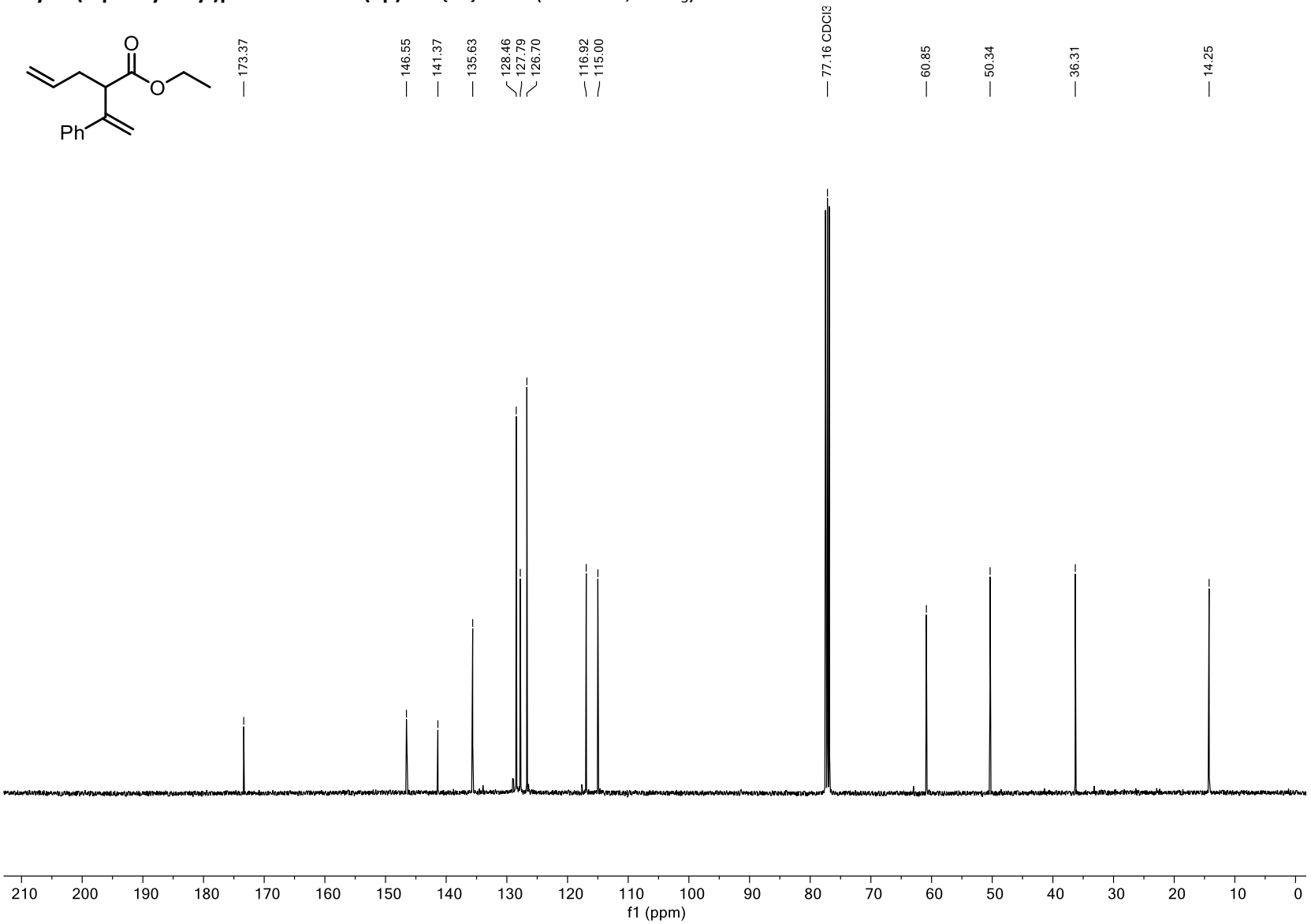
Ethyl 2-benzoylpent-4-enoate (S16): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



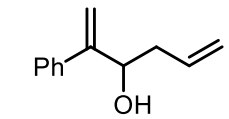
Ethyl 2-(1-phenylvinyl)pent-4-enoate (1p): ^{1}H NMR (300 MHz, $CDCl_3$)



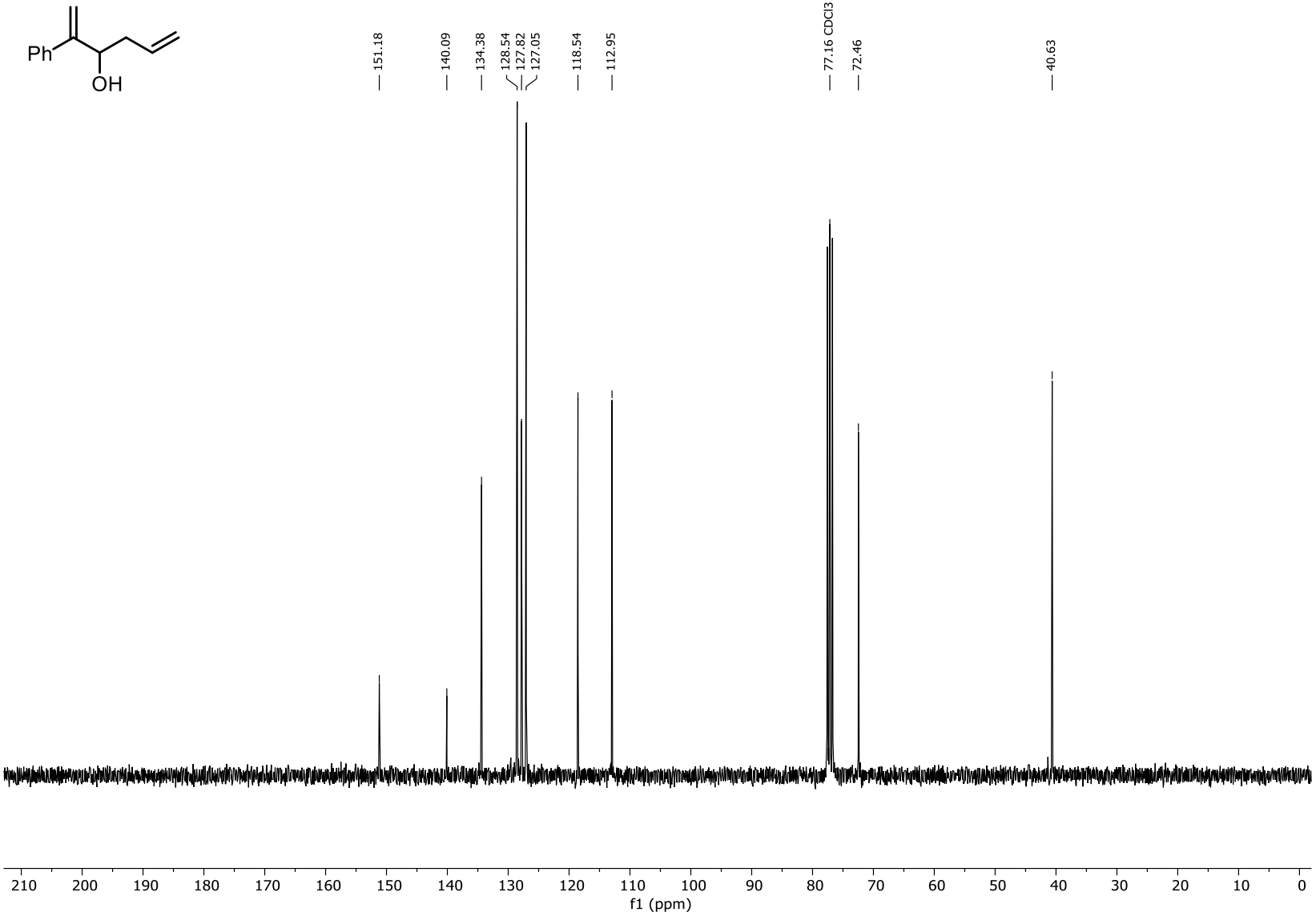
Ethyl 2-(1-phenylvinyl)pent-4-enoate (1p): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



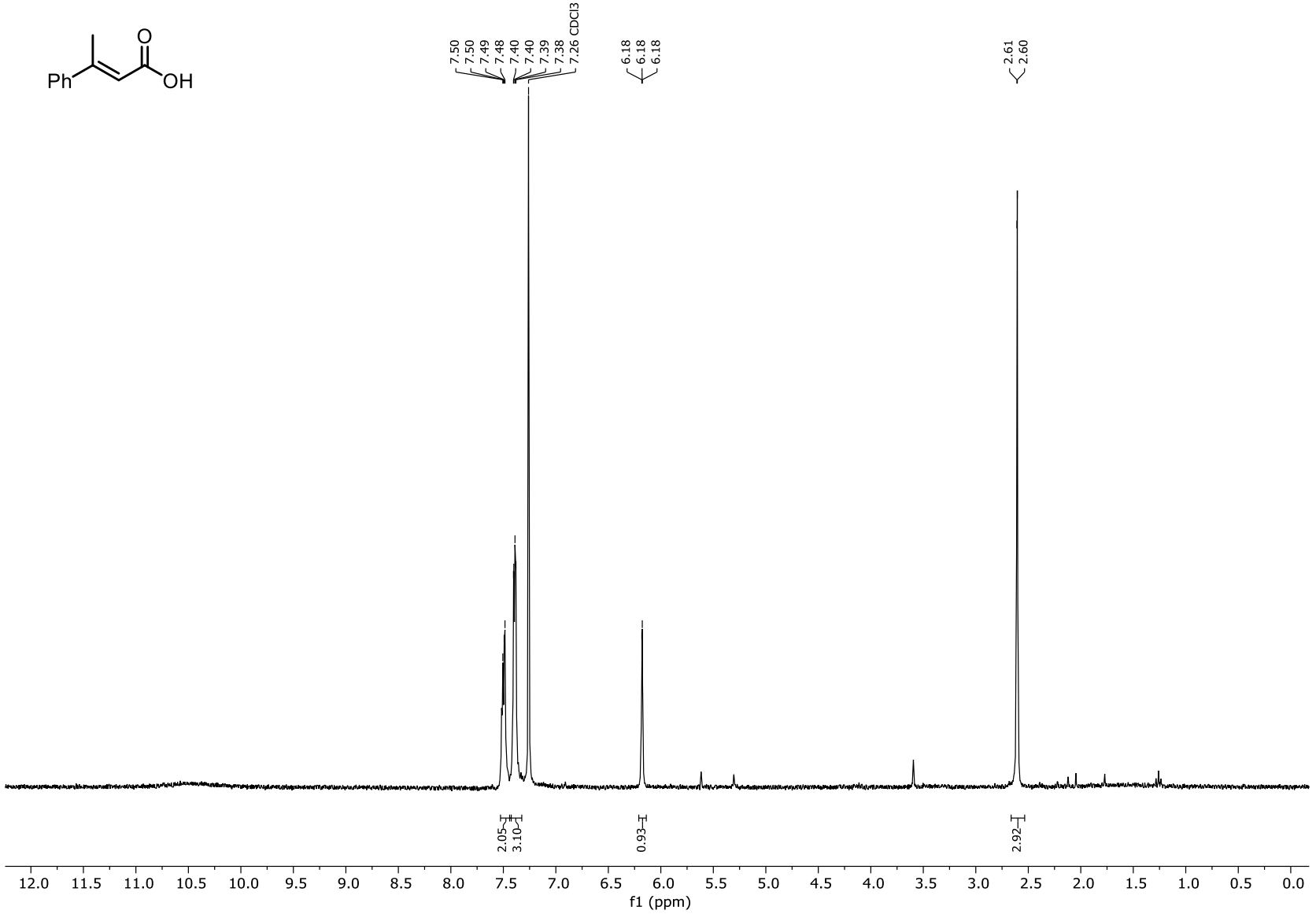
2-Phenylhexa-1,5-dien-3-ol (1q): ^{1}H NMR (300 MHz, $CDCl_3$)



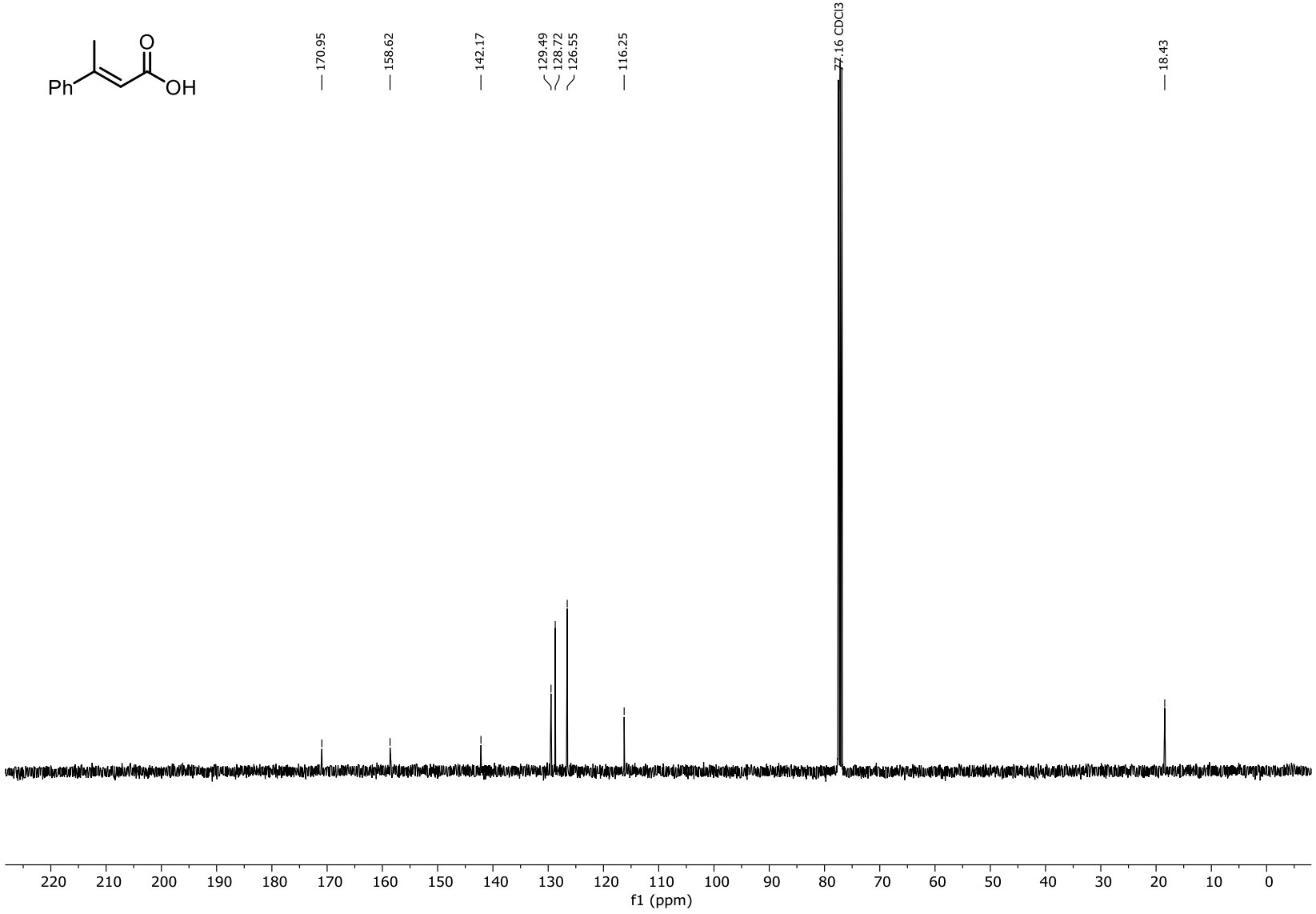
2-Phenylhexa-1,5-dien-3-ol (1q): $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



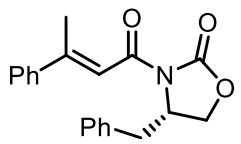
(*E*)-3-phenylbut-2-enoic acid (S17): ^{1}H NMR (300 MHz, $CDCl_3$)



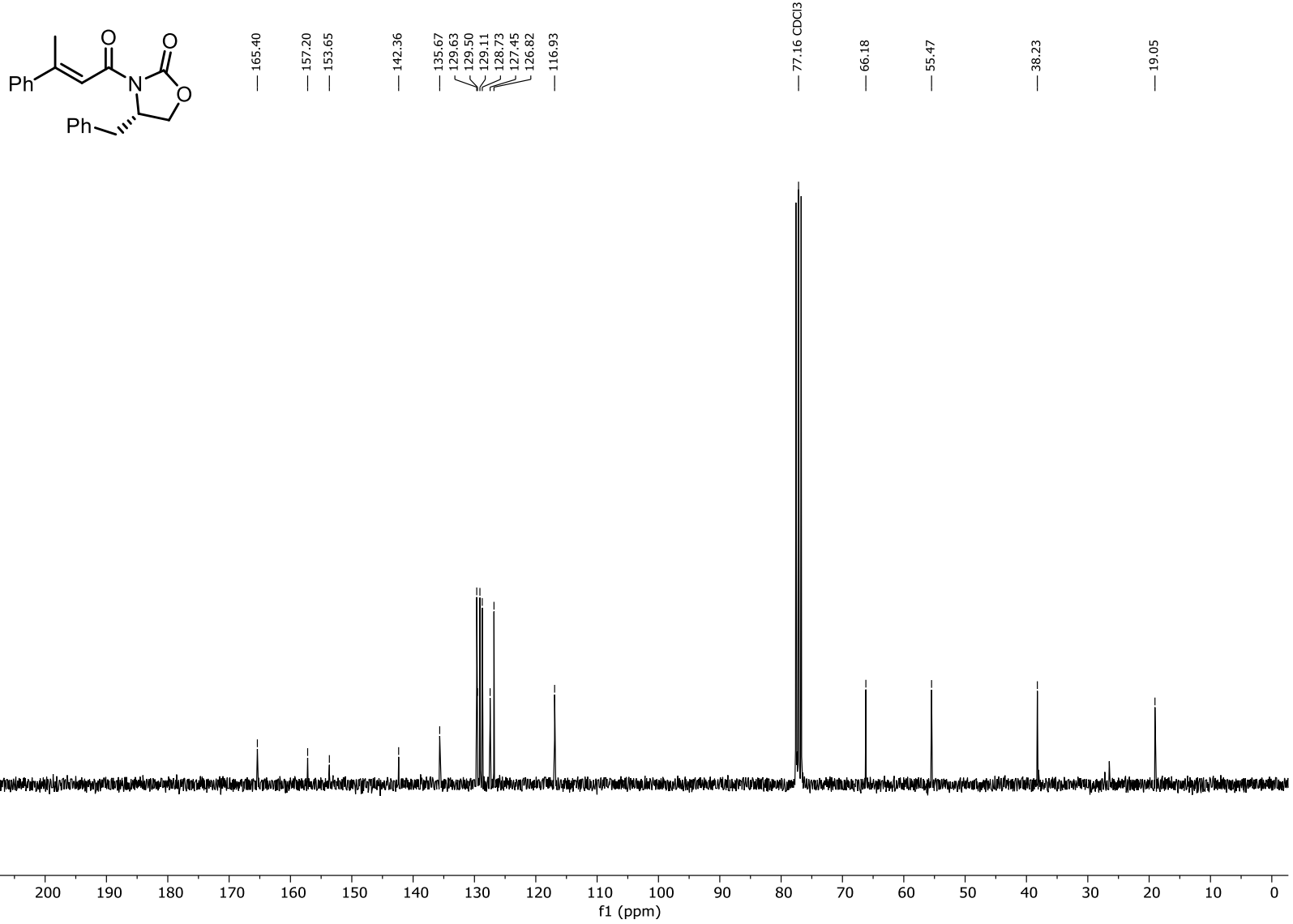
(*E*)-3-phenylbut-2-enoic acid (S17): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



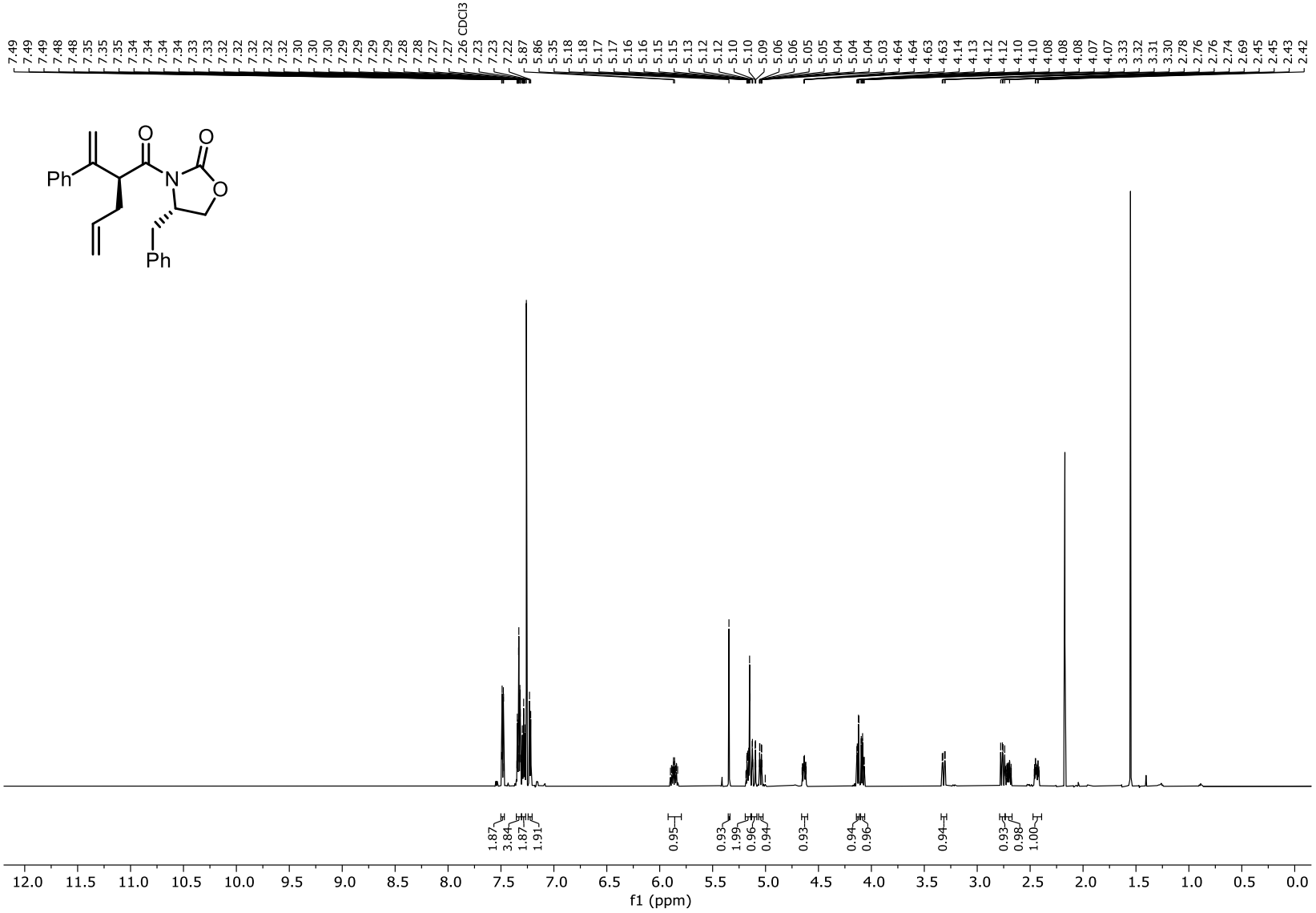
(*S,E*)-4-benzyl-3-(3-phenylbut-2-enoyl)oxazolidin-2-one (S18): ^{1}H NMR (300 MHz, $CDCl_3$)



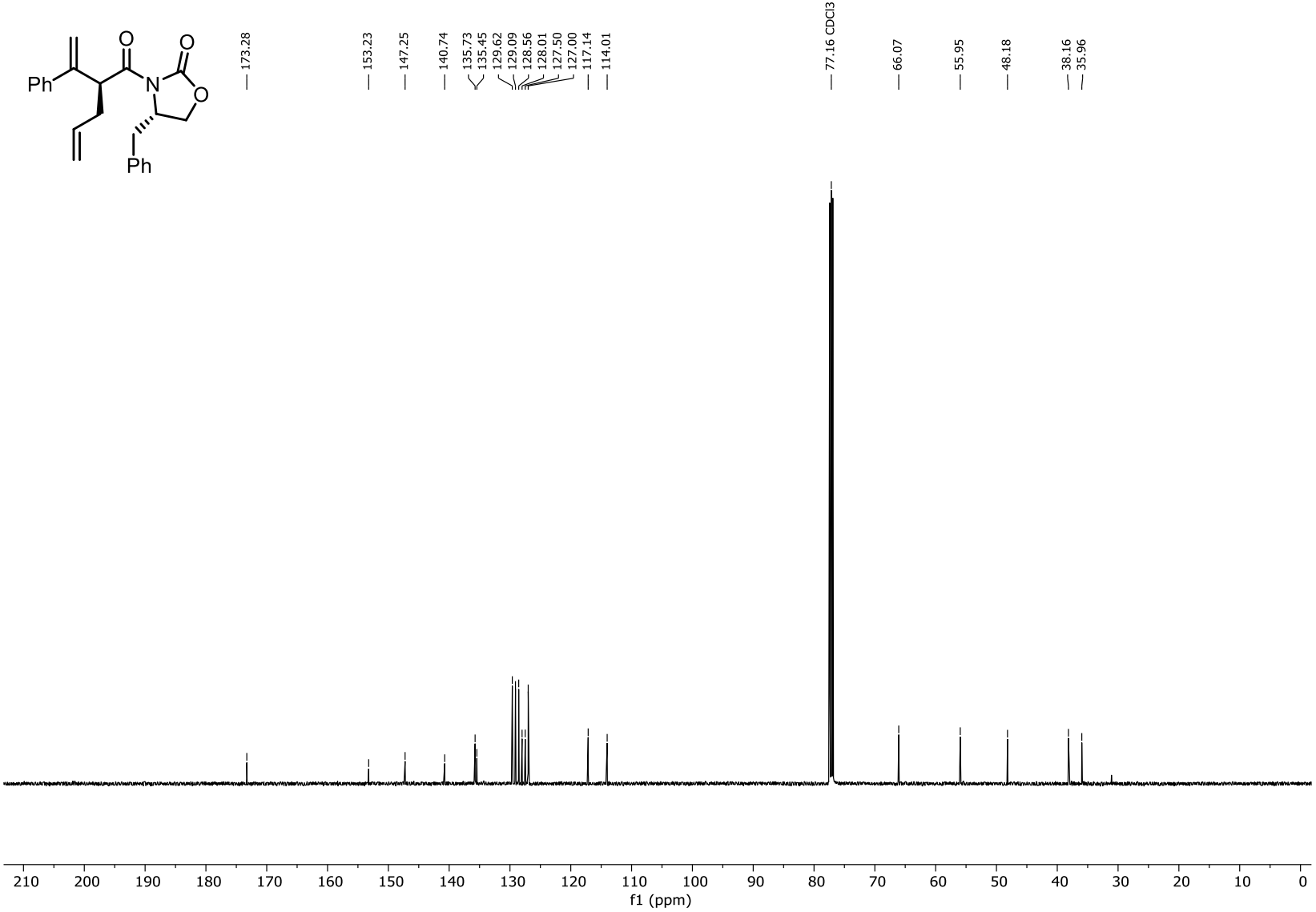
(*S,E*)-4-benzyl-3-(3-phenylbut-2-enoyl)oxazolidin-2-one (S18): $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



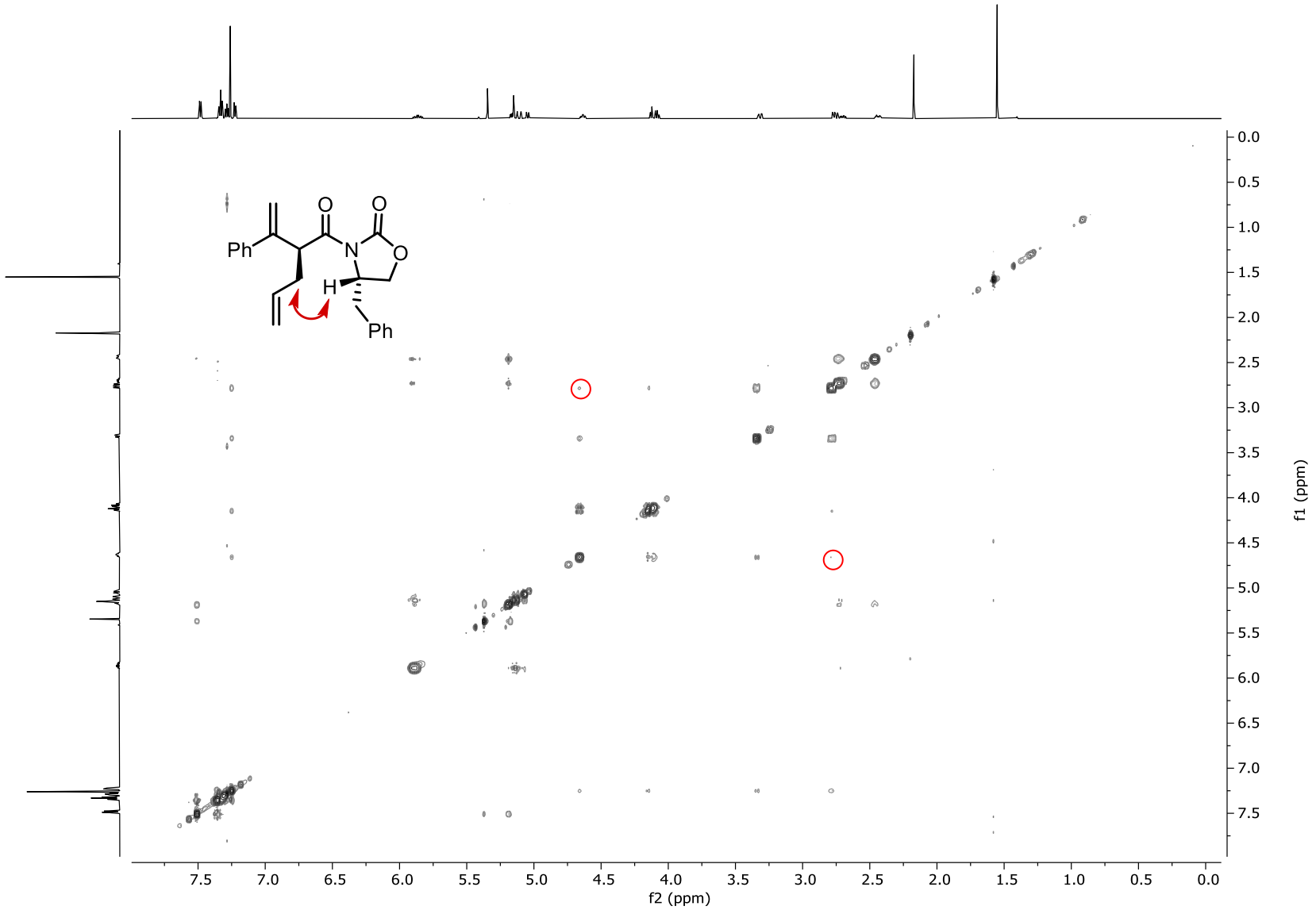
(*S*)-4-Benzyl-3-((*S*)-2-(1-phenylvinyl)pent-4-enoyl)oxazolidin-2-one (1r): ^{1}H NMR (600 MHz, $CDCl_3$)



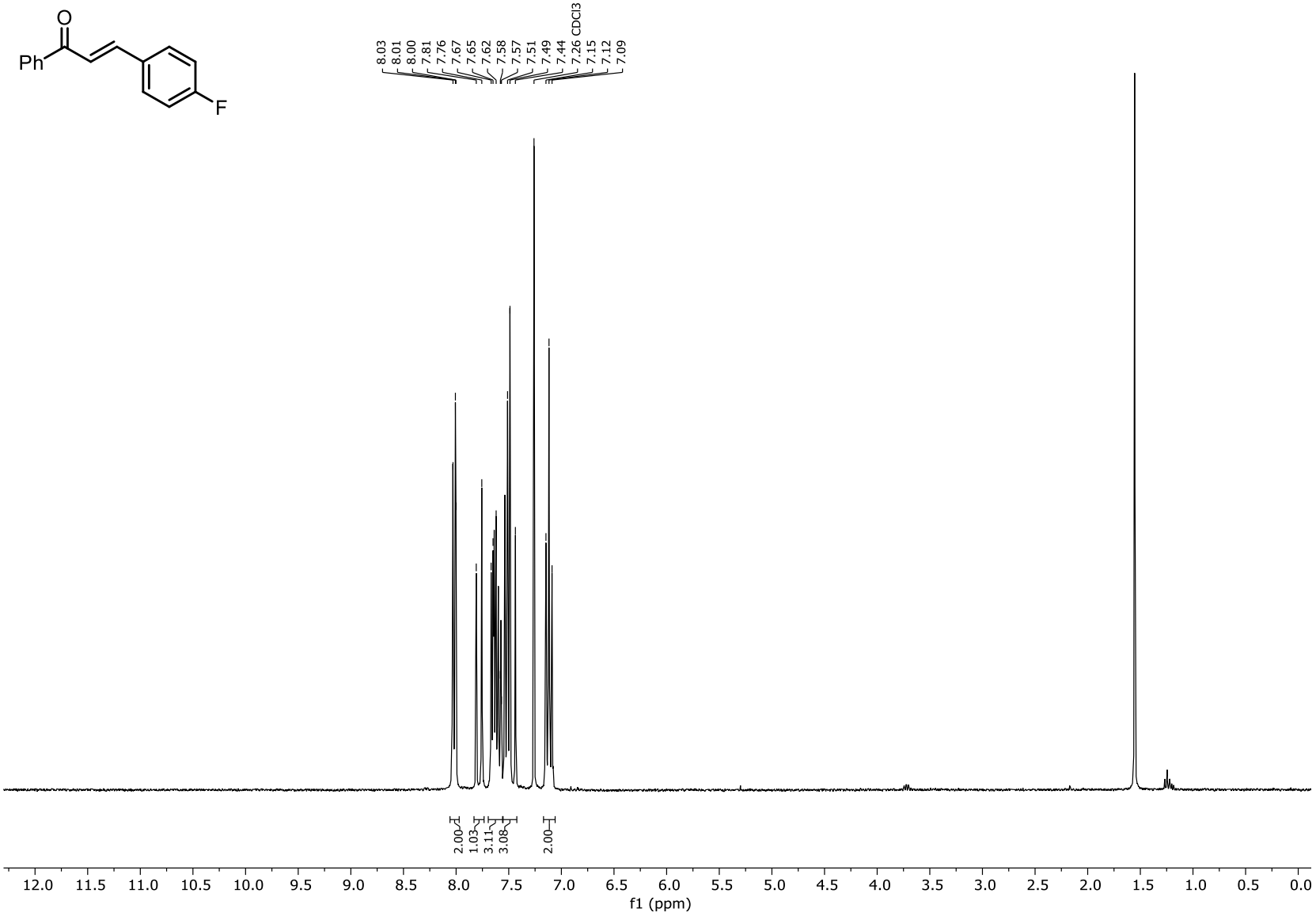
(*S*)-4-Benzyl-3-((*S*)-2-(1-phenylvinyl)pent-4-enoyl)oxazolidin-2-one (1q): $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



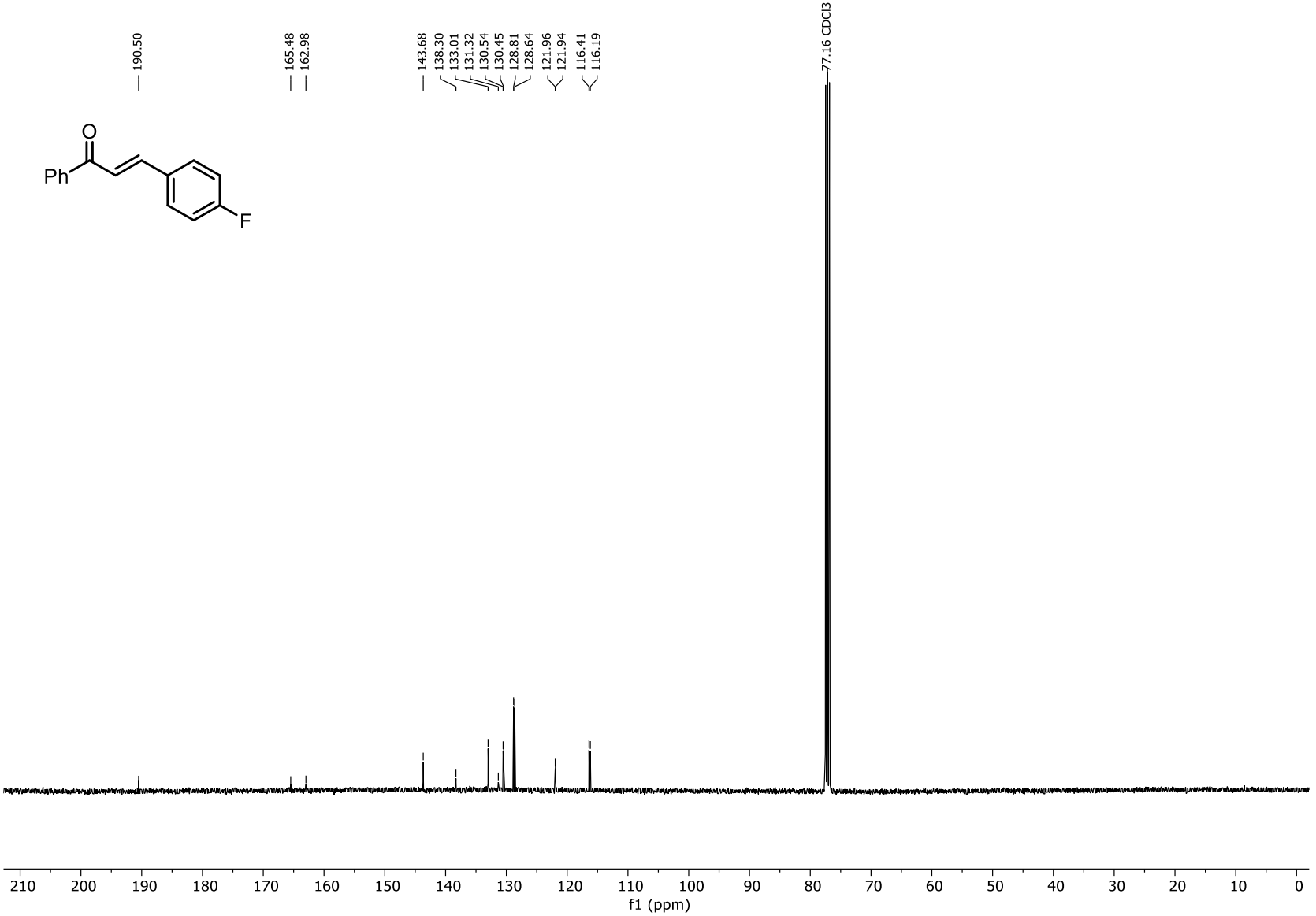
(*S*)-4-Benzyl-3-((*S*)-2-(1-phenylvinyl)pent-4-enoyl)oxazolidin-2-one (1q): NOESY (600 MHz, $CDCl_3$)



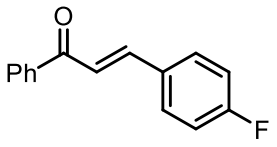
(*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (S19): ^{1}H NMR (300 MHz, $CDCl_3$)



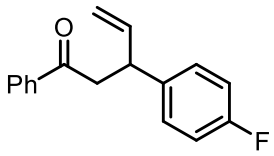
(*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (S19): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



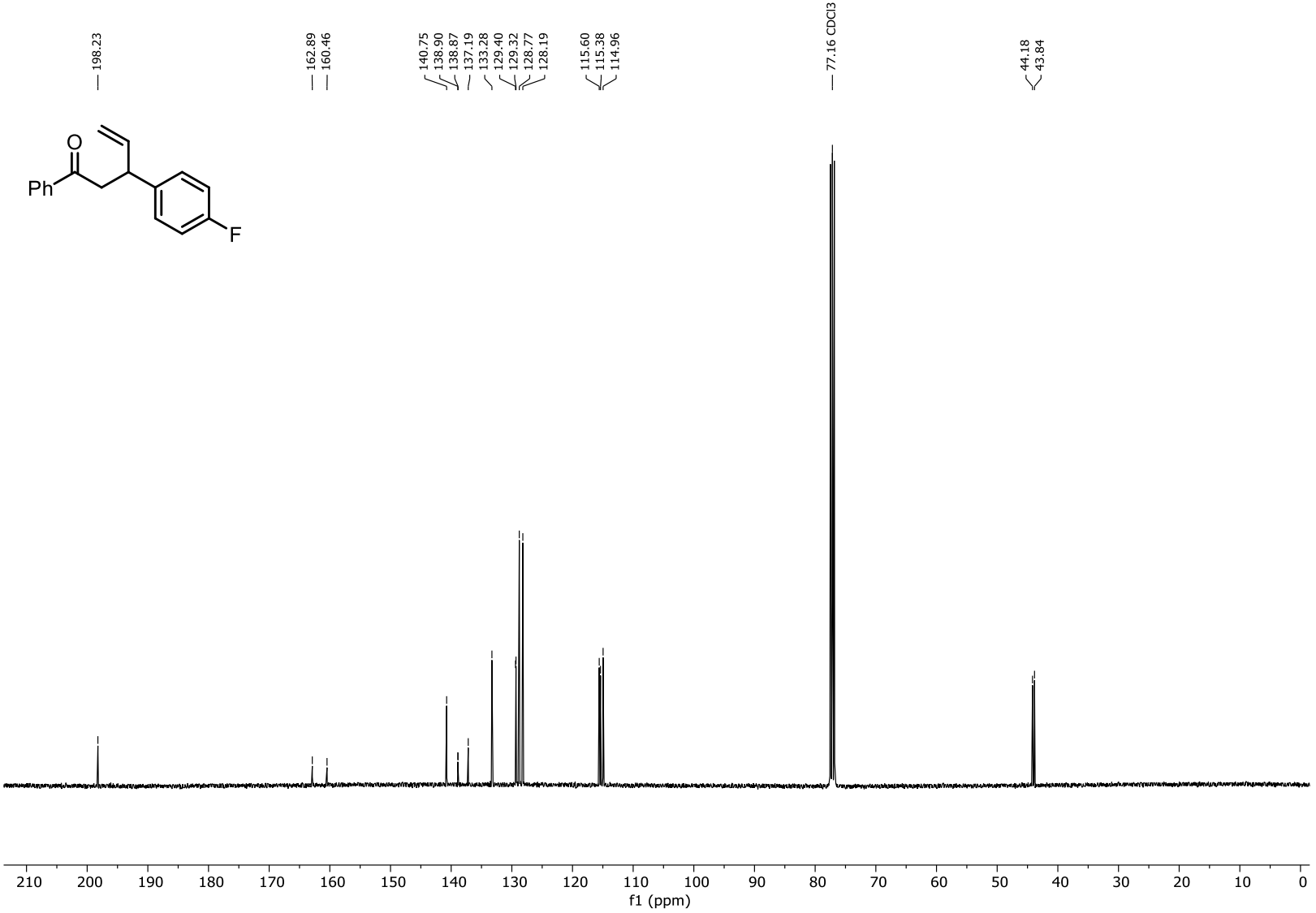
(*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (S19): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



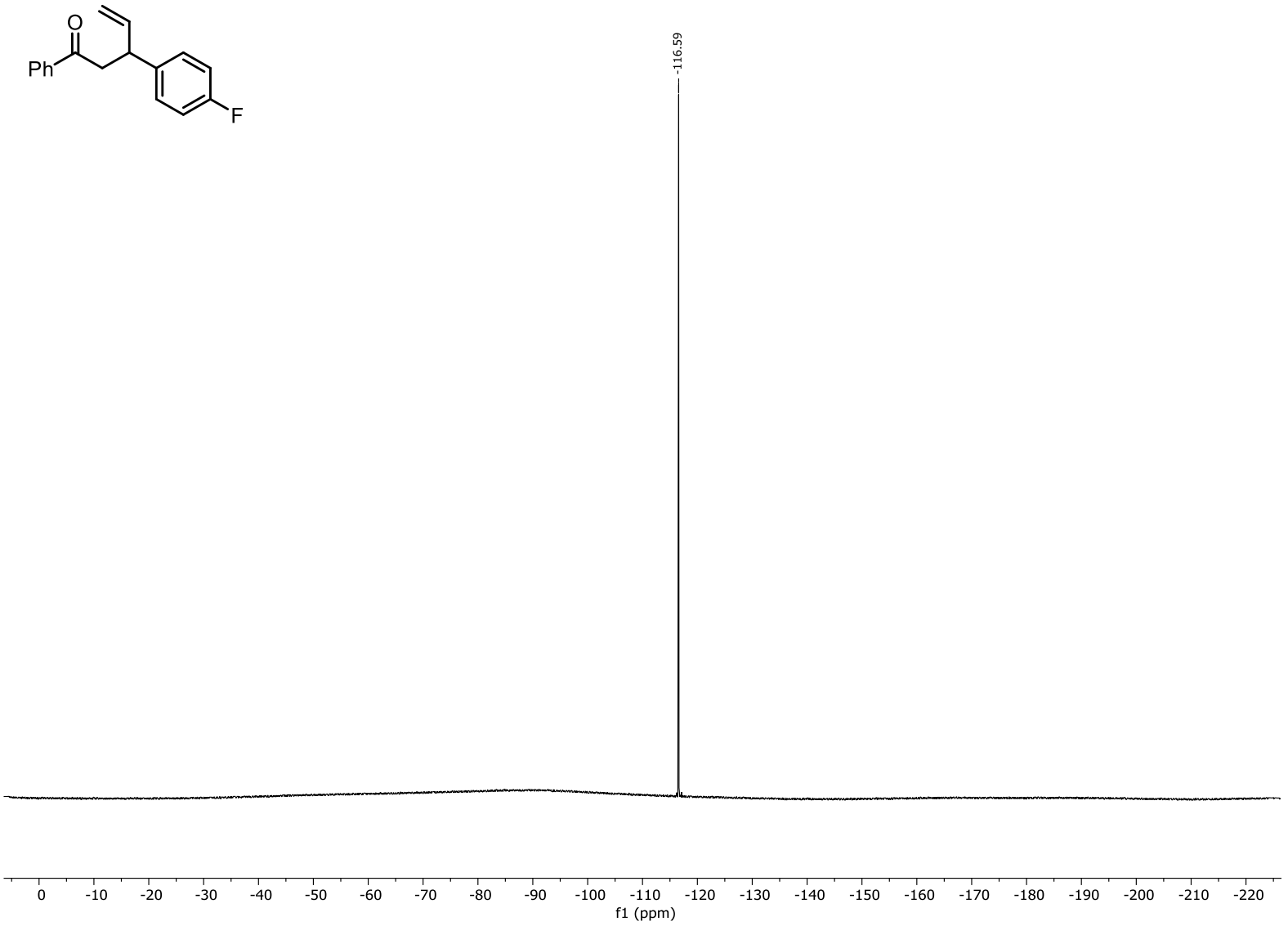
3-(4-Fluorophenyl)-1-phenylpent-4-en-1-one (S20): ^{1}H NMR (300 MHz, $CDCl_3$)



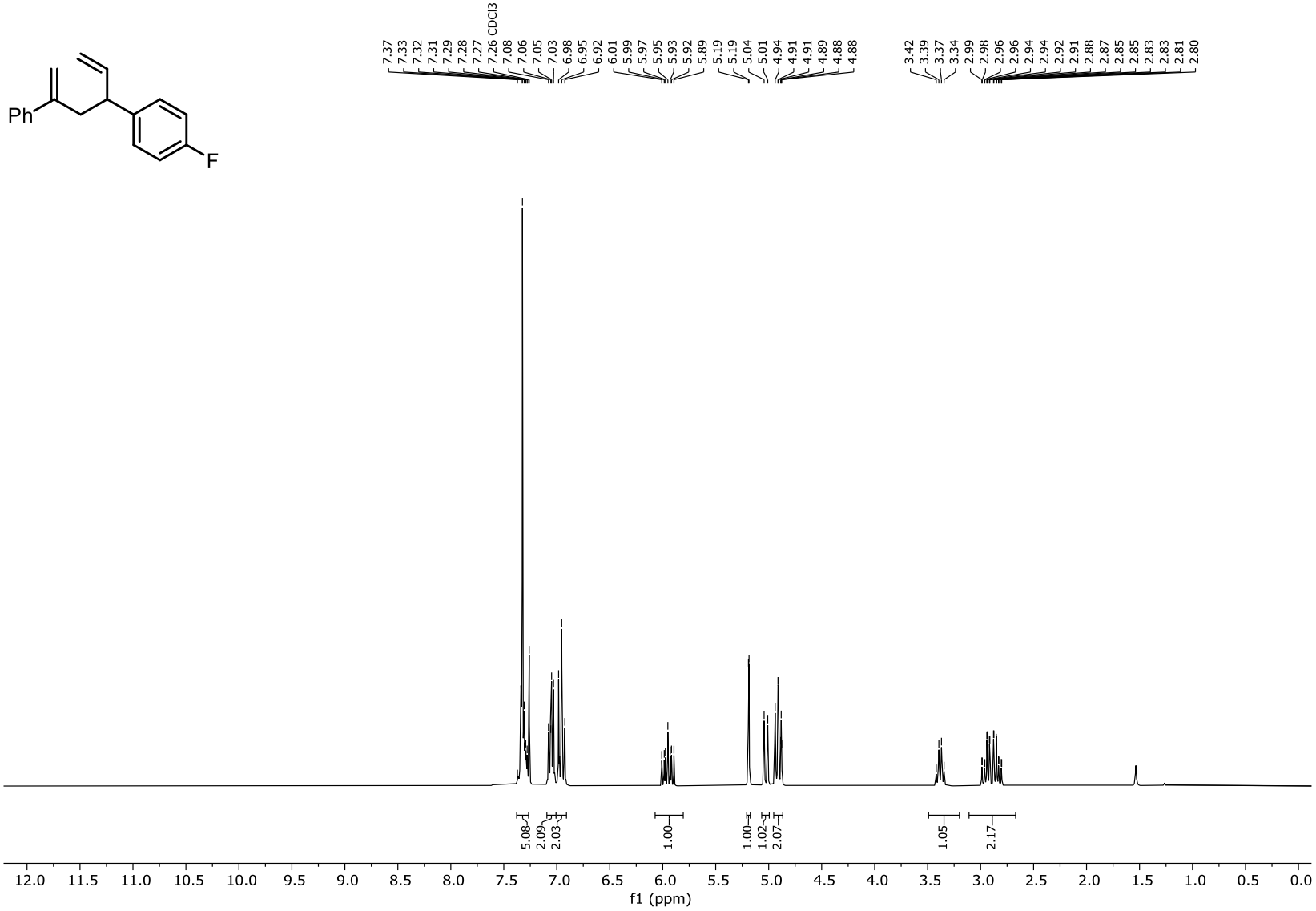
3-(4-Fluorophenyl)-1-phenylpent-4-en-1-one (S20): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



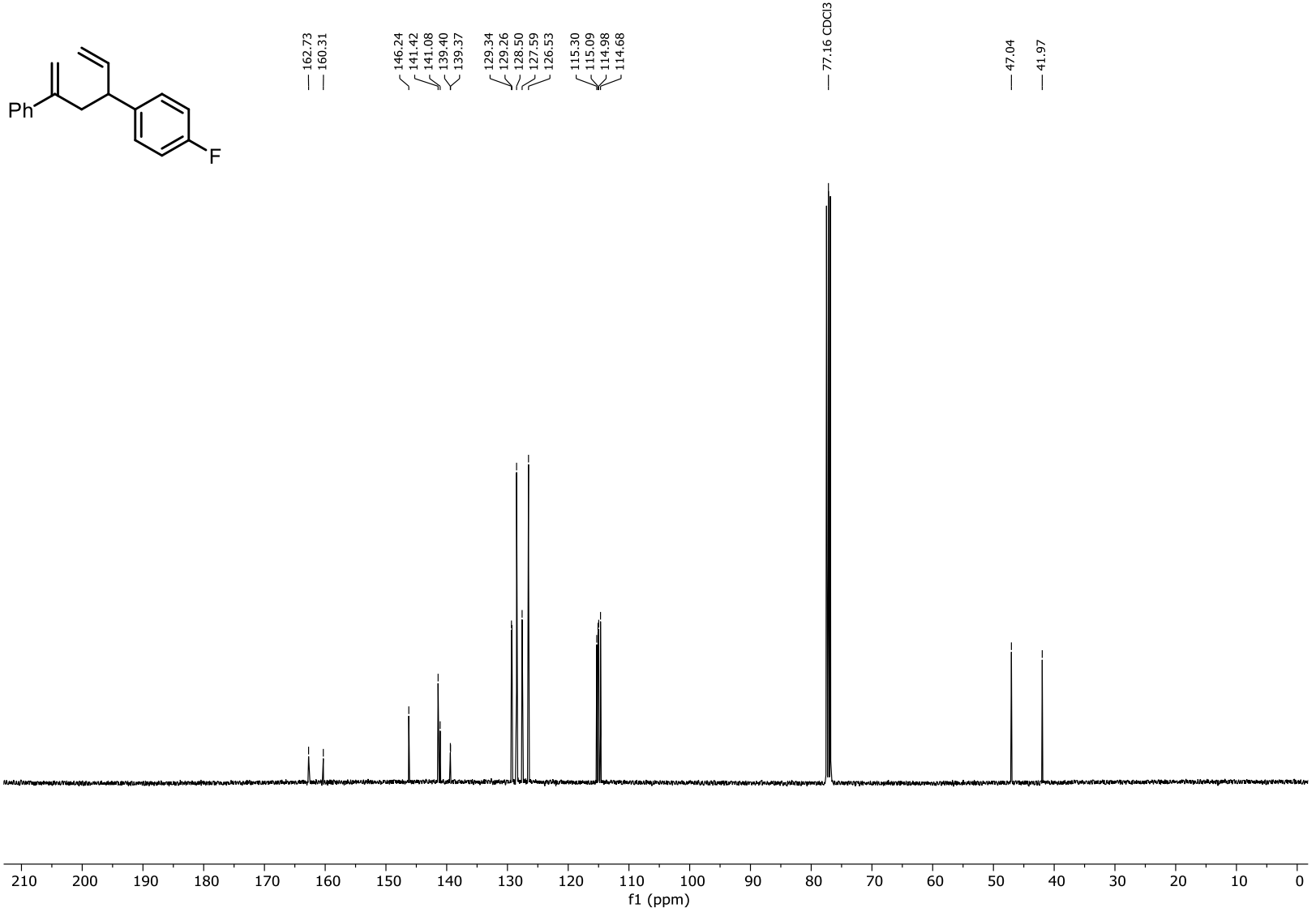
3-(4-Fluorophenyl)-1-phenylpent-4-en-1-one (S20): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



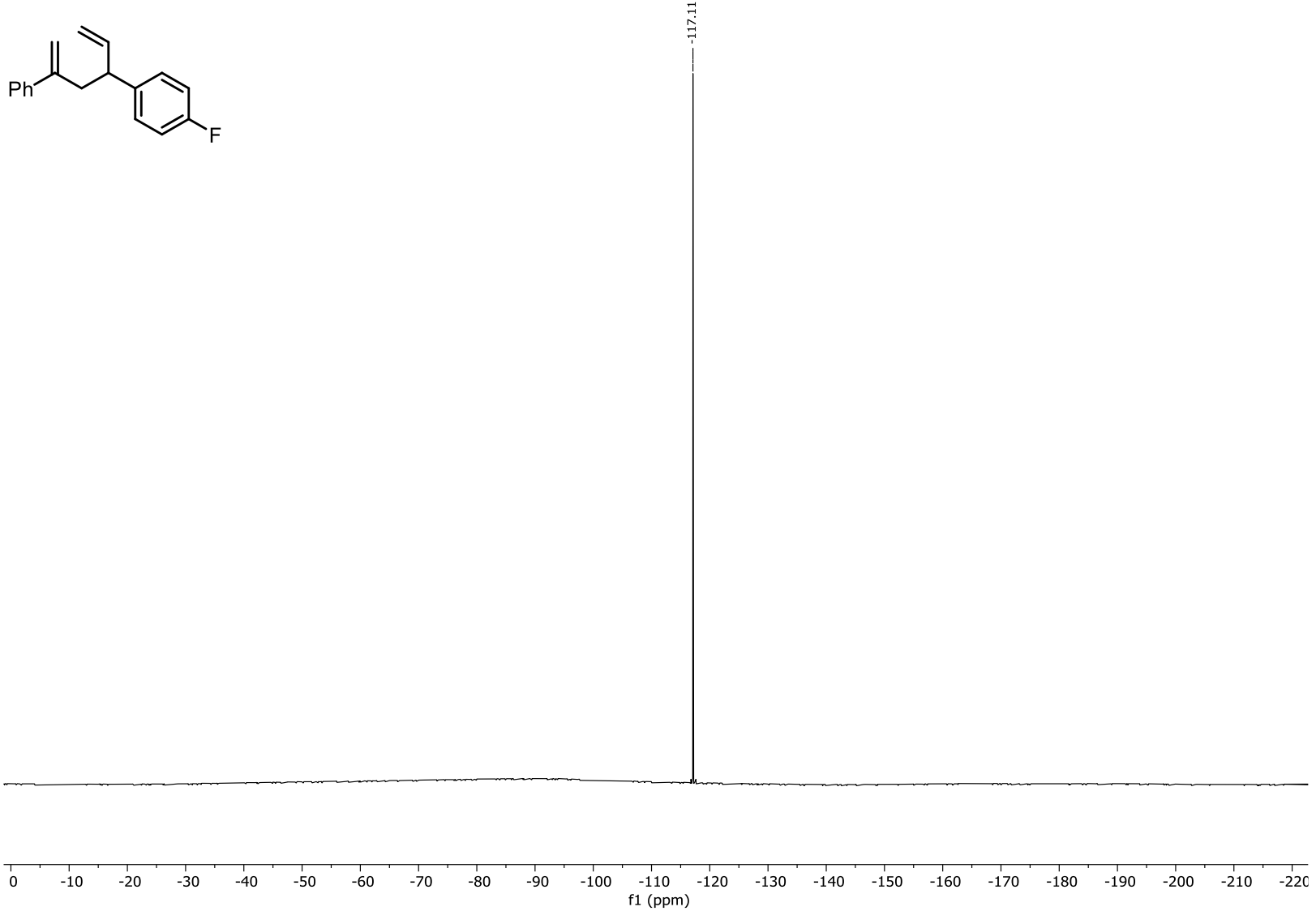
1-Fluoro-4-(5-phenylhexa-1,5-dien-3-yl)benzene (S20): ^{1}H NMR (300 MHz, $CDCl_3$)



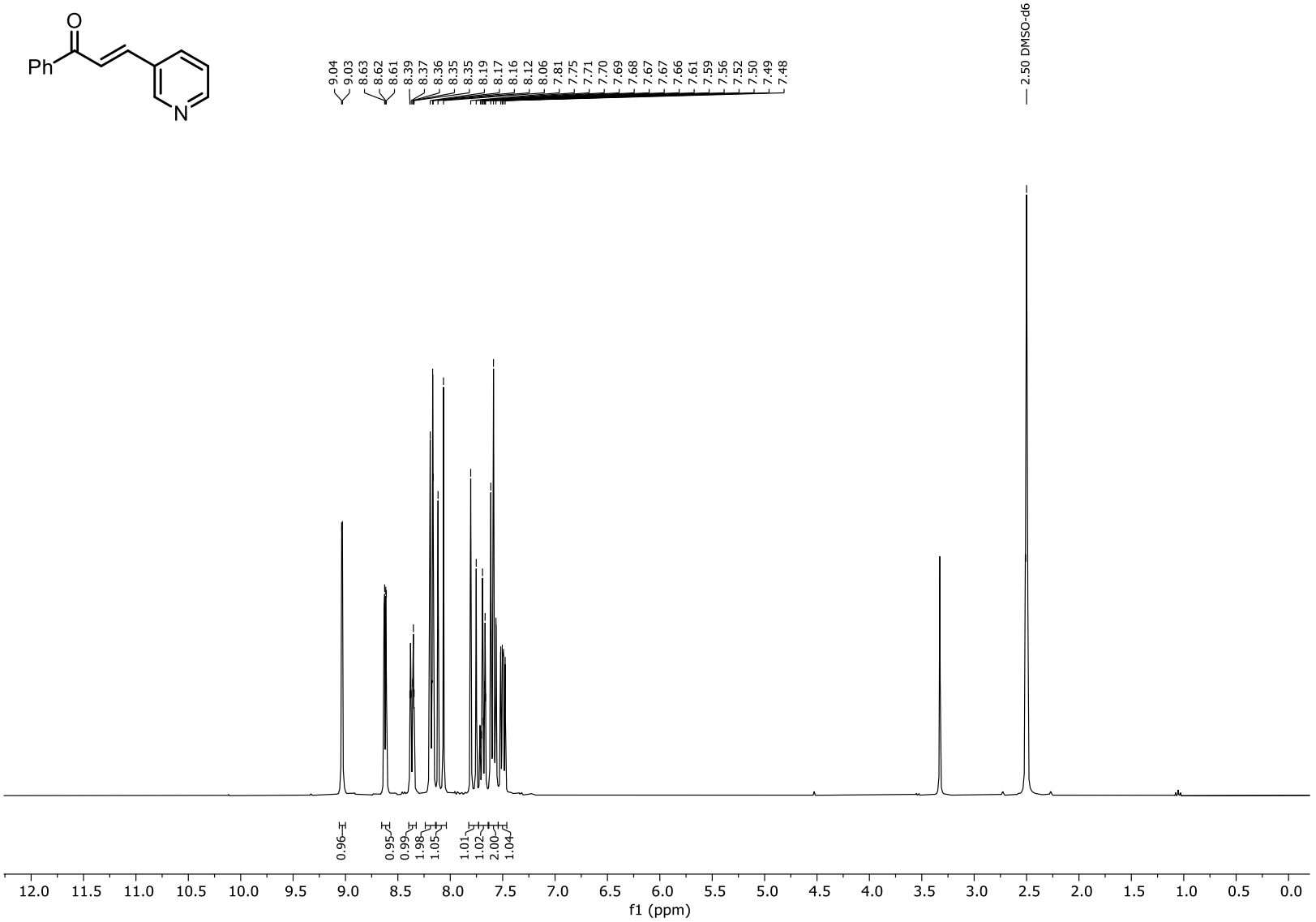
1-Fluoro-4-(5-phenylhexa-1,5-dien-3-yl)benzene (1s): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



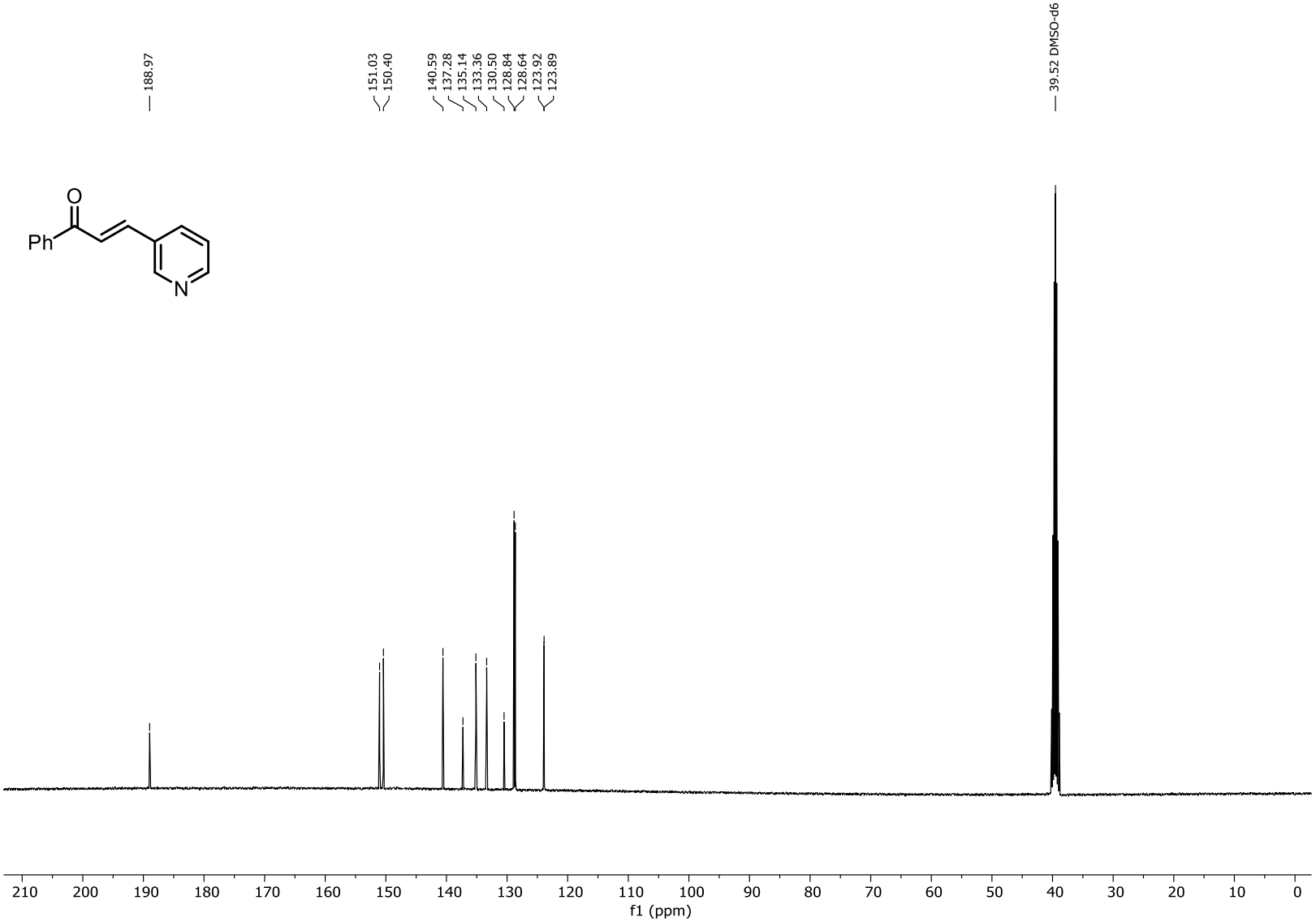
1-Fluoro-4-(5-phenylhexa-1,5-dien-3-yl)benzene (1s): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



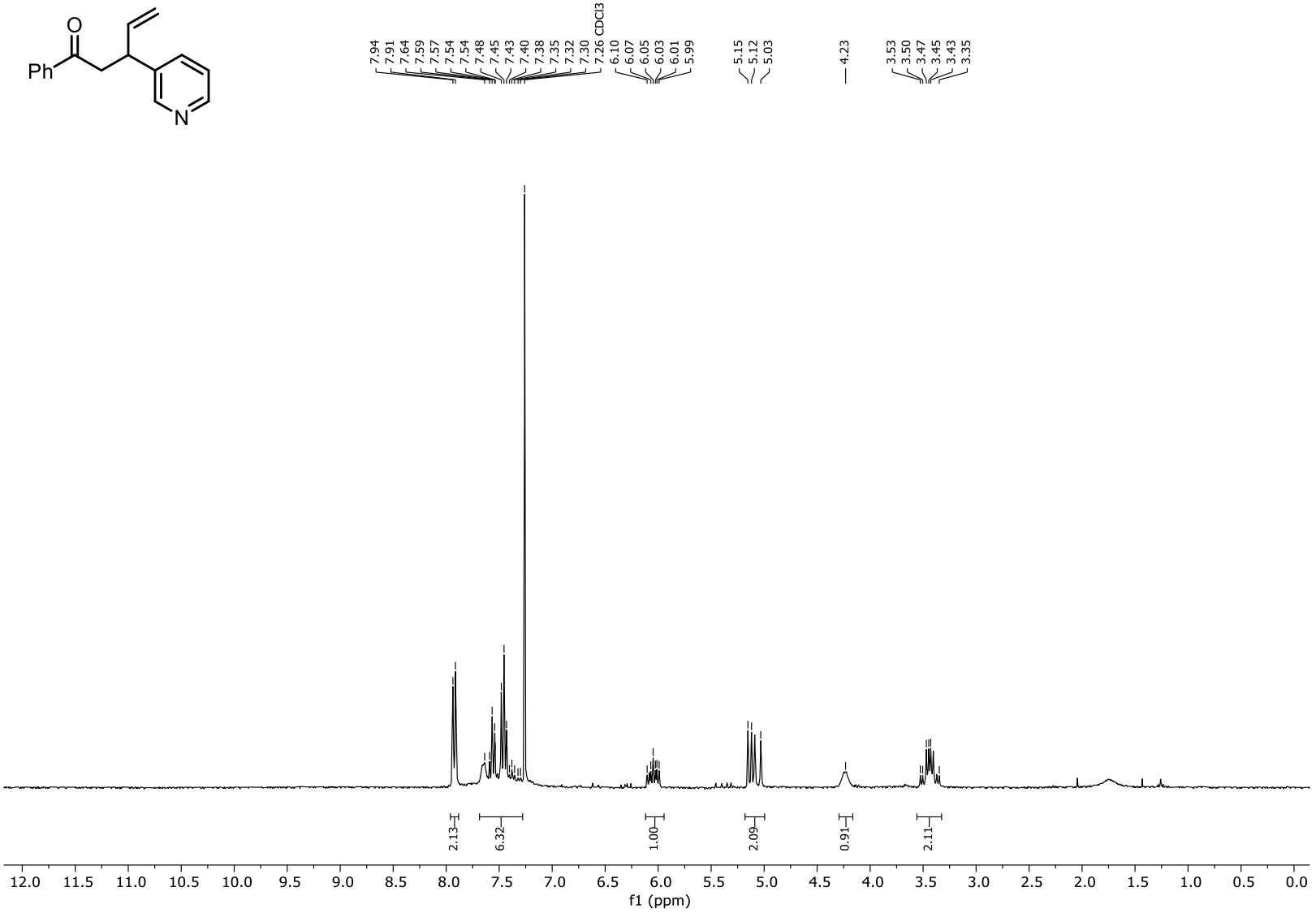
(*E*)-1-phenyl-3-(pyridin-3-yl)prop-2-en-1-one (S21): ^{1}H NMR (300 MHz, DMSO-*d*6)



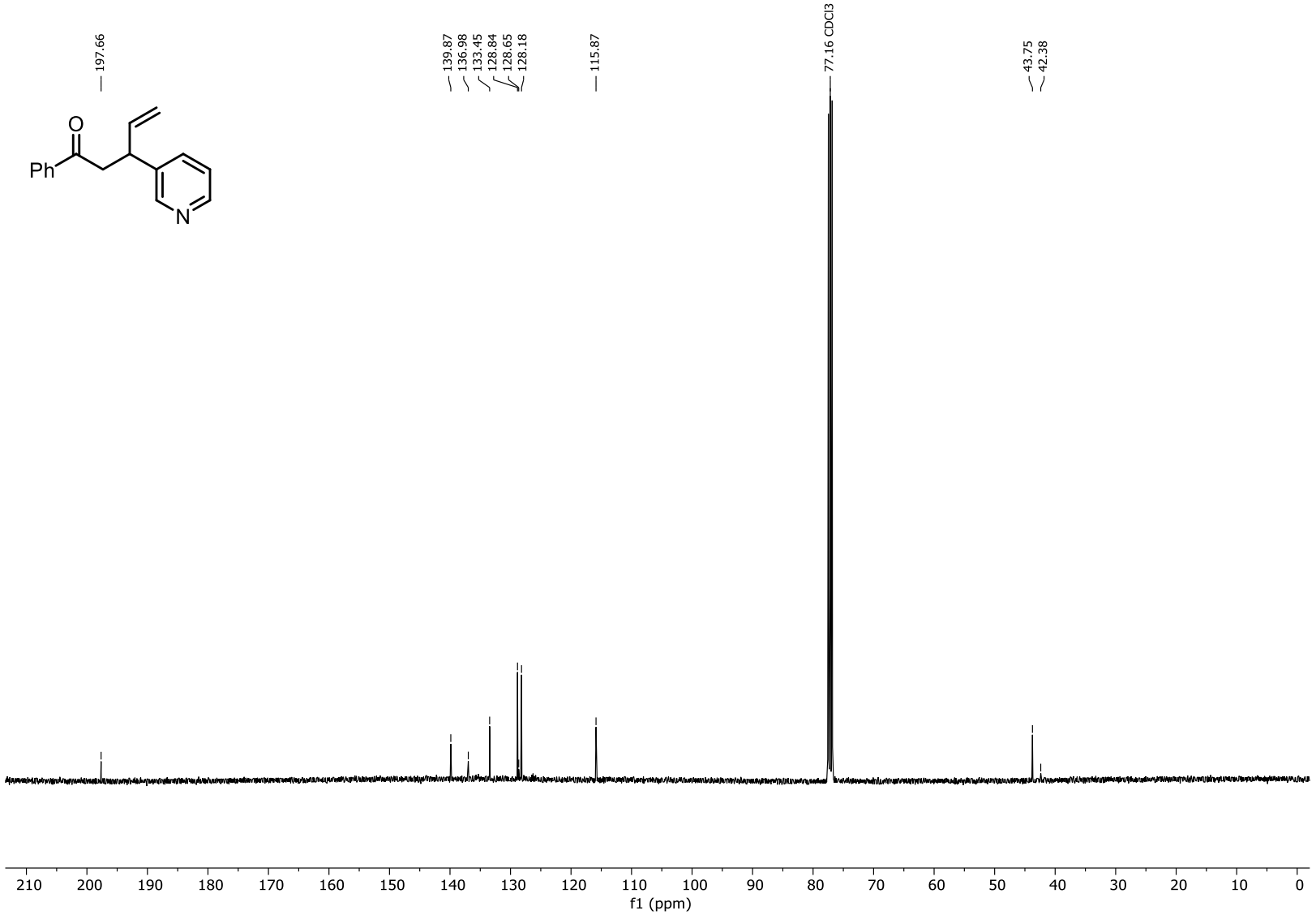
(*E*)-1-phenyl-3-(pyridin-3-yl)prop-2-en-1-one (S21): $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-*d*6)



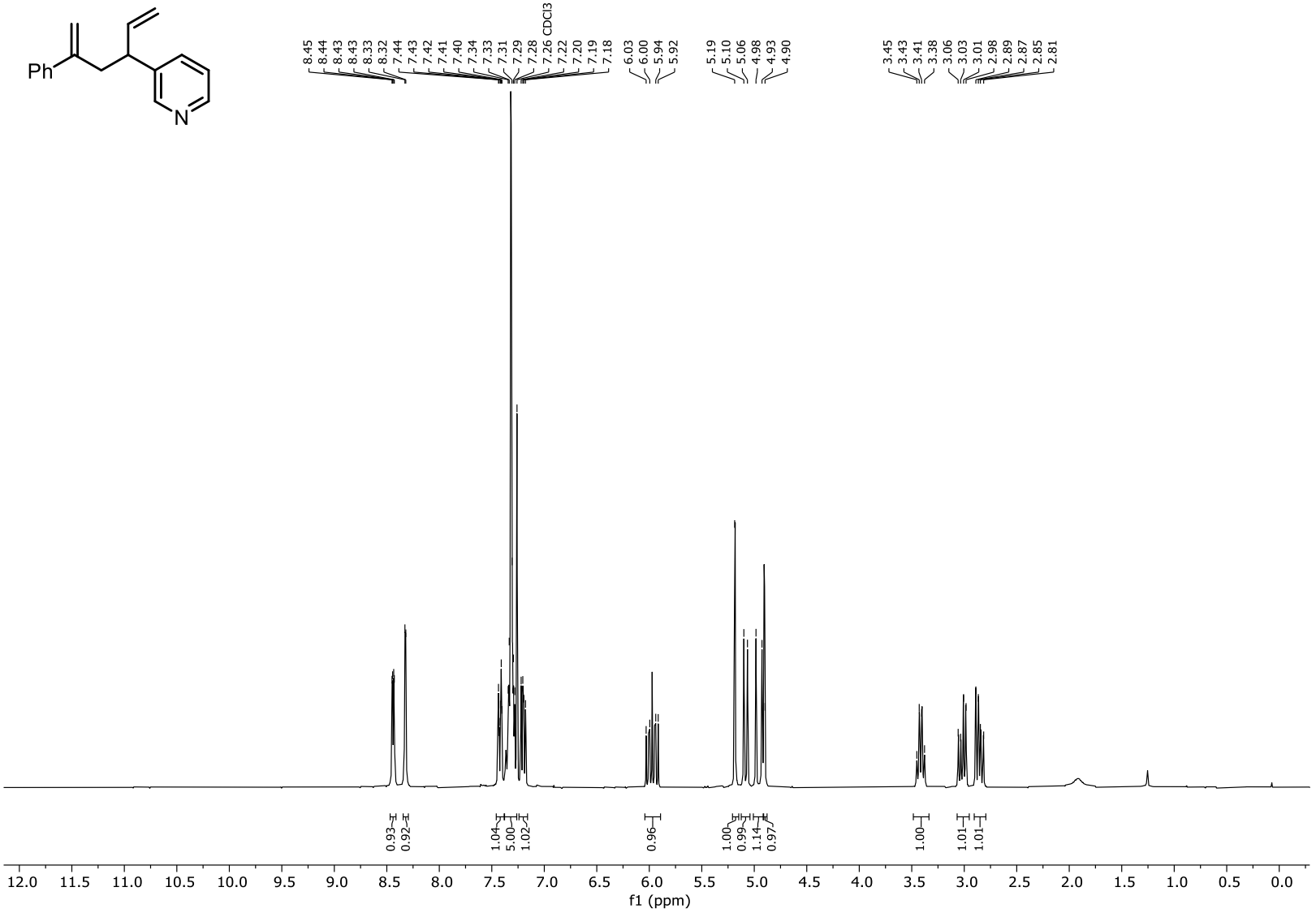
1-Phenyl-3-(pyridin-3-yl)pent-4-en-1-one (S22): ^{1}H NMR (300 MHz, $CDCl_3$)



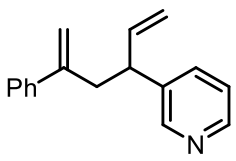
1-Phenyl-3-(pyridin-3-yl)pent-4-en-1-one (S22): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



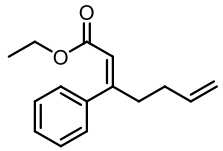
3-(5-Phenylhexa-1,5-dien-3-yl)pyridine (1t): ^{1}H NMR (300 MHz, $CDCl_3$)



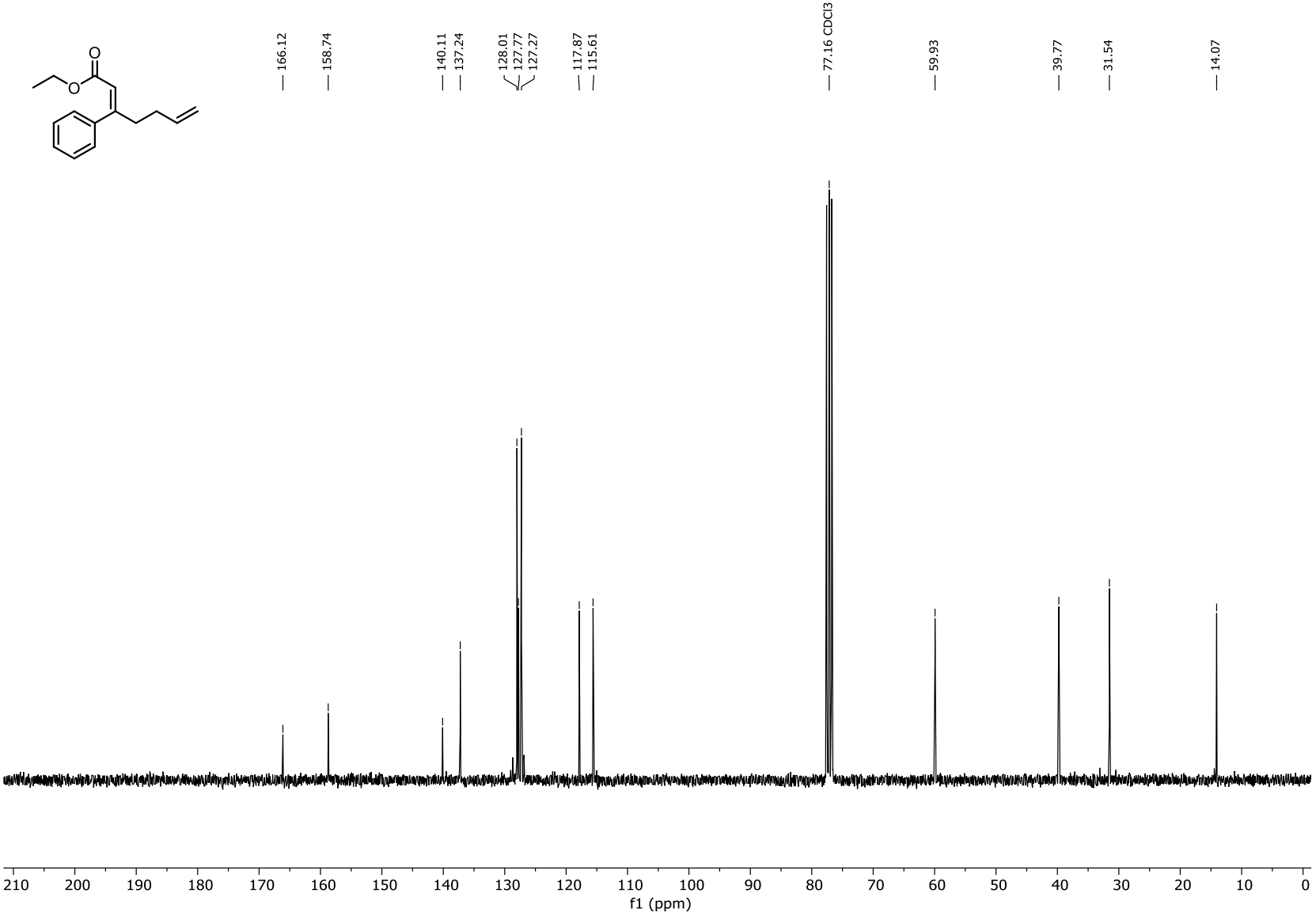
3-(5-Phenylhexa-1,5-dien-3-yl)pyridine (1t): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



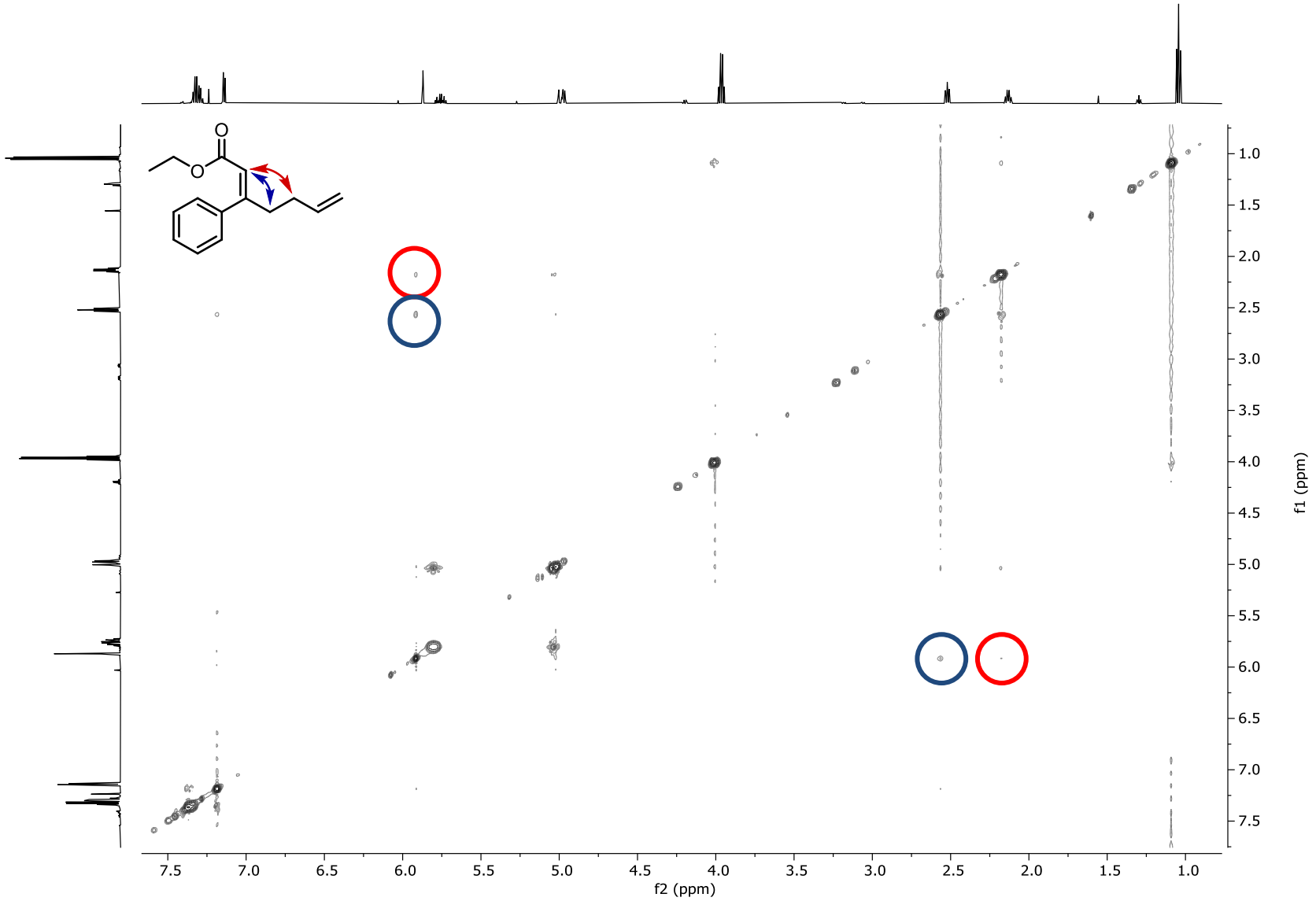
Ethyl 3-phenylhepta-2,6-dienoate (1u): ^{1}H NMR (300 MHz, $CDCl_3$)



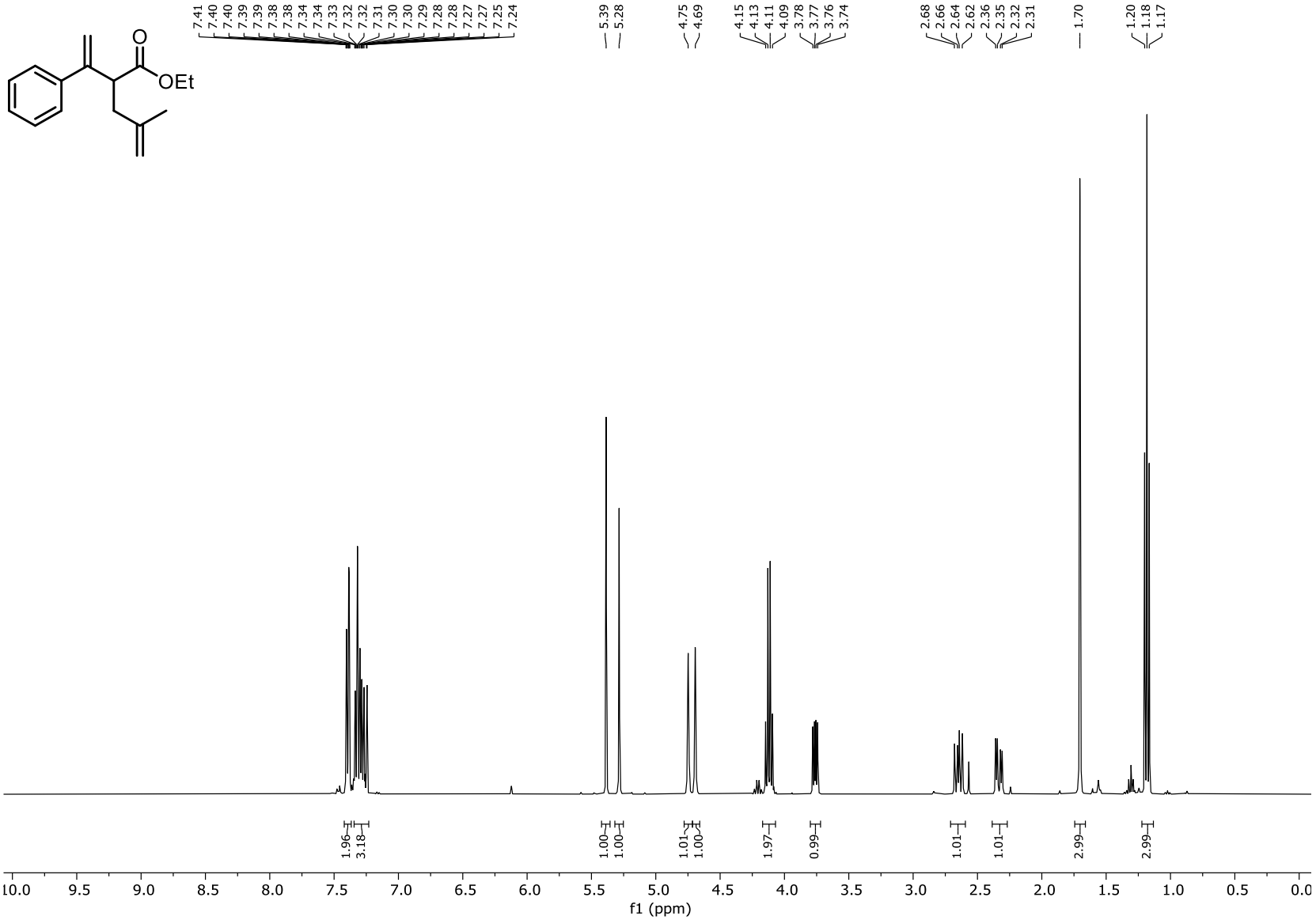
Ethyl 3-phenylhepta-2,6-dienoate (1u): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



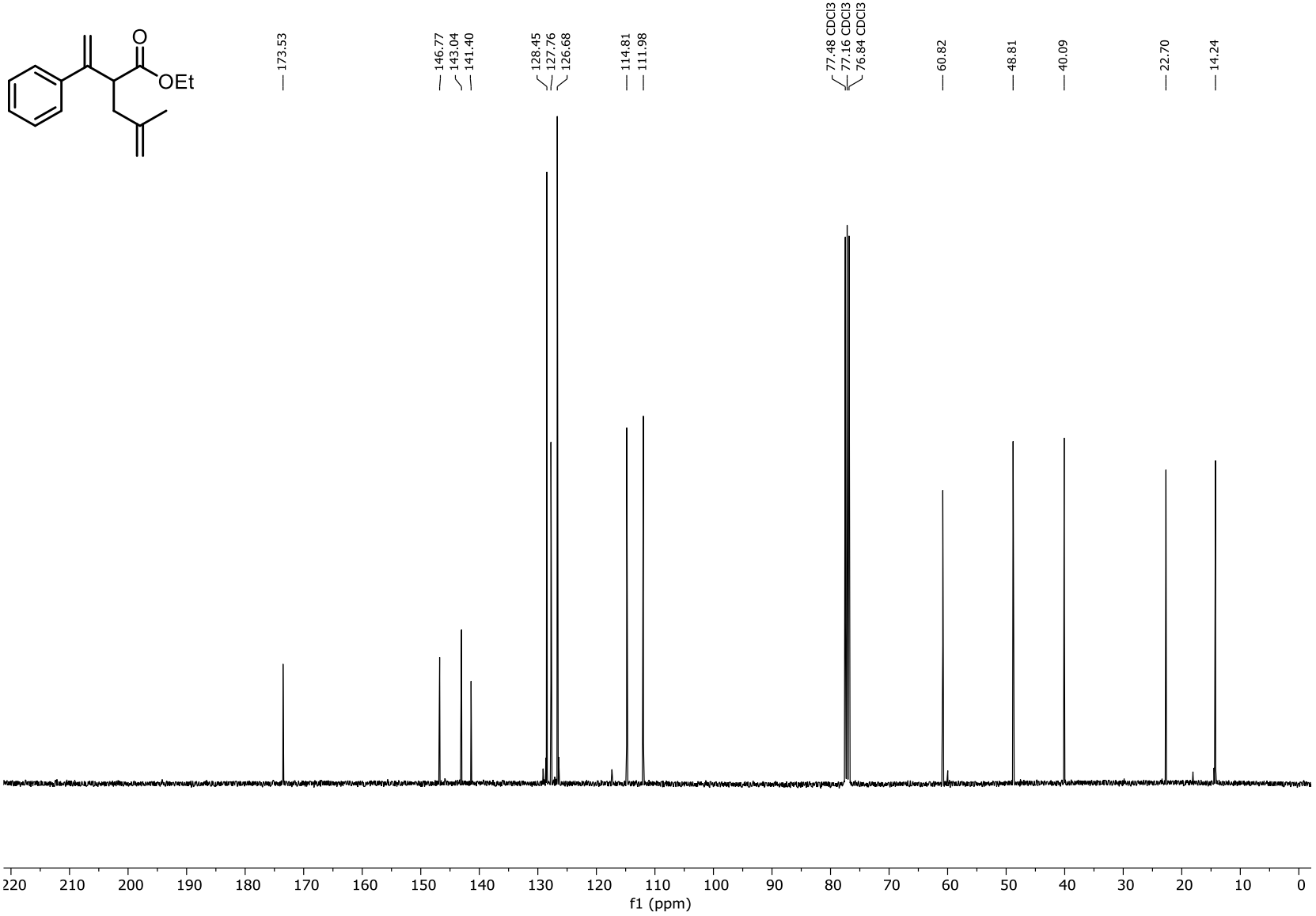
Ethyl (*E*)-3-phenylhepta-2,6-dienoate (1u): ^{1}H NOESY (400 MHz, $CDCl_3$)



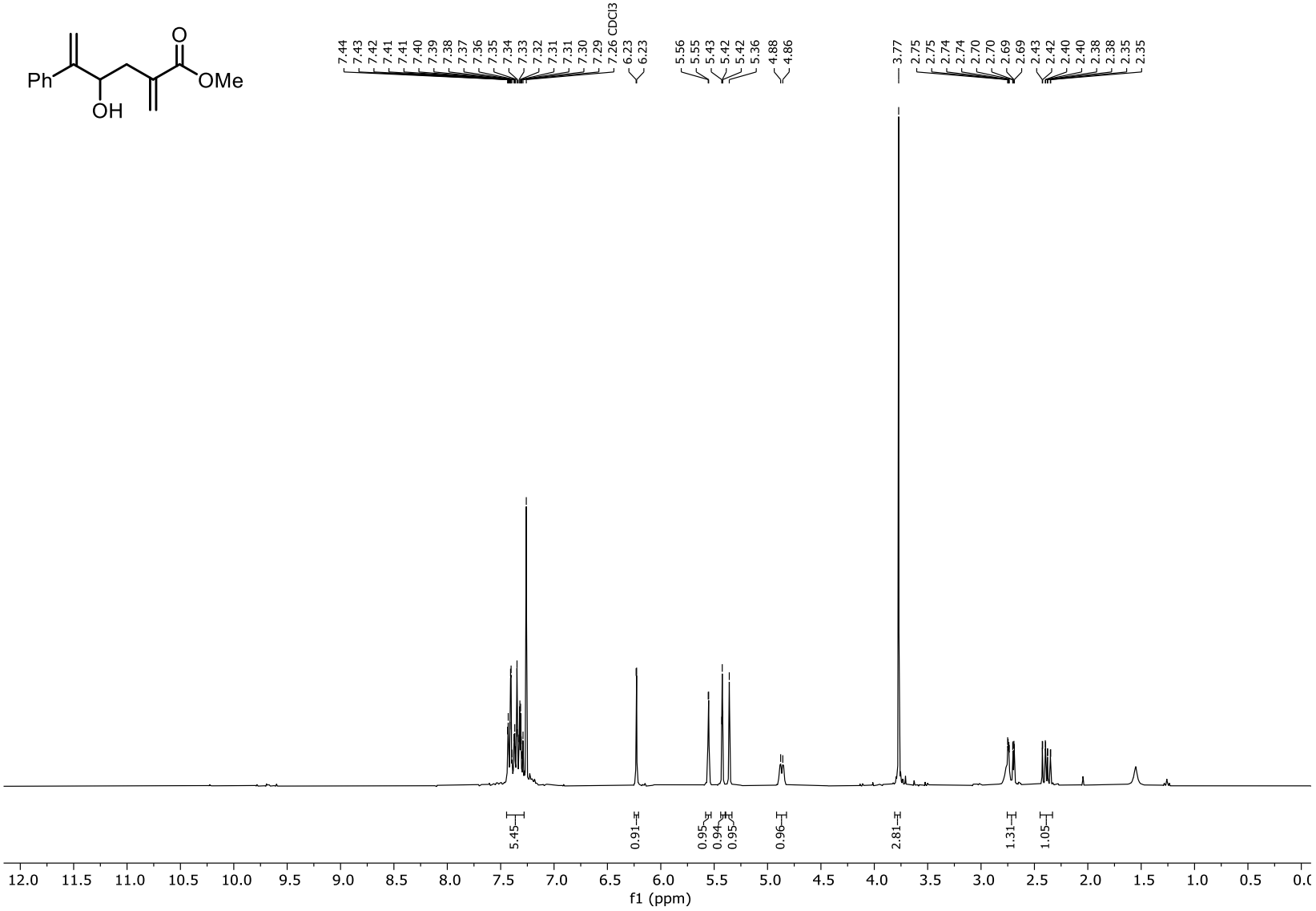
Ethyl 4-methyl-2-(1-phenylvinyl)pent-4-enoate (1v): ^{1}H NMR (400 MHz, $CDCl_3$)



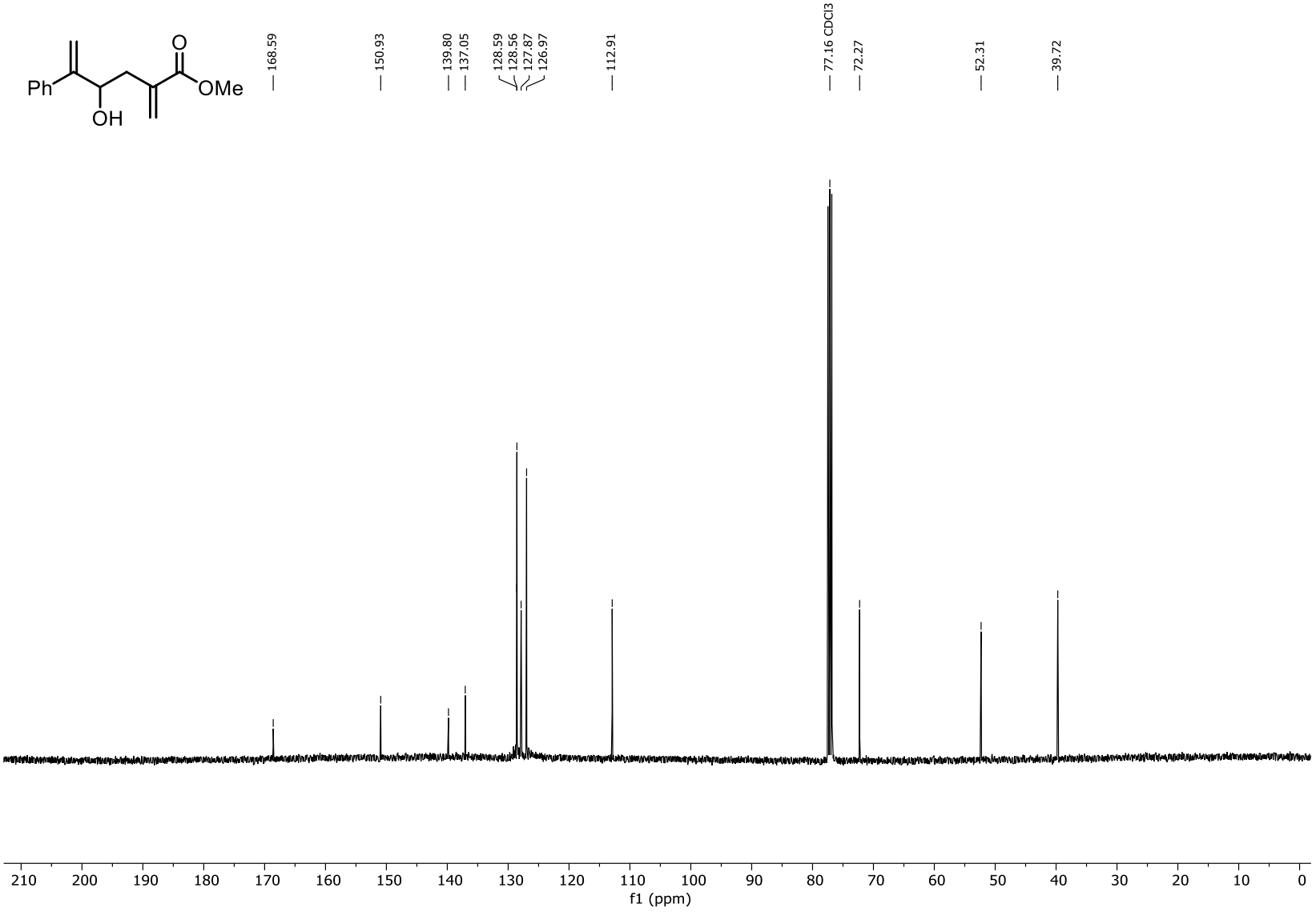
Ethyl 4-methyl-2-(1-phenylvinyl)pent-4-enoate (1v): ^{13}C NMR (101 MHz, $CDCl_3$)



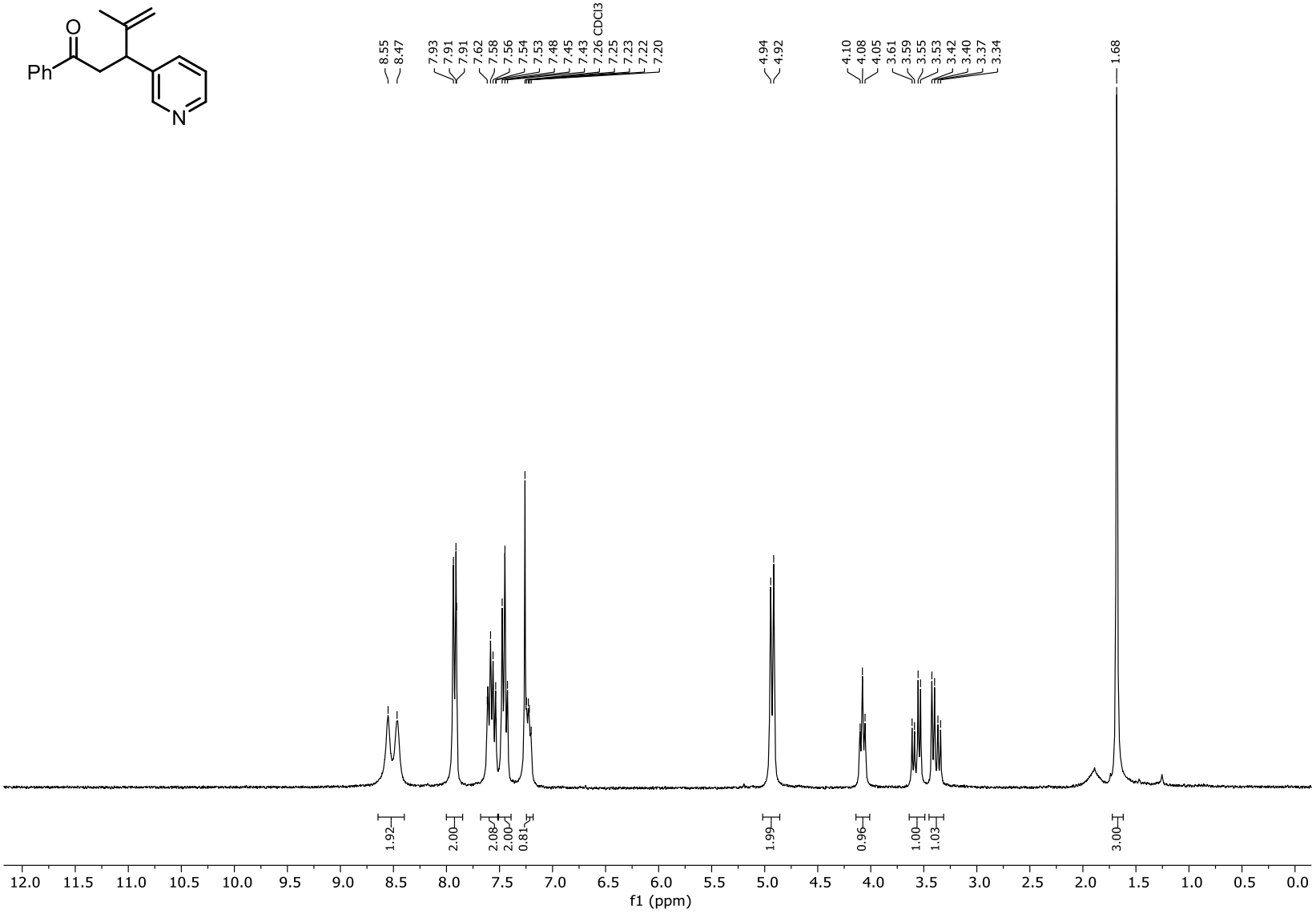
Methyl 4-hydroxy-2-methylene-5-phenylhex-5-enoate (1w): ^{1}H NMR (300 MHz, $CDCl_3$)



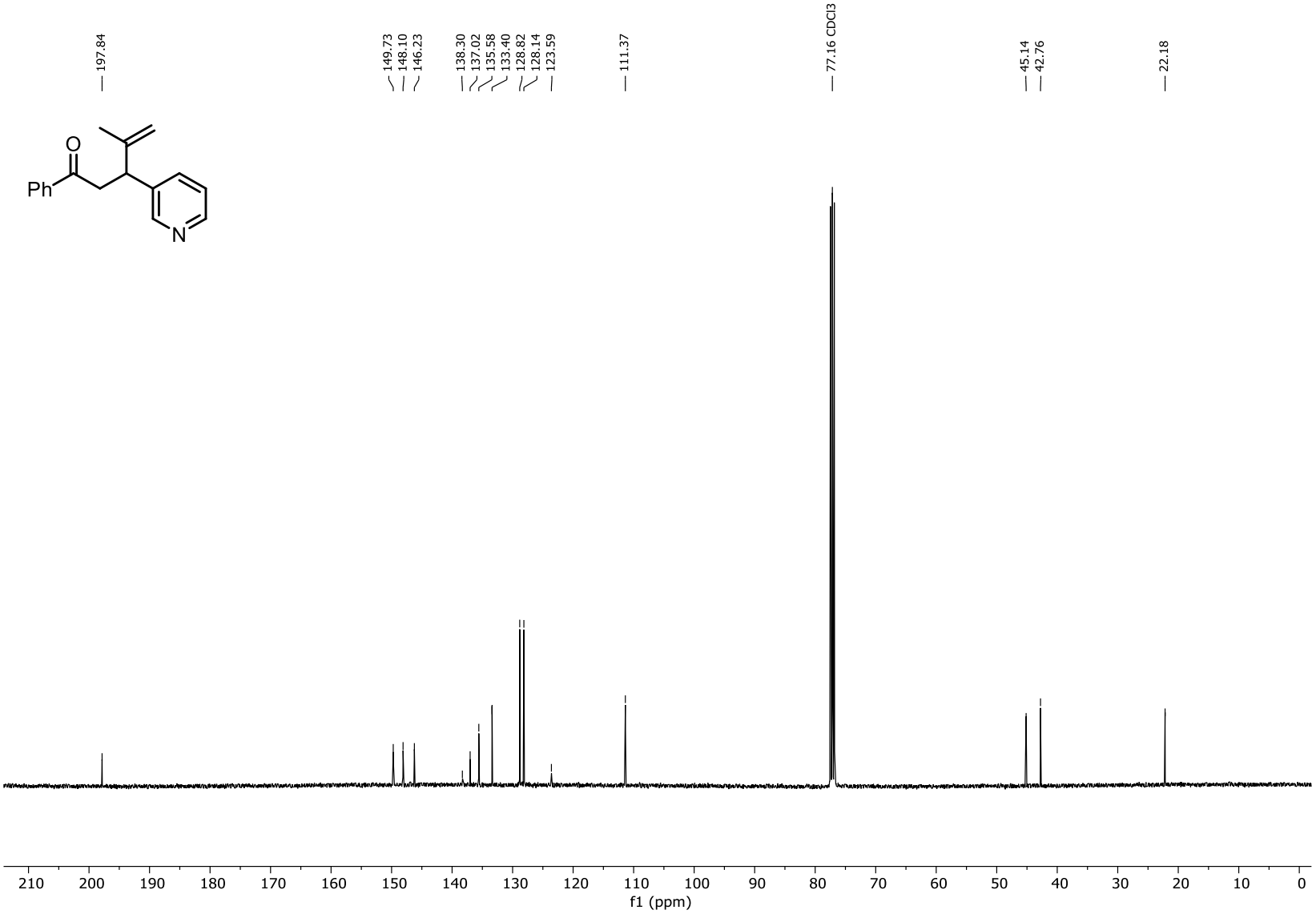
Methyl 4-hydroxy-2-methylene-5-phenylhex-5-enoate (1w): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



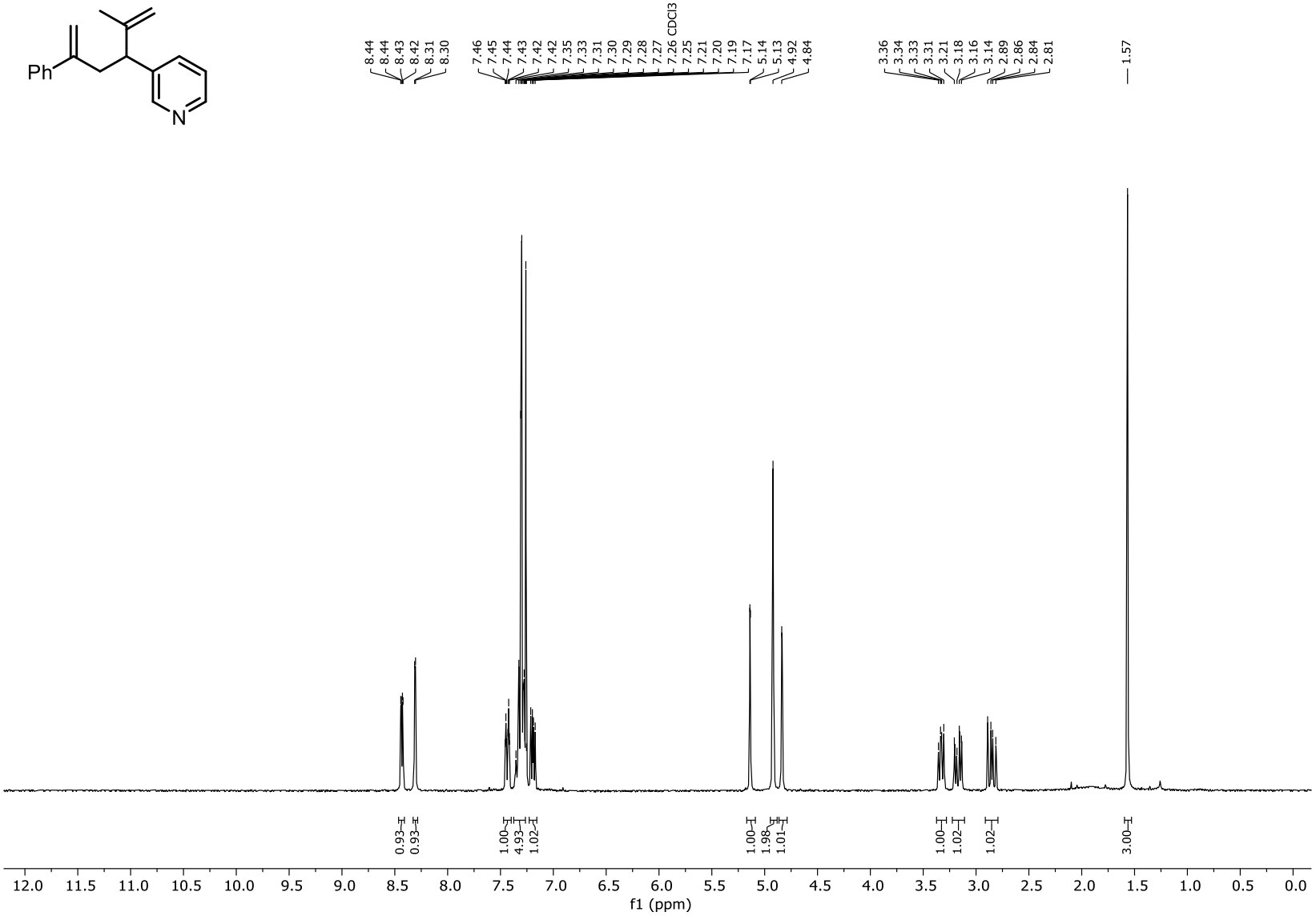
4-Methyl-1-phenyl-3-(pyridin-3-yl)pent-4-en-1-one (S23): ^{1}H NMR (300 MHz, $CDCl_3$)



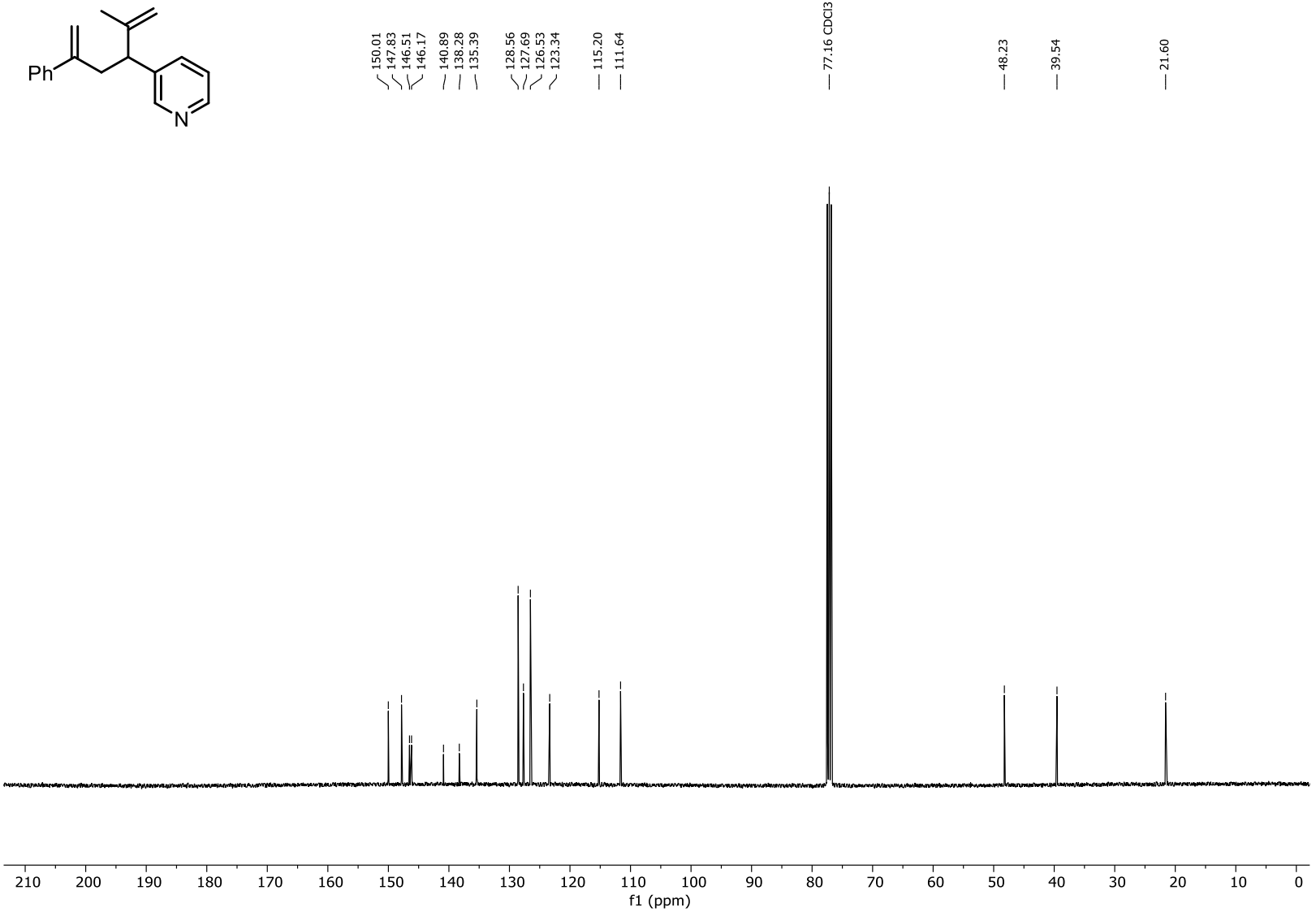
4-Methyl-1-phenyl-3-(pyridin-3-yl)pent-4-en-1-one (S23): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



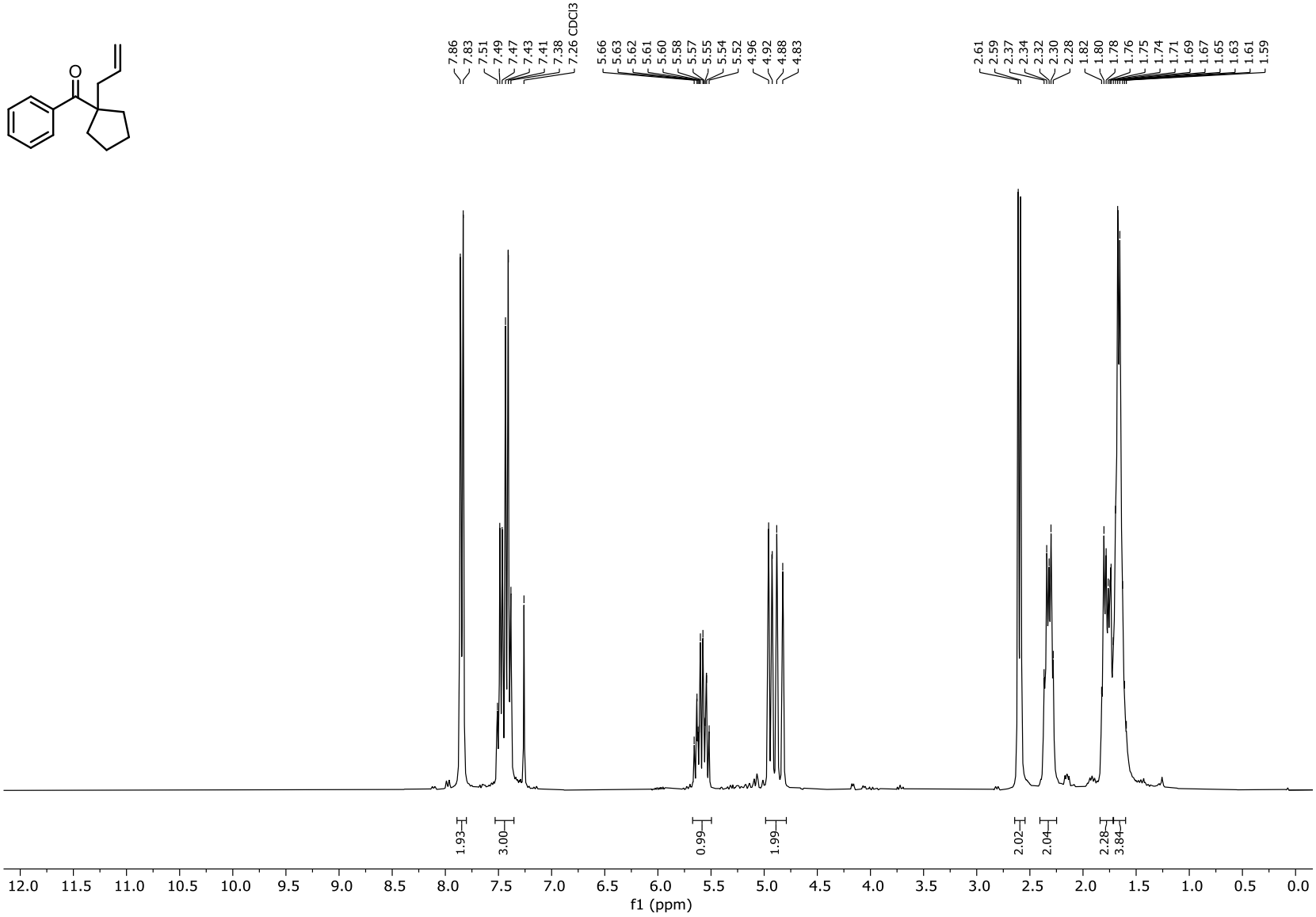
3-(2-Methyl-5-phenylhexa-1,5-dien-3-yl)pyridine (1x): ^{1}H NMR (300 MHz, $CDCl_3$)



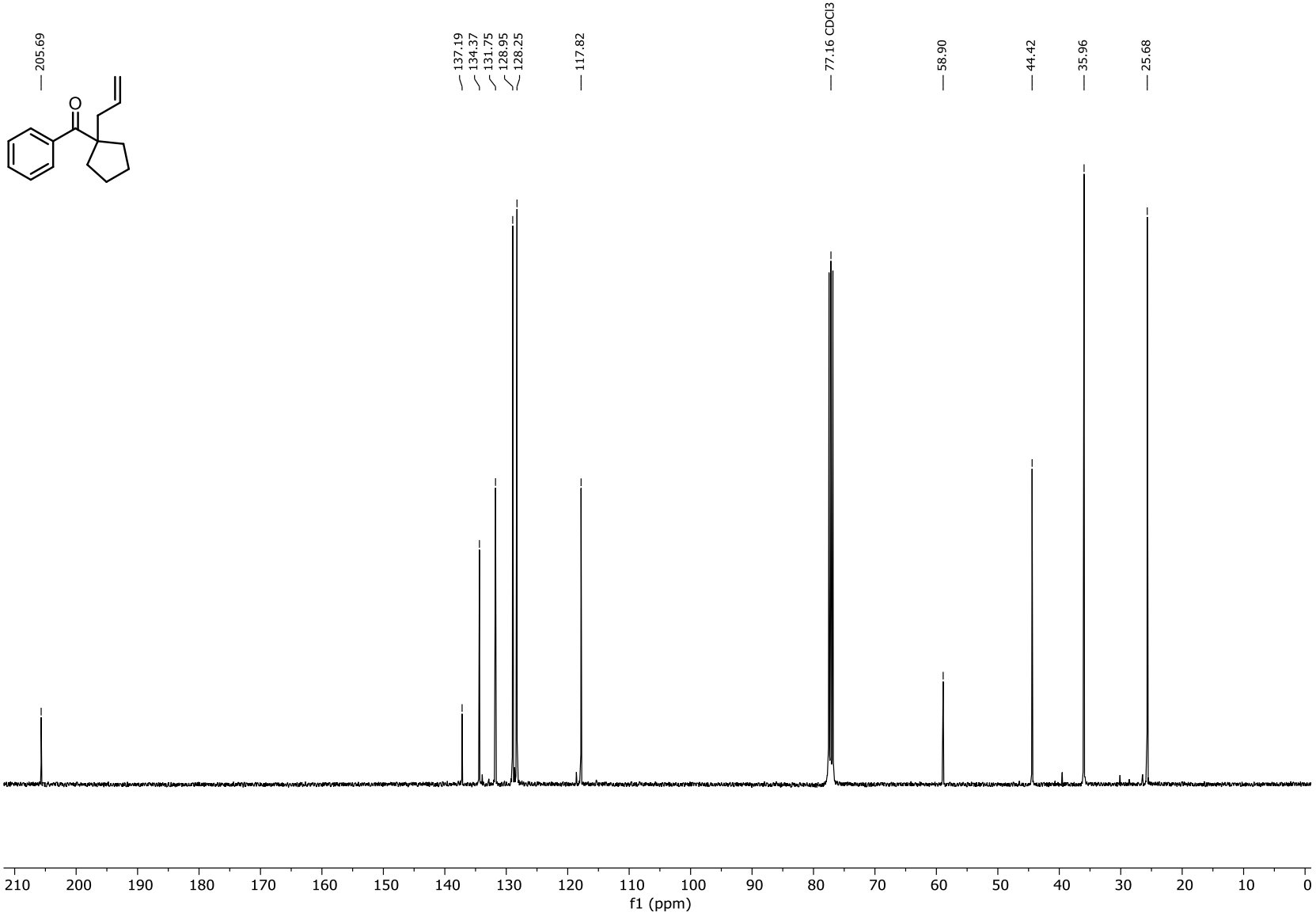
3-(2-Methyl-5-phenylhexa-1,5-dien-3-yl)pyridine (1x): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



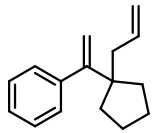
(1-Allylcyclopentyl)(phenyl)methanone (S24): ^{1}H NMR (300 MHz, $CDCl_3$)



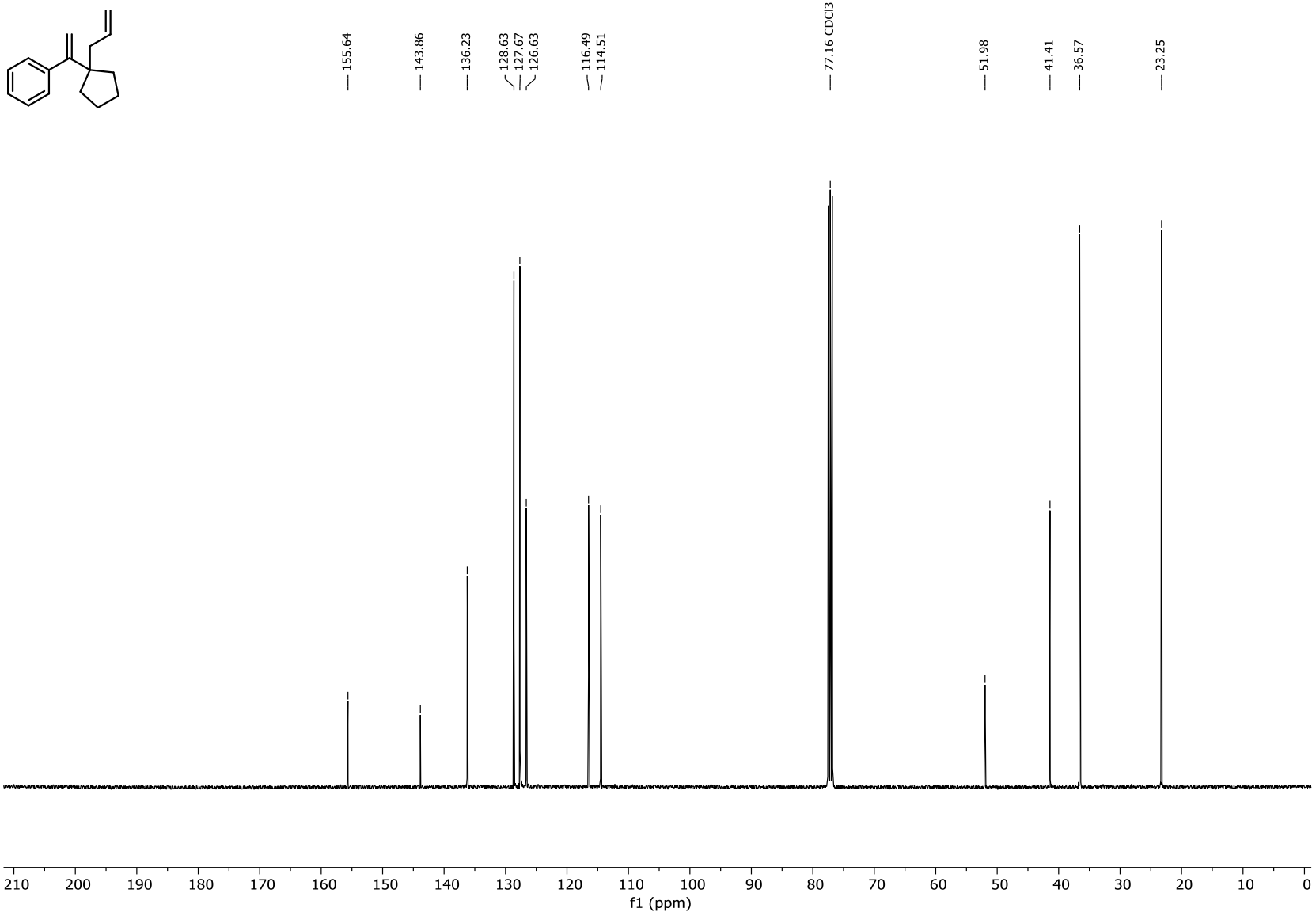
(1-Allylcyclopentyl)(phenyl)methanone (S24): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



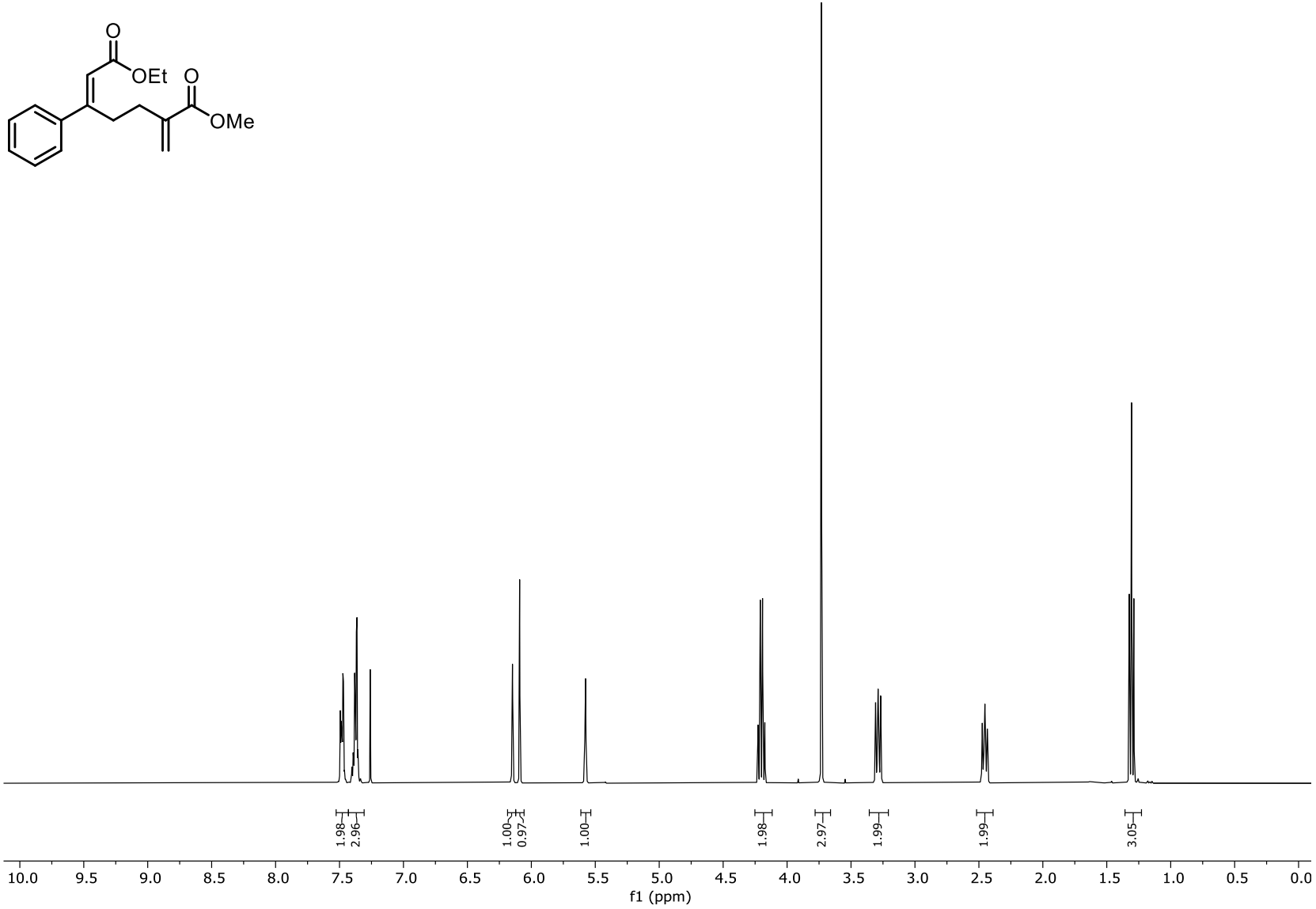
(1-(1-Allylcyclopentyl)vinyl)benzene (1y): ^{1}H NMR (300 MHz, $CDCl_3$)



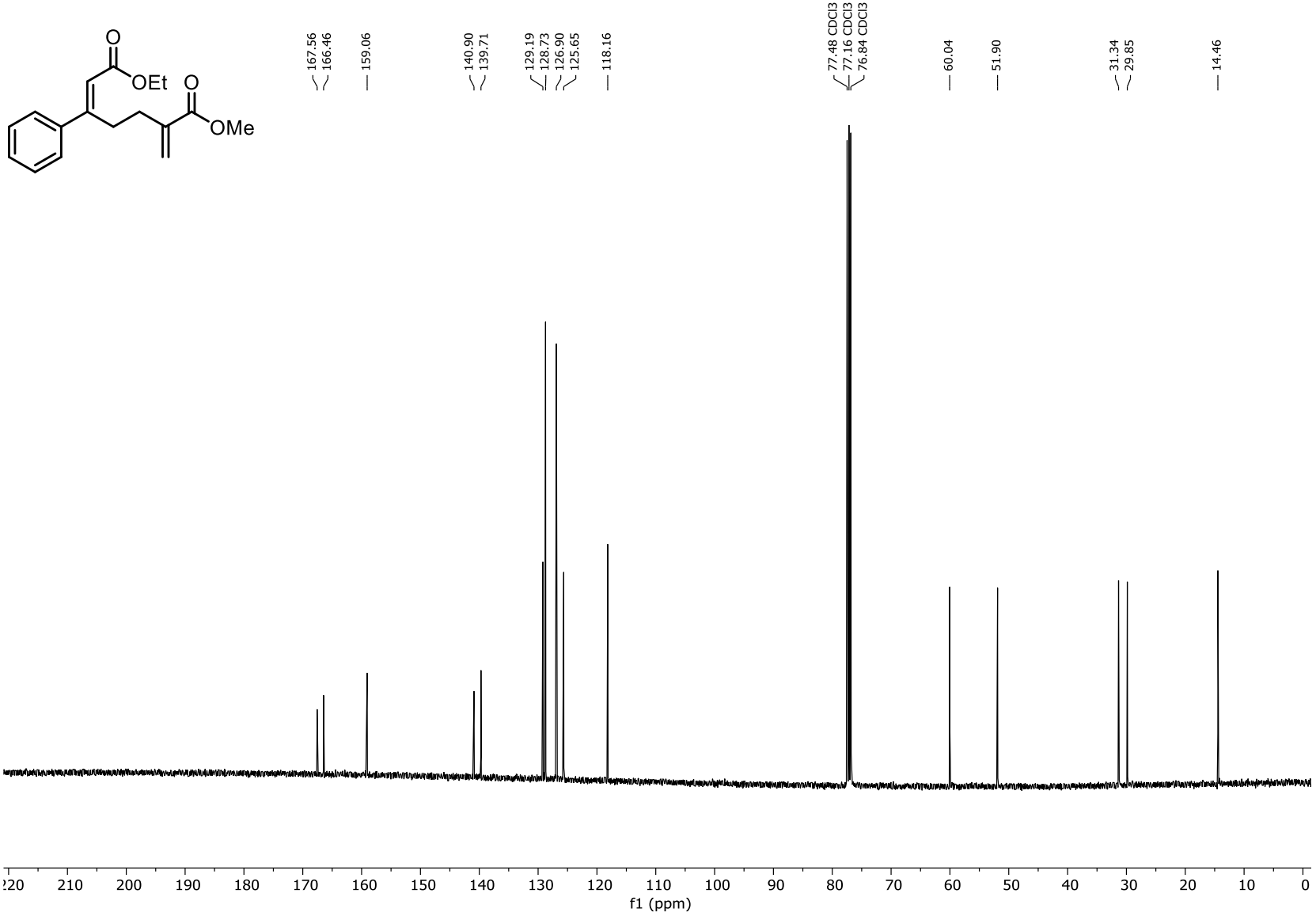
(1-(1-Allylcyclopentyl)vinyl)benzene (1y): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



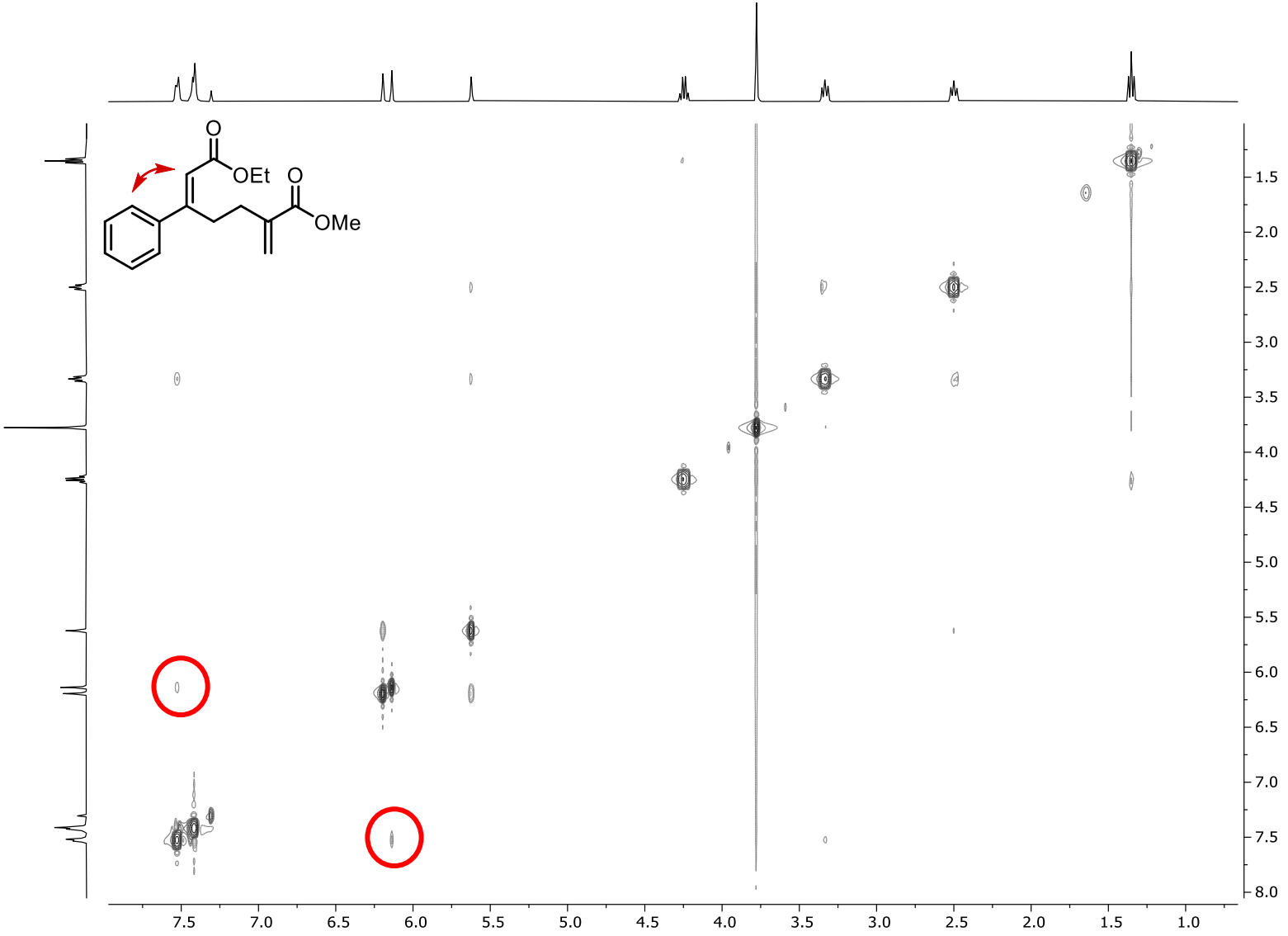
1-Ethyl 7-methyl (*E*)-6-methylene-3-phenylhept-2-enedioate (1z): ^{1}H NMR (400 MHz, $CDCl_3$)



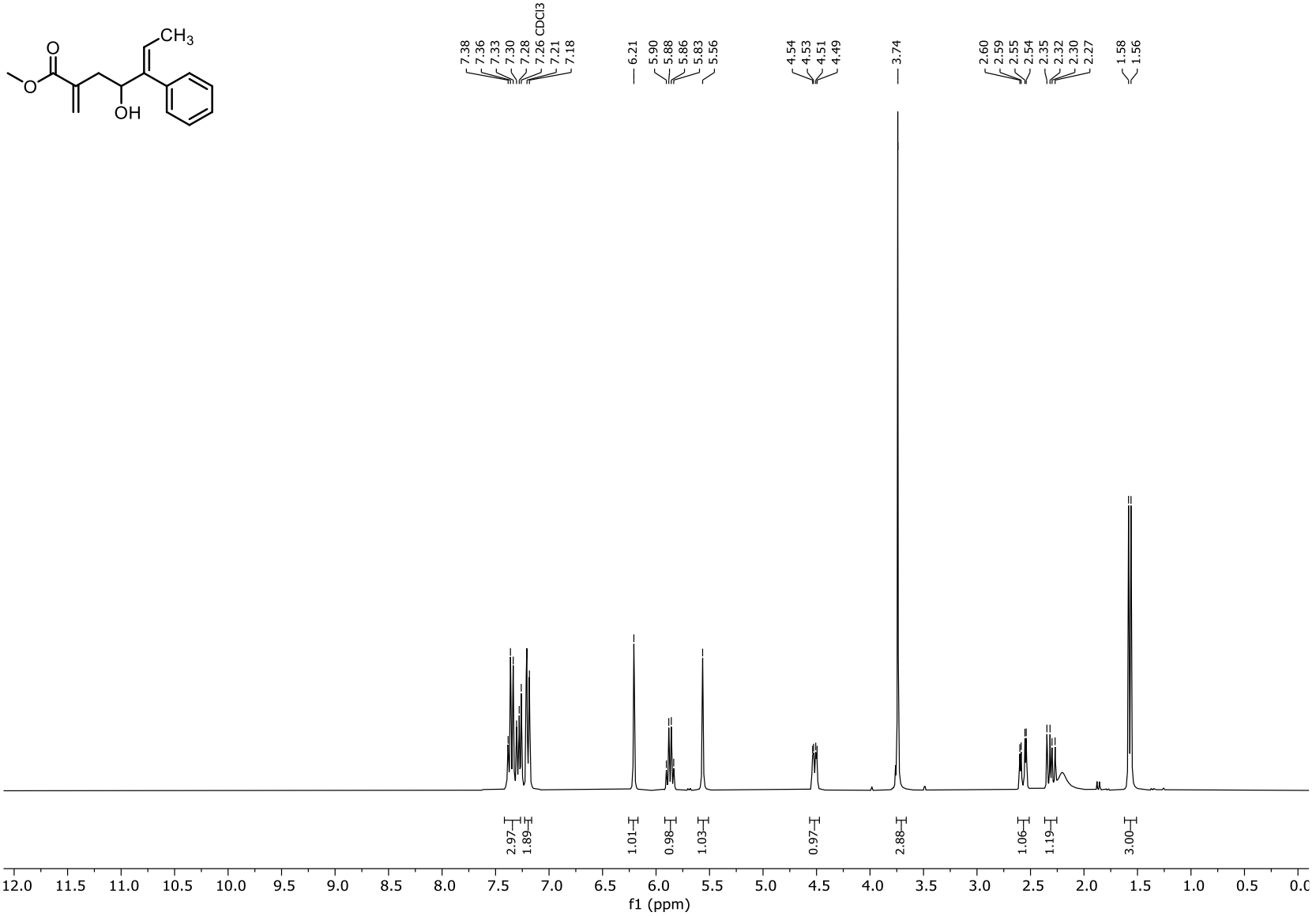
1-Ethyl 7-methyl (*E*)-6-methylene-3-phenylhept-2-enedioate (1z): ^{13}C NMR (101 MHz, $CDCl_3$)



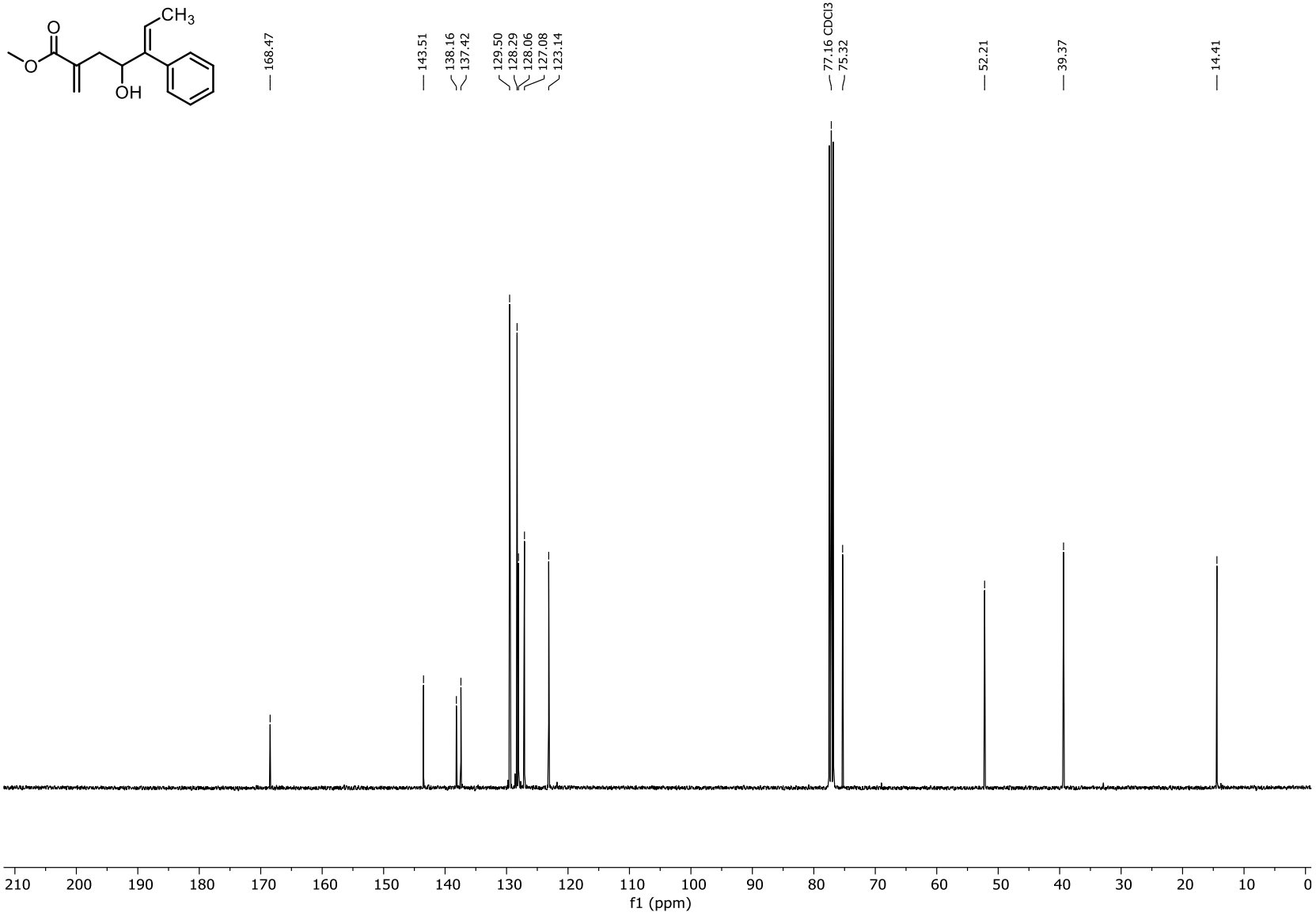
1-Ethyl 7-methyl (*E*)-6-methylene-3-phenylhept-2-enedioate (1z): NOESY (400 MHz, $CDCl_3$)



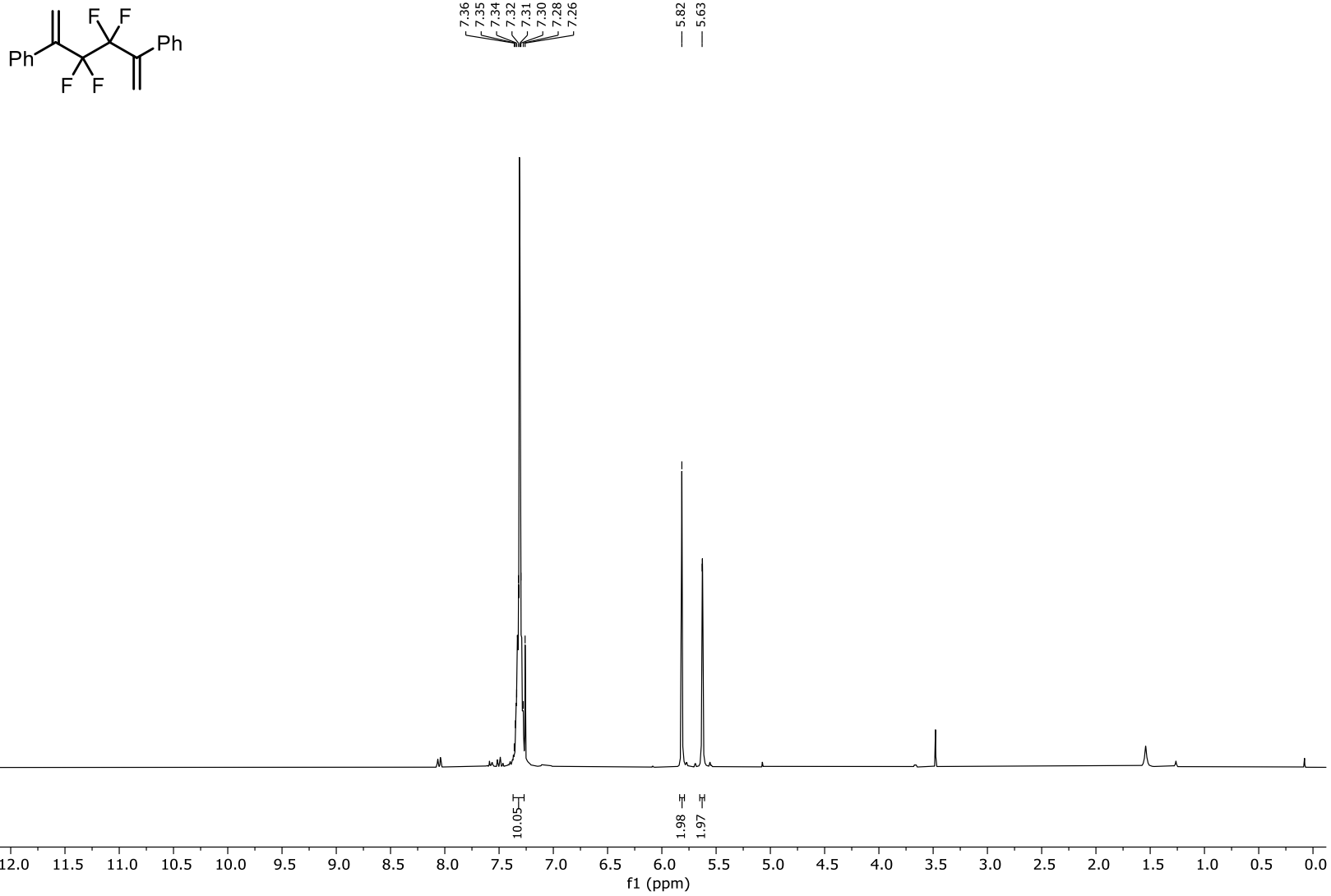
Methyl 4-hydroxy-2-methylene-5-phenylhept-5-enoate (1aa): ^{1}H NMR (300 MHz, $CDCl_3$)



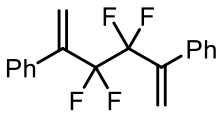
Methyl 4-hydroxy-2-methylene-5-phenylhept-5-enoate (1aa): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



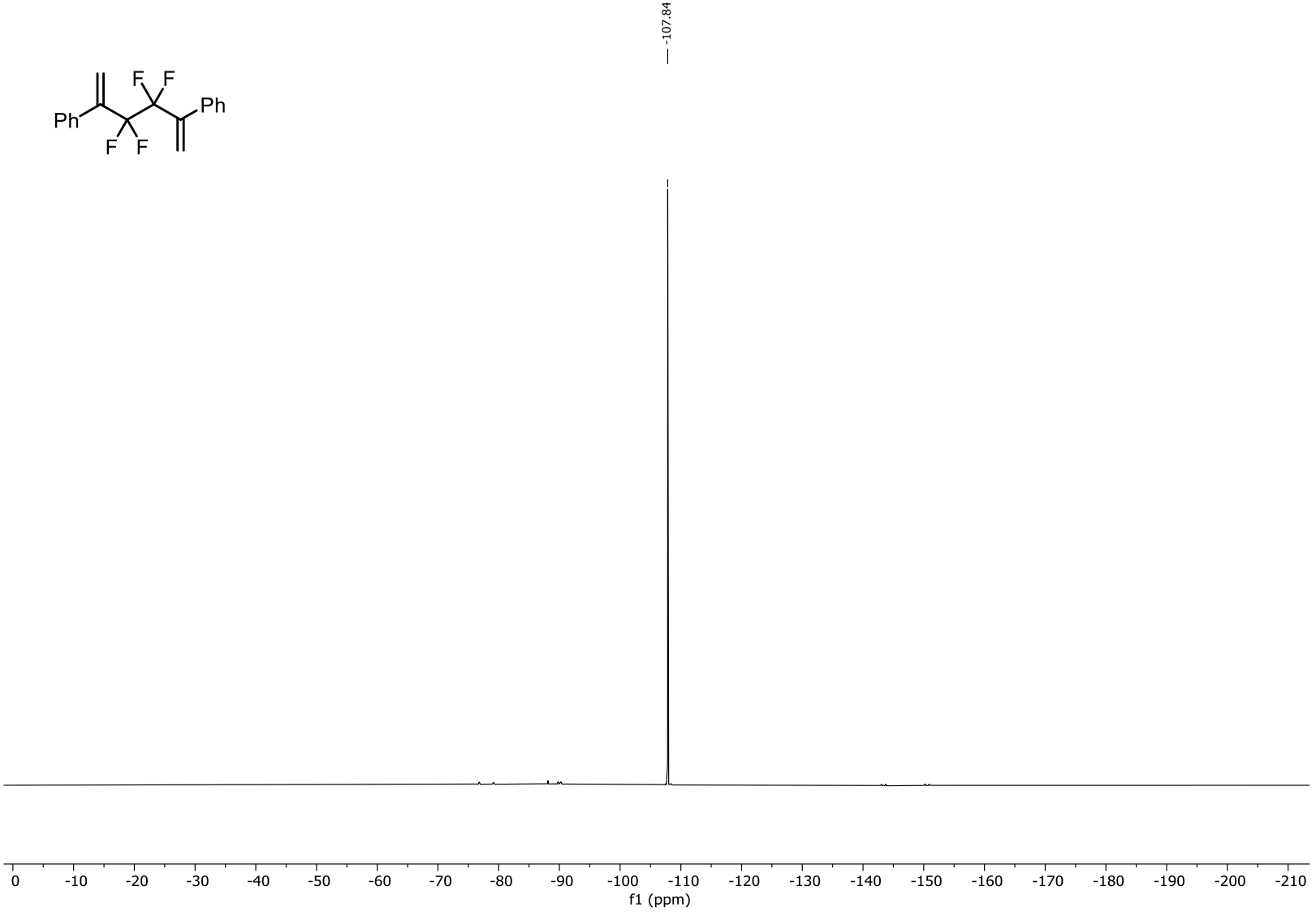
(3,3,4,4-tetrafluorohexa-1,5-diene-2,5-diyl)dibenzene (1ab): ^{1}H NMR (300 MHz, $CDCl_3$)



(3,3,4,4-tetrafluorohexa-1,5-diene-2,5-diyl)dibenzene (1ab): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

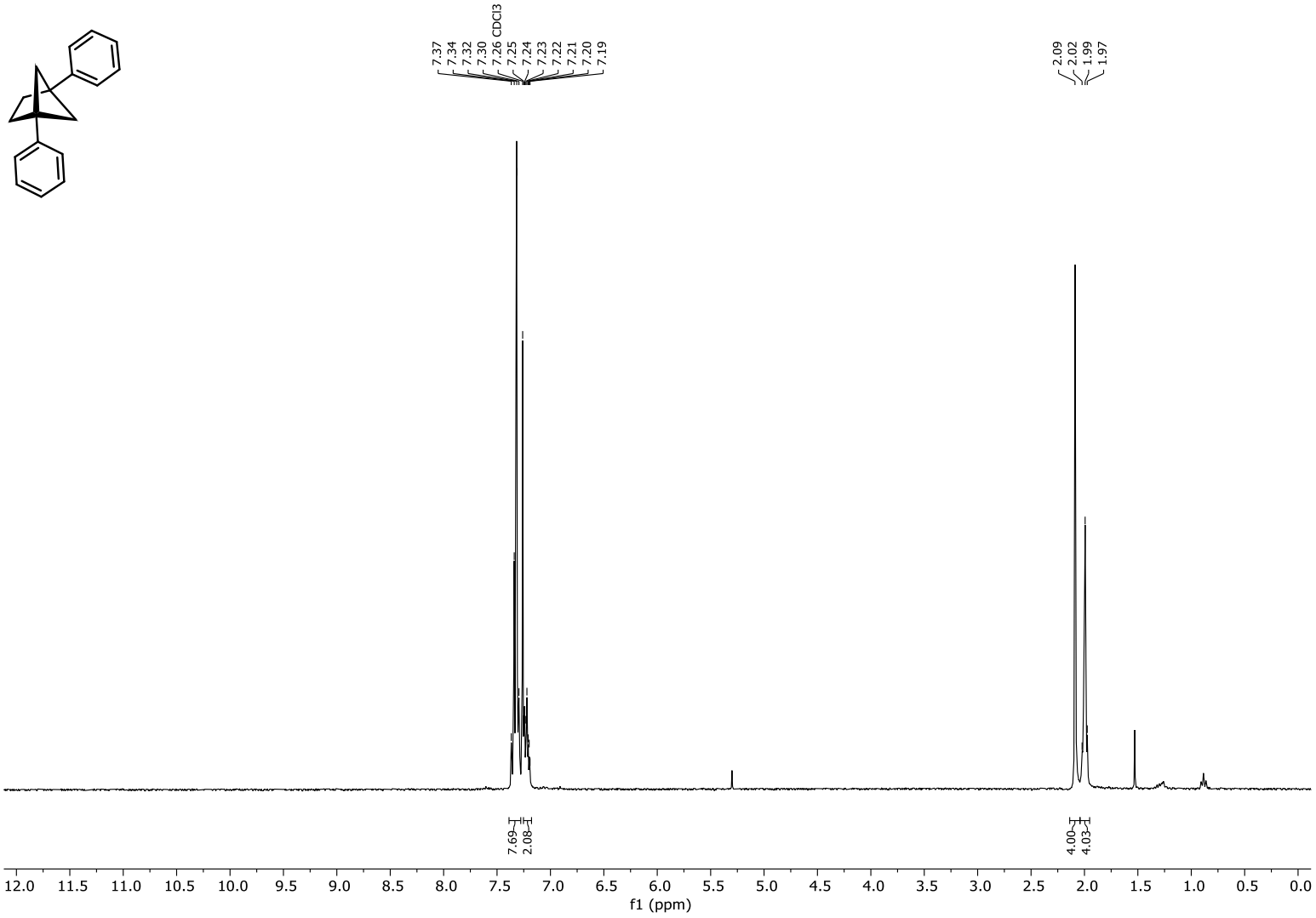


(3,3,4,4-tetrafluorohexa-1,5-diene-2,5-diyl)dibenzene (1ab): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)

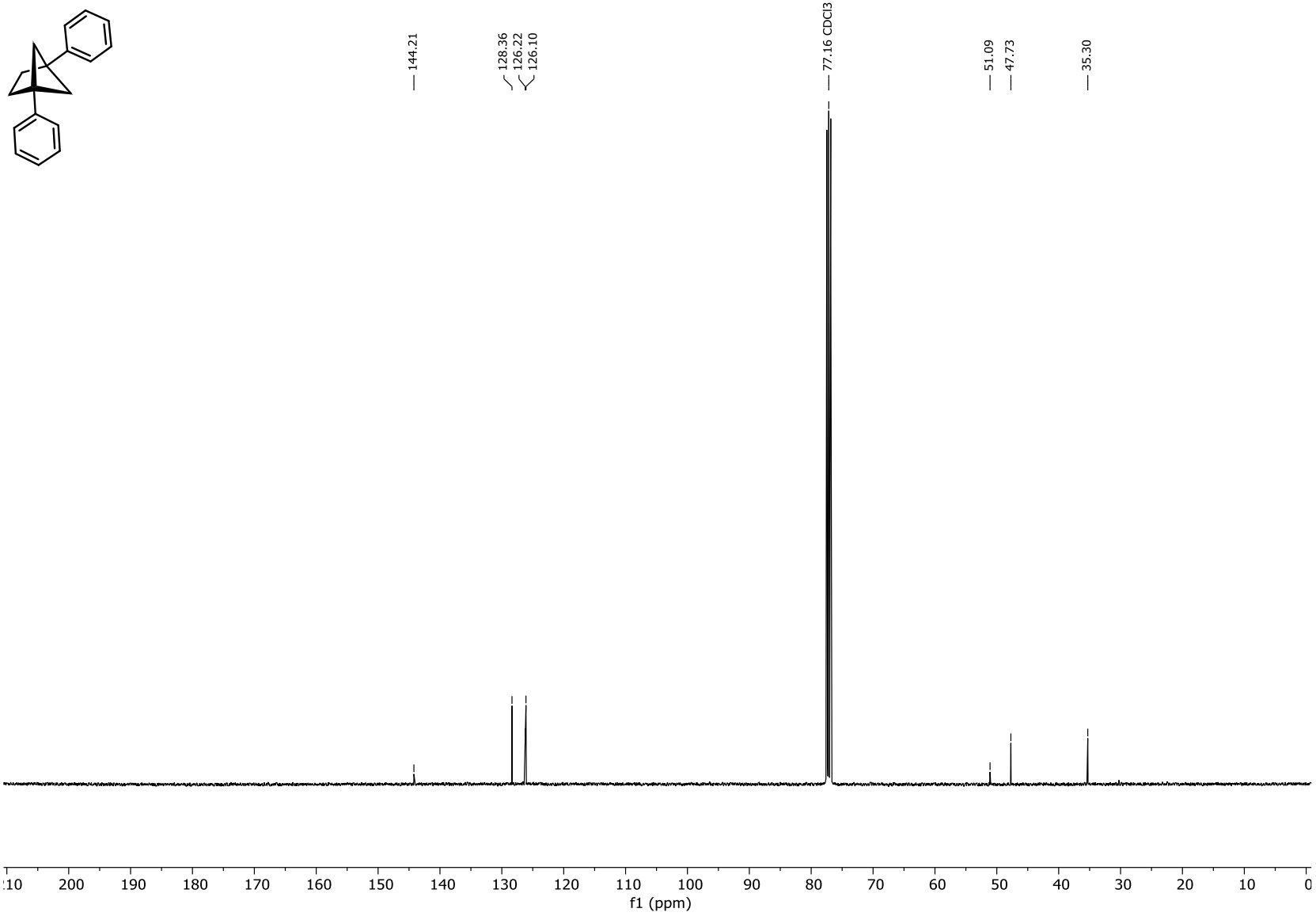


7.2 NMR Spectra of BCH 2a–2ab

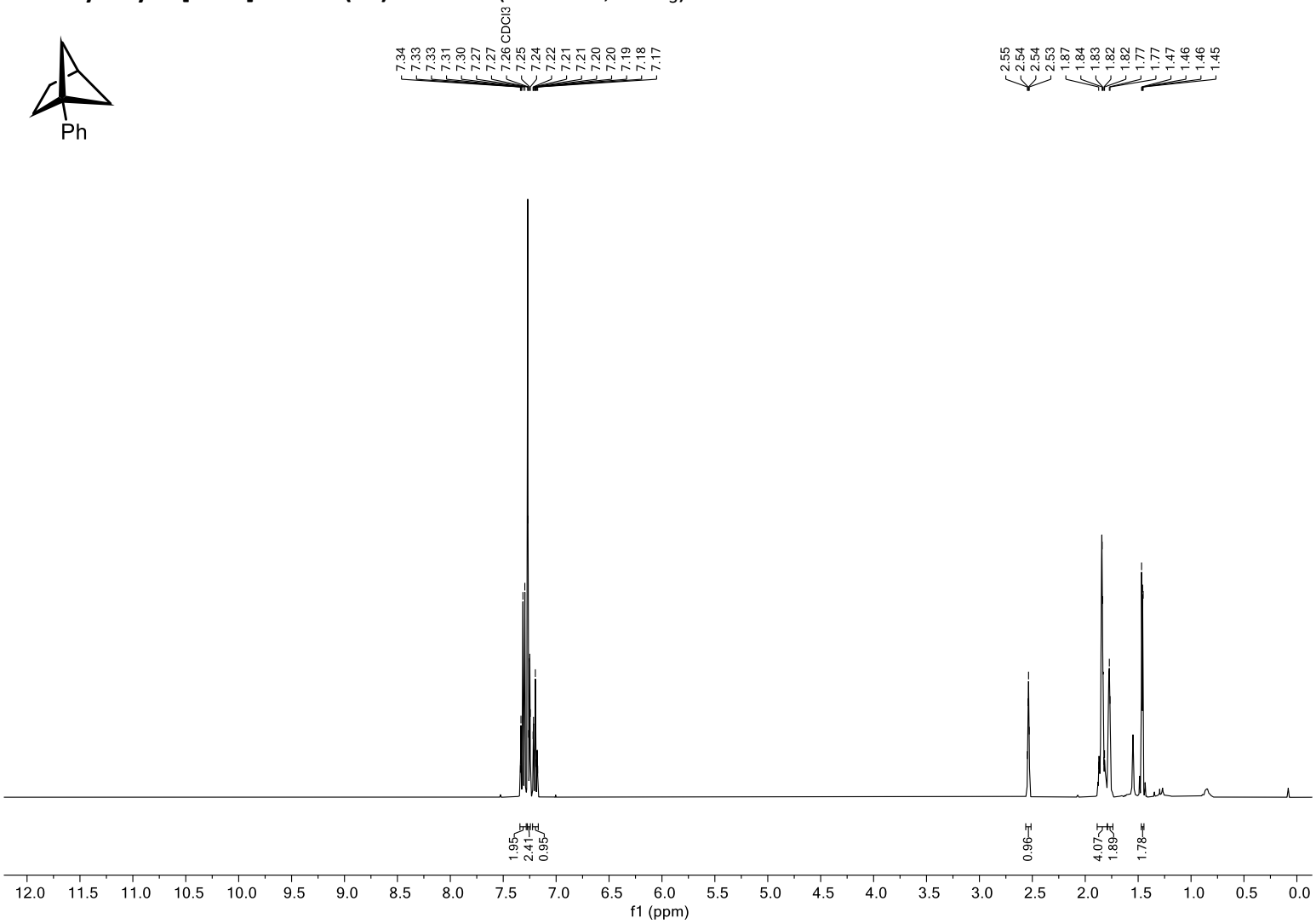
1,4-Diphenylbicyclo[2.1.1]hexane (2a): ^{1}H NMR (300 MHz, $CDCl_3$)



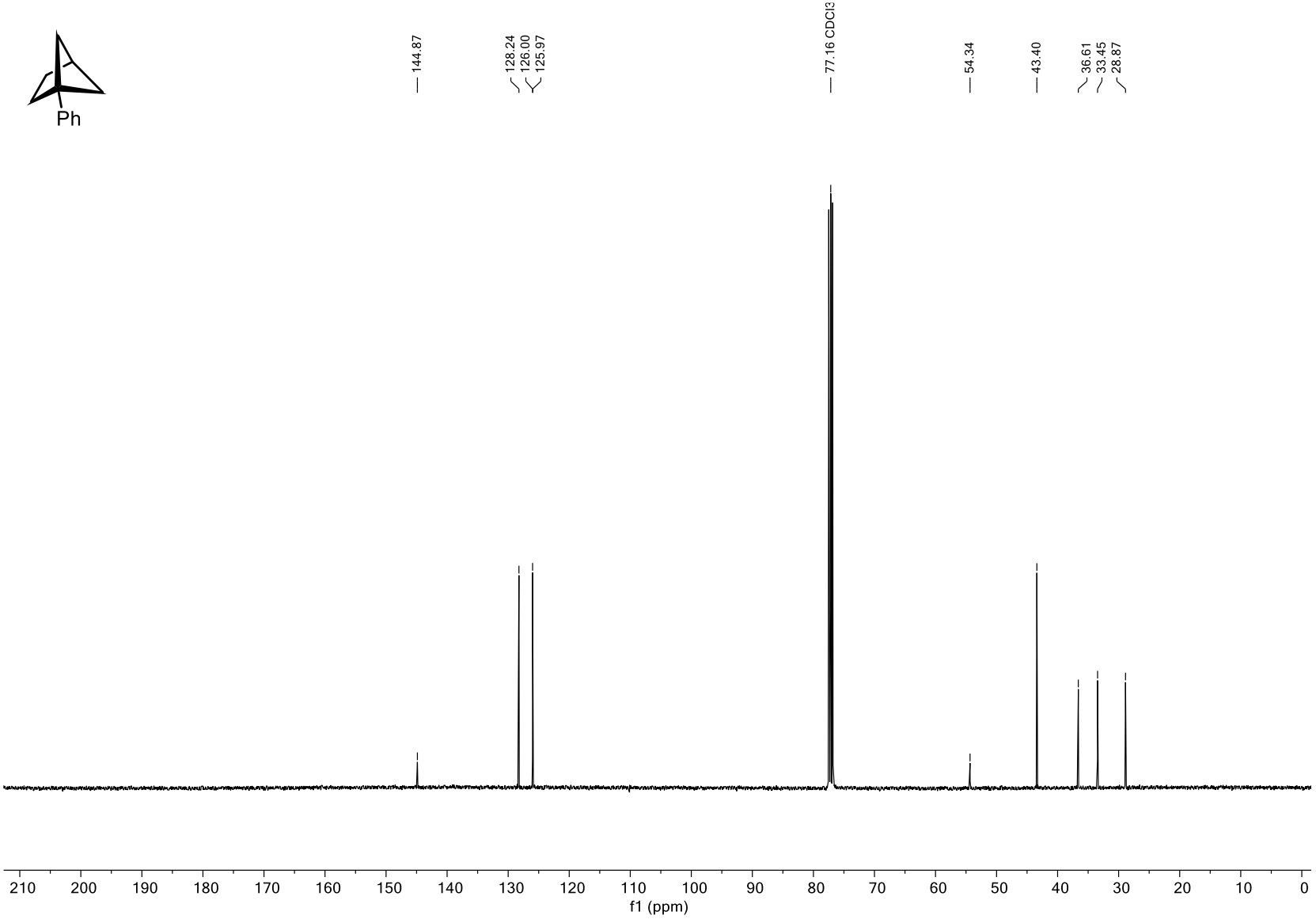
1,4-Diphenylbicyclo[2.1.1]hexane (2a): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



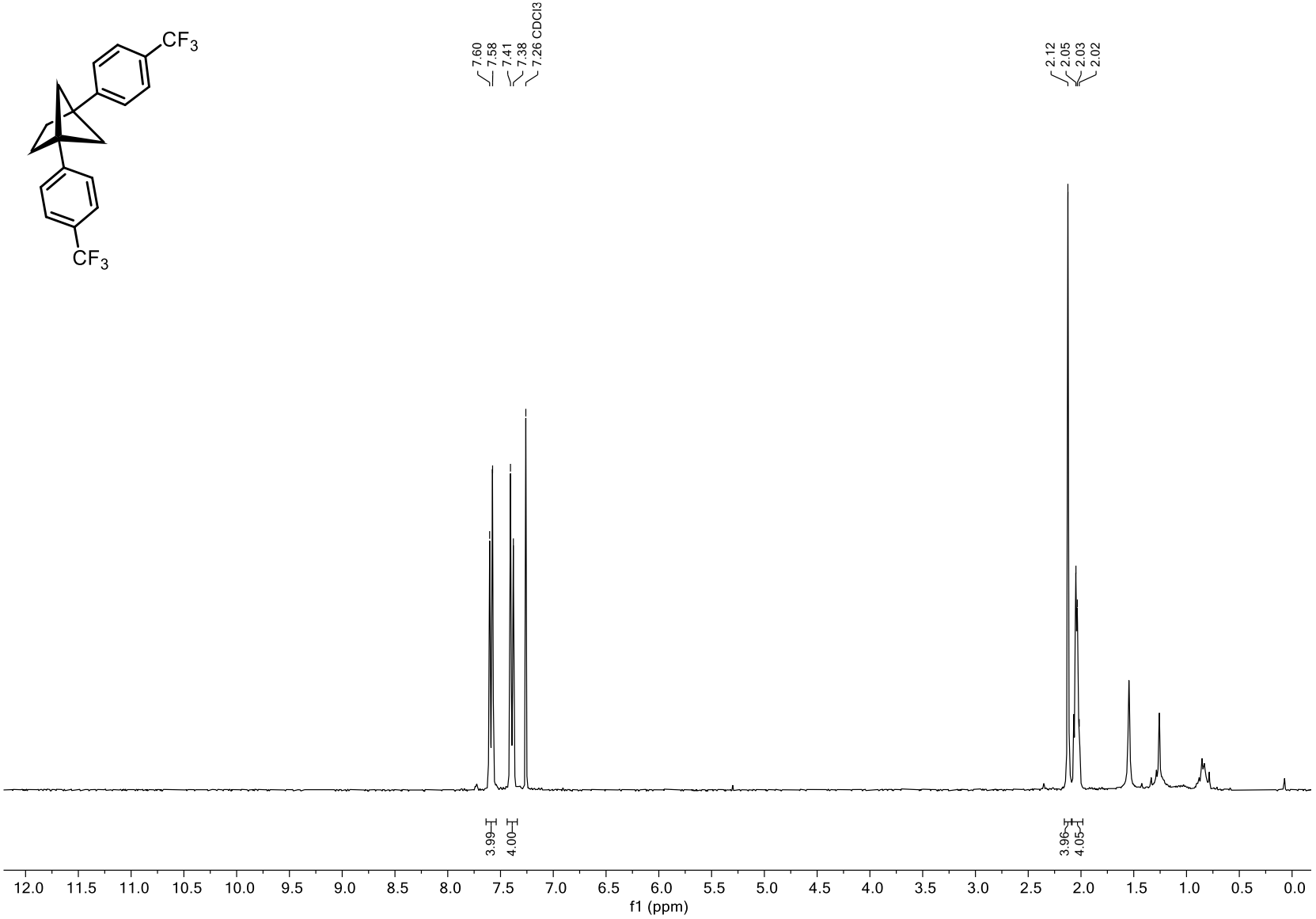
1-Phenylbicyclo[2.1.1]hexane (2b): ^{1}H NMR (300 MHz, $CDCl_3$)



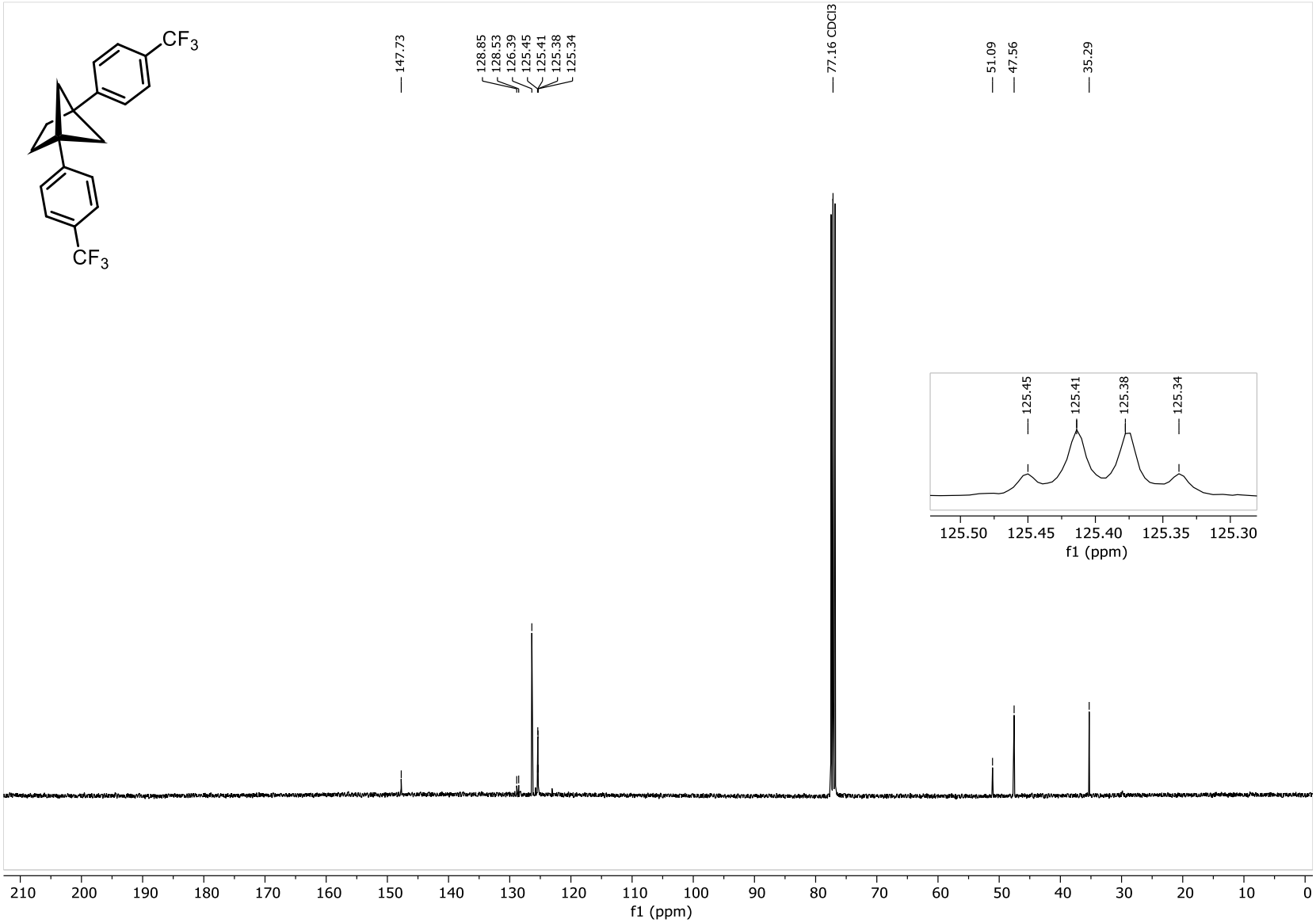
1-Phenylbicyclo[2.1.1]hexane (2b): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



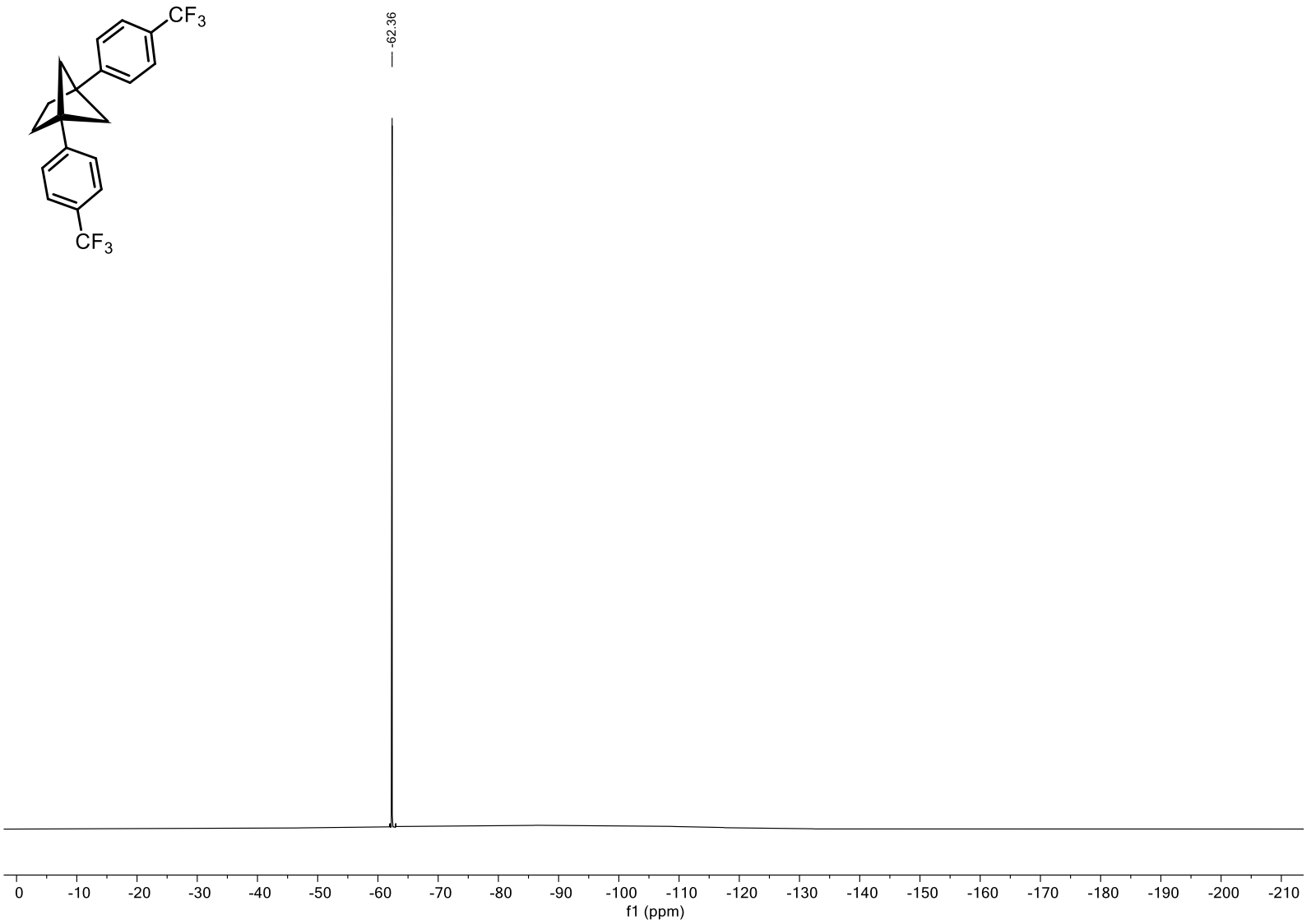
1,4-Bis(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (2c): ^{1}H NMR (300 MHz, $CDCl_3$)



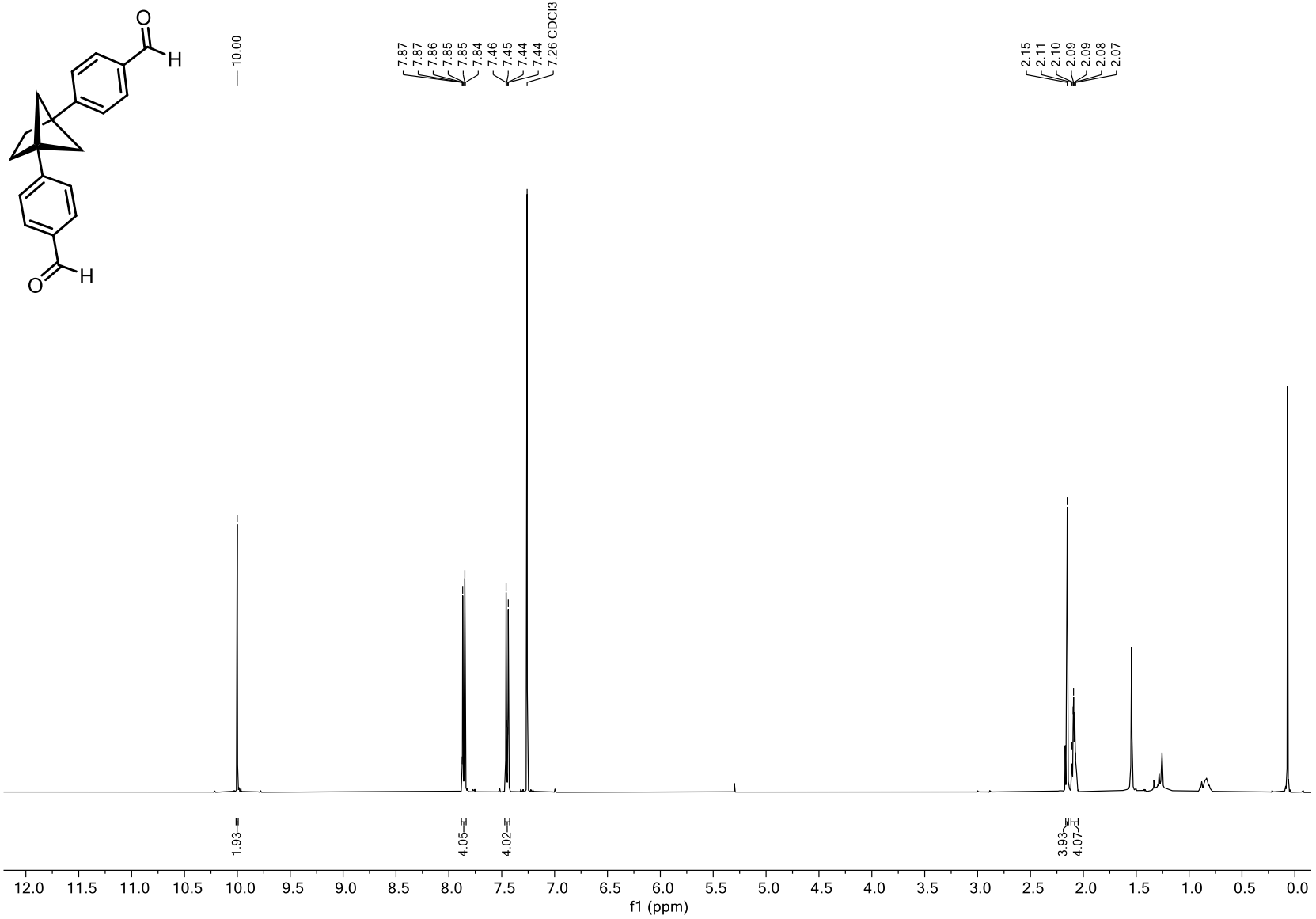
1,4-Bis(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (2c): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



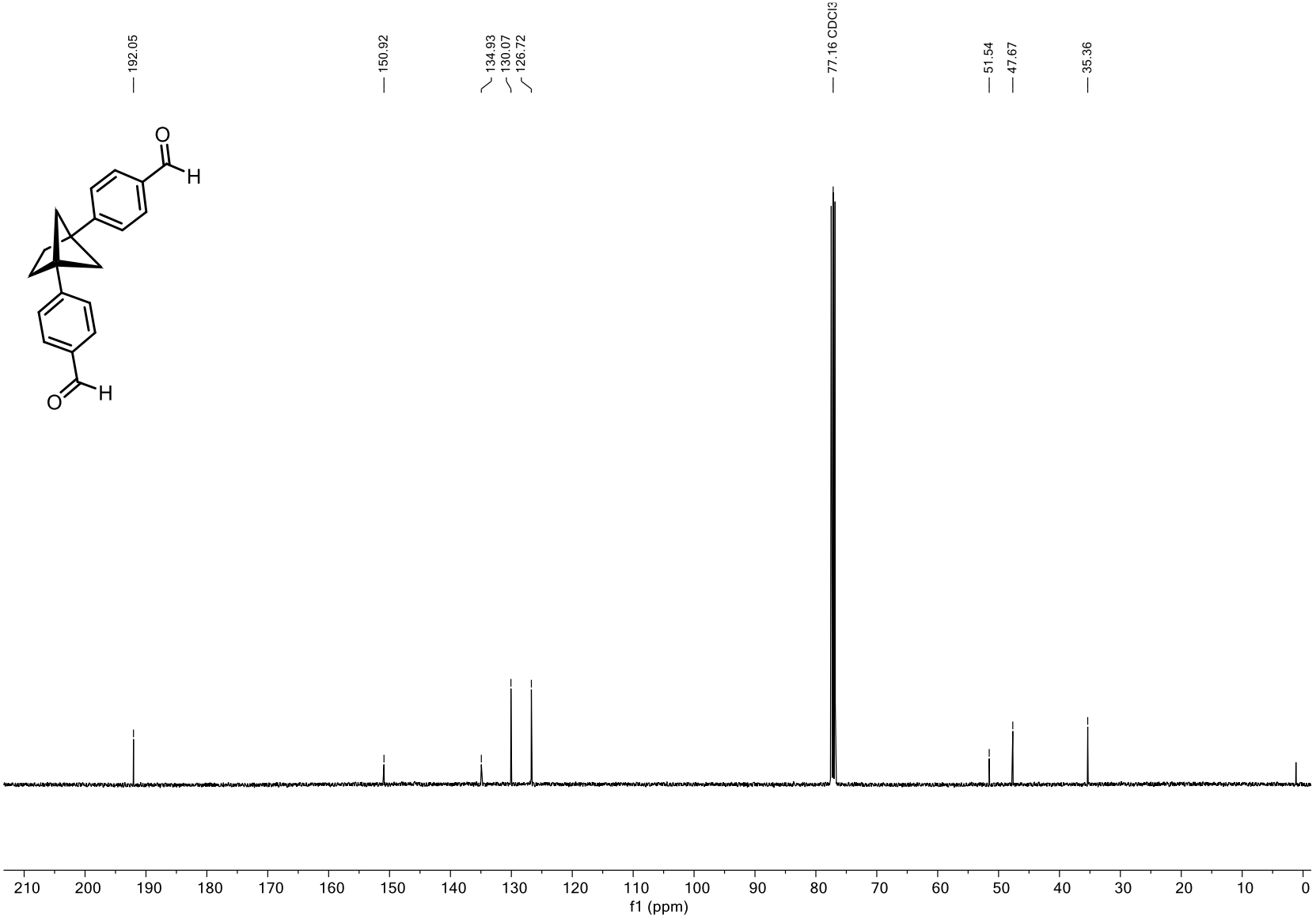
1,4-Bis(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (2c): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



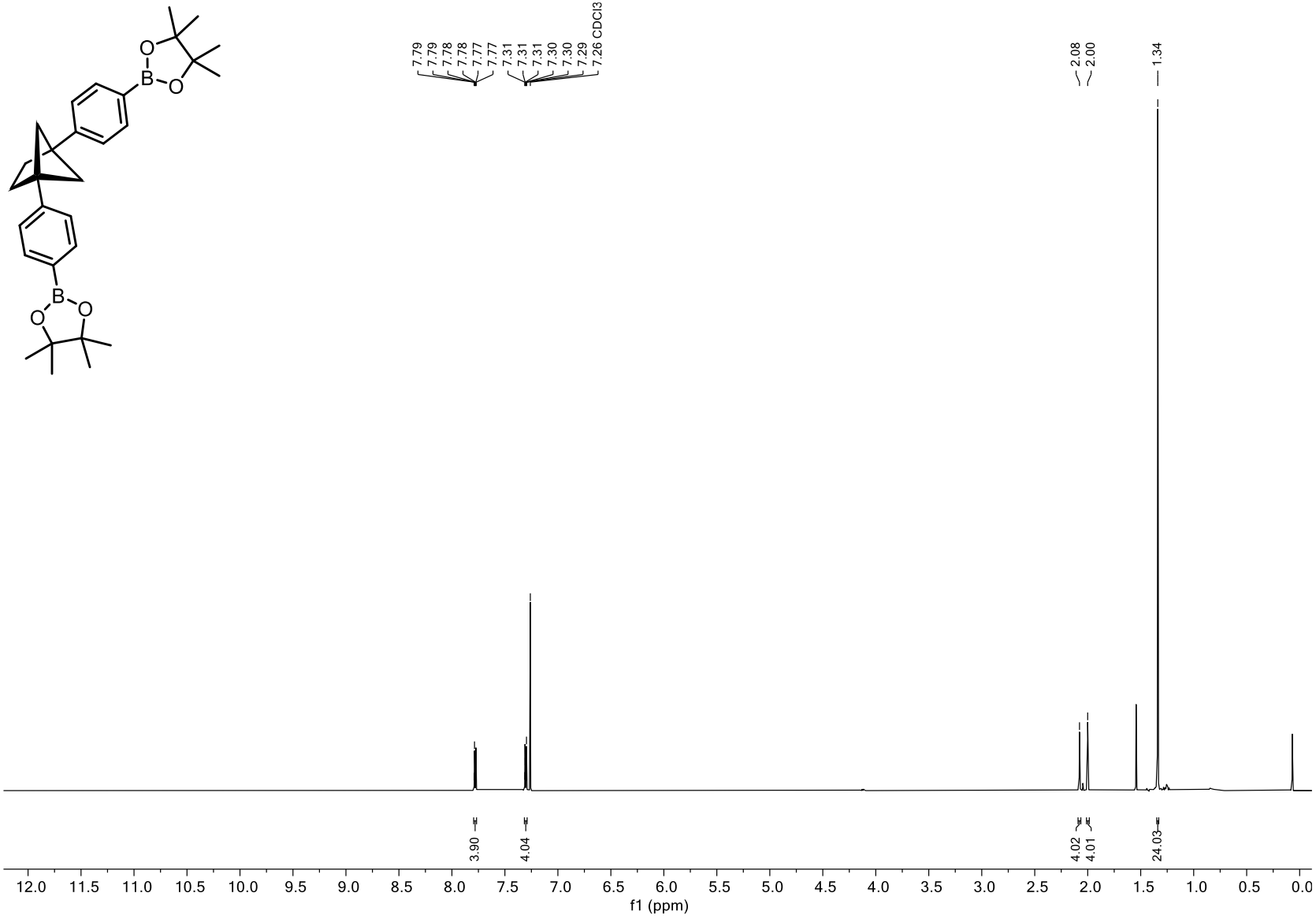
4,4'-(Bicyclo[2.1.1]hexane-1,4-diyl)dibenzaldehyde (2d): ^{1}H NMR (300 MHz, $CDCl_3$)



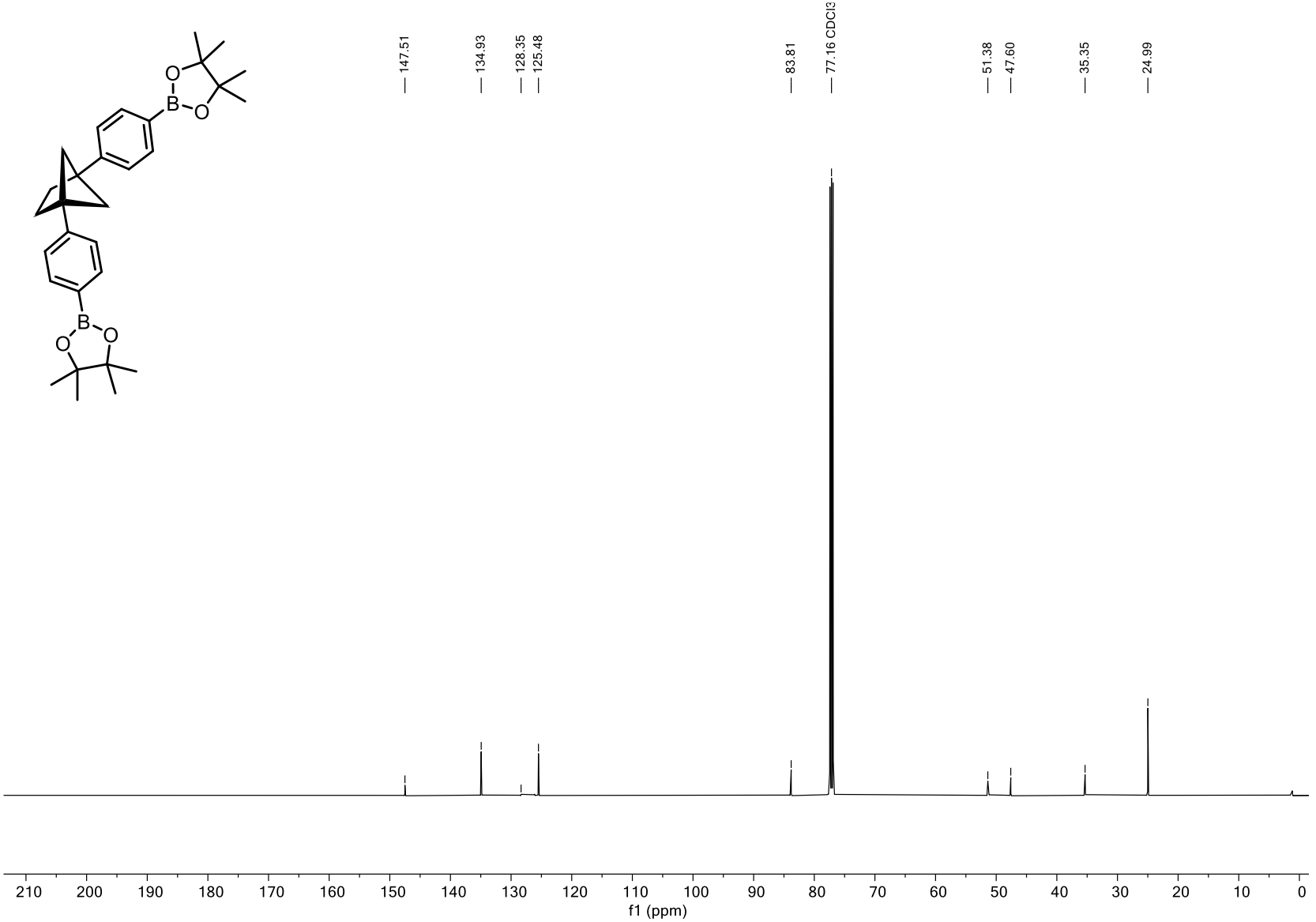
4,4'-(Bicyclo[2.1.1]hexane-1,4-diyl)dibenzaldehyde (2d): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



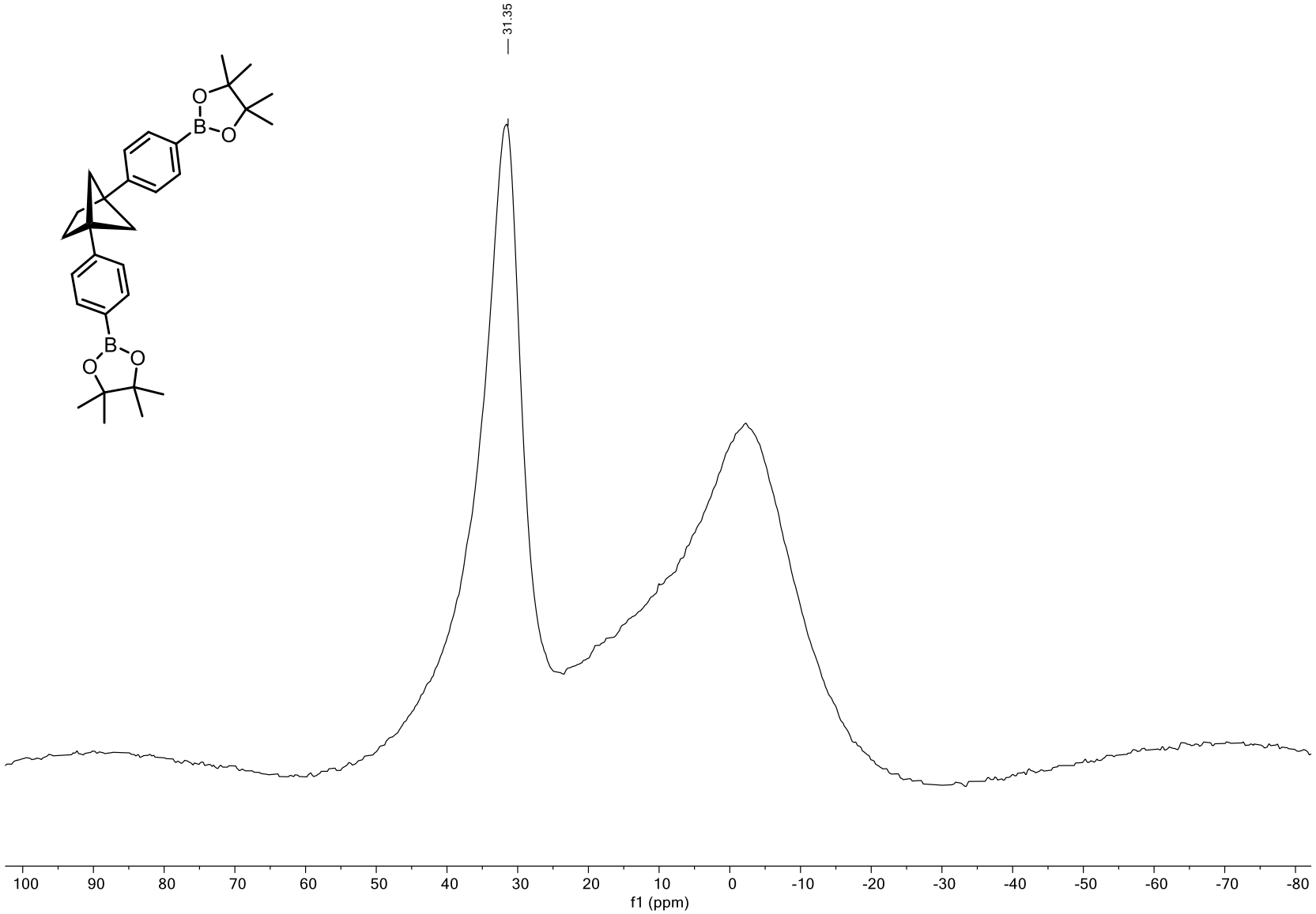
1,4-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)bicyclo[2.1.1]hexane (2e): ^{1}H NMR (300 MHz, $CDCl_3$)



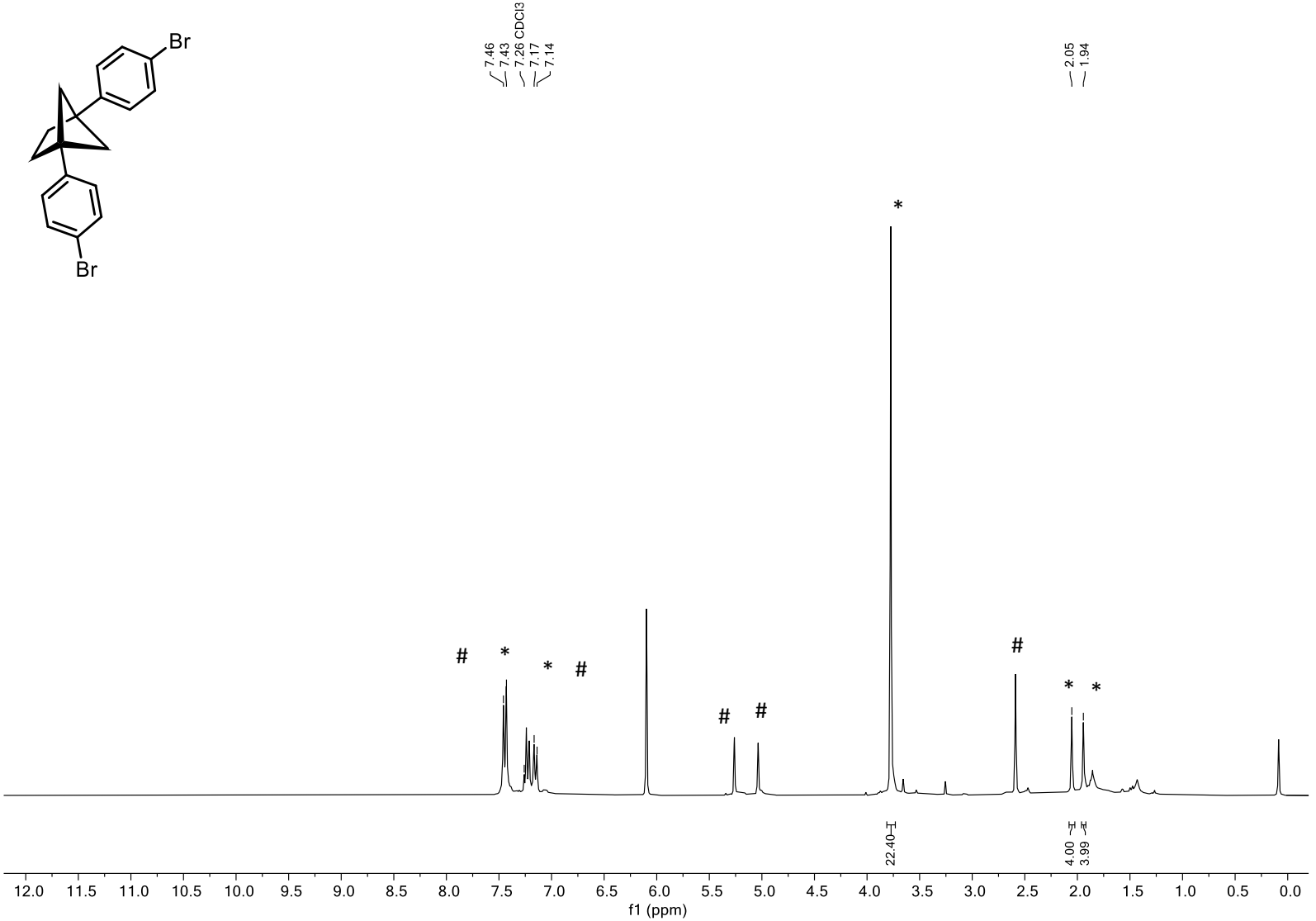
1,4-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)bicyclo[2.1.1]hexane (2e): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



1,4-Bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)bicyclo[2.1.1]hexane (2e): ^{11}B NMR (161 MHz, $CDCl_3$)

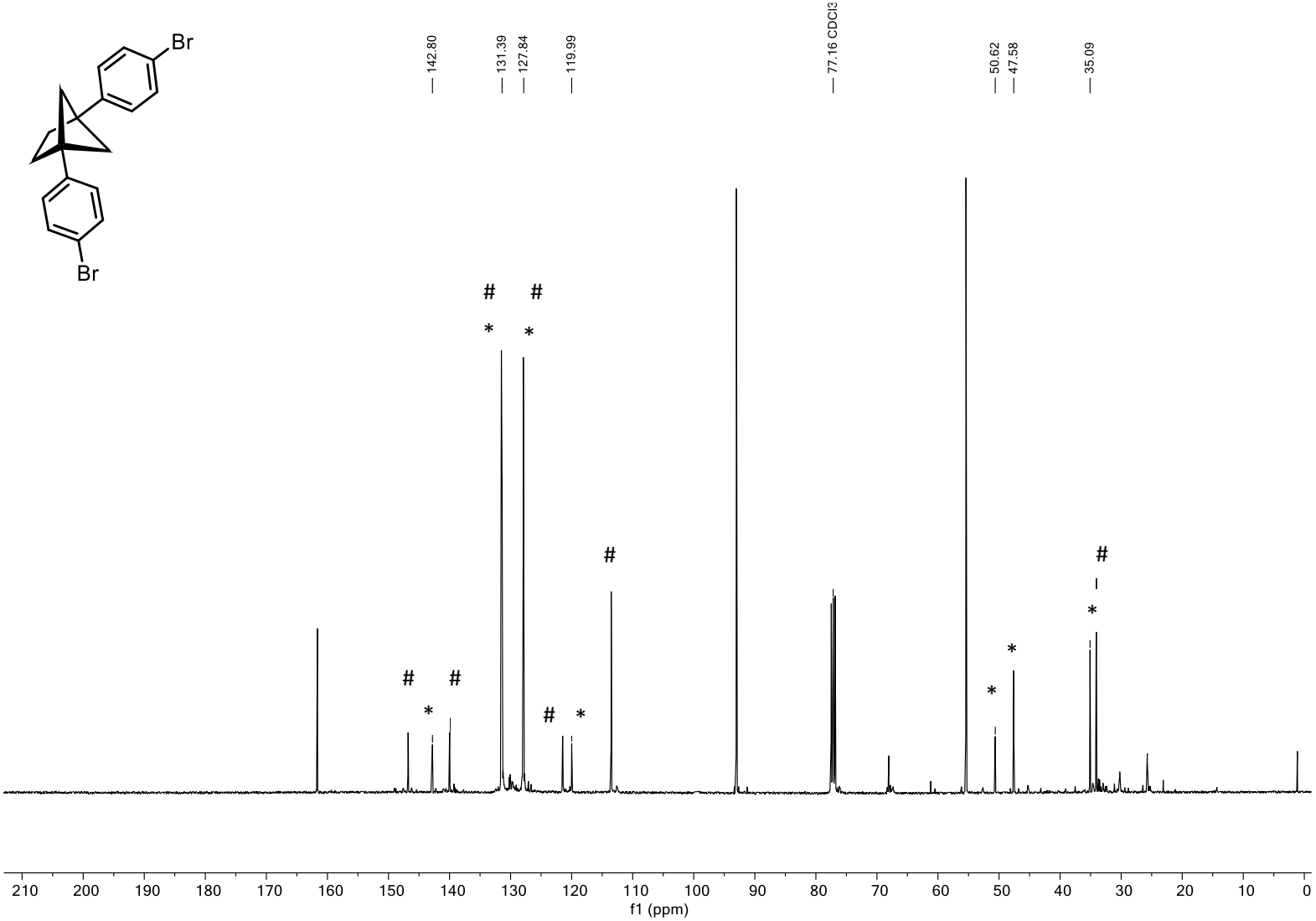


1,4-Bis(4-bromophenyl)bicyclo[2.1.1]hexane (2f): ^{1}H NMR (300 MHz, $CDCl_3$)



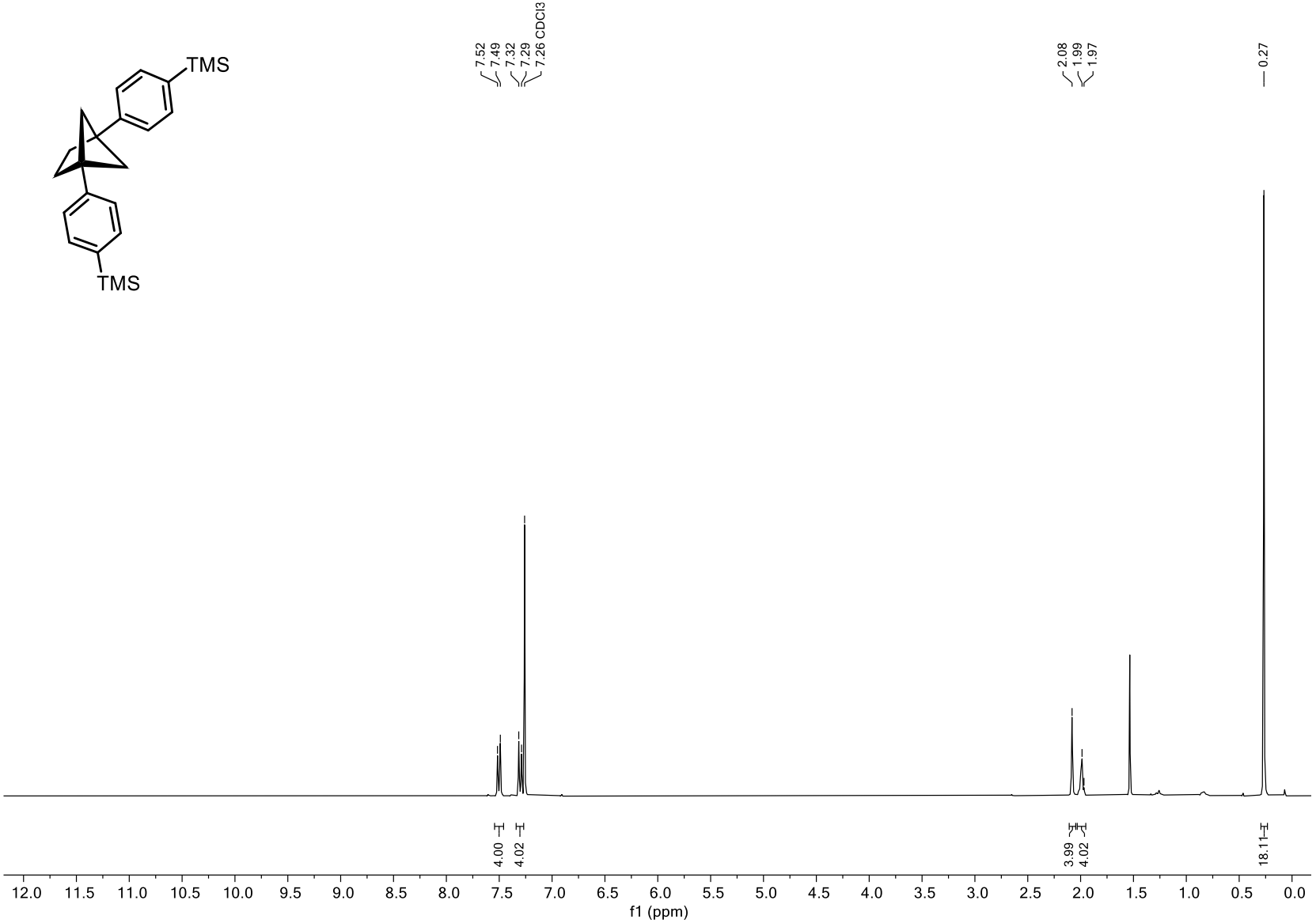
= diene **1m**, * = BCH **2m**

1,4-Bis(4-bromophenyl)bicyclo[2.1.1]hexane (2f): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

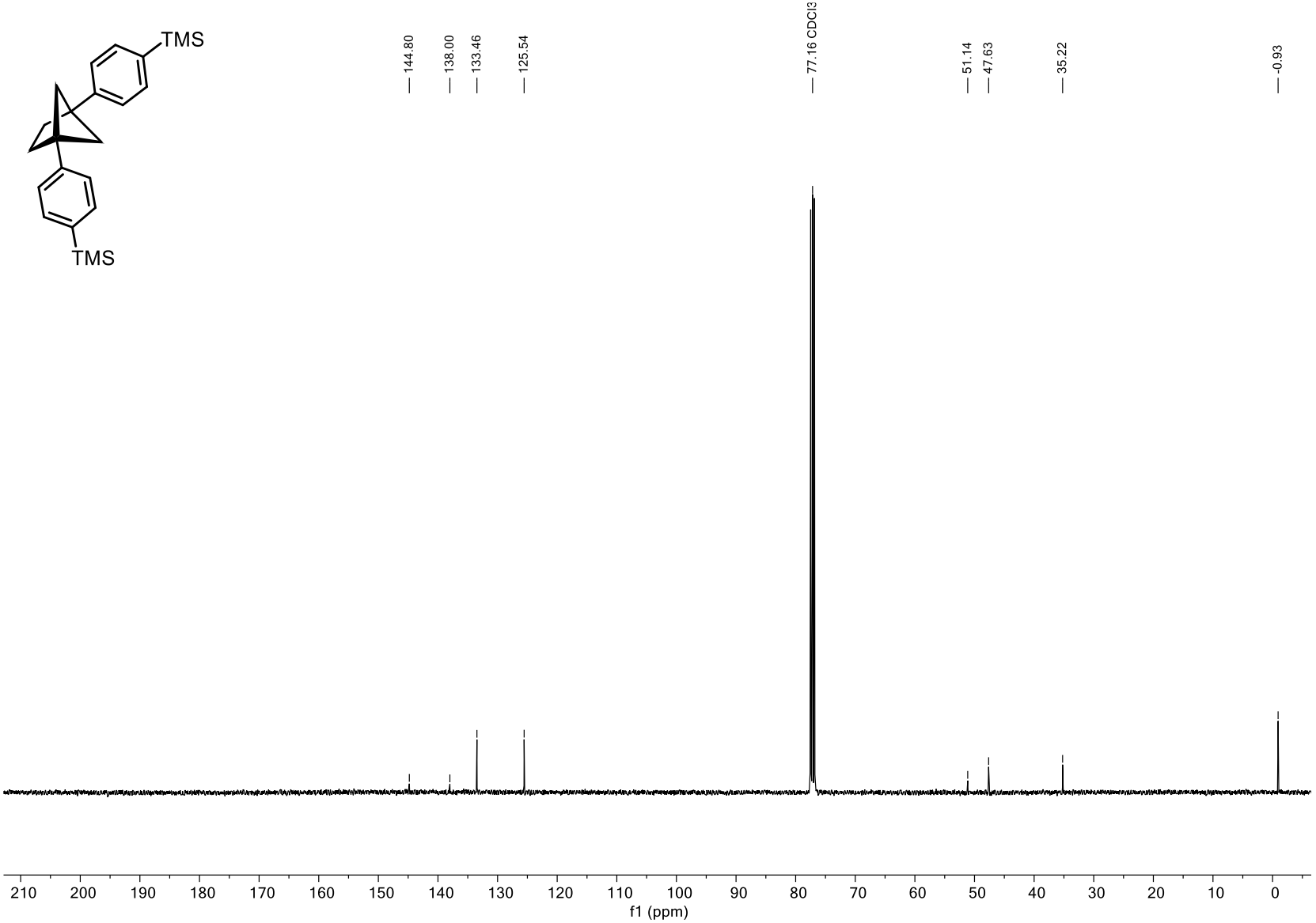


= diene **1f**, * = BCH **2f**

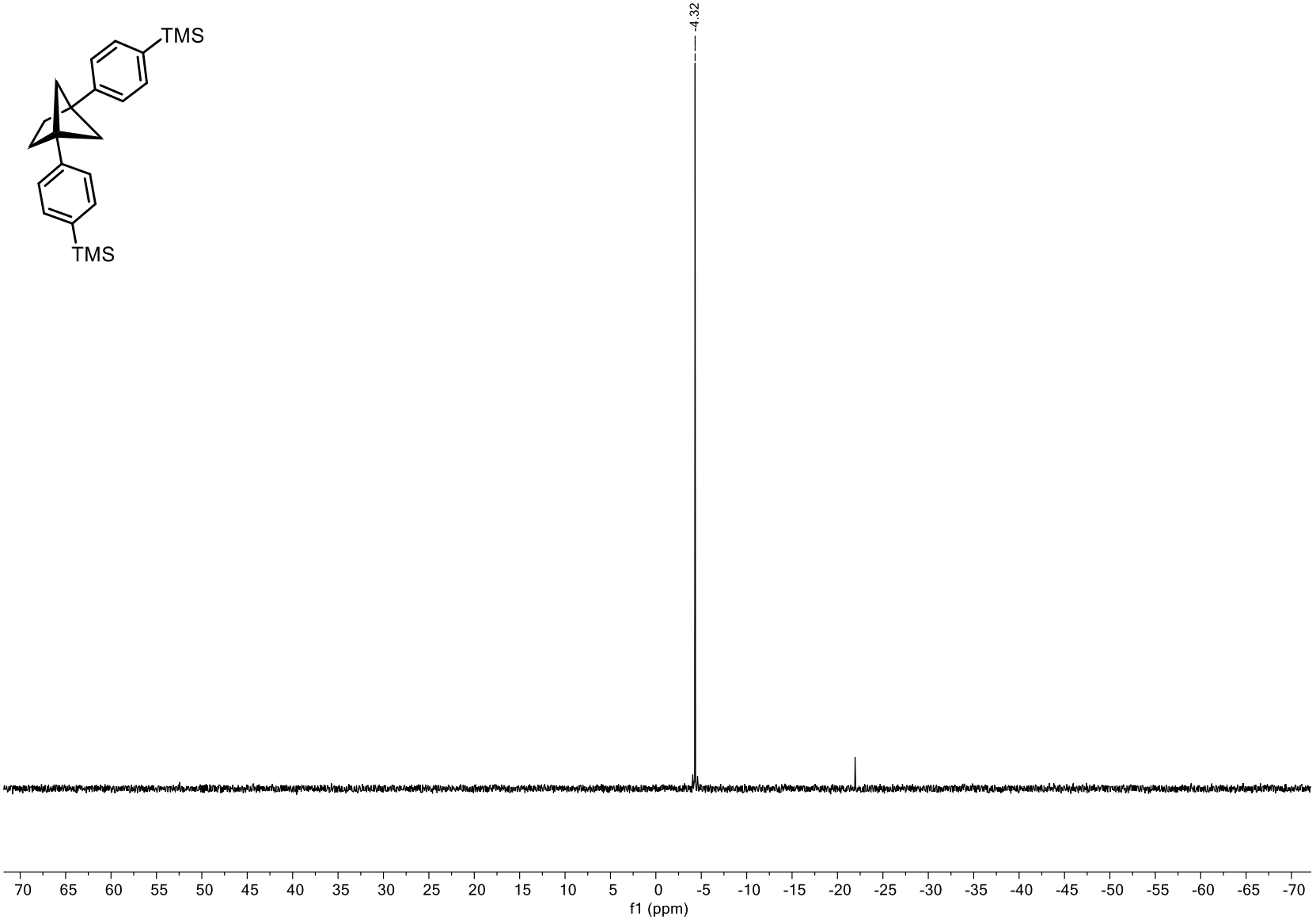
1,4-Bis(4-(trimethylsilyl)phenyl)bicyclo[2.1.1]hexane (2g): ^{1}H NMR (300 MHz, $CDCl_3$)



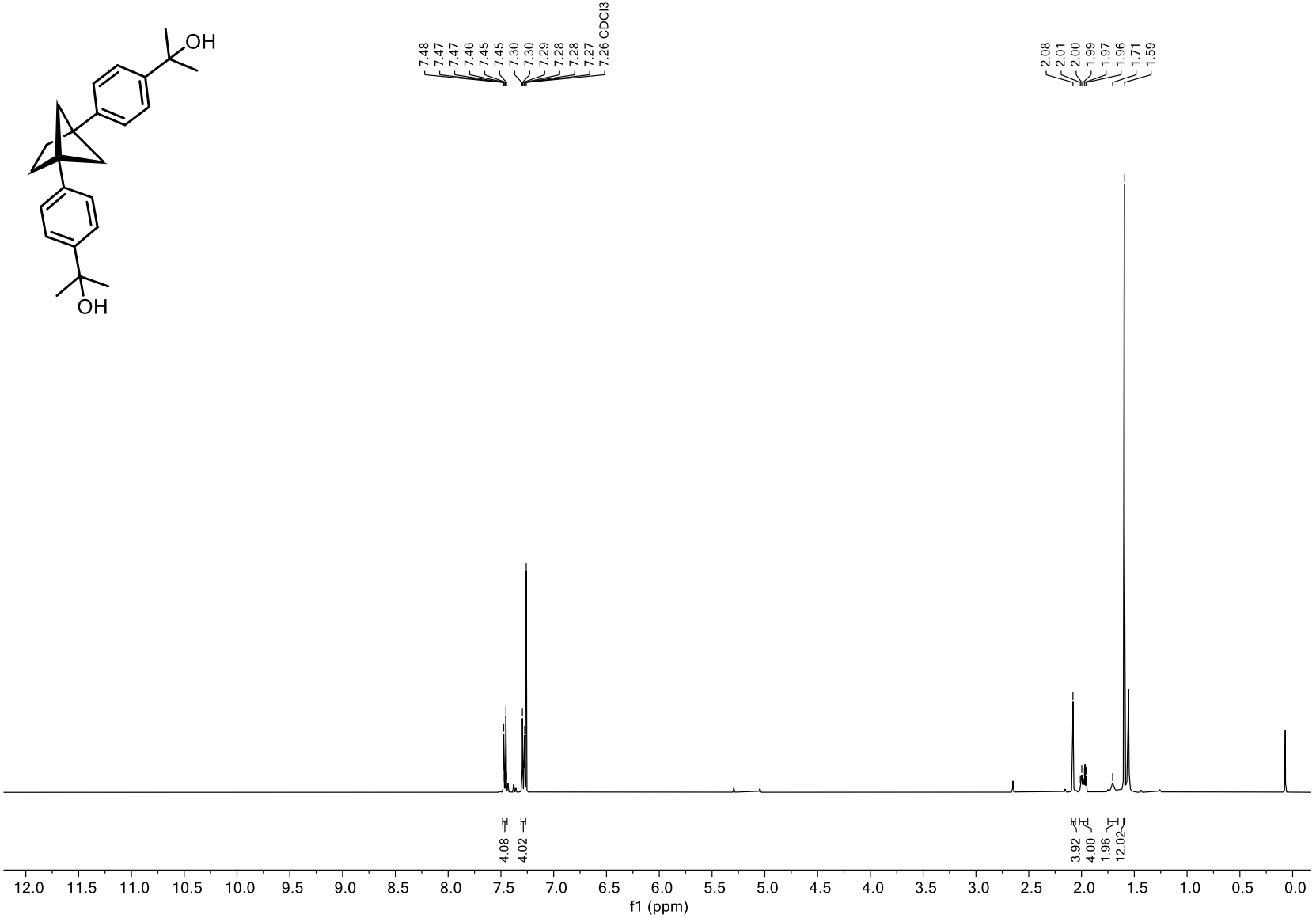
1,4-Bis(4-(trimethylsilyl)phenyl)bicyclo[2.1.1]hexane (2g): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



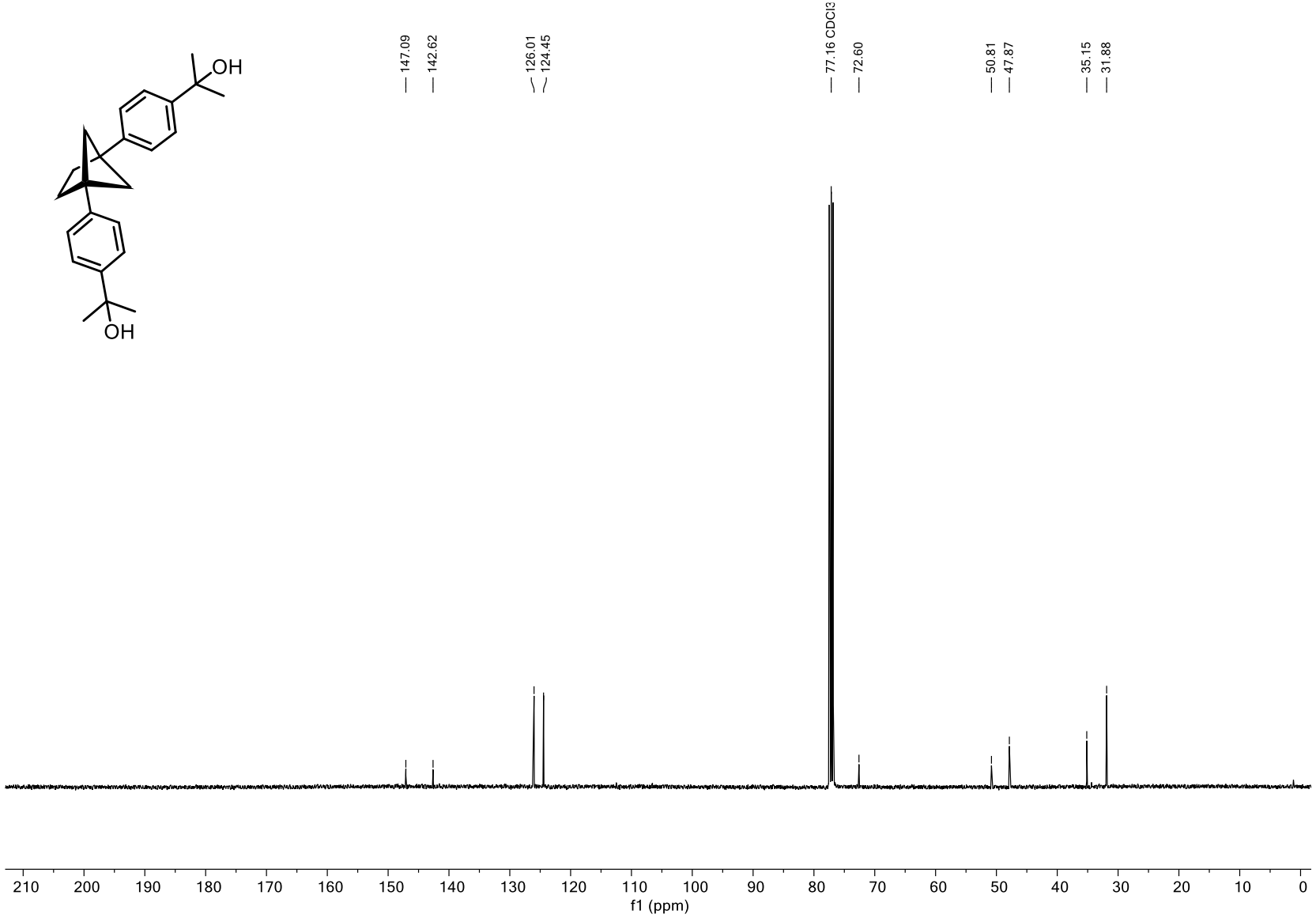
1,4-Bis(4-(trimethylsilyl)phenyl)bicyclo[2.1.1]hexane (2g): INEPT $^{29}Si\{^{1}H\}$ NMR (99 MHz, $CDCl_3$)



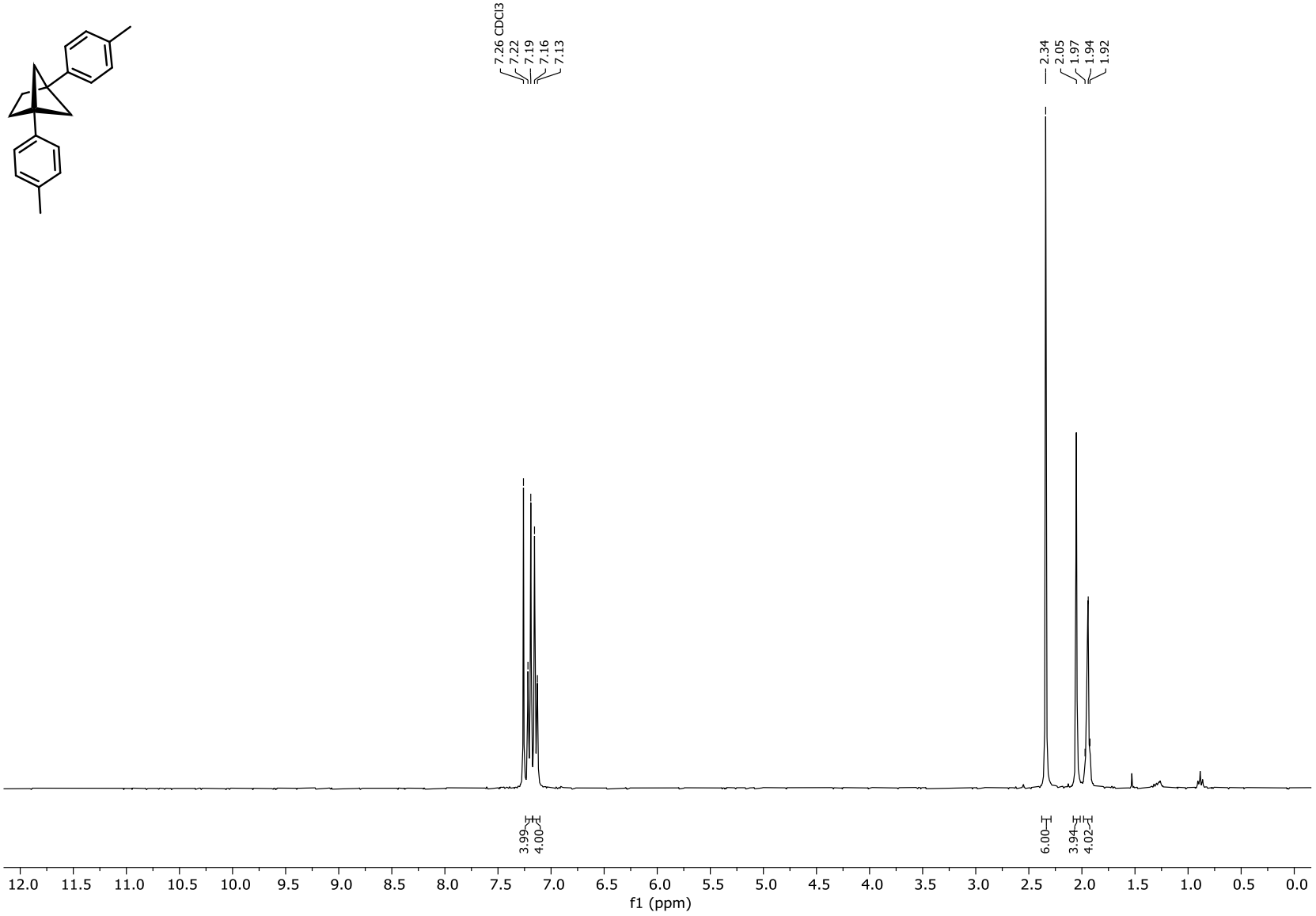
2,2'-((Bicyclo[2.1.1]hexane-1,4-diyl)bis(4,1-phenylene))bis(propan-2-ol) (2h): ^{1}H NMR (300 MHz, $CDCl_3$)



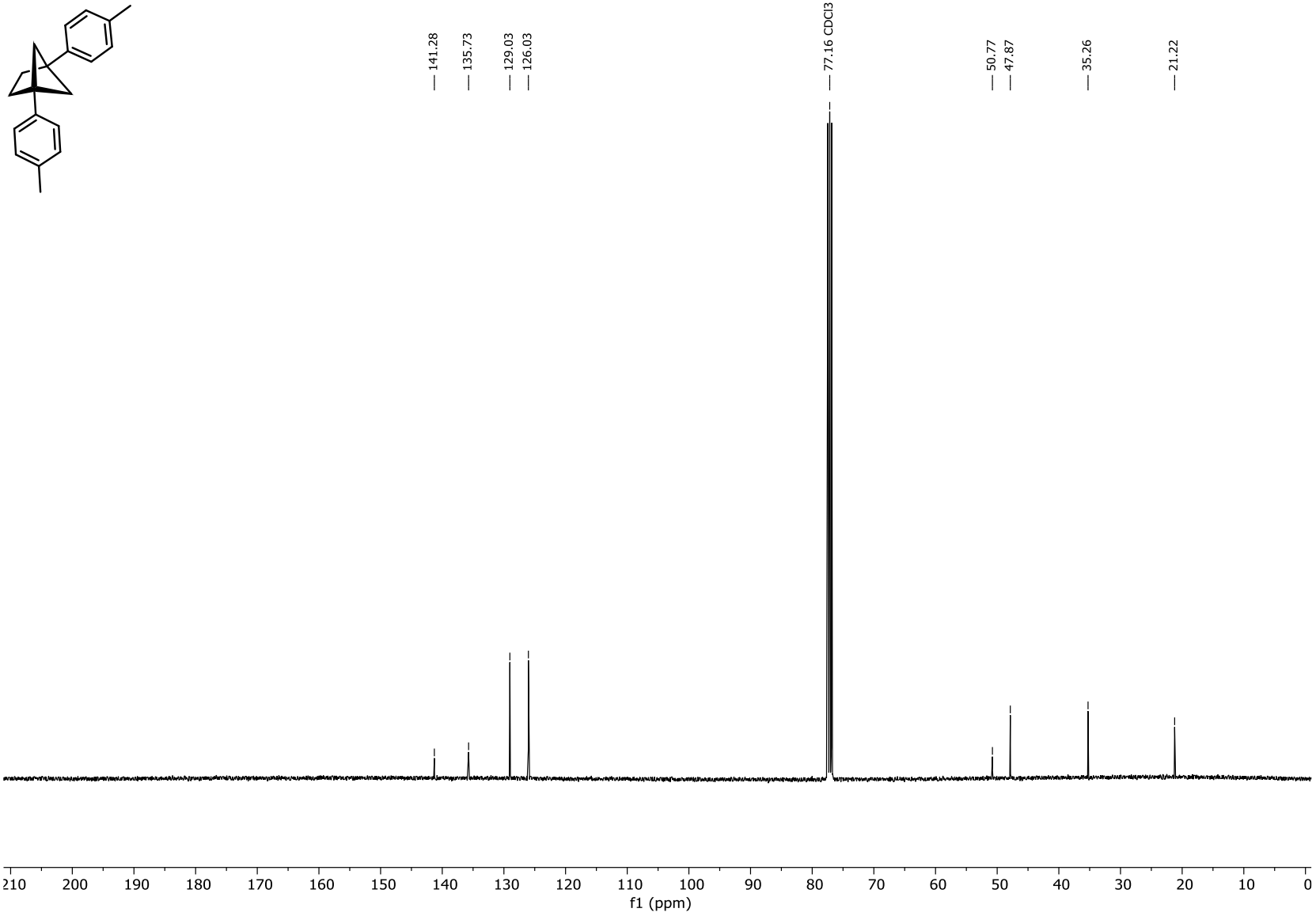
2,2'-((Bicyclo[2.1.1]hexane-1,4-diyl)bis(4,1-phenylene))bis(propan-2-ol) (2h): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



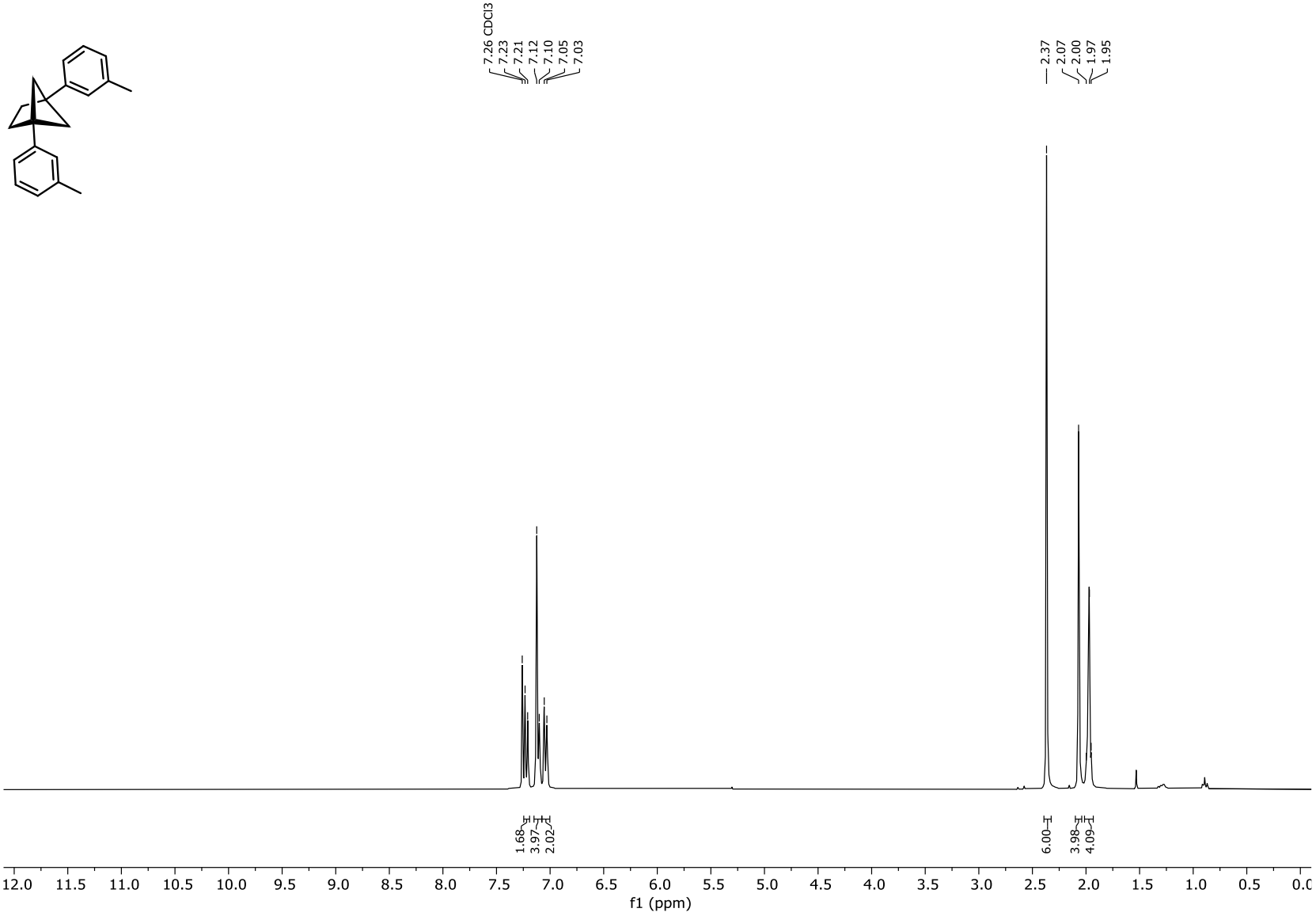
1,4-Di-*p*-tolylbicyclo[2.1.1]hexane (2i): ^{1}H NMR (300 MHz, $CDCl_3$)



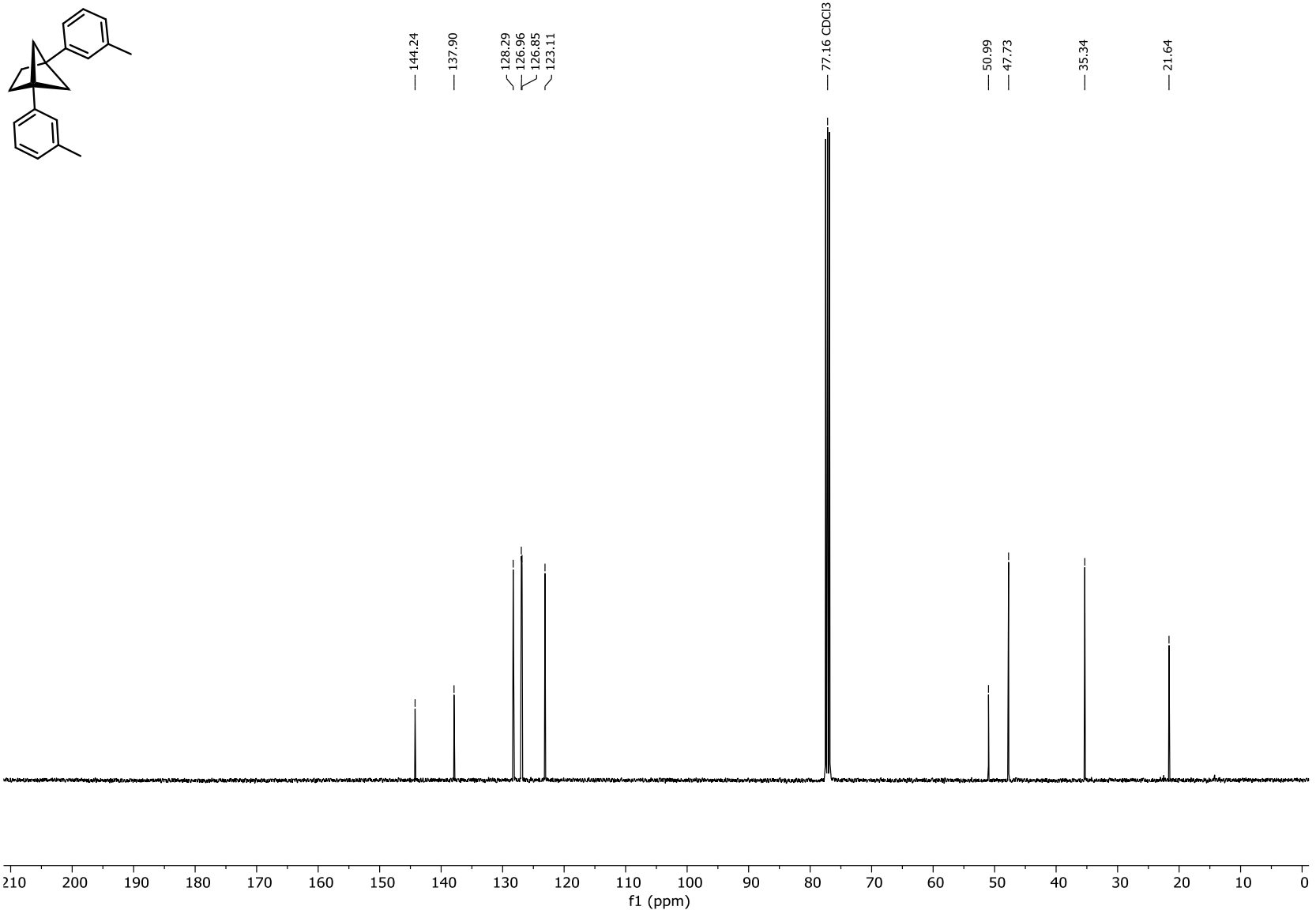
1,4-Di-*p*-tolylbicyclo[2.1.1]hexane (2i): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



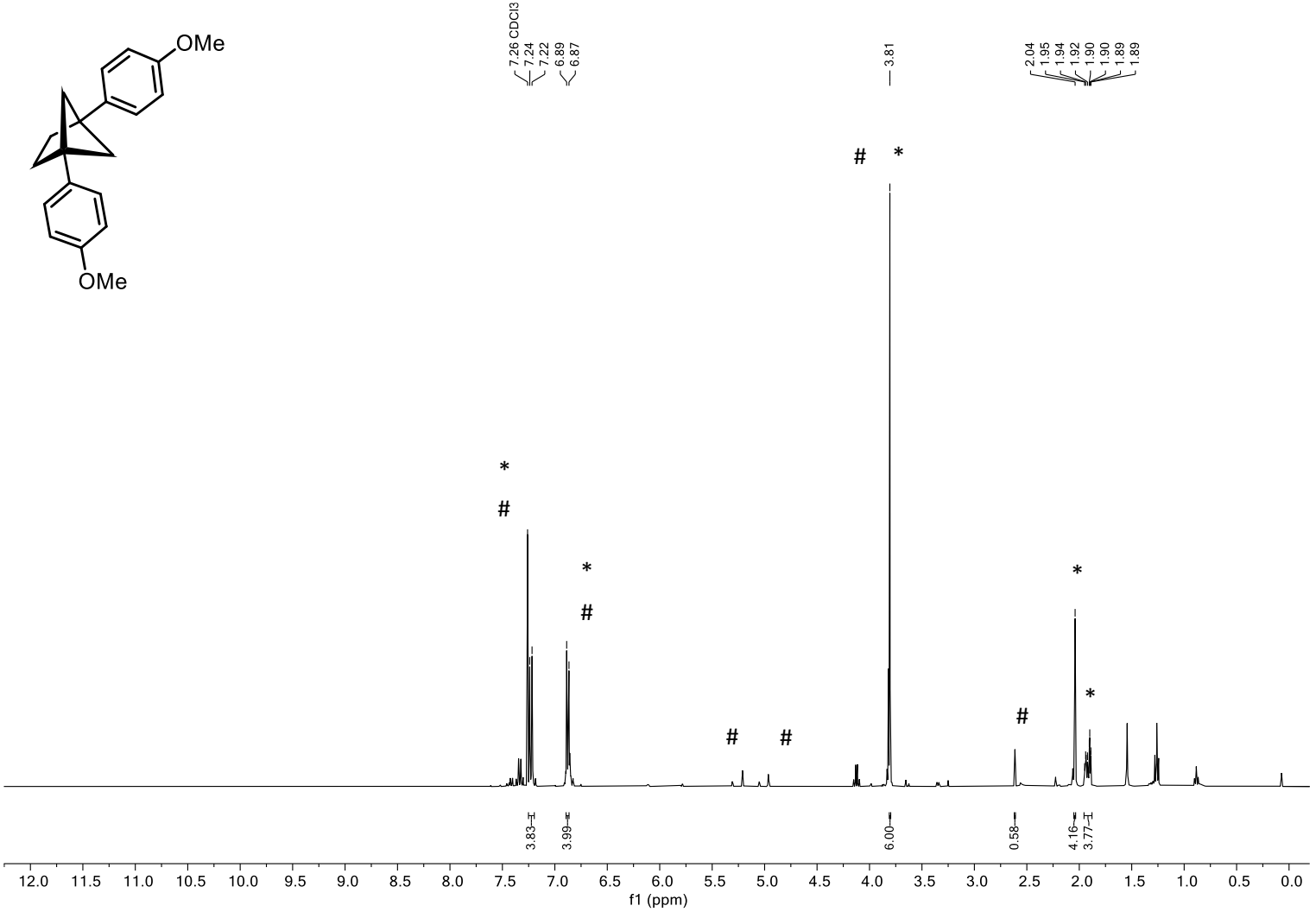
1,4-Di-*m*-tolylbicyclo[2.1.1]hexane (2j): ^{1}H NMR (300 MHz, $CDCl_3$)



1,4-Di-*m*-tolylbicyclo[2.1.1]hexane (2j): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

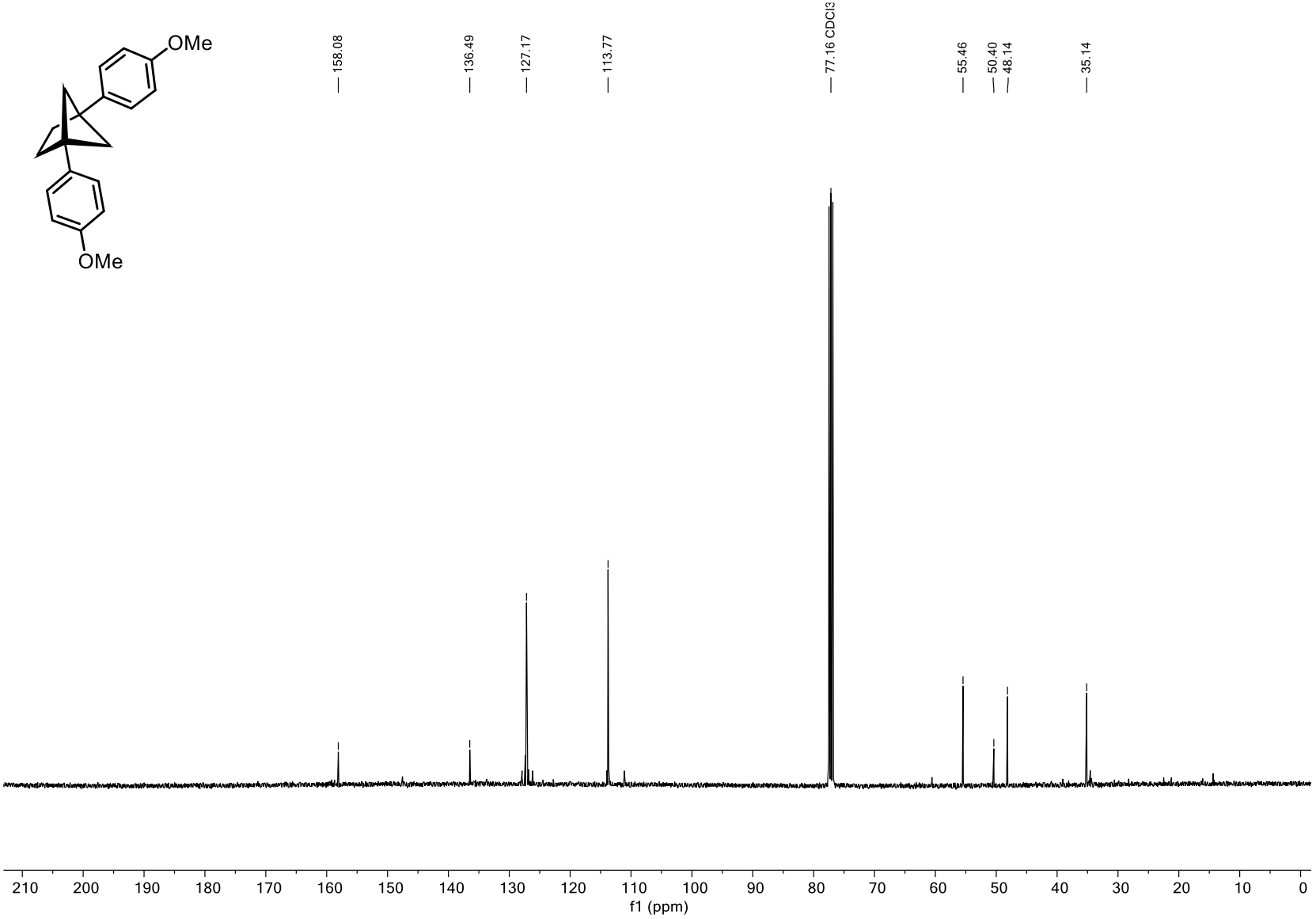


1,4-Bis(4-methoxyphenyl)bicyclo[2.1.1]hexane (2l): ^{1}H NMR (300 MHz, $CDCl_3$)

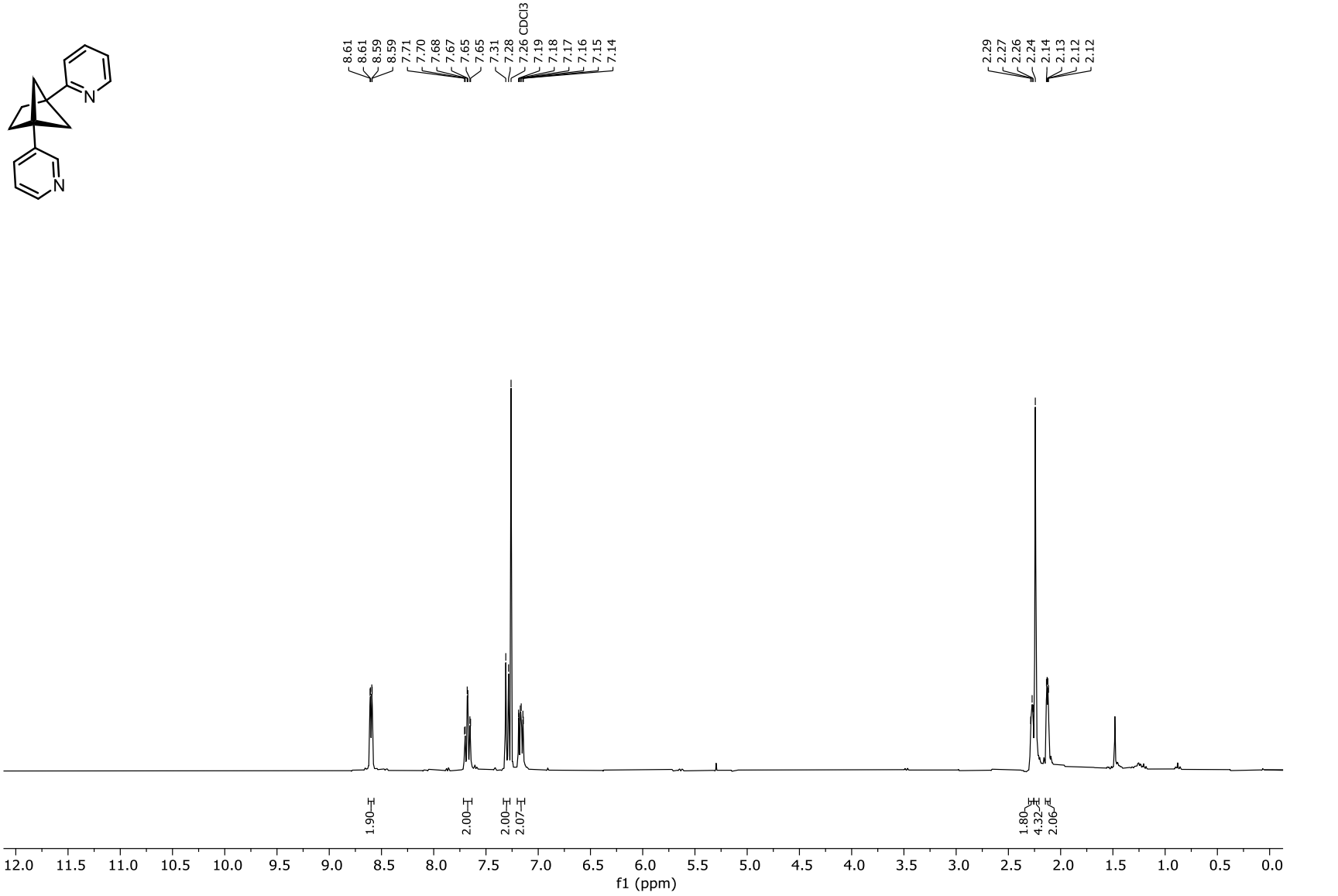


= diene **1l**, * = BCH **2l**

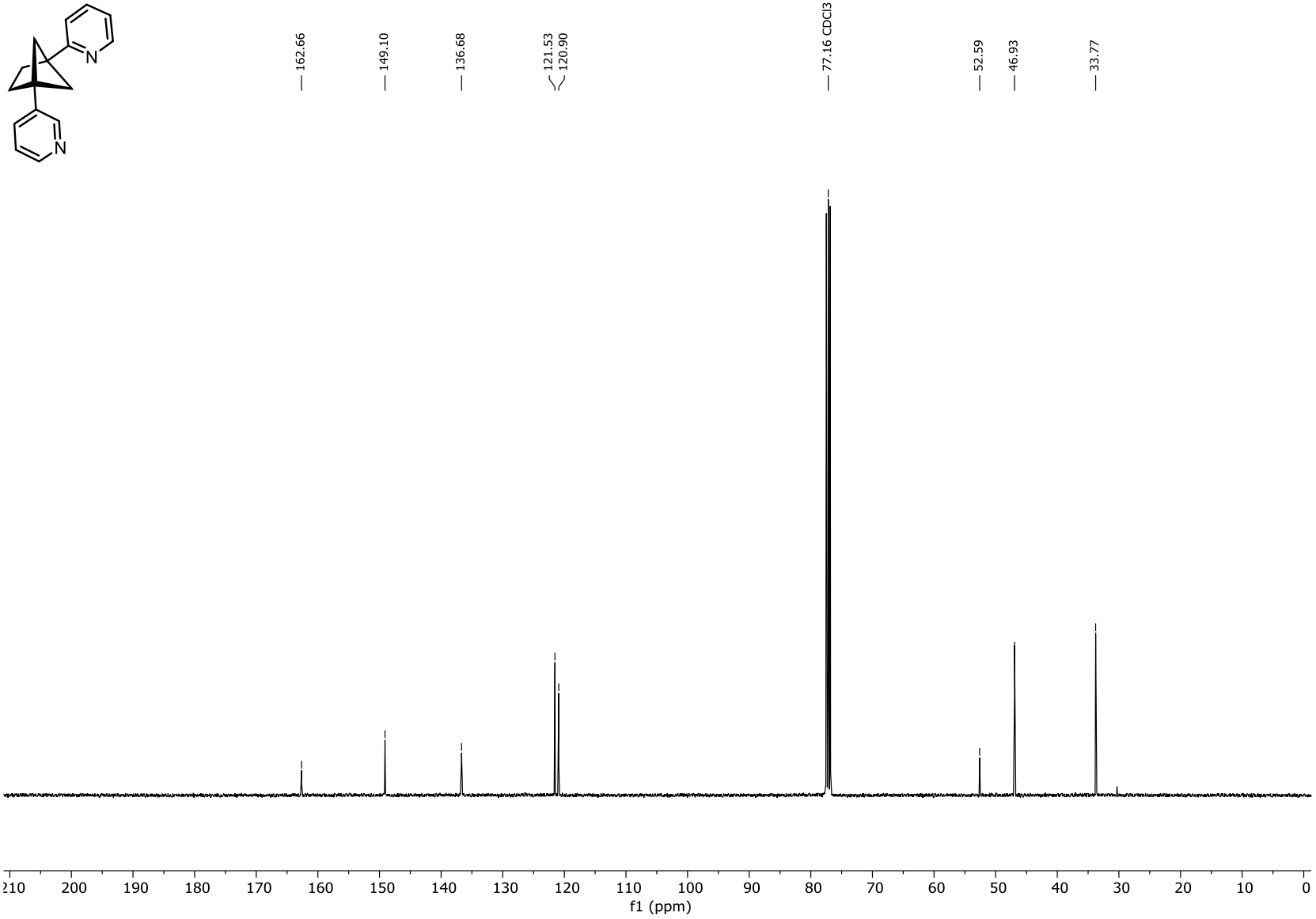
1,4-Bis(4-methoxyphenyl)bicyclo[2.1.1]hexane (2l): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



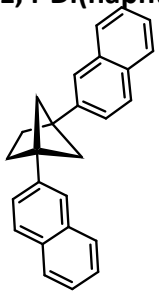
1,4-Di(pyridin-2-yl)bicyclo[2.1.1]hexane (2m): ^{1}H NMR (300 MHz, $CDCl_3$)



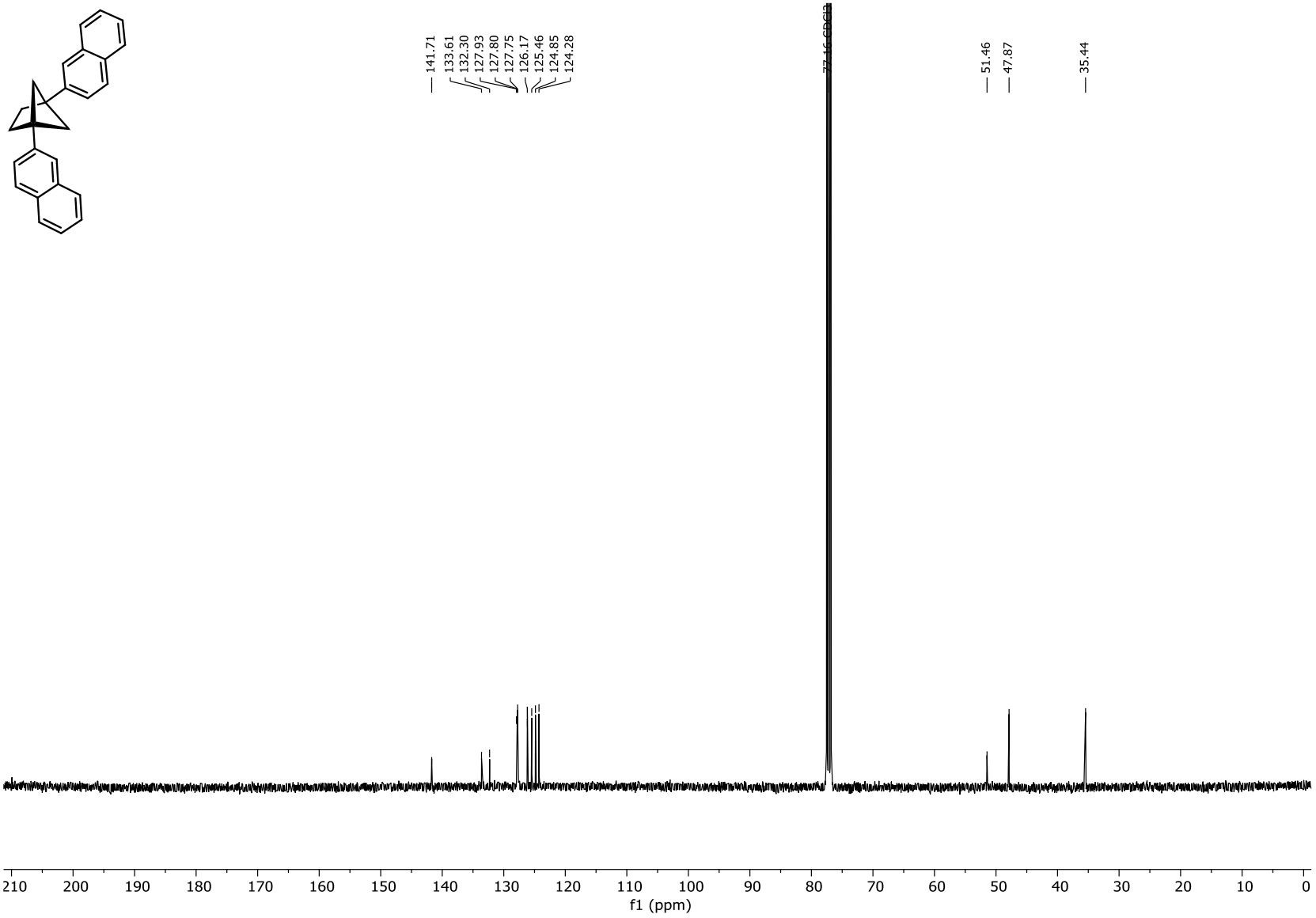
1,4-Di(pyridin-2-yl)bicyclo[2.1.1]hexane (2m): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



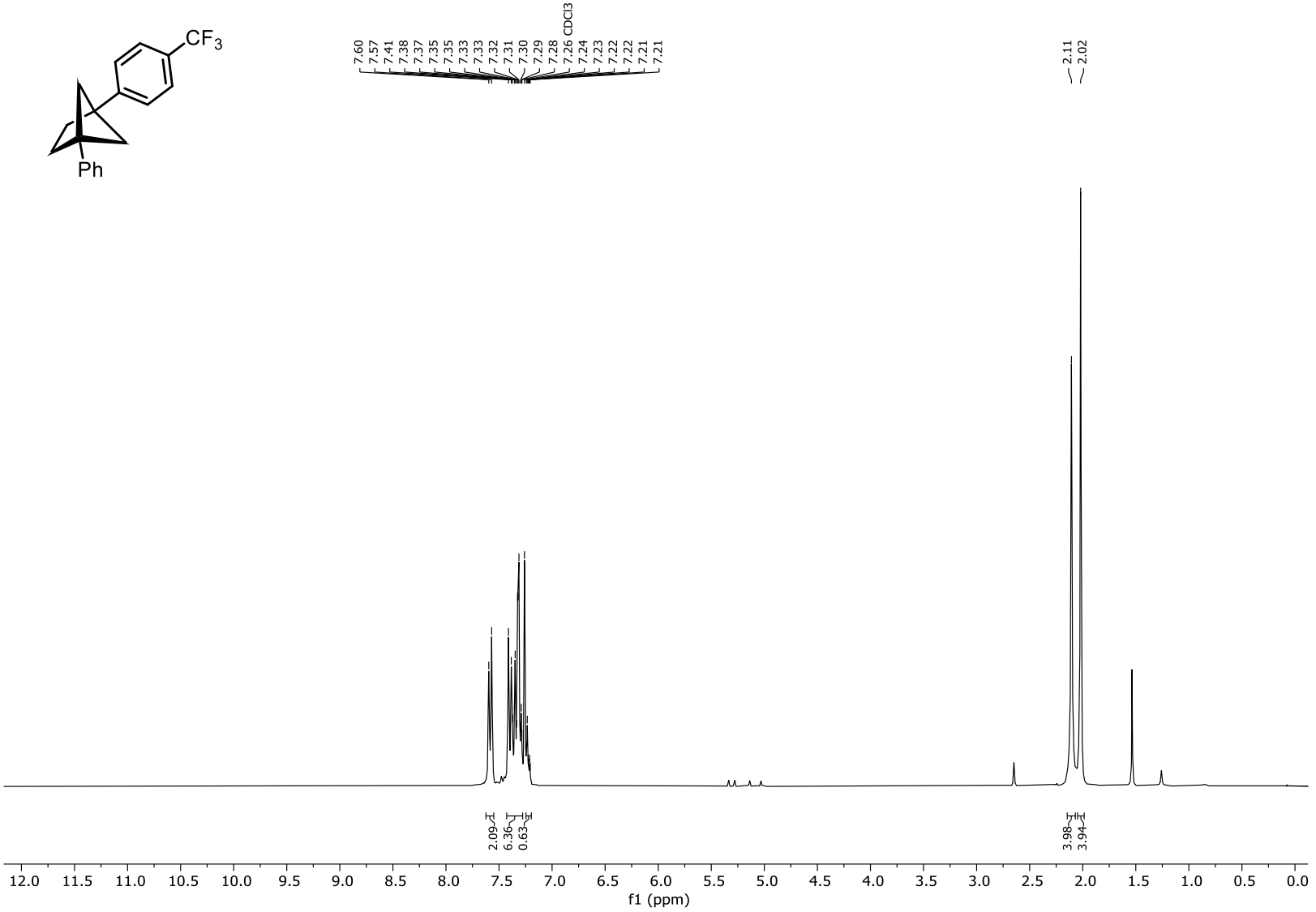
1,4-Di(naphthalen-2-yl)bicyclo[2.1.1]hexane (2n): ^{1}H NMR (300 MHz, $CDCl_3$)



1,4-Di(naphthalen-2-yl)bicyclo[2.1.1]hexane (2n): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

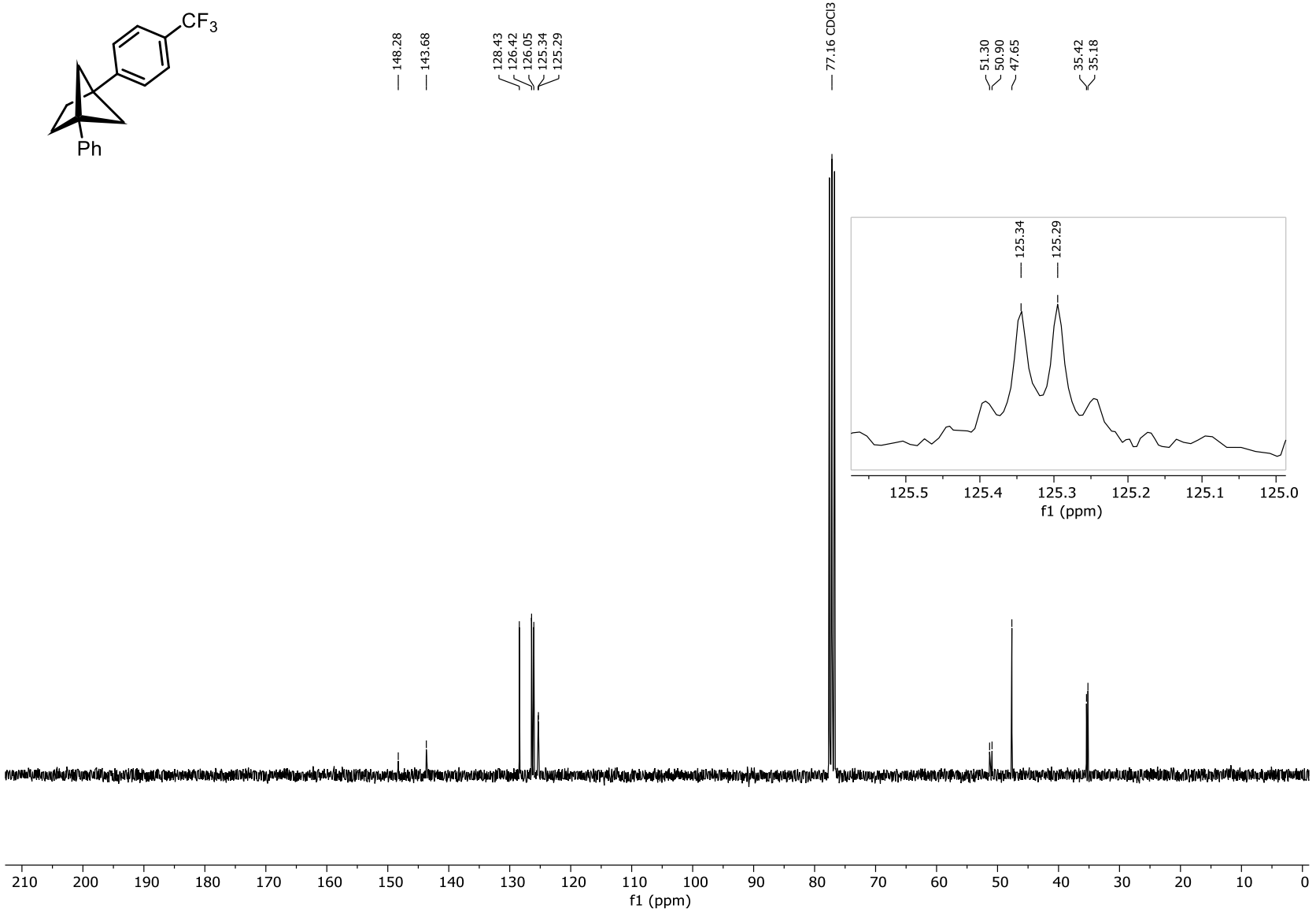


1-Phenyl-4-(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (2o): ^{1}H NMR (300 MHz, $CDCl_3$)

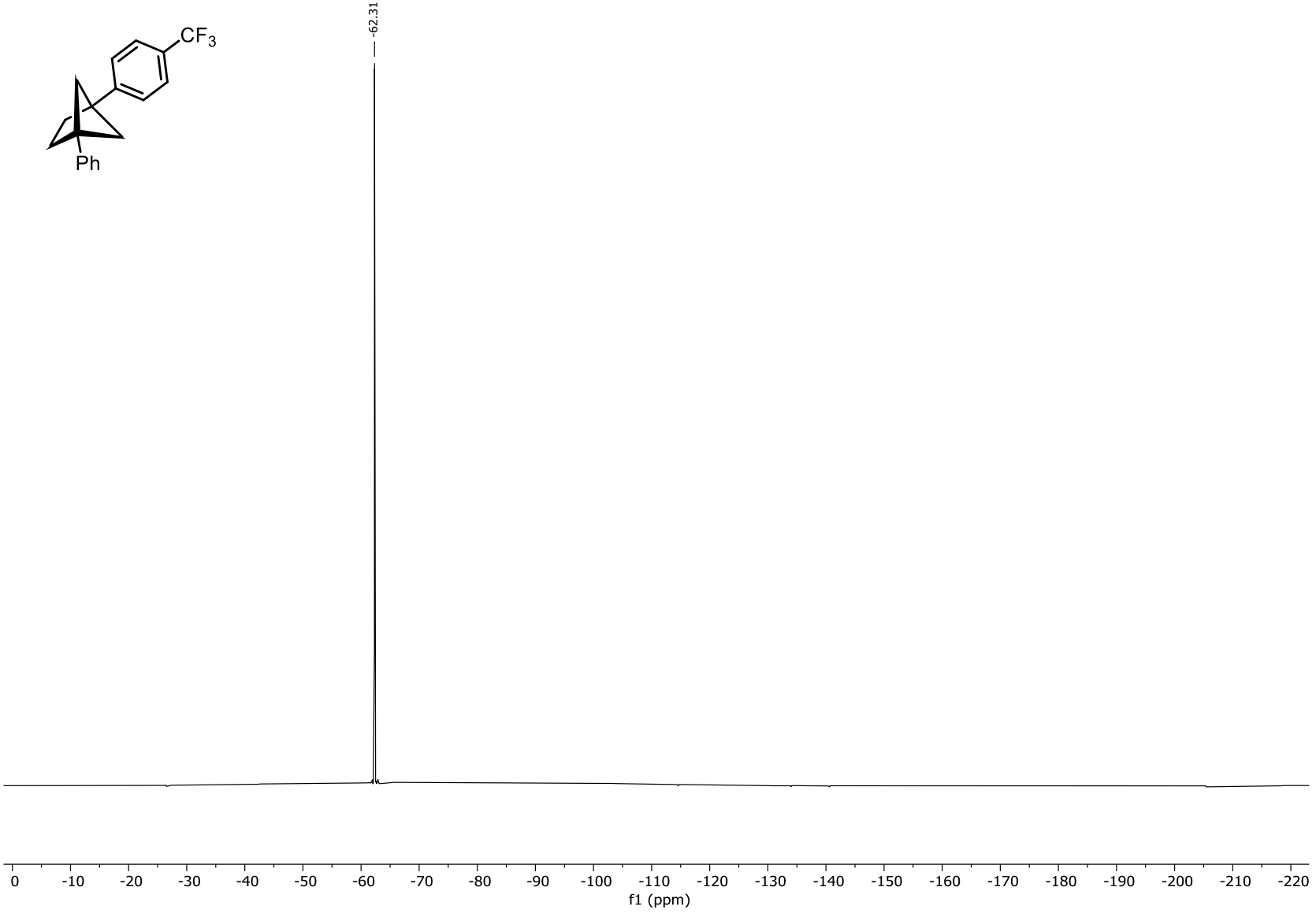


1-Phenyl-4-(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (xx): $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

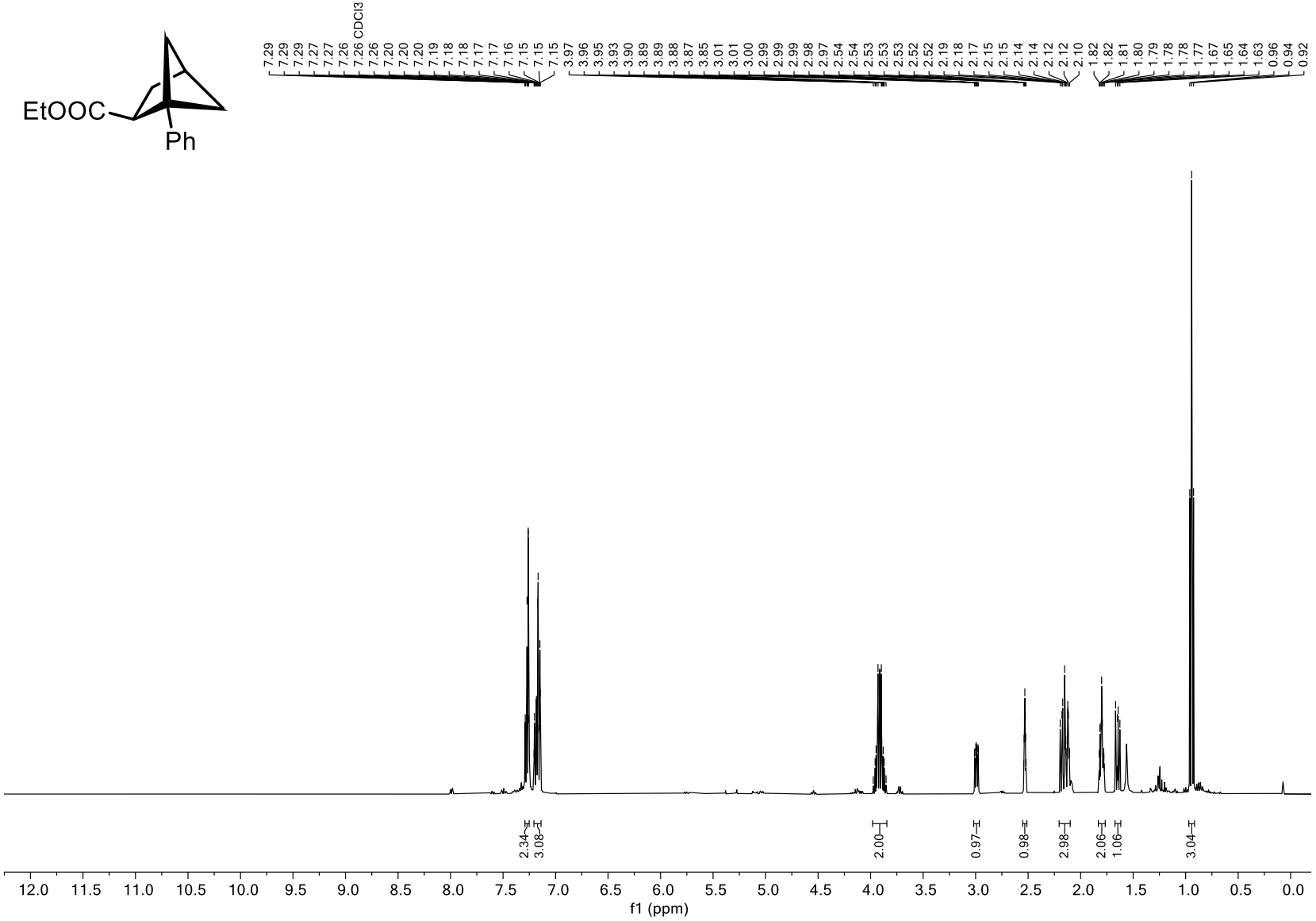
1-Phenyl-4-(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (2o): $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



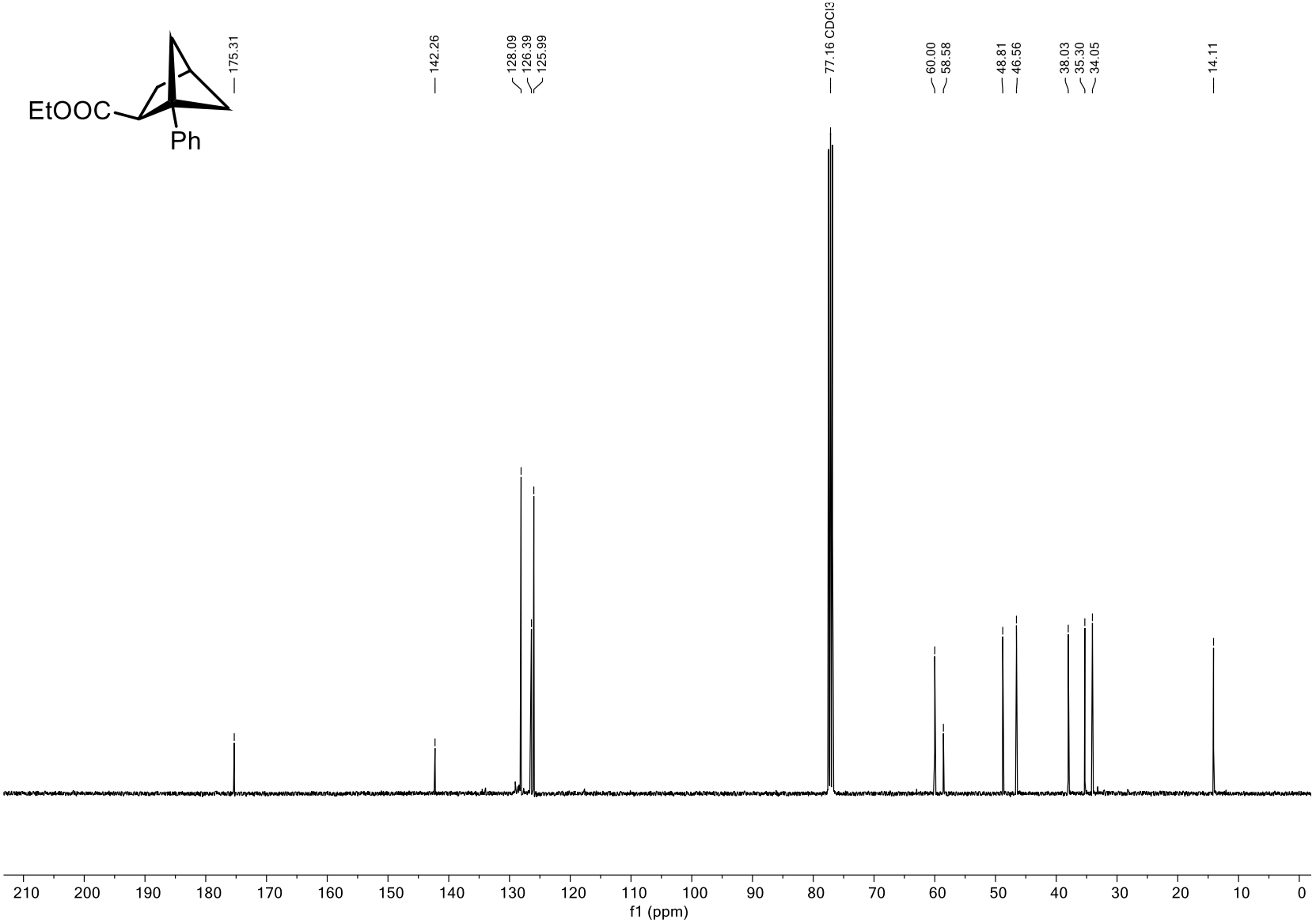
1-Phenyl-4-(4-(trifluoromethyl)phenyl)bicyclo[2.1.1]hexane (2o): $^{19}F\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



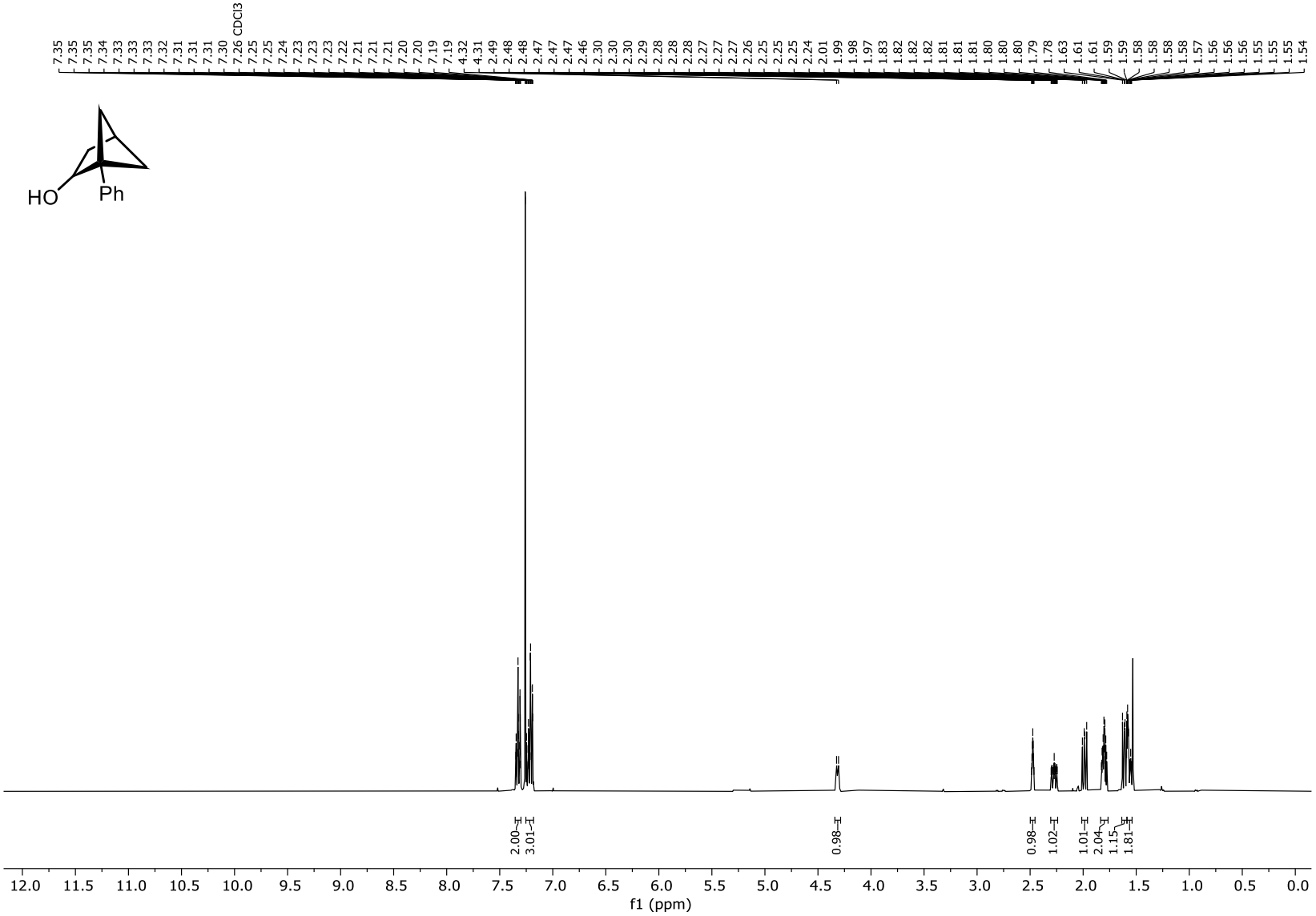
Ethyl 1-phenylbicyclo[2.1.1]hexane-2-carboxylate (2p): ^{1}H NMR (300 MHz, $CDCl_3$)



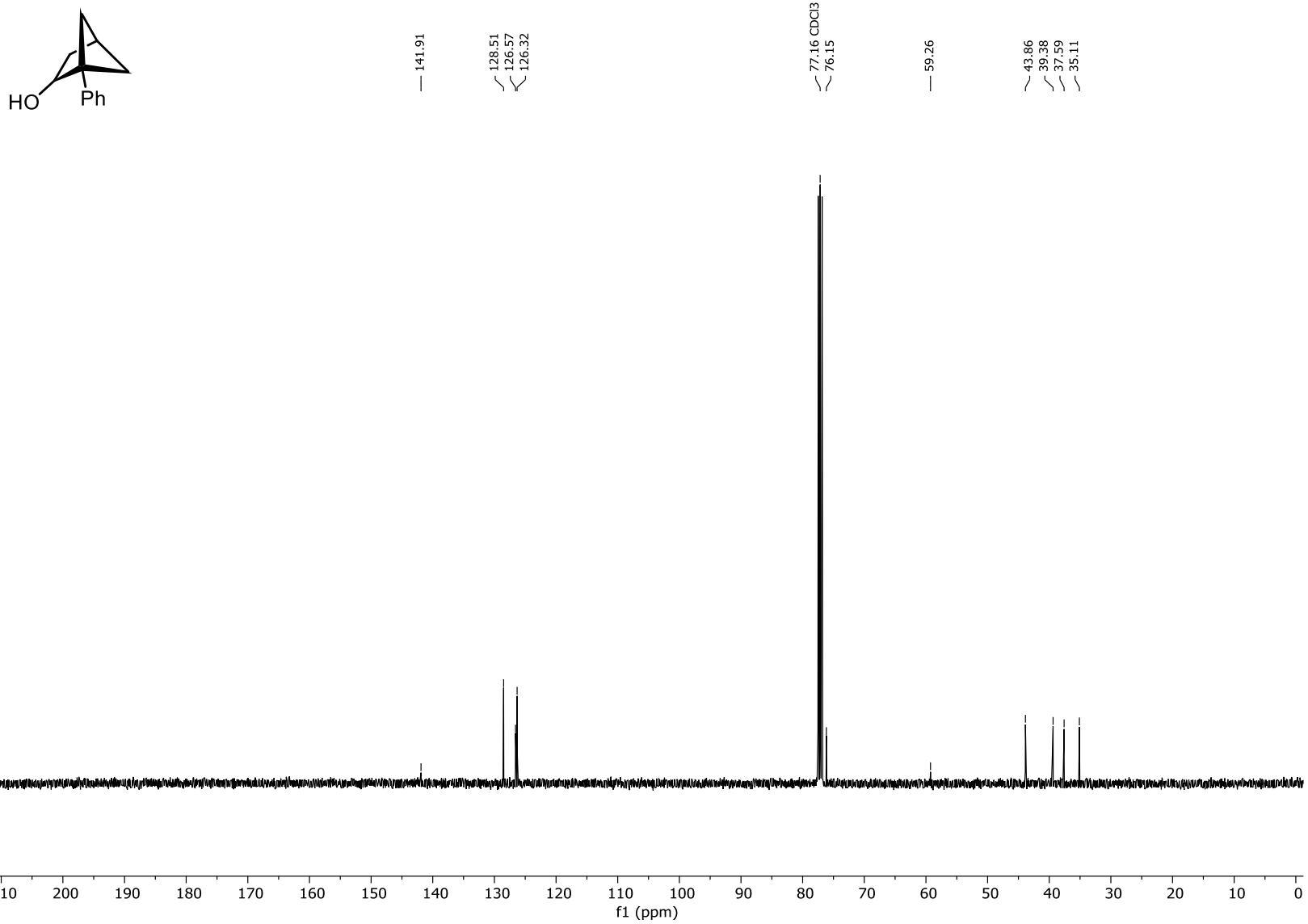
Ethyl 1-phenylbicyclo[2.1.1]hexane-2-carboxylate (2p): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



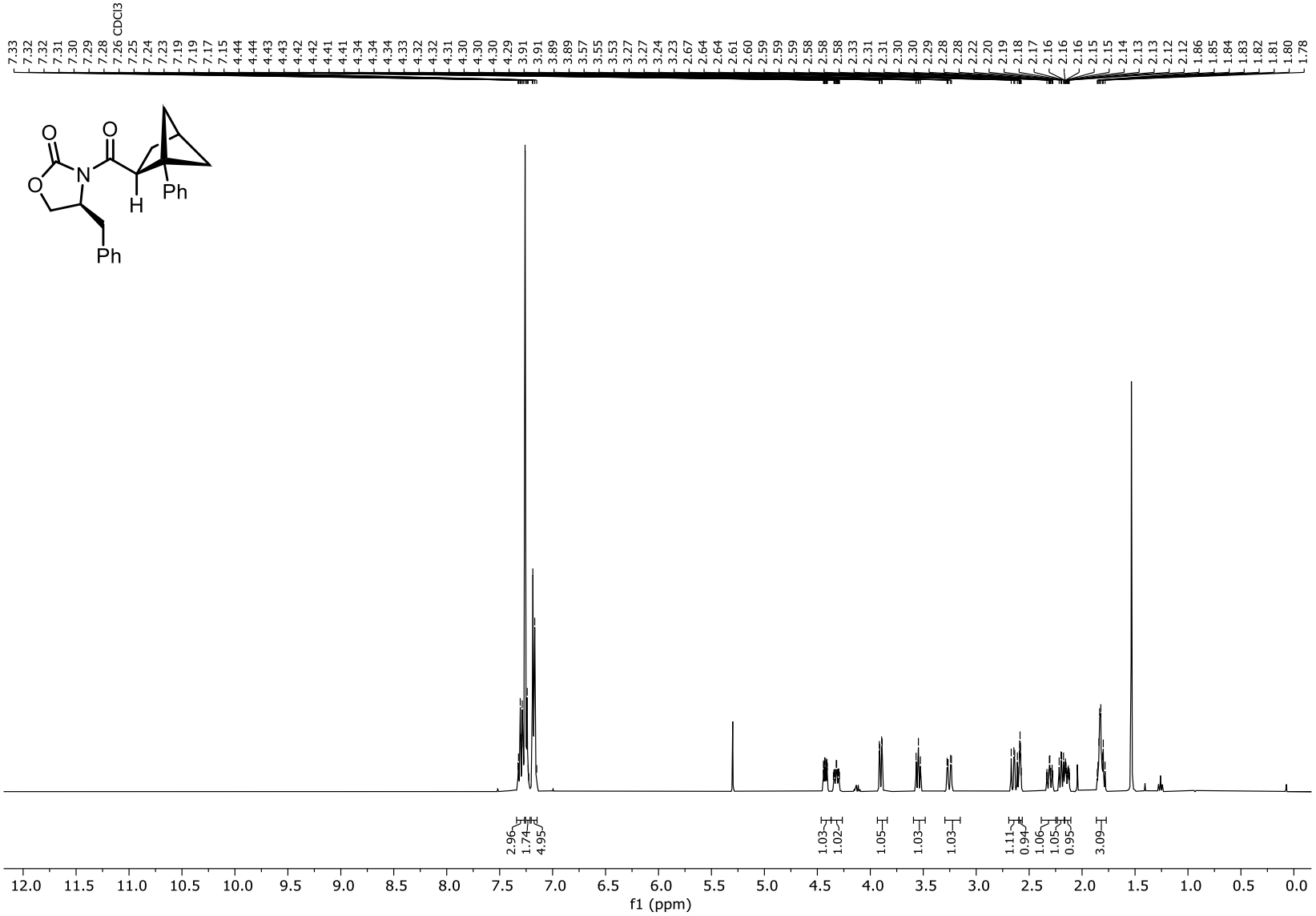
Phenylbicyclo[2.1.1]hexan-2-ol (2q): ^{1}H NMR (400 MHz, $CDCl_3$)



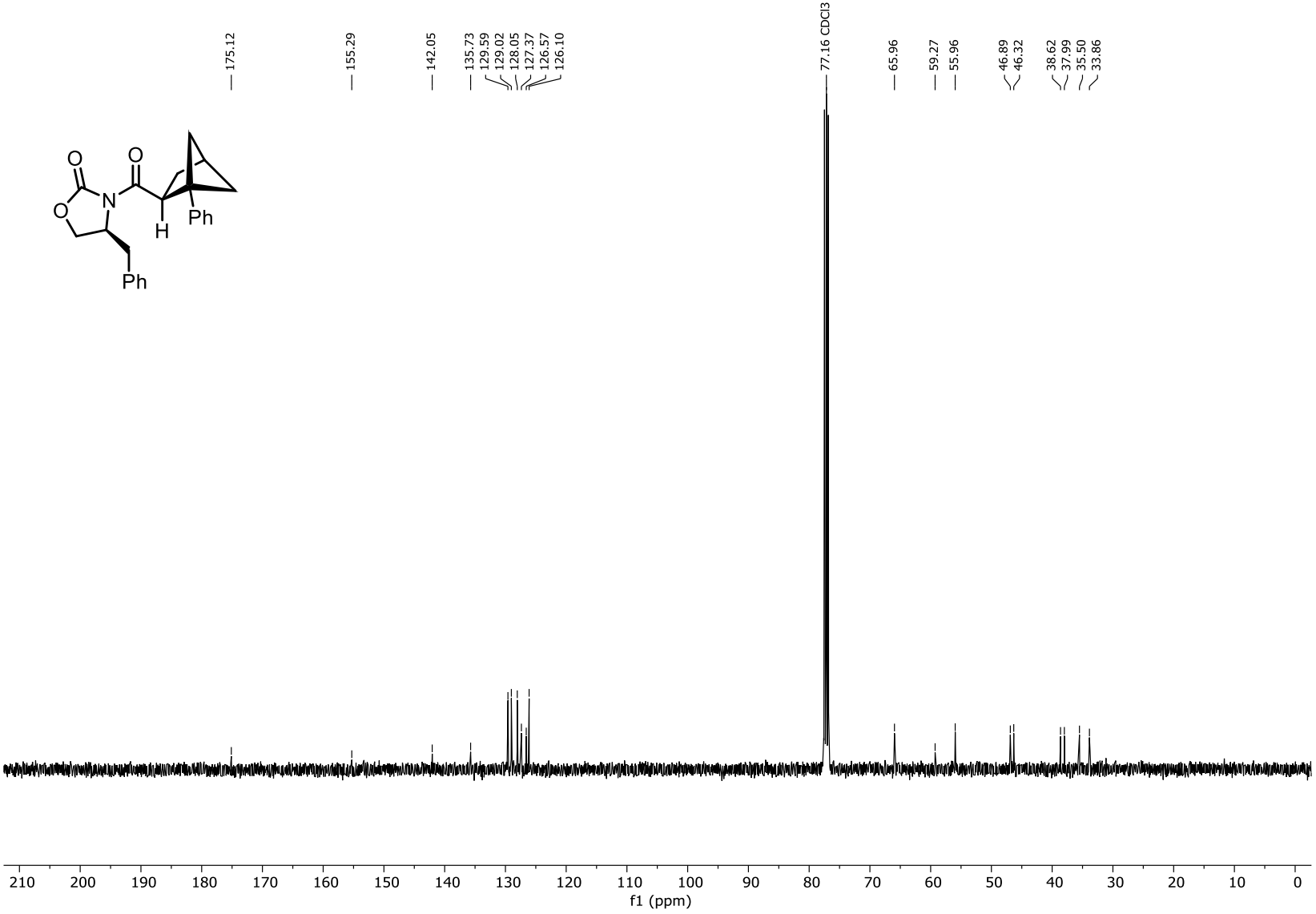
1-Phenylbicyclo[2.1.1]hexan-2-ol (2q): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



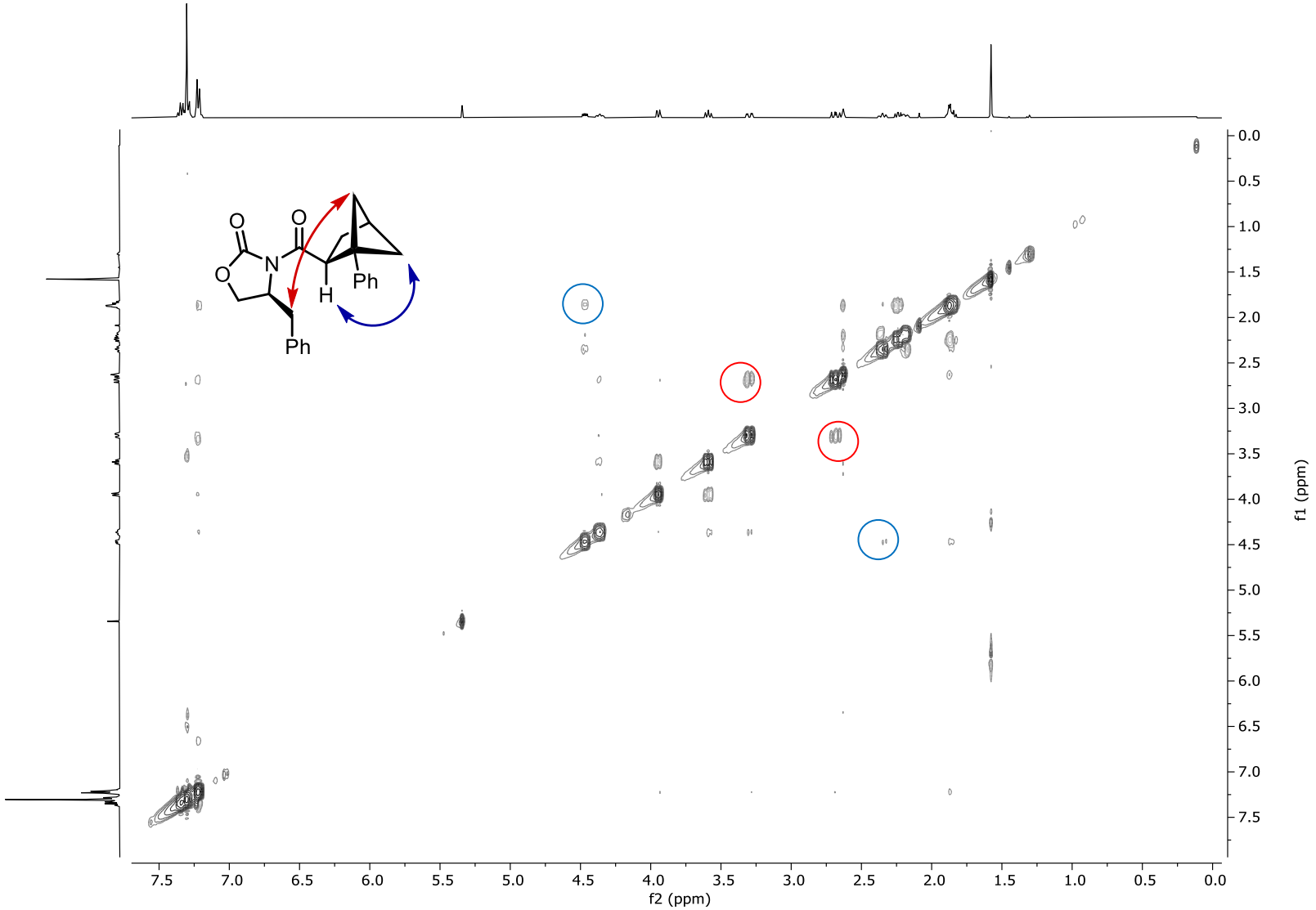
(*S*)-4-benzyl-3-((2*S*)-1-phenylbicyclo[2.1.1]hexane-2-carbonyl)oxazolidin-2-one (2r): ^{1}H NMR (400 MHz, $CDCl_3$)



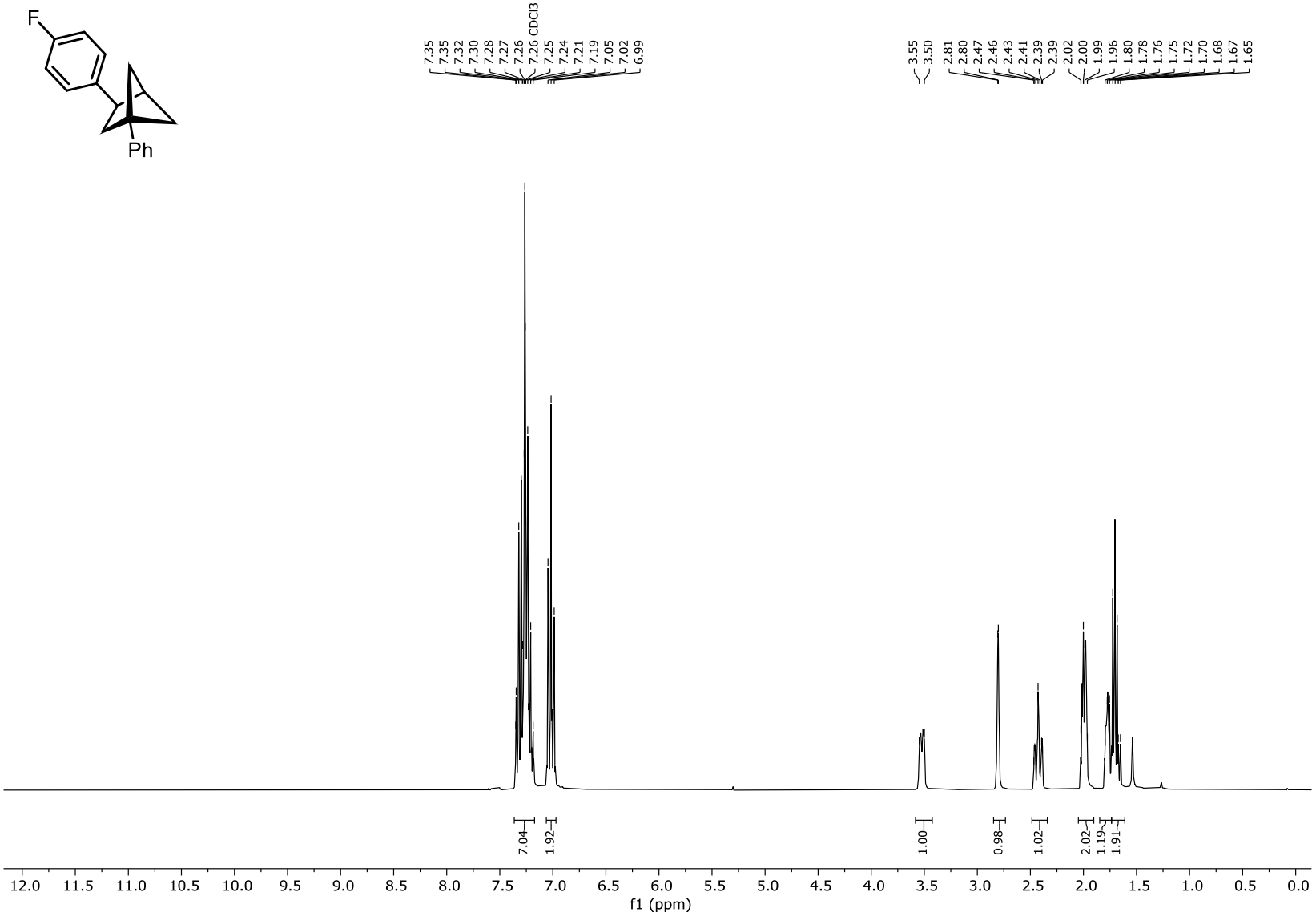
(*S*)-4-benzyl-3-((2*S*)-1-phenylbicyclo[2.1.1]hexane-2-carbonyl)oxazolidin-2-one (2r): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



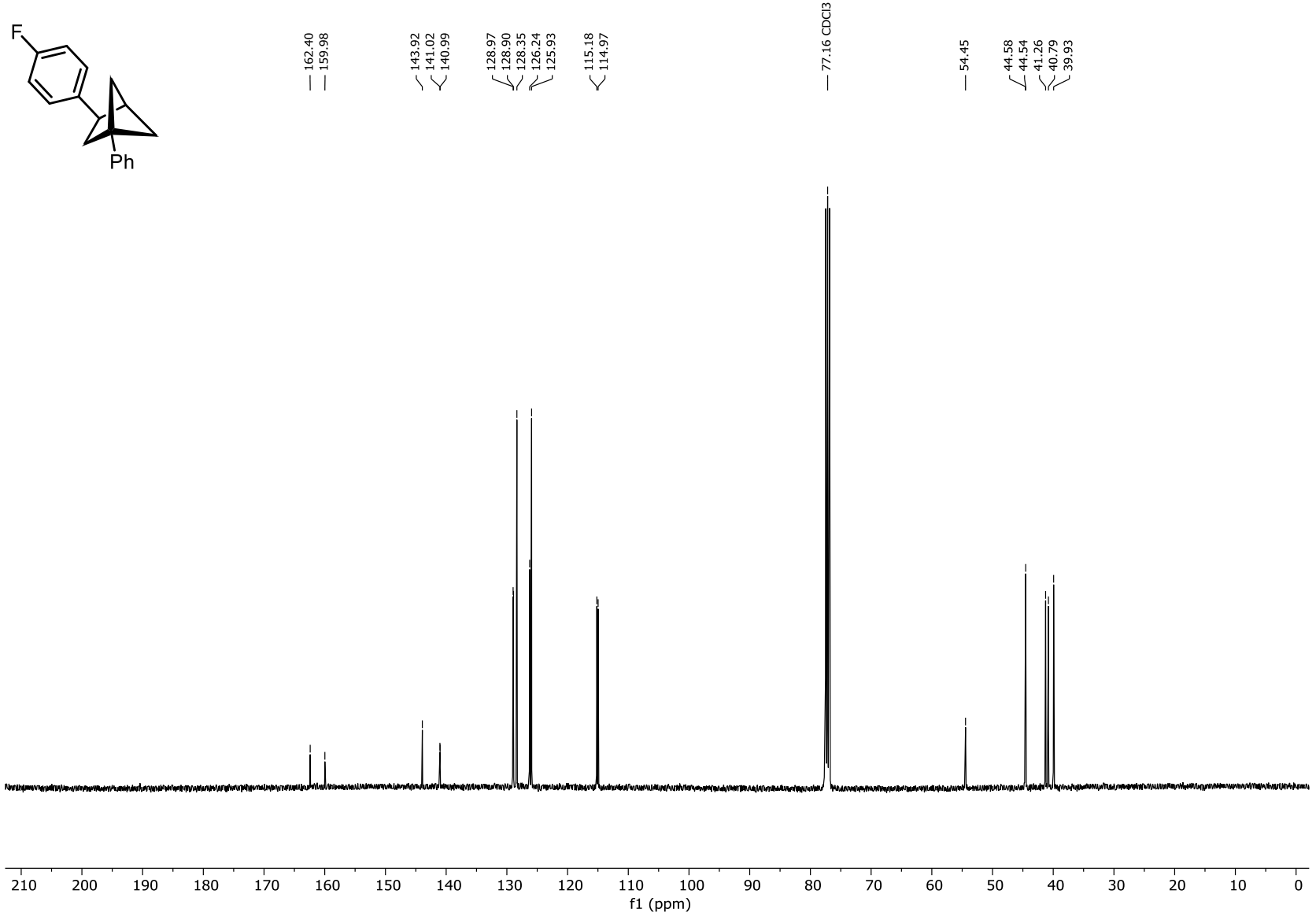
(*S*)-4-benzyl-3-((2*S*)-1-phenylbicyclo[2.1.1]hexane-2-carbonyl)oxazolidin-2-one (2r): NOESY (400 MHz, $CDCl_3$)



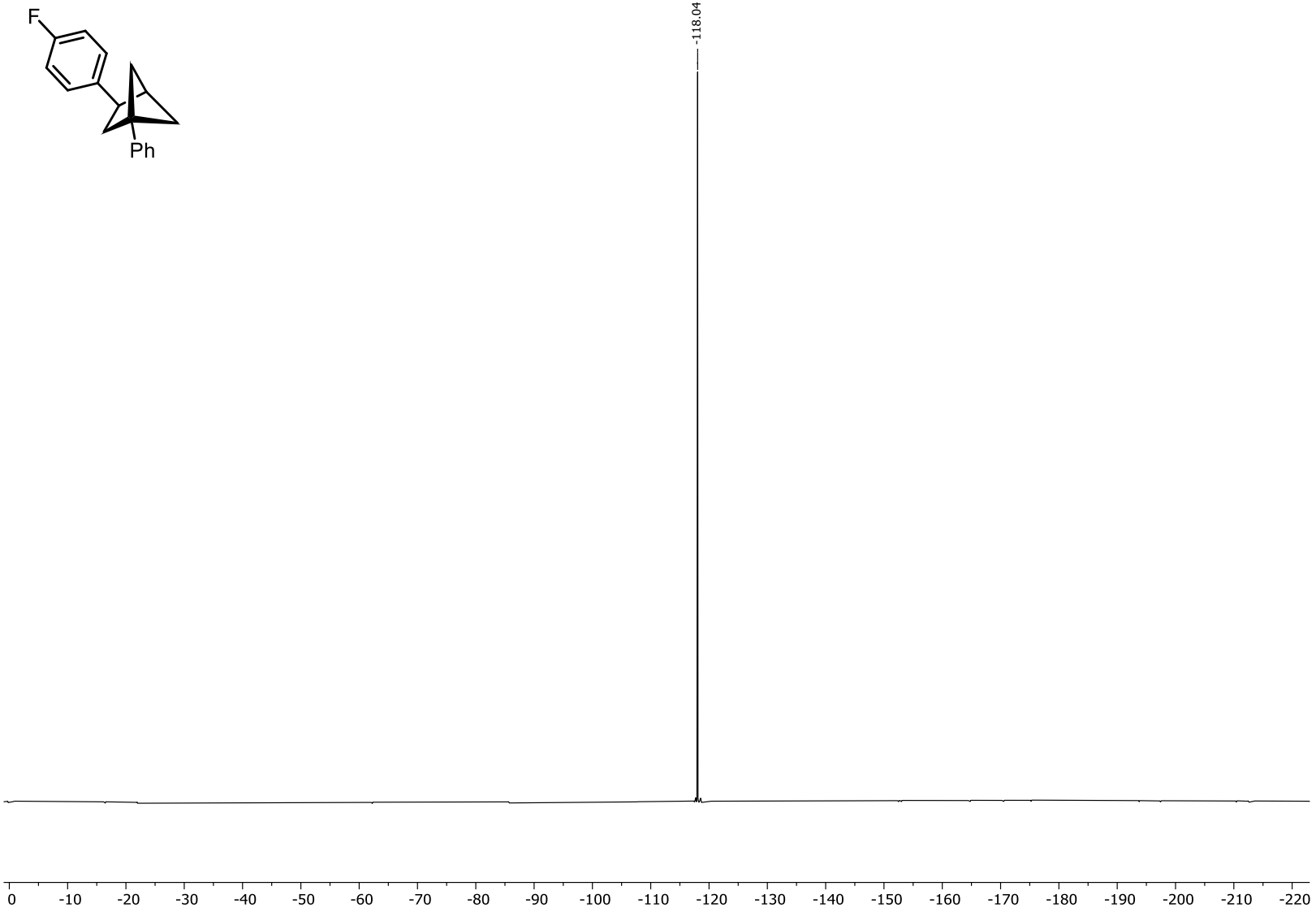
3-(4-Fluorophenyl)-1-phenylbicyclo[2.1.1]hexane (2s): ^{1}H NMR (300 MHz, $CDCl_3$)



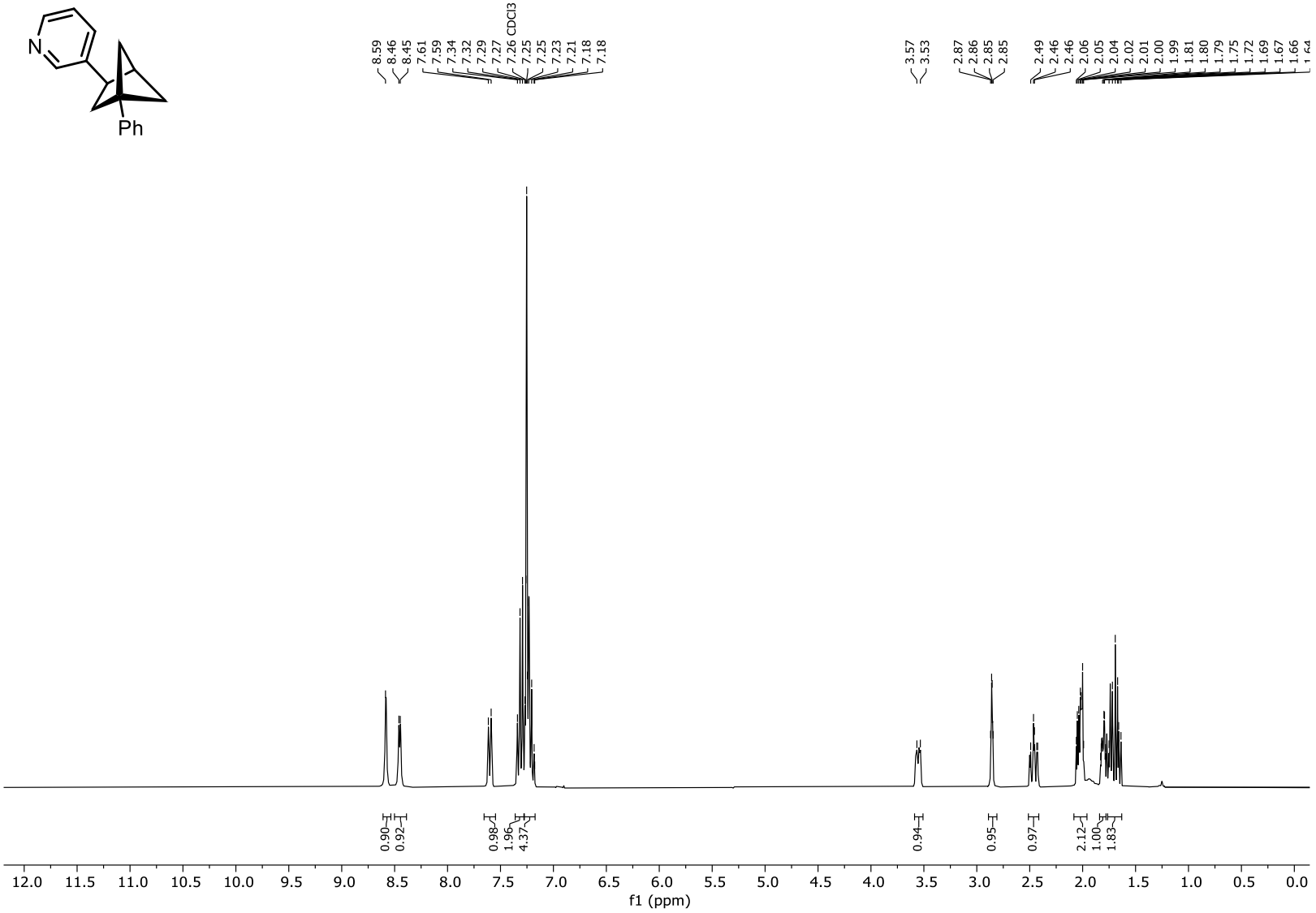
3-(4-Fluorophenyl)-1-phenylbicyclo[2.1.1]hexane (2s): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



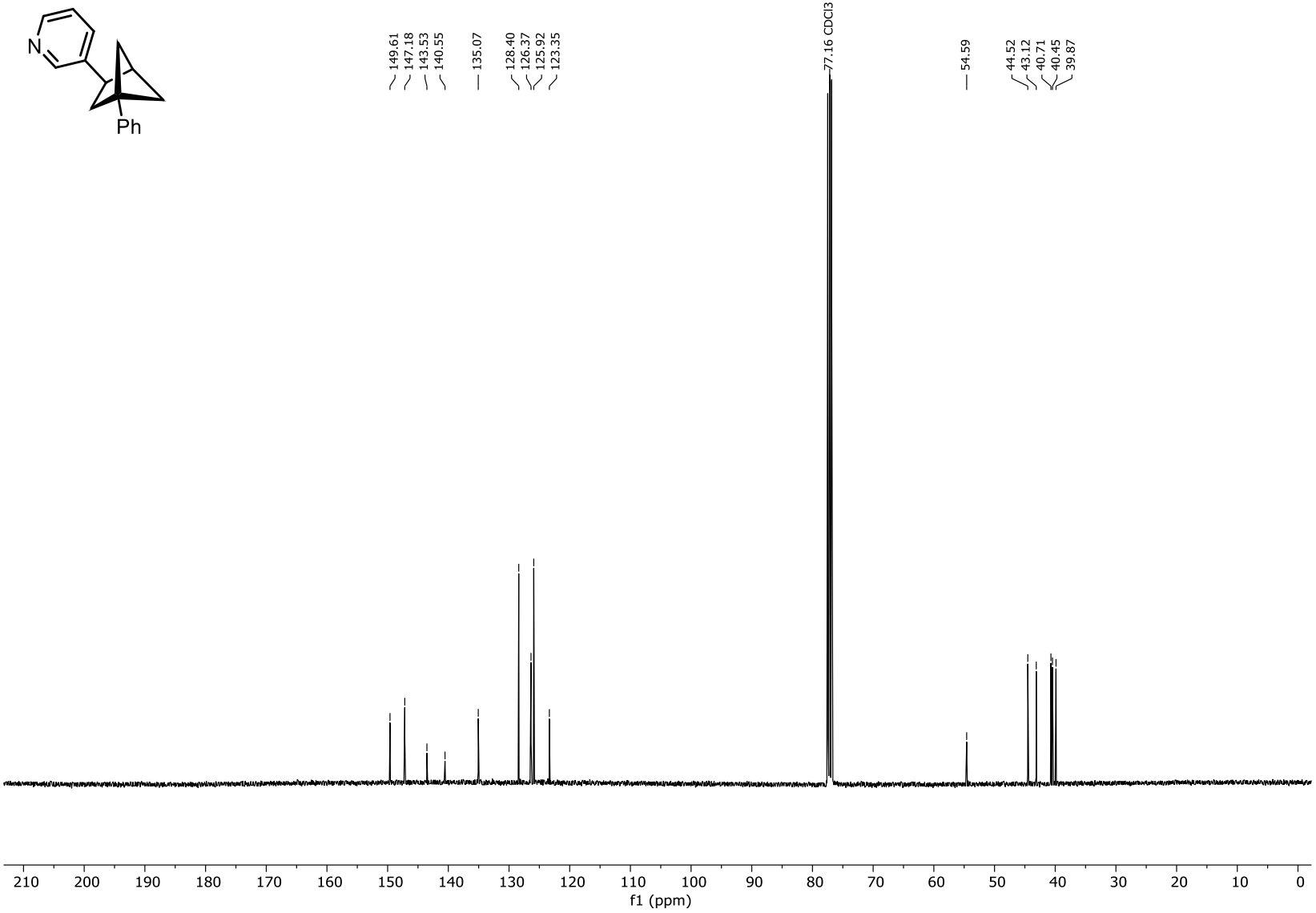
3-(4-Fluorophenyl)-1-phenylbicyclo[2.1.1]hexane (2s): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)



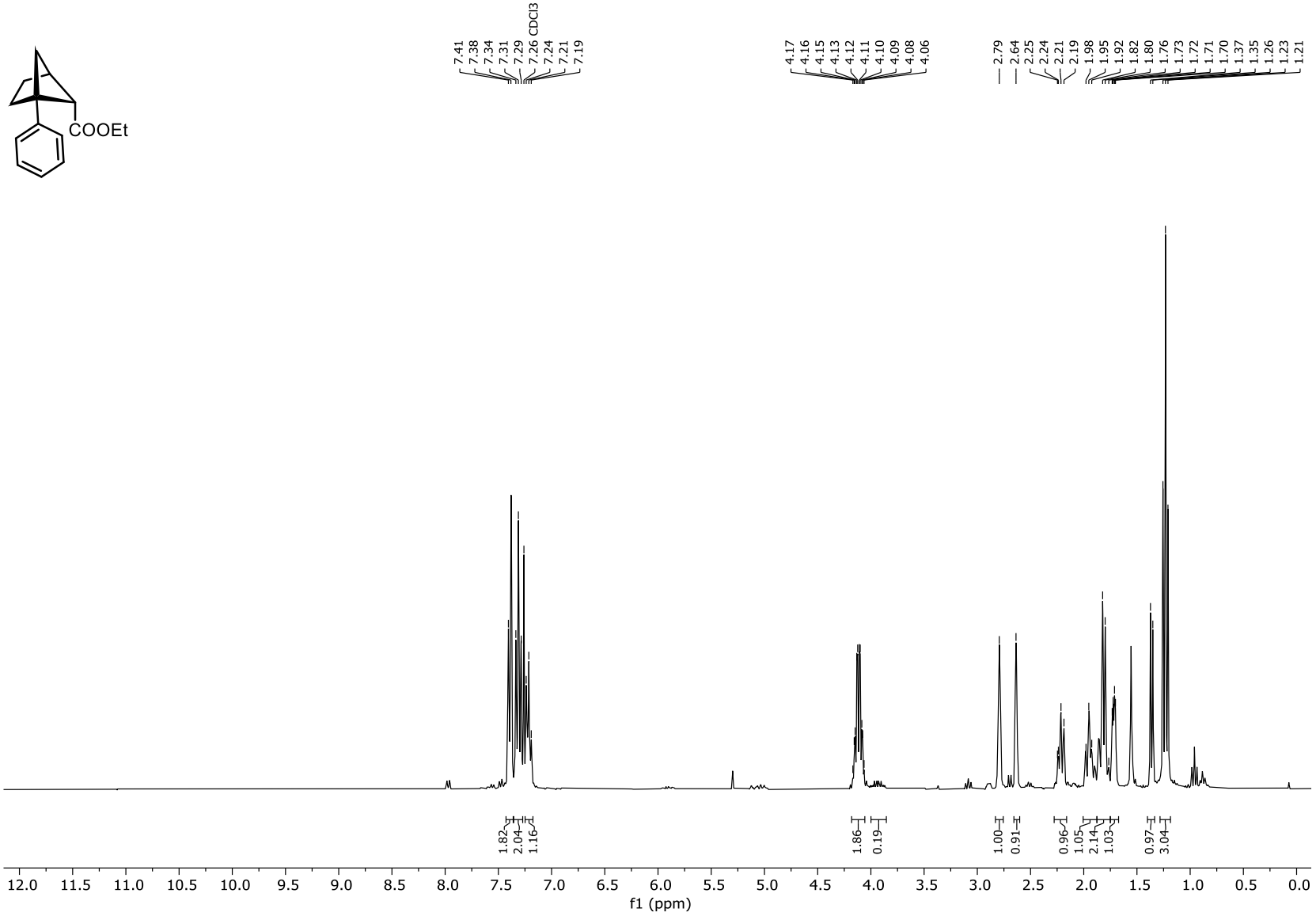
3-(4-Phenylbicyclo[2.1.1]hexan-2-yl)pyridine (2t): ^{1}H NMR (300 MHz, $CDCl_3$)



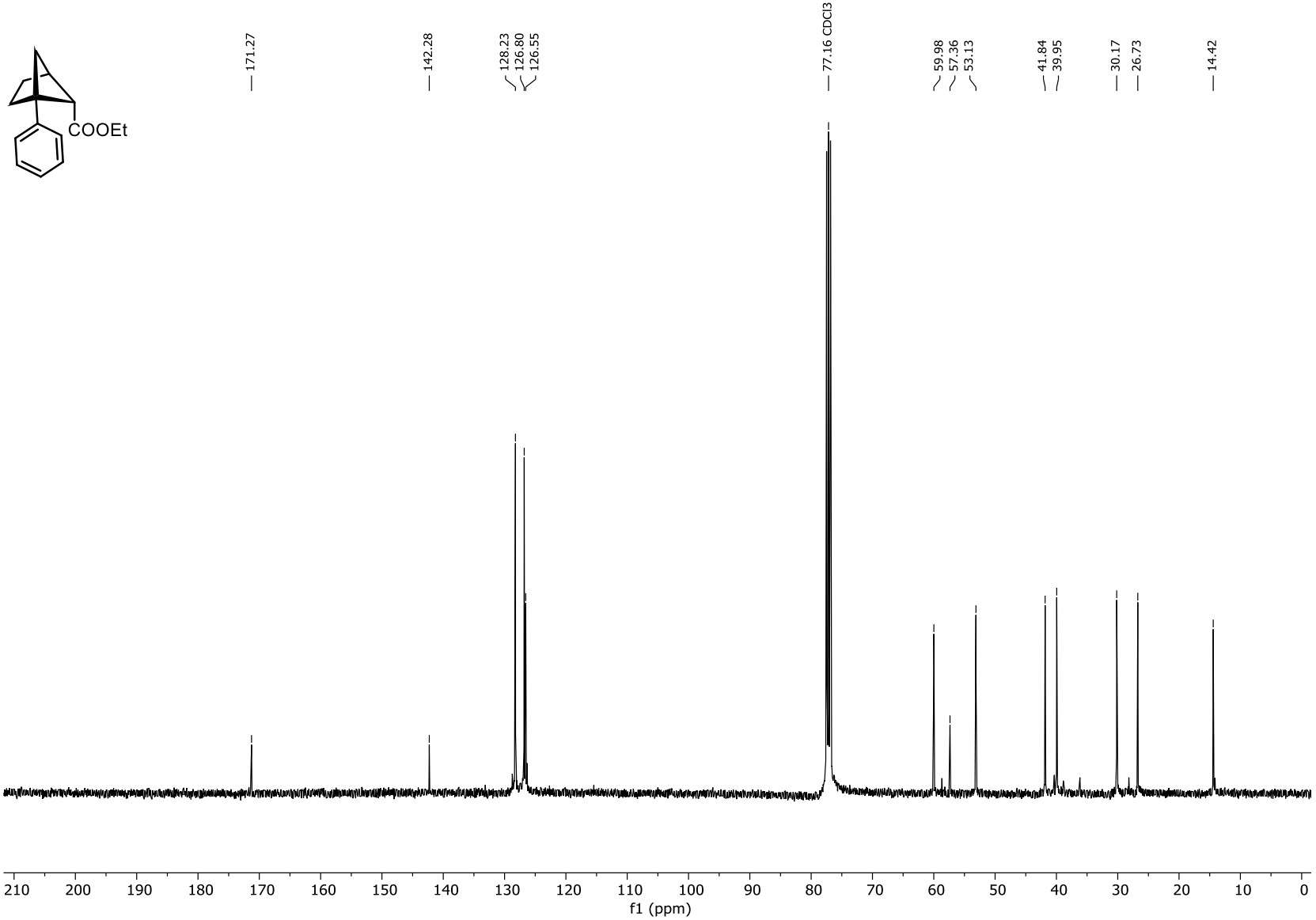
3-(4-Phenylbicyclo[2.1.1]hexan-2-yl)pyridine (2t): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



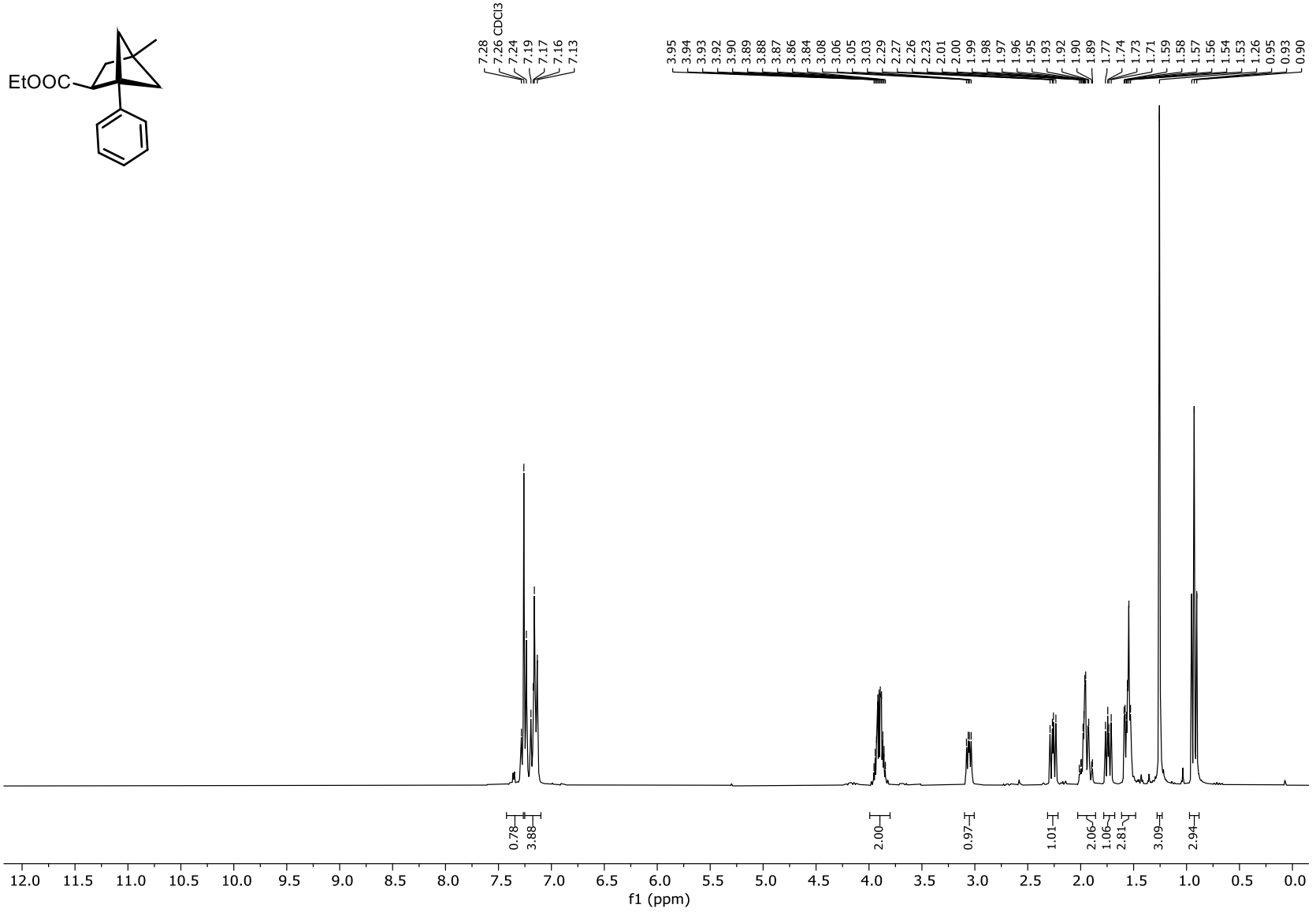
Ethyl 1-phenylbicyclo[2.1.1]hexane-5-carboxylate (2u): ^{1}H NMR (300 MHz, $CDCl_3$)



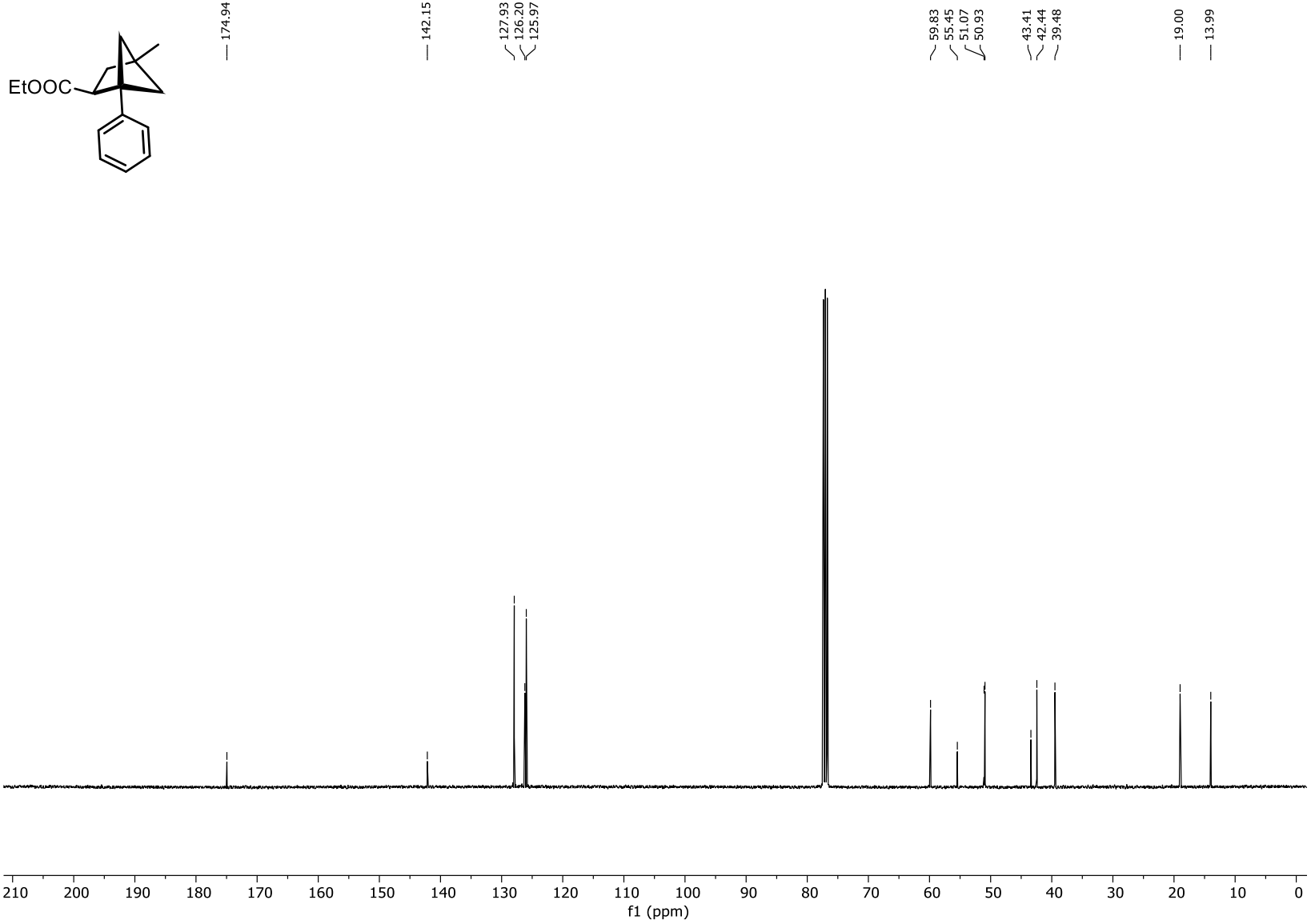
Ethyl 1-phenylbicyclo[2.1.1]hexane-5-carboxylate (2u): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



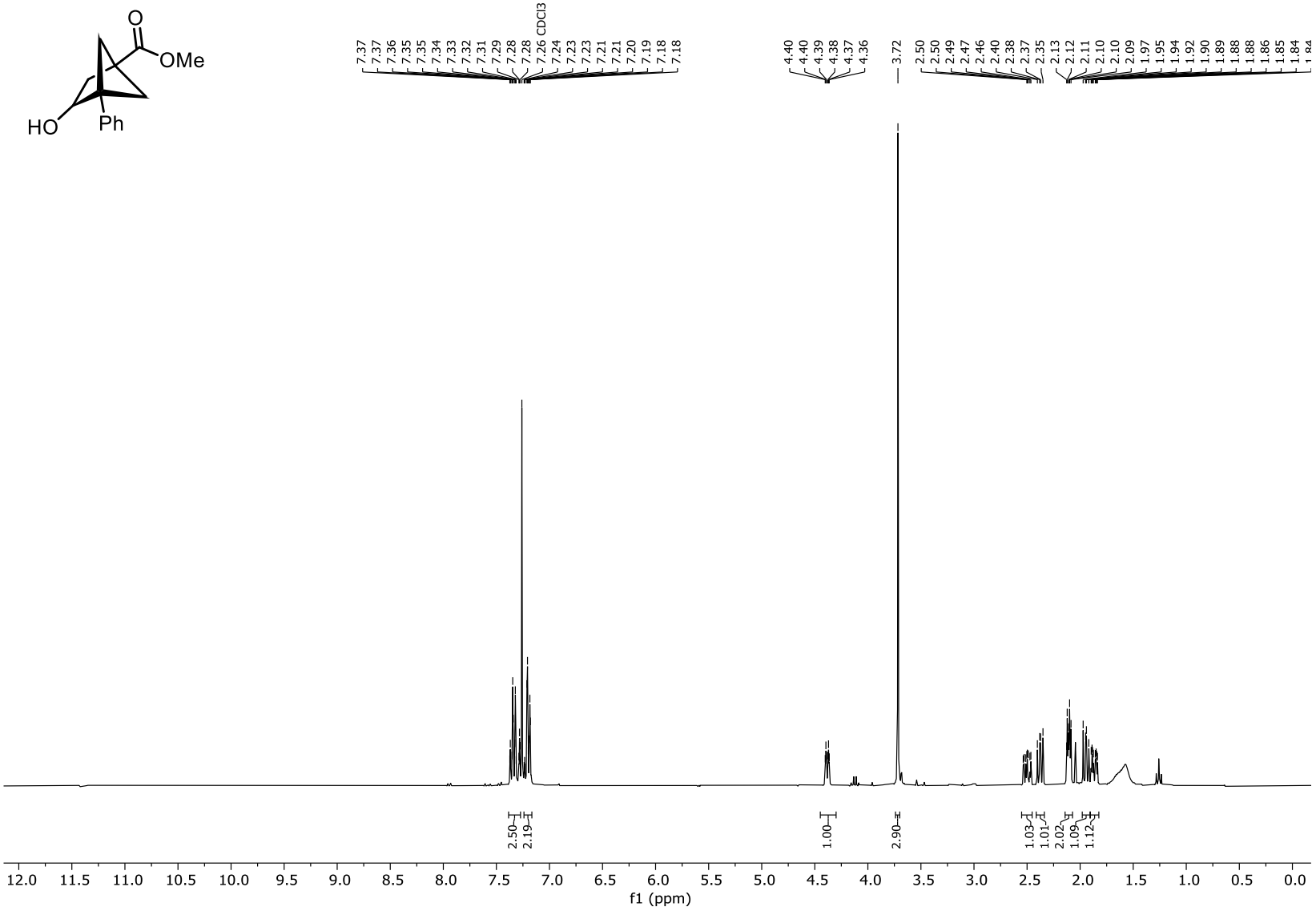
Ethyl 4-methyl-1-phenylbicyclo[2.1.1]hexane-2-carboxylate (2v): ^{1}H NMR (300 MHz, $CDCl_3$)



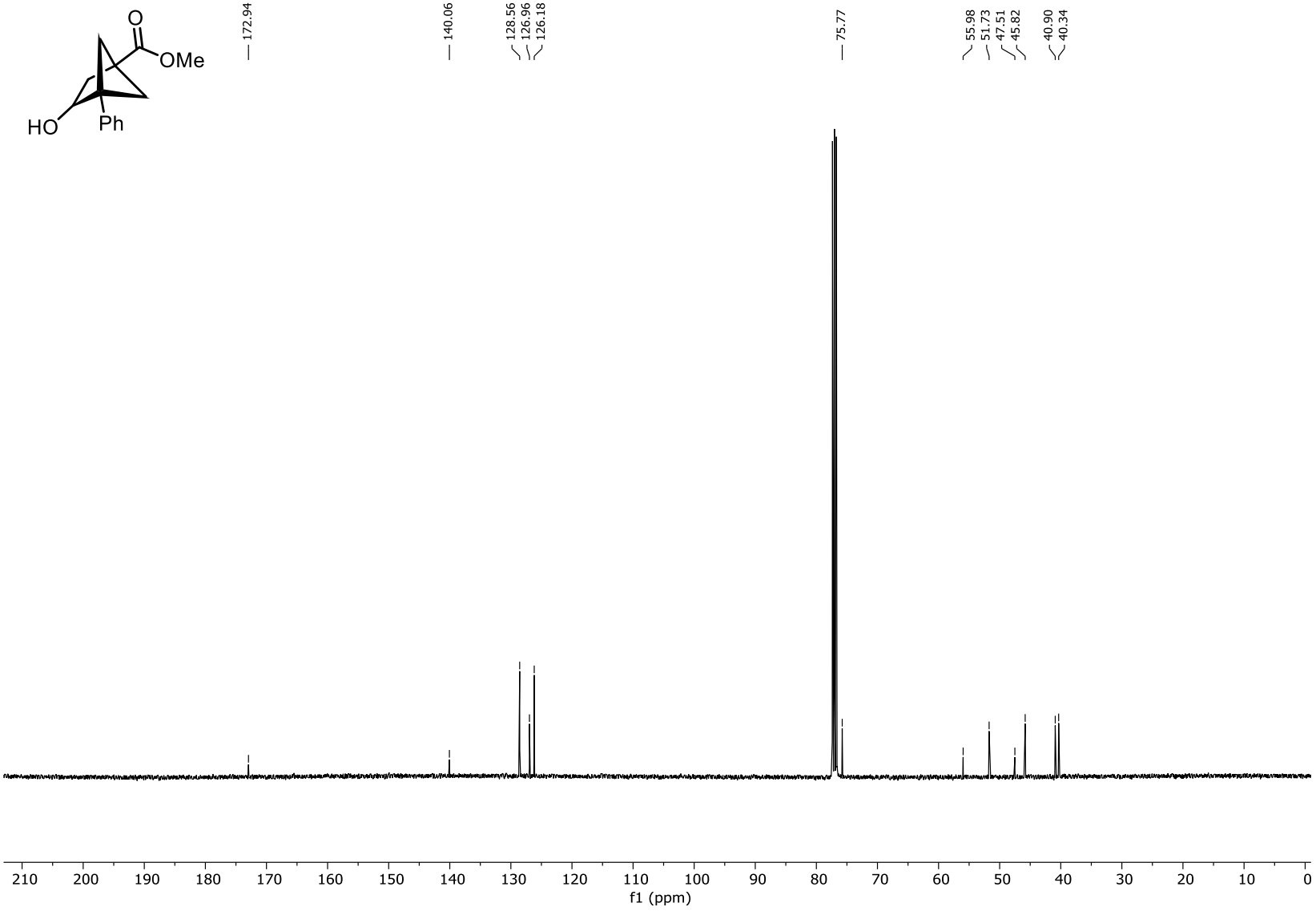
Ethyl 4-methyl-1-phenylbicyclo[2.1.1]hexane-2-carboxylate (2v): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



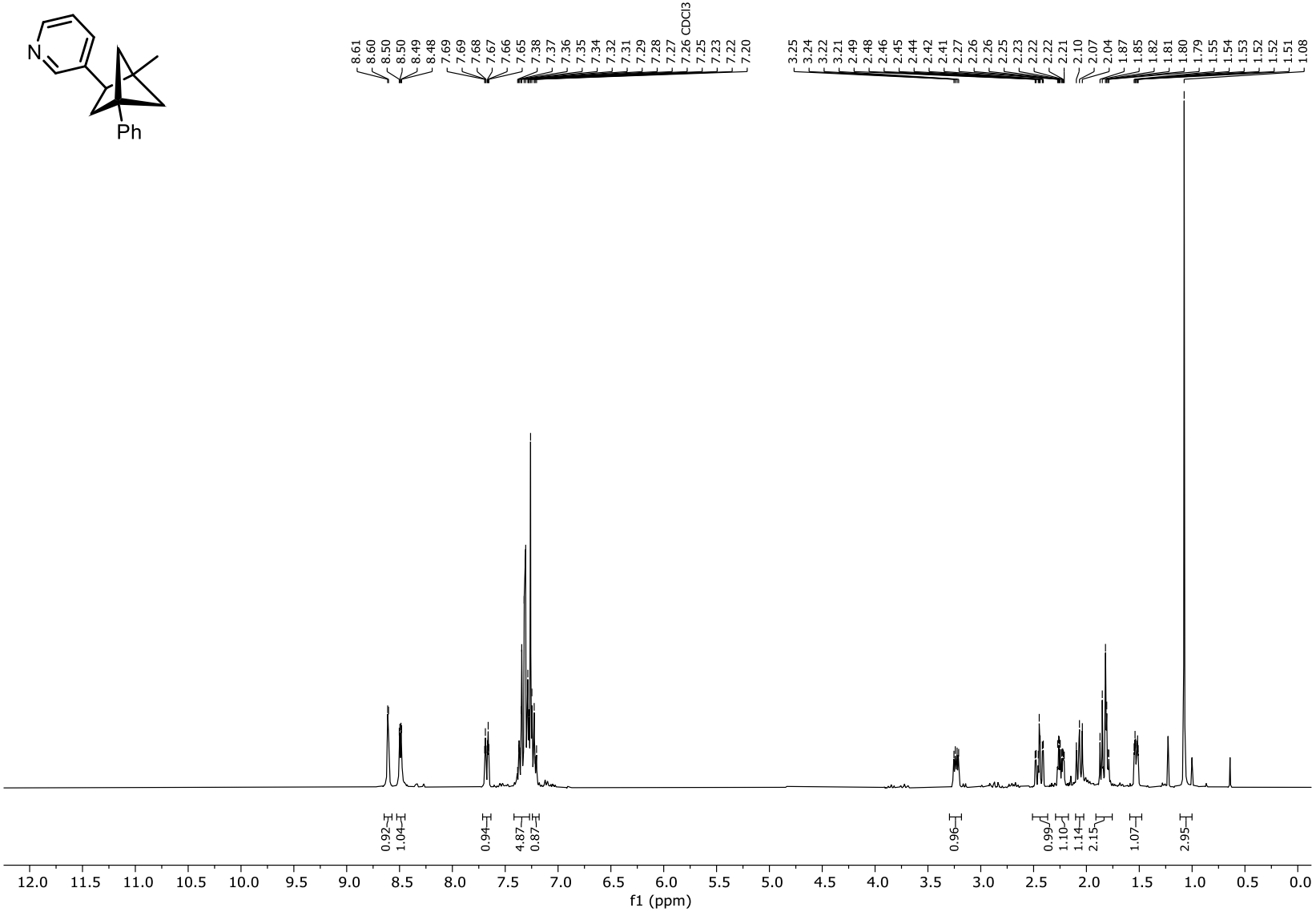
Methyl-3-hydroxy-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2w): ^{1}H NMR (300 MHz, $CDCl_3$)



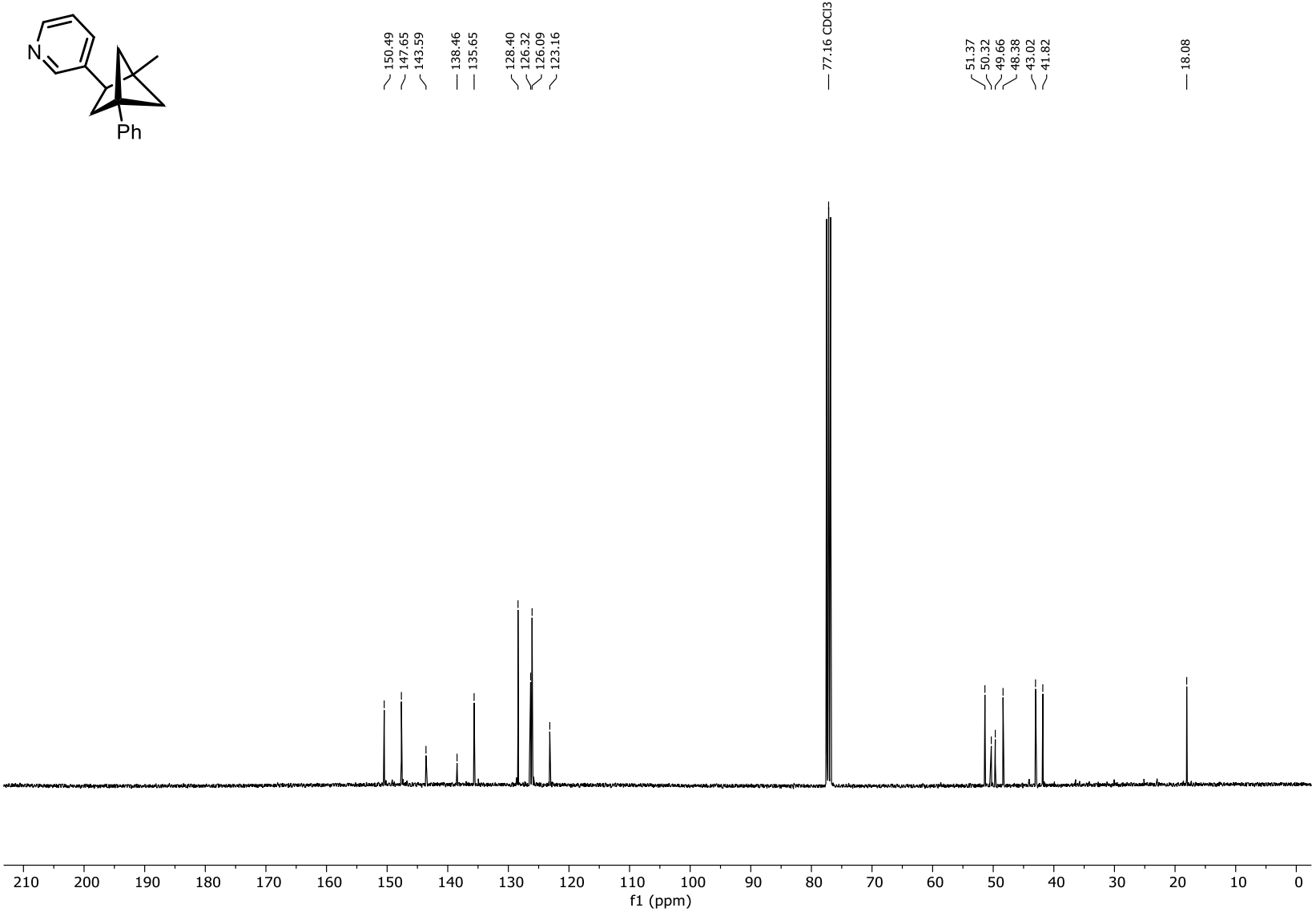
Methyl-3-hydroxy-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2w): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



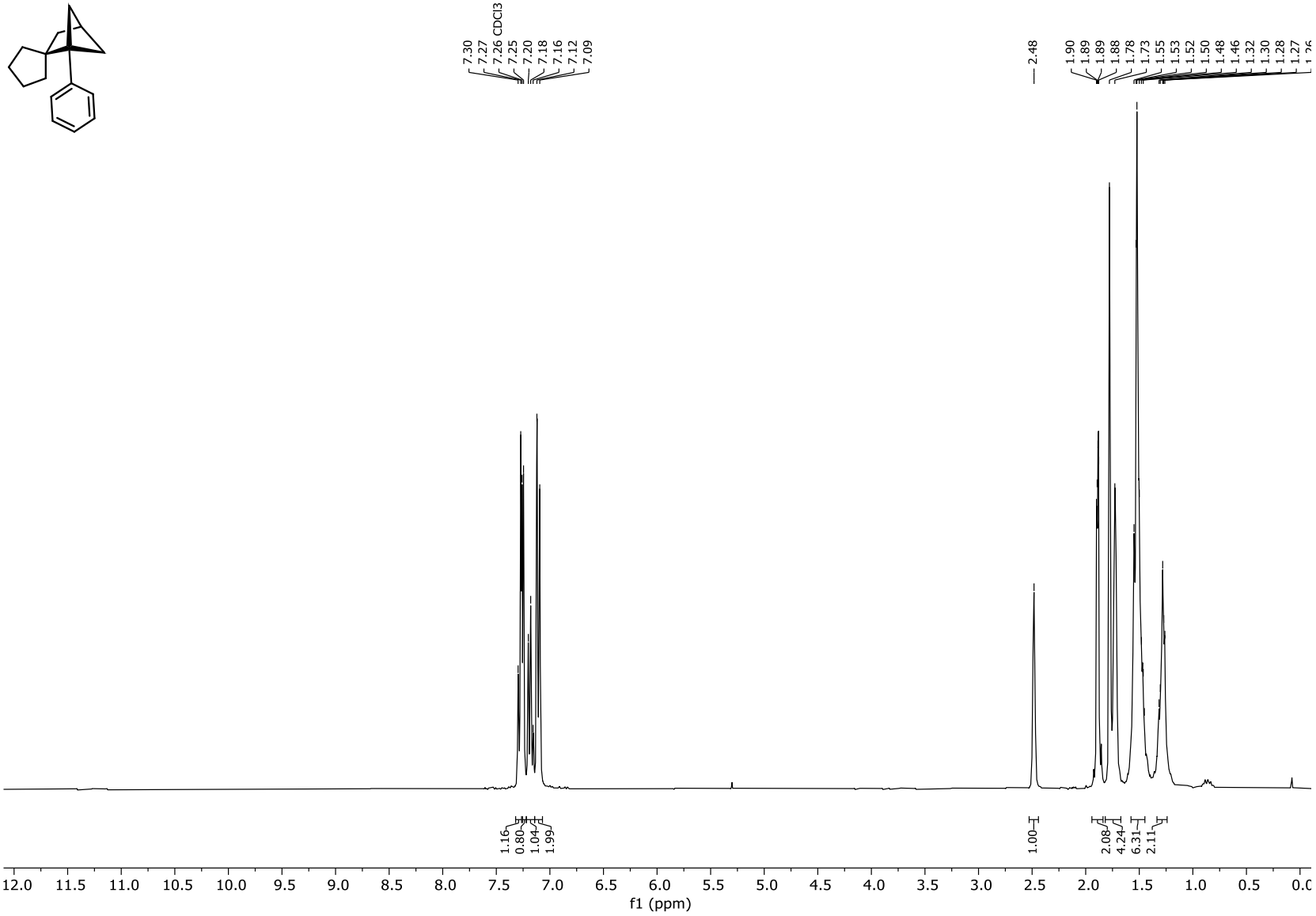
3-(1-methyl-4-phenylbicyclo[2.1.1]hexan-2-yl)pyridine (2x):



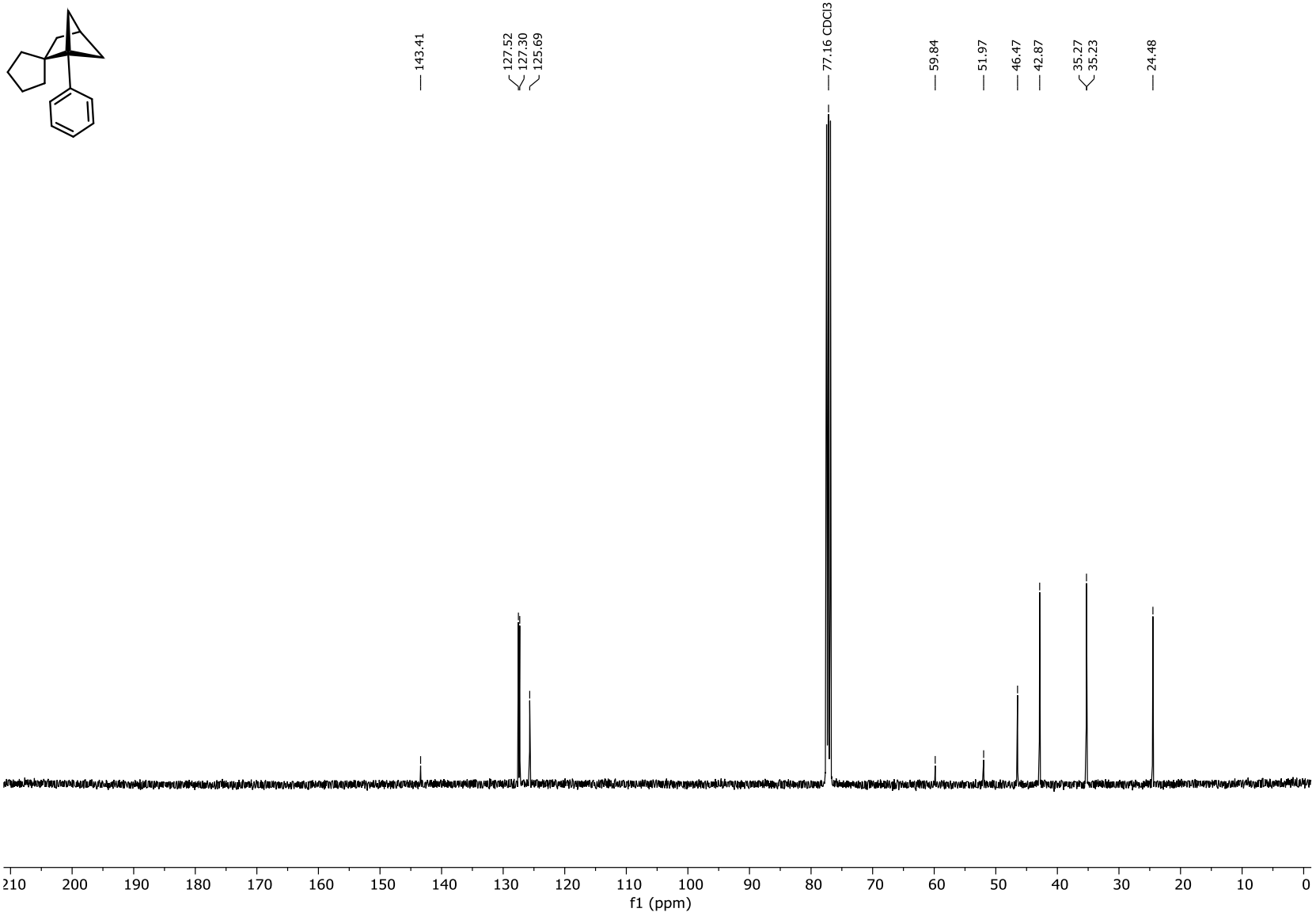
3-(1-methyl-4-phenylbicyclo[2.1.1]hexan-2-yl)pyridine (2x):



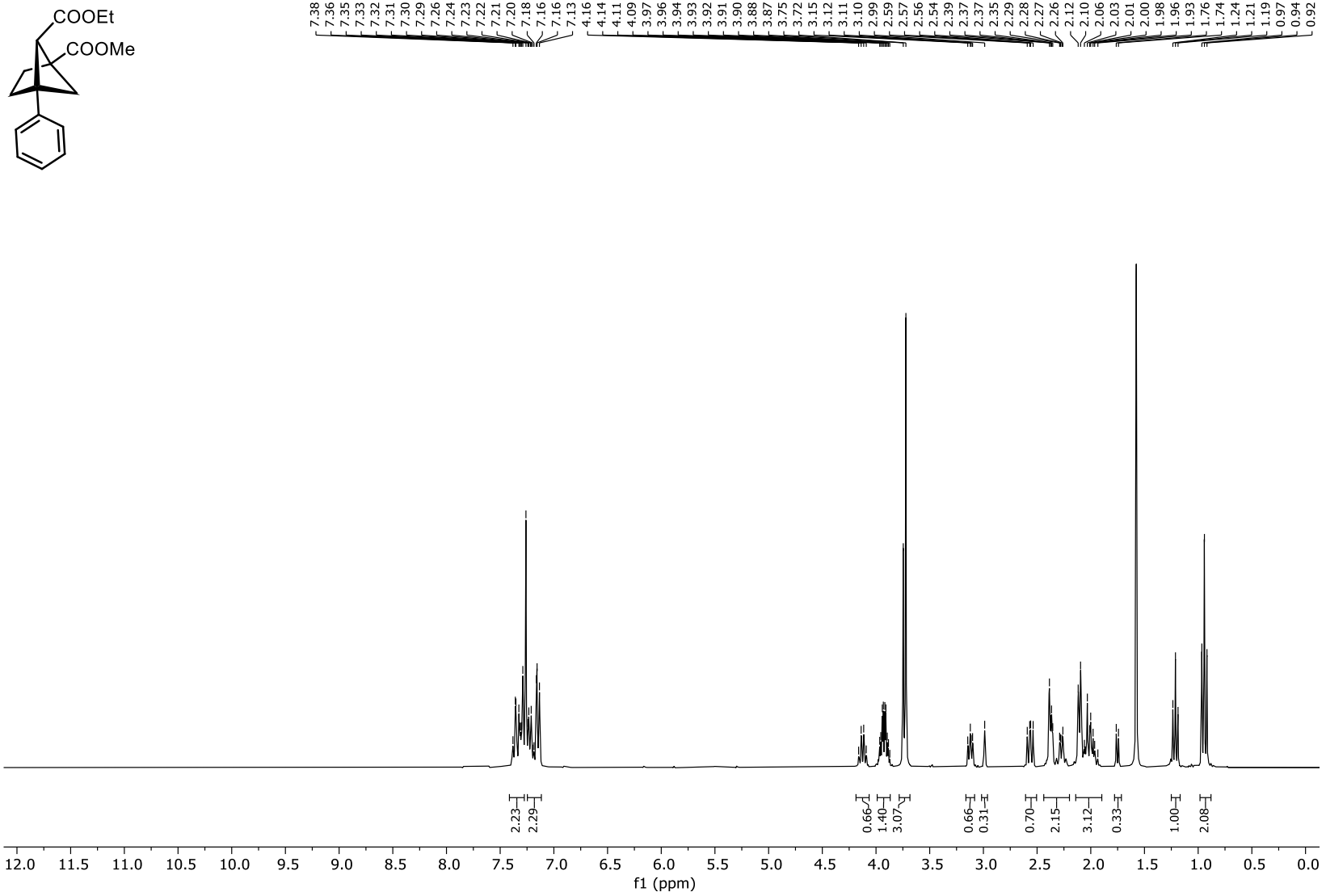
1-Phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclopentane] (2y): ^{1}H NMR (300 MHz, $CDCl_3$)



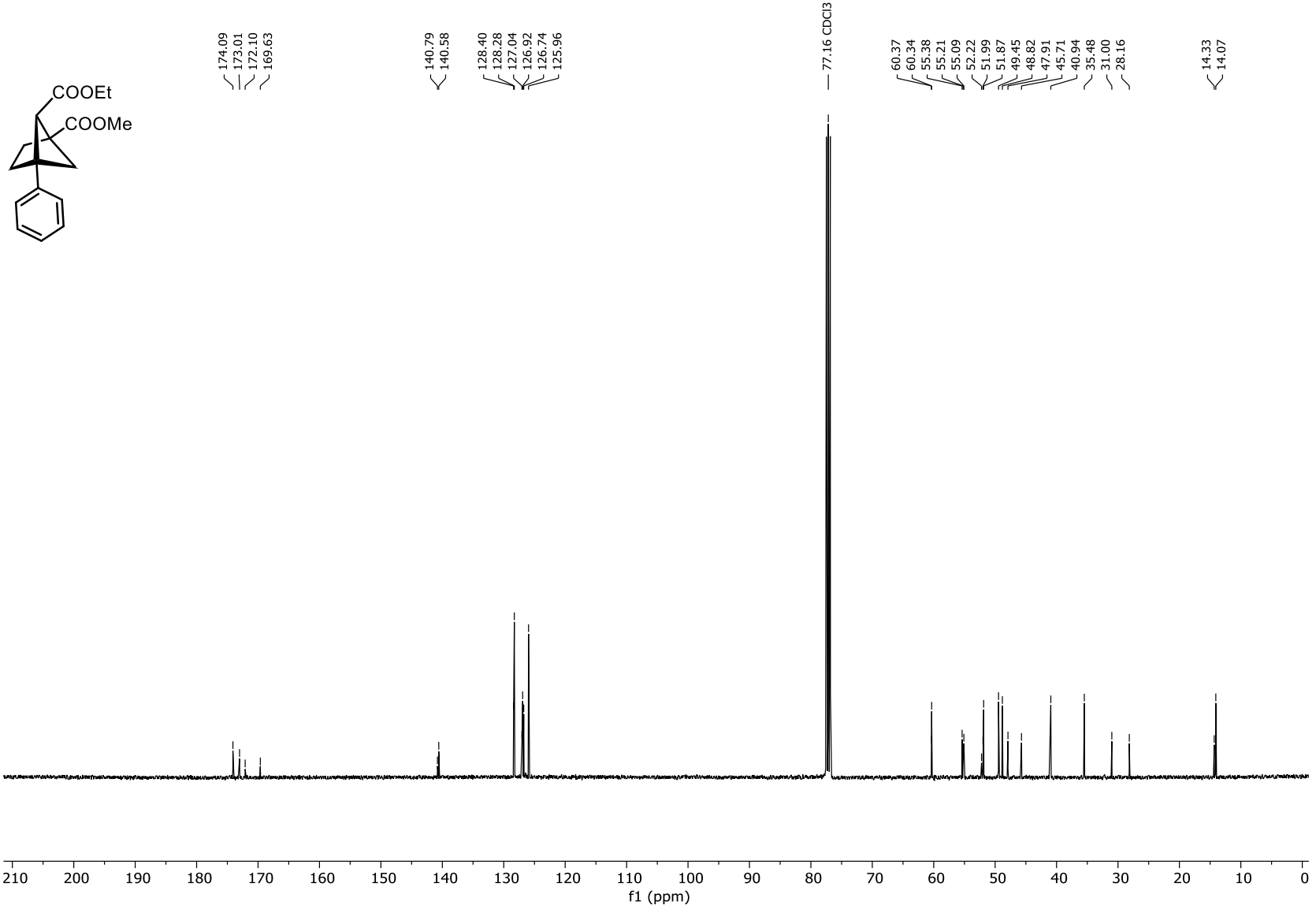
1-Phenylspiro[bicyclo[2.1.1]hexane-2,1'-cyclopentane] (2y): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



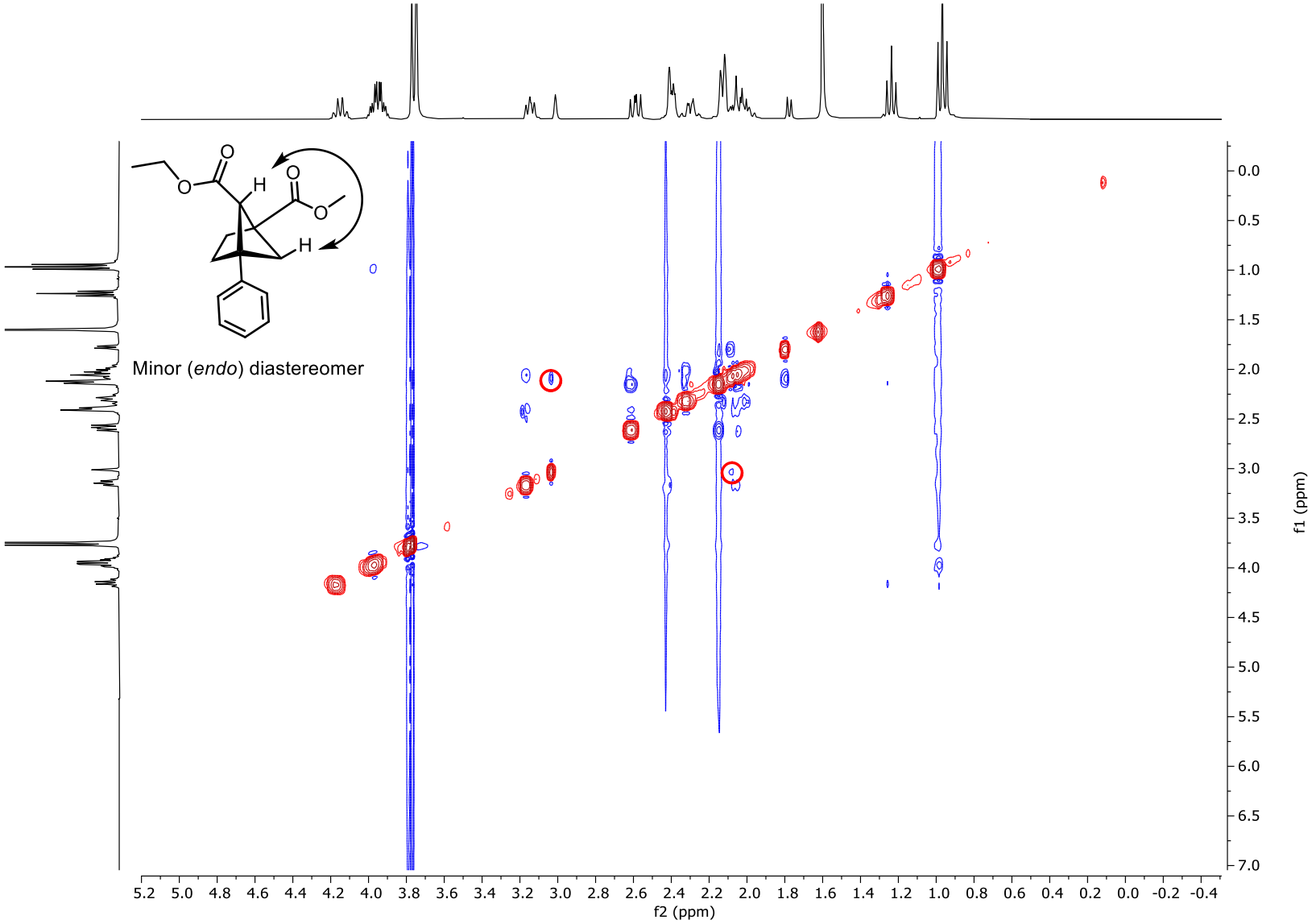
5-Ethyl 1-methyl-4-phenylbicyclo[2.1.1]hexane-1,5-dicarboxylate (2z): ^{1}H NMR (300 MHz, $CDCl_3$)



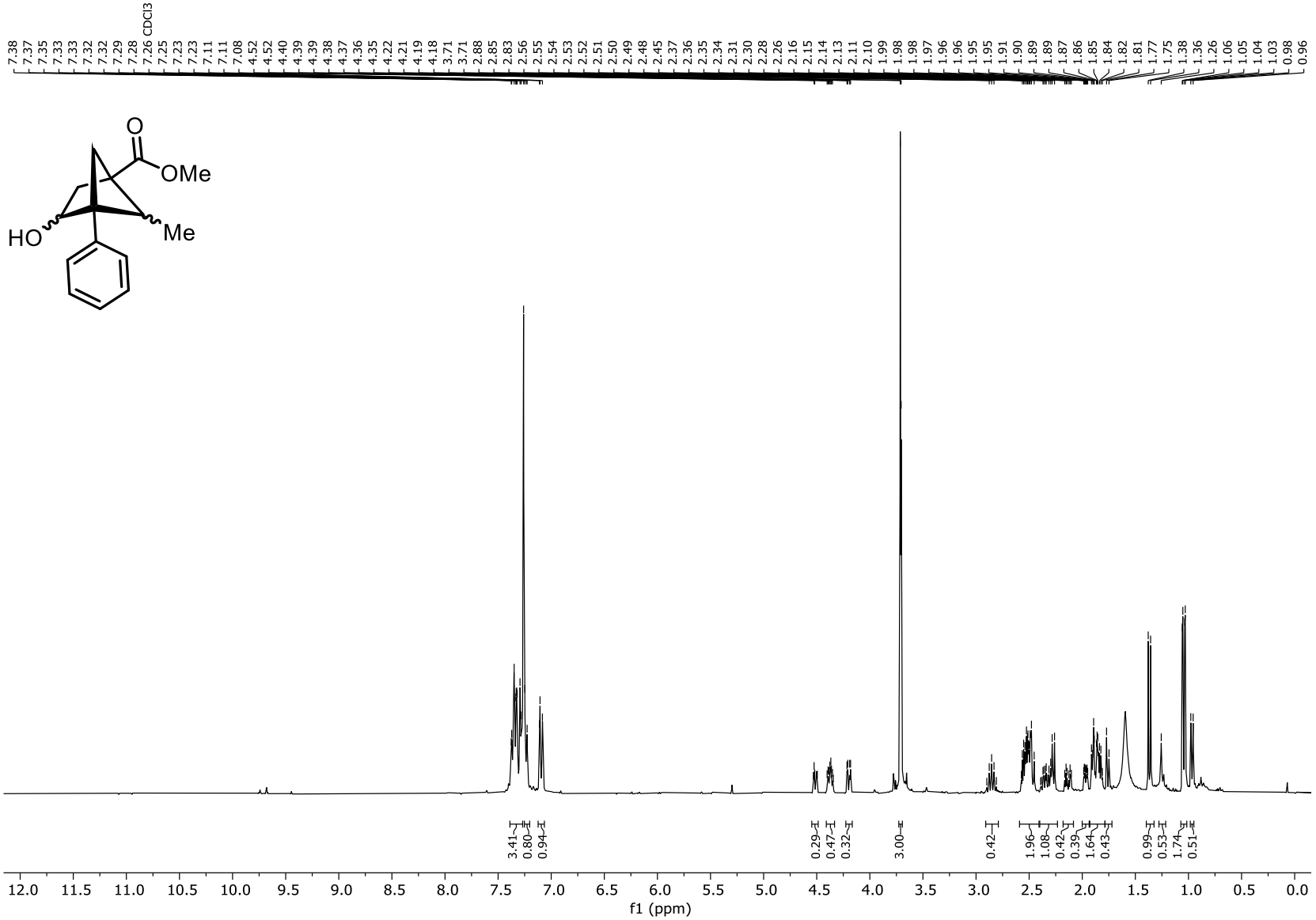
5-Ethyl 1-methyl-4-phenylbicyclo[2.1.1]hexane-1,5-dicarboxylate (2z): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



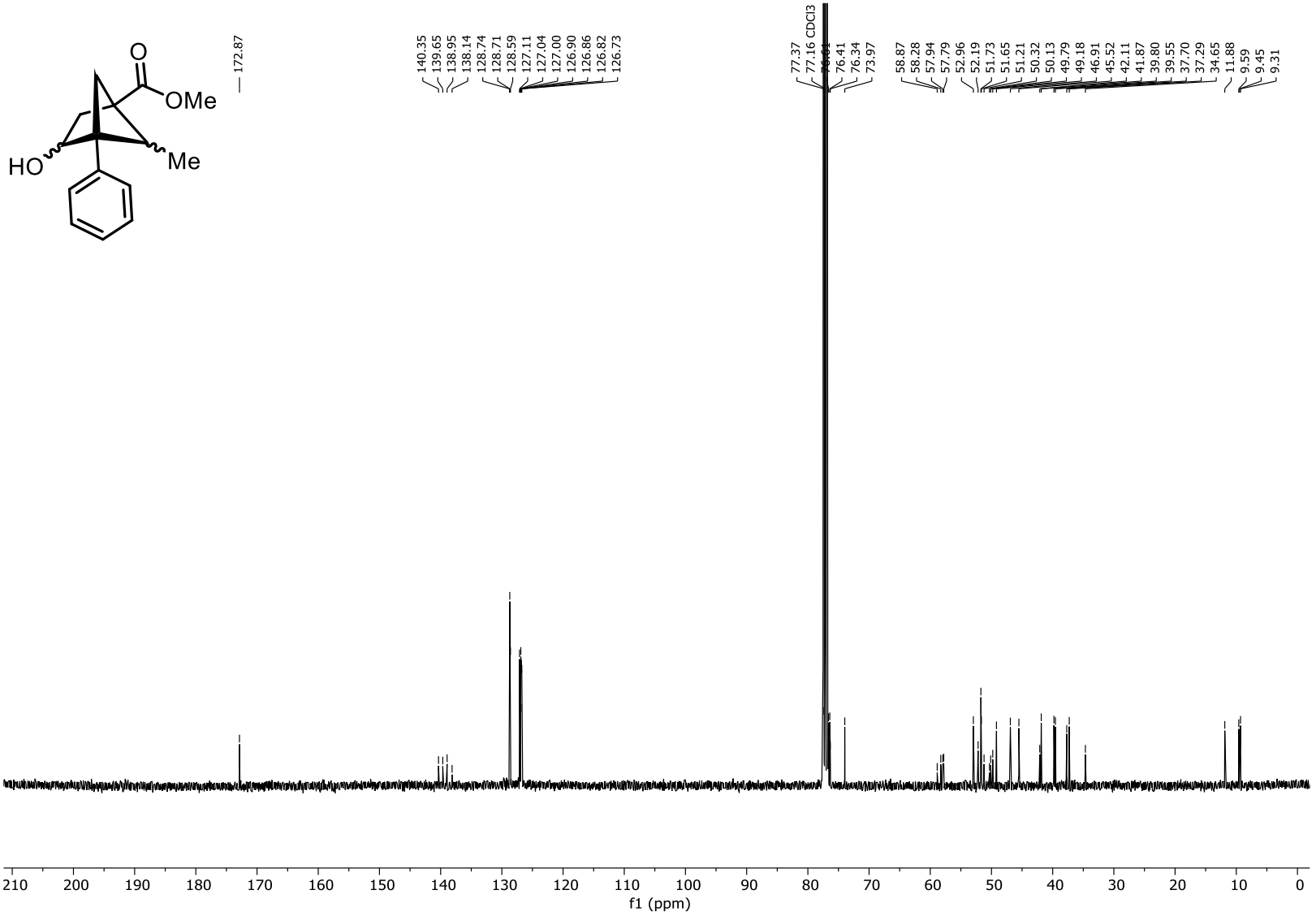
5-Ethyl 1-methyl-4-phenylbicyclo[2.1.1]hexane-1,5-dicarboxylate (2z): NOESY (400 MHz, $CDCl_3$)



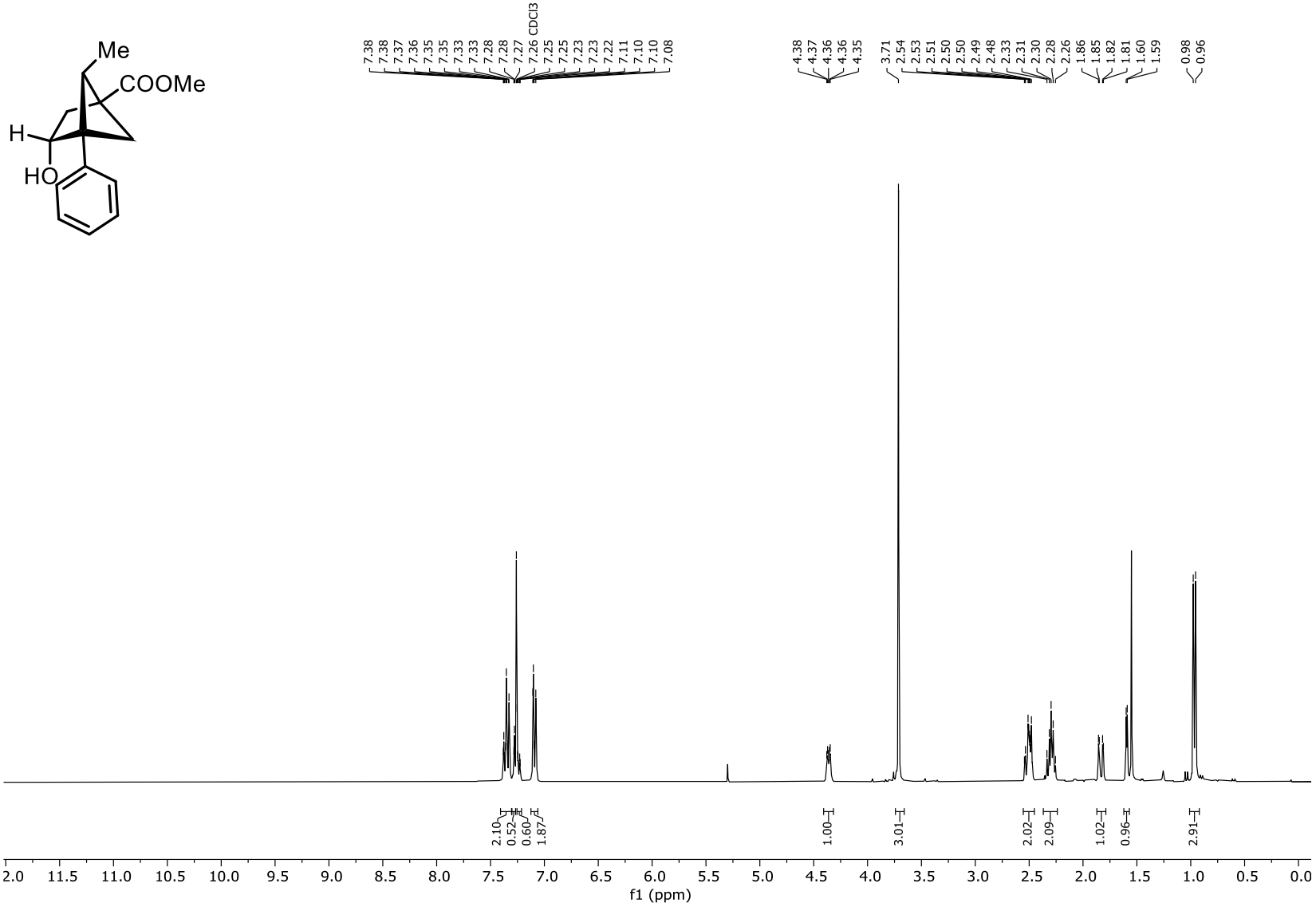
Methyl-3-hydroxy-5-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NMR (300 MHz, $CDCl_3$)



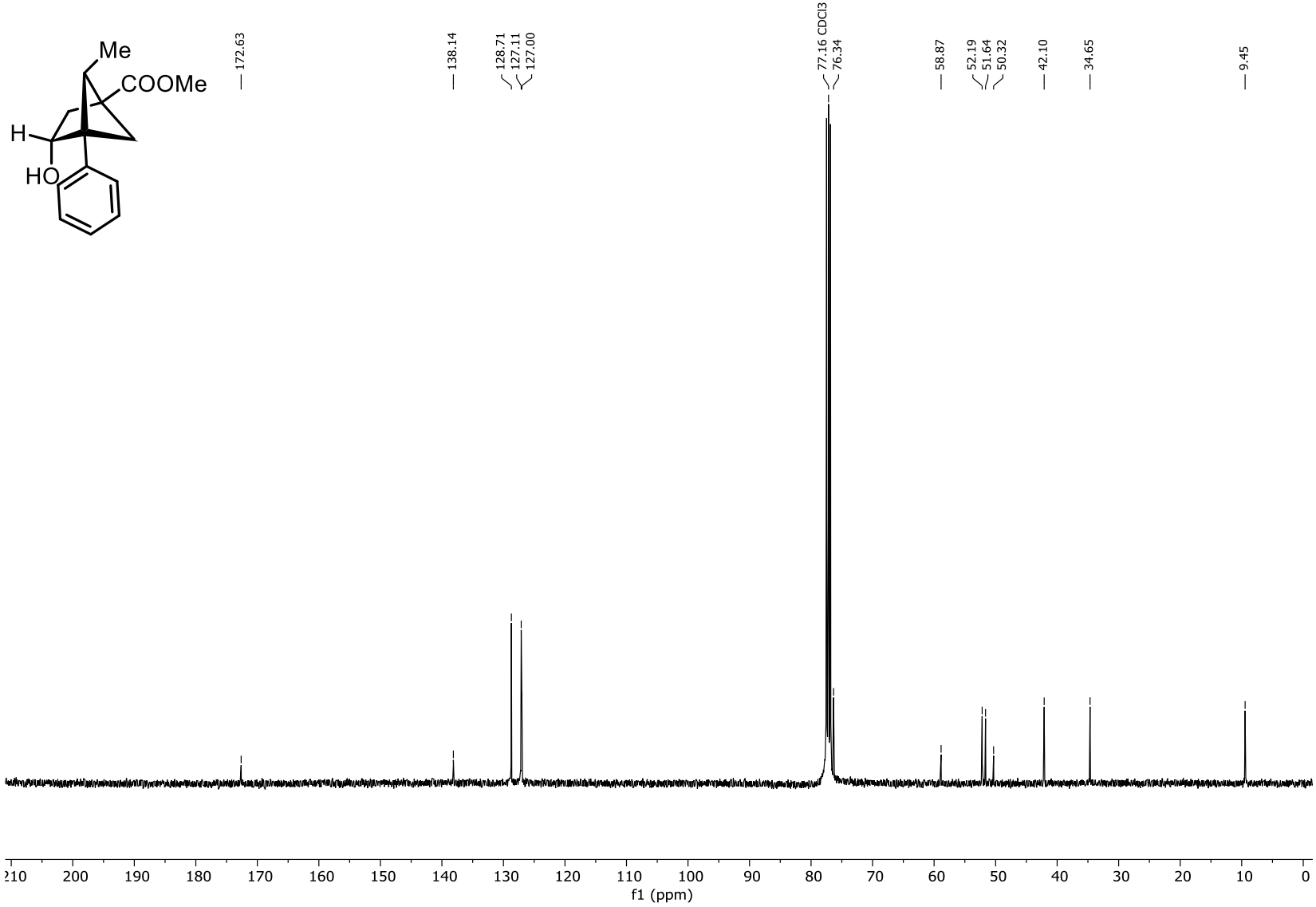
Methyl 3-hydroxy-5-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



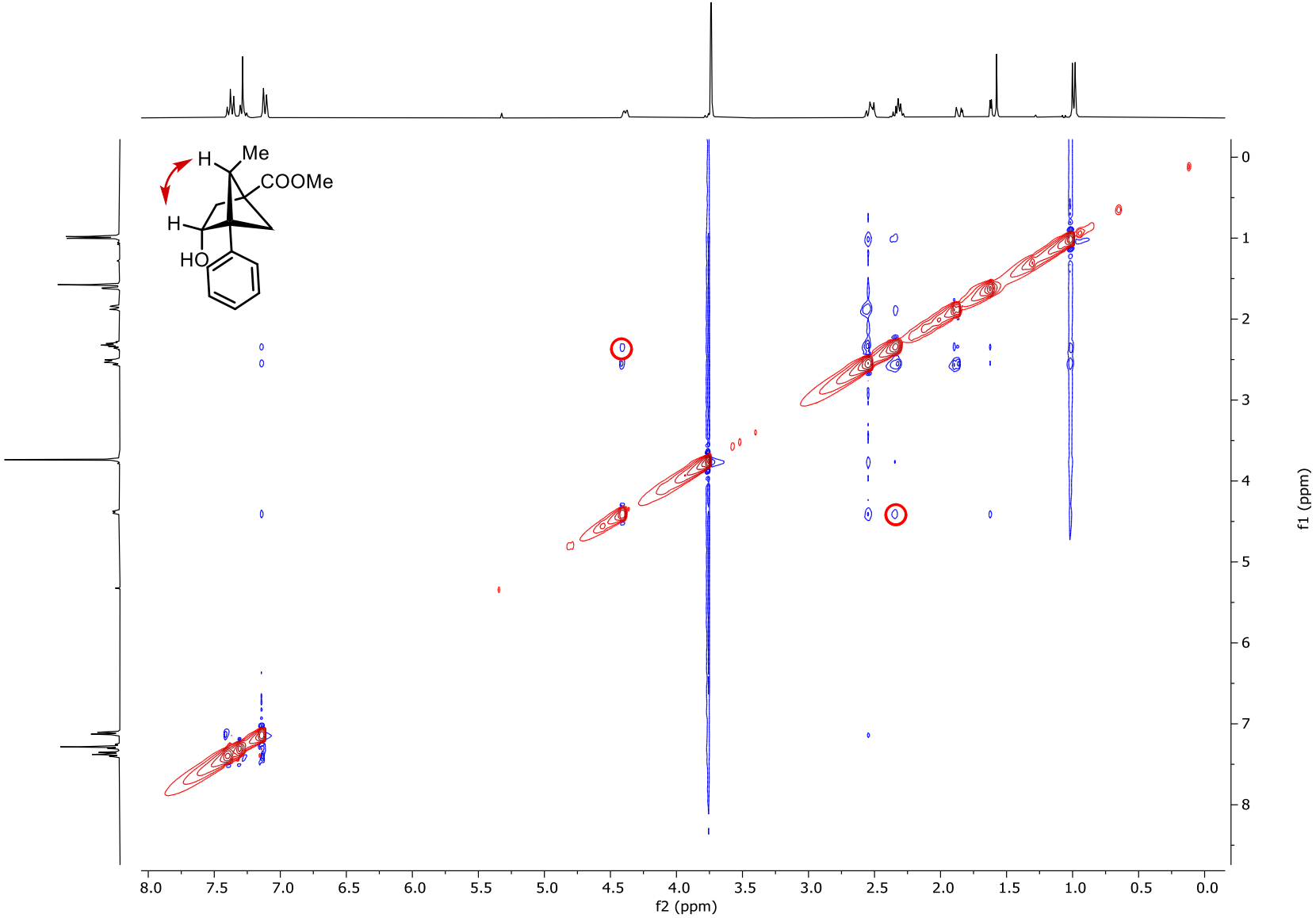
Methyl 2-*exo*-hydroxy-5-*exo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NMR (300 MHz, $CDCl_3$)



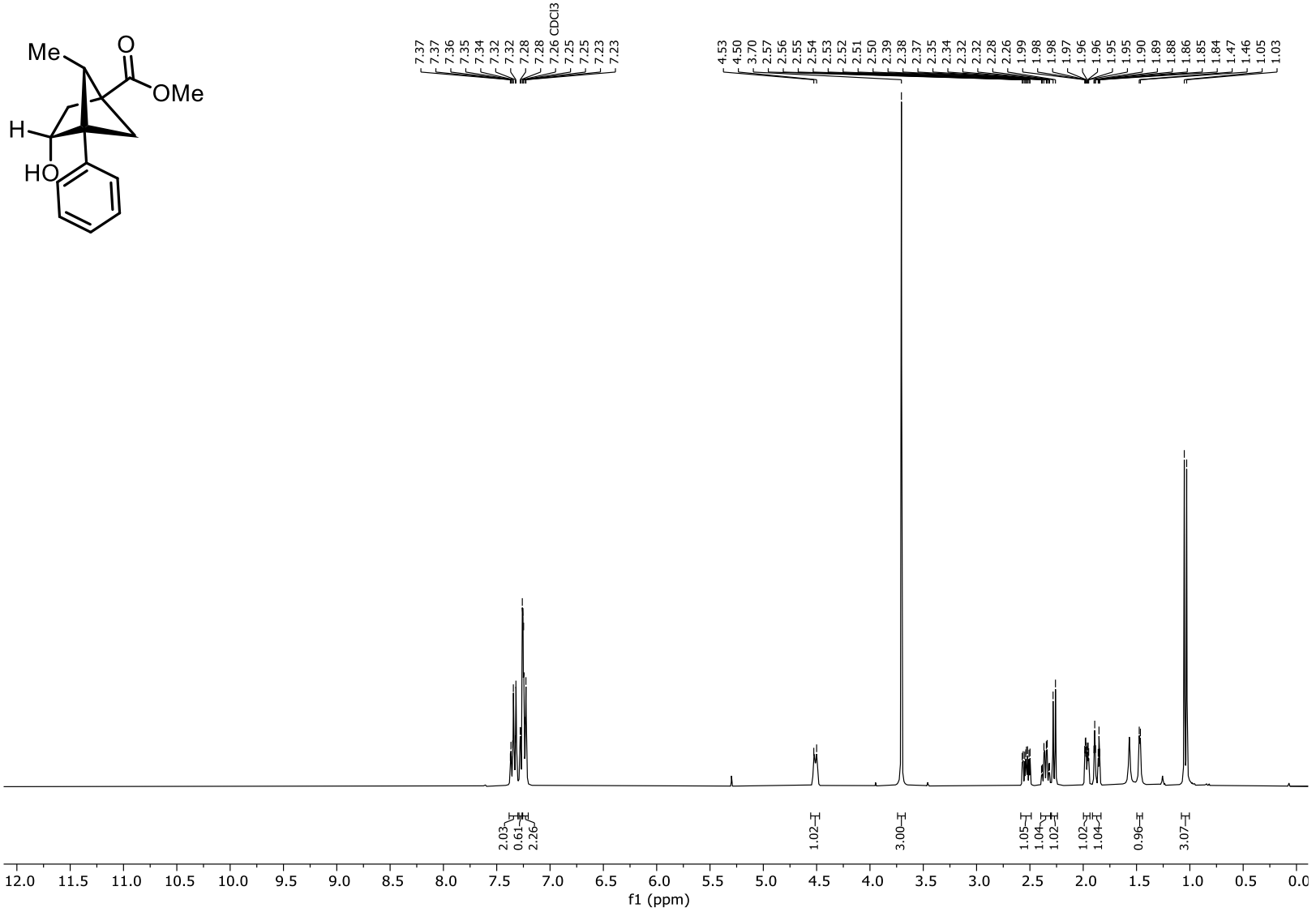
Methyl 2-exo-hydroxy-5-exo-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



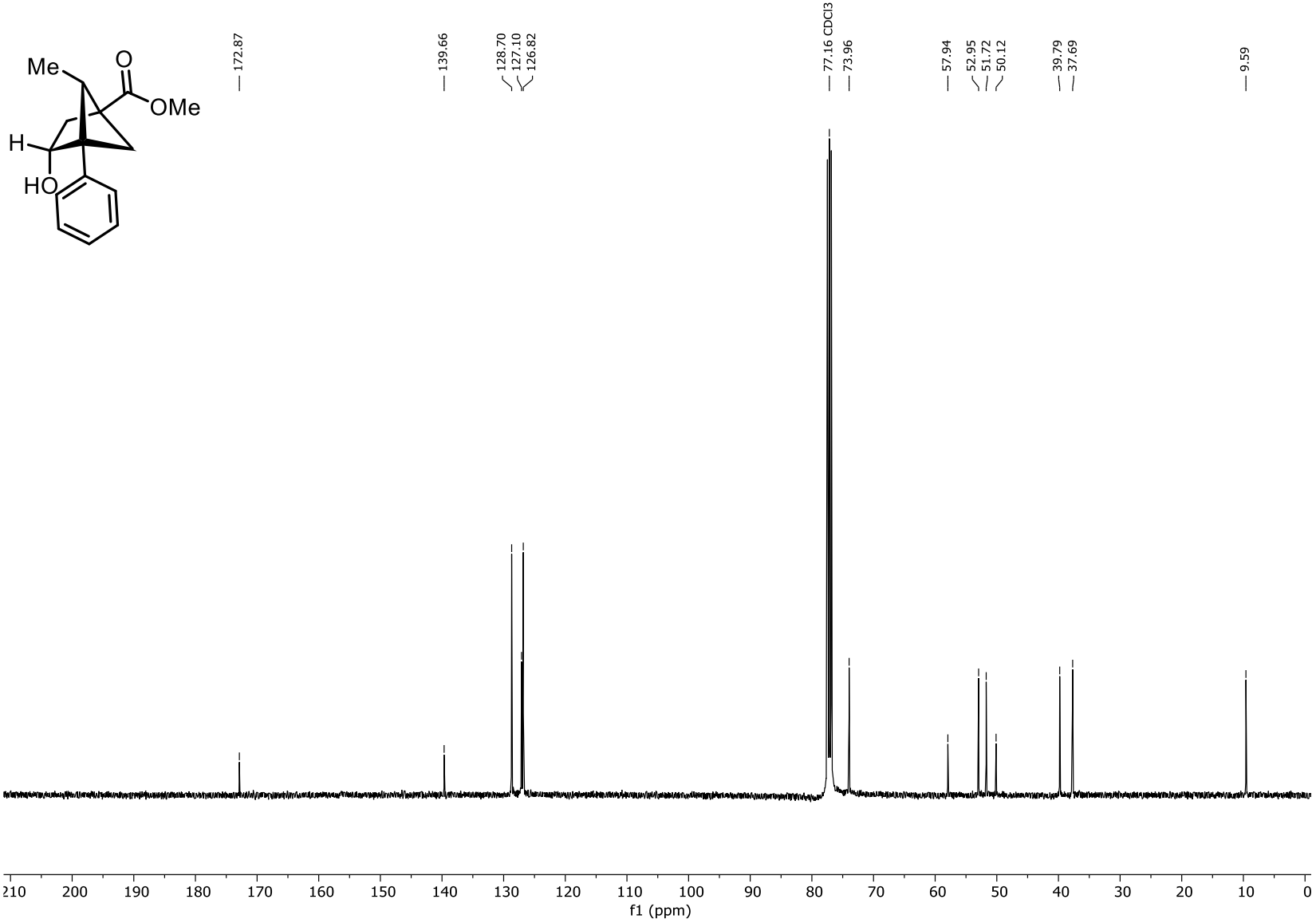
Methyl 2-*exo*-hydroxy-5-*exo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NOESY (400 MHz, $CDCl_3$)



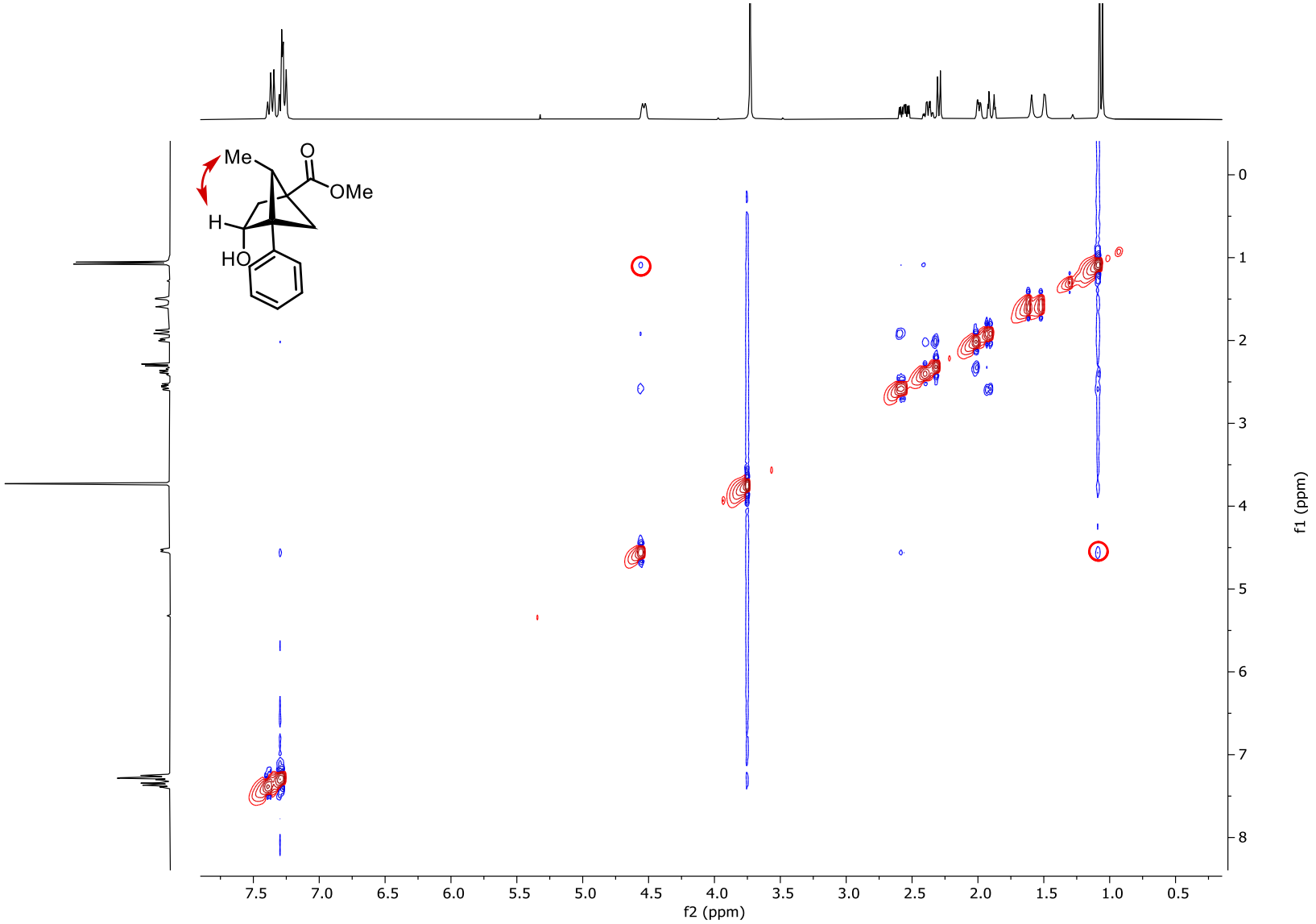
Methyl 2-*exo*-hydroxy-5-*endo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NMR (300 MHz, $CDCl_3$)



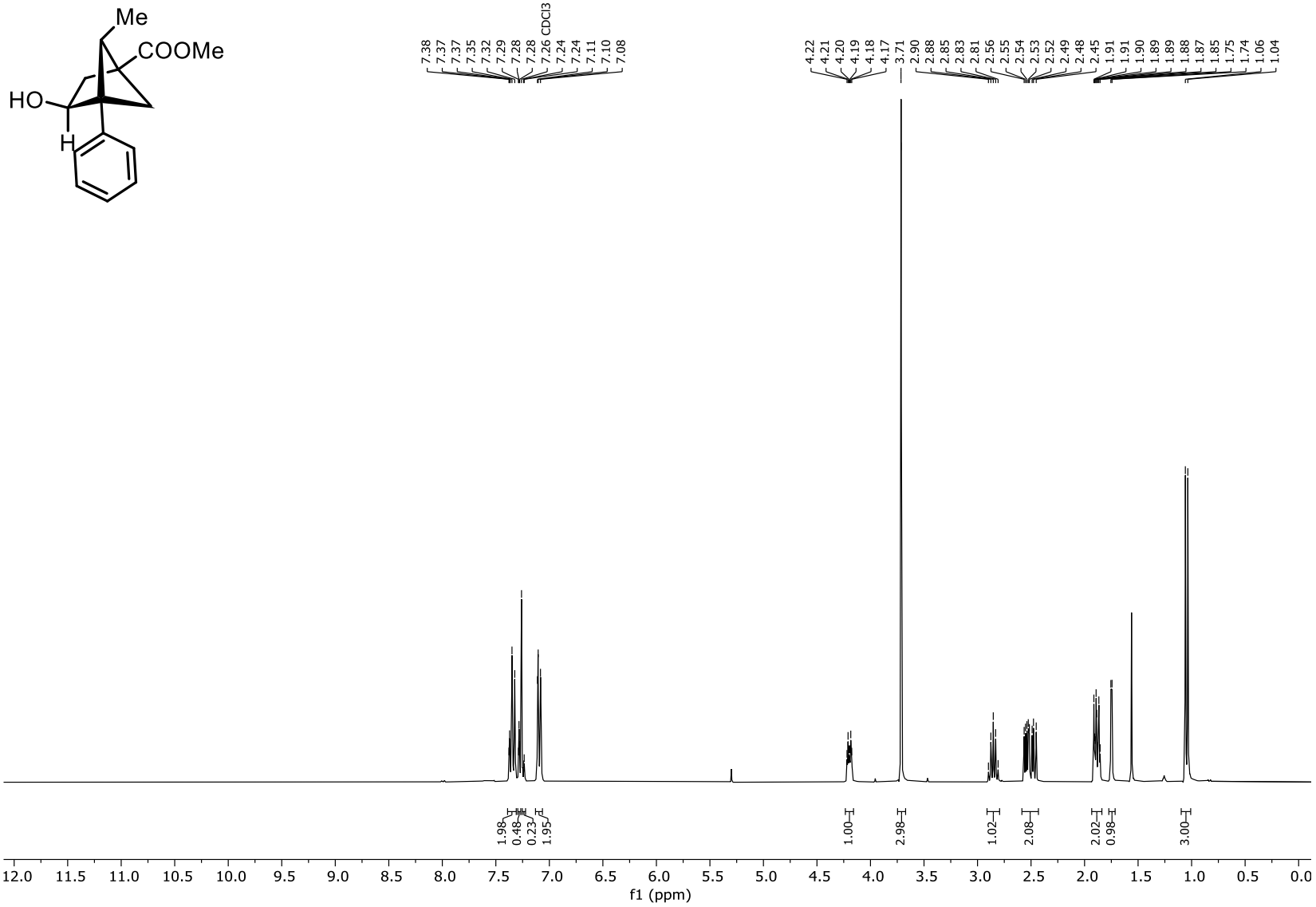
Methyl 2-*exo*-hydroxy-5-*endo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



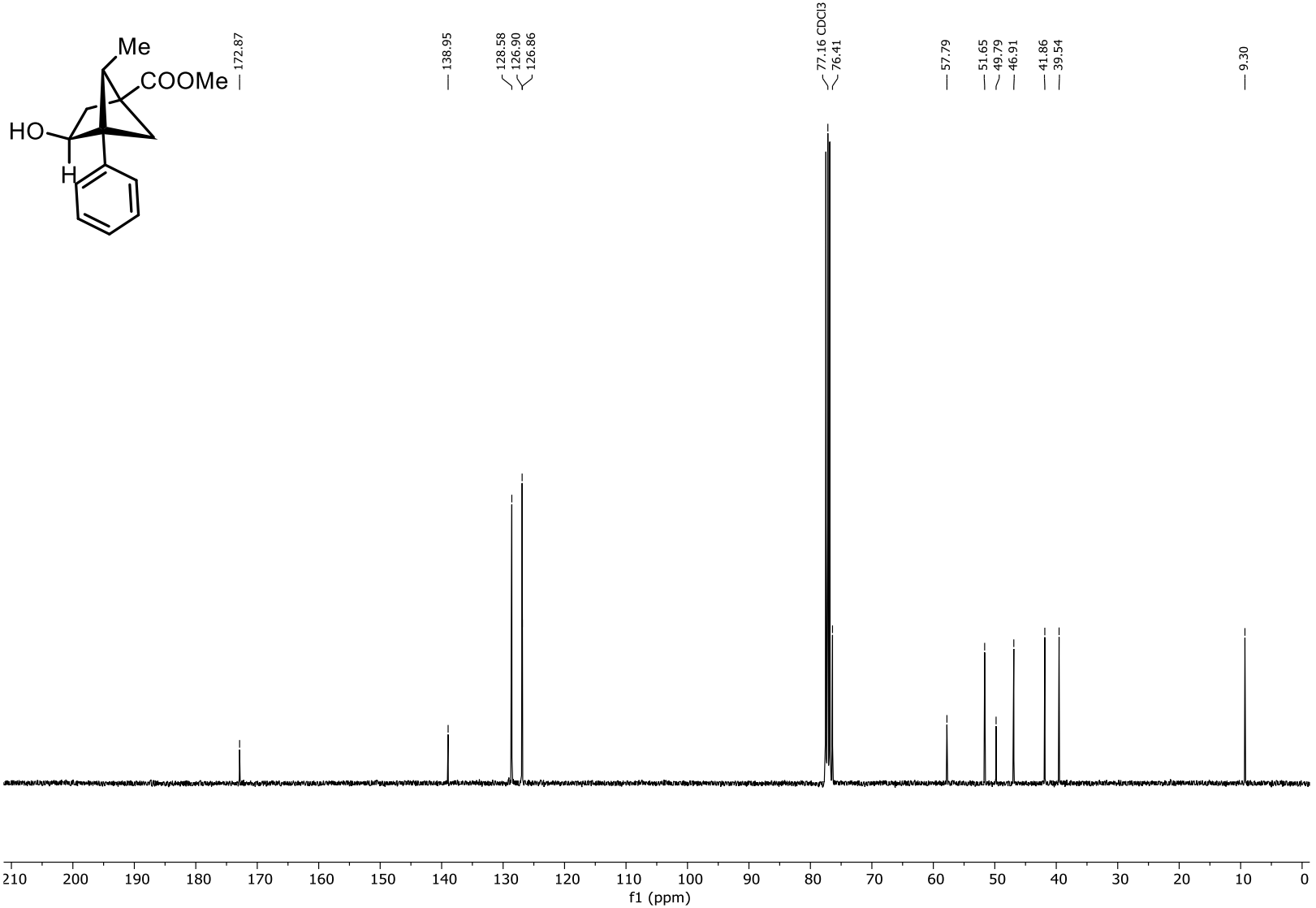
Methyl 2-*exo*-hydroxy-5-*endo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NOESY (400 MHz, $CDCl_3$)



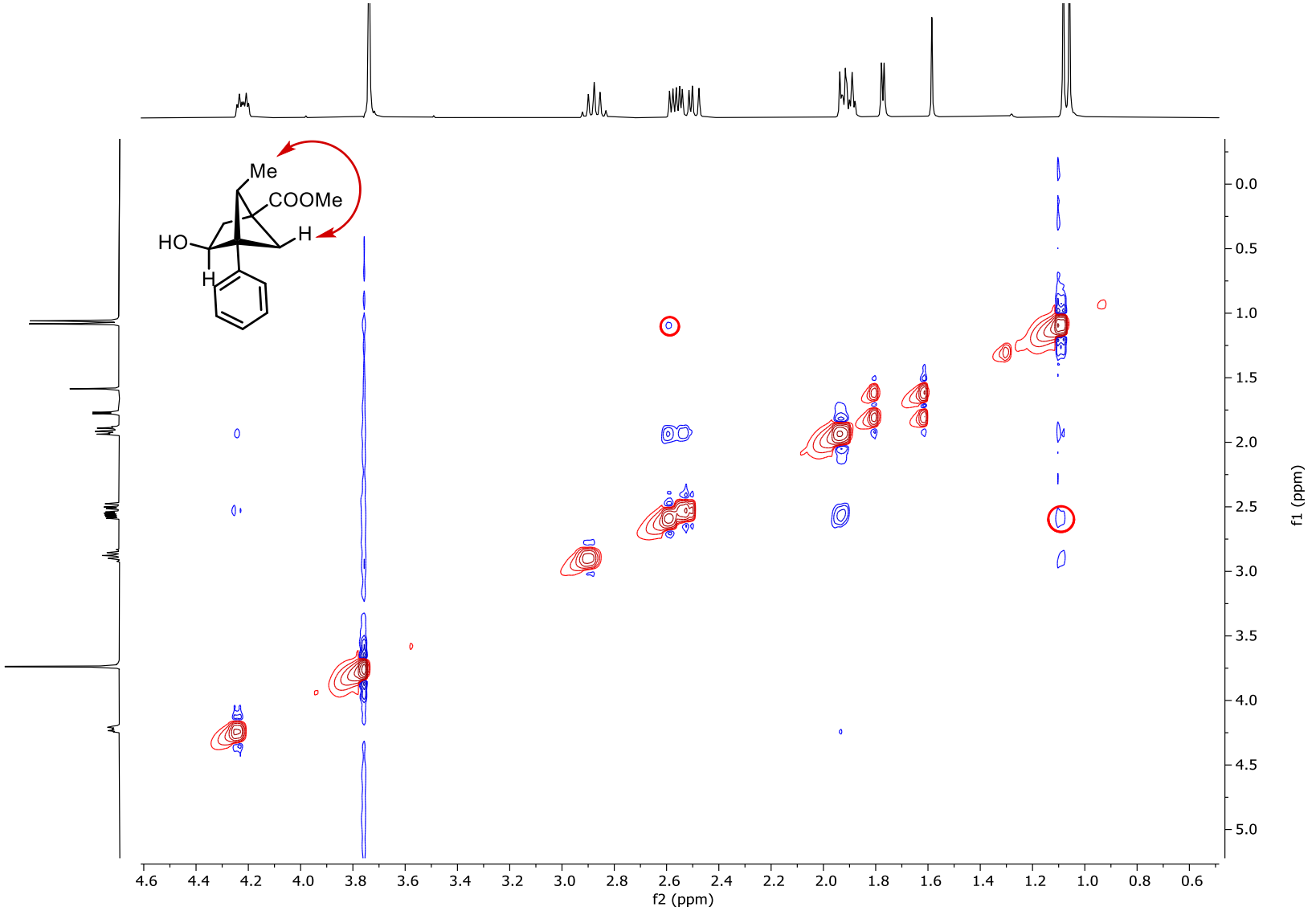
Methyl 2-*endo*-hydroxy-5-*exo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NMR (300 MHz, $CDCl_3$)



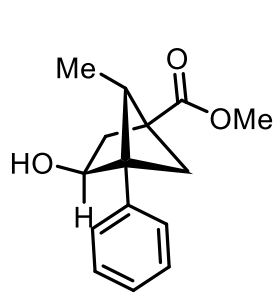
Methyl2-*endo*-hydroxy-5-*exo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



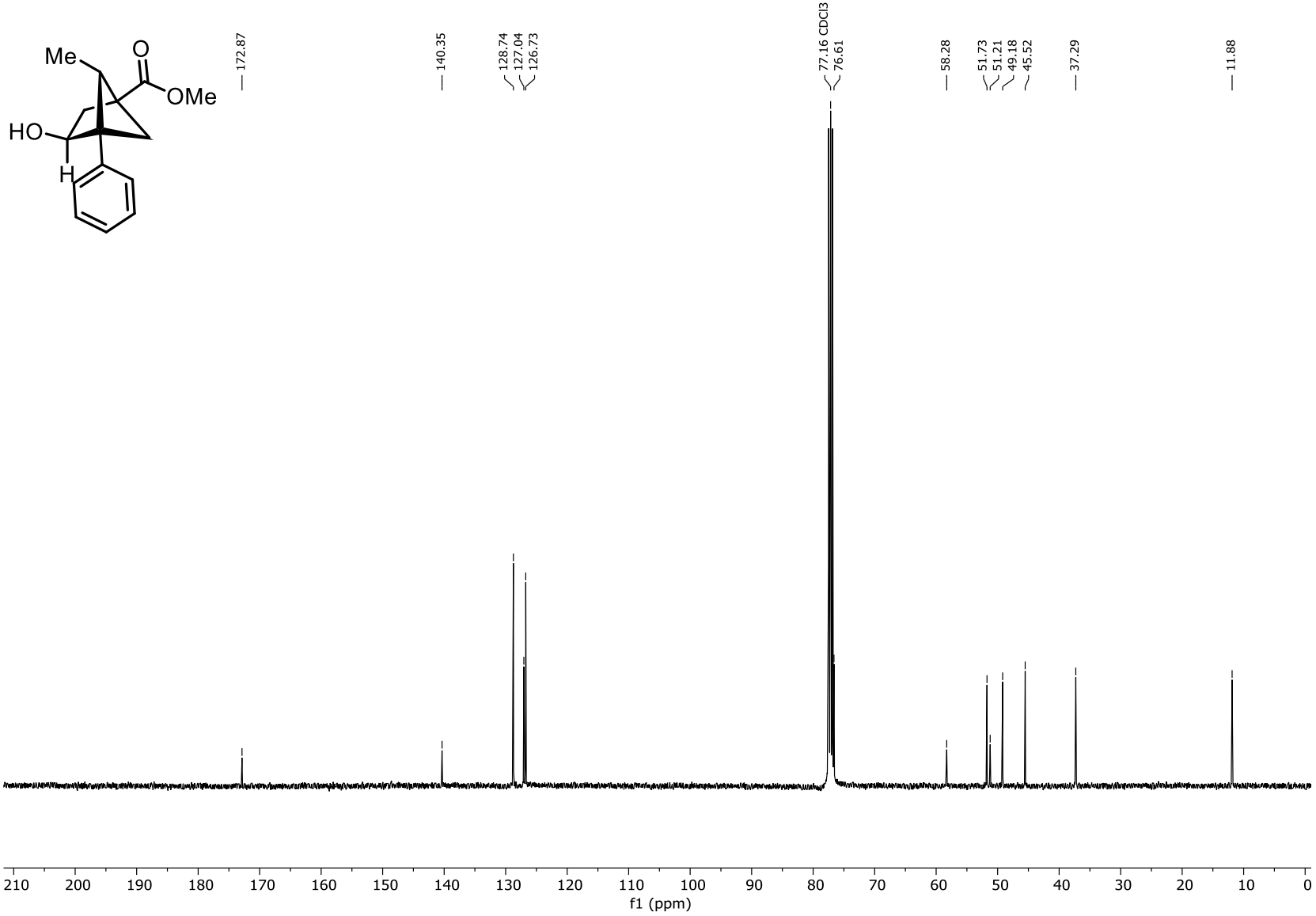
Methyl 2-*endo*-hydroxy-5-*exo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NOESY (400 MHz, $CDCl_3$)



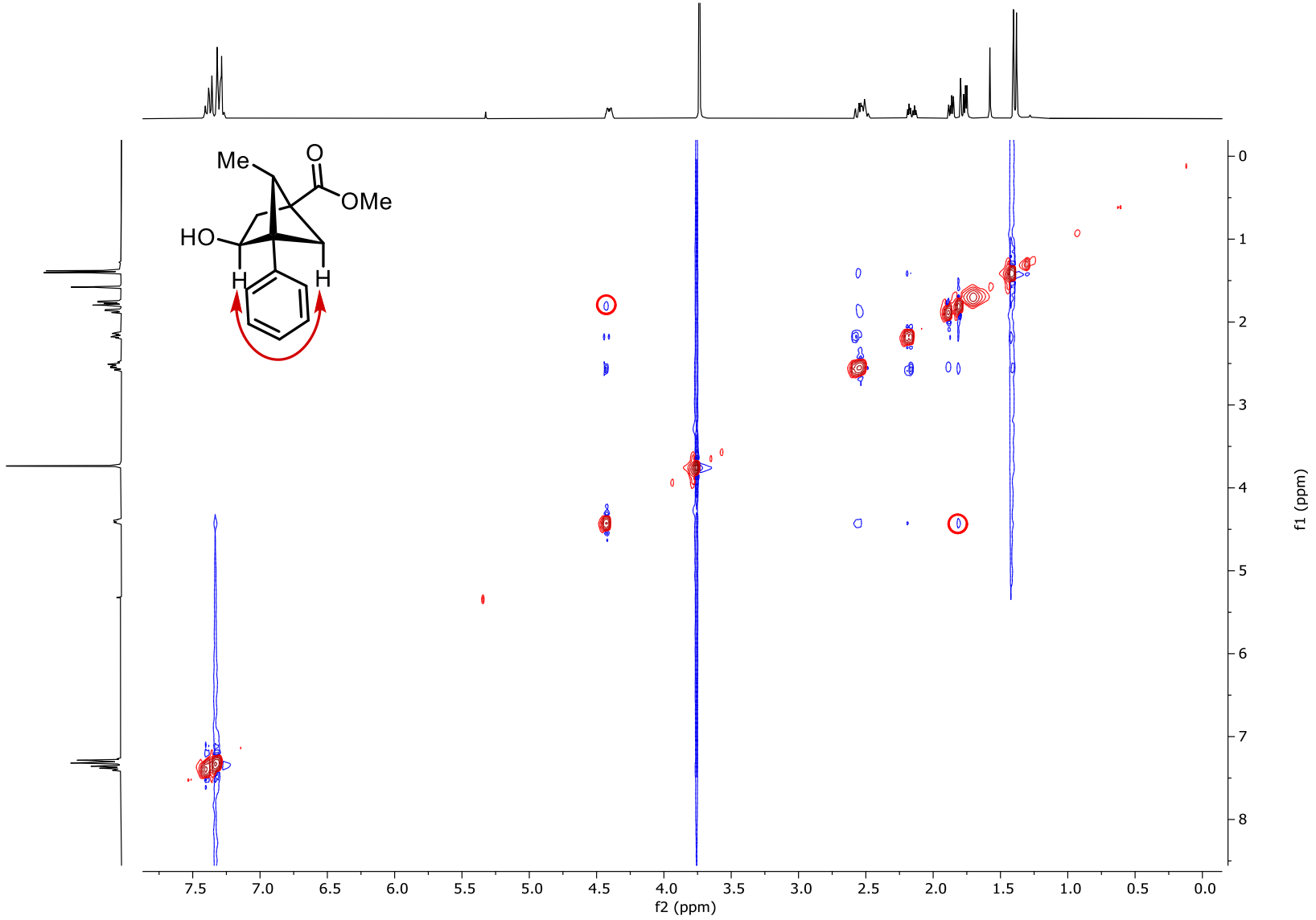
Methyl 2-*endo*-hydroxy-5-*endo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NMR (300 MHz, $CDCl_3$)



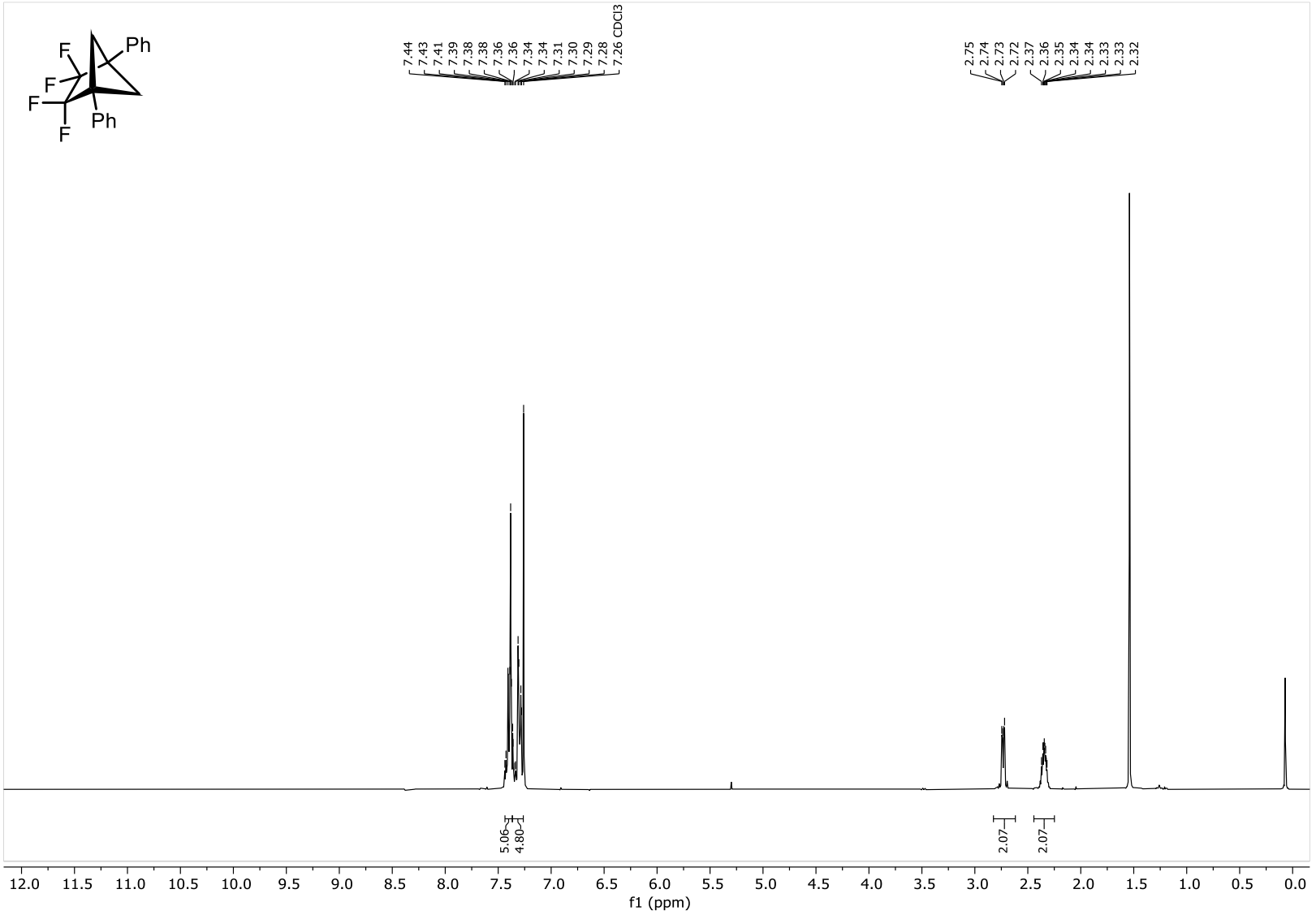
Methyl 2-*endo*-hydroxy-5-*endo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



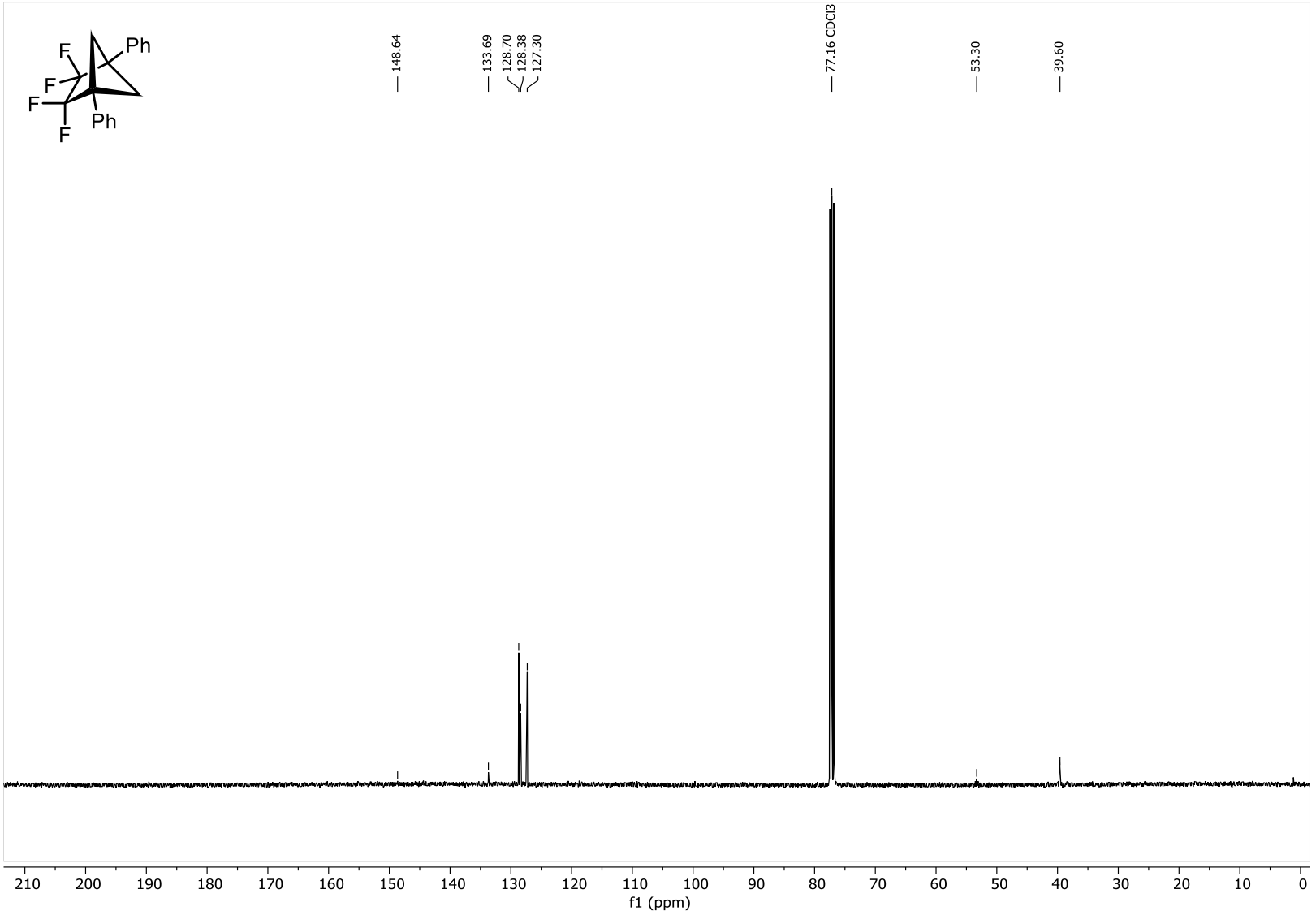
Methyl 2-*endo*-hydroxy-5-*endo*-methyl-4-phenylbicyclo[2.1.1]hexane-1-carboxylate (2aa): ^{1}H NOESY (400 MHz, $CDCl_3$)



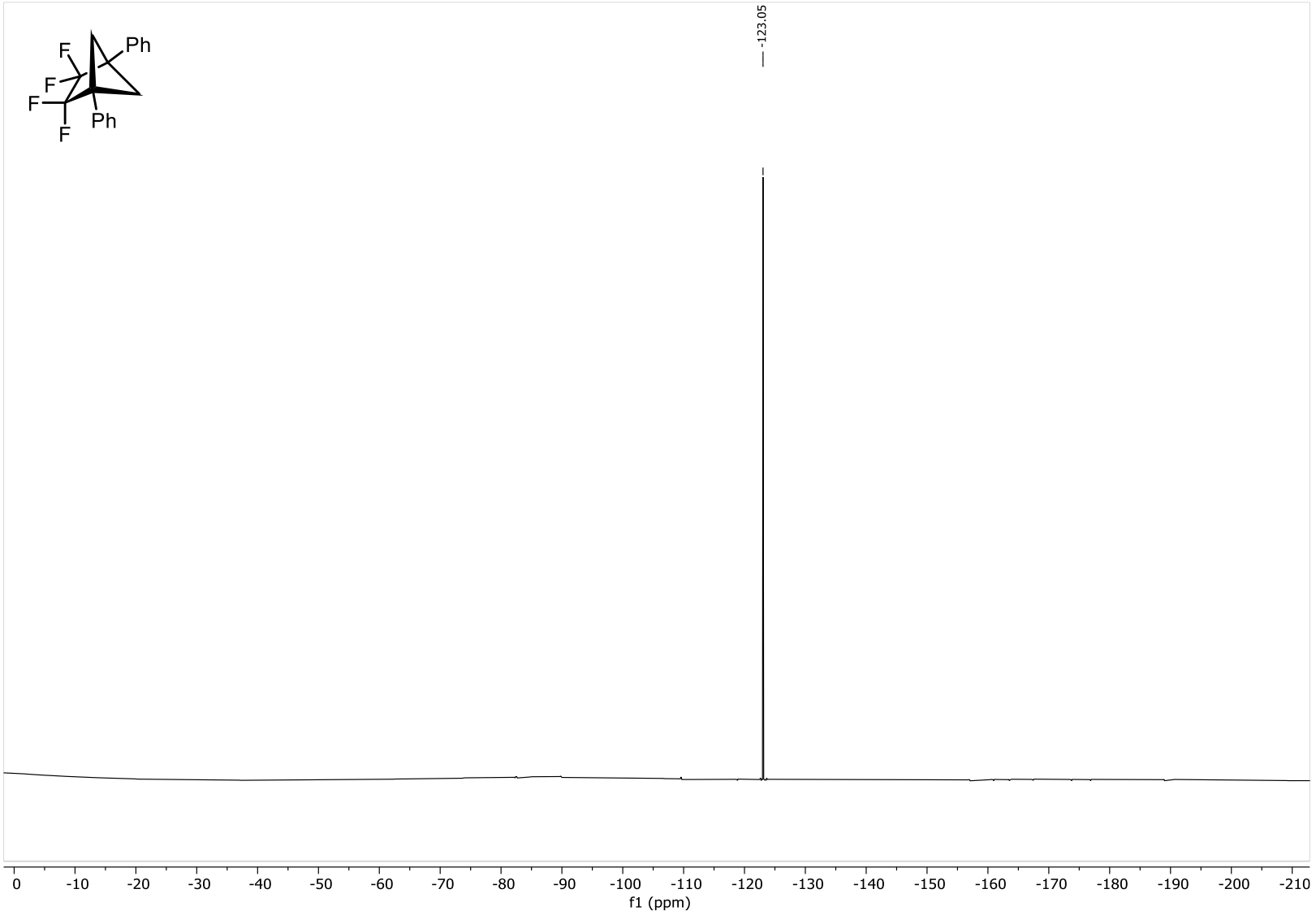
(1s,4s)-2,2,3,3-tetrafluoro-1,4-diphenylbicyclo[2.1.1]hexane (2ab): ^{1}H NMR (300 MHz, $CDCl_3$)



(1s,4s)-2,2,3,3-tetrafluoro-1,4-diphenylbicyclo[2.1.1]hexane (2ab): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

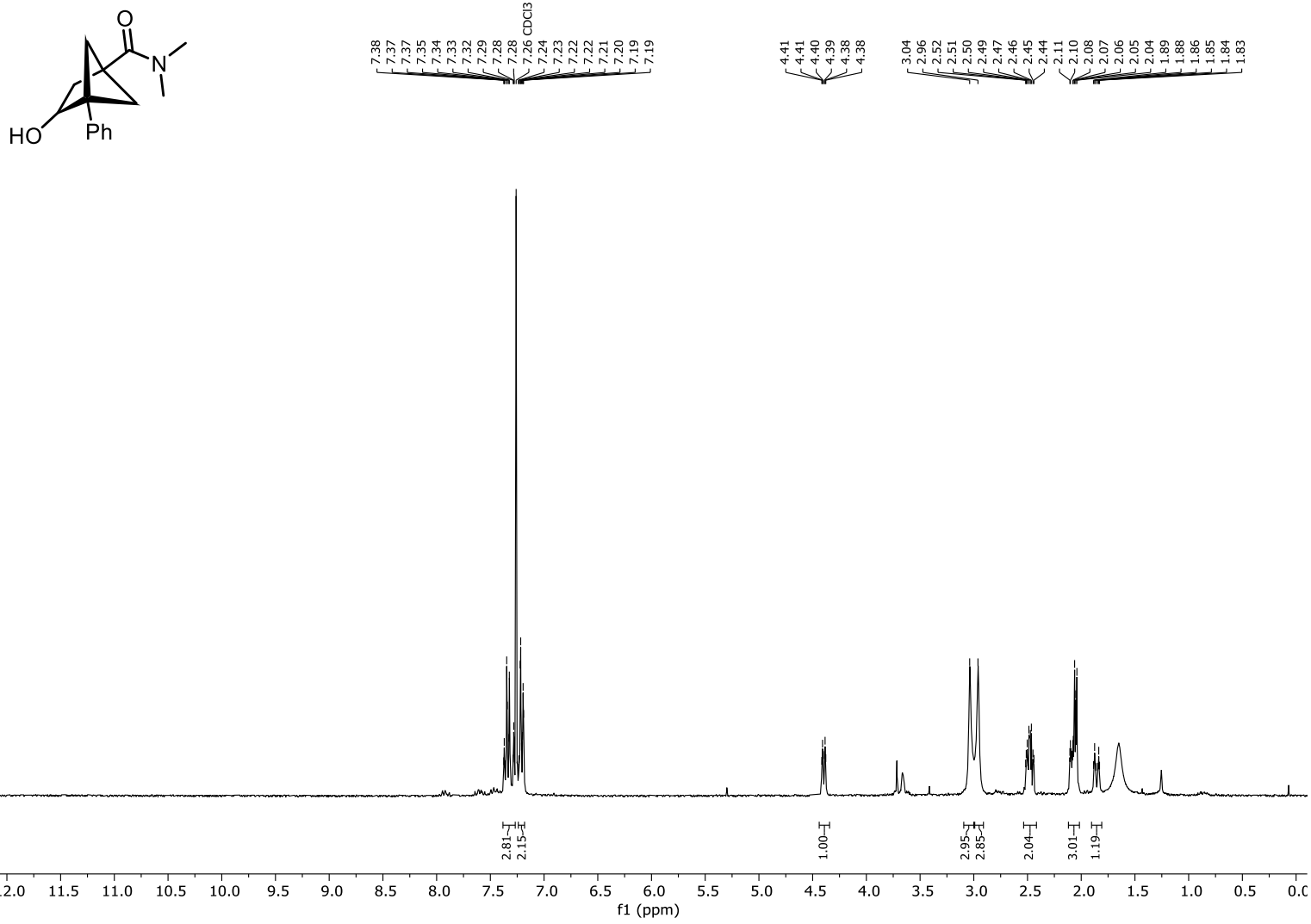


(1s,4s)-2,2,3,3-tetrafluoro-1,4-diphenylbicyclo[2.1.1]hexane (2ab): $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$)

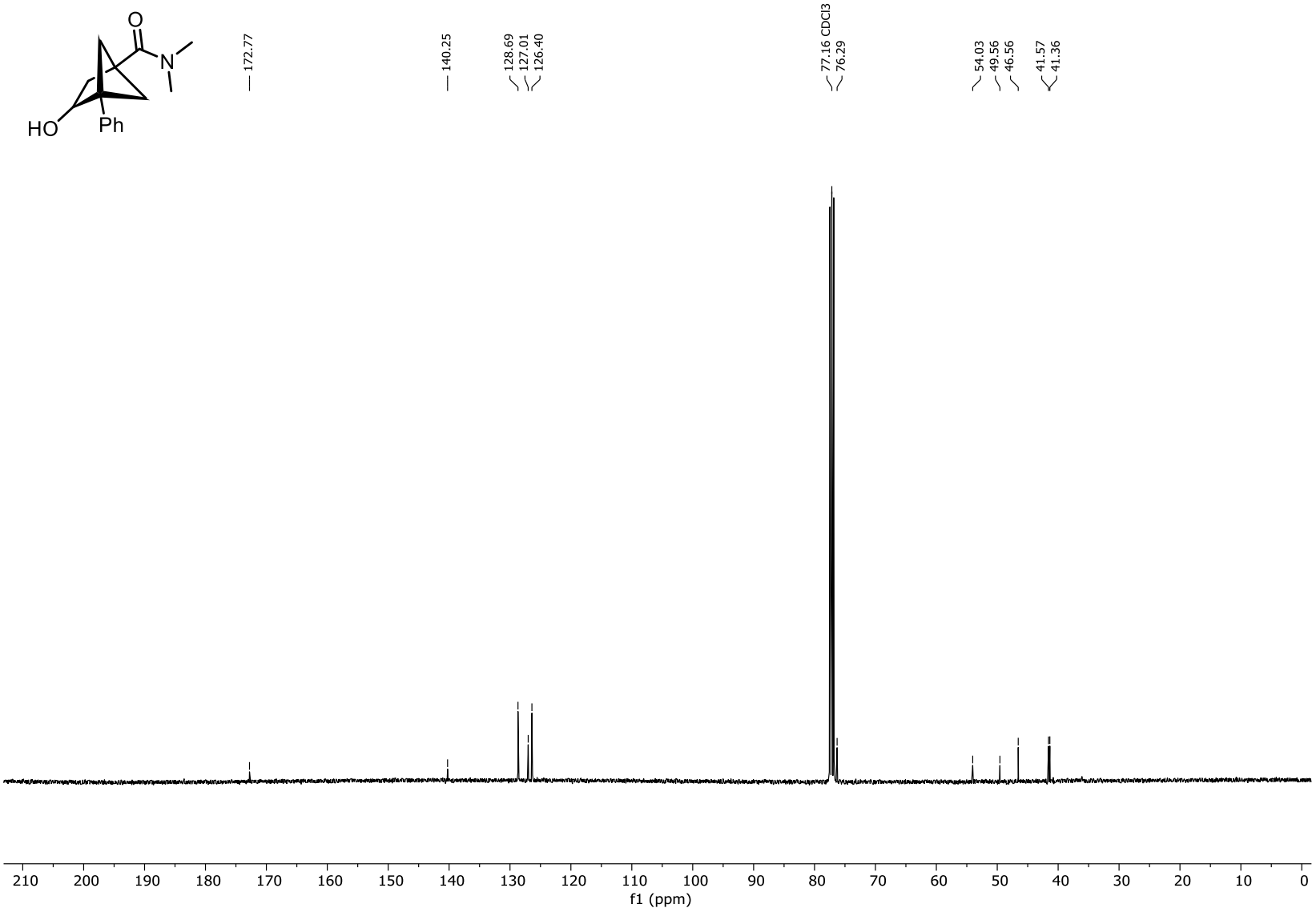


7.3 NMR Spectra of BCH 3, 4, 6, 8-10:

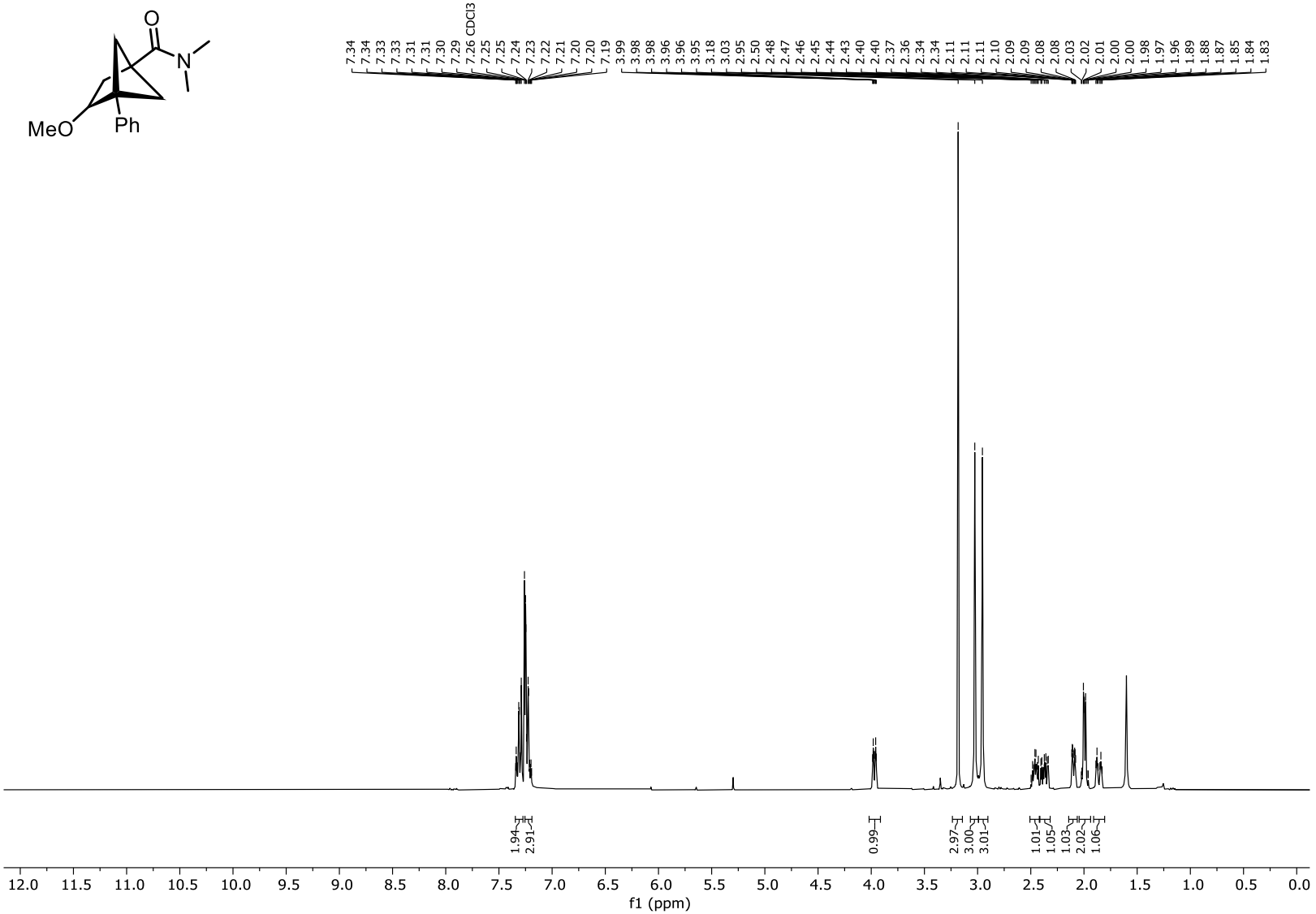
3-Hydroxy-N,N-dimethyl-4-phenylbicyclo[2.1.1]hexane-1-carboxamide (3): ^{1}H NMR (300 MHz, $CDCl_3$)



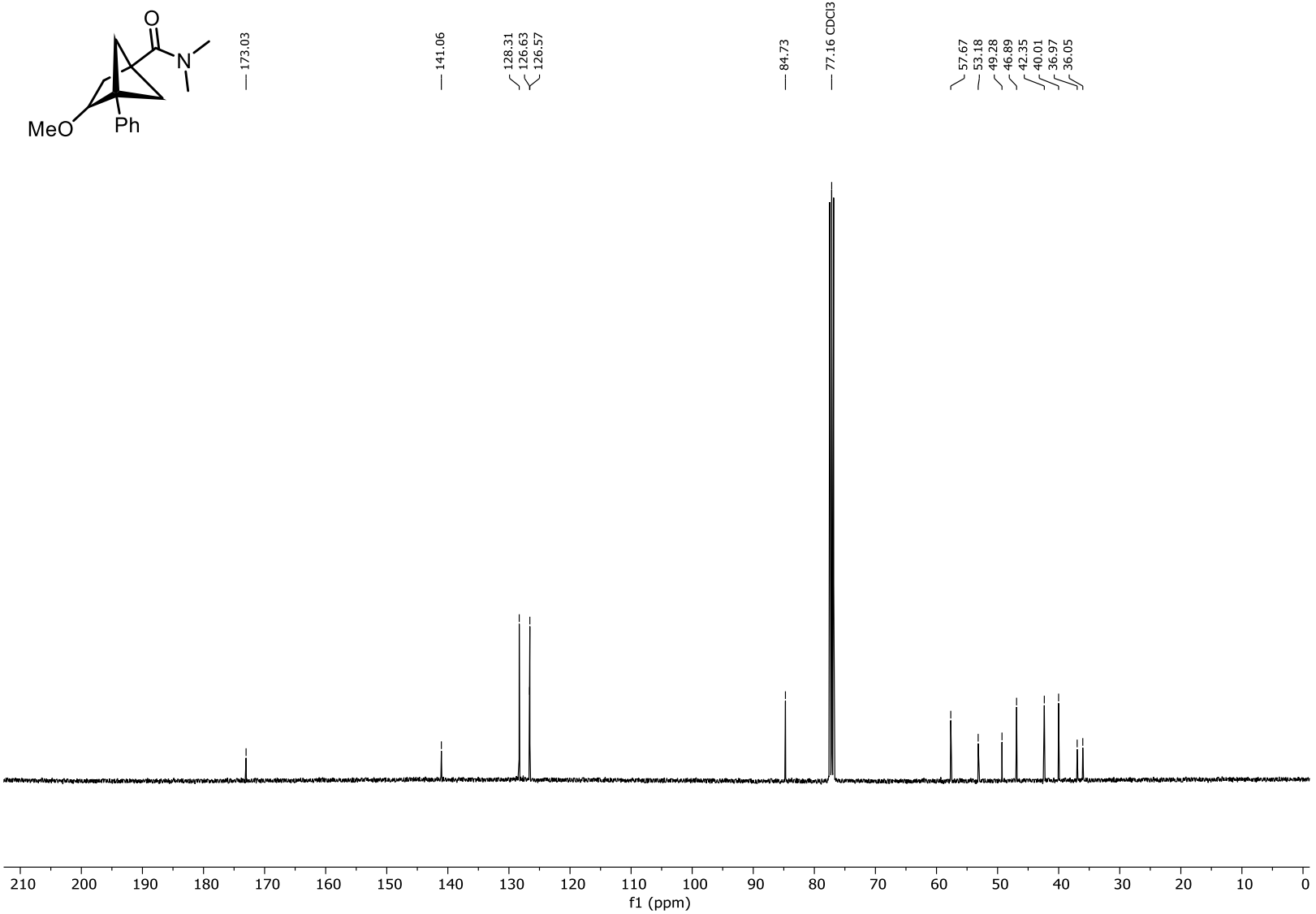
3-Hydroxy-N,N-dimethyl-4-phenylbicyclo[2.1.1]hexane-1-carboxamide (3): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



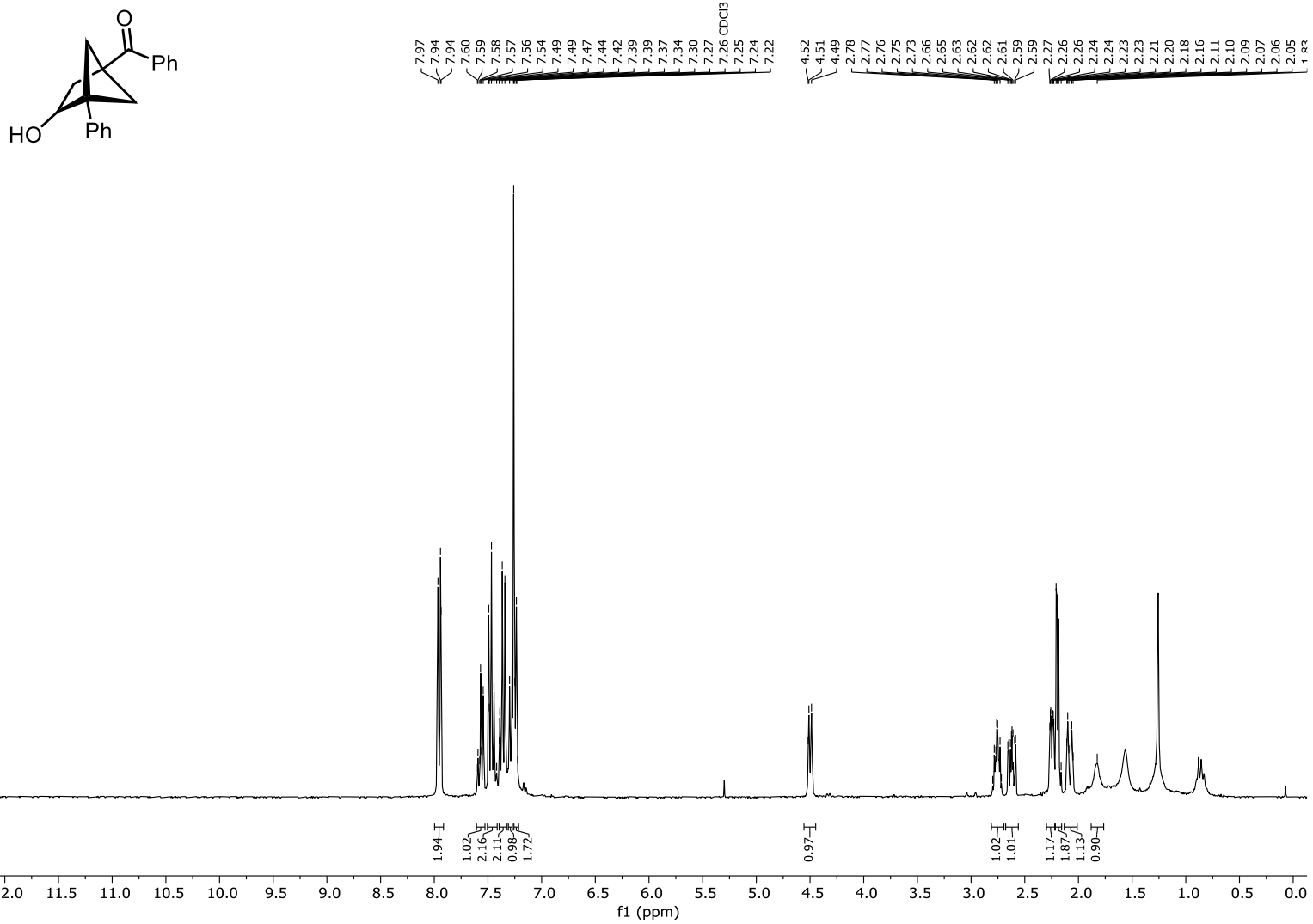
3-Methoxy-N,N-dimethyl-4-phenylbicyclo[2.1.1]hexane-1-carboxamide (4): ^{1}H NMR (300 MHz, $CDCl_3$)



3-Methoxy-N,N-dimethyl-4-phenylbicyclo[2.1.1]hexane-1-carboxamide (4): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

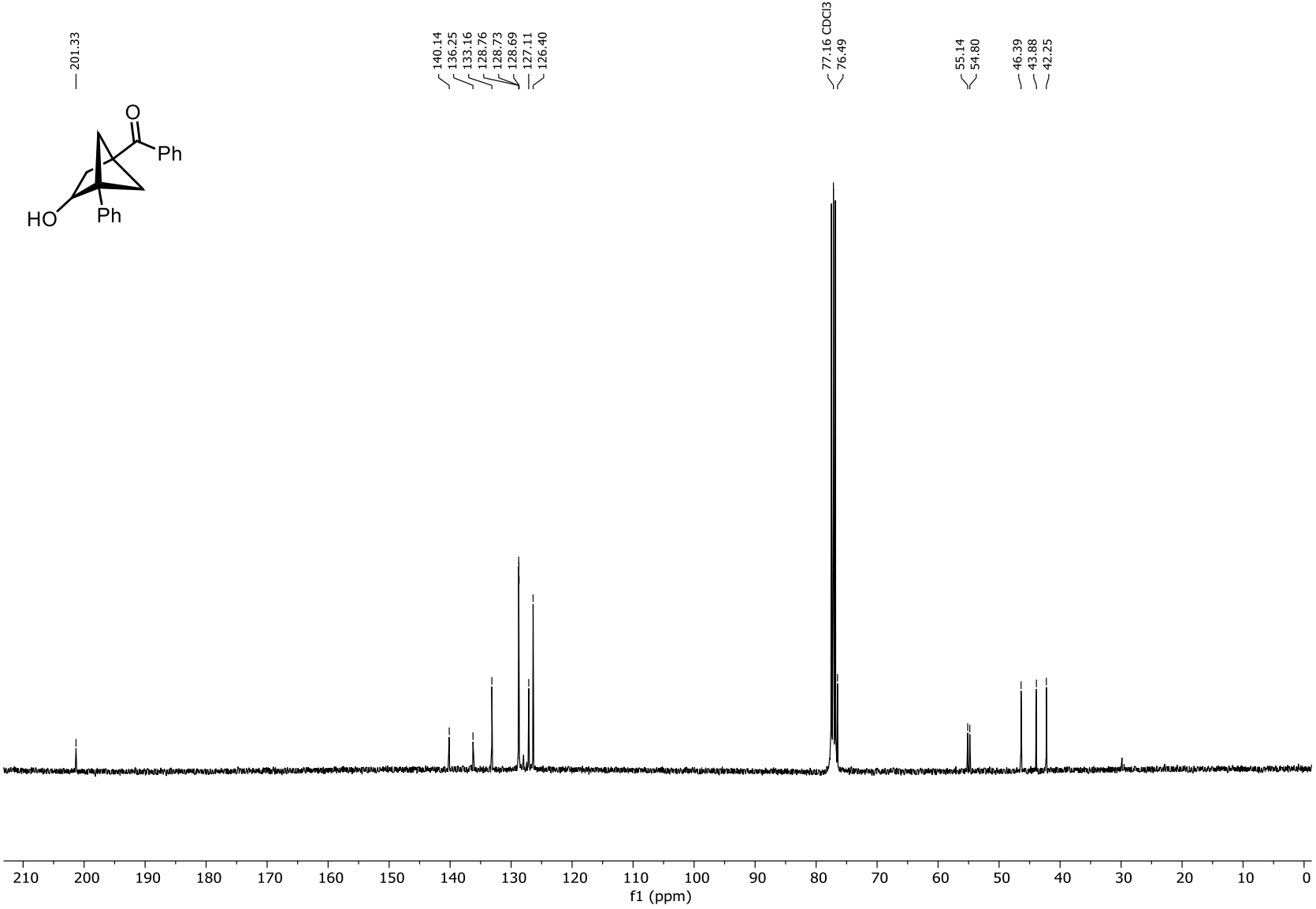


3-Hydroxy-4-phenylbicyclo[2.1.1]hexan-1-yl)(phenyl)methanone (6): ^{1}H NMR (300 MHz, $CDCl_3$)

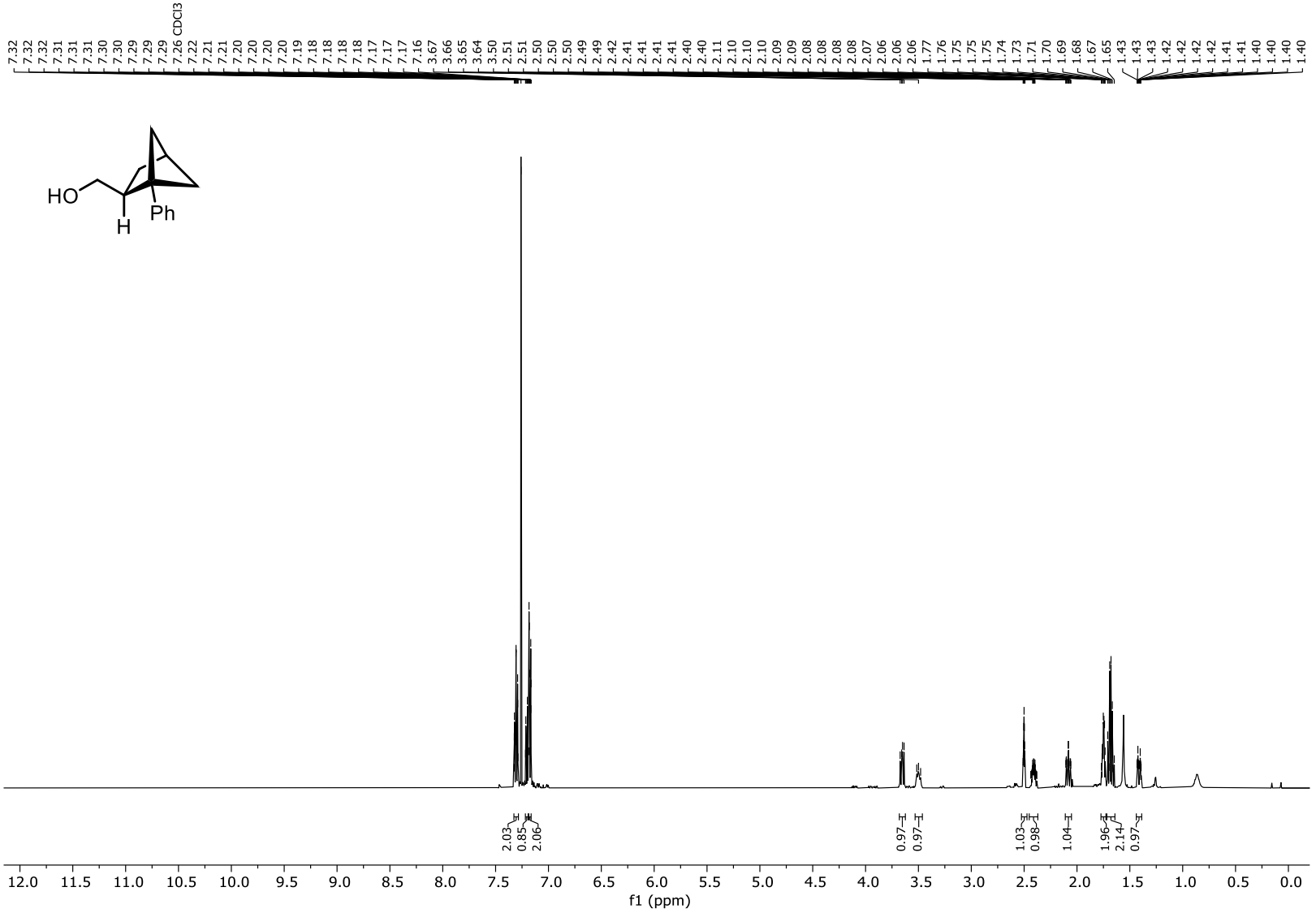


The resonances at 1.26 and 0.86 ppm are consistent with that reported for H grease.[22]

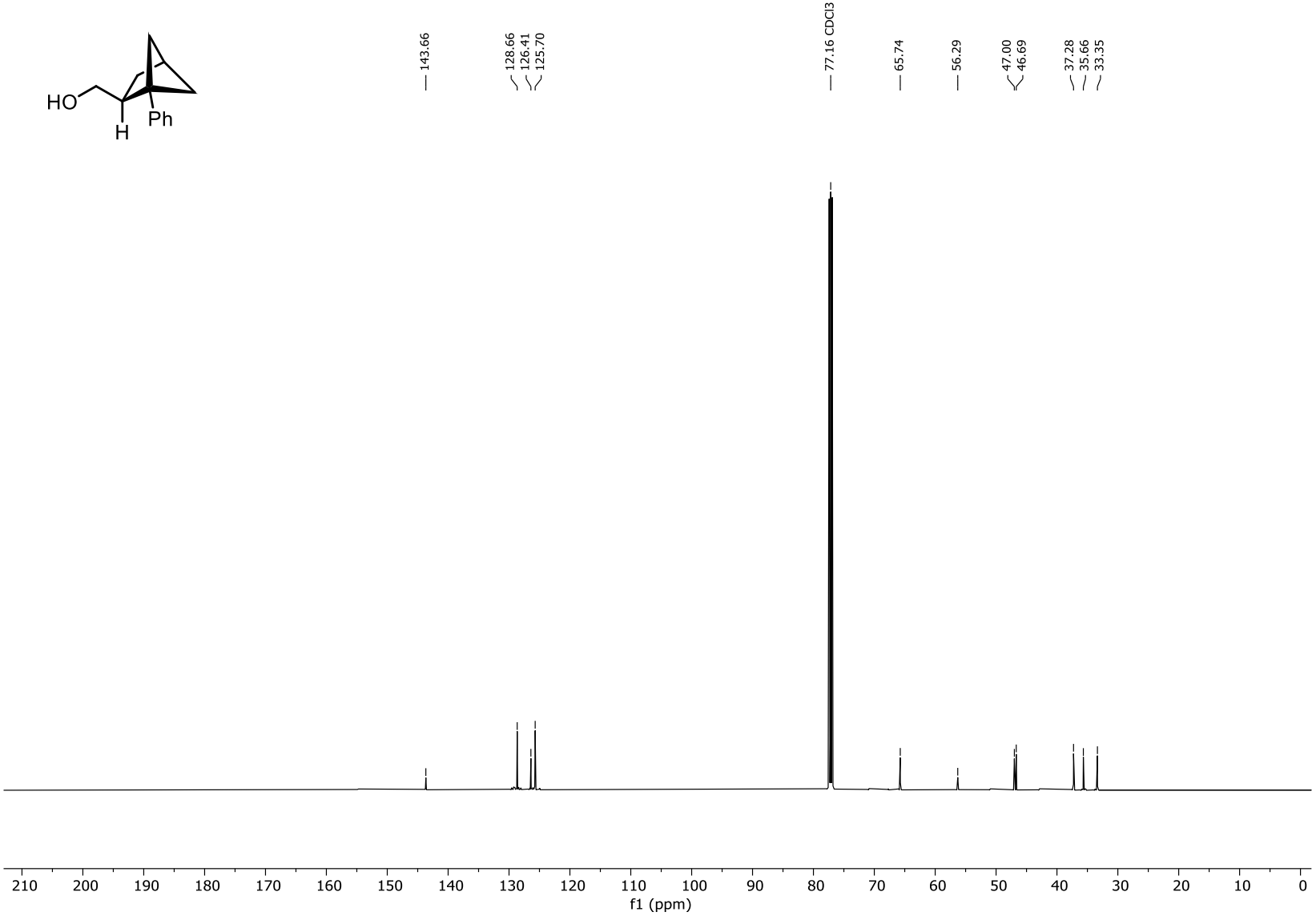
3-Hydroxy-4-phenylbicyclo[2.1.1]hexan-1-yl)(phenyl)methanone (6): $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



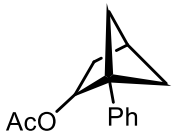
(2*S*-Phenylbicyclo[2.1.1]hexan-2-yl)methanol (8): ^{1}H NMR (500 MHz, $CDCl_3$)



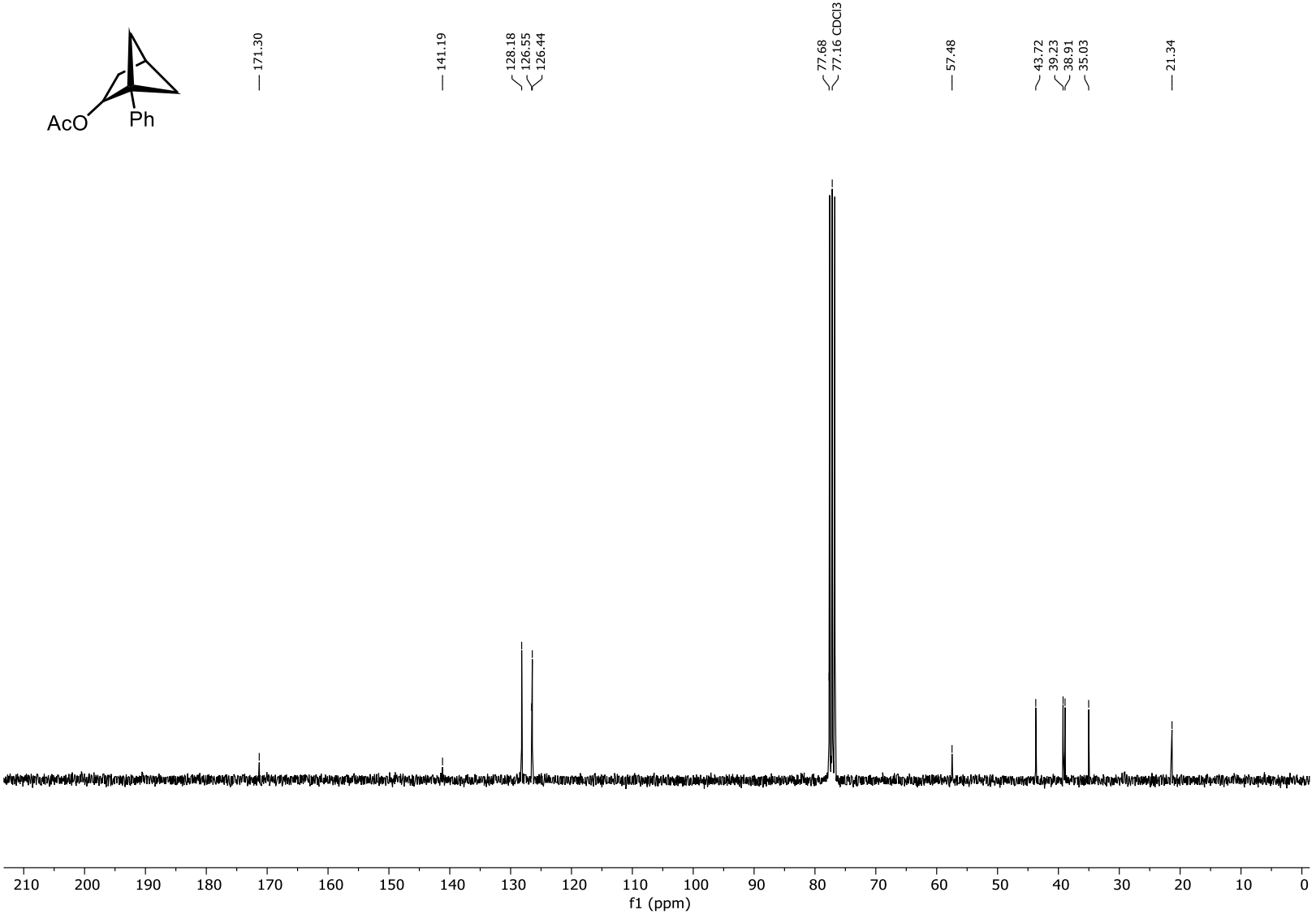
(2*S*-Phenylbicyclo[2.1.1]hexan-2-yl)methanol (8): $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



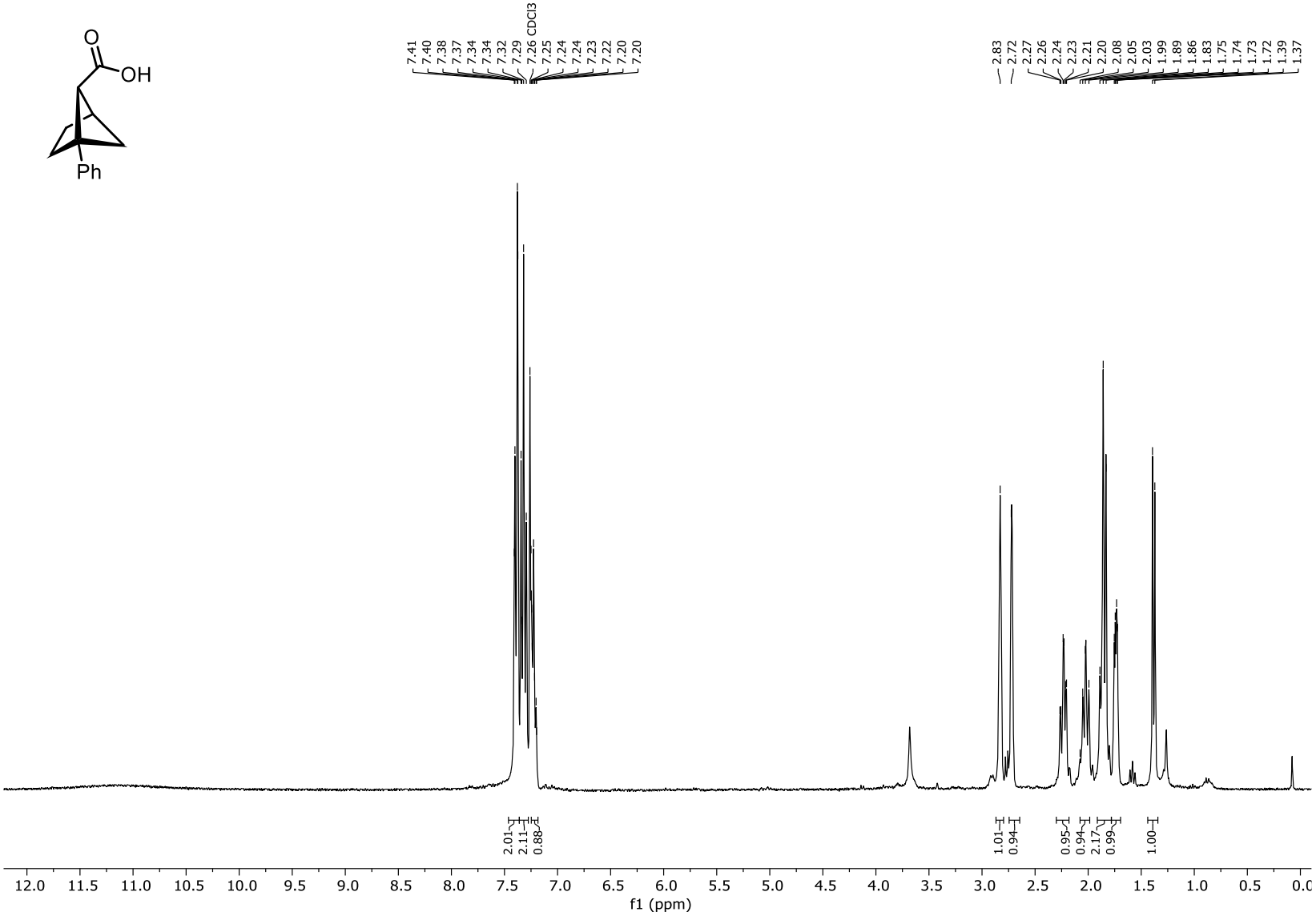
1-Phenylbicyclo[2.1.1]hexan-2-yl acetate (9): ^{1}H NMR (300 MHz, $CDCl_3$)



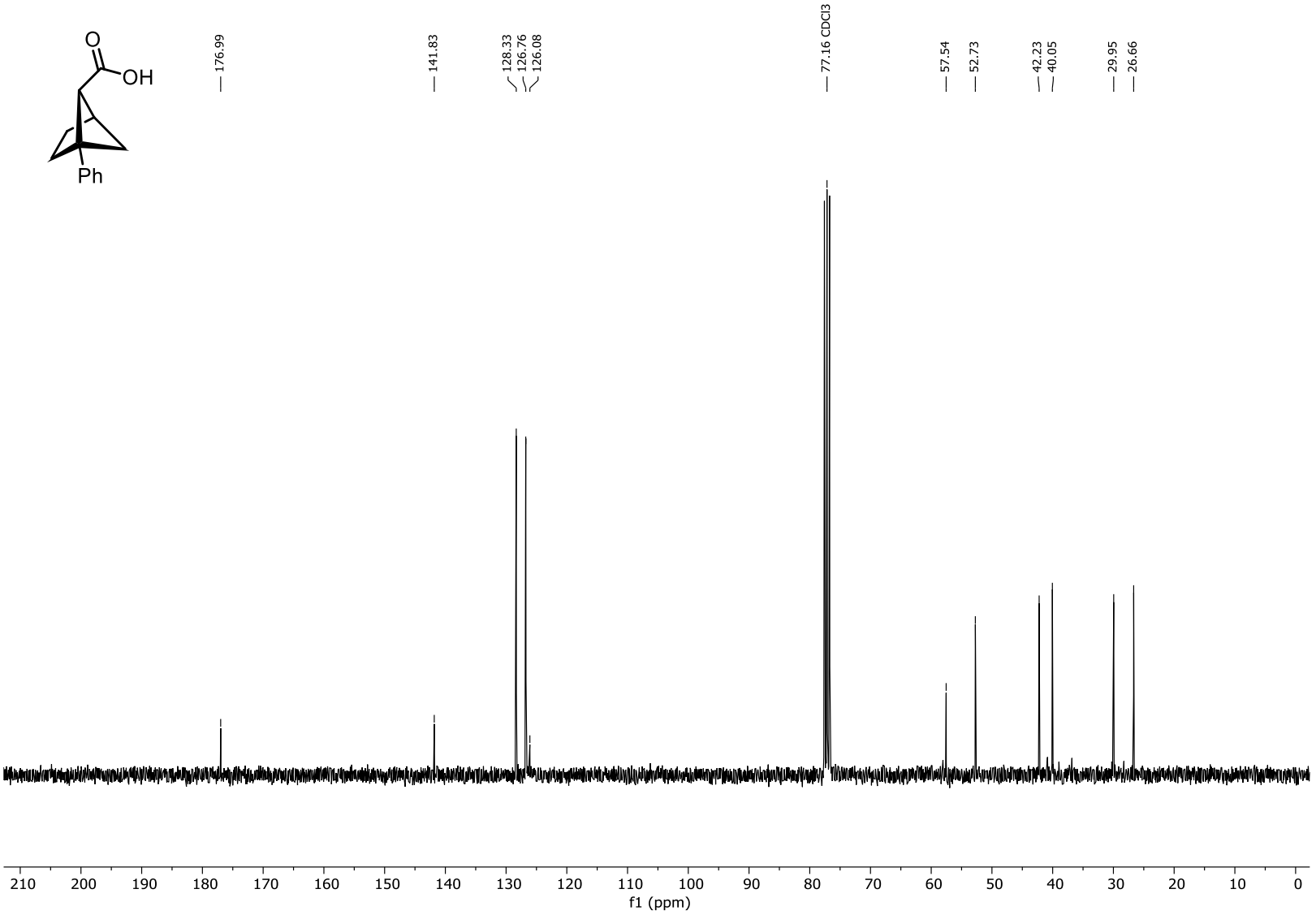
1-Phenylbicyclo[2.1.1]hexan-2-yl acetate (9): $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



1-Phenylbicyclo[2.1.1]hexane-5-carboxylic acid (10): ^{1}H NMR (300 MHz, $CDCl_3$)



1-Phenylbicyclo[2.1.1]hexane-5-carboxylic acid (10): $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



8 Crystallographic Supplement

Refinement table and details for 1,4-Diphenylbicyclo[2.1.1]hexane (**2a**)

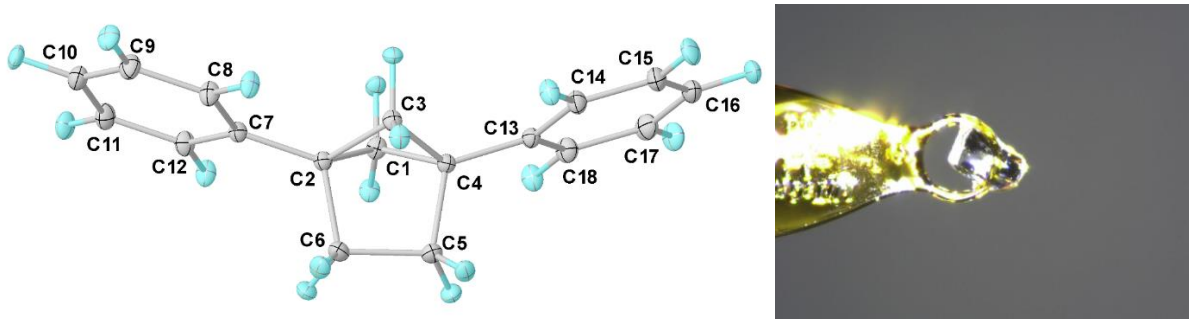


Figure S2. Molecular structure of **2a** in the solid state and picture of used crystal.

Displacement ellipsoids are drawn at 50% probability level. The crystals were obtained from dichloromethane.

Table S6. Crystal data and structure refinement.

CCDC number	2262000	**2θ range [°]**	3.81 to 107.88 (0.44 Å)
Empirical formula	$C_{18}H_{18}$		
Formula weight	234.343	**Index ranges**	−24 ≤ h ≤ 24 −13 ≤ k ≤ 13 −46 ≤ l ≤ 46
Temperature [K]	100		
Crystal system	Monoclinic		
Space group (number)	$P2_1/c$ (14)	**Reflections collected**	251577
***a* [Å]**	10.7190(15)	**Independent reflections**	15981 R_{int} = 0.0244 R_{sigma} = 0.0091
***b* [Å]**	5.9192(12)		
***c* [Å]**	20.494(3)		
α [°]	90	**Completeness to θ = 25.242°**	100.0 %
β [°]	94.366(6)		
γ [°]	90	**Data / Restraints / Parameters**	15981/0/325
Volume [Å^3]	1296.5(4)		
Z	4	**Goodness-of-fit on F^2**	1.0841
ρ_{calc} [gcm^{-3}]	1.201		
μ [mm^{-1}]	0.067	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0139 wR_2 = 0.0257
***F*(000)**	504.248		
Crystal size [mm^3]	0.342×0.204×0.116	**Final *R* indexes [all data]**	R_1 = 0.0197 wR_2 = 0.0273
Crystal colour	colourless		
Crystal shape	block	**Largest peak/hole [eÅ^{-3}]**	0.17/-0.12
Radiation	MoK_α (λ=0.71073 Å)		

Refinement table and details for 1,4-Bis(4-(trimethylsilyl)phenyl)bicyclo[2.1.1]hexane **(2g)**

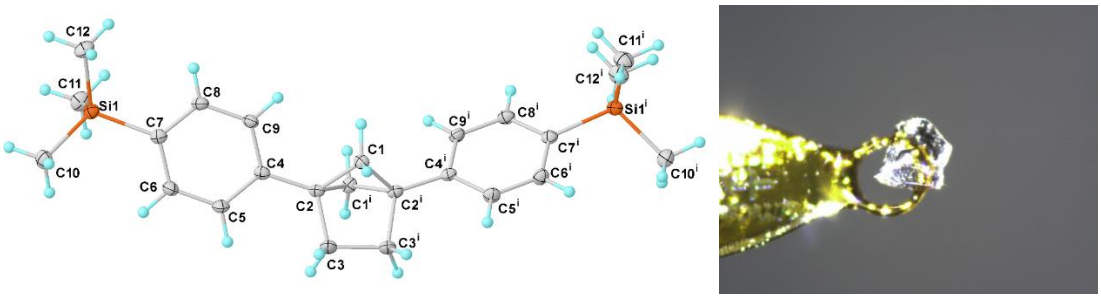


Figure S3. Molecular structure of **2g** in the solid state and picture of used crystal.

Second half of the molecule generated by symmetry i = 1-x, y,0.5-z. Displacement ellipsoids are drawn at 50% probability level. The crystals were obtained from dichloromethane.

Table S7. Crystal data and structure refinement.

CCDC number	2262001	**2θ range [°]**	5.49 to 59.24 (0.72 Å)
Empirical formula	$C_{24}H_{34}Si_2$		
Formula weight	378.69	**Index ranges**	−40 ≤ h ≤ 39 −8 ≤ k ≤ 8 −14 ≤ l ≤ 16
Temperature [K]	100.00		
Crystal system	monoclinic		
Space group (number)	$C2/c$ (15)	**Reflections collected**	20285
***a* [Å]**	29.688(2)	**Independent reflections**	3121 R_{int} = 0.0405 R_{sigma} = 0.0237
***b* [Å]**	6.2911(5)		
***c* [Å]**	11.9420(8)		
α [°]	90	**Completeness to θ = 25.242°**	99.8%
β [°]	90.063(3)		
γ [°]	90	**Data / Restraints / Parameters**	3121/0/121
Volume [Å^3]	2230.4(3)		
Z	4	**Goodness-of-fit on *F*^{2}**	1.088
ρ_{calc} [gcm^{-3}]	1.128		
μ [mm^{-1}]	0.164	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0377 wR_2 = 0.0929
***F*(000)**	824		
Crystal size [mm^3]	0.393×0.326×0.059	**Final *R* indexes [all data]**	R_1 = 0.0452 wR_2 = 0.0993
Crystal colour	colourless		
Crystal shape	plate	**Largest peak/hole [eÅ^{-3}]**	0.41/-0.26
Radiation	MoK_α (λ=0.71073 Å)		

Refinement table and details for 1,4-Di(naphthalen-2-yl)bicyclo[2.1.1]hexane (**2n**)

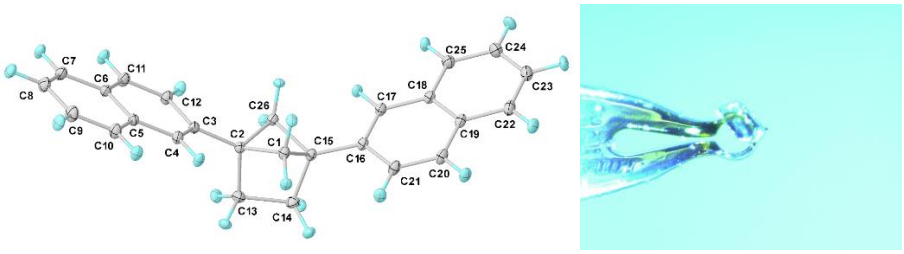


Figure S4. Molecular structure of **2n** in the solid state and picture of used crystal.

Displacement ellipsoids are drawn at 50% probability level. The crystals were obtained from dichloromethane.

Table S8. Crystal data and structure refinement.

CCDC number	2289323	**2θ range [°]**	4.68 to 67.48 (0.64 Å)
Empirical formula	$C_{26}H_{22}$		
Formula weight	334.464	**Index ranges**	−27 ≤ h ≤ 27 −8 ≤ k ≤ 9 −27 ≤ l ≤ 27
Temperature [K]	100.00		
Crystal system	Monoclinic		
Space group (number)	$P2_1/c$ (14)	**Reflections collected**	93855
***a* [Å]**	17.5616(13)	**Independent reflections**	7088 R_{int} = 0.0271 R_{sigma} = 0.0119
***b* [Å]**	5.8909(5)		
***c* [Å]**	17.9060(16)		
α [°]	90	**Completeness to θ = 25.242°**	100.0 %
β [°]	106.549(4)		
γ [°]	90	**Data / Restraints / Parameters**	7088/0/433
Volume [Å^3]	1775.7(3)		
Z	4	**Goodness-of-fit on F^2**	1.0321
ρ_{calc} [gcm^{-3}]	1.251		
μ [mm^{-1}]	0.070	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0130 wR_2 = 0.0233
***F*(000)**	712.358		
Crystal size [mm^3]	0.294×0.168×0.131	**Final *R* indexes [all data]**	R_1 = 0.0179 wR_2 = 0.0253
Crystal colour	Colorless		
Crystal shape	Block	**Largest peak/hole [eÅ^{-3}]**	0.11/-0.10
Radiation	Mo K_α (λ=0.71073 Å)		

Refinement table and details for (*S*)-4-benzyl-3-((2*S*)-1-phenylbicyclo[2.1.1]hexane-2-carbonyl)oxazolidin-2-one (**2r**):

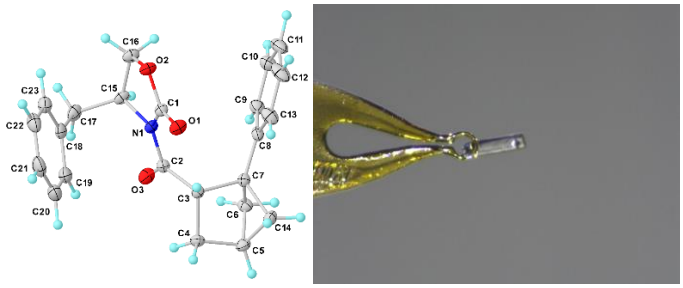


Figure S5. Molecular structure of **2r** in the solid state and picture of used crystal.

Displacement ellipsoids are drawn at 50% probability level. The crystals were obtained from ethylacetate.

Table S9. Crystal data and structure refinement.

CCDC number	2289325	**Index ranges**	$-7 \le h \le 7$ $-20 \le k \le 20$ $-23 \le l \le 23$
Empirical formula	$C_{23}H_{23}NO_3$		
Formula weight	361.42	**Reflections collected**	60017
Temperature [K]	100.00		
Crystal system	Orthorhombic		
Space group (number)	$P2_12_12_1$ (19)	**Independent reflections**	4010 R_{int} = 0.0486 R_{sigma} = 0.0157
***a* [Å]**	6.2717(8)	**Completeness to θ = 25.242°**	100.0 %
***b* [Å]**	16.1815(16)		
***c* [Å]**	18.3606(18)		
α [°]	90	**Data / Restraints / Parameters**	4010/0/337
β [°]	90		
γ [°]	90	**Goodness-of-fit on F^2**	1.021
Volume [Å^3]	1863.3(4)		
Z	4	**Final *R* indexes [$I \ge 2\sigma(I)$]**	R_1 = 0.0241 wR_2 = 0.0634
ρ_{calc} [gcm^{-3}]	1.288		
μ [mm^{-1}]	0.680	**Final *R* indexes [all data]**	R_1 = 0.0246 wR_2 = 0.0637
***F*(000)**	768		
Crystal size [mm^3]	0.376×0.066×0.052	**Largest peak/hole [eÅ^{-3}]**	0.21/-0.12
Crystal colour	Colorless		
Crystal shape	Needle	**Flack X parameter**	-0.04(3)
Radiation	CuK_α (λ=1.54178 Å)	**Extinction coefficient**	0.0029(3)
2θ range [°]	7.28 to 159.46 (0.78 Å)		

Refinement table and details for 3-(4-Fluorophenyl)-1-phenylbicyclo[2.1.1]hexane (**2s**)

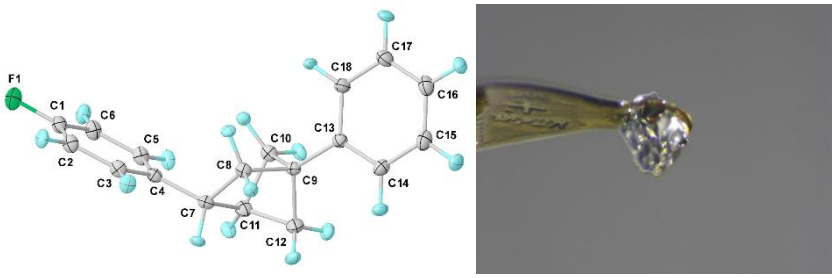


Figure S6. Molecular structure of **2s** in the solid state and picture of used crystal

Displacement ellipsoids are drawn at 50% probability level. The crystals were obtained from dichloromethane.

Table S10. Crystal data and structure refinement.

CCDC number	2289324	**2θ range [°]**	4.44 to 67.52 (0.64 Å)
Empirical formula	$C_{18}H_{17}F$		
Formula weight	252.334	**Index ranges**	−15 ≤ h ≤ 15 −8 ≤ k ≤ 9 −33 ≤ l ≤ 32
Temperature [K]	100.00		
Crystal system	Monoclinic		
Space group (number)	$P2_1/n$ (14)	**Reflections collected**	47752
***a* [Å]**	10.1015(9)	**Independent reflections**	5339 R_{int} = 0.0351 R_{sigma} = 0.0176
***b* [Å]**	6.0988(5)		
***c* [Å]**	21.7233(17)		
α [°]	90	**Completeness to θ = 25.242°**	99.7 %
β [°]	90.575(4)		
γ [°]	90	**Data / Restraints / Parameters**	5339/0/325
Volume [Å^3]	1338.24(19)		
Z	4	**Goodness-of-fit on F^2**	1.1368
ρ_{calc} [gcm^{-3}]	1.252		
μ [mm^{-1}]	0.080	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0190 wR_2 = 0.0453
***F*(000)**	536.320		
Crystal size [mm^3]	0.485×0.312×0.282	**Final *R* indexes [all data]**	R_1 = 0.0219 wR_2 = 0.0469
Crystal colour	Colorless		
Crystal shape	Block	**Largest peak/hole [eÅ^{-3}]**	0.27/-0.11
Radiation	Mo K_α (λ=0.71073 Å)		

Refinement table and details for (1s,4s)-2,2,3,3-tetrafluoro-1,4-diphenylbicyclo[2.1.1]hexane (**2ab**)

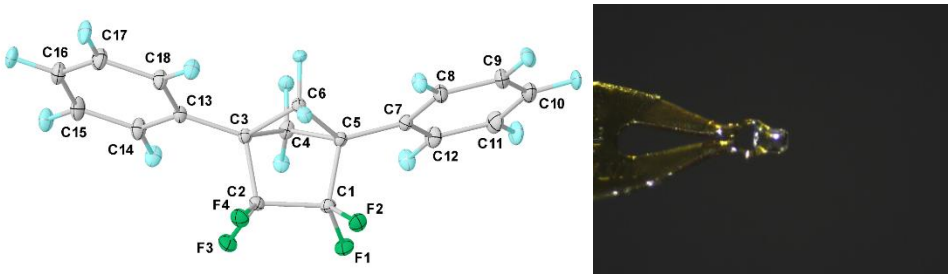


Figure S7. Molecular structure of **2ab** in the solid state and picture of used crystal.

Displacement ellipsoids are drawn at 50% probability level. The crystals were obtained from dichloromethane.

Table S11. Crystal data and structure refinement.

CCDC number	2261999	**2θ range [°]**	3.98 to 86.27 (0.52 Å)
Empirical formula	$C_{18}H_{14}F_4$		
Formula weight	306.29	**Index ranges**	−20 ≤ h ≤ 20 −12 ≤ k ≤ 12 −39 ≤ l ≤ 39
Temperature [K]	100.00		
Crystal system	monoclinic		
Space group (number)	$P2_1/c$ (14)	**Reflections collected**	182274
***a* [Å]**	10.8425(8)	**Independent reflections**	10412 R_{int} = 0.0431 R_{sigma} = 0.0133
***b* [Å]**	6.2990(8)		
***c* [Å]**	20.5750(19)		
α [°]	90	**Completeness to θ = 25.242°**	100.0 %
β [°]	96.030(2)		
γ [°]	90	**Data / Restraints / Parameters**	10411/4/325
Volume [Å^3]	1397.4(2)		
Z	4	**Goodness-of-fit on F^2**	1.063
ρ_{calc} [gcm^{-3}]	1.456		
μ [mm^{-1}]	0.121	**Final *R* indexes [*I*≥2σ(*I*)]**	R_1 = 0.0193 wR_2 = 0.0428
***F*(000)**	632		
Crystal size [mm^3]	0.175×0.121×0.078	**Final *R* indexes [all data]**	R_1 = 0.0256 wR_2 = 0.0455
Crystal colour	colourless		
Crystal shape	block	**Largest peak/hole [eÅ^{-3}]**	0.26/-0.18
Radiation	MoK_α (λ=0.71073 Å)		

9 References

1 W. C. Still, M. Khan and A. Mitra, *J. Org. Chem*., 1978, **43**, 2923–2925.
2 G. M. Sheldrick, *Acta Crystallogr. A,* 2008, **A64**, 112–122.
3 a) O. V. Dolomanov, L. J. Bourhis, R. J Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.,* 2009, **42**, 339–341; b) D. Kratzert, *FinalCif*, V106, https://dkratzert.de/finalcif.html.
4 T. Kottke and D. Stalke, *J. Appl. Cryst*., 1993, **26**, 615–619.
5 F. Kleemiss, O.V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, M. Midgley, L.J. Bourhis, A. Genoni, L.A. Malaspina, D. Jayatilaka, J.L. Spencer, F. White, B. Grundkoetter-Stock, S. Steinhauer, D. Lentz, H. Puschmann and S.Grabowsky, *Chem. Sci*., 2021, **12**, 1675–1692.
6 M. Golfmann, L. Glagow, A. Giakoumidakis, C. Golz and J. C. L. Walker, *Chem. Eur. J.,* 2023, **29**, e202202373.
7 M. Y. Wong, S. Krotkus, G. Copley, W. Li, C. Murawski, D. Hall, G. J. Hedley, M. Jaricot, D. B. Cordes, A. M. Z. Slawin, Y. Olivier, D. Beljonne, L. Muccioli, M. Moral, J.-C. Sancho-Garcia, M. C. Gather, I. D. W. Samuel and E. Zysman-Colman, *ACS Appl. Mater. Interfaces*., 2018, **10**, 33360–33372.
8 E. Speckmeier, T. G. Fischer and K. Zeitler, *J. Am. Chem. Soc.,* 2018, **140**, 15353–15365.
9 K. P. Bryliakov, E. P. Talsi and M. Bochmann, *Organometallics,* 2003, **23**, 149–152.
10 C. Peppe and R. P. das Chagas, *Synlett,* 2004, 1187–1190.
11 D. V. Gribkov, K. C. Hultzsch and F. Hampel, *J. Am. Chem. Soc*., 2006, **128**, 3748–3759.
12 M. Imai, M. Tanaka, K. Tanaka, Y. Yamamoto, N. Imai-Ogata, M. Shimowatari, S. Nagumo, N. Kawahara and H. Suemune, J*. Org. Chem*., 2004, **69**, 1144–1150.
13 a) K. Moriyama, T. Hamada, Y. Nakamura and H. Togo, *Chem. Commun*., 2017, **53**, 6565–6568; b) X.-Y. Guan, Z. Al-Misba'a and K.-W. Huang, *Arab. J. Chem*., 2015, **8**, 892–896.
14 H. Ikeda, K. Matsuo, Y. Matsui, M. Matsuoka and K. Mizuno, *Bull. Chem. Soc. Jpn*., 2011, **84**, 537–543.
15 S. A. Chacko, P. G. Wenthold, *J. Org. Chem*. 2006, ***72***, 494–501.
[16] R. Liu, Z. Yang, Y. Ni, K. Song, K. Shen, S. Lin, Q. Pan*, J. Org. Chem.* 2017, **82**, 15, 8023–8030.
[17] M. S. Chen, P. Narayanasamy, N. A. Labenz, M. C. White, *J. Am. Chem. Soc.* 2005, 127, **19**, 6970–6971.
[18] A. Shimizu, G. Hirata, G. Onodera and M. Kimura, *Adv. Synth. Catal*., 2018, **360**, 1954–1960.
[19] R. Liu, Z. Yang, Y. Ni, K. Song, K. Shen, S. Lin, Q. Pan*, J. Org. Chem.* 2017, **82**, 15, 8023–8030.
[20] A. Denisenko, P. Garbuz, S. V. Shishkina, N. M. Voloshchuk and P. K. Mykhailiuk, *Angew. Chem. Int. Ed.,* 2020, **59**, 20515–20521.
[21]A. Denisenko, P. Garbuz, S. V. Shishkina, N. M. Voloshchuk, P. K. Mykhailiuk, *Angew. Chem.* 2020, ***132***, 20696–20702.
[22] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics,* 2010, **29**, 2176–2179.