

Supporting Information

Reductive Activation and Hydrofunctionalization of Olefins by Multiphoton Tandem Photoredox Catalysis

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Experimental Procedures

General Information

Synthesis and General Instrumentation: Unless otherwise stated, reagents and solvents were purchased from commercial sources and used without further purification. $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]\text{PF}_6$ was prepared according to a literature procedure.¹

Analytical Thin Layer Chromatography (TLC) was carried out using aluminium-backed Merck Kieselgel KG60 F254 silica plates. Preparative TLC was conducted using Analtech silica gel matrix preparative TLC plates (1.00 mm). The plates were visualized by irradiation with short-wave ultraviolet light. Flash chromatography was performed on SiliaFlash® P60 R12030B 40-63 micron silica gel.

All light promoted reactions were performed using two PR160 (40 W, 440 nm) Kessil LED lights (www.kessil.com) (Figure S1). Vials were placed on a square metal frame fitted with PC cooling fans and heat sinks for temperature control (internal temperature of reactor typically reaches 27 ± 5 °C overnight). The power of the light source can be varied with four levels of intensity control.

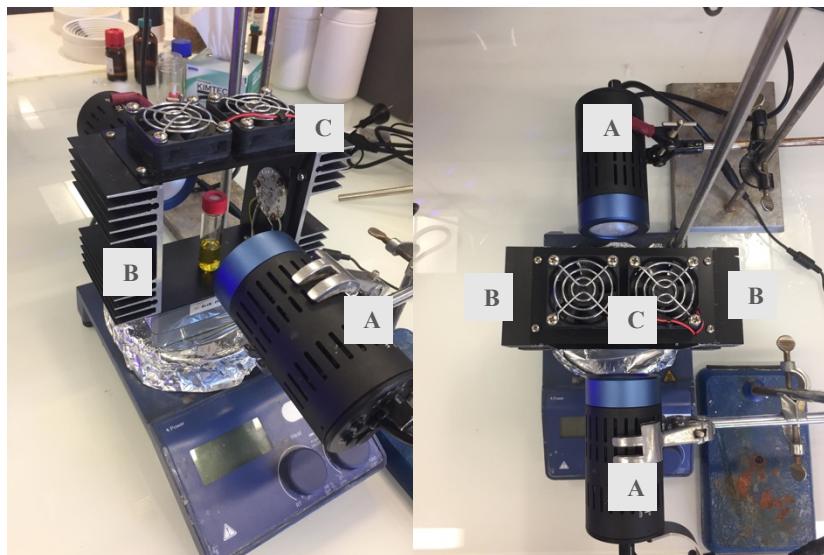


Figure S1. Photoreaction assembly; a) Kessil 440 nm LED light; b) heat sinks; c) PC cooling fans.

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on Varian MR-400 (400 MHz), Agilent DD2 (500 MHz) and Varian INOVA (600 MHz). Chemical shifts are expressed in parts per million (PPM) and are referenced to the internal solvent peaks.

Mass spectrometry

Accurate mass measurement was performed by the Monash Analytical Platform using an Agilent 6220 Accurate Mass LC-TOF system with Agilent 1200 Series HPLC. MS was fitted with the Agilent Multimode Source (ESI/APCI). Reference mass correction used for all accurate mass work was Purine/HP0921 mix. **Scan** from 100 m/z to 3000 m/z; **Source Conditions:** 8 L/min N₂, 325 degrees drying gas temp. Capillary voltage – 3000V. Samples were directly injected into the source using a syringe pump (KD Scientific Syringe pump running at 600uL/h).

Transient absorption (TA) spectroscopy

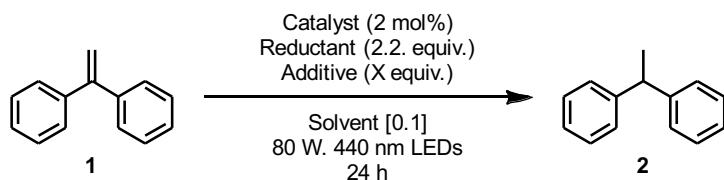
Nanosecond transient absorption measurements were performed using the 355 nm output from a nanosecond optical parametric oscillator (Eskpla NT340) as the excitation source (pump) (~5 ns pulses at 10 Hz). A Xenon lamp (ILC Cermax) was used as probe with a monochromator (Acton SpectraPro 300i), a long-pass filter (370 nm), photomultiplier tube (Hamamatsu R928), and digital oscilloscope (Teledyne/LeCroy WaveSurfer 10). The wavelengths detected were 380 nm and 540 nm.

Fluorescent quenching experiments

Steady-state luminescent spectra were recorded using an Agilent Cary Eclipse Fluorescence Spectrophotometer. Samples were excited at 440 nm, slit widths were 5 nm and the area under the spectra were used for determining the Stern-Volmer quenching values.

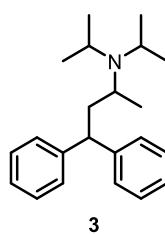
Optimization

Table S1: Reaction optimization



Solvent	Reductant	Additive (equiv.)	Catalyst	Conversion [%] ^a	Yield of 2 [%] ^a
DMF	Triethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	90	3
MeCN	Triethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	100	4
DMSO	Triethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	100	2
MeOH	Triethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	92	14
EtOH	Triethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	99	7
Toluene	Triethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	100	0
THF	Triethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	96	0
MeOH	Tributylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	100	6
MeOH	1,2,2,6,6-Pentamethylpiperidine		Ir(ppy) ₂ (dtb-bpy)PF ₆	100	7
MeOH	<i>N,N</i> -Diisopropylethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	100	37
MeOH	Tetrahydroisoquinoline		Ir(ppy) ₂ (dtb-bpy)PF ₆	18	8
MeOH	Tetramethylethylenediamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	47	11
MeOH	<i>N,N</i> -Dicyclohexylmethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	92	20
MeOH/H ₂ O (9:1)	<i>N,N</i> -Diisopropylethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	98	55
MeOH/H ₂ O (8:2)	<i>N,N</i> -Diisopropylethylamine		Ir(ppy) ₂ (dtb-bpy)PF ₆	90	29 ^b
MeOH/H ₂ O (9:1)	<i>N,N</i> -Diisopropylethylamine	HCOOH (2.5)	Ir(ppy) ₂ (dtb-bpy)PF ₆	100	74
MeOH/H ₂ O (9:1)	<i>N,N</i> -Diisopropylethylamine	HCOOH (2.8)	Ir(ppy) ₂ (dtb-bpy)PF ₆	100	82
MeOH/H ₂ O (9:1)	<i>N,N</i> -Diisopropylethylamine	HCOOH (3.0)	Ir(ppy) ₂ (dtb-bpy)PF ₆	100	79
MeOH/H ₂ O (9:1)	<i>N,N</i> -Diisopropylethylamine	HCOOH (2.8)	<i>fac</i> -Ir(ppy) ₃	23	20
MeOH/H ₂ O (9:1)	<i>N,N</i> -Diisopropylethylamine	HCOOH (2.8)	Ru(bpy) ₃ Cl ₂	N.D.	N.D.

^aYield determined by ¹H NMR spectroscopy using sulfolene as an internal standard.^b α -amino adduct **3** was the major by-product. ND = Not Detected



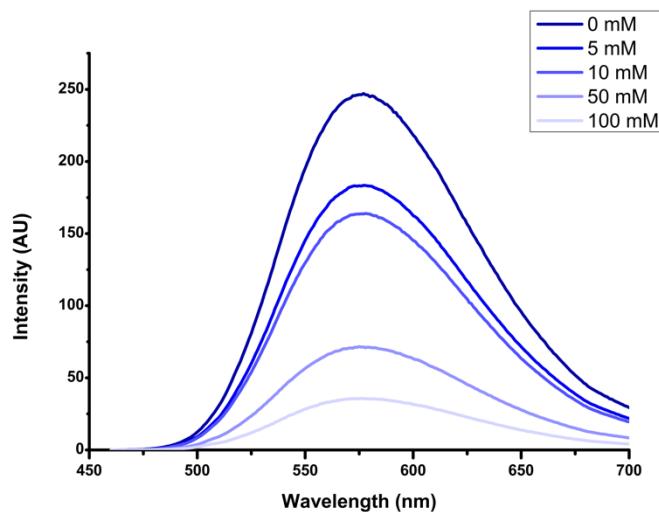
Mechanistic Studies

Stern-Volmer Fluorescence Quenching Studies

Quenching of $[\text{Ir1}]^{**}$

A standard solution of $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]\text{PF}_6$ in methanol (0.1 mM) was prepared in a 10 mL volumetric flask. An aliquot (2 mL) was transferred to a septum capped quartz cuvette. A solution containing an appropriate amount of quencher in methanol (1 mL) was added. The sample was sparged with N_2 for 1 min prior to fluorescence measurement being taken.

A



B

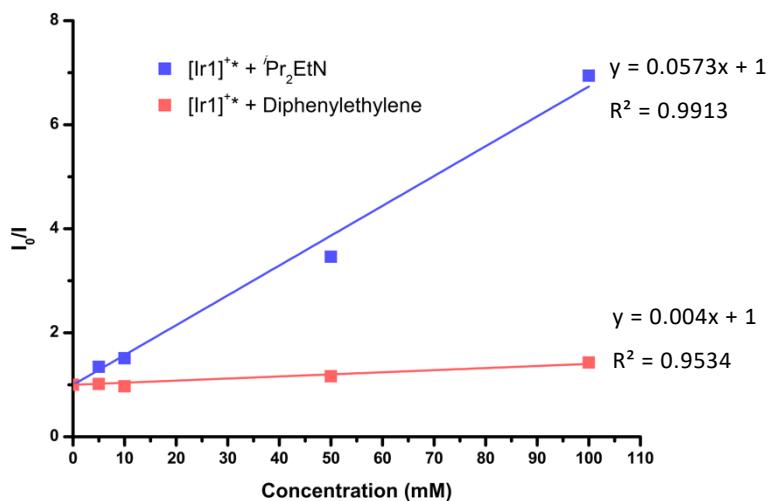


Figure S2: (A) Photoluminescence quenching of $[\text{Ir1}]^{**}$ in methanol by $i\text{Pr}_2\text{EtN}$. (B) Stern-Volmer plot of fluorescence intensity of $[\text{Ir1}]^{**}$ in the presence of $i\text{Pr}_2\text{EtN}$ (blue) and diphenylethylene (red).

Quenching of $[\text{Ir}2]^{0*}$:

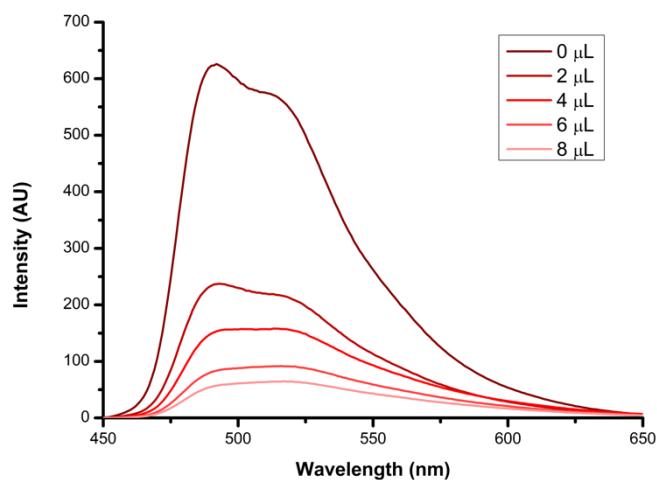
Emission from $[\text{Ir}2]^{0}$ in the absence of the quencher:*

A standard solution containing $^3\text{Pr}_2\text{EtN}$ (50 mM) and $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]\text{PF}_6$ (0.1 mM) in methanol was prepared in a 10 mL volumetric flask. An aliquot (3 mL) was transferred to a septum capped quartz cuvette, degassed for 1 min with N_2 and irradiated for 10 min with 14W, 447 nm blue LED light, under a positive pressure of N_2 . Fluorescence measurement was taken immediately after the sample was removed from the blue LED reactor.

Quenching studies:

Neat diphenylethylene was added, in 2 μL increments, to the quartz cuvette via an air-tight microsyringe. Following each incremental addition, the sample was sparged with N_2 for 1 minute and irradiated with 14W, 447 nm blue LED light under a positive pressure of N_2 for 10 minutes. Each time the fluorescence measurement was taken immediately after the sample was removed from the blue LED reactor.

A



B

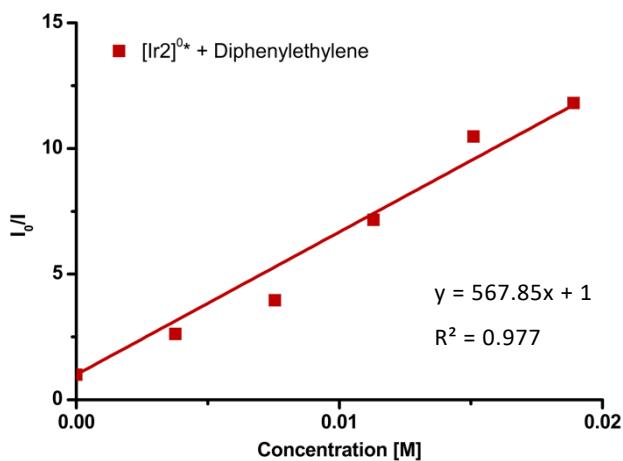


Figure S3: (A) Photoluminescence quenching of $[\text{Ir}2]^{0*}$ by diphenylethylene. (B) Stern-Volmer plot of fluorescence intensity in the presence of diphenylethylene.

Transient Absorption Spectroscopy

Samples for transient-absorption studies were prepared in the following manner:

A standard solution containing $^i\text{Pr}_2\text{EtN}$ (50 mM) and $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]\text{PF}_6$ (0.1 mM) in methanol was prepared in a 10 mL volumetric flask. An aliquot (3 mL) was transferred to a septum capped quartz cuvette. Neat diphenylethylene (53 μL) was added to the cuvette via an air-tight microsyringe, and the sample was sparged with nitrogen for 1 minute, and irradiated with 14W, 447 nm blue LED light under a positive pressure of N_2 for 10 minutes. The transient absorption measurement was then recorded immediately after the sample was removed from the blue LED reactor.

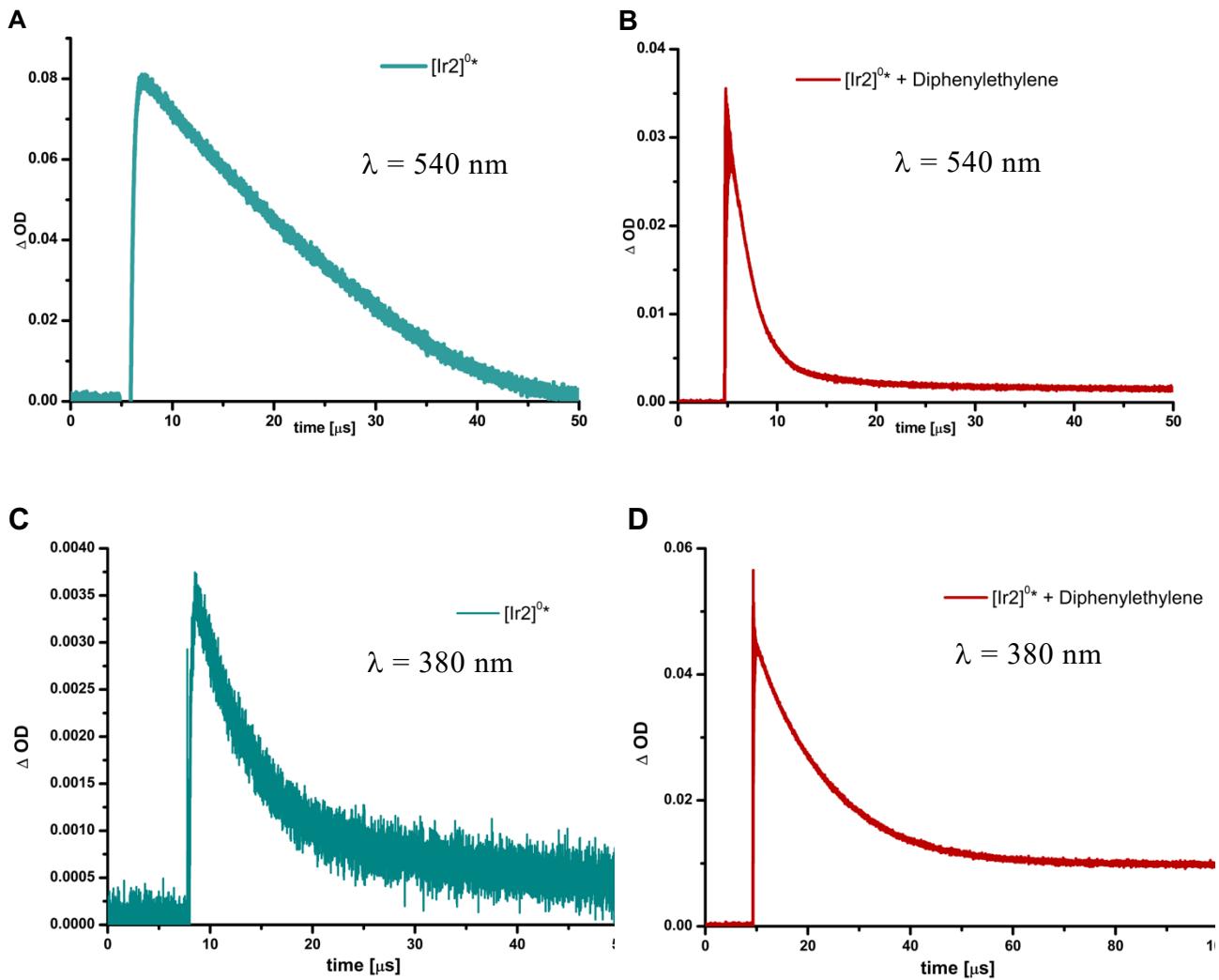


Figure S4: (A) Transient absorption decay profile of $[\text{Ir}2]^{0*}$ following excitation at $\lambda_{\text{ex}} = 355 \text{ nm}$, probe = 540 nm (B) Transient absorption decay profile of $[\text{Ir}2]^{0*}$ following excitation at $\lambda_{\text{ex}} = 355 \text{ nm}$, probe = 540 nm in the presence of diphenylethylene (100 mM). C) Transient absorption decay profile of $[\text{Ir}2]^{0*}$ following excitation at $\lambda_{\text{ex}} = 355 \text{ nm}$, probe = 380 nm (D) Transient absorption decay profile of $[\text{Ir}2]^{0*}$ following excitation at $\lambda_{\text{ex}} = 355 \text{ nm}$, probe = 380 nm in the presence of diphenylethylene (100 mM).

Radical Clock Experiment

In polar solvents, a radical anion derived from diarylethylene (**Int-A**) is quenched by a proton donor resulting in a formation of a neutral radical at the more stabilized benzylic position (**Int-B**).² To enable detection of **Int-B** in our reaction, we subjected (1-cyclopropylvinyl)benzene (**39**) to the optimized photoredox hydrogenation protocol. The tertiary benzylic radical **Int-B39** has been reported to undergo a relatively slow ($k \approx 4 \times 10^5 \text{ s}^{-1}$)³ ring opening rearrangement resulting in the formation of open chained product **40**. Thus, it was hypothesized that there should be competition between formation of **40** and **41** if **Int-B39** is an intermediate along the main reaction pathway.

As shown in Figure S5 below, rearranged open-chain olefin **40**, the reduced unrearranged **41** as well as and the Markovnikov methanol adduct **42** were detected in the ^1H NMR spectrum of the crude reaction mixture (Figure S5 below), in the ratio of approx. **40** : **41** : **42** = 1 : 1.6 : 0.4. All three products derive from **Int-B39**. Oxidation of the benzylic radicals to a carbocations, followed by a nucleophilic attack by solvent is known,^{2, 4} and yet it is a minor product here despite high nucleophilicity of the C-C bond in the cyclopropane ring.

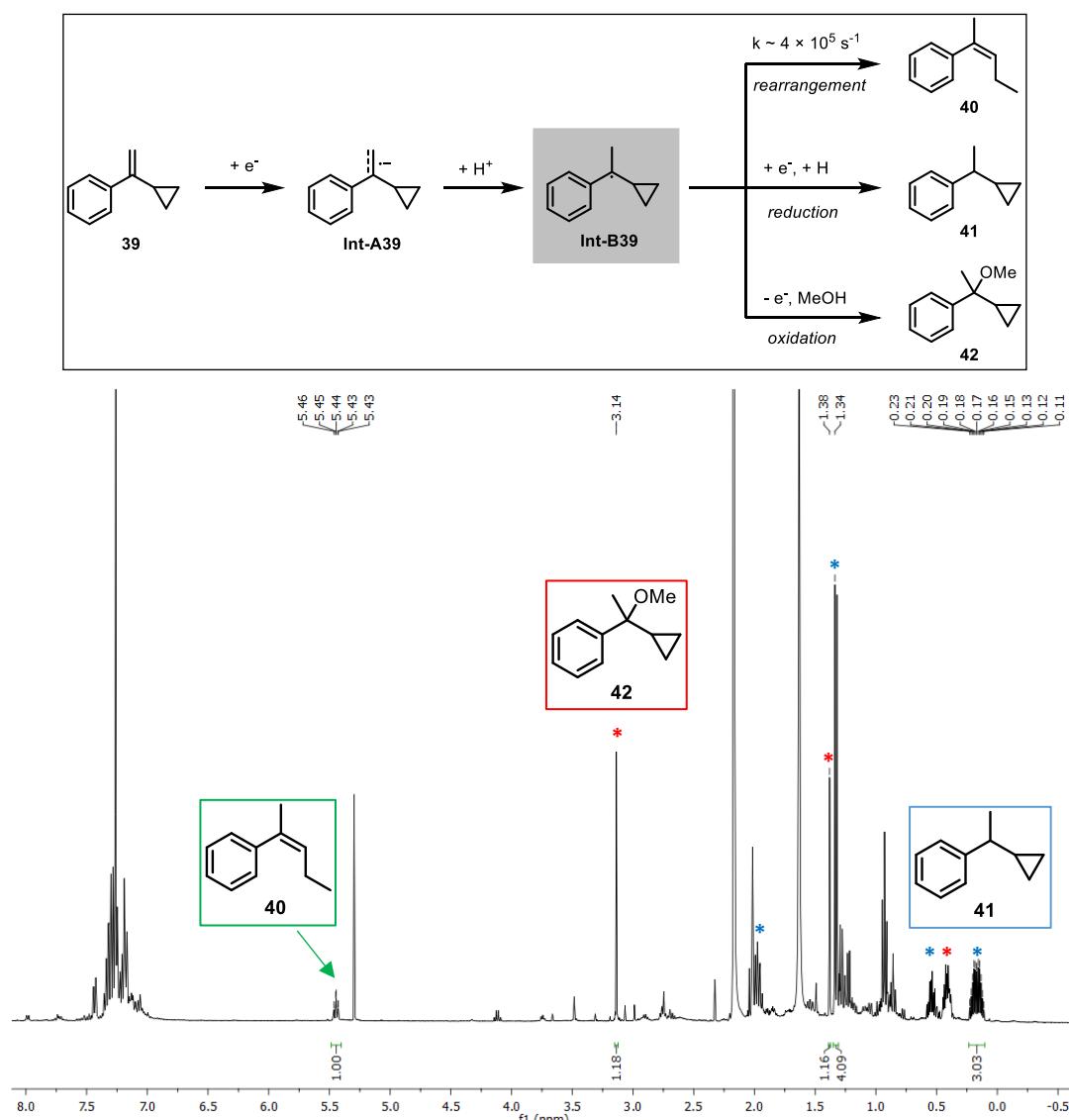


Figure S5: Top: formation of **40**, **41** and **42** from **Int-B39**. Bottom: ^1H NMR spectrum (CDCl_3 , 400 MHz) of the crude reaction mixture. **40**,⁵ **41**,⁶ and **42**,⁷ are known compounds and the chemical shifts match those reported in the literature.

Reactivity of Int-B

To determine how **Int-B** converts into fully hydrogenated product, we conducted deuterium labelling experiments using substrate **16a**. Two plausible pathways were identified. Path A involves a hydrogen atom transfer (HAT) from the $^3\text{Pr}_2\text{EtN}$ radical cation, a mechanism previously reported for transfer hydrogenation of ketimines under similar reaction conditions,⁸ or the ammonium formate complex.⁹ In path B, a sequential single electron transfer (SET) step generates an anionic **Int-C**, which is quenched by protic solvent or formic acid. Alternatively, **Int-A** could undergo direct HAT from the ammonium formate complex to give **Int-C** in one step.

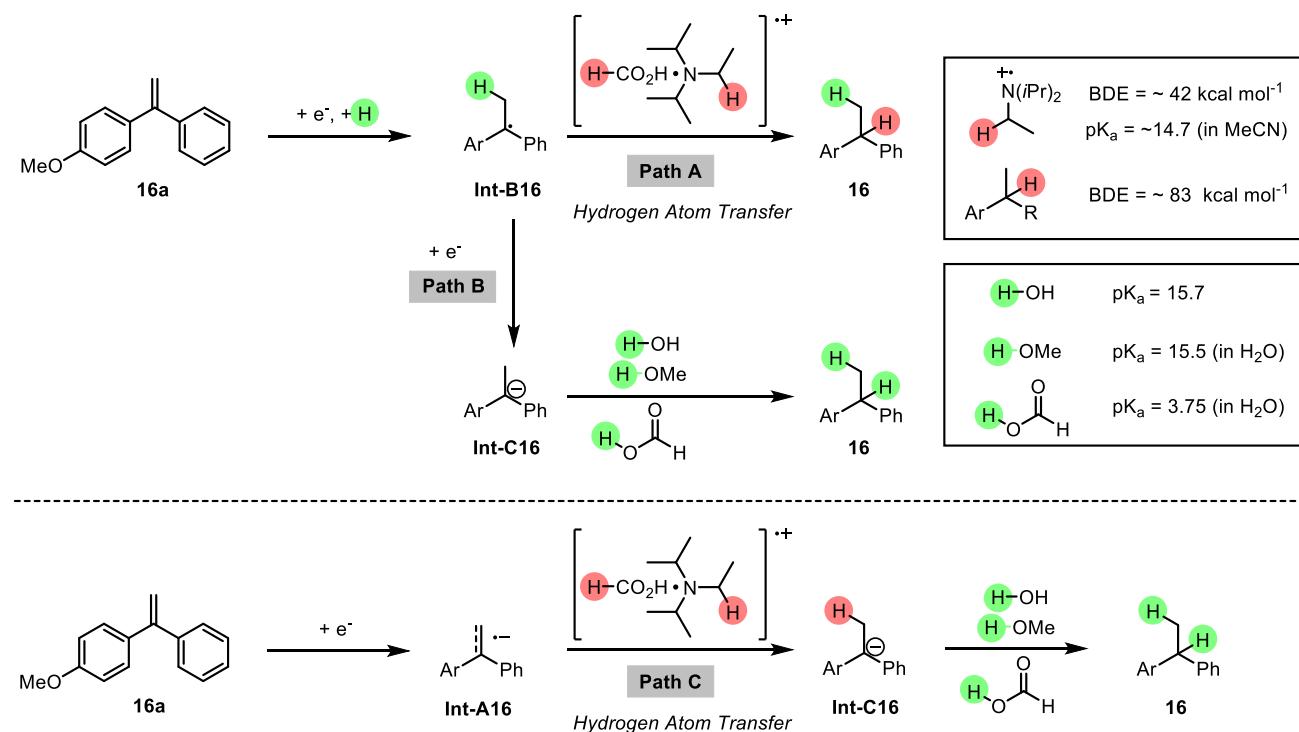
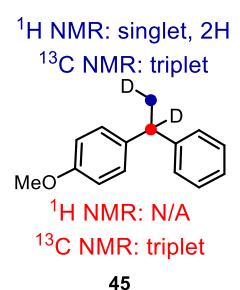
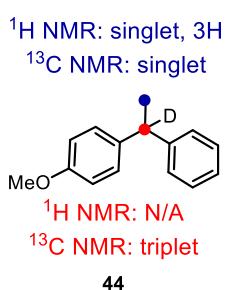
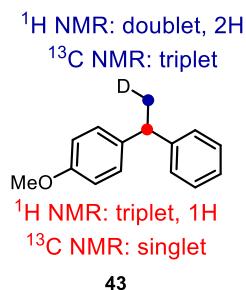


Figure S6: Path A: formation of product **16** through direct hydrogen atom transfer to **IntB-16** from the radical cation of the formate salt of $^3\text{Pr}_2\text{EtN}$; Path B: formation of product **16** through two sequential single electron transfers and protonation; Path C: formation of product **16** through direct hydrogen atom transfer to **Int-A16** from the radical cation of the formate salt of $^3\text{Pr}_2\text{EtN}$

Replacing $^3\text{Pr}_2\text{EtN}$ with $d_{15}\text{-NEt}_3$ was not informative, as only traces of the reduced product could be detected in the ^1H NMR spectrum of the crude reaction mixture. Consequently, $d_4\text{-MeOH}$, D_2O and HCO_2D were used as solvents with $^3\text{Pr}_2\text{EtN}$ as the reductive quencher. Mass spectrometry of the crude reaction mixture revealed that both mono-deuterated products, **43** and/or **44** ($m/z = 214.12$) and bis-deuterated product **45** ($m/z = 215.13$) were generated under these reaction conditions. Reduced product **16** with no deuterium incorporation was not detected in the ^1H NMR spectrum of the crude reaction mixture.



HRMS (ESI) m/z calc. for C₁₅H₁₆DO
 $[M+H]^+$ 214.1342 found 214.1217

HRMS (ESI) m/z calc. for C₁₅H₁₅D₂O
 $[M+H]^+$ 215.1405 found 215.1253

Figure S7 Three possible deuterated products detected in the mass spectrum of the crude reaction mixture and their ¹H NMR and ¹³C NMR splitting patterns.¹⁰

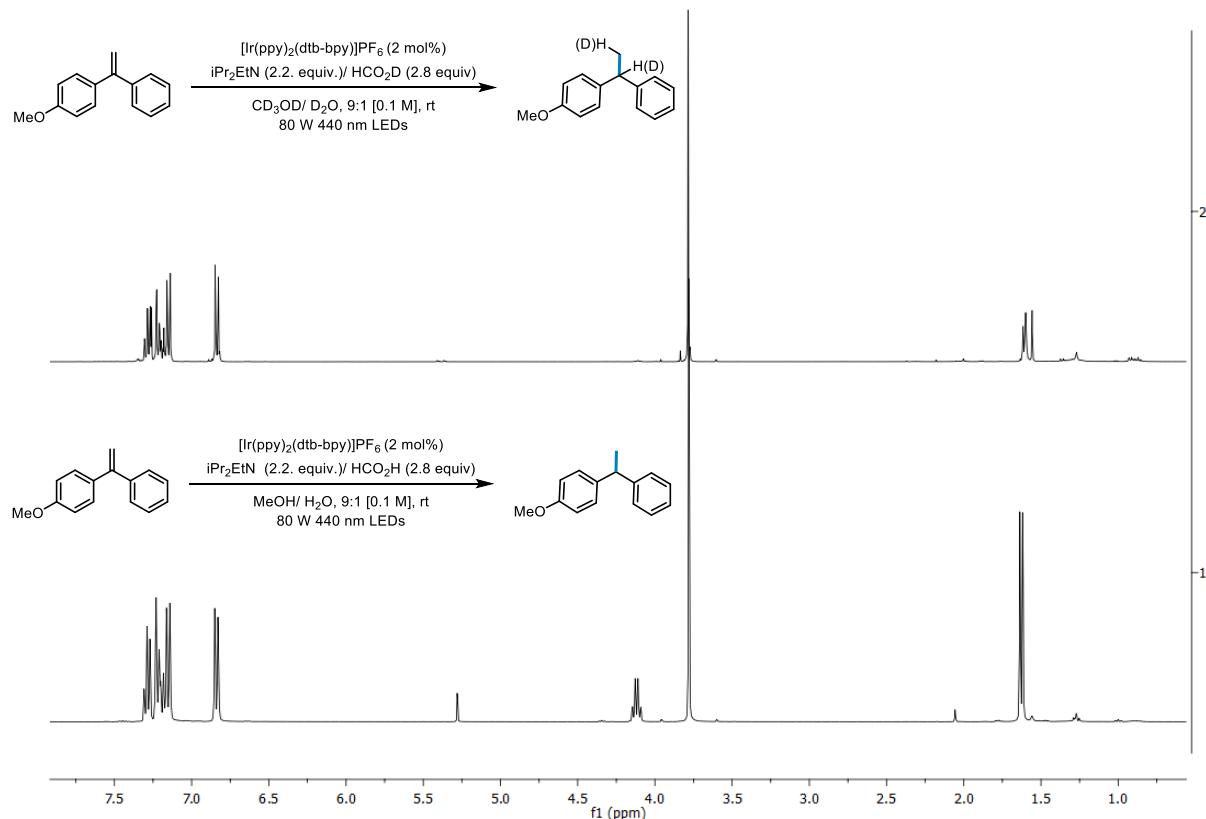


Figure S8: Comparison of the ¹H NMR spectrum (CDCl₃, 400 MHz) of the reduced product run in non-deuterated solvents (bottom) and deuterated solvents (top).

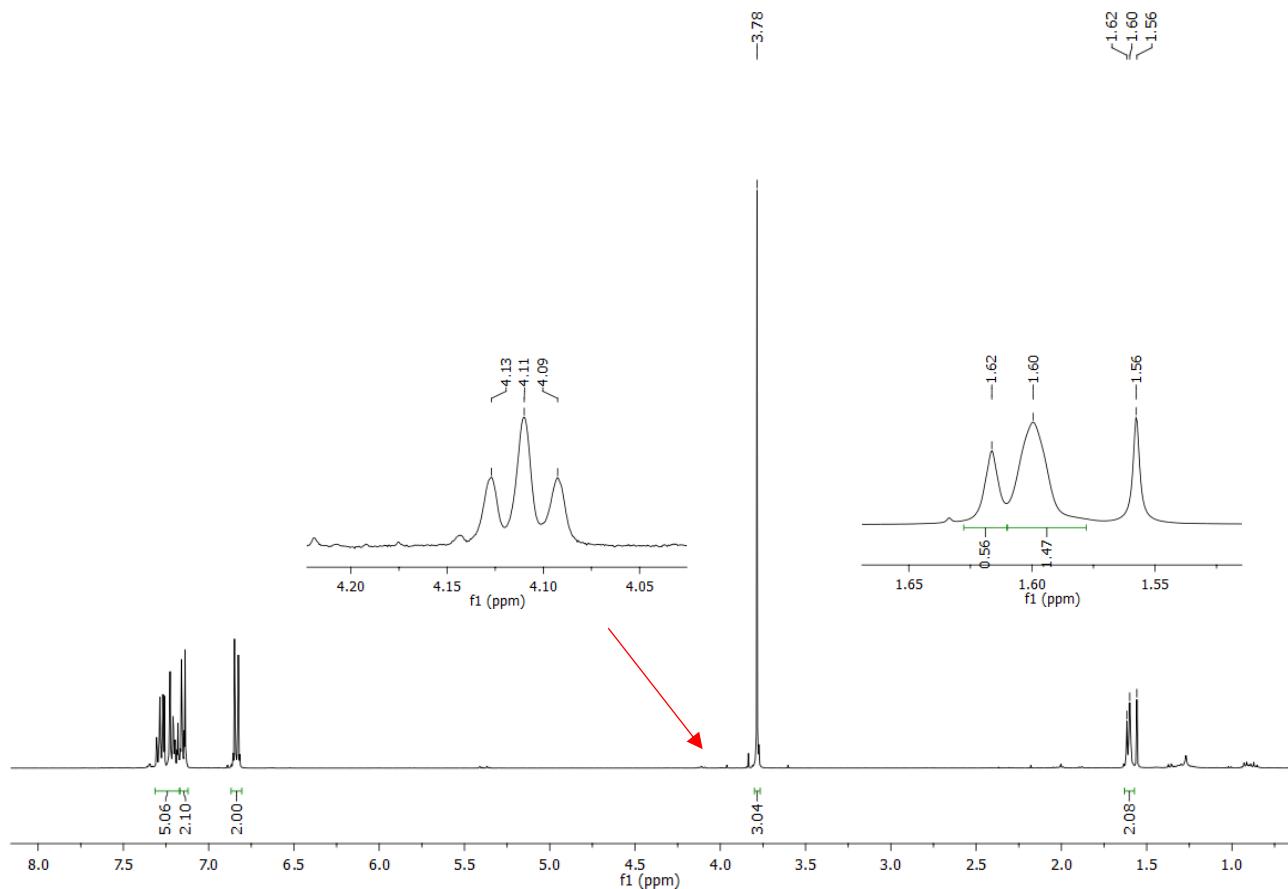


Figure S9: ^1H NMR spectrum (CDCl_3 , 500 MHz) of hydrogenation reaction of substrate **16a** run in MeOH-d_4 , D_2O and HCOOD .

Baseline triplet at 4.11 ppm (Figure S9) suggested that compound **43** formed in trace quantities. This indicated that resonances at 1.62 ppm and 1.60 ppm, are both singlets corresponding to products **44** and **45**. ^{13}C NMR spectrum (Figure S10) confirmed that resonances at 44.5 ppm and 22.2 ppm both split into a singlet and a triplet, confirming incomplete deuterium incorporation at both distal and proximal positions, and ^1H - ^{13}C HSQC spectrum revealed 2D correlation between the major singlet in ^1H NMR spectrum at 1.60 ppm and a triplet in ^{13}C NMR spectrum at 21.8 ppm, verifying that bis-deuterated product **45** is the major product from this reaction.

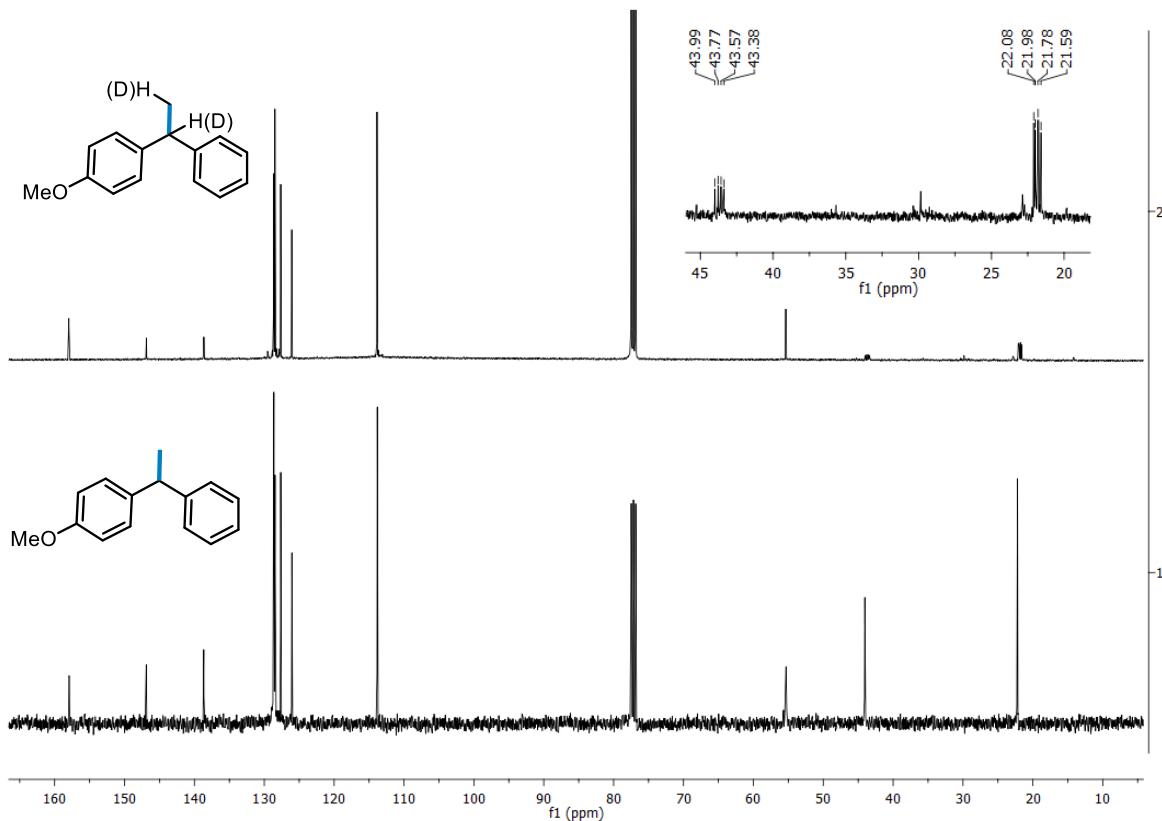


Figure S10: Comparison of the ^{13}C NMR spectra (CDCl_3 , 125 MHz) of the reduced product run in non-deuterated solvents (bottom) and deuterated solvents (top).

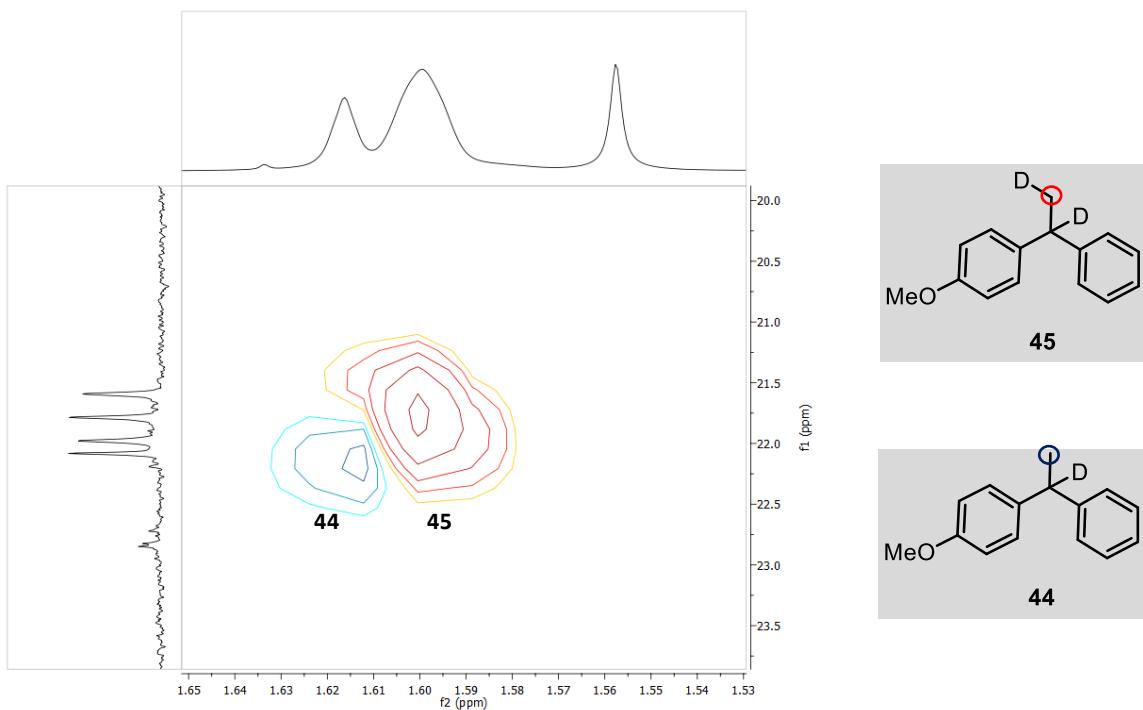


Figure S11: Partial ^1H - ^{13}C HSQC spectrum demonstrating correlation between the major singlet in ^1H NMR (1.60 ppm) and the triplet in ^{13}C NMR spectra, consistent with structure **45**.

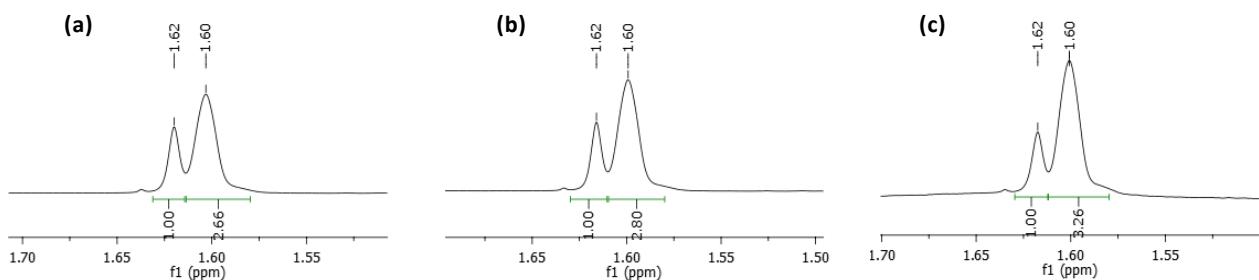


Figure S12: Comparison of partial ^1H NMR spectra (CDCl_3 , 400 MHz) of the crude reaction mixtures run with MeOD-d_4 and D_2O and (a) HCOOH (b) HCOOD and (c) DCOOH . The proportion of bis-deuterated product slightly increases from (a) to (b) to (c), suggesting that the ammonium formate complex can act as a HAT reagent (path c).

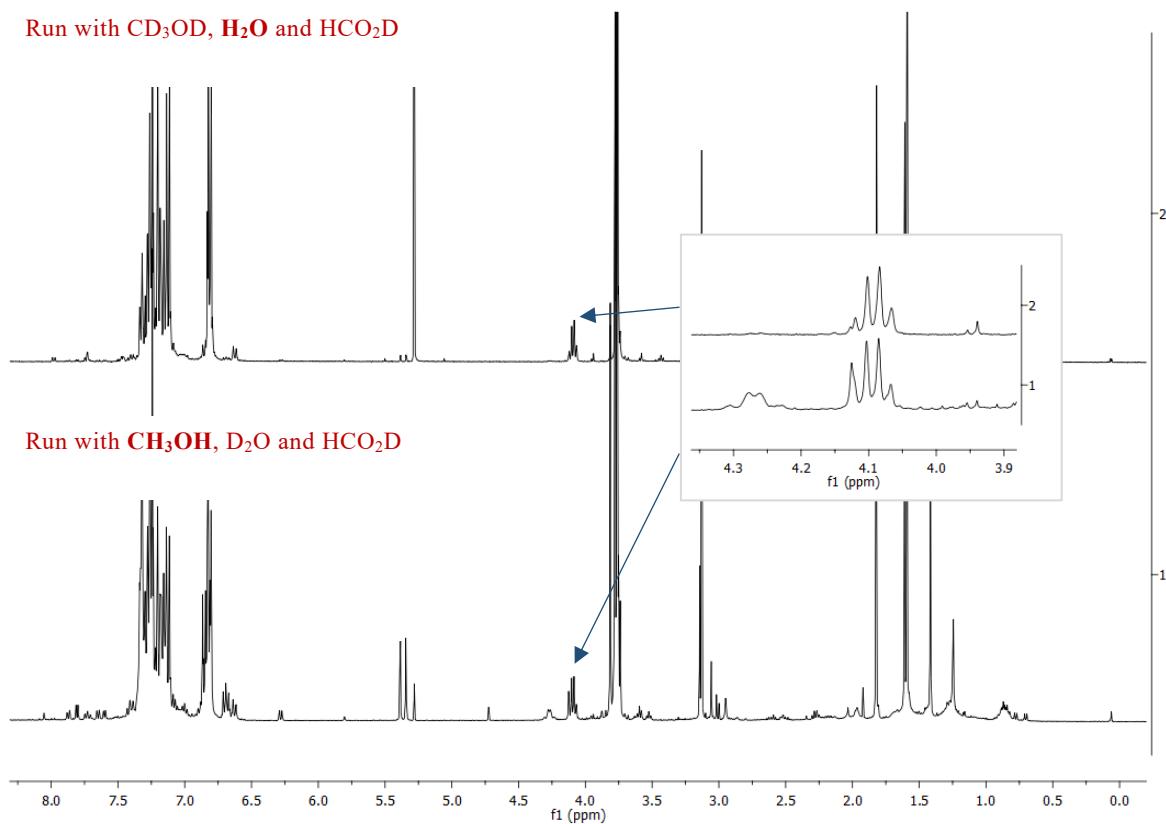


Figure S13: Comparison of ^1H NMR spectra (CDCl_3 , 400 MHz) of the crude reaction mixtures run with methanol and D_2O (bottom) or with CD_3OD and water (top). The characteristic quartet around 4.1 ppm shows the presence of non-deuterated reduced product **16**, signifying that solvents are the major sources of protons in this reaction.

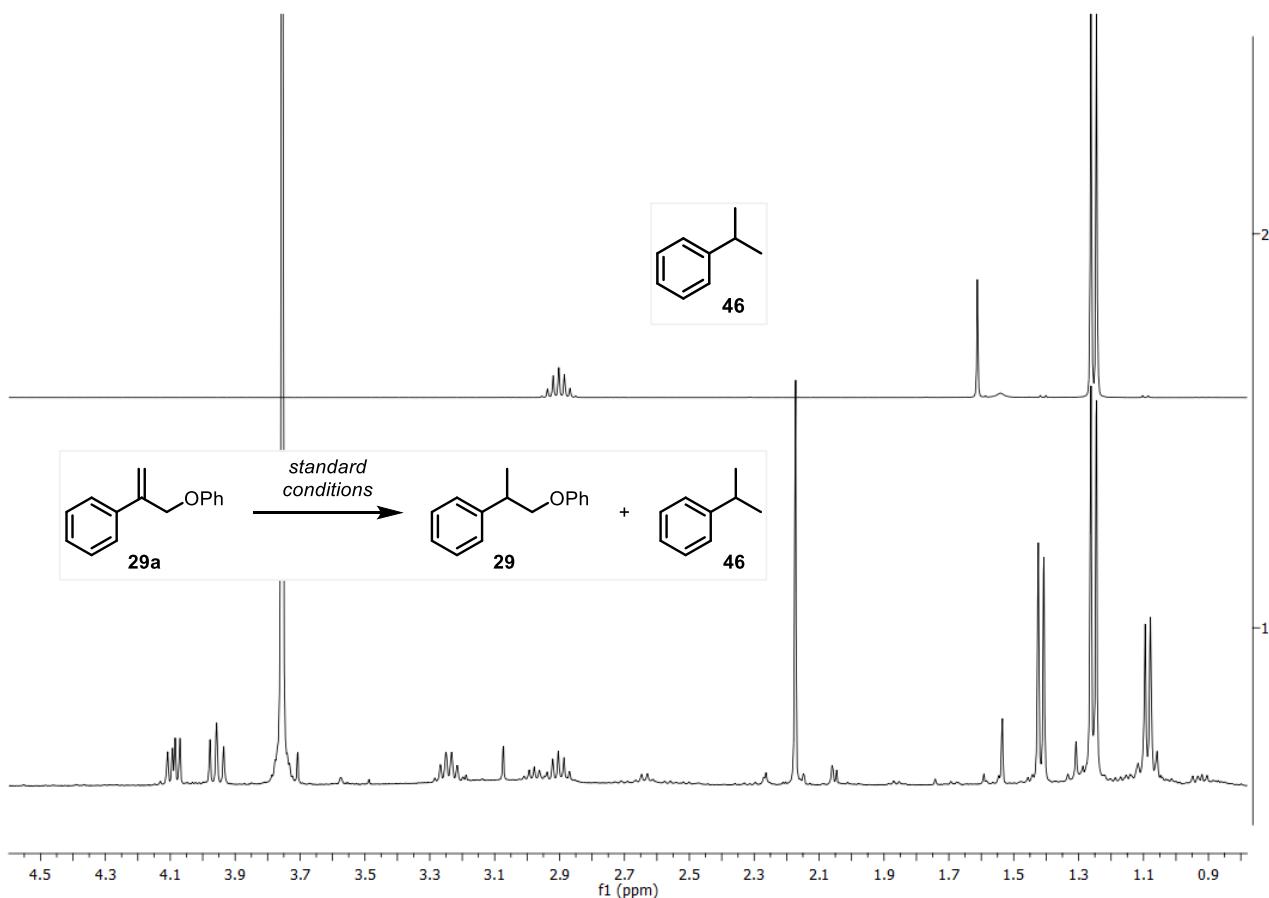


Figure S14: ¹H NMR spectra (CDCl₃, 400 MHz) of the crude for the reduction of **29a** (bottom) and an authentic sample of cumene **46** (top). The presence of cumene **46** is consistent with the formation of **Int-C** and elimination of the phenoxy group, followed by reduction of the resulting α -methyl styrene.

Addition to Ketones: Mechanistic Hypothesis

We hypothesize that product **48** arises from the direct nucleophilic addition of Int-A to a carbonyl group, to generate a benzylic radical. As established previously, the resulting benzylic radical is further reduced to carbanion, which could be quenched by the amine radical cation, or be protonated by traces of water in the solvent. No side products were observed in the ¹H NMR of the crude reaction mixture, and we did not observe any difunctionalisation adducts. The reaction was slow and did not go to completion even after extended reaction times (60 hours).

Alternatively, product **48** could also arise from the radical addition to the carbonyl group, however this is known to be difficult, as the resulting alkoxyl radical undergoes facile β -fragmentation.¹¹

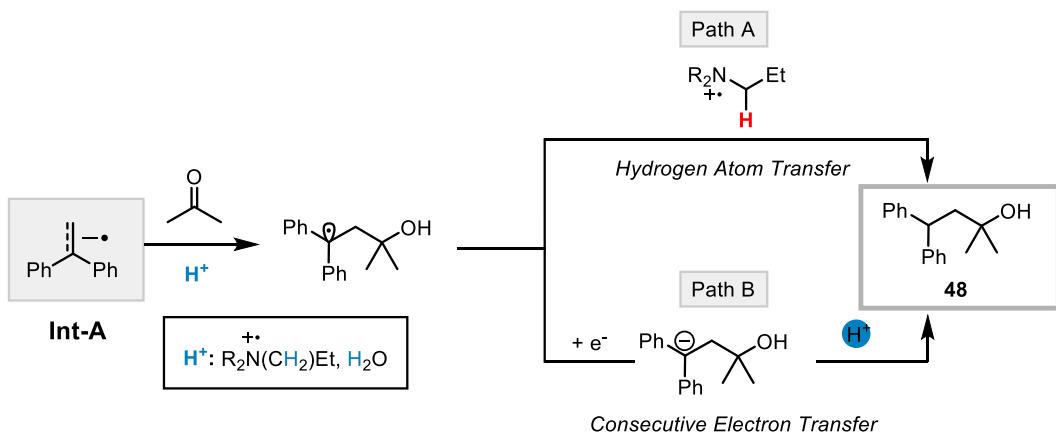
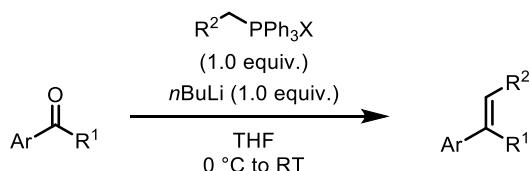


Figure S15: Path A: formation of product **48** through direct hydrogen atom transfer from the radical cation of the tertiary amine; Path B: formation of product **48** through two sequential single electron transfers and protonation.

Synthesis and Characterization

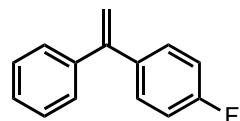
Preparation of styrene derivatives

Method A:¹²



A solution of *n*BuLi in hexanes (C = 1.6 M, 4.0 mmol, 1.0 equiv.) was added dropwise, at 0 °C, to a solution of a Wittig salt (4.0 mmol, 1.0 equiv.) in dry THF (30 mL). The reaction mixture was stirred at 0 °C for 30 minutes. A solution of the carbonyl compound (4.0 mmol, 1.0 equiv.) in dry THF (10 mL) was added dropwise at 0 °C, and the reaction mixture was stirred at room temperature overnight. It was then diluted with brine and extracted with EtOAc (3 × 40 mL). The combined organic extracts were washed with brine (3×) and dried with MgSO₄. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica eluting with 1 - 5% EtOAc/nhexane to yield the desired product.

Substrates synthesized using method A:



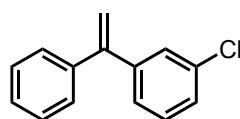
1-Fluoro-4-(1-phenylvinyl)benzene (4a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.57 g, 72% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.39-7.31 (m, 7H), 7.07-7.01 (m, 2H), 5.46 (d, *J* = 1.1 Hz, 1H), 5.44 (d, *J* = 1.1 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 162.7 (d, *J*_{C-F} = 245.4 Hz), 149.2, 141.4, 137.7 (d, *J*_{C-F} = 3.0 Hz), 130.0 (d, *J*_{C-F} = 7.90 Hz), 128.4, 128.3, 128.0, 115.3 (d, *J*_{C-F} = 21.4 Hz), 114.4.

¹⁹F NMR (376 MHz, CDCl₃): δ = -114.8.

Data matched that reported in the literature.¹³

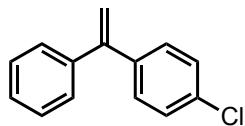


1-Chloro-3-(1-phenylvinyl)benzene (6a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/hexane afforded the desired product as a yellow liquid (0.64 g, 74% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.39-7.21 (m, 9H), 5.51 (d, *J* = 0.9 Hz, 1H), 5.48 (d, *J* = 0.9 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 149.0, 143.5, 140.9, 134.2, 129.5, 128.44, 128.43, 128.3, 128.1, 127.9, 126.6, 115.4.

Data matched that reported in the literature.¹⁴

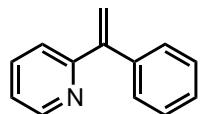


1-Chloro-4-(1-phenylvinyl)benzene (7a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/hexane afforded the desired product as a colourless liquid (0.59 g, 68% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.38-7.27 (m, 9H), 5.48 (d, *J* = 1.1 Hz, 1H), 5.46 (d, *J* = 1.1 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 149.1, 141.1, 140.1, 133.7, 129.7, 128.5, 128.4, 128.3, 128.1, 114.8.

Data matched that reported in the literature.¹⁵

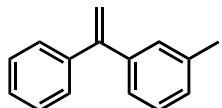


2-(1-Phenylvinyl)pyridine (11a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 50% EtOAc/nhexane afforded the desired product as a red liquid (0.52 g, 71% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 8.66 - 8.64 (m, 1H), 7.65 - 7.61 (m, 1H), 7.37 - 7.33 (m, 5H), 7.28 - 7.26 (m, 1H), 7.23 - 7.21 (m, 1H), 6.00 (d, *J* = 1.4 Hz, 1H), 5.62 (d, *J* = 1.4 Hz, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 158.6, 149.5, 149.2, 140.4, 136.4, 128.5, 128.4, 127.9, 123.0, 122.5, 117.9.

Data matched that reported in the literature.¹⁶

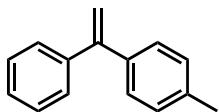


1-Methyl-3-(1-phenylvinyl)benzene (13a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid. (0.66 g, 85% yield)

¹H NMR (CDCl₃, 400 MHz): δ = 7.38-7.33 (m, 5H), 7.25 (m, 1H), 7.17 (m, 3H), 5.47 (s, 2H), 2.37 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 150.3, 141.7, 141.6, 137.9, 129.1, 128.6, 128.4, 128.3, 128.2, 127.8, 125.6, 114.3, 21.6.

Data matched that reported in the literature.¹⁷

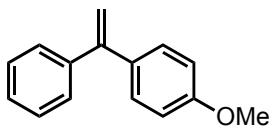


1-Methyl-4-(1-phenylvinyl)benzene (14a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.54 g, 70 % yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.38-7.33 (m, 5H), 7.27 (m, 2H), 7.17 (m, 2H), 5.46 (d, J = 1.3 Hz, 1H), 5.43 (d, J = 1.3 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 150.0, 141.8, 138.7, 137.6, 129.0, 128.4, 128.3, 128.2, 127.8, 113.8, 21.3.

Data matched that reported in the literature.¹⁵

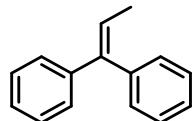


1-Methoxy-4-(1-phenylvinyl)benzene (16a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a white crystalline solid (0.64 g, 76% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.36-7.31 (m, 5H), 7.30 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.40 (d, J = 1.1 Hz, 1H), 5.36 (d, J = 1.1 Hz, 1H), 3.83 (s, 3H)

^{13}C NMR (CDCl_3 , 100 MHz): δ = 159.5, 149.6, 142.0, 134.1, 129.5, 128.5, 128.3, 127.8, 113.7, 113.1, 55.4.

Data matched that reported in the literature.¹⁰

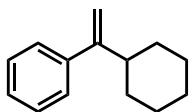


Prop-1-ene-1,1-diyldibenzene (20a): prepared with ethyltriphenylphosphonium bromide; flash chromatography eluting with 2% EtOAc/nhexane afforded the desired product as a white solid (0.58 g, 49% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.40 – 7.36 (m, 2H), 7.33 – 7.19 (m, 8H), 6.19 (q, J = 7.2 Hz, 1H), 1.77 (d, J = 7.2 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 143.1, 142.6, 140.2, 130.2, 128.3, 128.2, 127.3, 127.0, 126.9, 124.3, 124.2, 15.9.

Data matched that reported in the literature.¹⁷

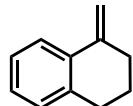


(1-Cyclohexylvinyl)benzene (21a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.47 g, 63% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.38-7.25 (m, 5H), 5.16 (s, 1H), 5.03 (s, 1H), 2.44 (m, 1H), 1.88-1.71 (m, 5H), 1.40-1.14 (m, 5H).

¹³C NMR (CDCl₃, 100 MHz): δ = 155.1, 143.1, 128.2, 127.1, 126.8, 110.5, 42.7, 32.8, 27.0, 26.6.

Data matched that reported in the literature.¹⁸

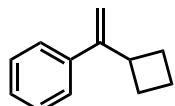


1-Methylene-1,2,3,4-tetrahydronaphthalene (22a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.17 g, 29% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.67-7.63 (m, 1H), 7.20-7.09 (m, 3H), 5.48 (m, 1H), 4.95 (m, 1H), 2.87-2.84 (m, 2H), 2.57-2.53 (m, 2H), 1.92-1.86 (m, 2H).

¹³C NMR (CDCl₃, 126 MHz): δ = 143.6, 137.5, 134.9, 129.3, 127.7, 126.0, 124.3, 108.0, 33.4, 30.6, 24.0.

Data matched that reported in the literature.¹⁹

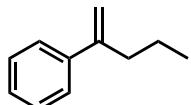


(1-Cyclobutylvinyl)benzene (23a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.49 g, 78% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.41-7.38 (m, 2H), 7.33 (m, 2H), 7.29-7.25 (m, 1H), 5.37 (m, 1H), 5.06 (m, 1H), 3.53-3.44 (m, 1H), 2.29-2.18 (m, 2H), 2.06-1.94 (m, 3H), 1.86-1.74 (m, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ = 152.1, 140.8, 128.3, 127.3, 126.2, 109.9, 39.7, 28.5, 17.9.

Data matched that reported in the literature.²⁰

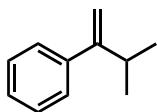


Pent-1-en-2-ylbenzene (25a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.28 g, 48% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.43 (d, *J* = 7.8 Hz, 2H), 7.37-7.33 (m, 2H), 7.30-7.26 (m, 1H), 5.30 (s, 1H), 5.08 (s, 1H), 2.53-2.49 (m, 2H), 1.55-1.46 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 148.6, 141.6, 128.3, 127.4, 126.3, 112.3, 37.6, 21.5, 13.9.

Data matched that reported in the literature.²¹

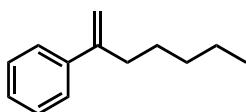


(3-Methylbut-1-en-2-yl)benzene (26a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.27 g, 46% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.39-7.26 (m, 5H), 5.17 (m, 1H), 5.06 (m, 1H), 2.86 (m, 1H), 1.13 (d, J = 6.8 Hz, 6H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 155.9, 143.0, 128.3, 127.2, 126.7, 110.1, 32.4, 22.2.

Data matched that reported in the literature.²⁰

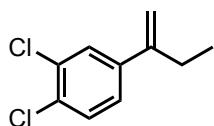


Hept-1-en-2-ylbenzene (27a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.34 g, 49% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.44-7.42 (m, 2H), 7.37-7.32 (m, 2H), 7.30-7.26 (m, 1H), 5.28 (d, J = 1.5 Hz, 1H), 5.08 (d, J = 1.4 Hz, 1H), 2.53-2.50 (m, 2H), 1.51-1.44 (m, 2H), 1.37-1.28 (m, 4H), 0.90 (m, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 148.9, 141.6, 128.4, 127.4, 126.2, 112.1, 35.5, 31.7, 28.1, 22.7, 14.2.

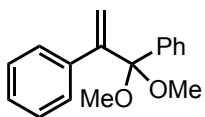
Data matched that reported in the literature.²²



4-(But-1-en-2-yl)-1,2-dichlorobenzene (28a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.44 g, 54% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.48 (d, J = 2.1 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.23 (dd, J = 8.4, 2.1 Hz, 1H), 5.28 (m, 1H), 5.11 (m, 1H), 2.46 (m, 2H), 1.09 (m, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 148.0, 141.7, 132.4, 131.2, 130.2, 128.1, 125.5, 112.7, 28.0, 12.9.



(1,1-Dimethoxyprop-2-ene-1,2-diyl)dibenzene (30a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.51 g, 50% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.53 – 7.51 (m, 2H), 7.30-7.20 (m, 3H), 7.17-7.10 (m, 5H), 6.02 (d, J = 1.9 Hz, 1H), 5.59 (d, J = 1.9 Hz, 1H), 3.16 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ = 148.4, 140.2, 139.6, 128.0, 127.9, 127.8, 127.7, 127.5, 127.2, 118.5, 102.4, 49.1.

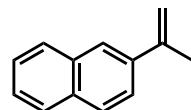


1-(But-1-en-2-yl)-2-fluorobenzene (31a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.17 g, 28% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.27-7.20 (m, 2H), 7.11-7.01 (m, 2H), 5.22 (m, 1H), 5.14 (m, 1H), 2.48 (q, J = 7.4 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 160.0 (d, J_{C-F} = 247.0 Hz), 146.8, 130.4 (d, J_{C-F} = 14.7 Hz), 130.1 (d, J_{C-F} = 3.9 Hz), 128.7 (d, J_{C-F} = 8.2 Hz), 124.0 (d, J_{C-F} = 3.3 Hz), 115.8 (d, J_{C-F} = 23.0 Hz), 114.5, 29.5, 12.8.

¹⁹F NMR (376 MHz, CDCl₃): δ = -115.5.

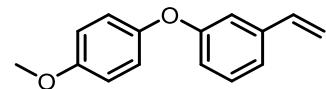


2-(Prop-1-en-2-yl)naphthalene (32a): prepared with methyltriphenylphosphonium bromide; flash chromatography eluting with 1% EtOAc/nhexane afforded the desired product as a white crystalline solid (0.53g, 79% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.88-7.80 (m, 4H), 7.72-7.69 (m, 1H), 7.51-7.47 (m, 2H), 5.57 (m, 1H), 5.23-5.22 (m, 1H), 2.30-2.29 (m, 3H).

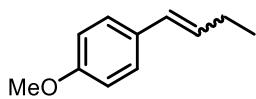
¹³C NMR (CDCl₃, 100 MHz): δ = 143.1, 138.4, 133.5, 132.9, 128.4, 127.8, 127.6, 126.2, 125.9, 124.4, 124.0, 113.2, 22.0.

Data matched that reported in the literature.²³



¹H NMR (CDCl₃, 400 MHz): δ = 7.25 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 7.00-6.98 (m, 3H), 6.90 – 6.88 (m, 2H), 6.84 (dd, J = 7.6, 2.4 Hz, 1H), 6.66 (dd, J = 17.6, 10.8 Hz, 1H), 5.72 (d, J = 17.6 Hz, 1H), 5.25 (d, J = 10.8 Hz, 1H), 3.82 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 158.6, 156.0, 150.2, 139.4, 136.5, 129.8, 120.9, 120.7, 117.1, 115.3, 115.0, 114.6, 55.8.



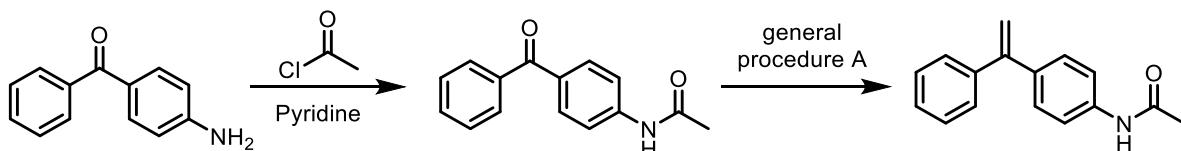
1-(But-1-en-1-yl)-4-methoxybenzene (38a): prepared with *n*-propyltriphenylphosphonium iodide; flash chromatography eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.12 g, 63% yield, 2.6:1 *E/Z* ratio).

¹H NMR (CDCl₃, 400 MHz): δ = 7.29 – 7.27 (m, 2H, *E* isomer), 7.23 – 7.21 (m, 2H, *Z* isomer), 6.88 – 6.86 (m, 2H, *Z* isomer), 6.85 – 6.83 (m, 2H, *E* isomer), 6.34 – 6.30 (m, 1H, both isomers), 6.13 (dt, *J* = 15.6, 6.4 Hz, 1H, *E* isomer), 5.57 (dt, *J* = 11.6, 7.2 Hz, 1H, *Z* isomer), 3.81 (s, 3H, *Z* isomer), 3.80 (s, 3H, *E* isomer), 2.38 – 2.30 (m, 2H, *Z* isomer), 2.25 – 2.17 (m, 2H, *E* isomer), 1.08 (m, 3H, both isomers).

¹³C NMR (CDCl₃, 100 MHz): δ = 158.7 (*E* isomer), 158.3 (*Z* isomer), 130.7 (*Z* isomer), 130.6 (*E* isomer), 130.0 (*Z* isomer), 128.2 (*E* isomer), 127.8 (*Z* isomer), 127.1 (*E* isomer), 114.0 (*E* isomer), 113.7 (*Z* isomer), 55.4 (both isomers), 26.2 (*E* isomer), 22.1 (*Z* isomer), 14.7 (*Z* isomer), 14.0 (*E* isomer).

Data matched that reported in the literature.²⁴

Synthesis of *N*-(4-(1-phenylvinyl)phenyl)acetamide (10a)



4-Aminobenzophenone (5.0 mmol 1.0 equiv.) was taken up in pyridine and the solution was cooled to 0 °C. Acetyl chloride (6.0 mmol, 1.1 equiv.) was added dropwise at 0 °C and the solution was stirred at room temperature for 5 hours. The reaction mixture was diluted with dichloromethane and washed with aqueous HCl solution (1M) and water. The organic layer was dried with MgSO₄ and the solvent removed under reduced pressure. The crude material was used directly in the next step without further purification.

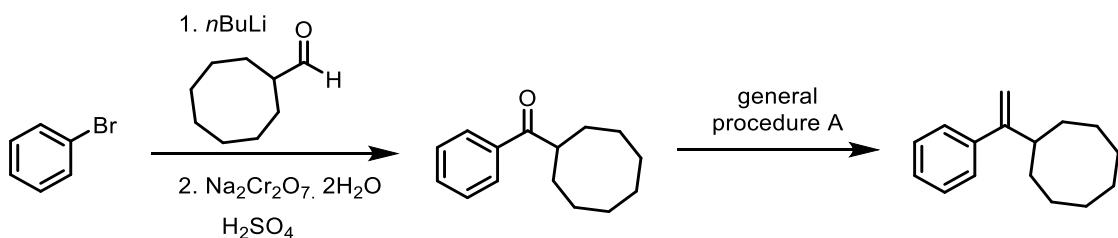
The crude reaction mixture was then subjected to general procedure A. The product was purified by flash chromatography on silica, eluting with 50% EtOAc/petroleum ether to give the desired product as an orange crystalline solid. (0.34 g, 28% yield over 2 steps)

¹H NMR (CDCl₃, 400 MHz): δ = 7.63 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 7H), 5.43 (s, 1H), 5.40 (s, 1H), 2.18 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 168.7, 149.5, 141.5, 137.58, 137.57, 128.9, 128.4, 128.3, 127.9, 119.7, 114.0, 24.7.

Data matched that reported in the literature.¹³

Synthesis of (1-phenylvinyl)cyclooctane (24a)



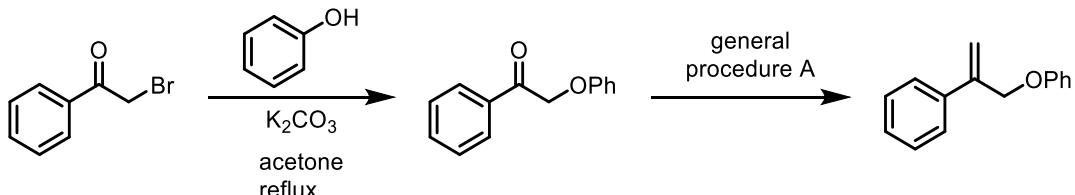
A solution of *n*BuLi in hexanes ($C = 1.6$ M, 12 mmol, 1.2 equiv.) was added dropwise, at -78°C , to a solution of bromobenzene (10 mmol, 1.0 equiv.) in THF (100 mL). The reaction mixture was stirred at -78°C for 1 hour. Cyclooctanecarbaldehyde (11 mmol, 1.1 equiv.) was added dropwise at -78°C and the reaction mixture was stirred at room temperature overnight. It was quenched with saturated NH_4Cl solution and extracted with EtOAc (3×40 mL). The combined organic layers were washed with brine ($3 \times$) and dried (MgSO_4). The solvent was removed under reduced pressure. The residue was then dissolved in DMSO and added to a stirred suspension of sodium dichromate dihydrate (5.28 mmol, 0.66 equiv.) in DMSO. The reaction mixture was cooled to 0°C and concentrated sulfuric acid (21.3 mmol, 2.66 equiv.) was added dropwise. After stirring at room temperature for 30 minutes the reaction mixture was poured onto ice and extracted with Et_2O (2×40 mL). The combined organic extracts were washed with saturated aqueous NaHCO_3 solution, dried with MgSO_4 and concentrated under reduced pressure.

The crude reaction mixture was subjected to general procedure A. Purification by flash chromatography on silica eluting with 1% EtOAc/nhexane afforded the desired product as a colourless liquid (0.33 g, 19% yield over 3 steps)

^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.38\text{-}7.24$ (m, 5H), 5.15 (s, 1H), 5.03 (s, 1H), 2.75-2.70 (m, 1H), 1.84-1.49 (m, 14H).

^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 156.3, 143.5, 128.3, 127.1, 126.8, 111.0, 42.4, 31.7, 27.3, 26.4, 25.7$.

Synthesis of (3-phenoxyprop-1-en-2-yl)benzene (29a)



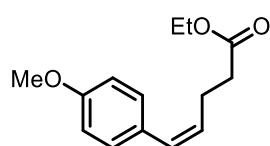
A solution of 2-bromoacetophenone (5.0 mmol, 1.0 equiv.) in acetone (50 mL) was added dropwise, at room temperature, to a suspension of phenol (5.5 mmol, 1.1 equiv.) and K_2CO_3 (7.6 mmol, 1.5 equiv.) in acetone. The reaction mixture was heated at reflux for 4 hours. The suspension was filtered through a plug of Celite with dichloromethane and the filtrate was concentrated under reduced pressure. Recrystallization from petroleum ether gave 2-phenoxy-1-phenylethan-1-one as a white solid (0.66 g, 62% yield).

2-Phenoxy-1-phenylethan-1-one was subjected to general procedure A. Purification by flash chromatography on silica, eluting with 10% EtOAc/nhexane gave the title compound as a colourless liquid (0.40 g, 61% yield).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.51$ (m, 2H), 7.41-7.30 (m, 5H), 7.02-6.98 (m, 3H), 5.65 (d, $J = 0.8$ Hz, 1H), 5.50 (d, $J = 1.1$ Hz, 1H), 4.93 (s, 2H).

^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 158.7, 143.1, 138.5, 129.6, 128.6, 128.1, 126.2, 121.1, 115.04, 114.96, 69.9$.

Synthesis of ethyl (Z)-5-(4-methoxyphenyl)pent-4-enoate (37a)



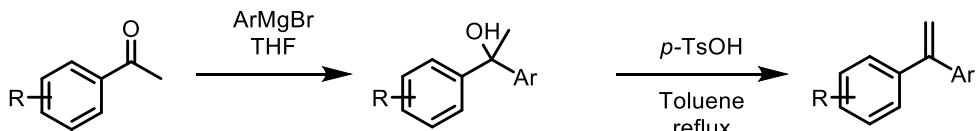
A solution of NaHMDS in toluene ($C = 0.6$ M, 1.1 mmol, 1.0 equiv.) was added dropwise, at $0\text{ }^\circ\text{C}$, to a solution of a (3-ethoxycarbonylpropyl)triphenylphosphonium bromide (1.1 mmol, 1.0 equiv.) in dry THF (5 mL). The reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 30 minutes. A solution of 4-methoxybenzaldehyde (1.1 mmol, 1.0 equiv.) in dry THF (3 mL) was added dropwise at $0\text{ }^\circ\text{C}$, and the reaction mixture was stirred at room temperature overnight. It was then diluted with brine and extracted with EtOAc (3×40 mL). The combined organic extracts were washed with brine (3 \times) and dried with MgSO_4 . The solvent removed under reduced pressure and the residue was purified by flash chromatography on silica eluting with 10% EtOAc/nhexane to yield the desired product as a colourless oil (0.052 g, 20% yield).

^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.23 - 7.21$ (m, 2H), 6.89 – 6.86 (m, 2H), 6.40 (d, $J = 11.6$ Hz, 1H), 5.52 (dt, $J = 11.6, 7.2$ Hz, 1H), 4.13 (q, $J = 7.2$ Hz, 2H), 3.81 (s, 3H), 2.68 – 2.62 (m, 2H), 2.45 – 2.41 (m, 2H), 1.24 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 173.2, 158.5, 130.1, 130.0, 129.6, 128.9, 113.8, 60.6, 55.5, 34.6, 34.4, 24.2, 22.9, 14.4$.

Data matched that reported in the literature.²⁵

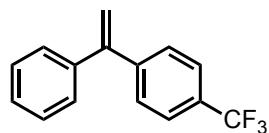
Method B



A suspension of Mg turnings (9.0 mmol, 1.5 equiv.) and several crystals of iodine in dry THF (10 mL) was stirred at room temperature for 10 minutes. Aryl bromide (9.0 mmol, 1.5 equiv.) was added dropwise at room temperature, and the reaction mixture was then stirred at $40\text{ }^\circ\text{C}$ for 1 hour. After cooling to $0\text{ }^\circ\text{C}$, acetophenone (6.0 mmol, 1.0 equiv.) was added dropwise, and the reaction mixture was stirred at room temperature overnight. It was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc (3×40 mL). The combined organic extracts were washed with brine (3 \times) and dried (MgSO_4). The solvent was removed by reduced pressure and the residue used directly without further purification.

The crude reaction mixture was taken up in toluene containing *p*-toluene sulfonic acid (0.8 mmol, 20 mol%). The solution was heated at reflux overnight under Dean-Stark conditions. It was cooled to room temperature, washed with brine and extracted with EtOAc (3×40 mL). The combined organic extracts were washed with brine (3 \times) and dried (MgSO_4). The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica eluting with 1-5% EtOAc/nhexane to yield the desired product.

Substrates synthesized using method B:



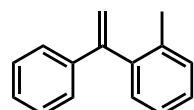
1-(1-Phenylvinyl)-4-(trifluoromethyl)benzene (5a): prepared using acetophenone and 4-trifluoromethylphenylmagnesium bromide; flash chromatography on silica eluting with 1% EtOAc/nhexane afforded the desired product as a light yellow solid (1.33 g, 67% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.61 (m, 2H), 7.46 (m, 2H), 7.39-7.31 (m, 5H), 5.58 (d, J = 0.8 Hz, 1H), 5.53 (d, J = 0.8 Hz, 1H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 149.1, 145.2, 140.8, 129.9 (q, J = 32.4 Hz), 128.7, 128.5, 128.3, 128.2, 125.3 (q, J = 3.8 Hz), 124.4 (q, J = 272.7 Hz), 116.1.

^{19}F NMR (376 MHz, CDCl_3): δ = -62.5.

Data matched that reported in the literature.¹³

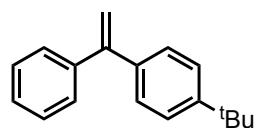


1-Methyl-2-(1-phenylvinyl)benzene (12a): prepared using 2'-methylacetophenone and phenylmagnesium bromide; flash chromatography on silica eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (0.63 g, 81% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.34-7.21 (m, 9H), 5.80 (d, J = 1.1 Hz, 1H), 5.23 (d, J = 1.1 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 149.6, 141.7, 140.7, 136.3, 130.2, 130.1, 128.5, 127.69, 127.65, 126.6, 125.8, 115.0, 20.3.

Data matched that reported in the literature.¹³

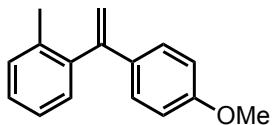


1-(tert-Butyl)-4-(1-phenylvinyl)benzene (15a): prepared using acetophenone and 4-*tert*-butylphenylmagnesium bromide; flash chromatography on silica eluting with 1% EtOAc/nhexane afforded the desired product as a colourless oil (0.09 g, 5% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.38-7.26 (m, 9H), 5.46 (s, 1H), 5.41 (s, 1H), 1.34 (s, 9H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 150.9, 149.9, 141.8, 138.5, 128.5, 128.2, 128.0, 127.7, 125.2, 113.9, 34.7, 31.5.

Data matched that reported in the literature.¹⁵

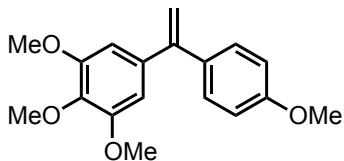


1-(1-(4-Methoxyphenyl)vinyl)-2-methylbenzene (17a): prepared using 2'-methylacetophenone and 4-methoxyphenylmagnesium bromide; vacuum distillation (135-145 °C, ± 1 mbar) afforded the desired product as a colourless liquid (0.75 g, 84% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.28-7.17 (m, 6H), 6.83-6.80 (m, 2H), 5.68 (d, *J* = 1.4 Hz, 1H), 5.08 (d, *J* = 1.4 Hz, 1H), 3.80 (s, 3H), 2.06 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 159.3, 148.9, 142.0, 136.3, 133.3, 130.15, 130.05, 127.8, 127.5, 125.8, 113.8, 113.0, 55.4, 20.2.

Data matched that reported in the literature.¹⁷



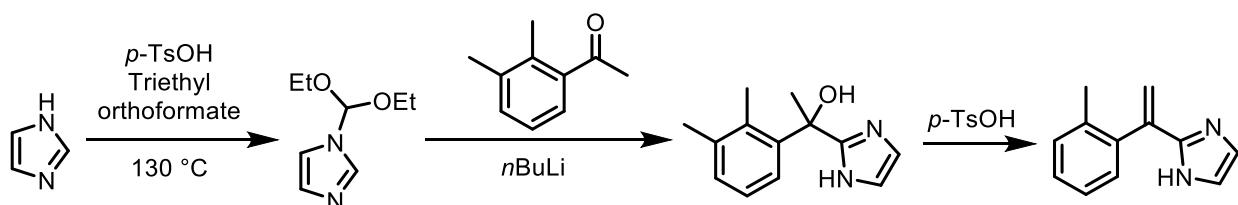
1,2,3-Trimethoxy-5-(1-(4-methoxyphenyl)vinyl)benzene (19a): prepared using 3',4',5'-trimethoxy acetophenone and 4-methoxyphenylmagnesium bromide; flash chromatography on silica eluting with 50% EtOAc/nhexane afforded the desired product as a pale yellow oil (0.76 g, 53% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.32-7.28 (m, 2H), 6.89-6.85 (m, 2H), 6.56 (s, 2H), 5.37 (d, *J* = 1.2 Hz, 1H), 5.32 (d, *J* = 1.2 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.81 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ = 159.5, 152.9, 149.6, 137.8, 137.7, 133.8, 129.5, 113.6, 112.6, 105.7, 61.1, 56.2, 55.4.

Data matched that reported in the literature.²⁶

Synthesis of 2-(1-(2,3-dimethylphenyl)vinyl)-1*H*-imidazole (18a)²⁷



Imidazole (10 mmol, 1.0 equiv.) and *p*-toluene sulfonic acid (0.3 mmol, 3.0 mol%) were dissolved in triethyl orthoformate (40 mmol, 4.0 equiv.) and the reaction mixture was stirred at 130 °C until all methanol was distilled. The remaining triethyl orthoformate was removed by vacuum distillation (75 -79 °C, ± 4 mbar) affording the product as a clear oil. (1.45 g, 42% yield.).

1-(Diethoxymethyl)-1*H*-imidazole (5.0 mmol, 1.0 equiv.) was dissolved in dry THF and cooled to -78 °C. A solution of *n*BuLi in hexanes (C = 1.6 M, 5 mmol, 1.0 equiv.) was added dropwise, and the reaction mixture was stirred at -78 °C for 3 hours. 1-(2,3-Dimethylphenyl)ethanone (5.5 mmol, 1.1 equiv.) was added dropwise at -78 °C and the

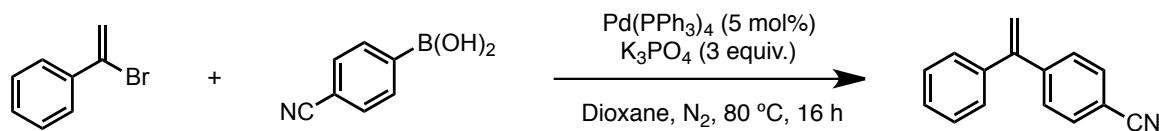
solution was stirred at -78°C for 10 minutes, and at room temperature overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl solution and extracted with EtOAc ($3 \times 40 \text{ mL}$). The combined organic layers were washed with brine ($3 \times$) and dried (MgSO_4). The solvent was removed under reduced pressure and the residue was taken directly to the next step without further purification.

The crude reaction mixture was then subjected to general procedure B. Recrystallization from $\text{CH}_2\text{Cl}_2/n\text{hexane}$ yielded the desired product as a white crystalline solid (0.10 g, 10% yield over 2 steps).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.20-7.10 (m, 3H), 7.03 (s, 2H), 6.31 (d, J = 1.3 Hz, 1H), 5.23 (d, J = 1.2 Hz, 1H), 2.31 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 147.2, 138.8, 138.7, 137.5, 135.0, 130.0, 127.7, 125.8, 122.9, 116.4, 20.5, 16.5.

Synthesis of 4-(1-phenylvinyl)benzonitrile (8a)



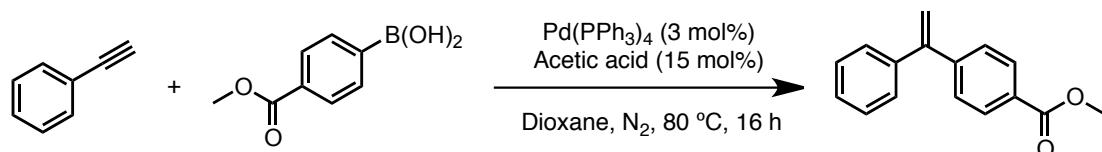
A Schlenk tube was charged with 4-cyanophenylboronic acid (5.2 mmol, 1.3 equiv), K_3PO_4 (12 mol, 3.0 equiv.) and $\text{Pd}(\text{PPh}_3)_4$ (0.2 mmol, 5.0 mol%). The flask was evacuated and backfilled with nitrogen 3 times. 1,4-Dioxane (50 mL), and α -bromo styrene (4.0 mmol, 1.0 equiv.) were added, and the reaction mixture was stirred at 80°C overnight. It was cooled to room temperature and filtered through a plug of Celite with dichloromethane. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica, eluting with 8% $\text{EtOAc}/n\text{hexane}$ to give the title product as a dark orange oil (0.43 g, 53% yield.)

^1H NMR (CDCl_3 , 400 MHz): δ = 7.63 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.38-7.27 (m, 5H), 5.59 (d, J = 0.7 Hz, 1H), 5.55 (d, J = 0.7 Hz, 1H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 148.8, 146.2, 140.3, 132.2, 129.0, 128.6, 128.4, 128.3, 119.0, 116.9, 111.5.

Data matched that reported in the literature.¹⁷

Synthesis of methyl 4-(1-phenylvinyl)benzoate (9a)²⁸



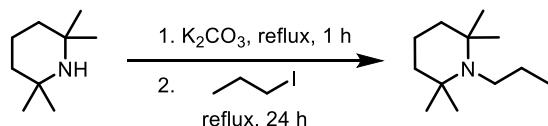
$\text{Pd}(\text{PPh}_3)_4$ (0.12 mmol, 3.0 mol%) and (4-(methoxycarbonyl)phenyl)boronic acid (6.0 mmol, 1.5 equiv.) were added an oven dried Schlenk tube. The flask was evacuated and backfilled with nitrogen 3 times and left under positive nitrogen pressure. Dry, degassed dioxane (10 mL) was added, followed by phenylacetylene (4.0 mmol, 1.0 equiv.) and acetic acid (0.6 mmol, 15 mol%). The reaction mixture was stirred at 80°C for 16 hours under positive nitrogen pressure. It was cooled to room temperature, diluted with Et_2O and filtered through a plug of Celite with Et_2O . The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica eluting with 100% dichloromethane to give the desired product as a crystalline white solid. (0.56 g, 59% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 8.01 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.37-7.30 (m, 5H), 5.55 (d, *J* = 1.0 Hz, 1H), 5.54 (d, *J* = 1.0 Hz, 1H), 3.93 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 167.0, 149.4, 146.2, 140.9, 129.6, 129.4, 128.4, 128.35, 128.33, 128.1, 116.0, 52.2.

Data matched that reported in the literature.¹⁸

Synthesis of 2,2,6,6-tetramethyl-1-propylpiperidine (47)



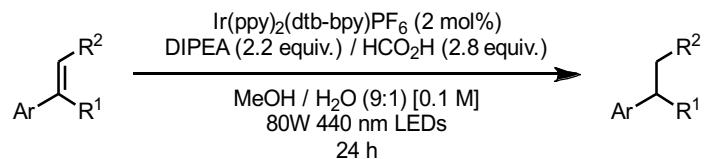
Synthesised according to a modified literature procedure.²⁹ A mixture of 2,2,6,6-tetramethylpiperidine (8.4 mL, 50 mmol) and K₂CO₃ (8.64 g, 63 mmol) in CH₃CN (10 mL) was heated at reflux for 1 hour. Iodopropane (4.9 mL, 50 mmol) was added in one portion, and the reaction mixture heated at reflux for 24 hours. It was cooled to room temperature and filtered through a plug of Celite with Et₂O. The reaction mixture was extracted with 1M aqueous HCl solution (3×) and washed with Et₂O (3×). The acidic extracts were neutralised with solid NaHCO₃ and extracted with Et₂O and dried (MgSO₄). The solvent was removed under reduced pressure to give the title compound as a colourless liquid (1.6 g, 17% yield).

¹H NMR (CDCl₃, 500 MHz): δ = 2.30 – 2.27 (m, 2H), 1.52 – 1.50 (m, 2H), 1.41 – 1.37 (m, 6H), 1.01 (s, 12H), 0.78 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ = 54.5, 47.3, 41.3, 28.9, 27.6, 17.9, 11.6.

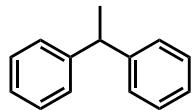
HRMS (ESI) *m/z* calc. for C₁₂H₂₆N [M+H]⁺ 184.2065 found 184.1890.

General procedure for the photoredox catalyzed hydrogenation reaction



Alkene (0.1 mmol, 1.0 equiv.) and photocatalyst (0.002 mmol, 2 mol%) were placed in a pressure relief sample vial and taken up in 9:1 methanol / water (1 mL). The reaction mixture was sparged with N₂ for 1 minute. *N,N*-Diisopropylethylamine (0.22 mmol, 2.2 equiv.) and formic acid (0.28 mmol, 2.8 equiv.) were added via an air tight syringe under a positive pressure of nitrogen, and the solution was sparged with N₂ for 30 seconds. The cap was wrapped in parafilm and the reaction mixture was stirred for 24 hours at room temperature, whilst being irradiated with 80W blue LEDs. The reaction mixture was diluted with CH₂Cl₂ and washed with saturated aqueous NaHCO₃ solution (1 × 10 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL) and the combined organic extracts were dried with MgSO₄. The solvent was removed under reduced pressure and the residue purified by preparative TLC eluting with 1 - 5% EtOAc/nhexane to yield the desired product.

Product Characterization Data

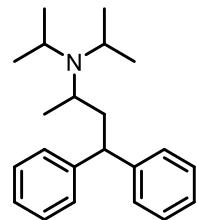


Ethane-1,1-diylbenzene (2): preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (15 mg, 80% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.33-7.18 (m, 10H), 4.18 (q, J = 7.2 Hz, 1H), 1.67 (d, J = 7.2 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 146.5, 128.5, 127.8, 126.1, 44.9, 22.0.

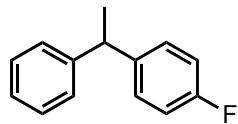
Data matched that reported in the literature.³⁰



***N,N*-Diisopropyl-4,4-diphenylbutan-2-amine (3)**

^1H NMR (400 MHz, CDCl_3): δ = 7.32 – 7.11 (m, 10H), 4.15 (dd, J = 9.0, 6.0 Hz, 1H), 3.21 – 3.07 (m, 2H), 2.78 (dq, J = 12.9, 6.5 Hz, 1H), 2.12 – 1.93 (m, 2H), 1.05 (d, J = 6.6 Hz, 3H), 0.95 (d, J = 6.6 Hz, 6H), 0.92 (d, J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ = 146.90, 144.68, 128.49, 128.46, 128.37, 127.99, 126.02, 125.88, 48.38, 47.17, 44.43, 42.78, 29.85, 24.41, 22.38, 21.03.



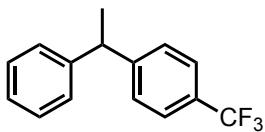
1-Fluoro-4-(1-phenylethyl)benzene (4): preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (14 mg, 68% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.32-7.28 (m, 2H), 7.22-7.16 (m, 5H), 7.00-6.94 (m, 2H), 4.15 (q, J = 7.2 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 161.5 (d, $J_{\text{C-F}}$ = 243.8 Hz), 146.30, 142.2 (d, $J_{\text{C-F}}$ = 3.2 Hz), 129.1 (d, $J_{\text{C-F}}$ = 7.8 Hz), 128.6, 127.7, 126.3, 115.2 (d, $J_{\text{C-F}}$ = 21.1 Hz), 44.2, 22.2.

^{19}F NMR (376 MHz, CDCl_3): δ = -117.5.

Data matched that reported in the literature.³⁰



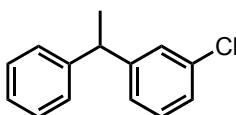
1-(1-Phenylethyl)-4-(trifluoromethyl)benzene (5): run at 0.3 mmol scale; preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (56 mg, 74% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.56 (d, J = 8.2 Hz, 2H), 7.36-7.31 (m, 4H), 7.26-7.22 (m, 3H), 4.23 (q, J = 7.2 Hz, 1H), 1.68 (d, J = 7.2 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 150.6, 145.4, 128.7, 128.1, 127.7, 126.6, 125.5 (q, $J_{\text{C-F}}$ = 3.4 Hz), 124.4 (q, $J_{\text{C-F}}$ = 270.3 Hz), 44.8, 21.8.

^{19}F NMR (376 MHz, CDCl_3): δ = -62.4.

Data matched that reported in the literature.³¹

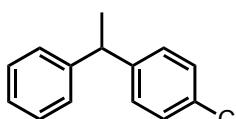


1-Chloro-3-(1-phenylethyl)benzene (6): run at 0.3 mmol scale; preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (53 mg, 81% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.36-7.30 (m, 2H), 7.27-7.18 (m, 6H), 7.14-7.12 (m, 1H), 4.16 (q, J = 7.2 Hz, 1H), 1.66 (d, J = 7.2 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 148.6, 145.6, 134.3, 129.7, 128.6, 127.9, 127.7, 126.4, 126.3, 126.0, 44.7, 21.8.

Data matched that reported in the literature.³²

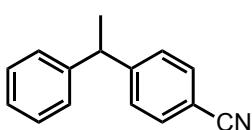


1-Chloro-4-(1-phenylethyl)benzene (7): preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (16 mg, 75% yield).

^1H NMR (CDCl_3 , 600 MHz): δ = 7.31-7.28 (m, 2H), 7.26-7.24 (m, 2H), 7.21-7.19 (m, 3H), 7.16-7.14 (m, 2H), 4.13 (q, J = 7.2 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H).

^{13}C NMR (CDCl_3 , 151 MHz): δ = 145.9, 145.0, 131.9, 129.1, 128.6, 128.6, 127.7, 126.4, 44.3, 21.9.

Data matched that reported in the literature.³³

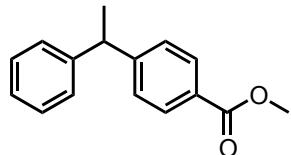


4-(1-Phenylethyl)benzonitrile (8): preparative TLC eluting with 15% EtOAc/nhexane afforded the desired product as a colourless liquid (9 mg, 42% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.33-7.29 (m, 4H), 7.23-7.17 (m, 3H), 4.20 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 152.0, 144.8, 132.4, 128.8, 128.6, 127.7, 126.8, 119.2, 110.0, 45.0, 21.6.

Data matched that reported in the literature.³⁴

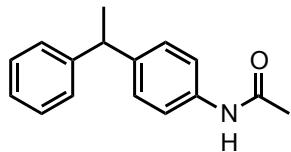


Methyl 4-(1-phenylethyl)benzoate (9): preparative TLC eluting with 50% EtOAc/nhexane afforded the desired product as a colourless liquid (14 mg, 58% yield)

¹H NMR (CDCl₃, 600 MHz): δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.31-7.28 (m, 4H), 7.21-7.19 (m, 3H), 4.21 (q, *J* = 7.2 Hz, 1H), 3.89 (s, 3H), 1.66 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 151 MHz): δ = 167.2, 151.9, 145.6, 129.9, 128.6, 128.2, 127.8, 127.7, 126.5, 52.1, 45.0, 21.7.

Data matched that reported in the literature.³⁵

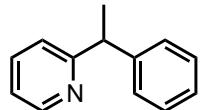


N-(4-(1-Phenylethyl)phenyl)acetamide (10): preparative TLC eluting with 30% DCM/nhexane afforded the desired product as a pale orange solid (17 mg, 69% yield)

¹H NMR (CDCl₃, 600 MHz): δ = 7.39 (d, *J* = 8.5 Hz, 2H), 7.29-7.26 (m, 2H), 7.20-7.19 (m, 4H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 1H), 2.15 (s, 3H), 1.61 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 151 MHz): δ = 168.3, 146.4, 142.6, 135.9, 128.5, 128.2, 127.7, 126.2, 120.2, 44.4, 24.7, 22.0.

Data matched that reported in the literature.³⁶

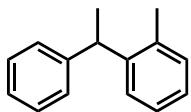


2-(1-Phenylethyl)pyridine (11): preparative TLC eluting with 20% EtOAc/nhexane afforded the desired product as a colourless liquid (13 mg, 68% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 8.57-8.55 (m, 1H), 7.56 (td, *J* = 7.7, 1.9 Hz, 1H), 7.31-7.29 (m, 4H), 7.23-7.17 (m, 1H), 7.13-7.07 (m, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 1.71 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 165.2, 149.3, 145.2, 136.5, 128.6, 127.8, 126.4, 122.3, 121.3, 47.5, 20.9.

Data matched that reported in the literature.³⁷

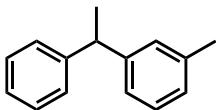


1-Methyl-2-(1-phenylethyl)benzene (12): preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (43 mg, 72% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.36-7.19 (m, 9H), 4.39 (q, *J* = 7.2 Hz, 1H), 2.30 (s, 3H), 1.68 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 146.3, 144.0, 136.2, 130.5, 128.4, 127.8, 126.8, 126.2, 126.1, 125.9, 41.1, 22.3.

Data matched that reported in the literature.³²

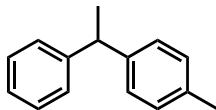


1-Methyl-3-(1-phenylethyl)benzene (13): run at 0.3 mmol scale; preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (53 mg, 90% yield)

¹H NMR (CDCl₃, 400 MHz): δ = 7.37-7.23 (m, 6H), 7.11-7.06 (m, 3H), 4.18 (q, *J* = 7.2 Hz, 1H), 2.38 (s, 3H), 1.70 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 146.6, 146.4, 138.0, 128.6, 128.5, 128.4, 127.7, 126.9, 126.1, 124.7, 44.9, 22.0, 21.6.

Data matched that reported in the literature.³⁸

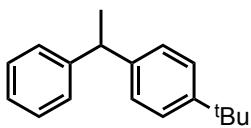


1-Methyl-4-(1-phenylethyl)benzene (14): run at 0.3 mmol scale; preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (46 mg, 79% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.36-7.14 (m, 8H), 4.18 (q, *J* = 7.2 Hz, 1H), 2.37 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 146.7, 143.5, 135.6, 129.2, 128.5, 127.7, 127.6, 126.1, 44.5, 22.1, 21.1.

Data matched that reported in the literature.³²

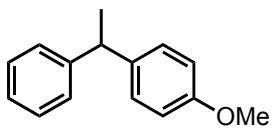


11-(tert-Butyl)-4-(1-phenylethyl)benzene (15): preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (15 mg, 63% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.32-7.23 (m, 6H), 7.21-7.15 (m, 3H), 4.13 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H), 1.31 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ = 148.8, 146.7, 143.4, 128.5, 127.8, 127.3, 126.1, 125.4, 44.5, 34.5, 31.5, 22.1.

Data matched that reported in the literature.³⁴

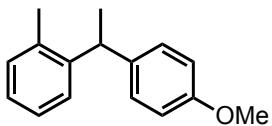


1-Methoxy-4-(1-phenylethyl)benzene (16): preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (18 mg, 67% yield)

¹H NMR (CDCl₃, 400 MHz): δ = 7.33-7.29 (m, 2H), 7.26-7.21 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 1H), 3.80 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 157.9, 146.9, 138.7, 128.6, 128.5, 127.6, 126.0, 113.8, 55.3, 44.0, 22.2, 19.9.

Data matched that reported in the literature.³⁰

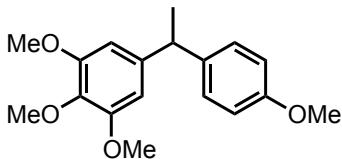


1-(1-(4-Methoxyphenyl)ethyl)-2-methylbenzene (17): run at 0.3 mmol scale; preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (53 mg, 79% yield)

¹H NMR (CDCl₃, 400 MHz): δ = 7.31-7.29 (m, 1H), 7.25-7.20 (m, 1H), 7.17-7.15 (m, 2H), 7.12-7.10 (m, 2H), 6.86-6.83 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 2.28 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 157.8, 144.4, 138.5, 136.1, 130.5, 128.7 (2C), 126.6, 126.1, 113.8, 55.3, 40.2, 22.4, 19.8.

Data matched that reported in the literature.³⁹

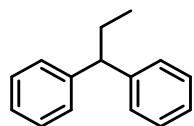


1,2,3-Trimethoxy-5-(1-(4-methoxyphenyl)ethyl)benzene (19): preparative TLC eluting with 50% EtOAc/nhexane afforded the desired product as a colourless liquid (14 mg, 47% yield).

¹H NMR (CDCl₃, 600 MHz): δ = 7.14 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.42 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 1H), 3.81 (s, 9H), 3.79 (s, 3H), 1.60 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (CDCl₃, 151 MHz): δ = 158.0, 153.2, 142.6, 138.5, 136.3, 128.5, 113.8, 104.7, 61.0, 56.2, 55.4, 44.3, 22.4.

Data matched that reported in the literature.⁴⁰

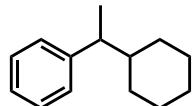


Propane-1,1-diylidibenzene (20): preparative TLC eluting with 8% toluene/nhexane afforded the desired product as a colourless oil (17 mg, 84% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.30 – 7.23 (m, 8H), 7.19 – 7.15 (m, 2H), 3.79 (t, J = 7.6 Hz, 1H), 2.08 (pent, J = 7.6 Hz, 2H), 0.90 (t, J = 7.6 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 145.3, 128.5, 128.1, 126.1, 53.4, 28.7, 12.9.

Data matched that reported in the literature.⁴¹

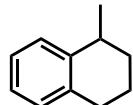


(1-Cyclohexylethyl)benzene (21): run at 0.3 mmol scale; preparative TLC eluting with 1% EtOAc/nhexane afforded the desired product as a colourless oil (46 mg, 80% yield).

¹H NMR (CDCl₃, 600 MHz): δ = 7.31-7.28 (m, 2H), 7.20-7.16 (m, 3H), 2.46 (m, 1H), 1.91-1.89 (m, 1H), 1.78-1.75 (m, 1H), 1.66-1.61 (m, 2H), 1.47-1.39 (m, 2H), 1.25 (d, J = 7.0 Hz, 3H), 1.16-1.10 (m, 2H), 0.99-0.93 (m, 1H), 0.86-0.80 (m, 1H).

¹³C NMR (CDCl₃, 151 MHz): δ = 147.2, 128.1, 127.8, 125.8, 46.1, 44.4, 31.6, 30.8, 26.7, 19.0.

Data matched that reported in the literature.⁴²

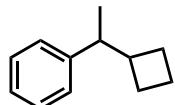


1-Methylene-1,2,3,4-tetrahydronaphthalene (22): run at 0.3 mmol scale; preparative TLC eluting with 1% EtOAc/nhexane afforded the desired product as a colourless liquid (27 mg, 62% yield).

¹H NMR (CDCl₃, 600 MHz): δ = 7.22-7.06 (m, 4H), 2.94-2.90 (m, 1H), 2.82-2.73 (m, 2H), 1.96-1.83 (m, 2H), 1.77-1.71 (m, 1H), 1.57-1.55 (m, 1H), 1.31 (d, J = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 151 MHz): δ = 142.3, 137.0, 129.1, 128.2, 125.7, 125.5, 32.6, 31.6, 30.1, 23.0, 20.6.

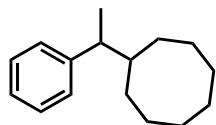
Data matched that reported in the literature.⁴³



(1-Cyclobutylethyl)benzene (23): run at 0.3 mmol scale; preparative TLC eluting with 1% EtOAc/nhexane afforded the desired product as a colourless liquid (40 mg, 82% yield)

¹H NMR (CDCl₃, 400 MHz): δ = 7.33-7.28 (m, 2H), 7.21-7.17 (m, 3H), 2.63 (dq, J = 10.0, 6.9 Hz, 1H), 2.48-2.42 (m, 1H), 2.17-2.11 (m, 1H), 1.83-1.74 (m, 4H), 1.67-1.60 (m, 1H), 1.17 (d, J = 6.9 Hz, 3H).

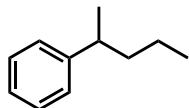
¹³C NMR (CDCl₃, 100 MHz): δ = 146.2, 128.3, 127.3, 125.9, 46.9, 42.9, 27.7, 27.3, 19.2, 17.6.



(1-Phenylethyl)cyclooctane (24): run at 0.3 mmol scale; preparative TLC eluting with 1% EtOAc/nhexane afforded the desired product as a colourless liquid (54 mg, 84% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.32-7.28 (m, 2H), 7.21-7.17 (m, 3H), 2.60-2.53 (m, 1H), 1.79-1.15 (m, 15H), overlapping with 1.25 (d, J = 7.0 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 147.6, 128.2, 127.8, 125.7, 46.3, 43.3, 31.1, 29.5, 27.3, 27.3, 26.7, 26.2, 25.7, 19.1.

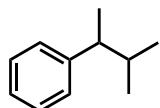


Pentan-2-ylbenzene (25)

^1H NMR (CDCl_3 , 400 MHz): δ = 7.32-7.29 (m, 2H), 7.21-7.18 (m, 3H), 2.76-2.67 (m, 1H), 1.64-1.50 (m, 2H), 1.32-1.20 (m, 5H), 0.89 (t, J = 7.3 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 148.1, 128.4, 127.1, 125.9, 40.9, 39.8, 22.4, 21.0, 14.3.

Data matched that reported in the literature.⁴⁴

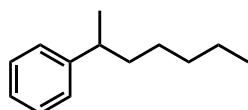


(3-Methylbutan-2-yl)benzene (26)

^1H NMR (CDCl_3 , 400 MHz): δ = 7.32-7.27 (m, 2H), 7.22-7.17 (m, 3H), 2.48-2.41 (m, 1H), 1.85-1.73 (m, 1H), 1.26 (d, J = 7.0 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H), 0.78 (d, J = 6.7 Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 147.2, 128.2, 127.8, 125.8, 47.0, 34.6, 21.3, 20.3, 18.9.

Data matched that reported in the literature.⁴³

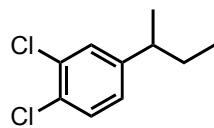


Heptan-2-ylbenzene (27): preparative TLC eluting with 1% EtOAc/nhexane afforded the desired product as a colourless liquid (16 mg, 90% yield).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.36-7.30 (m, 2H), 7.22-7.18 (m, 3H), 2.74-2.66 (m, 1H), 1.65-1.52 (m, 2H), 1.31-1.23 (m, 9H), 0.90-0.86 (m, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ = 148.1, 148.1, 128.4, 128.4, 127.1, 127.1, 125.9, 125.9, 40.1, 40.1, 38.6, 38.6, 32.1, 32.1, 27.6, 27.6, 22.8, 22.8, 22.5, 22.5, 14.2, 14.2.

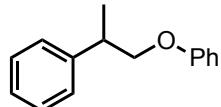
Data matched that reported in the literature.⁴⁵



4-(sec-Butyl)-1,2-dichlorobenzene (28): preparative TLC eluting with 1% EtOAc/nhexane afforded the desired product as a colourless liquid (43 mg, 71% yield).

¹H NMR (CDCl₃, 600 MHz): δ = 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 1H), 7.01 (dd, *J* = 8.2, 1.9 Hz, 1H), 2.59-2.54 (m, 1H), 1.62-1.51 (m, 2H), 1.21 (d, *J* = 7.1 Hz, 3H), 0.83-0.81 (m, 3H).

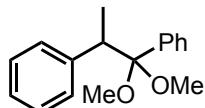
¹³C NMR (CDCl₃, 151 MHz): δ = 148.1, 132.3, 130.3, 129.6, 129.2, 126.7, 41.2, 31.1, 21.8, 12.2.



(1-Phenoxypropan-2-yl)benzene (29): preparative TLC eluting with 10% CH₂Cl₂/nhexane afforded the desired product as a colourless liquid (14 mg, 67% yield)

¹H NMR (CDCl₃, 600 MHz): δ = 7.35-7.25 (m, 7H), 6.95-6.89 (m, 3H), 4.11-4.09 (m, 1H), 3.98-3.96 (m, 1H), 3.28-3.22 (m, 1H), 1.43 (d, *J* = 7.0 Hz, 3H).

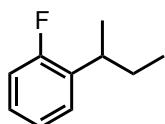
¹³C NMR (CDCl₃, 151 MHz): δ = 159.1, 143.8, 129.5, 128.6, 127.6, 126.7, 120.8, 114.8, 73.5, 39.7, 18.3.



(1,1-Dimethoxypropane-1,2-diyl)dibenzene (30): preparative TLC eluting with 10% dichloromethane/nhexane afforded the desired product as a white solid (20 mg, 76% yield).

¹H NMR (CDCl₃, 600 MHz): δ = 7.26-7.10 (m, 6H), 6.97-6.96 (m, 2H), 6.82-6.80 (m, 2H), 3.53 (q, *J* = 7.3 Hz, 1H), 3.42 (s, 3H), 3.10 (s, 3H), 1.16 (d, *J* = 7.3 Hz, 3H).

¹³C NMR (CDCl₃, 151 MHz): δ = 141.5, 137.1, 130.1, 129.0, 127.7, 127.1, 126.9, 126.3, 105.7, 49.6, 48.5, 44.5, 15.3.

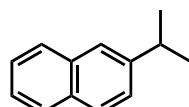


1-(sec-Butyl)-2-fluorobenzene (31)

¹H NMR (CDCl₃, 400 MHz): δ = 7.23-6.98 (m, 4H), 3.04-2.95 (m, 1H), 1.69-1.57 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (CDCl₃, 126 MHz): δ = 161.0 (d, *J* = 244.2 Hz), 134.2 (d, *J* = 14.7 Hz), 128.1 (d, *J* = 5.5 Hz), 127.2 (d, *J* = 8.3 Hz), 124.1 (d, *J* = 3.5 Hz), 115.3 (d, *J* = 23.1 Hz), 34.3 (d, *J* = 1.6 Hz), 30.1, 20.7, 12.3.

¹⁹F NMR (376 MHz, CDCl₃): δ = -119.2.

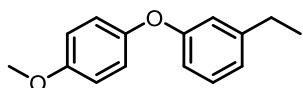


2-Isopropylnaphthalene (32): preparative TLC eluting with 1% EtOAc/nhexane afforded the desired product as a colourless liquid (6 mg, 37% yield)

¹H NMR (CDCl₃, 600 MHz): δ = 7.81–1.78 (m, 3H), 7.65 (s, 1H), 7.46–7.39 (m, 3H), 3.08 (septet, *J* = 6.9 Hz, 1H), 1.35 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (CDCl₃, 151 MHz): δ = 146.5, 133.8, 132.2, 128.0, 127.7, 127.7, 125.9, 125.9, 125.2, 124.2, 34.4, 24.1.

Data matched that reported in the literature.⁴⁶

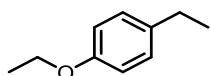


3-Ethyl-4'-methoxy-1,1'-biphenyl (33): preparative TLC eluting with 10% EtOAc/nhexane afforded the desired product as a colourless liquid (14 mg, 67% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.22 – 7.18 (m, 1H), 6.99 – 6.97 (m, 2H), 6.89 – 6.87 (m, 3H), 6.81 (m, 1H), 6.75 – 6.73 (m, 1H), 3.81 (s, 3H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 158.6, 155.9, 150.4, 146.4, 129.5, 129.4, 122.2, 120.9, 117.3, 114.9, 55.8, 28.9, 15.6.

Data matched that reported in the literature.⁴⁷

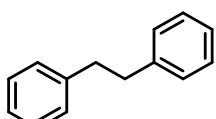


1-Ethoxy-4-ethylbenzene (34)

¹H NMR (CDCl₃, 400 MHz): δ = 7.10 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 157.1, 136.4, 128.8, 114.5, 63.6, 28.1, 16.1, 15.1.

Data matched that reported in the literature.⁴⁸

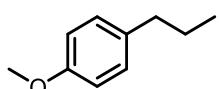


1,2-Diphenylethane (35): preparative TLC eluting with 8% EtOAc/nhexane afforded the desired product as a colourless solid (17 mg, 93% yield).

¹H NMR (400 MHz, CDCl₃): δ = 7.33 – 7.27 (m, 4H), 7.24 – 7.17 (m, 6H), 2.94 (s, 4H).

¹³C NMR (100 MHz, CDCl₃): δ = 141.91, 128.58, 128.47, 126.05, 38.10.

Data matched that reported in the literature.⁴⁹

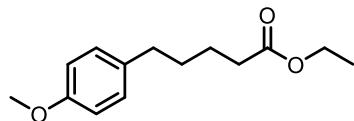


1-Methoxy-4-propylbenzene (36): preparative TLC eluting with 3% EtOAc/nhexane afforded the desired product as a colourless liquid (11 mg 70% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.10 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.61 (sept. *J* = 7.6 Hz, 2H), 0.93 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 157.7, 135.0, 129.4, 113.7, 55.4, 37.3, 25.0, 13.9.

Data matched that reported in the literature.⁵⁰

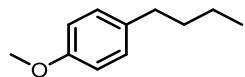


Ethyl 5-(4-methoxyphenyl)pentanoate (37): preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (20 mg, 87% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.11 – 7.08 (m, 2H), 6.85 – 6.80 (m, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.59 – 2.55 (m, 2H), 2.33 – 2.29 (m, 2H), 1.65 – 1.60 (m, 5H), 1.25 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 173.8, 157.8, 134.4, 129.4, 113.8, 60.4, 55.4, 34.8, 34.3, 31.3, 24.7, 14.4.

Data matched that reported in the literature.⁵¹



1-Butyl-4-methoxybenzene (38): preparative TLC eluting with 5% EtOAc/nhexane afforded the desired product as a colourless liquid (12 mg, 75% yield).

¹H NMR (CDCl₃, 400 MHz): δ = 7.10 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 2.57 – 2.54 (m, 2H), 1.61 – 1.53 (m, 2H), 1.39 – 1.30 (m, 2H), 0.94 – 0.91 (m, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ = 157.7, 135.2, 129.4, 113.7, 55.4, 34.9, 34.1, 22.5, 14.1.

Data matched that reported in the literature.⁵²

Derivatisation of 1-(2-(1-(2,3-dimethylphenyl)ethyl)-1*H*-imidazol-1-yl)ethanone (18)

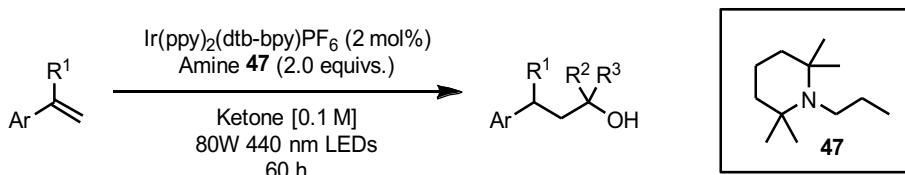


Olefin **18a** was subjected to the general conditions for the photoredox-catalysed hydrogenation reaction. After work up, the crude reaction mixture was dissolved in dichloromethane (3 mL) and treated with acetic anhydride (3 mmol, 10 equiv.), dropwise at room temperature. The reaction mixture was stirred at room temperature overnight. It was quenched with saturated aqueous NaHCO₃ solution (2 mL) and extracted with dichloromethane (2 × 2 mL). The combined organic extracts were dried with MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by preparative TLC eluting with 50% EtOAc/nhexane to yield the desired product as a white crystalline solid (8 mg, 38% yield over 2 steps).

¹H NMR (CDCl₃, 400 MHz): δ = 7.23 (d, *J* = 1.8 Hz, 1H), 7.04 (d, *J* = 1.8 Hz, 1H), 6.99–6.90 (m, 2H), 6.59–6.57 (m, 1H), 5.08 (q, *J* = 7.1 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H), 1.61 (d, *J* = 7.1 Hz, 3H).

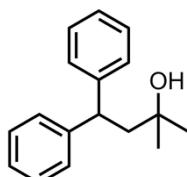
¹³C NMR (CDCl₃, 100 MHz): δ = 158.0, 153.1, 142.6, 138.4, 136.2, 128.5, 113.8, 104.6, 60.9, 56.2, 55.3, 44.3, 22.3.

General procedure for the photoredox catalyzed hydrofunctionalization with ketones



Alkene (0.1 mmol, 1.0 equiv.), photocatalyst (0.002 mmol, 2 mol%) and amine **47** (0.2 mmol, 2.0 equiv.) were placed in a pressure relief sample vial and taken up in acetone (1 mL). The reaction mixture was sparged with N₂ for 1 minute. The cap was wrapped in parafilm and the reaction mixture was stirred for 60 hours at room temperature, whilst being irradiated with 80W blue LEDs. The solvent was removed under reduced pressure and the residue purified by preparative TLC eluting with 20% EtOAc/nhexane to yield the desired product.

Product Characterization Data

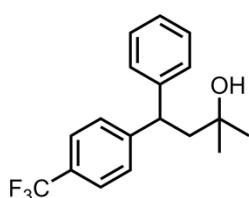


2-Methyl-4,4-diphenylbutan-2-ol (48): preparative TLC eluting with 20% EtOAc/nhexane afforded the desired product as a colourless liquid (10 mg, 42% yield).

¹H NMR (CDCl₃, 500 MHz): δ = 7.33 – 7.26 (m, 8H), 7.17 – 7.15 (m, 2H), 4.22 (t, *J* = 7.0 Hz, 1H), 2.38 (d, *J* = 7.0 Hz, 2H), 1.18 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ = 145.8, 128.8, 127.9, 126.4, 71.5, 48.9, 47.7, 30.4.

HRMS (APCI/ESI) *m/z* calc. for C₁₇H₁₉⁺ [M-OH]⁺ 223.1481 found 223.1472

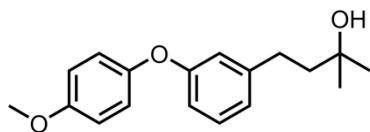


2-Methyl-4-phenyl-4-(4-(trifluoromethyl)phenyl)butan-2-ol (49): preparative TLC eluting with 20% EtOAc/nhexane afforded the desired product as a colourless liquid (13 mg, 41% yield).

¹H NMR (CDCl₃, 500 MHz): δ = 7.53 – 7.52 (m, 2H), 7.43 – 7.41 (m, 2H), 7.30 – 7.29 (m, 4H), 7.19 – 7.18 (m, 1H), 4.30 (t, J = 7.0 Hz, 1H), 2.43 – 2.32 (m, 2H), 1.18 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ = 150.2, 144.9, 129.0, 128.7 (q, J_{C-F} = 32.1 Hz), 128.2, 127.9, 126.8, 125.7 (q, J_{C-F} = 3.8 Hz), 123.0, 71.4, 48.8, 47.6, 30.4, 30.3.

HRMS (APCI/ESI) *m/z* calc. for C₁₈H₁₈F₃⁺ [M-OH]⁺ 291.1355 found 291.1341.

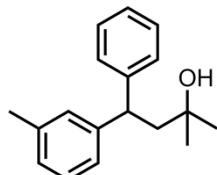


4-(3-(4-Methoxyphenoxy)phenyl)-2-methylbutan-2-ol (50): preparative TLC eluting with 20% EtOAc/nhexane afforded the desired product as a colourless liquid (15 mg, 52% yield).

¹H NMR (CDCl₃, 500 MHz): δ = 7.21 – 7.18 (m, 1H), 6.98 – 6.96 (m, 2H), 6.89 – 6.87 (m, 2H), 6.80 (s, 1H), 6.76 – 6.74 (m, 1H), 3.81 (s, 3H), 2.68 – 2.64 (m, 2H), 1.78 – 1.75 (m, 2H), 1.27 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): δ = 158.7, 155.9, 150.3, 144.6, 129.6, 122.6, 120.9, 117.7, 115.1, 115.0, 71.0, 55.8, 45.6, 30.8, 29.5.

HRMS (APCI/ESI) *m/z* calc. for C₁₈H₂₂O₃ [M]⁺ 286.1569 found 286.1567.

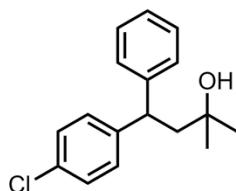


2-Methyl-4-phenyl-4-(*m*-tolyl)butan-2-ol (51): preparative TLC eluting with 20% EtOAc/nhexane afforded the desired product as a colourless liquid (13 mg, 52% yield).

¹H NMR (CDCl₃, 500 MHz): δ = 7.33 – 7.26 (m, 4H), 7.19 – 7.12 (m, 4H), 6.98 – 6.97 (m, 2H), 4.18 (t, J = 7.0 Hz, 1H), 2.37 (d, J = 7.0 Hz, 2H), 2.31 (s, 3H), 1.19 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ = 145.9, 145.7, 138.4, 128.8, 128.8, 128.7, 127.9, 127.2, 126.4, 124.9, 71.6, 48.9, 47.7, 30.3, 30.2, 21.7.

HRMS (APCI/ESI) *m/z* calc. for C₁₈H₂₁⁺ [M-OH]⁺ 237.1638 found 237.1634.

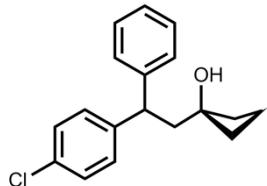


2-Methyl-4-phenyl-4-(*m*-tolyl)butan-2-ol (52): preparative TLC eluting with 20% EtOAc/nhexane afforded the desired product as a colourless liquid (13 mg, 54% yield).

¹H NMR (CDCl₃, 500 MHz): δ = 7.30 – 7.26 (m, 8H), 7.21 – 7.19 (m, 1H), 4.23 (t, *J* = 7.0 Hz, 1H), 2.39 – 2.33 (m, 2H), 1.19 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ = 145.4, 144.5, 132.1, 129.2, 128.9, 128.9, 127.8, 126.6, 71.4, 48.9, 47.1, 30.4, 30.3.

HRMS (APCI/ESI) *m/z* calc. for C₁₇H₁₈Cl⁺ [M-OH]⁺ 257.1092 found 257.1089



1-(2-(4-Chlorophenyl)-2-phenylethyl)cyclobutan-1-ol (53): preparative TLC eluting with 20% EtOAc/nhexane afforded the desired product as a colourless liquid (15 mg, 51% yield).

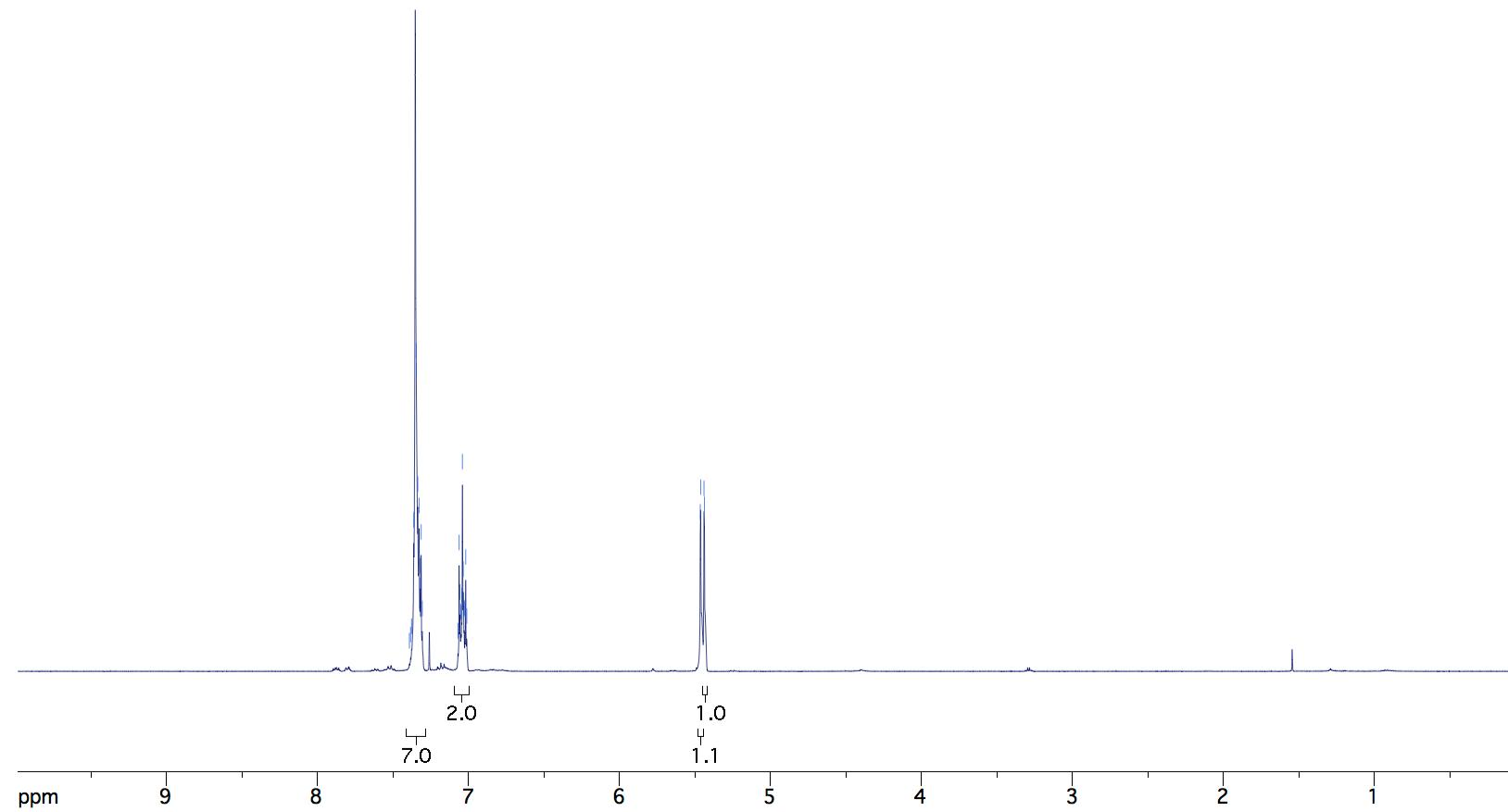
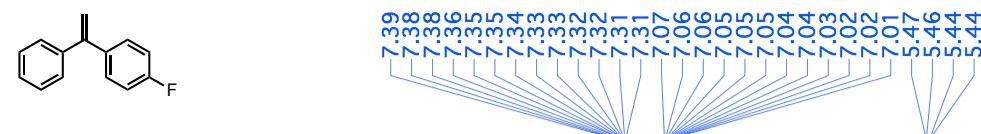
¹H NMR (CDCl₃, 500 MHz): δ = 7.28 – 7.16 (m, 9H, overlapping with CDCl₃), 4.08 (t, *J* = 8.0 Hz, 1H), 3.14 – 3.13 (m, 1H), 3.03 – 2.87 (m, 2H), 2.49 – 2.41 (m, 1H), 2.21 – 2.06 (m, 2H), 1.61 – 1.62 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz): δ = 143.8, 143.6, 142.9, 142.7, 132.3, 132.3, 129.4, 129.2, 128.8, 128.8, 127.9, 127.8, 126.8, 126.8, 58.7, 48.2, 48.1, 44.7, 35.6, 17.4, 17.4.

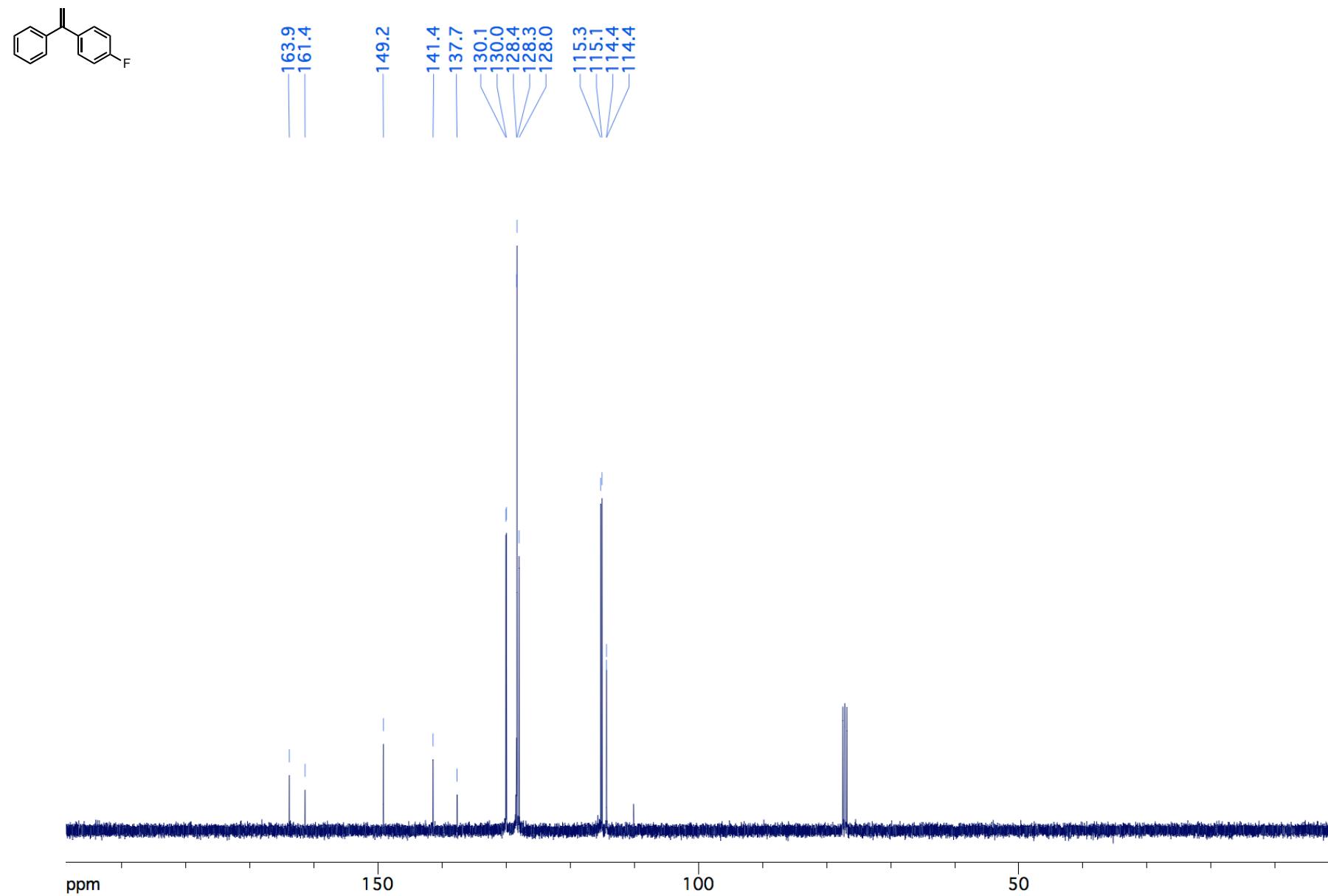
HRMS (APCI/ESI) *m/z* calc. for C₁₈H₁₈ClO [M-H]⁺ 285.1046 found 285.1039.

^1H , ^{13}C and ^{19}F NMR Spectra

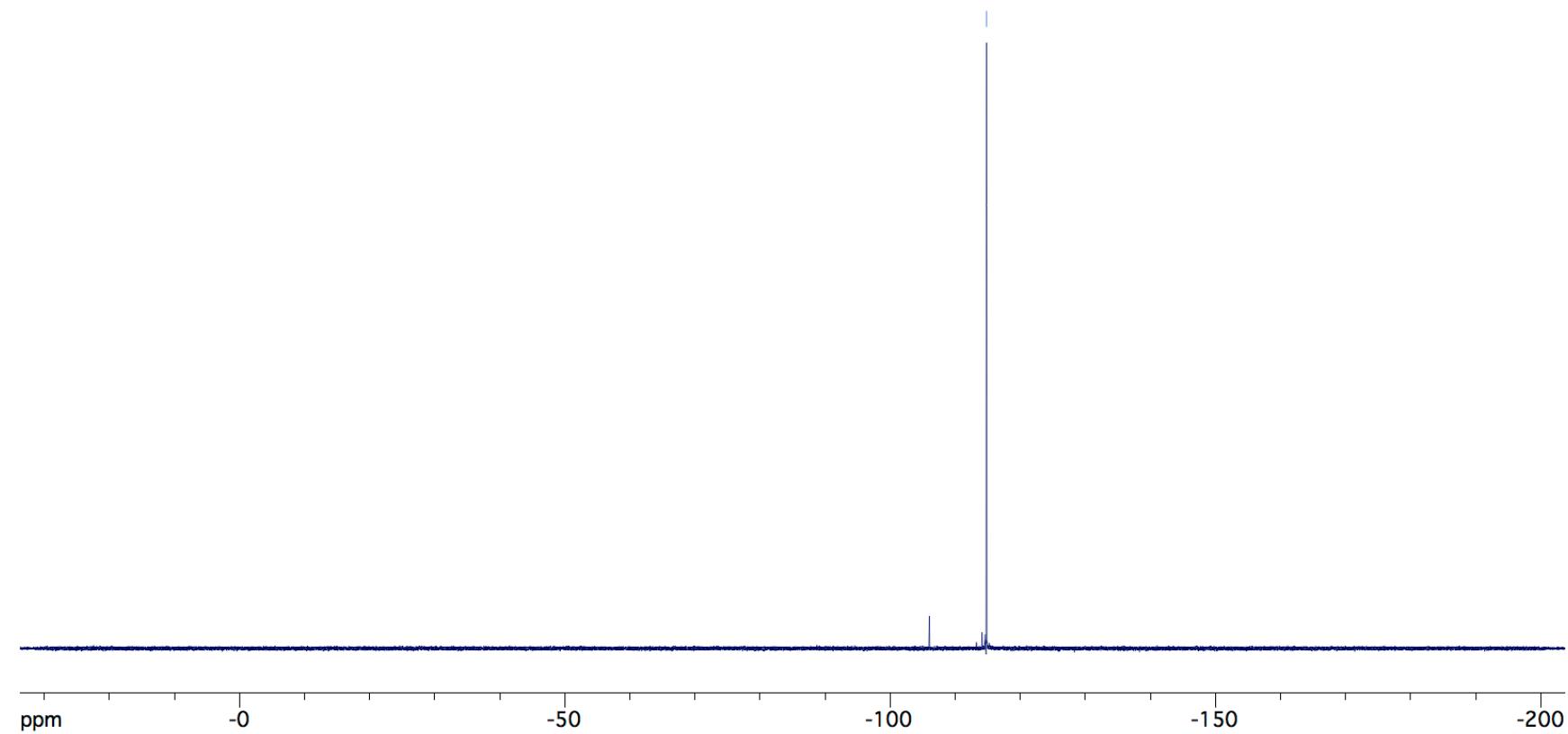
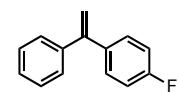
1-Fluoro-4-(1-phenylvinyl)benzene (4a) ^1H NMR (CDCl_3 , 400 MHz)



1-Fluoro-4-(1-phenylvinyl)benzene (4a) ^{13}C NMR (CDCl_3 , 100 MHz)

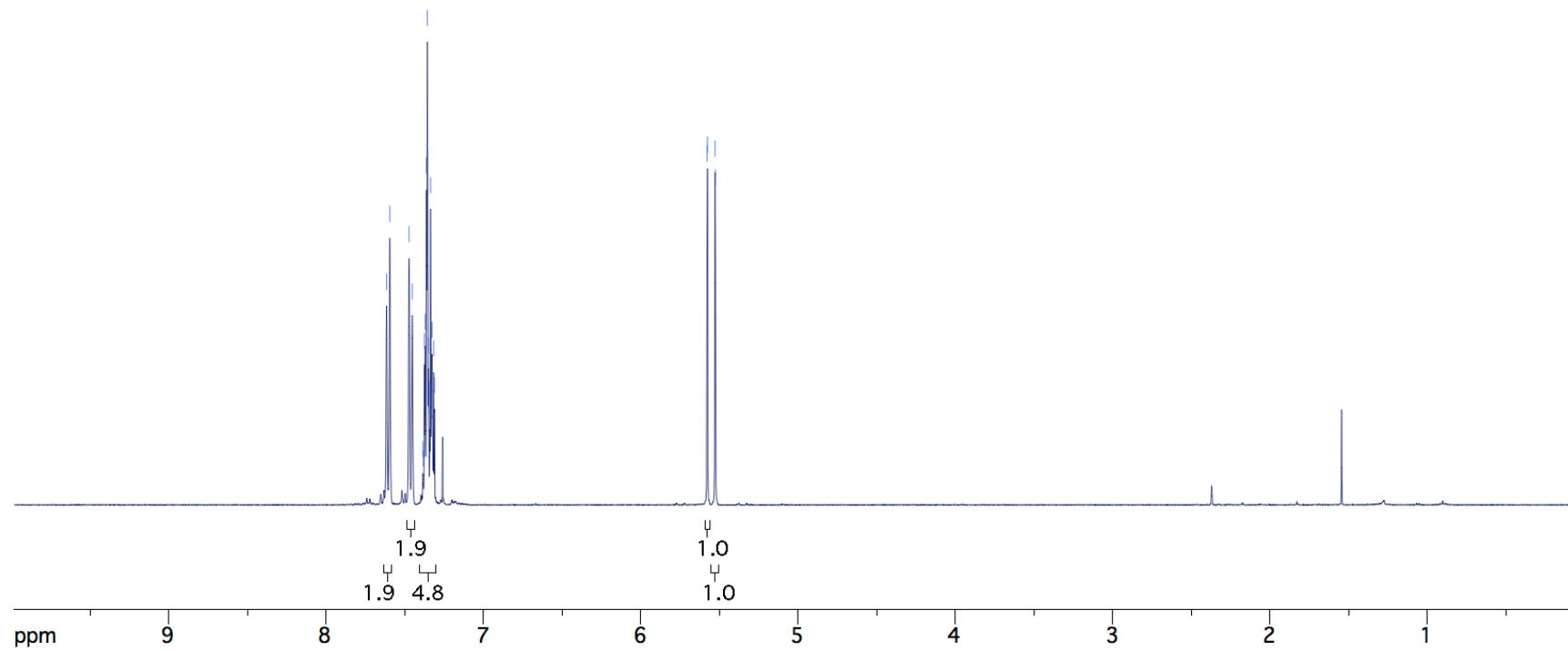
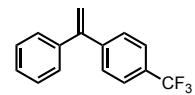


1-Fluoro-4-(1-phenylvinyl)benzene (4a) ^{19}F -NMR (CDCl_3 , 376 MHz)



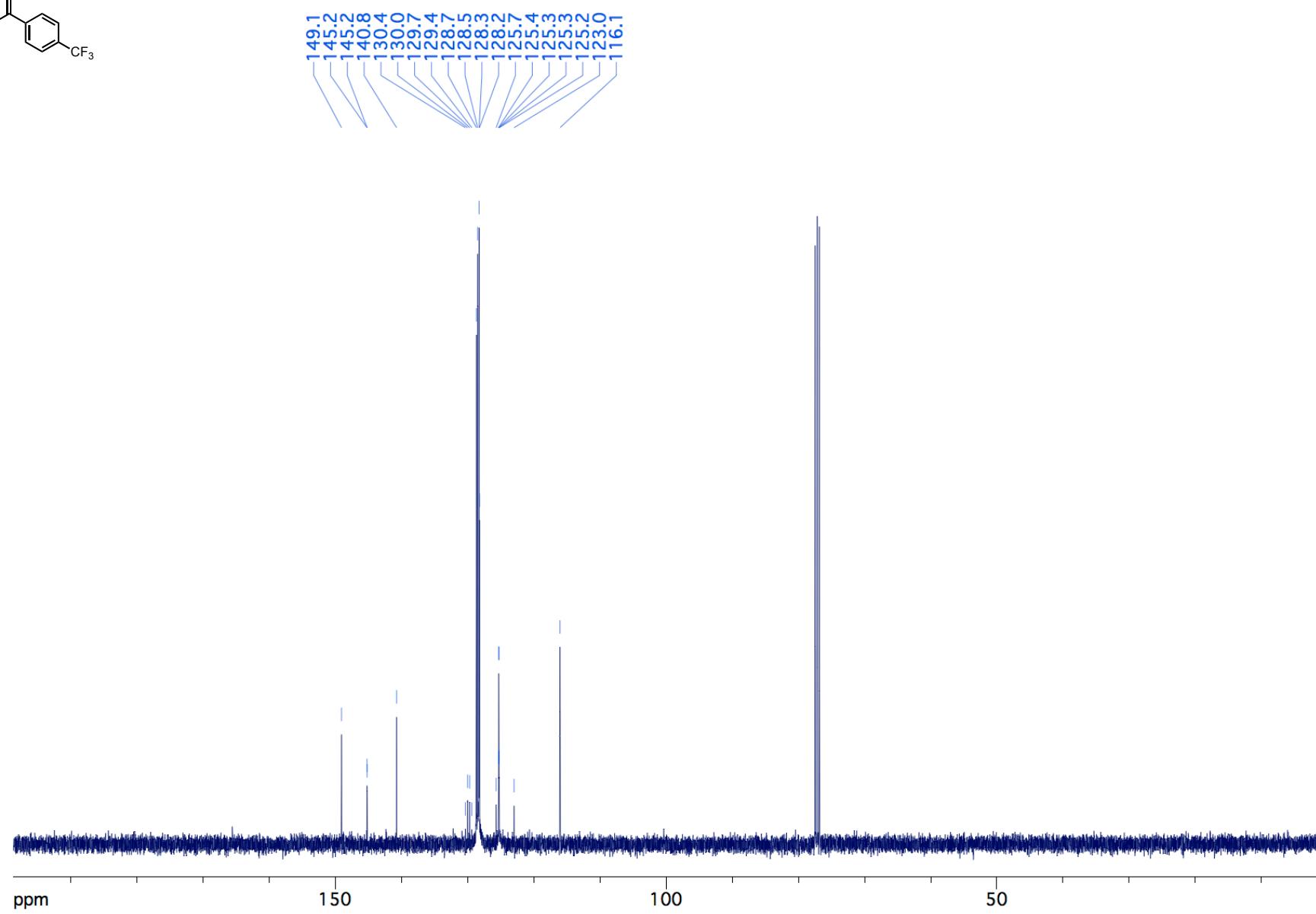
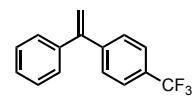
1-(1-Phenylvinyl)-4-(trifluoromethyl)benzene (5a)

¹H NMR (CDCl₃, 400 MHz)



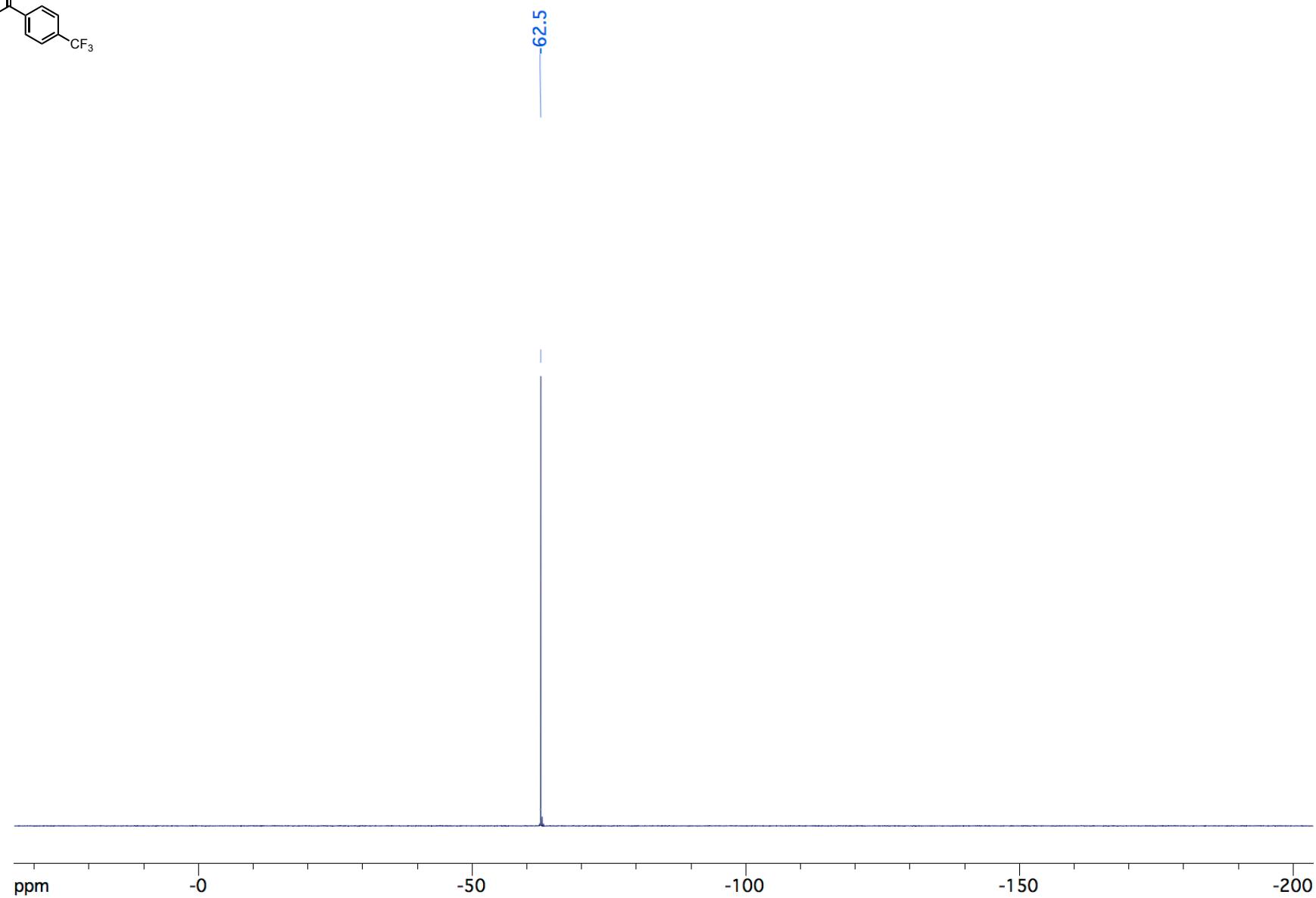
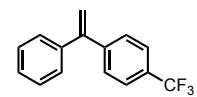
1-(1-Phenylvinyl)-4-(trifluoromethyl)benzene (5a)

¹³C NMR (CDCl₃, 100 MHz)

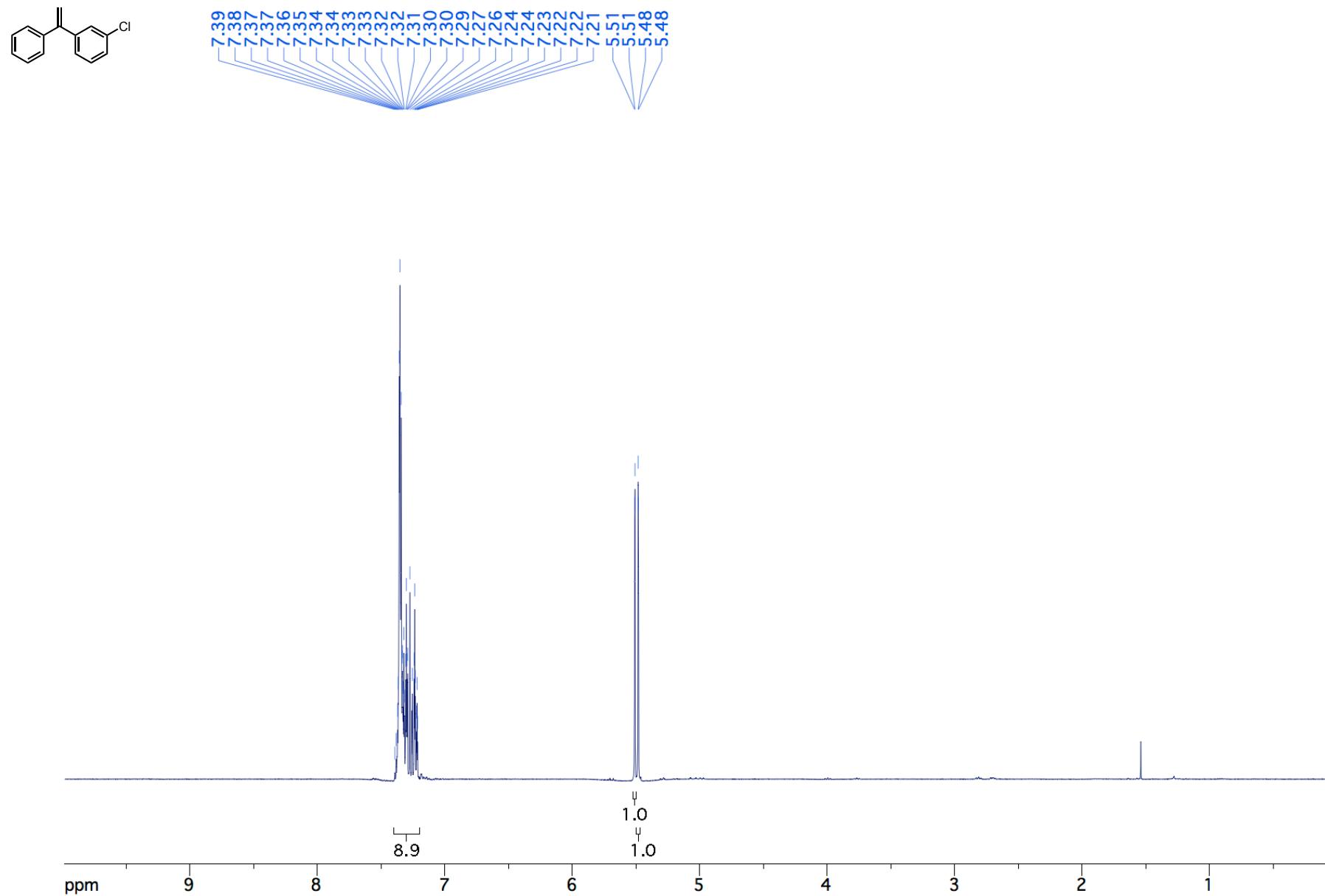


1-(1-Phenylvinyl)-4-(trifluoromethyl)benzene (5a)

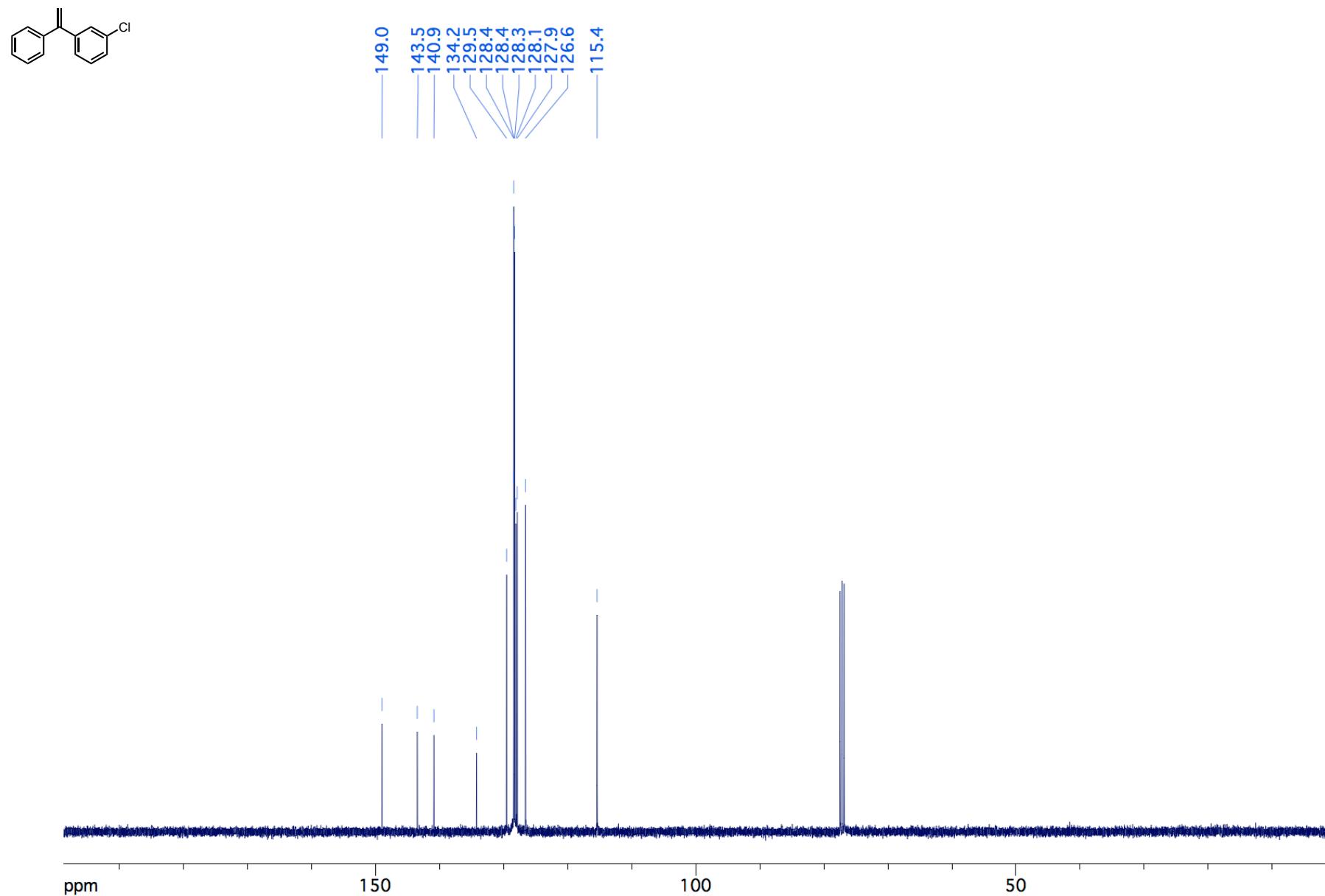
^{19}F -NMR (CDCl_3 , 376 MHz)



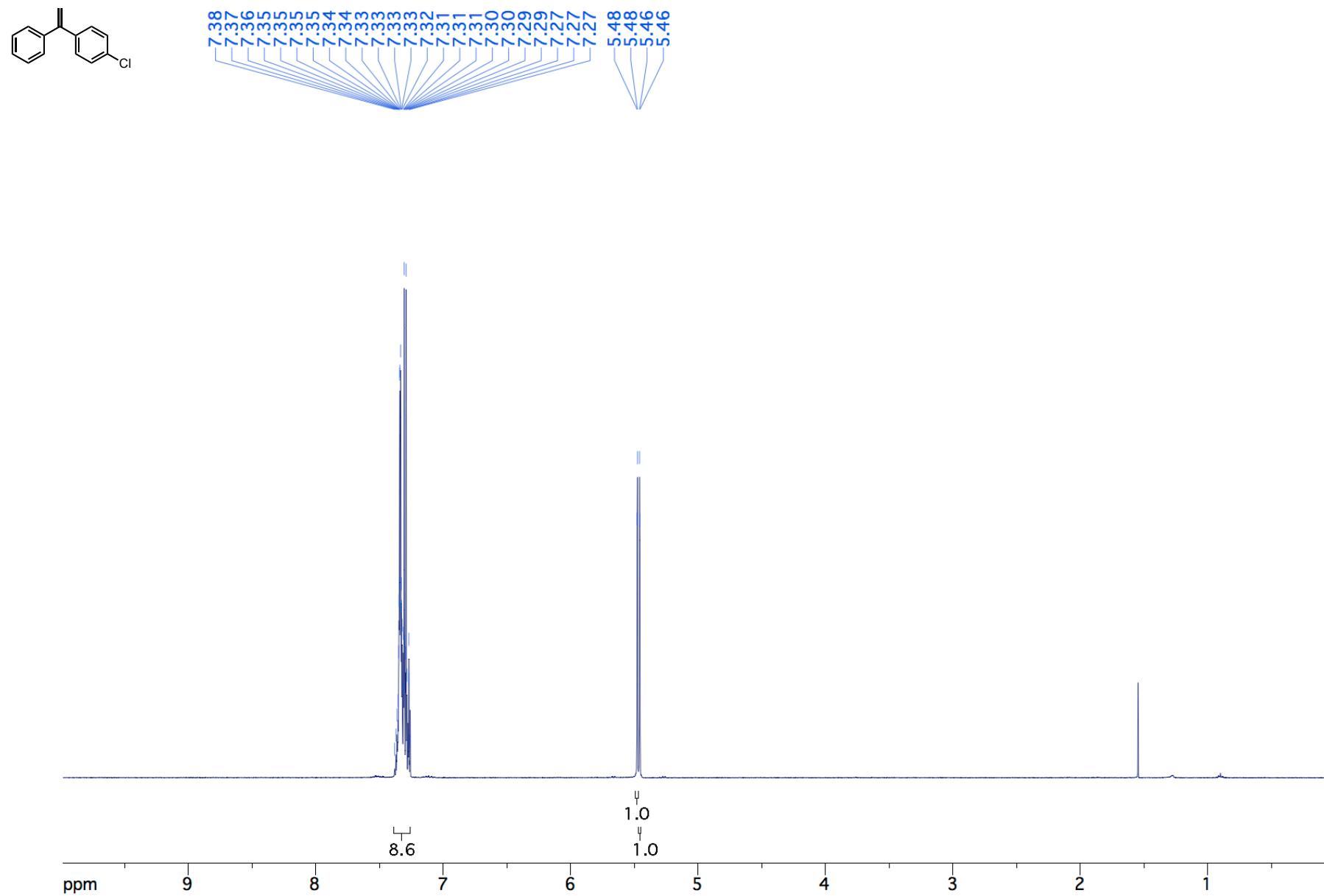
1-Chloro-3-(1-phenylvinyl)benzene (6a) ^1H NMR (CDCl_3 , 400 MHz)



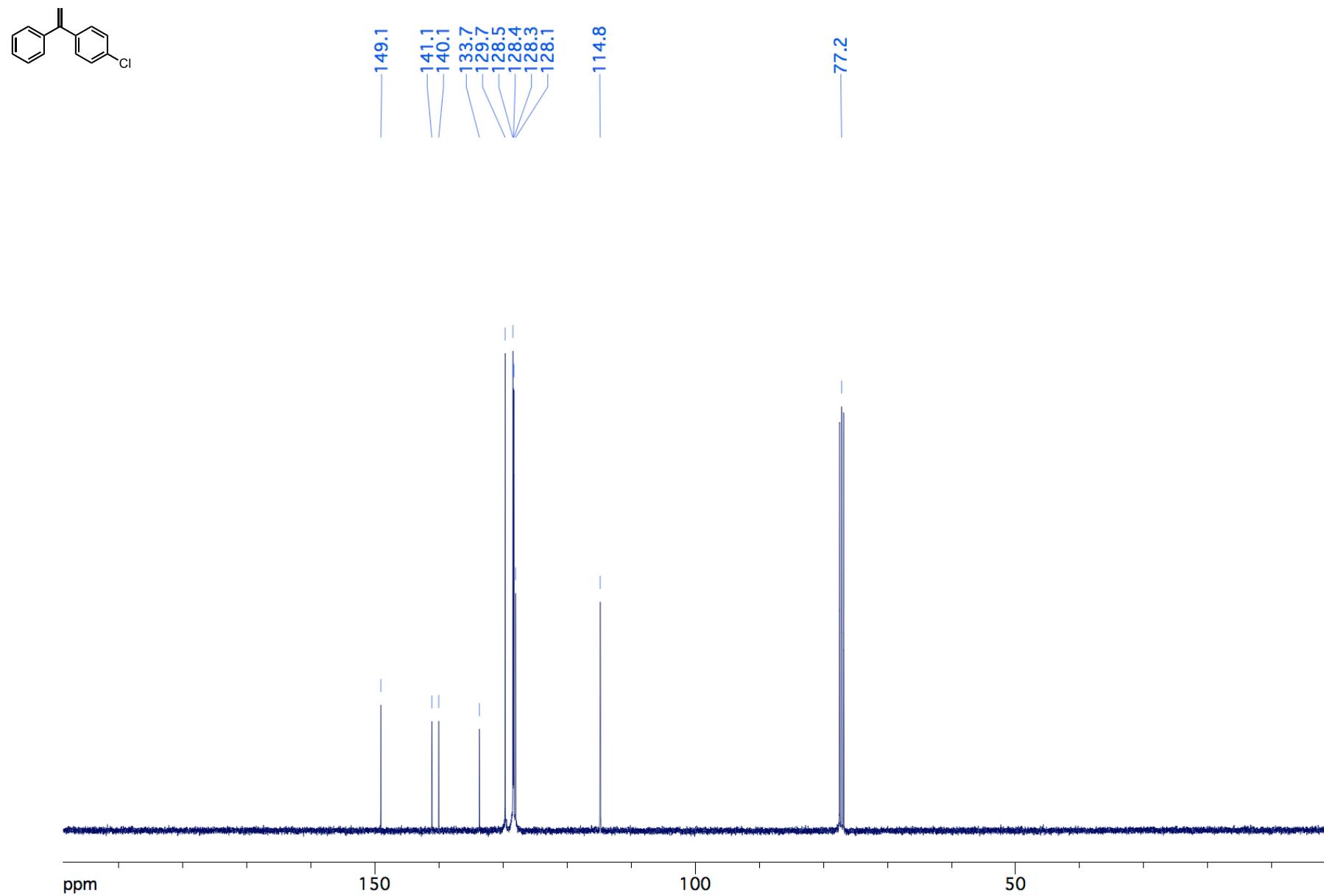
1-Chloro-3-(1-phenylvinyl)benzene (6a) ^{13}C NMR (CDCl_3 , 100 MHz)



1-Chloro-4-(1-phenylvinyl)benzene (7a) ^1H NMR (CDCl_3 , 400 MHz)

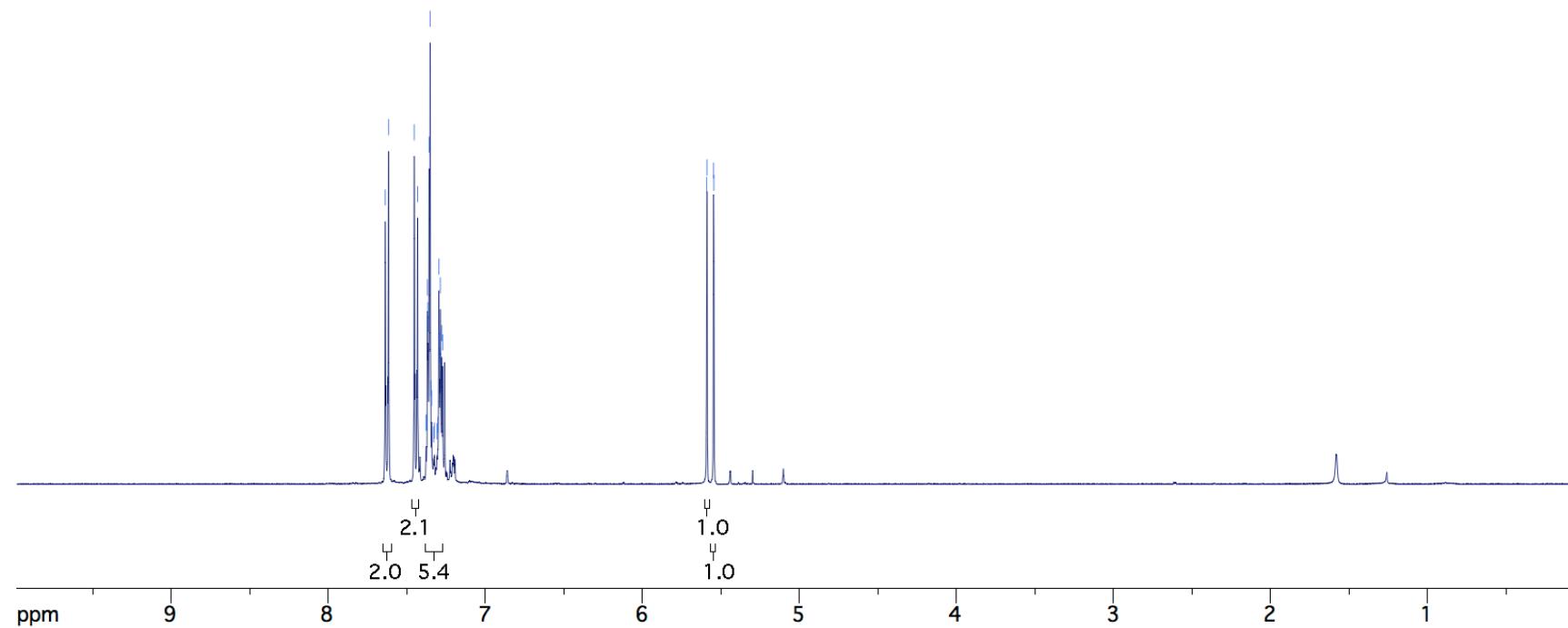
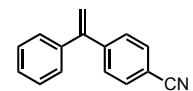


1-Chloro-4-(1-Phenylvinyl)benzene (7a) ^{13}C NMR (CDCl_3 , 100 MHz)



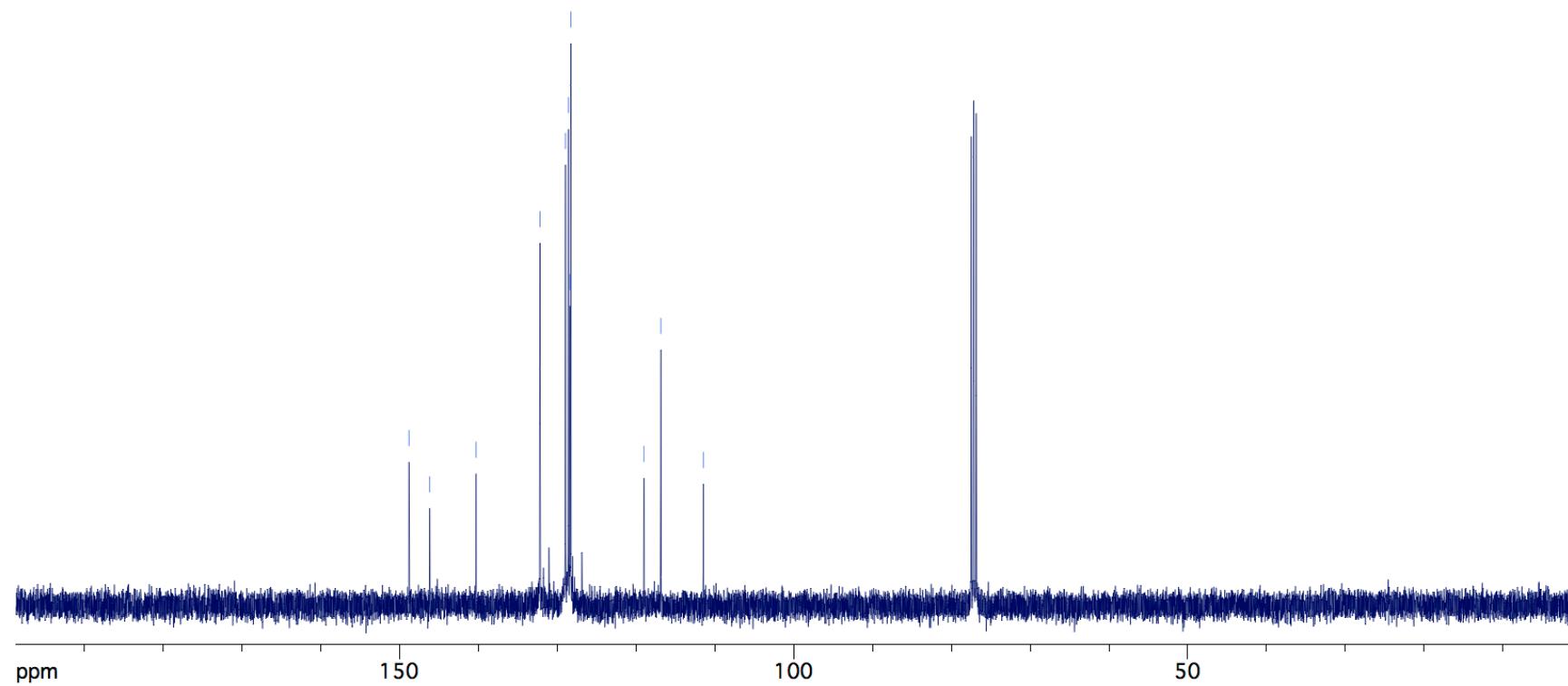
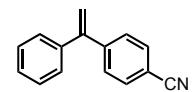
4-(1-Phenylvinyl)benzonitrile (8a)

^1H NMR (CDCl_3 , 400 MHz)

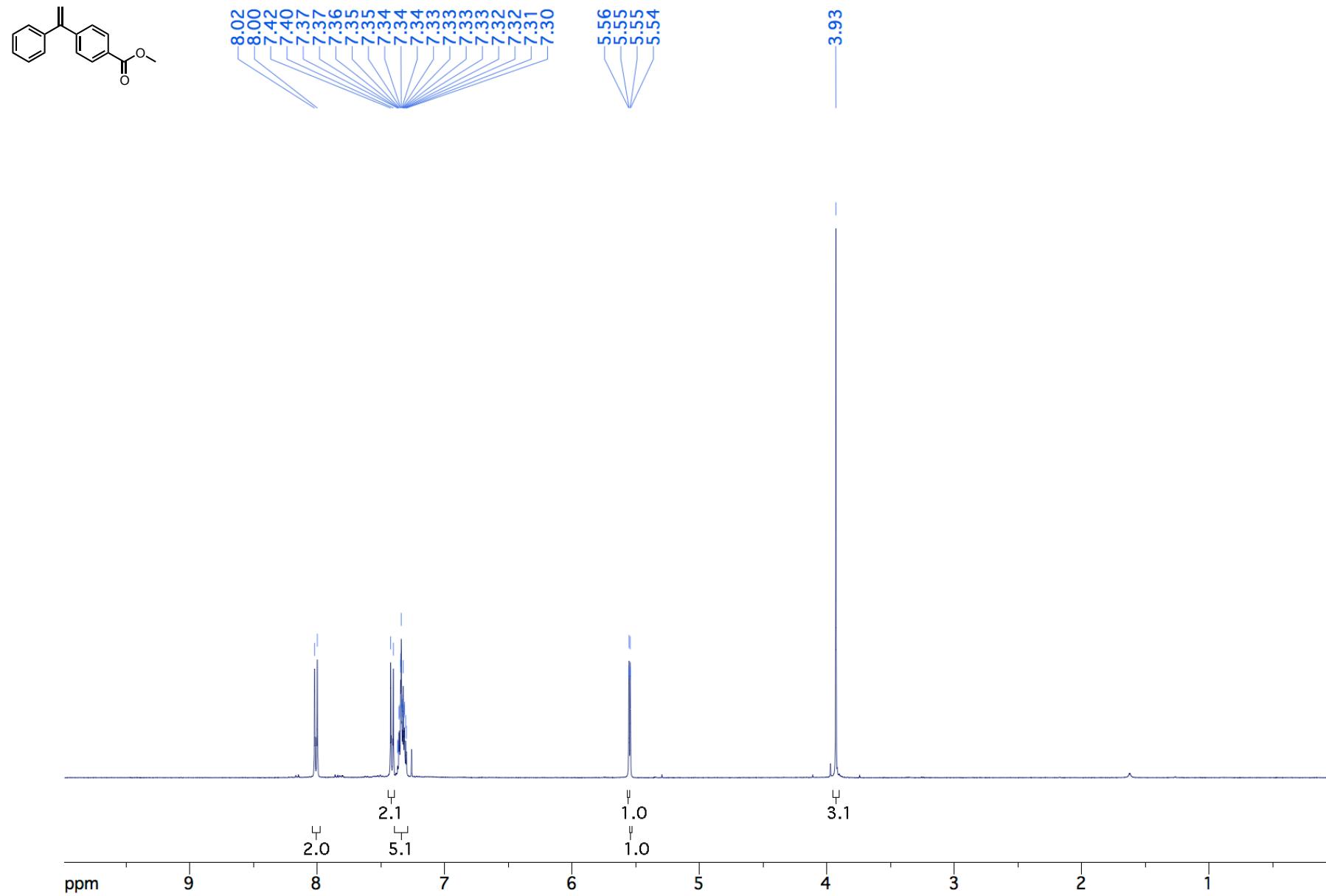


4-(1-Phenylvinyl)benzonitrile (8a)

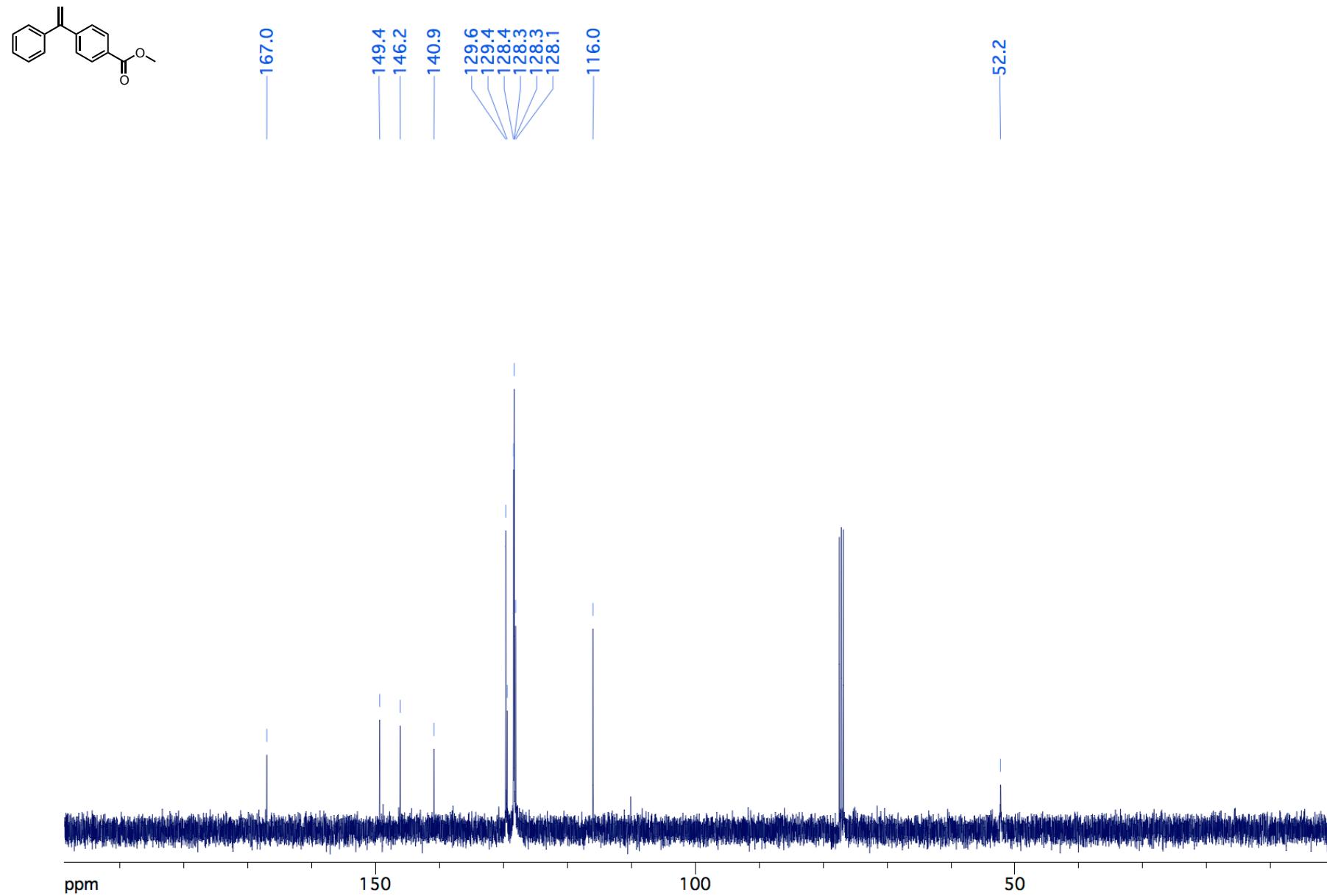
^{13}C NMR (CDCl_3 , 100 MHz)



Methyl 4-(1-phenylvinyl)benzoate (9a) ^1H NMR (CDCl_3 , 400 MHz)

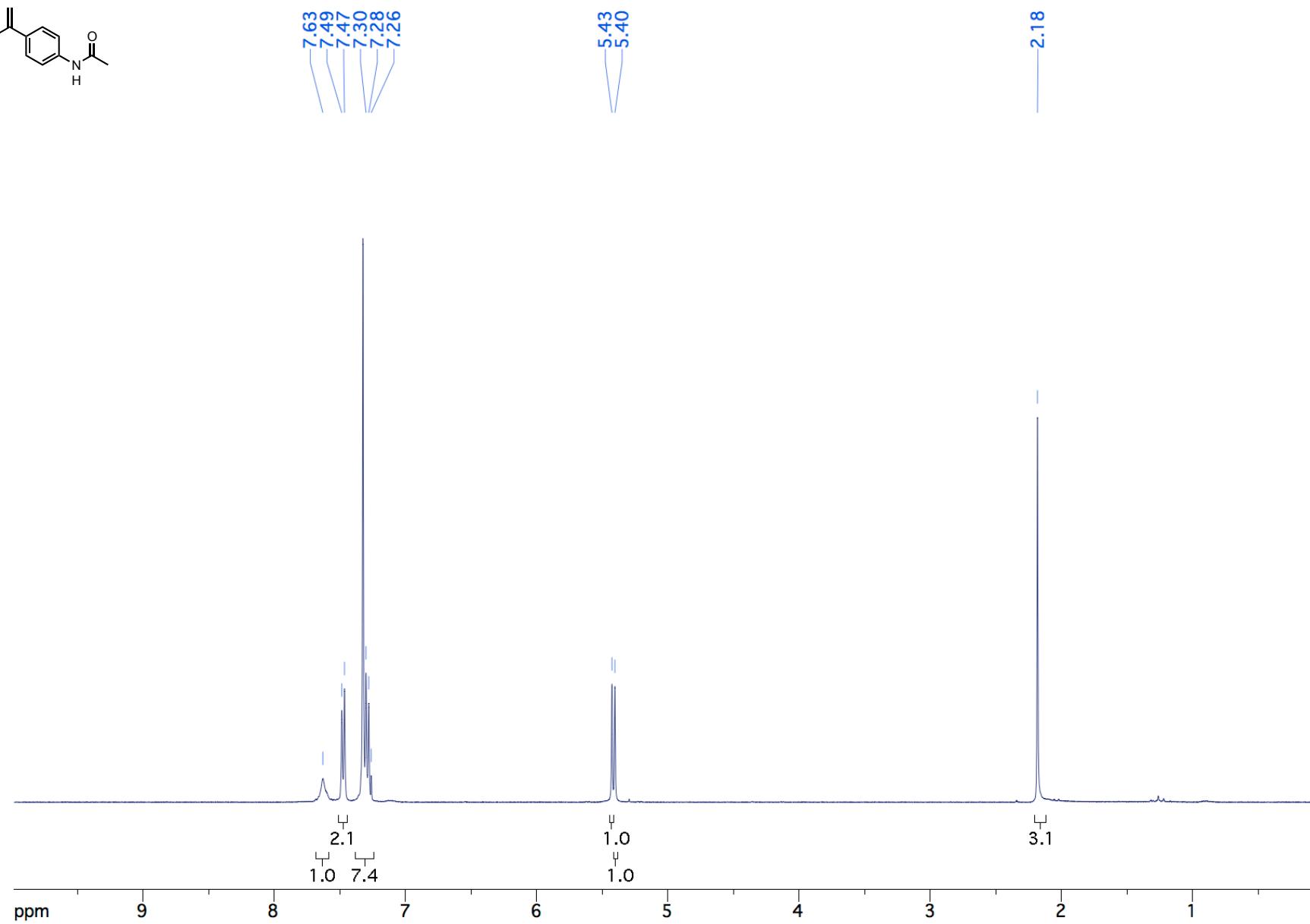
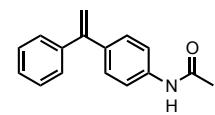


Methyl 4-(1-phenylvinyl)benzoate (9a) ^{13}C NMR (CDCl_3 , 100 MHz)



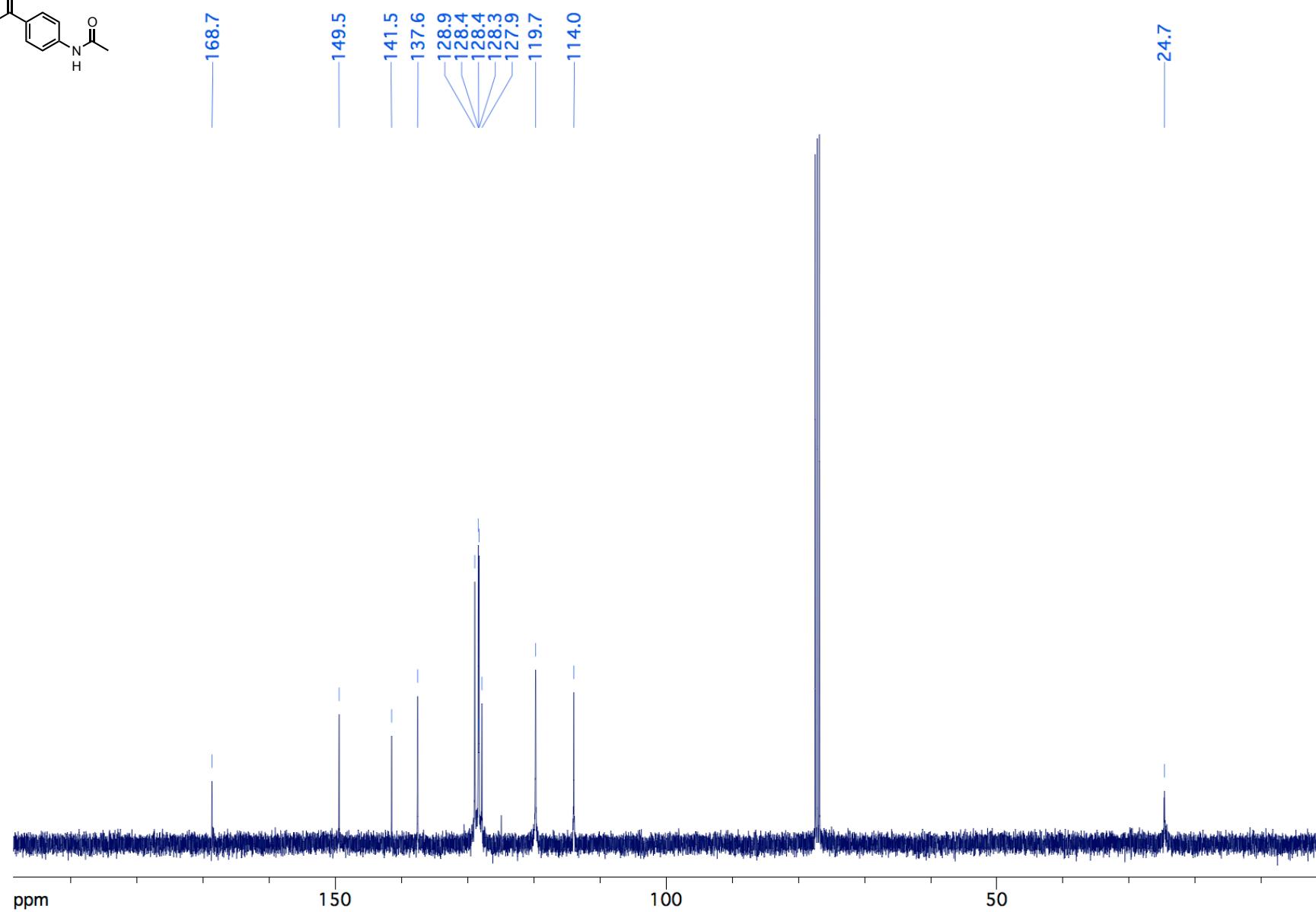
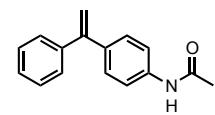
N-(4-(1-Phenylvinyl)phenyl)acetamide (10a)

^1H NMR (CDCl_3 , 400 MHz)

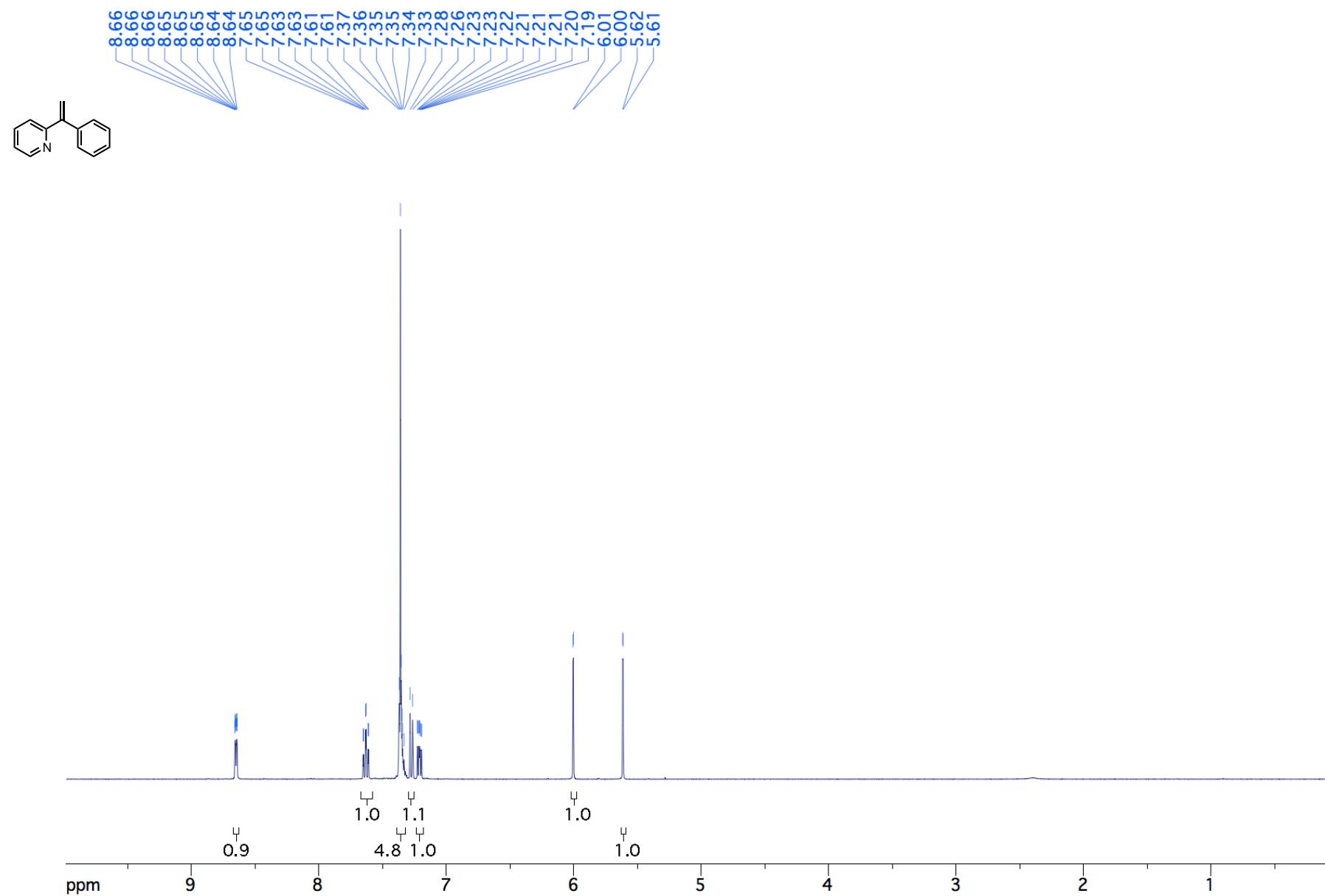


N-(4-(1-Phenylvinyl)phenyl)acetamide (10a)

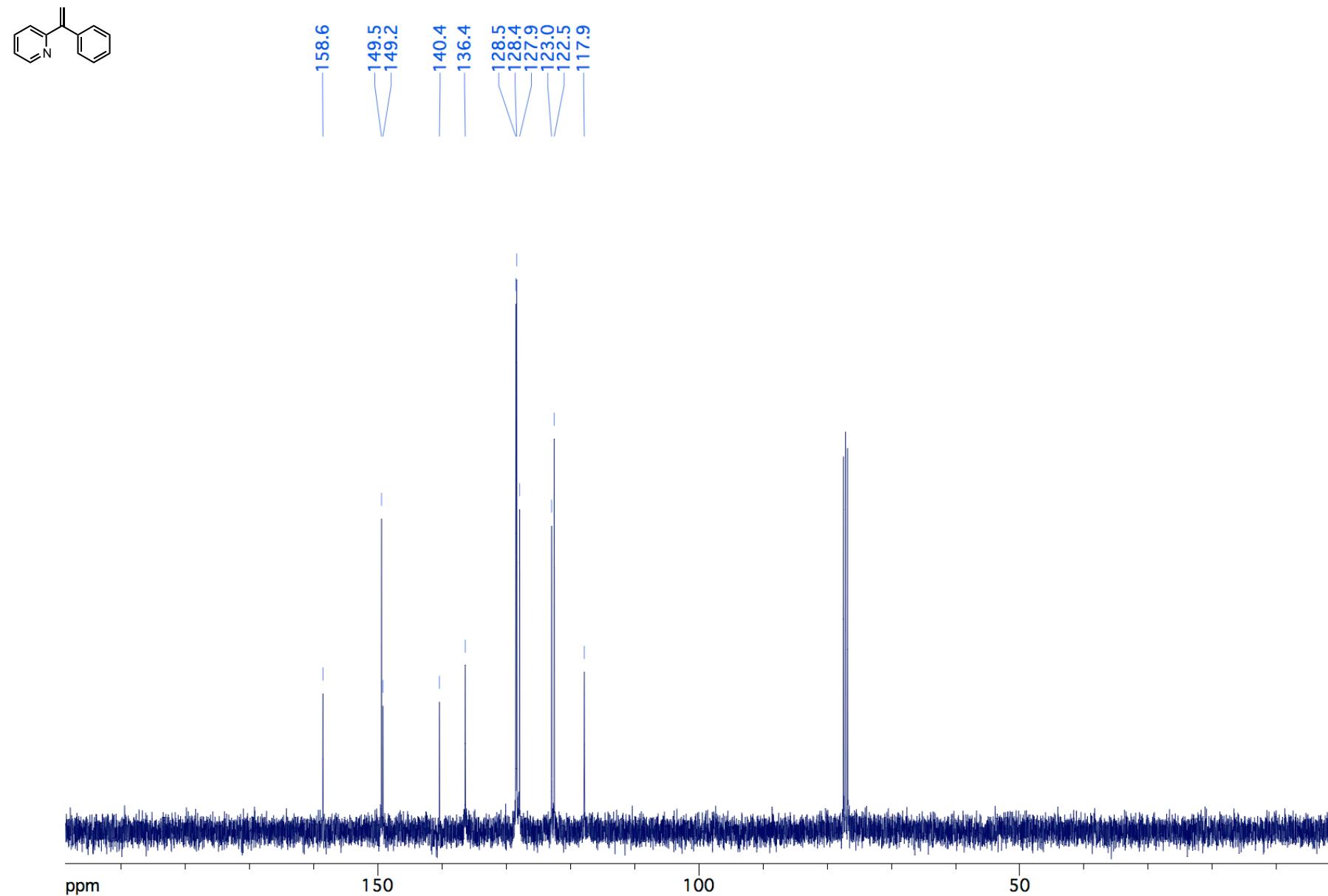
^{13}C NMR (CDCl_3 , 100 MHz)



2-(1-Phenylvinyl)pyridine (11a) ^1H NMR (CDCl_3 , 400 MHz)

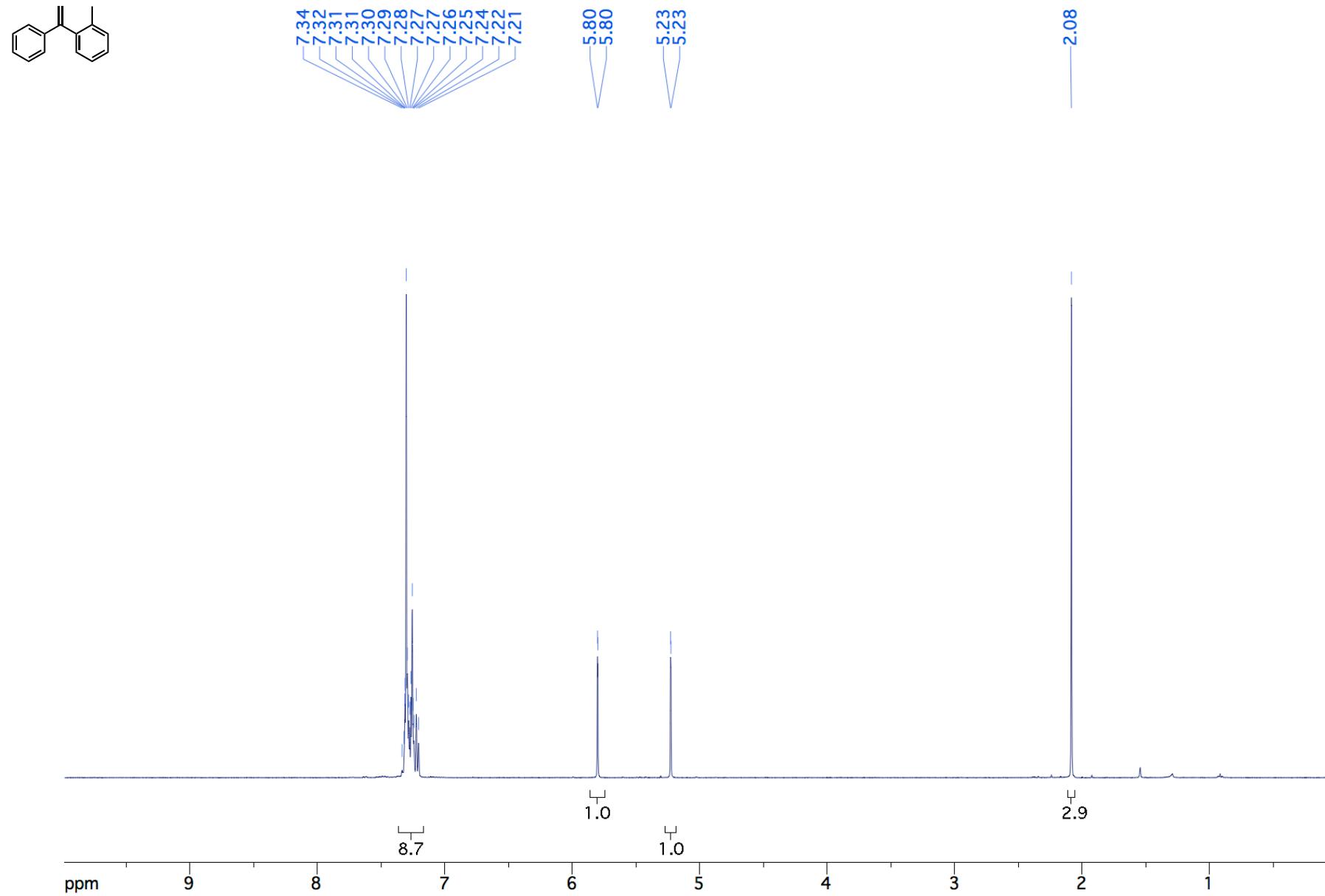


2-(1-Phenylvinyl)pyridine (11a) ^{13}C NMR (CDCl_3 , 100 MHz)



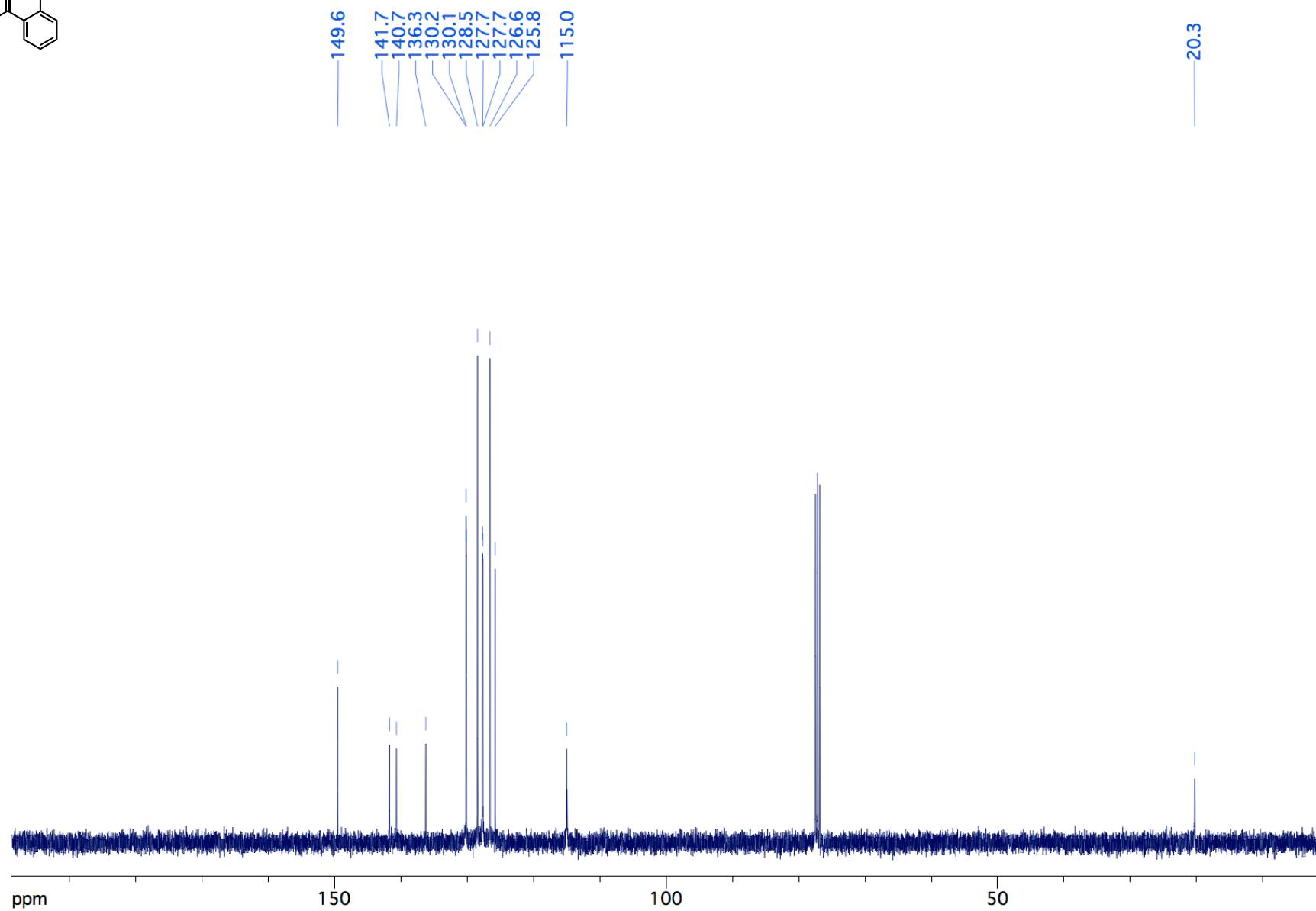
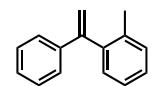
1-Methyl-2-(1-phenylvinyl)benzene (12a)

^1H NMR (CDCl_3 , 400 MHz)



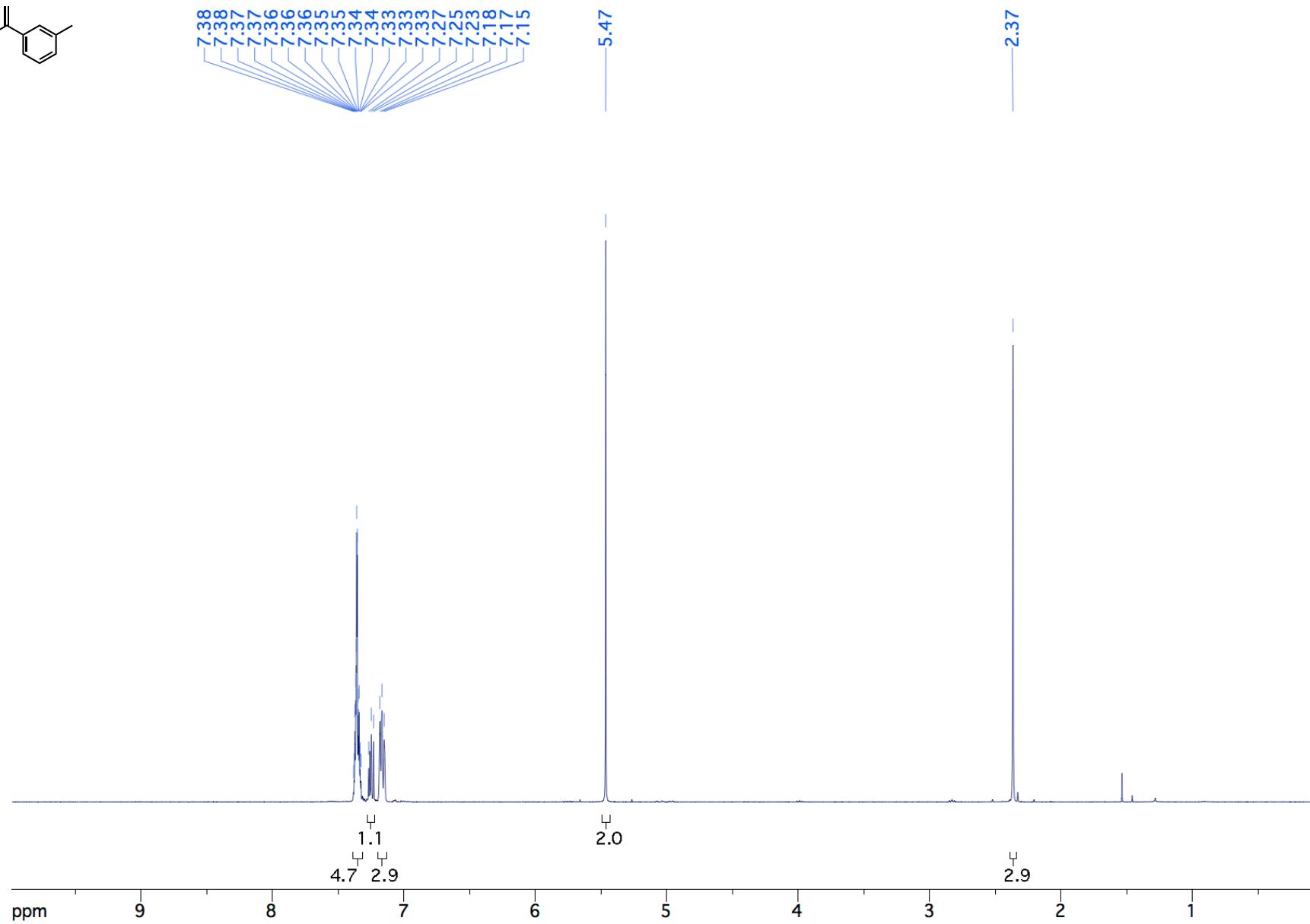
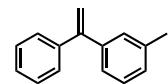
1-Methyl-2-(1-phenylvinyl)benzene (12a)

^{13}C NMR (CDCl_3 , 100 MHz)



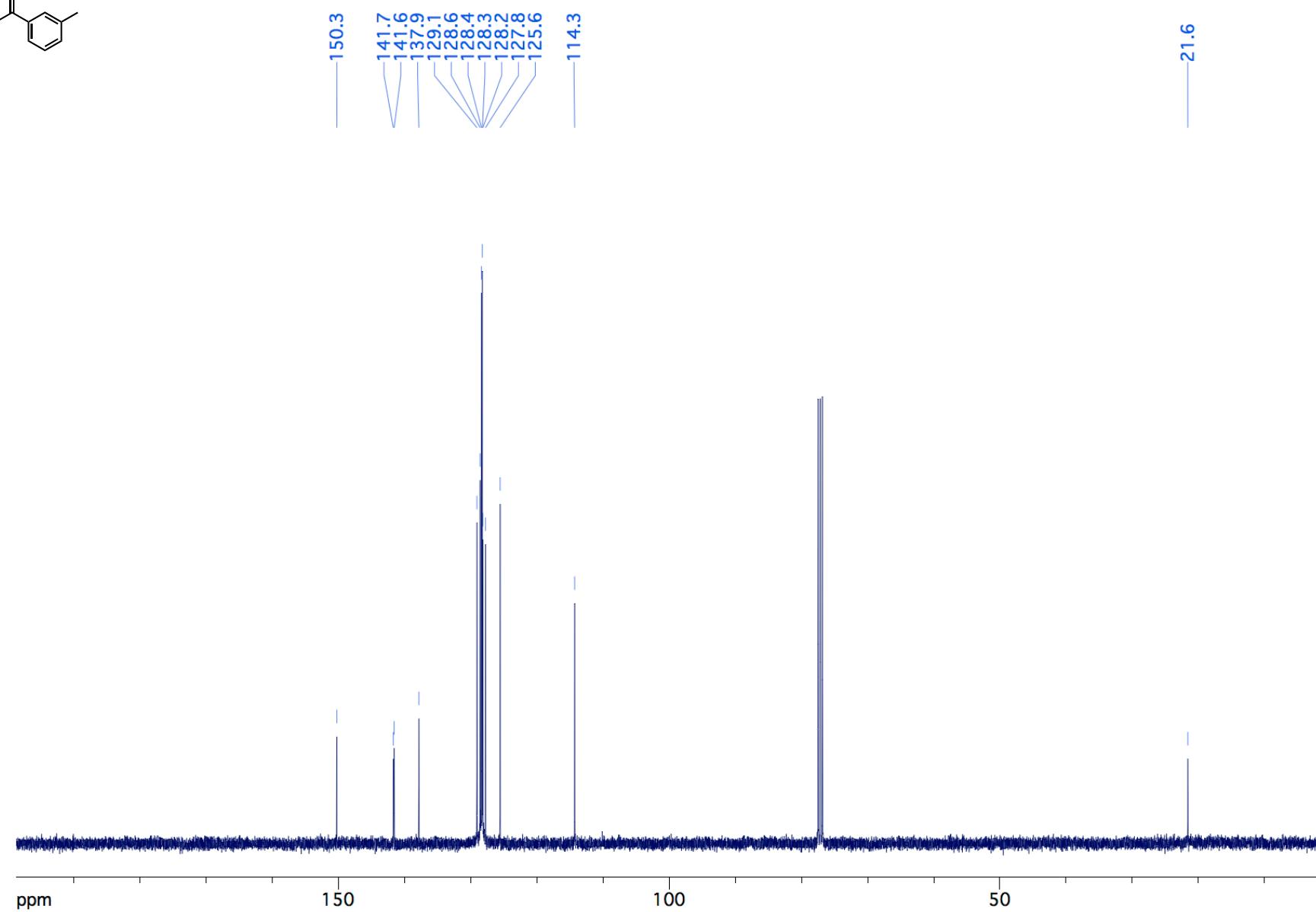
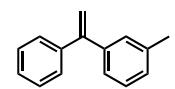
1-Methyl-3-(1-phenylvinyl)benzene (13a)

^1H NMR (CDCl_3 , 400 MHz)



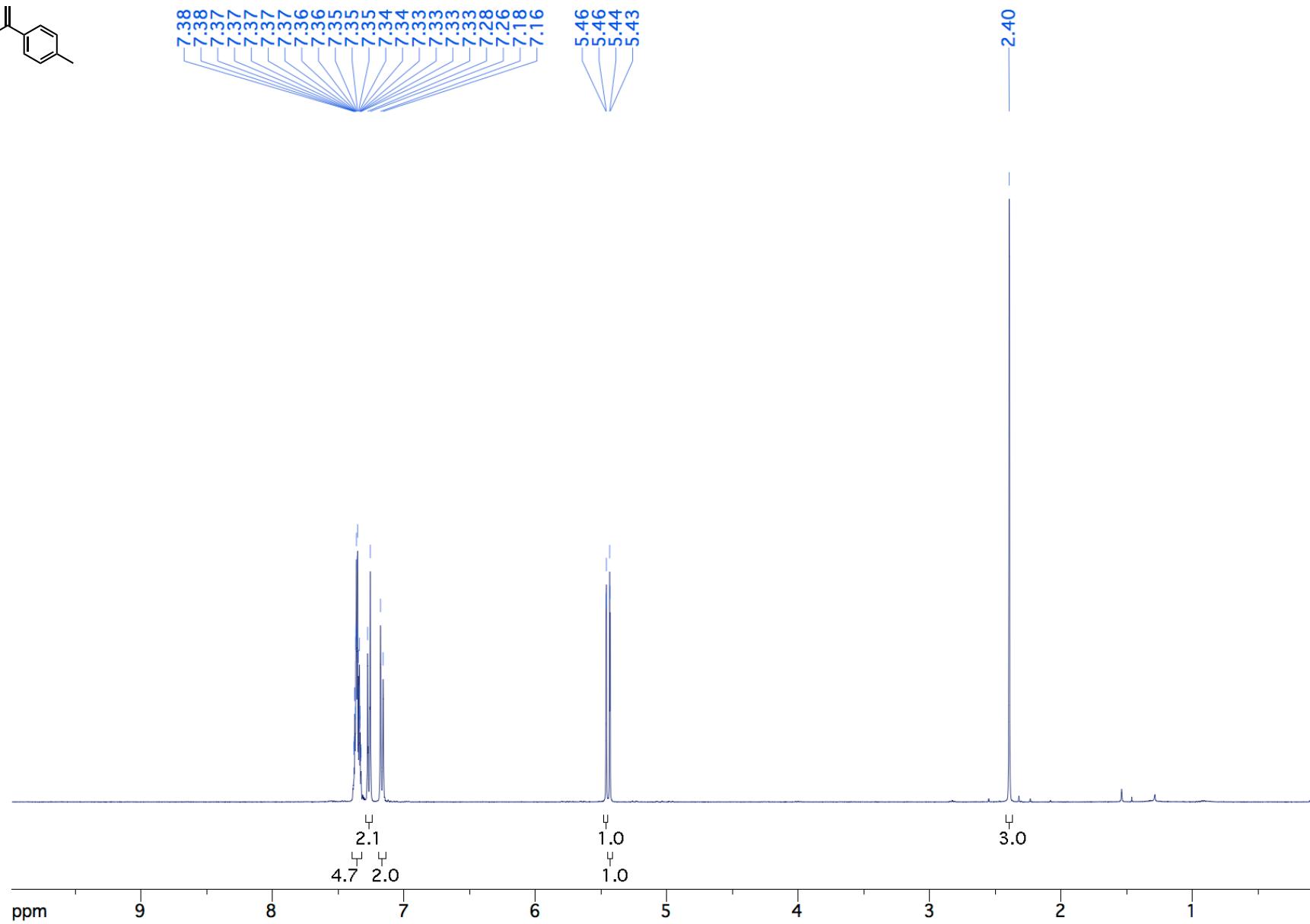
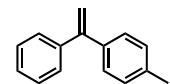
1-Methyl-3-(1-phenylvinyl)benzene (13a)

^{13}C NMR (CDCl_3 , 100 MHz)



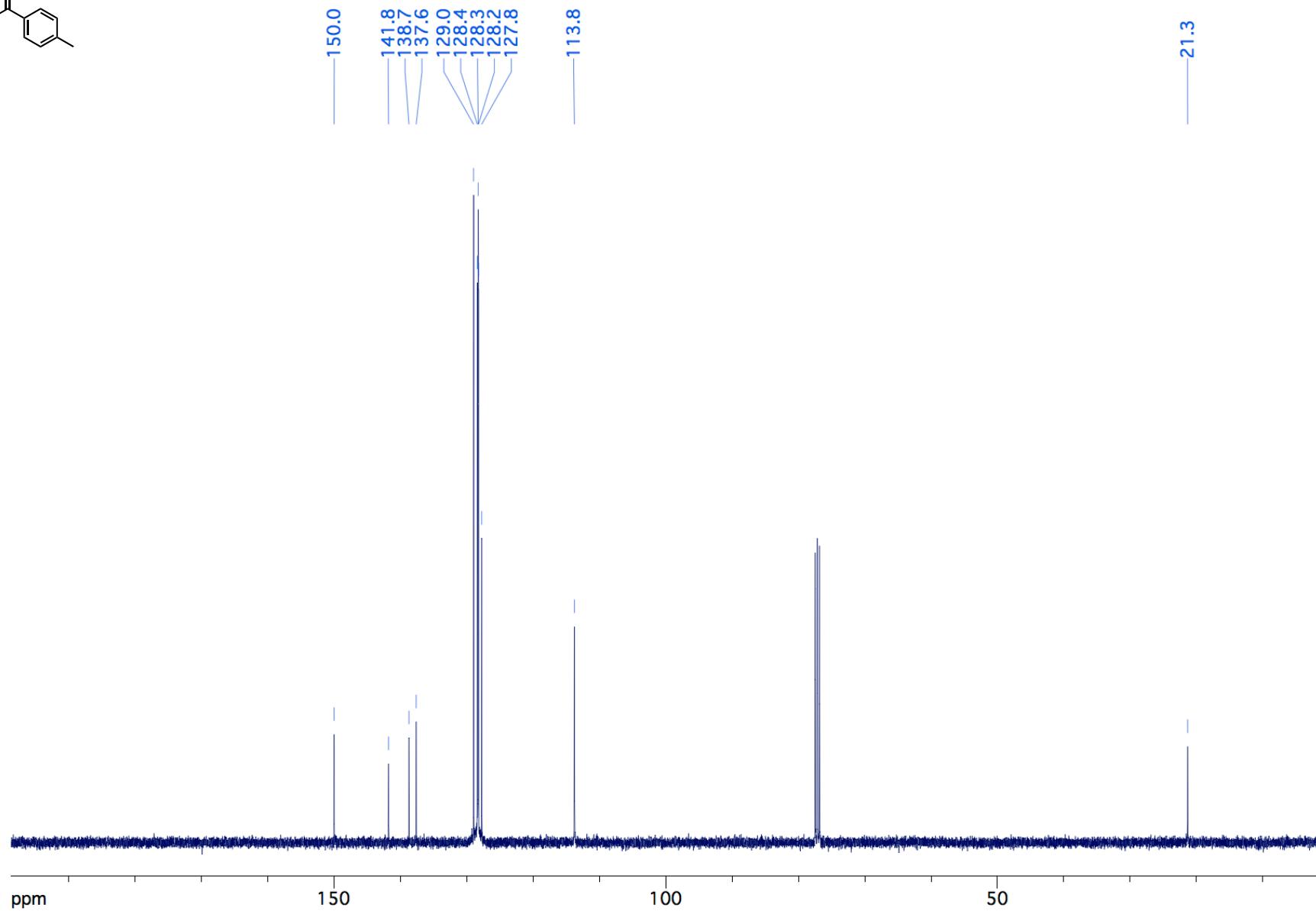
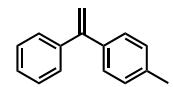
1-Methyl-4-(1-phenylvinyl)benzene (14a)

^1H NMR (CDCl_3 , 400 MHz)



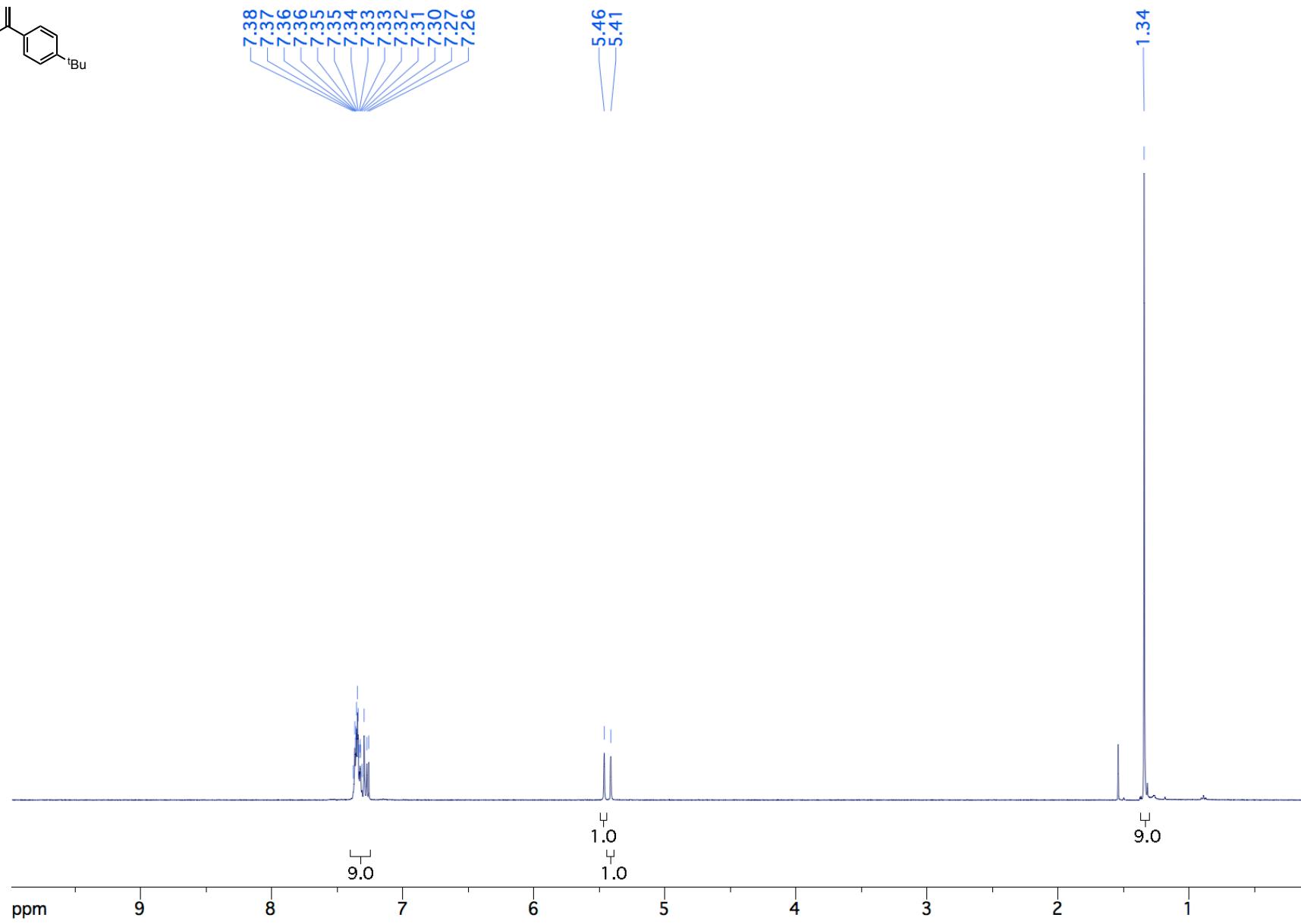
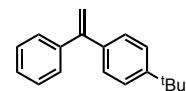
1-Methyl-4-(1-phenylvinyl)benzene (14a)

^{13}C NMR (CDCl_3 , 100 MHz)



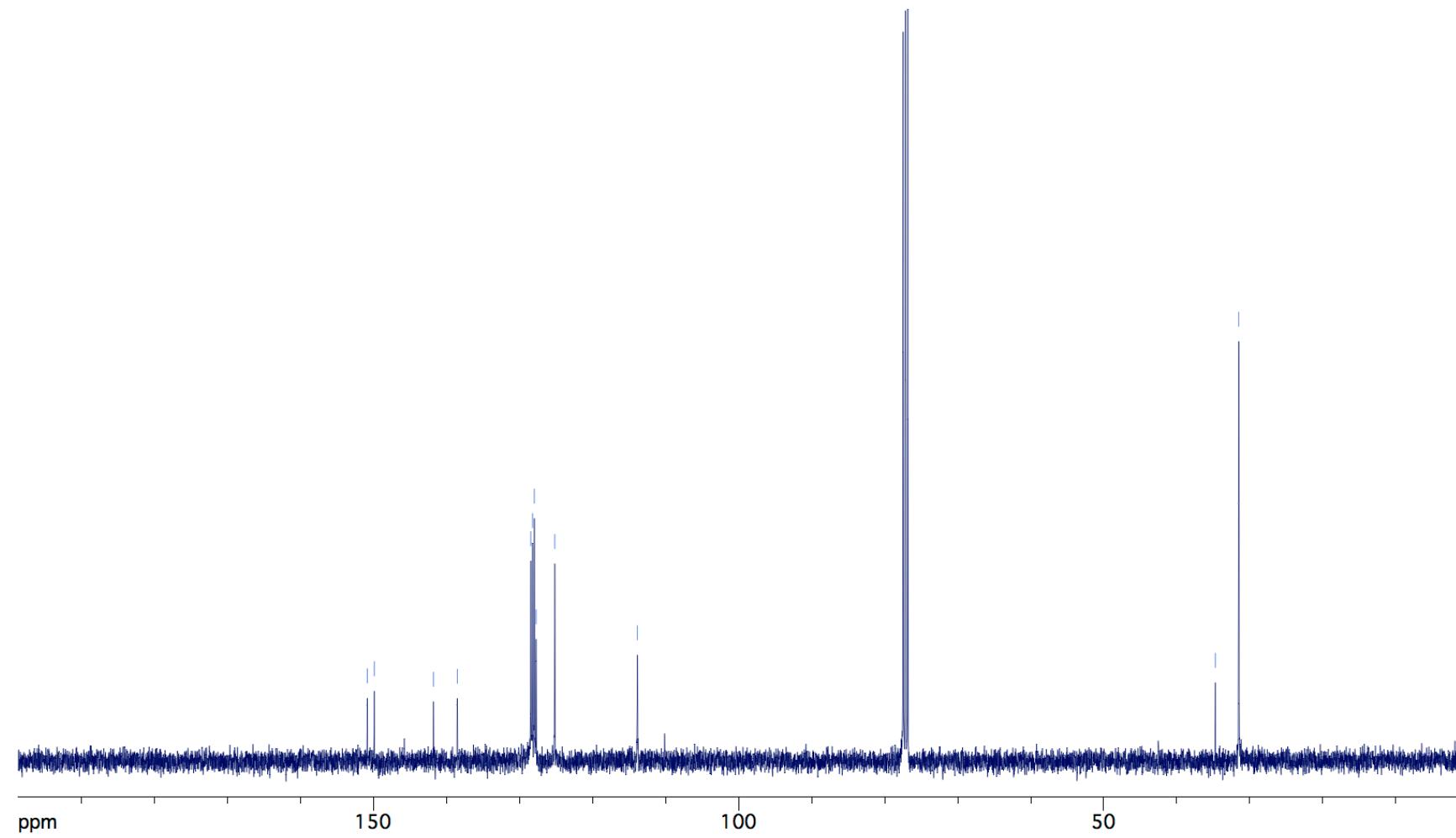
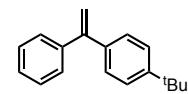
1-(*tert*-Butyl)-4-(1-phenylvinyl)benzene (15a)

¹H NMR (CDCl₃, 400 MHz)



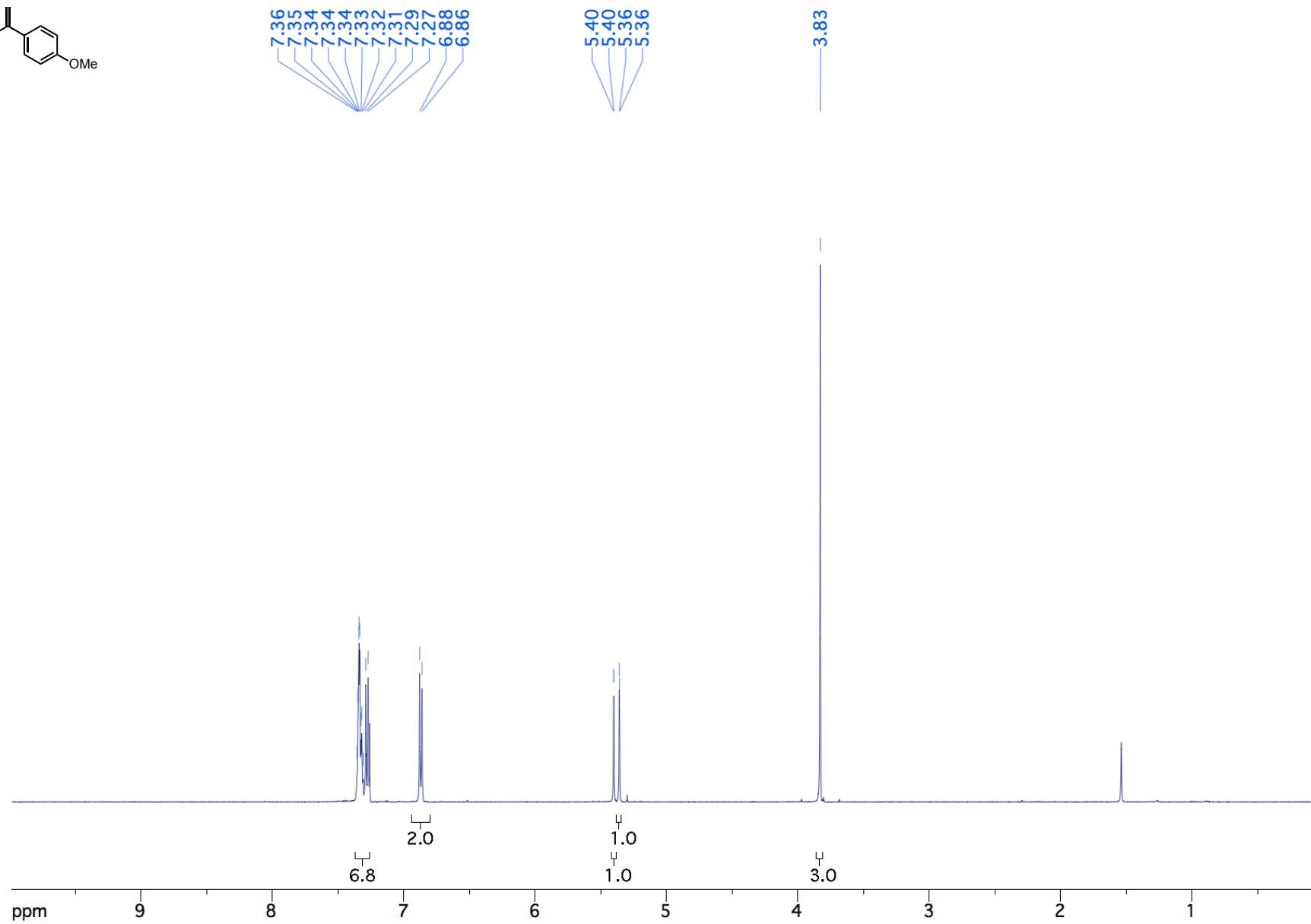
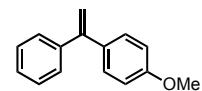
1-(*tert*-Butyl)-4-(1-phenylvinyl)benzene (15a)

^{13}C NMR (CDCl_3 , 100 MHz)



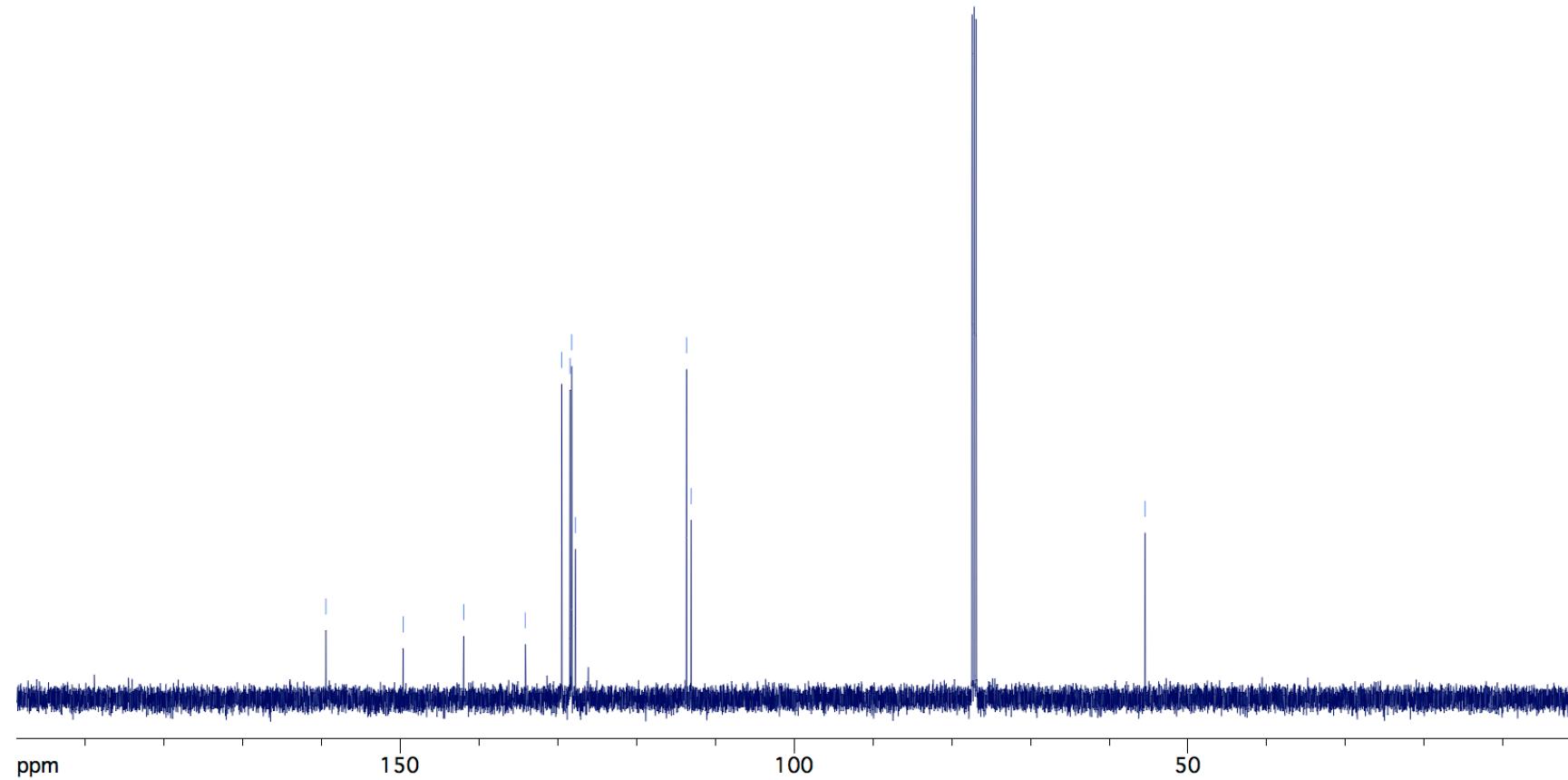
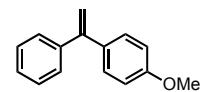
1-Methoxy-4-(1-phenylvinyl)benzene (16a)

^1H NMR (CDCl_3 , 400 MHz)

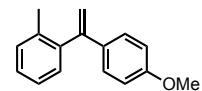


1-Methoxy-4-(1-phenylvinyl)benzene (16a)

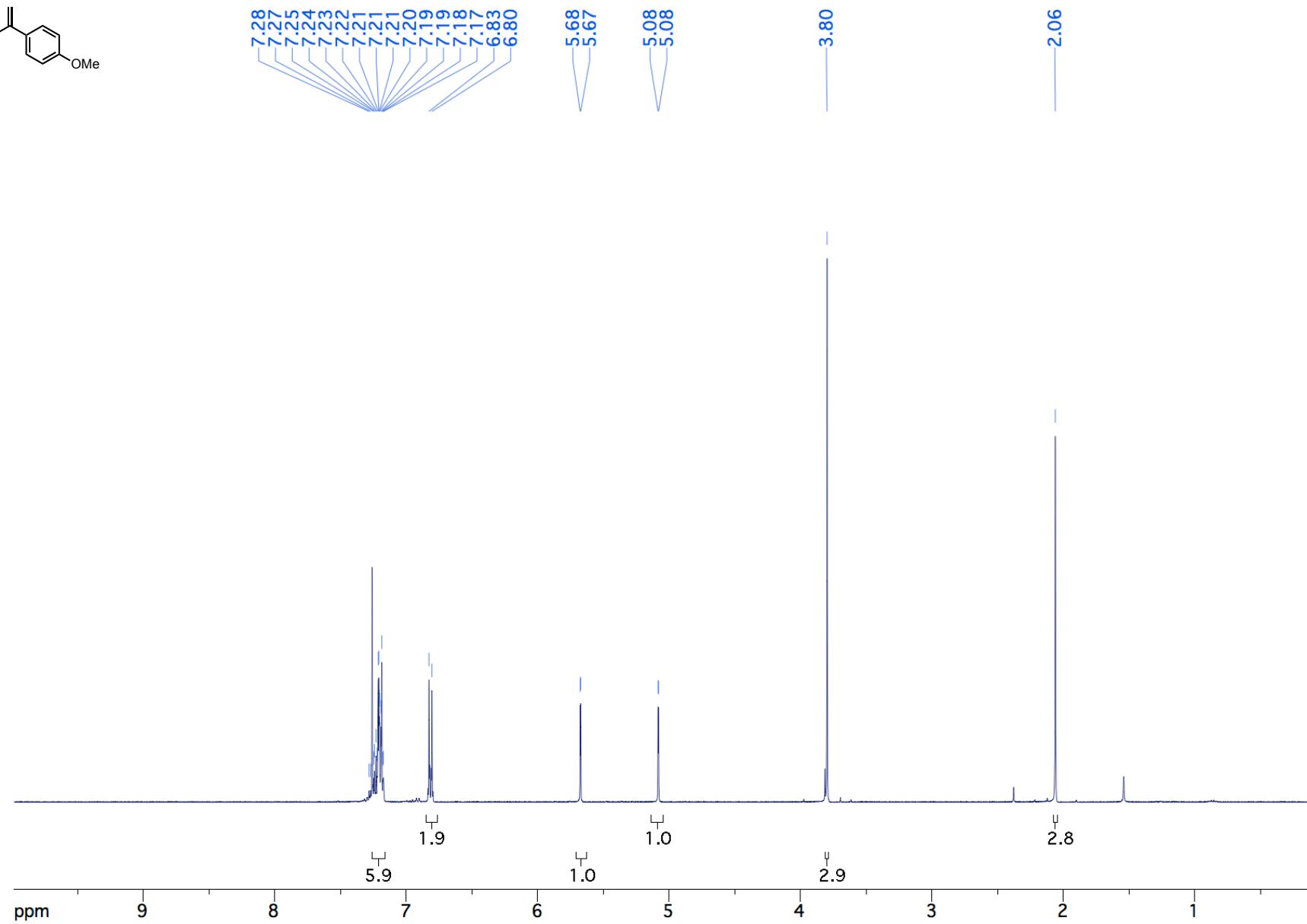
^{13}C NMR (CDCl_3 , 100 MHz)



1-(1-(4-Methoxyphenyl)vinyl)-2-methylbenzene (17a)

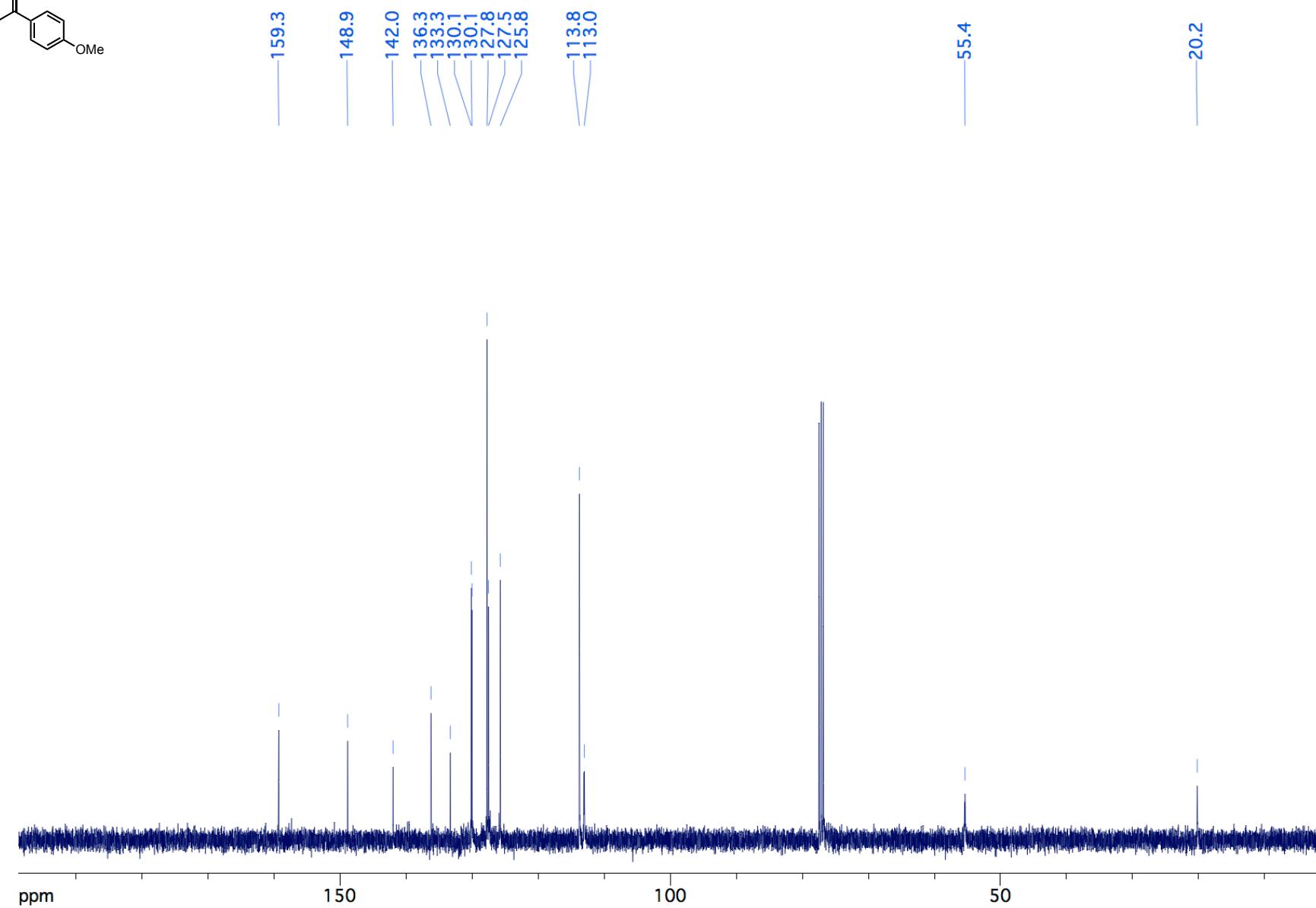
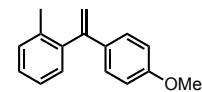


¹H NMR (CDCl₃, 400 MHz)



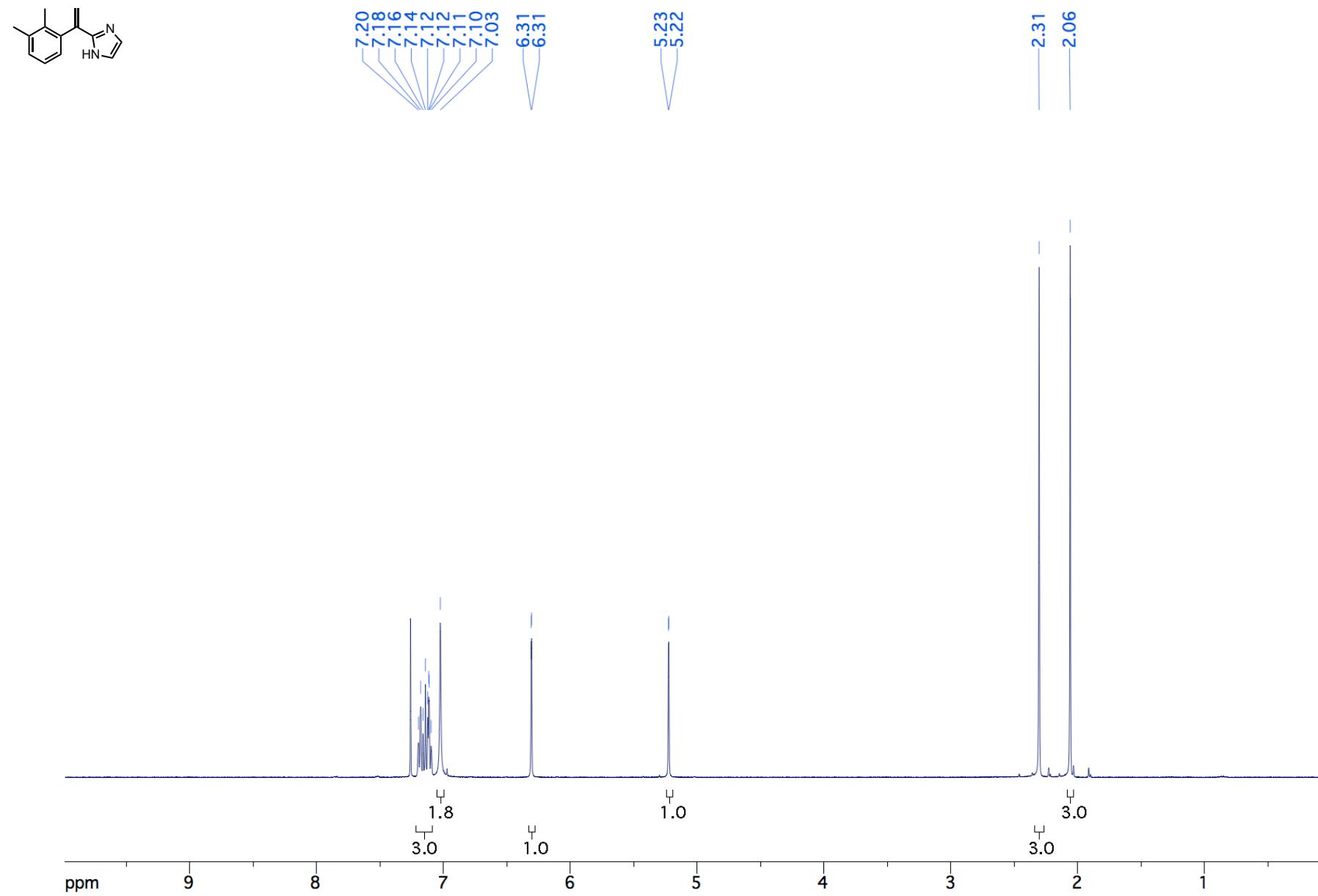
1-(1-(4-Methoxyphenyl)vinyl)-2-methylbenzene (17a)

^{13}C NMR (CDCl_3 , 100 MHz)



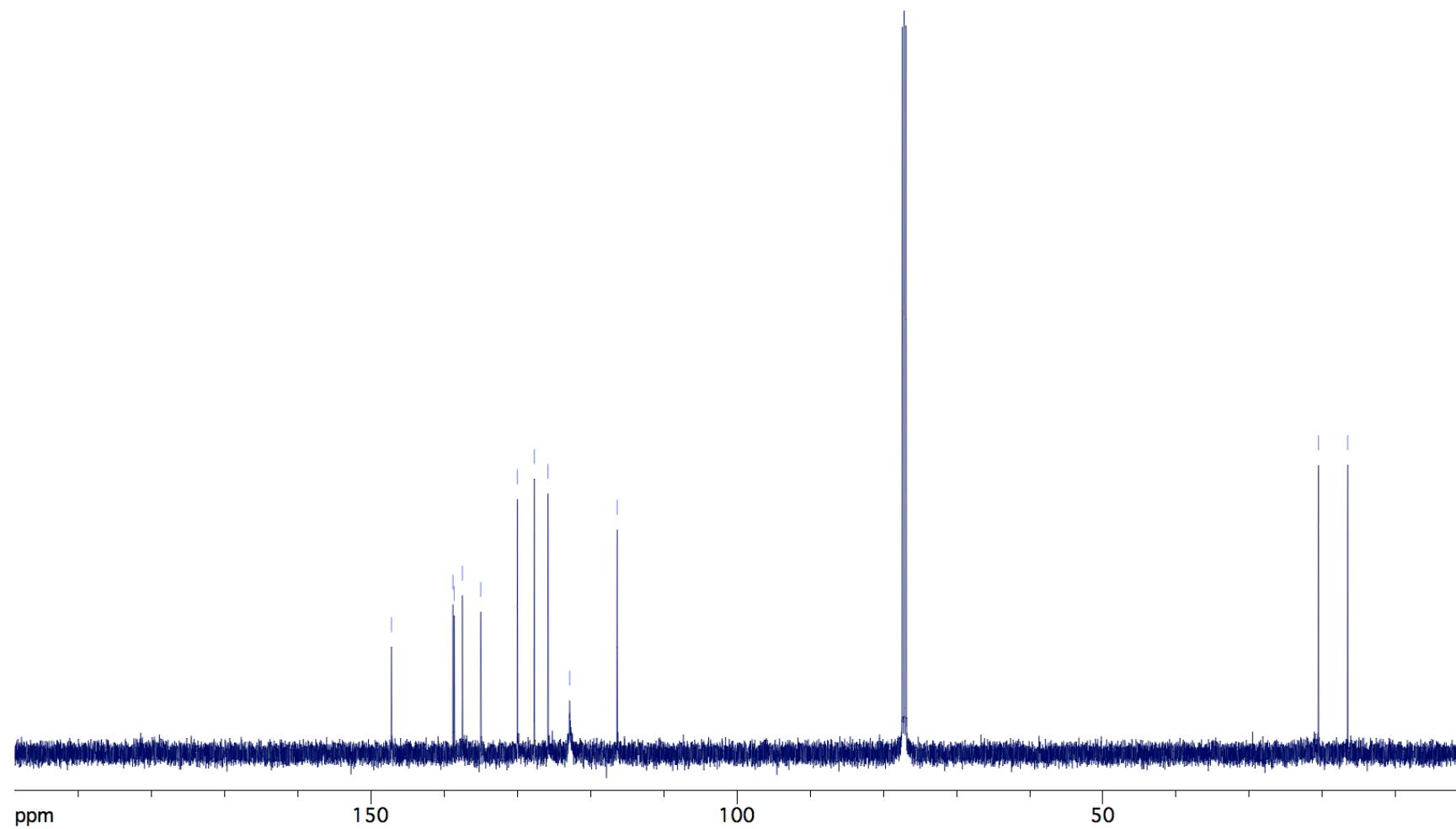
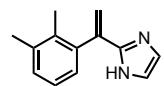
2-(1-(2,3-Dimethylphenyl)vinyl)-1*H*-imidazole (18a)

^1H NMR (CDCl_3 , 400 MHz)

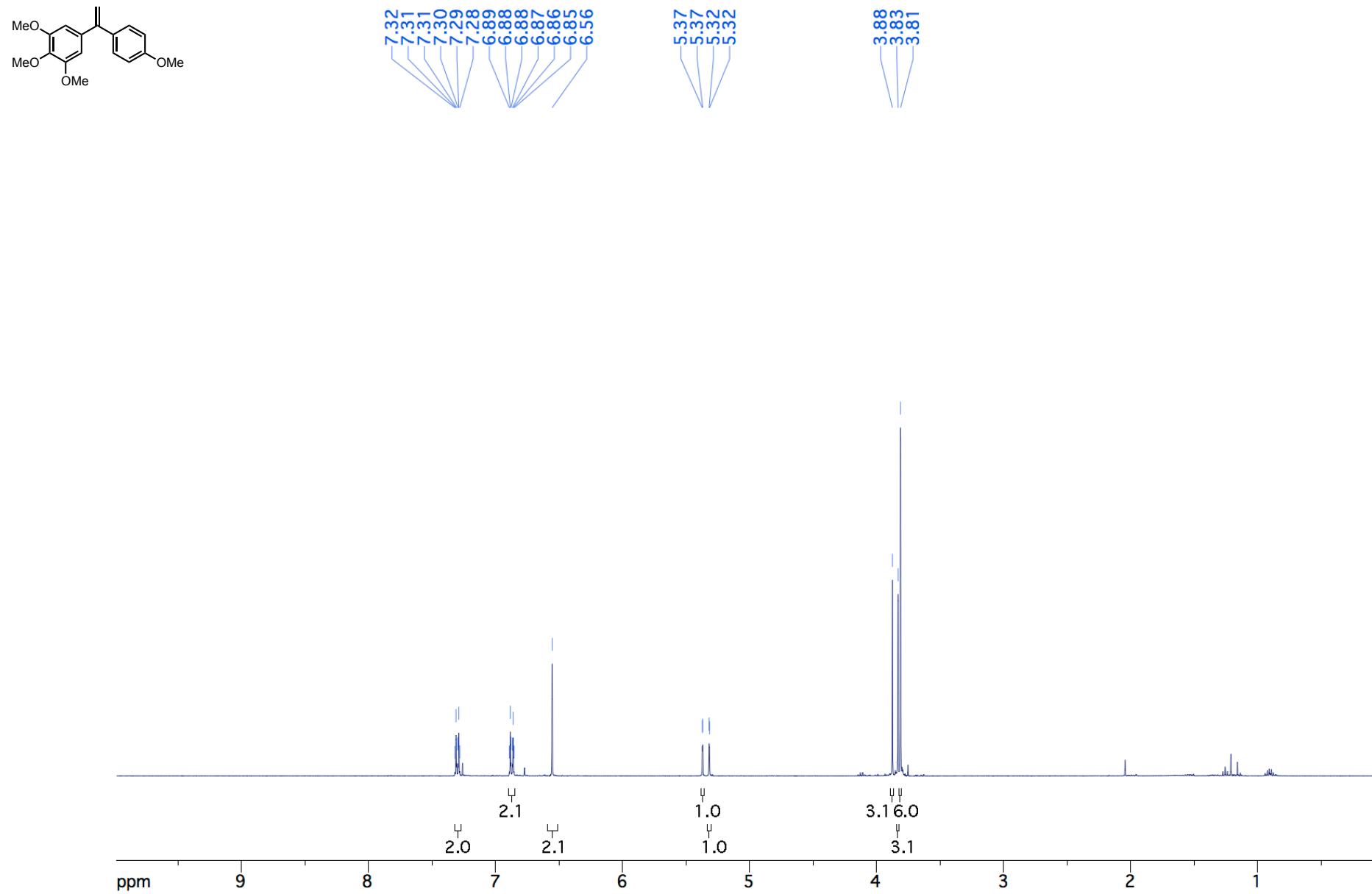


2-(1-(2,3-Dimethylphenyl)vinyl)-1*H*-imidazole (18a)

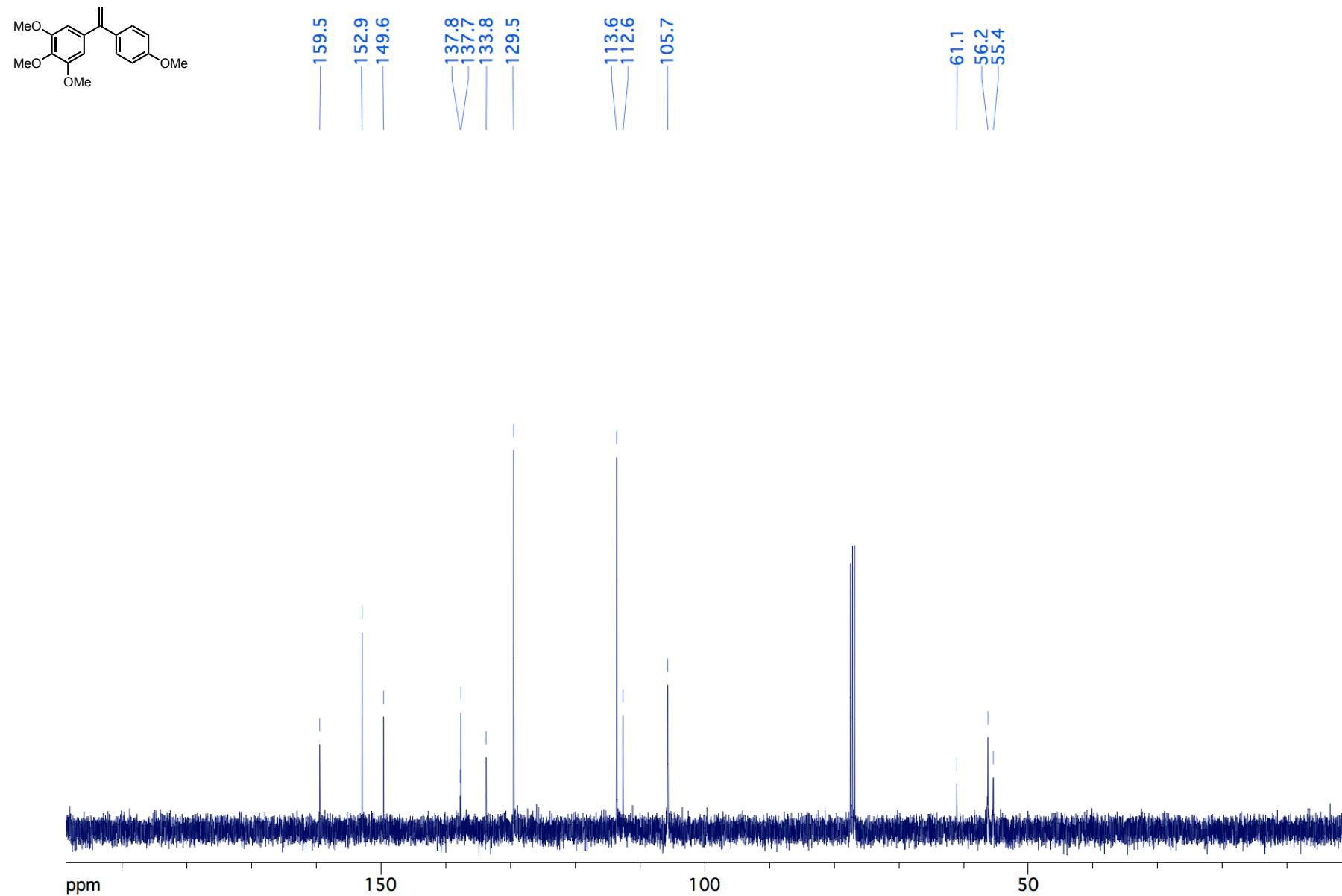
^{13}C NMR (CDCl_3 , 100 MHz)



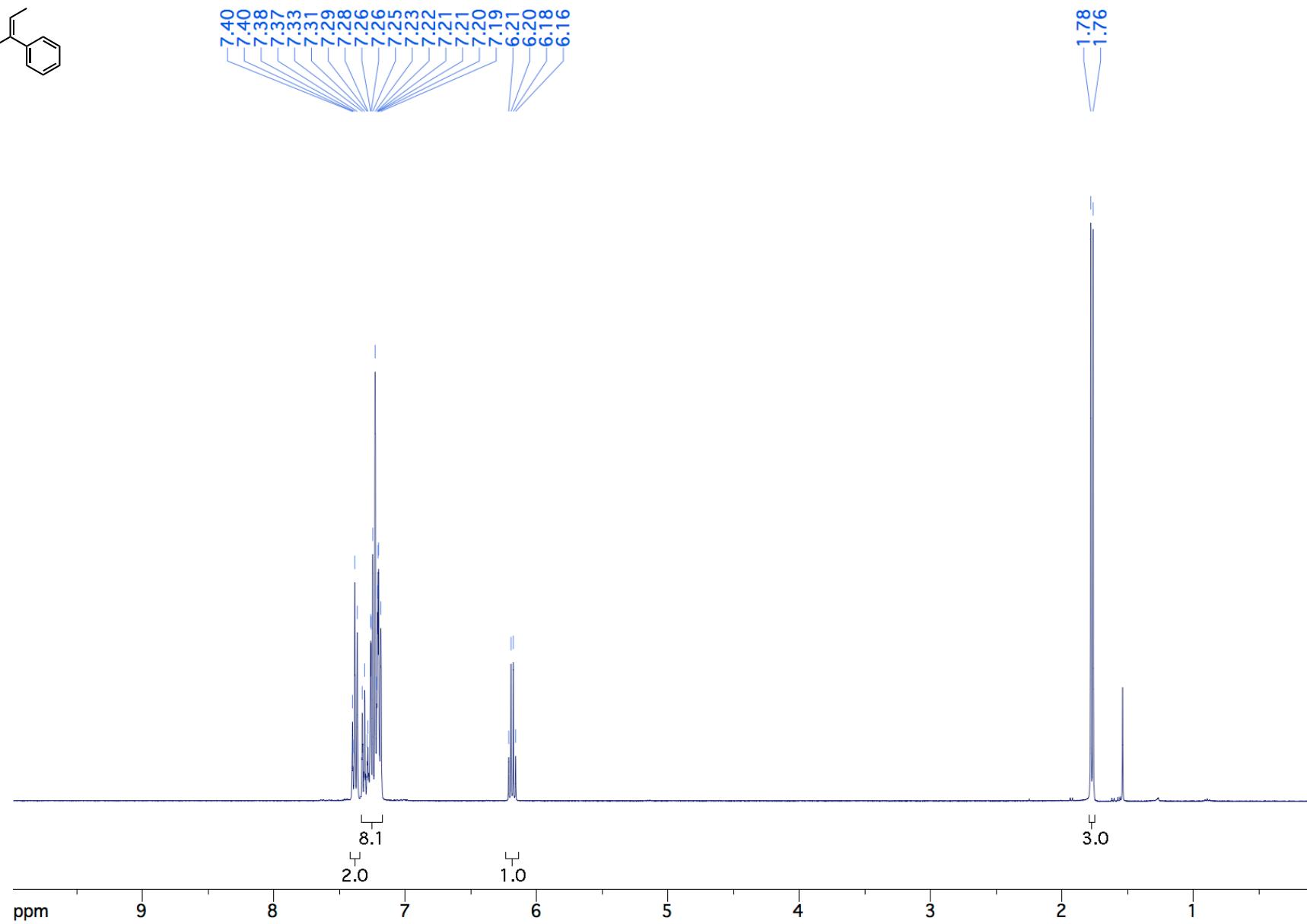
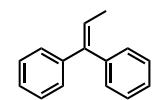
1,2,3-Trimethoxy-5-(1-(4-methoxyphenyl)vinyl)benzene (19a) ^1H NMR (CDCl_3 , 400 MHz)



1,2,3-Trimethoxy-5-(1-(4-methoxyphenyl)vinyl)benzene (19a) ^{13}C NMR (CDCl_3 , 100 MHz)

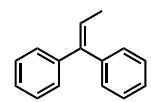


Prop-1-ene-1,1-diylbenzene (20a) ^1H NMR (CDCl_3 , 400 MHz)



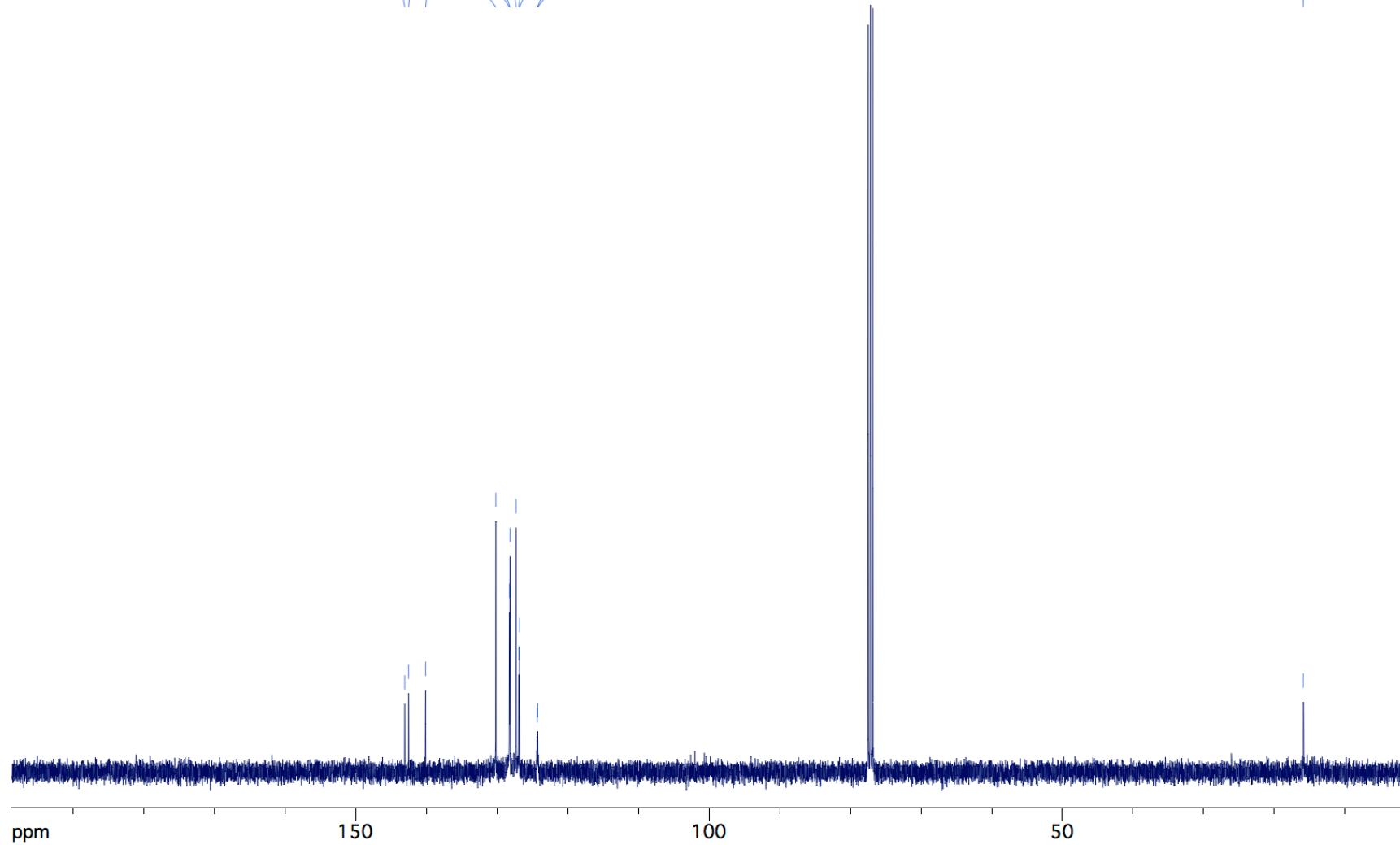
Prop-1-ene-1,1-diylbenzene (20a)

^{13}C NMR (CDCl_3 , 100 MHz)



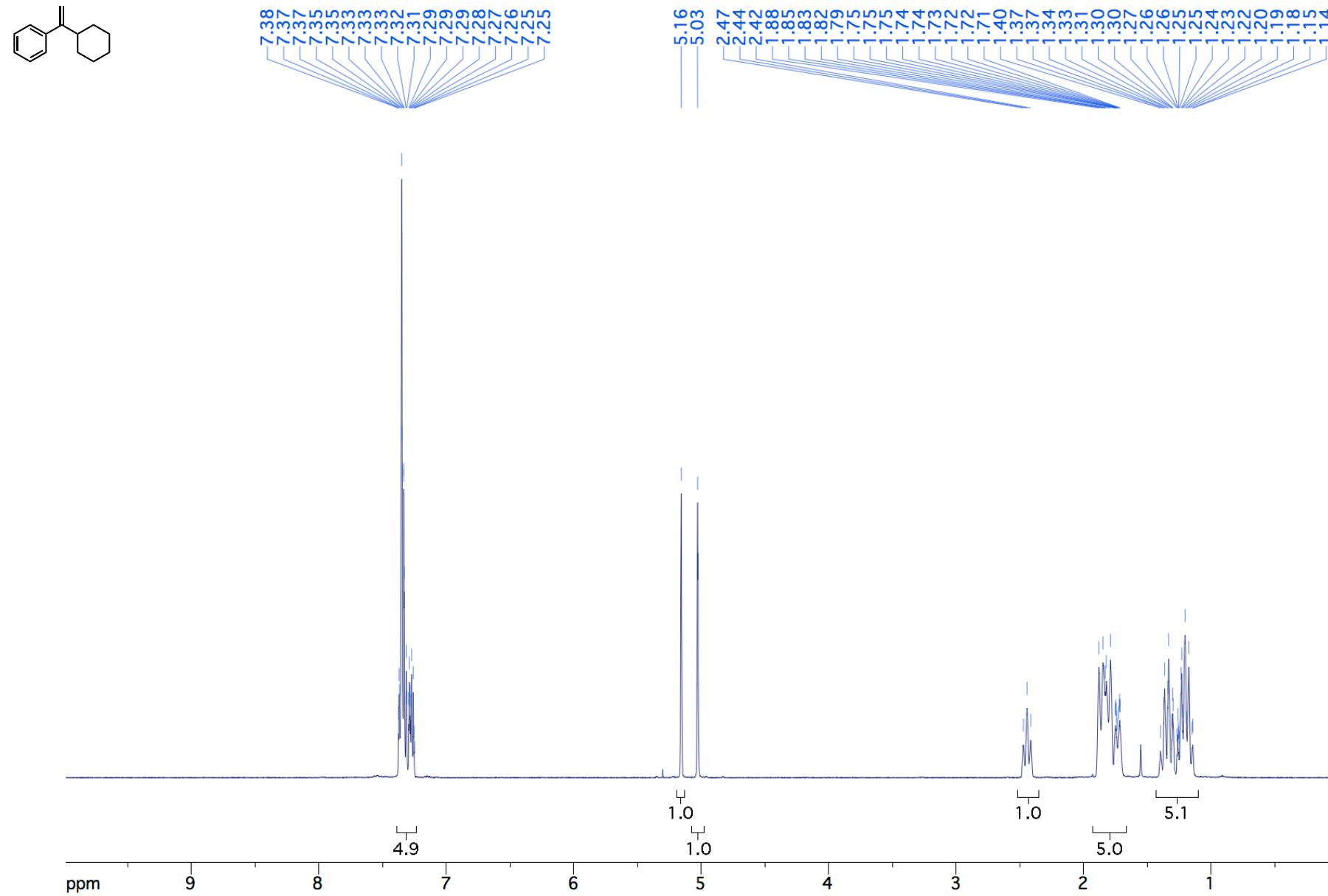
143.1
142.5
140.1
130.2
128.3
128.2
127.3
127.0
126.8
124.3
124.3

15.9



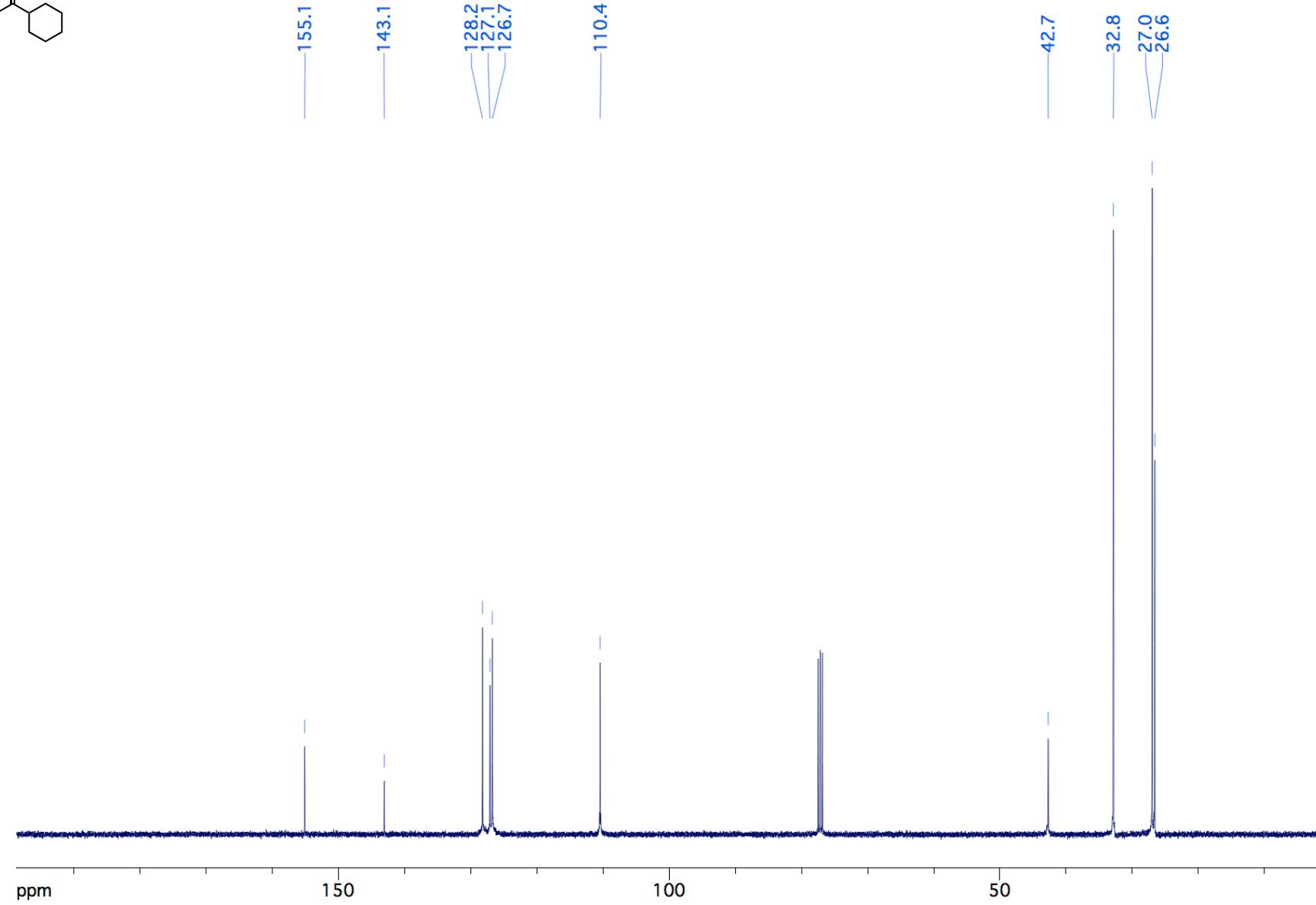
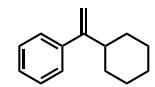
(1-Cyclohexylvinyl)benzene (21a)

^1H NMR (CDCl_3 , 400 MHz)



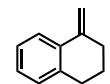
(1-Cyclohexylvinyl)benzene (21a)

^{13}C NMR (CDCl_3 , 100 MHz)



1-Methylene-1,2,3,4-tetrahydronaphthalene (22a)

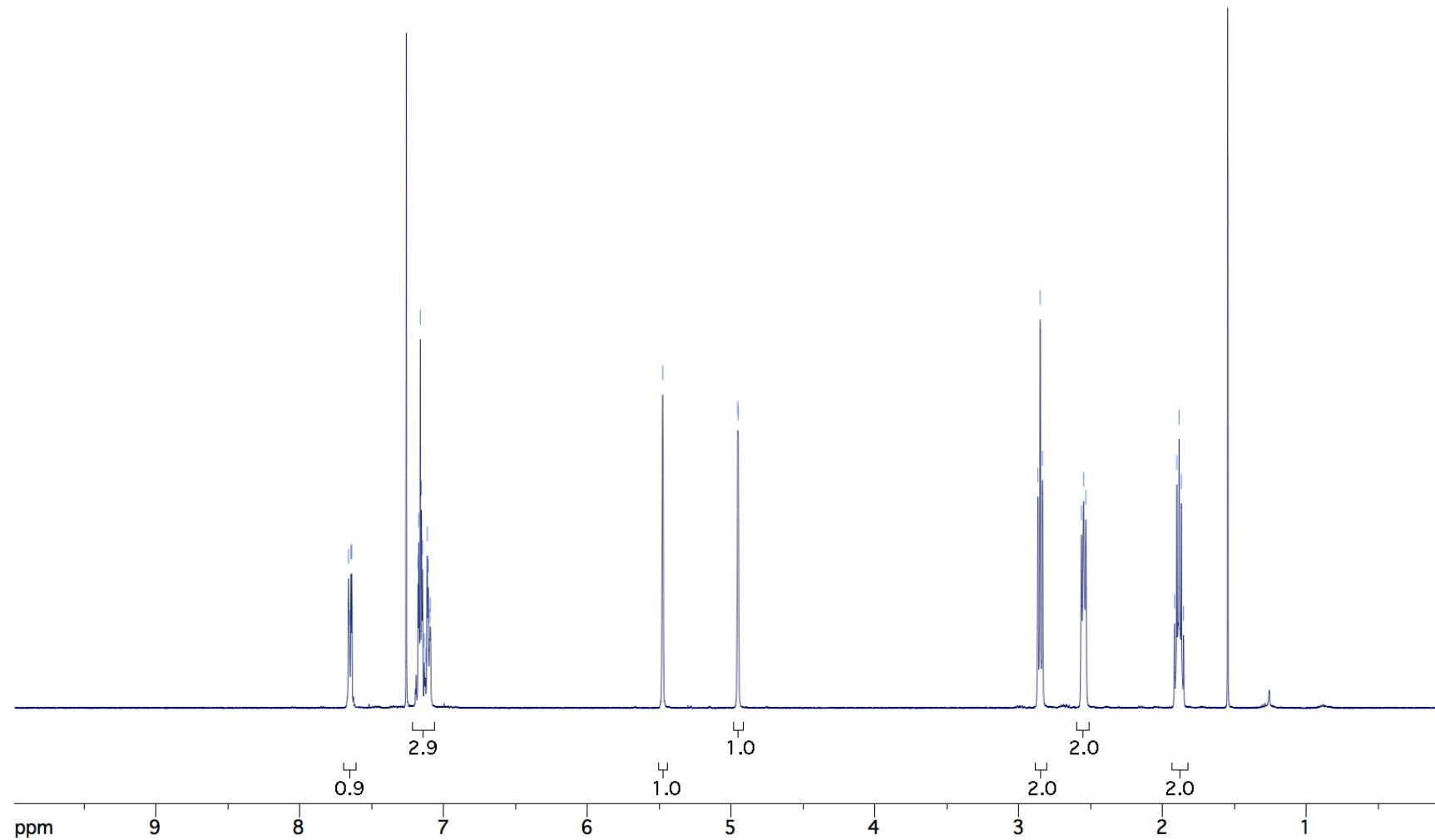
^1H NMR (CDCl_3 , 400 MHz)



7.66
7.64
7.64
7.18
7.18
7.18
7.18
7.16
7.15
7.15
7.13
7.13
7.11
7.11
7.10
7.09

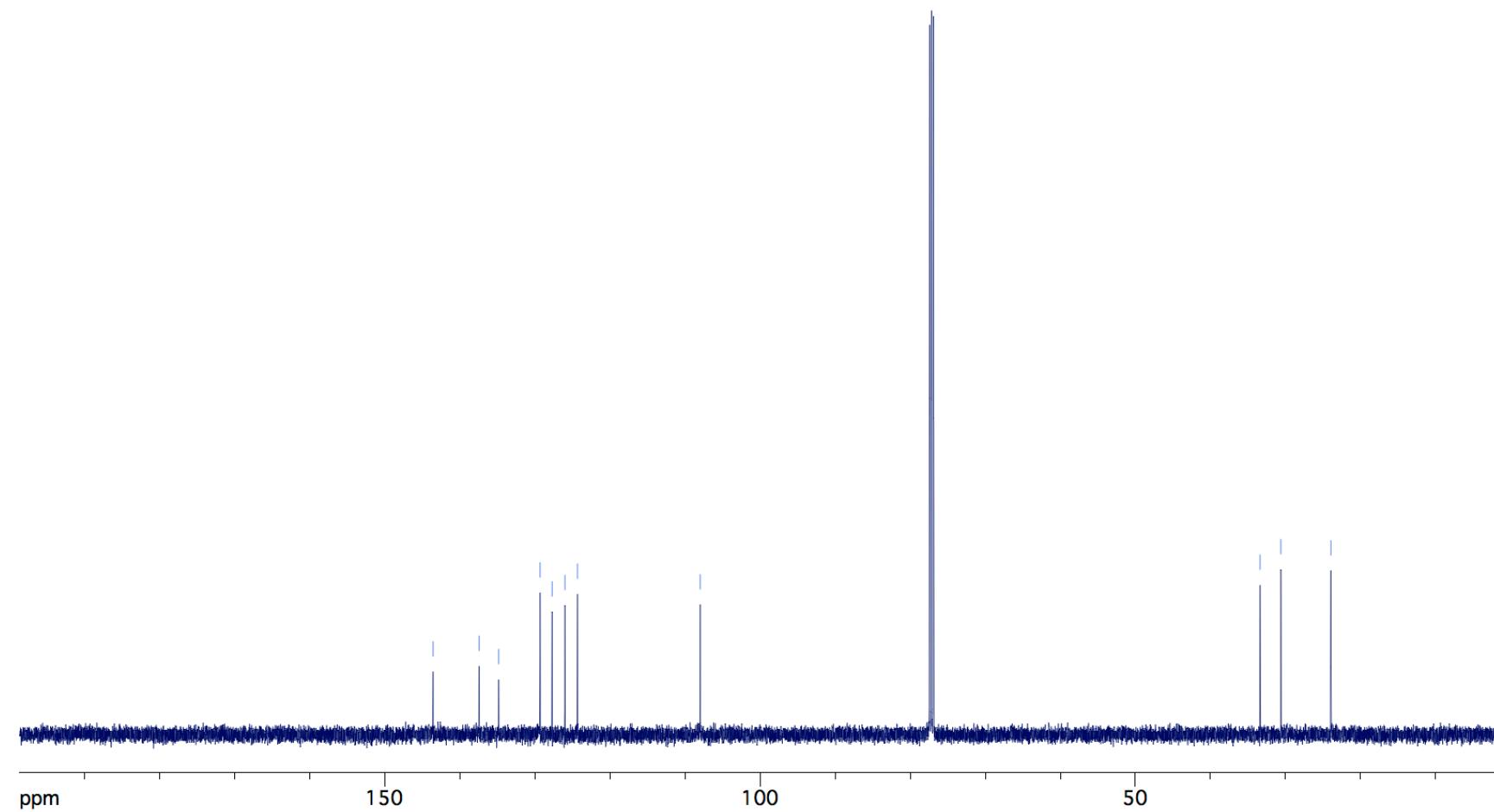
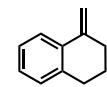
5.48
4.95

2.87
2.85
2.84
2.57
2.55
2.53
1.92
1.90
1.89
1.87
1.86



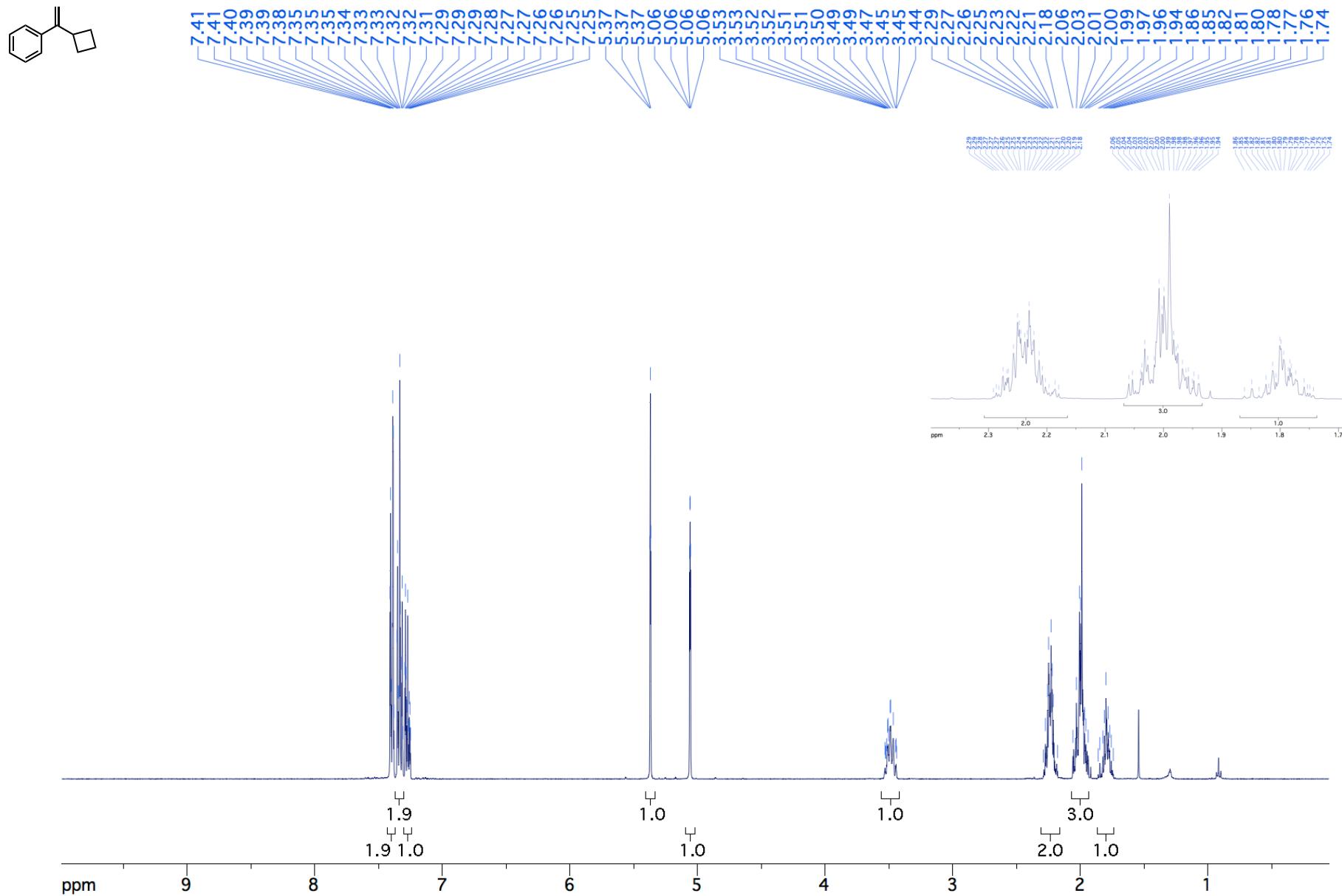
1-Methylene-1,2,3,4-tetrahydronaphthalene (22a)

^{13}C NMR (CDCl_3 , 100 MHz)



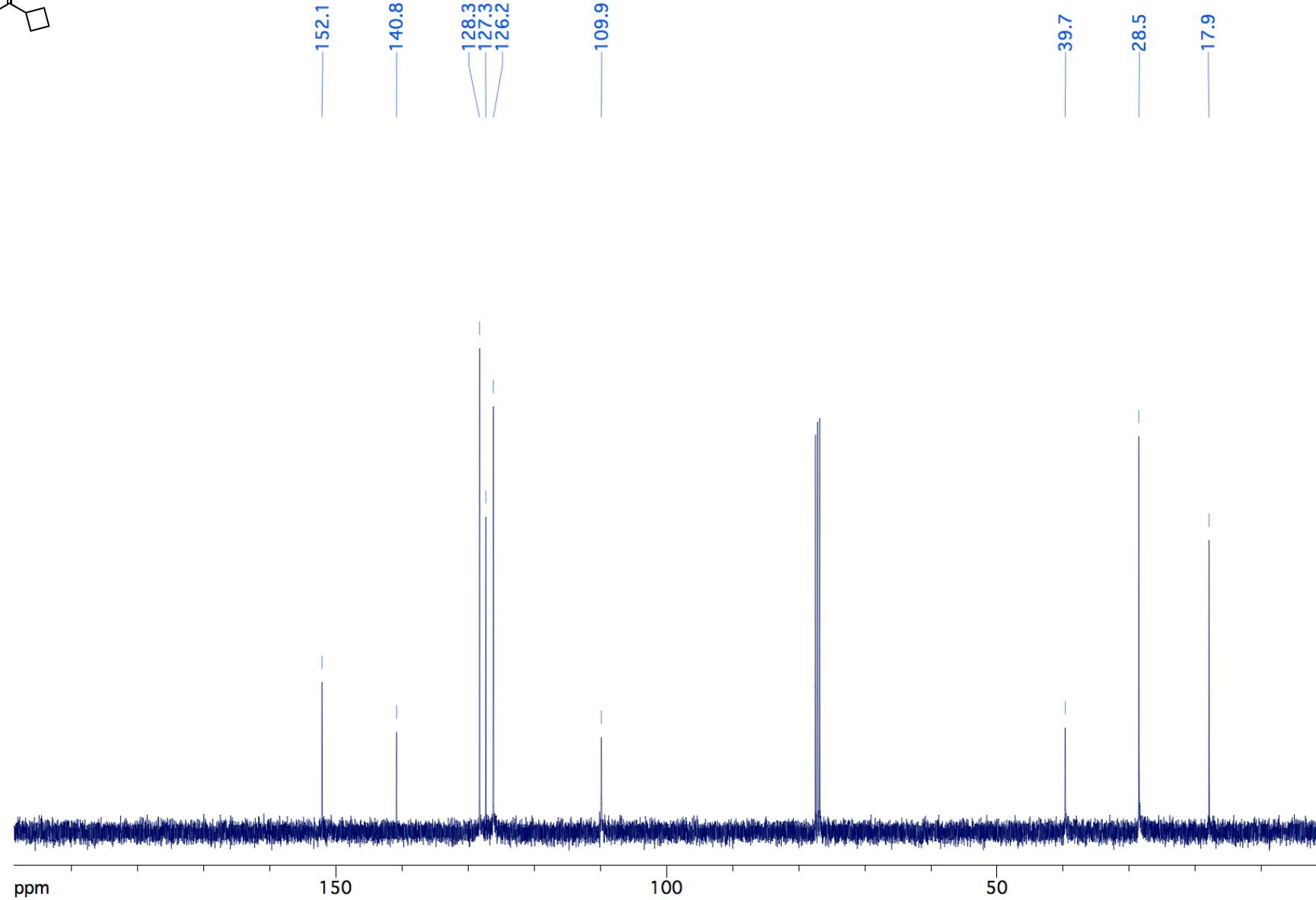
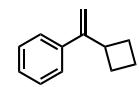
(1-Cyclobutylvinyl)benzene (23a)

^1H NMR (CDCl_3 , 400 MHz)



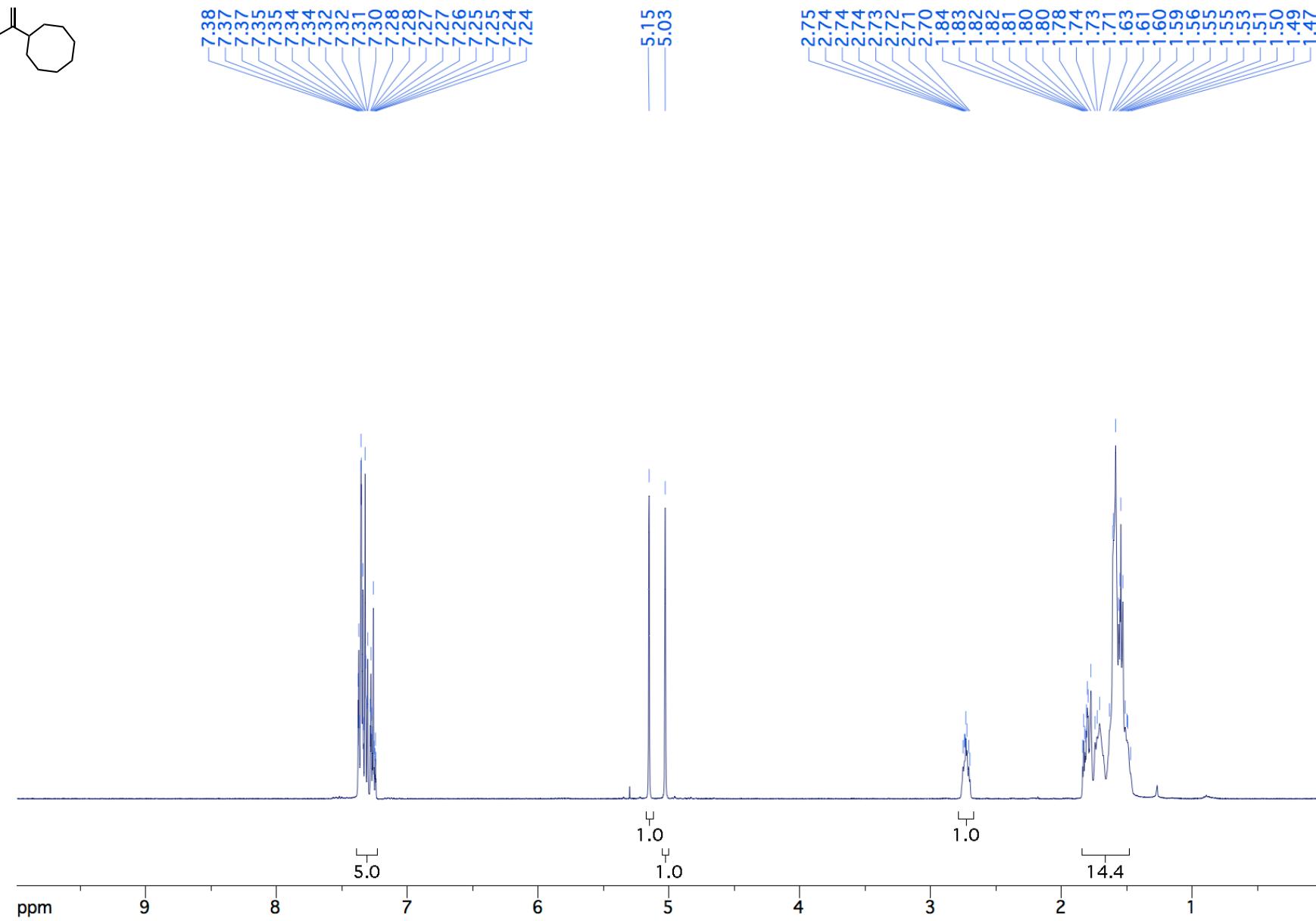
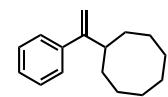
(1-Cyclobutylvinyl)benzene (23a)

^{13}C NMR (CDCl_3 , 100 MHz)



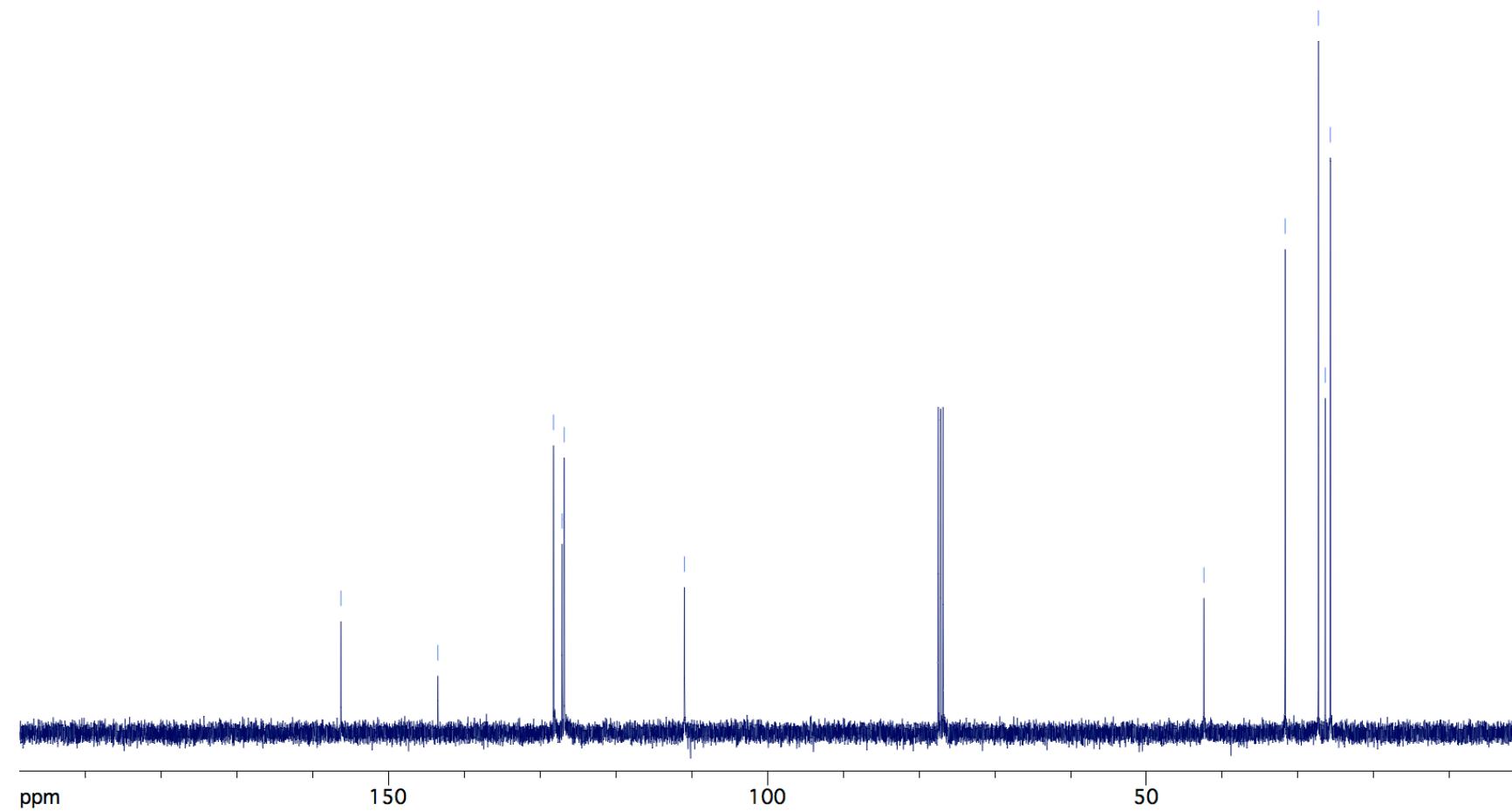
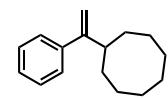
(1-Phenylvinyl)cyclooctane (24a)

^1H NMR (CDCl_3 , 400 MHz)

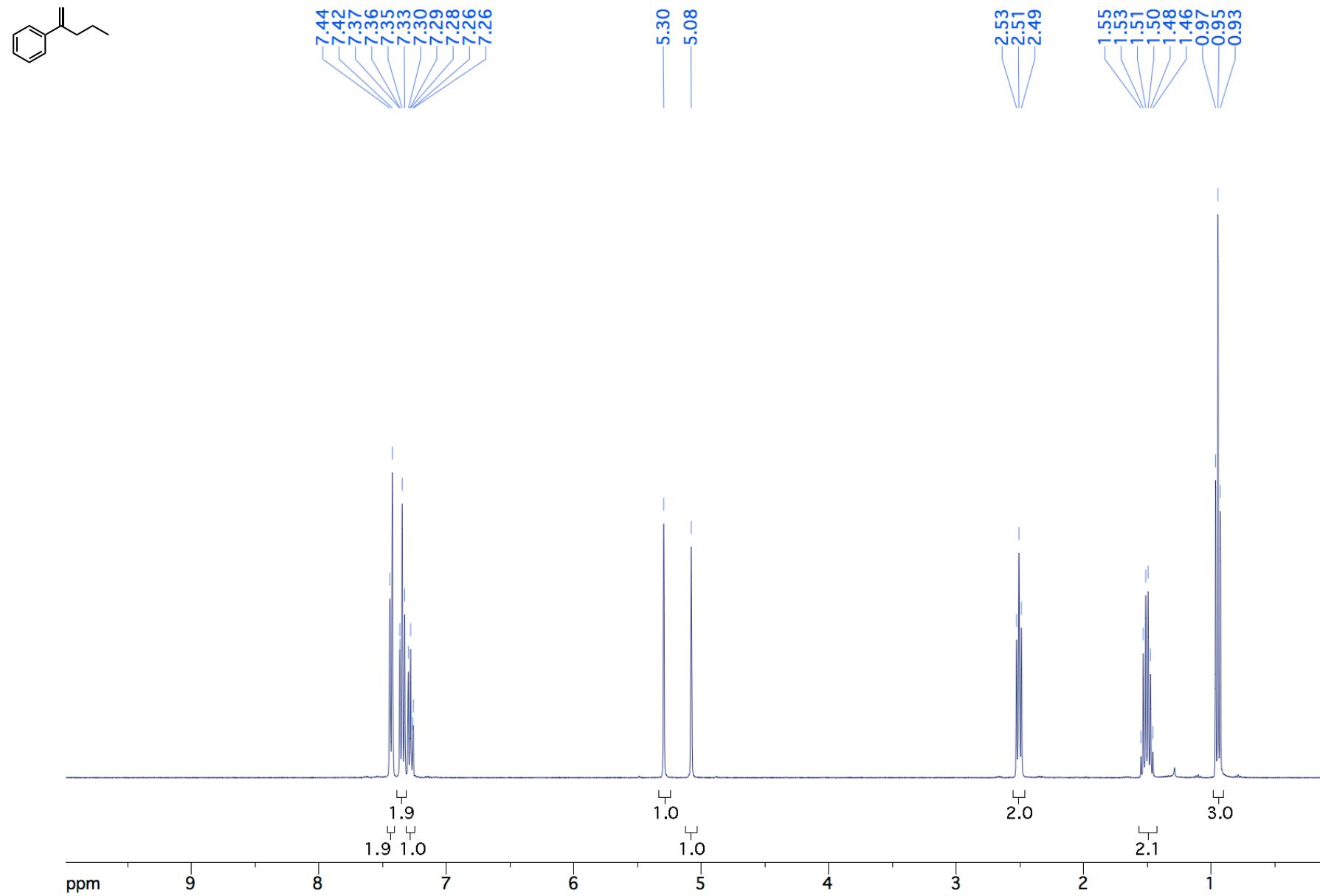


(1-Phenylvinyl)cyclooctane (24a)

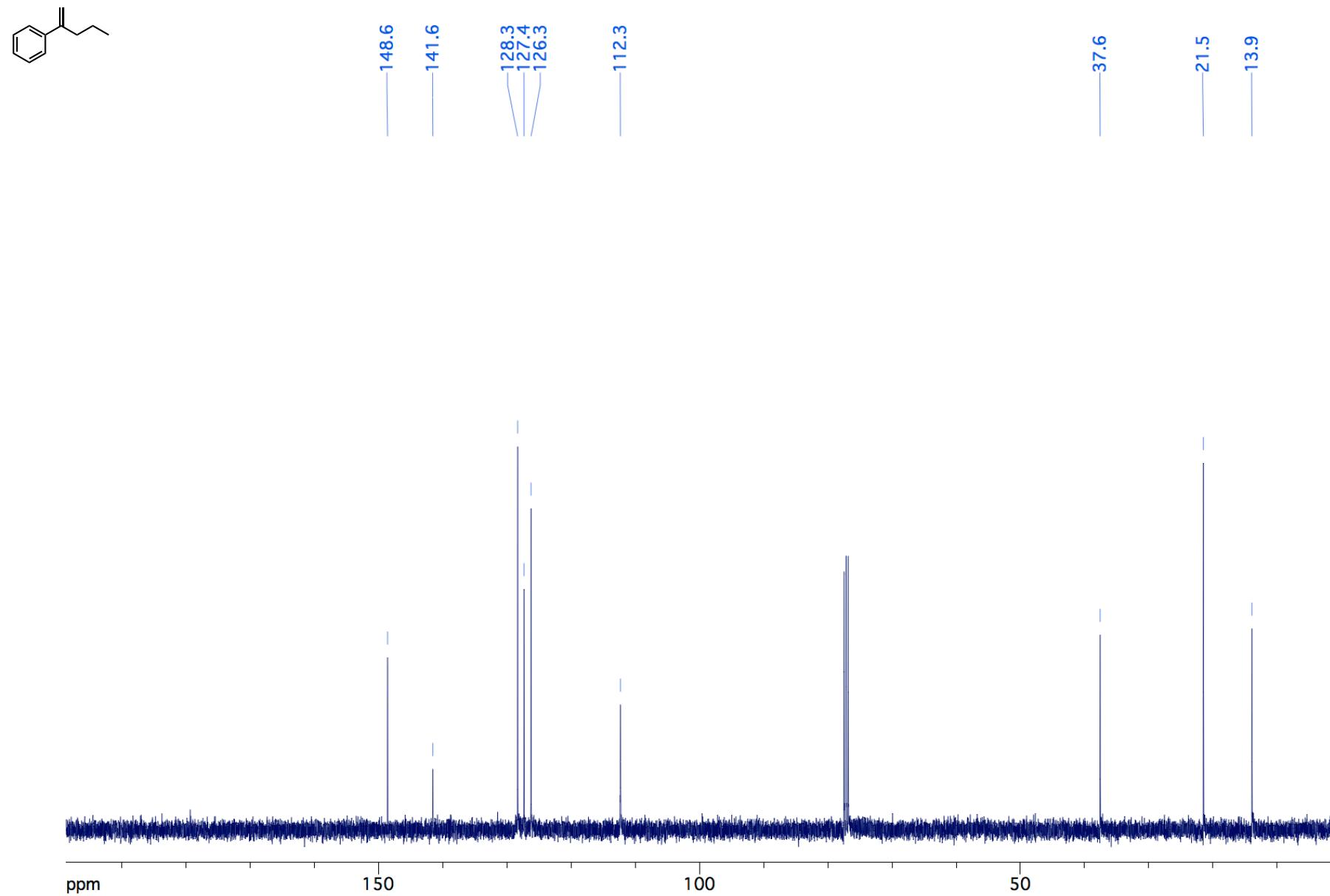
^{13}C NMR (CDCl_3 , 100 MHz)



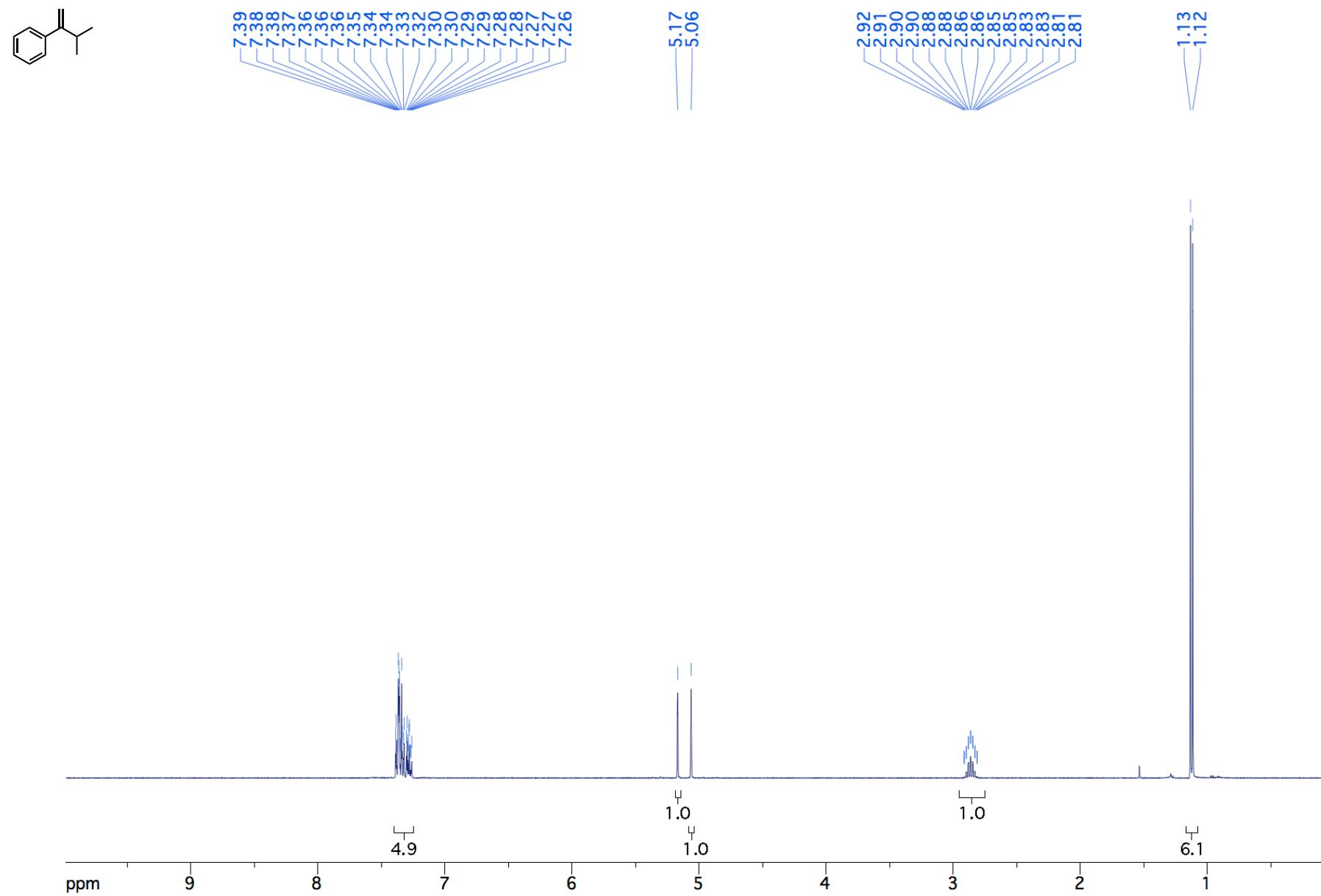
Pent-1-en-2-ylbenzene (25a) ^1H NMR (CDCl_3 , 400 MHz)



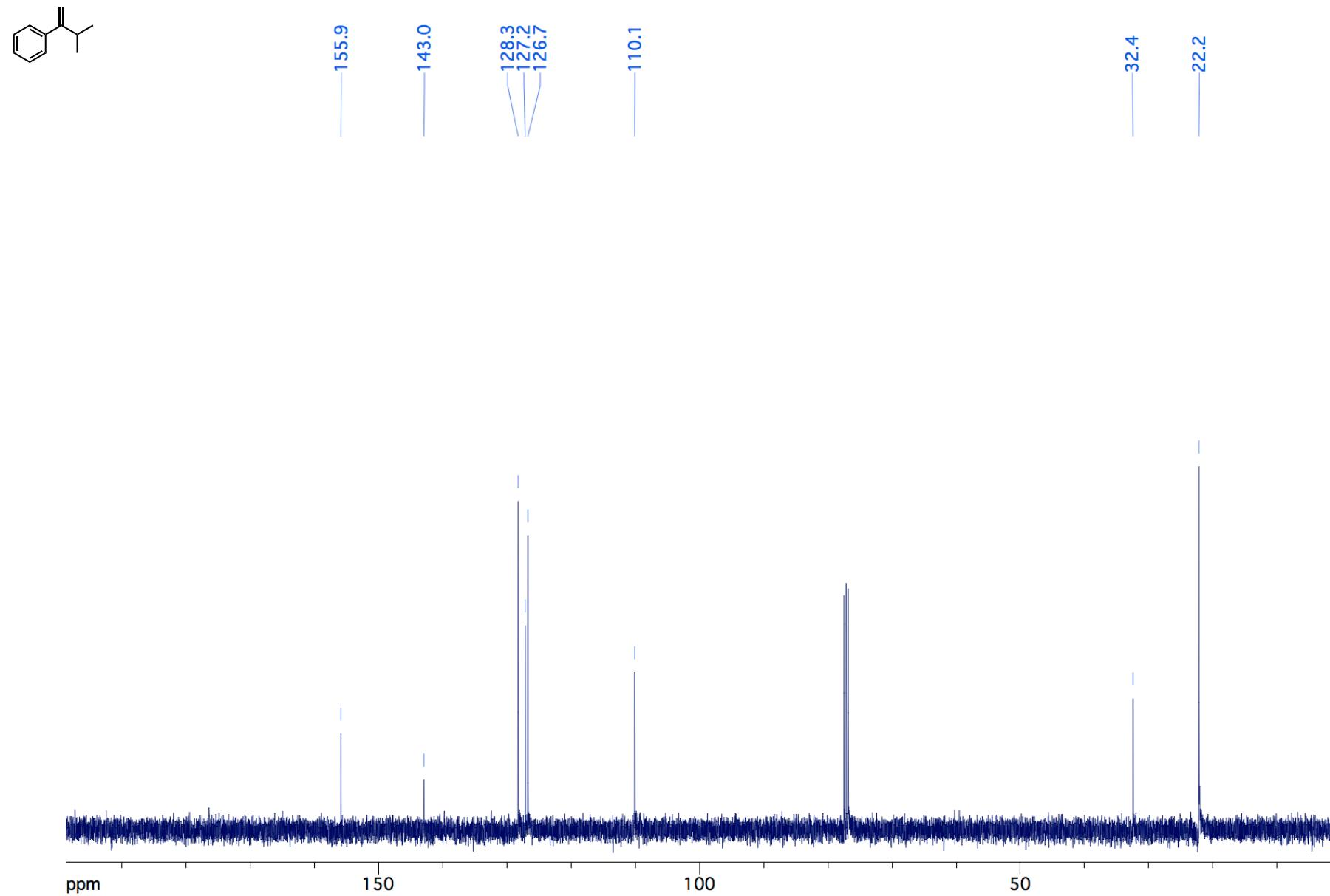
Pent-1-en-2-ylbenzene (25a) ^{13}C NMR (CDCl_3 , 100 MHz)



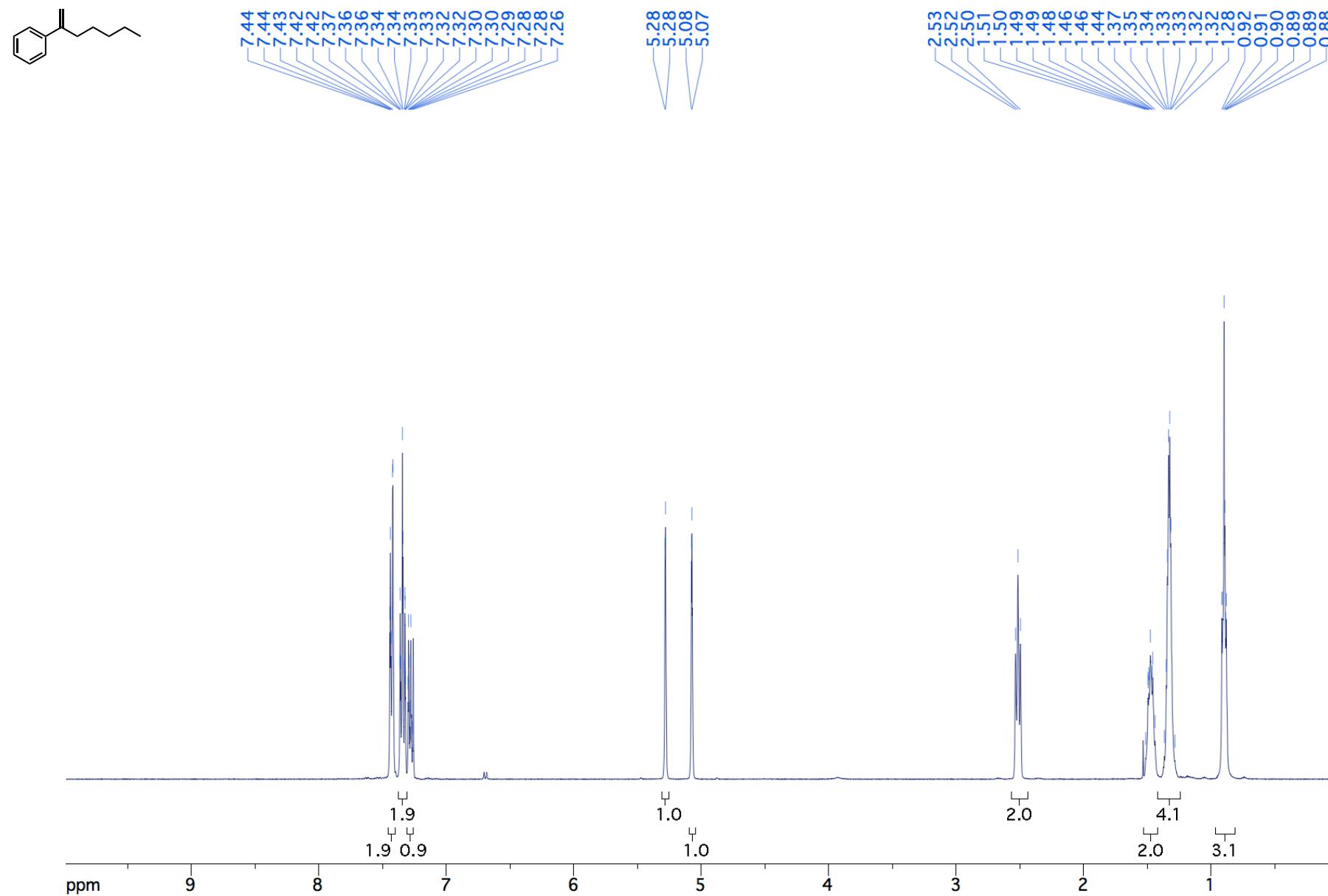
(3-Methylbut-1-en-2-yl)benzene (26a) ^1H NMR (CDCl_3 , 400 MHz)



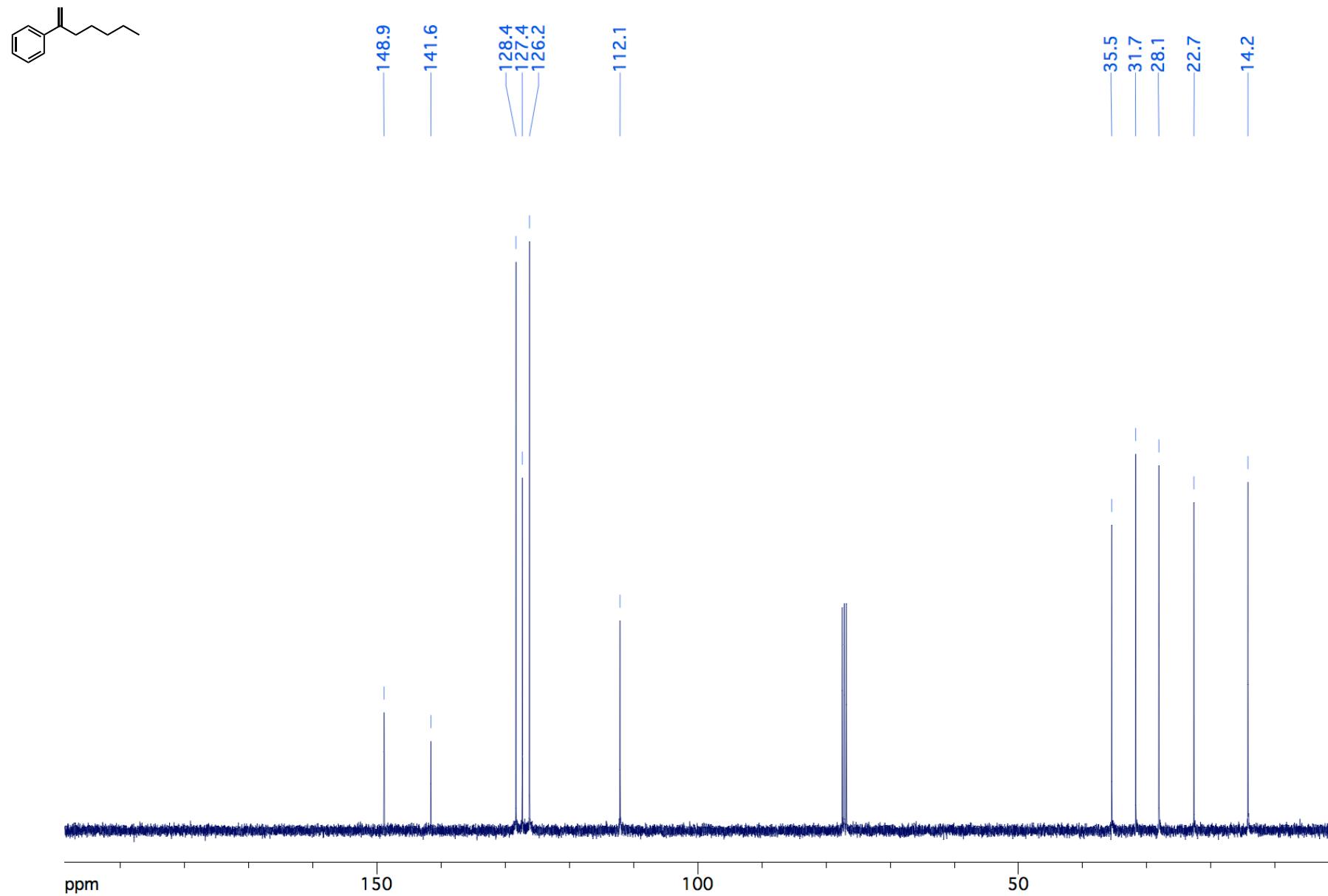
(3-Methylbut-1-en-2-yl)benzene (26a) ^{13}C NMR (CDCl_3 , 100 MHz)



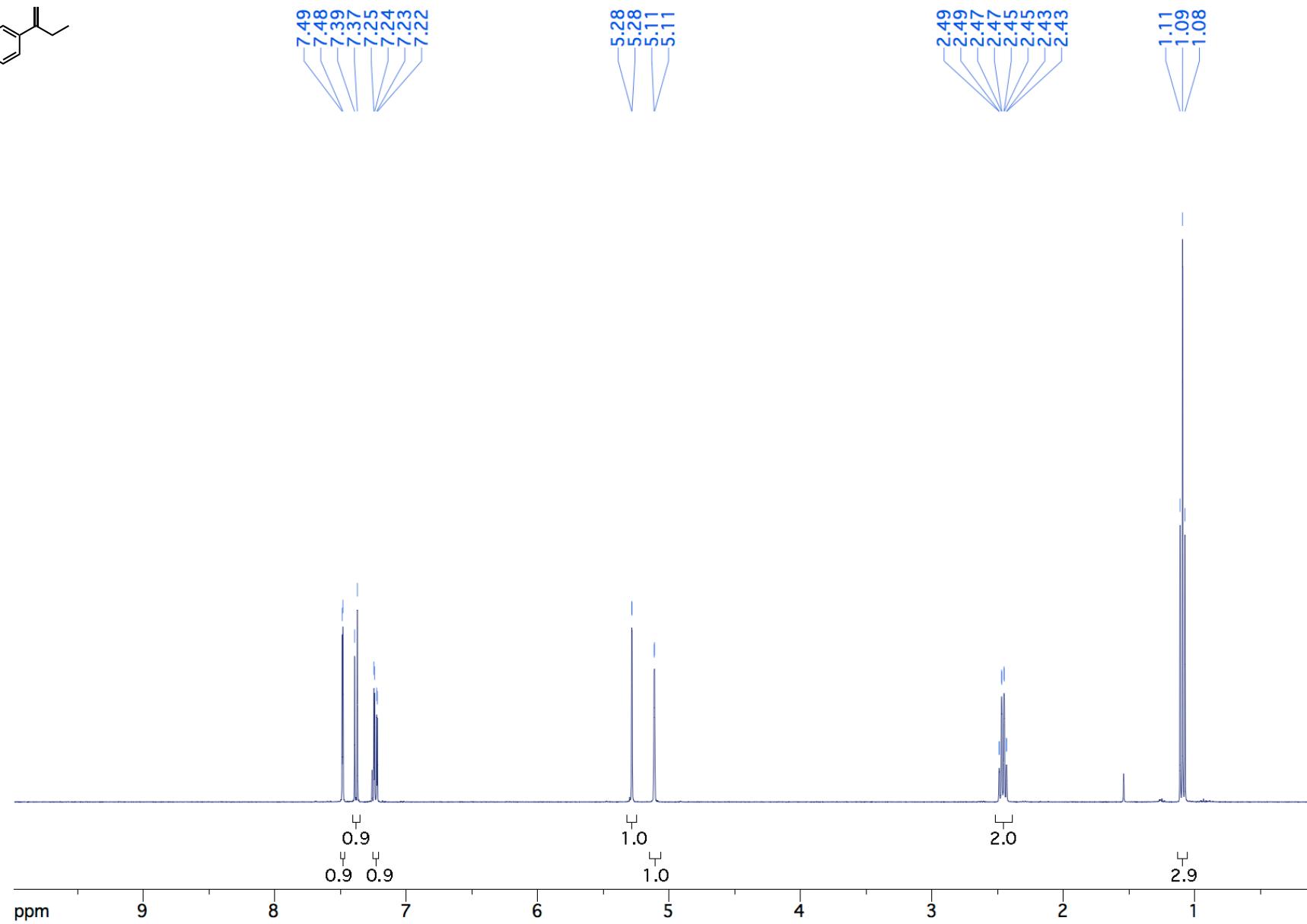
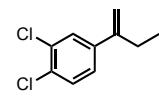
Hept-1-en-2-ylbenzene (27a) ^1H NMR (CDCl_3 , 400 MHz)



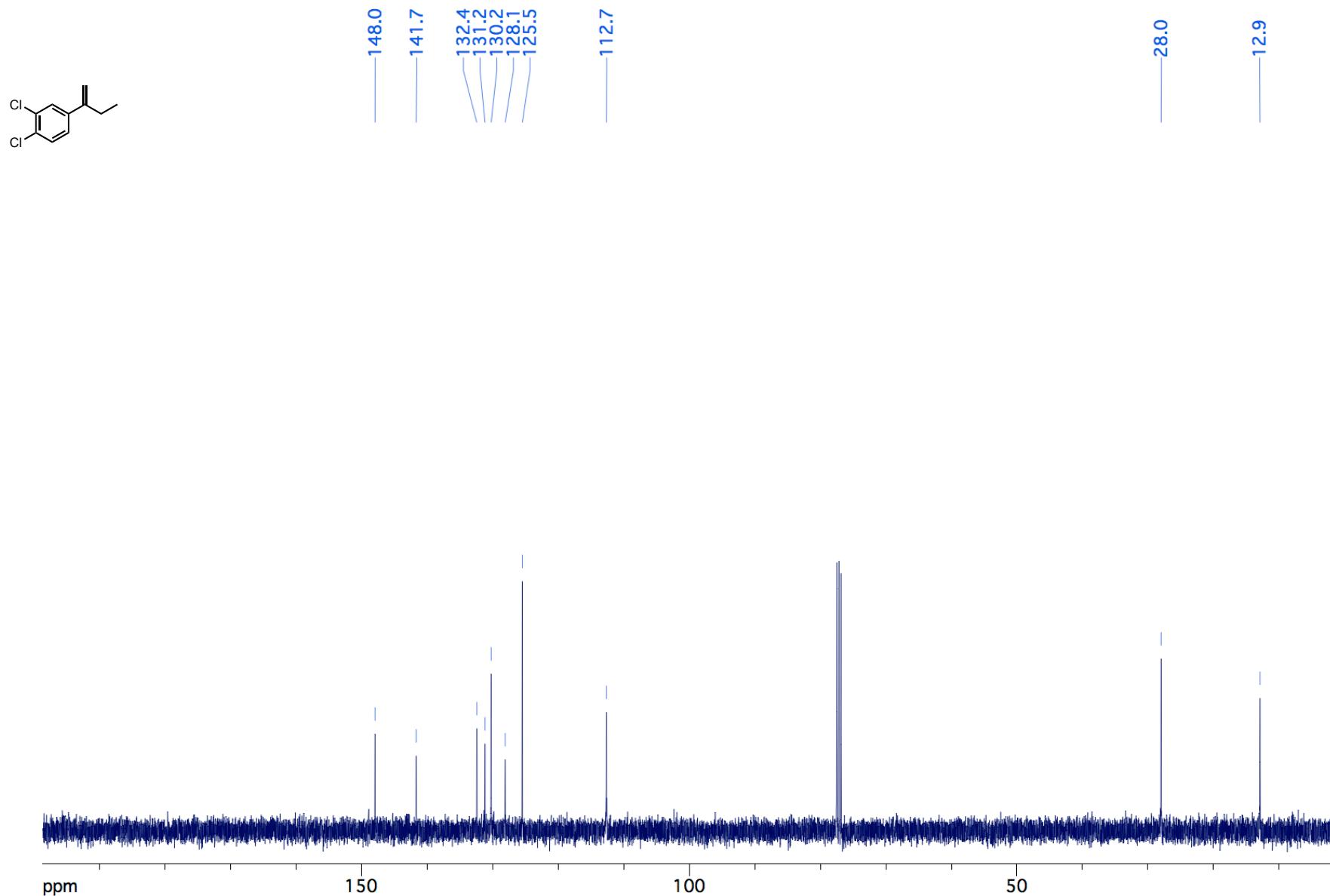
Hept-1-en-2-ylbenzene (27a) ^{13}C NMR (CDCl_3 , 100 MHz)



4-(But-1-en-2-yl)-1,2-dichlorobenzene (28a) ^1H NMR (CDCl_3 , 400 MHz)

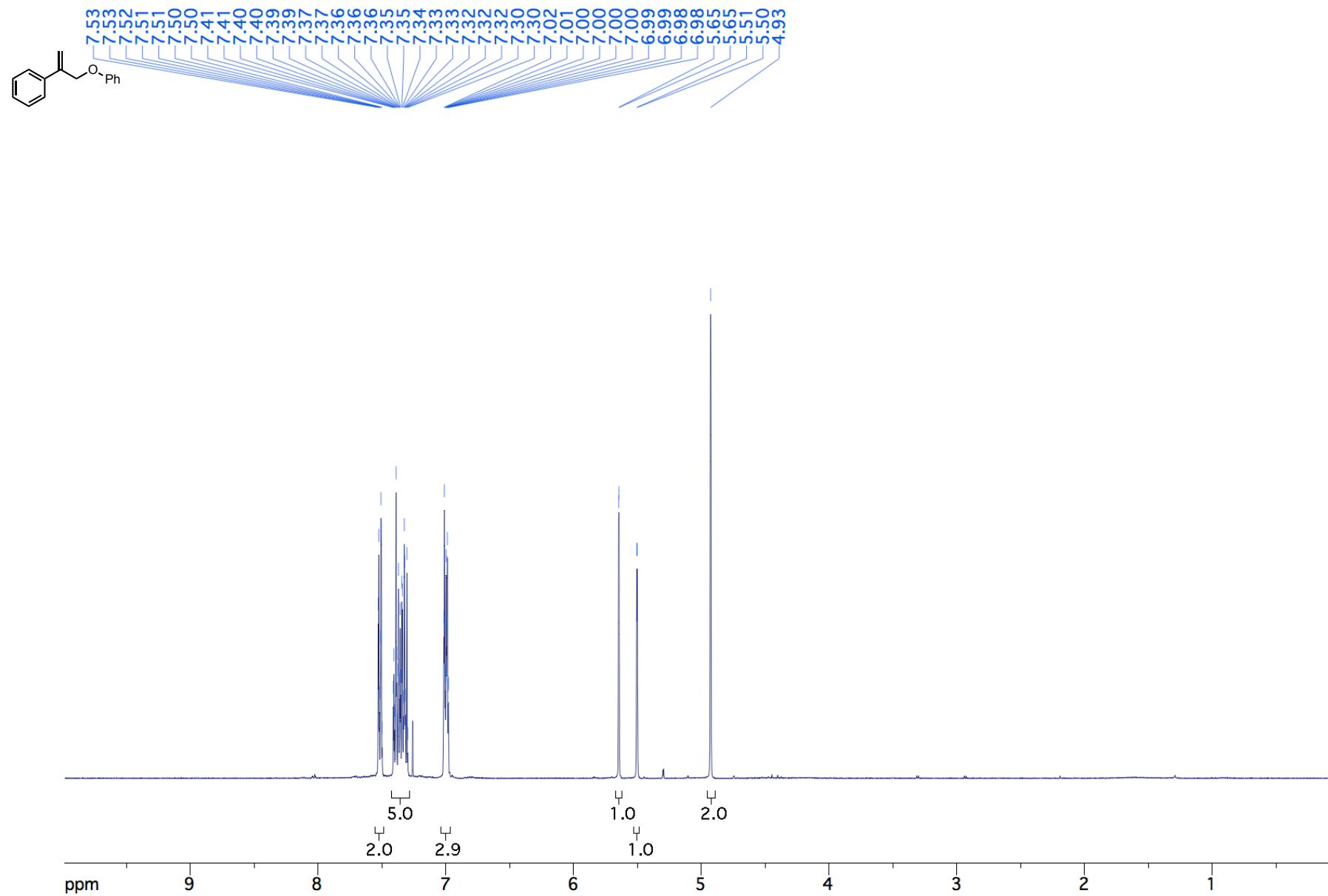


4-(But-1-en-2-yl)-1,2-dichlorobenzene (28a) ^{13}C NMR (CDCl_3 , 100 MHz)



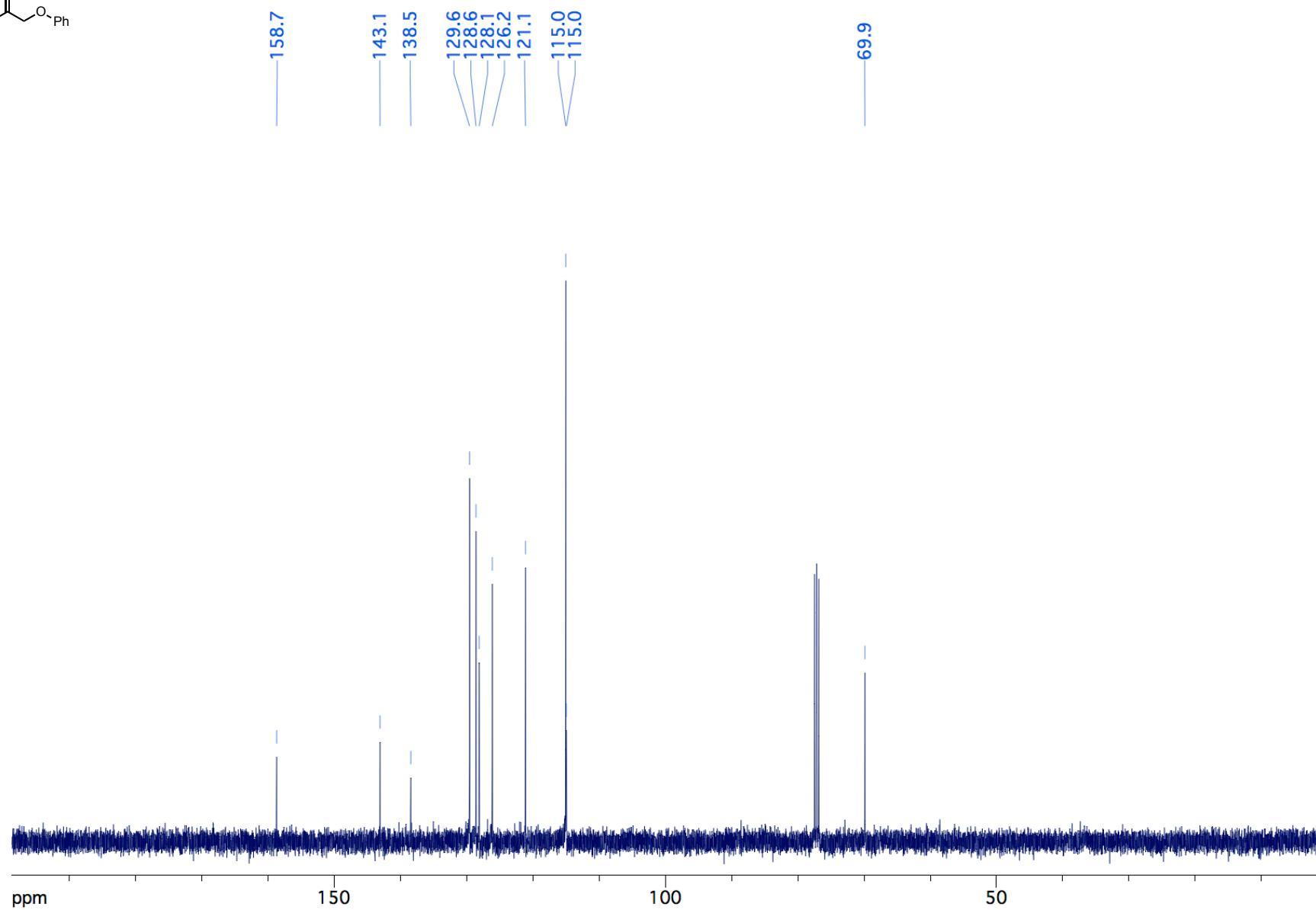
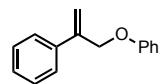
(3-Phenoxyprop-1-en-2-yl)benzene (29a)

^1H NMR (CDCl_3 , 400 MHz)



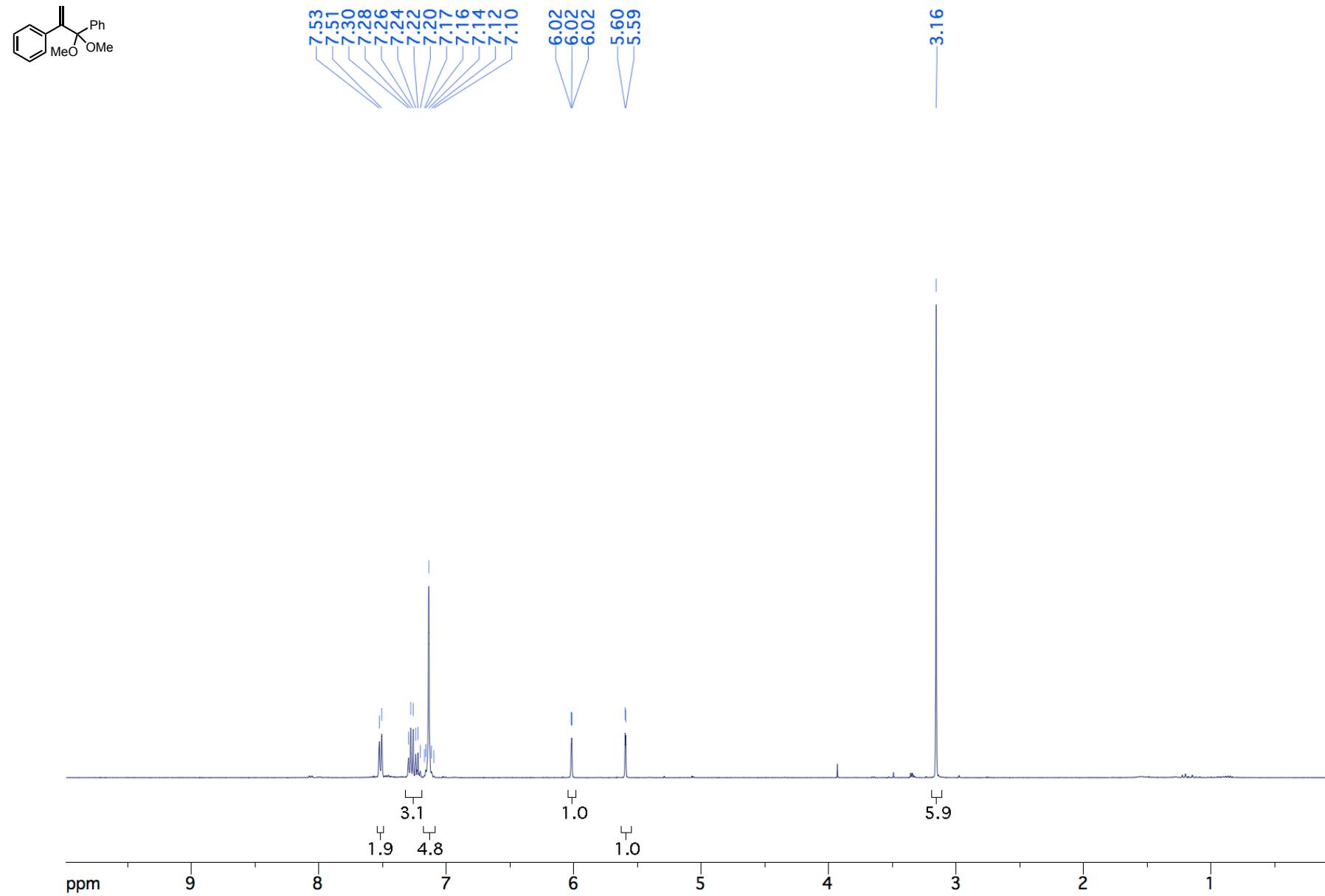
(3-Phenoxyprop-1-en-2-yl)benzene (29a)

^{13}C NMR (CDCl_3 , 100 MHz)



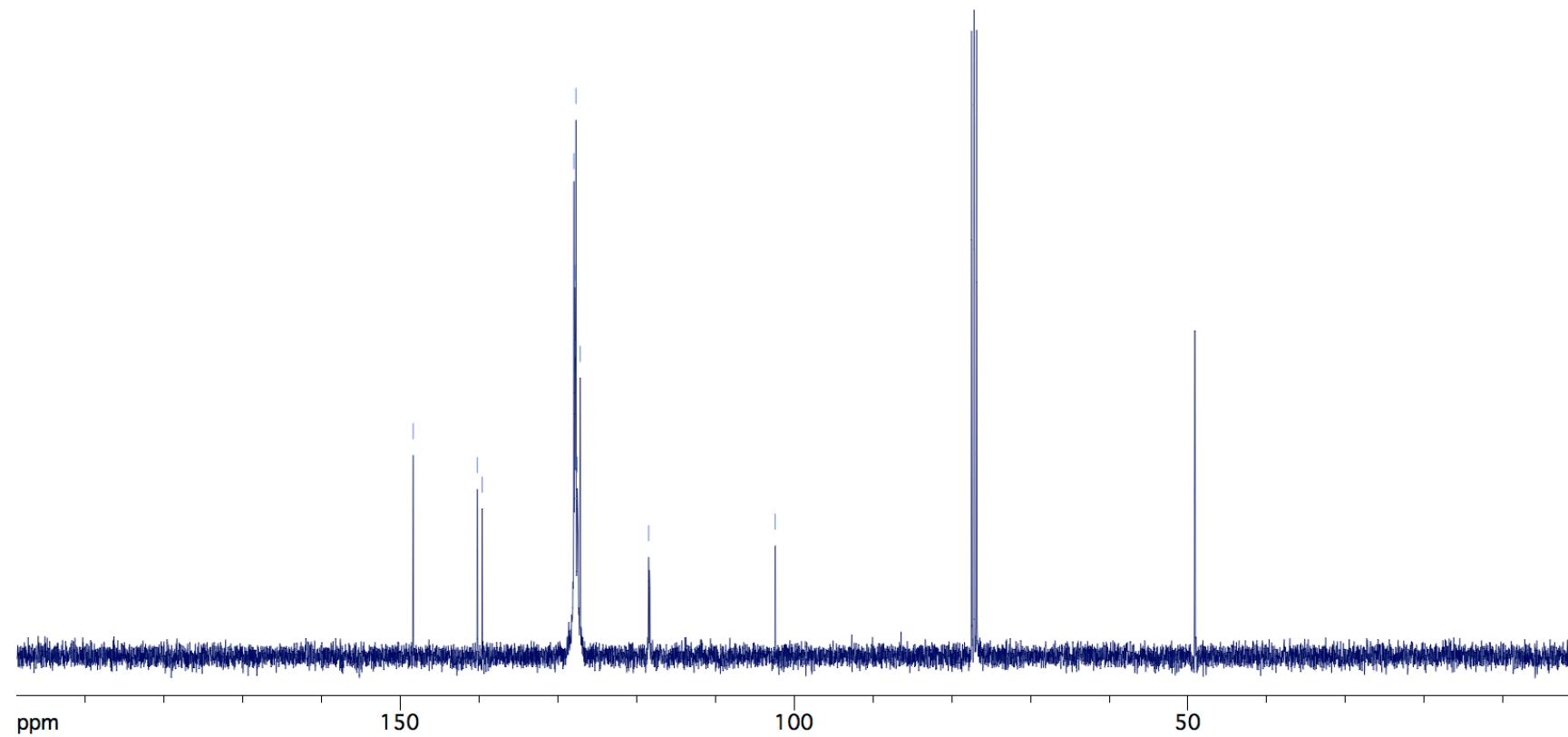
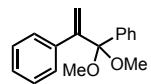
(1,1-Dimethoxyprop-2-ene-1,2-diyil)dibenzene (30a)

¹H NMR (CDCl₃, 400 MHz)



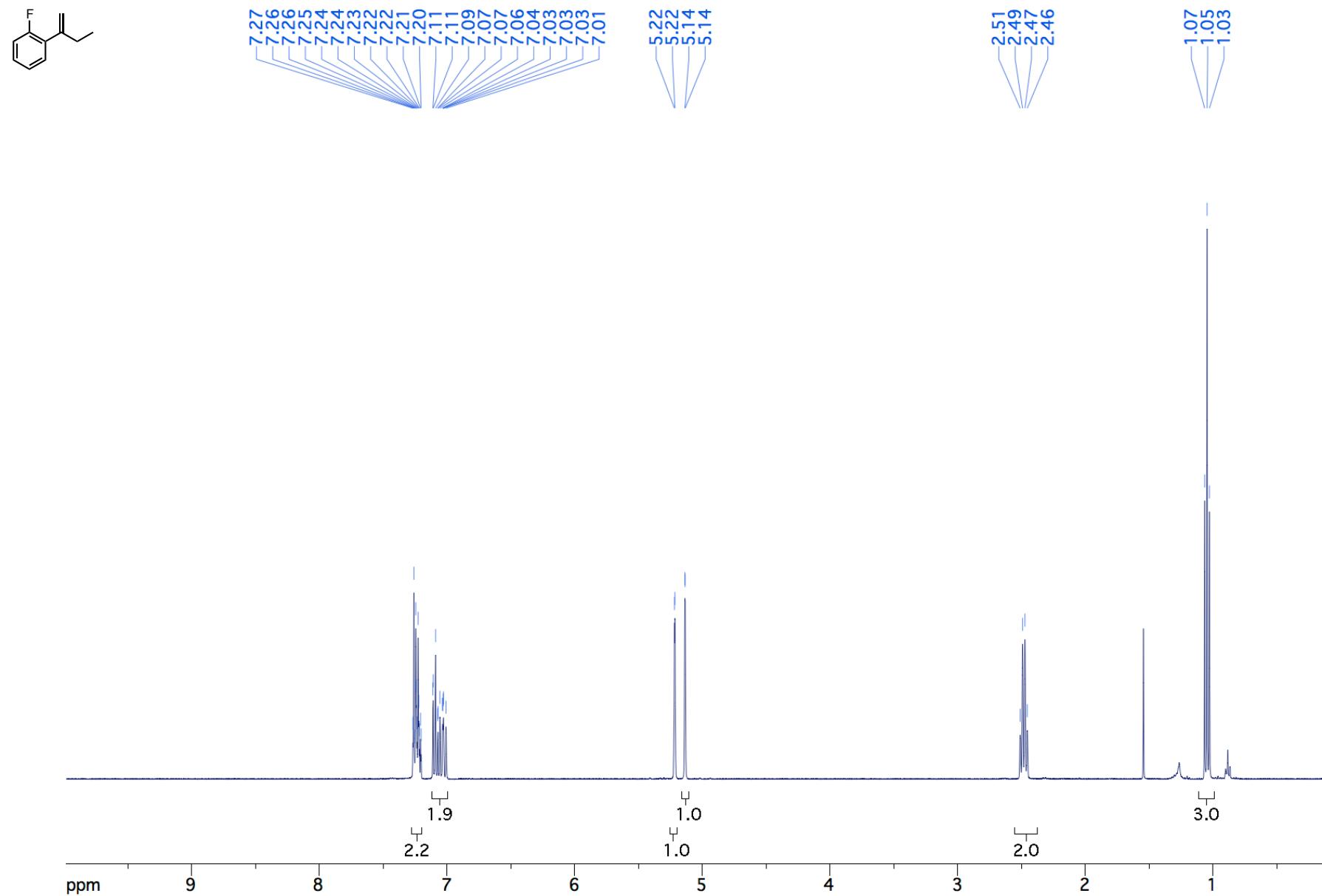
(1,1-Dimethoxyprop-2-ene-1,2-diyl)dibenzene (30a)

^{13}C NMR (CDCl_3 , 100 MHz)



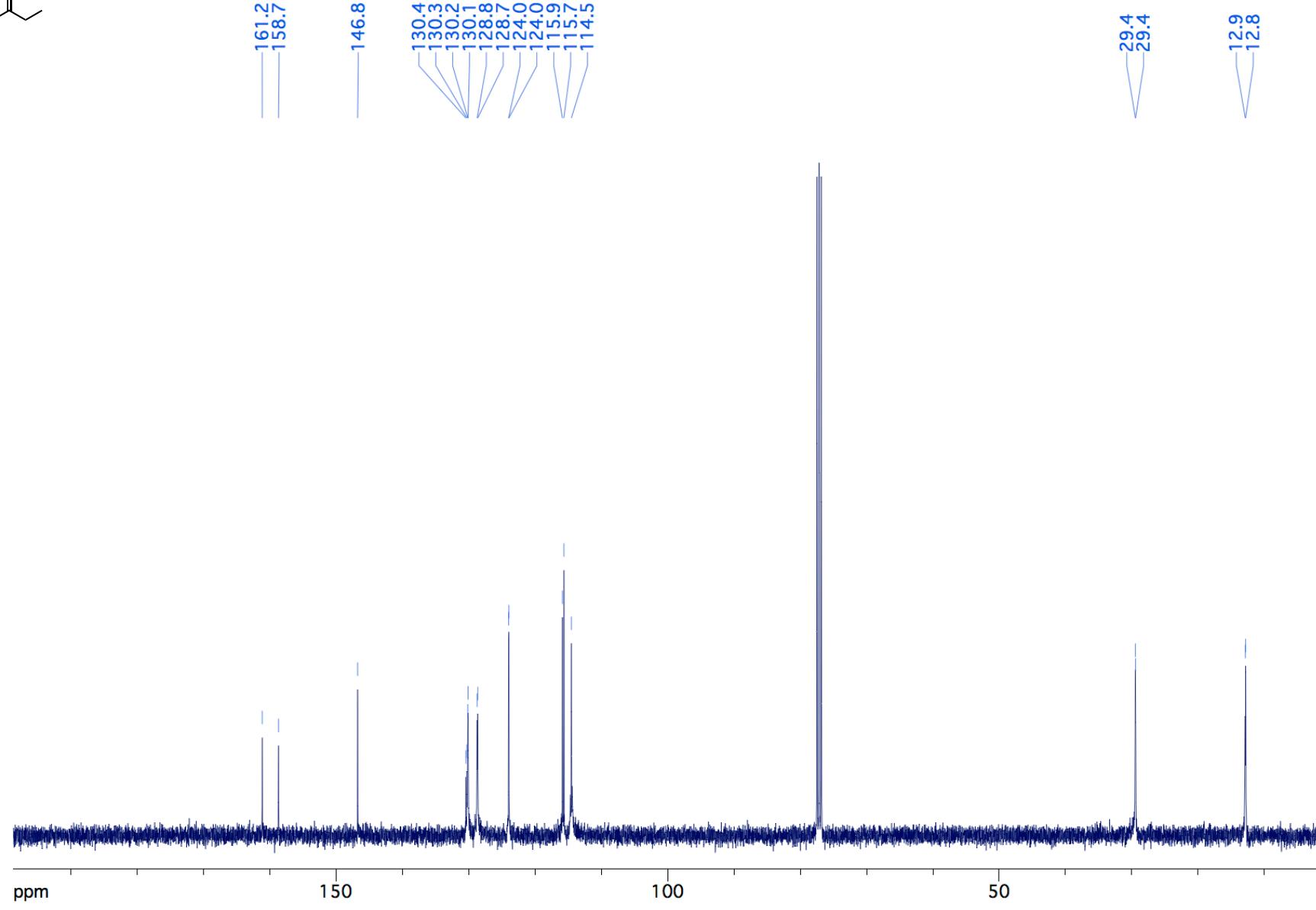
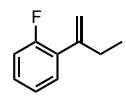
1-(But-1-en-2-yl)-2-fluorobenzene (31a)

¹H NMR (CDCl₃, 400 MHz)



1-(But-1-en-2-yl)-2-fluorobenzene (31a)

¹³C NMR (CDCl₃, 100 MHz)



ppm

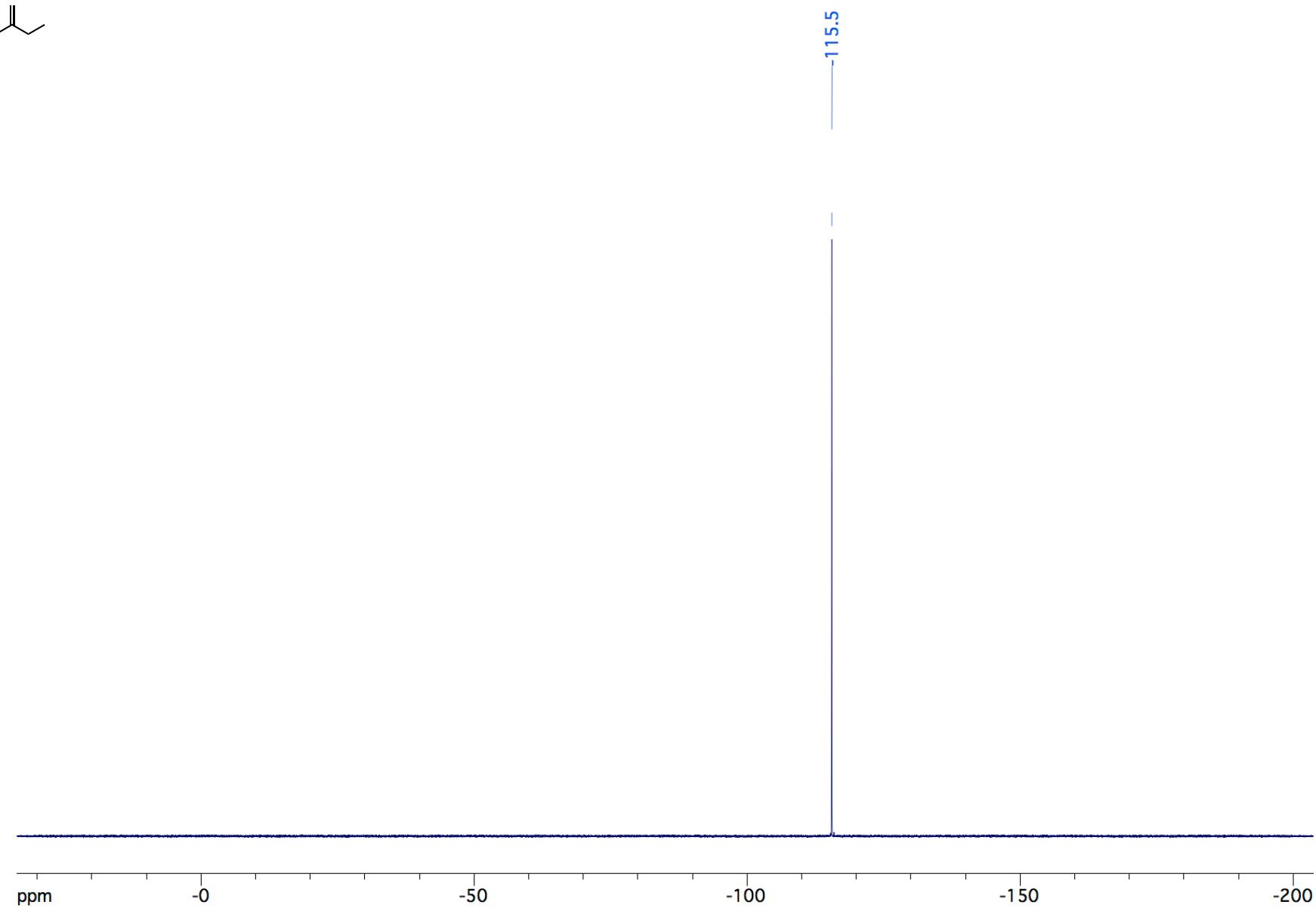
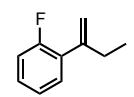
150

100

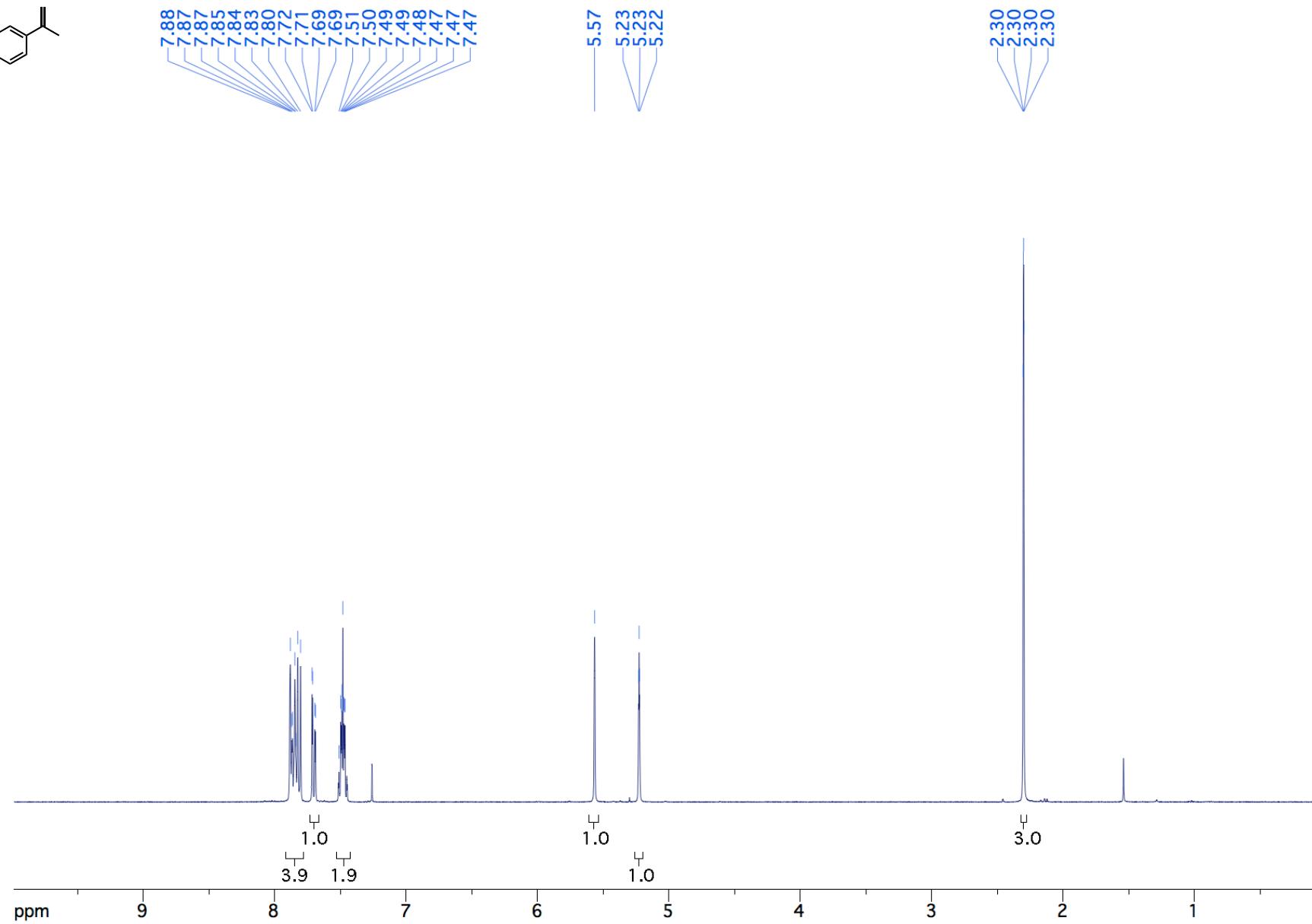
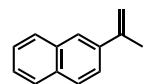
50

100

1-(But-1-en-2-yl)-2-fluorobenzene (31a) ^{19}F -NMR (CDCl_3 , 376 MHz)

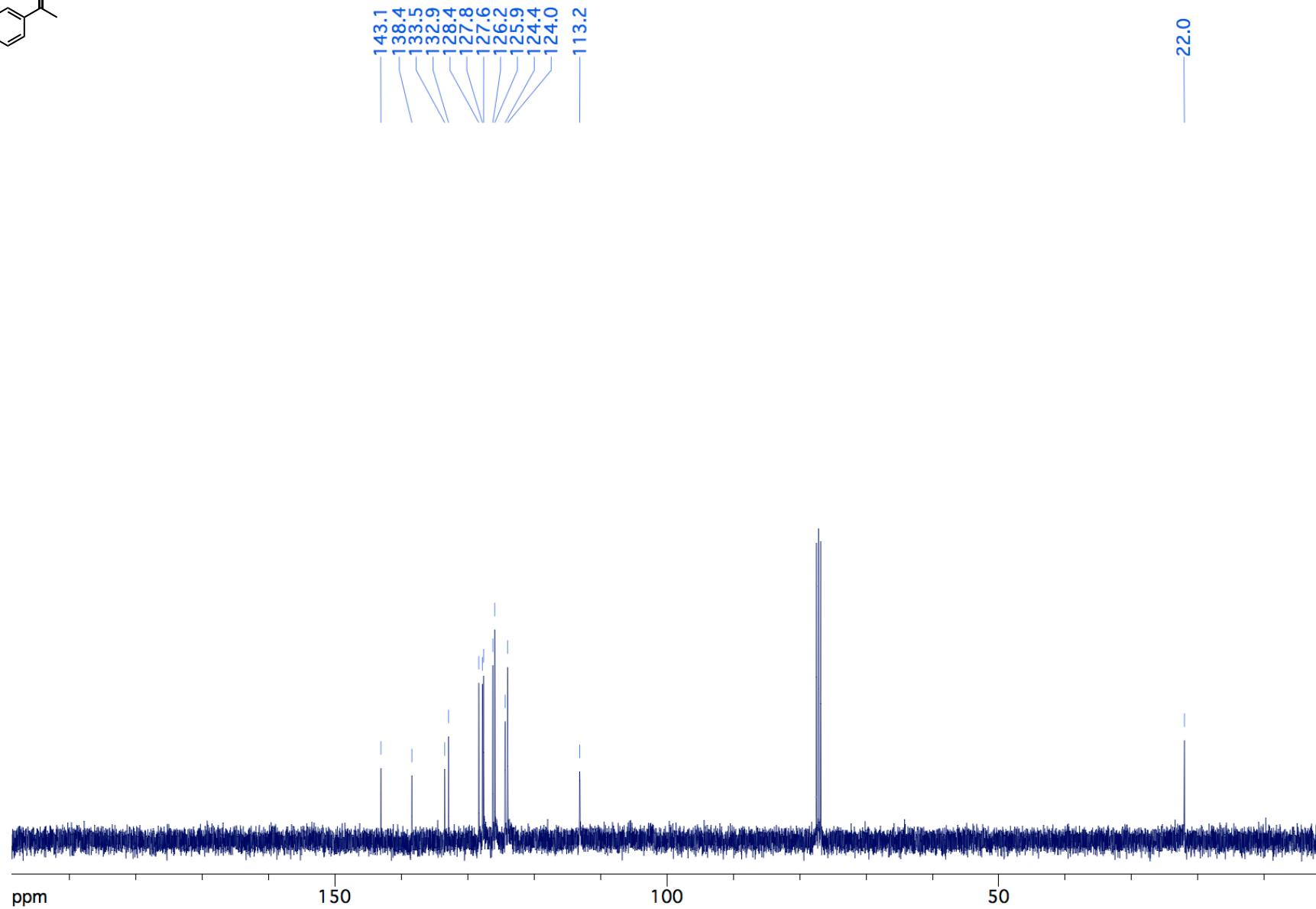
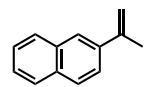


2-(Prop-1-en-2-yl)naphthalene (32a) ^1H NMR (CDCl_3 , 400 MHz)

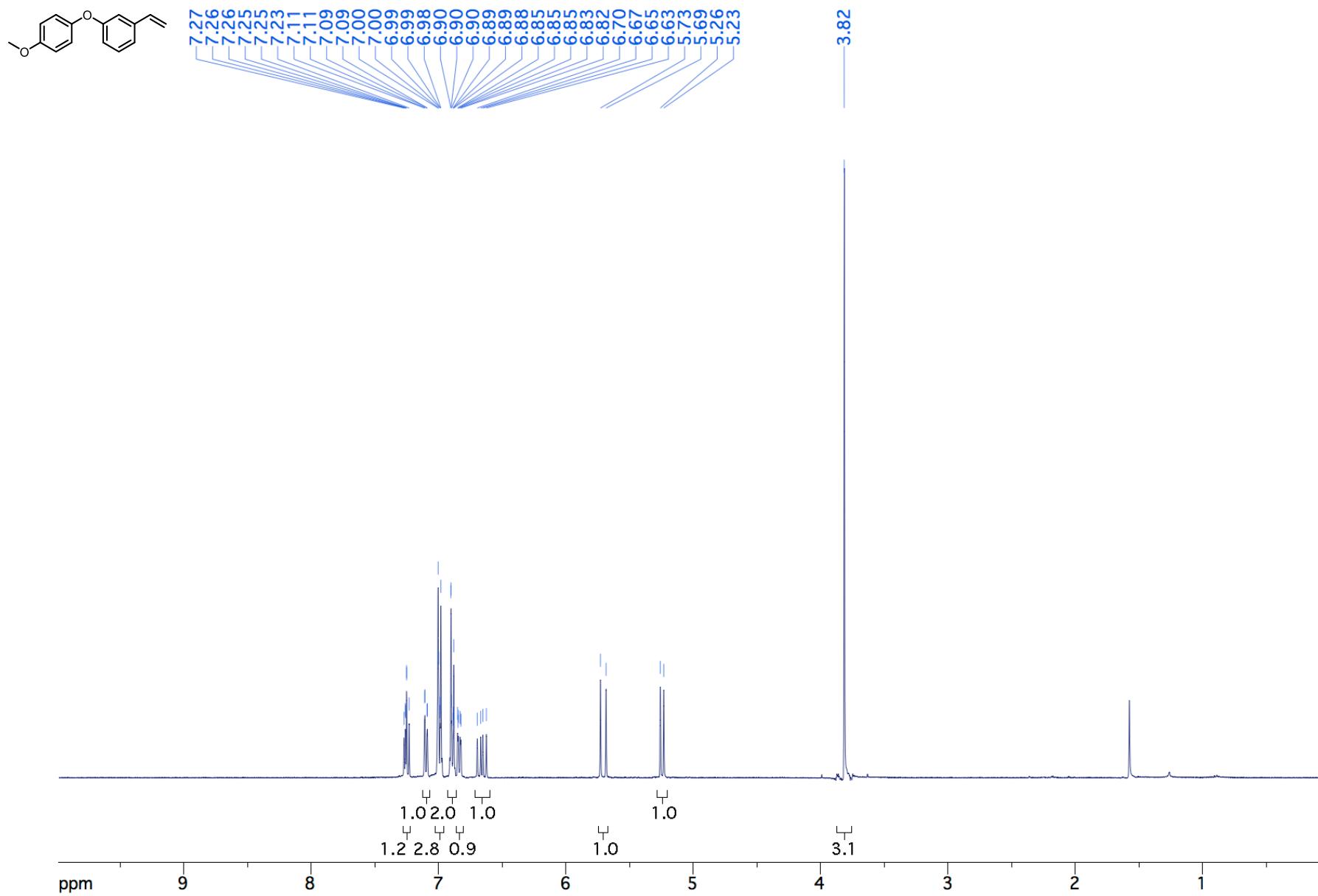


2-(Prop-1-en-2-yl)naphthalene (32a)

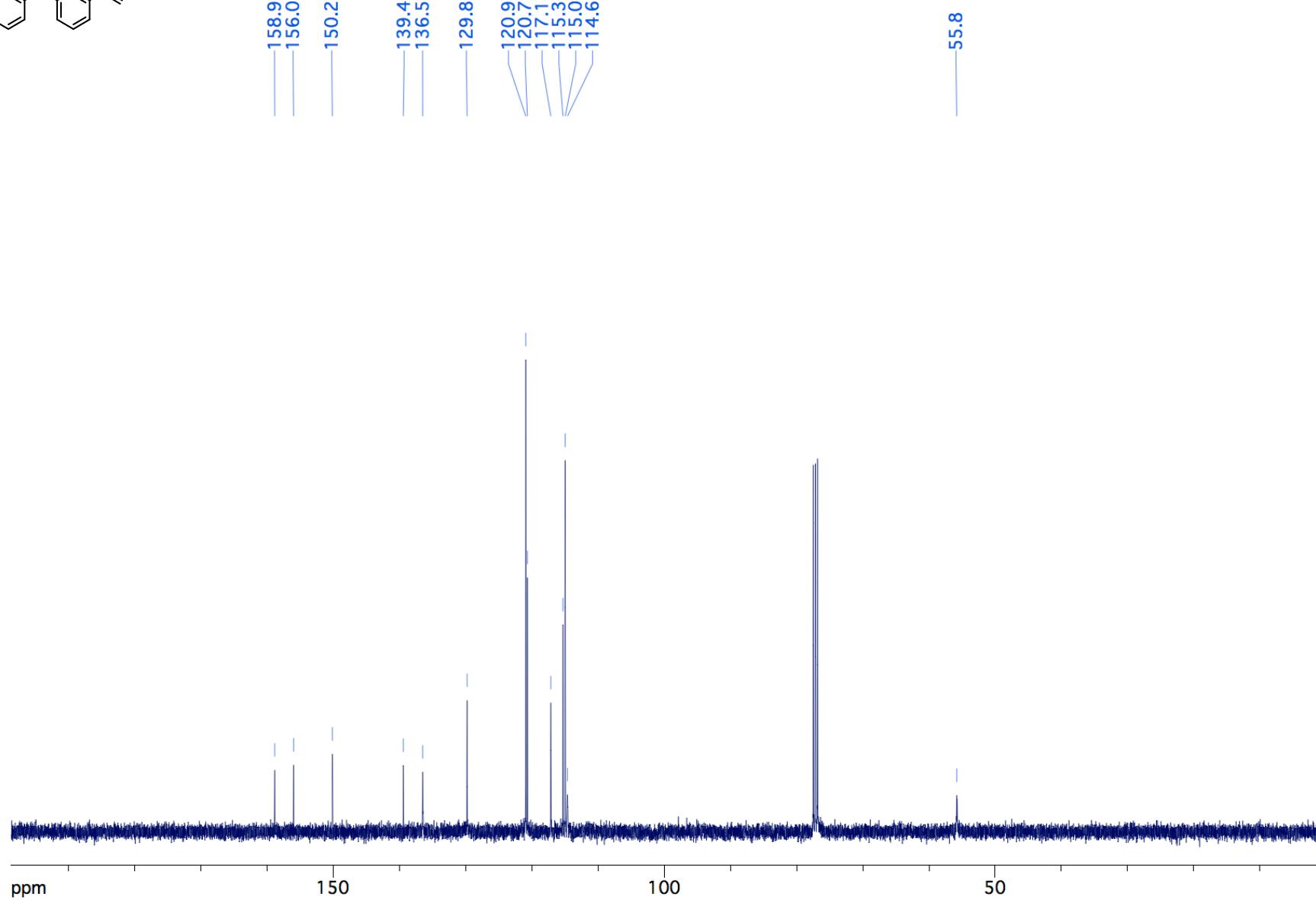
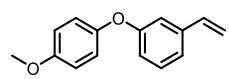
^{13}C NMR (CDCl_3 , 100 MHz)



4'-Methoxy-3-vinyl-1,1'-biphenyl (33a) ^1H NMR (CDCl_3 , 400 MHz)

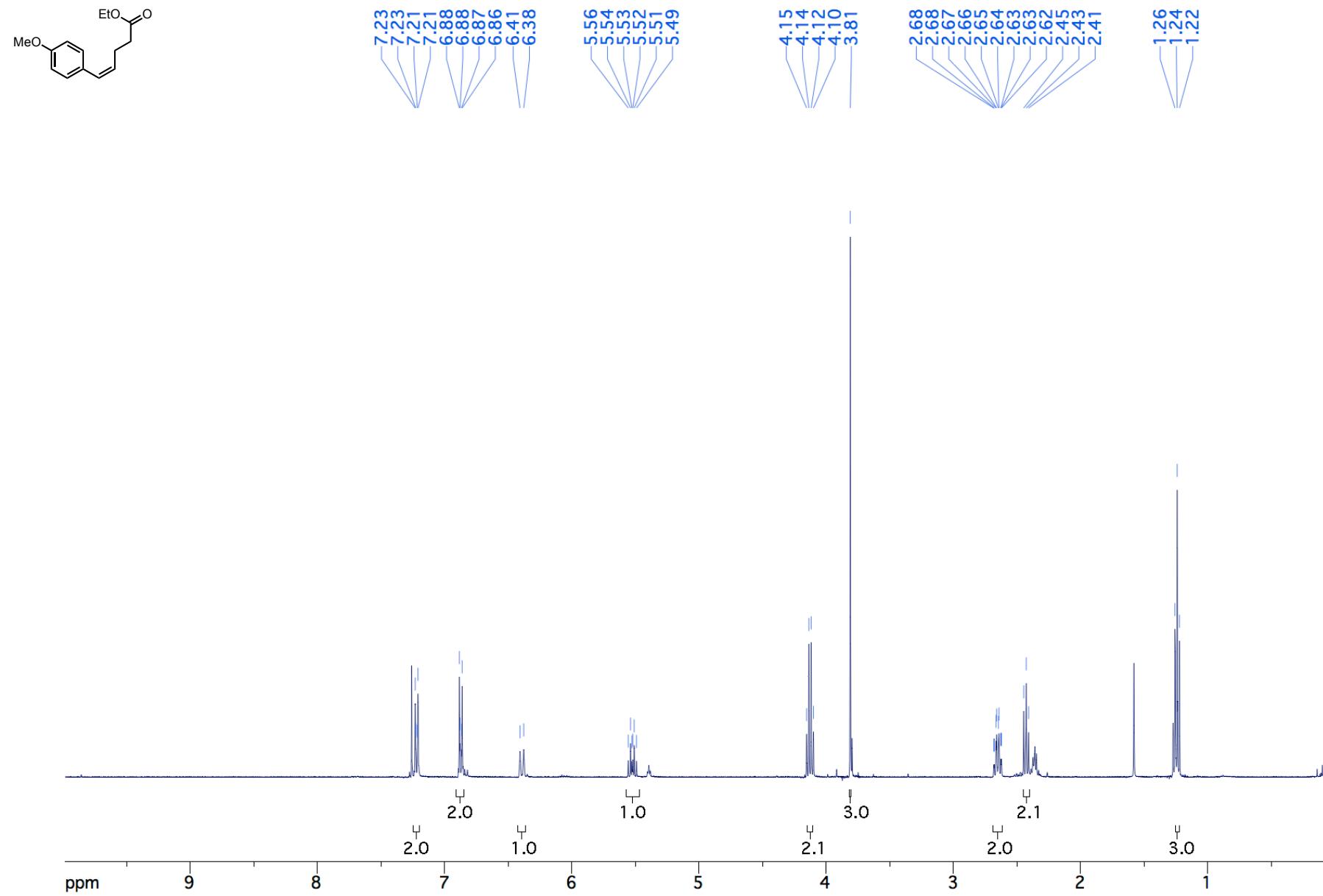


4'-Methoxy-3-vinyl-1,1'-biphenyl (33a) ^{13}C NMR (CDCl_3 , 100 MHz)

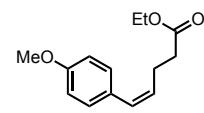


(Z)-Ethyl 5-(4-methoxyphenyl)pent-4-enoate (37a)

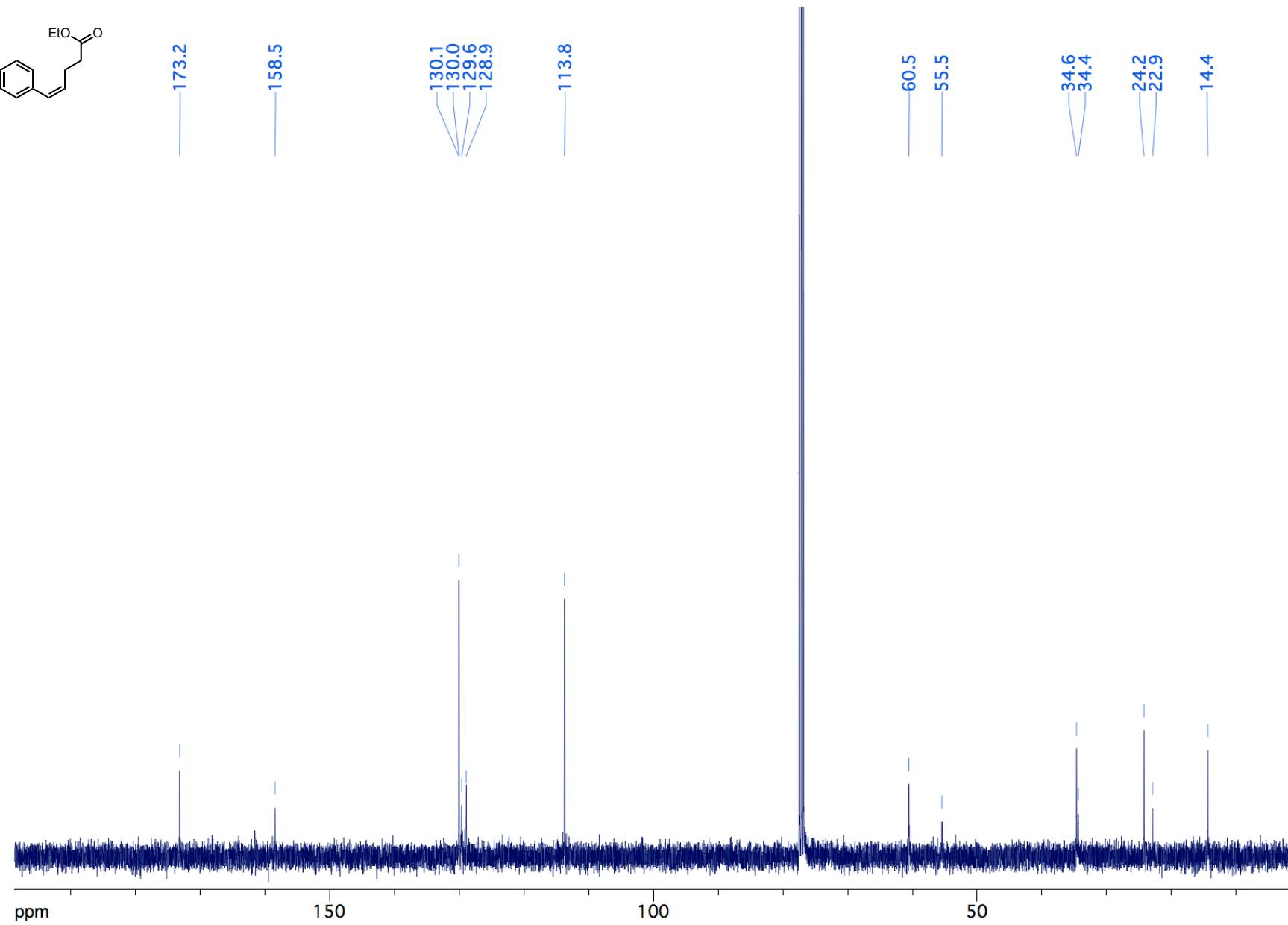
¹H NMR (CDCl₃, 400 MHz)



(Z)-Ethyl 5-(4-methoxyphenyl)pent-4-enoate (37a)

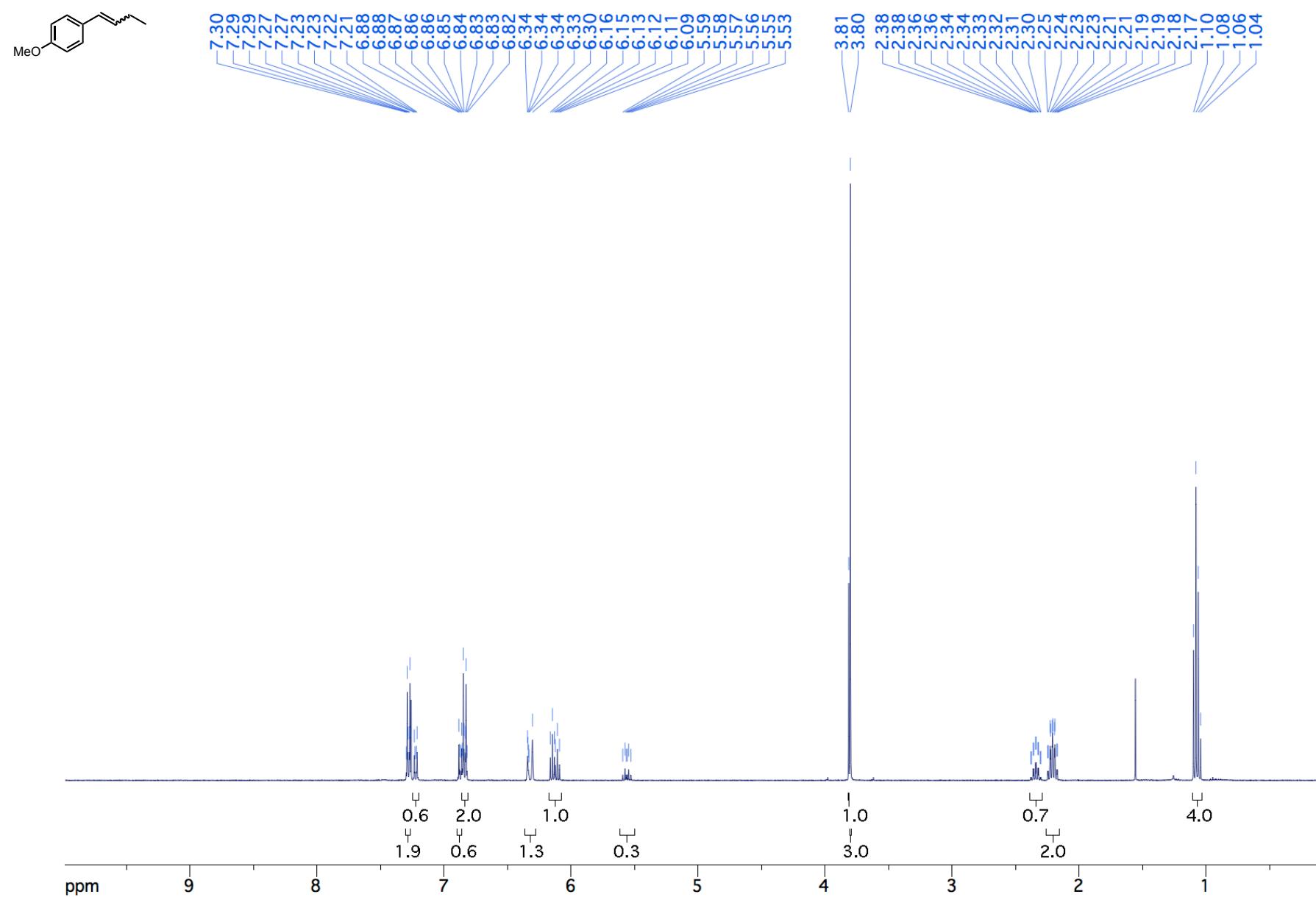


¹³C NMR (CDCl₃, 100 MHz)

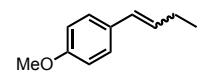


1-(But-1-en-1-yl)-4-methoxybenzene (38a)

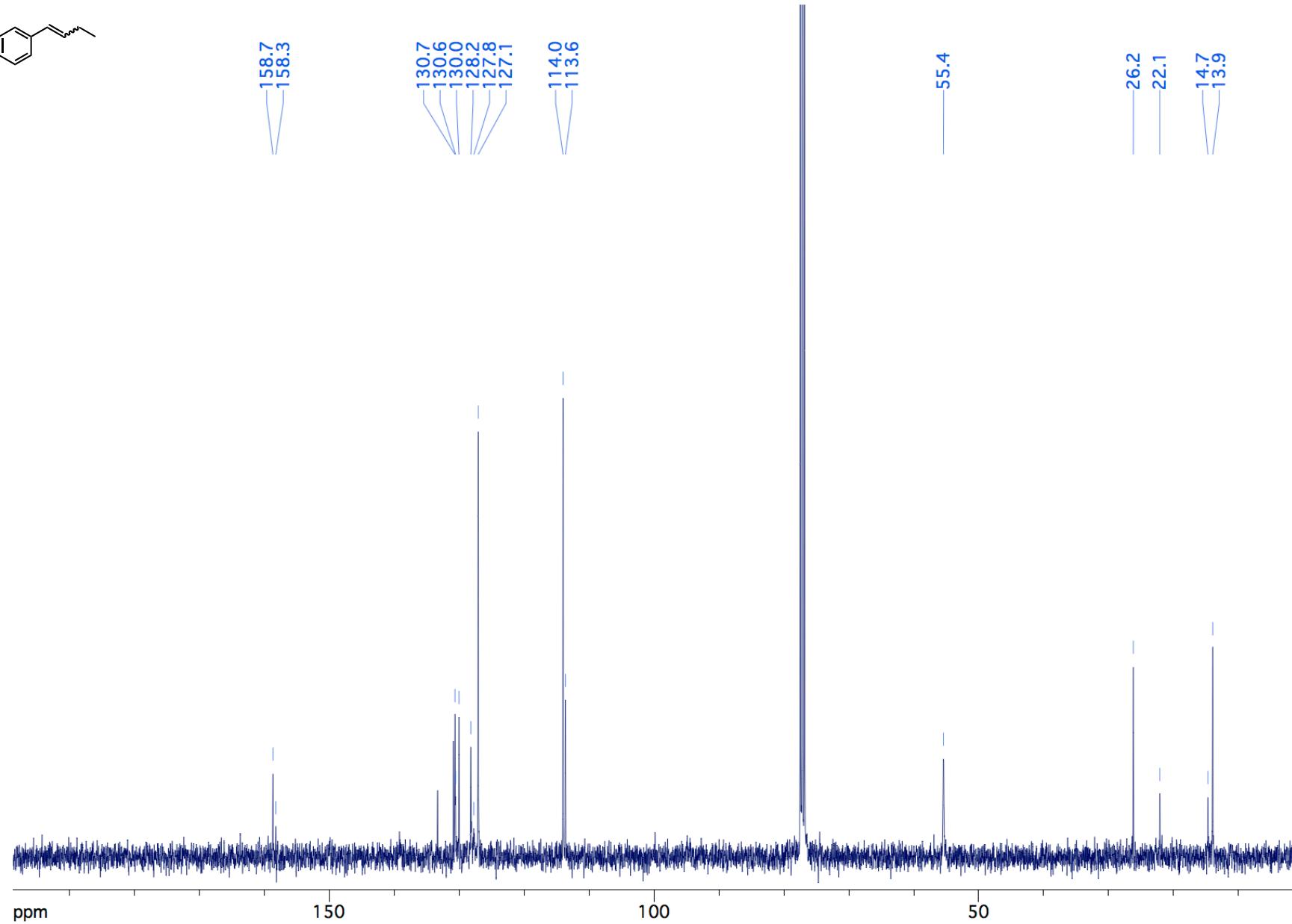
^1H NMR (CDCl_3 , 400 MHz)



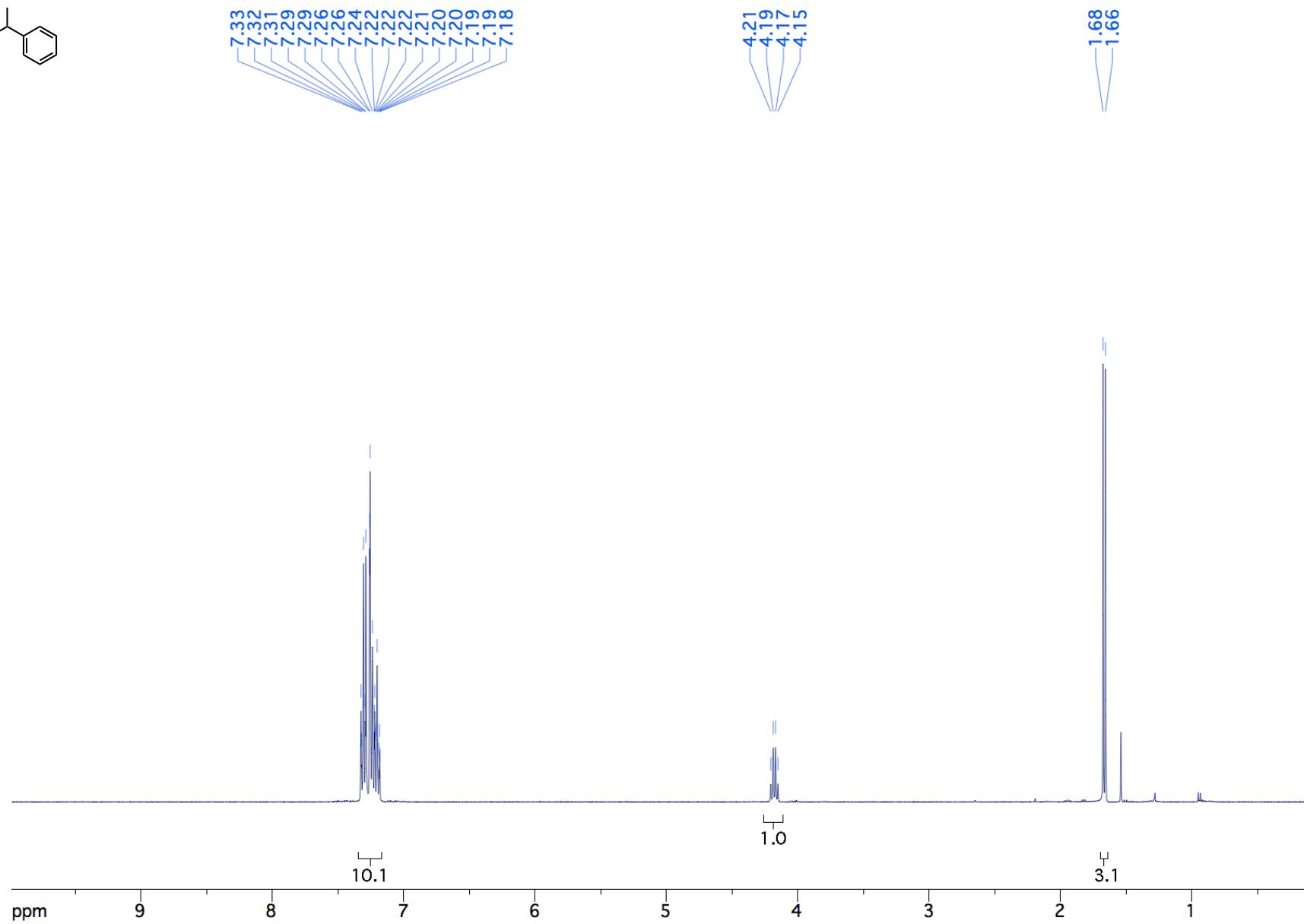
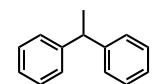
1-(But-1-en-1-yl)-4-methoxybenzene (38a)



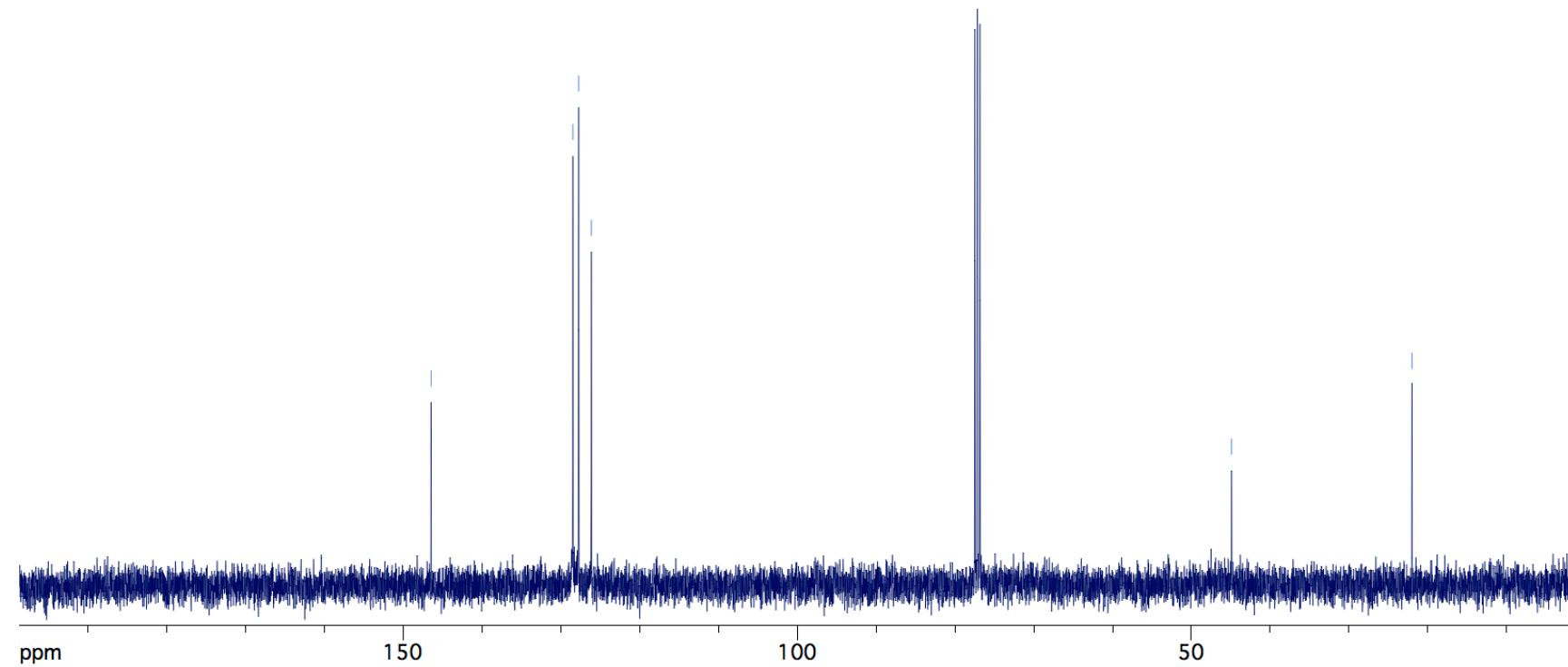
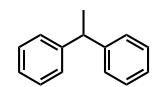
^{13}C NMR (CDCl_3 , 100 MHz)



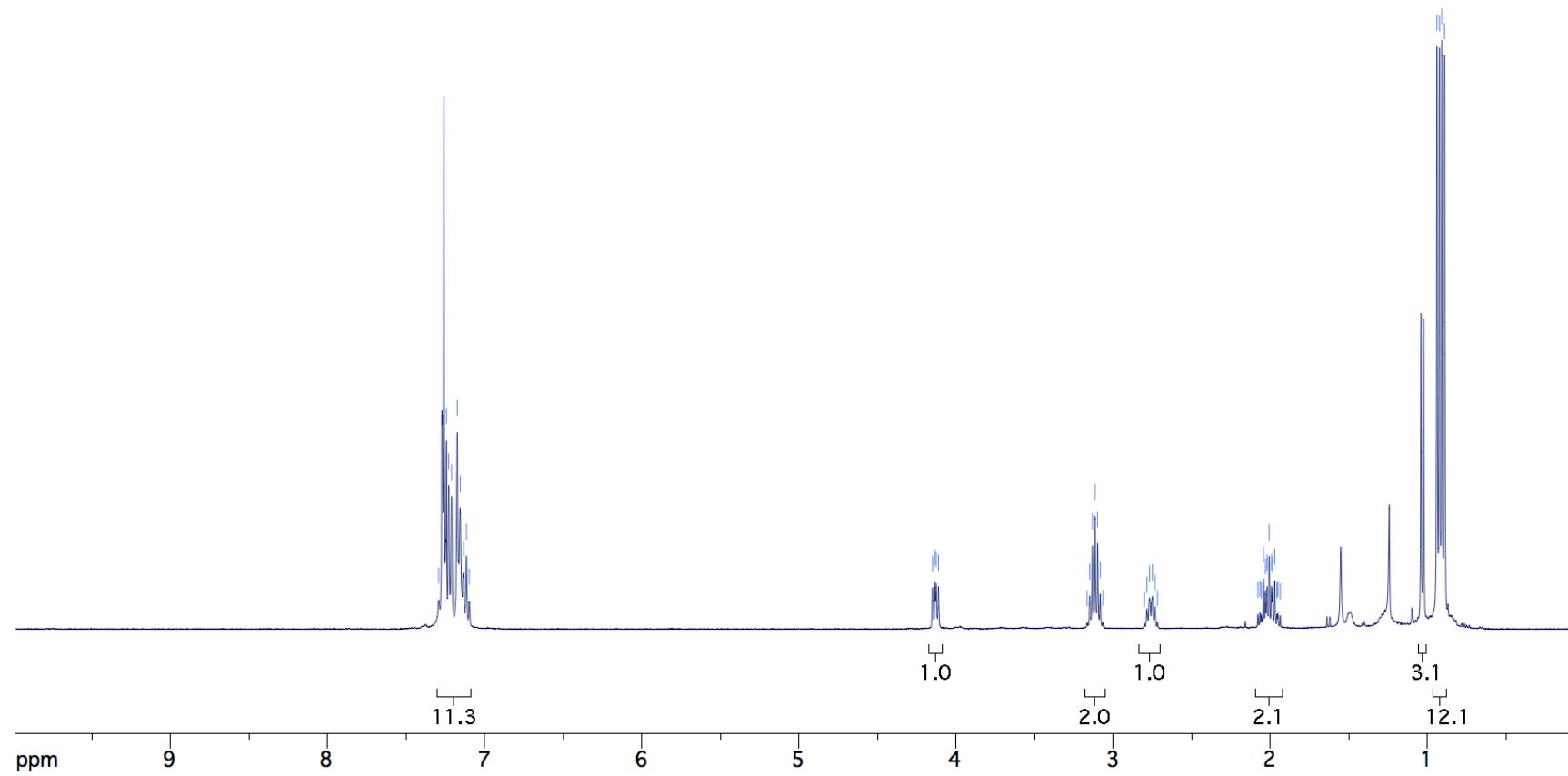
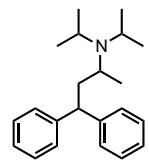
Ethane-1,1-diylbibenzene (2) ^1H NMR (CDCl_3 , 400 MHz)



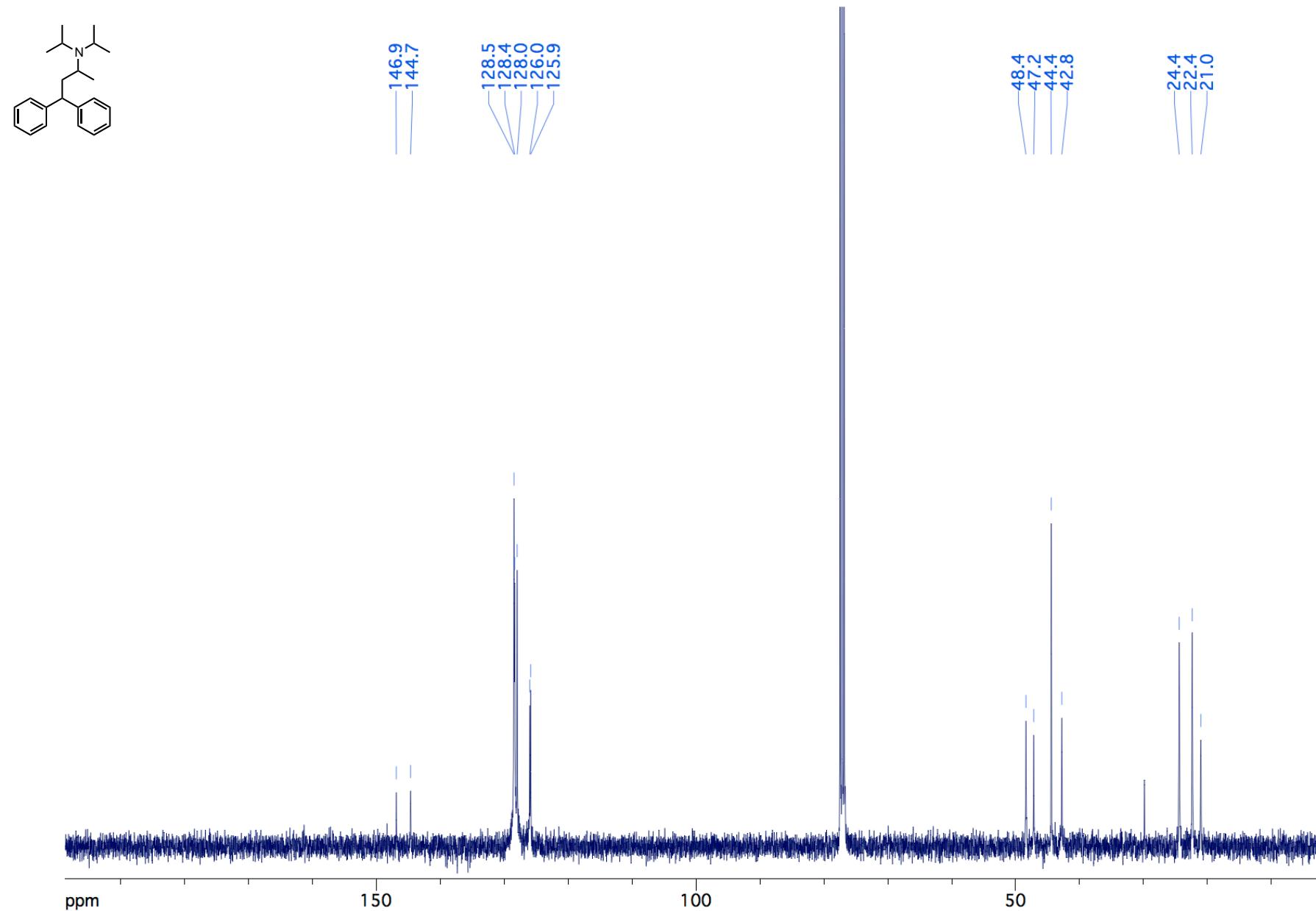
Ethane-1,1-diylbibenzene (2) ^{13}C NMR (CDCl_3 , 100 MHz)



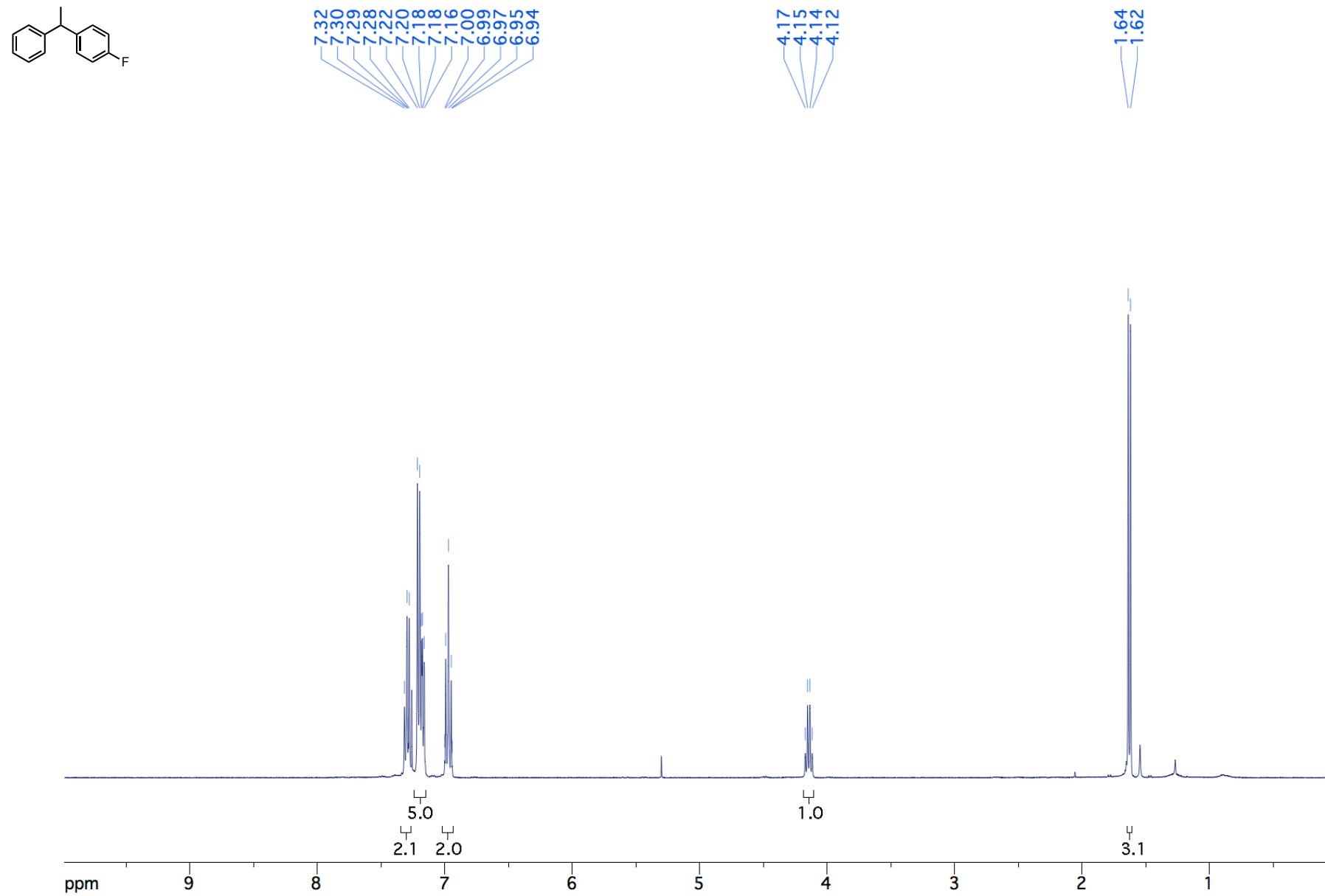
***N,N*-diisopropyl-4,4-diphenylbutan-2-amine (3)** ^1H NMR (CDCl_3 , 400 MHz)



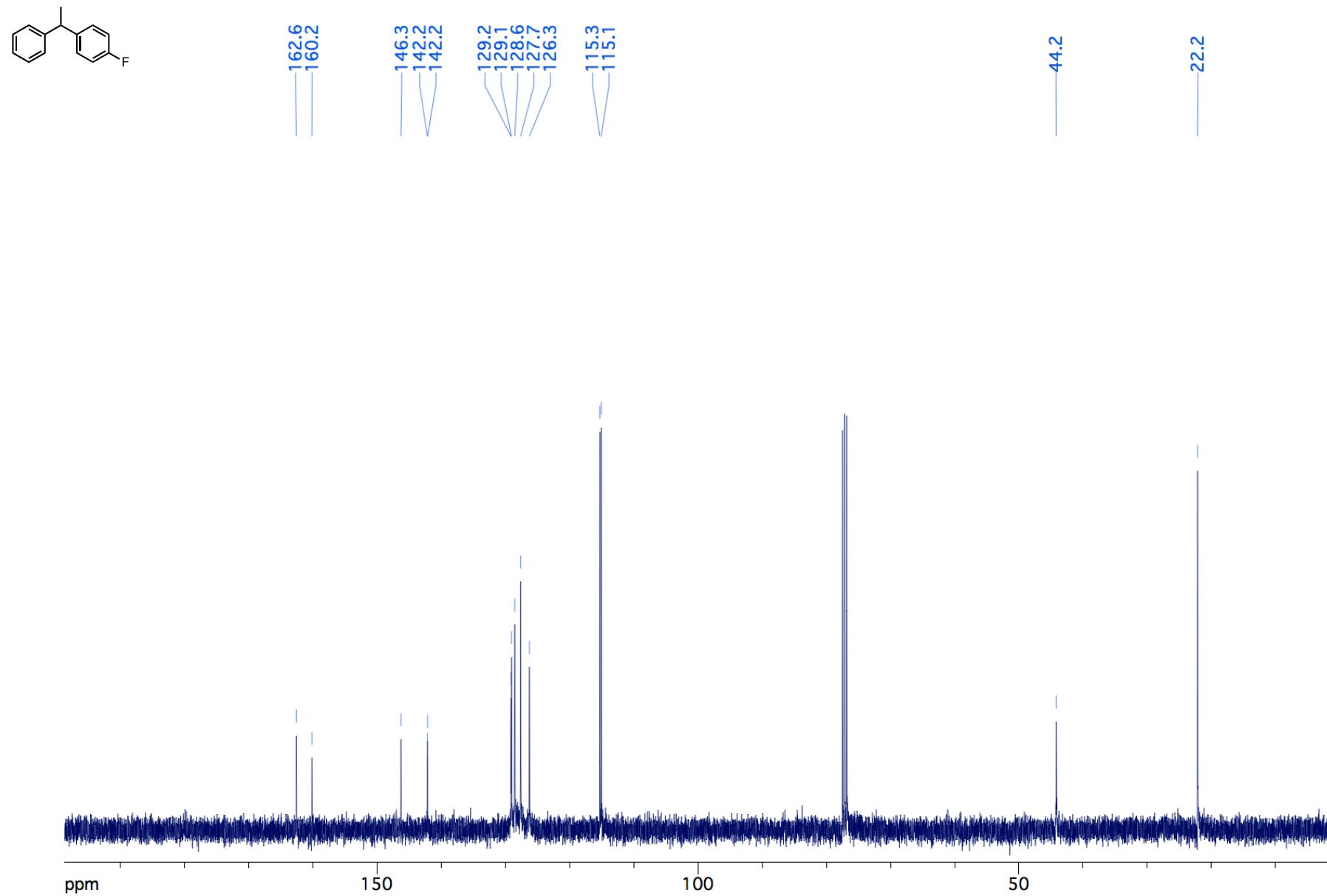
N,N-diisopropyl-4,4-diphenylbutan-2-amine (3) ^{13}C NMR (CDCl_3 , 100 MHz)



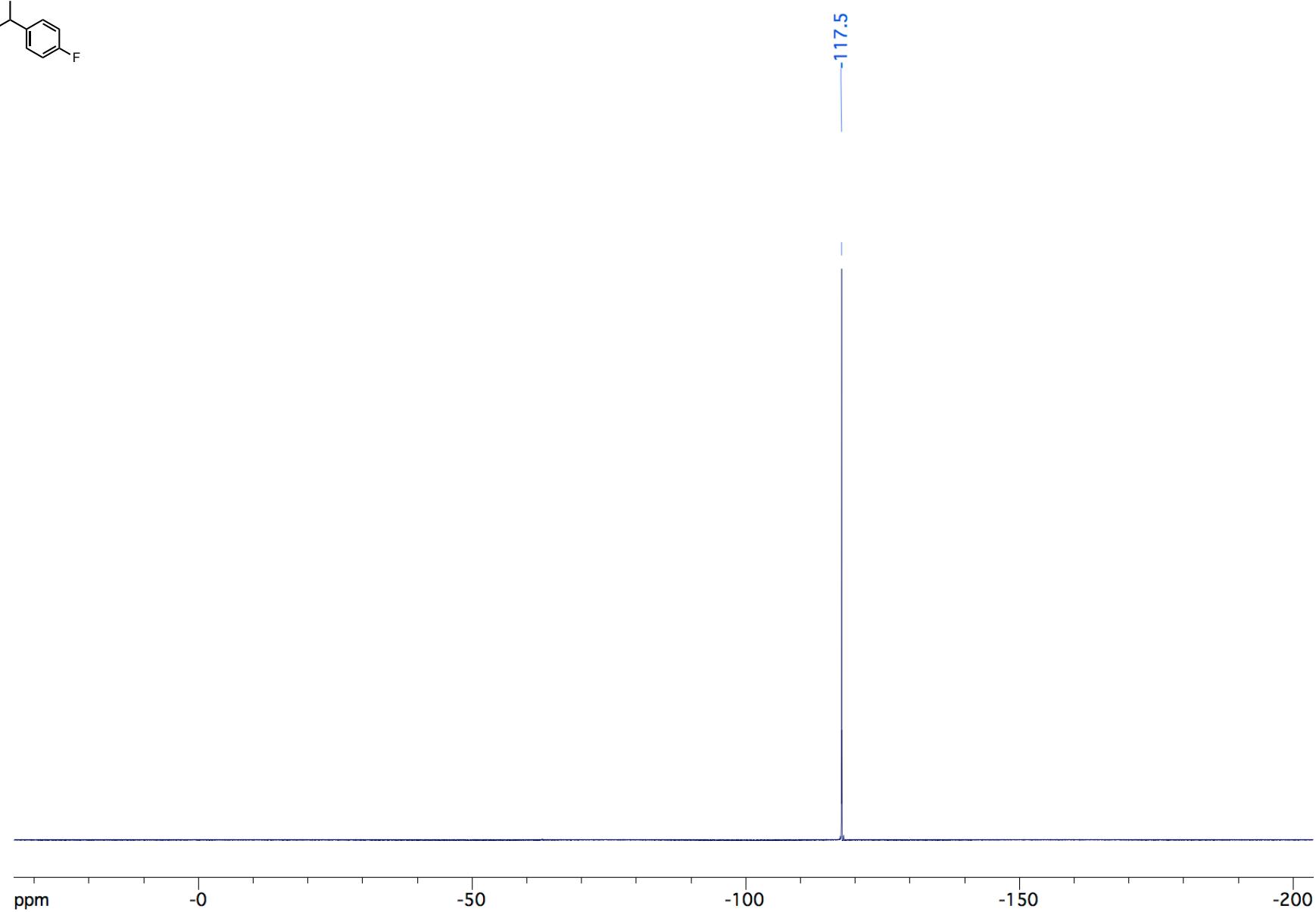
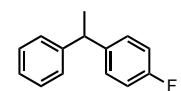
1-Fluoro-4-(1-phenylethyl)benzene (4) ^1H NMR (CDCl_3 , 400 MHz)



1-Fluoro-4-(1-phenylethyl)benzene (4) ^{13}C NMR (CDCl_3 , 100 MHz)

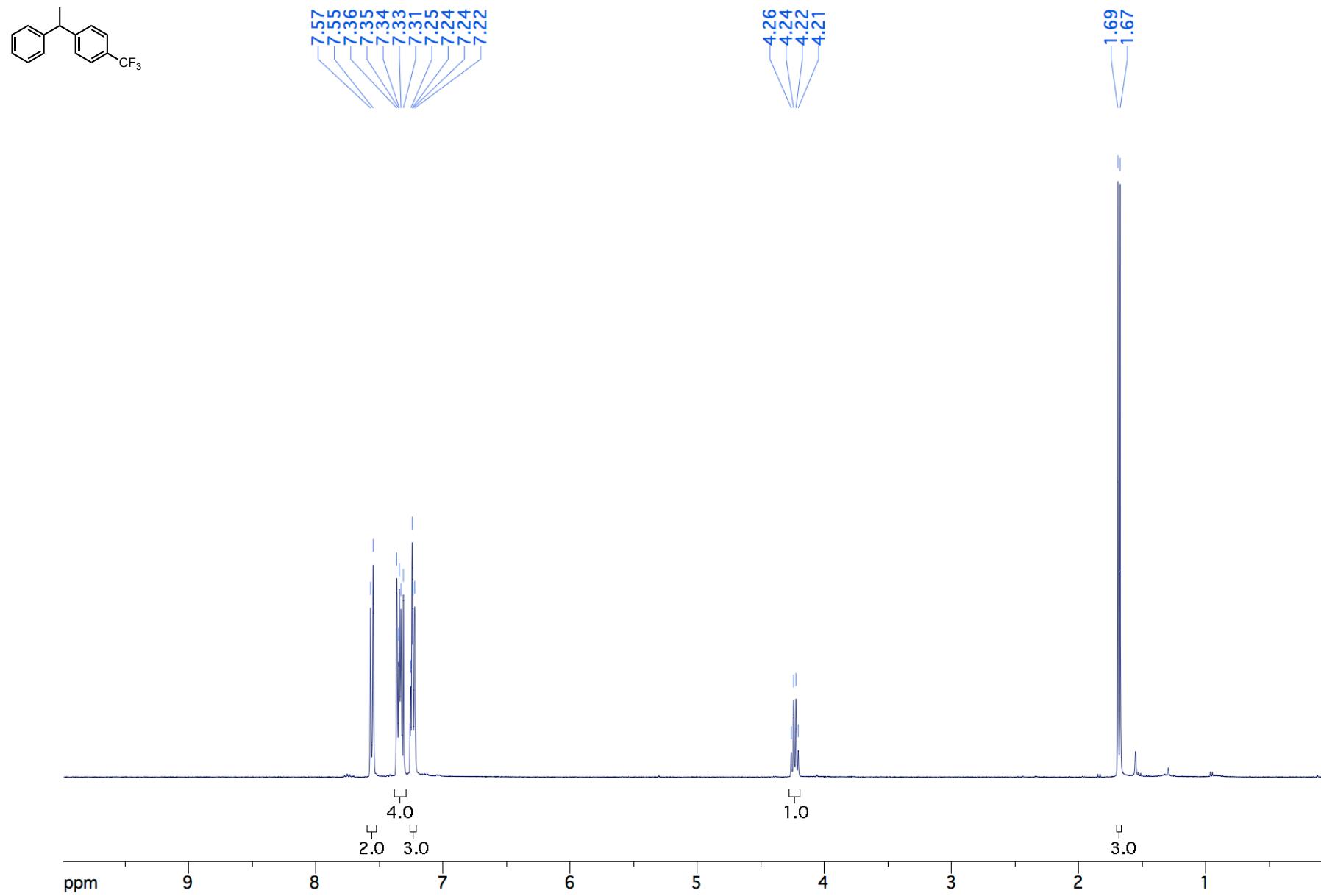


1-Fluoro-4-(1-phenylethyl)benzene (4) ^{19}F -NMR (CDCl_3 , 376 MHz)



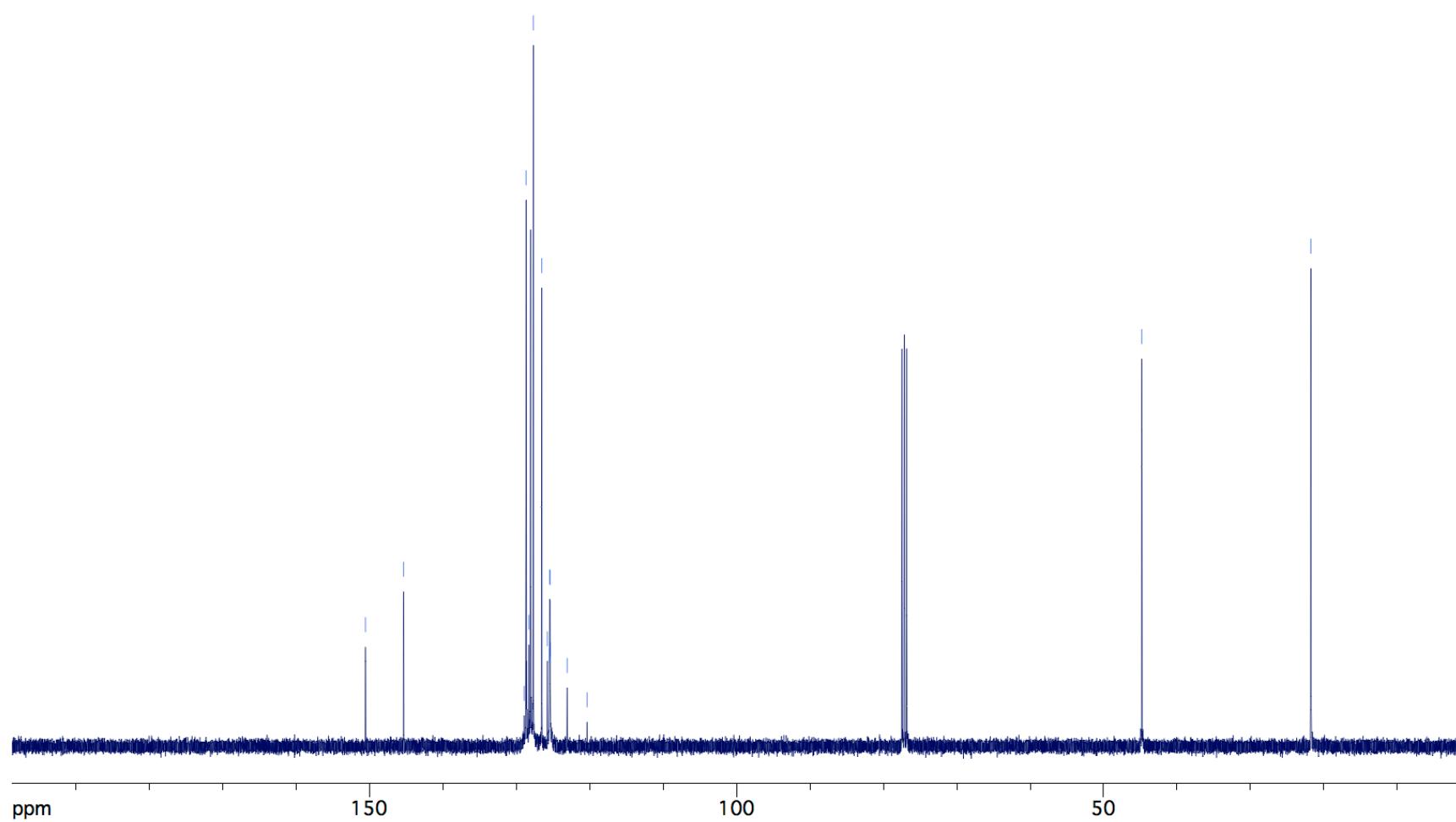
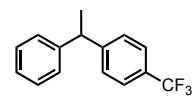
1-(1-Phenylethyl)-4-(trifluoromethyl)benzene (5)

^1H NMR (CDCl_3 , 400 MHz)



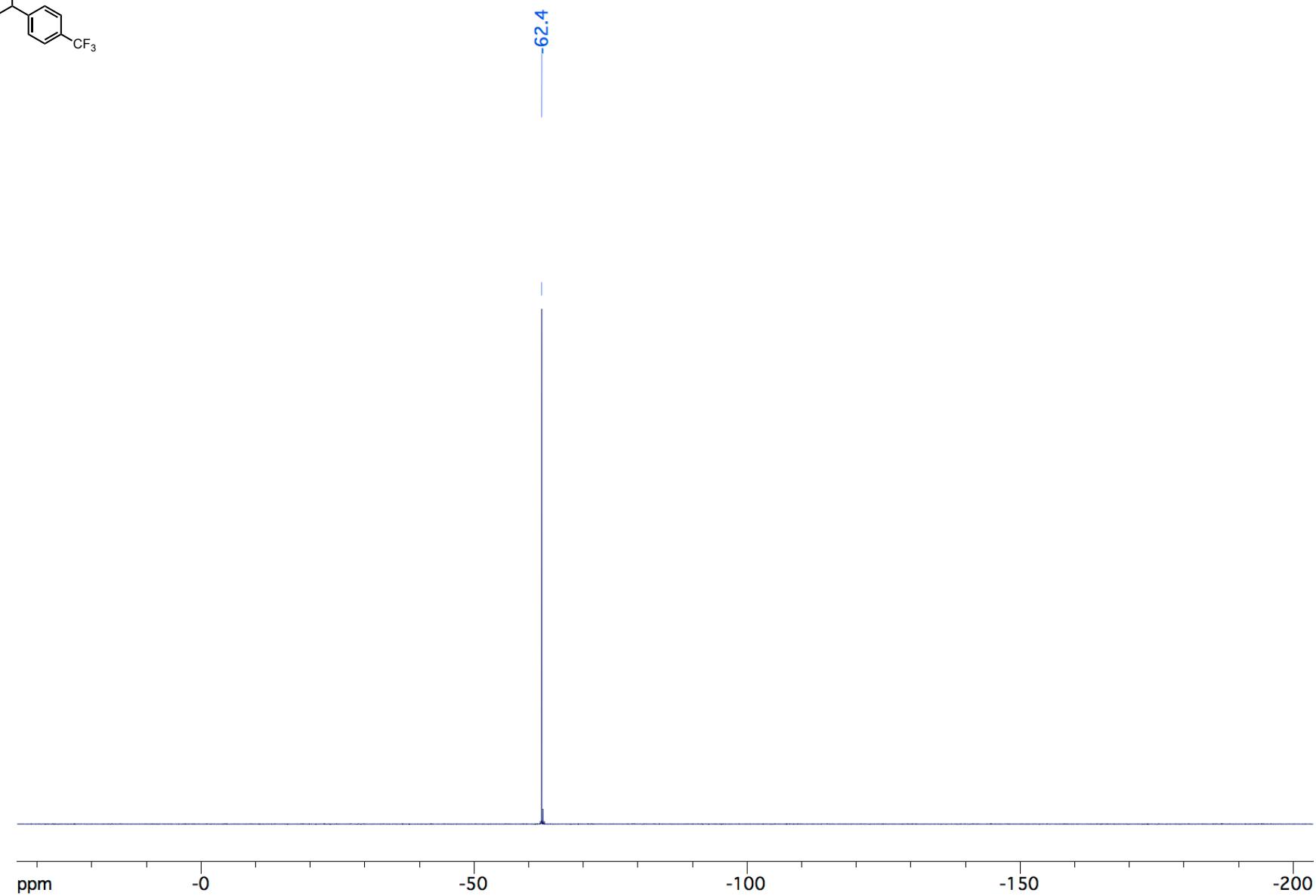
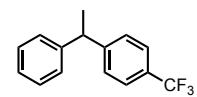
1-(1-Phenylethyl)-4-(trifluoromethyl)benzene (5)

^{13}C NMR (CDCl_3 , 100 MHz)

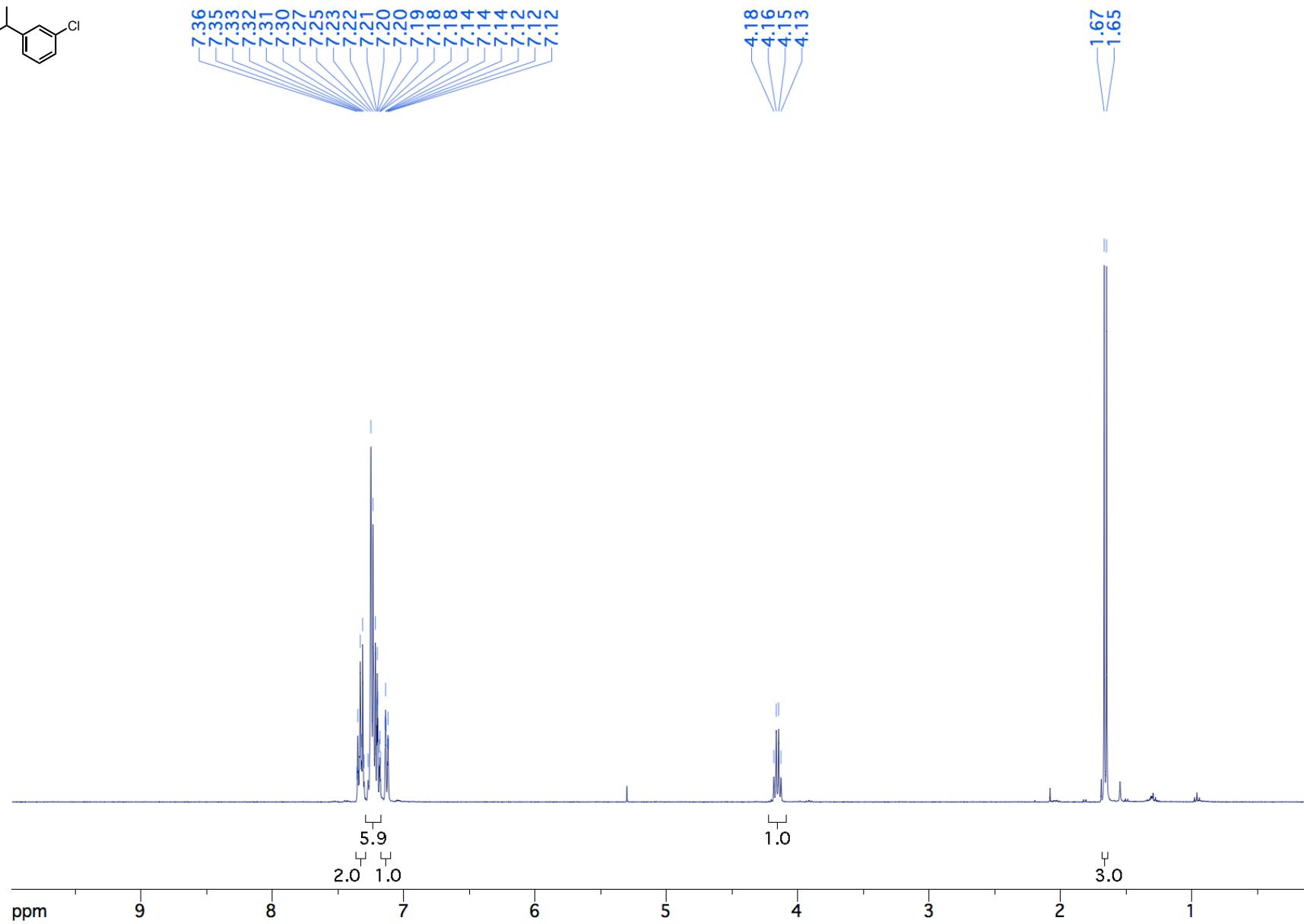
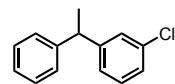


1-(1-Phenylethyl)-4-(trifluoromethyl)benzene (5)

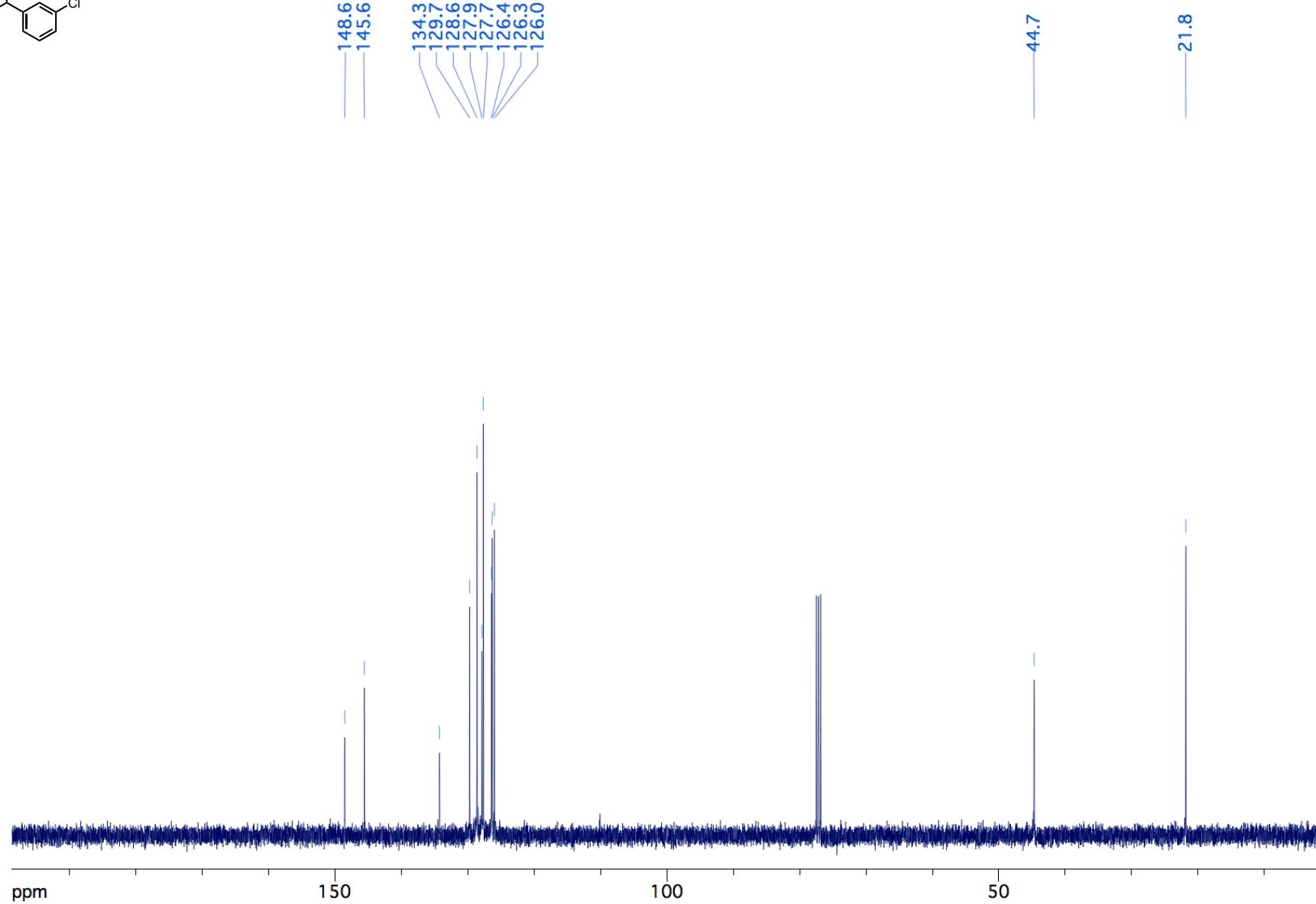
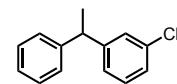
^{19}F -NMR (CDCl_3 , 376 MHz)



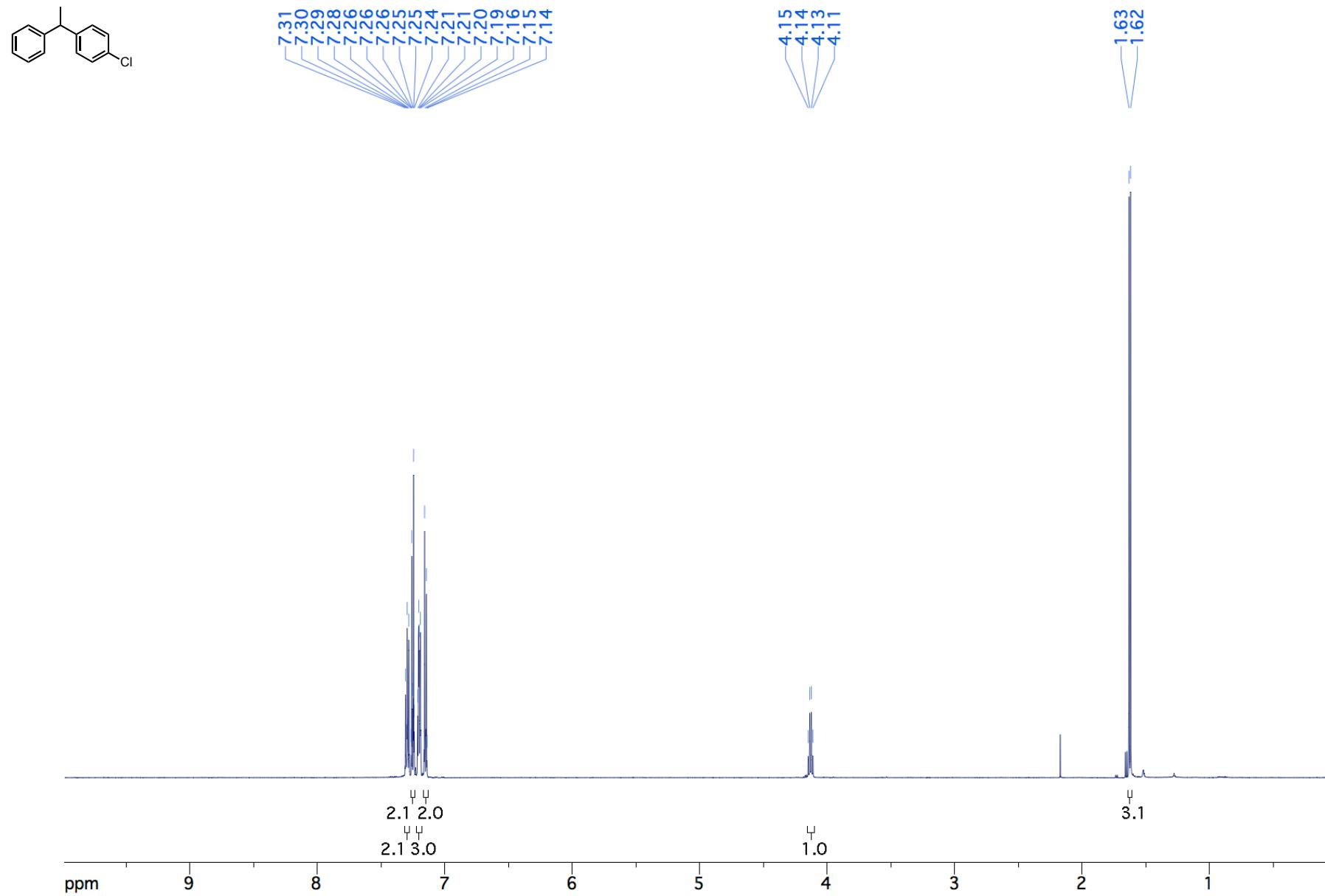
1-Chloro-3-(1-phenylethyl)benzene (6) ^1H NMR (CDCl_3 , 400 MHz)



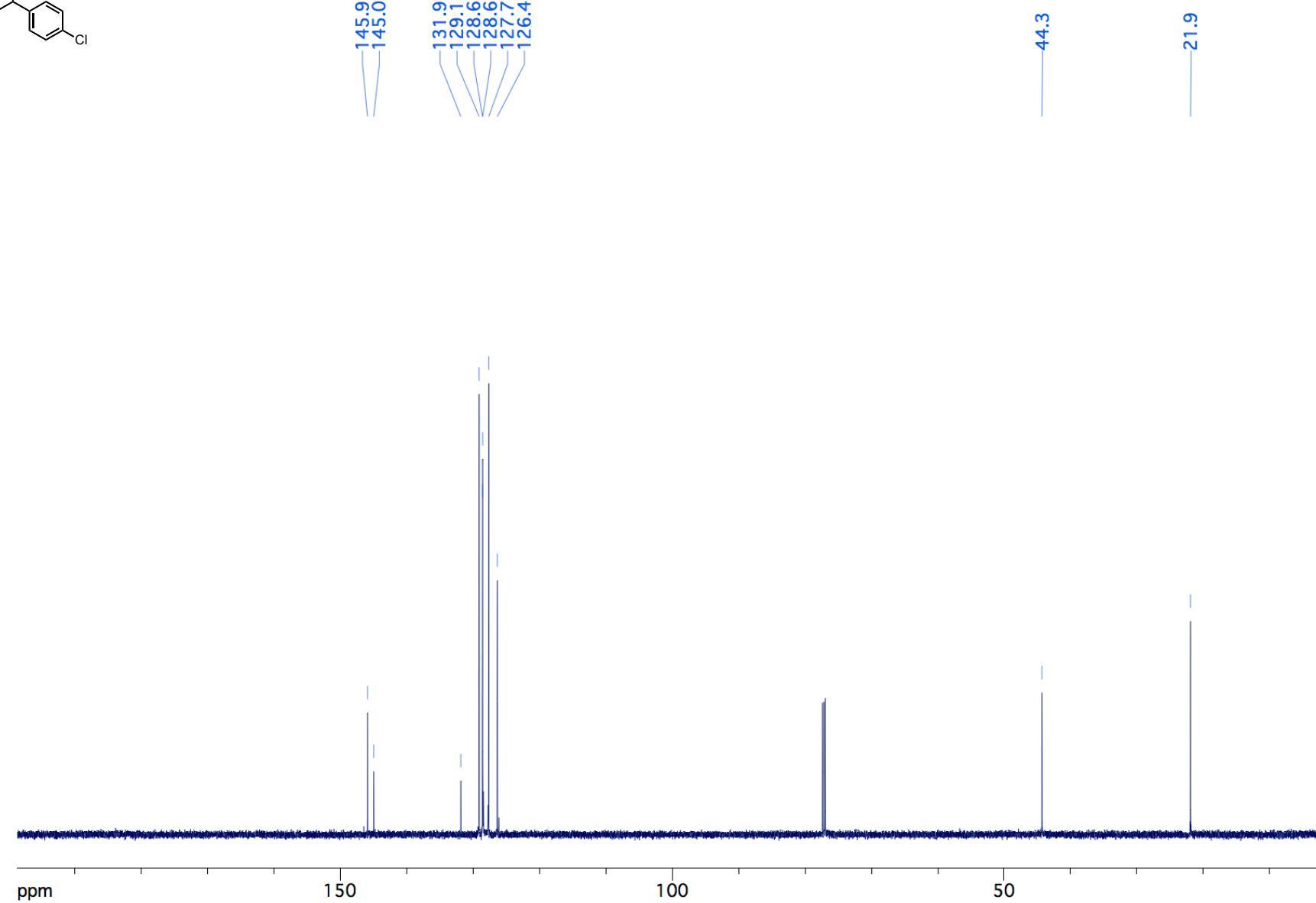
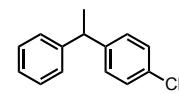
1-Chloro-3-(1-phenylethyl)benzene (6) ^{13}C NMR (CDCl_3 , 100 MHz)



1-Chloro-4-(1-phenylethyl)benzene (7) ^1H NMR (CDCl_3 , 600 MHz)

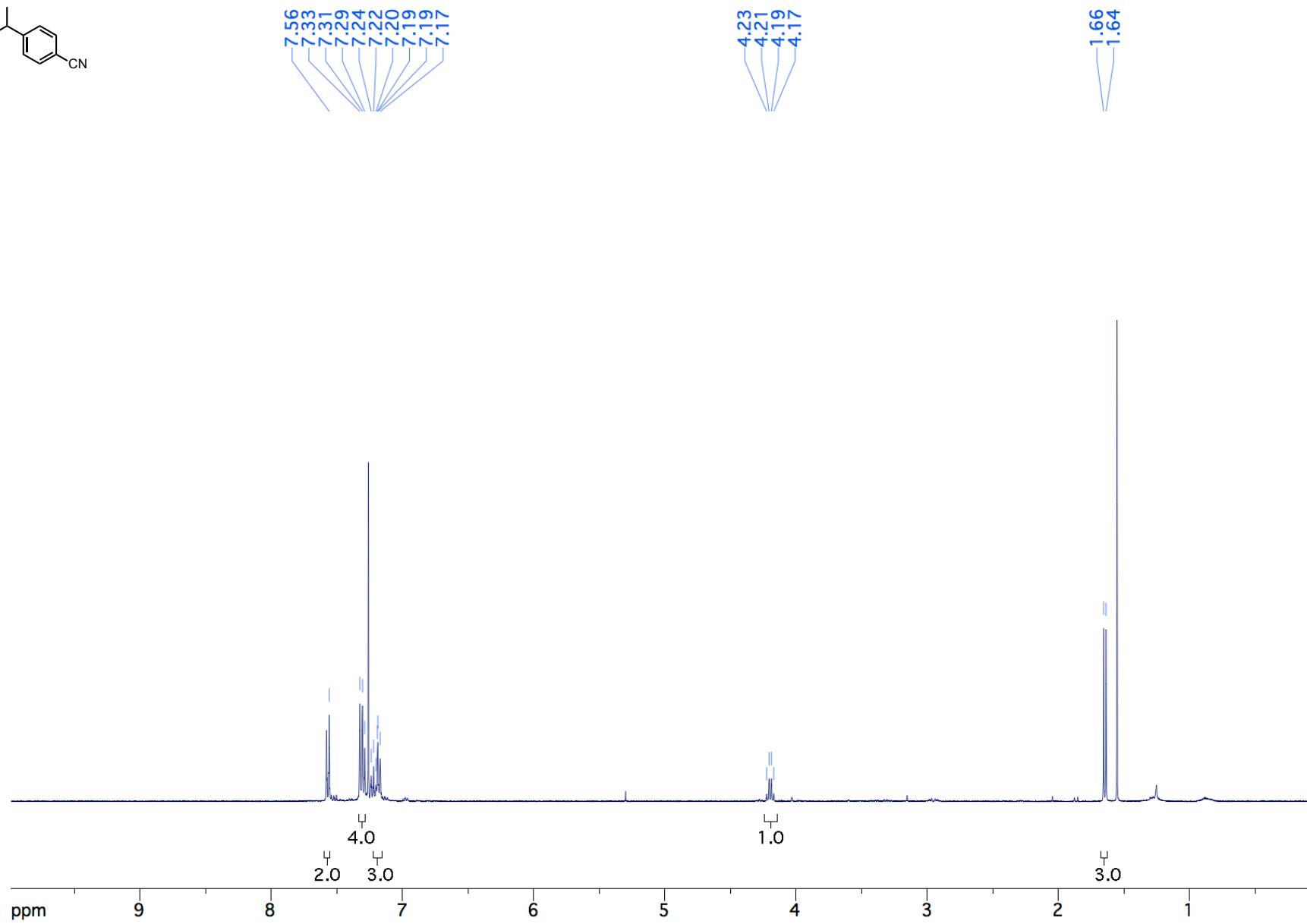
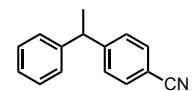


1-Chloro-4-(1-phenylethyl)benzene (7) ^{13}C NMR (CDCl_3 , 151 MHz)

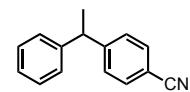


4-(1-Phenylethyl)benzonitrile (8)

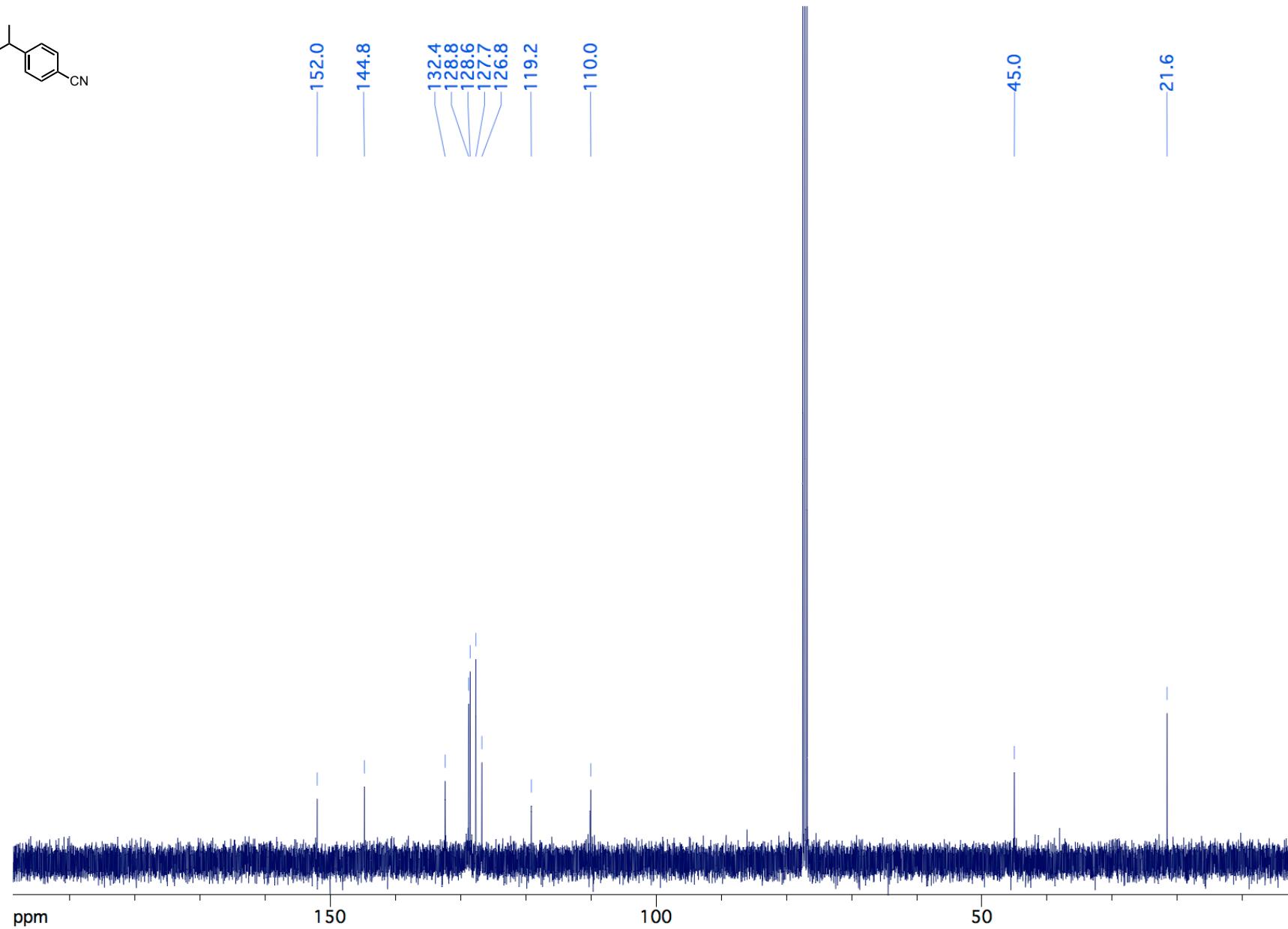
^1H NMR (CDCl_3 , 400 MHz)



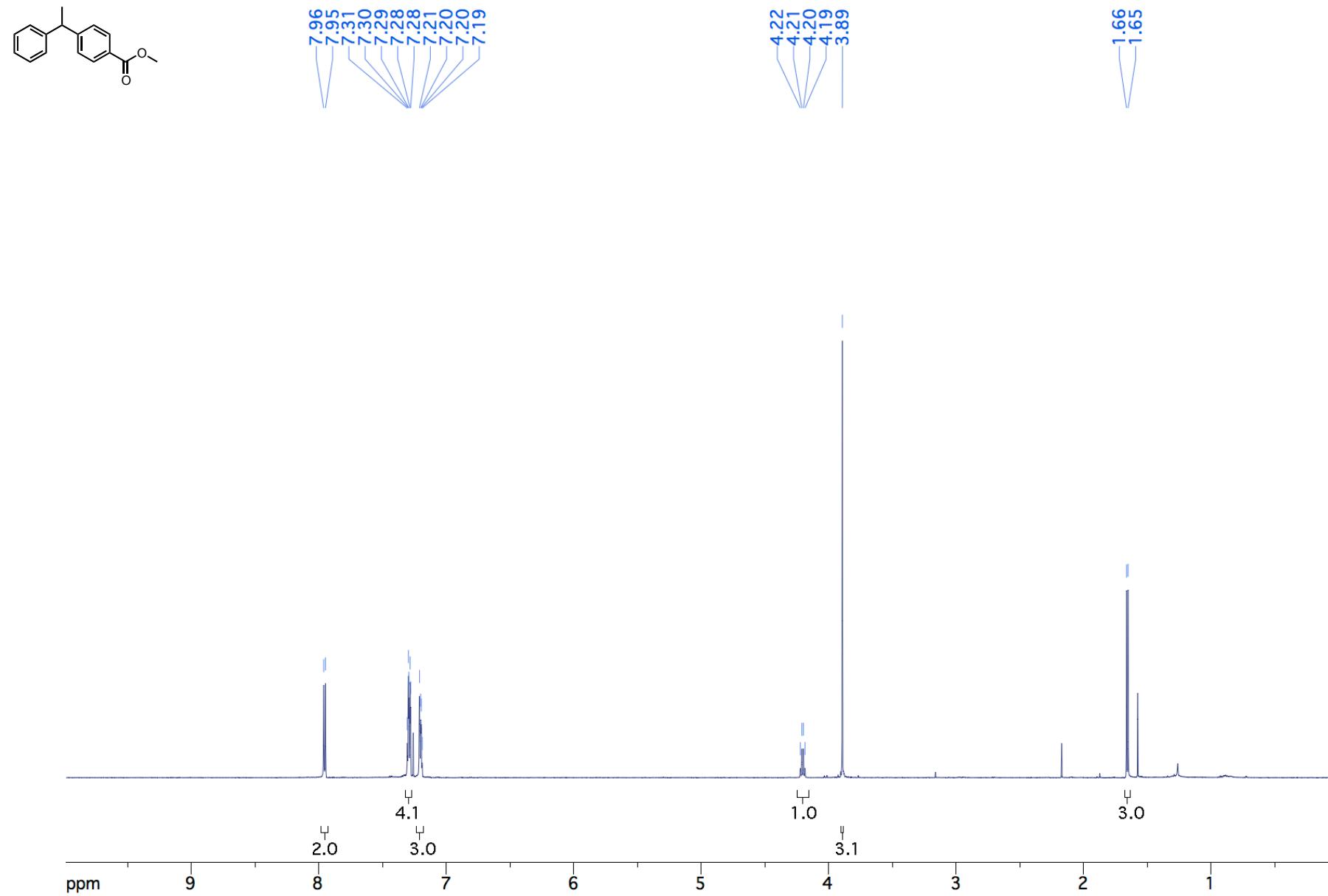
4-(1-Phenylethyl)benzonitrile (8)



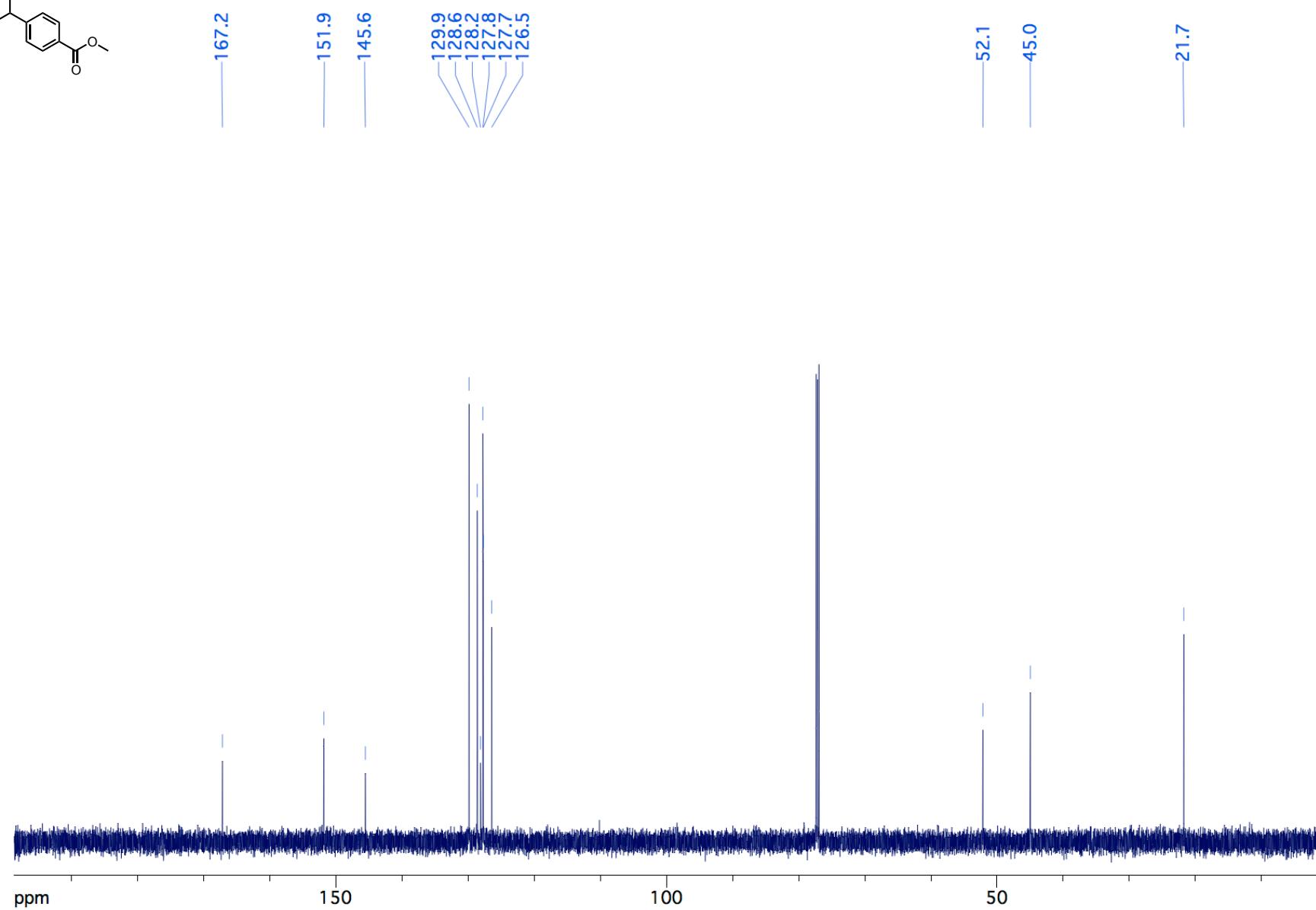
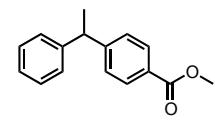
^{13}C NMR (CDCl_3 , 100 MHz)



Methyl 4-(1-phenylethyl)benzoate (9) ^1H NMR (CDCl_3 , 600 MHz)

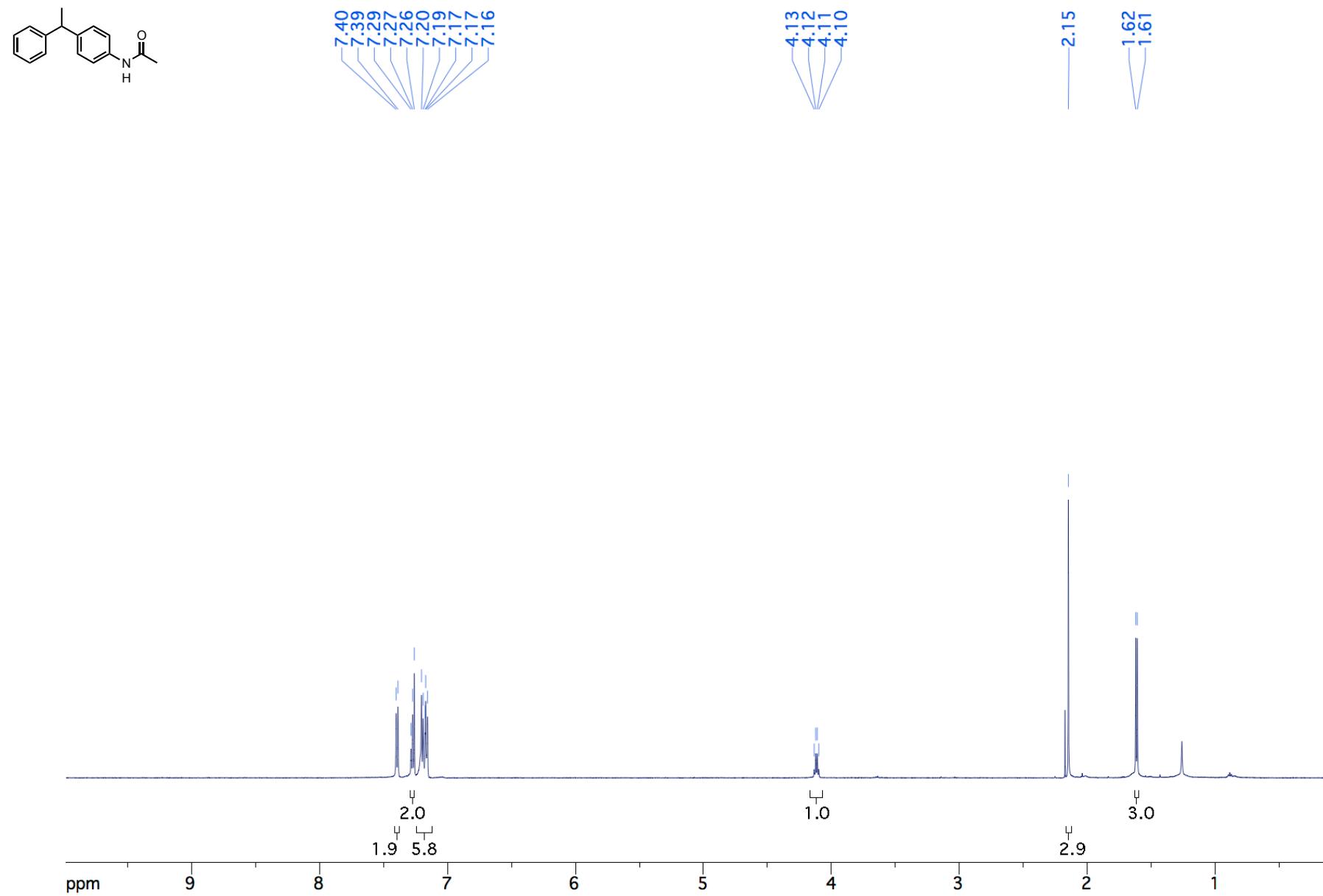


Methyl 4-(1-phenylethyl)benzoate (9) ^{13}C NMR (CDCl_3 , 151 MHz)



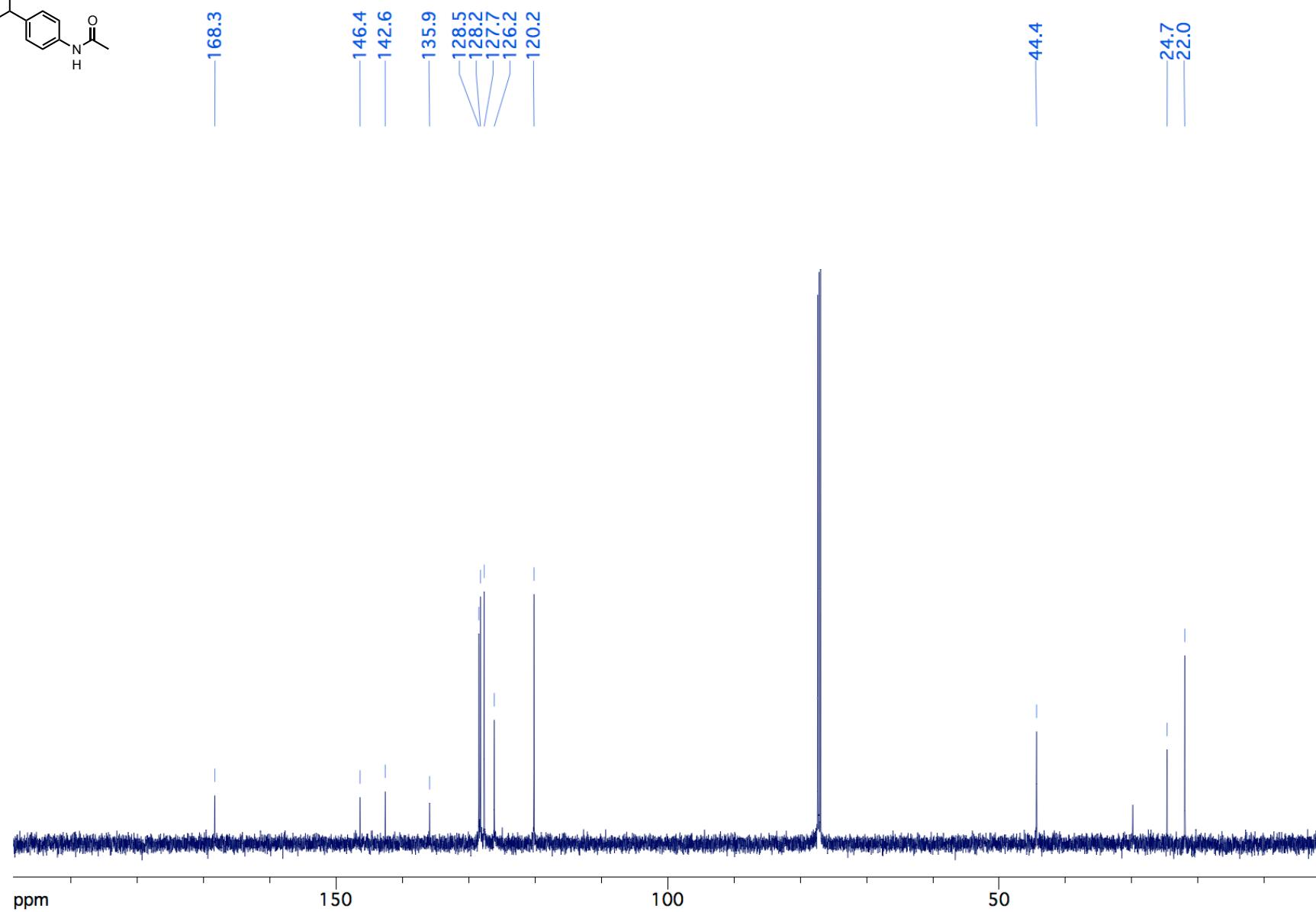
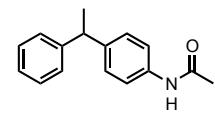
N-(4-(1-Phenylethyl)phenyl)acetamide (10)

^1H NMR (CDCl_3 , 600 MHz)

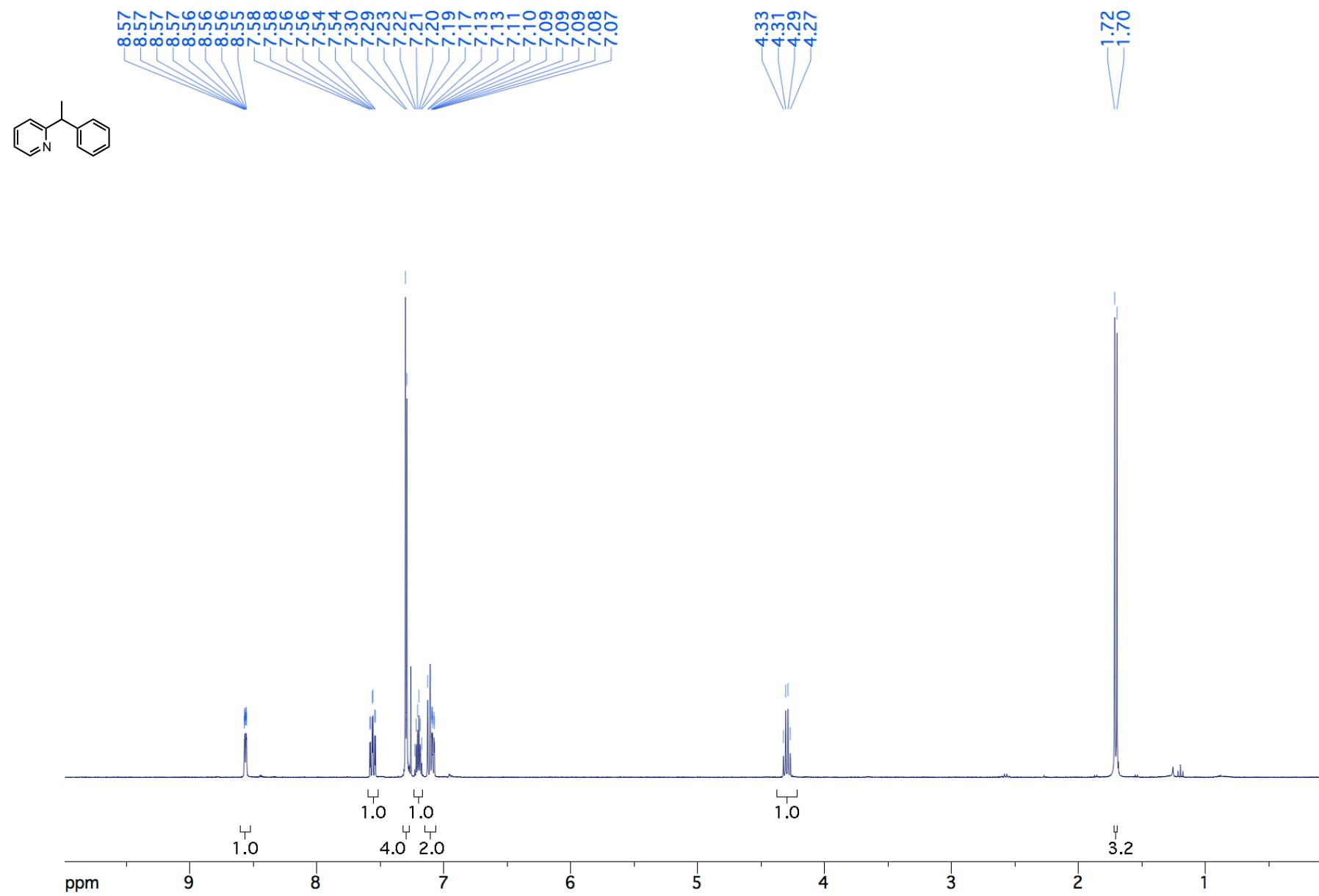


N-(4-(1-Phenylethyl)phenyl)acetamide (10)

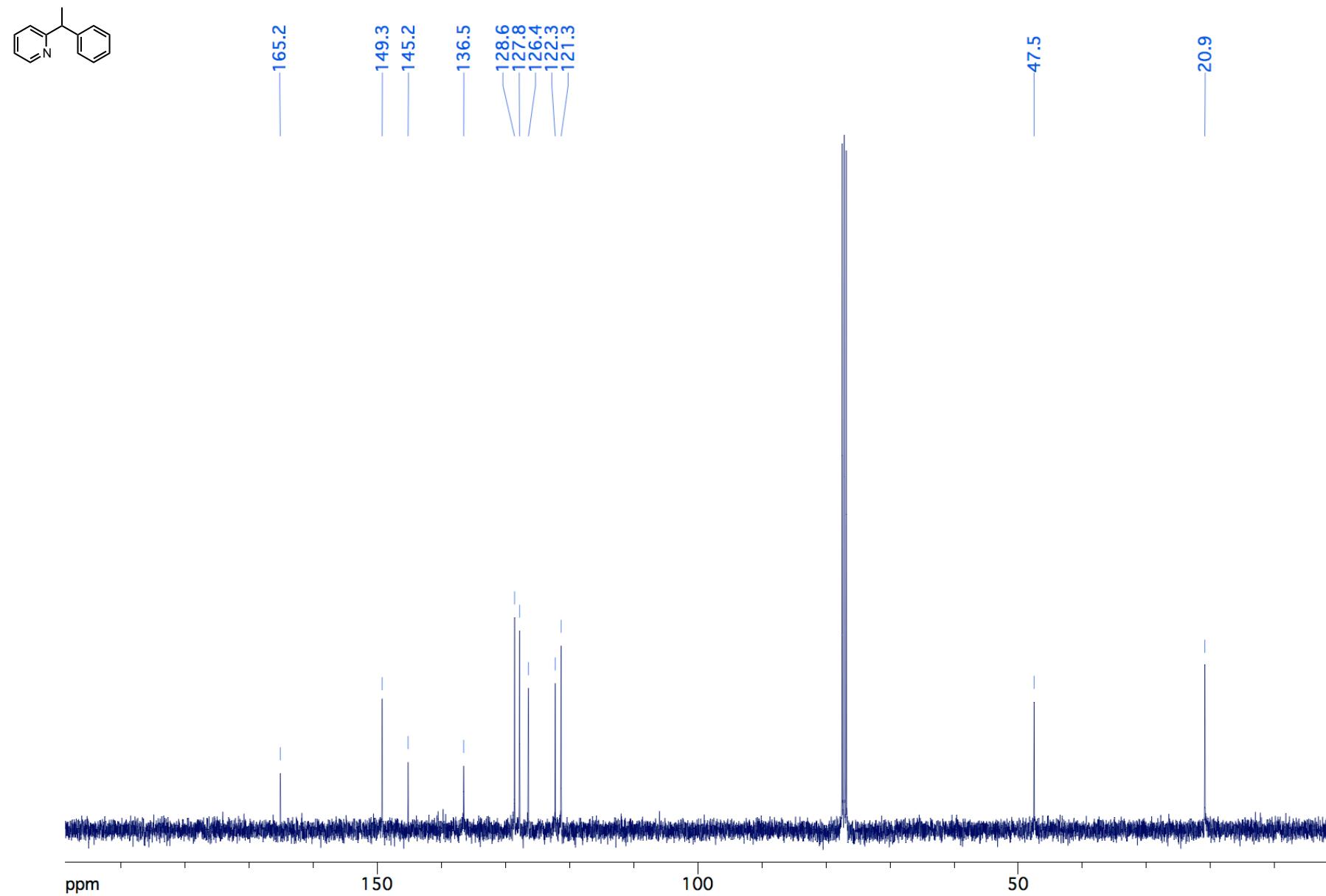
^{13}C NMR (CDCl_3 , 151 MHz)



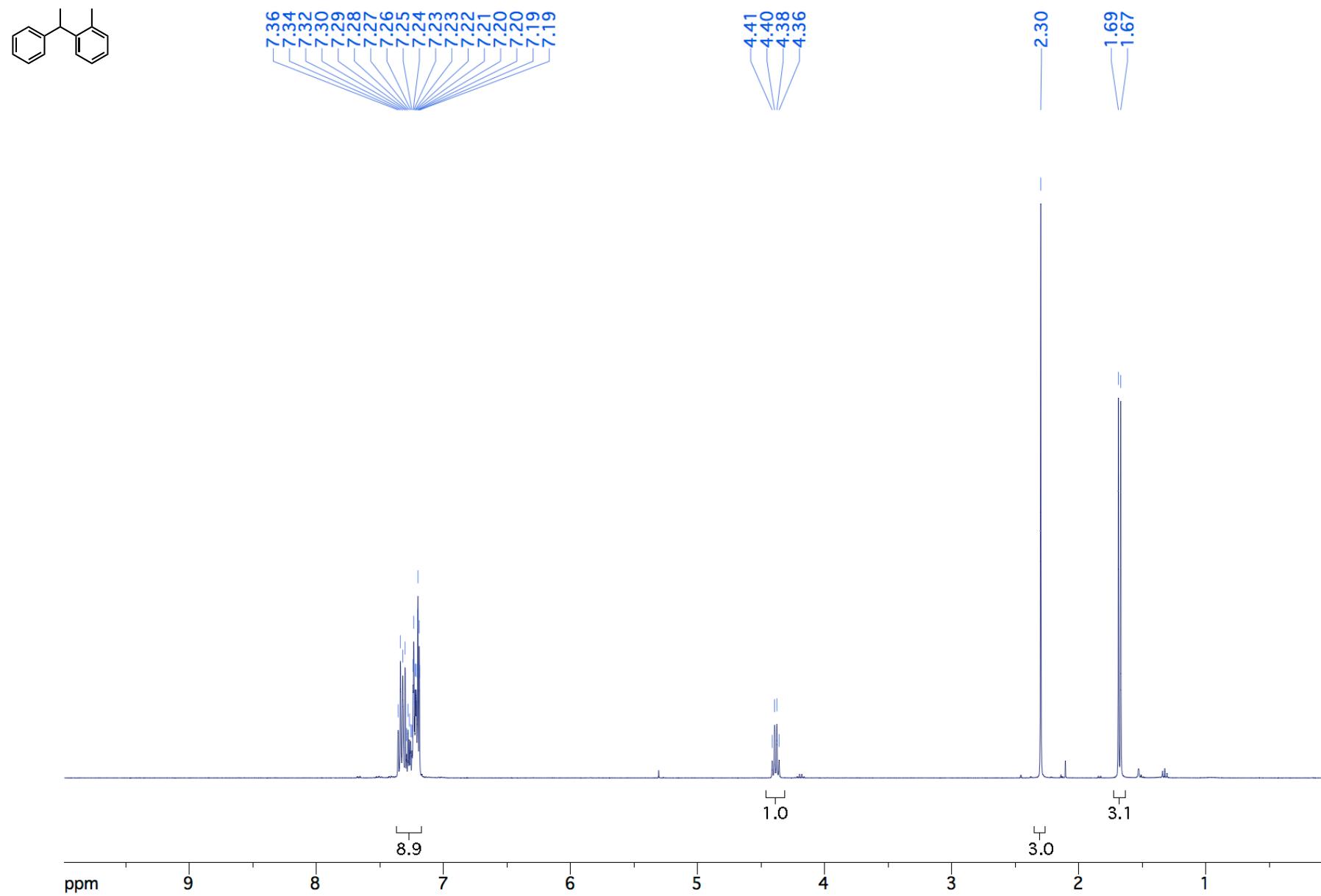
2-(1-Phenylethyl)pyridine (11) ^1H NMR (CDCl₃, 400 MHz)



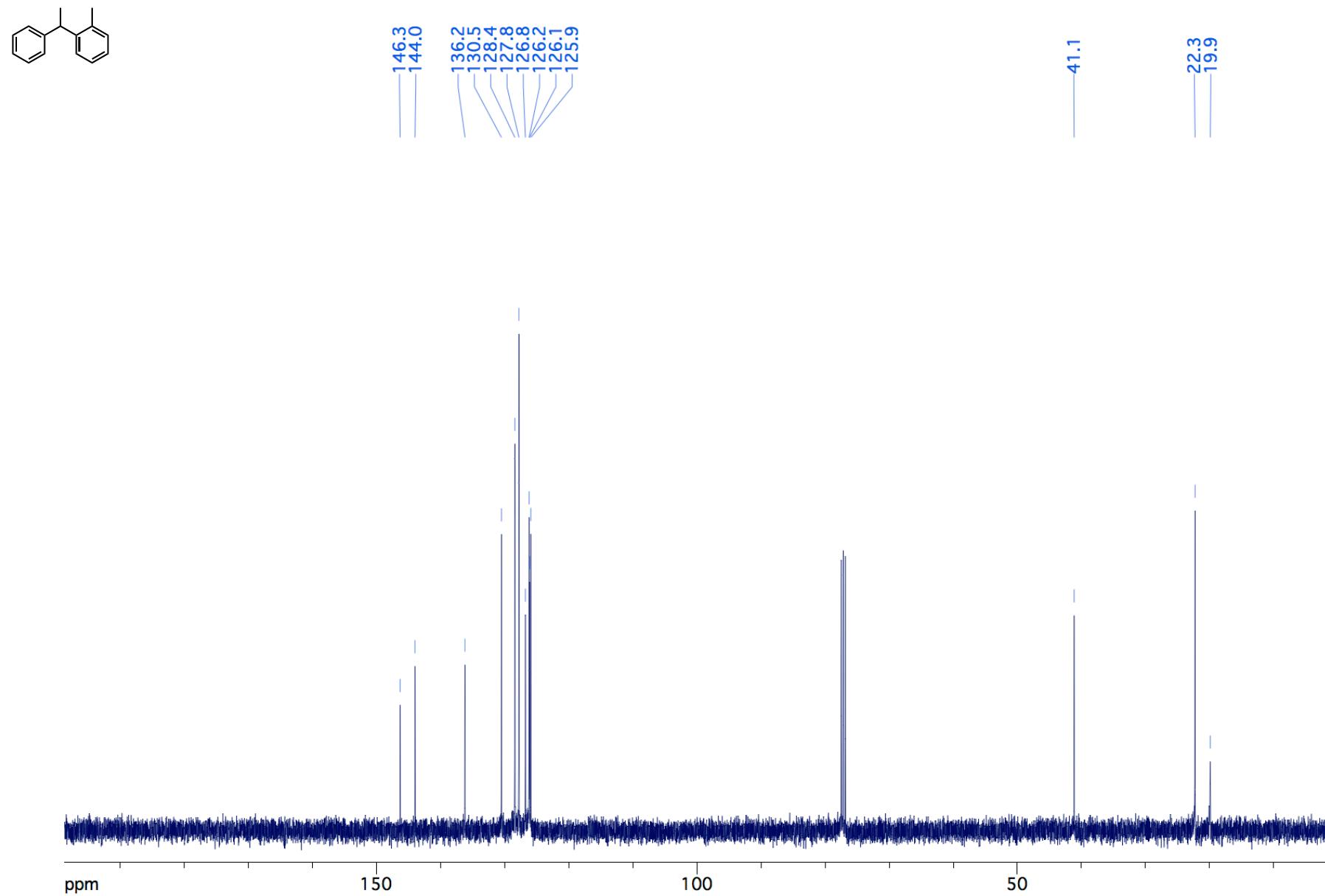
2-(1-Phenylethyl)pyridine (11) ^{13}C NMR (CDCl_3 , 100 MHz)



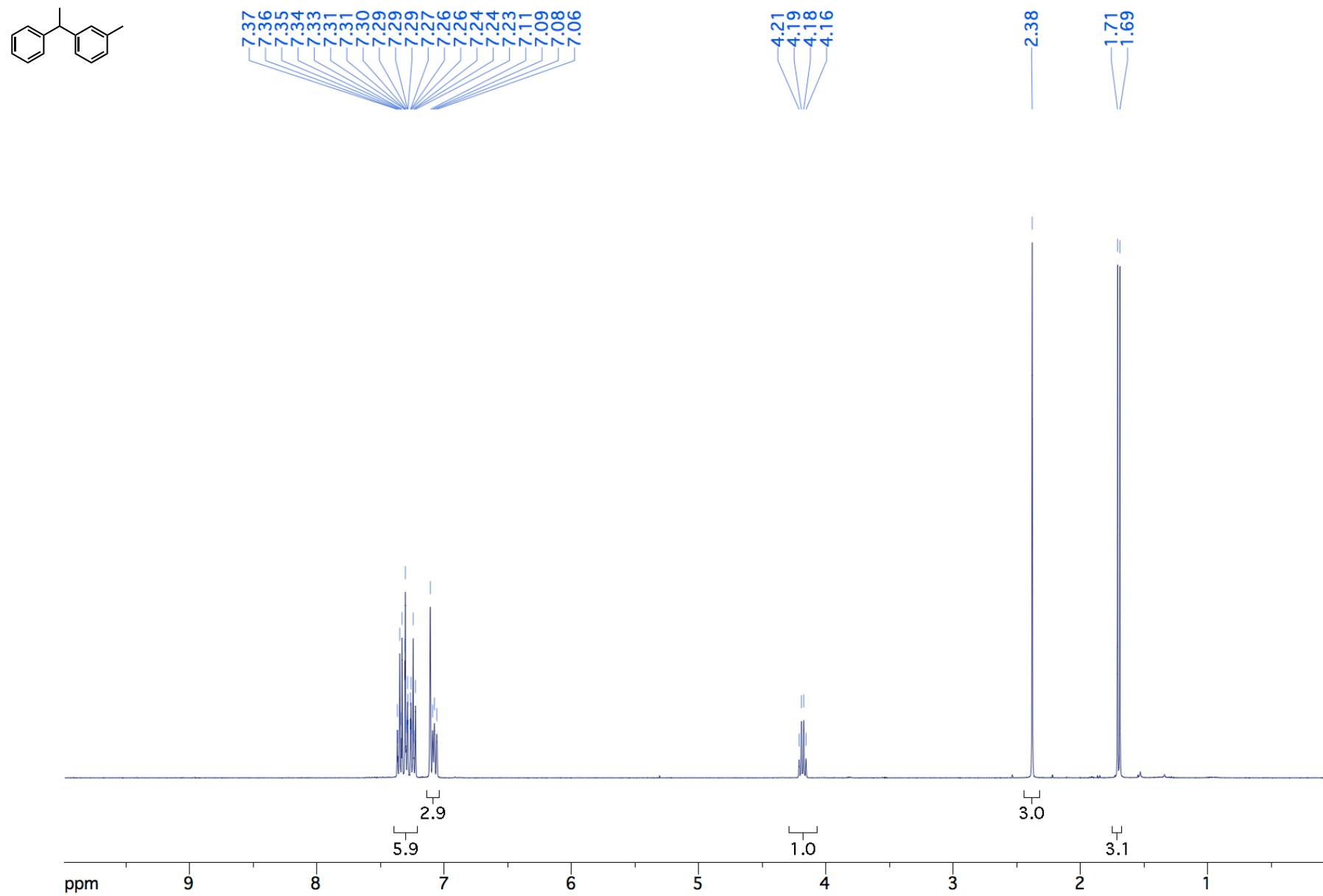
1-Methyl-2-(1-phenylethyl)benzene (12) ^1H NMR (CDCl_3 , 400 MHz)



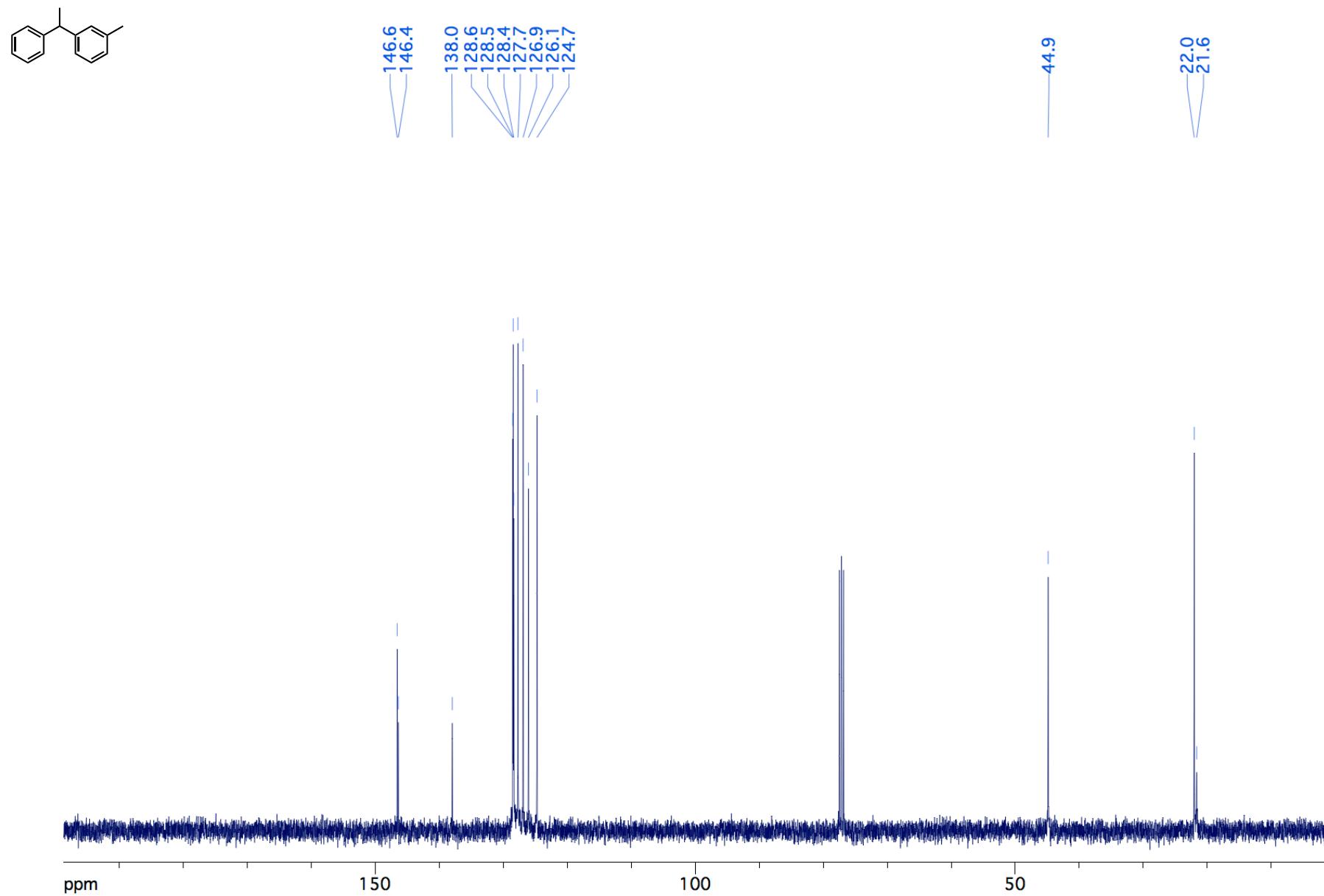
1-Methyl-2-(1-phenylethyl)benzene (12) ^{13}C NMR (CDCl_3 , 100 MHz)



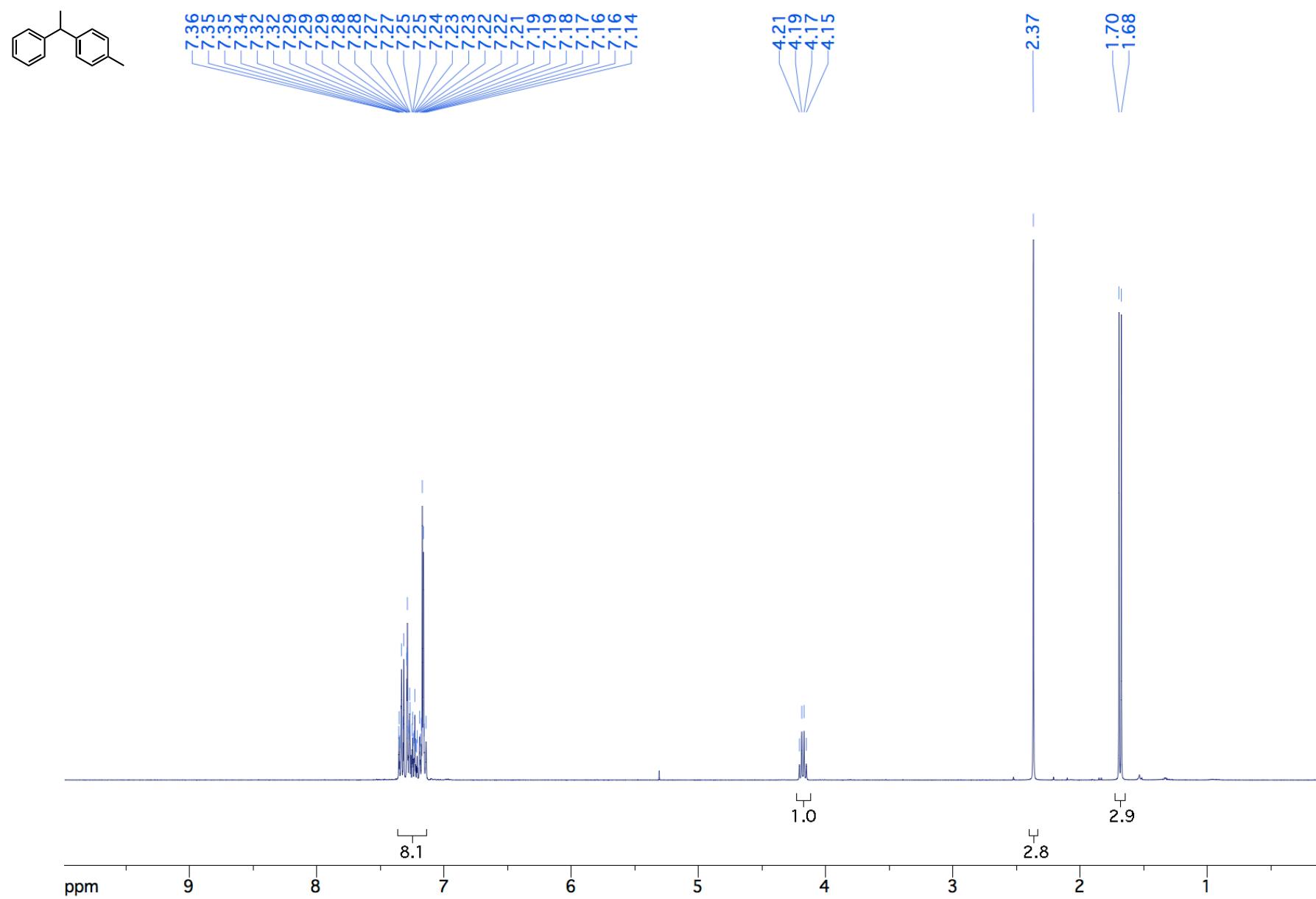
1-Methyl-3-(1-phenylethyl)benzene (13) ^1H NMR (CDCl_3 , 400 MHz)



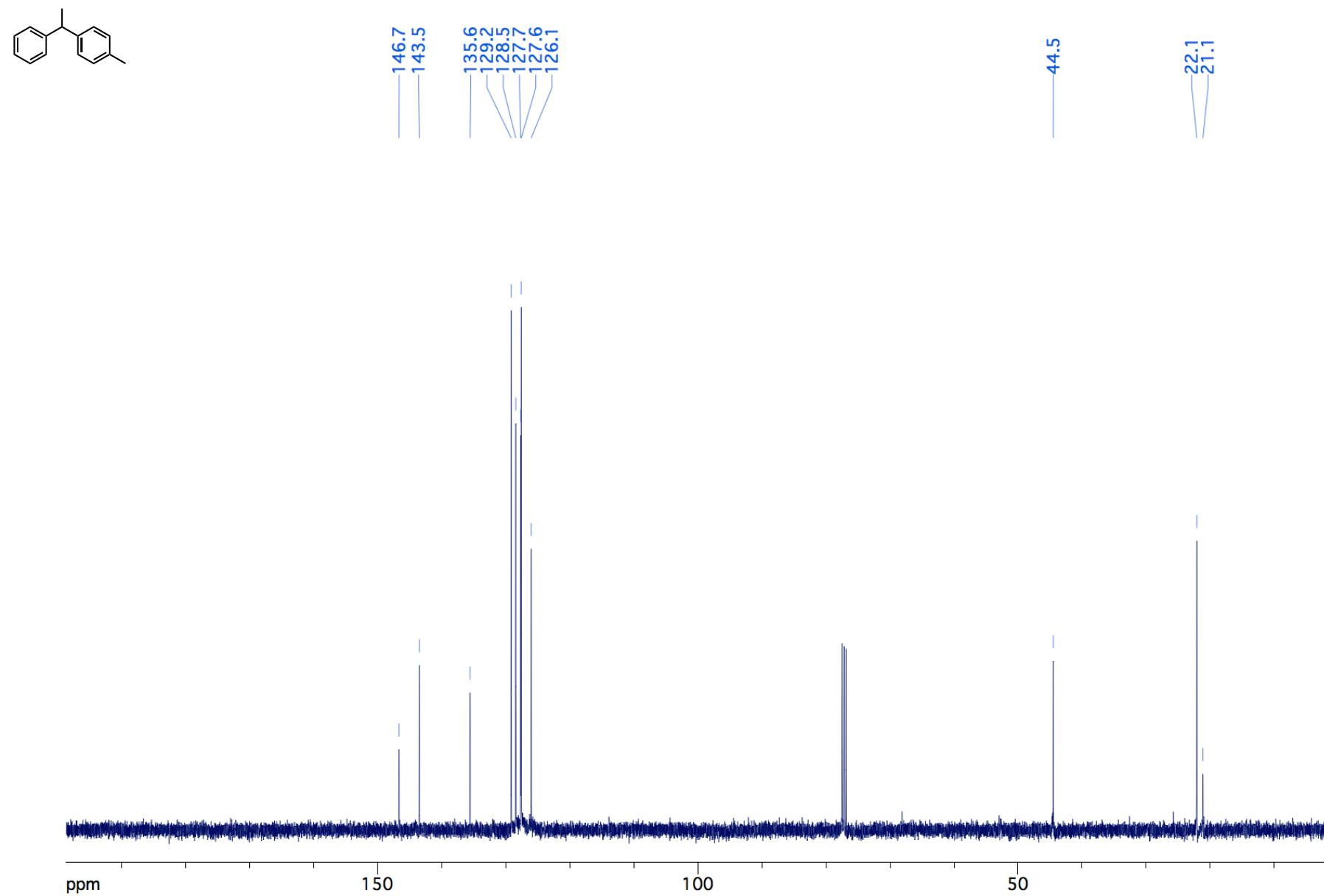
1-Methyl-3-(1-phenylethyl)benzene (13) ^{13}C NMR (CDCl_3 , 100 MHz)



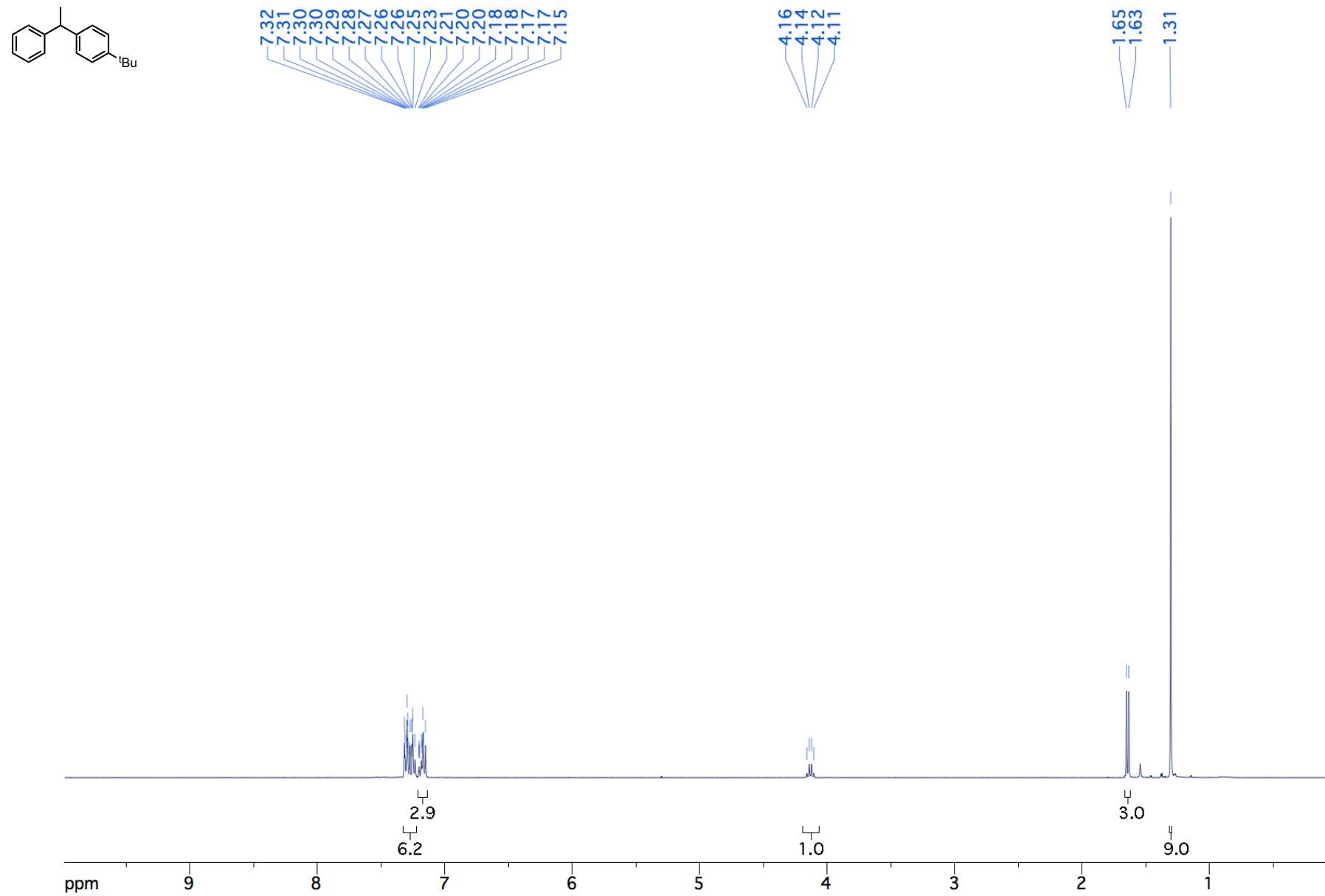
1-Methyl-4-(1-phenylethyl)benzene (14) ^1H NMR (CDCl_3 , 400 MHz)



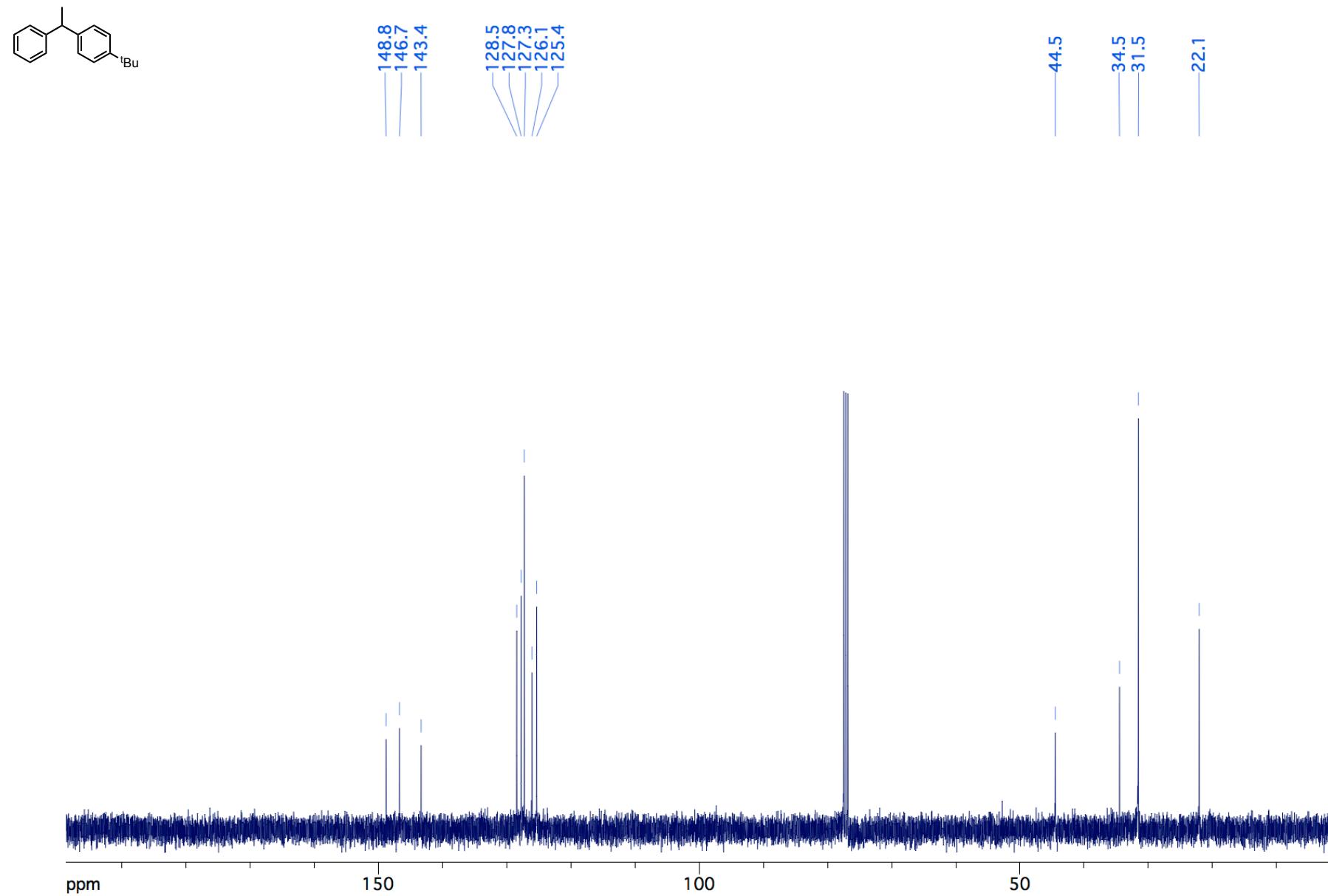
1-Methyl-4-(1-phenylethyl)benzene (14) ^{13}C NMR (CDCl_3 , 100 MHz)



11-(*tert*-Butyl)-4-(1-phenylethyl)benzene (15) ^1H NMR (CDCl_3 , 400 MHz)

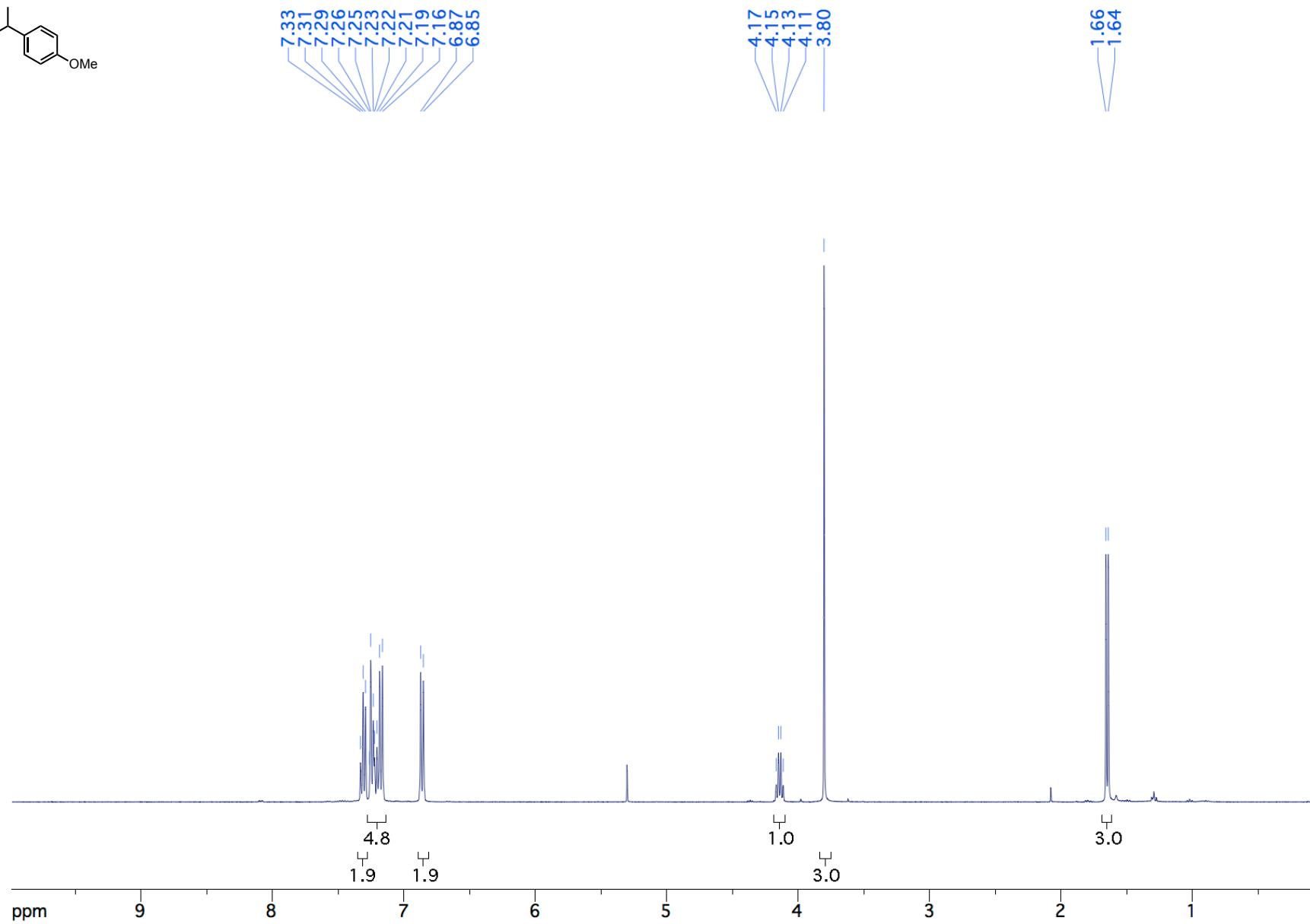
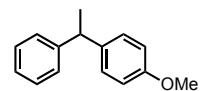


11-(*tert*-Butyl)-4-(1-phenylethyl)benzene (15) ^{13}C NMR (CDCl_3 , 100 MHz)



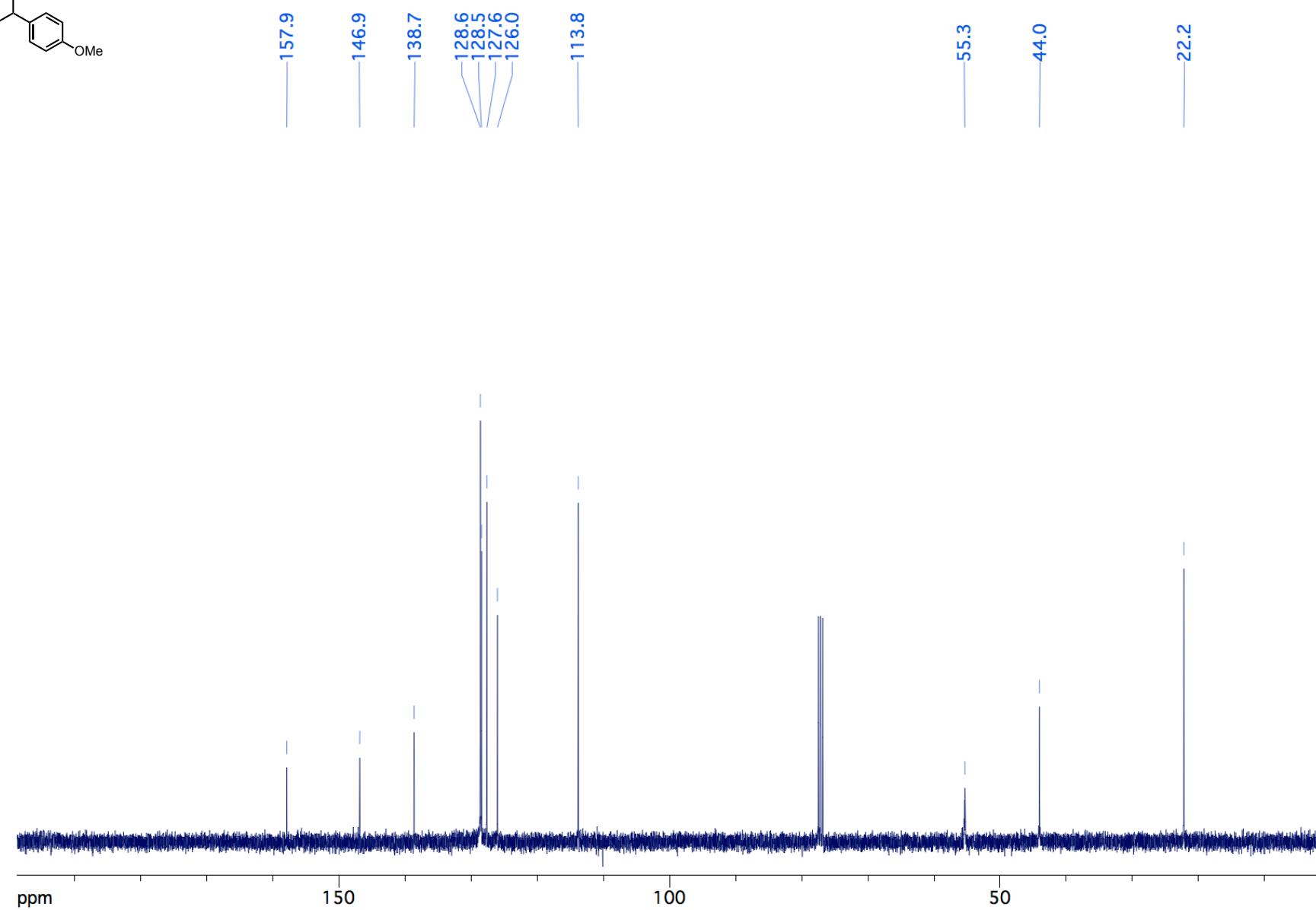
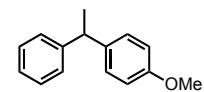
1-Methoxy-4-(1-phenylethyl)benzene (16)

¹H NMR (CDCl₃, 400 MHz)



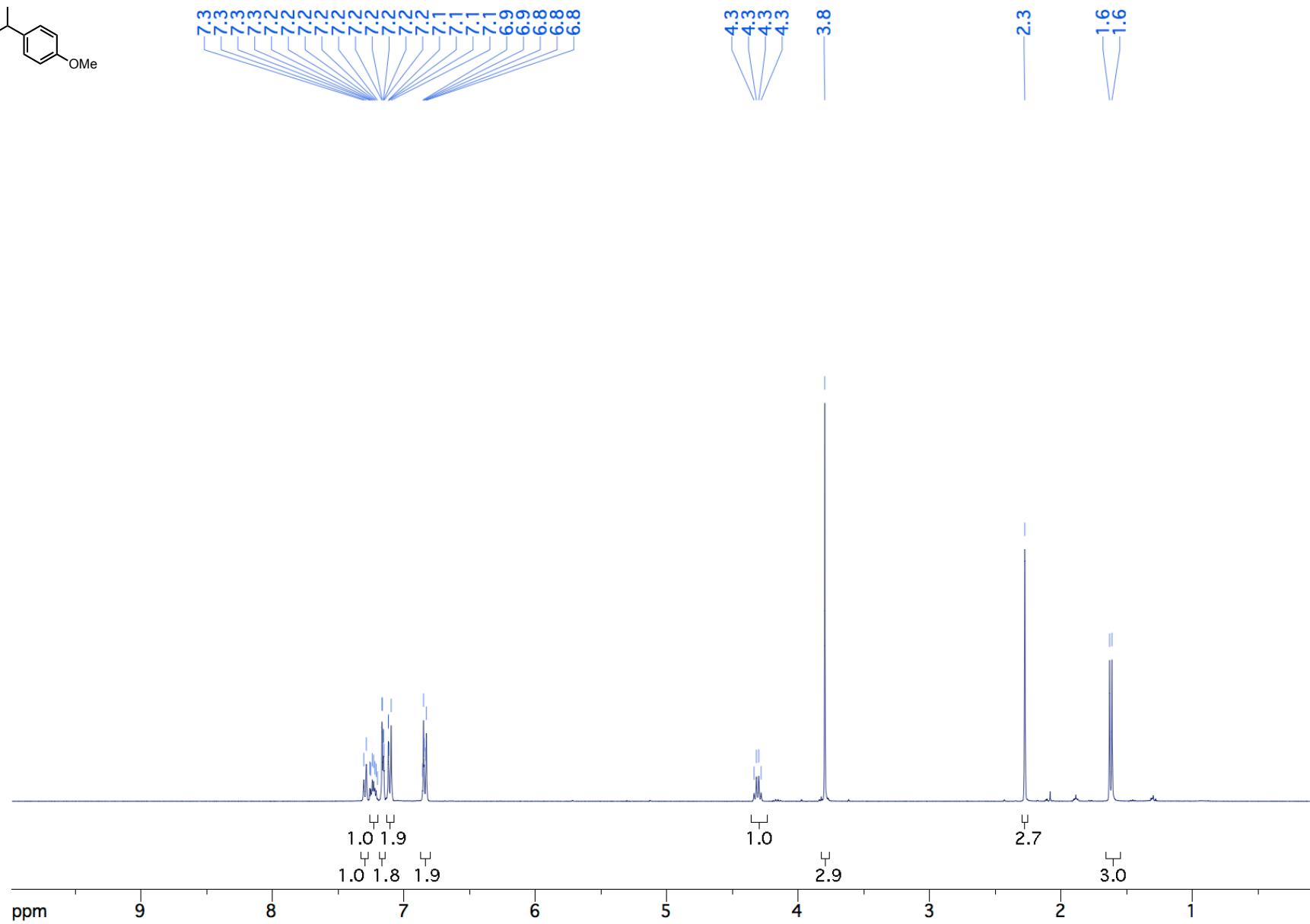
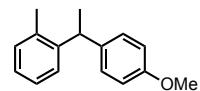
1-Methoxy-4-(1-phenylethyl)benzene (16)

^{13}C NMR (CDCl_3 , 100 MHz)



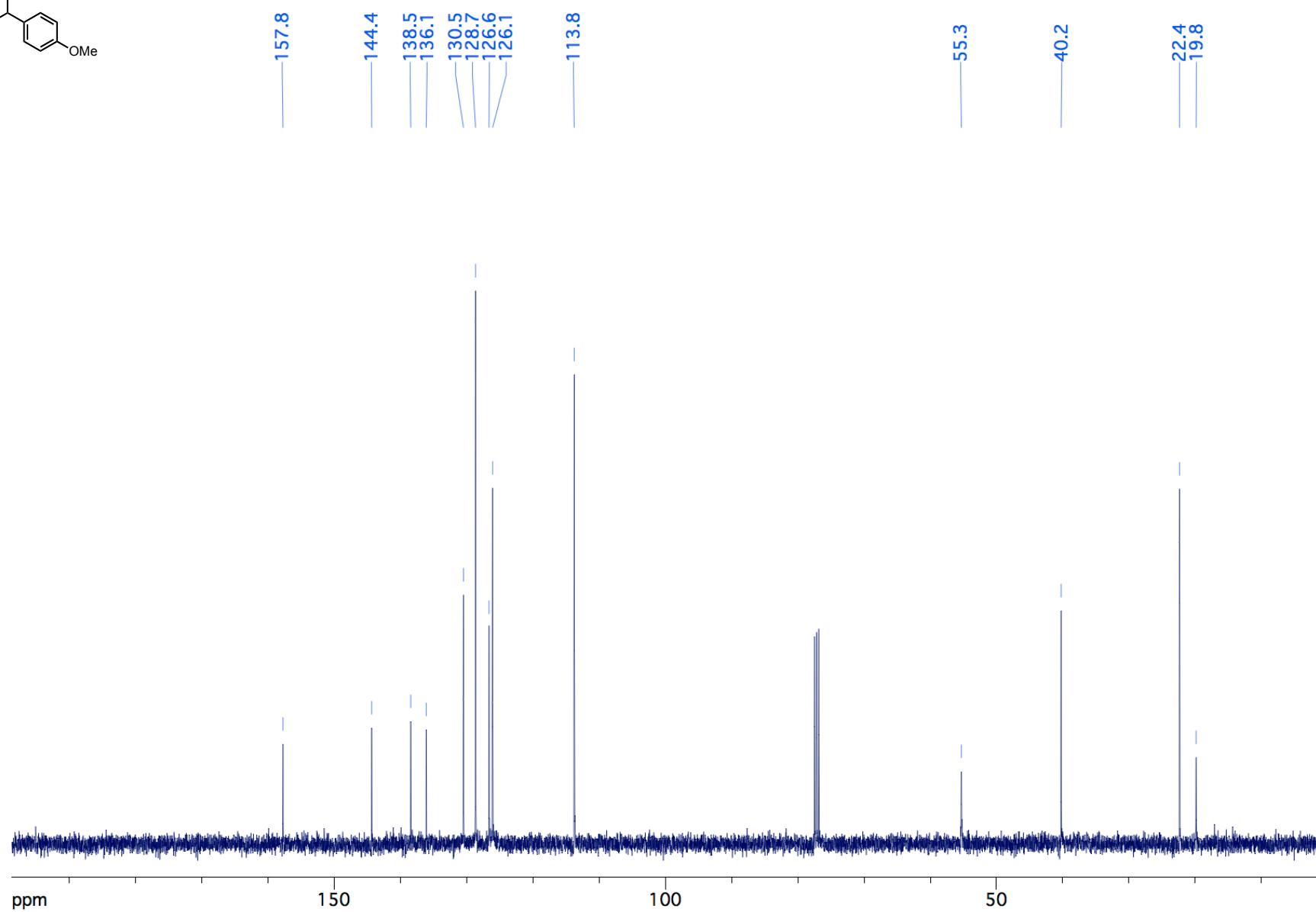
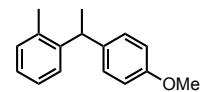
1-(1-(4-Methoxyphenyl)ethyl)-2-methylbenzene (17)

¹H NMR (CDCl₃, 400 MHz)



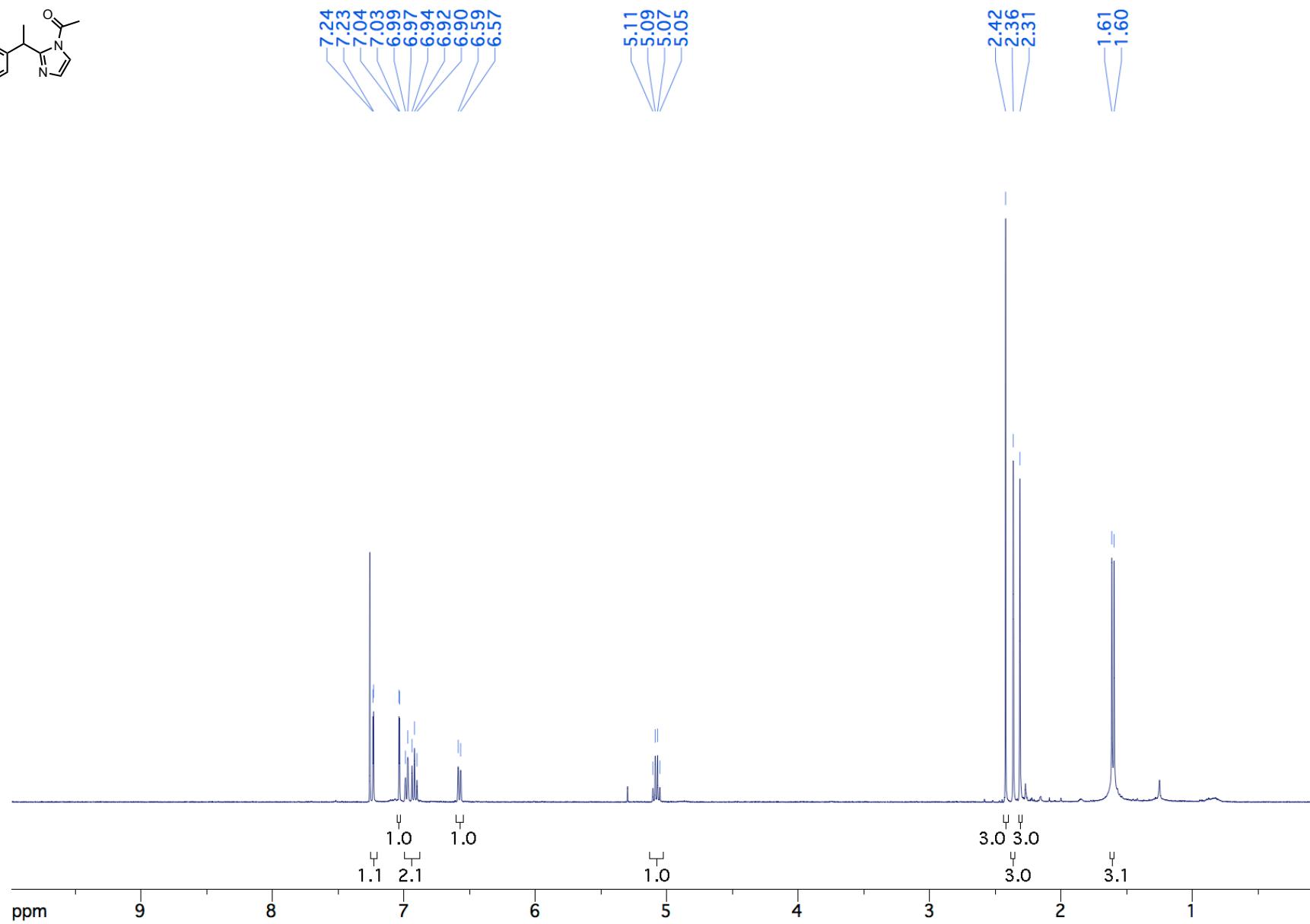
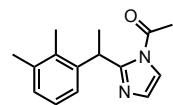
1-(1-(4-Methoxyphenyl)ethyl)-2-methylbenzene (17)

^{13}C NMR (CDCl_3 , 100 MHz)



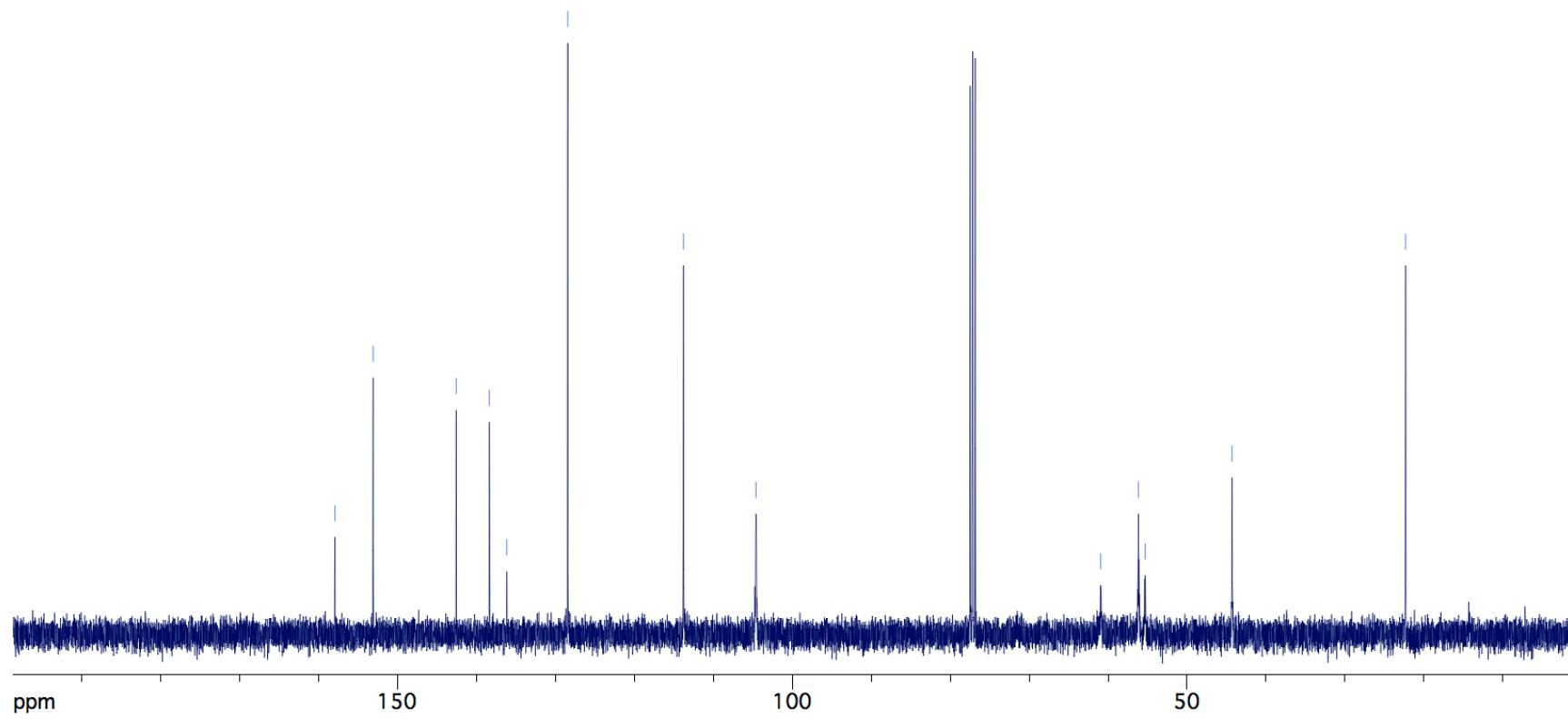
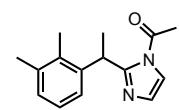
1-(2-(1-(2,3-Dimethylphenyl)ethyl)-1*H*-imidazol-1-yl)ethanone (18)

¹H NMR (CDCl₃, 400 MHz)



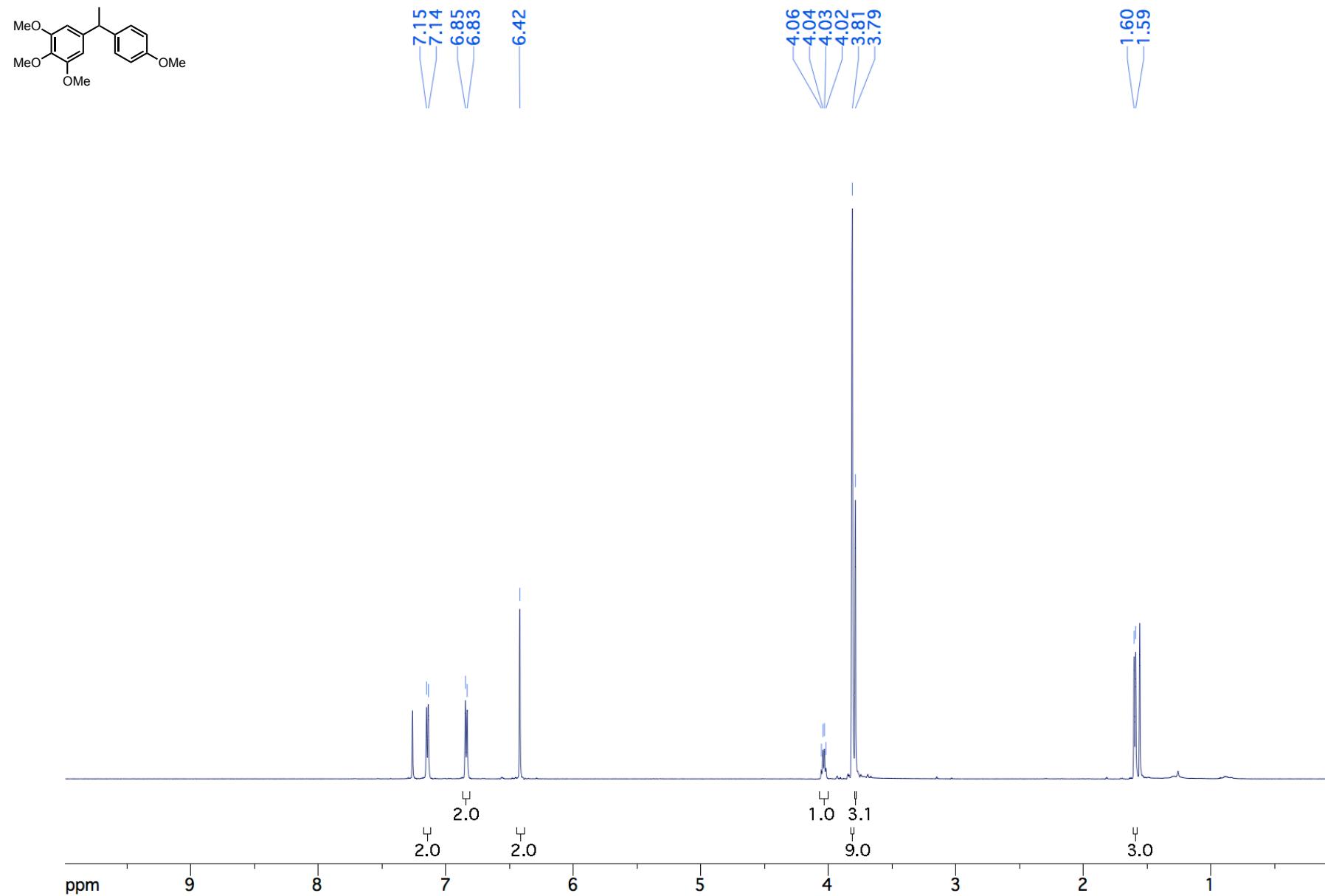
1-(2-(1-(2,3-Dimethylphenyl)ethyl)-1*H*-imidazol-1-yl)ethanone (18)

¹³C NMR (CDCl₃, 100 MHz)

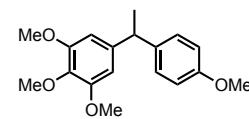


1,2,3-Trimethoxy-5-(1-(4-methoxyphenyl)ethyl)benzene (19)

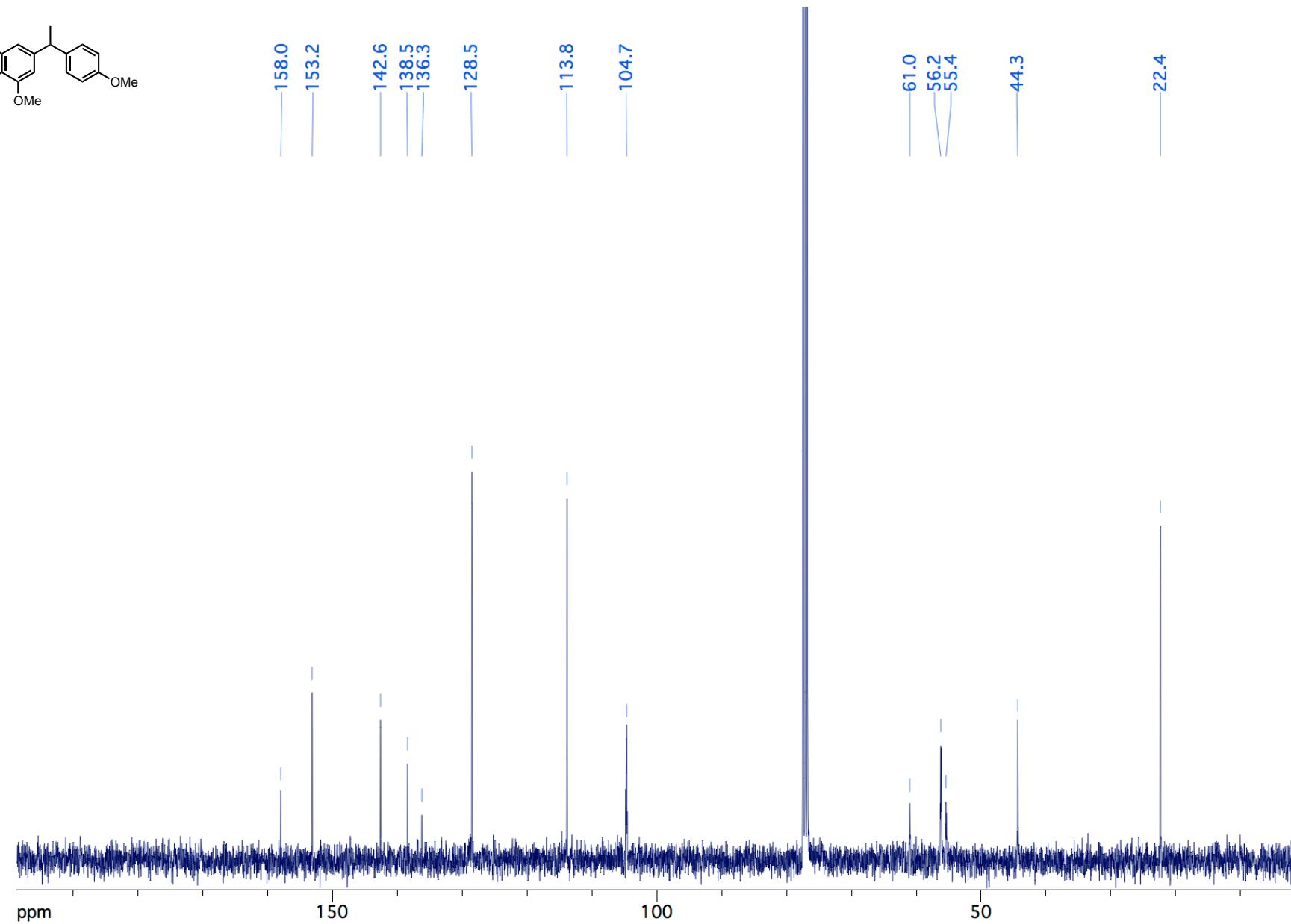
¹H NMR (CDCl₃, 600 MHz)



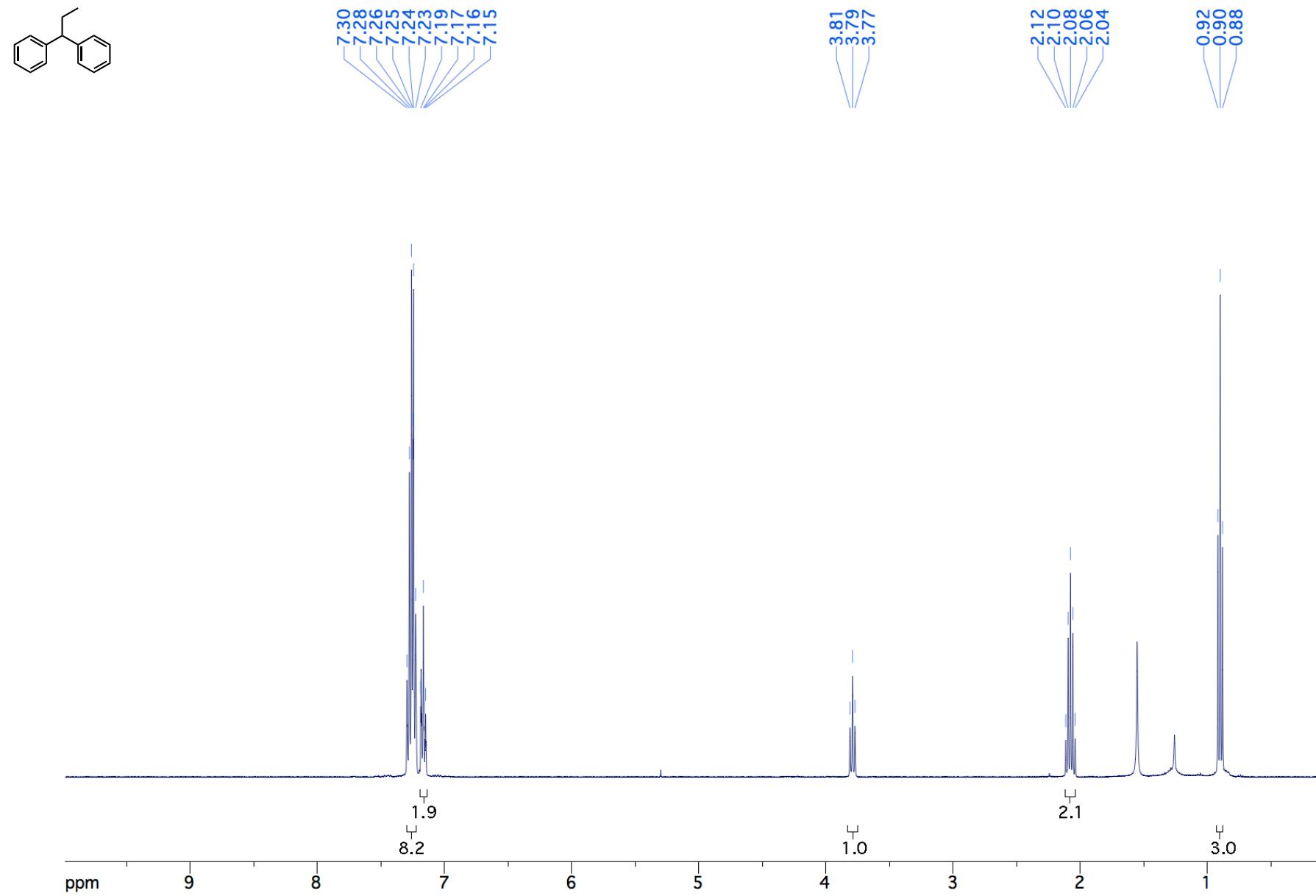
1,2,3-Trimethoxy-5-(1-(4-methoxyphenyl)ethyl)benzene (19)



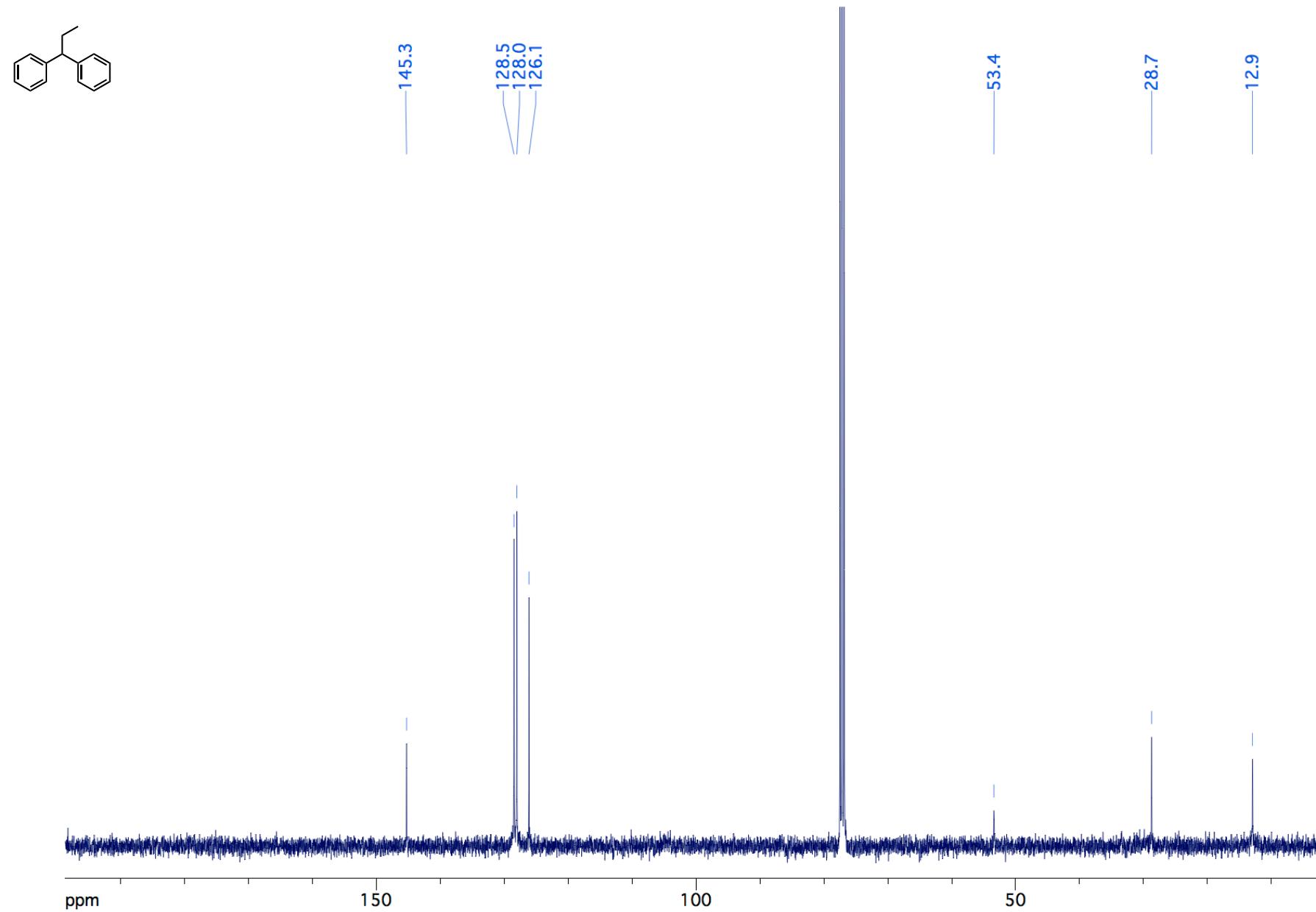
^{13}C NMR (CDCl_3 , 151 MHz)



Propane-1,1-diylbenzene (20) ^1H NMR (CDCl_3 , 400 MHz)

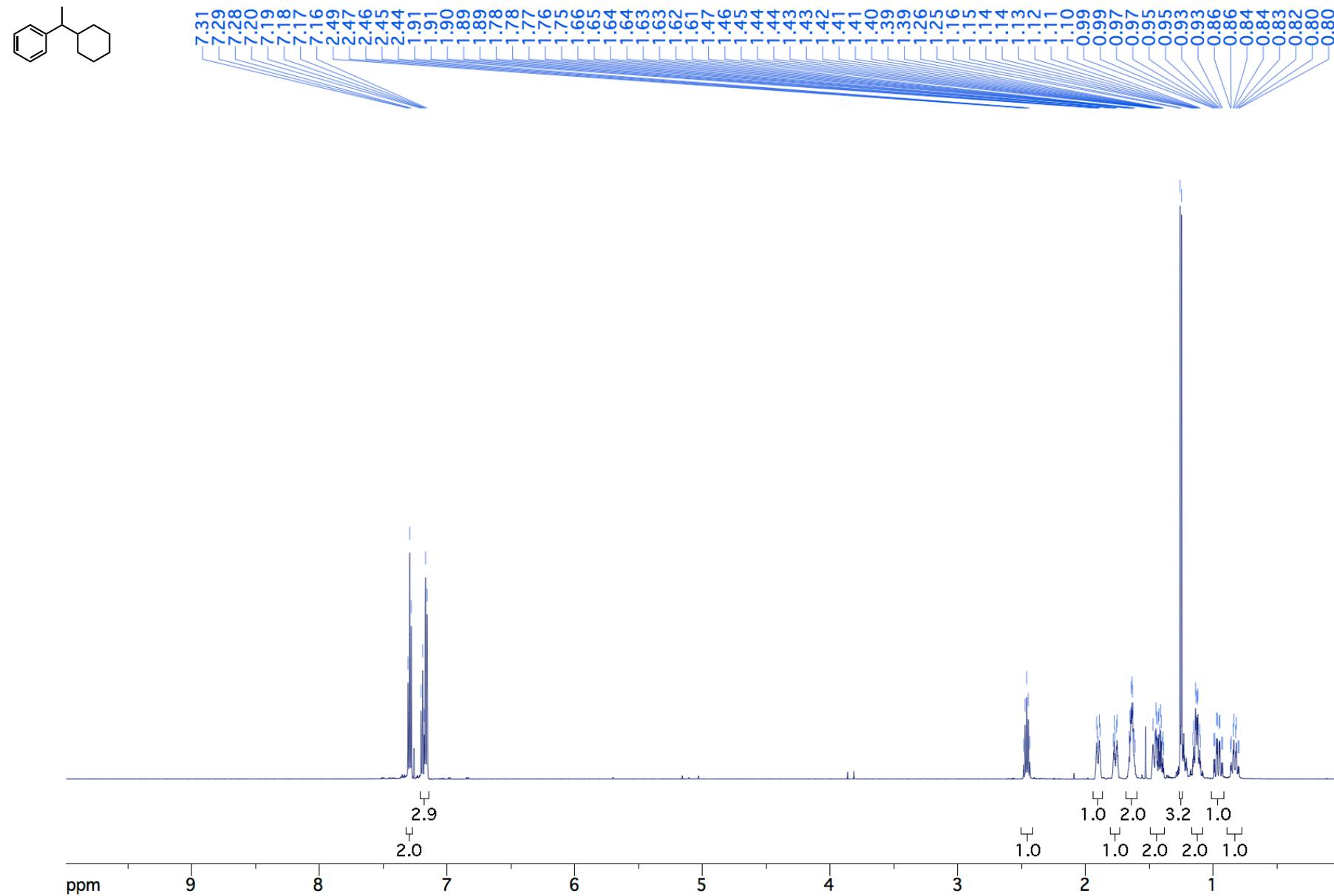


Propane-1,1-diylbenzene (20) ^{13}C NMR (CDCl_3 , 100 MHz)



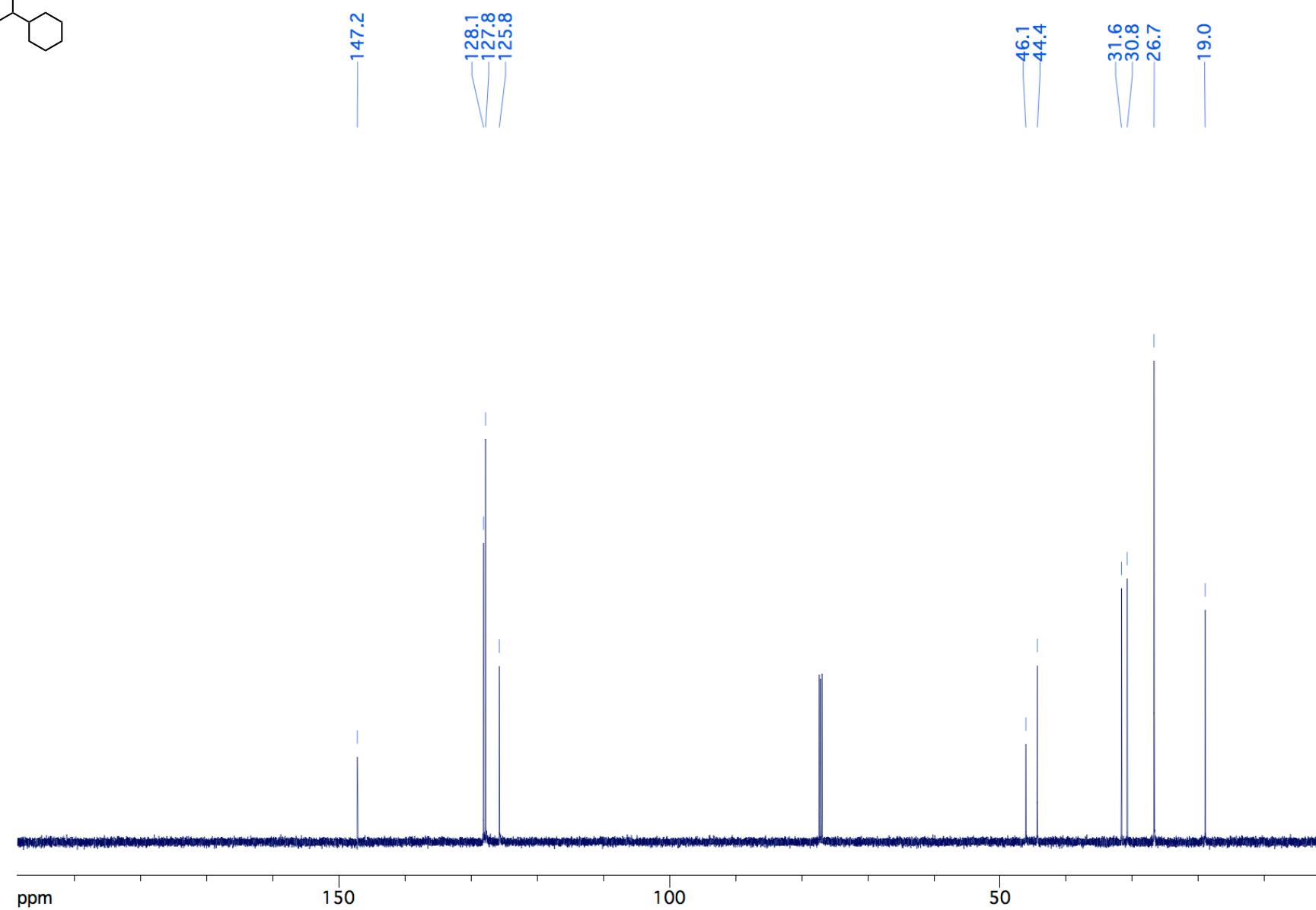
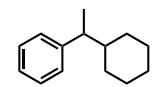
(1-Cyclohexylethyl)benzene (21)

^1H NMR (CDCl_3 , 600 MHz)

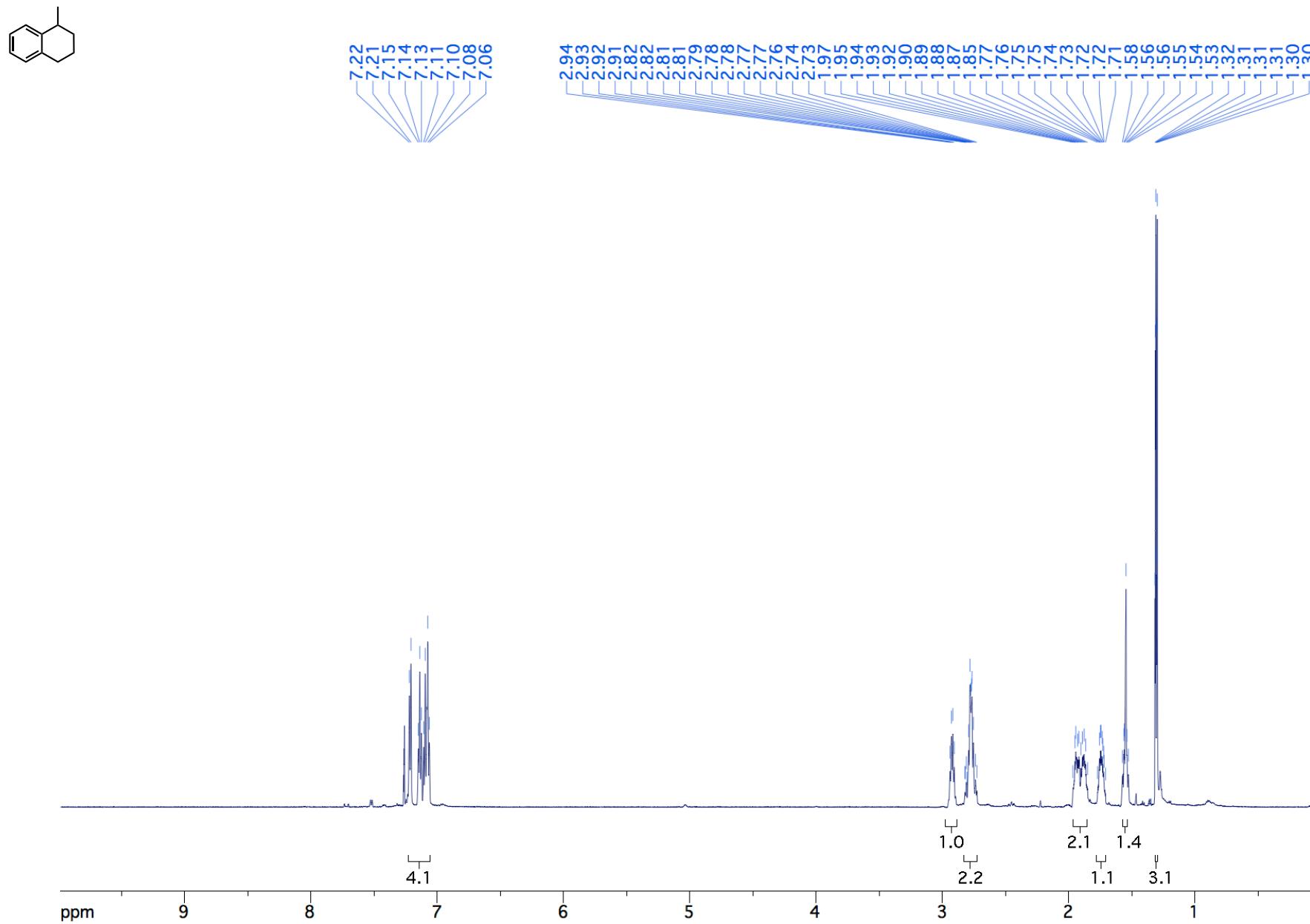


(1-Cyclohexylethyl)benzene (21)

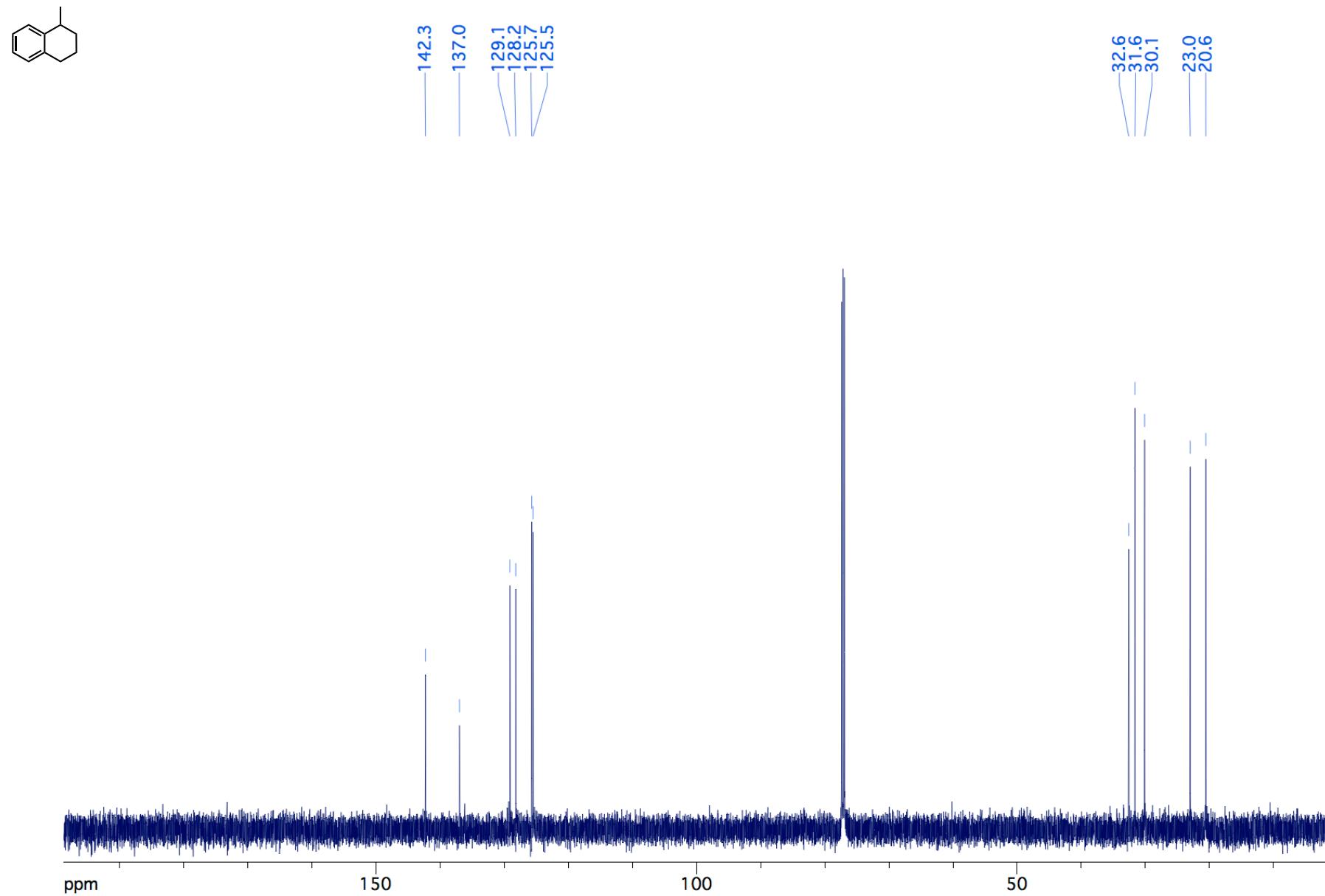
^{13}C NMR (CDCl_3 , 151 MHz)



1-Methylene-1,2,3,4-tetrahydronaphthalene (22) ^1H NMR (CDCl_3 , 600 MHz)

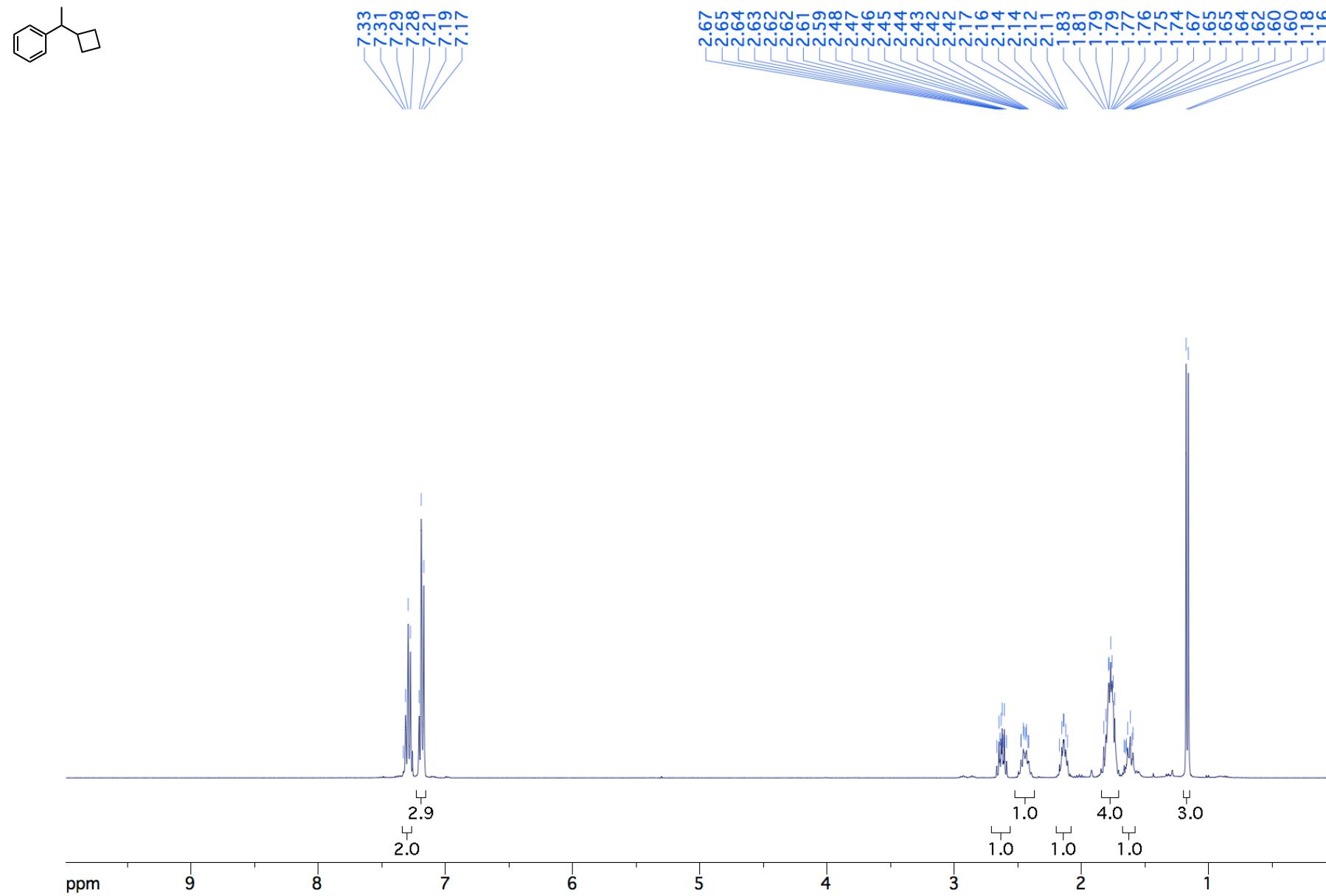


1-Methylene-1,2,3,4-tetrahydronaphthalene (22)¹³C NMR (CDCl₃, 151 MHz)



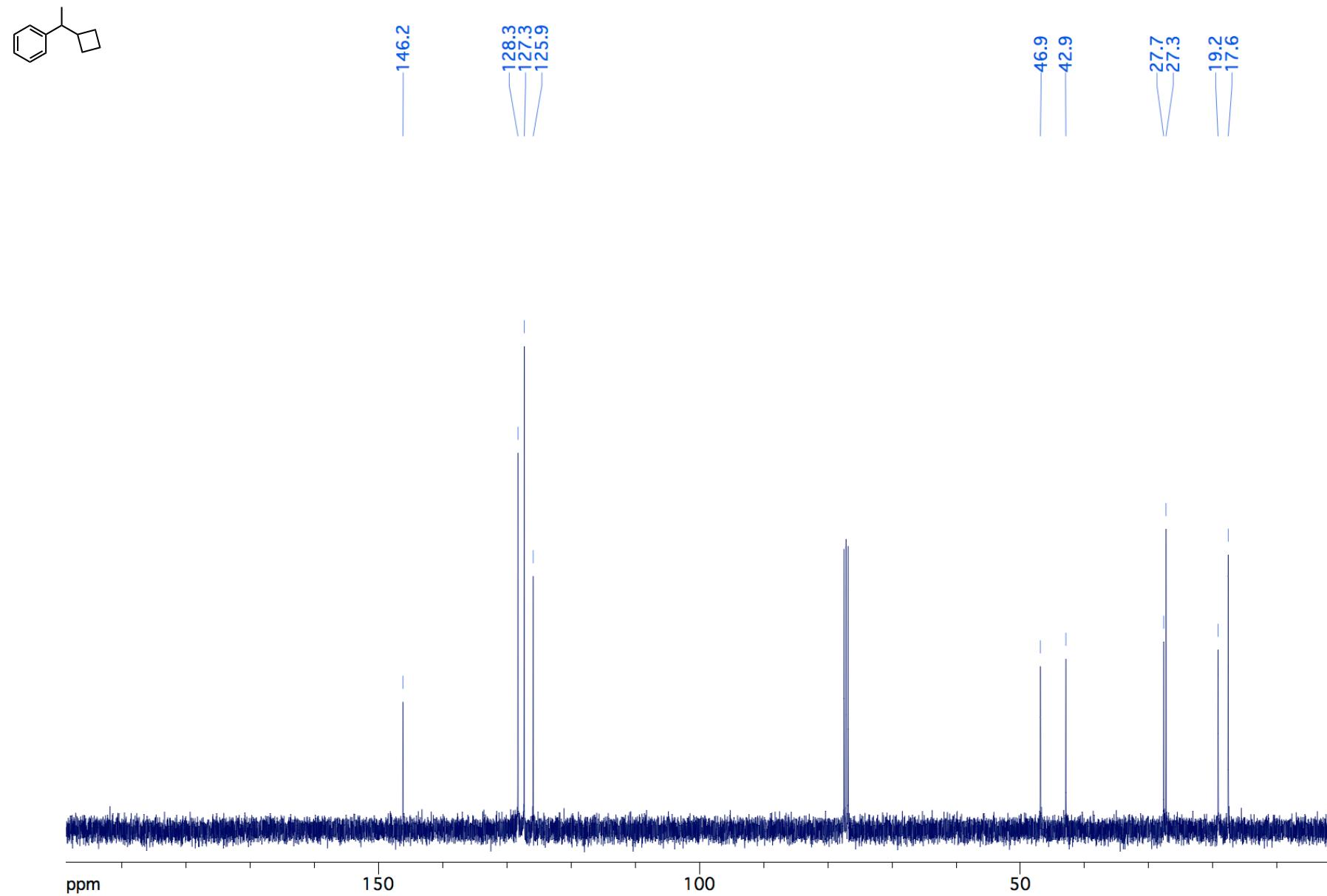
(1-Cyclobutylethyl)benzene (23)

¹H NMR (CDCl₃, 400 MHz)



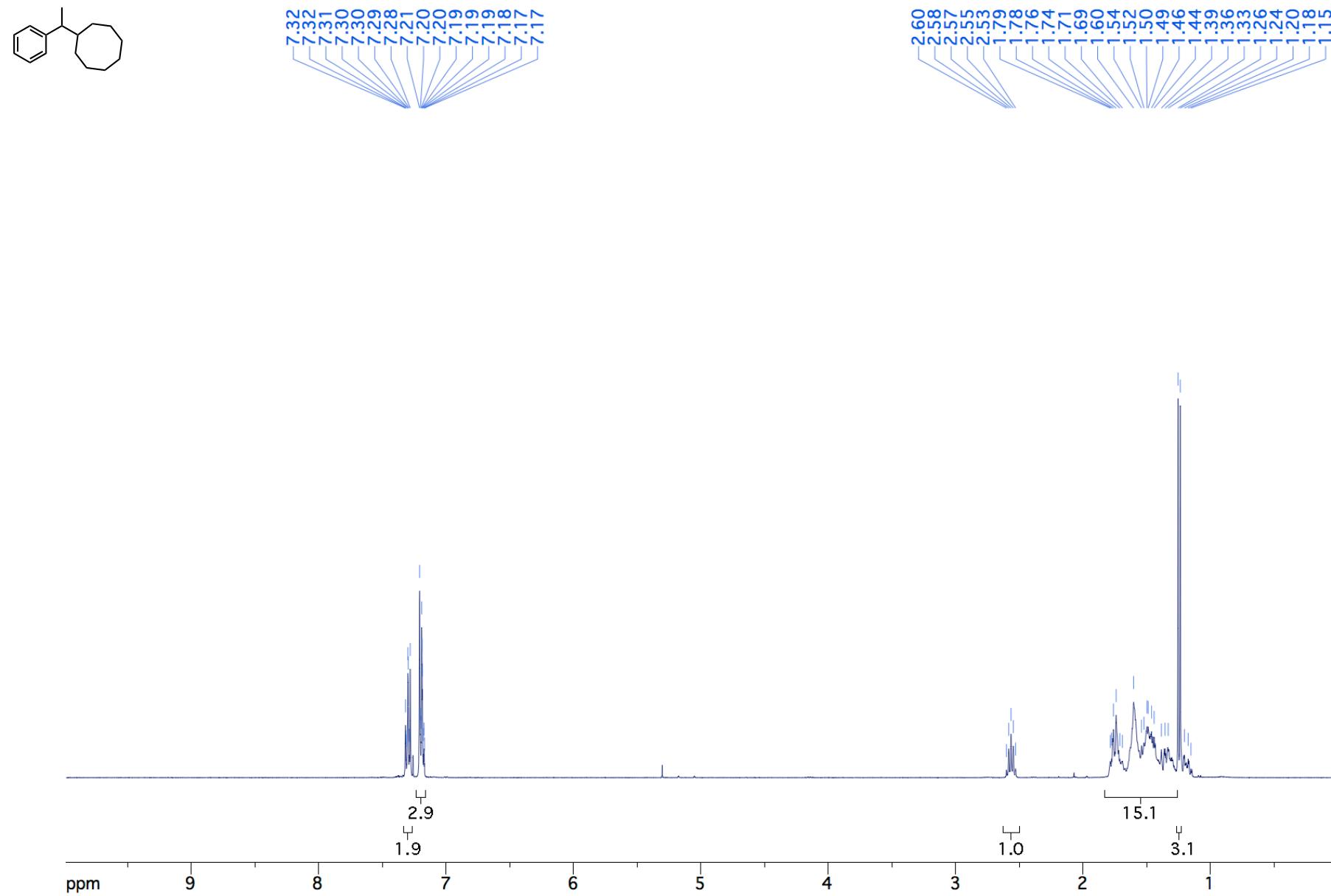
(1-Cyclobutylethyl)benzene (23)

^{13}C NMR (CDCl_3 , 100 MHz)



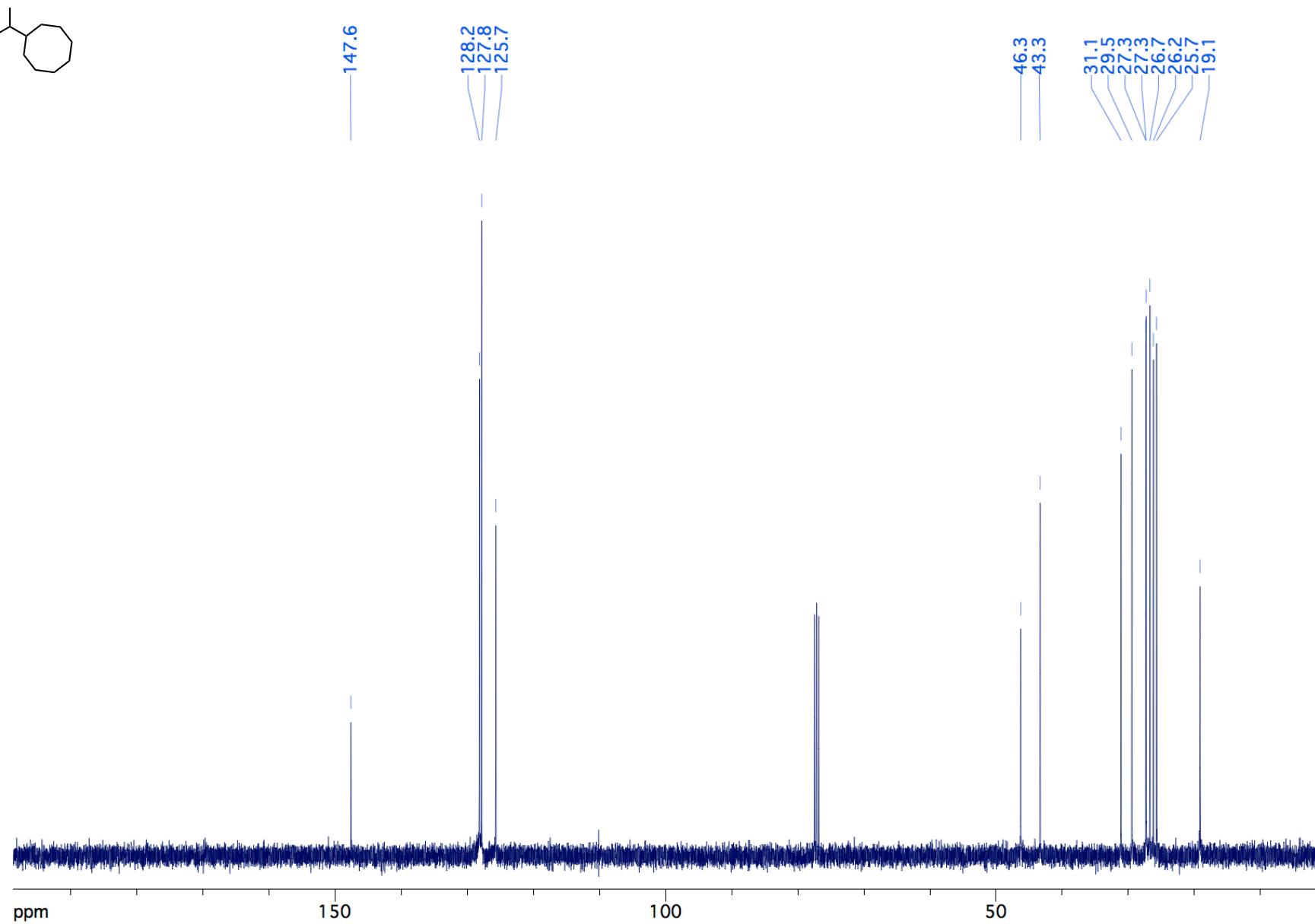
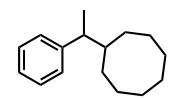
(1-Phenylethyl)cyclooctane (24)

^1H NMR (CDCl_3 , 400 MHz)



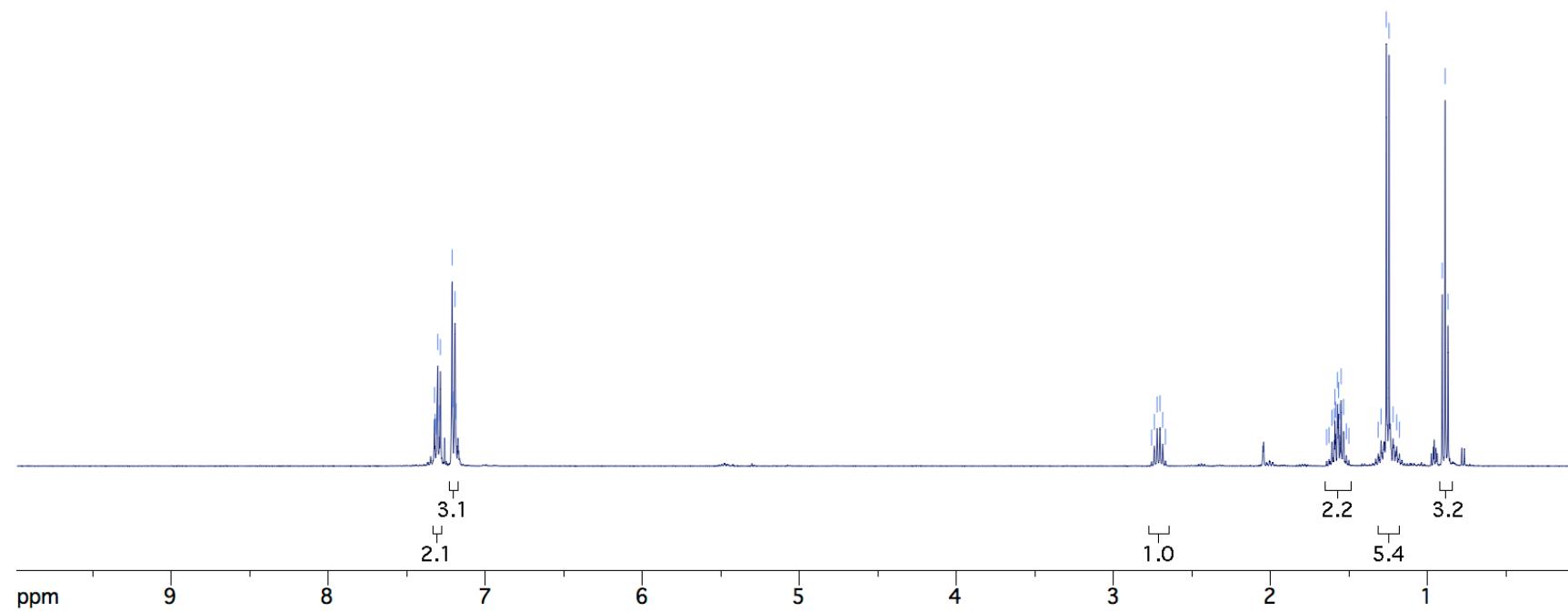
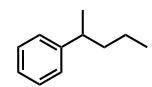
(1-Phenylethyl)cyclooctane (24)

^{13}C NMR (CDCl_3 , 100 MHz)



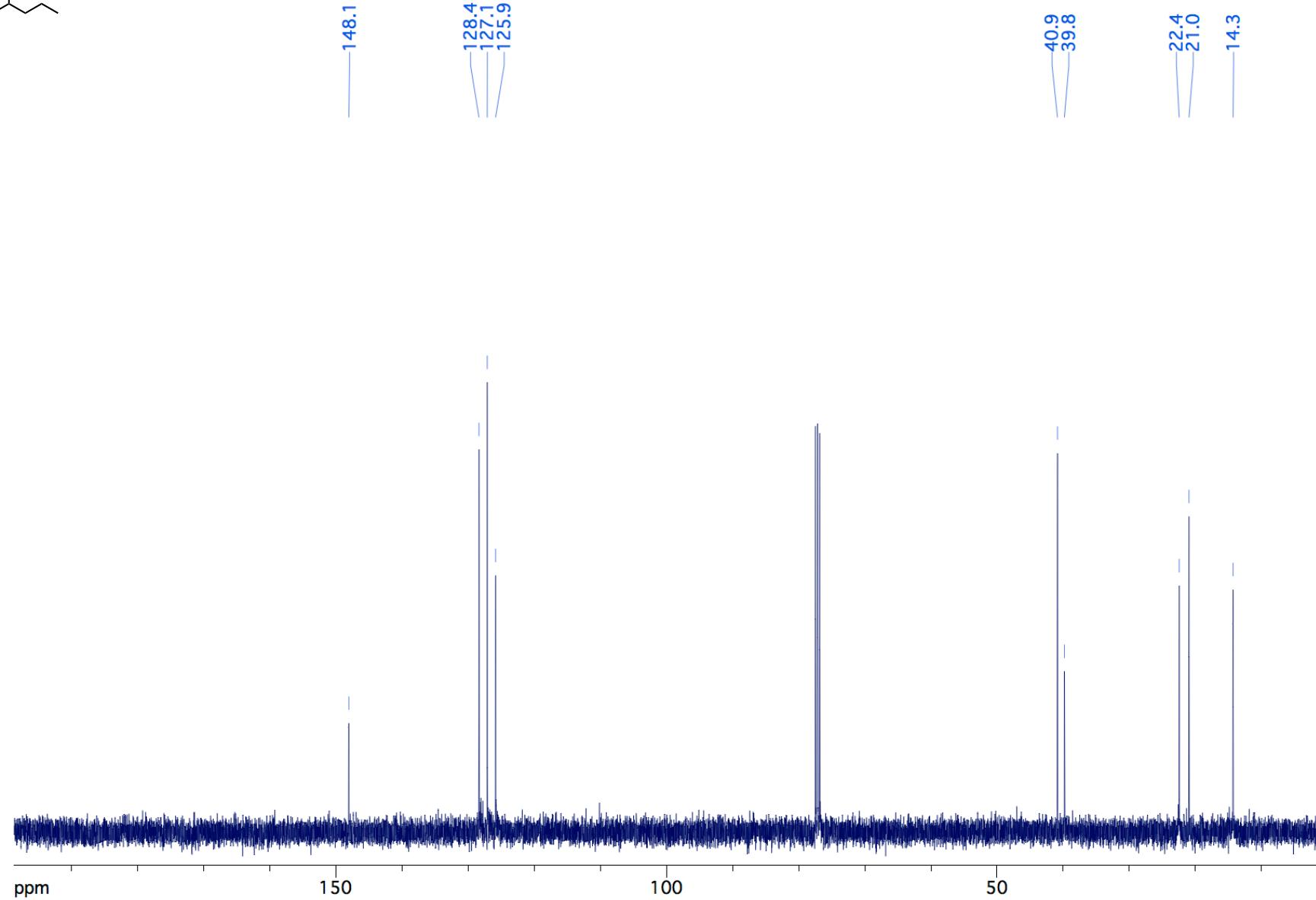
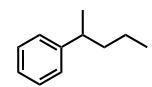
Pentan-2-ylbenzene (25)

^1H NMR (CDCl_3 , 400 MHz)



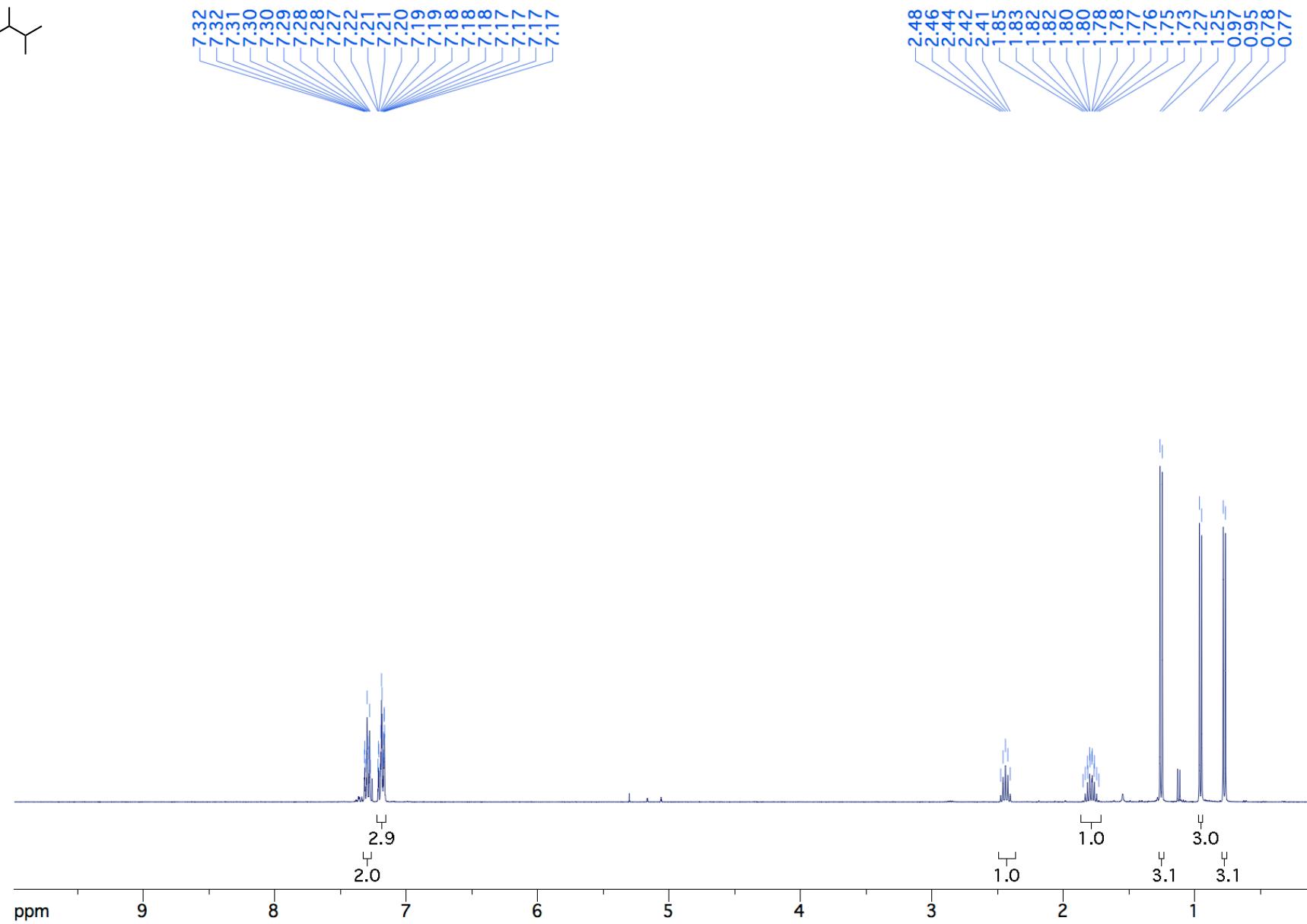
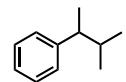
Pentan-2-ylbenzene (25)

^{13}C NMR (CDCl_3 , 100 MHz)



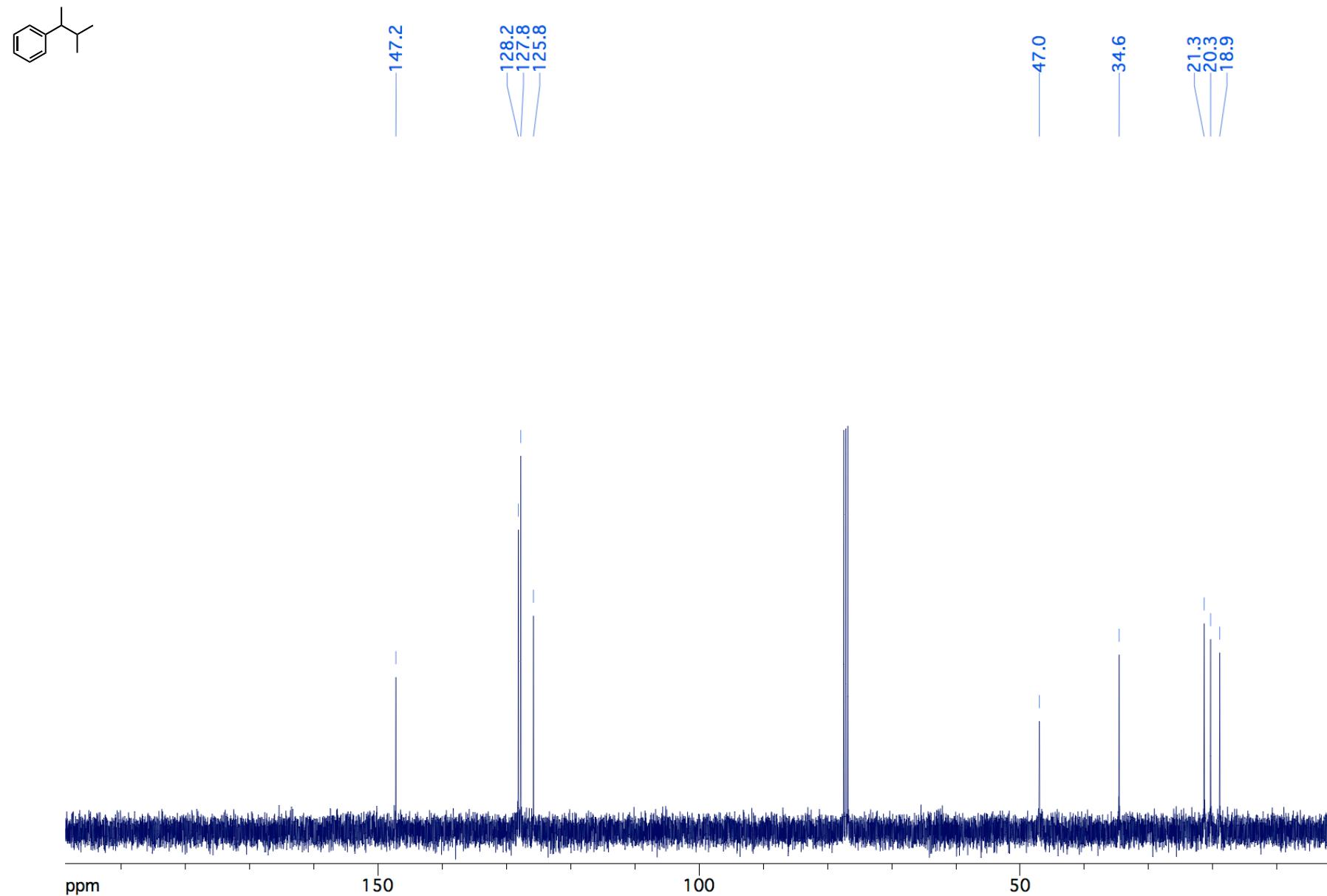
(3-Methylbutan-2-yl)benzene (26)

¹H NMR (CDCl₃, 400 MHz)



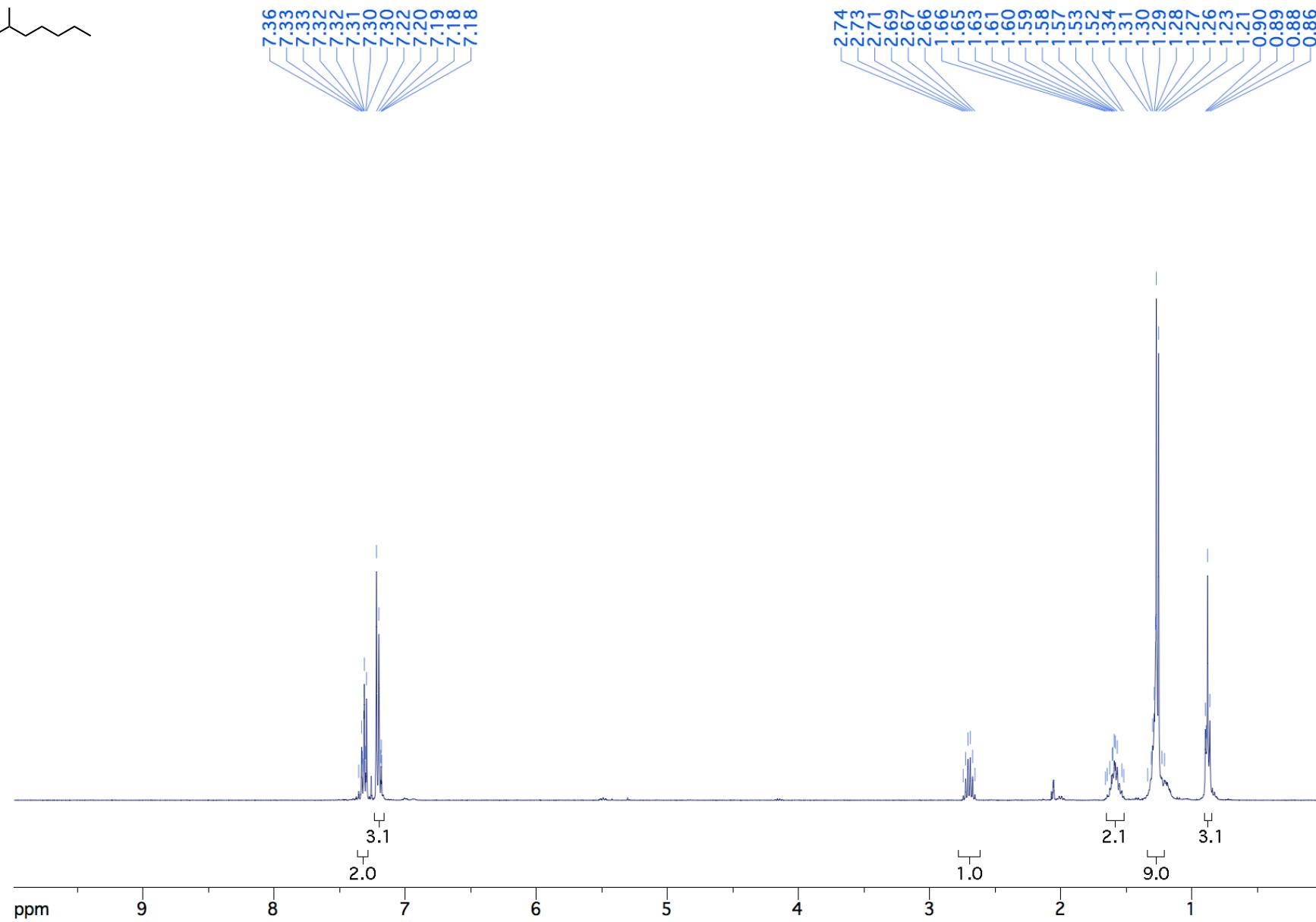
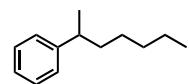
(3-Methylbutan-2-yl)benzene (26)

^{13}C NMR (CDCl_3 , 100 MHz)



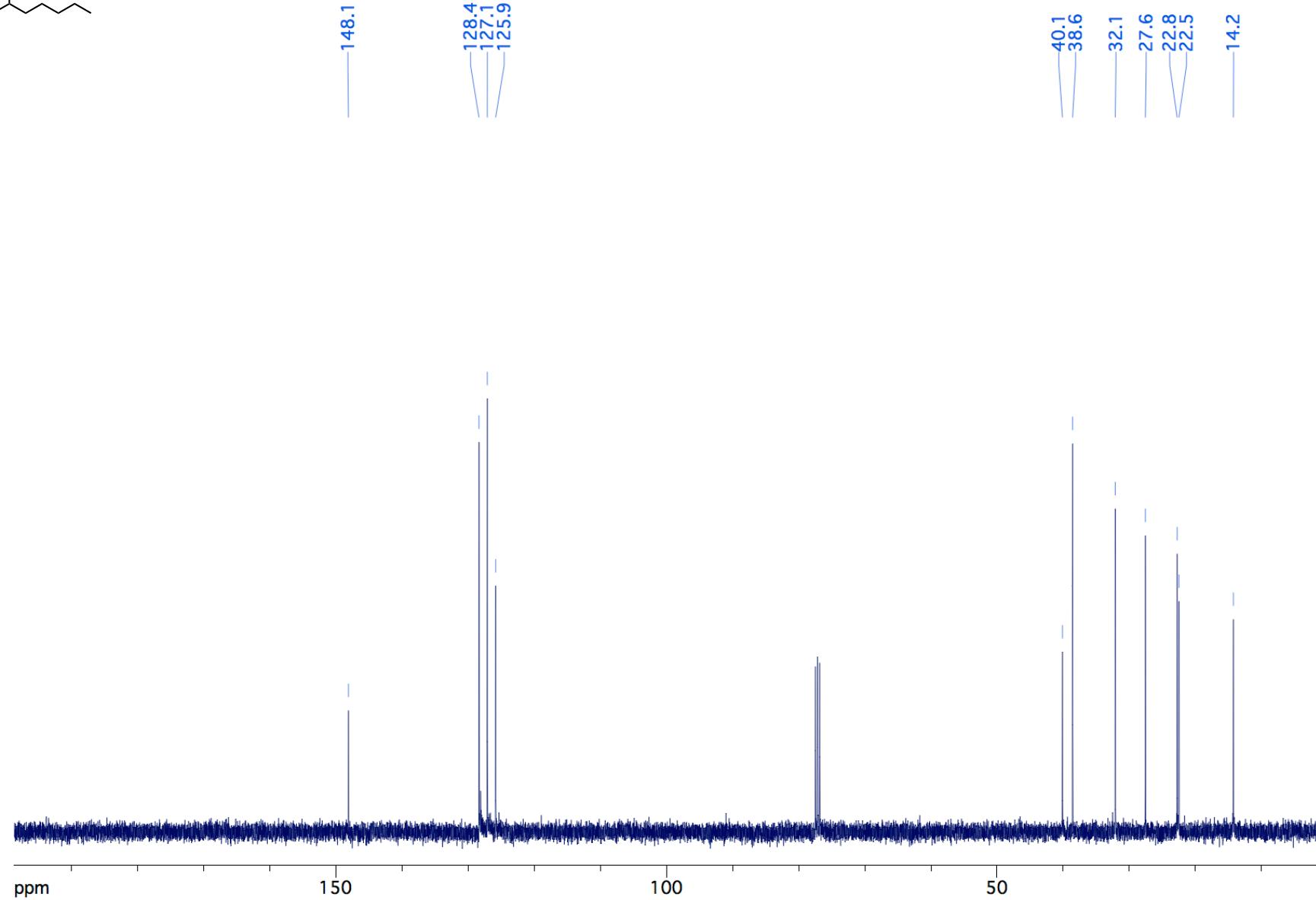
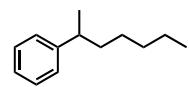
Heptan-2-ylbenzene (27)

¹H NMR (CDCl₃, 400 MHz)

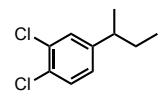


Heptan-2-ylbenzene (27)

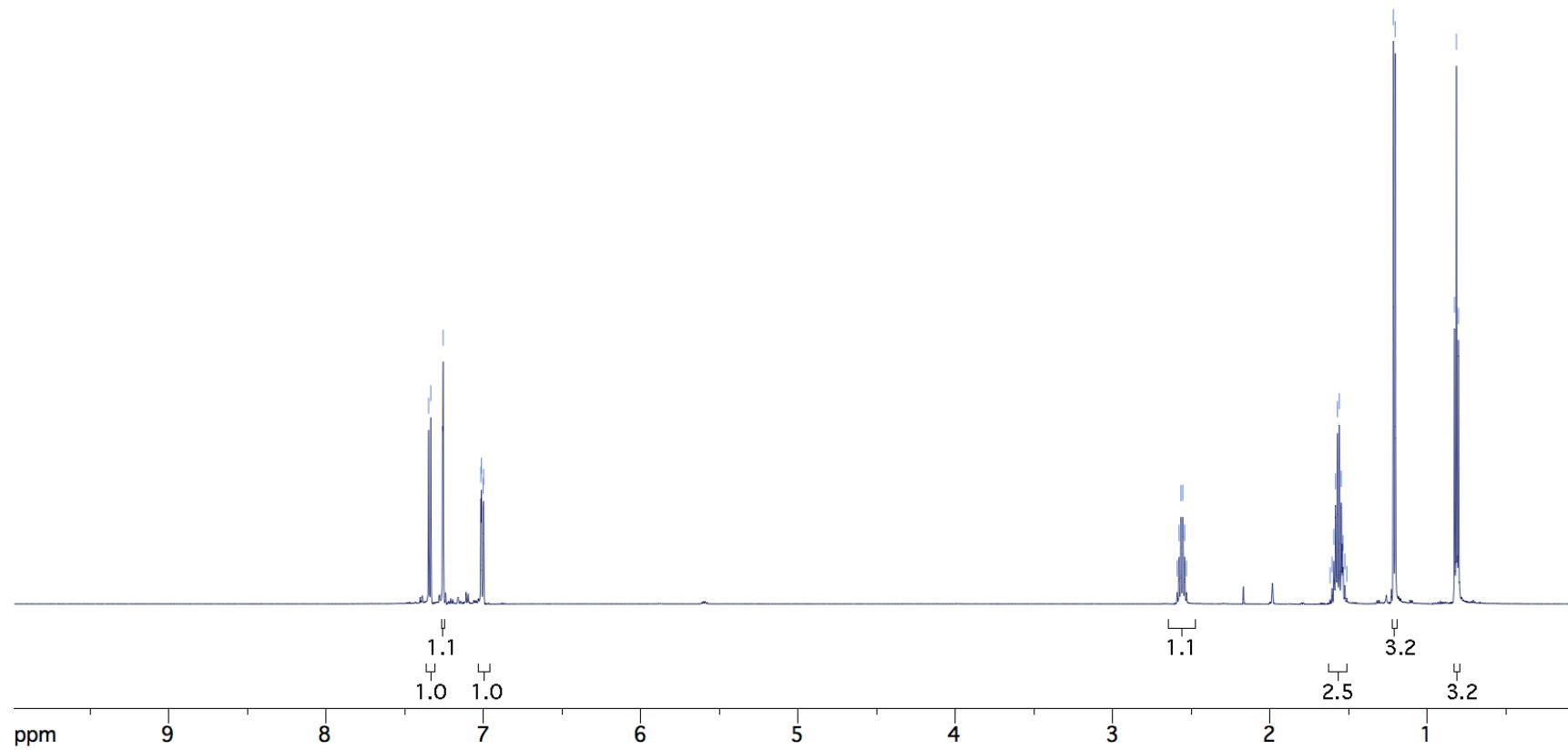
^{13}C NMR (CDCl_3 , 100 MHz)



4-(sec-Butyl)-1,2-dichlorobenzene (28) ^1H NMR (CDCl_3 , 600 MHz)

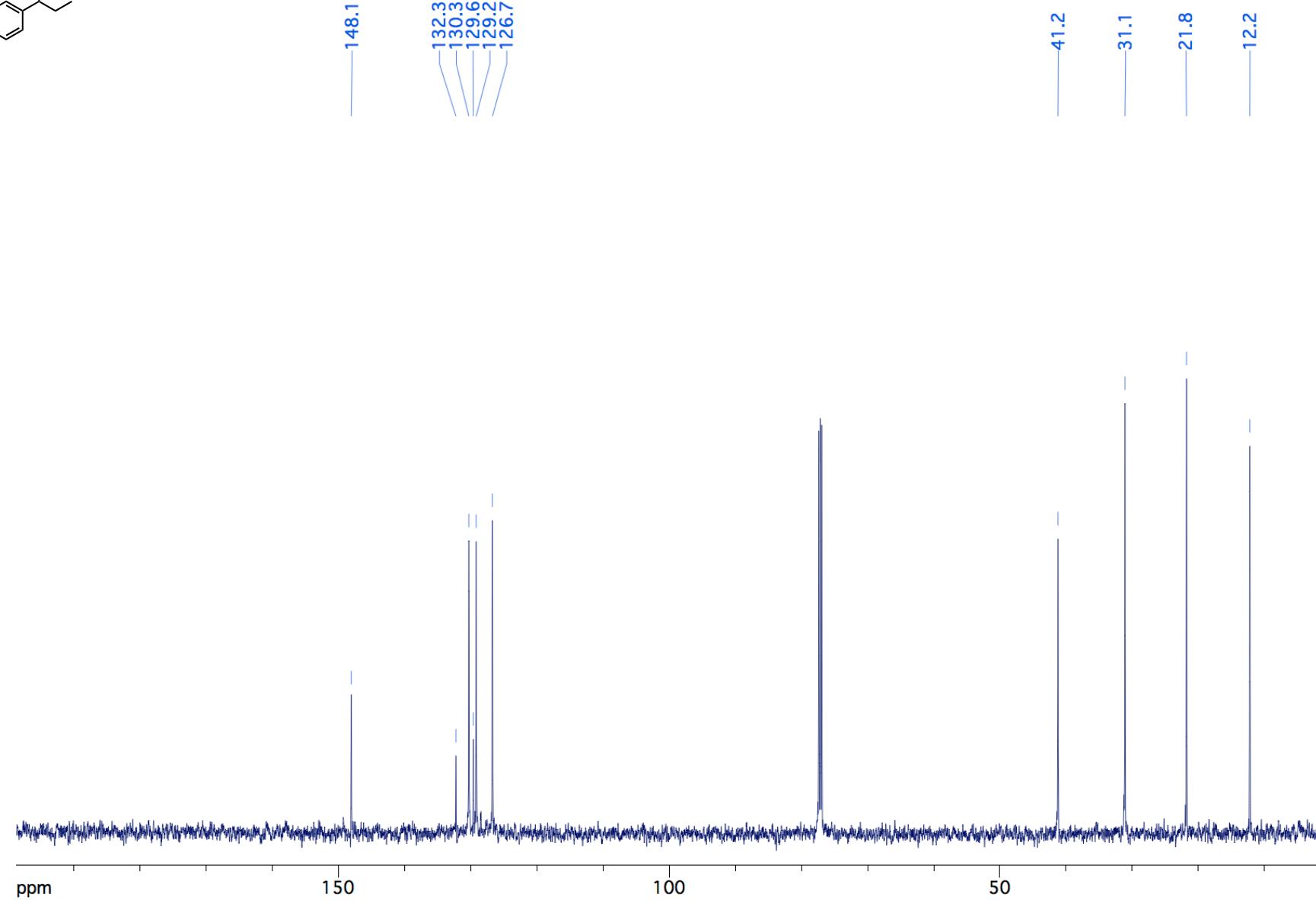
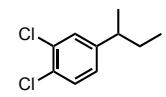


7.35
7.34
7.26
7.02
7.01
7.00

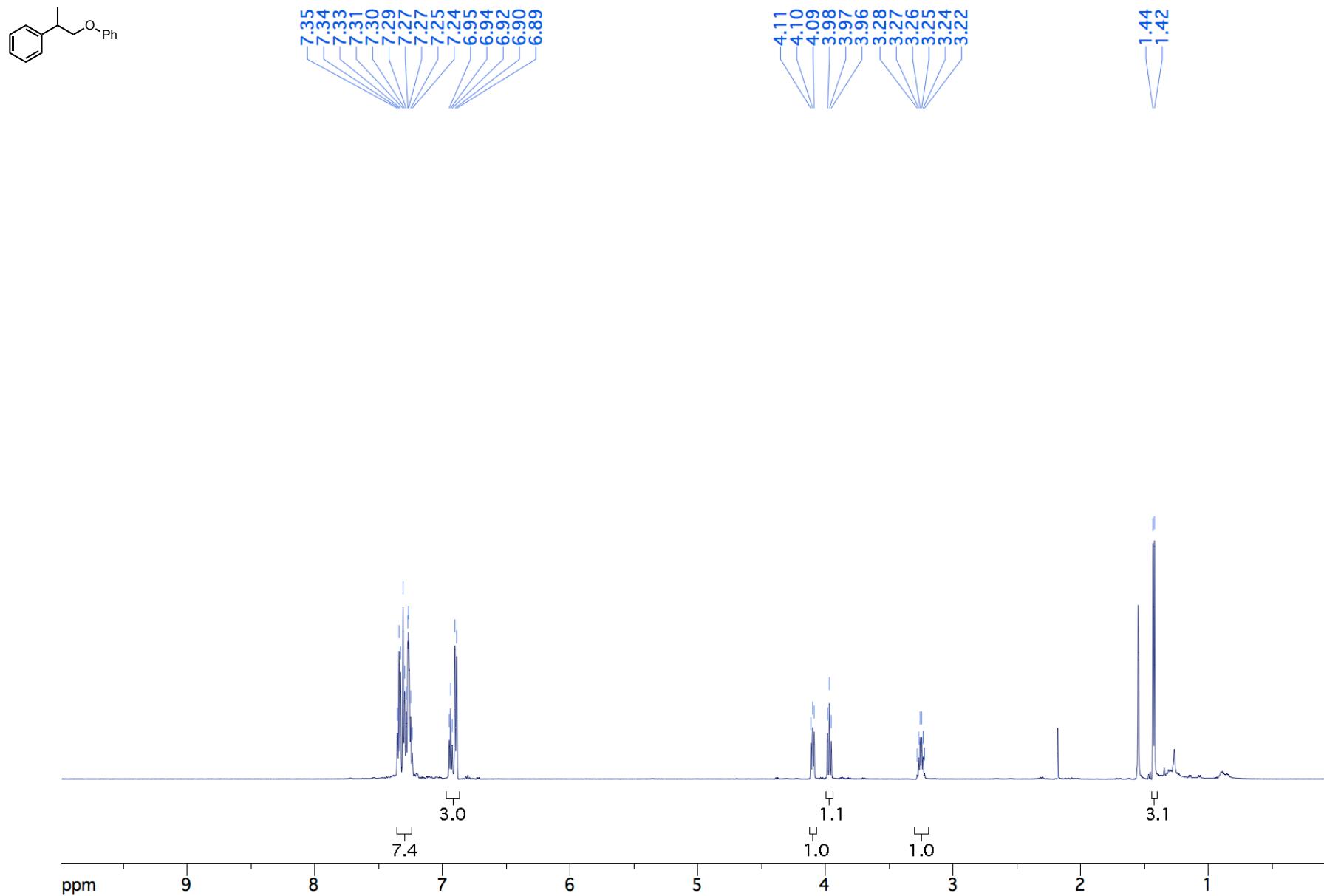


4-(sec-Bbutyl)-1,2-dichlorobenzene (28)

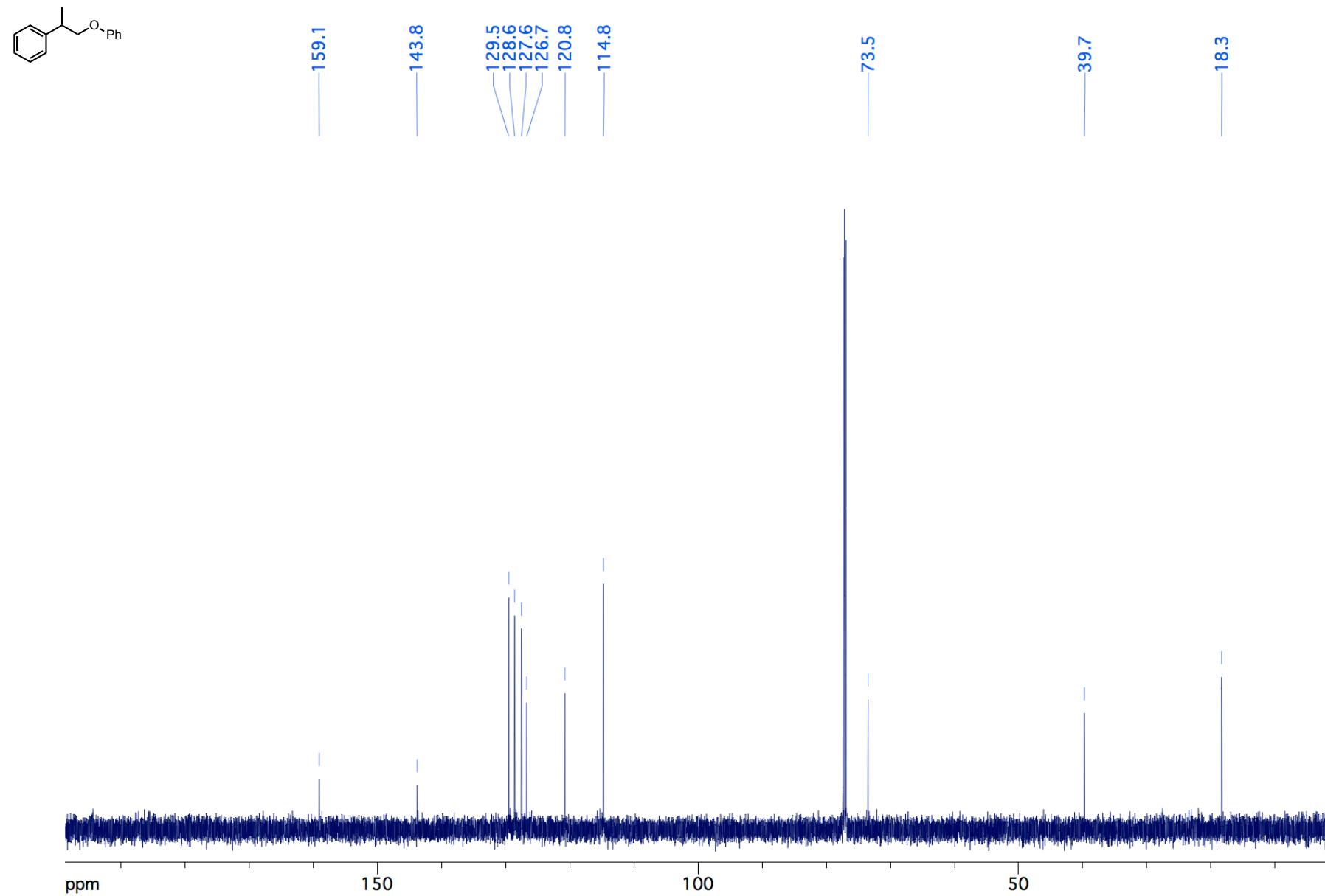
^{13}C NMR (CDCl_3 , 151 MHz)



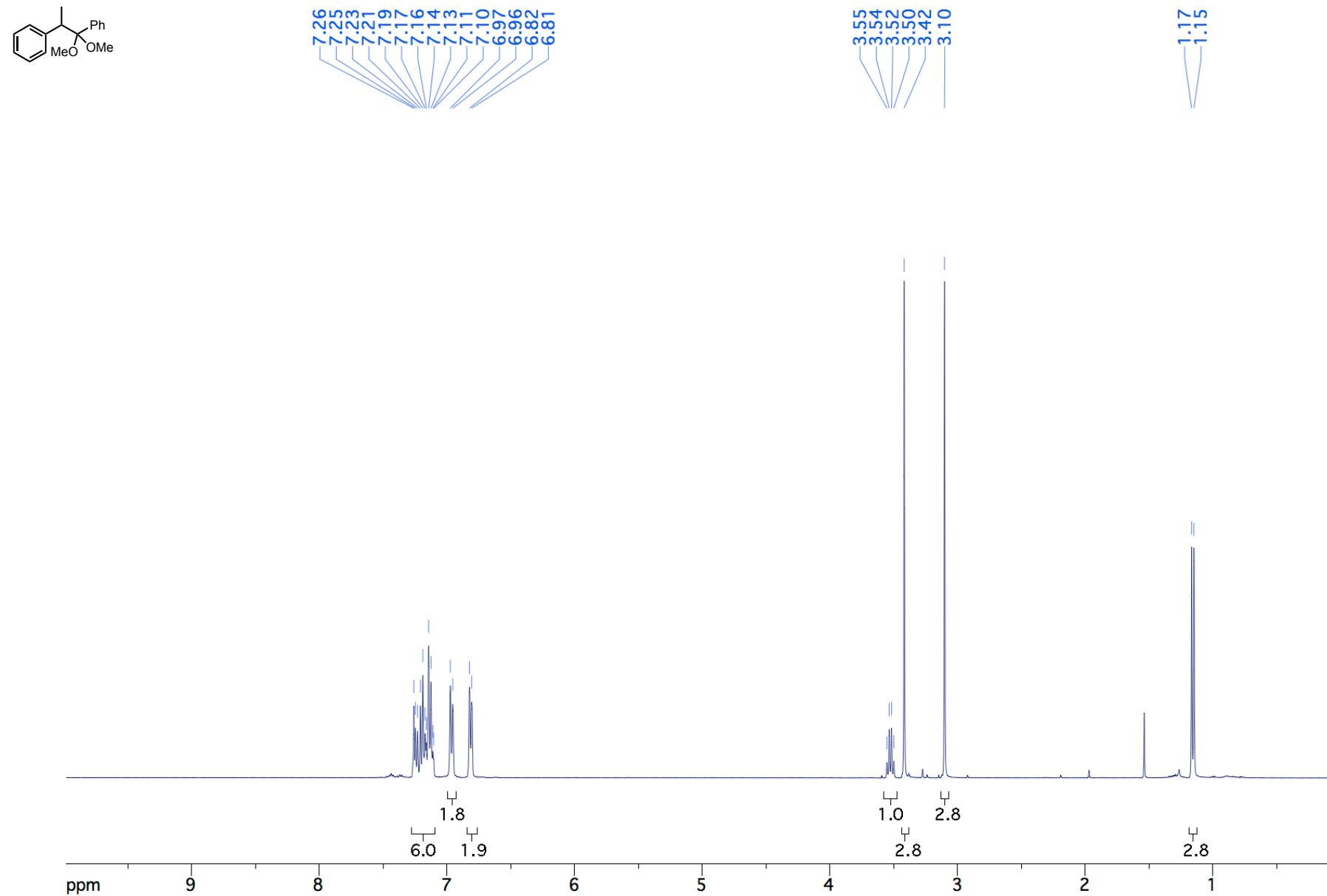
(1-Phenoxypropan-2-yl)benzene (29) ^1H NMR (CDCl_3 , 600 MHz)



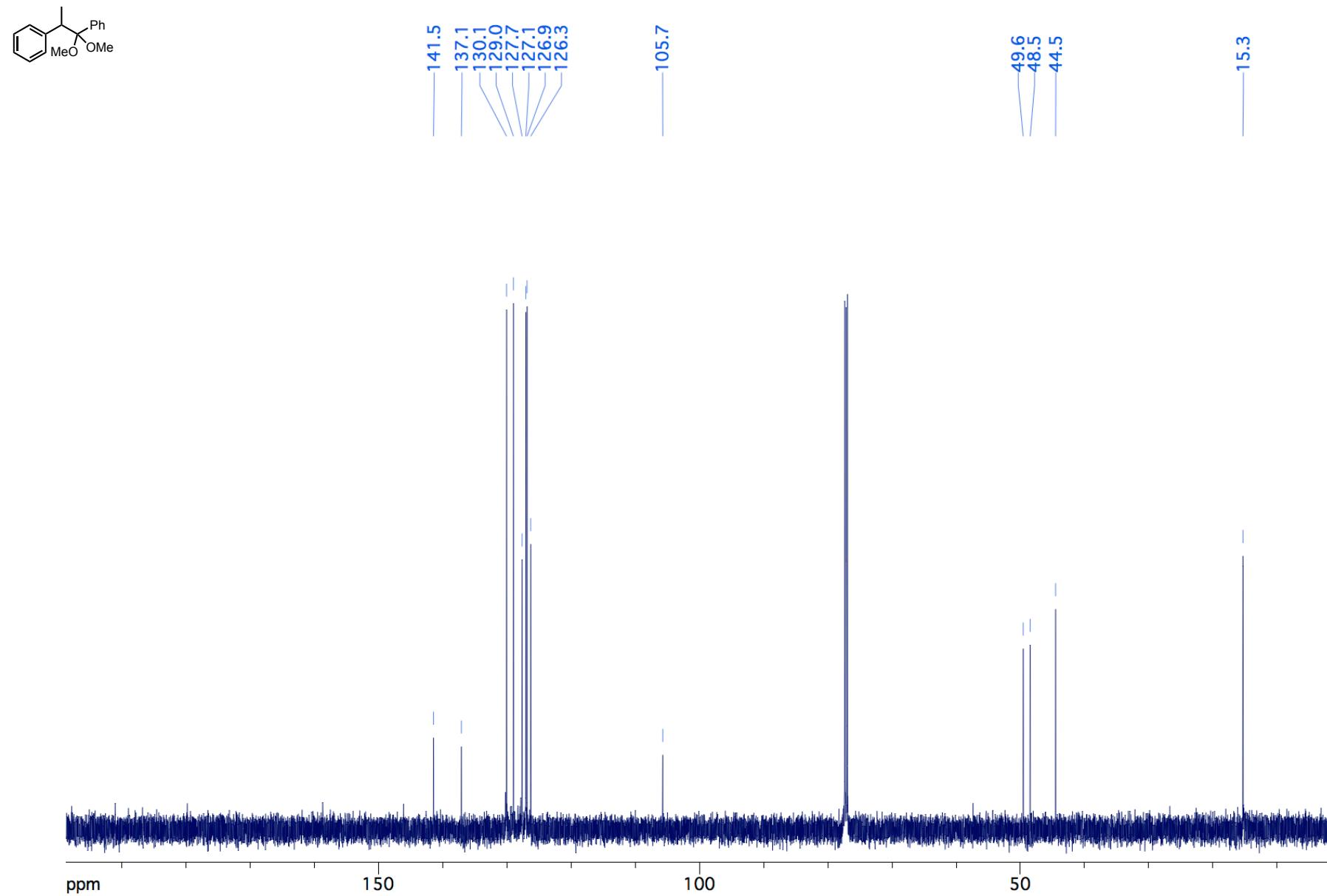
(1-Phenoxypropan-2-yl)benzene (29) ^{13}C NMR (CDCl_3 , 151 MHz)



(1,1-Dimethoxypropane-1,2-diyl)dibenzene (30) ^1H NMR (CDCl_3 , 600 MHz)

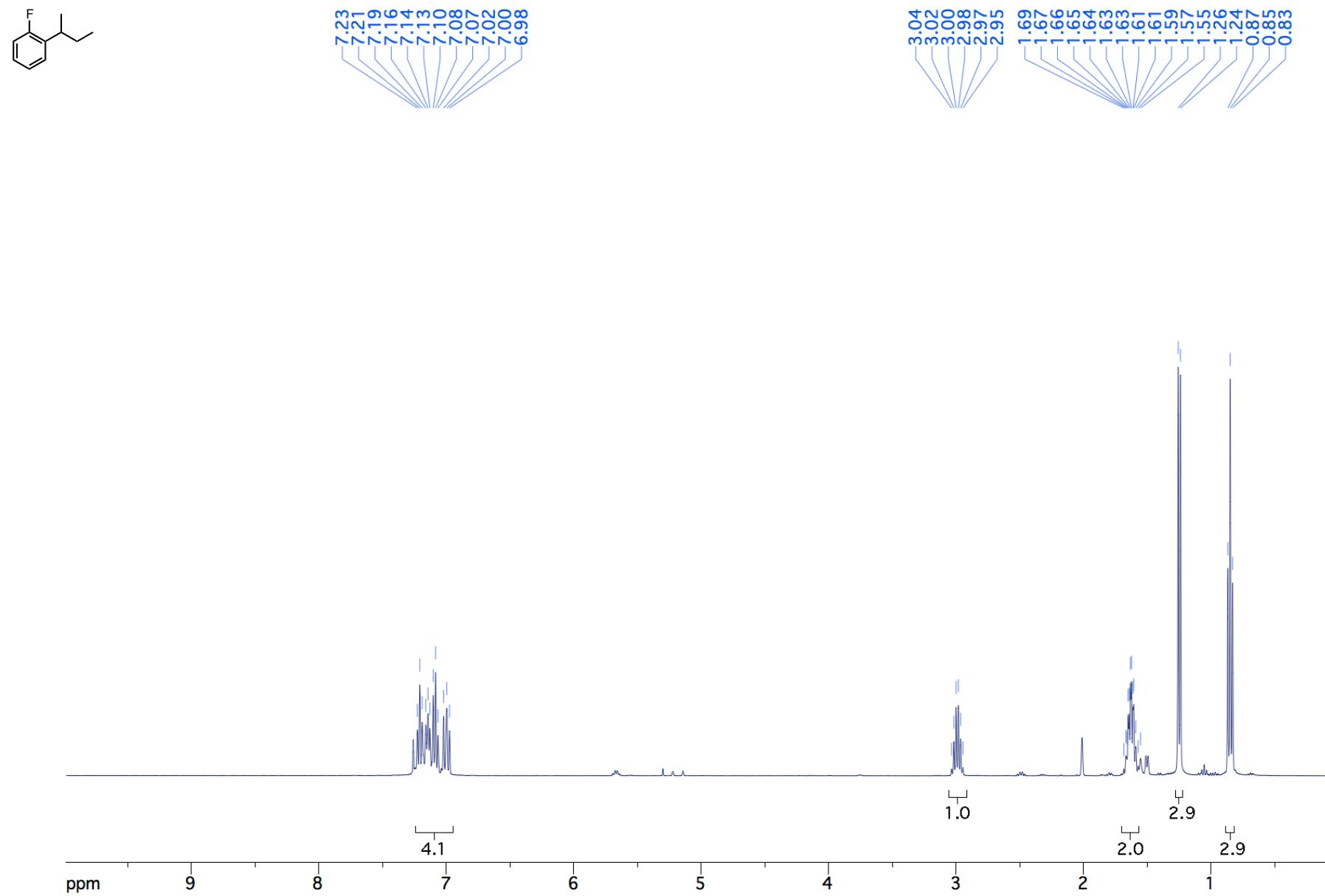


(1,1-Dimethoxypropane-1,2-diyl)dibenzene (30) ^{13}C NMR (CDCl_3 , 151 MHz)



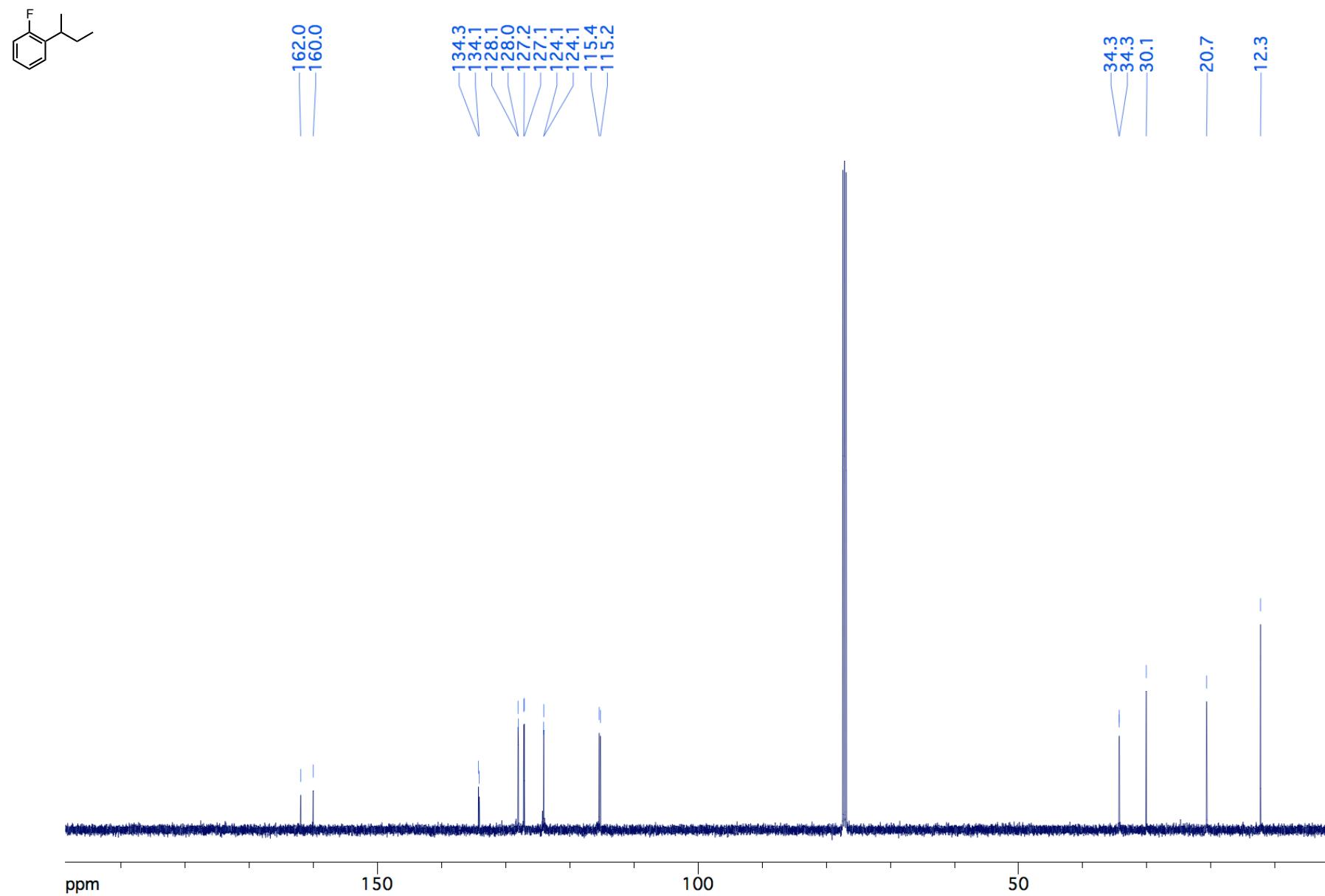
1-(sec-Butyl)-2-fluorobenzene (31)

^1H NMR (CDCl_3 , 400 MHz)



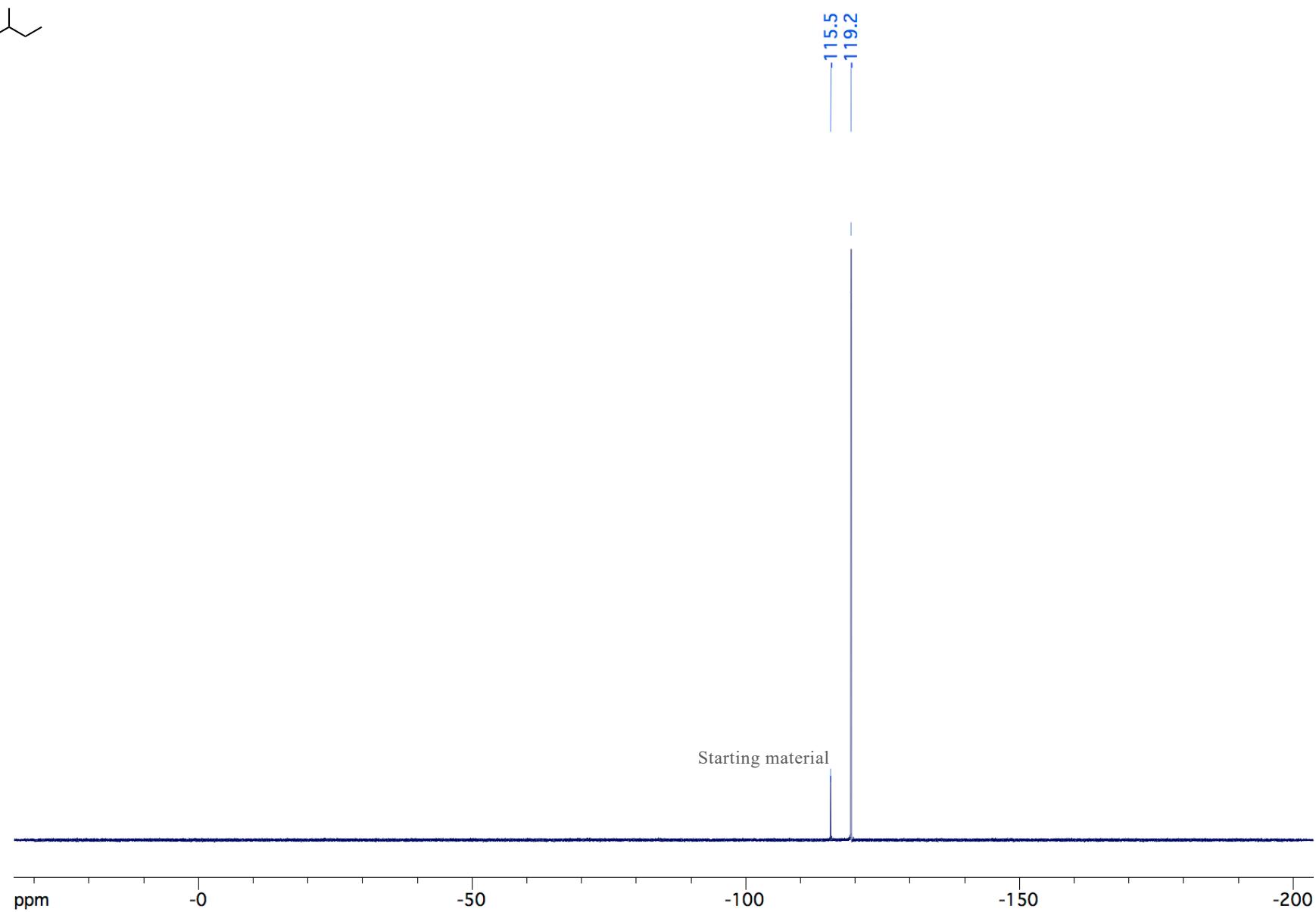
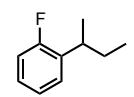
1-(sec-Butyl)-2-fluorobenzene (31)

^{13}C NMR (CDCl_3 , 100 MHz)

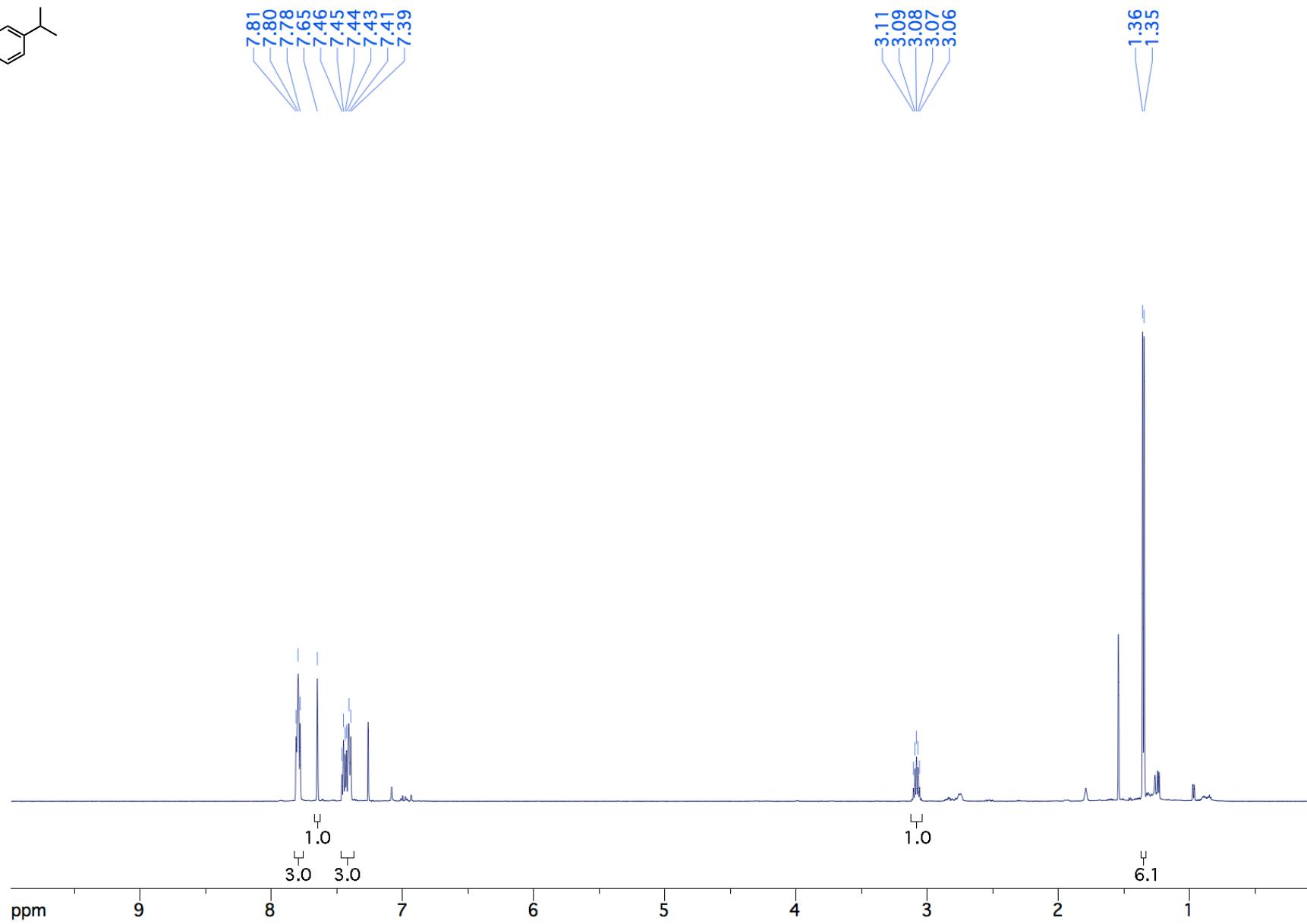
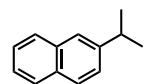


1-(sec-Butyl)-2-fluorobenzene (31)

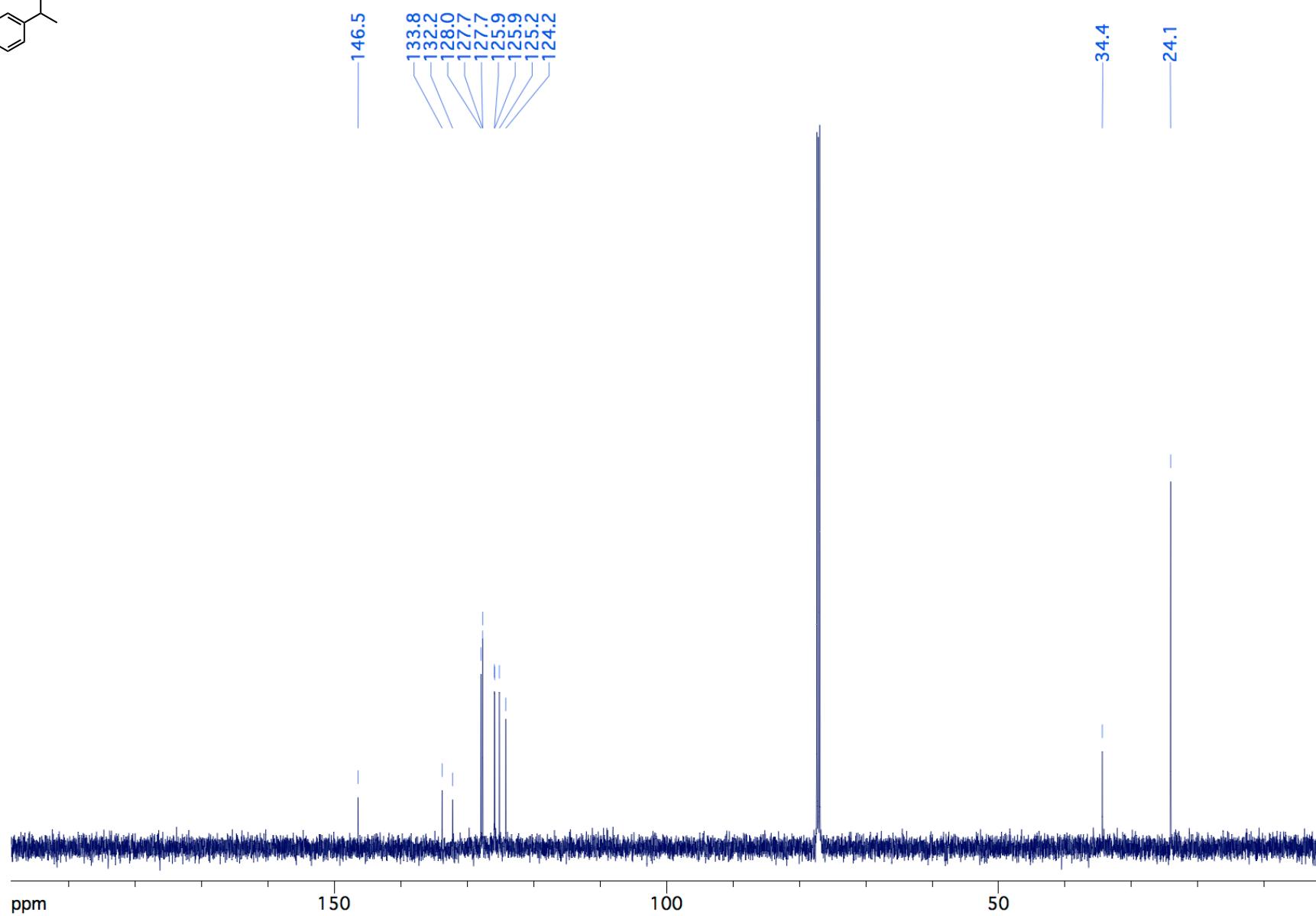
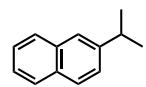
^{19}F -NMR (CDCl_3 , 376 MHz)



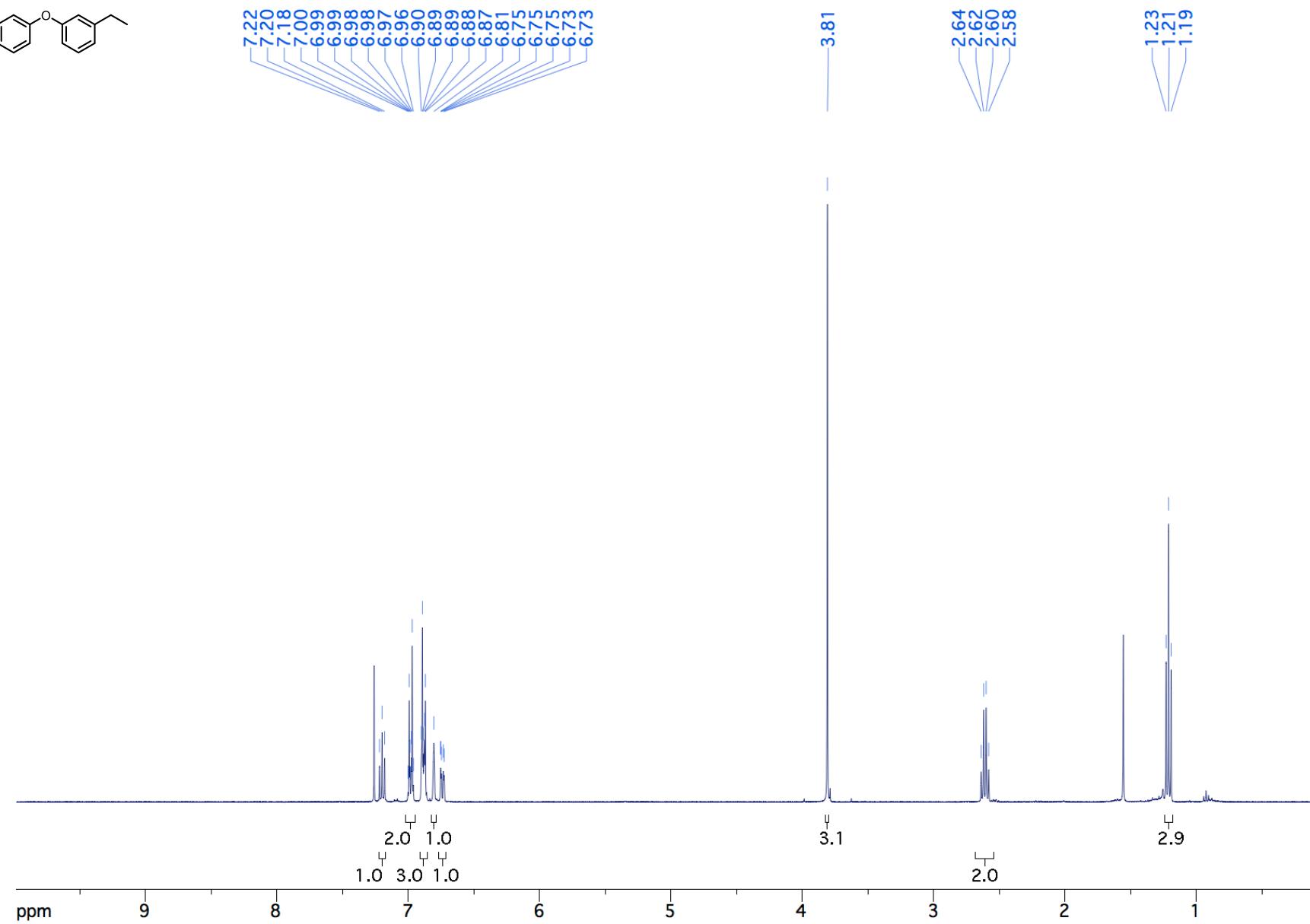
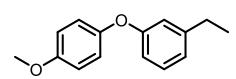
2-Isopropylnaphthalene (32) ^1H NMR (CDCl_3 , 600 MHz)



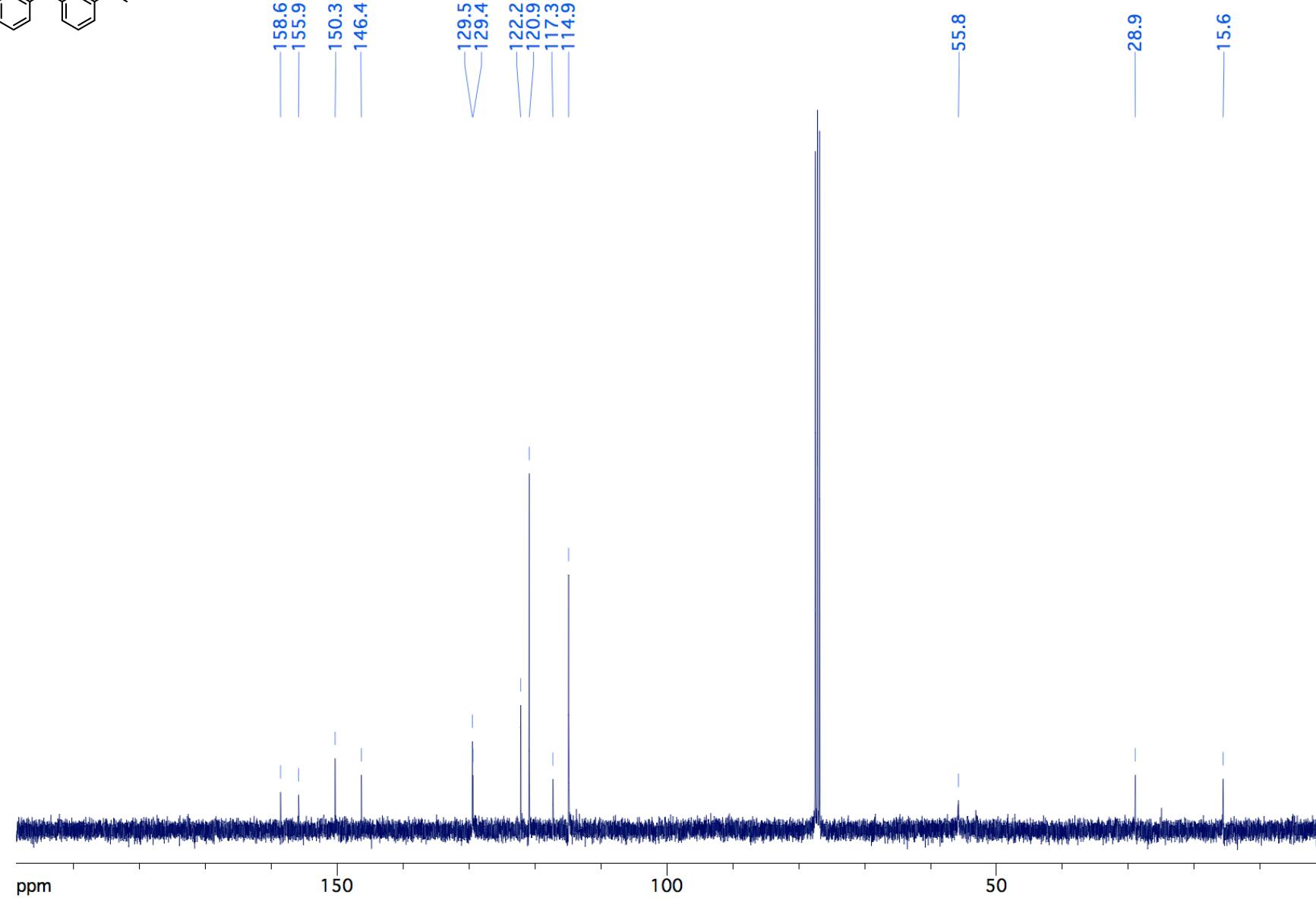
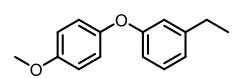
2-Isopropylnaphthalene (32) ^{13}C NMR (CDCl_3 , 151 MHz)



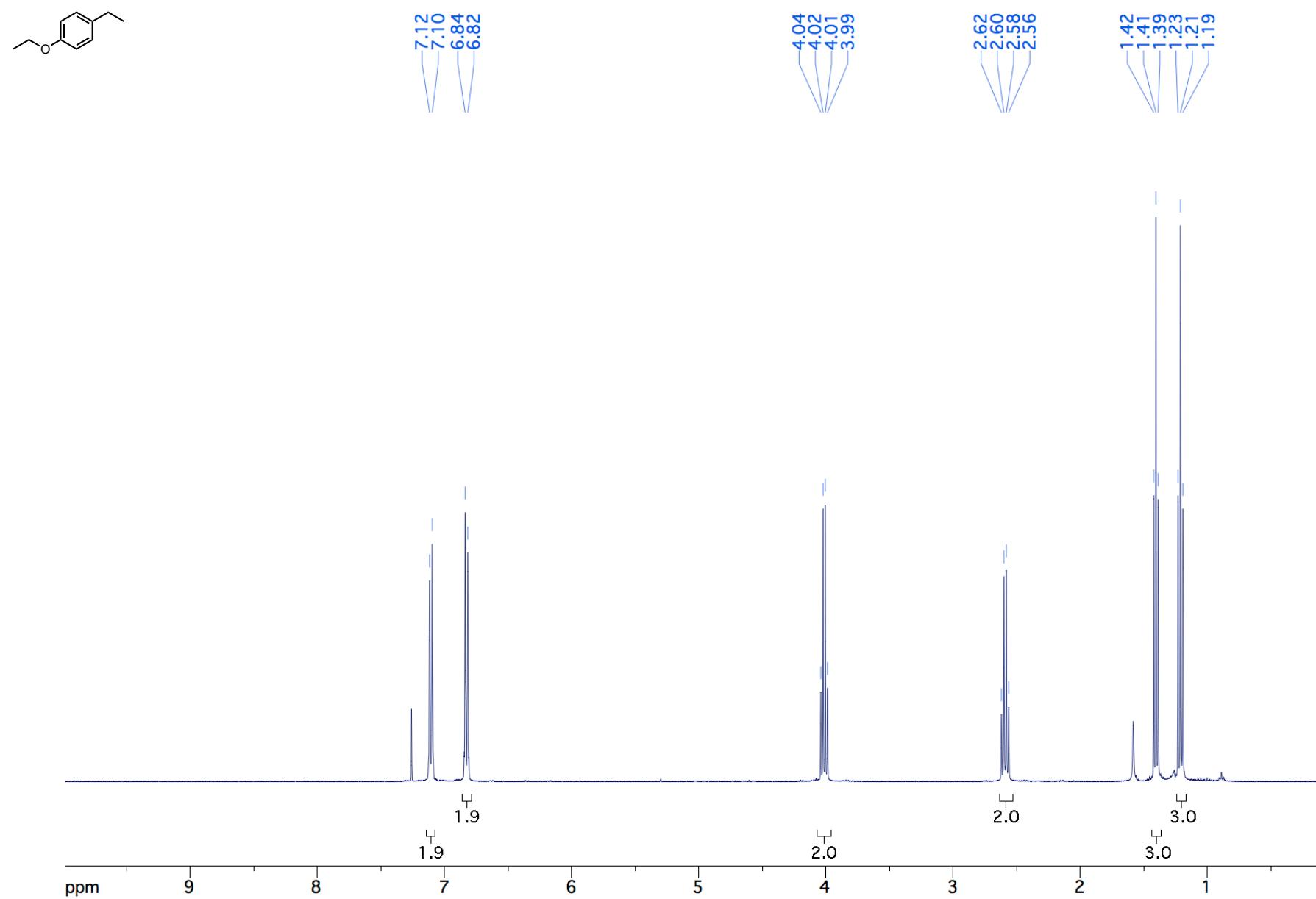
3-Ethyl-4'-methoxy-1,1'-biphenyl (33) ^1H NMR (CDCl_3 , 400 MHz)



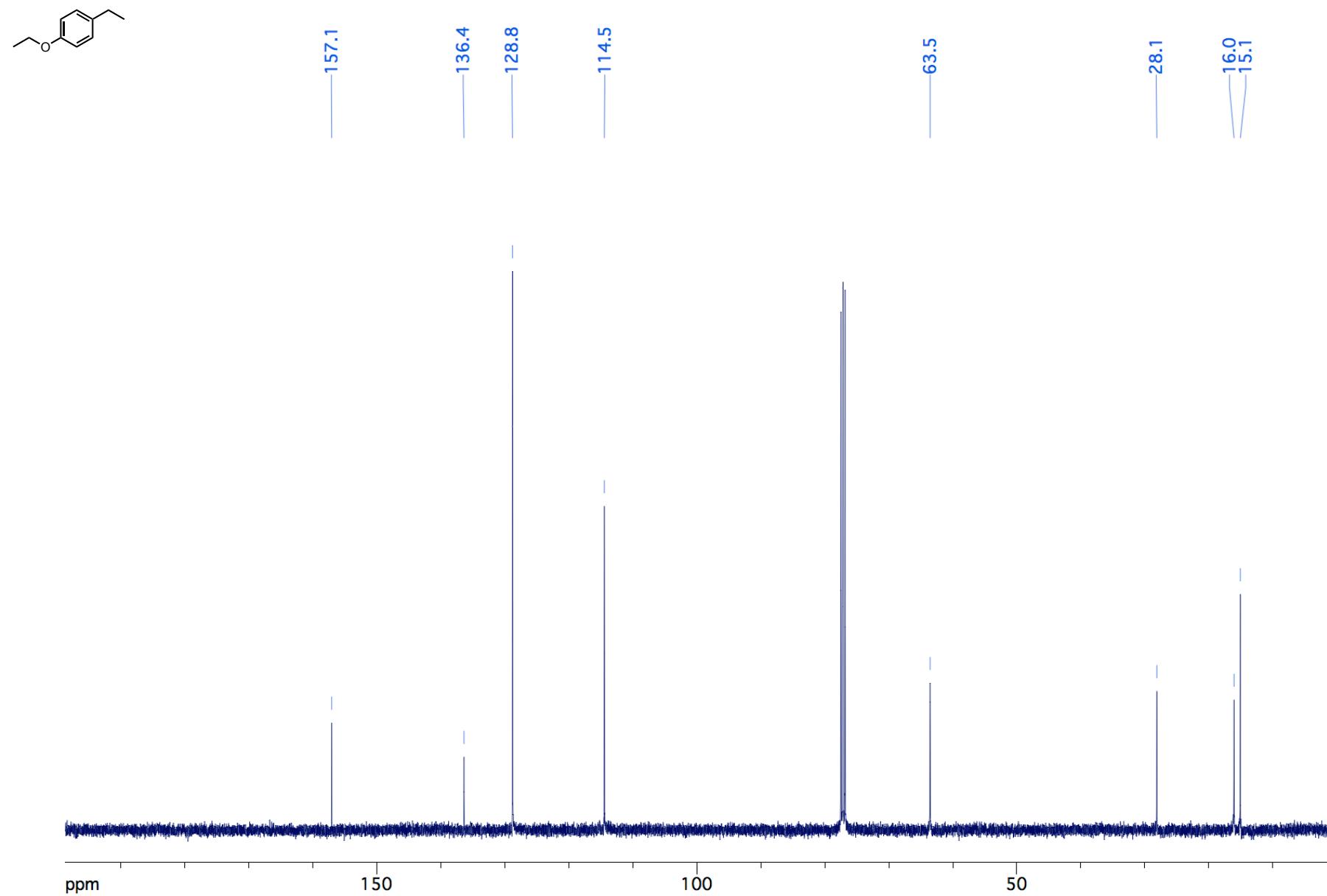
3-Ethyl-4'-methoxy-1,1'-biphenyl (33) ^{13}C NMR (CDCl_3 , 100 MHz)



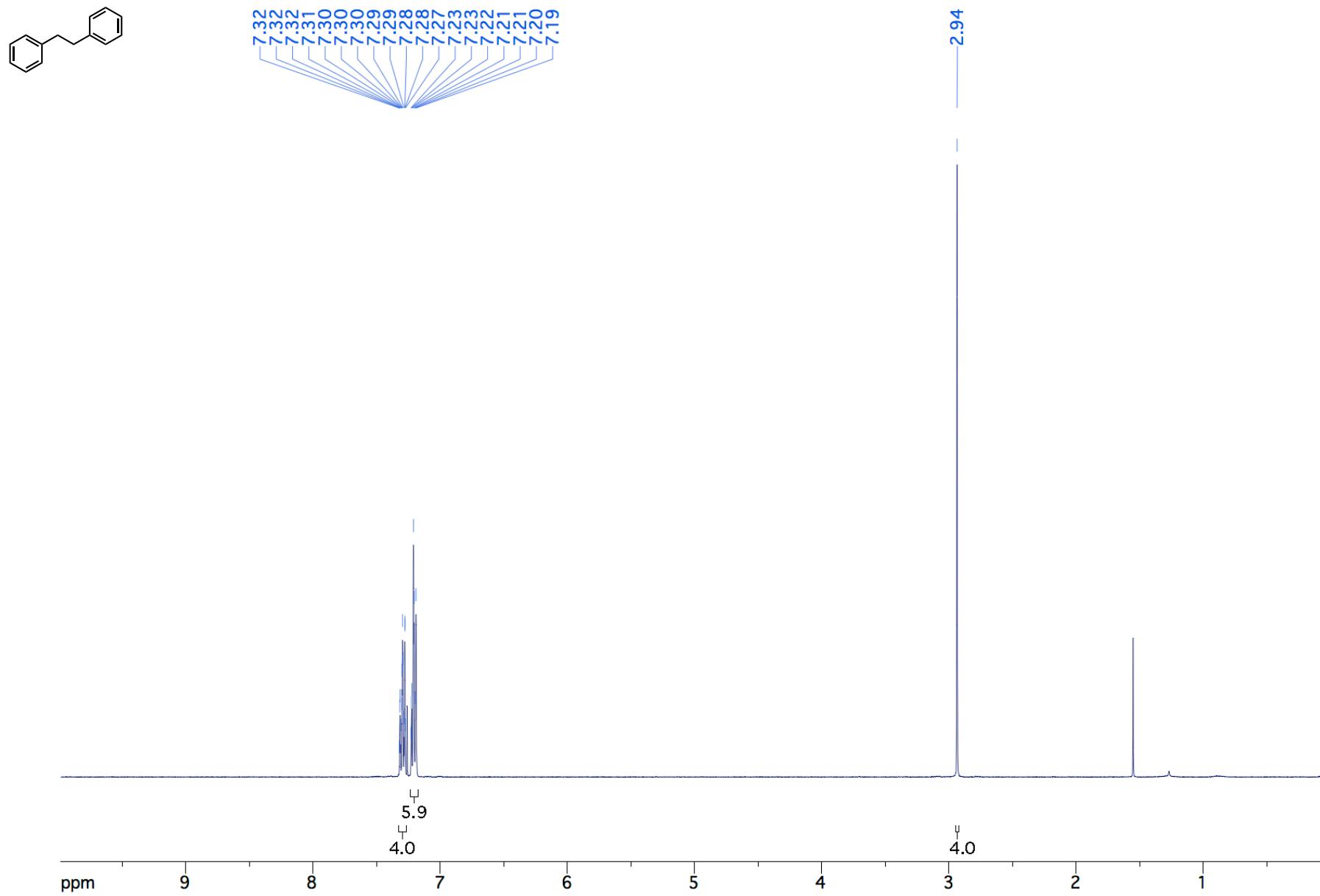
1-Ethoxy-4-ethylbenzene (34) ^1H NMR (CDCl_3 , 400 MHz)



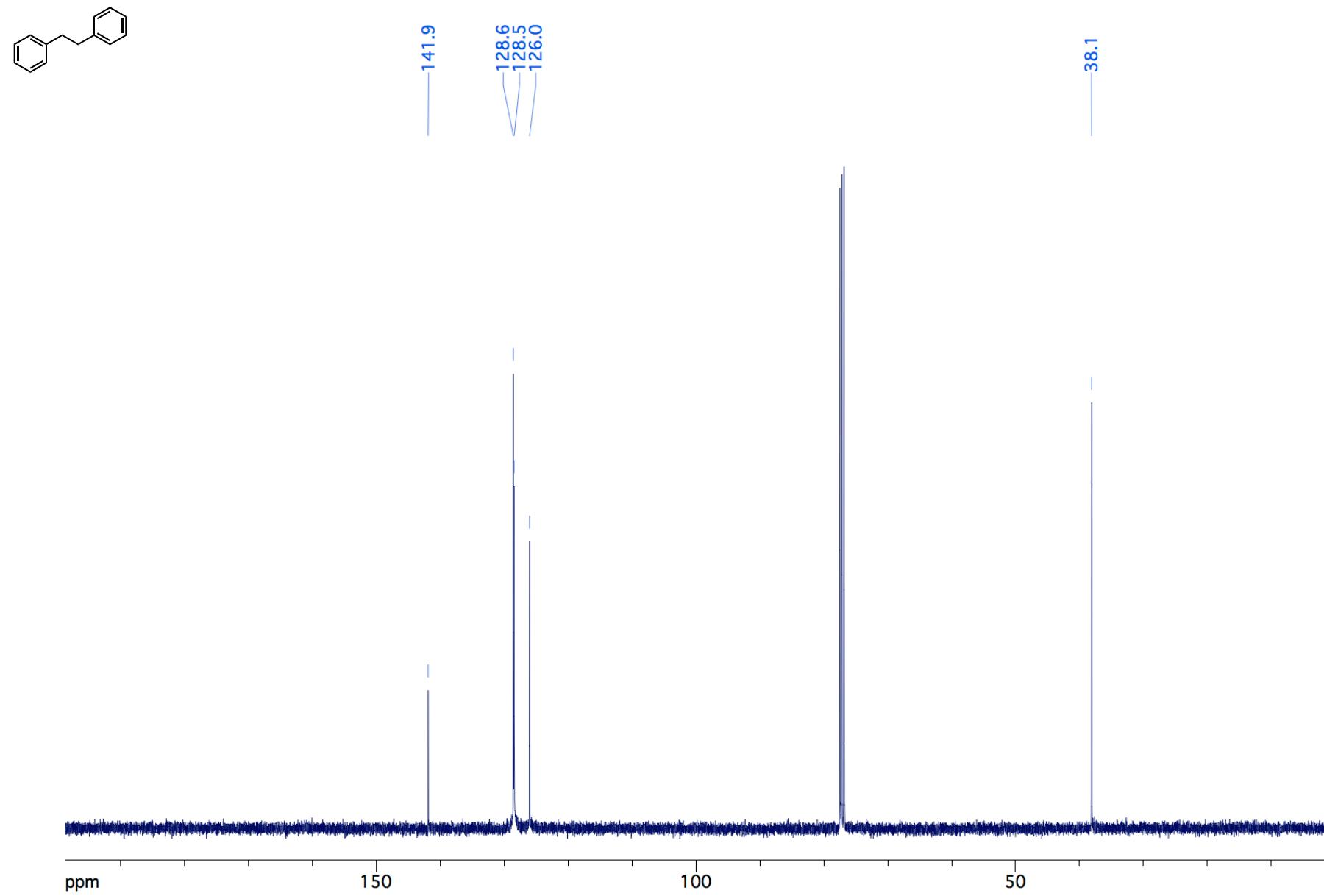
1-Ethoxy-4-ethylbenzene (34) ^{13}C NMR (CDCl_3 , 100 MHz)



1,2-diphenylethane (35) ^1H NMR (CDCl_3 , 400 MHz)

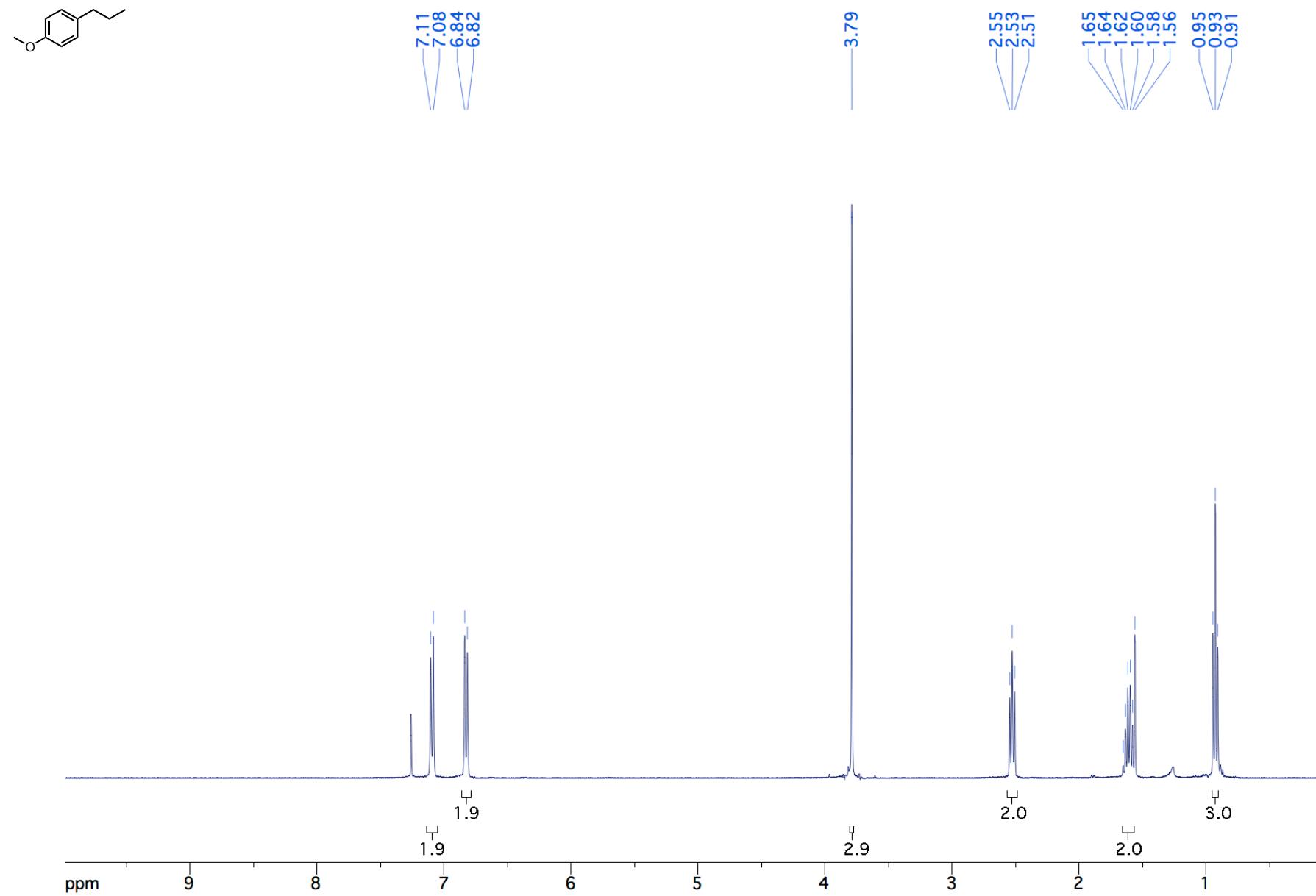


1,2-diphenylethane (35) ^{13}C NMR (CDCl_3 , 100 MHz)



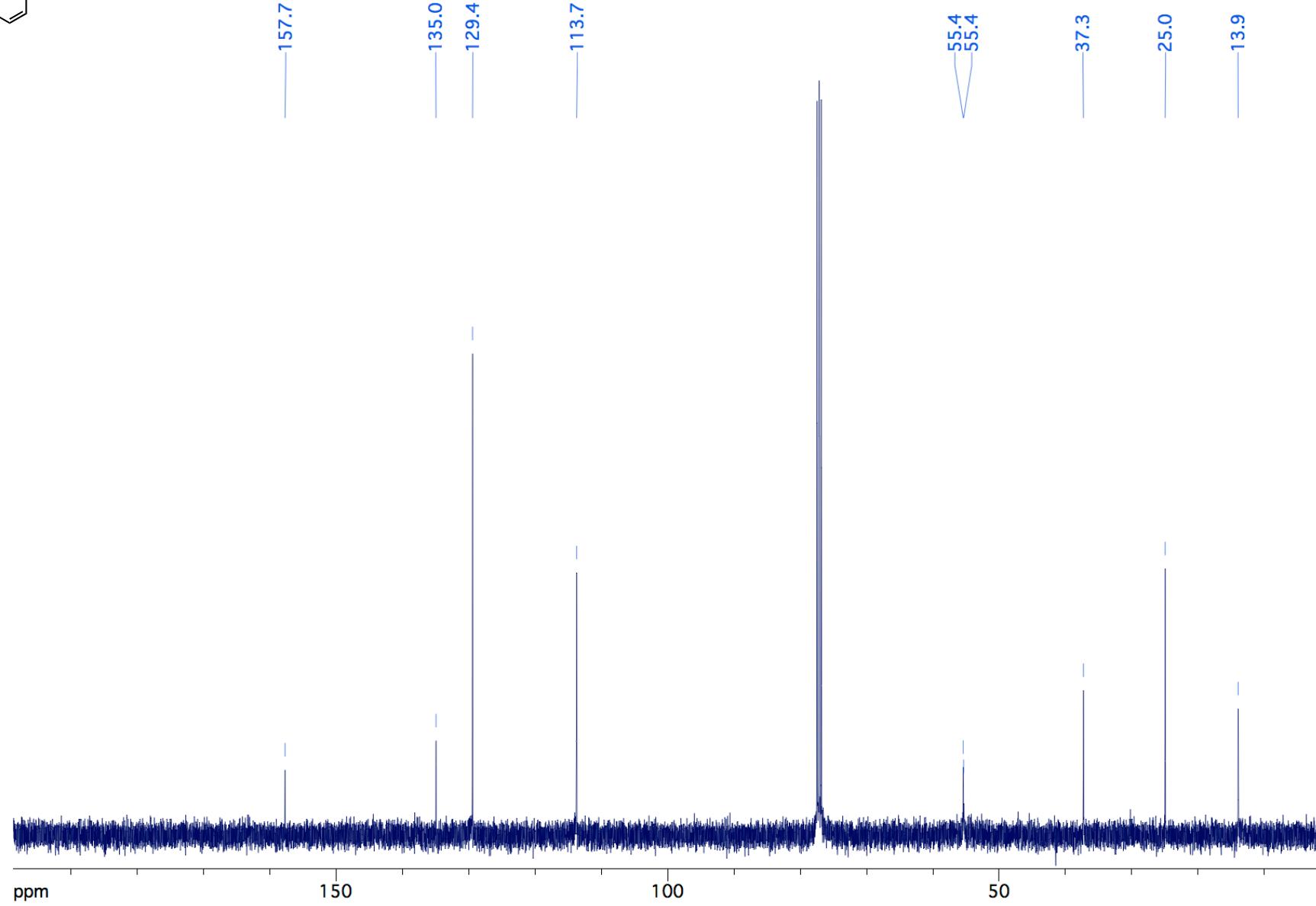
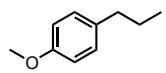
1-Methoxy-4-propylbenzene (36)

^1H NMR (CDCl_3 , 400 MHz)



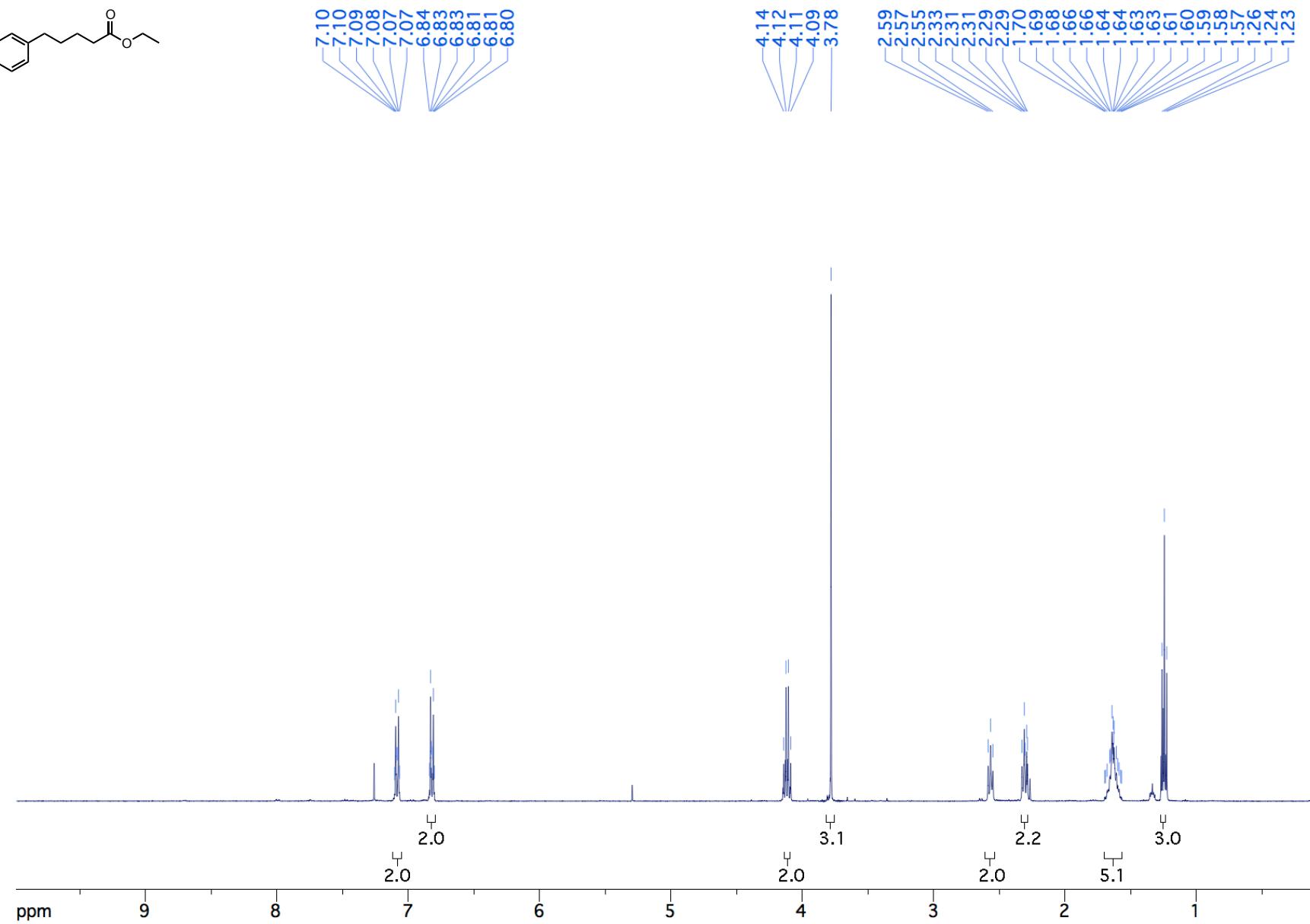
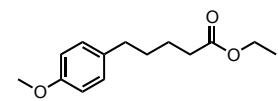
1-Methoxy-4-propylbenzene (36)

^{13}C NMR (CDCl_3 , 100 MHz)



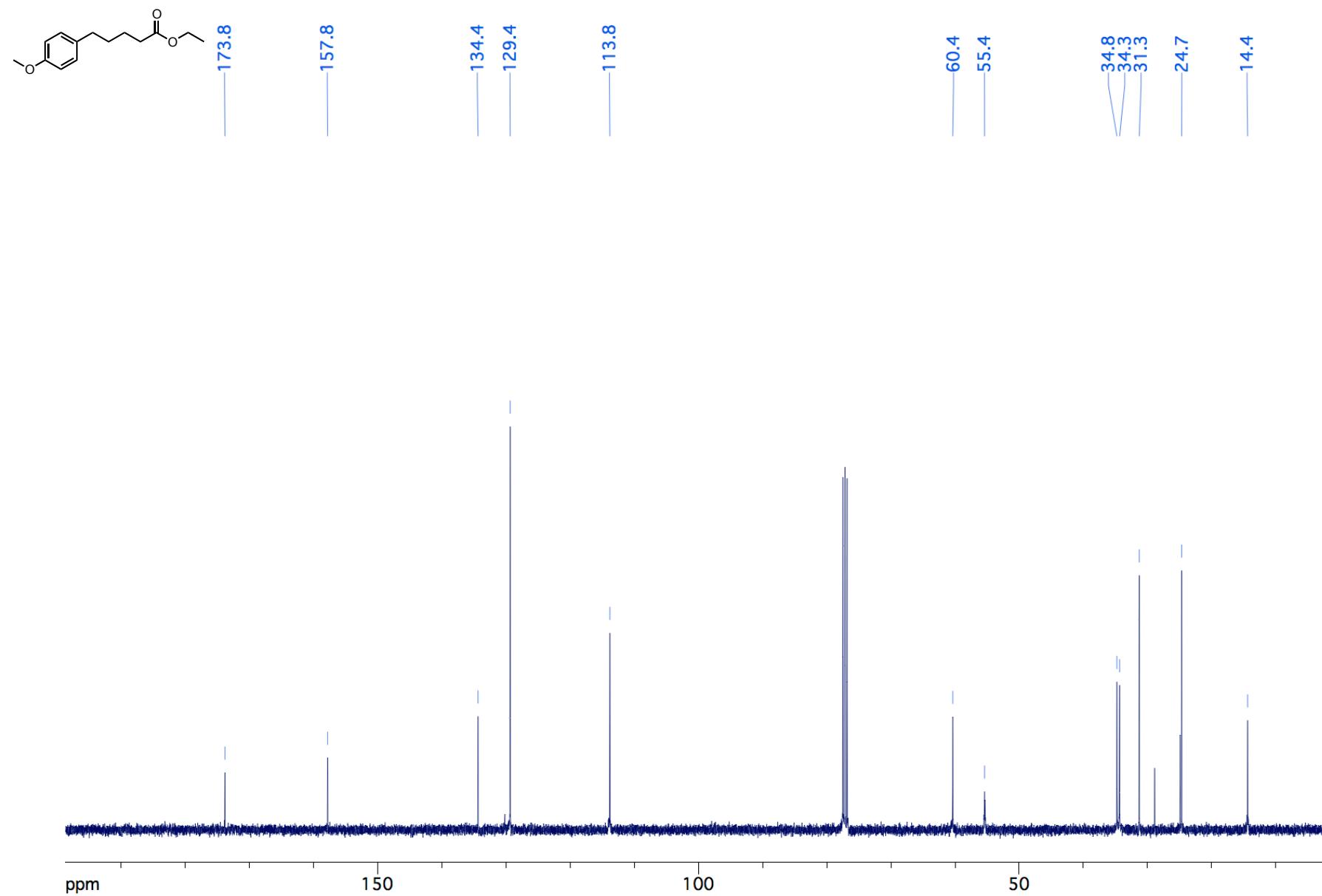
Ethyl 5-(4-methoxyphenyl)pentanoate (37)

¹H NMR (CDCl₃, 400 MHz)

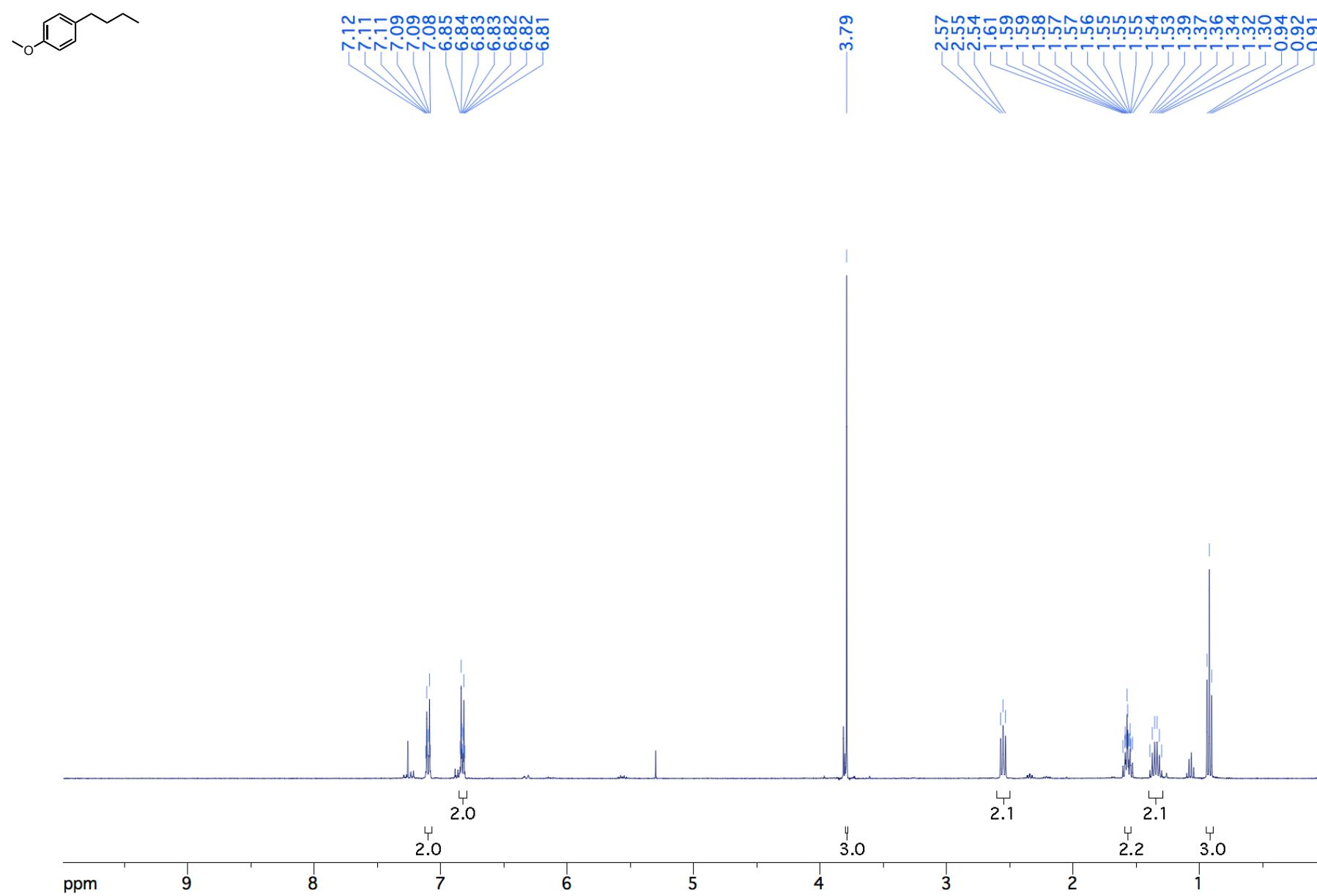


Ethyl 5-(4-methoxyphenyl)pentanoate (37)

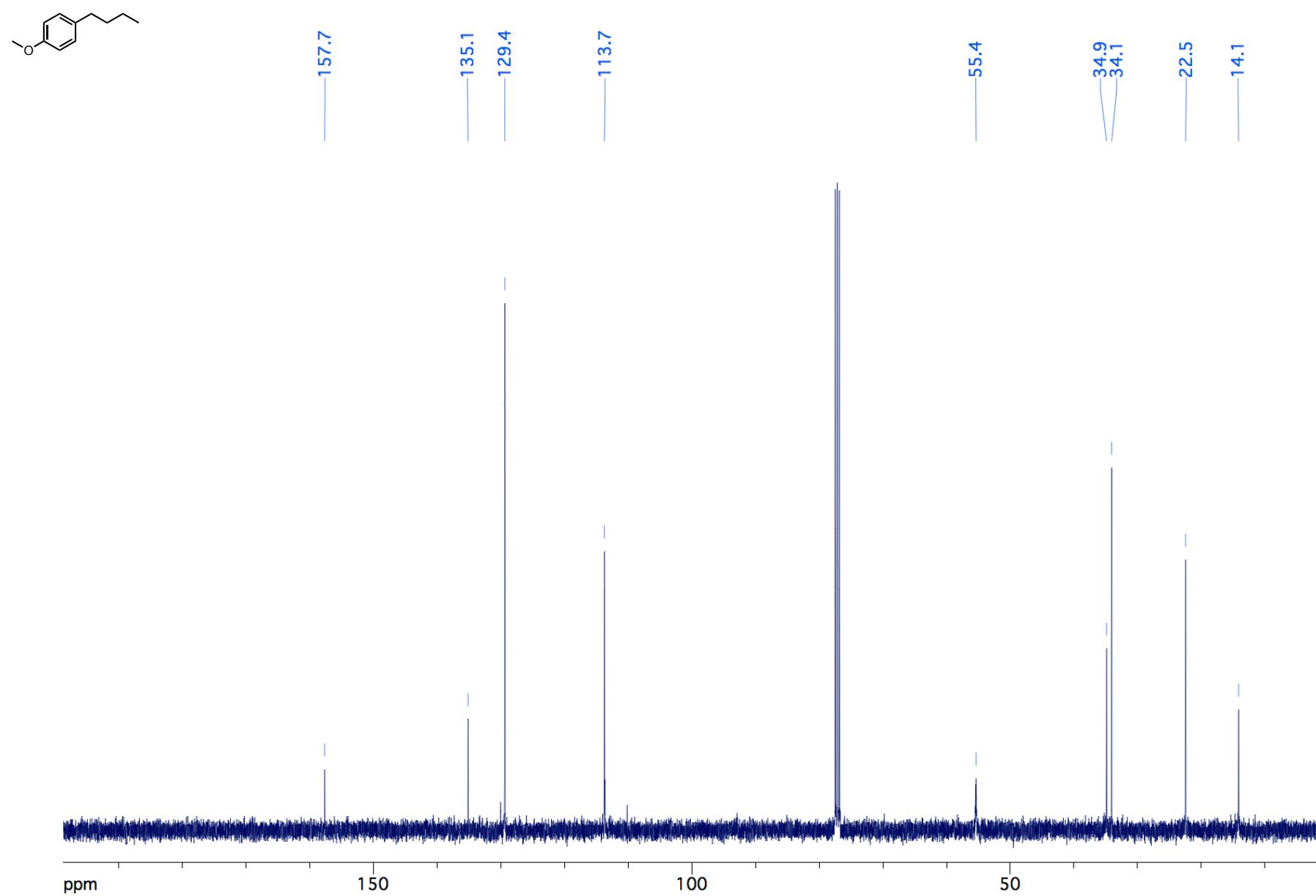
^{13}C NMR (CDCl_3 , 100 MHz)



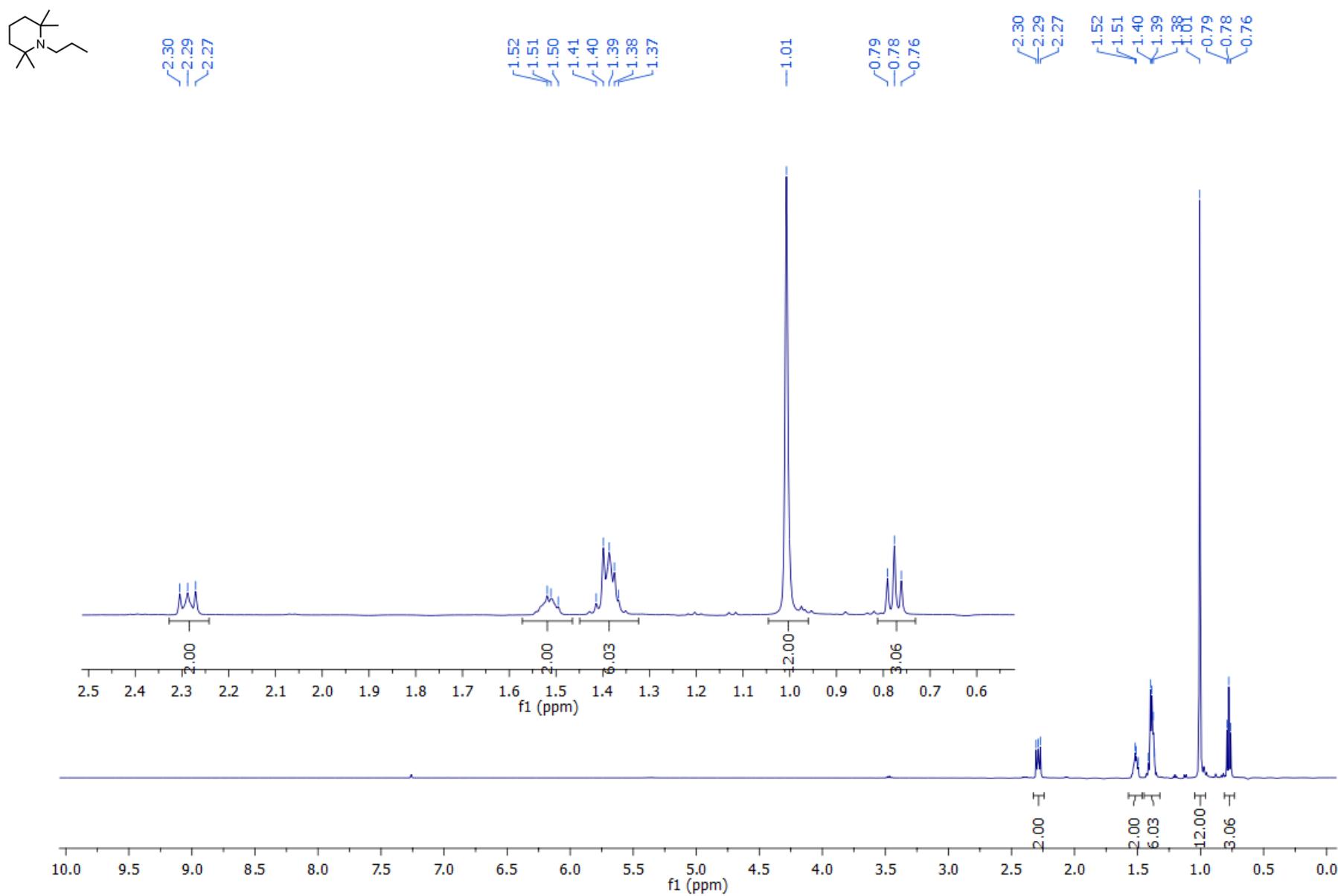
1-Butyl-4-methoxybenzene (38) ^1H NMR (CDCl_3 , 400 MHz)



1-Butyl-4-methoxybenzene (38) ^{13}C NMR (CDCl_3 , 100 MHz)

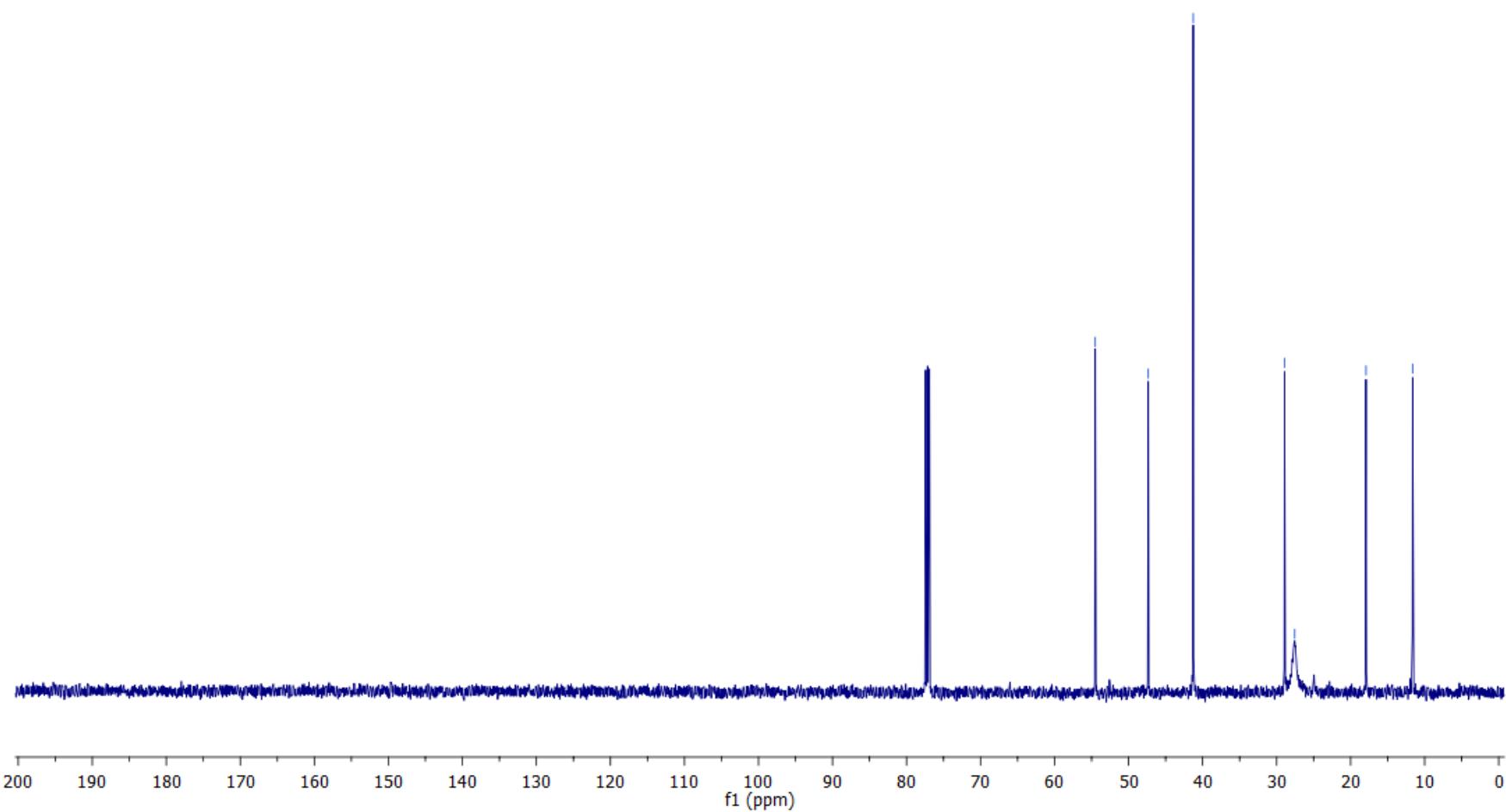
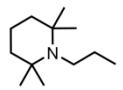


2,2,6,6-Tetramethyl-1-propylpiperidine (47) ^1H NMR (CDCl_3 , 500 MHz)

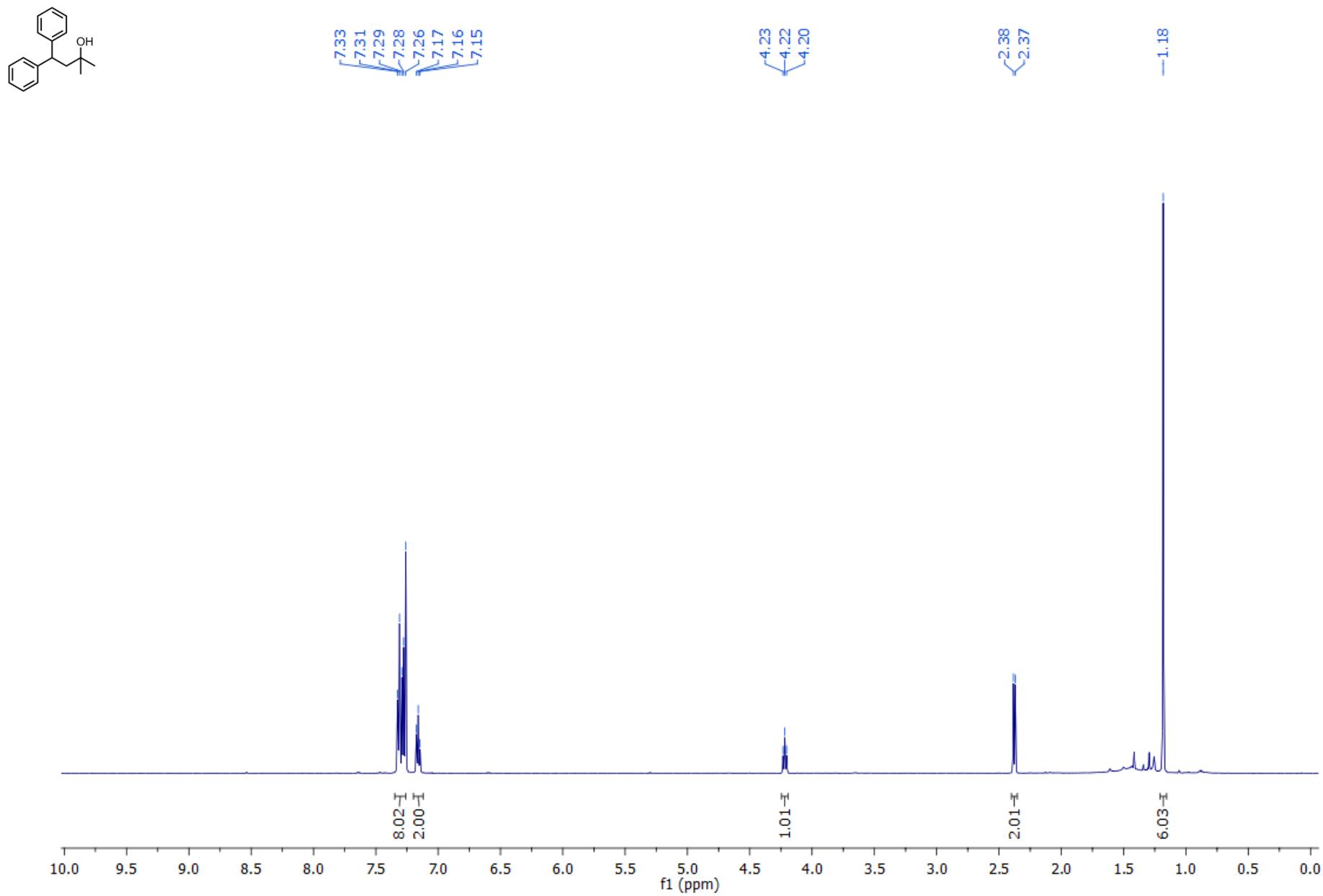


2,2,6,6-Tetramethyl-1-propylpiperidine (47)

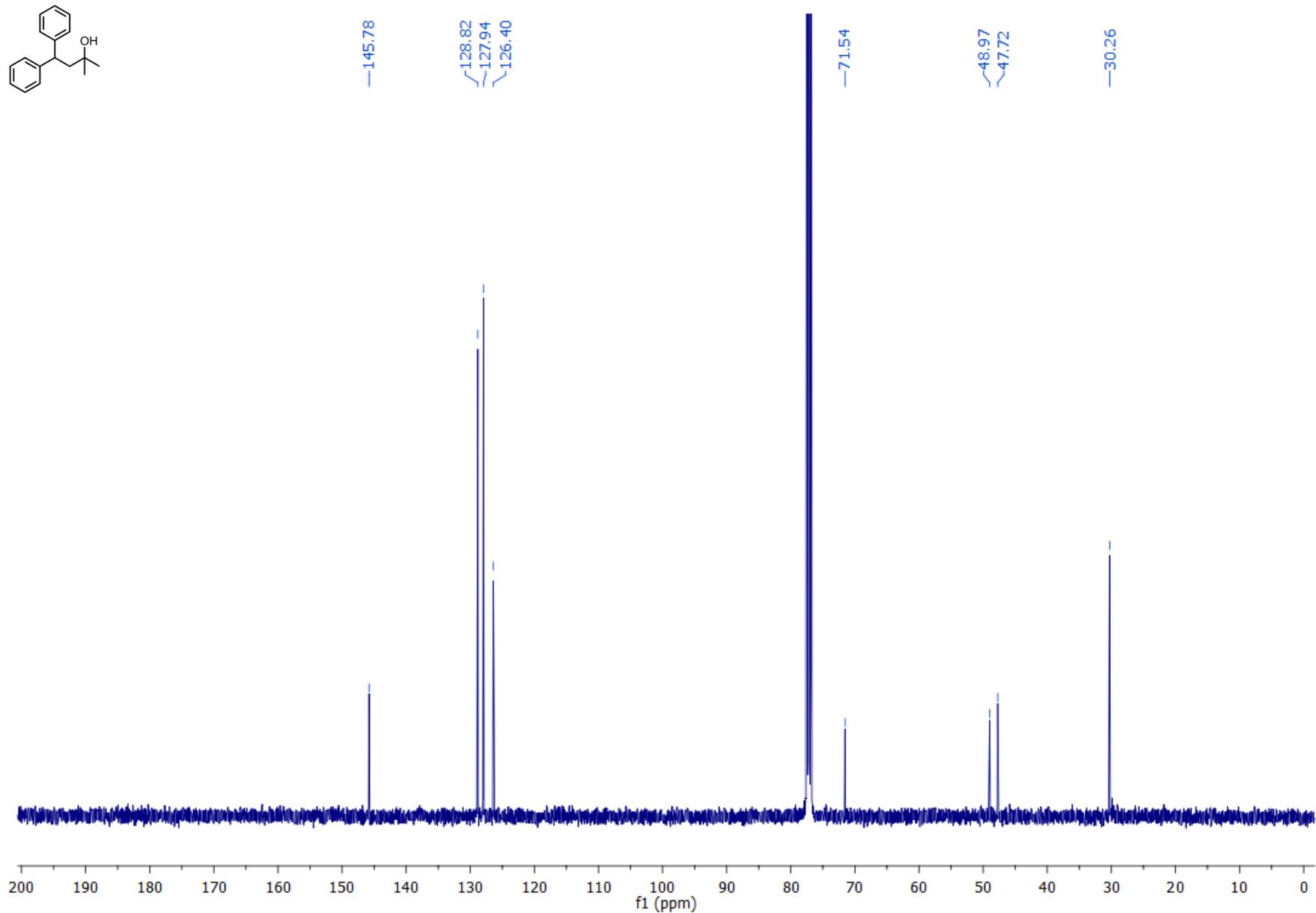
^{13}C NMR (CDCl_3 , 125 MHz)



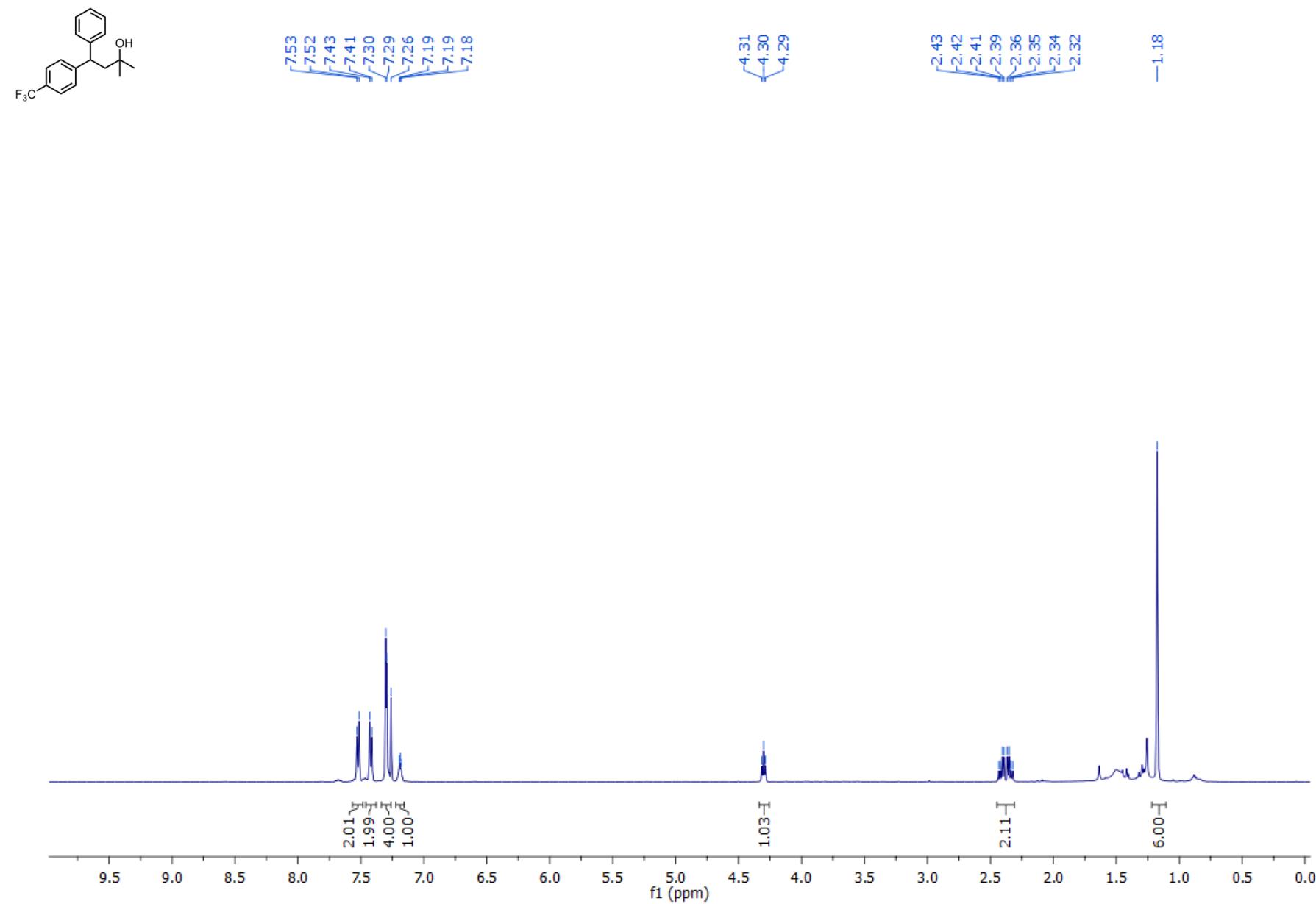
2-Methyl-4,4-diphenylbutan-2-ol (48) ^1H NMR (CDCl_3 , 500 MHz)



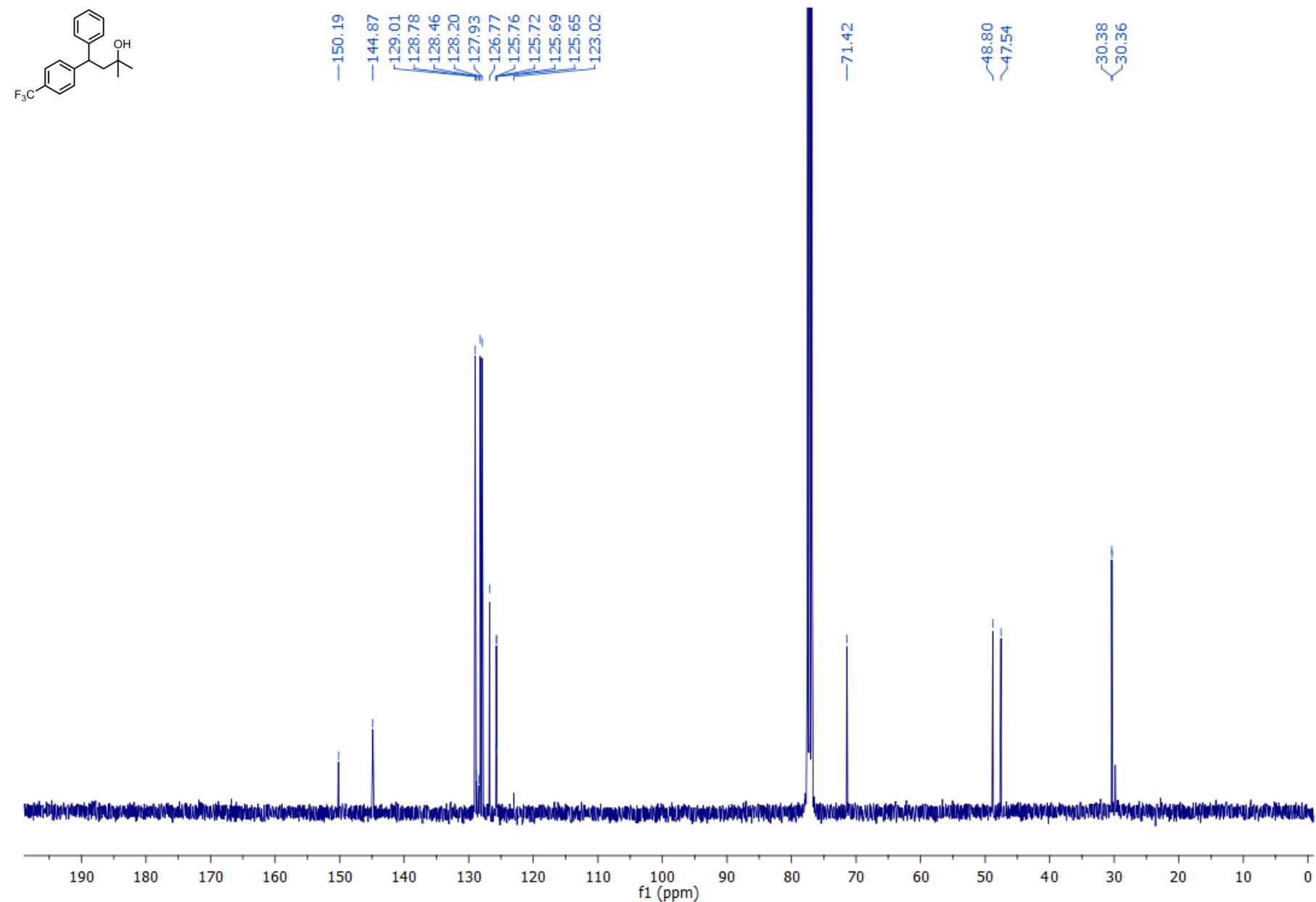
2-Methyl-4,4-diphenylbutan-2-ol (48) ^{13}C NMR (CDCl_3 , 100 MHz)



2-Methyl-4-phenyl-4-(4-(trifluoromethyl)phenyl)butan-2-ol (49) ^1H NMR (CDCl_3 , 500 MHz)

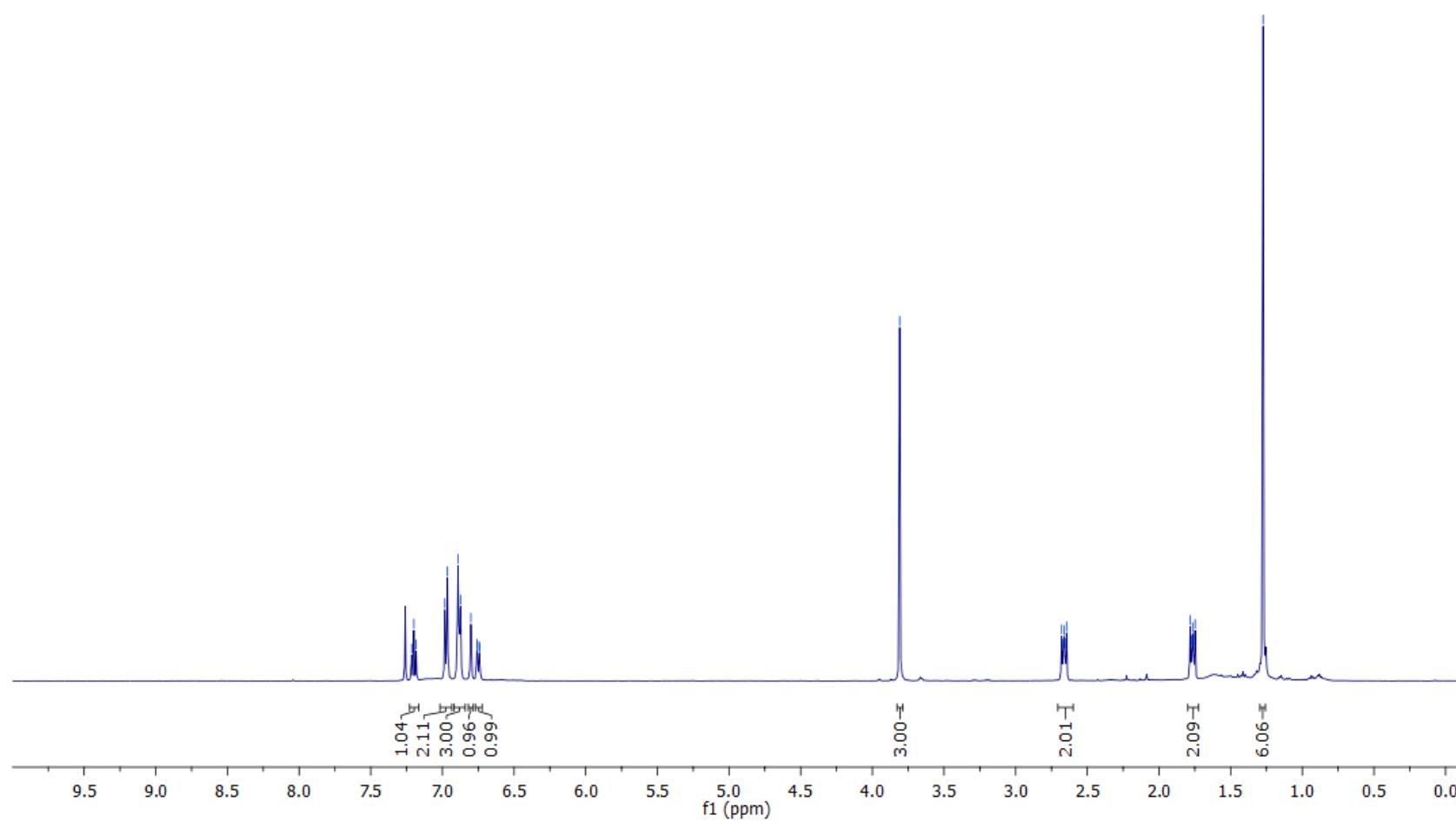
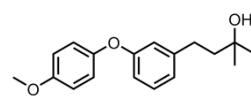


2-Methyl-4-phenyl-4-(4-(trifluoromethyl)phenyl)butan-2-ol (49) ^{13}C NMR (CDCl_3 , 100 MHz)

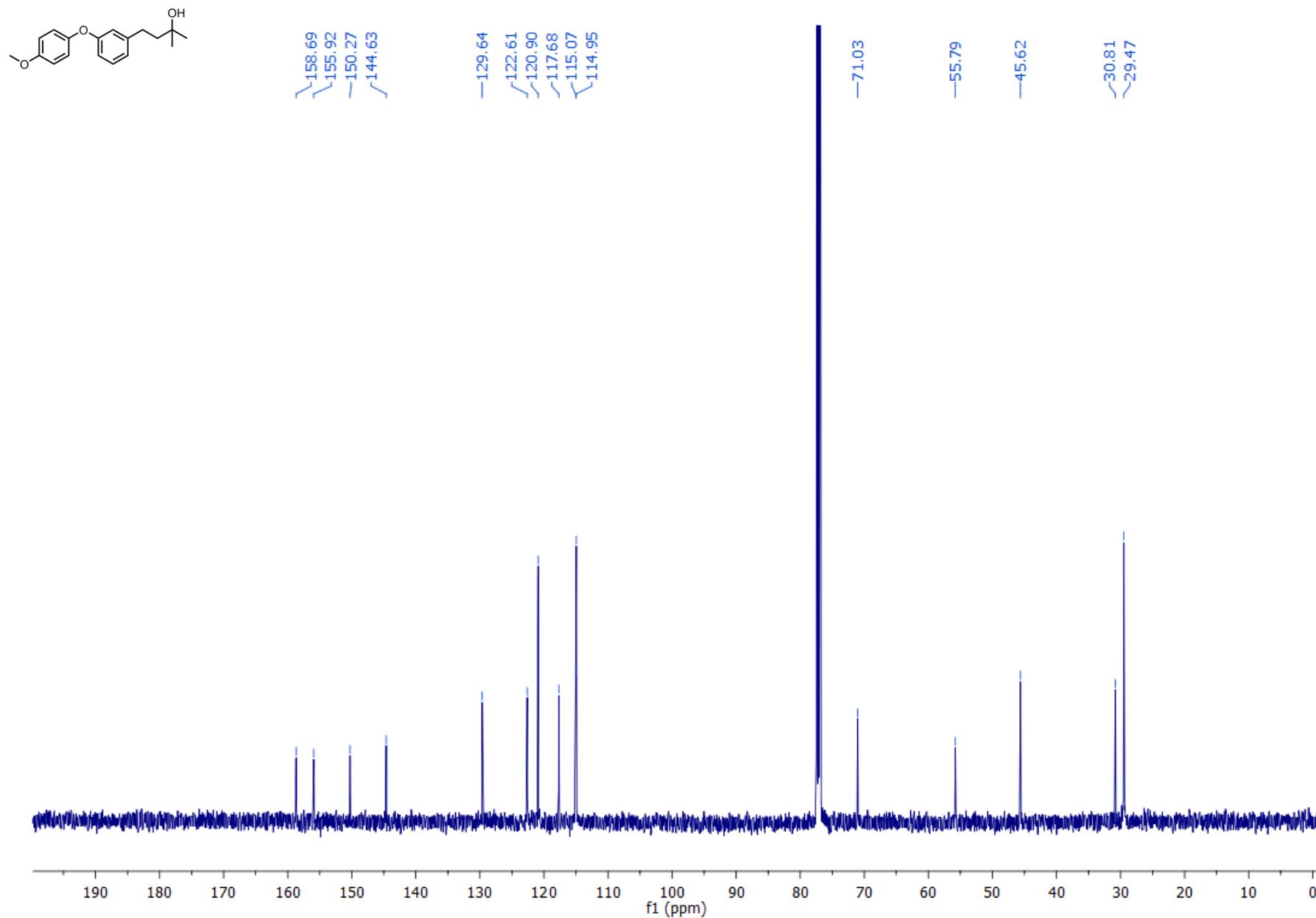


4-(3-(4-Methoxyphenoxy)phenyl)-2-methylbutan-2-ol (50)

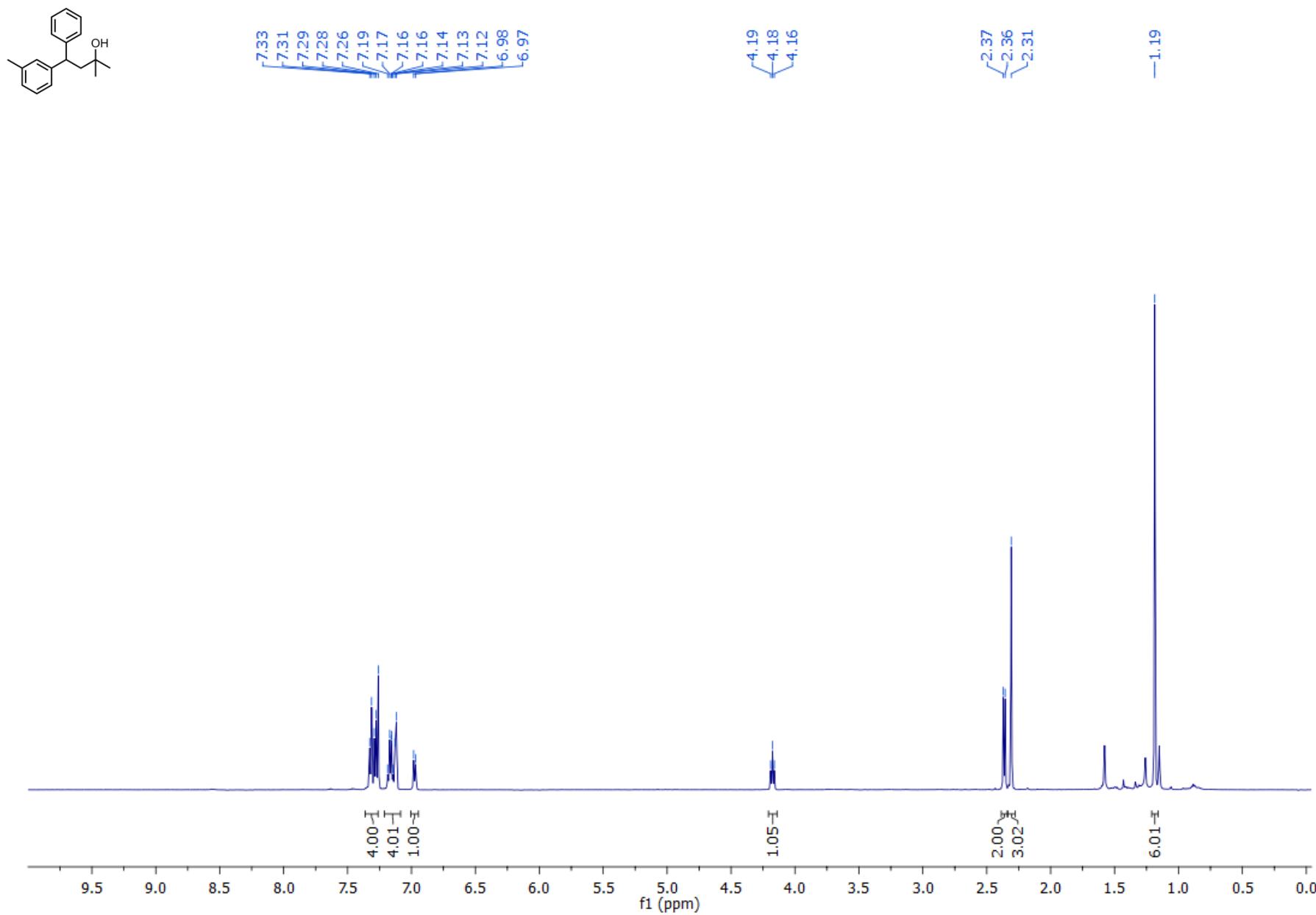
¹H NMR (CDCl₃, 500 MHz)



4-(3-(4-Methoxyphenoxy)phenyl) -2-methylbutan-2-ol (50) ^{13}C NMR (CDCl_3 , 125 MHz)

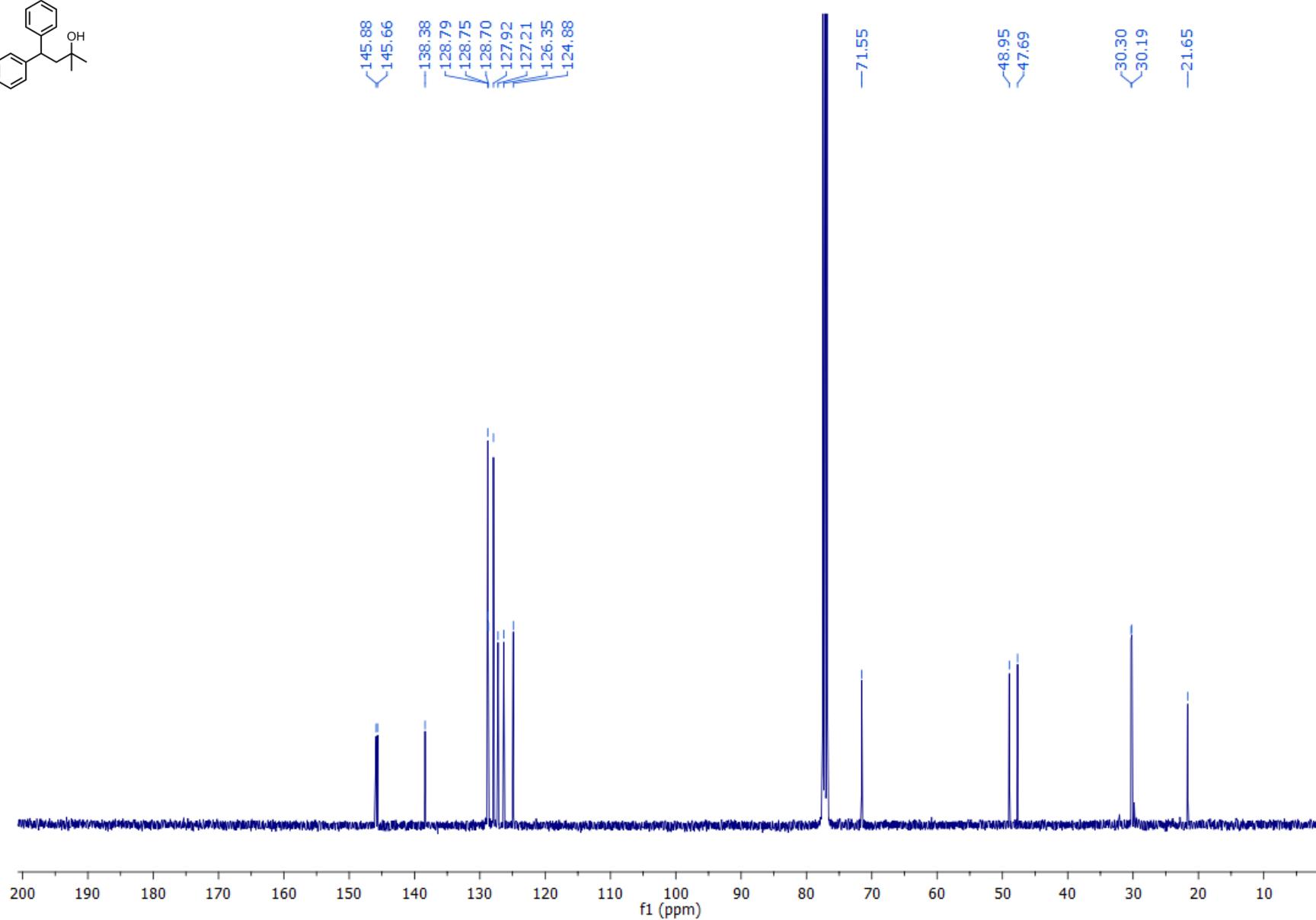
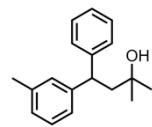


2-Methyl-4-phenyl-4-(m-tolyl)butan-2-ol (51) ^1H NMR (CDCl_3 , 500 MHz)

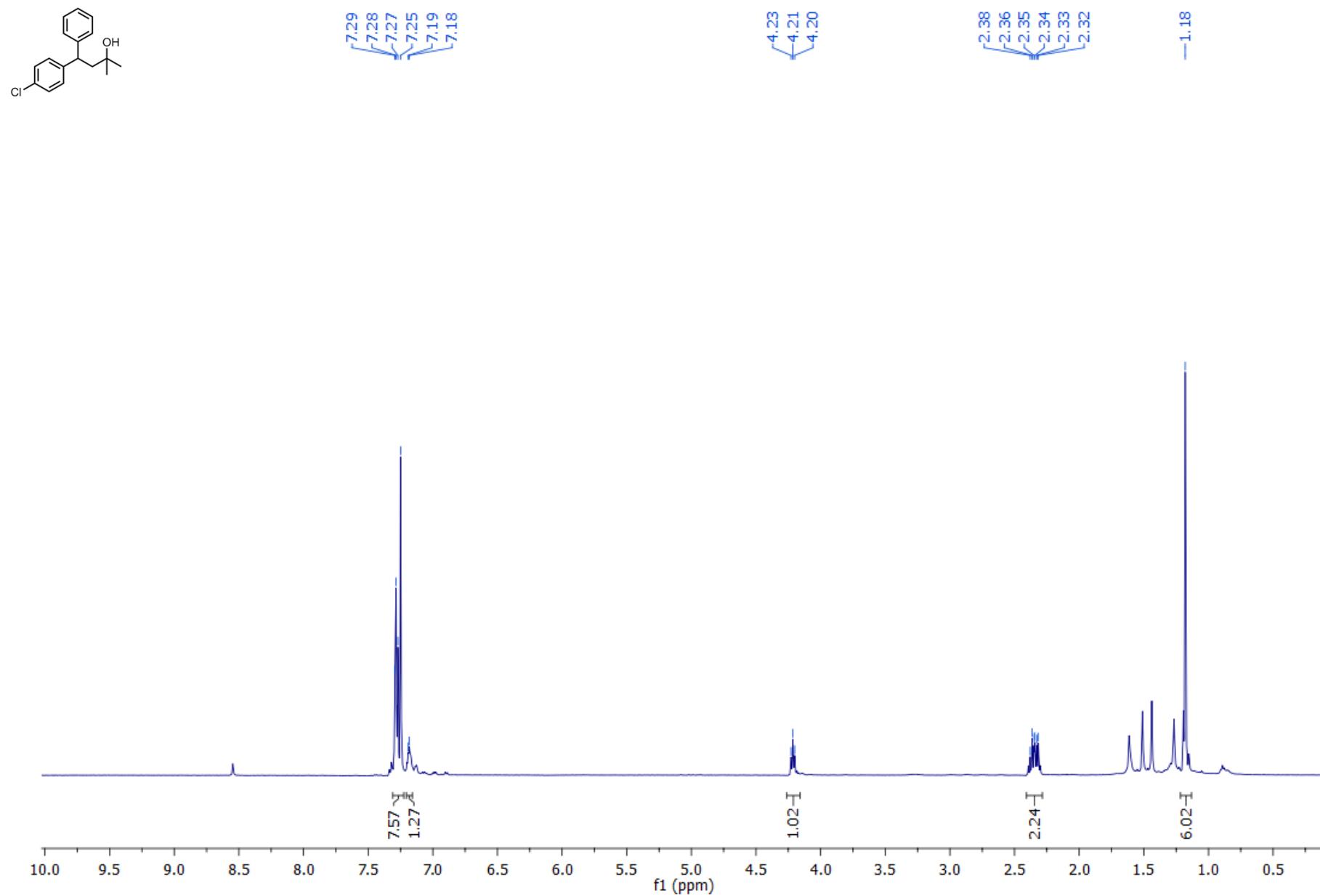


2-Methyl-4-phenyl-4-(m-tolyl)butan-2-ol (51)

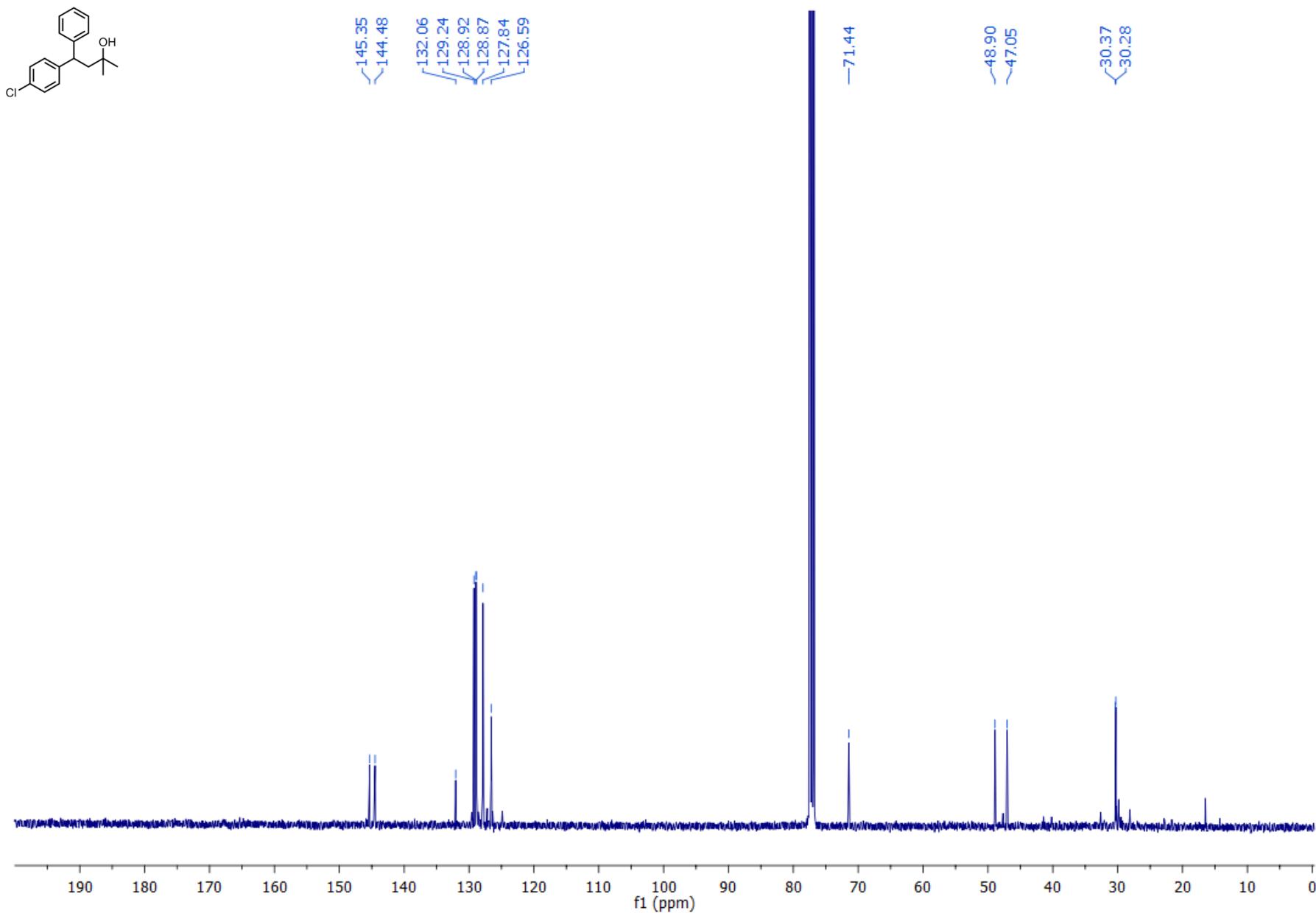
^{13}C NMR (CDCl_3 , 100 MHz)



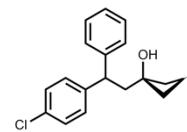
4-(4-Chlorophenyl)-2-methyl-4-phenylbutan-2-ol (52) ^1H NMR (CDCl_3 , 500 MHz)



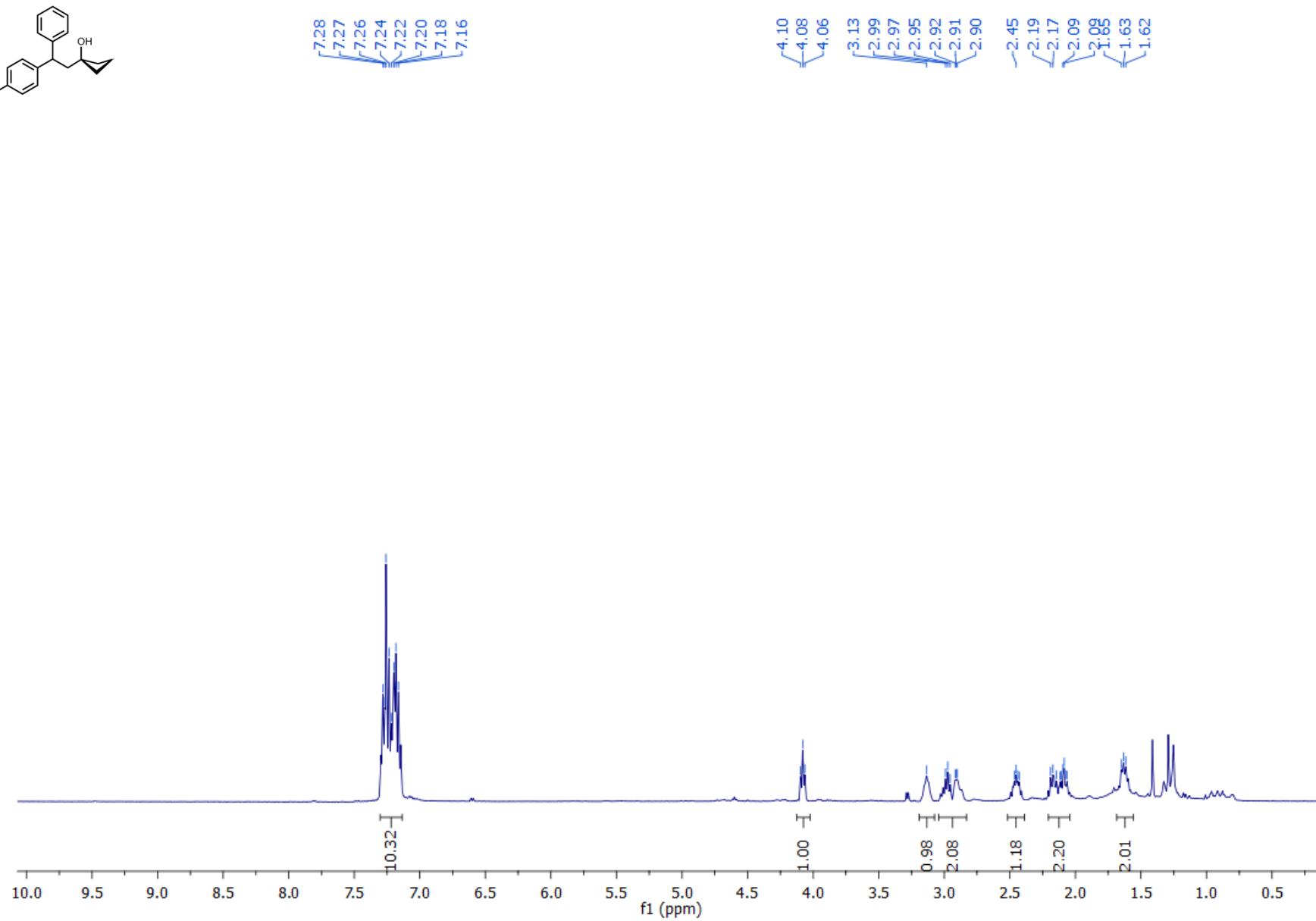
4-(4-Chlorophenyl)-2-methyl-4-phenylbutan-2-ol (52) ^{13}C NMR (CDCl_3 , 100 MHz)



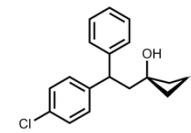
1-(2-(4-Chlorophenyl)-2-phenylethyl)cyclobutan-1-ol (53)



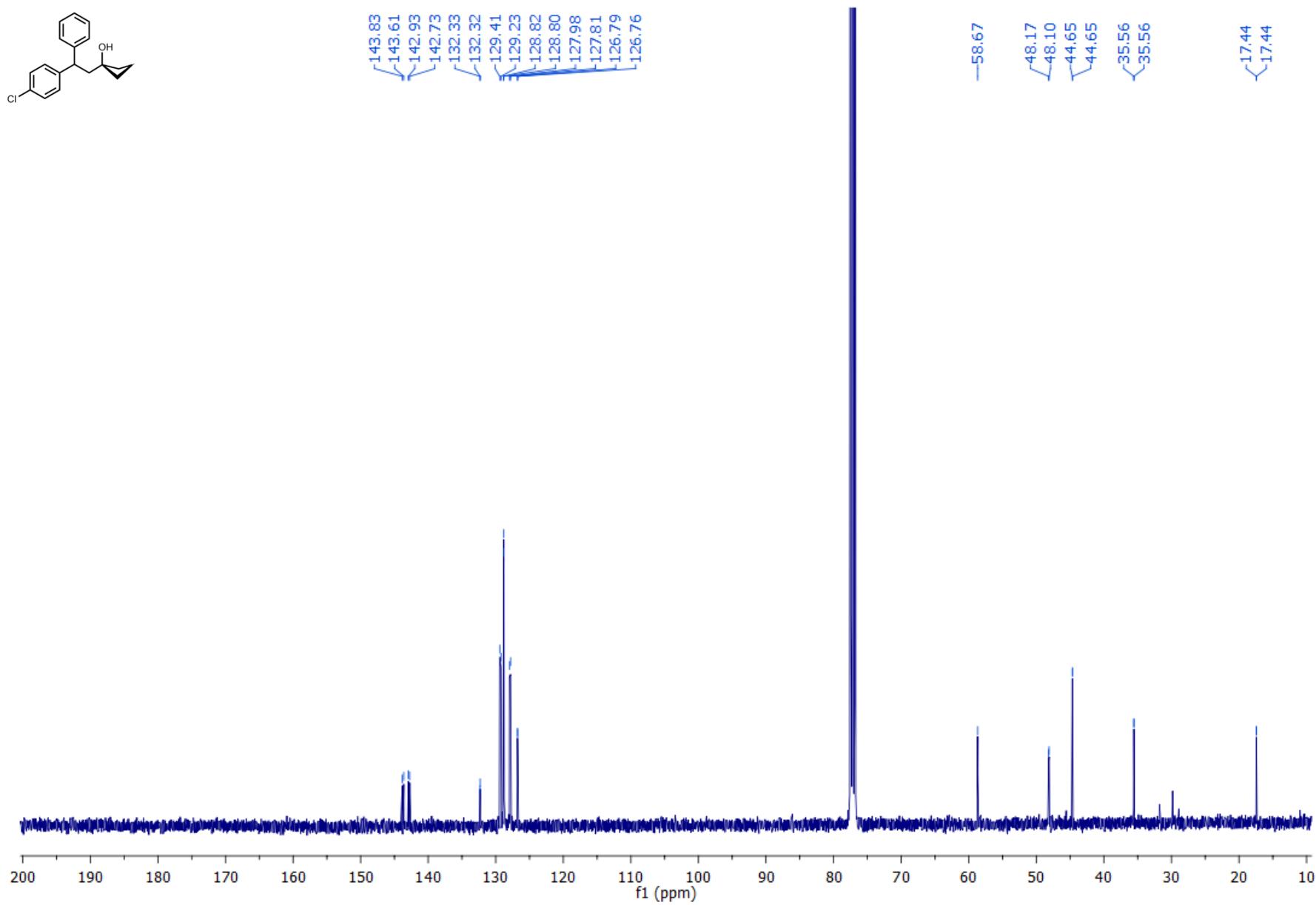
¹H NMR (CDCl₃, 500 MHz)



1-(2-(4-Chlorophenyl)-2-phenylethyl)cyclobutan-1-ol (53)



^{13}C NMR (CDCl_3 , 100 MHz)



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