Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

SUPPORTING INFORMATION

Piperazine-promoted gold-catalyzed hydrogenations: the influence of capping ligands

Jhonatan L. Fiorio,[a] *Eduardo C. M. Barbosa,*[a] *Danielle K. Kikuchi,*[a] *Pedro H. C. Camargo,*[a]
Matthias Rudolph,[b] *A. Stephen K. Hashmi,*[b] *Liane M. Rossi*[a]*

[a] Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo,
Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo, SP, Brazil.

[b] Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg University, Im
Neuenheimer Feld 270, 69120 Heidelberg, Germany

*Correspondence to: lrossi@iq.usp.br.

Table of contents

1. Materials and methods 3
2. Supplementary figures and tables 4
3. ^{1}H and ^{13}C NMR Spectra of Products 9

1. Materials and methods

All the reagents used for the support and catalyst preparations were of analytical grade, purchased from Sigma-Aldrich and used as received. Tetrachloroauric(III) acid was purchased as a 30 wt% aqueous solution in dilute HCl (Sigma-Aldrich). Commercial reagents were purchased from Sigma Aldrich, and used as received. The glass reactors were thoroughly cleaned with aqua regia ($HCl:HNO_3 = 3:1$ v/v), rinsed with copious pure water, and then dried in an oven prior to use.

UV-Vis spectra were recorded on a Shimadzu UV-1700. Gold content in the catalyst was measured by FAAS analysis, on a Shimadzu AA-6300 spectrophotometer using an Au hollow cathode lamp (Photron). Metal leaching into the supernatant solution was measured by inductively coupled plasma atomic emission spectroscopy measurements, performed on a Spectro Arcos ICP-OES. TEM analyses were performed with a JEOL 2100. Catalyst samples for TEM were prepared by sonicating the catalyst powder in propan-2-ol. A drop of the resulting dispersion was placed on a carbon-coated copper grid (Ted Pella, Inc.). The histogram of nanoparticle size distribution was obtained from the measurement of about 200 particles. NMR spectra was recorded on Bruker 500 or 300 MHz spectrometers. ^{1}H NMR spectra were referenced to the residual solvent signals (δ_H 7.26 ppm for $CDCl_3$). Elemental analyses (C, H, and N) were obtained on a Perkin Elmer 2400 II instrument.

2. Supplementary figures and tables

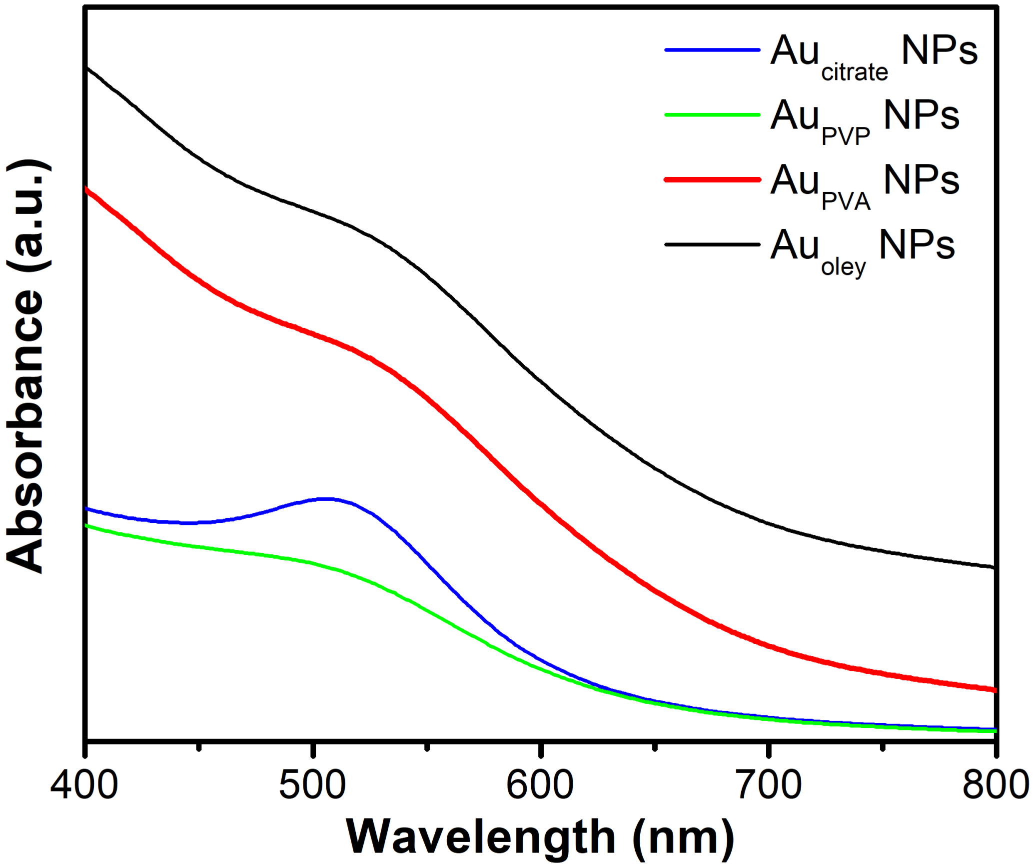


Figure S1. UV-vis spectra of Au NPs according to the different stabilizers.

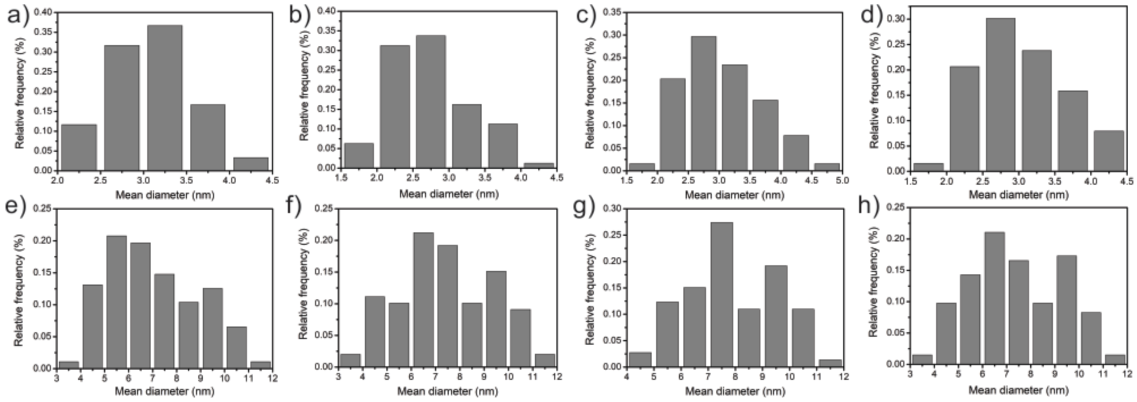


Figure S2. Size distribution of Au NPs before and after thermal (a, e) Au$_{PVA}$/C, (b, f) Au$_{PVP}$/C, (c, g) Au$_{oley}$/C, (d, h) Au$_{citrate}$/C.

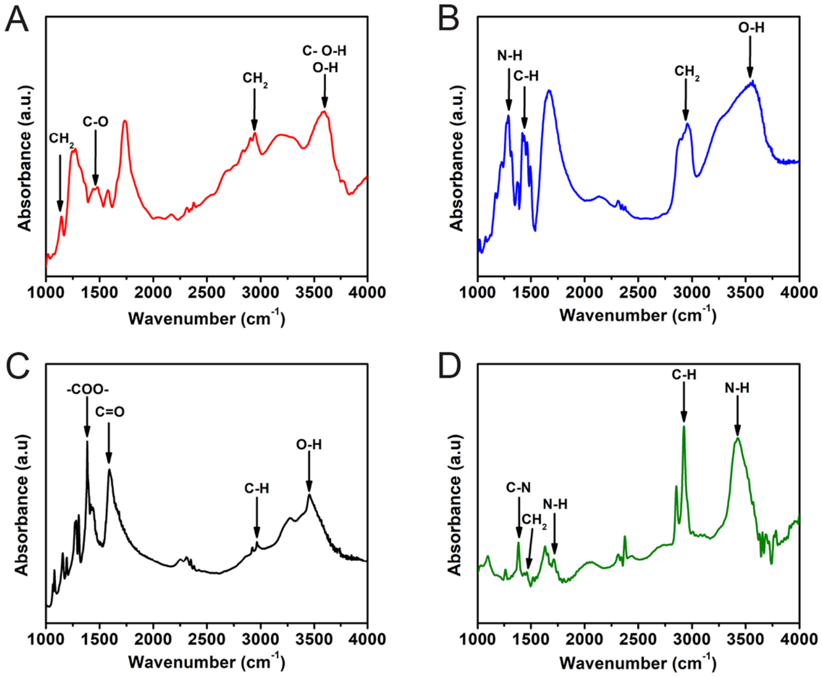


Figure S3. FTIR spectra of the (a) Au$_{PVA}$/C, (b) Au$_{PVP}$/C, (c) Au$_{Cit}$/C, (d) Au$_{Oley}$/C catalysts.

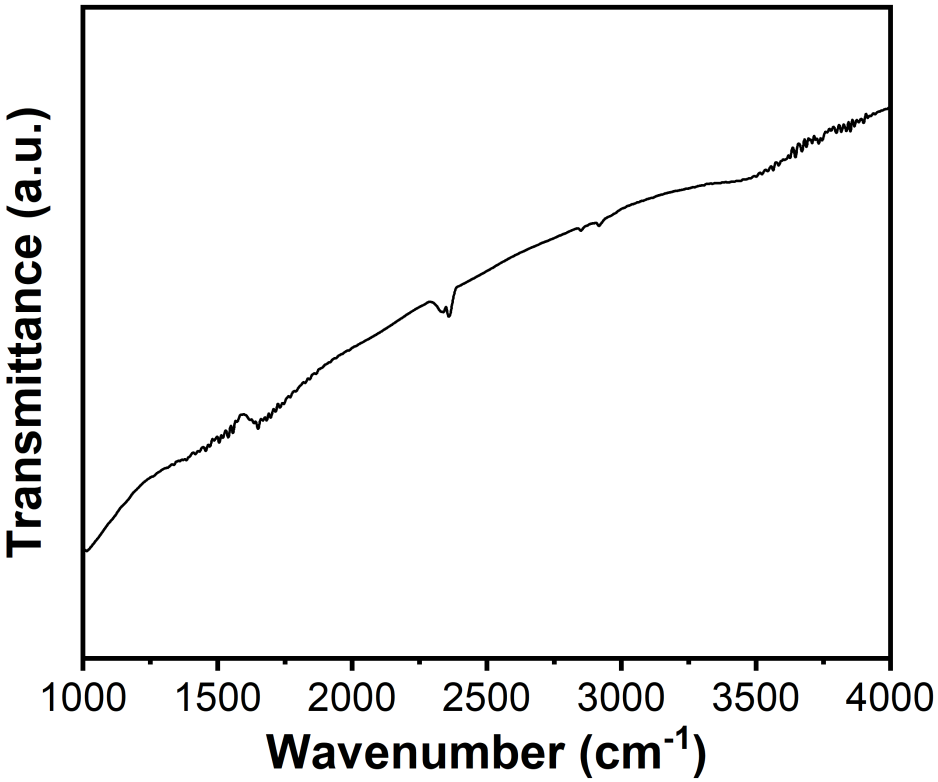


Figure S4. FTIR spectra of the Au$_{PVA}$/C catalyst after thermal treatment.

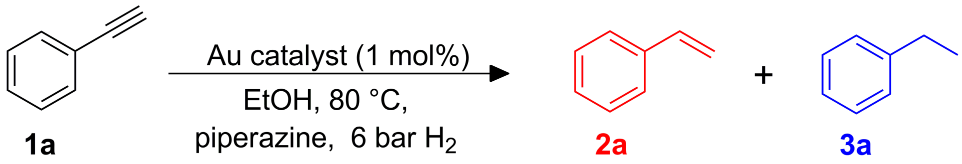
Table S1. ICP-AES analysis of the reaction mixture - Leaching experiments

Run	Gold content (ppm)
1	<0.1
2	<0.1
3	<0.1
4	<0.1
5	<0.1

Table S2. Carbon analysis of the as-prepared catalysts and calcined samples.

Entry	Catalyst	Treatment to remove ligands	Carbon content (%)
1	Au$_{PVA}$/C	No	90.86
2	Au$_{PVA}$/C	Calcined at 400 ºC	90.35
3	Au$_{Citr}$/C	No	90.91
4	Au$_{Citr}$/C	Calcined at 400 ºC	90.47
3	Au$_{Oley}$/C	No	90.32
4	Au$_{Oley}$/C	Calcined at 400 ºC	90.10

Table S3. Catalytic activity of Au catalysts in the hydrogenation of phenylacetylene **1a**.[a]



Entry	Catalyst	Refluxed at 90 ºC	Amine	Conversion (%)	Selectivity to **2a** (%)
1	Au$_{PVA}$/C	No	No	6	>99
2	Au$_{PVA}$/C	No	Yes	3	>99
3	Au$_{PVA}$/C	Yes	No	15	>99
4	Au$_{PVA}$/C	Yes	Yes	93	>99
5	Au$_{Citr}$/C	No	No	5	>99
6	Au$_{Citr}$/C	No	Yes	3	>99
7	Au$_{Citr}$/C	Yes	No	13	>99
8	Au$_{Citr}$/C	Yes	Yes	95	>99

[a]Reaction conditions: 1 mmol of alkyne, 0.5 mol% of Au, 1 mmol of piperazine, 2 mL of EtOH, 80 °C, 6 bar of H_2, 24 h. Conversion and selectivity were determined by GC using the internal standard technique.

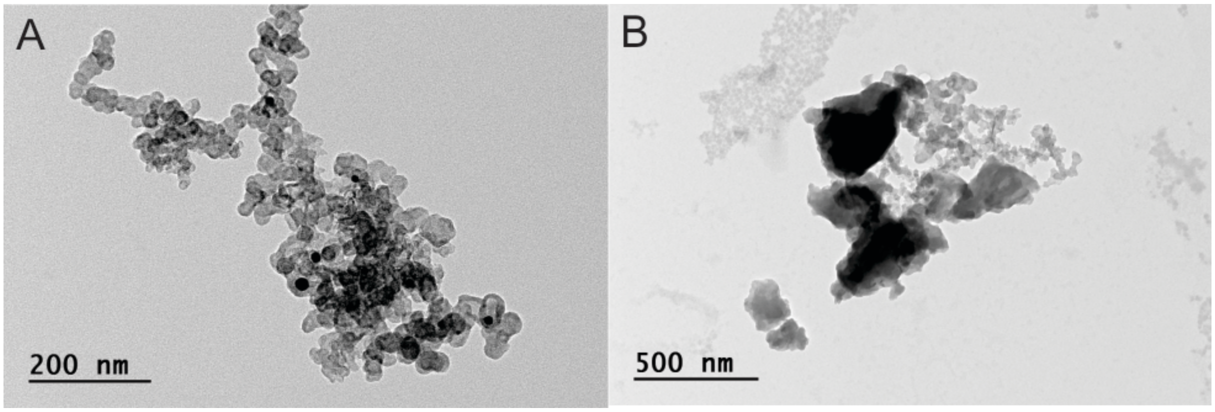


Figure S5. TEM images of Au_{PVA}/C thermally treated at a) 500 ºC and b) 800 ºC.

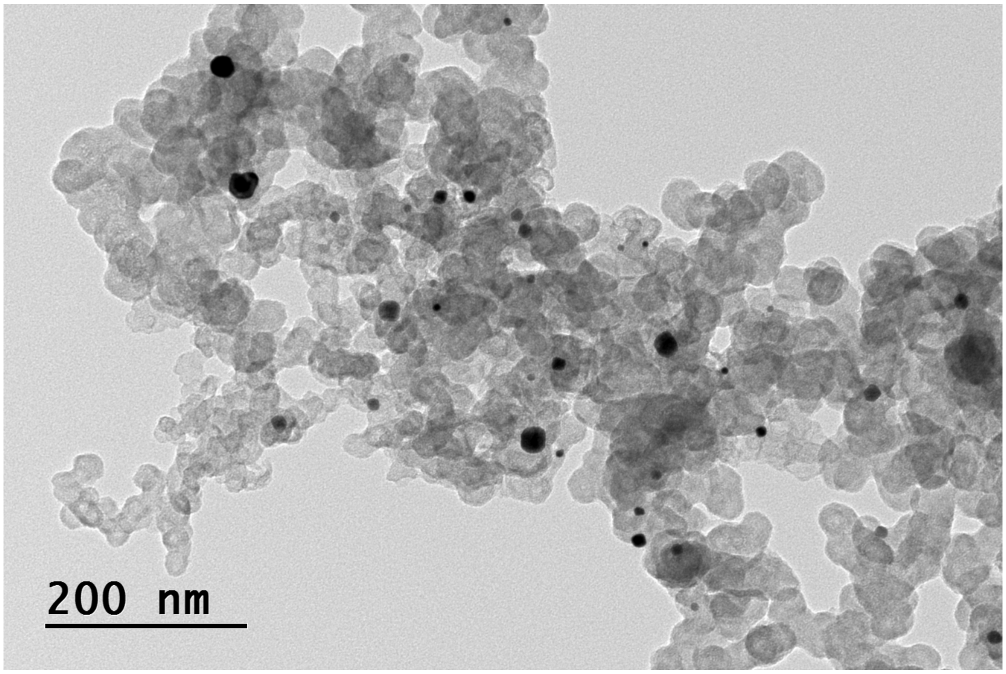


Figure S6. TEM image of Au_{PVA}/C thermal treated after fifth-run reactions

3. ^{1}H and ^{13}C NMR Spectra of Products

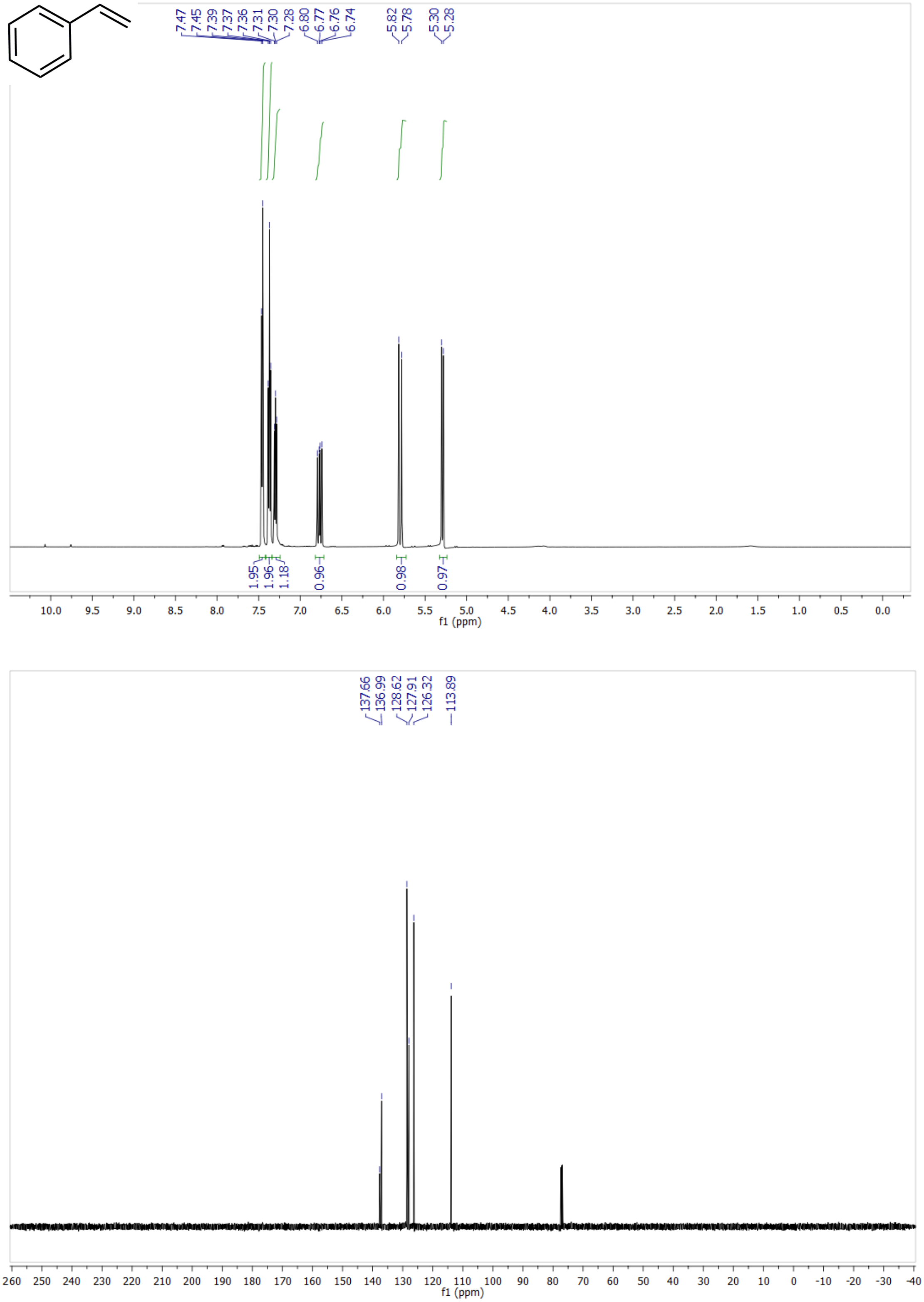


Figure S7. ^{1}H and ^{13}C NMR Spectrum of **2a**

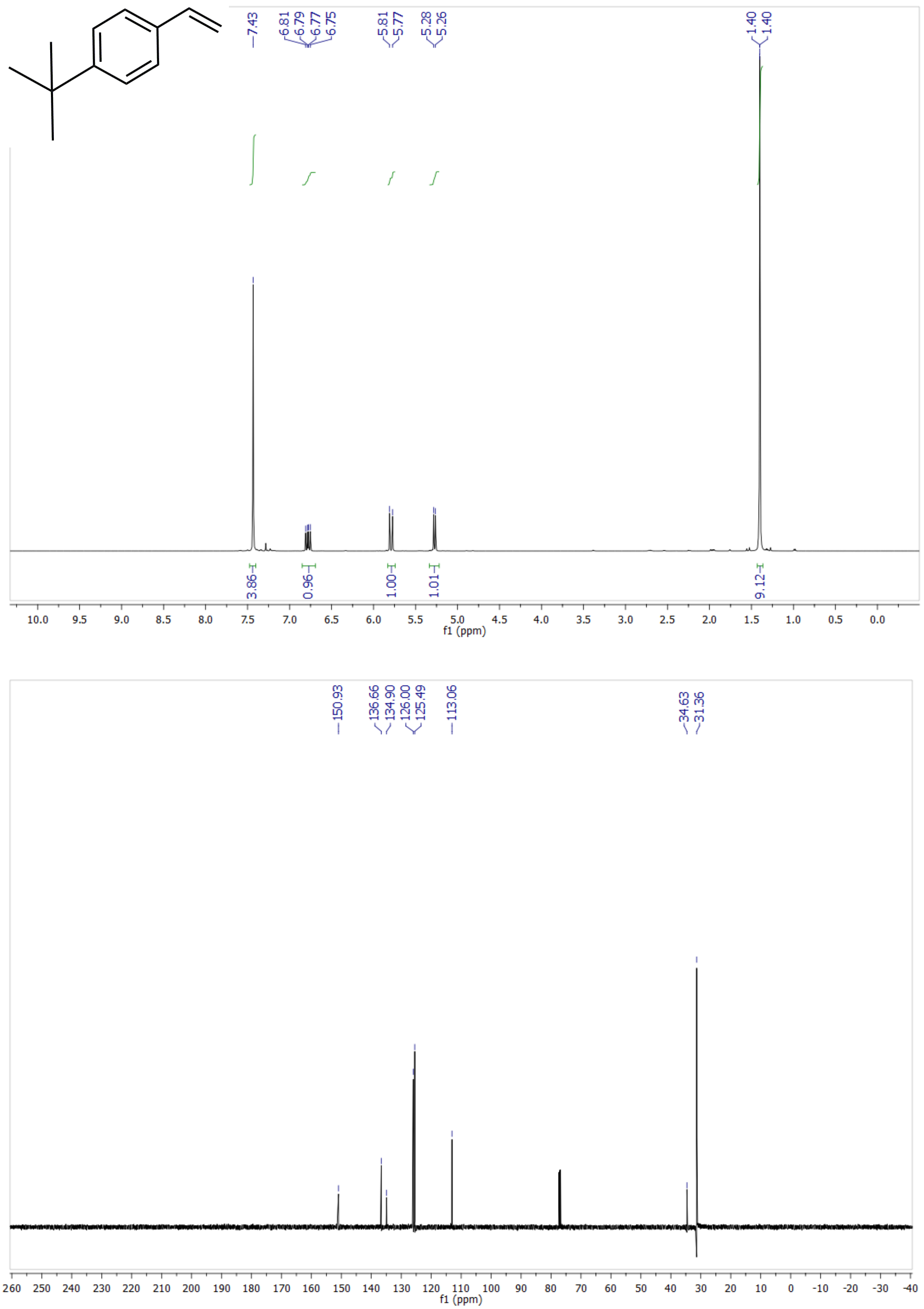


Figure S8. ^{1}H and ^{13}C NMR Spectrum of **2b**

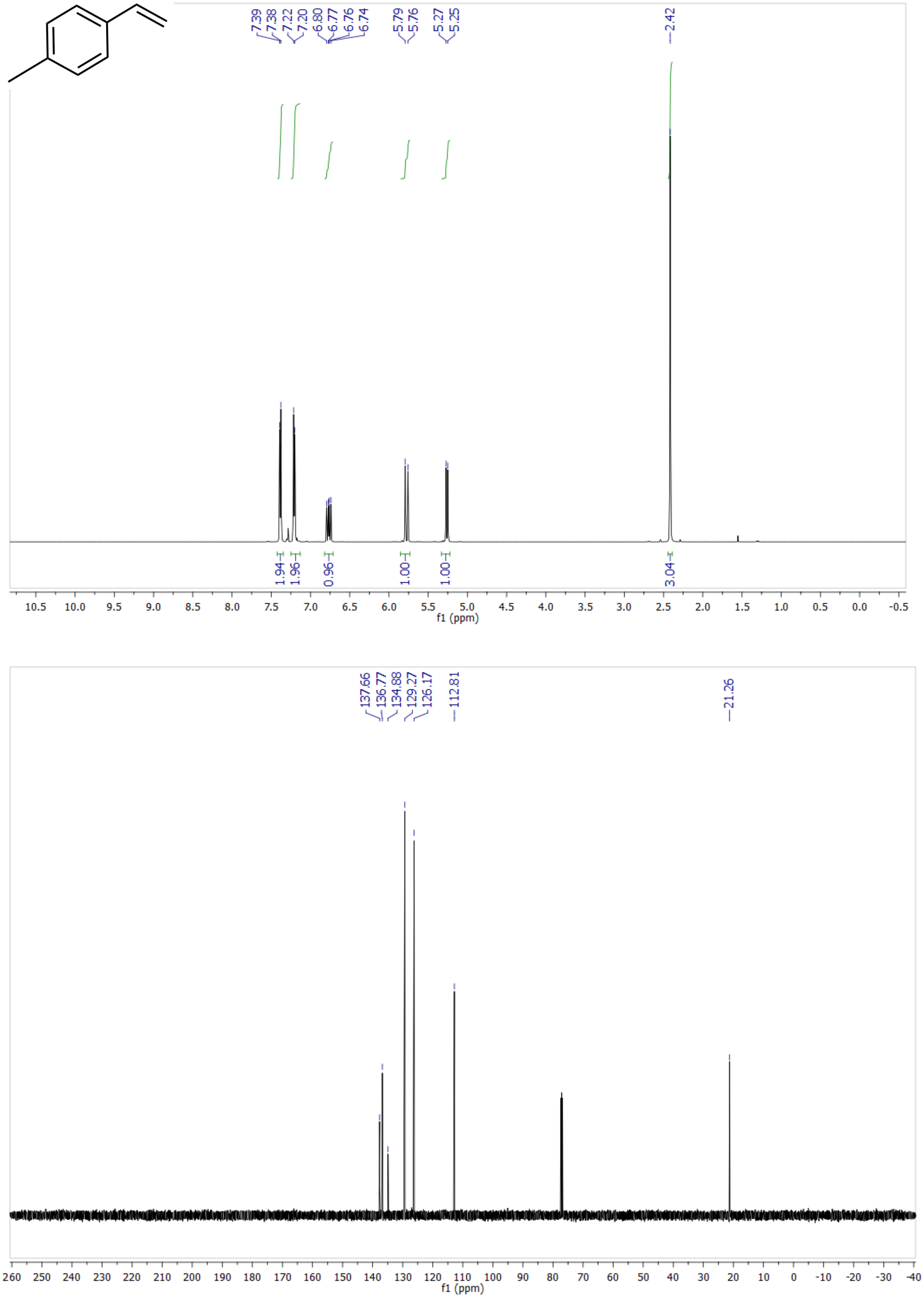


Figure S9. ^{1}H and ^{13}C NMR Spectrum of **2c**

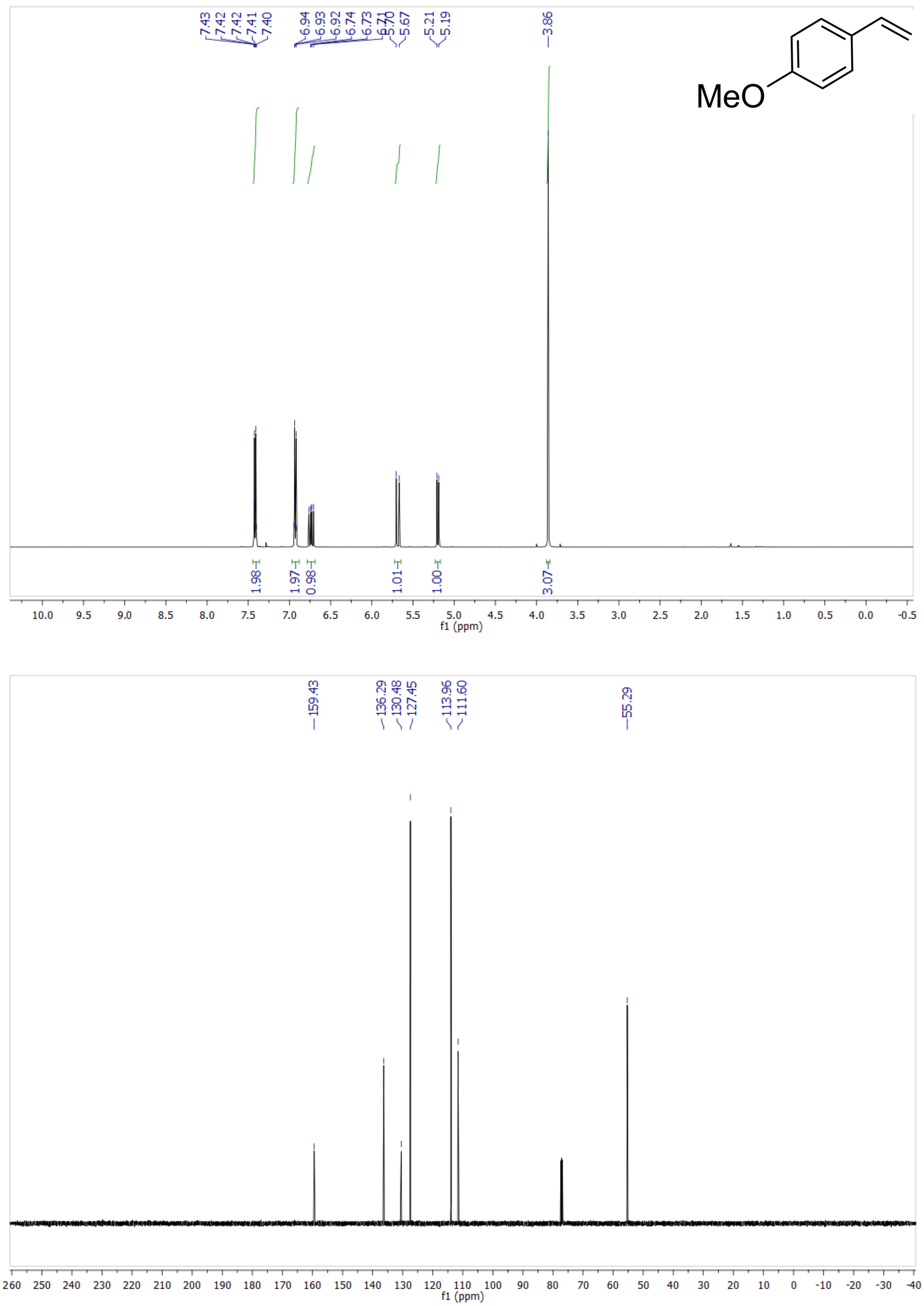


Figure S10. ^{1}H and ^{13}C NMR Spectrum of **2d**

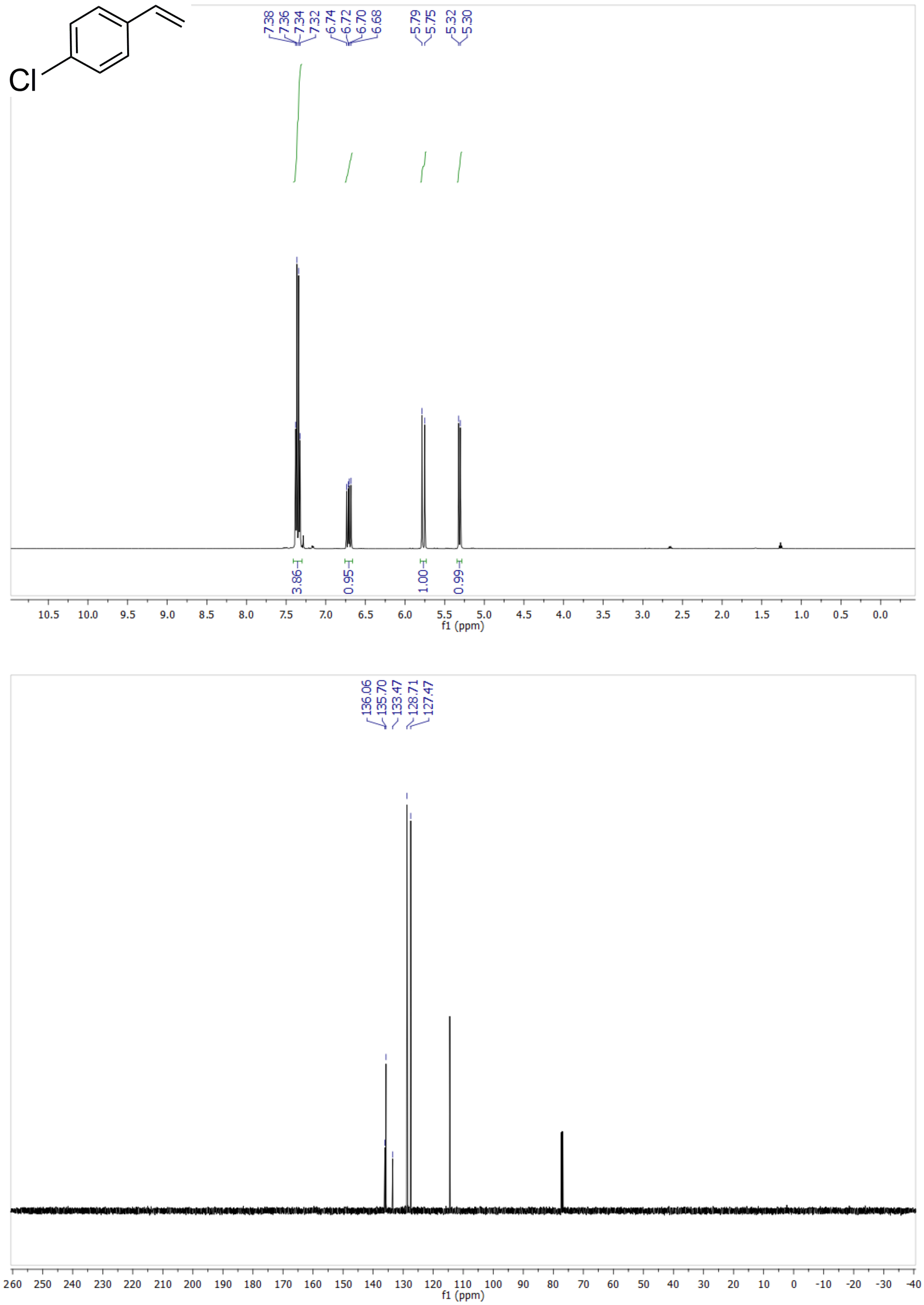


Figure S11. ^{1}H and ^{13}C NMR Spectrum of **2f**

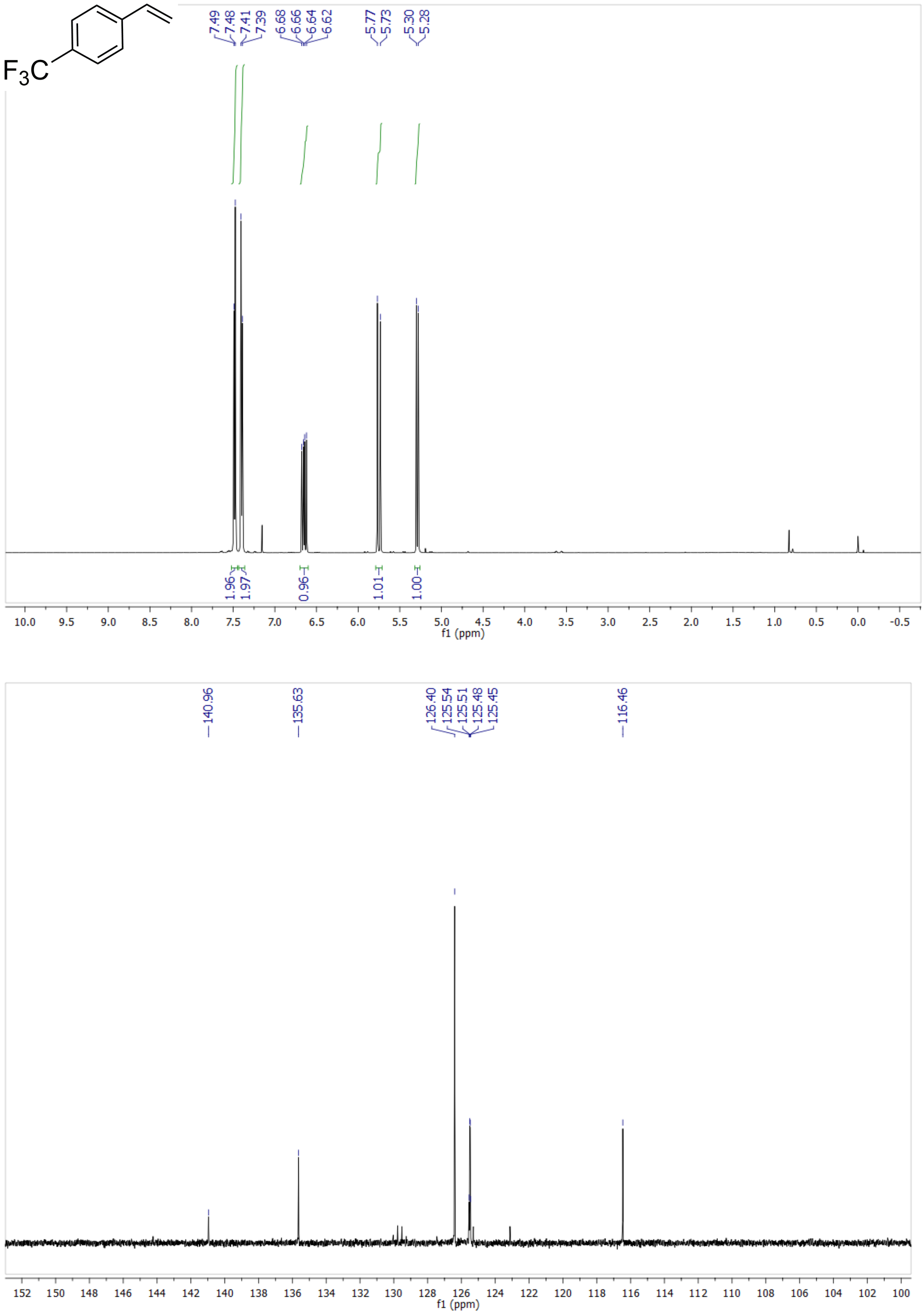


Figure S12. ^{1}H and ^{13}C NMR Spectrum of **2h**

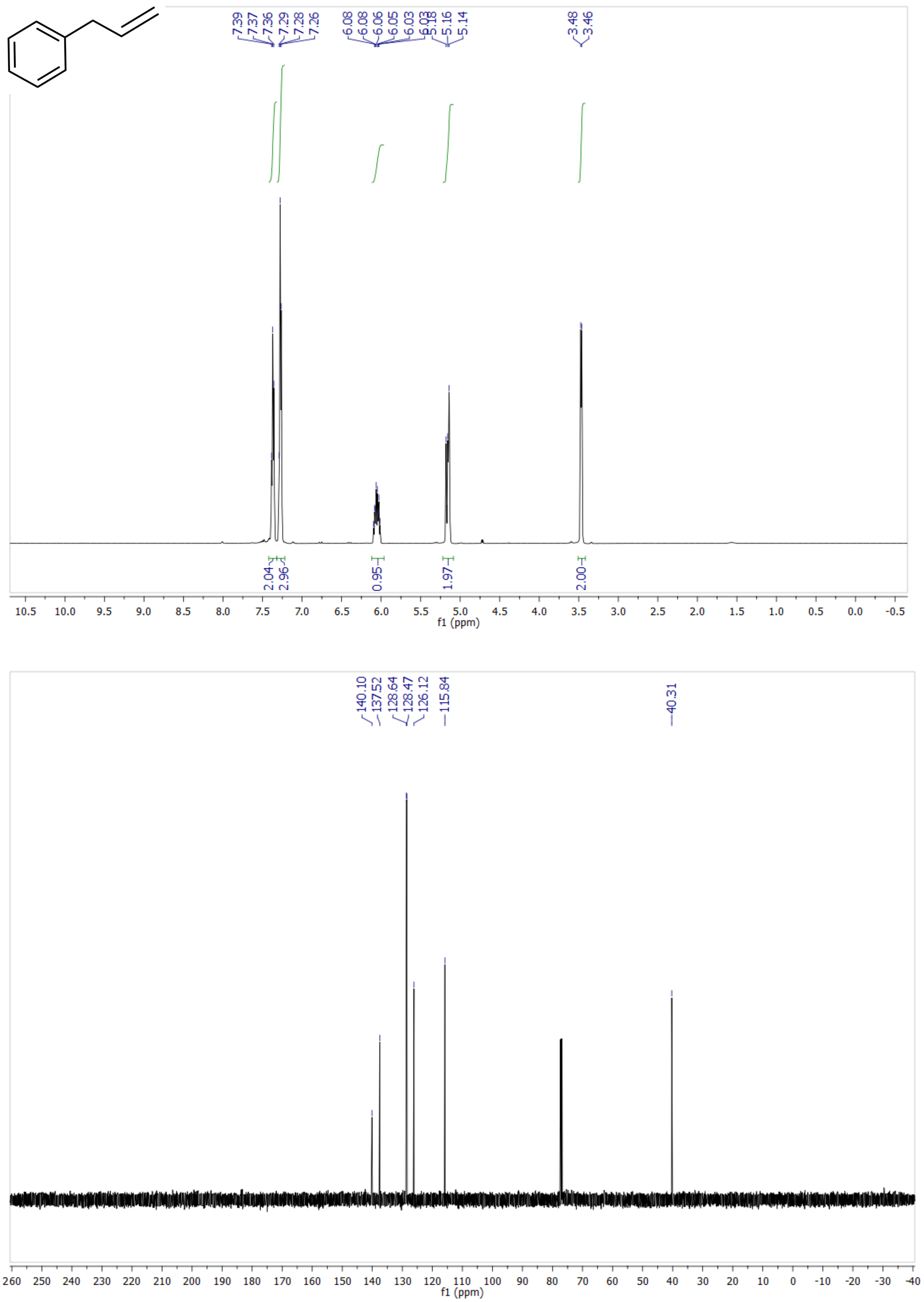


Figure S13. ^{1}H and ^{13}C NMR Spectrum of **2i**

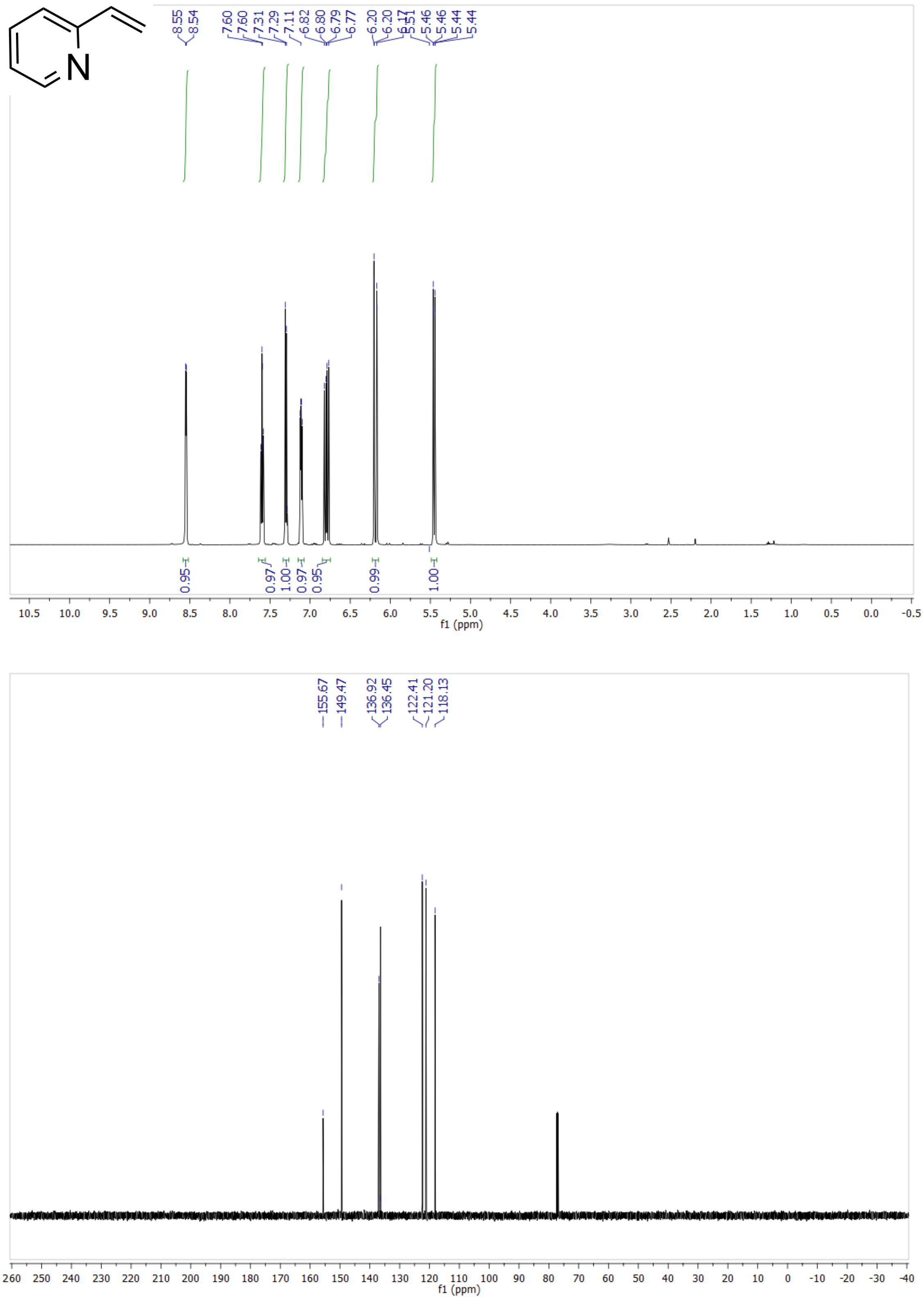


Figure S14. ^{1}H and ^{13}C NMR Spectrum of **2k**

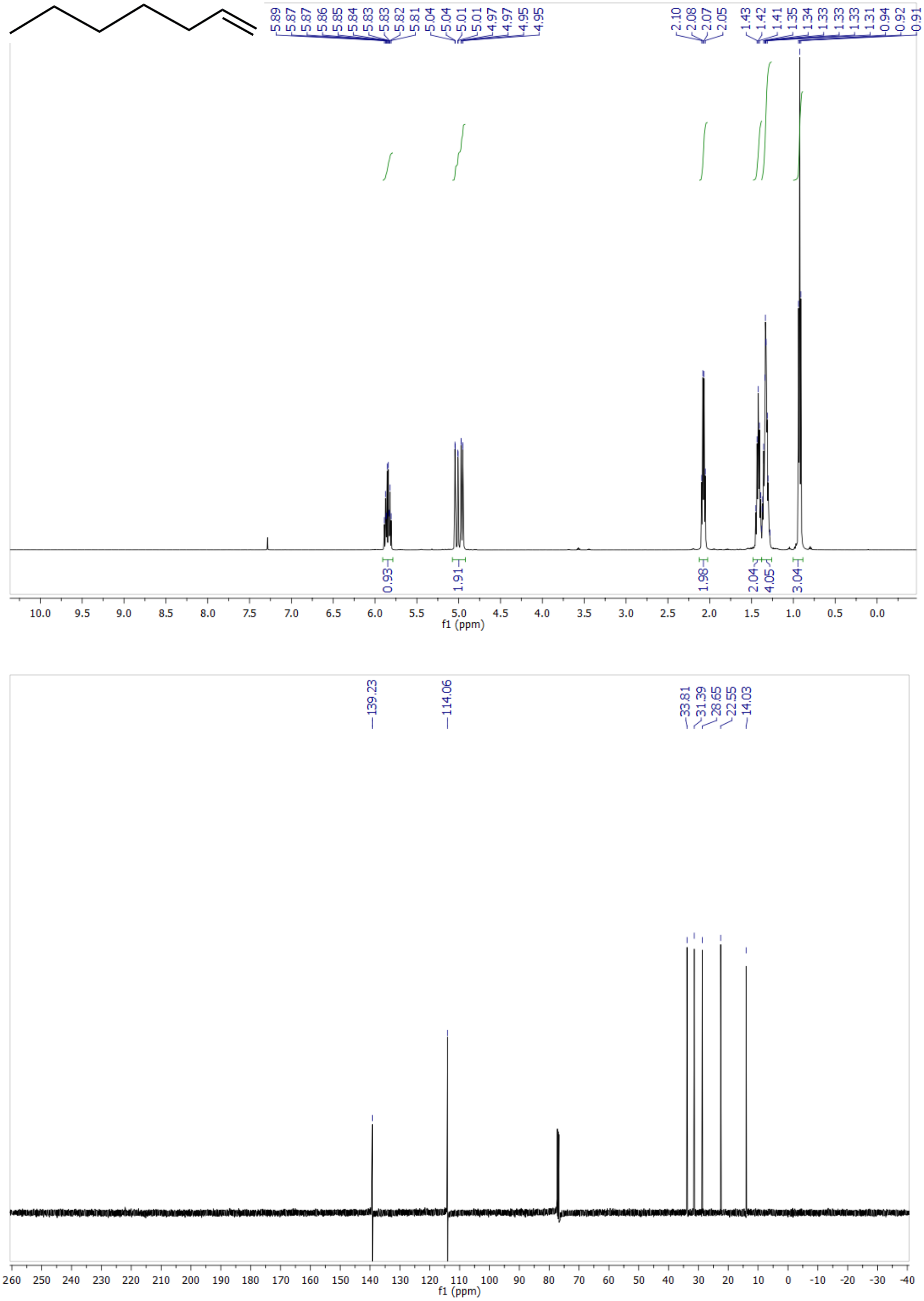


Figure S15. ^{1}H and ^{13}C NMR Spectrum of **2r**

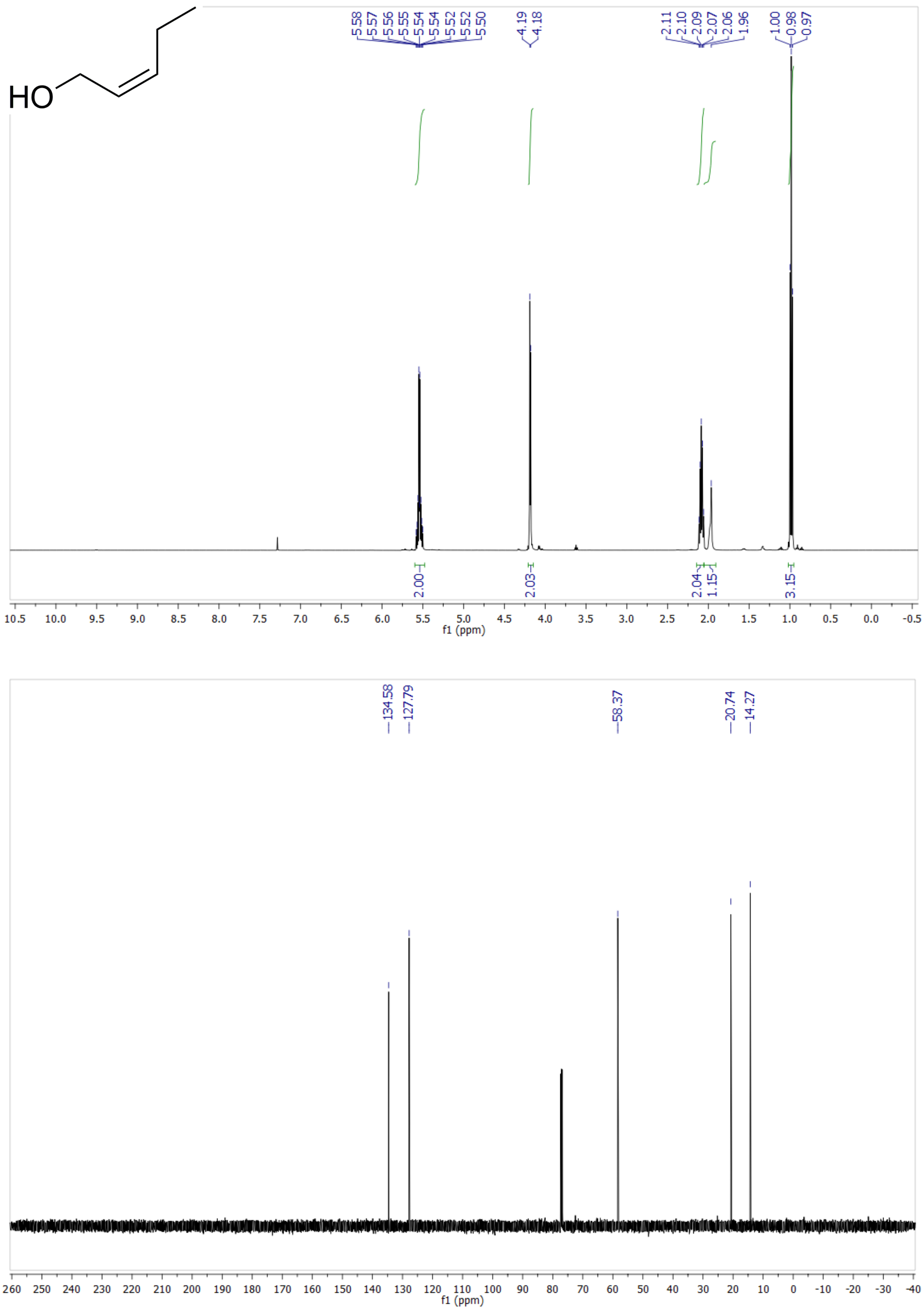


Figure S16. ^{1}H and ^{13}C NMR Spectrum of **2y**

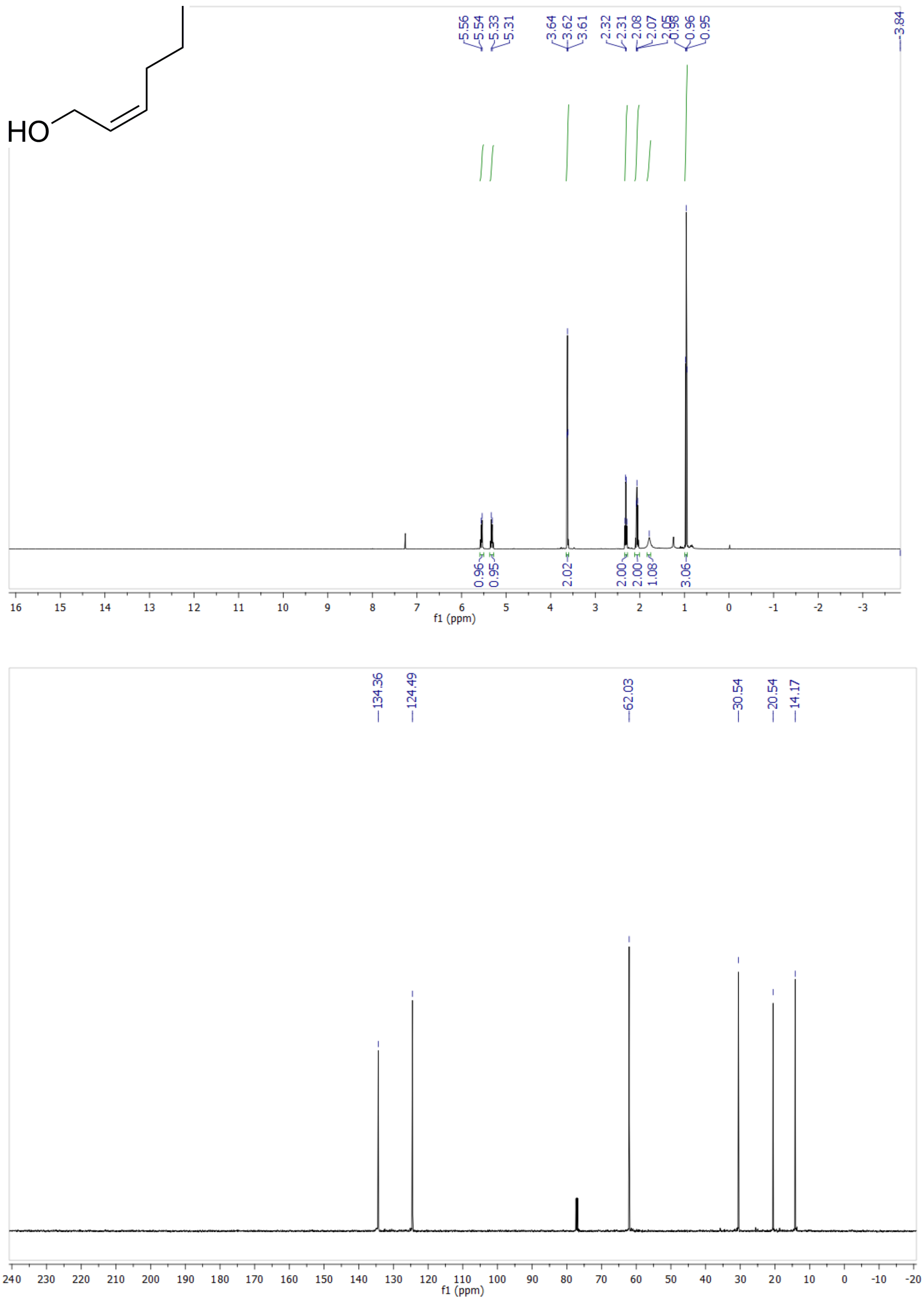


Figure S17. ^{1}H and ^{13}C NMR Spectrum of **2aa**

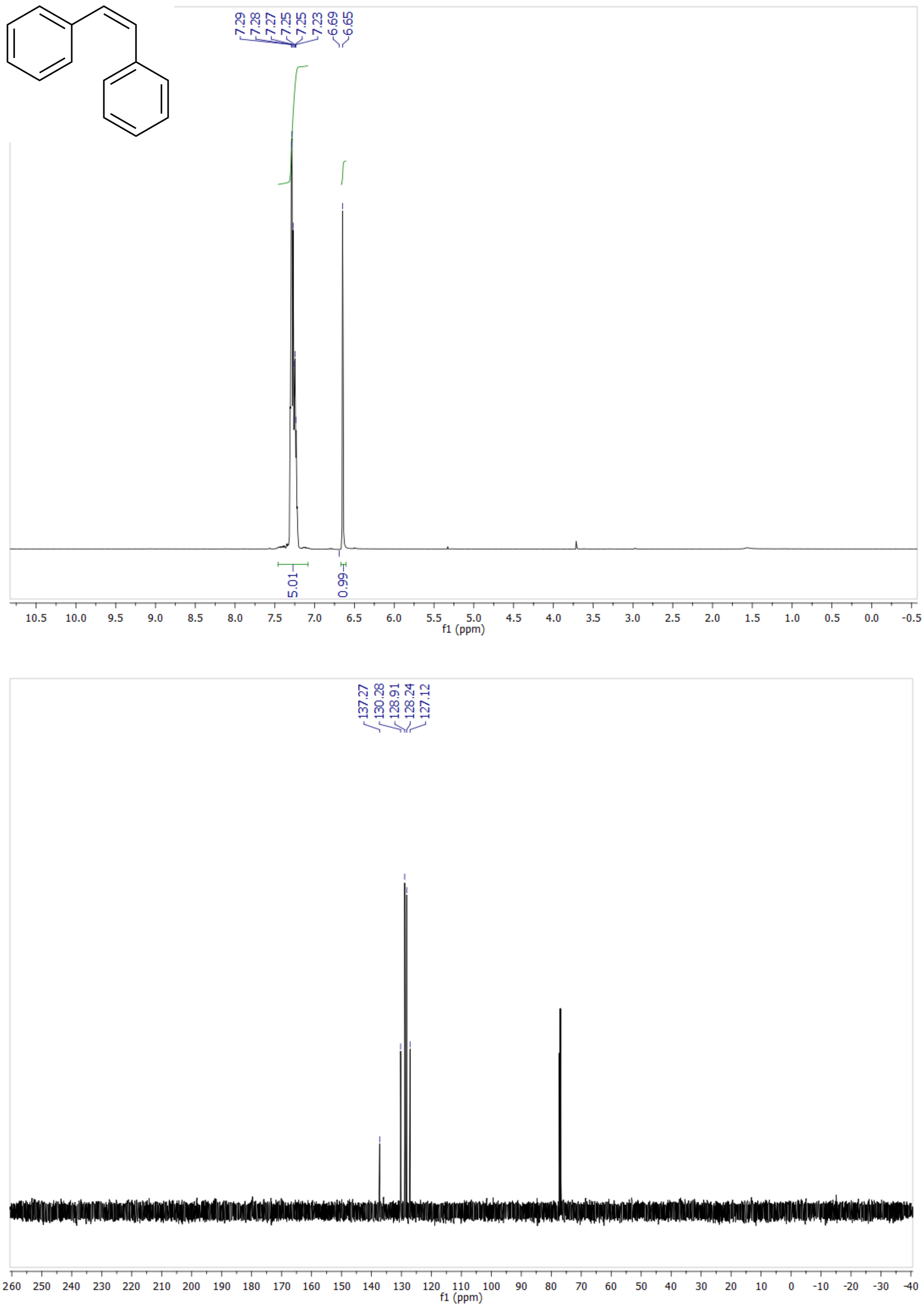


Figure S18. ^{1}H and ^{13}C NMR Spectrum of **2ae**