Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

(NHC-olefin)-nickel(0) nanoparticles as catalysts for the (*Z*)-selective semi-hydrogenation of alkynes and ynamides

Marta G. Avello,[a] Stéphane Golling,[a] Lai Truong-Phuoc,[b] Loïc Vidal,[c] Thierry Romero,[b] Vasiliki Papaefthimiou,[b] Nathalie Gruber,[d] Michael J. Chetcuti,[a] Frédéric R. Leroux,[a] Morgan Donnard,[a] Vincent Ritleng,[a] Cuong Pham-Huu,*[b] and Christophe Michon*[a]*

[a] Université de Strasbourg, Université de Haute-Alsace, Ecole Européenne de Chimie, Polymères et Matériaux, CNRS, LIMA, UMR 7042, 25 rue Becquerel, 67087 Strasbourg, France.
E-mail: cmichon@unistra.fr
[b] Université de Strasbourg, Ecole Européenne de Chimie, Polymères et Matériaux, CNRS, ICPEES, UMR 7515, 25 rue Becquerel, 67087 Strasbourg, France.
E-mail: cuong.pham-huu@unistra.fr
[c] Université de Haute-Alsace, CNRS, IS2M UMR UMR 7361, 15, rue Jean Starcky - BP 2488, 68057 Mulhouse cedex, France
[d] Université de Strasbourg, Fédération de chimie Le Bel – FR2010, BP 296R8 1, rue Blaise Pascal, 67008 Strasbourg Cedex, France

I) General methods and instrumentation.

All solvents were dried using standard methods and stored over molecular sieves (4 Å).

Alkynes substrates were purchased from usual chemical providers and used as received.

Except for the catalytic hydrogenations which were performed in pressurised Parr autoclaves, all reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon.

Analytical thin layer chromatography (TLC) was performed on Merck pre-coated 0.20 mm silica gel Alugram Sil 60 G/UV$_{254}$ plates.

Flash chromatography was carried out with Macherey silica gel (Kielselgel 60).

Gas chromatography analyses were done on GC Agilent with FID detectors using Agilent HP1 column (30 m, 0.35 mm, 0.25 μm), with hydrogen as gas carrier and with tetradecane as the internal standard.

^{1}H (300 or 400 MHz) and ^{13}C (75 or 100 MHz) spectra were acquired on Bruker Avance III spectrometers. DEPT 135 ^{13}C spectra were recorded to help in the ^{13}C signal assignments of complexes **2a** and **2b**. An HMBC ^{15}N spectrum of **2a** at 298 K was recorded with the following parameters: TD (^{15}N) = 32 and NS = 64. The chemical shifts are referenced to the residual deuterated or ^{13}C solvent peaks. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. 1,3,5-trimethoxybenzene and 1,2,4,5-tetrachlorobenzene were used as internal standards when needed.

Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, Institut de Chimie, UMR 7177, Université de Strasbourg.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were performed by the Plateforme Analytique des Inorganiques, IPHC, UMR 7178, CNRS /Université de Strasbourg.

High-resolution mass spectra were recorded on a Bruker micrOTOF or Bruker micrOTOF-Q mass spectrometer by the Service de Spectrométrie de Masse, Institut de Chimie, UMR 7177 or the Laboratoire de Spectrométrie de Masse BioOrganique, IPHC, UMR 7178 of the Université de Strasbourg.

Single-crystal X-ray diffraction data were collected at 120(2) K on a Bruker APEX II DUO Kappa CCD area detector diffractometer equipped with an Oxford Cryosystem liquid N_2 device using Mo-Kα radiation (λ = 0.71073 Å). A summary of crystal data, data collection parameters and structure refinements is given in Table S1. The cell parameters were determined from reflections taken from three sets of twelve frames, each at ten seconds exposure, using APEX2 software. The structures were solved using direct methods with SHELXS-2014 and refined against F^2 for all reflections using the SHELXL-2014 software.[S1] A semi-empirical absorption correction was applied using SADABS in APEX II.[S2] All non-hydrogen atoms were refined with anisotropic displacement parameters, using weighted full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters.

Powder X-ray Diffraction (PXRD) measurements were carried out on a Bruker D-8 Advance diffractometer equipped with a Vantec detector (Cu Kα radiation) working at 40 kV and 40 mA. X-ray diffractograms were recorded in the 20-80° 2θ region at room temperature in air.

Dynamic Light Scattering (DLS) measurements were performed on an Anton Paar DLS system at 25 °C.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed in an ultrahigh vacuum (UHV) spectrometer equipped with a RESOLVE 120 MCD5 hemispherical electron analyzer. The Al Kα hv=1486.6 eV dual anode X-ray source was used as incident radiation. The C 1s peak at 285 eV was used as peak reference. The constant pass energy mode was used to record both survey and high-resolution spectra, with pass energies 100 and 20 eV respectively.

Scanning electron microscopy (SEM) measurements were recorded with a Hitachi SU8010 FE-SEM microscope at 1 kV at room temperature. No metallization of the samples was done, but their borders were covered with a metallic tape to evacuate the excess of charge.

Elemental mapping by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) was investigated with a Zeiss Gemini SEM 500 FEG EDAX Octane Elite EDX detector. The X-rays emitted upon electron irradiation were acquired in the range 0–20 keV. Quantification was done using the standard-less ZAF correction method in the Team EDS software from EDAX.

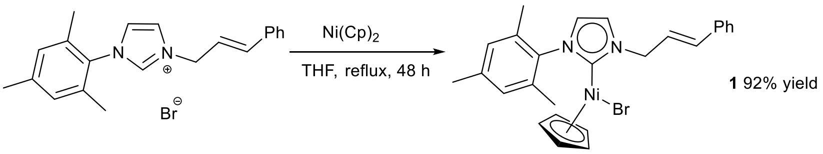
Transmission electron microscopy was performed on a JEOL JSM-7900F. This field emission microscope allowed the user to work under the following modes:

- TEM, HRTEM: conventional microscopy, high resolution and micro-diffraction
- EDS: microanalysis by energy dispersion of the photons emitted by the sample under the impact effect of the incident electrons.

Raman analysis was performed on a LabRAM ARAMIS Horiba Jobin Yvon system.

II. Additional experimental and analytical data:

II.1. Synthesis, characterisation and X-ray diffraction analyses on single crystals of complex 1



Scheme S1. Synthesis of Ni(II) complex **1**.

A Schlenk tube containing a stirring bar was loaded with 3-cinnamyl-1-mesityl-1H-imidazol-3-ium bromide[S3] (600 mg, 1.56 mmol, 1.0 eq), and nickelocene[S4] (343 mg, 1.56 mmol, 1.0 eq). The mixture was stirred, under Ar, in refluxing THF (12 mL) for 48h, until the solution colour change to red burgundy. The resulting mixture was filtered through a Celite pad and washed with THF (3 x 10 mL). The solvent was removed under *vacuum*, and the resulting residue was washed with pentane (x3) to afford the pure complex as a pink powder (717 mg, 1.41 mmol, 92% yield) after removal of the solvents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.39 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 7.21 (d, *J* = 1.9 Hz, 1H, NC*H*CHN), 7.09 (bs, 2H, Mes), 6.87 (d, *J* = 1.9 Hz, 1H, NCHC*H*N), 6.70 – 6.53 (m, 2H, CH=CH), 5.86 (bs, 2H, CH_2), 4.81 (s, 5H, Cp), 2.43 (s, 3H, CH_3), 2.14 (bs, 6H, $2CH_3$).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.8 (C C-Ni), 139.3 (2C), 136.8 (C), 136.3 (C), 133.9 (CH CH=CH), 129.3 (2CH Mes), 128.9 (2CH), 128.3 (CH), 126.8 (2CH), 125.4 (CH CH=CH), 123.7 (CH NC*H*CHN), 123.2 (C), 122.8 (CH NCHC*H*N), 91.7 (5CH, Cp), 54.4 (CH_2), 21.3 (CH_3), 18.5 ($2CH_3$).

HRMS (ESI+): m/z 425.1528 calcd. for $C_{26}H_{27}N_2Ni$ $[M-Br]^+$, found 425.1524.

Elemental analysis. Calculated for $C_{26}H_{27}BrN_2Ni + 0.5\ H_2O$: C, 60.62; H, 5.44; N, 5.44. Found: C, 60.59; H, 5.42; N, 5.77.

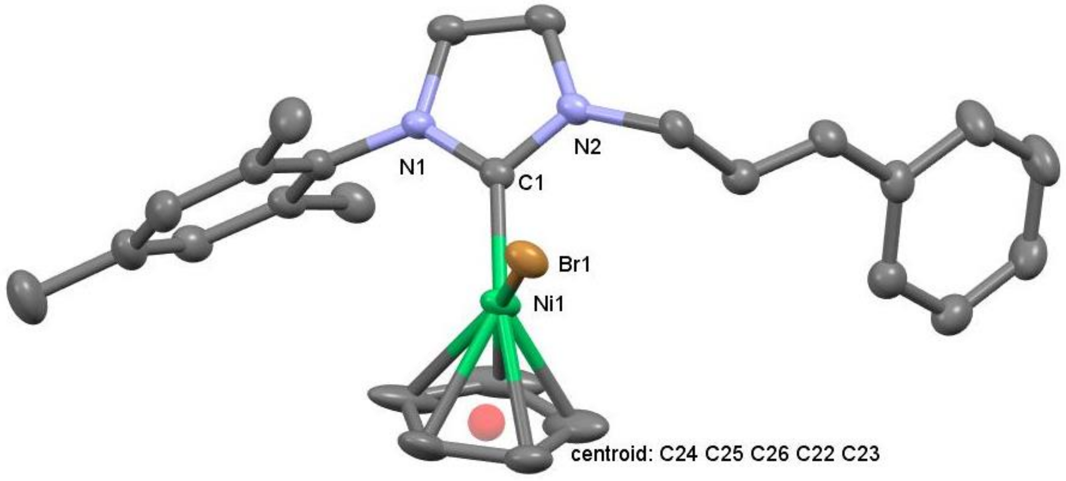


Figure S1. ORTEP of complex **1**. Hydrogens were omitted for clarity. Ellipsoids are shown at the 50% probability level. Main bond lengths in Å: (C1-Ni1) 1.880(3), (Ni1-Br1) 2.3359(4), (Ni1-Centroid$_{C24C25C26C22C23}$) 1.749(6). CCDC 2208403.

Table S1. X-ray crystallographic data and data collection parameters for **1**.

CCDC number	2208403
Identification code	emccm211201
Empirical formula	C26 H27 Br N2 Ni
Formula weight	506.11
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.5740(4) A alpha = 101.953(2) deg.
	b = 11.7216(6) A beta = 104.814(2) deg.
	c = 12.8822(6) A gamma = 104.574(2) deg.
Volume	1159.27(10) A^3
Z, Calculated density	2, 1.450 Mg/m^3
Absorption coefficient	2.575 mm^-1
F(000)	520
Crystal size	0.200 x 0.200 x 0.140 mm
Theta range for data collection	1.876 to 29.230 deg.
Limiting indices	-11<=h<=11, -16<=k<=16, -17<=l<=17
Reflections collected / unique	58451 / 6291 [R(int) = 0.0630]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6605
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6291 / 0 / 273
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0695
R indices (all data)	R1 = 0.0488, wR2 = 0.0778
Extinction coefficient	n/a
Largest diff. peak and hole	0.532 and -0.392 e.A^-3

II.2. Experimental procedures for the catalytic hydrogenations.

All catalytic results are the average of at least 2 runs.

Method A (for solid alkynes)

A 10 mL Schlenk tube containing a stirring bar was loaded with the nickel precatalyst **1** (7.6 mg, 0.015 mmol, 3 mol%), dry toluene (5 mL) and 1.0-1.5 M solution of MeMgBr in THF (45 µL, 0.045 mmol, 9 mol%). The solution was stirred at 100 °C for 2h. A change of colour was observed, from pink to dark brown. The resulting solution was transferred to the rea ctor, where the alkyne (0.5 mmol, 1.0 eq) was previously dried under *vacuum* for one hour. The reactor was loaded with 10 bar of H_2 and the bath was set to the corresponding temperature. The conversion was determined by GC or ^{1}H NMR spectroscopy (after filtration through a pad of SiO_2), and the product was purified by preparative TLC or flash chromatography.

Method A2 (for solid alkynes and ynamides in EtOH)

A 10 mL Schlenk tube containing a stirring bar was loaded with the nickel precatalyst **1** (7.6 mg, 0.015 mmol, 3 mol%), dry toluene (3 mL) and 1.0-1.5 M solution of MeMgBr in THF (45 µL, 0.045 mmol, 9 mol%). The solution was stirred at 100 °C for 2h. A change of colour was observed, from pink to dark brown. The solvent is evaporated under *vacuum*, and dry EtOH (5 mL) was added. The resulting solution was transferred to the reactor, where the alkyne/ ynamide (0.5 mmol, 1.0 eq) was previously dried under *vacuum* for one hour. The reactor was loaded with 10 bar of H_2 and the bath was set to the corresponding temperature. The conversion was determined by GC or ^{1}H NMR spectroscopy (after filtration through a pad of SiO_2), and the product was purified by preparative TLC or flash chromatography.

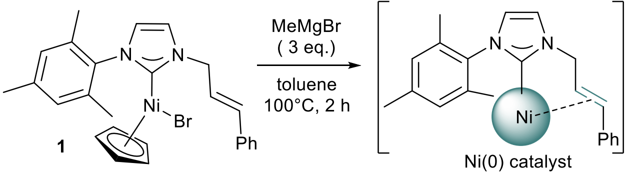
Method B (for liquid alkynes)

A 10 mL Schlenk tube containing a stirring bar was loaded with the nickel precatalyst **1** (7.6 mg, 0.015 mmol, 3 mol%), dry toluene (5 mL) and 1.0-1.5 M solution of MeMgBr in THF (45 µL, 0.045 mmol, 9 mol%). The solution was stirred at 100 °C for 2h. A change of colour was observed, from pink to dark brown. The alkyne (0.5 mmol, 1.0 eq) was added to the solution, and the resulting mixture is transferred to the reactor, previously dried under *vacuum* for one hour. The reactor was loaded with 10 bar of H_2 and the bath was set to the corresponding temperature. The conversion was determined by GC or ^{1}H NMR spectroscopy (after filtration through a pad of SiO_2), and the product was purified by preparative TLC or flash chromatography.

Method B2 (for liquid alkynes and ynamides in EtOH)

A 10 mL Schlenk tube containing a stirring bar was loaded with the nickel precatalyst (7.6 mg, 0.015 mmol, 3 mol%), dry toluene (3 mL) and 1.0-1.5 M solution of MeMgBr in THF (45 µL, 0.045 mmol, 9 mol%). The solution was stirred at 100 °C for 2h. A change of colour was observed, from pink to dark brown. The solvent is evaporated under *vacuum* and the alkyne/ynamide (0.5 mmol, 1.0 eq) was added to the Schlenk. Dry EtOH (5 mL) was added, and the resulting mixture is transferred to the reactor, previously dried for one hour. The reactor was loaded with 10 bar of H_2 and the bath was set to the corresponding temperature. The conversion was determined by GC or ^{1}H NMR spectroscopy (after filtration through a pad of SiO_2), and the product was purified by preparative TLC or flash chromatography.

II.3. Reduction of complex 1: experimental observations and development of the catalytic conditions.



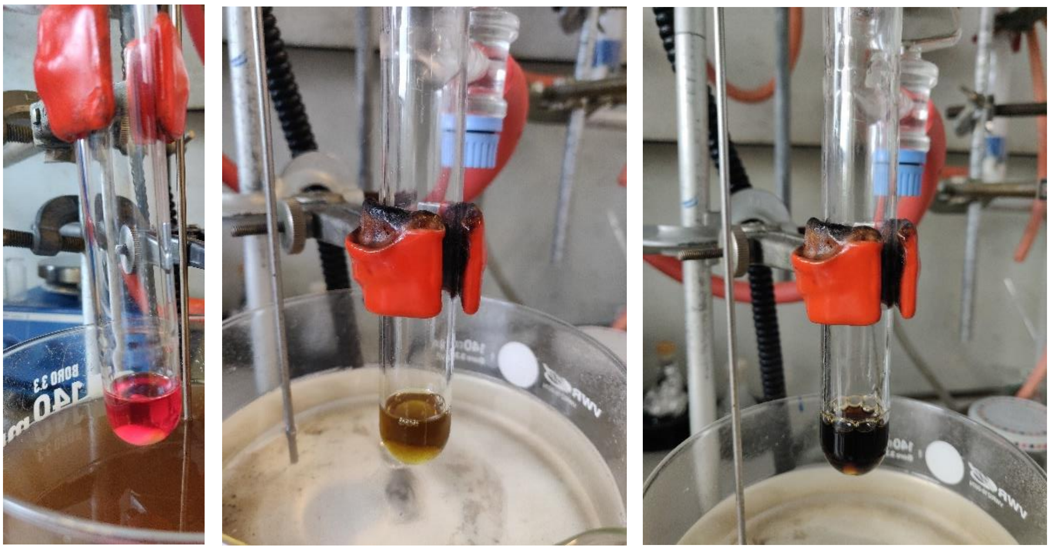
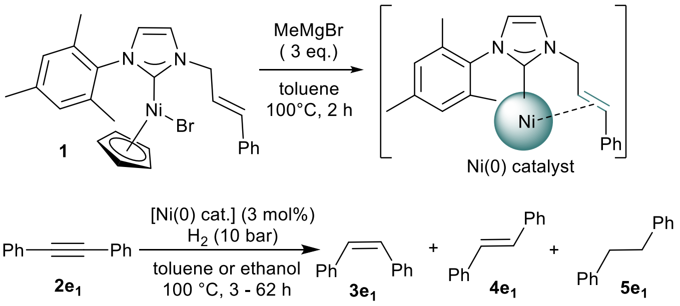


Figure S2. Reduction of complex **1** with MeMgBr: a) before adding the MeMgBr (pink solution); b) after adding it (yellow solution); c) after 2 hours of stirring at 100°C (brown solution).

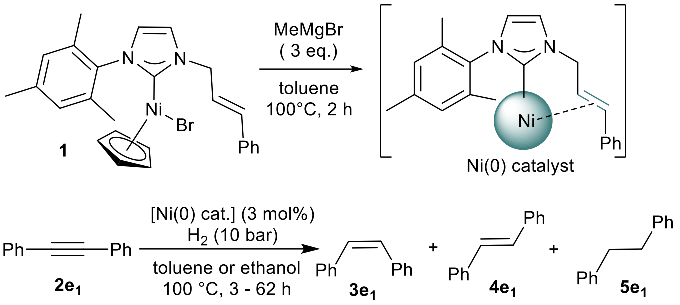
Table S2. Development of the semi-hydrogenation of diphenylacetylene using reduced complex **1**.



Entry	Reducing agent (eq.)	Solvent	T (°C)	t (h)	Yield (%)[a]	3d / 4d / 5d
1	none	toluene	60	13	0	-
2	MeMgBr (1.6)	toluene	60	13	8	67 / 0 / 33
3	MeMgBr (3)	toluene	60	13	98	96 / 0 / 4
4	MeMgBr (3)	toluene	40	13	100 (78)	91 / 0 / 9
5	MeMgBr (3)	toluene	25	62	85	82 / 6 /12
6	MeMgBr (3)	ethanol	25	3	86	85 / 0 / 15

a) GC yields. b) Ratio determined by GC and ^{1}H NMR.

Table S3. Screening of pressure, temperature, loading and solvent.

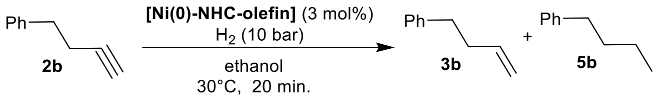


Entry	Solvent	Pressure (bar)	Catalyst loading	T (°C)	time (h)	Conversion (%)	alkane /alkene (%)
1	Toluene	10	3 mol%	40	13	Full	9/91
2	Toluene	10	2 mol%	40	48	96	10/87(*Z*)/3(*E*)
3	Toluene	10	2 mol%	40	13	24	6/90(*Z*)/4(*E*)
4	Toluene	4	3 mol%	40	13	37	3/93(*Z*)/4(*E*)
5	Toluene	4	3 mol%	40	36	Full	90/10
6	Toluene	4	3 mol%	60	13	85	2/98
7	EtOH	10	3 mol%	30	3	86	85/15
8	EtOH	10	1 mol%	40	13	Full	62/38
9[c]	EtOH	10	1 mol%	40	13	30	11/83(*Z*)/6(*E*)
10	EtOH	10	1 mol%	40	62	Full	100% Alkane
11	EtOH	10	1 mol%	40	5	77	5/93(*Z*)/2(*E*)
12	EtOH	10	1 mol%	40	7	81	9/89(*Z*)/2(*E*)
13	EtOH	10	1 mol%	60	3	Full	75/25
14	EtOH	4	1 mol%	40	13	98	90/10
15	EtOH	1	1 mol%	60	13	10	6/82(*Z*)/12(*E*)

a) GC yields. b) Ratio determined by GC and ^{1}H NMR. c) using an isolated catalyst stored and transferred in a glovebox.

II.4. Recycling of catalyst:

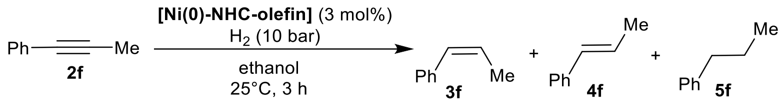
Table S4: recycling of catalyst during the hydrogenation of terminal alkyne 2b.



Run[a]	**Yield**[b]	**Selectivity (%)**[b]	
		3b /	**5b**
1	Quant.	76	24
2	90	80	20
3	89	79	21
4	84	80	20
5	81	84	16
6	68	85	15

a) After a cycle, hydrogen pressure was released and an aliquot was taken under an argon stream. Afterwards, solvent, reagents and products were evaporated under vacuum. The autoclave was then filled with solvent and reagent under an argon stream and a pressure of 10 bar H_2 was applied. The new reaction cycle was then started for 20 min. b) Determined by GC.

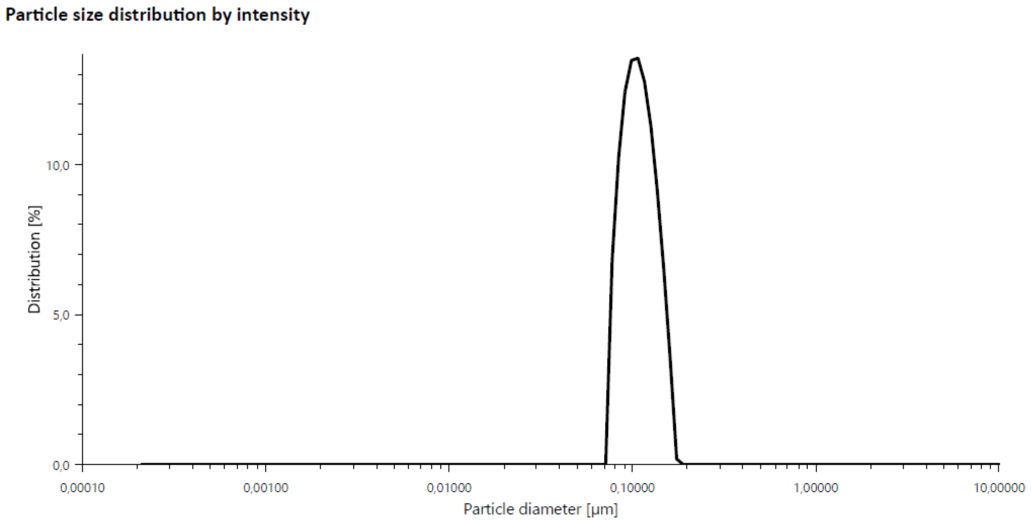
Table S5: recycling of catalyst during the hydrogenation of internal alkyne 2f.



Run[a]	**Yield**[b]	**Selectivity (%)**[b]		
		3f /	**4f** /	**5f**
1	100	86	3	11
2	48	92	2	6
3	41	91	3	6
4	29	92	3	5
5	29	92	2	6
6	20	92	3	5

a) After a cycle, hydrogen pressure was released and an aliquot was taken under an argon stream. Afterwards, solvent, reagents and products were evaporated under vacuum. The autoclave was then filled with solvent and reagent under an argon stream and a pressure of 10 bar H_2 was applied. The new reaction cycle was then started for 3 hours. b) Determined by GC.

II.5. Diffusion Light-Scattering (DLS) measurements


Particle size distribution by intensity

Particle size distribution peaks (intensity)

	Size [µm]	Area [%]	Standard deviation [µm]
Peak 1	0,11023	100,00	0,02144
Peak 2	-	-	-
Peak 3	-	-	-

Figure S3. DLS measurement on a sample of reduced complex **1** in toluene.

II.6. X-ray diffraction analysis by reflection on powder of reduced complex 1

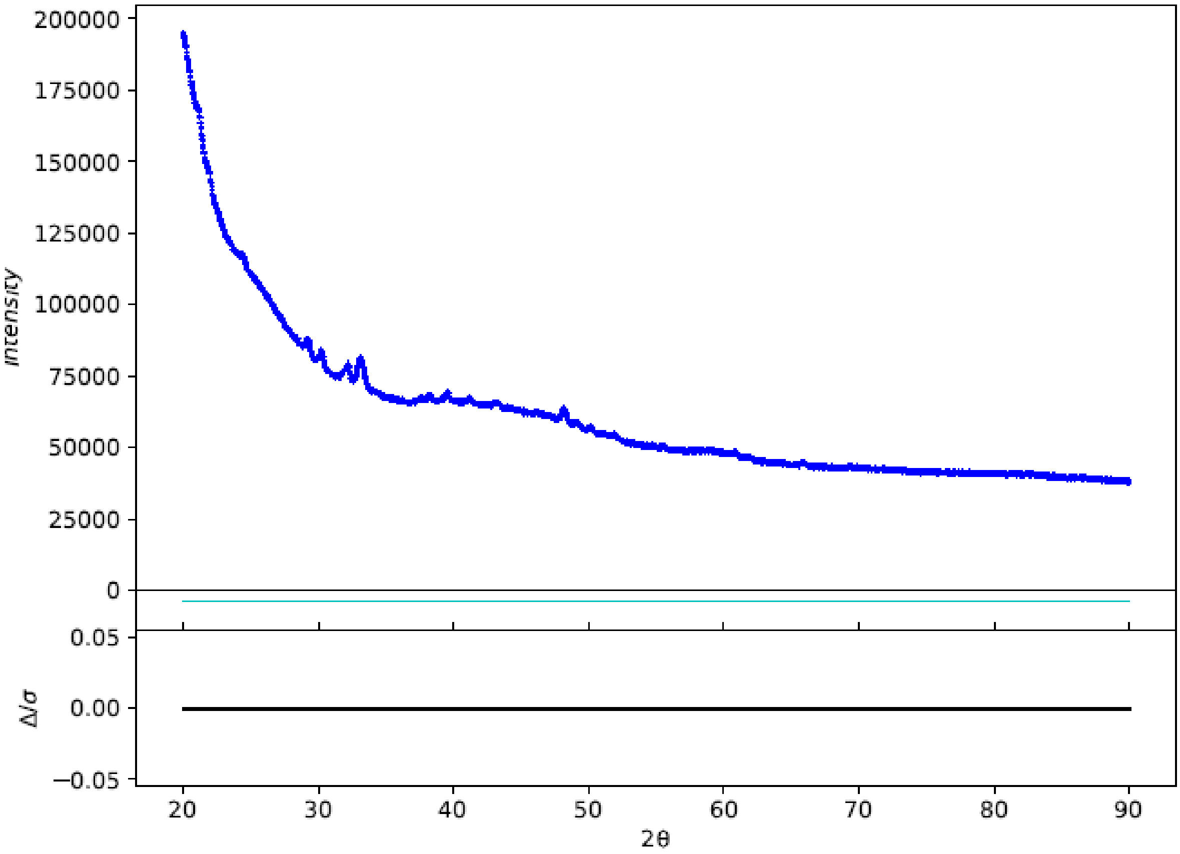


Figure S4. X-ray diffraction analysis by reflection on powder of reduced complex **1**

II.7. XPS results

The X-ray photoelectron spectroscopy (XPS) measurements were performed in an ultrahigh vacuum (UHV) spectrometer equipped with a RESOLVE 120 MCD5 hemispherical electron analyzer. The Al Kα hv=1486.6 eV dual anode X-ray source was used as incident radiation. The C 1s peak at 285 eV was used as peak reference. The constant pass energy mode was used to record both survey and high resolution spectra, with pass energies 100 and 20 eV respectively.

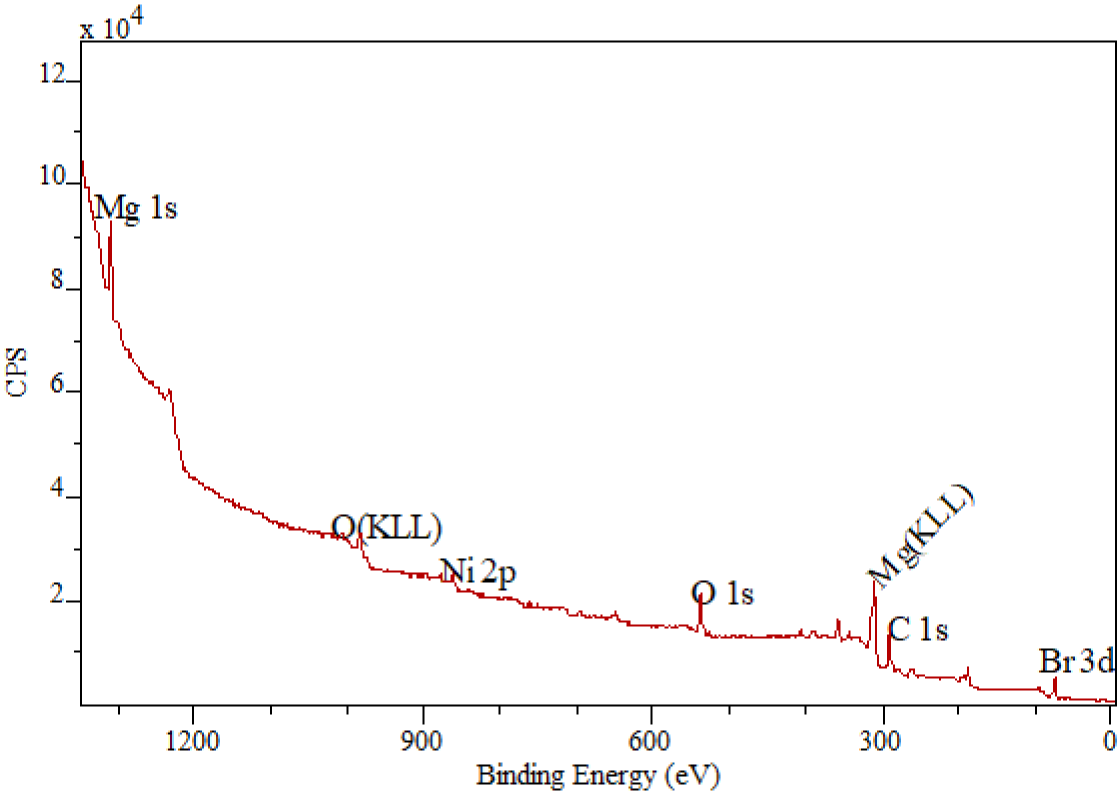


Figure S5: Survey scan spectra of reduced complex **1**.

The XPS peaks of all elements that exist in the samples surface are detected in the survey scans. In figure 1, the survey spectra of the two samples are shown (the main peaks are noted). High resolution spectra (C1s, Mg 1s, O 1s, Ni 2p and Br 3d) were also acquired.

- Ni 2p3/2 spectra:

  In both samples there is a peak at ca. 854.8 eV with a satellite at ca 861.9 eV. If we compare these spectra with reference spectra of metallic Ni and NiO powder (given below) we can deduce that they correspond to oxidised Ni species.[S5]

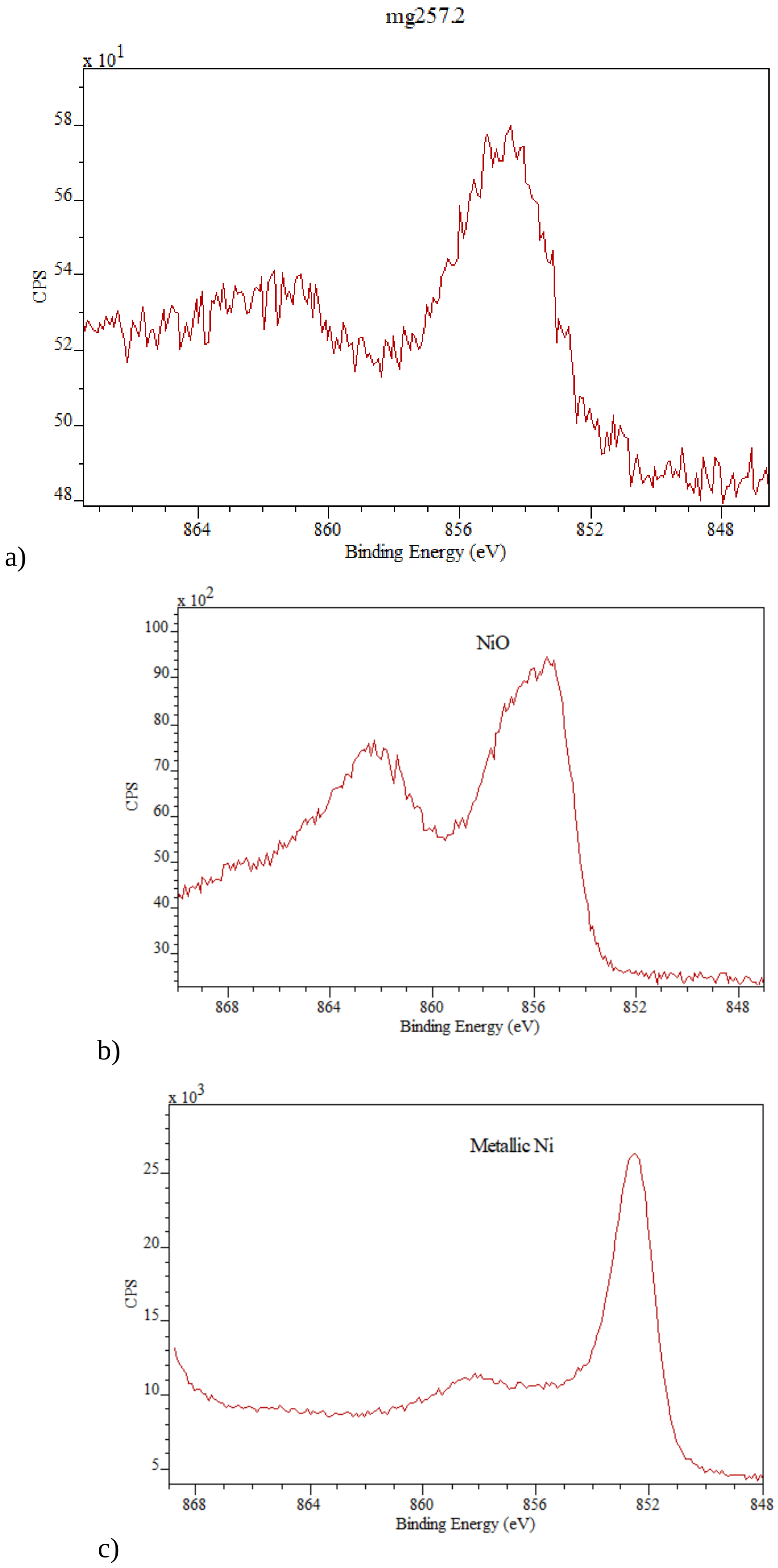


Figure S6: XPS spectrum of Ni 2p3/2 for reduced complex **1** (top, a) and reference spectra of NiO and metallic Ni (below, b and c).

Quantitative analysis:

The % surface ratio of all elements was calculated by using the area of the core level peaks, normalized to the photoemission cross section by assuming a homogeneous distribution arrangement model. The surface atomic ratios of all elements of the samples are summarized in Table 1.

SAMPLE	%O	%C	%Mg	%Br	%Ni	%N
MG257	17,9	55,1	10,1	8,3	2,2	6,4

Table S6: Surface atomic ratios of all elements measured by XPS.

II.8. Raman analysis

No evidence of Ni oxides (150-430 cm^{-1}) and Ni hydroxides (3100-3650 cm^{-1}) was observed. However, significant bands were observed at 1367 cm^{-1} (weak, C-CH$_3$ vibrations), 1600 cm^{-1} (weak, vibrations of aromatic and heterocyclic rings) and 2919 cm^{-1} (strong, aliphatic CH and aromatic CH vibrations).

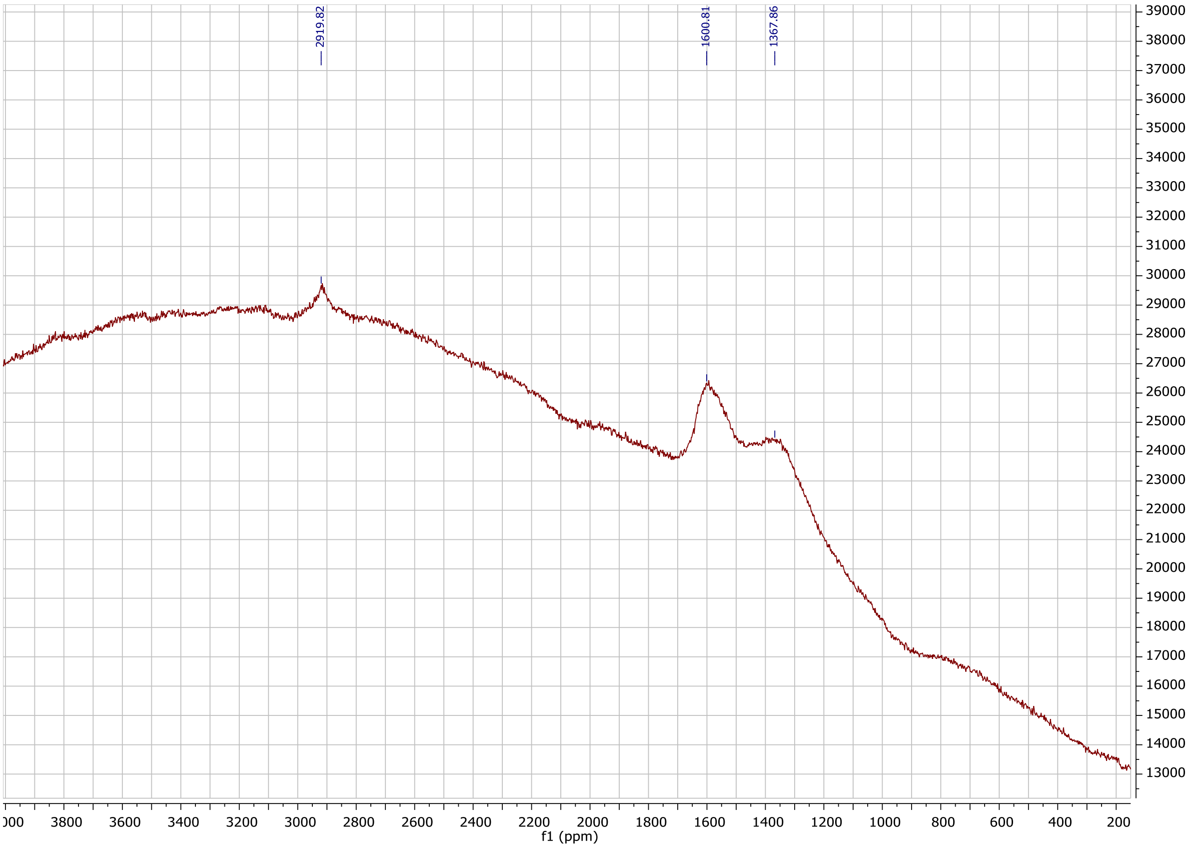
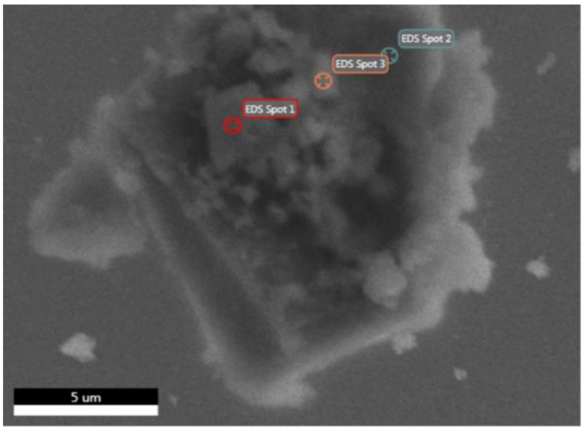
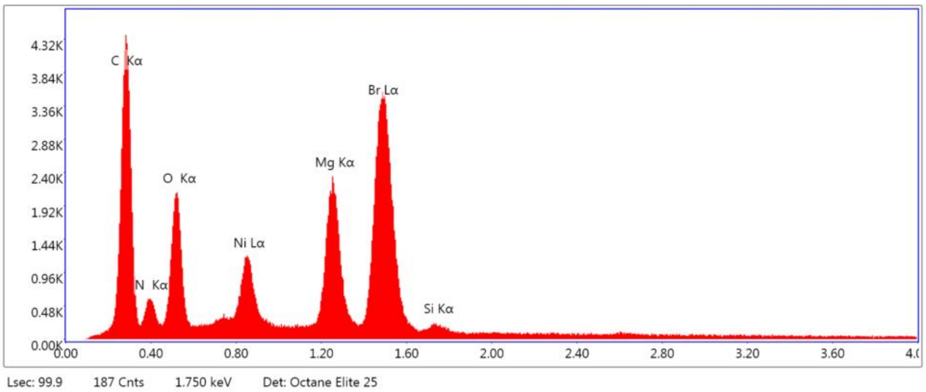


Figure S7: Raman spectrum of fresh reduced complex **1**

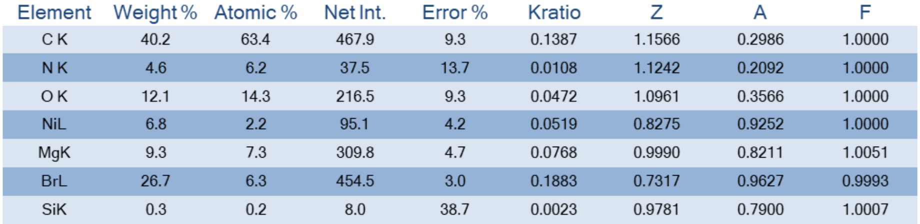
II.9. MEB and SEM-EDS analyses of catalyst.



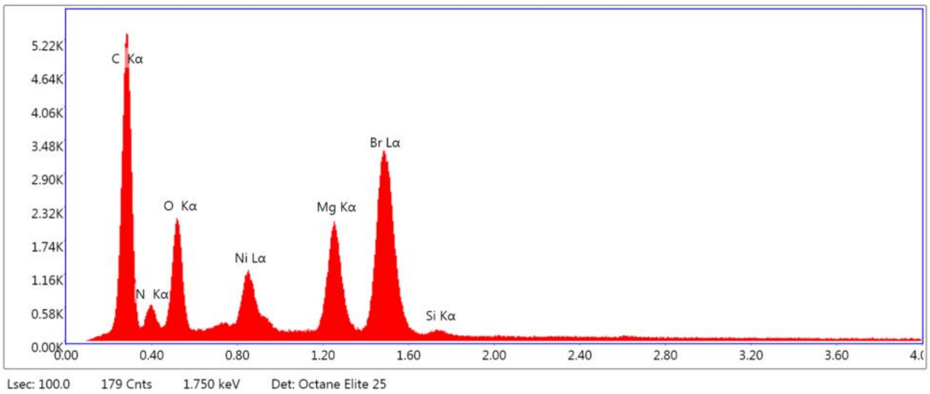


EDS-Spot1

Lsec: 99.9 187 Cnts 1.750 keV Det: Octane Elite 25

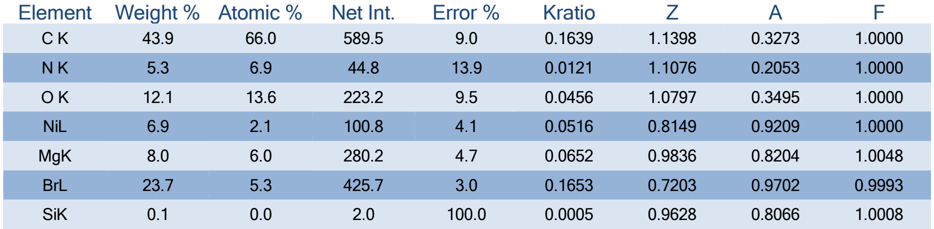


Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	40.2	63.4	467.9	9.3	0.1387	1.1566	0.2986	1.0000
N K	4.6	6.2	37.5	13.7	0.0108	1.1242	0.2092	1.0000
O K	12.1	14.3	216.5	9.3	0.0472	1.0961	0.3566	1.0000
NiL	6.8	2.2	95.1	4.2	0.0519	0.8275	0.9252	1.0000
MgK	9.3	7.3	309.8	4.7	0.0768	0.9990	0.8211	1.0051
BrL	26.7	6.3	454.5	3.0	0.1883	0.7317	0.9627	0.9993
SiK	0.3	0.2	8.0	38.7	0.0023	0.9781	0.7900	1.0007



EDS-Spot 3

Lsec: 100.0 179 Cnts 1.750 keV Det: Octane Elite 25



Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
C K	43.9	66.0	589.5	9.0	0.1639	1.1398	0.3273	1.0000
N K	5.3	6.9	44.8	13.9	0.0121	1.1076	0.2053	1.0000
O K	12.1	13.6	223.2	9.5	0.0456	1.0797	0.3495	1.0000
NiL	6.9	2.1	100.8	4.1	0.0516	0.8149	0.9209	1.0000
MgK	8.0	6.0	280.2	4.7	0.0652	0.9836	0.8204	1.0048
BrL	23.7	5.3	425.7	3.0	0.1653	0.7203	0.9702	0.9993
SiK	0.1	0.0	2.0	100.0	0.0005	0.9628	0.8066	1.0008

Figure S8. SEM-EDX spectrum of reduced complex **1**. Cu and Si elements were also present respectively due to the sample holder and the synthetic process.

II.10. TEM and STEM EDS analyses of catalyst.

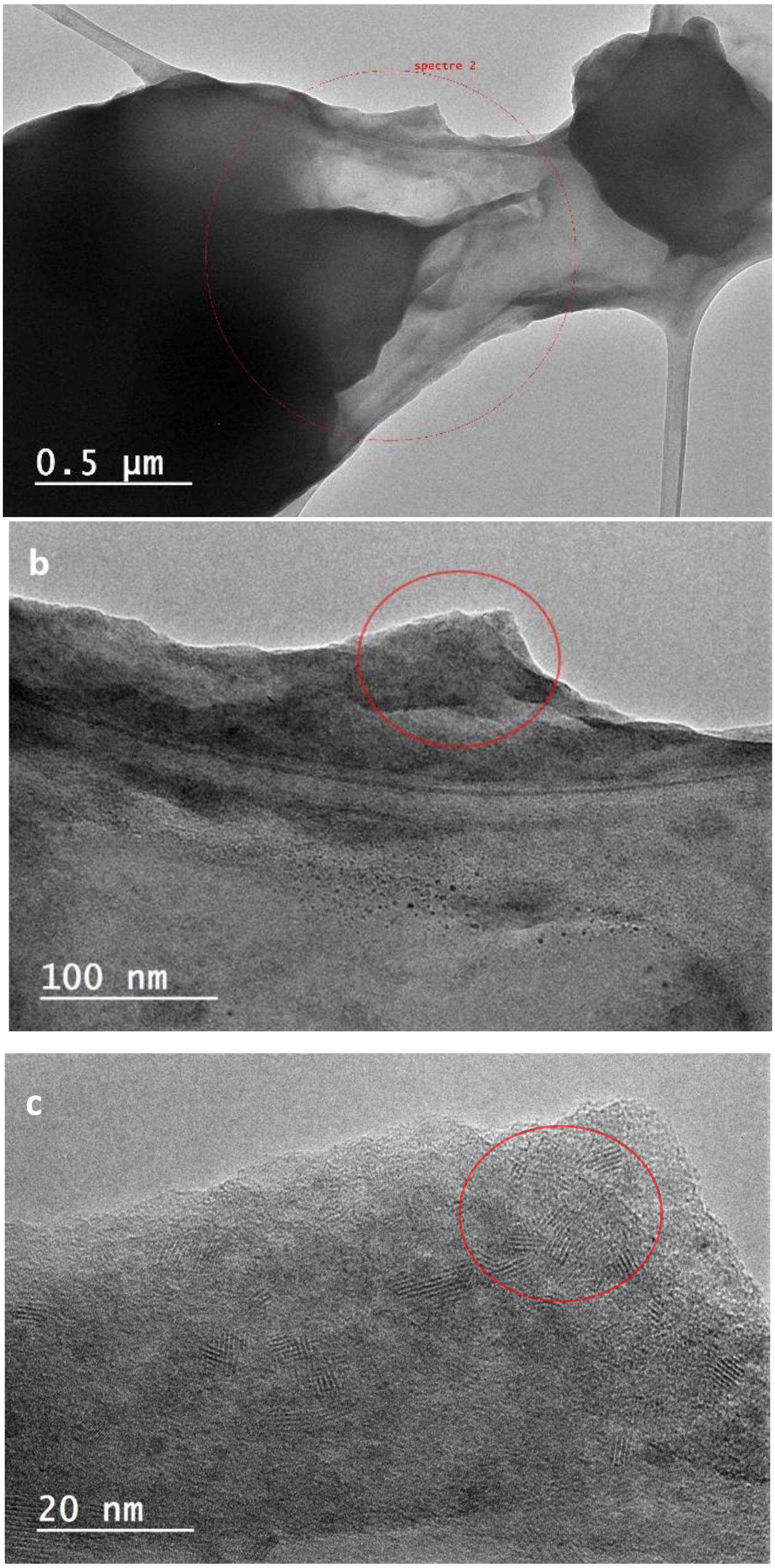


Figure S9. TEM of reduced complex **1**..

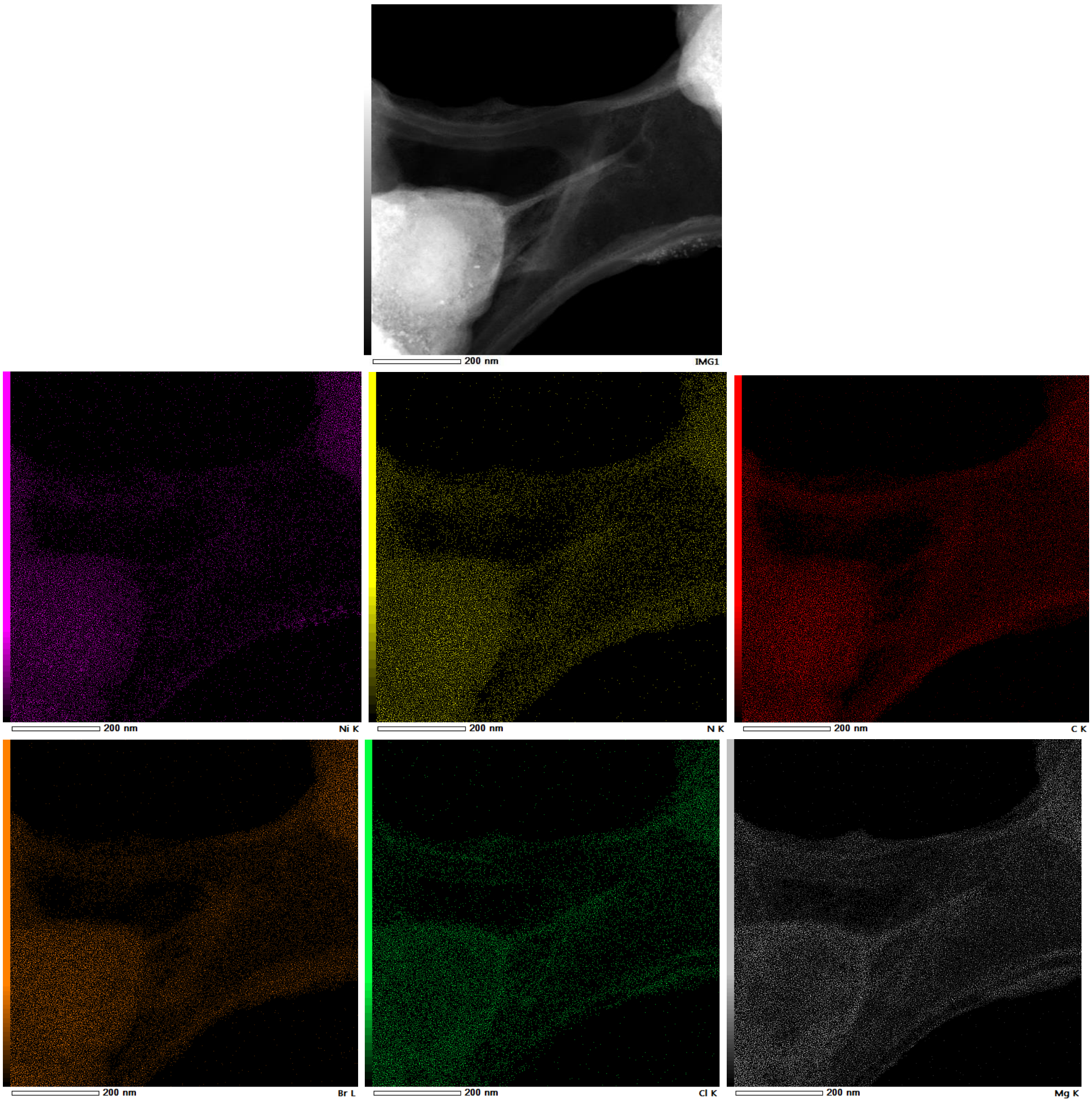
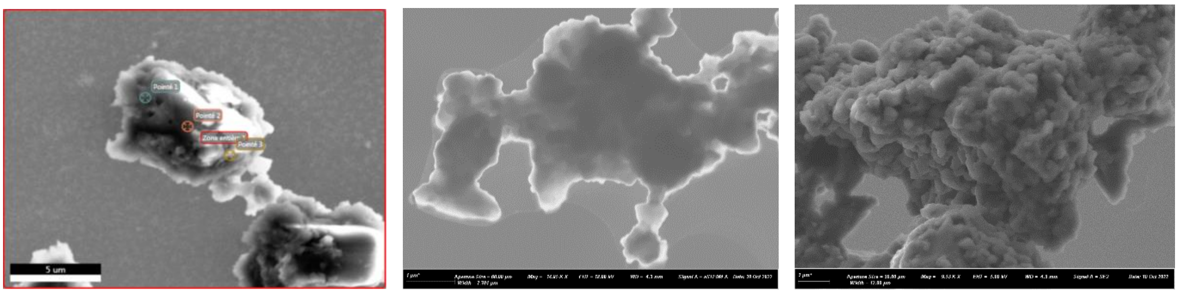
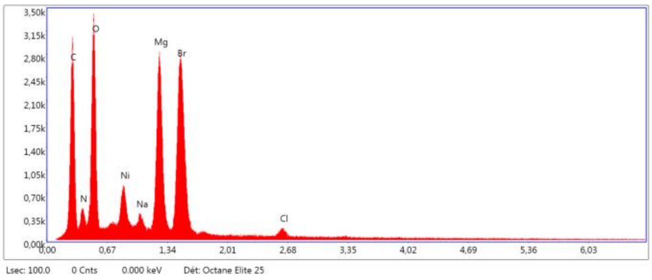


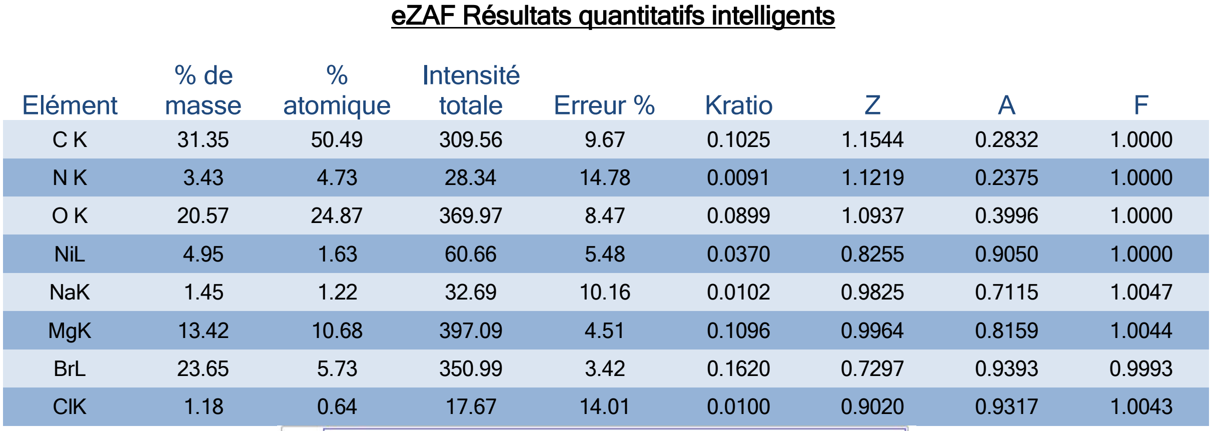
Figure S10. Elemental mapping area for Ni, N, C, Br, Cl, Mg by STEM-EDS of reduced complex **1**.

II.11. MEB and SEM-EDX analyses of spent catalyst.



EDS spot1

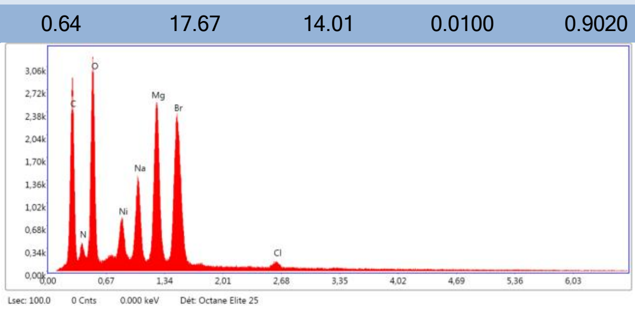


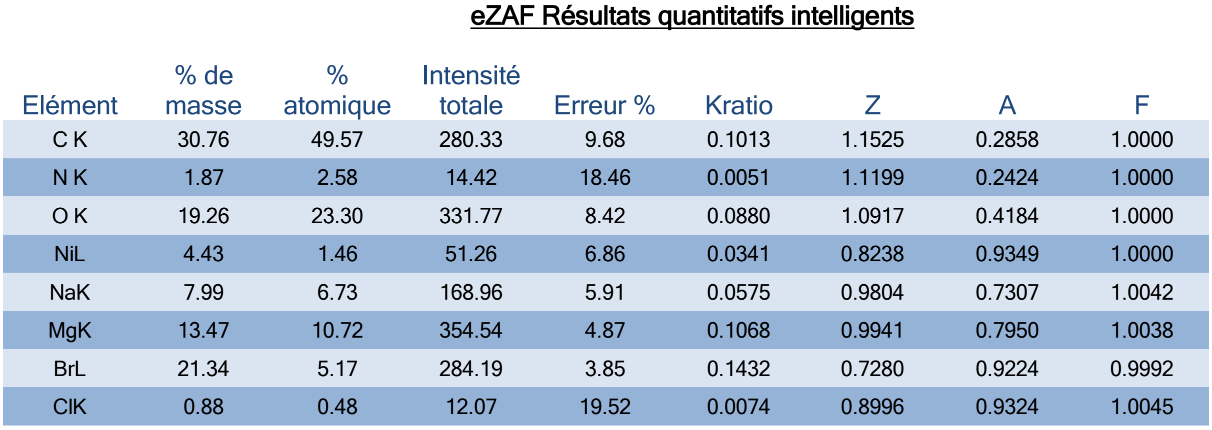


eZAF Résultats quantitatifs intelligents

Elément	% de masse	% atomique	Intensité totale	Erreur %	Kratio	Z	A	F
C K	31.35	50.49	309.56	9.67	0.1025	1.1544	0.2832	1.0000
N K	3.43	4.73	28.34	14.78	0.0091	1.1219	0.2375	1.0000
O K	20.57	24.87	369.97	8.47	0.0899	1.0937	0.3996	1.0000
NiL	4.95	1.63	60.66	5.48	0.0370	0.8255	0.9050	1.0000
NaK	1.45	1.22	32.69	10.16	0.0102	0.9825	0.7115	1.0047
MgK	13.42	10.68	397.09	4.51	0.1096	0.9964	0.8159	1.0044
BrL	23.65	5.73	350.99	3.42	0.1620	0.7297	0.9393	0.9993
ClK	1.18	0.64	17.67	14.01	0.0100	0.9020	0.9317	1.0043

EDS spot2





eZAF Résultats quantitatifs intelligents

Elément	% de masse	% atomique	Intensité totale	Erreur %	Kratio	Z	A	F
C K	30.76	49.57	280.33	9.68	0.1013	1.1525	0.2858	1.0000
N K	1.87	2.58	14.42	18.46	0.0051	1.1199	0.2424	1.0000
O K	19.26	23.30	331.77	8.42	0.0880	1.0917	0.4184	1.0000
NiL	4.43	1.46	51.26	6.86	0.0341	0.8238	0.9349	1.0000
NaK	7.99	6.73	168.96	5.91	0.0575	0.9804	0.7307	1.0042
MgK	13.47	10.72	354.54	4.87	0.1068	0.9941	0.7950	1.0038
BrL	21.34	5.17	284.19	3.85	0.1432	0.7280	0.9224	0.9992
ClK	0.88	0.48	12.07	19.52	0.0074	0.8996	0.9324	1.0045

Figure S11. SEM-EDX spectrum of reduced complex **1** after 6 catalytic runs – see part II.3 and table S5.

II.12. TEM and STEM-EDS analyses of spent catalyst.

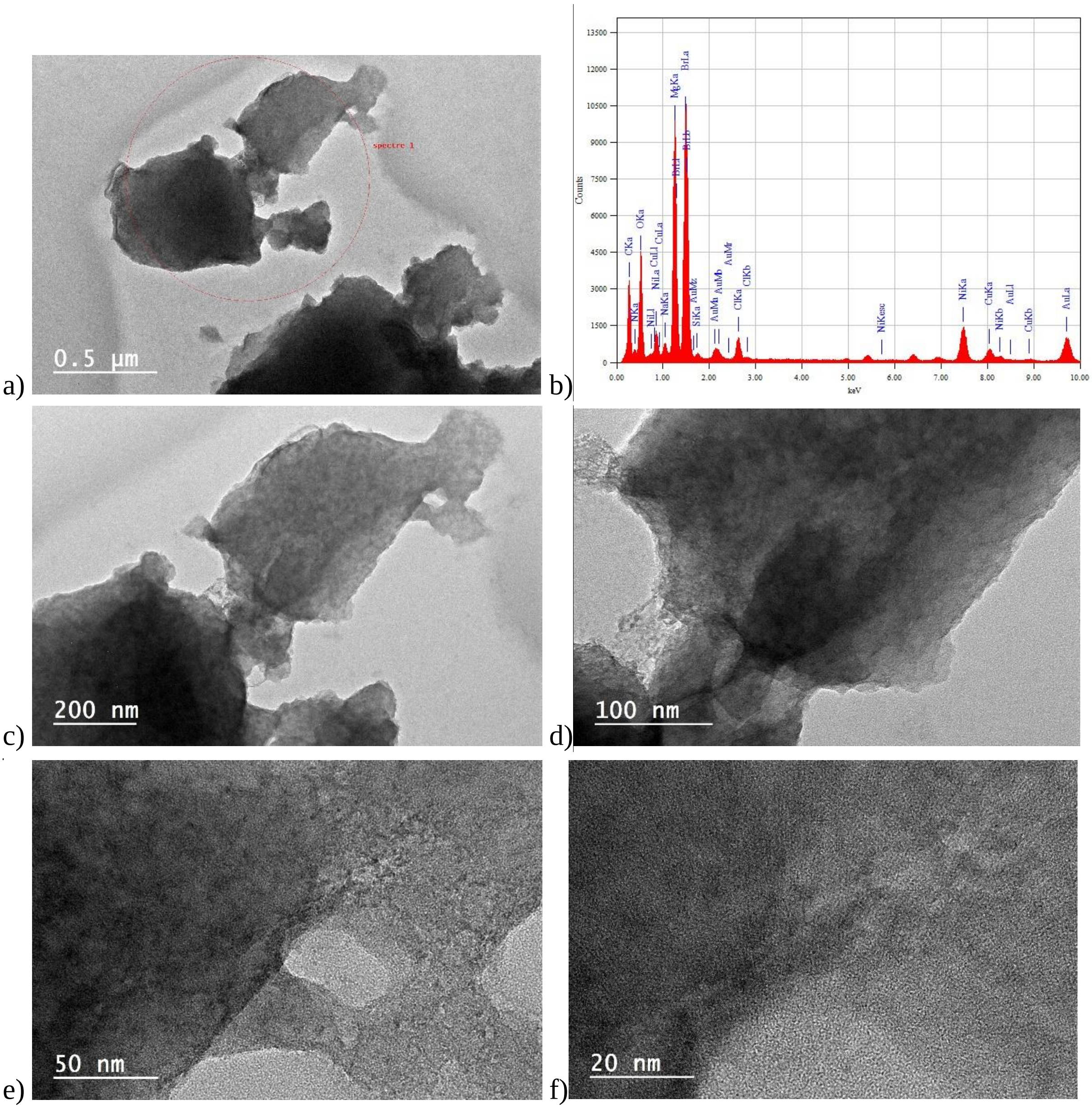
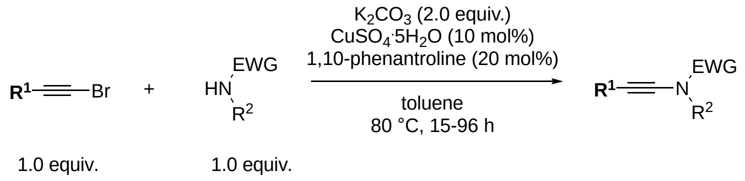


Figure S12. TEM of reduced complex **1** after 6 catalytic runs – see part II.3 and table S5. Cu, Au and Si elements were also present respectively due to the sample holder and the synthetic process.

III. Synthesis and characterization of compounds

III.1. Synthesis of ynamides

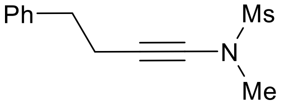
General procedure (GP): copper-catalysed alkynylation of nitrogen nucleophiles with bromoalkynes



Following Hsung's procedure,[S6] a 30-mL sealed tube was charged with the nitrogen nucleophile (1.0 eq.), potassium carbonate (2.0 eq.), $CuSO_4\cdot5H_2O$ (10 mol%), 1,10-phenanthroline (20 mol%) under Ar. The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon three times. Dry and degassed toluene (1 M) and alkynyl bromide (1.0 eq.) were added, the rubber septum was replaced by a Teflon-coated screw cap and the mixture was stirred at 80 °C for 15 - 96 hours. The reaction mixture was then cooled to room temperature, filtered over a plug of Celite (washed with EtOAc) and concentrated under reduced pressure. The crude residue was purified by flash column chromatography over silica gel.

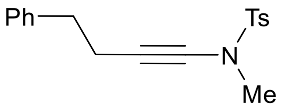
Modified general procedure (Modified GP): for the coupling of bromoalkynes and *N*-Moc-protected amines, K_3PO_4 (2.0 eq.) was the base of choice.

***N*-methyl-*N*-(4-phenylbut-1-yn-1-yl)methanesulfonamide, CAS [1821320-90-4] (2j):**



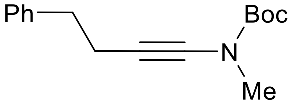
Prepared following the GP from (4-bromobut-3-yn-1-yl)benzene (11.48 mmol, 2.40 g, 1.2 eq). Reaction time: 66 h. TLC: R*f*: 0.35 (pentane/EtOAc 7:1). Purification by flash column chromatography over silica gel (pentane/ EtOAc 7:1) afforded the title compound (2.29 g, 9.65 mmol) as a pale yellow oil. 84 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.32 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 3.11 (s, 3H), 2.91 (s, 3H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.59 (t, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ (ppm) 140.6, 128.7, 128.5, 126.5, 75.2, 68.6, 39.2, 36.0, 35.3, 20.7.

***N*,4-dimethyl-*N*-(4-phenylbut-1-yn-1-yl)benzenesulfonamide, CAS [1966112-17-3] (2k)**

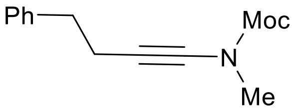


Prepared following the GP in 31% yield (5.40 mmol ; 1.40 g) from (4-bromobut-3- yn-1-yl)benzene (17.15 mmol ; 3.59 g). Yellow oil. TLC R*f*: 0.25 (pentane/EtOAc 80:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.37 – 7.19 (m, 7H), 3.01 (s, 3H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.5, 140.6, 133.2, 129.7 (x2), 128.5 (x2), 128.4 (x2), 127.8 (x2), 126.3, 75.7, 67.9, 39.3, 35.2, 21.7, 20.5.

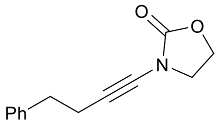
Tert-butyl methyl(4-phenylbut-1-yn-1-yl)carbamate, CAS [2727894-28-0] (2l): Prepared following the GP in 31% yield (5.32 mmol ; 1.37 g) from (4-bromobut-3-yn-1-yl)benzene (17.15 mmol ; 3.59 g). Yellow oil. TLC R*f* : 0.30 (pentane/EtOAc 90:10). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.16 (m, 3H), 3.01 (s, 3H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 1.46 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.9, 154.9, 153.4, 142.0, 128.5 (x2), 128.3 (x2), 126.2, 81.9, 67.6, 35.6, 28.1 (x3), 20.8.



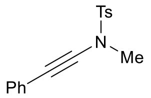
Methyl methyl(4-phenylbut-1-yn-1-yl)carbamate, CAS [2763576-63-0] (2m): Prepared following the modified GP from (4-bromobut-3-yn-1-yl)benzene (7.32 mmol, 6.0 g, 1.3 eq). Reaction time: 72 h. TLC: R*f*: 0.35 (pentane/EtOAc 95:5). Purification by flash column chromatography over silica gel (pentane/ EtOAc = 95:5) afforded the title compound (1.03 g, 4.74 mmol) as a colorless oil. 65 % yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 3.79 (s, 3H), 3.10 (s, 3H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.59 (t, *J* = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 156.5, 140.9, 128.7, 128.4, 126.4, 75.8, 68.3, 54.0, 38.0, 35.6, 20.8.



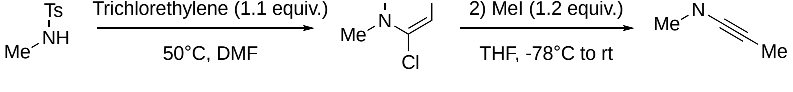
3-(4-phenylbut-1-yn-1-yl)oxazolidin-2-one, CAS [849093-07-8] (2n): Prepared following the GP from (4-bromobut-3-yn-1-yl)benzene (28.70 mmol, 6.0 g, 1.2 eq). Reaction time: 66 h. TLC: R*f*: 0.35 (pentane/EtOAc 7:3). Purification by flash column chromatography over silica gel (pentane/ EtOAc = 7:3) afforded a yellow solid. The resulting solid was washed with pentane over a frit to give the title compound (4.0 g, 21.65 mmol) as a colorless solid. 78 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 4.43 – 4.38 (m, 2H), 3.86 – 3.80 (m, 2H), 2.85 (t, *J* = 7.6, 2H), 2.63 – 2.58 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 156.7, 140.7, 128.6, 128.5, 126.5, 70.9, 70.7, 62.9, 47.1, 35.3, 20.8.

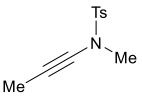


***N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide, CAS [1005500-77-5] (2o):** Prepared following the GP from 1-(bromoethynyl)benzene (8.42 mmol, 1.52 g, 1.2 eq). Reaction time: 86 h. TLC: R*f*: 0.30 (pentane/EtOAc 20:1). Purification by flash column chromatography over silica gel (gradient from pentane to pentane/EtOAc = 10:1) afforded the title compound (1.46 g, 5.12 mmol) as a colorless solid. 73 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.31 – 7.27 (m, 4H), 3.16 (s, 3H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.9, 133.4, 131.5, 129.9, 128.4, 128.0, 128.0, 122.8, 84.1, 69.2, 39.5, 21.8.



***N*,4-dimethyl-*N*-(prop-1-yn-1-yl)benzenesulfonamide, CAS [1005500-76-4] (2p)**: Synthesized following Anderson's procedure[S7]

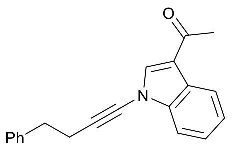


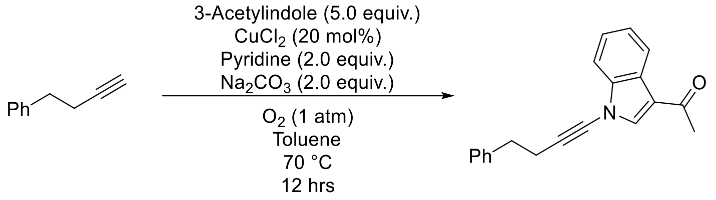


Step 1 : To a stirring suspension of *N*-tosyl-*N*-methylamine (3.91 g ; 21.108 mmol ; 1 equiv.), Cs_2CO_3 (10.32 g ; 31.66 mmol ; 1.5 equiv.) and DMF (20 mL) at 50 °C was added trichloroethylene (2.089 mL, 23.22 mmol, 1.1 equiv.) dropwise over 10 minutes. The resulting mixture was stirred at 50 °C until reaction completion, as monitored by TLC. The organic layer was separated and further washed three times with water. The organic layer was then dried (Na_2SO_4), filtered and concentrated *in vacuo.*

Step 2 : To an oven dried, argon flushed flask was added *N*-[(*E*)-1,2-dichloroethenyl]-*N*,4-dimethylbenzene-1- sulfonamide (500 mg ; 1.78 mmol ; 1.0 equiv.) and THF (18.75 mL) , and cooled to -78 °C whilst stirring. A solution of PhLi (2.708 mL, 3.93 mmol, 2.2 equiv.) was then added dropwise over 10 minutes, and left to stir at- 78 °C. After completion of the starting material (followed by TLC), MeI (0.13 mL ; 2.14 mmol ; 1.2 equiv.) was added to the solution and the mixture was allowed to warm at 25 °C and stirred for 1 hour. Upon reaction completion, as monitored by TLC, the reaction mixture was quenched with water, followed by extraction with Et_2O (×2). The organic extracts were combined and dried (Na_2SO_4), filtered and concentrated *in vacuo* to obtain the crude product which was purified by column chromatography on silica gel. The title compound was obtained in 45% yield (0.80 mmol ; 179 mg) from *N*-[(*E*)-1,2-dichloroethenyl]- *N*,4-dimethylbenzene-1-sulfonamide (1.78 mmol ; 500 mg). White solid. TLC R*f* : 0.35 (pentane/EtOAc 70:30). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 – 7.76 (m, 2H), 7.41 – 7.34 (m, 2H), 3.03 (s, 3H), 2.47 (s, 3H), 1.89 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.5, 133.3, 129.7 (x2), 127.8 (x2), 73.7, 64.1, 39.3, 21.6, 3.2.

1-(1-(4-phenylbut-1-yn-1-yl)-1*H*-indol-3-yl)ethan-1-one, CAS [1677697-97-0] (2q): Synthesized following Stahl's procedure.[S8,S9]





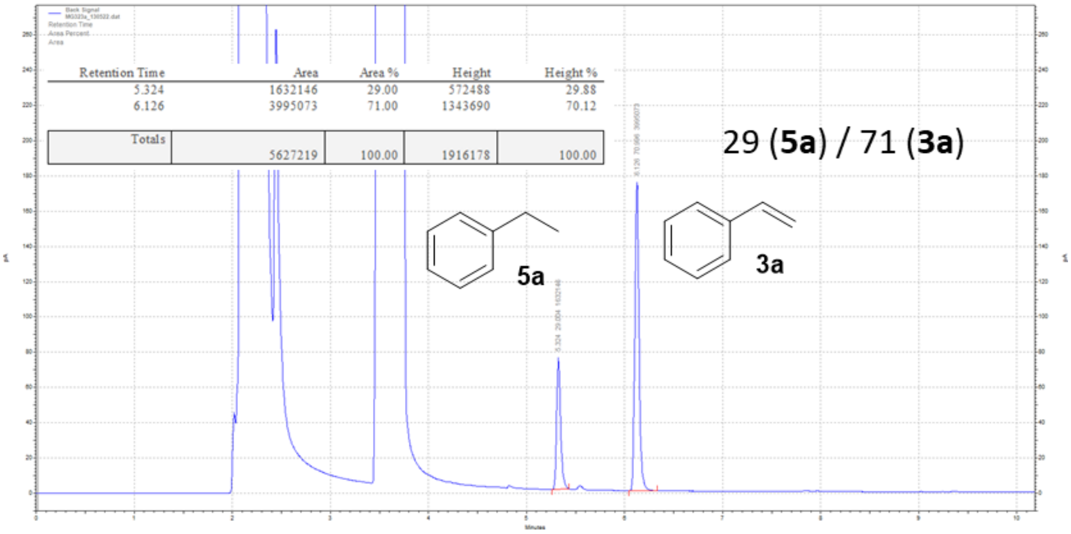
In a 250 ml three-neck round-bottom flask equipped with a stir-bar, $CuCl_2$ (20 mol%), 3-acetylindole (5.0 equiv.) and Na_2CO_3 (2.0 equiv.) were combined. The reaction flask was purged with oxygen gas for 15 minutes. A solution of pyridine (2.0 equiv.) in dry toluene (0.4 M) was added to the reaction flask *via* a syringe. A balloon filled with oxygen gas was connected to the reaction flask *via* a needle. The flask was placed in an oil-bath and heated to 70 °C. A solution of 4-phenyl-1-butyne in dry toluene (0.3 M) was added to the flask over 4 hours by using a syringe pump. After the addition of alkyne/toluene solution, the reaction mixture was allowed to stir at 70 °C for another 8 hours and then cooled to room temperature. After completion of the starting material, the solution was concentrated under reduced pressure and purified by column chromatography on silica gel (pentane/EtOAc) to afford the corresponding ynamide. TLC R*f* : 0.40 (pentane/EtOAc 80:20). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (m, 1H), 6.91 – 6.73 (m, 9H), 2.48 (t, *J* = 7.3 Hz, 2H), 2.30 (t, *J* = 7.3 Hz, 2H), 2.02 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 193.3, 140.6, 139.1, 135.8, 129.0 (x2), 127.0, 125.3, 125.06, 124.3, 123.1, 119.5, 111.6, 71.8, 71.6, 35.4, 28.0, 20.9.

Methyl N-(methylsulfonyl)-N-(4-phenylbut-1-yn-1-yl)glycinate (2r):

Prepared following the GP in 15% yield (1.79 mmol; 0.529 g) from (4-bromobut-3-yn-1-yl)benzene (12.2 mmol; 2.57 g). Brown solid. TLC Rf: 0.25 (Pentane/EtOAc 70:30). IR (neat) νmax 3026, 2953, 2257, 1752, 1352, 1160, 1217, 1160, 1097 cm-1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.23 – 7.20 (m, 3H), 4.22 (s, 2H), 3.78 (s, 3H), 3.16 (s, 3H), 2.82 (t, J = 7.3 Hz, 2H), 2.59 (t, J = 7.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.6, 140.5, 128.6 (x2), 128.4 (x2), 126.3, 73.3, 70.0, 52.6, 52.4, 39.0, 35.1, 20.6. HRMS (ESI+) m/z: calcd for ($C_{14}H_{17}O_4NLiS$) [M + Li] 302.10328; found 302.10330.

III.2. Characterisations of hydrogenated products.

styrene (3a)^{S10} CAS [100-42-5]



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6.126	3995073	71.00	1343690	70.12
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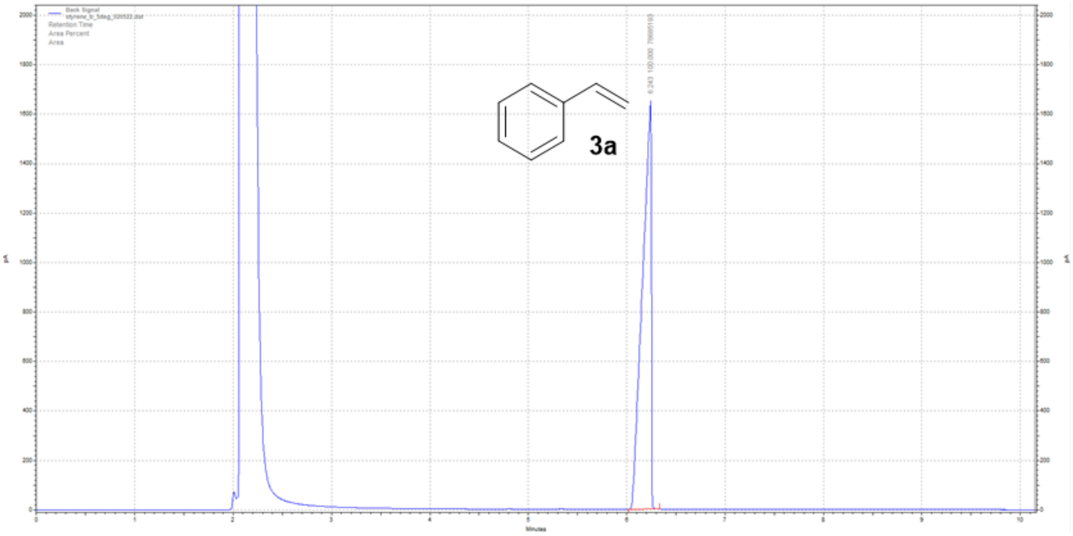

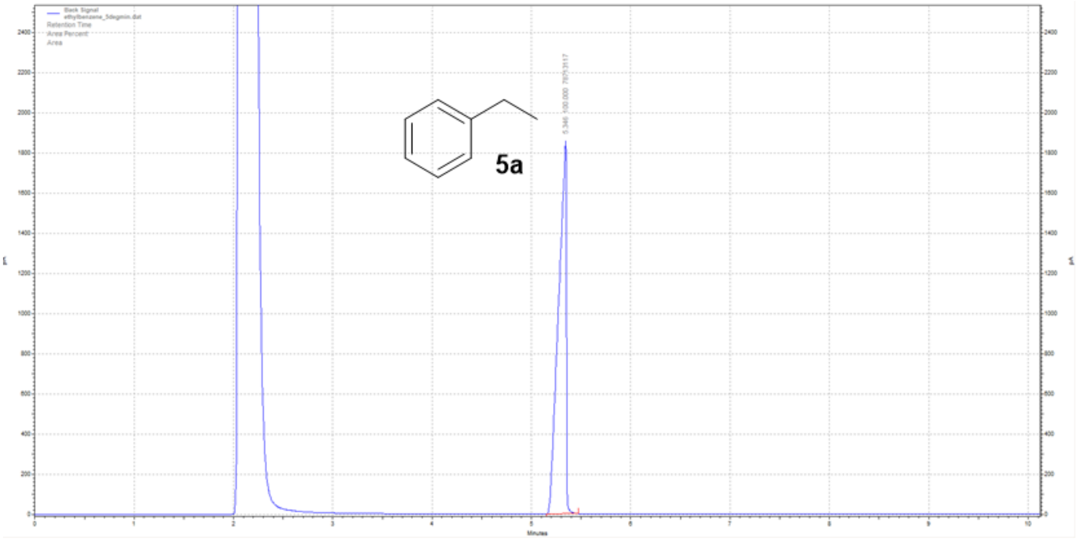
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Area Percent
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pA
Minutes
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2
3
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7
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9
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400
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800
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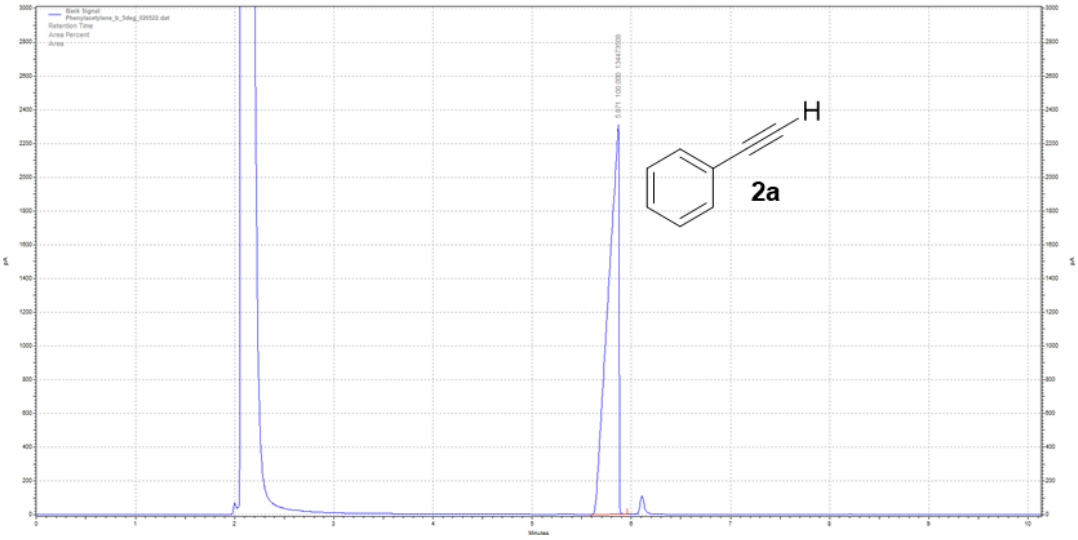
1200
1400
1600
1800
2000
2200
2400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3
4
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7
8
9
10
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400
600
800
1000
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1400
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2000
2200
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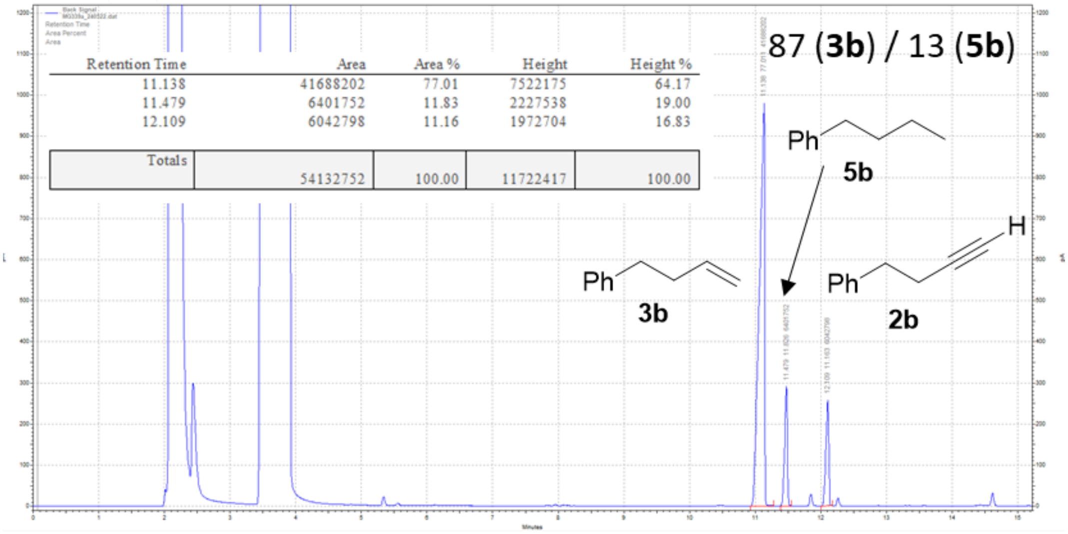
2600
2800
3000

but-3-en-1-ylbenzene (3b)^{S11} CAS [768-56-9]



Retention Time	Area	Area %	Height	Height %
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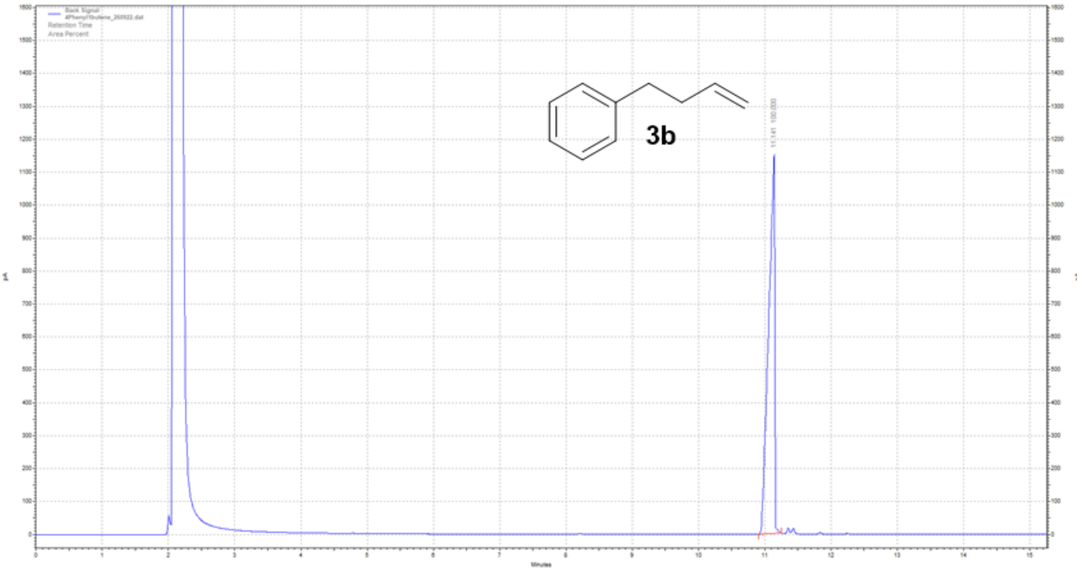
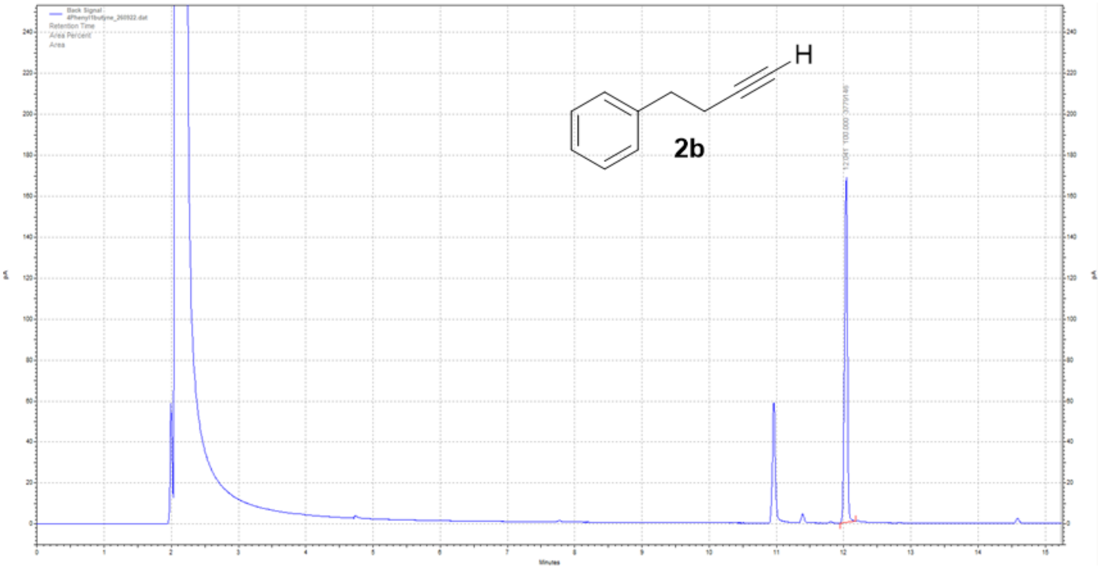
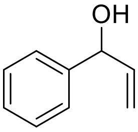
11.479	6401752	11.83	2227538	19.00
12.109	6042798	11.16	1972704	16.83
Totals	54132752	100.00	11722417	100.00





1-phenylprop-2-en-1-ol (3c)[S12]

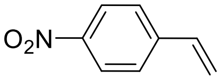


Method B. R.T. 13h in toluene. 75% yield (by NMR). The compound was purified by prep TLC (Petroleum ether: AcOEt 95:5) to give **3c** in 18% yield (12 mg, 0.09 mmol) (volatile) as a transparent oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 6.10 – 6.01 (m, 1H), 5.35 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.22 – 5.18 (m, 2H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 142.8 (C), 140.4 (CH), 128.7 (2CH), 127.9 (CH), 126.5 (2CH), 115.3 (CH$_2$), 75.5 (CH).

1-nitro-4-vinylbenzene (3d)[S13]

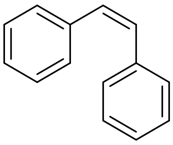


Method B. 40ºC, 62h in toluene. 90% conversion, 81% alkene *Z* , 14% alkane (by GC). The compound was purified by prep. TLC (P.E: AcOEt 97:3) to give **3d** in 63 % yield (47 mg, 0.32 mmol) as a transparent oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (t, *J* = 2.0 Hz, 1H), 8.10 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.70 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H, C*H*=CH$_2$), 5.90 (d, *J* = 17.6 Hz, 1H, CH=C*H*$_2$), 5.44 (d, *J* = 10.9 Hz, 1H, CH=C*H*$_2$).

^{13}C NMR (101 MHz, CDCl$_3$) δ 148.8 (C), 139.4 (C), 134.9 (CH), 132.2 (CH), 129.6 (CH), 122.6 (CH), 121.0 (CH), 117.2 (CH$_2$).

(*Z*)-1,2-diphenylethene (3e$_1$)[S14]

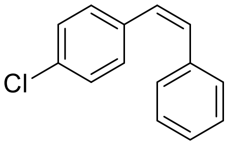


Method A. 40ºC, 13h in toluene, 91% yield (by GC). The compound was purified by prep. TLC (Hexane) to give **3d** in 78 % yield (70 mg, 0.39 mmol) as a transparent oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 – 7.17 (m, 5H), 6.61 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 137.4 (C), 130.4 (CH), 129.0 (2CH), 128.3 (2CH), 127.2 (CH).

(*Z*)-1-chloro-4-styrylbenzene (3e$_2$)^{S15}

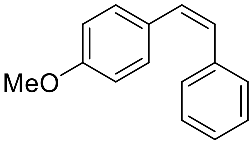


Method A. 80ºC, 13h in toluene. Full conversion, 90% alkene *Z*, 10% alkane (by GC). The compound was purified by prep. TLC (Petroleum ether) to give **3e$_2$** in 75 % yield (81 mg, 0.38 mmol) as a transparent oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.03 (m, 9H), 6.54 (d, *J* = 12.2 Hz, 1H, CH=CH), 6.44 (d, *J* = 12.2 Hz, 1H, CH=CH).

^{13}C NMR (101 MHz, CDCl$_3$) δ 137.0 (C), 135.8 (C), 132.9 (C), 131.1 (CH), 130.4 (2CH), 129.1 (CH), 128.9 (2CH), 128.6 (2CH), 128.5 (2CH), 127.5 (CH).

(*Z*)-1-methoxy-4-styrylbenzene (3e$_3$)^{S15}

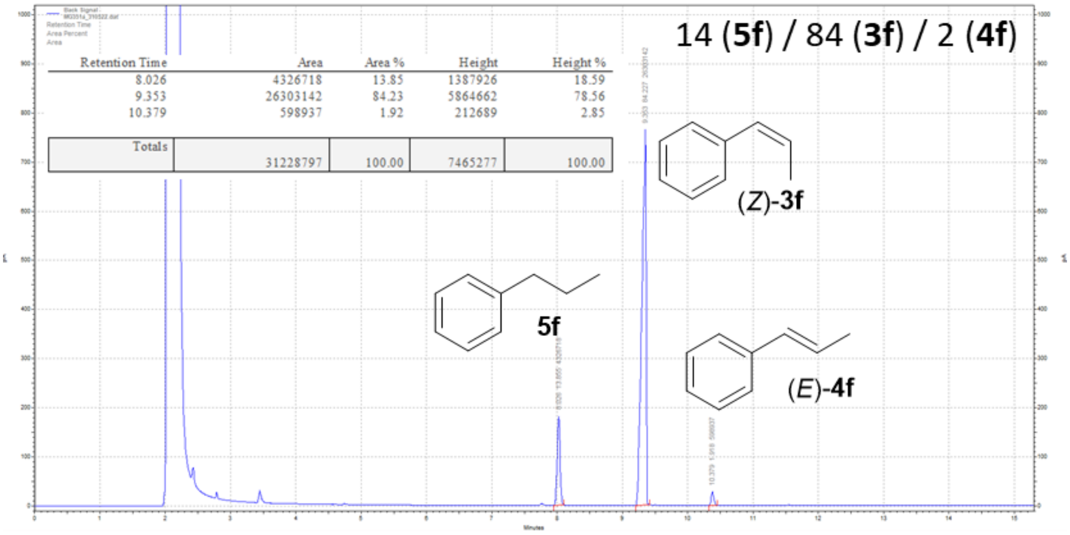


Method A. 80ºC, 48h in toluene. 87% alkene *Z* (by GC). The compound was purified by prep. TLC (P.E: Et$_2$O 95:5) to give **3e$_3$** in 69 % yield (72 mg, 0.34 mmol) as a transparent oil.

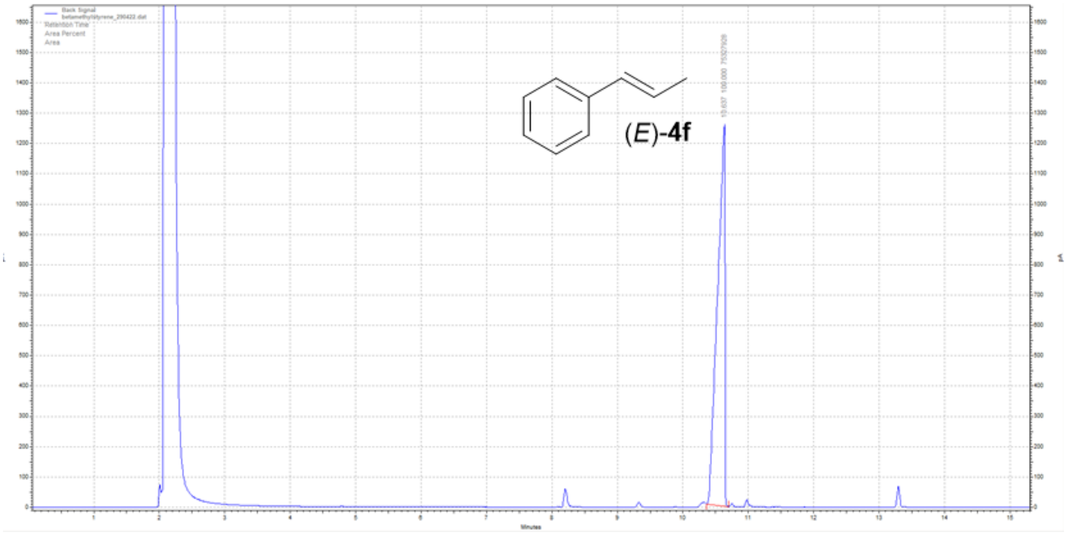
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.07 (m, 7H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.46 (d, *J* = 12.3 Hz, 1H CH=CH), 6.43 (d, *J* = 12.3 Hz, 1H CH=CH), 3.71 (s, 3H, OCH$_3$).

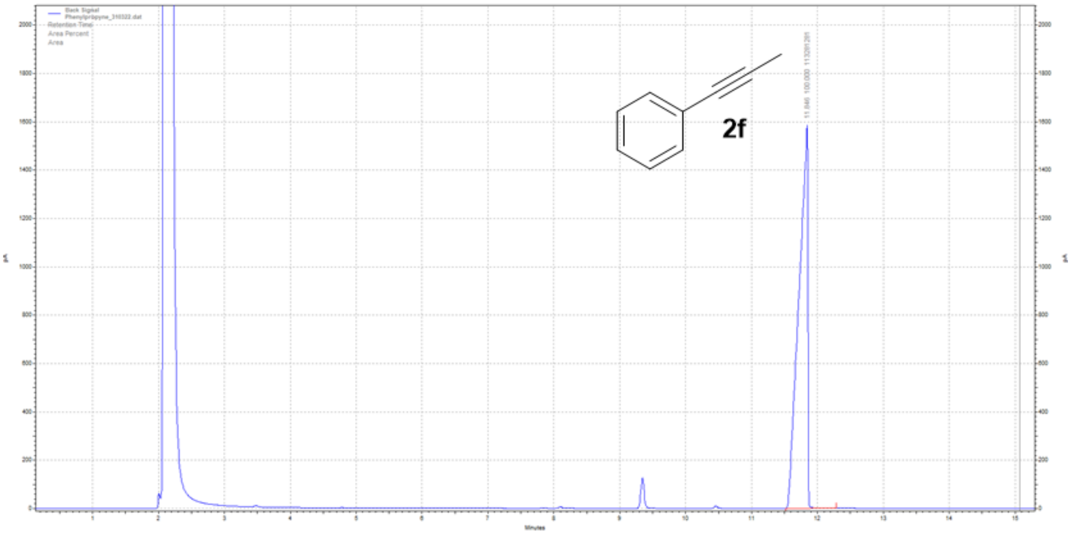
^{13}C NMR (101 MHz, CDCl$_3$) δ 158.8 (C), 137.8 (C), 130.3 (2CH), 129.9 (CH), 129.8 (C), 129.0 (2CH), 128.9 (CH), 128.4 (2CH), 127.0 (CH), 113.7 (2CH), 55.3 (OCH$_3$).

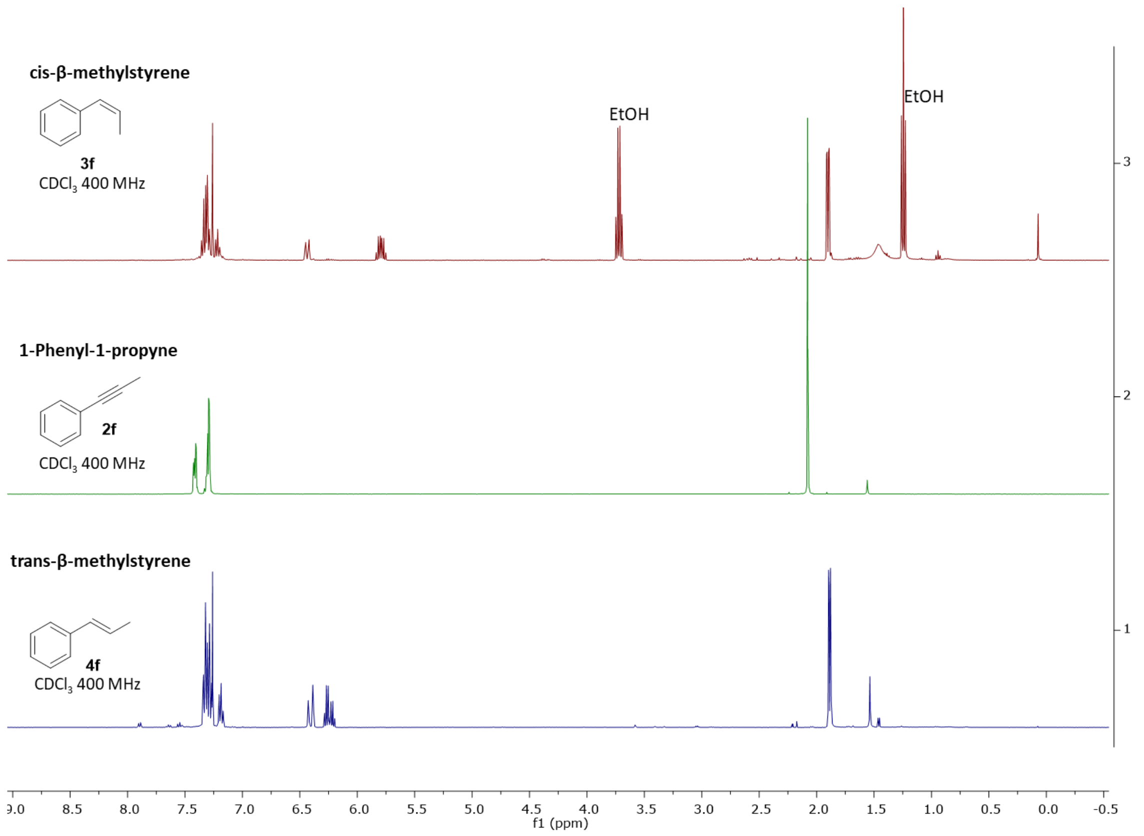
(*Z*)-prop-1-en-1-ylbenzene 3f^{S16}



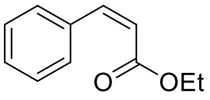
Retention Time	Area	Area %	Height	Height %
8.026	4326718	13.85	1387926	18.59
9.353	26303142	84.23	5864662	78.56
10.379	598937	1.92	212689	2.85
Totals	31228797	100.00	7465277	100.00







Ethyl (*Z*)-3-phenylacrylate (3g)[S17]

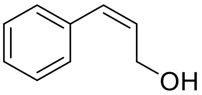


Method B2. R.T. 13h in EtOH. 78% yield (by GC). The compound was purified by prep TLC (Petroleum ether: AcOEt 98:2) to give **3e** in 63% yield (55 mg, 0.31 mmol) as a transparent oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 – 7.55 (m, 2H), 7.39 – 7.30 (m, 3H), 6.95 (d, *J* = 12.7 Hz, 1H, CH=CH), 5.95 (d, *J* = 12.6 Hz, 1H, CH=CH), 4.18 (q, *J* = 7.1 Hz, 2H, CH$_2$), 1.24 (t, *J* = 7.1 Hz, 3H, CH$_3$).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 166.4 (C), 143.1 (CH), 135.1 (C), 129.8 (2CH), 129.1 (CH), 128.1 (2CH), 120.1 (CH), 60.4 (CH$_2$), 14.2 (CH$_3$).

(*Z*)-3-phenylprop-2-en-1-ol (3h)[S18]

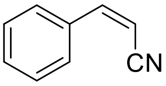


Method B2. R.T. 4h 30 min in EtOH. 88% yield (by GC). The compound was purified by prep TLC (Petroleum ether: AcOEt 8:2) to give **3g** in 81% yield (54 mg, 0.40 mmol) as a yellowish oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.24 (m, 2H), 7.23 – 7.17 (m, 1H), 7.17 – 7.10 (m, 2H), 6.50 (d, *J* = 11.7 Hz, 1H, CH=CH), 5.80 (dt, *J* = 11.8, 6.4 Hz, 1H, CH=CH), 4.37 (dd, *J* = 6.4, 1.7 Hz, 2H, CH$_2$).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 136.6 (C), 131.3 (CH), 131.2 (CH), 128.9 (2CH), 128.4 (2CH), 127.4 (CH), 59.9 (CH$_2$).

(*Z*)-3-phenylacrylonitrile (3i)[S19]

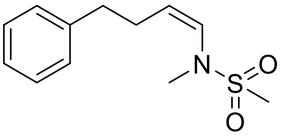


Method B2. R.T. 13h in EtOH. 93% yield (by GC). The compound was purified by prep TLC (Petroleum ether: AcOEt 97:3) to give **3h** in 88% yield (57 mg, 0.44 mmol) as a transparent oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 – 7.76 (m, 2H), 7.49 – 7.39 (m, 3H), 7.13 (d, *J* = 12.1 Hz, 1H, CH=CH), 5.45 (d, *J* = 12.1 Hz, 1H, CH=CH).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 148.9 (CH), 133.7 (C), 131.1 (CH), 129.2 (2CH), 129.1 (2CH), 117.5 (C), 95.2 (CH).

(*Z*)-N-methyl-N-(4-phenylbut-1-en-1-yl)methanesulfonamide (3j)



Method B2. 60ºC 48h in EtOH. 88% yield (by ^{1}H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 8:2) to give **3i** in 74% yield (89 mg, 0.37 mmol) as a transparent oil.

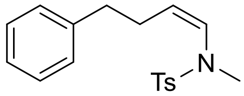
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 5.80 (dt, *J* = 7.9, 1.6 Hz, 1H, CH=CH), 5.41 (q, *J* = 7.5 Hz, 1H, CH=CH), 2.87 (s, 3H, CH$_3$), 2.75 (s, overlapped 3H, CH$_3$), 2.75 – 2.70 (m, overlapped 2H, CH$_2$), 2.61 – 2.55 (m, 2H, CH$_2$).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 141.4 (C), 130.3 (CH), 128.7 (2CH), 128.5 (2CH), 127.1 (CH), 126.2 (CH), 37.5 (CH$_3$), 35.4 (CH$_3$), 35.2 (CH$_2$), 28.8 (CH$_2$).

HRMS (ESI+): m/z 246.1140 calcd. for $C_{12}H_{17}LiNO_2$ $[M+Li]^+$, found 246.1137.

HRMS (ESI+): m/z 262.0878 calcd. for $C_{12}H_{17}NNaO_2$ $[M+Na]^+$, found 262.0875.

(*Z*)-N,4-dimethyl-N-(4-phenylbut-1-en-1-yl)benzenesulfonamide (3k)



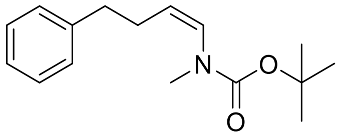
Method A2. 60ºC 62h in EtOH. 92% yield (by ^{1}H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 9:1) to give **3j** in 80% yield (124 mg, 0.39 mmol) as a transparent oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H, Ts), 7.31 (d, *J* = 7.7 Hz, 2H, Ts), 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 5.45 (dt, *J* = 7.8, 1.3 Hz, 1H, CH=CH), 5.43 – 5.38 (m, 1H, CH=CH), 2.70 (s, 3H, N-CH_3 overlapped), 2.68 (m, 2H, CH_2 overlapped), 2.57 (qt, *J* = 7.3, 1.3 Hz, 2H, CH_2), 2.43 (s, 3H, CH_3 Ts).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 143.7 (C), 141.6 (C), 134.1 (C), 131.3 (CH), 129.7 (2CH), 128.7 (2CH), 128.4 (2CH), 127.8 (2CH), 127.4 (CH), 126.1 (CH), 37.8 (N-CH_3), 35.2 (CH_2), 28.8 (CH_2), 21.7 (CH_3).

HRMS (ESI+): m/z 316.1366 calcd. for $C_{18}H_{22}NO_2S$ $[M+H]^+$, found 316.1367.

tert-butyl (*Z*)-methyl(4-phenylbut-1-en-1-yl)carbamate (3l)



Method B2. 60ºC 62h in EtOH. 92% yield (by ^{1}H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 97:3) to give **3k** in 72% yield (94 mg, 0.36 mmol) as a transparent oil.

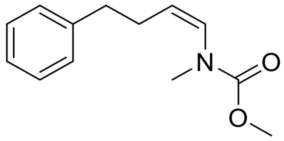
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.26 (m, 2H), 7.22 – 7.16 (m, 3H), 6.18 (bs, 1H, CH=CH), 4.89 (bs, 1H, CH=CH), 2.98 (s, 3H, CH_3), 2.71 (d, *J* = 7.1 Hz, 2H, CH_2), 2.45 – 2.39 (m, 2H, CH_2), 1.47 (s, 9H, 3CH_3, ^{t}Bu).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 154.8 (C=O), 141.7 (C), 129.1 (CH), 128.6 (2CH), 128.5 (2CH), 126.1 (CH), 119.1 (CH, broad), 80.4 (C, ^{t}Bu), 35.8 (CH_2), 29.1 (CH_2 broad), 28.6 (CH_3), 28.5 (3CH_3, ^{t}Bu).

HRMS (ESI+): m/z 268.1883 calcd. for $C_{16}H_{23}LiNO_2$ $[M+Li]^+$, found 268.1894.

HRMS (ESI+): m/z 284.1621 calcd. for $C_{16}H_{23}NNaO_2$ $[M+Na]^+$, found 284.1621.

methyl (*Z*)-methyl(4-phenylbut-1-en-1-yl)carbamate (3m)



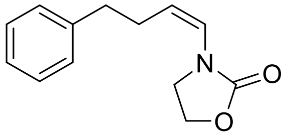
Method A2. 60ºC 48h in EtOH. 85% yield (by ^{1}H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 95:5) to give **3l** in 79% yield (86 mg, 0.39 mmol) as a transparent oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 – 7.33 (m, 2H), 7.28 – 7.23 (m, 3H), 6.22 (bs, 1H, CH=CH), 5.09 (q, *J* = 7.2 Hz, 1H, CH=CH), 3.79 (s, 3H, CH$_3$), 3.08 (s, 3H, CH$_3$), 2.80 – 2.73 (m, 2H, CH$_2$), 2.47 (qd, *J* = 7.8, 7.3, 1.7 Hz, 2H, CH$_2$).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 156.1 (C=O), 141.6 (C), 128.5 (2CH), 128.5 (2CH), 128.4 (broad CH), 126.1 (CH), 121.8 (broad CH), 53.1 (CH$_3$), 36.4 (CH$_3$), 35.6 (CH$_2$), 29.0 (CH$_2$).

HRMS (ESI+): m/z 220.1332 calcd. for $C_{13}H_{18}NO_2$ $[M+H]^+$, found 220.1335.

(*Z*)-3-(4-phenylbut-1-en-1-yl)oxazolidin-2-one (3n)[S20]



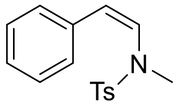
Method A2. 60ºC 13h in EtOH. 89% yield (by ^{1}H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 8:2) to give **3m** in 72% yield (78 mg, 0.36 mmol) as a transparent oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 6.24 (dt, *J* = 9.5, 1.6 Hz, 1H, CH=CH), 4.88 (dt, *J* = 9.5, 7.6 Hz, 1H, CH=CH), 4.32 – 4.27 (m, 2H, CH$_2$), 3.78 – 3.72 (m, 2H, CH$_2$), 2.72 (t, *J* = 7.5 Hz, 2H, CH$_2$), 2.49 (qd, *J* = 7.6, 1.6 Hz, 2H, CH$_2$).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 156.9 (C=O), 141.3 (C), 128.6 (2CH), 128.5 (2CH), 126.3 (CH), 123.1 (CH), 114.6 (CH), 62.2 (CH$_2$), 45.6 (CH$_2$), 36.3 (CH$_2$), 28.7 (CH$_2$).

HRMS (ESI+): m/z 217.1103 calcd. for $C_{13}H_{16}NO_2$ $[M+H]^+$, found 217.1049.

(Z)-N,4-dimethyl-N-styrylbenzenesulfonamide (3o)[S21]



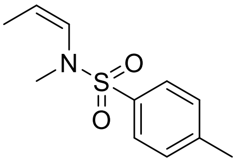
Method A2. 60ºC 62h in EtOH. 94% yield (by ^{1}H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 8:2) to give **3n** in 84% yield (120 mg, 0.42 mmol) as a transparent oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H, Ts), 7.39 (d, *J* = 7.7 Hz, 2H, Ts), 7.31 – 7.21 (m, 5H), 6.29 (d, *J* = 9.0 Hz, 1H, CH=CH), 6.04 (d, *J* = 9.0 Hz, 1H, CH=CH), 2.78 (s, 3H, N-CH$_3$), 2.49 (s, 3H, CH$_3$ Ts).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 144.1 (C), 135.0 (C), 134.3 (C), 129.9 (2CH), 129.1 (2CH), 128.3 (2CH), 127.7 (CH), 127.6 (2CH), 127.4 (CH), 121.1 (CH), 36.7 (CH$_3$), 21.7 (CH$_3$).

HRMS (ESI+): m/z 288.1053 calcd. for $C_{16}H_{18}NO_2S$ [M+H]$^+$, found 288.1053

(*Z*)-N,4-dimethyl-N-(prop-1-en-1-yl)benzenesulfonamide (3p)[S22]



Method A2. 60ºC 36h in EtOH. 74% yield (by ^{1}H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 97:3) to give **3o** in 62% yield (70 mg, 0.31 mmol) as a transparent oil.

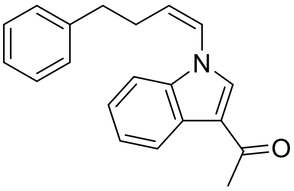
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.52 – 5.44 (m, 2H CH=CH), 2.83 (s, 3H, CH$_3$), 2.43 (s, 3H, CH$_3$), 1.75 (dd, *J* = 6.4, 1.2 Hz, 3H, CH$_3$).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 143.7 (C), 134.2 (C), 129.7 (2CH), 128.0 (CH, CH=CH), 127.8 (2CH), 126.8 (CH, CH=CH), 37.7 (CH$_3$), 21.7 (CH$_3$), 12.9 (CH$_3$).

HRMS (ESI+): m/z 232.0978 calcd. for $C_{11}H_{15}LiNO_2S$ [M+Li]$^+$, found 232.0978.

HRMS (ESI+): m/z 248.0716 calcd. for $C_{11}H_{15}NNaO_2S$ [M+Na]$^+$, found 248.0716.

(*Z*)-1-(1-(4-phenylbut-1-en-1-yl)-1H-indol-3-yl)ethan-1-one (3q)



Method A2. 60ºC 13h in EtOH. 70% yield (by ^{1}H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 8:2) to give **3q** in 61% yield (88 mg, 0.31 mmol) as a transparent oil.

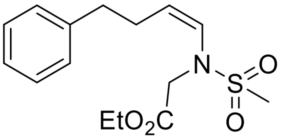
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.38 – 8.35 (m, 1H), 7.41 (s, 1H), 7.33 – 7.19 (m, 6H), 7.16 – 7.12 (m, 2H), 6.75 (dt, *J* = 8.4, 1.7 Hz, 1H, CH=CH), 5.75 (t, *J* = 7.6 Hz, 1H, CH=CH), 2.78 (t, *J* = 7.3 Hz, 2H, CH$_2$), 2.52 (qd, *J* = 7.4, 1.7 Hz, 2H, CH$_2$), 2.48 (s, 3H, CH$_3$).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 193.4 (C=O), 140.7 (C), 137.3 (C), 134.3 (CH), 128.7 (4CH), 128.4 (CH), 126.5 (CH), 125.9 (C), 123.9 (CH), 123.7 (CH), 123.1 (CH), 122.7 (CH), 118.2 (C), 110.5 (CH), 35.4 (CH_2), 29.0 (CH_2), 27.9 (CH_3).

HRMS (ESI+): m/z 296.1621 calcd. for $C_{20}H_{19}LiNO$ $[M+Li]^+$, found 296.1630.

HRMS (ESI+): m/z 312.1359 calcd. for $C_{20}H_{19}NNaO$ $[M+Na]^+$, found 312.1365.

ethyl (*Z*)-N-(methylsulfonyl)-N-(4-phenylbut-1-en-1-yl)glycinate (3r)



Method B2. 70ºC 13h in EtOH. 76% alkene (*Z*), 5% alkene (*E*) (19% ynamide reagent recovered with CO_2Et) (by ^1H NMR). The compound was purified by flash chromatography (gradient from 100% petroleum ether to petroleum ether: AcOEt 85:15) to give **3r** in 72% yield (112 mg, 0.36 mmol) as a transparent oil.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 7.28 – 7.23 (m, 3H), 6.12 (dt, *J* = 7.7, 1.6 Hz, 1H, CH=CH), 5.61 (q, *J* = 7.5 Hz, 1H, CH=CH), 4.24 (q, *J* = 7.1 Hz, 2H, OCH_2), 4.03 (s, 2H, NCH_2), 3.06 (s, 3H, CH_3 Mes), 2.79 (t, *J* = 7.4 Hz, 2H, CH_2), 2.62 (qdd, *J* = 7.3, 1.6, 0.6 Hz, 2H, CH_2), 1.33 (t, *J* = 7.2 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4 (C, C=O), 141.2 (C), 133.1 (CH), 128.6 (2CH), 128.5 (2CH), 126.2 (CH), 125.4 (CH), 61.6 (CH_2), 51.8 (CH_2), 39.3 (CH_3), 35.0 (CH_2), 28.8 (CH_2), 14.2 (CH_3).

HRMS (ESI+): m/z 318.13458 calcd. for $C_{15}H_{21}NO_4LiS$ $[M+Li]^+$, found 318.13460.

IV. References

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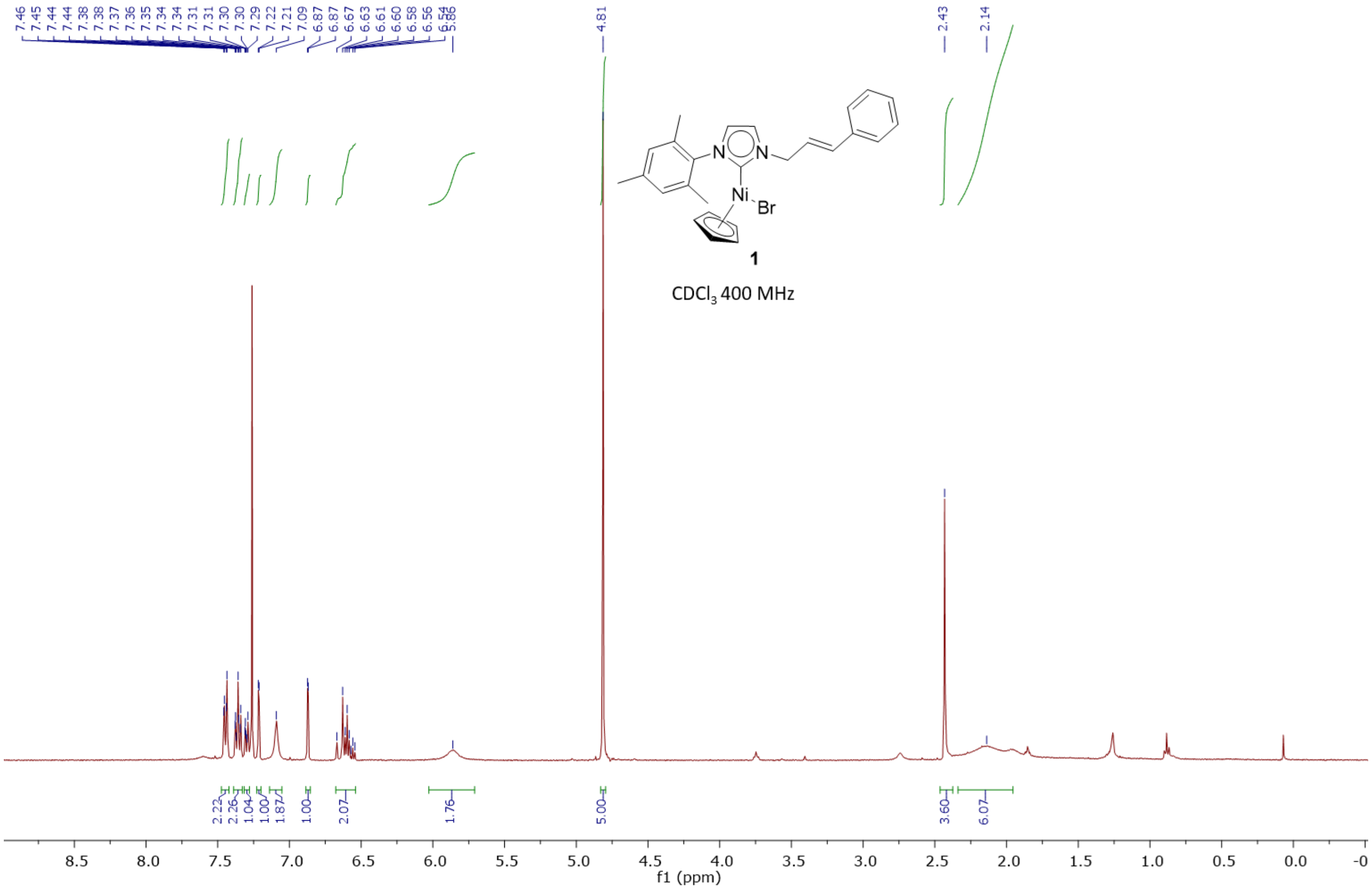
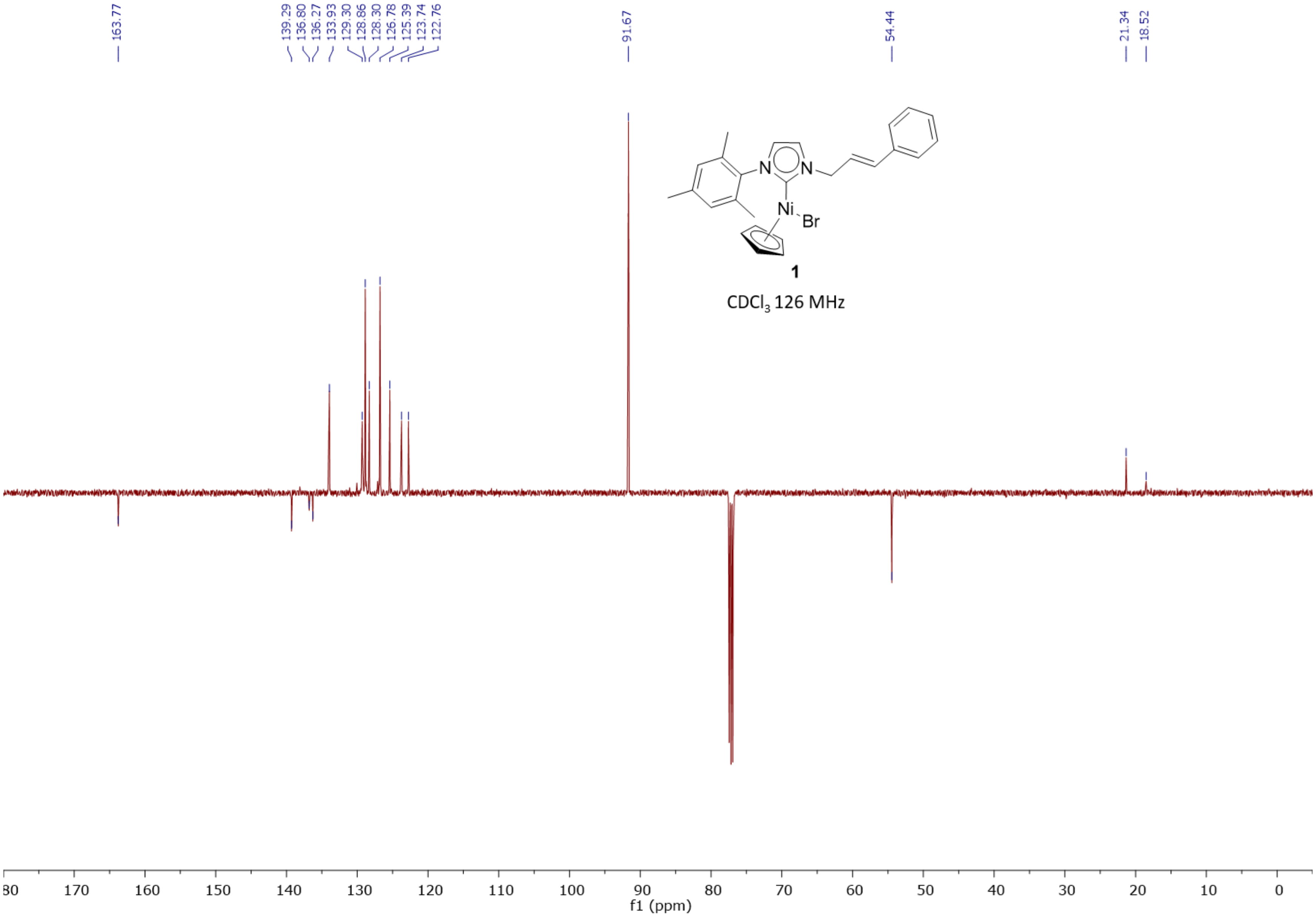
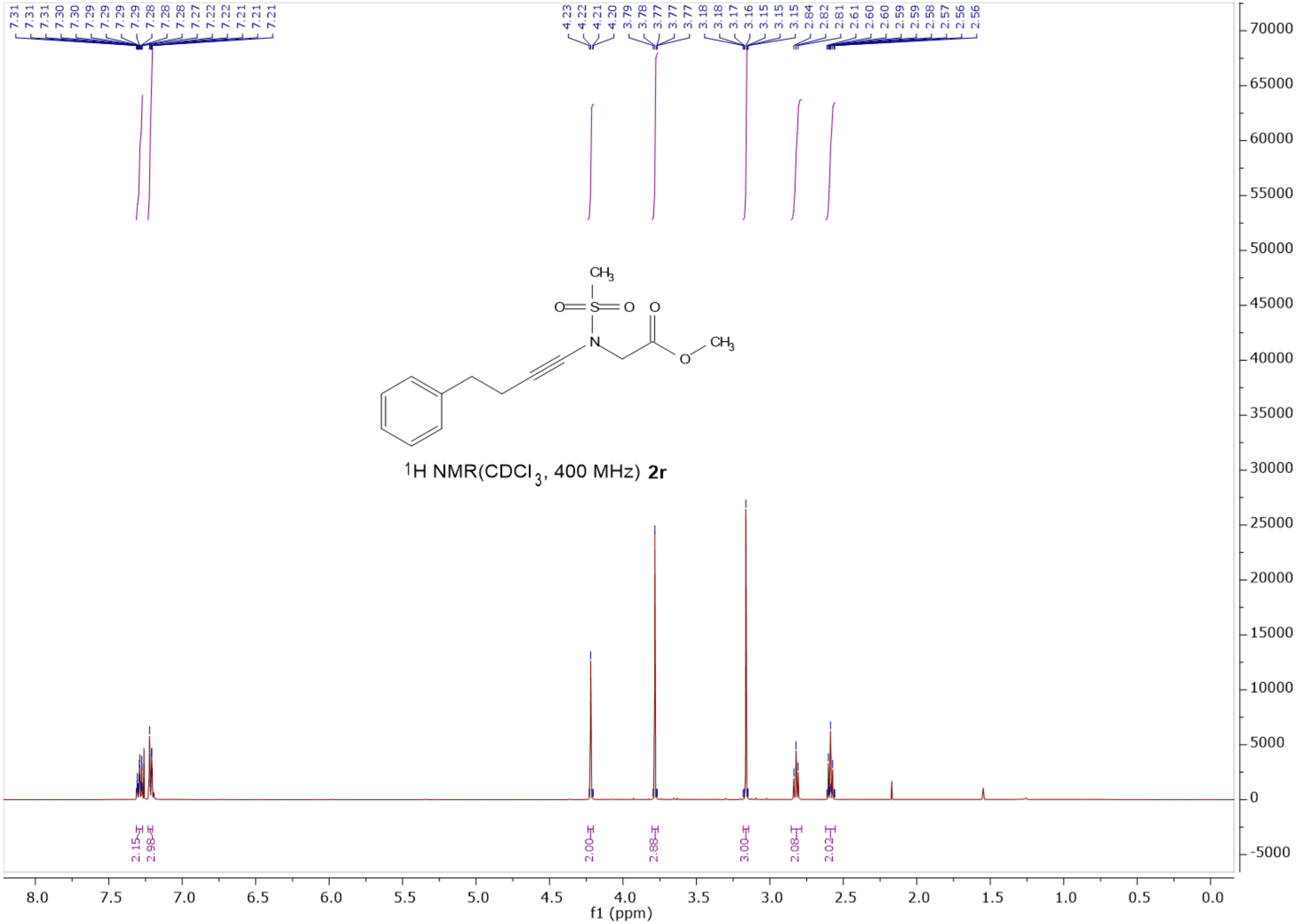
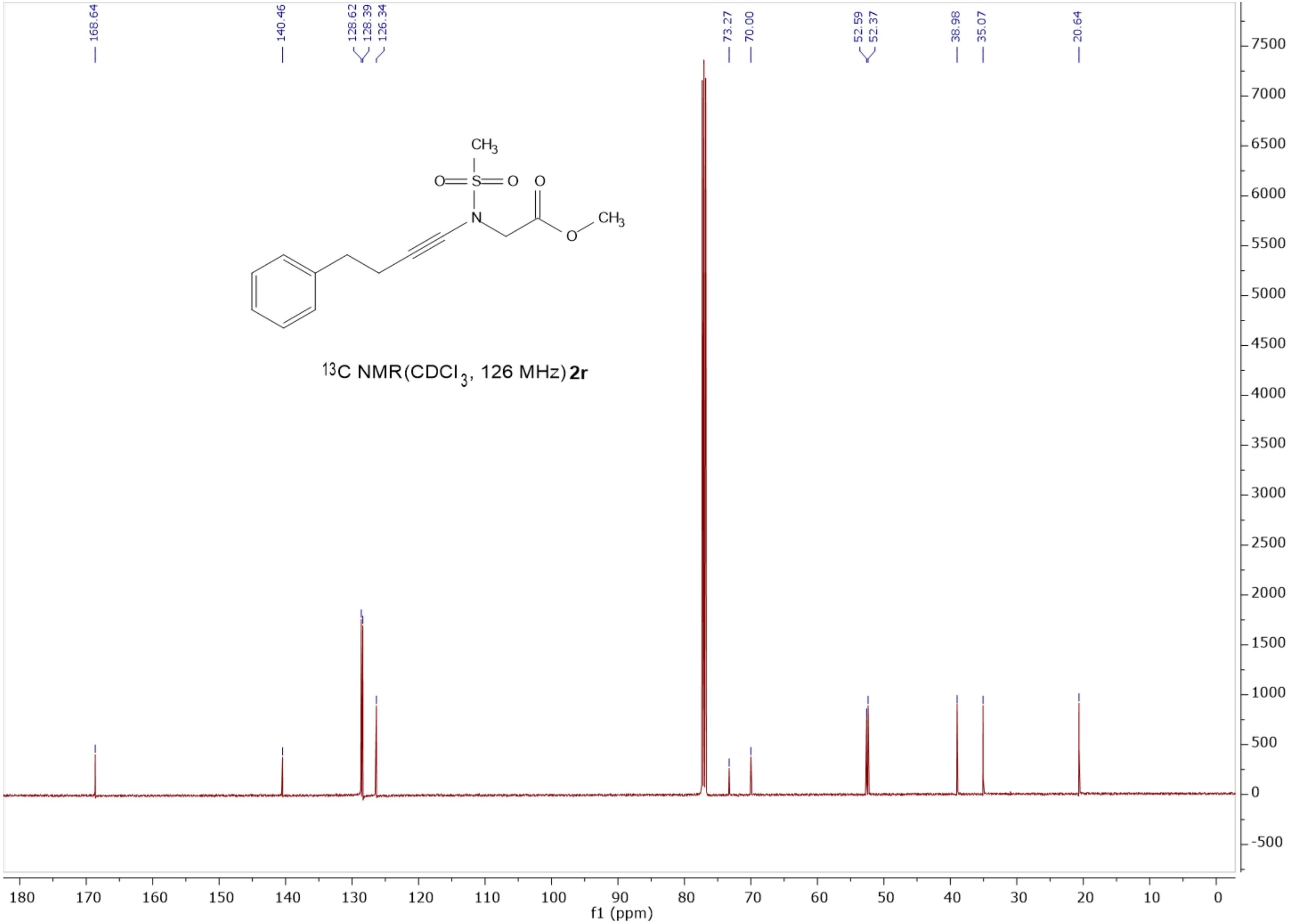
V. ^{1}H, ^{13}C NMR spectra of isolated compounds

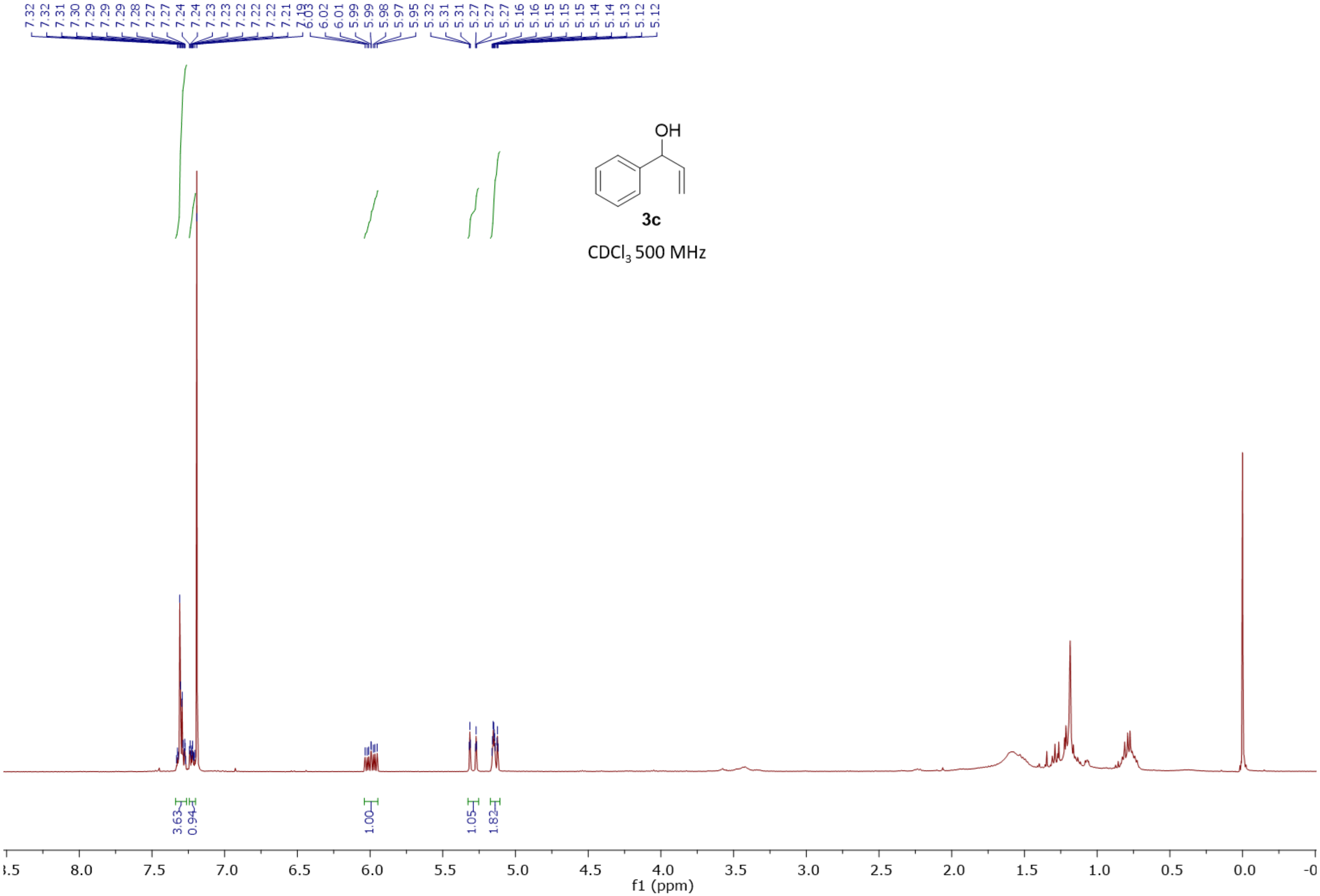


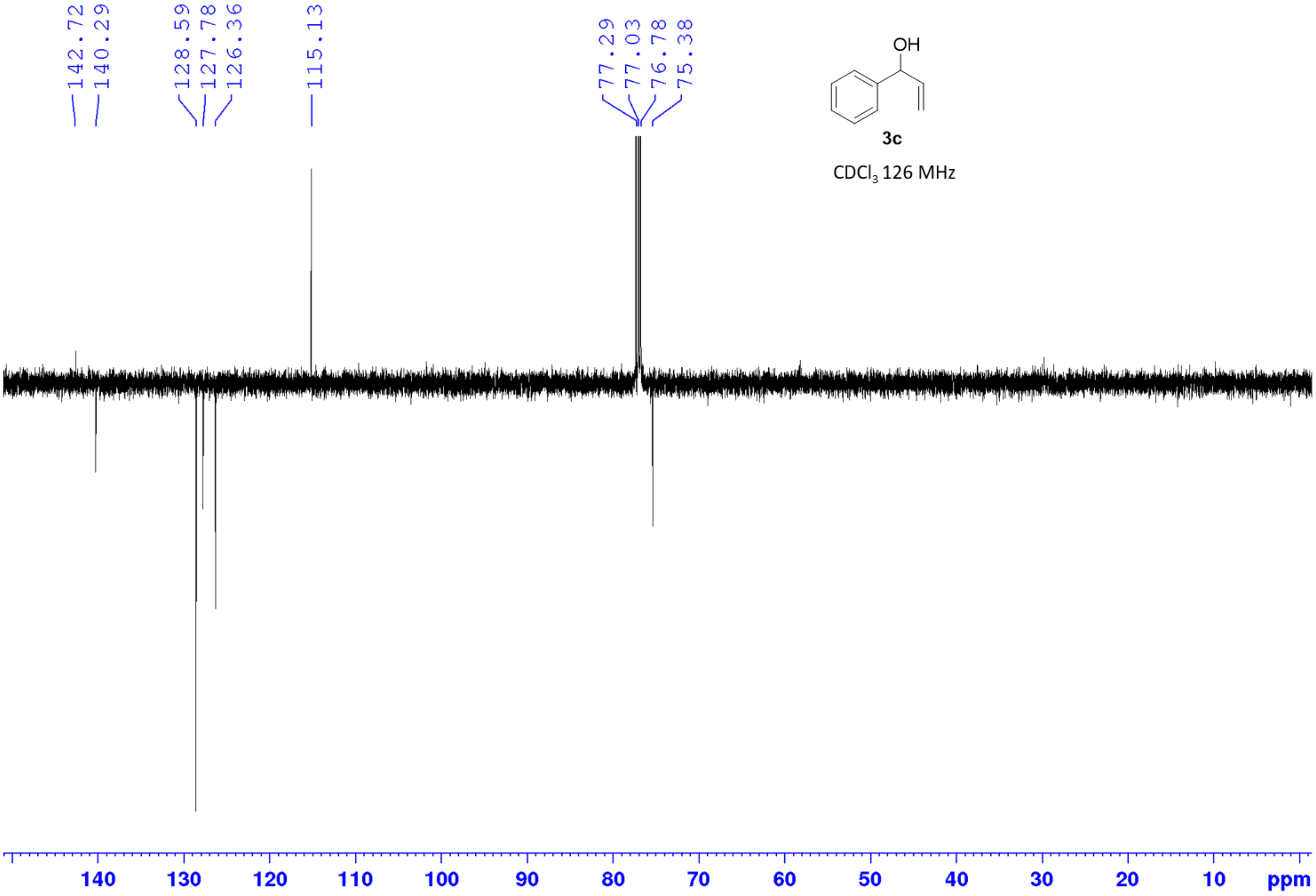

163.77
139.29
136.80
136.27
133.93
129.30
128.86
128.30
126.78
125.39
123.74
122.76
91.67
54.44
21.34
18.52
N
N
Ni
Br
1
CDCl$_3$ 126 MHz
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{1}H NMR(CDCl$_3$, 400 MHz) **2r**

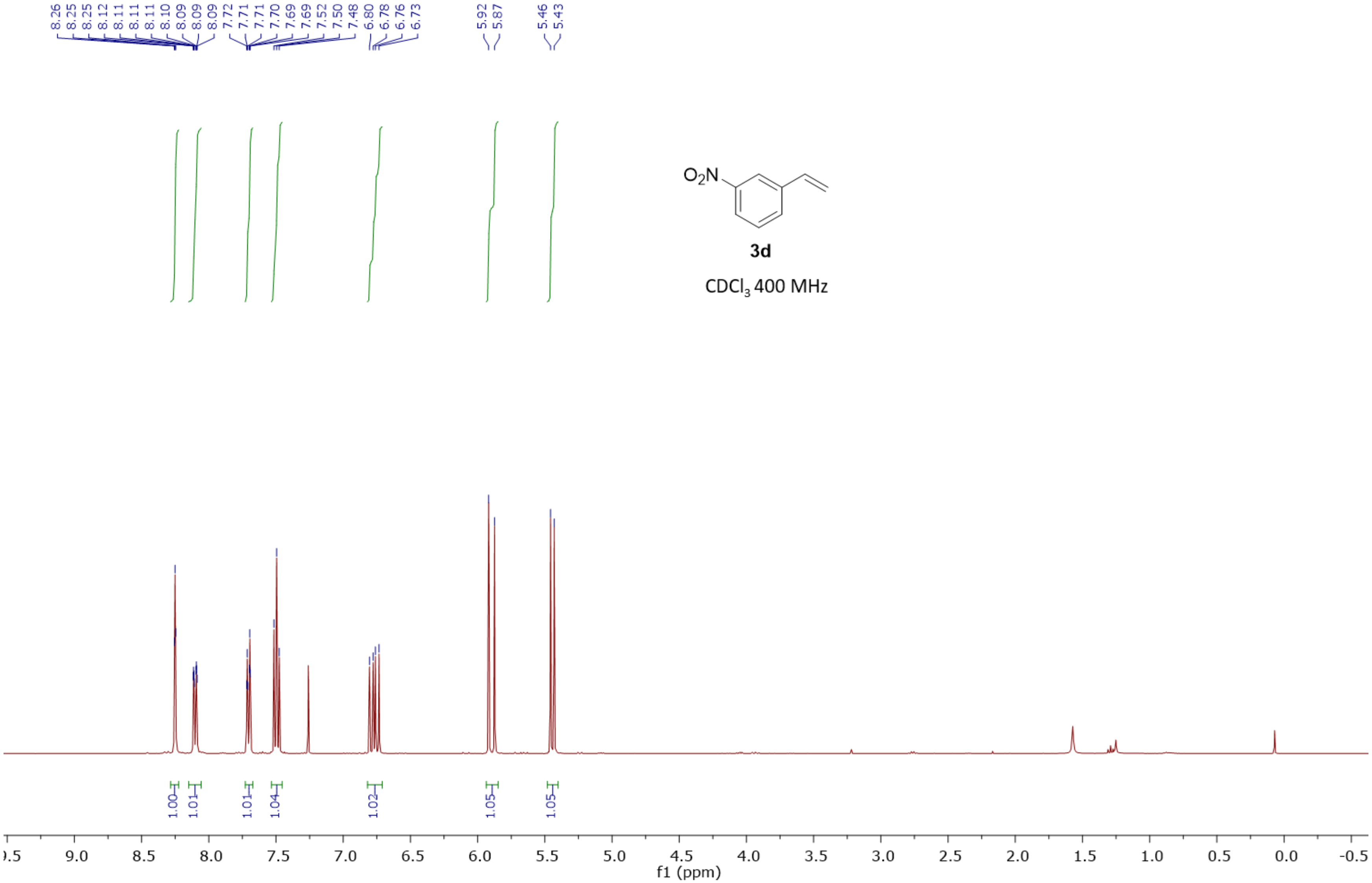

168.64
140.46
128.62
128.39
126.34
73.27
70.00
52.59
52.37
38.98
35.07
20.64
CH3
O
S
O
O
N
O
CH3
^{13}C NMR(CDCl$_3$, 126 MHz) **2r**
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.32
7.32
7.31
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.24
7.24
7.23
7.23
7.22
7.22
7.22
7.21
7.19
6.03
6.02
6.01
5.99
5.99
5.98
5.97
5.95
5.32
5.31
5.31
5.27
5.27
5.27
5.27
5.16
5.16
5.15
5.15
5.15
5.14
5.14
5.13
5.12
5.12
OH
3c
CDCl$_3$ 500 MHz
3.63
0.94
1.00
1.05
1.82
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)



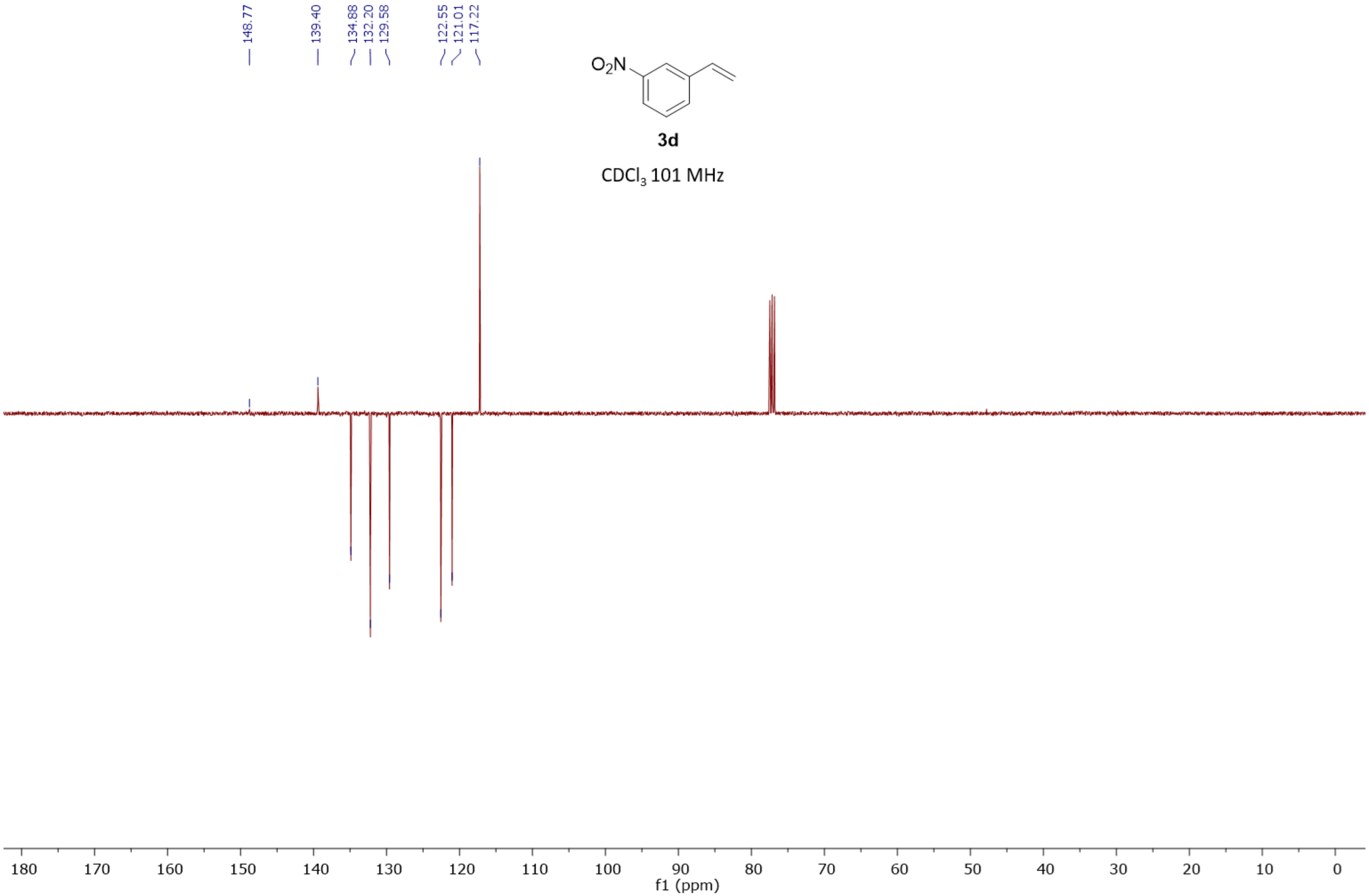
3c

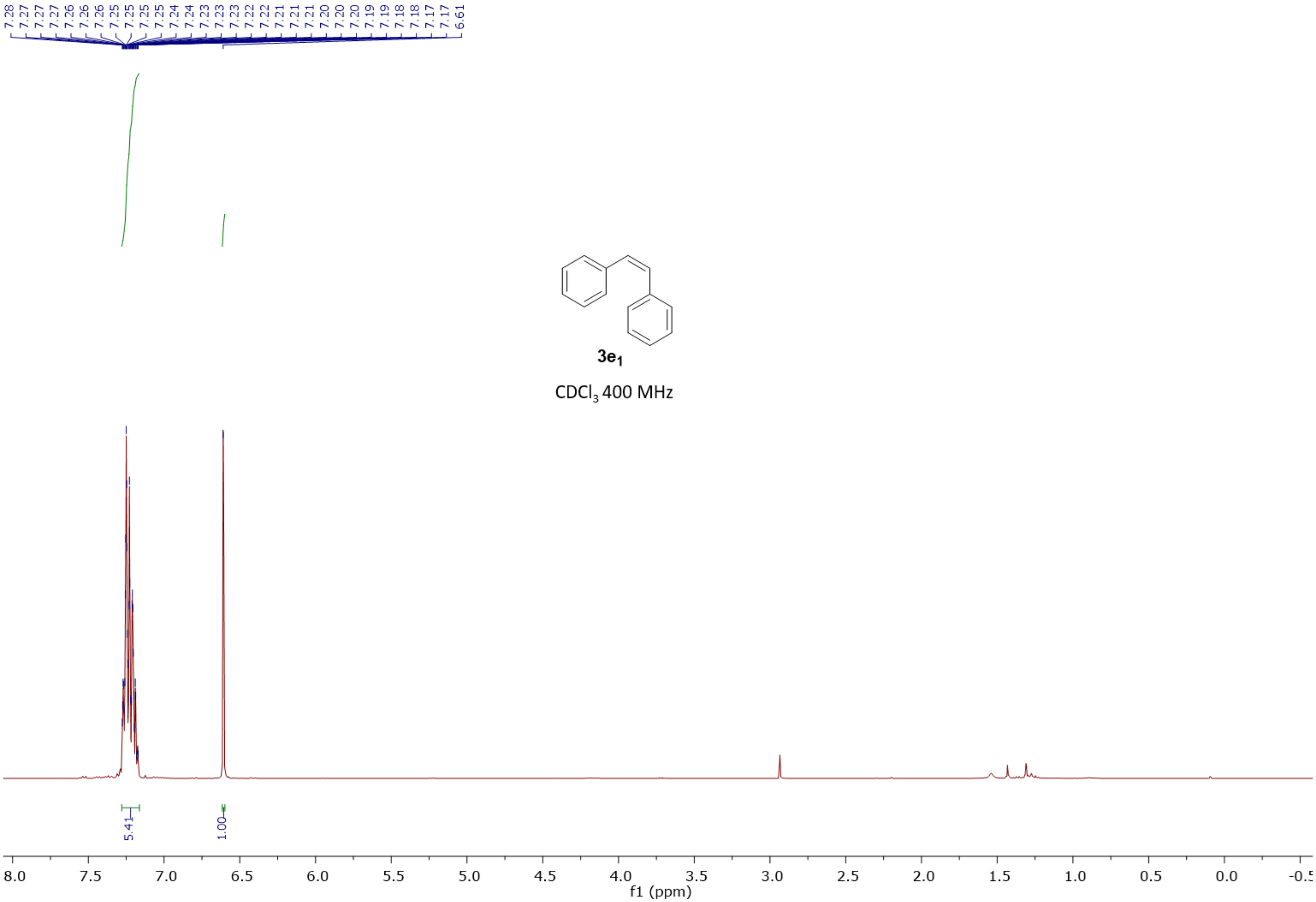
CDCl$_3$ 126 MHz



3d

CDCl$_3$ 400 MHz


148.77
139.40
134.88
132.20
129.58
122.55
121.01
117.22
O_2N
3d
$CDCl_3$ 101 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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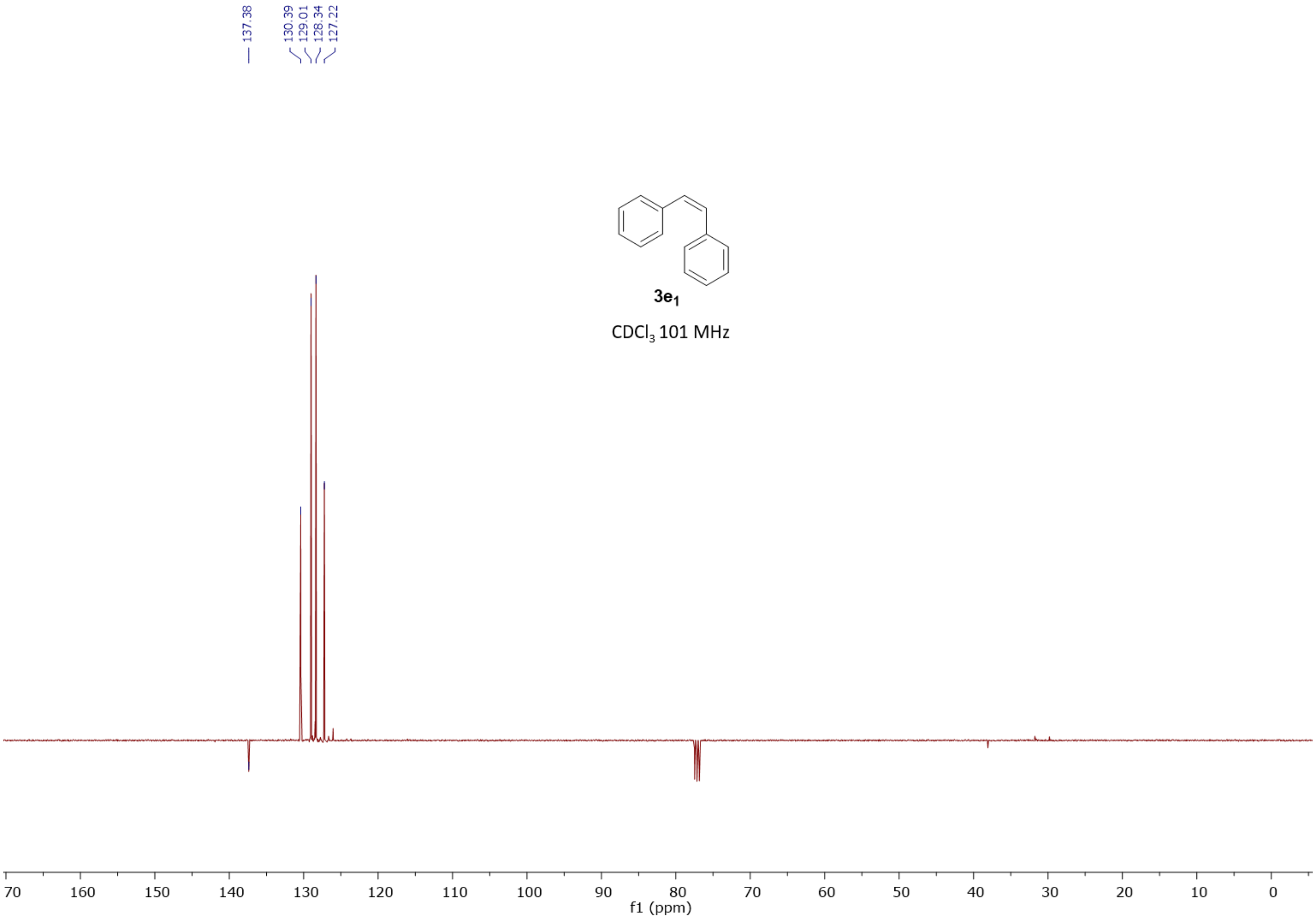
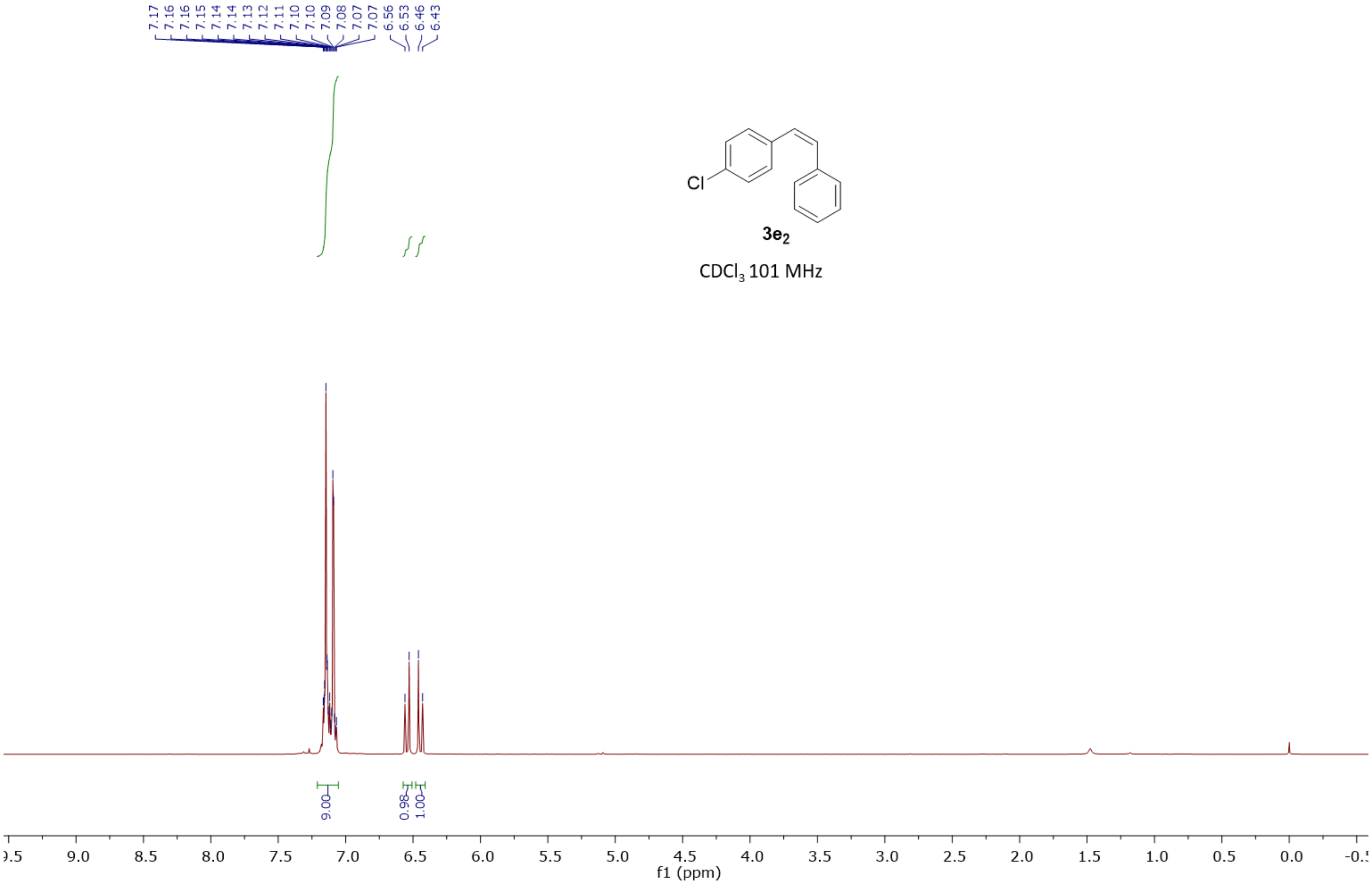
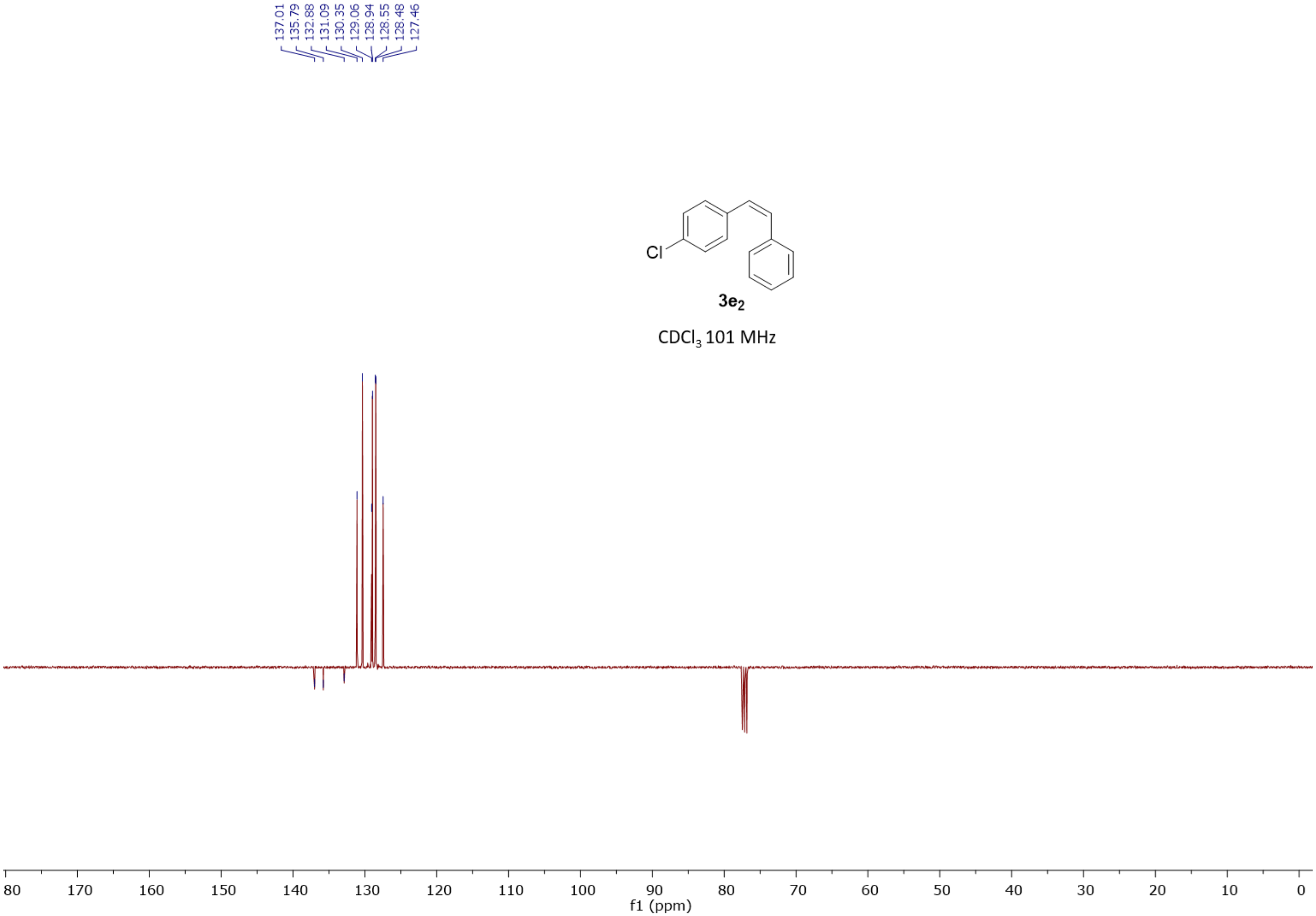
7.27
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.25
7.25
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.17
6.61
3e1
CDCl3 400 MHz
5.41
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


137.38
130.39
129.01
128.34
127.22
$3e_1$
$CDCl_3$ 101 MHz
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



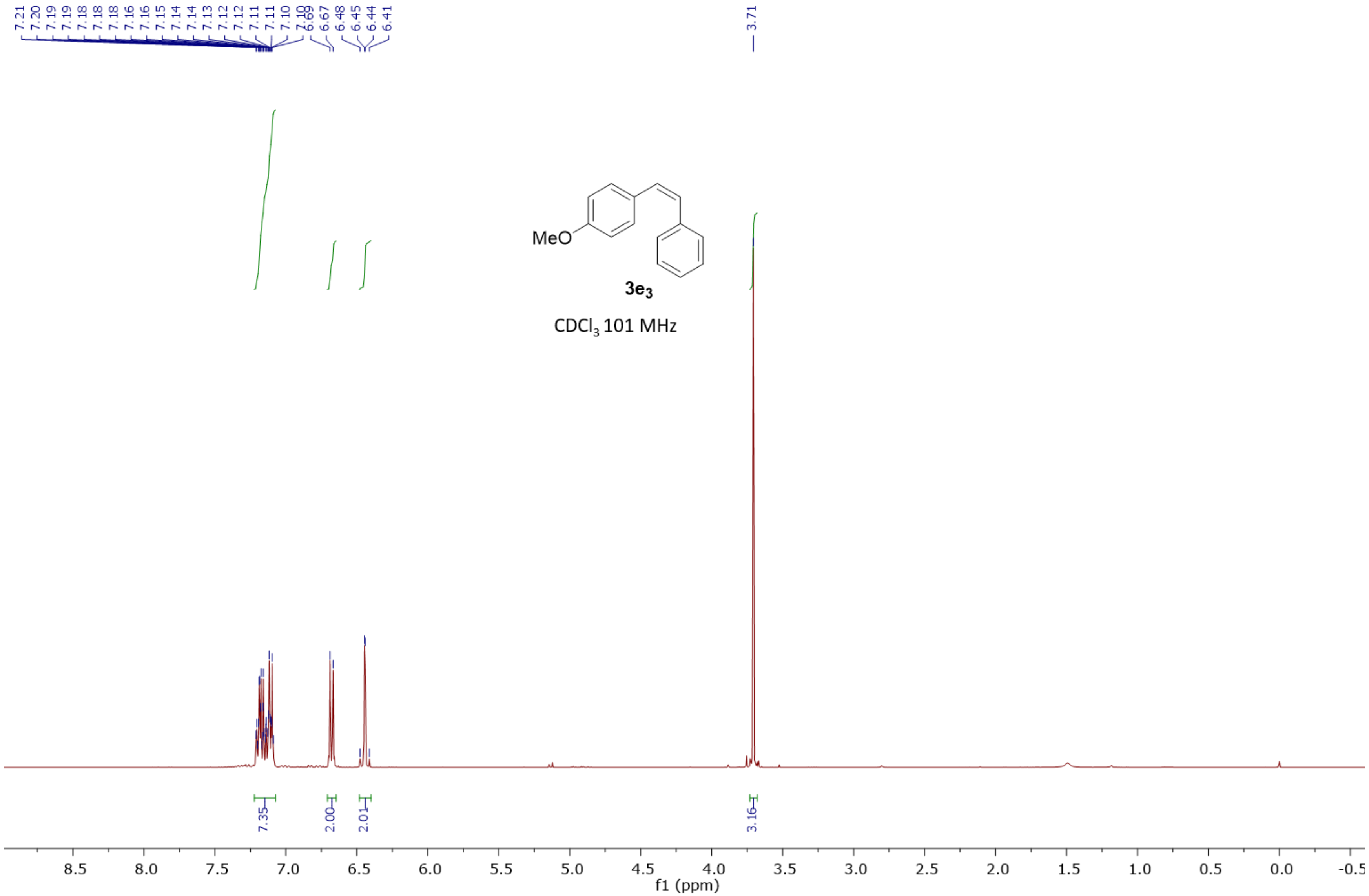
3e$_2$

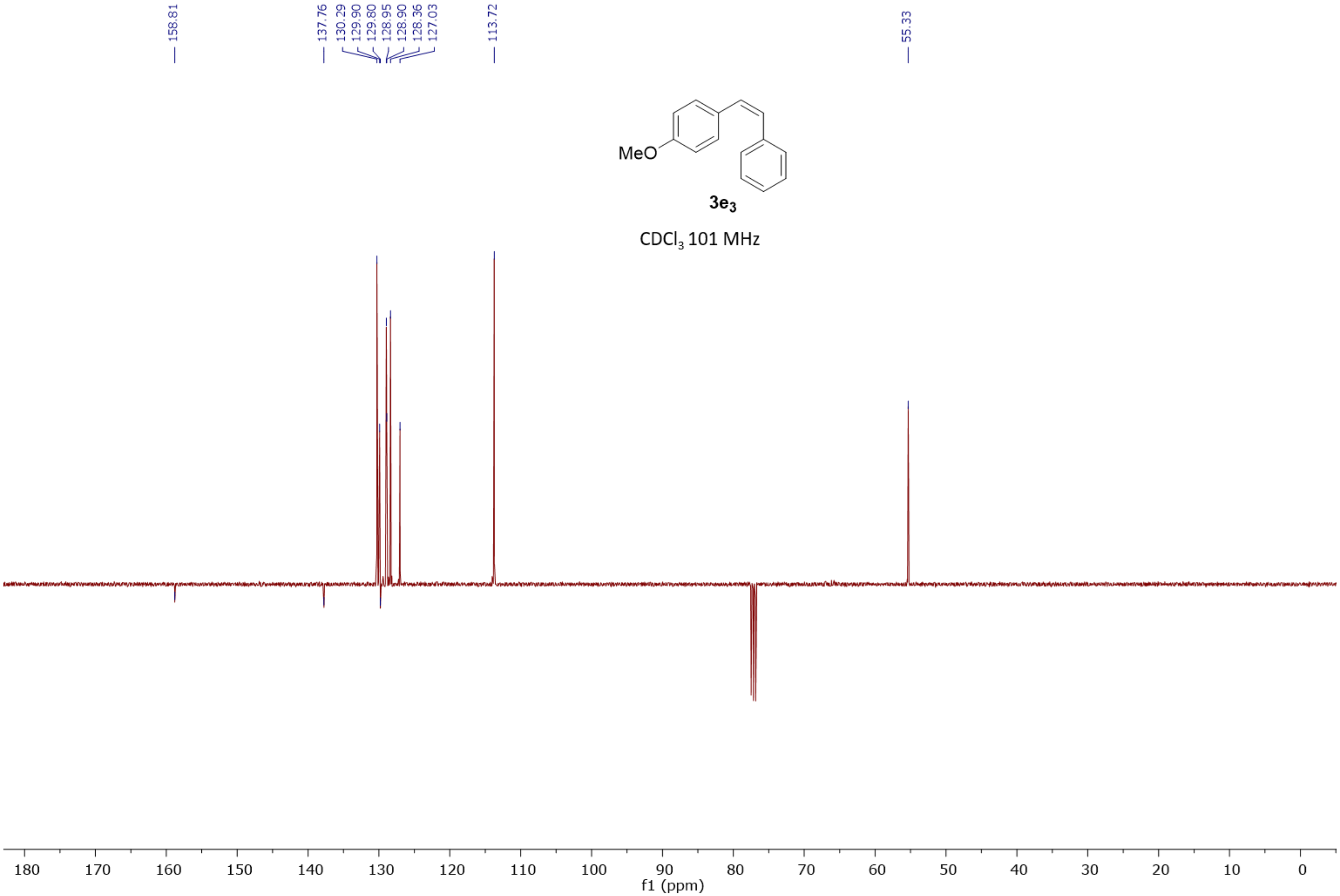
CDCl$_3$ 101 MHz



$3e_2$

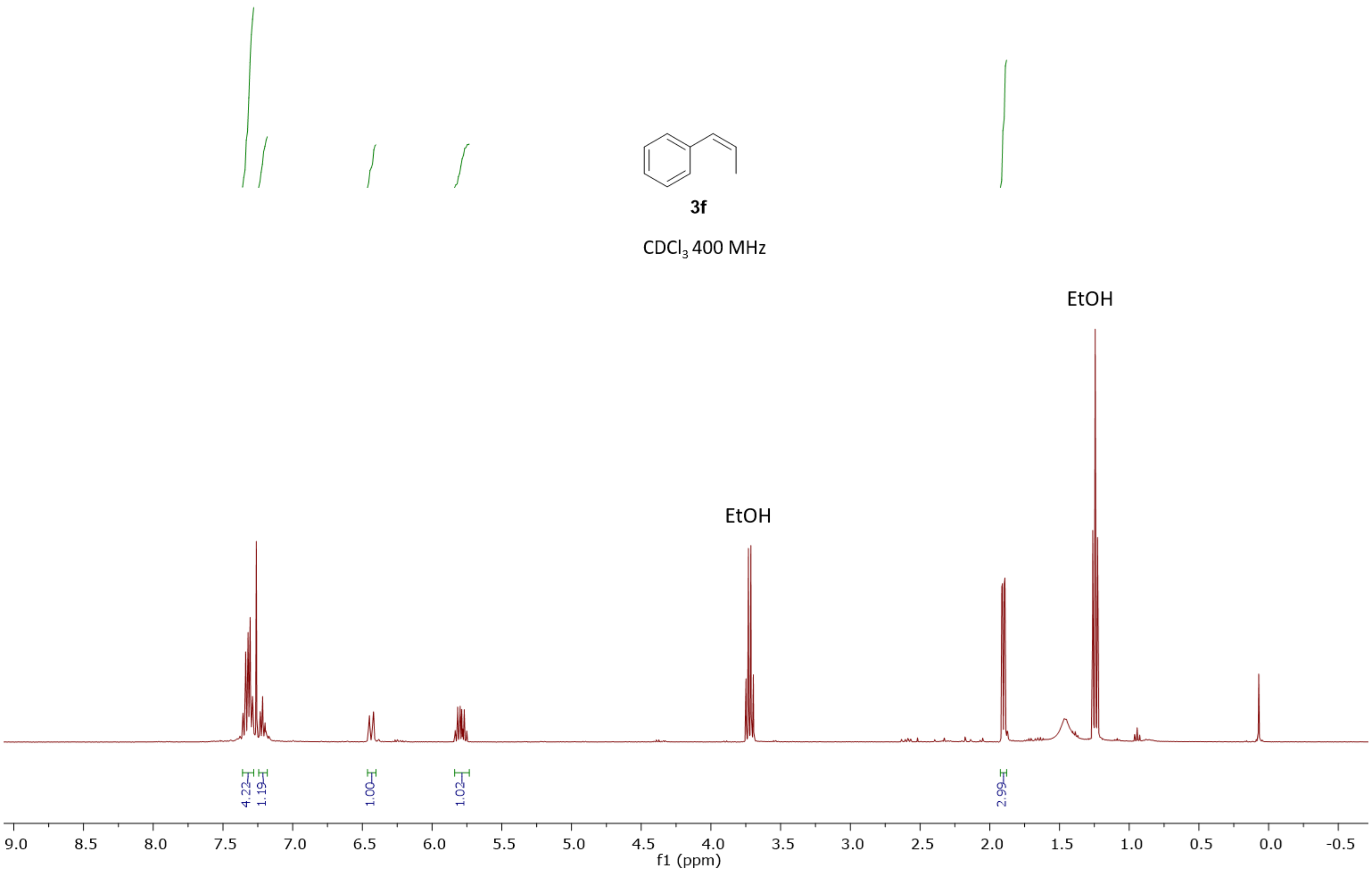
$CDCl_3$ 101 MHz

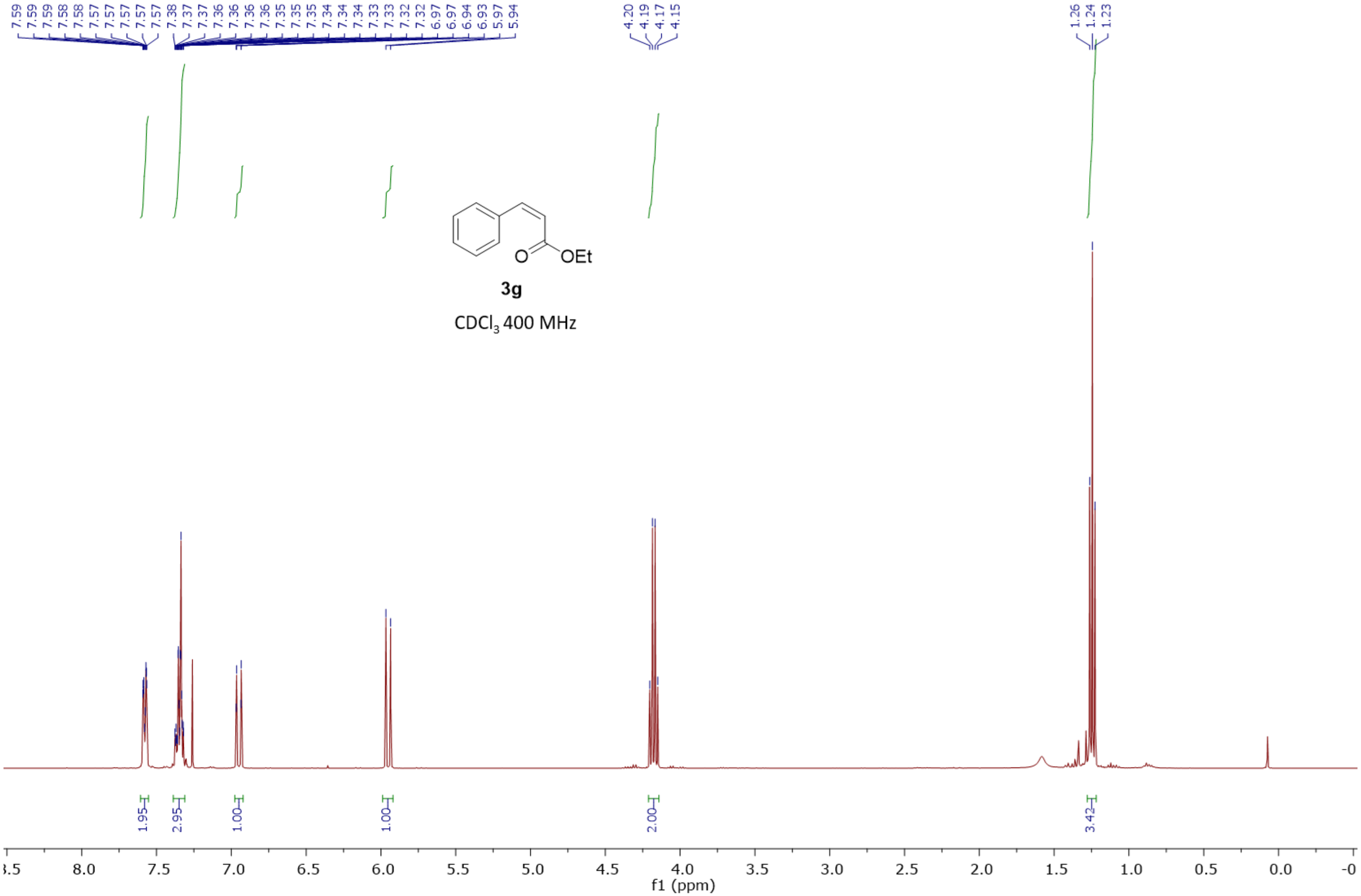

7.21
7.20
7.19
7.19
7.18
7.18
7.18
7.16
7.16
7.15
7.14
7.14
7.13
7.12
7.12
7.11
7.11
7.10
7.10
6.69
6.67
6.48
6.45
6.44
6.41
3.71
MeO
3e3
CDCl3 101 MHz
7.35
2.00
2.01
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



$3e_3$

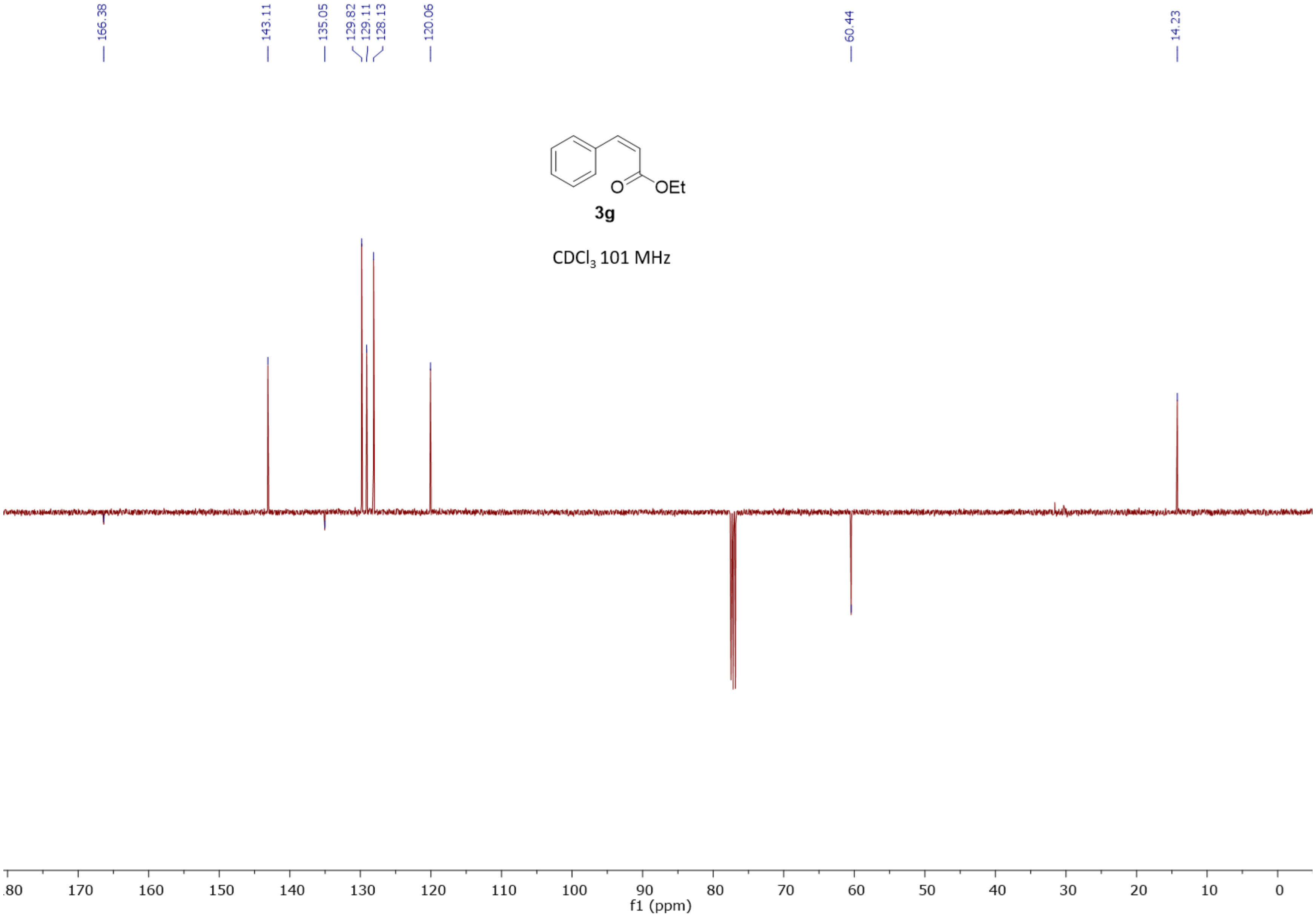
$CDCl_3$ 101 MHz

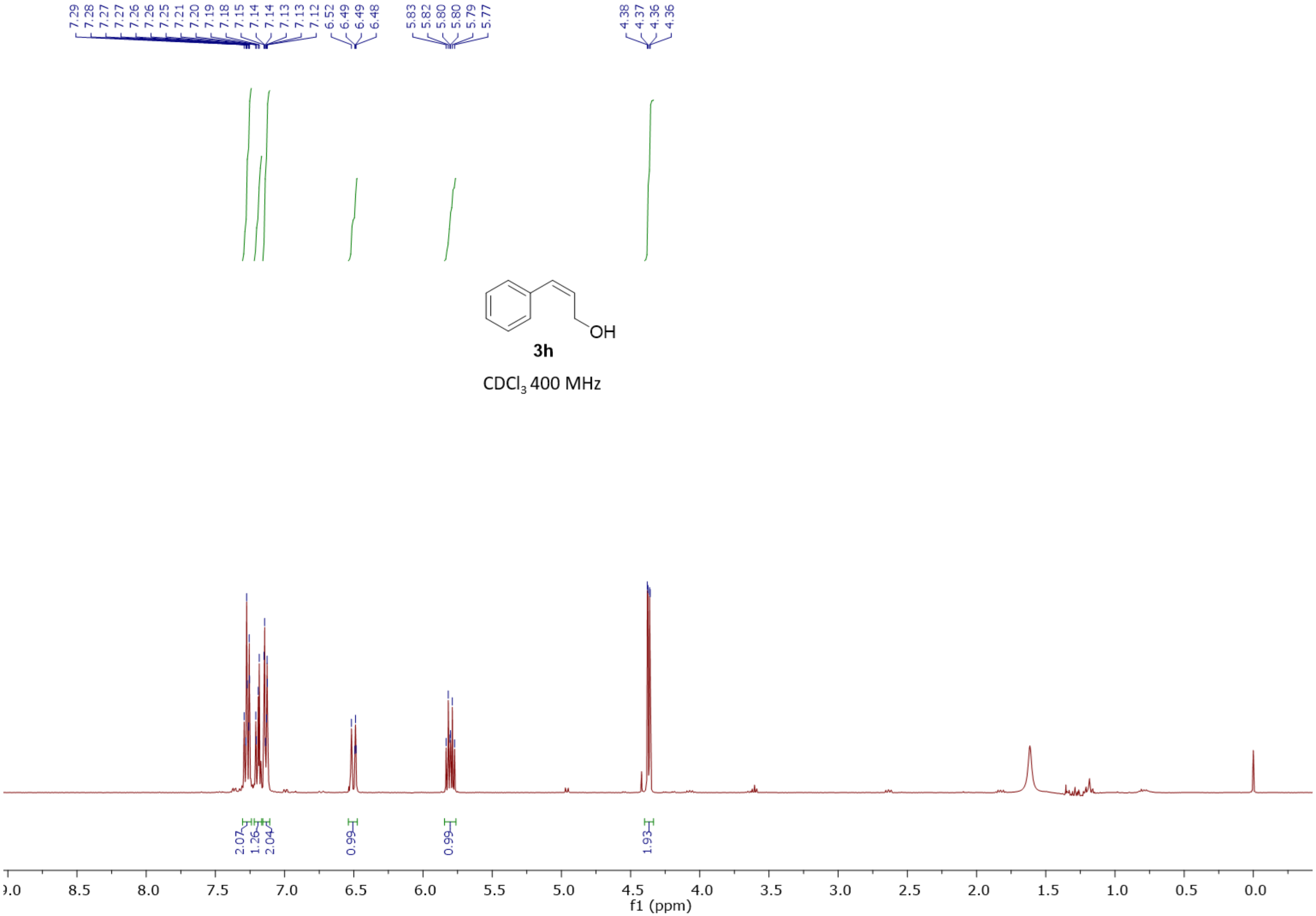

3f
$CDCl_3$ 400 MHz
EtOH
EtOH
4.22
1.19
1.00
1.02
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



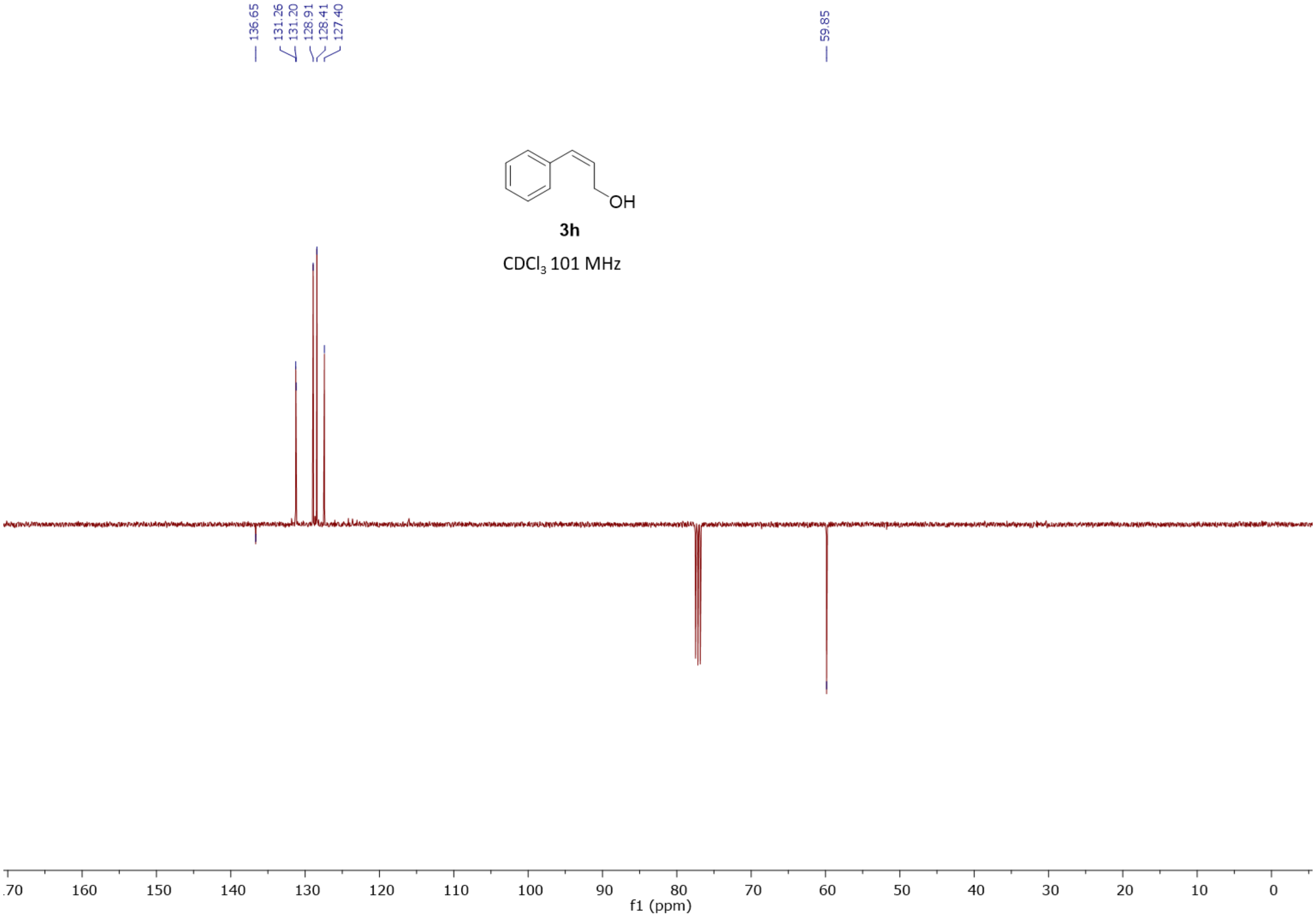
3g

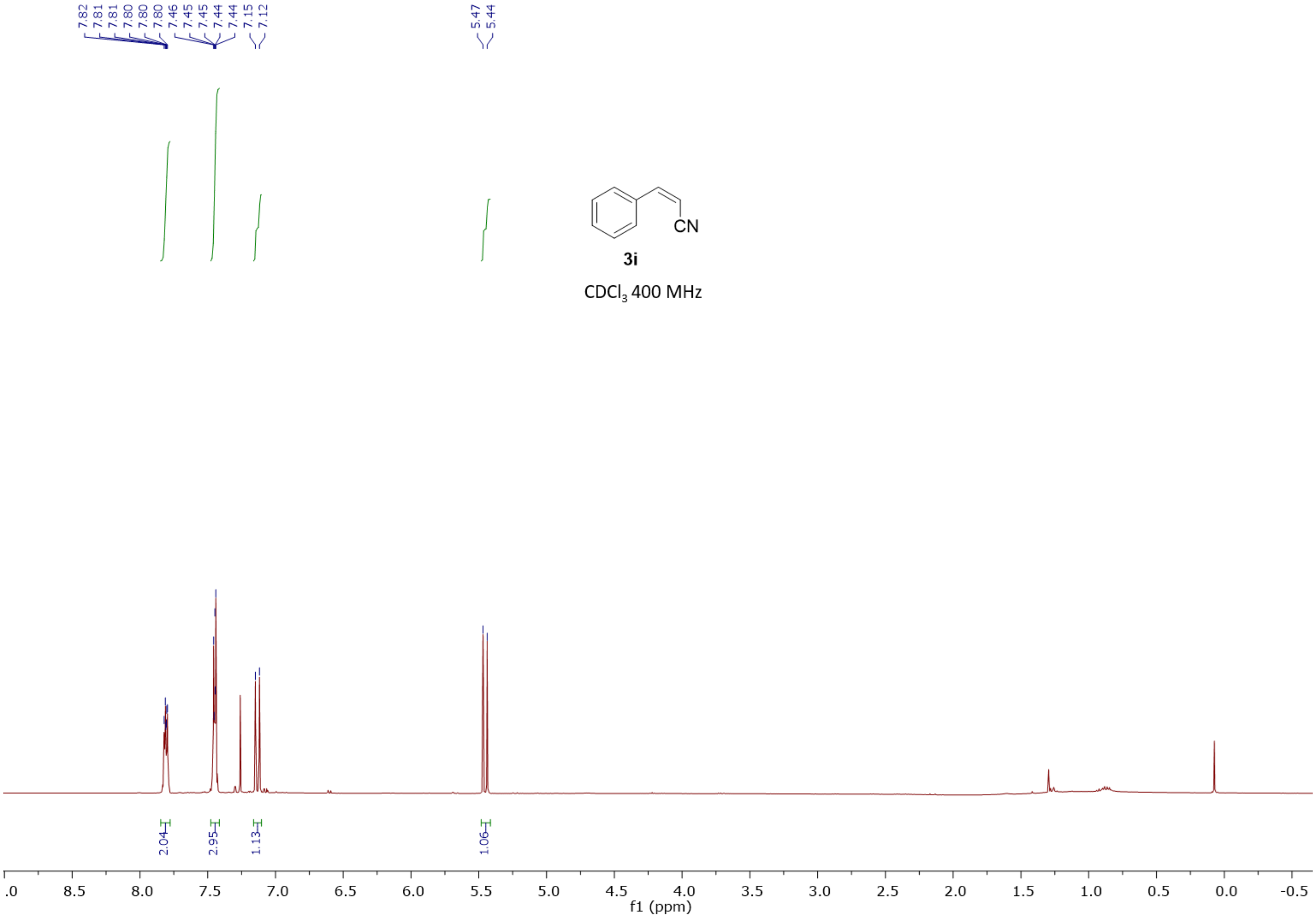
CDCl$_3$ 400 MHz

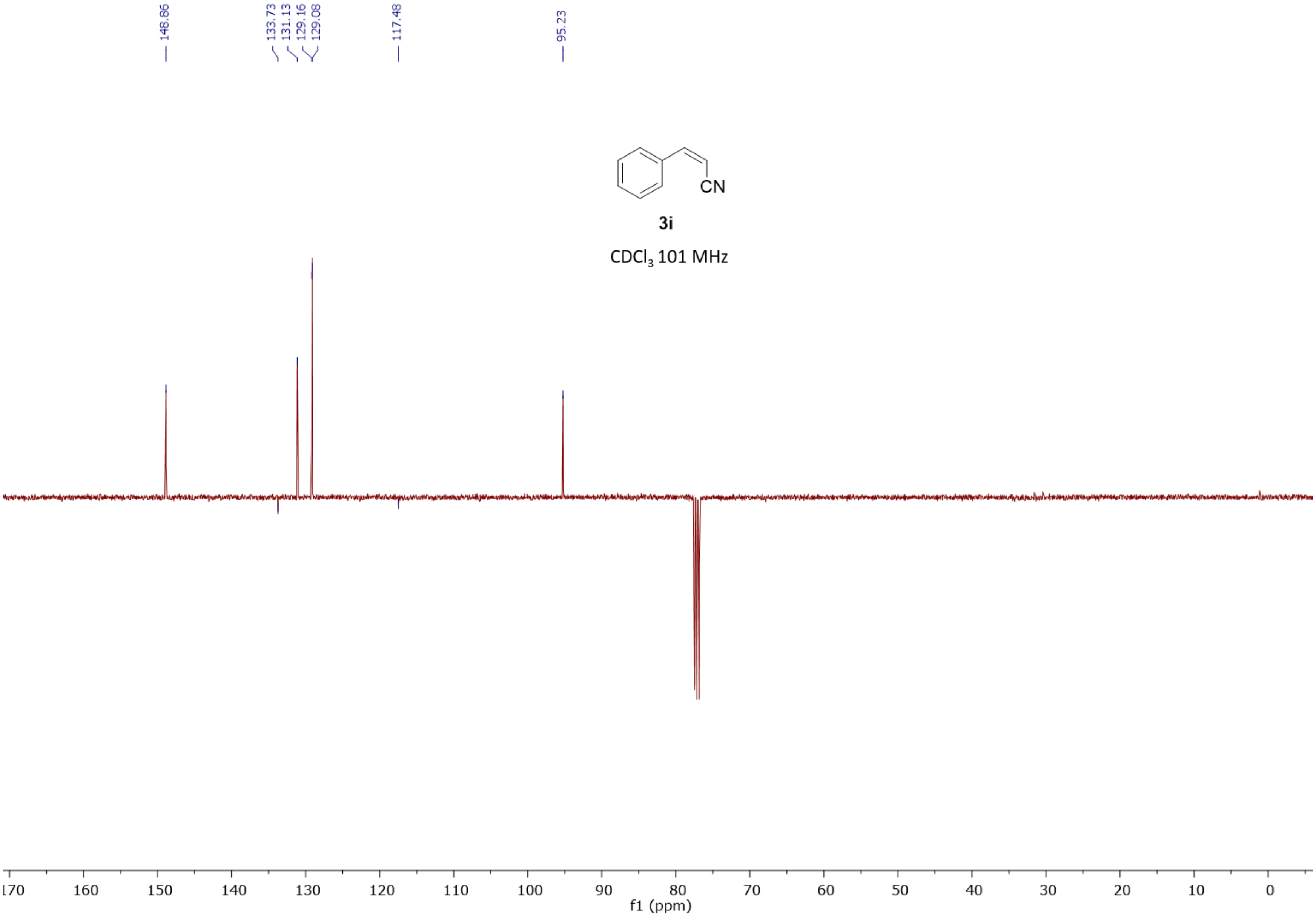

166.38
143.11
135.05
129.82
129.11
128.13
120.06
60.44
14.23
O
OEt
3g
CDCl$_3$ 101 MHz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

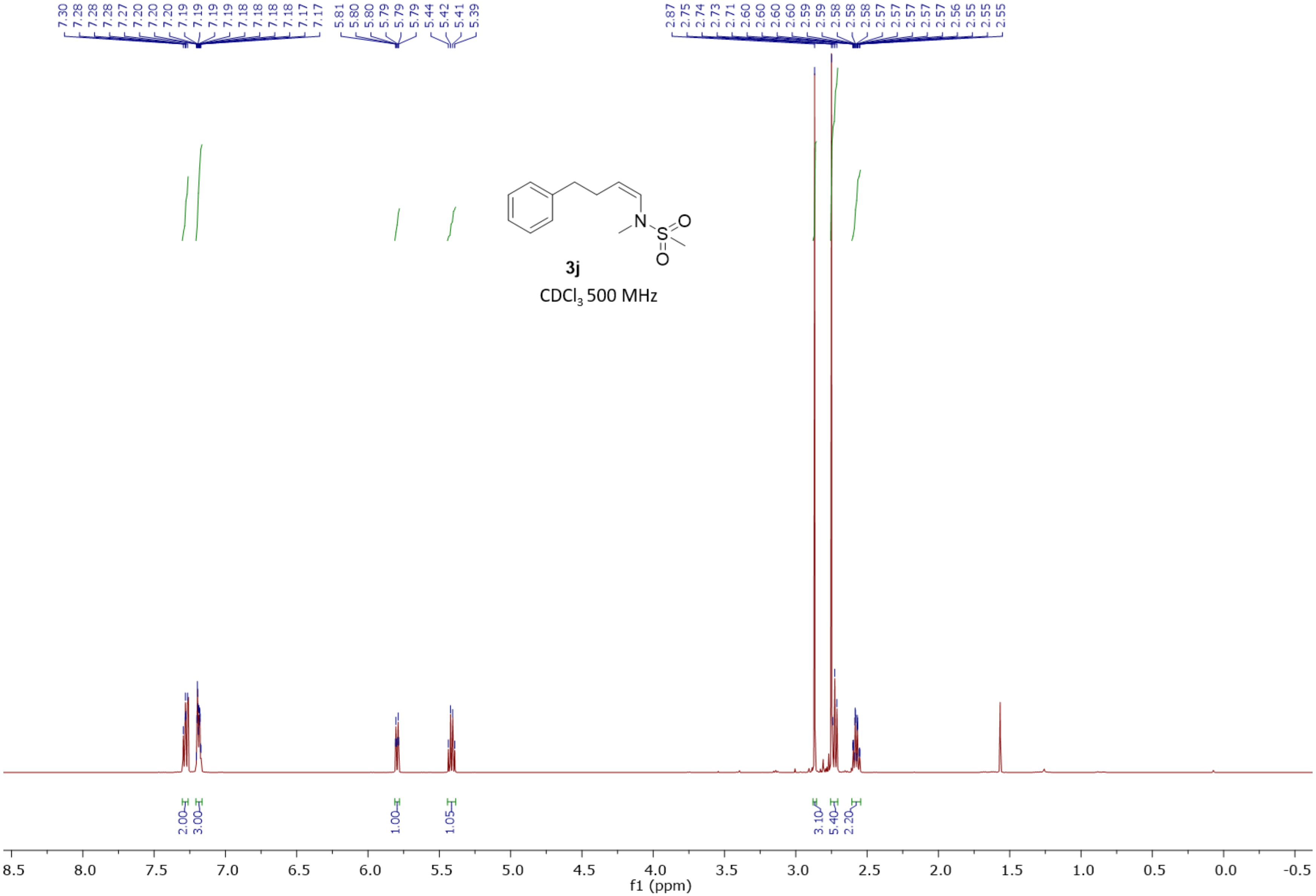

3h

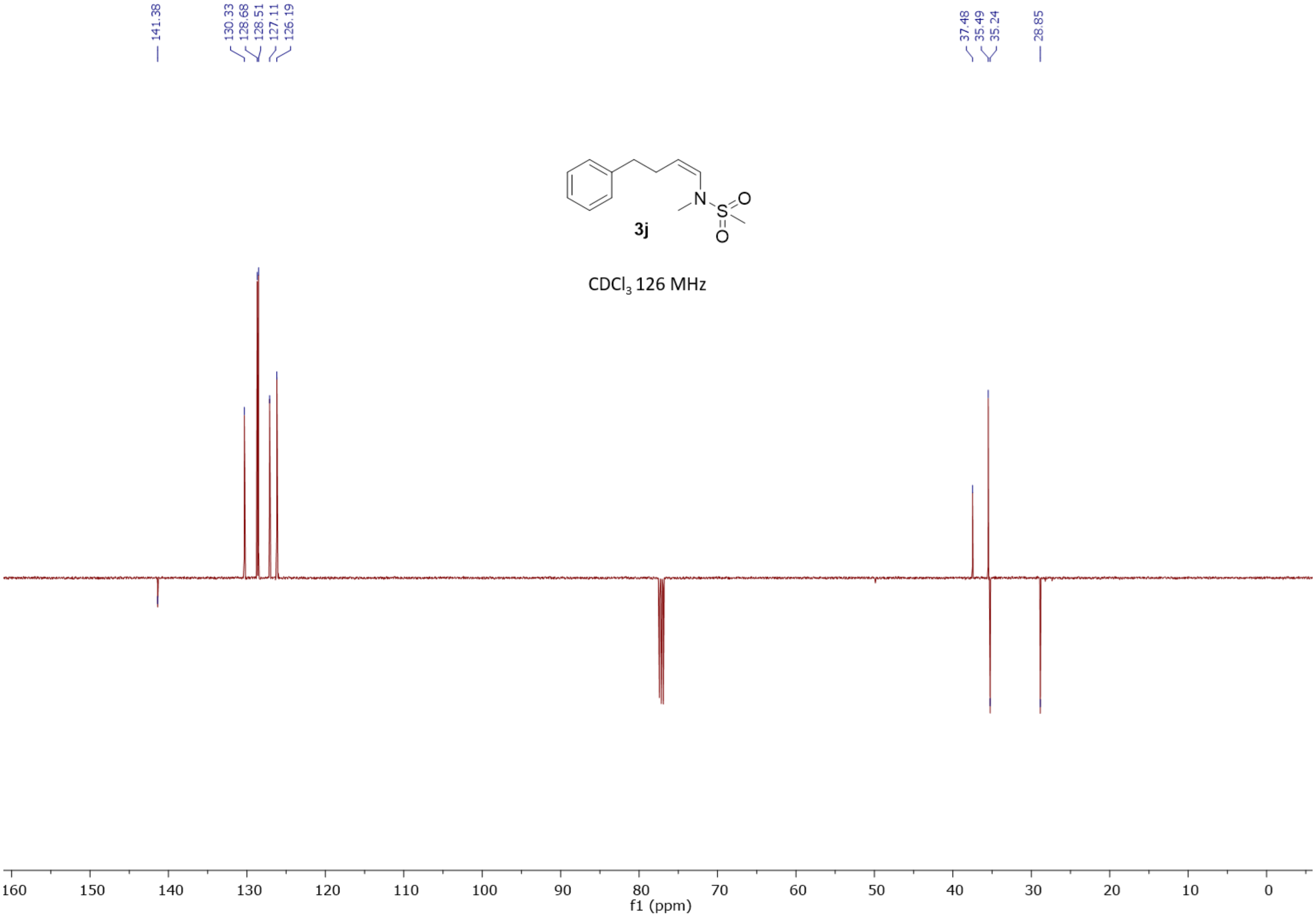
$CDCl_3$ 400 MHz


136.65
131.26
131.20
128.91
128.41
127.40
59.85
OH
3h
$CDCl_3$ 101 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.82
7.81
7.81
7.80
7.80
7.80
7.46
7.45
7.45
7.44
7.44
7.15
7.12
5.47
5.44
CN
3i
$CDCl_3$ 400 MHz
2.04
2.95
1.13
1.06
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

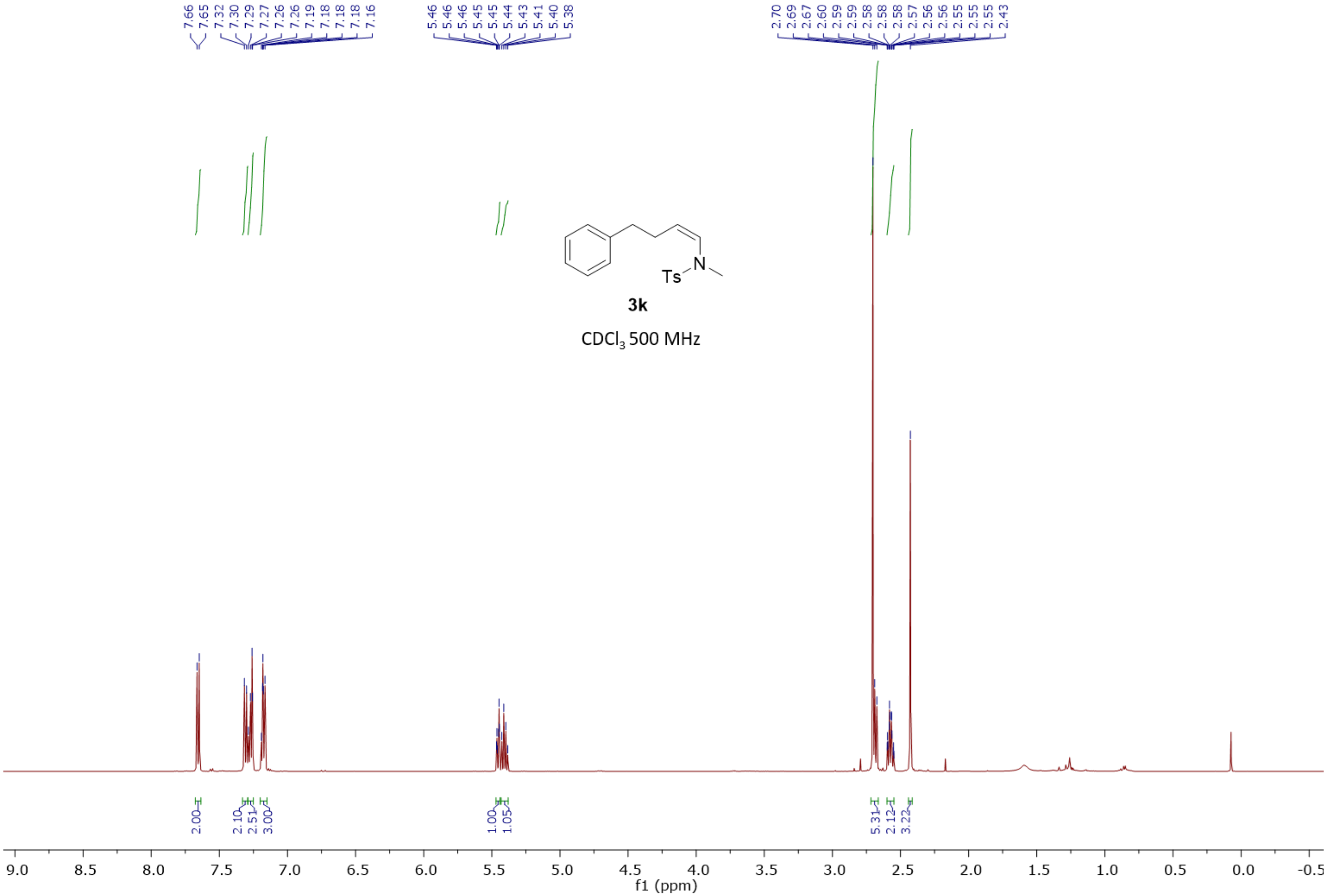

148.86
133.73
131.13
129.16
129.08
117.48
95.23
CN
3i
CDCl$_3$ 101 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.30 7.28 7.28 7.28 7.27 7.20 7.20 7.20 7.19 7.19 7.19 7.19 7.18 7.18 7.18 7.18 7.17 7.17
5.81 5.80 5.80 5.79 5.79 5.79 5.44 5.42 5.41 5.39
2.87 2.75 2.74 2.73 2.71 2.60 2.60 2.60 2.60 2.59 2.59 2.58 2.58 2.58 2.57 2.57 2.57 2.57 2.57 2.56 2.55 2.55 2.55
N
S
O
O
3j
CDCl3 500 MHz
2.00
3.00
1.00
1.05
3.10
5.40
2.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



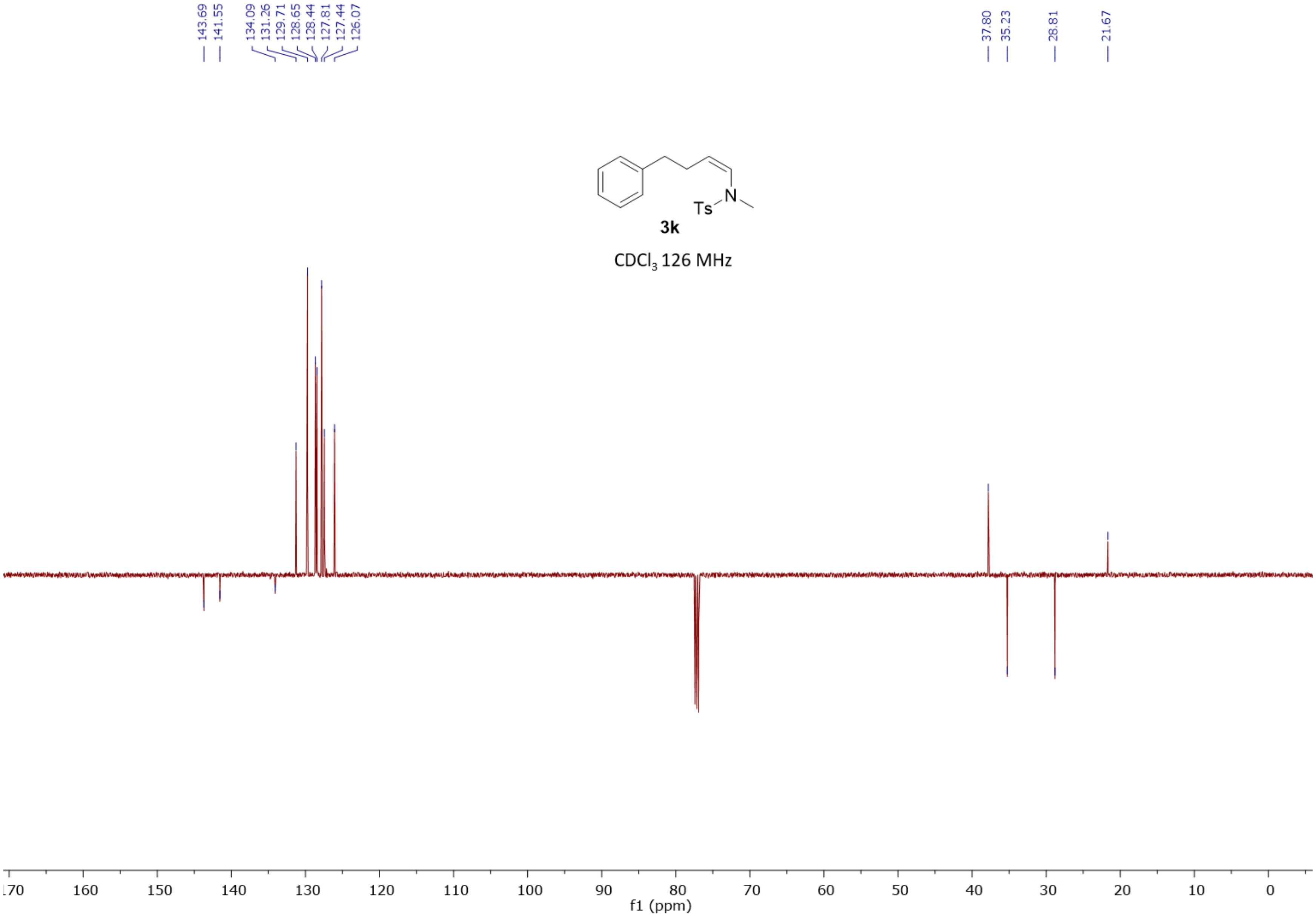
3j

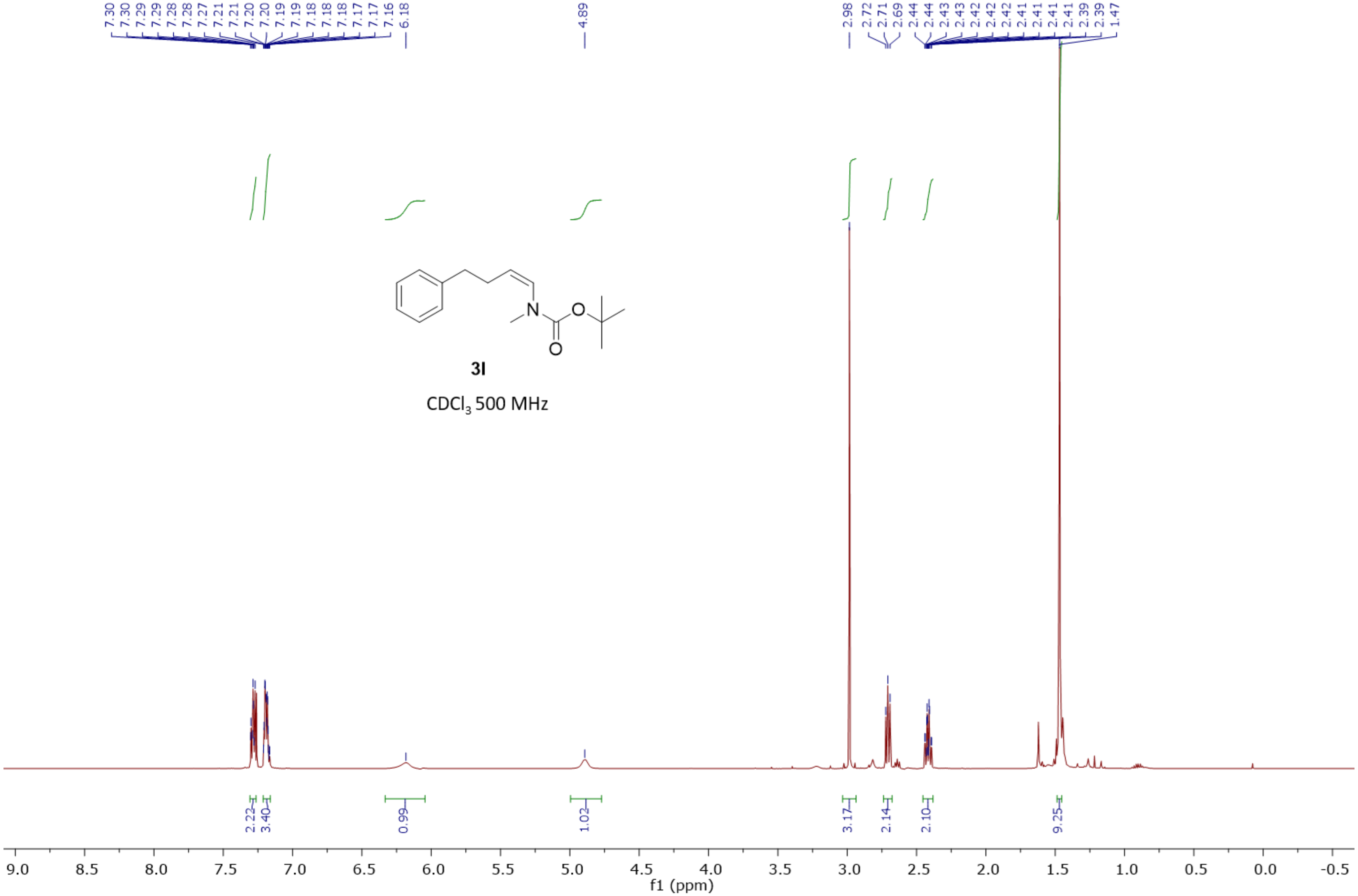
$CDCl_3$ 126 MHz



3k

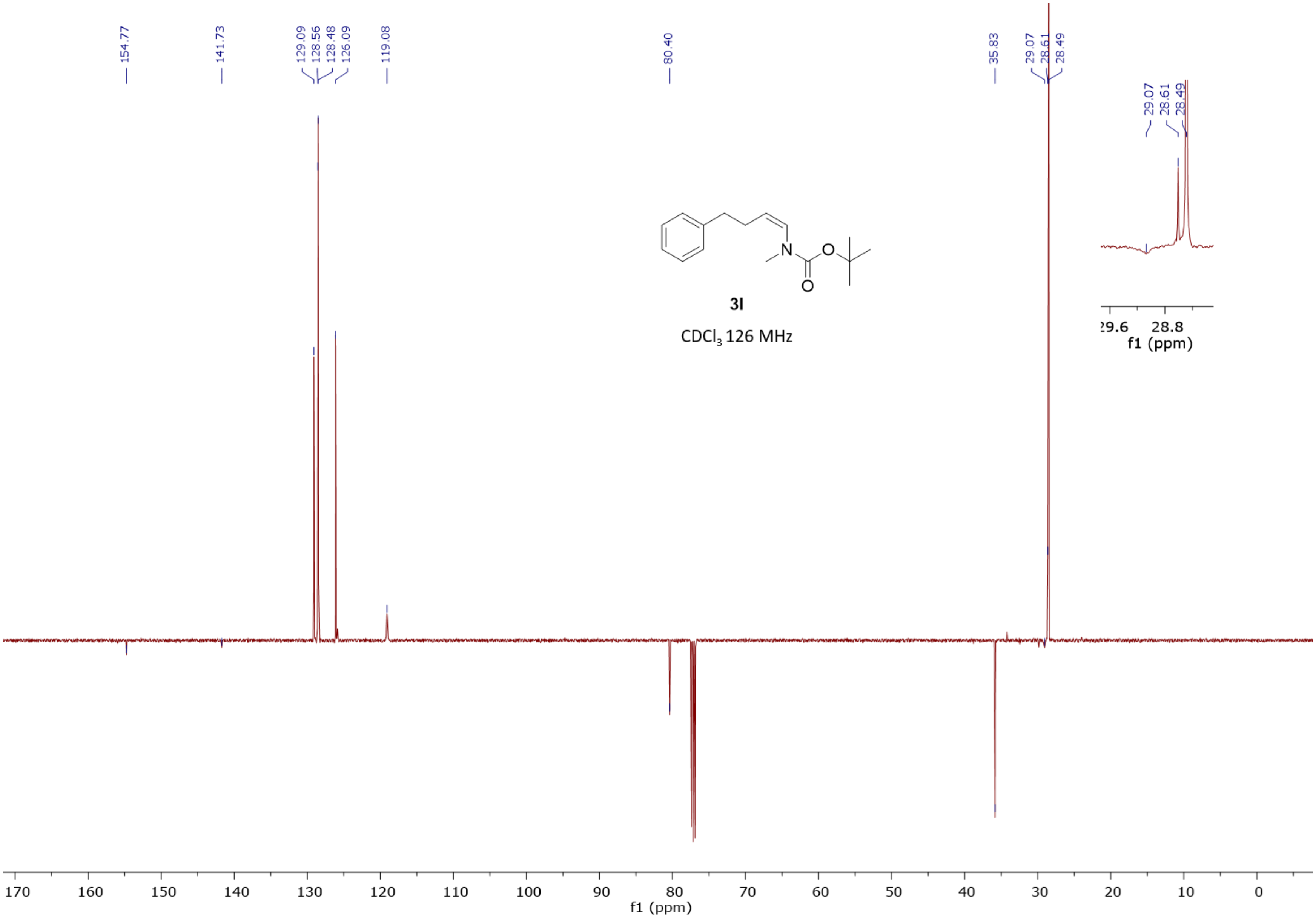
$CDCl_3$ 500 MHz

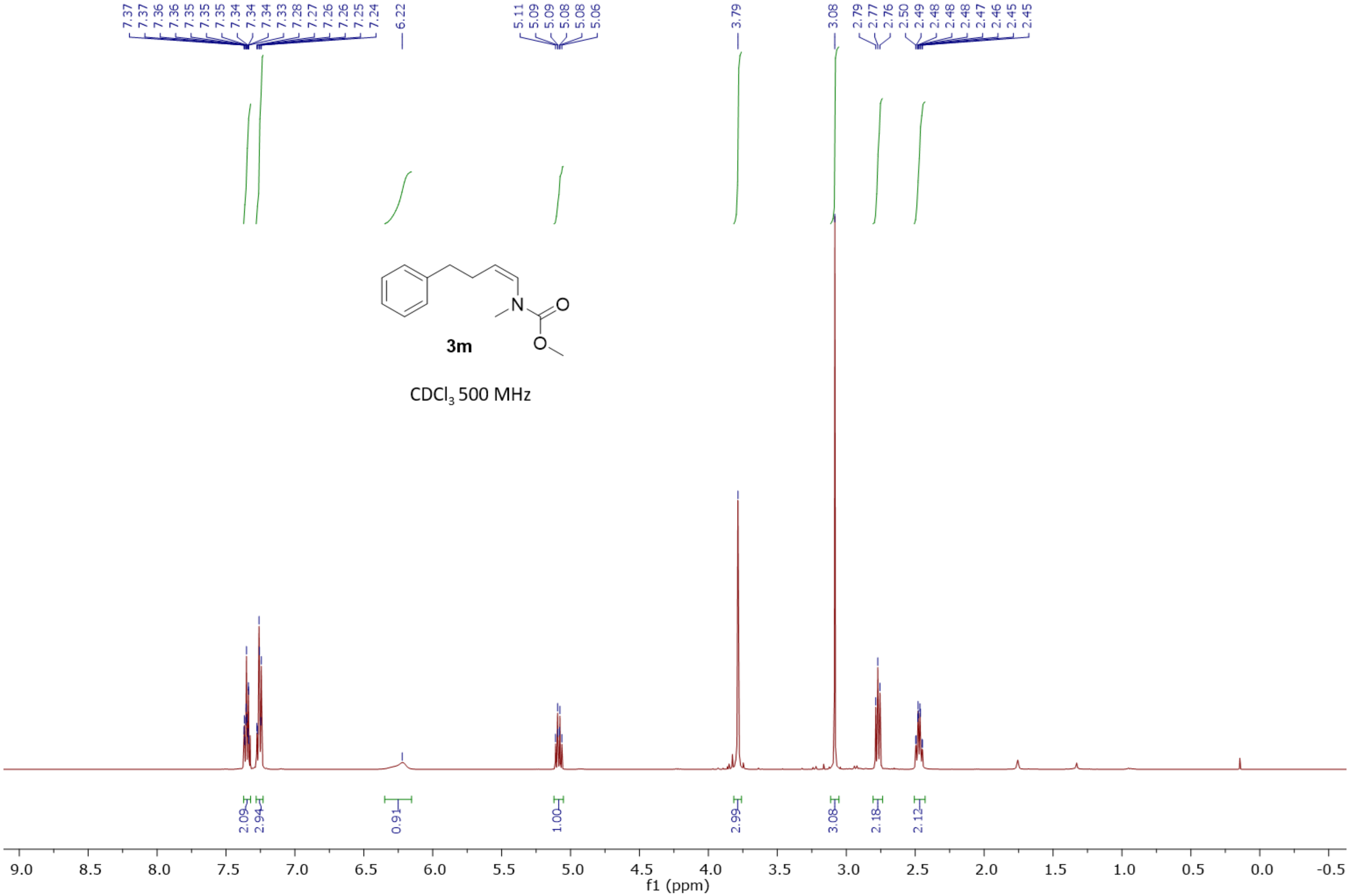

143.69
141.55
134.09
131.26
129.71
128.65
128.44
127.81
127.44
126.07
37.80
35.23
28.81
21.67
Ts
N
3k
CDCl$_3$ 126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

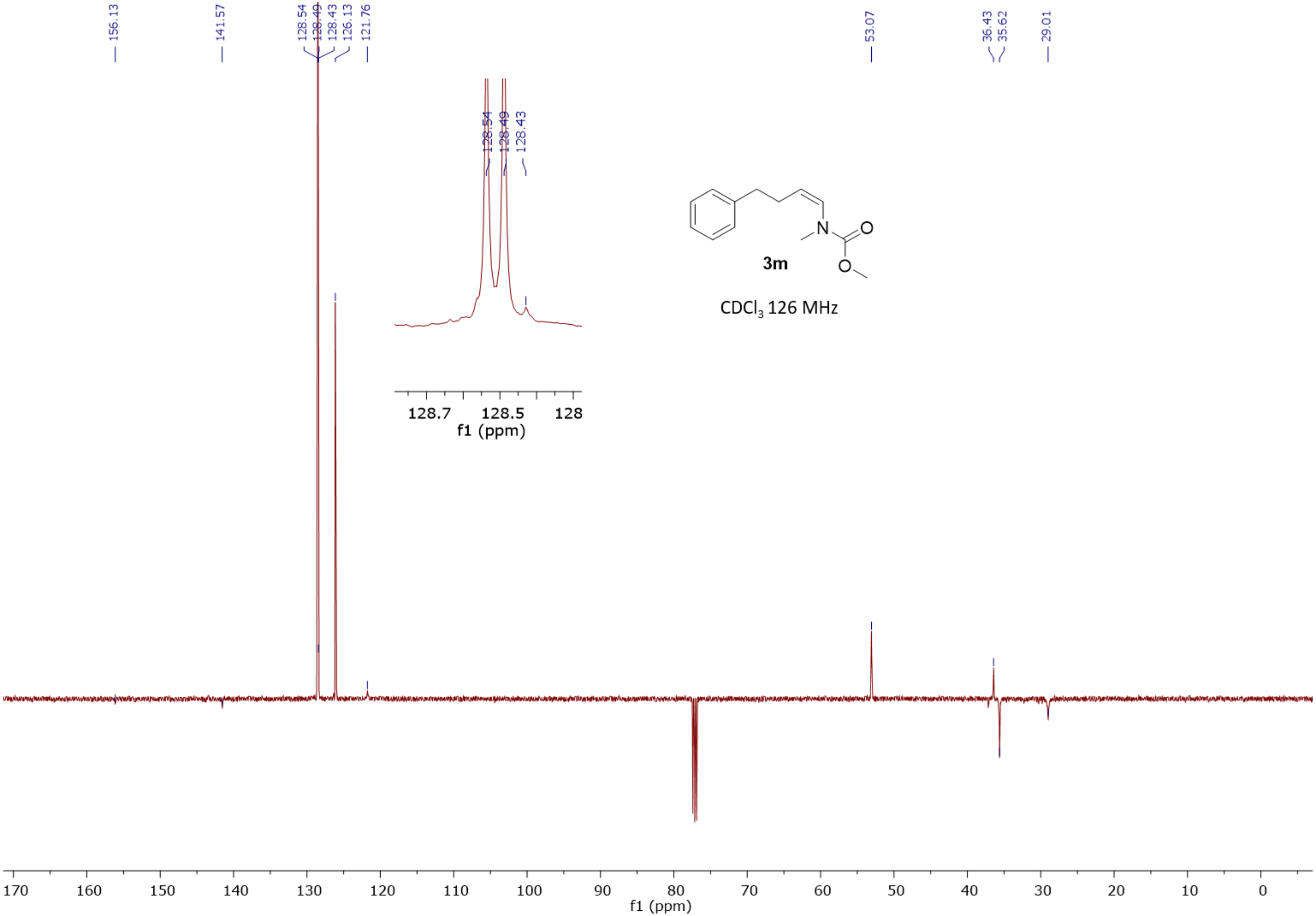


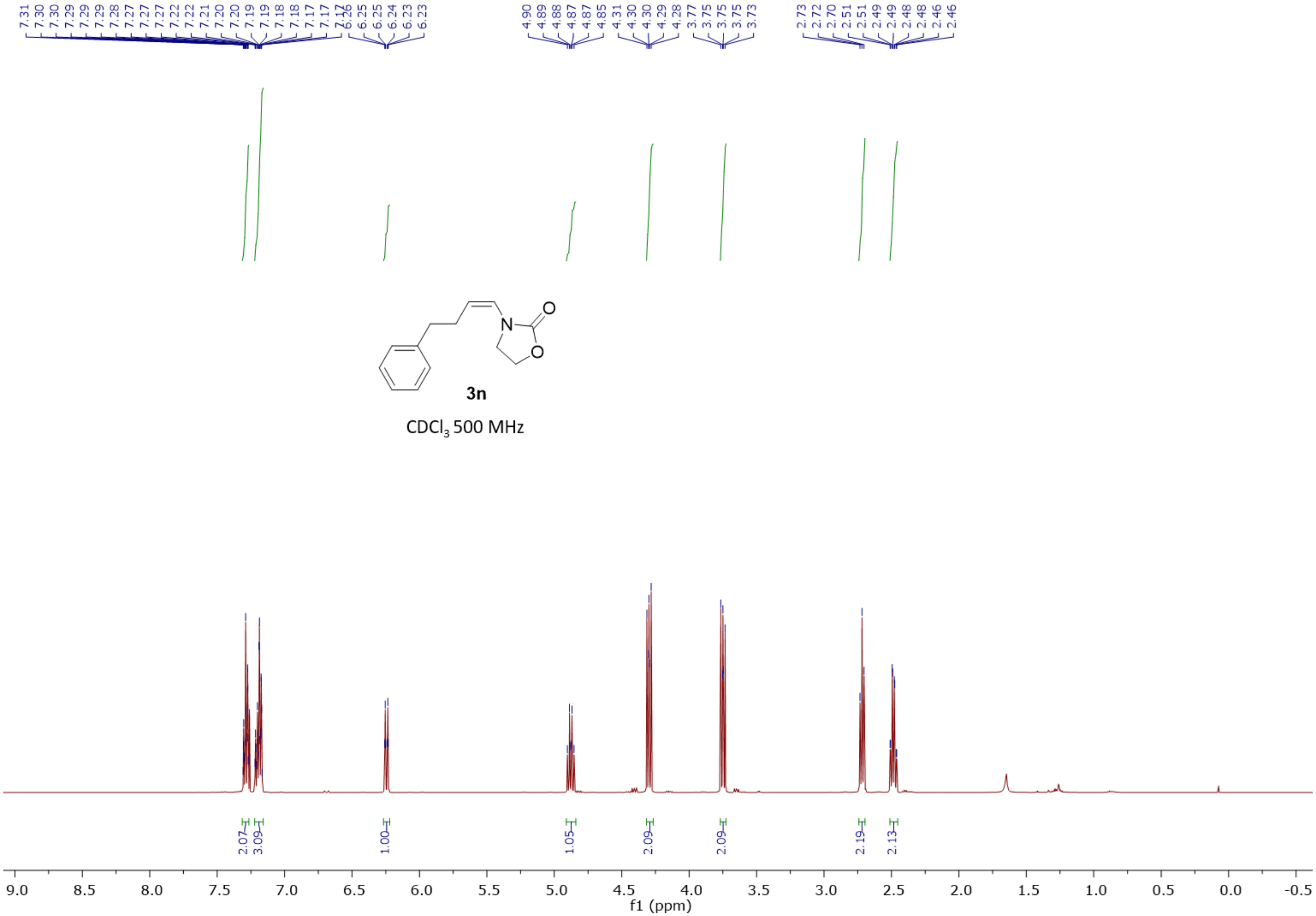
3l

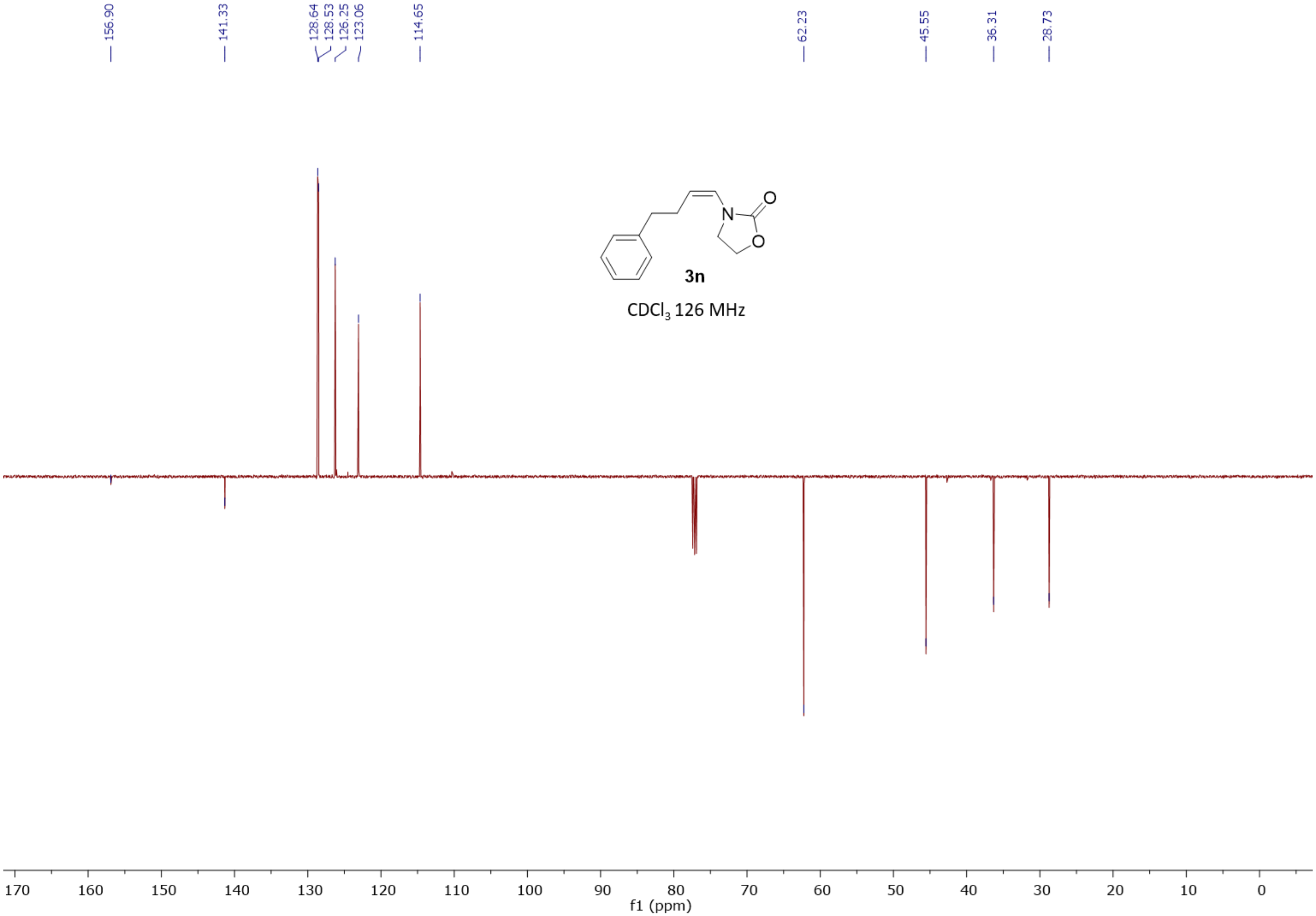
CDCl$_3$ 500 MHz


154.77
141.73
129.09
128.56
128.48
126.09
119.08
80.40
35.83
29.07
28.61
28.49
N
O
O
3l
CDCl$_3$ 126 MHz
29.07
28.61
28.49
29.6
28.8
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.28 7.27 7.26 7.26 7.25 7.24
6.22
5.11 5.09 5.09 5.08 5.08 5.06
3.79
3.08 2.79 2.77 2.76 2.50 2.49 2.48 2.48 2.48 2.47 2.46 2.45 2.45
N
O
O
3m
CDCl$_3$ 500 MHz
2.09
2.94
0.91
1.00
2.99
3.08
2.18
2.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

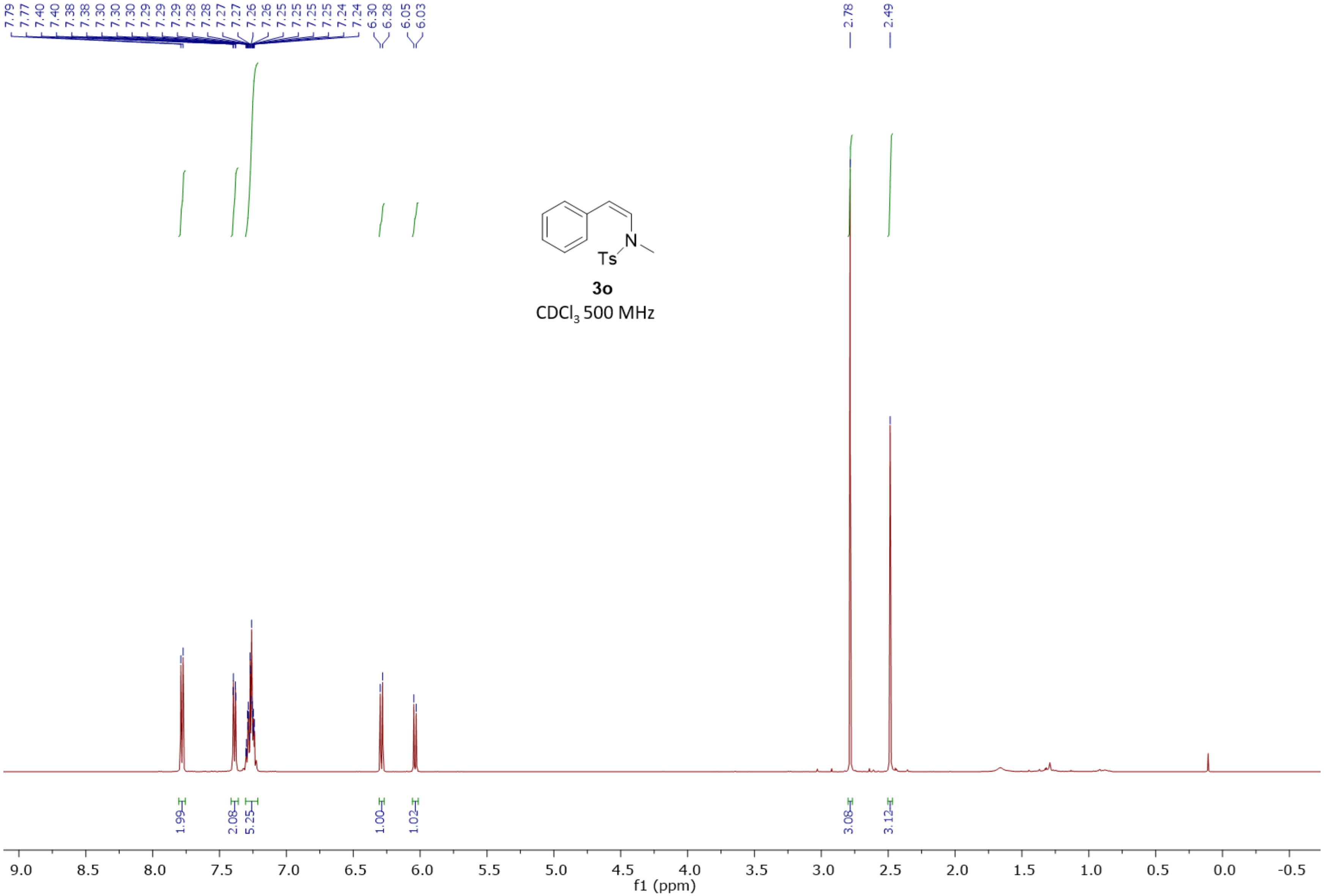

156.13
141.57
128.54
128.49
128.43
126.13
121.76
53.07
36.43
35.62
29.01
128.54
128.49
128.43
128.7
128.5
128
f1 (ppm)
N
O
O
3m
CDCl$_3$ 126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

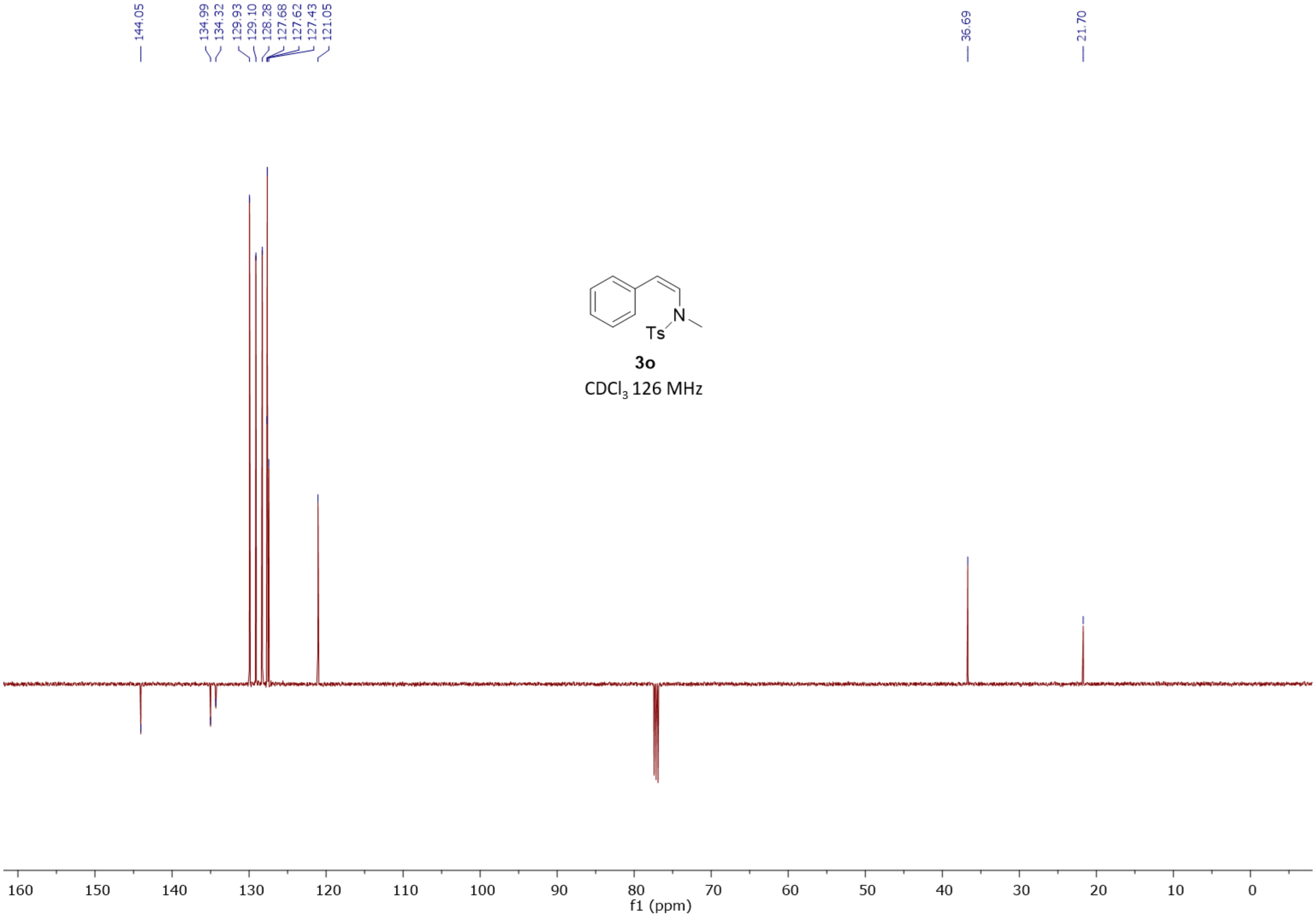

7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.27
7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.17
6.26
6.25
6.25
6.24
6.23
6.23
4.90
4.89
4.88
4.87
4.87
4.85
4.31
4.30
4.30
4.29
4.28
3.77
3.75
3.75
3.75
3.73
2.73
2.72
2.70
2.51
2.51
2.49
2.49
2.48
2.48
2.46
2.46
N
O
O
3n
CDCl3 500 MHz
2.07
3.09
1.00
1.05
2.09
2.09
2.19
2.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

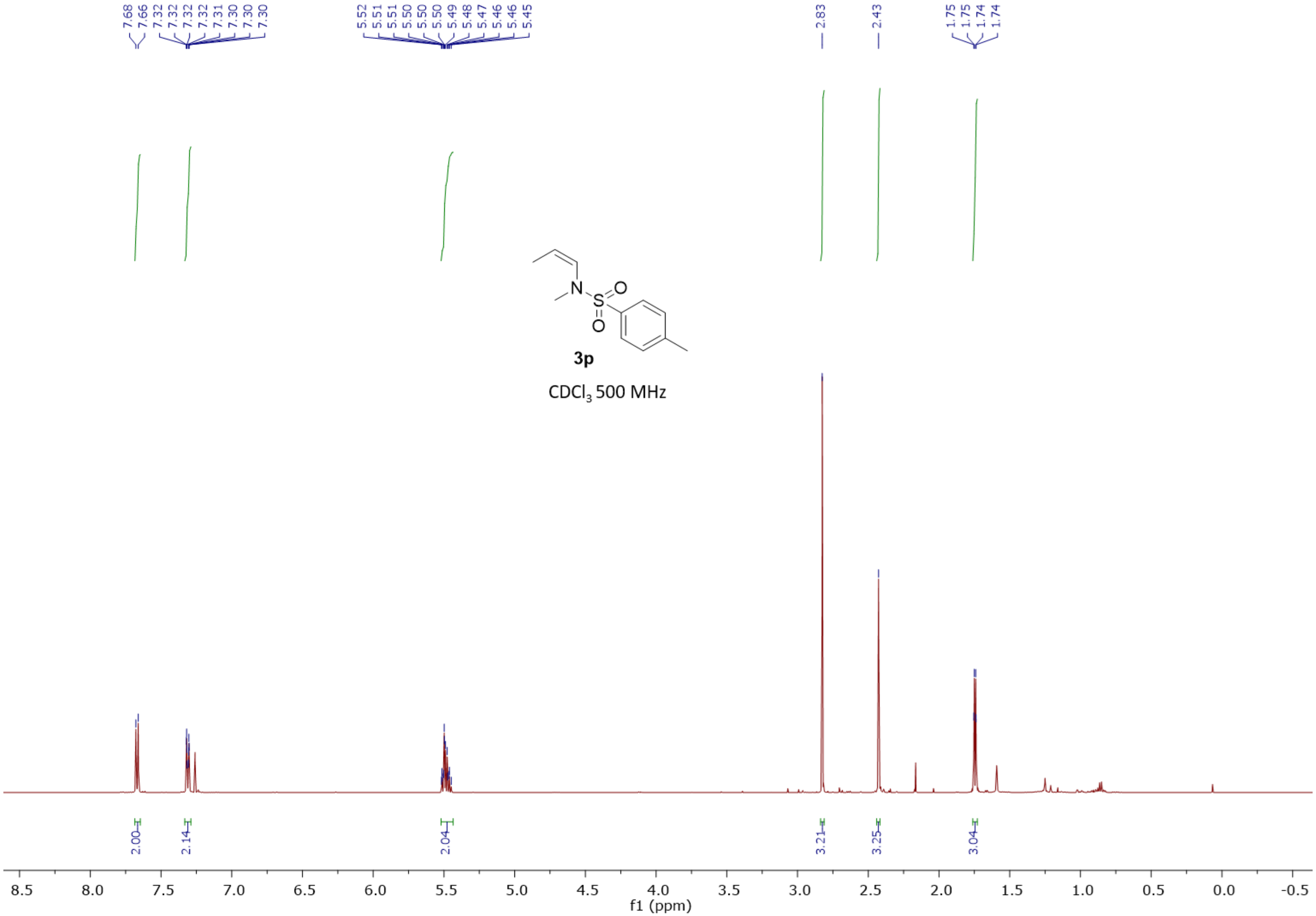


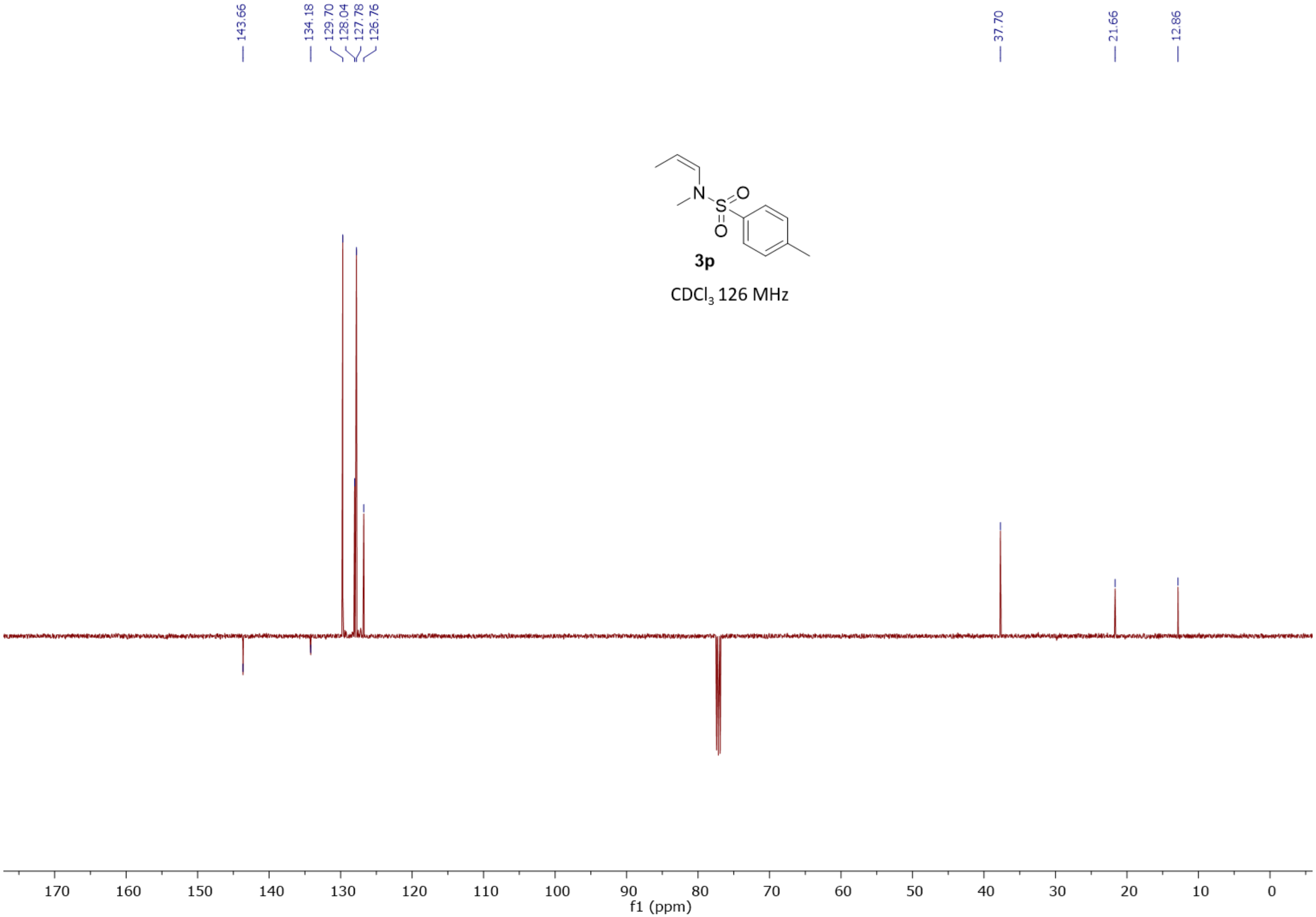
3n

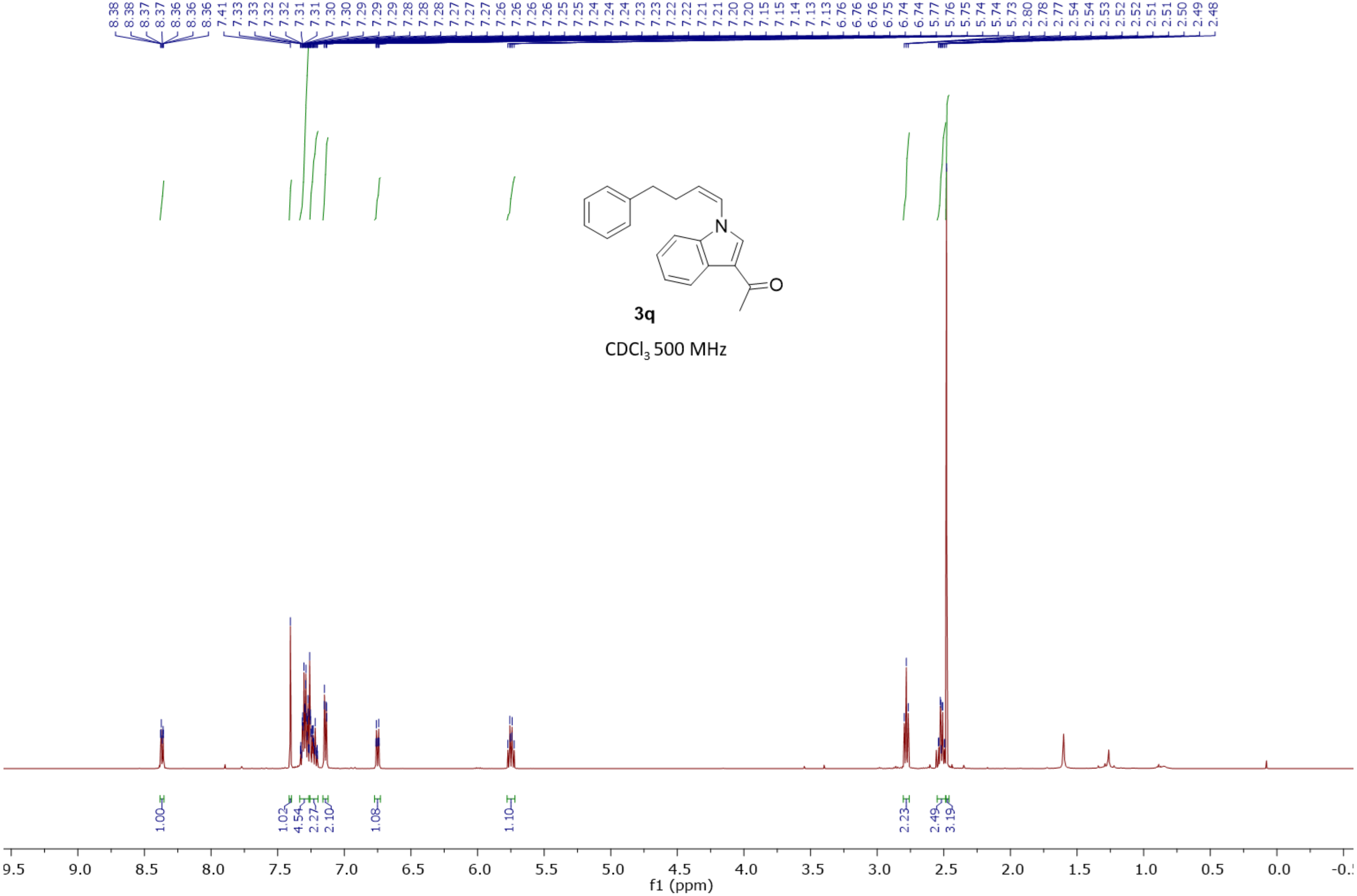
$CDCl_3$ 126 MHz

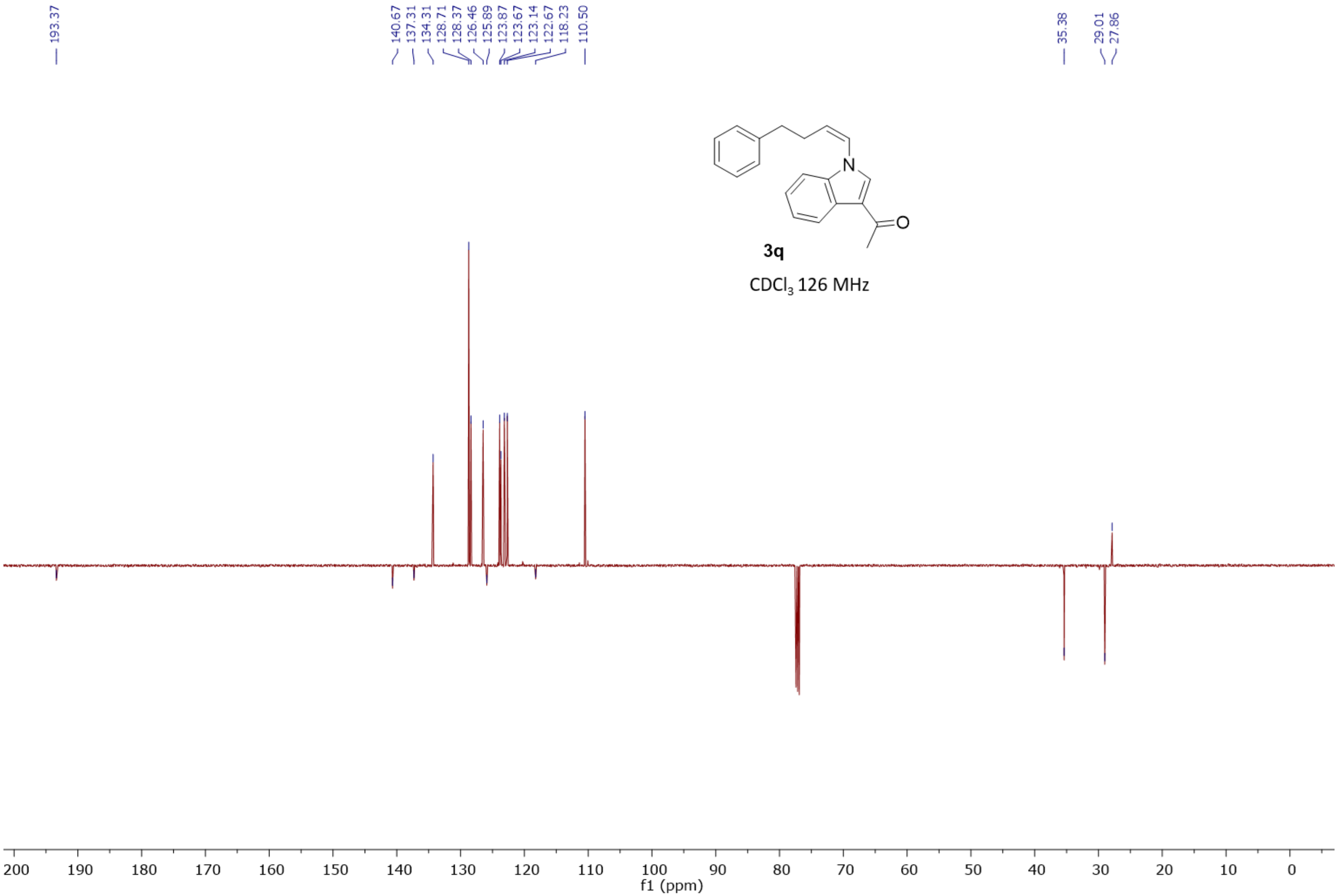

7.79
7.77
7.40
7.40
7.38
7.38
7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.25
7.25
7.24
7.24
6.30
6.28
6.05
6.03
2.78
2.49
N
Ts
3o
CDCl$_3$ 500 MHz
1.99
2.08
5.25
1.00
1.02
3.08
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

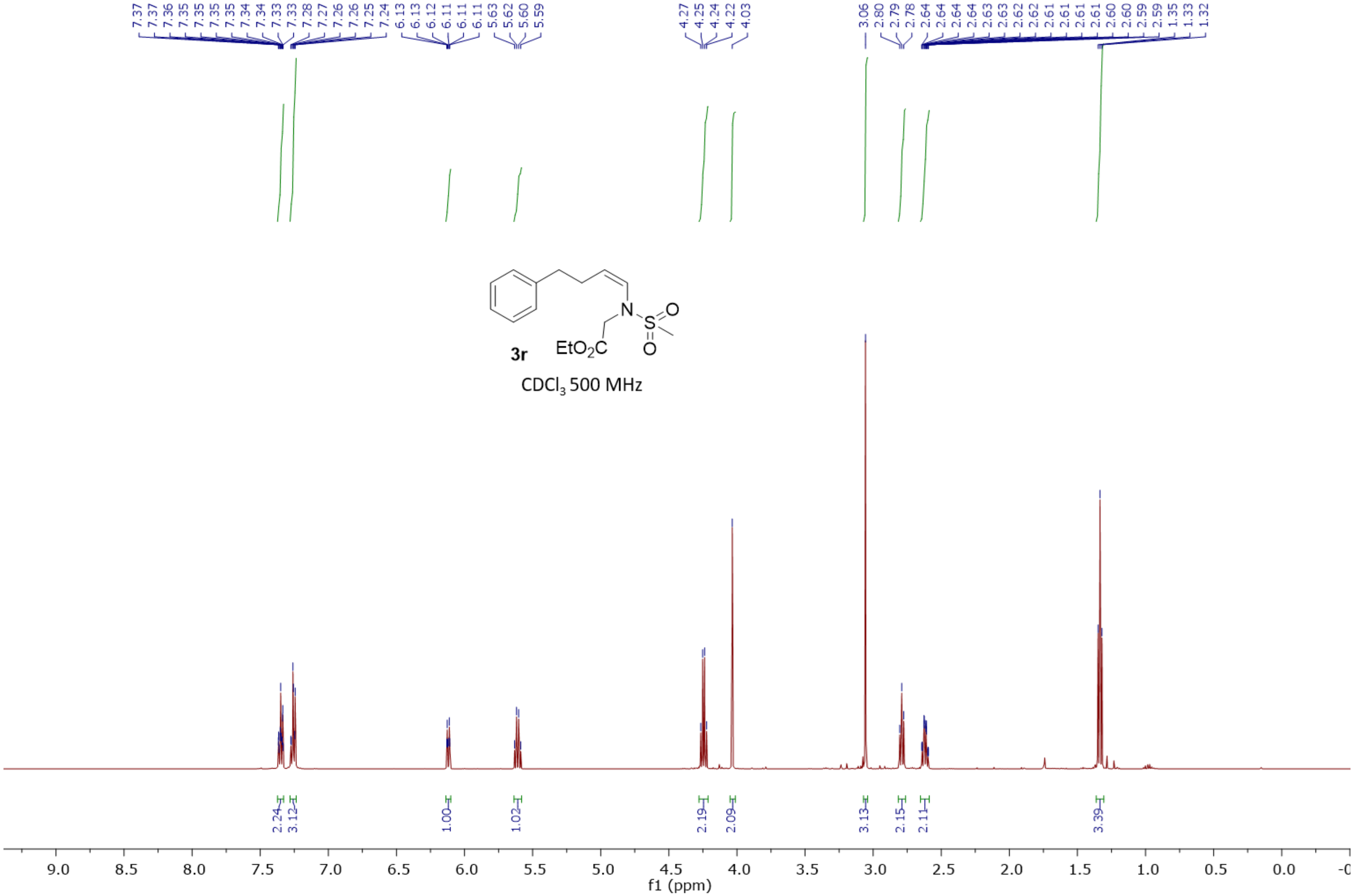

144.05
134.99
134.32
129.93
129.10
128.28
127.68
127.62
127.43
121.05
36.69
21.70
N
Ts
3o
CDCl3 126 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

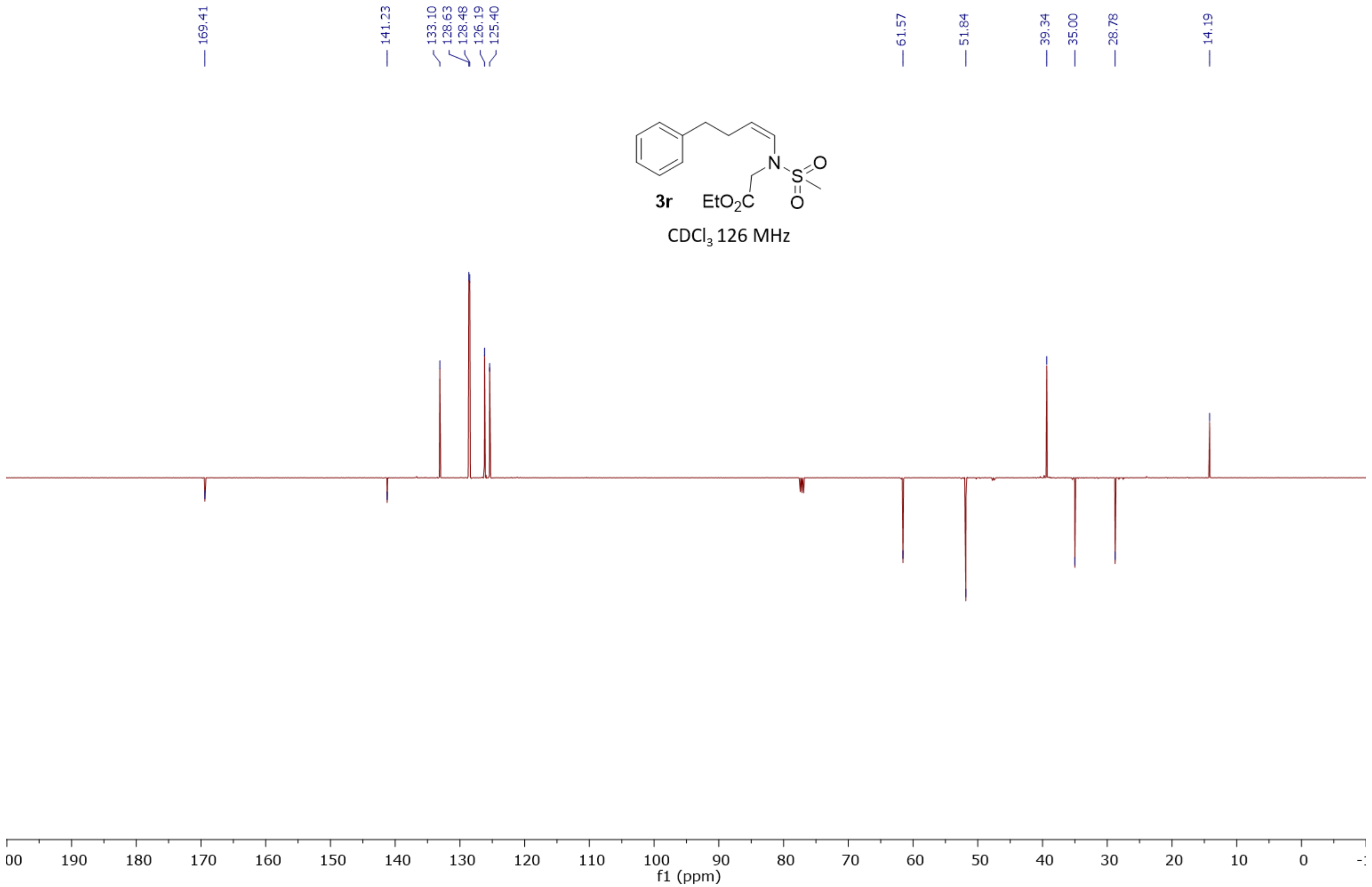

7.68
7.66
7.32
7.32
7.32
7.32
7.31
7.30
7.30
7.30
5.52
5.51
5.51
5.50
5.50
5.50
5.49
5.48
5.47
5.46
5.45
2.83
2.43
1.75
1.75
1.74
1.74
N
S
O
O
3p
CDCl$_3$ 500 MHz
2.00
2.14
2.04
3.21
3.25
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


143.66
134.18
129.70
128.04
127.78
126.76
37.70
21.66
12.86
3p
CDCl3 126 MHz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.38
8.38
8.37
8.37
8.36
8.36
8.36
7.41
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.15
7.15
7.14
7.13
7.13
6.76
6.76
6.75
6.74
6.74
5.77
5.76
5.75
5.74
5.74
5.73
2.80
2.78
2.77
2.54
2.54
2.53
2.52
2.52
2.51
2.51
2.50
2.49
2.48
N
O
3q
CDCl$_3$ 500 MHz
1.00
1.02
4.54
2.27
2.10
1.08
1.10
2.23
2.49
3.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


193.37
140.67
137.31
134.31
128.71
128.37
126.46
125.89
123.87
123.67
123.14
122.67
118.23
110.50
35.38
29.01
27.86
N
O
3q
CDCl$_3$ 126 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37
7.37
7.36
7.35
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.28
7.27
7.26
7.26
7.25
7.24
6.13
6.13
6.12
6.11
6.11
6.11
5.63
5.62
5.60
5.59
4.27
4.25
4.24
4.22
4.03
3.06
2.80
2.79
2.78
2.64
2.64
2.64
2.64
2.63
2.63
2.62
2.62
2.62
2.61
2.61
2.61
2.61
2.60
2.59
2.59
1.35
1.33
1.32
N
S
O
O
EtO2C
3r
CDCl3 500 MHz
2.24
3.12
1.00
1.02
2.19
2.09
3.13
2.15
2.11
3.39
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


169.41
141.23
133.10
128.63
128.48
126.19
125.40
61.57
51.84
39.34
35.00
28.78
14.19
N
S
O
O
3r
EtO$_2$C
CDCl$_3$ 126 MHz
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)