Radical Germylzincation of *α*-Heteroatom-Substituted Alkynes

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Supporting Information

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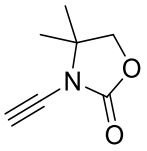
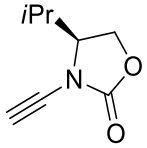
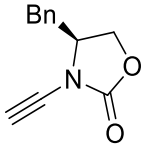
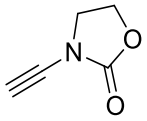
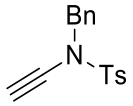
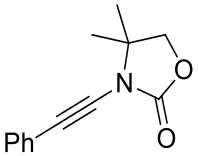
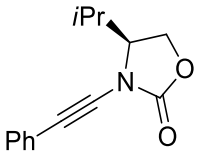
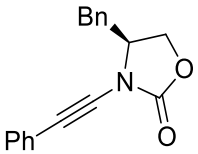
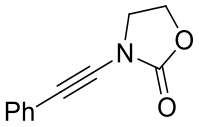
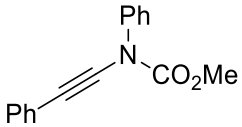
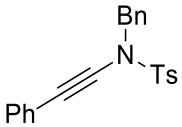
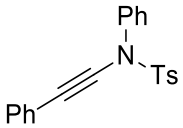
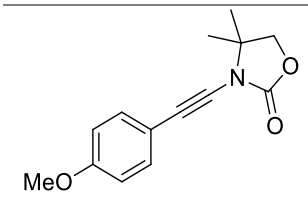
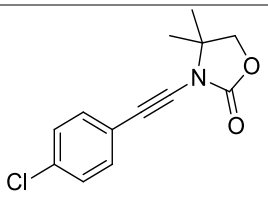
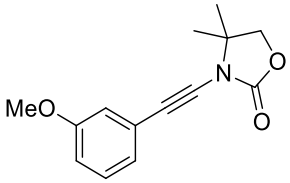
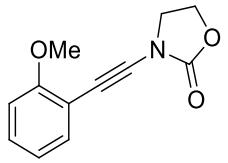
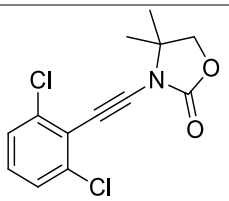
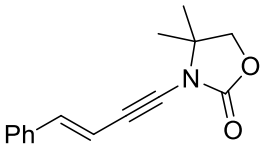
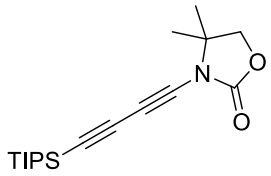
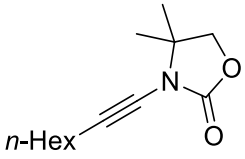
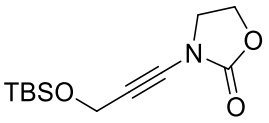
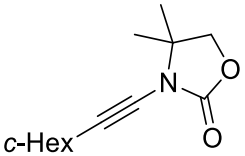
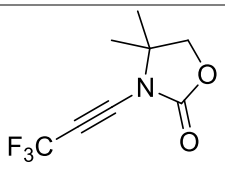
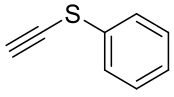
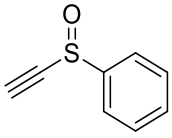
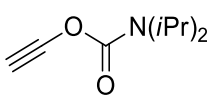
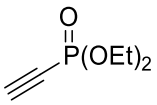
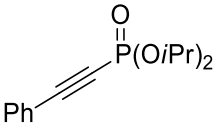
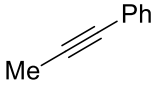
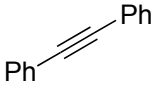
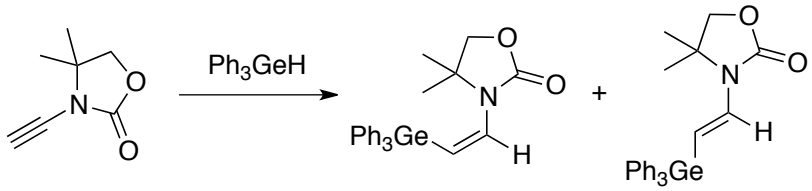
 **1**	 **S1**	 **S2**	 **S3**
 **S4**	 **S5**	 **S6**	 **S7**
 **S8**	 **S9**	 **S10**	 **S11**
 **S12**	 **S13**	 **S14**	 **S15**
 **S16**	 **S17**	 **S18**	 **S19**
 **S20**	 **S21**	 **S22**	 **S23**
 **S24**	 **S25**	 **S26**	 **S27**
 **S28**	 **S29**		

II Additional Data and Discussion

II.1 Optimization of the Hydrogermylation of Ynamide 1 with Ph_3GeH and Verification of the Radical Mechanism



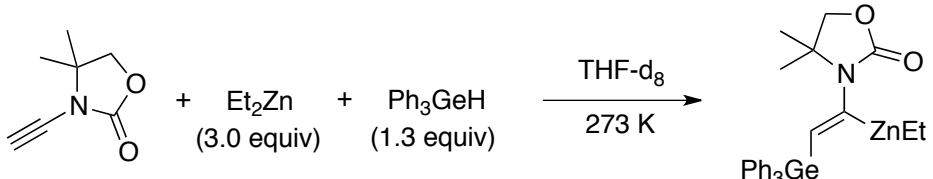
1 *Z*-**2** *E*-**2**

Entry	Conditions	Additive	Ph_3GeH (equiv)	2/1[a] (ratio)	d.r. 2 (*Z*/*E*)[a]	Yield 2 (%)[b] [*Z*/*E*]
1	*n*-hexane, 0 °C, 3 h	–	1.3	59:41	>98:2	–
2	THF, 0 °C, 3 h	–	1.3	48:52	>98:2	–
3	THF, rt, 16 h	–	1.3	80:20	96:4	–
4	**THF, rt, 16 h**	**–**	**2.0**	**98:2**	**96:4**	**84 [96:4]**
5	THF, 40 °C, 4 h	–	2.0	100:0	93:7	91 [93:7]
6	THF, 0 °C, 3 h	TEMPO (10 mol%)	1.3	0:100	–	–
7	THF, 40 °C, 4 h	TEMPO (20 mol%)	2.0	0:100	–	–

[a]Determined by ^{1}H NMR prior to purification. [b]Yield of isolated **2** as a mixture of diastereomers.

II.2 ^{1}H NMR Monitoring Experiments

II.2.1 Monitoring of the Reaction between Ph_3GeH / Et_2Zn and Ynamide 1 in THF at 0 °C



1 (1.0 equiv) **VII**

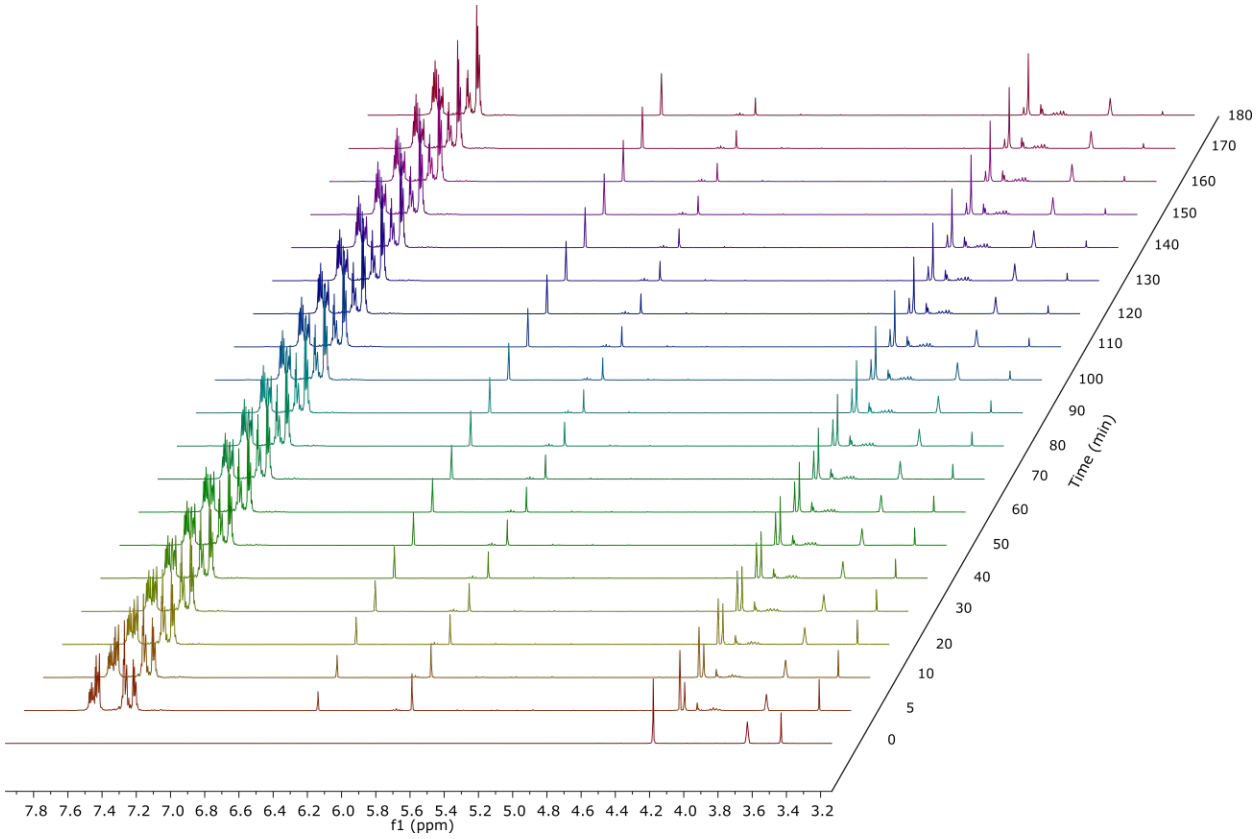
Procedure:

A reference spectrum (used for t = 0) was recorded at 273 K for ynamide **1** (8 mg, 0.06 mmol) dissolved in THF-d_8 (0.5 mL).

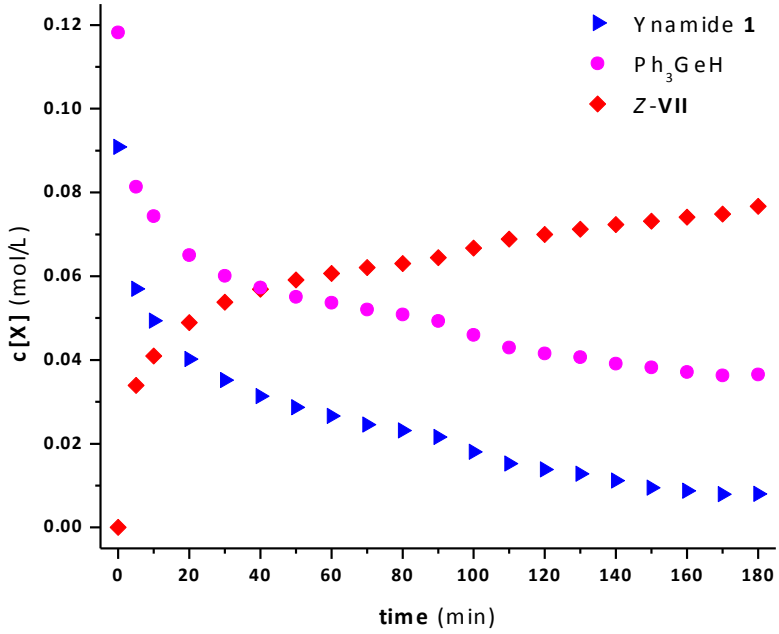
Then, the monitored sample was prepared. In a dry Schlenk tube, ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) was dissolved in THF-d_8 (1.5 mL) and cooled to 0 °C. Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv), followed by Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) in THF-d_8

(0.5 mL) were added (**t = 0**) and an aliquot (~0.5 mL) was transferred to a J Young NMR tube under argon atmosphere. The tube was immediately placed in the NMR probe at 273 K. ^{1}H NMR spectra were recorded every 5 min during 3 h.

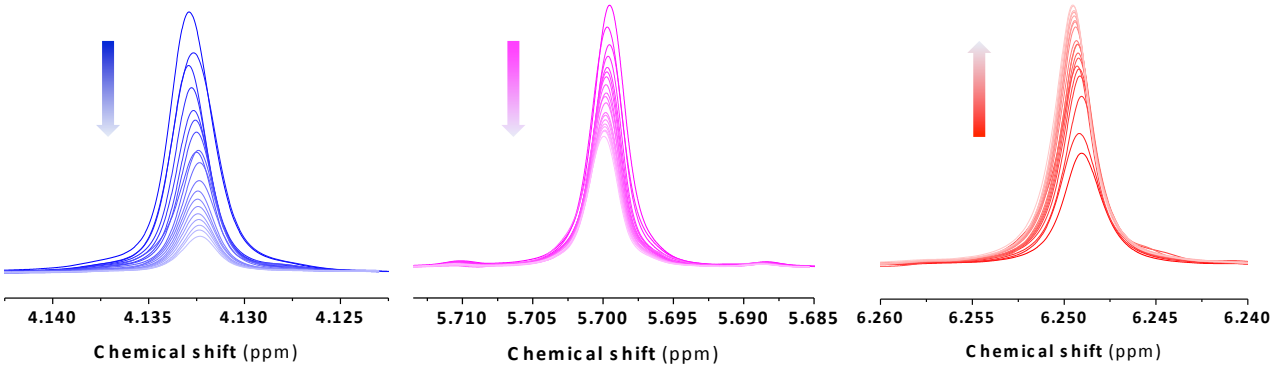
Evolution of the [8.0–3.0 ppm] region of the ^{1}H NMR spectra:

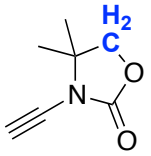


*Evolution of the concentration of **1**, Ph_3GeH and Z-**VII**:*



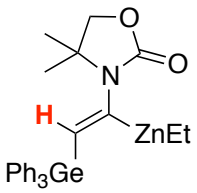
The concentration of **1**, Ph_3GeH and (*Z*)-**VII** was determined on the basis of the integration of the following signals in the ^1H NMR spectra:





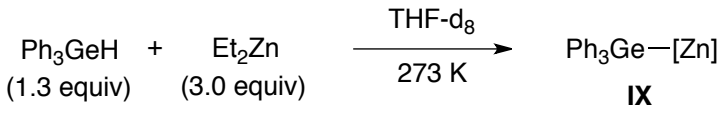
1

Ph_3GeH



Z-**VII**

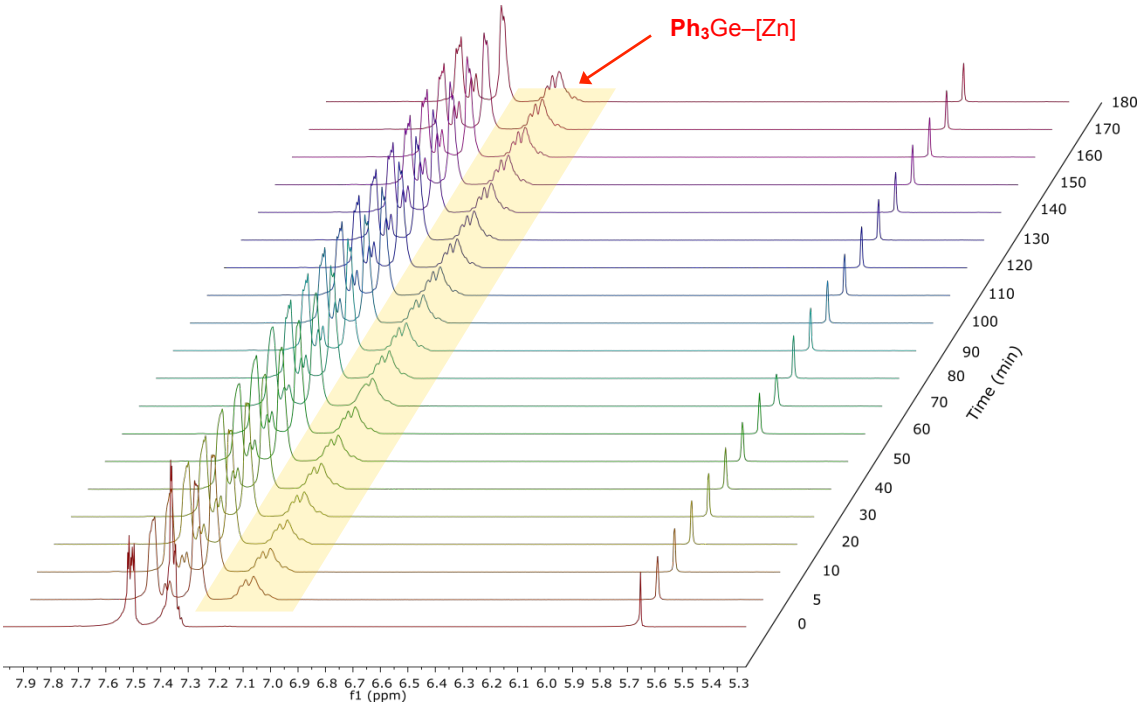
II.2.2 Monitoring of the Reaction Between Ph_3GeH and Et_2Zn in THF at 0 °C



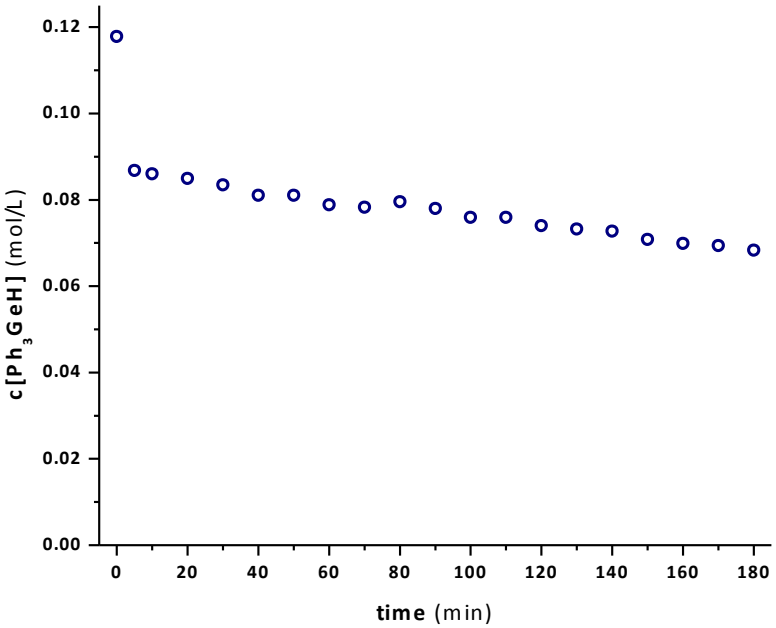
Procedure:

In a J Young NMR tube under argon atmosphere, Ph_3GeH (25 mg, 0.08 mmol) was dissolved in THF-d_8 (0.5 mL). A first spectrum (used for t = 0) was recorded at 273 K. The NMR tube was then placed in an ice-bath and Et_2Zn (1.0 M in hexane, 0.18 mL, 0.18 mmol, 3.0 equiv) was introduced. At the end of the addition (**t = 0**), the tube was immediately placed in the NMR probe at 273 K and ^1H NMR spectra were recorded every 5 min during 3 h.

Evolution of the [8.0–5.3 ppm] region of the ^1H NMR spectra:

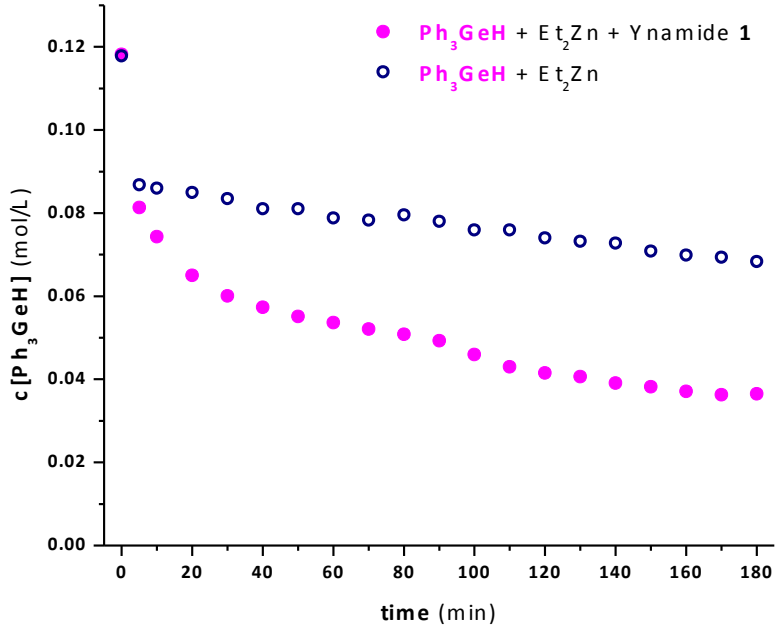


Evolution of the concentration of Ph_3GeH (determined on the basis of the integration of the signal at 5.65 ppm of the ^1H NMR spectra):

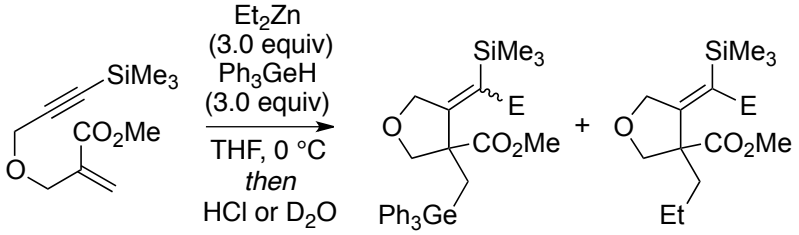


II.2.3 Comparison of the rate of depletion of Ph_3GeH upon contact with Et_2Zn in the presence or absence of 1 (THF, 0 °C)

Comparison of the evolution of the concentration of Ph_3GeH in the two previous experiments:



II.3 Control Experiments with Acceptor X



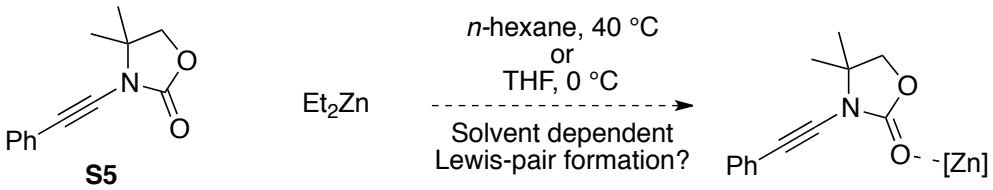
X **XI** (E=H) *Z*-**XII** (E=H)

[^{2}H]-**XI** (E=D) *Z*-[^{2}H]-**XII** (E=D)

Entry	Quench	Products [ratio][a]	dr of product XI (*Z*/*E*)[a]	Yield (%)[b]
1	aq. HCl (1.0 M)	**XI**/*Z*-**XII** [41:59]	85:15	92
2	D_2O	[^{2}H]-**XI**/*Z*-[^{2}H]-**XII** [39:61]	86 (80% D):14 (<10%D)[c]	nc

[a]Determined by ^{1}H NMR prior to purification. [b]Combined yield of products isolated as mixtures after chromatography. [c]The percentage of deuterium incorporation is given in parenthesis for each isomer.

II.4 IR *in situ* Monitoring of Lewis-pair Formation Between Ynamide S5 and Et_2Zn in *n*-hexane or THF



S5

For these studies, Ph-substituted internal ynamide **S5** was selected as model substrate instead of terminal ynamide **1,** in order to avoid complications associated with competing deprotonation of **1** by Et_2Zn.

Reaction setup:

React IR 15 with MCT Detector using HappGenzel apodization was used to collect IR reaction spectra. The instrument was fitted with a DiComp (Diamond) probe connected via AgX 6mm x 1.5m silver halide fiber. All data were collected at 8 cm^{-1} resolution from 3000 to 650 cm^{-1}. 125 scans were collected to obtain 1 spectrum. An air background was collected prior to the experiments and Mettler Toledo iCIR version 4.3 was used for instrument control and data analysis. Baseline offset correction was applied.

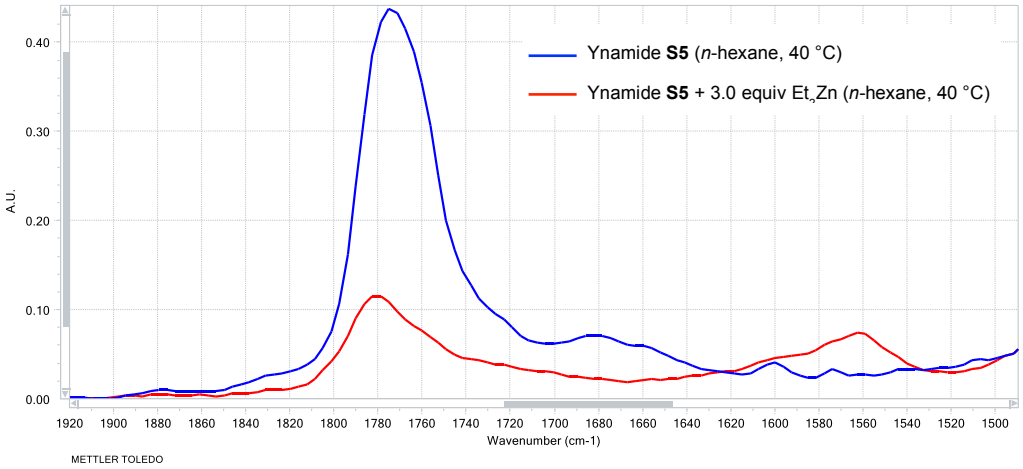
Monitoring of the interaction between ynamide S5 and Et_2Zn in n-hexane at 40 °C:

Procedure:

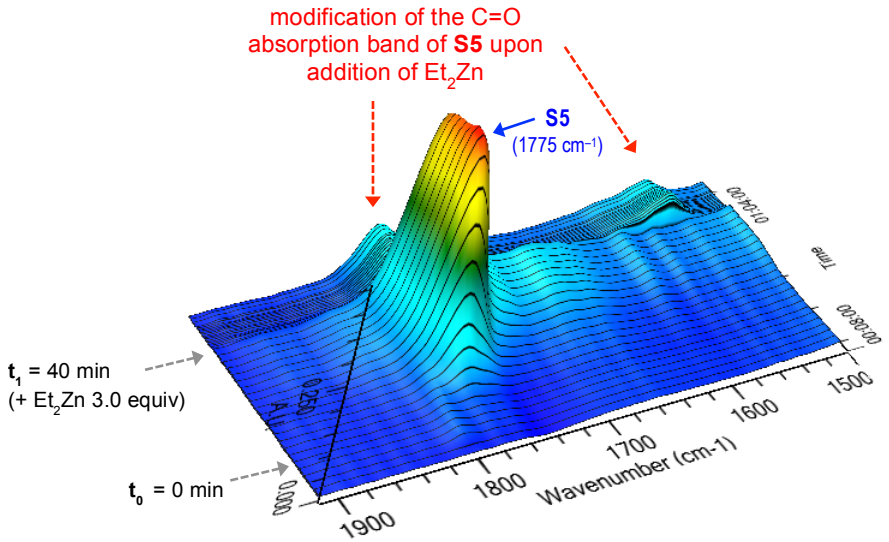
Under argon atmosphere, *n*-hexane (2.0 mL) was introduced into a three-necked round-flask equipped with the DiComp probe and heated to 40 °C. Evolution of the system was monitored at

1–2 min intervals. Ynamide **S5** (54 mg, 0.25 mmol) was introduced ($\mathbf{t_0}$) and a suspension was obtained. After ~ 40 min, most of the ynamide had dissolved and the system reached a steady state. Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) was then added ($\mathbf{t_1}$) and the turbid solution became clear.

Selected IR spectra [1900–1500 cm^{-1}] region:



IR in-situ monitoring [1900–1500 cm^{-1}] region:



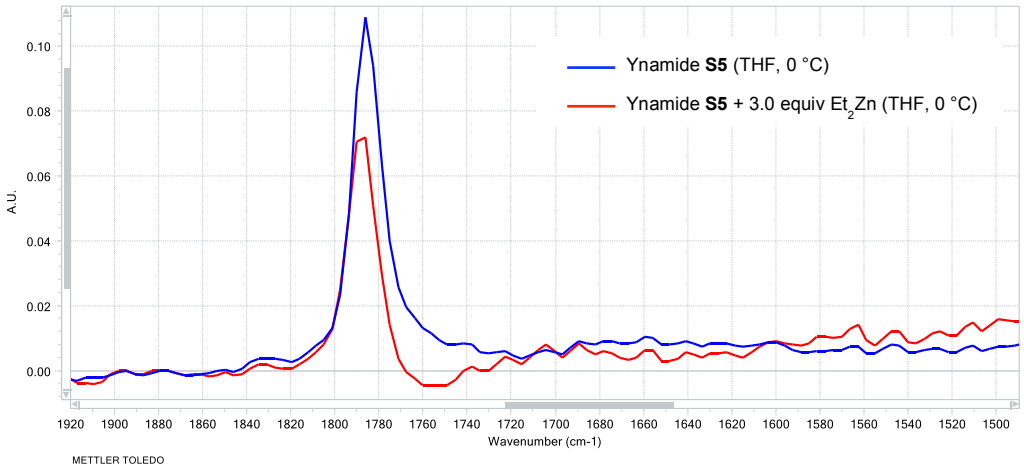
Monitoring of the interaction between ynamide S5 and Et_2Zn in THF at 0 °C:

Procedure:

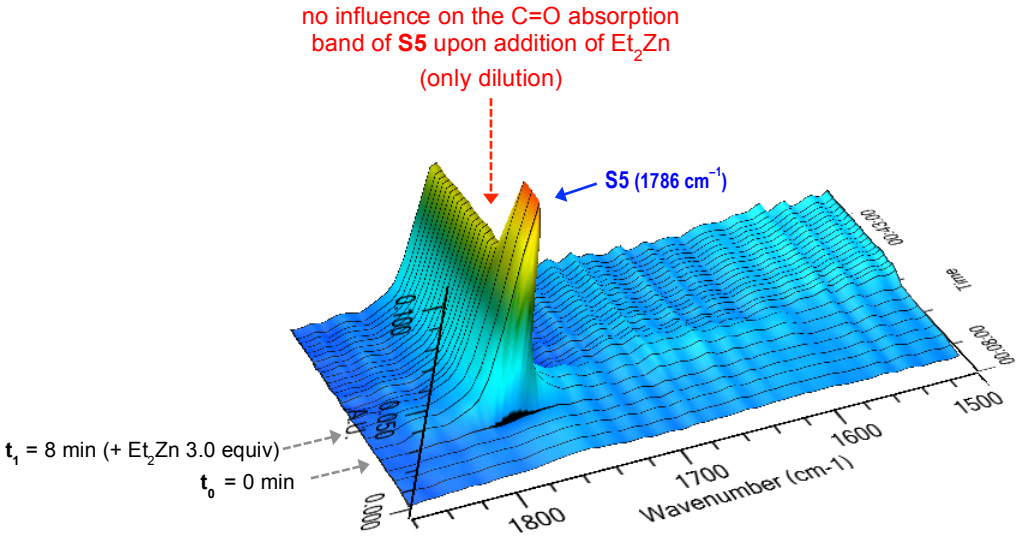
Under argon atmosphere, THF (2.0 mL) was introduced into a three-necked round-flask equipped with the DiComp probe and cooled to 0 °C. Evolution of the system was monitored at 1–2 min intervals. Ynamide **S5** (54 mg, 0.25 mmol) was introduced ($\mathbf{t_0}$) and a colorless solution

was obtained. After stabilization of the system, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) was added ($\mathbf{t_1}$).

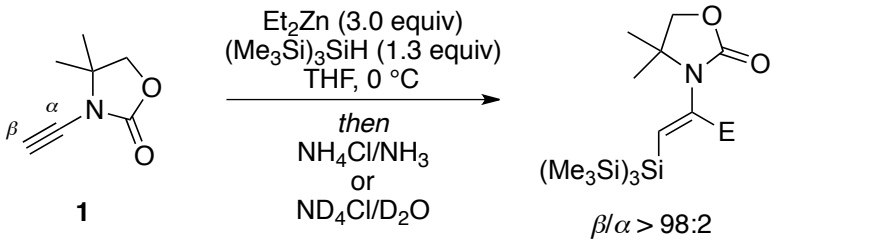
Selected IR spectra [1900–1500 cm^{-1}] region:



IR in-situ monitoring [1900–1500 cm^{-1}] region:



II.5 Silylzincation of Ynamide 1 in THF



1

$\beta/\alpha > 98{:}2$

S30 (E=H): 78% (*E*/*Z* = 90:10)

[^{2}H]-**S30** (E=D): 70% (*E*/*Z* = 95:5)

III Experimental Details

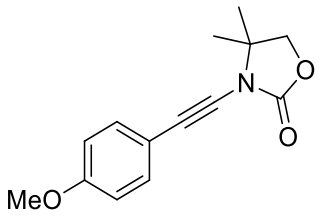
III.1 General Information

Experiments involving organometallic compounds were carried out in dried glassware under a positive pressure of dry argon. THF, toluene, DMF, and CH_2Cl_2 were distilled to remove stabilizers and dried with a Solvent Purification System. Et_2Zn (Aldrich), triphenylgermanium hydride (Aldrich), tributylgermanium hydride (Aldrich), triethylgermanium hydride (Alfa Aesar), 1,4-dioxane (anhydrous, 99.8%, Aldrich), *n*-hexane (Aldrich), 1-phenyl-1-propyne (Acros), and all other reagents were of commercial quality and were used without purification. Flash column chromatography was performed using the indicated solvents on silica gel 60 (40–63 μm, 230–400 mesh, ASTM) by Merck. ^{1}H NMR and ^{13}C NMR (or JMod) spectra were recorded with a Bruker AV 300 or 400 spectrometers. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 or C_6H_6: δ = 7.16 for ^{1}H NMR and $CDCl_3$: δ = 77.16 ppm or C_6D_6: δ= 128.06 ppm for ^{13}C NMR or JMod). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, hept = heptaplet, m = multiplet), coupling constant (Hz) and integration. Infrared (IR) spectra were recorded with a Bruker Tensor 27 ATR diamond spectrophotometer and are reported in wavenumbers (cm^{-1}). Melting points (mp) were determined with Stuart Scientific SMP3 melting point apparatus and are not corrected. Optical rotations were measured on a JASCO P-2000 polarimeter with $[\alpha]_D$ values reported in 10^{-1} ($°\cdot cm^2\cdot g^{-1}$); concentration *c* is in g/100 mL. High resolution mass spectra (HRMS) were obtained on a Bruker MicrOTOF.

III.2 Experimental Procedures and Compound Characterization Data

III.2.1 Starting Materials

The following substrates are known compounds: 3-ethynyl-4,4-dimethyloxazolidin-2-one (**1**),[1] (*S*)-3-ethynyl-4-isopropyloxazolidin-2-one (**S1**),[1] (*S*)-4-benzyl-3-ethynyloxazolidin-2-one (**S2**),[1,2] 3-ethynyloxazolidin-2-one (**S3**),[1,3] *N*-benzyl-*N*-ethynyl-4-methylbenzenesulfonamide (**S4**),[1,4] 4,4-dimethyl-3-(phenylethynyl)oxazolidin-2-one (**S5**),[5,6] (*S*)-4-isopropyl-3-(phenylethynyl)oxazolidin-2-one (**S6**),[6,7] (*S*)-4-benzyl-3-(phenylethynyl)oxazolidin-2-one (**S7**),[1,7] 3-(phenylethynyl)oxazolidin-2-one (**S8**),[6,8] methyl phenyl(phenylethynyl)carbamate (**S9**),[6,9] *N*-benzyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (**S10**),[6] 4-methyl-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide (**S11**),[1,7] 3-((2-methoxyphenyl)ethynyl)oxazolidin-2-one (**S15**),[10] 3-(3-((*tert*-butyldimethylsilyl)oxy)prop-1-yn-1-yl)oxazolidin-2-one (**S20**),[8] ethynyl phenyl sulfide (**S23**),[11] ethynyl *p*-tolyl (*R*)-sulfoxide (**S24**),[12] ethynyl *N,N*-diisopropylcarbamate (**S25**),[13] diethyl ethynylphosphonate (**S26**),[14] diisopropyl (phenylethynyl)phosphonate (**S27**),[10,15] tri(2-furyl)germane.[16]



$C_{14}H_{15}NO_3$

M = 245.27 g·mol^{-1}

S12

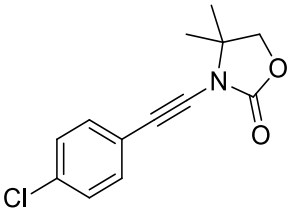
3-((4-methoxyphenyl)ethynyl)-4,4-dimethyloxazolidin-2-one (S12): Prepared by the method reported by Evano *et al*[6] from 4,4-dimethyloxazolidin-2-one (0.50 g, 4.34 mmol, 1.0 equiv) and 1-(2,2-dibromovinyl)-4-methoxybenzene[17] (1.90 g, 6.51 mmol, 1.5 equiv), using Cs_2CO_3 (5.66 g, 17.36 mmol, 4.0 equiv), CuI (103 mg, 0.54 mmol, 0.1 equiv), and *N*,*N*'-dimethylethylenediamine (72 mg, 0.81 mmol, 0.2 equiv), in dioxane (8 mL), with a reaction time of 25 h. Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = gradient from 50:50 to 30:70) afforded analytically pure **S12** (0.85 g, 80%) as a white solid; mp 115–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 7.42–7.39 (m, 2H), 6.86–6.82 (m, 2H), 4.18 (s, 2H), 3.81 (s, 3H), 1.48 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.8, 155.3, 133.7, 114.5, 114.0, 75.8, 74.9, 73.3, 60.4, 55.4, 25.0.

IR (neat): ν (cm^{-1}) 2967, 2927, 1751, 1409, 1245, 1074, 828, 751.

HRMS (ESI): *m/z* calculated for $[C_{14}H_{15}NO_3 + Na]^+$ 268.0944; found 268.0943.



$C_{13}H_{12}ClNO_2$

M = 249.69 g·mol^{-1}

S13

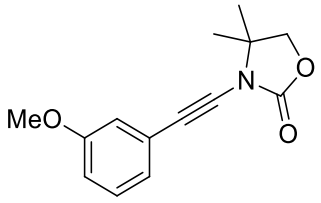
3-((4-chlorophenyl)ethynyl)-4,4-dimethyloxazolidin-2-one (S13): Prepared by the method reported by Evano *et al*[6] from 4,4-dimethyloxazolidin-2-one (1.00 g, 8.69 mmol, 1.0 equiv) and 1-chloro-4-(2,2-dibromovinyl)benzene[17] (3.86 g, 13.03 mmol, 1.5 equiv), using Cs_2CO_3 (11.32 g, 34.74 mmol, 4.0 equiv), CuI (207 mg, 1.09 mmol, 0.1 equiv), and *N*,*N*'-dimethylethylenediamine (144 mg, 1.63 mmol, 0.2 equiv), in dioxane (16 mL), with a reaction time of 24 h. Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = gradient from 70:30 to 50:50) afforded analytically pure **S13** (1.48 g, 68%) as a pale yellow solid; mp 100–102 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 7.39–7.36 (m, 2H), 7.30–7.26 (m, 2H), 4.19 (s, 2H), 1.49 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 134.3, 132.9, 128.8, 121.1, 77.4, 75.9, 72.7, 60.5, 25.1.

IR (neat): ν (cm^{-1}) 2976, 1763, 1401, 1273, 1176, 1078, 829, 751.

HRMS (ESI): *m/z* calculated for $[C_{13}H_{12}ClNO_2 + Na]^+$ 272.0449; found 272.0456.



$C_{14}H_{15}NO_3$

M = 245.27 g·mol^{-1}

S14

3-((3-methoxyphenyl)ethynyl)-4,4-dimethyloxazolidin-2-one (S14): Prepared by the method reported by Evano *et al*[6] from 4,4-dimethyloxazolidin-2-one (1.00 g, 8.69 mmol, 1.0 equiv) and 1-(2,2-dibromovinyl)-3-methoxybenzene[17,18] (3.80 g, 13.03 mmol, 1.5 equiv) using Cs_2CO_3 (11.32 g, 34.74 mmol, 4.0 equiv), CuI (207 mg, 1.09 mmol, 0.1 equiv), and *N*,*N*'-dimethylethylenediamine (144 mg, 1.63 mmol, 0.2 equiv), in dioxane (16 mL), with a reaction time of 24 h. Purification of the crude product by flash chromatography on silica gel

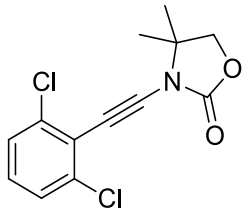
(pentane/Et_2O = 50:50) afforded analytically pure **S14** (1.61 g, 76%) as a pale yellow solid; mp 91–94 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 7.23–7.19 (m, 1H), 7.04 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 6.98 (dd, *J* = 2.7 Hz, *J* = 1.2 Hz, 1H), 6.86 (ddd, *J* = 8.3 Hz, *J* = 2.7 Hz, *J* = 1.2 Hz, 1H), 4.19 (s, 2H), 3.80 (s, 3H), 1.50 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.5, 155.1, 129.5, 124.2, 123.6, 116.5, 114.9, 76.3, 75.8, 73.7, 60.5, 55.5, 25.1.

IR (neat): ν (cm^{-1}) 3073, 2974, 1769, 1574, 1393, 1281, 1169, 1076.

HRMS (ESI): *m/z* calculated for $[C_{14}H_{15}NO_3 + Na]^+$ 268.0944; found 268.0948.



$C_{13}H_{11}Cl_2NO_2$

M = 284.14 g·mol^{-1}

S16

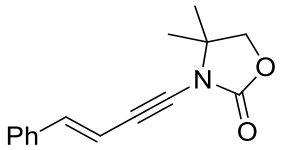
3-((2,6-dichlorophenyl)ethynyl)-4,4-dimethyloxazolidin-2-one (S16): Prepared by the method reported by Evano *et al*[6] from 4,4-dimethyloxazolidin-2-one (1.00 g, 8.69 mmol, 1.0 equiv) and 1,3-dichloro-2-(2,2-dibromovinyl)benzene[17,19] (4.91 g, 13.03 mmol, 1.5 equiv), using Cs_2CO_3 (11.32 g, 34.74 mmol, 4.0 equiv), CuI (207 mg, 1.09 mmol, 0.1 equiv), and *N*,*N*'-dimethylethylenediamine (144 mg, 1.63 mmol, 0.2 equiv), in dioxane (16 mL), with a reaction time of 24 h. Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = gradient from 70:30 to 50:50) afforded analytically pure **S16** (665 mg, 27%) as a pale brown solid; mp 98–100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 7.31–7.29 (m, 2H), 7.12 (dd, *J* = 8.6 Hz, *J* = 7.7 Hz, 1H), 4.21 (s, 2H), 1.55 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 136.2, 128.5, 127.5, 123.0, 87.1, 75.9, 68.7, 60.9, 25.0.

IR (neat): ν (cm^{-1}) 2977, 1772, 1390, 1371, 1272, 1200, 1076, 783.

HRMS (ESI): *m/z* calculated for $[C_{13}H_{11}Cl_2NO_2 + Na]^+$ 306.0059; found 306.0062.



$C_{15}H_{15}NO_2$

M = 241.29 g·mol^{-1}

S17

***(E)*-4,4-dimethyl-3-(4-phenylbut-3-en-1-yn-1-yl)oxazolidin-2-one (S17):** Prepared by the method reported by Evano *et al*[6] from 4,4-dimethyloxazolidin-2-one (500 mg, 4.34 mmol, 1.0 equiv) and (*E*)-(4,4-dibromobuta-1,3-dien-1-yl)benzene[17,20] (1.64 g, 6.51 mmol, 1.5 equiv), using Cs_2CO_3 (5.66 g, 17.36 mmol, 4.0 equiv), CuI (103 mg, 0.54 mmol, 0.1 equiv), and *N*,*N*'-dimethylethylenediamine (72 mg, 0.81 mmol, 0.2 equiv), in dioxane (8 mL), with a reaction time of 25 h. Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = gradient from 50:50 to 30:70) afforded analytically pure **S17** (676 mg, 65%) as a yellow solid; mp 104–105 °C.

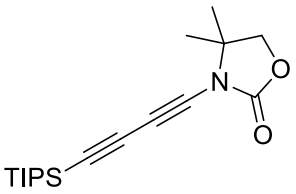
^{1}H NMR (400 MHz, $CDCl_3$): 7.41–7.27 (m, 5H), 6.95 (d, J_{trans} = 16.2 Hz, 1H), 6.31 (d, J_{trans} = 16.2 Hz, 1H), 4.18 (s, 2H), 1.49 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 140.3, 136.3, 128.8, 128.5, 126.2, 107.2, 78.4, 75.8, 73.3, 60.4, 25.0.

IR (neat): ν (cm^{-1}) 2974, 2920, 2231, 1759, 1400, 1167, 741, 686.

HRMS (ESI): *m/z* calculated for $[C_{15}H_{15}NO_2 + Na]^+$ 264.0995; found 264.0989.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 16.2 Hz).



$C_{18}H_{29}NO_2Si$

M = 319.51 g·mol^{-1}

S18

4,4-dimethyl-3-((triisopropylsilyl)buta-1,3-diyn-1-yl)oxazolidin-2-one (S18): Prepared by the method reported by Lei *et al*[21] from ynamide **1** (200 mg, 1.44 mmol, 1.2 equiv) and (bromoethynyl)triisopropylsilane[22] (314 mg, 1.20 mmol, 1.0 equiv), using $Pd(dba)_2$ (28 mg, 0.05 mmol, 4 mol%), PPh_3 (13 mg, 0.05 mmol, 4 mol%), CuI (5 mg, 0.02 mmol, 2 mol%), and Et_3N (243 mg, 2.40 mmol, 2.0 equiv), in dry DMF (2 mL), with an overnight reaction time. Purification

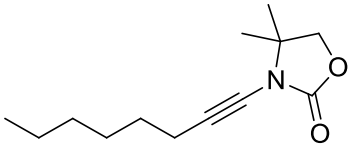
of the crude product by flash chromatography on silica gel (pentane/Et_2O = 90:10) afforded analytically pure **S18** (131 mg, 34%) as a pale yellow solid; mp 123–125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 4.14 (s, 2H), 1.47 (s, 6H), 1.08 (s, 21H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.3, 88.8, 87.7, 76.0, 62.4, 61.8, 60.8, 25.1, 18.7, 11.4.

IR (neat): ν (cm^{-1}) 2950, 2862, 2231, 1764, 1402, 1376, 1169, 669.

HRMS (ESI): *m/z* calculated for $[C_{18}H_{29}NO_2Si + Na]^+$ 342.1860; found 342.1870.



$C_{13}H_{21}NO_2$

M = 223.31 g·mol^{-1}

S19

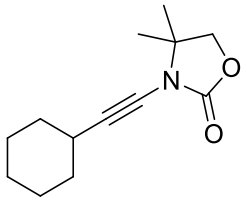
4,4-dimethyl-3-(oct-1-yn-1-yl)oxazolidin-2-one (S19): Prepared according to a reported literature procedure for ynamide formation[1] from 4,4-dimethyloxazolidin-2-one (1.00 g, 8.69 mmol, 1.3 equiv) and 1-bromooct-1-yne[23] (1.32 g, 6.98 mmol, 1.0 equiv), using 1,10-phenanthroline (252 mg, 1.40 mmol, 0.2 equiv), $CuSO_4 \cdot 5H_2O$ (174 mg, 0.70 mmol, 0.1 equiv), and K_2CO_3 (2.07 g, 15.01 mmol, 2.2 equiv) in toluene (40 mL) with a reaction time of 6 days. Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **S19** (333 mg, 21%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): 4.09 (s, 2H), 2.32 (td, *J* = 7.0 Hz, *J* = 0.5 Hz, 2H), 1.56–1.48 (m, 2H), 1.42–1.34 (m, 8H), 1.32–1.22 (m, 4H), 0.88–0.85 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.8, 75.5, 73.3, 67.2, 59.7, 31.2, 28.8, 28.4, 24.6, 22.5, 18.5, 14.0.

IR (neat): ν (cm^{-1}) 2967, 2926, 2858, 1766, 1401, 1168, 1072, 1021.

HRMS (ESI): *m/z* calculated for $[C_{13}H_{21}NO_2 + Na]^+$ 246.1465; found 246.1462.



$C_{13}H_{19}NO_2$

M = 221.30 g·mol^{-1}

S21

3-(cyclohexylethynyl)-4,4-dimethyloxazolidin-2-one (S21): Prepared by the method reported by Evano *et al*[6] from 4,4-dimethyloxazolidin-2-one (1.00 g, 8.69 mmol, 1.0 equiv) and (2,2-

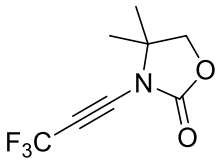
dibromovinyl)cyclohexane[17] (3.49 g, 13.03 mmol, 1.5 equiv), using Cs_2CO_3 (11.32 g, 34.74 mmol, 4.0 equiv), CuI (207 mg, 1.09 mmol, 0.1 equiv), and *N*,*N*'-dimethylethylenediamine (144 mg, 1.63 mmol, 0.2 equiv), in dioxane (16 mL), with a reaction time of 24 h. Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **S21** (1.16 g, 60%) as a white solid; mp 74–75 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 4.07 (s, 2H), 2.52 (tt, *J* = 8.7 Hz, *J* = 3.9 Hz, 1H), 1.80–1.74 (m, 2H), 1.69–1.62 (m, 2H), 1.49–1.41 (m, 3H), 1.36 (s, 6H), 1.33–1.28 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.6, 77.3, 75.5, 67.5, 59.8, 32.9, 28.8, 25.9, 24.7, 24.66.

IR (neat): ν (cm^{-1}) 2929, 2854, 1765, 1404, 1171, 1074, 1022, 753.

HRMS (ESI): *m/z* calculated for $[C_{13}H_{19}NO_2 + Na]^+$ 244.1308; found 244.1299.



$C_8H_8F_3NO_2$

M = 207.15 g·mol^{-1}

S22

4,4-dimethyl-3-(3,3,3-trifluoroprop-1-yn-1-yl)oxazolidin-2-one (S22): Prepared by the method reported by Evano and Blanchard[24] from 3-ethynyl-4,4-dimethyloxazolidin-2-one (300 mg, 2.16 mmol, 1.0 equiv) and $TMSCF_3$ (1.23 g, 8.64 mmol, 4.0 equiv), using CuI (617 mg, 3.24 mmol, 1.5 equiv), TMEDA (377 mg, 3.24 mmol, 1.5 equiv), and K_2CO_3 (896 mg, 6.48 mmol, 3.0 equiv), in dry DMF (10 mL), with a reaction time of 48 h. Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = gradient from 70:30 to 60:40) afforded analytically pure **S22** (68 mg, 15%) as a white solid; mp 53–55 °C.

^{1}H NMR (400 MHz, $CDCl_3$): 4.20 (s, 2H), 1.48 (s, 6H).

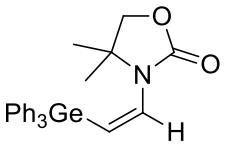
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.9, 115.4 (q, J_{CF} = 256.9 Hz), 76.3, 75.3 (q, J_{CF} = 5.9 Hz), 62.6 (q, J_{CF} = 54.5 Hz), 61.0, 24.9.

^{19}F NMR (376 MHz, $CDCl_3$): –48.5 (s).

IR (neat): ν (cm^{-1}) 2923, 2279, 2256, 1781, 1272, 1122, 1018, 680.

HRMS (ESI): *m/z* calculated for $[C_8H_8F_3NO_2 + Na]^+$ 230.0399; found 230.0399.

III.2.2 Hydrogermylation of Ynamide 1



$C_{25}H_{25}GeNO_2$

M = 444.11 g·mol^{-1}

Z-**2**

***(Z)*-4,4-dimethyl-3-[2-(triphenylgermyl)vinyl]oxazolidin-2-one (*Z*-2):** In a dry Schlenk tube under argon atmosphere, ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) was dissolved in dry THF (2 mL). The solution was degassed by 3 freeze-pump-thaw cycles and Ph_3GeH (152 mg, 0.50 mmol, 2.0 equiv) was added. The reaction mixture was stirred for 16 h at rt and aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product (*Z*/*E* = 96:4). Purification by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **2** (93 mg, 84%, *Z*/*E* = 96:4) as a white solid; mp 142–145 °C.

^{1}H NMR (400 MHz, $CDCl_3$): (*Z*-isomer) δ 7.66–7.62 (m, 6H), 7.41–7.34 (m, 9H), 6.65 (d, *J* = 10.6 Hz, 1H), 6.19 (d, *J* = 10.6 Hz, 1H), 3.30 (s, 2H), 1.16 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*Z*-isomer) δ 154.9, 137.2, 135.3, 133.6, 128.9, 128.0, 121.8, 74.2, 58.7, 24.1.

IR (neat): ν (cm^{-1}) 3057, 2928, 2860, 1755, 1607, 1027, 911, 732, 697.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{25}GeNO_2 + Na]^+$ 468.0994; found 468.0991.

Note: The Z configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 10.6 Hz).

III.2.3 Germylzincation of Terminal Ynamides (GP I and GP II):

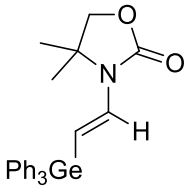
General procedure for germylzincation of terminal ynamides (**GP I**)*:*

In a dry Schlenk tube under argon atmosphere, the appropriate ynamide (0.25 mmol, 1.0 equiv) was dissolved in dry THF (2 mL) and the solution was degassed by 3 freeze-pump-thaw cycles. At 0 ºC, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) and the appropriate germanium hydride (0.33–0.50 mmol, 1.3–2.0 equiv) were successively added. The reaction mixture was stirred at this temperature for the given reaction time and then aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and

the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product.

General procedure for germylzincation – D-labeling of terminal ynamides (**GP II**):

In a dry Schlenk tube under argon atmosphere, the appropriate ynamide (0.25 mmol, 1.0 equiv) was dissolved in dry THF (2 mL) and the solution was degassed by 3 freeze-pump-thaw cycles. At 0 ºC, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) and the appropriate germanium hydride (0.33–0.50 mmol, 1.3–2.0 equiv) were successively added. The reaction mixture was stirred at this temperature for the given reaction time. A solution of ND_4Cl (300 mg) in D_2O (2 mL) was added and the mixture was stirred for 1 h at rt before adding aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product.



$C_{25}H_{25}GeNO_2$

M = 444.11 g·mol^{-1}

E-**2**

(*E*)-4,4-dimethyl-3-[2-(triphenylgermyl)vinyl]oxazolidin-2-one (*E*-2): Prepared according to **GP I** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) with Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure *E*-**2** (97 mg, 87%, *E*/*Z* > 98:2) as a white solid; mp 139–142 °C.

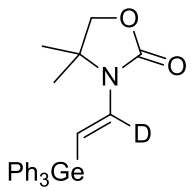
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.50 (m, 6H), 7.41–7.36 (m, 9H), 6.50 (d, *J* = 17.5 Hz, 1H), 5.97 (d, *J* = 17.5 Hz, 1H), 4.02 (s, 2H), 1.51 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 136.3, 135.1, 134.6, 129.3, 128.4, 102.9, 75.2, 58.8, 25.1.

IR (neat): ν (cm^{-1}) 2920, 2853, 1746, 1611, 1325, 1062, 739, 698.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{25}GeNO_2 + Na]^+$ 468.0994; found 468.1005.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 17.5 Hz).



$C_{25}H_{24}DGeNO_2$

M = 445.12 g·mol^{-1}

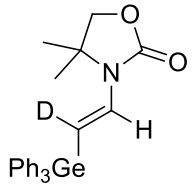
E-[^{2}H(*α*)]-**2**

***E*-[^{2}H(*α*)]-2:** Prepared according to **GP II** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) with Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure *E*-[^{2}H(*α*)]-**2** (95 mg, 86%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.53 (m, 6H), 7.44–7.38 (m, 9H), 6.00 (s, 1H), 4.02 (s, 2H), 1.52 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 136.3, 135.0, 134.3 (t, *J* = 26.4 Hz), 129.2, 128.4, 102.6, 75.2, 58.7, 25.1.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{24}DGeNO_2 + Na]^+$ 469.1057; found 469.1046.



$C_{25}H_{24}DGeNO_2$

M = 445.12 g·mol^{-1}

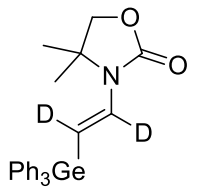
E-[^{2}H(*β*)]-**2**

***E*-[^{2}H(*β*)]-2:** Prepared according to **GP I** from ynamide [^{2}H]-**1** (30 mg, 0.21 mmol, 1.0 equiv) with Ph_3GeH (85 mg, 0.28 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure *E*-[^{2}H(*β*)]-**2** (94 mg, 99%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.51 (m, 6H), 7.44–7.37 (m, 9H), 6.52 (s, 1H), 4.02 (s, 2H), 1.52 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 136.3, 135.1, 134.5, 129.3, 128.4, 102.6 (t, *J* = 23.4 Hz), 75.3, 58.8, 25.1.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{24}DGeNO_2 + Na]^+$ 469.1057; found 469.1039.



$C_{25}H_{23}D_2GeNO_2$

M = 446.12 g·mol^{-1}

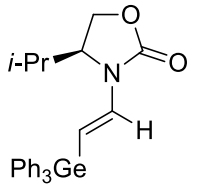
E-[^{2}H(*α*),^{2}H(*β*)]-**2**

***E*-[^{2}H(*α*),^{2}H(*β*)]-2:** Prepared according to **GP II** from ynamide [^{2}H]-**1** (30 mg, 0.21 mmol, 1.0 equiv) with Ph_3GeH (85 mg, 0.28 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure *E*-[^{2}H(*α*),^{2}H(*β*)]-**2** in (85 mg, 89%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.52 (m, 6H), 7.45–7.38 (m, 9H), 4.02 (s, 2H), 1.52 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 136.3, 135.1, 134.2 (t, *J* = 25.1 Hz), 129.3, 128.4, 102.4 (t, *J* = 21.4 Hz), 75.3, 58.8, 25.1.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{23}D_2GeNO_2 + Na]^+$ 470.1120; found 470.1110.



$C_{26}H_{27}GeNO_2$

M = 458.14 g·mol^{-1}

4

***(S,E)*-4-isopropyl-3-[2-(triphenylgermyl)vinyl]oxazolidin-2-one (4):** Prepared according to **GP I** from ynamide **S1** (38 mg, 0.25 mmol, 1.0 equiv) with Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **4** (76 mg, 66%, *E*/*Z* > 98:2) as a white solid; mp 141–143 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.49 (m, 6H), 7.47–7.26 (m, 9H), 6.90 (d, *J* = 17.1 Hz, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 4.32–4.24 (m, 2H), 4.21 (dt, *J* = 8.6 Hz, *J* = 3.3 Hz, 1H), 2.57–2.49 (m, 1H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H).

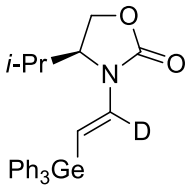
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.3, 136.2, 135.6, 135.0, 129.3, 128.5, 100.7, 63.2, 58.1, 26.5, 18.1, 14.1.

IR (neat): ν (cm^{-1}) 3071, 2965, 2873, 1756, 1608, 1399, 732, 696.

HRMS (ESI): *m/z* calculated for $[C_{26}H_{27}GeNO_2 + Na]^+$ 482.1151; found 482.1170.

$[\alpha]_D^{20}$: 12.0 (*c* 1.0, CH_2Cl_2).

Note: The E configuration was determined on the basis of the ^1H NMR coupling constant of the vinylic protons (J = 17.1 Hz).



$C_{26}H_{26}DGeNO_2$

M = 459.14 g·mol^{-1}

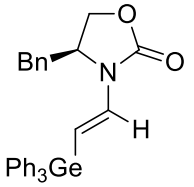
[^{2}H]-**4**

[^{2}H]-4: Prepared according to **GP II** from ynamide **S1** (38 mg, 0.25 mmol, 1.0 equiv) with Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure [^{2}H]-**4** (89 mg, 77%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.52 (m, 6H), 7.47–7.39 (m, 9H), 5.37 (s, 1H), 4.33–4.25 (m, 2H), 4.22 (dt, *J* = 8.5 Hz, *J* = 3.4 Hz, 1H), 2.58–2.51 (m, 1H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.3, 136.2, 135.0, 129.3, 128.5, 100.4, 63.2, 58.1, 26.5, 18.1, 14.1. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{26}H_{26}DGeNO_2 + Na]^+$ 483.1214; found 483.1211.



$C_{30}H_{27}GeNO_2$

M = 506.18 g·mol^{-1}

5

***(S,E)*-4-benzyl-3-(2-(triphenylgermyl)vinyl)oxazolidin-2-one (5):** Prepared according to **GP I** from ynamide **S2** (50 mg, 0.25 mmol, 1.0 equiv) with Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 16 h. The reaction quench was modified by adding CuTC (48 mg, 0.25 mmol, 1.0 equiv) and, 5 min after, NH_4Cl (300 mg) in H_2O (2 mL) and stirring the resulting mixture for 1 h at rt before workup with aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (toluene/Et_2O = 90:10) afforded analytically pure **5** (89 mg, 70%, *E*/*Z* > 98:2) as a white solid; mp 111–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.56 (m, 6H), 7.45–7.41 (m, 9H), 7.38–7.34 (m, 2H), 7.32–7.28 (m, 1H), 7.23–7.21 (m, 2H), 6.96 (d, *J* = 17.2 Hz, 1H), 5.50 (d, *J* = 17.2 Hz, 1H), 4.49 (tt, *J* = 8.5 Hz, *J* = 3.1 Hz, 1H), 4.28 (dd, *J* = 9.0 Hz, *J* = 7.7 Hz, 1H), 4.23 (dd, *J* = 9.0 Hz, *J* = 3.1 Hz, 1H), 3.35 (dd, *J* = 13.9 Hz, *J* = 3.3 Hz, 1H), 2.89 (dd, *J* = 13.9 Hz, *J* = 8.8 Hz, 1H).

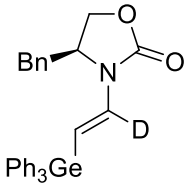
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.8, 136.1, 135.5, 135.3, 135.0, 129.393, 129.387, 129.1, 128.5, 127.5, 101.1, 66.7, 54.6, 36.5.

IR (neat): ν (cm^{-1}) 3068, 1752, 1608, 1400, 1089, 907, 727, 696.

HRMS (ESI): *m/z* calculated for $[C_{30}H_{27}GeNO_2 + Na]^+$ 530.1152; found 530.1167.

$[\alpha]_D^{20}$: 11.7 (*c* 1.0, CH_2Cl_2).

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 17.2 Hz).



$C_{30}H_{26}DGeNO_2$

M = 507.19 g·mol^{-1}

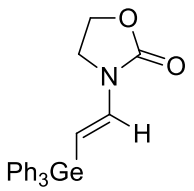
[^{2}H]-**5**

[^{2}H]-5: Prepared according to **GP II** from ynamide **S2** (50 mg, 0.25 mmol, 1.0 equiv) with Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 16h. The reaction quench was modified by adding CuTC (48 mg, 0.25 mmol, 1.0 equiv) 5 min before ND_4Cl in D_2O. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (toluene/Et_2O = 90:10) afforded analytically pure [^{2}H]-**5** in (96 mg, 76%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.55 (m, 6H), 7.45–7.41 (m, 9H), 7.38–7.34 (m, 2H), 7.32–7.28 (m, 1H), 7.23–7.21 (m, 2H), 5.49 (s, 1H), 4.52–4.46 (m, 1H), 4.28 (dd, *J* = 9.0 Hz, *J* = 7.7 Hz, 1H), 4.23 (dd, *J* = 9.0 Hz, *J* = 3.0 Hz, 1H), 3.35 (dd, *J* = 13.9 Hz, *J* = 3.3 Hz, 1H), 2.89 (dd, *J* = 13.9 Hz, *J* = 8.9 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.8, 136.1, 135.3, 135.0, 129.4, 129.38, 129.1, 128.5, 127.5, 100.9, 66.7, 54.6, 36.5. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{30}H_{26}DGeNO_2 + Na]^+$ 531.1215; found 531.1224.



$C_{23}H_{21}GeNO_2$

M = 416.06 g·mol^{-1}

6

***(E)*-3-(2-(triphenylgermyl)vinyl)oxazolidin-2-one (6):** Prepared according to **GP I** from ynamide **S3** (28 mg, 0.25 mmol, 1.0 equiv) with Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 3 h. The reaction quench was modified by adding CuTC (48 mg, 0.25 mmol, 1.0 equiv) and, 5 min after, NH_4Cl (300 mg) in H_2O (2 mL) and stirring the resulting mixture for 1 h at rt before workup with aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = gradient from 70:30 to 50:50) afforded analytically pure **6** (73 mg, 70%, *E*/*Z* > 98:2) as a white solid; mp 121–124 °C.

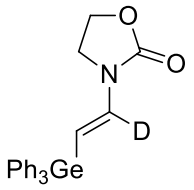
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.50 (m, 6H), 7.45–7.36 (m, 9H), 7.00 (d, *J* = 16.8 Hz, 1H), 5.21 (d, *J* = 16.8 Hz, 1H), 4.46–4.42 (m, 2H), 3.86–3.82 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.0, 136.4, 136.1, 135.0, 129.3, 128.5, 100.6, 62.4, 42.2.

IR (neat): ν (cm^{-1}) 3058, 1761, 1608, 1402, 1184, 1084, 733, 697.

HRMS (ESI): *m/z* calculated for $[C_{23}H_{21}GeNO_2 + Na]^+$ 440.0681; found 440.0671.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 16.8 Hz).



$C_{23}H_{20}DGeNO_2$

M = 417.06 g·mol^{-1}

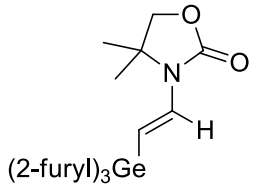
[^{2}H]-**6**

[^{2}H]-6: Prepared according to **GP II** from ynamide **S3** (28 mg, 0.25 mmol, 1.0 equiv) with Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 3 h. The reaction quench was modified by adding CuTC (48 mg, 0.25 mmol, 1.0 equiv) 5 min before ND_4Cl/D_2O. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = gradient from 70:30 to 50:50) afforded analytically pure [^{2}H]-**6** (69 mg, 66%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.50 (m, 6H), 7.44–7.36 (m, 9H), 5.20 (s, 1H), 4.47–4.43 (m, 2H), 3.86–3.82 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.0, 136.1, 135.0, 129.3, 128.5, 100.4, 62.4, 42.2. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{23}H_{20}DGeNO_2 + Na]^+$ 441.0743; found 441.0743.



$C_{19}H_{19}GeNO_5$

M = 414.00 g·mol^{-1}

7

***(E)*-4,4-dimethyl-3-(2-(tri(furan-2-yl)germyl)vinyl)oxazolidin-2-one (7):** Prepared according to **GP I** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) with (2-furyl)$_3$GeH (89 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 3 h. The reaction quench was modified by adding CuTC (48 mg, 0.25 mmol, 1.0 equiv) and, 5 min after, NH_4Cl (300 mg) in H_2O (2 mL) and stirring the resulting mixture for 1 h at rt before workup with aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/EtOAc = 70:30) afforded analytically pure **7** (75 mg, 72%, *E*/*Z* > 98:2) as a white solid; mp 142–145 °C.

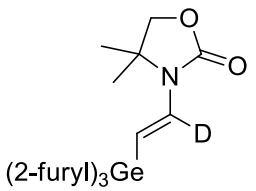
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 1.7 Hz, *J* = 0.6 Hz, 3H), 6.81 (dd, *J* = 3.2 Hz, *J* = 0.6 Hz, 3H), 6.75 (d, *J* = 17.5 Hz, 1H), 6.47 (dd, *J* = 3.2 Hz, *J* = 1.7 Hz, 3H), 5.78 (d, *J* = 17.5 Hz, 1H), 4.01 (s, 2H), 1.51 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.0, 152.5, 147.7, 135.4, 121.6, 110.0, 99.1, 75.3, 58.8, 25.1.

IR (neat): ν (cm^{-1}) 2978, 1754, 1612, 1326, 1066, 1001, 891, 748.

HRMS (ESI): *m/z* calculated for $[C_{19}H_{19}GeNO_5 + Na]^+$ 438.0371; found 438.0375.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 17.5 Hz).



$C_{19}H_{18}DGeNO_5$

M = 415.00 g·mol^{-1}

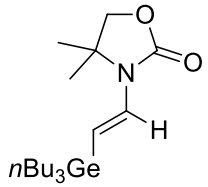
[^{2}H]-**7**

[^{2}H]-7: Prepared according to **GP II** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) with (2-furyl)$_3$GeH (89 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 3 h. The reaction quench was modified by adding CuTC (48 mg, 0.25 mmol, 1.0 equiv) 5 min before ND_4Cl/D_2O. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/EtOAc = 70:30) afforded analytically pure [^{2}H]-**7** in (86 mg, 83%, *E*/*Z* > 98:2) as white crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 1.7 Hz, *J* = 0.6 Hz, 3H), 6.81 (dd, *J* = 3.3 Hz, *J* = 0.6 Hz, 3H), 6.47 (dd, *J* = 3.3 Hz, *J* = 1.7 Hz, 3H), 5.77 (s, 1H), 4.01 (s, 2H), 1.51 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.0, 152.5, 147.7, 135.1 (t, *J* = 26.9 Hz), 121.6, 110.0, 98.8, 75.3, 58.7, 25.0.

HRMS (ESI): *m/z* calculated for $[C_{19}H_{18}DGeNO_5 + Na]^+$ 439.0434; found 439.0420.



$C_{19}H_{37}GeNO_2$

M = 384.14 g·mol^{-1}

8

***(E)*-4,4-dimethyl-3-(2-(tributylgermyl)vinyl)oxazolidin-2-one (8):** Prepared according to **GP I** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) with *n*Bu$_3$GeH (123 mg, 0.50 mmol, 2.0 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* = 96:4) by flash chromatography on silica gel (pentane/Et_2O = 90:10) afforded analytically pure **8** (74 mg, 77%, *E*/*Z* = 96:4) as a colorless oil.

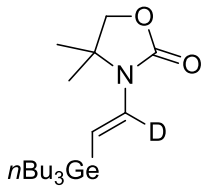
^{1}H NMR (400 MHz, $CDCl_3$): (*E*-isomer) δ 6.39 (d, *J* = 17.9 Hz, 1H), 5.34 (d, *J* = 17.9 Hz, 1H), 3.98 (s, 2H), 1.50 (s, 6H), 1.36–1.29 (m, 12H), 0.89–0.86 (m, 9H), 0.81–0.77 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*E*-isomer) δ 155.5, 130.9, 106.8, 75.4, 58.7, 27.5, 26.5, 25.0, 13.9, 13.1.

IR (neat): ν (cm^{-1}) 2961, 2921, 1755, 1610, 1325, 1182, 1067, 789, 689.

HRMS (ESI): *m/z* calculated for $[C_{19}H_{37}GeNO_2 + Na]^+$ 408.1932; found 408.1945.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 17.9 Hz).



$C_{19}H_{36}DGeNO_2$

M = 385.15 g·mol^{-1}

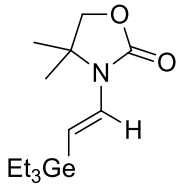
[^{2}H]-**8**

[^{2}H]-8: Prepared according to **GP II** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) with *n*Bu_3GeH (123 mg, 0.50 mmol, 2.0 equiv) and a reaction time of 16 h. Purification of the crude product (*E/Z* = 96:4) by flash chromatography on silica gel (pentane/Et_2O = 90:10) afforded analytically pure [^{2}H]-**8** (64 mg, 67%, *E*/*Z* > 98:2) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.33 (t, *J* = 2.3 Hz, 1H), 3.98 (s, 2H), 1.50 (s, 6H), 1.37–1.28 (m, 12H), 0.90–0.86 (m, 9H), 0.81–0.77 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.5, 130.6 (t, *J* = 26.7), 106.6, 75.4, 58.7, 27.5, 26.5, 25.0, 13.9, 13.2.

HRMS (ESI): *m/z* calculated for $[C_{19}H_{36}DGeNO_2 + Na]^+$ 409.1994; found 409.1994.



$C_{13}H_{25}GeNO_2$

M = 299.98 g·mol^{-1}

9

***(E)*-4,4-dimethyl-3-(2-(triethylgermyl)vinyl)oxazolidin-2-one (9):** Prepared according to **GP I** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) with Et_3GeH (80 mg, 0.50 mmol, 2.0 equiv) and a reaction time of 16 h. Purification of the crude product (*E/Z* = 95:5) by flash chromatography on silica gel (pentane/EtOAc = 90:10) afforded analytically pure **9** (57 mg, 76%, *E/Z* = 95:5) as a colorless oil.

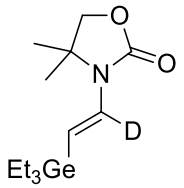
^{1}H NMR (400 MHz, $CDCl_3$): (*E*-isomer) δ 6.39 (d, *J* = 17.9 Hz, 1H), 5.32 (d, *J* = 17.9 Hz, 1H), 3.98 (s, 2H), 1.49 (s, 6H), 1.03–0.99 (m, 9H), 0.82–0.76 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*E*-isomer) δ 155.4, 131.2, 105.6, 75.4, 58.7, 25.0, 9.0, 4.6.

IR (neat): ν (cm^{-1}) 2952, 1752, 1609, 1325, 1181, 1066, 790, 703.

HRMS (ESI): *m/z* calculated for [$C_{13}H_{25}GeNO_2$ + Na]$^+$ 324.0991; found 324.1004.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 17.9 Hz).



$C_{13}H_{24}DGeNO_2$

M = 300.99 g·mol^{-1}

[^{2}H]-**9**

[^{2}H]-9: Prepared according to **GP II** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) with Et_3GeH (80 mg, 0.50 mmol, 2.0 equiv) and a reaction time of 16 h. Purification of the crude product (*E/Z* = 91:9) by flash chromatography on silica gel (pentane/EtOAc = 90:10) afforded analytically pure [^{2}H]-**9** (69 mg, 92%, *E/Z* = 87:13) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): (*E*-isomer) δ 5.31 (t, *J* = 2.5 Hz, 1H), 3.97 (s, 2H), 1.49 (s, 6H), 1.03–0.98 (m, 9H), 0.81–0.75 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*E*-isomer) δ 155.4, 130.9 (t, *J* = 26.8 Hz), 105.3, 75.4, 58.6, 24.9, 9.0, 4.6.

HRMS (ESI): *m/z* calculated for [$C_{13}H_{24}DGeNO_2$ + Na]$^+$ 325.1054; found 325.1055.

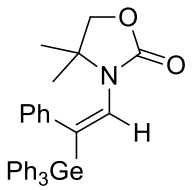
III.2.4 Germylzincation of Internal Ynamides (GP III and GP IV):

General procedure for germylzincation of internal ynamides (**GP III**)*:*

In a dry Schlenk tube under argon atmosphere, the appropriate ynamide (0.15 mmol, 1.0 equiv) was suspended in dry *n*-hexane (1.2 mL). At 0 ºC, Et_2Zn (1.0 M in hexane, 0.45 mL, 0.45 mmol, 3.0 equiv) and the corresponding germanium hydride (0.20–0.30 mmol, 1.3–2.0 equiv) were successively added. The reaction mixture was then heated at 40 ºC and the resulting solution stirred for the given reaction time. The reaction mixture was then cooled to rt and aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product.

General procedure for germylzincation – D-labeling of internal ynamides (**GP IV**):

In a dry Schlenk tube under argon atmosphere, the appropriate ynamide (0.15 mmol, 1.0 equiv) was suspended in dry *n*-hexane (1.2 mL). At 0 ºC, Et_2Zn (1.0 M in hexane, 0.45 mL, 0.45 mmol, 3.0 equiv) and the corresponding germanium hydride (0.20–0.30 mmol, 1.3–2.0 equiv) were successively added. The reaction mixture was then heated at 40 ºC and the resulting solution stirred for the given reaction time. After cooling the reaction mixture to rt, a solution of ND_4Cl (300 mg) in D_2O (2 mL) was added followed by THF (2 mL) 10 min after. The mixture was stirred for 1 h at rt and then aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product.



$C_{31}H_{29}GeNO_2$

M = 520.21 g·mol^{-1}

10

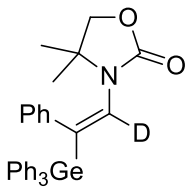
***(E)*-4,4-dimethyl-3-[2-phenyl-2-(triphenylgermyl)vinyl]oxazolidin-2-one (10):** Prepared according to **GP III** from ynamide **S5** (32 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **10** (72 mg, 92%, *E*/*Z* > 98:2) as a white solid; mp 162–166 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.44 (m, 6H), 7.40–7.33 (m, 9H), 7.15–7.13 (m, 3H), 7.07–7.05 (m, 2H), 6.00 (s, 1H), 3.87 (s, 2H), 1.16 (s, 6H).

JMod (100 MHz, $CDCl_3$): δ 154.9, 141.9, 139.5, 135.5, 135.3, 129.4, 128.4, 128.0 (2C), 127.9, 126.6, 75.0, 59.7, 24.9.

IR (neat): ν (cm^{-1}) 3058, 2971, 1755, 1338, 735, 698.

HRMS (ESI): *m/z* calculated for $[C_{31}H_{29}GeNO_2 + Na]^+$ 544.1309; found 544.1296.



$C_{31}H_{28}DGeNO_2$

M = 521.21 g·mol^{-1}

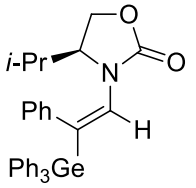
[^{2}H]-**10**

[^{2}H]-10: Prepared according to **GP IV** from ynamide **S5** (32 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure [^{2}H]-**10** (69 mg, 88%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.44 (m, 6H), 7.42–7.33 (m, 9H), 7.18–7.12 (m, 3H), 7.09–7.06 (m, 2H), 3.88 (s, 2H), 1.16 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.8, 141.5, 139.4, 135.5, 135.3, 129.3, 128.4, 128.0 (2C), 126.5, 74.9, 59.6, 24.9. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{31}H_{28}DGeNO_2 + Na]^+$ 545.1371; found 545.1383.



$C_{32}H_{31}GeNO_2$

M = 534.23 g·mol^{-1}

11

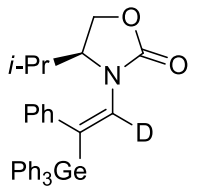
***(S,E)*-4-isopropyl-3-(2-phenyl-2-(triphenylgermyl)vinyl)oxazolidin-2-one (11):** Prepared according to **GP III** from ynamide **S6** (34 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* = 92:8) by flash chromatography on silica gel (pentane/Et_2O = 80:20) afforded analytically pure **11** (69 mg, 86%, *E*/*Z* > 98:2) as a white solid; mp 147–150 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.32 (m, 15H), 7.19–7.15 (m, 3H), 6.99–6.97 (m, 2H), 6.83 (s, 1H), 4.03–3.95 (m, 2H), 3.21 (dt, *J* = 8.2 Hz, *J* = 3.0 Hz, 1H), 1.97 (heptd, *J* = 7.0 Hz, *J* = 3.0 Hz, 1H), 0.76 (d, *J* = 7.0 Hz, 3H), 0.37 (d, *J* = 7.0 Hz, 3H).

JMod (100 MHz, $CDCl_3$): δ 156.8, 139.7, 135.5, 135.45, 129.6, 129.3, 128.9, 128.4, 128.3, 126.6, 122.7, 62.6, 58.5, 26.9, 17.4, 13.4.

IR (neat): ν (cm^{-1}) 3059, 2920, 2871, 1756, 1611, 1218, 909, 730, 698.

HRMS (ESI): *m/z* calculated for $[C_{32}H_{31}GeNO_2 + Na]^+$ 558.1466; found 558.1484.
$[\alpha]_D^{20}$: –171.2 (*c* 1.0, CH_2Cl_2).

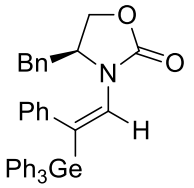


$C_{32}H_{30}DGeNO_2$
M = 535.24 g·mol^{-1}

[^{2}H]-**11**

[^{2}H]-11: Prepared according to **GP IV** from ynamide **S6** (34 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* = 90:10) by flash chromatography on silica gel (pentane/Et_2O = 80:20) afforded [^{2}H]-**11** (66 mg, 83%, *E/Z* = 86:14) as a white solid, contaminated with 6% of unidentified triphenylgermyl-containing residues.

^{1}H NMR (400 MHz, $CDCl_3$): (*E*-isomer) δ 7.46–7.31 (m, 15H), 7.20–7.11 (m, 3H), 6.99–6.96 (m, 2H), 4.04–3.94 (m, 2H), 3.21 (dt, *J* = 8.3 Hz, *J* = 3.0 Hz, 1H), 1.97 (heptd, *J* = 7.0 Hz, *J* = 3.0 Hz, 1H), 0.75 (d, *J* = 7.0 Hz, 3H), 0.37 (d, *J* = 7.0 Hz, 3H).
JMod (100 MHz, $CDCl_3$): (*E*-isomer) δ 156.8, 139.7, 135.6, 135.5, 129.3, 128.9, 128.35, 128.28, 126.6, 122.7, 62.6, 58.4, 26.9, 17.4, 13.4. *One C is not observed.*
HRMS (ESI): *m/z* calculated for $[C_{32}H_{30}DGeNO_2 + Na]^+$ 559.1528; found 559.1547.



$C_{36}H_{31}GeNO_2$
M = 582.28 g·mol^{-1}

12

***(S,E)*-4-benzyl-3-(2-phenyl-2-(triphenylgermyl)vinyl)oxazolidin-2-one (12):** Prepared according to **GP III** from ynamide **S7** (42 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 75:25) afforded analytically pure **12** (74 mg, 85%, *E*/*Z* > 98:2) as a white solid; mp 173–176 °C.

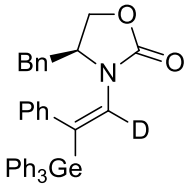
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.32 (m, 15H), 7.29–7.23 (m, 3H), 7.19–7.07 (m, 5H), 6.89 (s, 1H), 6.62–6.54 (m, 2H), 3.96–3.85 (m, 2H), 3.76 (ddt, *J* = 10.5 Hz, *J* = 6.8 Hz, *J* = 3.6 Hz, 1H), 3.01 (dd, *J* = 13.3 Hz, *J* = 3.6 Hz, 1H), 2.37 (dd, *J* = 13.3 Hz, *J* = 10.5 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.5, 139.9, 135.6, 135.5, 135.3, 129.6, 129.4, 129.37, 129.3, 128.8, 128.7, 128.4, 127.1, 126.9, 121.8, 65.6, 55.2, 37.0.

IR (neat): ν (cm^{-1}) 3060, 2920, 1761, 1395, 1085, 734, 699.

HRMS (ESI): *m/z* calculated for $[C_{36}H_{31}GeNO_2 + Na]^+$ 606.1467; found 606.1468.

$[\alpha]_D^{20}$: –168.5 (*c* 0.25, CH_2Cl_2).



$C_{36}H_{30}DGeNO_2$

M = 583.28 g·mol^{-1}

[^{2}H]-**12**

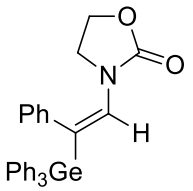
[^{2}H]-12: Prepared according to **GP IV** from ynamide **S7** (42 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 75:25) afforded analytically pure [^{2}H]-**12** (63 mg, 72%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.31 (m, 15H), 7.29–7.23 (m, 3H), 7.17–7.06 (m, 5H), 6.60–6.45 (m, 2H), 3.96–3.84 (m, 2H), 3.82–3.71 (m, 1H), 3.00 (dd, *J* = 13.3 Hz, *J* = 3.5 Hz, 1H), 2.36 (dd, *J* = 13.3 Hz, *J* = 10.5 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.4, 139.8, 135.6, 135.5, 135.3, 129.4, 129.37, 129.3, 128.8, 128.7, 128.4, 127.1, 126.9, 121.5, 65.6, 55.2, 37.0. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{36}H_{30}DGeNO_2 + Na]^+$ 607.1529; found 607.1549.

The E configuration was determined by X-ray crystallographic analysis.



$C_{29}H_{25}GeNO_2$

M = 492.15 g·mol^{-1}

13

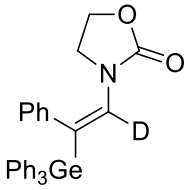
***(E)*-3-(2-phenyl-2-(triphenylgermyl)vinyl)oxazolidin-2-one (13):** Prepared according to **GP III** from ynamide **S8** (28 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **13** (51 mg, 69%, *E*/*Z* > 98:2) as a white solid; mp 217–220 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.30 (m, 15H), 7.14–7.11 (m, 3H), 6.97–6.94 (m, 2H), 6.89 (s, 1H), 4.13–4.09 (m, 2H), 3.18–3.14 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.7, 139.4, 135.5, 135.4, 130.5, 129.6, 129.3, 128.3, 127.8, 126.5, 119.5, 62.5, 45.1.

IR (neat): ν (cm^{-1}) 3059, 1757, 1395, 1229, 1082, 907, 731, 695.

HRMS (ESI): *m/z* calculated for $[C_{29}H_{25}GeNO_2 + Na]^+$ 516.0995; found 516.1015.



$C_{29}H_{24}DGeNO_2$

M = 493.16 g·mol^{-1}

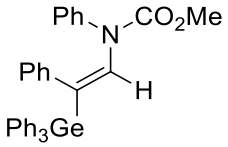
[^{2}H]-**13**

[^{2}H]-13: Prepared according to **GP IV** from ynamide **S8** (28 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure [^{2}H]-**13** (59 mg, 80%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.31 (m, 15H), 7.15–7.12 (m, 3H), 6.97–6.95 (m, 2H), 4.13–4.09 (m, 2H), 3.18–3.14 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.7, 139.3, 135.5, 135.4, 129.6, 129.3, 128.3, 127.8, 126.5, 119.2, 62.6, 45.1. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{29}H_{24}DGeNO_2 + Na]^+$ 517.1058; found 517.1073.



$C_{34}H_{29}GeNO_2$

M = 556.24 g·mol^{-1}

14

***(E)*-methyl phenyl(2-phenyl-2-(triphenylgermyl)vinyl)carbamate (14):** Prepared according to **GP III** from ynamide **S9** (38 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 90:10) afforded analytically pure **14** (61 mg, 73%, *E*/*Z* > 98:2) as a white solid; mp 136–138 °C.

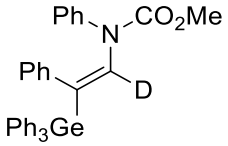
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.31 (m, 15H), 7.05 (s, 1H), 7.02–6.98 (m, 2H), 6.96–6.89 (m, 3H), 6.87–6.81 (m, 3H), 6.60–6.58 (m, 2H), 3.65 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.3, 140.7, 139.2, 136.3, 135.8, 135.6, 129.2, 128.5, 128.3, 128.2, 127.6, 127.4, 126.0, 125.6, 53.4. *One C is not observed.*

IR (neat): ν (cm^{-1}) 3059, 1717, 1601, 1437, 1329, 1289, 733, 696.

HRMS (ESI): *m/z* calculated for $[C_{34}H_{29}GeNO_2 + Na]^+$ 580.1310; found 580.1329.

The E configuration was determined by X-ray crystallographic analysis.



$C_{34}H_{28}DGeNO_2$

M = 557.25 g·mol^{-1}

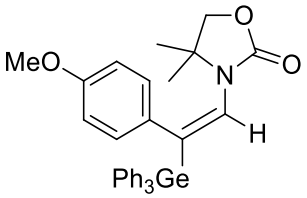
[^{2}H]-**14**

[^{2}H]-14: Prepared according to **GP IV** from ynamide **S9** (38 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 90:10) afforded analytically pure [^{2}H]-**14** (61 mg, 73%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.32 (m, 15H), 7.03–6.98 (m, 2H), 6.96–6.90 (m, 3H), 6.88–6.81 (m, 3H), 6.61–6.59 (m, 2H), 3.66 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 155.3, 140.7, 139.1, 135.8, 135.5, 129.2, 128.5, 128.3, 128.2, 127.6, 127.4, 126.0, 125.5, 53.4. *Two Cs are not observed.*

HRMS (ESI): *m/z* calculated for $[C_{34}H_{28}DGeNO_2 + Na]^+$ 581.1372; found 581.1365.



$C_{32}H_{31}GeNO_3$

M = 550.23 g·mol^{-1}

15

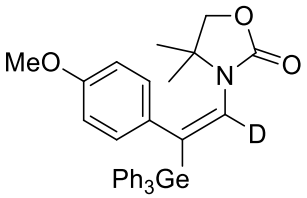
***(E)*-3-(2-(4-methoxyphenyl)-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (15):** Prepared according to **GP III** from ynamide **S12** (37 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = gradient from 60:40 to 50:50) afforded analytically pure **15** (78 mg, 94%, *E*/*Z* > 98:2) as a white solid; mp 151–153 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.46 (m, 6H), 7.42–7.34 (m, 9H), 7.04–7.00 (m, 2H), 6.73–6.70 (m, 2H), 5.99 (s, 1H), 3.89 (s, 2H), 3.74 (s, 3H), 1.15 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.3, 155.0, 141.7, 135.5, 135.47, 131.6, 129.3, 129.2, 128.4, 127.8, 113.5, 74.9, 59.7, 55.1, 24.9.

IR (neat): ν (cm^{-1}) 3058, 2969, 1750, 1510, 1244, 1030, 735, 698.

HRMS (ESI): *m/z* calculated for $[C_{32}H_{31}GeNO_3 + Na]^+$ 574.1415; found 574.1431.



$C_{32}H_{30}DGeNO_3$

M = 551.24 g·mol^{-1}

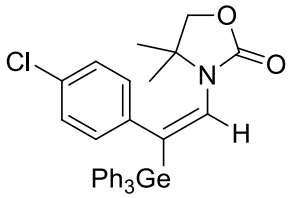
[^{2}H]-**15**

[^{2}H]-15: Prepared according to **GP IV** from ynamide **S12** (37 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = gradient from 60:40 to 50:50) afforded analytically pure [^{2}H]-**15** (75 mg, 90%, *E*/*Z* > 98:2) as a white solid.

^1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.45 (m, 6H), 7.42–7.33 (m, 9H), 7.03–7.00 (m, 2H), 6.73–6.69 (m, 2H), 3.89 (s, 2H), 3.74 (s, 3H), 1.15 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.3, 155.0, 141.4, 135.5, 135.48, 131.6, 129.3, 129.2, 128.4, 113.5, 75.0, 59.7, 55.2, 24.9. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{32}H_{30}DGeNO_3 + Na]^+$ 575.1478; found 575.1497.



$C_{31}H_{28}ClGeNO_2$

M = 554.65 g·mol^{-1}

16

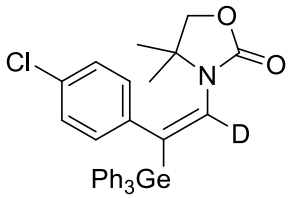
***(E)*-3-(2-(4-chlorophenyl)-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (16):** Prepared according to **GP III** from ynamide **S13** (38 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 65:35) afforded analytically pure **16** (74 mg, 89%, *E*/*Z* > 98:2) as a white solid; mp 168–170 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.35 (m, 15H), 7.15–7.11 (m, 2H), 7.01–6.97 (m, 2H), 6.00 (s, 1H), 3.90 (s, 2H), 1.19 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.5, 140.3, 138.1, 135.5, 134.9, 132.3, 129.5, 129.3, 128.5, 128.3, 128.2, 74.9, 59.5, 24.9.

IR (neat): ν (cm^{-1}) 3059, 2972, 1756, 1338, 1084, 912, 734, 698.

HRMS (ESI): *m/z* calculated for $[C_{31}H_{28}ClGeNO_2 + Na]^+$ 578.0915; found 578.0932.



$C_{31}H_{27}DClGeNO_2$

M = 555.66 g·mol^{-1}

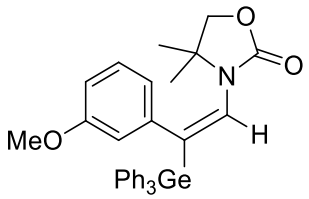
[^{2}H]-**16**

[^{2}H]-16: Prepared according to **GP IV** from ynamide **S13** (38 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 65:35) afforded analytically pure [^{2}H]-**16** (72 mg, 87%, *E*/*Z* > 98:2) as a white solid.

^1H NMR (400 MHz, $CDCl_3$): δ 7.47–7.34 (m, 15H), 7.14–7.11 (m, 2H), 7.00–6.97 (m, 2H), 3.90 (s, 2H), 1.18 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 154.5, 140.0, 138.1, 135.5, 134.9, 132.3, 129.5, 129.3, 128.5, 128.3, 74.9, 59.5, 24.9. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{31}H_{27}DClGeNO_2 + Na]^+$ 579.0977; found 579.0987.



$C_{32}H_{31}GeNO_3$

M = 550.23 g·mol^{-1}

17

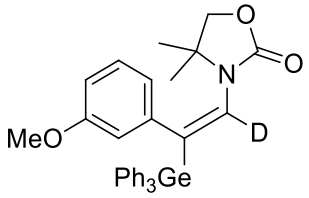
***(E)*-3-(2-(3-methoxyphenyl)-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (17):** Prepared according to **GP III** from ynamide **S14** (37 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 4 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **17** (69 mg, 83%, *E*/*Z* > 98:2) as a white solid; mp 130–132 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.45 (m, 6H), 7.42–7.34 (m, 9H), 7.07 (dd, *J* = 8.3 Hz, *J* = 7.6 Hz, 1H), 6.68 (dtd, *J* = 7.6 Hz, *J* = 2.5 Hz, *J* = 1.6 Hz, 2H), 6.61 (dd, *J* = 2.5 Hz, *J* = 1.6 Hz, 1H), 6.00 (s, 1H), 3.89 (s, 2H), 3.53 (s, 3H), 1.16 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.2, 155.0, 142.1, 140.7, 135.5, 135.3, 129.4, 129.0, 128.4, 127.9, 120.4, 113.1, 113.0, 75.0, 59.7, 55.0, 24.9.

IR (neat): ν (cm^{-1}) 3059, 2969, 1754, 1602, 1338, 1082, 735, 698.

HRMS (ESI): *m/z* calculated for $[C_{32}H_{31}GeNO_3 + Na]^+$ 574.1415; found 574.1432.



$C_{32}H_{30}DGeNO_3$

M = 551.24 g·mol^{-1}

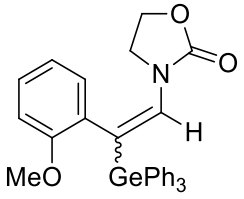
[^{2}H]-**17**

[^{2}H]-17: Prepared according to **GP IV** from ynamide **S14** (37 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 5 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure [^{2}H]-**17** (73 mg, 88%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.45 (m, 6H), 7.42–7.34 (m, 9H), 7.07 (dd, *J* = 8.3 Hz, *J* = 7.5 Hz, 1H), 6.70–6.67 (m, 2H), 6.61 (dd, *J* = 2.5 Hz, *J* = 1.6 Hz, 1H), 3.89 (s, 2H), 3.53 (s, 3H), 1.16 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 155.0, 141.7, 140.7, 135.5, 135.3, 129.4, 129.0, 128.4, 120.4, 113.1, 113.0, 75.0, 59.7, 55.0, 24.9. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{32}H_{30}DGeNO_3 + Na]^+$ 575.1478; found 575.1489.



$C_{30}H_{27}GeNO_3$

M = 522.18 g·mol^{-1}

18

3-(2-(2-methoxyphenyl)-2-(triphenylgermyl)vinyl)oxazolidin-2-one (18): Prepared according to **GP III** from ynamide **S15** (33 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 6 h. Purification of the crude product (*E*/*Z* = 60:40) by flash chromatography on silica gel (pentane/Et_2O = gradient from 70:30 to 60:40) afforded two fractions containing, respectively, analytically pure *E*-**18** (38 mg, 49%, *E*/*Z* > 98:2) and analytically pure *Z*-**18** (25 mg, 32%, *Z*/*E* > 98:2), as white solids.

E-**18**

mp 151–153 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.26 (m, 15H), 7.10 (ddd, *J* = 8.2 Hz, *J* = 7.4 Hz, *J* = 1.8 Hz, 1H), 6.95 (dd, *J* = 7.4 Hz, *J* = 1.8 Hz, 1H), 6.89 (s, 1H), 6.77 (td, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H), 6.51 (dd, *J* = 8.2 Hz, *J* = 1.1 Hz, 1H), 4.14 (t, *J* = 8.1 Hz, 2H), 3.33–3.22 (m, 2H), 3.20 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.8, 156.6, 136.3, 135.4, 130.5, 130.48, 129.0, 128.3 128.1, 128.0, 119.9, 116.1, 110.3, 62.5, 54.8, 44.4.

IR (neat): ν (cm^{-1}) 3059, 1759, 1629, 1397, 1236, 1082, 740, 700.

HRMS (ESI): *m/z* calculated for $[C_{30}H_{27}GeNO_3 + Na]^+$ 546.1101; found 546.1122.

Z-**18:**

mp 151–153 ºC.

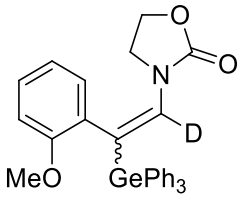
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.48 (m, 6H), 7.45 (s, 1H), 7.34–7.23 (m, 10H), 7.00 (ddd, *J* = 8.1 Hz, *J* = 7.4 Hz, *J* = 1.7 Hz, 1H), 6.83 (td, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H), 6.27 (dd, *J* = 8.1 Hz, *J*

= 1.1 Hz, 1H), 3.79 (dd, *J* = 8.7 Hz, *J* = 7.0 Hz, 2H), 3.41 (dd, *J* = 8.7 Hz, *J* = 7.0 Hz, 2H), 3.20 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 157.0, 156.4, 138.0, 135.4, 134.9, 132.6, 129.9, 129.0, 128.1, 128.0, 120.4, 118.8, 109.4, 62.3, 54.1, 45.8.

IR (neat): ν (cm^{-1}) 3059, 1760, 1610, 1483, 1399, 911, 737, 698.

HRMS (ESI): *m/z* calculated for $[C_{30}H_{27}GeNO_3 + Na]^+$ 546.1101; found 546.1103.



$C_{30}H_{26}DGeNO_3$

M = 523.19 g·mol^{-1}

[^{2}H]-**18**

[^{2}H]-18: Prepared according to **GP IV** from ynamide **S15** (33 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 6 h. Purification of the crude product (*E*/*Z* = 52:48) by flash chromatography on silica gel (pentane/Et_2O = gradient from 70:30 to 60:40) afforded two fractions containing, respectively, analytically pure *E*-[^{2}H]-**18** (33 mg, 42%, *E*/*Z* > 98:2) and analytically pure *Z*-[^{2}H]-**18** (33 mg, 42%, *Z*/*E* > 98:2), as white solids.

E-[^{2}H]-**18**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.27 (m, 15H), 7.11 (ddd, *J* = 8.2 Hz, *J* = 7.4 Hz, *J* = 1.8 Hz, 1H), 6.96 (dd, *J* = 7.4 Hz, *J* = 1.8 Hz, 1H), 6.78 (td, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H), 6.52 (dd, *J* = 8.2 Hz, *J* = 1.1 Hz, 1H), 4.14 (t, *J* = 8.1 Hz, 2H), 3.34–3.23 (m, 2H), 3.21 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 156.8, 156.6, 136.2, 135.4, 130.5, 129.0, 128.3 128.1, 128.0, 119.9, 115.9, 110.3, 62.5, 54.8, 44.3. *One C is not observed.*

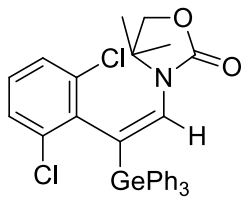
HRMS (ESI): *m/z* calculated for $[C_{30}H_{26}DGeNO_3 + Na]^+$ 547.1164; found 547.1144.

Z-[^{2}H]-**18**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.47 (m, 6H), 7.32–7.22 (m, 10H), 6.99 (ddd, *J* = 8.2 Hz, *J* = 7.4 Hz, *J* = 1.8 Hz, 1H), 6.81 (td, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H), 6.25 (dd, *J* = 8.2 Hz, *J* = 1.1 Hz, 1H), 3.77 (dd, *J* = 8.7 Hz, *J* = 7.0 Hz, 2H), 3.40 (dd, *J* = 8.7 Hz, *J* = 7.0 Hz, 2H), 3.18 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 157.0, 156.4, 138.0, 134.9, 132.6, 129.9, 128.9, 128.1, 128.0, 120.4, 118.5, 109.4, 62.3, 54.1, 45.8. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{30}H_{26}DGeNO_3 + Na]^+$ 547.1164; found 547.1184.



$C_{31}H_{27}Cl_2GeNO_2$

M = 589.10 g·mol^{-1}

19

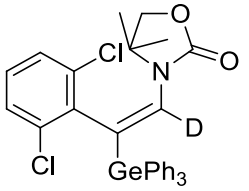
***(E)*-3-(2-(2,6-dichlorophenyl)-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (19):** Prepared according to **GP III** from ynamide **S16** (43 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **19** (61 mg, 69%, *E*/*Z* > 98:2) as a white solid; mp 159–160 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.53 (m, 6H), 7.39–7.29 (m, 9H), 7.10–7.08 (m, 2H), 6.91 (dd, *J* = 8.5, 7.6 Hz, 1H), 6.17 (s, 1H), 3.95 (s, 2H), 1.31 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.2, 138.4, 136.1, 135.3, 133.9, 130.3, 129.2, 128.0, 127.6, 127.5, 126.7, 74.8, 60.1, 25.2.

IR (neat): ν (cm^{-1}) 3059, 1765, 1432, 1340, 1083, 912, 734, 697.

HRMS (ESI): *m/z* calculated for $[C_{31}H_{27}Cl_2GeNO_2 + Na]^+$ 612.0521; found 612.0546.



$C_{31}H_{26}DCl_2GeNO_2$

M = 590.10 g·mol^{-1}

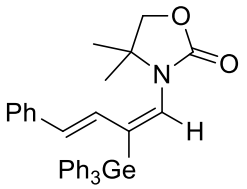
[^{2}H]-**19**

[^{2}H]-19: Prepared according to **GP IV** from ynamide **S16** (43 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. The reaction quench was modified by adding CuTC (48 mg, 0.25 mmol, 1.7 equiv) and stirring for 5 min before the addition of ND_4Cl/D_2O. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure [^{2}H]-**19** (64 mg, 72%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.53 (m, 6H), 7.37–7.30 (m, 9H), 7.10–7.08 (m, 2H), 6.92 (dd, *J* = 8.5, 7.5 Hz, 1H), 3.95 (s, 2H), 1.31 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.2, 138.4, 136.1, 135.3, 133.9, 129.1, 128.0, 127.6, 127.5, 126.3, 74.7, 60.0, 25.2. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{31}H_{26}DCl_2GeNO_2 + Na]^+$ 613.0584; found 613.0604.



$C_{33}H_{31}GeNO_2$

M = 546.24 g·mol^{-1}

20

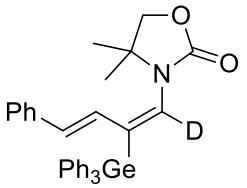
4,4-dimethyl-3-((1*E*,3*E*)-4-phenyl-2-(triphenylgermyl)buta-1,3-dien-1-yl)oxazolidin-2-one (20): Prepared according to **GP III** from ynamide **S17** (36 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **20** (70 mg, 85%, *E*/*Z* > 98:2) as a yellow solid; mp 149–151 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.65 (m, 6H), 7.45–7.38 (m, 9H), 7.33 (dd, J_{trans} = 16.2 Hz, *J* = 1.0 Hz, 1H), 7.24–7.14 (m, 5H), 6.53 (d, J_{trans} = 16.2 Hz, 1H), 5.63 (t, *J* = 1.0 Hz, 1H), 4.10 (s, 2H), 1.22 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 137.6, 136.1, 135.4, 135.2, 132.8, 129.3, 128.6, 128.5, 128.46, 127.7, 127.1, 126.7, 74.9, 59.7, 24.9.

IR (neat): ν (cm^{-1}) 3071, 2970, 1752, 1338, 1074, 909, 734, 697.

HRMS (ESI): *m/z* calculated for $[C_{33}H_{31}GeNO_2 + Na]^+$ 570.1466; found 570.1470.



$C_{33}H_{30}DGeNO_2$

M = 547.25 g·mol^{-1}

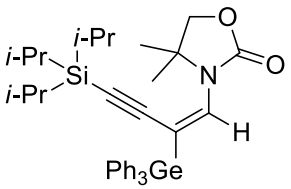
[^{2}H]-**20**

[^{2}H]-20: Prepared according to **GP IV** from ynamide **S17** (36 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure [^{2}H]-**20** (66 mg, 80%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.65 (m, 6H), 7.43–7.38 (m, 9H), 7.33 (d, J_{trans} = 16.2 Hz, 1H), 7.23–7.16 (m, 5H), 6.53 (d, J_{trans} = 16.2 Hz, 1H), 4.10 (s, 2H), 1.22 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 137.6, 136.1, 135.4, 135.1, 132.5, 129.3, 128.5, 128.46, 127.7, 127.1, 126.7, 74.9, 59.7, 24.9. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{33}H_{30}DGeNO_2 + Na]^+$ 571.1529; found 571.1545.



$C_{36}H_{45}GeNO_2Si$

M = 624.47 g·mol^{-1}

21

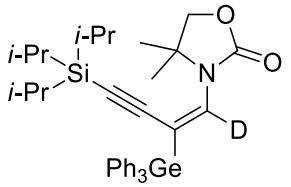
***(E)*-4,4-dimethyl-3-(4-(triisopropylsilyl)-2-(triphenylgermyl)but-1-en-3-yn-1-yl) oxazolidin-2-one (21):** Prepared according to **GP III** from ynamide **S18** (48 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/EtOAc = 95:5) afforded analytically pure **21** (42 mg, 45%, *E*/*Z* > 98:2) as a white solid; mp 147–149 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.63 (m, 6H), 7.42–7.39 (m, 9H), 6.24 (s, 1H), 3.84 (s, 2H), 1.11 (s, 6H), 1.08 (s, 21H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.9, 147.5, 135.52, 135.47, 129.5, 128.9, 128.6, 102.1, 101.4, 76.1, 61.5, 26.2, 18.7, 11.4.

IR (neat): ν (cm^{-1}) 2938, 2863, 1749, 1345, 1080, 738, 702, 669.

HRMS (ESI): *m/z* calculated for $[C_{36}H_{45}GeNO_2Si + Na]^+$ 648.2331; found 648.2357.



$C_{36}H_{44}DGeNO_2Si$

M = 625.48 g·mol^{-1}

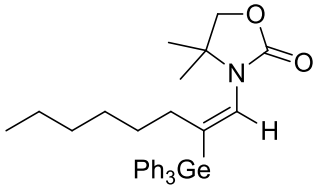
[^{2}H]-**21**

[^{2}H]-21: Prepared according to **GP IV** from ynamide **S18** (48 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/EtOAc = 95:5) afforded analytically pure [^{2}H]-**21** (42 mg, 45%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.64 (m, 6H), 7.42–7.39 (m, 9H), 3.84 (s, 2H), 1.12 (s, 6H), 1.09 (s, 21H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.9, 147.4, 135.53, 135.5, 129.5, 128.6, 102.1, 101.4, 76.1, 61.5, 26.2, 18.7, 11.4. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{36}H_{44}DGeNO_2Si + Na]^+$ 649.2386; found 649.2385.



$C_{31}H_{37}GeNO_2$

M = 528.27 g·mol^{-1}

22

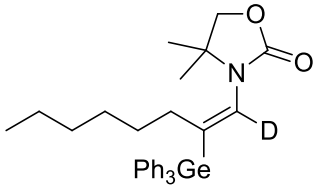
***(E)*-4,4-dimethyl-3-(2-(triphenylgermyl)oct-1-en-1-yl)oxazolidin-2-one (22):** Prepared according to **GP III** from ynamide **S19** (34 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E/Z* = 90:10) by flash chromatography on silica gel (toluene/Et_2O = 90:10) afforded analytically pure **22** (67 mg, 85%, *E/Z* = 90:10) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): (*E*-isomer) δ 7.59–7.53 (m, 6H), 7.43–7.36 (m, 9H), 5.71 (t, *J* = 1.1 Hz, 1H), 4.05 (s, 2H), 2.37–2.33 (m, 2H), 1.29–0.90 (m, 14H), 0.79–0.74 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*E*-isomer) δ 154.6, 141.6, 136.0, 135.4, 129.3, 128.4, 126.5, 75.0, 59.2, 31.37, 31.35, 29.7, 28.7, 24.9, 22.6, 14.1.

IR (neat): ν (cm^{-1}) 2964, 2923, 2857, 1755, 1613, 1335, 739, 701.

HRMS (ESI): *m/z* calculated for $[C_{31}H_{37}GeNO_2 + Na]^+$ 552.1935; found 552.1950.



$C_{31}H_{36}DGeNO_2$

M = 529.28 g·mol^{-1}

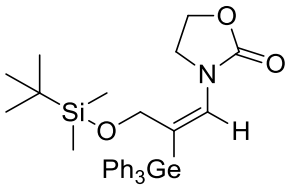
[^{2}H]-**22**

[^{2}H]-22: Prepared according to **GP IV** from ynamide **S19** (34 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E/Z* = 92:8) by flash chromatography on silica gel (toluene/Et_2O = 90:10) afforded analytically pure [^{2}H]-**22** (69 mg, 87%, *E/Z* = 92:8) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): (*E*-isomer) δ 7.59–7.53 (m, 6H), 7.43–7.36 (m, 9H), 4.05 (s, 2H), 2.37–2.33 (m, 2H), 1.28–0.90 (m, 14H), 0.79–0.74 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*E*-isomer) δ 154.6, 141.3, 136.1, 135.4, 129.3, 128.4, 75.0, 59.2, 31.4, 31.3, 29.7, 28.7, 24.9, 22.6, 14.1. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{31}H_{36}DGeNO_2 + Na]^+$ 553.1997; found 553.2019.



$C_{30}H_{37}GeNO_3Si$

M = 560.35 g·mol^{-1}

23

***(E)*-3-(3-((tert-butyldimethylsilyl)oxy)-2-(triphenylgermyl)prop-1-en-1-yl)oxazolidin-2-one (23):** Prepared according to **GP III** from ynamide **S20** (38 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **23** (44 mg, 52%, *E*/*Z* > 98:2) as colorless crystals; mp 116–119 °C.

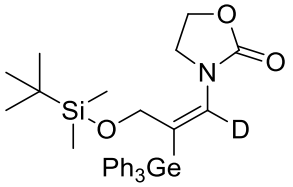
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.55 (m, 6H), 7.39–7.35 (m, 9H), 6.41 (t, *J* = 1.3 Hz, 1H), 4.45 (d, *J* = 1.3 Hz, 2H), 4.40–4.36 (m, 2H), 4.10–4.07 (m, 2H), 0.73 (s, 9H), –0.25 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.5, 136.4, 135.5, 132.3, 129.1, 128.3, 121.4, 62.3, 60.4, 45.6, 25.9, 18.3, –5.7.

IR (neat): ν (cm^{-1}) 3058, 2926, 2854, 1761, 1622, 1092, 843, 736, 700.

HRMS (ESI): *m/z* calculated for $[C_{30}H_{37}GeNO_3Si + Na]^+$ 584.1653; found 584.1664.

The E configuration was determined by X-ray crystallographic analysis.



$C_{30}H_{36}DGeNO_3Si$

M = 561.35 g·mol^{-1}

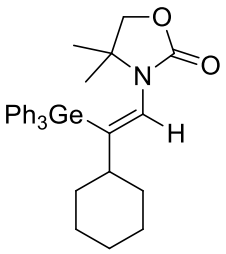
[^{2}H]-**23**

[^{2}H]-23: Prepared according to **GP IV** from ynamide **S20** (38 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 3 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure [^{2}H]-**23** (35 mg, 42%, *E*/*Z* > 98:2) as white crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.55 (m, 6H), 7.39–7.35 (m, 9H), 4.45 (s, 2H), 4.40–4.36 (m, 2H), 4.11–4.07 (m, 2H), 0.73 (s, 9H), –0.26 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.5, 136.4, 135.5, 129.1, 128.3, 120.9, 62.3, 60.3, 45.5, 25.9, 18.3, –5.8. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{30}H_{36}DGeNO_3Si + Na]^+$ 585.1716; found 585.1732.



$C_{31}H_{35}GeNO_2$

M = 526.26 g·mol^{-1}

24

***(Z)*-3-(2-cyclohexyl-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (24):** Prepared according to **GP III** from ynamide **S21** (33 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (92 mg, 0.30 mmol, 2.0 equiv) and a reaction time of 16 h. Purification of the crude product (*Z/E* = 92:8) by flash chromatography on silica gel (toluene/Et_2O = 92:8) afforded analytically pure **24** (50 mg, 63%, *Z/E* = 92:8) as a white solid; mp 155–158 ºC.

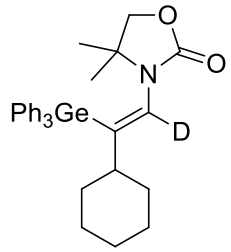
^{1}H NMR (400 MHz, $CDCl_3$): (*Z*-isomer) δ 7.67–7.63 (m, 6H), 7.40–7.33 (m, 9H), 6.35 (d, *J* = 1.0 Hz, 1H), 3.13 (s, 2H), 2.16–2.09 (m, 1H), 1.82–1.78 (m, 2H), 1.65–1.53 (m, 3H), 1.28–1.18 (m, 2H), 1.15 (s, 6H), 1.12–1.04 (m, 1H), 1.01–0.90 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*Z*-isomer) δ 155.7, 145.0, 137.4, 135.8, 128.8, 128.1, 127.9, 74.0, 59.3, 42.8, 34.6, 27.0, 26.2, 23.6.

IR (neat): ν (cm^{-1}) 2927, 2851, 1753, 1370, 1091, 911, 734, 698.

HRMS (ESI): *m/z* calculated for $[C_{31}H_{35}GeNO_2 + Na]^+$ 550.1778; found 550.1766.

The Z configuration was assigned by analogy with **25**.



$C_{31}H_{34}DGeNO_2$

M = 527.26 g·mol^{-1}

[^{2}H]-**24**

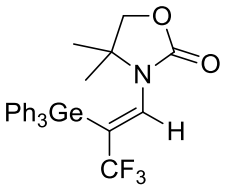
[^{2}H]-24: Prepared according to **GP IV** from ynamide **S21** (33 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (92 mg, 0.30 mmol, 2.0 equiv) and a reaction time of 16 h. The reaction quench was modified by adding CuTC (48 mg, 0.25 mmol, 1.7 equiv) and stirring for 5 min before the

addition of ND_4Cl/D_2O. Purification of the crude product (*Z*/*E* = 98:2) by flash chromatography on silica gel (toluene/Et_2O = 92:8) afforded analytically pure [^{2}H]-**24** (50 mg, 63%, *Z*/*E* = 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.64 (m, 6H), 7.40–7.32 (m, 9H), 3.13 (s, 2H), 2.13 (tt, *J* = 11.7 Hz, *J* = 3.0 Hz, 1H), 1.83–1.78 (m, 2H), 1.65–1.54 (m, 3H), 1.29–1.16 (m, 2H), 1.16 (s, 6H), 1.14–1.05 (m, 1H), 1.02–0.90 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.6, 144.7, 137.4, 135.8, 128.7, 127.9, 74.0, 59.2, 42.8, 34.6, 27.0, 26.2, 23.6. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{31}H_{34}DGeNO_2 + Na]^+$ 551.1841; found 551.1834.



$C_{26}H_{24}F_3GeNO_2$

M = 512.11 g·mol^{-1}

25

***(Z)*-4,4-dimethyl-3-(3,3,3-trifluoro-2-(triphenylgermyl)prop-1-en-1-yl)oxazolidin-2-one (25):** Prepared according to **GP III** from ynamide **S22** (31 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **25** (44 mg, 57%, *Z*/*E* > 98:2) as a white solid; mp 203–206 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.62 (m, 6H), 7.40–7.33 (m, 9H), 7.07 (q, $^4J_{HF}$ = 1.7 Hz, 1H), 3.29 (s, 2H), 1.28 (s, 6H).

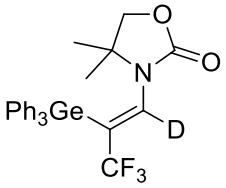
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.8, 137.0 (q, $^3J_{CF}$ = 1.7 Hz), 135.7, 135.6, 129.1, 128.0, 126.4 (q, $^1J_{CF}$ = 273.7 Hz), 122.2 (q, $^2J_{CF}$ = 30.2 Hz), 74.3, 59.6, 24.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ –53.8 (d, $^4J_{FH}$ = 1.7 Hz).

IR (neat): ν (cm^{-1}) 2974, 1769, 1614, 1268, 1228, 1118, 739, 697.

HRMS (ESI): *m/z* calculated for $[C_{26}H_{24}F_3GeNO_2 + Na]^+$ 536.0868; found 536.0869.

The Z configuration was determined by X-ray crystallographic analysis.



$C_{26}H_{23}DF_3GeNO_2$

M = 513.12 g·mol^{-1}

[^{2}H]-**25**

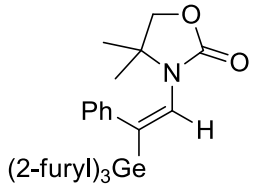
[^{2}H]-25: Prepared according to **GP IV** from ynamide **S22** (31 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*Z*/*E* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure [^{2}H]-**25** (42 mg, 55%, *Z*/*E* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.63 (m, 6H), 7.41–7.34 (m, 9H), 3.29 (s, 2H), 1.28 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.8, 135.7, 135.5, 129.1, 127.9, 126.5 (q, $^1J_{CF}$ = 274.0 Hz), 121.8 (q, $^2J_{CF}$ = 30.2 Hz), 74.3, 59.6, 24.0. *One C is not observed.*

^{19}F NMR (376 MHz, $CDCl_3$): δ –53.8 (s).

HRMS (ESI): *m/z* calculated for [$C_{26}H_{23}DF_3GeNO_2$ + Na]$^+$ 537.0931; found 537.0950.



$C_{25}H_{23}GeNO_5$

M = 490.09 g·mol^{-1}

26

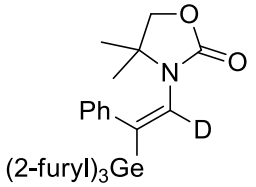
***(E)*-4,4-dimethyl-3-(2-phenyl-2-(tri(furan-2-yl)germyl)vinyl)oxazolidin-2-one (26):** Prepared according to **GP III** from ynamide **S5** (32 mg, 0.15 mmol, 1.0 equiv) with (2-furyl)$_3$GeH (74 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/EtOAc = 70:30) afforded analytically pure **26** (65 mg, 88%, *E*/*Z* > 98:2) as a white solid; mp 133–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 1.7 Hz, *J* = 0.6 Hz, 3H), 7.26–7.11 (m, 5H), 6.71 (dd, *J* = 3.3 Hz, *J* = 0.6 Hz, 3H), 6.45 (dd, *J* = 3.3 Hz, *J* = 1.7 Hz, 3H), 6.18 (s, 1H), 3.90 (s, 2H), 1.21 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 151.6, 147.7, 138.4, 136.9, 128.1, 128.08, 127.9, 126.9, 122.4, 110.1, 75.0, 59.8, 24.9.

IR (neat): ν (cm^{-1}) 2974, 1759, 1341, 1204, 1003, 897, 752, 698.

HRMS (ESI): *m/z* calculated for [$C_{25}H_{23}GeNO_5$ + Na]$^+$ 514.0685; found 514.0702.



$C_{25}H_{22}DGeNO_5$

M = 491.10 g·mol^{-1}

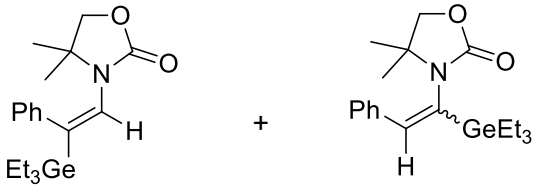
[^{2}H]-**26**

[^{2}H]-26: Prepared according to **GP IV** from ynamide **S5** (32 mg, 0.15 mmol, 1.0 equiv) with (2-furyl)$_3$GeH (74 mg, 0.20 mmol, 1.3 equiv) and a reaction time of 16 h. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/EtOAc = 70:30) afforded analytically pure [^{2}H]-**26** (65 mg, 88%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 1.7 Hz, *J* = 0.6 Hz, 3H), 7.24–7.11 (m, 5H), 6.71 (dd, *J* = 3.3 Hz, *J* = 0.6 Hz, 3H), 6.45 (dd, *J* = 3.3 Hz, *J* = 1.7 Hz, 3H), 3.90 (s, 2H), 1.22 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 151.6, 147.7, 138.4, 136.5, 128.1, 127.9, 126.9, 122.4, 110.1, 75.0, 59.7, 24.9. *One C is not observed.*

HRMS (ESI): *m/z* calculated for [$C_{25}H_{22}DGeNO_5$ + Na]$^+$ 515.0748; found 515.0746.



$C_{19}H_{29}GeNO_2$

M = 376.08 g·mol^{-1}

27 (β-isomer) **27** (α-isomer)

***(E)*-4,4-dimethyl-3-(2-phenyl-2-(triethylgermyl)vinyl)oxazolidin-2-one / 4,4-dimethyl-3-(2-phenyl-1-(triethylgermyl)vinyl)oxazolidin-2-one (27):** Prepared according to **GP III** from ynamide **S5** (32 mg, 0.15 mmol, 1.0 equiv) with Et_3GeH (48 mg, 0.30 mmol, 2.0 equiv) and a reaction time of 16 h. A mixture of regioisomers (β/α = 55:45) was obtained in the crude and they could not be separated during purification. Flash chromatography on silica gel (pentane/EtOAc = 90:10) afforded **27** (35 mg, 63%, mixture of regioisomers β/α = 55:45) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.16 (m, 2H$_{\beta\text{-isomer}}$ + 6H$_{\alpha\text{-isomer}}$), 7.10–7.06 (m, 1H$_{\beta\text{-isomer}}$), 6.99–6.97 (m, 2H$_{\beta\text{-isomer}}$), 5.76 (s, 1H$_{\beta\text{-isomer}}$), 4.01 (s, 2H$_{\alpha\text{-isomer}}$), 3.77 (s, 2H$_{\beta\text{-isomer}}$), 1.37 (s, 6H$_{\alpha\text{-}}$

$_{isomer}$), 1.07 (s, 6H$_{\beta\text{-isomer}}$), 0.98–0.93 (m, 9H$_{\beta\text{-isomer}}$), 0.89–0.85 (m, 9H$_{\alpha\text{-isomer}}$), 0.82–0.75 (m, 6H$_{\beta\text{-isomer}}$), 0.72–0.66 (m, 6H$_{\alpha\text{-isomer}}$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.2 ($C_{\alpha\text{-isomer}}$), 156.0 ($C_{\beta\text{-isomer}}$), 147.2 ($C_{\beta\text{-isomer}}$), 142.9 ($C_{\alpha\text{-isomer}}$), 141.1 ($C_{\alpha\text{-isomer}}$), 140.6 ($C_{\beta\text{-isomer}}$), 137.0 ($C_{\alpha\text{-isomer}}$), 128.7 ($C_{\alpha\text{-isomer}}$), 128.2 ($C_{\alpha\text{-isomer}}$), 128.0 ($C_{\beta\text{-isomer}}$), 127.96 ($C_{\alpha\text{-isomer}}$), 127.3 ($C_{\beta\text{-isomer}}$), 126.1 ($C_{\beta\text{-isomer}}$), 123.9 ($C_{\beta\text{-isomer}}$), 76.2 ($C_{\alpha\text{-isomer}}$), 75.0 ($C_{\beta\text{-isomer}}$), 60.9 ($C_{\alpha\text{-isomer}}$), 59.8 ($C_{\beta\text{-isomer}}$), 26.5 ($C_{\alpha\text{-isomer}}$), 24.8 ($C_{\beta\text{-isomer}}$), 9.1 ($C_{\alpha\text{-isomer}}$), 8.9 ($C_{\beta\text{-isomer}}$), 6.7 ($C_{\alpha\text{-isomer}}$), 4.3 ($C_{\beta\text{-isomer}}$).

HRMS (ESI): *m/z* calculated for $[C_{19}H_{29}GeNO_2 + Na]^+$ 400.1302; found 400.1304.

III.2.5 Domino Ynamide Germylzincation – Cu(I)-Mediated Electrophilic Trapping (GP V and GP VI)

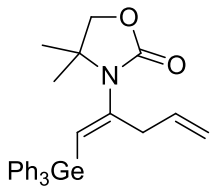
General procedure for domino germylzincation – Cu(I)-mediated electrophilic trapping of terminal ynamides (**GP V**):

In a dry Schlenk tube under argon atmosphere, the appropriate ynamide (0.25 mmol, 1.0 equiv) was dissolved in dry THF (2 mL) and the solution was degassed by 3 freeze-pump-thaw cycles. At 0 ºC, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) and Ph_3GeH (0.33 mmol, 1.3 equiv) were successively added. The reaction mixture was stirred at this temperature for 3 h and then cooled to –30 °C. The appropriate Cu(I)-salt (0.75 mmol, 3.0 equiv) followed by the appropriate electrophile (1.75 mmol, 7.0 equiv) were added at this temperature and the reaction mixture was allowed to warm slowly to rt overnight under stirring. Then, aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added and after 1 h stirring the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product.

General procedure for domino germylzincation – Cu(I)-mediated electrophilic trapping of internal ynamides (**GP VI**):

In a dry Schlenk tube under argon atmosphere, the appropriate ynamide (0.15 mmol, 1.0 equiv) was suspended in dry *n*-hexane (1.2 mL). At 0 ºC, Et_2Zn (1.0 M in hexane, 0.45 mL, 0.45 mmol, 3.0 equiv) and Ph_3GeH (0.20–0.30 mmol, 1.3–2.0 equiv) were successively added. The reaction mixture was then heated at 40 ºC and the resulting solution stirred for the given reaction time. After cooling the reaction mixture to –30 °C, the appropriate Cu(I)-salt (0.45 mmol, 3.0 equiv), followed by the appropriate electrophile (1.05 mmol, 7.0 equiv) and THF (1 mL) were added and the reaction mixture was allowed to warm slowly to rt overnight under stirring. Then, aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added and after 1 h stirring the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed

with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product.



$C_{28}H_{29}GeNO_2$

M = 484.18 g·mol^{-1}

28

***(E)*-4,4-dimethyl-3-(1-(triphenylgermyl)penta-1,4-dien-2-yl)oxazolidin-2-one (28):** Prepared according to **GP V** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) using CuCN·2LiCl (1.0 M in THF, 0.75 mL, 0.75 mmol, 3.0 equiv) and allyl bromide (212 mg, 1.75 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **28** (111 mg, 92%, *E*/*Z* > 98:2) as a white solid; mp 131–133 °C.

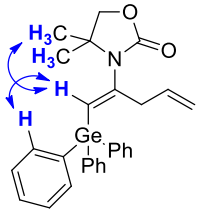
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.57 (m, 6H), 7.42–7.39 (m, 9H), 5.86 (s, 1H), 5.40–5.29 (m, 1H), 4.87 (ddt, J_{cis} = 10.1 Hz, *J* = 2.0 Hz, *J* = 1.1 Hz, 1H), 4.76 (dq, J_{trans} = 17.0 Hz, *J* = 1.5 Hz, 1H), 4.02 (s, 2H), 3.20 (dt, *J* = 7.0 Hz, *J* = 1.3 Hz, 2H), 1.47 (s, 6H).

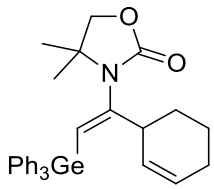
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.4, 148.3, 136.5, 134.9, 133.9, 129.3, 128.6, 119.0, 118.2, 76.1, 60.6, 39.2, 26.2.

IR (neat): ν (cm^{-1}) 3075, 2974, 1746, 1332, 1063, 733, 696.

HRMS (ESI): *m/z* calculated for $[C_{28}H_{29}GeNO_2 + Na]^+$ 508.1308; found 508.1320.

The E configuration was confirmed by the following NOESY enhancements:





$C_{31}H_{33}GeNO_2$

M = 524.24 g·mol^{-1}

29

((*E*)-3-(1-(cyclohex-2-en-1-yl)-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (29): Prepared according to **GP V** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) using CuCN·2LiCl (1.0 M in THF, 0.75 mL, 0.75 mmol, 3.0 equiv) and 3-bromocyclohex-1-ene (282 mg, 1.75 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **29** (106 mg, 81%, *E*/*Z* > 98:2) as a white solid; mp 146–148 °C.

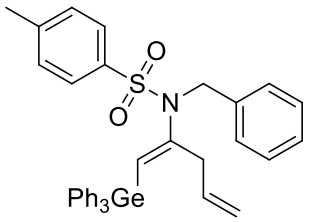
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 6H), 7.41–7.38 (m, 9H), 6.10 (s, 1H), 5.52–5.49 (m, 1H), 5.29–5.25 (m, 1H), 4.04 (s, 2H), 3.28–3.24 (m, 1H), 1.79–1.73 (m, 2H), 1.60–1.48 (m, 3H), 1.38 (s, 3H), 1.377 (s, 3H), 1.03–0.97 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.3, 153.7, 136.5, 135.0, 129.8, 129.3, 128.7, 128.6, 128.5, 76.2, 60.3, 43.9, 27.2, 27.0, 26.3, 24.6, 21.7.

IR (neat): ν (cm^{-1}) 3073, 2933, 1742, 1596, 1331, 910, 732, 695.

HRMS (ESI): *m/z* calculated for $[C_{31}H_{33}GeNO_2 + Na]^+$ 548.1622; found 548.1612.

The E configuration was assigned by analogy with **28**.



$C_{37}H_{35}GeNO_2S$

M = 630.38 g·mol^{-1}

30

***(E)*-*N*-benzyl-4-methyl-*N*-(1-(triphenylgermyl)penta-1,4-dien-2-yl)benzenesulfonamide (30):** Prepared according to **GP V** from ynamide **S4** (71 mg, 0.25 mmol, 1.0 equiv) using CuTC (143 mg, 0.75 mmol, 3.0 equiv) and allyl bromide (212 mg, 1.75 mmol, 7.0 equiv). The work up procedure was modified. The reaction mixture was filtered directly through a Celite® pad and the residue rinsed with THF. The filtrate was concentrated under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (pentane/Et_2O = 90:10 + 1% Et_3N) afforded analytically pure **30** (137 mg, 87%, *E*/*Z* > 98:2) as a white solid; mp 120–123 °C.

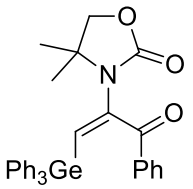
^{1}H NMR (400 MHz, C_6D_6): δ 7.84–7.80 (m, 2H), 7.46–7.43 (m, 6H), 7.22–7.19 (m, 2H), 7.16–7.11 (m, 9H), 7.07–7.05 (m, 3H), 6.78–6.75 (m, 2H), 5.81 (s, 1H), 5.24 (ddt, J_{trans} = 17.0 Hz, J_{cis} = 10.1 Hz, J = 7.0 Hz, 1H), 4.59 (ddd, J_{cis} = 10.1 Hz, J = 2.1 Hz, J = 1.1 Hz, 1H), 4.52 (s, 2H), 4.52–4.47 (m, 1H), 3.14 (dt, J = 7.0 Hz, J = 1.4 Hz, 2H), 1.91 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.3, 143.7, 136.2, 135.7, 135.2, 134.8, 134.5, 133.4, 129.9, 129.4, 129.2, 128.4, 128.1, 127.9, 123.7, 117.3, 53.5, 41.8, 21.7.

IR (neat): ν (cm^{-1}) 3072, 1427, 1158, 1090, 908, 728, 699, 650.

HRMS (ESI): *m/z* calculated for $[C_{37}H_{35}GeNO_2S + Na]^+$ 654.1499; found 654.1524.

The E configuration was assigned by analogy with **28**



$C_{32}H_{29}GeNO_3$

M = 548.22 g·mol^{-1}

31

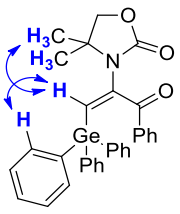
***(E)*-4,4-dimethyl-3-(3-oxo-3-phenyl-1-(triphenylgermyl)prop-1-en-2-yl)oxazolidin-2-one (31):** Prepared according to **GP V** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) using CuCN·2LiCl (1.0 M in THF, 0.75 mL, 0.75 mmol, 3.0 equiv) and benzoyl chloride (246 mg, 1.75 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded **31** (104 mg, 76%, *E*/*Z* > 98:2) contaminated with product **2** (23 mg, 17%, *E*/*Z* = 50:50); mp 142–144 °C.

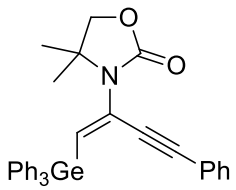
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 2H), 7.53–7.47 (m, 6H), 7.42–7.35 (m, 3H), 7.30–7.18 (m, 9H), 6.68 (s, 1H), 3.99 (s, 2H), 1.34 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 193.3, 155.5, 145.4, 135.9, 135.4, 135.1, 133.1, 129.6, 129.2, 129.1, 128.2, 128.1, 75.6, 60.6, 25.4.

HRMS (ESI): *m/z* calculated for $[C_{32}H_{29}GeNO_3 + Na]^+$ 572.1258; found 572.1267.

The E configuration was confirmed by the following NOESY enhancements:





$C_{33}H_{29}GeNO_2$

M = 544.23 g·mol^{-1}

32

***(E)*-4,4-dimethyl-3-(4-phenyl-1-(triphenylgermyl)but-1-en-3-yn-2-yl)oxazolidin-2-one (32):** Prepared according to **GP V** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) using CuCN·2LiCl (1.0 M in THF, 0.75 mL, 0.75 mmol, 3.0 equiv) and (bromoethynyl)benzene (317 mg, 1.75 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **32** (128 mg, 94%, *E*/*Z* > 98:2) as a yellow solid; mp 113–115 °C.

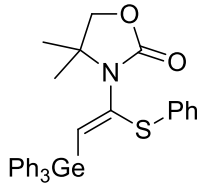
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.58 (m, 6H), 7.36–7.31 (m, 9H), 7.24–7.19 (m, 1H), 7.13–7.09 (m, 2H), 6.76 (s, 1H), 6.70–6.68 (m, 2H), 4.06 (s, 2H), 1.58 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.5, 136.1, 135.1, 132.9, 131.4, 129.2, 128.9, 128.85, 128.4, 128.1, 121.7, 92.7, 87.6, 75.6, 60.4, 26.0.

IR (neat): ν (cm^{-1}) 3058, 2971, 1750, 1351, 965, 911, 730, 694.

HRMS (ESI): *m/z* calculated for $[C_{33}H_{29}GeNO_2 + Na]^+$ 568.1309; found 568.1300.

The E configuration was assigned by analogy with **31**.



$C_{31}H_{29}GeNO_2S$

M = 552.27 g·mol^{-1}

33

***(Z)*-4,4-dimethyl-3-(1-(phenylthio)-2-(triphenylgermyl)vinyl)oxazolidin-2-one (33):** Prepared according to **GP V** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) using CuCN·2LiCl (1.0 M in THF, 0.75 mL, 0.75 mmol, 3.0 equiv) and S-phenyl benzenethiosulfonate (438 mg, 1.75 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **33** (104 mg, 75%, *Z*/*E* > 98:2) as colorless crystals; mp 184–187 °C.

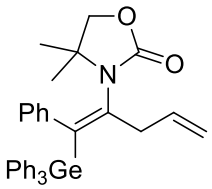
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.65 (m, 6H), 7.40–7.36 (m, 9H), 7.20–7.10 (m, 5H), 6.57 (s, 1H), 3.82 (s, 2H), 1.32 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.4, 142.2, 136.5, 135.1, 134.8, 133.0, 130.5, 129.1, 128.8, 128.3, 127.2, 75.5, 60.3, 25.6.

IR (neat): ν (cm^{-1}) 3058, 1749, 1558, 1322, 1078, 913, 734, 695.

HRMS (ESI): *m/z* calculated for $[C_{31}H_{29}GeNO_2S + Na]^+$ 576.1028; found 576.1032.

The E configuration was assigned by analogy with **31**.



$C_{34}H_{33}GeNO_2$

M = 560.27 g·mol^{-1}

34

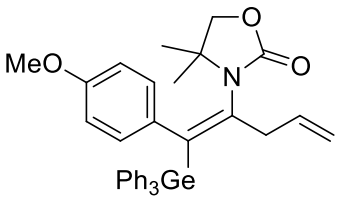
***(E)*-4,4-dimethyl-3-(1-phenyl-1-(triphenylgermyl)penta-1,4-dien-2-yl)oxazolidin-2-one (34):** Prepared according to **GP VI** from ynamide **S5** (32 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv), a reaction time of 3 h, and using CuCN·2LiCl (1.0 M in THF, 0.45 mL, 0.45 mmol, 3.0 equiv) and allyl bromide (127 mg, 1.05 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **34** (80 mg, 95%, *E*/*Z* > 98:2) as a white solid; mp 138–139 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.47 (m, 6H), 7.36–7.28 (m, 9H), 7.25–6.45 (m, 5H), 5.65 (dddd, J_{trans} = 17.0 Hz, J_{cis} = 10.1 Hz, *J* = 8.0 Hz, *J* = 5.5 Hz, 1H), 4.89 (dq, J_{cis} = 10.1 Hz, *J* = 1.5 Hz, 1H), 4.72 (dq, J_{trans} = 17.0 Hz, *J* = 1.6 Hz, 1H), 3.83 (d, *J* = 7.8 Hz, 1H), 3.48 (d, *J* = 7.8 Hz, 1H), 3.38 (ddt, *J* = 16.0 Hz, *J* = 5.5 Hz, *J* = 1.8 Hz, 1H), 2.81 (ddt, *J* = 16.0 Hz, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 1.34 (s, 3H), 0.90 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.1, 143.7, 140.5, 140.0, 136.2, 135.2, 134.0, 129.1, 128.7 (br), 128.4, 126.0, 118.1, 76.4, 60.4, 42.7, 26.9, 25.1. *One CH(Ar) signal is not observed.*

IR (neat): ν (cm^{-1}) 3058, 2980, 2898, 1739, 1338, 912, 731, 695.

HRMS (ESI): *m/z* calculated for $[C_{34}H_{33}GeNO_2 + Na]^+$ 584.1623; found 584.1642.



$C_{35}H_{35}GeNO_3$

M = 590.30 g·mol^{-1}

35

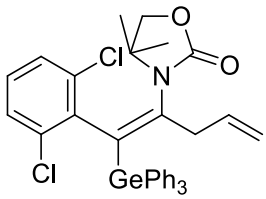
***(E)*-3-(1-(4-methoxyphenyl)-1-(triphenylgermyl)penta-1,4-dien-2-yl)-4,4-dimethyloxazolidin-2-one (35):** Prepared according to **GP VI** from ynamide **S12** (245 mg, 1.0 mmol, 1.0 equiv), Et_2Zn (1.0 M in hexane, 3.0 mL, 3.0 mmol, 3.0 equiv), and Ph_3GeH (396 mg, 1.3 mmol, 1.3 equiv), with a reaction time of 6 h, followed by addition of CuCN·2LiCl (1.0 M in THF, 3.0 mL, 3.0 mmol, 3.0 equiv) and allyl bromide (847 mg, 7.0 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **35** (503 mg, 85%, *E*/*Z* > 98:2) as a white solid; mp 196–199 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.47 (m, 6H), 7.36–7.29 (m, 9H), 7.25–6.10 (br m, 4H), 5.65 (dddd, J_{trans} = 17.1 Hz, J_{cis} = 10.1 Hz, *J* = 8.0 Hz, *J* = 5.5 Hz, 1H), 4.89 (dd, J_{cis} = 10.1 Hz, *J* = 1.3 Hz, 1H), 4.72 (dd, J_{trans} = 17.1Hz, *J* = 1.5 Hz, 1H), 3.84 (d, *J* = 7.8 Hz, 1H), 3.67 (s, 3H), 3.53 (d, *J* = 7.8 Hz, 1H), 3.37 (ddt, *J* = 16.0 Hz, *J* = 5.5 Hz, *J* = 1.8 Hz, 1H), 2.79 (ddt, *J* = 16.0 Hz, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 1.34 (s, 3H), 0.91 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.9, 157.2, 143.3, 140.1, 136.3, 135.2, 134.1, 132.9, 129.9 (br), 129.1, 128.3, 118.0, 113.0, 76.4, 60.4, 55.3, 42.8, 26.9, 25.3.

IR (neat): ν (cm^{-1}) 3062, 1743, 1510, 1340, 1248, 1035, 735, 699.

HRMS (ESI): *m/z* calculated for $[C_{35}H_{35}GeNO_3 + Na]^+$ 614.1729; found 614.1719.



$C_{34}H_{31}Cl_2GeNO_2$

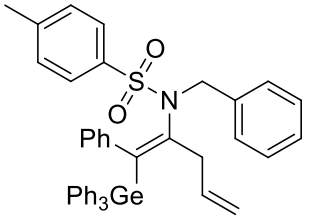
M = 629.16 g·mol^{-1}

36

***(E)*-3-(1-(2,6-dichlorophenyl)-1-(triphenylgermyl)penta-1,4-dien-2-yl)-4,4-dimethyloxazolidin-2-one (36):** Prepared according to **GP VI** from ynamide **S16** (43 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv), a reaction time of 16 h, and using CuCN·2LiCl (1.0 M in THF, 0.45 mL, 0.45 mmol, 3.0 equiv) and allyl bromide (127 mg, 1.05 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel

(pentane/Et_2O = 70:30) afforded analytically pure **36** (74 mg, 79%, *E*/*Z* > 98:2) as a white solid; mp 221–224 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50–6.50 (br m, 15H), 7.20 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.82 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 5.51 (dddd, J_{trans} = 16.8 Hz, J_{cis} = 10.1 Hz, *J* = 8.4 Hz, *J* = 6.0 Hz, 1H), 5.01–4.93 (m, 2H), 3.90–3.83 (m, 2H), 3.78 (dd, *J* = 15.4 Hz, *J* = 8.4 Hz, 1H), 3.23 (dd, *J* = 15.4 Hz, *J* = 6.0 Hz, 1H), 1.39 (s, 3H), 0.63 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.0, 145.1, 138.9, 136.3 (br), 135.4 (br), 135.2, 135.0, 134.5, 134.4, 129.0 (br), 128.7, 128.4, 128.0 (br), 127.4, 119.3, 77.7, 61.7, 40.7, 26.1, 23.6.
IR (neat): ν (cm^{-1}) 3059, 1743, 1605, 1428, 1319, 910, 731, 695.
HRMS (ESI): *m/z* calculated for $[C_{34}H_{31}Cl_2GeNO_2 + Na]^+$ 652.0835; found 652.0840.



$C_{43}H_{39}GeNO_2S$
M = 706.48 g·mol^{-1}

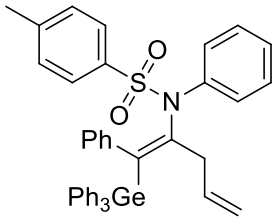
37

***(E)-N*-benzyl-4-methyl-*N*-(1-phenyl-1-(triphenylgermyl)penta-1,4-dien-2-yl) benzenesulfonamide (37):** Prepared according to **GP VI** from ynamide **S10** (54 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (92 mg, 0.30 mmol, 2.0 equiv), a reaction time of 24 h at rt, and using CuTC (86 mg, 0.45 mmol, 3.0 equiv) and allyl bromide (127 mg, 1.05 mmol, 7.0 equiv). The work up procedure was modified. The reaction mixture was filtered directly through a Celite® pad and the residue rinsed with CH_2Cl_2. The filtrate was concentrated under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (pentane/Et_2O = 90:10 + 1% Et_3N) afforded analytically pure **37** (93 mg, 88%, *E*/*Z* > 98:2) as a white solid; mp 167–169 °C.

^{1}H NMR (400 MHz, C_6D_6): δ 7.59–7.56 (m, 6H), 7.44–7.42 (m, 2H), 7.16–7.11 (m, 11H), 7.04–6.87 (m, 8H), 6.68–6.66 (m, 2H), 5.36 (ddt, J_{trans} = 17.2 Hz, J_{cis} = 10.3 Hz, *J* = 7.0 Hz, 1H), 4.60 (dq, J_{cis} = 10.3 Hz, *J* = 1.5 Hz, 1H), 4.37–4.31 (m, 2H), 4.14 (d, *J* = 14.3 Hz, 1H), 3.68–3.61 (m, 1H), 3.40–3.35 (m, 1H), 1.84 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 143.4, 142.8, 141.9, 140.8, 139.1, 136.9, 136.3, 135.7, 134.0, 130.8, 129.7 (br), 129.3, 129.2, 128.6, 128.56, 128.2, 128.1, 127.9, 125.9, 117.6, 52.5, 42.2, 21.1.

IR (neat): ν (cm^{-1}) 3072, 1430, 1333, 1155, 1088, 912, 731, 699.

HRMS (ESI): *m/z* calculated for $[C_{43}H_{39}GeNO_2S + Na]^+$ 730.1814; found 730.1839.



$C_{42}H_{37}GeNO_2S$

M = 692.45 g·mol^{-1}

38

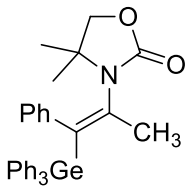
***(E)*-4-methyl-*N*-phenyl-*N*-(1-phenyl-1-(triphenylgermyl)penta-1,4-dien-2-yl) benzenesulfonamide (38):** Prepared according to **GP VI** from ynamide **S11** (52 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (92 mg, 0.30 mmol, 2.0 equiv), a reaction time of 24 h at rt, and using CuTC (86 mg, 0.45 mmol, 3.0 equiv) and allyl bromide (127 mg, 1.05 mmol, 7.0 equiv). The work up procedure was modified. The reaction mixture was filtered directly through a Celite® pad and the residue rinsed with CH_2Cl_2. The filtrate was concentrated under reduced pressure to afford the crude product. Purification by flash chromatography on silica gel (benzene) afforded **38** (80 mg, 77%, *E/Z* = 92:8) as a white solid; mp 181–183 °C.

^{1}H NMR (400 MHz, C_6D_6) (*E*-isomer): δ 7.63–7.61 (m, 6H), 7.49–7.47 (m, 2H), 7.34–7.31 (m, 2H), 7.17–7.09 (m, 13H), 6.93–6.89 (m, 2H), 6.84–6.82 (m, 2H), 6.53–6.51 (m, 2H), 5.43 (ddt, J_{trans} = 17.2 Hz, J_{cis} = 10.1 Hz, J = 7.0 Hz, 1H), 4.64 (dd, J_{cis} = 10.1 Hz, J = 1.7 Hz, 1H), 4.10 (dd, J_{trans} = 17.2 Hz, J = 1.7 Hz, 1H), 4.25–3.80 (br s, 1H), 3.80–3.50 (br s, 1H), 1.72 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, C_6D_6) (*E*-isomer): δ 147.6, 142.9, 142.1, 141.8, 140.7, 139.2, 136.8, 136.0, 135.7, 134.5, 129.4, 129.334, 129.328, 128.63, 128.6, 127.6, 127.5, 125.9, 125.8, 117.9, 41.9, 21.0.

IR (neat): ν (cm^{-1}) 3061, 1348, 1159, 1088, 907, 733, 696, 605.

HRMS (ESI): *m/z* calculated for $[C_{42}H_{37}GeNO_2S + Na]^+$ 716.1657; found 716.1666.



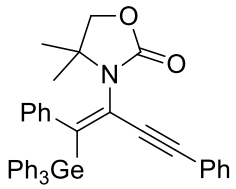
$C_{32}H_{31}GeNO_2$

M = 534.23 g·mol^{-1}

39

***(E)*-4,4-dimethyl-3-(1-phenyl-1-(triphenylgermyl)prop-1-en-2-yl)oxazolidin-2-one (39):** Prepared according to **GP VI** from ynamide **S5** (32 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv), a reaction time of 3 h, and using CuCN·2LiCl (1.0 M in THF, 0.45 mL, 0.45 mmol, 3.0 equiv) and methyl iodide (149 mg, 1.05 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **39** (36 mg, 45%, *E*/*Z* > 98:2) as a white solid; mp 207–210 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.47 (m, 6H), 7.34–7.29 (m, 9H), 7.22–6.65 (br m, 5H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.56 (d, *J* = 8.0 Hz, 1H), 1.90 (s, 3H), 1.32 (s, 3H), 0.81 (s, 3H).
JMod (100 MHz, $CDCl_3$): δ 156.7, 142.9, 140.6, 138.2, 136.2, 135.1, 129.1, 128.4, 127.4 (br), 126.0, 76.1, 60.8, 27.1, 25.5, 25.0. *One CH(Ar) signal is not observed.*
IR (neat): ν (cm^{-1}) 2974, 1742, 1394, 1339, 1085, 1036, 736, 699.
HRMS (ESI): *m/z* calculated for $[C_{32}H_{31}GeNO_2 + Na]^+$ 558.1466; found 558.1472.



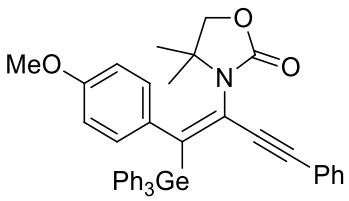
$C_{39}H_{33}GeNO_2$
M = 620.32 g·mol^{-1}

40

(*E*)-3-(1,4-diphenyl-1-(triphenylgermyl)but-1-en-3-yn-2-yl)-4,4-dimethyloxazolidin-2-one (40): Prepared according to **GP VI** from ynamide **S5** (32 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv), a reaction time of 3 h, and using CuCN·2LiCl (1.0 M in THF, 0.45 mL, 0.45 mmol, 3.0 equiv) and (bromoethynyl)benzene (190 mg, 1.05 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **40** (88 mg, 95%, *E*/*Z* > 98:2) as a pale yellow solid; mp 209–211 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 6H), 7.32–7.24 (m, 9H), 7.17–7.13 (m, 1H), 7.06–6.98 (m, 7H), 6.60–6.58 (m, 2H), 3.92 (br s, 1H), 3.63 (br s, 1H), 1.52 (br s, 3H), 1.01 (br s, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.3, 154.3, 139.2, 135.7, 135.3, 131.3, 128.9, 128.6, 128.18, 128.16, 127.8, 127.5, 126.6, 123.2, 122.0, 94.3, 89.6, 76.0, 61.1, 25.7 (br), 25.1 (br).
IR (neat): ν (cm^{-1}) 3058, 2972, 1746, 1340, 1080, 911, 730, 693.
HRMS (ESI): *m/z* calculated for $[C_{39}H_{33}GeNO_2 + Na]^+$ 644.1624; found 644.1618.

The E configuration was determined by X-ray crystallographic analysis.



$C_{40}H_{35}GeNO_3$

M = 650.35 g·mol^{-1}

41

***(E)*-3-(1-(4-methoxyphenyl)-4-phenyl-1-(triphenylgermyl)but-1-en-3-yn-2-yl)-4,4-dimethyloxazolidin-2-one (41):** Prepared according to **GP VI** from ynamide **S12** (245 mg, 1.0 mmol, 1.0 equiv), Et_2Zn (1.0 M in hexane, 3.0 mL, 3.0 mmol, 3.0 equiv), and Ph_3GeH (396 mg, 1.30 mmol, 1.3 equiv) with a reaction time of 6 h, followed by addition of CuTC (572 mg, 3.0 mmol, 3.0 equiv), dry THF (4 mL) and (bromoethynyl)benzene (1.27 g, 7.0 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **41** (350 mg, 54%, *E*/*Z* > 98:2) as a pale orange solid; mp 240–241 °C.

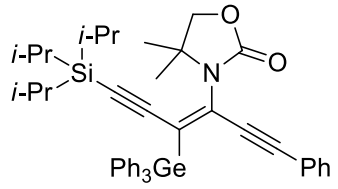
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.43 (m, 6H), 7.22–7.15 (m, 9H), 7.07–7.03 (m, 1H), 6.97–6.92 (m, 2H), 6.83–6.81 (m, 2H), 6.51–6.48 (m, 4H), 3.84 (br s, 1H), 3.59 (s, 3H), 3.58 (br s, 1H), 1.41 (br s, 3H), 0.89 (br s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.4, 156.4, 153.9, 135.9, 135.3, 131.5, 131.2, 129.6, 128.9, 128.5, 128.1, 127.8, 123.1, 122.1, 112.9, 94.2, 89.7, 75.9, 61.1, 55.2, 25.8 (br), 25.1 (br).

IR (neat): ν (cm^{-1}) 3059, 1746, 1499, 1247, 1031, 911, 732, 695.

HRMS (ESI): *m/z* calculated for $[C_{40}H_{35}GeNO_3 + Na]^+$ 674.1730; found 674.1755.

The E configuration was assigned by analogy with **40**.



$C_{44}H_{49}GeNO_2Si$

M = 724.59 g·mol^{-1}

42

***(E)*-4,4-dimethyl-3-(1-phenyl-6-(triisopropylsilyl)-4-(triphenylgermyl)hexa-3-en-1,5-diyn-3-yl)oxazolidin-2-one (42):** Prepared according to **GP VI** from ynamide **S18** (48 mg, 0.15 mmol, 1.0 equiv) with Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv), a reaction time of 16 h, and using CuCN·2LiCl (1.0 M in THF, 0.45 mL, 0.45 mmol, 3.0 equiv) and (bromoethynyl)benzene (190

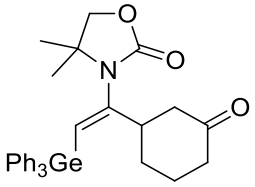
mg, 1.05 mmol, 7.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 80:20) afforded analytically pure **42** (22 mg, 20%, *E*/*Z* > 98:2) as a yellow gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.73 (m, 6H), 7.35–7.33 (m, 9H), 7.18–7.14 (m, 1H), 7.07–7.03 (m, 2H), 6.57–6.55 (m, 2H), 3.97 (d, *J* = 8.0 Hz, 1H), 3.60 (d, *J* = 8.0 Hz, 1H), 1.56 (s, 3H), 1.54 (s, 3H), 1.13–1.12 (m, 21H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.8, 151.0, 135.7, 135.5, 131.4, 129.2, 128.8, 128.4, 127.9, 126.5, 122.0, 102.6, 99.1, 97.6, 87.4, 76.2, 62.6, 26.9, 26.1, 18.8, 11.5.

IR (neat): ν (cm^{-1}) 2935, 2862, 1743, 1433, 914, 732, 692, 663.

HRMS (ESI): *m/z* calculated for $[C_{44}H_{49}GeNO_2Si + Na]^+$ 748.2647; found 748.2634.



$C_{31}H_{33}GeNO_3$

M = 540.24 g·mol^{-1}

43

(*E*)-4,4-dimethyl-3-(1-(3-oxocyclohexyl)-2-(triphenylgermyl)vinyl)oxazolidin-2-one (43): In a dry Schlenk tube under argon atmosphere, ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) was dissolved in dry THF (2 mL) and the solution was degassed by 3 freeze-pump-thaw cycles. At 0 ºC, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) and Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) were successively added. The reaction mixture was stirred at this temperature for 3 h and then cooled to –30 °C. CuCN·2LiCl (1.0 M in THF, 0.75 mL, 0.75 mmol, 3.0 equiv) was added and the reaction was further cooled to –78 °C. Chlorotrimethylsilane (380 mg, 3.50 mmol, 14.0 equiv) and cyclohex-2-enone (168 mg, 1.75 mmol, 7.0 equiv) were added at this temperature and the reaction mixture was allowed to warm slowly to rt overnight under stirring. Then, aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added and after 1 h stirring the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product. Purification by flash chromatography on silica gel (pentane/Et_2O = 75:25) afforded analytically pure **43** (90 mg, 67%, *E*/*Z* > 98:2) as a white solid; mp 165–168 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.53 (m, 6H), 7.43–7.37 (m, 9H), 6.11 (s, 1H), 4.11–4.06 (m, 2H), 2.75–2.69 (m, 1H), 2.42–2.35 (m, 1H), 2.26–2.21 (m, 1H), 2.08–2.04 (m, 1H), 2.00–1.95 (m, 1H), 1.69–1.60 (m, 3H), 1.46 (s, 3H), 1.41 (s, 3H), 0.77–0.65 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 209.9, 157.0, 151.8, 136.0, 134.8, 129.6, 128.7, 127.4, 76.1, 61.5, 46.1, 45.9, 40.7, 30.8, 27.0, 26.4, 24.6.

IR (neat): ν (cm^{-1}) 2969, 2936, 1748, 1707, 1597, 1328, 734, 697.

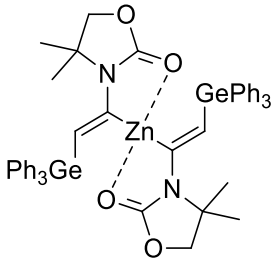
HRMS (ESI): *m/z* calculated for $[C_{31}H_{33}GeNO_3 + Na]^+$ 564.1571; found 564.1591.

The E configuration was assigned by analogy with **28**.

III.2.6 Domino Ynamide Germylzincation – Cu(I)-Mediated Electrophilic Trapping via Divinylzinc Intermediates (GP VII and GP VIII)

Characterization of divinylzinc intermediates (**GP VII**):

In a dry Schlenk tube under argon atmosphere, the appropriate ynamide (0.25 mmol, 1.0 equiv) was dissolved in dry THF (2 mL) and the solution was degassed by 3 freeze-pump-thaw cycles. At 0 ºC, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) and Ph_3GeH (0.33 mmol, 1.3 equiv) were successively added. The reaction mixture was stirred at this temperature for 3 h and then concentrated under vacuum (1 mmHg) to remove all the volatiles. After placing the residue under argon, C_6D_6 (2 mL) was added and the mixture concentrated again under vacuum (the procedure was repeated two times) to afford the crude product.



$C_{50}H_{48}Ge_2N_2O_4Zn$

M = 951.59 g·mol^{-1}

44

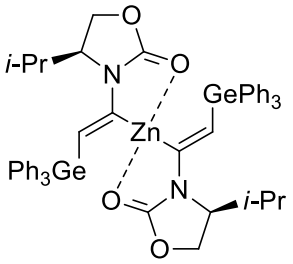
***bis*((*Z*)-1-(4,4-dimethyl-2-oxooxazolidin-3-yl)-2-(triphenylgermyl)vinyl)zinc (44):** Prepared according to **GP VII** from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = gradient from 60:40 to 0:100) afforded **44** (79 mg, 33%) as a white solid contaminated with 5% of product *E*-**2**. White crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from pentane/CH_2Cl_2.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.39 (m, 12H), 7.30–7.20 (m, 18H), 5.96 (s, 2H), 3.99 (d, *J* = 8.1 Hz, 2H), 3.89 (d, *J* = 8.1 Hz, 2H), 1.63 (s, 6H), 1.57 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 165.7, 161.8, 138.0, 135.6, 128.6, 128.0, 109.3, 75.3, 60.0, 25.6.

HRMS (ESI): *m/z* calculated for $[C_{50}H_{48}Ge_2N_2O_4Zn + Na]^+$ 975.1223; found 975.1231.

The structure was confirmed by X-ray crystallographic analysis.



$C_{52}H_{52}Ge_2N_2O_4Zn$

M = 979.64 g·mol^{-1}

45

***bis*((*Z*)-1-((*S*)-4-isopropyl-2-oxooxazolidin-3-yl)-2-(triphenylgermyl)vinyl)zinc (45):** Prepared according to **GP VII** from ynamide **S1** (38 mg, 0.25 mmol, 1.0 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = gradient from 50:50 to 0:100) afforded **45** (105 mg, 43%) as a white solid contaminated with 5% of product *E*-**4**. White crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from pentane/CH_2Cl_2.

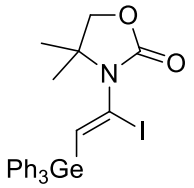
^{1}H NMR (400 MHz, C_6D_6): δ 7.49–7.46 (m, 12H), 6.96–6.89 (m, 18H), 5.38 (s, 2H), 3.43–3.38 (m, 4H), 3.33–3.29 (m, 2H), 2.21–2.14 (m, 2H), 0.30 (d, *J* = 7.0 Hz, 6H), 0.09 (d, *J* = 7.0 Hz, 6H).
JMod (100 MHz, C_6D_6): δ 164.9, 162.4, 138.4, 136.1, 128.7, 128.4, 108.3, 64.7, 57.8, 26.2, 17.6, 13.7.
HRMS (ESI): *m/z* calculated for $[C_{52}H_{52}Ge_2N_2O_4Zn + Na]^+$ 1003.1536; found 1003.1559.

The structure was confirmed by X-ray crystallographic analysis.

*General procedure for domino terminal ynamide germylzincation – Cu(I)-mediated electrophilic trapping via divinylzinc intermediate **44*** (**GP VIII**):

Divinylzinc intermediate **44** was prepared from ynamide **1** (35 mg , 0.25 mmol, 1.0 equiv) according to **GP VII**. The resulting solid was redissolved in dry and degassed THF (2 mL) and cooled to –30°C. The appropriate Cu(I)-salt (0.50–0.55 mmol, 2.0–2.2 equiv) followed by the appropriate electrophile (0.50–0.63 mmol, 2.0–2.5 equiv) were added at this temperature and the reaction mixture was allowed to warm slowly to rt overnight under stirring. Then, aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added and after 1 h stirring the layers were separated. The

aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product.



$C_{25}H_{24}GeINO_2$

M = 570.01 g·mol^{-1}

46

***(Z)*-3-(1-iodo-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (46):** Prepared according to **GP VIII** using CuCN·2LiCl (1.0 M in THF, 0.50 mL, 0.50 mmol, 2.0 equiv) and I_2 (1.0 M in THF, 0.50 mL, 0.50 mmol, 2.0 equiv) (addition at –40 ºC). The reaction was left to warm slowly to 0 ºC overnight after addition of the electrophile. Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **46** (94 mg, 66%, *Z*/*E* > 98:2) as white crystals; mp 113–116 °C.

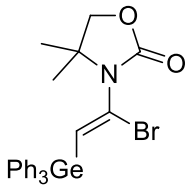
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.63 (m, 6H), 7.44–7.40 (m, 9H), 7.15 (s, 1H), 4.07 (s, 2H), 1.53 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.2, 144.4, 135.2, 134.6, 129.5, 128.5, 100.3, 75.9, 61.5, 25.5.

IR (neat): ν (cm^{-1}) 2972, 1757, 1587, 1320, 1078, 911, 734, 697.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{24}GeINO_2 + Na]^+$ 593.9961; found 593.9979.

The Z configuration was assigned by analogy with **31**.



$C_{25}H_{24}BrGeNO_2$

M = 523.01 g·mol^{-1}

47

***(Z)*-3-(1-bromo-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (47):** Prepared according to **GP VIII** using CuCN·2LiCl (1.0 M in THF, 0.50 mL, 0.50 mmol, 2.0 equiv) and *N*-bromo succinimide (89 mg, 0.50 mmol, 2.0 equiv) (addition at –40 ºC). The reaction was left to warm slowly to 0 ºC overnight after addition of the electrophile. Purification of the crude product

by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded **47** (60 mg, 46%, *Z*/*E* > 98:2) contaminated with 6% of product **2**; mp 160–163 ºC.

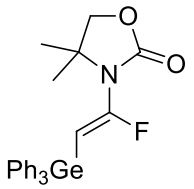
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.60 (m, 6H), 7.43–7.39 (m, 9H), 6.75 (s, 1H), 4.09 (s, 2H), 1.50 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.4, 135.6, 135.1, 135.0, 129.5, 128.5, 126.3, 76.0, 61.1, 25.7.

IR (neat): ν (cm^{-1}) 2973, 1762, 1604, 1323, 1079, 911, 735, 698.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{24}BrGeNO_2 + Na]^+$ 546.0093; found 546.0081.

The Z configuration was assigned by analogy with **31**.



$C_{25}H_{24}FGeNO_2$

M = 462.10 g·mol^{-1}

48

***(Z)*-3-(1-fluoro-2-(triphenylgermyl)vinyl)-4,4-dimethyloxazolidin-2-one (48):** Prepared according to **GP VIII** using CuCN·2LiCl (1.0 M in THF, 0.55 mL, 0.55 mmol, 2.2 equiv) and 1-fluoropyridinium tetrafluoroborate (116 mg, 0.63 mmol, 2.5 equiv). Purification of the crude product by flash chromatography on silica gel (pentane/Et_2O = 60:40) afforded analytically pure **48** (68 mg, 59%, *Z*/*E* > 98:2) as a white solid; mp 122–126 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 6H), 7.42–7.38 (m, 9H), 5.51 (d, $^3J_{HF}$ = 52.7 Hz, 1H), 4.06 (s, 2H), 1.46 (d, $^5J_{HF}$ = 1.3 Hz, 6H).

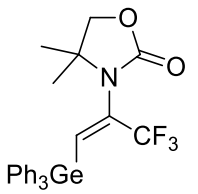
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.3 (d, $^3J_{CF}$ = 3.1 Hz), 152.5 (d, $^1J_{CF}$ = 255.3 Hz), 136.1, 134.8, 129.3, 128.4, 92.8 (d, $^2J_{CF}$ = 39.3 Hz), 75.3, 60.3 (d, $^3J_{CF}$ = 3.4 Hz), 26.0 (d, $^4J_{CF}$ = 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ –71.0 (d, $^3J_{FH}$ = 52.7 Hz).

IR (neat): ν (cm^{-1}) 3069, 1762, 1648, 1339, 1078, 908, 730, 696.

HRMS (ESI): *m/z* calculated for $[C_{25}H_{24}FGeNO_2 + Na]^+$ 486.0900; found 486.0906.

The Z configuration was assigned by analogy with **28**.



$C_{26}H_{24}F_3GeNO_2$

M = 512.11 g·mol^{-1}

49

***(E)*-4,4-dimethyl-3-(3,3,3-trifluoro-1-(triphenylgermyl)prop-1-en-2-yl)oxazolidin-2-one (49):** Prepared according to **GP VIII** using CuCN·2LiCl (1.0 M in THF, 0.55 mL, 0.55 mmol, 2.2 equiv) and 5-(trifluoromethyl)dibenzothiophenium tetrafluoroborate (Umemoto's reagent) (213 mg, 0.63 mmol, 2.5 equiv). Purification of the crude product by flash chromatography on silica gel (toluene/Et_2O = 92:8) afforded analytically pure **49** (50 mg, 39%, *E/Z* = 92:8) as a white solid; mp 178–180 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): (*E*-isomer) δ 7.55–7.53 (m, 6H), 7.45–7.38 (m, 9H), 6.85 (q, $^4J_{HF}$ = 1.2 Hz, 1H), 4.14 (s, 2H), 1.40 (s, 6H).

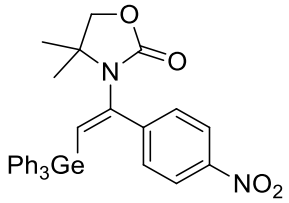
^{13}C NMR (100 MHz, $CDCl_3$): (*E*-isomer) δ 156.1, 143.1 (q, $^3J_{CF}$ = 2.8 Hz), 136.3 (m), 135.0, 134.8, 129.6, 128.6, 120.7 (q, $^1J_{CF}$ = 276.5 Hz), 76.1, 60.9, 25.9.

^{19}F NMR (376 MHz, $CDCl_3$): (*E*-isomer) δ –62.5 (s).

IR (neat): ν (cm^{-1}) 2992, 1759, 1325, 1173, 1123, 895, 735, 698.

HRMS (ESI): *m/z* calculated for $[C_{26}H_{24}F_3GeNO_2 + Na]^+$ 536.0863; found 536.0863.

The E configuration was assigned by analogy with **28***.*



$C_{31}H_{28}GeN_2O_4$

M = 565.21 g·mol^{-1}

50

***(E)*-4,4-dimethyl-3-(1-(4-nitrophenyl)-2-(triphenylgermyl)vinyl)oxazolidin-2-one (50):** Divinylzinc intermediate **44** was prepared from ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) according to **GP VII**. The resulting solid was redissolved in dry and degassed THF (1 mL) and a THF (1 mL) solution of Pd_2dba_3 (11 mg, 0.0125 mmol, 5 mol%), tri(2-furyl)phosphine (6 mg, 0.030 mmol, 10 mol%), and 1-bromo-4-nitrobenzene (101 mg, 0.50 mmol, 2.0 equiv) was then added drop-wise at rt. The reaction mixture was heated at 65 °C for 40 h under stirring. It was then cooled to rt and filtered over a pad of silica gel using CH_2Cl_2 as eluent, and concentrated

under reduce pressure to afford the crude product. Purification by flash chromatography on silica gel (pentane/Et_2O/toluene = 50:40:10) afforded analytically pure **50** (79 mg, 56%, *E*/*Z* > 98:2) as a pale yellow solid; mp 157–159 °C.

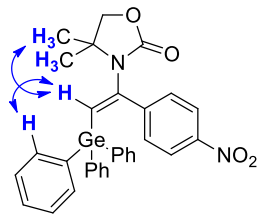
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.54 (m, 2H), 7.35–7.31 (m, 6H), 7.26–7.15 (m, 11H), 6.49 (s, 1H), 4.00 (s, 2H), 1.21 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.1, 147.6, 145.7, 144.8, 136.0, 134.7, 129.8, 129.3, 128.9, 128.5, 123.0, 75.7, 60.5, 26.3.

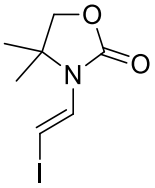
IR (neat): ν (cm^{-1}) 2973, 1747, 1517, 1338, 909, 859, 728, 696.

HRMS (ESI): *m/z* calculated for $[C_{31}H_{28}GeN_2O_4 + Na]^+$ 589.1153; found 589.1160.

The E configuration was confirmed by NOESY enhancements:



III.2.7 Halodegermylation of *β*-Triphenylgermylenamides



$C_7H_{10}INO_2$

M = 267.06 g·mol^{-1}

51

***(E)*-3-(2-iodovinyl)-4,4-dimethyloxazolidin-2-one (51):** To a stirred solution of *E*-**2** (44 mg, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (0.40 mL) at –78 ºC, ICl (1.0 M in CH_2Cl_2, 0.12 mL, 0.12 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at –78 ºC for 1 h and then at rt for 2 h. The mixture was then concentrated under vacuum to afford the crude product. Purification by flash chromatography on silica gel (pentane/Et_2O = 70:30) afforded analytically pure **51** (25 mg, 93%, *E*/*Z* > 98:2) as a white solid; mp 62–65 °C.

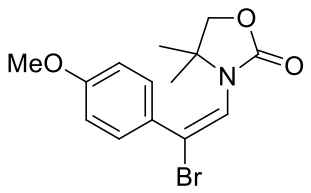
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (d, *J* = 14.1 Hz, 1H), 6.17 (d, *J* = 14.1 Hz, 1H), 4.03 (s, 2H), 1.45 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.7, 131.6, 75.2, 59.4, 58.9, 25.4.

IR (neat): ν (cm^{-1}) 2975, 1744, 1396, 1371, 1324, 1169, 1070, 762.

HRMS (ESI): *m/z* calculated for $[C_7H_{10}INO_2 + Na]^+$ 289.9648; found 289.9644.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 14.1 Hz).



$C_{14}H_{16}BrNO_3$

M = 326.19 g·mol^{-1}

52

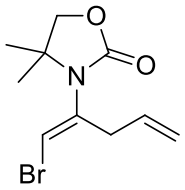
***(E)*-3-(2-bromo-2-(4-methoxyphenyl)vinyl)-4,4-dimethyloxazolidin-2-one (52):** To a stirred solution of *E*-**15** (55 mg, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (0.40 mL) at –78 ºC, Br_2 (1.0 M in CH_2Cl_2, 0.10 mL, 0.10 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred at –78 ºC for 1 h and then at rt for 15 min. The mixture was then concentrated under vacuum to afford the crude product. Purification by flash chromatography on silica gel (pentane/EtOAc = 60:40) afforded analytically pure **52** (24 mg, 73%, *E*/*Z* > 98:2) as a colorless gum.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.40 (m, 2H), 6.85–6.83 (m, 2H), 6.36 (s, 1H), 3.93 (s, 2H), 3.80 (s, 3H), 1.18 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.3, 155.7, 130.3, 129.2, 129.1, 120.2, 113.7, 75.3, 60.5, 55.4, 24.6.

IR (neat): ν (cm^{-1}) 2972, 1753, 1409, 1250, 1175, 1074, 1027, 833.

HRMS (ESI): *m/z* calculated for $[C_{14}H_{16}BrNO_3 + Na]^+$ 348.0206; found 348.0210.



$C_{10}H_{14}BrNO_2$

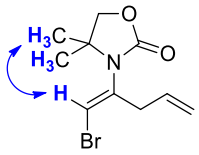
M = 260.13 g·mol^{-1}

53

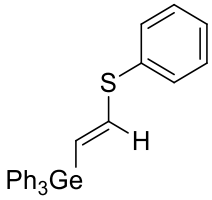
***(E)*-3-(1-bromopenta-1,4-dien-2-yl)-4,4-dimethyloxazolidin-2-one (53):** To a stirred solution of *E*-**28** (48 mg, 0.10 mmol, 1.0 equiv) in CH_2Cl_2 (0.40 mL) at –78 ºC, Br_2 (1.0 M in CH_2Cl_2, 0.10 mL, 0.10 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred at –78 ºC for 1 h and then at rt for 15 min. The mixture was then concentrated under vacuum to afford the crude product. Purification of the crude product by flash chromatography on silica gel (pentane/EtOAc = 60:40) afforded analytically pure **53** (11 mg, 43%, *E*/*Z* > 98:2) as a white solid; mp 66–68 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (s, 1H), 5.79 (ddt, *J* = 16.9 Hz, *J* = 10.0 Hz, *J* = 6.8 Hz, 1H), 5.21–5.13 (m, 2H), 4.04 (s, 2H), 3.29 (dtd, *J* = 6.8 Hz, *J* = 1.5 Hz, *J* = 0.6 Hz, 2H), 1.34 (s, 6H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.8, 137.2, 132.5, 118.6, 109.2, 75.9, 60.3, 36.9, 26.5.
IR (neat): ν (cm^{-1}) 2976, 1745, 1406, 1386, 1343, 1186, 1071, 764.
HRMS (ESI): *m/z* calculated for $[C_{10}H_{14}BrNO_2 + Na]^+$ 282.0100; found 282.0090.

The E configuration was confirmed by the following NOESY enhancements:



III.2.8 Germylzincation of *α*-Heteroatom-Substituted Alkynes



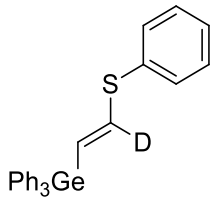
$C_{26}H_{22}GeS$
M = 439.16 g·mol^{-1}

54

***E*-triphenyl(2-(phenylthio)vinyl)germane (54):** Prepared following the same procedure as **GP I** with ethynyl(phenyl)sulfane **S23** (34 mg, 0.25 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv), Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and 3 h reaction time. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 99:1) afforded analytically pure **54** (58 mg, 53%, *E*/*Z* > 98:2) as a white solid; mp 107–110 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.38 (m, 6H), 7.31–7.27 (m, 9H), 7.26–7.13 (m, 5H), 6.65 (d, *J* = 17.7 Hz, 1H), 6.31 (d, *J* = 17.7 Hz, 1H).
JMod (100 MHz, $CDCl_3$): δ 141.4, 136.2, 135.1, 133.6, 131.6, 129.4, 129.3, 128.4, 127.7, 122.8.
IR (neat): ν (cm^{-1}) 3058, 1528, 1428, 1091, 951, 792, 736, 691.
HRMS (ESI): *m/z* calculated for $[C_{26}H_{22}GeS + Na]^+$ 463.0550; found 463.0552.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 17.7 Hz).



$C_{26}H_{21}DGeS$

M = 440.16 g·mol^{-1}

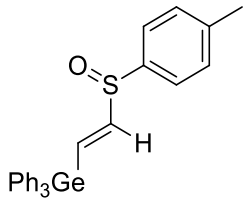
[^{2}H]-**54**

[^{2}H]-54: Prepared following the same procedure as **GP II** with ethynyl(phenyl)sulfane **S23** (34 mg, 0.25 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv), Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and 3 h reaction time. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 99:1) afforded analytically pure [^{2}H]-**54** (66 mg, 60%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.39 (m, 6H), 7.33–7.27 (m, 9H), 7.27–7.15 (m, 5H), 6.31 (t, *J* = 2.3 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 136.2, 135.1, 133.5, 131.6, 129.4, 129.3, 128.4, 127.7, 122.6. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{26}H_{21}DGeS + Na]^+$ 464.0613; found 464.0603.



$C_{27}H_{24}GeOS$

M = 469.18 g·mol^{-1}

55

***(E)*-triphenyl(2-(*p*-tolylsulfinyl)vinyl)germane (55):** Prepared following the same procedure as **GP I** with ethynyl *p*-tolyl (*R*)-sulfoxide **S24** (41 mg, 0.25 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv), Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and 3 h reaction time. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = gradient from 80:20 to 70:30) afforded analytically pure **55** (53 mg, 45%, *E*/*Z* > 98:2) as a white solid; mp 147–150 °C.

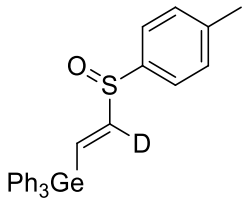
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 17.4 Hz, 1H), 7.51–7.49 (m, 2H), 7.47–7.45 (m, 6H), 7.43–7.35 (m, 9H), 7.31–7.29 (m, 2H), 6.74 (d, *J* = 17.4 Hz, 1H), 2.41 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.1, 142.0, 140.2, 135.0, 134.9, 131.0, 130.3, 129.6, 128.6, 125.3, 21.6.

IR (neat): ν (cm^{-1}) 3046, 2920, 1483, 1429, 1092, 1051, 737, 696.

HRMS (ESI): *m/z* calculated for $[C_{27}H_{24}GeOS + Na]^+$ 493.0652; found 493.0650.

Note: The E configuration was determined on the basis of the ^1H NMR coupling constant of the vinylic protons (J = 17.4 Hz).



$C_{27}H_{23}DGeOS$

M = 470.19 g·mol^{-1}

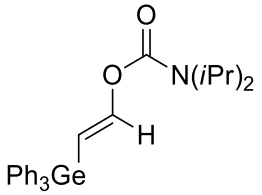
[^{2}H]-**55**

[^{2}H]-55: Prepared following the same procedure as **GP II** with ethynyl *p*-tolyl (*R*)-sulfoxide **S24** (41 mg, 0.25 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv), Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and 3 h reaction time. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = gradient from 80:20 to 70:30) afforded analytically pure [^{2}H]-**55** (51 mg, 43%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.51–7.49 (m, 2H), 7.47–7.45 (m, 6H), 7.43–7.35 (m, 9H), 7.31–7.29 (m, 2H), 2.41 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.7 (t, *J* = 26.0 Hz), 142.0, 140.2, 135.0, 134.9, 130.8, 130.3, 129.6, 128.6, 125.3, 21.6.

HRMS (ESI): *m/z* calculated for $[C_{27}H_{23}DGeOS + Na]^+$ 494.0715; found 494.0713.



$C_{27}H_{31}GeNO_2$

M = 474.18 g·mol^{-1}

56

***(E)*-2-(triphenylgermyl)vinyl diisopropylcarbamate (56):** Prepared following the same procedure as **GP I** with ethynyl *N,N*-diisopropylcarbamate **S25** (25 mg, 0.15 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.45 mL, 0.45 mmol, 3.0 equiv), Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and 3 h reaction time. Purification of the crude product (*E*/*Z* > 98:2) by flash

chromatography on silica gel (pentane/Et_2O = 95:5) afforded analytically pure **56** (26 mg, 37%, *E*/*Z* > 98:2) as a white solid; mp 107–109 °C.

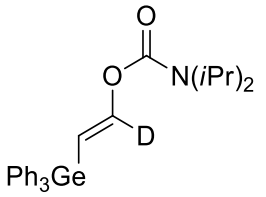
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (m, 6H), 7.40–7.36 (m, 9H), 7.24 (d, *J* = 14.6 Hz, 1H), 5.68 (d, *J* = 14.6 Hz, 1H), 4.10–3.80 (m, 2H), 1.28–1.22 (m, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.5, 147.3, 136.3, 135.1, 129.3, 128.4, 100.6, 46.7 (br), 46.1 (br), 21.8 (br), 20.5 (br).

IR (neat): ν (cm^{-1}) 2963, 2934, 1711, 1611, 1429, 1310, 962, 739.

HRMS (ESI): *m/z* calculated for $[C_{27}H_{31}GeNO_2 + Na]^+$ 498.1459; found 498.1456.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 14.6 Hz).



$C_{27}H_{30}DGeNO_2$

M = 475.19 g·mol^{-1}

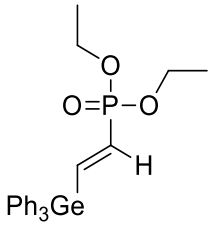
[^{2}H]-**56**

[^{2}H]-56: Prepared following the same procedure as **GP II** with ethynyl *N,N*-diisopropylcarbamate **S25** (25 mg, 0.15 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.45 mL, 0.45 mmol, 3.0 equiv), Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv) and 3 h reaction time. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/Et_2O = 95:5) afforded analytically pure [^{2}H]-**56** (20 mg, 28%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (m, 6H), 7.41–7.35 (m, 9H), 5.67 (s, 1H), 4.10–3.80 (m, 2H), 1.28–1.22 (m, 12H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.5, 136.3, 135.1, 129.3, 128.4, 100.4, 46.7 (br), 46.1 (br), 21.8 (br), 20.5 (br). *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{27}H_{30}DGeNO_2 + Na]^+$ 499.1522; found 499.1519.



$C_{24}H_{27}GeO_3P$

M = 467.08 g·mol^{-1}

57

***(E)*-diethyl (2-(triphenylgermyl)vinyl)phosphonate (57):** In a dry Schlenk tube under argon atmosphere, diethyl ethynylphosphonate **S26** (41 mg, 0.25 mmol, 1.0 equiv) was dissolved in dry *n*-hexane (1.2 mL). At 0 ºC, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) was added and the mixture stirred for 1 h. Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) was then added at the same temperature and the reaction was stirred for 16 h at rt. Then, aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product (*E*/*Z* > 98:2). Purification by flash chromatography on silica gel (pentane/EtOAc = 50:50) afforded analytically pure **57** (82 mg, 70%, *E*/*Z* > 98:2) as colorless crystals; mp 98–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, J_{HP} = 31.6 Hz, J_{HH} = 20.1 Hz, 1H), 7.49–7.45 (m, 6H), 7.44–7.36 (m, 9H), 6.37 (dd, J_{HP} = 27.0 Hz, J_{HH} = 20.1 Hz, 1H), 4.10 (dqd, J_{HP} = 8.3 Hz, J_{HH} = 7.1 Hz, J_{HH} = 1.2 Hz, 4H), 1.32 (t, J_{HH} = 7.1 Hz, 6H).

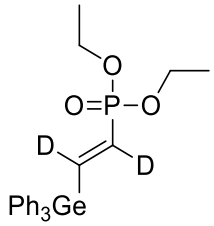
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.8 (d, $^2J_{CP}$ = 3.7 Hz), 135.8 (d, $^1J_{CP}$ = 171.8 Hz), 135.2, 134.6, 129.6, 128.6, 62.1 (d, $^2J_{CP}$ = 5.7 Hz), 16.5 (d, $^3J_{CP}$ = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 15.5 (ddquint, J_{PH} = 31.6 Hz, J_{PH} = 27.0 Hz, J_{PH} = 8.3 Hz).

IR (neat): ν (cm^{-1}) 2984, 2905, 2858, 1483, 1244, 959, 738, 701.

HRMS (ESI): *m/z* calculated for $[C_{24}H_{27}GeO_3P + Na]^+$ 491.0807; found 491.0819.

Note: The E configuration was determined on the basis of the ^{1}H NMR coupling constant of the vinylic protons (J = 20.1 Hz).



$C_{24}H_{25}D_2GeO_3P$

M = 469.10 g·mol^{-1}

[^{2}H]-**57**

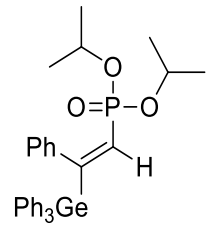
[^{2}H]-57: In a dry Schlenk tube under argon atmosphere, diethyl ethynylphosphonate **S26** (41 mg, 0.25 mmol, 1.0 equiv) was dissolved in dry *n*-hexane (1.2 mL). At 0 ºC, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) was added and the mixture stirred for 1 h. Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) was then added at the same temperature and the reaction was stirred for 16 h at rt. A solution of ND_4Cl (300 mg) in D_2O (2 mL) was added followed by THF (2 mL) 10 min after. The mixture was stirred for 1 h at rt and then aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product (*E*/*Z* > 98:2). Purification of the crude product by flash chromatography on silica gel (pentane/EtOAc = 50:50) afforded analytically pure [^{2}H]-**57** (73 mg, 62%, *E*/*Z* > 98:2) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.47 (m, 6H), 7.45–7.37 (m, 9H), 4.11 (dqd, J_{HP} = 8.2 Hz, J_{HH} = 7.1 Hz, J_{HH} = 1.1 Hz, 4H), 1.33 (t, J_{HH} = 7.1 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.2 (m), 135.5 (dm, $^1J_{CP}$ = 171.8 Hz), 135.1, 134.6, 129.6, 128.6, 62.0 (d, $^2J_{CP}$ = 5.8 Hz), 16.5 (d, $^3J_{CP}$ = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 16.5 (s).

HRMS (ESI): *m/z* calculated for $[C_{24}H_{25}D_2GeO_3P + Na]^+$ 493.0927; found 493.0926.



$C_{32}H_{35}GeO_3P$

M = 571.23 g·mol^{-1}

58

***(E)*-diisopropyl (2-phenyl-2-(triphenylgermyl)vinyl)phosphonate (58):** Prepared following the same procedure as **GP III** with diisopropyl (phenylethynyl)phosphonate **S27** (40 mg, 0.15 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.45 mL, 0.45 mmol, 3.0 equiv), Ph_3GeH (60

mg, 0.20 mmol, 1.3 equiv), and 16 h reaction time. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/EtOAc = 75:25) afforded analytically pure **58** (60 mg, 70%, *E*/*Z* > 98:2) as colorless crystals; mp 82–86 °C.

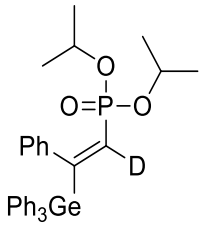
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.29 (m, 15H), 7.19–7.13 (m, 3H), 7.11–7.05 (m, 2H), 6.27 (d, J_{HP} = 23.1 Hz, 1H), 4.47 (dhept, J_{HP} = 7.8 Hz, J_{HH} = 6.2 Hz, 2H), 1.14 (d, J = 6.2 Hz, 6H), 1.03 (d, J = 6.2 Hz, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.5 (d, $^3J_{CP}$ = 5.7 Hz), 141.2 (d, $^2J_{CP}$ = 12.3 Hz), 135.6, 134.7, 131.4 (d, $^1J_{CP}$ = 171.7 Hz), 129.5, 128.4, 127.7, 127.5 (d, $^4J_{CP}$ = 2.0 Hz), 127.0, 70.4 (d, $^2J_{CP}$ = 6.4 Hz), 24.0 (d, $^3J_{CP}$ = 4.0 Hz), 23.8 (d, $^3J_{CP}$ = 5.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 11.8 (dt, $^2J_{PH}$ = 23.1 Hz, $^3J_{PH}$ = 7.8 Hz).

IR (neat): ν (cm^{-1}) 3058, 2979, 1433, 1237, 979,786, 737, 699.

HRMS (ESI): *m/z* calculated for $[C_{32}H_{35}GeO_3P + Na]^+$ 595.1435; found 595.1451.



$C_{32}H_{34}DGeO_3P$

M = 572.24 g·mol^{-1}

[^{2}H]-**58**

[^{2}H]-58: Prepared following the same procedure as **GP IV** with diisopropyl (phenylethynyl)phosphonate **S27** (40 mg, 0.15 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.45 mL, 0.45 mmol, 3.0 equiv), Ph_3GeH (60 mg, 0.20 mmol, 1.3 equiv), and 16 h reaction time. Purification of the crude product (*E*/*Z* > 98:2) by flash chromatography on silica gel (pentane/EtOAc = 75:25) afforded analytically pure [^{2}H]-**58** (58 mg, 68%, *E*/*Z* > 98:2) as colorless crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.31 (m, 15H), 7.18–7.14 (m, 3H), 7.10–7.06 (m, 2H), 4.47 (dhept, J_{HP} = 7.8 Hz, J_{HH} = 6.2 Hz, 2H), 1.14 (d, J = 6.2 Hz, 6H), 1.03 (d, J = 6.2 Hz, 6H).

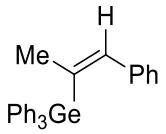
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.4 (d, $^3J_{CP}$ = 5.7 Hz), 141.2 (d, $^2J_{CP}$ = 12.2 Hz), 135.5, 134.7, 129.0, 127.9, 127.2, 127.0 (d, $^4J_{CP}$ = 2.1 Hz), 126.5, 69.9 (d, $^2J_{CP}$ = 6.4 Hz), 23.5 (d, $^3J_{CP}$ = 4.0 Hz), 23.2 (d, $^3J_{CP}$ = 5.0 Hz). *One C is not observed.*

^{31}P NMR (162 MHz, $CDCl_3$): δ 11.8 (t, $^3J_{PH}$ = 7.8 Hz).

HRMS (ESI): *m/z* calculated for $[C_{32}H_{34}DGeO_3P + Na]^+$ 596.1497; found 596.1519.

The E configuration was determined by X-ray crystallographic analysis.

III.2.9 Germylzincation of 1-Phenyl-1-Propyne and Diphenylacetylene



$C_{27}H_{24}Ge$

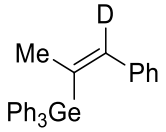
M = 421.12 g·mol^{-1}

59

***(Z)*-triphenyl(1-phenylprop-1-en-2-yl)germane (59):** Prepared following the same procedure as **GP I** using 1-phenyl-1-propyne **S28** (29 mg, 0.25 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv), Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 16 h at 40 °C. Purification of the crude product (*Z/E* = 90:10) by flash chromatography on silica gel (pentane/Et_2O = 99:1) afforded analytically pure **59** (42 mg, 40%, *Z/E* = 87:13) as a white solid. The spectral data was in good agreement with that previously reported.[25]

^{1}H NMR (400 MHz, $CDCl_3$): (*Z*-isomer) δ 7.54 (s, 1H), 7.51–7.48 (m, 6H), 7.34–7.28 (m, 9H), 7.10–7.06 (m, 2H), 6.91–6.81 (m, 3H), 2.09 (d, *J* = 1.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): (*Z*-isomer) δ 143.1, 138.1, 137.1, 135.2, 135.0, 128.7, 128.6, 128.1, 127.4, 126.8, 28.0.



$C_{27}H_{23}DGe$

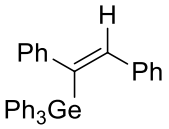
M = 422.13 g·mol^{-1}

[^{2}H]-59

[^{2}H]-59: Prepared following the same procedure as **GP II** using 1-phenyl-1-propyne **S28** (29 mg, 0.25 mmol, 1.0 equiv) as substrate, Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv), Ph_3GeH (99 mg, 0.33 mmol, 1.3 equiv) and a reaction time of 16 h at 40 °C. Purification of the crude product (*Z*/*E* = 90:10) by flash chromatography on silica gel (eluent pentane:Et_2O = 99:1) afforded analytically pure [^{2}H]-**59** (45 mg, 43%, *Z/E* = 91:9) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): (*Z*-isomer) δ 7.52–7.50 (m, 6H), 7.36–7.29 (m, 9H), 7.11–7.09 (m, 2H), 6.93–6.83 (m, 3H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): (*Z*-isomer) δ 138.0, 137.1, 135.2, 134.9, 128.7, 128.6, 128.1, 127.4, 126.8, 27.9. *One C is not observed.*



$C_{32}H_{26}Ge$

M = 483.19 g·mol^{-1}

60

***(Z)*-(1,2-diphenylvinyl)triphenylgermane (60):**

In a dry tube under argon atmosphere, diphenylacetylene **S29** (45 mg, 0.25 mmol, 1.0 equiv), Ph_3GeH (153 mg, 0.50 mmol, 2.0 equiv), and AIBN (10 mg, 0.06 mmol, 25 mol%) were dissolved in dry THF (0.64 mL). The tube was then sealed with a cap with septum, and Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) was added at rt. The reaction mixture was placed in an oil bath heated at 80 °C and stirred for 1 h at that temperature. After cooling the reaction mixture to rt, aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product. Purification by flash chromatography on silica gel (gradient from pentane to pentane/Et_2O = 99:1) afforded analytically pure **60** (81 mg, 67%, *Z/E* = 92:8) as a white solid; mp 104–106 °C.

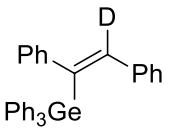
^{1}H NMR (400 MHz, $CDCl_3$): (*Z*-isomer) δ 7.54 (s, 1H), 7.31–7.27 (m, 6H), 7.16–7.03 (m, 13H), 7.01–6.95 (m, 3H), 6.82–6.78 (m, 1H), 6.76–6.72 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*Z*-isomer) δ 146.3, 146.1, 141.3, 137.6, 137.2, 135.3, 128.9, 128.6, 128.3, 128.0, 127.8, 127.5, 127.3, 126.1.

IR (neat): ν (cm^{-1}) 3051, 1595, 1496, 1431, 1089, 763, 734, 696.

HRMS (ESI): *m/z* calculated for $[C_{32}H_{26}Ge + Na]^+$ 507.1145; found 507.1172.

The Z configuration was assigned by analogy with **59**.



$C_{32}H_{25}DGe$

M = 484.20 g·mol^{-1}

[^{2}H]-60

[^{2}H]-60: In a dry tube under argon atmosphere, diphenylacetylene **S29** (45 mg, 0.25 mmol, 1.0 equiv), Ph_3GeH (153 mg, 0.50 mmol, 2.0 equiv), and AIBN (10 mg, 0.06 mmol, 25 mol%) were dissolved in dry THF (0.64 mL). The tube was then sealed with a cap with septum, and Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) was added at rt. The reaction mixture was placed in an oil bath heated at 80 °C and stirred for 1 h at that temperature. After cooling the reaction mixture to rt, a solution of ND_4Cl (300 mg) in D_2O (2 mL) was added followed by THF (2 mL) 10 min after. The mixture was stirred for 2 h at rt and then aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product. Purification by flash chromatography on silica gel (gradient from pentane to pentane/Et_2O = 99:1) afforded analytically pure **[^{2}H]-60** (86 mg, 71%, *Z/E* = 92:8) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.26 (m, 6H), 7.16–7.02 (m, 13H), 7.01–6.93 (m, 3H), 6.82–6.78 (m, 1H), 6.76–6.71 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): (*Z*-isomer) δ 146.1, 141.2, 137.5, 137.1, 135.3, 128.9, 128.6, 128.3, 128.0, 127.8, 127.5, 127.3, 126.0. *One C is not observed.*

HRMS (ESI): *m/z* calculated for $[C_{32}H_{25}DGe + Na]^+$ 508.1208; found 508.1234.

III.2.10 Reaction with Acceptor X

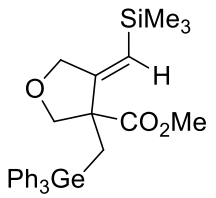
In a dry Schlenk tube under argon atmosphere, β-(propargyloxy)enoate **X** (40 mg, 0.18 mmol) was dissolved in dry THF (4.5 mL) and the solution was degassed by 3 freeze-pump-thaw cycles. At 0 ºC, Ph_3GeH (165 mg, 0.54 mmol, 3.0 equiv) and Et_2Zn (1.0 M in hexane, 0.54 mL, 0.54 mmol, 3.0 equiv) were successively added and the reaction mixture was stirred for 16 h at 0 °C. Et_2O (5 mL) and 1M aq. HCl (5 mL) were added. The aqueous layer was extracted with Et_2O (x3) and the combined organics were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product contained *Z*-**XI**, *E*-**XI**, and *Z*-**XII** in *Z*-**XI**/*E*-**XI**/*Z*-**XII** = 35:6:59 ratio. Purification by flash chromatography on silica gel (pentane/Et_2O = 90:10) afforded two fractions containing mixtures of **XI** and *Z*-**XII**.

Fraction 1 (38 mg): **XI** (32 mg, *Z/E* = 86:14, 34%) + *Z*-**XII**[26] (6 mg, 13%).

Fraction 2 (24 mg): *Z*-**XII** (18 mg, 39%) + **XI** (6 mg, *Z*/*E* = 64:36, 6%).

Deuterium labeling:

The above-described procedure was followed, but D_2O (1 mL) was added and the mixture stirred for 1 h at rt prior to the acidic quench. The crude product contained *Z*-[^{2}H]-**XI** (80% D-incorporation), *E*-**XI** (<10% D-incorporation), and *Z*-[^{2}H]-**XII**[26] (80% D-incorporation) in *Z*-[^{2}H]-**XI**/*E*-**XI**/*Z*-[^{2}H]-**XII** = 34:5:61 ratio.



$C_{29}H_{34}GeO_3Si$

M = 531.30 g·mol^{-1}

XI

Methyl 4-((trimethylsilyl)methylene)-3-((triphenylgermyl)methyl)tetrahydrofuran-3-carboxylate (XI):

Characterization data for both isomers of **XI** could be extracted from the analysis of *Fraction 1.*

Z-**XI:**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (m, 6H$_Z$), 7.38–7.36 (m, 9H$_Z$), 5.72 (t, *J* = 2.4 Hz, 1H$_Z$), 4.34 (t$_{app}$, *J* = 2.4 Hz, 2H$_Z$), 4.12 (dd, *J* = 9.0 Hz, *J* = 1.0 Hz, 1H$_Z$), 3.65 (d, *J* = 9.0 Hz, 1H$_Z$), 3.22 (s, 3H$_Z$), 2.38 (dd, *J* = 14.0 Hz, *J* = 1.0 Hz, 1H$_Z$), 1.93 (d, *J* = 14.0 Hz, 1H$_Z$), 0.07 (s, 9H$_Z$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 173.4, 161.1, 136.9, 135.2, 129.1, 128.31, 119.2, 76.0, 70.7, 57.2, 52.1, 23.7, -0.58.

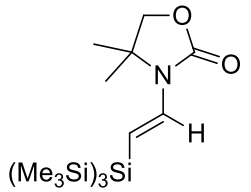
E-**XI:**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (m, 6H$_E$), 7.38–7.36 (m, 9H$_E$), 5.40 (t, *J* = 2.0 Hz, 1H$_E$), 4.32–4.30 (m, 1H$_E$), 4.23 (dd, *J* = 13.1 Hz, *J* = 2.0 Hz, 1H$_E$), 3.97 (d, *J* = 9.0 Hz, 1H$_E$), 3.75 (d, *J* = 9.0 Hz, 1H$_E$), 3.34 (s, 3H$_E$), 2.54 (dd, *J* = 13.9 Hz, *J* = 1.1 Hz, 1H$_E$), 2.00–1.90 (m, 1H$_E$), 0.17 (s, 9H$_E$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 174.0, 161.6, 137.3, 135.3, 129.0, 128.3, 119.9, 79.3, 75.5, 55.5, 52.2, 23.5, 0.9.

HRMS (ESI): *m/z* calculated for [$C_{29}H_{34}GeO_3Si$ + Na]$^+$ 555.1381; found 555.1388.

III.2.11 Silylzincation of Ynamide 1 in THF



$C_{16}H_{37}NO_2Si_4$

M = 387.81 g·mol^{-1}

S30

3-(2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)vinyl)-4,4-dimethyloxazolidin-2-one (S30): In a dry Schlenk tube under argon atmosphere, ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) was dissolved in dry THF (2 mL) and the solution was degassed by 3 freeze-pump-thaw cycles. At 0 ºC, $(Me_3Si)_3SiH$ (80 mg, 0.33 mmol, 1.3 equiv) and Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) were successively added. The reaction mixture was stirred at this temperature for 3 h and then aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2 were added. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product (*E/Z* = 90:10). Purification by flash chromatography on silica gel (pentane/Et_2O = gradient from 95:5 to 80:20) afforded analytically pure *Z*-**S30**[1] (15 mg, 14%, *Z/E* > 98:2) and *E*-**S30** (62 mg, 64%, *E/Z* > 98:2) as colorless liquids.

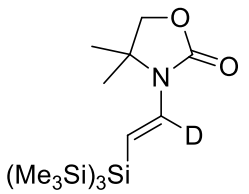
E-**S30:**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.46 (d, *J* = 17.7 Hz, 1H), 5.22 (d, *J* = 17.7 Hz, 1H), 3.97 (s, 2H), 1.47 (s, 6H), 0.18 (s, 27H).

JMod (100 MHz, $CDCl_3$): δ 155.1, 132.2, 100.4, 75.2, 58.7, 25.2, 0.9.

IR (neat): ν (cm^{-1}) 2969, 2898, 1748, 1380, 1035, 938, 836, 693.

HRMS (ESI): *m/z* calculated for $[C_{16}H_{37}NO_2Si_4 + Na]^+$ 410.1794; found 410.1795.



$C_{16}H_{36}DNO_2Si_4$

M = 388.82 g·mol^{-1}

[^{2}H]-**S30**

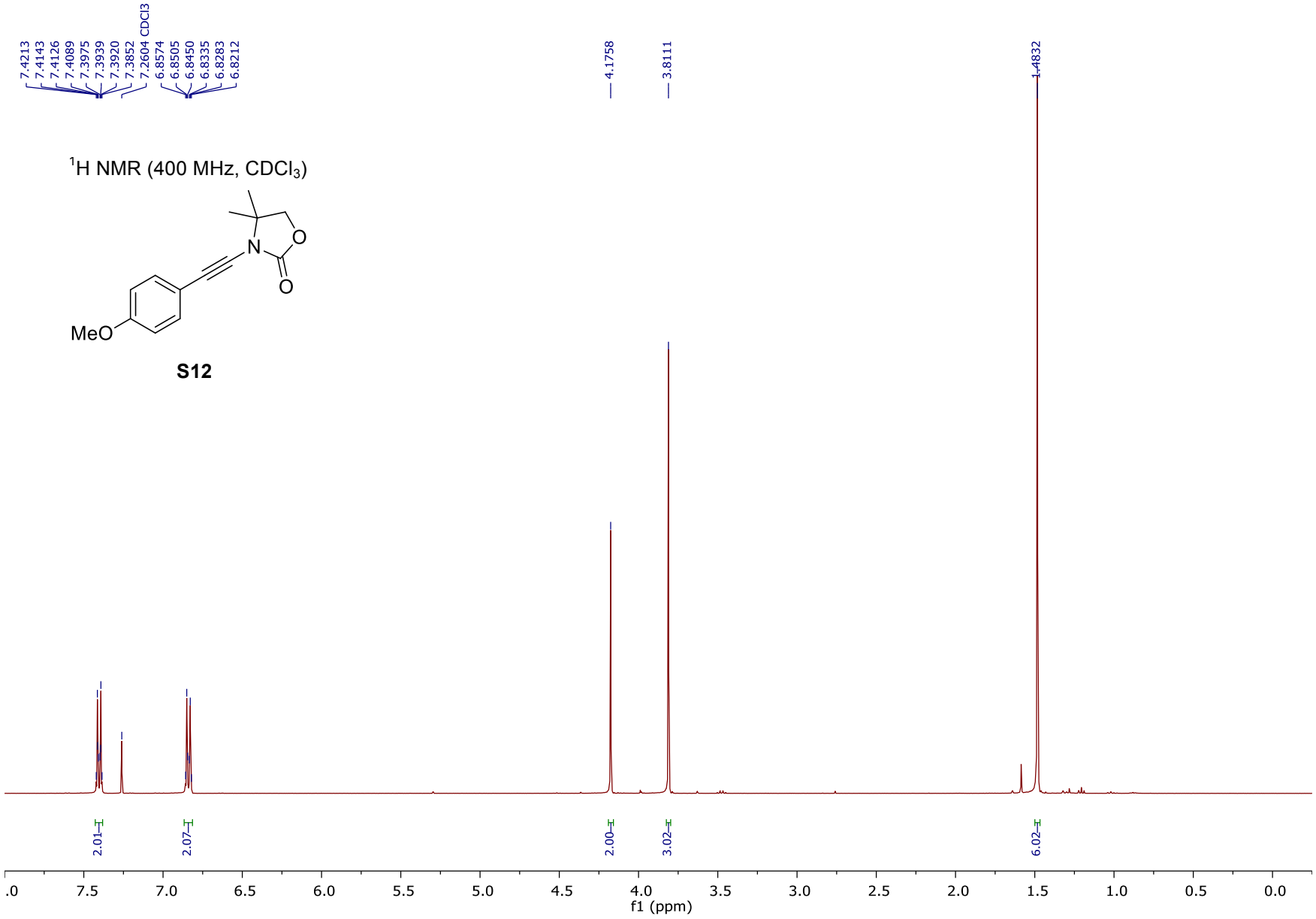
***E*-[^{2}H]-S30:** In a dry Schlenk tube under argon atmosphere, ynamide **1** (35 mg, 0.25 mmol, 1.0 equiv) was dissolved in dry THF (2 mL) and the solution was degassed by 3 freeze-pump-thaw cycles. At 0 ºC, $(Me_3Si)_3SiH$ (80 mg, 0.33 mmol, 1.3 equiv) and Et_2Zn (1.0 M in hexane, 0.75 mL, 0.75 mmol, 3.0 equiv) were successively added and the reaction mixture was stirred at this temperature for 3 h. A solution of ND_4Cl (300 mg) in D_2O (2 mL) was added and the mixture was stirred for 1 h at rt before adding aq NH_4Cl/NH_3 (2:1) and CH_2Cl_2. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (x3), and the combined organic layers were washed with brine (x2), dried over Na_2SO_4, filtered, and concentrated under reduce pressure to afford the crude product (*E/Z* = 95:5). Purification by flash chromatography on silica gel (pentane/Et_2O = gradient from 95:5 to 80:20) afforded analytically pure (*E*)-[^{2}H]-**S30** (68 mg, 70%, *E/Z* > 98:2).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.21 (t, *J* = 2.4 Hz, 1H), 3.98 (s, 2H), 1.47 (s, 6H), 0.18 (s, 27H).

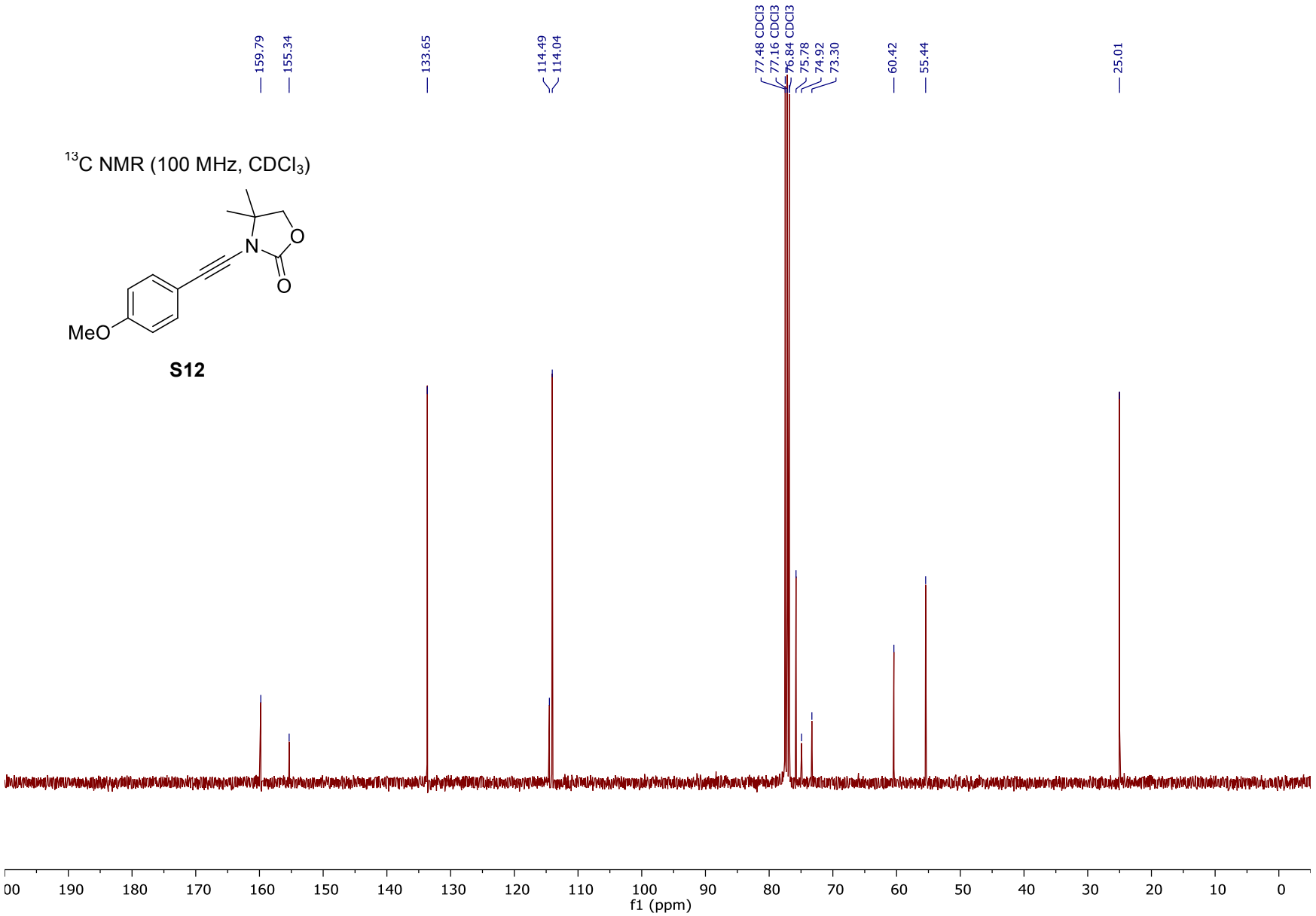
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 131.9 (t, *J* = 27.2 Hz), 100.2, 75.2, 58.6, 25.2, 0.9.

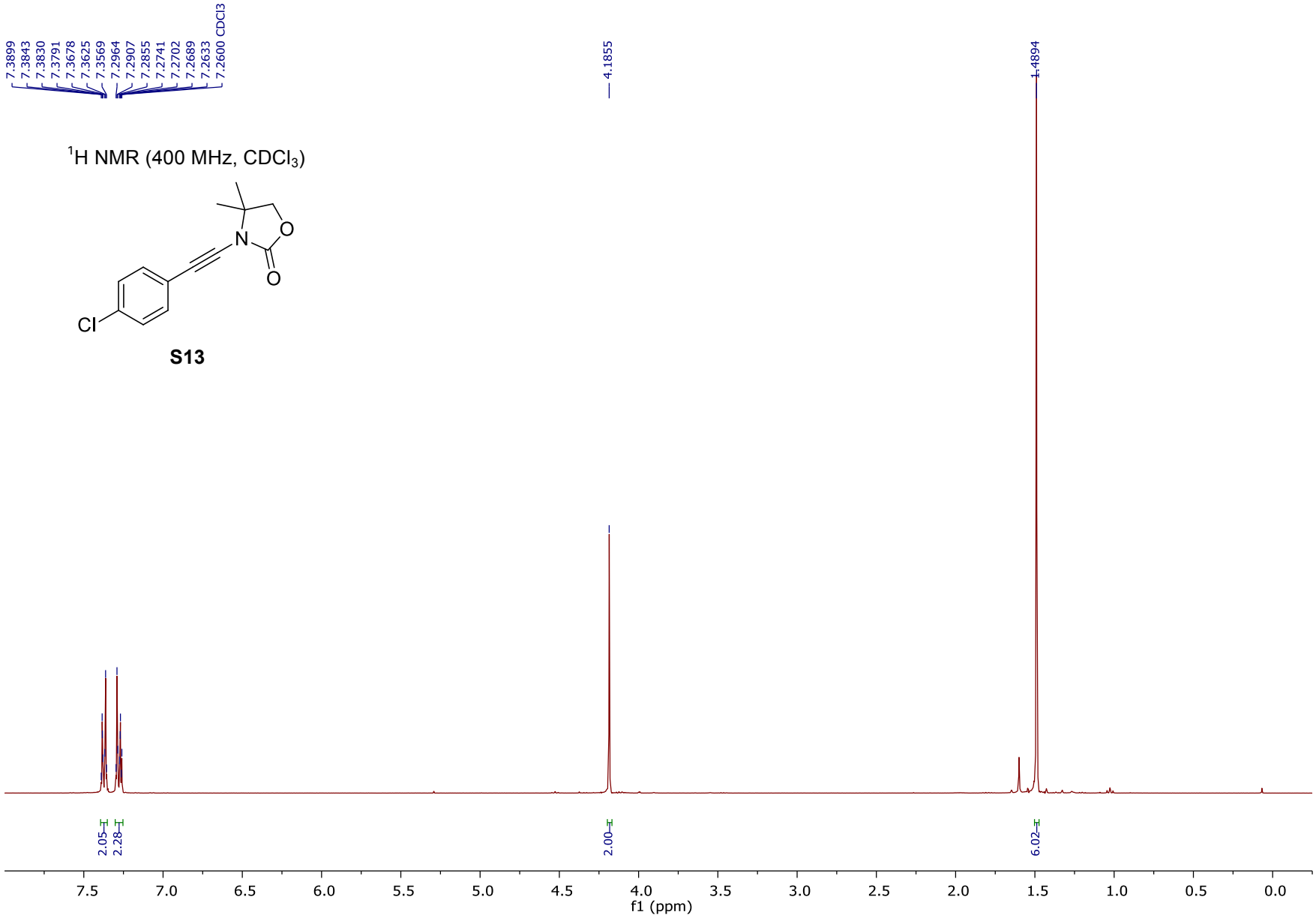
HRMS (ESI): *m/z* calculated for $[C_{16}H_{36}DNO_2Si_4 + H]^+$ 389.2037; found 389.2039.

IV NMR Spectra for New Compounds


7.4213
7.4143
7.4126
7.4089
7.3975
7.3939
7.3920
7.3852
7.2604 CDCl3
6.8574
6.8505
6.8450
6.8335
6.8283
6.8212
4.1758
3.8111
1.4832
^{1}H NMR (400 MHz, $CDCl_3$)
N
O
O
MeO
2.01
2.07
2.00
3.02
6.02
f1 (ppm)

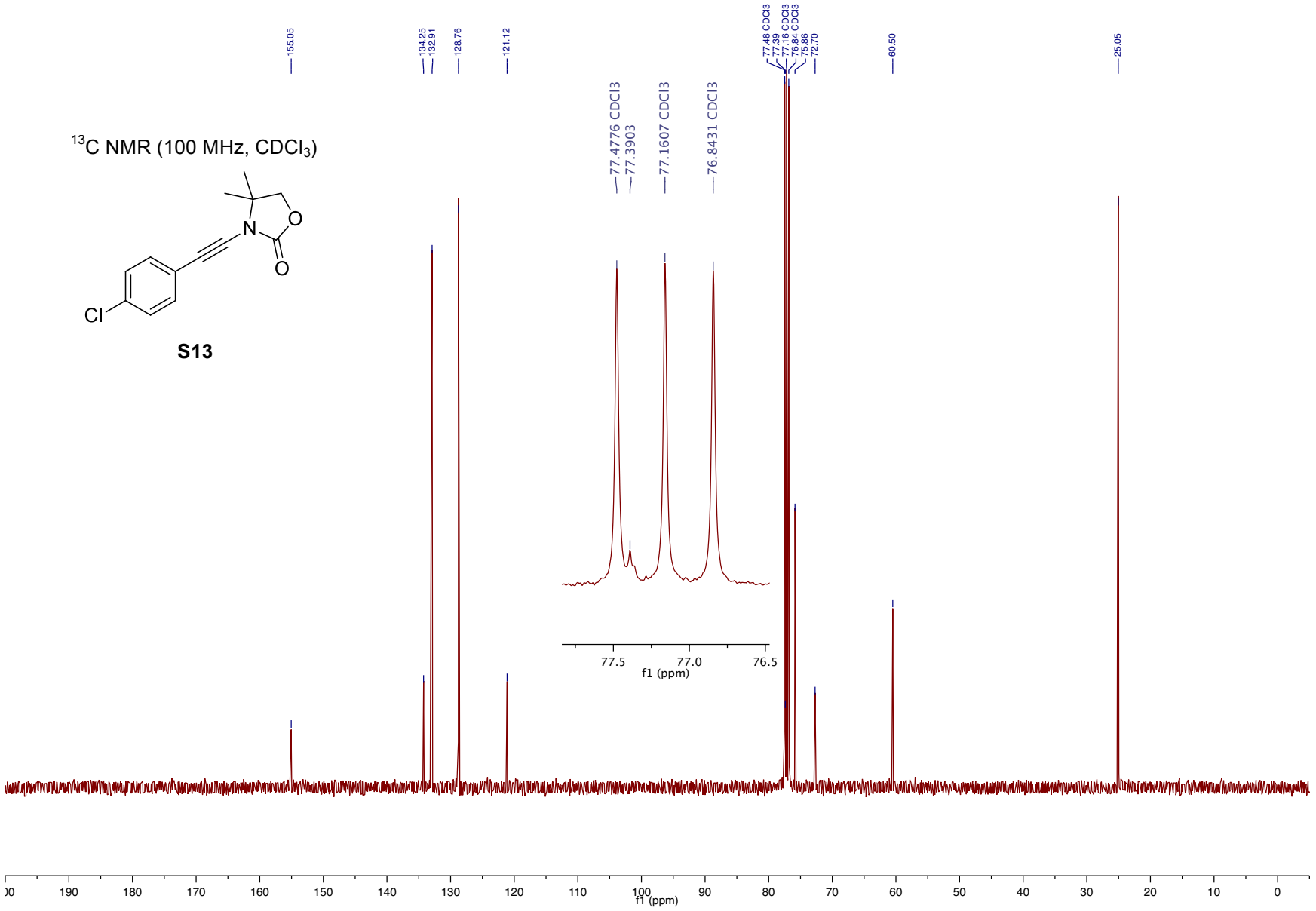
S12


159.79
155.34
133.65
114.49
114.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.78
74.92
73.30
60.42
55.44
25.01
13C NMR (100 MHz, CDCl3)
N
O
O
O
MeO
S12
f1 (ppm)



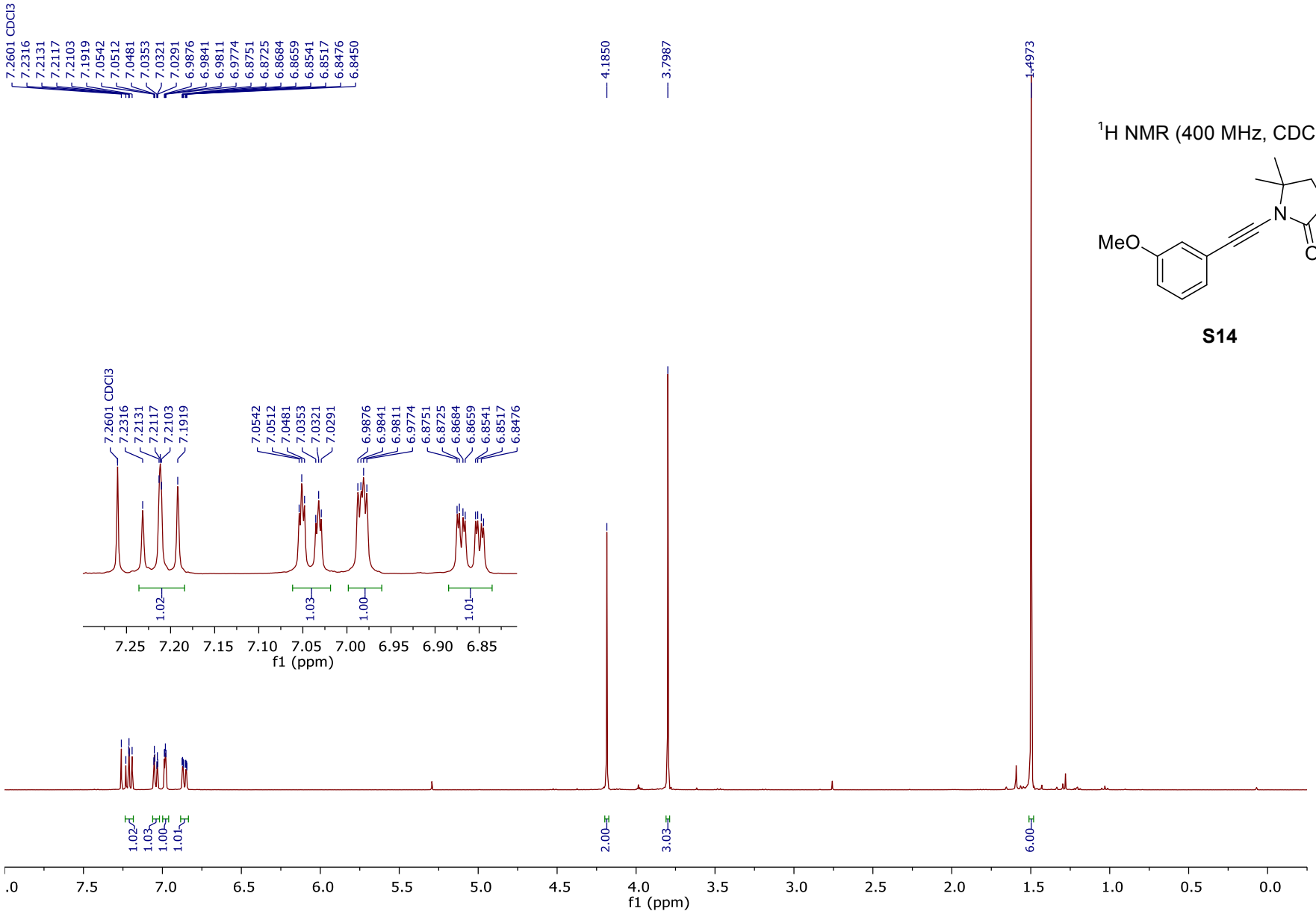
^{1}H NMR (400 MHz, $CDCl_3$)

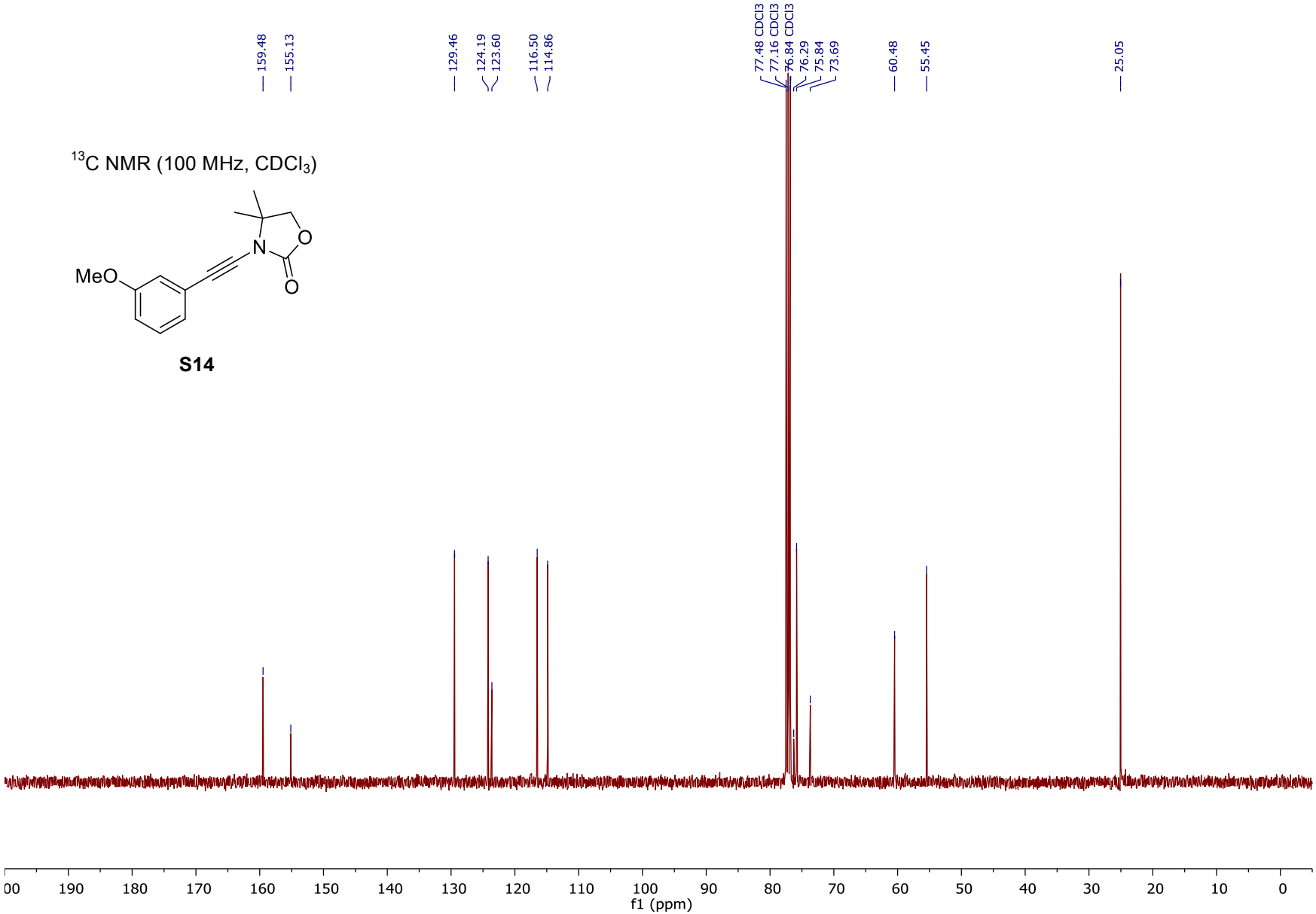
S13

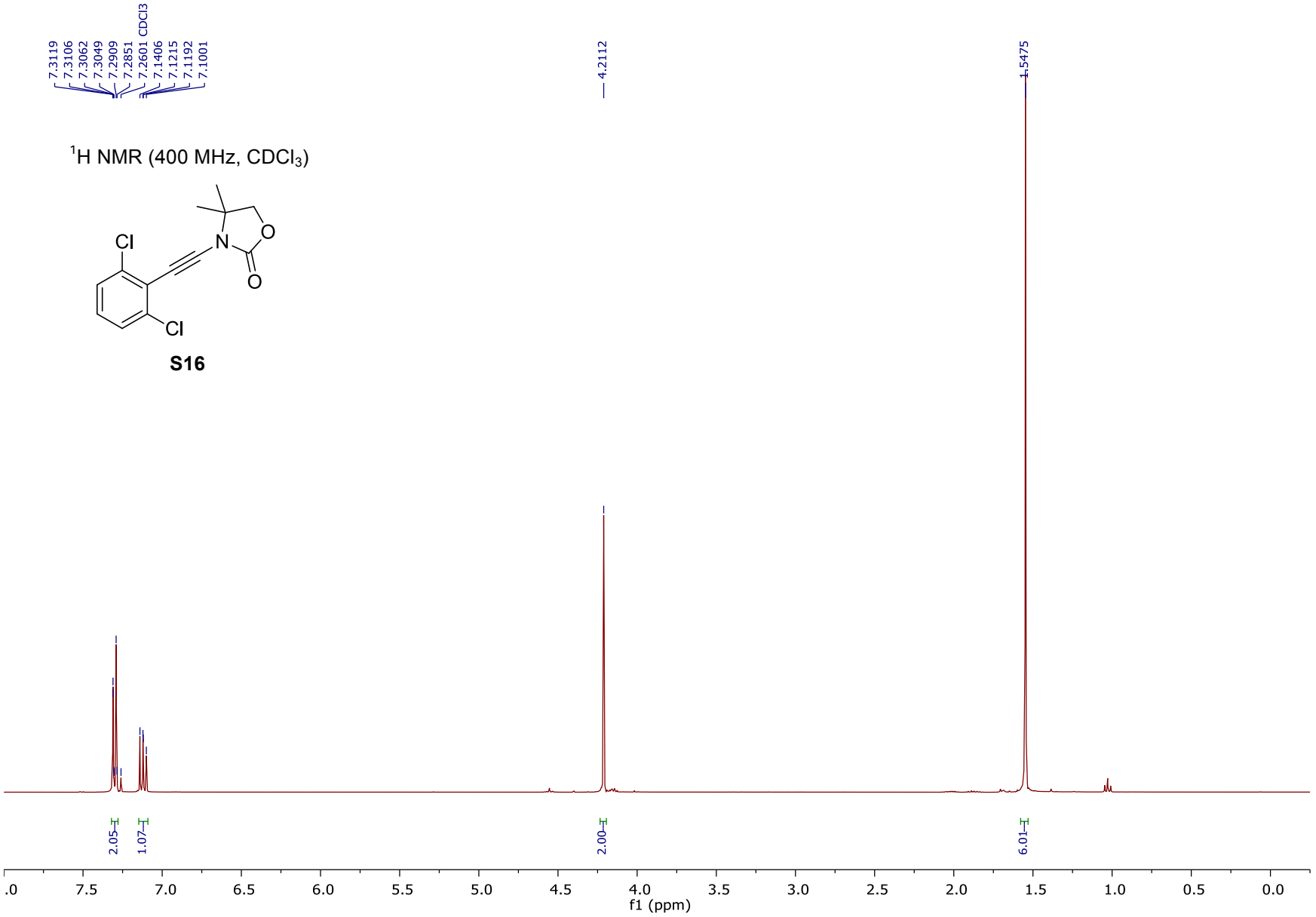


^{13}C NMR (100 MHz, $CDCl_3$)

S13


7.2601 CDCl3
7.2316
7.2131
7.2117
7.2103
7.1919
7.0542
7.0512
7.0481
7.0353
7.0321
7.0291
6.9876
6.9841
6.9811
6.9774
6.8751
6.8725
6.8684
6.8659
6.8541
6.8517
6.8476
6.8450
4.1850
3.7987
1.4973
1.02
1.03
1.00
1.01
2.00
3.03
6.00
f1 (ppm)
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
N
O
O
S14

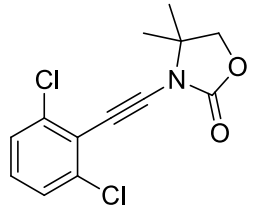

159.48
155.13
129.46
124.19
123.60
116.50
114.86
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.29
75.84
73.69
60.48
55.45
25.05
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
N
O
O
S14
f1 (ppm)



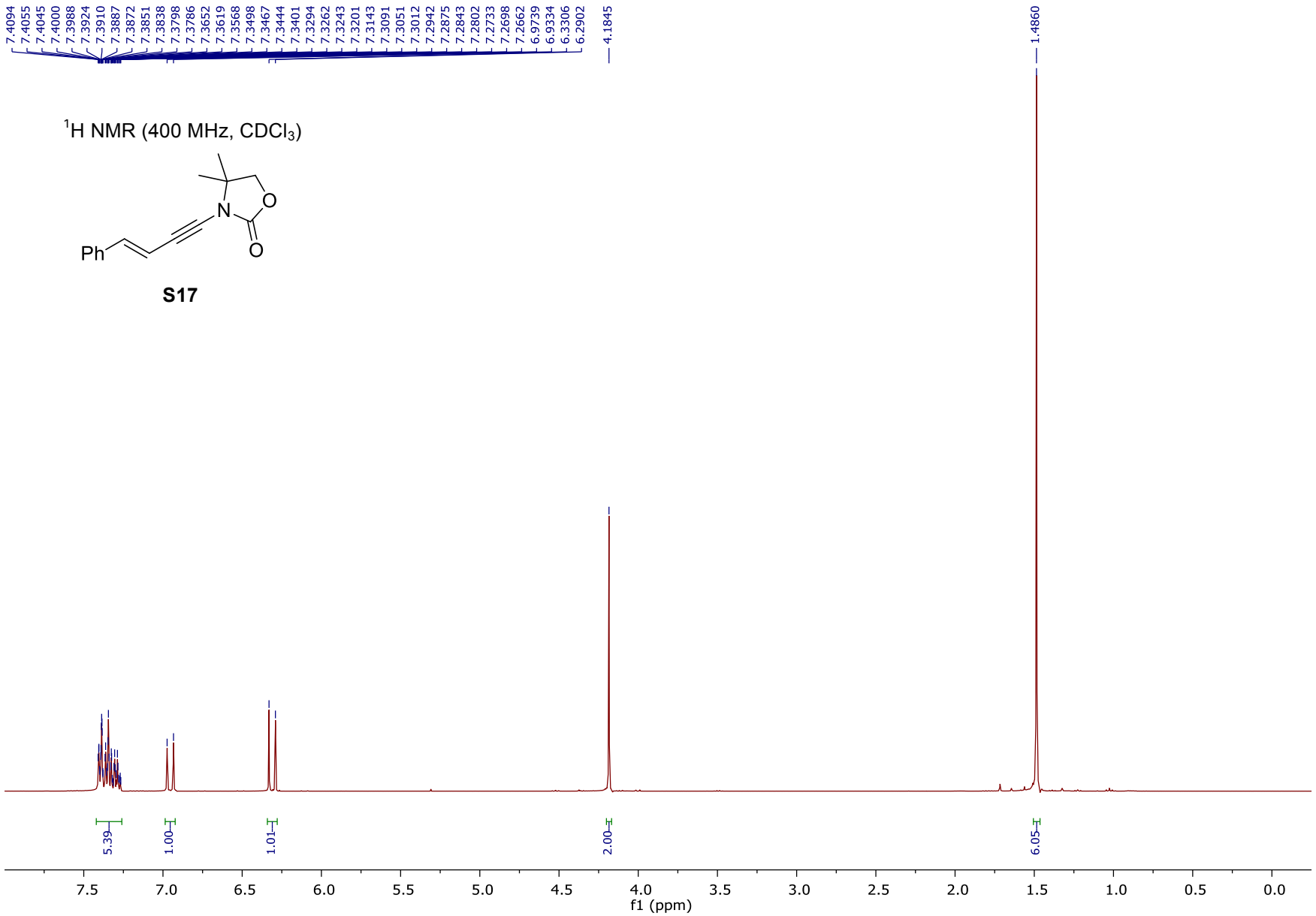
^{1}H NMR (400 MHz, $CDCl_3$)

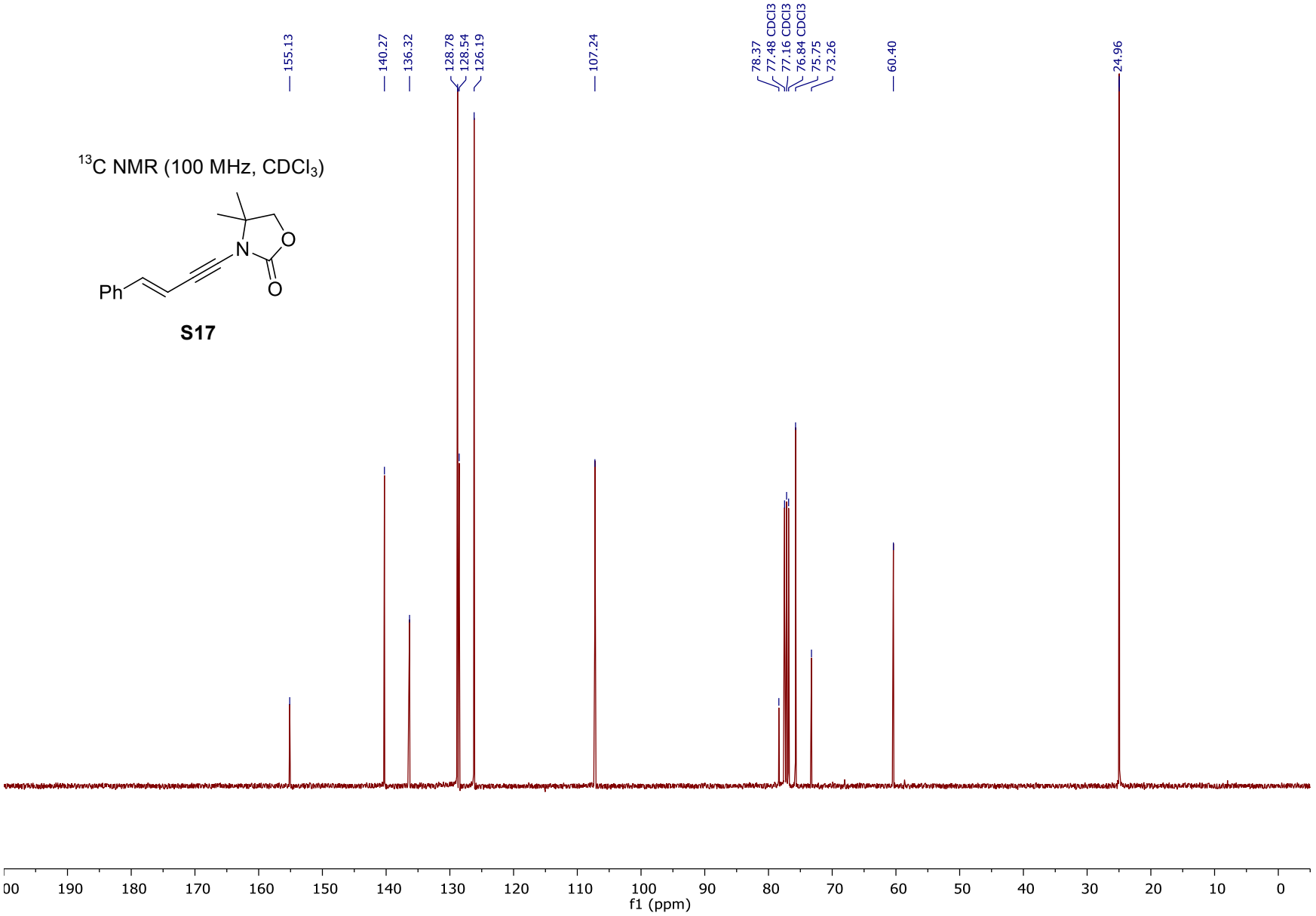
S16

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



S16

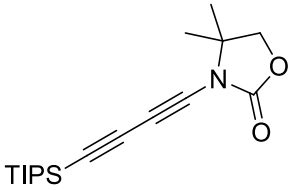

7.4094
7.4055
7.4045
7.4000
7.3988
7.3924
7.3910
7.3887
7.3872
7.3851
7.3838
7.3798
7.3786
7.3652
7.3619
7.3568
7.3498
7.3467
7.3444
7.3401
7.3294
7.3262
7.3243
7.3201
7.3143
7.3091
7.3051
7.3012
7.2942
7.2875
7.2843
7.2802
7.2733
7.2698
7.2662
6.9739
6.9334
6.3306
6.2902
4.1845
1.4860
^{1}H NMR (400 MHz, $CDCl_3$)
N
O
O
Ph
S17
5.39
1.00
1.01
2.00
6.05
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
f1 (ppm)



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

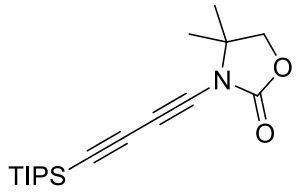
S17

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

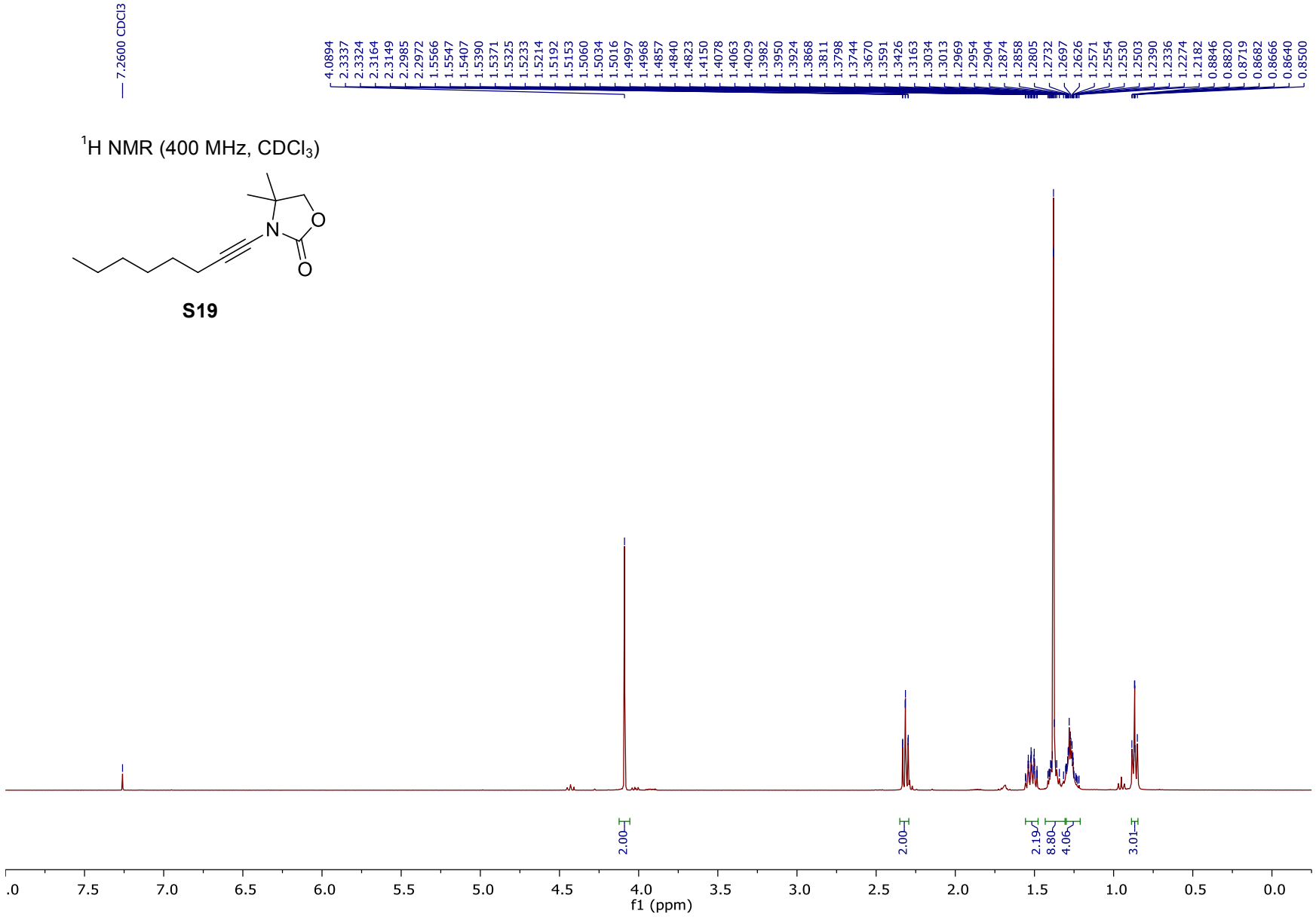


S18

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



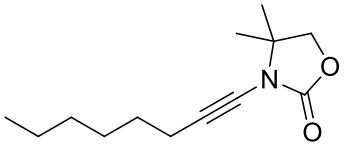
S18



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

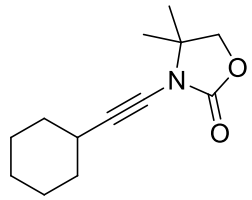
S19

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



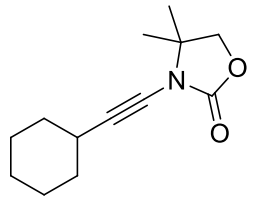
S19

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



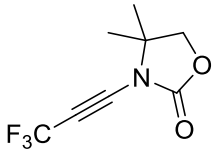
S21

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



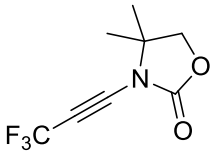
S21

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



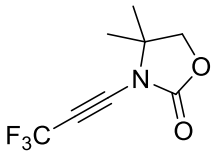
S22

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

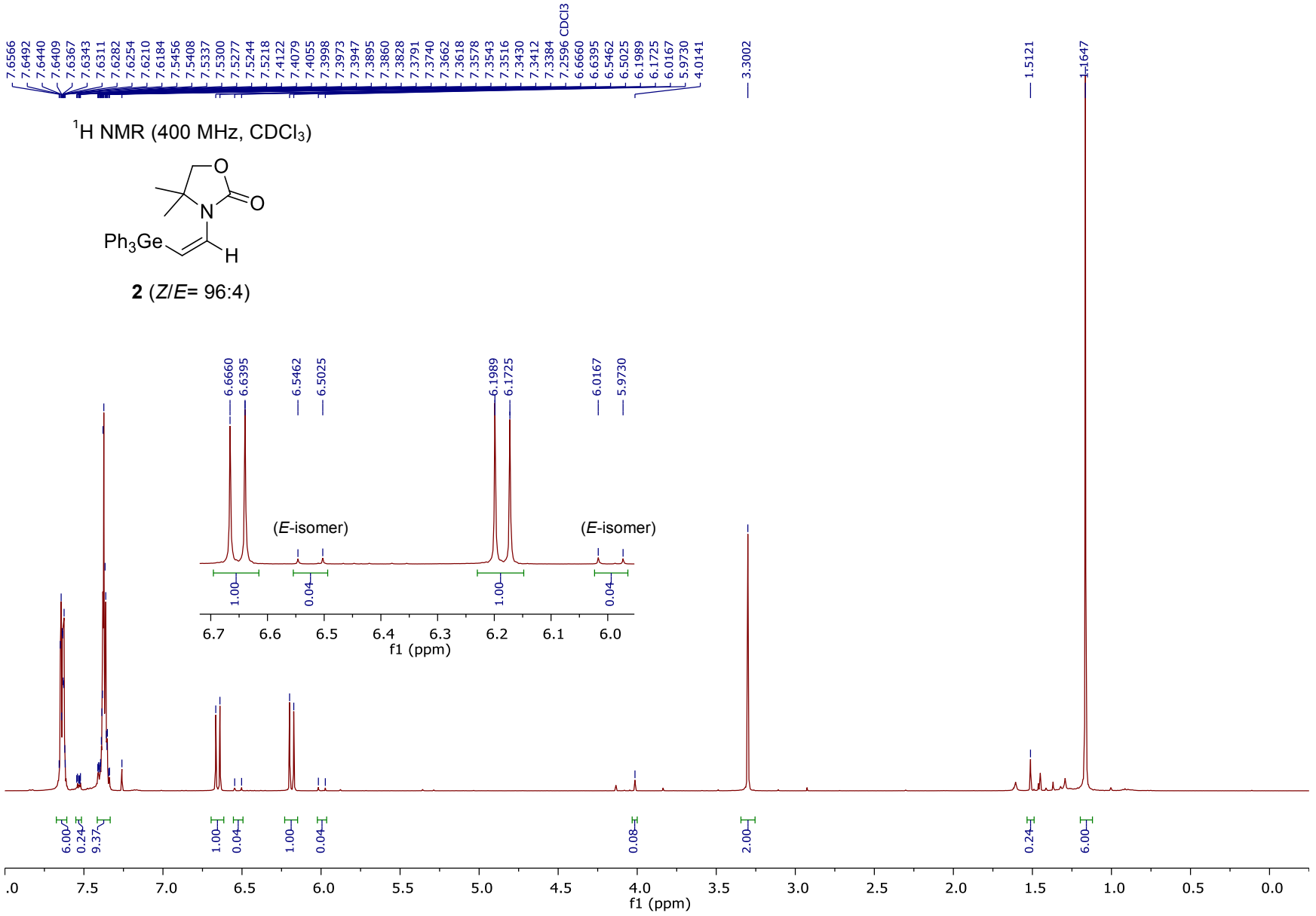


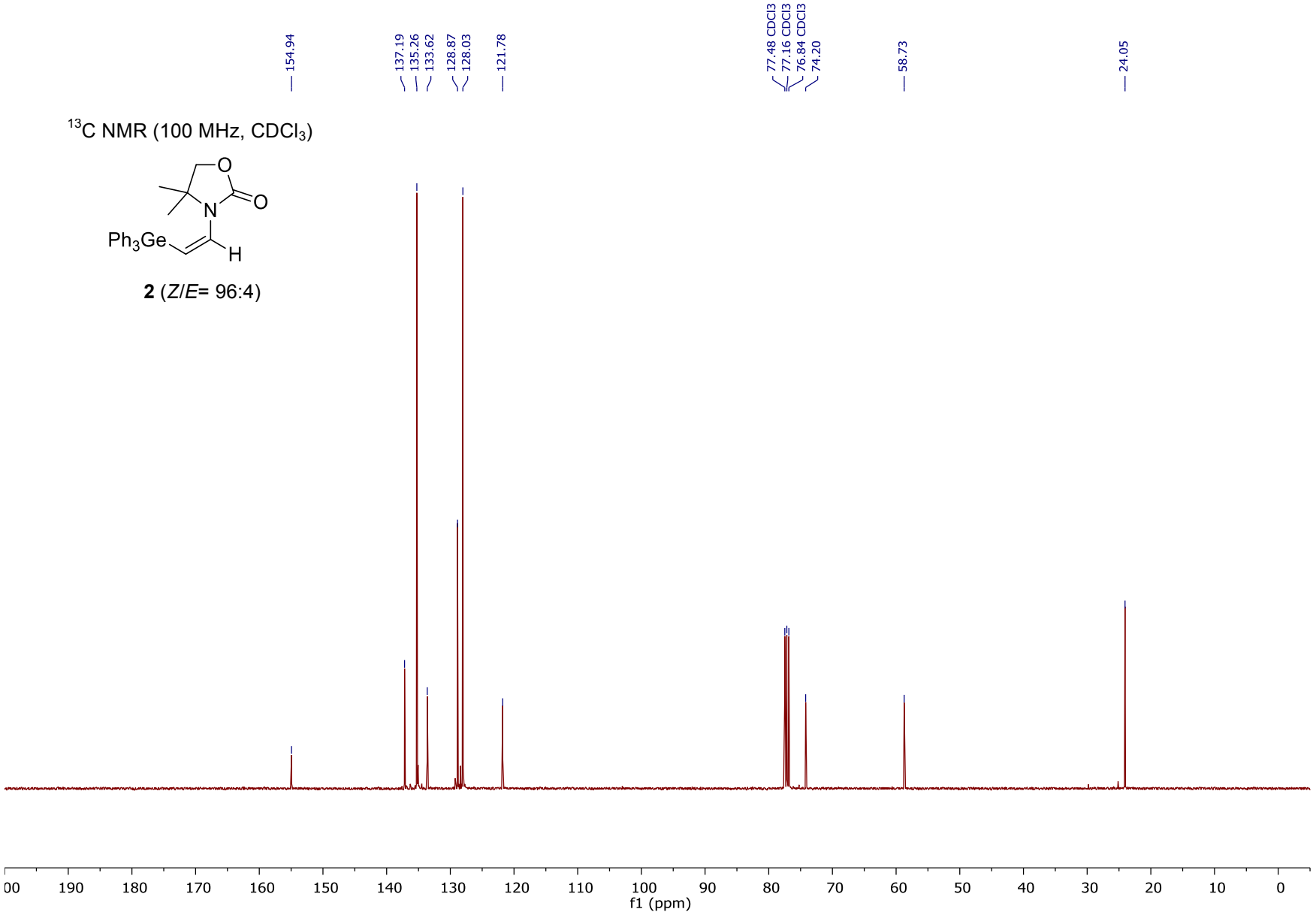
S22

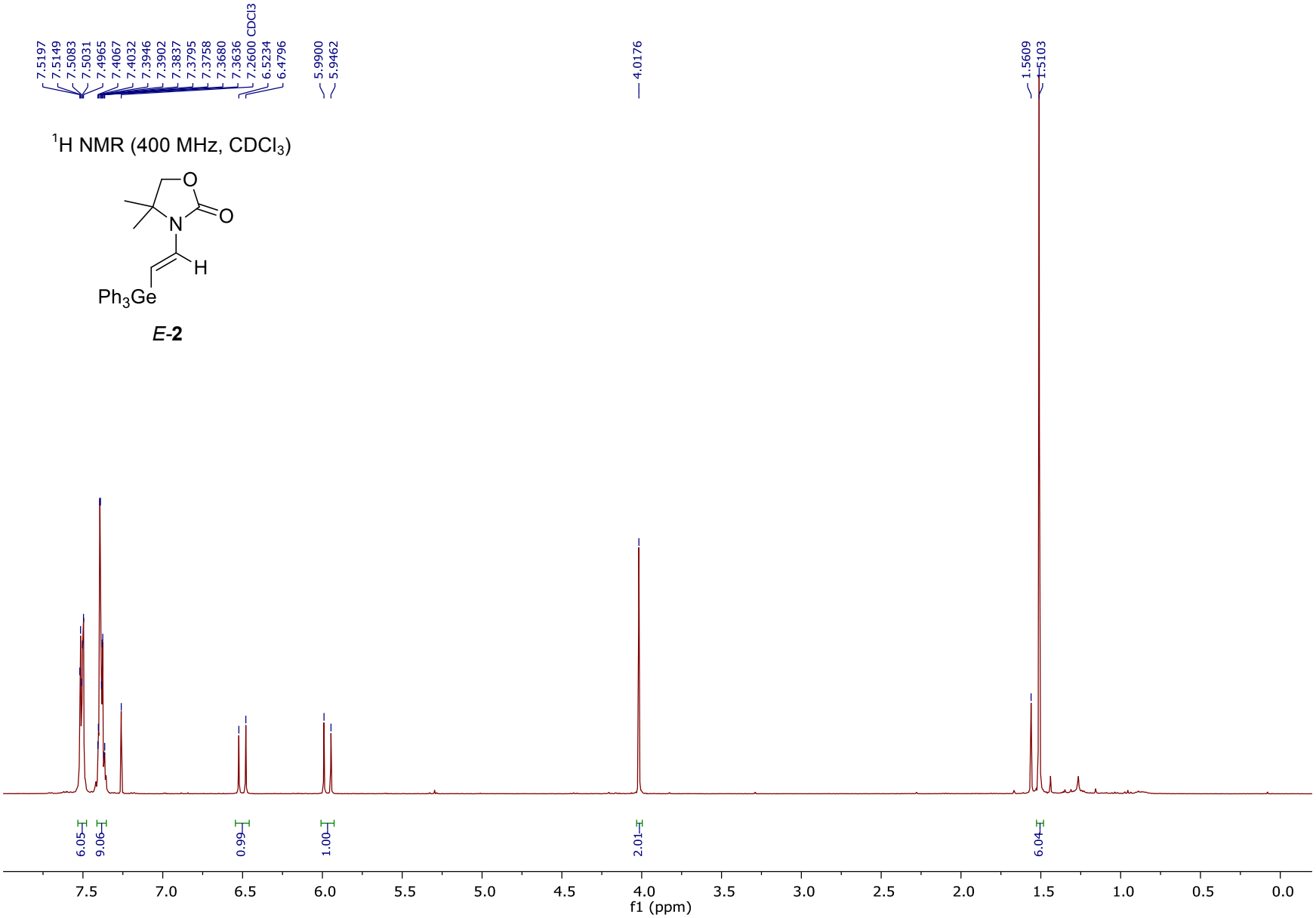
^{19}F NMR (376 MHz, $CDCl_3$)



S22

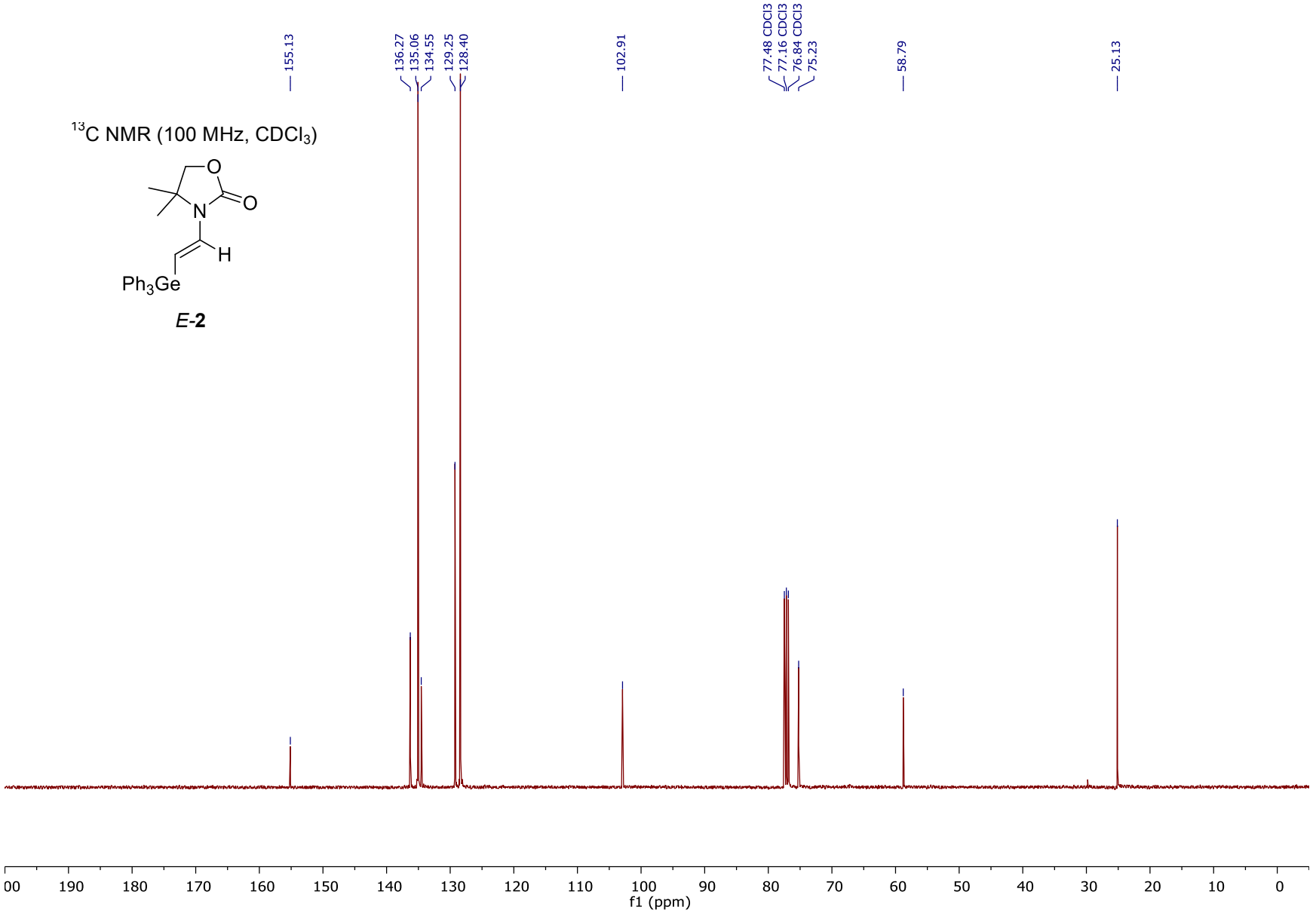

7.6566
7.6492
7.6440
7.6409
7.6367
7.6343
7.6311
7.6282
7.6254
7.6210
7.6184
7.5456
7.5408
7.5337
7.5300
7.5277
7.5244
7.5218
7.4122
7.4079
7.4055
7.3998
7.3973
7.3947
7.3895
7.3860
7.3828
7.3791
7.3740
7.3662
7.3618
7.3578
7.3543
7.3516
7.3430
7.3412
7.3384
7.2596 CDCl3
6.6660
6.6395
6.5462
6.5025
6.1989
6.1725
6.0167
5.9730
4.0141
3.3002
1.5121
1.1647
^{1}H NMR (400 MHz, $CDCl_3$)
Ph_3Ge
2 (*Z*/*E*= 96:4)
(*E*-isomer)
(*E*-isomer)
1.00
0.04
1.00
0.04
f1 (ppm)
6.00
0.24
9.37
1.00
0.04
1.00
0.04
0.08
2.00
0.24
6.00
f1 (ppm)

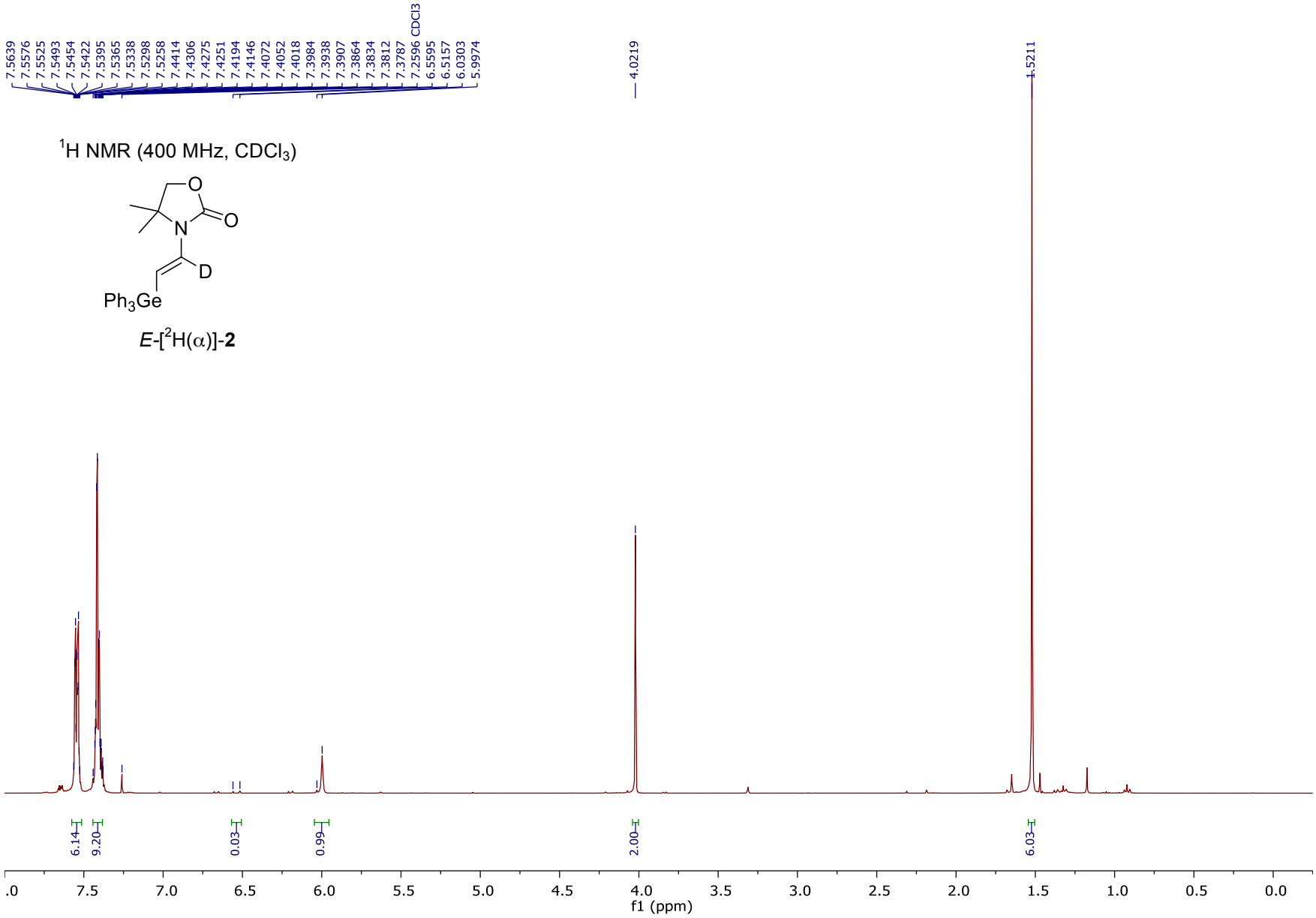

154.94
137.19
135.26
133.62
128.87
128.03
121.78
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.20
58.73
24.05
^{13}C NMR (100 MHz, $CDCl_3$)
O
N
O
Ph_3Ge
H
2 (*Z*/*E*= 96:4)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



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

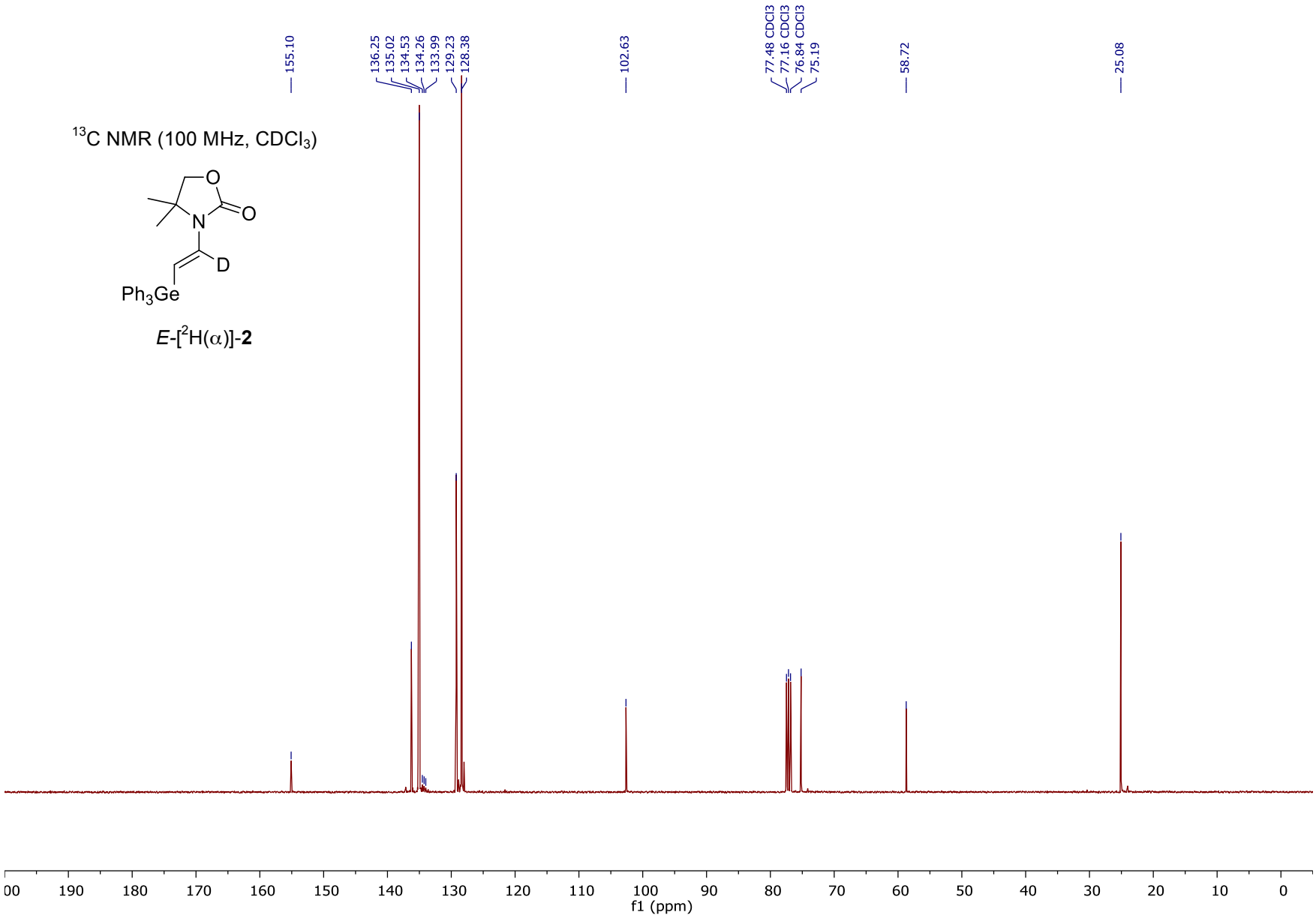
***E*-2**

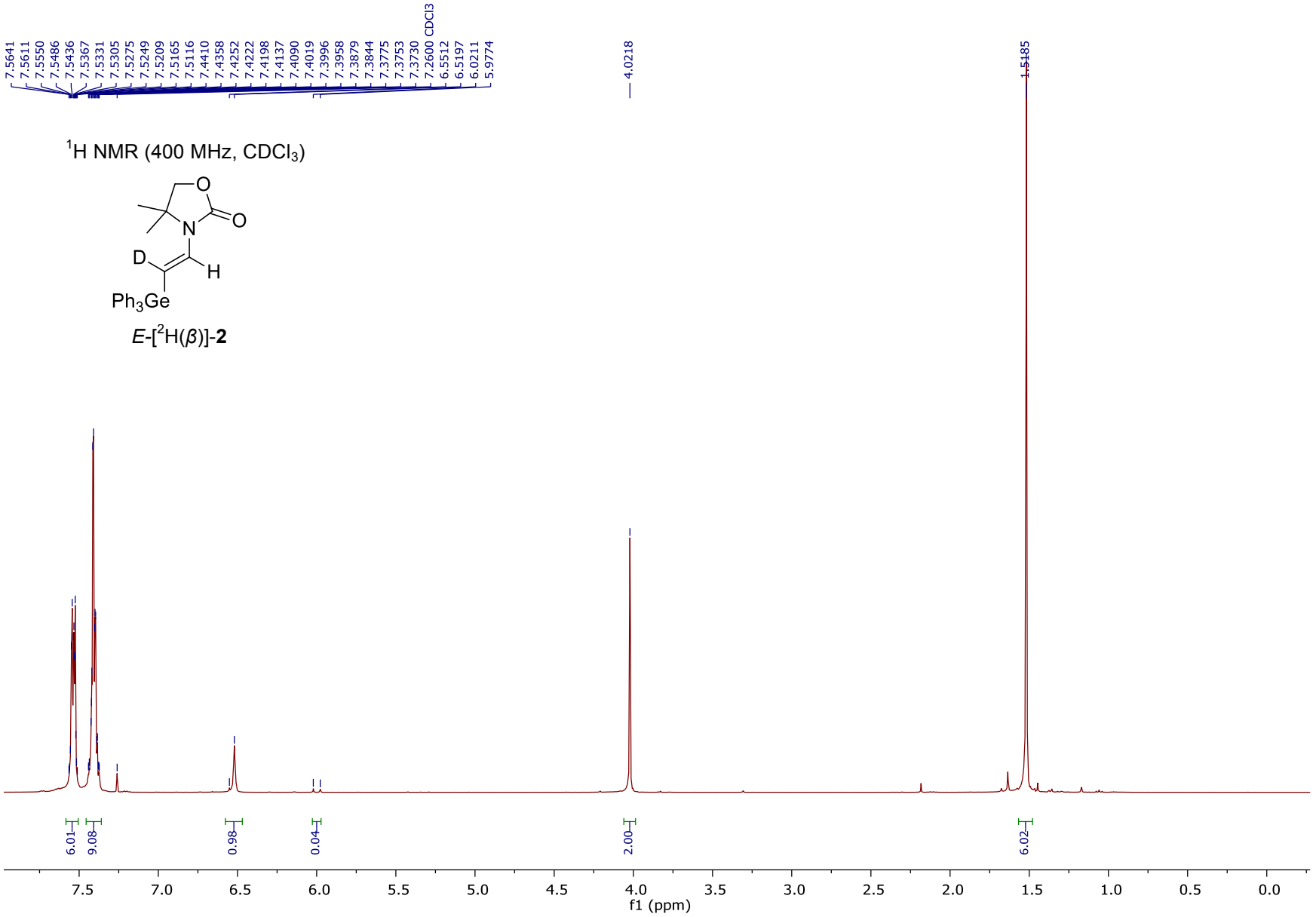

155.13
136.27
135.06
134.55
129.25
128.40
102.91
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.23
58.79
25.13
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
H
Ph_3Ge
E-**2**
f1 (ppm)



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

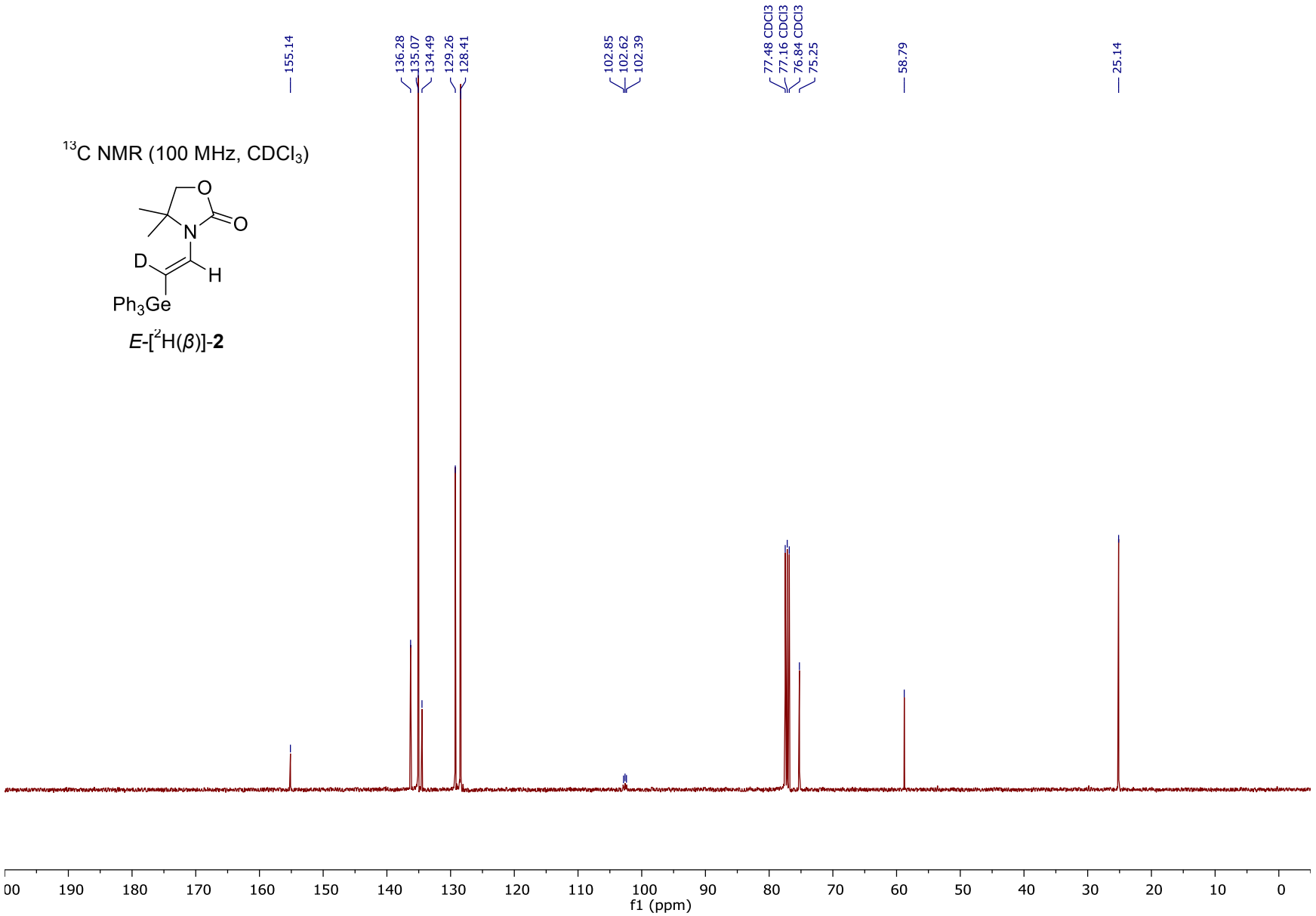
E-[^{2}H(α)]-**2**

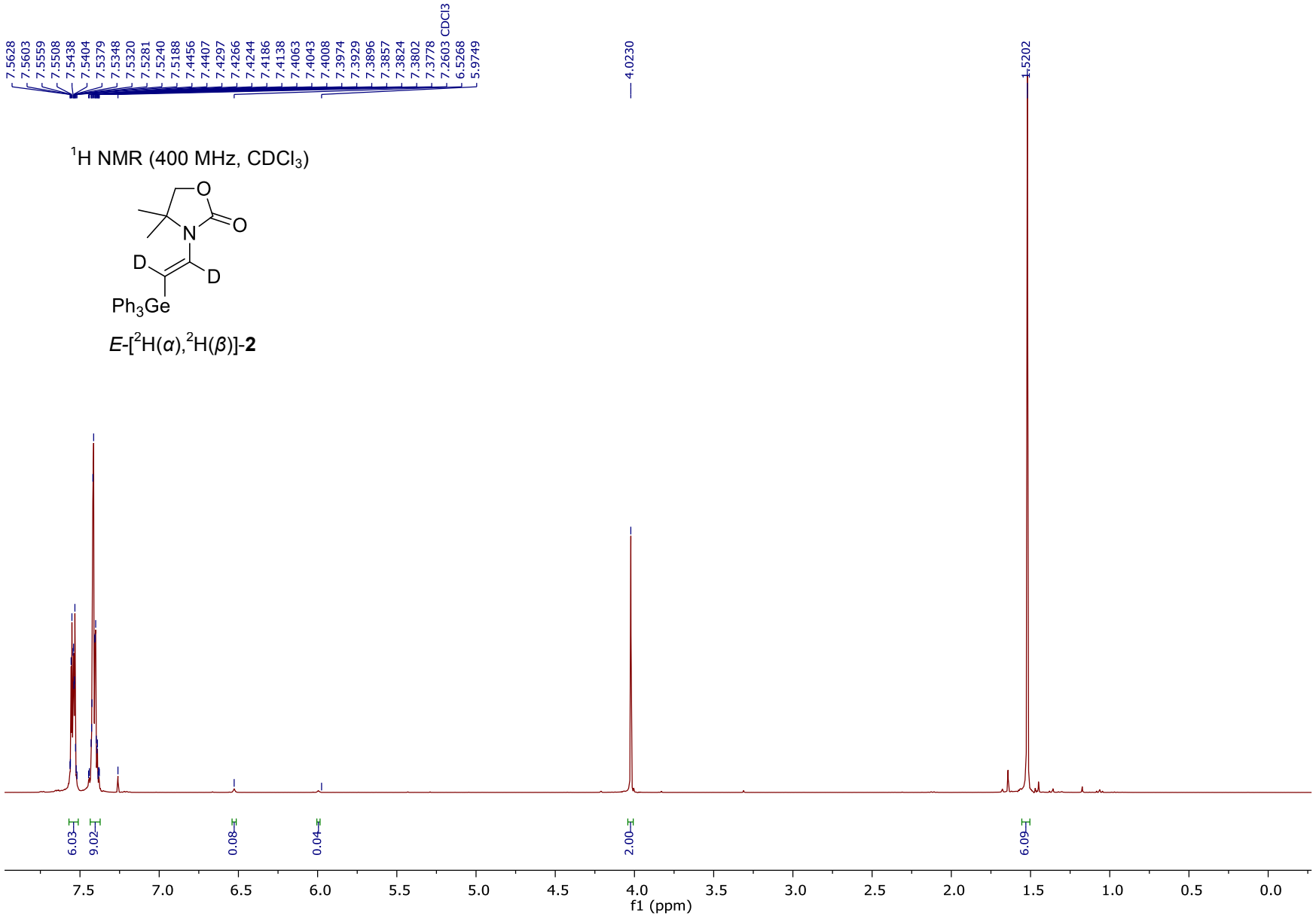

155.10
136.25
135.02
134.53
134.26
133.99
129.23
128.38
102.63
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.19
58.72
25.08
13C NMR (100 MHz, CDCl3)
O
O
N
D
Ph3Ge
E-[2H(α)]-2
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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

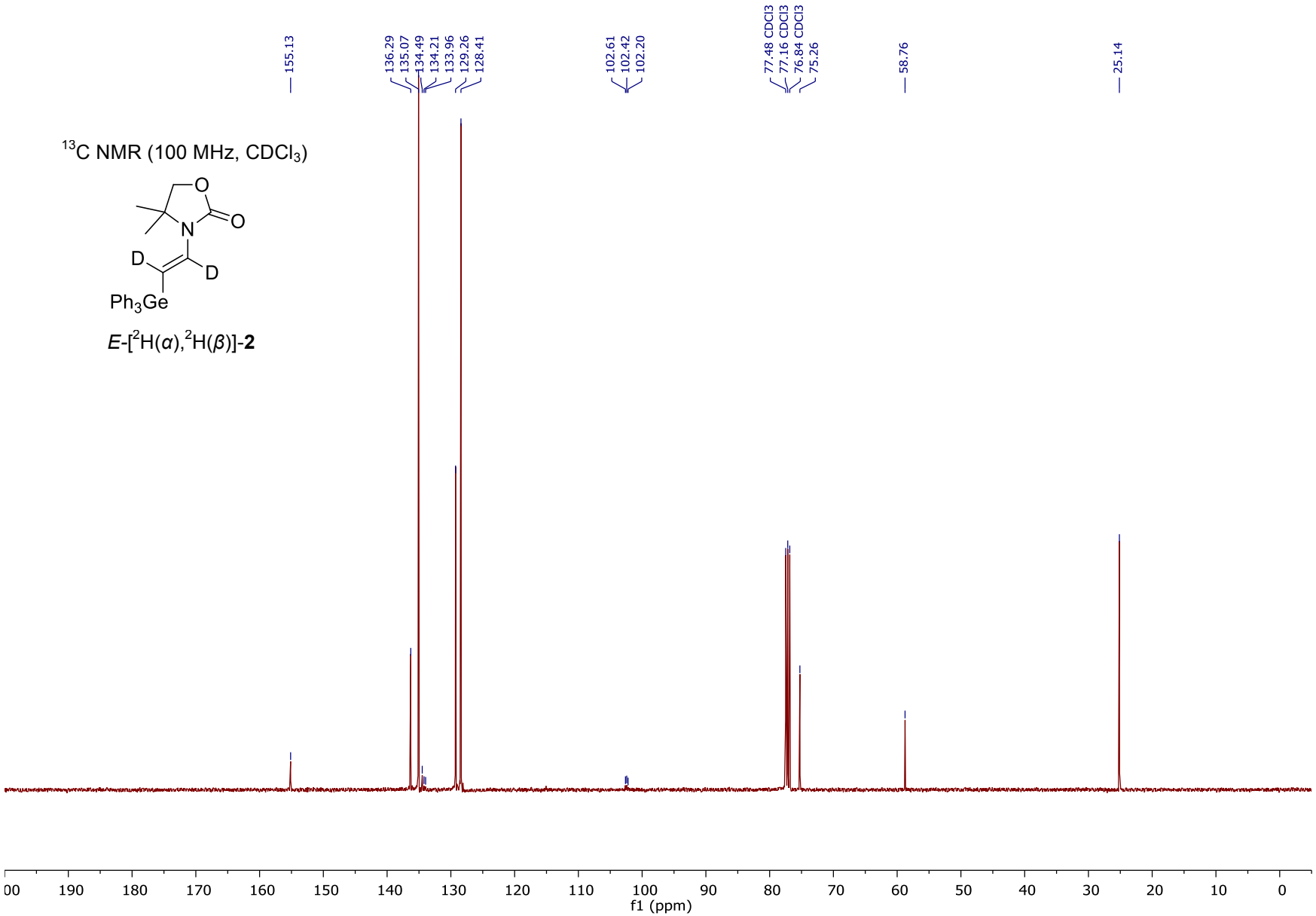
E-[^{2}H(*β*)]-**2**

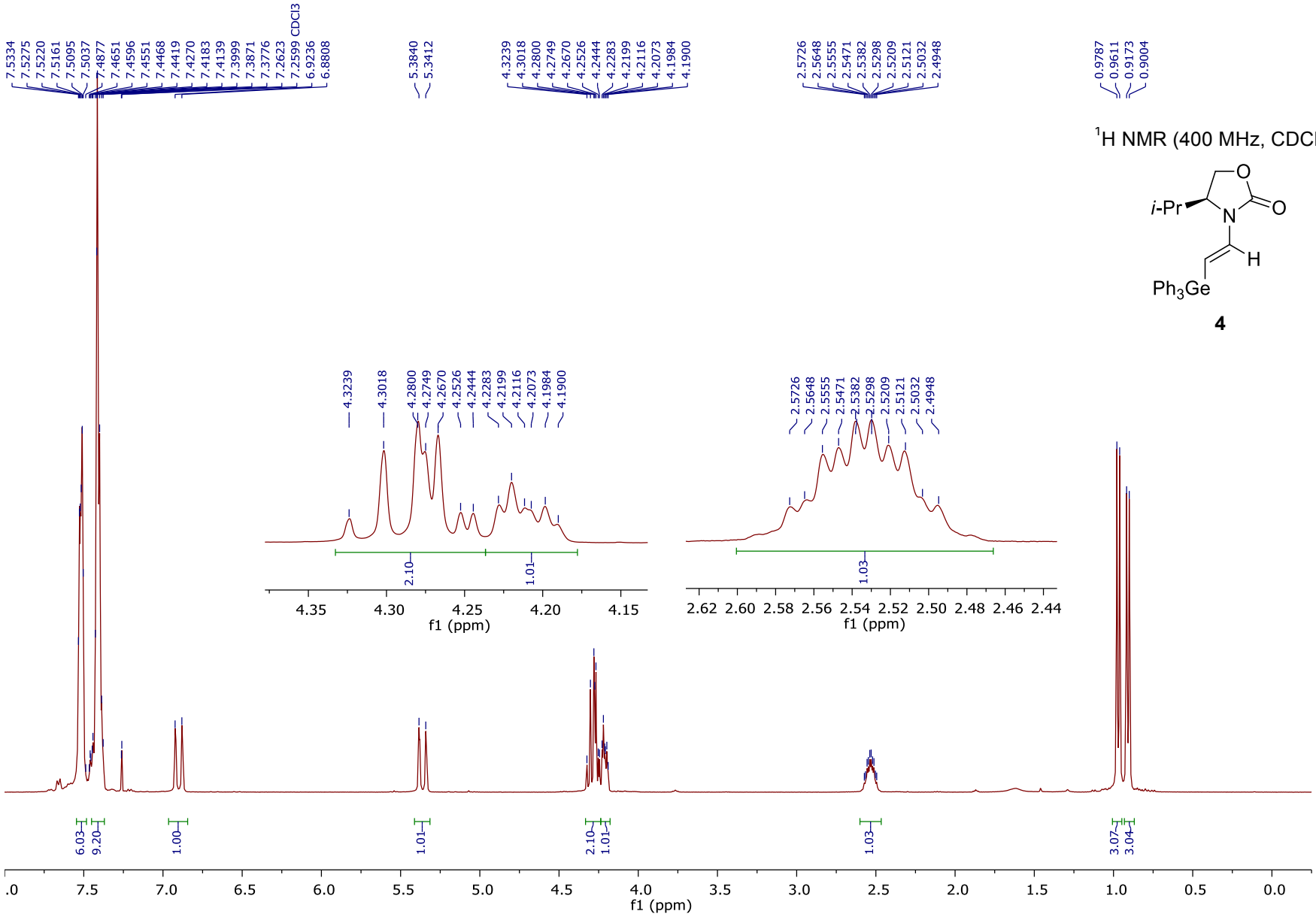

155.14
136.28
135.07
134.49
129.26
128.41
102.85
102.62
102.39
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.25
58.79
25.14
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
D
H
Ph_3Ge
E-[^{2}H(*β*)]-**2**
f1 (ppm)



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

E-[^{2}H(*α*),^{2}H(*β*)]-**2**

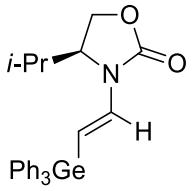

155.13
136.29
135.07
134.49
134.21
133.96
129.26
128.41
102.61
102.42
102.20
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.26
58.76
25.14
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
D
D
Ph_3Ge
E-[^{2}H(*α*),^{2}H(*β*)]-**2**
f1 (ppm)



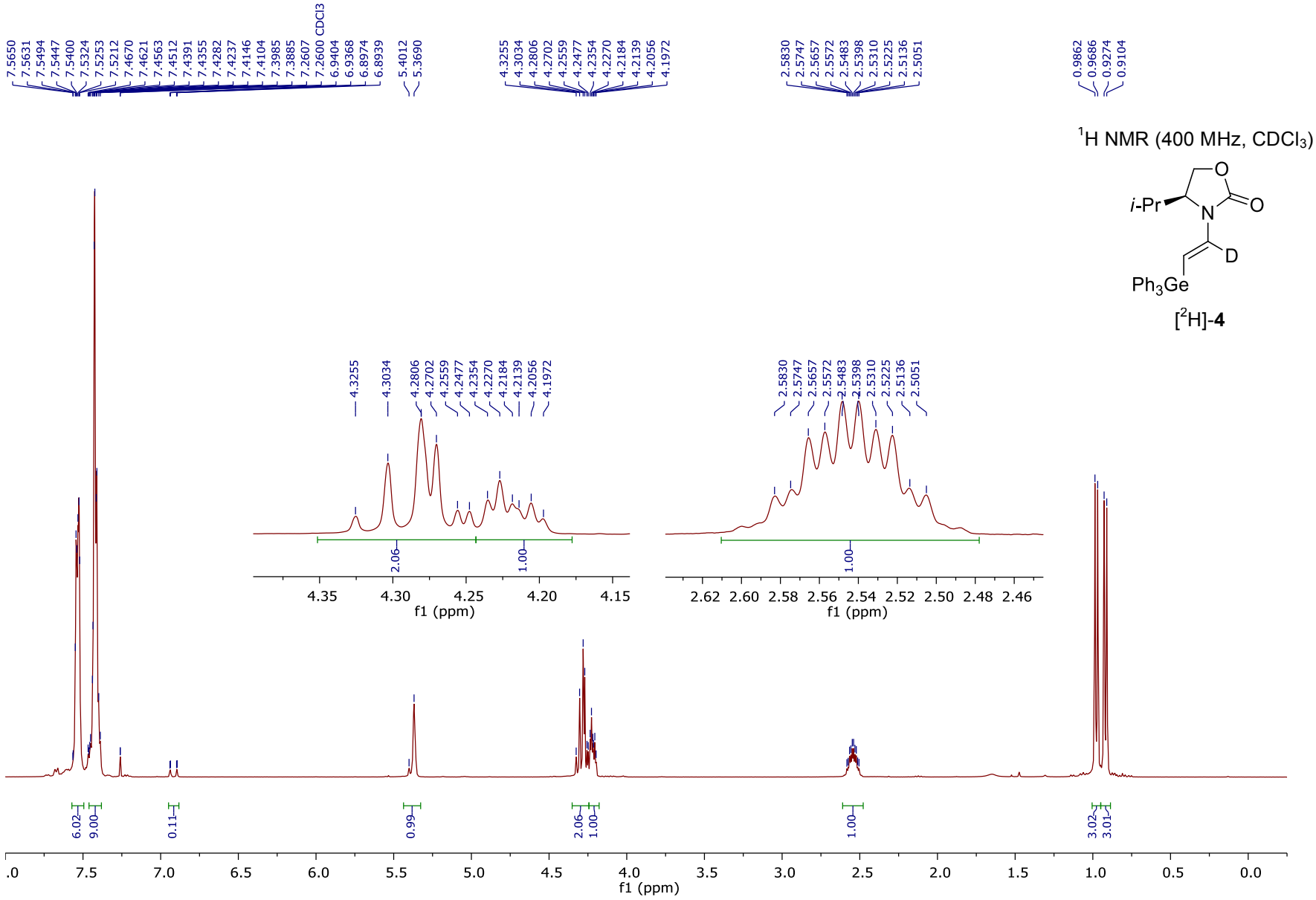
^{1}H NMR (400 MHz, $CDCl_3$)

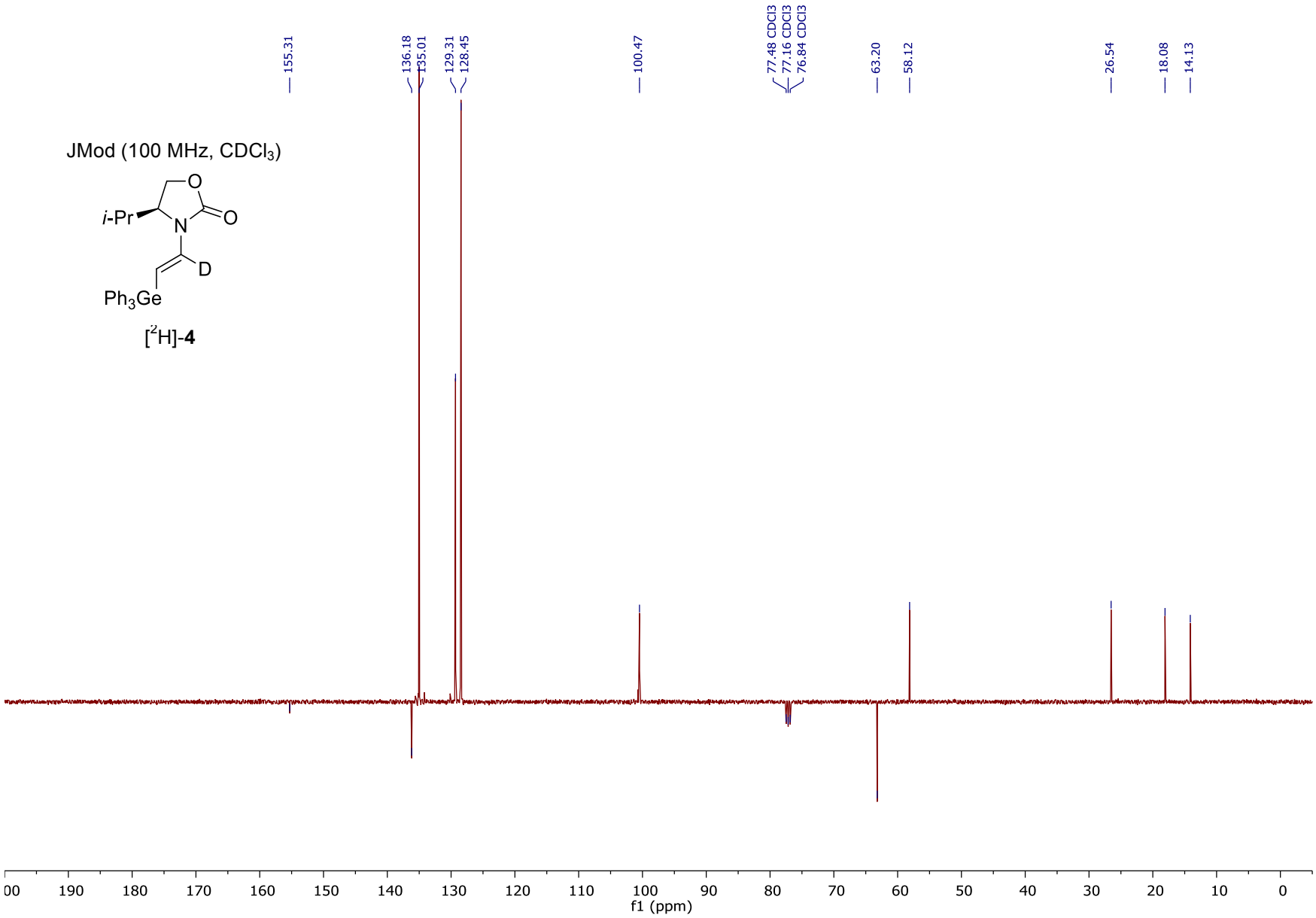
4

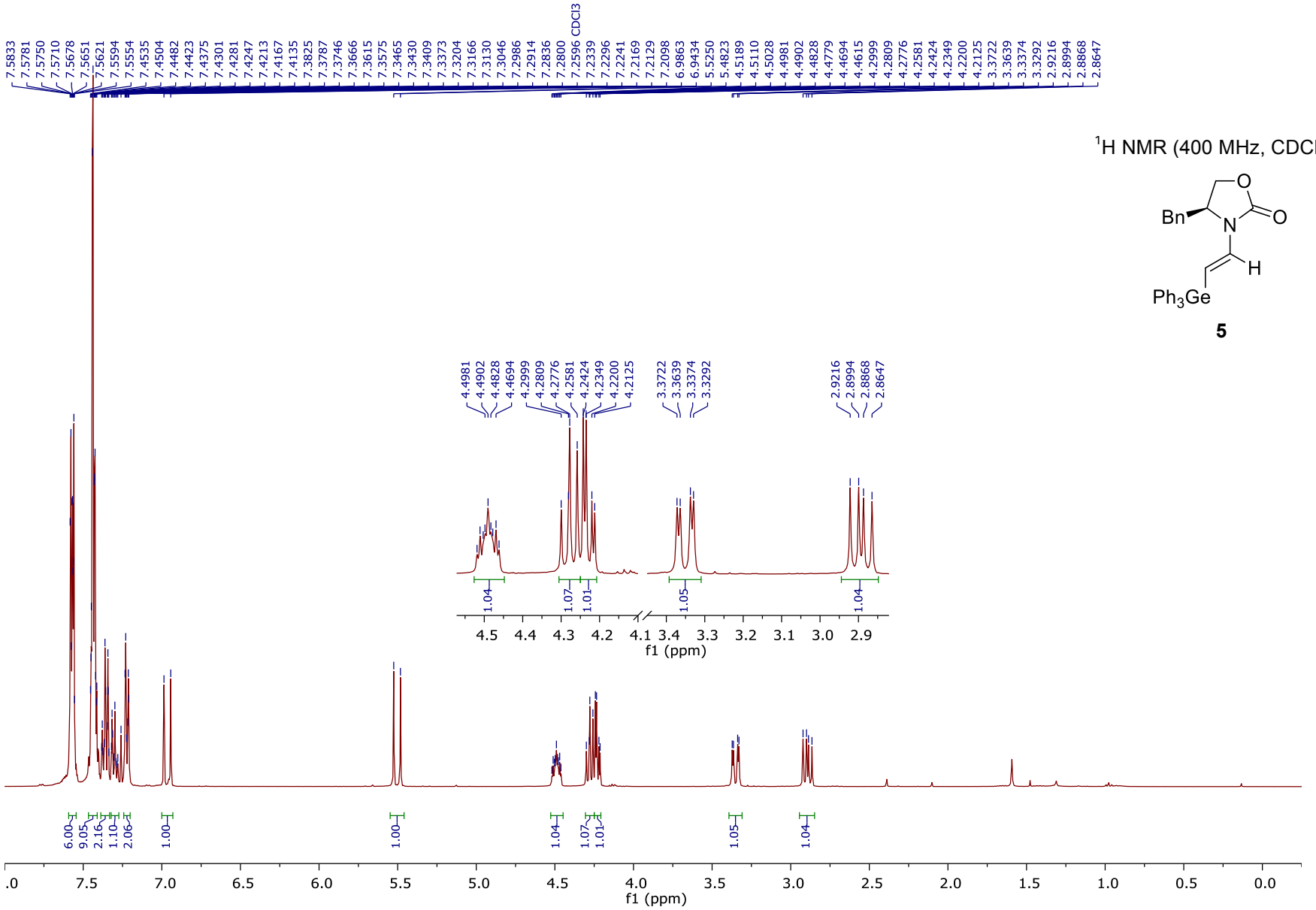
^{13}C NMR (100 MHz, $CDCl_3$)



4

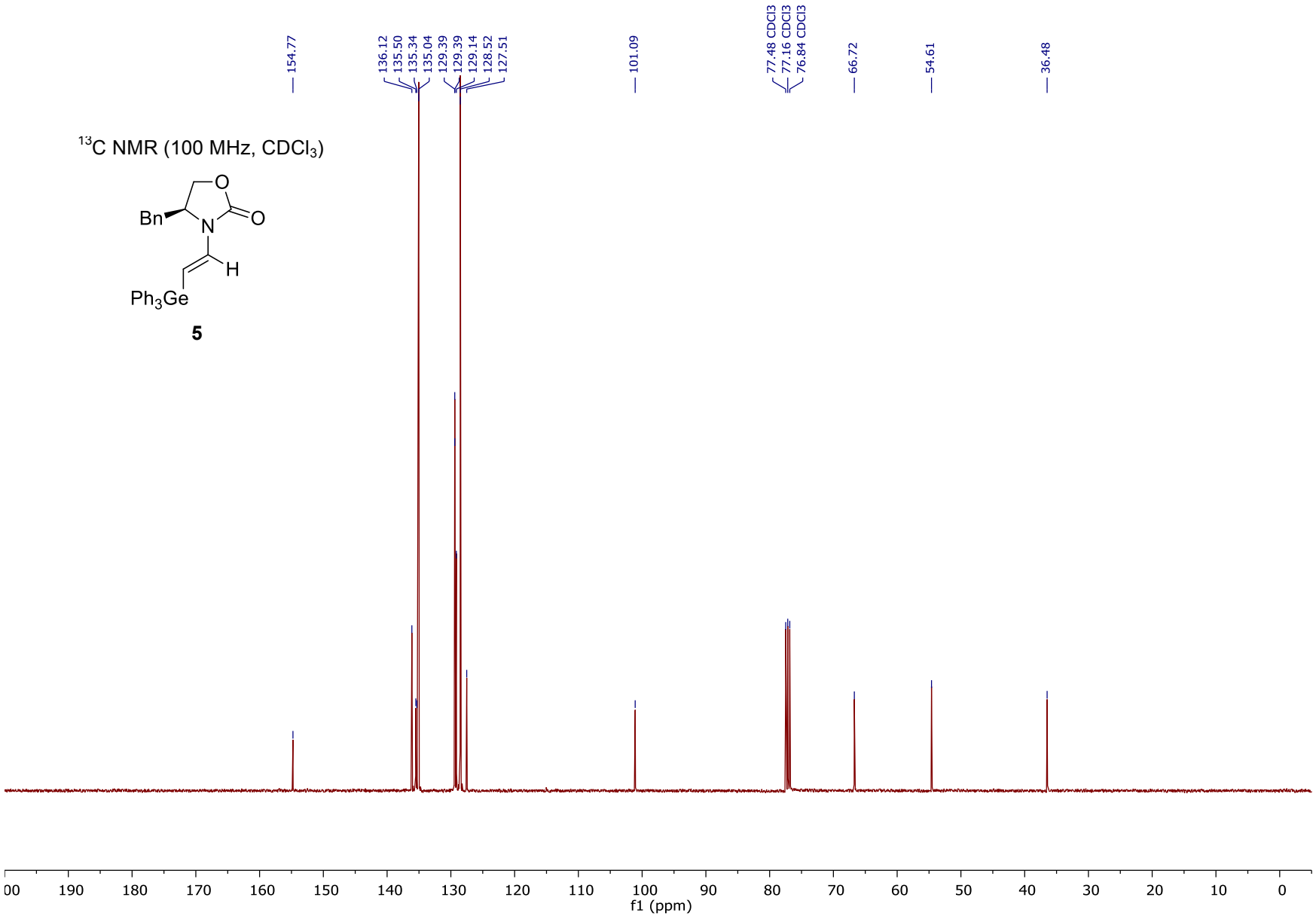

7.5650
7.5631
7.5494
7.5447
7.5400
7.5324
7.5253
7.5212
7.4670
7.4621
7.4563
7.4512
7.4391
7.4355
7.4282
7.4237
7.4146
7.4104
7.3985
7.3885
7.2607
7.2600 CDCl3
6.9404
6.9368
6.8974
6.8939
5.4012
5.3690
4.3255
4.3034
4.2806
4.2702
4.2559
4.2477
4.2354
4.2270
4.2184
4.2139
4.2056
4.1972
2.5830
2.5747
2.5657
2.5572
2.5483
2.5398
2.5310
2.5225
2.5136
2.5051
0.9862
0.9686
0.9274
0.9104
1H NMR (400 MHz, CDCl3)
i-Pr
O
N
O
D
Ph3Ge
[2H]-4
2.06
1.00
4.35
4.30
4.25
4.20
4.15
f1 (ppm)
1.00
2.62 2.60 2.58 2.56 2.54 2.52 2.50 2.48 2.46
f1 (ppm)
6.02
9.00
0.11
0.99
2.06
1.00
1.00
3.02
3.01
.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
f1 (ppm)


155.31
136.18
135.01
129.31
128.45
100.47
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.20
58.12
26.54
18.08
14.13
JMod (100 MHz, CDCl3)
i-Pr
O
O
N
O
D
Ph3Ge
[2H]-4
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



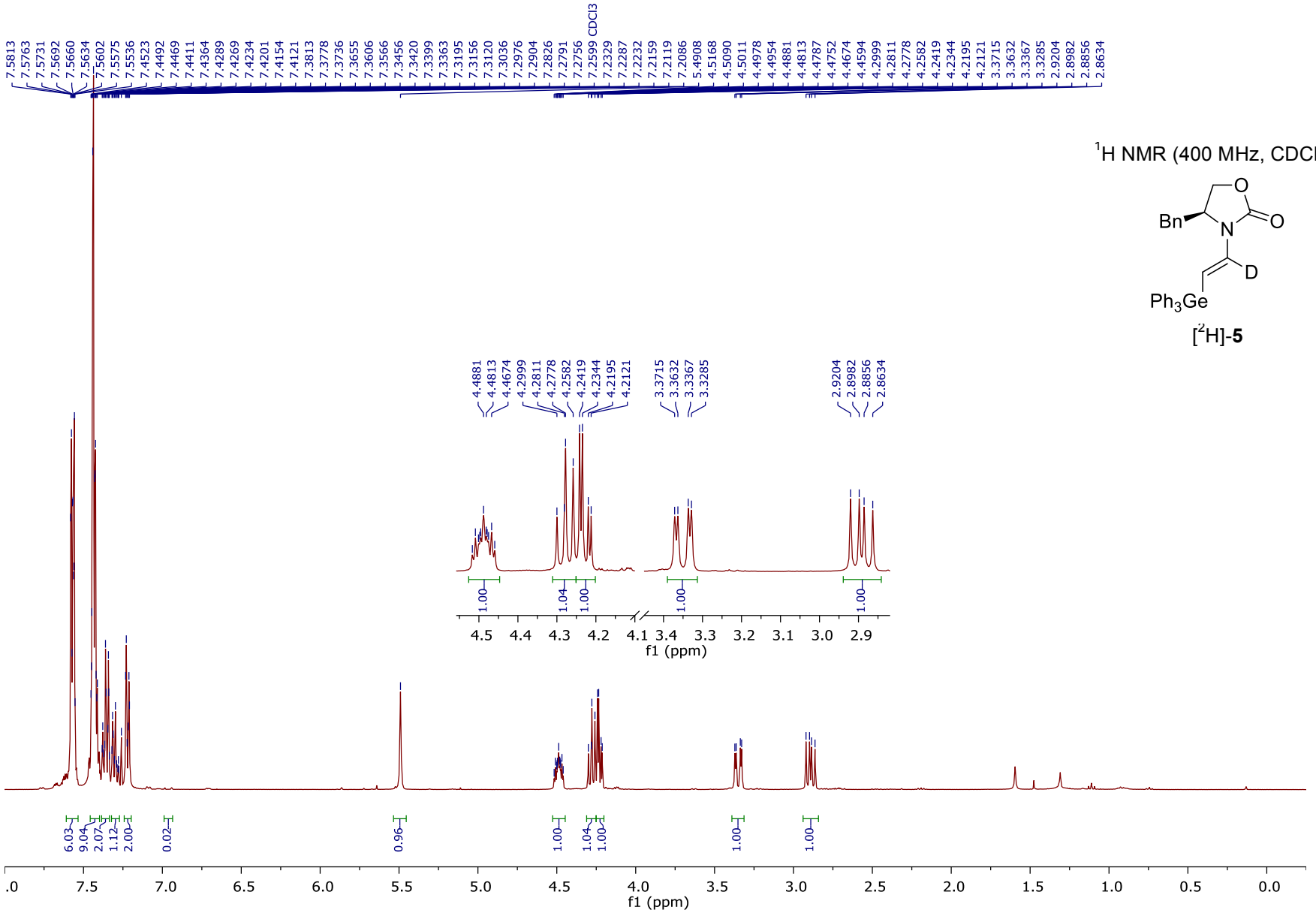
^{1}H NMR (400 MHz, $CDCl_3$)

5



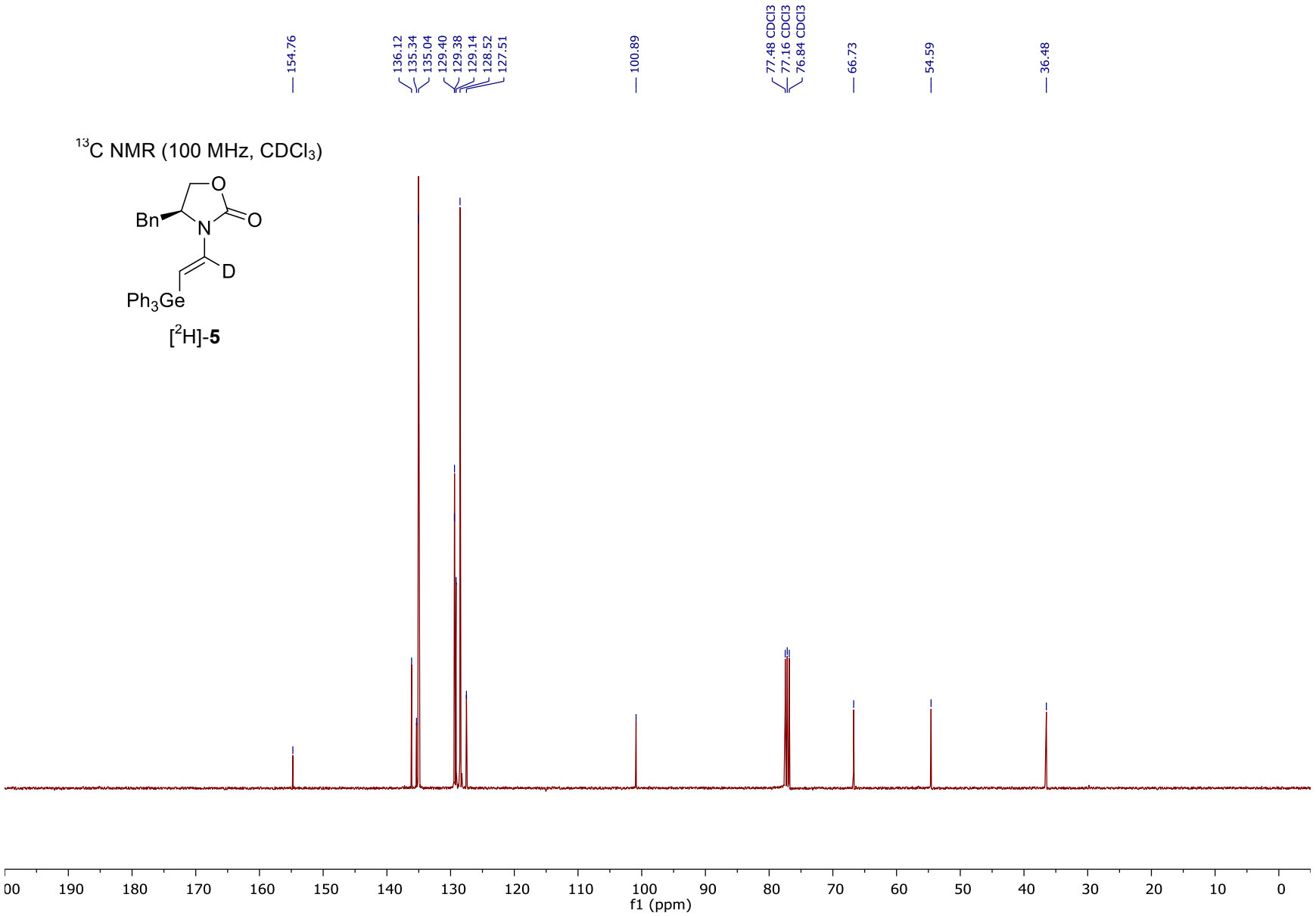
^{13}C NMR (100 MHz, $CDCl_3$)

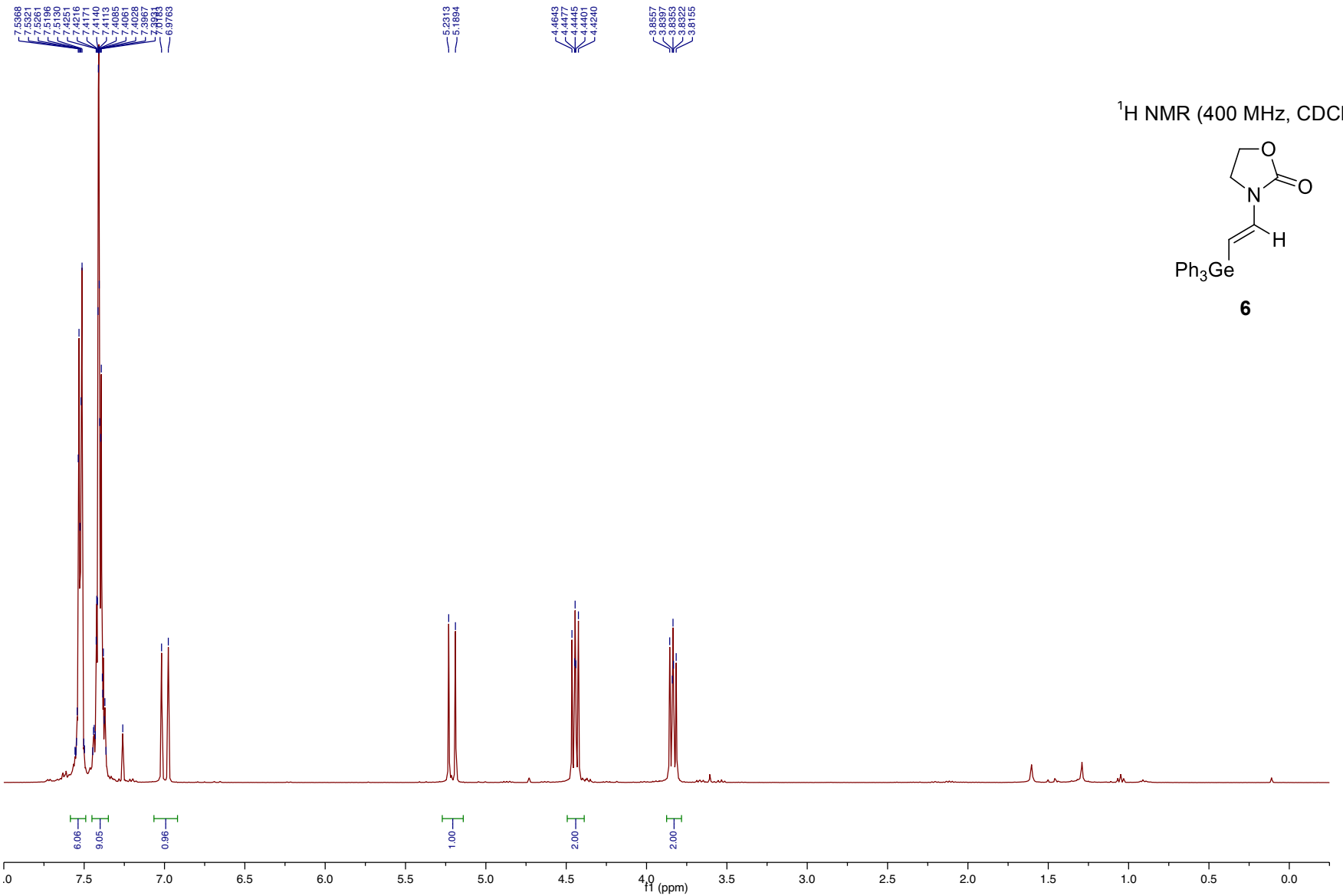
5



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

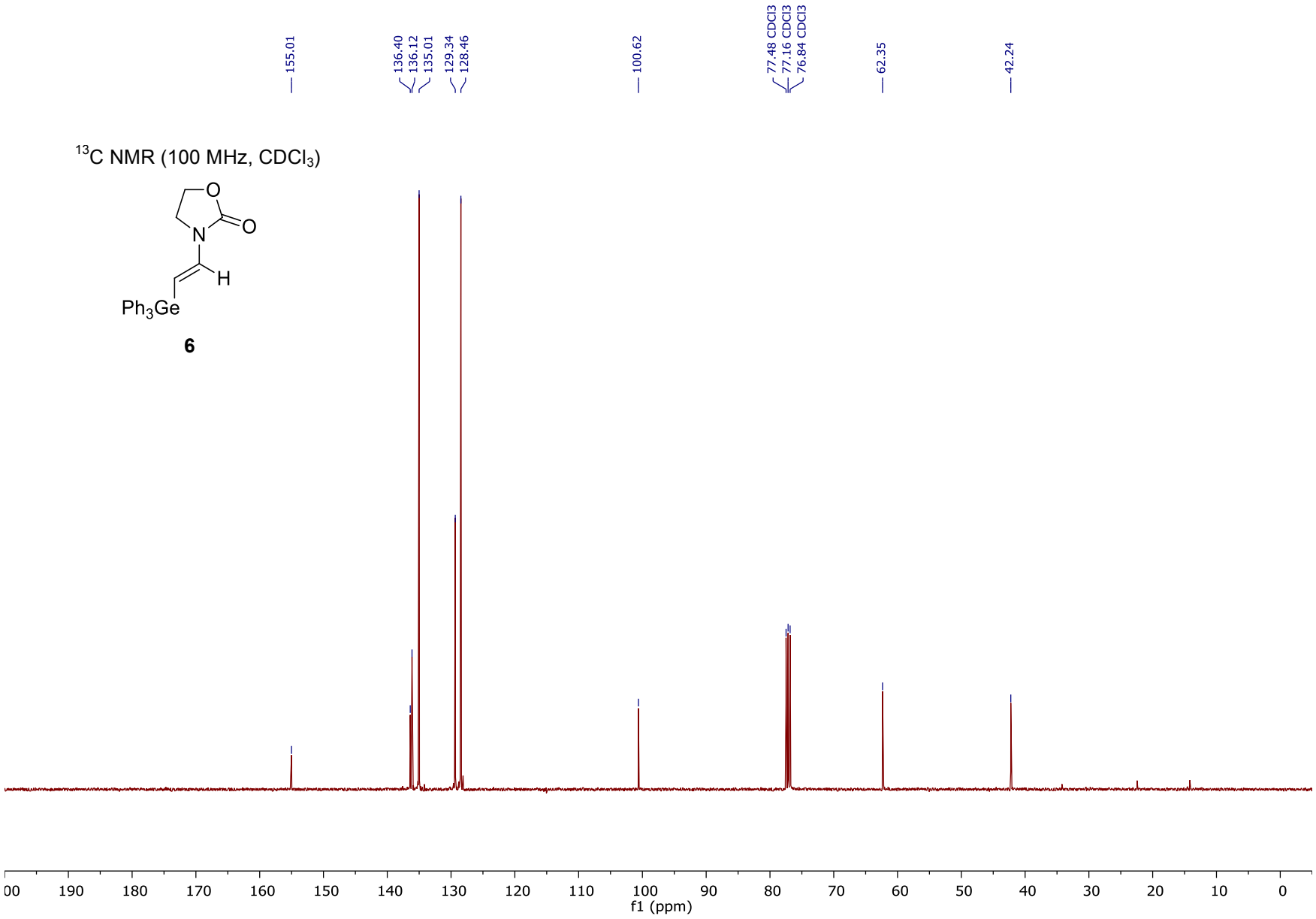
[^{2}H]-**5**

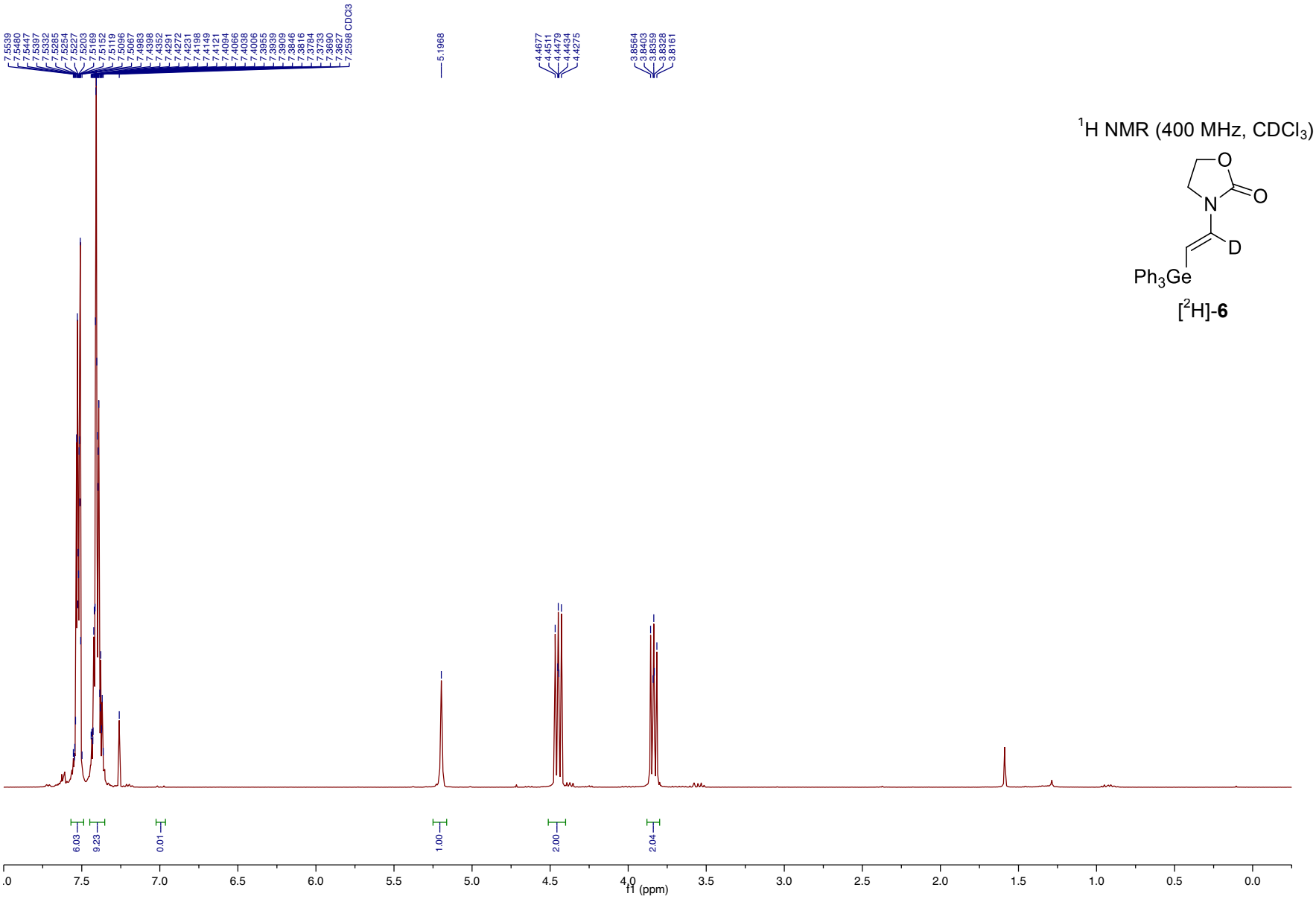

154.76
136.12
135.34
135.04
129.40
129.38
129.14
128.52
127.51
100.89
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
66.73
54.59
36.48
^{13}C NMR (100 MHz, $CDCl_3$)
Bn
O
N
O
D
Ph_3Ge
[^{2}H]-**5**
f1 (ppm)



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

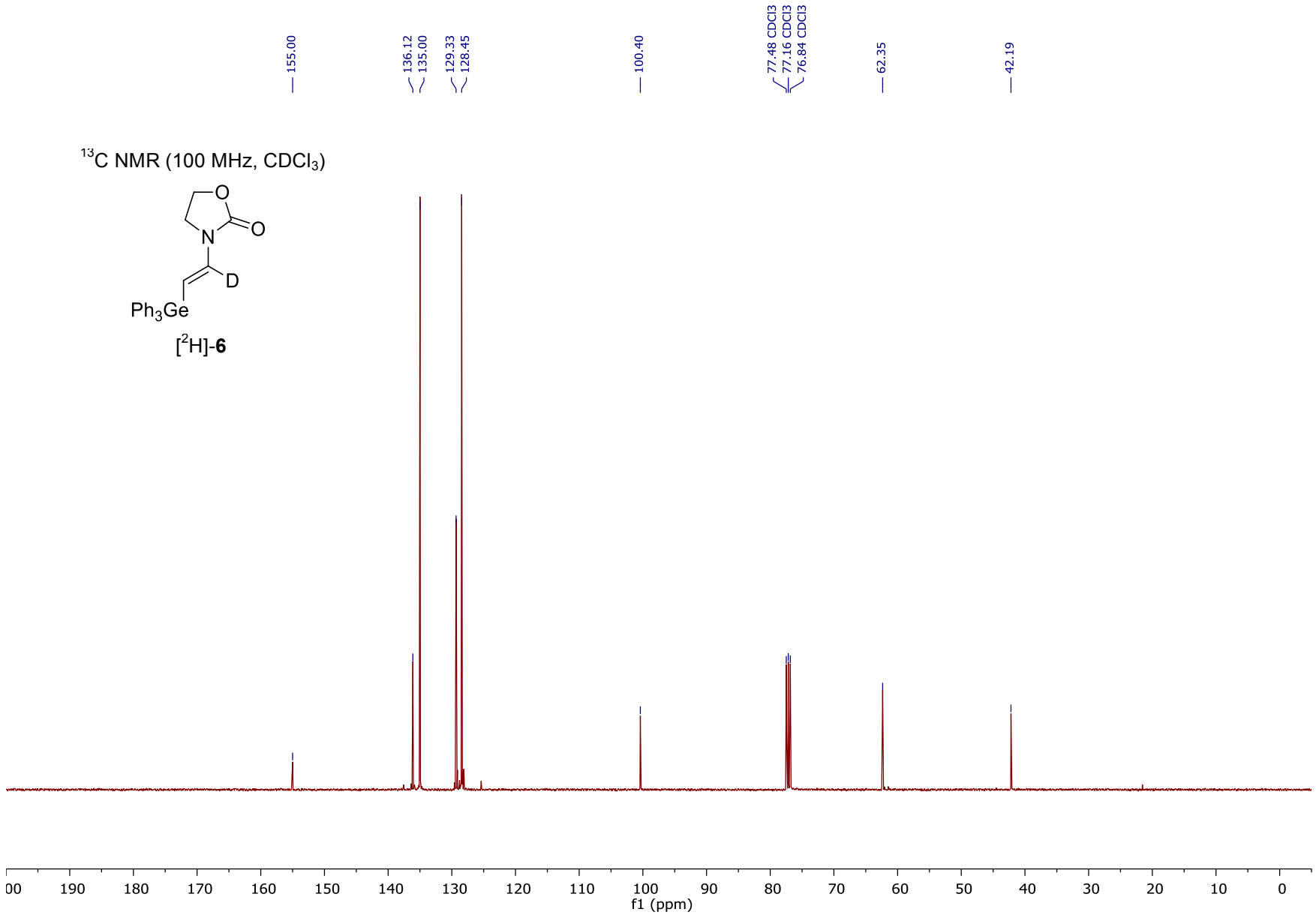
6

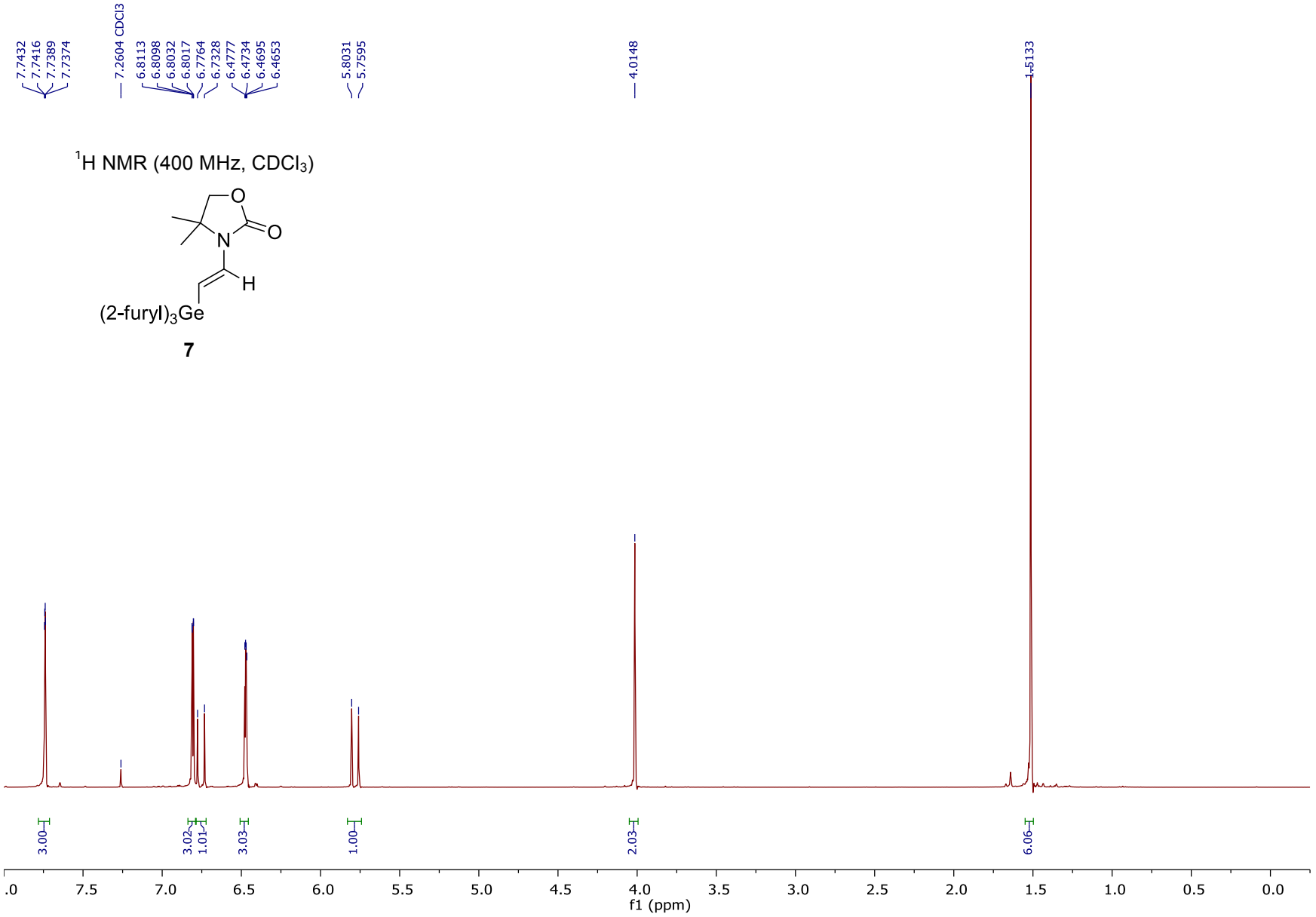

155.01
136.40
136.12
135.01
129.34
128.46
100.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.35
42.24
13C NMR (100 MHz, CDCl3)
O
O
N
H
Ph3Ge
6
f1 (ppm)

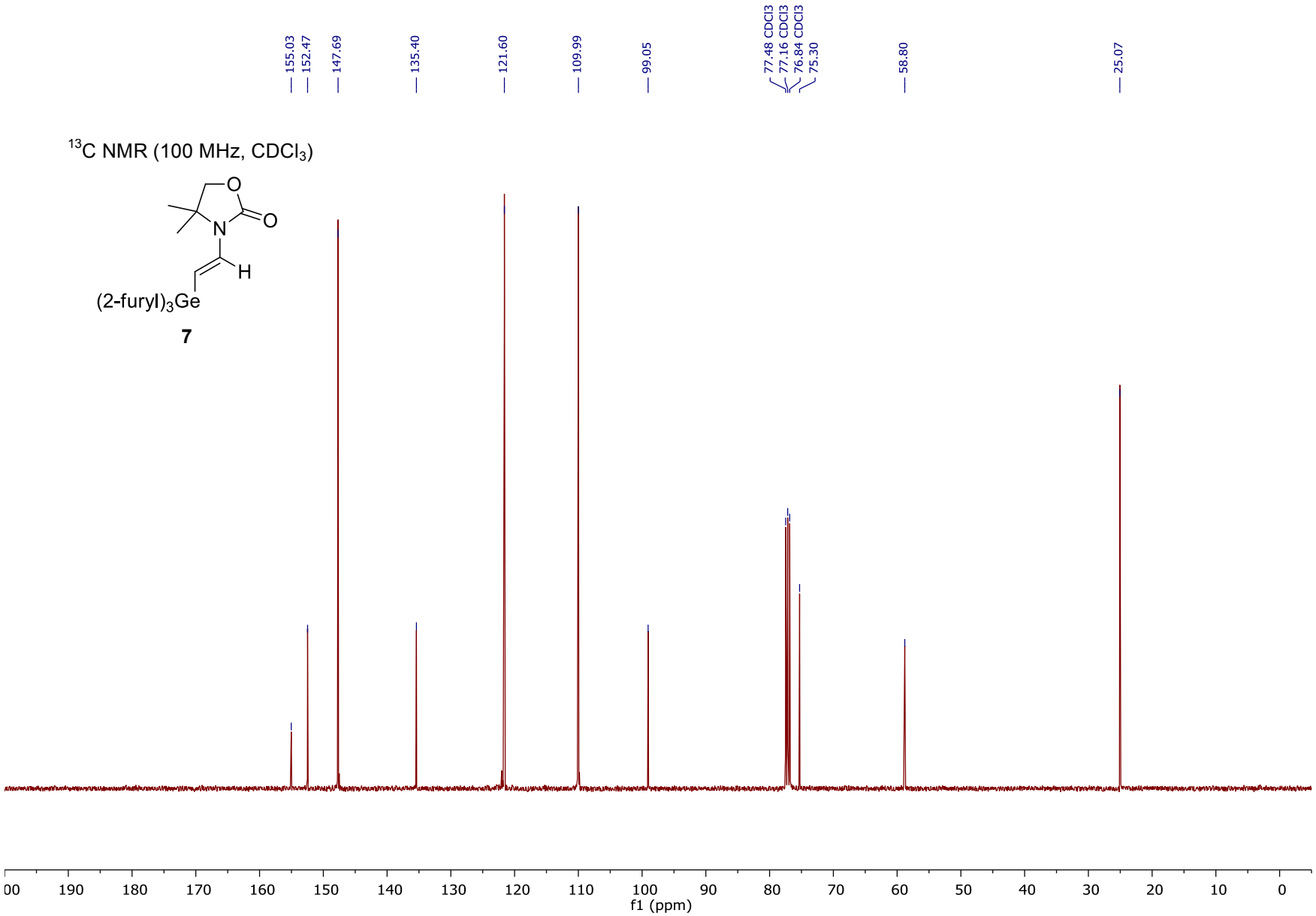


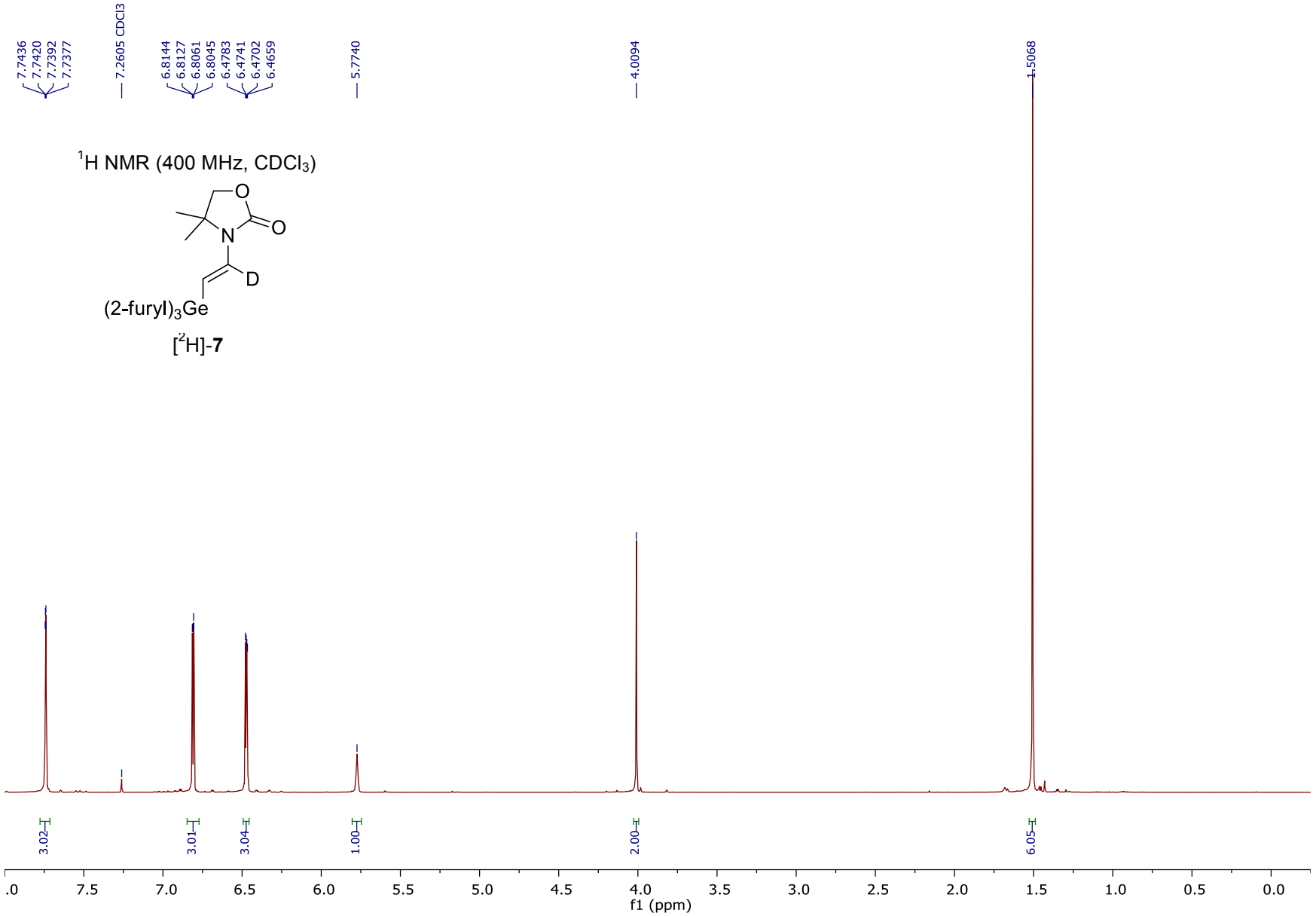
^{1}H NMR (400 MHz, $CDCl_3$)

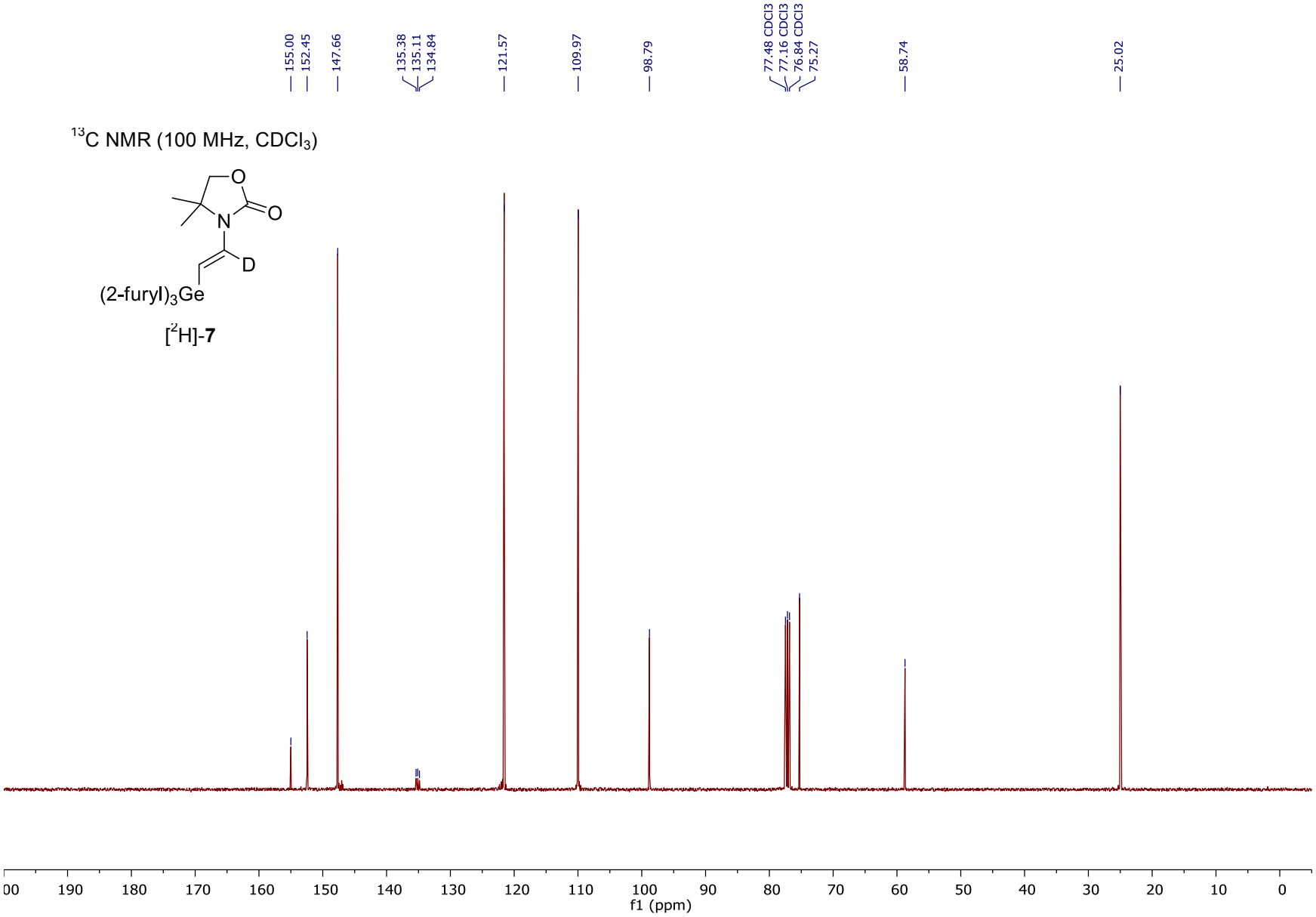
[^{2}H]-**6**

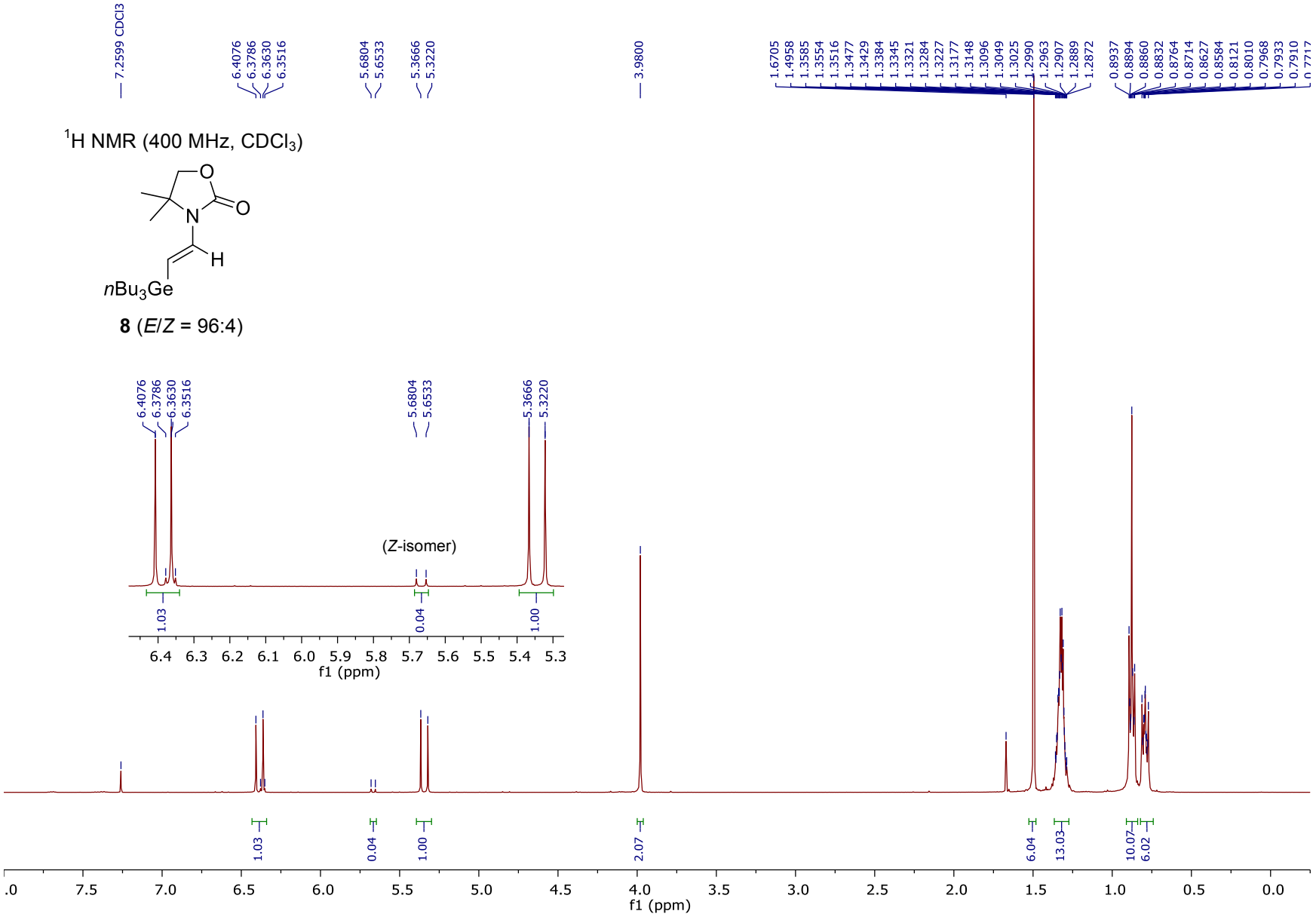

155.00
136.12
135.00
129.33
128.45
100.40
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.35
42.19
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
D
Ph_3Ge
[^{2}H]-**6**
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

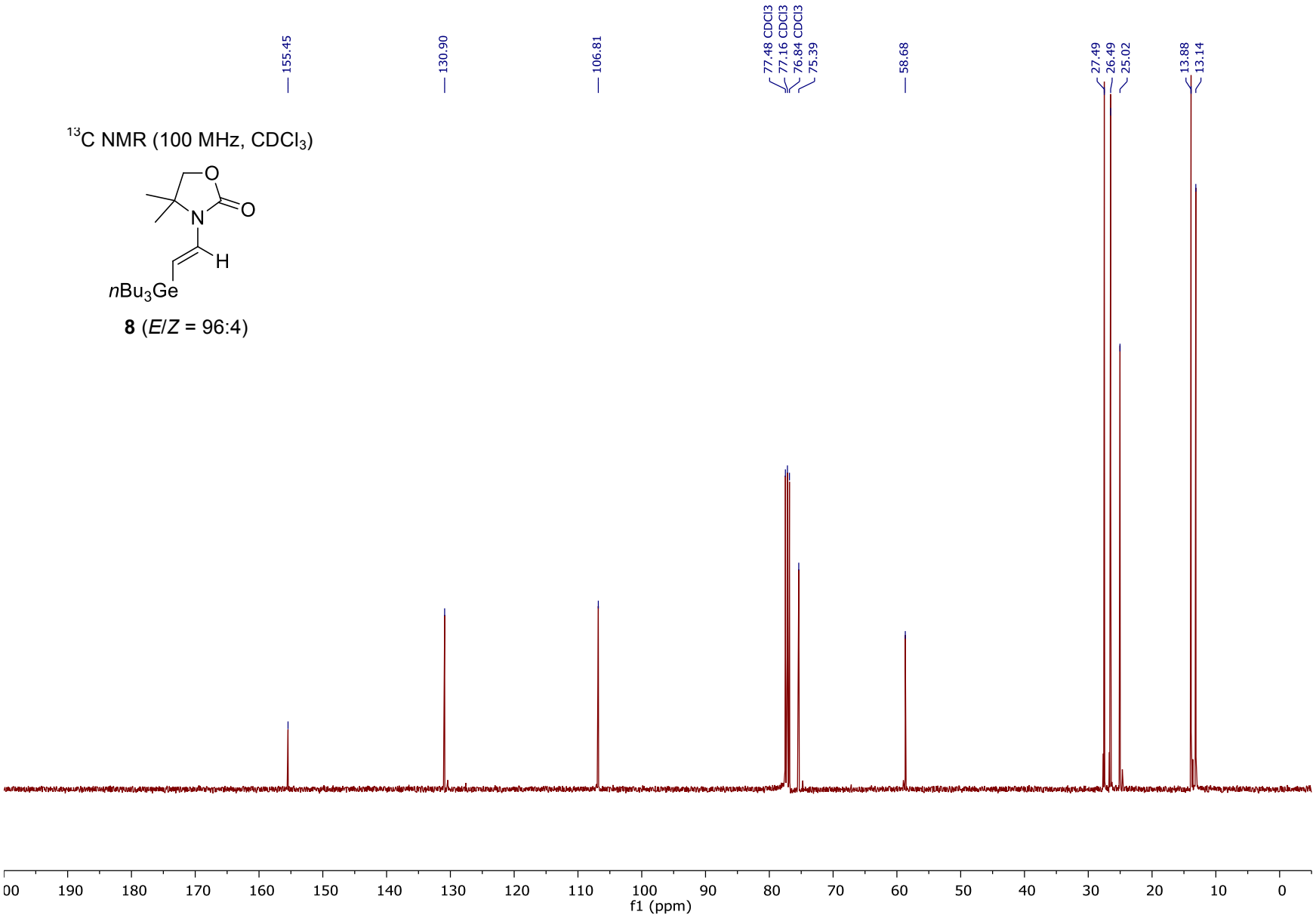

7.7432
7.7416
7.7389
7.7374
7.2604 CDCl3
6.8113
6.8098
6.8032
6.8017
6.7764
6.7328
6.4777
6.4734
6.4695
6.4653
5.8031
5.7595
4.0148
1.5133
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
H
(2-furyl)$_3$Ge
7
3.00
3.02
1.01
3.03
1.00
2.03
6.06
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.03
152.47
147.69
135.40
121.60
109.99
99.05
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.30
58.80
25.07
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
H
(2-furyl)$_3$Ge
7
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.7436
7.7420
7.7392
7.7377
7.2605 CDCl3
6.8144
6.8127
6.8061
6.8045
6.4783
6.4741
6.4702
6.4659
5.7740
4.0094
1.5068
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
D
(2-furyl)$_3$Ge
[^{2}H]-**7**
3.02
3.01
3.04
1.00
2.00
6.05
.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
f1 (ppm)


155.00
152.45
147.66
135.38
135.11
134.84
121.57
109.97
98.79
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.27
58.74
25.02
13C NMR (100 MHz, CDCl3)
O
O
N
D
(2-furyl)3Ge
[2H]-7
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

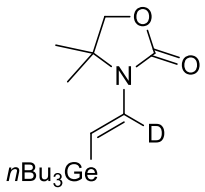

7.2599 CDCl3
6.4076
6.3786
6.3630
6.3516
5.6804
5.6533
5.3666
5.3220
3.9800
1.6705
1.4958
1.3585
1.3554
1.3516
1.3477
1.3429
1.3384
1.3345
1.3321
1.3284
1.3227
1.3177
1.3148
1.3096
1.3049
1.3025
1.2990
1.2963
1.2907
1.2889
1.2872
0.8937
0.8894
0.8860
0.8832
0.8764
0.8714
0.8627
0.8584
0.8121
0.8010
0.7968
0.7933
0.7910
0.7717
1H NMR (400 MHz, CDCl3)
O
O
N
H
nBu3Ge
8 (E/Z = 96:4)
(Z-isomer)
1.03
0.04
1.00
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3
f1 (ppm)
1.03
0.04
1.00
2.07
6.04
13.03
10.07
6.02
.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
f1 (ppm)



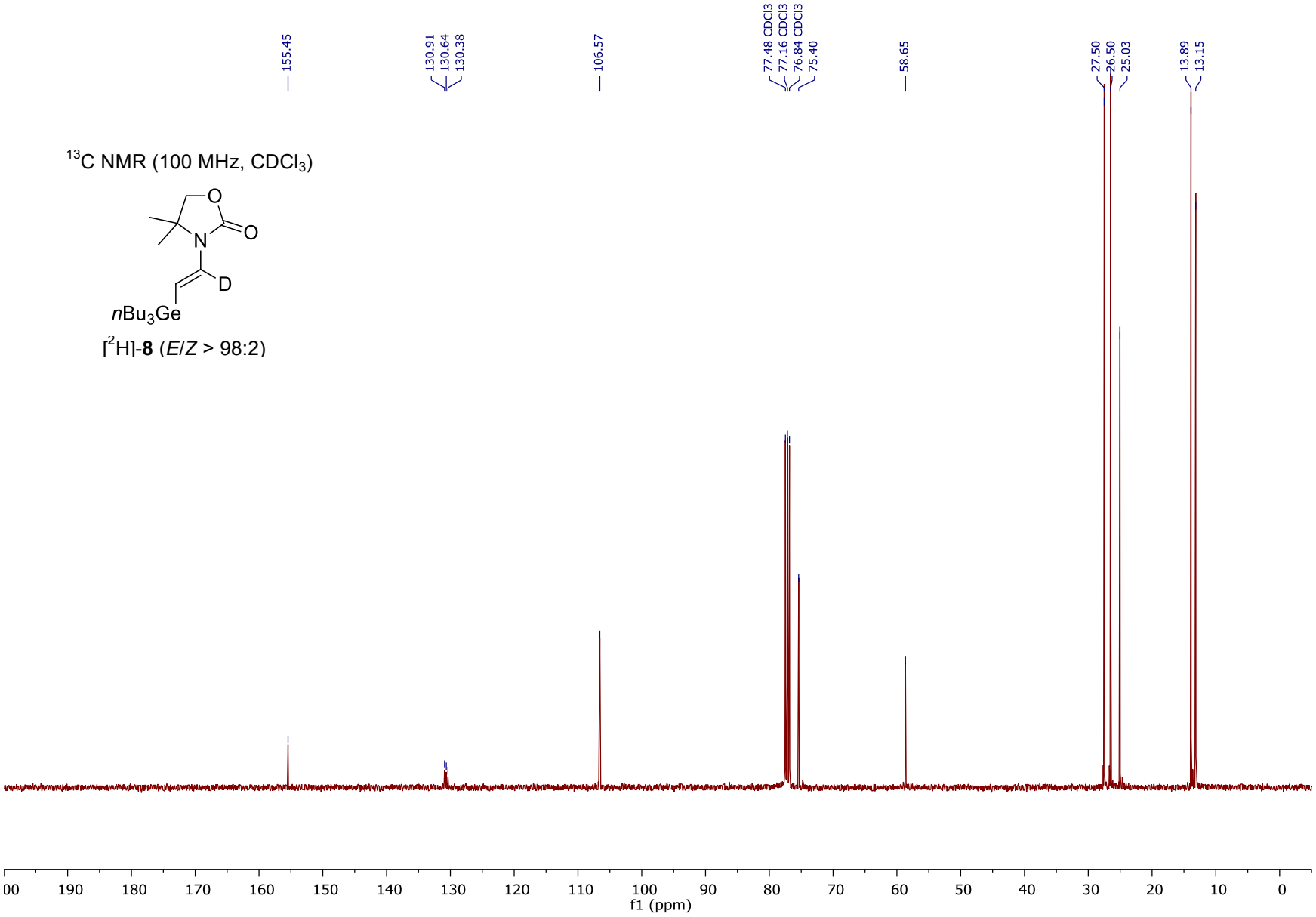
^{13}C NMR (100 MHz, $CDCl_3$)

8 (*E*/*Z* = 96:4)

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

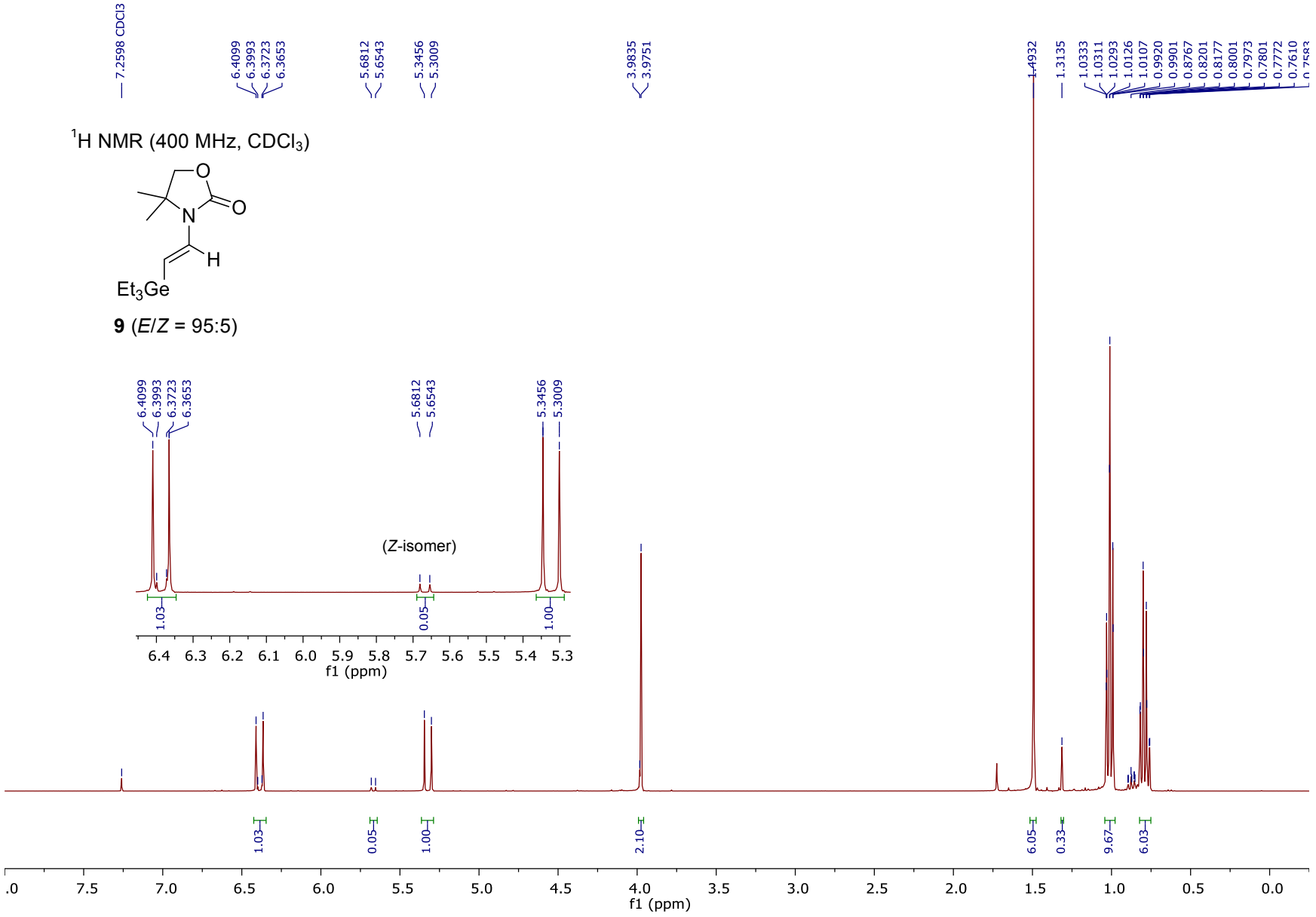


[^{2}H]-**8** (*E*/*Z* > 98:2)

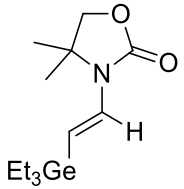


^{13}C NMR (100 MHz, $CDCl_3$)

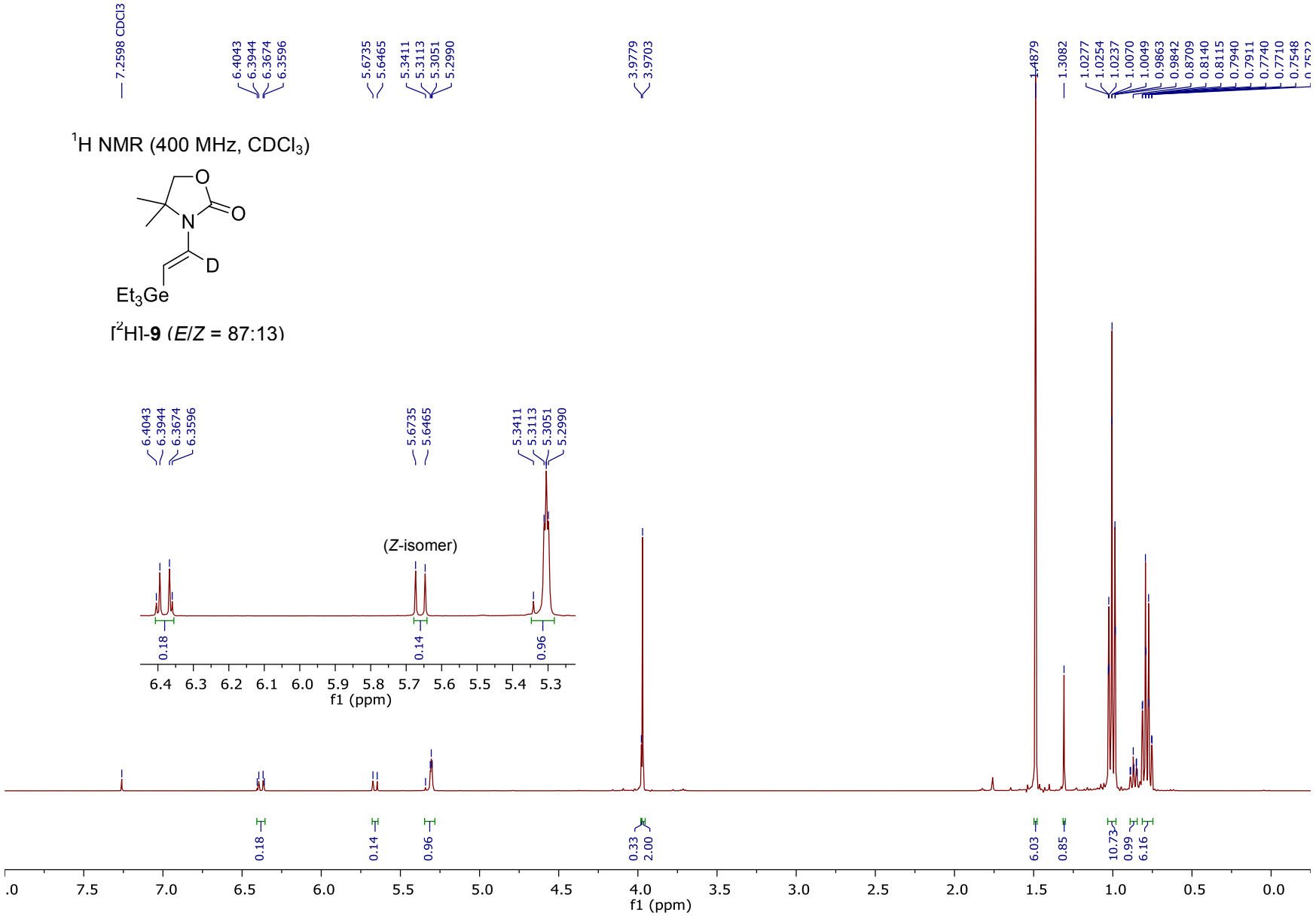
[^{2}H]-**8** (*E*/*Z* > 98:2)


7.2598 CDCl3
6.4099
6.3993
6.3723
6.3653
5.6812
5.6543
5.3456
5.3009
3.9835
3.9751
1.4932
1.3135
1.0333
1.0311
1.0293
1.0126
1.0107
0.9920
0.9901
0.8767
0.8201
0.8177
0.8001
0.7973
0.7801
0.7772
0.7610
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
H
Et_3Ge
9 (*E*/*Z* = 95:5)
(*Z*-isomer)
1.03
0.05
1.00
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3
f1 (ppm)
1.03
0.05
1.00
2.10
6.05
0.33
9.67
6.03
.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
f1 (ppm)

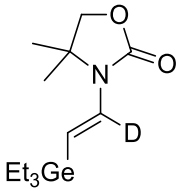
^{13}C NMR (100 MHz, $CDCl_3$)



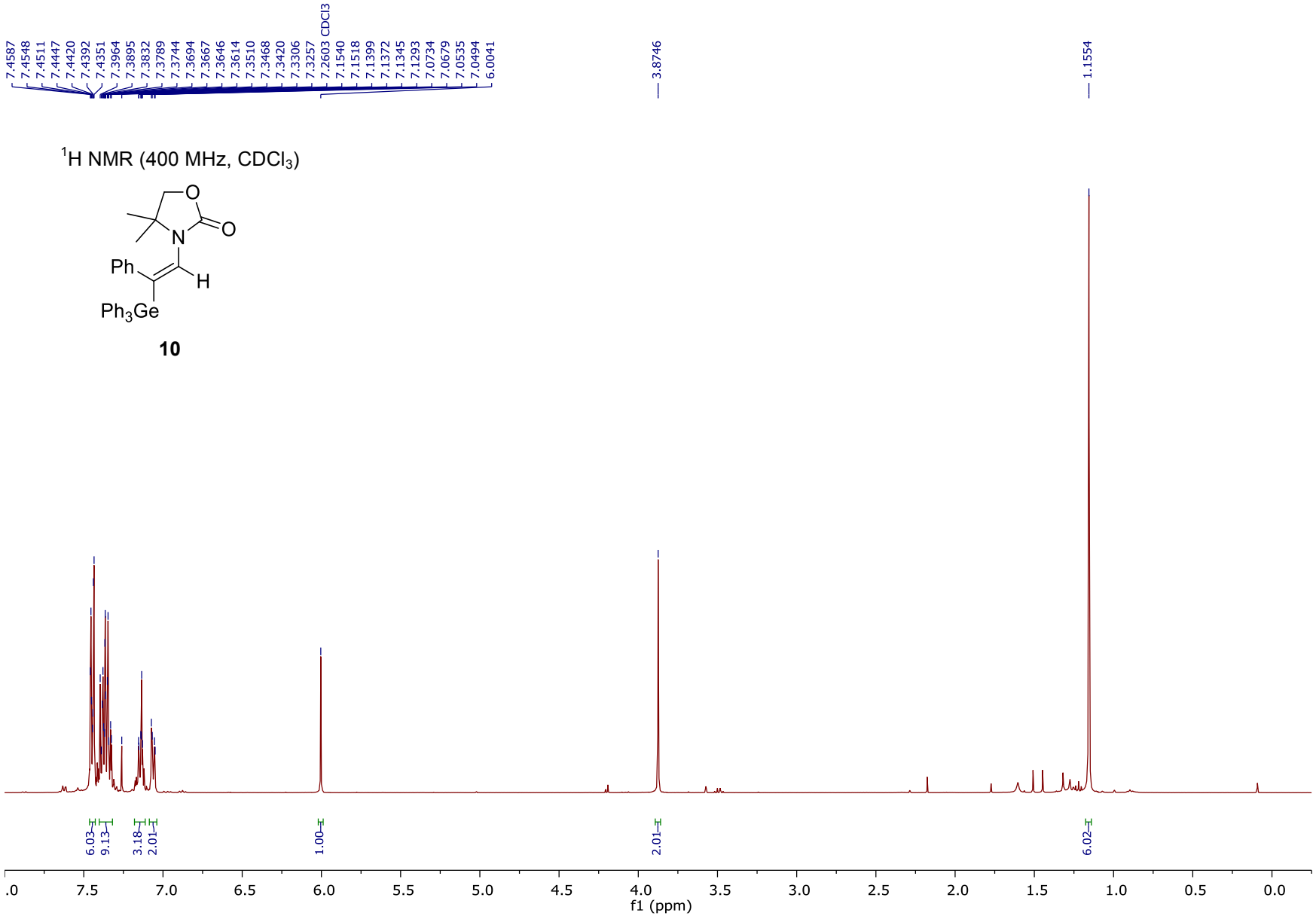
9 (*E*/*Z* = 95:5)


7.2598 CDCl3
6.4043
6.3944
6.3674
6.3596
5.6735
5.6465
5.3411
5.3113
5.3051
5.2990
3.9779
3.9703
1.4879
1.3082
1.0277
1.0254
1.0237
1.0070
1.0049
0.9863
0.9842
0.8709
0.8140
0.8115
0.7940
0.7911
0.7740
0.7710
0.7548
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
D
Et_3Ge
[^{2}H1-**9** (*E*/*Z* = 87:13)
(*Z*-isomer)
0.18
0.14
0.96
f1 (ppm)
0.33
2.00
6.03
0.85
10.73
0.99
6.16
f1 (ppm)

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

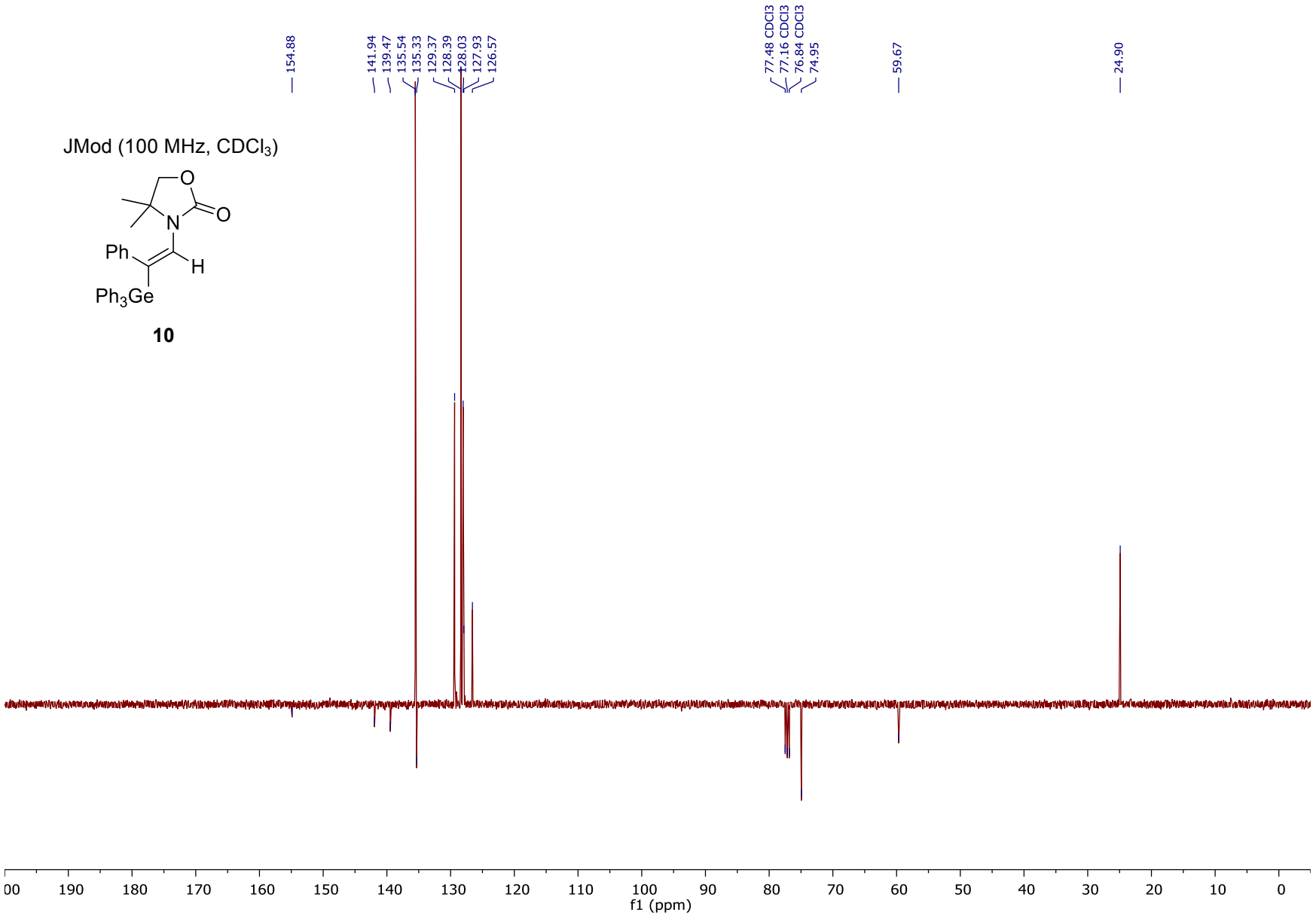


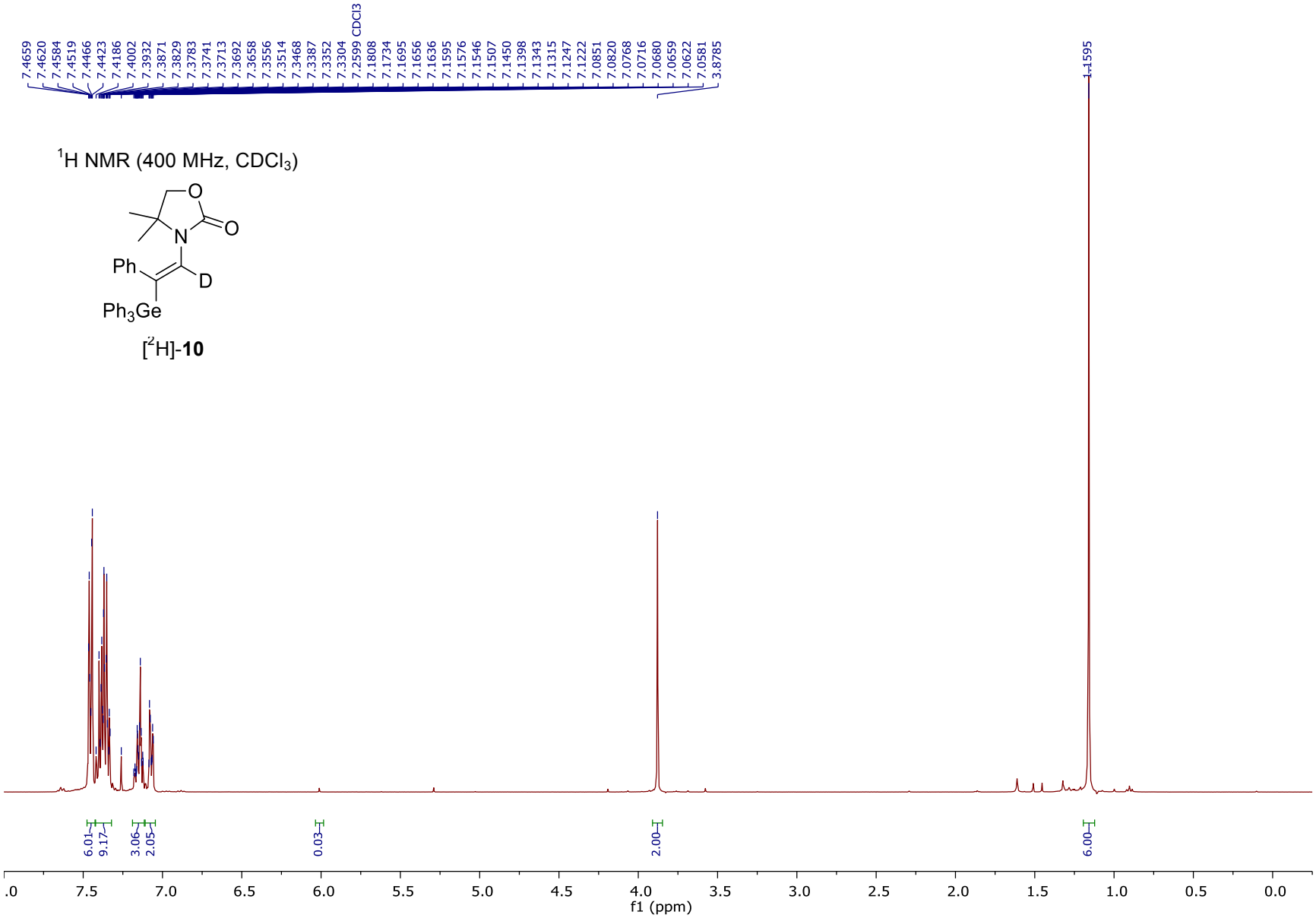
[^{2}H]-**9** (*E*/*Z* = 87:13)



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

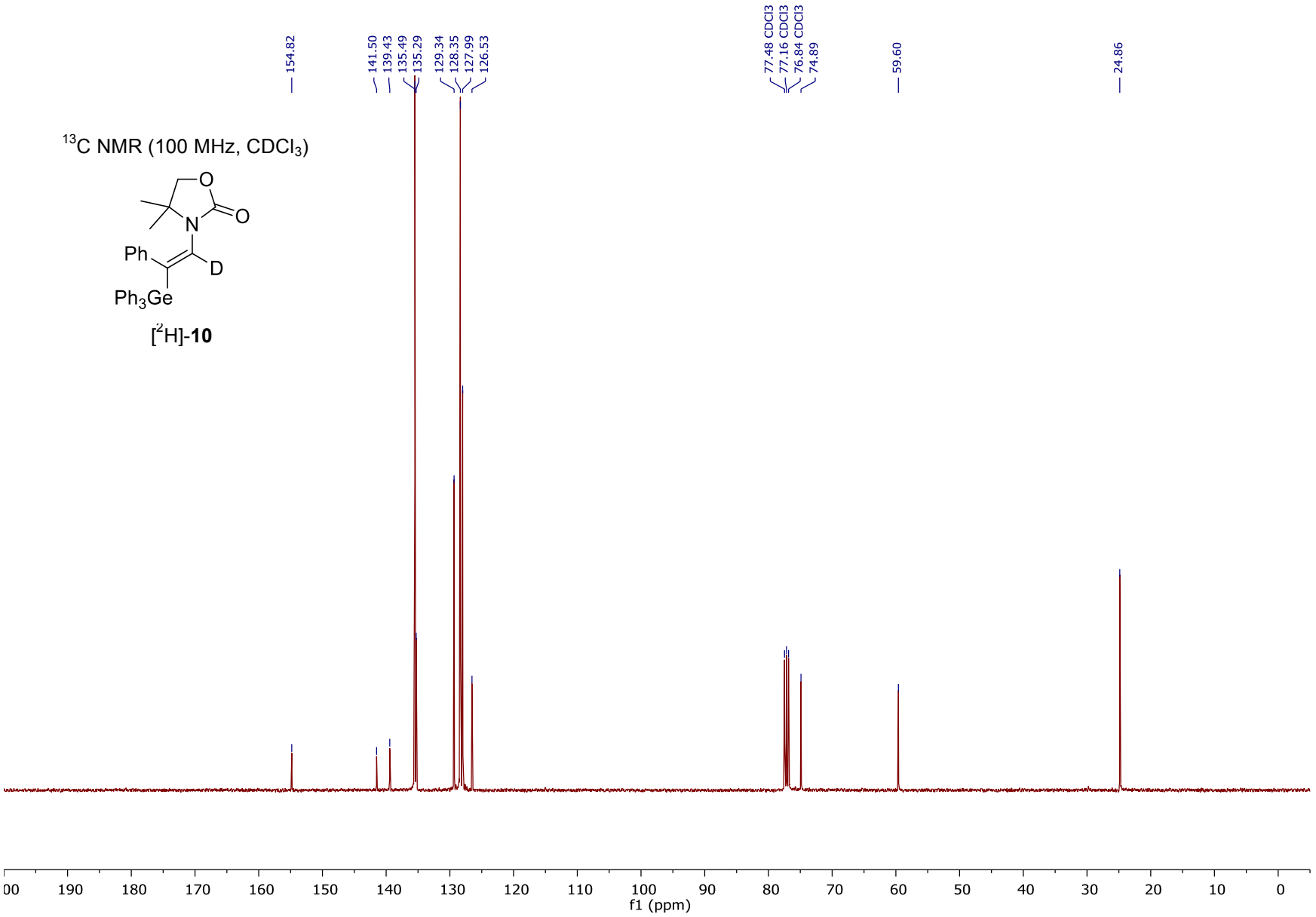
10

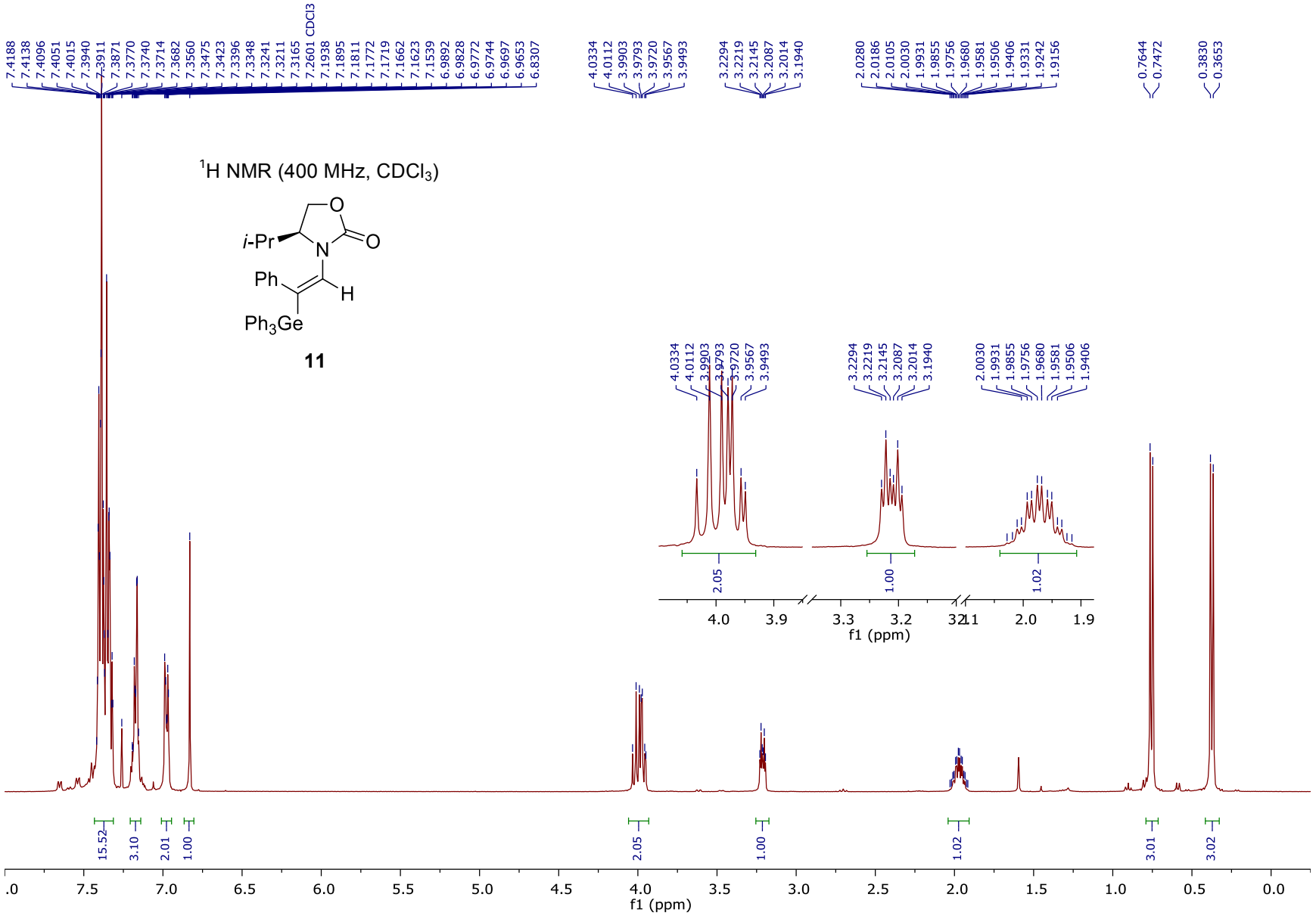

154.88
141.94
139.47
135.54
135.33
129.37
128.39
128.03
127.93
126.57
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.95
59.67
24.90
JMod (100 MHz, CDCl3)
O
N
O
Ph
H
Ph3Ge
10
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

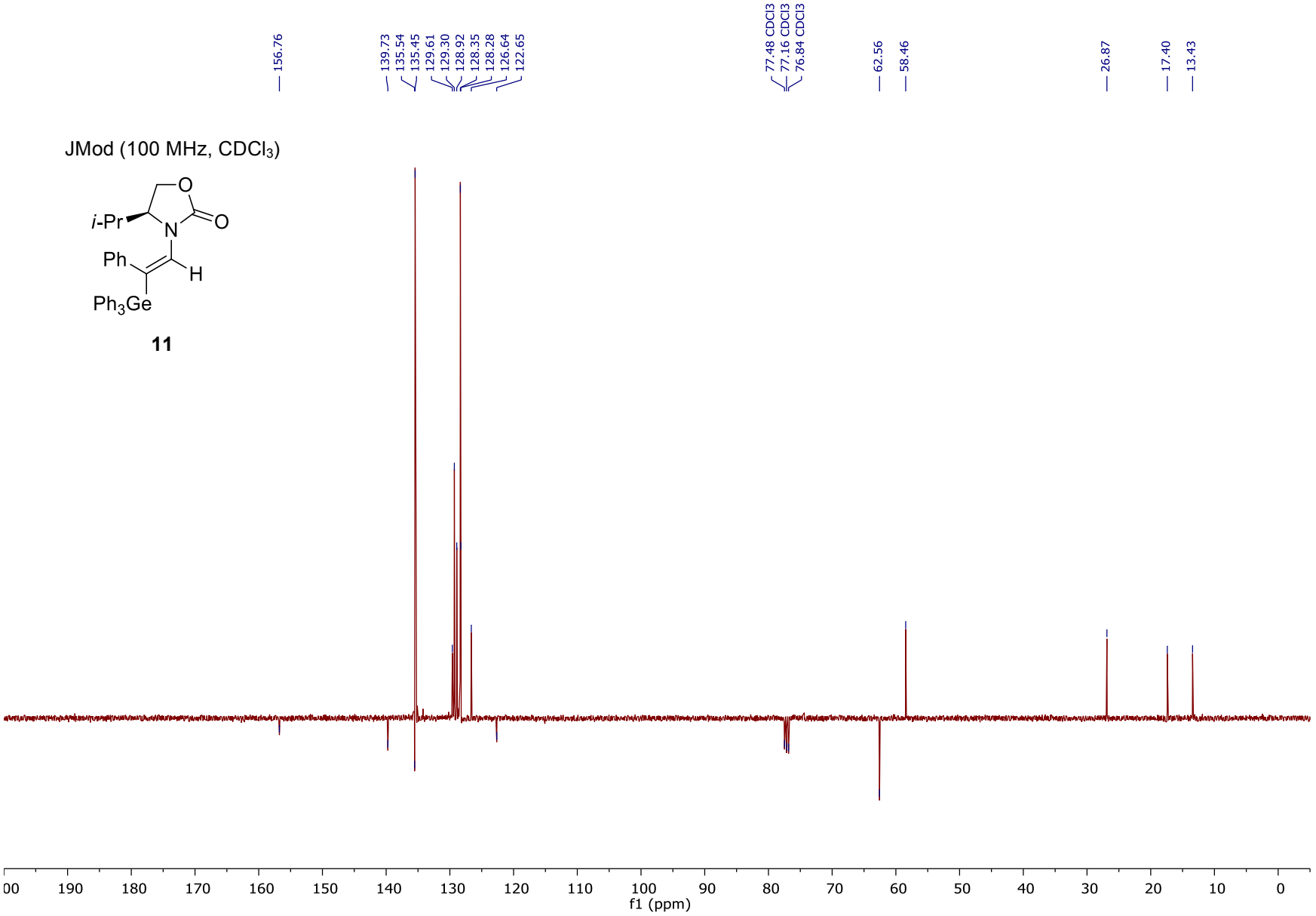


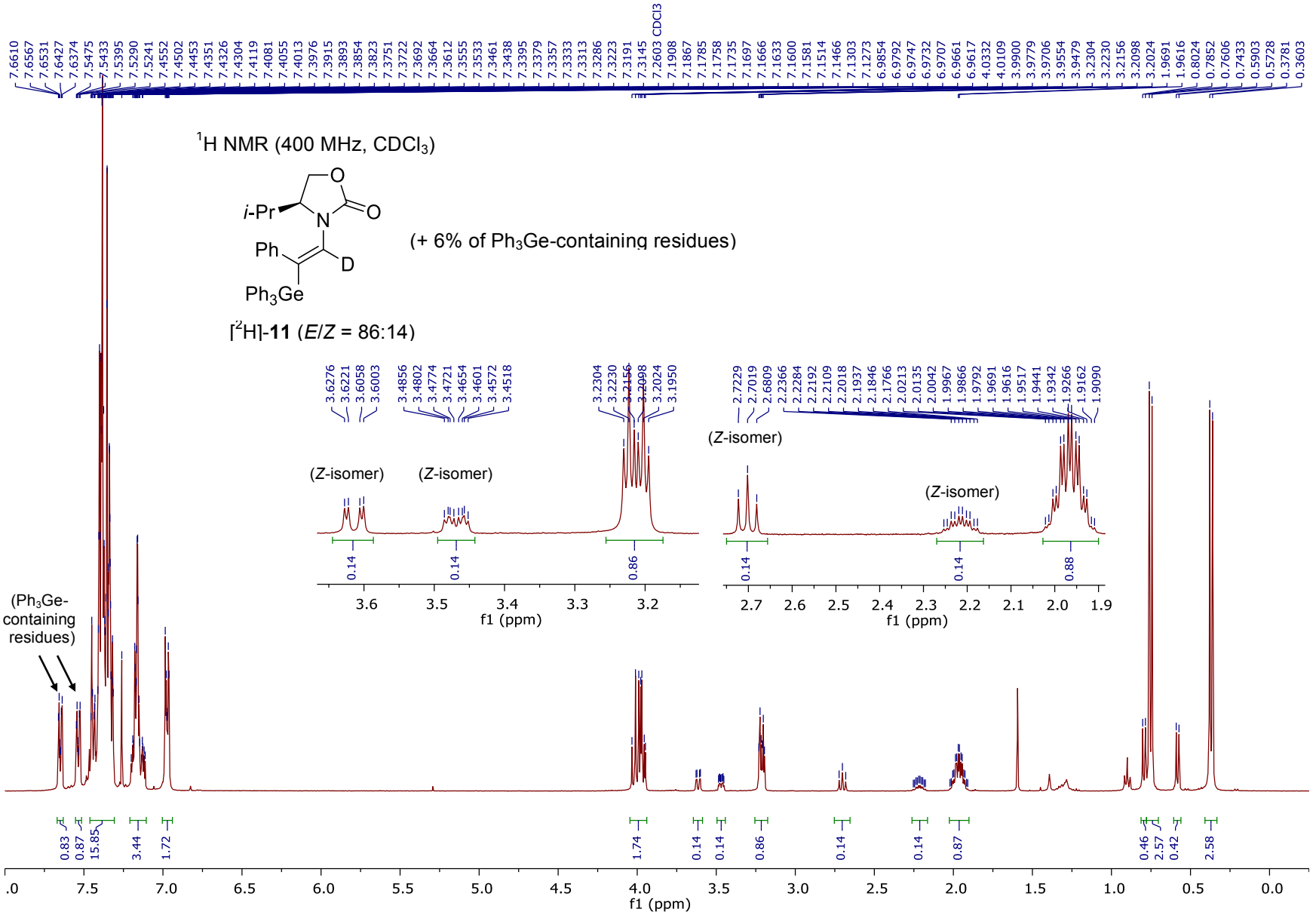
^{1}H NMR (400 MHz, $CDCl_3$)

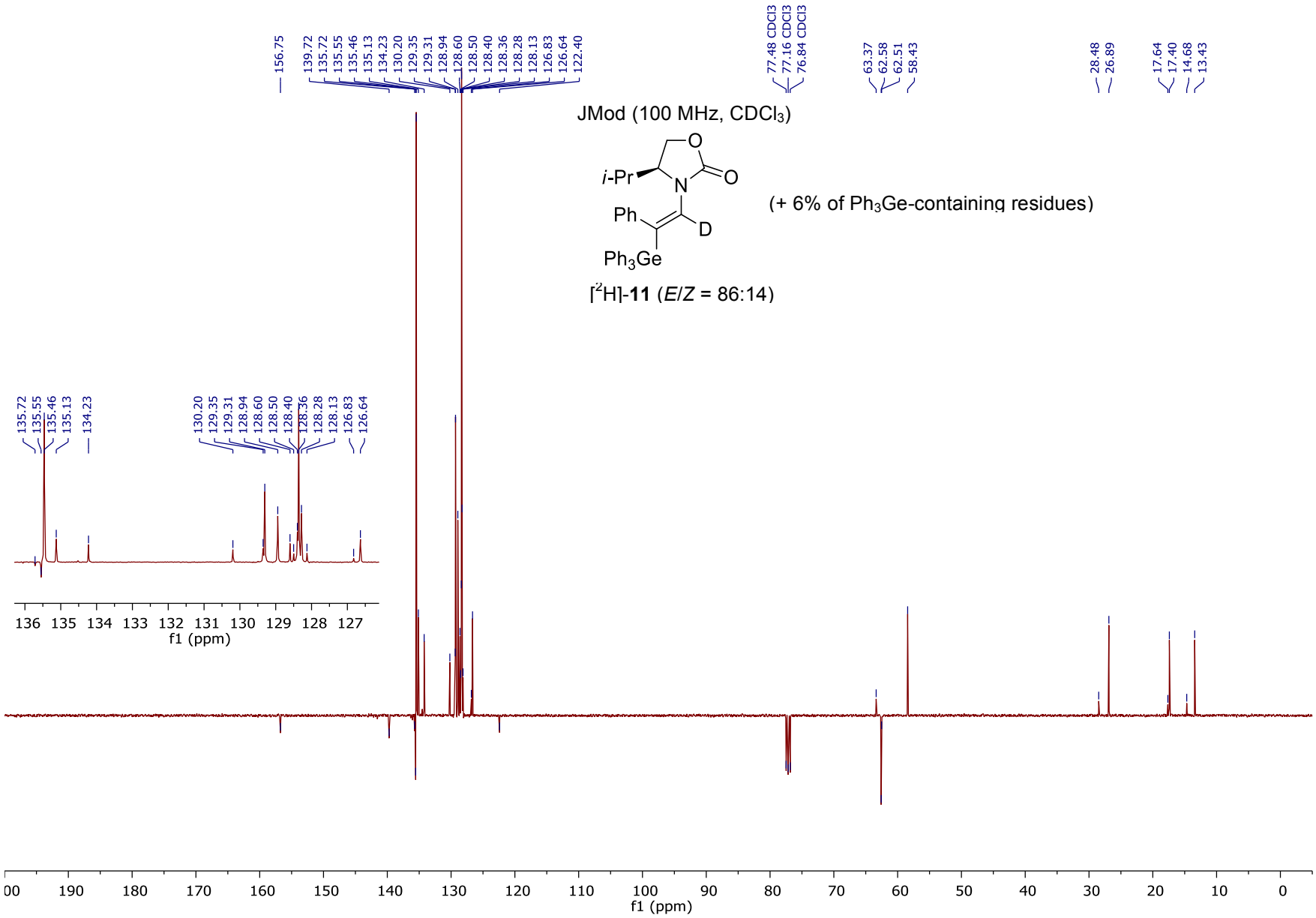
[^{2}H]-**10**

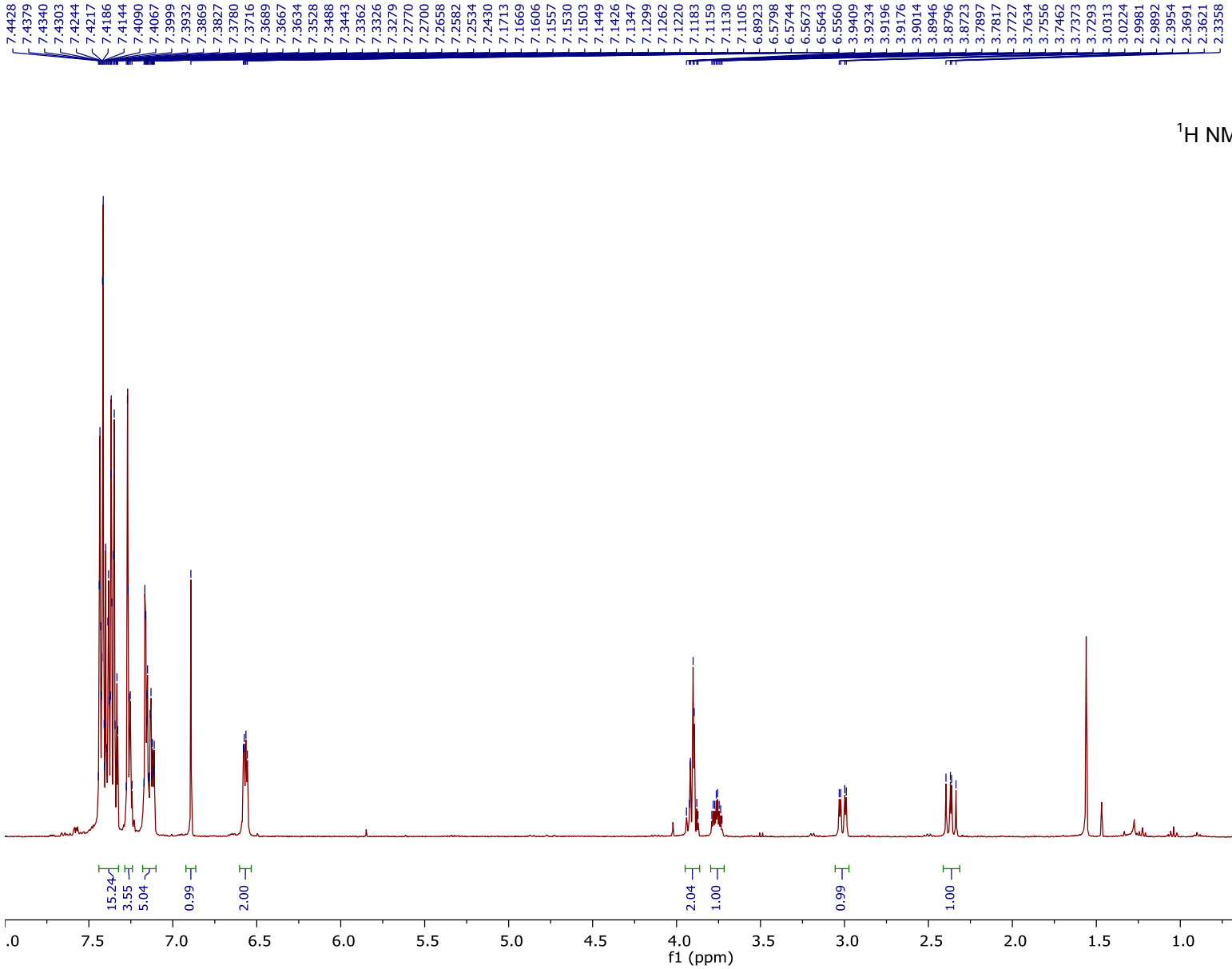

154.82
141.50
139.43
135.49
135.29
129.34
128.35
127.99
126.53
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.89
59.60
24.86
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph
D
Ph_3Ge
[^{2}H]-**10**
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


^{1}H NMR (400 MHz, $CDCl_3$)
11
f1 (ppm)

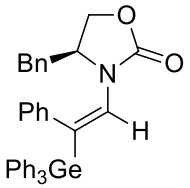

156.76
139.73
135.54
135.45
129.61
129.30
128.92
128.35
128.28
126.64
122.65
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.56
58.46
26.87
17.40
13.43
JMod (100 MHz, CDCl3)
i-Pr
N
O
O
Ph
H
Ph3Ge
11
f1 (ppm)


^{1}H NMR (400 MHz, $CDCl_3$)
i-Pr
Ph
D
Ph_3Ge
(+ 6% of Ph_3Ge-containing residues)
[^{2}H]-**11** (*E*/*Z* = 86:14)
(Ph_3Ge-containing residues)
(*Z*-isomer)
(*Z*-isomer)
(*Z*-isomer)
(*Z*-isomer)
f1 (ppm)
f1 (ppm)
f1 (ppm)

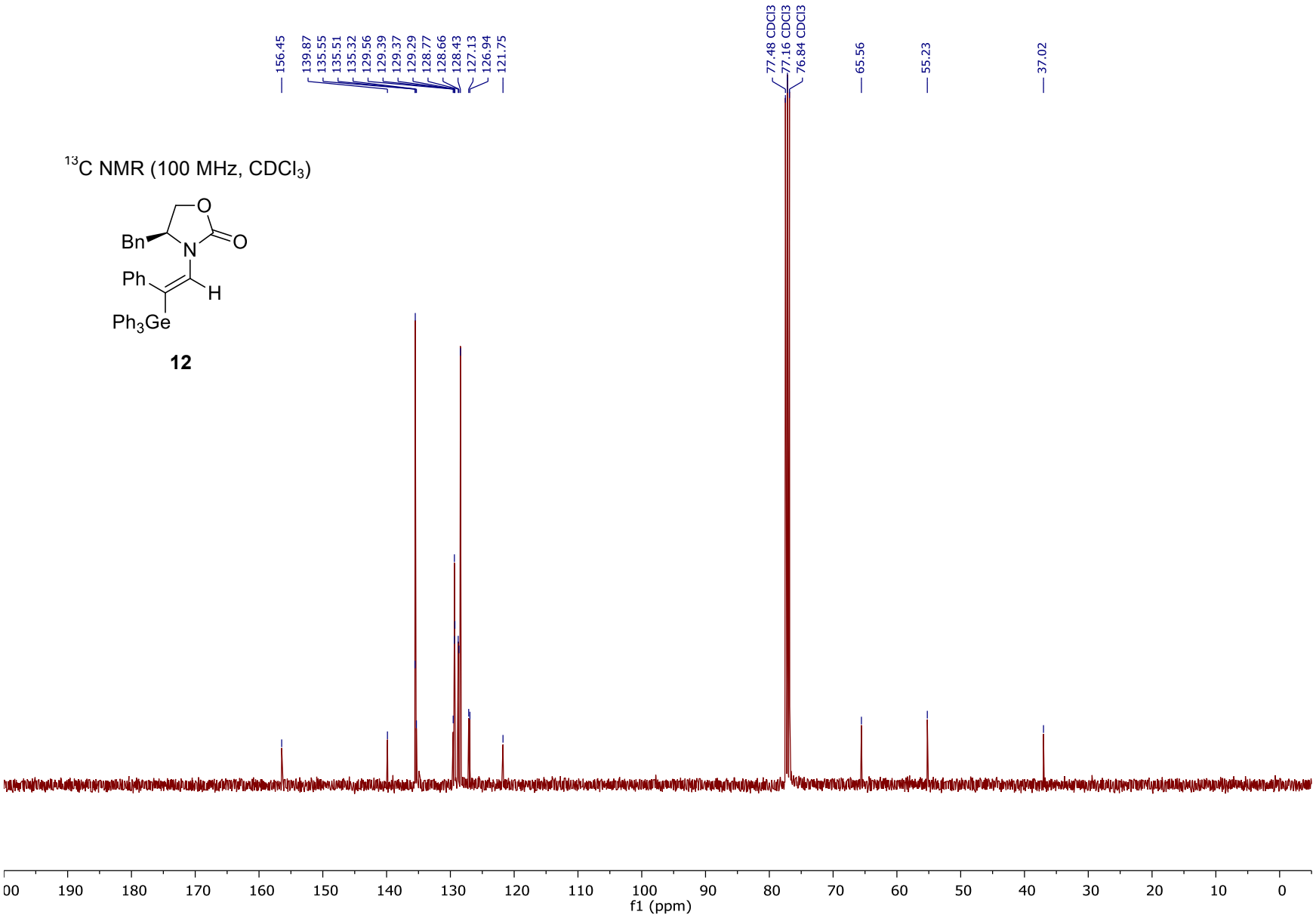

156.75
139.72
135.72
135.55
135.46
135.13
134.23
130.20
129.35
129.31
128.94
128.60
128.50
128.40
128.36
128.28
128.13
126.83
126.64
122.40
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
63.37
62.58
62.51
58.43
28.48
26.89
17.64
17.40
14.68
13.43
JMod (100 MHz, CDCl3)
i-Pr
O
O
N
Ph
D
Ph3Ge
(+ 6% of Ph3Ge-containing residues)
[2H]-11 (E/Z = 86:14)
f1 (ppm)

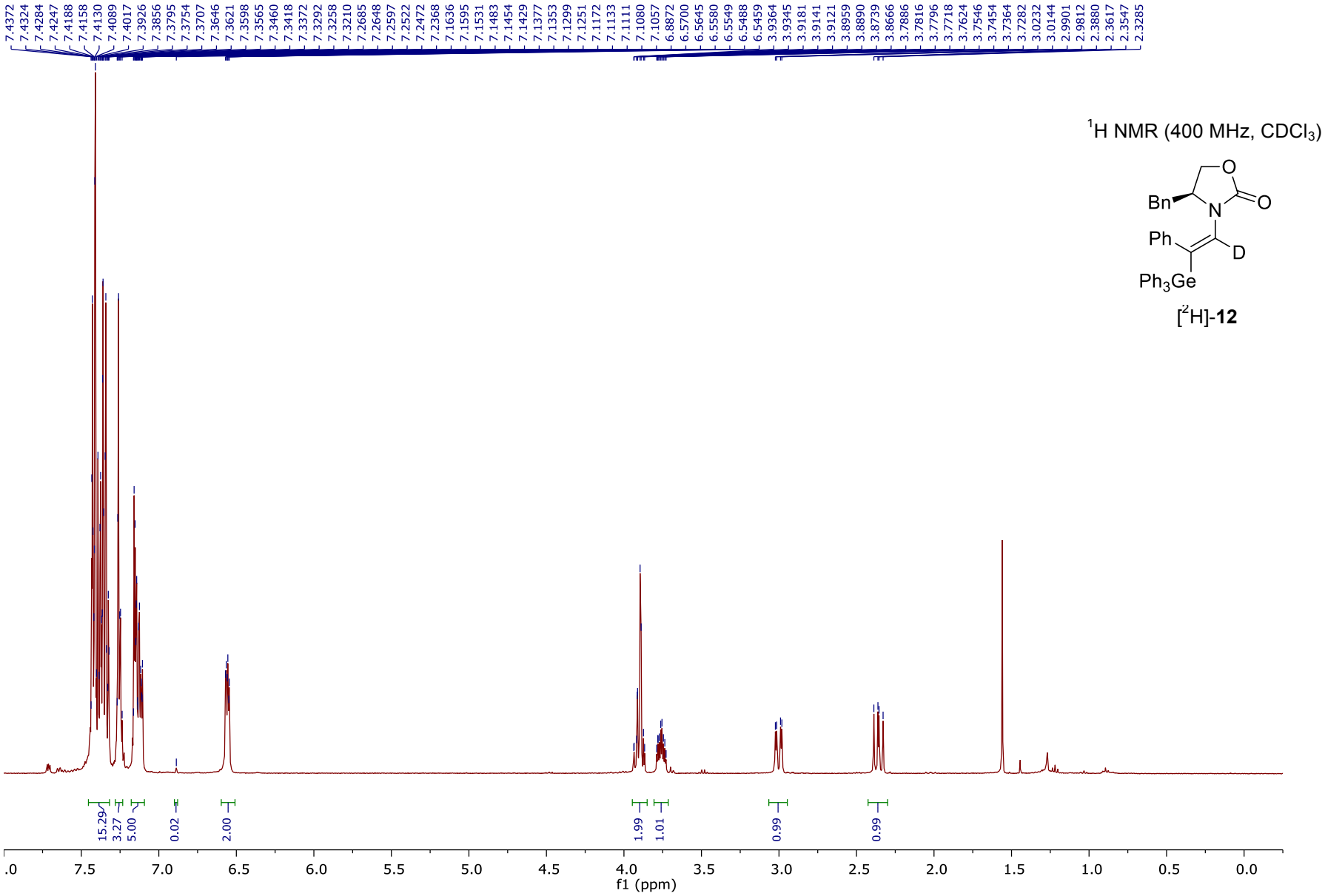


^{1}H NMR (400 MHz, $CDCl_3$)



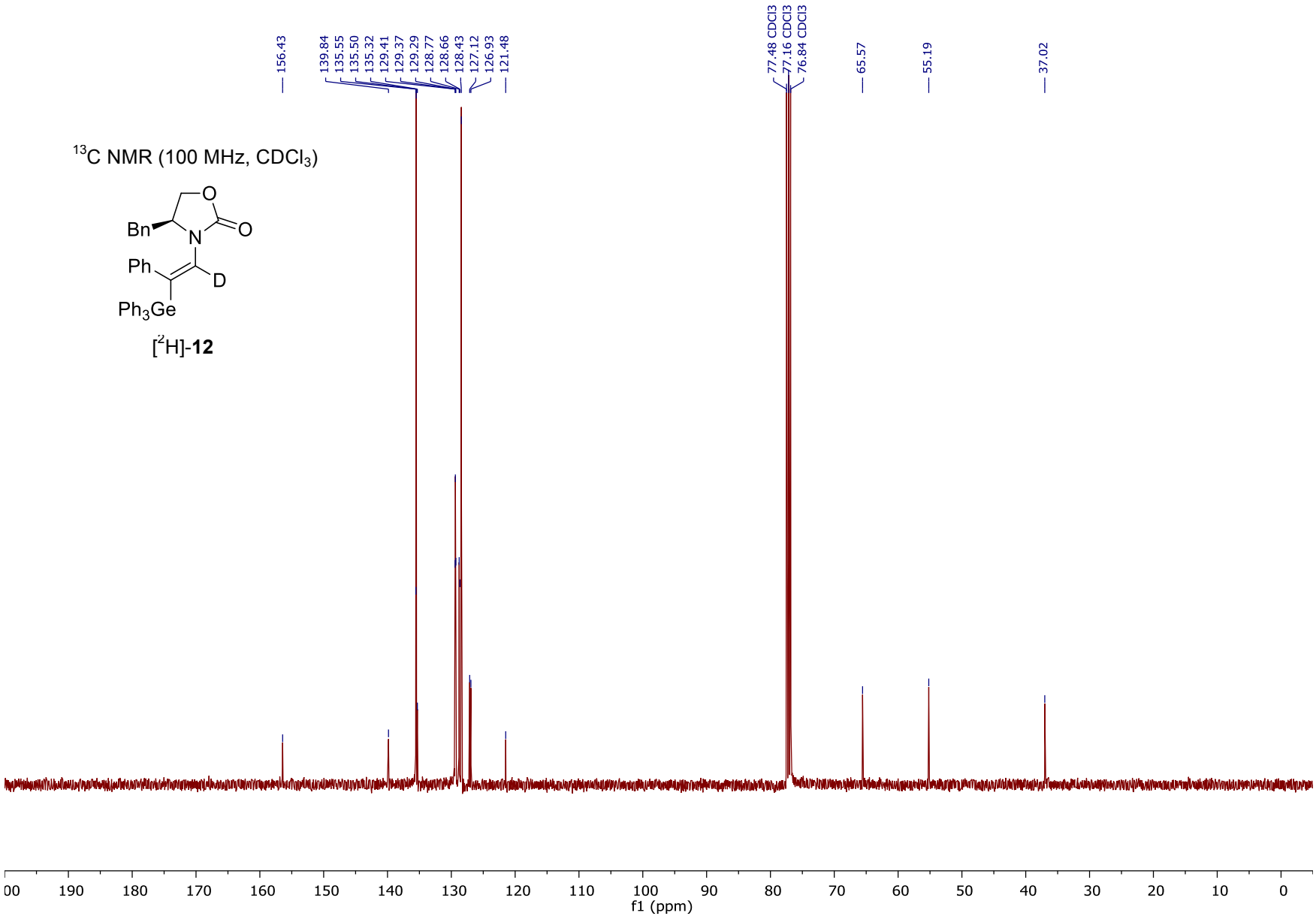
12

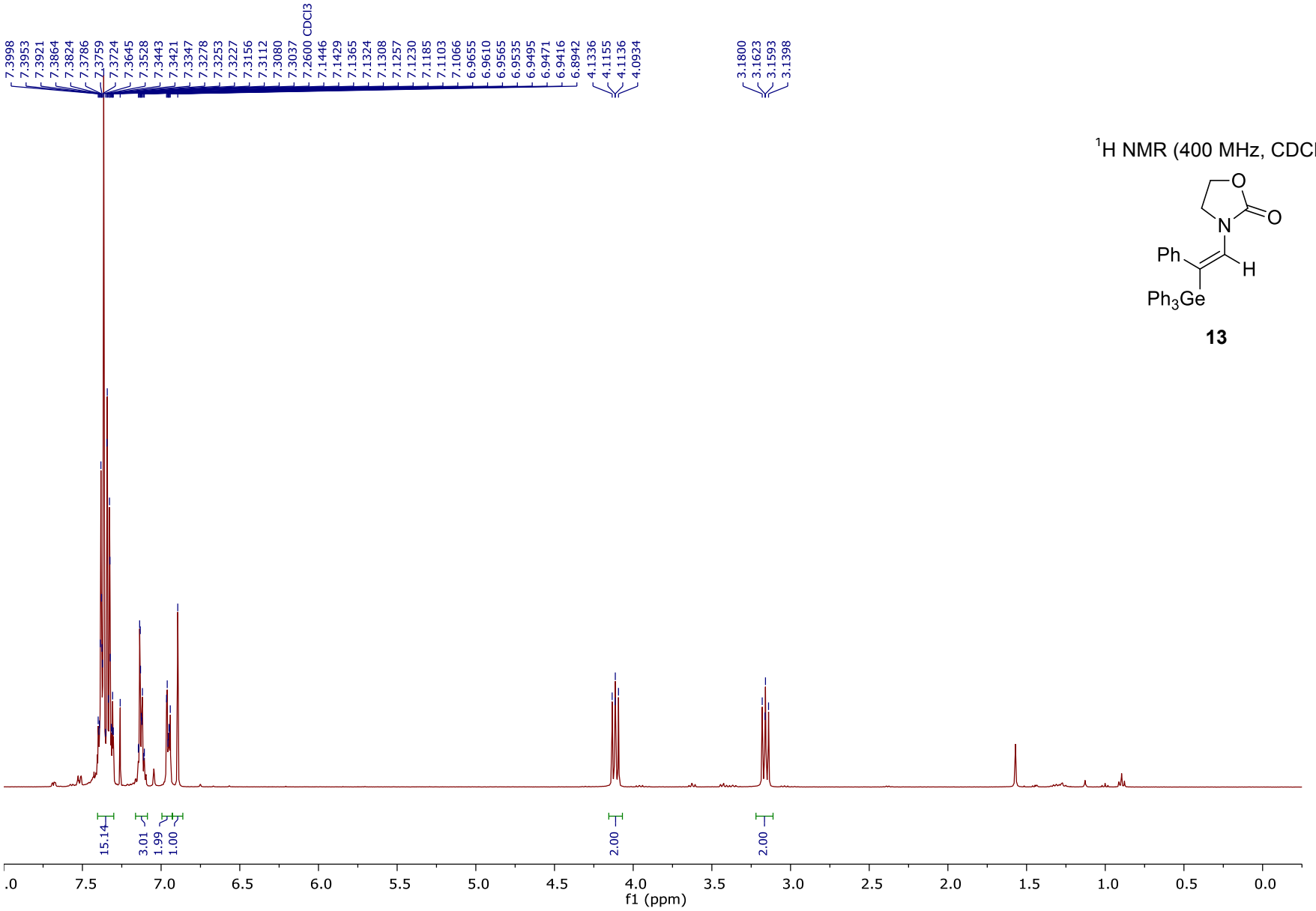

156.45
139.87
135.55
135.51
135.32
129.56
129.39
129.37
129.29
128.77
128.66
128.43
127.13
126.94
121.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.56
55.23
37.02
^{13}C NMR (100 MHz, $CDCl_3$)
Bn
N
O
O
Ph
H
Ph_3Ge
12
f1 (ppm)



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

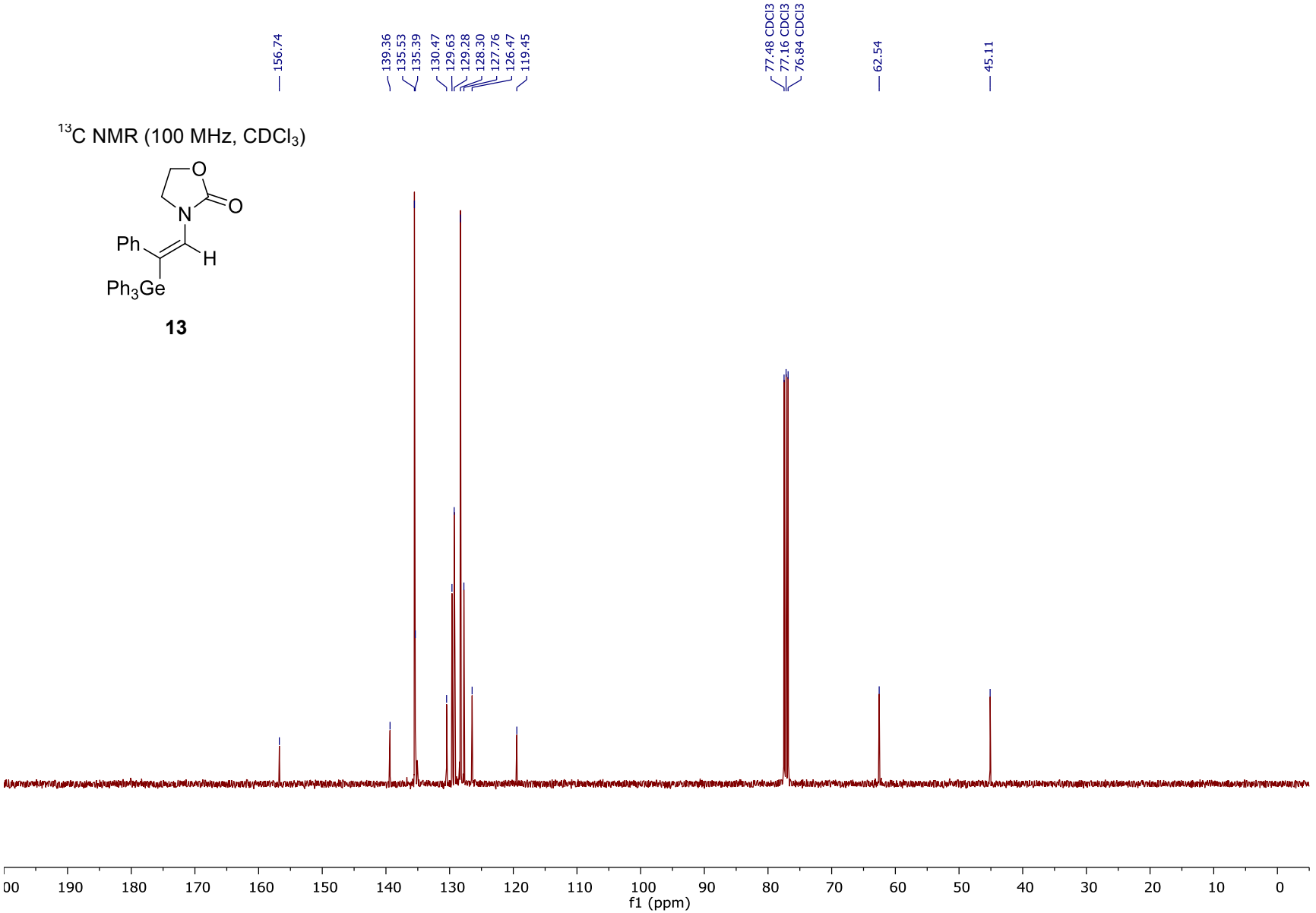
[^{2}H]-**12**


156.43
139.84
135.55
135.50
135.32
129.41
129.37
129.29
128.77
128.66
128.43
127.12
126.93
121.48
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.57
55.19
37.02
^{13}C NMR (100 MHz, $CDCl_3$)
Bn
N
O
O
Ph
D
Ph_3Ge
[^{2}H]-**12**
f1 (ppm)



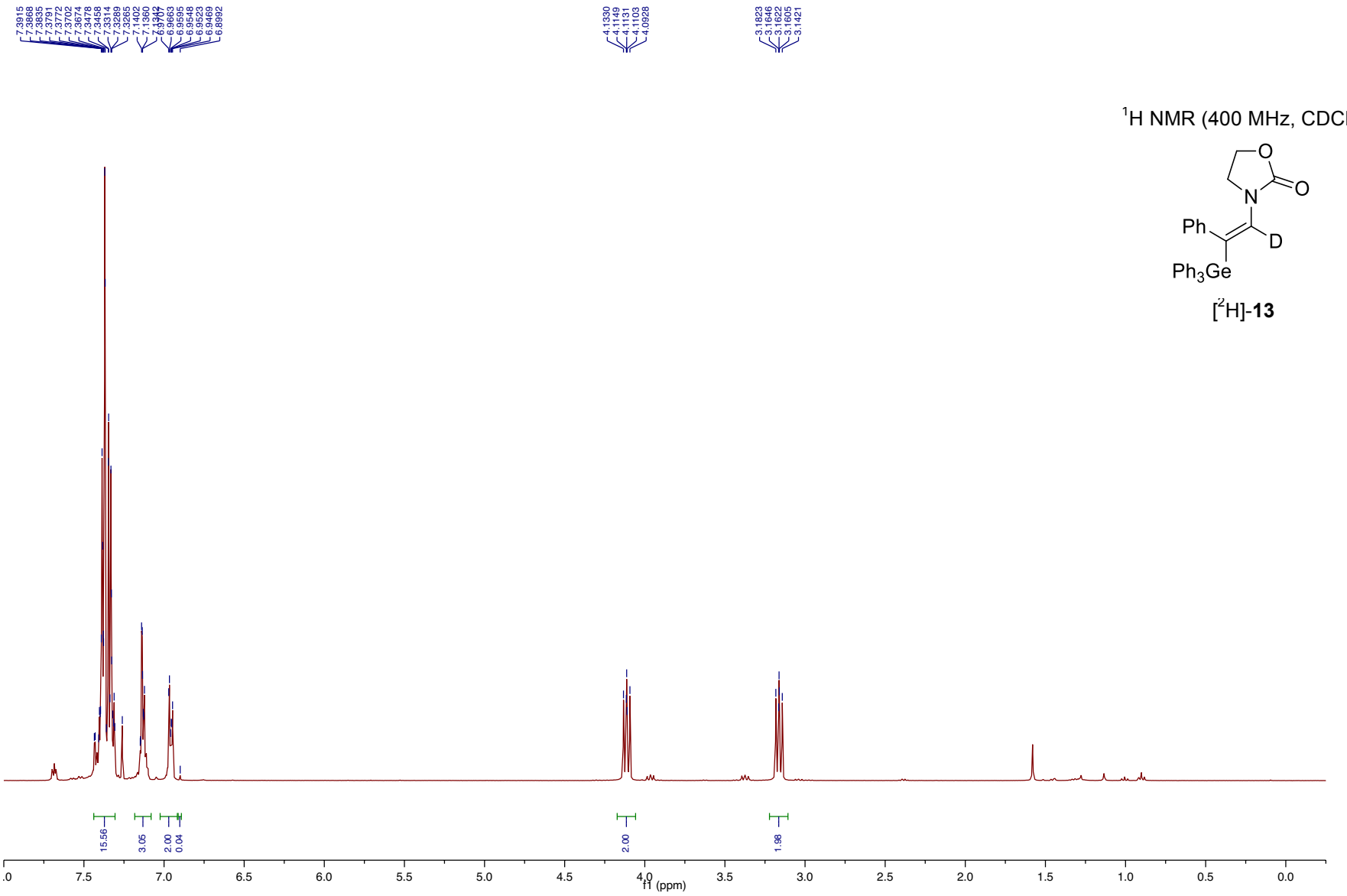
^{1}H NMR (400 MHz, $CDCl_3$)

13



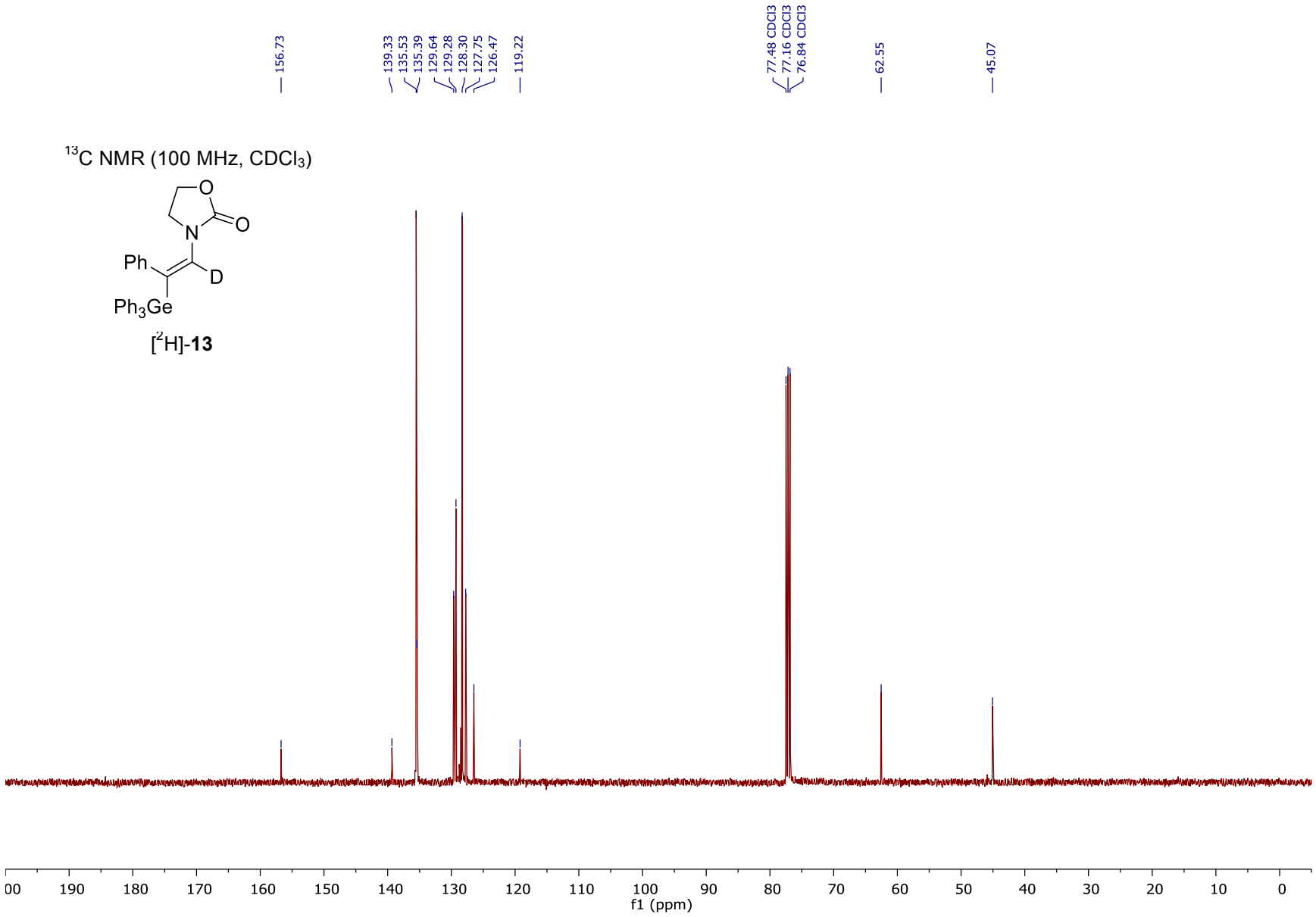
^{13}C NMR (100 MHz, $CDCl_3$)

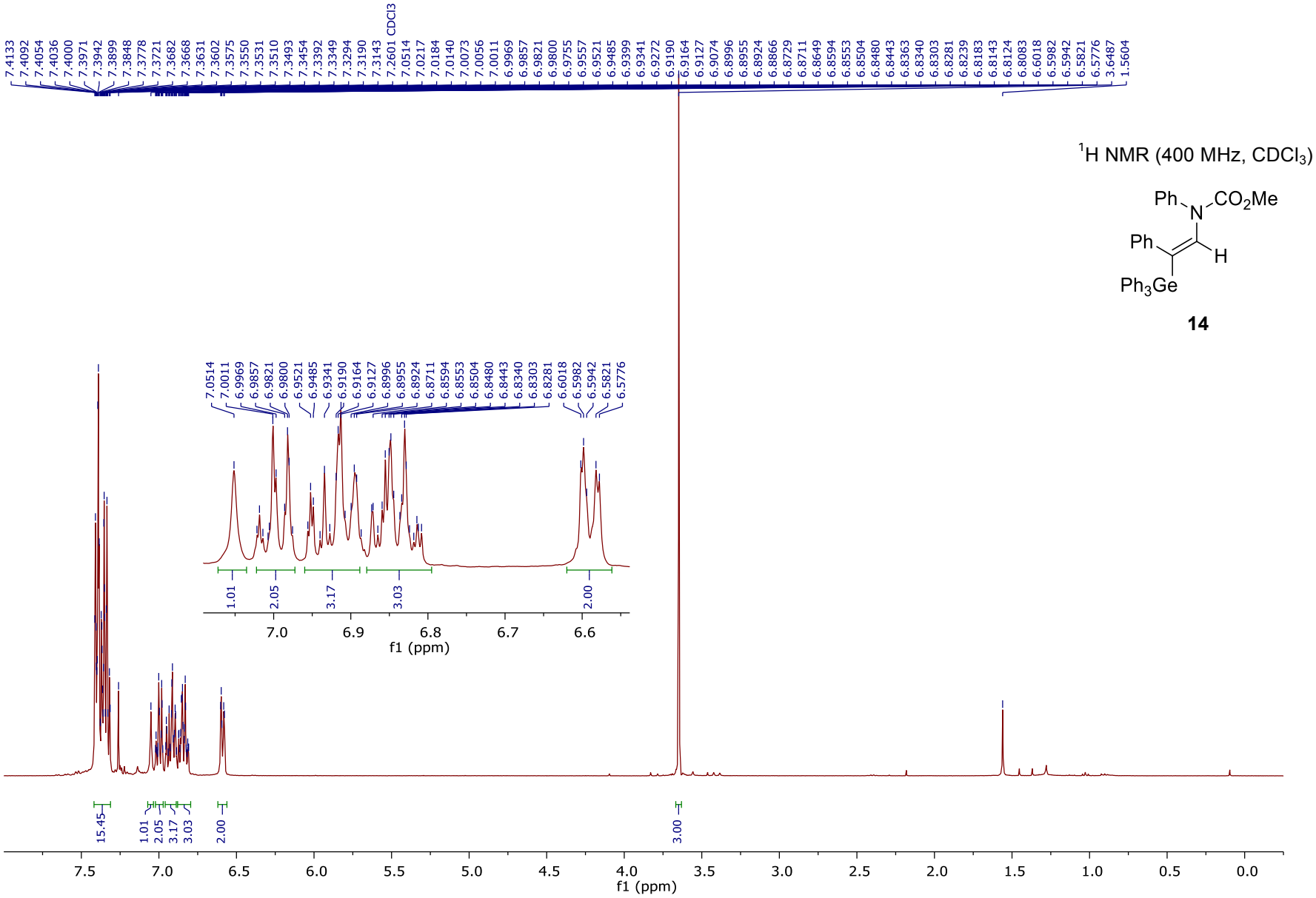
13

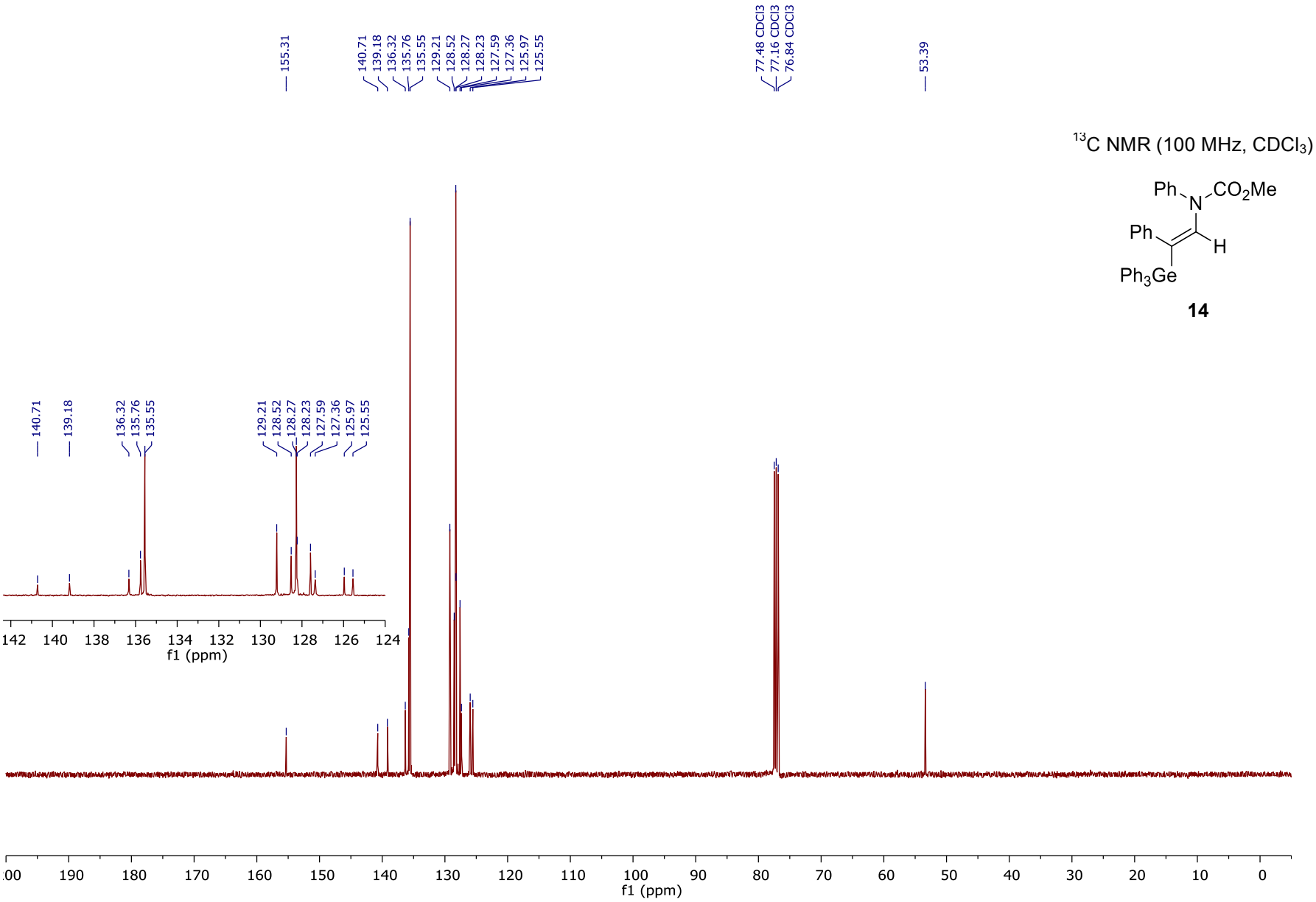


^{1}H NMR (400 MHz, $CDCl_3$)

[^{2}H]-**13**

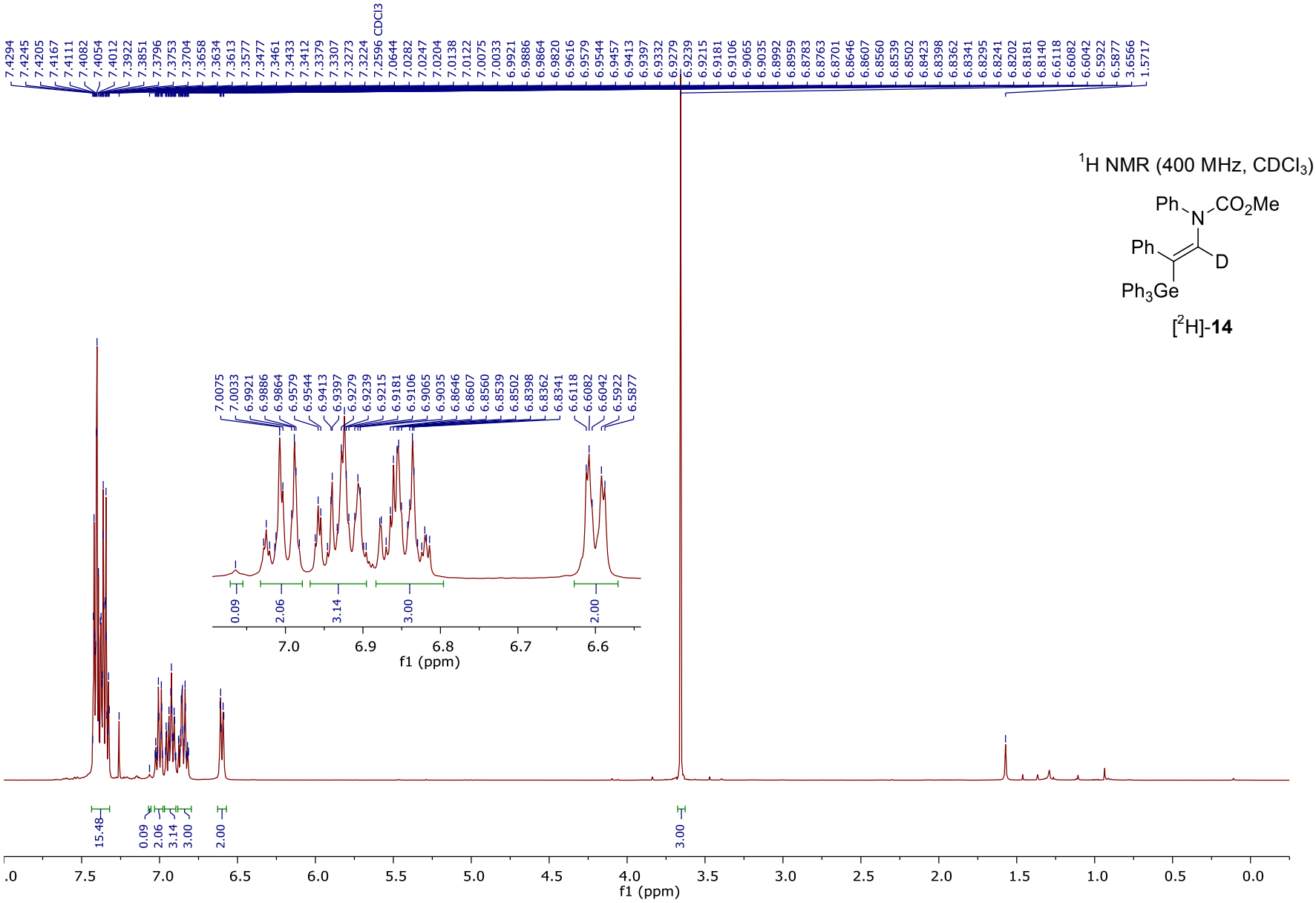

156.73
139.33
135.53
135.39
129.64
129.28
128.30
127.75
126.47
119.22
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.55
45.07
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph
D
Ph_3Ge
[^{2}H]-**13**
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

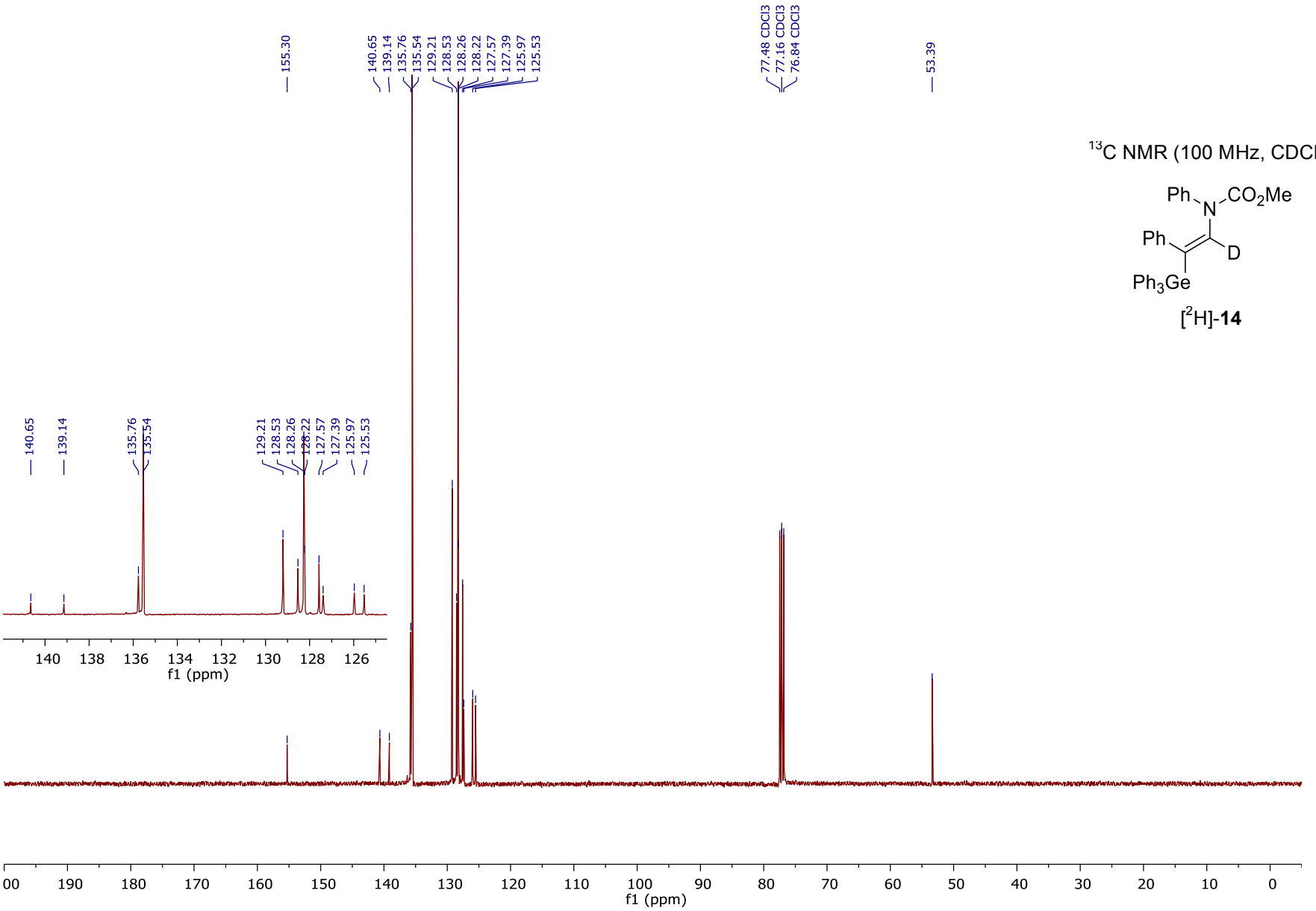

7.4133 7.4092 7.4054 7.4036 7.4000 7.3971 7.3942 7.3899 7.3848 7.3778 7.3721 7.3682 7.3668 7.3631 7.3602 7.3575 7.3550 7.3531 7.3510 7.3493 7.3454 7.3392 7.3349 7.3294 7.3190 7.3143 7.2601 CDCl3 7.0514 7.0217 7.0184 7.0140 7.0073 7.0056 7.0011 6.9969 6.9857 6.9821 6.9800 6.9755 6.9557 6.9521 6.9485 6.9399 6.9341 6.9272 6.9190 6.9164 6.9127 6.9074 6.8996 6.8955 6.8924 6.8866 6.8729 6.8711 6.8649 6.8594 6.8553 6.8504 6.8480 6.8443 6.8363 6.8340 6.8303 6.8281 6.8239 6.8183 6.8143 6.8124 6.8083 6.6018 6.5982 6.5942 6.5821 6.5776 3.6487 1.5604
^{1}H NMR (400 MHz, $CDCl_3$)
Ph N CO_2Me Ph H Ph_3Ge
14
7.0514 7.0011 6.9969 6.9857 6.9821 6.9800 6.9521 6.9485 6.9341 6.9190 6.9164 6.9127 6.8996 6.8955 6.8924 6.8711 6.8594 6.8553 6.8504 6.8480 6.8443 6.8340 6.8303 6.8281 6.6018 6.5982 6.5942 6.5821 6.5776
1.01 2.05 3.17 3.03 2.00
7.0 6.9 6.8 6.7 6.6
f1 (ppm)
15.45 1.01 2.05 3.17 3.03 2.00 3.00
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
f1 (ppm)

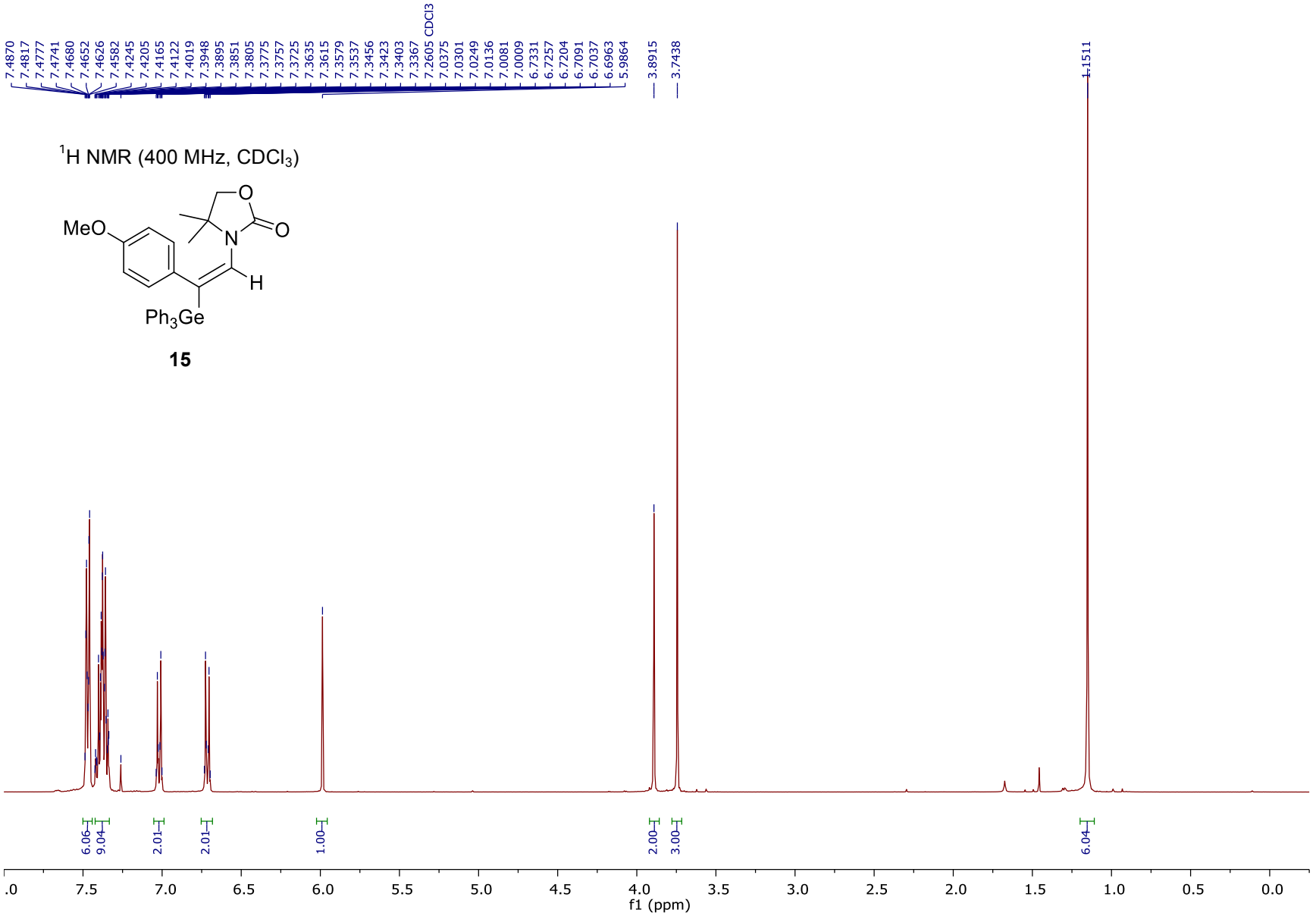


^{13}C NMR (100 MHz, $CDCl_3$)

14

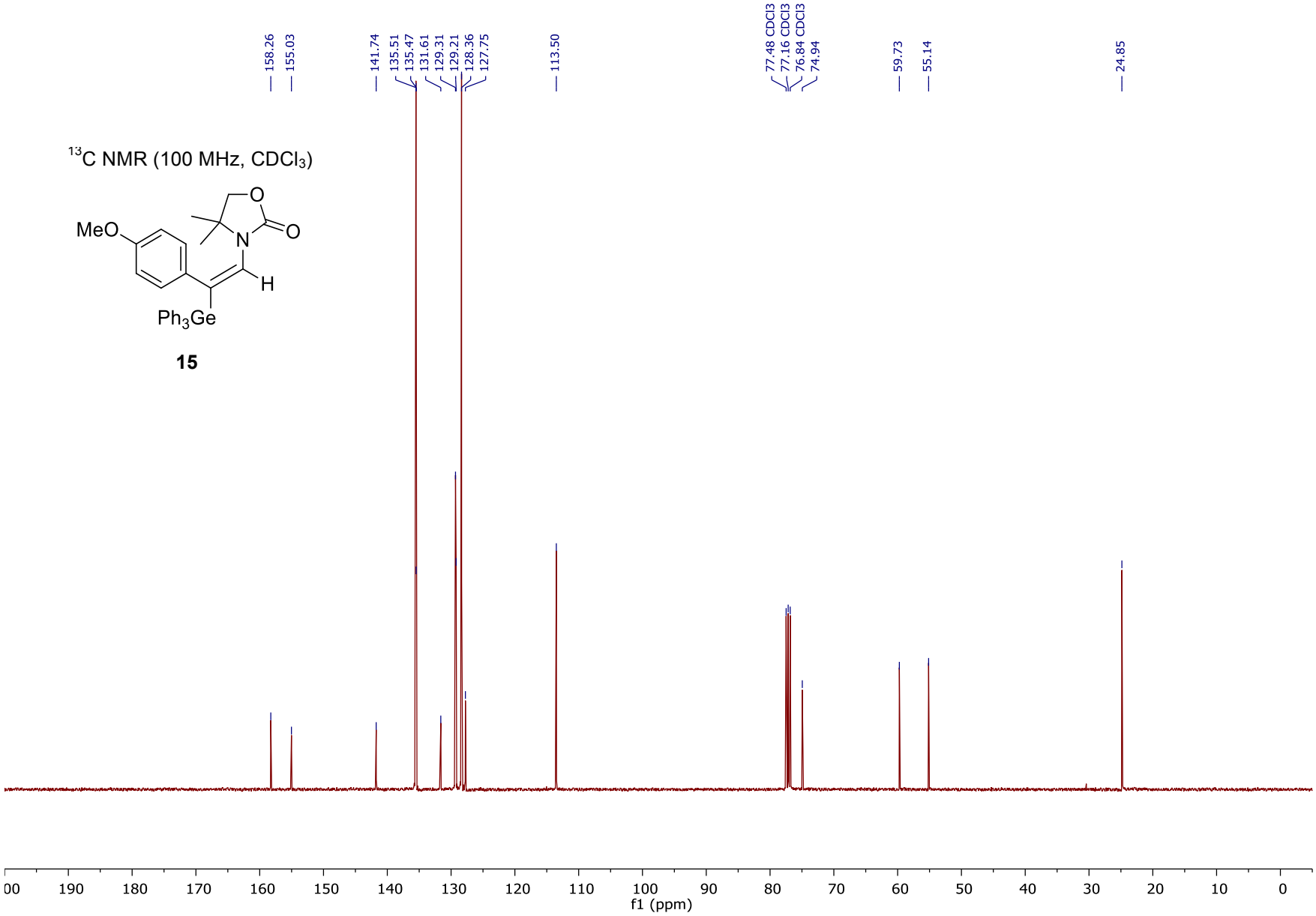

7.4294 7.4245 7.4205 7.4167 7.4111 7.4082 7.4054 7.4012 7.3922 7.3851 7.3796 7.3753 7.3704 7.3658 7.3634 7.3613 7.3577 7.3477 7.3461 7.3433 7.3412 7.3379 7.3307 7.3273 7.3224 7.2596 CDCl3 7.0644 7.0282 7.0247 7.0204 7.0138 7.0122 7.0075 7.0033 6.9921 6.9886 6.9864 6.9820 6.9616 6.9579 6.9544 6.9457 6.9413 6.9397 6.9332 6.9279 6.9239 6.9215 6.9181 6.9106 6.9065 6.9035 6.8992 6.8959 6.8783 6.8763 6.8701 6.8646 6.8607 6.8560 6.8539 6.8502 6.8423 6.8398 6.8362 6.8341 6.8295 6.8241 6.8202 6.8181 6.8140 6.8118 6.8082 6.8042 6.5922 6.5877 3.6566 1.5717
^{1}H NMR (400 MHz, $CDCl_3$)
Ph N CO_2Me Ph D Ph_3Ge
[^{2}H]-**14**
7.0075 7.0033 6.9921 6.9886 6.9864 6.9579 6.9544 6.9413 6.9397 6.9279 6.9239 6.9215 6.9181 6.9106 6.9065 6.9035 6.8646 6.8607 6.8560 6.8539 6.8502 6.8398 6.8362 6.8341 6.6118 6.6082 6.6042 6.5922 6.5877
0.09 2.06 3.14 3.00 2.00
7.0 6.9 6.8 6.7 6.6
f1 (ppm)
15.48 0.09 2.06 3.14 3.00 2.00 3.00
.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
f1 (ppm)

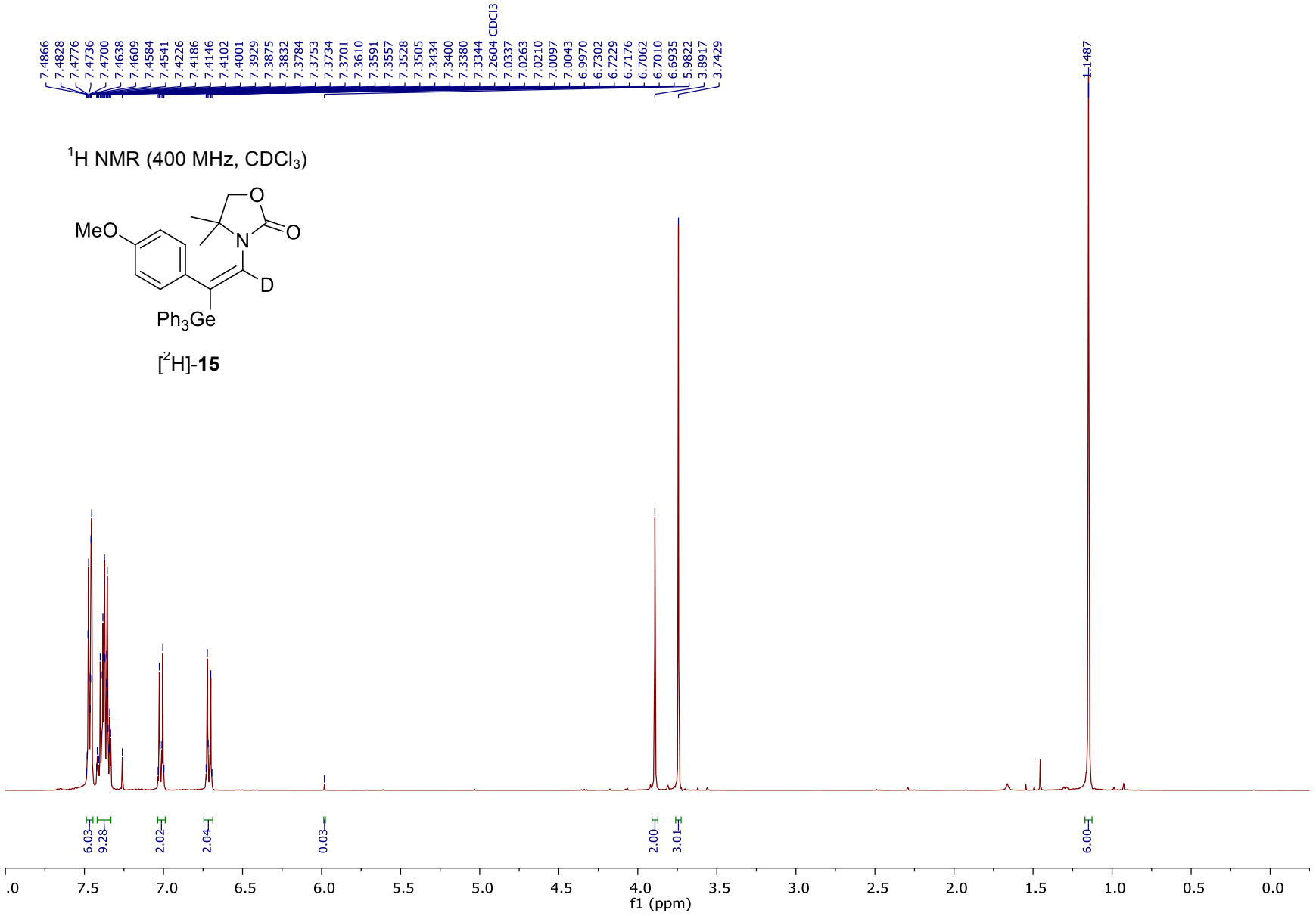

155.30
140.65
139.14
135.76
135.54
129.21
128.53
128.26
128.22
127.57
127.39
125.97
125.53
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.39
f1 (ppm)
^{13}C NMR (100 MHz, $CDCl_3$)
Ph
N
CO_2Me
Ph
D
Ph_3Ge
[^{2}H]-**14**

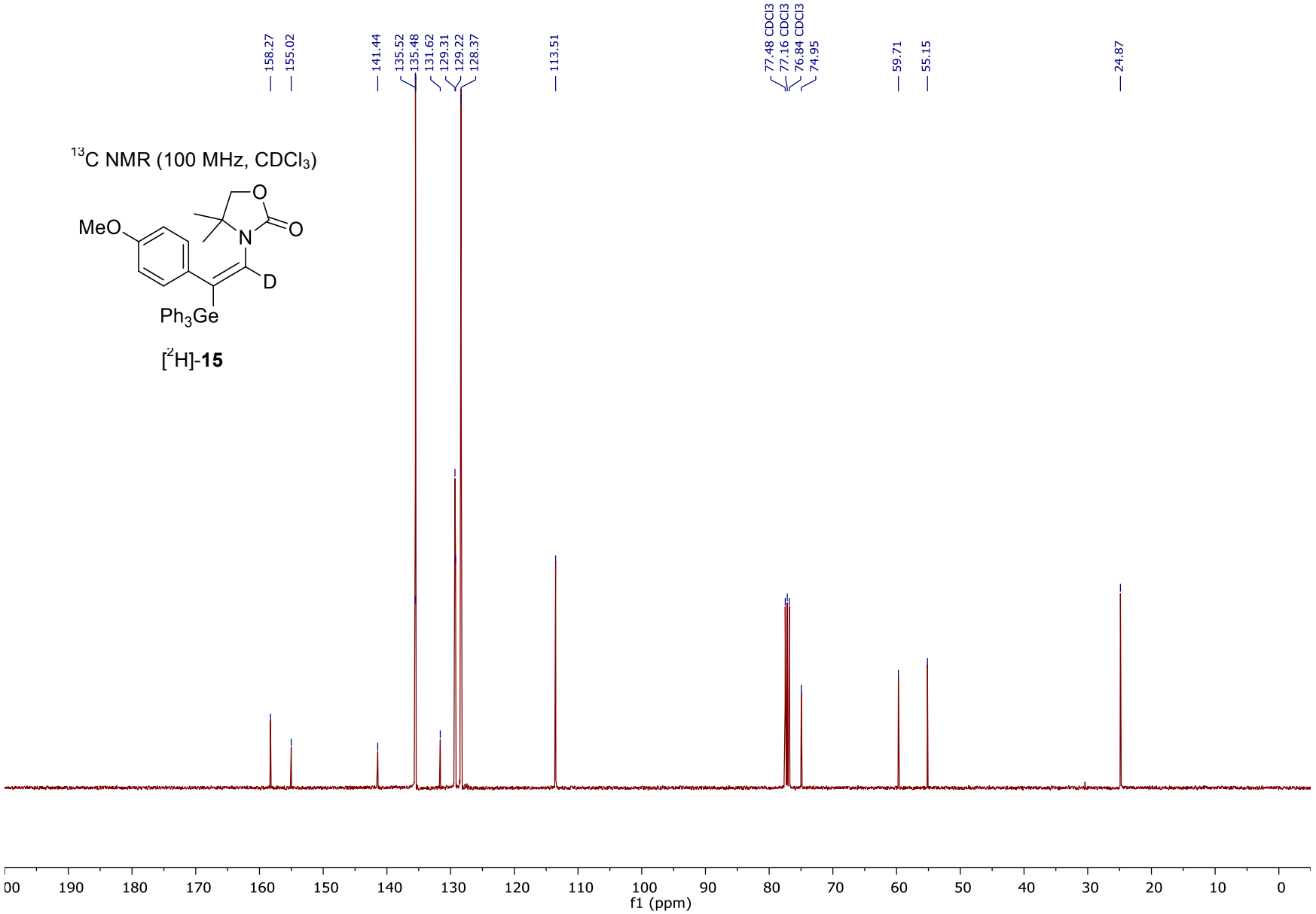


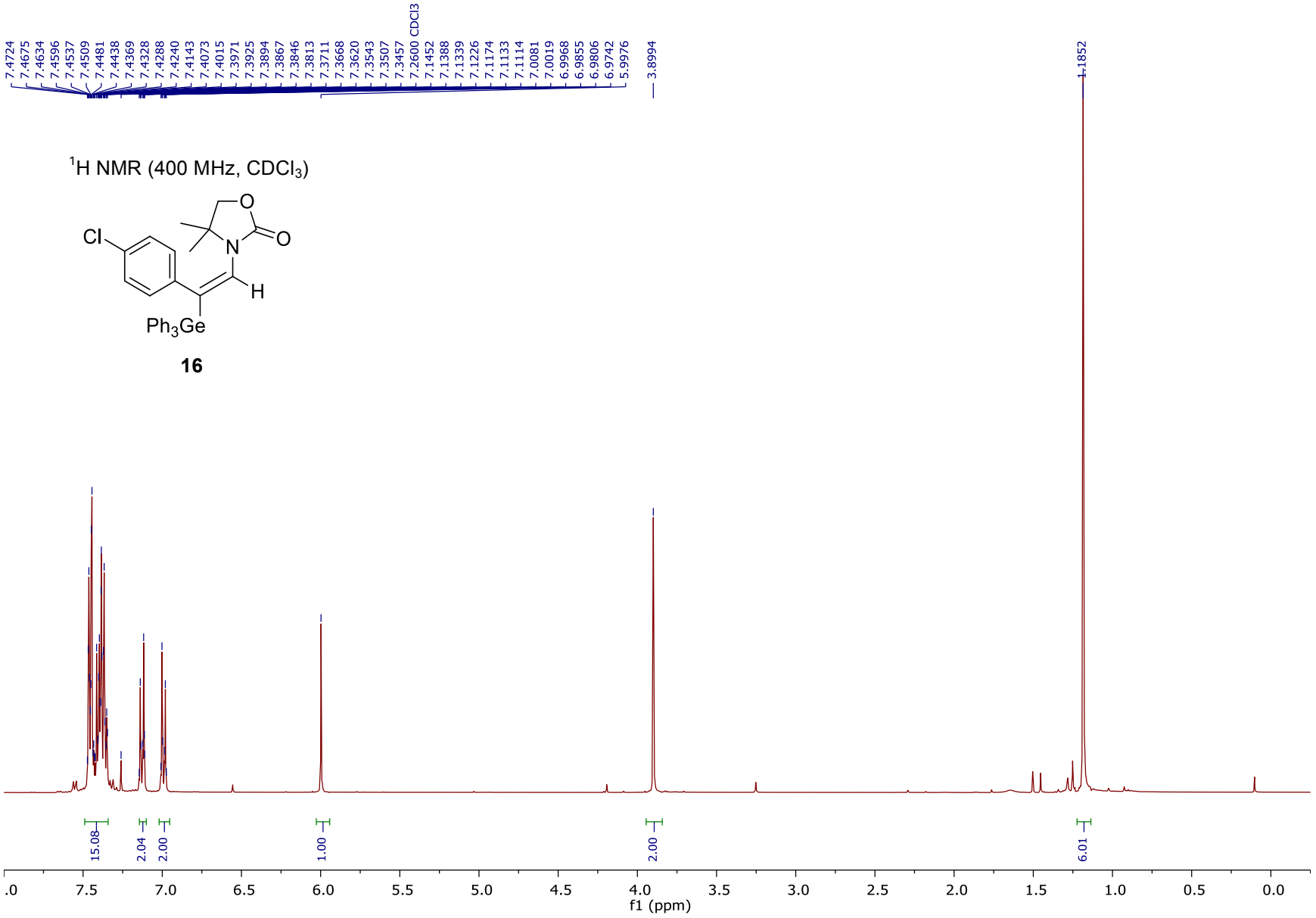
^{1}H NMR (400 MHz, $CDCl_3$)

15


158.26
155.03
141.74
135.51
135.47
131.61
129.31
129.21
128.36
127.75
113.50
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.94
59.73
55.14
24.85
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
O
O
N
H
Ph_3Ge
15
f1 (ppm)

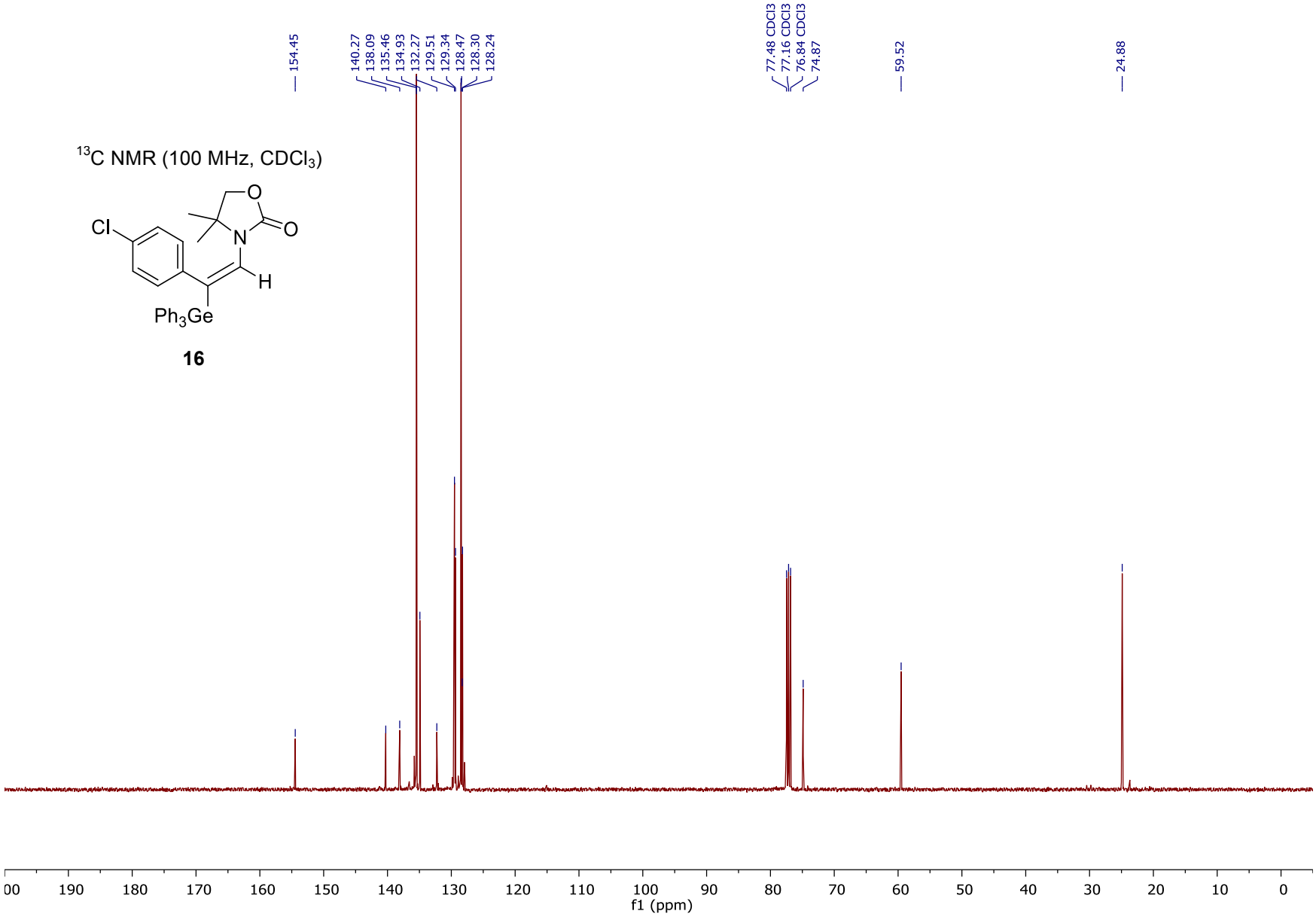

7.4866
7.4828
7.4776
7.4736
7.4700
7.4638
7.4609
7.4584
7.4541
7.4226
7.4186
7.4146
7.4102
7.4001
7.3929
7.3875
7.3832
7.3784
7.3753
7.3734
7.3701
7.3610
7.3591
7.3557
7.3528
7.3505
7.3434
7.3400
7.3380
7.3344
7.2604 CDCl3
7.0337
7.0263
7.0210
7.0097
7.0043
6.9970
6.7302
6.7229
6.7176
6.7062
6.7010
6.6935
5.9822
3.8917
3.7429
1.1487
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
O
O
N
D
Ph_3Ge
[^{2}H]-**15**
6.03
9.28
2.02
2.04
0.03
2.00
3.01
6.00
f1 (ppm)

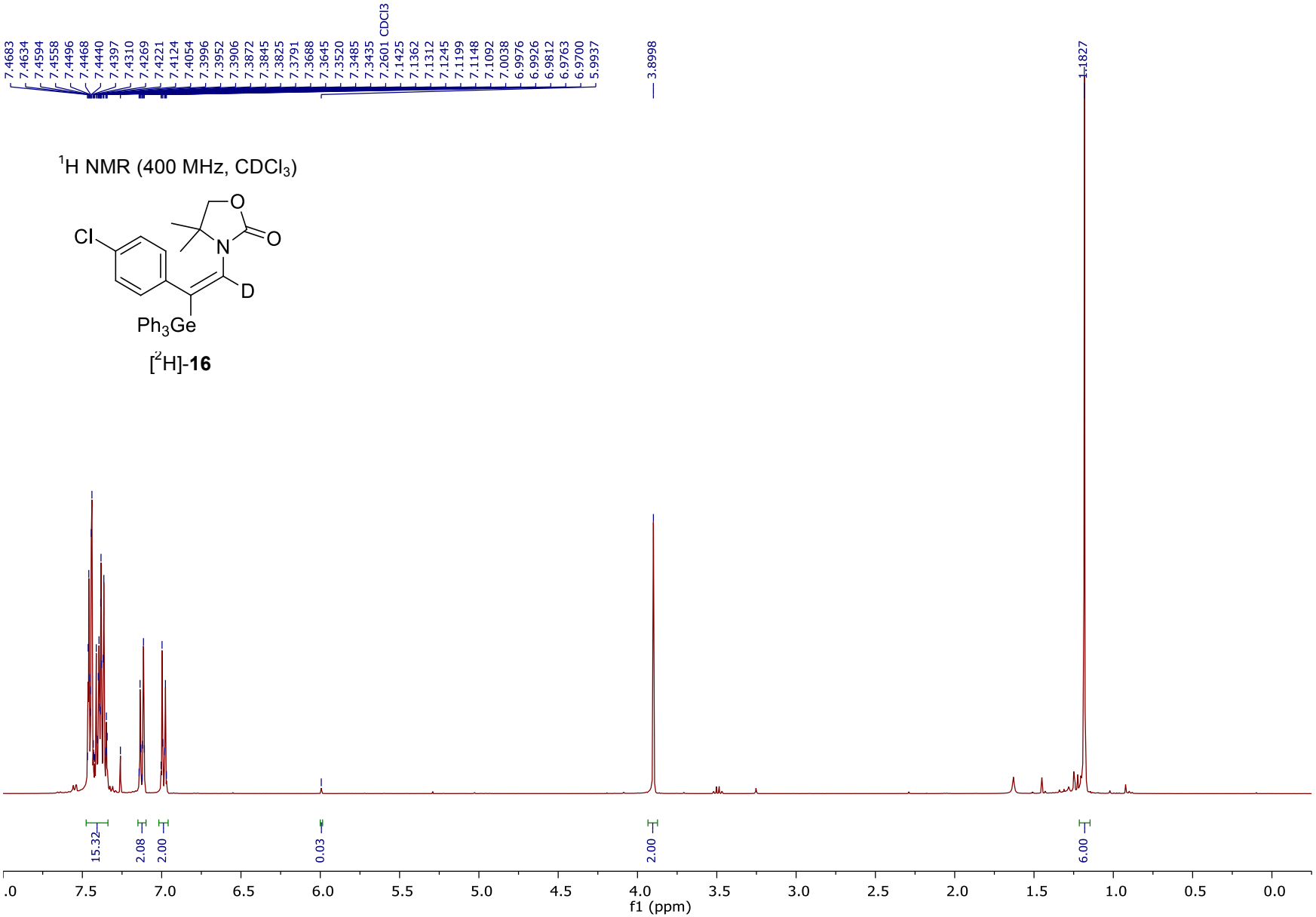

158.27
155.02
141.44
135.52
135.48
131.62
129.31
129.22
128.37
113.51
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.95
59.71
55.15
24.87
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
O
O
N
D
Ph_3Ge
[^{2}H]-**15**
f1 (ppm)



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

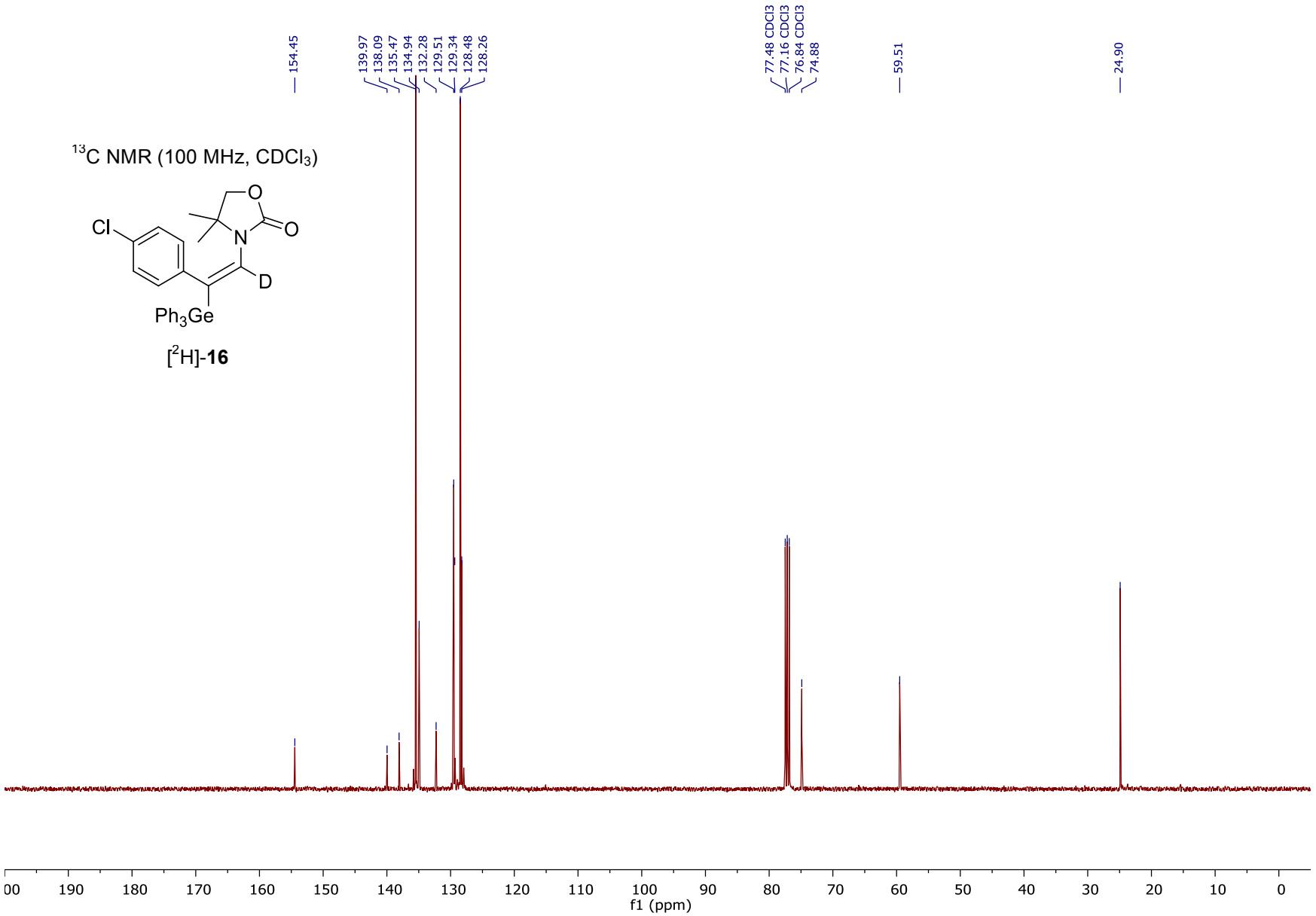
16

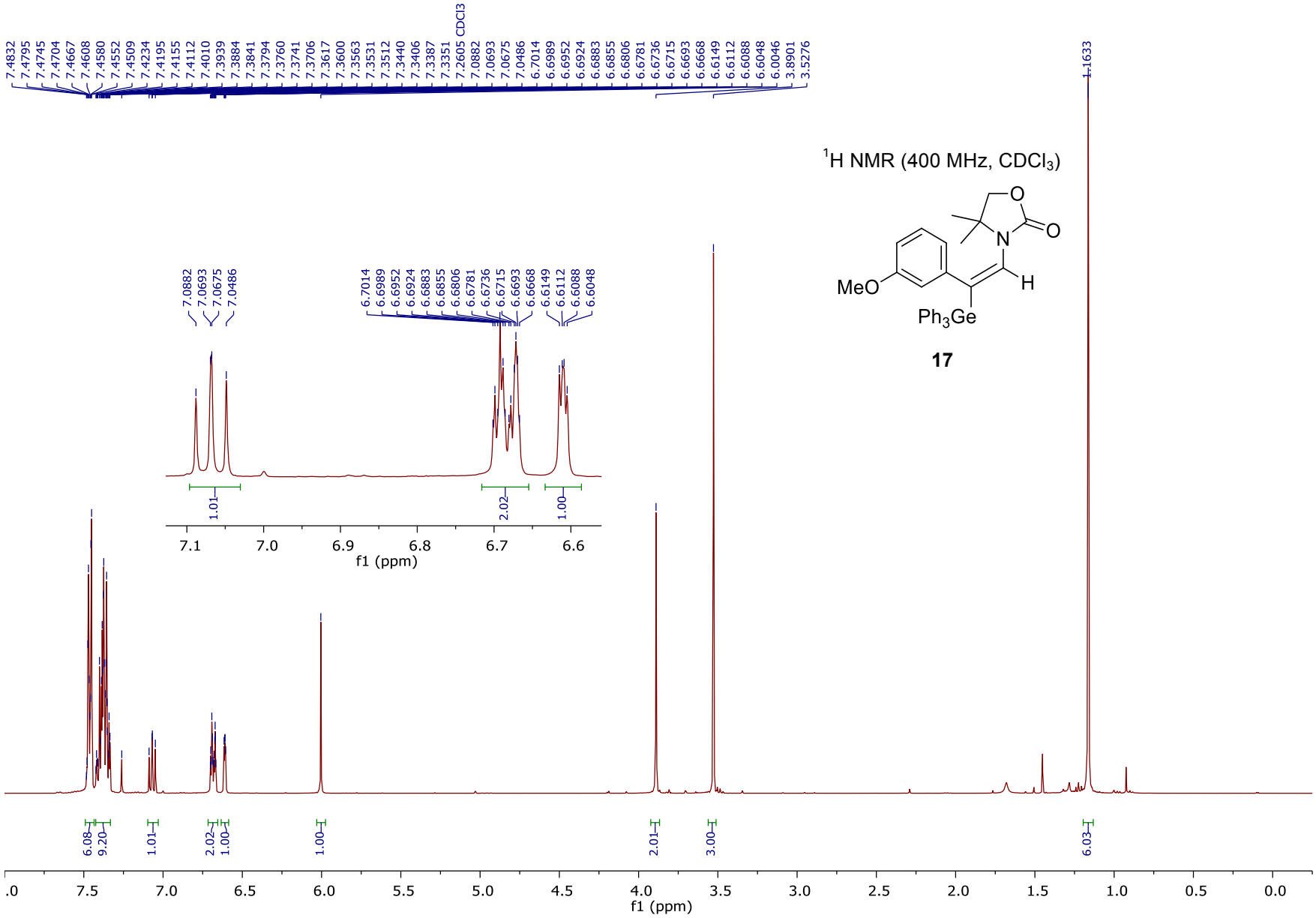

154.45
140.27
138.09
135.46
134.93
132.27
129.51
129.34
128.47
128.30
128.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.87
59.52
24.88
^{13}C NMR (100 MHz, $CDCl_3$)
Cl
O
O
N
H
Ph_3Ge
16
f1 (ppm)

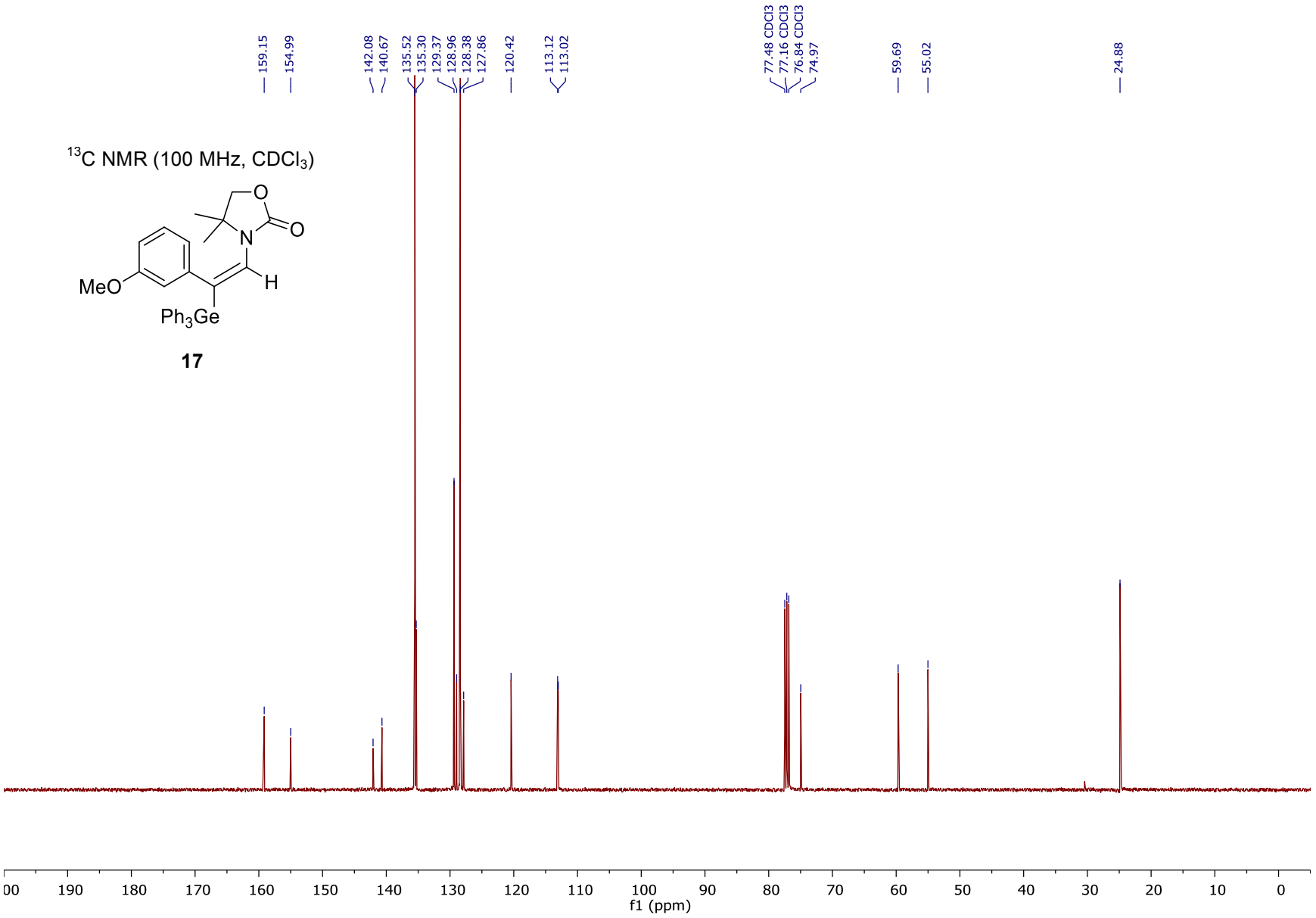


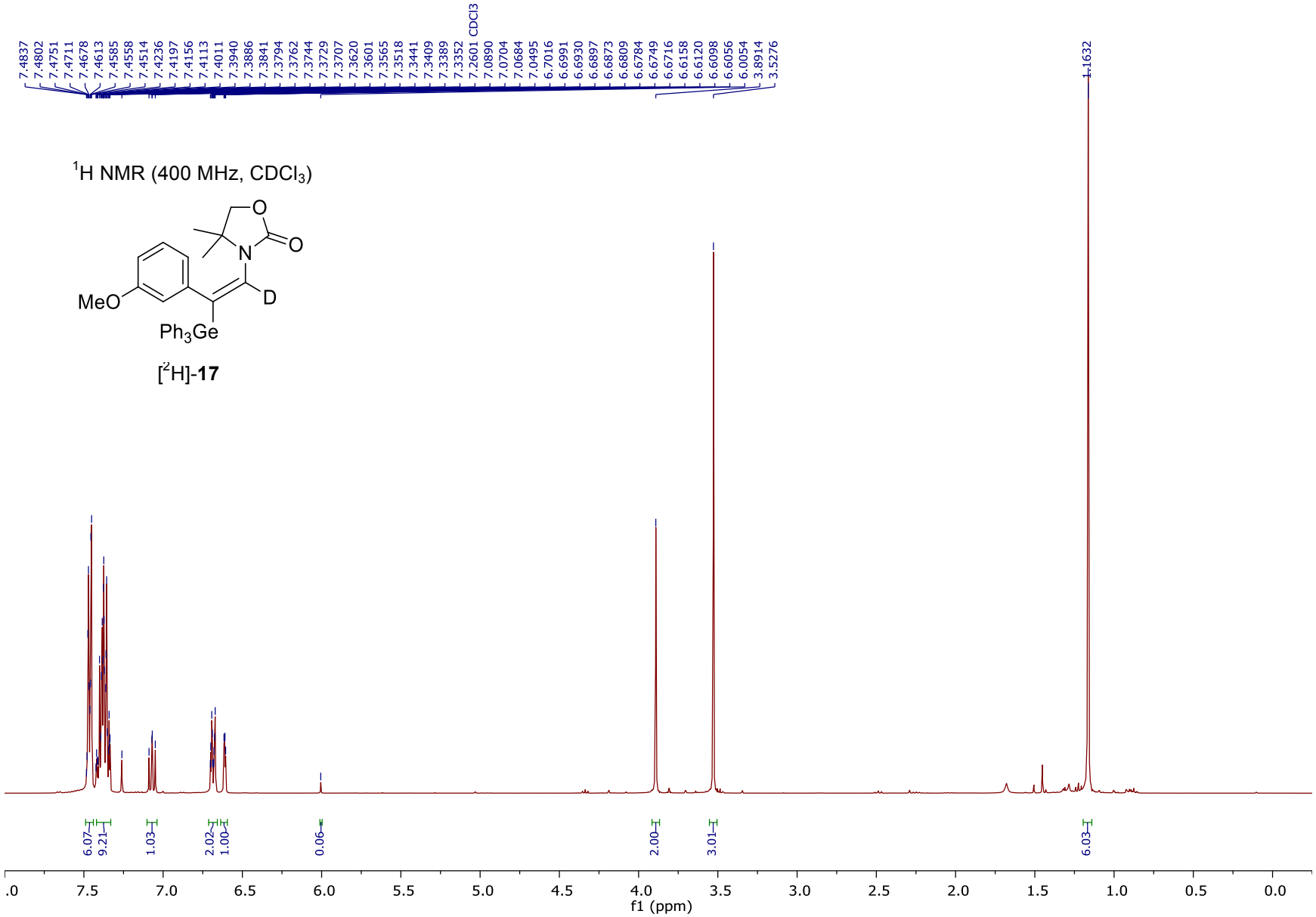
^{1}H NMR (400 MHz, $CDCl_3$)

[^{2}H]-**16**


154.45
139.97
138.09
135.47
134.94
132.28
129.51
129.34
128.48
128.26
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.88
59.51
24.90
^{13}C NMR (100 MHz, $CDCl_3$)
Cl
O
O
N
D
Ph_3Ge
[^{2}H]-**16**
f1 (ppm)

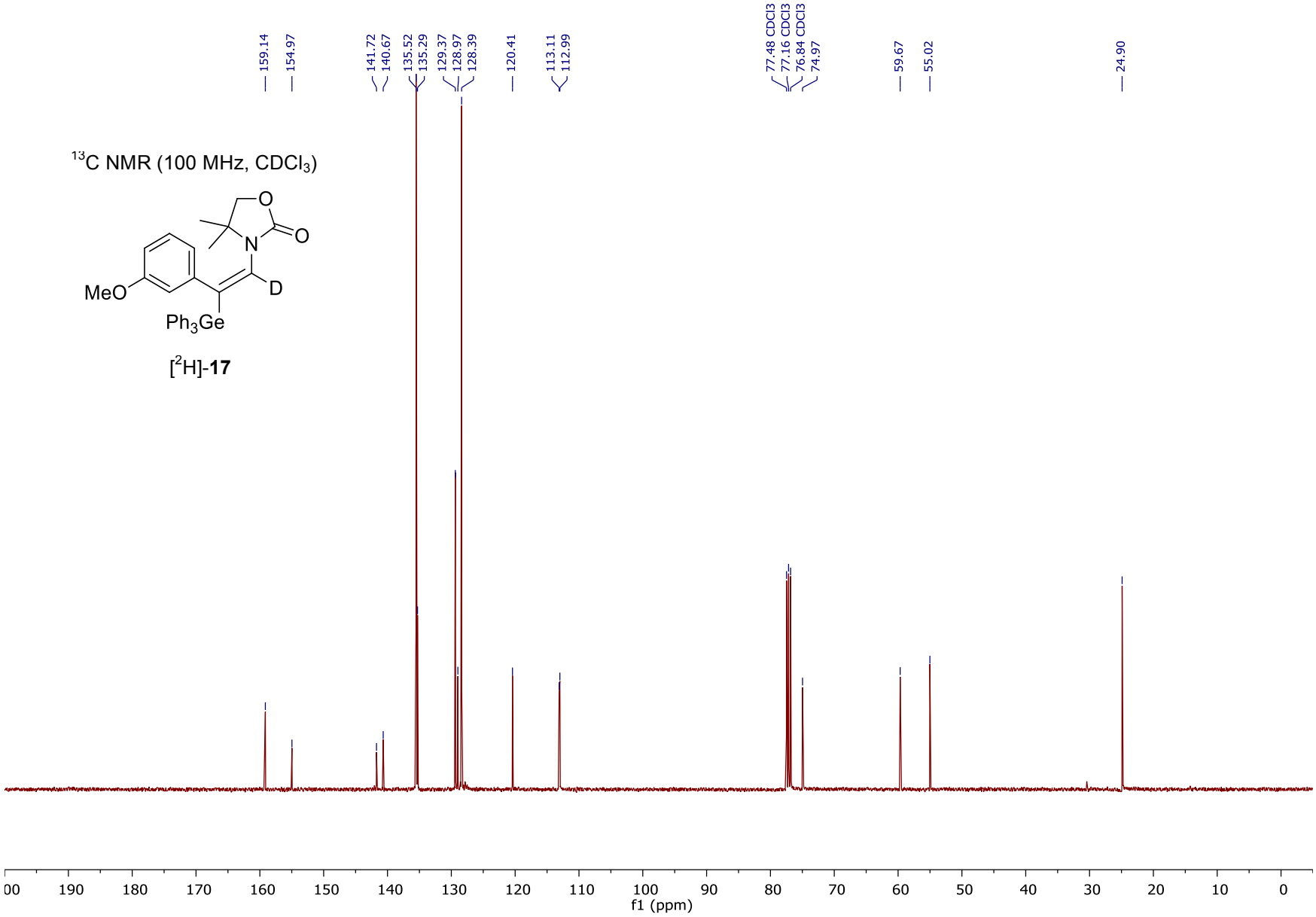

7.4832 7.4795 7.4745 7.4704 7.4667 7.4608 7.4580 7.4552 7.4509 7.4234 7.4195 7.4155 7.4112 7.4010 7.3939 7.3884 7.3841 7.3794 7.3760 7.3741 7.3706 7.3617 7.3600 7.3563 7.3531 7.3512 7.3440 7.3406 7.3387 7.3351 7.2605 CDCl3 7.0882 7.0693 7.0675 7.0486 6.7014 6.6989 6.6952 6.6924 6.6883 6.6855 6.6806 6.6781 6.6736 6.6715 6.6693 6.6668 6.6149 6.6112 6.6088 6.6048 6.0046 3.8901 3.5276 1.1633
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
H
Ph_3Ge
17
1.01 2.02 1.00
7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
6.08 9.20 1.01 2.02 1.00 1.00 2.01 3.00 6.03
.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
f1 (ppm)

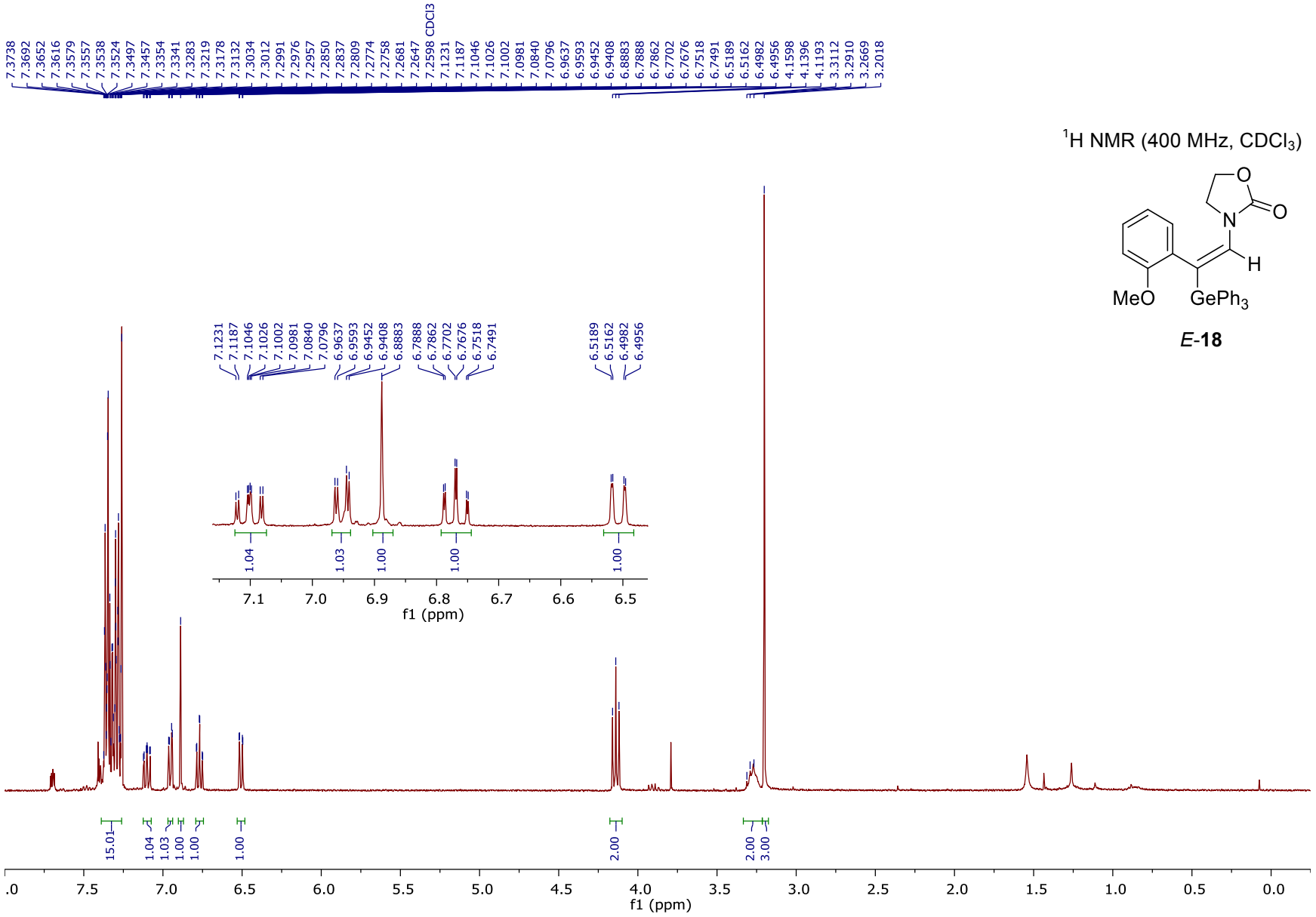

159.15
154.99
142.08
140.67
135.52
135.30
129.37
128.96
128.38
127.86
120.42
113.12
113.02
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.97
59.69
55.02
24.88
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
MeO
H
Ph_3Ge
17
f1 (ppm)

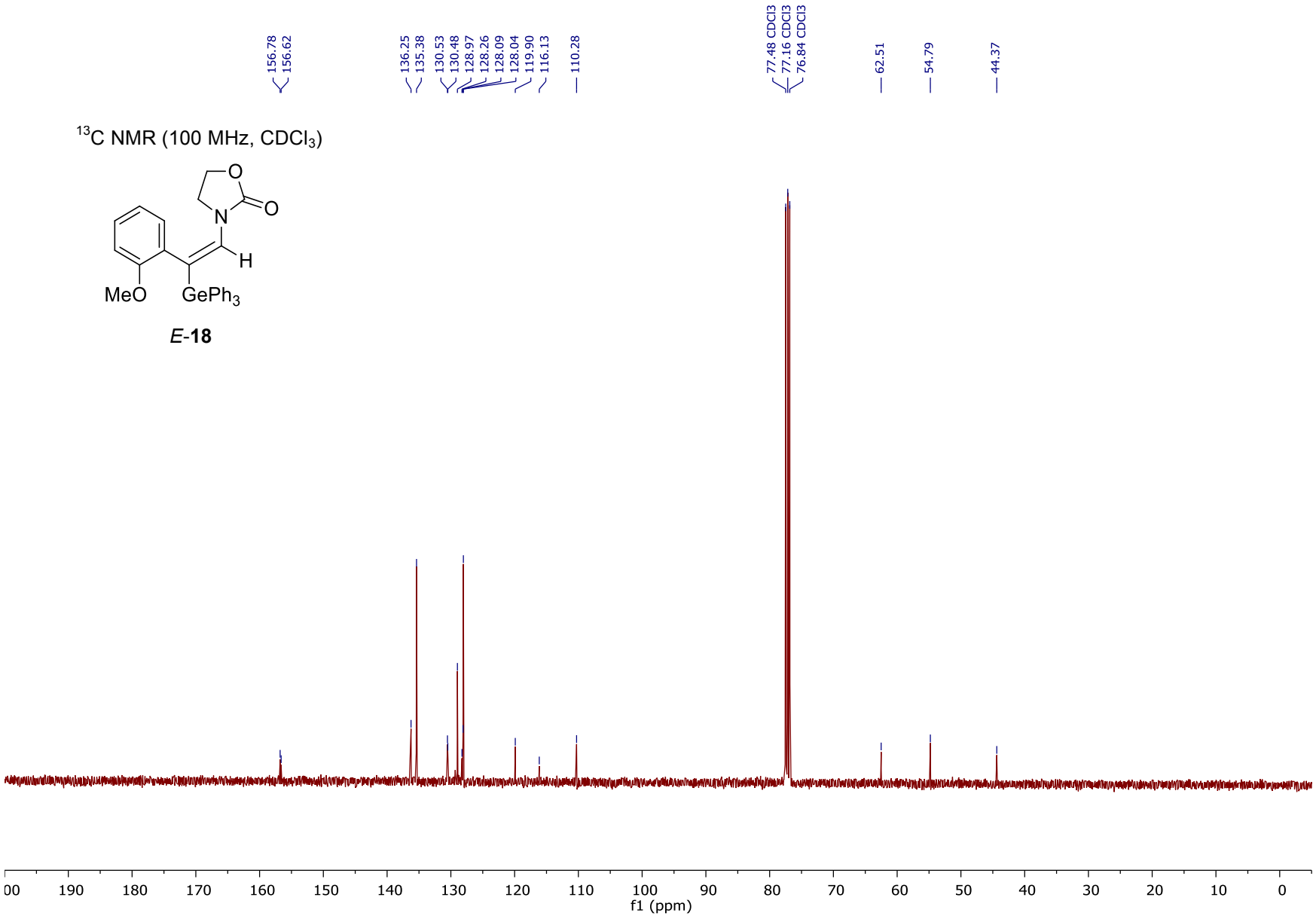


^{1}H NMR (400 MHz, $CDCl_3$)

[^{2}H]-**17**

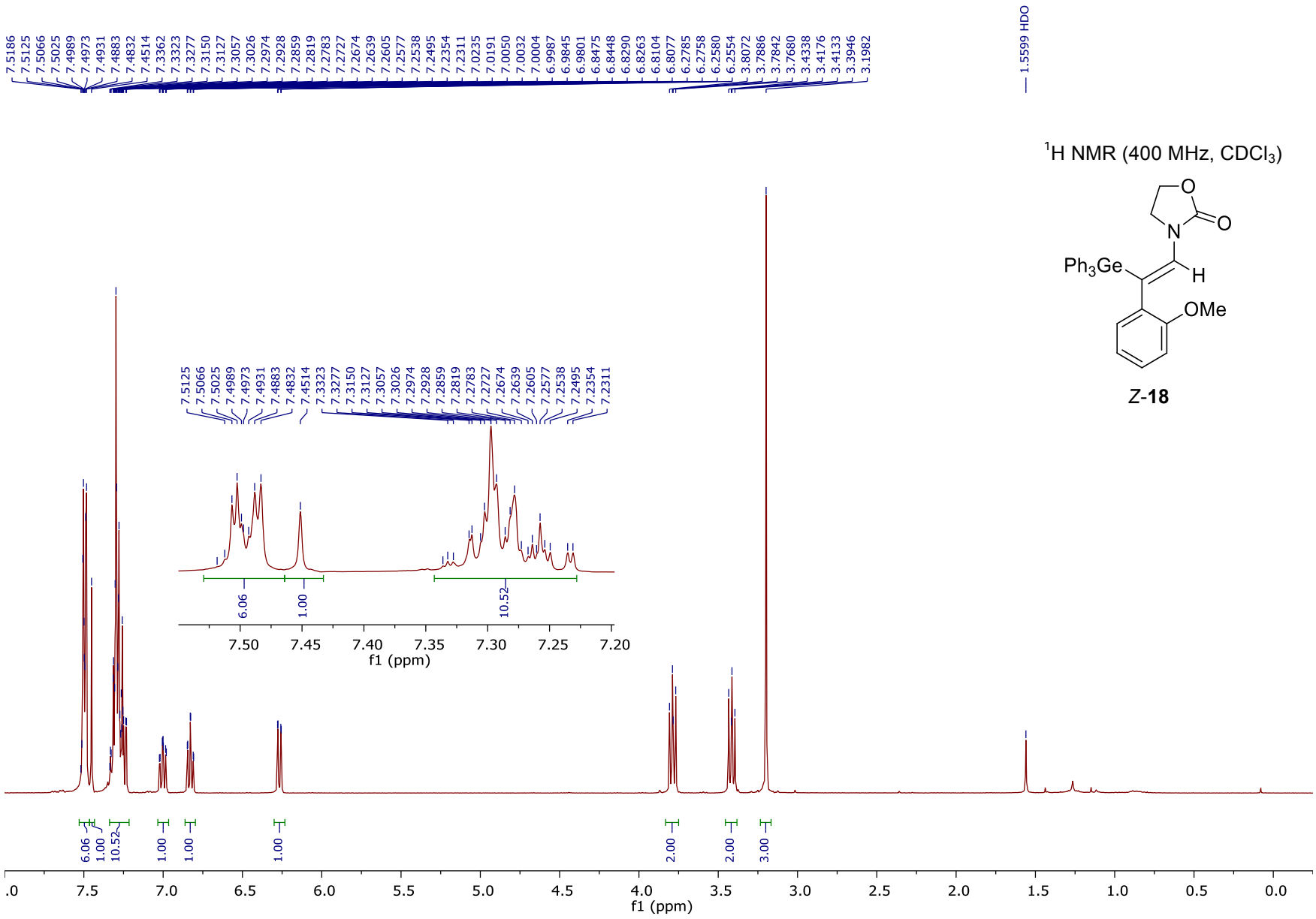

159.14
154.97
141.72
140.67
135.52
135.29
129.37
128.97
128.39
120.41
113.11
112.99
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.97
59.67
55.02
24.90
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
D
Ph_3Ge
[^{2}H]-**17**
f1 (ppm)

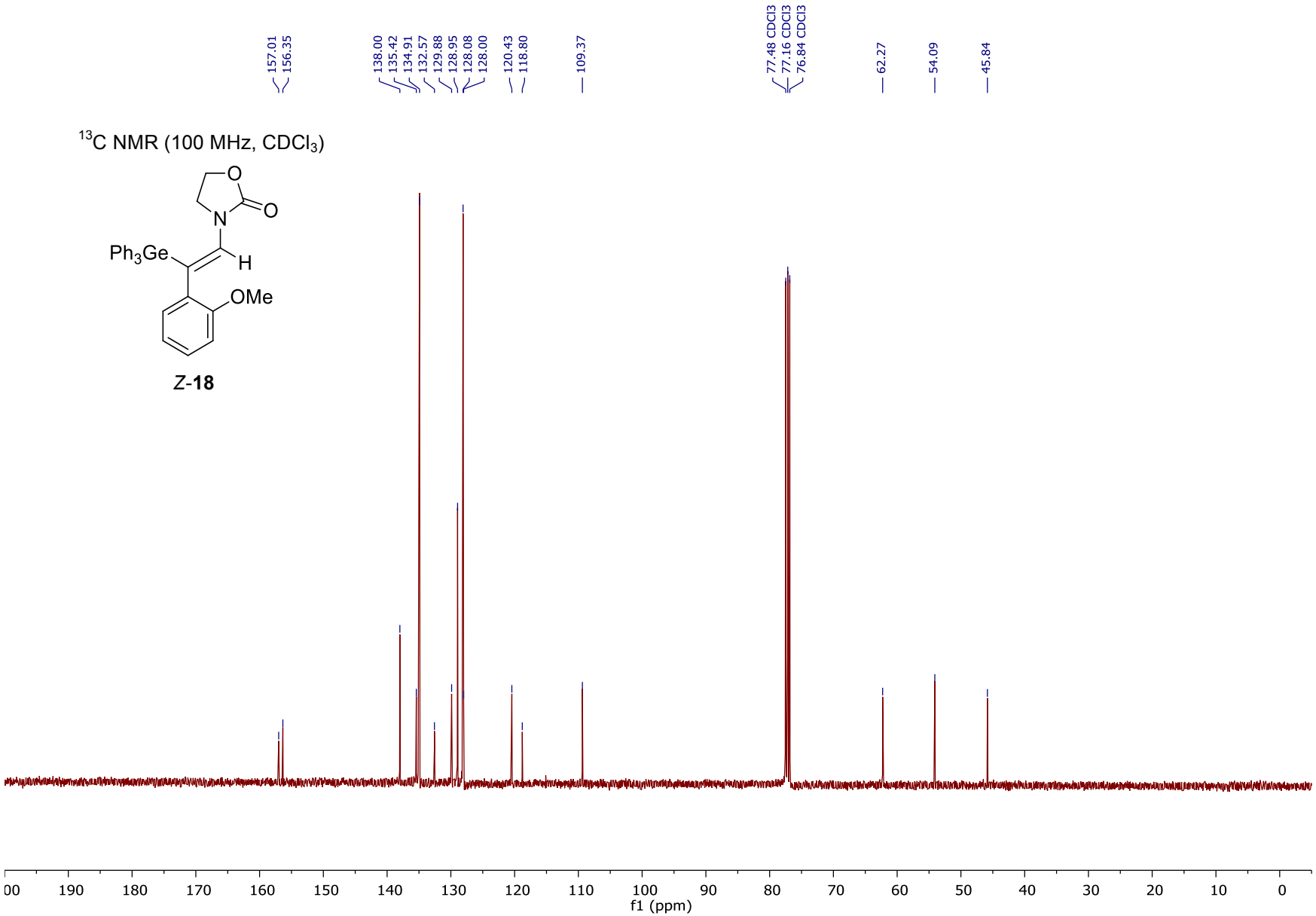

7.3738 7.3692 7.3652 7.3616 7.3579 7.3557 7.3538 7.3524 7.3497 7.3457 7.3354 7.3341 7.3283 7.3219 7.3178 7.3132 7.3034 7.3012 7.2991 7.2976 7.2957 7.2850 7.2837 7.2809 7.2774 7.2758 7.2681 7.2647 7.2598 CDCl3 7.1231 7.1187 7.1046 7.1026 7.1002 7.0981 7.0840 7.0796 6.9637 6.9593 6.9452 6.9408 6.8883 6.7888 6.7862 6.7702 6.7676 6.7518 6.7491 6.5189 6.5162 6.4982 6.4956 4.1598 4.1396 4.1193 3.3112 3.2910 3.2669 3.2018
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
$GePh_3$
H
N
O
O
E-**18**
15.01
1.04
1.03
1.00
1.00
1.00
2.00
2.00
3.00
f1 (ppm)
1.04
1.03
1.00
1.00
1.00
f1 (ppm)

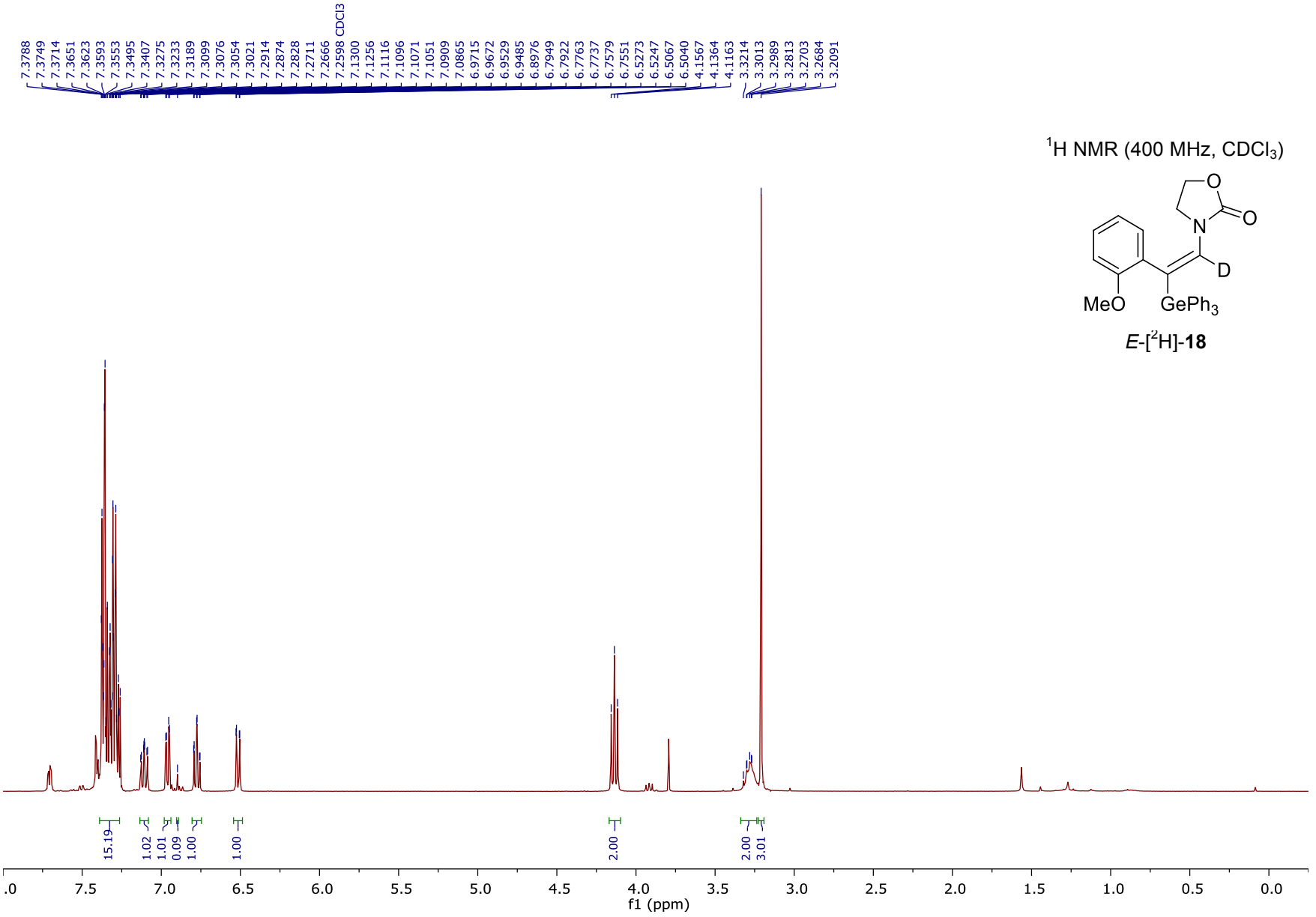


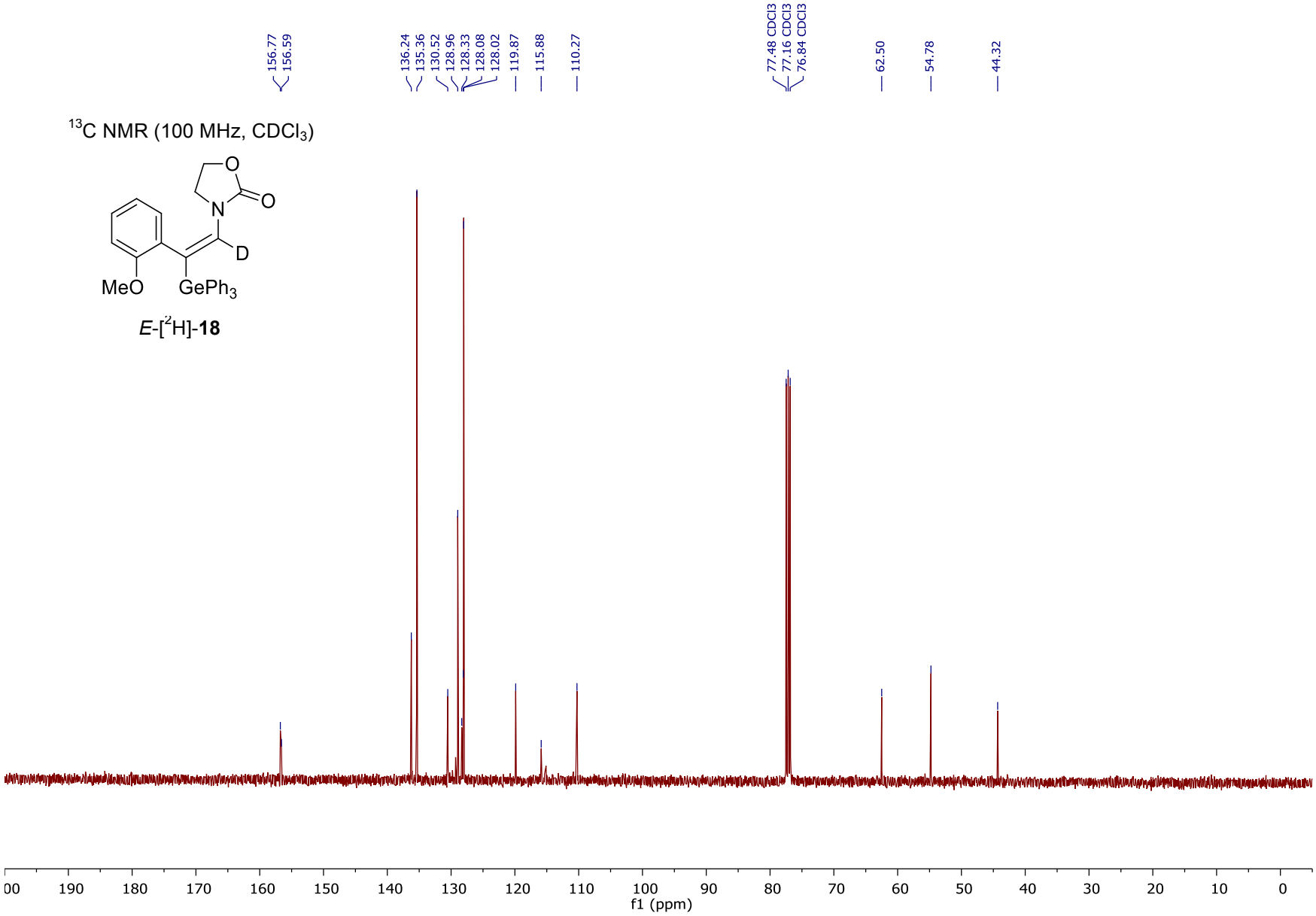
^{13}C NMR (100 MHz, $CDCl_3$)

E-**18**


7.5186
7.5125
7.5066
7.5025
7.4989
7.4973
7.4931
7.4883
7.4832
7.4514
7.3362
7.3323
7.3277
7.3150
7.3127
7.3057
7.3026
7.2974
7.2928
7.2859
7.2819
7.2783
7.2727
7.2674
7.2639
7.2605
7.2577
7.2538
7.2495
7.2354
7.2311
7.0191
7.0050
7.0032
7.0004
6.9987
6.9845
6.9801
6.8475
6.8448
6.8290
6.8263
6.8104
6.8077
6.2785
6.2758
6.2580
6.2554
3.8072
3.7886
3.7842
3.7680
3.4338
3.4176
3.4133
3.3946
3.1982
1.5599 HDO
6.06
1.00
10.52
1.00
1.00
1.00
2.00
2.00
3.00
f1 (ppm)
^{1}H NMR (400 MHz, $CDCl_3$)
Ph_3Ge
O
N
O
H
OMe
***Z*-18**

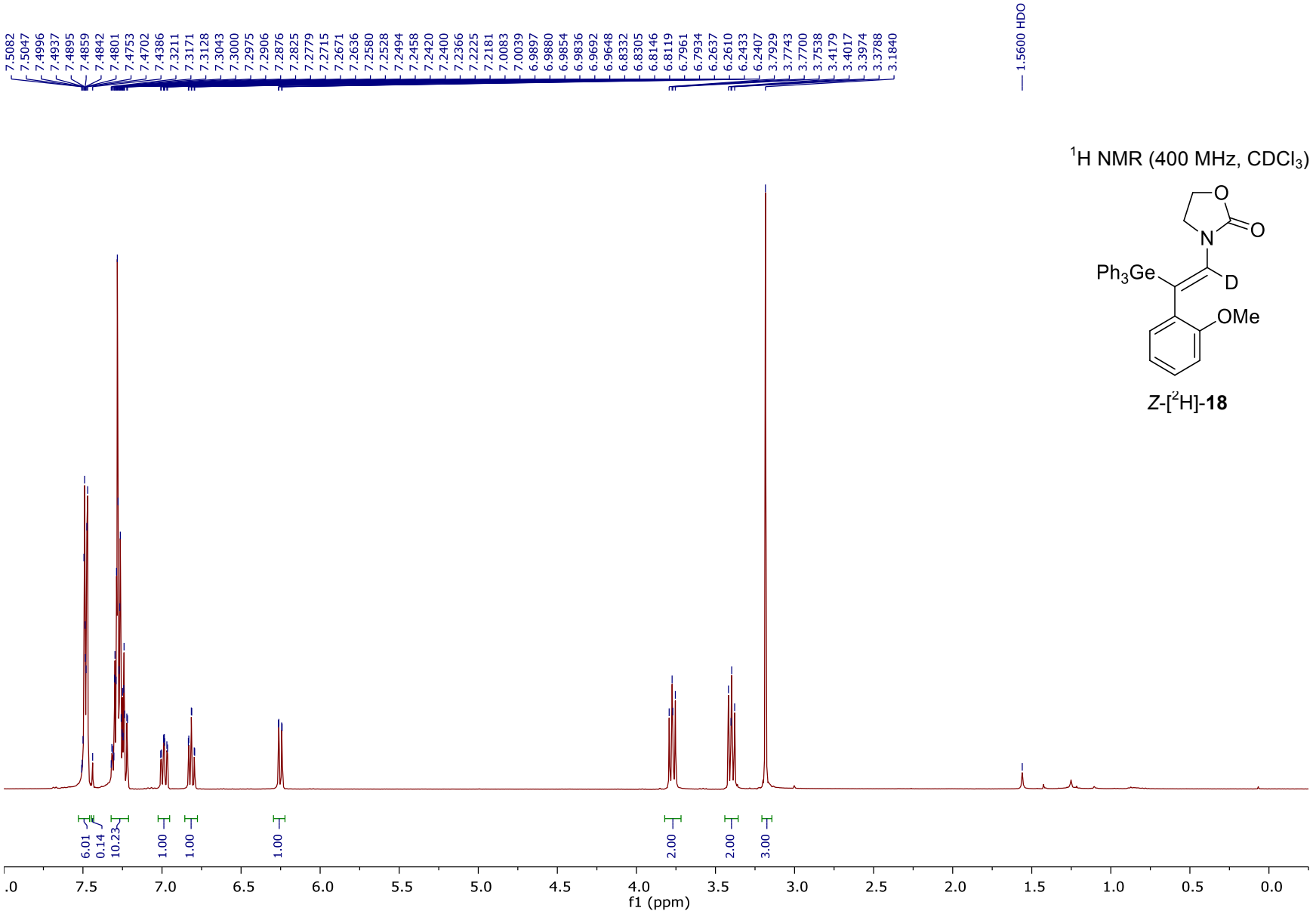

157.01
156.35
138.00
135.42
134.91
132.57
129.88
128.95
128.08
128.00
120.43
118.80
109.37
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.27
54.09
45.84
13C NMR (100 MHz, CDCl3)
O
O
N
Ph3Ge
H
OMe
Z-18
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.3788
7.3749
7.3714
7.3651
7.3623
7.3593
7.3553
7.3495
7.3407
7.3275
7.3233
7.3189
7.3099
7.3076
7.3054
7.3021
7.2914
7.2874
7.2828
7.2711
7.2666
CDCl3
7.2598
7.1300
7.1256
7.1116
7.1096
7.1071
7.1051
7.0909
7.0865
6.9715
6.9672
6.9529
6.9485
6.8976
6.7949
6.7922
6.7763
6.7737
6.7579
6.7551
6.5273
6.5247
6.5067
6.5040
4.1567
4.1364
4.1163
3.3214
3.3013
3.2989
3.2813
3.2703
3.2684
3.2091
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
N
D
MeO
GePh$_3$
E-[^{2}H]-**18**
15.19
1.02
1.01
0.09
1.00
1.00
2.00
2.00
3.01
.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
f1 (ppm)



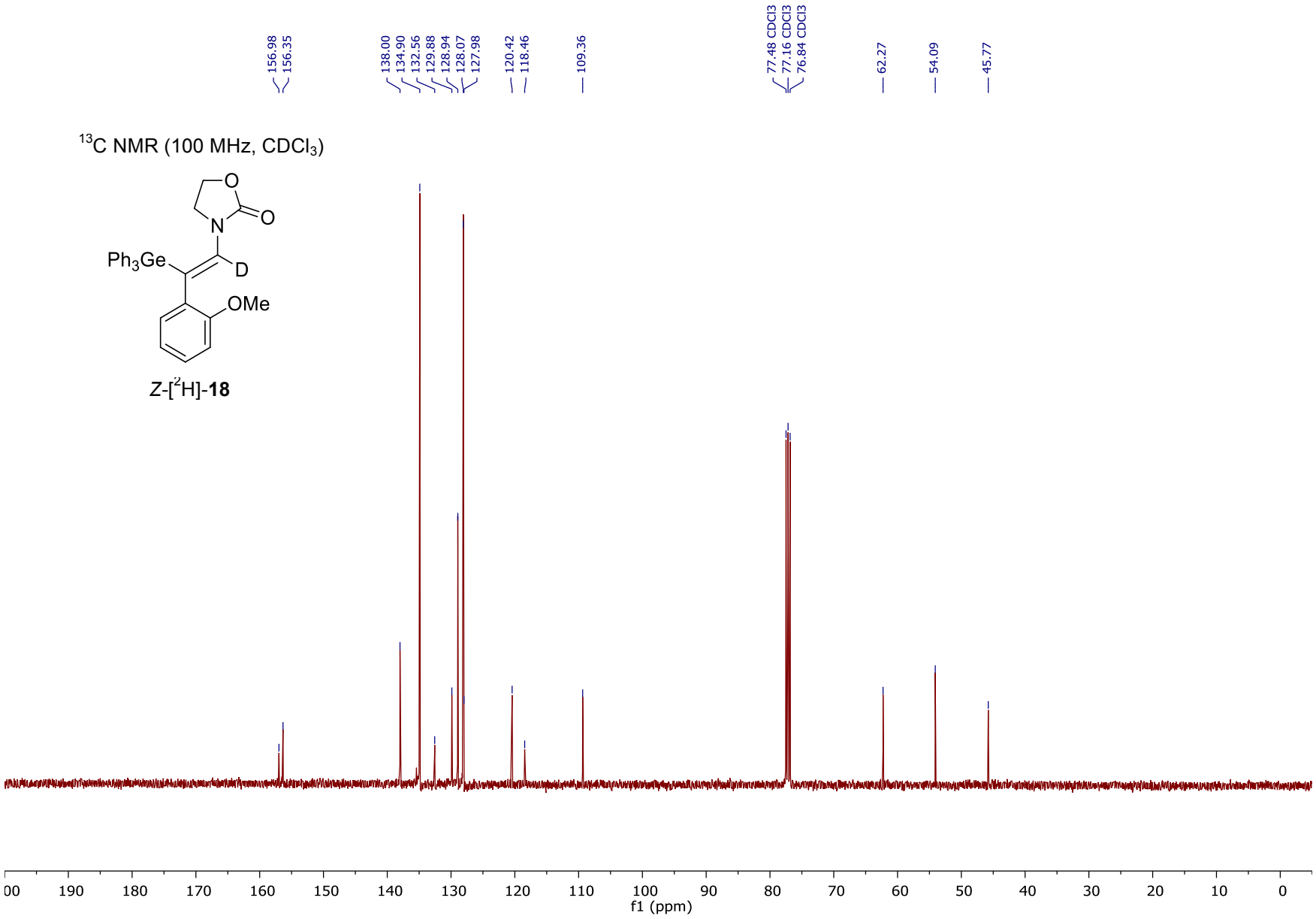
^{13}C NMR (100 MHz, $CDCl_3$)

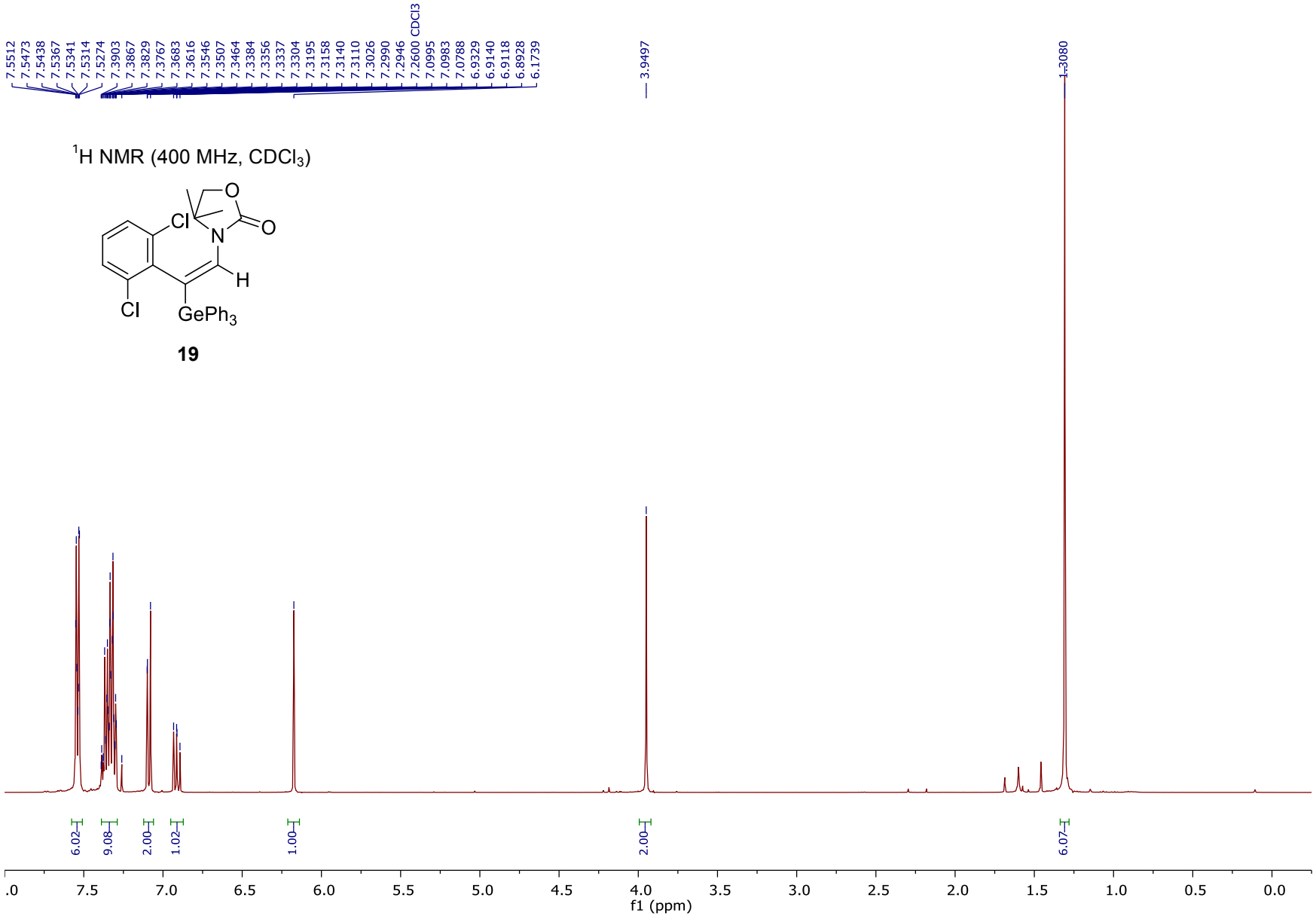
E-[^{2}H]-**18**



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

Z-[^{2}H]-**18**

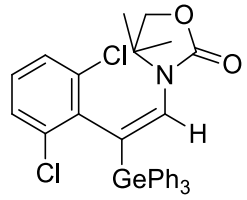

156.98
156.35
138.00
134.90
132.56
129.88
128.94
128.07
127.98
120.42
118.46
109.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.27
54.09
45.77
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph_3Ge
D
OMe
Z-[^{2}H]-**18**
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



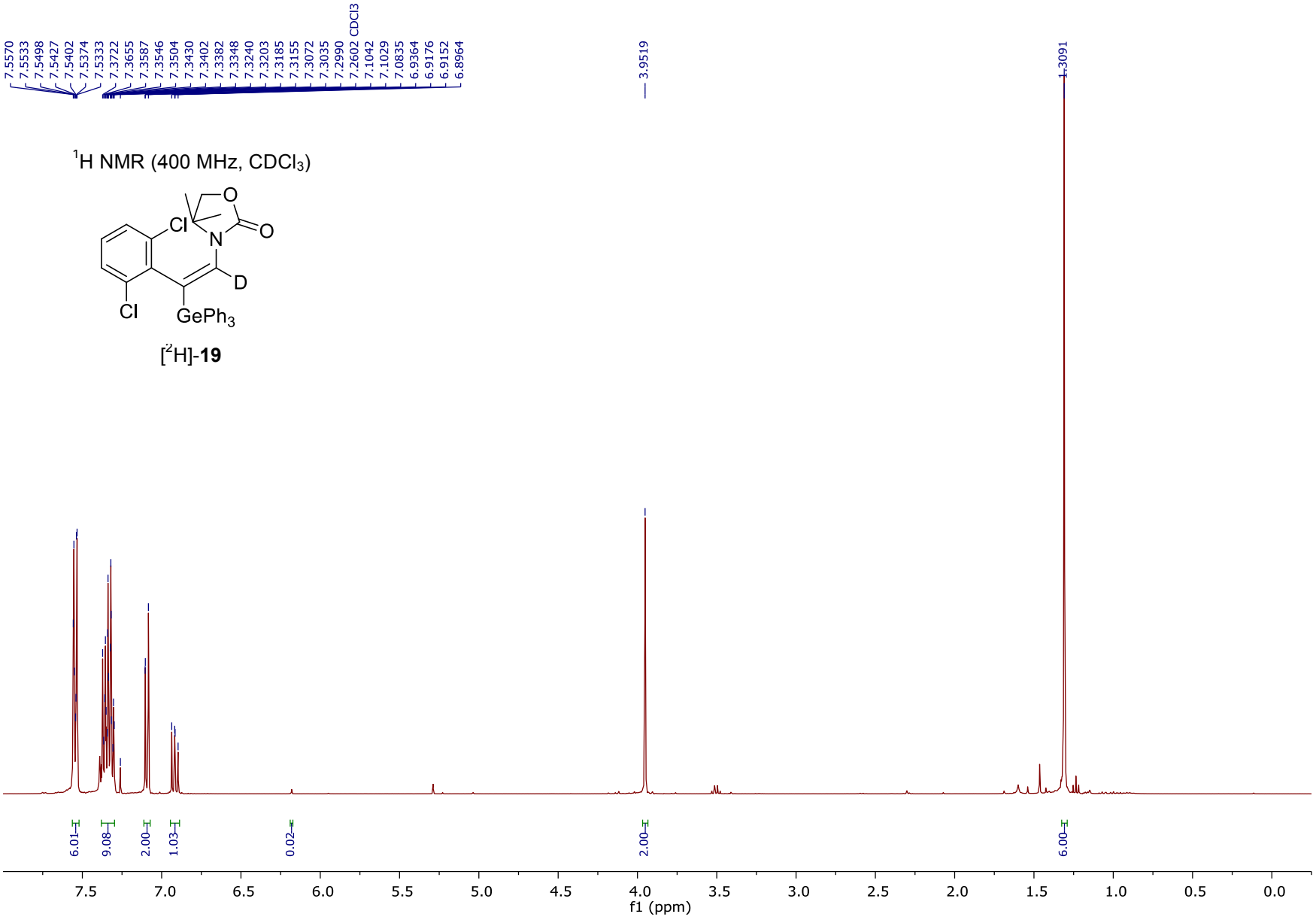
^{1}H NMR (400 MHz, $CDCl_3$)

19

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

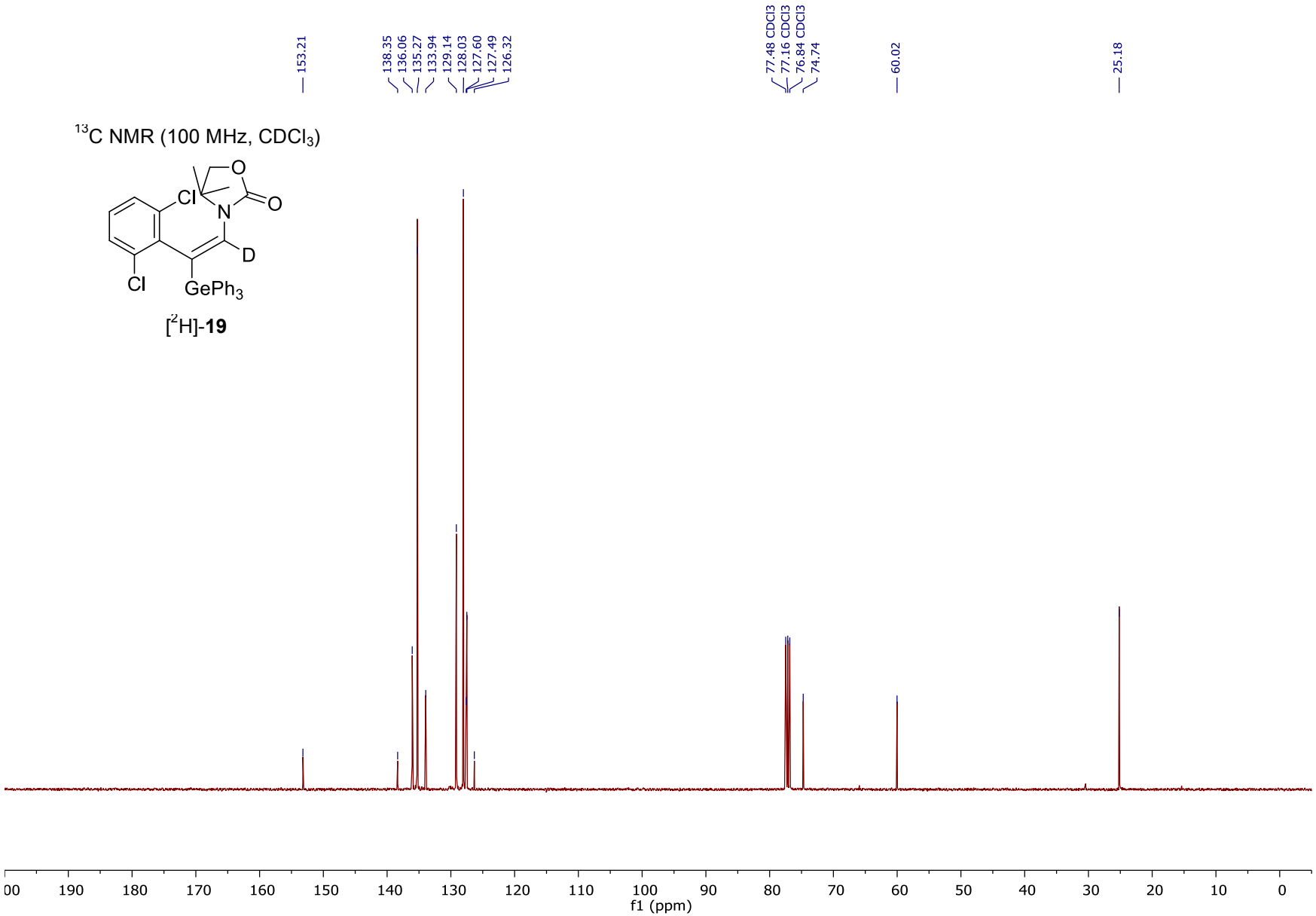


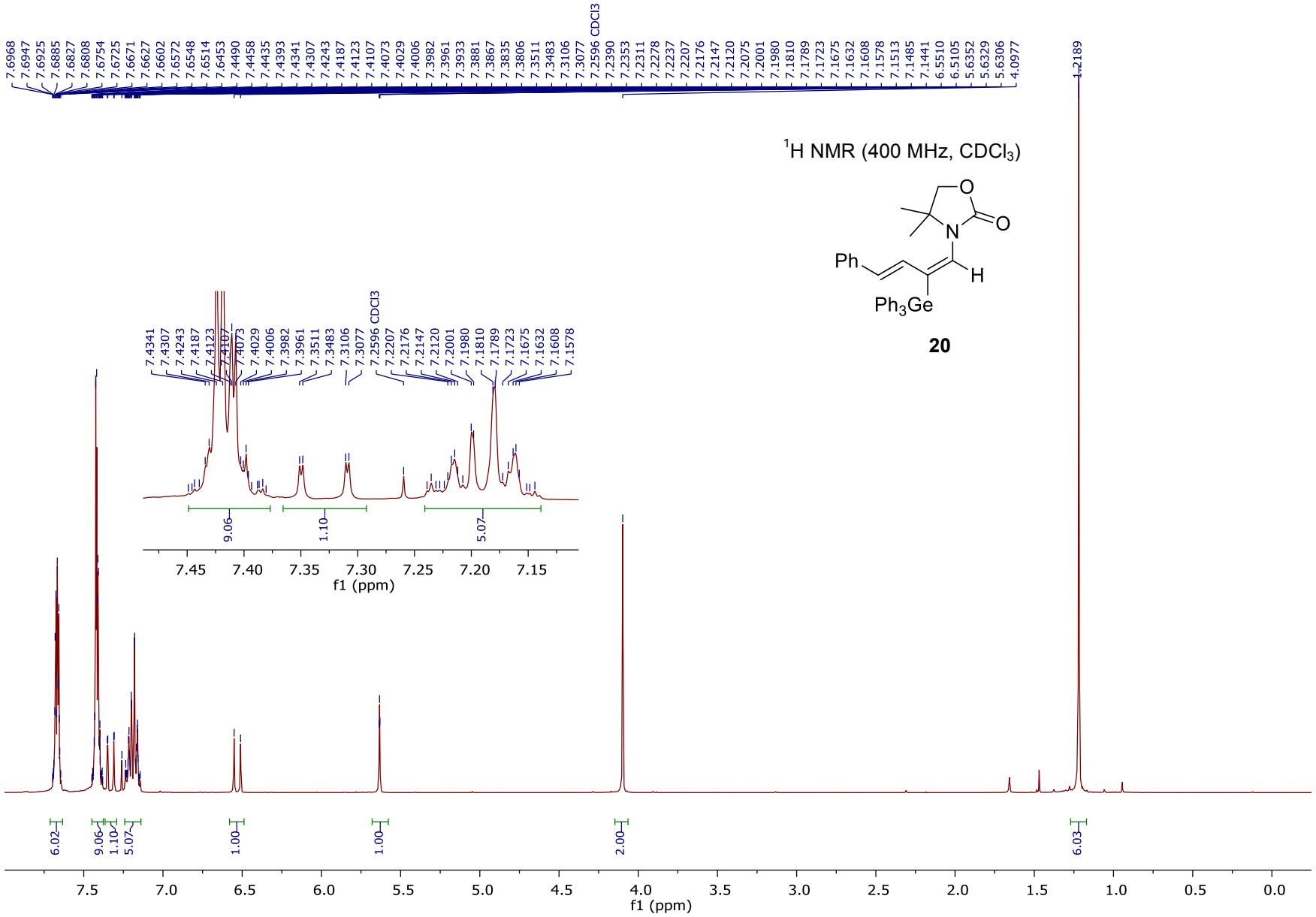
19

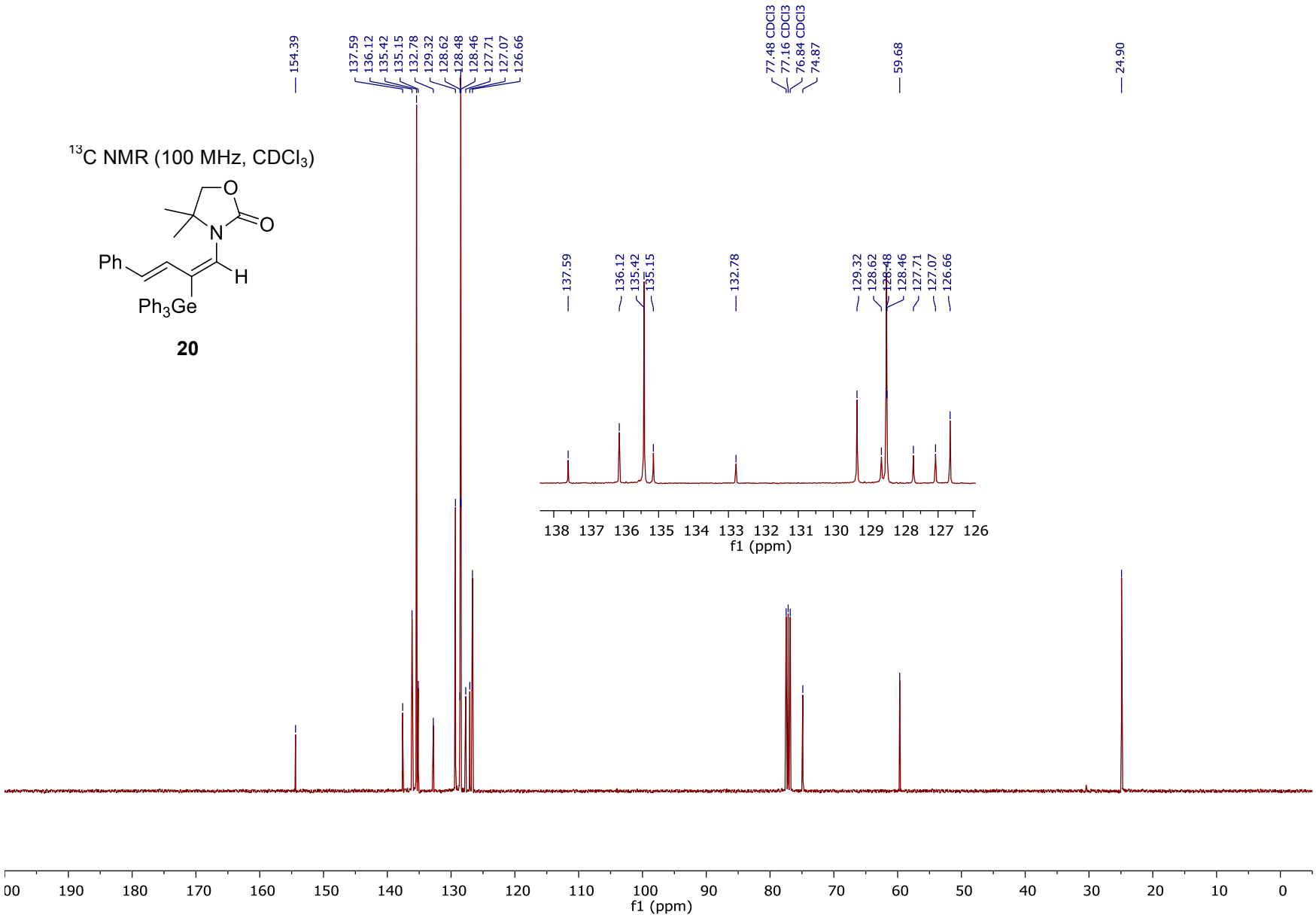


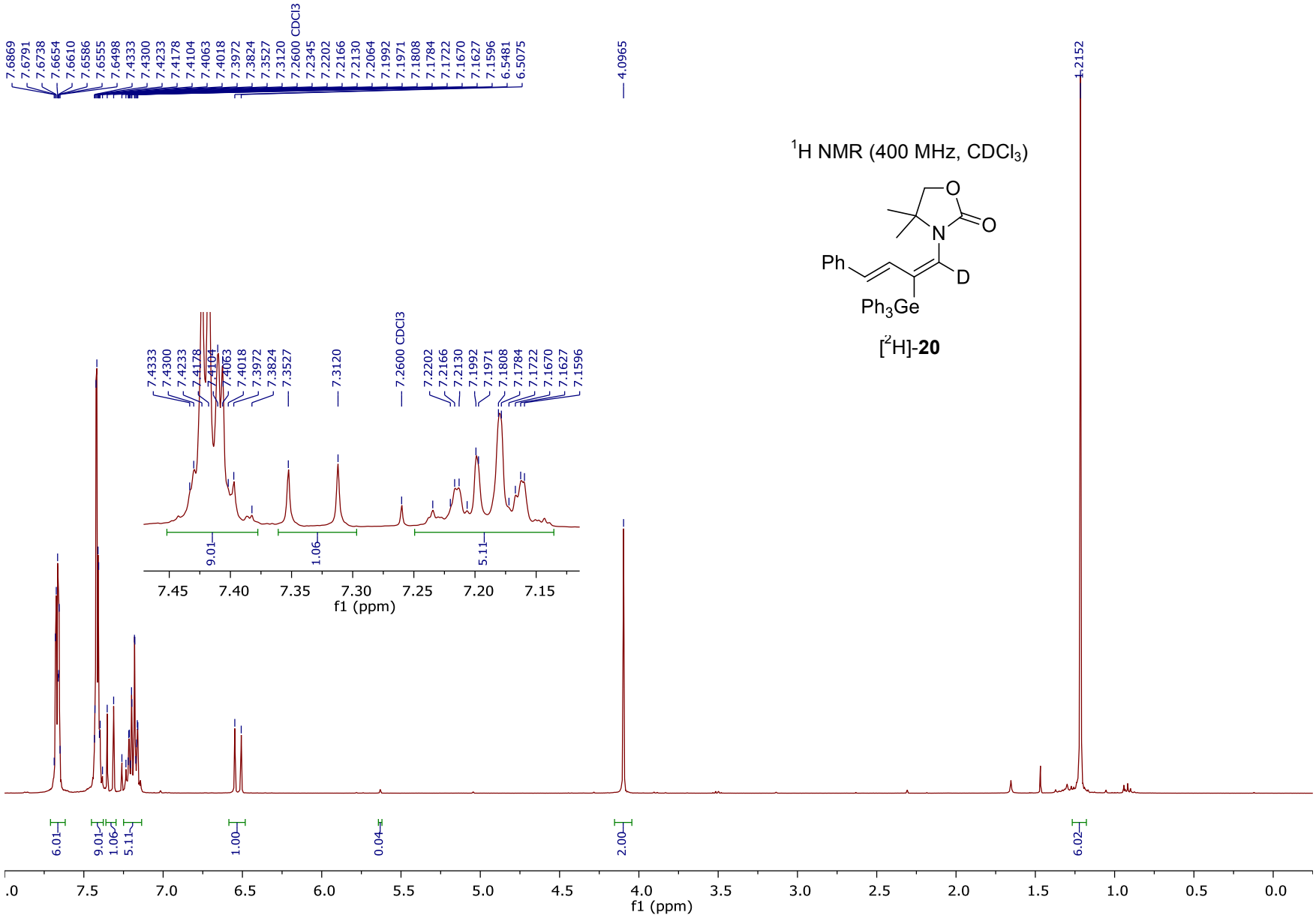
^{1}H NMR (400 MHz, $CDCl_3$)

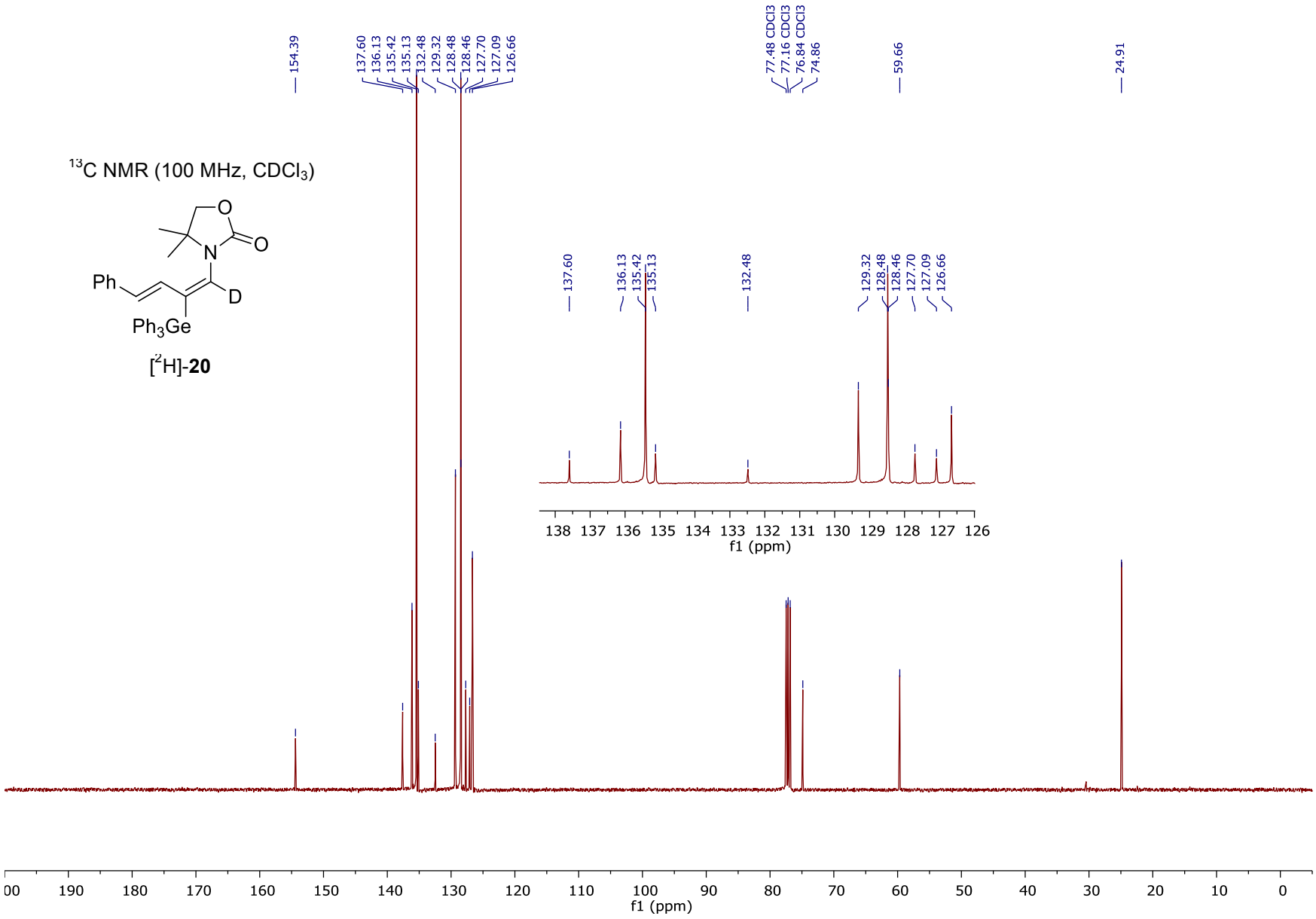
[^{2}H]-**19**

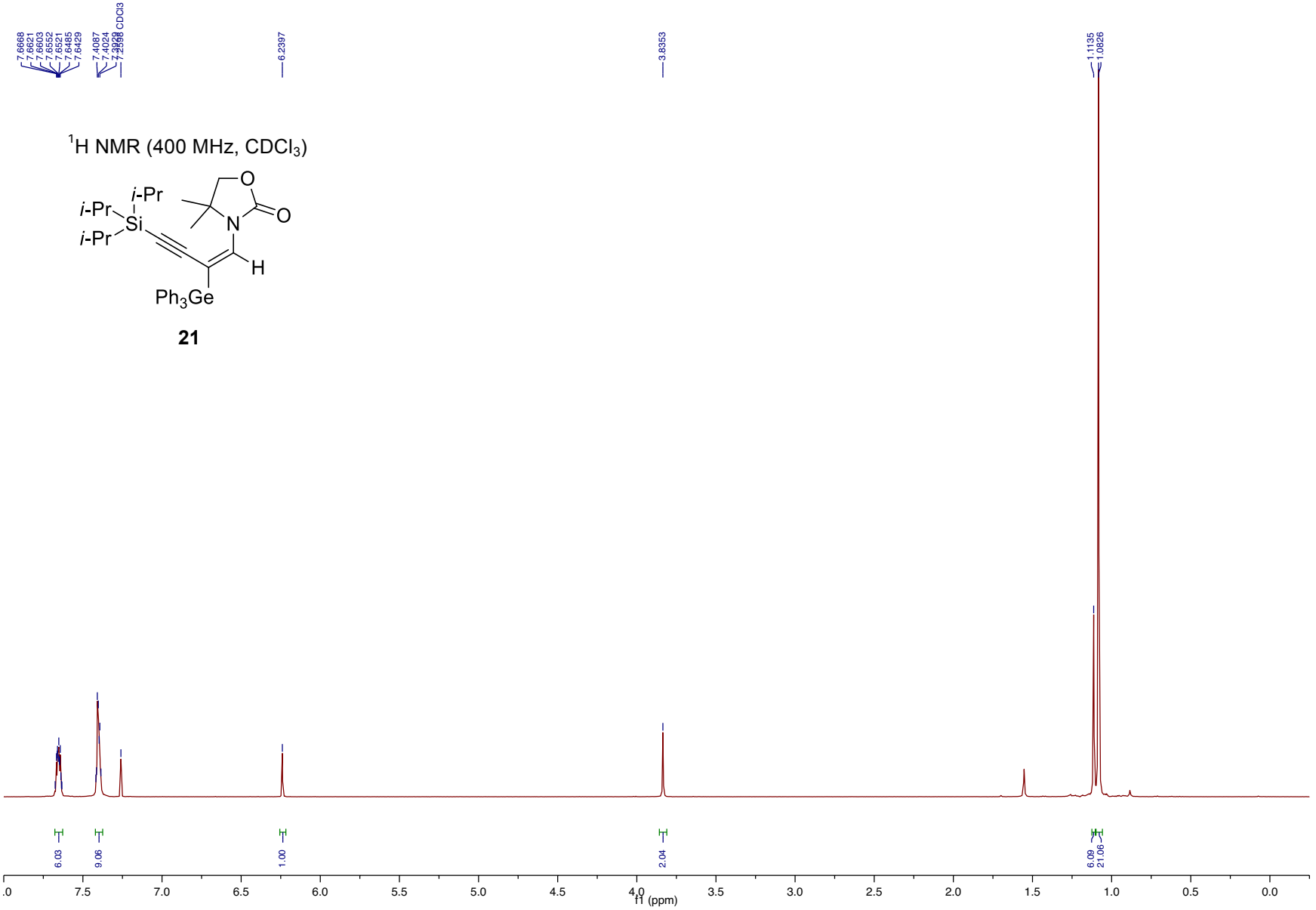

153.21
138.35
136.06
135.27
133.94
129.14
128.03
127.60
127.49
126.32
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.74
60.02
25.18
^{13}C NMR (100 MHz, $CDCl_3$)
O
Cl
N
O
D
Cl
$GePh_3$
[^{2}H]-**19**
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


^{1}H NMR (400 MHz, $CDCl_3$)
Ph
H
Ph_3Ge
O
N
O
20
CDCl3
f1 (ppm)


154.39
137.59
136.12
135.42
135.15
132.78
129.32
128.62
128.48
128.46
127.71
127.07
126.66
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.87
59.68
24.90
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph
H
Ph_3Ge
20
f1 (ppm)
f1 (ppm)

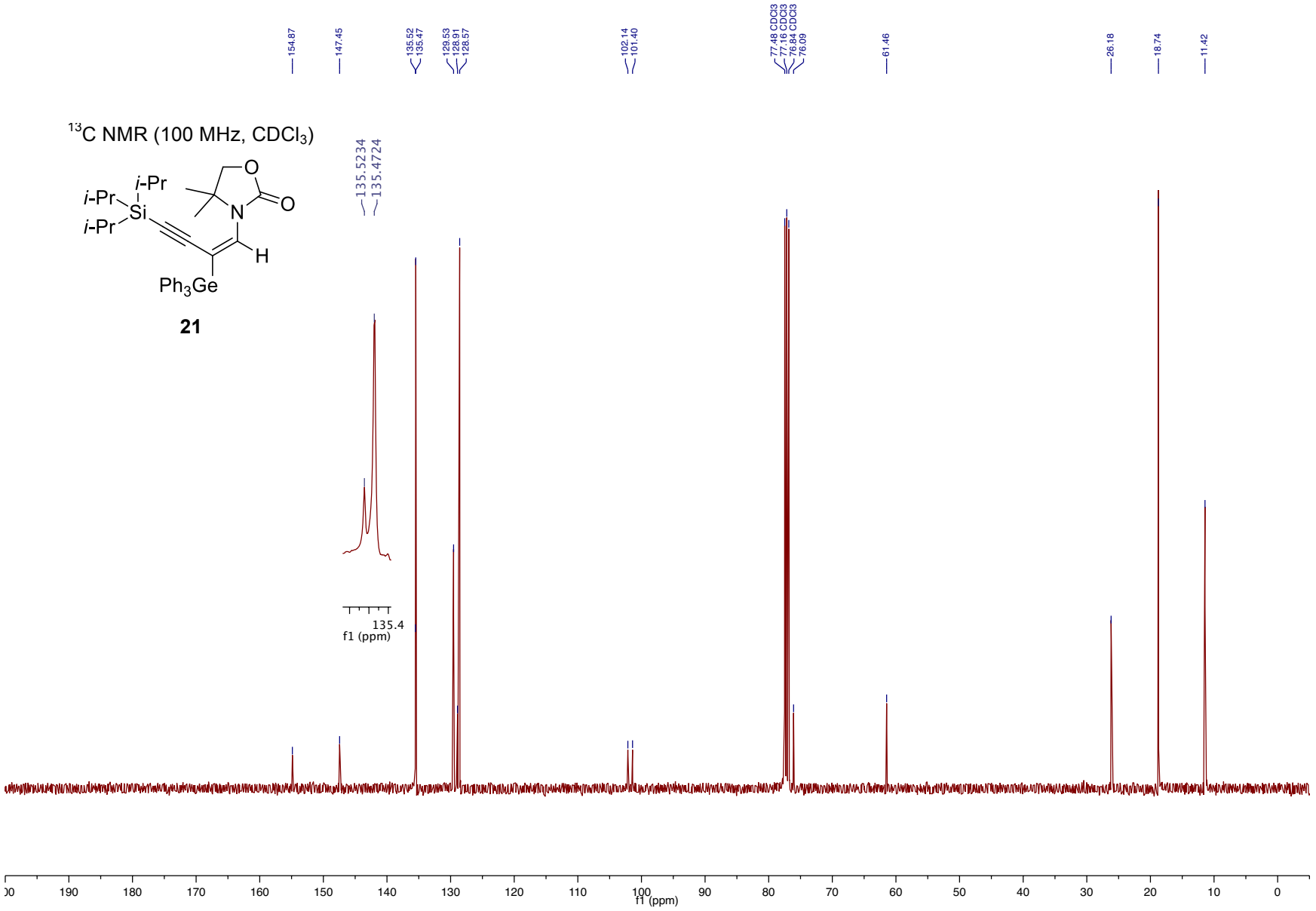

7.6869
7.6791
7.6738
7.6654
7.6610
7.6586
7.6555
7.6498
7.4333
7.4300
7.4233
7.4178
7.4104
7.4063
7.4018
7.3972
7.3824
7.3527
7.3120
7.2600 CDCl3
7.2345
7.2202
7.2166
7.2130
7.2064
7.1992
7.1971
7.1808
7.1784
7.1722
7.1670
7.1627
7.1596
6.5481
6.5075
4.0965
1.2152
[1]H NMR (400 MHz, CDCl3)
O
O
N
Ph
D
Ph3Ge
[2H]-20
9.01
1.06
5.11
7.45
7.40
7.35
7.30
7.25
7.20
7.15
f1 (ppm)
6.01
9.01
1.06
5.11
1.00
0.04
2.00
6.02
.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
f1 (ppm)


154.39
137.60
136.13
135.42
135.13
132.48
129.32
128.48
128.46
127.70
127.09
126.66
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.86
59.66
24.91
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph
D
Ph_3Ge
[^{2}H]-**20**
f1 (ppm)
f1 (ppm)



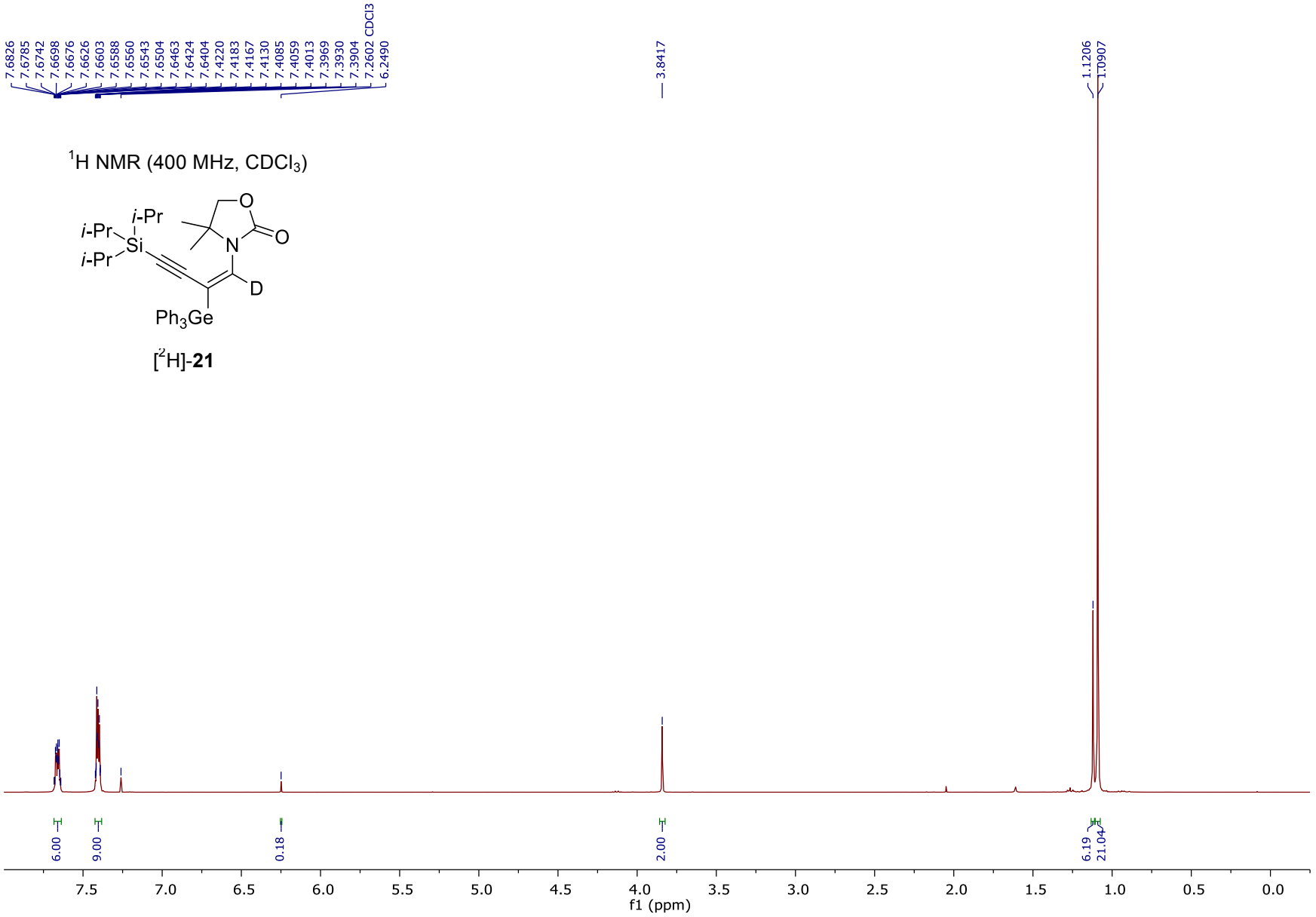
^{1}H NMR (400 MHz, $CDCl_3$)

21



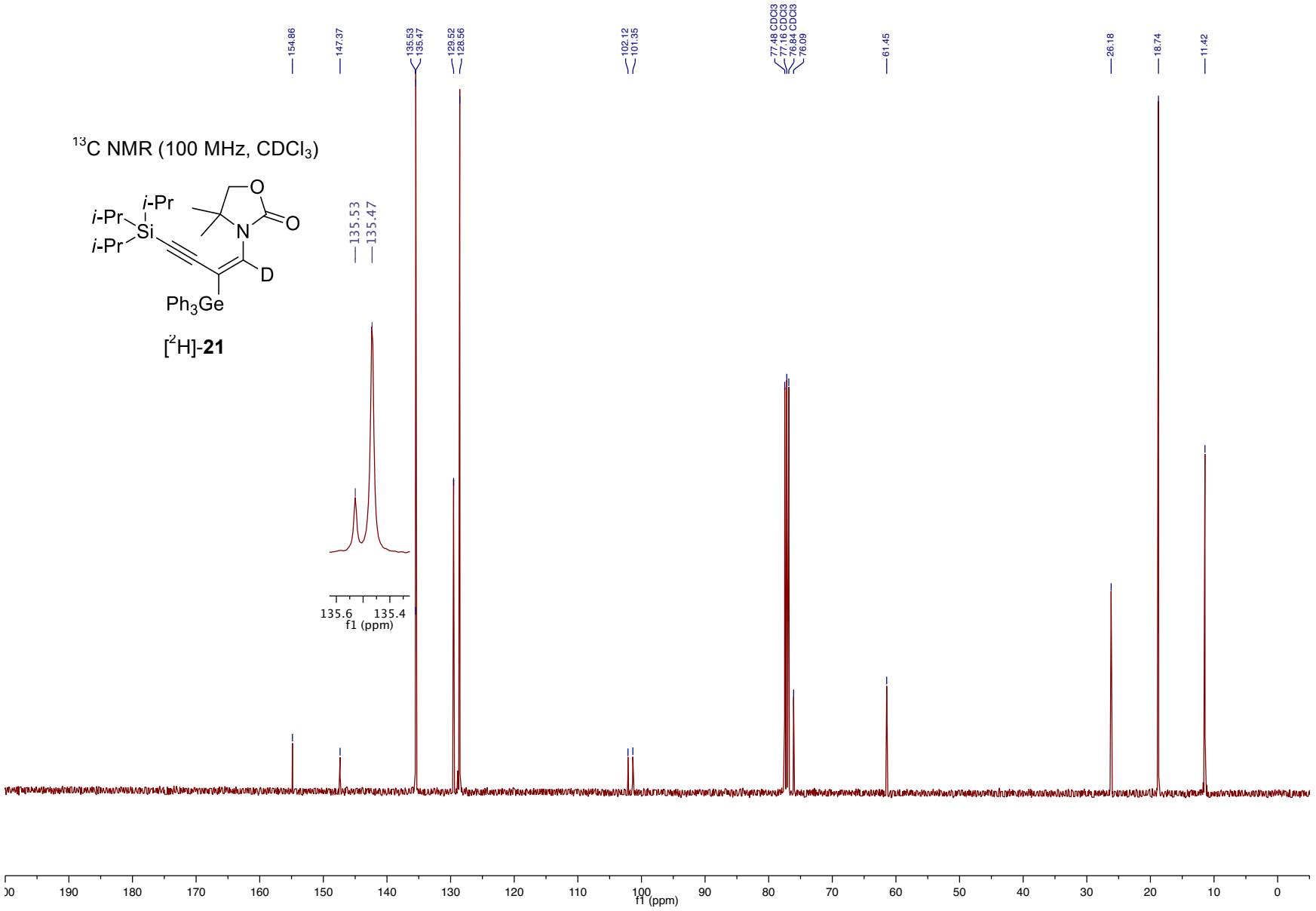
^{13}C NMR (100 MHz, $CDCl_3$)

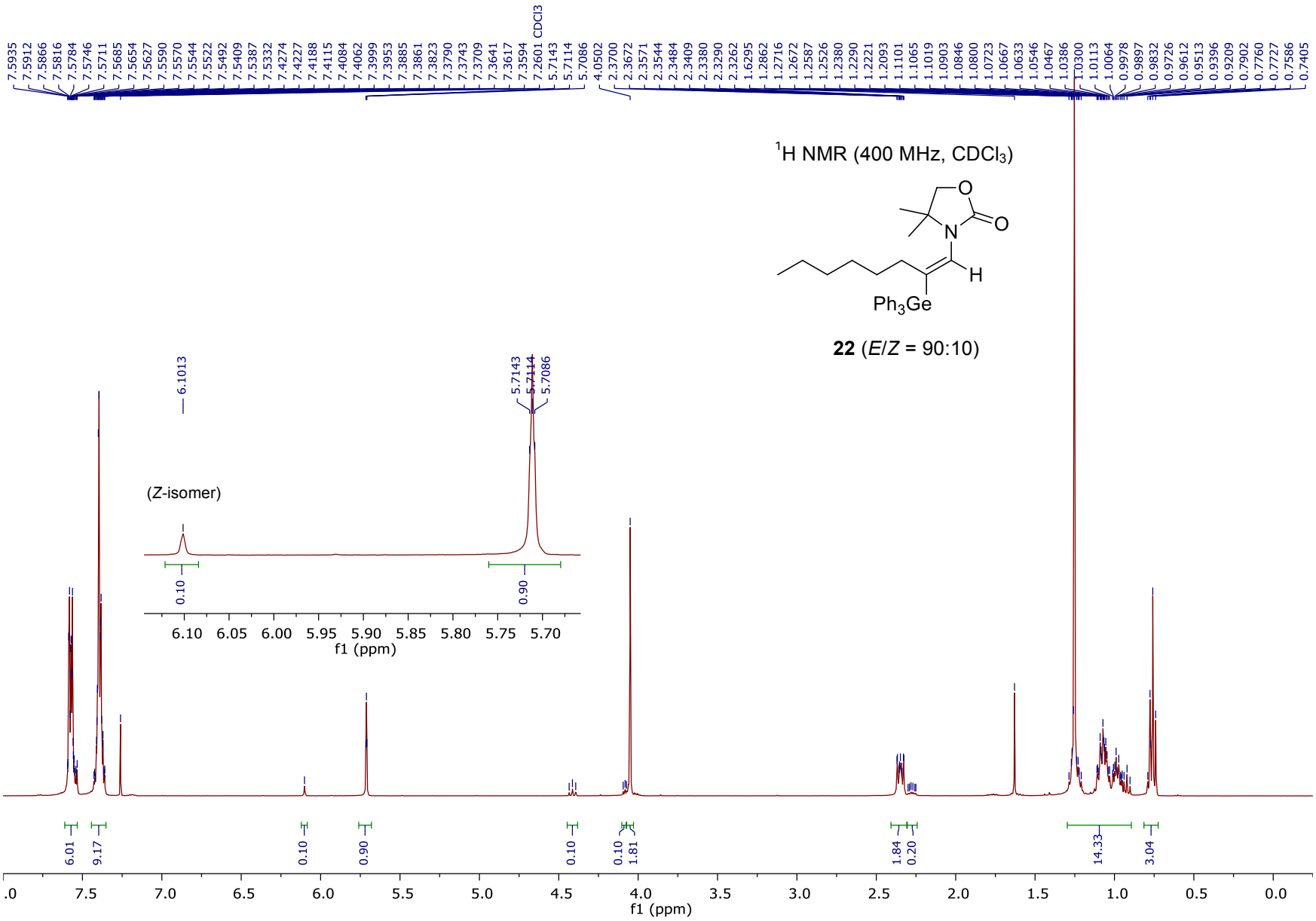
21

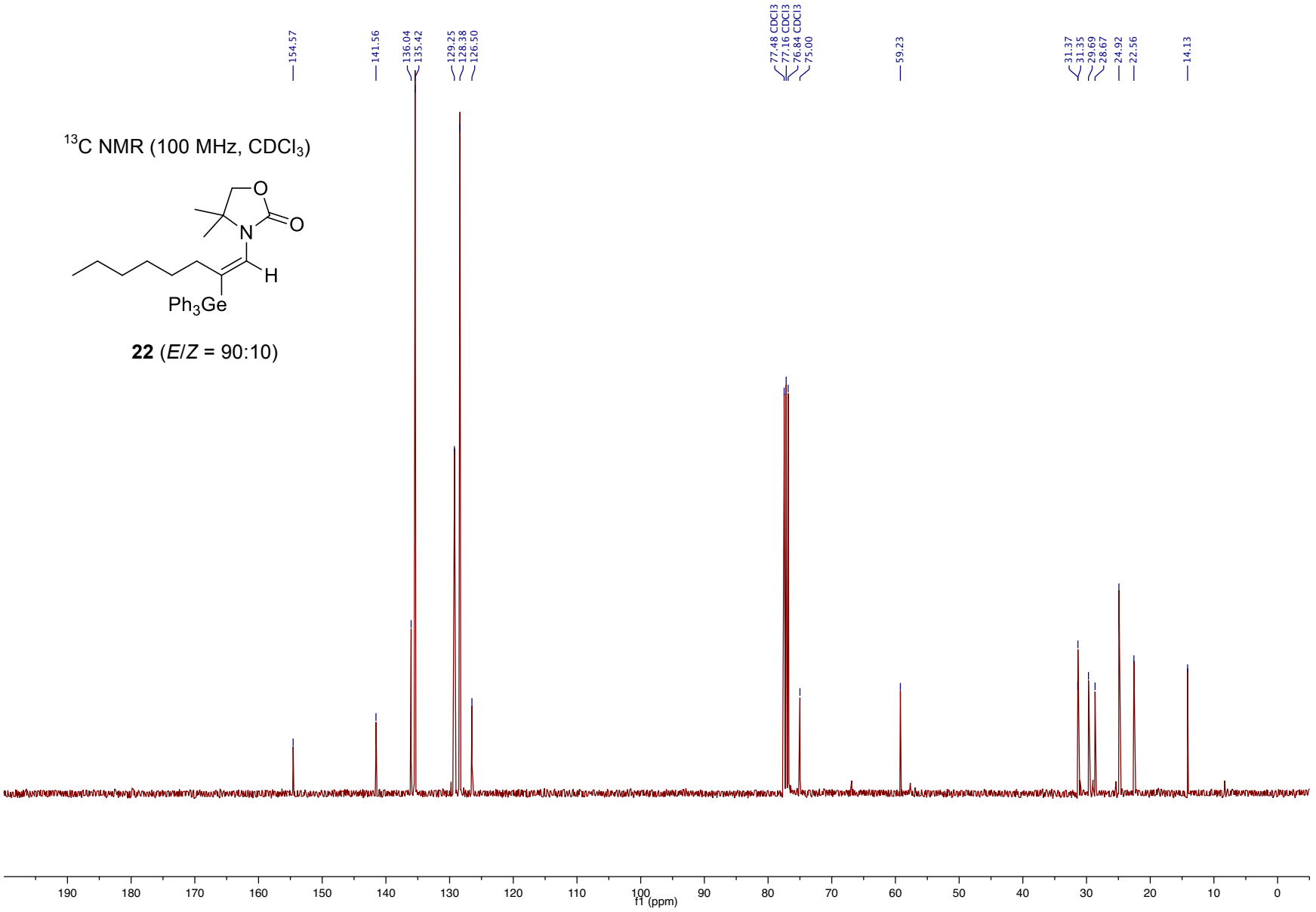


^{1}H NMR (400 MHz, $CDCl_3$)

[^{2}H]-**21**

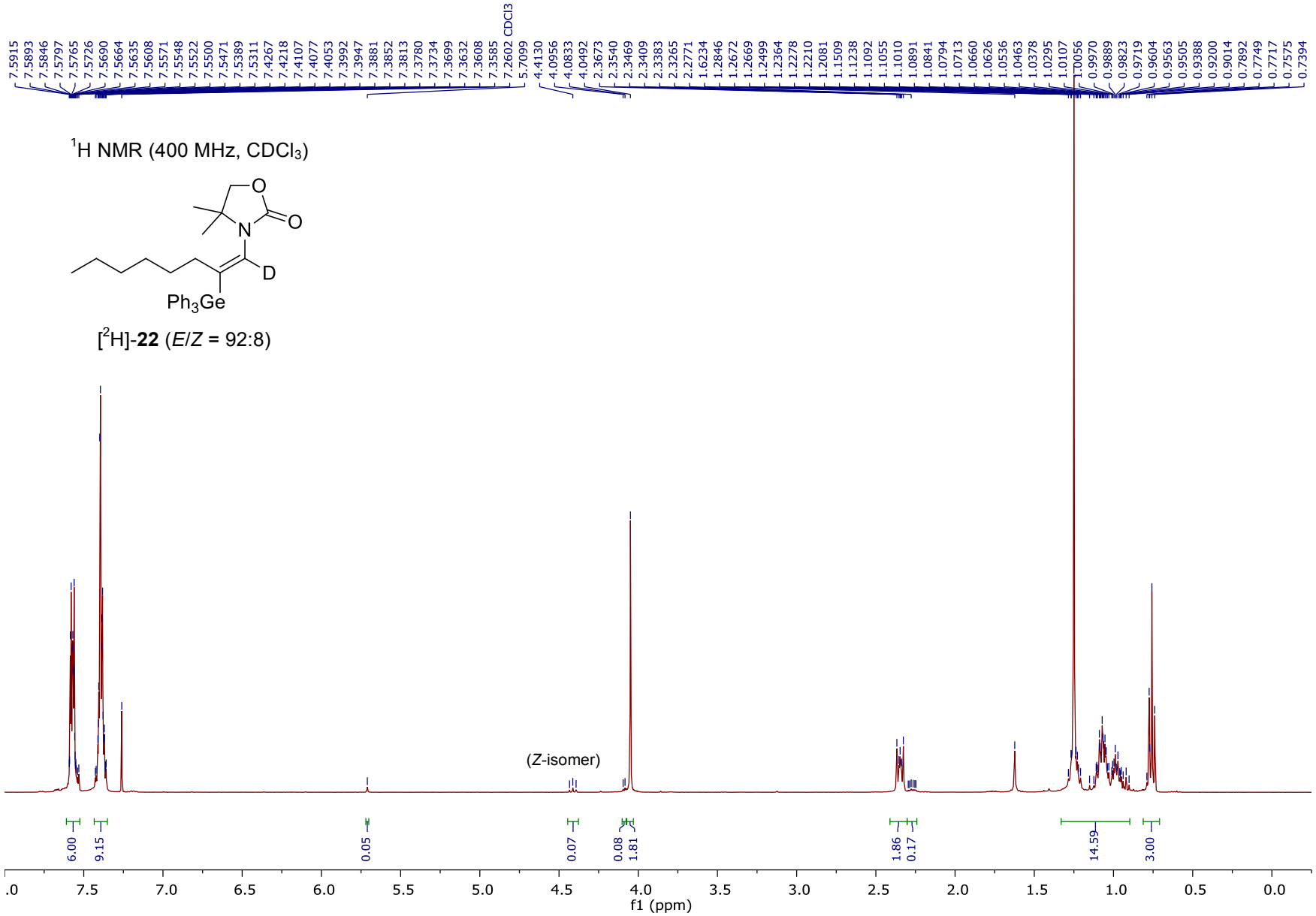

154.86
147.37
135.53
135.47
129.52
128.56
102.12
101.35
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.09
61.45
26.18
18.74
11.42
^{13}C NMR (100 MHz, $CDCl_3$)
i-Pr
i-Pr
Si
i-Pr
O
O
N
D
Ph_3Ge
[^{2}H]-**21**
135.6
135.4
f1 (ppm)
f1 (ppm)

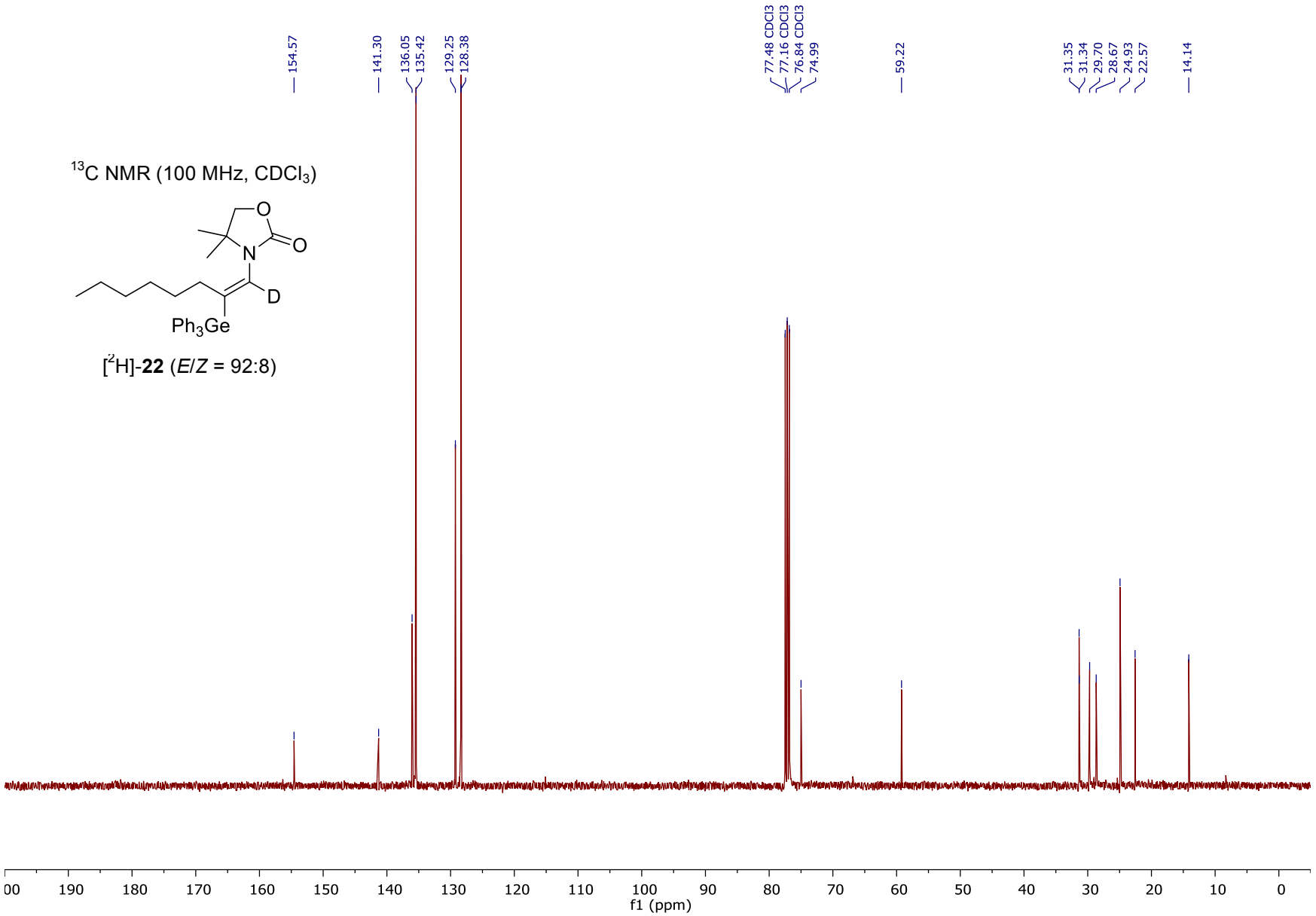

^{1}H NMR (400 MHz, $CDCl_3$)
22 (*E*/*Z* = 90:10)
(*Z*-isomer)
f1 (ppm)

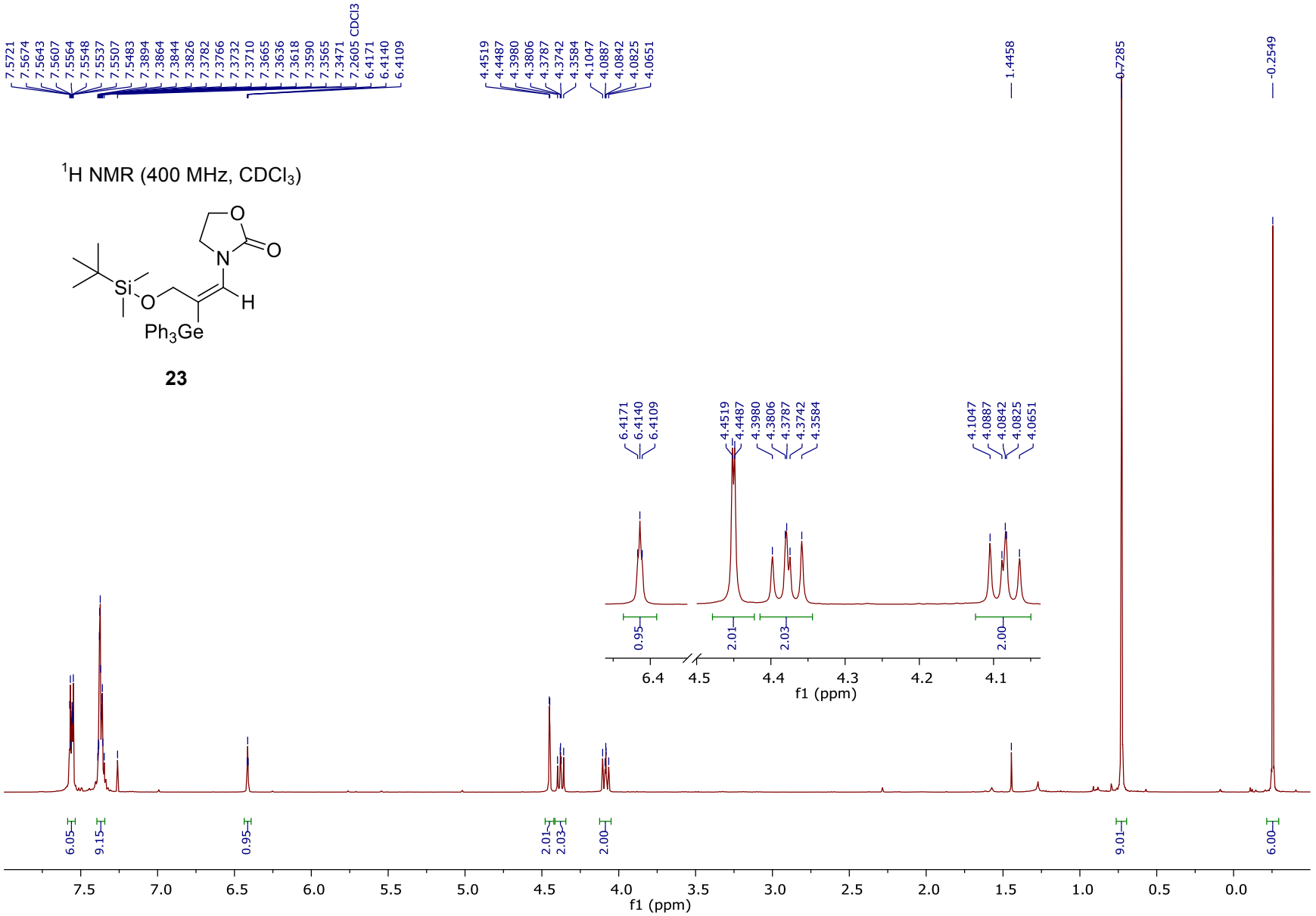


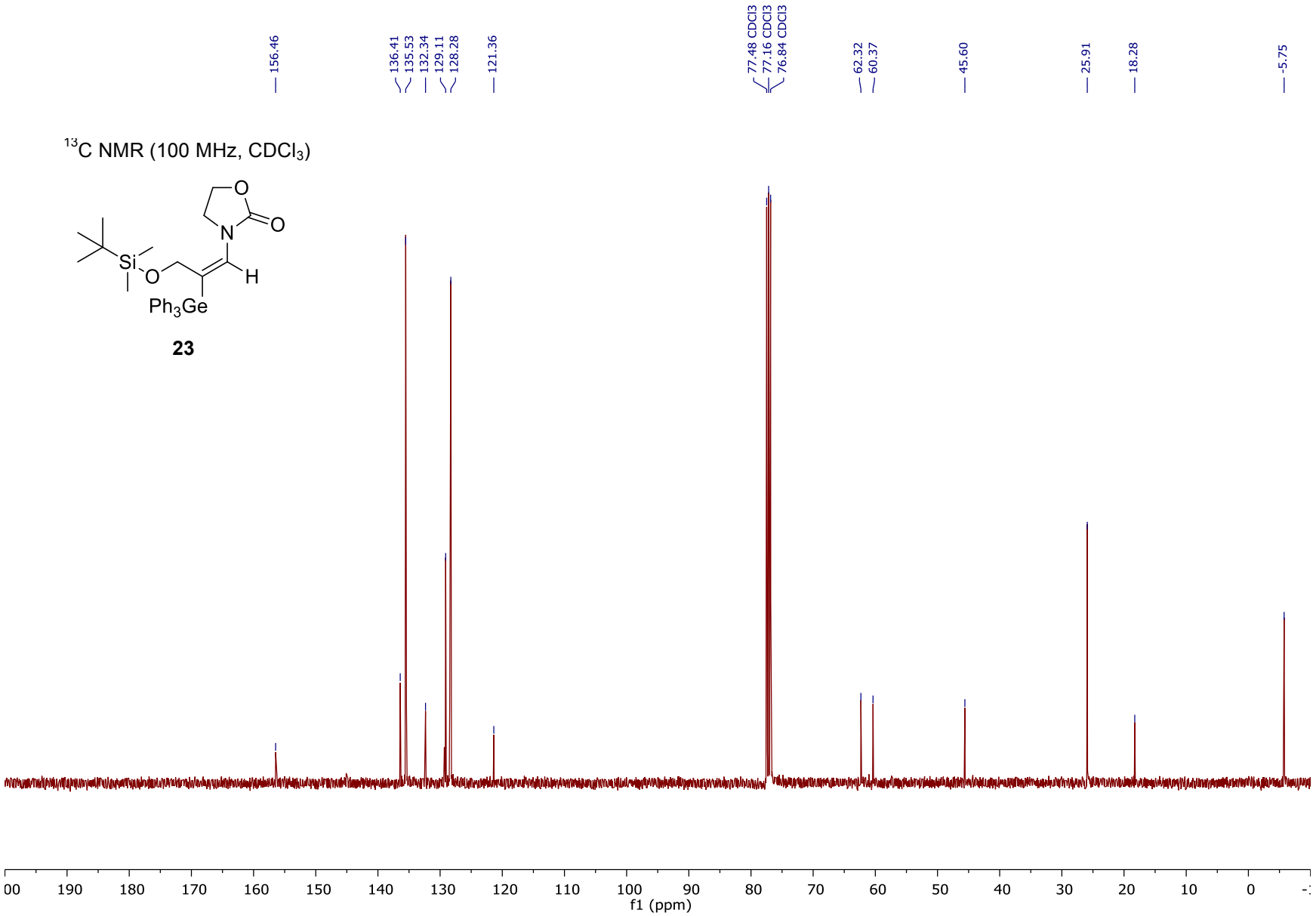
^{13}C NMR (100 MHz, $CDCl_3$)

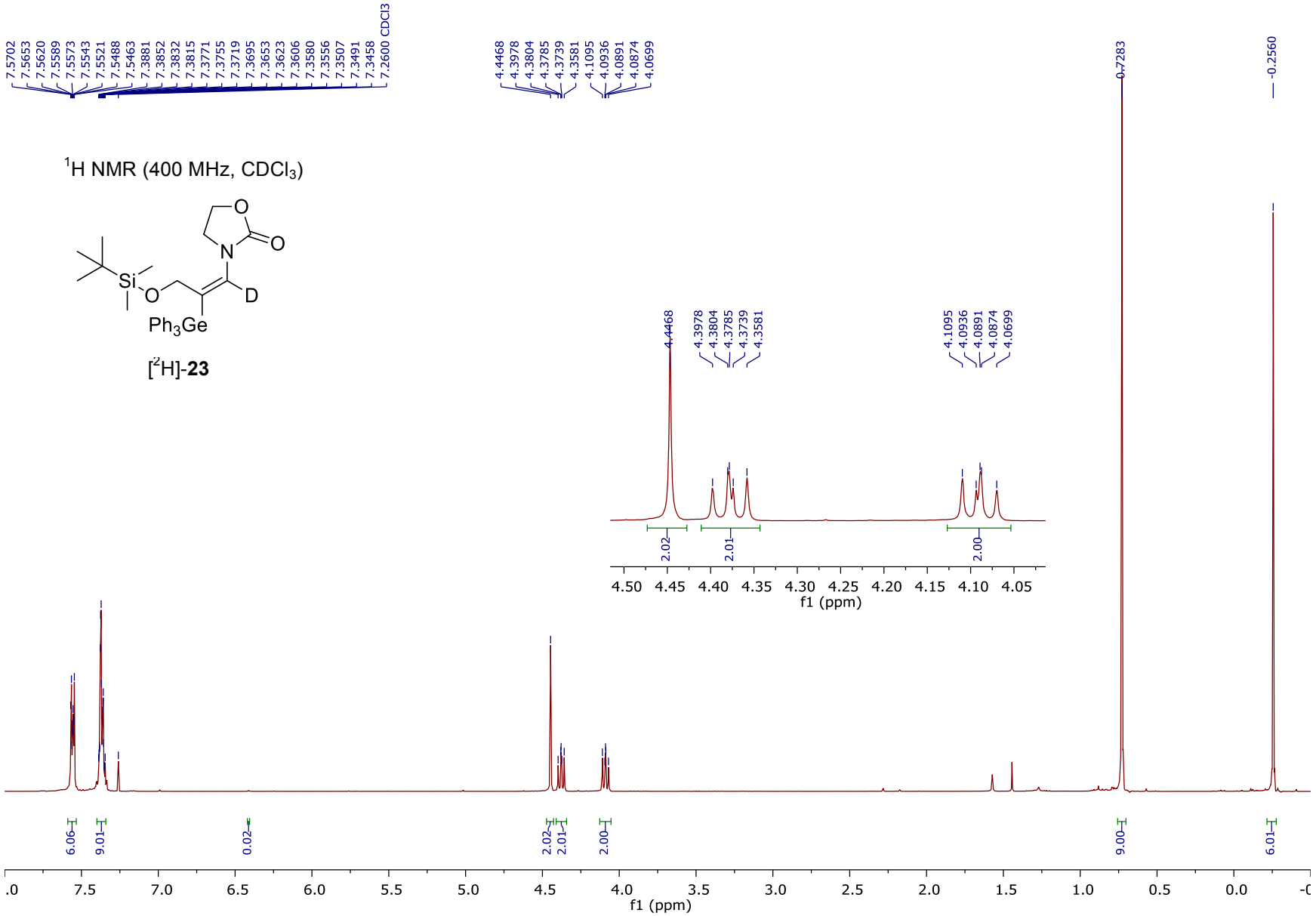
22 (*E*/*Z* = 90:10)

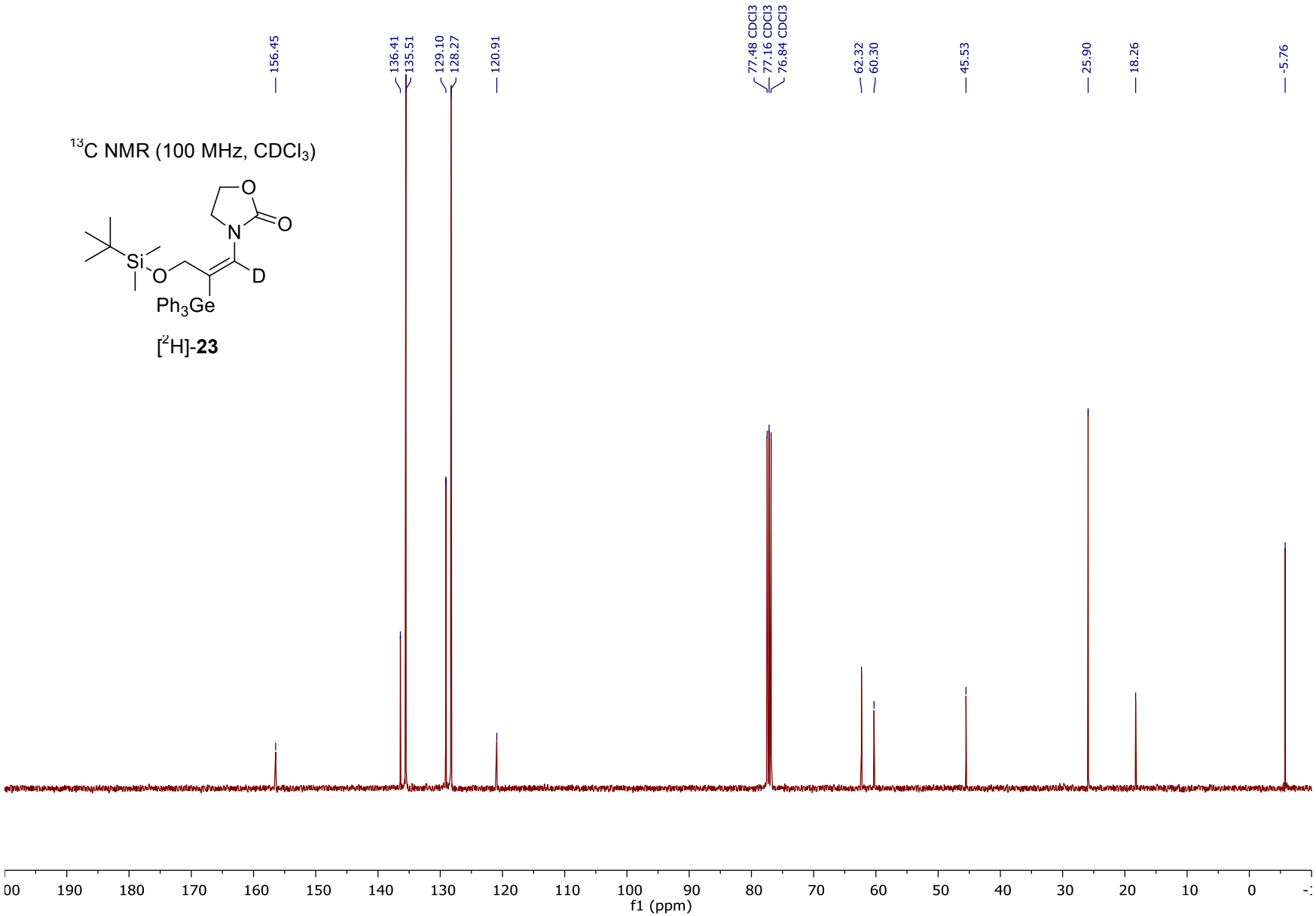

7.5915 7.5893 7.5846 7.5797 7.5765 7.5726 7.5690 7.5664 7.5635 7.5608 7.5571 7.5548 7.5522 7.5500 7.5471 7.5389 7.5311 7.4267 7.4218 7.4107 7.4077 7.4053 7.3992 7.3947 7.3881 7.3852 7.3813 7.3780 7.3734 7.3699 7.3632 7.3608 7.3585 7.2602 CDCl3 5.7099 4.4130 4.0956 4.0833 4.0492 2.3673 2.3540 2.3469 2.3409 2.3383 2.3265 2.2771 1.6234 1.2846 1.2672 1.2669 1.2499 1.2364 1.2278 1.2210 1.2081 1.1509 1.1238 1.1092 1.1055 1.1010 1.0891 1.0841 1.0794 1.0713 1.0660 1.0626 1.0536 1.0463 1.0378 1.0295 1.0107 1.0056 0.9970 0.9889 0.9823 0.9719 0.9604 0.9563 0.9505 0.9388 0.9200 0.9014 0.7892 0.7749 0.7717 0.7575 0.7394
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
O
D
Ph_3Ge
[^{2}H]-**22** (*E*/*Z* = 92:8)
(*Z*-isomer)
6.00
9.15
0.05
0.07
0.08
1.81
1.86
0.17
14.59
3.00
.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
f1 (ppm)


154.57
141.30
136.05
135.42
129.25
128.38
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.99
59.22
31.35
31.34
29.70
28.67
24.93
22.57
14.14
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
D
Ph_3Ge
[^{2}H]-**22** (*E*/*Z* = 92:8)
f1 (ppm)


7.5721
7.5674
7.5643
7.5607
7.5564
7.5548
7.5537
7.5507
7.5483
7.3894
7.3864
7.3844
7.3826
7.3782
7.3766
7.3732
7.3710
7.3665
7.3636
7.3618
7.3590
7.3565
7.3471
7.2605 CDCl3
6.4171
6.4140
6.4109
4.4519
4.4487
4.3980
4.3806
4.3787
4.3742
4.3584
4.1047
4.0887
4.0842
4.0825
4.0651
1.4458
0.7285
-0.2549
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
Si
O
H
Ph_3Ge
23
0.95
2.01
2.03
2.00
6.4
4.5
4.4
4.3
4.2
4.1
f1 (ppm)
6.05
9.15
0.95
2.01
2.03
2.00
9.01
6.00
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
f1 (ppm)


156.46
136.41
135.53
132.34
129.11
128.28
121.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.32
60.37
45.60
25.91
18.28
-5.75
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Si
O
H
Ph_3Ge
23
f1 (ppm)

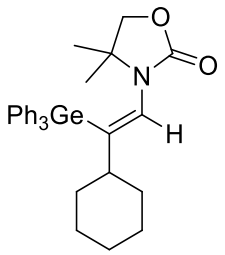

7.5702
7.5653
7.5620
7.5589
7.5573
7.5543
7.5521
7.5488
7.5463
7.3881
7.3852
7.3832
7.3815
7.3771
7.3755
7.3719
7.3695
7.3653
7.3623
7.3606
7.3580
7.3556
7.3507
7.3491
7.3458
7.2600 CDCl3
4.4468
4.3978
4.3804
4.3785
4.3739
4.3581
4.1095
4.0936
4.0891
4.0874
4.0699
0.7283
-0.2560
1H NMR (400 MHz, CDCl3)
O
O
N
Si
O
D
Ph3Ge
[2H]-23
2.02
2.01
2.00
4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05
f1 (ppm)
6.06
9.01
0.02
2.02
2.01
2.00
9.00
6.01
.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
f1 (ppm)



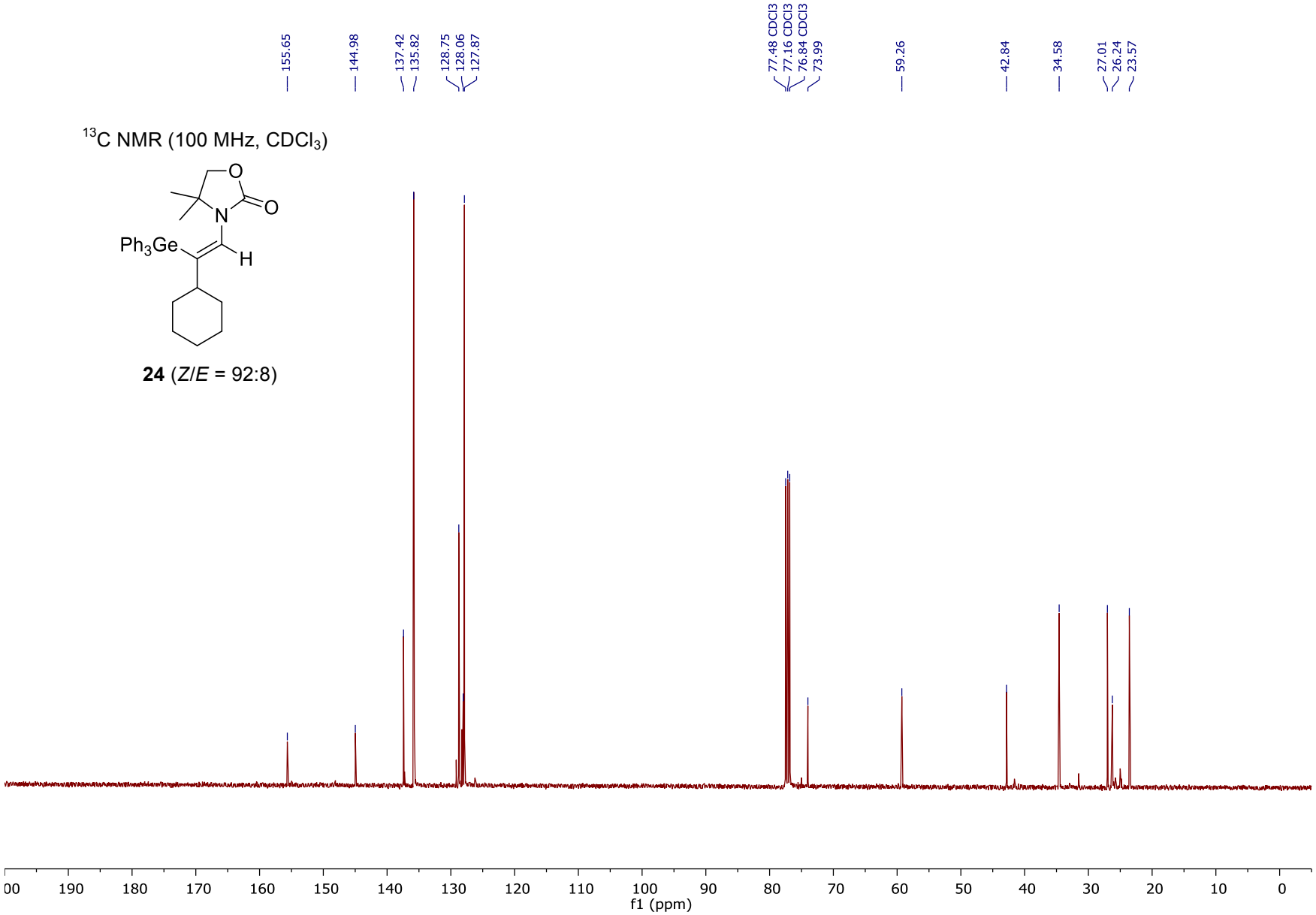
^{13}C NMR (100 MHz, $CDCl_3$)

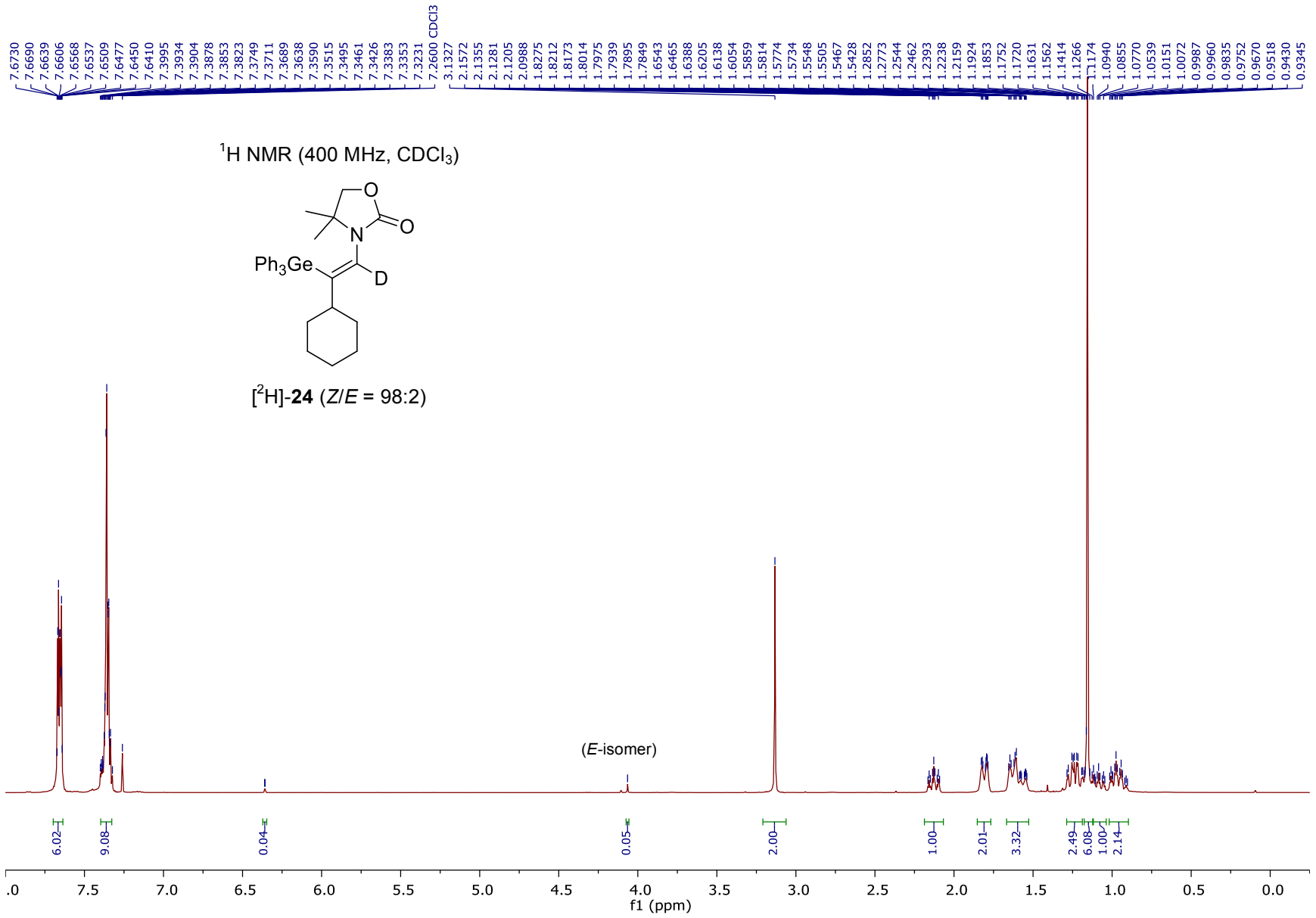
[^{2}H]-**23**

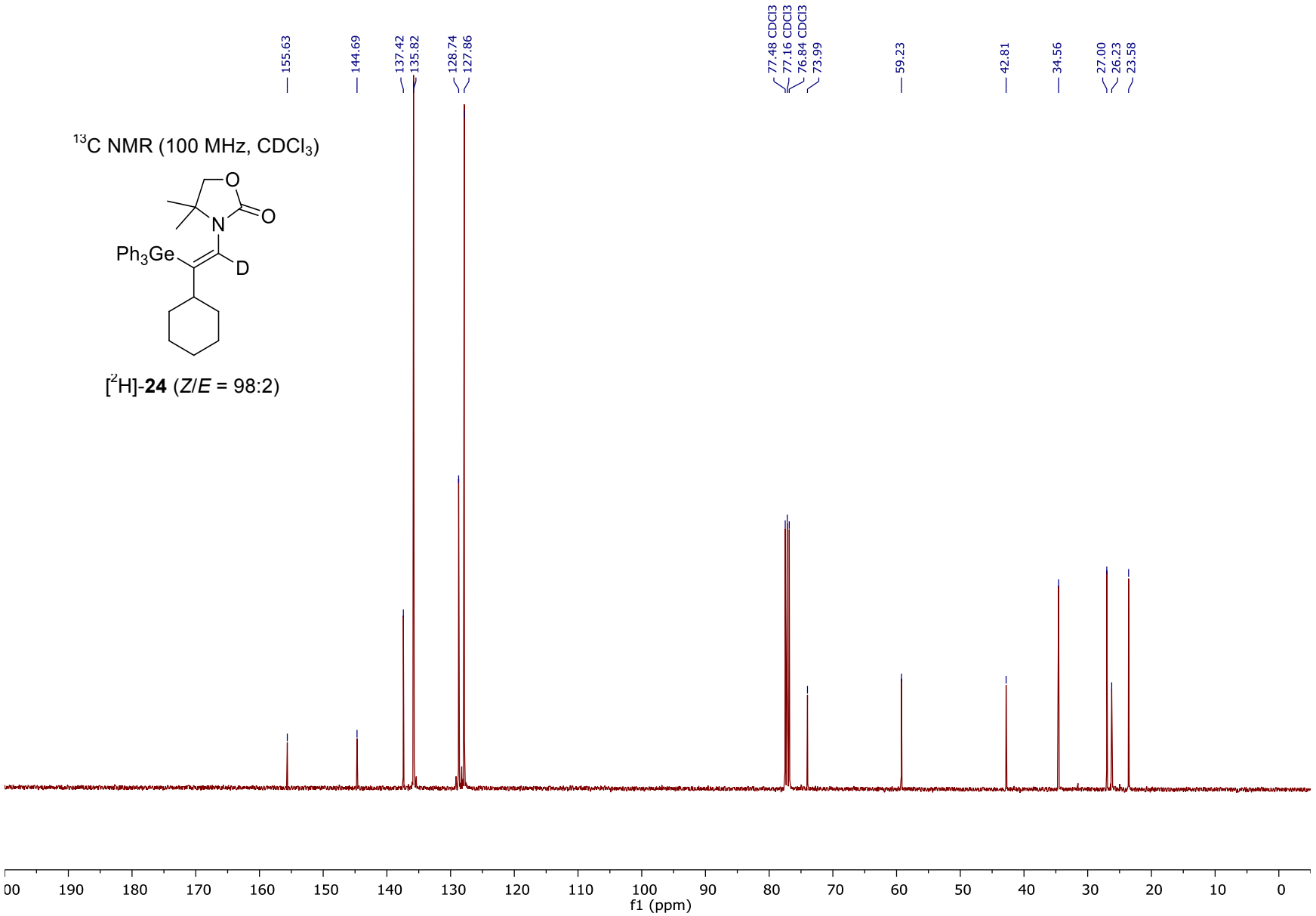
^{1}H NMR (400 MHz, $CDCl_3$)

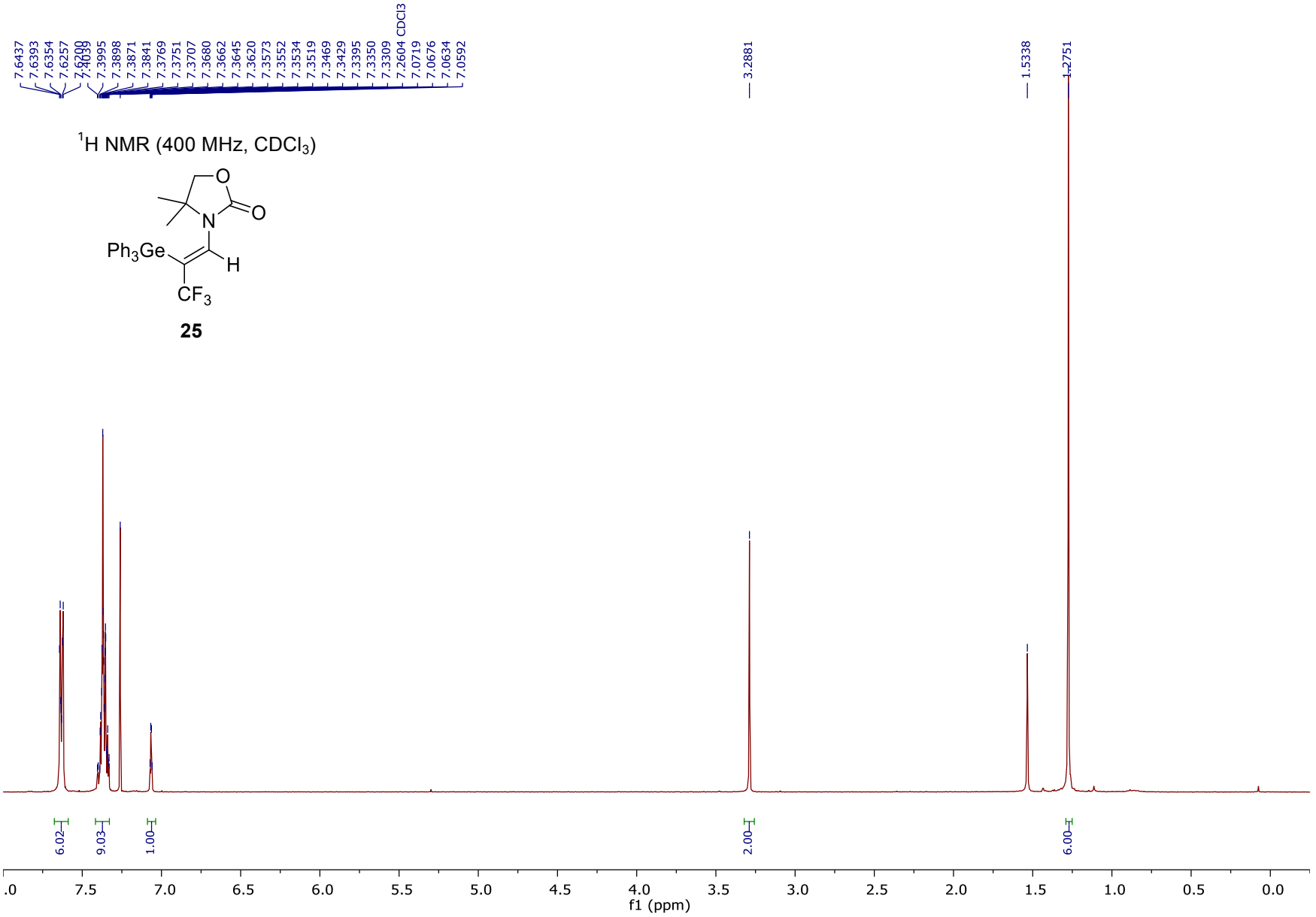


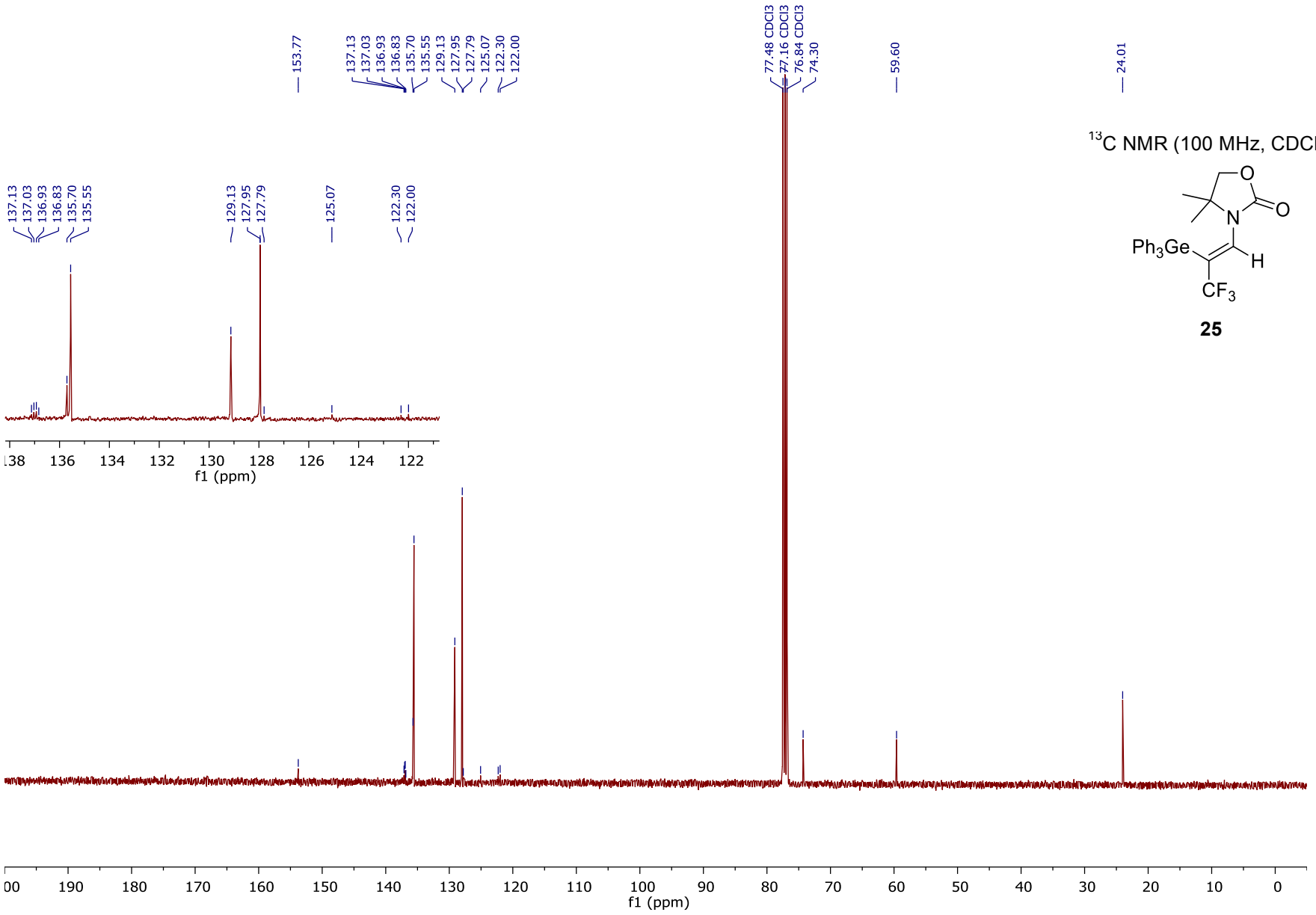
24 (*Z*/*E* = 92:8)


155.65
144.98
137.42
135.82
128.75
128.06
127.87
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.99
59.26
42.84
34.58
27.01
26.24
23.57
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph_3Ge
H
24 (*Z*/*E* = 92:8)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.6730 7.6690 7.6639 7.6606 7.6568 7.6537 7.6509 7.6477 7.6450 7.6410 7.3995 7.3934 7.3904 7.3878 7.3853 7.3823 7.3749 7.3711 7.3689 7.3638 7.3590 7.3515 7.3495 7.3461 7.3426 7.3383 7.3353 7.3231 7.2600 CDCl3
3.1327 2.1572 2.1355 2.1281 2.1205 2.0988 1.8275 1.8212 1.8173 1.8014 1.7975 1.7939 1.7895 1.7849 1.6543 1.6465 1.6388 1.6205 1.6138 1.6054 1.5859 1.5814 1.5774 1.5734 1.5548 1.5505 1.5467 1.5428 1.2852 1.2773 1.2544 1.2462 1.2393 1.2238 1.2159 1.1924 1.1853 1.1752 1.1720 1.1631 1.1562 1.1414 1.1266 1.1174 1.0940 1.0855 1.0770 1.0539 1.0151 1.0072 0.9987 0.9960 0.9835 0.9752 0.9670 0.9518 0.9430 0.9345
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
Ph_3Ge
D
[^{2}H]-**24** (*Z*/*E* = 98:2)
(*E*-isomer)
6.02 9.08 0.04 0.05 2.00 1.00 2.01 3.32 2.49 6.08 1.00 2.14
.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
f1 (ppm)

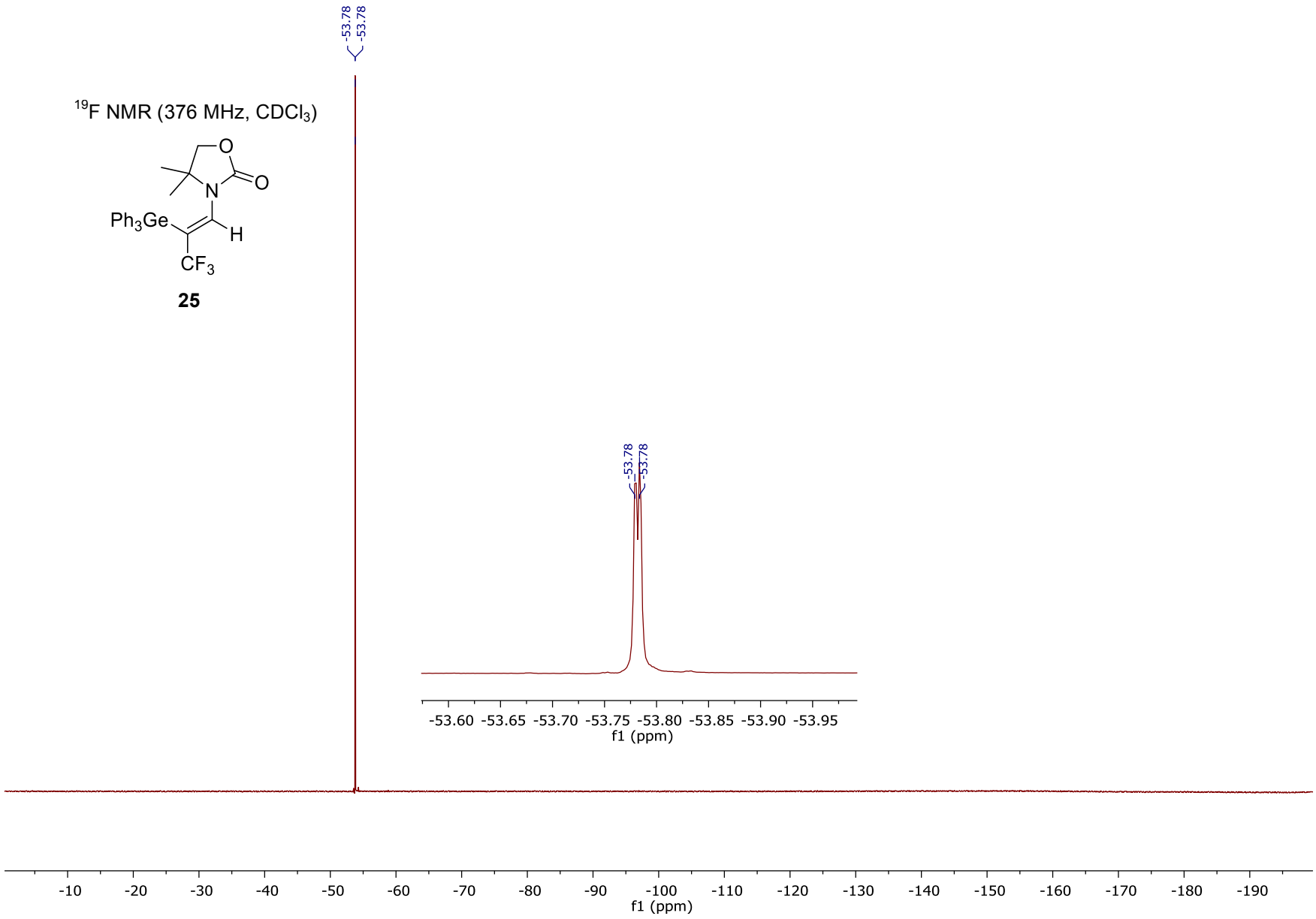

155.63
144.69
137.42
135.82
128.74
127.86
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.99
59.23
42.81
34.56
27.00
26.23
23.58
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph_3Ge
D
[^{2}H]-**24** (*Z*/*E* = 98:2)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

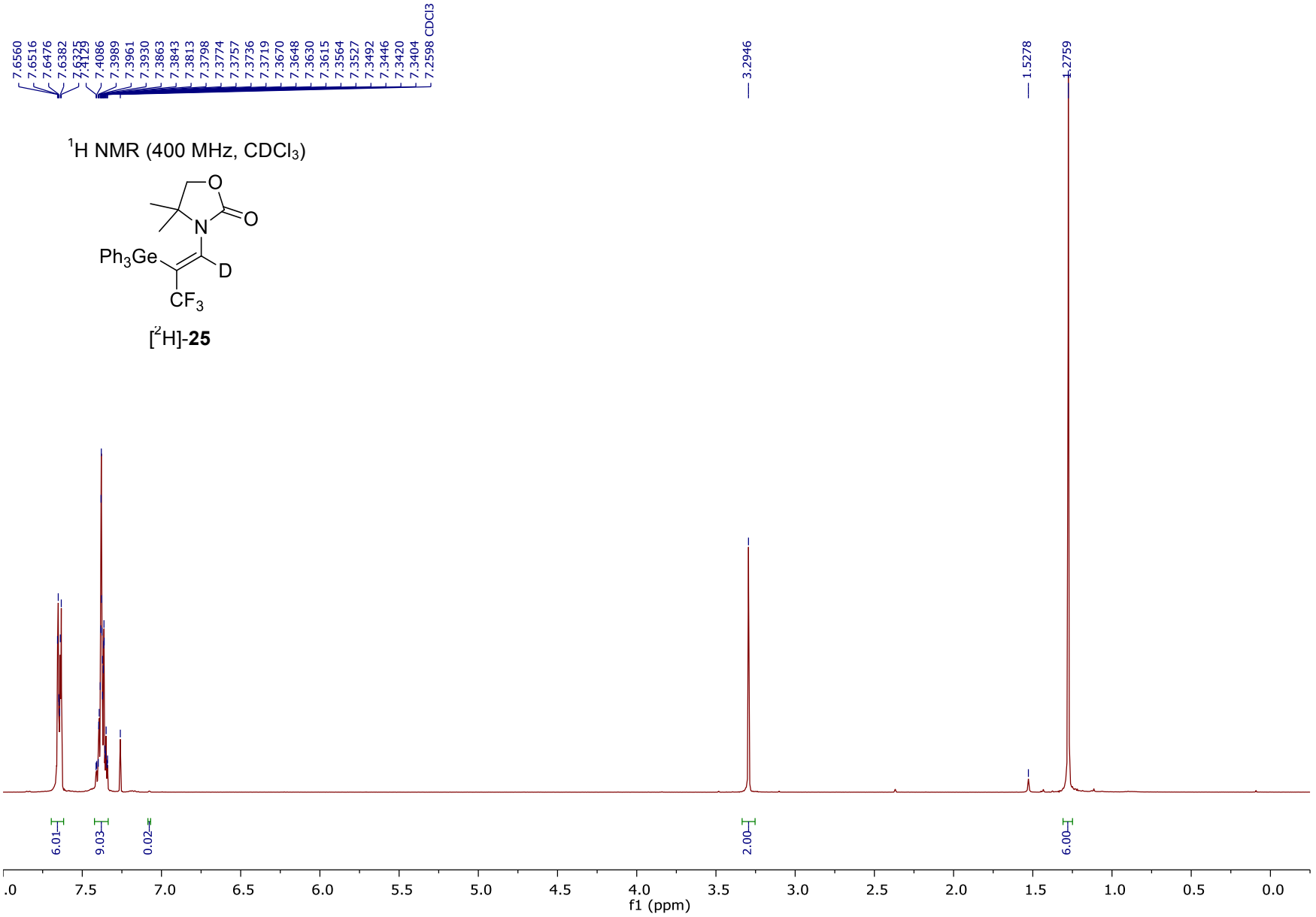

7.6437
7.6393
7.6354
7.6257
7.6200
7.4039
7.3995
7.3898
7.3871
7.3841
7.3769
7.3751
7.3707
7.3680
7.3662
7.3645
7.3620
7.3573
7.3552
7.3534
7.3519
7.3469
7.3429
7.3395
7.3350
7.3309
7.2604 CDCl3
7.0719
7.0676
7.0634
7.0592
3.2881
1.5338
1.2751
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
Ph_3Ge
H
CF_3
25
6.02
9.03
1.00
2.00
6.00
.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
f1 (ppm)



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

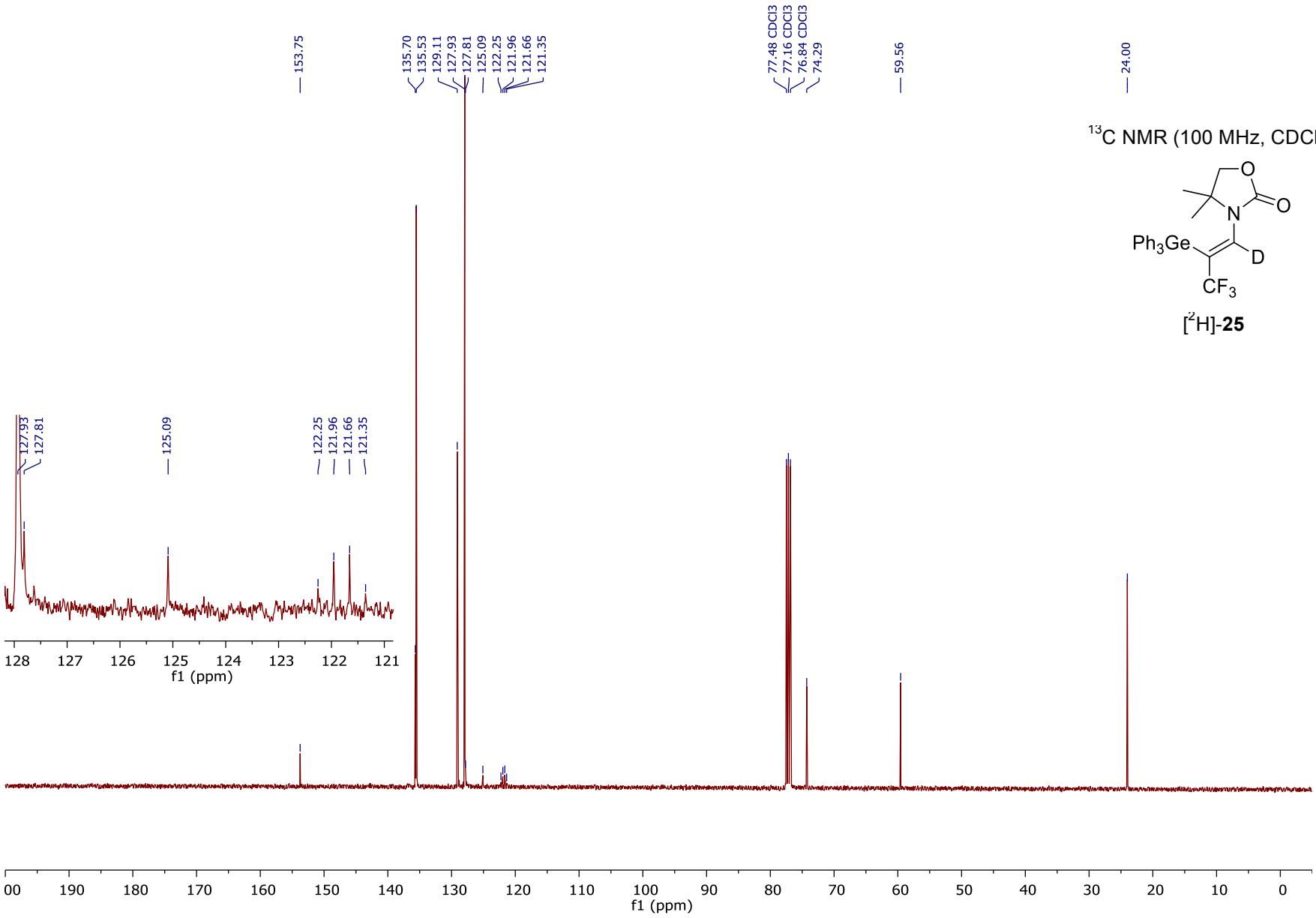
25


-53.78
-53.78
^{19}F NMR (376 MHz, $CDCl_3$)
O
N
O
Ph_3Ge
H
CF_3
25
-53.78
-53.78
-53.60 -53.65 -53.70 -53.75 -53.80 -53.85 -53.90 -53.95
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

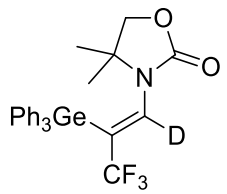


^{1}H NMR (400 MHz, $CDCl_3$)

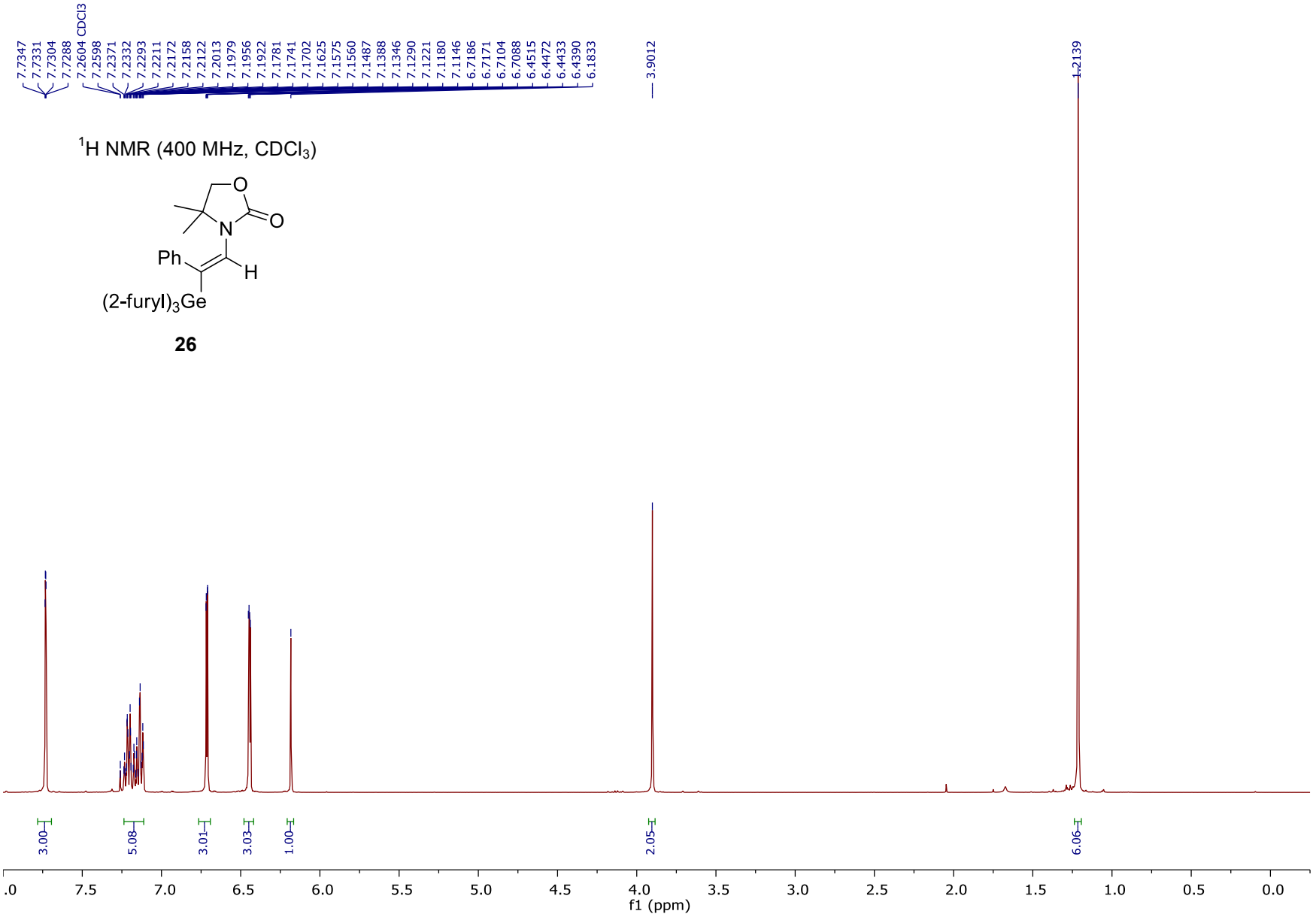
[^{2}H]-**25**


153.75
135.70
135.53
129.11
127.93
127.81
125.09
122.25
121.96
121.66
121.35
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.29
59.56
24.00
f1 (ppm)
^{13}C NMR (100 MHz, $CDCl_3$)
Ph_3Ge
D
CF_3
[^{2}H]-**25**

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

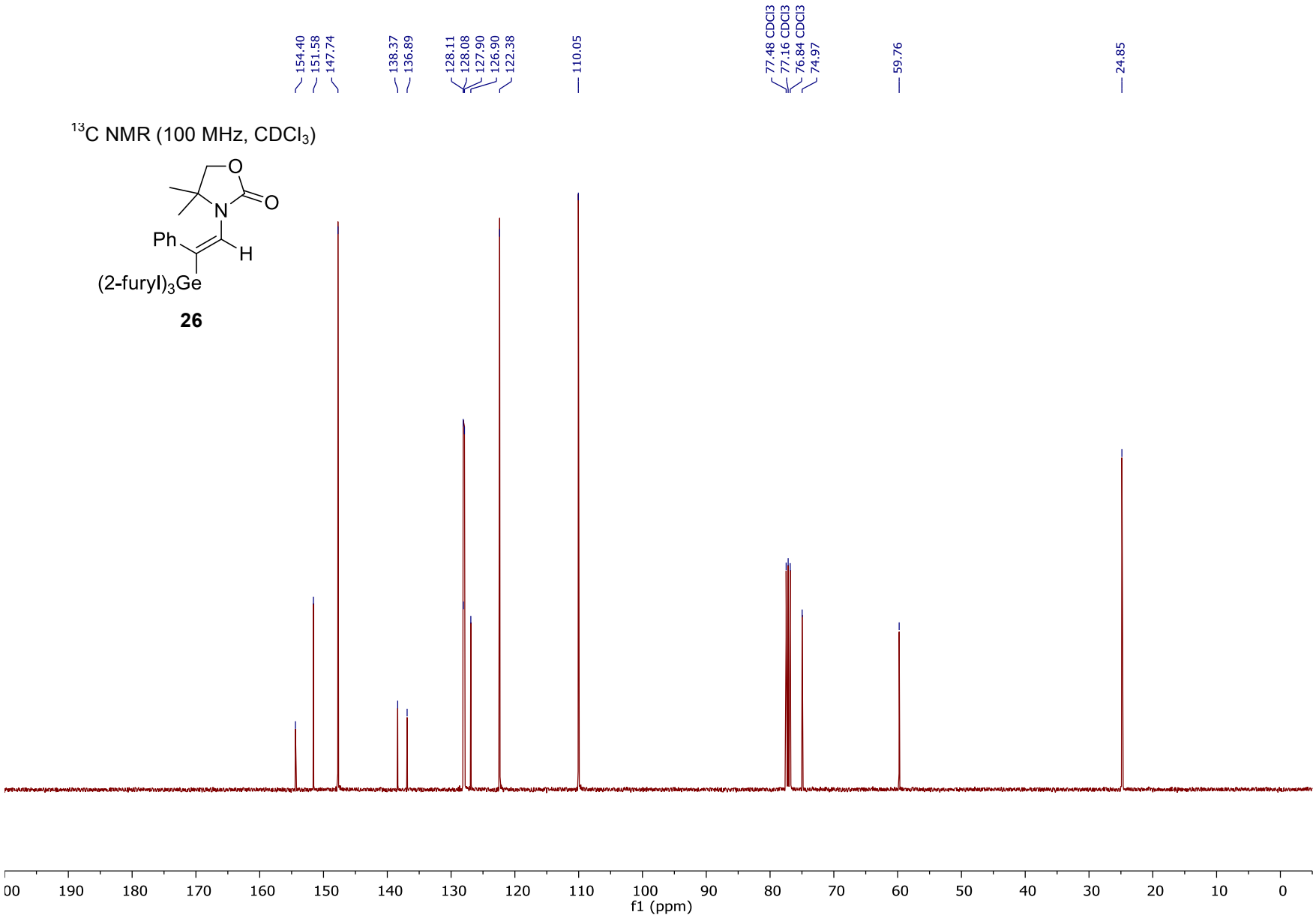


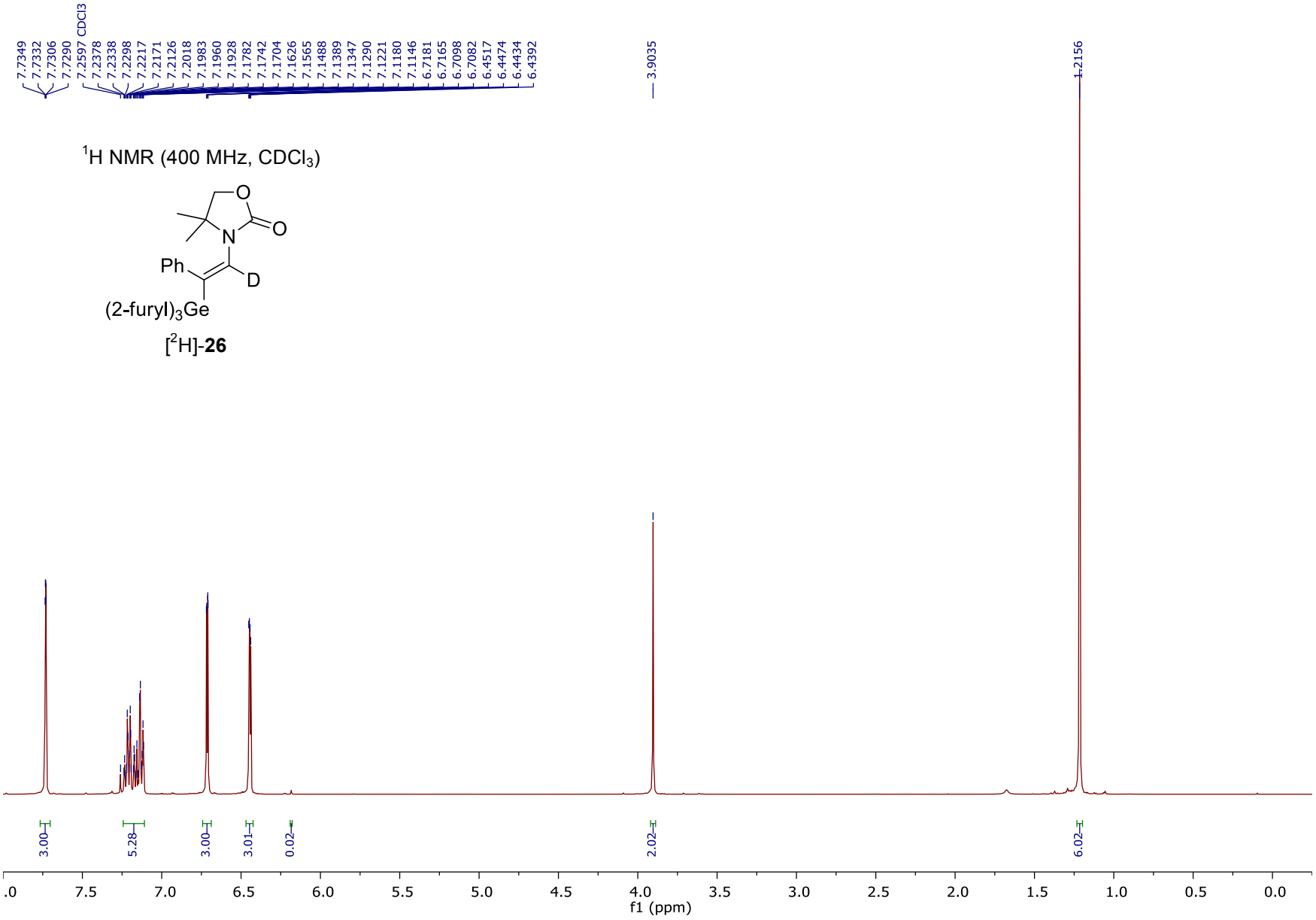
[^{2}H]-**25**



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

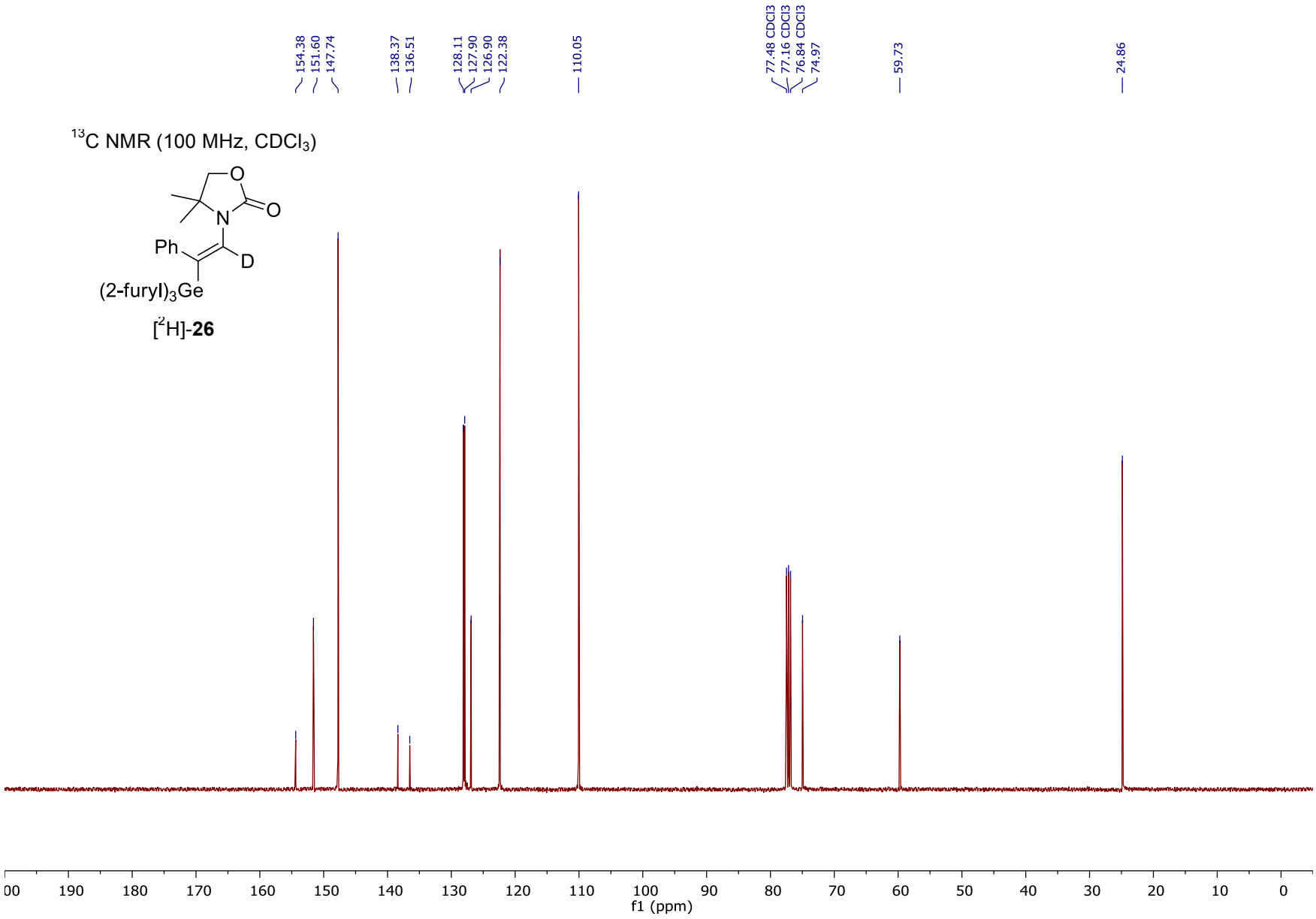
26

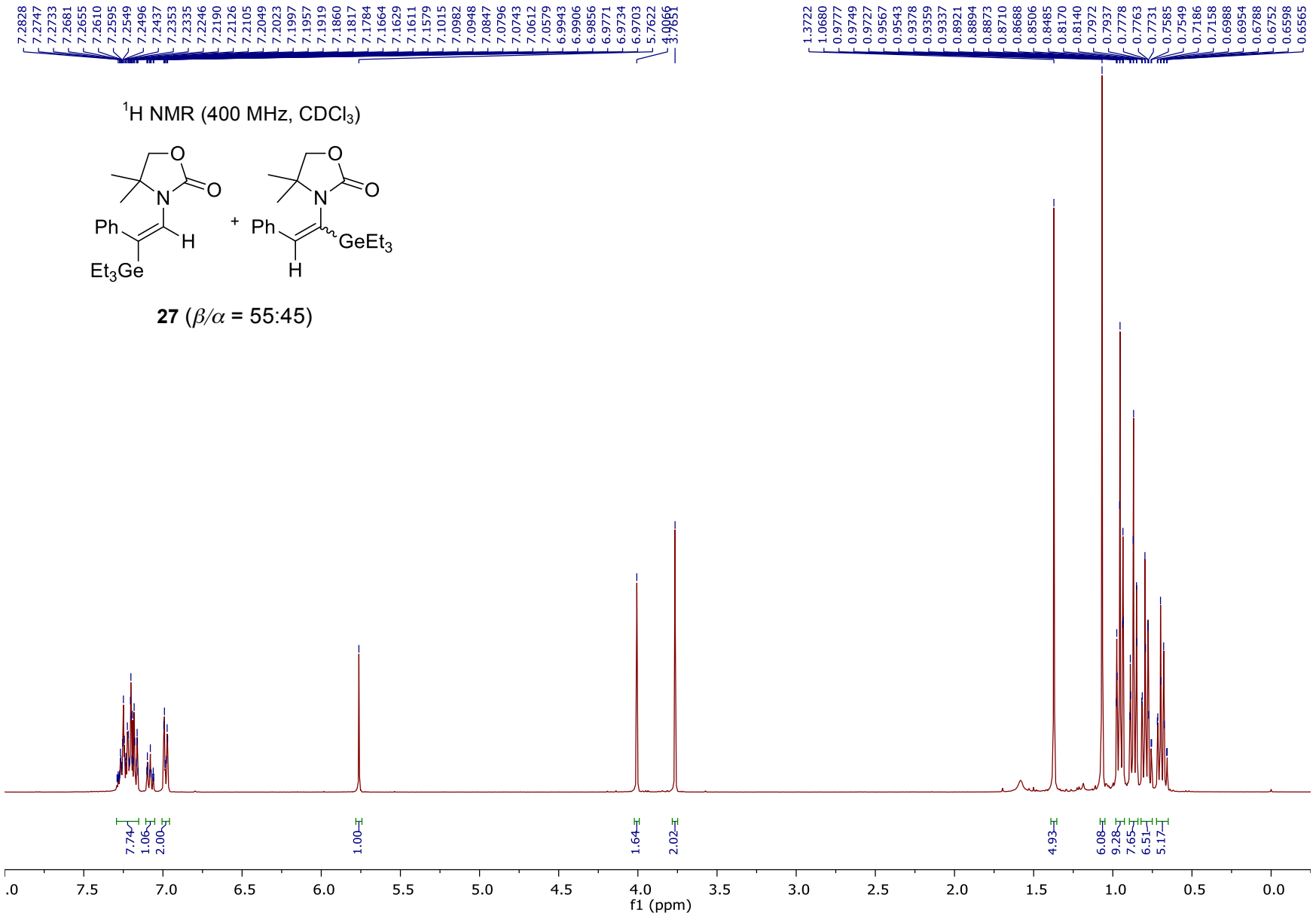

154.40
151.58
147.74
138.37
136.89
128.11
128.08
127.90
126.90
122.38
110.05
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.97
59.76
24.85
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph
H
(2-furyl)$_3$Ge
26
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

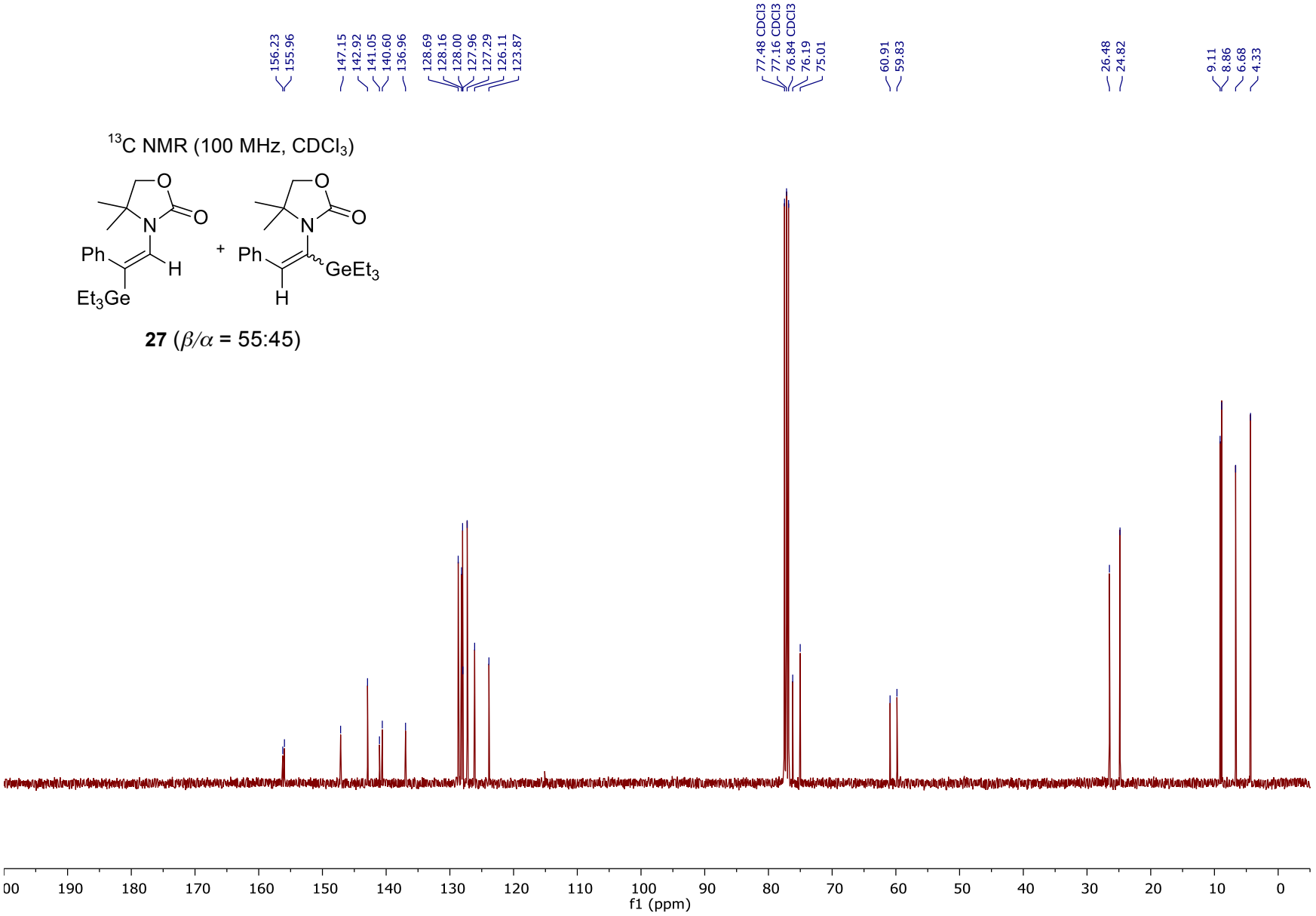


^{1}H NMR (400 MHz, $CDCl_3$)

[^{2}H]-**26**

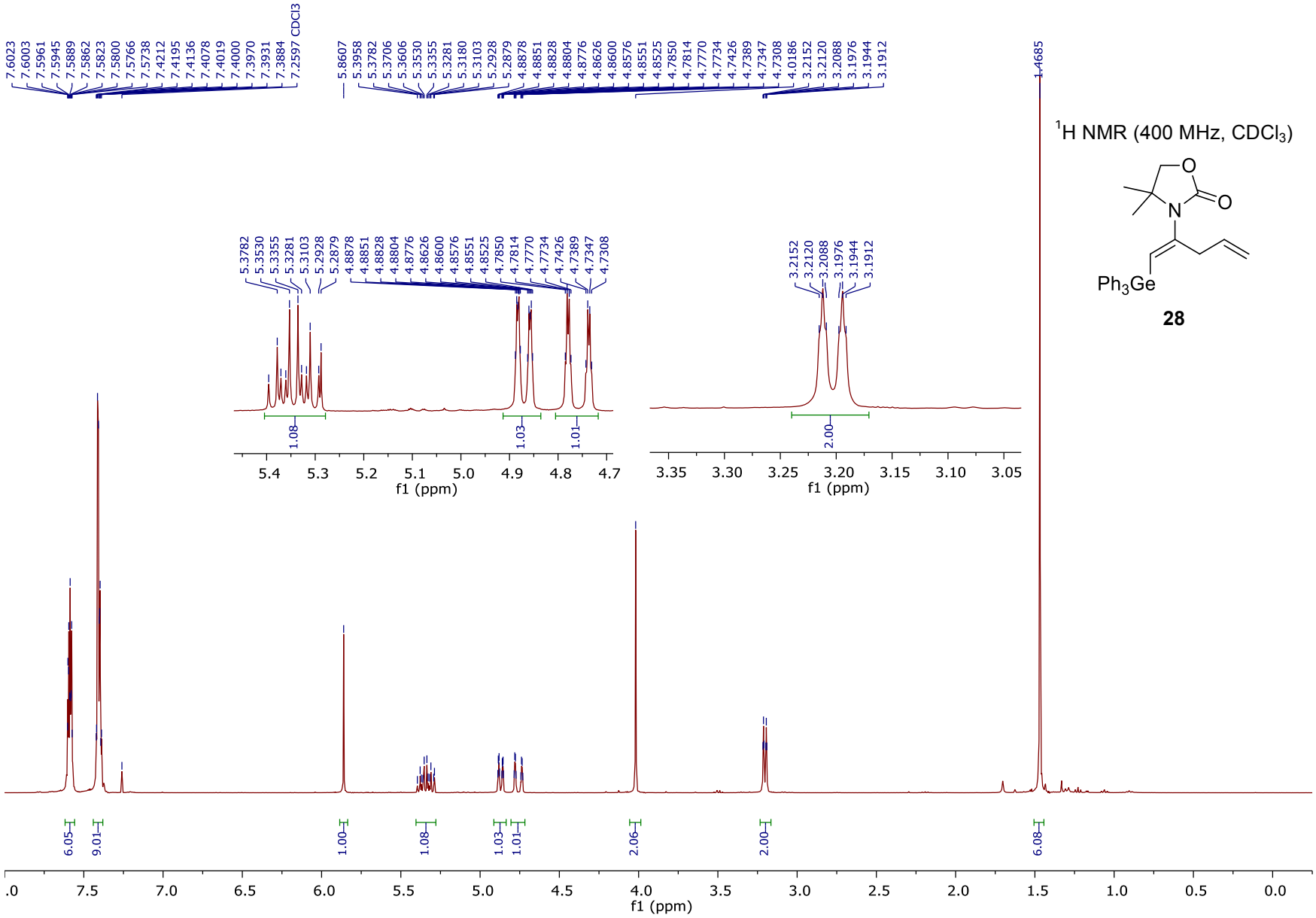

154.38
151.60
147.74
138.37
136.51
128.11
127.90
126.90
122.38
110.05
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
74.97
59.73
24.86
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph
D
(2-furyl)$_3$Ge
[^{2}H]-**26**
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

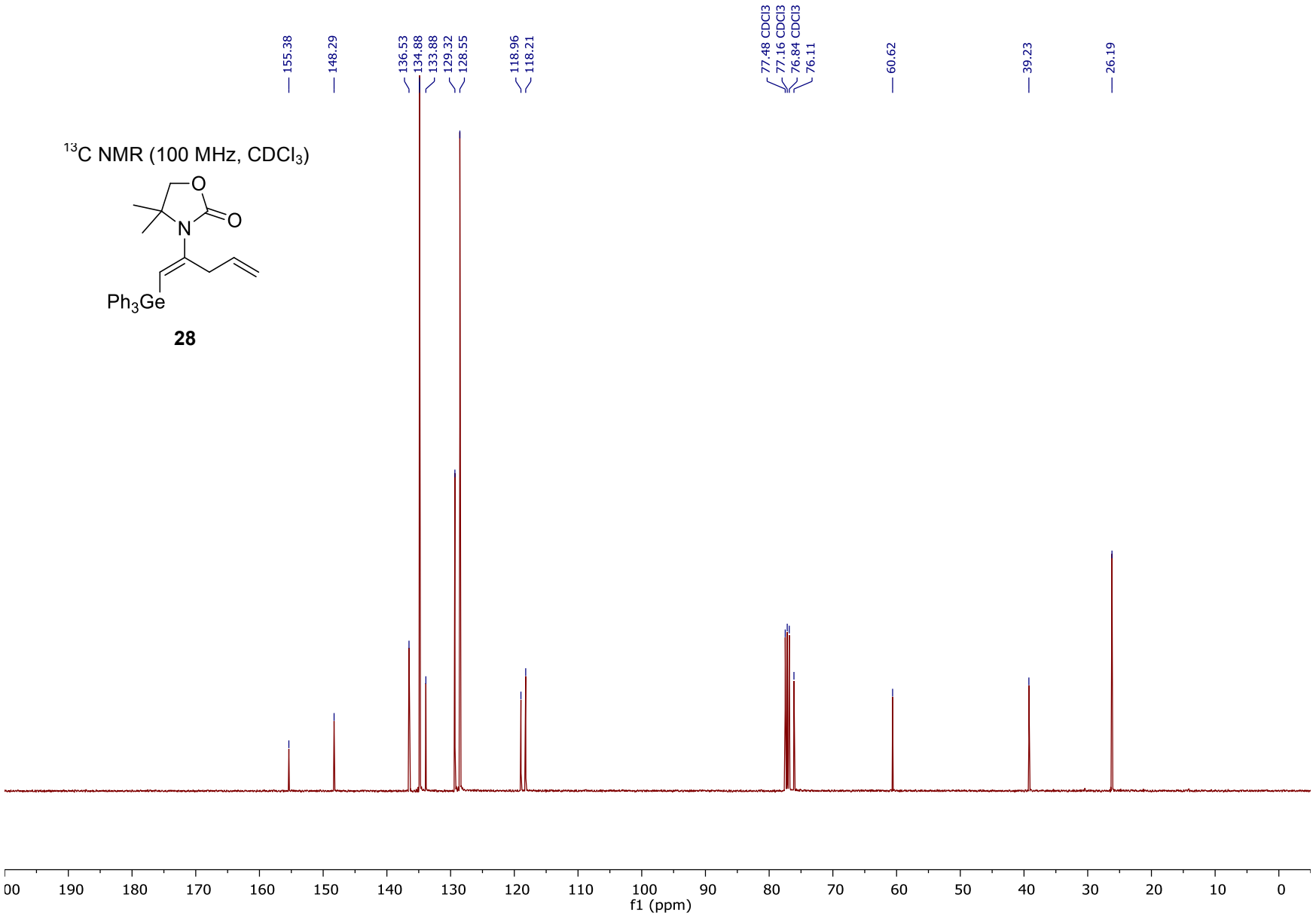

7.2828 7.2747 7.2733 7.2681 7.2655 7.2610 7.2595 7.2549 7.2496 7.2437 7.2353 7.2335 7.2246 7.2190 7.2126 7.2105 7.2049 7.2023 7.1997 7.1957 7.1919 7.1860 7.1817 7.1784 7.1664 7.1629 7.1611 7.1579 7.1015 7.0982 7.0948 7.0847 7.0796 7.0743 7.0612 7.0579 6.9943 6.9906 6.9856 6.9771 6.9734 6.9703 5.7622 4.1066 3.7851
1.3722 1.0680 0.9777 0.9749 0.9727 0.9567 0.9543 0.9378 0.9359 0.9337 0.8921 0.8894 0.8873 0.8710 0.8688 0.8506 0.8485 0.8170 0.8140 0.7972 0.7937 0.7778 0.7763 0.7731 0.7585 0.7549 0.7186 0.7158 0.6988 0.6954 0.6788 0.6752 0.6598 0.6565
1H NMR (400 MHz, CDCl3)
Ph
H
Et3Ge
+
Ph
GeEt3
H
27 (β/α = 55:41)
7.74 1.06 2.00 1.00 1.64 2.02 4.93 6.08 9.28 7.65 6.51 5.17
.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
f1 (ppm)

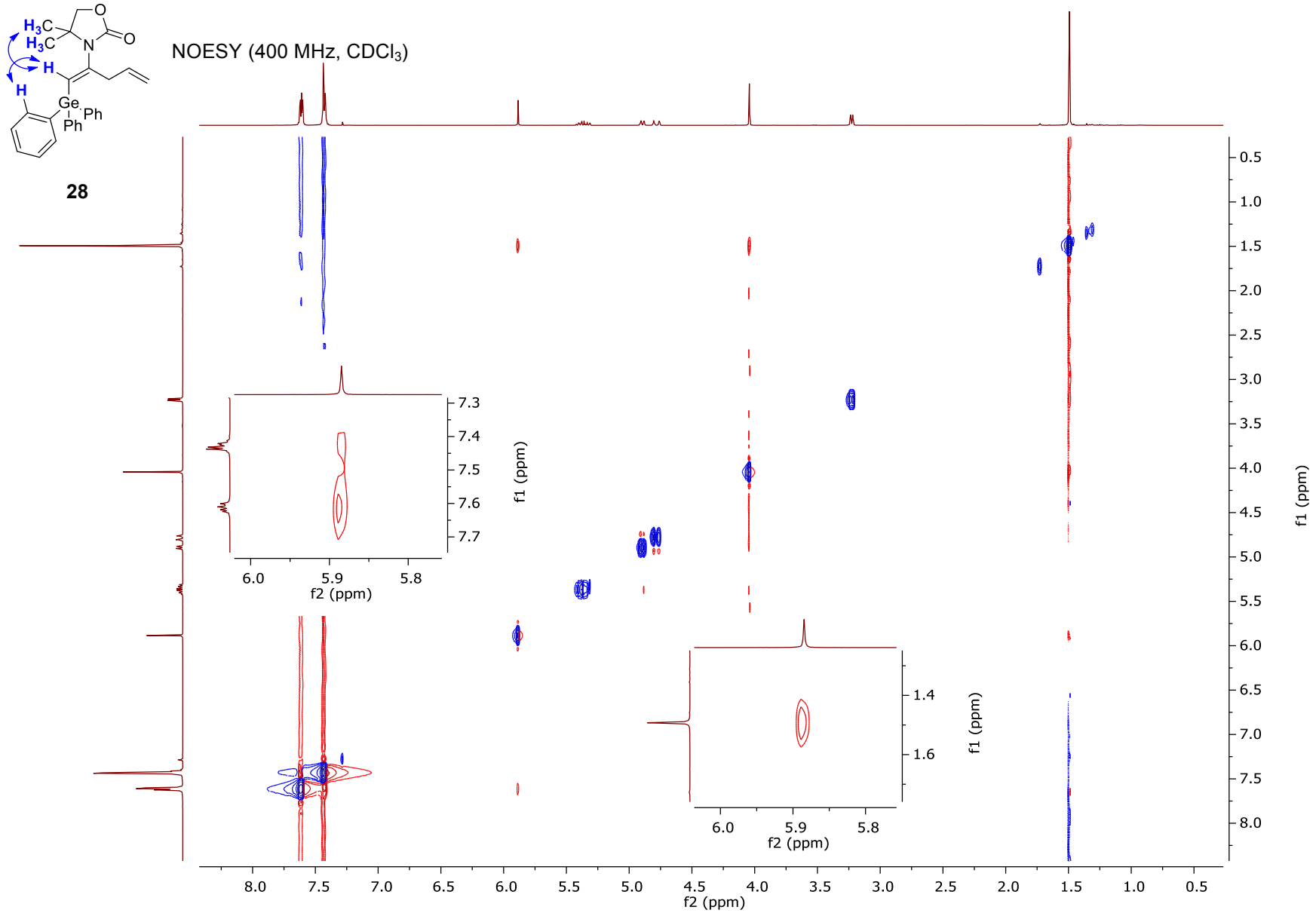


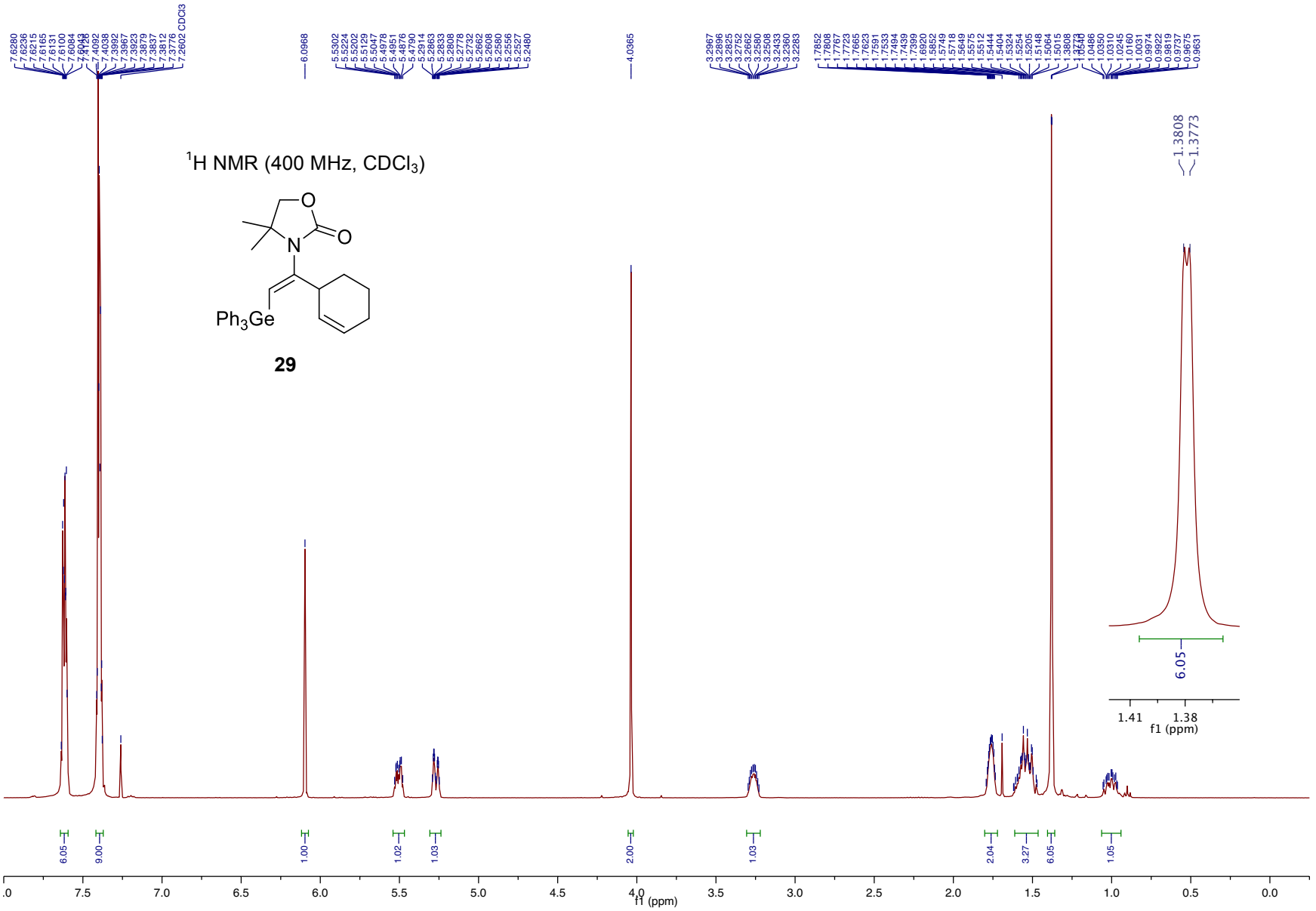
^{13}C NMR (100 MHz, $CDCl_3$)

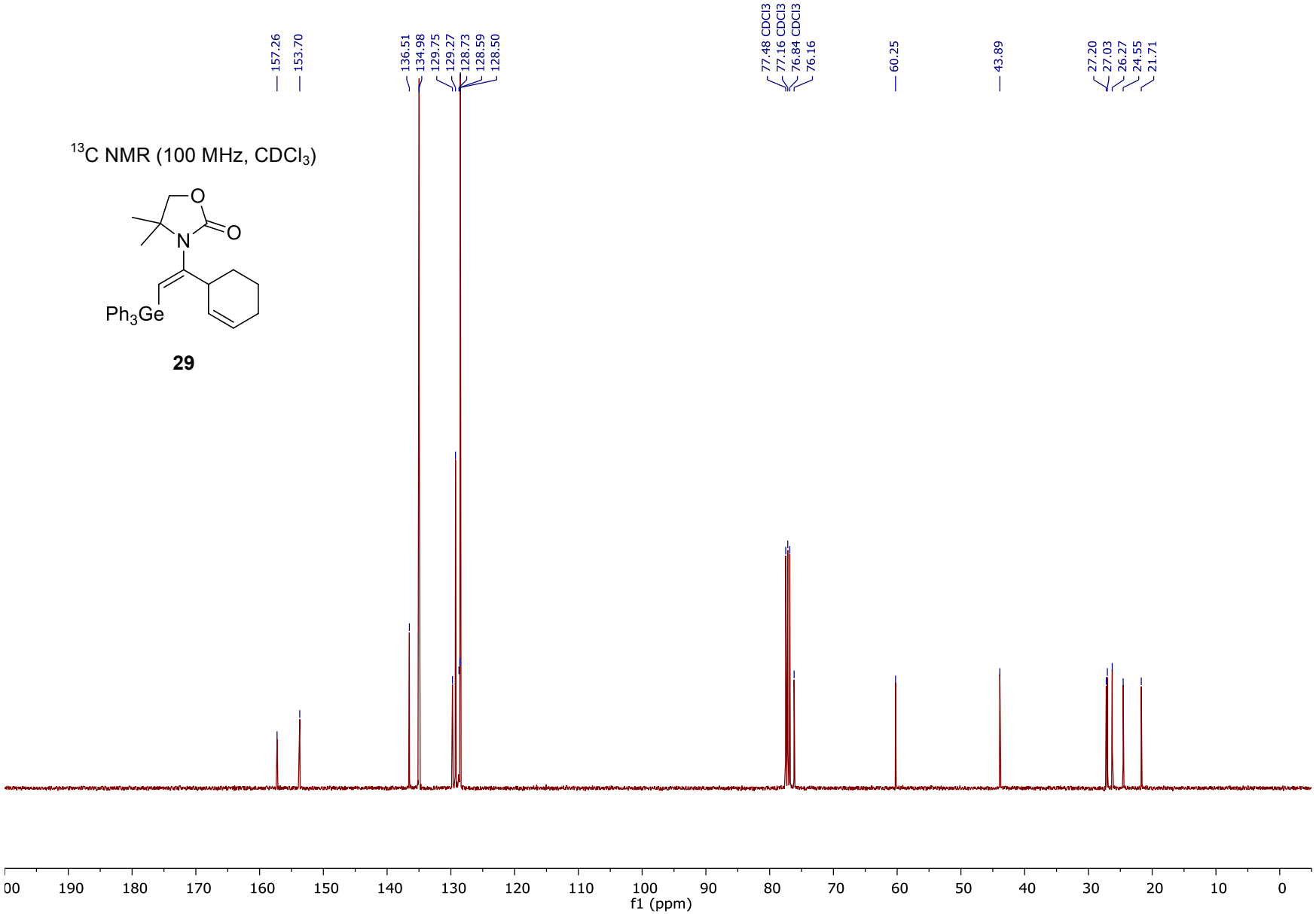
27 (β/α = 55:45)

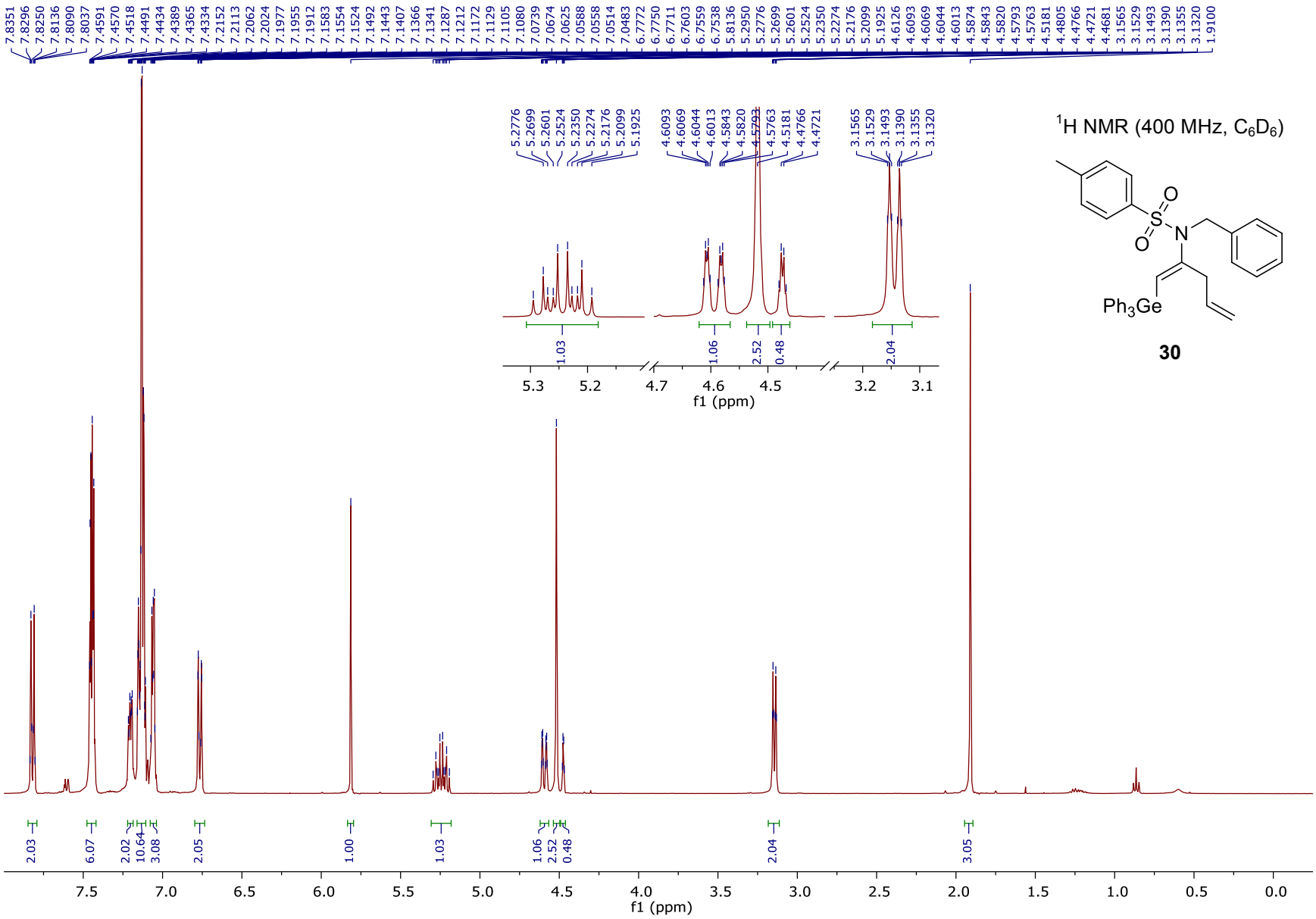

^{1}H NMR (400 MHz, $CDCl_3$)
Ph_3Ge
28
f1 (ppm)

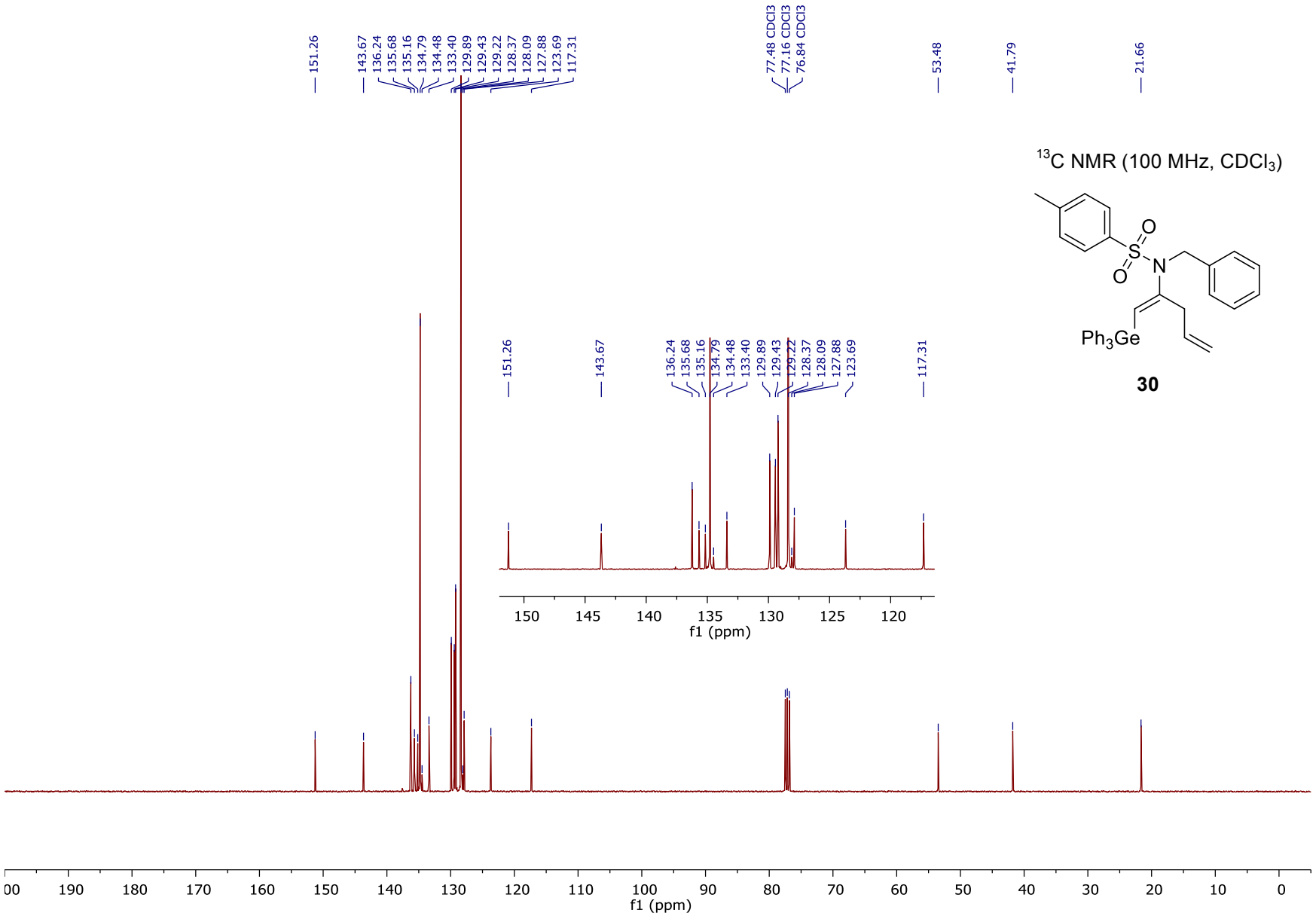

155.38
148.29
136.53
134.88
133.88
129.32
128.55
118.96
118.21
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.11
60.62
39.23
26.19
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph_3Ge
28
f1 (ppm)


NOESY (400 MHz, CDCl3)
28
f2 (ppm)
f1 (ppm)

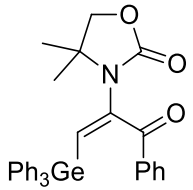

^{1}H NMR (400 MHz, $CDCl_3$)
Ph$_3$Ge
29
f1 (ppm)


157.26
153.70
136.51
134.98
129.75
129.27
128.73
128.59
128.50
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.16
60.25
43.89
27.20
27.03
26.27
24.55
21.71
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph_3Ge
29
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


^{1}H NMR (400 MHz, C_6D_6)
Ph_3Ge
30
f1 (ppm)

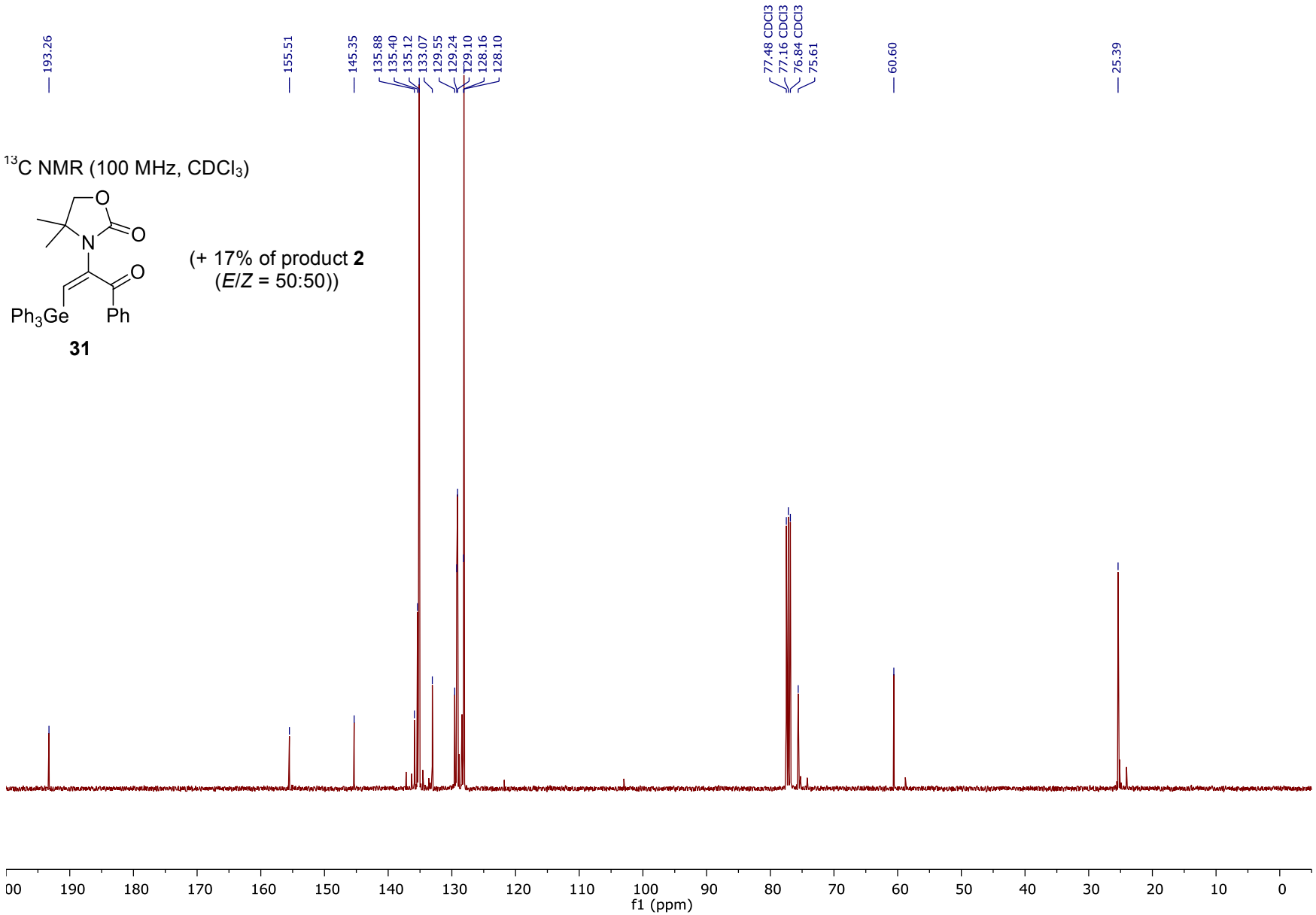

151.26
143.67
136.24
135.68
135.16
134.79
134.48
133.40
129.89
129.43
129.22
128.37
128.09
127.88
123.69
117.31
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.48
41.79
21.66
f1 (ppm)
^{13}C NMR (100 MHz, $CDCl_3$)
O
S
O
N
Ph_3Ge
30

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



31

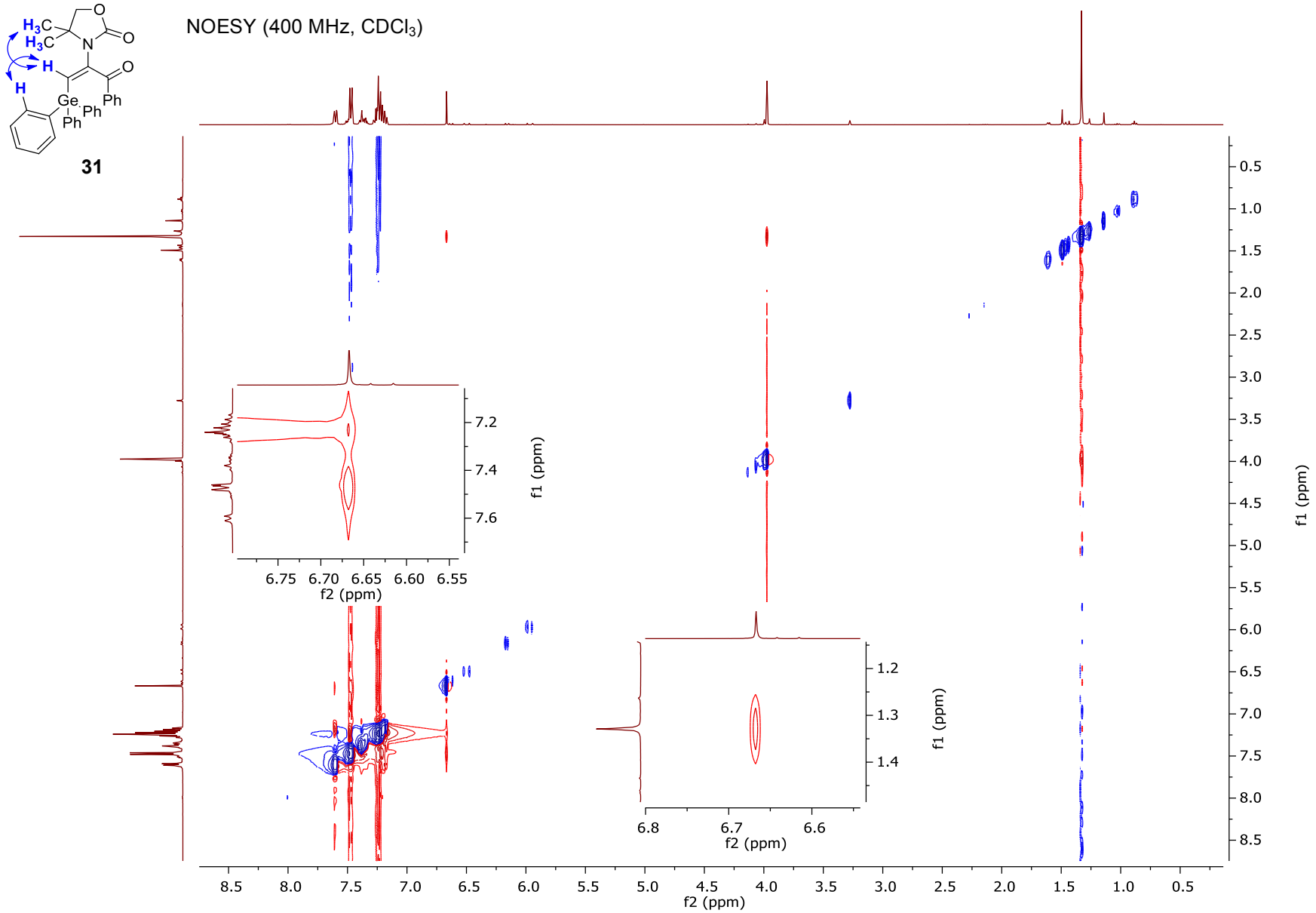
(+ 17% of product **2** (*E*/*Z* = 50:50))



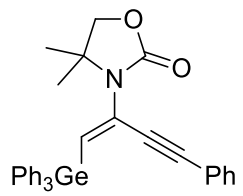
^{13}C NMR (100 MHz, $CDCl_3$)

31

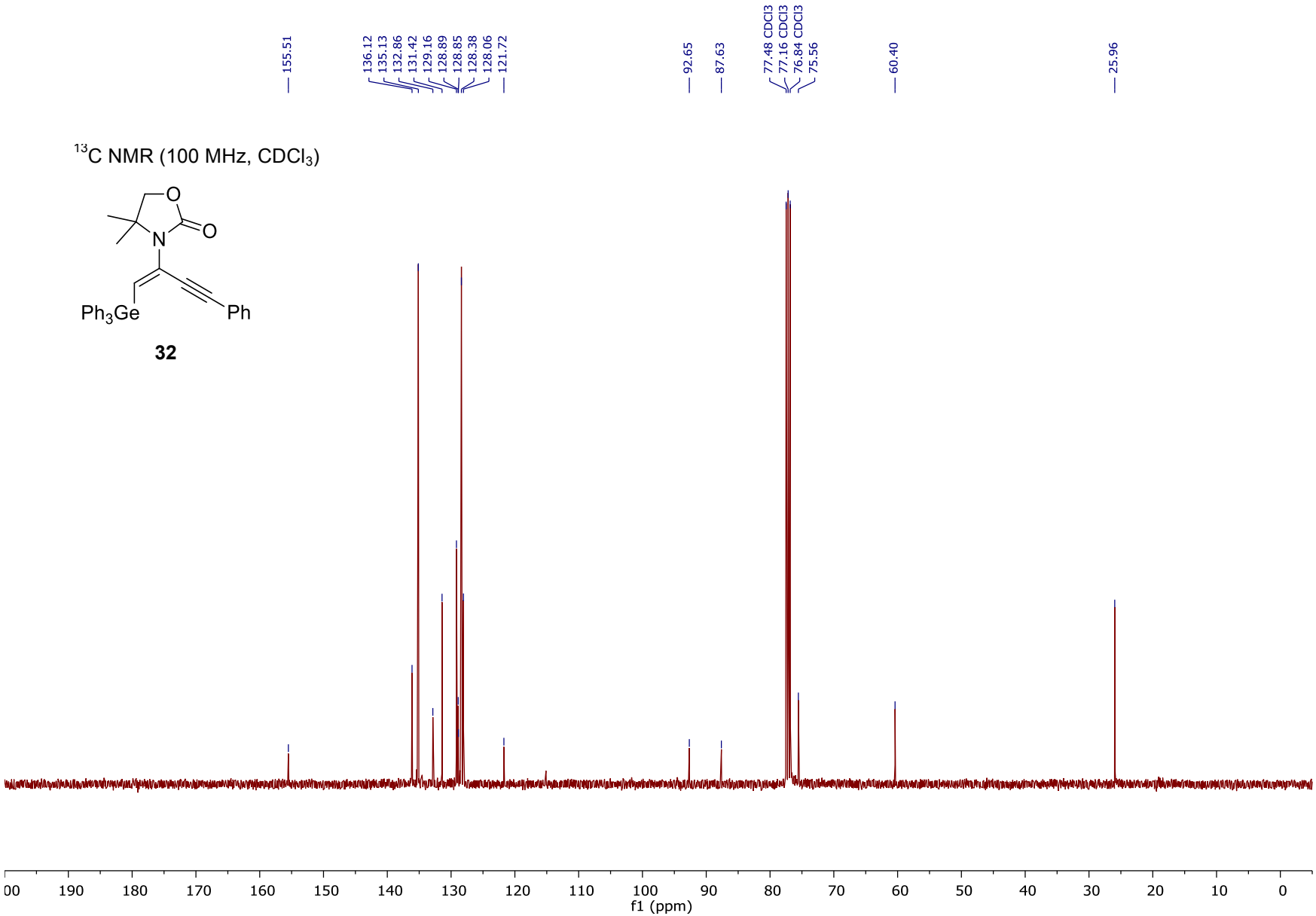
(+ 17% of product **2**
(*E*/*Z* = 50:50))

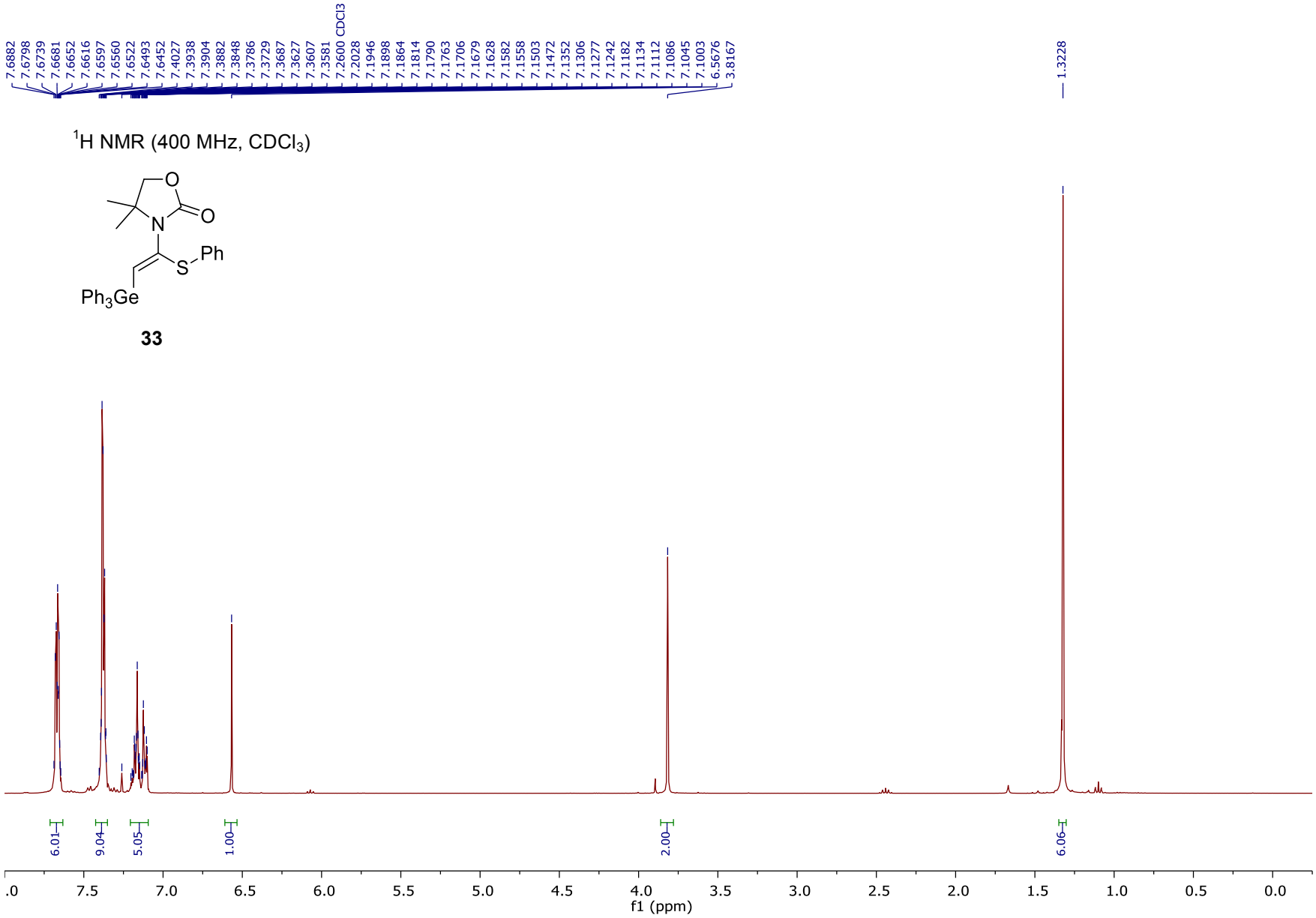

NOESY (400 MHz, CDCl3)
31
f2 (ppm)
f1 (ppm)

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

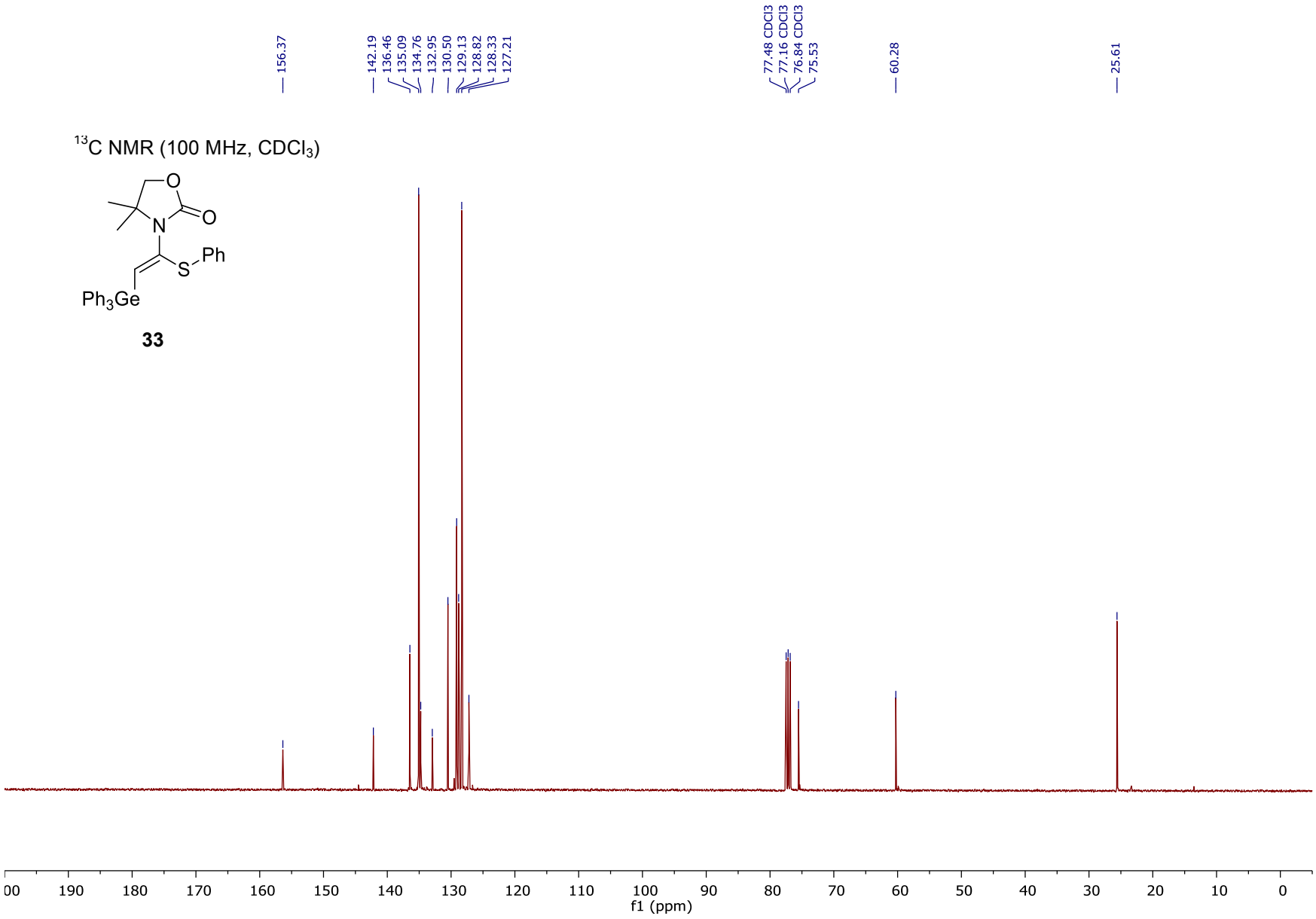


32

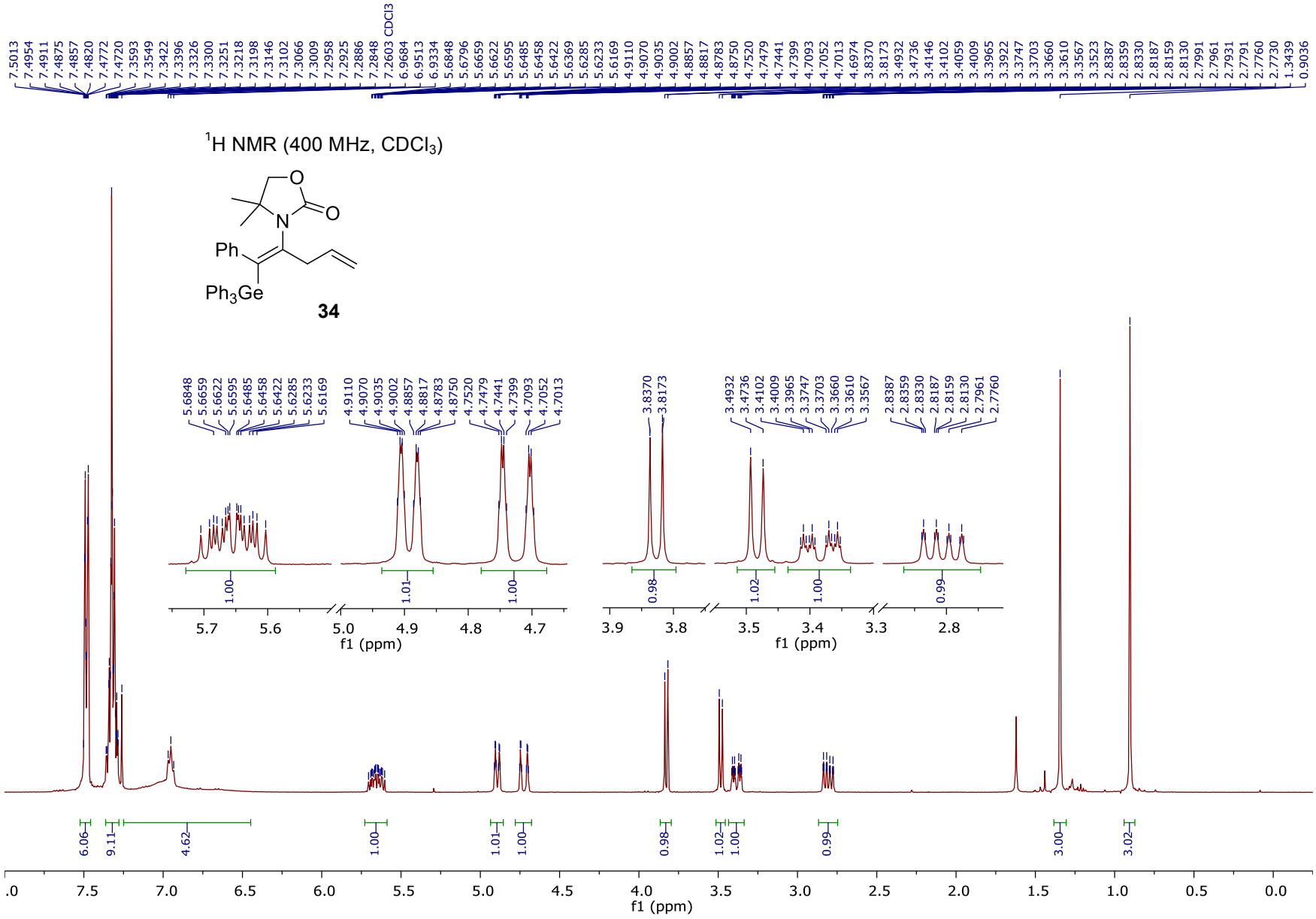

155.51
136.12
135.13
132.86
131.42
129.16
128.89
128.85
128.38
128.06
121.72
92.65
87.63
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.56
60.40
25.96
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph_3Ge
Ph
32
f1 (ppm)

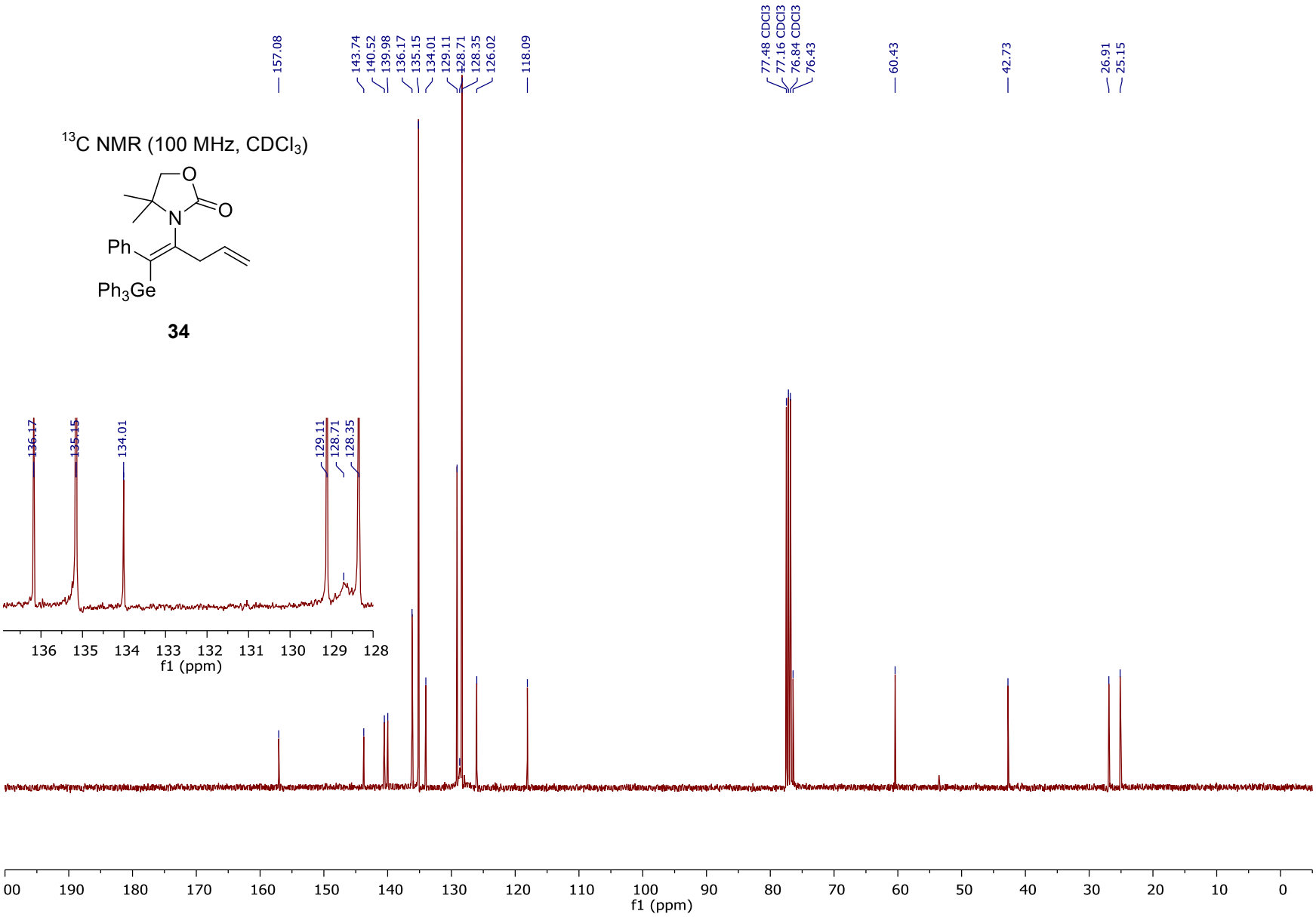

7.6882
7.6798
7.6739
7.6681
7.6652
7.6616
7.6597
7.6560
7.6522
7.6493
7.6452
7.4027
7.3938
7.3904
7.3882
7.3848
7.3786
7.3729
7.3687
7.3627
7.3607
7.3581
7.2600 CDCl3
7.2028
7.1946
7.1898
7.1864
7.1814
7.1790
7.1763
7.1706
7.1679
7.1628
7.1582
7.1558
7.1503
7.1472
7.1352
7.1306
7.1277
7.1242
7.1182
7.1134
7.1112
7.1086
7.1045
7.1003
6.5676
3.8167
1.3228
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
Ph
S
Ph_3Ge
6.01
9.04
5.05
1.00
2.00
6.06
f1 (ppm)

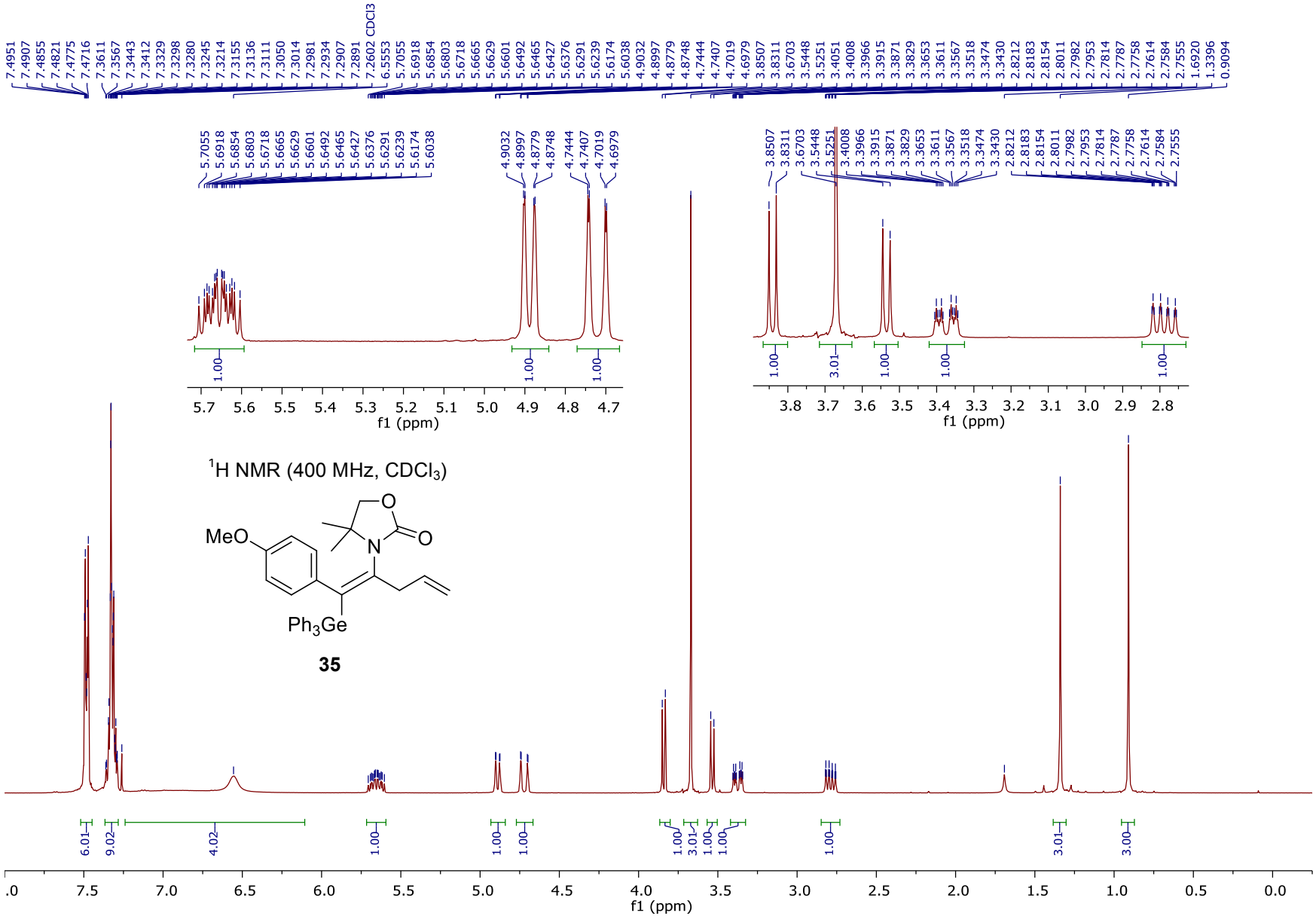
33

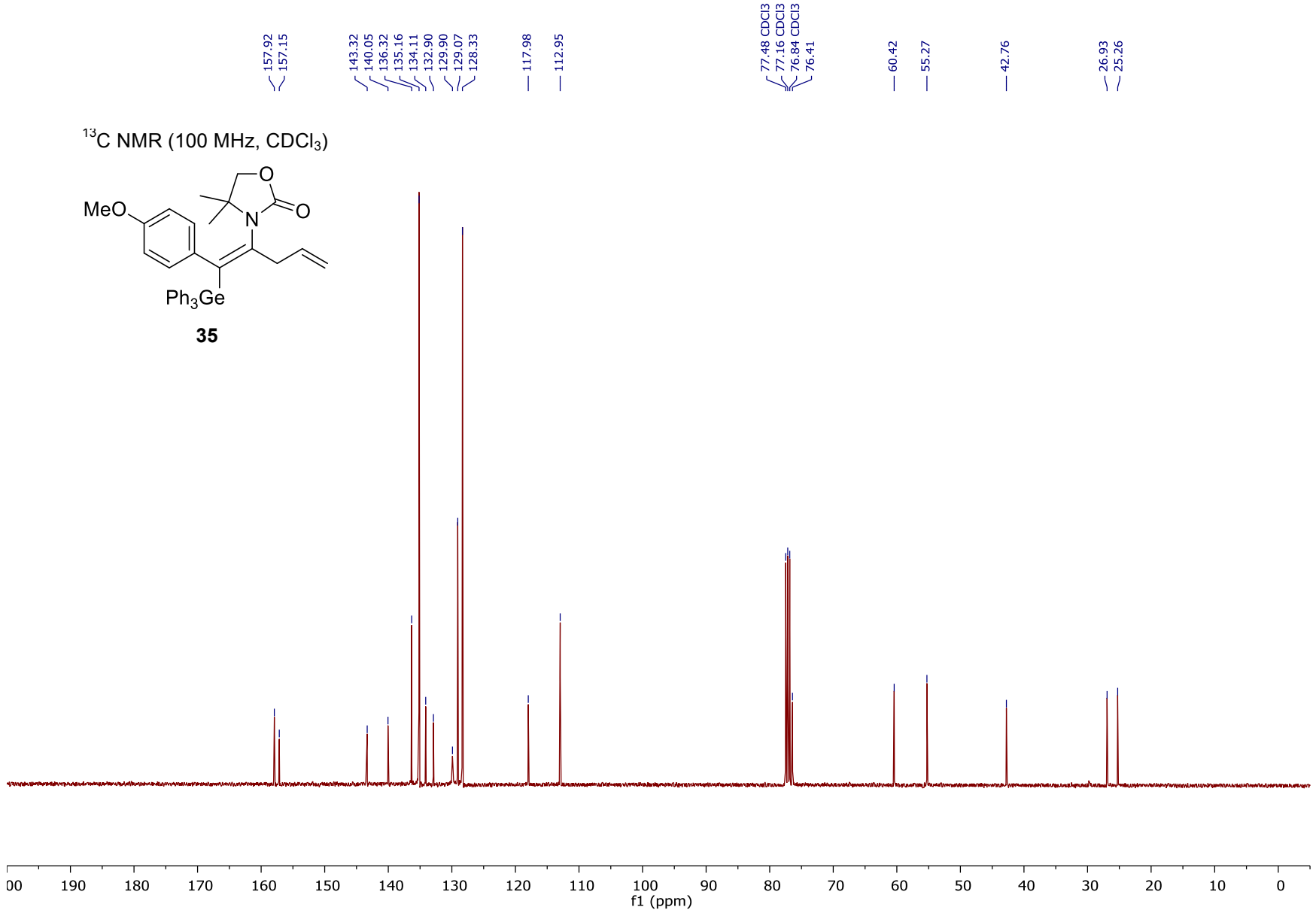

156.37
142.19
136.46
135.09
134.76
132.95
130.50
129.13
128.82
128.33
127.21
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.53
60.28
25.61
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
S
Ph
Ph_3Ge
f1 (ppm)

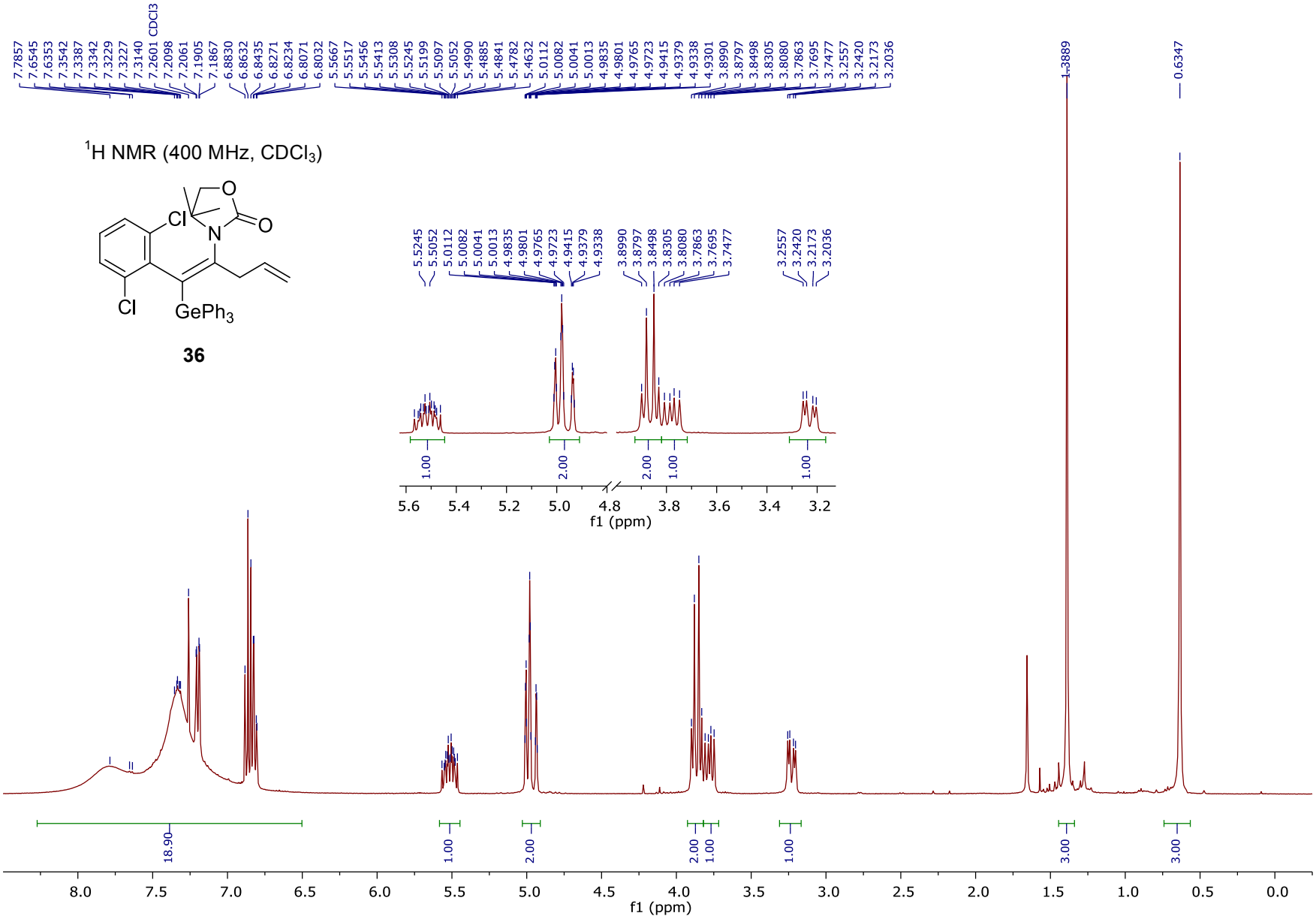
33

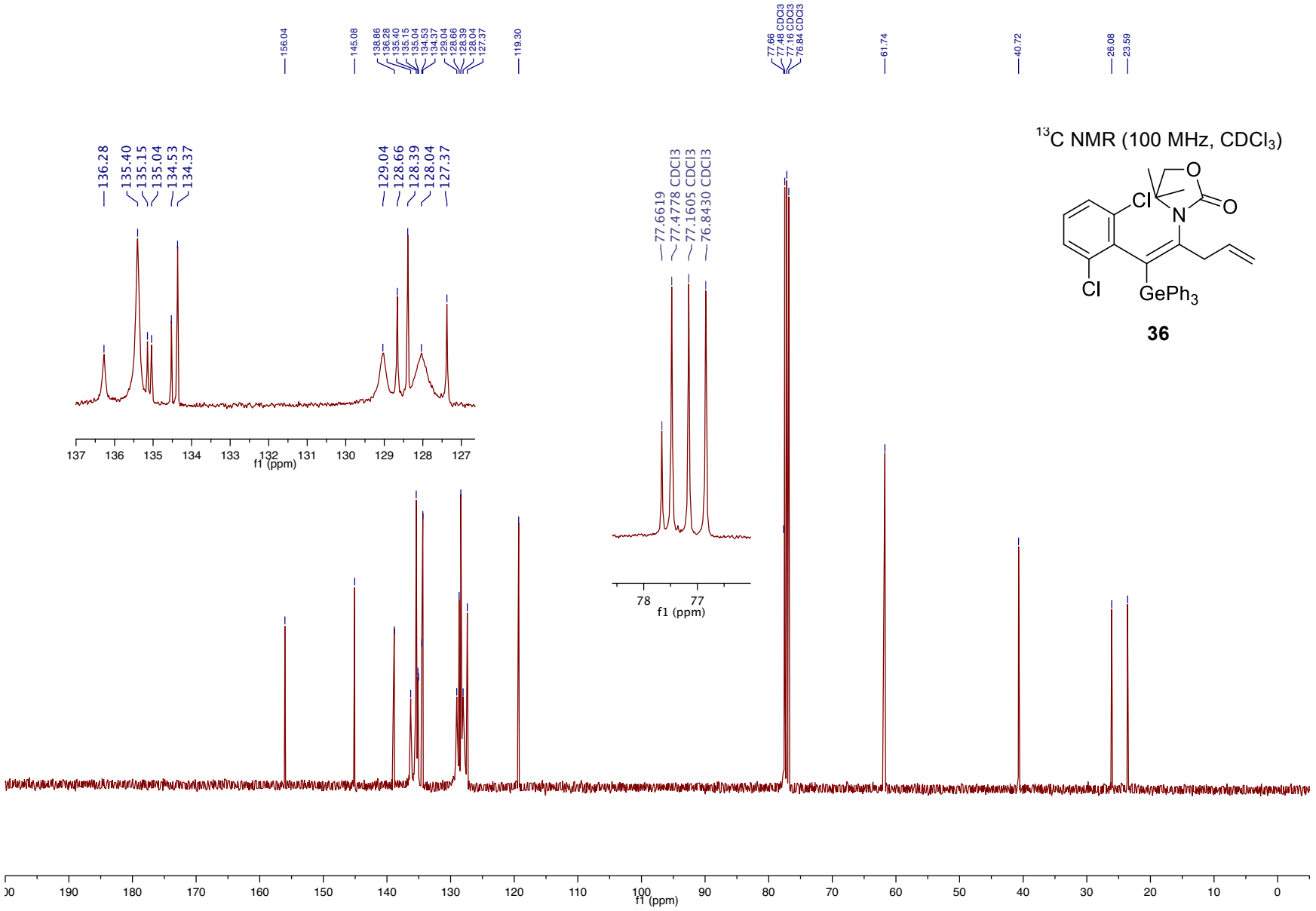

7.5013 7.4954 7.4911 7.4875 7.4857 7.4820 7.4772 7.4720 7.3593 7.3549 7.3422 7.3396 7.3326 7.3300 7.3251 7.3218 7.3198 7.3146 7.3102 7.3066 7.3009 7.2958 7.2925 7.2886 7.2848 7.2603 CDCl3 6.9684 6.9513 6.9334 5.6848 5.6796 5.6659 5.6622 5.6595 5.6485 5.6458 5.6422 5.6369 5.6285 5.6233 5.6169 4.9110 4.9070 4.9035 4.9002 4.8857 4.8817 4.8783 4.8750 4.7520 4.7479 4.7441 4.7399 4.7093 4.7052 4.7013 4.6974 3.8370 3.8173 3.4932 3.4736 3.4102 3.4059 3.4009 3.3965 3.3747 3.3703 3.3660 3.3610 3.3567 3.3523 2.8387 2.8359 2.8330 2.8187 2.8159 2.8130 2.7991 2.7961 2.7931 2.7791 2.7760 2.7730 1.3439 0.9036
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
Ph
Ph_3Ge
34
f1 (ppm)
6.06 9.11 4.62 1.00 1.01 1.00 0.98 1.02 1.00 0.99 3.00 3.02

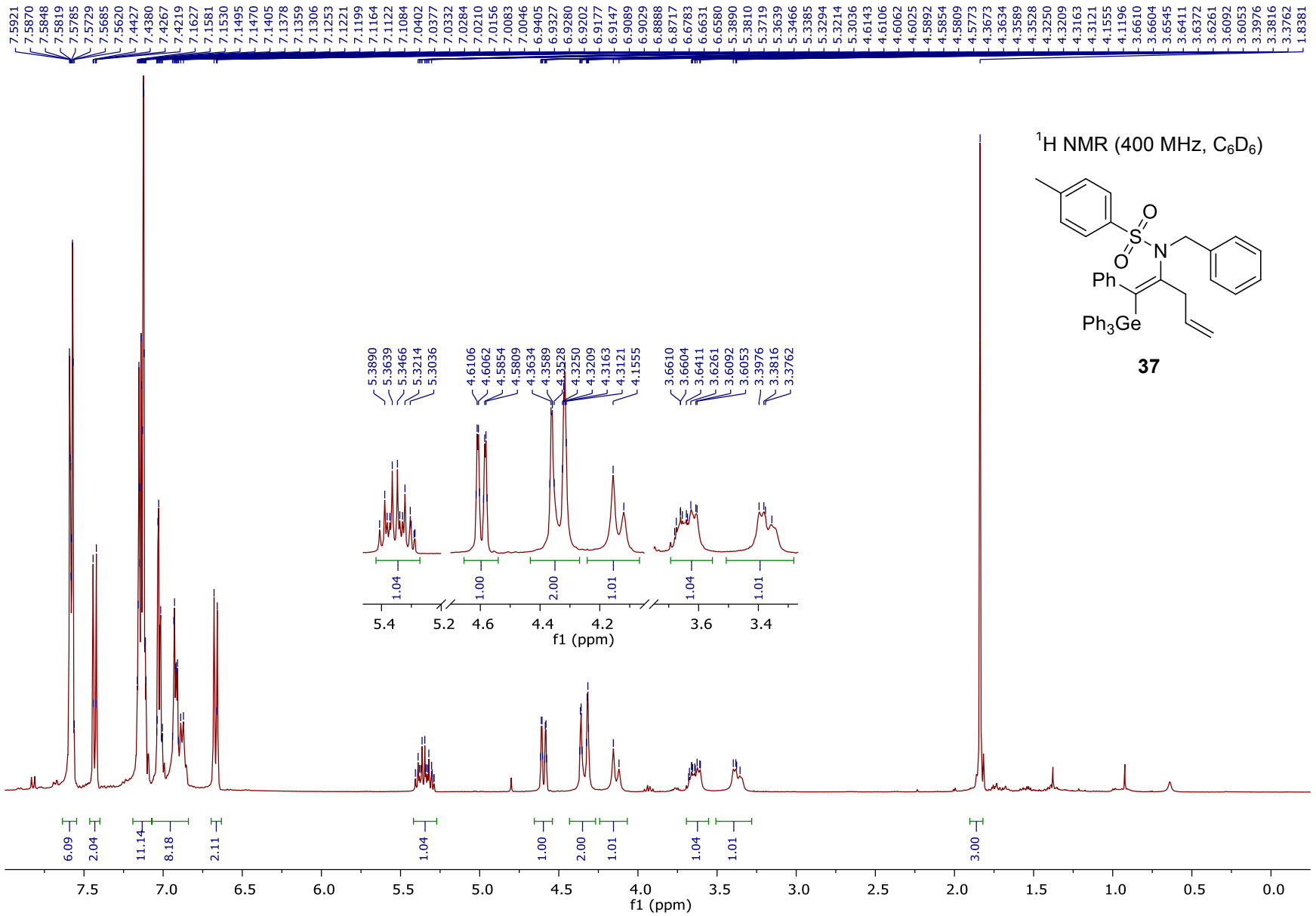

157.08
143.74
140.52
139.98
136.17
135.15
134.01
129.11
128.71
128.35
126.02
118.09
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.43
60.43
42.73
26.91
25.15
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph
Ph_3Ge
34
f1 (ppm)
f1 (ppm)

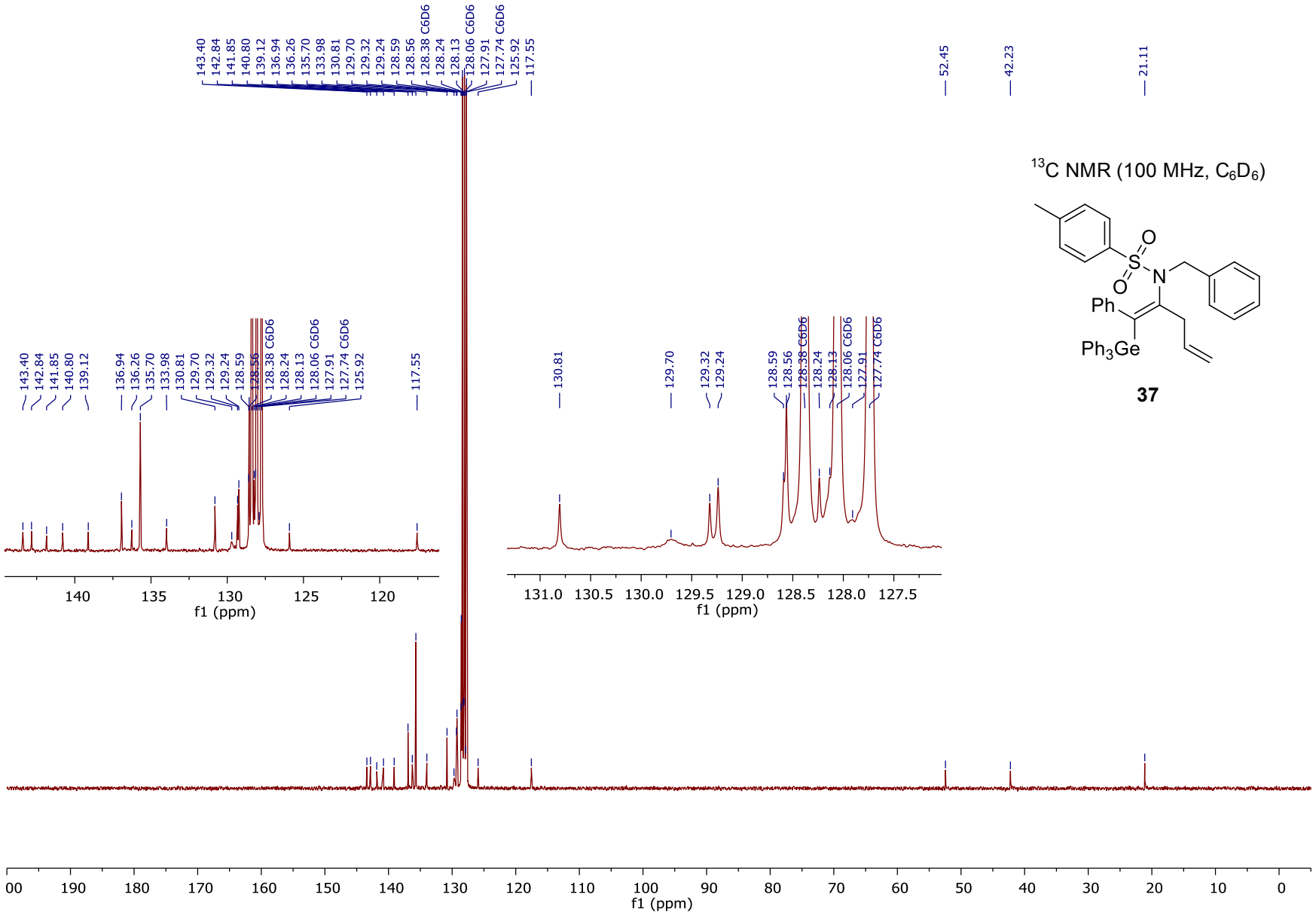

7.4951 7.4907 7.4855 7.4821 7.4775 7.4716 7.3611 7.3567 7.3443 7.3412 7.3329 7.3298 7.3280 7.3245 7.3214 7.3155 7.3136 7.3111 7.3050 7.3014 7.2981 7.2934 7.2907 7.2891 7.2602 CDCl3 6.6553 5.7055 5.6918 5.6854 5.6803 5.6718 5.6665 5.6629 5.6601 5.6492 5.6465 5.6427 5.6376 5.6291 5.6239 5.6174 5.6038 4.9032 4.8997 4.8779 4.8748 4.7444 4.7407 4.7019 4.6979 4.8997 4.8779 4.8748 4.7444 4.7407 4.7019 4.6979 3.8507 3.8311 3.6703 3.5448 3.5251 3.4051 3.4008 3.3966 3.3915 3.3871 3.3829 3.3653 3.3611 3.3567 3.3518 3.3474 3.3430 2.8212 2.8183 2.8154 2.8011 2.7982 2.7953 2.7814 2.7787 2.7758 2.7614 2.7584 2.7555 1.6920 1.3396 0.9094
1.00 1.00 1.00
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7
f1 (ppm)
1.00 3.01 1.00 1.00 1.00
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8
f1 (ppm)
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
O
O
N
Ph_3Ge
35
6.01 9.02 4.02 1.00 1.00 1.00 1.00 3.01 1.00 1.00 3.01 3.00
.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
f1 (ppm)

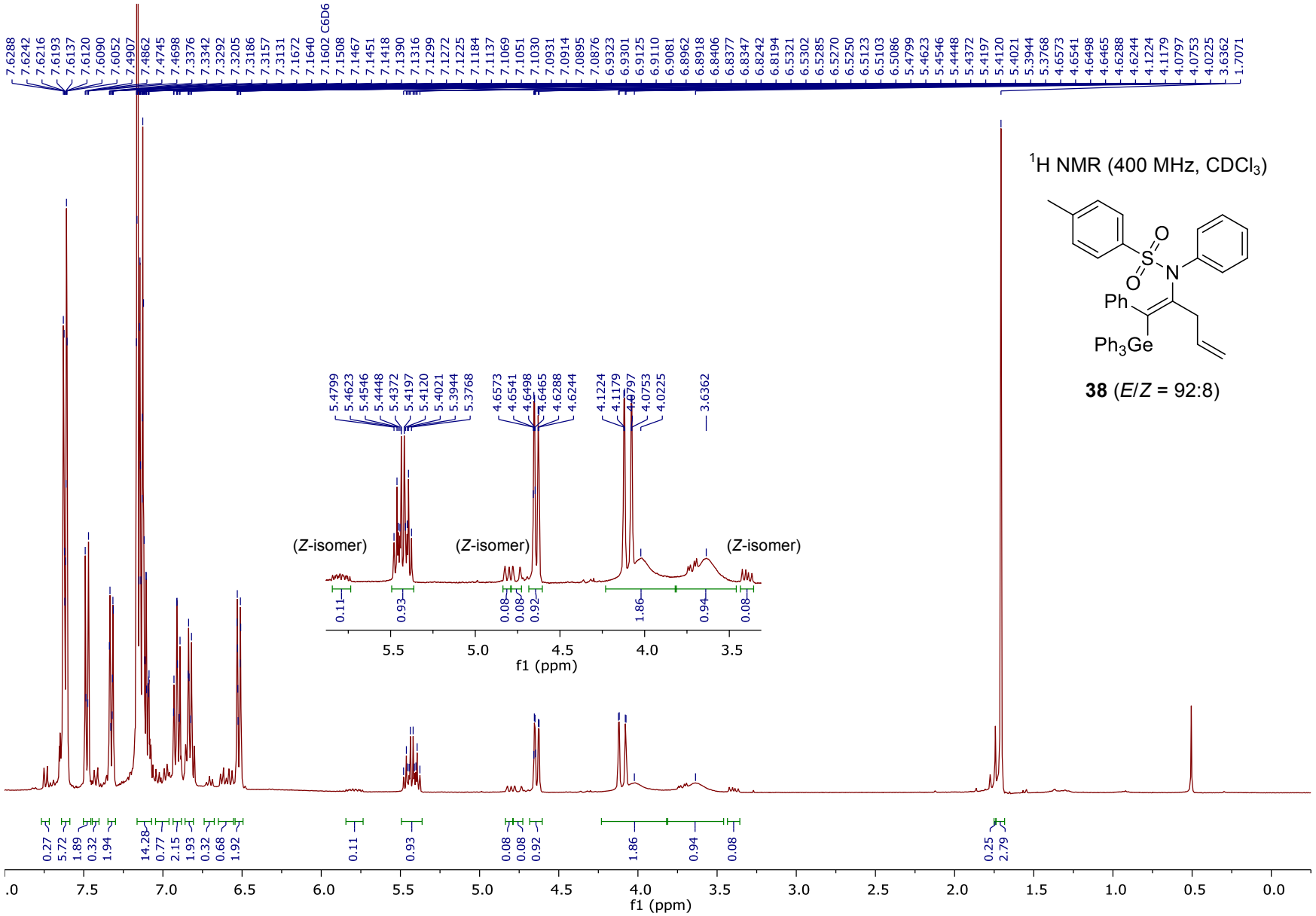

157.92
157.15
143.32
140.05
136.32
135.16
134.11
132.90
129.90
129.07
128.33
117.98
112.95
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.41
60.42
55.27
42.76
26.93
25.26
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
O
N
O
Ph_3Ge
35
f1 (ppm)

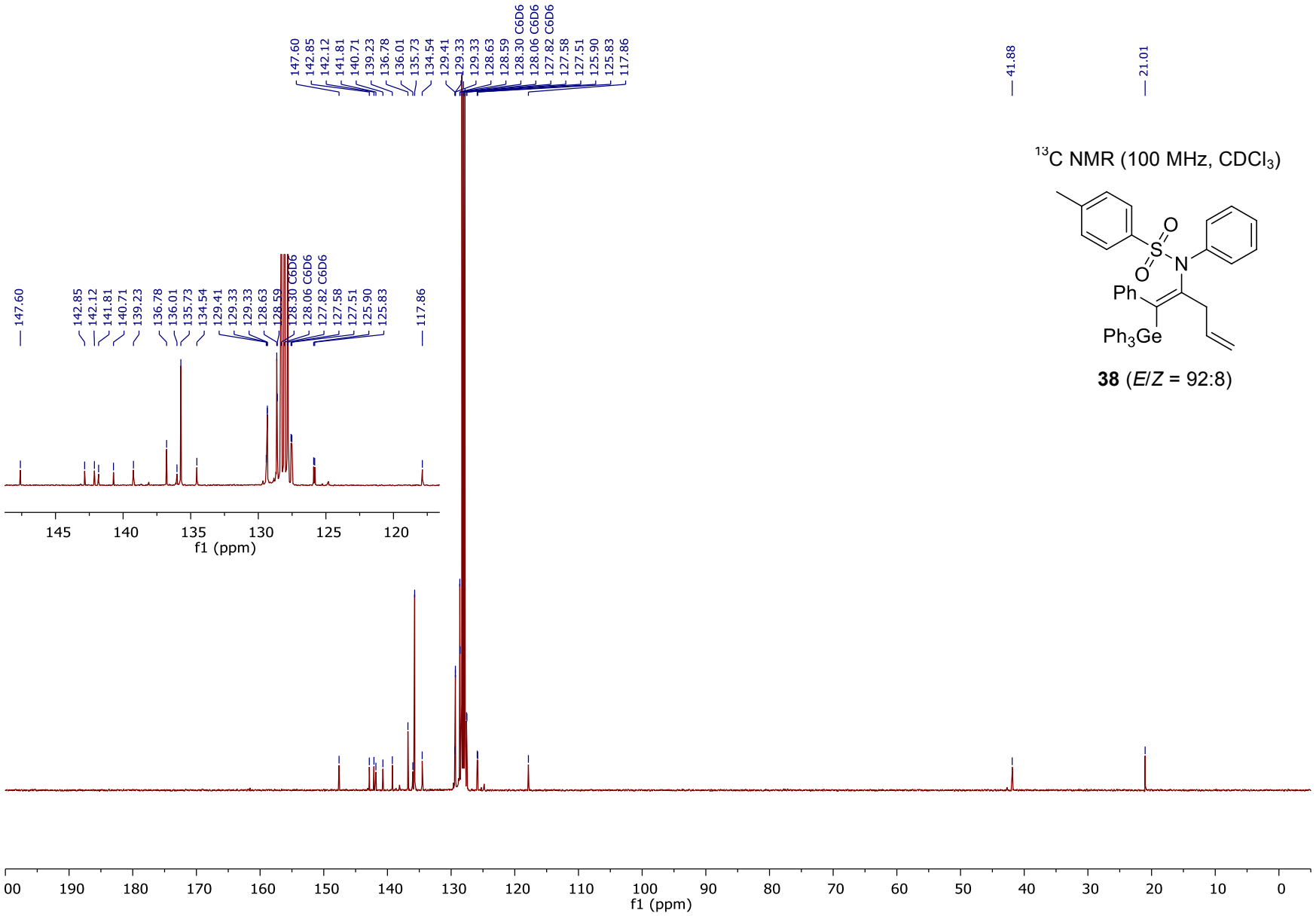

7.7857
7.6545
7.6353
7.3542
7.3387
7.3342
7.3229
7.3227
7.3140
7.2601 CDCl3
7.2098
7.2061
7.1905
7.1867
6.8830
6.8632
6.8435
6.8271
6.8234
6.8071
6.8032
5.5667
5.5517
5.5456
5.5413
5.5308
5.5245
5.5199
5.5097
5.5052
5.4990
5.4885
5.4841
5.4782
5.4632
5.0112
5.0082
5.0041
5.0013
4.9835
4.9801
4.9765
4.9723
4.9415
4.9379
4.9338
4.9301
3.8990
3.8797
3.8498
3.8305
3.8080
3.7863
3.7695
3.7477
3.2557
3.2420
3.2173
3.2036
1.3889
0.6347
1H NMR (400 MHz, CDCl3)
Cl
O
N
O
Cl
GePh3
36
1.00
2.00
2.00
1.00
1.00
5.6
5.4
5.2
5.0
4.8
3.8
3.6
3.4
3.2
f1 (ppm)
18.90
1.00
2.00
2.00
1.00
1.00
3.00
3.00
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
f1 (ppm)

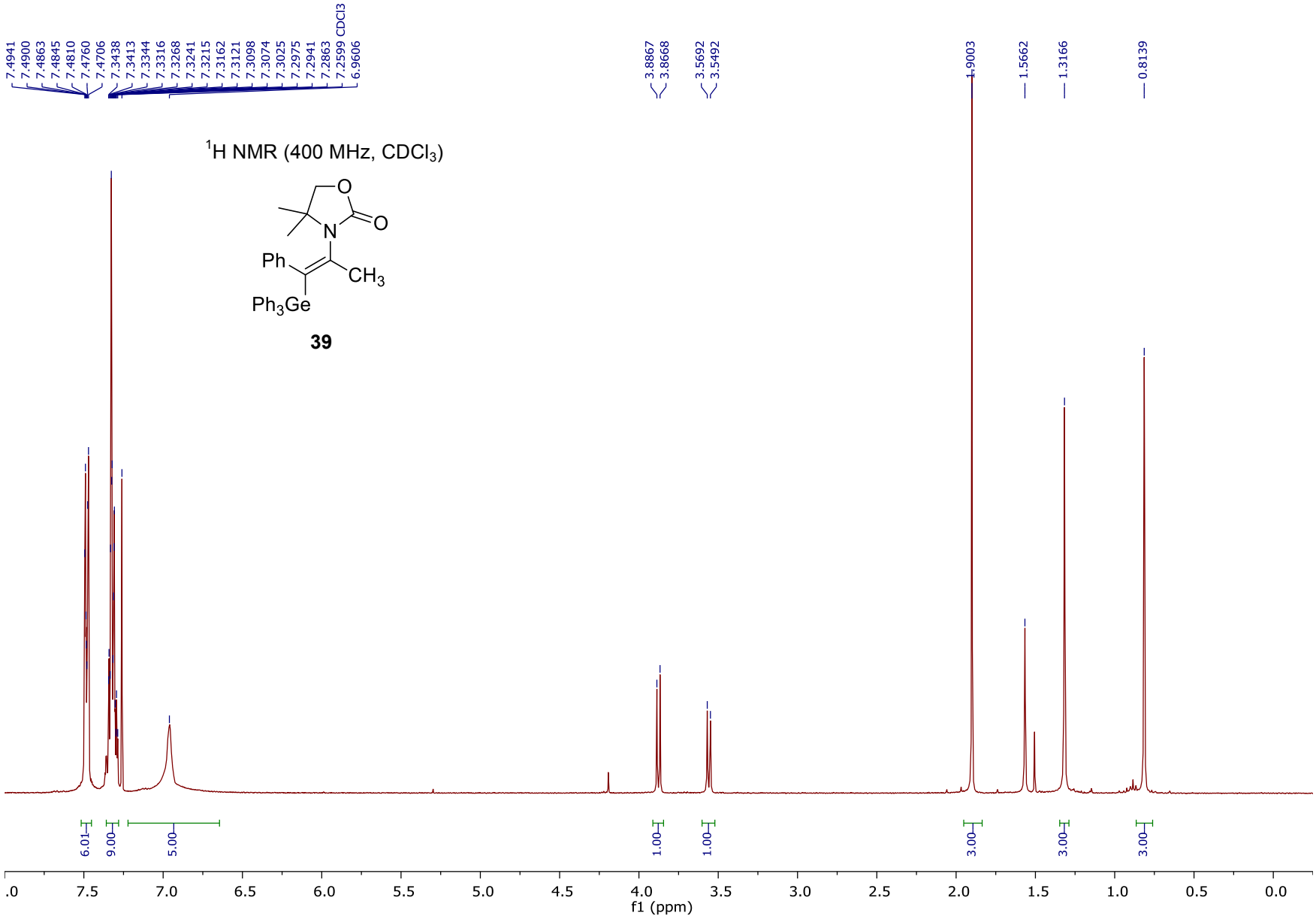

156.04
145.08
138.86
136.28
135.40
135.15
135.04
134.53
134.37
129.04
128.66
128.39
128.04
127.37
119.30
77.66
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.74
40.72
26.08
23.59
136.28
135.40
135.15
135.04
134.53
134.37
129.04
128.66
128.39
128.04
127.37
77.6619
77.4778 CDCl3
77.1605 CDCl3
76.8430 CDCl3
f1 (ppm)
^{13}C NMR (100 MHz, $CDCl_3$)
Cl
O
N
O
Cl
$GePh_3$
36

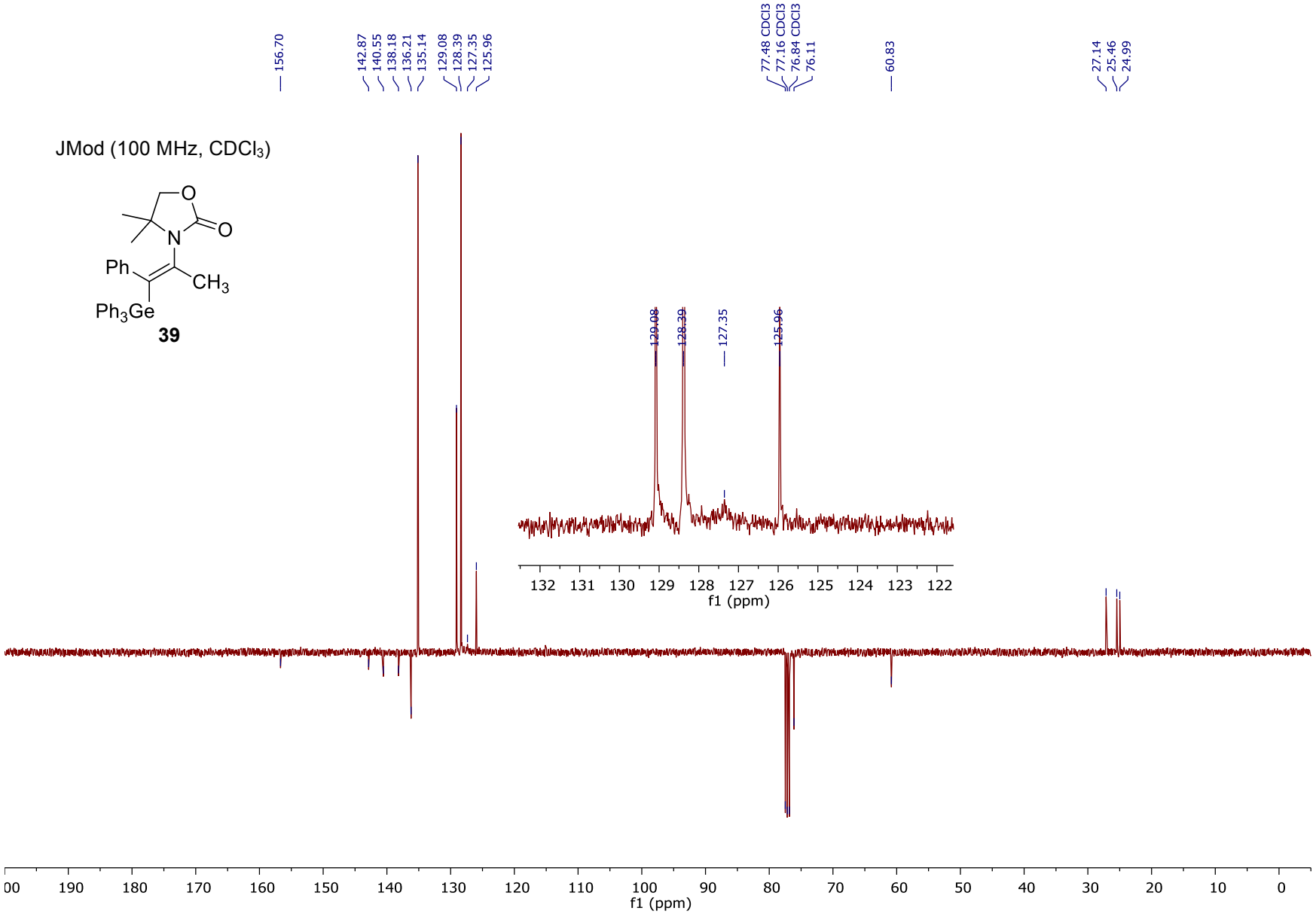

^{1}H NMR (400 MHz, C_6D_6)
Ph
Ph_3Ge
37
f1 (ppm)

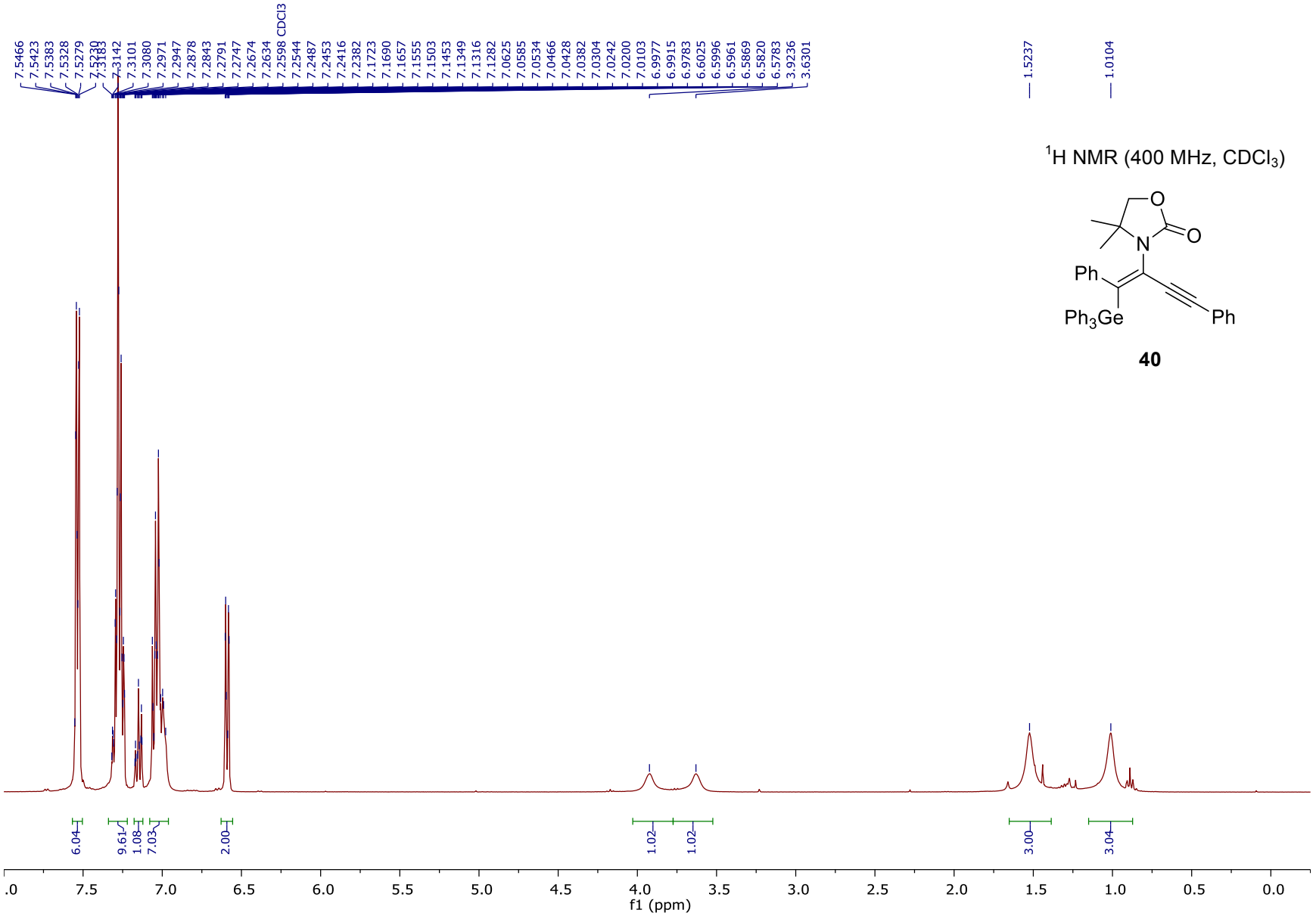

143.40
142.84
141.85
140.80
139.12
136.94
136.26
135.70
133.98
130.81
129.70
129.32
129.24
128.59
128.38 C6D6
128.24
128.13
128.06 C6D6
127.91
127.74 C6D6
125.92
117.55
52.45
42.23
21.11
f1 (ppm)
^{13}C NMR (100 MHz, C_6D_6)
Ph
Ph_3Ge
37


^{1}H NMR (400 MHz, $CDCl_3$)
38 (*E*/*Z* = 92:8)
Ph
Ph_3Ge
(*Z*-isomer)
(*Z*-isomer)
(*Z*-isomer)
f1 (ppm)


147.60
142.85
142.12
141.81
140.71
139.23
136.78
136.01
135.73
134.54
129.41
129.33
129.33
128.63
128.59
128.30 C6D6
128.06 C6D6
127.82 C6D6
127.58
127.51
125.90
125.83
117.86
41.88
21.01
f1 (ppm)
^{13}C NMR (100 MHz, $CDCl_3$)
Ph
Ph_3Ge
38 (*E*/*Z* = 92:8)

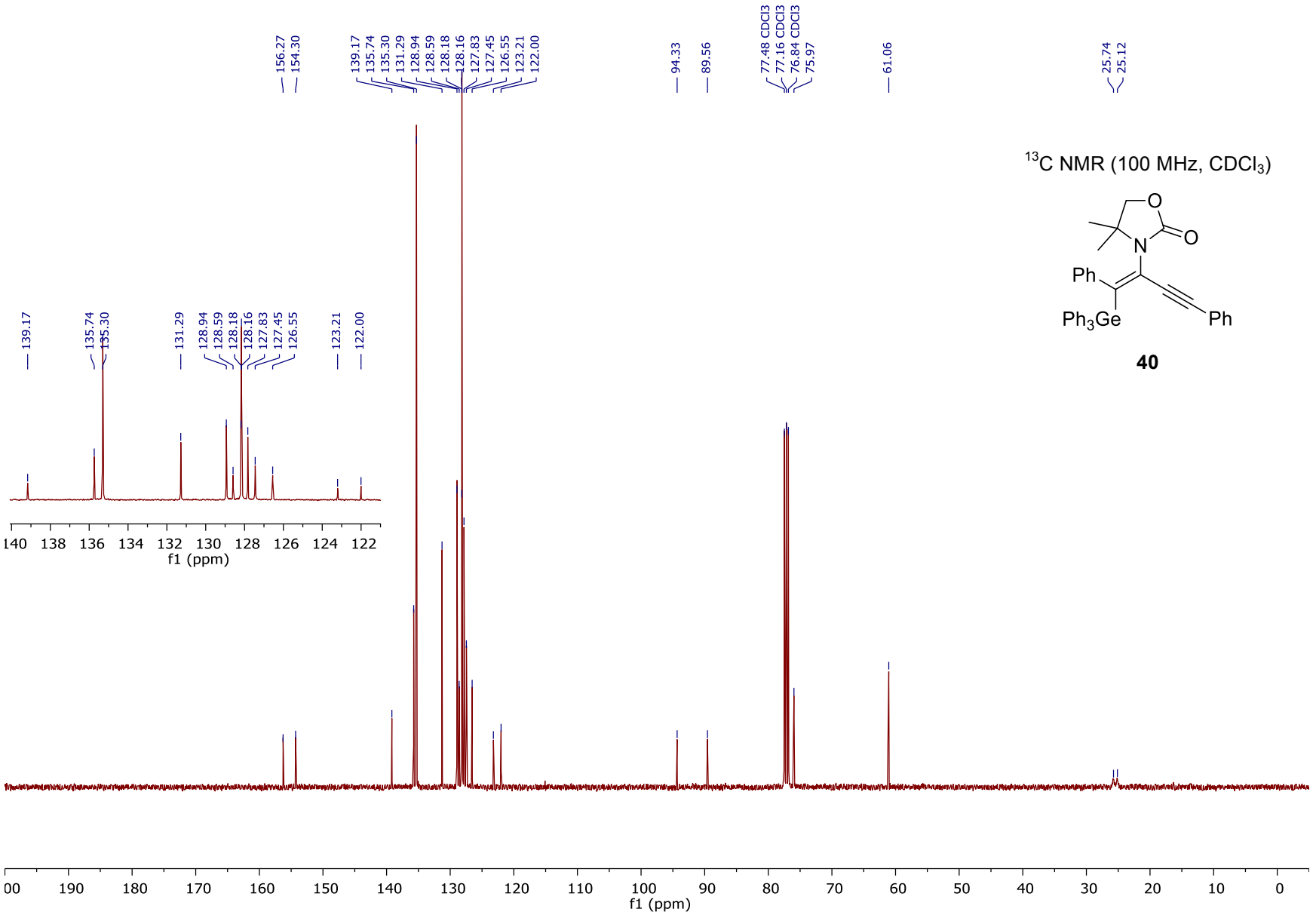

7.4941
7.4900
7.4863
7.4845
7.4810
7.4760
7.4706
7.3438
7.3413
7.3344
7.3316
7.3268
7.3241
7.3215
7.3162
7.3121
7.3098
7.3074
7.3025
7.2975
7.2941
7.2863
7.2599 CDCl3
6.9606
3.8867
3.8668
3.5692
3.5492
1.9003
1.5662
1.3166
0.8139
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
Ph
CH_3
Ph_3Ge
39
6.01
9.00
5.00
1.00
1.00
3.00
3.00
3.00
.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
f1 (ppm)

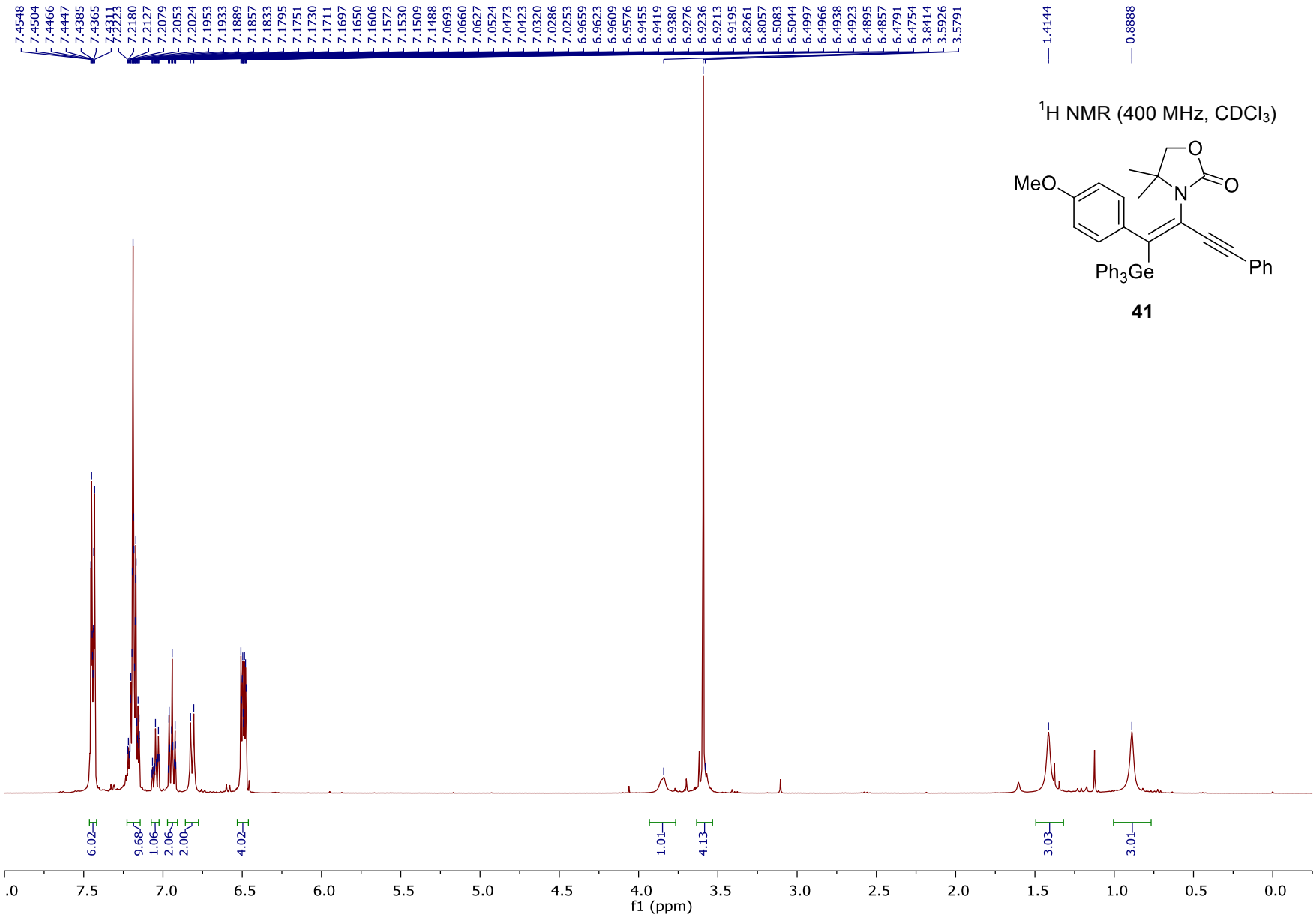

156.70
142.87
140.55
138.18
136.21
135.14
129.08
128.39
127.35
125.96
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.11
60.83
27.14
25.46
24.99
JMod (100 MHz, CDCl3)
O
O
N
Ph
CH3
Ph3Ge
39
f1 (ppm)
f1 (ppm)



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

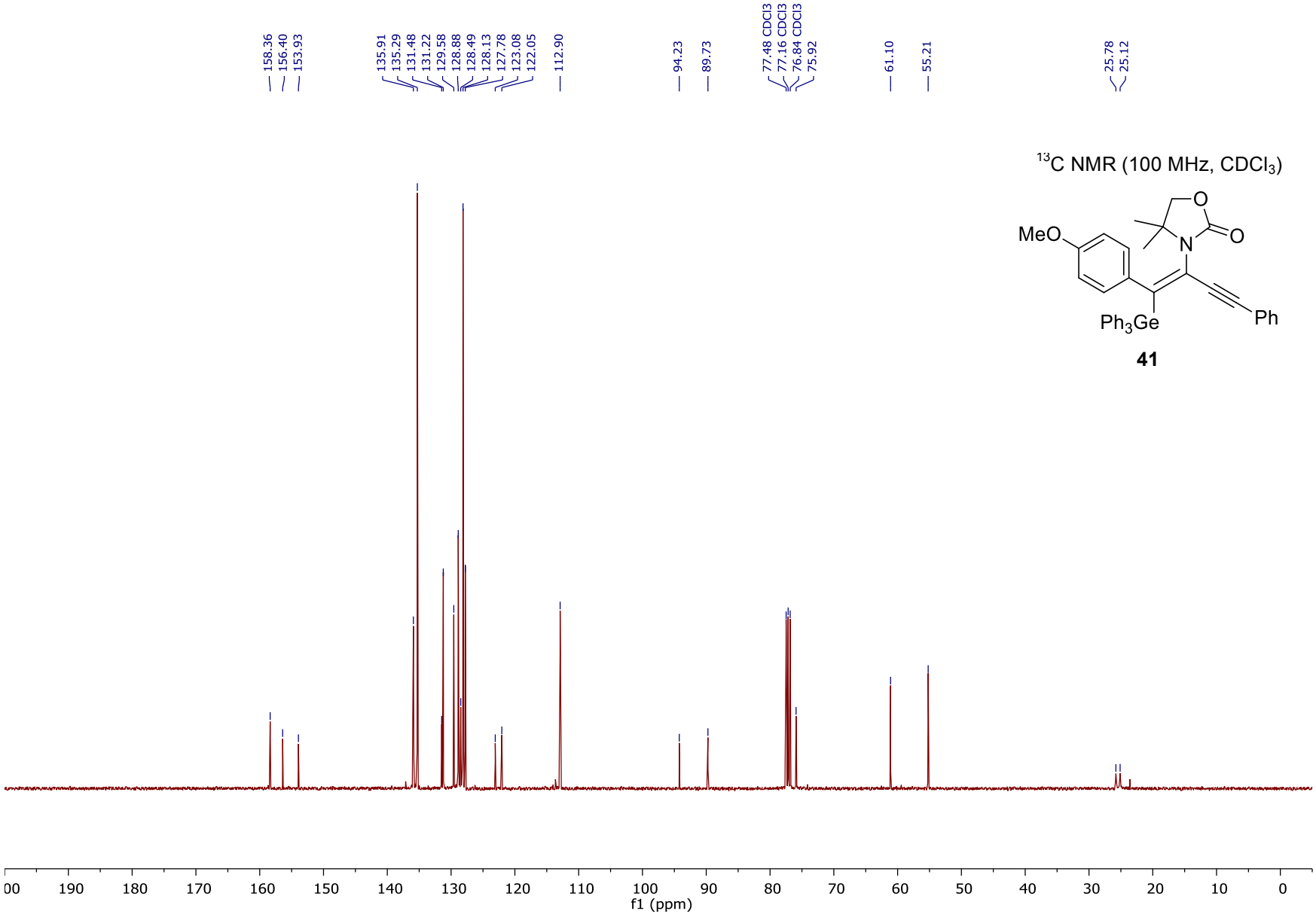
40


156.27
154.30
139.17
135.74
135.30
131.29
128.94
128.59
128.18
128.16
127.83
127.45
126.55
123.21
122.00
94.33
89.56
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.97
61.06
25.74
25.12
f1 (ppm)
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
Ph
Ph_3Ge
Ph
40



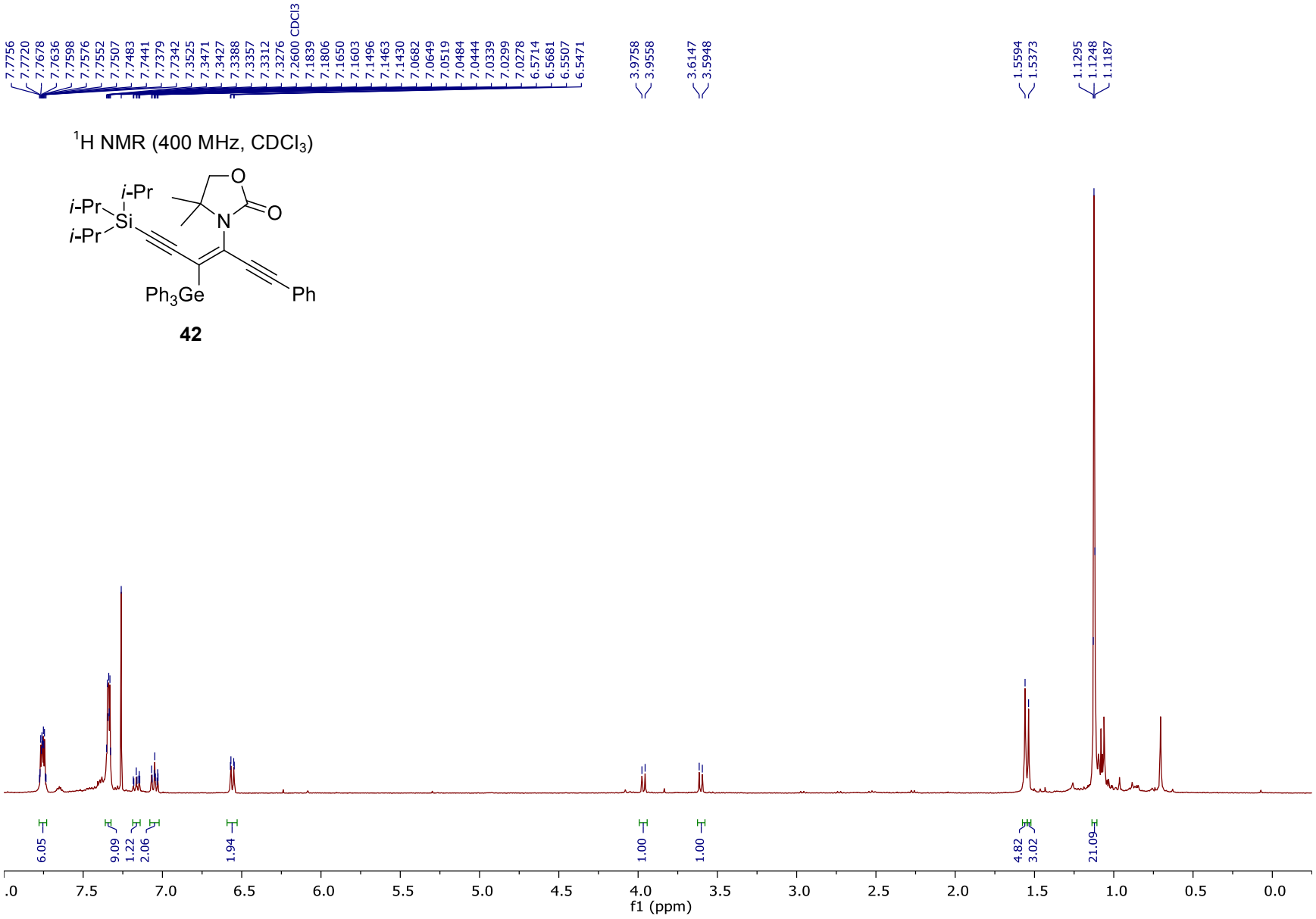
^{1}H NMR (400 MHz, $CDCl_3$)

41



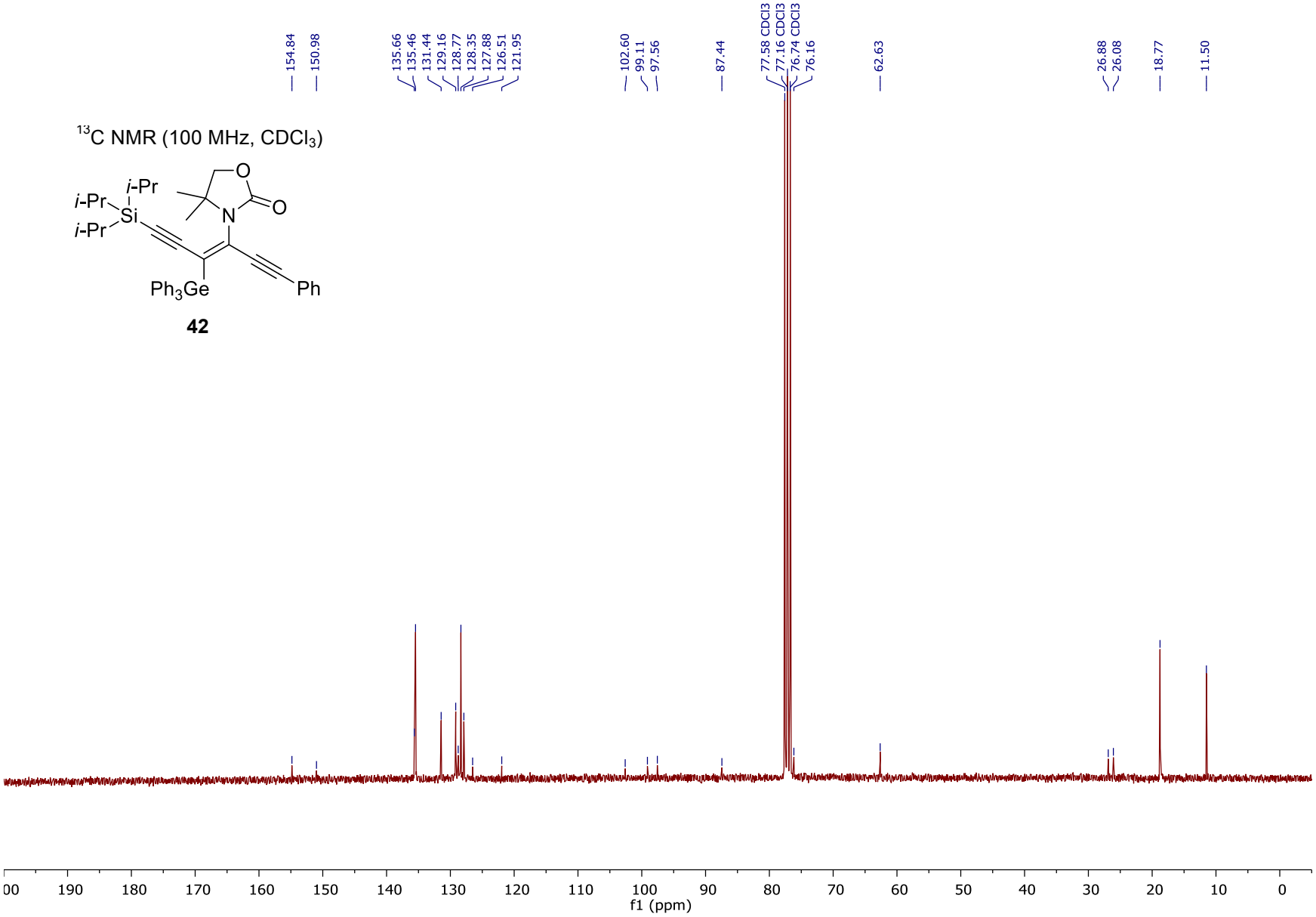
^{13}C NMR (100 MHz, $CDCl_3$)

41



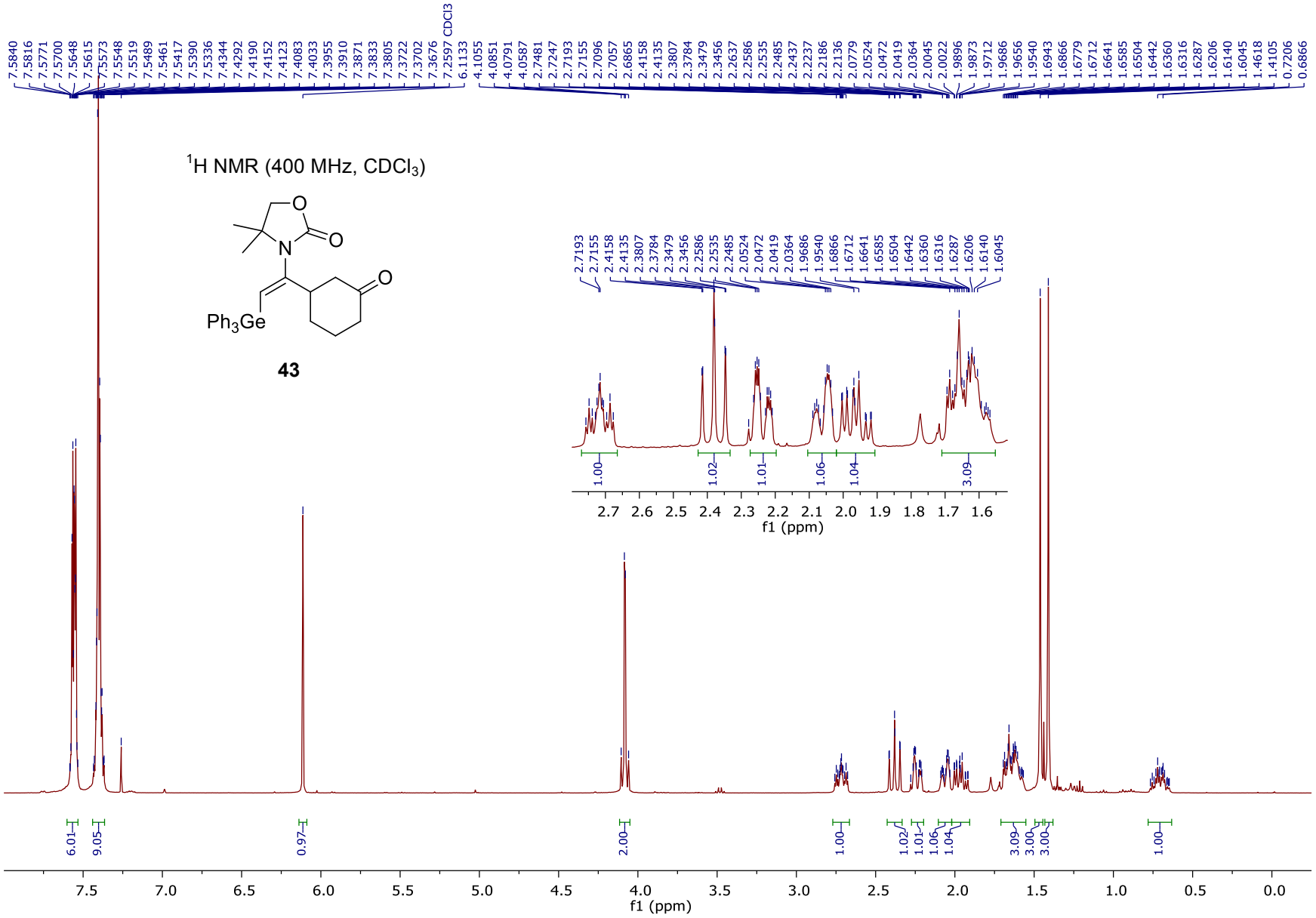
^{1}H NMR (400 MHz, $CDCl_3$)

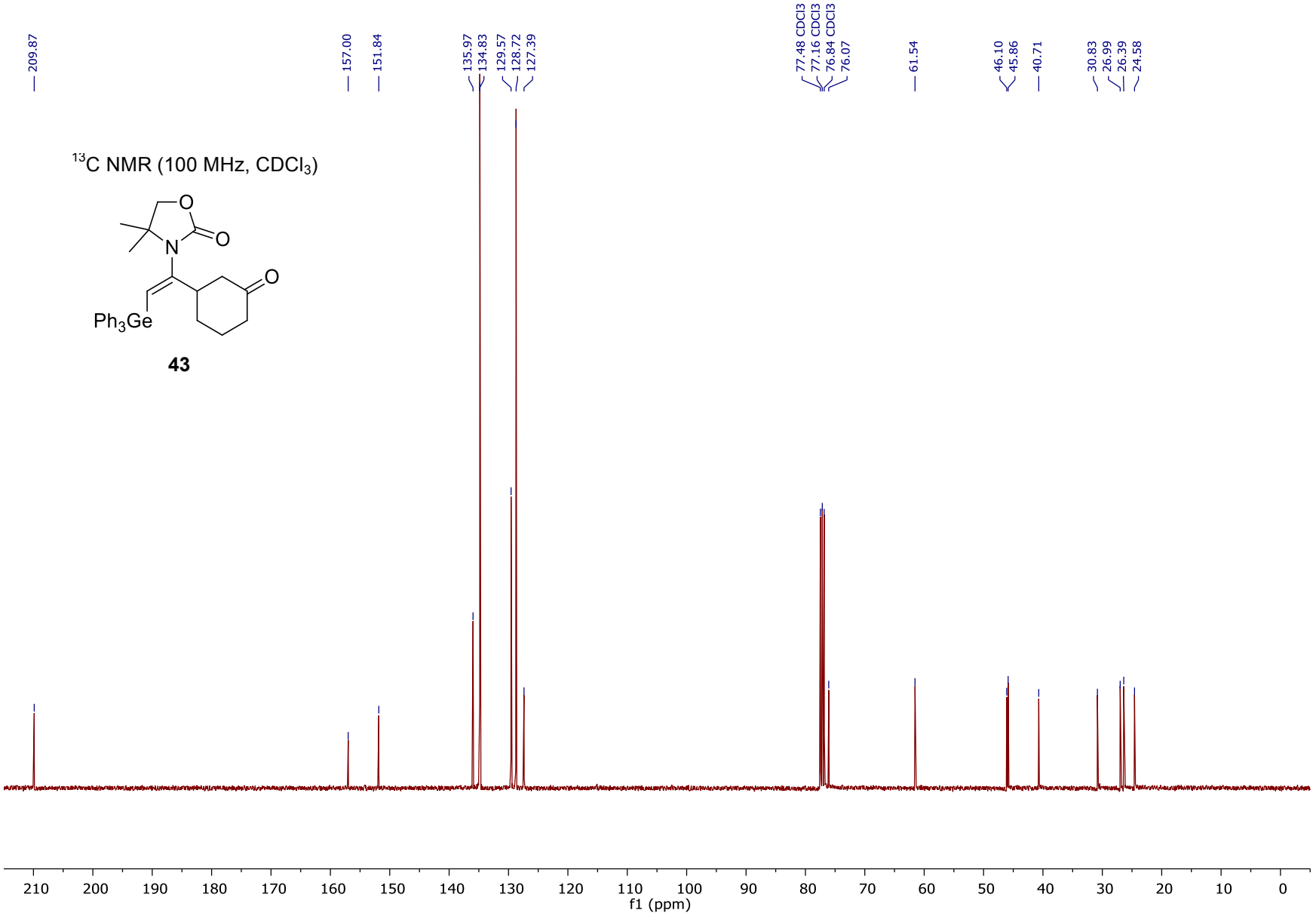
42



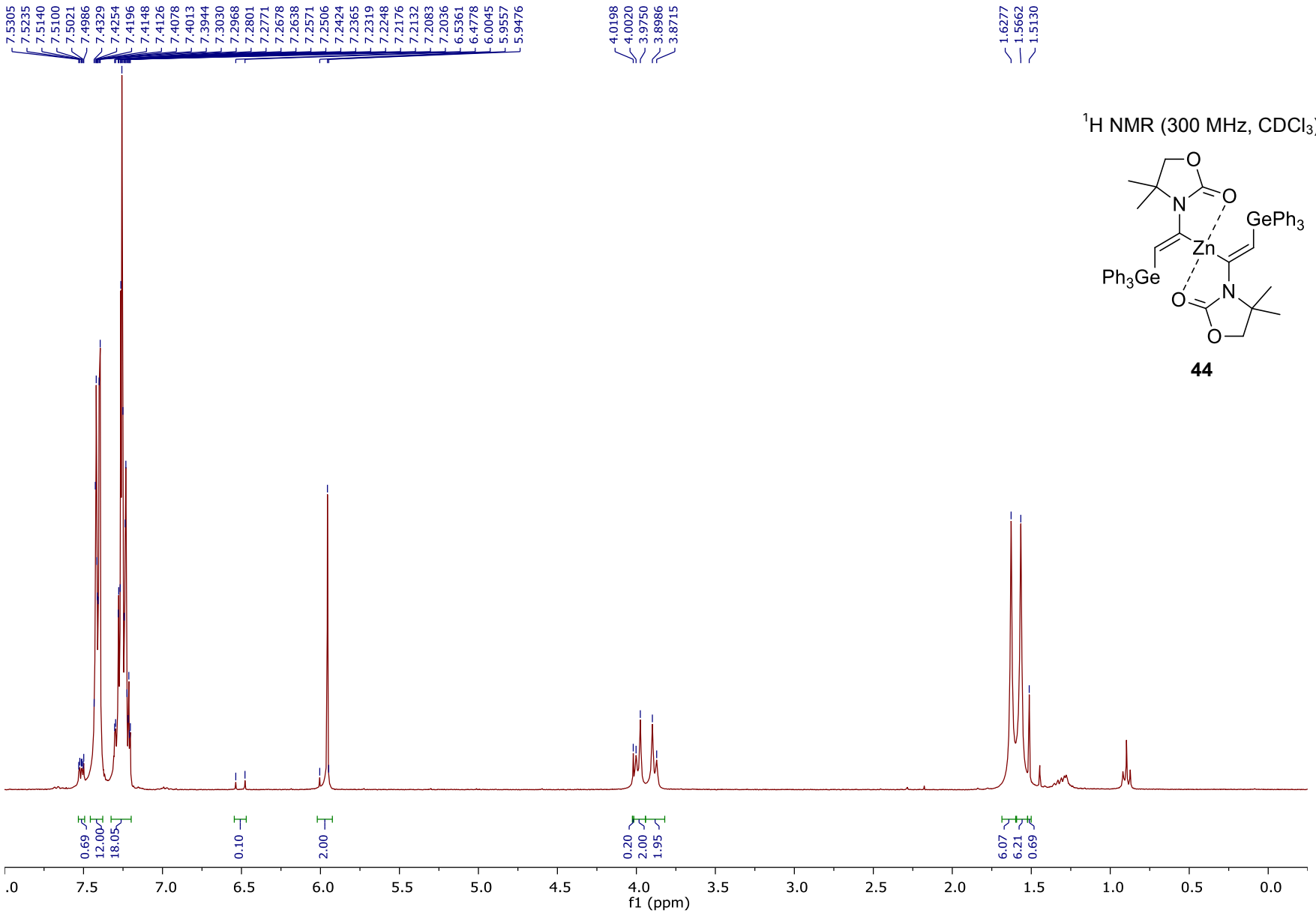
^{13}C NMR (100 MHz, $CDCl_3$)

42


^{1}H NMR (400 MHz, $CDCl_3$)
Ph_3Ge
43
f1 (ppm)

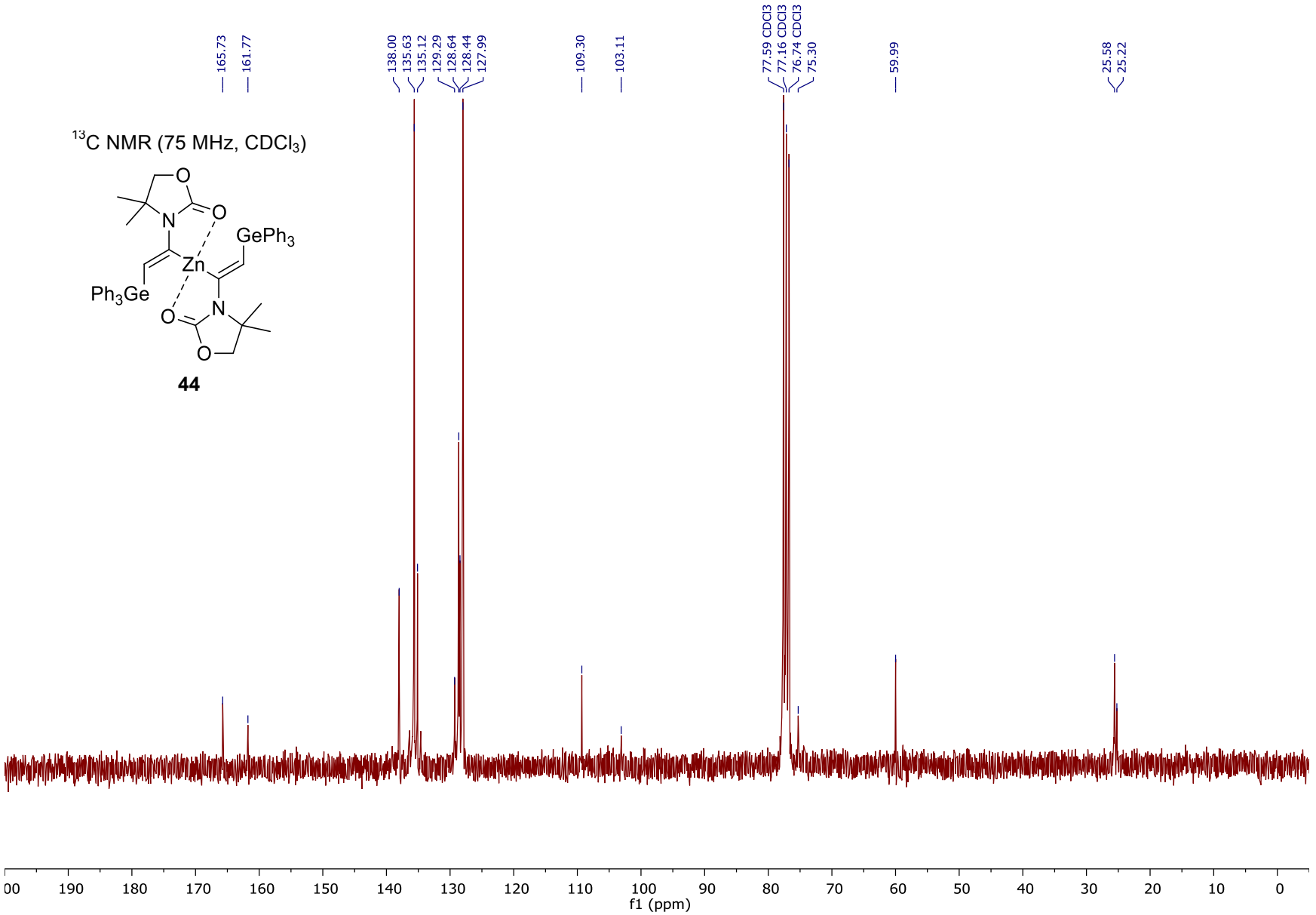

209.87
157.00
151.84
135.97
134.83
129.57
128.72
127.39
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.07
61.54
46.10
45.86
40.71
30.83
26.99
26.39
24.58
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
O
Ph_3Ge
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

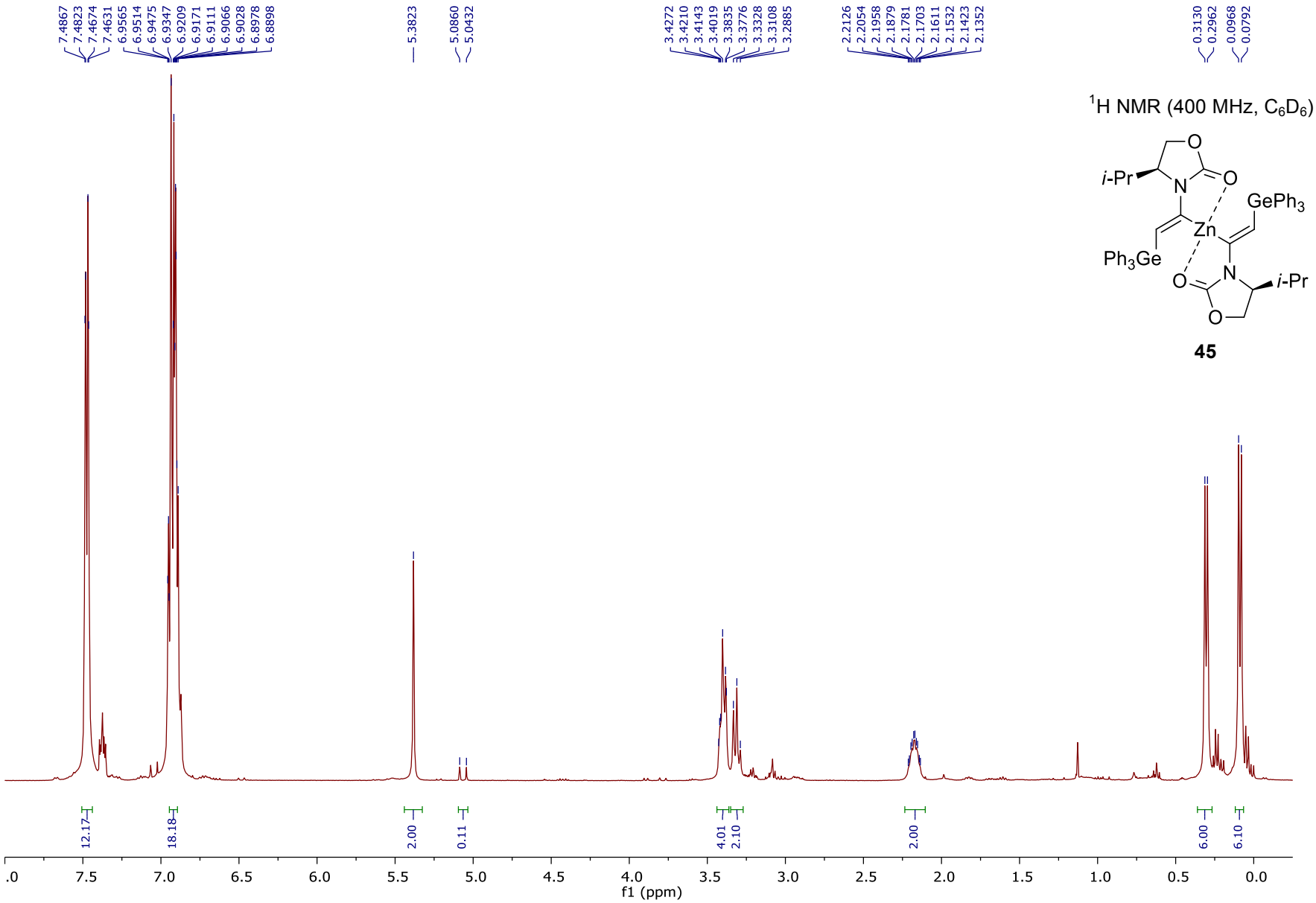
43



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

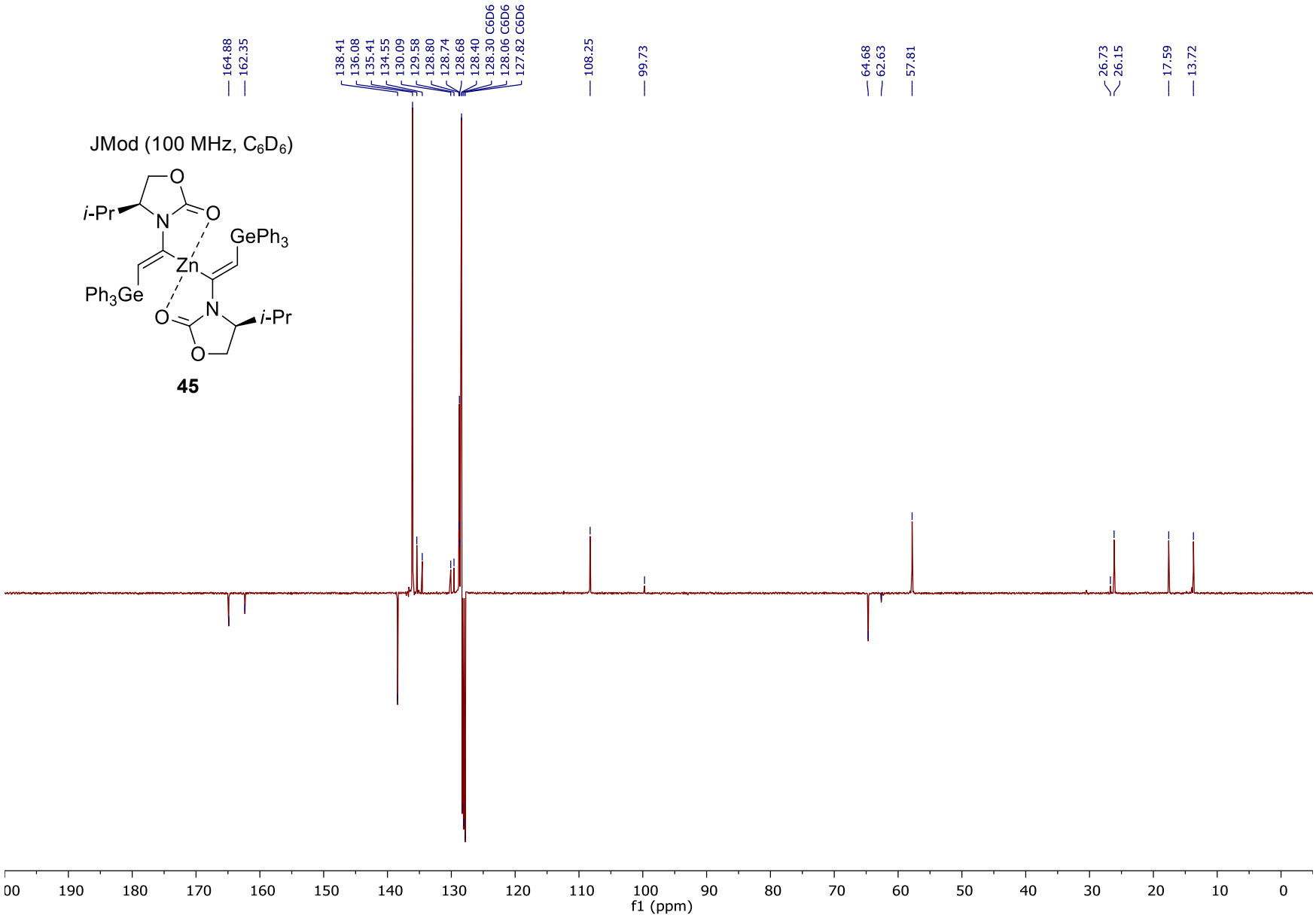
44

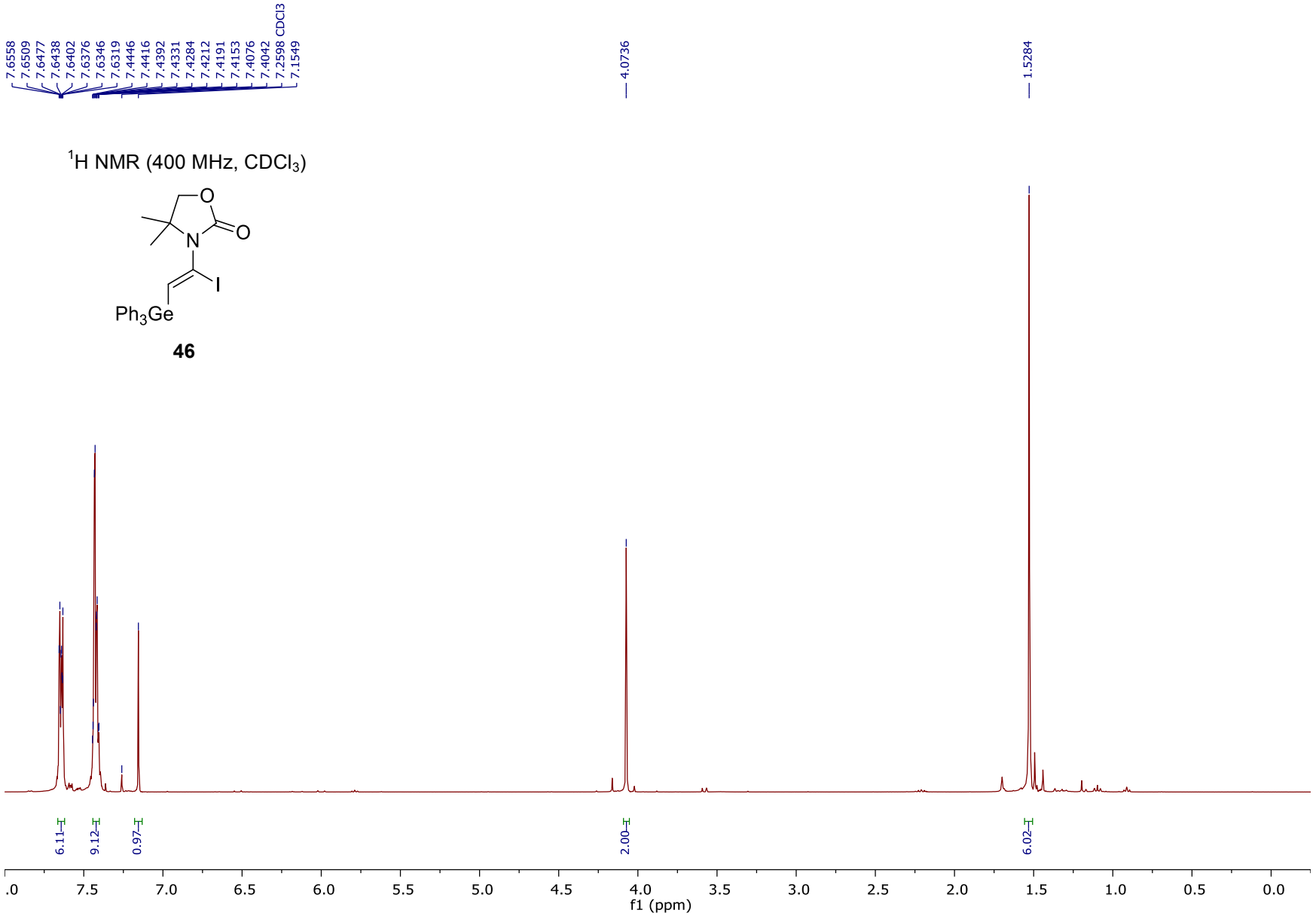

165.73
161.77
138.00
135.63
135.12
129.29
128.64
128.44
127.99
109.30
103.11
77.59 CDCl3
77.16 CDCl3
76.74 CDCl3
75.30
59.99
25.58
25.22
13C NMR (75 MHz, CDCl3)
O
N
O
GePh3
Zn
Ph3Ge
O
N
O
44
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{1}H NMR (400 MHz, C_6D_6)

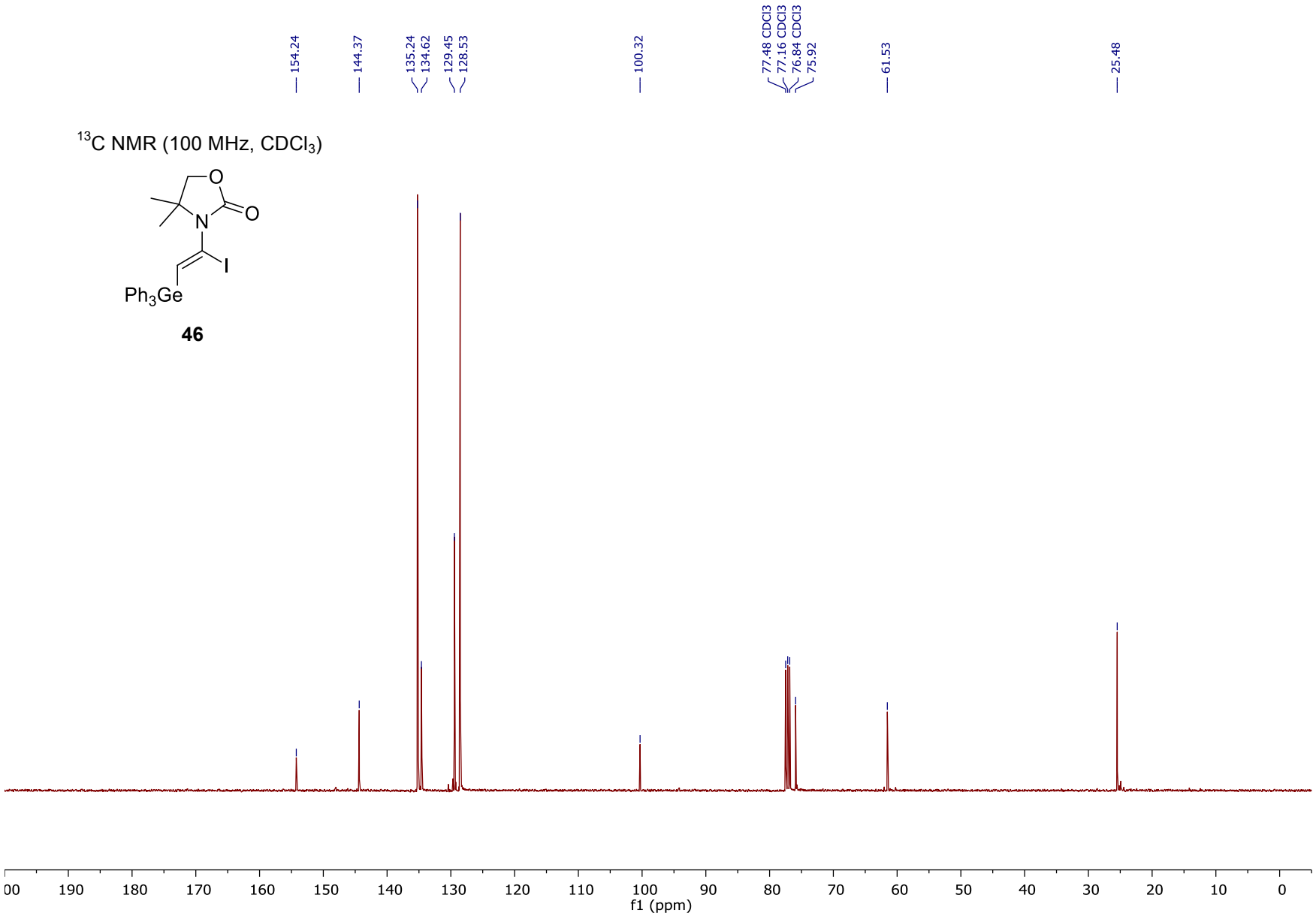
45

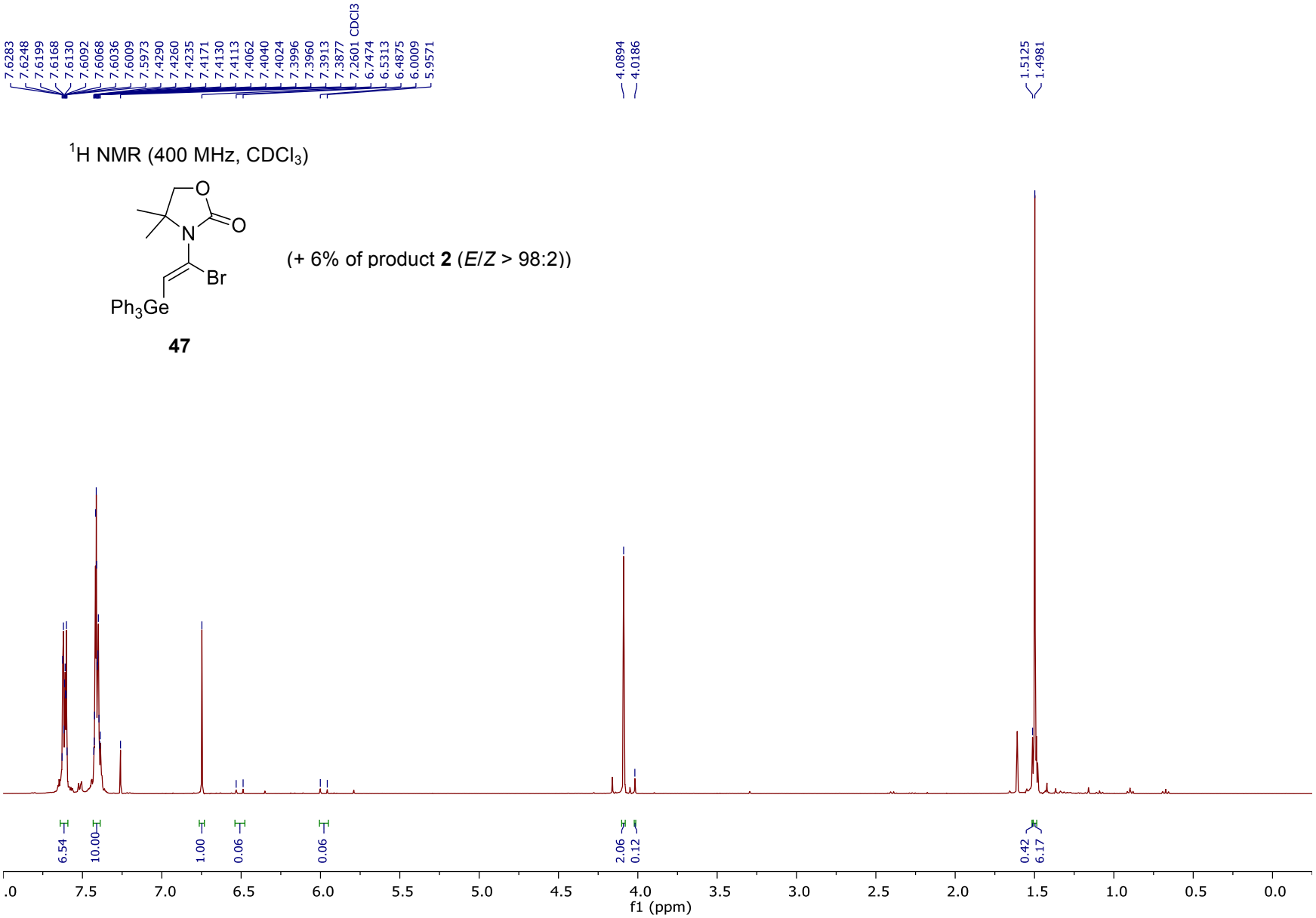

JMod (100 MHz, C6D6)
i-Pr
GePh3
Zn
Ph3Ge
i-Pr
45
164.88
162.35
138.41
136.08
135.41
134.55
130.09
129.58
128.80
128.74
128.68
128.40
128.30 C6D6
128.06 C6D6
127.82 C6D6
108.25
99.73
64.68
62.63
57.81
26.73
26.15
17.59
13.72
f1 (ppm)



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

46


154.24
144.37
135.24
134.62
129.45
128.53
100.32
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.92
61.53
25.48
13C NMR (100 MHz, CDCl3)
O
O
N
I
Ph3Ge
46
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

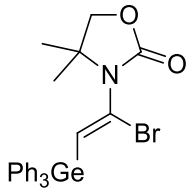


^{1}H NMR (400 MHz, $CDCl_3$)

47

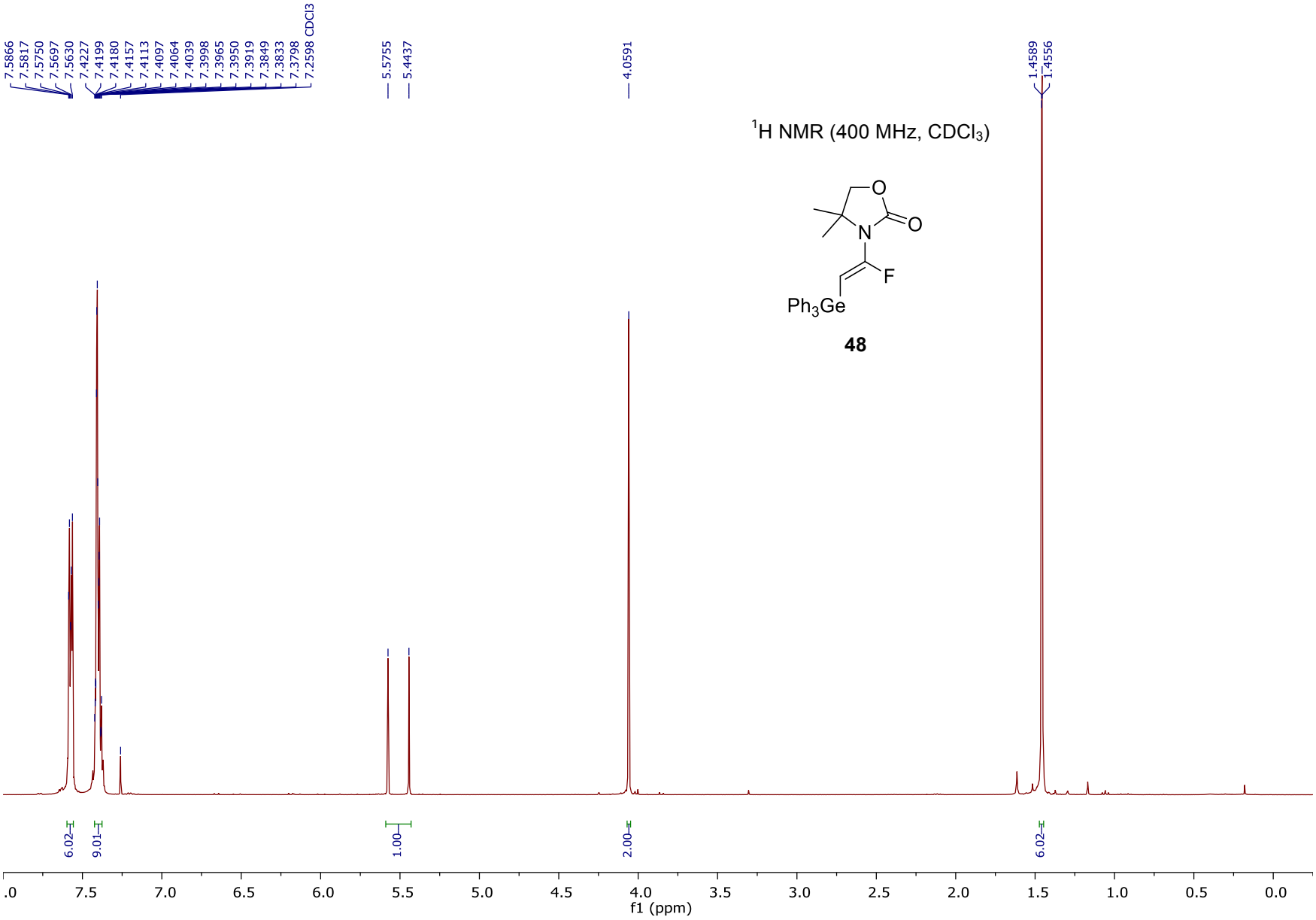
(+ 6% of product **2** (*E*/*Z* > 98:2))

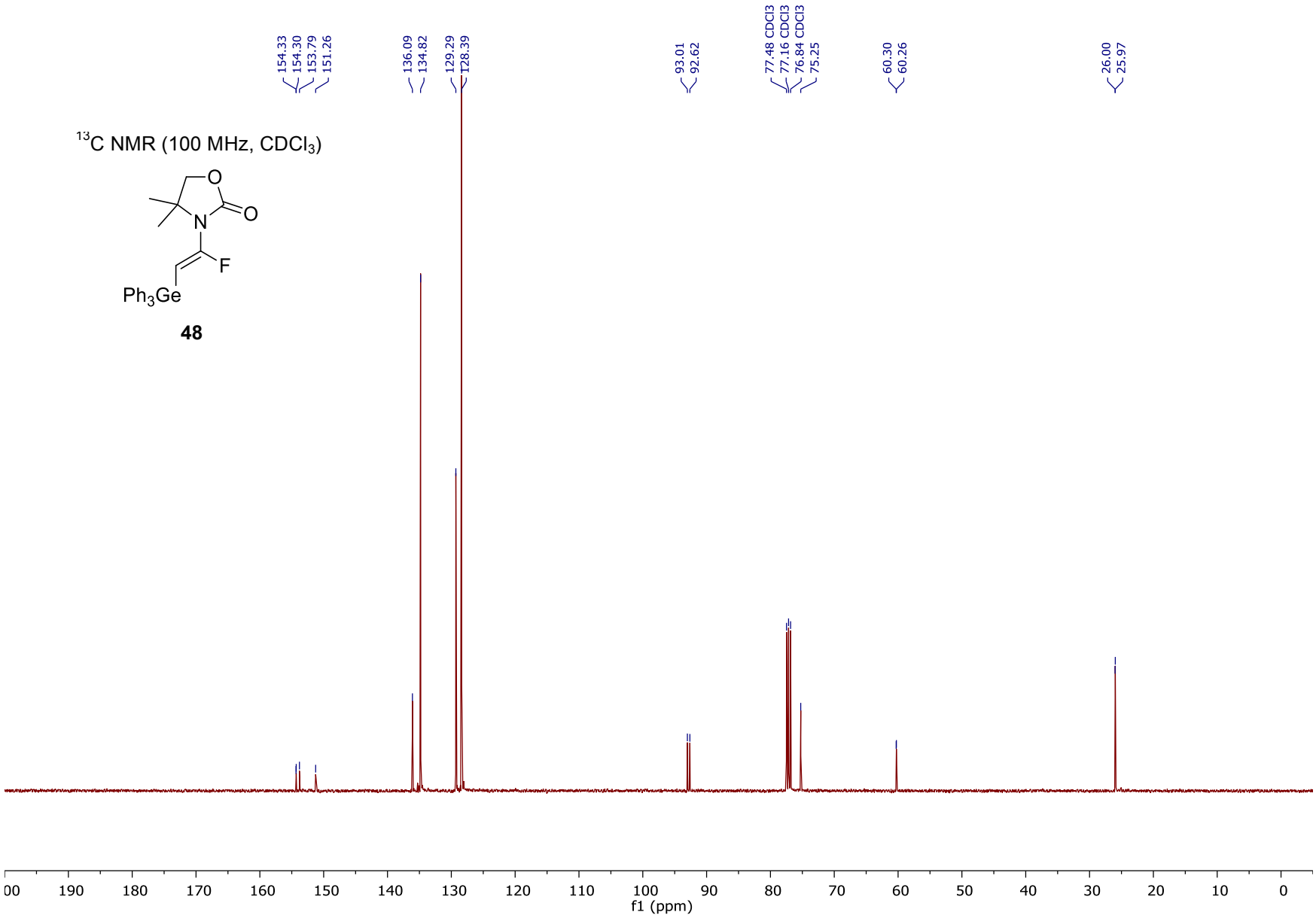
^{13}C NMR (100 MHz, $CDCl_3$)



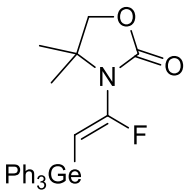
47

(+ 6% of product **2** (*E*/*Z* > 98:2))

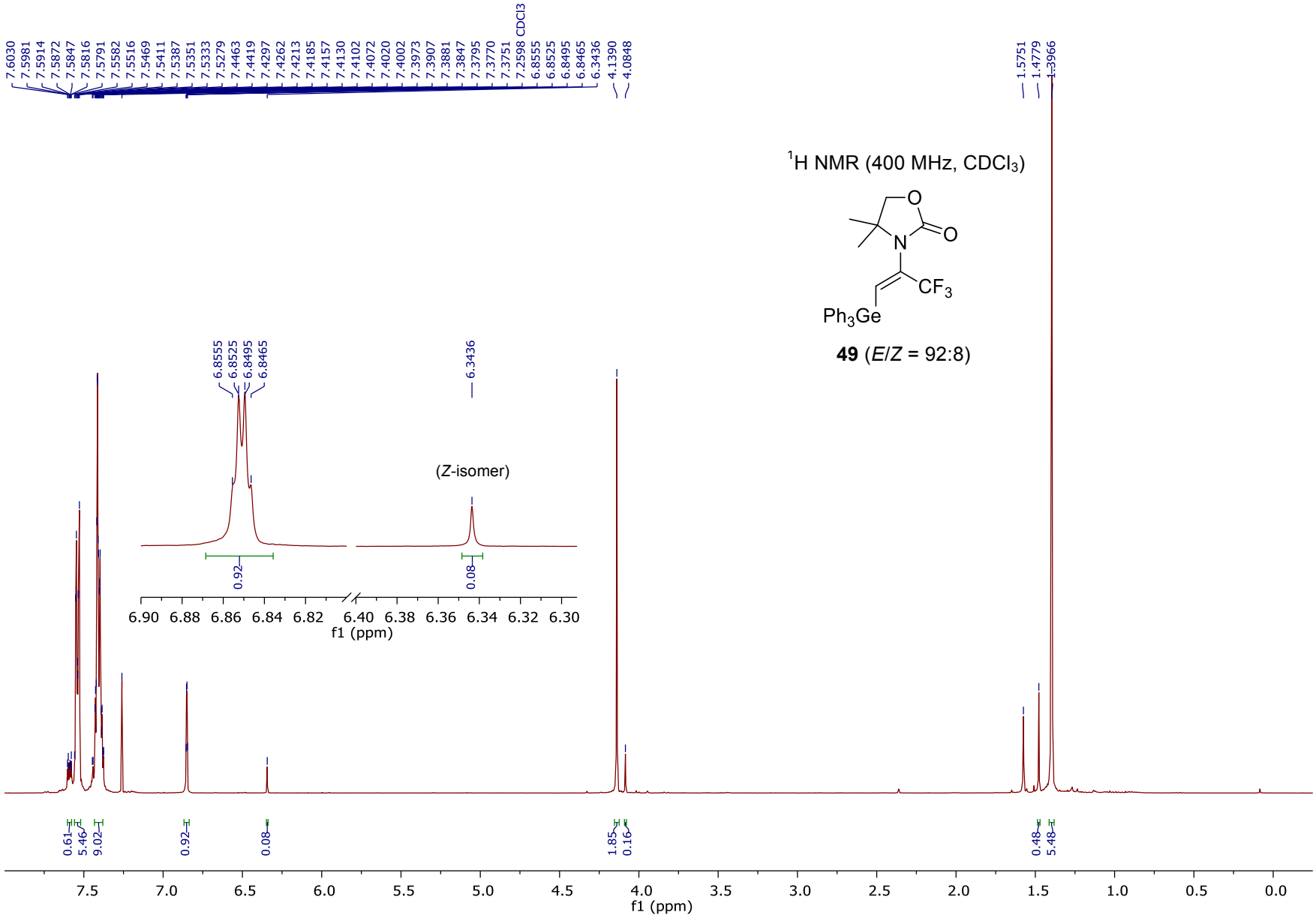

7.5866
7.5817
7.5750
7.5697
7.5630
7.4227
7.4199
7.4180
7.4157
7.4113
7.4097
7.4064
7.4039
7.3998
7.3965
7.3950
7.3919
7.3849
7.3833
7.3798
7.2598 CDCl3
5.5755
5.4437
4.0591
1.4589
1.4556
^{1}H NMR (400 MHz, $CDCl_3$)
O
O
N
F
Ph_3Ge
48
6.02
9.01
1.00
2.00
6.02
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

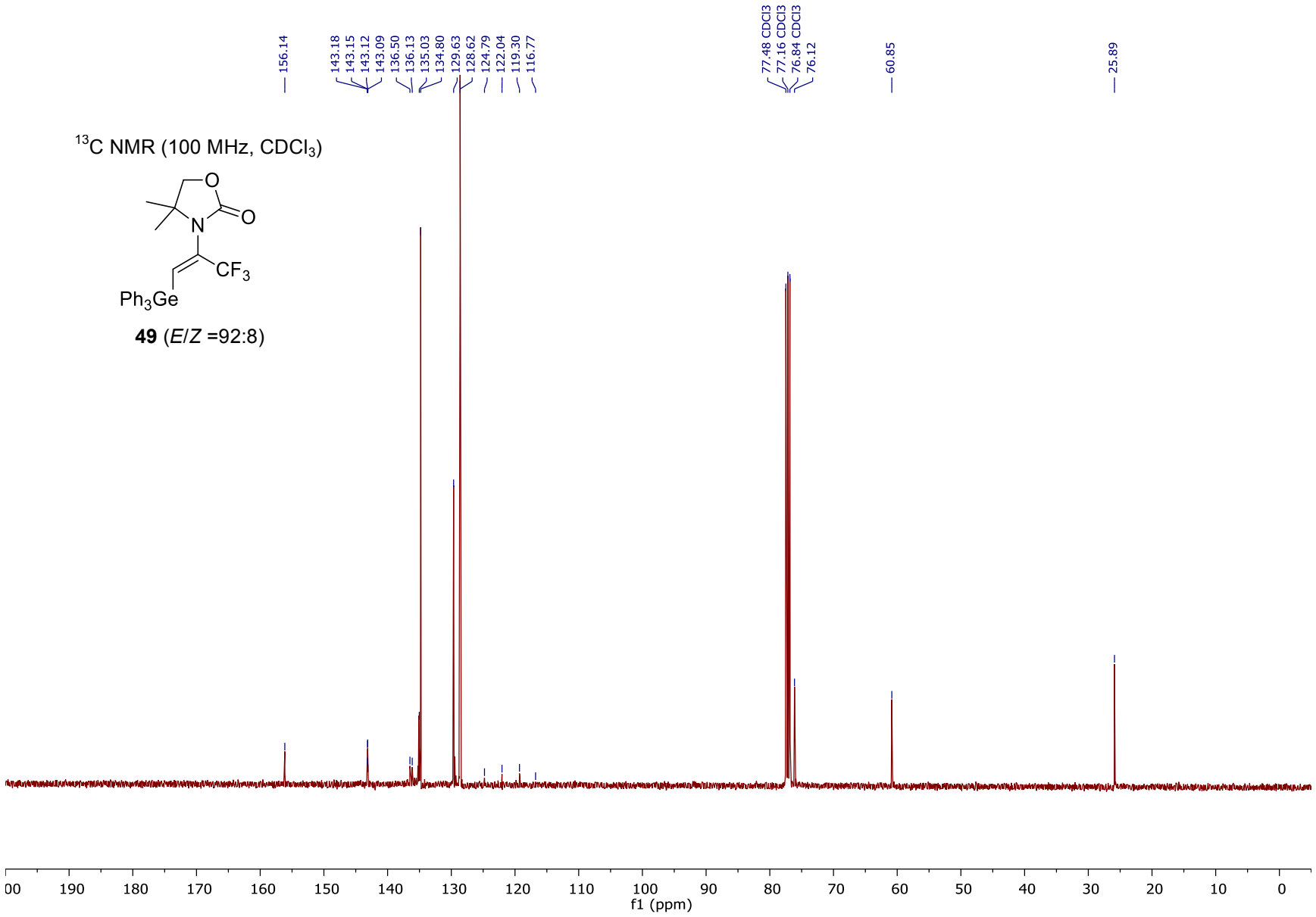

154.33
154.30
153.79
151.26
136.09
134.82
129.29
128.39
93.01
92.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.25
60.30
60.26
26.00
25.97
13C NMR (100 MHz, CDCl3)
O
O
N
F
Ph3Ge
48
f1 (ppm)

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



48

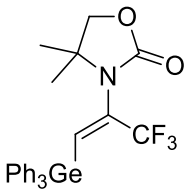

7.6030
7.5981
7.5914
7.5872
7.5847
7.5816
7.5791
7.5582
7.5516
7.5469
7.5411
7.5387
7.5351
7.5333
7.5279
7.4463
7.4419
7.4297
7.4262
7.4213
7.4185
7.4157
7.4130
7.4102
7.4072
7.4020
7.4002
7.3973
7.3907
7.3881
7.3847
7.3795
7.3770
7.3751
CDCl3
7.2598
6.8555
6.8525
6.8495
6.8465
6.3436
4.1390
4.0848
1.5751
1.4779
1.3966
^{1}H NMR (400 MHz, $CDCl_3$)
49 (*E*/*Z* = 92:8)
(*Z*-isomer)
0.92
0.08
6.90 6.88 6.86 6.84 6.82 6.40 6.38 6.36 6.34 6.32 6.30
f1 (ppm)
0.61
5.46
9.02
0.92
0.08
1.85
0.16
0.48
5.48
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
f1 (ppm)



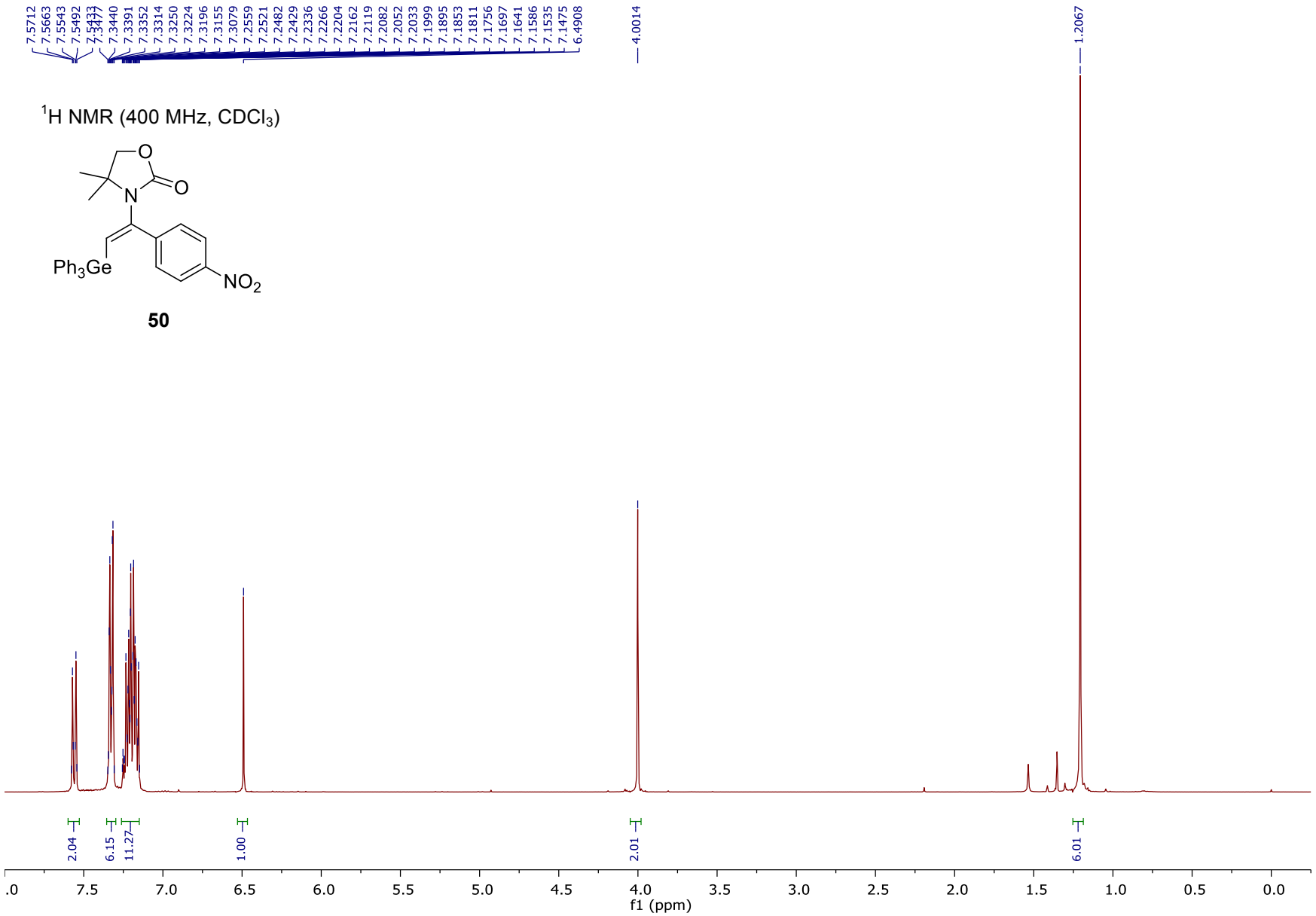
^{13}C NMR (100 MHz, $CDCl_3$)

49 (*E*/*Z* =92:8)

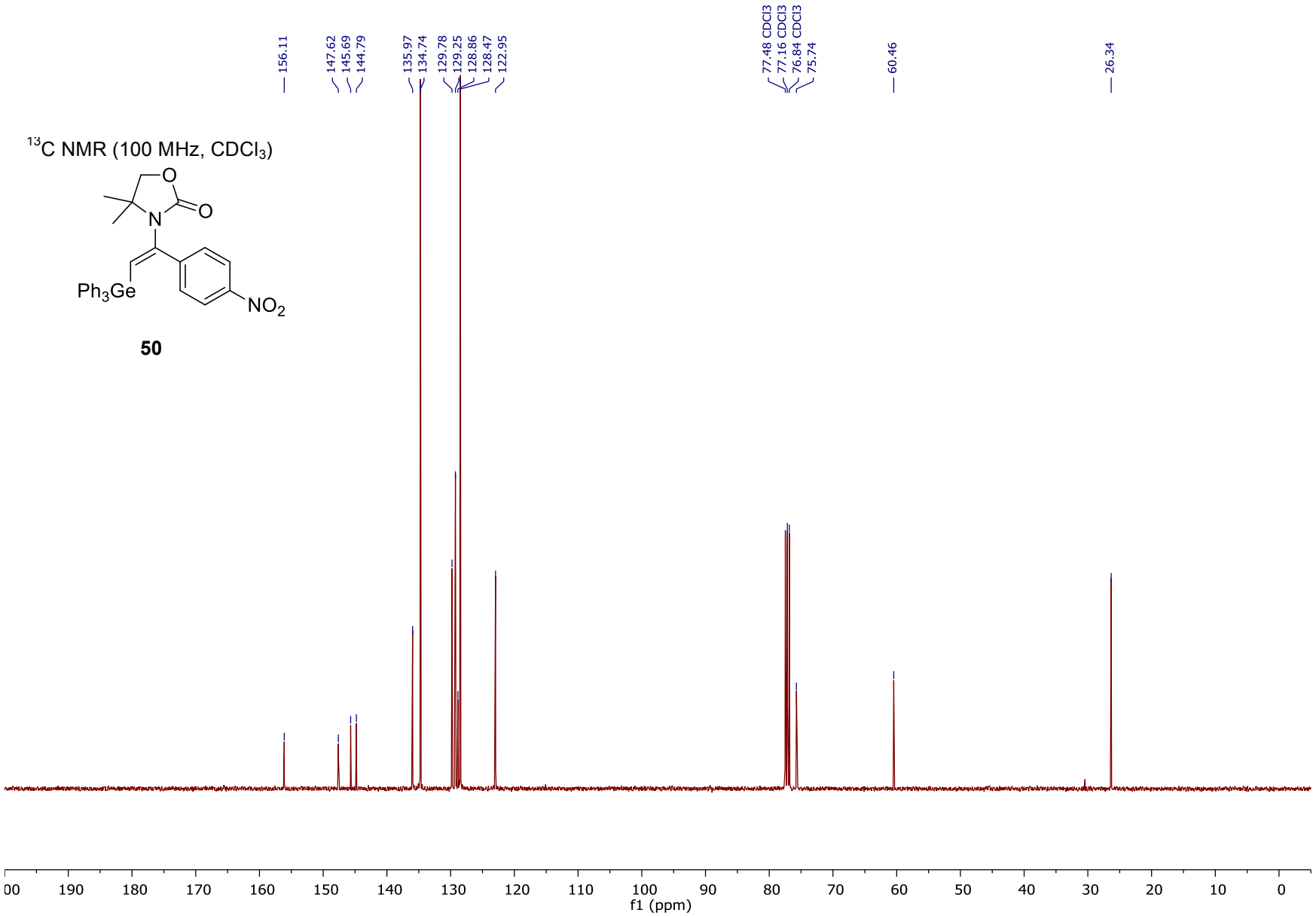
^{19}F NMR (376 MHz, $CDCl_3$)



49 (*E*/*Z* =92:8)

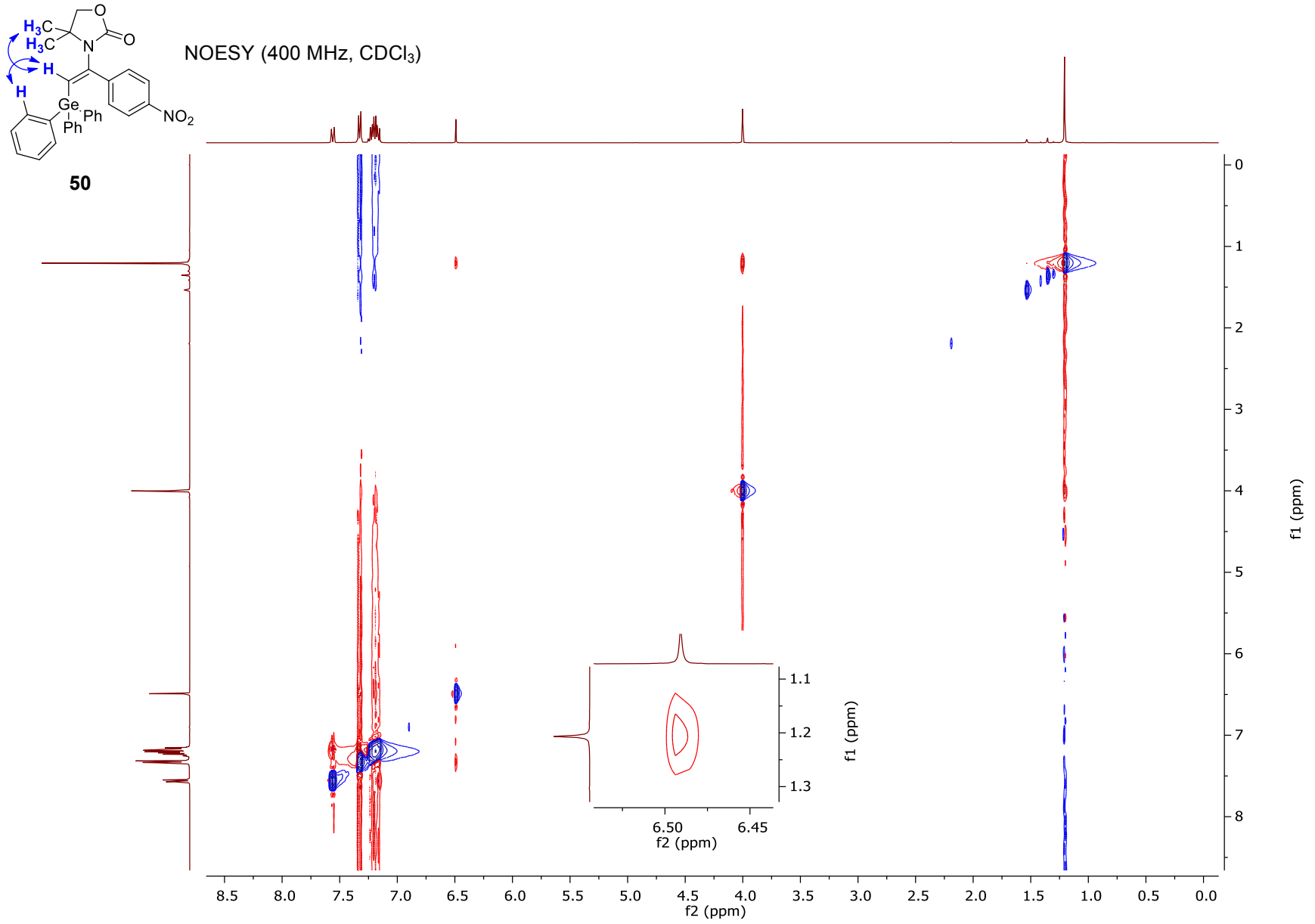

7.5712
7.5663
7.5543
7.5492
7.5433
7.5377
7.3440
7.3391
7.3352
7.3314
7.3250
7.3224
7.3196
7.3155
7.3079
7.2559
7.2521
7.2482
7.2429
7.2336
7.2266
7.2204
7.2162
7.2119
7.2082
7.2052
7.2033
7.1999
7.1895
7.1853
7.1811
7.1756
7.1697
7.1641
7.1586
7.1535
7.1475
6.4908
4.0014
1.2067
^{1}H NMR (400 MHz, $CDCl_3$)
O
N
O
Ph_3Ge
NO_2
2.04
6.15
11.27
1.00
2.01
6.01
.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
f1 (ppm)

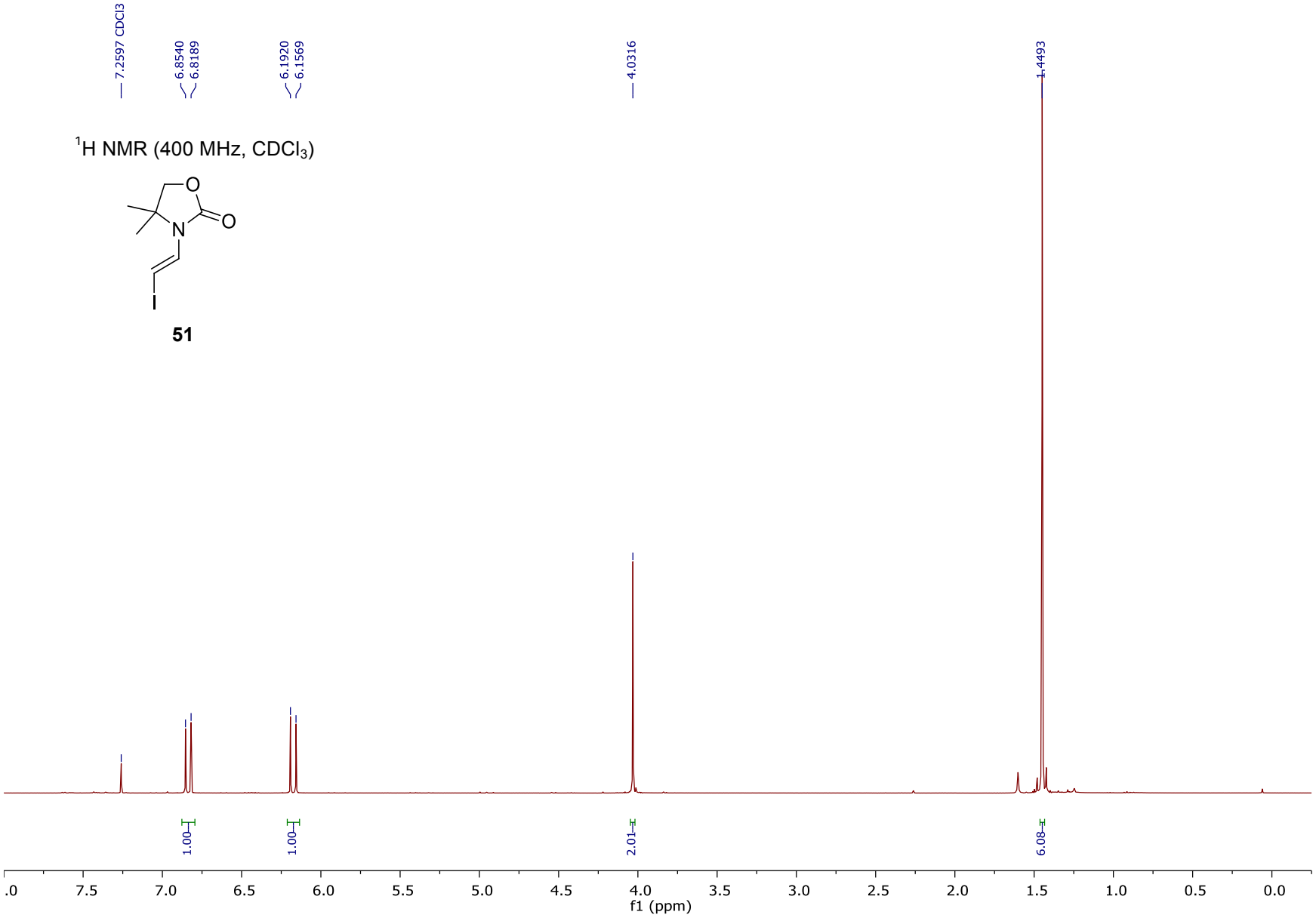
50



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

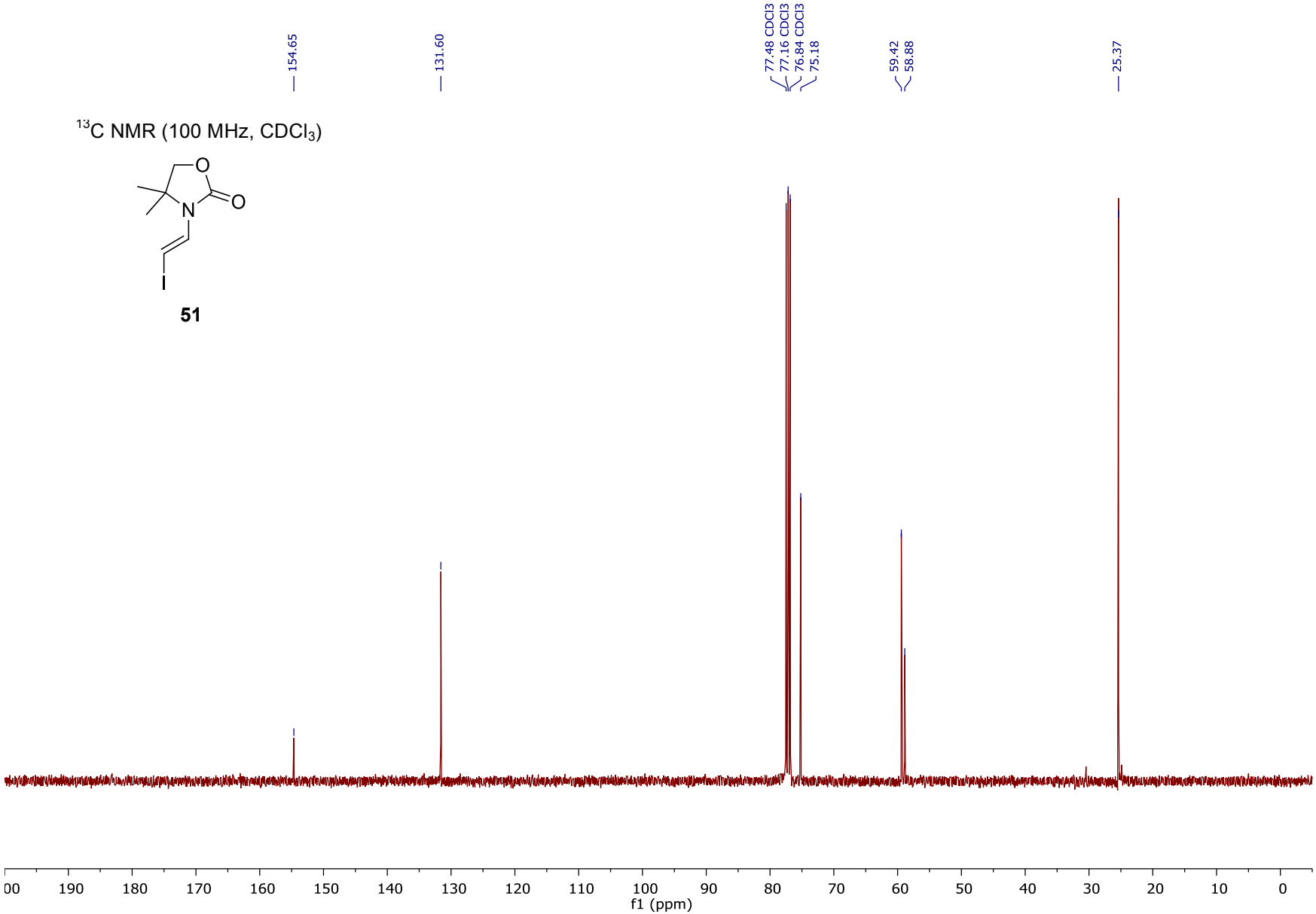
50


NOESY (400 MHz, $CDCl_3$)
50
f2 (ppm)
f1 (ppm)
6.50
6.45
1.1
1.2
1.3



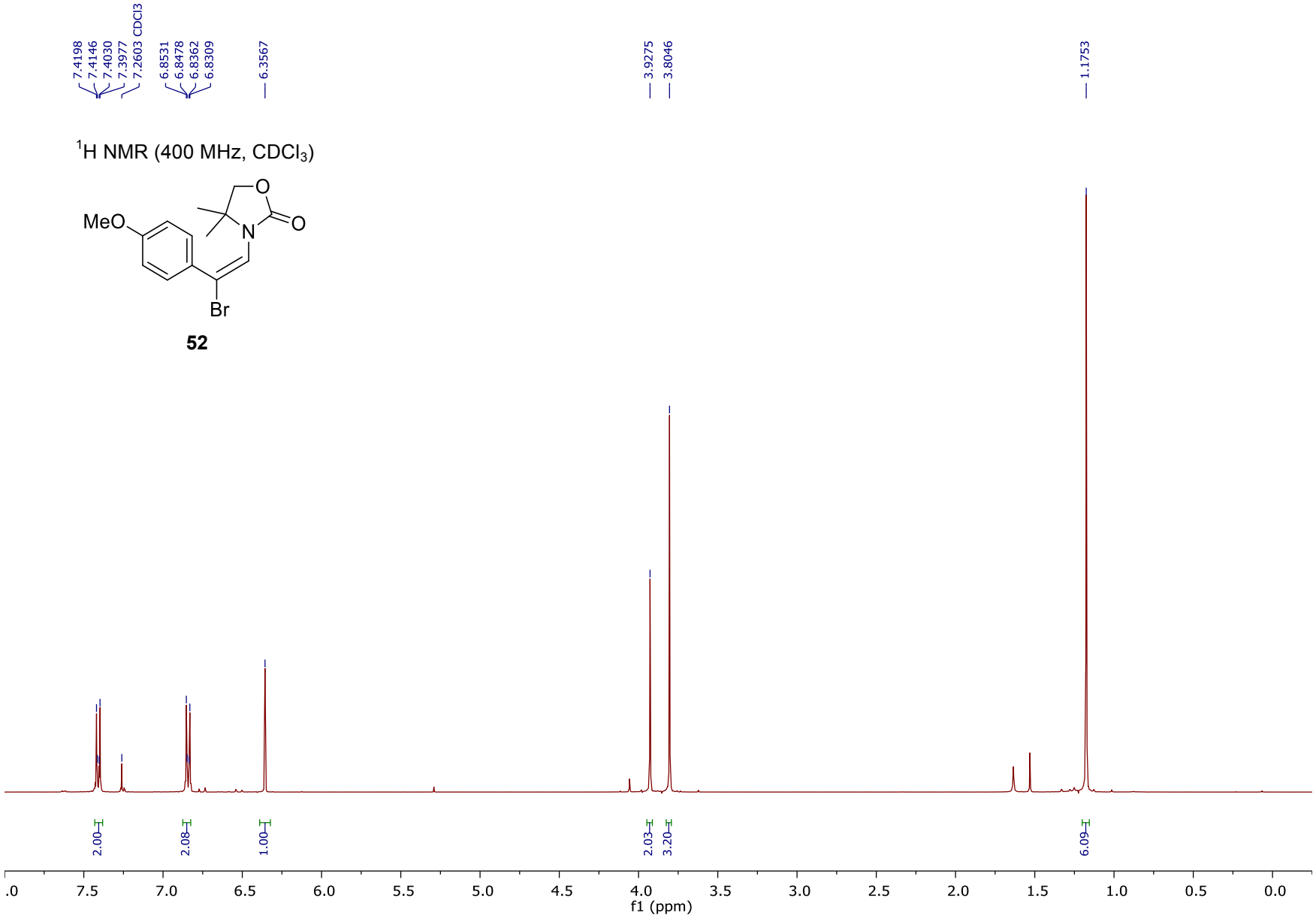
^{1}H NMR (400 MHz, $CDCl_3$)

51



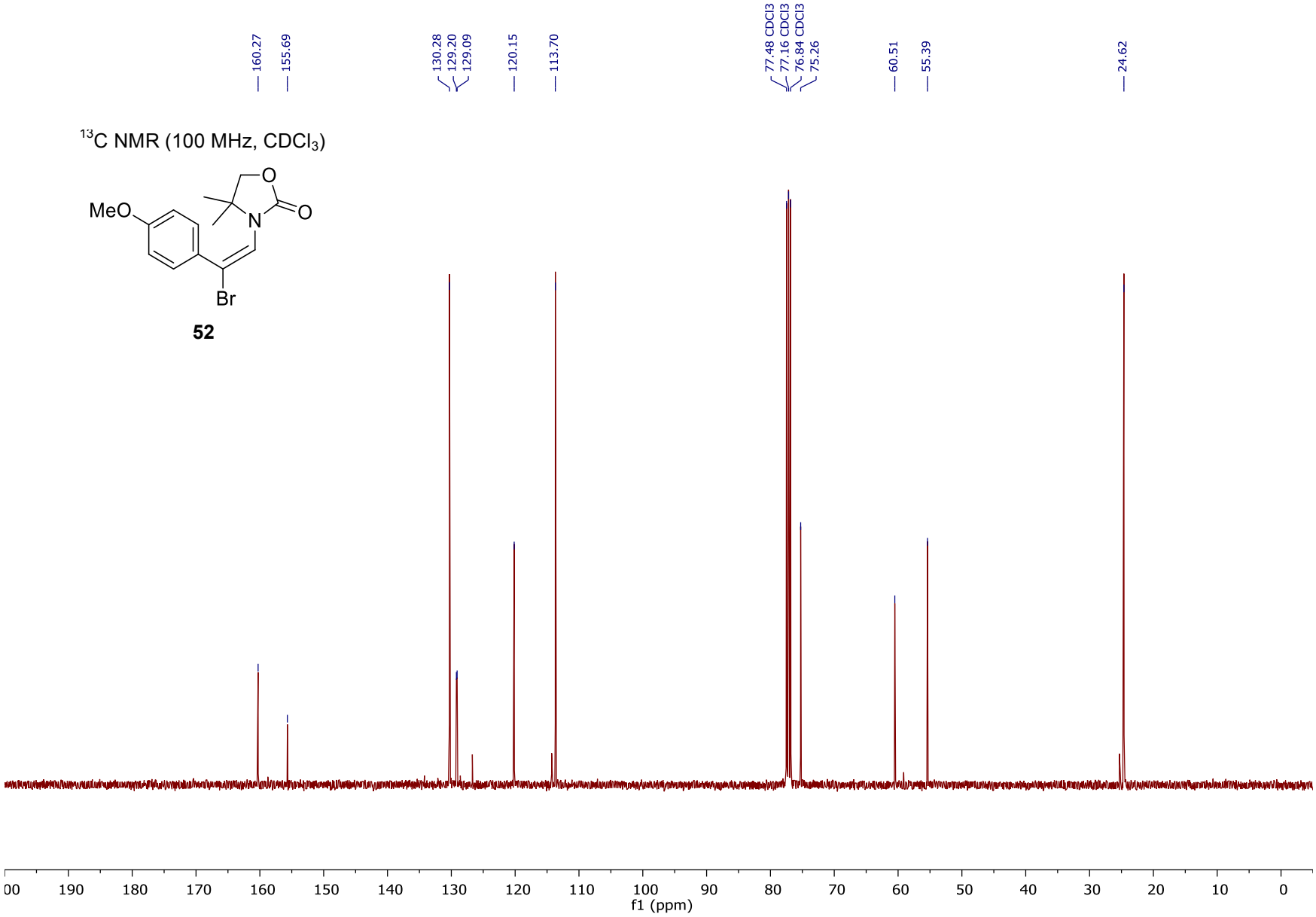
^{13}C NMR (100 MHz, $CDCl_3$)

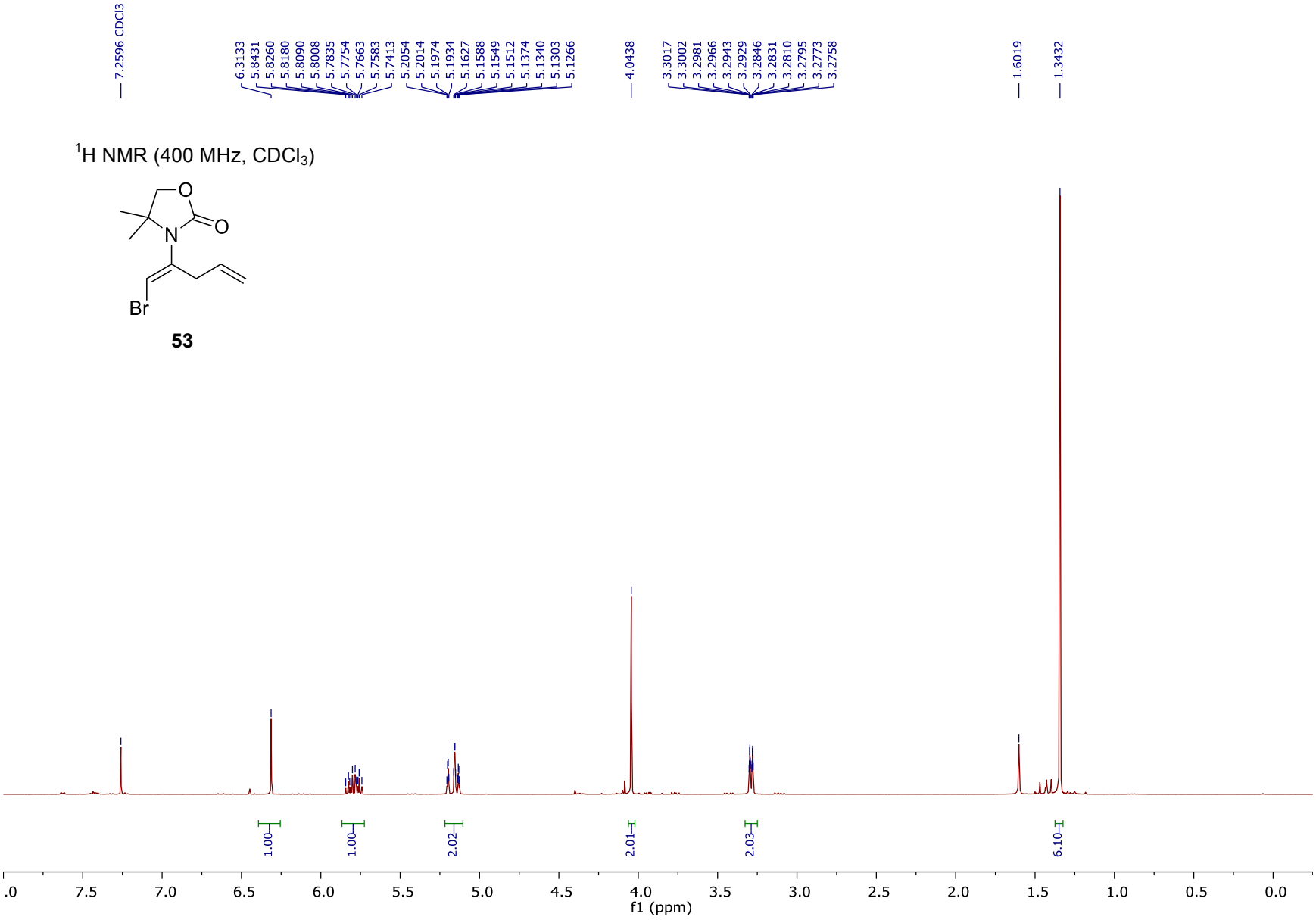
51



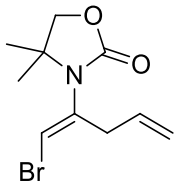
^{1}H NMR (400 MHz, $CDCl_3$)

52

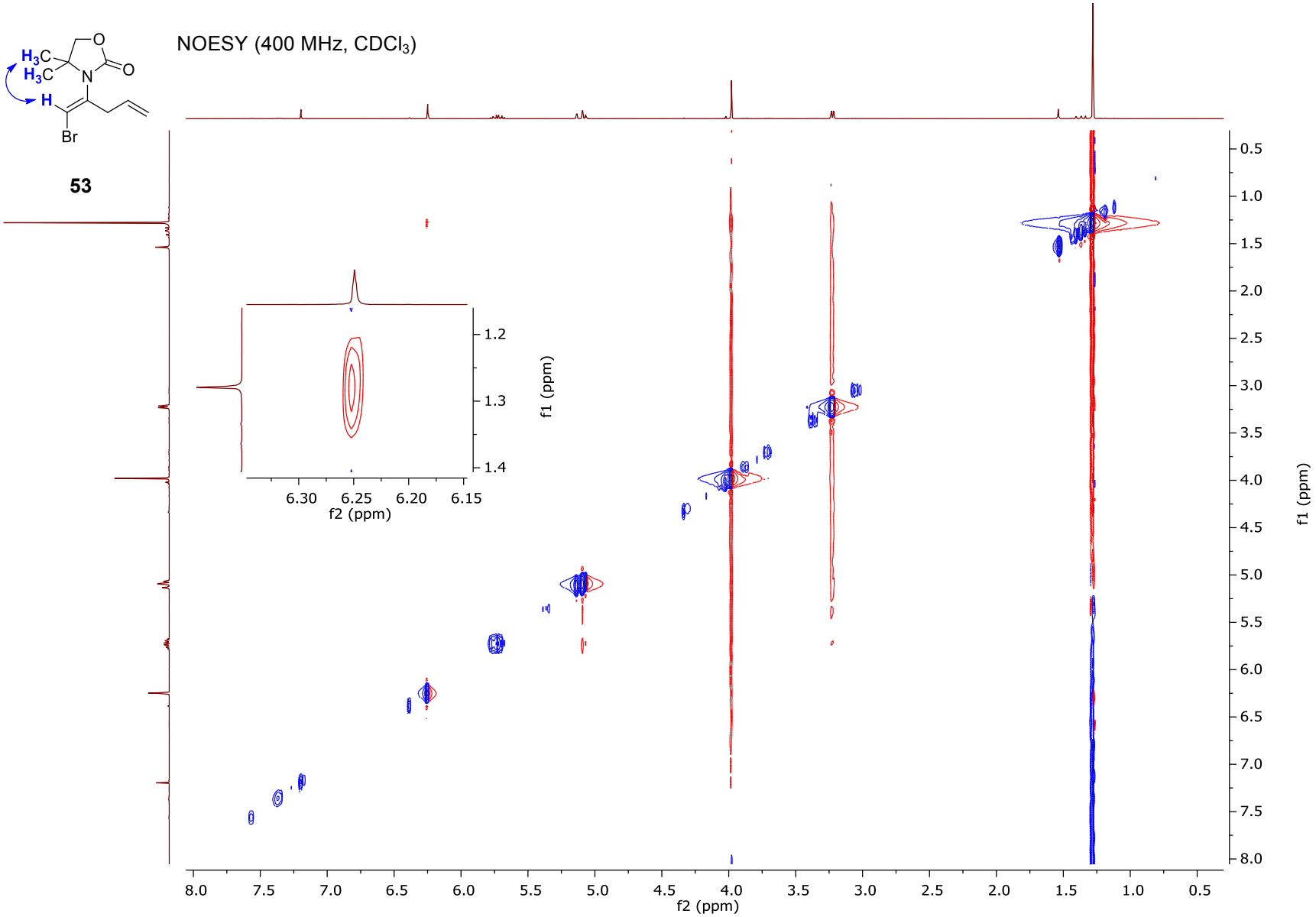

160.27
155.69
130.28
129.20
129.09
120.15
113.70
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.26
60.51
55.39
24.62
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
O
N
O
Br
52
f1 (ppm)

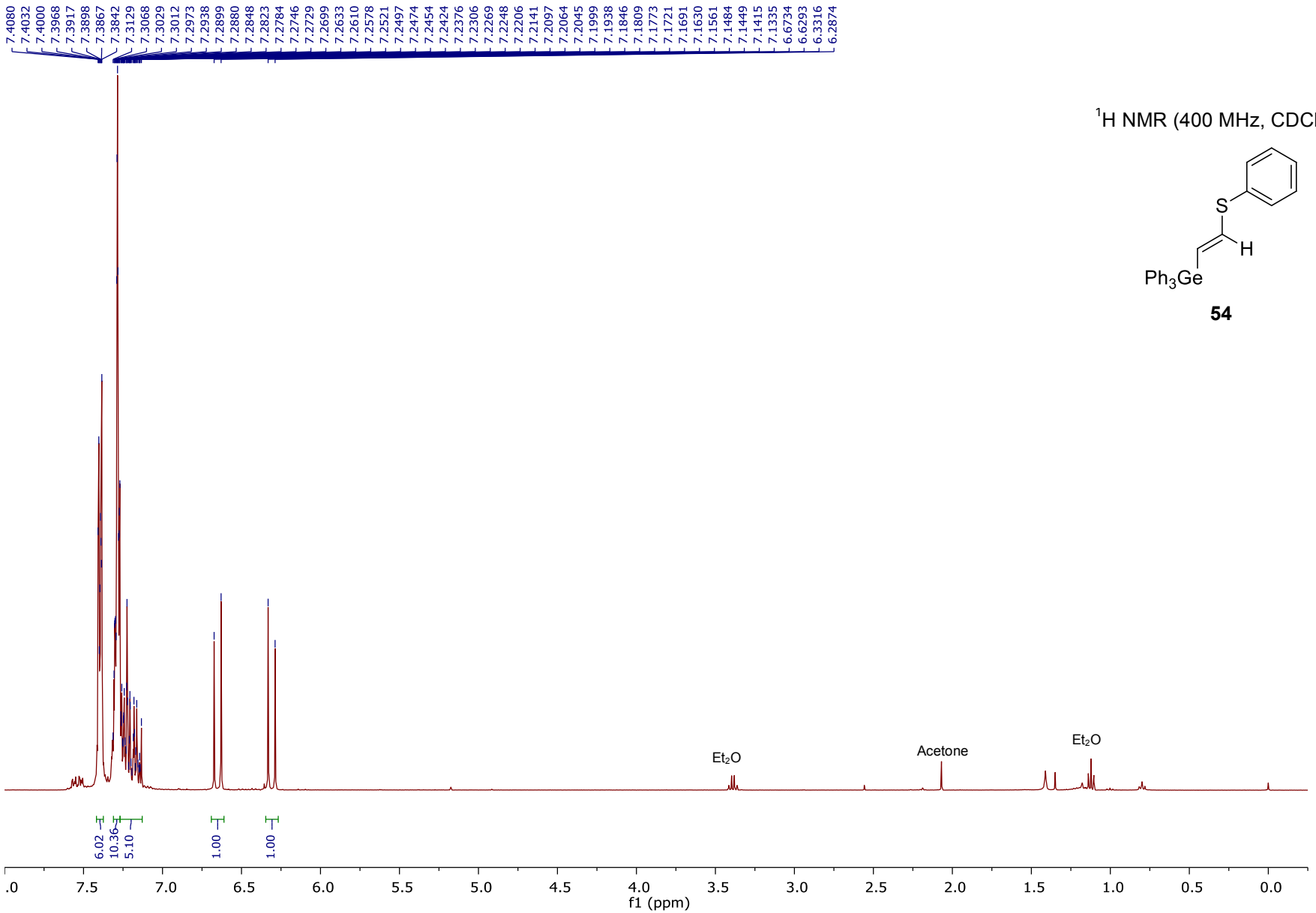

7.2596 CDCl3
6.3133
5.8431
5.8260
5.8180
5.8090
5.8008
5.7835
5.7754
5.7663
5.7583
5.7413
5.2054
5.2014
5.1974
5.1934
5.1627
5.1588
5.1549
5.1512
5.1374
5.1340
5.1303
5.1266
4.0438
3.3017
3.3002
3.2981
3.2966
3.2943
3.2929
3.2846
3.2831
3.2810
3.2795
3.2773
3.2758
1.6019
1.3432
1H NMR (400 MHz, CDCl3)
O
O
N
Br
53
1.00
1.00
2.02
2.01
2.03
6.10
.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
f1 (ppm)

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



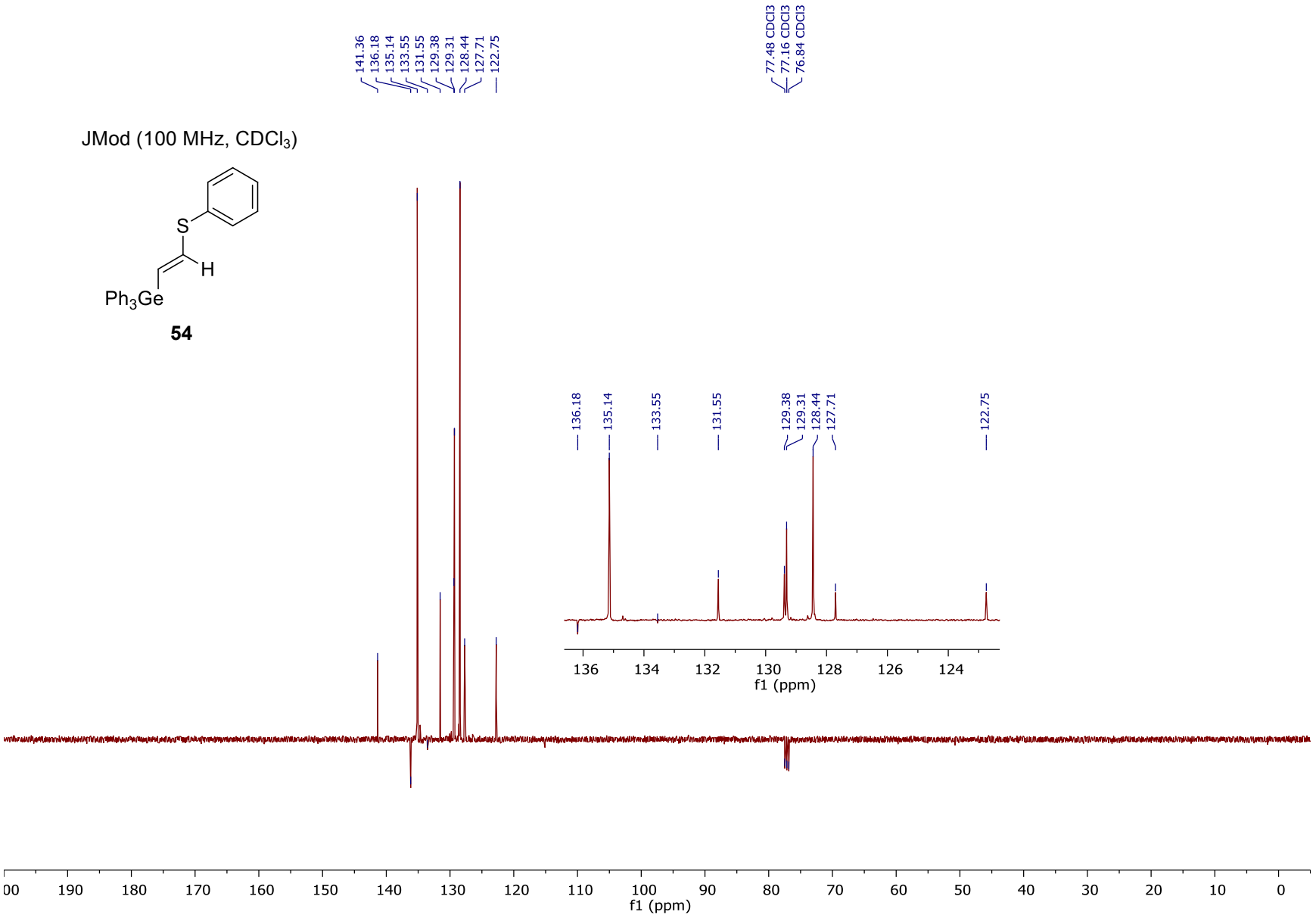
53

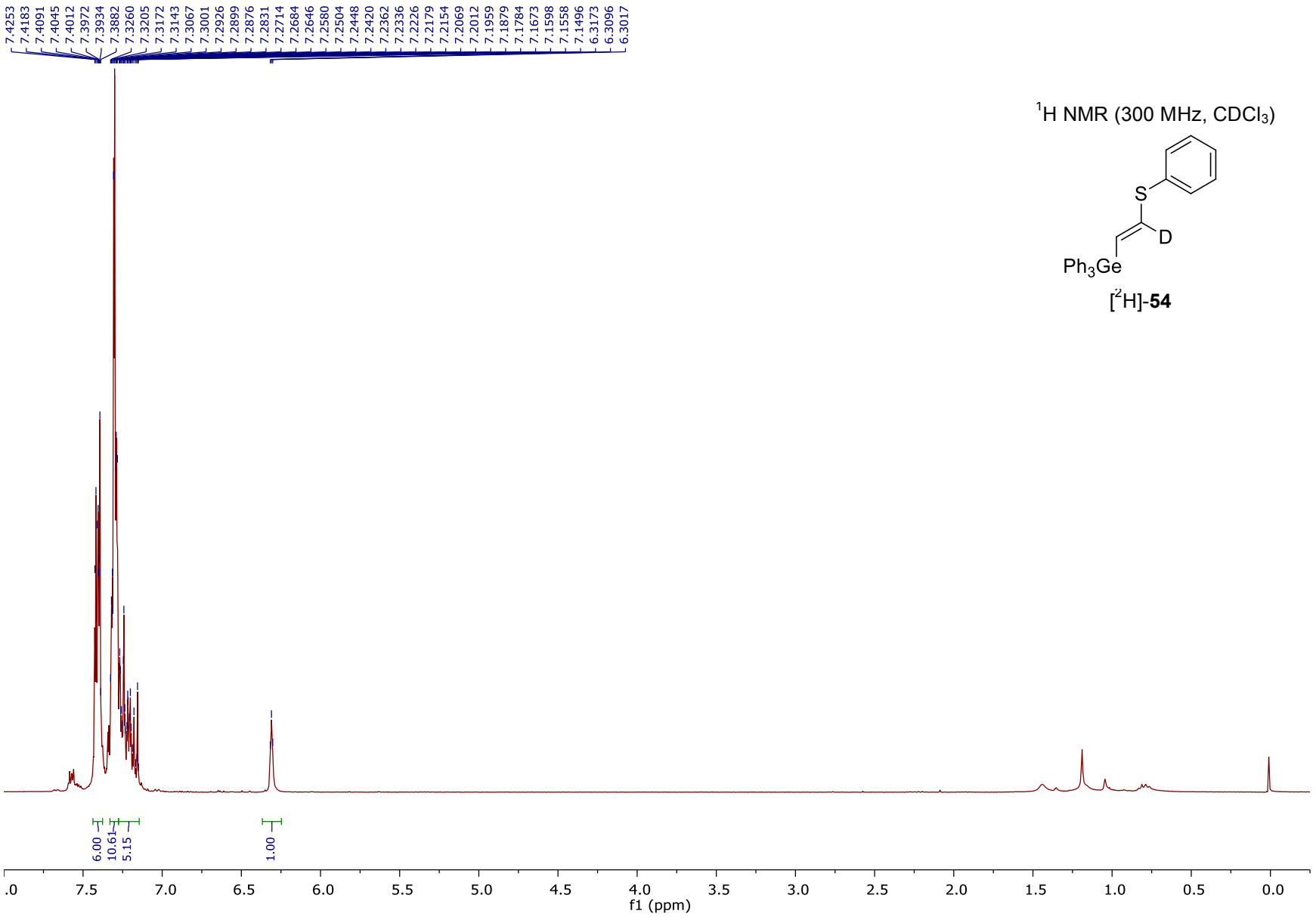

NOESY (400 MHz, CDCl3)
H3C
H3C
O
N
O
H
Br
53
f1 (ppm)
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.2
1.3
1.4
6.30
6.25
6.20
6.15



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

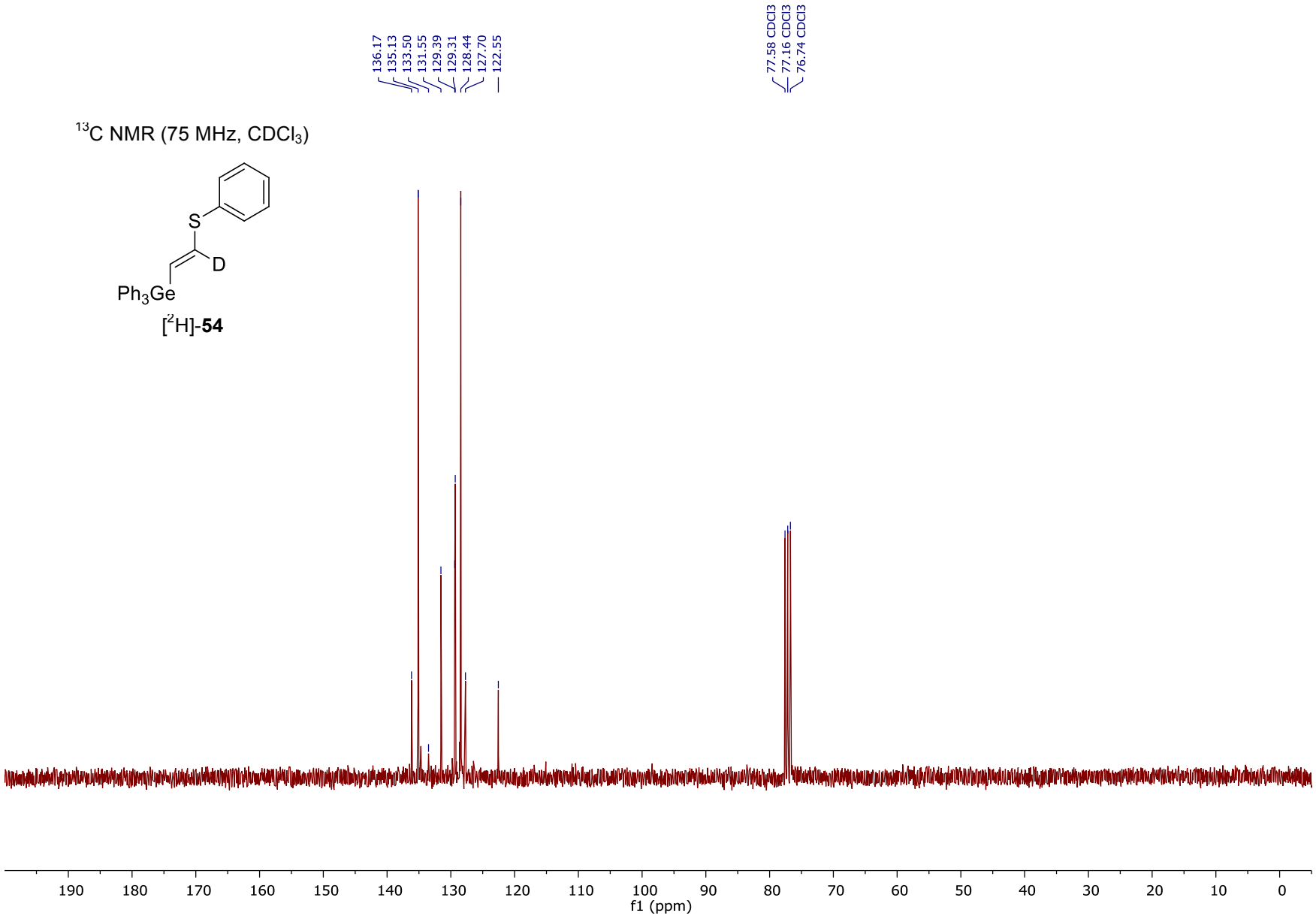
54

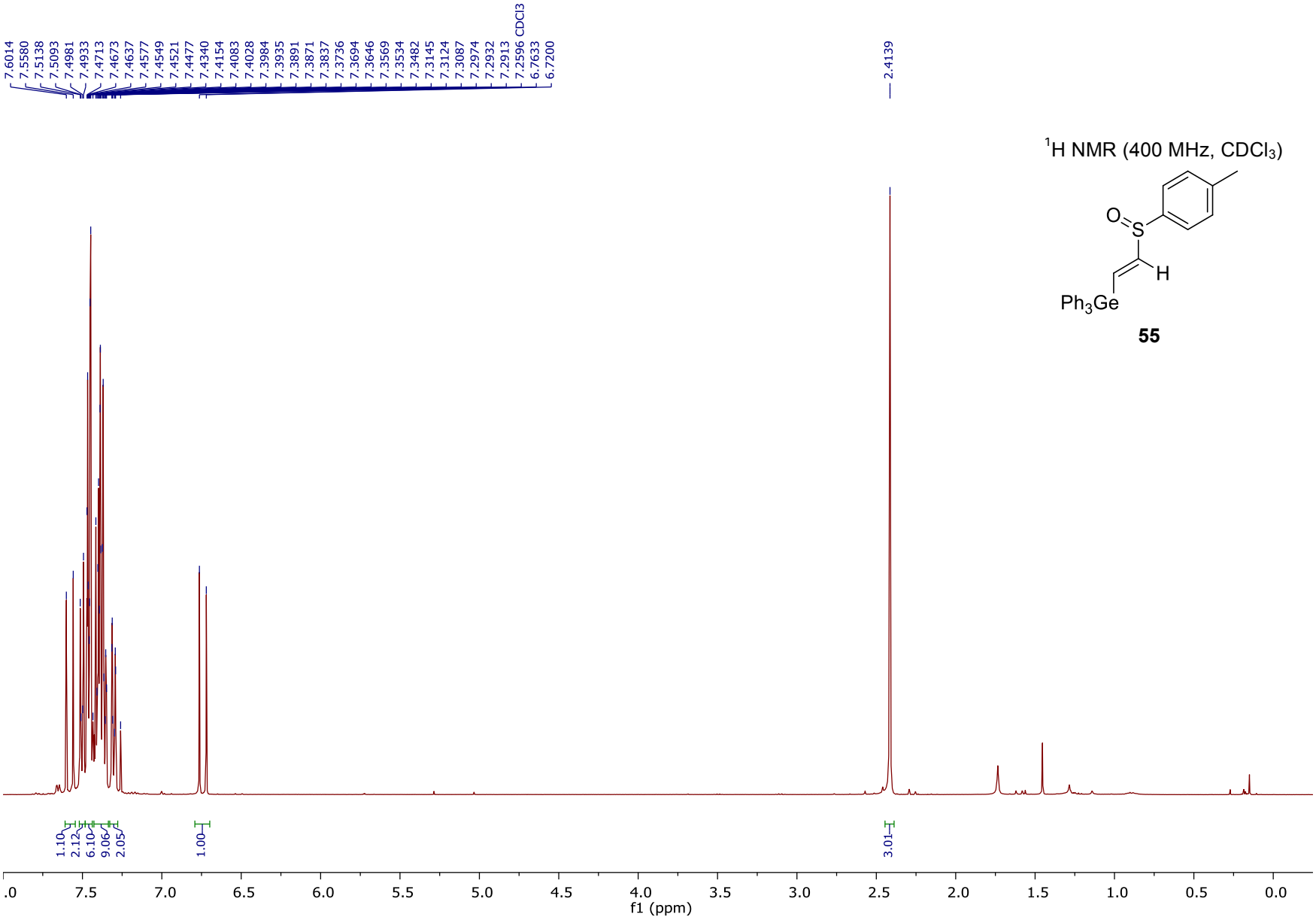

141.36
136.18
135.14
133.55
131.55
129.38
129.31
128.44
127.71
122.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
JMod (100 MHz, CDCl3)
S
H
Ph3Ge
54
136.18
135.14
133.55
131.55
129.38
129.31
128.44
127.71
122.75
136
134
132
130
128
126
124
f1 (ppm)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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

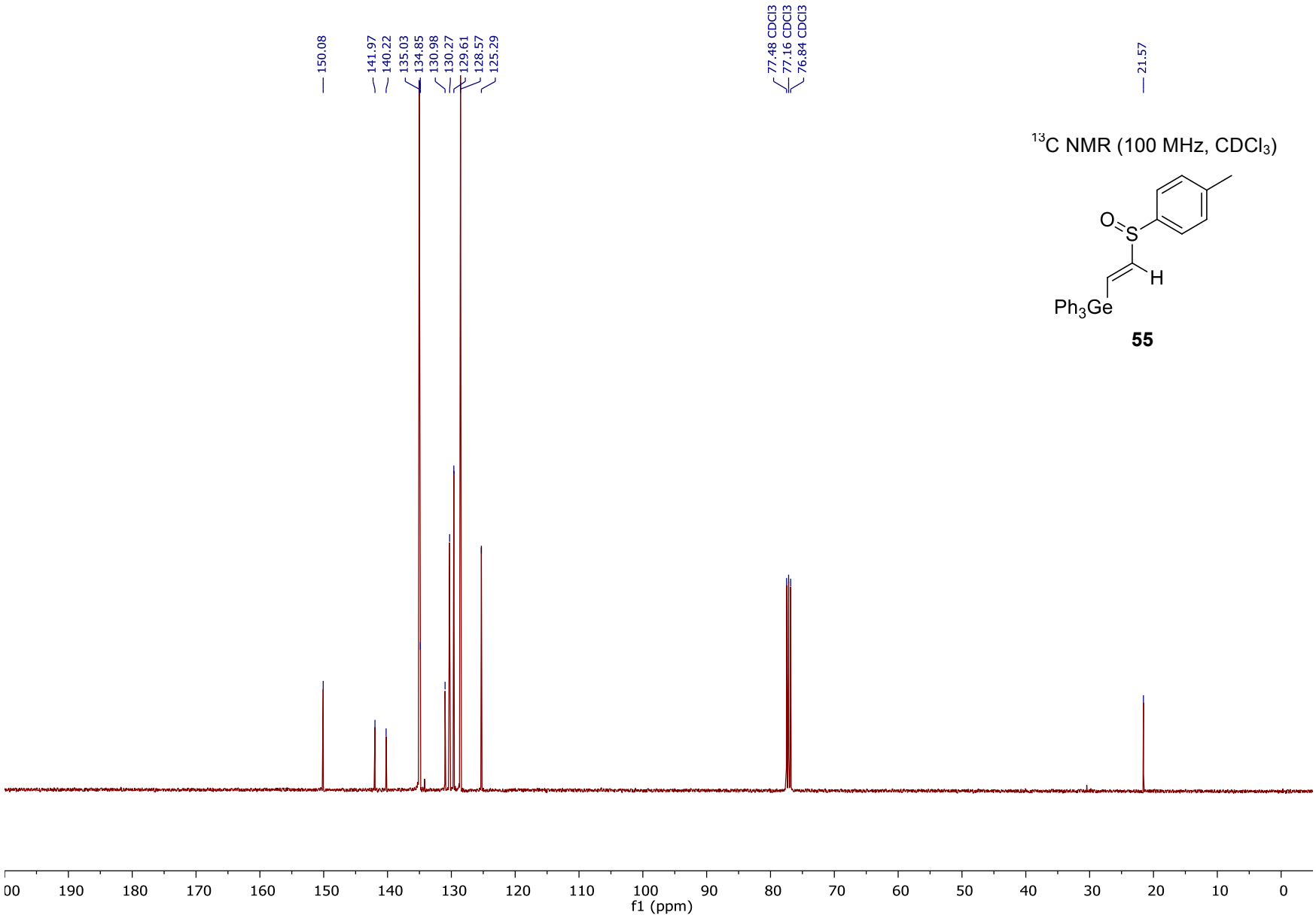
[^{2}H]-**54**


136.17
135.13
133.50
131.55
129.39
129.31
128.44
127.70
122.55
77.58 CDCl3
77.16 CDCl3
76.74 CDCl3
^{13}C NMR (75 MHz, $CDCl_3$)
S
D
Ph_3Ge
[^{2}H]-**54**
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



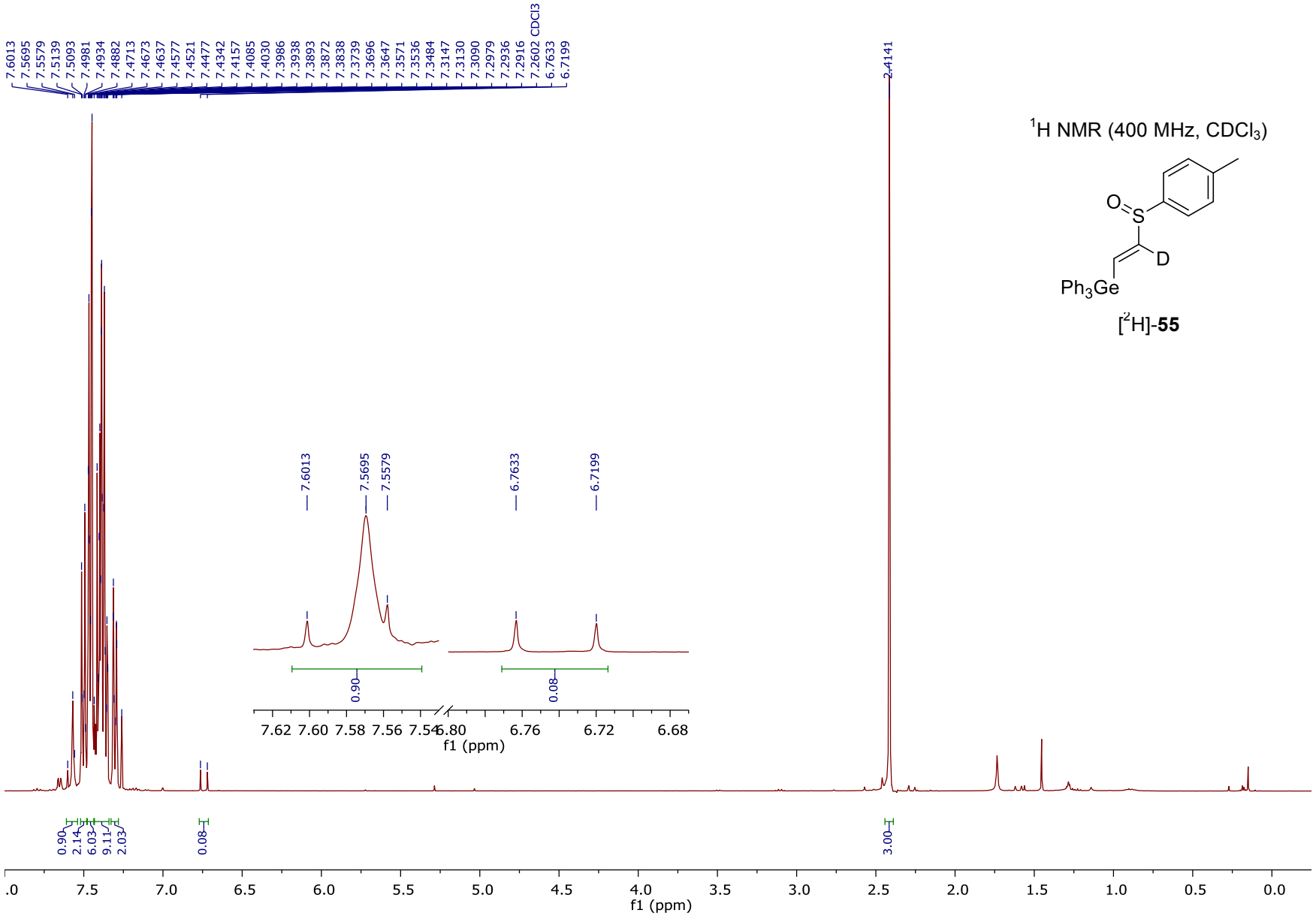
^{1}H NMR (400 MHz, $CDCl_3$)

55



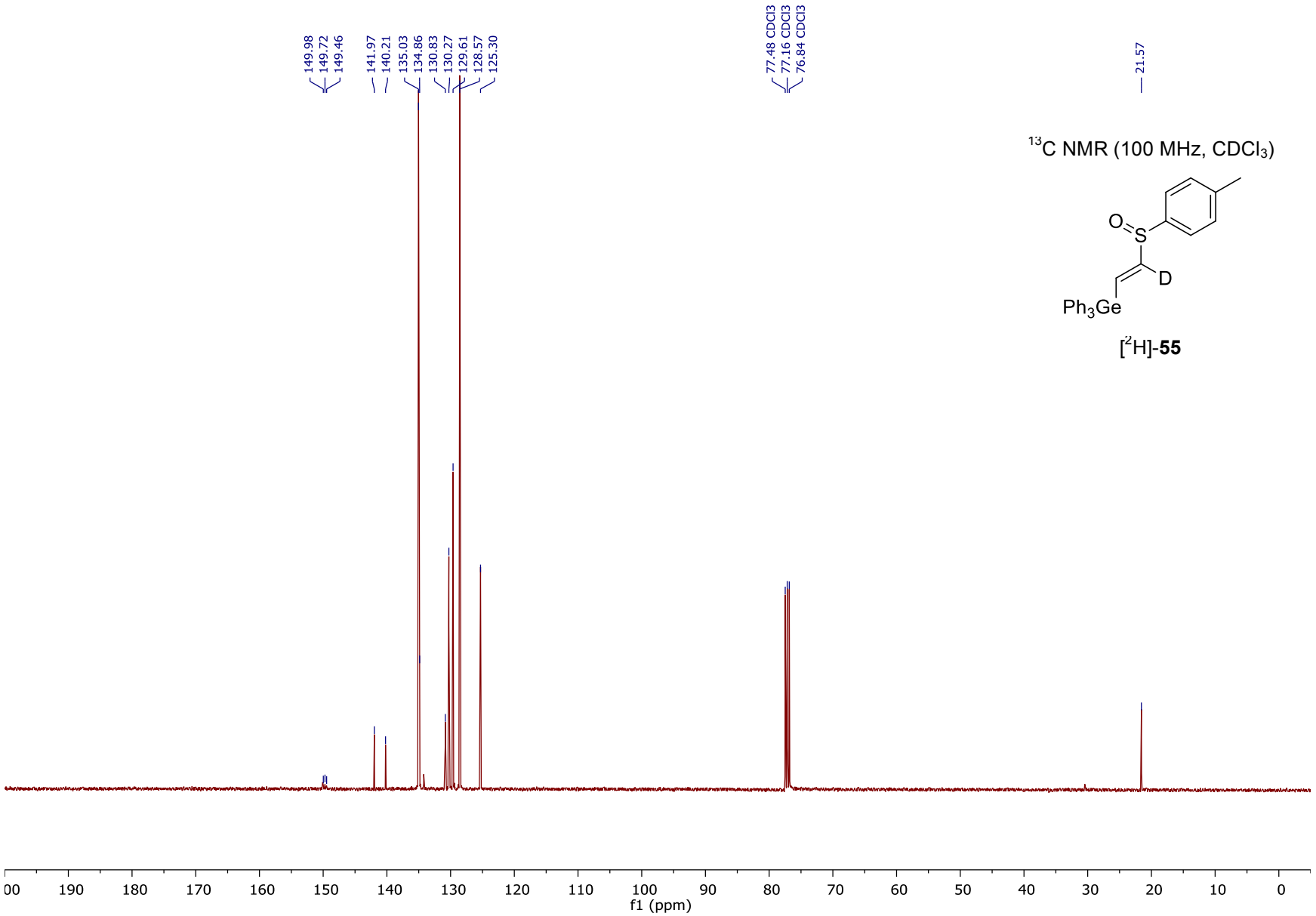
^{13}C NMR (100 MHz, $CDCl_3$)

55



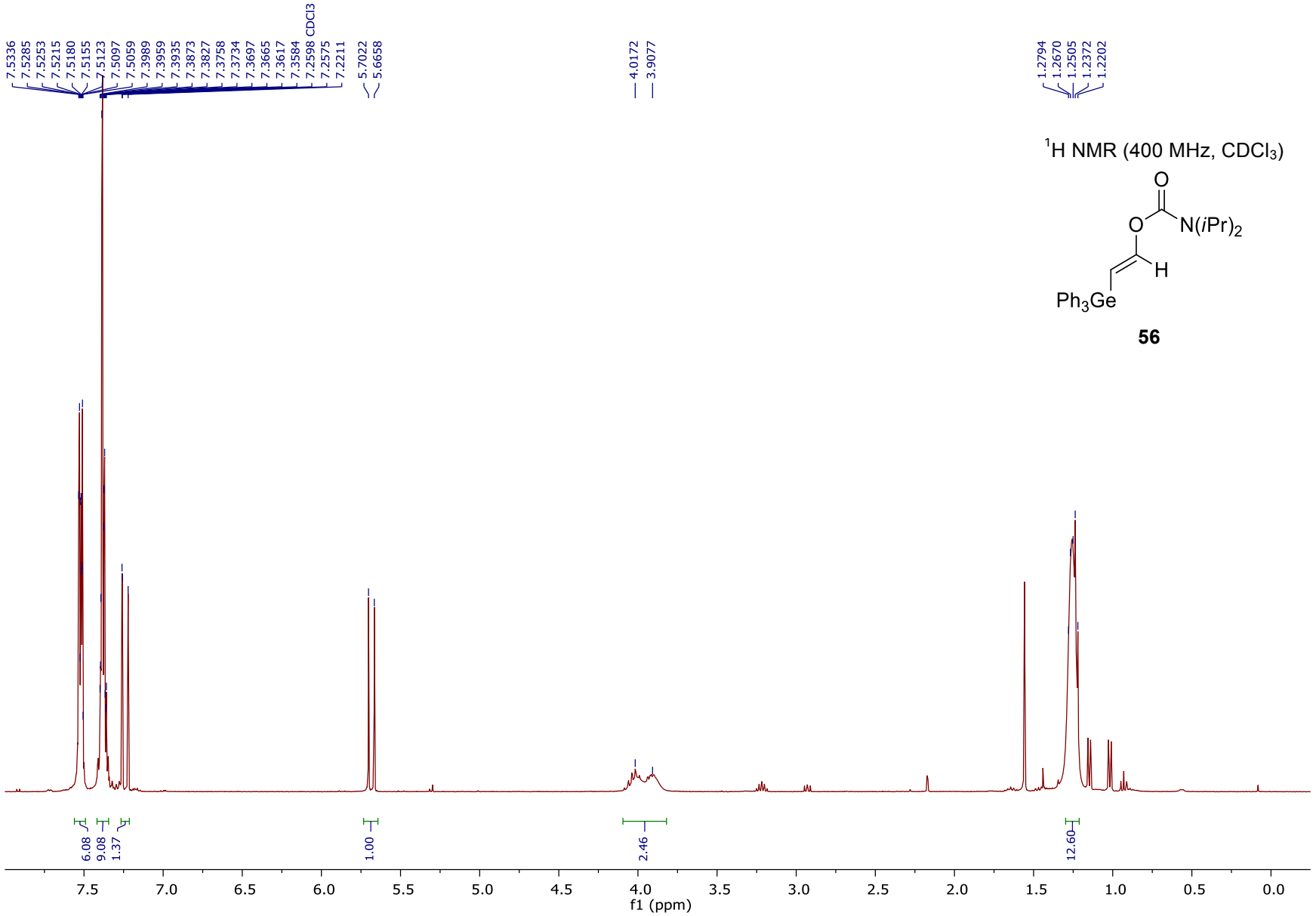
^{1}H NMR (400 MHz, $CDCl_3$)

[^{2}H]-**55**



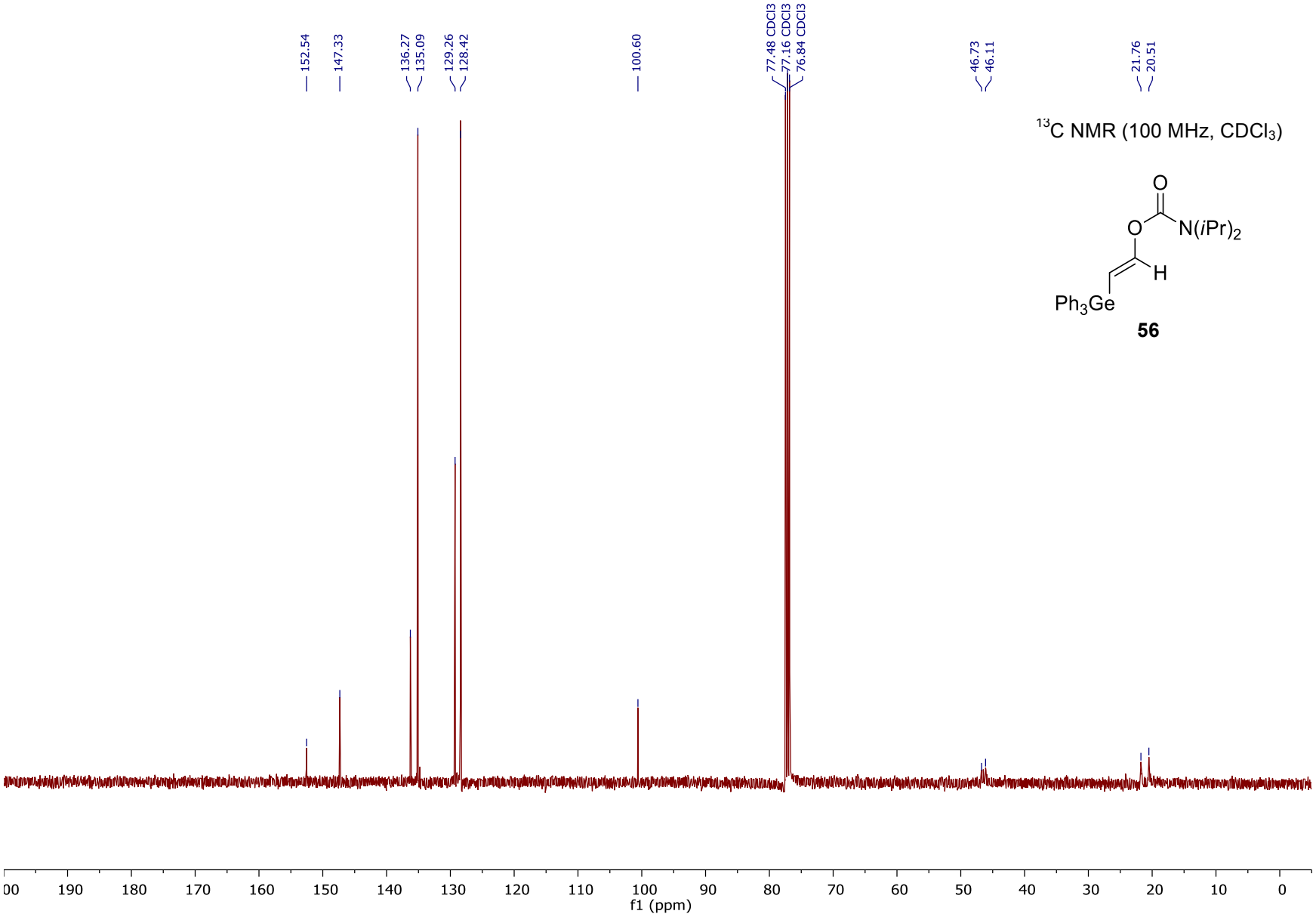
^{13}C NMR (100 MHz, $CDCl_3$)

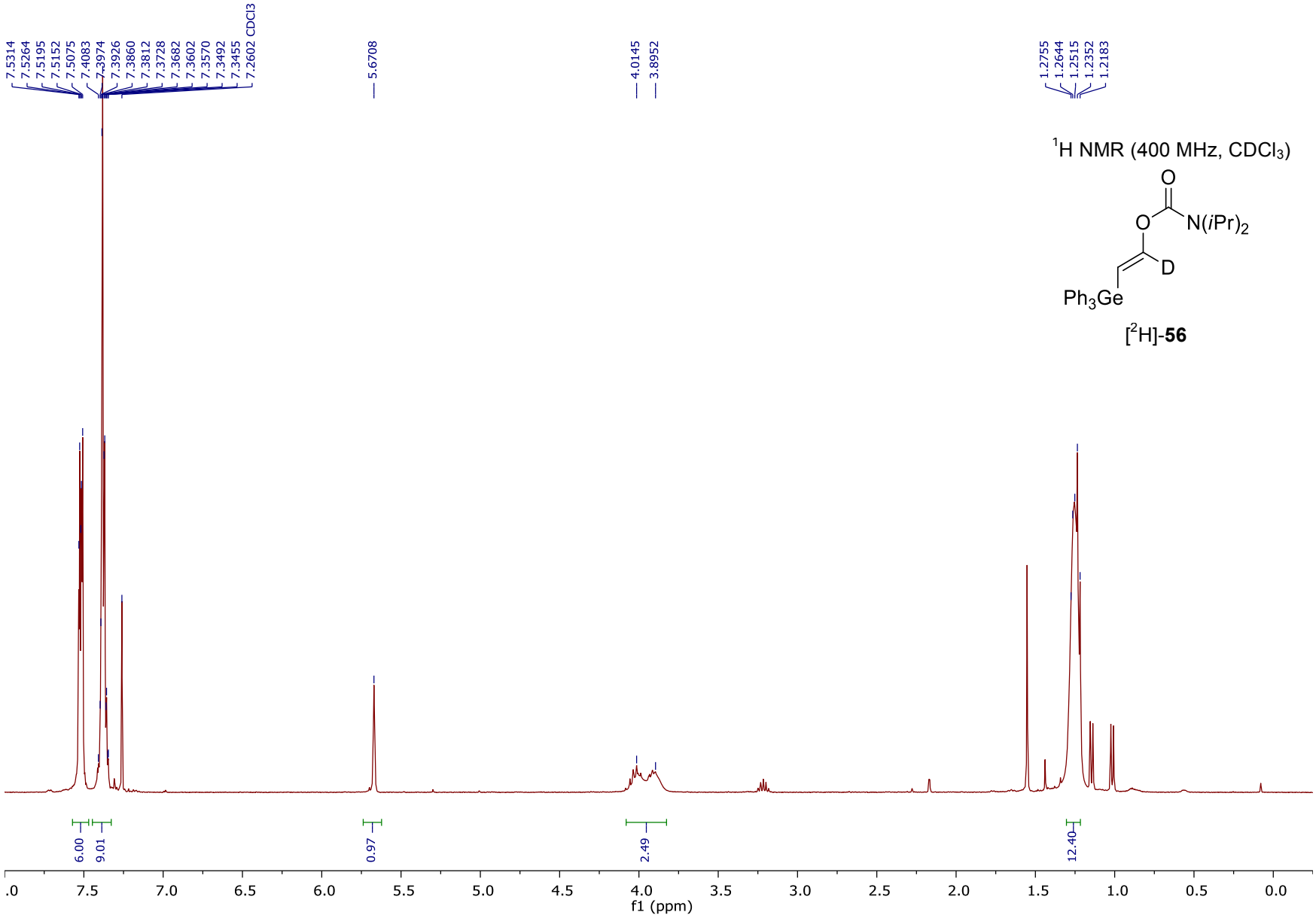
[^{2}H]-**55**



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

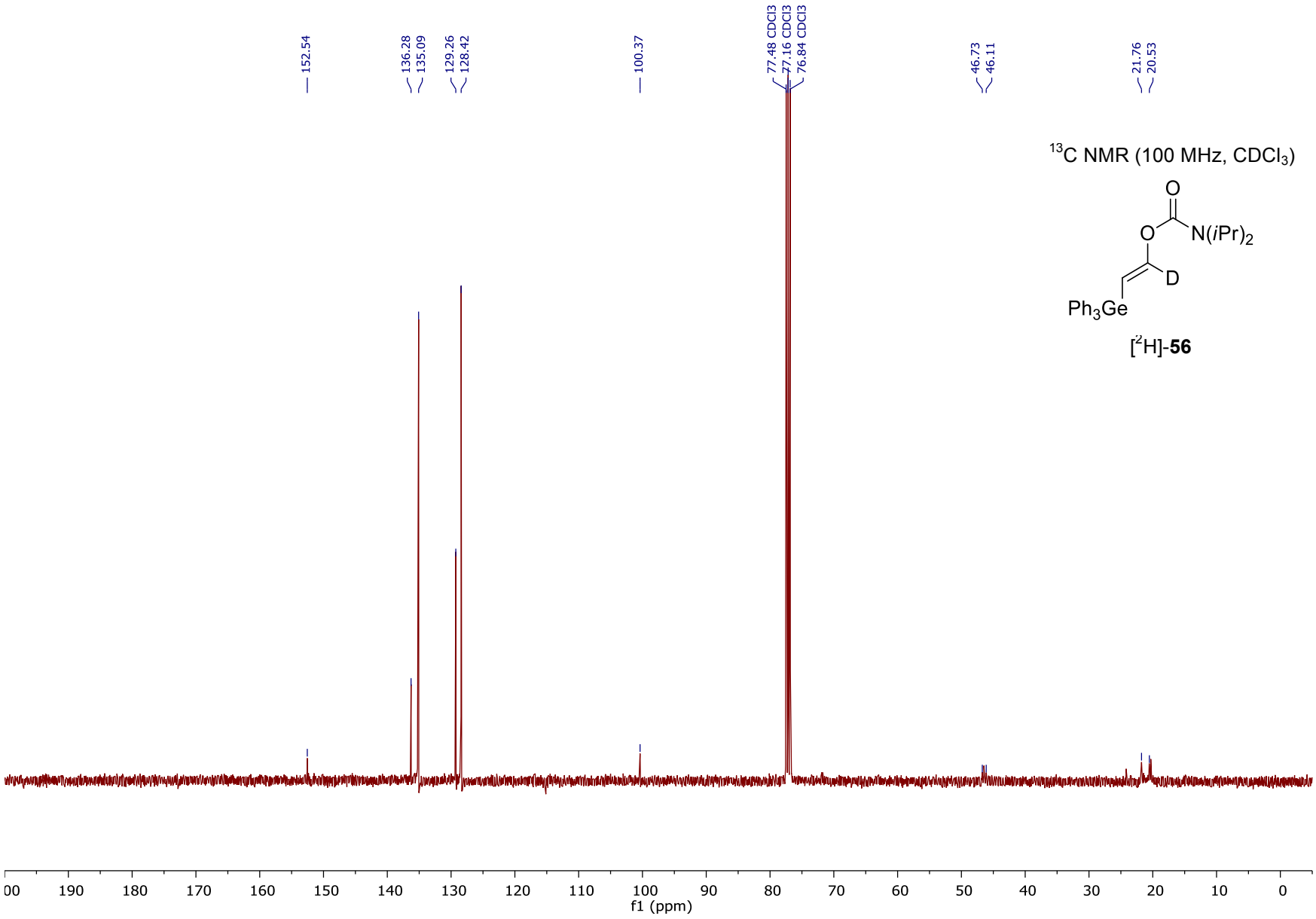
56

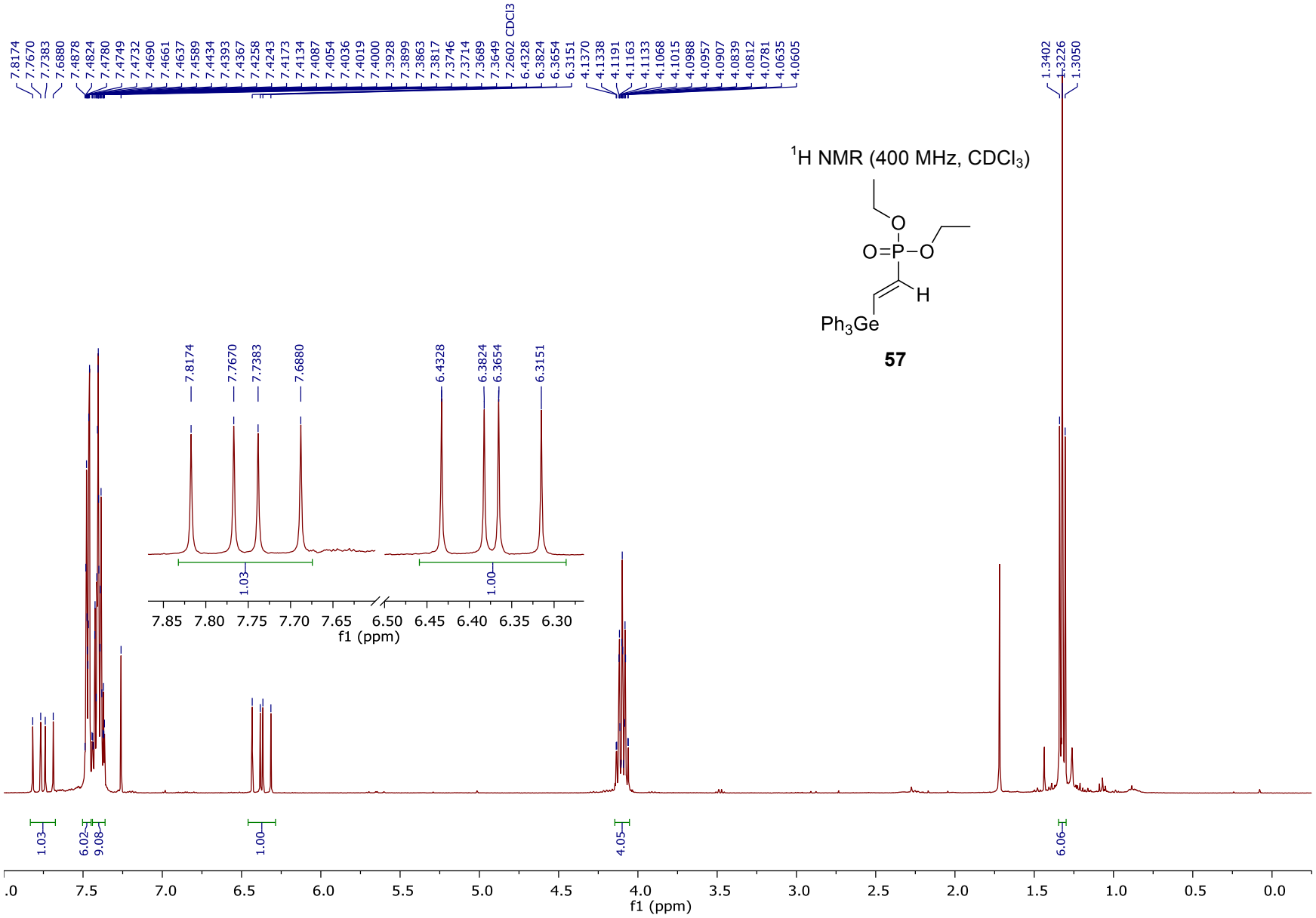

152.54
147.33
136.27
135.09
129.26
128.42
100.60
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
46.73
46.11
21.76
20.51
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N(*i*Pr)$_2$
H
Ph$_3$Ge
56
f1 (ppm)

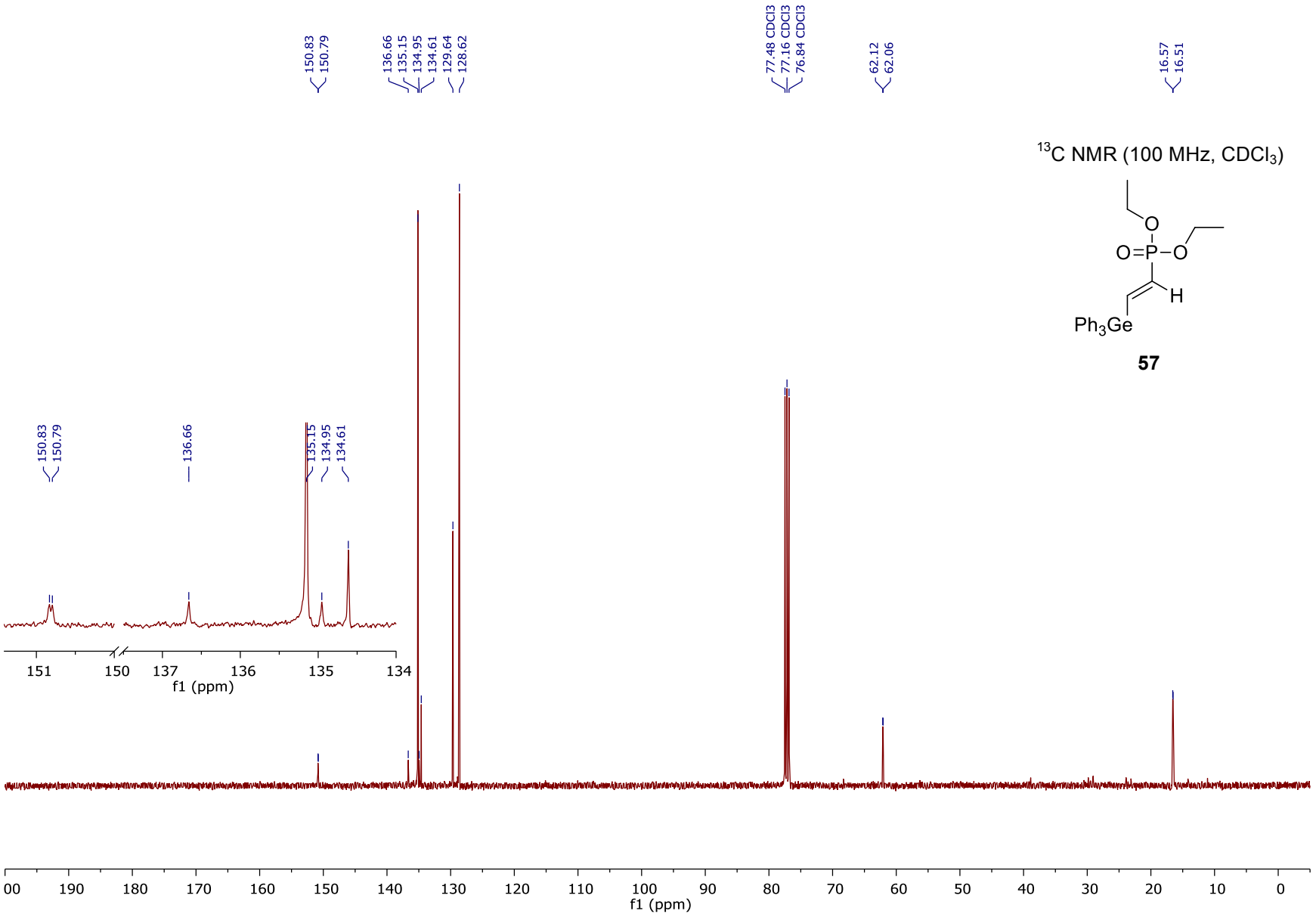


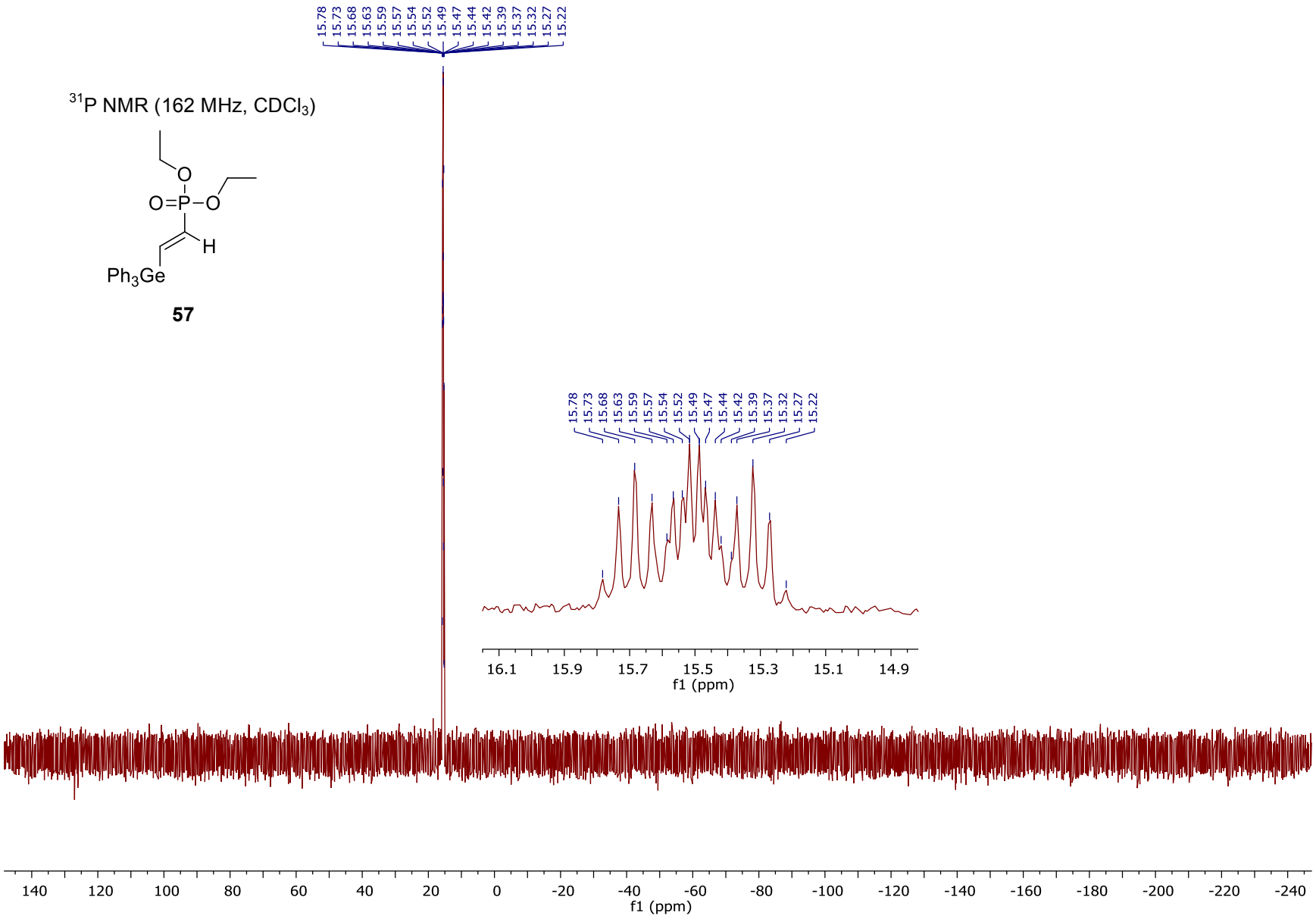
^{1}H NMR (400 MHz, $CDCl_3$)

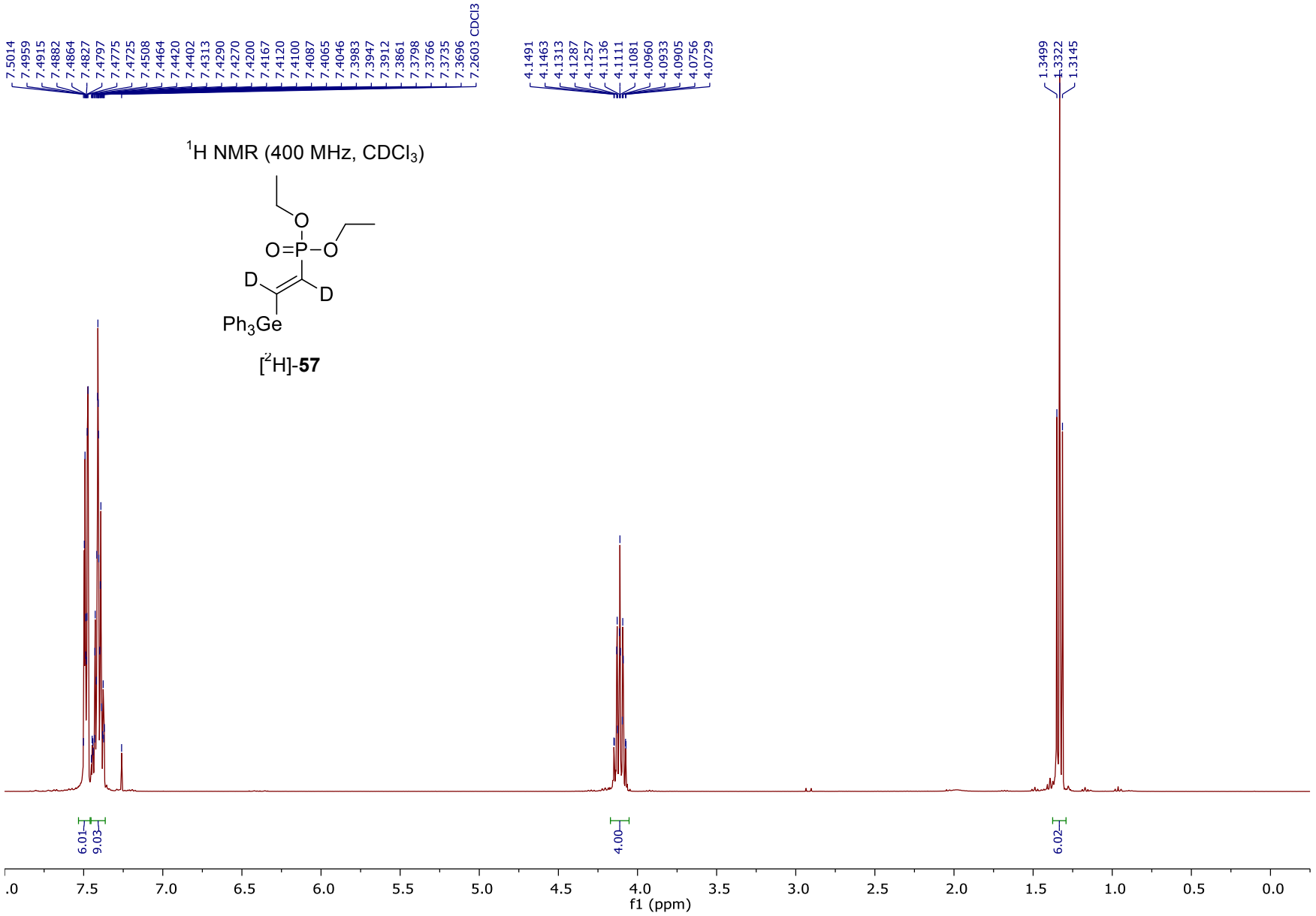
[^{2}H]-**56**

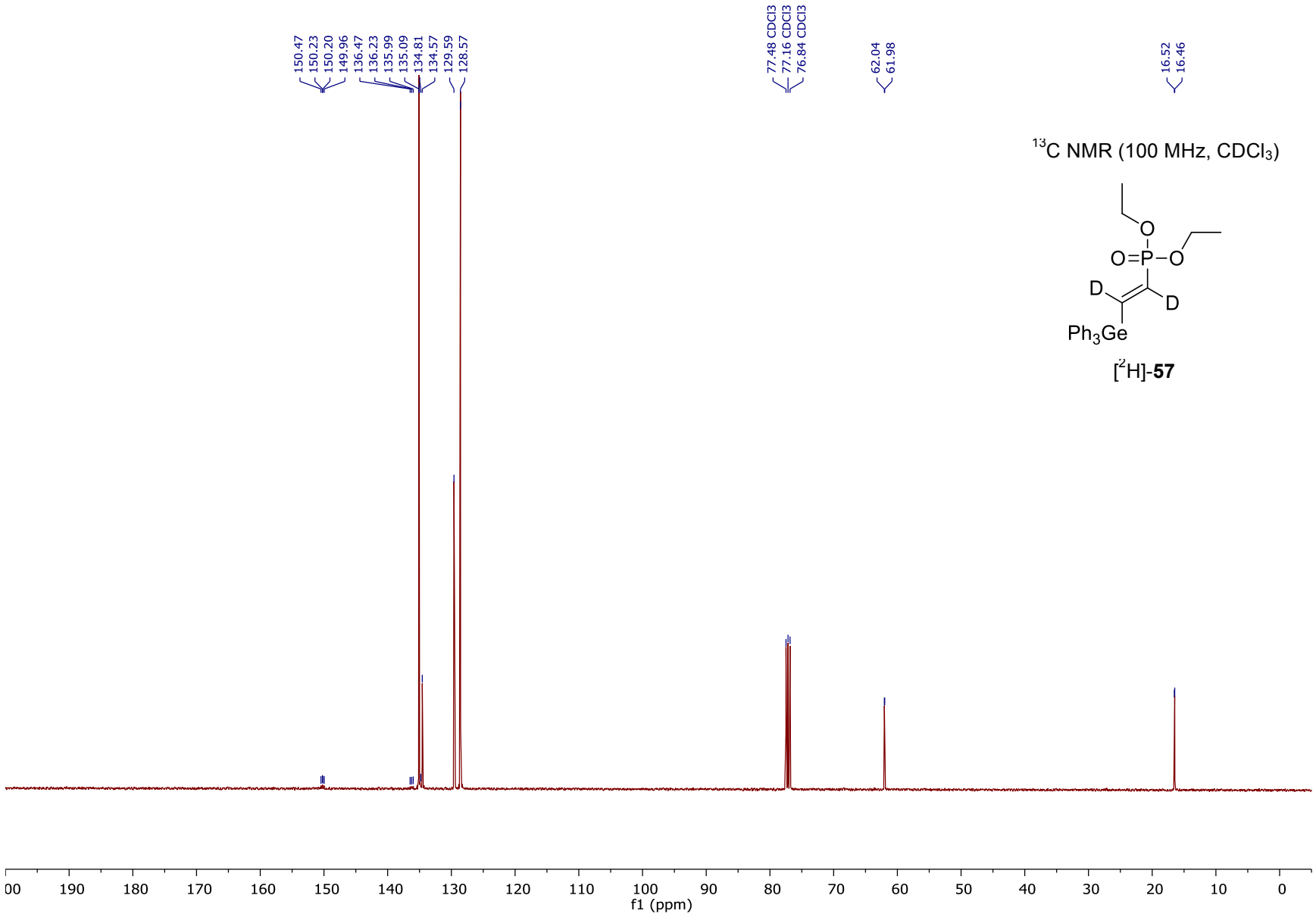

152.54
136.28
135.09
129.26
128.42
100.37
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
46.73
46.11
21.76
20.53
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N(*i*Pr)$_2$
D
Ph$_3$Ge
[^{2}H]-**56**
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.8174
7.7670
7.7383
7.6880
7.4878
7.4824
7.4780
7.4749
7.4732
7.4690
7.4661
7.4637
7.4589
7.4434
7.4393
7.4367
7.4258
7.4243
7.4173
7.4134
7.4087
7.4054
7.4036
7.4019
7.4000
7.3928
7.3899
7.3863
7.3817
7.3746
7.3714
7.3689
7.3649
7.2602 CDCl3
6.4328
6.3824
6.3654
6.3151
4.1370
4.1338
4.1191
4.1163
4.1133
4.1068
4.1015
4.0988
4.0957
4.0907
4.0839
4.0812
4.0781
4.0635
4.0605
1.3402
1.3226
1.3050
^{1}H NMR (400 MHz, $CDCl_3$)
O
O=P–O
H
Ph_3Ge
57
1.03
6.02
9.08
1.00
4.05
6.06
f1 (ppm)


150.83
150.79
136.66
135.15
134.95
134.61
129.64
128.62
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.12
62.06
16.57
16.51
^{13}C NMR (100 MHz, $CDCl_3$)
O
O=P–O
H
Ph_3Ge
57
f1 (ppm)
f1 (ppm)


15.78
15.73
15.68
15.63
15.59
15.57
15.54
15.52
15.49
15.47
15.44
15.42
15.39
15.37
15.32
15.27
15.22
31P NMR (162 MHz, CDCl3)
O
O=P–O
H
Ph3Ge
57
16.1
15.9
15.7
15.5
15.3
15.1
14.9
f1 (ppm)
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

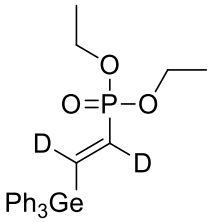

7.5014
7.4959
7.4915
7.4882
7.4864
7.4827
7.4797
7.4775
7.4725
7.4508
7.4464
7.4420
7.4402
7.4313
7.4290
7.4270
7.4200
7.4167
7.4120
7.4100
7.4087
7.4065
7.4046
7.3983
7.3947
7.3912
7.3861
7.3798
7.3766
7.3735
7.3696
7.2603 CDCl3
4.1491
4.1463
4.1313
4.1287
4.1257
4.1136
4.1111
4.1081
4.0960
4.0933
4.0905
4.0756
4.0729
1.3499
1.3322
1.3145
^{1}H NMR (400 MHz, $CDCl_3$)
O
O=P–O
D
D
Ph_3Ge
[^{2}H]-**57**
6.01
9.03
4.00
6.02
.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
f1 (ppm)



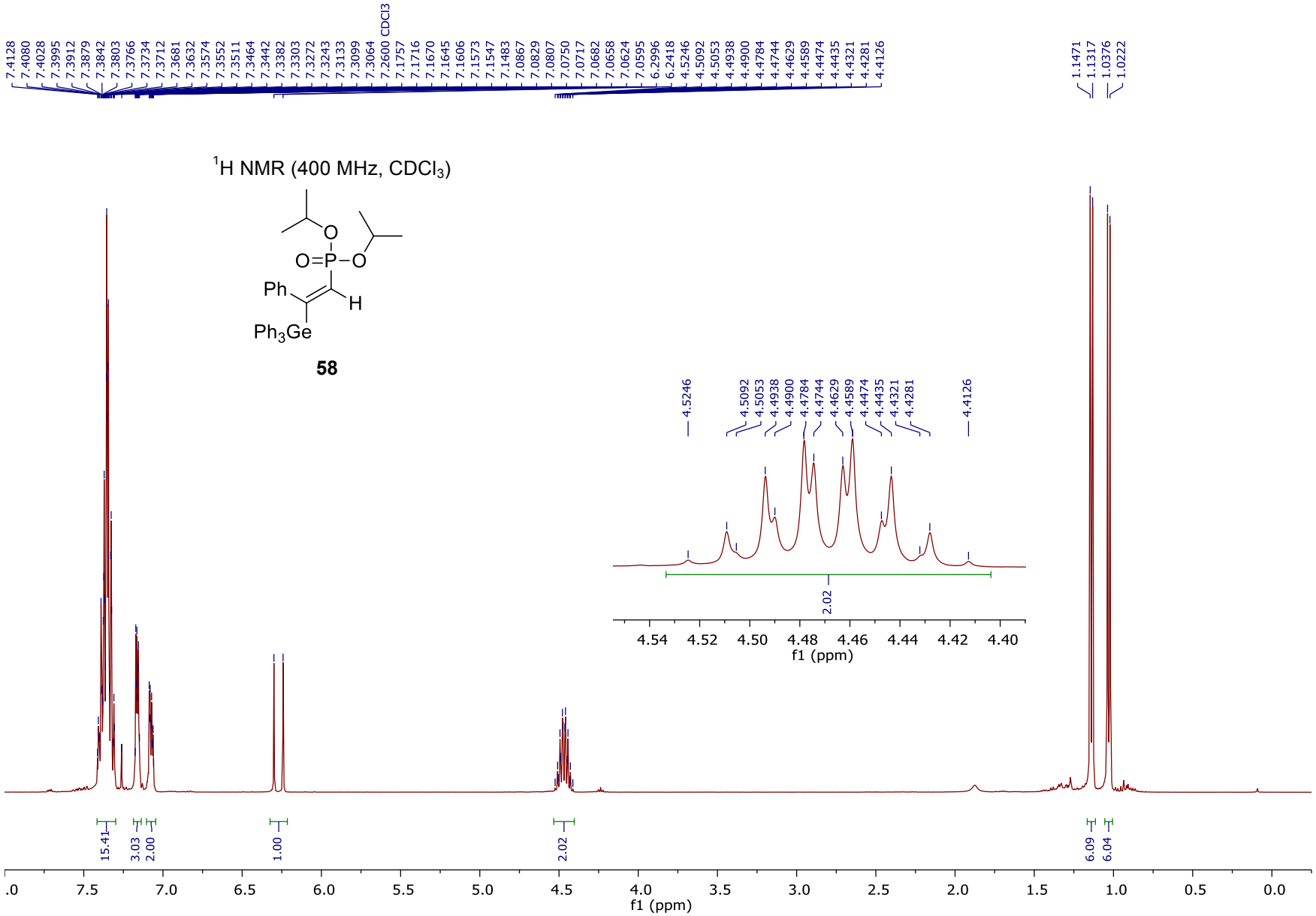
^{13}C NMR (100 MHz, $CDCl_3$)

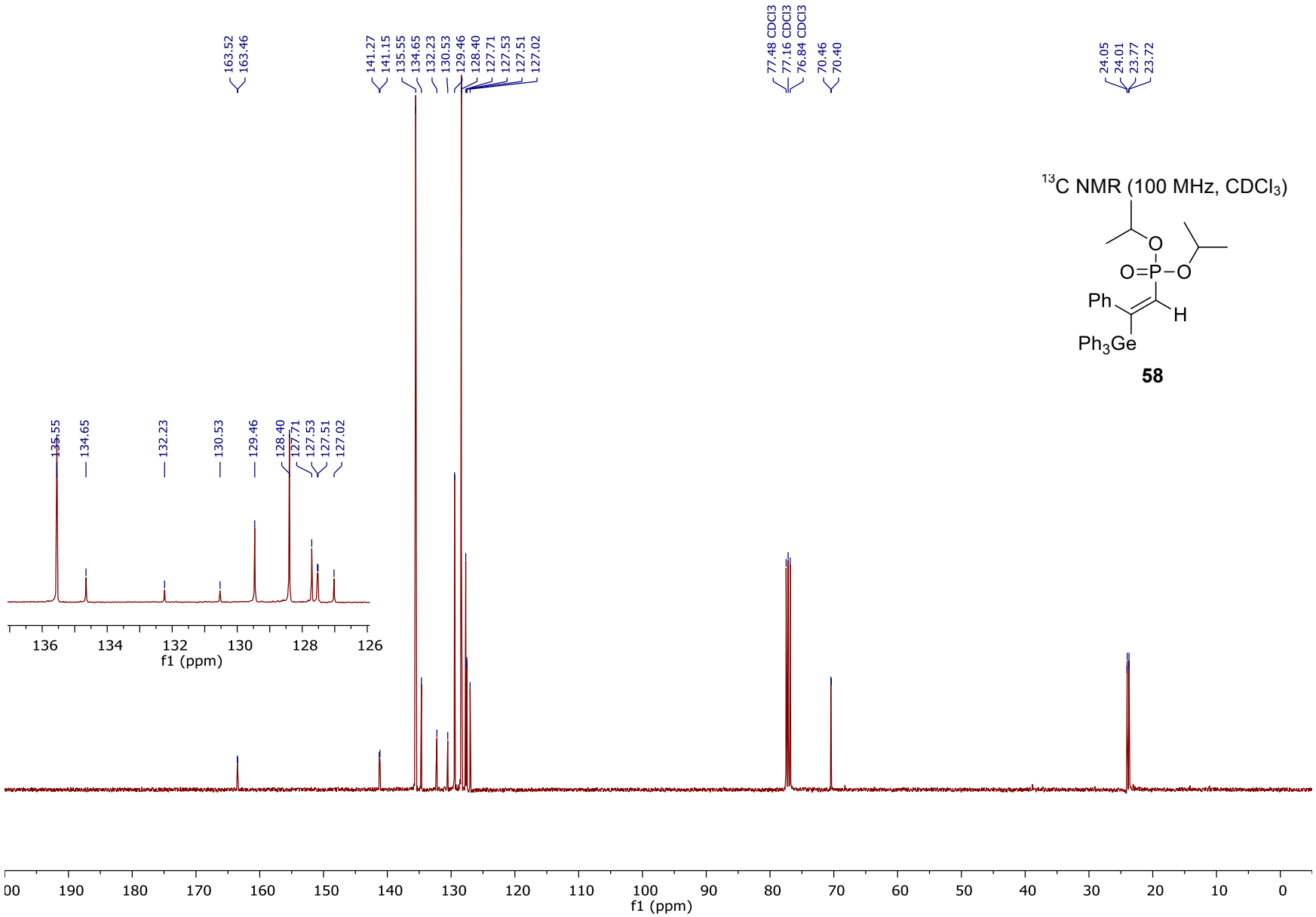
[^{2}H]-**57**

^{31}P NMR (162 MHz, $CDCl_3$)

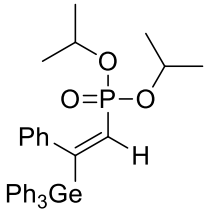


[^{2}H]-**57**

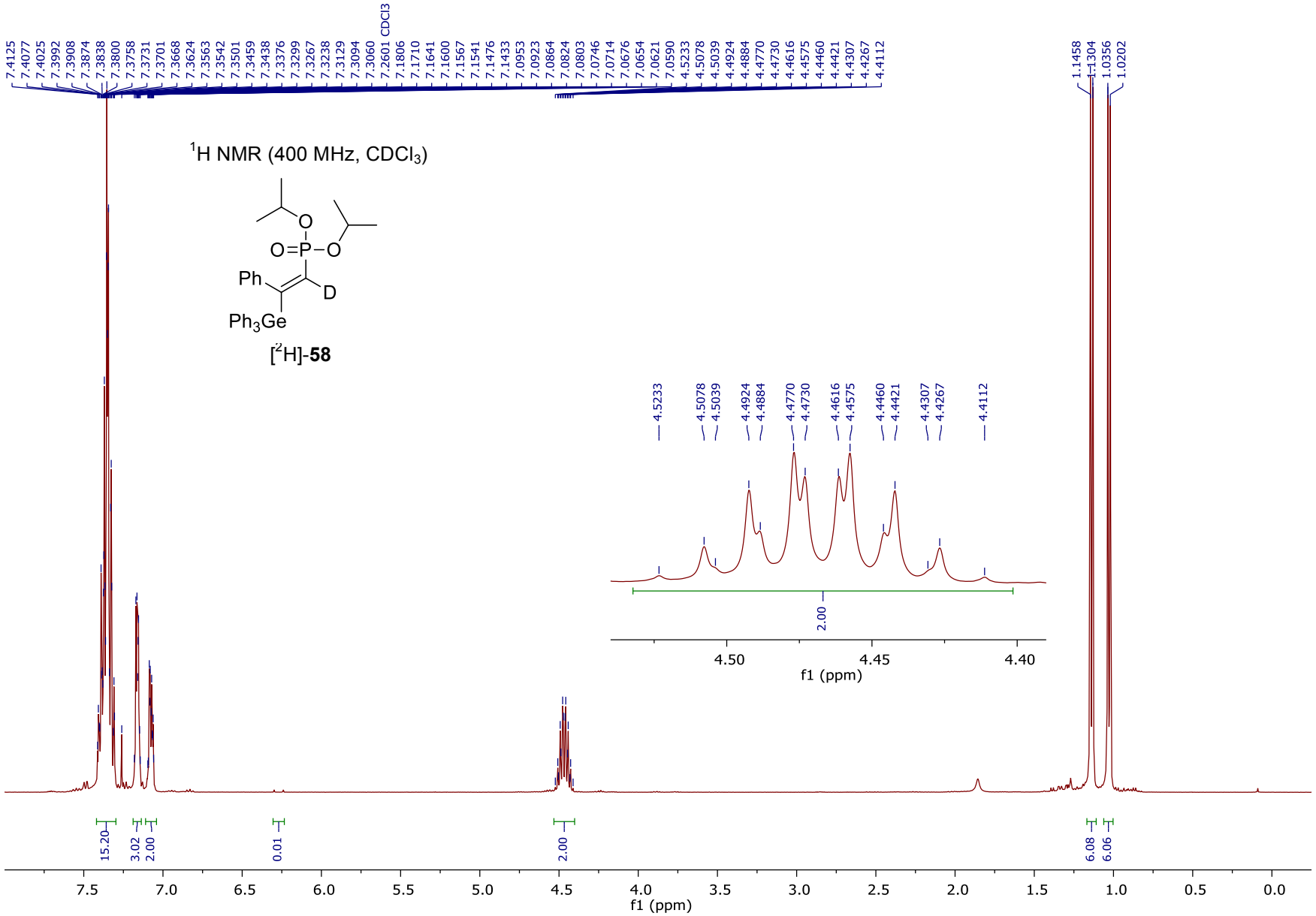

7.4128 7.4080 7.4028 7.3995 7.3912 7.3879 7.3842 7.3803 7.3766 7.3734 7.3712 7.3681 7.3632 7.3574 7.3552 7.3511 7.3464 7.3442 7.3382 7.3303 7.3272 7.3243 7.3133 7.3099 7.3064 7.2600 CDCl3 7.1757 7.1716 7.1670 7.1645 7.1606 7.1573 7.1547 7.1483 7.0867 7.0829 7.0807 7.0750 7.0717 7.0682 7.0658 7.0624 7.0595 6.2996 6.2418 4.5246 4.5092 4.5053 4.4938 4.4900 4.4784 4.4744 4.4629 4.4589 4.4474 4.4435 4.4321 4.4281 4.4126
1.1471 1.1317 1.0376 1.0222
^{1}H NMR (400 MHz, $CDCl_3$)
O
O=P–O
Ph
H
Ph_3Ge
58
4.5246 4.5092 4.5053 4.4938 4.4900 4.4784 4.4744 4.4629 4.4589 4.4474 4.4435 4.4321 4.4281 4.4126
2.02
4.54 4.52 4.50 4.48 4.46 4.44 4.42 4.40
f1 (ppm)
15.41 3.03 2.00 1.00 2.02 6.09 6.04
.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
f1 (ppm)

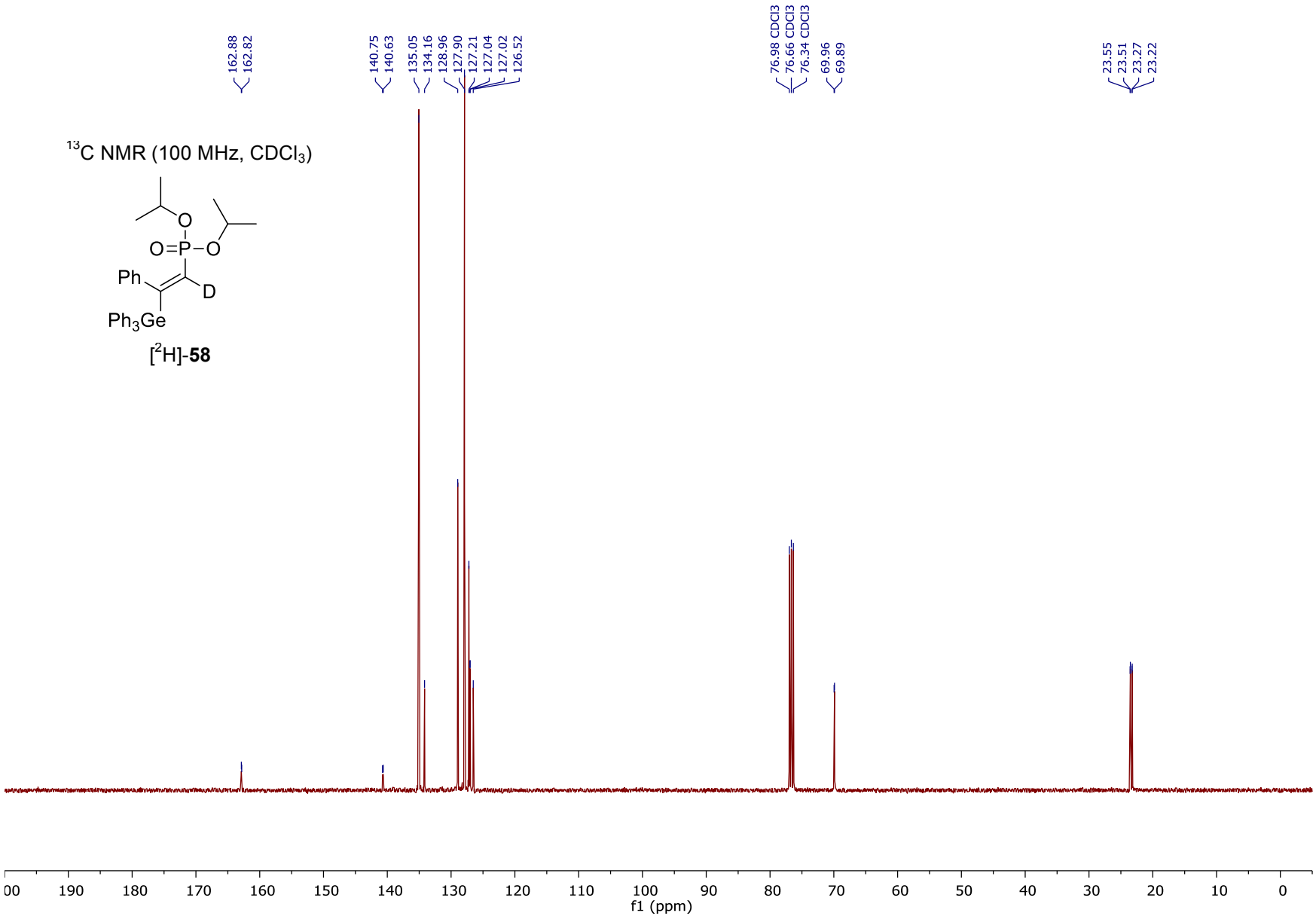

163.52
163.46
141.27
141.15
135.55
134.65
132.23
130.53
129.46
128.40
127.71
127.53
127.51
127.02
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.46
70.40
24.05
24.01
23.77
23.72
f1 (ppm)
^{13}C NMR (100 MHz, $CDCl_3$)
O
O=P–O
Ph
H
Ph_3Ge
58

^{31}P NMR (162 MHz, $CDCl_3$)

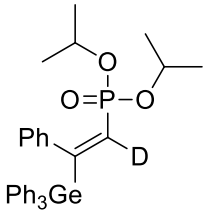


58

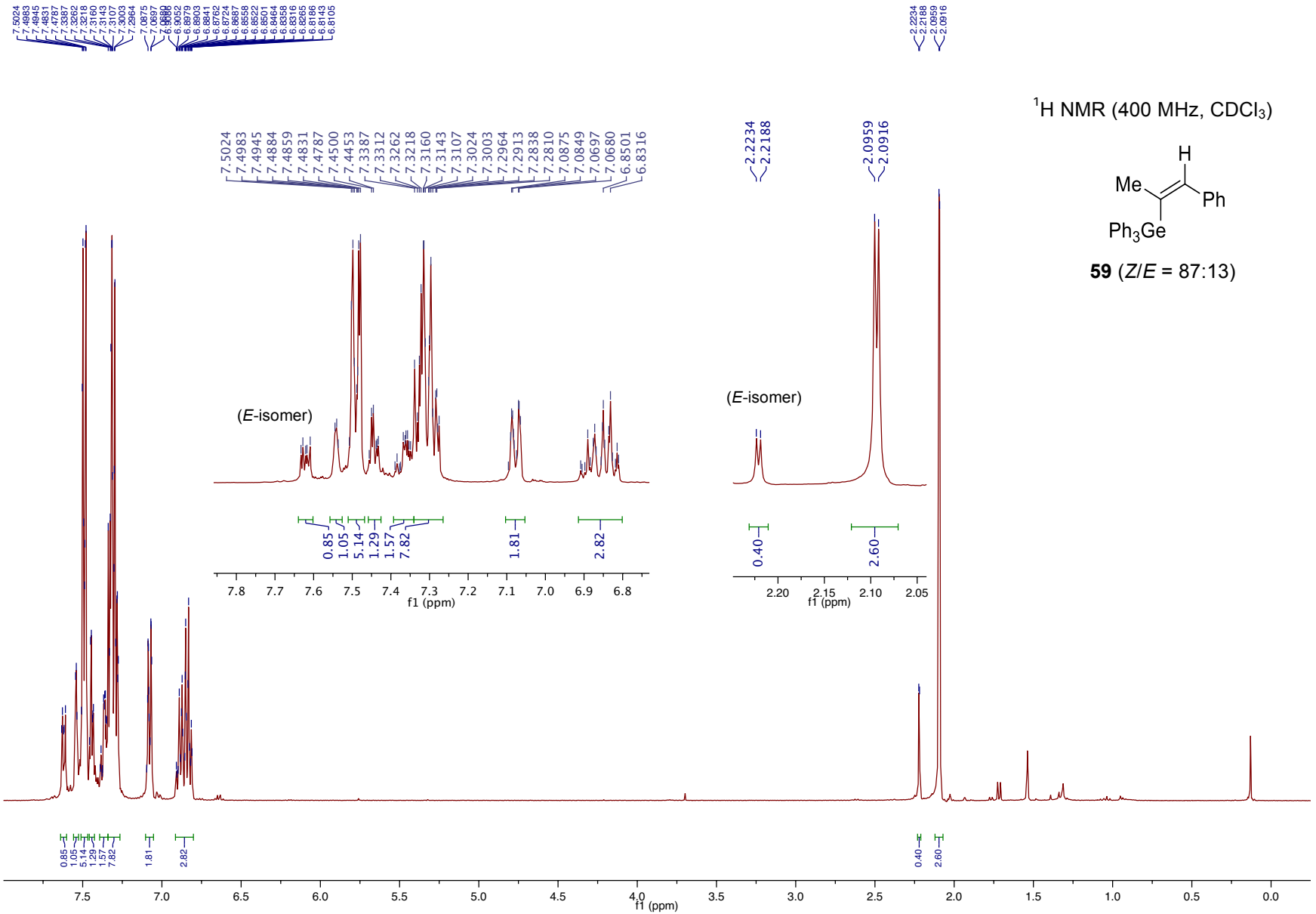

7.4125
7.4077
7.4025
7.3992
7.3908
7.3874
7.3838
7.3800
7.3758
7.3731
7.3701
7.3668
7.3624
7.3563
7.3542
7.3501
7.3459
7.3438
7.3376
7.3299
7.3267
7.3238
7.3129
7.3094
7.3060
7.2601 CDCl3
7.1806
7.1710
7.1641
7.1600
7.1567
7.1541
7.1476
7.1433
7.0953
7.0923
7.0864
7.0824
7.0803
7.0746
7.0714
7.0676
7.0654
7.0621
7.0590
4.5233
4.5078
4.5039
4.4924
4.4884
4.4770
4.4730
4.4616
4.4575
4.4460
4.4421
4.4307
4.4267
4.4112
1.1458
1.1304
1.0356
1.0202
^{1}H NMR (400 MHz, $CDCl_3$)
O
O=P–O
Ph
D
Ph_3Ge
[^{2}H]-**58**
2.00
4.50
4.45
4.40
f1 (ppm)
15.20
3.02
2.00
0.01
2.00
6.08
6.06
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
f1 (ppm)


162.88
162.82
140.75
140.63
135.05
134.16
128.96
127.90
127.21
127.04
127.02
126.52
76.98 CDCl3
76.66 CDCl3
76.34 CDCl3
69.96
69.89
23.55
23.51
23.27
23.22
^{13}C NMR (100 MHz, $CDCl_3$)
O
O=P–O
Ph
D
Ph_3Ge
[^{2}H]-**58**
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

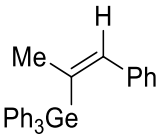
^{31}P NMR (162 MHz, $CDCl_3$)



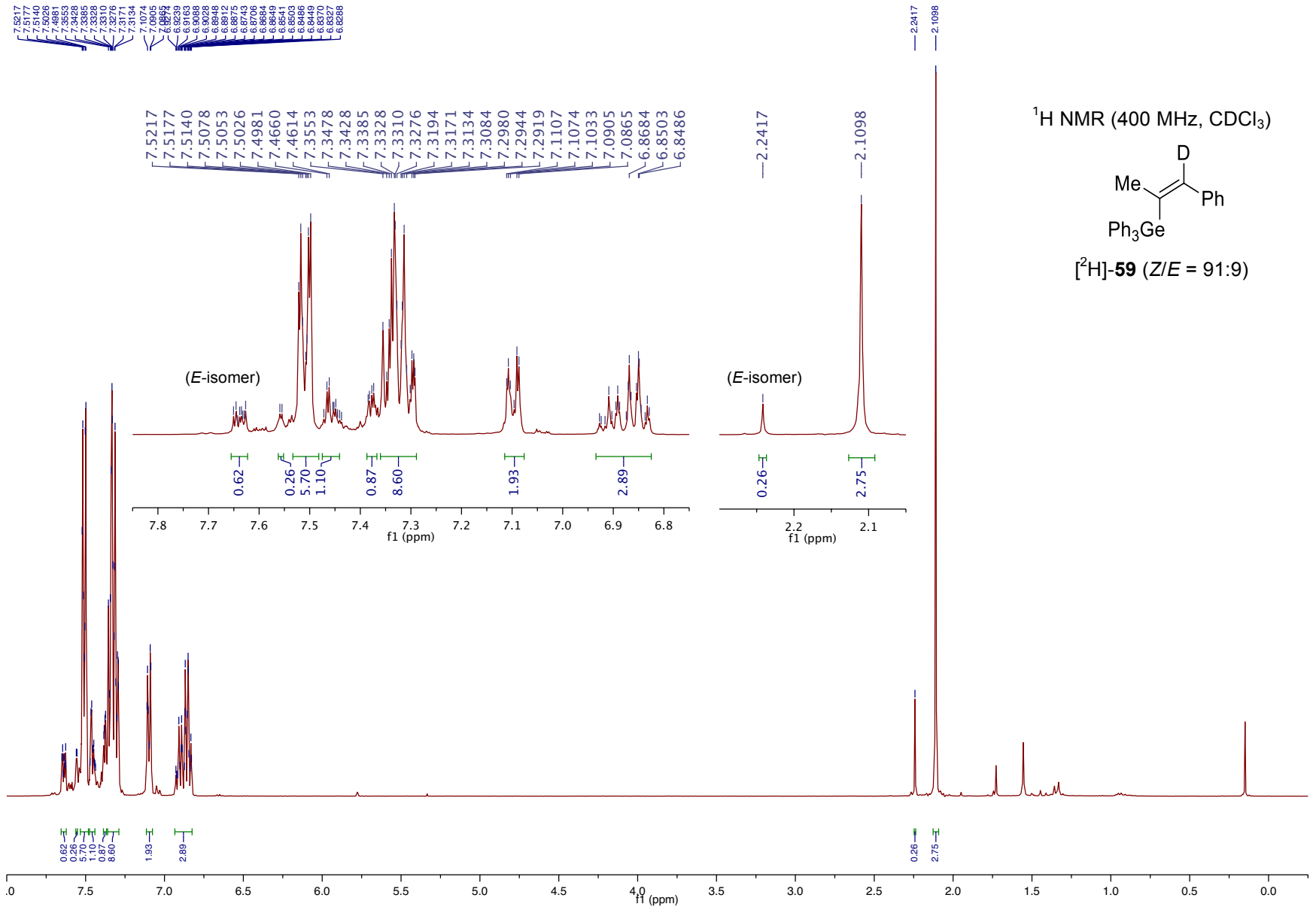
[^{2}H]-**58**


^{1}H NMR (400 MHz, $CDCl_3$)
H
Me
Ph
Ph_3Ge
59 (*Z*/*E* = 87:13)
(*E*-isomer)
(*E*-isomer)
f1 (ppm)

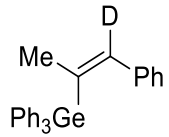
^{13}C NMR (100 MHz, $CDCl_3$)



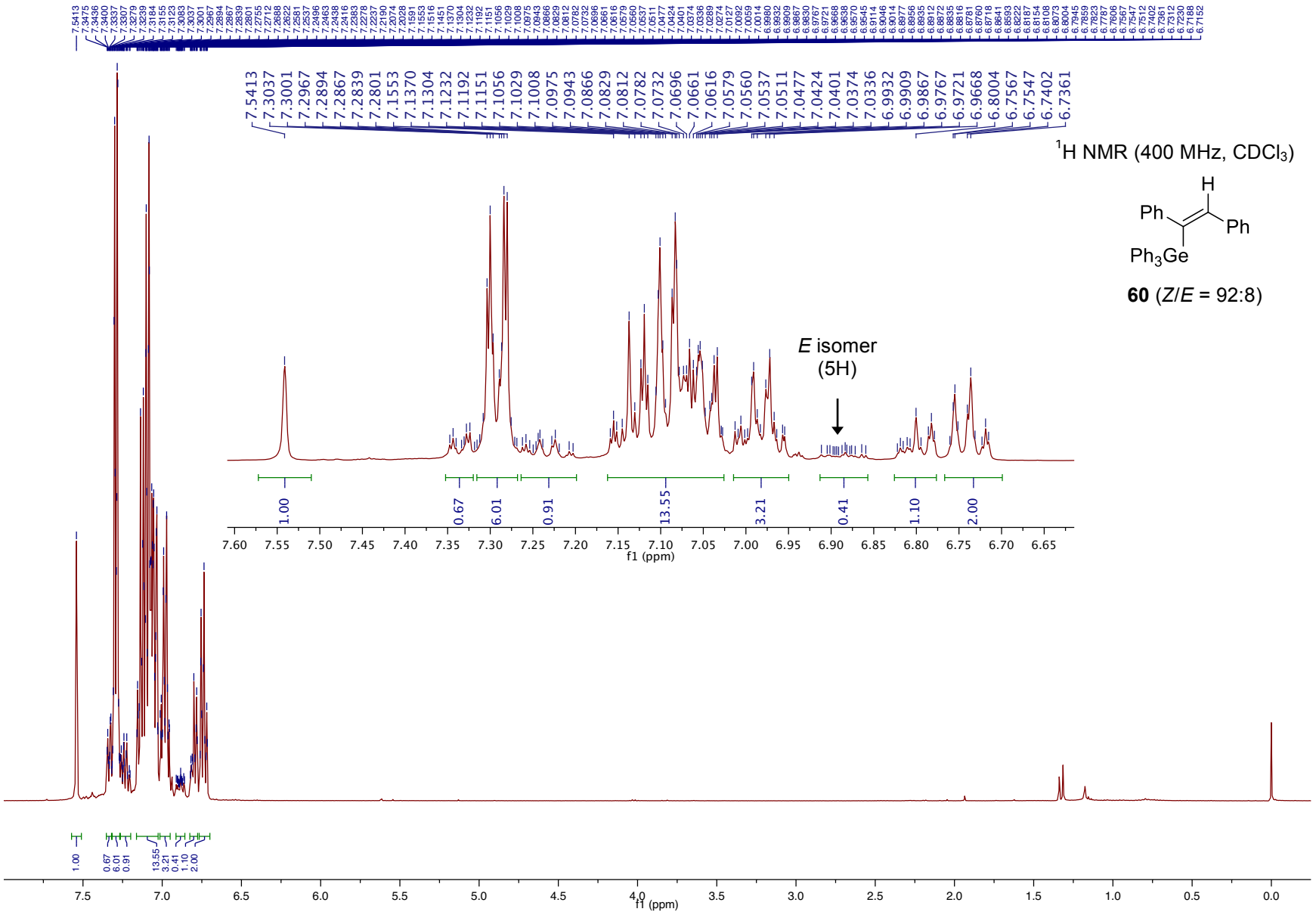
59 (*Z*/*E* = 87:13)


^{1}H NMR (400 MHz, $CDCl_3$)
D
Me
Ph
Ph_3Ge
[^{2}H]-**59** (*Z*/*E* = 91:9)
(*E*-isomer)
(*E*-isomer)
f1 (ppm)

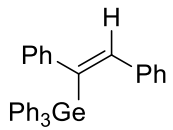
^{13}C NMR (100 MHz, $CDCl_3$)



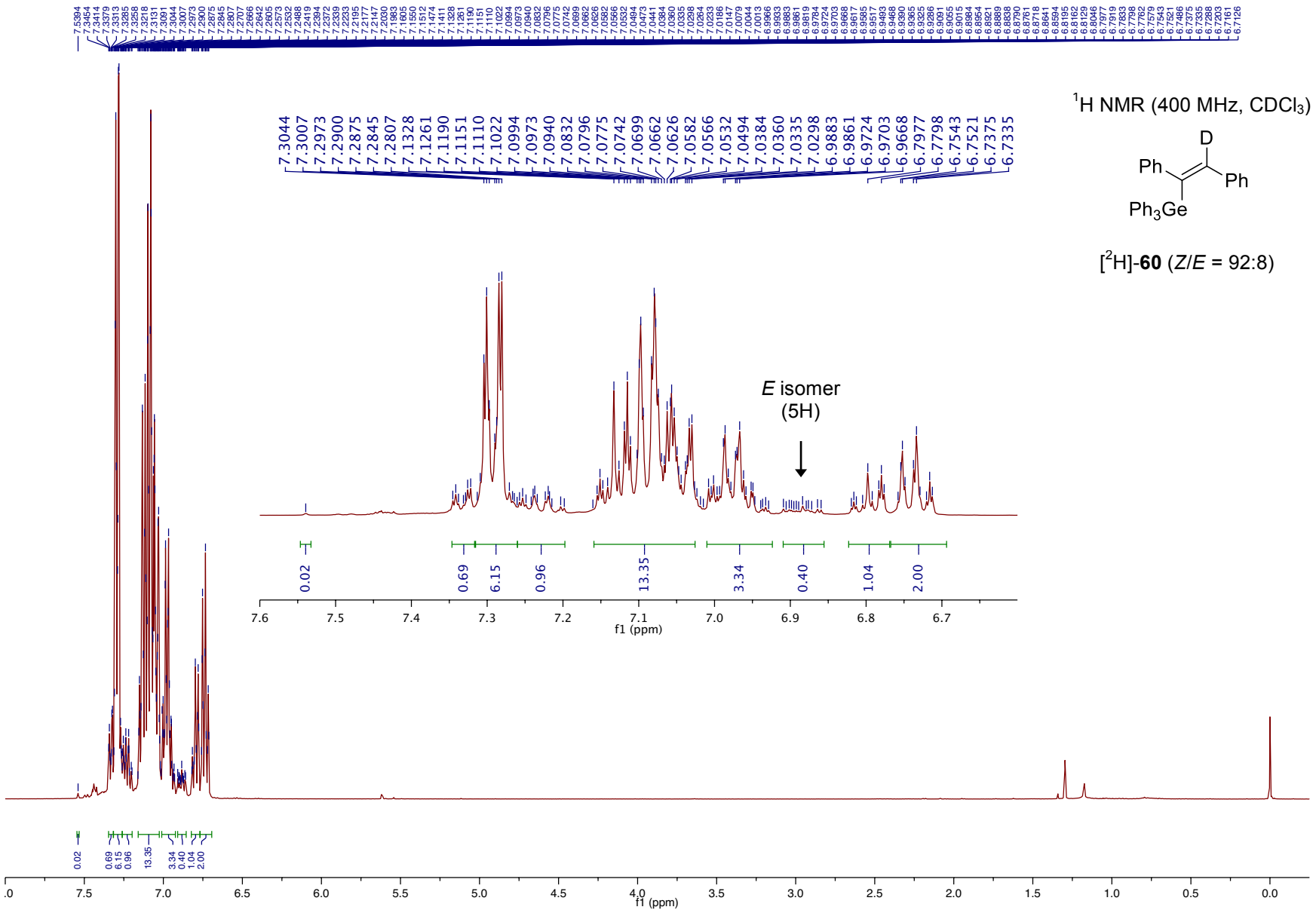
[^{2}H]-**59** (*Z*/*E* = 91:9)


^{1}H NMR (400 MHz, $CDCl_3$)
H
Ph
Ph
Ph_3Ge
60 (*Z*/*E* = 92:8)
E isomer
(5H)
f1 (ppm)

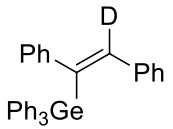
^{13}C NMR (100 MHz, $CDCl_3$)



60 (*Z*/*E* = 92:8)

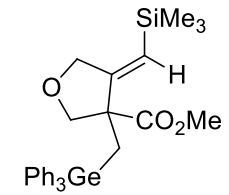

^{1}H NMR (400 MHz, $CDCl_3$)
D
Ph
Ph
Ph_3Ge
[^{2}H]-**60** (*Z*/*E* = 92:8)
E isomer
(5H)
0.02
0.69
6.15
0.96
13.35
3.34
0.40
1.04
2.00
f1 (ppm)

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

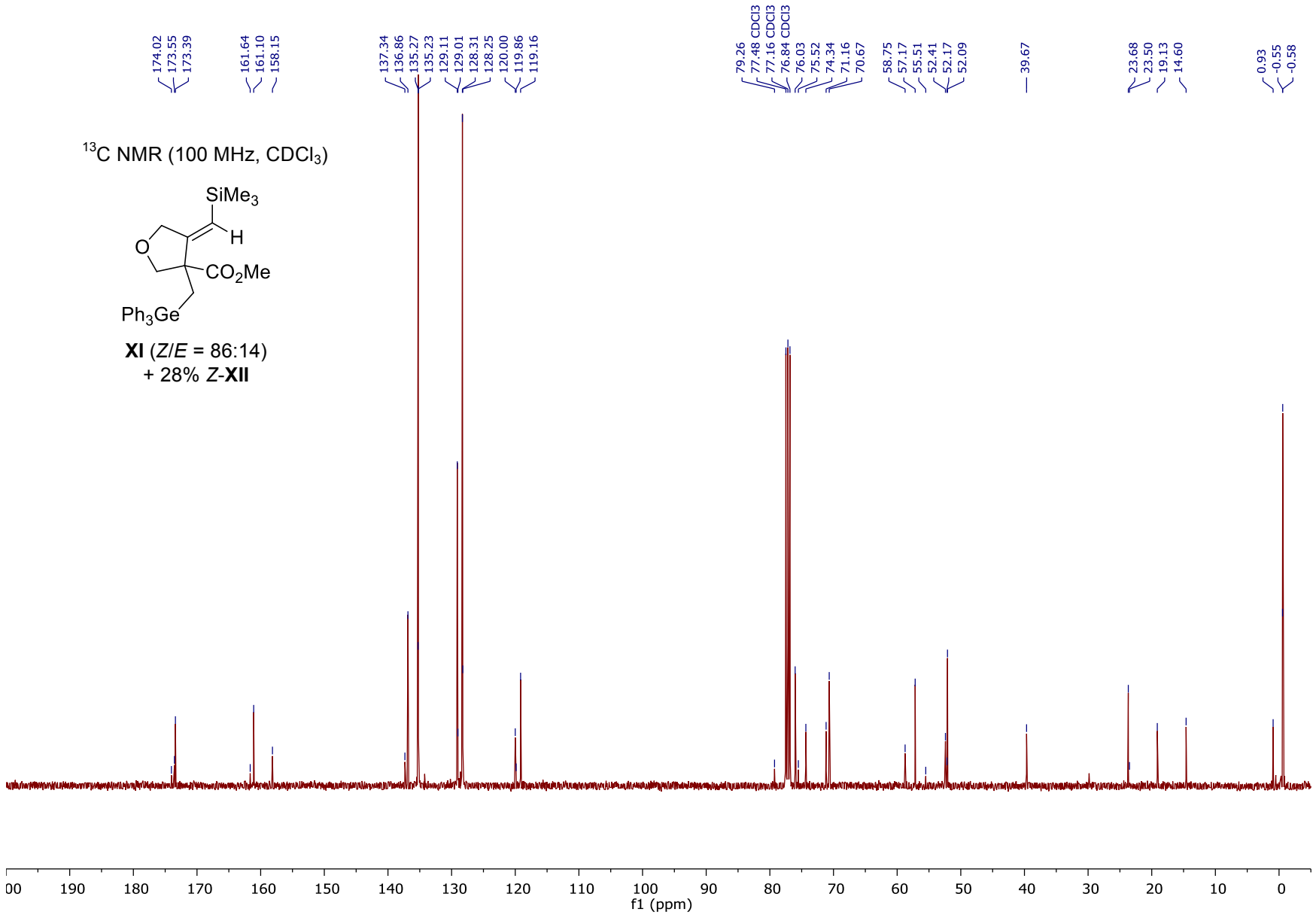


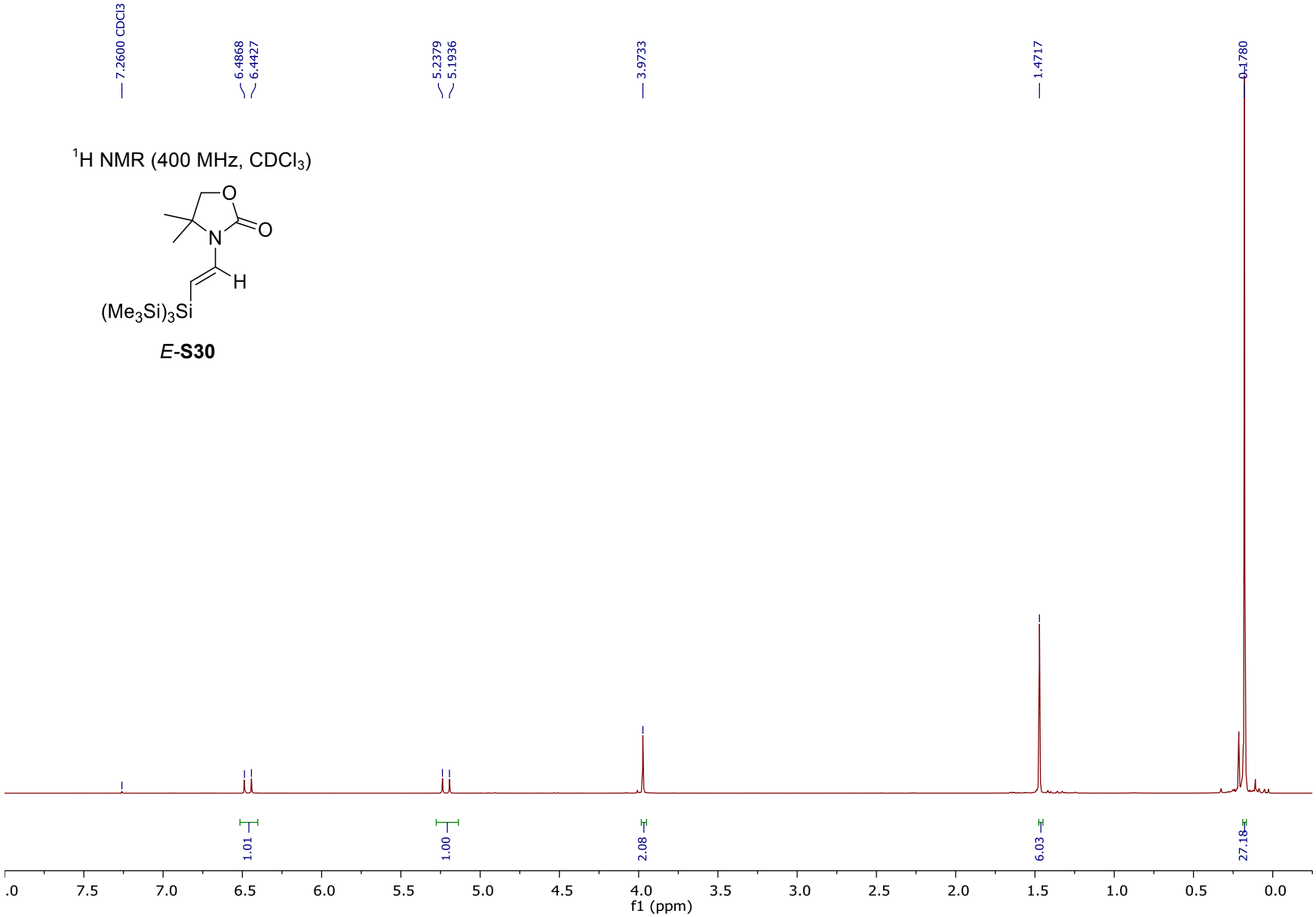
[^{2}H]-**60** (*Z*/*E* = 92:8)

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



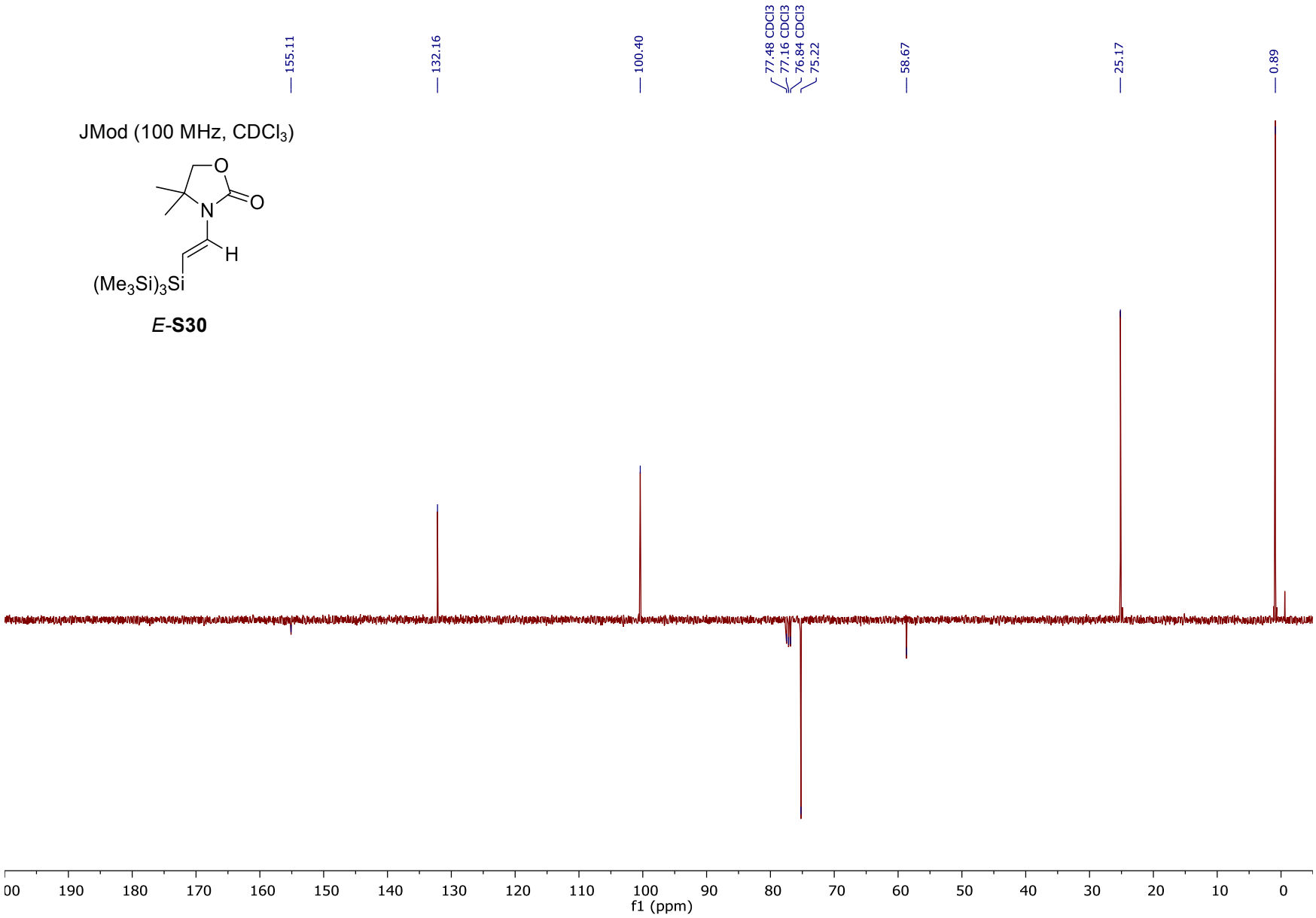
XI (*Z*/*E* = 86:14)
+ 28% *Z*-**XII**

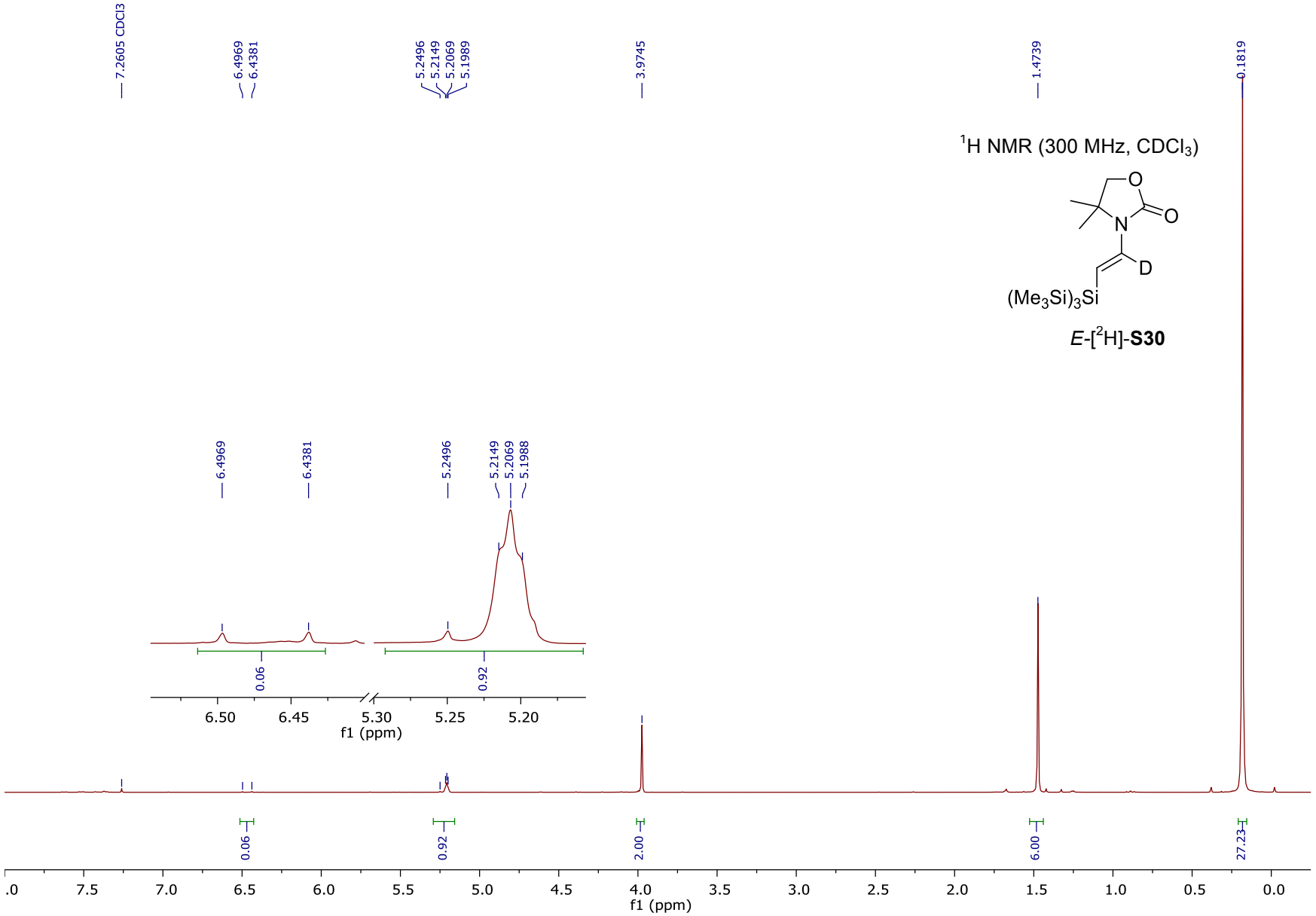

174.02
173.55
173.39
161.64
161.10
158.15
137.34
136.86
135.27
135.23
129.11
129.01
128.31
128.25
120.00
119.86
119.16
79.26
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
76.03
75.52
74.34
71.16
70.67
58.75
57.17
55.51
52.41
52.17
52.09
39.67
23.68
23.50
19.13
14.60
0.93
-0.55
-0.58
^{13}C NMR (100 MHz, $CDCl_3$)
SiMe3
H
O
CO2Me
Ph3Ge
XI (*Z*/*E* = 86:14)
+ 28% *Z*-**XII**
f1 (ppm)

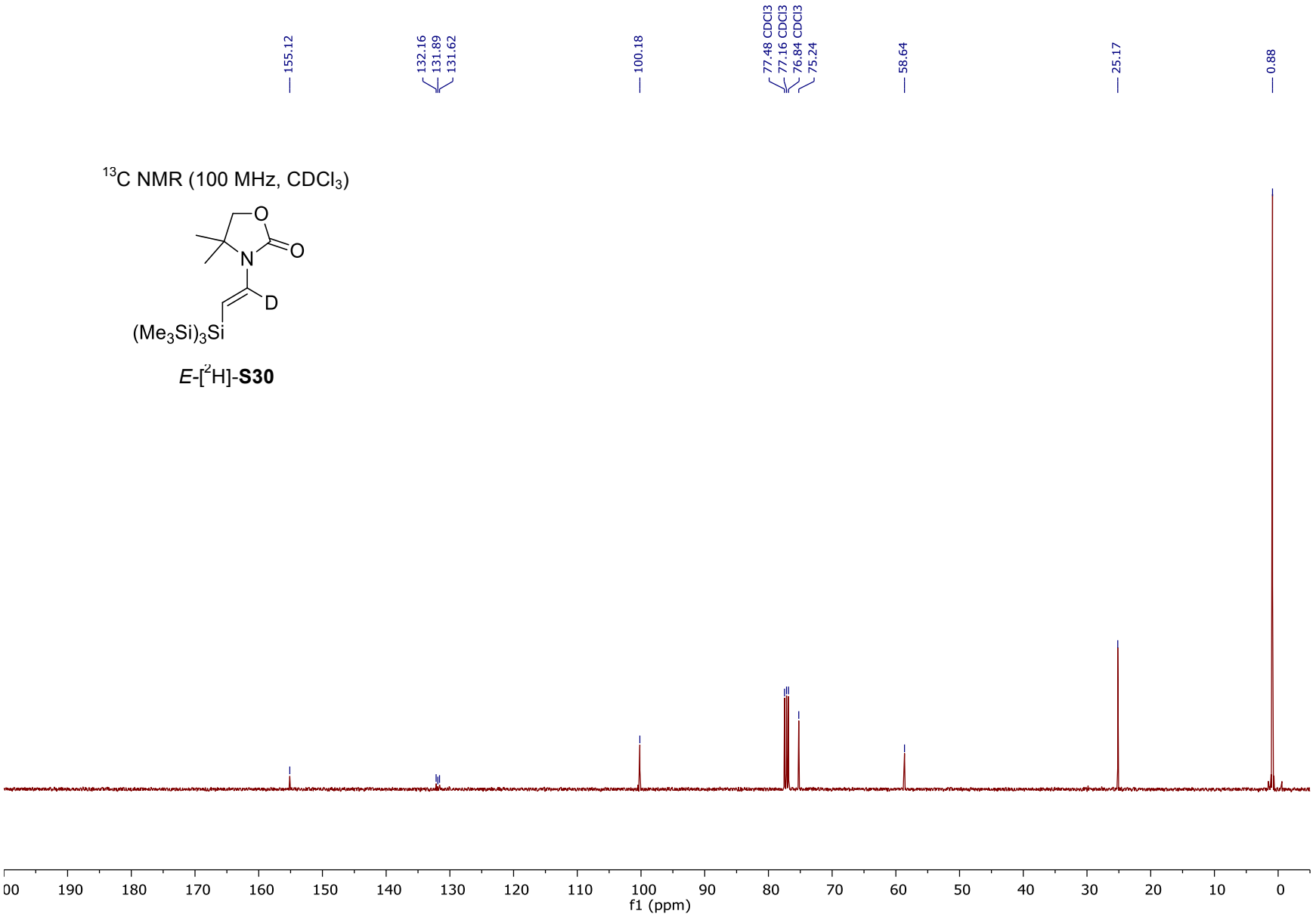


^{1}H NMR (400 MHz, $CDCl_3$)

***E*-S30**


155.11
132.16
100.40
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.22
58.67
25.17
0.89
JMod (100 MHz, CDCl3)
O
O
N
H
(Me3Si)3Si
E-S30
f1 (ppm)


7.2605 CDCl3
6.4969
6.4381
5.2496
5.2149
5.2069
5.1989
3.9745
1.4739
0.1819
^{1}H NMR (300 MHz, $CDCl_3$)
O
O
N
D
$(Me_3Si)_3Si$
E-[^{2}H]-**S30**
0.06
0.92
2.00
6.00
27.23
f1 (ppm)


155.12
132.16
131.89
131.62
100.18
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.24
58.64
25.17
0.88
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
N
D
$(Me_3Si)_3Si$
E-[^{2}H]-**S30**
f1 (ppm)

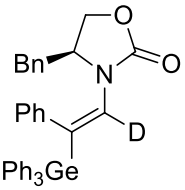
V X-Ray Crystal Structure Determination of Compounds [^{2}H]-12, 14, 23, 25, 40, 44, 45, [^{2}H]-58

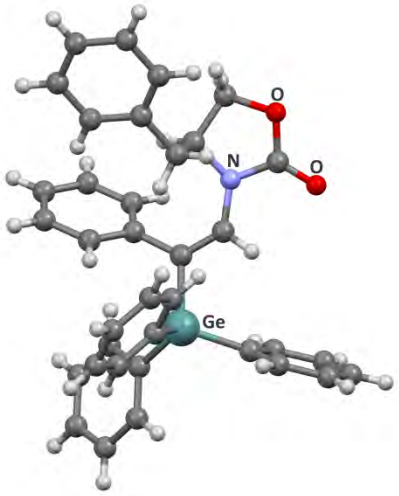
Single crystals were selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with Bruker Kappa-APEX2 systems using micro-source Cu-Kα or fine-focus sealed tube Mo-Kα radiation. Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried out with the Bruker APEX2 suite of programs. The structures were solved with SHELXT-2014[27] and refined by full-matrix least-squares methods with SHELXL-2014[27] using WinGX[28] or Olex2.[29] Crystal absolute structures for compounds [^{2}H]-**12** and **45** were determined by anomalous scattering effects analysis.[30] Compound **44** was refined as a 2-component inversion twin. All structures were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 1862400–1862407 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Compound	**12**	**14**	**23**	**25**
Empirical formula	C_{36} H_{31} Ge N O_2	C_{34} H_{29} Ge N O_2	C_{30} H_{37} Ge N O_3 Si	C_{26} H_{24} F_3 Ge N O_2
Formula weight	582.21	556.17	560.28	512.05
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic
Space group	P 4_1 2_1 2	P 2_1/c	P 2_1/n	P 2_1/c
Unit cell dimensions	a = 9.5716(4) Å	a = 10.4058(3) Å	a = 11.7444(5) Å	a = 11.4162(3) Å
	b = 9.5716(4) Å	b = 20.8929(7) Å	b = 15.9338(8) Å	b = 16.8675(5) Å
	c = 64.226(3) Å	c = 13.6211(5) Å	c = 32.3292(16) Å	c = 24.7995(7) Å
	α = 90°	α = 90°	α = 90°	α = 90°
	β = 90°	β = 111.976(2)°	β = 92.830(3)°	β = 96.907(2)°
	γ = 90°	γ = 90°	γ = 90°	γ = 90°
Volume	5884.1(6) $Å^3$	2746.16(16) $Å^3$	6042.5(5) $Å^3$	4740.8(2) $Å^3$
Z	8	4	8	8
Crystal description	colourless fragment	colourless block	colourless bar	colourless fragment
Crystal size	0.15 x 0.15 x 0.05 mm^3	0.21 x 0.17 x 0.17 mm^3	0.6 x 0.1 x 0.05 mm^3	0.35 x 0.15 x 0.05 mm^3
Density (calculated)	1.314 $g.cm^{-3}$	1.345 $g.cm^{-3}$	1.232 $g.cm^{-3}$	1.435 $g.cm^{-3}$
Absorption coefficient	1.662 mm^{-1}	1.147 mm^{-1}	1.981 mm^{-1}	1.339 mm^{-1}
Min. and max. transmission	0.74 and 0.87	0.68 and 0.75	0.53 and 0.90	0.80 and 0.95
Temperature	200(1) K	200(1) K	200(1) K	200(1) K
Wavelength	1.54178 Å	0.71073 Å	1.54178 Å	0.71073 Å
θ range for data collection	3.02° to 30.07°	1.89° to 30.16°	2.74° to 66.66°	2.05° to 30.56°
Index ranges	-8 <= h <= 10	-14 <= h <= 14	-13 <= h <= 10	-15 <= h <= 16
	-11 <= k<= 11	-23 <= k<= 29	-18 <= k<= 18	-24 <= k<= 24
	-76 <= l <= 76	-19 <= l <= 11	-38 <= l <= 38	-30 <= l <= 35
Reflections (all / independent)	41850 / 5180	38870 / 8095	47637 / 10414	61522 / 14521
R(int)	7.44 %	1.82 %	7.91 %	3.19 %
Completeness	99.8 %	99.5 %	97.5 %	99.8 %
Data / parameters / restraints	5180 / 361 / 0	8095 / 344 / 0	10414 / 712 / 60	14521 / 595 / 0
Goodness-of-fit on F^2	1.065	1.021	1.031	1.006
Final R indices [I > 2σ(I)]	R1 = 3.07 % wR2 = 7.73 %	R1 = 2.55 % wR2 = 6.35 %	R1 = 4.55 % wR2 = 12.39 %	R1 = 3.33 % wR2 = 7.16 %
Final R indices (all data)	R1 = 3.18 % wR2 = 7.80 %	R1 = 3.34 % wR2 = 6.74 %	R1 = 5.58 % wR2 = 13.19 %	R1 = 5.61 % wR2 = 7.87 %
Largest difference peak and hole	0.35 and -0.35 e.$Å^{-3}$	0.38 and -0.28 e.$Å^{-3}$	0.37 and -0.40 e.$Å^{-3}$	0.46 and -0.35 e.$Å^{-3}$
Absolute structure parameter	-0.005(12)	/	/	/

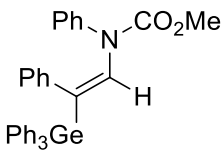
Compound	**40**	**44**	**45**	**58**
Empirical formula	C_{39} H_{33} Ge N O_2	C_{52} H_{52} Cl_4 Ge_2 N_2 O_4 Zn	C_{54} H_{56} Cl_4 Ge_2 N_2 O_4 Zn	C_{32} H_{35} Ge O_3 P
Formula weight	620.25	1121.30	1149.35	571.16
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	P 2_1/n	P c a 2_1	P 2_1 2_1 2_1	C 2/c
Unit cell dimensions	a = 11.0689(2) Å	a = 21.4118(5) Å	a = 13.4291(6) Å	a = 16.3298(9) Å
	b = 17.7248(3) Å	b = 12.0493(2) Å	b = 17.2102(8) Å	b = 12.8553(7) Å
	c = 16.4657(3) Å	c = 39.1926(8) Å	c = 23.7226(12) Å	c = 28.1785(16) Å
	α = 90°	α = 90°	α = 90°	α = 90°
	β = 90.862(1)°	β = 90°	β = 90°	β = 97.582(2)°
	γ = 90°	γ = 90°	γ = 90°	γ = 90°
Volume	3230.1(1) $Å^3$	10111.6(4) $Å^3$	5482.7(4) $Å^3$	5863.6(6) $Å^3$
Z	4	8	4	8
Crystal description	colourless fragment	colourless prism	colourless fragment	colourless fragment
Crystal size	0.55 x 0.4 x 0.25 mm^3	0.3 x 0.05 x 0.02 mm^3	0.4 x 0.2 x 0.02 mm^3	0.25 x 0.2 x 0.15 mm^3
Density (calculated)	1.275 $g.cm^{-3}$	1.473 $g.cm^{-3}$	1.392 $g.cm^{-3}$	1.294 $g.cm^{-3}$
Absorption coefficient	0.982 mm^{-1}	1.909 mm^{-1}	3.946 mm^{-1}	1.129 mm^{-1}
Min. and max. transmission	0.70 and 0.84	1.00 and 0.70	0.54 and 1.00	0.70 and 0.75
Temperature	200(1) K	200(1) K	200(1) K	200(1) K
Wavelength	0.71073 Å	0.71073 Å	1.54178 Å	0.71073 Å
θ range for data collection	1.69° to 30.57°	1.69° to 26.39°	3.18° to 66.93°	2.21° to 30.54°
Index ranges	-15 <= h <= 15	-26 <= h <= 23	-14 <= h <= 15	-23 <= h <= 22
	-25 <= k<= 20	-8 <= k<= 15	-20 <= k<= 20	-18 <= k<= 18
	-23 <= l <= 23	-48 <= l <= 43	-28 <= l <= 28	-40 <= l <= 40
Reflections (all / independent)	37208 / 9896	46305 / 18058	25916 / 9520	34893 / 8973
R(int)	2.18 %	4.39 %	9.35 %	1.79 %
Completeness	99.8 %	99.8 %	99.5 %	99.8 %
Data / parameters / restraints	9896 / 388 / 0	18058 / 1172 / 13	9520 / 622 / 10	8973 / 334 / 0
Goodness-of-fit on F^2	1.075	1.023	1.040	1.050
Final R indices [I > 2σ(I)]	R1 = 3.85 % wR2 = 9.36 %	R1 = 4.86 % wR2 = 11.56 %	R1 = 6.28 % wR2 = 16.09 %	R1 = 2.73 % wR2 = 6.53 %
Final R indices (all data)	R1 = 5.55 % wR2 = 10.16 %	R1 = 7.26 % wR2 = 12.60 %	R1 = 7.76 % wR2 = 17.32 %	R1 = 3.38 % wR2 = 6.83 %
Largest difference peak and hole	1.10 and -0.39 e.$Å^{-3}$	0.68 and -0.86 e.$Å^{-3}$	1.00 and -0.79 e.$Å^{-3}$	0.38 and -0.29 e.$Å^{-3}$
Absolute structure parameter	/	0.292(15)	0.02(2)	/

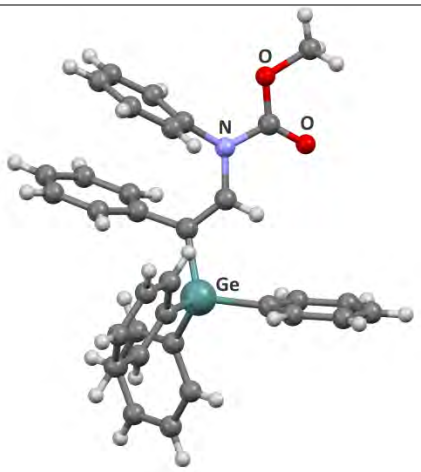
X-ray structure of compound [^{2}H]-**12** (1862400)



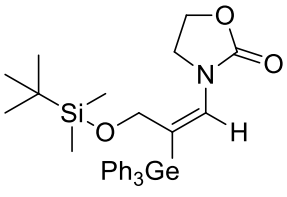


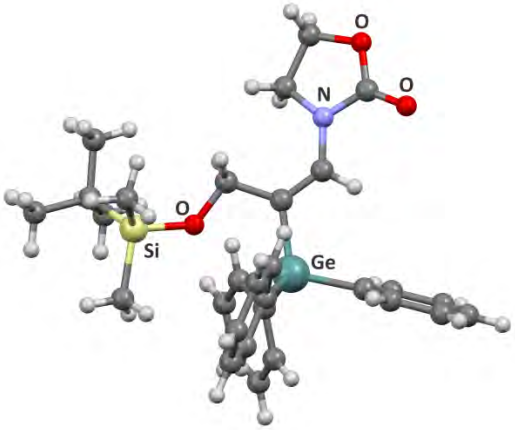
X-ray structure of compound 14 (1862401)



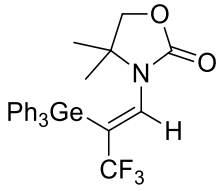


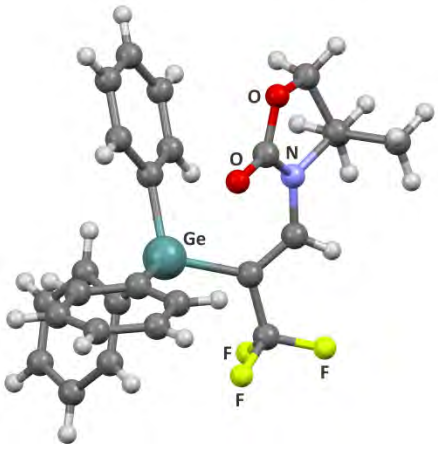
X-ray structure of compound 23 (1862402)



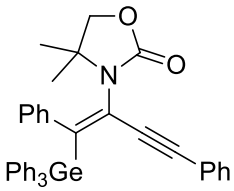


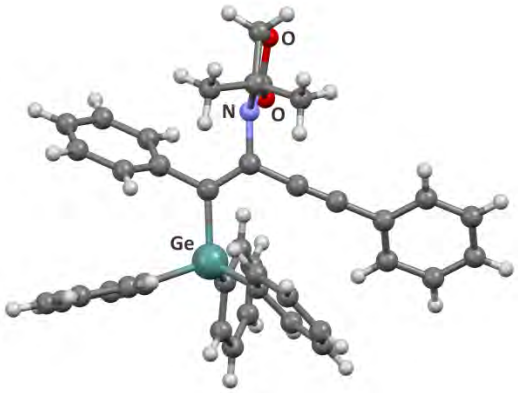
X-ray structure of compound 25 (1862403)



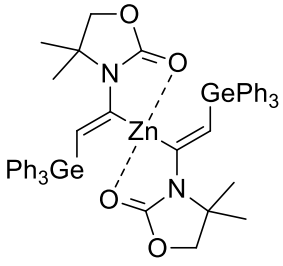


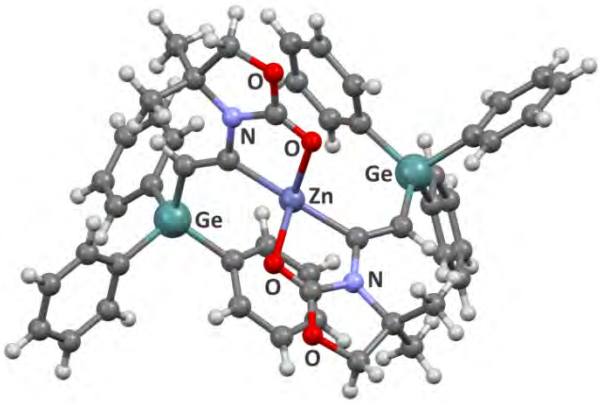
X-ray structure of compound 40 (1862404)



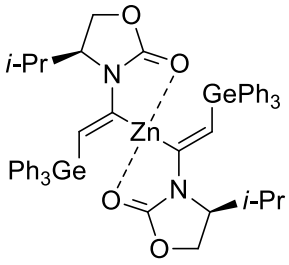


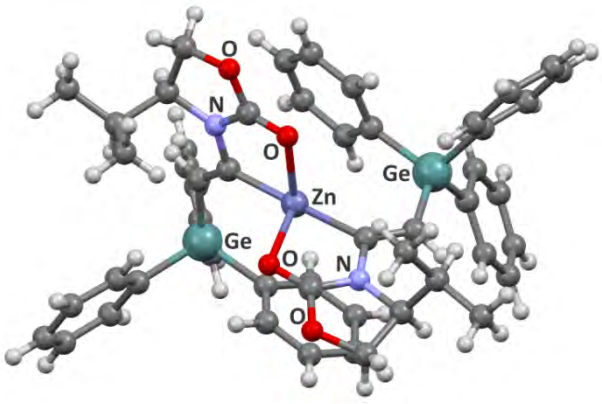
X-ray structure of compound 44 (1862405)



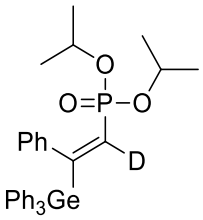


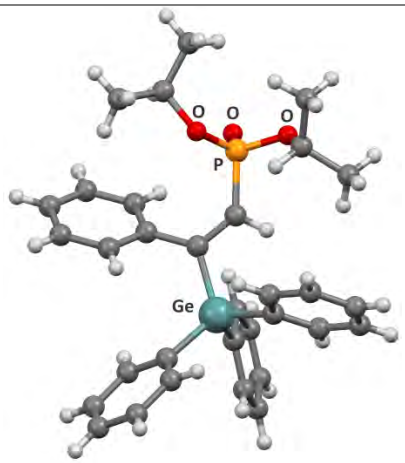
X-ray structure of compound 45 (1862406)





X-ray structure of compound [^{2}H]-**58** (1862407)





VI References

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