

SUPPORTING INFORMATION FOR:

The Palladium-Catalyzed Intramolecular Alder-ene Reactions of *O*- and *N*-Linked 1,6-Enynes Incorporating Triethylsilyl Capping Groups

Jeremy Nugent, Eliska Matoušová, Martin G. Banwell* and Anthony C. Willis

Research School of Chemistry, Institute of Advanced Studies,

The Australian National University, Canberra, ACT 2601, Australia

CONTENTS	PAGE
ORTEP Derived from the Single-crystal X-ray Analysis of Compound 20	S2
¹ H and ¹³ C NMR spectra of compounds 3a-e , 4a/5a , 4b/5b , 4c/5c , 4d/5d , 4e , 6 (and precursor), 7 , 8 , 9/10 , 11 (and precursors), 12 , 13 (and precursors), 14 , 15 (and precursor), 16 , 17 (and precursor), 18 , 19 (and precursor), 20 , 21 , 22 , 23 (and precursor), 24/25 , 26 , 27/28 , 29 (and precursor), 30 , 31 (and precursor), 32 , 33 , 34 , 35 (and precursors), 36-44 , 45 (and precursor), 46-56 , 57 (and precursor), 58 (and precursors), 59 , 60 (and precursor), 61 , 62 , 63 , 64/65 , 66/67 , 68 , 69 .	S3-S178

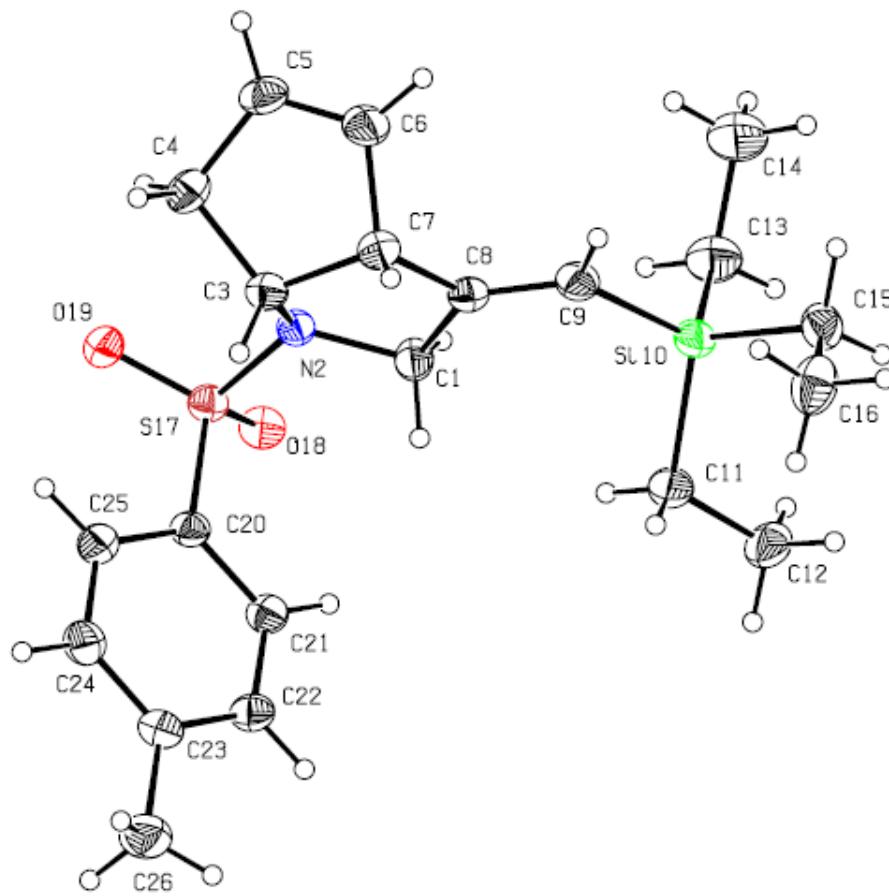
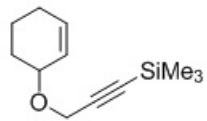
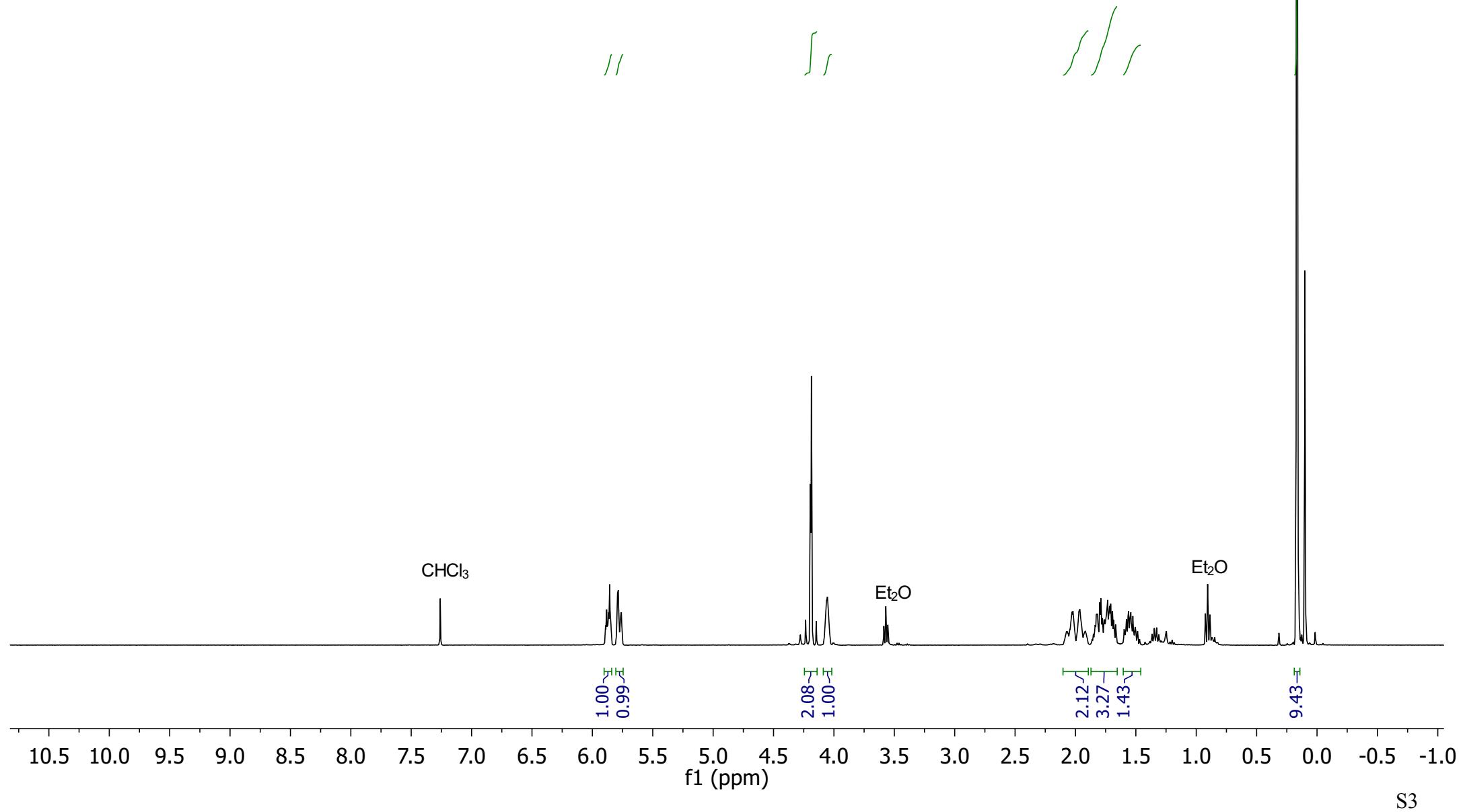
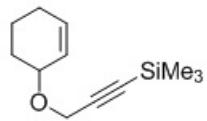


Figure S1: Structure of compound **20** (CCDC 1572856) with labeling of selected atoms. Anisotropic displacement ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

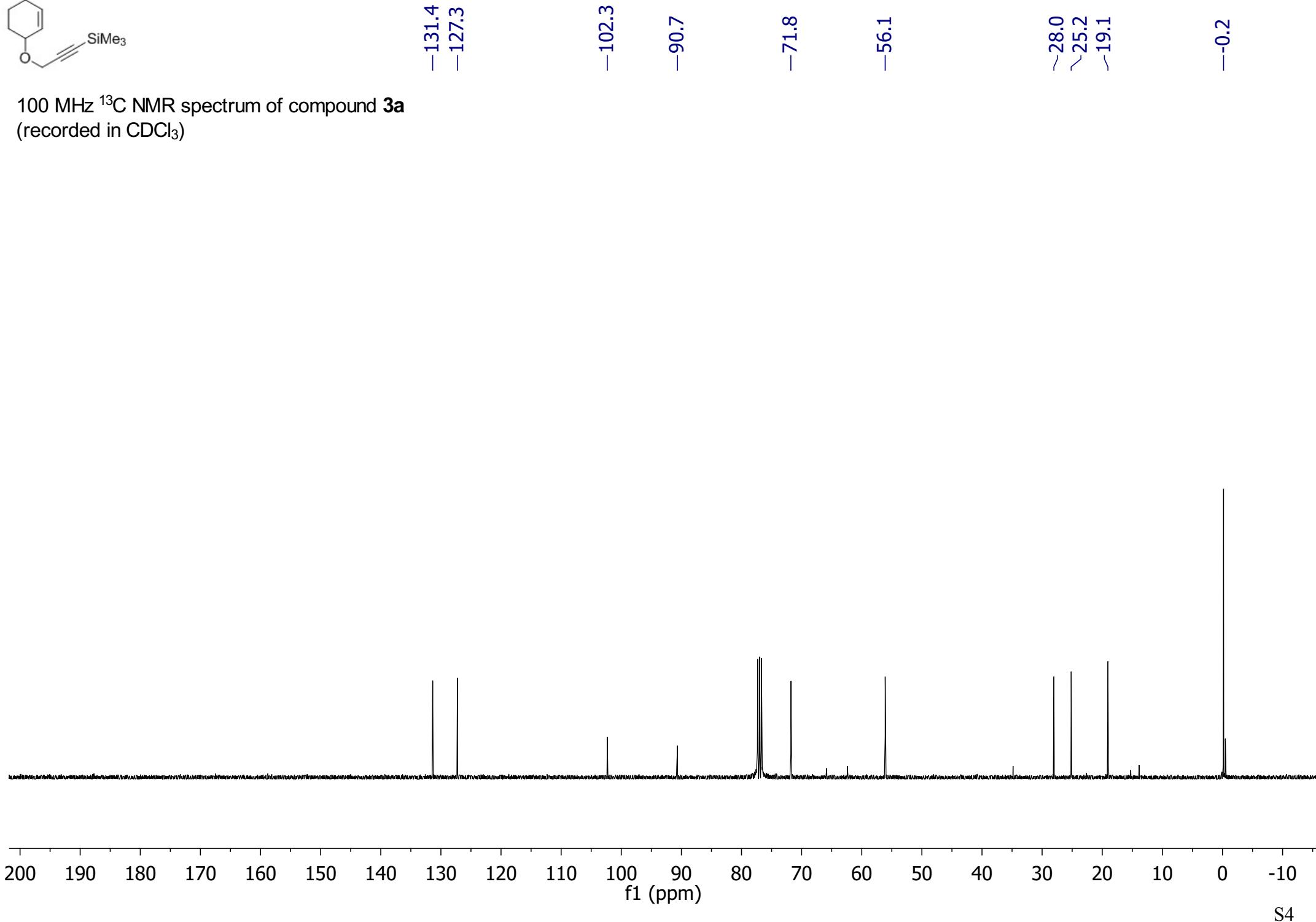


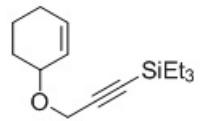
400 MHz ¹H NMR spectrum of compound 3a
(recorded in CDCl₃)



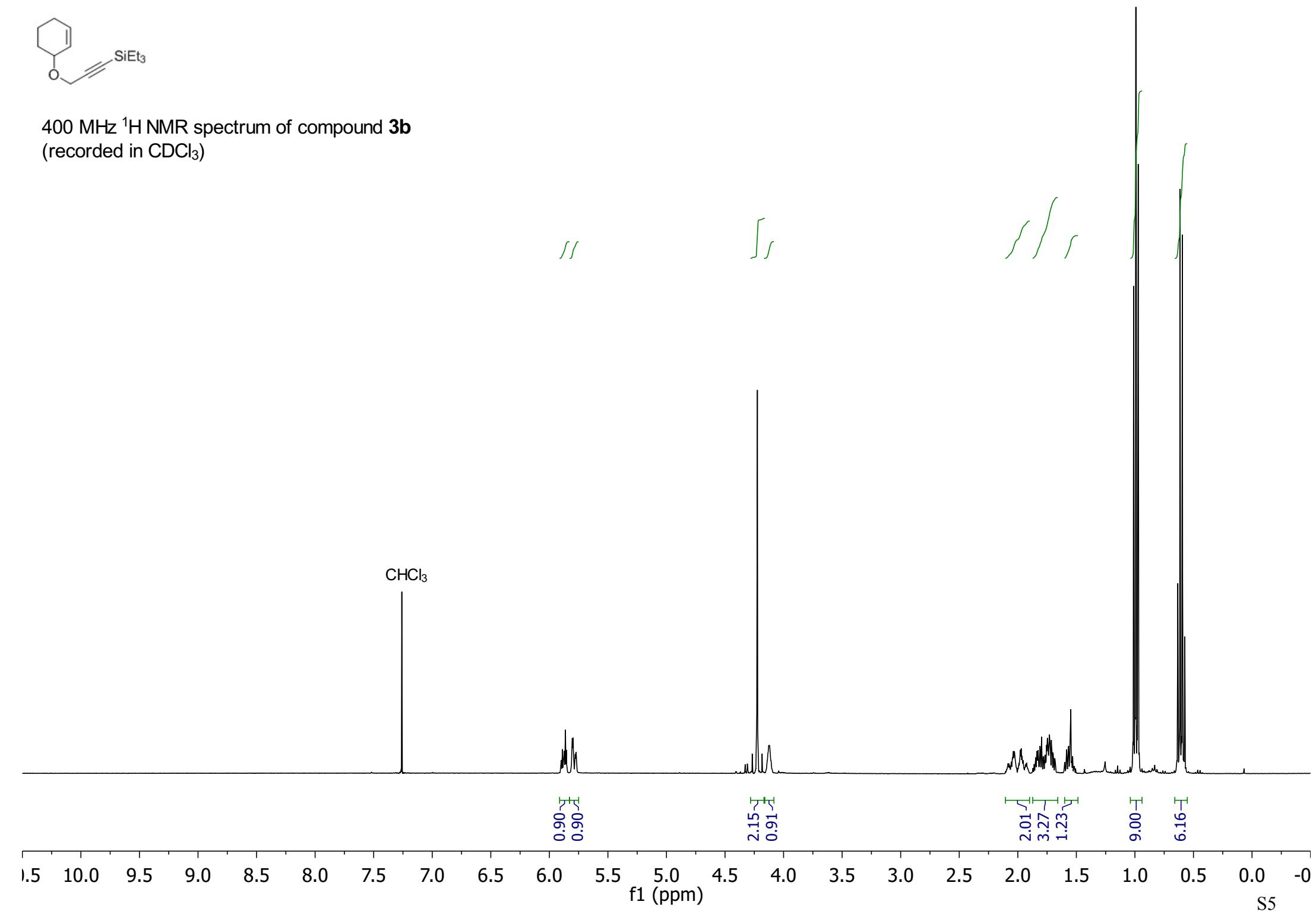


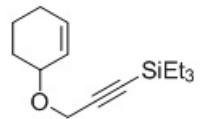
100 MHz ¹³C NMR spectrum of compound 3a
(recorded in CDCl₃)





400 MHz ^1H NMR spectrum of compound **3b**
(recorded in CDCl_3)





100 MHz ^{13}C NMR spectrum of compound **3b**
(recorded in CDCl_3)

-131.5
-127.5

-103.6

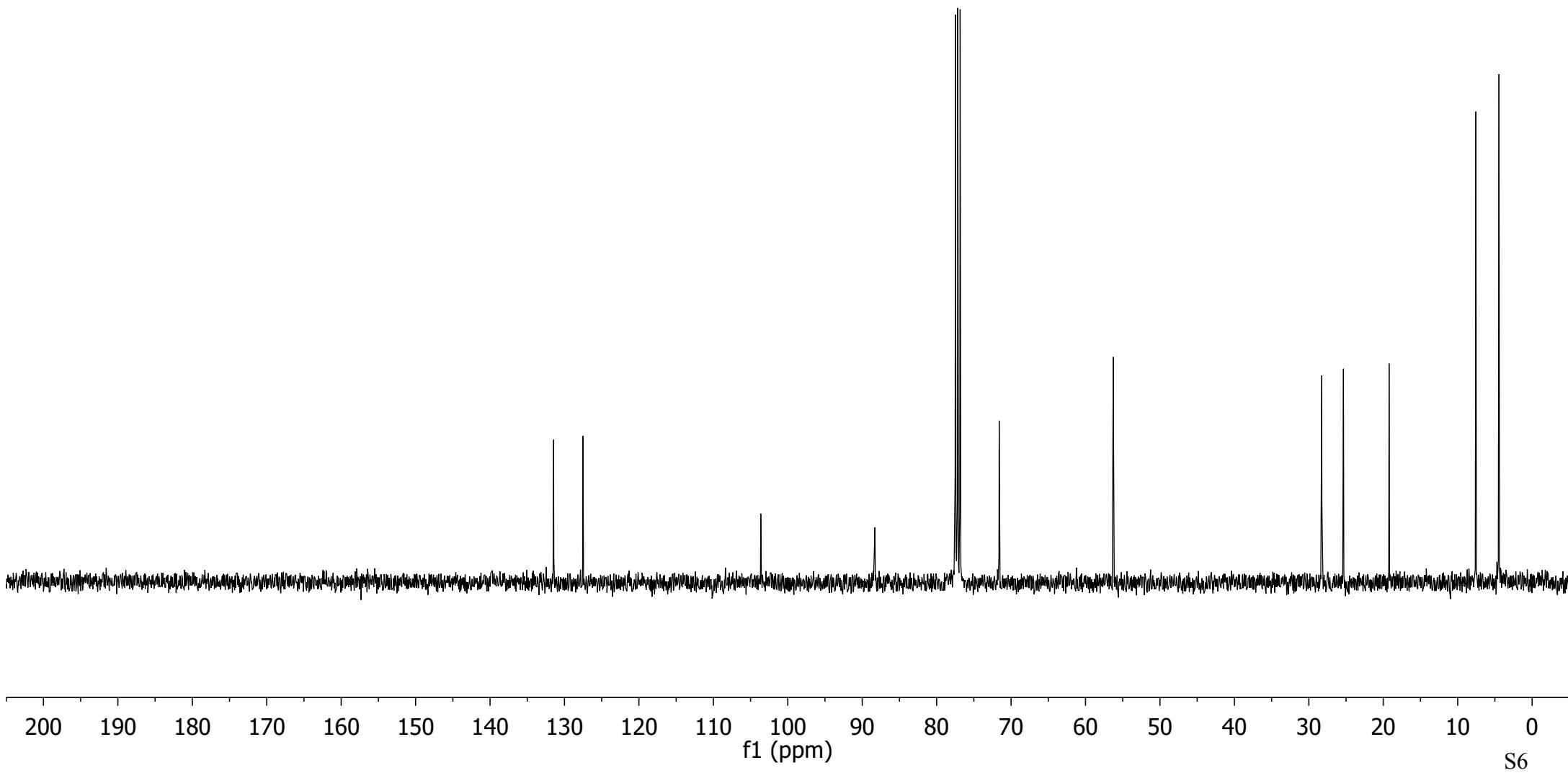
-88.3

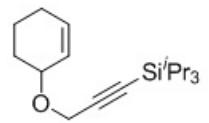
-71.6

-56.3

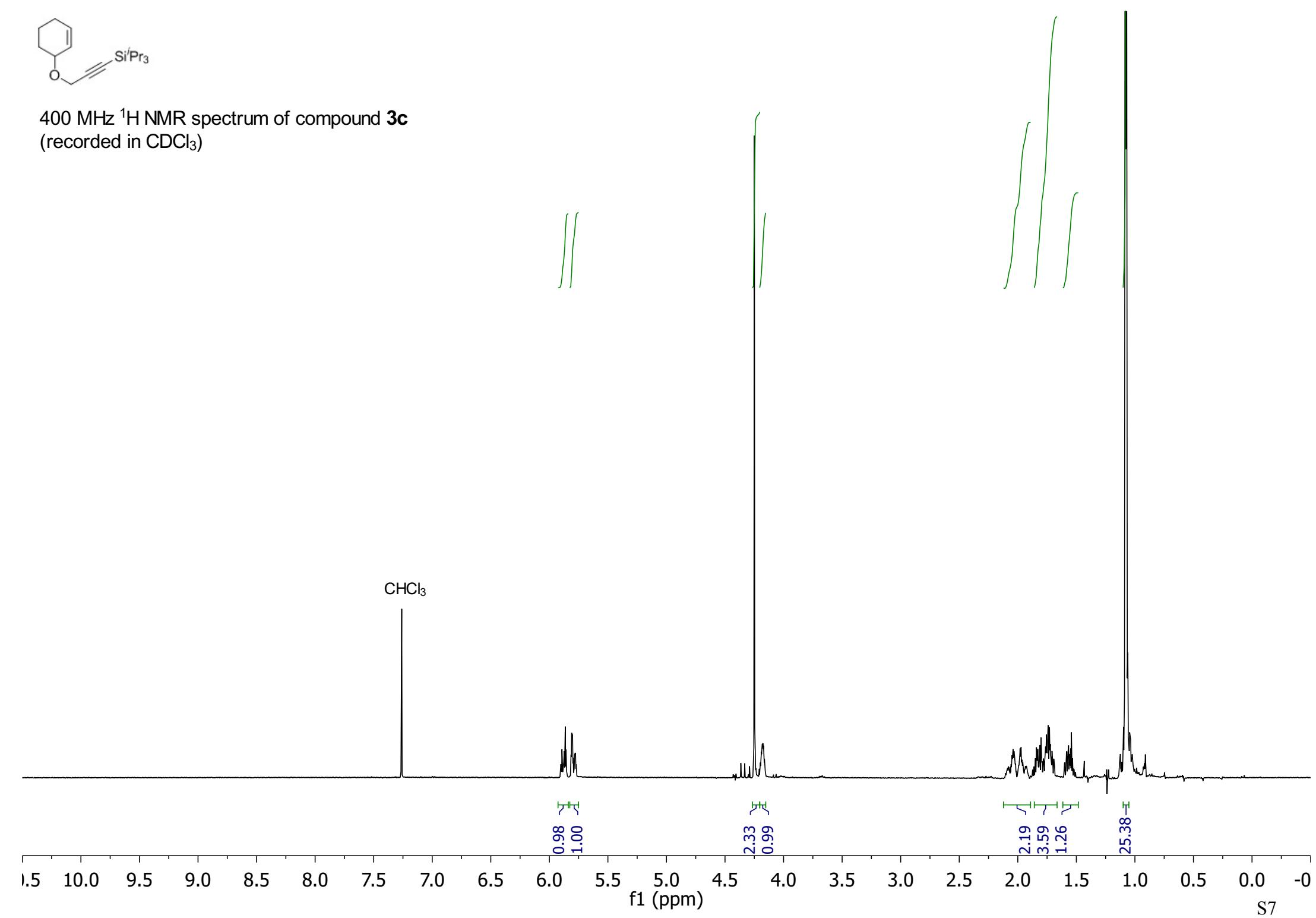
 \sim 28.3
 \sim 25.4
 \sim 19.2

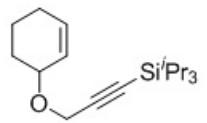
-7.6
-4.5





400 MHz ^1H NMR spectrum of compound **3c**
(recorded in CDCl_3)





100 MHz ^{13}C NMR spectrum of compound **3c**
(recorded in CDCl_3)

—131.4
—127.6

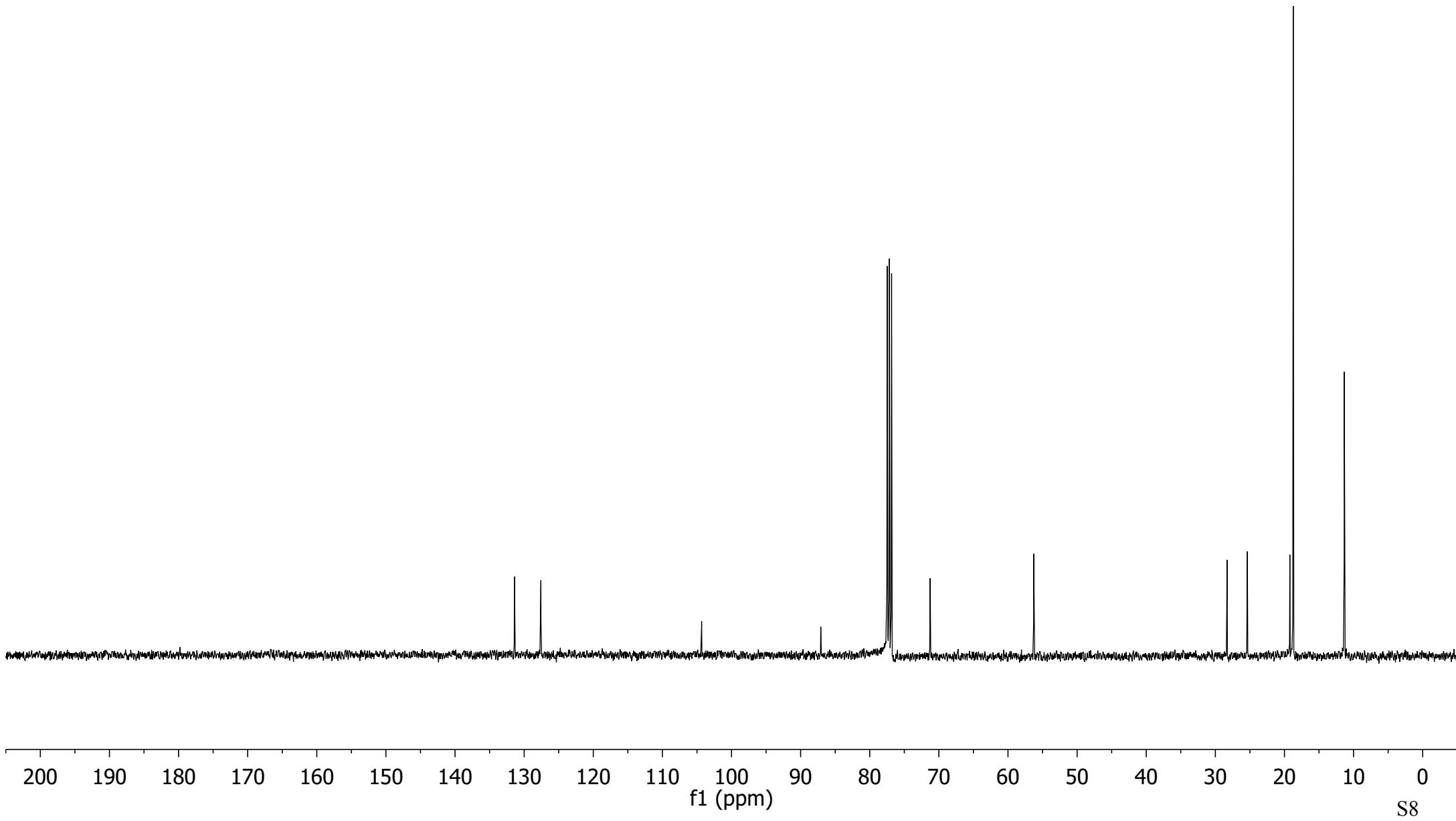
—104.3

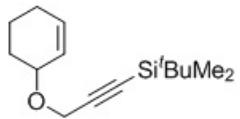
—87.1

—71.3

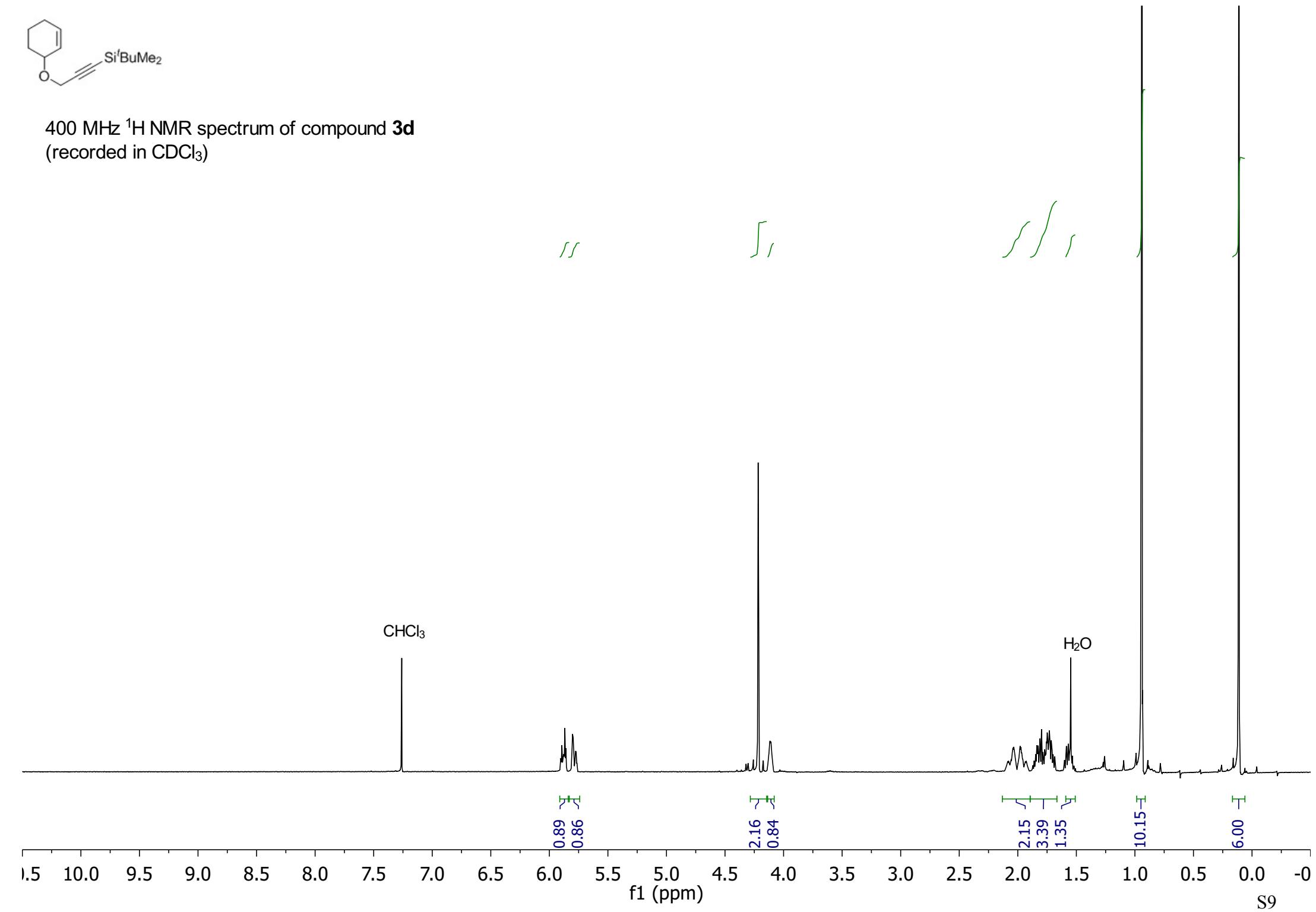
—56.3

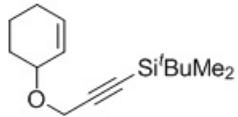
—28.3
—25.4
—19.2
—18.7
—11.3



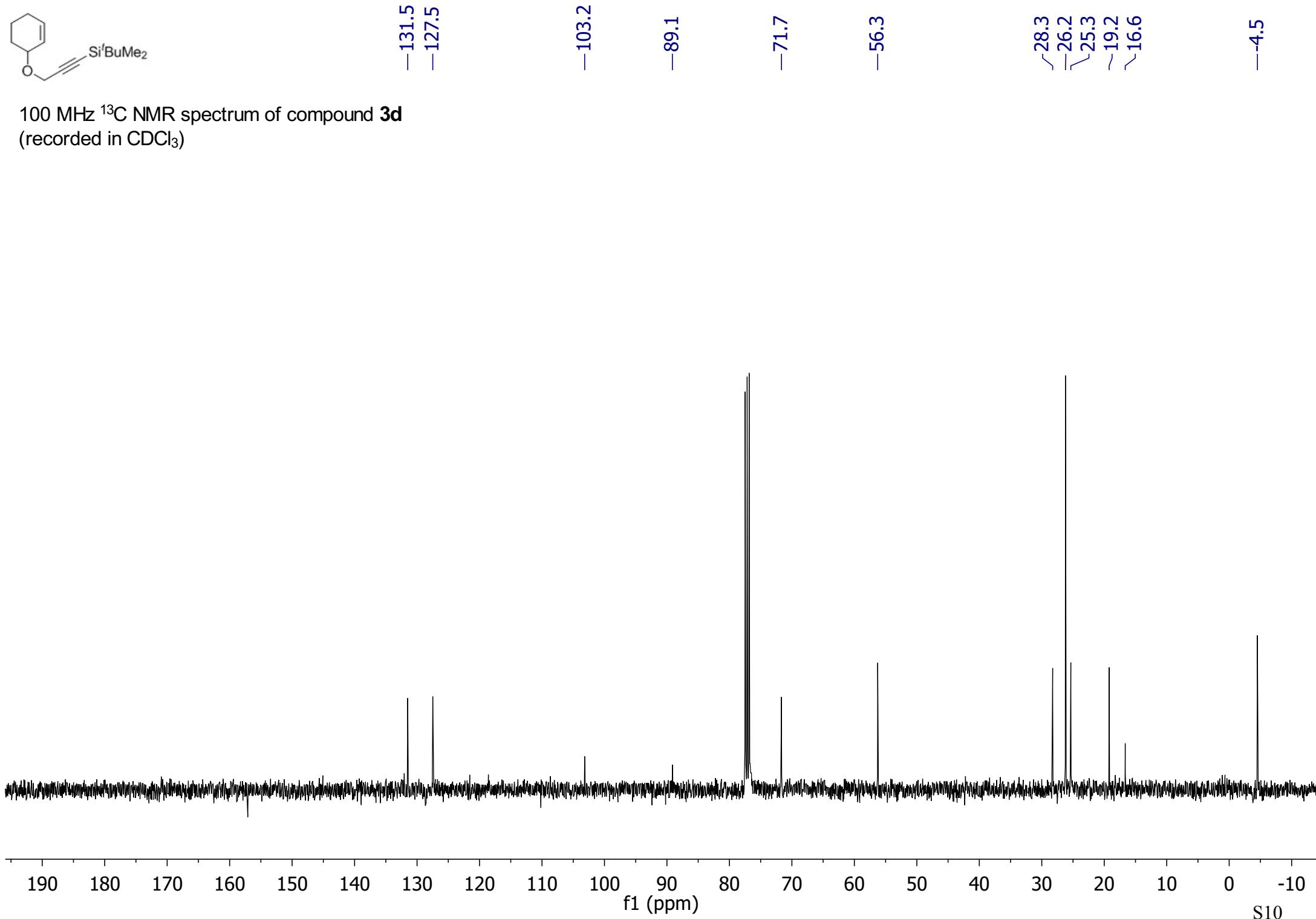


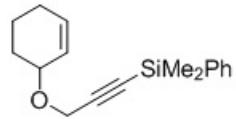
400 MHz ^1H NMR spectrum of compound **3d**
(recorded in CDCl_3)



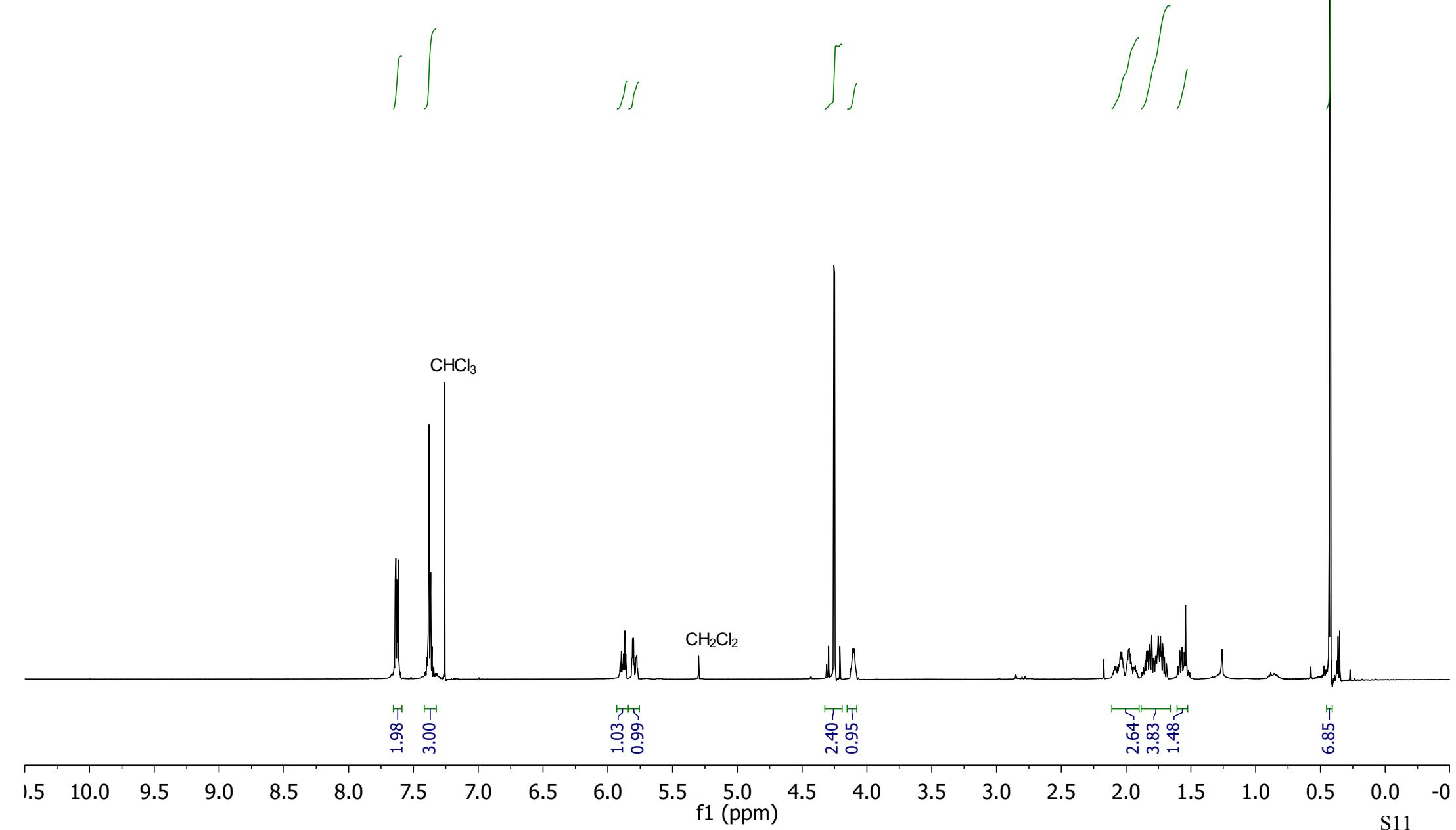


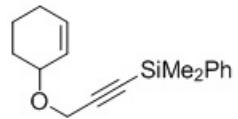
100 MHz ^{13}C NMR spectrum of compound **3d**
(recorded in CDCl_3)



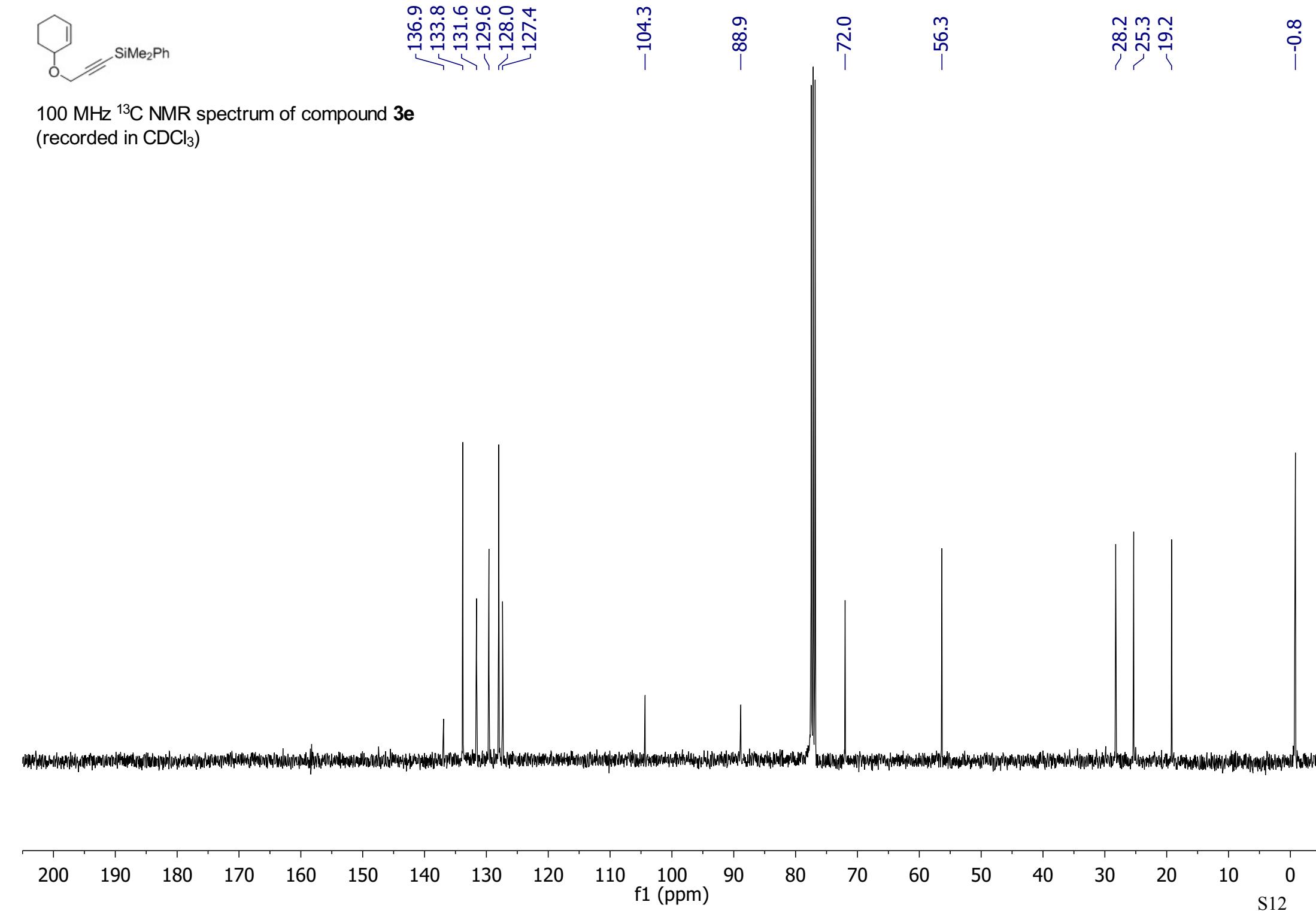


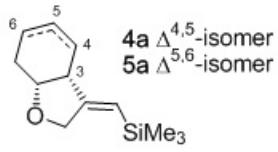
400 MHz ^1H NMR spectrum of compound **3e**
(recorded in CDCl_3)



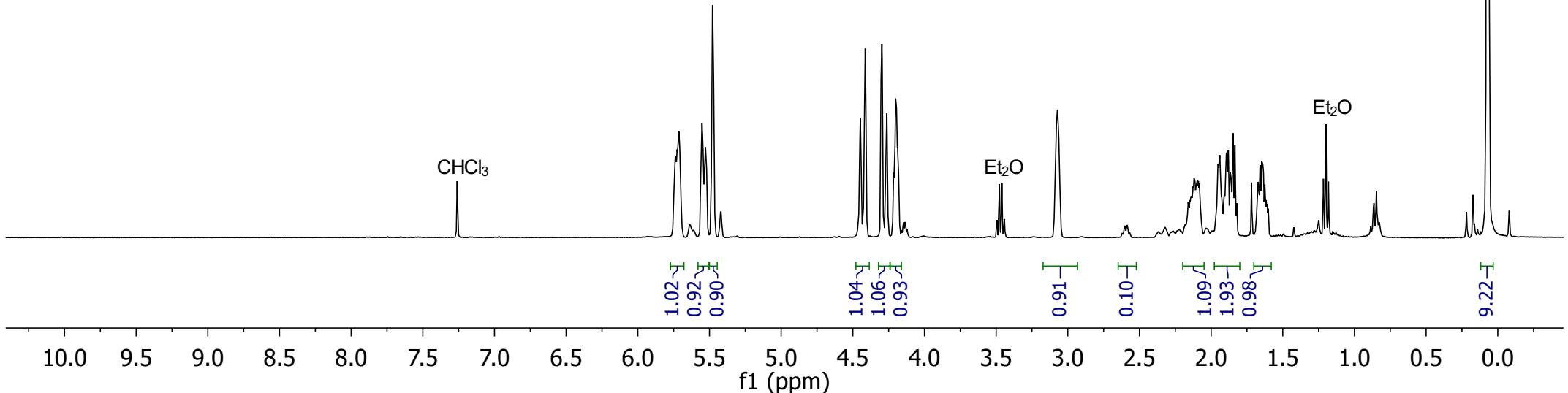
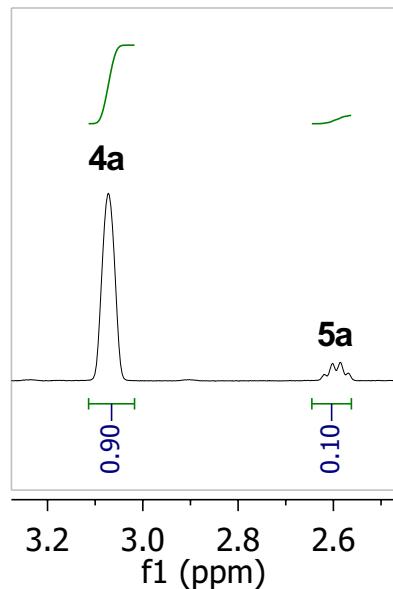


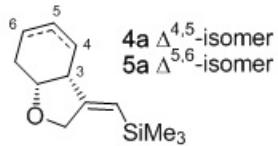
100 MHz ^{13}C NMR spectrum of compound **3e**
(recorded in CDCl_3)





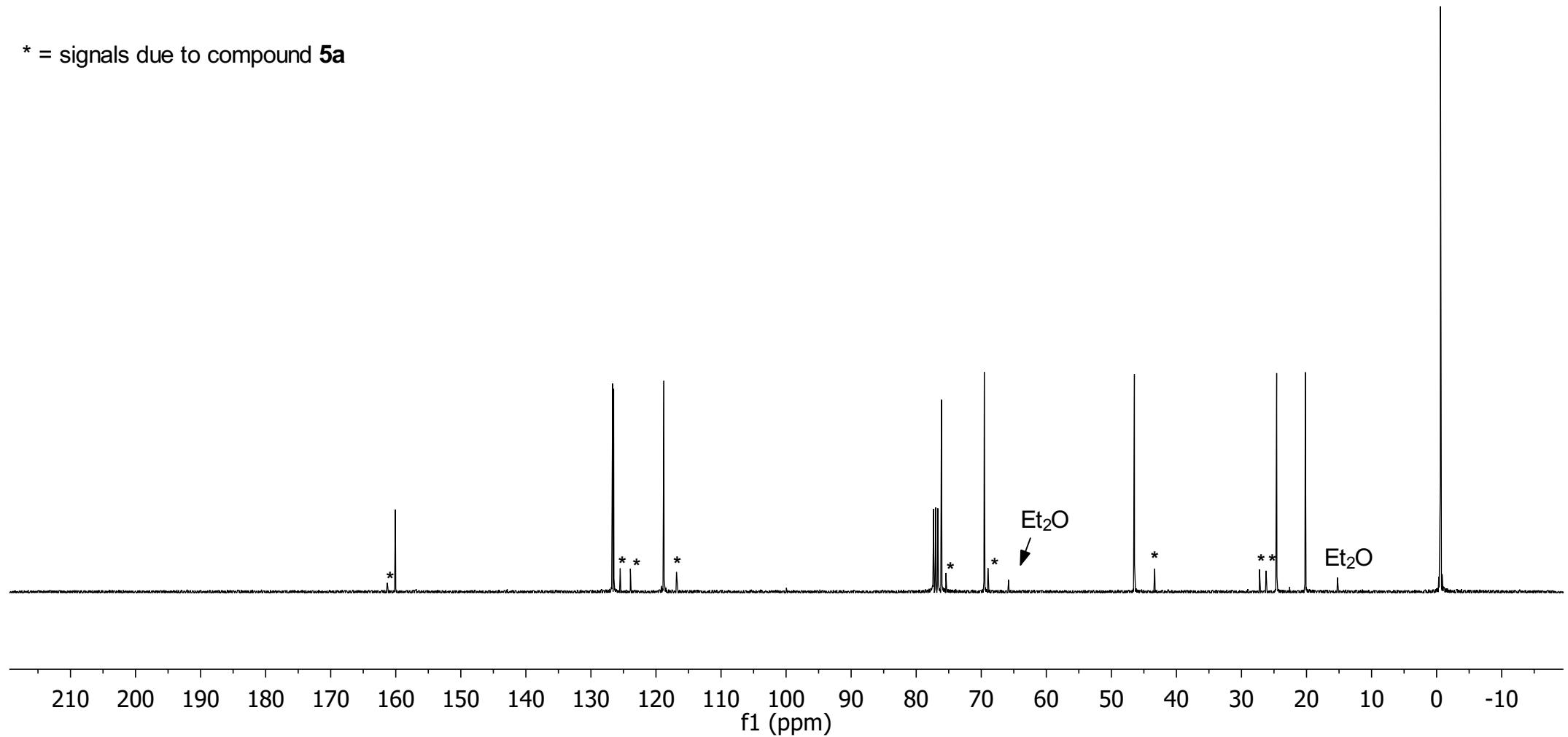
400 MHz ^1H NMR spectrum of a ca 9:1 mixture of compounds **4a** and **5a**
 (recorded in CDCl_3)

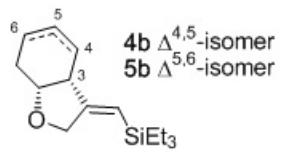




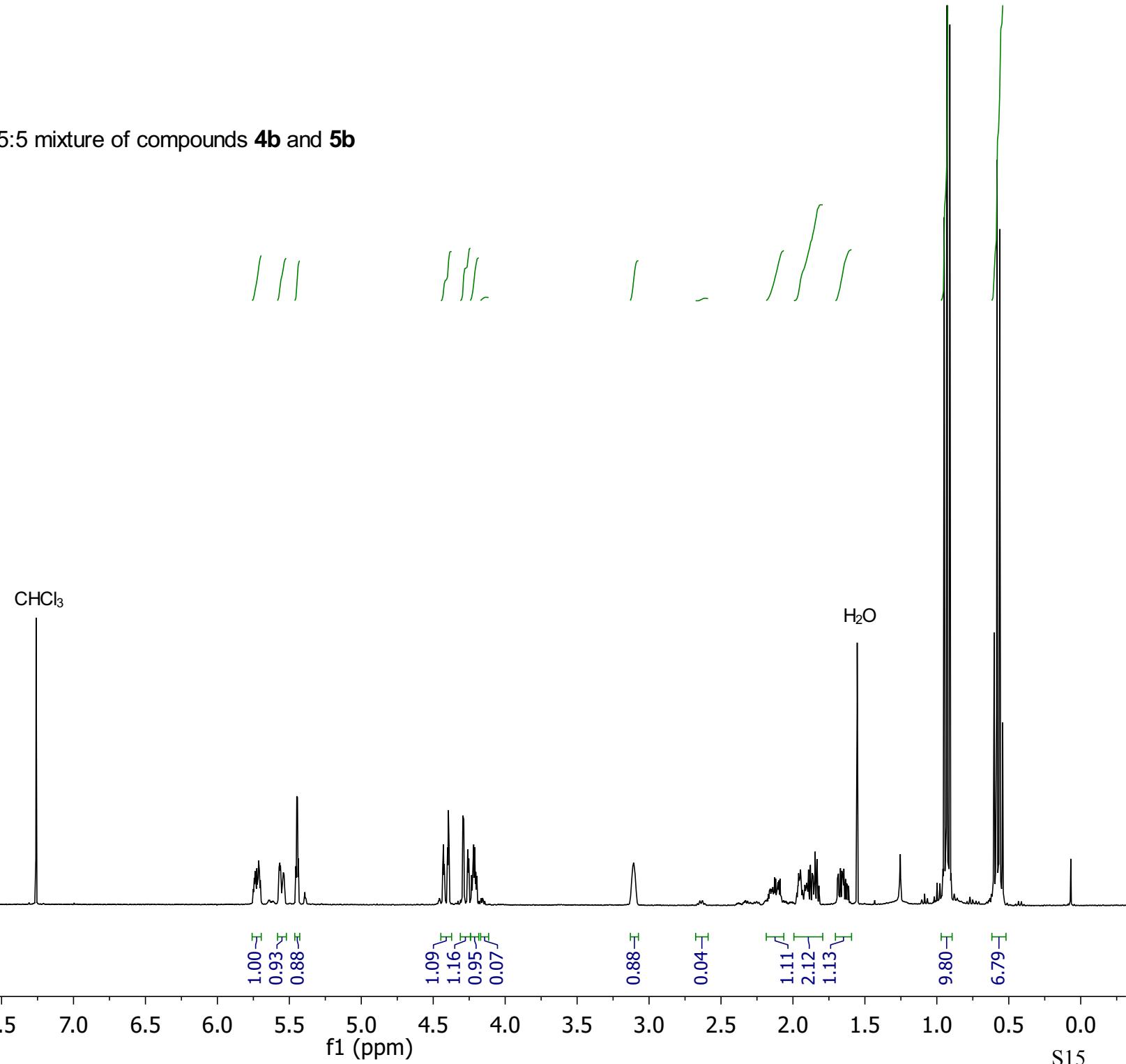
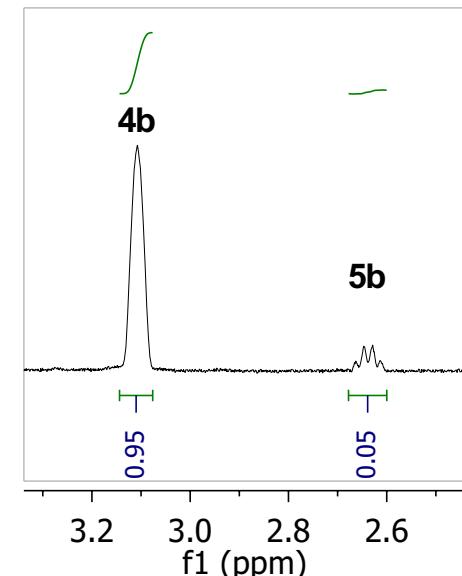
100 MHz ^{13}C NMR spectrum of a ca 9:1 mixture of compounds **4a** and **5a**
(recorded in CDCl_3)

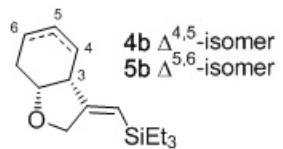
* = signals due to compound **5a**



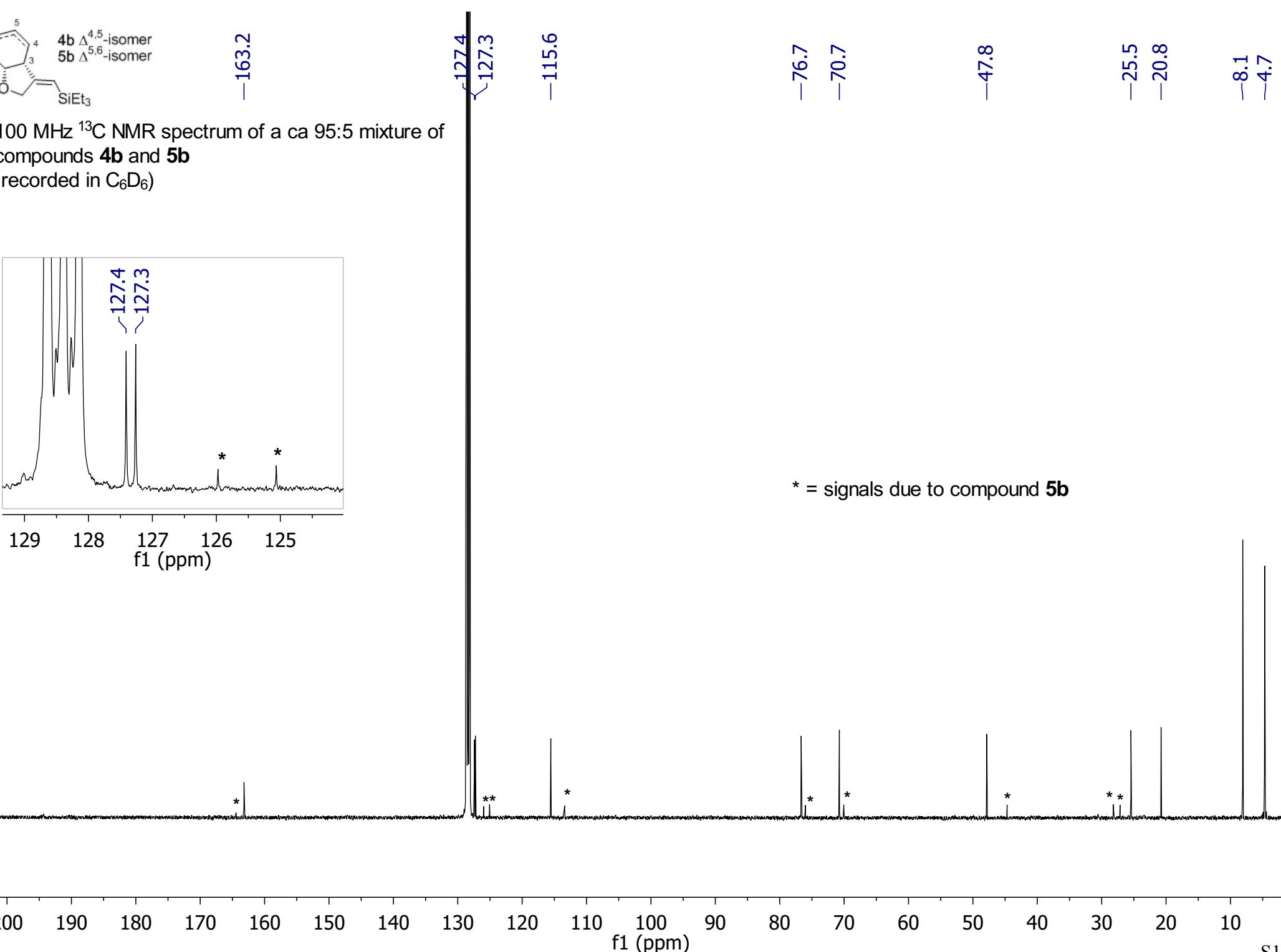
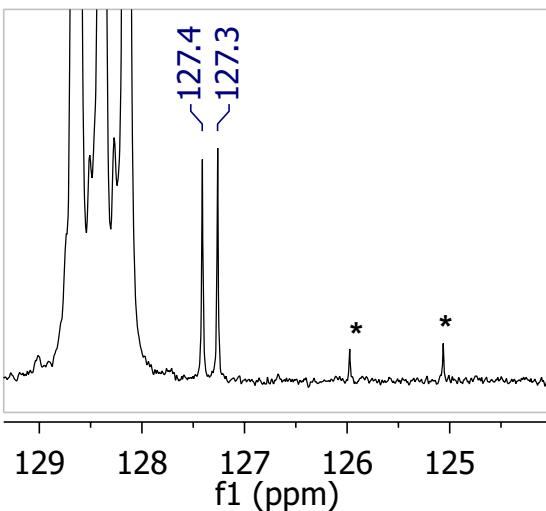


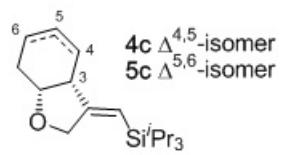
400 MHz ^1H NMR spectrum of a ca 95:5 mixture of compounds **4b** and **5b**
 (recorded in CDCl_3)



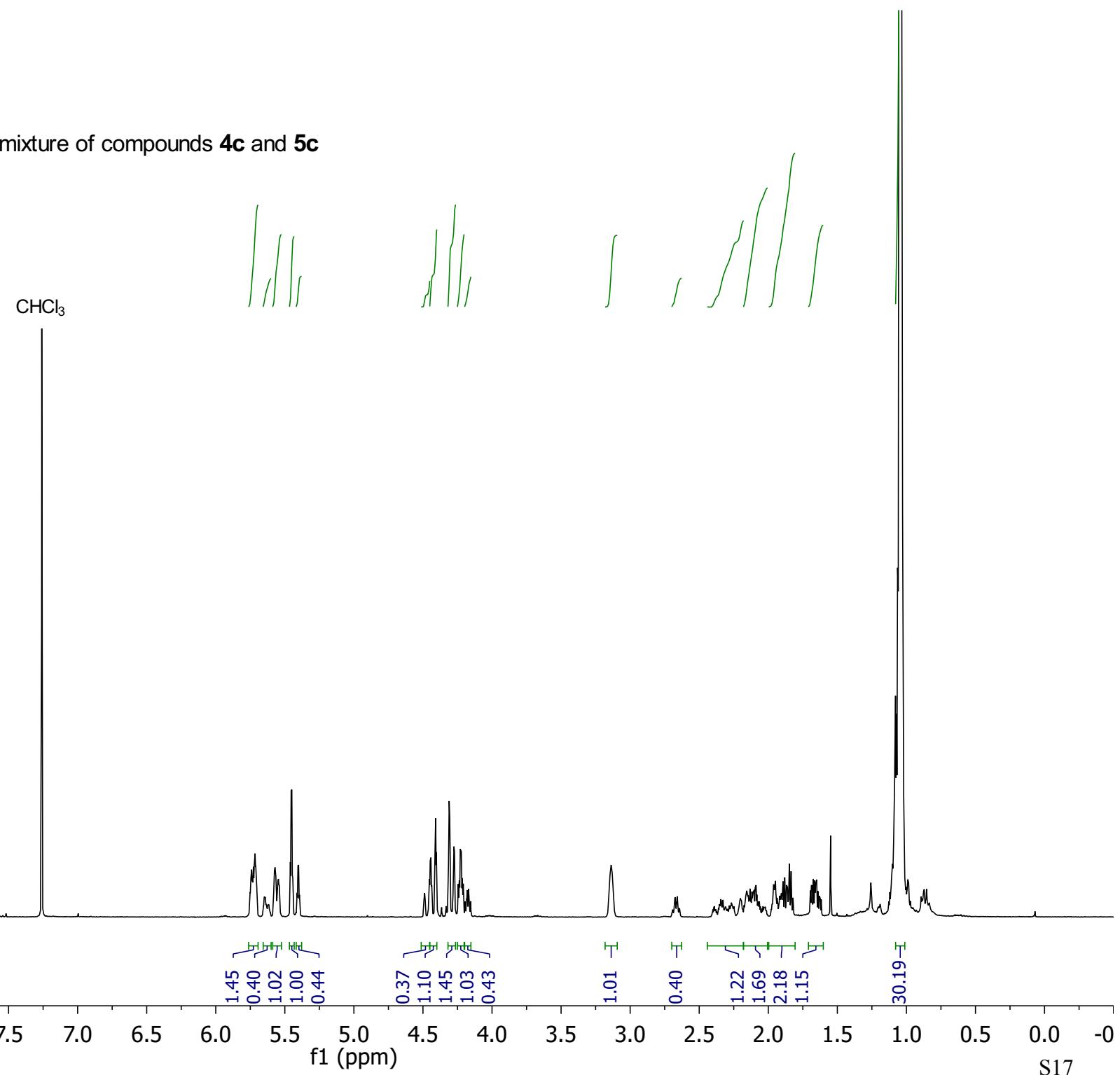
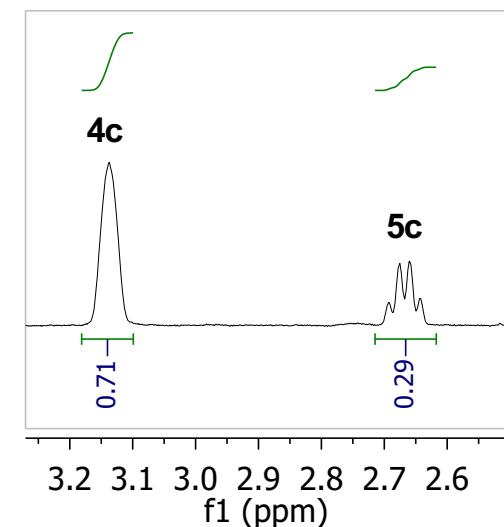


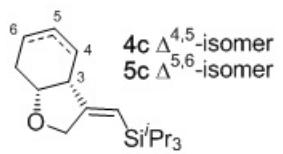
100 MHz ^{13}C NMR spectrum of a ca 95:5 mixture of compounds **4b** and **5b**
(recorded in C_6D_6)





400 MHz ^1H NMR spectrum of a ca 7:3 mixture of compounds **4c** and **5c**
 (recorded in CDCl_3)





162.9
161.7

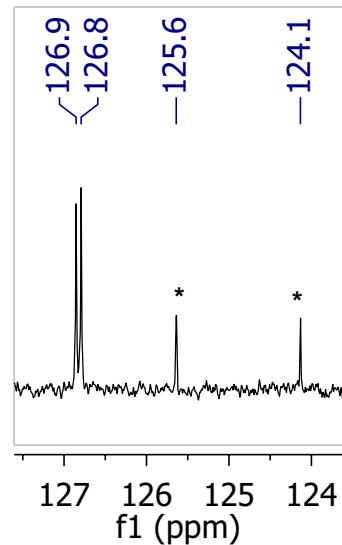
126.9
126.8
125.6
124.1
114.4
112.4

76.3
75.6
70.4
69.9

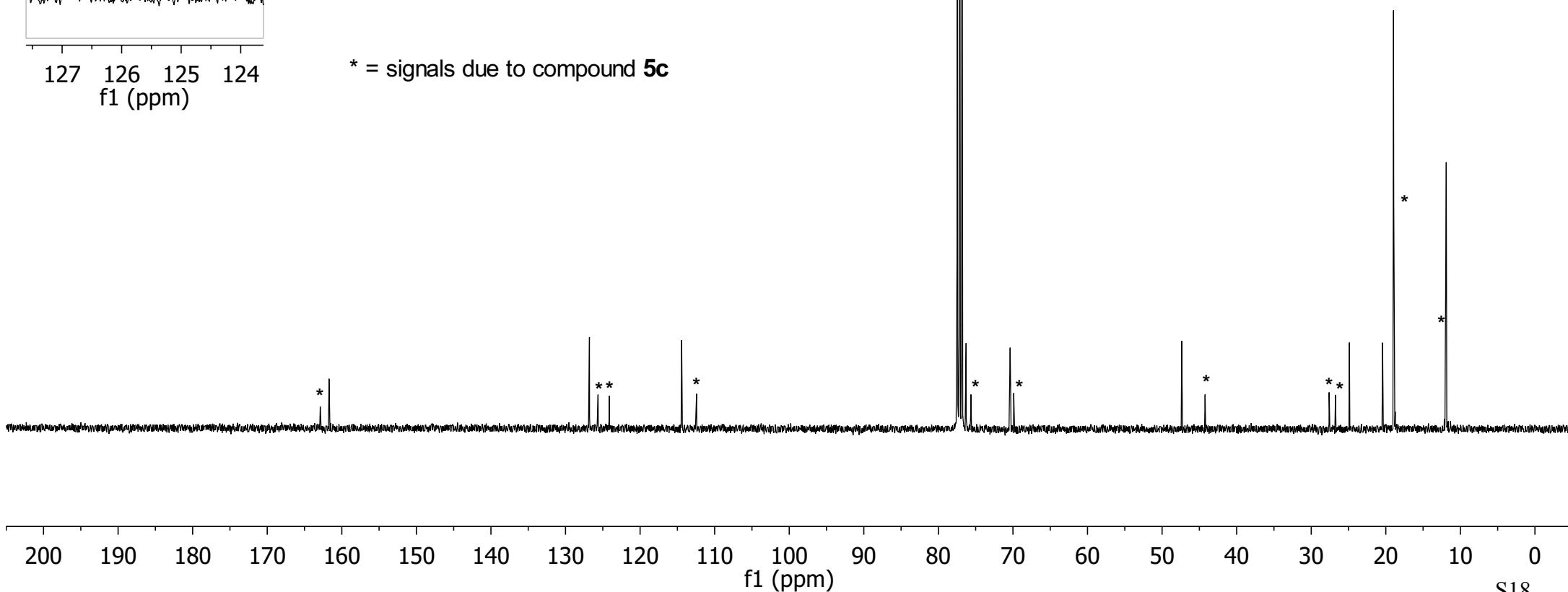
47.4
44.2

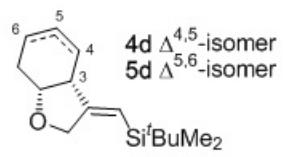
27.6
26.7
24.9
20.4
19.0
18.9
11.9
11.9

100 MHz ^{13}C NMR spectrum of a ca 7:3 mixture of compounds **4c** and **5c**
(recorded in CDCl_3)

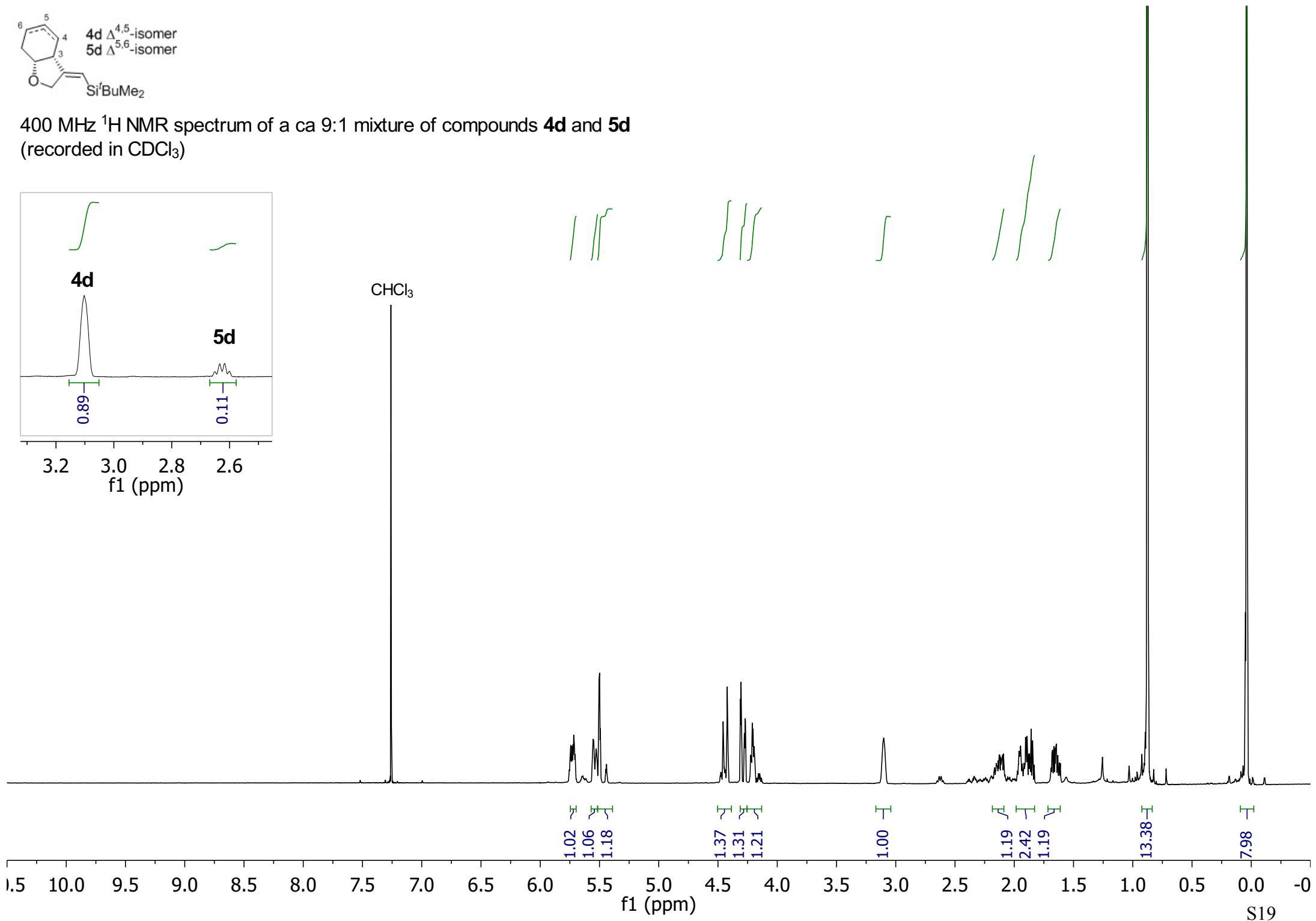
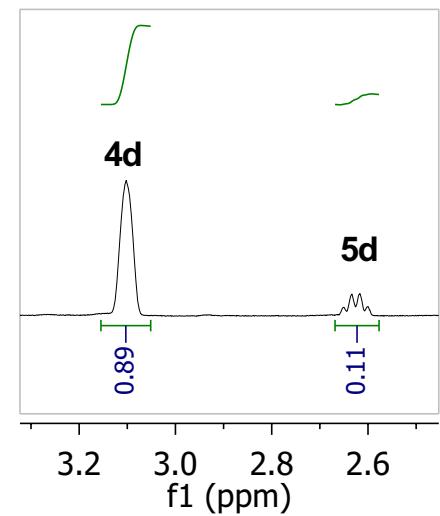


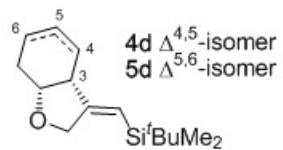
* = signals due to compound **5c**





400 MHz ^1H NMR spectrum of a ca 9:1 mixture of compounds **4d** and **5d**
 (recorded in CDCl_3)





—161.3

126.8
 126.8

—116.3

—76.2

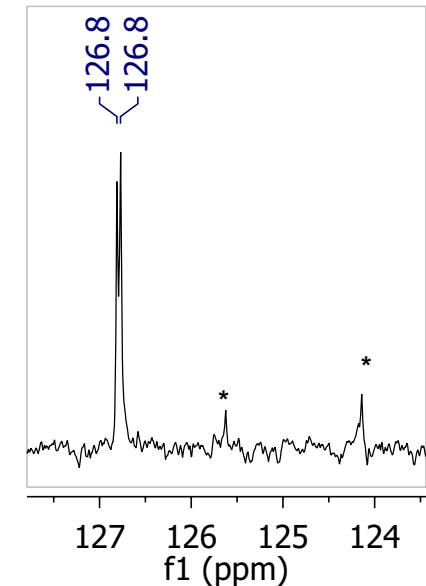
—70.1

—47.0

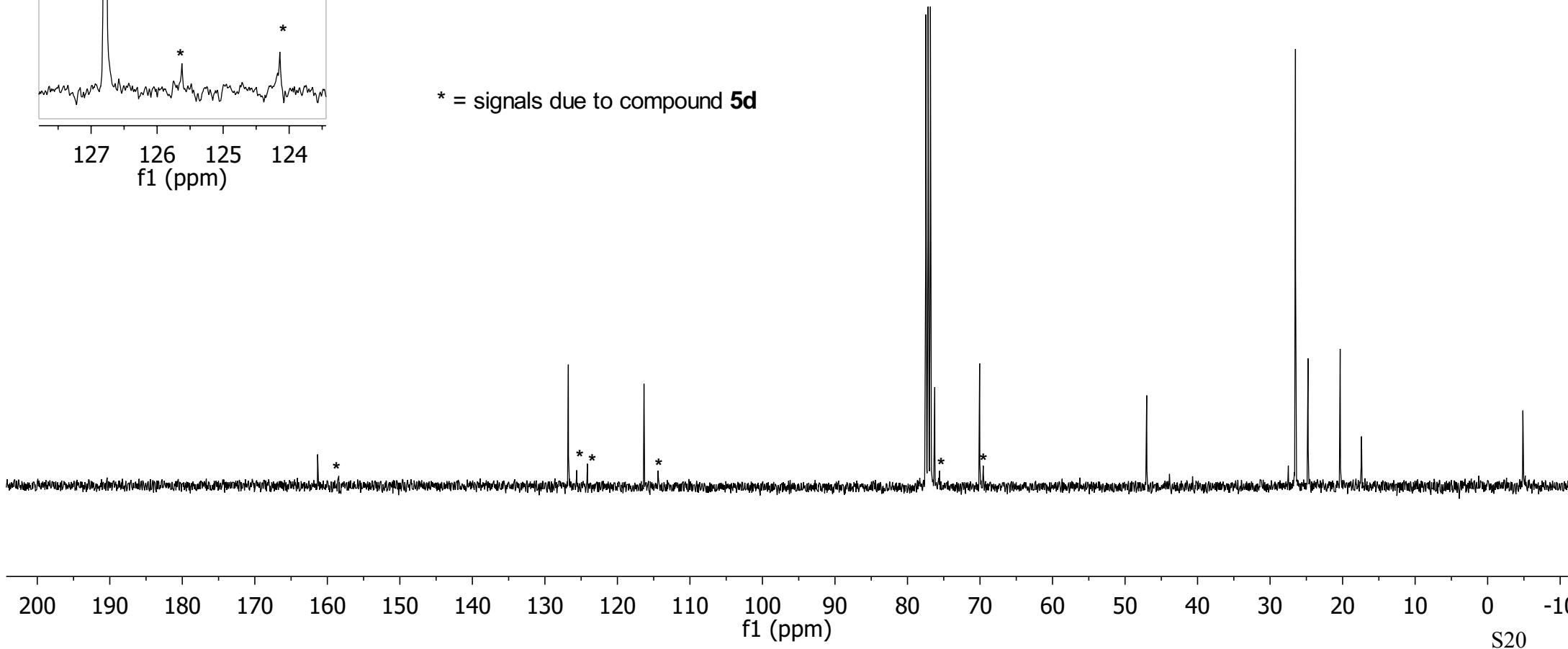
26.5
 24.8
 20.3
 17.4

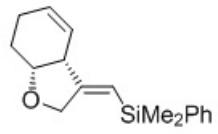
—4.9
 —4.9

100 MHz ^{13}C NMR spectrum of a ca 9:1 mixture of compounds **4d** and **5d**
 (recorded in CDCl_3)

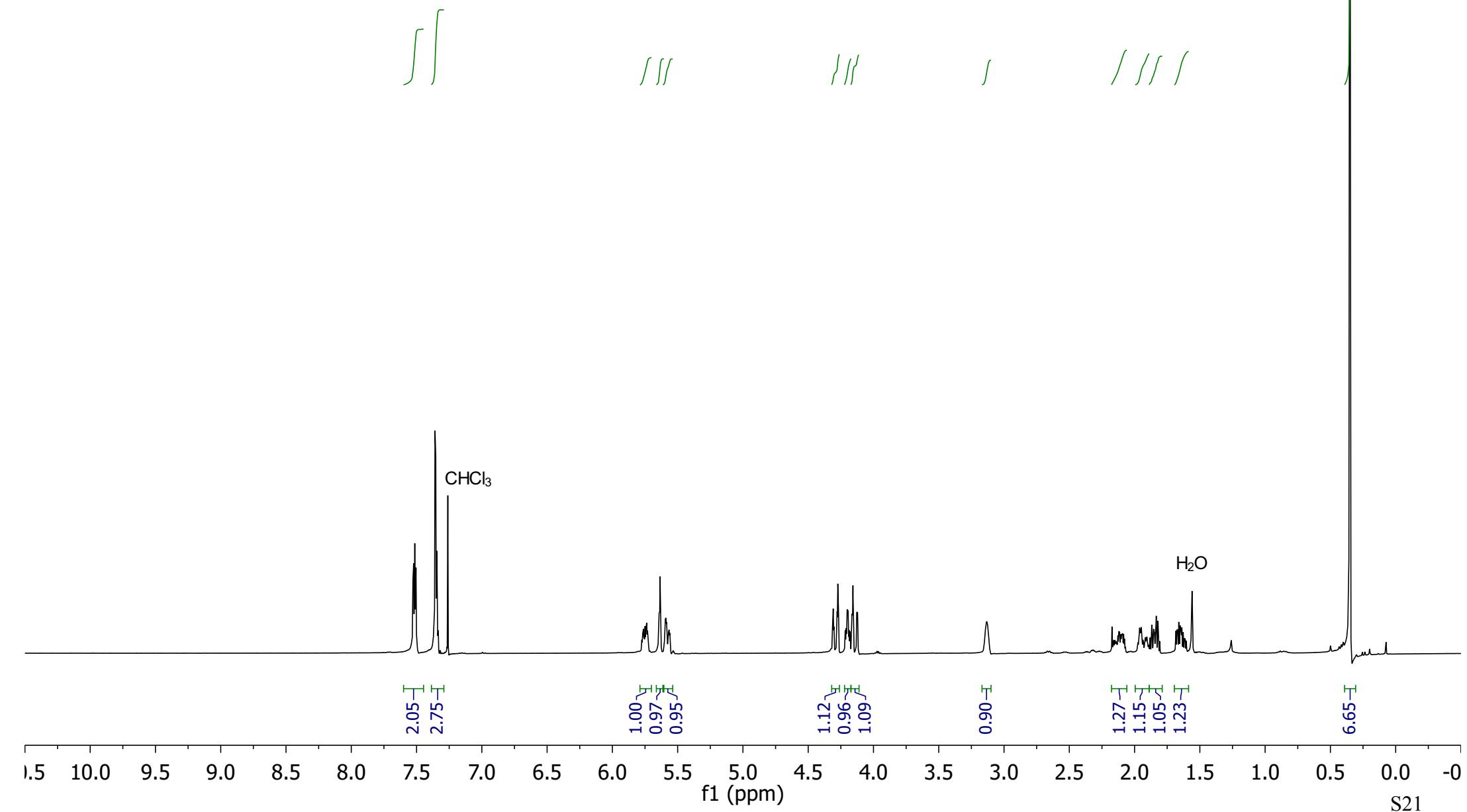


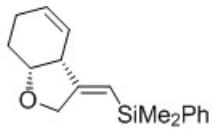
* = signals due to compound **5d**



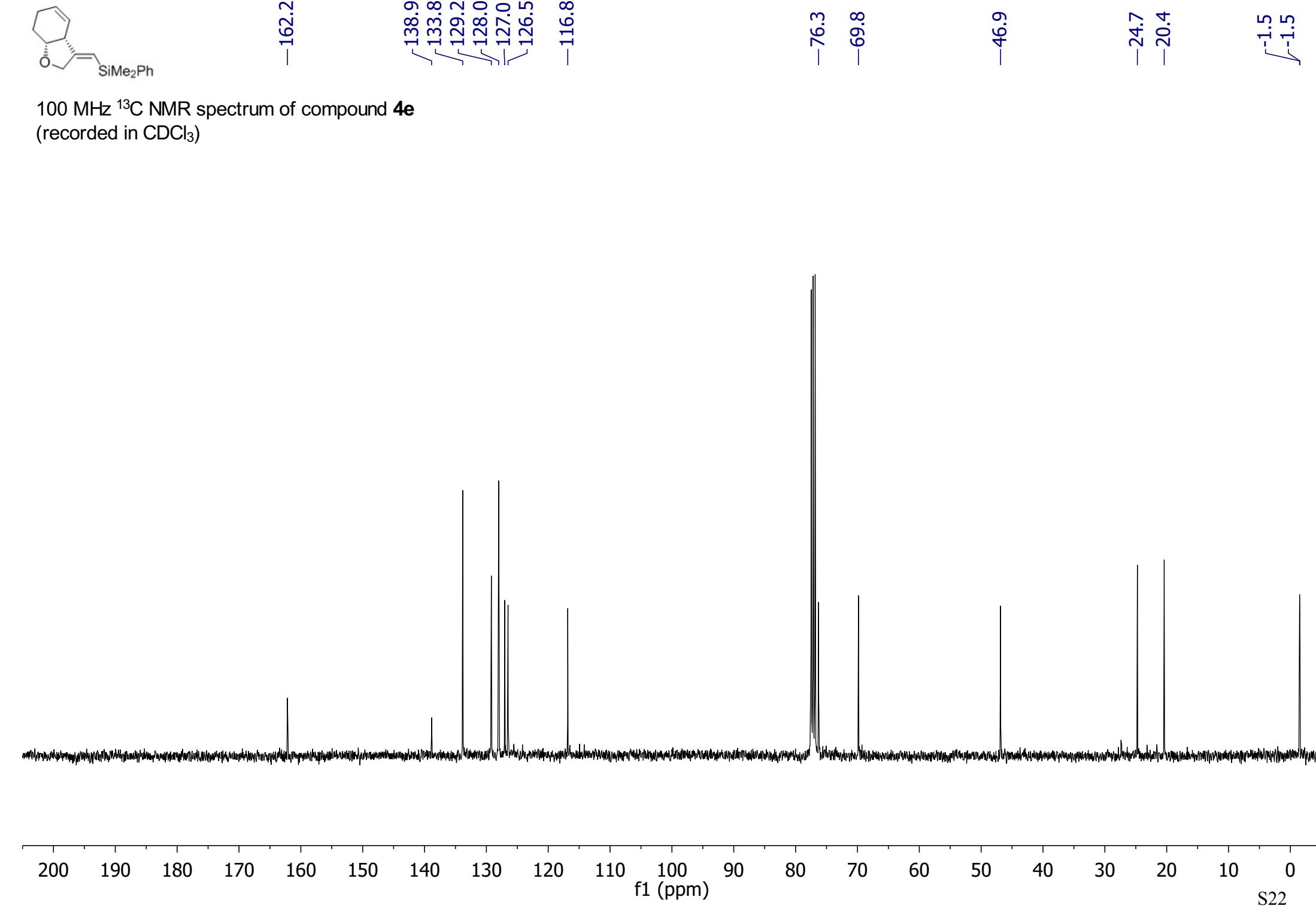


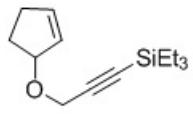
400 MHz ^1H NMR spectrum of compound **4e**
(recorded in CDCl_3)



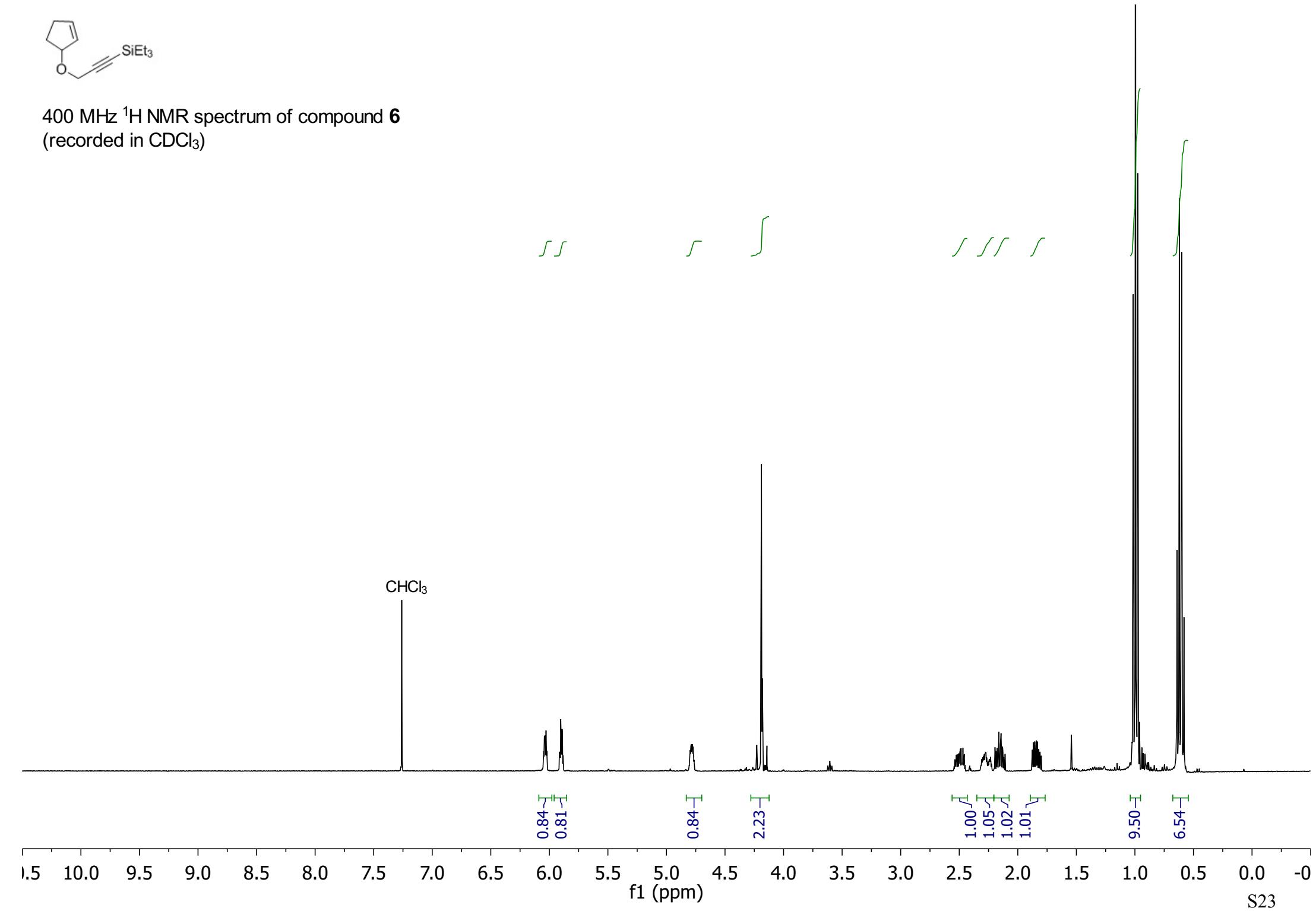


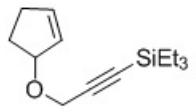
100 MHz ^{13}C NMR spectrum of compound **4e**
(recorded in CDCl_3)



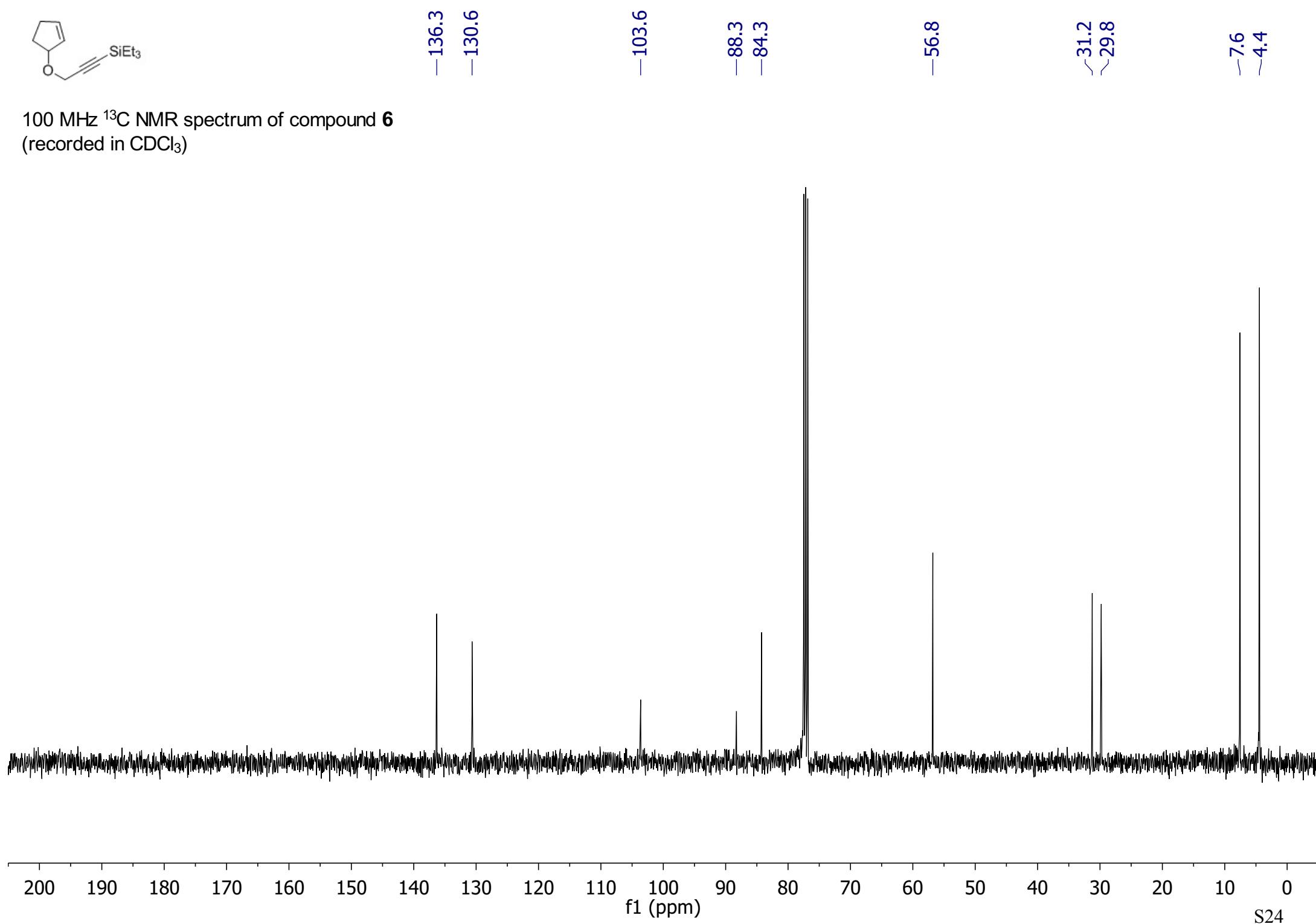


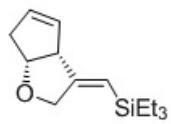
400 MHz ^1H NMR spectrum of compound **6**
(recorded in CDCl_3)



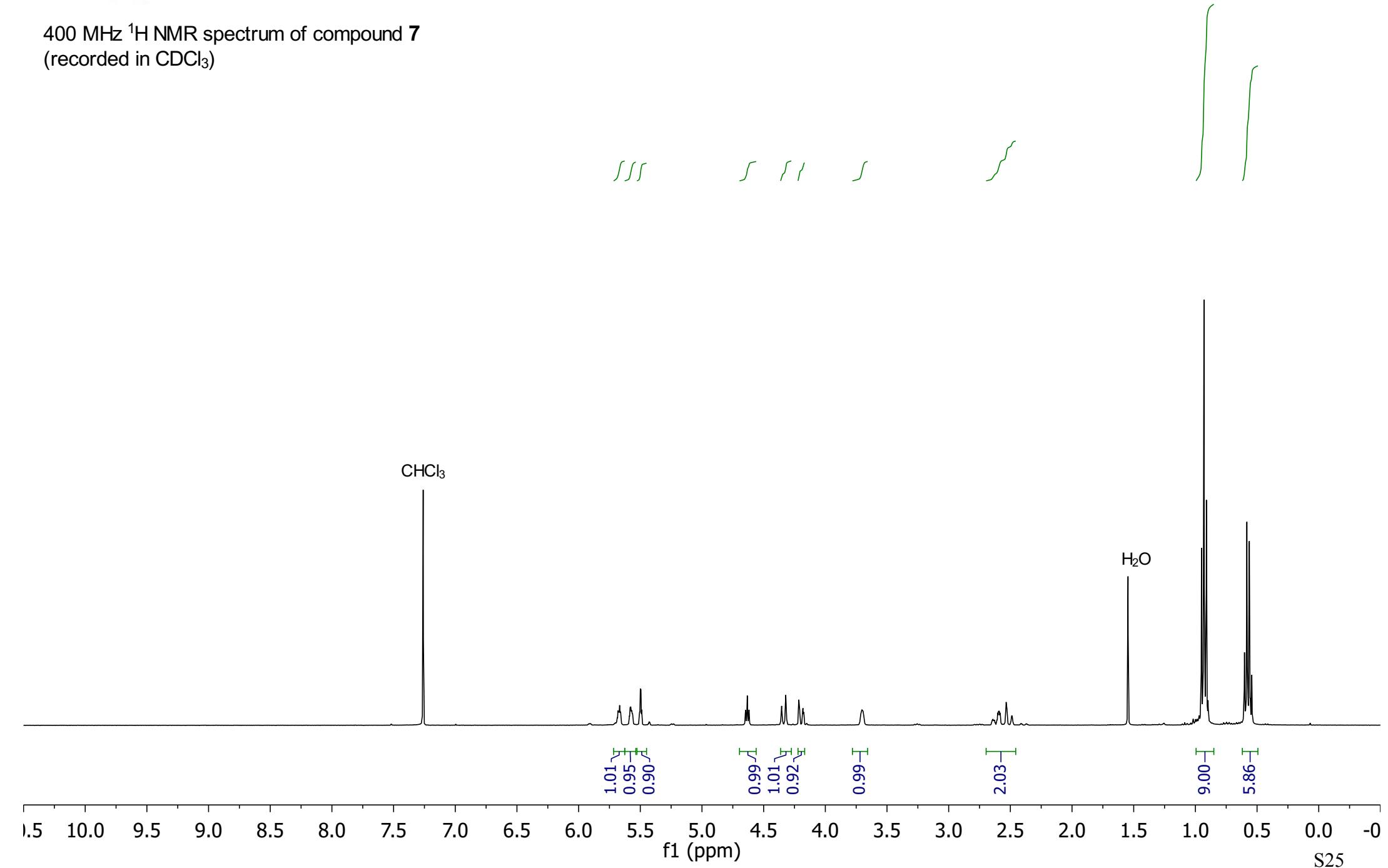


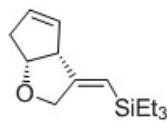
100 MHz ^{13}C NMR spectrum of compound **6**
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound 7
(recorded in CDCl_3)





-158.4

-132.2
-128.7

-115.6

-81.8

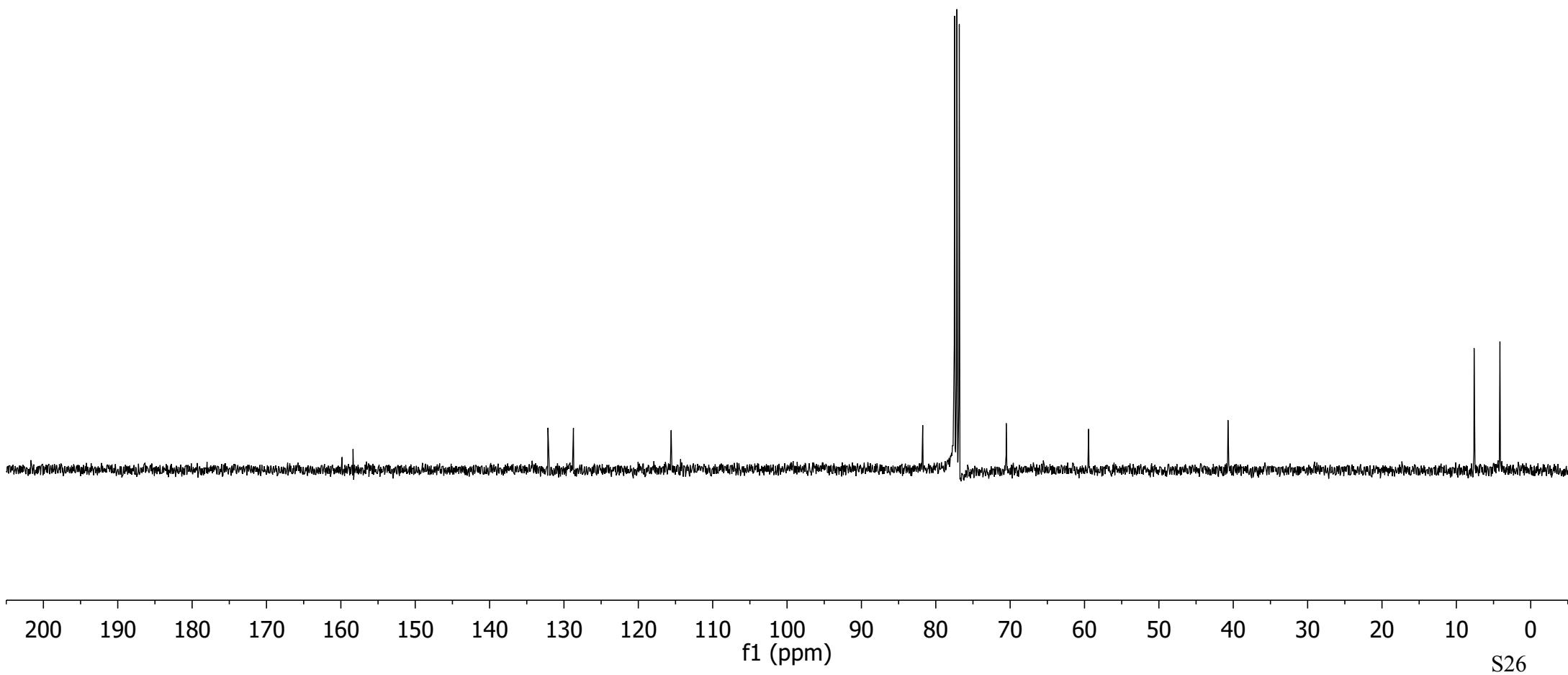
-70.5

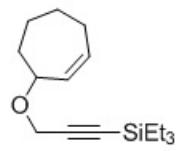
-59.5

-40.7

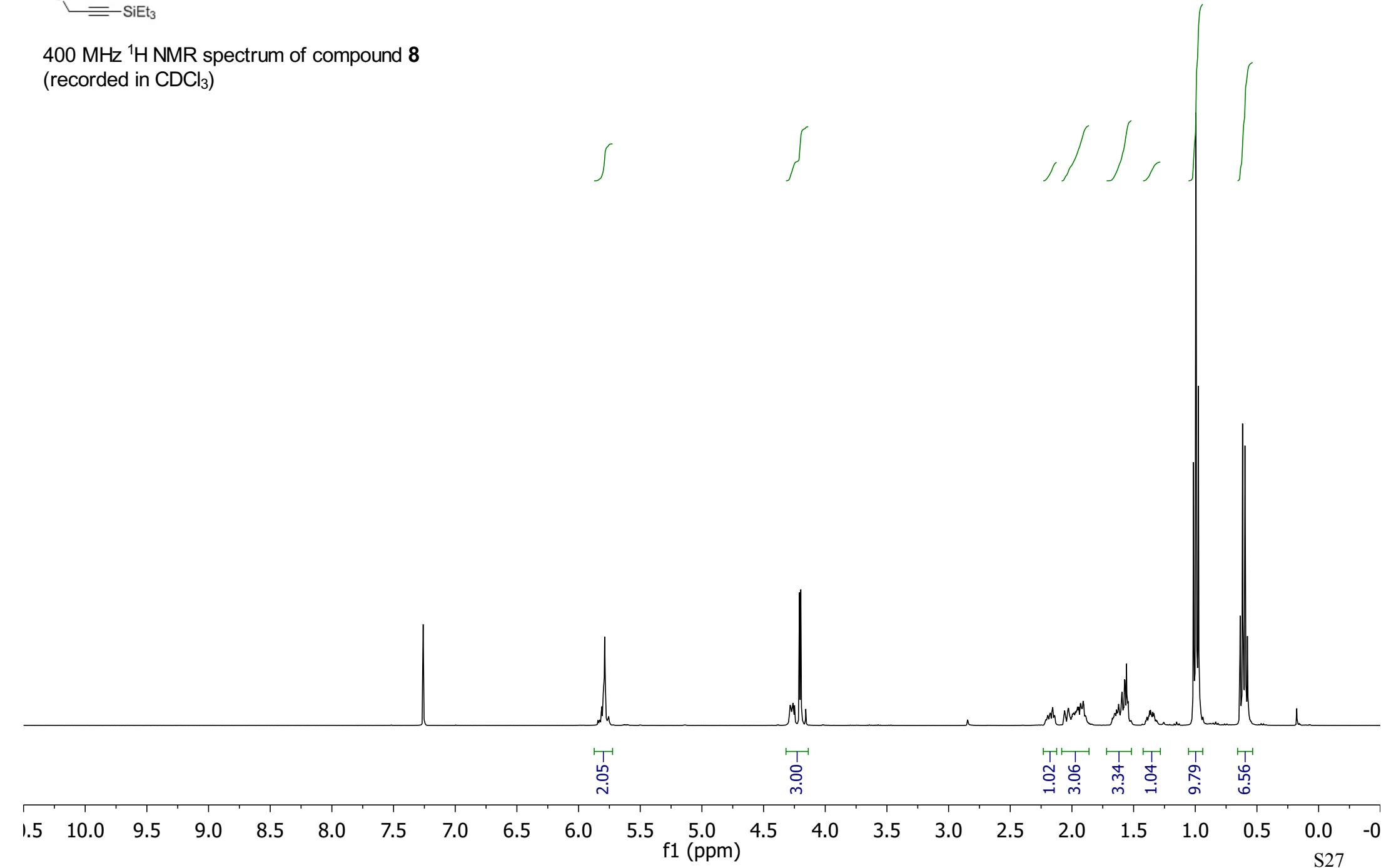
-7.6
-4.1

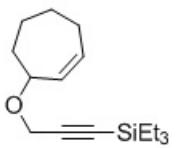
100 MHz ^{13}C NMR spectrum of compound 7
(recorded in CDCl_3)



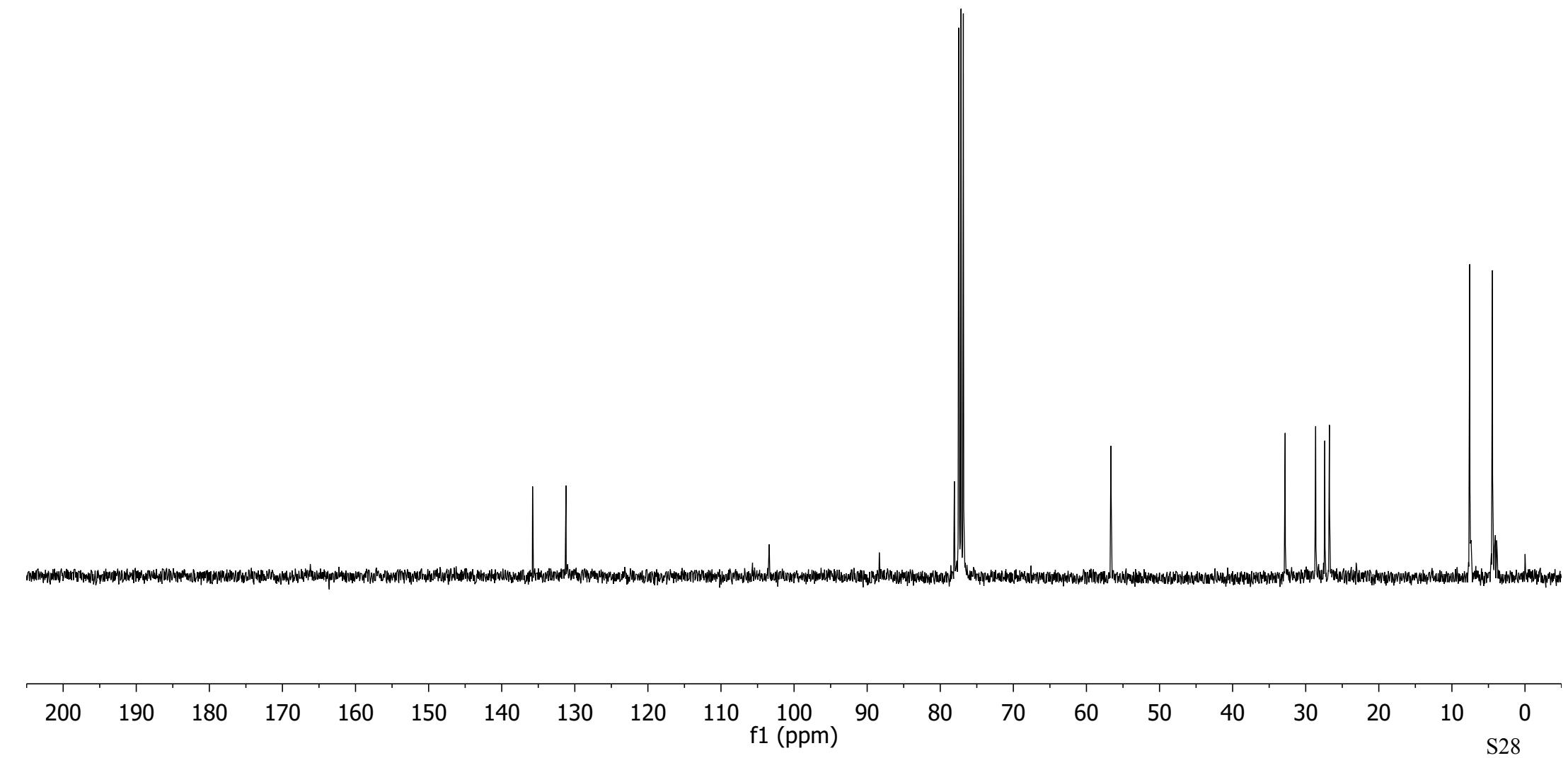


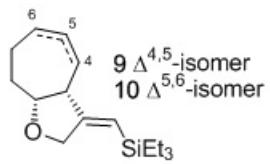
400 MHz ^1H NMR spectrum of compound **8**
(recorded in CDCl_3)



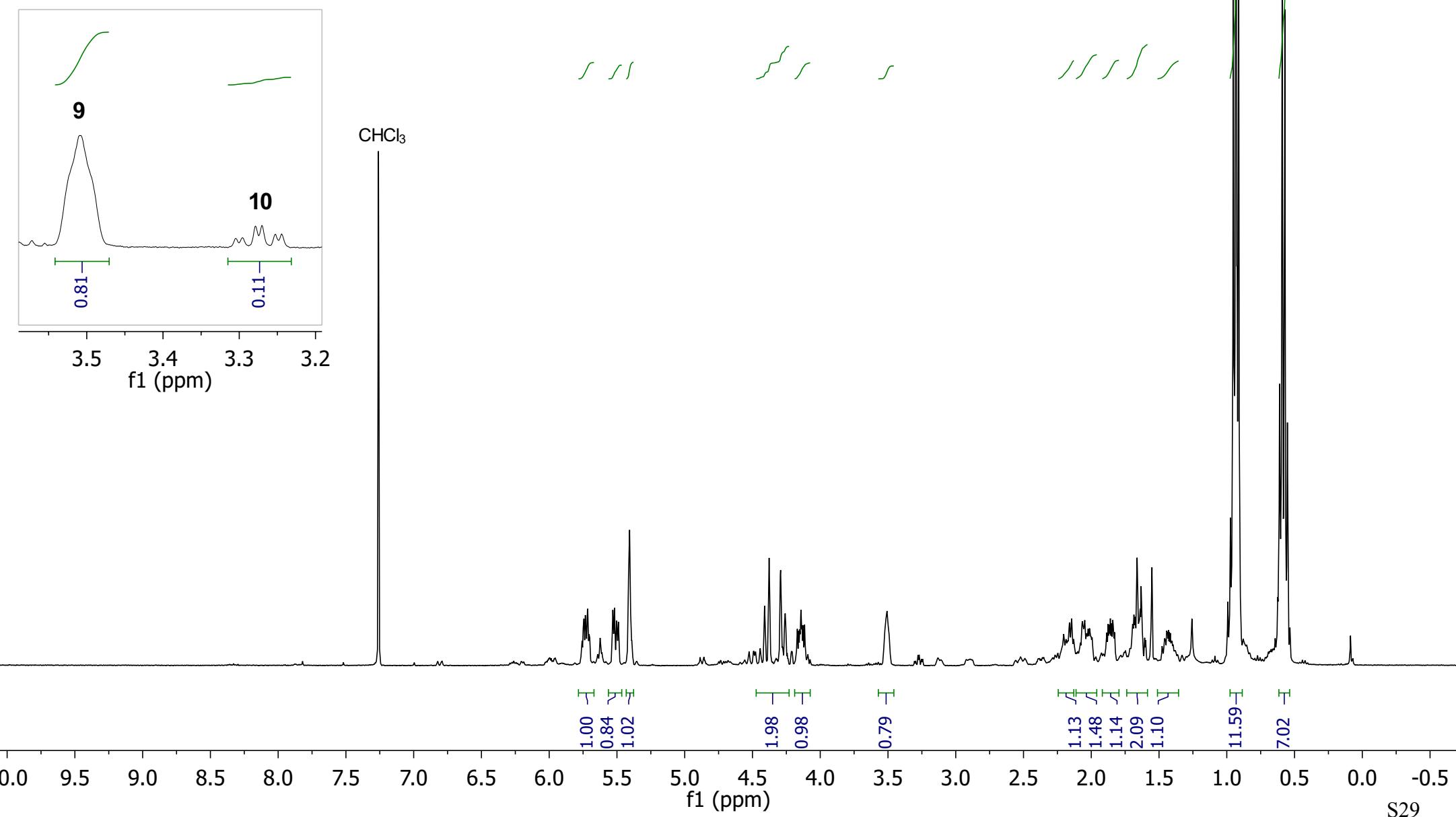


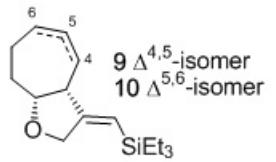
100 MHz ^{13}C NMR spectrum of compound **8**
(recorded in CDCl_3)



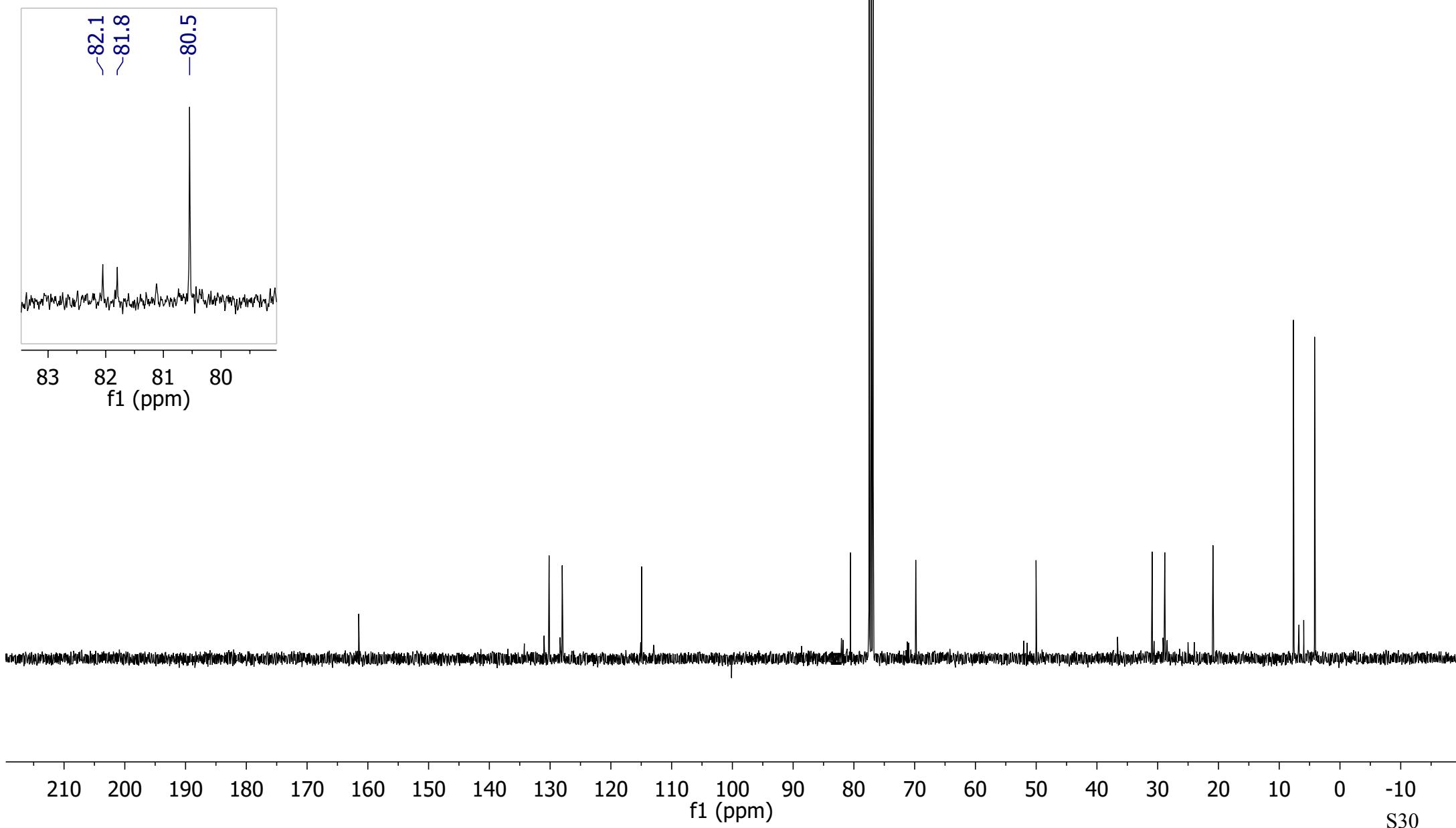


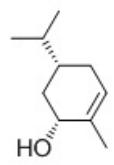
400 MHz ^1H NMR spectrum of a ca 8:1 mixture of compounds **9** and **10**
 (recorded in CDCl_3)



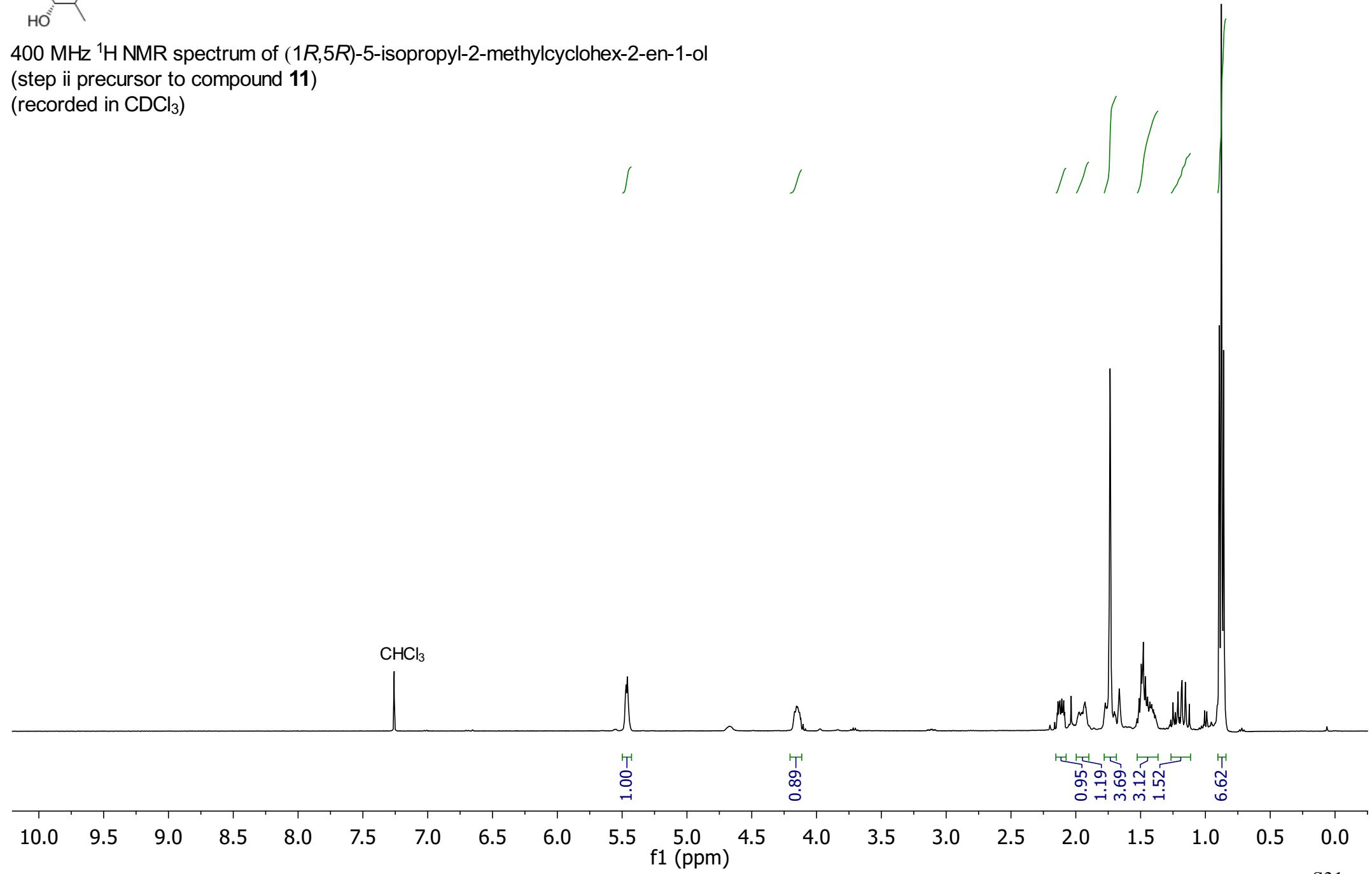


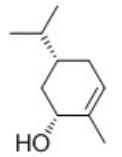
100 MHz ¹³C NMR spectrum of a ca 8:1 mixture of compounds **9** and **10**
(recorded in CDCl₃)



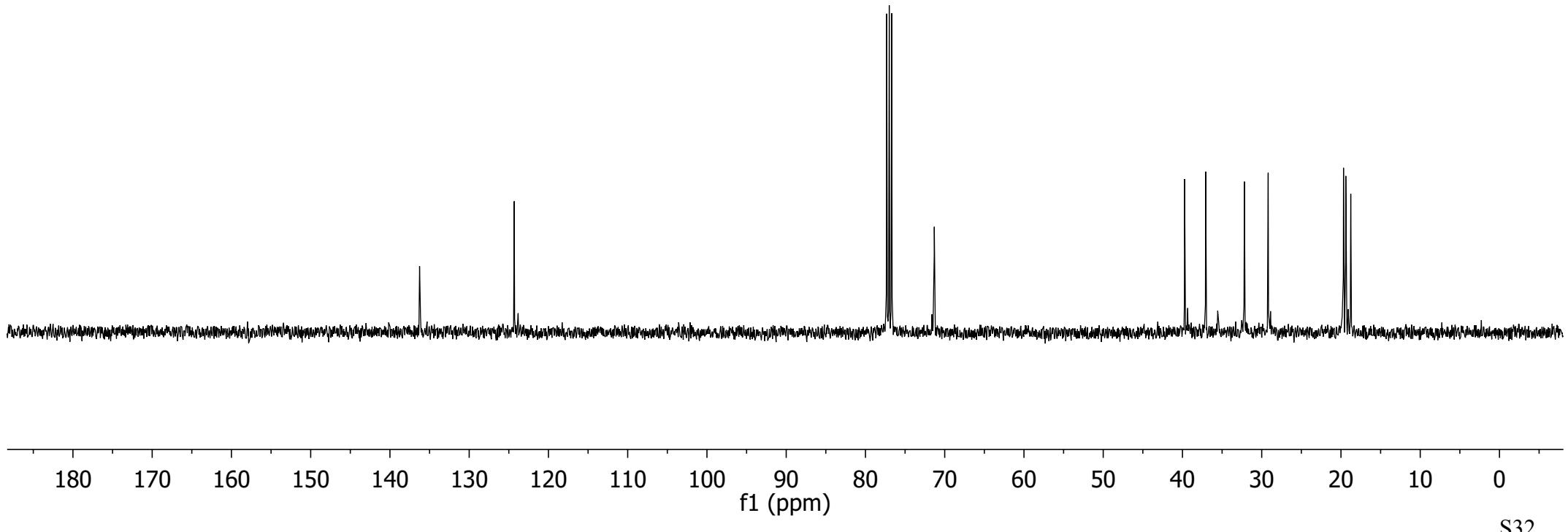


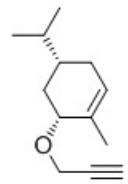
400 MHz ^1H NMR spectrum of (*1R,5R*)-5-isopropyl-2-methylcyclohex-2-en-1-ol
(step ii precursor to compound **11**)
(recorded in CDCl_3)



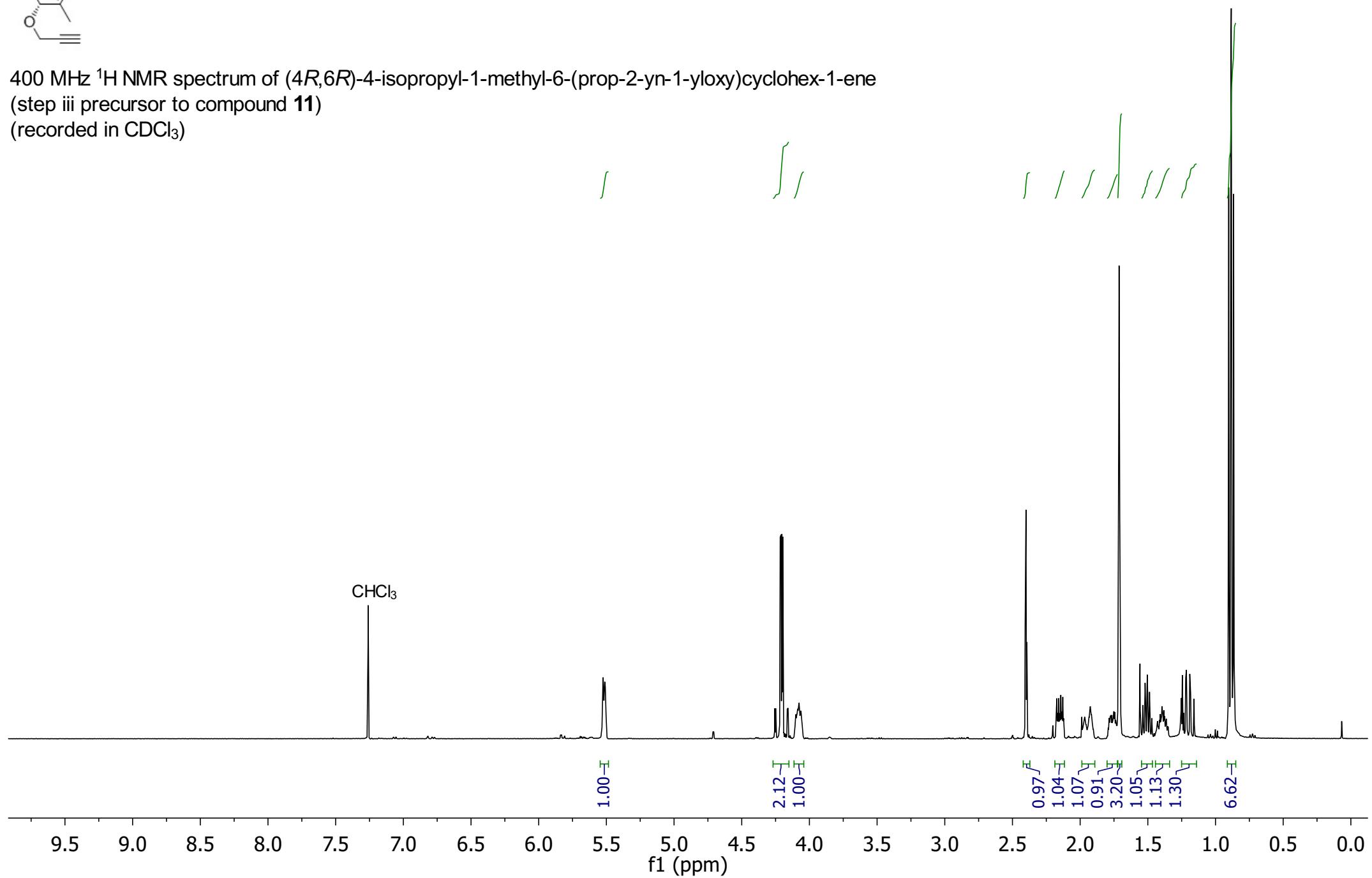


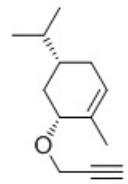
100 MHz ^{13}C NMR spectrum of (*1R,5R*)-5-isopropyl-2-methylcyclohex-2-en-1-ol
(step ii precursor to compound **11**)
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of (*4R,6R*)-4-isopropyl-1-methyl-6-(prop-2-yn-1-yloxy)cyclohex-1-ene
(step iii precursor to compound **11**)
(recorded in CDCl_3)





—134.9
—125.4

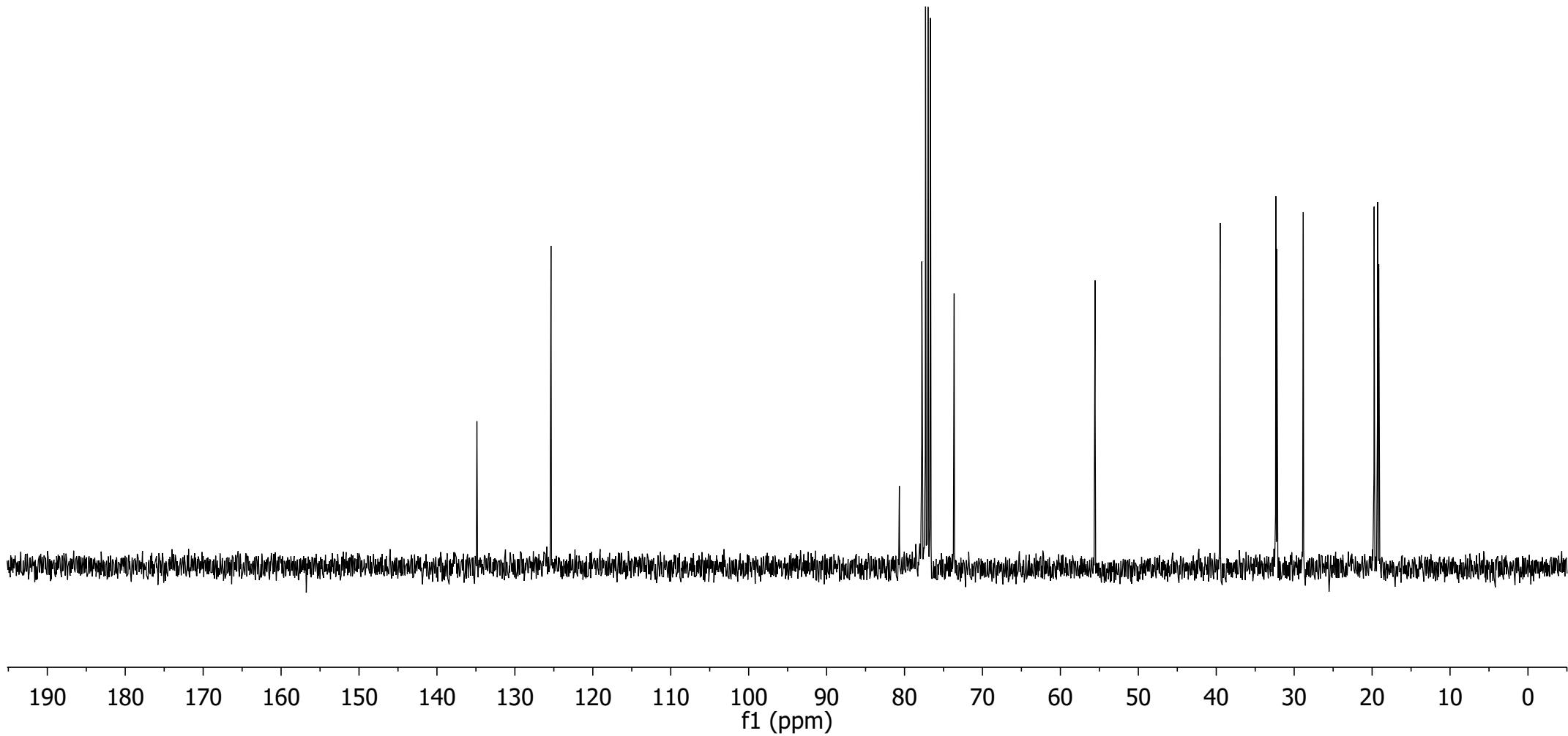
—80.7
~77.8
—73.6

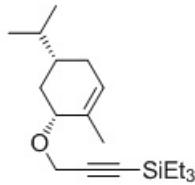
—55.6

—39.5
/ 32.4
/ 32.2
—28.8

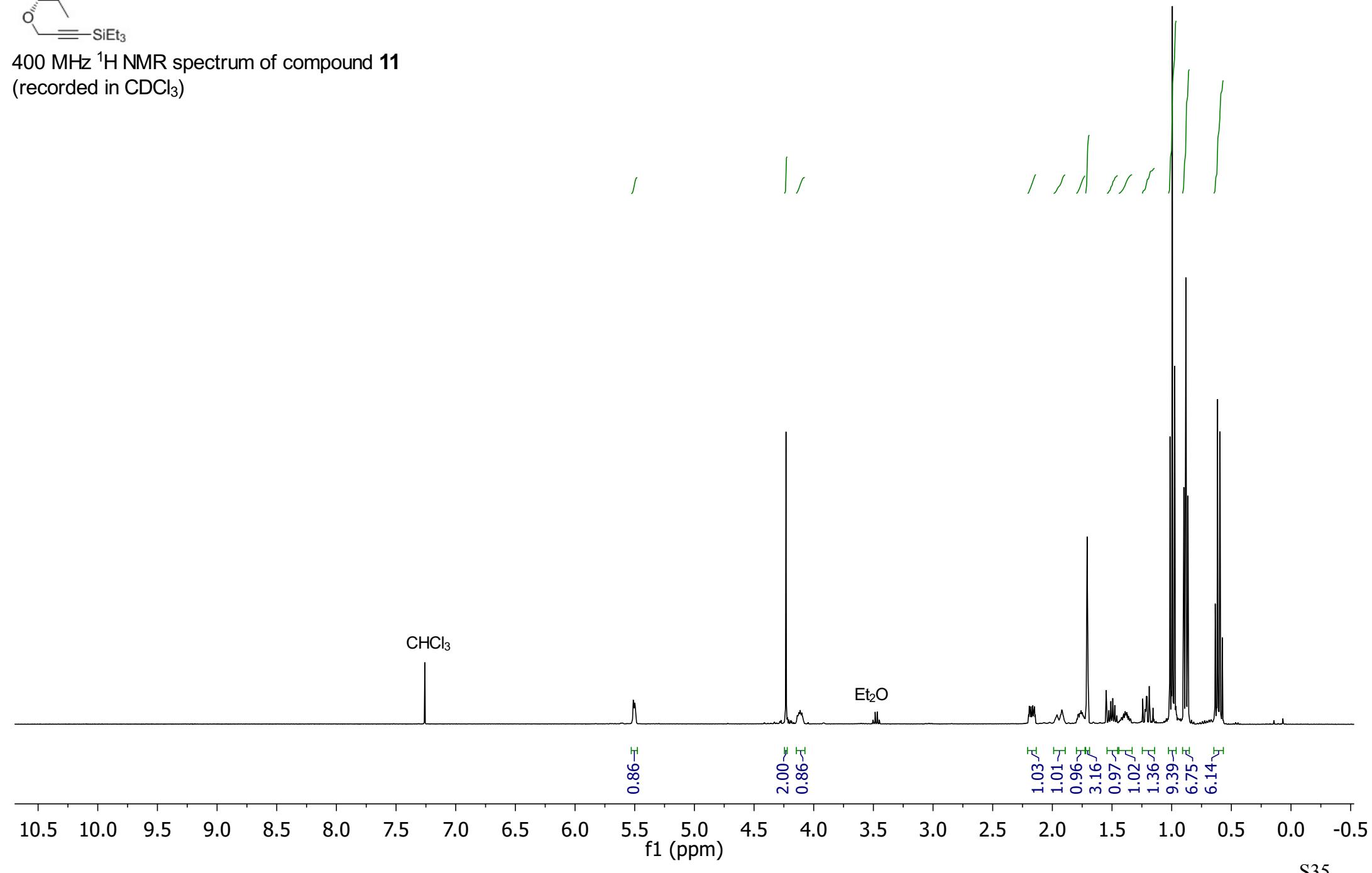
19.7
/ 19.3
/ 19.2

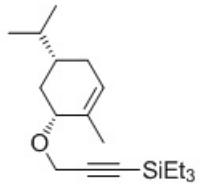
100 MHz ^{13}C NMR spectrum of (*4R,6R*)-4-isopropyl-1-methyl-6-(prop-2-yn-1-yloxy)cyclohex-1-ene
(step ii precursor to compound **11**)
(recorded in CDCl_3)



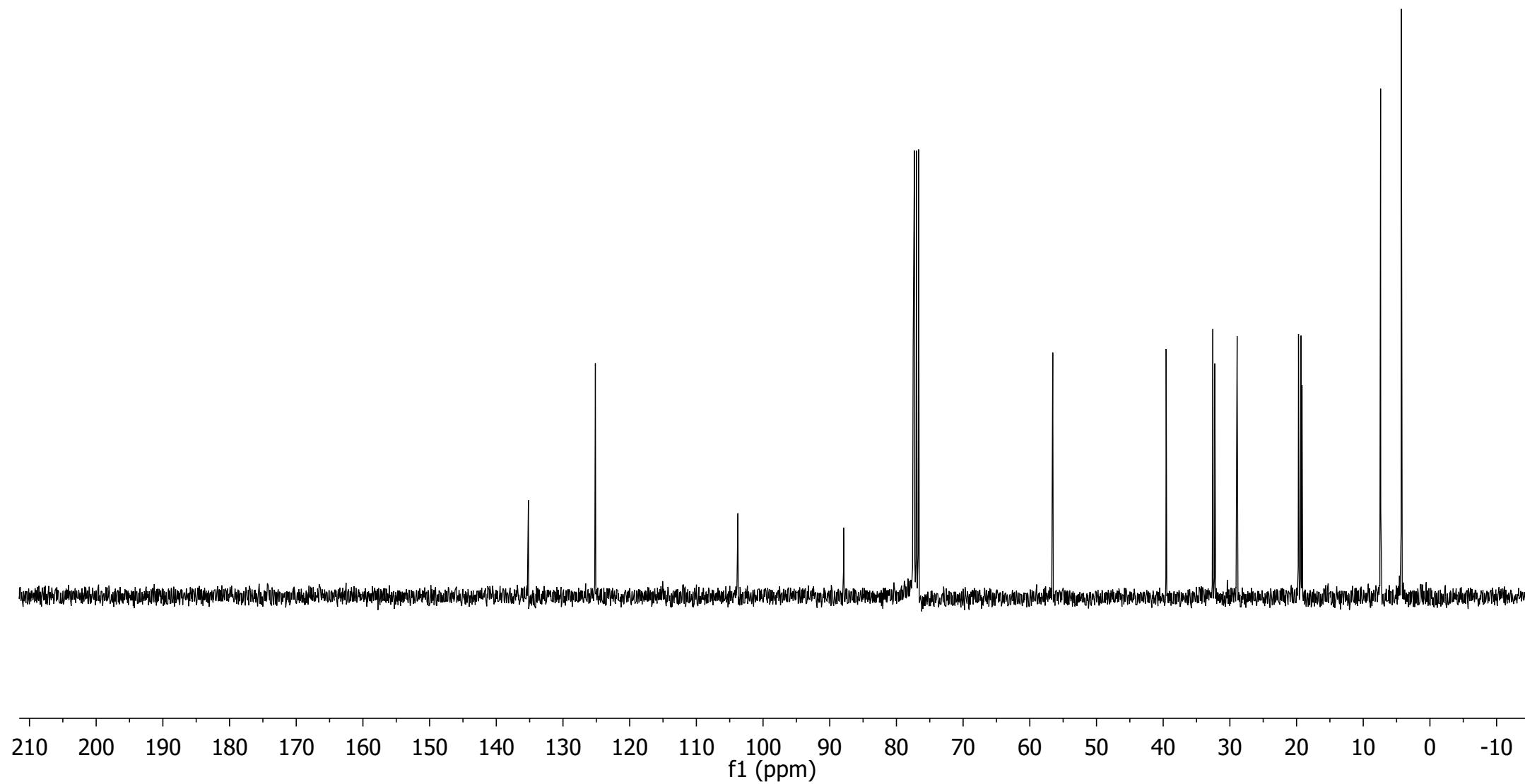


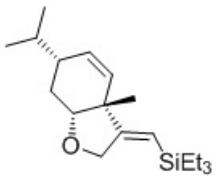
400 MHz ^1H NMR spectrum of compound **11**
 (recorded in CDCl_3)





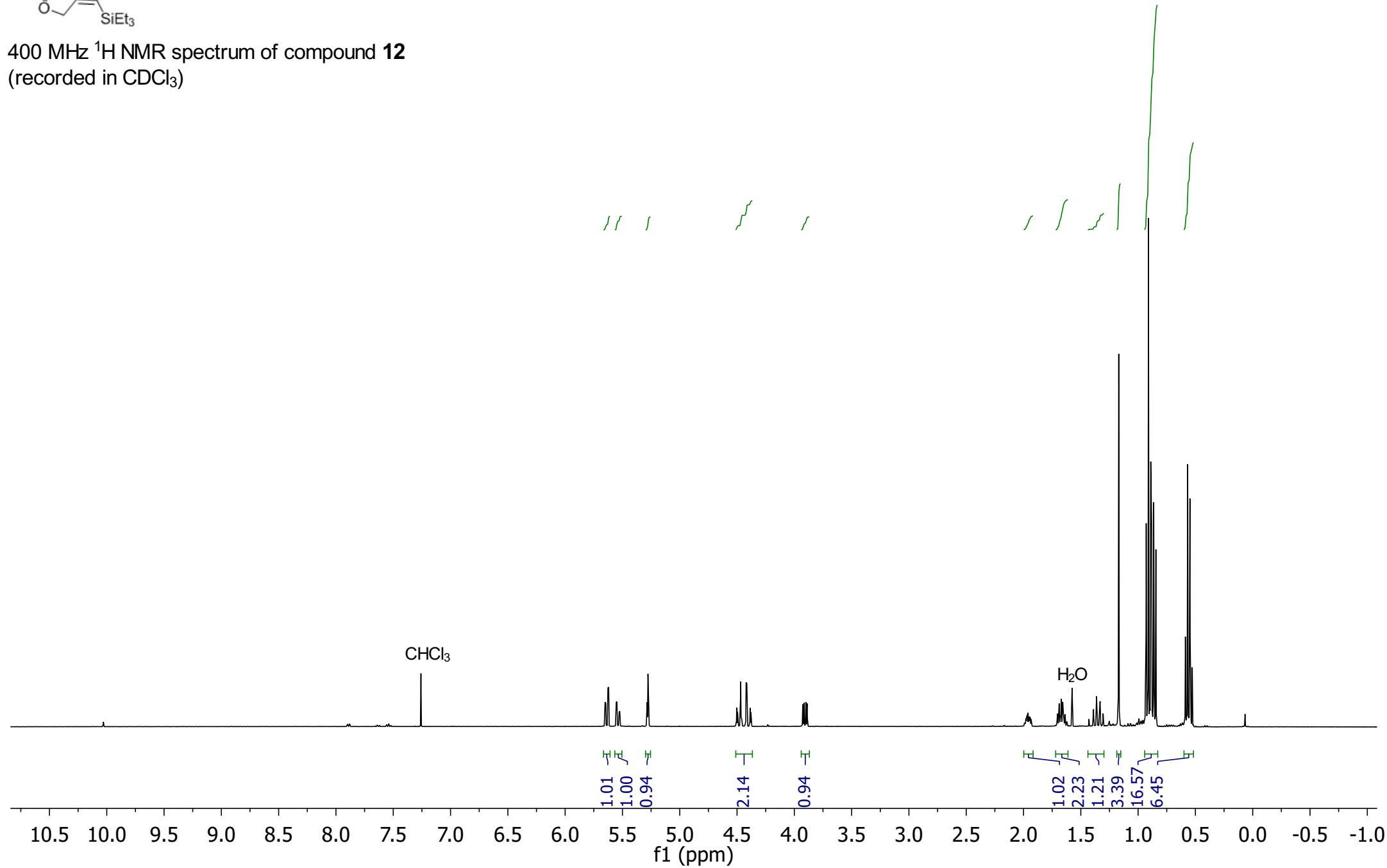
100 MHz ^{13}C NMR spectrum of compound **11**
(recorded in CDCl_3)

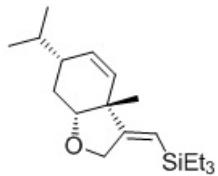




400 MHz ^1H NMR spectrum of compound **12**

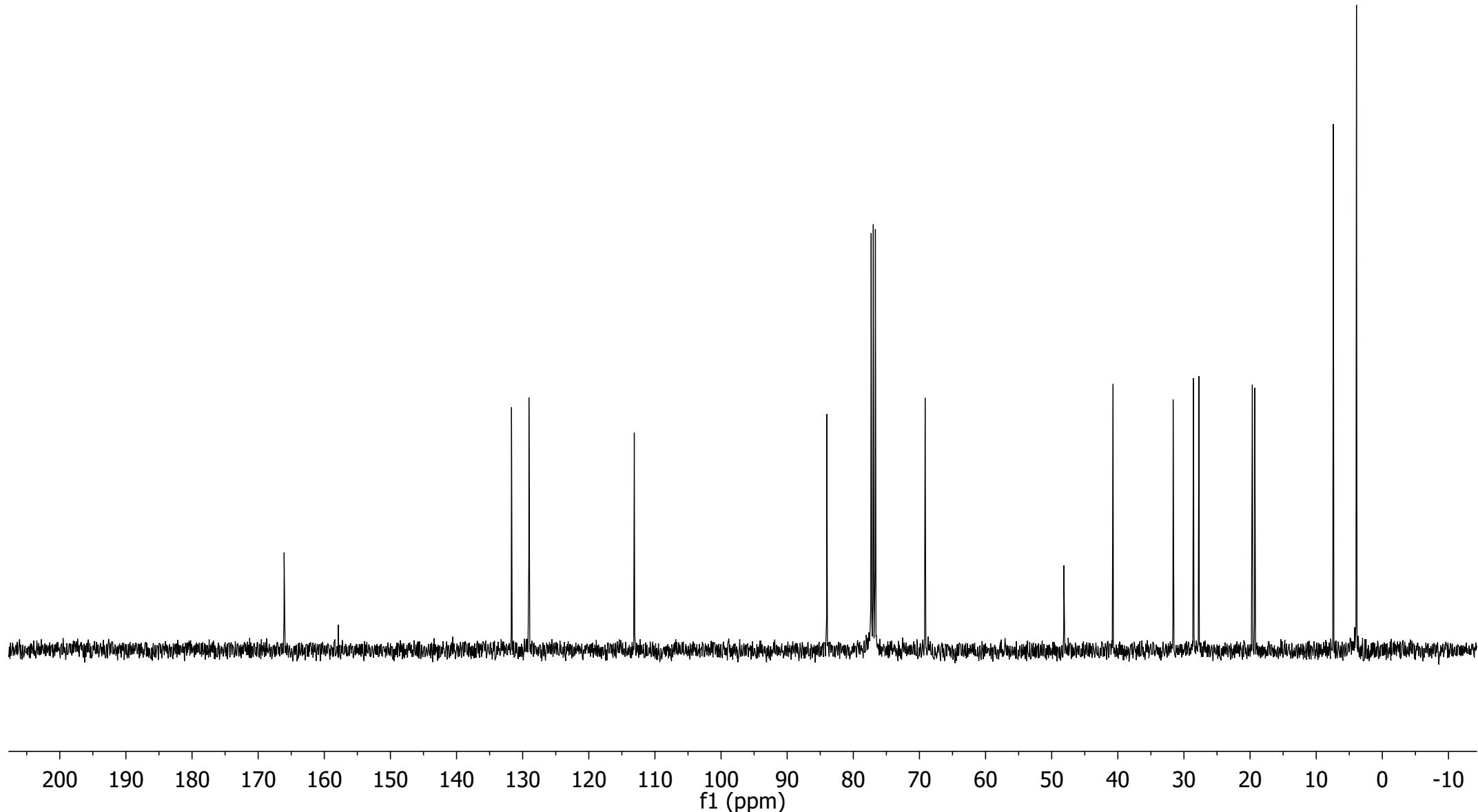
(recorded in CDCl_3)

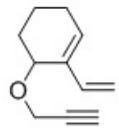




-166.1
-131.7
-129.1
-113.1
-84.0
-69.1
-48.2
-40.7
-31.6
-28.6
-27.7
-19.7
-19.3
-7.4
-3.9

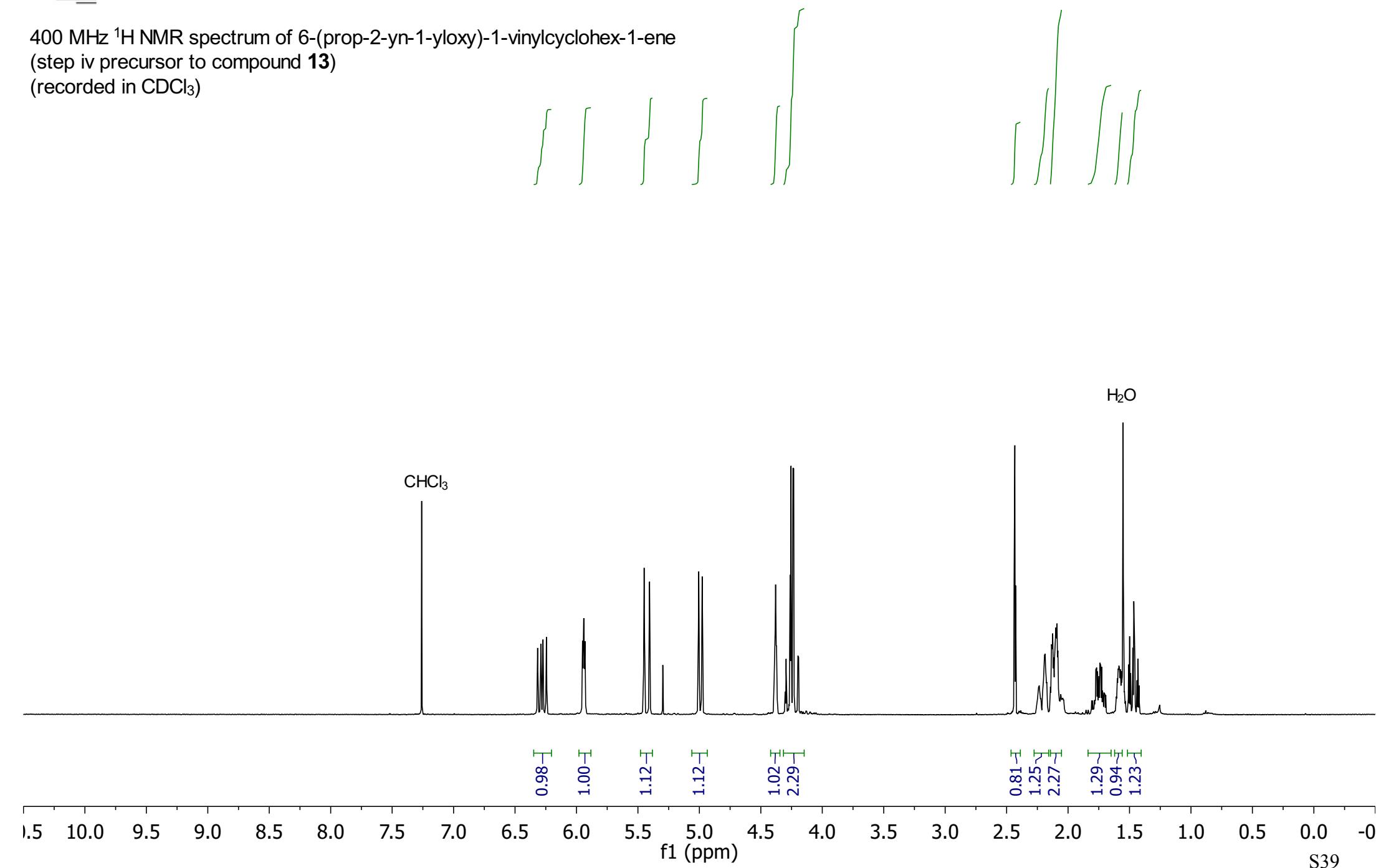
100 MHz ^{13}C NMR spectrum of compound **12**
(recorded in CDCl_3)

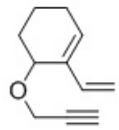




400 MHz ^1H NMR spectrum of 6-(prop-2-yn-1-yloxy)-1-vinylcyclohex-1-ene
(step iv precursor to compound **13**)

(recorded in CDCl_3)





138.0
135.7
133.6

111.6

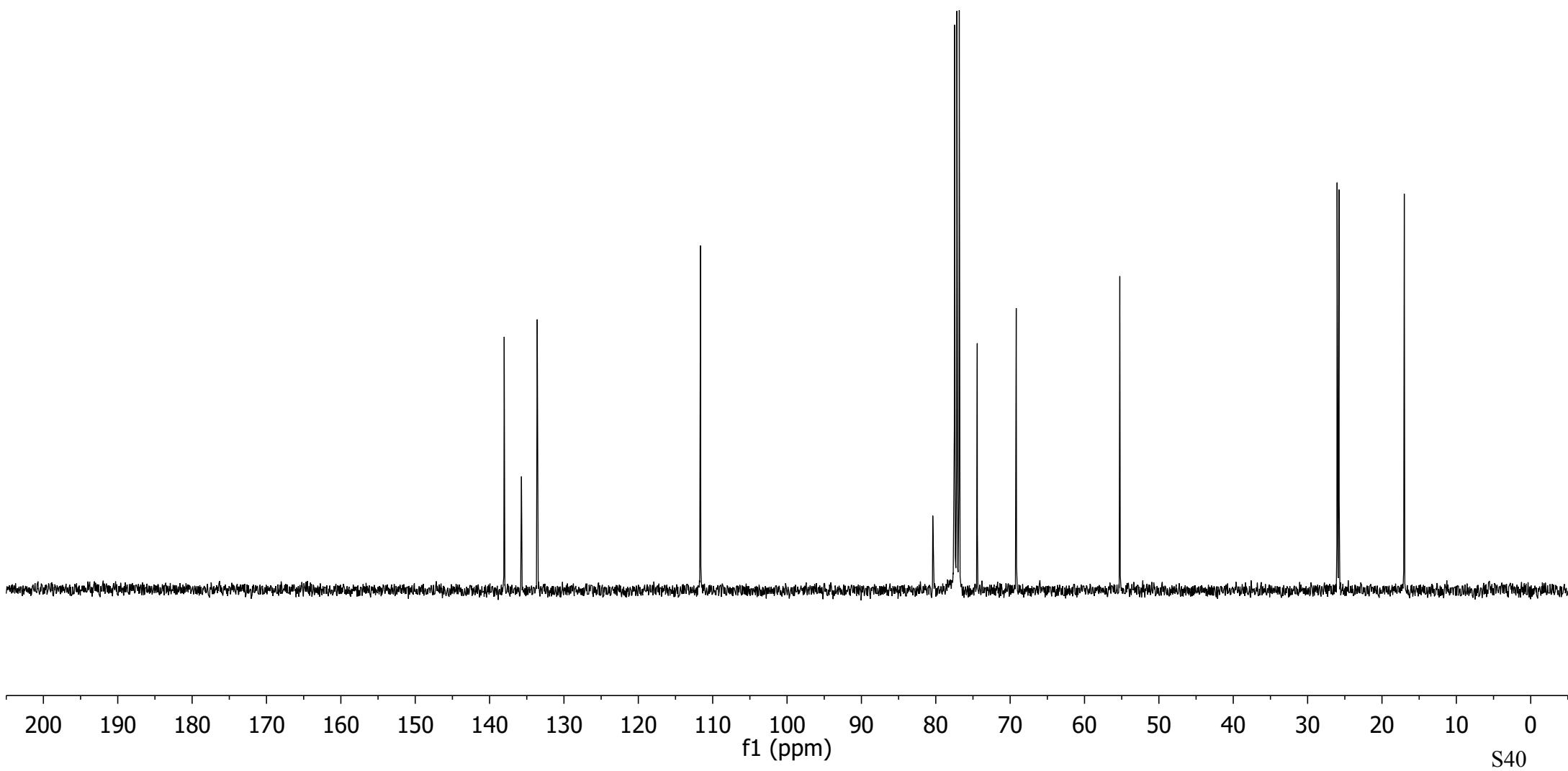
80.4
74.4
69.2

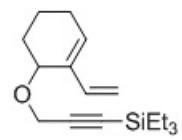
55.3

26.0
25.8

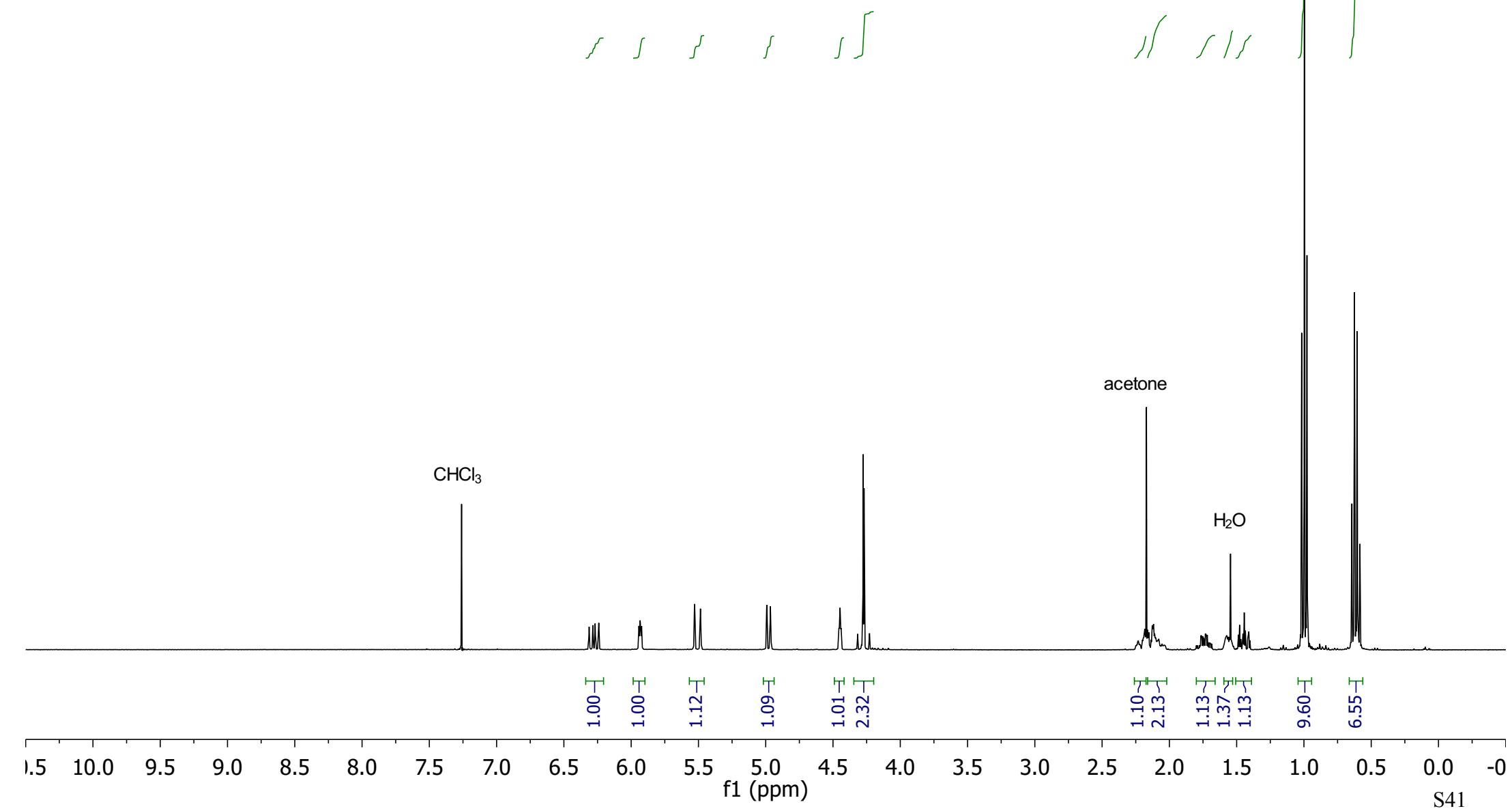
17.0

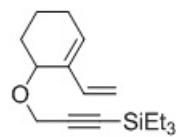
100 MHz ^{13}C NMR spectrum of 6-(prop-2-yn-1-yloxy)-1-vinylcyclohex-1-ene
(step iv precursor to compound **13**)
(recorded in CDCl_3)



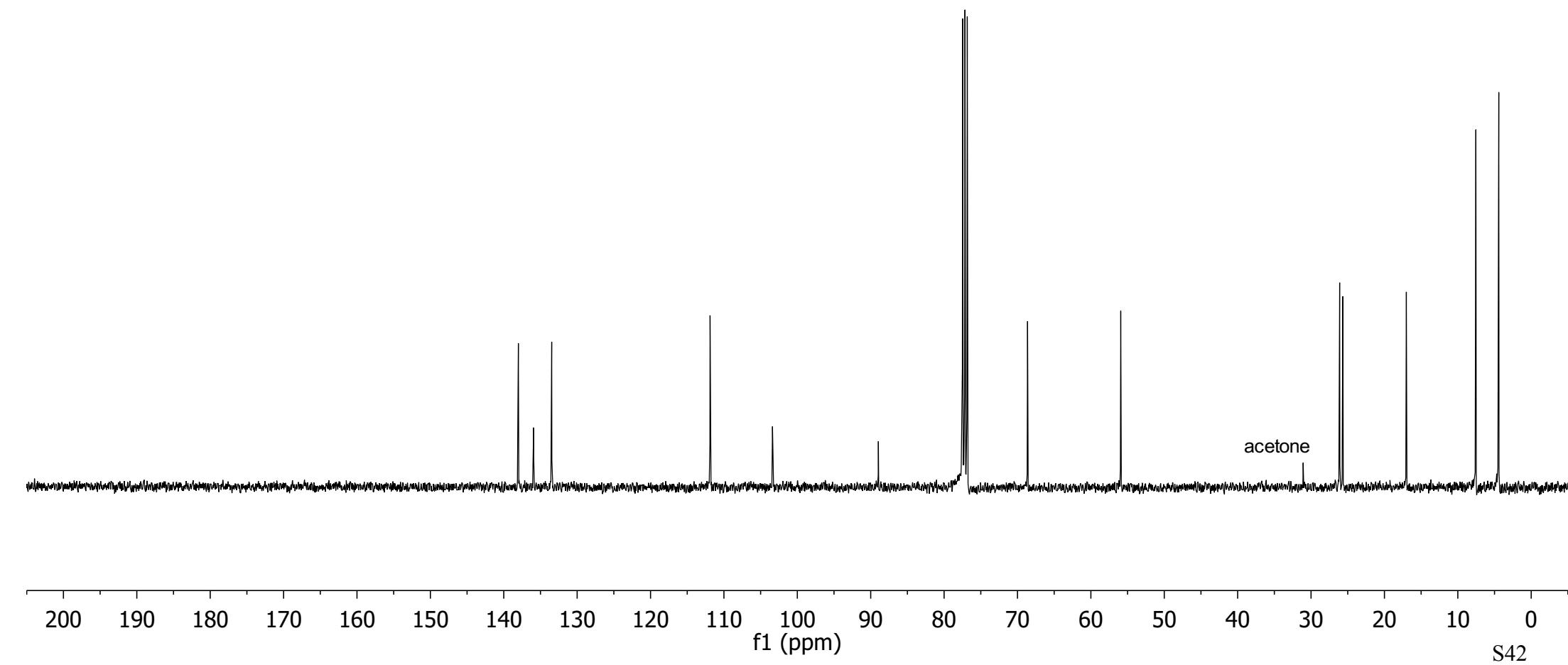


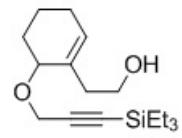
400 MHz ^1H NMR spectrum of compound **55**
(recorded in CDCl_3)



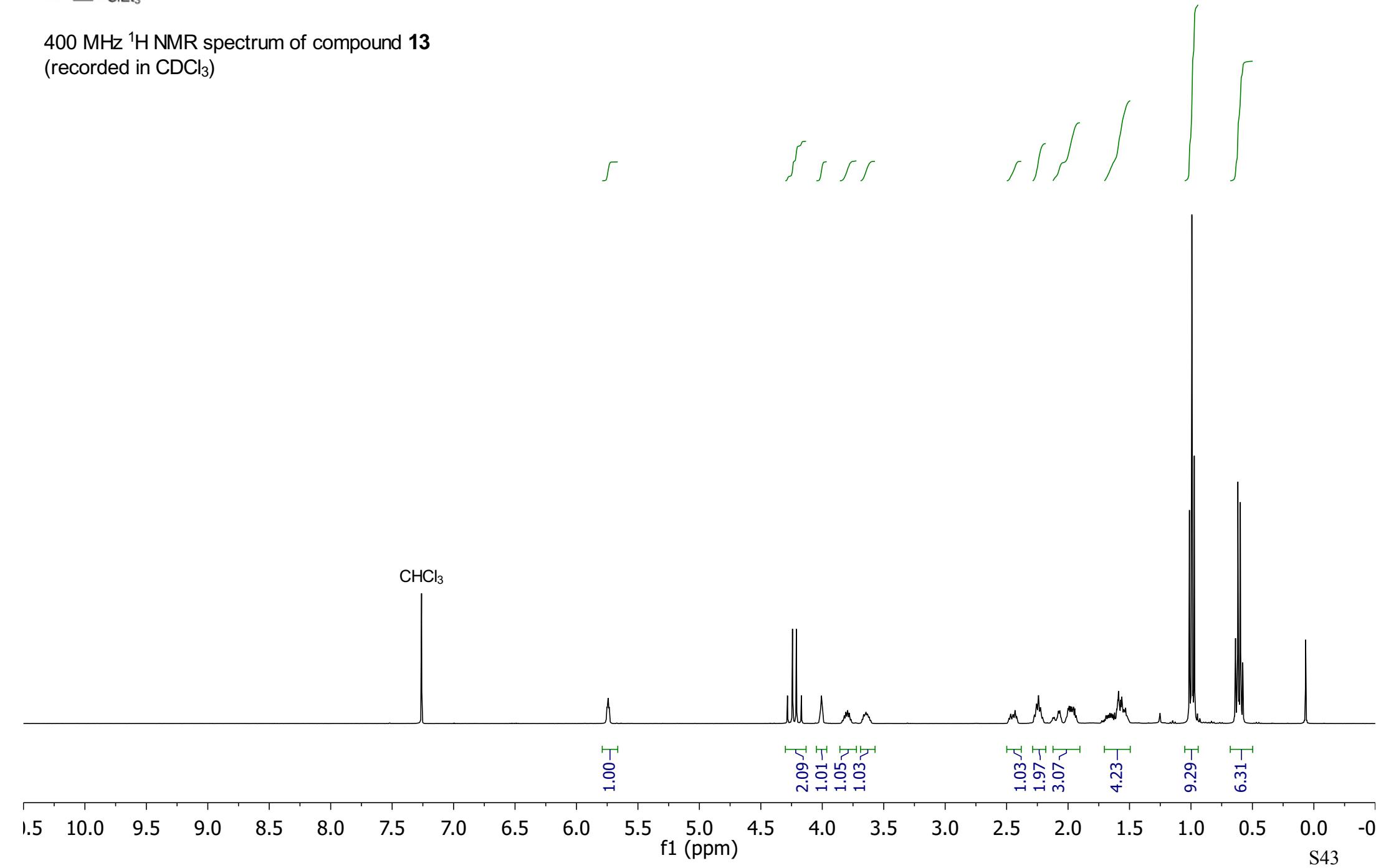


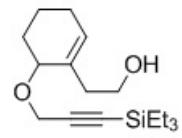
100 MHz ^{13}C NMR spectrum of compound **55**
(recorded in CDCl_3)



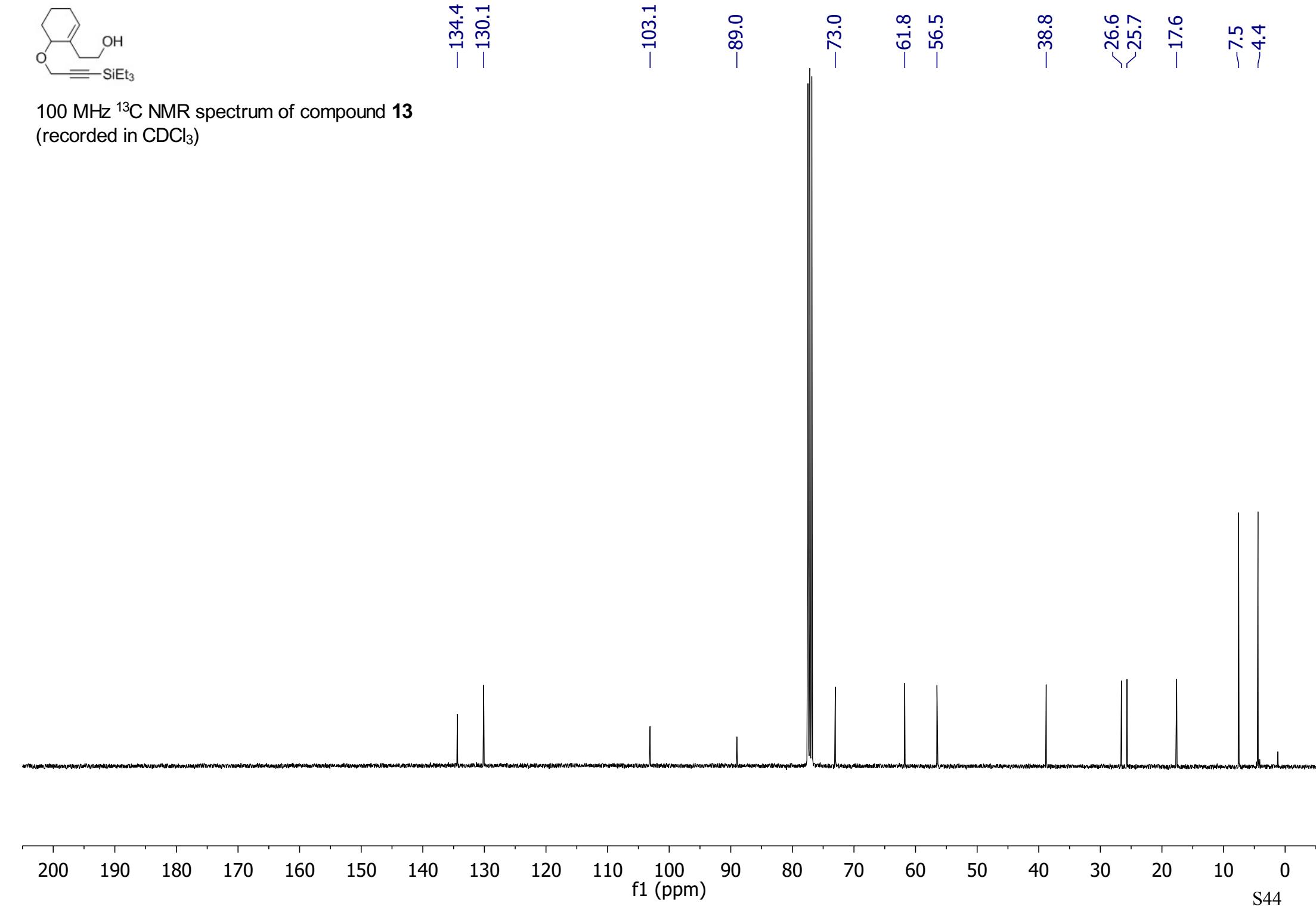


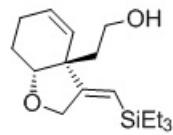
400 MHz ^1H NMR spectrum of compound **13**
(recorded in CDCl_3)



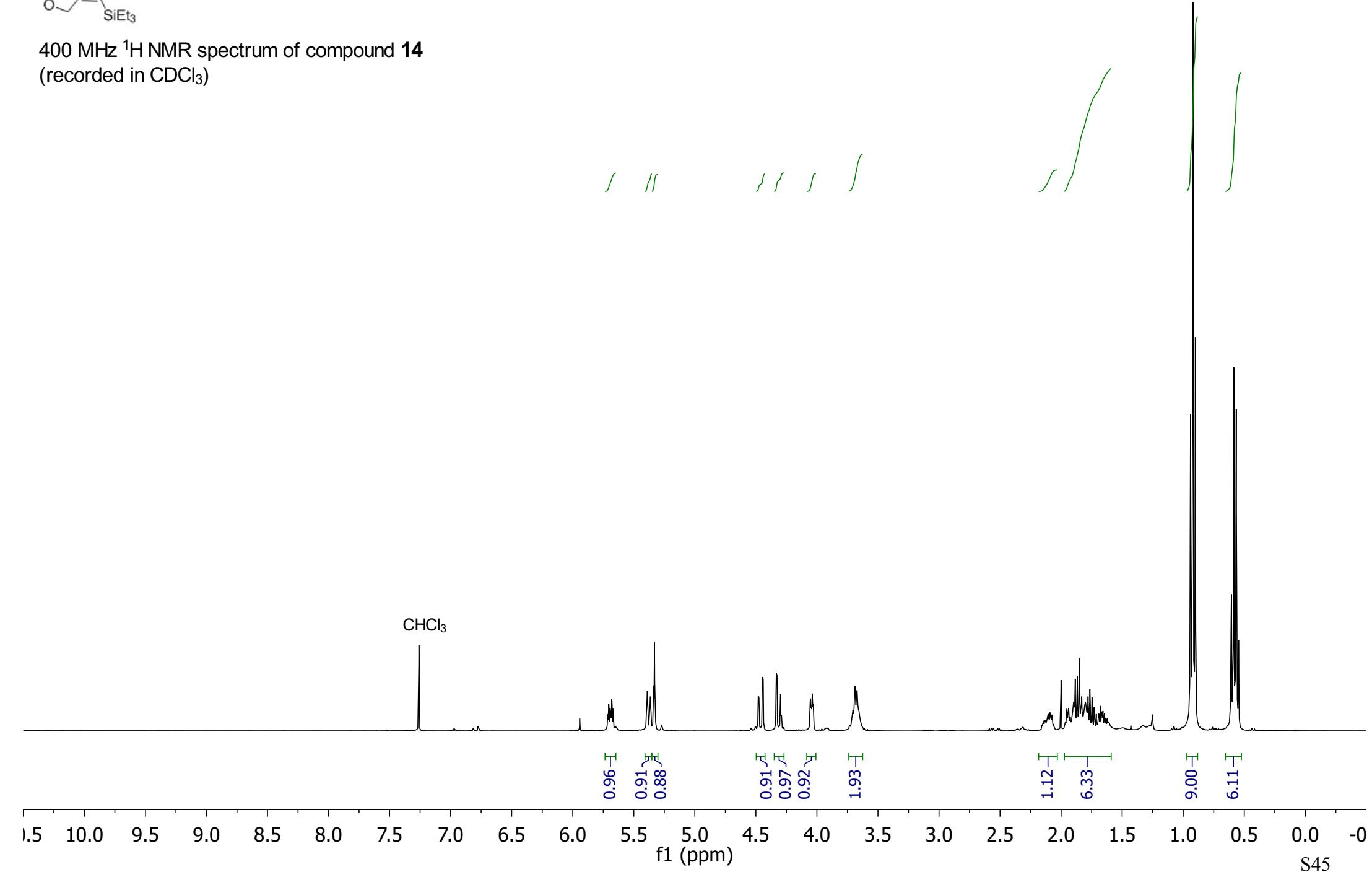


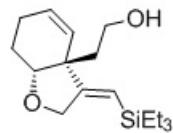
100 MHz ^{13}C NMR spectrum of compound **13**
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound **14**
(recorded in CDCl_3)





-164.4

-131.5

-126.1

-114.4

-80.7

-70.2

-60.0

-49.7

-41.6

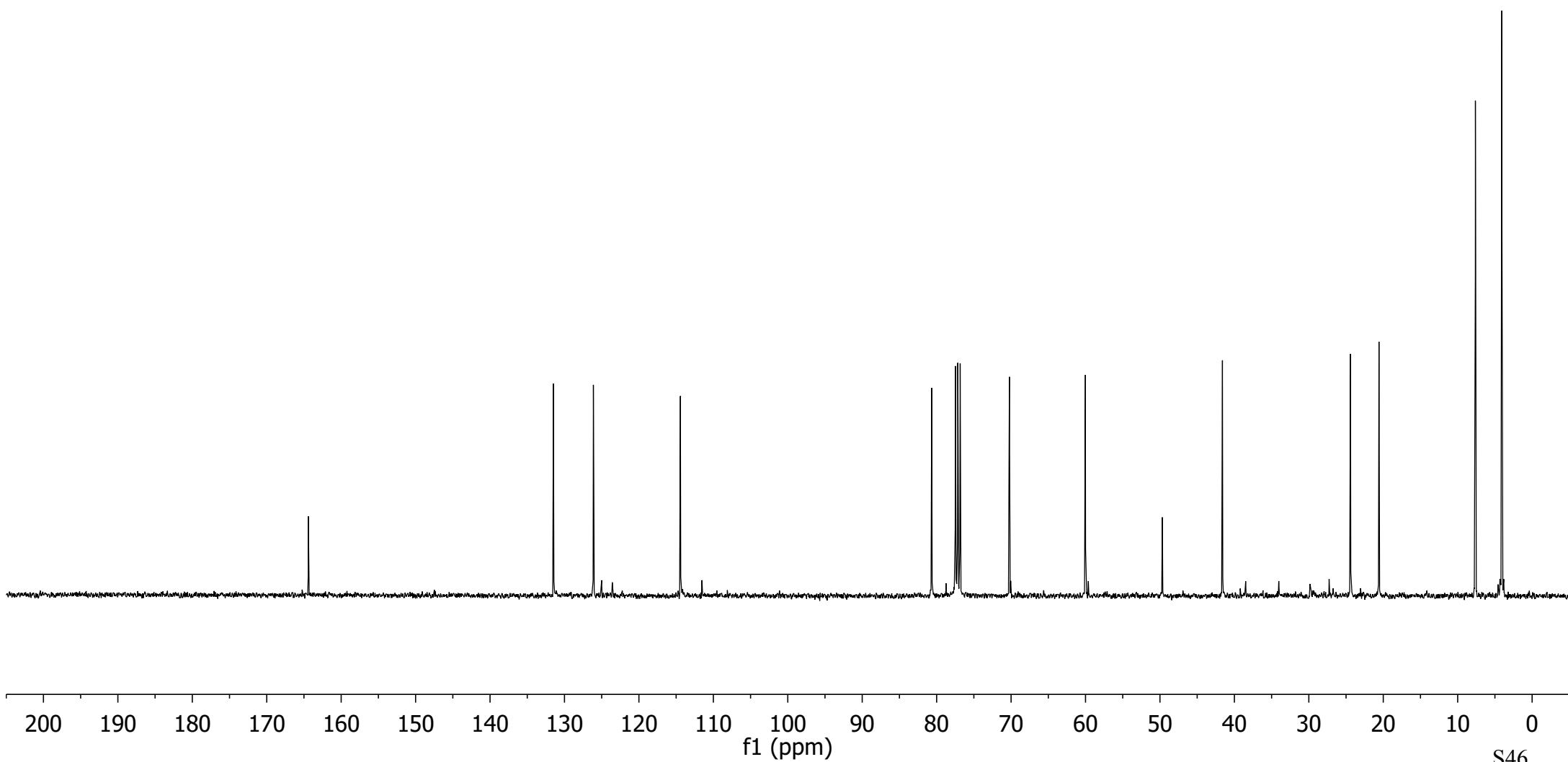
-24.4

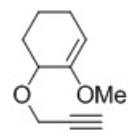
-20.6

-7.6

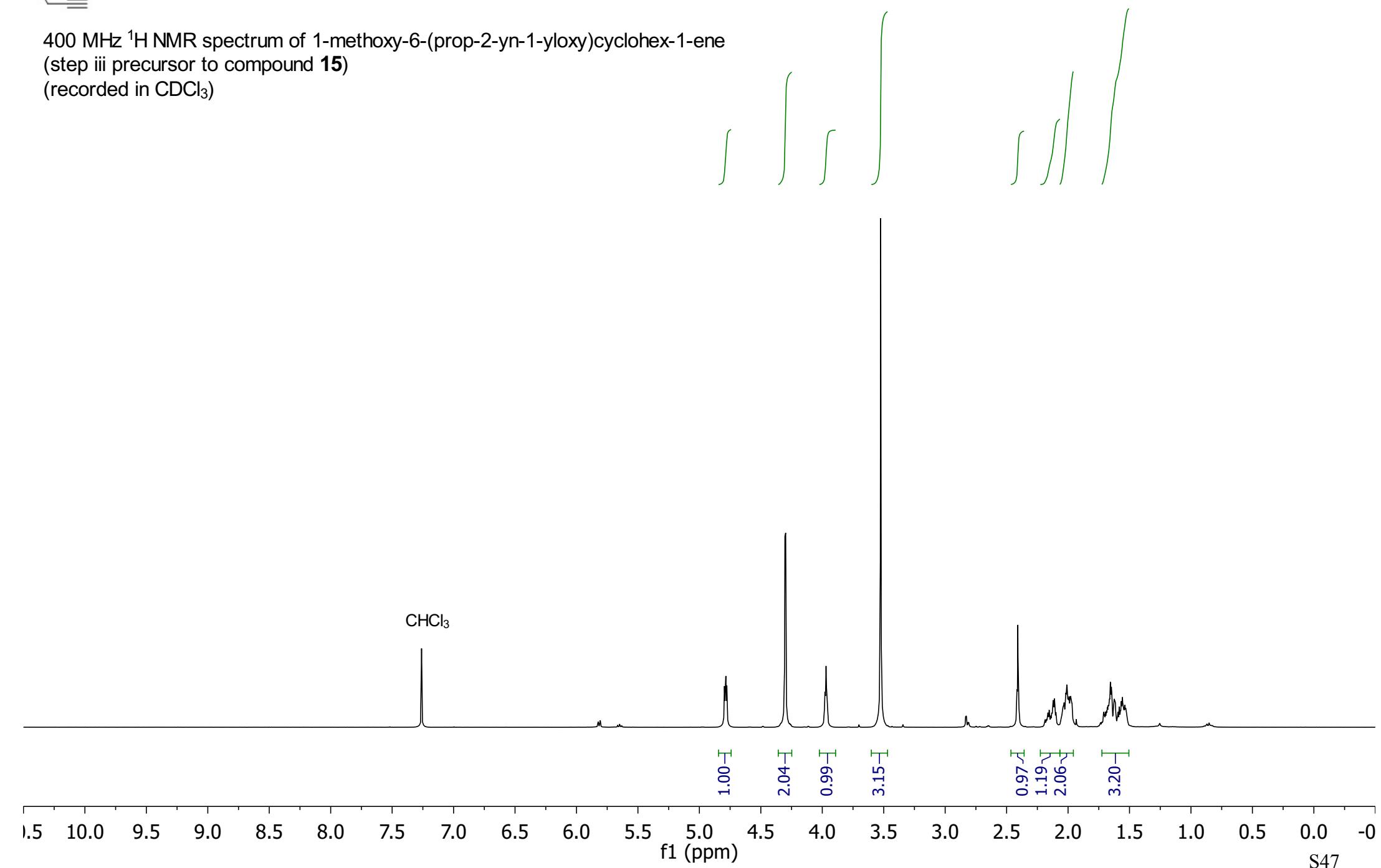
-4.1

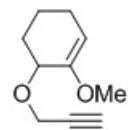
100 MHz ^{13}C NMR spectrum of compound **14**
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of 1-methoxy-6-(prop-2-yn-1-yloxy)cyclohex-1-ene
(step iii precursor to compound **15**)
(recorded in CDCl_3)



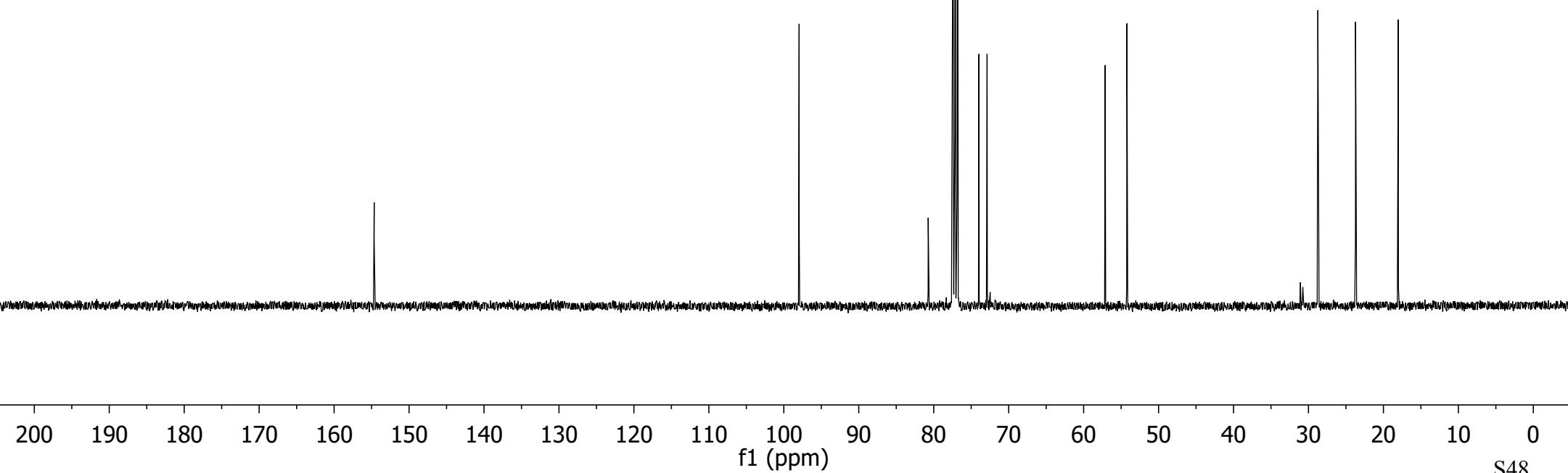


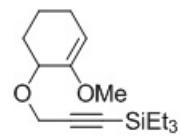
-154.7

-98.0

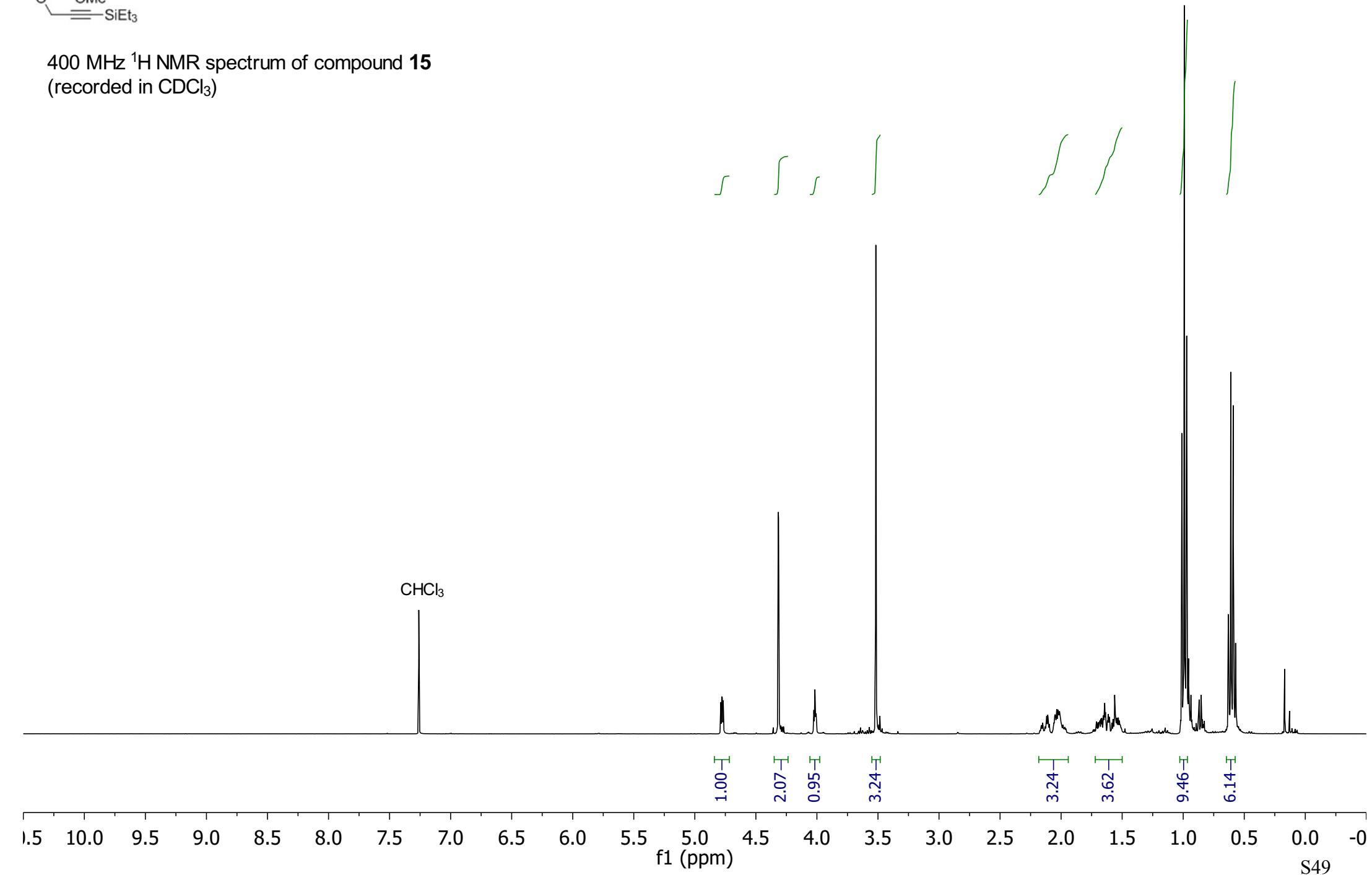
-80.7
-74.0
-72.9-57.1
-54.2~28.7
~23.7
~18.0

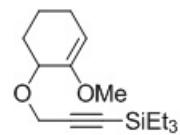
100 MHz ^{13}C NMR spectrum of 1-methoxy-6-(prop-2-yn-1-yloxy)cyclohex-1-ene
(step iii precursor to compound **15**)
(recorded in CDCl_3)



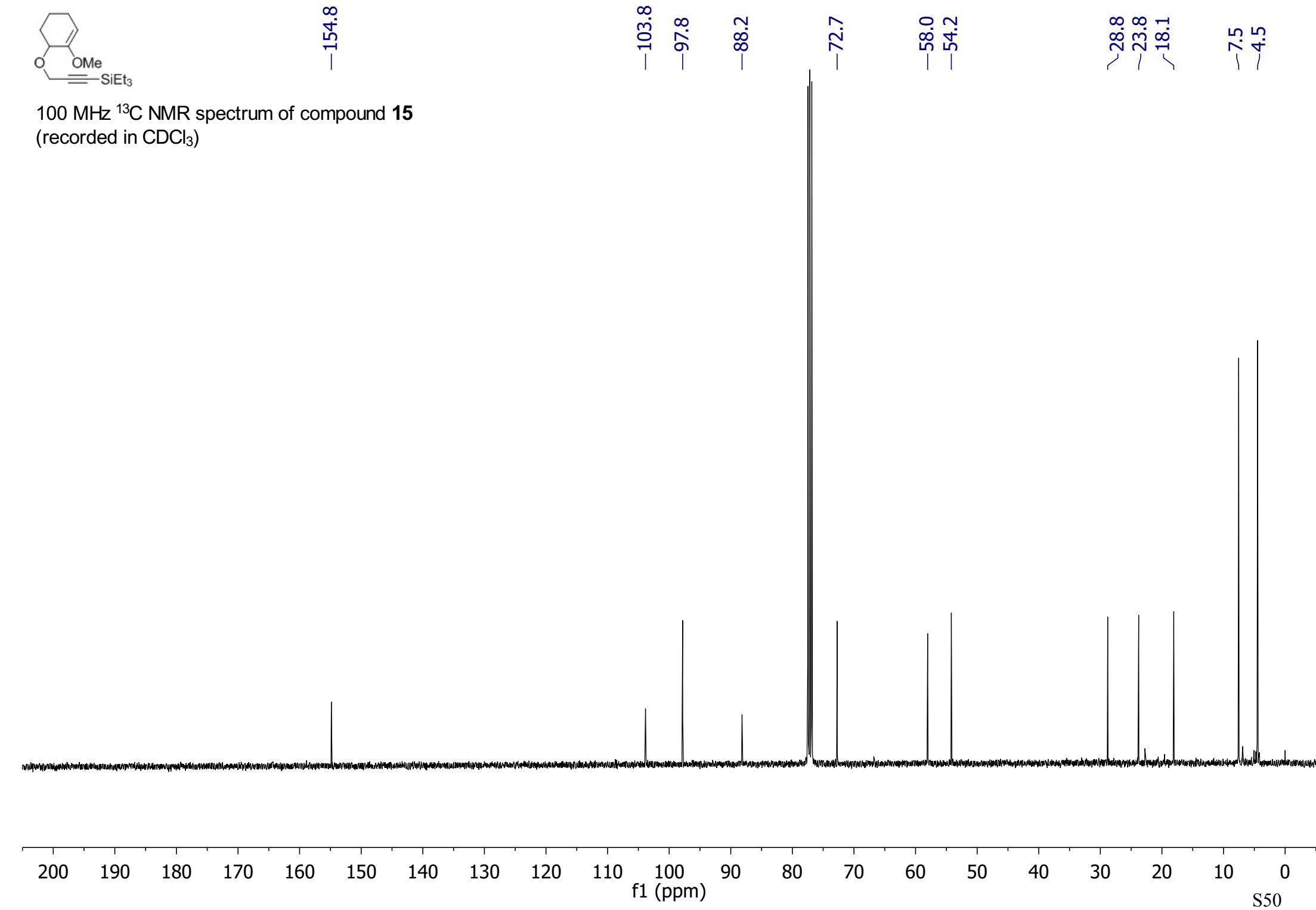


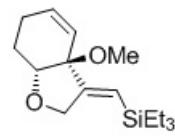
400 MHz ^1H NMR spectrum of compound **15**
(recorded in CDCl_3)



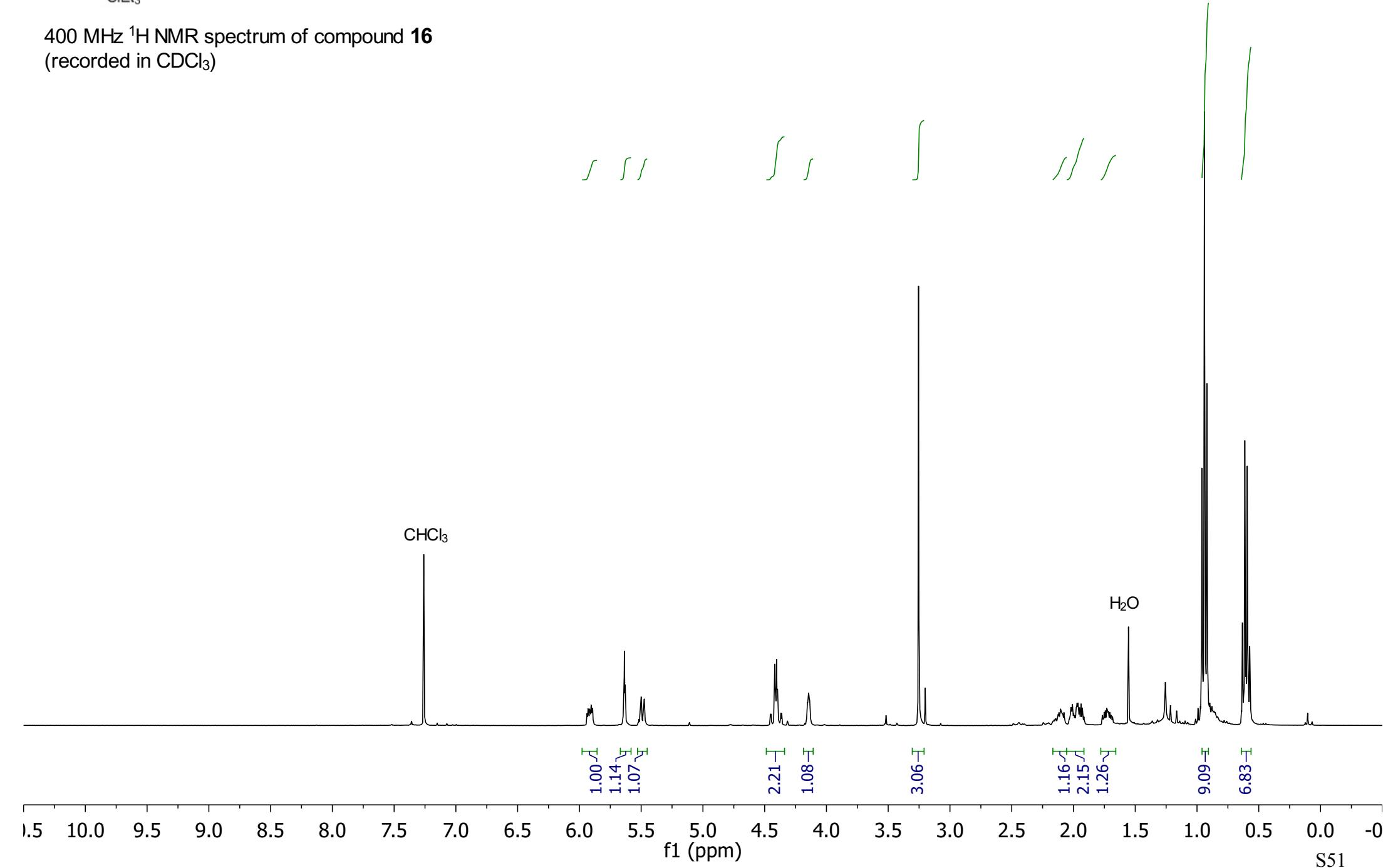


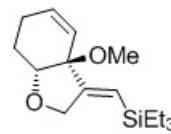
100 MHz ^{13}C NMR spectrum of compound 15
(recorded in CDCl_3)



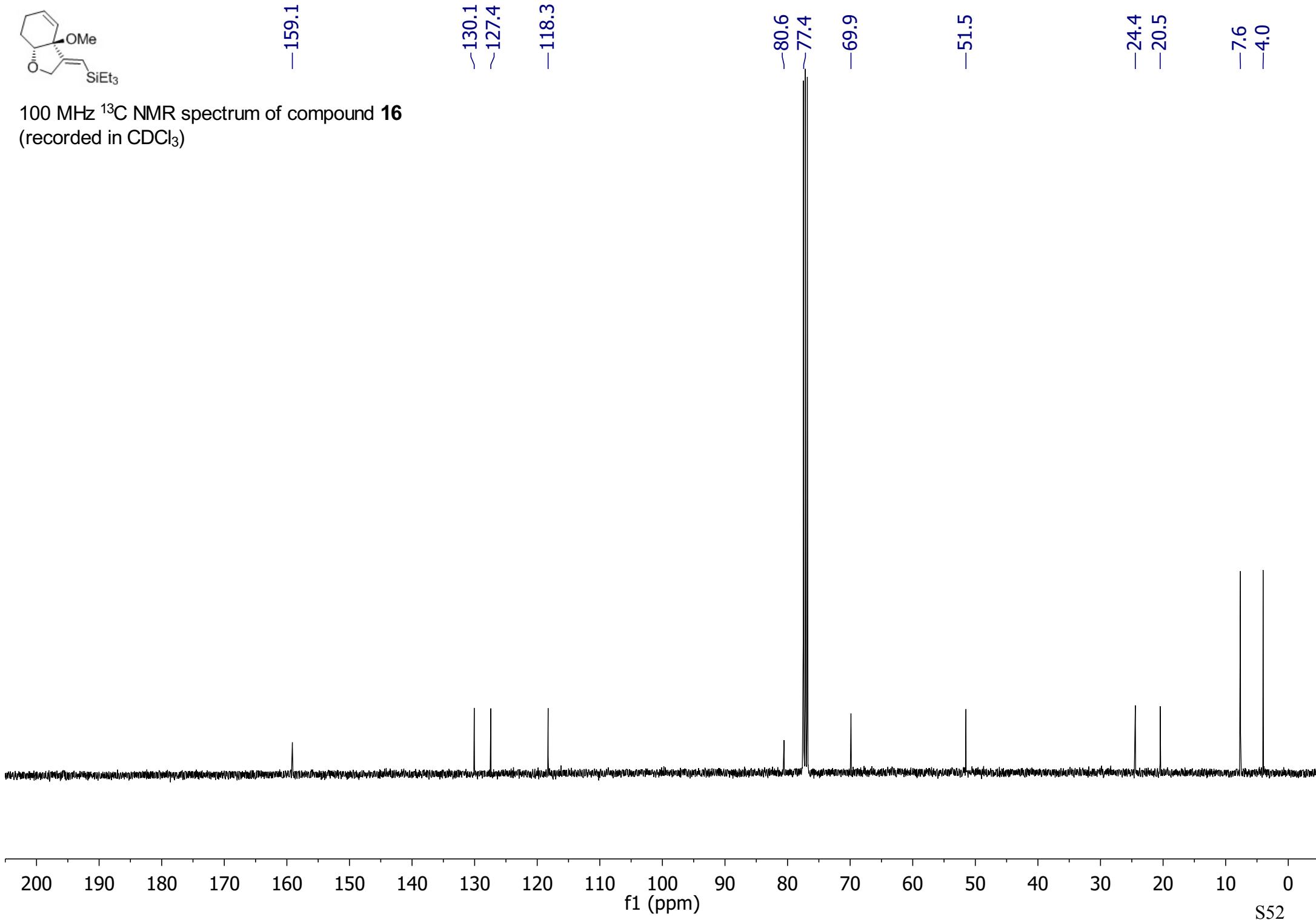


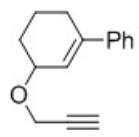
400 MHz ^1H NMR spectrum of compound **16**
(recorded in CDCl_3)



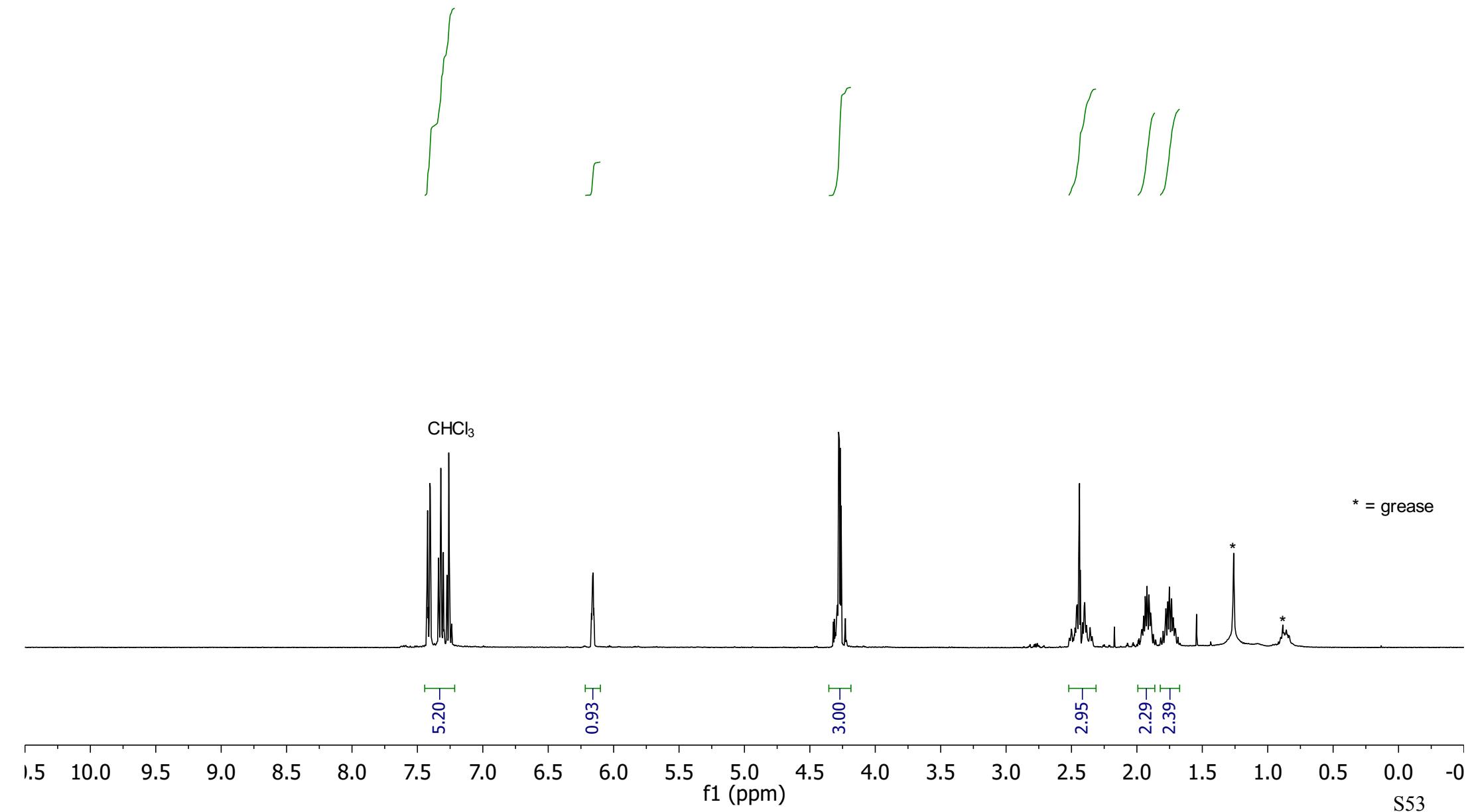


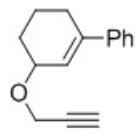
100 MHz ^{13}C NMR spectrum of compound **16**
(recorded in CDCl_3)





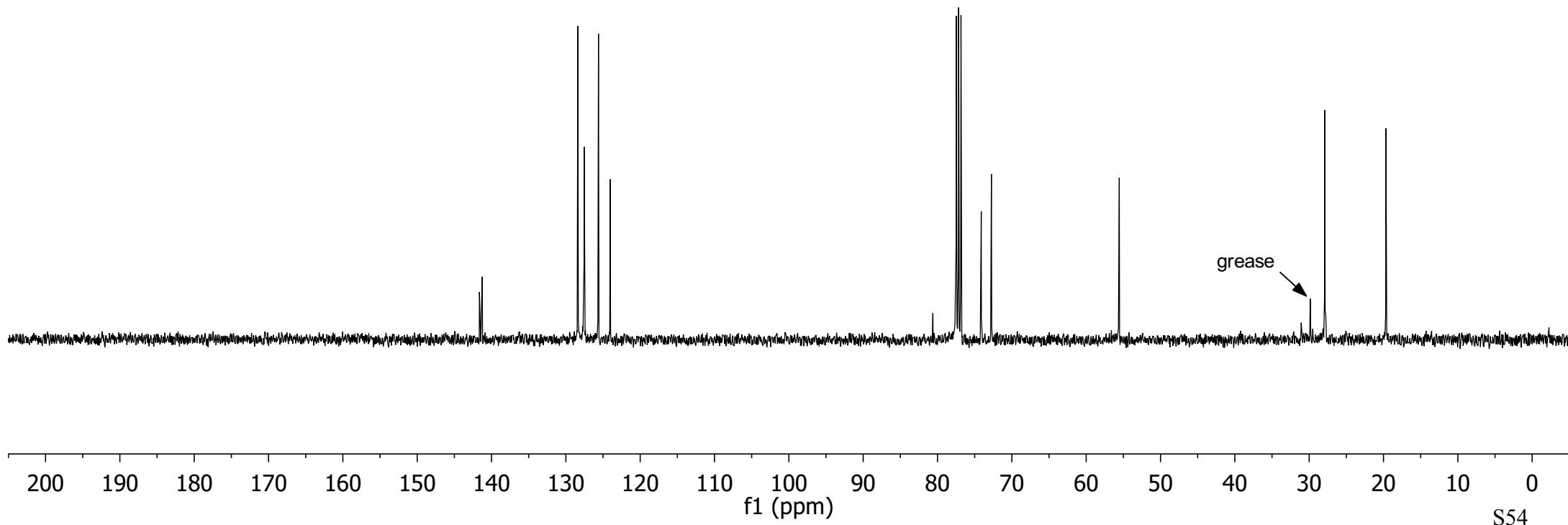
400 MHz ^1H NMR spectrum of 5-(prop-2-yn-1-yloxy)-2,3,4,5-tetrahydro-1,1'-biphenyl
(step iii precursor to compound **17**)
(recorded in CDCl_3)

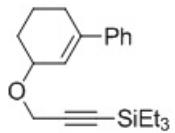




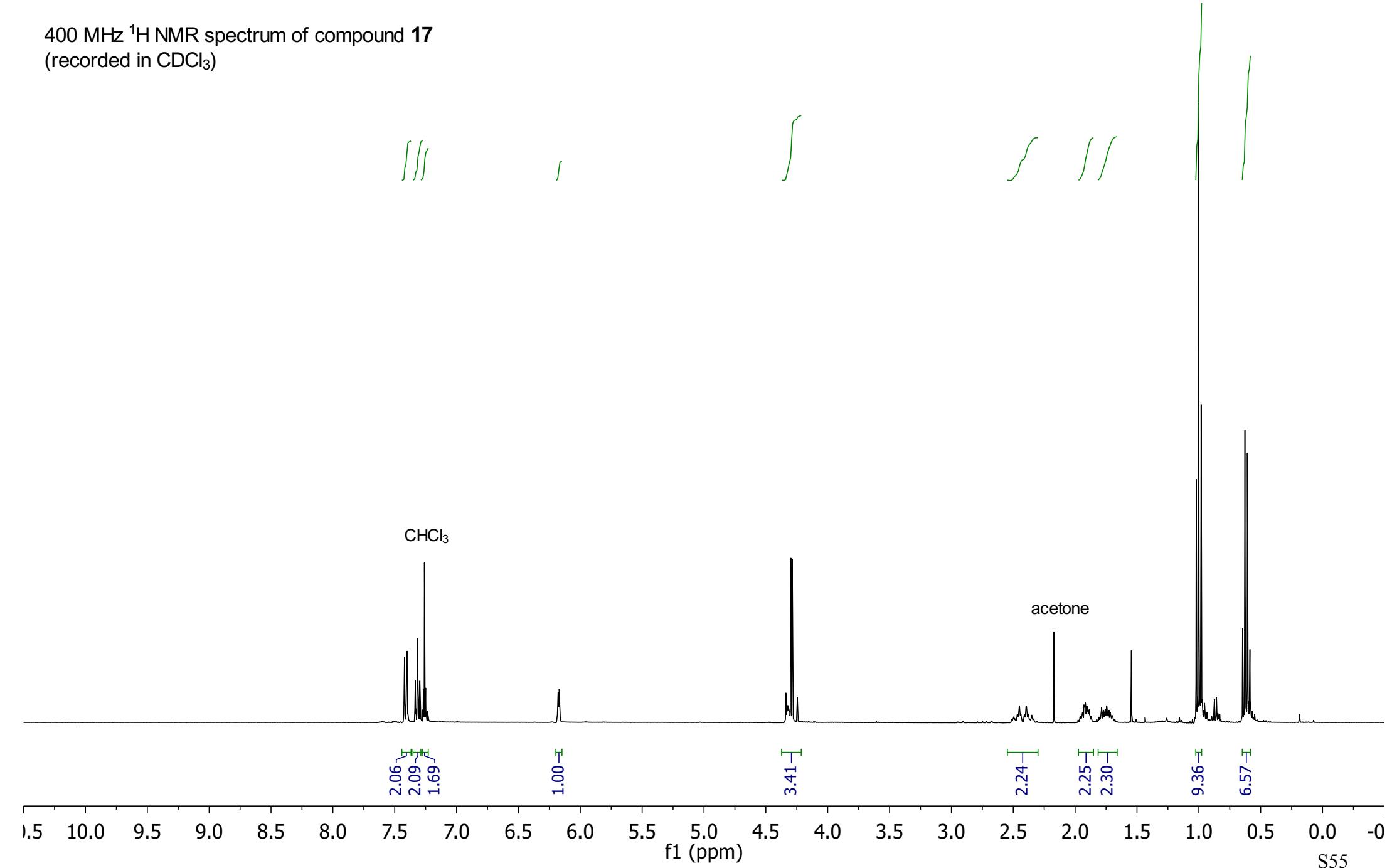
141.6
141.3
128.4
127.5
125.6
124.0
80.6
74.1
72.8
55.5
27.9
27.8
19.7

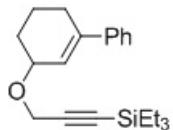
100 MHz ^{13}C NMR spectrum of 5-(prop-2-yn-1-yloxy)-2,3,4,5-tetrahydro-1,1'-biphenyl
(step iii precursor to compound **17**)
(recorded in CDCl_3)





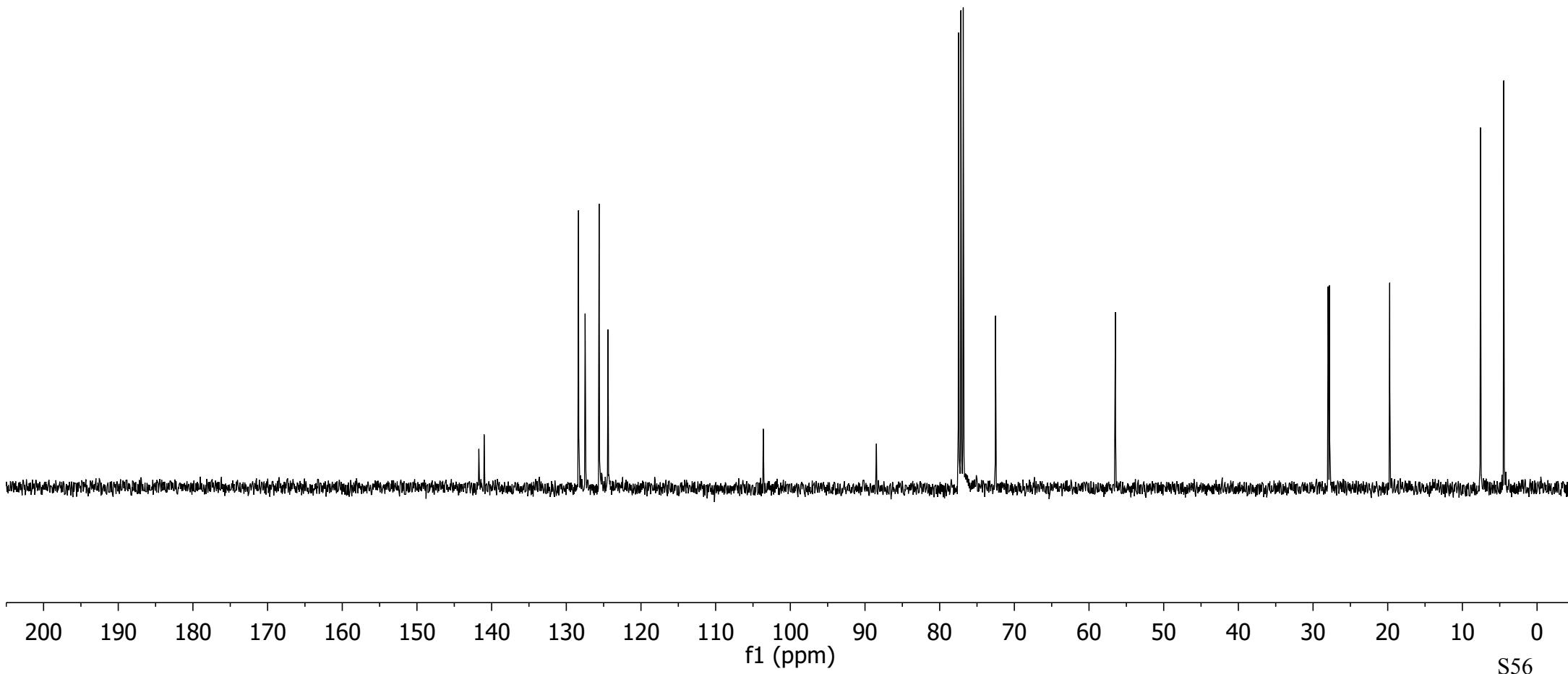
400 MHz ^1H NMR spectrum of compound **17**
(recorded in CDCl_3)

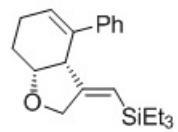




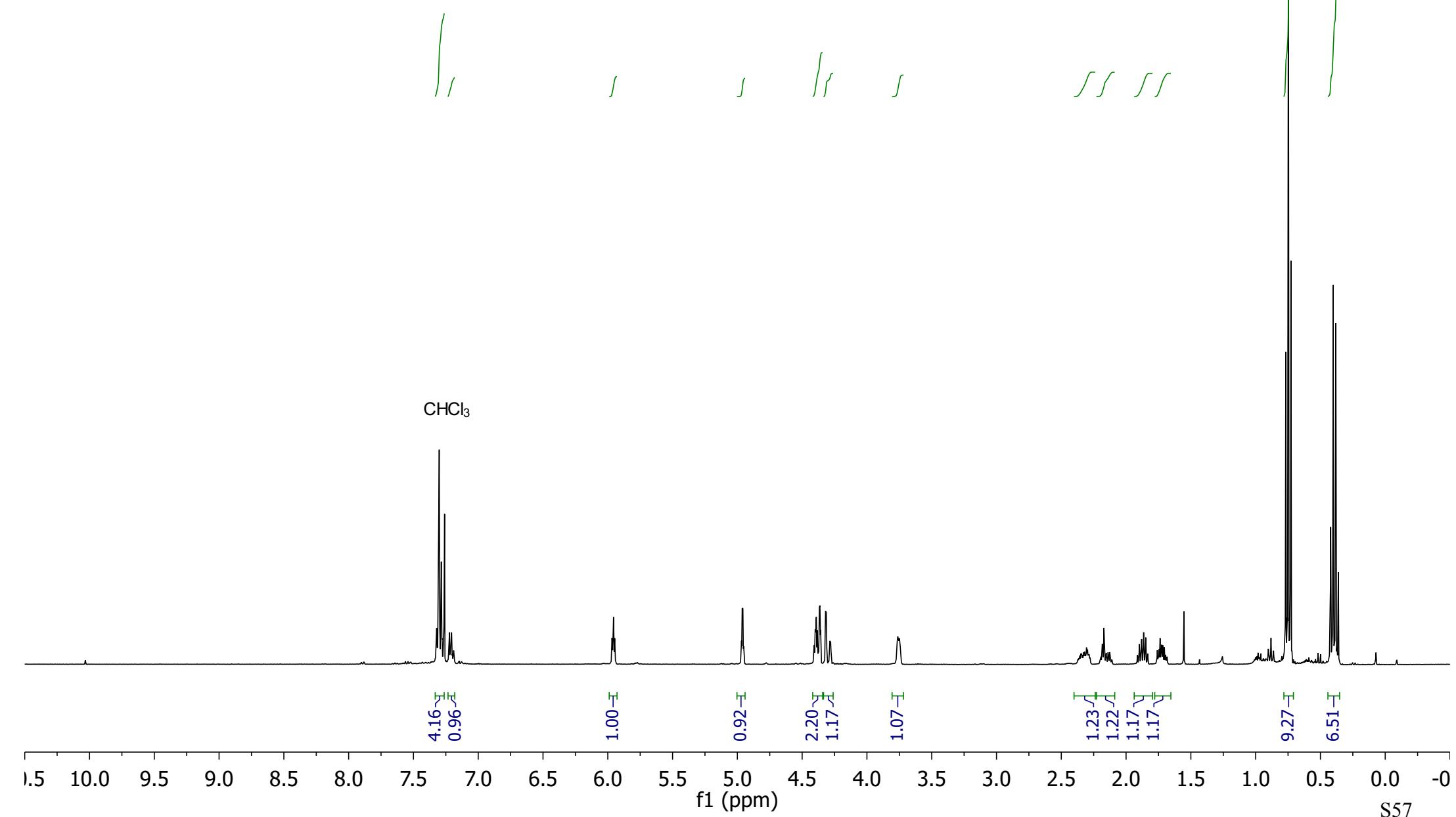
100 MHz ^{13}C NMR spectrum of compound **17**
(recorded in CDCl_3)

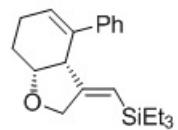
141.7
141.0
128.4
127.5
125.6
124.4
103.6
88.5
72.5
56.5
28.0
27.8
19.7
7.6
4.5





400 MHz ^1H NMR spectrum of compound **18**
(recorded in CDCl_3)





-158.3

-142.1
-136.9
128.2
127.0
126.8
126.1
-118.0

-76.9

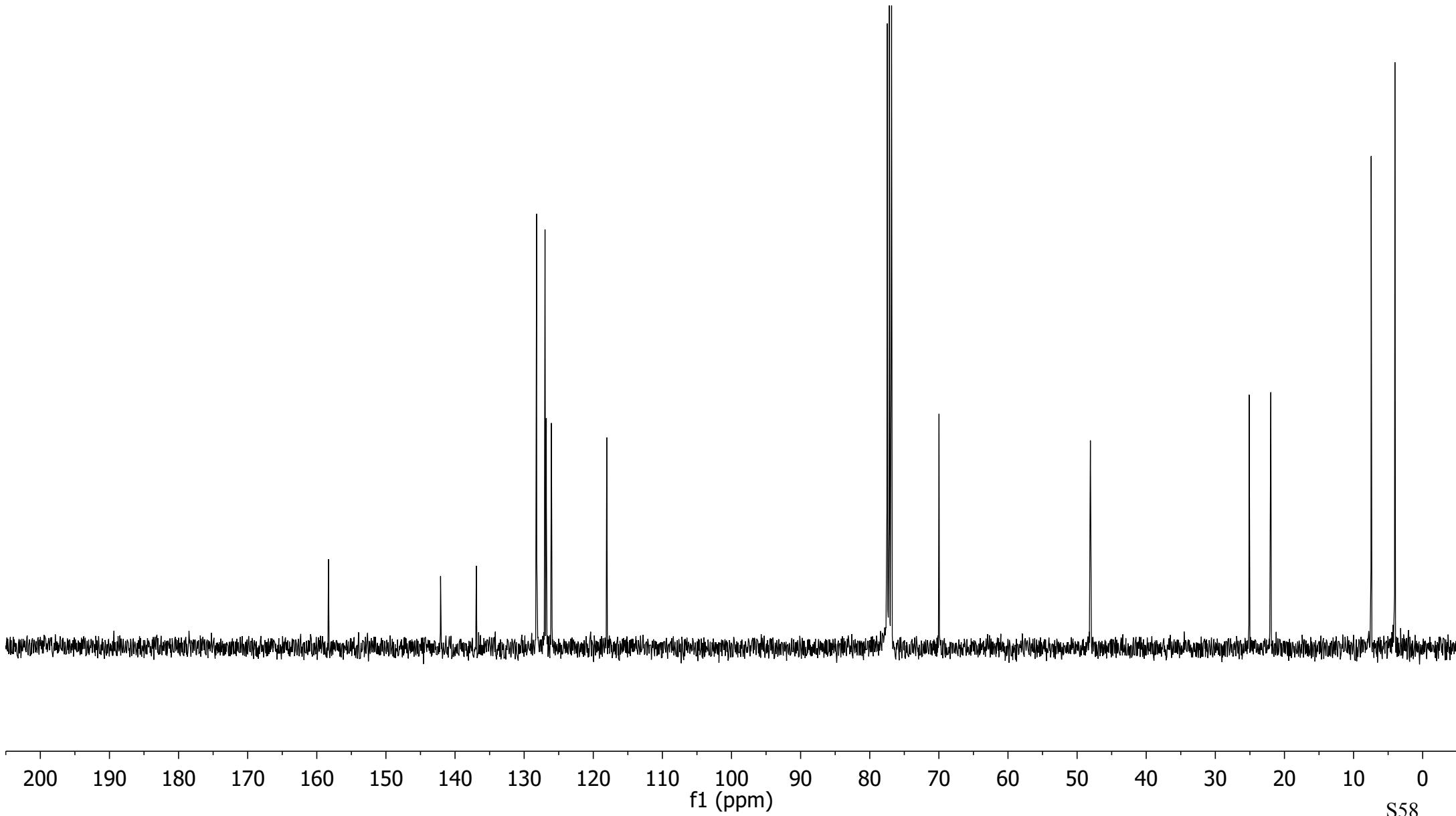
-70.0

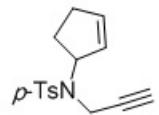
-48.1

-25.1
-22.0

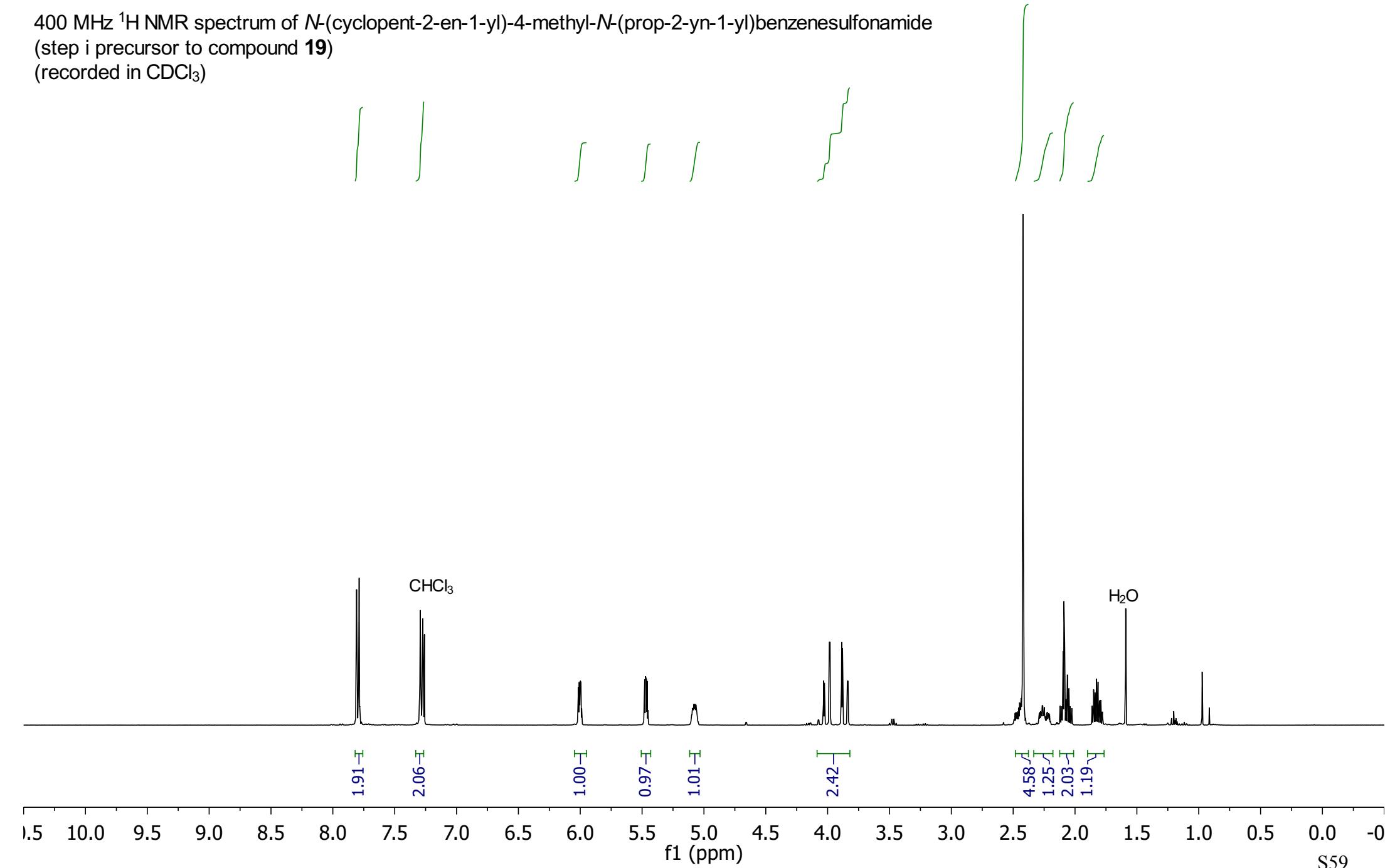
-7.5
-4.0

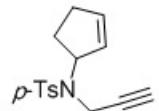
100 MHz ¹³C NMR spectrum of compound **18**
(recorded in CDCl₃)





400 MHz ^1H NMR spectrum of *N*-(cyclopent-2-en-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide
(step i precursor to compound **19**)
(recorded in CDCl_3)



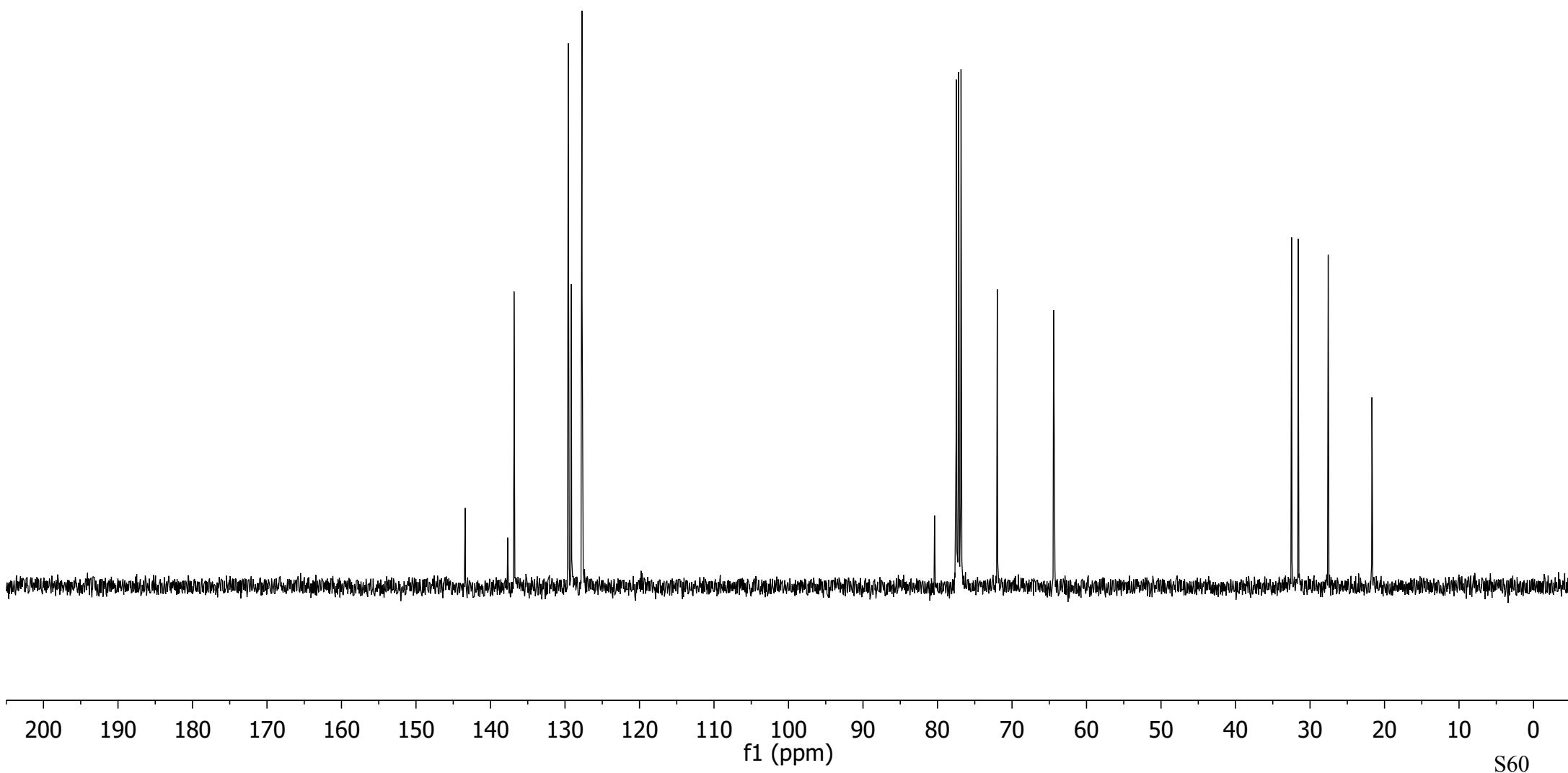


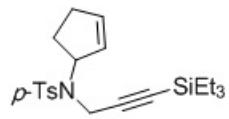
143.4
137.7
136.8
129.6
129.1
127.7

-80.4
-72.0
-64.4

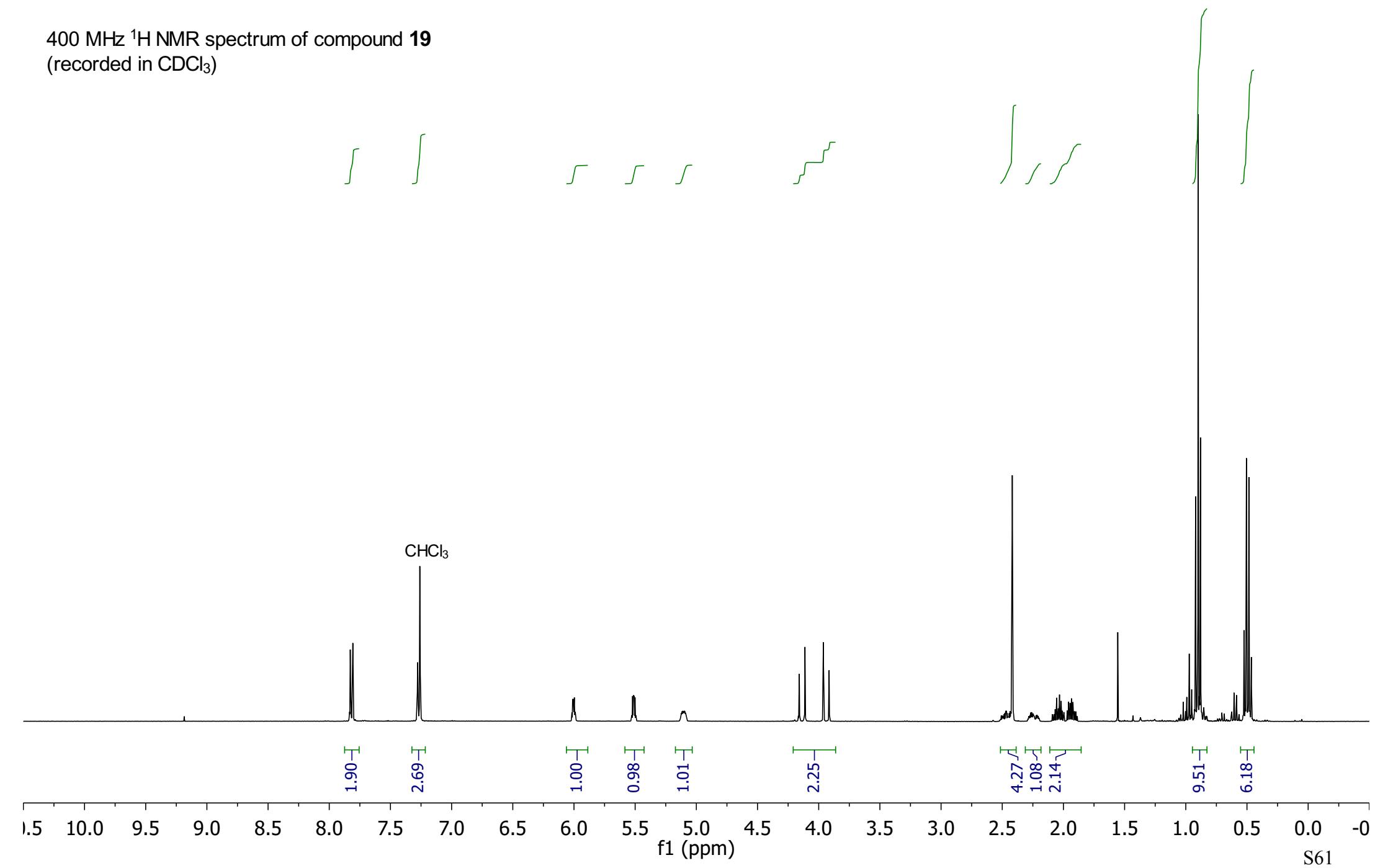
32.5
31.6
27.6
21.7

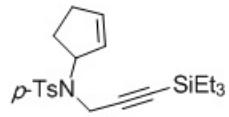
100 MHz ^{13}C NMR spectrum of *N*-(cyclopent-2-en-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide
(step i precursor to compound **19**)
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound **19**
 (recorded in CDCl_3)





100 MHz ^{13}C NMR spectrum of compound **19**
(recorded in CDCl_3)

143.2
138.1
136.7
129.5
129.3
127.7

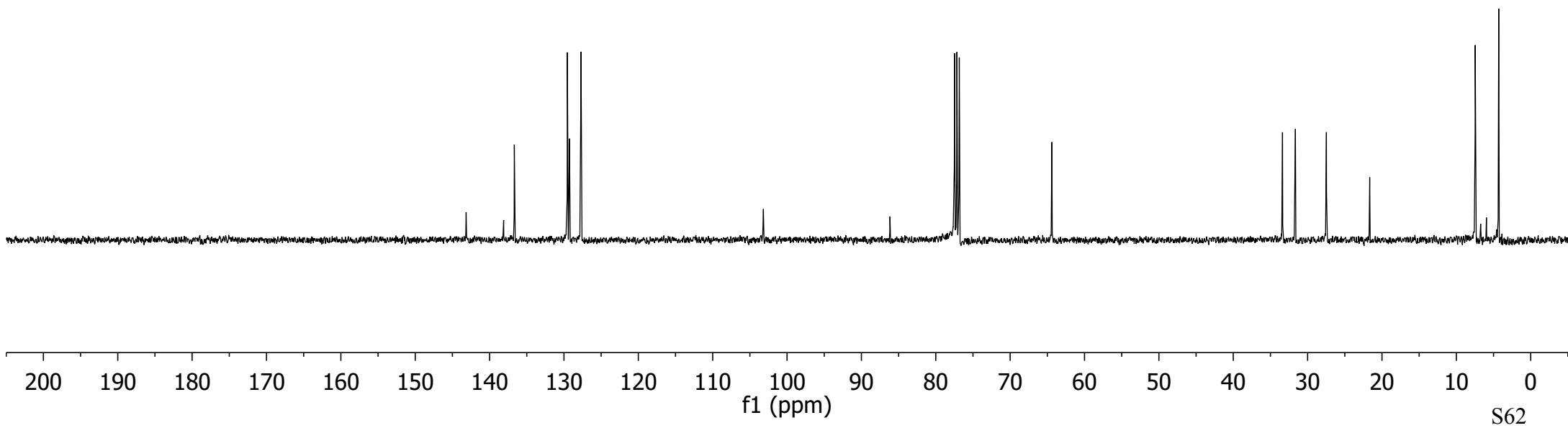
—103.2

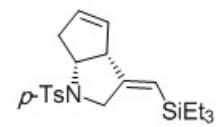
—86.2

—64.4

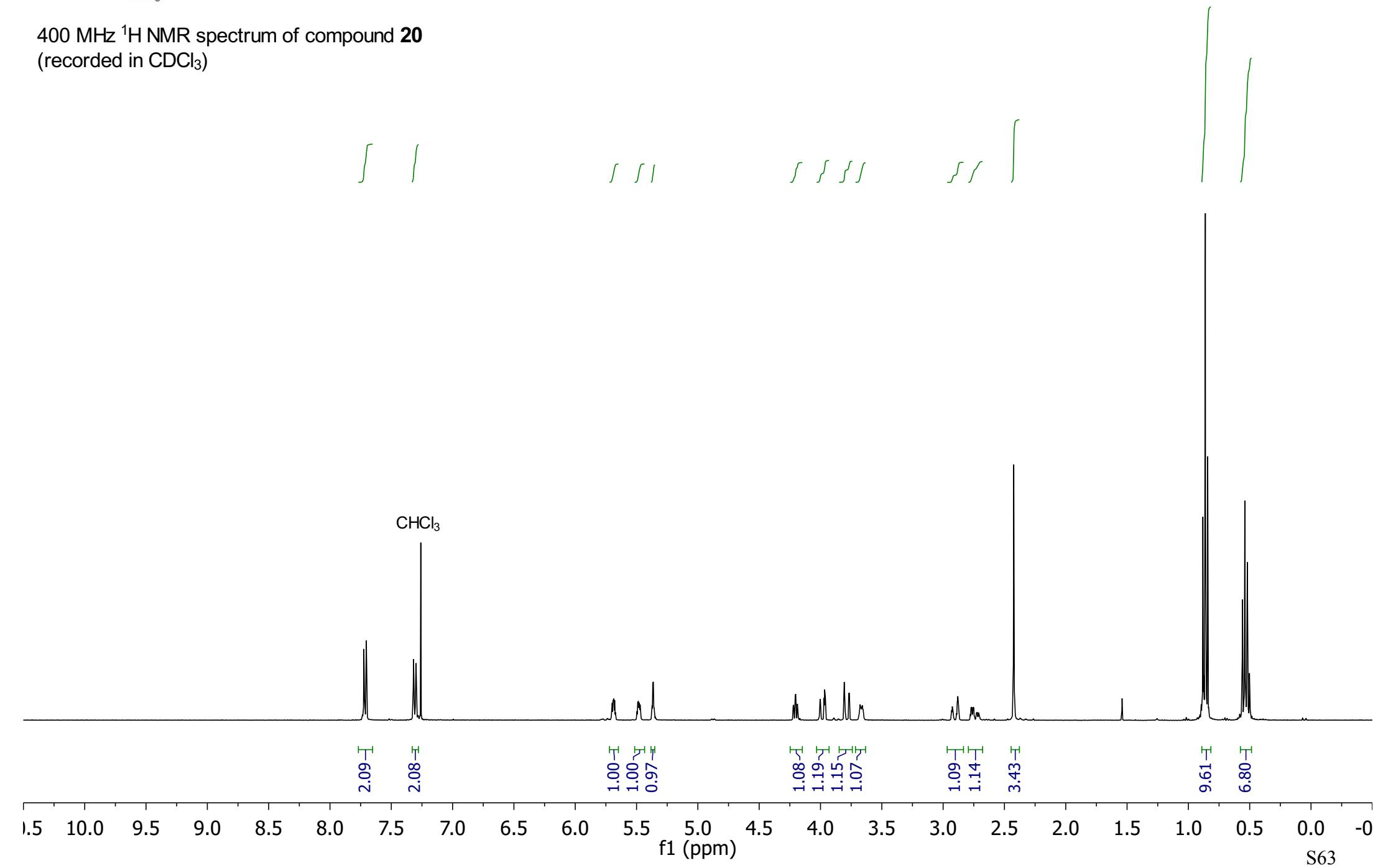
—33.4
—31.6
—27.5
—21.7

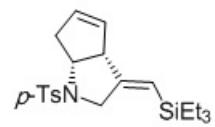
—7.5
—4.3



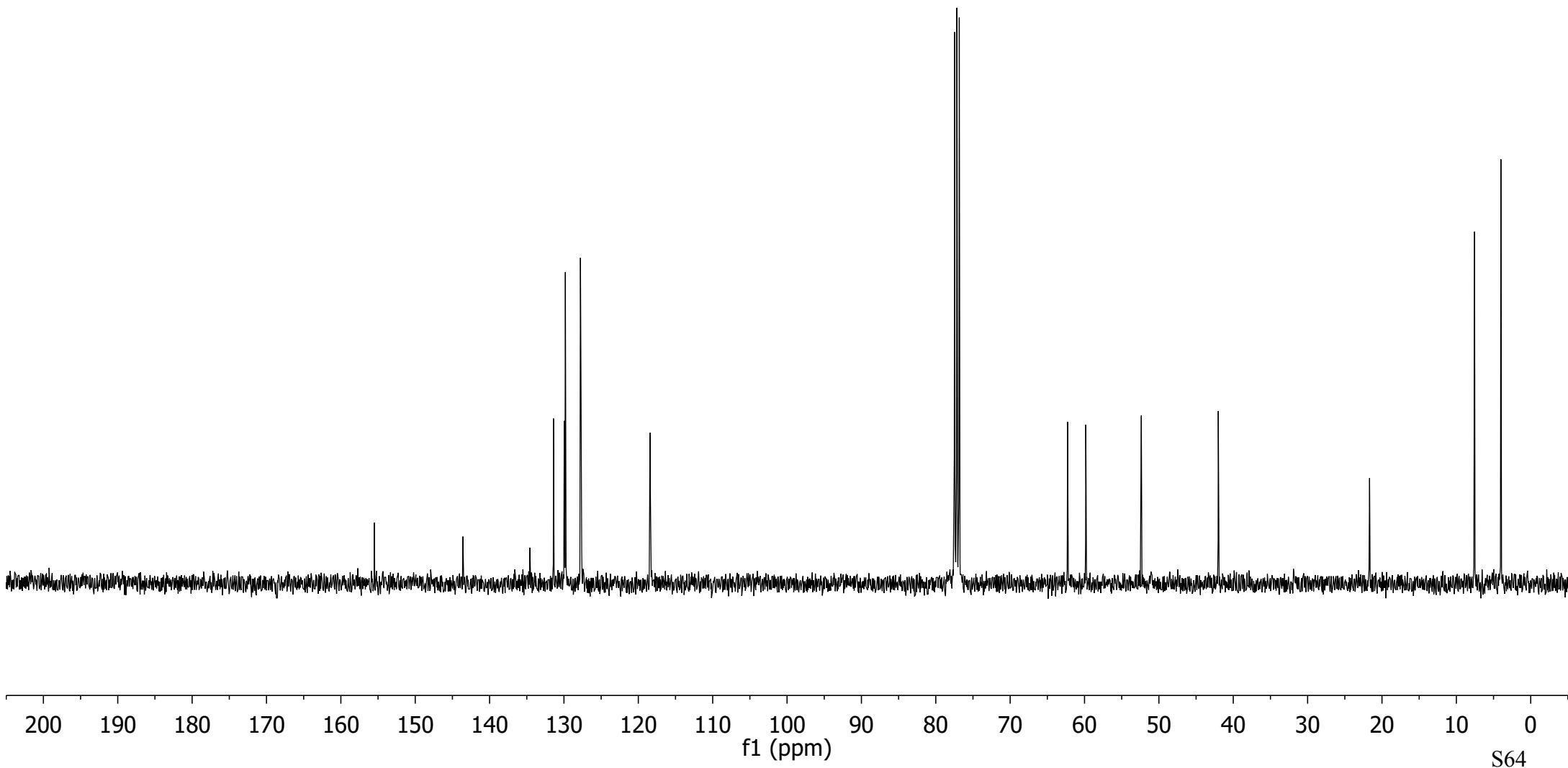


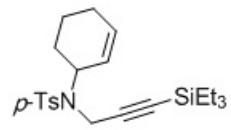
400 MHz ^1H NMR spectrum of compound **20**
(recorded in CDCl_3)



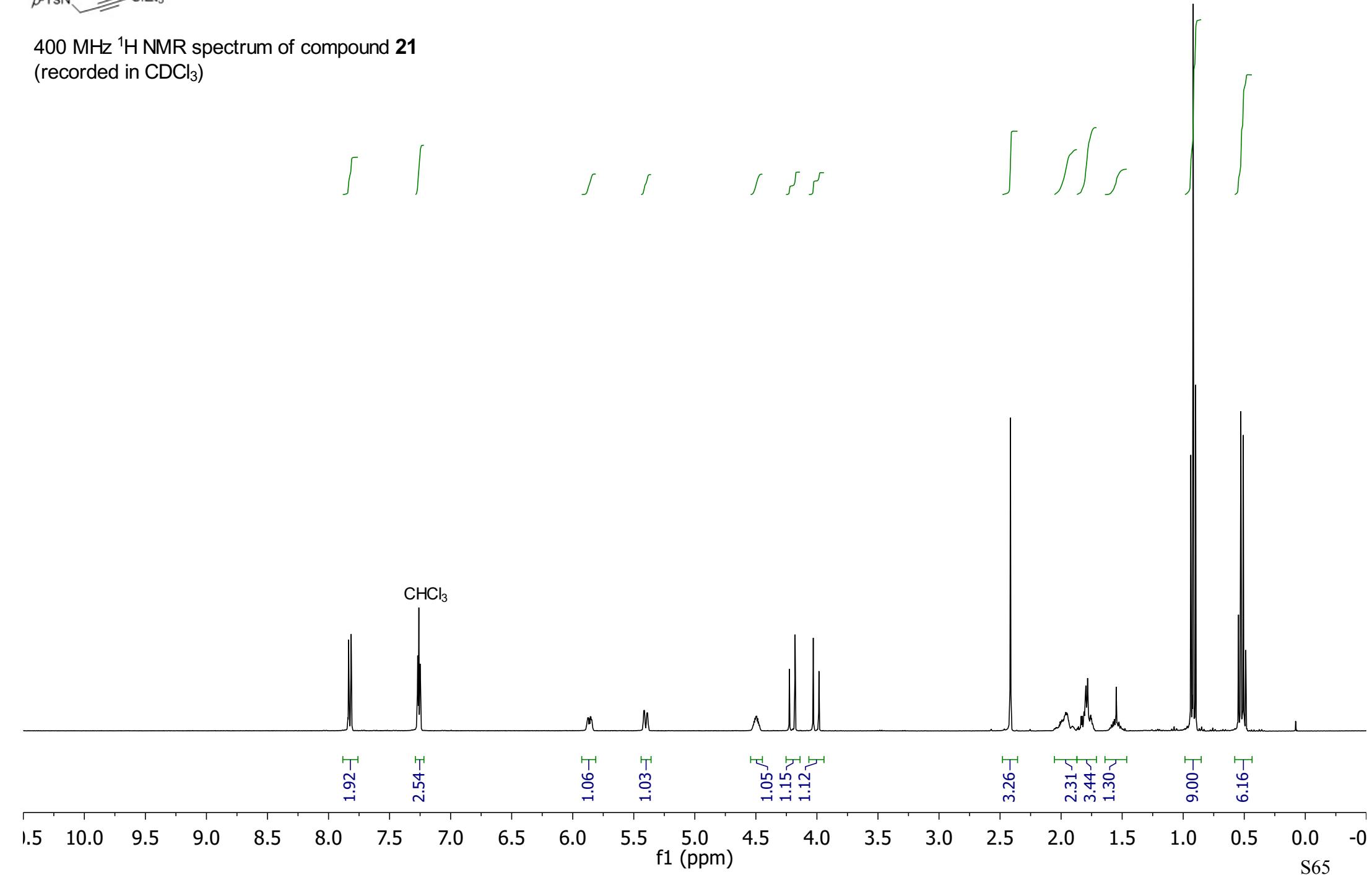


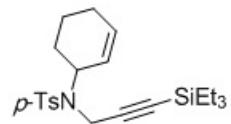
100 MHz ^{13}C NMR spectrum of compound **20**
(recorded in CDCl_3)





400 MHz ¹H NMR spectrum of compound **21**
(recorded in CDCl₃)





100 MHz ^{13}C NMR spectrum of compound **21**
(recorded in CDCl_3)

—143.1
—138.5
✓ 132.9
✓ 129.5
—127.6

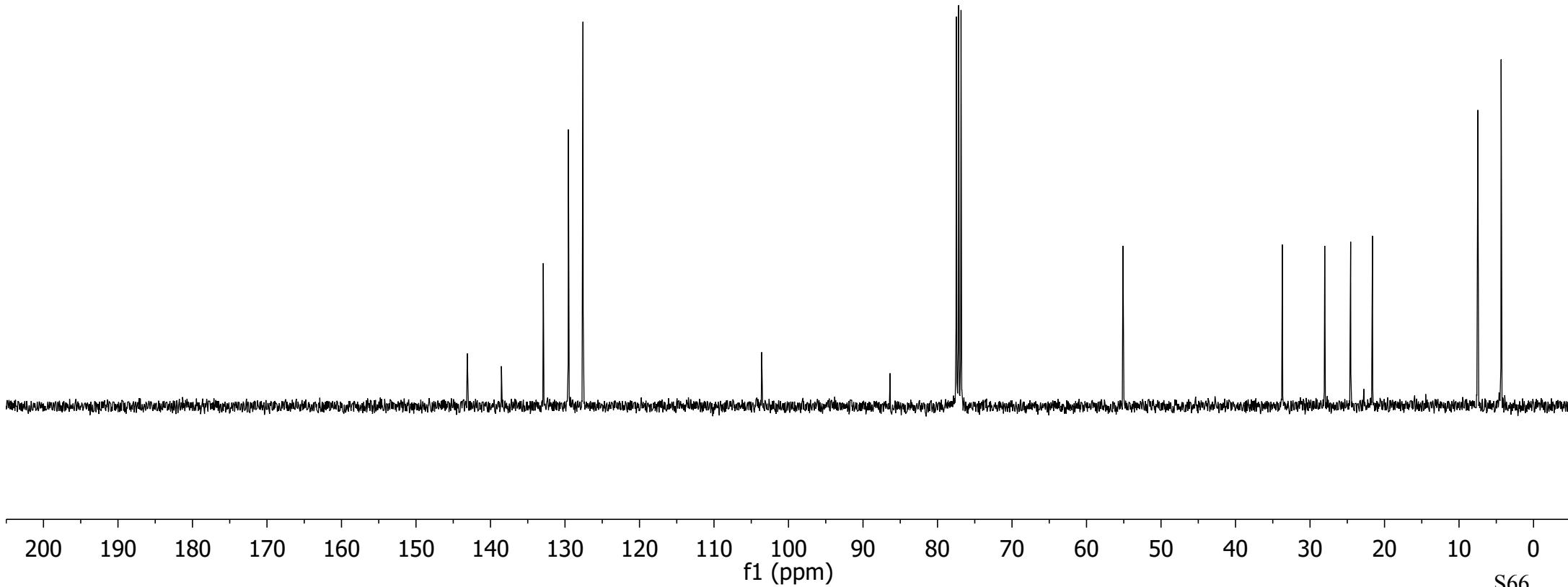
—103.6

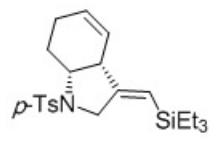
—86.4

—55.1

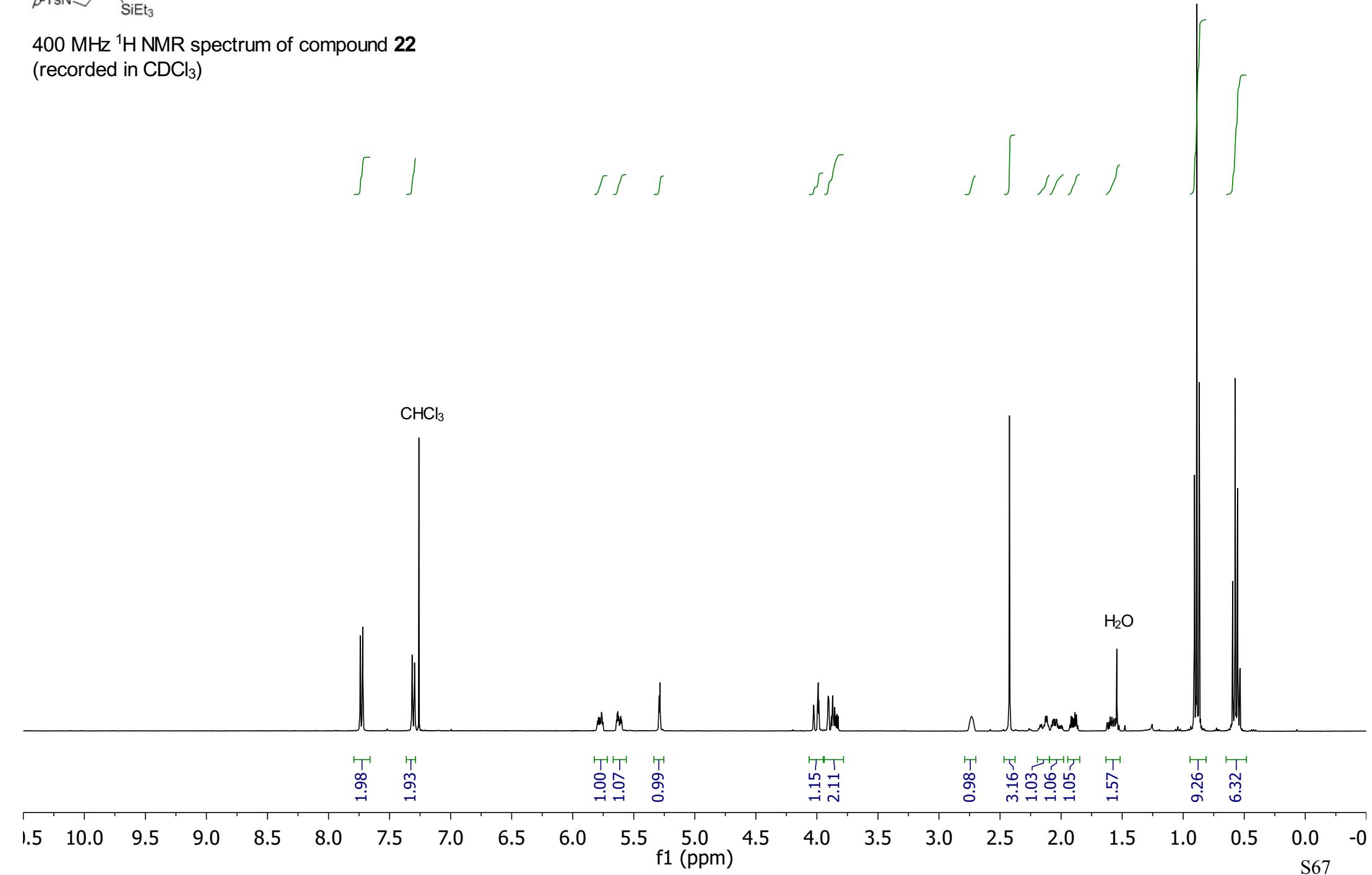
✓ 33.7
✓ 28.0
✓ 24.5
✓ 21.7
✓ 21.6

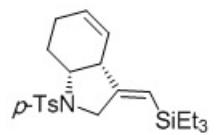
—7.5
—4.3



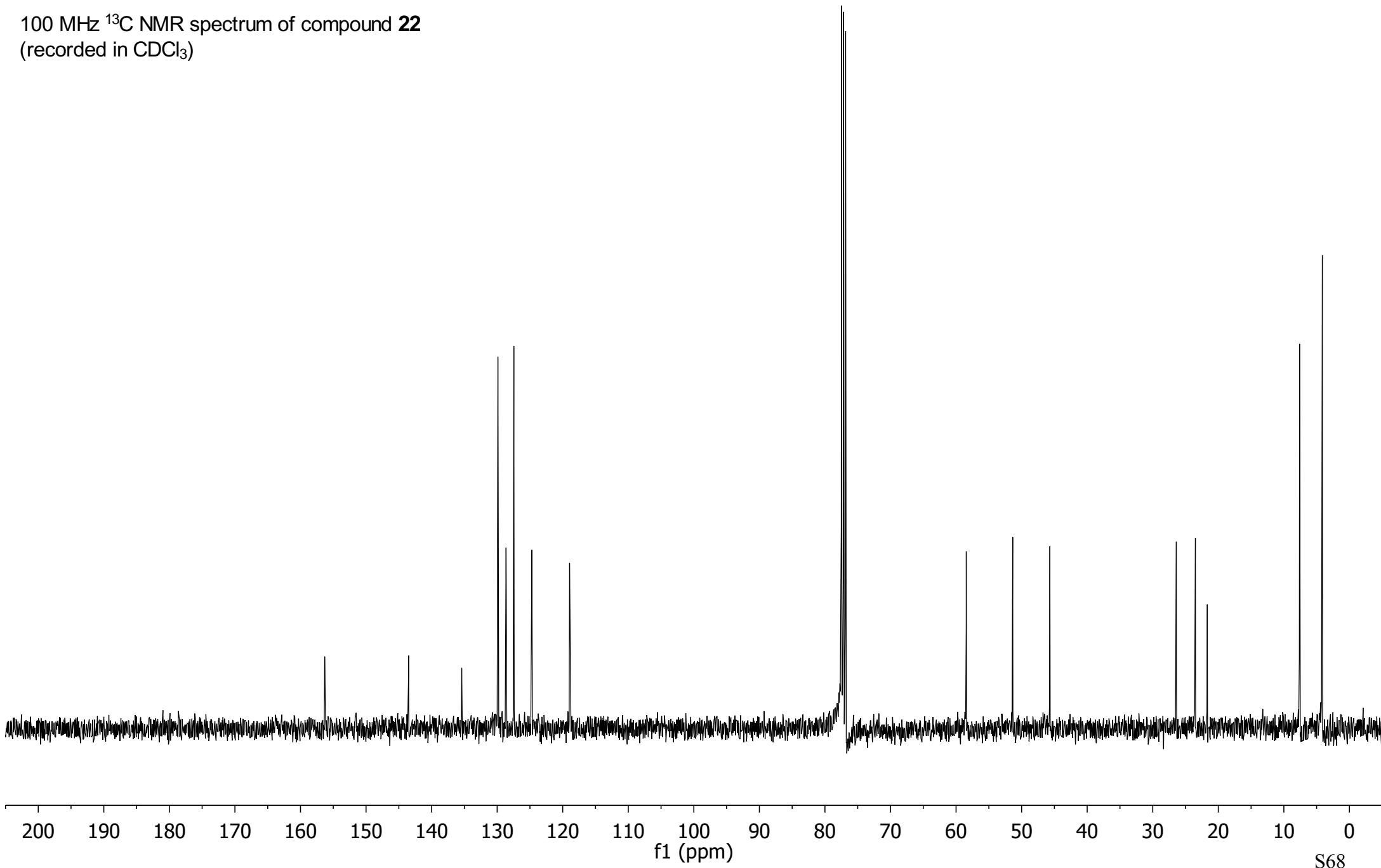


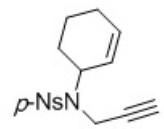
400 MHz ^1H NMR spectrum of compound **22**
(recorded in CDCl_3)



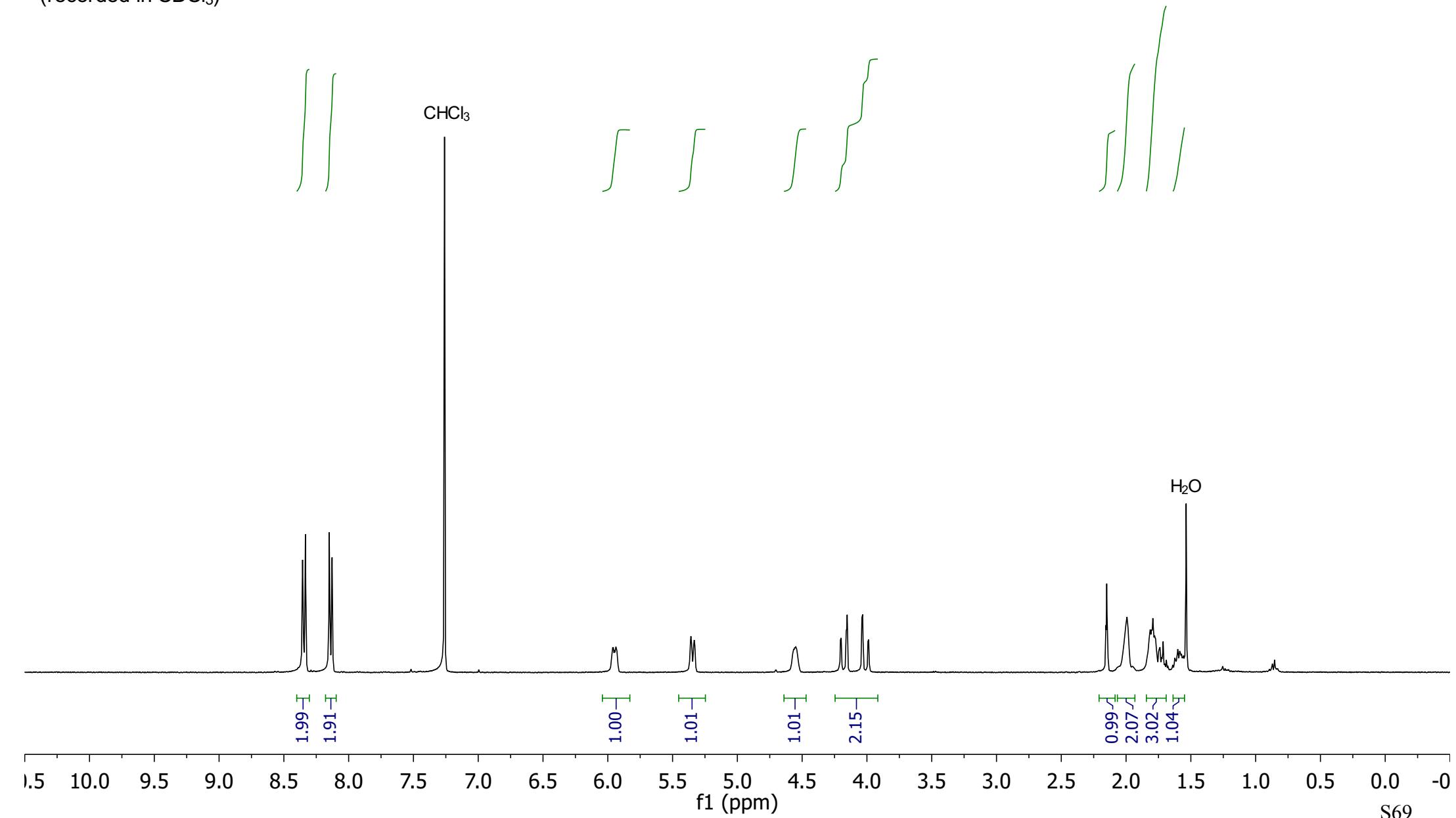


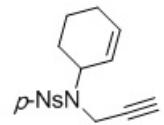
100 MHz ^{13}C NMR spectrum of compound **22**
(recorded in CDCl_3)



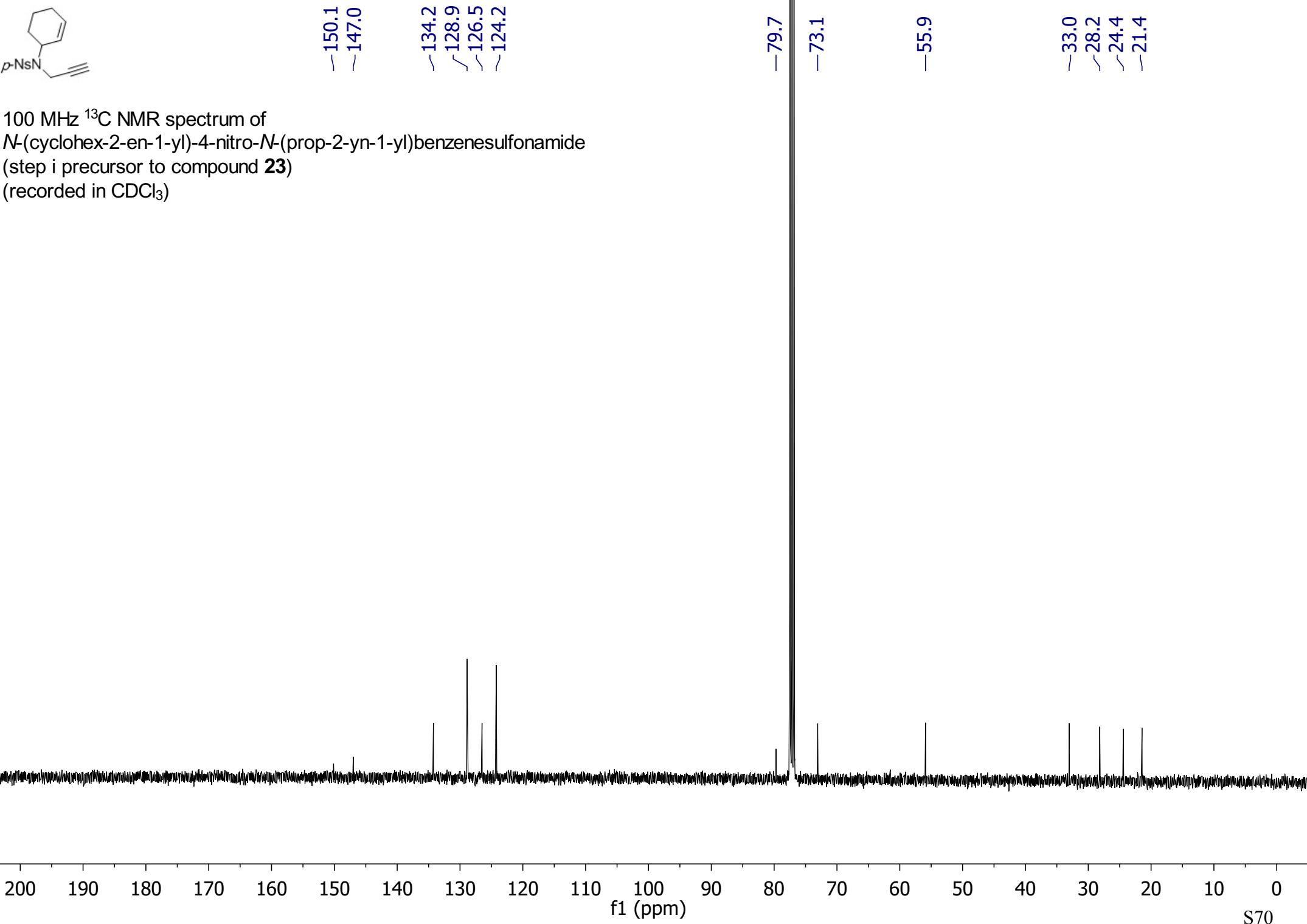


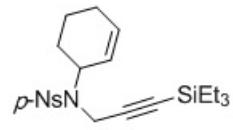
400 MHz ^1H NMR spectrum of *N*-(cyclohex-2-en-1-yl)-4-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide
(step i precursor to compound **23**)
(recorded in CDCl_3)



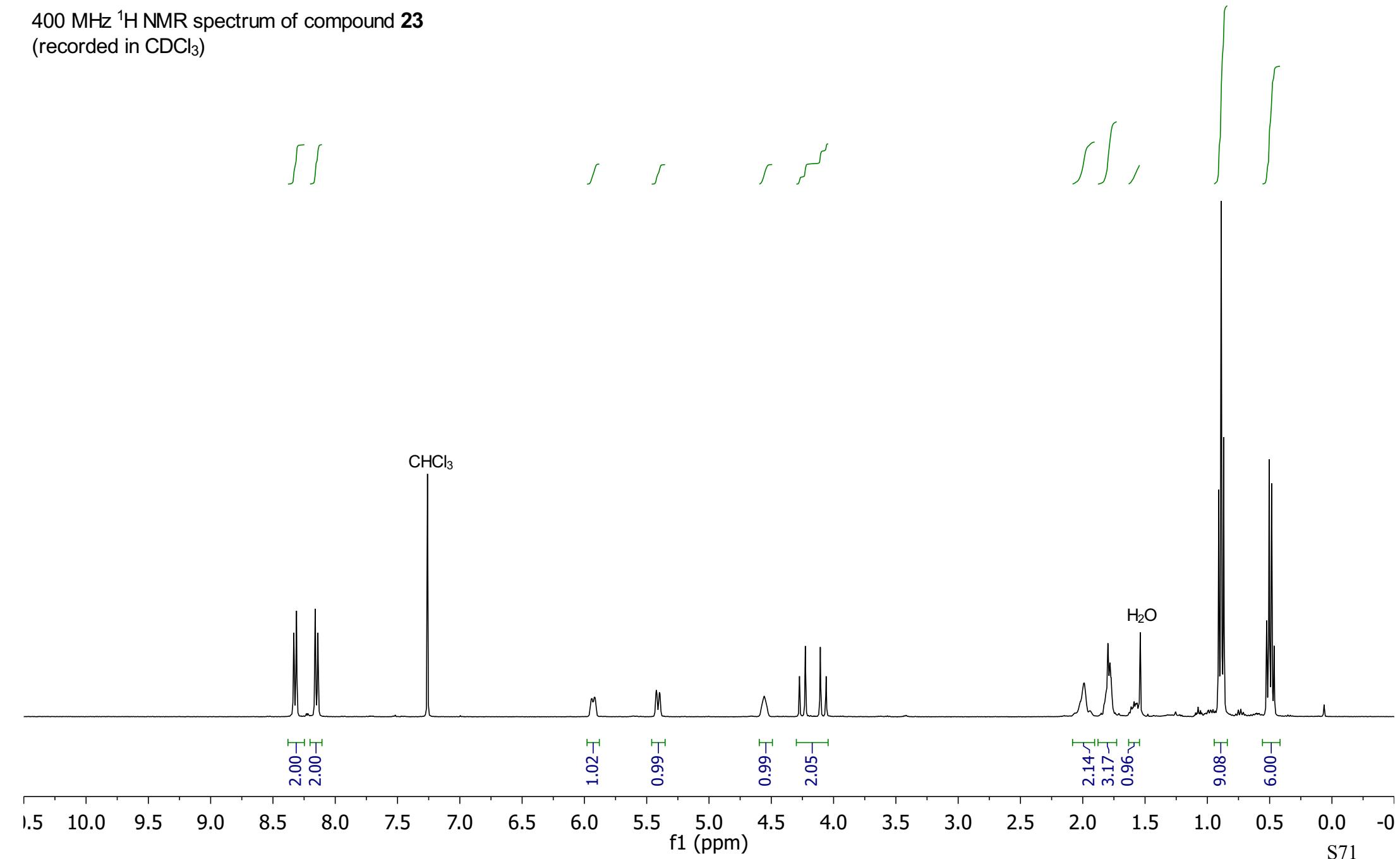


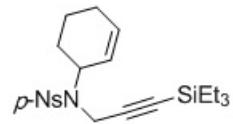
100 MHz ^{13}C NMR spectrum of
N-(cyclohex-2-en-1-yl)-4-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide
(step i precursor to compound **23**)
(recorded in CDCl_3)



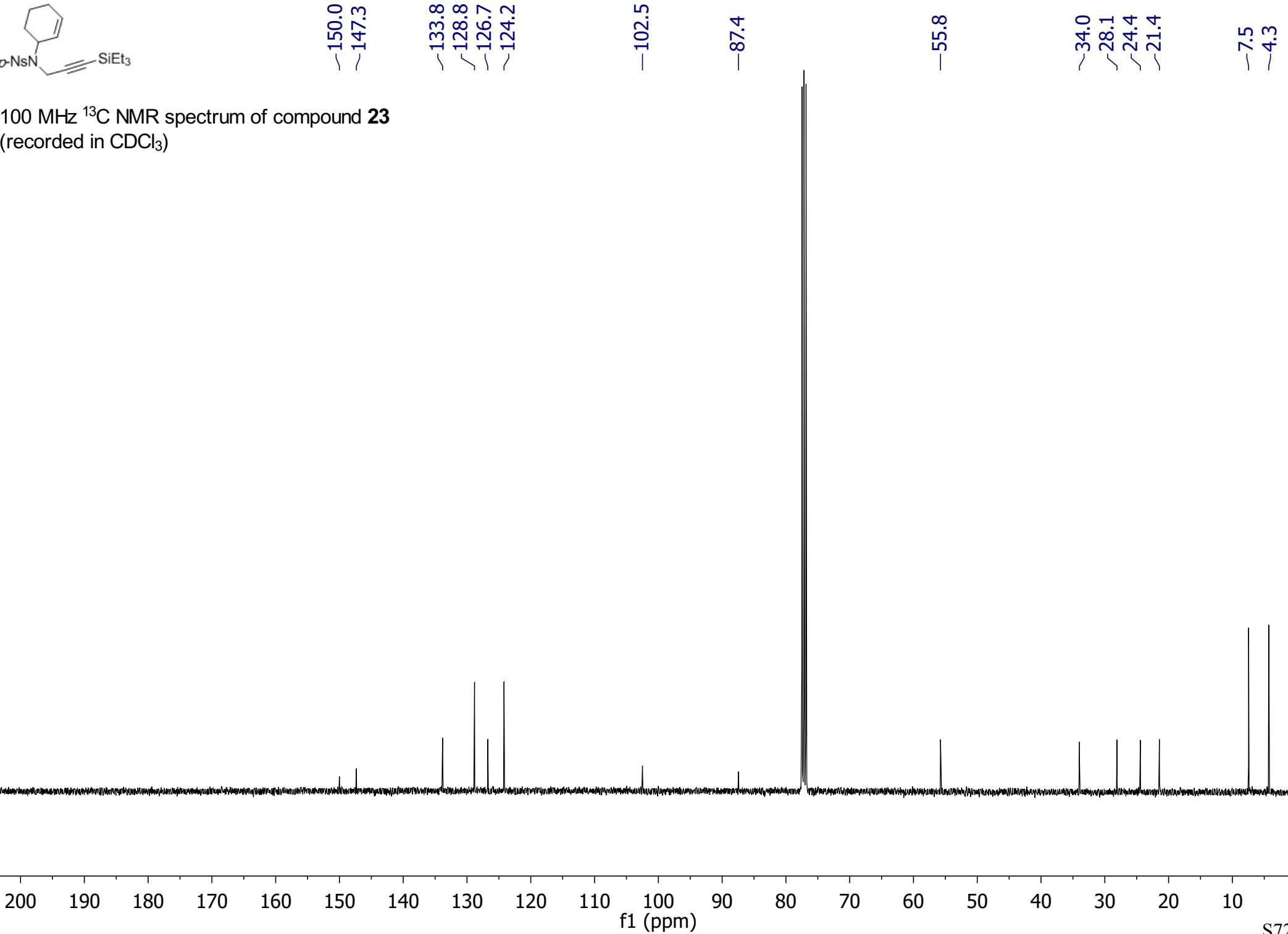


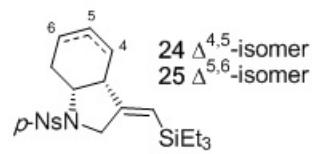
400 MHz ^1H NMR spectrum of compound **23**
(recorded in CDCl_3)



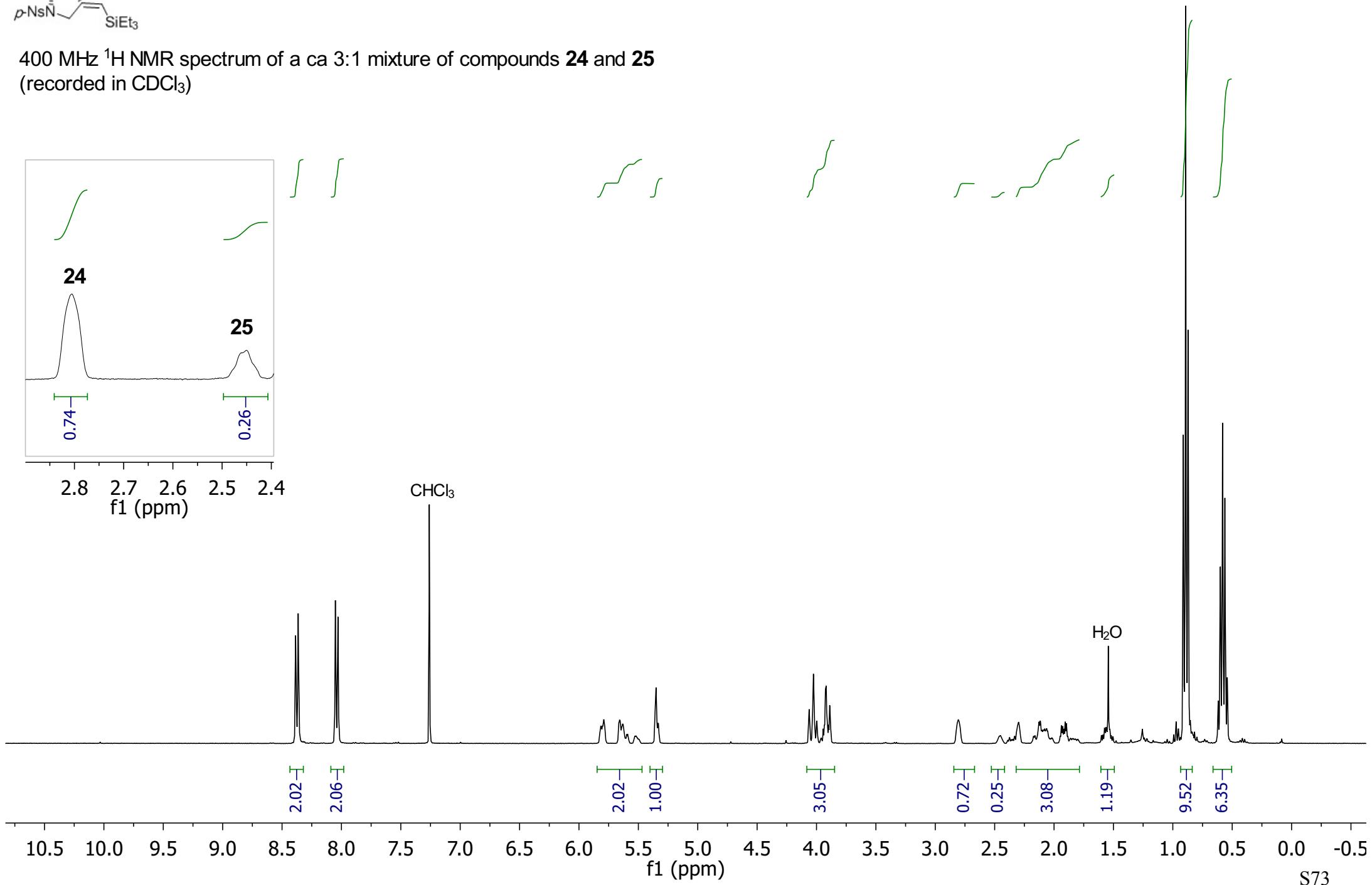


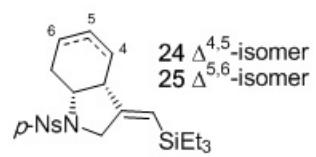
100 MHz ^{13}C NMR spectrum of compound **23**
(recorded in CDCl_3)



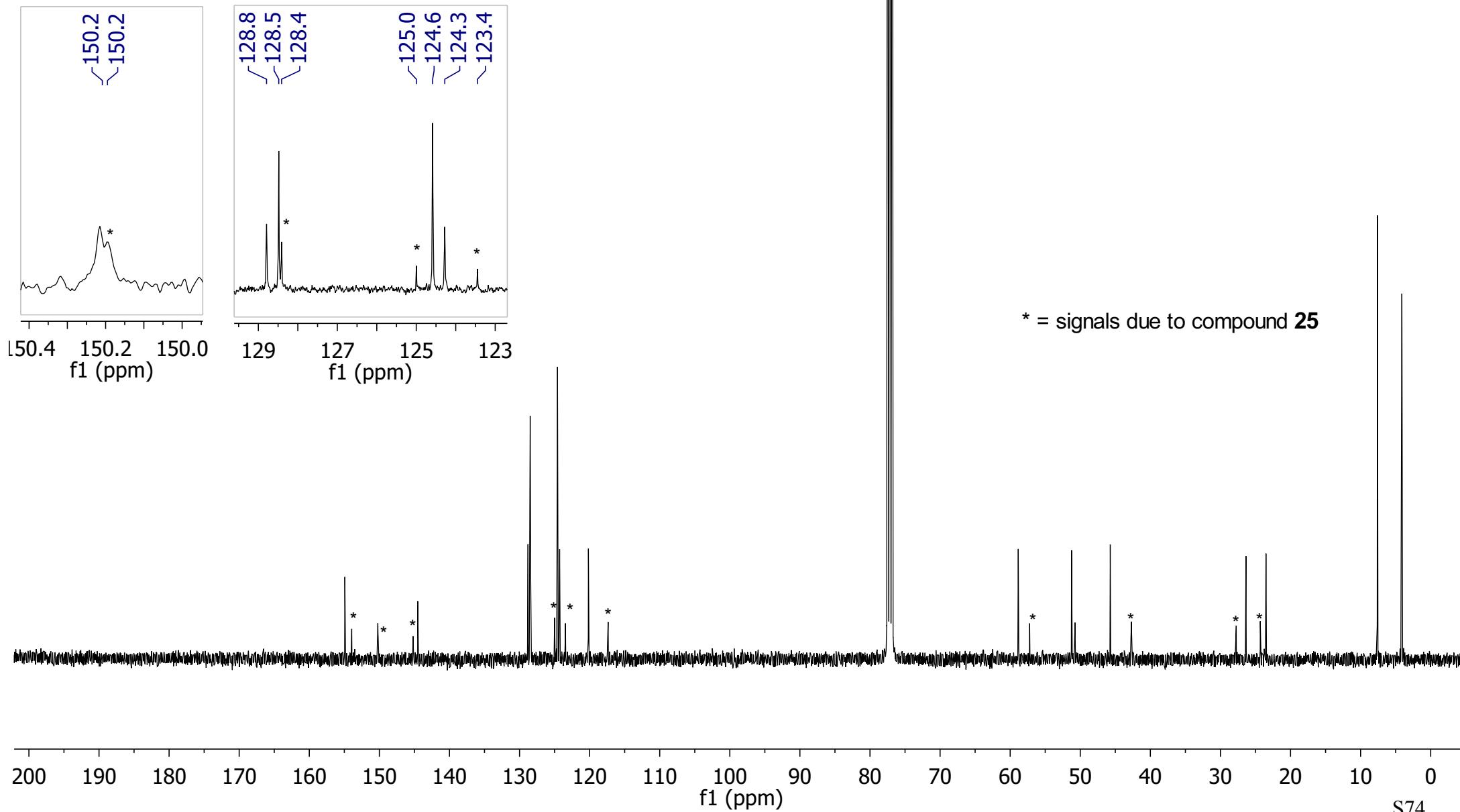


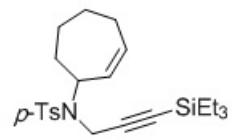
400 MHz ^1H NMR spectrum of a ca 3:1 mixture of compounds **24** and **25**
 (recorded in CDCl_3)



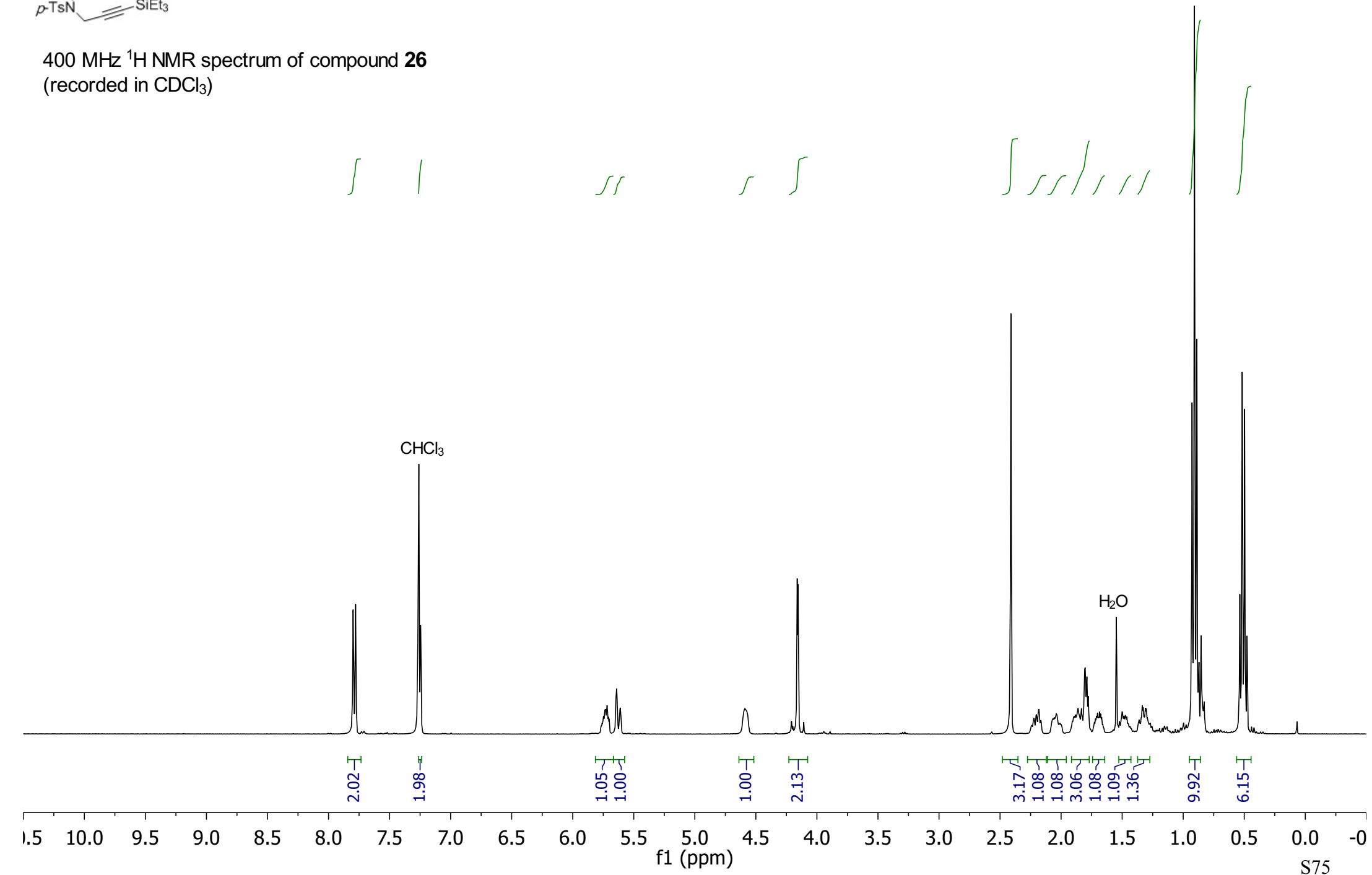


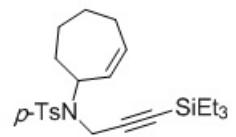
100 MHz ^{13}C NMR spectrum of a ca 3:1 mixture of compounds **24** and **25**
 (recorded in CDCl_3)





400 MHz ¹H NMR spectrum of compound **26**
(recorded in CDCl₃)





100 MHz ^{13}C NMR spectrum of compound **26**
(recorded in CDCl_3)

143.1
138.3
133.7
132.3
129.5
127.6

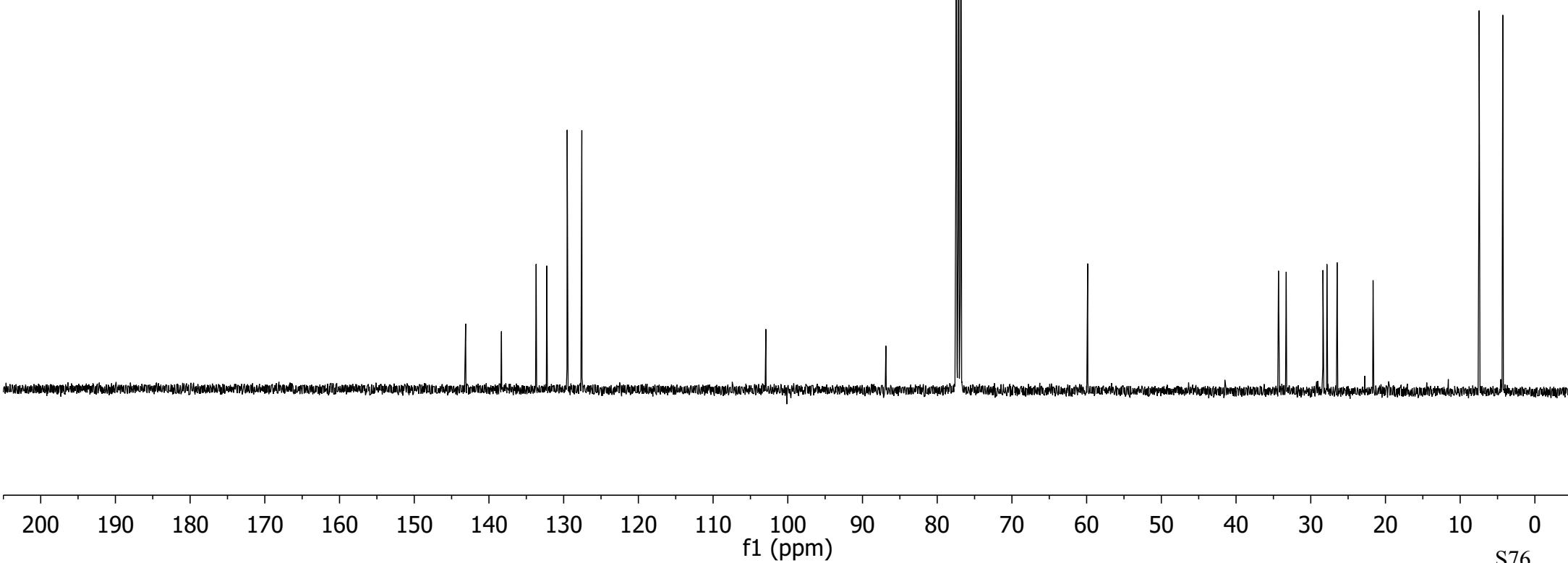
-102.9

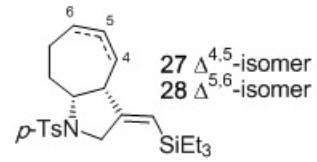
-86.9

-59.9

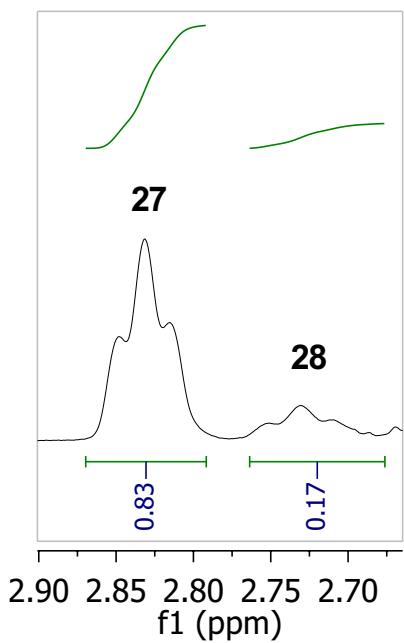
34.3
33.3
28.4
27.8
26.5
21.7

-7.5
-4.3

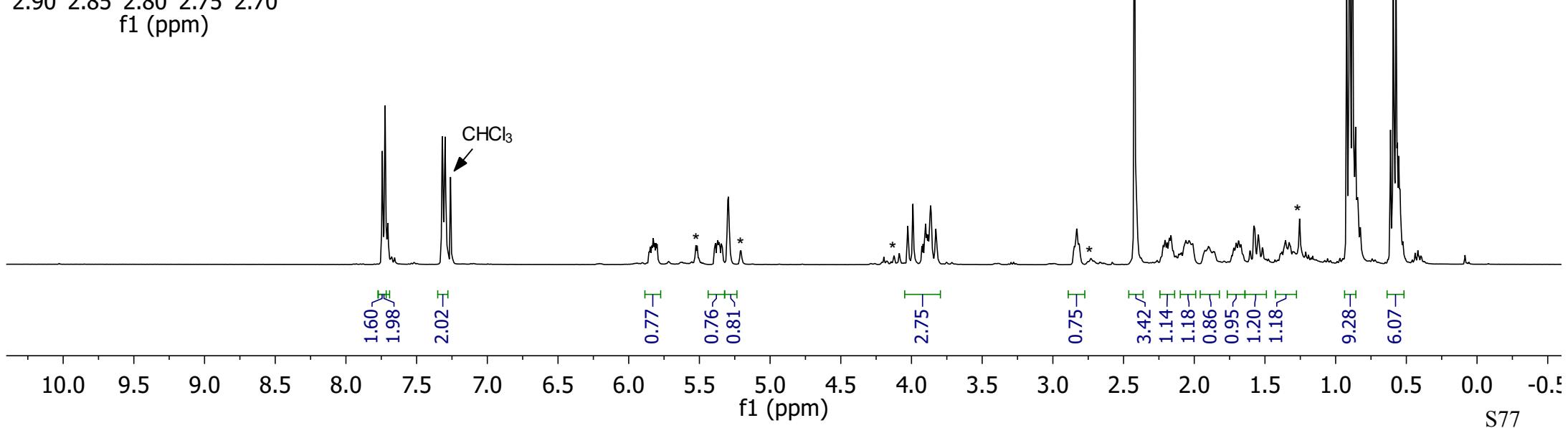


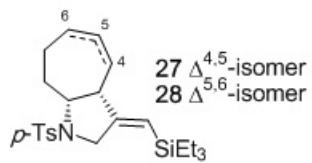


400 MHz ^1H NMR spectrum of a ca 4:1 mixture of compounds **27** and **28** (recorded in CDCl_3)

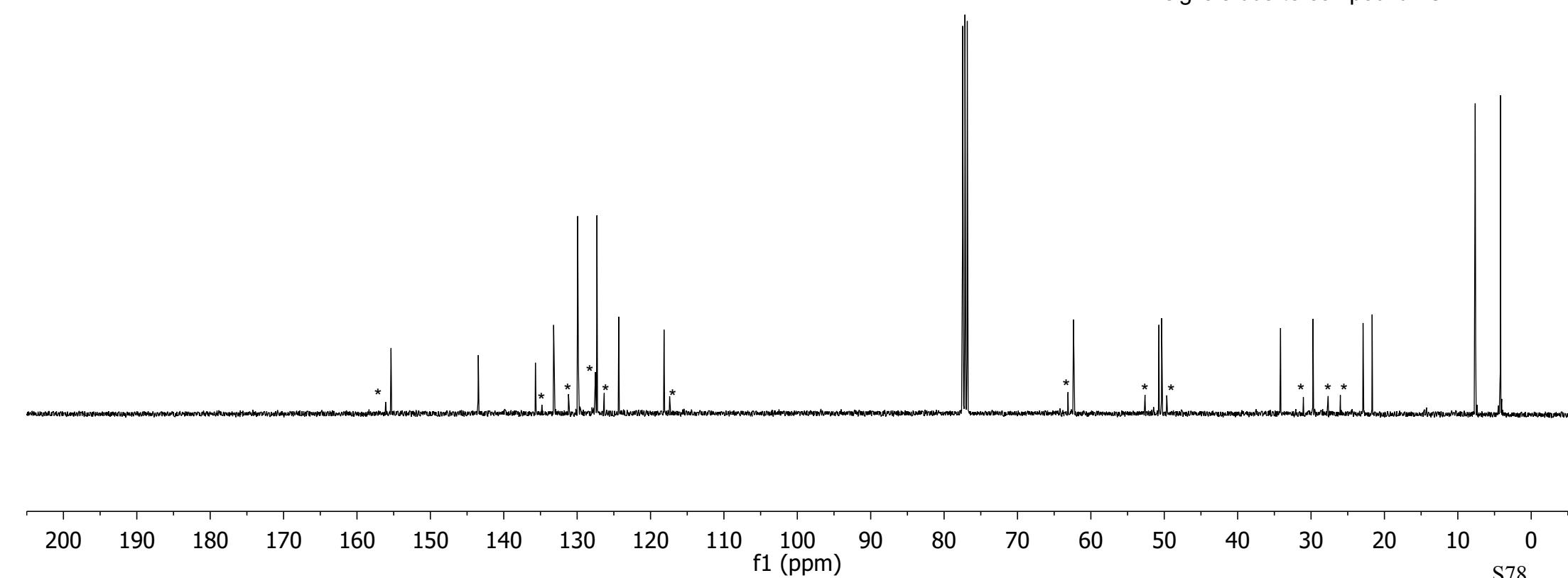


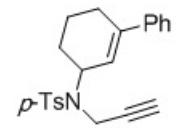
* = signals due to compound **28**



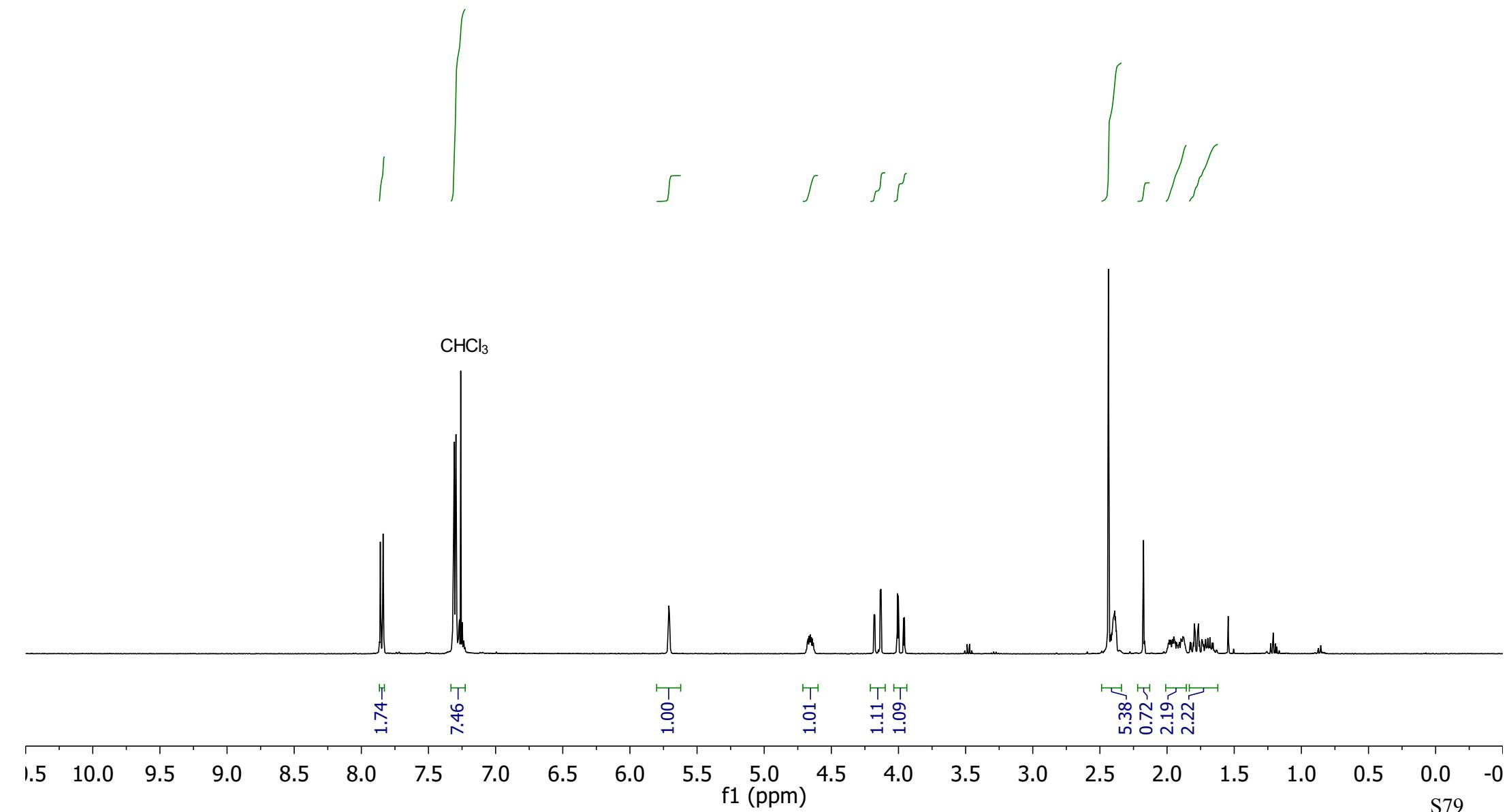


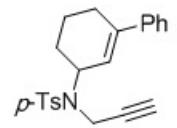
100 MHz ^{13}C NMR spectrum of a ca 4:1 mixture of compounds **27** and **28**
 (recorded in CDCl_3)





400 MHz ^1H NMR spectrum of 4-methyl- N -(prop-2-yn-1-yl)- N -(3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)benzenesulfonamide
(step i precursor to compound **29**)
(recorded in CDCl_3)



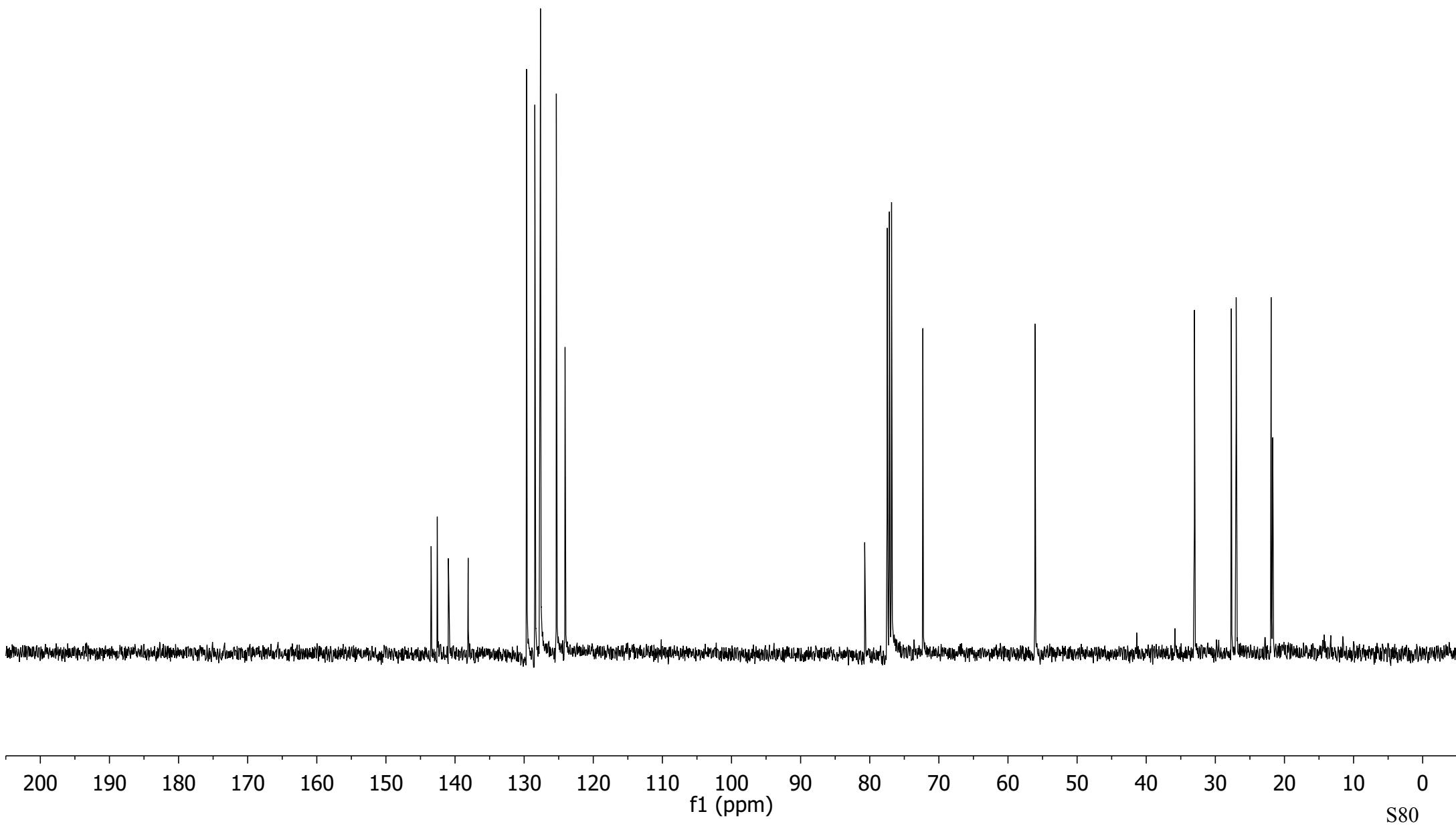


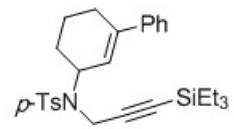
143.5
142.6
141.0
138.1
129.6
128.5
127.7
127.6
125.3
124.1

-80.7
-72.3
-56.1

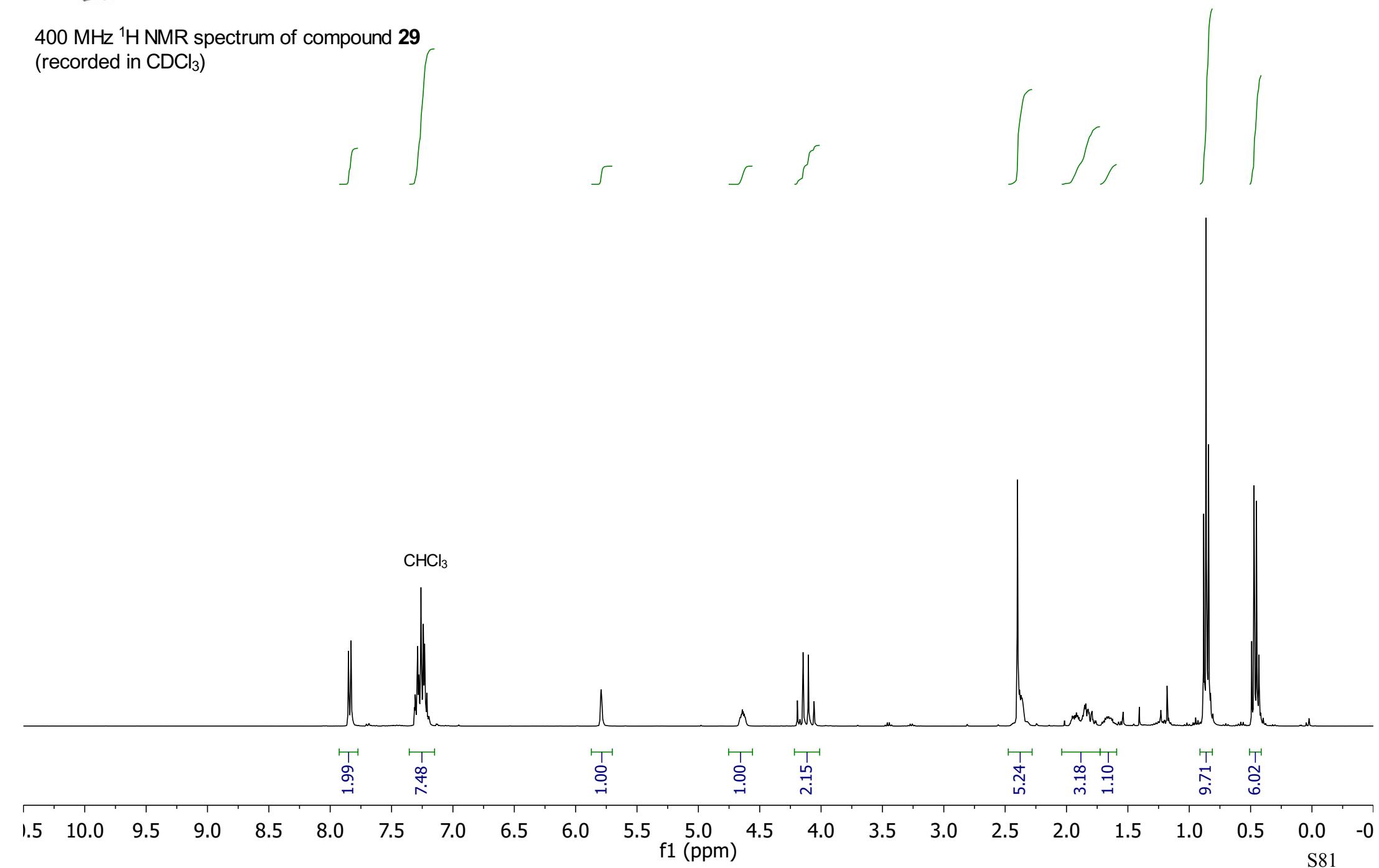
33.0
27.7
27.0
21.9
21.7

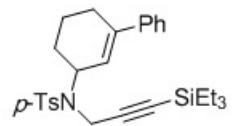
100 MHz ^{13}C NMR spectrum of 4-methyl- N -(prop-2-yn-1-yl)- N -(3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)benzenesulfonamide
(step i precursor to compound **29**)
(recorded in CDCl_3)





400 MHz ¹H NMR spectrum of compound **29**
(recorded in CDCl₃)





100 MHz ^{13}C NMR spectrum of compound **29**
(recorded in CDCl_3)

143.2
142.3
141.1
138.5
129.6
128.4
127.7
127.6
125.4
124.3

-103.5

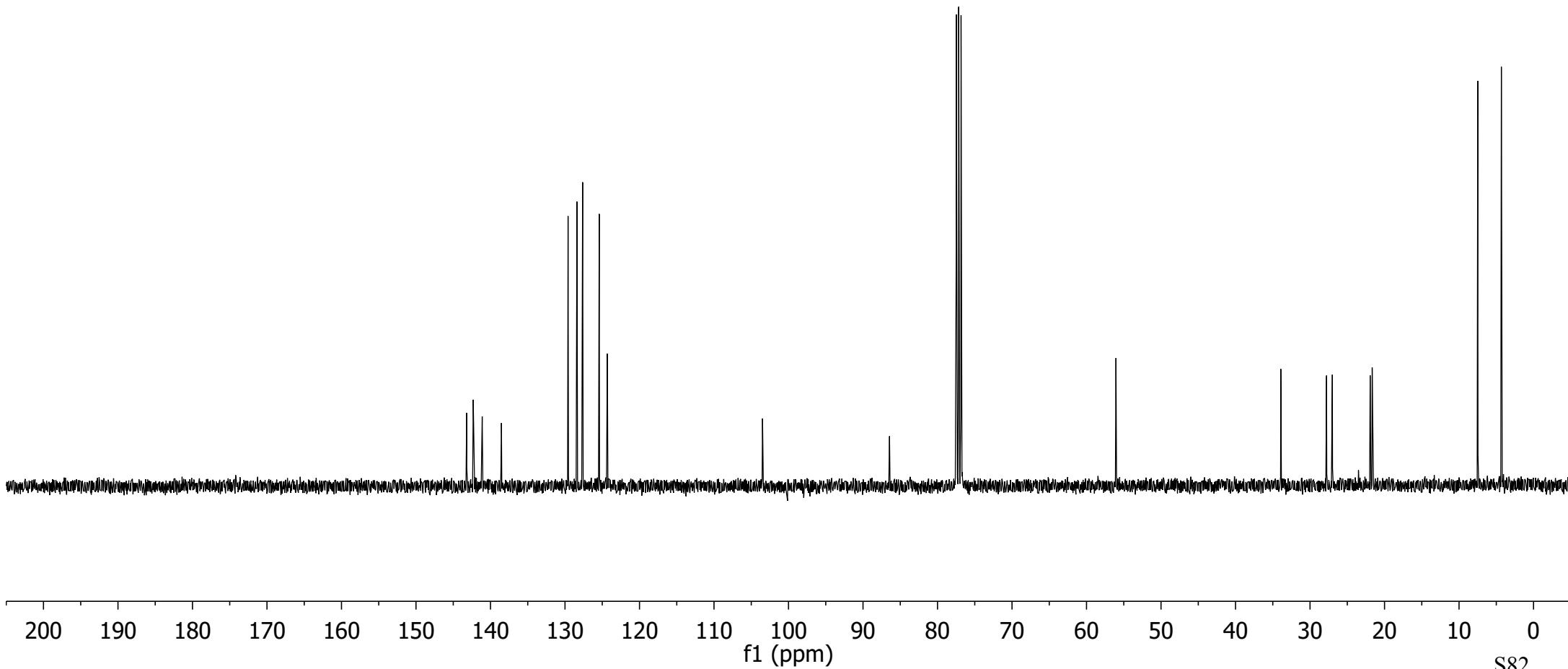
-86.4

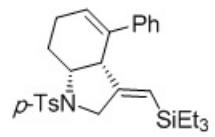
-56.0

33.9
27.8
27.0
21.9
21.7

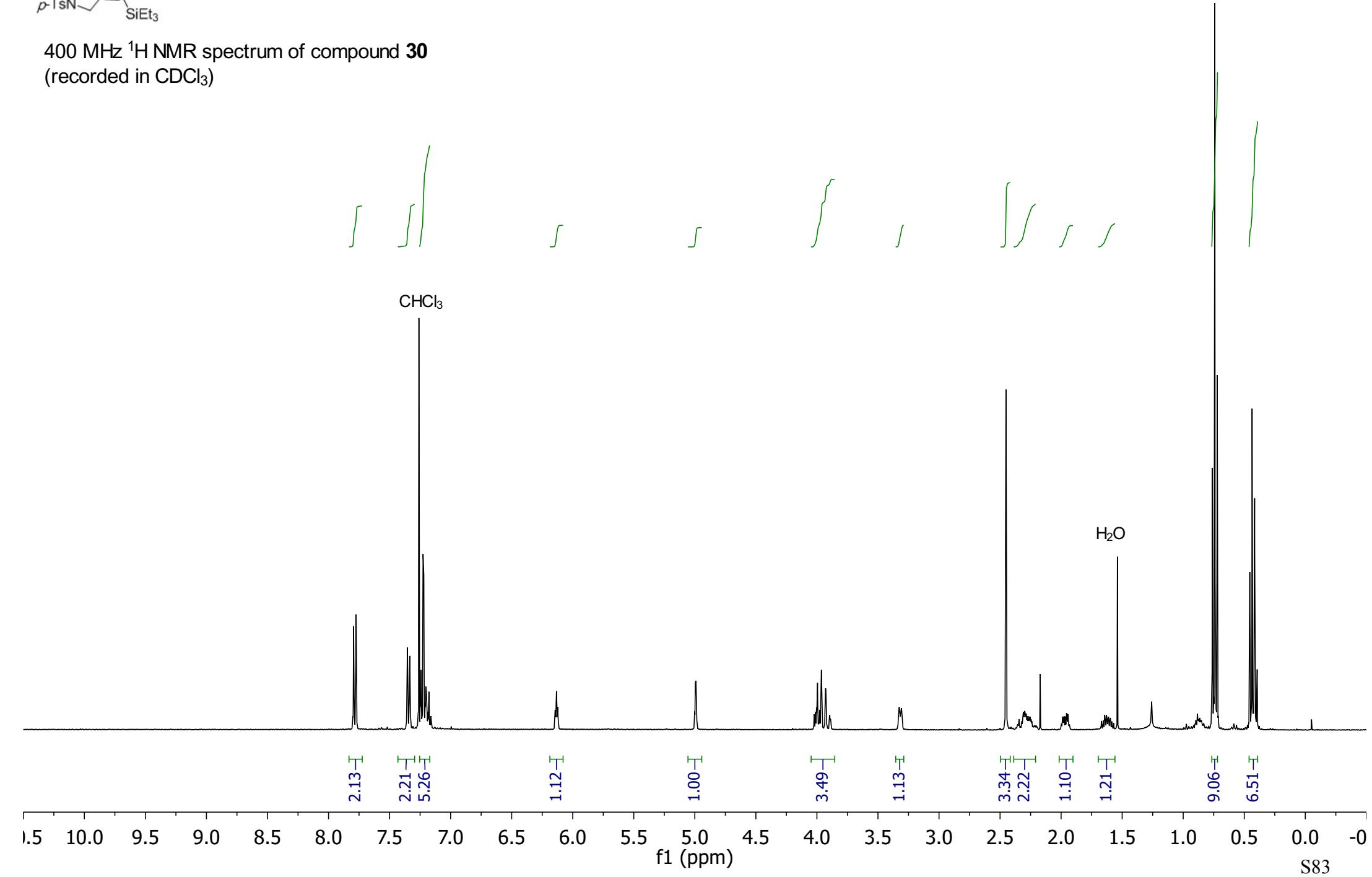
-7.5

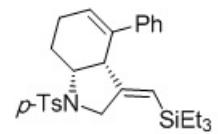
-4.3



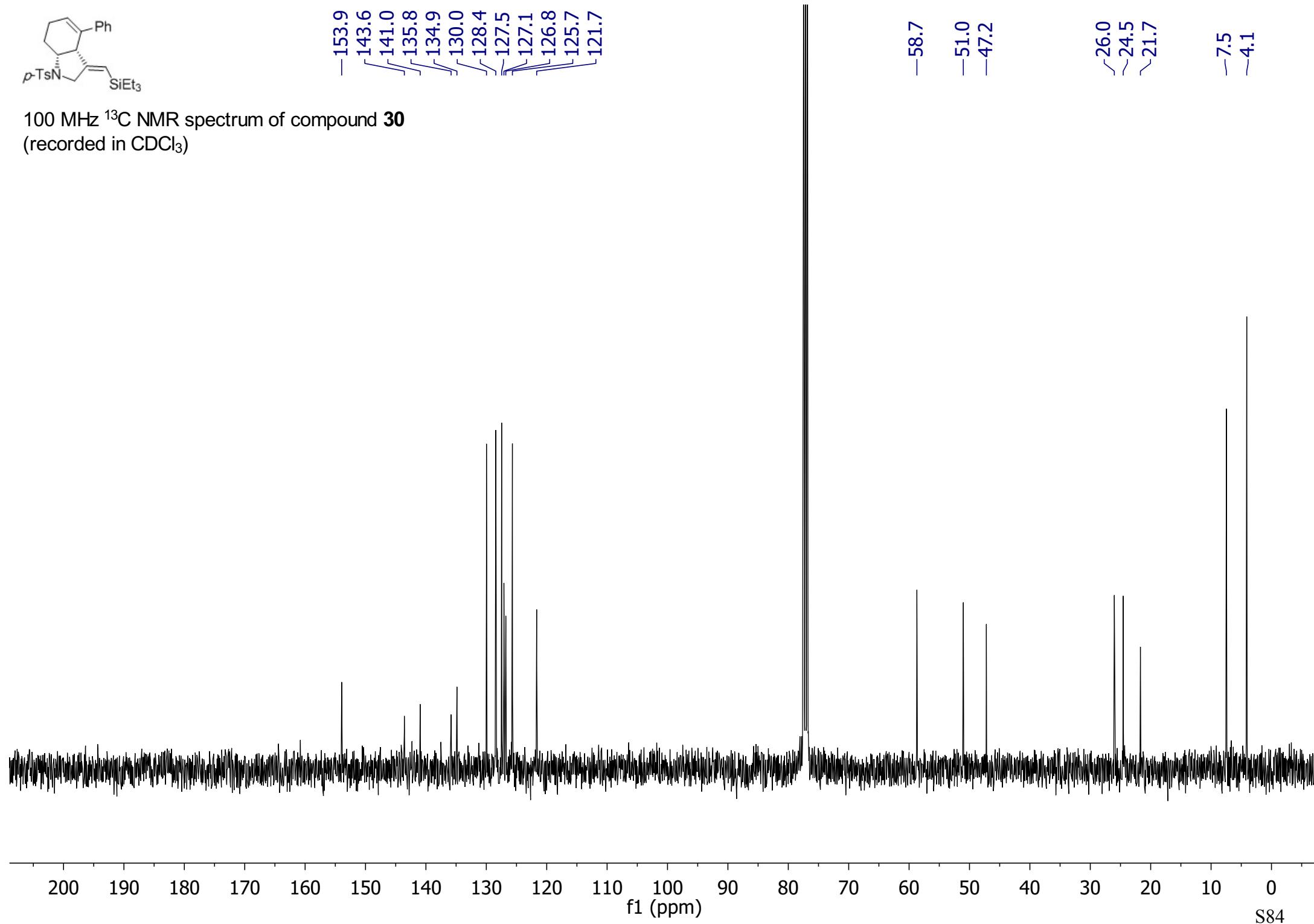


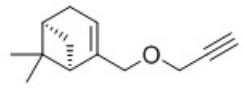
400 MHz ^1H NMR spectrum of compound **30**
(recorded in CDCl_3)



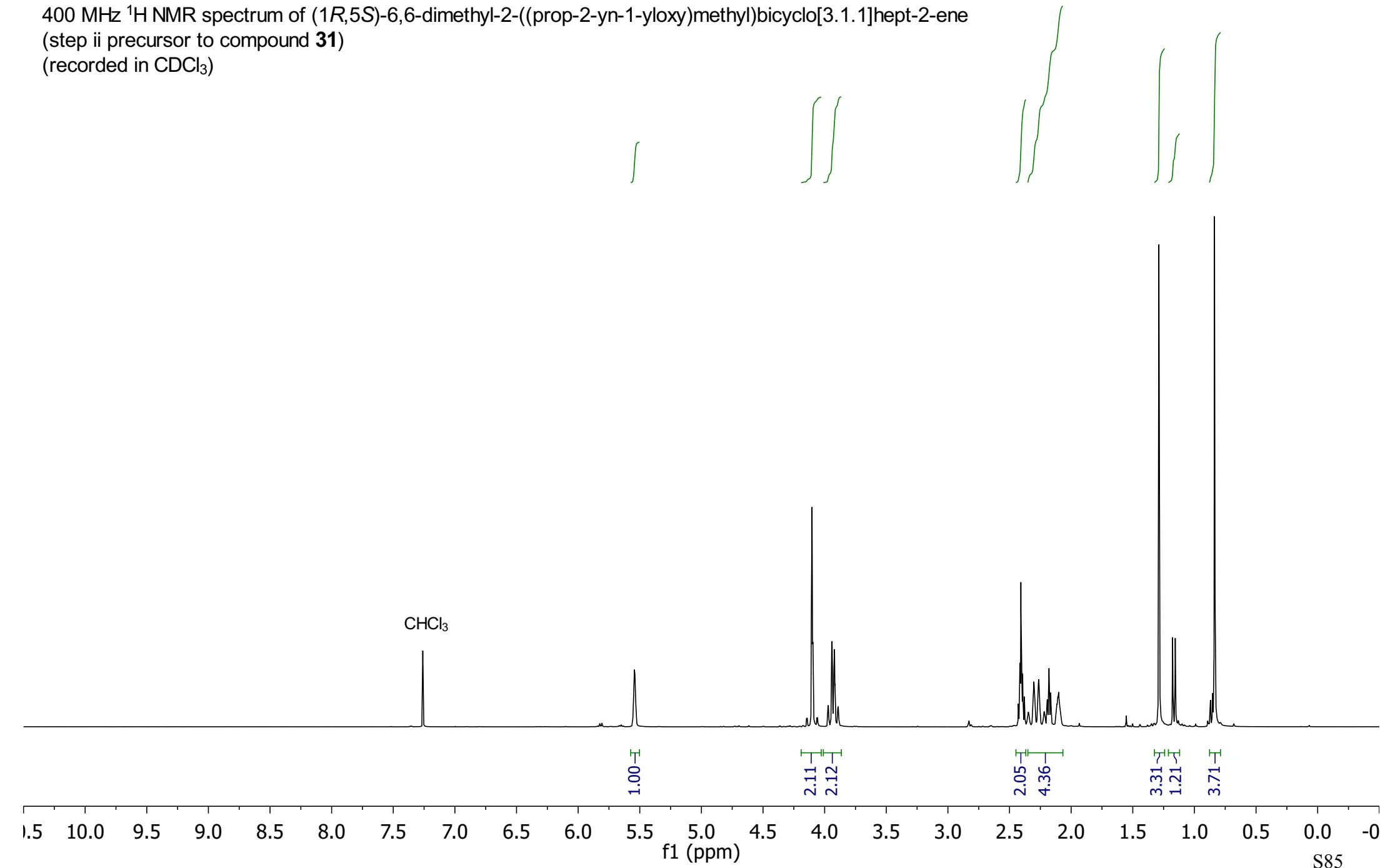


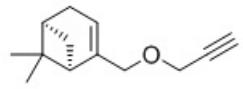
100 MHz ^{13}C NMR spectrum of compound **30**
(recorded in CDCl_3)





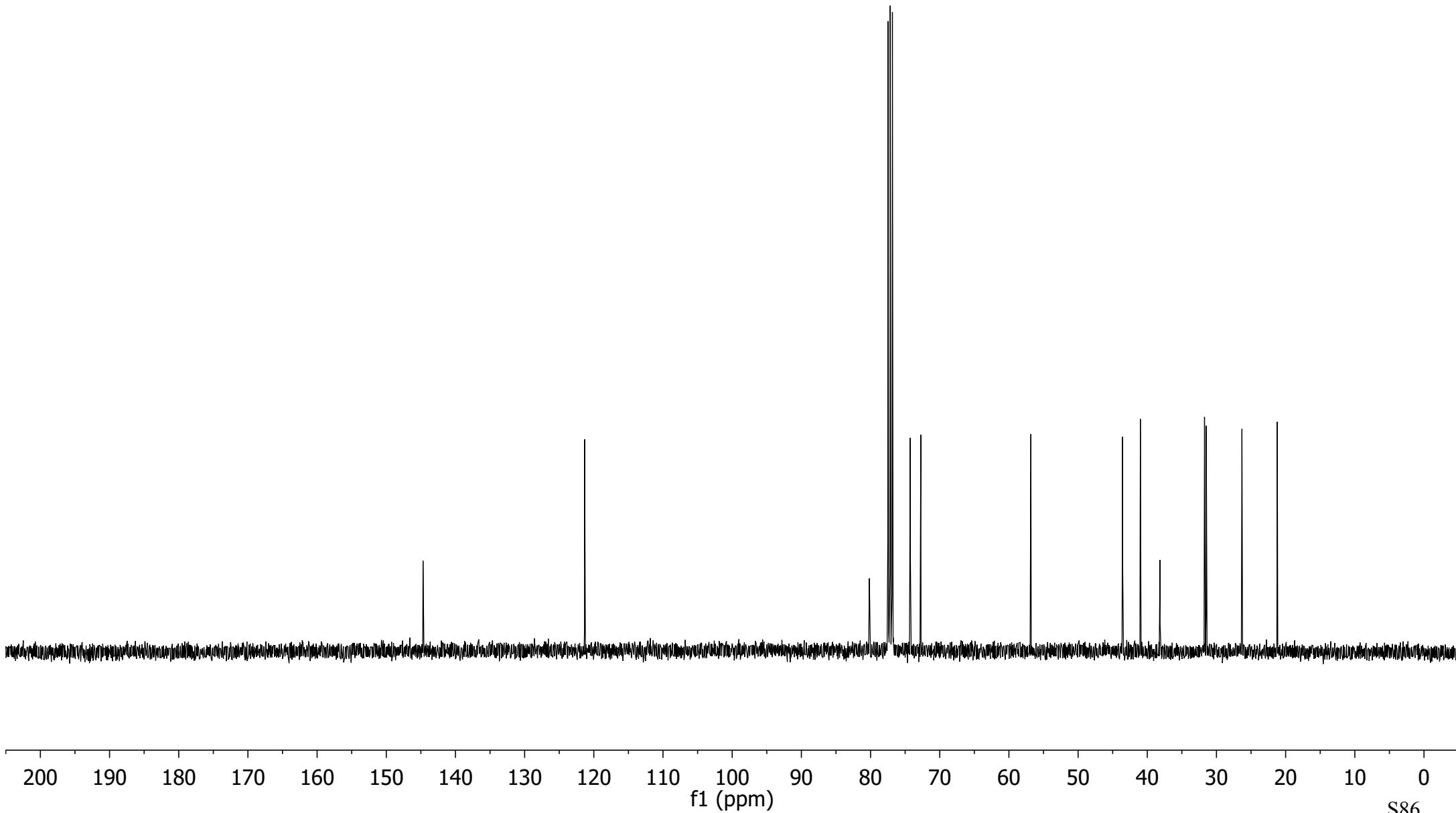
400 MHz ^1H NMR spectrum of (*1R,5S*)-6,6-dimethyl-2-((prop-2-yn-1-yloxy)methyl)bicyclo[3.1.1]hept-2-ene
(step ii precursor to compound **31**)
(recorded in CDCl_3)

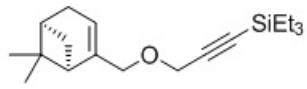




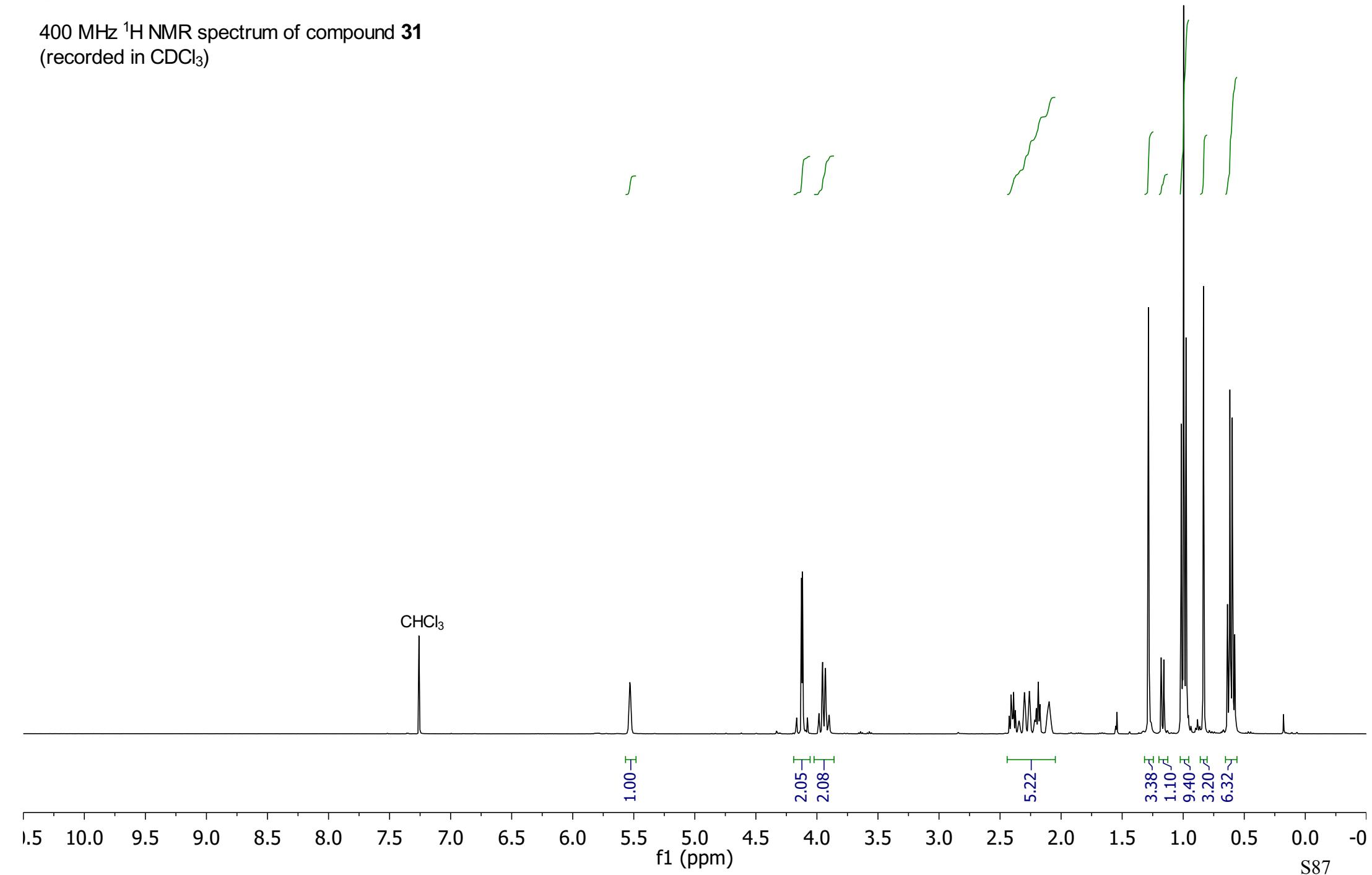
—144.7
—121.3
—80.2
—74.3
—72.7
—56.8
—43.6
—41.0
—38.2
—31.7
—31.5
—26.3
—21.2

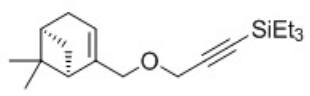
100 MHz ^{13}C NMR spectrum of (*1R,5S*)-6,6-dimethyl-2-((prop-2-yn-1-yloxy)methyl)bicyclo[3.1.1]hept-2-ene
(step ii precursor to compound **31**)
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound **31**
(recorded in CDCl_3)





-144.9

-121.2

-103.1

-88.7

-72.4

-57.6

-43.6

~41.0

~38.2

~31.7

~31.5

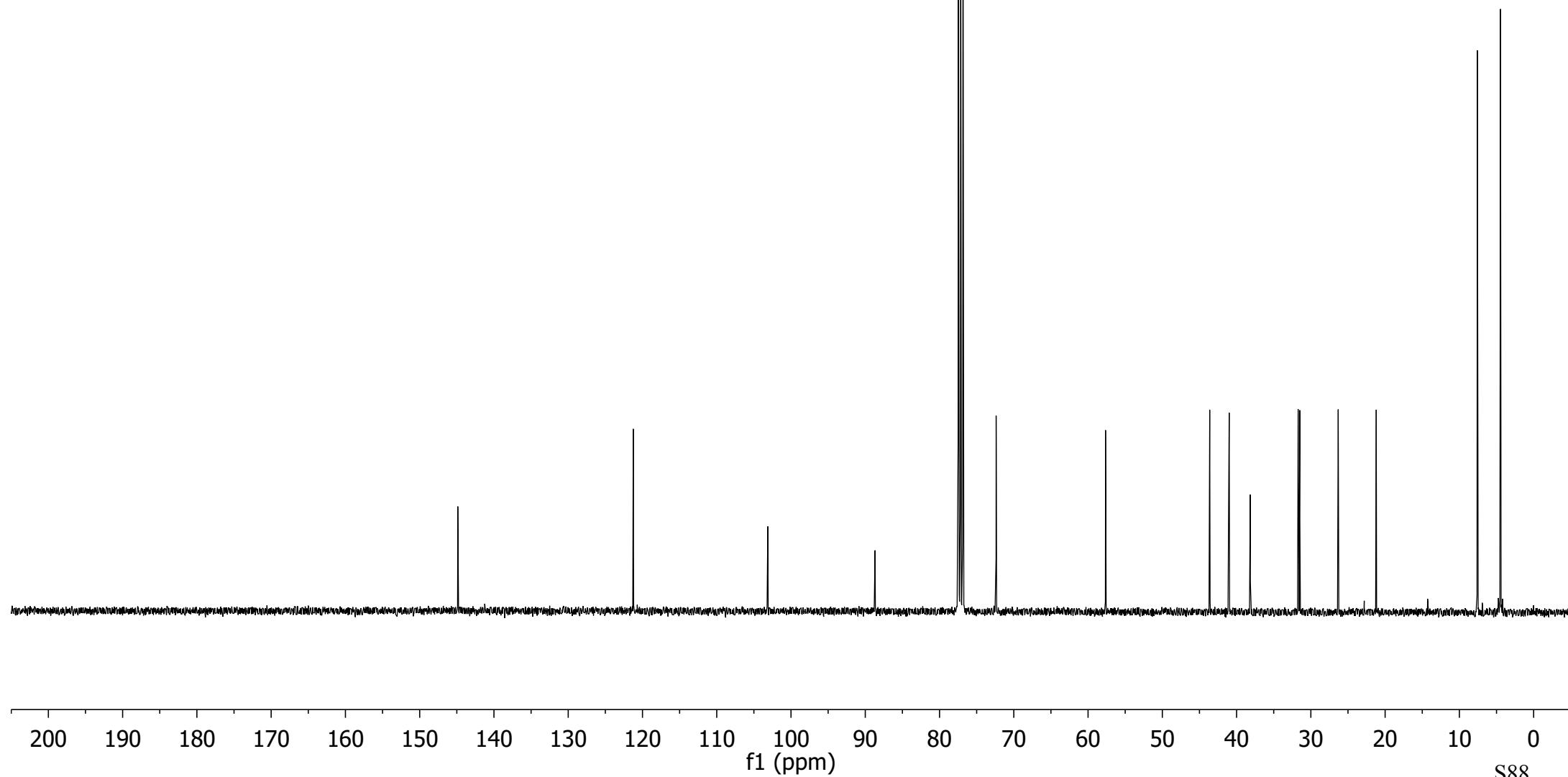
~26.3

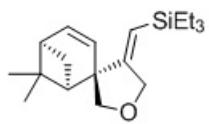
-21.2

-7.6

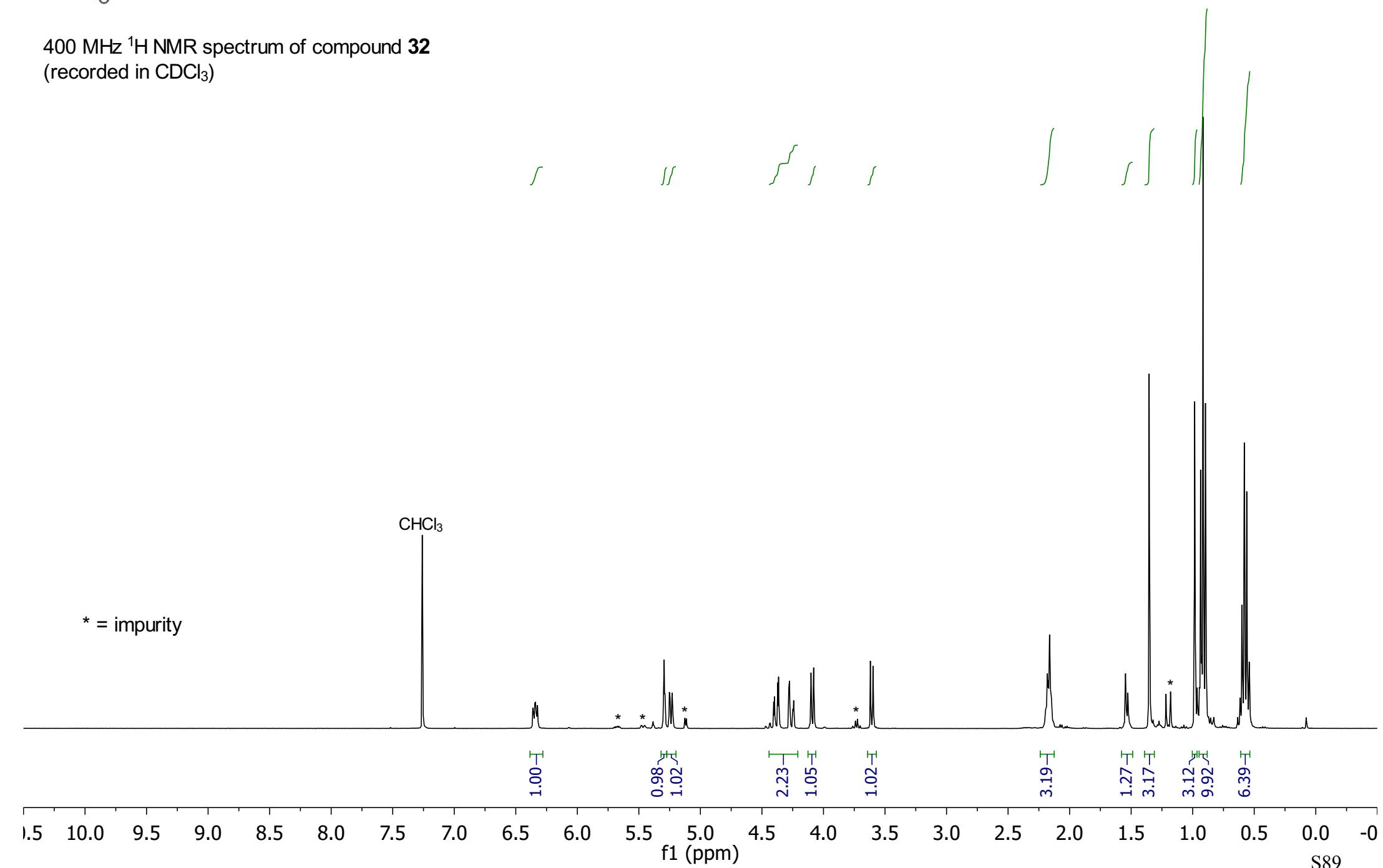
-4.5

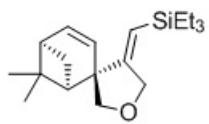
100 MHz ^{13}C NMR spectrum of compound **31**
(recorded in CDCl_3)



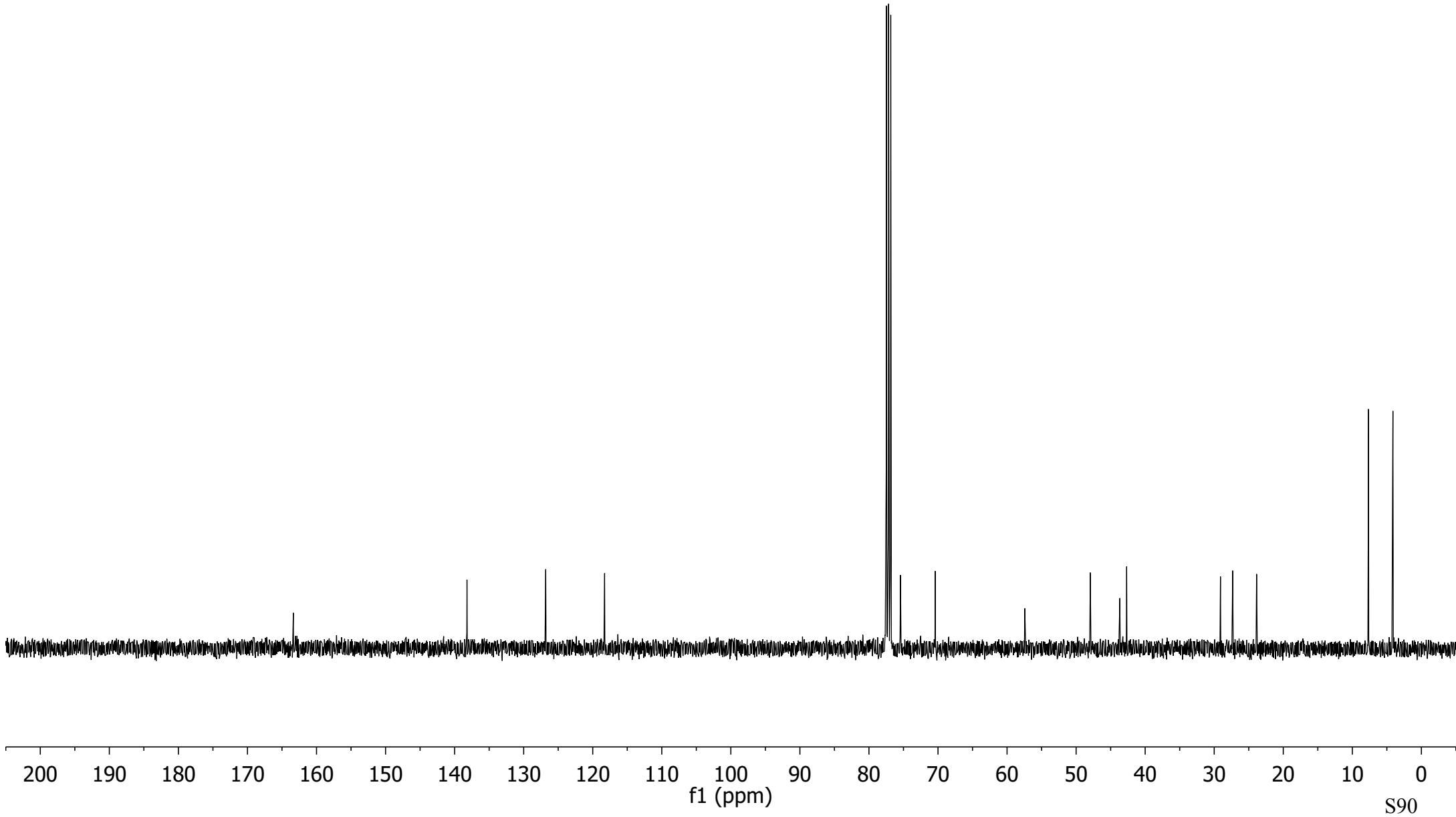


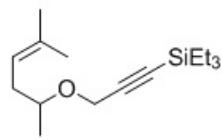
400 MHz ^1H NMR spectrum of compound 32
(recorded in CDCl_3)



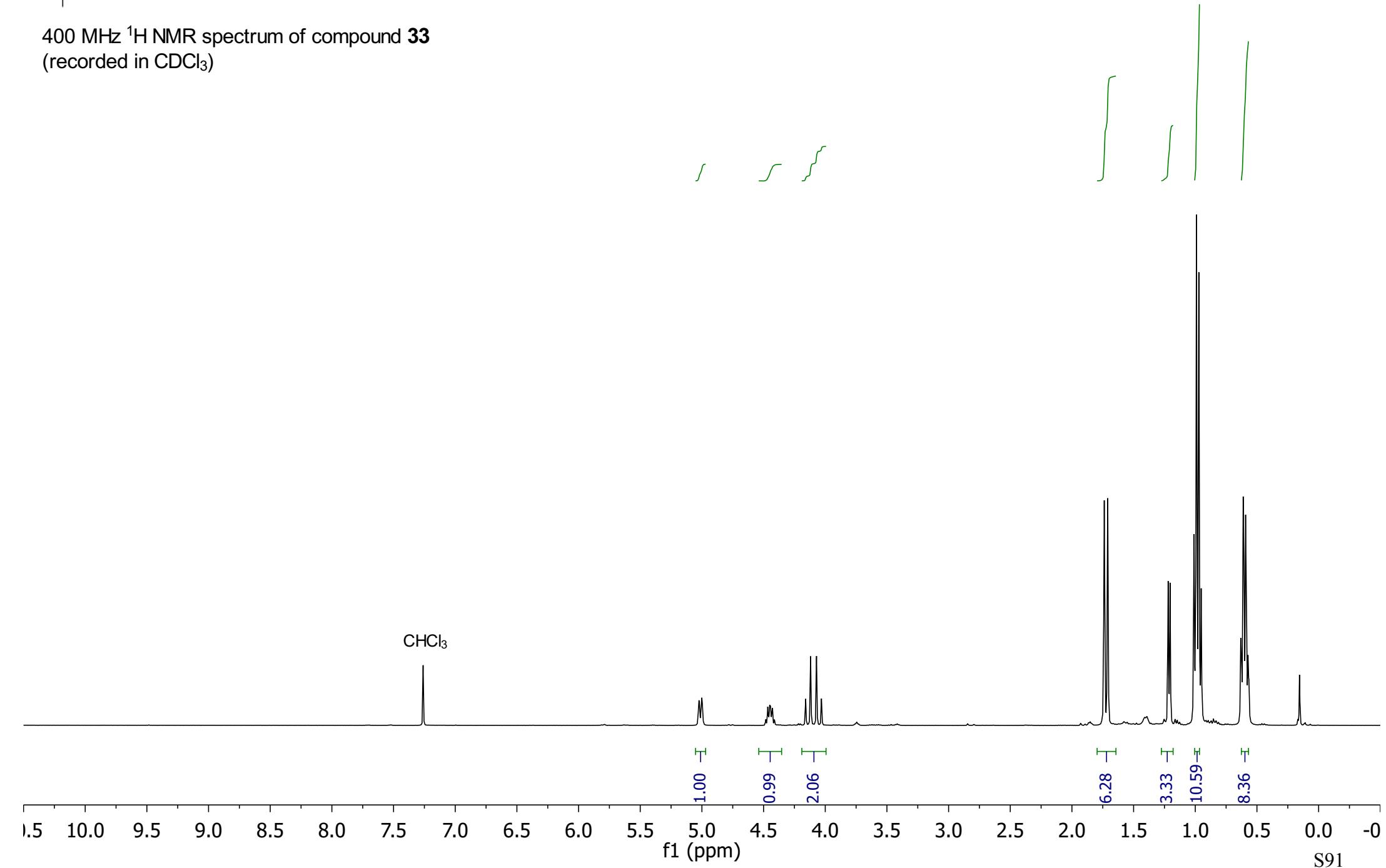


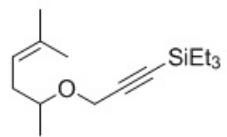
100 MHz ^{13}C NMR spectrum of compound 32
(recorded in CDCl_3)



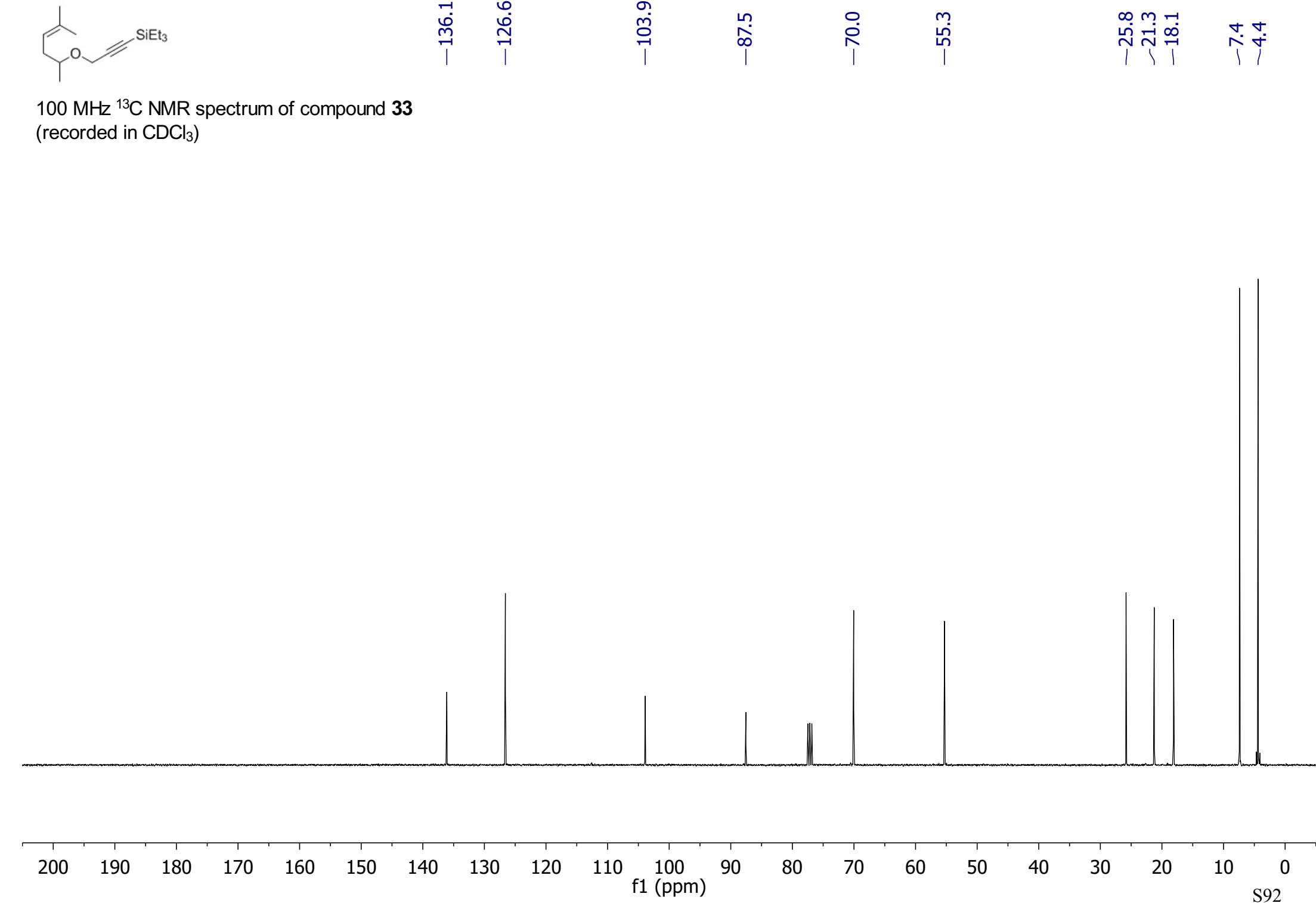


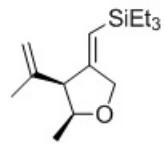
400 MHz ^1H NMR spectrum of compound 33
(recorded in CDCl_3)



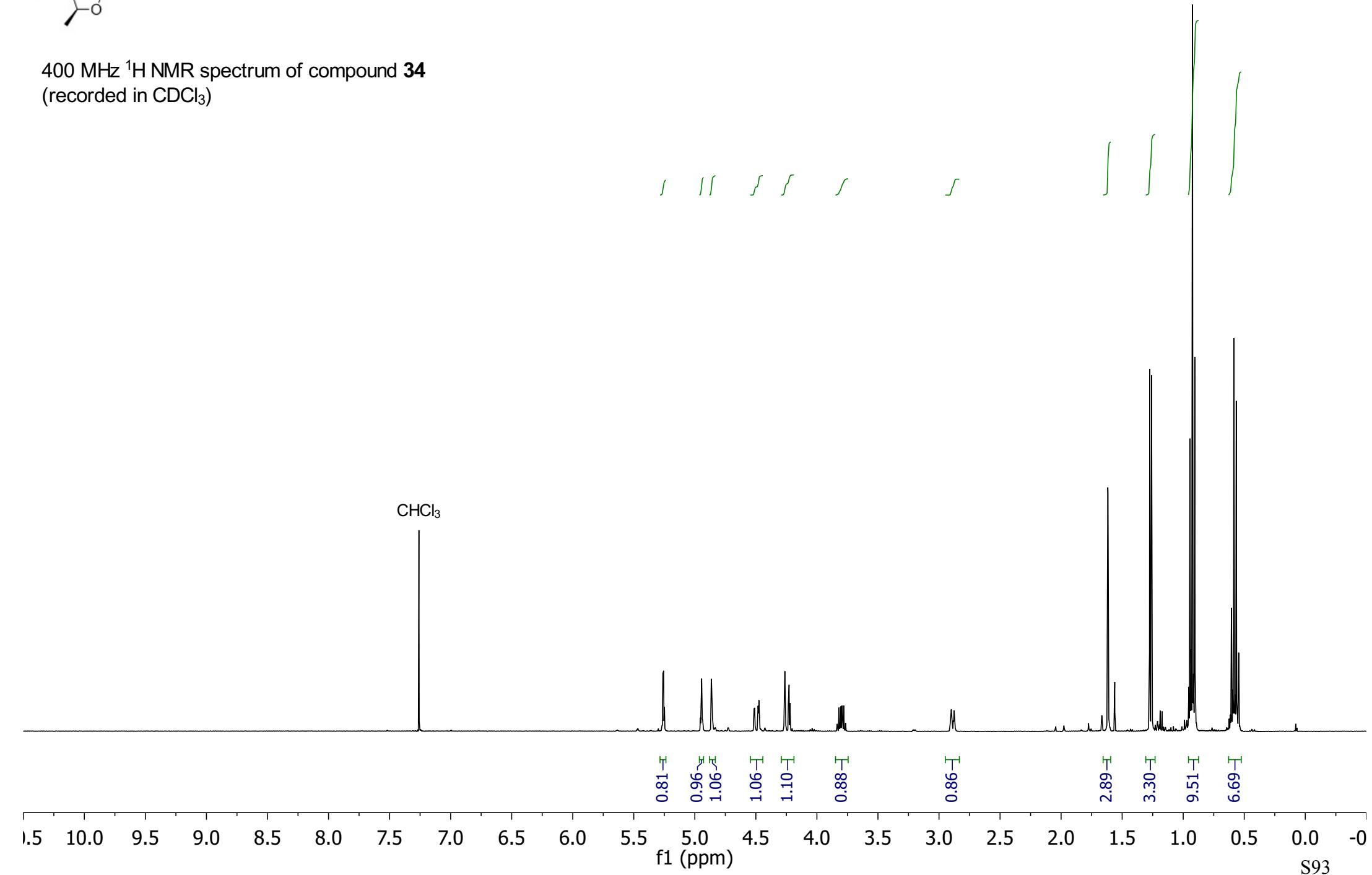


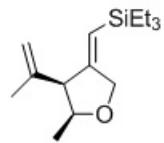
100 MHz ^{13}C NMR spectrum of compound 33
(recorded in CDCl_3)



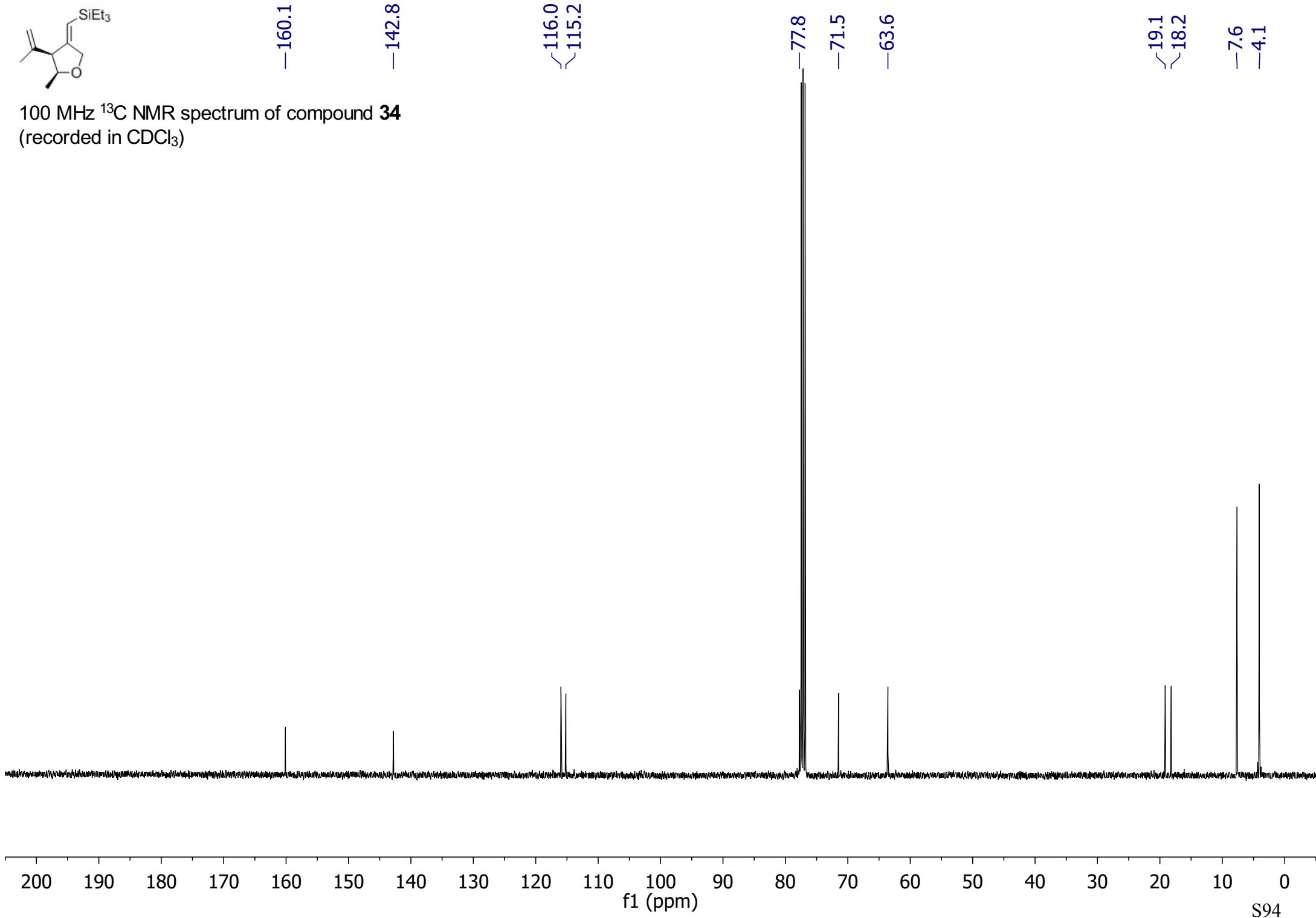


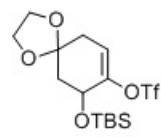
400 MHz ¹H NMR spectrum of compound **34**
(recorded in CDCl₃)



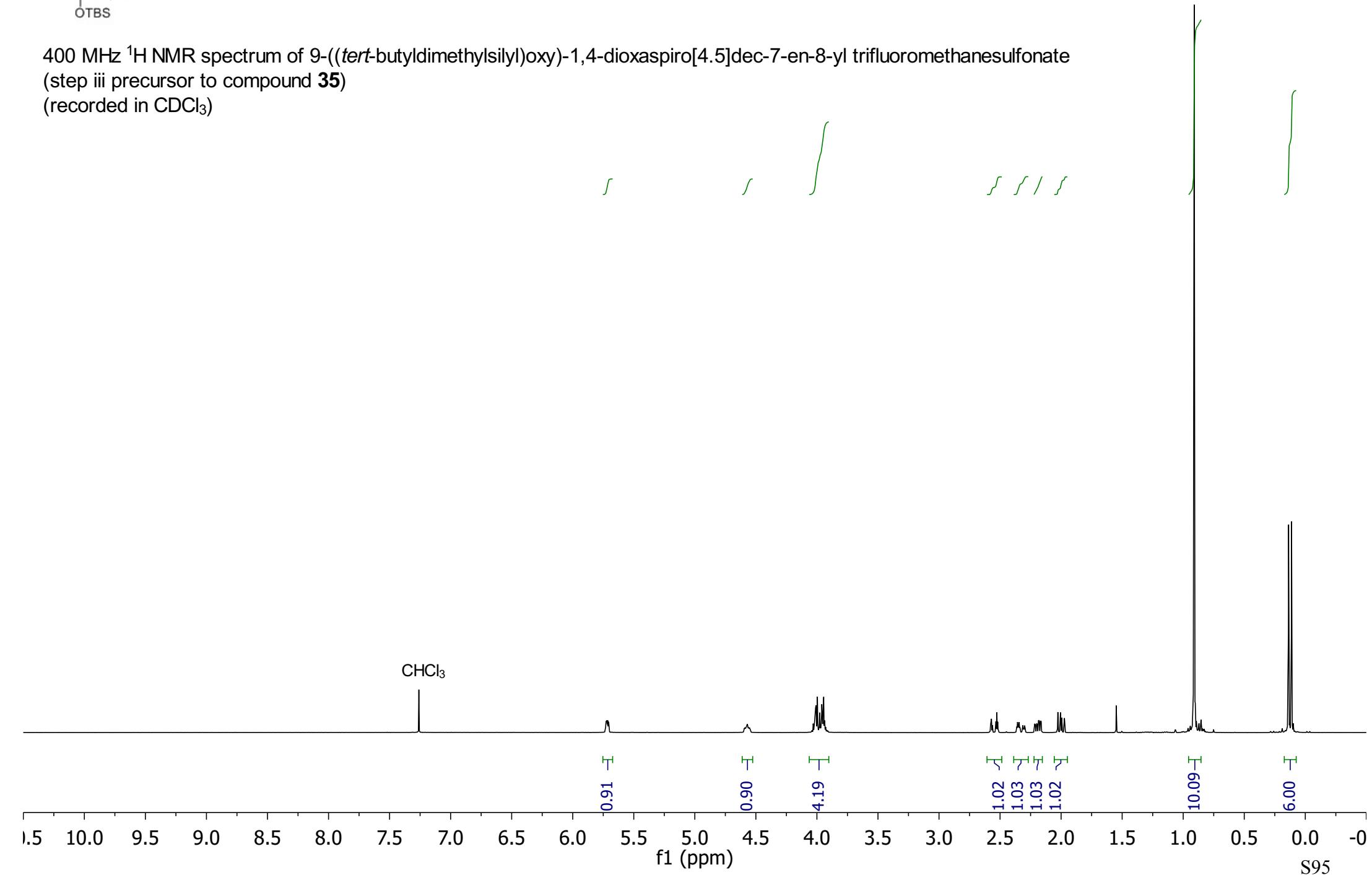


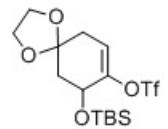
100 MHz ^{13}C NMR spectrum of compound **34**
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of 9-((*tert*-butyldimethylsilyl)oxy)-1,4-dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate
(step iii precursor to compound **35**)
(recorded in CDCl_3)





-149.1

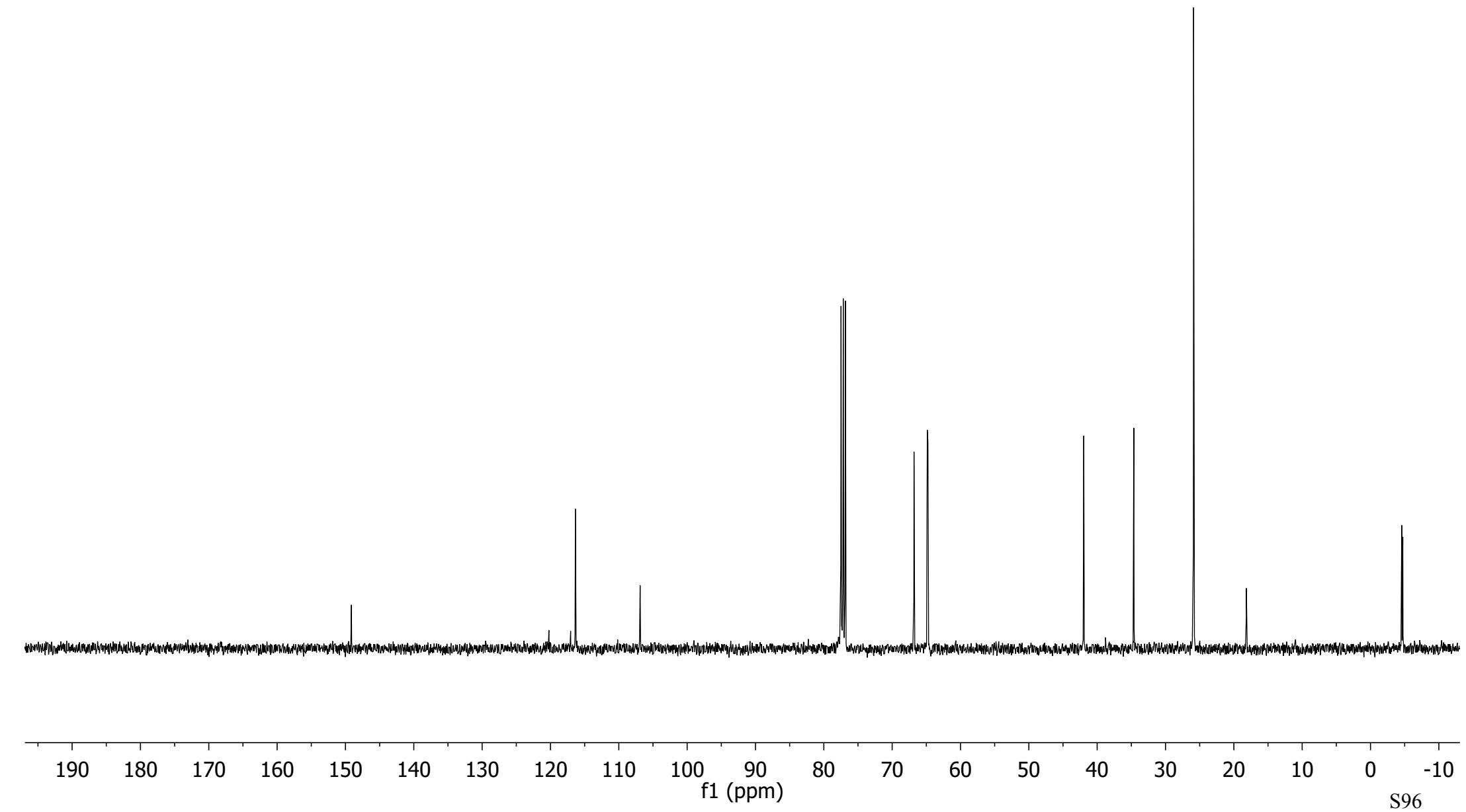
~123.4
~120.2
~117.0
~116.4
~113.9
~106.9

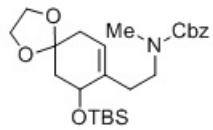
66.8
64.9
64.8

-42.0
-34.6
-25.9
-18.2

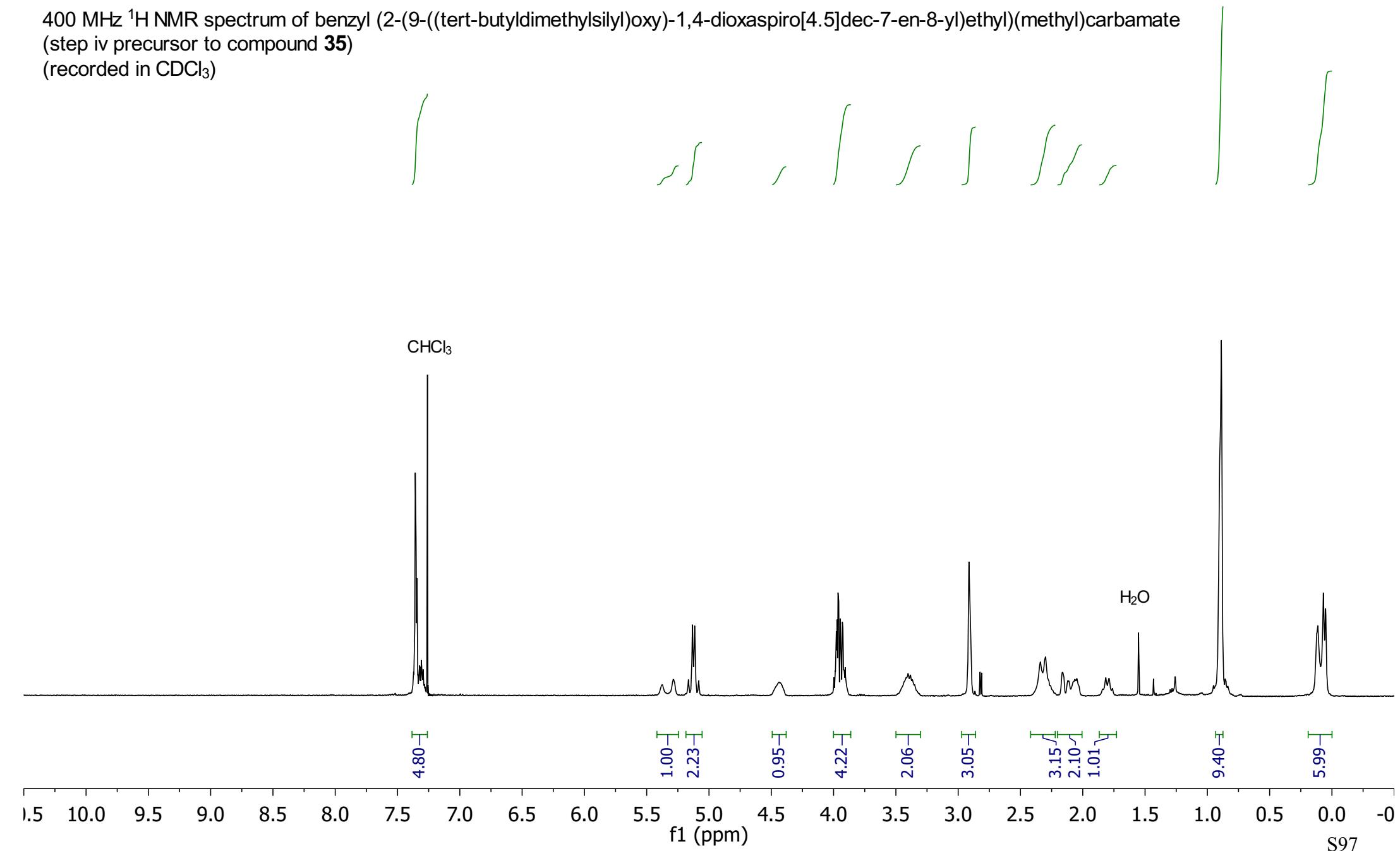
-4.6
-4.7

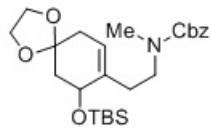
100 MHz ^{13}C NMR spectrum of 9-((tert-butyldimethylsilyl)oxy)-1,4-dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate
(step iii precursor to compound **35**)
(recorded in CDCl_3)





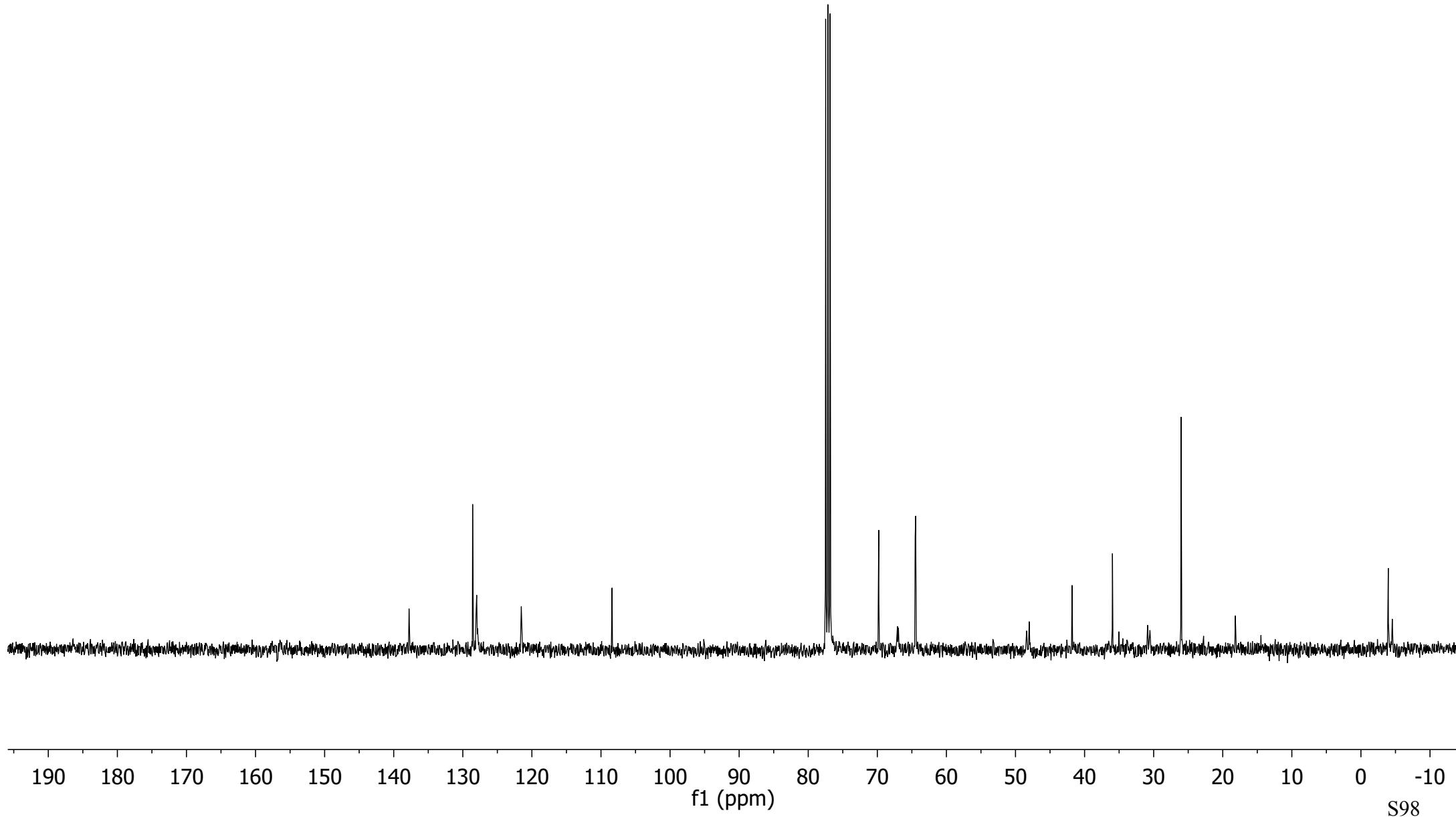
400 MHz ^1H NMR spectrum of benzyl (2-((tert-butyldimethylsilyl)oxy)-1,4-dioxaspiro[4.5]dec-7-en-8-yl)ethyl)(methyl)carbamate
(step iv precursor to compound **35**)
(recorded in CDCl_3)

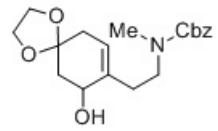




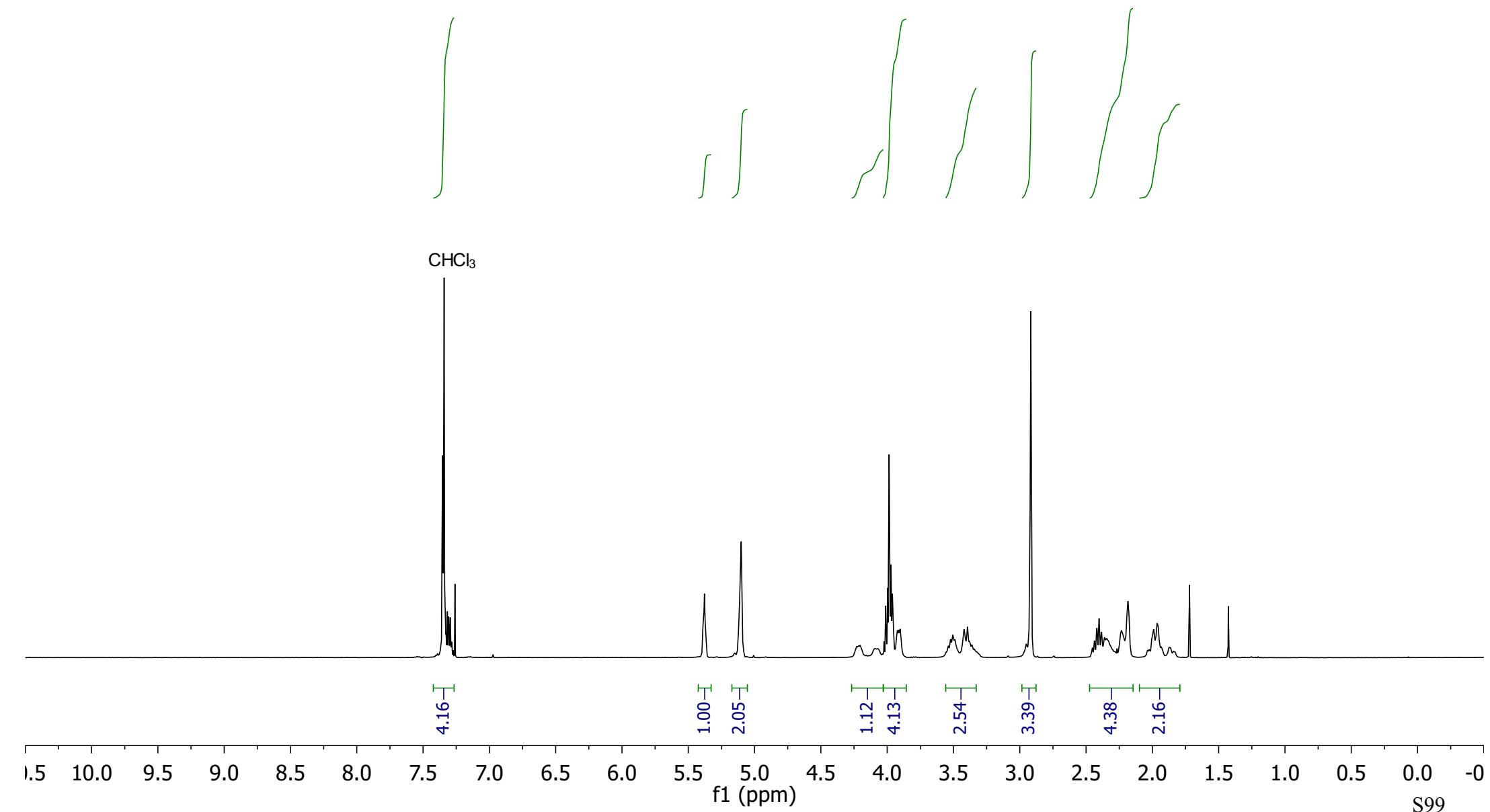
-137.8
 -128.6
 -128.1
 -128.0
 -127.9
 -127.8
 -121.5
 -108.4
 -69.8
 -67.1
 -66.9
 -64.5
 -64.5
 -48.0
 -41.8
 -36.0
 -35.0
 -30.9
 -26.0
 -18.2
 -4.0
 -4.5

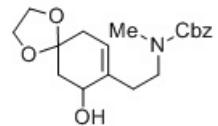
100 MHz ^{13}C NMR spectrum of benzyl (2-((tert-butyldimethylsilyl)oxy)-1,4-dioxaspiro[4.5]dec-7-en-8-yl)ethyl(methyl)carbamate
 (step iv precursor to compound **35**)
 (recorded in CDCl_3)





400 MHz ^1H NMR spectrum of benzyl (2-(9-hydroxy-1,4-dioxaspiro[4.5]dec-7-en-8-yl)ethyl)(methyl)carbamate
(step v precursor to compound **35**)
(recorded in CDCl_3)





156.6
156.3

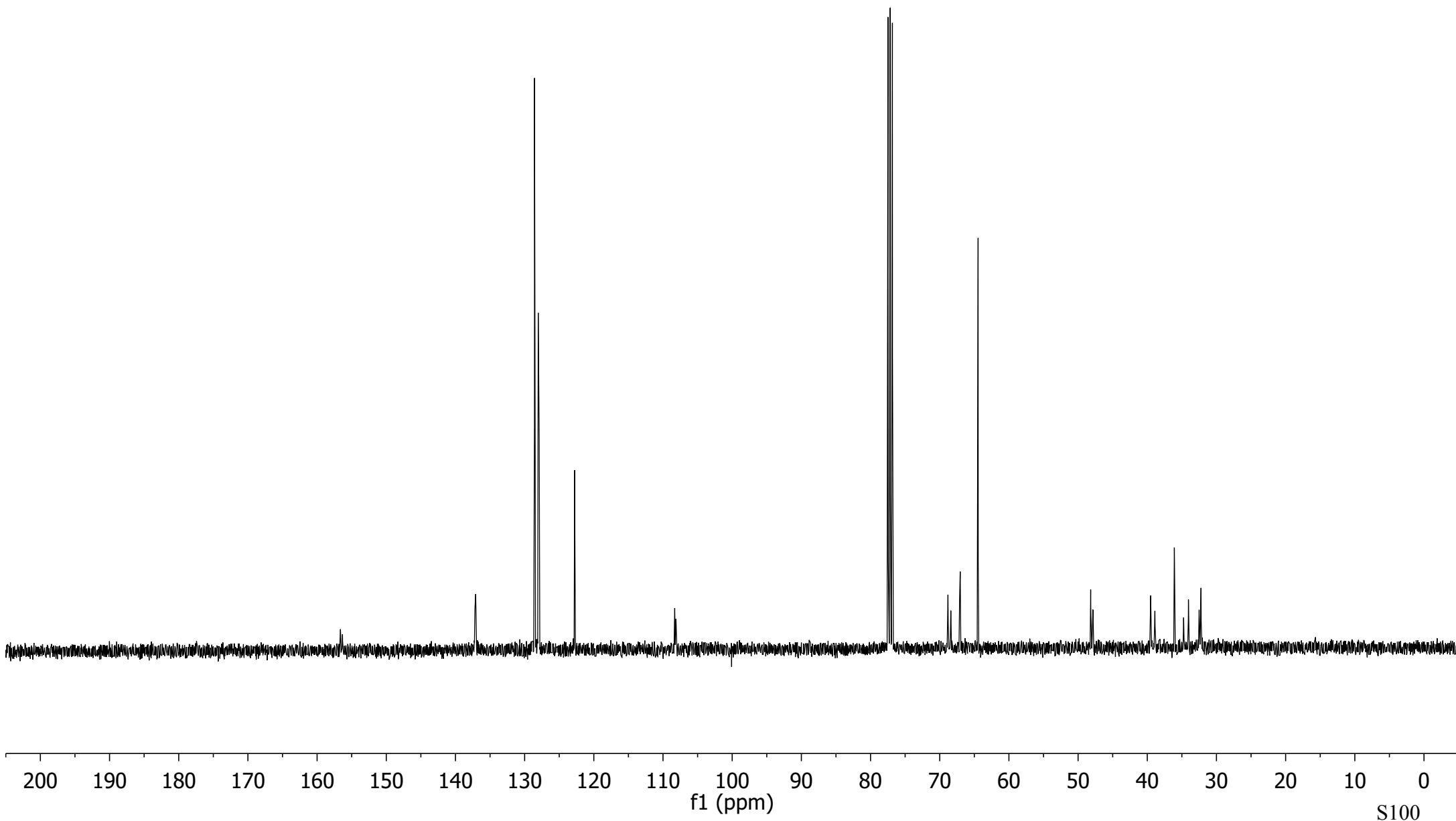
137.2
137.1
128.6
128.0
127.9
127.9
122.8

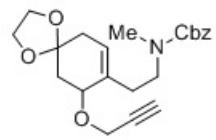
108.3
108.1

68.8
68.4
67.1
67.0
64.5

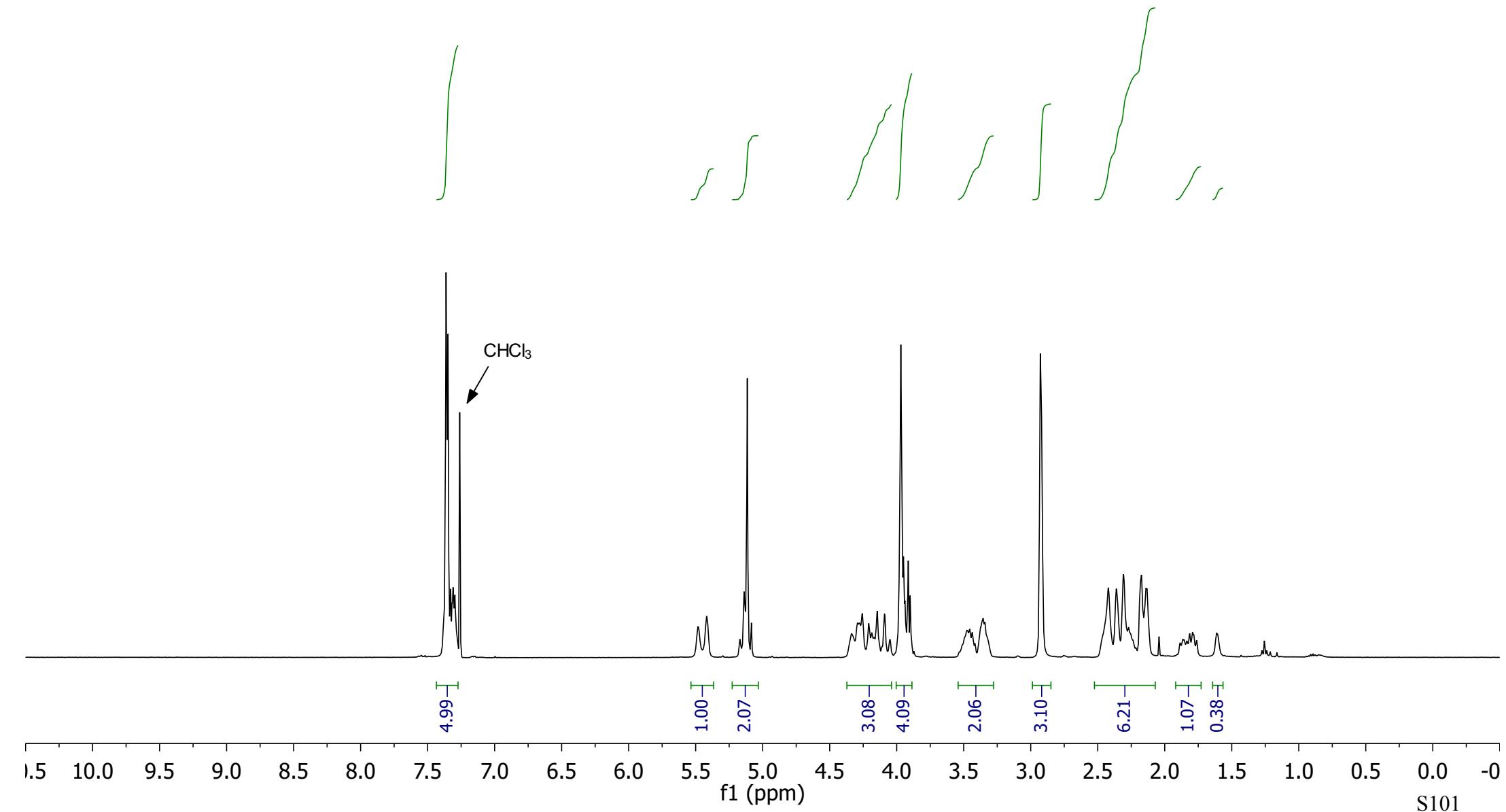
48.2
47.9
39.5
38.9
36.1
34.7
34.0
32.5
32.2

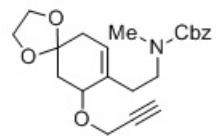
100 MHz ^{13}C NMR spectrum of benzyl (2-(9-hydroxy-1,4-dioxaspiro[4.5]dec-7-en-8-yl)ethyl)(methyl)carbamate
(step v precursor to compound **35**)
(recorded in CDCl_3)





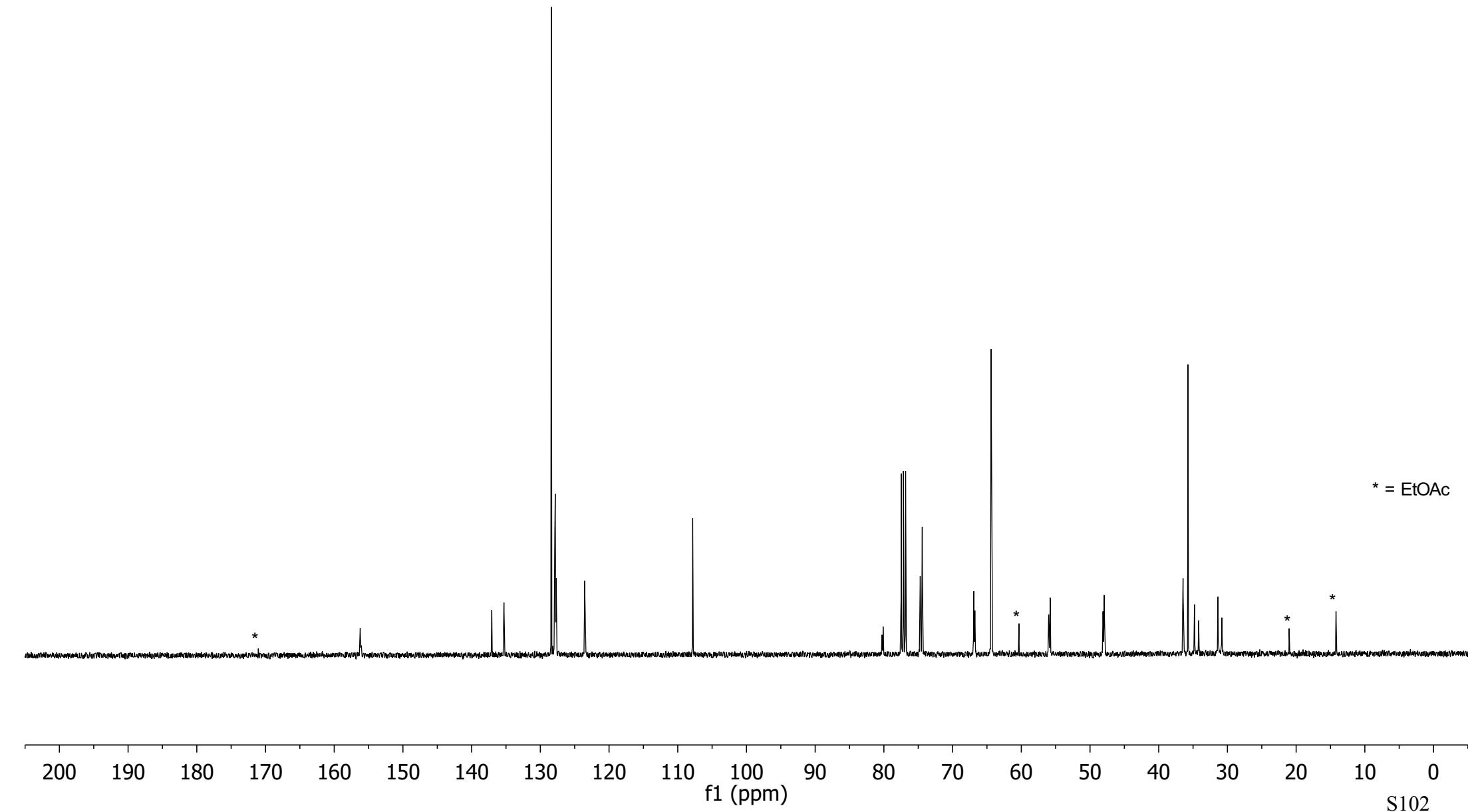
400 MHz ^1H NMR spectrum of benzyl methyl(2-(9-(prop-2-yn-1-yloxy)-1,4-dioxaspiro[4.5]dec-7-en-8-yl)ethyl)carbamate
(step vi precursor to compound **35**)
(recorded in CDCl_3)

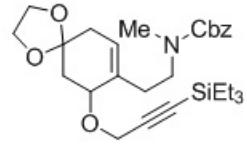




156.2
156.1
137.1
135.3
128.4
127.9
127.8
127.7
123.5
123.5
-107.8
80.3
80.1
74.8
74.7
74.4
66.9
66.8
64.4
64.3
56.0
55.8
48.1
47.9
36.5
36.4
35.7
34.8
34.2
31.4
30.8

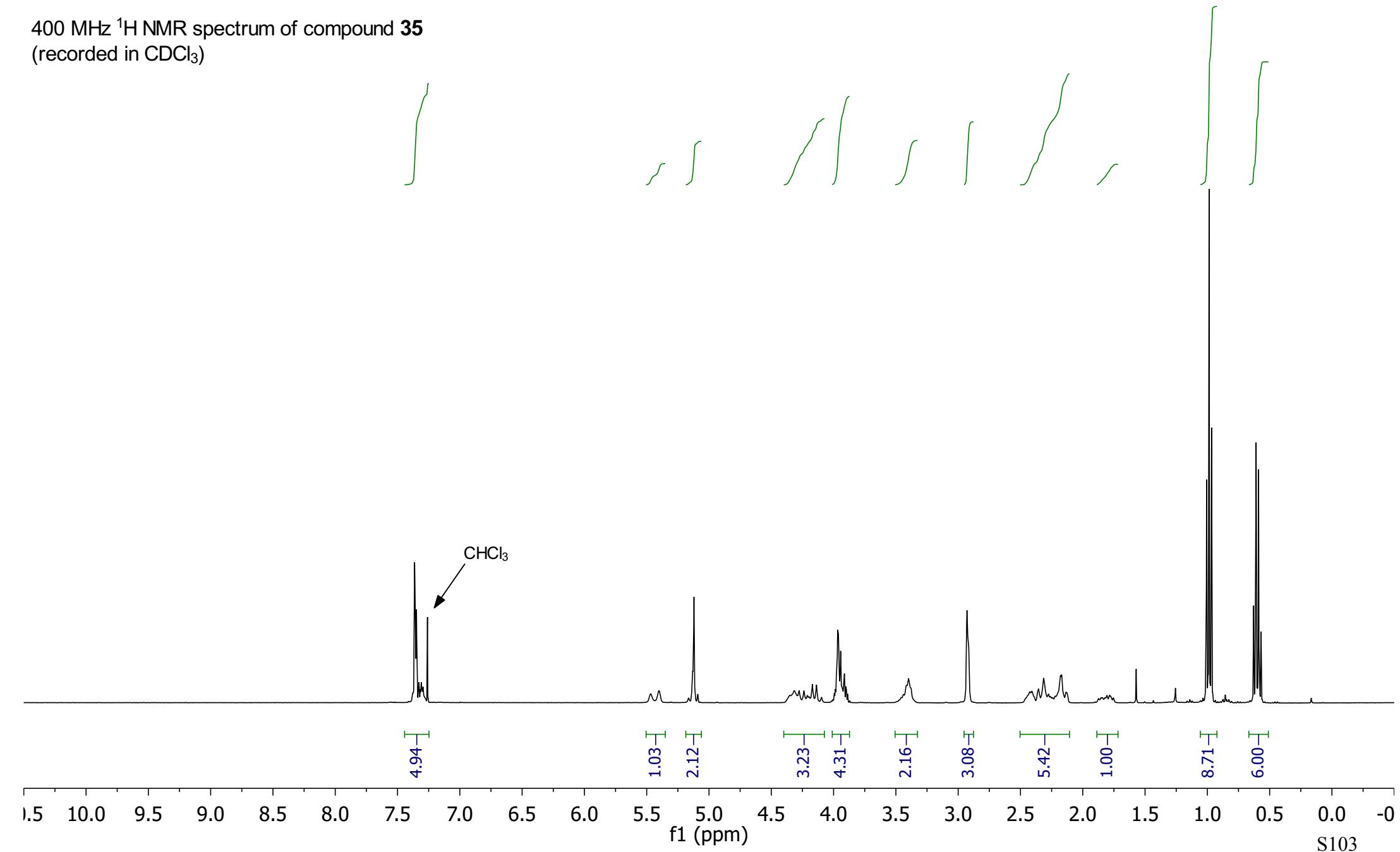
100 MHz ^{13}C NMR spectrum of benzyl methyl(2-(prop-2-yn-1-yloxy)-1,4-dioxaspiro[4.5]dec-7-en-8-yl)ethyl)carbamate
(step vi precursor to compound **35**)
(recorded in CDCl_3)

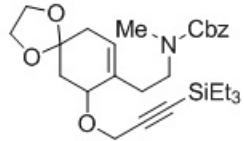




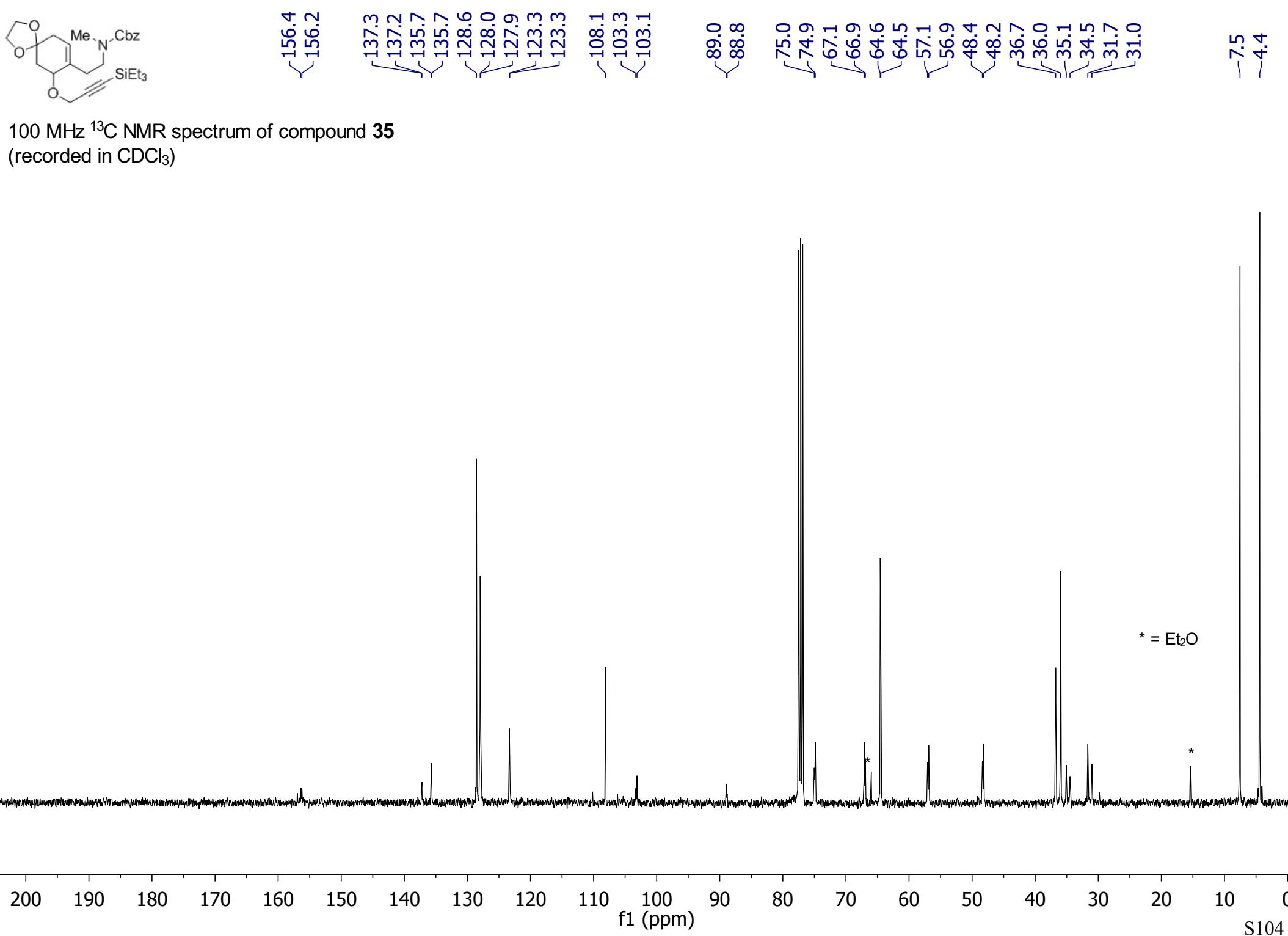
400 MHz ^1H NMR spectrum of compound **35**

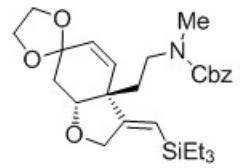
(recorded in CDCl_3)



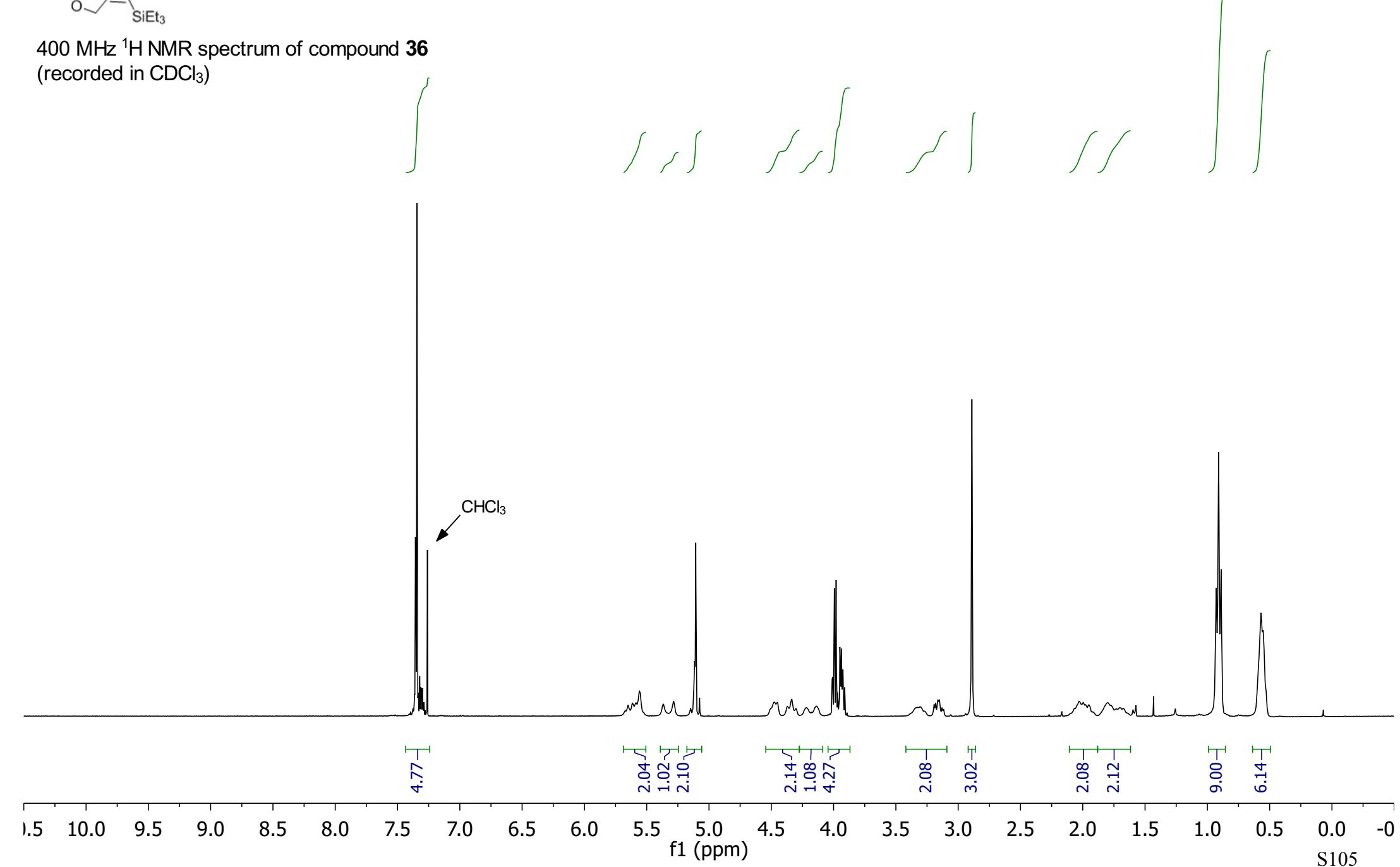


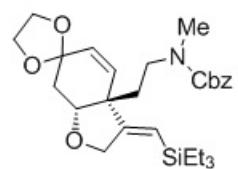
100 MHz ^{13}C NMR spectrum of compound **35**
(recorded in CDCl_3)





400 MHz ¹H NMR spectrum of compound **36**
(recorded in CDCl₃)





162.5
162.3
~156.1

137.0
134.4
128.6
128.1
128.0
128.0
126.8
-115.8

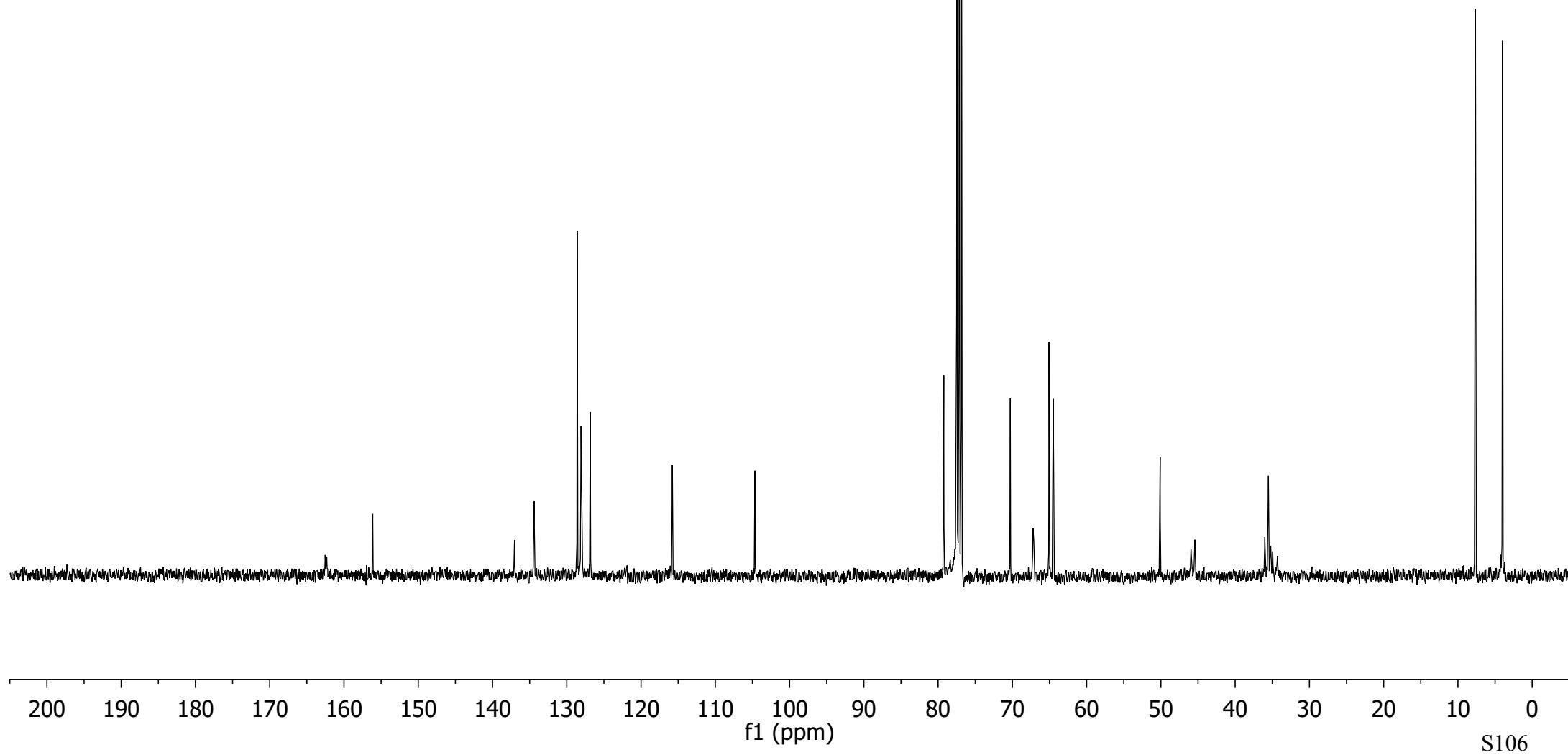
-104.7

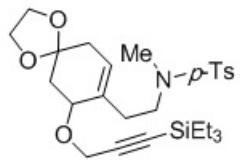
-79.2
70.3
67.2
67.1
65.1
64.5

50.1
45.9
45.4
36.0
35.5
35.2
34.9
34.3

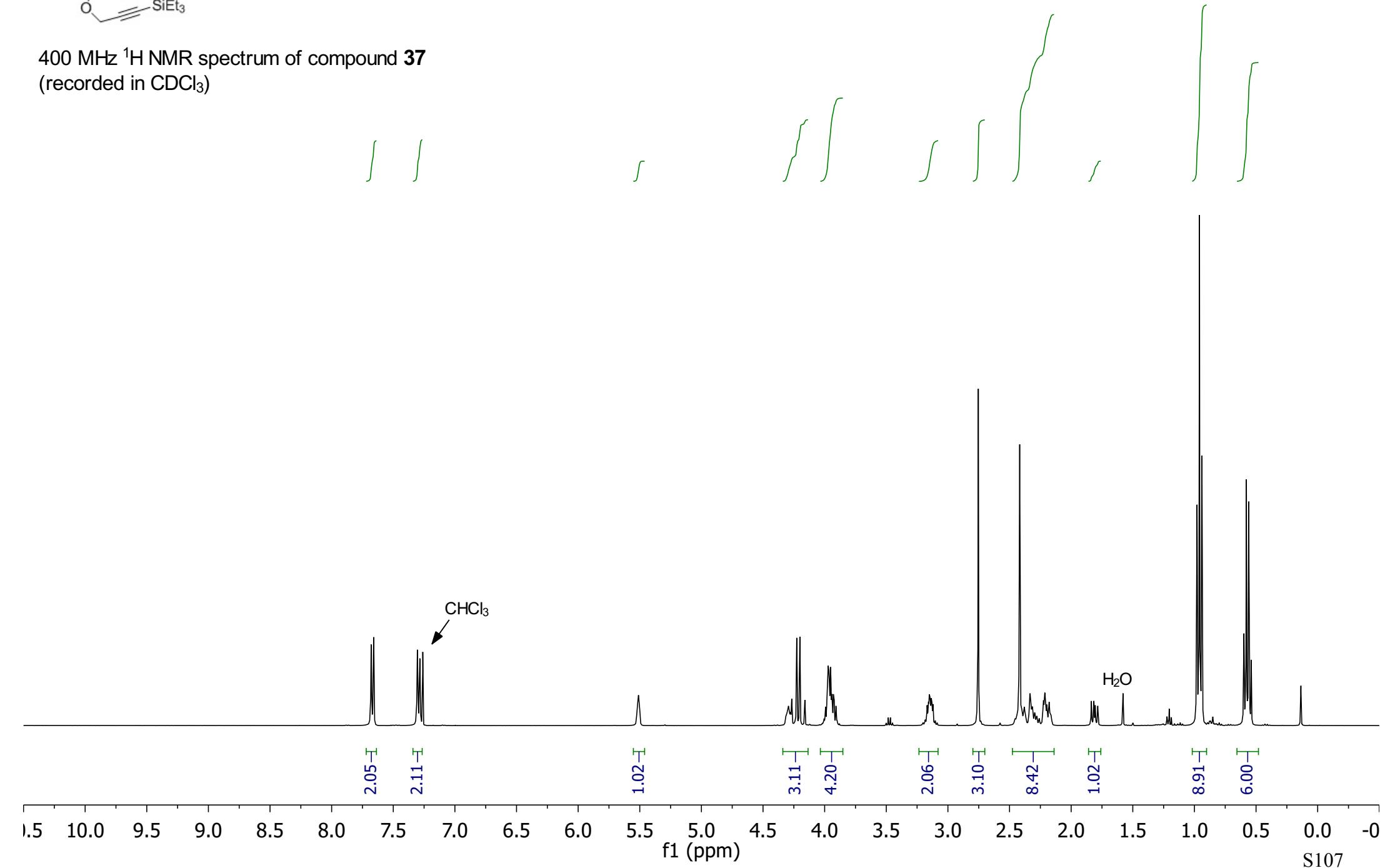
-7.6
-4.0

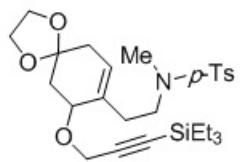
100 MHz ^{13}C NMR spectrum of compound **36**
(recorded in CDCl_3)



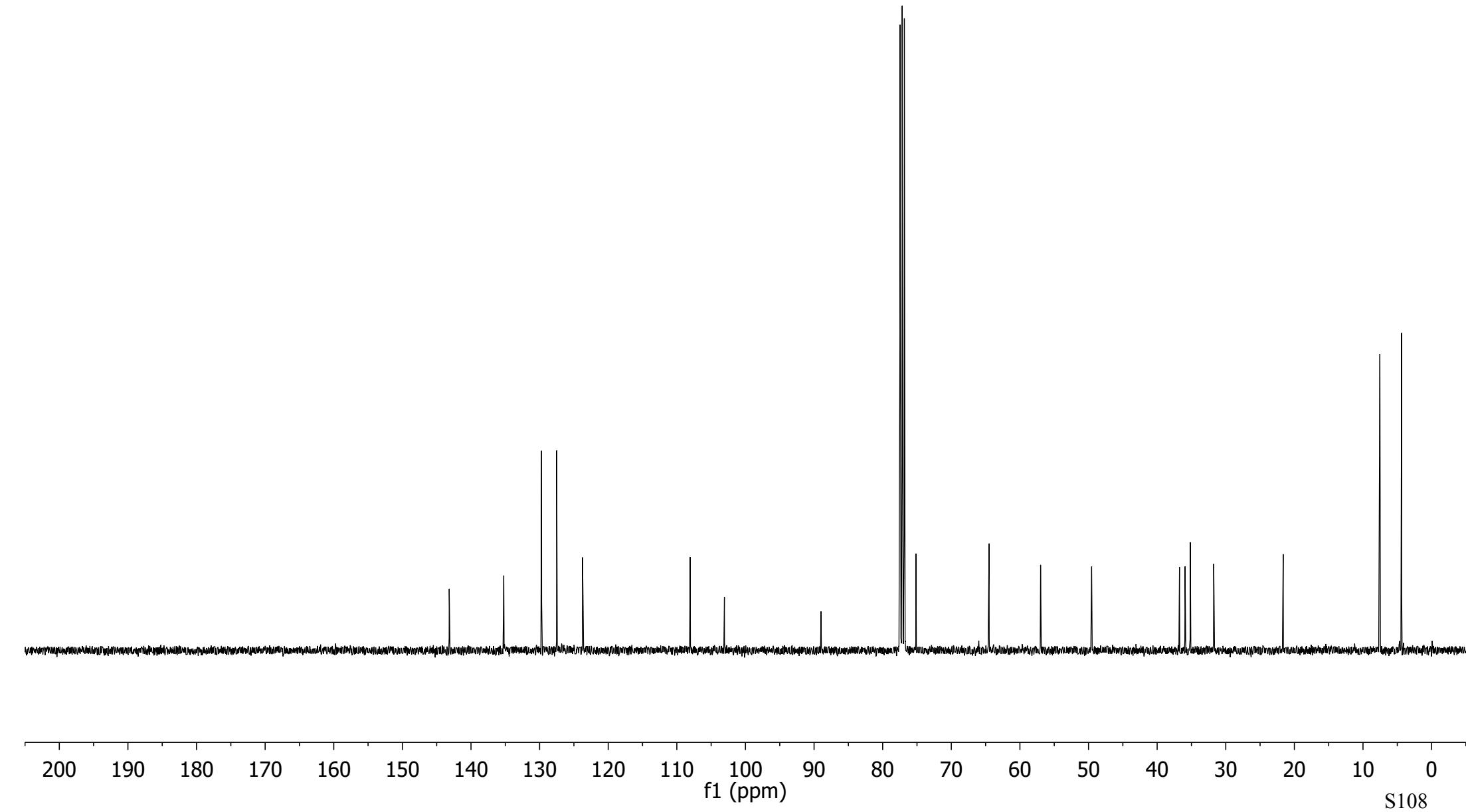


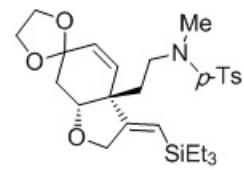
400 MHz ^1H NMR spectrum of compound **37**
(recorded in CDCl_3)



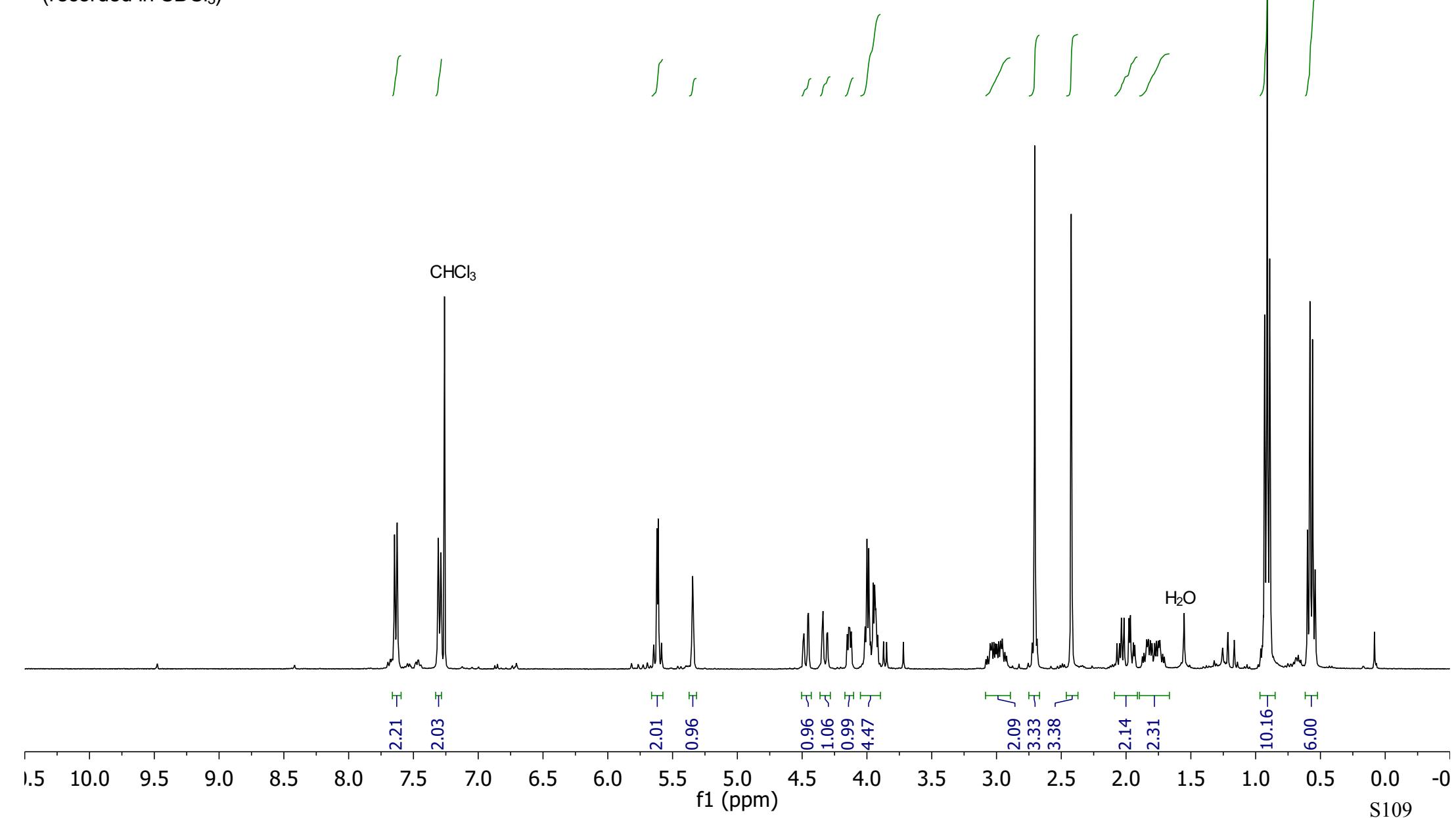


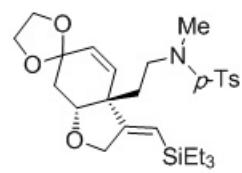
100 MHz ¹³C NMR spectrum of compound **37**
(recorded in CDCl₃)



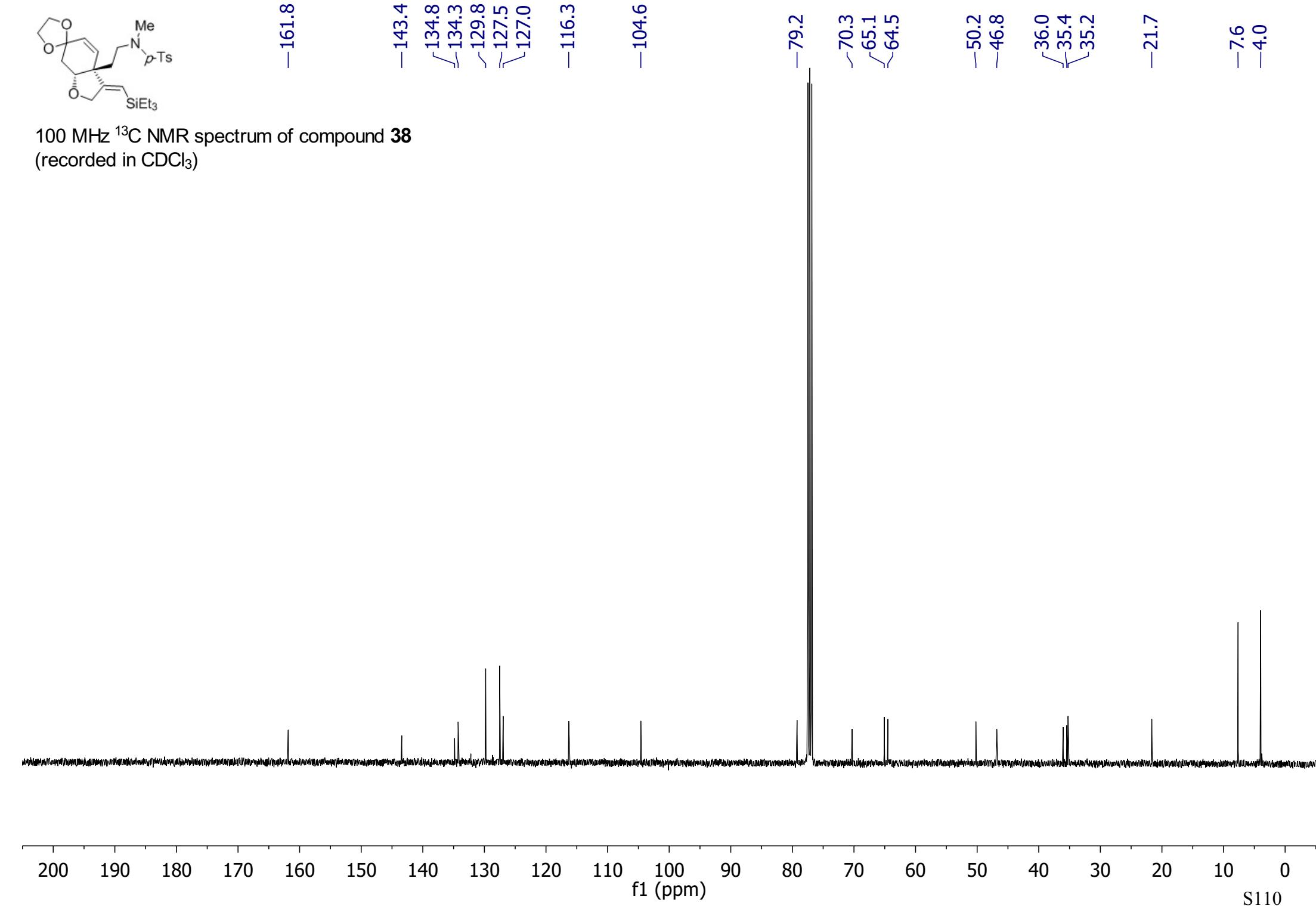


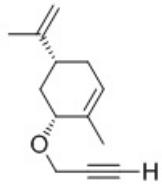
400 MHz ¹H NMR spectrum of compound **38**
(recorded in CDCl₃)



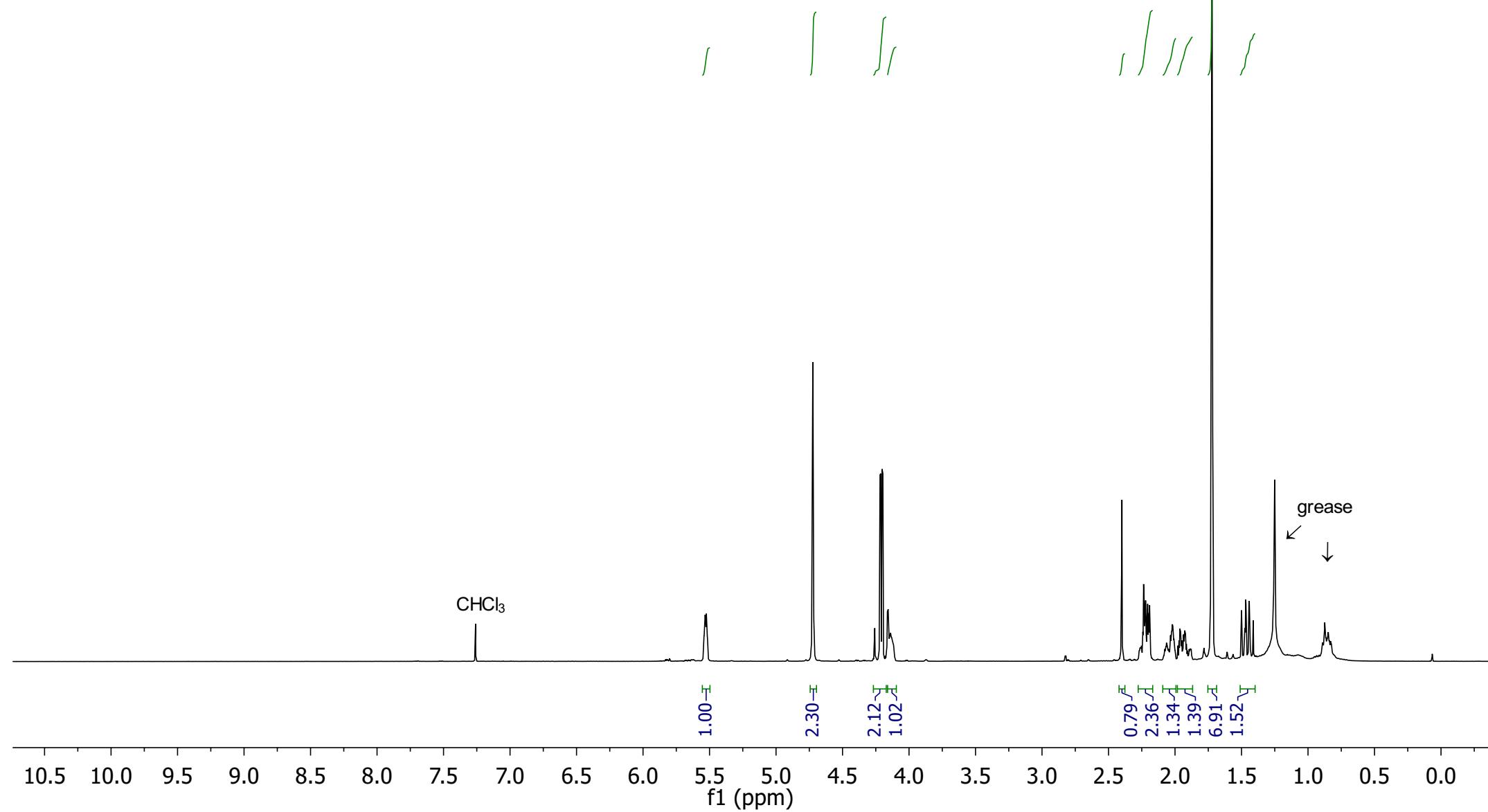


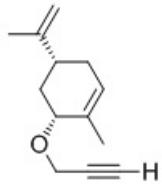
100 MHz ¹³C NMR spectrum of compound 38
(recorded in CDCl₃)



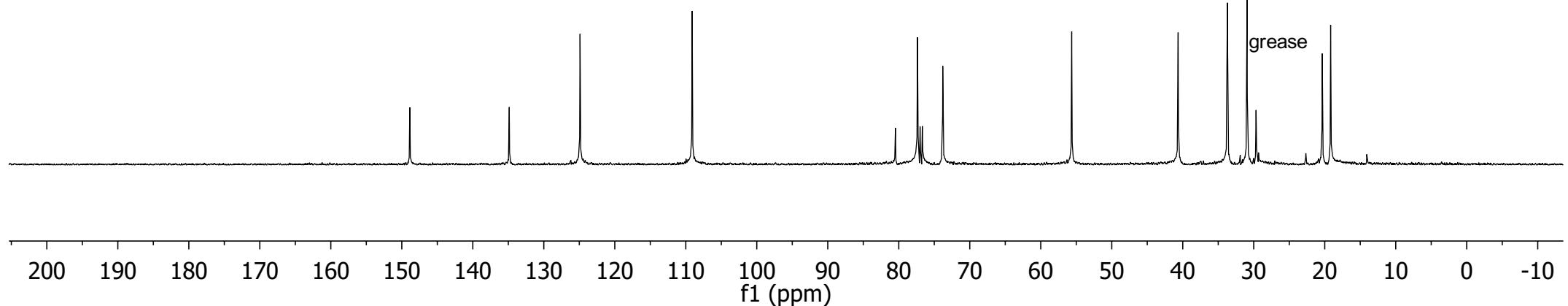


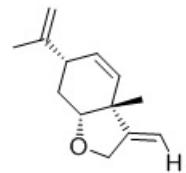
400 MHz ^1H NMR spectrum of compound **39**
(recorded in CDCl_3)



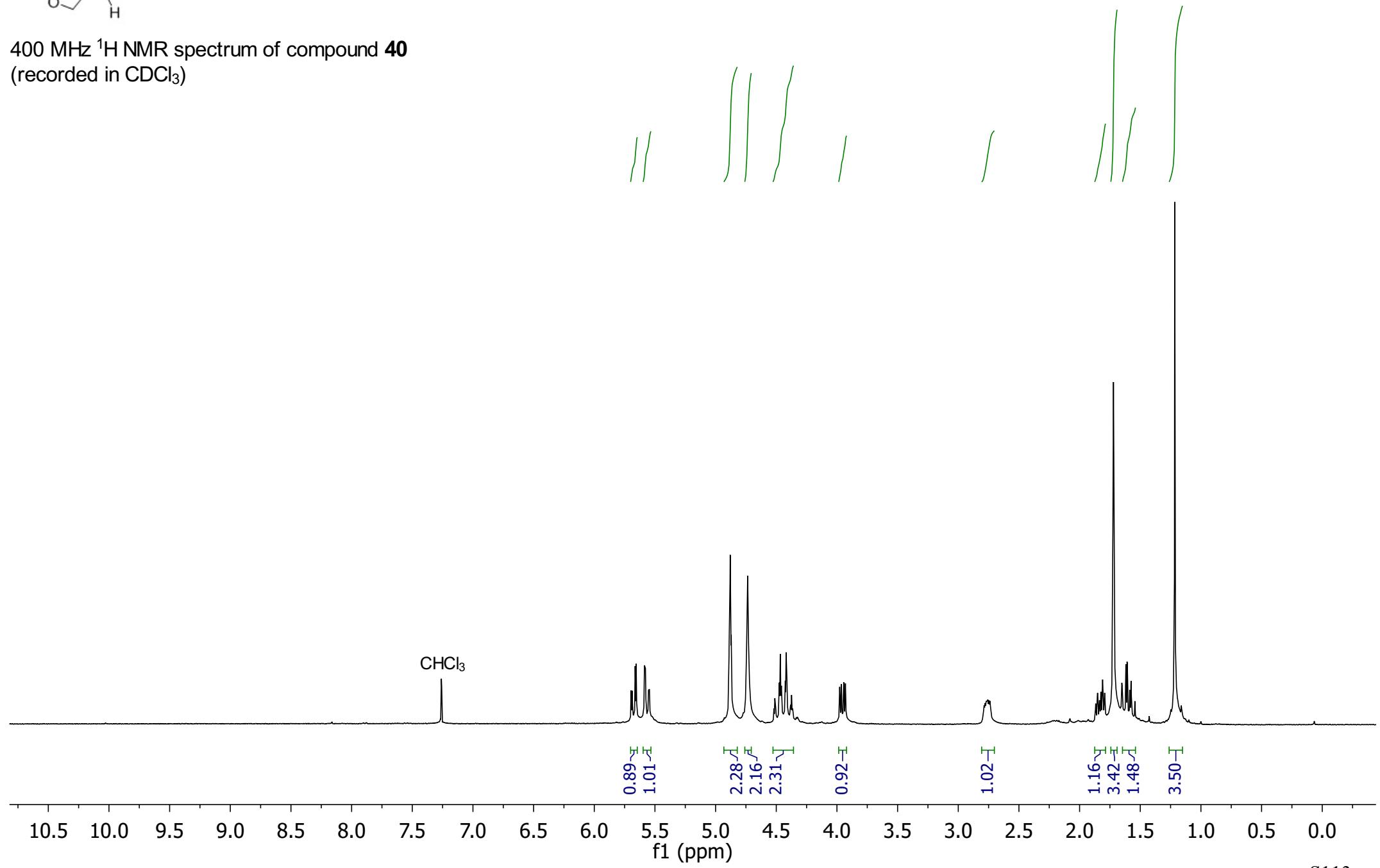


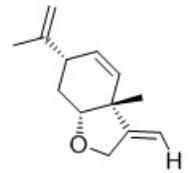
100 MHz ^{13}C NMR spectrum of compound **39**
(recorded in CDCl_3)



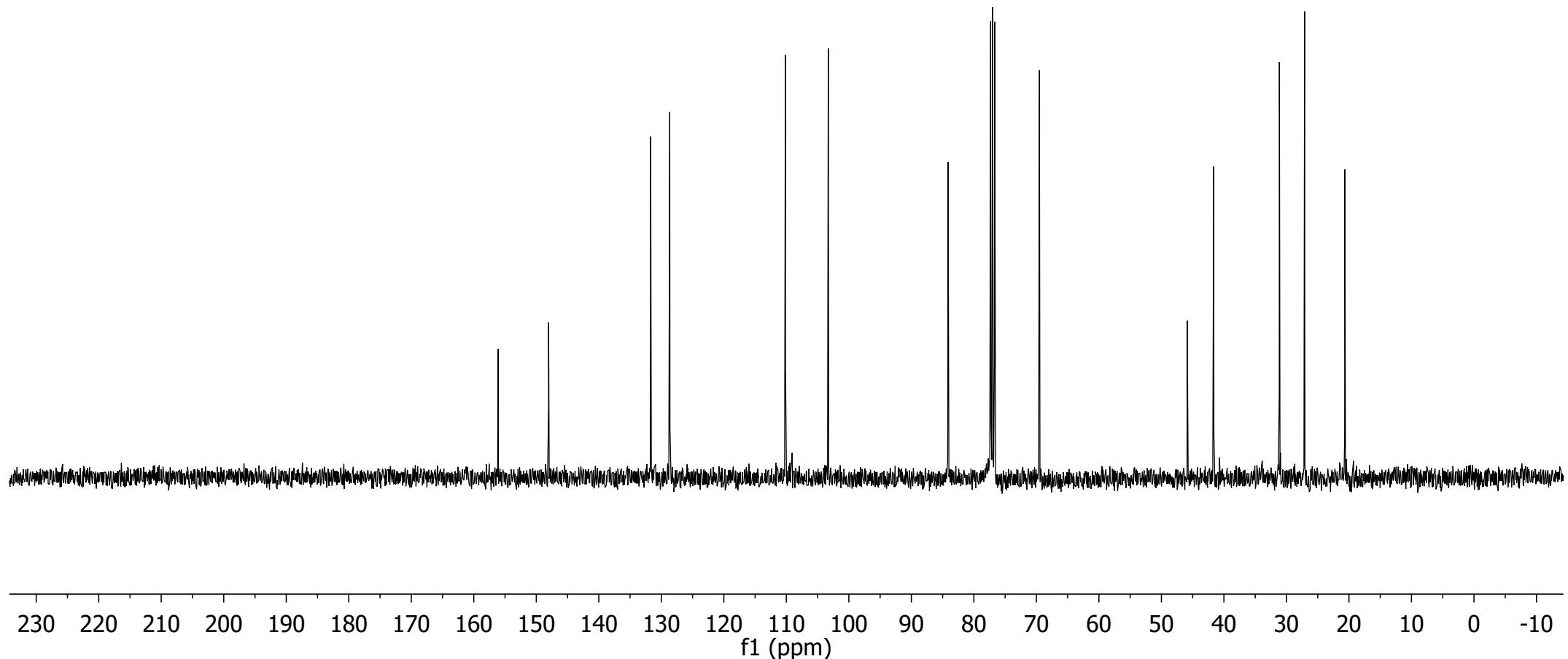


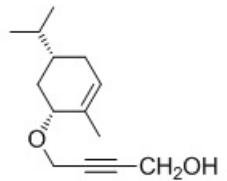
400 MHz ^1H NMR spectrum of compound **40**
(recorded in CDCl_3)



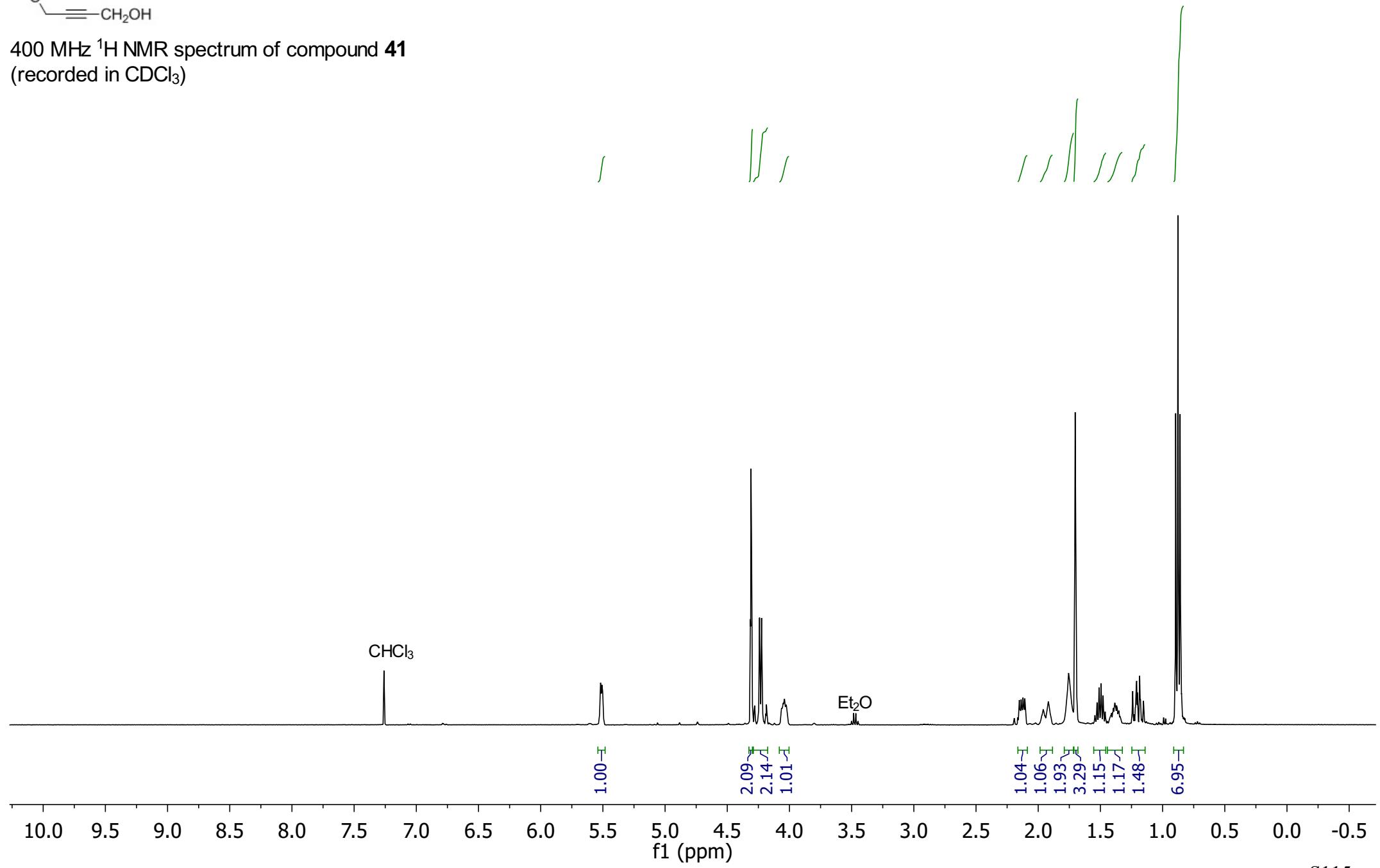


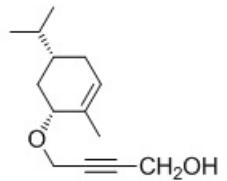
100 MHz ^{13}C NMR spectrum of compound **40**
(recorded in CDCl_3)



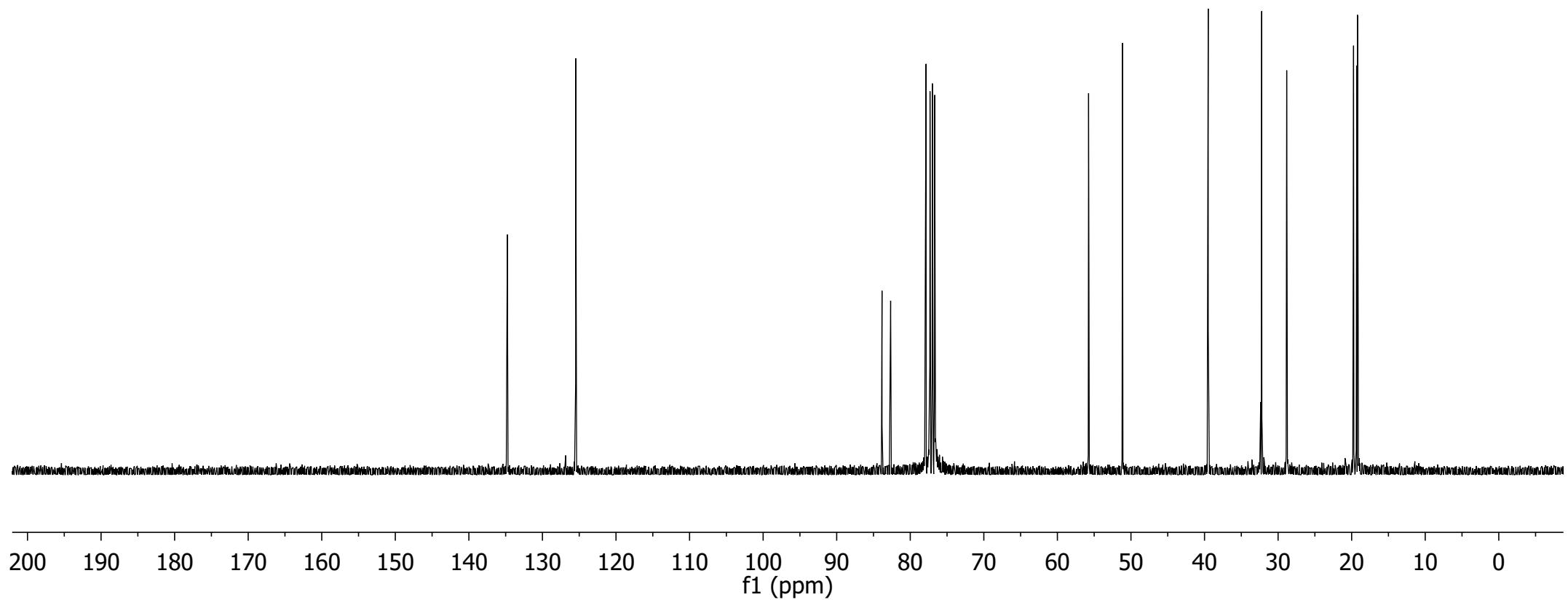


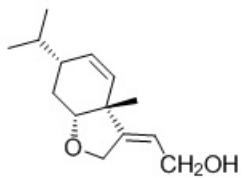
400 MHz ^1H NMR spectrum of compound **41**
(recorded in CDCl_3)



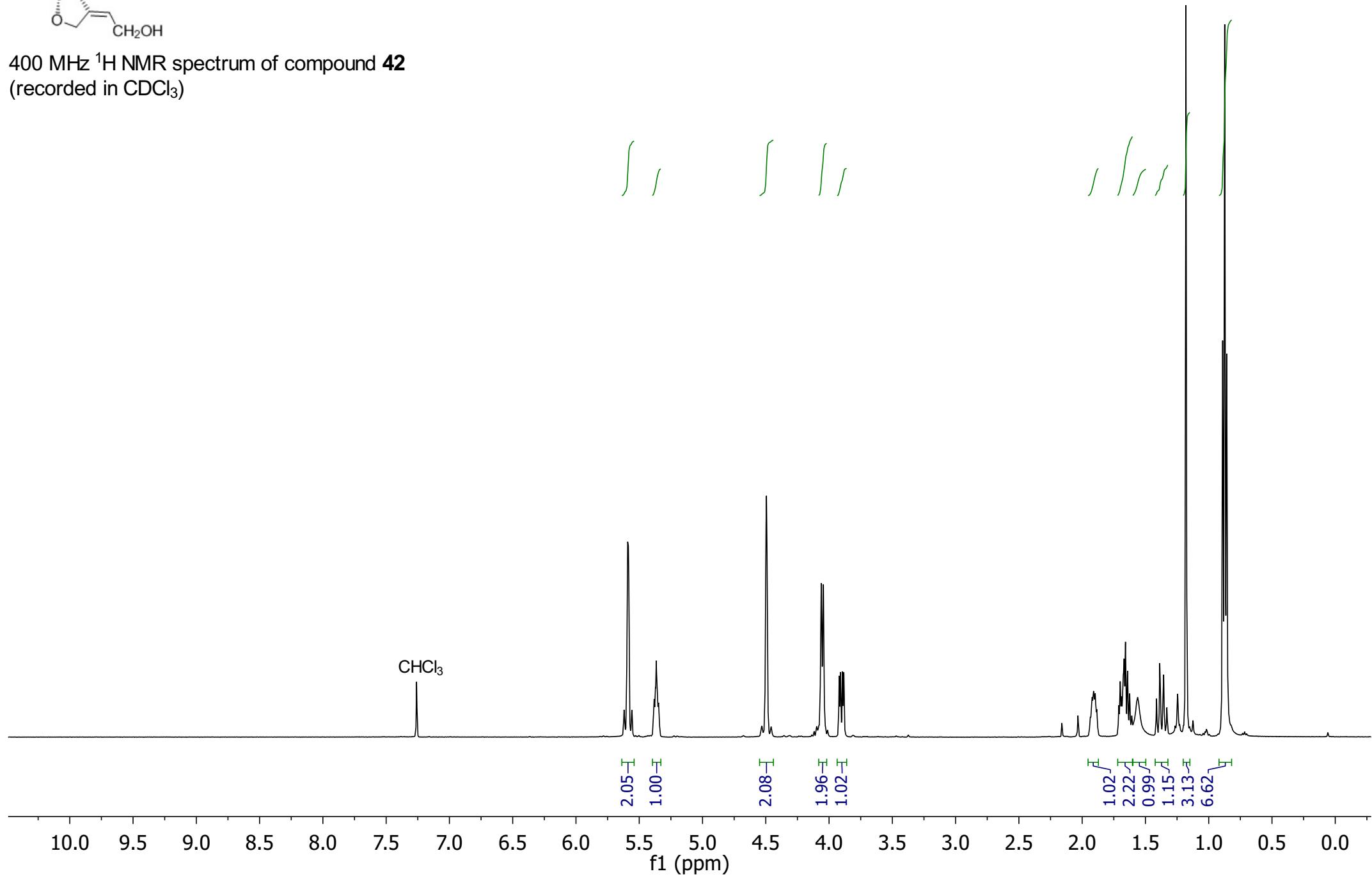


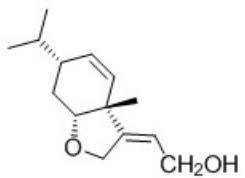
100 MHz ^{13}C NMR spectrum of compound **41**
(recorded in CDCl_3)



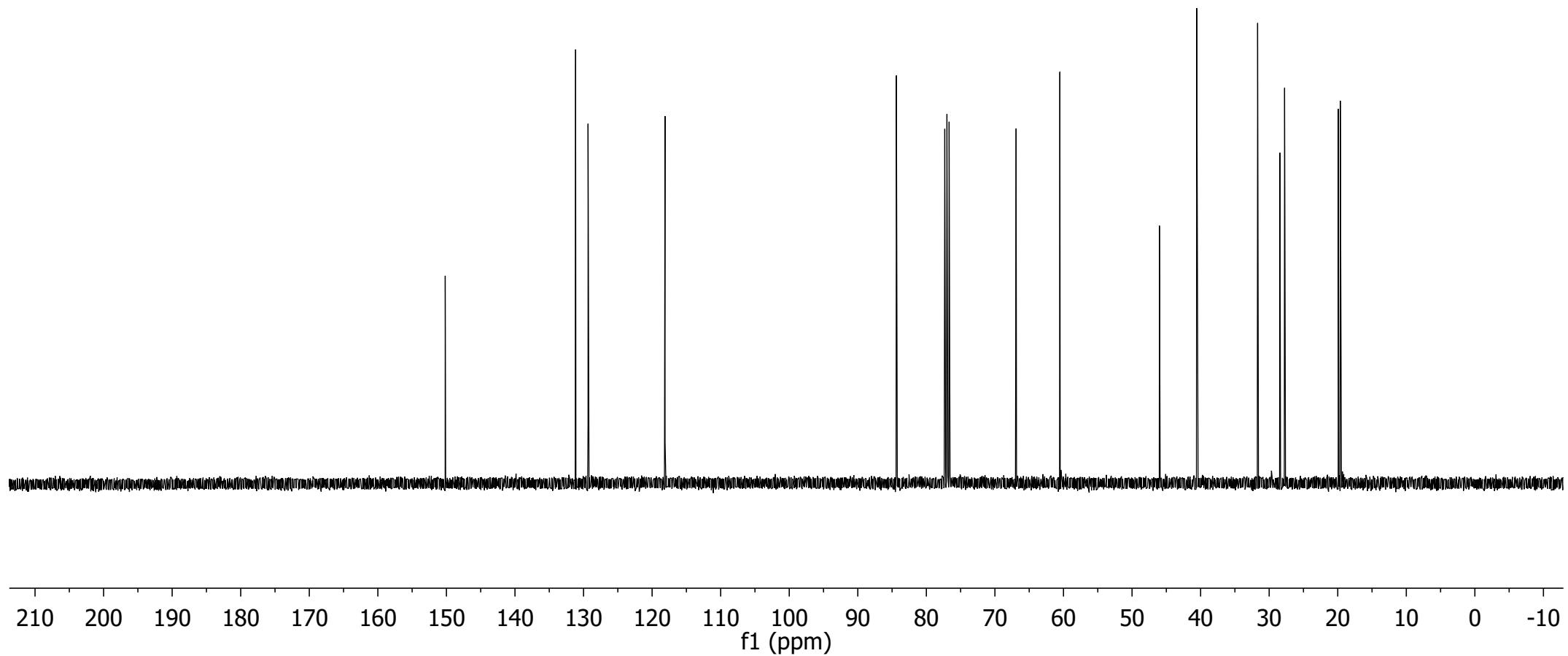


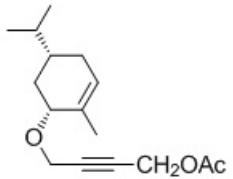
400 MHz ^1H NMR spectrum of compound **42**
(recorded in CDCl_3)



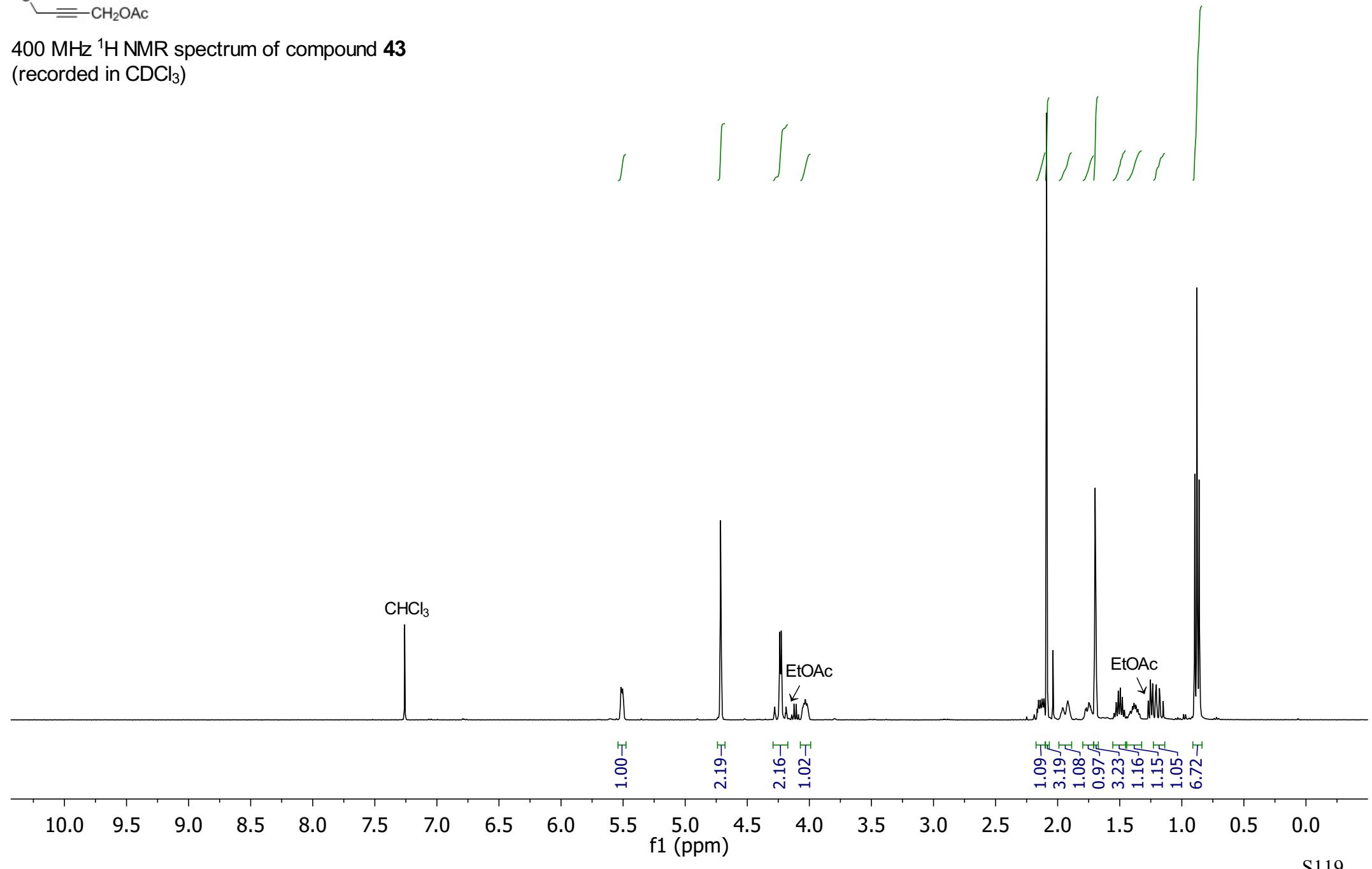


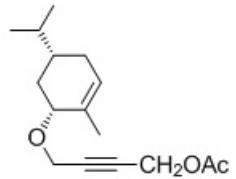
100 MHz ^{13}C NMR spectrum of compound **42**
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound **43**
(recorded in CDCl_3)





-170.2

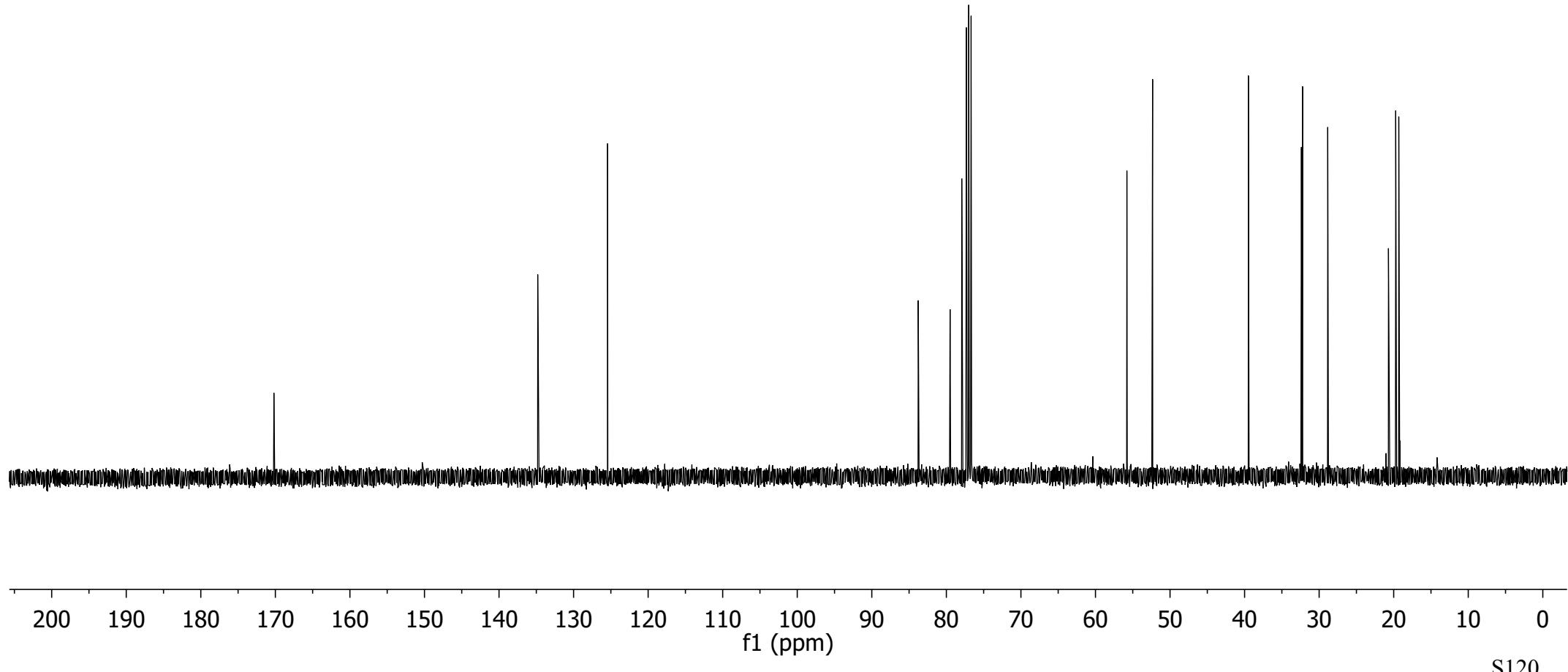
-125.4

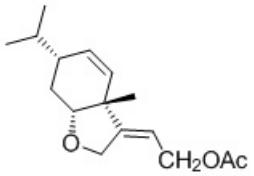
~83.8
~79.5
~77.9

-55.8
-52.3

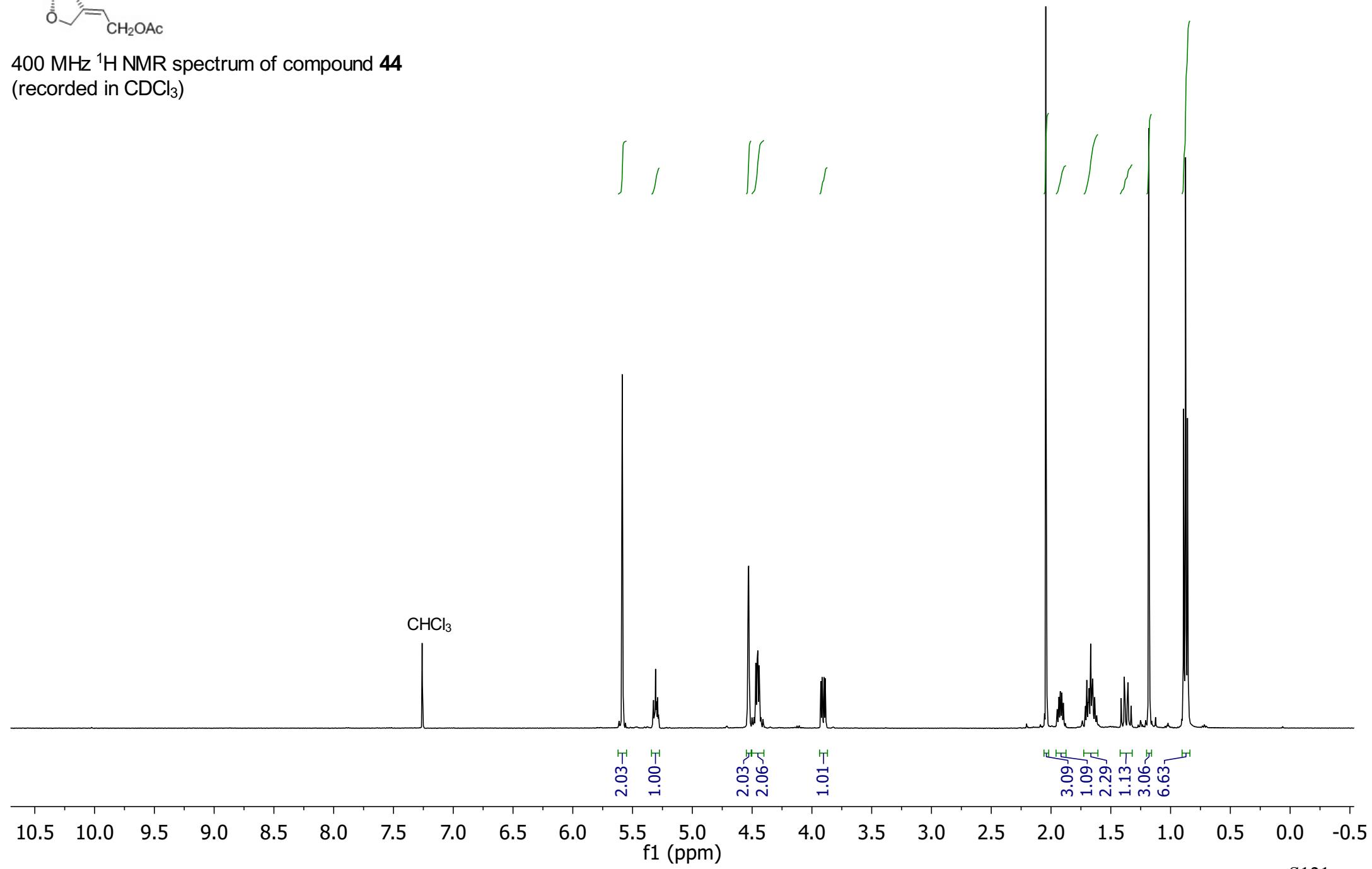
-39.5
-32.4
-32.2
-28.8
-20.7
~19.7
~19.3
19.2

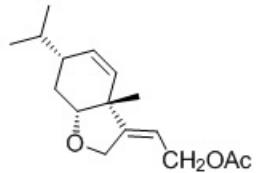
100 MHz ¹³C NMR spectrum of compound **43**
(recorded in CDCl₃)



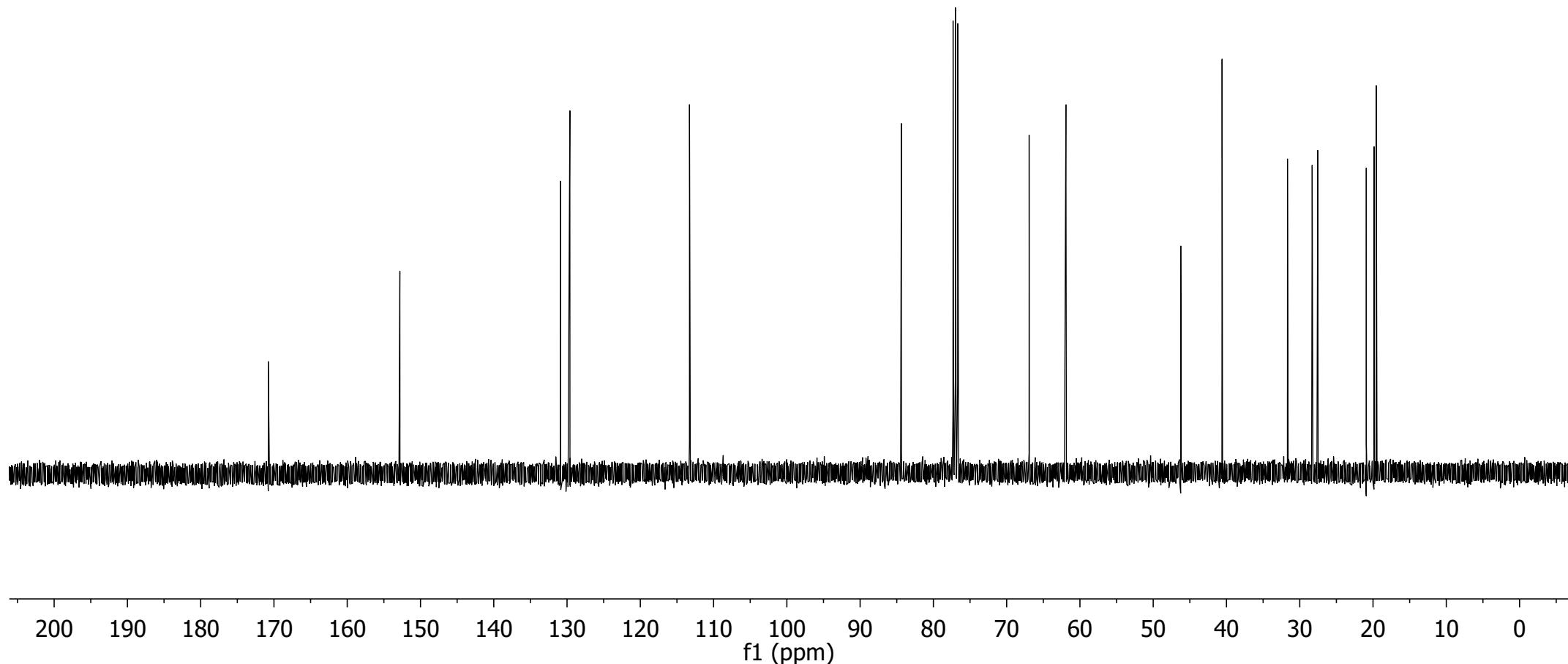


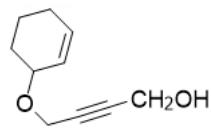
400 MHz ^1H NMR spectrum of compound **44**
(recorded in CDCl_3)



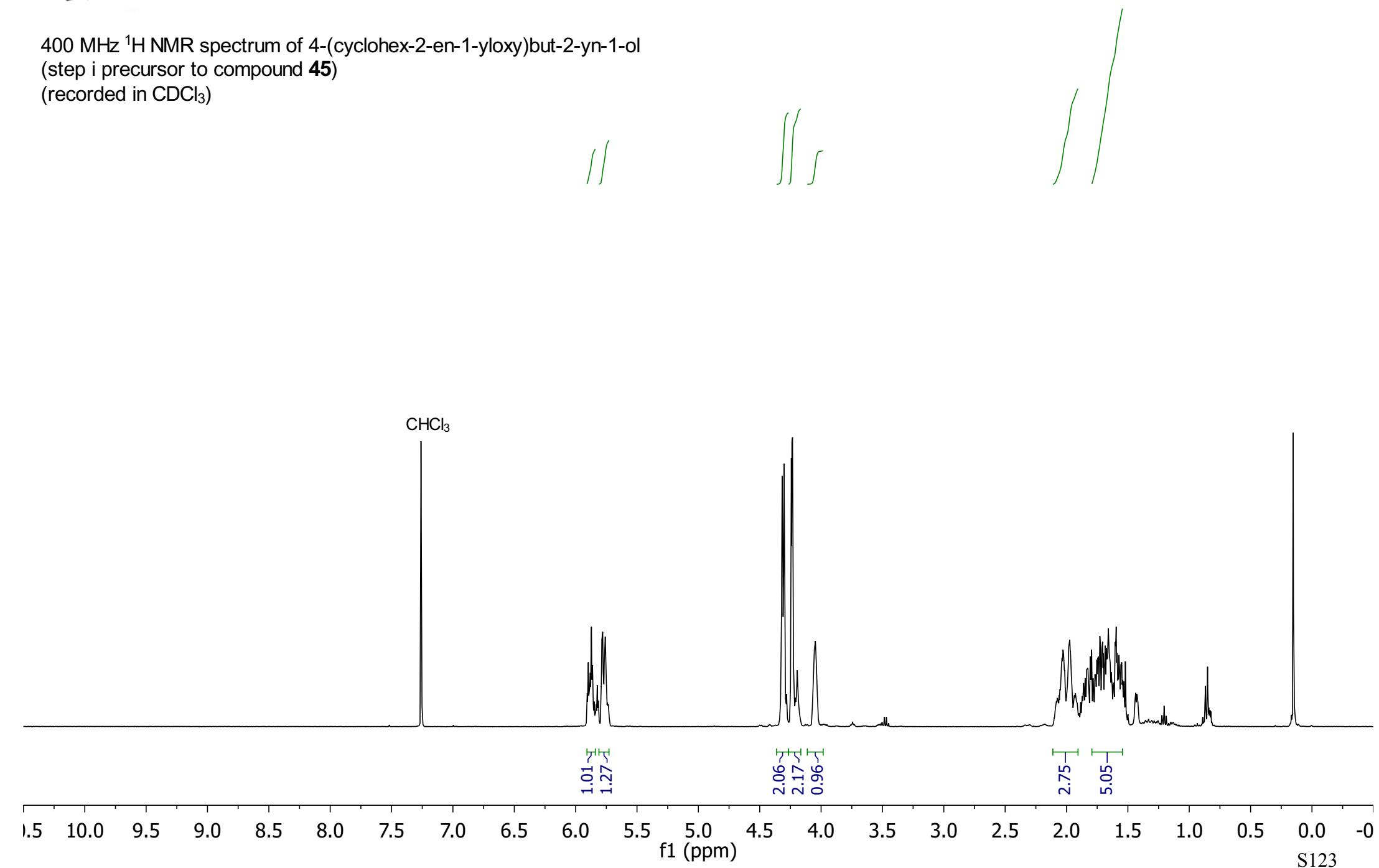


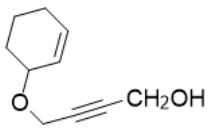
100 MHz ^{13}C NMR spectrum of compound **44**
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of 4-(cyclohex-2-en-1-yloxy)but-2-yn-1-ol
(step i precursor to compound **45**)
(recorded in CDCl_3)





-131.7
-127.1

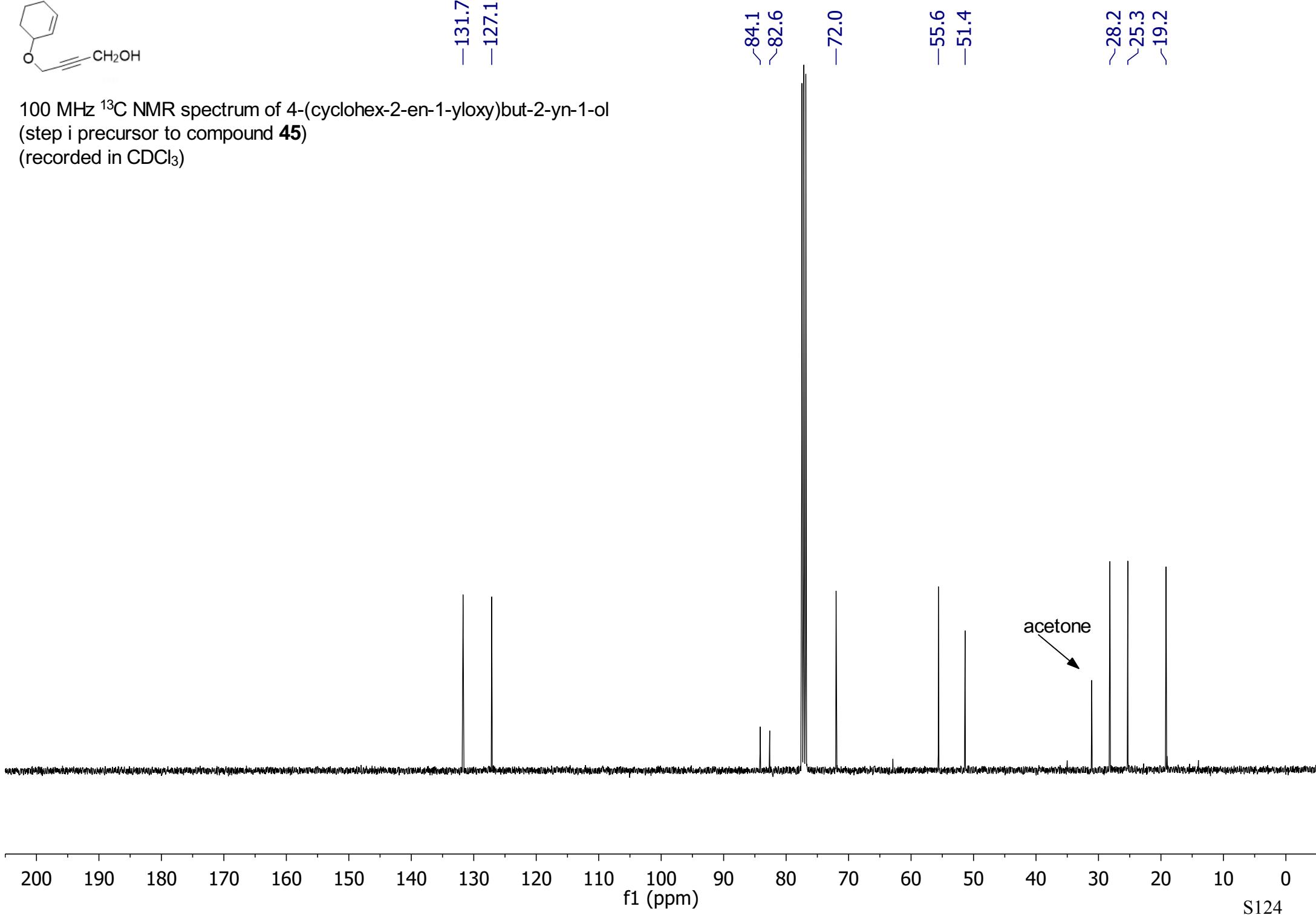
~84.1
~82.6

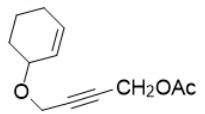
-72.0

-55.6
-51.4

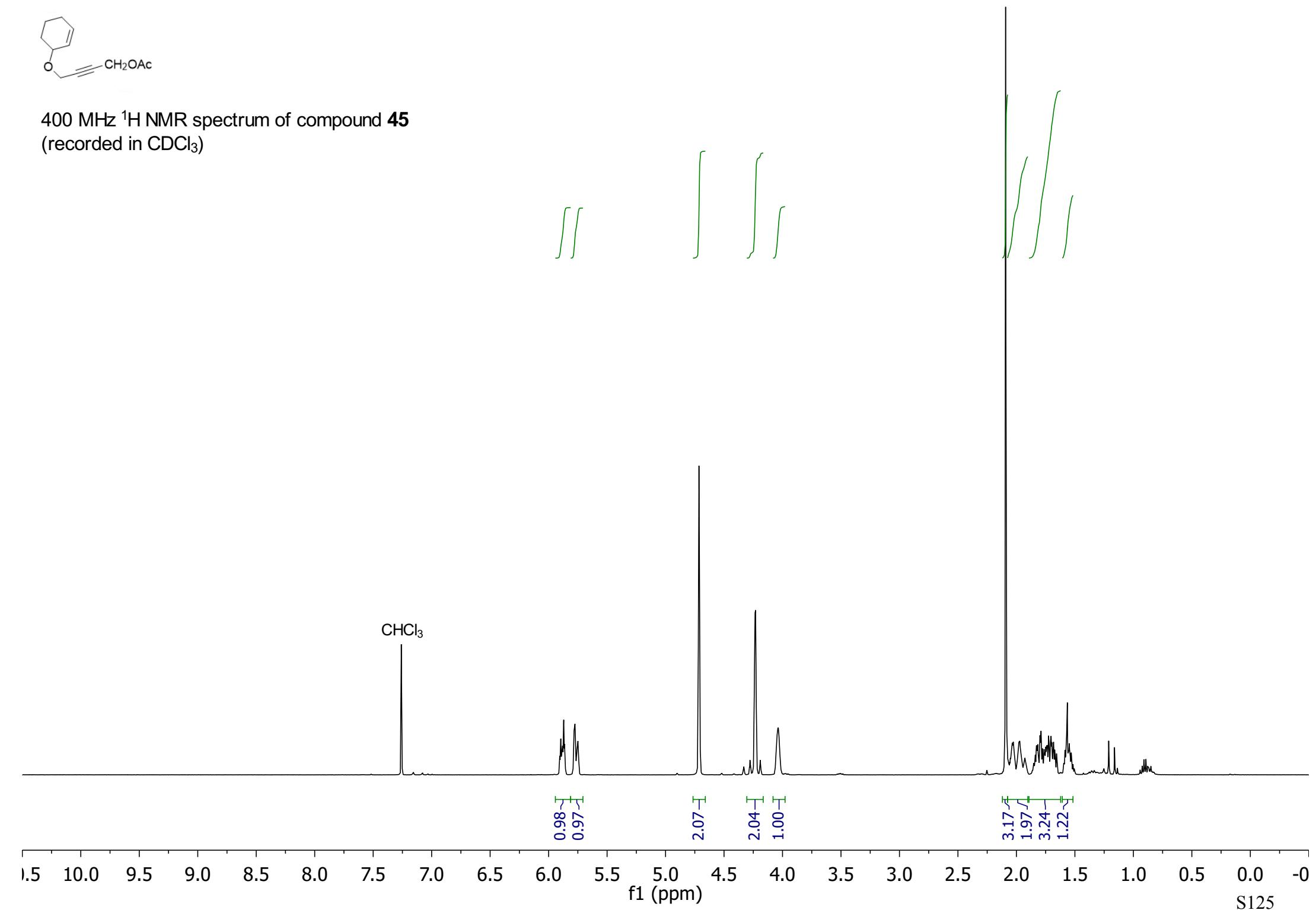
~28.2
~25.3
~19.2

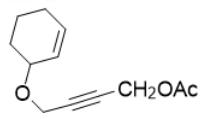
100 MHz ^{13}C NMR spectrum of 4-(cyclohex-2-en-1-yloxy)but-2-yn-1-ol
(step i precursor to compound **45**)
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound **45**
(recorded in CDCl_3)





-170.4

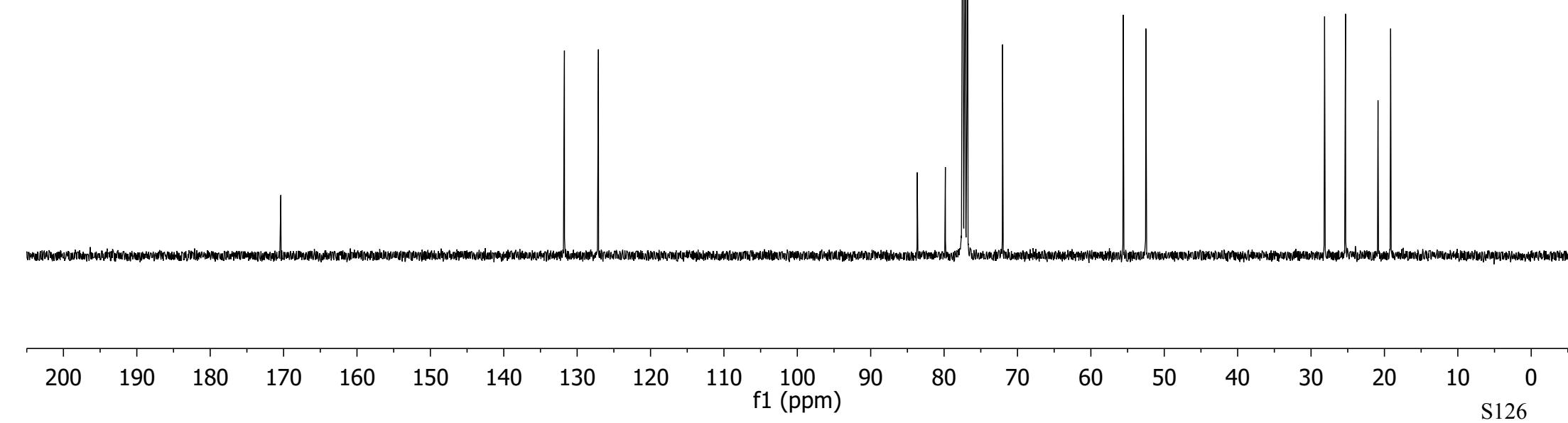
-131.7
-127.1

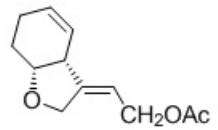
-83.7
-79.8
-72.0

-55.6
-52.5

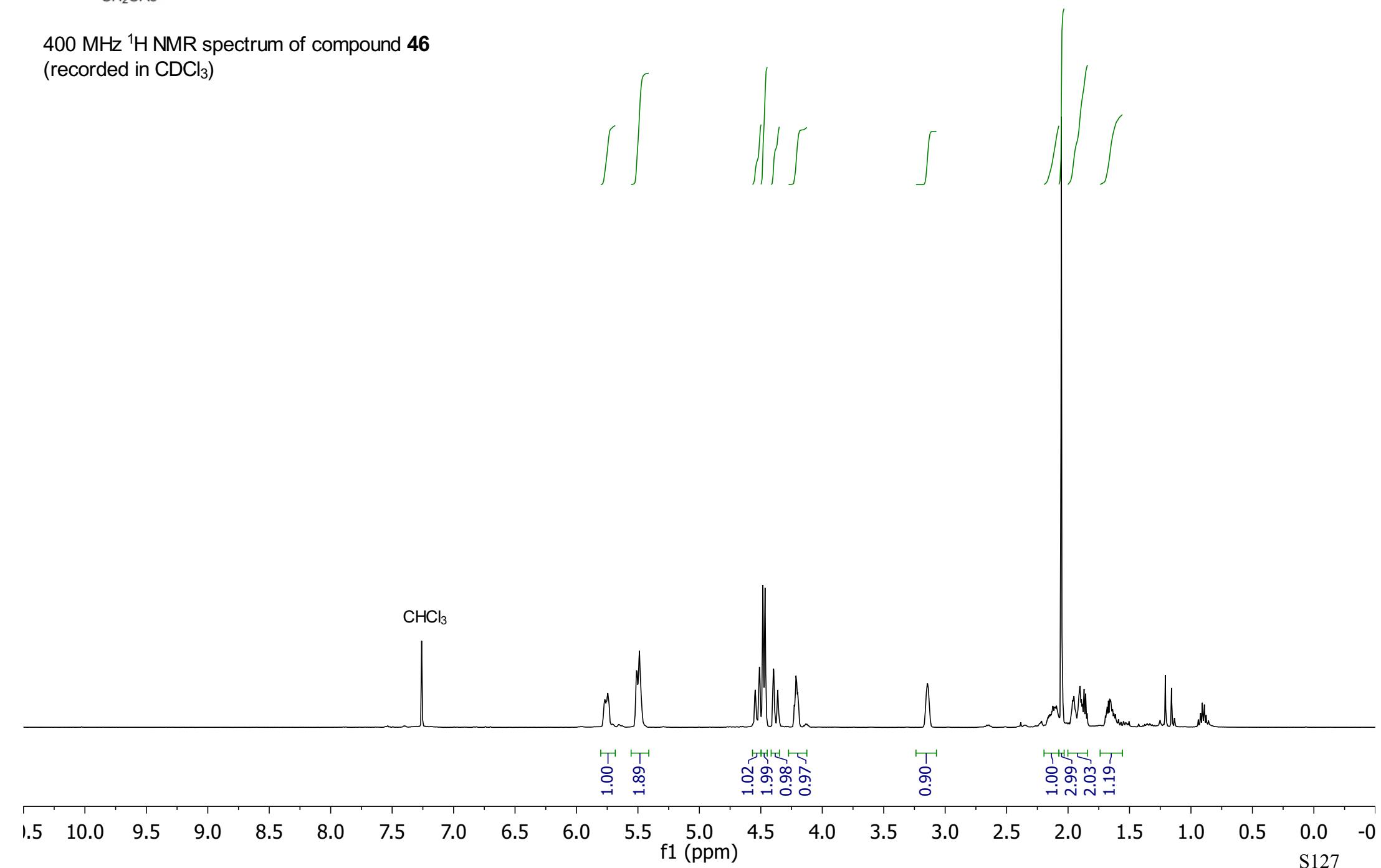
-28.2
-25.3
-20.9
-19.2

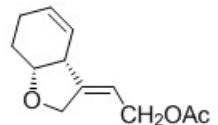
100 MHz ^{13}C NMR spectrum of compound **45**
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound **46**
(recorded in CDCl_3)





-171.0

-148.6

~127.5
~126.0

-114.8

-76.6

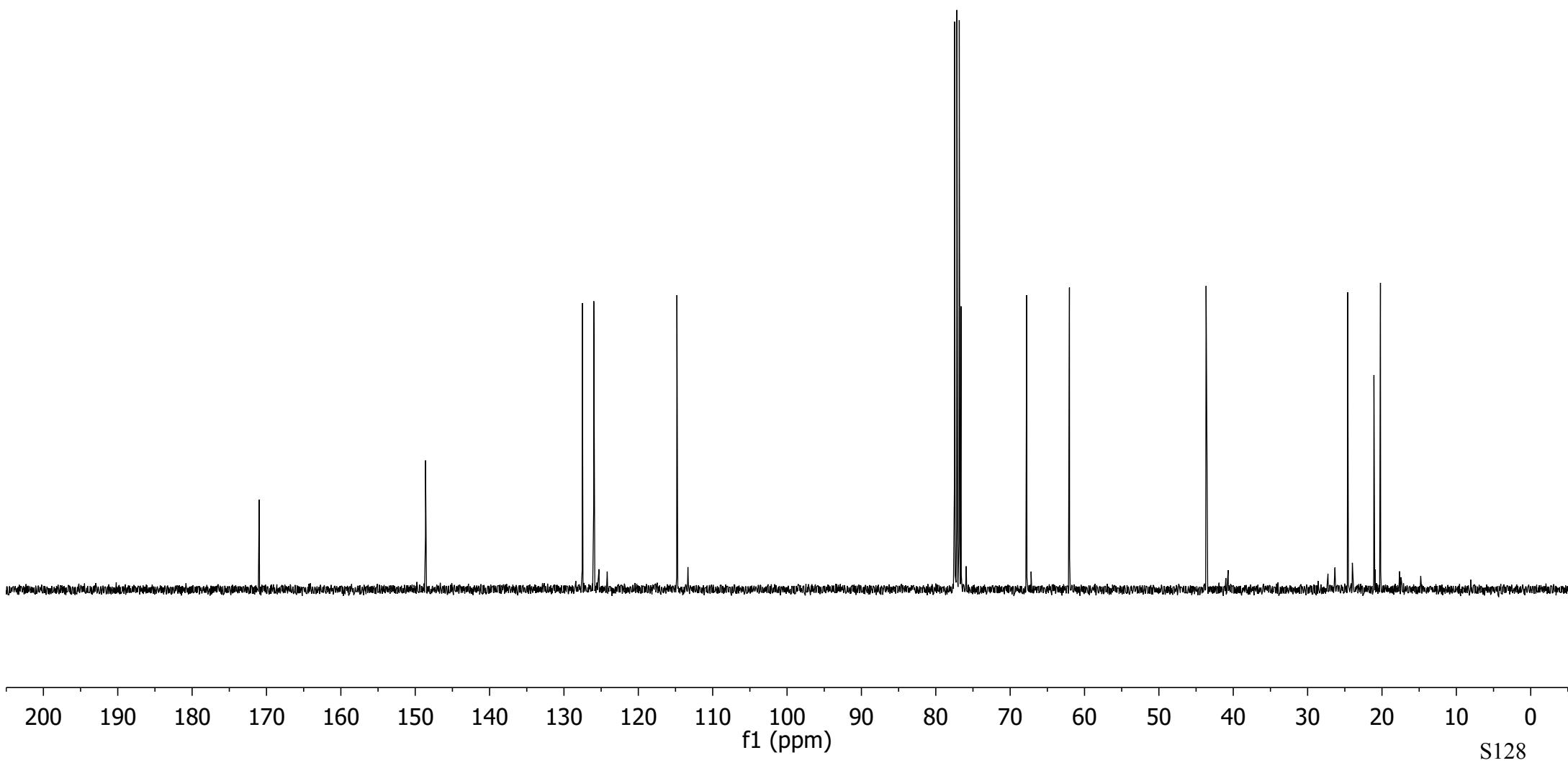
-67.8

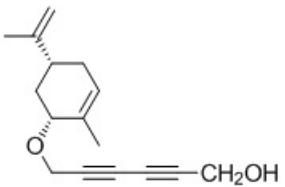
-62.0

-43.7

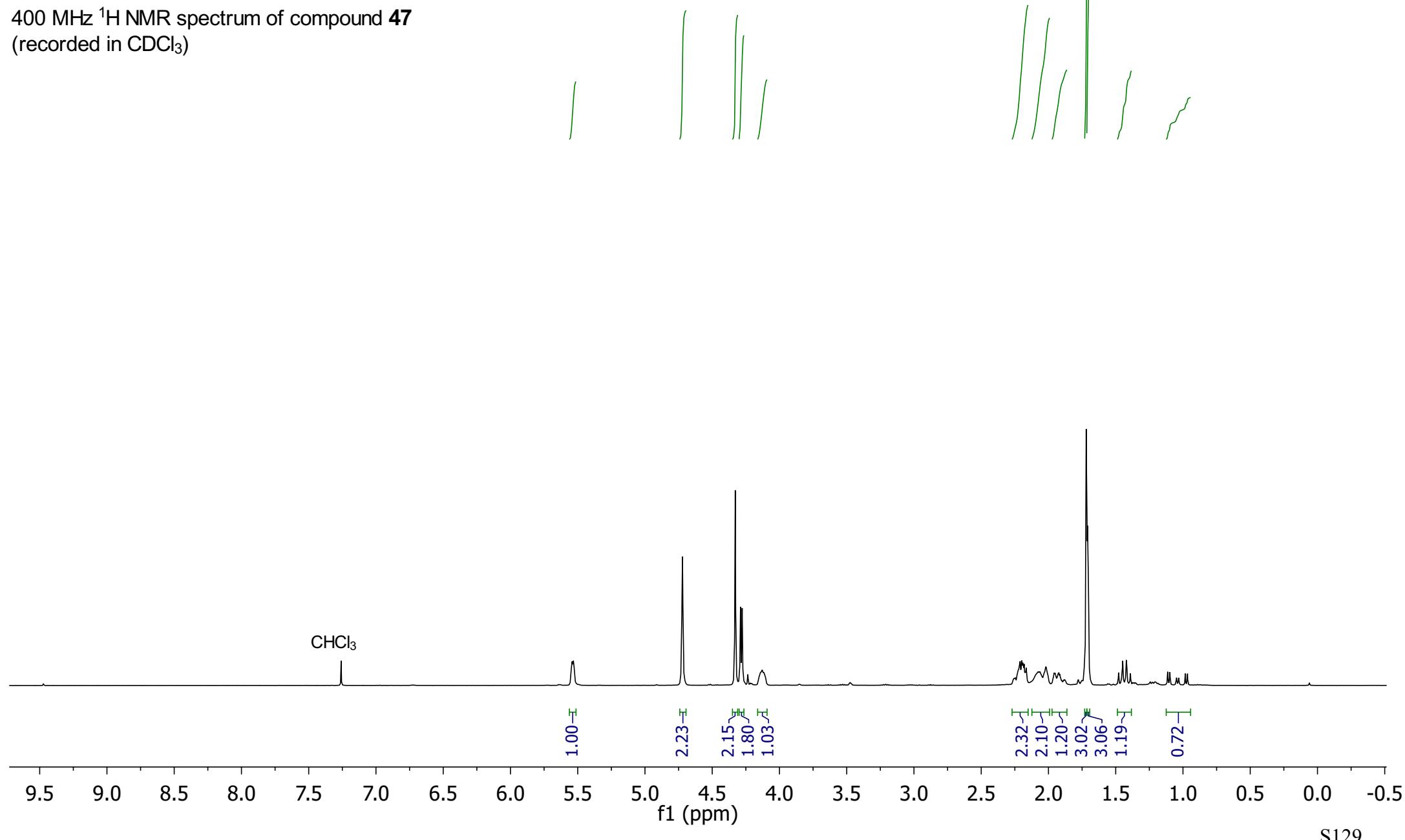
~24.6
~21.1
~20.2

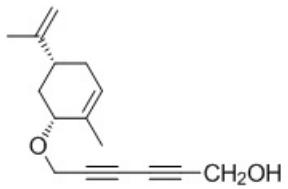
100 MHz ^{13}C NMR spectrum of compound **46**
(recorded in CDCl_3)



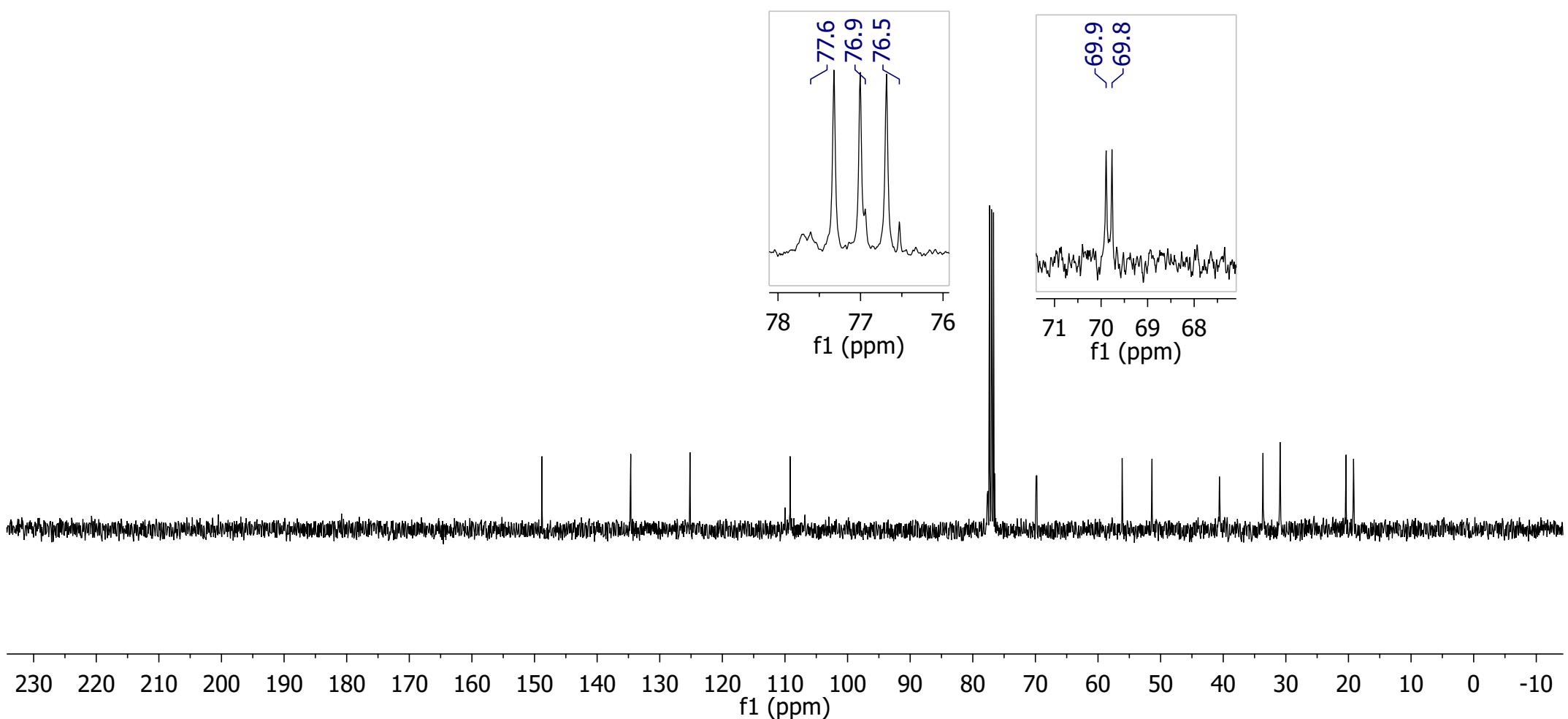


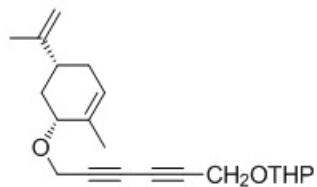
400 MHz ^1H NMR spectrum of compound **47**
(recorded in CDCl_3)



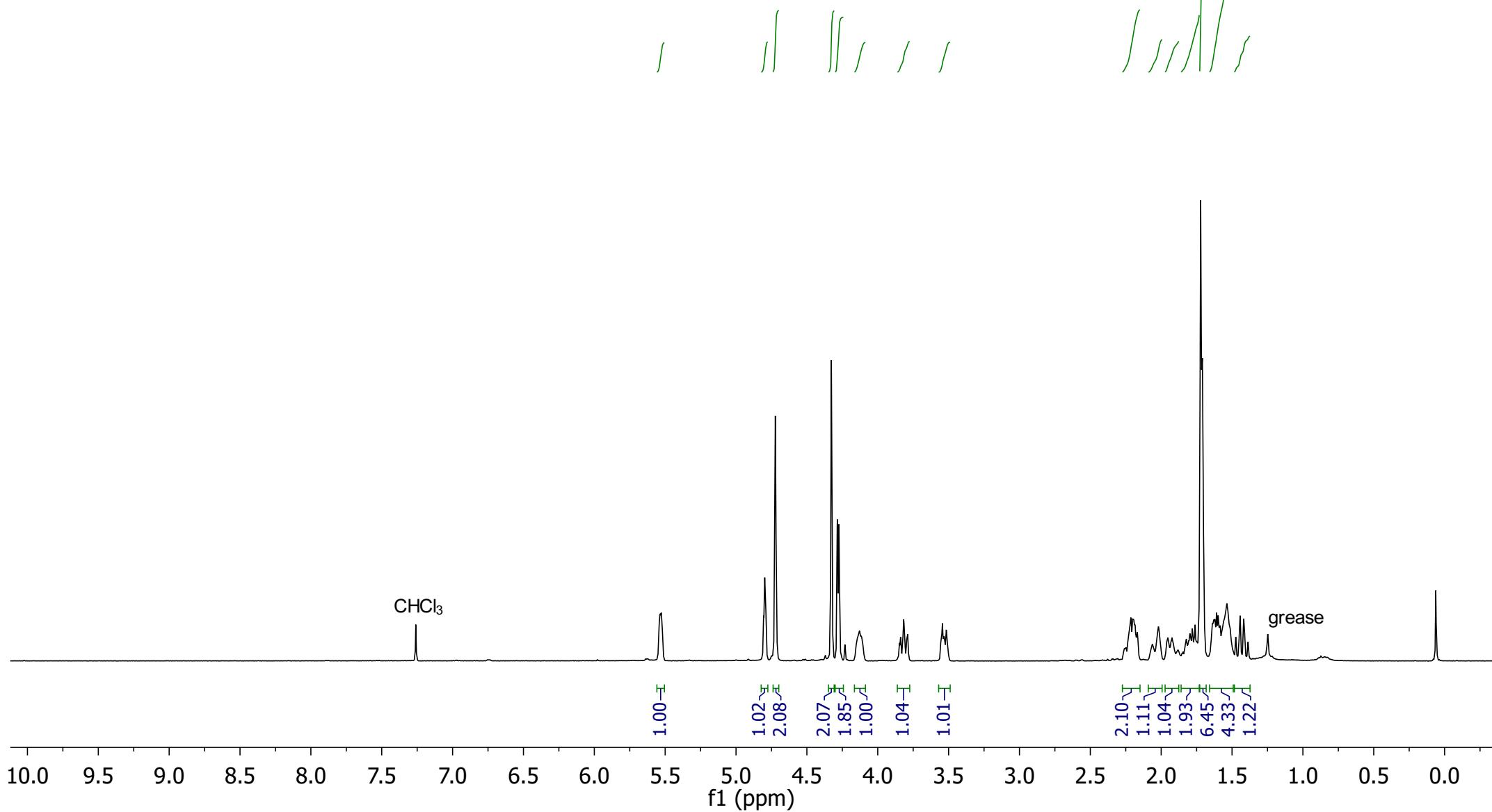


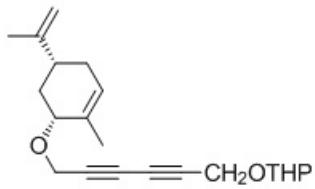
100 MHz ^{13}C NMR spectrum of compound **47**
(recorded in CDCl_3)



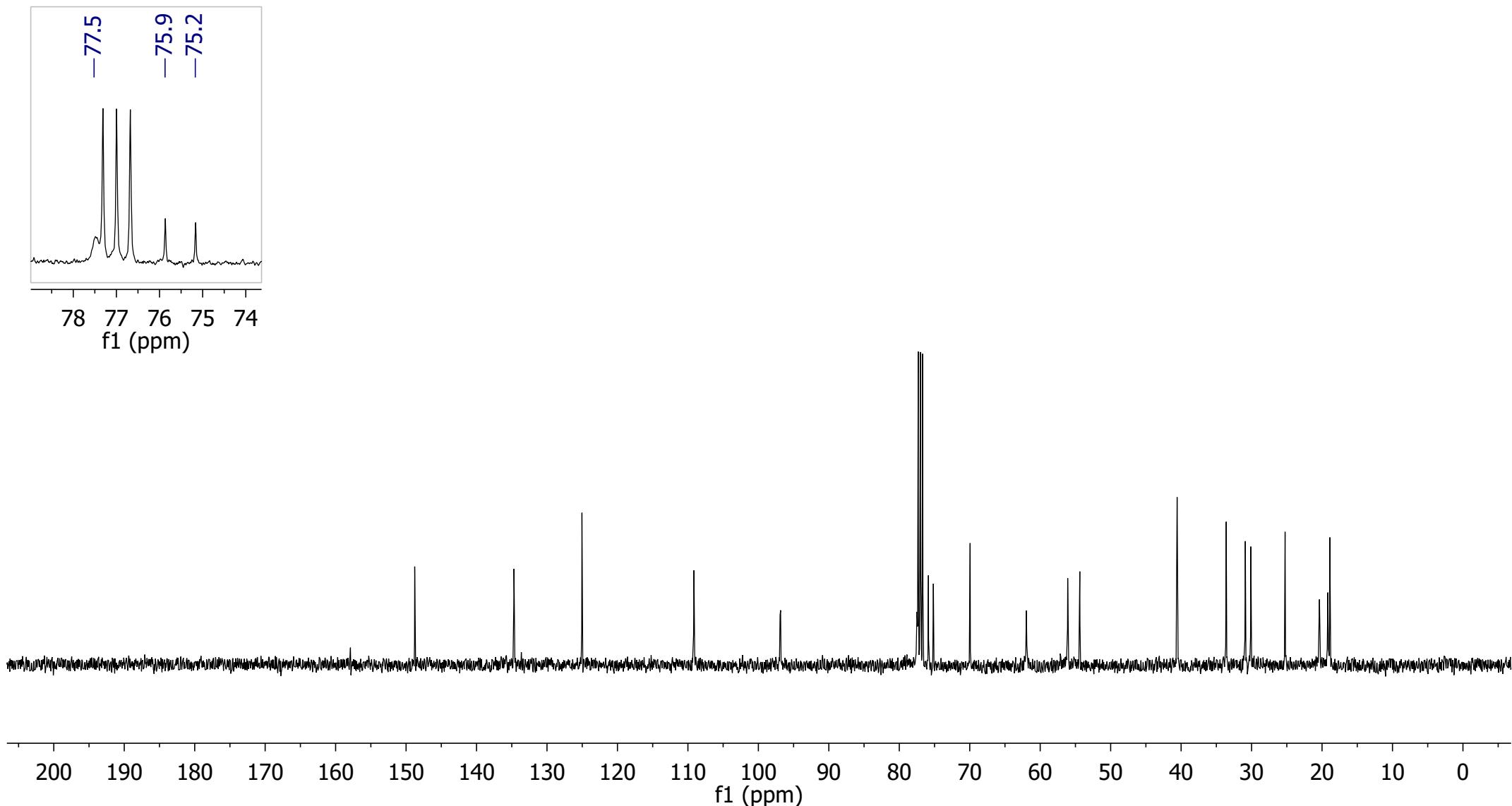


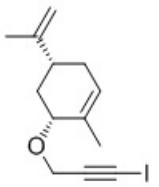
400 MHz ^1H NMR spectrum of compound **48**
(recorded in CDCl_3)



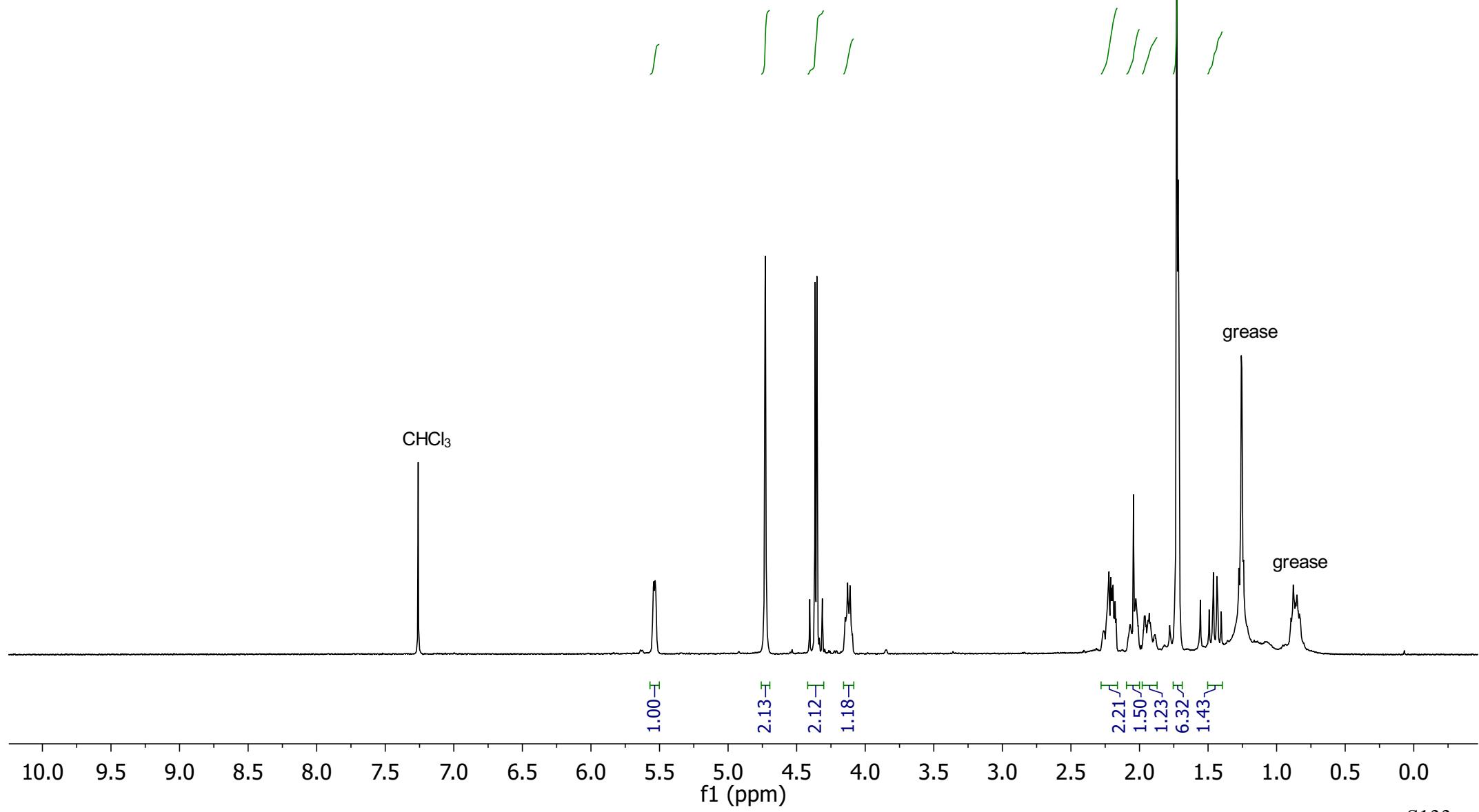


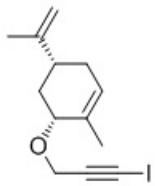
100 MHz ¹³C NMR spectrum of compound **48**
(recorded in CDCl₃)



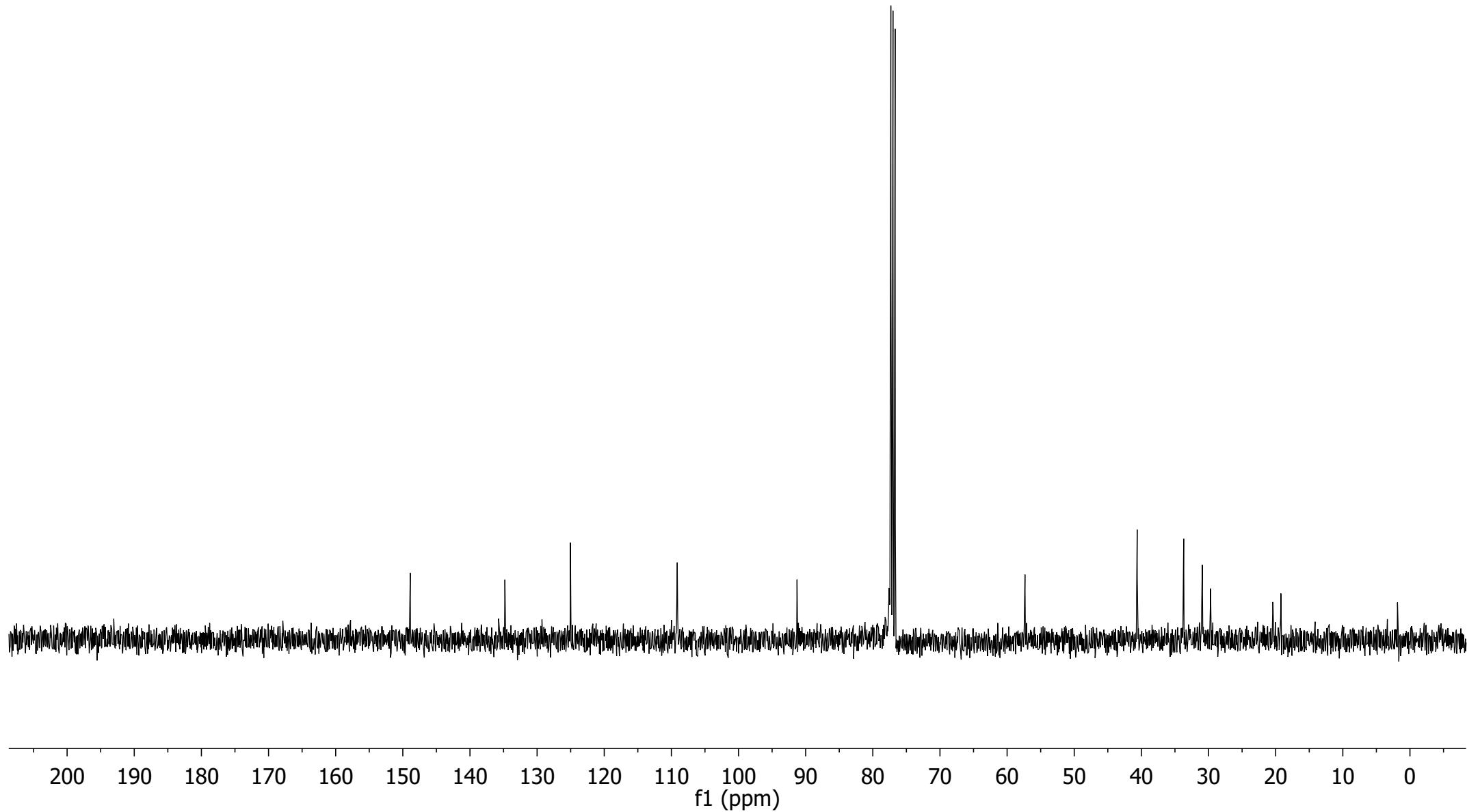


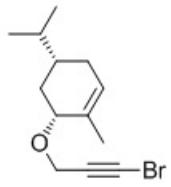
400 MHz ^1H NMR spectrum of compound **49**
(recorded in CDCl_3)



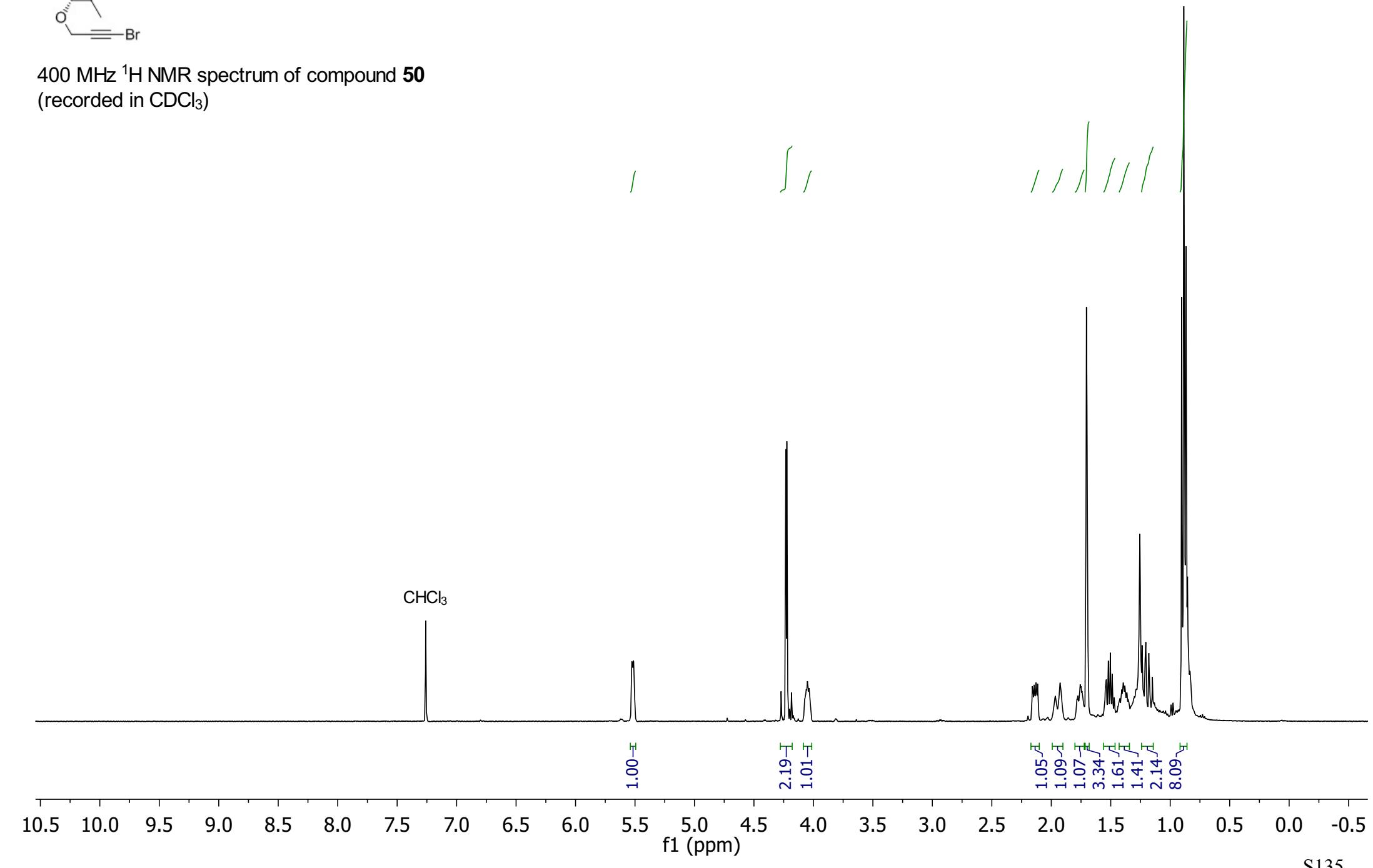


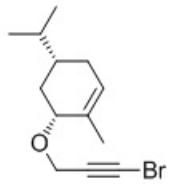
100 MHz ^{13}C NMR spectrum of compound **49**
(recorded in CDCl_3)



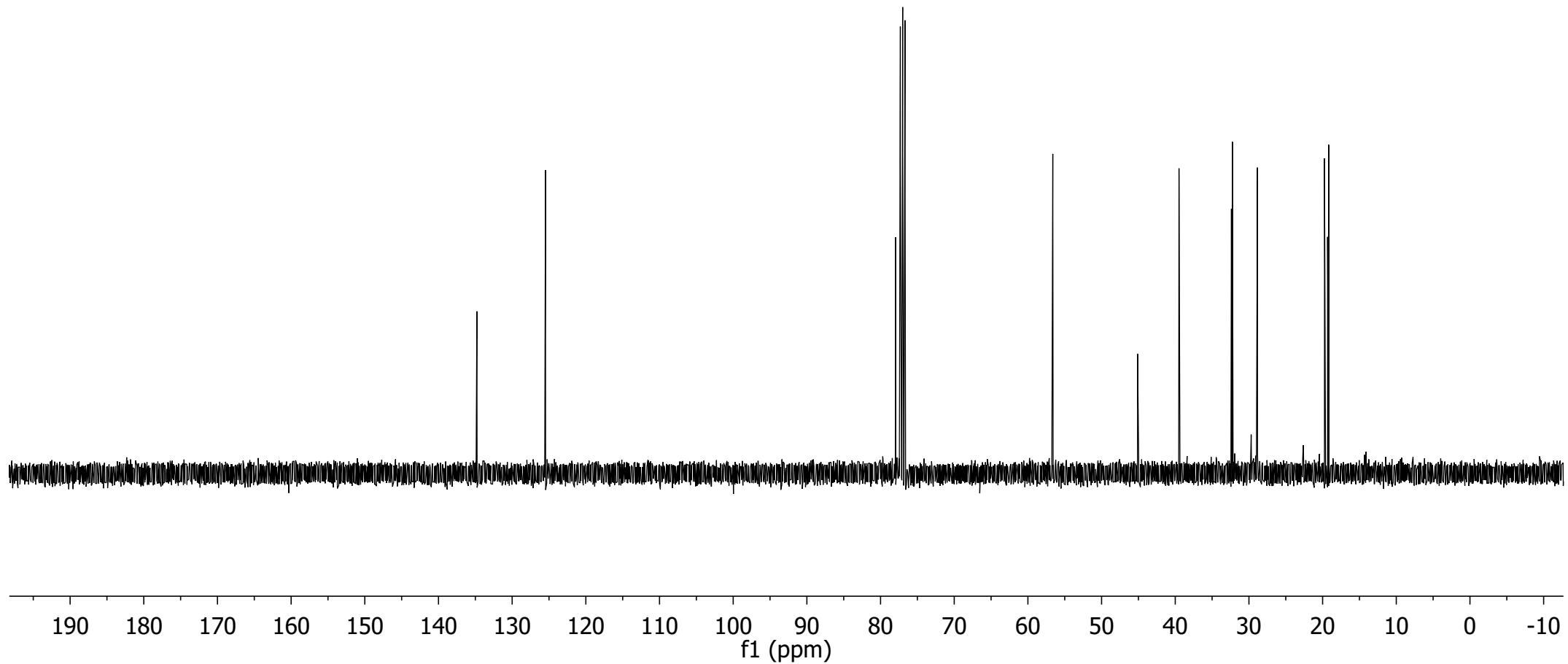


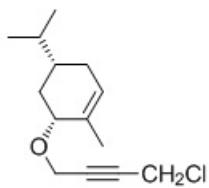
400 MHz ¹H NMR spectrum of compound **50**
(recorded in CDCl₃)



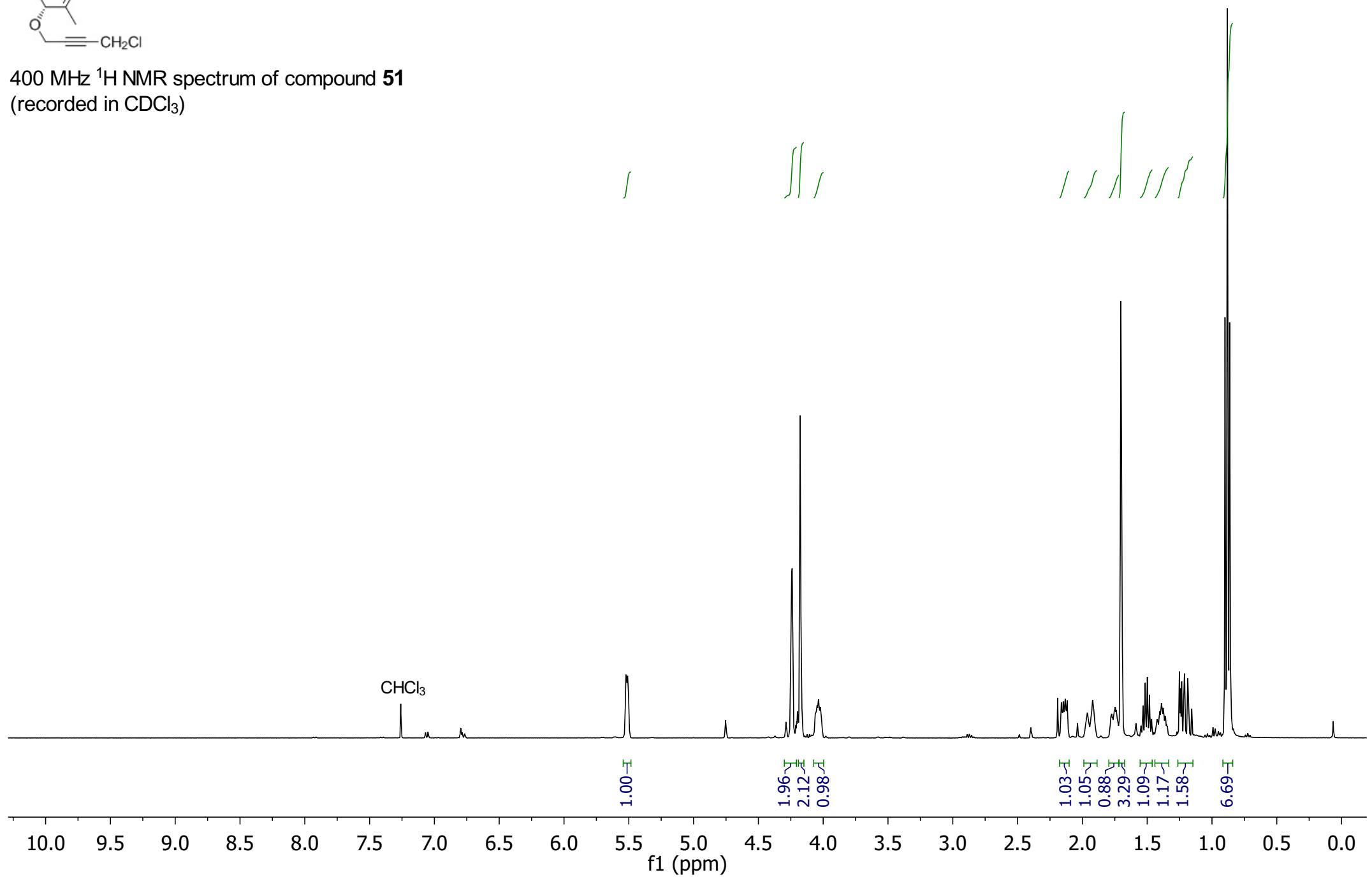


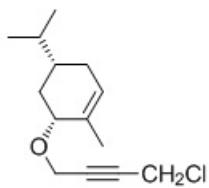
100 MHz ^{13}C NMR spectrum of compound **50**
(recorded in CDCl_3)



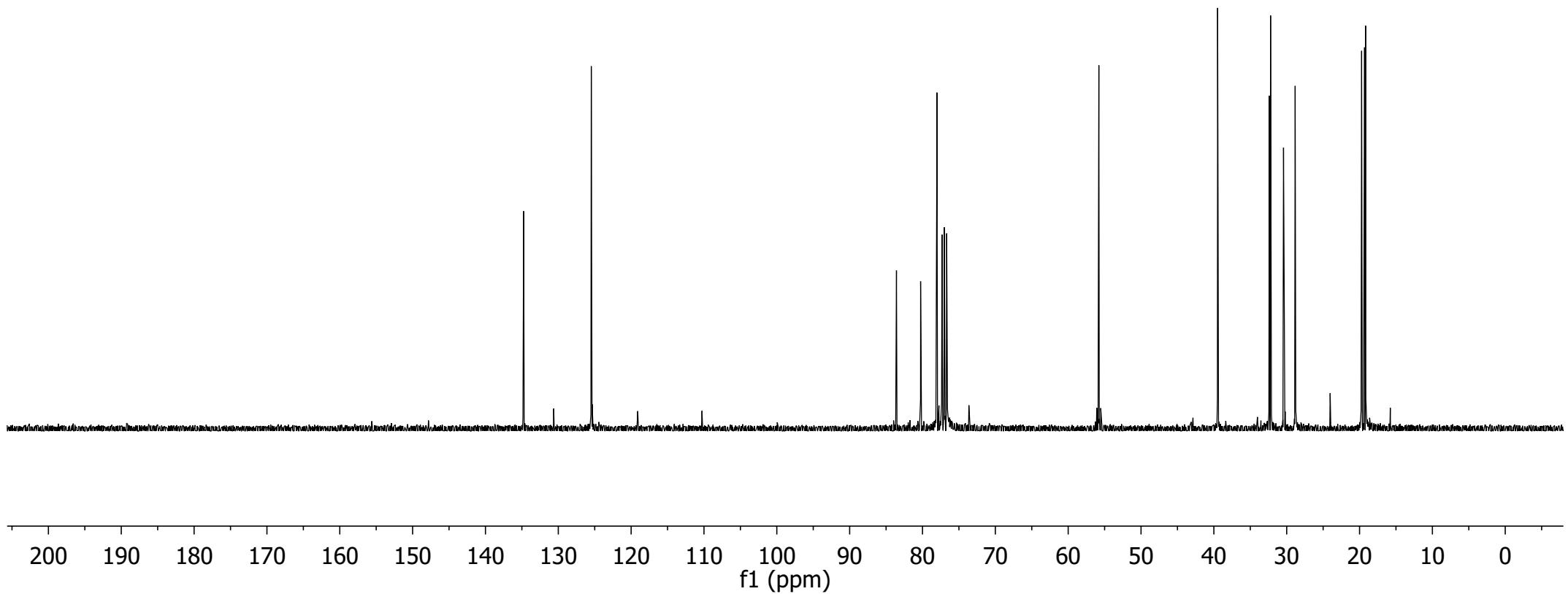


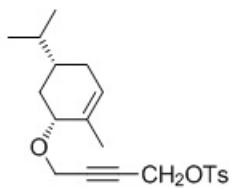
400 MHz ^1H NMR spectrum of compound **51**
(recorded in CDCl_3)



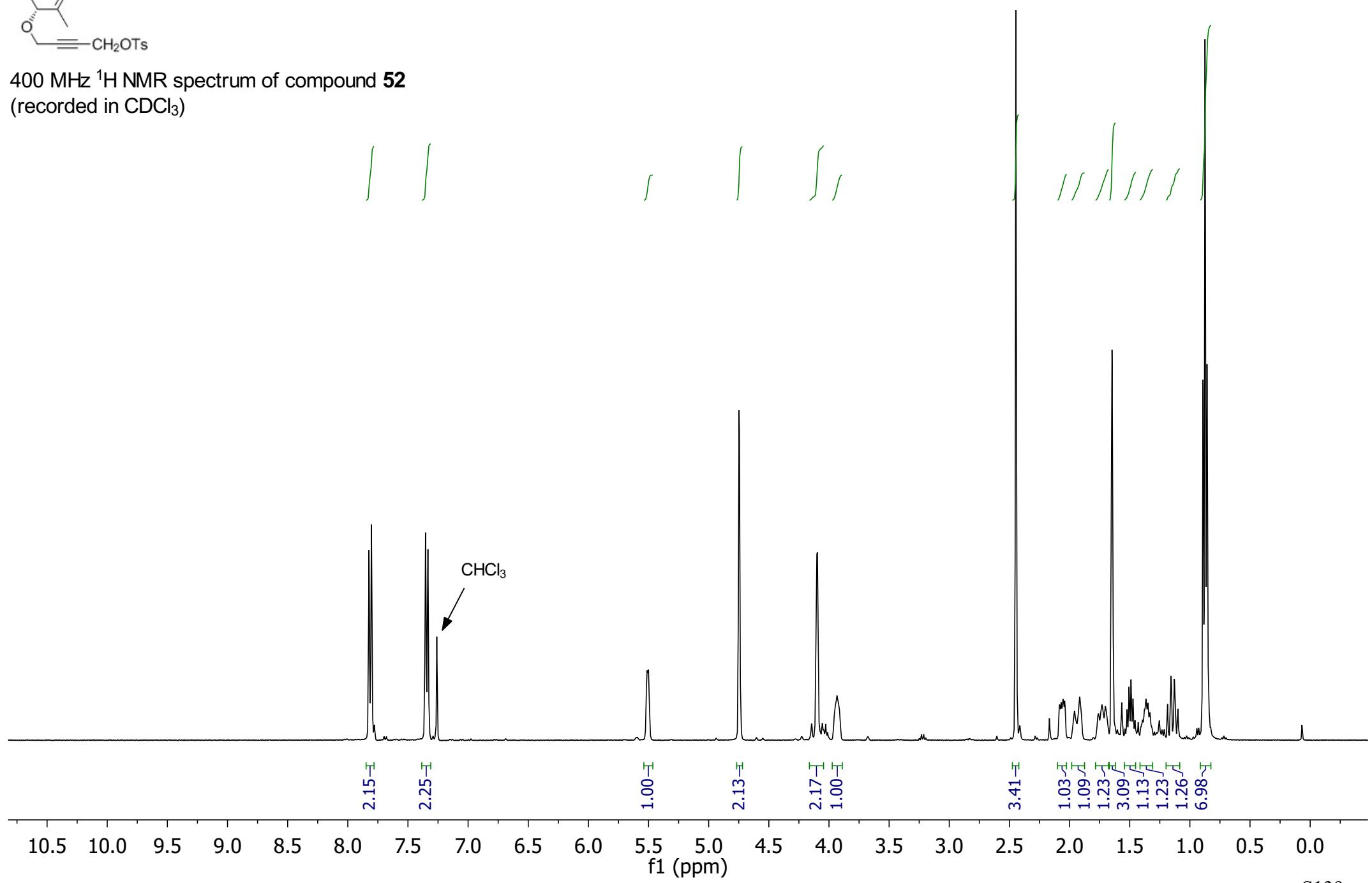


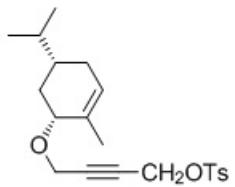
100 MHz ^{13}C NMR spectrum of compound **51**
(recorded in CDCl_3)





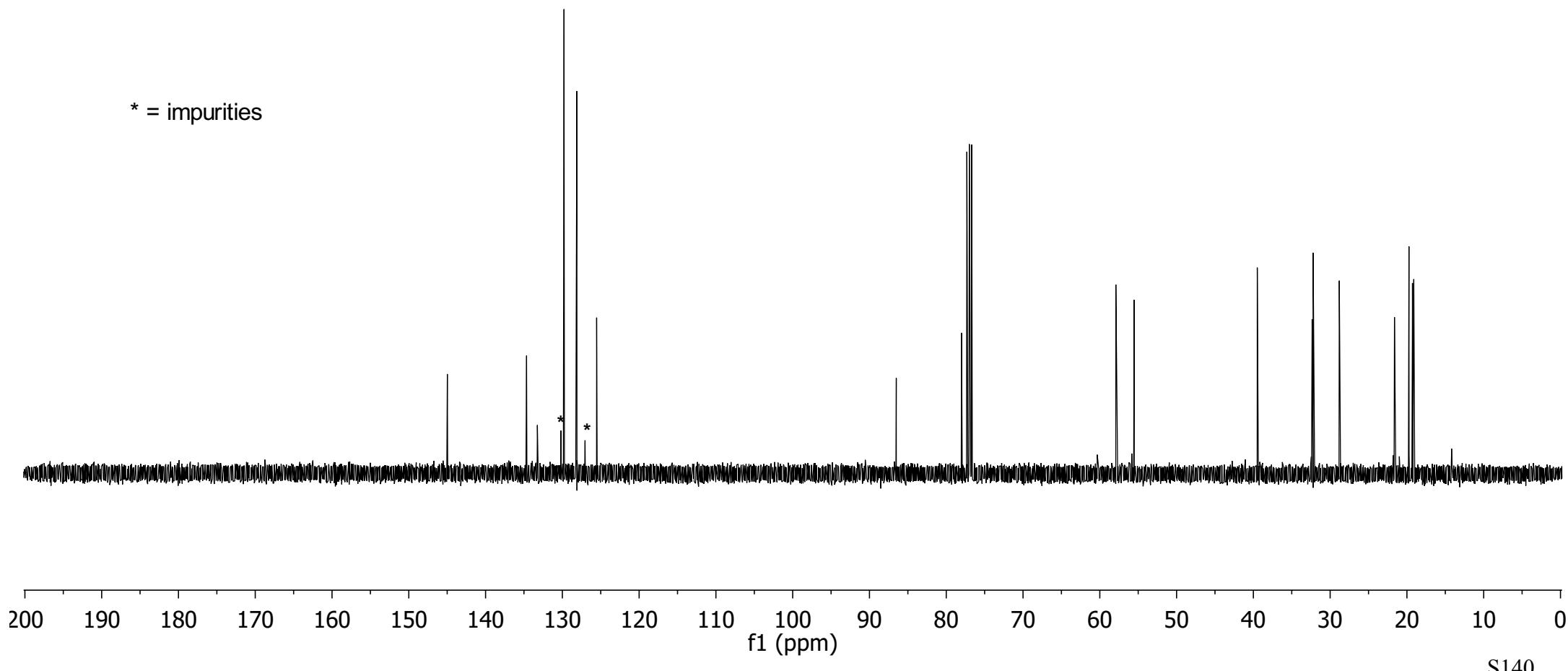
400 MHz ^1H NMR spectrum of compound **52**
(recorded in CDCl_3)

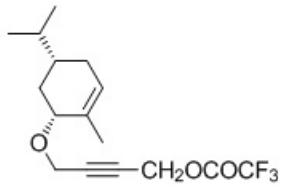




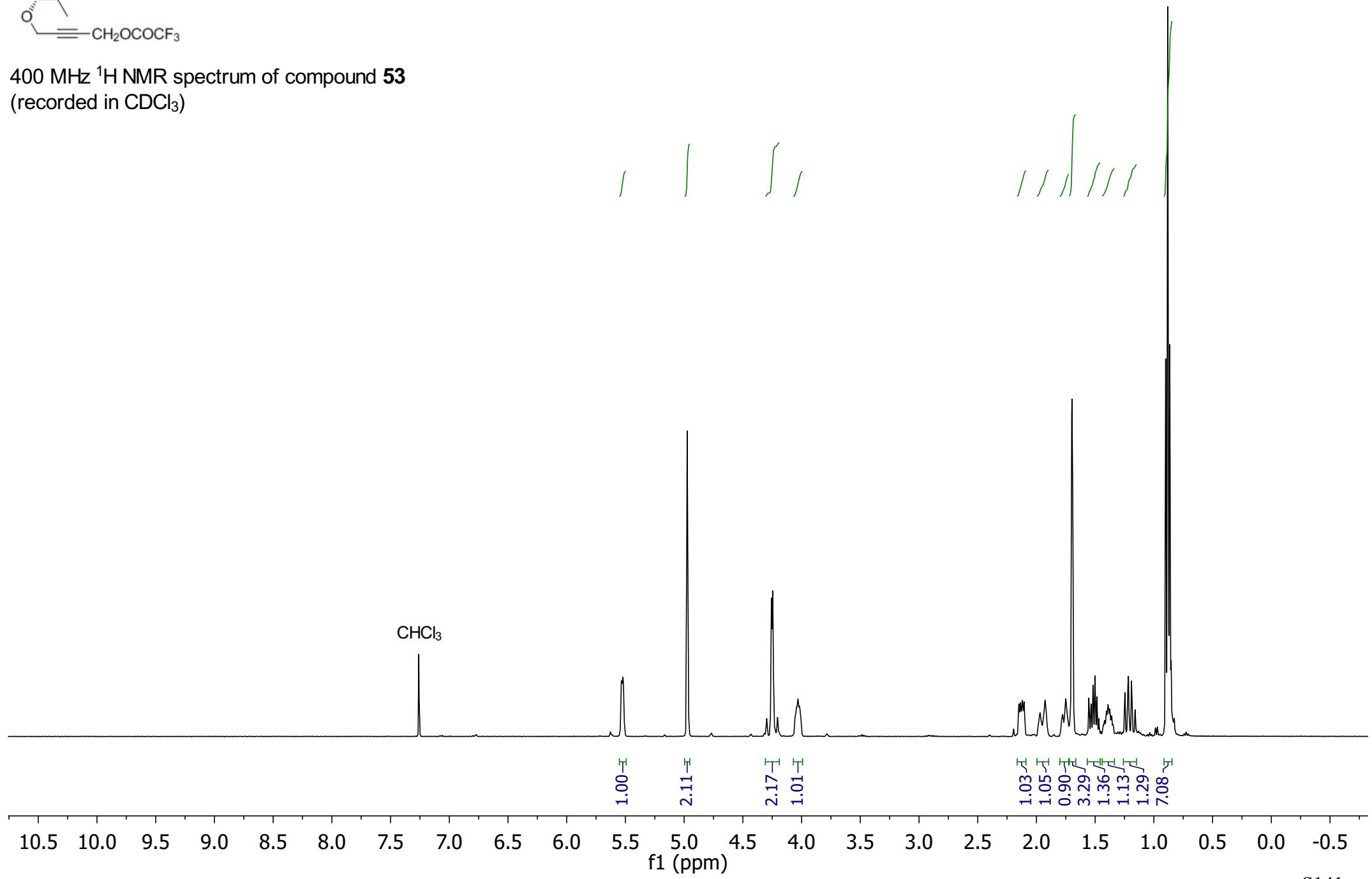
100 MHz ^{13}C NMR spectrum of compound **52**
(recorded in CDCl_3)

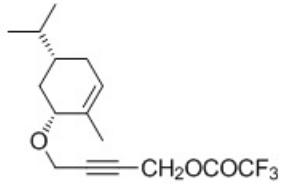
* = impurities



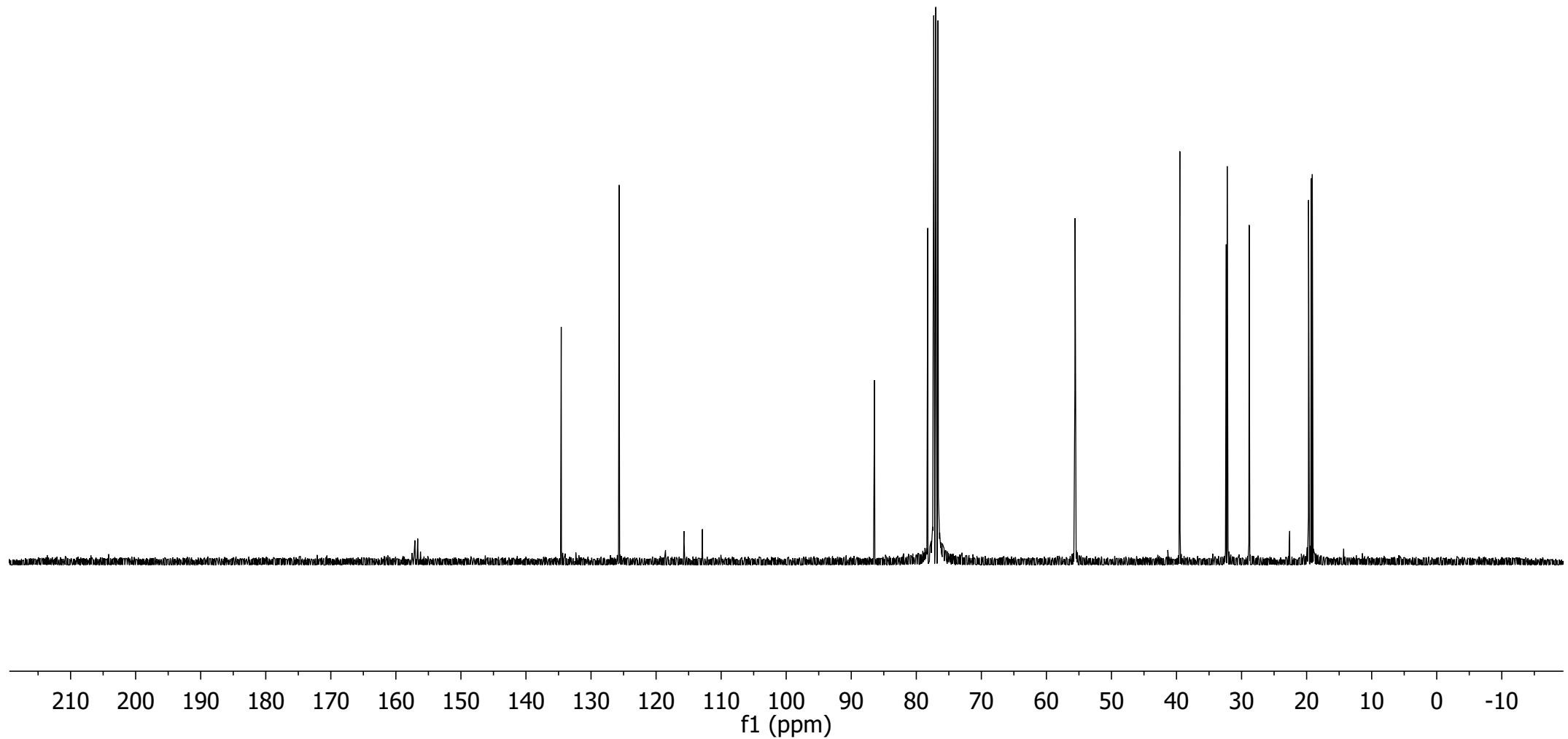


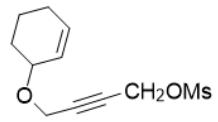
400 MHz ^1H NMR spectrum of compound **53**
(recorded in CDCl_3)



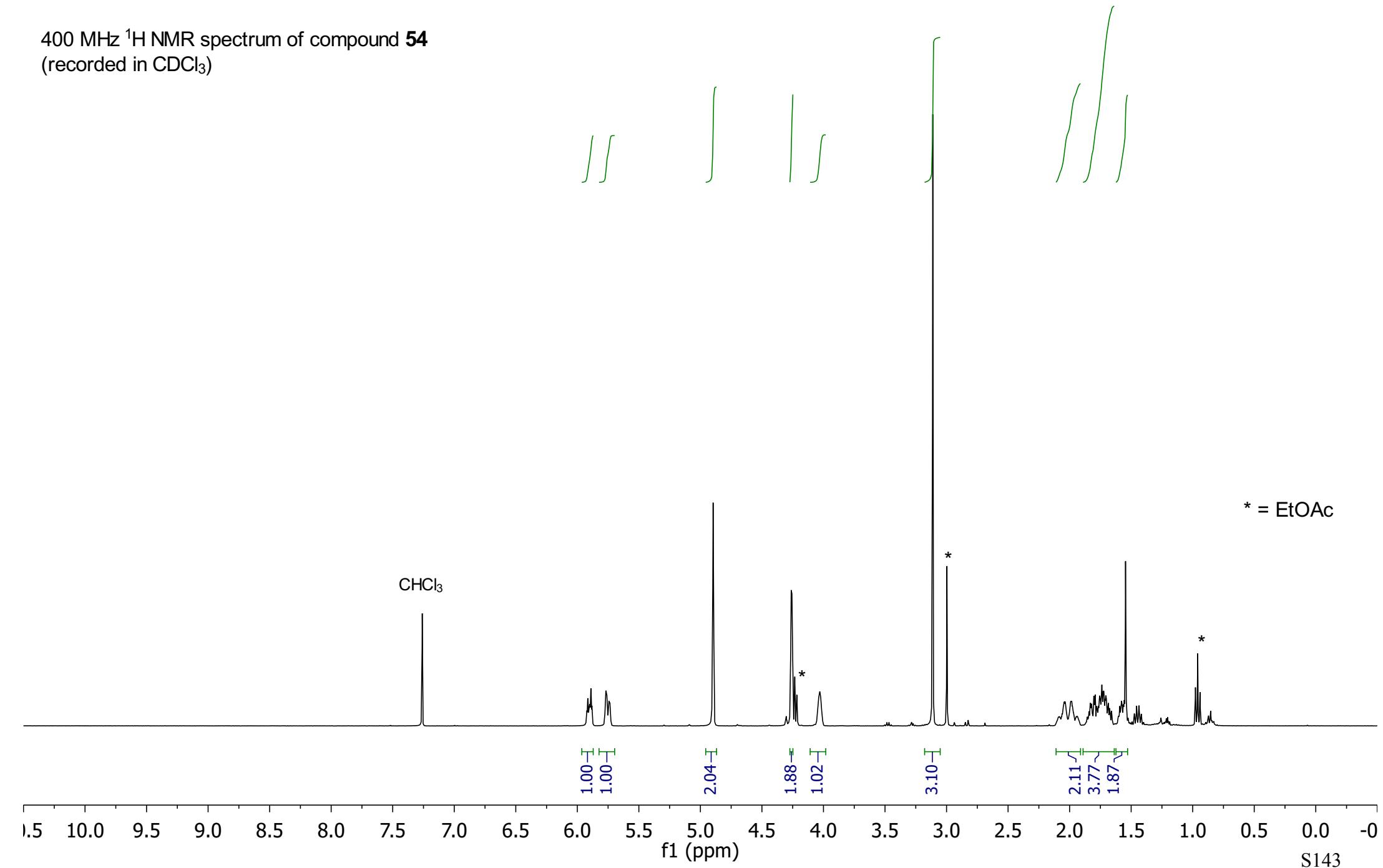


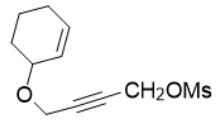
100 MHz ^{13}C NMR spectrum of compound 53
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound **54**
(recorded in CDCl_3)





100 MHz ^{13}C NMR spectrum of compound **54**
(recorded in CDCl_3)

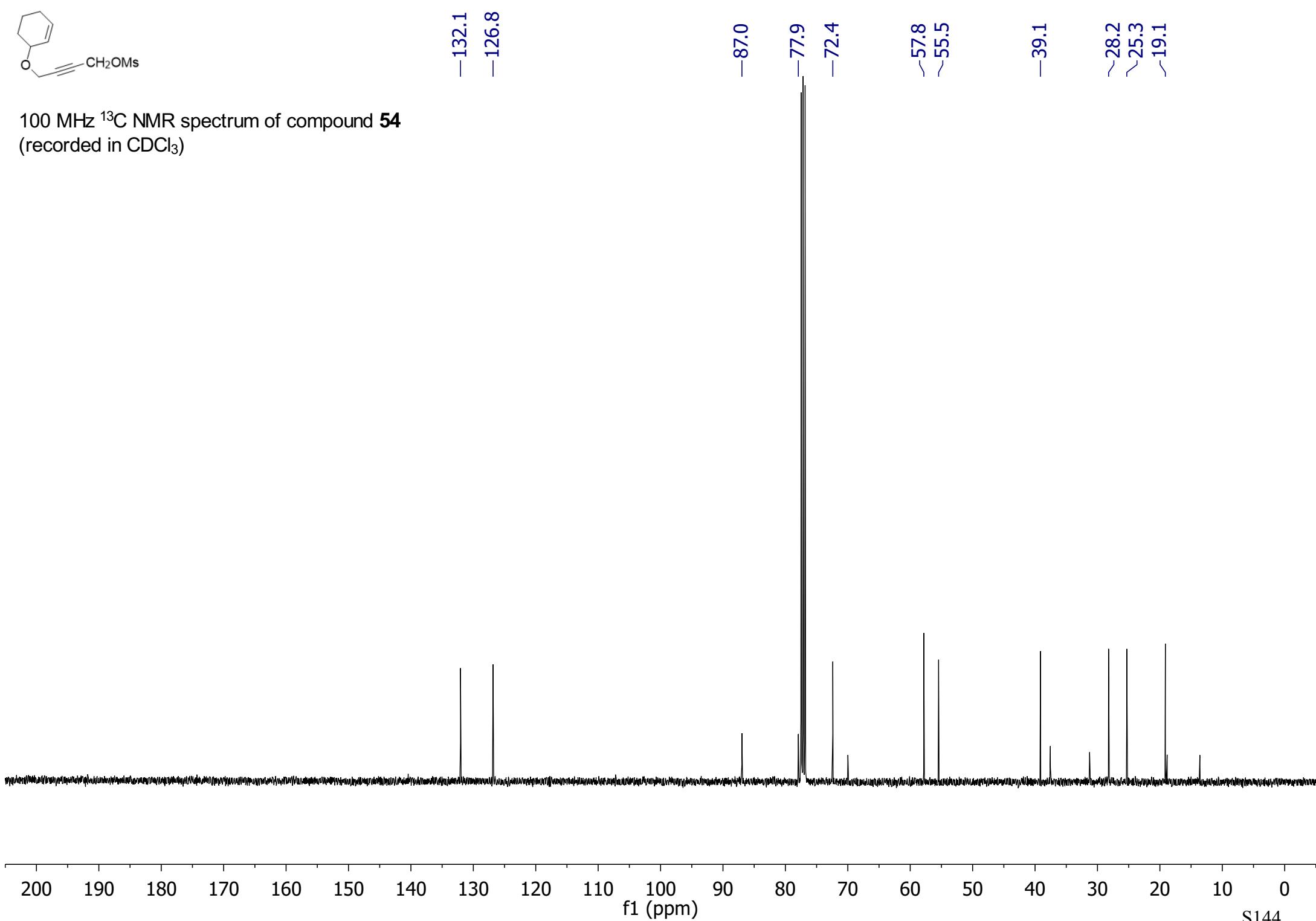
—132.1
—126.8

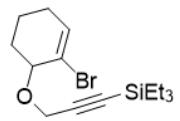
—87.0
—77.9
—72.4

—57.8
—55.5

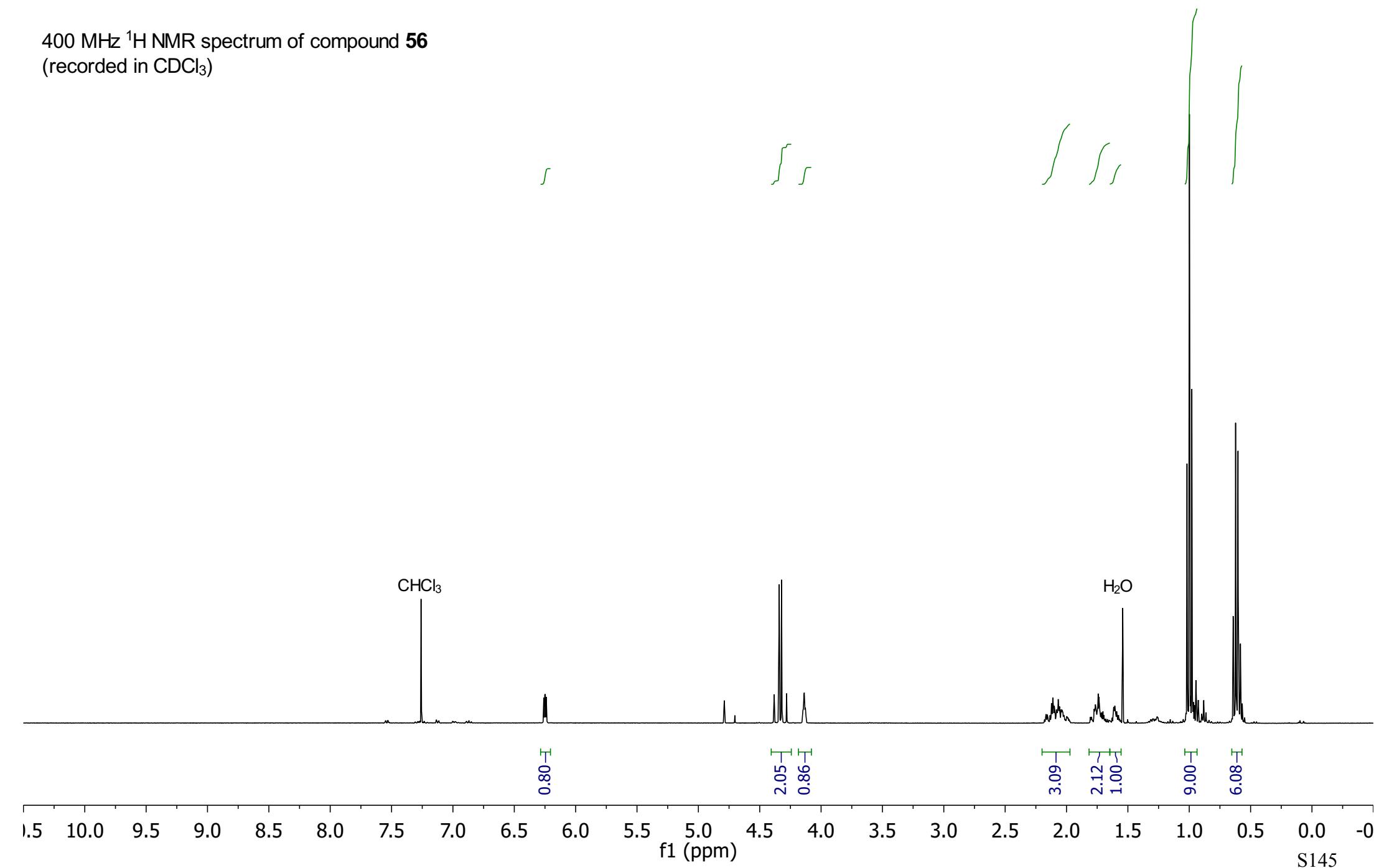
—39.1

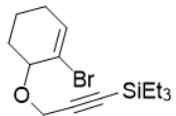
~28.2
~25.3
~19.1



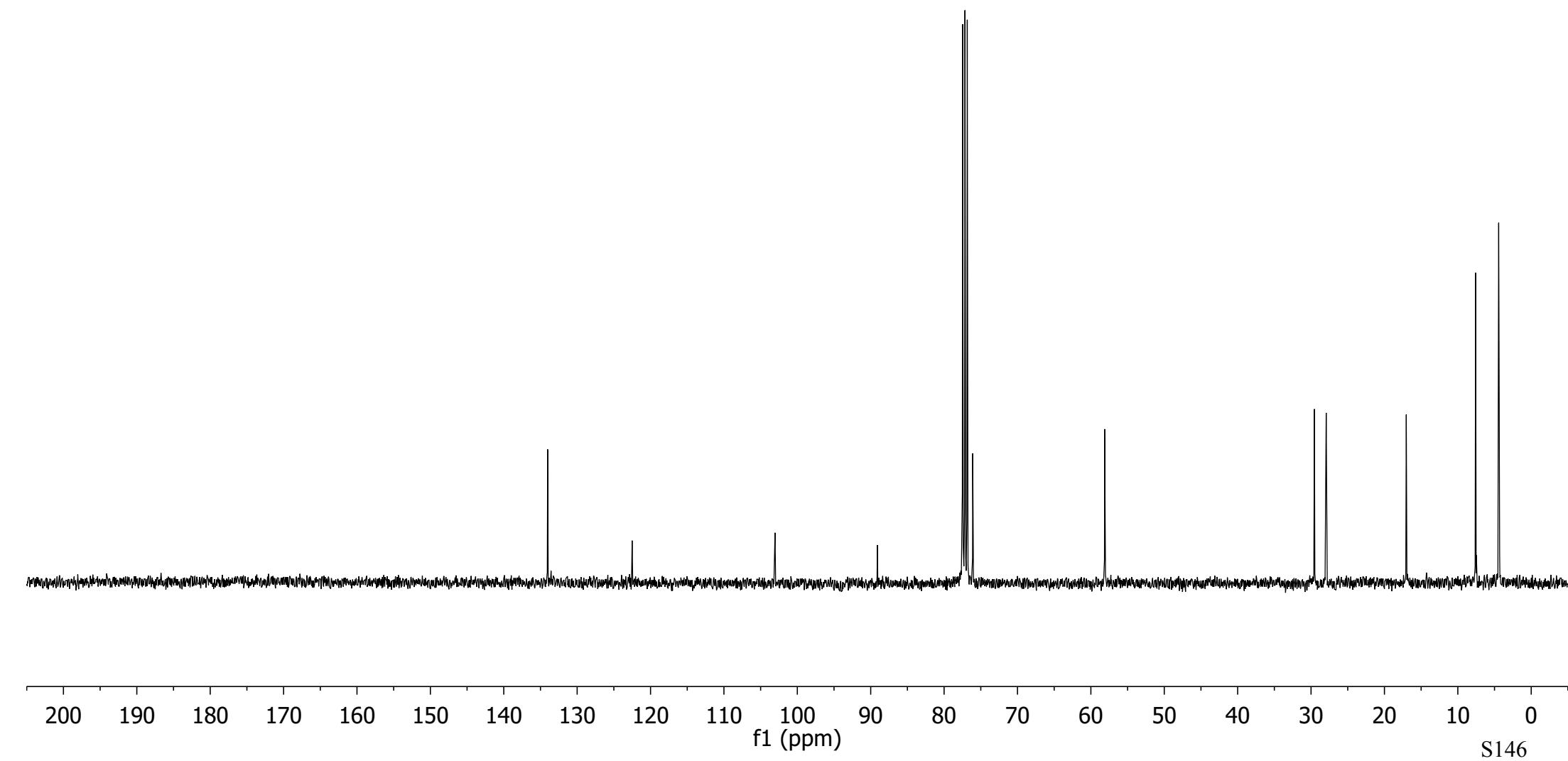


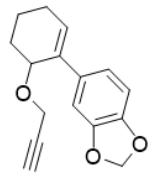
400 MHz ^1H NMR spectrum of compound **56**
(recorded in CDCl_3)



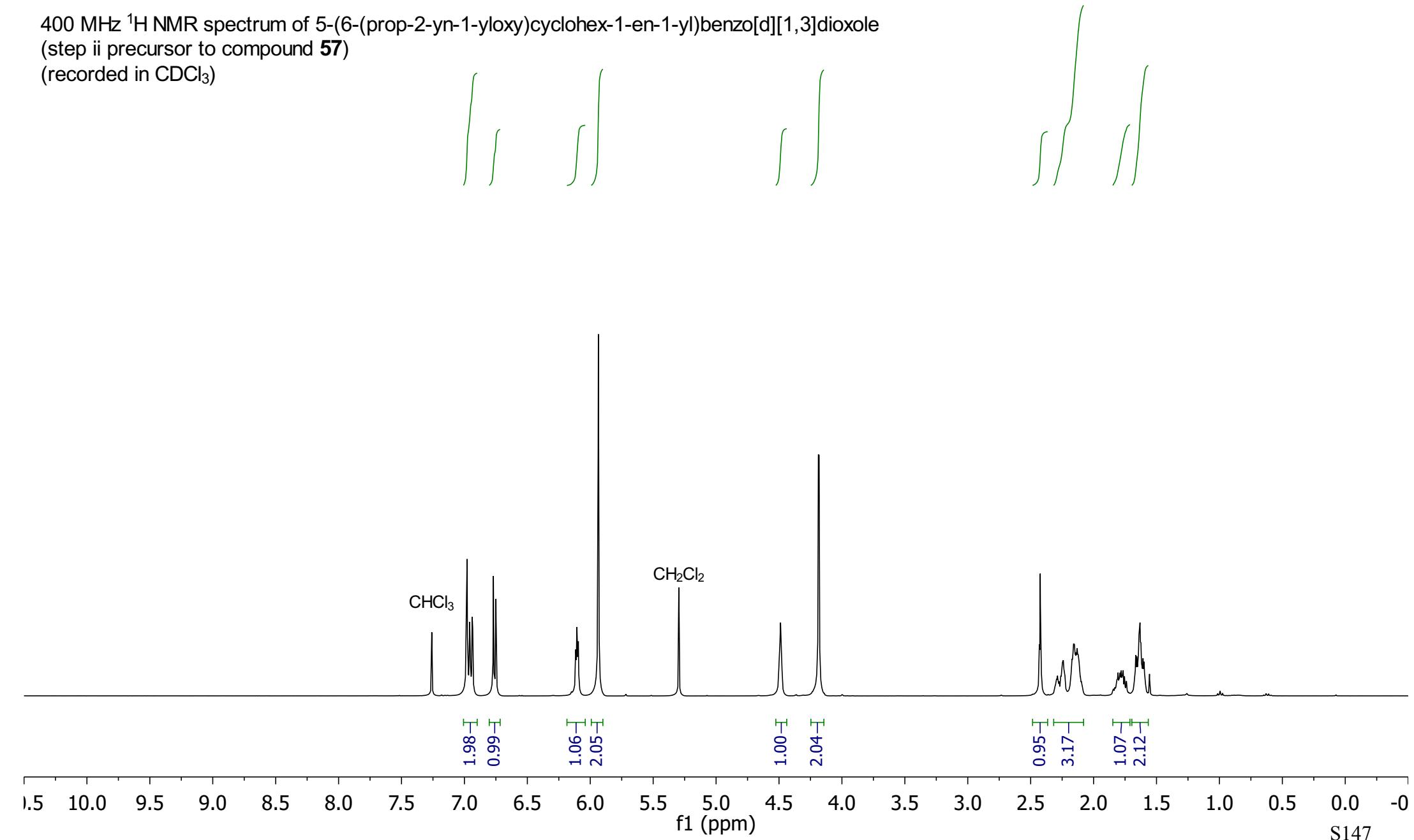


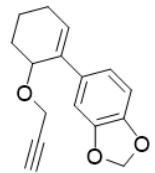
100 MHz ^{13}C NMR spectrum of compound **56**
(recorded in CDCl_3)





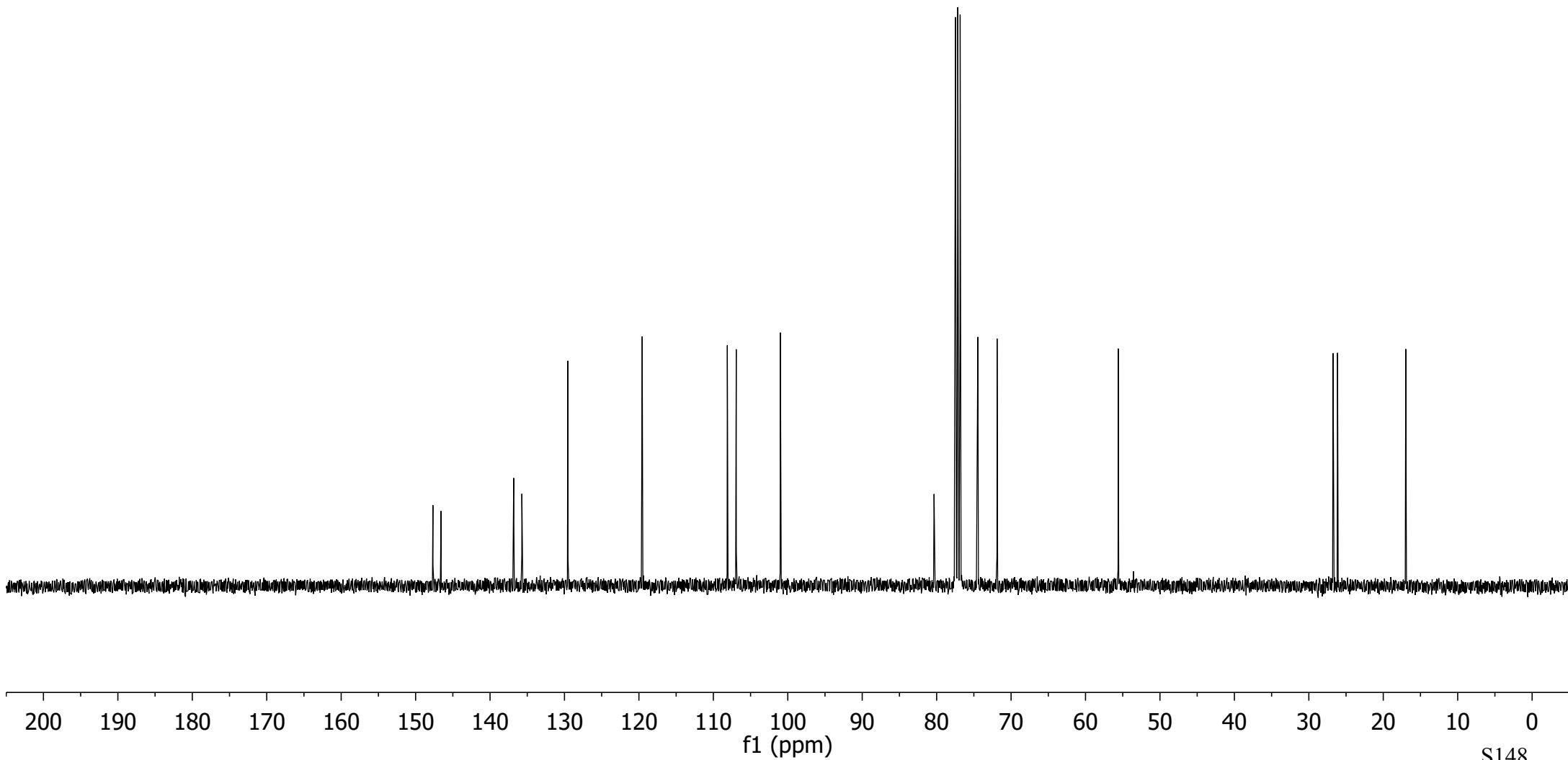
400 MHz ^1H NMR spectrum of 5-(6-(prop-2-yn-1-yloxy)cyclohex-1-en-1-yl)benzo[d][1,3]dioxole
(step ii precursor to compound **57**)
(recorded in CDCl_3)

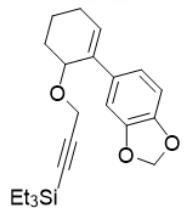




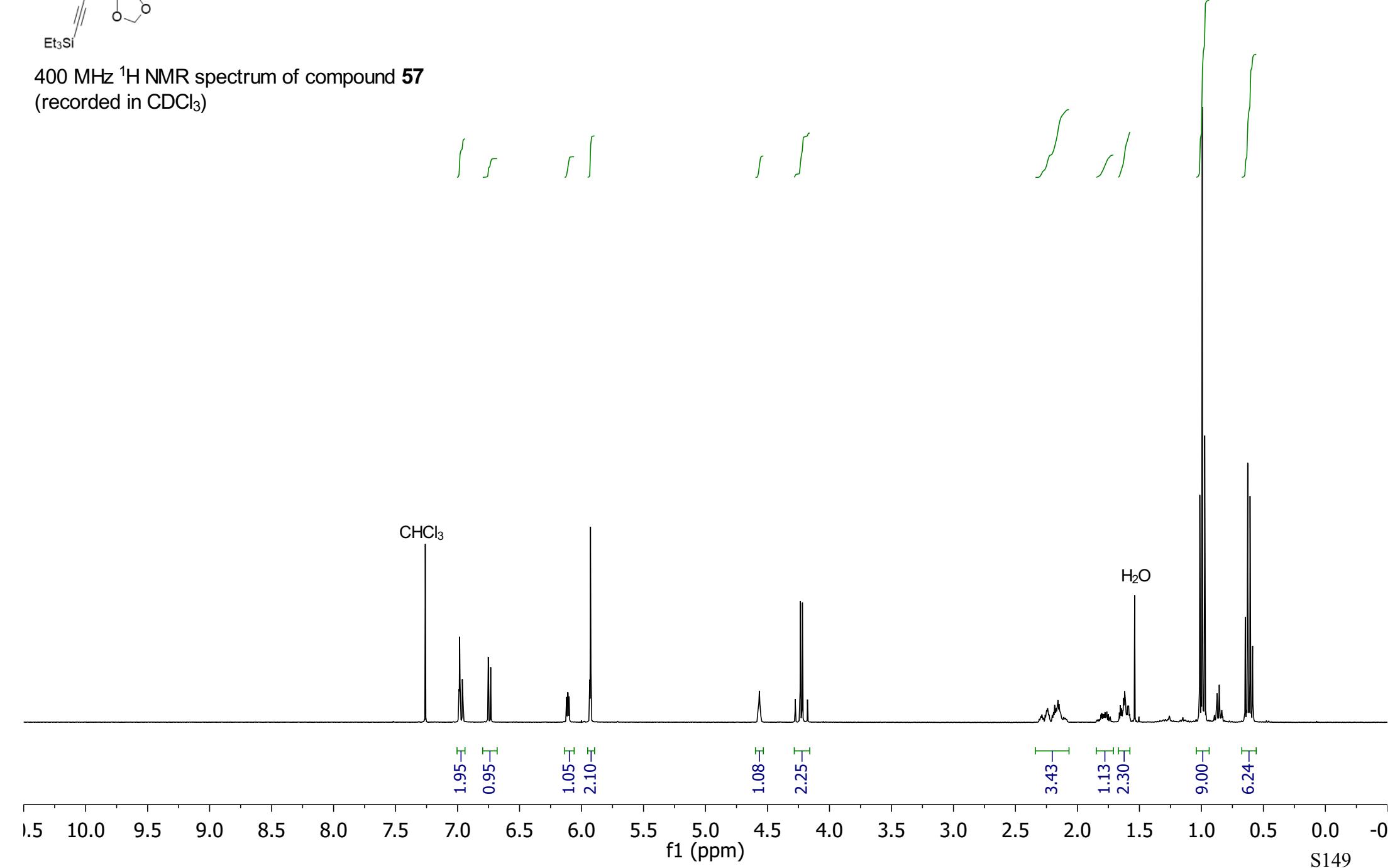
100 MHz ^{13}C NMR spectrum of 5-(6-(prop-2-yn-1-yloxy)cyclohex-1-en-1-yl)benzo[d][1,3]dioxole
(step ii precursor to compound **57**)
(recorded in CDCl_3)

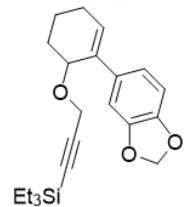
147.7
146.6
136.8
135.7
129.6
119.6
108.1
106.9
101.0
80.3
74.5
71.9
55.6
26.7
26.1
17.0



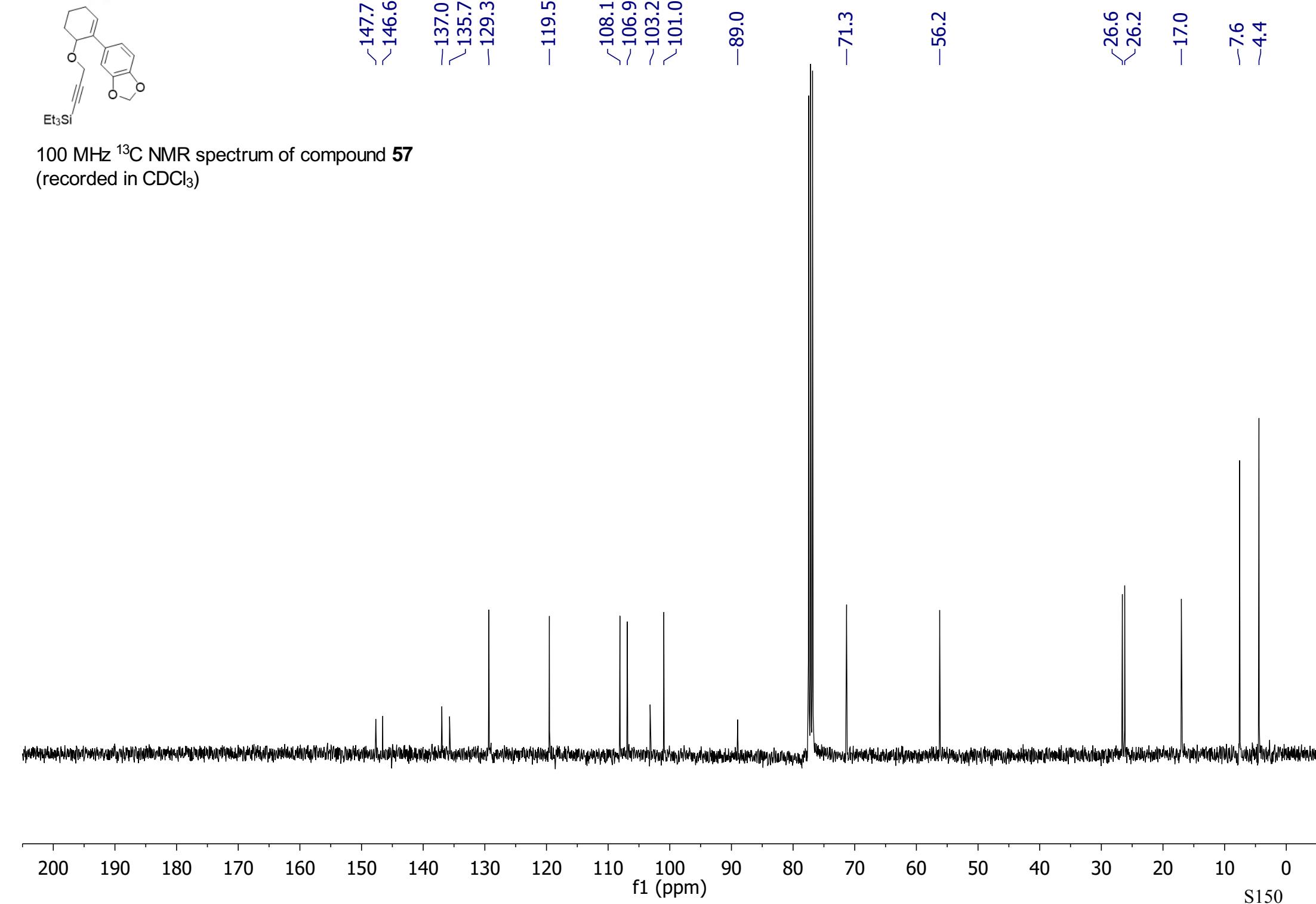


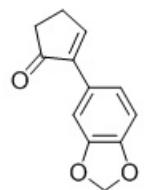
400 MHz ¹H NMR spectrum of compound **57**
(recorded in CDCl₃)



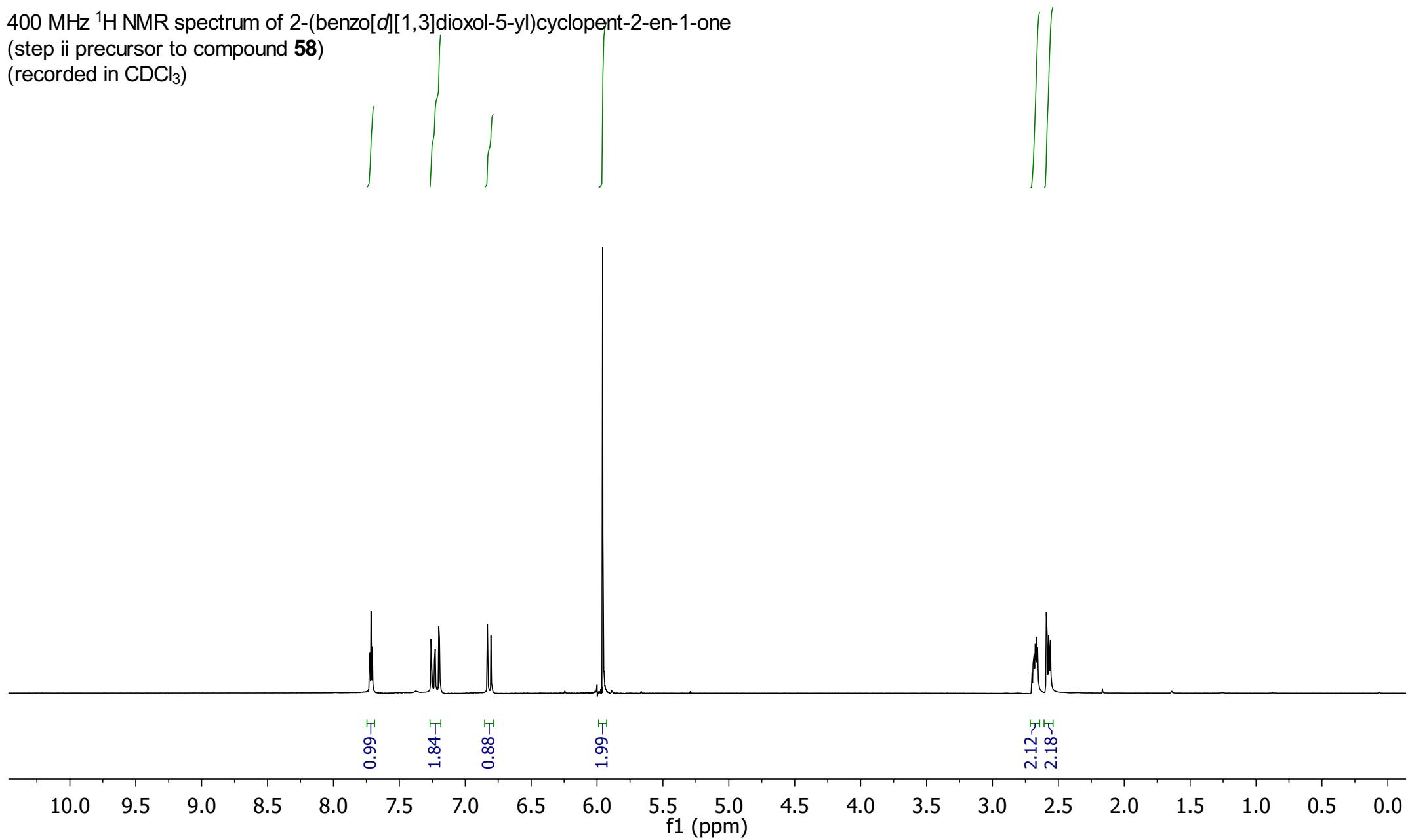


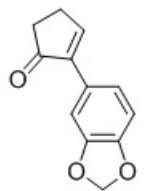
100 MHz ¹³C NMR spectrum of compound **57**
(recorded in CDCl₃)



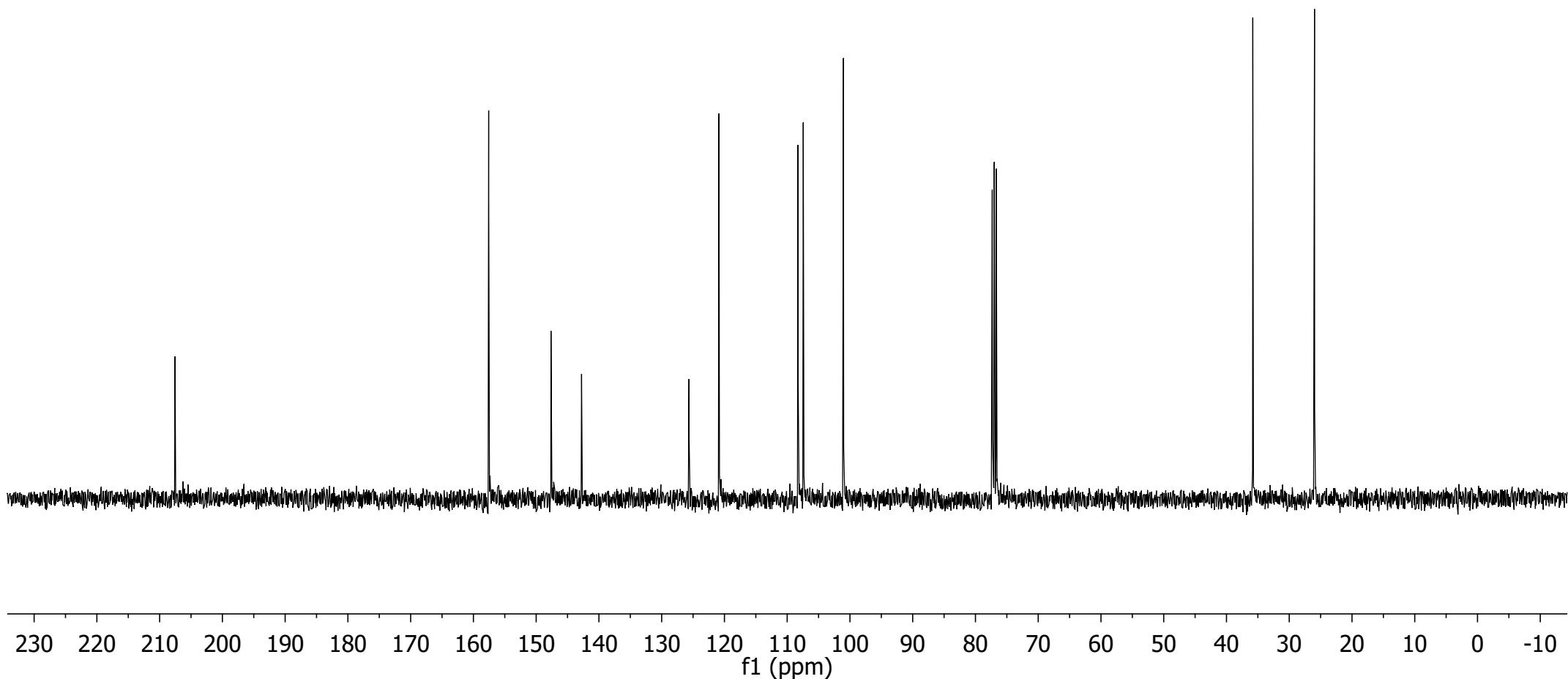


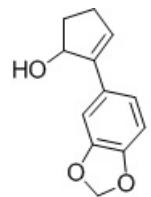
400 MHz ^1H NMR spectrum of 2-(benzo[*d*][1,3]dioxol-5-yl)cyclopent-2-en-1-one
(step ii precursor to compound **58**)
(recorded in CDCl_3)



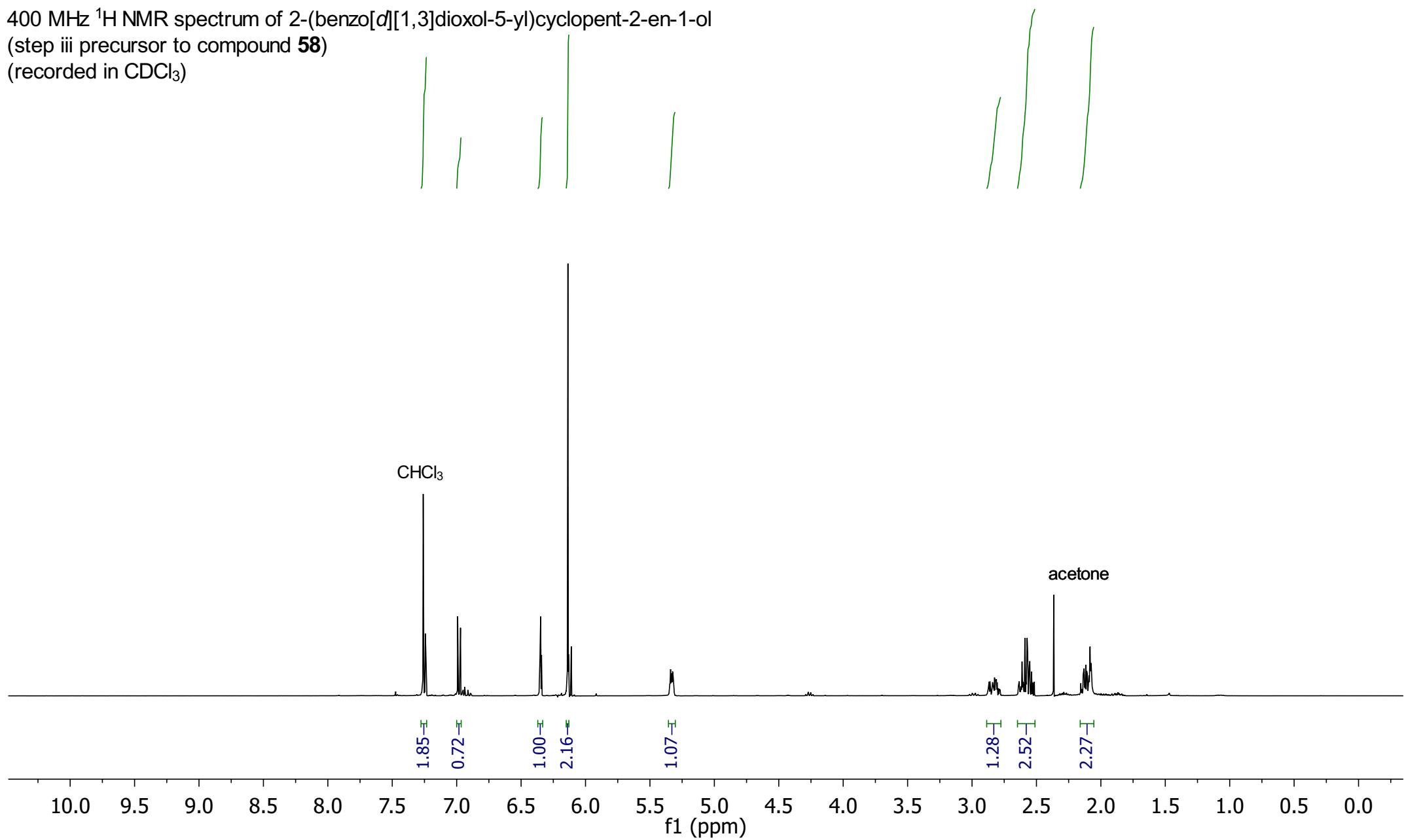


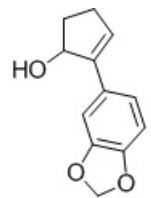
100 MHz ^{13}C NMR spectrum of 2-(benzo[*d*][1,3]dioxol-5-yl)cyclopent-2-en-1-one
(step ii precursor to compound **58**)
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of 2-(benzo[*d*][1,3]dioxol-5-yl)cyclopent-2-en-1-ol
(step iii precursor to compound **58**)
(recorded in CDCl_3)





147.9
146.9
144.1

129.2
128.6

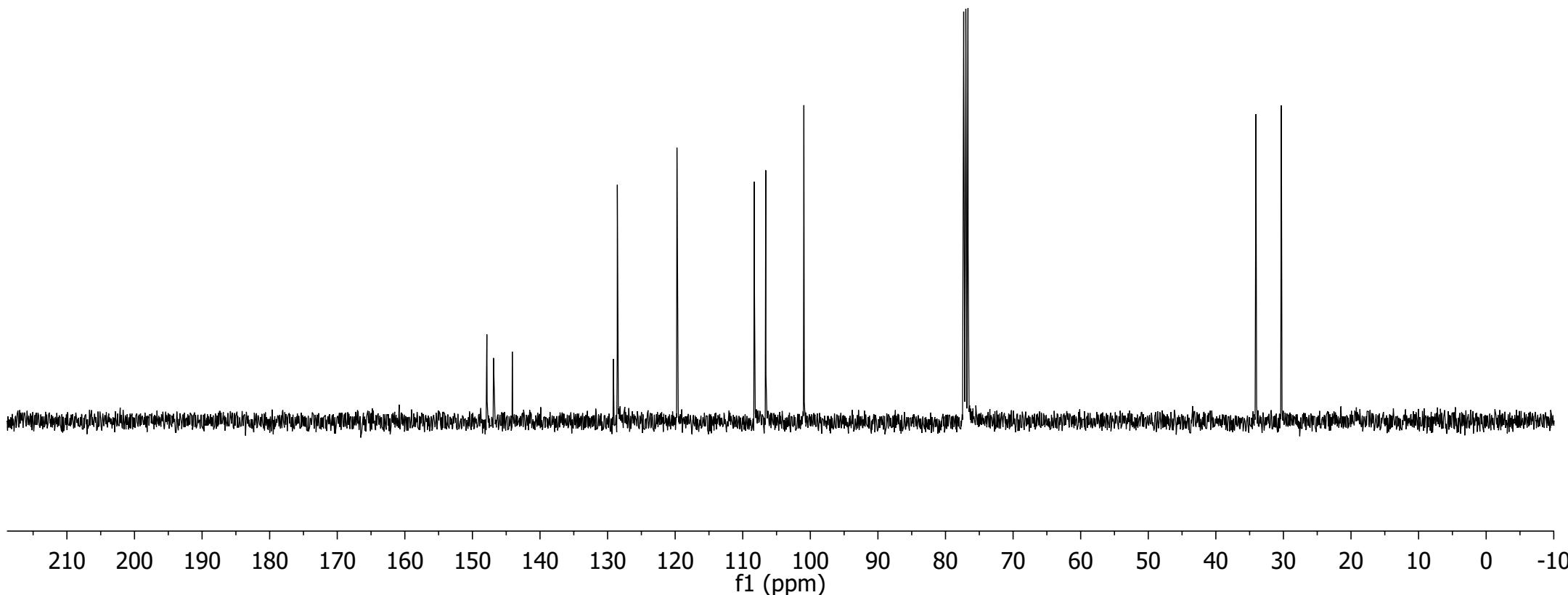
119.7

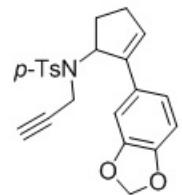
108.3
106.6
101.0

77.4

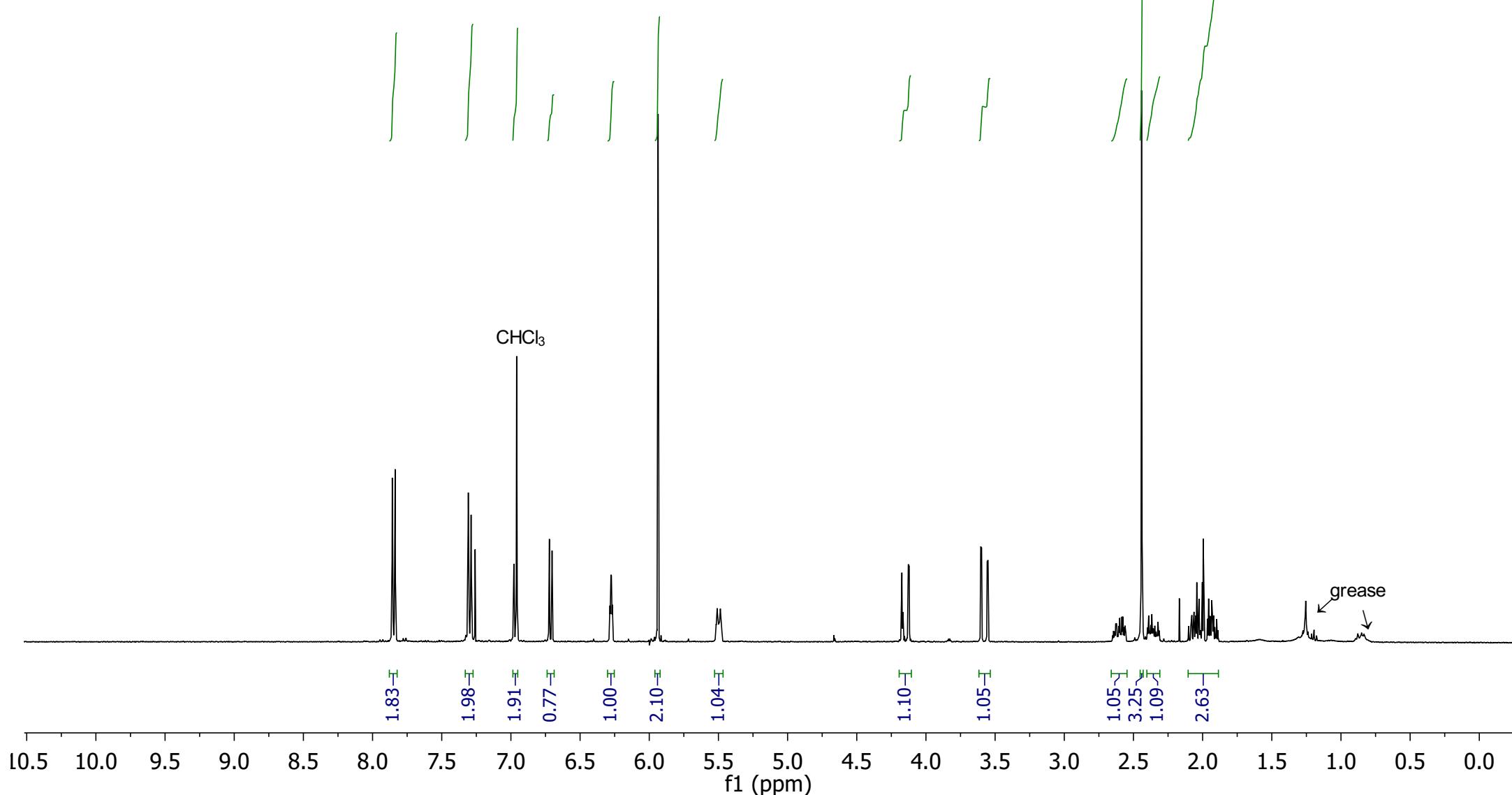
34.1
30.3

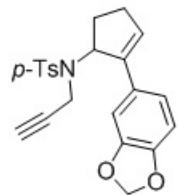
100 MHz ^{13}C NMR spectrum of 2-(benzo[*d*][1,3]dioxol-5-yl)cyclopent-2-en-1-ol
(step iii precursor to compound **58**)
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of *N*-(2-(benzo[*d*][1,3]dioxol-5-yl)cyclopent-2-en-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benz-enesulfonamide
(step iv precursor to compound **58**)
(recorded in CDCl_3)





147.7
147.1
143.3
139.1
137.6
131.6
129.3
128.1
127.9
-120.0

-108.3
-106.5
-100.9

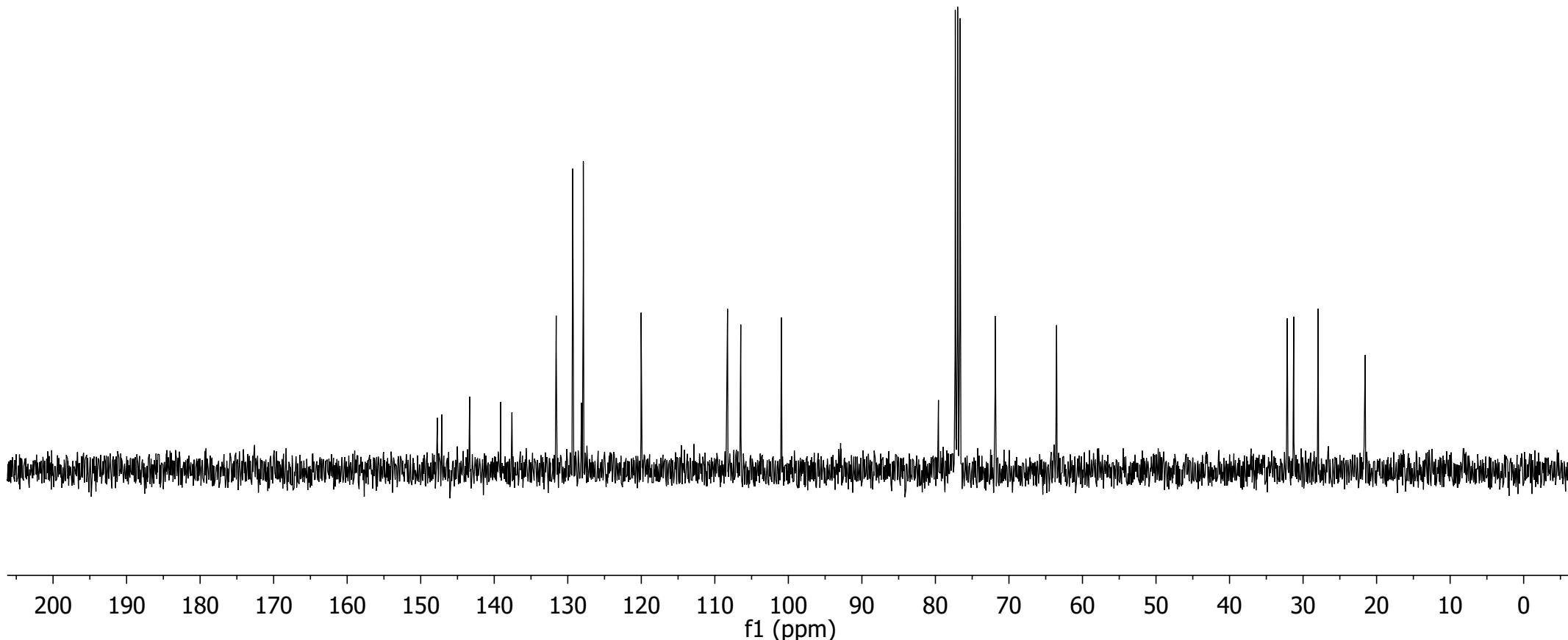
-79.6

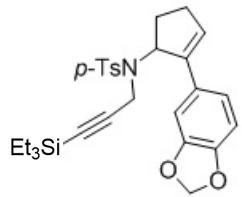
-71.9

-63.5

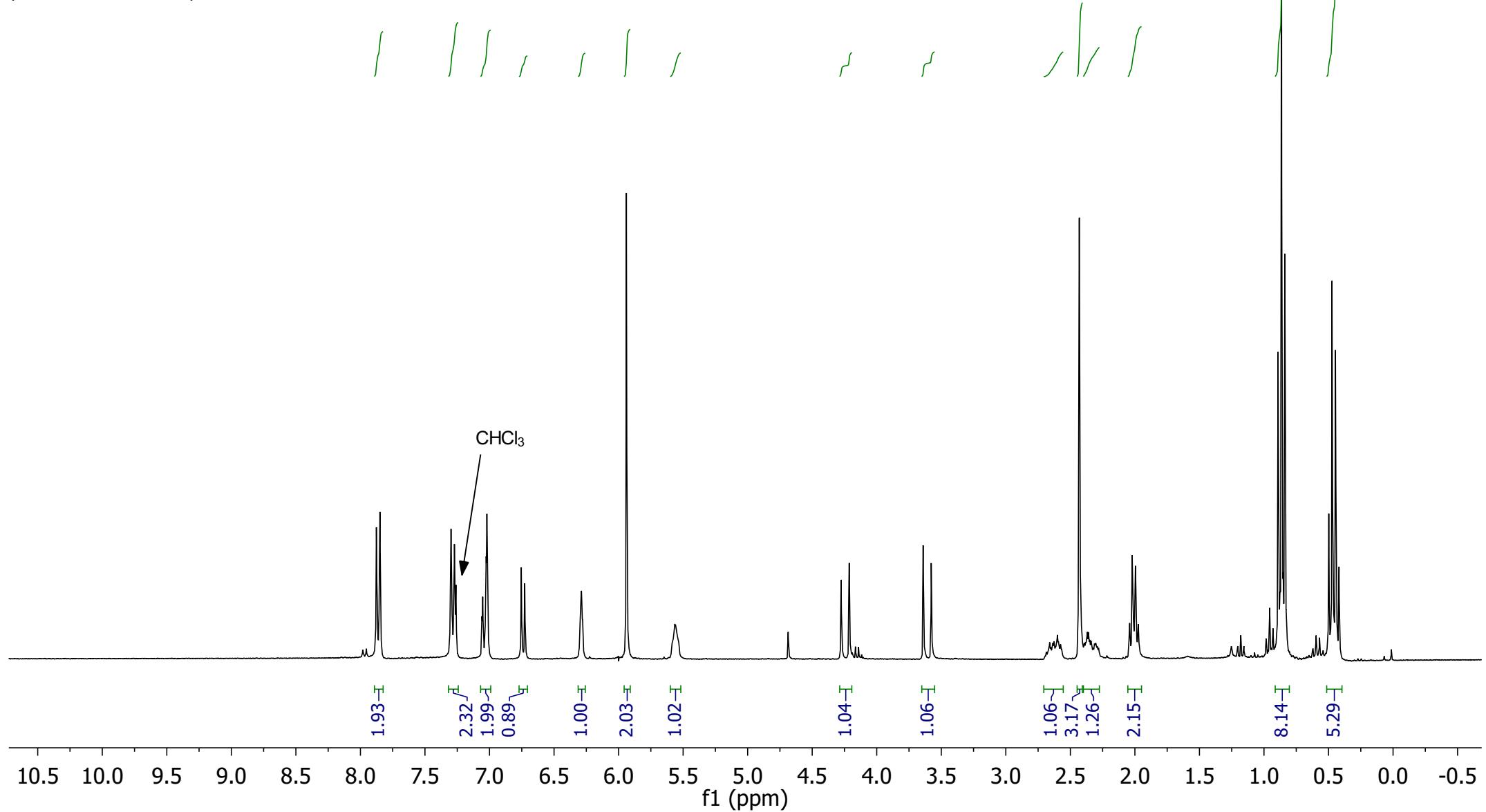
32.2
31.3
28.0
21.6

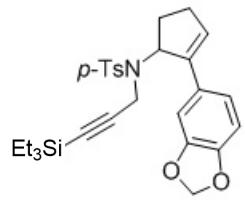
100 MHz ^{13}C NMR spectrum of *N*-(2-(benzo[*d*][1,3]dioxol-5-yl)cyclopent-2-en-1-yl)-4-methyl-*N*-(prop-2-yn-1-yl)benz-enesulfonamide
(step iv precursor to compound **58**)
(recorded in CDCl_3)



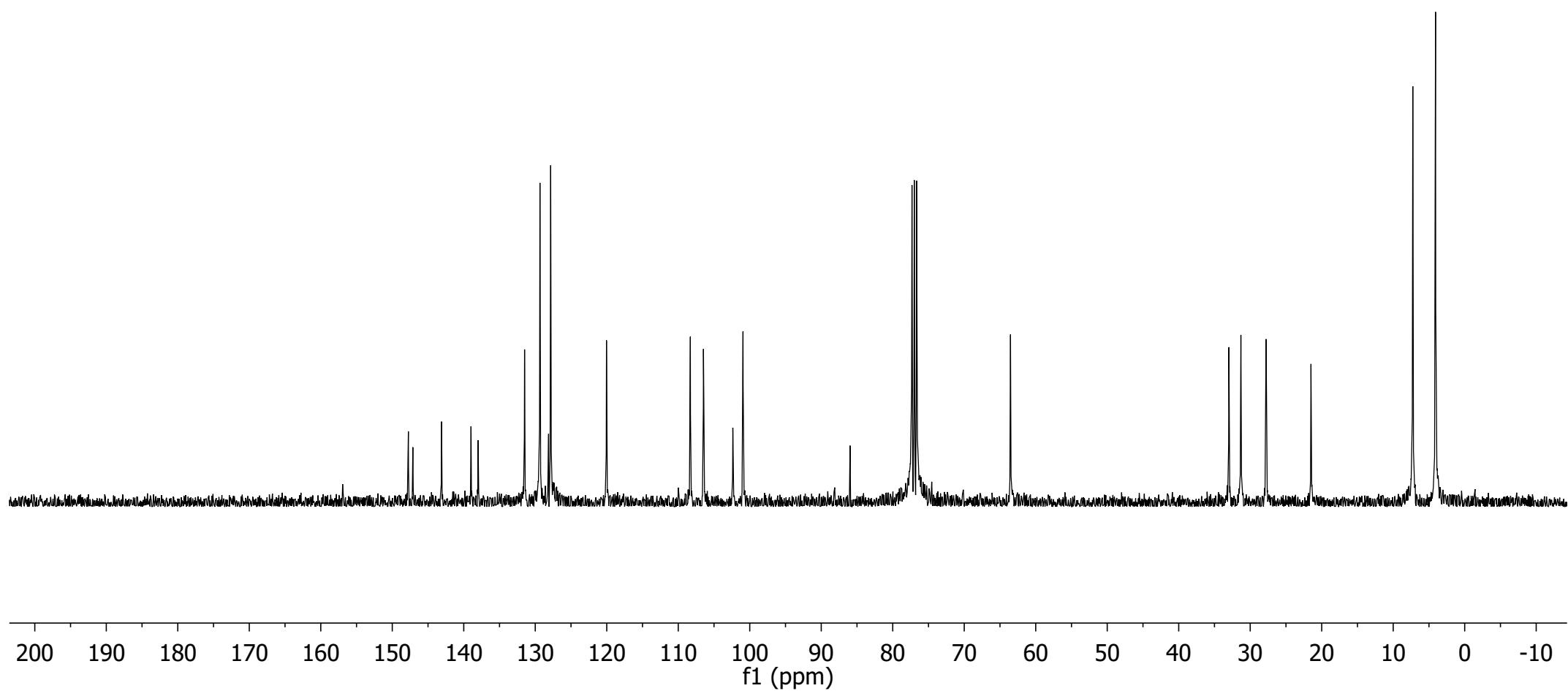


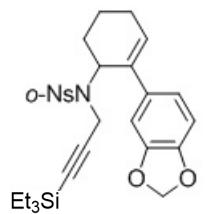
400 MHz ^1H NMR spectrum of compound **58**
(recorded in CDCl_3)



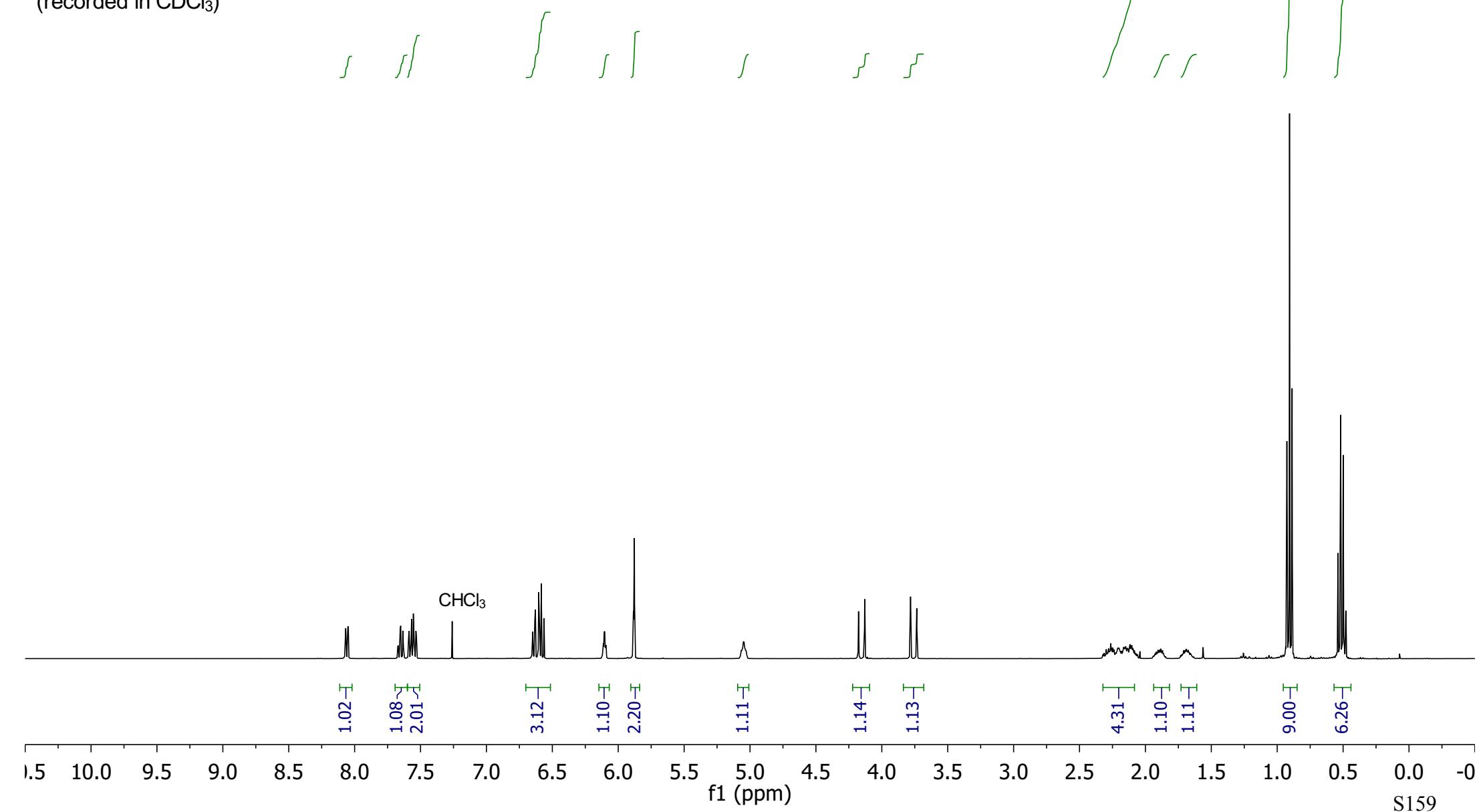


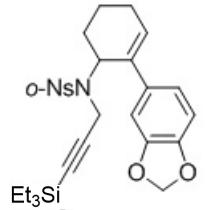
100 MHz ^{13}C NMR spectrum of compound **58**
(recorded in CDCl_3)





400 MHz ^1H NMR spectrum of compound **59**
(recorded in CDCl_3)





100 MHz ^{13}C NMR spectrum of compound **59**
(recorded in CDCl_3)

148.3
147.3
146.8
136.6
134.3
134.2
134.1
133.3
131.4
131.3
-123.9
-120.4

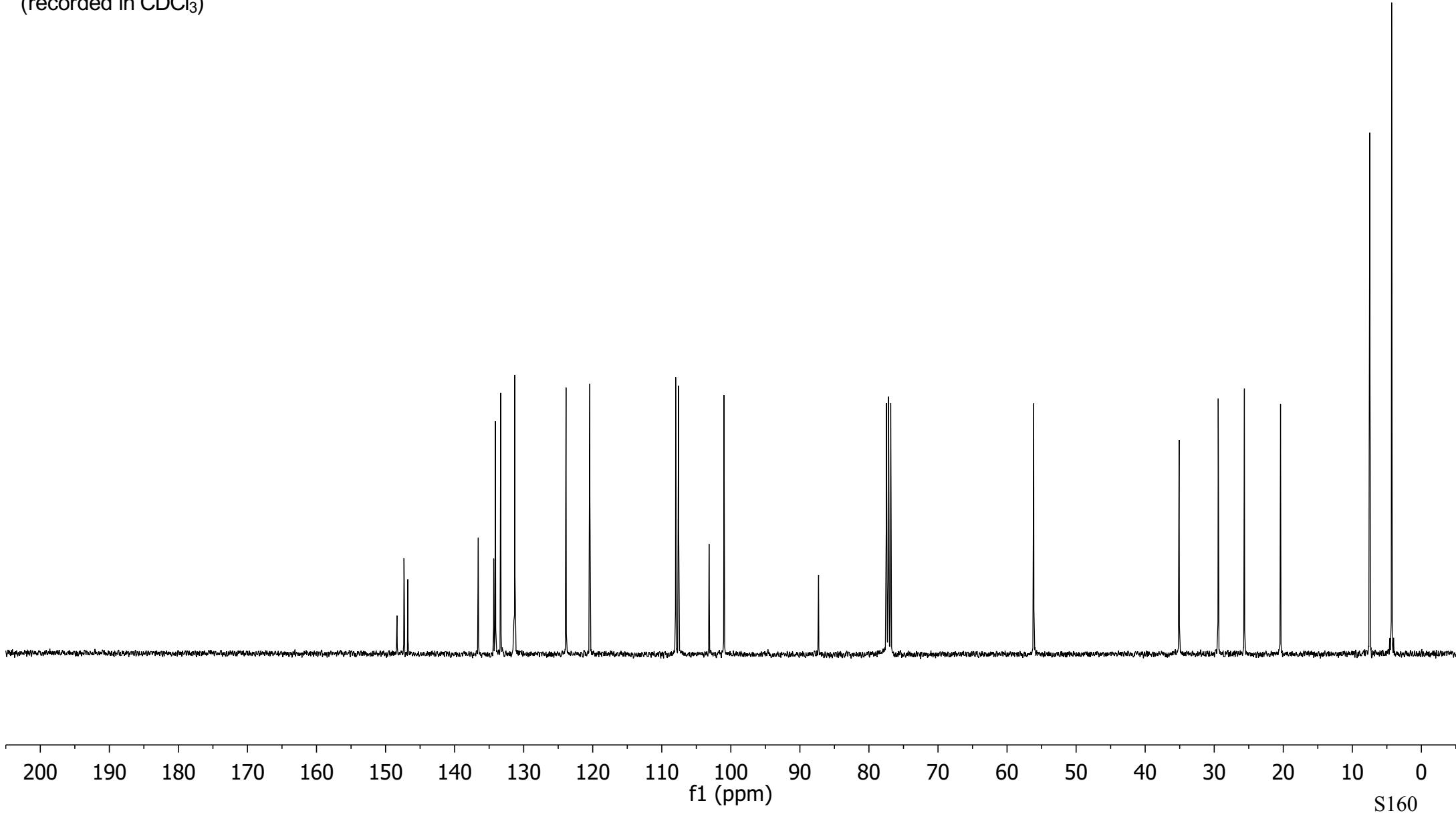
108.0
107.6
103.2
101.0

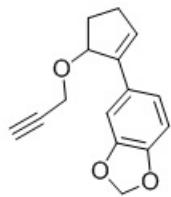
-87.3

-56.1

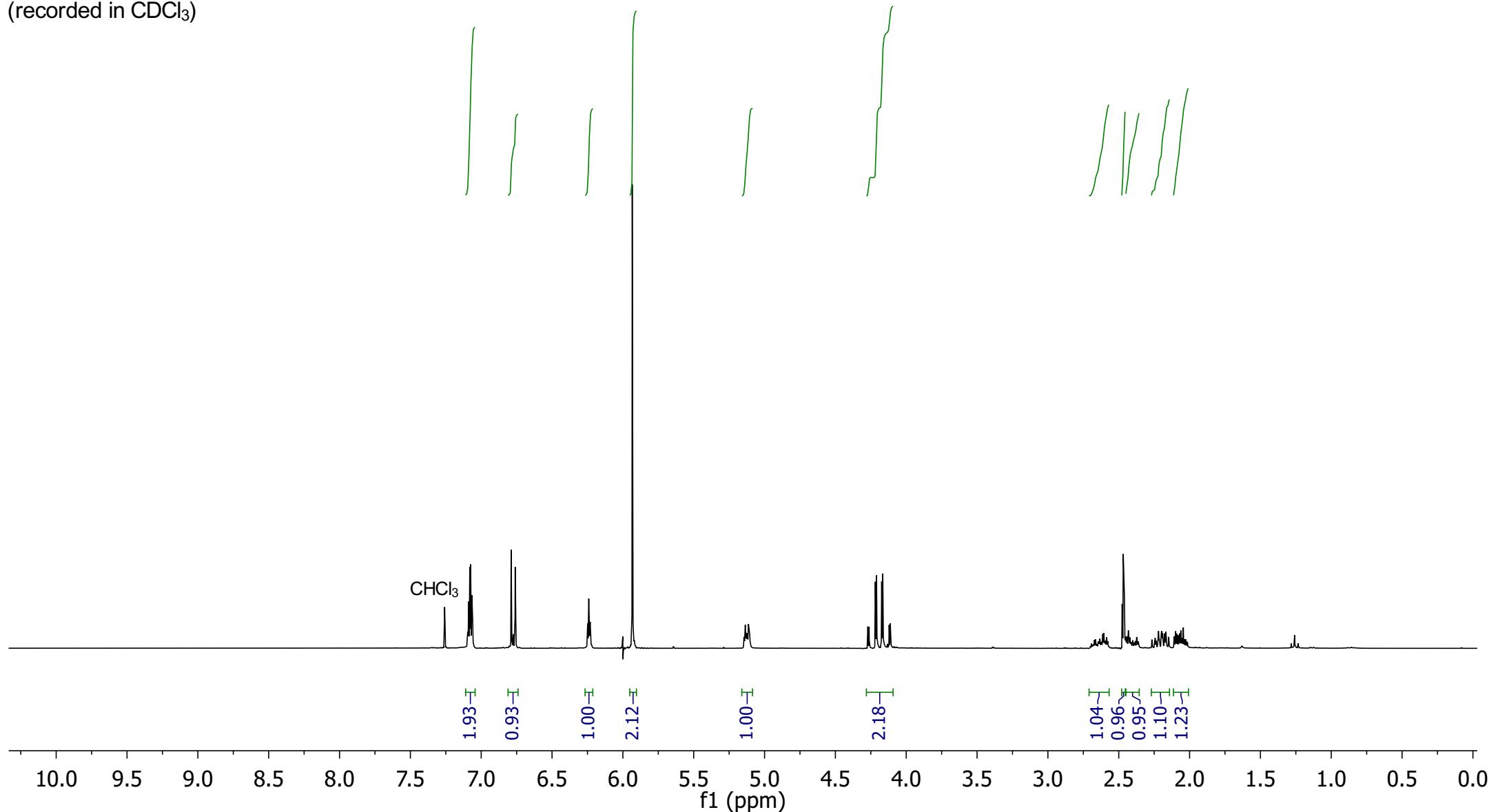
-35.1
-29.4
-25.6
20.4

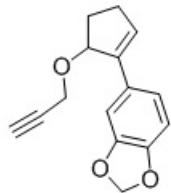
-7.5
-4.3





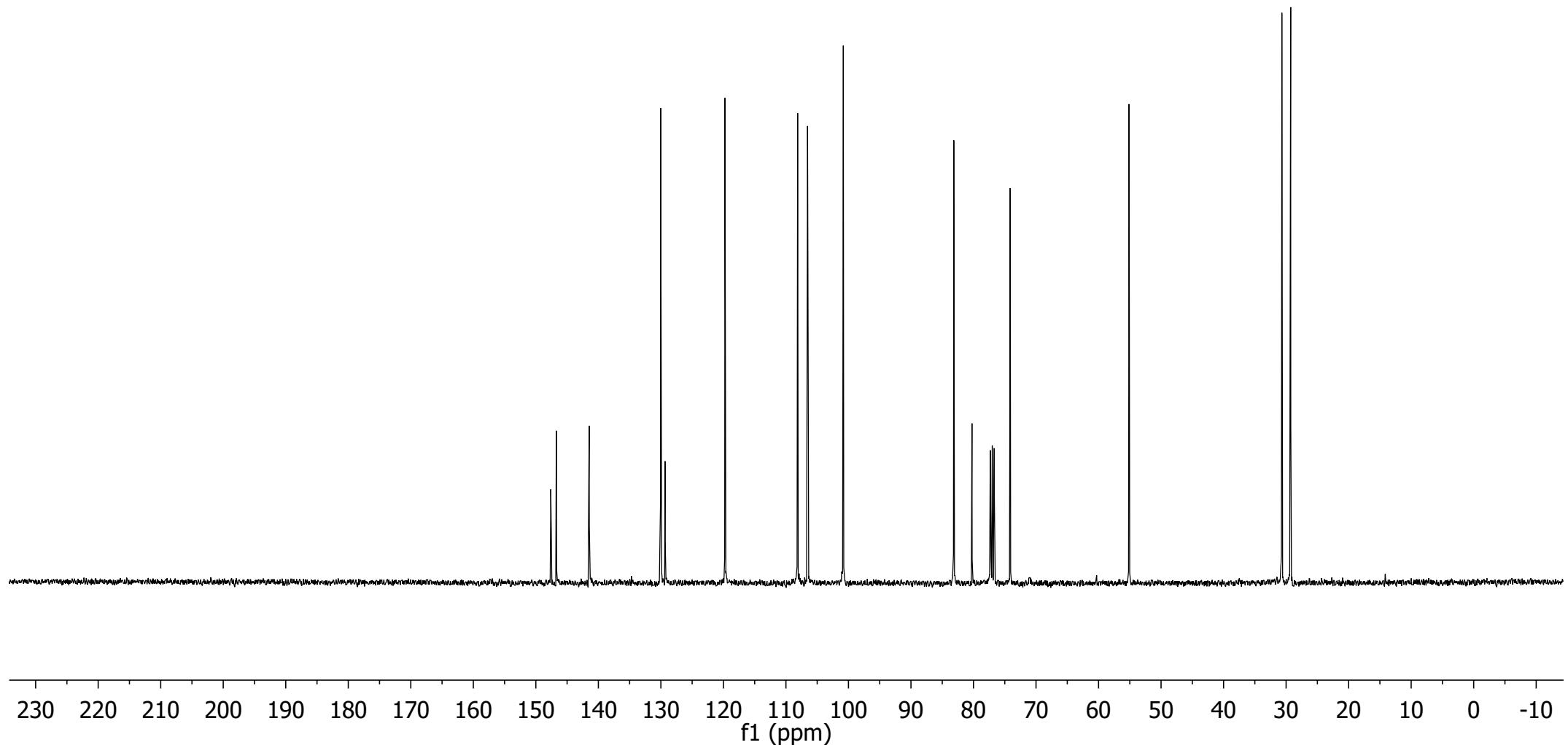
400 MHz ^1H NMR spectrum of 5-(5-(prop-2-yn-1-yloxy)cyclopent-1-en-1-yl)benzo[*d*][1,3]dioxole
(step i precursor to compound **60**)
(recorded in CDCl_3)

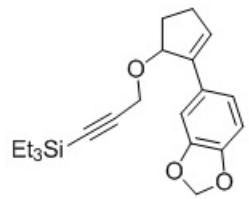




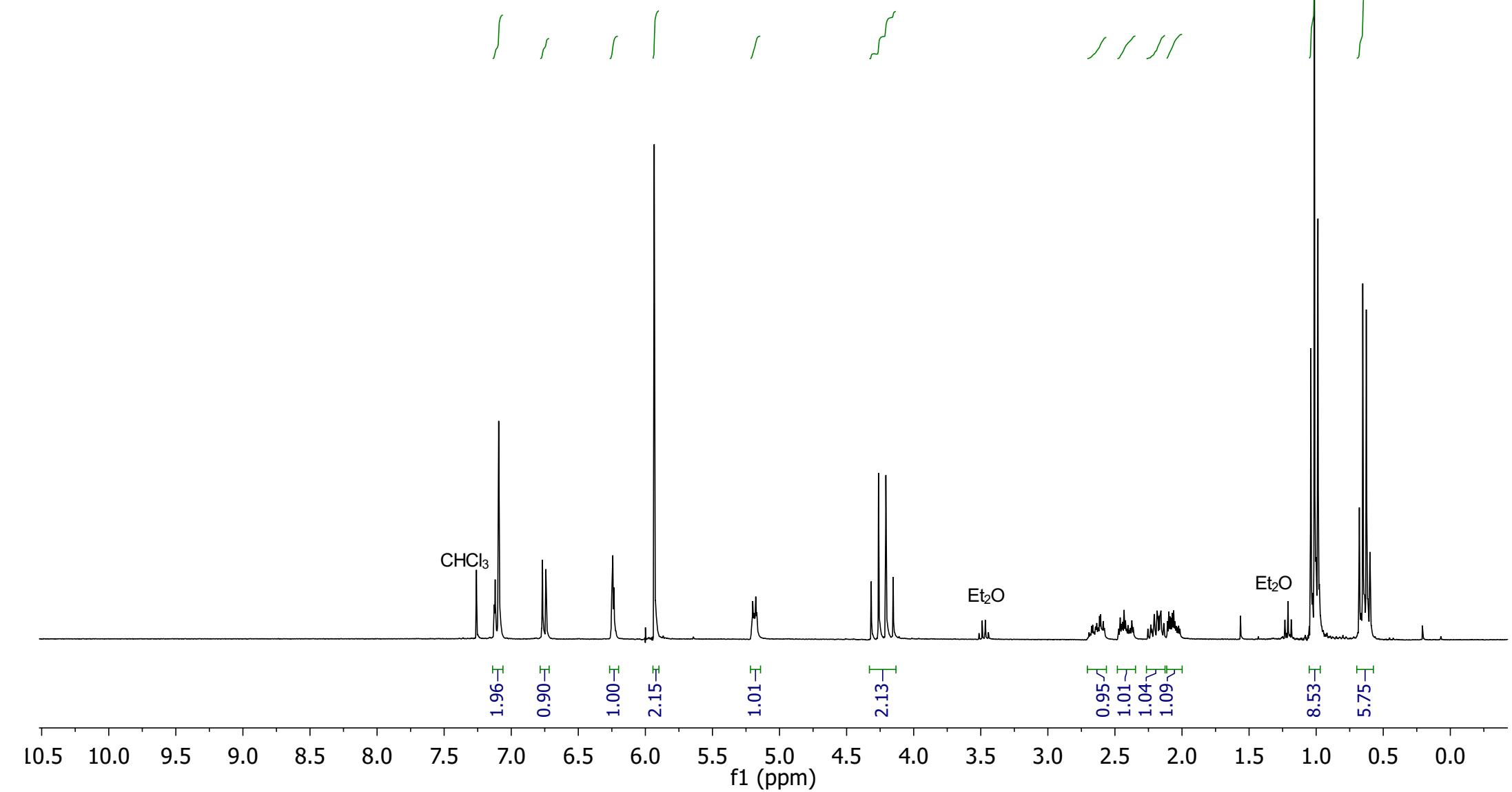
147.6
146.7
141.5
130.0
129.3
119.8
108.1
106.5
100.8
83.2
80.2
74.1
55.1
30.7
29.3

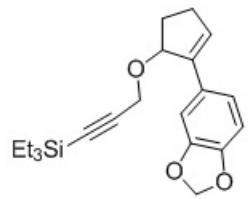
100 MHz ^{13}C NMR spectrum of 5-(5-(prop-2-yn-1-yloxy)cyclopent-1-en-1-yl)benzo[*d*][1,3]dioxole
(step i precursor to compound **60**)
(recorded in CDCl_3)



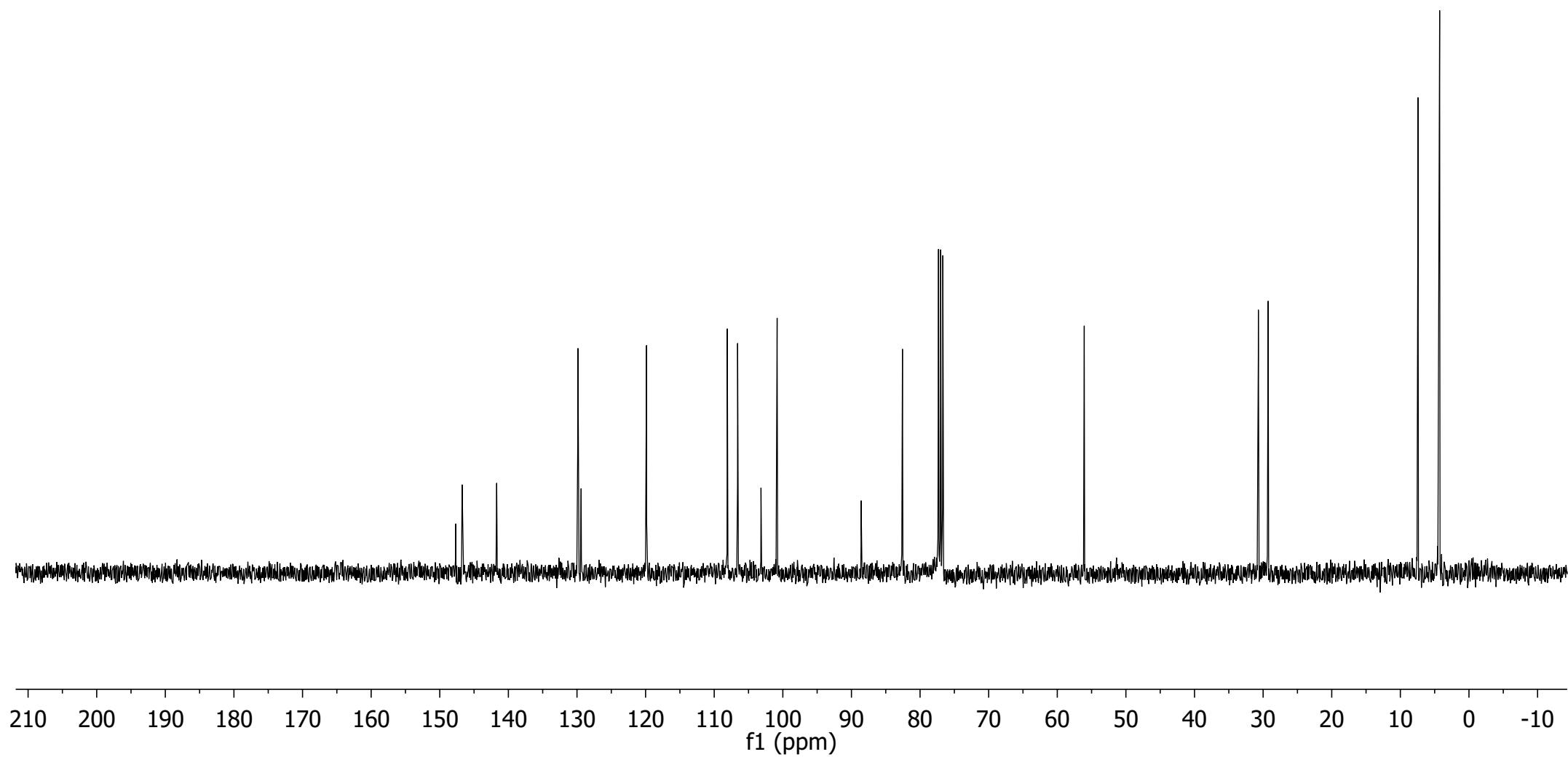


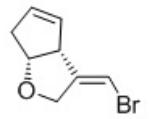
400 MHz ^1H NMR spectrum of compound **60**
(recorded in CDCl_3)



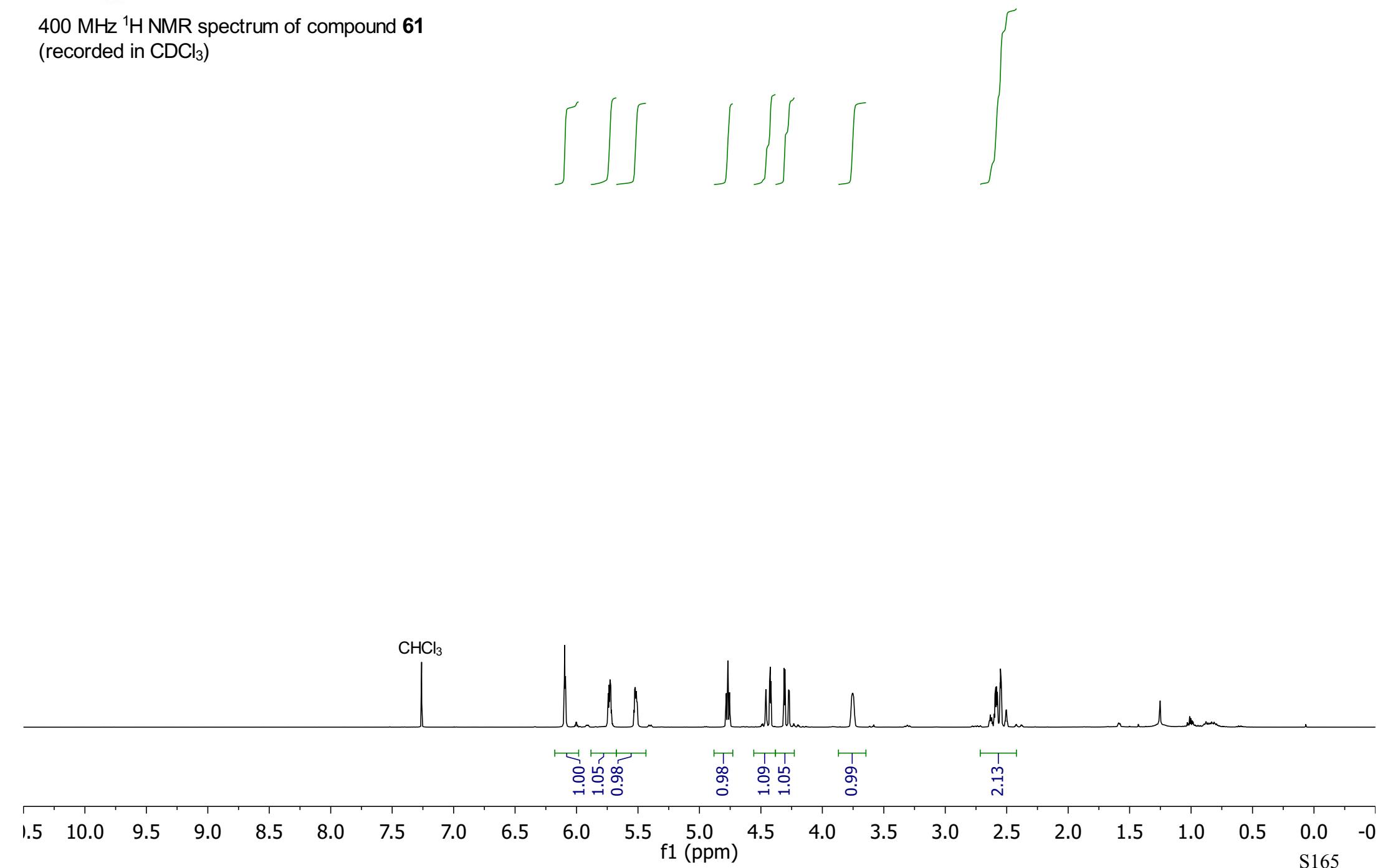


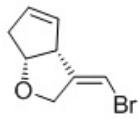
100 MHz ^{13}C NMR spectrum of compound **60**
(recorded in CDCl_3)



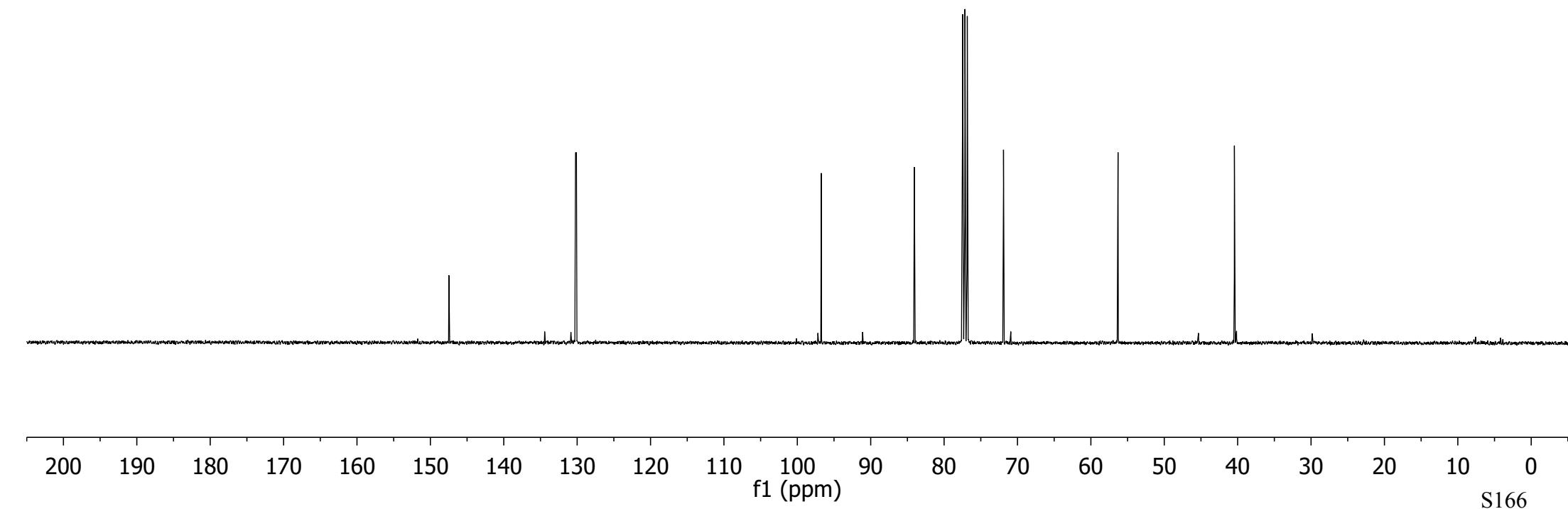


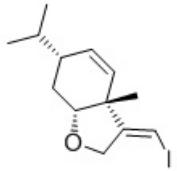
400 MHz ^1H NMR spectrum of compound **61**
(recorded in CDCl_3)



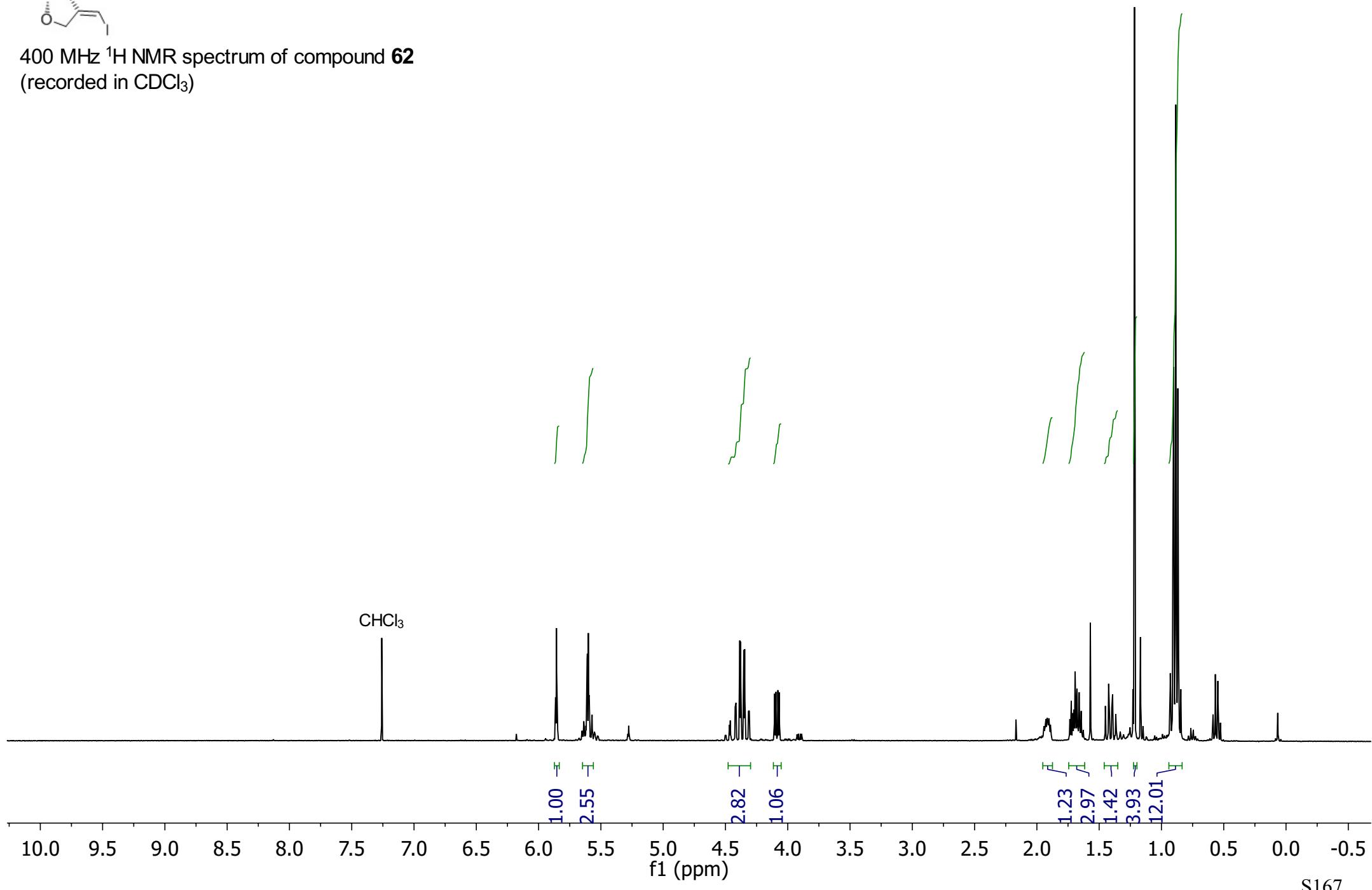


100 MHz ^{13}C NMR spectrum of compound **61**
(recorded in CDCl_3)





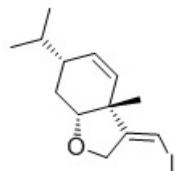
400 MHz ^1H NMR spectrum of compound **62**
(recorded in CDCl_3)



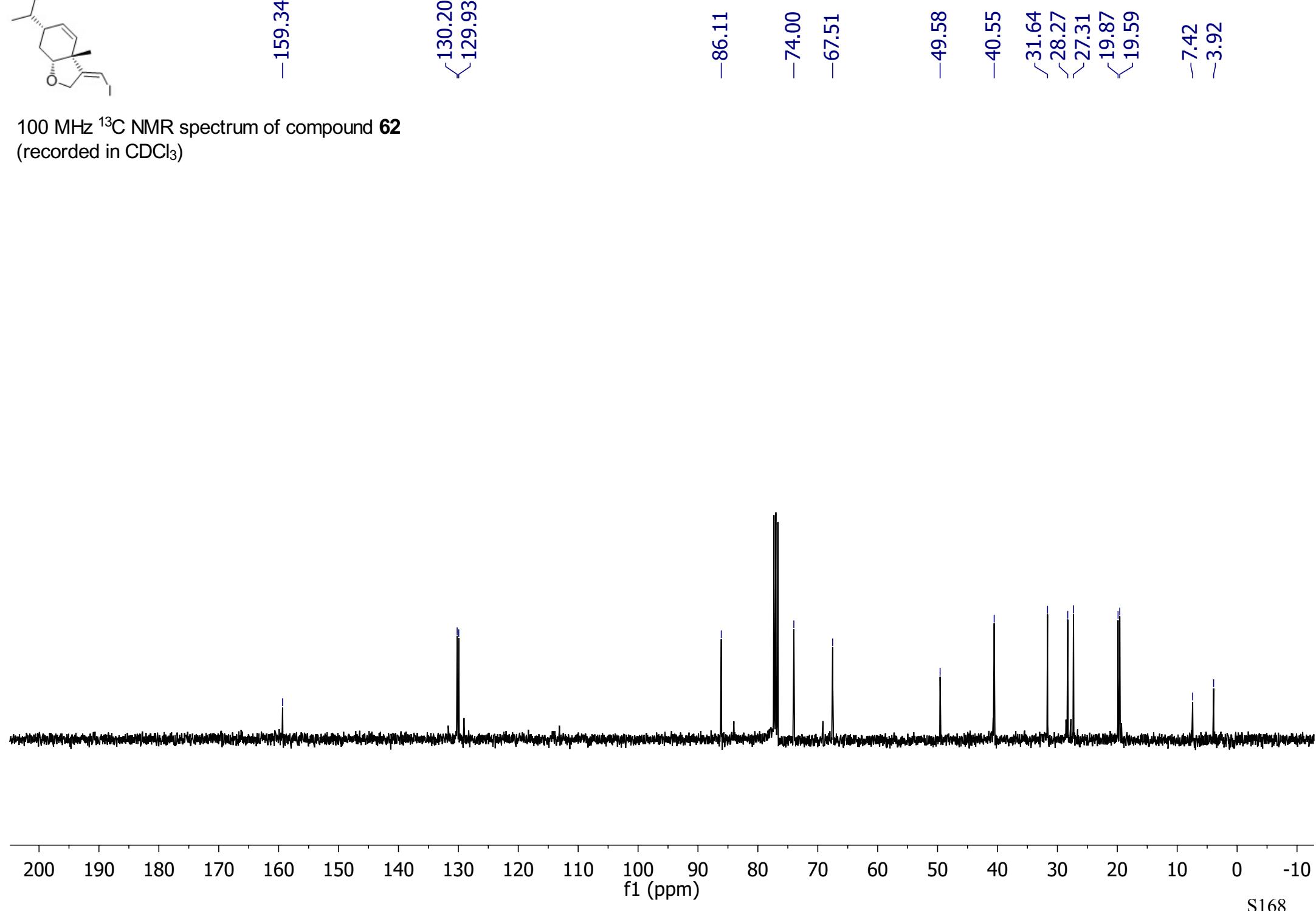
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

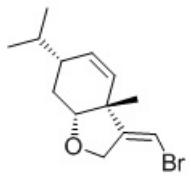
f1 (ppm)

S167

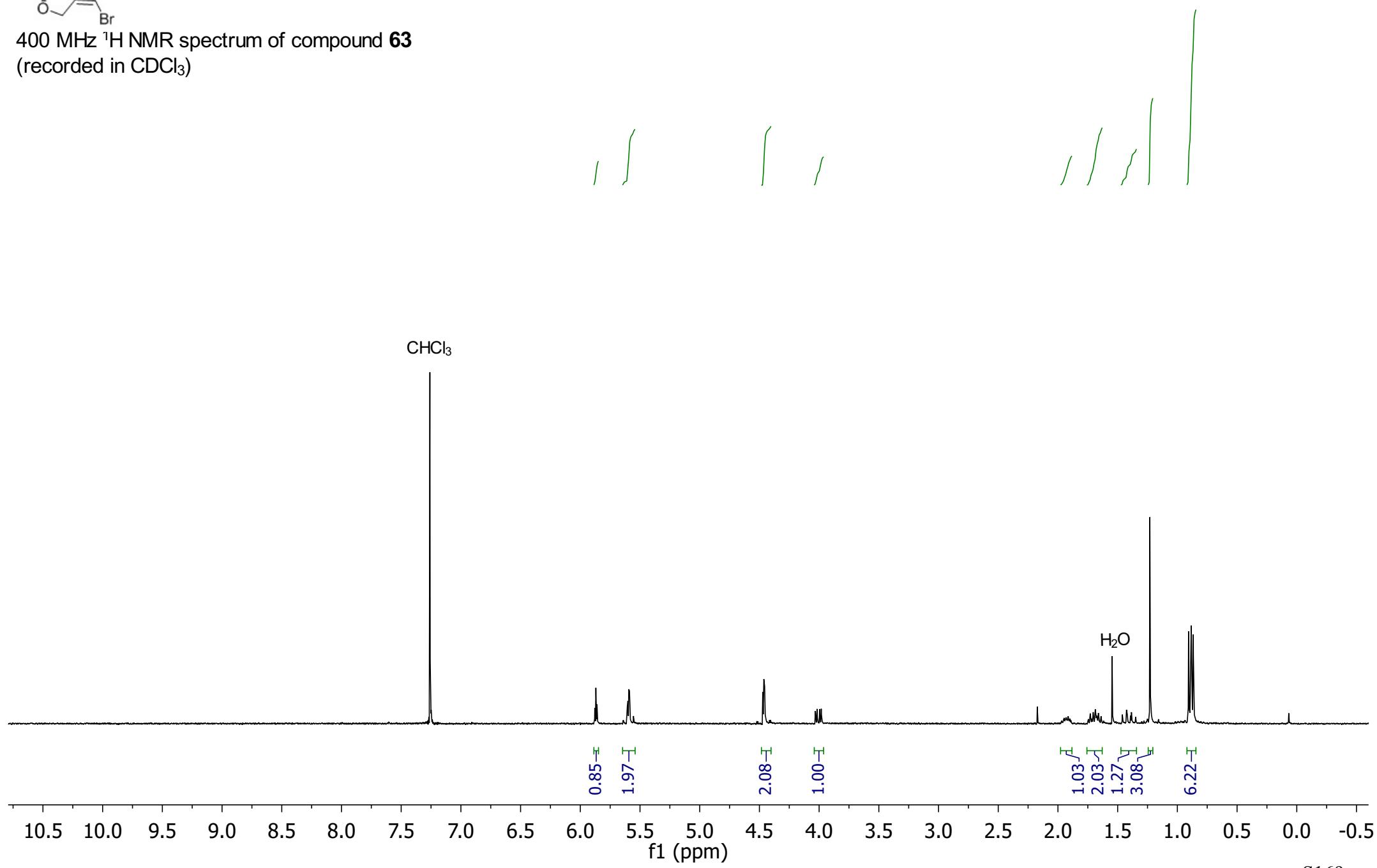


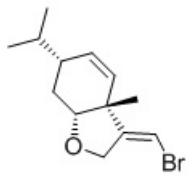
100 MHz ^{13}C NMR spectrum of compound **62**
(recorded in CDCl_3)



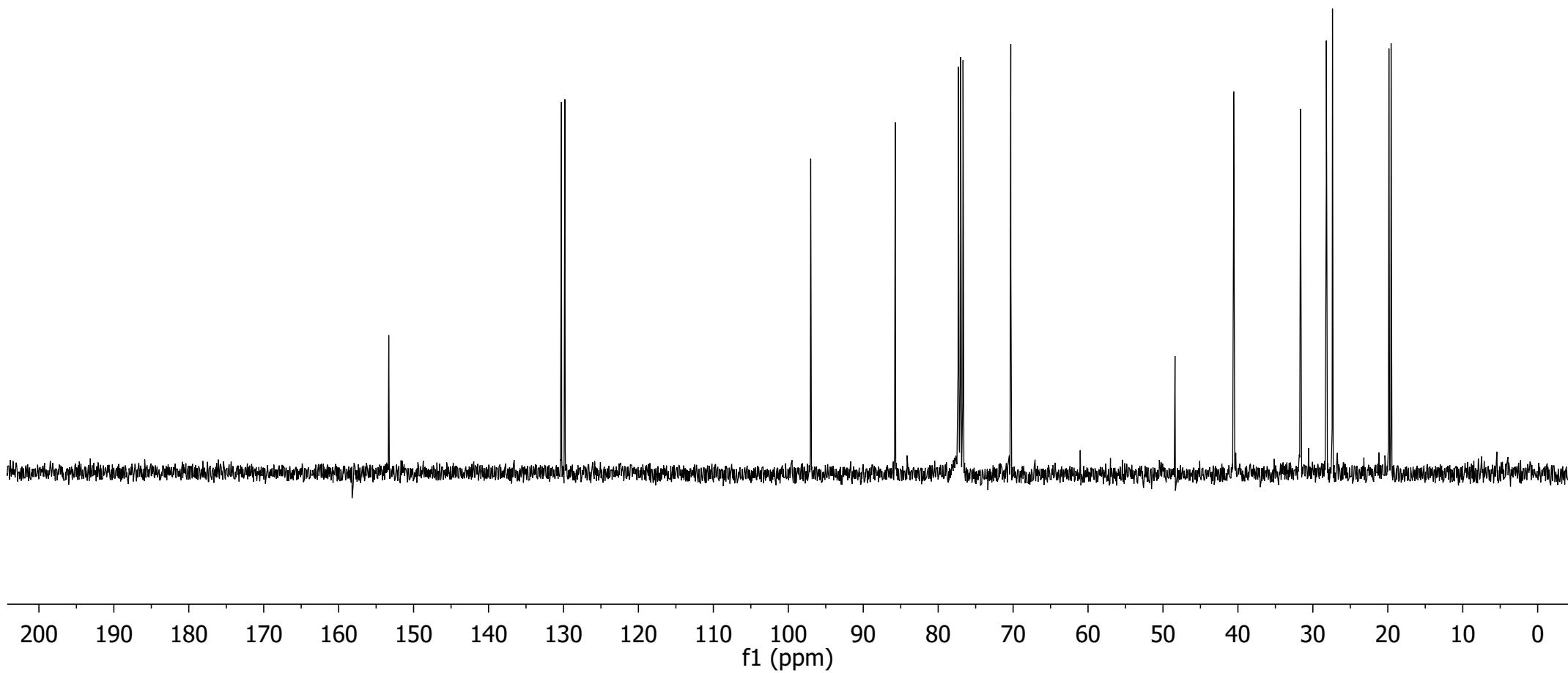


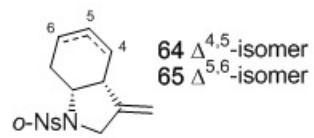
400 MHz ^1H NMR spectrum of compound **63**
(recorded in CDCl_3)



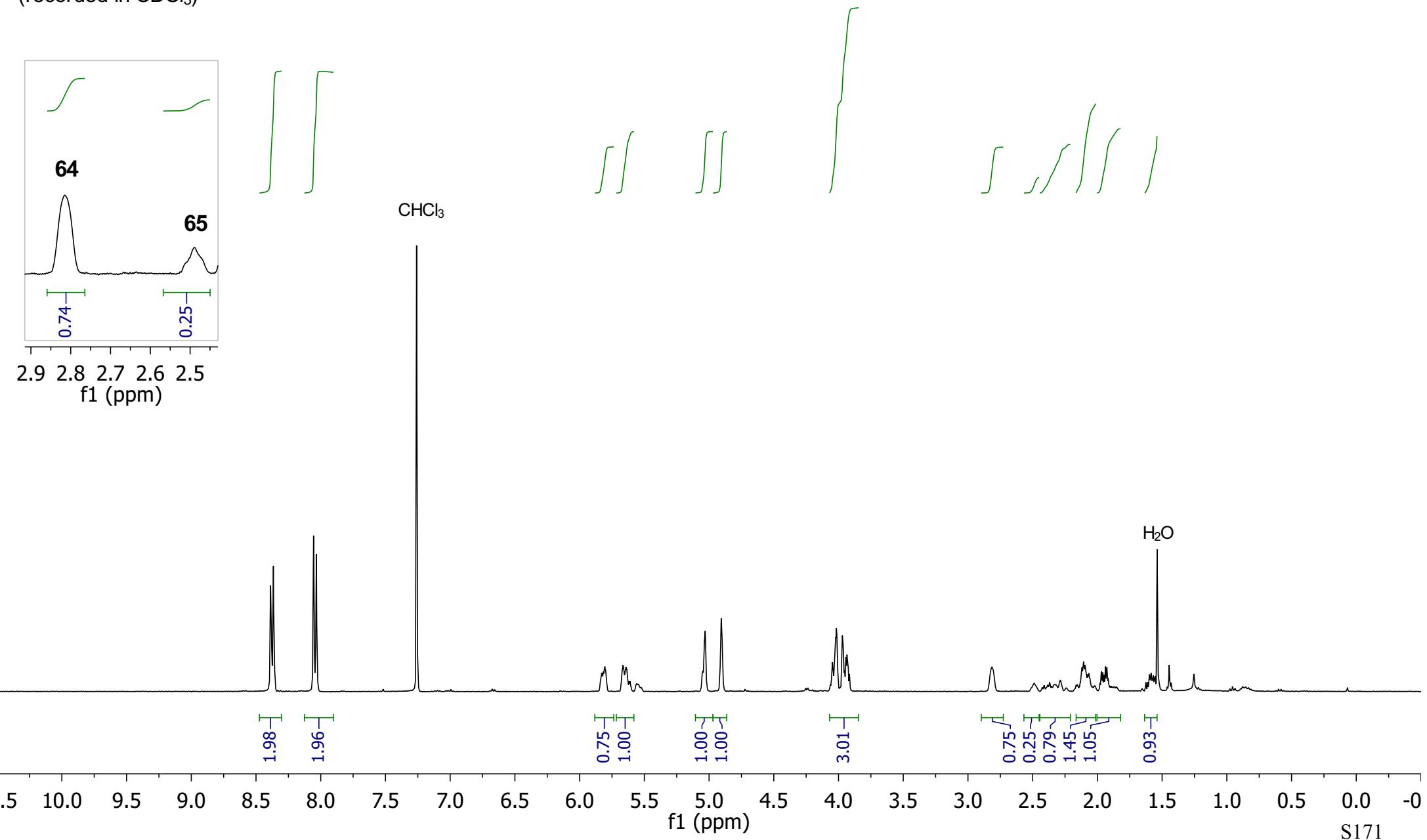


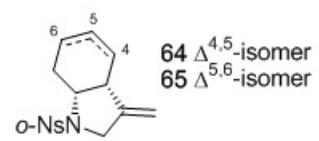
100 MHz ^{13}C NMR spectrum of compound **63**
 (recorded in CDCl_3)





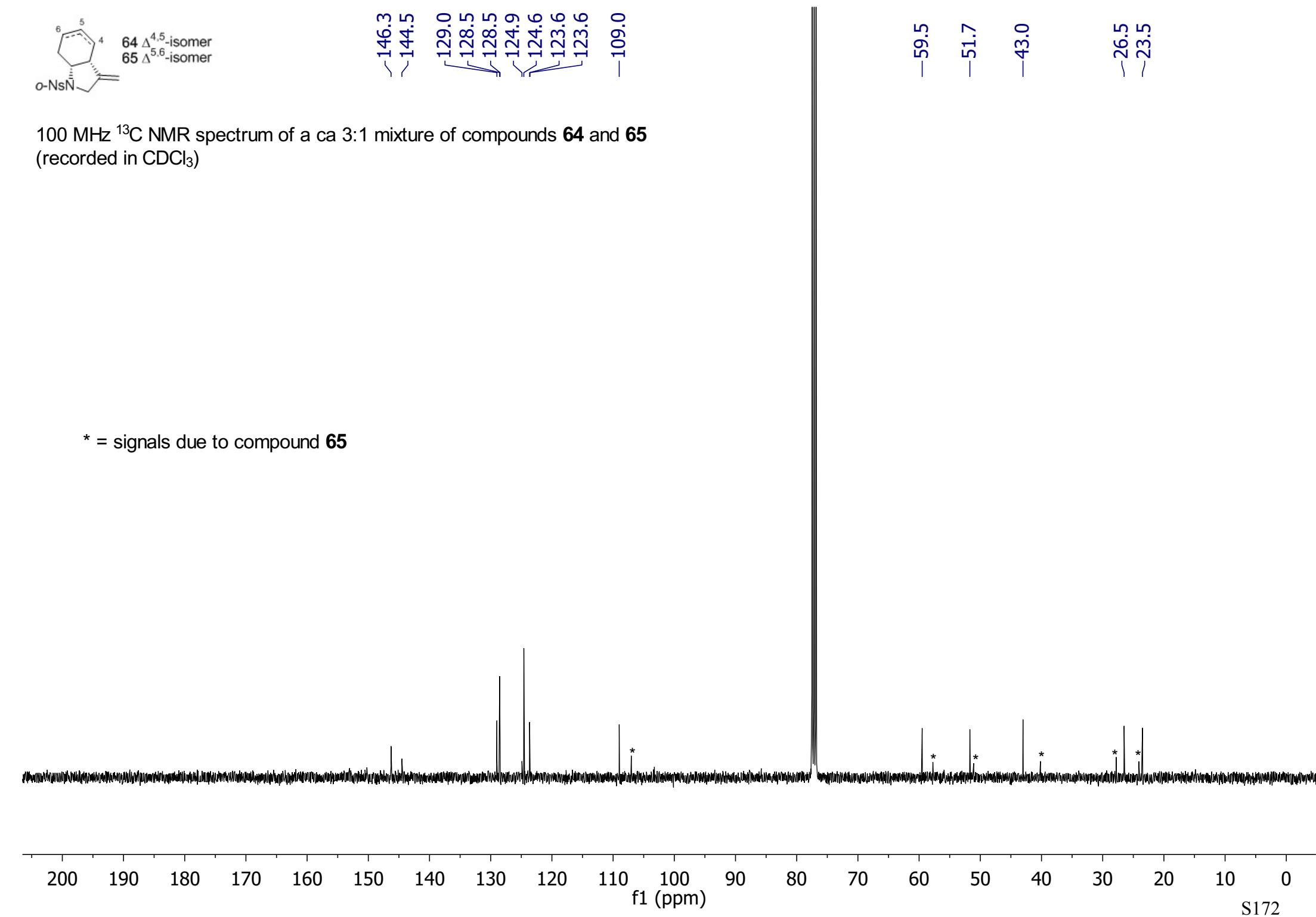
400 MHz ^1H NMR spectrum of a ca 3:1 mixture of compounds **64** and **65**
 (recorded in CDCl_3)

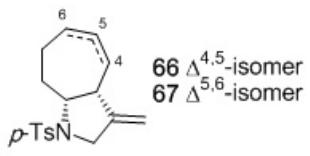




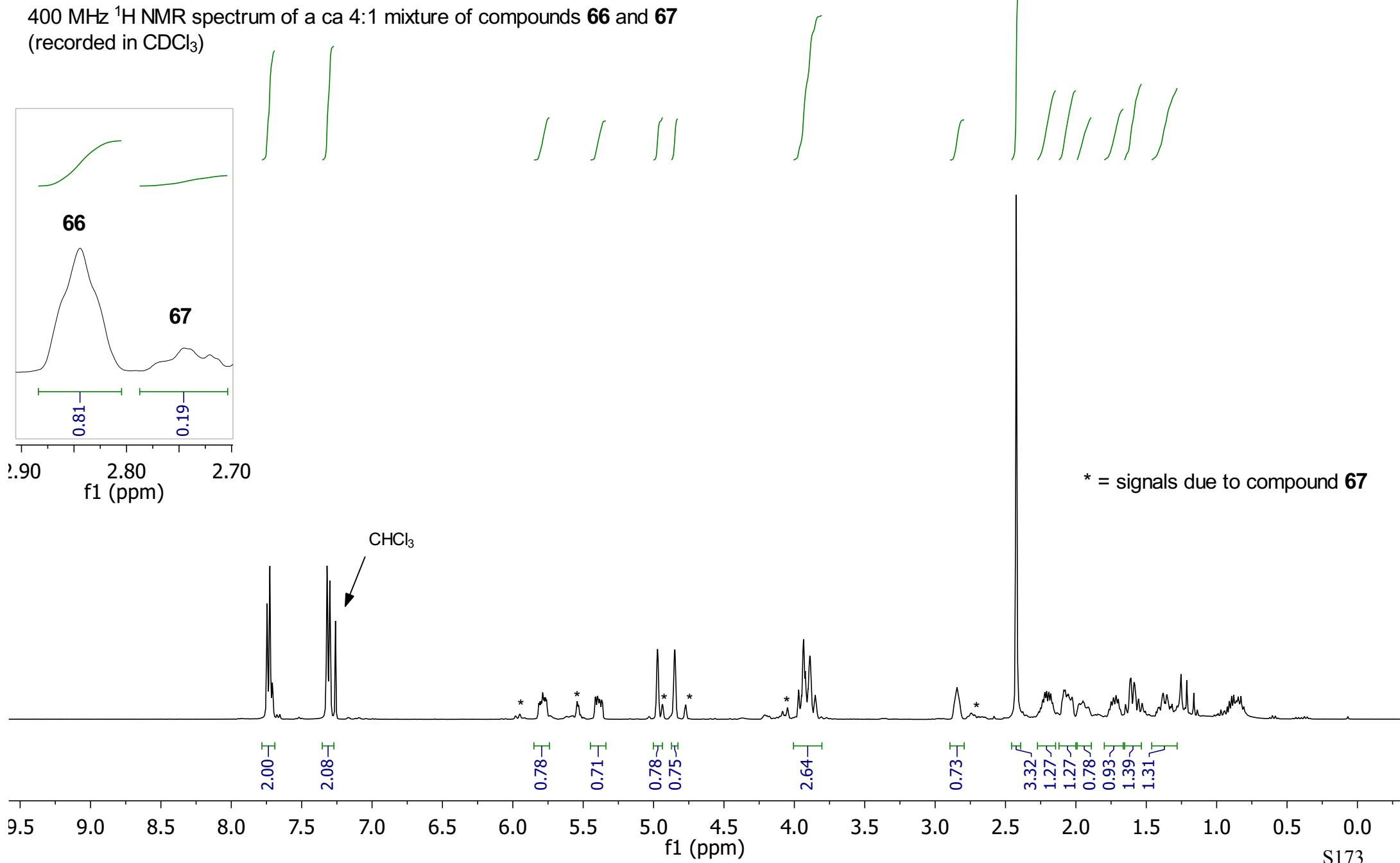
100 MHz ^{13}C NMR spectrum of a ca 3:1 mixture of compounds **64** and **65**
 (recorded in CDCl_3)

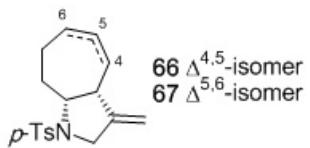
* = signals due to compound **65**



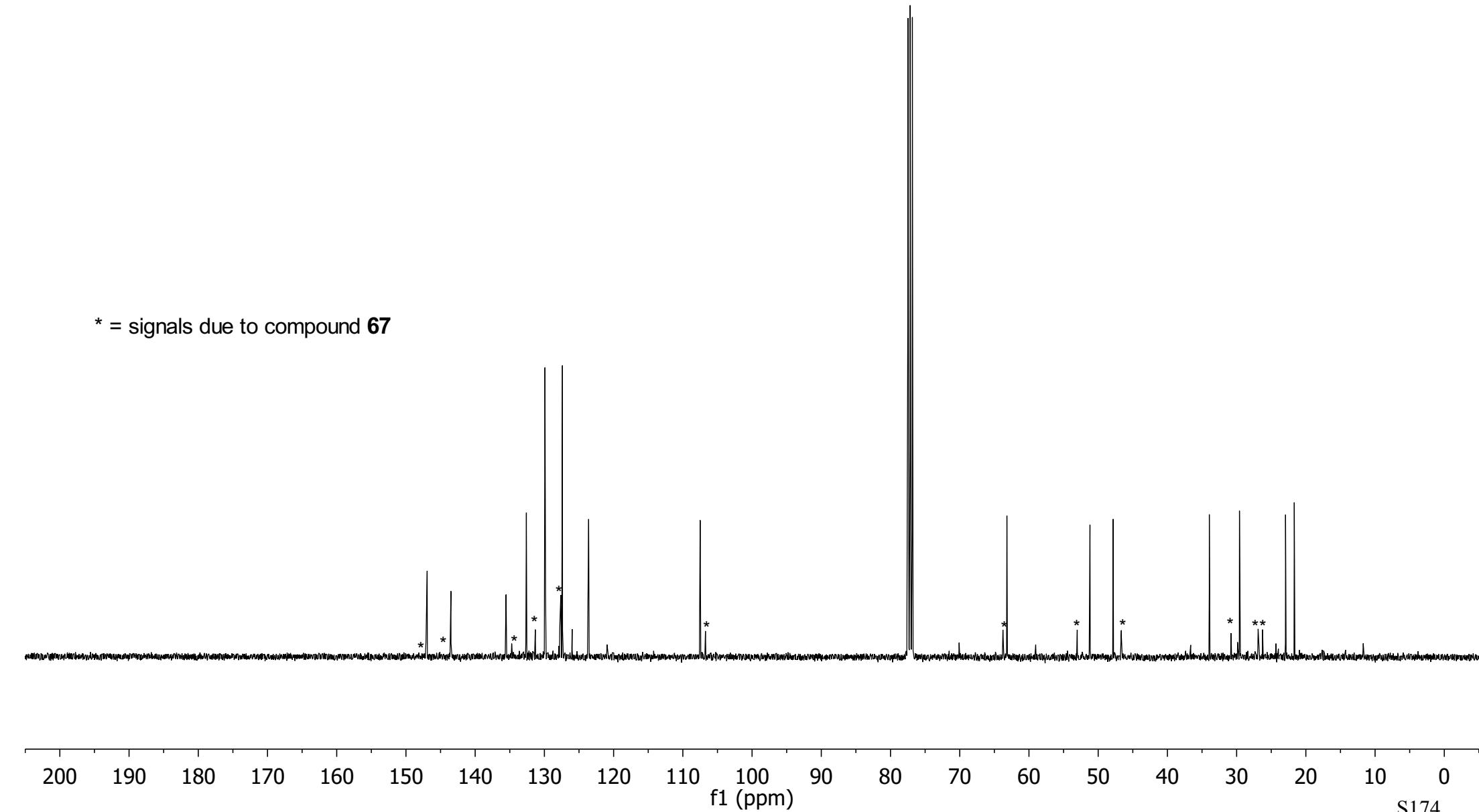


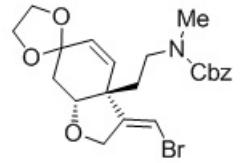
400 MHz ^1H NMR spectrum of a ca 4:1 mixture of compounds **66** and **67**
 (recorded in CDCl_3)





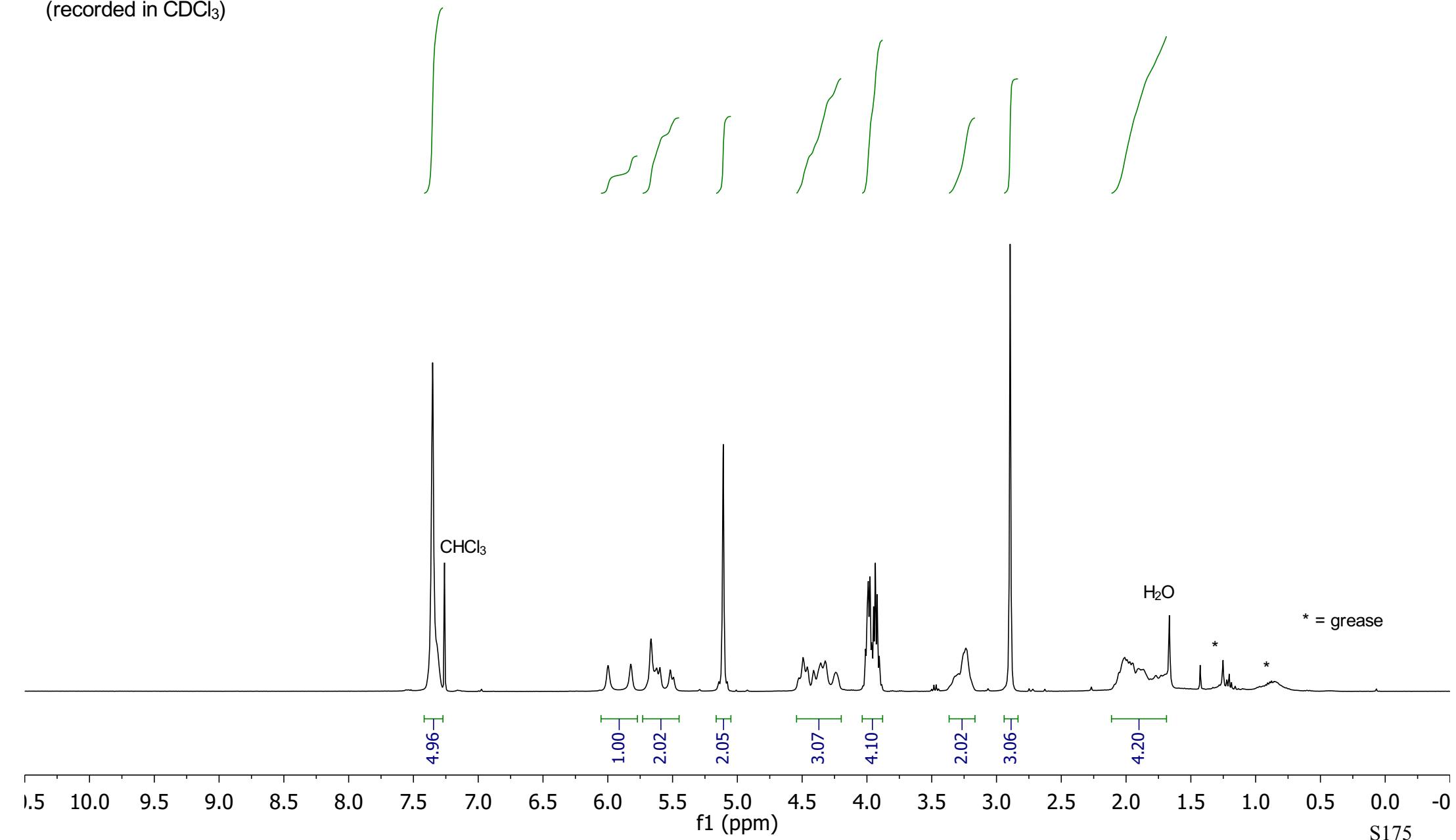
100 MHz ^{13}C NMR spectrum of a ca 7:1 mixture of compounds **66** and **67**
(recorded in CDCl_3)

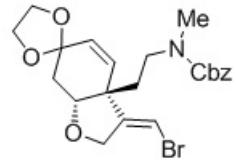




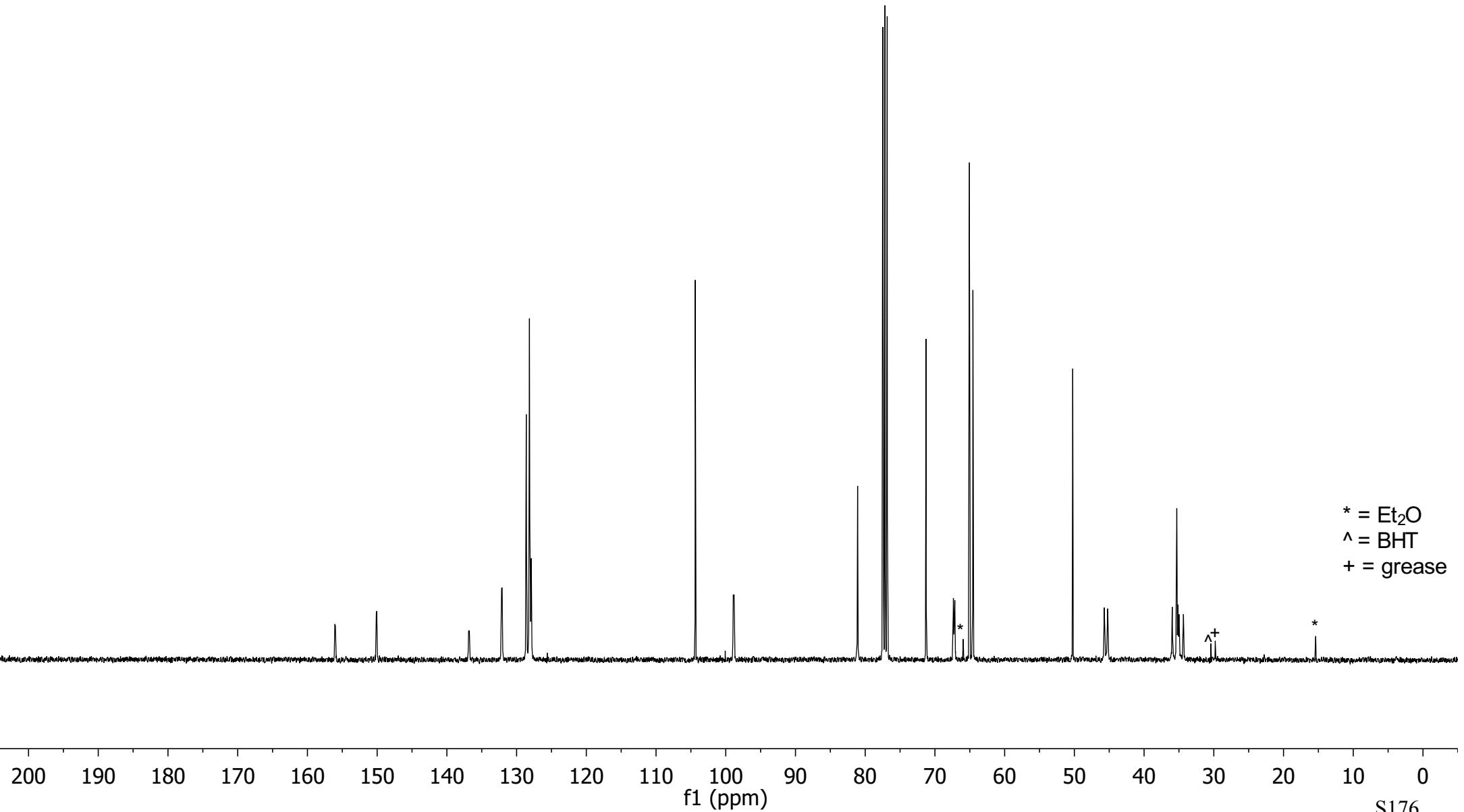
400 MHz ^1H NMR spectrum of compound **68**

(recorded in CDCl_3)

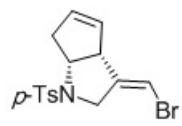




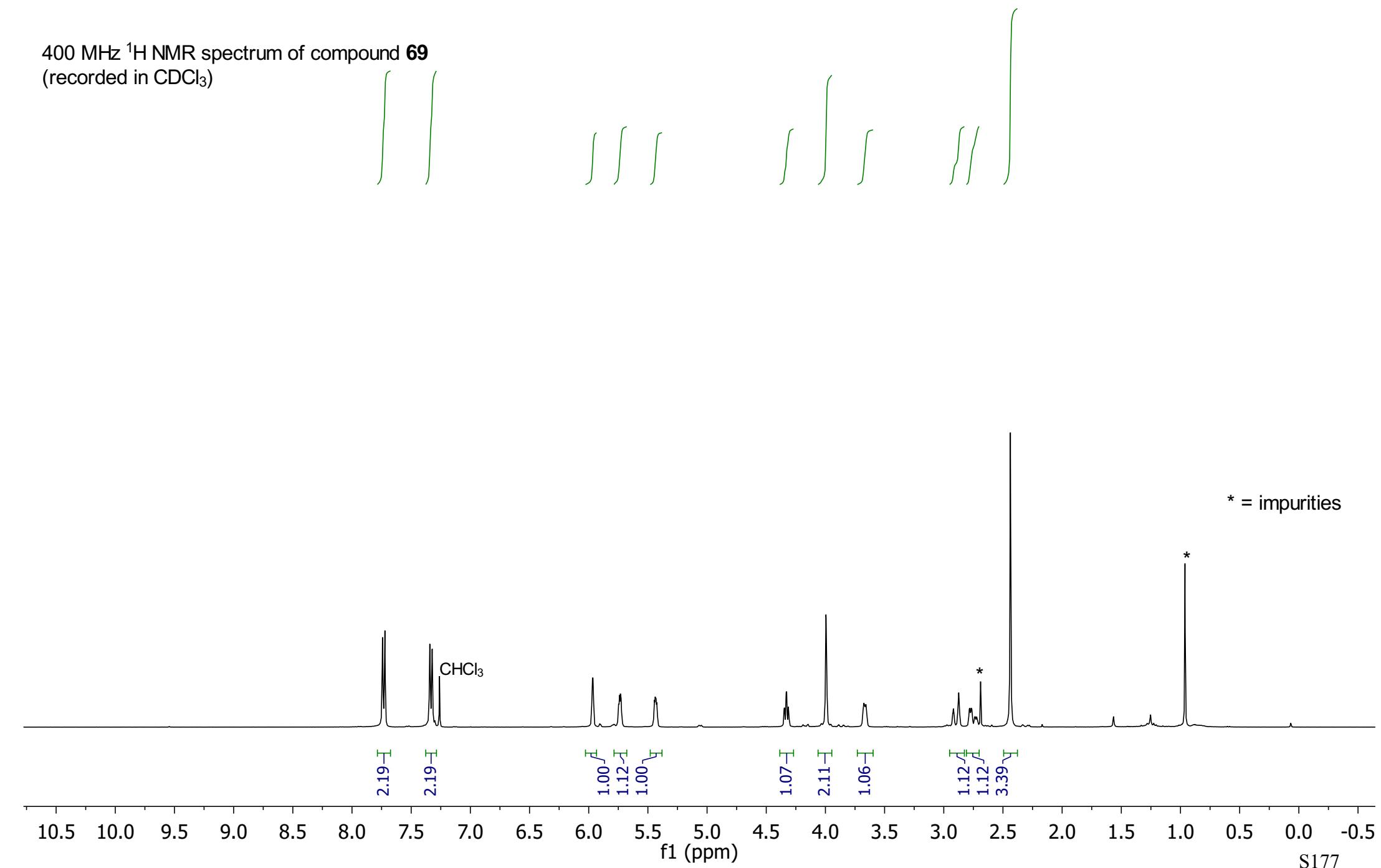
100 MHz ¹³C NMR spectrum of compound **68**
(recorded in CDCl₃)

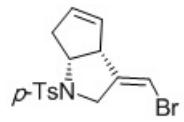


* = Et₂O
^ = BHT
+ = grease



400 MHz ^1H NMR spectrum of compound **69**
(recorded in CDCl_3)





100 MHz ^{13}C NMR spectrum of compound **69**
(recorded in CDCl_3)

