Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Copper(I)-Catalysed Transfer Hydrogenations with Ammonia Borane

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1 General information

All reactions were carried out in flame dried glassware under a nitrogen atmosphere using standard Schlenk techniques. Glassware and stir bars contaminated with transition metals were treated with *aqua regia* (conc. HCl/conc. HNO_3 3:1) prior to cleaning. For cleaning, glassware and stir bars were kept in a ^{i}PrOH/KOH overnight, rinsed with H_2O, kept in a citric acid/H_2O bath overnight and finally rinsed with dest. H_2O and dried at 120 °C. Solutions and reagents were added with nitrogen-flushed disposable syringes/needles. Solvents were added using glass syringes and stainless steel needles (stored at 120 °C). Analytical thin layer chromatography (TLC) was performed on silica gel 60 G/UV_{254} aluminium sheets (*Macherey-Nagel*). Flash column chromatography was performed on silica gel Davisil LC60A (40-63 µm, pore size 60 Å, *Grace*) using the indicated solvents.

NMR spectra were recorded on AV400 or AV500 instruments (*Bruker*). Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard according to the standard literature.[1] Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, m_c = centrosymmetric multiplet, app = apparent), coupling constants (Hz), integration and – if possible – atom assignment. The assignment refers to the atom number shown in the corresponding molecule figure and was achieved by analysis of DEPT (DEPT 135) and 2D-NMR spectra (COSY, HMQC, HMBC). If a distinct assignment was not possible, atoms were marked with "*" and can be interchanged. Designation "*Ar*" refers to atoms of an aromatic system where a distinct assignment was not possible. Melting points (m.p.) were determined using a Leica Galen III melting point apparatus (*Wagner & Munz*). Infrared (IR) spectra were recorded on a Cary 630 FT-IR spectrometer equipped with an ATR unit (*Agilent Technologies).* Mass spectra (HRMS) were obtained from the Analytical Facility at the Institut für Chemie at *Technische Universität Berlin* (ESI/APCI: LTQ Orbitrap XL, *Thermo Scientific*; EI: GC-system 5975C, HP-5MS, *Agilent Technologies*).

1.1 Solvents

THF and 1,4-dioxane were dried over sodium/benzophenone and distilled under a N_2 atmosphere prior to use. Et_3N, CH_2Cl_2 and Et_2O were dried over CaH_2 and distilled under a N_2 atmosphere prior to use. Acetonitrile (99.9%, extra dry) was purchased from *Acros*. Benzene (puriss., absolute) was purchased from *Sigma Aldrich*. Solvents (technical grade)

for extraction/chromatography (EtOAc, cyclohexane, CH_2Cl_2, Et_2O, *tert*-butyl methyl ether) were distilled under reduced pressure prior to use.

1.2 Chemicals

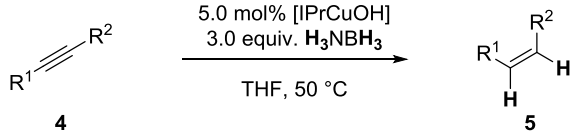
Compounds methyl non-2-ynoate (**6a**), methyl 3-phenylpropiolate (**6b**), ethynylbenzene (**S2**) 1,2-diphenylethylene (**4l**), dodec-6-yne (**4q**), ethyl cinnamate (**9c**), ethyl (*E*)-3-phenylbut-2-enoate (**9l**) were obtained commercially and used as is.

Synthesis of alkynes: Compounds ((pent-4-yn-1-yloxy)methyl)benzene (**S1**), (5-(benzyloxy)pent-1-yn-1-yl)benzene (**1**), methyl 4-(5-(benzyloxy)pent-1-yn-1-yl)benzoate (**4h**), 1-(5-(benzyloxy)pent-1-yn-1-yl)-4-methoxybenzene, (**4c**), 1-(4-(5-(benzyloxy)pent-1-yn-1-yl)phenyl)ethan-1-one (**4k**),[2] 4-(5-(benzyloxy)pent-1-yn-1-yl)benzonitrile (**4i**), 6-(benzyloxy)hex-2-yn-1-ol (**S4**), were prepared according to literature procedures.

Synthesis of esters: Compounds 4-(benzyloxy)benzaldehyde (**S6**),[3] ethyl 3-(4-methoxyphenyl)propanoate (**9c**)[4], ethyl 3-(4-(trifluoromethyl)phenyl)propanoate (**9i**),[4] ethyl 3-cyclohexylpropanoate (**9g**)[4], ethyl 3-(thiophen-2-yl)propanoate (**9f**),[4] methyl (*Z*)-3-(4-(benzyloxy)phenyl)acrylate (**9e**), ethyl (*E*)-3-(naphthalen-2-yl)but-2-enoate (**9j**),[5] ethyl 3,3-diphenylacrylate (**9l**)[6] were prepared according to literature procedures.

Synthesis of catalysts: The Cu complexes [IPrCuX], [sIPrCuCl], [IMesCuX] and [sIMesCuCl] were prepared according to a literature procedure[7] from the corresponding ligand precursor IPr·HCl.[8] [IPrCuOH] was obtained according to a literature procedure[9] from the corresponding precursor [IPrCuCl].

2 General Procedure alkyne transfer semihydrogenation with ammonia borane (GP3) (see also section 7.1.3)



4 5

A flame-dried 25 mL Schlenk-tube was charged with [IPrCuOH] (**x**) (5.00 mol%) and was dried under reduced pressure for 5 min. The catalyst was dissolved in THF (1.0 mL) and the alkyne (1.00 equiv.) was added as a solution in THF (1.0 mL). Ammonia borane (3.00 equiv.) was dissolved in THF (5.5 mL/mmol, c = 0.18 mmol/mL) and added dropwise to the reaction mixture over 3 h with a syringe pump. The resulting mixture was stirred at 50 °C until full conversion of the starting material was detected (GC- and NMR-analysis; samples for ^{1}H NMR spectroscopy and GC analysis were prepared by taking an aliquot of 0.3 mL from the reaction mixture, filtration through a pad of silica (0.5 x 3 cm) and elution with *tert*-butyl methyl ether (5 mL)). After full conversion of the alkyne was detected (for reaction times see corresponding substrates), the reaction mixture was filtered over a pad of silica (2.5 x 2.5 cm) eluted with *tert*-butyl methyl ether (15 mL) and all volatiles were removed under reduced pressure. The residue was purified via flash column chromatography to give the desired alkene.

3 Additional Screening data

This section contains tabular data about the optimization of the catalyst system.

In table 3.1.1, optimization data on the temperature of the reaction and the required amount of ammonia borane can be found. From the optimizations, it becomes clear that elevated temperatures are needed for high conversion of the alkyne **1**. The optimal temperature was found to be 40-50 °C. The following experiments were carried out at 50 °C. Furthermore, it was found that three equivalents of ammonia borane were necessary and that the reaction needs to be carried out in the absence of moisture in a closed system (pressure tube) for optimal results.

In table 3.2.1 to 3.2.5, the influence of the copper NHC complex, the counterion to copper and the base activation (if necessary) is investigated. It was found that NaO*t*Bu and K_2CO_3 can be used as activating agent, if the corresponding copper chloride NHC complexes were employed. A variety of simple NHC ligands to copper were tested with the result that IMes and IPr gave highest conversions of the alkynes. Finally, it was found that [IPrCuOH] alone could catalyze the transfer semihydrogenation with ammonia borane, rendering an additional activation unnecessary. Therefore, all further investigations have been carried out using this catalyst. It should be noted that whenever any conversion of the alkyne was detected, high *Z*-selectivity and negligible overreduction to the alkane were observed.

The addition mode of ammonia borane to the reaction mixture is crucial, as displayed from the experiments in table 3.3.1. A slow addition protocol leads to the highest conversions of the alkyne when the ammonia borane solution in THF was added over a period of at least three hours.

Table 3.4.1 shows the investigation of various solvents on the reaction, now still with the direct addition of three equivalents of ammonia borane directly at the beginning of the reaction. It was found that while many solvents tolerate the reaction to run, best results in terms of conversion were found in THF as solvent.

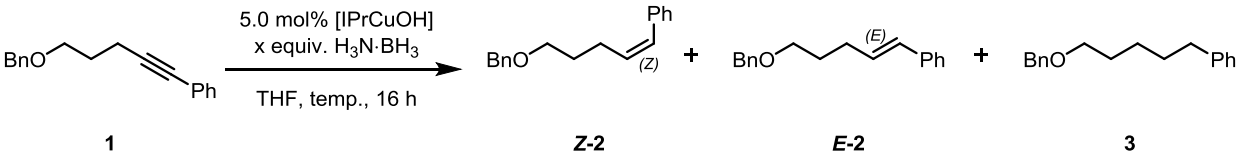
Table 3.5.1 displays that similar results could be obtained with even lower catalyst loadings of 1 mol-% if [IPrCuOH]. However, during the investigation of the substrate scope it was found that with functionalized substrates, generally 5 mol-% of catalyst were required for a general full conversion of substrates.

Table 3.6.1 shows an important feature of the catalytic system: The workup procedure is crucial for good yields of the desired alkene. The reason for this is most probably remaining borane compounds, which can lead to hydroboration of the desired alkenes, thereby

diminishing the overall yield. (Please see section 4 for the investigation and characterization of a hydroboration/oxidation product.) Best results in terms of yields were obtained by directly filtering the reaction mixture over silicagel and subsequent purification by column chromatography on silicagel.

3.1 Influence of the reaction temperature and amount of ammonia borane

Table 3.1.1. Cu-Catalyzed semihydrogenation of **1** with ammonia borane. Optimization of reaction temperature and amount of $H_3N{\cdot}BH_3$.



1 ***Z*-2** ***E*-2** **3**

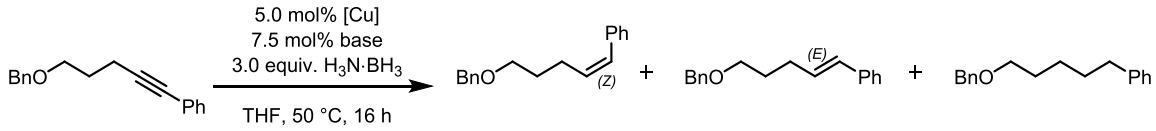
entry	temperature	equiv.of $H_3N{\cdot}BH_3$	comments	conversion[a]	selectivity *Z*-2/*E*-2/3[a]
1[b]	22 °C	3.0	---	12%	>99/0/0
2	22 °C	2.0	---	4%	>99/0/0
3	30 °C	3.0	---	68%	>99/0/0
4	30 °C	2.0	---	23%	>99/0/0
5	30 °C	1.0	---	14%	>99/0/0
6[b]	40 °C	10.0	---	19%	>99/0/0
7[b]	40 °C	5.0	---	92%	>99/0/0
8[b]	40 °C	3.0	---	35%	>99/0/0
9[c]	**40 °C**	**3.0**	**---**	**100%**	>99/0/0
10	40 °C	2.0	---	88%	>99/0/0
11	40 °C	20 mol%	H_2-balloon	20%	>99/0/0
12[b]	50 °C	4.0	---	99%	>99/0/0
13[b]	50 °C	3.0	---	87%	>99/0/0
15[c]	**50 °C**	**3.0**	**---**	**100%**	>99/0/0

entry	temperature	equiv.of $H_3N{\cdot}BH_3$	comments	conversion[a]	selectivity *Z*-2/*E*-2/3[a]
16	50 °C	3.0	in air, no moisture exclusion	7%	>99/0/0
17	50 °C	3.0	no [IPrCuOH]	0%	---
18[b]	60 °C	3.0	---	64%	>99/0/0

[a] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H NMR. [b] The reaction was carried out according to **GP3** in a 10 mL Schlenk-tube with a cooling condenser (closed system). [c] The reaction was carried out according to **GP3** in a 10 mL pressure tube (closed system).

3.2 Investigation of other NHC complexes, bases and counteranions to copper

Table 3.2.1. Cu-Catalyzed transfer semihydrogenation of **1** with ammonia borane. Influence of base and counteranion to copper.

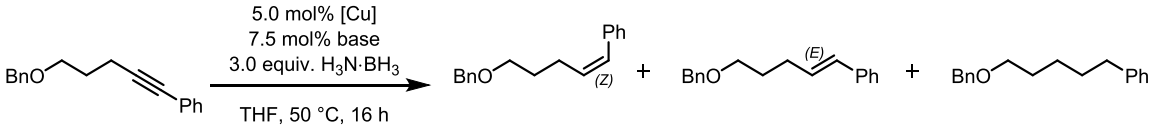


1 ***Z*-2** ***E*-2** **3**

entry	NHC-salt	base	conversion[a]	selectivity *Z*-2/*E*-2/3 [a]
1	IPrCuI	NaO*t*Bu	0%	>99/0/0
2	IPrCuBr	NaO*t*Bu	0%	>99/0/0
3	**IPrCuCl**	**NaO*t*Bu**	**100%**	**>99/0/0**
4	IPrCuCl	LiO*t*Bu	4%	>99/0/0
5	IPrCuCl	NaOMe	60%	>99/0/0
6	IPrCuCl	K_2CO_3	15%	>99/0/0
7	IPrCuCl	2.0 equiv. K_2CO_3	91%	>99/0/0
8	IPrCuCl	no base	0%	>99/0/0

[a] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H NMR. Reactions were carried out according to **GP3**.

Table 3.2.2. Cu-Catalyzed transfer semihydrogenation of **1** with ammonia borane. Influence of base and counteranion to copper.

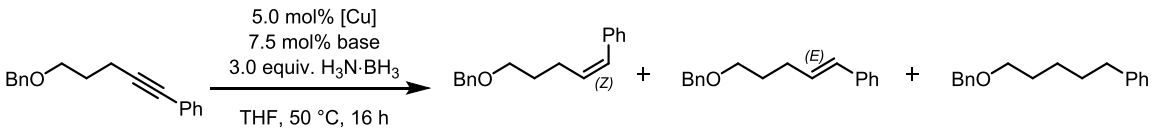


1 ***Z*-2** ***E*-2** **3**

entry	NHC-salt	base	comments	conversion[a]	selectivity *Z*-2/*E*-2/3 [a]
1	**sIPrCuCl**	**NaO*t*Bu**		**30%**	**>99/0/0**
2	sIPrCuCl	LiO*t*Bu		0%	>99/0/0
3	sIPrCuCl	no base		0%	>99/0/0

[a] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H NMR. Reactions were carried out according to **GP3**.

Table 3.2.3. Cu-Catalyzed transfer semihydrogenation of **1** with ammonia borane. Influence of base and counteranion to copper.

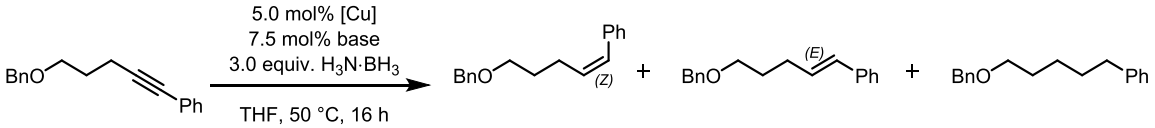


1 ***Z*-2** ***E*-2** **3**

entry	NHC-salt	base	comments	conversion[a]	selectivity *Z*-2/*E*-2/3 [a]
1	**IMesCuCl**	**NaO*t*Bu**		**100%**	**>99/0/0**
2	IMesCuCl	LiO*t*Bu		43%	>99/0/0
3	**IMesCuCl**	**K_2CO_3**		**100%**	**>99/0/0**
4	IMesCuCl	2.0 equiv. K_2CO_3		100%	>99/0/0
5	IMesCuCl	no base		16%	>99/0/0
6	IMesCuBr	NaO*t*Bu		0%	>99/0/0

[a] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H NMR. Reactions were carried out according to **GP3**.

Table 3.2.4. Cu-Catalyzed transfer semihydrogenation of **1** with ammonia borane. Influence of base and counteranion to copper.

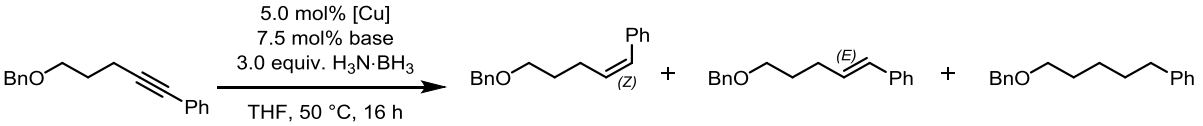


1 ***Z*-2** ***E*-2** **3**

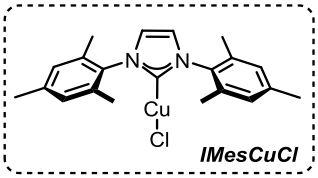
entry	NHC-salt	base	comments	conversion[a]	selectivity *Z*-2/*E*-2/3 [a]
1	**sIMesCuCl**	**NaO*t*Bu**		**100%**	**>99/0/0**
2	sIMesCuCl	LiO*t*Bu		26%	>99/0/0
3	sIMesCuCl	K_2CO_3		23%	>99/0/0
4	sIMesCuCl	2.0 equiv. K_2CO_3		19%	>99/0/0
5	sIMesCuCl	no base		0%	>99/0/0

[a] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H NMR. Reactions were carried out according to **GP3**.

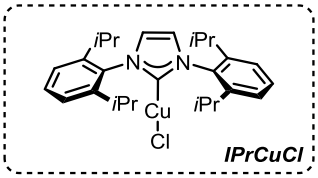
Table 3.2.5. Cu-Catalyzed semihydrogenation of **1** with ammonia borane. Investigation of NHC ligands.



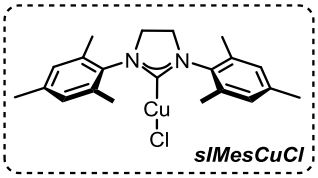
1 ***Z*-2** ***E*-2** **3**



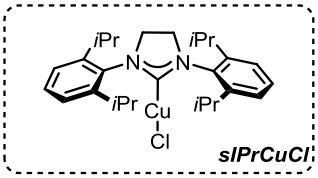
IMesCuCl



IPrCuCl



sIMesCuCl



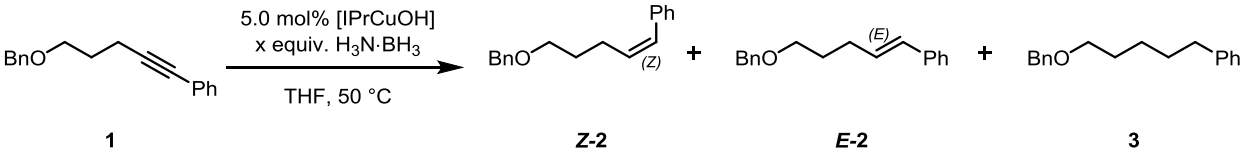
sIPrCuCl

entry	NHC-salt	base	comments	conversion[a]	selectivity *Z*-2/*E*-2/3 [a]
1	IPrCuCl	NaO*t*Bu		100%	>99/0/0
2	sIPrCuCl	NaO*t*Bu		30%	>99/0/0
3	IMesCuCl	NaO*t*Bu		100%	>99/0/0
4	IMesCuCl	K_2CO_3		100%	>99/0/0
5	sIMesCuCl	NaO*t*Bu		100%	>99/0/0
6	**IPrCuOH**	**no base**		**100%**	**>99/0/0**

[a] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H NMR. Reactions were carried out according to **GP3**.

3.3 Influence of the addition mode of ammonia borane

Table 3.3.1. Cu-Catalyzed transfer semihydrogenation of **1** with ammonia borane. Influence of addition mode of ammonia borane.



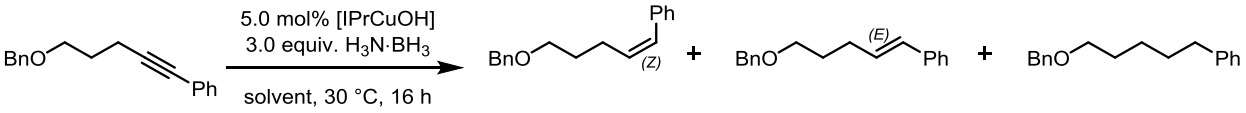
1 ***Z*-2** ***E*-2** **3**

entry	Timescale of AB addition[a]	Reaction time	equiv.of $H_3N{\cdot}BH_3$	conversion[b]	selectivity ***Z*-2/*E*-2/3** [b]
1	5 s	4.5 h	3.0	57%	>99/0/0
2	30 min	1 h	3.0	16%	>99/0/0
3	1 h	1.5 h	3.0	47%	>99/0/0
4	1.5 h	2 h	3.0	77%	>99/0/0
5	**3 h**	**3.5 h**	**3.0**	**100%**	**>99/0/0**
6	3 h	3.5 h	2.0	47%	>99/0/0
7	3 h	3.5 h	1.0	7%	>99/0/0
8	4 h	4.5 h	3.0	100%	>99/0/0
9	5 s	18 h	3.0	100%	>99/0/0

[a] Ammonia borane was added as a solution in THF (0.18 mol/L). [b] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H NMR. Reactions were carried out according to **GP3**.

3.4 Influence of the solvent

Table 3.4.1. Cu-Catalyzed semihydrogenation of **1** with ammonia borane. Solvent screening.



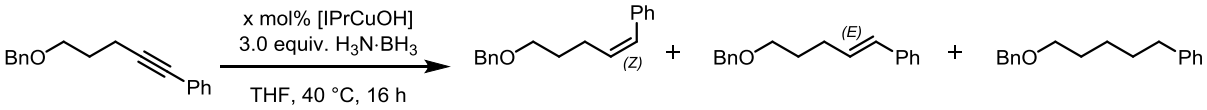
1 ***Z*-2** ***E*-2** **3**

entry	solvent	comments	conversion[a]	selectivity *Z*-2/*E*-2/3 [a]
1	**THF**	**---**	**68%**	>99/0/0
2	toluene	---	<5%	n.d.
3	1,4-dioxane	---	5%	>99/0/0
4	dichloromethane	---	6%	>99/0/0
5*	benzene	---	18%	>99/0/0
6*	*n*-hexane	---	10%	>99/0/0
7	chlorobenzene	---	19%	>99/0/0
8	diethyl ether	---	21%	>99/0/0
9	methyl-THF	---	14%	90/10/0

[a] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H-NMR.
[b] Hexaflouroisopropanol (HFIP).

3.5 Catalyst loading

Table 3.5.1. Cu-Catalyzed semihydrogenation of **1** with ammonia borane. Catalyst loading



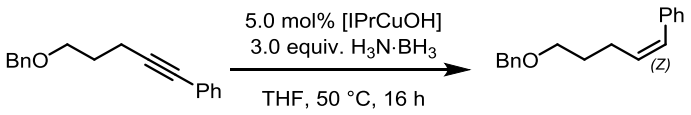
1 ***Z*-2** ***E*-2** **3**

entry	catalyst loading	comments	conversion[a]	selectivity *Z*-2/*E*-2/3 [a]
1	5.0 mol%	---	100%	98/2/0
2	4.0 mol%	---	96%	>99/0/0
3	3.0 mol%	---	83%	>99/0/0
4	2.0 mol%	---	98%	>99/0/0
5	1.0 mol%	---	100%	>99/0/0

[a] Conversion and *Z*-/*E*-alkene/alkane ratio (***Z*-2/*E*-2/3** ratio) were determined by ^{1}H-NMR.

3.6 Influence of the workup procedure on yield

Table 3.6.1. Influence of the workup procedure on the isolated yield.



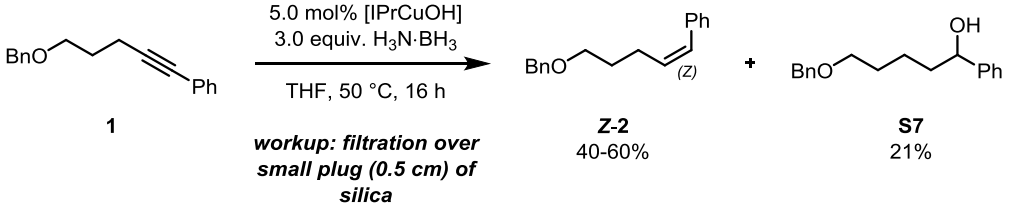
1 **Z-2**

entry	Work-up conditions	Yield after flash column chromatography
1	HCl in 1,4-dioxane; H_2O added; extracted with *t*BME; washed with aq. sat. $NaHCO_3$, H_2O, brine; dried over Na_2SO_4	61%
2	quenched with NaOH in H_2O; extracted with *t*BME; washed with HCl (2 M), H_2O, brine; dried over Na_2SO_4	41%
3	quenched with MeOH; concentrated under reduced pressure; procedure repeated three times	---
4	quenched with aq. sat. $NaHCO_3$;extracted with *t*BME; washed with HCl (2 M), H_2O, brine, dried over Na_2SO_4	24%
5[b]	**filtration of the crude reaction mixture over silica; afterwards evaporation of volatiles under reduced pessure, crude product loaded on silica, then flash column chromatography**	**96%**

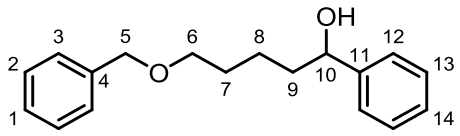
[a] The reactions were carried out according to **GP3**. After work-up crude products were purificated via flash column chromatography (SiO_2, 2.5 × 20 cm, cyclohexane/*t*BME 50:1, 10 mL). The reaction was carried out according to **GP3**. After work-up crude products were purificated via flash column chromatography (SiO_2, 2 × 11 cm, cyclohexane/*t*BME 50:1, 10 mL).

4 Identification of an hydroboration/oxidation product

From the reaction of **1** under the conditions shown below, we were able to isolate and characterize benzyl alcohol **S7** from the reaction mixture. The appearance of this product was observed whenever the initial filtration of the crude reaction mixture was carried out with a relatively small amount of silicagel. This hints at the fact that remaining ammonia borane (or decomposition products thereof) were still present in the crude mixture upon concentration. This could lead to hydroboration/oxidation to **S7** when oxygen is present as reported in the literature.[10]

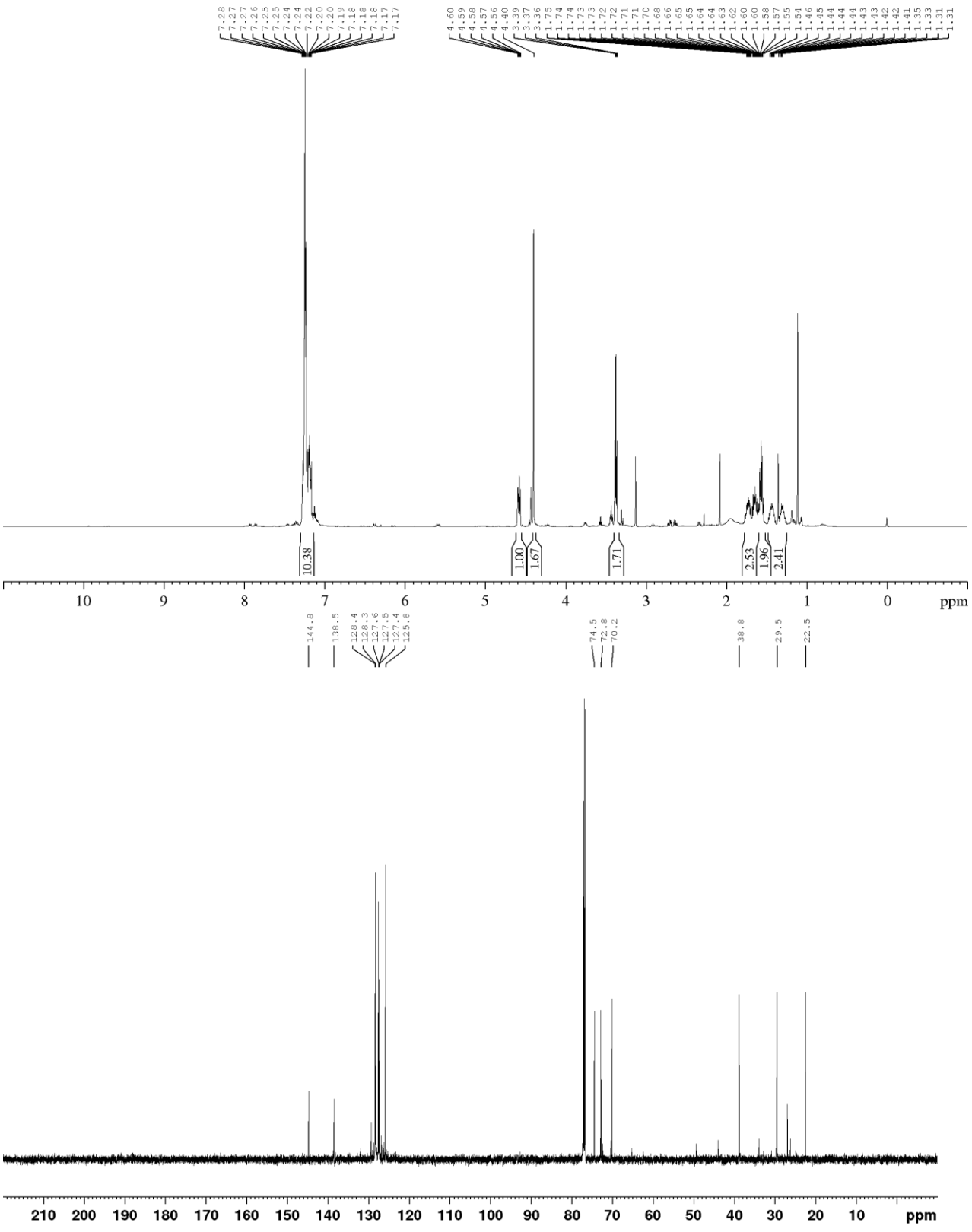


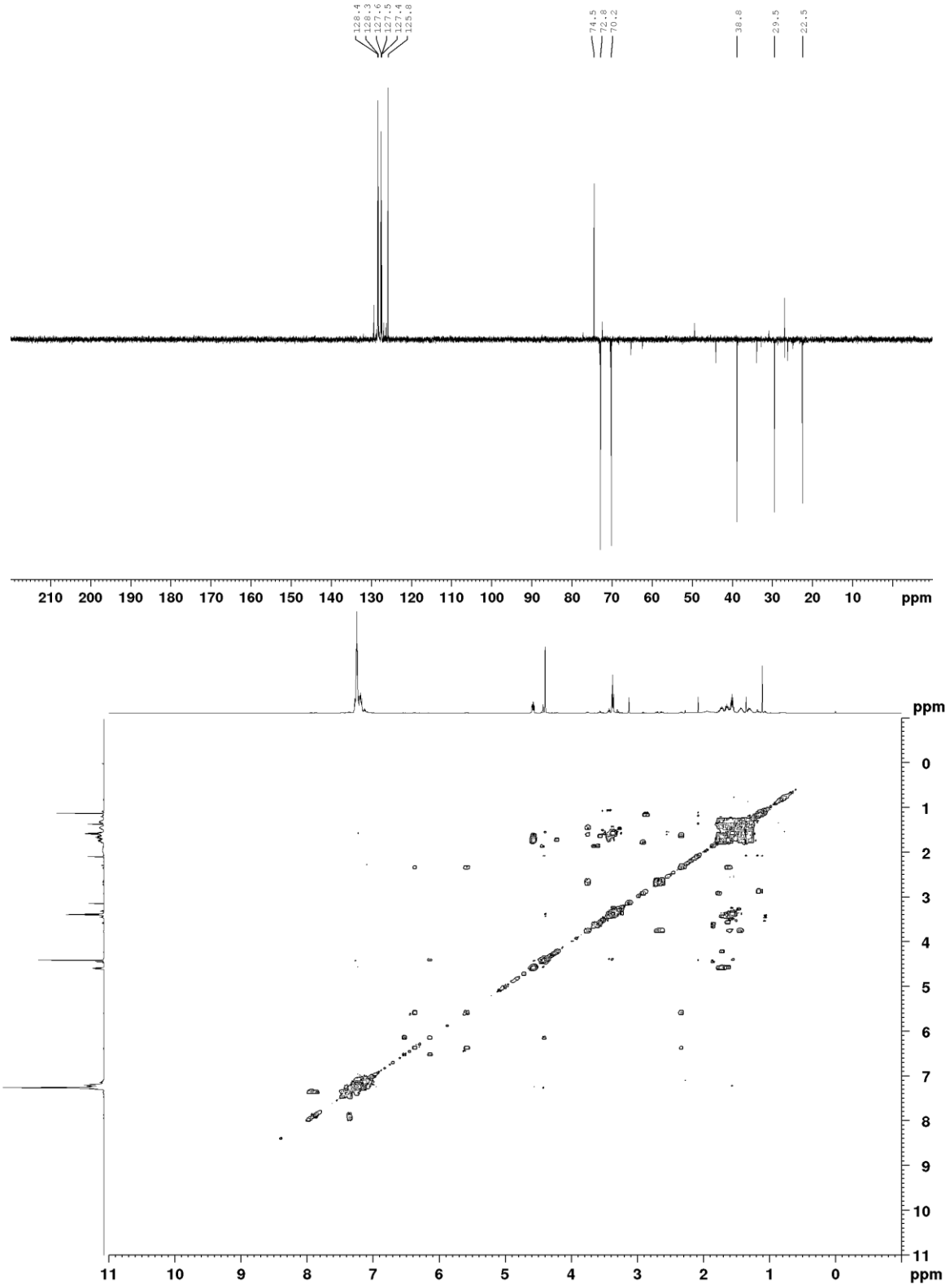
5-(Benzyloxy)-1-phenylpentan-1-ol (S7)

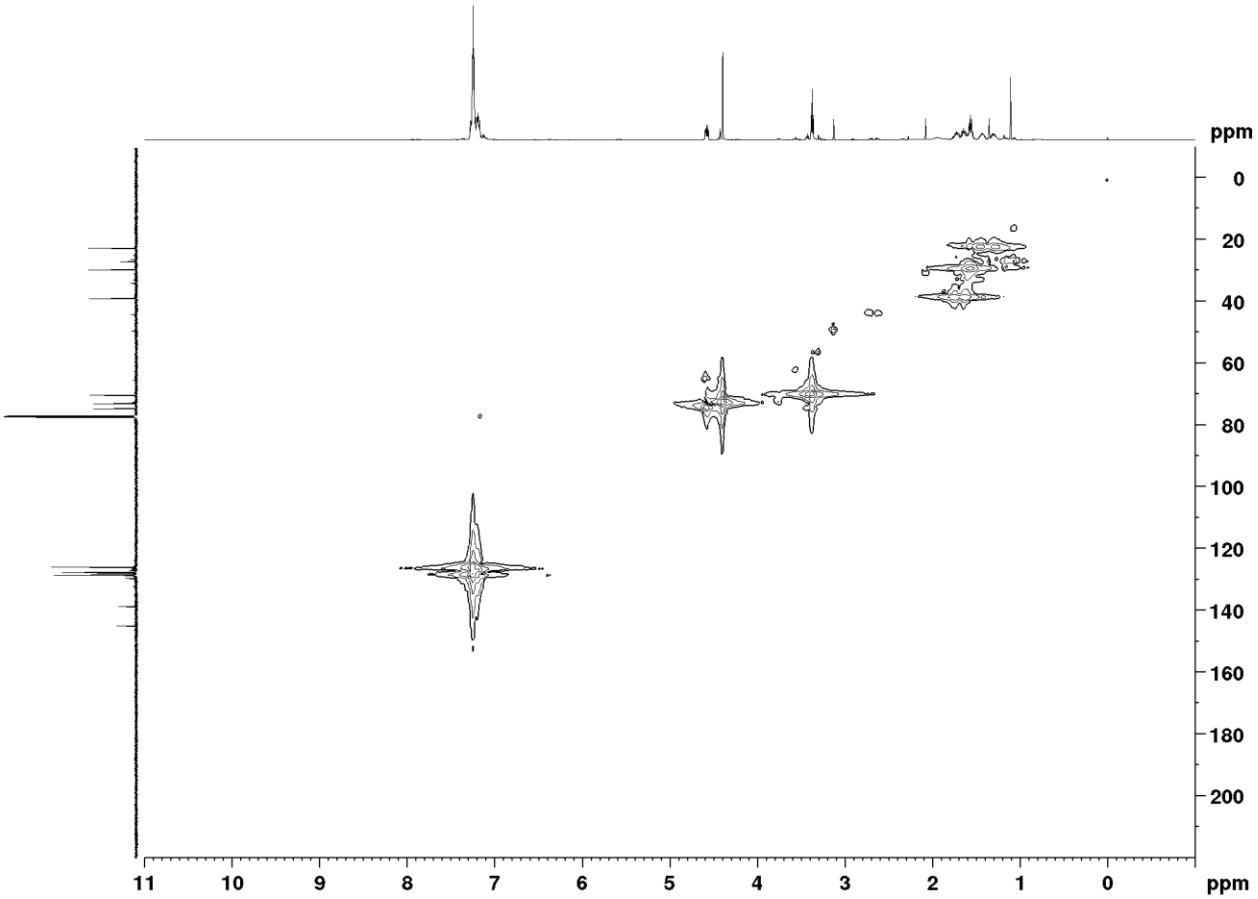


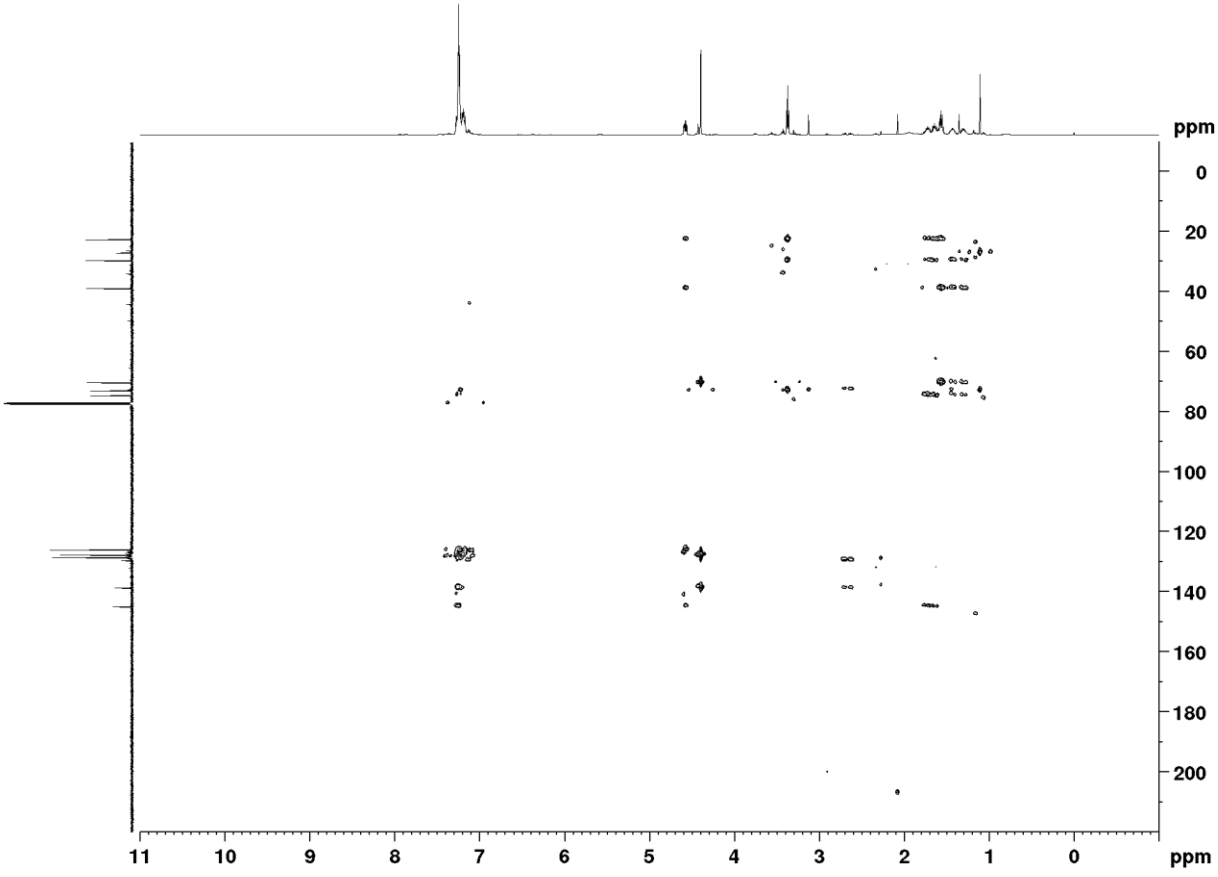
S7
$C_{18}H_{22}O_2$
M_W = 270.37 g/mol

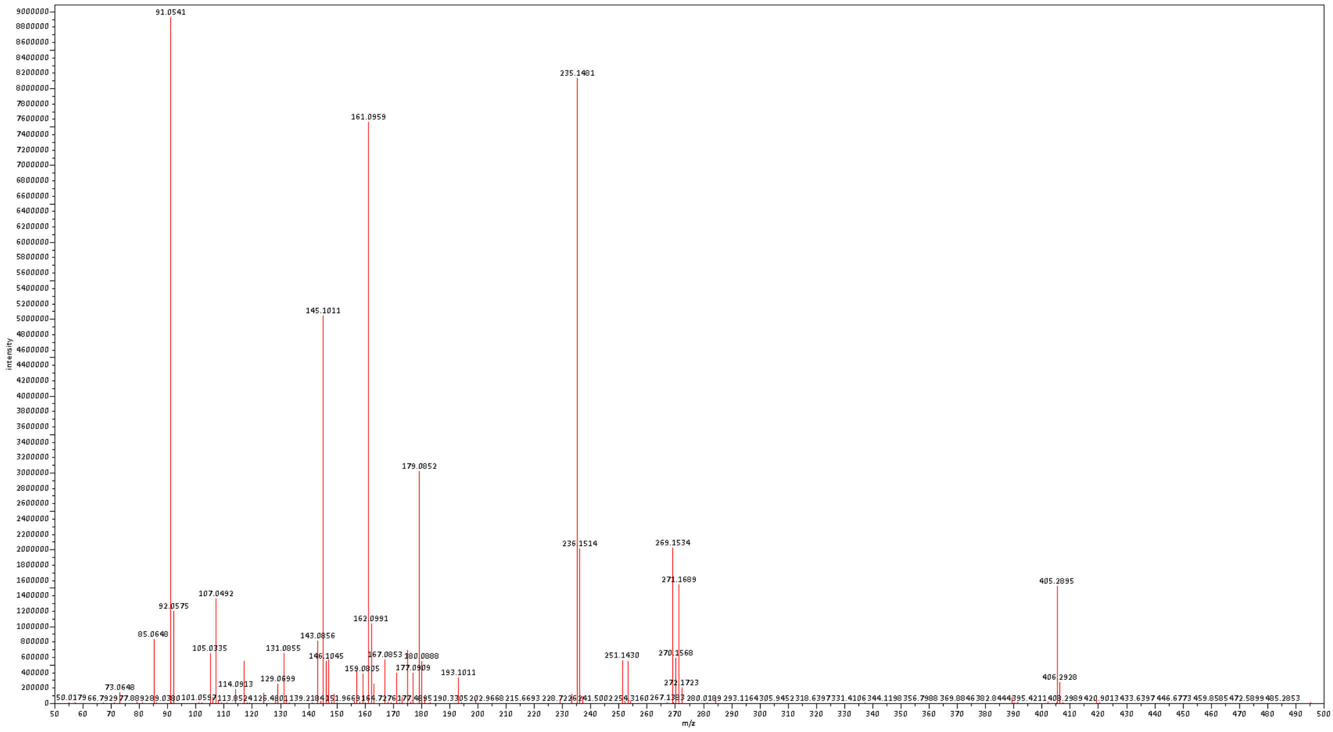
R_f = 0.10 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.27-1.35 (m, 2H, H-8), 1.41-1.42 (m, 2H, H-7), 1.42-1.44 (m, 2H, H-9), 3.37 (m_c, 2H, H-6), 4.40 (s, 2H, H-5), 6.56-4.60 (m, 1H, H-10), 7.17-7.28 (10H, H-Ar) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 22.5 (C-8), 29.5 (CC-7), 38.8 (C-9), 70.2 (C-6), 72.8 (C-5), 74.5 (C-10), 125.8 (C-Ar), 127.4 (C-Ar), 127.5 (C-Ar), 127.6 (C-Ar), 128.3 (C-Ar), 128.4 (C-Ar), 138.5 (C-4), 144.8 (C-11) ppm. **HRMS (APCI)** calcd. for $C_{18}H_{23}O_2^+$ [$(M+H)^+$]: 271.1698,, found: 271.1689.


7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.24 7.22 7.20 7.20 7.19 7.18 7.18 7.17 7.17
4.60 4.59 4.58 4.57 4.56 4.40 3.39 3.37 3.36 1.75 1.74 1.73 1.72 1.72 1.71 1.71 1.70 1.68 1.66 1.65 1.65 1.64 1.64 1.63 1.62 1.60 1.60 1.58 1.57 1.55 1.54 1.46 1.45 1.44 1.44 1.44 1.43 1.43 1.42 1.42 1.41 1.35 1.33 1.31 1.31
10.38
1.00
1.67
1.71
2.53
1.96
2.41
10 9 8 7 6 5 4 3 2 1 0 ppm
144.8 138.5 128.4 128.3 127.6 127.5 127.4 125.8
74.5 72.8 70.2
38.8 29.5 22.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


128.4
128.3
127.6
127.5
127.4
125.8
74.5
72.8
70.2
38.8
29.5
22.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
ppm
0 1 2 3 4 5 6 7 8 9 10 11
11 10 9 8 7 6 5 4 3 2 1 0 ppm


ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm


ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm


91.0541
235.1481
161.0959
145.1011
179.0852
236.1514
269.1534
271.1689
405.2895
107.0492
92.0575
162.0991
85.0648
143.0856
105.0335
131.0855
146.1045
167.0853
180.0888
270.1568
251.1430
159.0805
177.0909
193.1011
129.0699
114.0913
73.0648
272.1723
406.2928
intensity
m/z

5 Fate of ammonia borane, reaction control by ^{11}B-NMR

The reaction has been followed by ^{11}B NMR in order to gain insight into the ammonia borane decomposition products. In Figure 5.1, the ^{11}B NMR (THF-d_8) spectra of pure ammonia borane (A), a mixture of 10 mol% [IPrCuOH] and 1 equiv ammonia borane after 4 h in THF-d_8 at 50 °C (B) and a mixture of 1 equiv [IPrCuOH], 1 equiv alkyne **1** and 1 equiv ammonia borane after 4 h in THF-d_8 at 50 °C (C) are shown. From the chemical shift of the boron-containing products (around 0 ppm) in spectra B and C, it can be seen that (poly)aminoboranes are formed.[27] This accounts for the liberation of one equivalent H_2 per molecule ammonia borane.

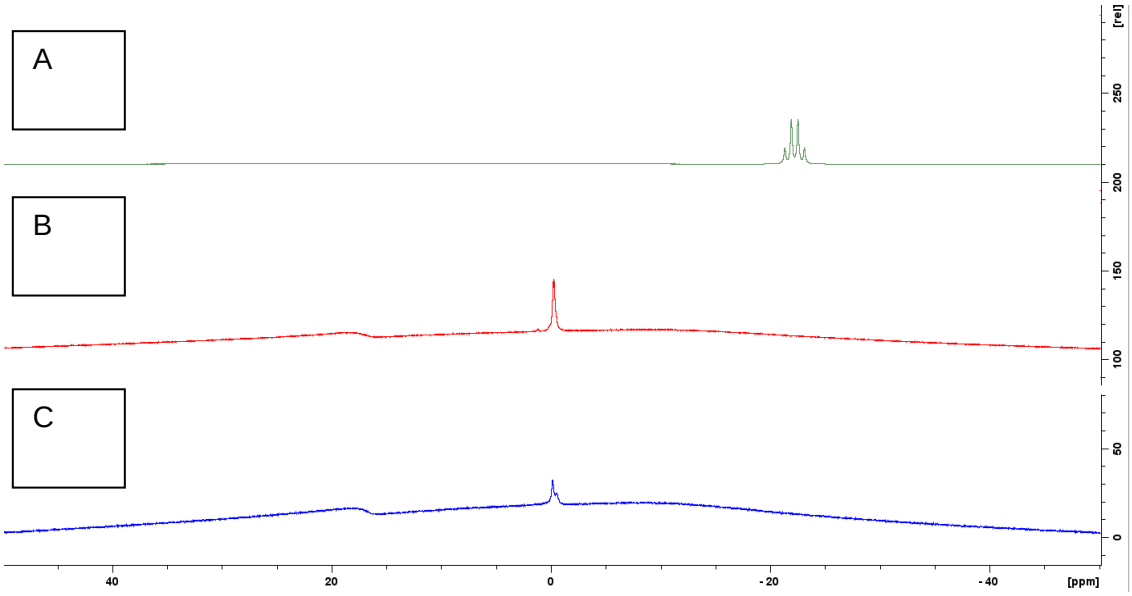


Figure 5.1: ^{11}B NMR of ammonia borane (A), 10 mol% [IPrCuOH] and 1 equiv ammonia borane after 4 h in THF-d_8 at 50 °C (B), mixture of 1 equiv [IPrCuOH], 1 equiv alkyne **1** and 1 equiv ammonia borane after 4 h in THF-d_8 at 50 °C (C) . All spectra recorded in THF-d_8.

Additionally, the ESI-MS of B and C were taken and delivered identical results. A representative spectrum can be seen in Figure 5.2. The major signals can be traced back to polyaminoboranes $(H_2NBH_2)_n$. (97: n = 3 + one B atom; 271: n = 9; 405: n = 14; 331: n = 11 + one B atom; 363: n = 12 + one N atom). The found masses can vary by small multiples of 2 from the calculated ones, most probably by additional unsaturations (B=N bonds). Since these iminoboranes are not observed in solution via ^{11}B NMR, they could arise during ionization in the mass spectrometer.

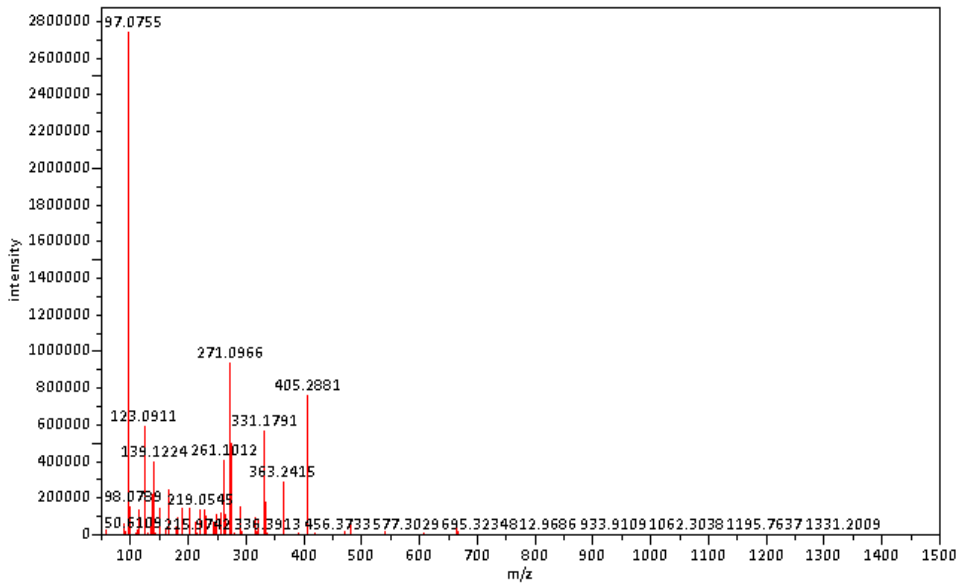


Figure 5.2: ESI-MS spectrum of a reaction mixture of 10 mol% [IPrCuOH] and 1 equiv ammonia borane after 4 h in THF-d_8 at 50 °C (B)

From the ^{1}H NMR spectrum of the stoichiometric reaction of alkyne **1**, [IPrCuOH] and ammonia borane (1:1:1) in THF-d8 (4 h at 50 °C), further insights into the reaction mechanism can be gained (Figures 5.4 and 5.5) In the shift region where the double bond hydrogen atoms are found, the formation of the desired product can be observed (resonances at 5.65 and 6.40 ppm). At the same time, an apparent triplet at 5.08 ppm is observed, which is an indication for a vinylcopper intermediate[28] such as the one shown in Figure 5.3. The observation of this intermediate hints at a reaction mechanism involving copper hydride intermediates (formation of the vinylcopper(I) intermediate by reaction of a copper hydride complex with an internal alkyne via insertion of the alkyne into the Cu–H bond).

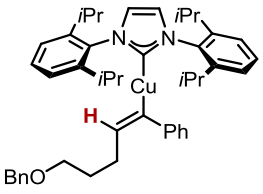


Figure 5.3.: Proposed vinylcopper intermediate.

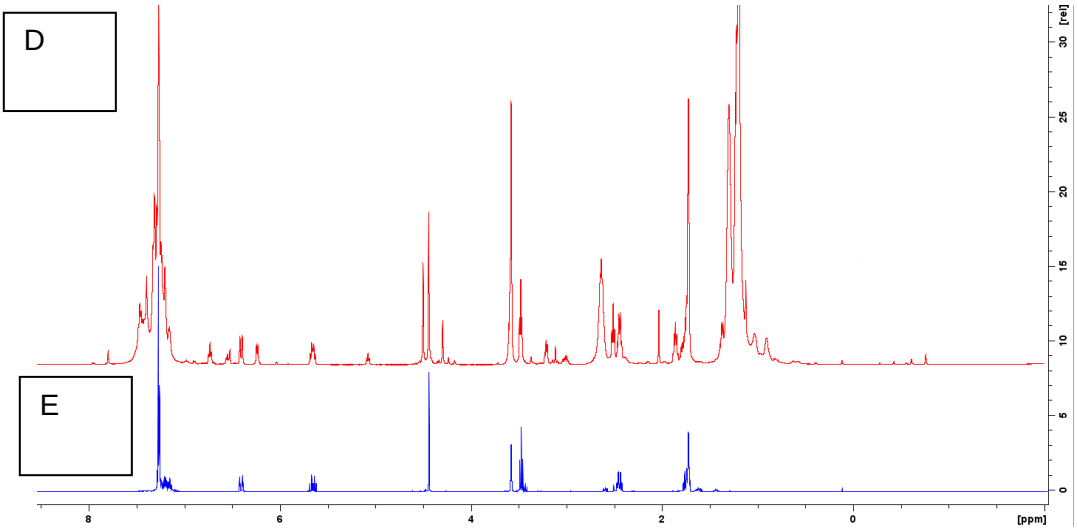


Figure 5.4: ^{1}H NMR of mixture of 1 equiv [IPrCuOH], 1 equiv alkyne **1** and 1 equiv ammonia borane after 4 h in THF-d_8 at 50 °C (D) and pure product *Z*-**2** (E).

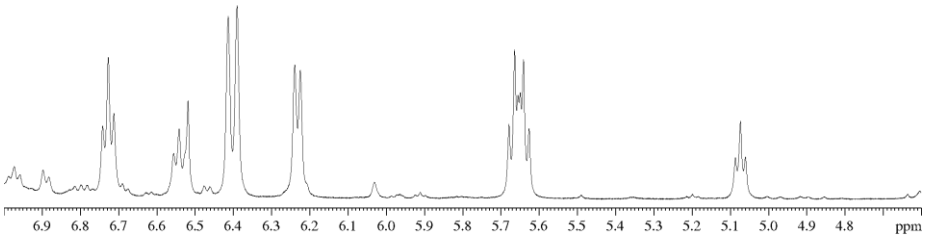
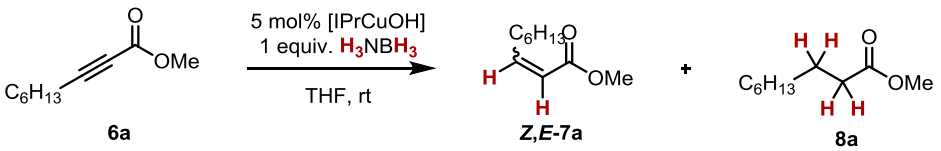


Figure 5.5: Extension of ^{1}H NMR spectrum D.

6 Transfer semihydrogenation of propiolates

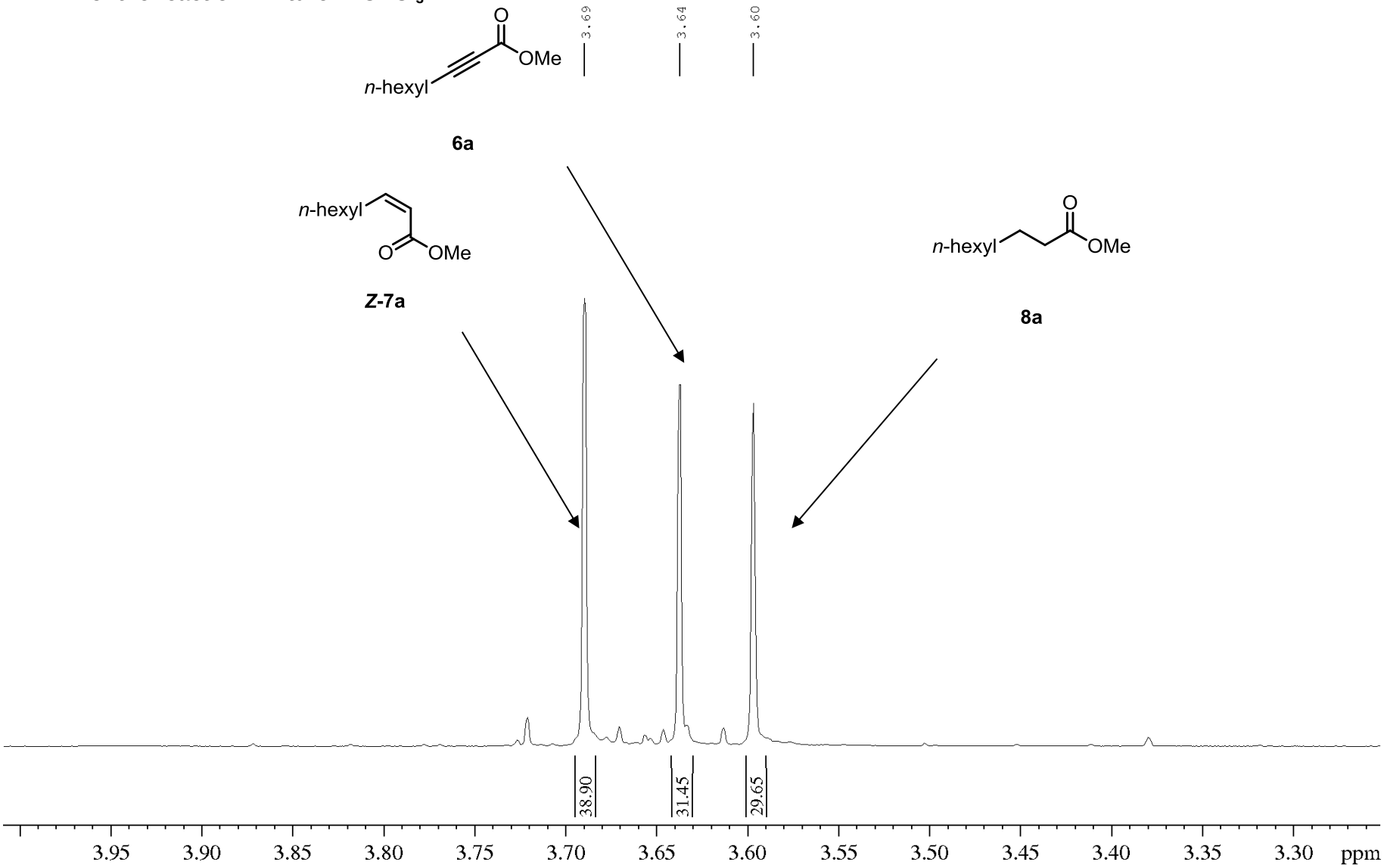
Reaction analysis of the transfer alkyne semihydrogenation of propiolates. For the reaction of **6a** as follows:

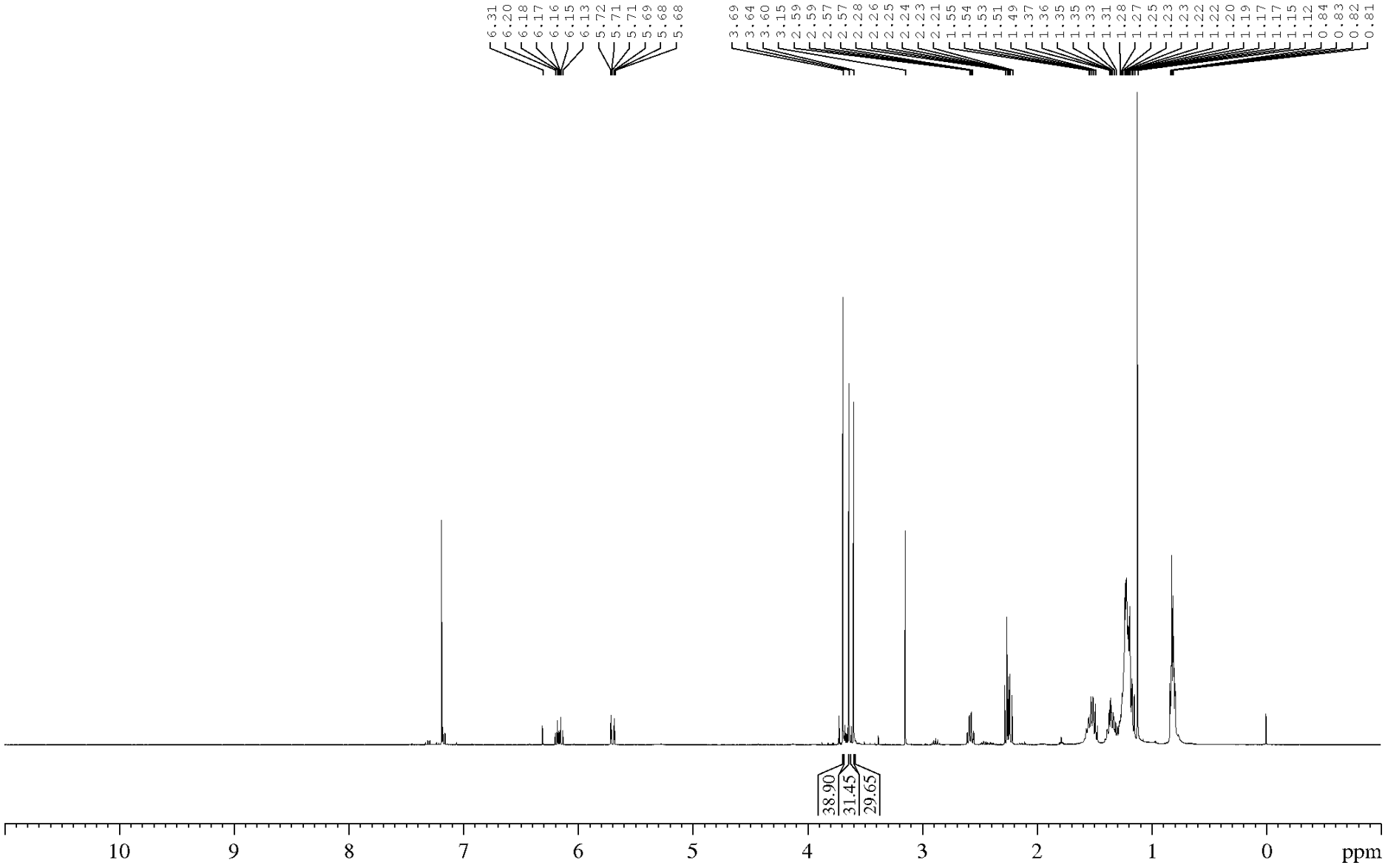


6a ***Z,E*-7a** **8a**

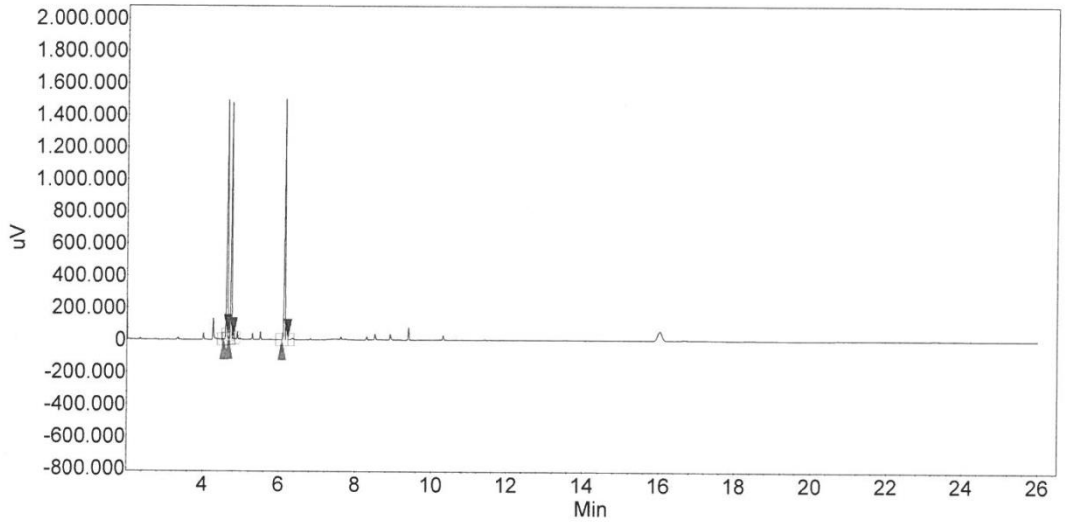
70% conv., ***Z*-7a**/***E*-7a**/**8a** = 54:0:46

^{1}H NMR of the reaction mixture in $CDCl_3$:




6.31
6.20
6.18
6.17
6.16
6.15
6.13
5.72
5.71
5.71
5.69
5.68
5.68
3.69
3.64
3.60
3.15
2.59
2.59
2.57
2.57
2.28
2.26
2.25
2.24
2.23
2.21
1.55
1.54
1.53
1.51
1.49
1.37
1.36
1.35
1.35
1.33
1.31
1.28
1.27
1.25
1.23
1.23
1.22
1.22
1.20
1.19
1.17
1.17
1.15
1.12
0.84
0.83
0.82
0.81
38.90
31.45
29.65
10
9
8
7
6
5
4
3
2
1
0
ppm

GC and GC/MS Data:



Peak results :

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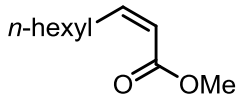
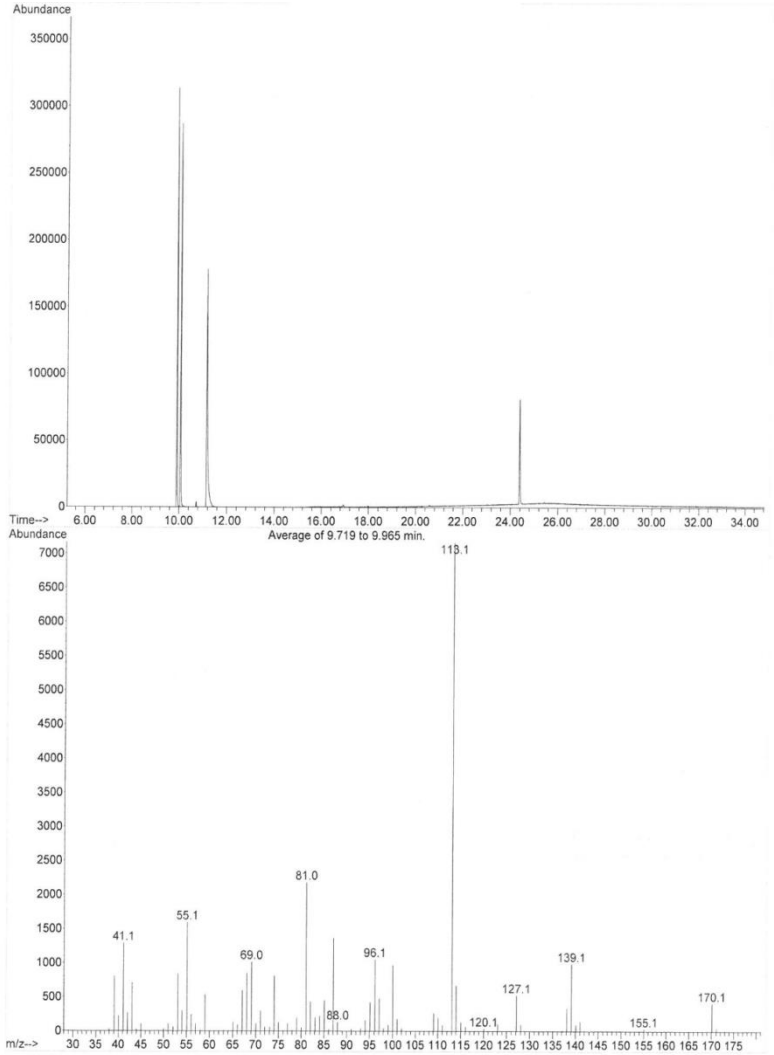
2	UNKNOWN	4,74	31,07	1469685,6	40041,7	31,068
3	UNKNOWN	6,14	32,70	1498977,5	42143,2	32,698
Total			100,00	4438120,8	128884,8	100,000


n-hexyl
O
OMe

***Z*-7a**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250000
200000
150000
100000
50000
0
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Average of 9.719 to 9.965 min.
Abundance
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
113.1
81.0
55.1
41.1
69.0
96.1
139.1
127.1
170.1
88.0
120.1
155.1
m/z-->
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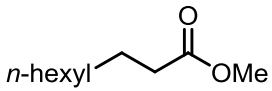
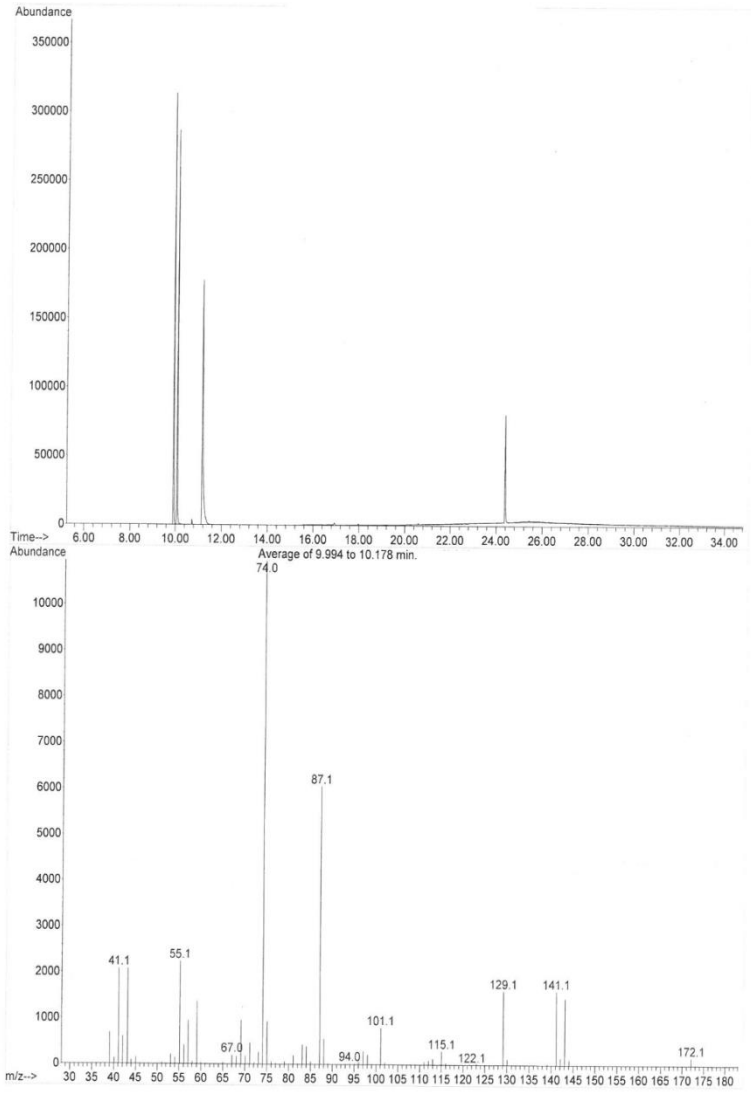

O
n-hexyl
OMe

8a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250000
200000
150000
100000
50000
0
Time-->
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Abundance
Average of 9.994 to 10.178 min.
74.0
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
87.1
41.1
55.1
67.0
94.0
101.1
115.1
122.1
129.1
141.1
172.1
m/z-->
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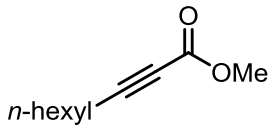
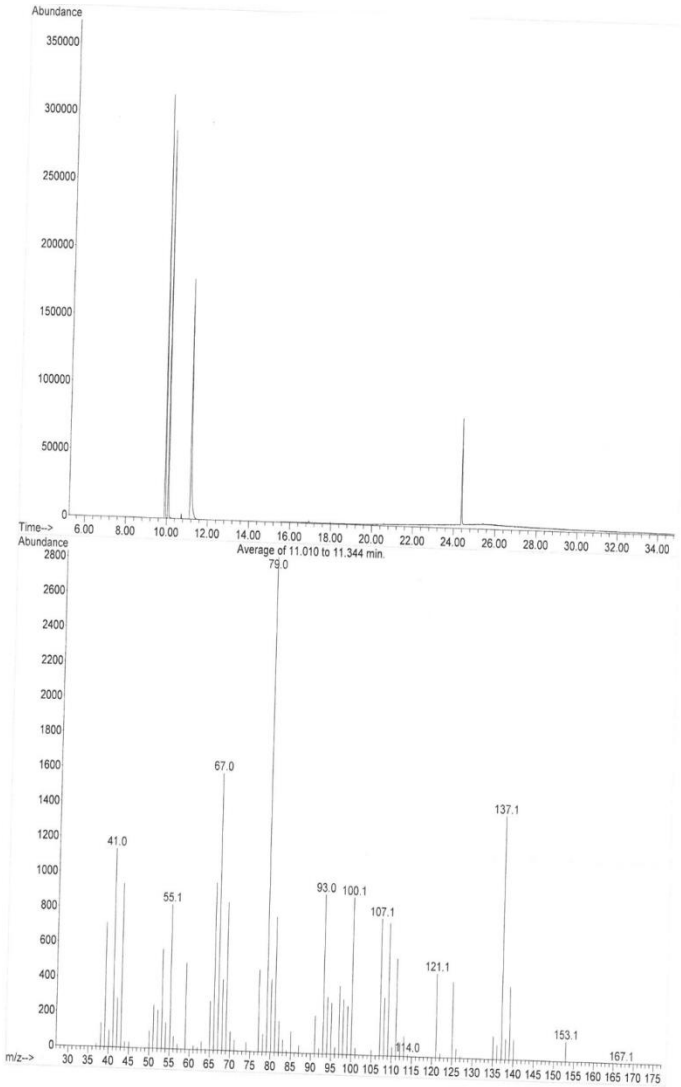

O
OMe
n-hexyl

6a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250000
200000
150000
100000
50000
0
Time-->
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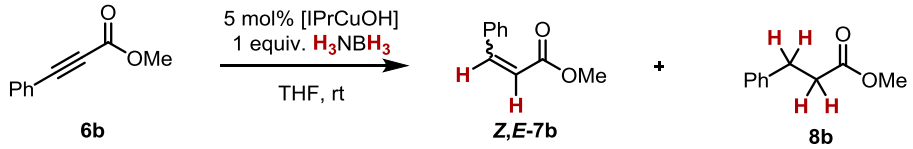
Average of 11.010 to 11.344 min.
Abundance
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
79.0
67.0
137.1
41.0
55.1
93.0
100.1
107.1
121.1
153.1
114.0
167.1
m/z-->
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175

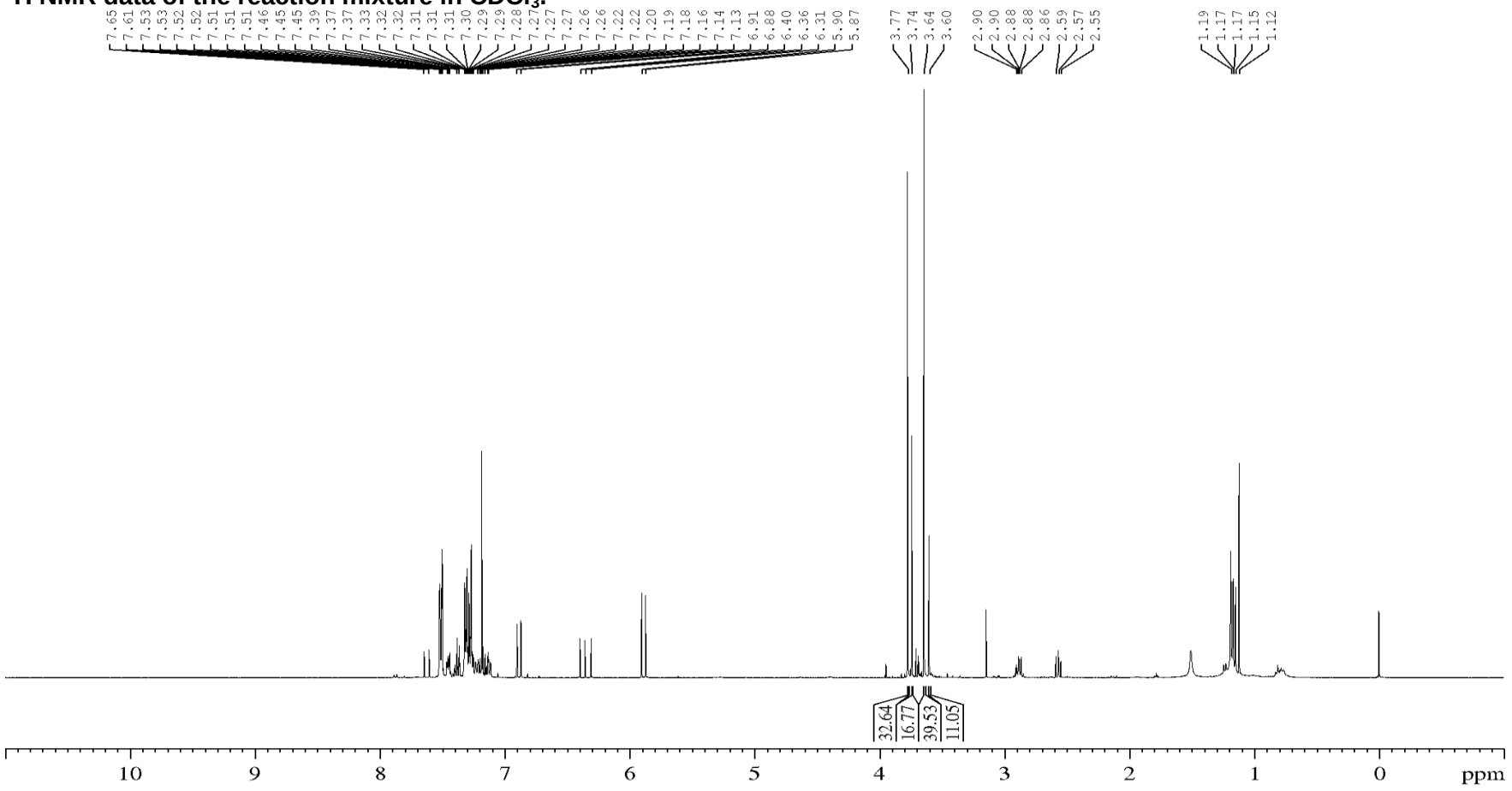
Reaction analysis of the transfer alkyne semihydrogenation of propiolates. For the reaction of **6b** as follows:

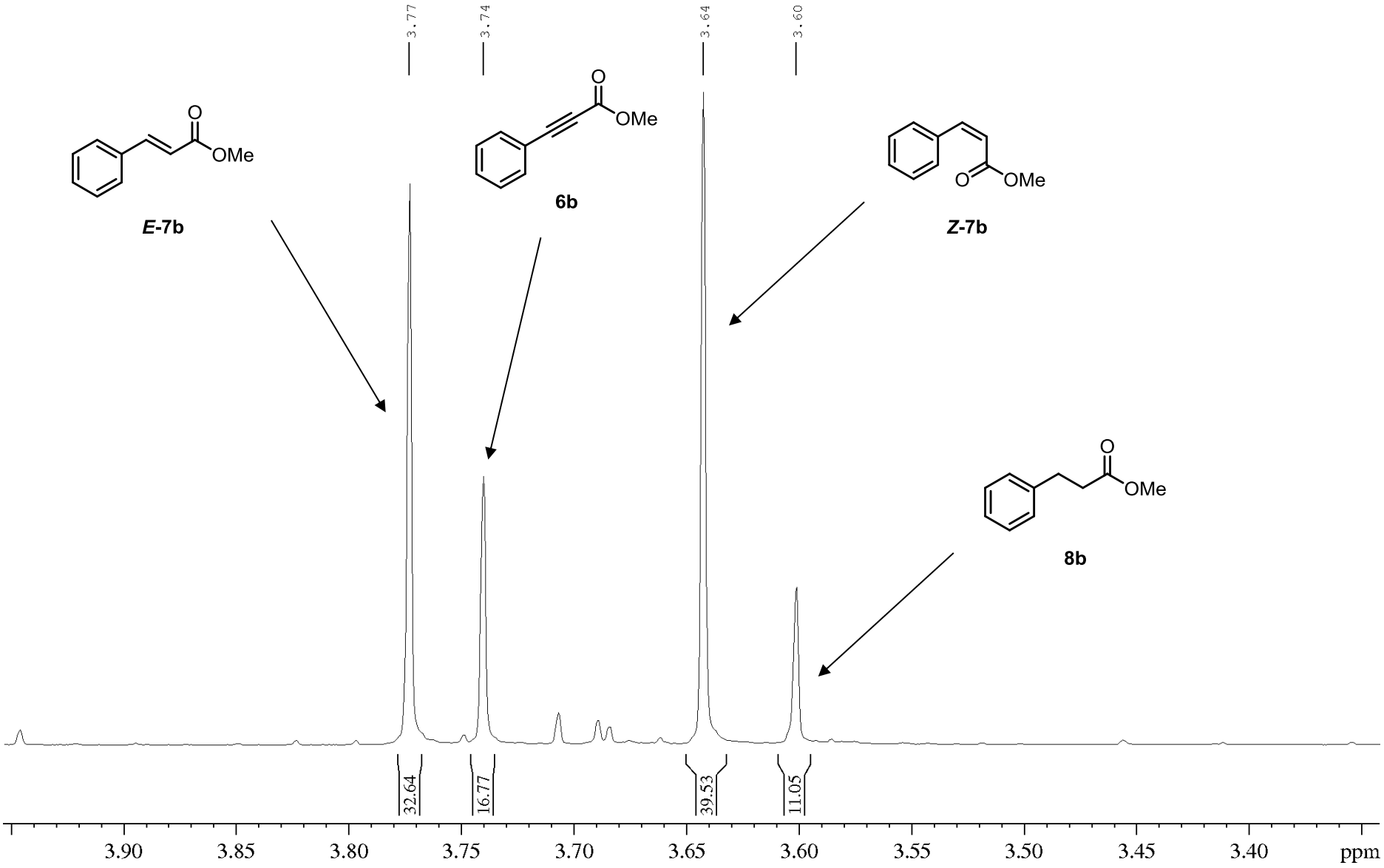


6b ***Z,E*-7b** **8b**

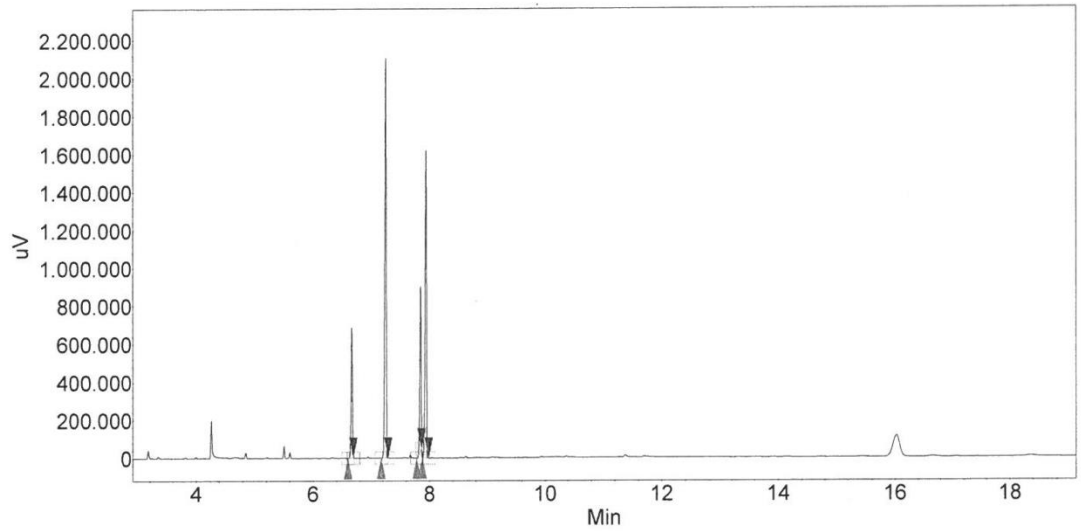
85% conv., ***Z*-7b**/***E*-7b**/**8b** = 48:37:15

^{1}H NMR data of the reaction mixture in $CDCl_3$.




3.77
3.74
3.64
3.60
O
OMe
E-7b
6b
Z-7b
8b
32.64
16.77
39.53
11.05
3.90
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
3.40
ppm

GC and GC/MS Data of the reaction mixture



Peak results :

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2	UNKNOWN	7,25	40,64	2103830,9	56179,5	40,637
3	UNKNOWN	7,85	15,50	867865,4	21425,8	15,498
4	UNKNOWN	7,94	31,16	1619649,7	43084,4	31,165
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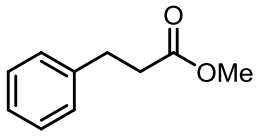
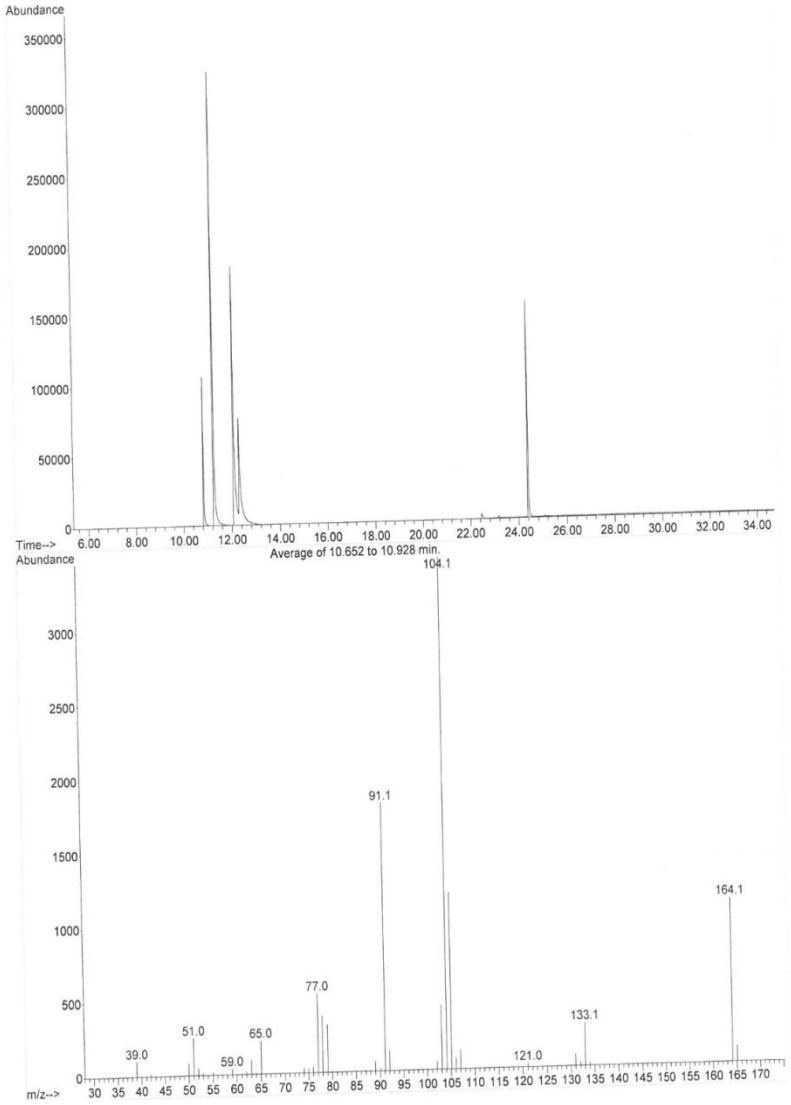

O
OMe

8b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150000
100000
50000
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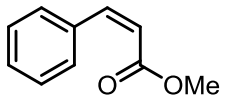
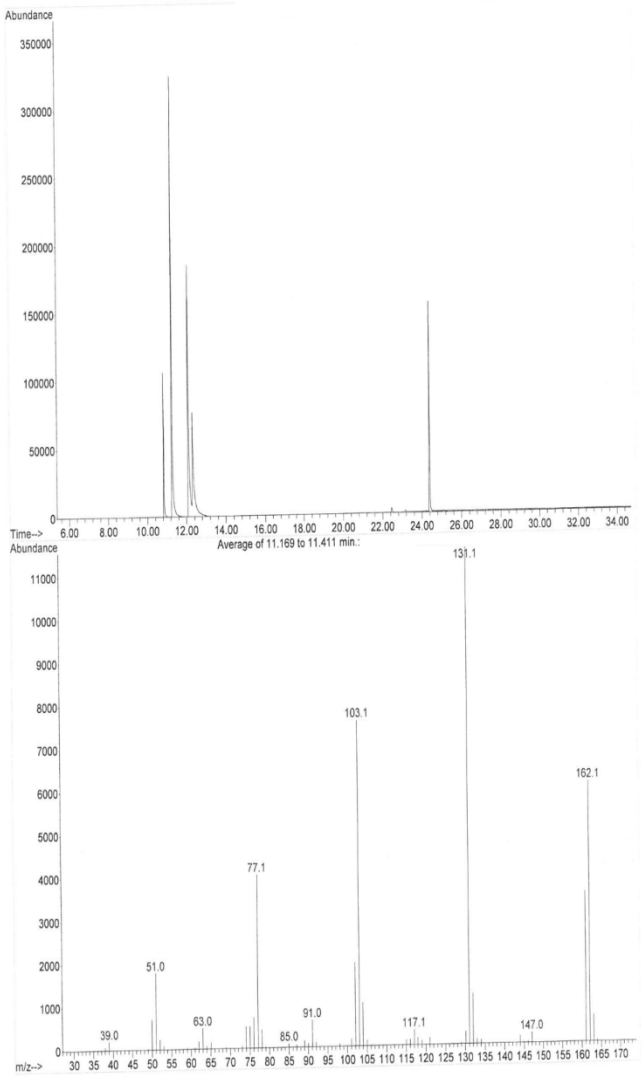
Time-->
Average of 10.652 to 10.928 min.
Abundance
104.1
3000
2500
2000
1500
1000
500
0
91.1
164.1
77.0
133.1
51.0
65.0
39.0
59.0
121.0
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170
m/z-->


O
OMe

Z-7b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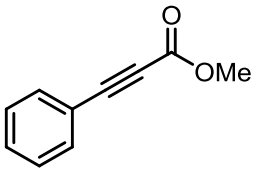
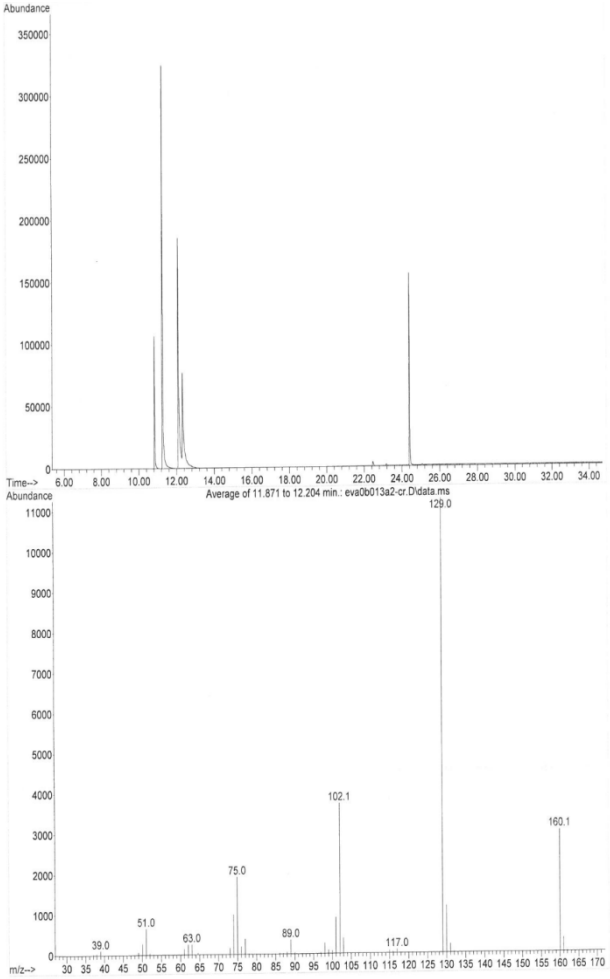
300000
250000
200000
150000
100000
50000
0
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Average of 11.169 to 11.411 min.:
Abundance
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
m/z-->
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170
131.1
103.1
162.1
77.1
51.0
91.0
63.0
39.0
85.0
117.1
147.0


O
OMe

6b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250000
200000
150000
100000
50000
0
Time-->
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Average of 11.871 to 12.204 min.: eva0b013a2-cr.D\data.ms
Abundance
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
129.0
102.1
160.1
75.0
51.0
89.0
63.0
39.0
117.0
m/z-->
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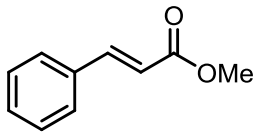
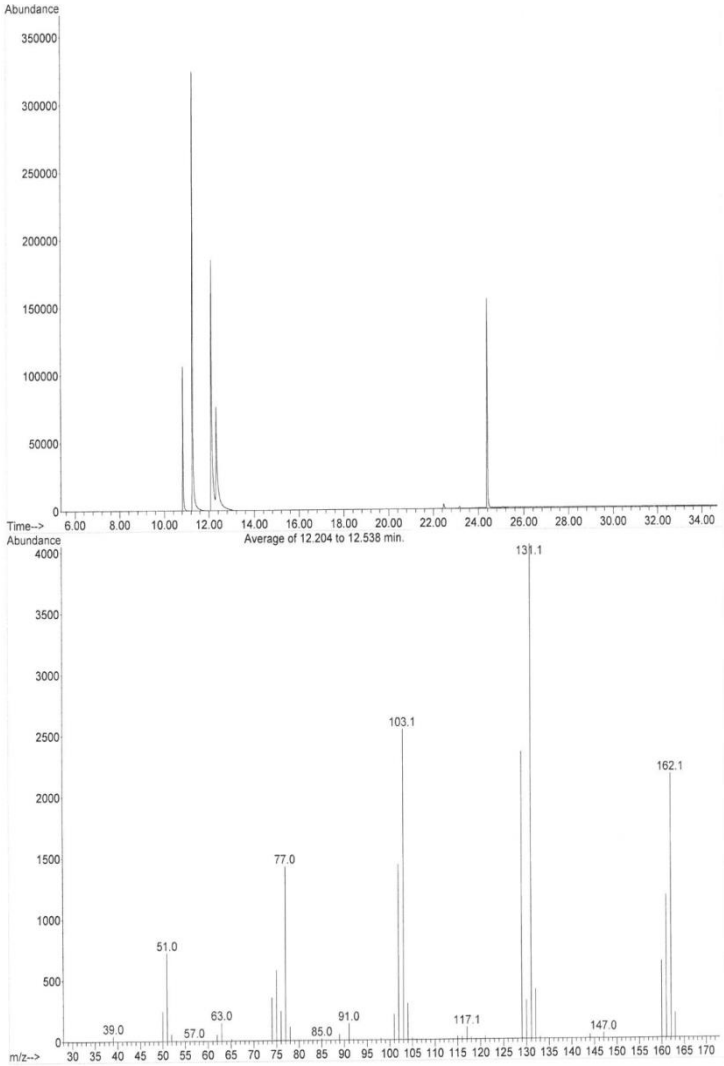

O
OMe

***E*-7b**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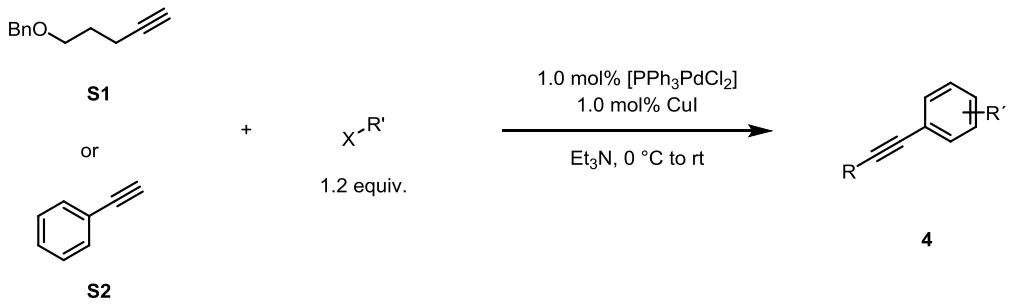
250000
200000
150000
100000
50000
0
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Average of 12.204 to 12.538 min.
Abundance
4000
3500
3000
2500
2000
1500
1000
500
0
131.1
103.1
162.1
77.0
51.0
63.0
91.0
117.1
147.0
39.0
57.0
85.0
m/z-->
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170

7 Experimental data

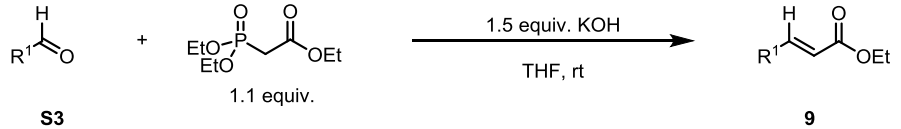
7.1 General procedures

7.1.1 General procedure for Sonogashira couplings (GP1)



According to a literature procedure[11] $[(PPh_3)_2PdCl_2]$ (1.00 mol%), CuI (1.00 mol%) and the corresponding aryl halide (1.20 equiv.) were dissolved in Et_3N (0.2 M) and cooled to 0 °C. The appropriate terminal alkyne (1.00 equiv.) was added dropwise to the stirred reaction mixture at 0 °C. After complete addition of the alkyne the mixture was allowed to warm to rt and was stirred until full conversion of the starting material was monitored by TLC or NMR analysis (for reaction times see corresponding substrates). The reaction was quenched by addition of H_2O (5 mL/mmol of alkyne) and subsequently, *tert*-butyl methyl ether (5 mL/mmol of alkyne) was added. The layers were seperated and the organic layer was washed with aq. HCl-solution (2 M, 5 mL/mmol of alkyne), brine (5 mL/mmol of alkyne) and dried over $MgSO_4$. After filtration, all volatiles were removed under reduced pressure to afford the crude product. Purification by flash column chromatography afforded the pure products.

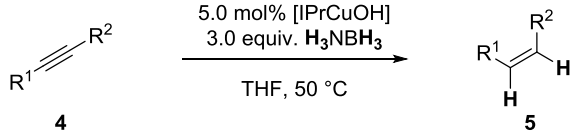
7.1.2 General procedure for *Horner-Wadsworth-Emmons* reactions (GP2)[4]



At room temperature, the corresponding aldehyde (1.00 equiv.) and KOH (1.50 equiv.) were suspended in THF (0.4M). Then, triethyl phosphonoacetate (1.10 equiv.) was added dropwise to the resulting suspension. The mixture was stirred at room temperature until full

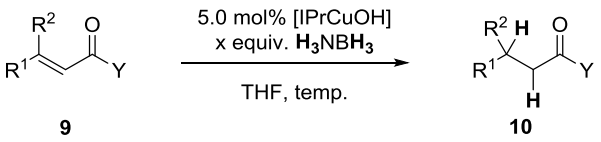
conversion of the starting material was detected (TLC monitoring). The reaction was quenched with sat. aq. NH_4Cl (3 mL/mmol). The aqueous layer was washed with EtOAc (3 mL/mmol) and the combined organic layers were washed with water (3 mL/mmol), sat. aq. $NaHCO_3$ (3 mL/mmol), dried over Na_2SO_4 and filtered. All volatiles were removed under reduced pressure. Purification by flash column chromatography afforded the pure products.

7.1.3 General procedure for copper(I)-catalyzed semihydogenation of alkynes with ammonia borane borane (GP3)



A flame-dried 25 mL Schlenk-tube was charged with [IPrCuOH] (**x**) (5.00 mol%) and was dried under reduced pressure for 5 min. The catalyst was dissolved in THF (1.0 mL) and the alkyne (1.00 equiv.) was added as a solution in THF (1.0 mL). Ammonia borane (3.00 equiv.) was dissolved in THF (5.5 mL/mmol, c = 0.18 mmol/mL) and added dropwise to the reaction mixture over 3 h with a syringe pump. The resulting mixture was stirred at 50 °C until full conversion of the starting material was detected (GC- and NMR-analysis; samples for ^1H NMR spectroscopy and GC analysis were prepared by taking an aliquot of 0.3 mL from the reaction mixture, filtration through a pad of silica (0.5 x 3 cm) and elution with *tert*-butyl methyl ether (5 mL)). After full conversion of the alkyne was detected (for reaction times see corresponding substrates), the reaction mixture was filtered over a pad of silica (2.5 x 2.5 cm) eluted with *tert*-butyl methyl ether (15 mL) and all volatiles were removed under reduced pressure. The residue was purified via flash column chromatography to give the desired alkene.

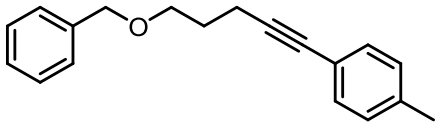
7.1.4 General procedure for copper(I)-catalyzed 1,4-reduction of α,β–unsaturated carbonyl compounds with ammonia borane (GP4)



A flame-dried 25 mL Schlenk-tube was charged with [IPrCuOH] (**84**) (5.00 mol%) and was dried under reduced pressure for 5 min. The catalyst was dissolved in THF (1.0 mL) and the corresponding substrate (1.00 equiv.) was added as a solution in THF (1.0 mL). Ammonia borane (for the amount of ammo*n*ia borane see corresponding substrates) was dissolved in THF (5.5 mL/mmol) and added dropwise to the reaction mixture over 3 h with a syringe pump. The resulting mixture was stirred at the indicated temperature until full conversion of the starting material was detected (NMR-analysis; samples for ^{1}H NMR spectroscopy were prepared by taking aliquots of 0.3 mL from the reaction mixture, filtration through a pad of silica (0.5 x 3 cm) and elution with *tert*-butyl methyl ether (5 mL). After full conversion of the α,β–unsaturated substrate (for reaction time see corresponding substrates) was reached, the reaction mixture was filtered over a pad of silica (2.5 x 2.5 cm) eluted with *tert*-butyl methyl ether (15 mL) and all volatiles were removed under reduced pressure. The residue was purified via flash column chromatography to give the desired product.

7.2 Synthesis of alkynes

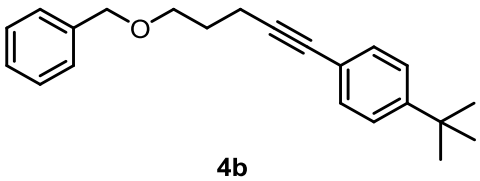
7.2.1 1-(5-(Benzyloxy)pent-1-yn-1-yl)-4-methylbenzene (4a)



4a
$C_{19}H_{20}O$
M_W = 264.37 g/mol

According to **GP1**, in a 50 mL round bottom flask $[(PPh_3)_2PdCl_2]$ (32.0 mg, 45.9 µmol, 1.00 mol%), CuI (8.70 mg, 45.9 µmol, 1.00 mol%) and 1-(methyl)-4-iodobenzene (1.40 g, 5.51 mmol, 1.20 equiv.) were dissolved in Et_3N (23 mL, 0.2M). ((Pent-4-yn-1-yloxy)methyl)benzene (**S1**) (0.80 g, 4.59 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 20 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 5.5 × 12 cm, cyclohexane/*t*BME 100:1) to obtain the desired alkyne **4a** (1.00 g, 3.78 mmol, 82%) as a colorless liquid. $\mathbf{R_f}$ = 0.75 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.80-1.85 (m, 2H), 2.25 (s, 3H), 2.45 (t, ^3J = 7.1 Hz, 2H), 3.55 (t, ^3J = 6.2 Hz, 2H), 4.46 (s, 2H), 7.00 (d, ^3J = 7.9 Hz, 2H), 7.17-7.20 (m, 3H), 7.24-7.29 (m, 4H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 16.3, 21.4, 29.0, 68.9, 73.0, 80.9, 88.7, 120.8, 127.5, 127.6, 128.4, 128.9, 131.4, 137.5, 138.5 ppm. **IR** (ATR) ν = 2922.6 (m, br), 1605.4 (w. br), 15090 (s), 1453.1 (m), 1103.6 (s, br), 815.3 (s), 734.7 (s), 696.7 (s) cm^{-1}. **HRMS (EI)** calcd. for $C_{19}H_{20}O$ [(M^+)]: 264.1509,
found: 264.1517.

7.2.2 1-(5-(Benzyloxy)pent-1-yn-1-yl)-4-(tert-butyl)benzene (4b)

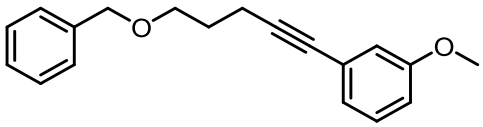


4b
$C_{22}H_{26}O$
M_W = 306.45 g/mol

According to **GP1**, in a 50 mL round bottom flask $[(PPh_3)_2PdCl_2]$ (32.0 mg, 45.9 µmol, 1.00 mol%), CuI (8.70 mg, 45.9 µmol, 1.00 mol%) and 1-(tert-butyl)-4-iodobenzene (1.43 g, 5.51 mmol, 1.20 equiv.) were dissolved in Et_3N (23 mL, 0.2M). ((Pent-4-yn-1-yloxy)methyl)benzene (**S1**) (0.80 g, 4.59 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 23 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 6 × 12 cm, cyclohexane/*t*BME 150:1) to obtain the desired alkyne **4b** (1.22 g, 4.01 mmol, 87%) as a colorless liquid. $\mathbf{R_f}$ = 0.63 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.22 (s, 9H, H-16), 1.80-1.85 (m, 2H, H-7), 2.45 (t, $^3J_{8,7}$ = 7.1 Hz, 2H, H-8), 3.55 (t, $^3J_{6,7}$ = 6.2 Hz, 2H, H-6), 4.46 (s, 2H, H-5), 7.17-7.23 (m, 5H, H-Ar), 7.24-7.29 (m, 4H, H-Ar) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 16.3 (C-8), 29.0 (C-7), 31.2 (C-16), 34.6 (C-15), 68.9 (C-6), 73.0 (C-5), 80.9 (C-10), 88.7 (C-9), 120.9 (C-11), 125.1 (C-Ar), 127.5 (C-Ar), 127.6 (C-Ar), 128.4

(C-Ar), 131.2 (C-Ar), 138.5 (C-4), 150.7 (C-14) ppm. **IR** (ATR) ν = 2956.8 (m), 2865.7 (m), 1503.7 (m), 1362.9 (m), 1106.9 (s), 1077.0 (s), 833.6 (s), 732.8 (s), 696.2 (s), 561.7 (s) cm^{-1}. **HRMS (EI)** calcd. for $C_{22}H_{26}O^+$ [(M^+)]: 306.1978, found: 306.1972.

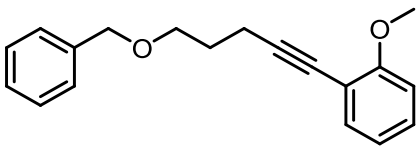
7.2.3 1-(5-(Benzyloxy)pent-1-yn-1-yl)-3-methoxybenzene (4d)



4d
$C_{19}H_{20}O_2$
M_W = 280.37 g/mol

According to **GP1**, in a 50 mL round bottom flask [$(PPh_3)_2PdCl_2$] (28.0 mg, 39.8 µmol, 1.00 mol%), CuI (7.60 mg, 39.8 µmol, 1.00 mol%) and 1-iodo-3-methoxybenzene (1.03 g, 4.42 mmol, 1.10 equiv.) were dissolved in Et_3N (20 mL, 0.2M). ((Pent-4-yn-1-yloxy)methyl)benzene (**S1**) (0.70 g, 4.02 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 20 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 6 × 10 cm, cyclohexane/*t*BME 100:1) to obtain the desired alkyne **4d** (1.07 g, 3.82 mmol, 95%) as yellow liquid. $\mathbf{R_f}$ = 0.45 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.80–1.86 (m, 2H), 2.46 (t, ^3J = 7.1 Hz, 2H), 3.55 (t, ^3J = 6.2 Hz, 2H), 3.70 (s, 3H,), 4.46 (s, 2H), 6.74-6.79 (m, 1H), 6.83 (s, 1H), 6.88-6.90 (m, 1H), 7.08-7.11 (m, 1H), 7.17-7.28 (m, 5H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 16.3, 28.9, 55.2, 68.8, 73.0, 80.8, 89.5, 114.1, 116.4, 124.1, 124.9, 127.5, 127.6, 128.4, 129.2, 138.5, 159.3 ppm. **IR** (ATR) ν = 2933.7 (m), 1595.3 (s), 1582.3 (s) 1479.1 (s), 1315.7 (m), 1285.3 (s), 1101.6 (s), 854.8 (w), 734.3 (s), 686.5 (s) cm^{-1}. **HRMS (EI)** calcd. For $C_{19}H_{20}O_2^+$ [(M^+)]:280.14578, found: 280.14502.

7.2.4 1-(5-(Benzyloxy)pent-1-yn-1-yl)-2-methoxybenzene (4e)

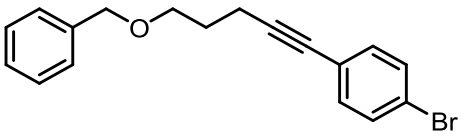


4e
$C_{19}H_{20}O_2$
M_W = 280.37 g/mol

According to **GP1**, in a 50 mL round bottom flask [$(PPh_3)_2PdCl_2$] (28.0 mg, 39.8 µmol, 1.00 mol%), CuI (7.60 mg, 39.8 µmol, 1.00 mol%) and 1-iodo-3-methoxybenzene (1.03 g, 4.42 mmol, 1.10 equiv.) were dissolved in Et_3N (20 mL, 0.2M). ((Pent-4-yn-1-yloxy)methyl)benzene (**S1**) (0.70 g, 4.02 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 20 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 6 × 10 cm, cyclohexane/*t*BME 100:1) to obtain the desired alkyne **4e** (1.10 g, 3.92 mmol, 98%) as a yellow liquid. $\mathbf{R_f}$ = 0.43

(SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.94–2.00 (m, 2H, H-7), 2.63 (t, ^3J = 7.1 Hz, 2H, H-8), 3.69 (t, ^3J = 6.2 Hz, 2H, H-6), 3.89 (s, 3H, H-15), 4.58 (s, 2H, H-5), 6.87-6.92 (m, 2H, H-Ar), 7.25-7.31 (m, 2H, H-Ar), 7.35-7.37 (m, 5H, H-1, H-2, H-3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 16.6 (C-8), 29.0 (C-7), 55.7 (C-17), 69.0 (C-6), 73.0 (C-5), 93.8 (C-9), 110.5 (C-Ar), 113.0 (C-10), 120.3 (C-Ar), 127.5 (C-Ar), 127.6 (C-Ar), 128.3 (C-Ar), 128.9 (C-Ar), 133.6 (C-Ar), 138.5 (C-4), 159.3 (C-12) ppm. The signal of C-11 was not detected. **IR** (ATR) ν = 2933.2 (w, br), 1595.3 (w), 1491.7 (m), 1259.8 (s), 1151.6 (m, br), 1024.0 (s), 749.7 (S), 697.1 (s) cm^{-1}. **HRMS (EI)** calcd. for $C_{19}H_{20}O_2^+$ [(M^+)]: 280.1458, found: 280.1456.

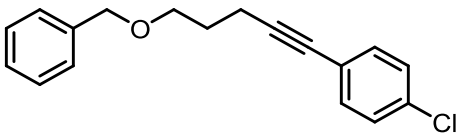
7.2.5 1-(5-(Benzyloxy)pent-1-yn-1-yl)-4-bromobenzene (4f)



4f
$C_{18}H_{17}BrO$
M_W = 329.24 g/mol

According to **GP1**, in a 100 mL round bottom flask [$(PPh_3)_2PdCl_2$] (40.0 mg, 57.0 µmol, 1.00 mol%), CuI (11.0 mg, 57.0 µmol, 1.00 mol%) and 1,4-dibromobenzene (1.60 g, 6.90 mmol, 1.20 equiv.) were dissolved in Et_3N (29 mL, 0.2M). ((Pent-4-yn-1-yloxy)methyl)benzene (**S1**) (1.00 g, 5.70 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 48 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 6 × 15 cm, cyclohexane/*t*BME 100:1) to obtain the desired alkyne **5f** (0.72 g, 2.20 mmol, 38%) as a colorless liquid. **R_f** = 0.35 (cyclohexane/*tert*-butyl methyl ether 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.91 (m_c, 2H), 2.53 (t, ^3J = 7.1 Hz, 2H), 3.62 (t, ^3J = 6.2 Hz, 2H), 4.54 (s, 2H), 7.22 (m_c, 2H), 7.27-7.30 (m, 1H), 7.33-7.37 (m, 4H), 7.41 (m_c, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 16.5, 28.9, 68.9, 73.1, 80.0, 91.1, 121.8, 123.1, 127.7, 127.8, 128.5, 131.5, 133.2, 138.6 ppm. . **IR** (ATR) ν = 2858(w), 1484 (s), 1453 (m), 1099 (s), 1069 (s), 1028 (s), 1010 (s), 822 (s), 735 (s), 697 (s), 522 (s), 457 (s) cm^{-1}. **HRMS (EI)** calcd for $C_{18}H_{17}BrO^+$ [($M)^+$]: 328.04573, found: 328.04605.

7.2.6 1-(5-(Benzyloxy)pent-1-yn-1-yl)-4-chlorobenzene (4g)

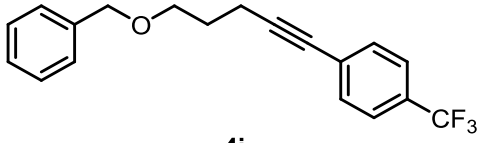


4g
$C_{18}H_{17}ClO$
M_W = 284.78 g/mol

According to **GP1**, in a 50 mL round bottom flask [$(PPh_3)_2PdCl_2$] (36.3 mg, 51.7 µmol, 1.00 mol%), CuI (9.80 mg, 51.7 µmol, 1.00 mol%) and 1-chloro-4-iodobenzene (1.48 g, 6.20 mmol, 1.20 equiv.) were dissolved in Et_3N (25 mL, 0.2M). ((Pent-4-yn-1-

yloxy)methyl)benzene (**S1**) (0.90 g, 5.17 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 20 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 6 × 15 cm, cyclohexane/*t*BME 100:1) to obtain the desired alkyne **4g** (0.80 g, 2.81 mmol, 54%) as a colorless liquid. $\mathbf{R_f}$ = 0.67 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.80-1.85 (m, 2H), 2.45 (t, $^3J_{8,7}$ = 7.1 Hz, 2H), 3.54 (t, ^3J = 6.2 Hz, 2H), 4.46 (s, 2H), 7.15-7.21 (m, 5H), 7.26-7.27 (m, 4H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 16.3, 28.8, 68.7, 73.0, 79.8, 90.7, 122.4, 127.5, 127.6, 128.4, 128.5, 132.8, 133.5, 138.5 ppm. **IR** (ATR) ν = 2856 (w), 1489 (s), 1453 (m), 1089 (s), 1027 (m), 1014 (s), 827 (s), 733 (s), 696 (s), 521 (s), 472 (m) cm^{-1}. **HRMS (APCI)** calcd. for $C_{18}H_{18}ClO^+$ [$(M+H^+)$]: 285.1041, found: 285.1035.

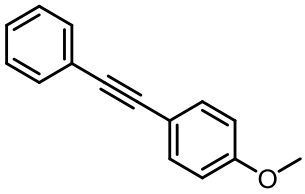
7.2.7 1-(5-(Benzyloxy)pent-1-yn-1-yl)-4-(trifluoromethyl)benzene (4j)



4j
$C_{19}H_{17}F_3O$
M_W = 318.34 g/mol

According to **GP1**, in a 100 mL round bottom flask $[(PPh_3)_2PdCl_2]$ (97.0 mg, 140 µmol, 1.00 mol%), CuI (26.0 mg, 140 µmol, 1.00 mol%) and 4-bromobenzotrifluoride (1.60 g, 8.27 mmol, 1.20 equiv.) were dissolved in Et_3N (35 mL, 0.2M). ((Pent-4-yn-1-yloxy)methyl)benzene (**S1**) (1.20 g, 6.90 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 48 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 6 × 15 cm, cyclohexane/*t*BME 100:1) to obtain the desired alkyne **4j** (0.72 g, 2.20 mmol, 38%) as a colorless liquid. $\mathbf{R_f}$ = 0.38 (cyclohexane/*tert*-butyl methyl ether 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.93 (m_c, 2H), 2.57 (t, ^3J = 7.1 Hz, 2H), 3.64 (t, ^3J = 6.1 Hz, 2H), 4.55 (s, 2H), 7.27-7.31 (m, 1H), 7.33-7.38 (m, 4H), 7.45-7.46 (m, 2H), 7.53-7.54 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 16.5, 28.9, 68.8, 73.1, 79.9, 92.6, 124.2 (q, ^1J = 272 Hz), 125.2 (q, ^3J = 4.0 Hz), 127.7, 127.8, 127.9, 128.5, 129.5 (q, ^2J = 32.5 Hz), 131.9, 138.6 ppm. **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -62.7 ppm. **IR** (ATR) ν = 2858 (w), 1615 (m), 1321 (s), 1164 (s), 1121 (s), 1104 (s), 1066 (s), 1017 (m), 841 (s), 735 (m), 697 (s), 598 (m) cm^{-1}. **HRMS (EI)** calcd for $C_{19}H_{17}FO^+$ [$(M)^+$]: 318.12260, found: 318.12293.

7.2.8 1-Methoxy-4-(phenylethynyl)benzene (4m)

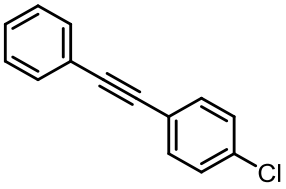


4m
$C_{15}H_{12}O$
M_W = 208.26 g/mol

According to **GP1**, in a 100 mL round bottom flask $[(PPh_3)_2PdCl_2]$ (69.0 mg, 98.0 µmol, 1.00 mol%), CuI (18.7 mg, 98.0 µmol, 1.00 mol%) and 1-iodo-4-methoxybenzene (2.50 g, 10.8 mmol, 1.10 equiv.) were dissolved in Et_3N (50 mL, 0.2M). Ethynylbenzene (**S2**) (1.00 g, 9.80 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 24 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 6 × 15 cm, cyclohexane/*t*BME 100:1) to obtain the desired alkyne **4m** (2.03 g, 9.80 mmol, 99%) as a beige solid. $\mathbf{R_f}$ = 0.54 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.89 (m_c, 2H), 7.30-7.36 (m, 3H), 7.48 (m_c, 2H), 7.52-7.53 (m, 2H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 55.3, 88.1, 89.4, 114.0, 115.4, 123.6, 127.9, 128.3, 131.4, 133.0, 159.6 ppm. **HRMS (EI)** calcd.for $C_{15}H_{12}O^+$ [(M^+)]: 208.0883, found: 208.0883.

The spectroscopic data is in accordance with the literature.[12]

7.2.9 1-Chloro-4-(phenylethynyl)benzene (4n)

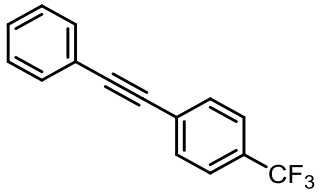


4n
$C_{14}H_9Cl$
M_W = 212.68 g/mol

According to **GP1**, in a 50 mL round bottom flask $[(PPh_3)_2PdCl_2]$ (28.0 mg, 40.0 µmol, 1.00 mol%), CuI (7.60 mg, 40.0 µmol, 1.00 mol%) and 1-chloro-4-iodobenzene (0.96 g, 4.80 mmol, 1.20 equiv.) were dissolved in Et_3N (15 mL, 0.2M). Ethynylbenzene (**S2**) (0.41 g, 4.00 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 24 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, pentane) to obtain the desired alkyne **4n** (0.64 g, 3.00 mmol, 75%) as white solid. $\mathbf{R_f}$ = 0.55 (SiO_2, cyclohexane). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.32-7.38 (m, 5H), 7.45-7.47 (m_c, 2H), 7.51-7.55 (m, 2H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 88.4, 90.5, 121.9, 123.1, 128.5, 128.5, 128.6, 128.8, 131.7, 133.0, 134.4 ppm. **HRMS (EI)** calcd. for $C_{14}H_9Cl^+$ [(M^+)]: 212.0387, found: 212.0393.

The spectroscopic data is in accordance with the literature.[13]

7.2.10 1-(Phenylethynyl)-4-(trifluoromethyl)benzene (4o)

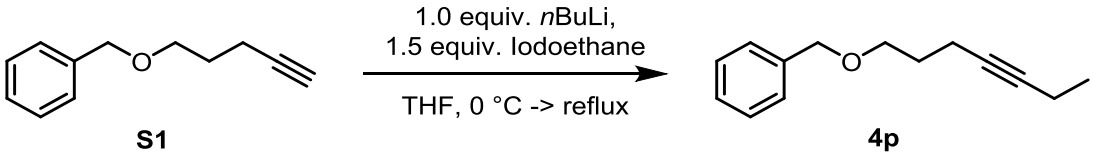


4o
$C_{15}H_9F_3$
M_W = 246.23 g/mol

According to **GP1**, in a 100 mL round bottom flask $[(PPh_3)_2PdCl_2]$ (69.0 mg, 98.0 µmol, 1.00 mol%), CuI (18.7 mg, 98.0 µmol, 1.00 mol%) and 1-iodo-4-(trifluoromethyl)benzene (2.90 g, 10.8 mmol, 1.10 equiv.) were dissolved in Et_3N (50 mL, 0.2M). Ethynylbenzene (**S2**) (1.00 g, 9.80 mmol, 1.00 equiv.) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred for 48 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 5.5 × 15 cm, cyclohexane/*t*BME 150:1) to obtain the desired alkyne **4o** (2.05 g, 8.33 mmol, 85%) as a beige solid. $\mathbf{R_f}$ = 0.85 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.37-7.38 (m, 3H), 7.54-7.57 (m, 2H), 7.62 (m_c, 4H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 88.0, 91.8, 122.6, 125.3 (q, ^3J = 3.5 Hz), 126.2 (q, ^1J = 273.0 Hz), 128.4, 128.8, 129.9 (q, ^2J = 32.6 Hz), 131.7, 131.8, 132.5 ppm. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -62.8 ppm. **HRMS (EI)** calcd. for $C_{15}H_9F_3^+$ [(M^+)]: 246.0651, found: 246.0657.

The spectroscopicspectroscopic data is in agreement with the literature.[12]

7.2.11 ((Hept-4-yn-1-yloxy)methyl)benzene (4p)



S1

4p
$C_{14}H_{18}O$
Mw = 202.30 g/mol

A solution of **S1** (0.70 g, 4.0 mmol, 1.0 equiv.) in THF (13 mL) was cooled to 0 °C. *n*BuLi-solution (2.5M in hexane, 1.6 mL, 4.0 mmol, 1.0 equiv.) was added dropwise. After 20 min the mixture was allowed to warm to rt. Then Iodoethane was added and the mixture was heated to reflux for 22 h. After cooling down to rt the reaction was quenched by the addition of H_2O (30 mL). The layers were separated und the aqueous layer was extracted with *t*BME (3 x 10 mL) and the combined organic layers were washed with brine (30 mL) and dried over Na_2SO_4. After filtration and concentration under reduced pressure the crude product was purified by flash column chromatography on silica gel using cyclohexane as eluent to yield **4p** (0.69 g, 3.4 mmol, 85%) as a slightly yellow solid. $\mathbf{R_f}$ = 0.31 (cyclohexane). **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = 6.43 (d, ^3J = 16.2 Hz, 1H), 7.07 (d, ^3J = 16.2 Hz, 1H), 7.30-7.38 (m,

6H), 7.44-7.51 (m, 4H) ppm. **^{13}C NMR** (126 MHz, CD_2Cl_2): δ = 89.2, 92.0, 108.4, 123.8, 126.7, 128.7, 128.8, 129.1, 129.2, 131.9, 136.7, 141.7 ppm. **HRMS (EI)** calcd for $C_{16}H_{12}^+$ [$(M)^+$]: 204.09390, found: 204.09302.
The data is in accordance with the literature.[2]

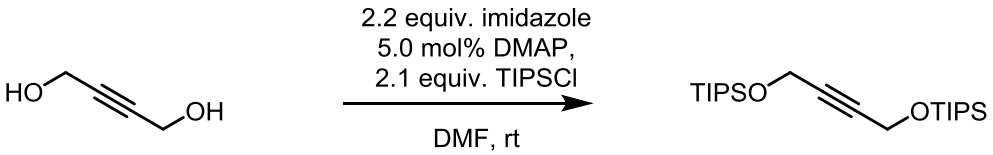
7.2.12 ((6-(Benzyloxy)hex-2-yn-1-yl)oxy)triisopropylsilane (4r)

S4

4r
$C_{22}H_{36}O_2Si$
Mw = 360.61 g/mol

In a flame-dried 25 mL Schlenk flask imidazole (0.32 g, 4.70 mmol, 1.20 equiv.), dimethylaminopyridine (DMAP, 29.0 mg, 0.24 mmol, 5.00 mol%), and propargylic alcohol **S4** (0.80 g, 3.92 mmol, 1.00 equiv.) were dissolved in DMF (8 mL) and stirred for 20 min at rt. After the reaction mixture became homogeneous, triisopropylsilylchloride (0.76 g, 3.92 mmol, 1.00 equiv.) was added dropwise and the solution was stirred for 24 h at rt. The reaction mixture was quenched by additon of water (30 mL), and was extracted with *t*BME (3 x 30 mL). The combined organic layers were washed with brine (3 x 30 mL) and dried over Na_2SO_4. The afforded crude product was purified via flash column chromatography (SiO_2, 5 × 15 cm, cyclohexane/*t*BME 50:1) to obtain the desired alkyne **4r** (1.00 g, 2.77 mmol, 59%) as a colorless liquid. $\mathbf{R_f}$ = 0.79 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.08-1.09 (m, 18H), 1.10-1.17 (m, 3H), 1.78-1.84 (m, 2H), 2.32-2.35 (m, 2H), 3.56 (t, ^3J = 6.2 Hz, 2H), 4.35 (t, ^5J = 2.1 Hz, 2H), 4.51 (s, 2H), 7.26-7.36 (m, 5H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 12.03, 15.7, 17.9, 28.8, 52.1, 68.9, 72.9, 79.1, 84.4, 127.5, 127.6, 128.3, 138.4 ppm. **^{29}Si-DEPT** (99 MHz, *J* = 20 Hz $CDCl_3$): δ = 16.0 ppm. **IR** (ATR) ν = 2942 (s), 2864 (s), 1454 (m), 1364 (m), 1141 (s), 1082 (s), 1065 (s), 882 (s), 733 (s), 680 (s), 659 (m) cm^{-1}. **HRMS (APCI)** calcd. for $C_{22}H_{35}O_2Si^+$ [$(M-H^+)$]: 359.2401, found: 359.2410.

7.2.13 3,3,10,10-Tetraisopropyl-2,11-dimethyl-4,9-dioxa-3,10-disiladodec-6-yne (4s)



S5

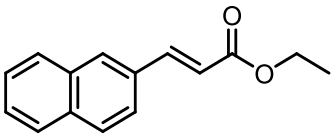
4s
$C_{22}H_{46}O_2Si_2$
Mw = 398.78 g/mol

In a flame-dried 25 mL Schlenk flask imidazole (60.4 mg, 8.84 mmol, 2.2 equiv.), dimethylaminopyridine (DMAP, 25.0 mg, 0.20 mmol, 5.00 mol%), and but-2-yne-1,4-diol (**S5**)

(0.35 g, 4.02 mmol, 1.00 equiv.) were dissolved in DMF (8 mL) and stirred for 20 min at rt. After the reaction mixture became homogeneous, triisopropylsilylchloride (1.63 g, 8.44 mmol, 2.10 equiv.) was added dropwise and the solution was stirred for 24 h at rt. The reaction mixture was quenched by additon of water (5 mL), and was extracted with *t*BME (3 x 5 mL). The combined organic layers were washed with brine (3 x 5 mL) and dried over Na_2SO_4. The afforded crude product was purified via flash column chromatography (SiO_2, 15 × 5 cm, cyclohexane/*t*BME 70:1) to obtain the desired alkyne **4s** (1.55 g, 3.89 mmol, 97%) as a colorless liquid. $\mathbf{R_f}$ = 0.56 (SiO_2, cyclohexane/*t*BME 50:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.05-1.08 (m, 36H), 1.12-1.22 (m, 6H), 4.41 (s, 4H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 12.0, 17.9, 52.0, 83.2 ppm. **^{29}Si-DEPT** (99 MHz, *J* = 20 Hz $CDCl_3$): δ = 16.3 ppm. **IR** (ATR) ν = 2942.8 (s), 2866.2 (s), 1463.2 (s), 1367.8 (m), 1260.3 (m), 1135.9 (s), 1061.1 (s), 881.3 (s), 681.2 (s), 684.6 (m) cm^{-1}. **HRMS (APCI)** calcd. for $C_{22}H_{47}O_2Si_2^+$ [$(M+H^+)$]: 399.3115, found: 399.3108.

7.3 Synthesis of α,β-unsaturated esters

7.3.1 Ethyl (*E*)-3-(naphthalen-2-yl)acrylate (9b)

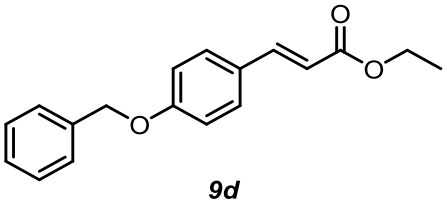


9b
$C_{15}H_{14}O_2$
M_W = 226.28 g/mol

According to **GP3**, in a 250 mL round bottom flask 2-naphthaldehyde (4.00 g, 25.6 mmol, 1.00 equiv.) and KOH (2.15 g, 38.4 mmol, 1.50 equiv.) were suspended in THF (60 mL) at rt. Then, triethyl phosphonoacetate (5.59 mL, 28.2 mmol, 1.10 equiv.) was added dropwise to the suspension. The mixture was stirred for 48 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 6 × 15 cm, cyclohexane/*t*BME = 20:1) to obtain the desired α,β-unsaturated ester **9b** (4.85 g, 21.4 mmol, 84%) as a white solid. $\mathbf{R_f}$ = 0.36 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.38 (t, ^3J = 7.1 Hz, 3H), 4.32 (q, ^3J= 7.1 Hz, 2H), 6.53 (d, ^3J = 15.8 Hz, 1H), 7.47-7.60 (m, 3H), 7.76 (m_c, 1H), 7.89 (m_c, 2H), 8.21 (m_c, 1H), 8.54 (d, ^3J = 15.8 Hz, 1H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.3, 60.6, 120.9, 123.4, 125.0, 125.4, 126.2, 126.8, 128.7, 130.4, 131.4, 131.8, 133.6, 141.6, 166.9 ppm. **HRMS (EI)** calcd. for $C_{15}H_{14}O_2^+$ [(M^+)]: 226.0988, found: 226.0993.

The spectroscopic data is in accordance with the literature.[14]

7.3.2 Ethyl (*E*)-3-(4-(benzyloxy)phenyl)acrylate (9d)



9d

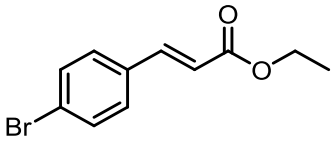
$C_{18}H_{18}O_3$

M_W = 282.34 g/mol

According to **GP3**, in a 25 mL round bottom flask 4-benzyloxybenzaldehyde **S6** (0.30 g, 1.41 mmol, 1.00 equiv.) and KOH (0.12 g, 2.12 mmol, 1.50 equiv.) were suspended in THF (5 mL) at room temperature. Then, triethyl phosphonoacetate (0.31 mL, 1.56 mmol, 1.10 equiv.) was added dropwise to the suspension. The mixture was stirred for 24 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 3.5 × 13 cm, cyclohexane/*t*BME = 20:1) to obtain the desired α,β-unsaturated ester **9d** (0.40 g, 1.40 mmol, 99%) as a white solid. $\mathbf{R_f}$ = 0.46 (SiO_2, cyclohexane/*t*BME 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.33 (t, ^3J = 7.1 Hz, 3H), 4.26 (q, ^3J = 7.1 Hz, 2H), 5.10 (s, 2H), 6.31 (d, ^3J = 15.8 Hz, 1H), 6.98 (m_c, 2H), 7.34-7.44 (m, 5H), 7.48 (m_c, 2H), 7.64 (d, ^3J = 15.8 Hz, 1H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.3, 60.3, 70.1, 115.2, 115.9, 127.4, 128.1, 128.6, 129.7, 136.5, 144.2, 160.5, 167.3 ppm. C-6 was not detected. **HRMS (EI)** calcd. for $C_{18}H_{18}O_3^+$ [(M^+)]: 282.1251, found: 282.1253.

The spectroscopic data is in accordance with the literature.[15]

7.3.3 Ethyl (*E*)-3-(4-bromophenyl)acrylate (9h)



9h

$C_{11}H_{11}BrO_2$

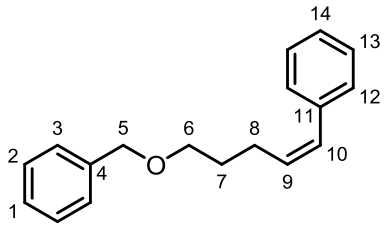
M_W = 255.11 g/mol

According to **GP3**, in a 25 mL round bottom flask 4-bromobenzaldehyde (0.60 g, 3.24 mmol, 1.00 equiv.) and KOH (0.27 g, 4.86 mmol, 1.50 equiv.) were suspended in THF (9 mL) at rt. Then, triethyl phosphonoacetate (0.71 mL, 3.57 mmol, 1.10 equiv.) was added dropwise to the suspension. The mixture was stirred for 20 h at rt. The afforded crude product was purified via flash column chromatography (SiO_2, 3.5 × 13 cm, cyclohexane/*t*BME = 20:1) to obtain the desired α,β-unsaturated ester **9h** (0.60 g, 2.35 mmol, 73%) as a white solid. $\mathbf{R_f}$ = 0.75 (SiO_2, cyclohexane/*t*BME 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.33 (t, ^3J = 7.1 Hz, 3H), 4.26 (q, $^3J_{2,1}$ = 7.1 Hz, 2H), 6.41 (d, ^3J = 16.0 Hz, 1H), 7.38 (m_c, 2H), 7.51 (m_c, 2H), 7.60 (d, ^3J = 16.0 Hz, 1H) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.3, 60.6, 119.0, 124.4, 129.4, 132.1, 133.4, 143.1, 166.7 ppm. **HRMS (EI)** calcd. for $C_{11}H_{11}BrO_2^+$ [(M^+)]: calculated: 253.9937, found: 253.9931.

The spectroscopic data is in accordance with the literature.[16]

7.4 Alkyne semihydrogenation

7.4.1 (*Z*)-(5-(Benzyloxy)pent-1-en-1-yl)benzene (2)



2

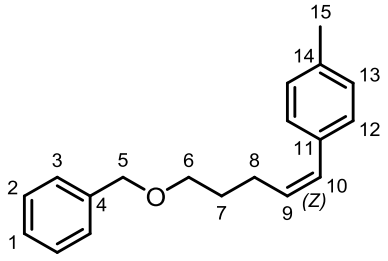
$C_{18}H_{20}O$

M_W = 252.36 g/mol

Prepared from **1** (96.0 mg, 0.38 mmol, 1.00 equiv.), [IPrCuOH] (9.80 mg, 19.2 µmol, 5.00 mol%) and a solution of ammonia borane (38.5 mg, 1.15 mmol, 3.00 equiv.) in THF (8 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 11 cm, cyclohexane/*t*BME = 50:1) afforded **2** (93.0 mg, 0.37 mmol, 96%) as a colorless oil. $\mathbf{R_f}$ = 0.65 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.67-73 (m, 2H, H-7), 2.37 (m_c, 2H, H-8), 3.42 (t, $^3J_{6,7}$ = 6.5 Hz, 2H, H-6), 4.40 (s, 2H, H-5), 5.58 (dt, $^3J_{9,10}$ = 11.7 Hz, $^3J_{9,8}$ = 7.4 Hz, 1H, H-9), 6.36 (d, $^3J_{10,9}$ = 11.7 Hz, 1H, H-10), 7.12-7.17 (m, 1H, H-14), 7.18-7.26 (m, 9H, H-Ar) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 25.4 (C-7), 30.0 (C-8), 69.7 (C-6), 72.9 (C-5), 126.5 (C-14), 127.5 (C-1), 127.6 (C-3), 128.1 (C-13)*, 128.3 (C- 2)*, 128.7 (C-12), 129.3 (C-10), 132.3 (C-9), 137.6 (C-11), 138.6 (C-4) ppm. **HRMS (APCI)** calcd. for $C_{18}H_{21}O^+$ [(M+H$^+$)]: 253.1587, found: 253.1589.

The spectroscopic data is in agreement with literature.[11]

7.4.2 (*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-methylbenzene (5a)



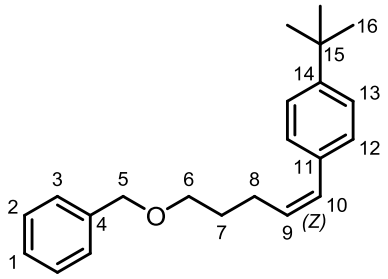
$C_{19}H_{22}O$

M_W = 266.38 g/mol

Prepared from **4a** (94.0 mg, 0.38 mmol, 1.00 equiv.), [IPrCuOH] (8.90 mg, 18.9 µmol, 5.00 mol%) and a solution of ammonia borane (35.0 mg, 1.14 mmol, 3.00 equiv.) in THF (6 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 13 cm, cyclohexane/*t*BME = 100:1) afforded **5a** (60.0 mg, 0.23 mmol, 63%) as a colorless oil. $\mathbf{R_f}$ = 0.75 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.79 (m_c, 2H, H-7), 2.35 (s, 3H, H-15), 2.45 (m_c, 2H, H-8),

3.51 (t, $^{3}J_{6,7}$ = 6.2 Hz, 2H, H-6), 4.48 (s, 2H, H-5), 5.62 (dt, $^{3}J_{9,10}$ = 11.7 Hz, $^{3}J_{9,8}$ = 7.6 Hz, 1H, H-9), 6.41 (d, $^{3}J_{10,9}$ = 11.7 Hz, 1H, H-10), 7.13 (m_c, 2H, H-13), 7.20 (m_c, 2H, H-12), 7.28-7.35 (m, 5H, H-1, H-2, H-3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 31.1. (C-15), 25.3 (C-8), 30.0 (C-7), 69.8 (C-6), 72.9 (C-5), 127.4 (C-1), 127.6 (C-3), 128.3 (C-3), 128.7 (C-12), 128.8 (C-13), 129.2 (C-10), 131.5 (C-9), 134.7 (C-11), 136.2 (C-14), 138.6 (C-4) ppm. **IR** (ATR) ν = 2921.1 (w), 1511.9 (m), 1453.1 (m), 1102.1 (s, br), 1027.9 (m), 823.5 (m, br), 732.8 (s), 696.2 (s), 606.0 (w, br) cm^{-1}. **HRMS (EI)** calcd. for $C_{19}H_{22}O^{+}$ [(M^{+})]: 266.1671, found: 266.1671.

7.4.3 (*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-(tert-butyl)benzene (5b)



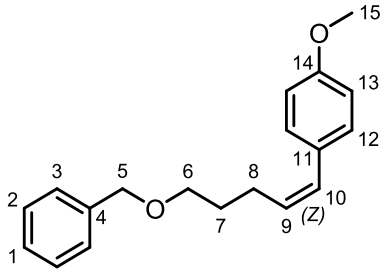
5b

$C_{22}H_{28}O$

M_W = 308.47 g/mol

Prepared from **4b** (94.0 mg, 0.31 mmol, 1.00 equiv.), [IPrCuOH] (7.70 mg, 16.4 µmol, 5.00 mol%) and a solution of ammonia borane (30.4 mg, 0.94 mmol, 3.00 equiv.) in THF (6 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 11 cm, cyclohexane/*t*BME = 100:1) afforded **5b** (50.0 mg, 0.16 mmol, 51%) as a colorless oil. $\mathbf{R_f}$ = 0.73 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ = 1.33 (s, 9H, H-16), 1.80 (m_c, 2H, H-7), 2.47 (m_c, 2H, H-8), 3.52 (t, $^{3}J_{6,7}$ = 6.2 Hz, 2H, H-6), 4.49 (s, 2H, H-5), 5.63 (dt, $^{3}J_{9,10}$ = 11.6 Hz, $^{3}J_{9,8}$ = 7.4 Hz, 1H, H-9), 6.40 (d, $^{3}J_{10,9}$ = 11.6 Hz, 1H, H-10), 7.25 (m_c, 2H, H-12), 7.26-7.35 (m, 7H, H-Ar) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ/ppm = 25.4 (C-8), 30.0 (C-7), 31.3 (C-16), 34.5 (C-15), 69.8 (C-6), 72.9 (C-5), 125.0 (C-Ar), 127.5 (C-3), 127.6 (C-Ar), 128.3 (C-Ar), 128.5 (C-12), 129.1 (C-10), 131.6 (C-9), 134.7 (C-11), 138.6 (C-4), 147.4 (C-14) ppm. **IR** (ATR) ν = 2960.7 (m), 1453.1 (m), 1362.0 (m), 1106.9 (s, br), 840.3 (s), 732.3 (s), 696.2 (s), 560.2 (m) cm^{-1}. **HRMS (APCI)** calcd. for $C_{22}H_{29}O^{+}$ [($M+H^{+}$)]: 309.2218, found: 309.2217.

7.4.4 (*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-methoxybenzene (5c)



5c

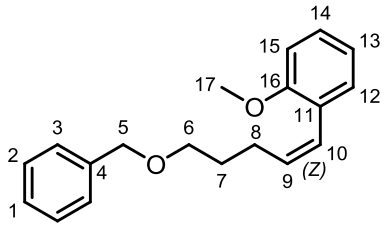
$C_{19}H_{22}O_2$

M_W = 282.16 g/mol

Prepared from **4c** (72.0 mg, 0.26 mmol, 1.00 equiv.), [IPrCuOH] (6.70 mg, 14.2 mmol, 5.00 mol%) and a solution of ammonia borane (26.0 mg, 0.86 mmol, 3.00 equiv.) in THF (6 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 19 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 100:1) afforded **5c** (49.0 mg, 0.18 mmol, 69%) as a colorless oil. $\mathbf{R_f}$ = 0.59 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.69 (m_c, 2H, H-7), 2.35 (m_c, 2H, H-8), 3.42 (t, $^3J_{6,7}$ = 6.4 Hz, 2H, H-6), 3.70 (s, 3H, H-15), 4.39 (s, 2H, H-5), 5.48 (dt, $^3J_{9,10}$ = 11.7 Hz, $^3J_{9,8}$ = 7.3 Hz, 1H, H-9), 6.28 (m_c, 1H, H-10), 6.76 (m_c, 2H, H-13), 7.14 (m_c, 2H, H-12), 7.18-7.25 (m, 5H, H-1, H-2, H-3) ppm. The ^{1}H NMR spectrum contains the *E*-isomer (5%). The ratio can be deduced from the ratio of the H-9 resonances (at 5.48 (for (*Z*)-**x**) and 5.98 (for (*E*)-**x**) ppm). **^{13}C-NMR** (126 MHz, $CDCl_3$): δ/ppm = 25.2 (C-8), 30.0 (C-7), 55.2 (C-15), 69.7 (C-6), 72.8 (C-5), 113.5 (C-13), 127.4 (C-1), 127.5 (C-2)*, 128.3 (C-3)*, 128.7 (C-10), 129.9 (C-12), 130.3 (C-4), 130.6 (C-9), 138.6 (C-4), 158.2 (C-14) ppm. **HRMS (EI)** calcd. for $C_{19}H_{22}O^+$ [(M^+)]: 282.1614, found: 282.1610.

The spectroscopic data is in agreement with literature.[11]

7.4.5 (*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-2-methoxybenzene (5e)



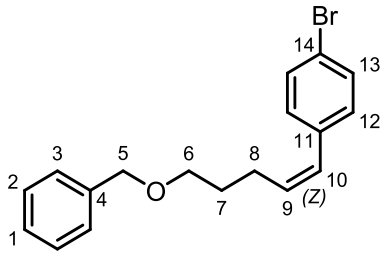
$C_{19}H_{22}O_2$

M_W = 282.16 g/mol

Prepared from **4e** (0.10 g, 0.36 mmol, 1.00 equiv.), [IPrCuOH] (8.40 mg, 17.9 mmol, 5.00 mol%) and a solution of ammonia borane (33.0 mg, 1.07 mmol, 3.00 equiv.) in THF (6 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 11 cm, cyclohexane/*t*BME = 100:1) afforded **5e** (72.0 mg, 0.26 mmol, 71%) as a colorless oil. $\mathbf{R_f}$ = 0.55 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.69 (m_c, 2H, H-7), 2.28 (m_c, 2H, H-8), 3.41 (t, $^3J_{6,7}$ = 6.5 Hz,

2H, H-6), 3.74 (s, 3H, H-17), 4.39 (s, 2H, H-5), 5.65 (dt, $^3J_{9,10}$ = 11.6 Hz, $^3J_{9,8}$ = 7.3 Hz, 1H, H-9), 6.46 (d, $^3J_{10,9}$ = 11.6 Hz, 1H, H-10), 6.79 (m_c, 1H, H-12), 6.83 (m_c, 1H, H-13), 7.13-7.26 (m, 7H, H-Ar) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 25.3 (C-8), 29.9 (C-7), 55.4 (C-17), 69.8 (C-6), 72.8 (C-5), 110.4 (C-12), 120.0 (C-13), 124.7 (C-10), 126.4 (C-11), 127.4 (C-Ar), 127.6 (C-3), 128.0 (C-Ar), 128.3 (C-Ar), 130.0 (C-Ar), 132.1 (C-9), 138.6 (C-4), 157.0 (C-16) ppm. **IR** (ATR) ν = 2932.7 (w), 1597.3 (m), 1486.8 (m), 1453.6 (m), 1239.0 (s), 1106.9 (s), 1027.4 (s), 750.2 (s), br , 696.7 (s), 605.1 (w, br) cm^{-1}. **HRMS (EI)** calcd. for $C_{19}H_{22}O^+$ [(M^+)]: 282.1614, found: 282.1610.

7.4.6 (*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-bromobenzene (5f)



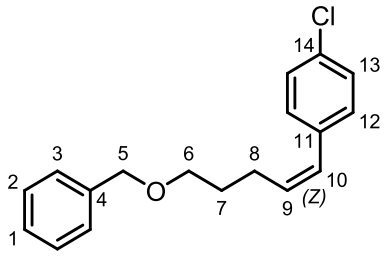
5f

$C_{18}H_{19}BrO$

M_W = 331.25 g/mol

Prepared from **4f** (0.12 g, 0.37 mmol, 1.00 equiv.), [IPrCuOH] (10.8 mg, 22.8 mmol, 5.00 mol%) and a solution of ammonia borane (42.3 mg, 0.91 mmol, 3.00 equiv.) in THF (7 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 48 h. Purification by flash column chromatography on silica gel (2 × 10 cm, cyclohexane/*t*BME = 100:1) afforded **5f** (95.0 mg, 0.29 mmol, 80%) as a colorless oil. $\mathbf{R_f}$ = 0.69 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.78 (m_c, 2H, H-7), 2.41 (m_c, 2H, H-8), 3.50 (t, $^3J_{6,7}$ = 6.4 Hz, 2H, H-6), 4.48 (s, 2H, H-5), 5.69 (dt, $^3J_{9,10}$ = 11.7 Hz, $^3J_{9,8}$ = 7.4 Hz, 1H, H-9), 6.37 (m_c, 1H, H-10), 7.15 (m_c, 2H, H-12), 7.27-7.30 (m, 3H, H-1, H-3), 7.33-7.36 (m, 2H, H-2), 7.43 (m_c, 2H, H-13) ppm. The ^{1}H NMR spectrum contains unknown impurities. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ/ppm = 25.2 (C-8), 29.8 (C-7), 69.6 (C-6), 72.9 (C-5), 120.3 (C-14), 127.5 (C-1), 127.6 (C-3), 128.2 (C-10), 128.3 (C-2), 130.4 (C-12), 131.2 (C-13), 133.0 (C-9), 136.4 (C-11), 138.5 (C-4) ppm. **IR** (ATR) ν = 2930 (m), 2856 (m), 1486 (s), 1453 (m), 1102 (s), 1071 (s), 1028 (m), 1009 (s), 837 (s), 734 (s), 696 (s) cm^{-1}. **HRMS (APCI)** calcd.for $C_{18}H_{20}BrO^+$ [($M+H^+$)]: 331.0692, found: 331.0689.

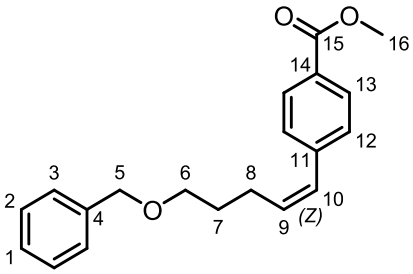
7.4.7 (*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-chlorobenzene (5g)



5g
$C_{18}H_{19}ClO$
M_W = 286.80 g/mol

Prepared from **4g** (94.0 mg, 0.35 mmol, 1.00 equiv.), [IPrCuOH] (8.30 mg, 17.5 mmol, 5.00 mol%) and a solution of ammonia borane (33.0 mg, 1.05 mmol, 3.00 equiv.) in THF (6 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 19 h. Purification by flash column chromatography on silica gel (2 × 13 cm, cyclohexane/*t*BME = 100:1) afforded **5g** (60.0 mg, 0.21 mmol, 63%) as a colorless oil. $\mathbf{R_f}$ = 0.59 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.78 (m_c, 2H, H-7), 2.42 (m_c, 2H, H-8), 3.51 (t, ^3J = 6.4 Hz, 2H, H-6), 4.48 (s, 2H, H-5), 5.69 (dt, $^3J_{9,10}$ = 11.7 Hz, $^3J_{9,8}$ = 7.4 Hz, 1H, H-9), 6.39 (d, $^3J_{10,9}$ = 11.7 Hz, 1H, H-10), 7.22 (m, 2H, H-12), 7.26-7.30 (m, 5H, H-13, H-Ar), 7.33-7.36 (m, 2H, H-2) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 25.2 (C-8), 29.8 (C-7), 69.6 (C-6), 72.9 (C-5), 127.5 (C-13), 127.6 (C-3), 128.2 (C-1), 128.3 (C-10), 128.4 (C-2), 130.0 (C-12), 132.2 (C-14), 132.9 (C-9), 136.0 (C-11), 138.5 (C-4) ppm. **IR** (ATR) ν = 2854 (m), 1490 (s), 1453 (m), 1362 (m), 1091 (s), 1013 (m), 840 (s), 734 (s), 696 (s) cm^{-1}. **HRMS (EI)** calcd. for $C_{18}H_{19}ClO^+$ [(M^+)]: 286.1119,, found: 286.1133.

7.4.8 Methyl (*Z*)-4-(5-(benzyloxy)pent-1-en-1-yl)benzoate (5h)



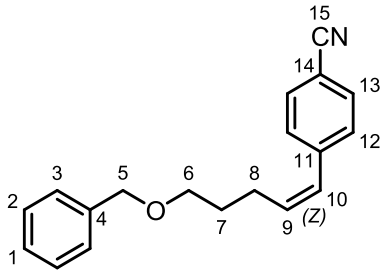
5h
$C_{20}H_{22}O_3$
M_W = 310.16 g/mol

Prepared from **4h** (93.0 mg, 0.32 mmol, 1.00 equiv.), [IPrCuOH] (7.60 mg, 16.2 mmol, 5.00 mol%) and a solution of ammonia borane (30.0 mg, 0.97 mmol, 3.00 equiv.) in THF (6 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 5 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 50:1) afforded **5h** (93.0 mg, 0.37 mmol, 96%) as a colorless oil, containing 20% of the corresponding alkane. $\mathbf{R_f}$ = 0.40 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ/ppm = 1.71 (m_c, 2H, H-7), 2.37 (m_c, 2H, H-8), 3.42 (t, $^3J_{6,7}$ = 6.4 Hz, 2H, H-6), 3.83 (s, 3H, H-16), 4.39 (s, 2H, H-

5), 5.70 (dt, $^3J_{9,10}$ = 11.7 Hz, $^3J_{9,8}$ = 7.4 Hz, 1H, H-9), 6.38 (d, $^3J_{10,9}$ = 11.7 Hz, 1H, H-10), 7.19-7.27 (m, 7H, H-1, H-2, H-3, H-12), 7.91 (m_c, 2H, H-13). The ^{1}H NMR spectrum contains 20% impurities of the overreduced alkane. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ/ppm = 25.4 (C-8), 29.8 (C-7), 52.0 (C-16), 69.6 (C-6), 72.9 (C-5), 127.5 (C-Ar), 127.6 (C-Ar), 128.3 (C-14), 128.6 (C-10), 128.7 (C-12), 129.5 (C-13), 129.6 (C-Ar), 134.4 (C-9), 138.5 (C-4), 142.3 (C-11), 167.0 (C-15). **HRMS (APCI)** calcd. for $C_{20}H_{23}O_3^+$ [($M+H^+$)]: 311.1647, found: 311.1645.

The spectroscopic data is in agreement with literature.[11]

7.4.9 (*Z*)-4-(5-(benzyloxy)pent-1-en-1-yl)benzonitrile (5i)

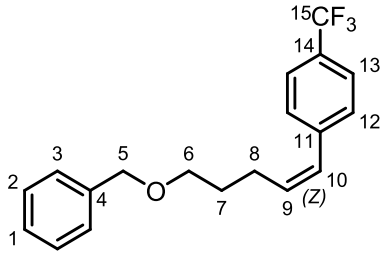


5i
$C_{19}H_{19}NO$
M_W = 277.37 g/mol

Prepared from **4i** (141 mg, 0.55 mmol, 1.00 equiv.), [IPrCuOH] (13.0 mg, 27.0 mmol, 5.00 mol%) and a solution of ammonia borane (50.0 mg, 1.63 mmol, 3.00 equiv.) in THF (10 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 17 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 50:1) afforded **5i** (70.0 mg, 0.26 mmol, 51%) as a colorless oil, containing 4% of the (*E*)-**5i** and 7% of the corresponding alkane. $\mathbf{R_f}$ = 0.59 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.70 (m_c, 2H, H-7), 2.35 (m_c, 2H, H-8), 3.42 (t, $^3J_{6,7}$ = 6.3 Hz, 2H, H-6), 4.39 (s, 2H, H-5), 5.74 (dt, $^3J_{9,10}$ = 11.8 Hz, $^3J_{9,8}$ = 7.5 Hz, 1H, H-9), 6.44 (d, $^3J_{10,9}$ = 11.8 Hz, 1H, H-10), 7.17-7.24 (m, 5H, H-1, H-2, H-3), 7.28 (m_c, 2H, H-12), 7.48 (m_c, 2H, H-13) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 25.4 (C-8), 29.7 (C-7), 69.4 (C-6), 72.9 (C-5), 109.9 (C-14), 119.0 (C-15), 127.5 (C-1)*, 127.6 (C-2)*, 127.9 (C-10), 128.3 (C-3)*, 129.3 (C-12), 131.9 (C-13), 135.5 (C-9), 138.4 (C-4), 142.1 (C-11) ppm. **HRMS (EI)** calcd. for $C_{19}H_{19}NO^+$ [(M^+)]: 277.1461, found: 277.1460.

The spectroscopic data is in agreement with literature.[11]

7.4.10 (*Z*)-1-(5-(Benzyloxy)pent-1-en-1-yl)-4-(trifluoromethyl)benzene (5j)



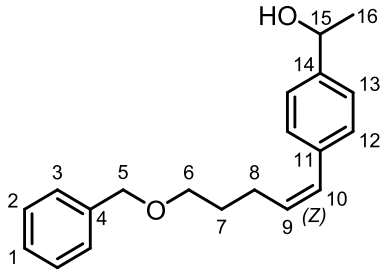
5j

$C_{19}H_{19}F_3O$

M_W = 320.36 g/mol

Prepared from **4j** (70.0 mg, 0.22 mmol, 1.00 equiv.), [IPrCuOH] (6.00 mg, 12.5 mmol, 5.00 mol%) and a solution of ammonia borane (23 mg, 0.75 mmol, 3.00 equiv.) in THF (4 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 48 h. Purification by flash column chromatography on silica gel (2 × 13 cm, cyclohexane/*t*BME = 100:1) afforded **5j** (50.0 mg, 0.16 mmol, 71%) as a colorless oil containing 19% of the corresponding alkane. $\mathbf{R_f}$ = 0.51 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.79 (m_c, 2H, H-7), 2.44 (m_c, 2H, H-8), 3.51 (t, $^3J_{6,7}$ = 6.3 Hz, 2H, H-6), 4.48 (s, 2H, H-5), 5.79 (dt, $^3J_{9,10}$ = 11.7 Hz, $^3J_{9,8}$ = 7.4 Hz, 1H, H-9), 6.46 (d, $^3J_{10,9}$ = 11.7 Hz, 1H, H-10), 7.27-7.35 (m, 5H, H-1, H-2, H-3), 7.38 (m_c, 2H, H-12), 7.56 (m_c, 2H, H-13) ppm. The ^{1}H NMR spectrum contains 19% of the corresponding alkane. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 25.3 (C-8), 29.8 (C-7), 69.5 (C-6), 72.9 (C-5), 124.2 (q, $^1J_{15,F}$ = 270 Hz, C-15), 125.1 (q, $^3J_{13,F}$ = 3.7 Hz, C-13), 127.5 (C-1), 127.6 (C-3), 128.1 (C-10), 128.3 (C-2), 128.9 (C-12), 134.1 (C-9), 138.4 (C-4), 141.1 (C-11) ppm. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -62.4 ppm. **IR** (ATR) ν = 2861 (w), 1616 (m), 1454 (m), 1323 (s), 1162 (s), 1112 (s), 1066 (s), 1016 (s), 852 (m), 744 (m), 697 (m) cm^{-1}. **HRMS** (EI) calcd. for $C_{12}H_{12}F_3O^+$ [(M^+)]: 321.1466, found: 321.1465.

7.4.11 (*Z*)-1-(4-(5-(Benzyloxy)pent-1-en-1-yl)phenyl)ethan-1-ol (5k)



5k

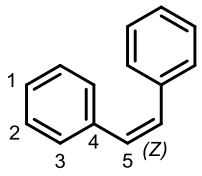
$C_{20}H_{24}O_2$

M_W = 296.41 g/mol

Prepared from **4k** (143 mg, 0.51 mmol, 1.00 equiv.), [IPrCuOH] (12.0 mg, 26.0 mmol, 5.00 mol%) and a solution of ammonia borane (48.0 mg, 1.54 mmol, 3.00 equiv.) in THF (10 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 16 h. Purification by flash column chromatography on silica gel (2 × 13 cm, cyclohexane/*t*BME = 10:1) afforded **5k** (80.0 mg, 0.26 mmol, 51%) as a colorless oil, containing 4% of the (*E*)-**5k** and 7% of the corresponding alkane. $\mathbf{R_f}$ = 0.33 (SiO_2, cyclohexane/*t*BME 2:1, $KMnO_4$). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.38 (d, $^3J_{16,15}$ = 6.4 Hz 3H, H-16), 1.68 (m_c, 2H, H-7), 2.35 (m_c, 2H, H-8), 3.40 (t, $^3J_{6,7}$ = 6.3 Hz, 2H, H-6), 4.37 (s, 2H, H-5), 4.75 (q, $^3J_{15,16}$ = 6.4 Hz, 1H, H-

15), 5.56 (dt, $^3J_{9,10}$ = 11.7 Hz, $^3J_{9,8}$ = 7.4 Hz, 1H, H-9), 6.33 (d, $^3J_{10,9}$ = 11.7 Hz, 1H, H-10), 7.25-7.38 (m, 5H, H-1, H-2, H-3), 7.37 (m_c, 2H, H-12), 7.90 (m_c, 2H, H-13) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 25.0 (C-8), 25.2 (C-16), 30.0 (C-7), 69.6 (C-6), 70.0 (C-15), 72.8 (C-5), 125.2 (C-Ar), 127.4 (C-Ar), 127.5 (C-Ar), 128.3 (C-Ar), 128.8 (C-10), 128.9 (C-Ar), 132.7 (C-9), 136.7 (C-14), 138.5 (C-4), 144.0 (C-11) ppm. **HRMS (APCI)** calcd. for $C_{20}H_{23}O^+$ [$(M\text{-}OH)^+$]: 279.1749, found: 279.1744.

7.4.12 (*Z*)-1,2-Diphenylethene (5l)

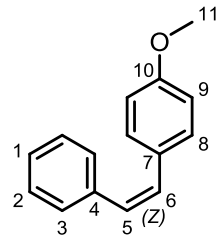


5l
$C_{14}H_{12}$
M_W = 180.25 g/mol

Prepared from **4l** (70.0 mg, 0.39 mmol, 1.00 equiv.), [IPrCuOH] (10.5 mg, 22.4 µmol, 5.00 mol%) and a solution of ammonia borane (41.0 mg, 0.95 mmol, 3.00 equiv.) in THF (7 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 20 h. Purification by flash column chromatography on silica gel (2 × 10 cm, cyclohexane) afforded **5l** (40.0 mg, 0.22 mmol, 57%) as a colorless oil. $\mathbf{R_f}$ = 0.58 (SiO_2, cyclohexane). **^{1}H NM**R (500 MHz, $CDCl_3$): δ = 6.52 (s, 2H, H-5), 7.08-7.18 (m, 10H, H-1, H-2, H-3) ppm. The ^{1}H NMR spectrum contains unknown impurities. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ/ppm = 127.1 (C-1), 128.2 (C-2), 128.8 (C-3), 130.2 (C-5), 137.2 (C-4) ppm. **HRMS (EI)** calcd. for $C_{14}H_{12}^+$ [(M^+)]: 180.0934, found: 180.0933.

The spectroscopic data is in agreement with literature.[11]

7.4.13 (*Z*)-1-Methoxy-4-styrylbenzene (5m)



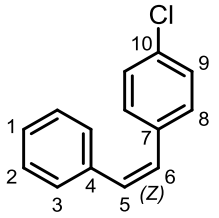
5m
$C_{15}H_{14}O$
M_W = 210.28g/mol

Prepared from **4m** (70.0 mg, 0.39 mmol, 1.00 equiv.), [IPrCuOH] (10.5 mg, 22.4 µmol, 5.00 mol%) and a solution of ammonia borane (41.0 mg, 0.95 mmol, 3.00 equiv.) in THF (7 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 20 h. Purification by flash

column chromatography on silica gel (2 × 10 cm, cyclohexane/*t*BME = 100:1) afforded **5m** (40.0 mg, 0.22 mmol, 57%) as a colorless oil. $\mathbf{R_f}$ = 0.64 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.69 (s, 3H, H-11), 6.44 (m_c, 2H, H-5, H-6), 6.67 (m_c, 2H, H-9), 7.09-7.10 (m_c, 3H, H-8, H-1). 7.13-7.20 (m, 4H, H-2, H-3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ/ppm = 55.1 (C-11), 113.6 (C-9), 126.9 (C-1), 128.2 (C-2), 128.7 (C-5), 128.8 (C-3), 129.6 (C-7), 129.7 (C-6), 130.1 (C-8), 137.6 (C-4), 158.7 (C-10) ppm. **HRMS (EI)** calcd. for $C_{15}H_{14}O^+$ [(M^+)]: 210.1039, found: 210.1045.

The spectroscopic data is in agreement with literature.[17]

7.4.14 (*Z*)-1-Chloro-4-styrylbenzene (5n)

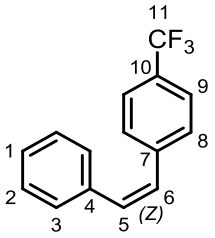


5n
$C_{14}H_{11}Cl$
M_W = 214.69 g/mol

Prepared from 4**n** (96.0 mg, 0.45 mmol, 1.00 equiv.), [IPrCuOH] (11.0 mg, 23.5 µmol, 5.00 mol%) and a solution of ammonia borane (43.5 mg, 1.41 mmol, 3.00 equiv.) in THF (8 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 12 h. Purification by flash column chromatography on silica gel (2 × 11 cm, pentane) afforded **5n** (75.0 mg, 0.35 mmol, 77%) as a colorless oil. $\mathbf{R_f}$ = 0.54 (SiO_2, pentane). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.54 (d, $^3J_{6,5}$ = 12.4 Hz, 1H, H-6), 6.64 (d, $^3J_{5,6}$ = 12.4 Hz, 1H, H-5), 7.18-7.23 (m_c, 4H, H-8, H-9), 7.24-7.28 (m, 5H, H-1, H-2, H-3) ppm. The ^{1}H NMR spectrum contains unknown impurities. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 127.3 (C-1), 128.3 (C-2), 128.4 (C-9), 128.8 (C-3), 128.9 (C-6), 130.2 (C-8), 130.9 (C-5), 132.7 (C-10), 135.6 (C-7), 136.9 (C-4) ppm. **HRMS (EI)** calcd. for $C_{14}H_{11}Cl^+$ [(M^+)]: 214.0544, found: 214.0534.

The spectroscopic data is in agreement with literature.[18]

7.4.15 (*Z*)-1-Styryl-4-(trifluoromethyl)benzene (5o)

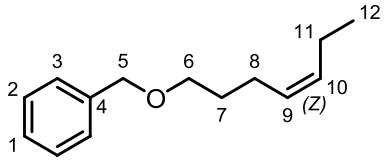


5o
$C_{15}H_{11}F_3$
M_W = 248.25 g/mol

Prepared from **4o** (94.0 mg, 0.38 mmol, 1.00 equiv.), [IPrCuOH] (9.50 mg, 20.3 µmol, 5.00 mol%) and a solution of ammonia borane (41.0 mg, 0.95 mmol, 3.00 equiv.) in THF (7 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 12 h. Purification by flash column chromatography on silica gel (2 × 10 cm, pentane) afforded **5o** (50.0 mg, 0.20 mmol, 50%) as a colorless oil containing 8% of the corresponding alkane. $\mathbf{R_f}$ = 0.56 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.62 (d, $^3J_{6,5}$ = 12.1 Hz, 1H, H-6), 6.65 (d, $^3J_{5,6}$ = 12.1 Hz, 1H, H-5), 7.13-7.17 (m, 5H, H-1, H-2, H-3), 7.26 (m_c, 2H, H-8), 7.39 (m_c, 2H, H-9) ppm. The ^{1}H NMR spectrum contains 8% of the corresponding alkane and unknown impurities. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ/ppm = 125.2 (q, $^3J_{9,F}$ = 3.7 Hz, C-9), 126.7 (q, $^2J_{10,F}$ = 25.0 Hz, C-10), 127.6 (C-1). 128.4 (C-2). 128.7 (C-6). 128.8 (C-3). 129.1 (C-8). 132.3 (C-5). 136.6 (C-7), 140.9 (C-4) ppm. The signal of C-11 was not detected. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -62.6 ppm. **HRMS (EI)** calcd. for $C_{15}H_{11}F_3$ [(M^+)]: 248.0807, found: 248.0811.

The spectroscopic data is in agreement with literature.[19]

7.4.16 (*Z*)-((Hept-4-en-1-yloxy)methyl)benzene (5p)



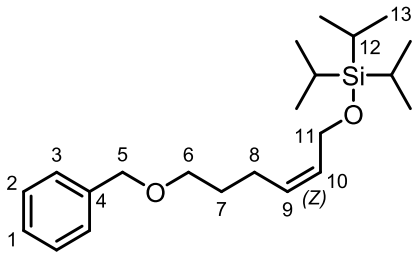
5p
$C_{14}H_{20}O$
M_W = 204.31 g/mol

Prepared from **4p** (95.0 mg, 0.50 mmol, 1.00 equiv.), [IPrCuOH] (12.0 mg, 25.0 µmol, 5.00 mol%) and a solution of ammonia borane (61.3 mg, 1.97 mmol, 4.00 equiv.) in THF (10 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 36 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 150:1) afforded **5p** (70.0 mg, 0.34 mmol, 74%) as a colorless oil. $\mathbf{R_f}$ = 0.79 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.96 (t, $^3J_{12,11}$ = 7.5 Hz, 3H, H-12), 1.68 (m_c, 2H, H-7), 2.05 (m_c, 2H, H-11), 2.14 (m_c, 2H, H-8), 3.49 (t, $^3J_{6,7}$ = 6.5 Hz, 2H, H-6), 4.51 (s, 2H, H-5), 5.33 (dtt, $^3J_{9,10}$ = 10.8 Hz, $^3J_{9,8}$ = 7.2 Hz, $^4J_{9,11}$ = 1.3 Hz, 1H, H-9), 5.39 (dtt, $^3J_{10,9}$ = 10.8 Hz, $^3J_{10,11}$ = 7.2 Hz, $^4J_{10,8}$ = 1.3 Hz, 1H, H-10), 7.27-7.31 (m, 1H, H-1), 7.33-7.35 (m, 4H, H-2, H-3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.3 (C-12), 20.5 (C-11), 23.7 (C-8), 29.8 (C-7), 69.9 (C-6),

72.9 (C-5), 127.5 (C-1), 127.6 (C-2)*, 128.3 (C-3)*, 128.4 (C-9), 132.2 (C-10), 138.7 (C-4) ppm. **HRMS (APCI)** calcd. for $C_{14}H_{21}O^+$ [(M+H$^+$)]: 205.1587, found: 205.1585.

The spectroscopic data is in agreement with literature.[11]

7.4.17 (*Z*)-((6-(Benzyloxy)hex-2-en-1-yl)oxy)triisopropylsilane (5r)



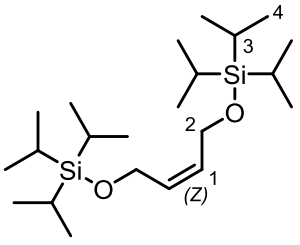
5r

$C_{22}H_{38}O_2Si$

M_W = 362.63 g/mol

Prepared from **4r** (95.0 mg, 0.50 mmol, 1.00 equiv.), [IPrCuOH] (12.0 mg, 25.0 µmol, 5.00 mol%) and a solution of ammonia borane (61.3 mg, 1.97 mmol, 3.00 equiv.) in THF (10 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 150:1) afforded **5r** (70.0 mg, 0.34 mmol, 74%) as a colorless oil. $\mathbf{R_f}$ = 0.68 (SiO_2, cyclohexane/*t*BME 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.05-1.11 (m, 21H, H-12, H-13), 1.69 (m_c, 2H, H-7), 2.14 (m_c, 2H, H-8), 3.48 (t, $^3J_{6,7}$ = 6.5 Hz, 2H, H-6), 4.30 (m_c, 2H, H-11), 4.50 (s, 2H, H-5), 5.42 (dtt, $^3J_{9,10}$ = 11.0 Hz, $^3J_{9,8}$ = 7.4 Hz, $^4J_{9,11}$ = 1.7 Hz, 1H, H-9), 5.57 (dtt, $^3J_{10,9}$ = 11.0 Hz, $^3J_{10,11}$ = 6.1 Hz, $^4J_{10,8}$ = 1.4 Hz, 1H, H-10), 7.27-7.30 (m, 1H, H-1), 7.32-7.35 (m, 4H, H-2, H-3) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ/ppm = 12.0 (C-12), 18.0 (C-13), 24.3 (C-8), 29.6 (C-7), 59.6 (C-11), 69.4 (C-6), 72.9 (C-5), 127.5 (C-1), 127.6 (C-2)*, 128.3 (C-3)*, 129.5 (C-9), 130.6 (C-10), 138.6 (C-4) ppm. **^{29}Si-DEPT** (99 MHz, *J* = 20 Hz $CDCl_3$): δ = 13.8 ppm. **IR** (ATR) ν = 2940.9 (m), 2864.3 (s), 1454.1 (m), 1094.4 (s, br), 1067.9 (s, br), 881.8 (s), 732.3 (m), 679.8 (s, br) cm^{-1}. **HRMS (EI)** calcd. for $C_{19}H_{31}O_2Si^+$ [(M-C_3H_7)$^+$]: 319.2088, found: 319.2095.

7.4.18 (*Z*)-3,3,10,10-Tetraisopropyl-2,11-dimethyl-4,9-dioxa-3,10-disiladodec-6-ene (5s)



$C_{22}H_{48}O_2Si_2$

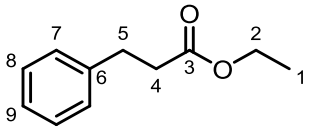
M_W = 400.79 g/mol

Prepared from **4s** (0.14 g, 0.35 mmol, 1.00 equiv.), [IPrCuOH] (8.80 mg, 18.8 µmol, 5.00 mol%) and a solution of ammonia borane (35.0 mg, 1.13 mmol, 3.00 equiv.) in THF (6 mL) following **GP3**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash

column chromatography on silica gel (2 × 11 cm, cyclohexane/*t*BME = 100:1) afforded **5s** (78.0 mg, 0.20 mmol, 56%) as a colorless oil. $\mathbf{R_f}$ = 0.28 (SiO_2, cyclohexane/*t*BME 50:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.05-1.14 (m, 42H, H-3, H-4), 4.30 (m_c, 4H, H-2), 5.58 (m_c, 2H, H-1) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 12.0 (C-3), 17.9 (C-4), 60.0 (C-2), 130.2 (C-1) ppm. **^{29}Si-DEPT** (99 MHz, *J* = 20 Hz $CDCl_3$): δ = 13.9 ppm. **IR** (ATR) ν = 2941.9 (m), 2865.2 (s), 1462.7 (m), 1088.1 (s), 1065.0 (s). 1012.9 (m), 880.8 (s), 788.7 (m, br), 679.3 (s), 656.6 (s) cm^{-1}. **HRMS (EI)** calcd. for $C_{19}H_{41}O_2Si_2$ [(M-C_3H_7)$^+$]: 357.2640,found: 357.2646.

7.5 1,4 Reduction of α,β-unsaturated substrates

7.5.1 Ethyl 3-phenylpropanoate (10a)

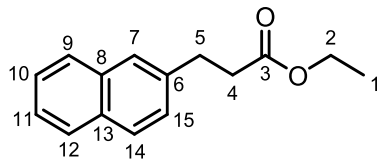


10a
$C_{11}H_{14}O_2$
M_W = 178.23 g/mol

Prepared from **9a** (97.0 mg, 0.57 mmol, 1.00 equiv.), [IPrCuOH] (13.0 mg, 28.4 µmol, 5.00 mol%) and a solution of ammonia borane (35.0 mg, 1.14 mmol, 2.00 equiv.) in THF (8 mL) following **GP4**. The reaction mixture was stirred at 50 °C for 16 h. Purification by flash column chromatography on silica gel (2 × 10 cm, cyclohexane/*t*BME = 20:1) afforded **10a** (80.0 mg, 0.45 mmol, 82%) as a yellow oil. $\mathbf{R_f}$ = 0.57 (SiO_2, cyclohexane/*t*BME = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.24 (t, $^3J_{1,2}$ = 7.2 Hz, 3H, H-1), 2.62 (m_c, 2H, H-4), 2.96 (t, $^3J_{5,4}$ = 8.1 Hz, 2H, H-5), 4.17 (q, $^3J_{2,1}$ = 7.2 Hz, 2H, H-2), 7.20-7.21 (m, 3H, H-9, H-8), 7.29 (m_c, 2H, H-7) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 28.1 (C-5), 35.2 (C-4), 60.5 (C-2), 126.2 (C-1), 128.3 (C-8), 128.5 (C-7), 140.6 (C-6), 172.9 (C-3) ppm. **HRMS (EI)** calcd. for $C_{11}H_{14}O_2^+$ [(M^+)]: 178.0988, found: 178.0992.

The spectroscopic data is in agreement with literature.[20]

7.5.2 Ethyl 3-(naphthalen-2-yl)propanoate (10b)

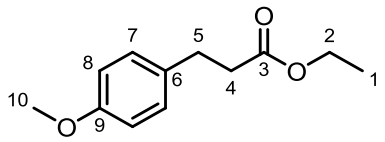


10b
$C_{15}H_{16}O_2$
M_W = 228.29 g/mol

Prepared from **9b** (0.15 g, 0.66 mmol, 1.00 equiv.), [IPrCuOH] (10.0 mg, 22.0 µmol, 5.00 mol%) and a solution of ammonia borane (41.0 mg, 1.33 mmol, 2.00 equiv.) in THF (8 mL) following **GP4**. The reaction mixture was stirred at 50 °C for 16 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 20:1) afforded **10b** (0.13 g, 0.55 mmol, 83%) as a yellow oil. $\mathbf{R_f}$ = 0.36 (SiO_2, cyclohexane/*t*BME = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.26 (t, $^3J_{1,2}$ = 7.3 Hz, 3H, H-1), 2.77 (t, $^3J_{4,5}$ = 8.1 Hz, 2H, H-4), 3.44 (t, $^3J_{5,4}$ = 8.1 Hz, 2H, H-5), 4.17 (q, $^3J_{2,1}$ = 7.3 Hz, 2H, H-2), 7.25-7.37 (m, 1H, H-), 7.39-7.42 (m, 1H, H-Ar), 7.48-7.56 (m, 2H, H-Ar), 7.74 (m_c, 1H, H-Ar), 7,87 (m_c, 1H, H-Ar), 8.05 (m_c, 1H, H-Ar) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 28.1 (C-5), 35.2 (C-4), 60.5 (C-2), 123.4 (C-Ar), 125.5 (C-Ar), 125.6 (C-Ar), 125.9 (C-Ar), 126.0 (C-Ar), 127.1 (C-Ar), 128.8 (C-Ar), 131.6 (C-8), 133.9 (C-13), 136.6 (C-6), 173.0 (C-3) ppm. **HRMS (EI)** calcd. for $C_{15}H_{16}O_2^+$ [(M^+)]: 228.1145, found: 228.1145.

The spectroscopic data is in agreement with literature.[21]

7.5.3 Ethyl 3-(4-methoxyphenyl)propanoate (10c)

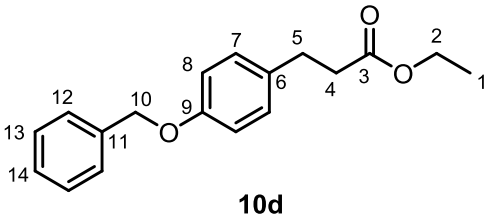


10c
$C_{12}H_{16}O_3$
M_W = 208.26 g/mol

Prepared from **9c** (0.10 g, 0.48 mmol, 1.00 equiv.), [IPrCuOH] (11.4 mg, 24.2 µmol, 5.00 mol%) and a solution of ammonia borane (30.0 mg, 0.97 mmol, 2.00 equiv.) in THF (6 mL) following **GP4**. The reaction mixture was stirred at 50 °C for 16 h. Purification by flash column chromatography on silica gel (2 × 10 cm, cyclohexane/*t*BME = 20:1) afforded **10c** (80.0 mg, 0.38 mmol, 83%) as a yellow oil. $\mathbf{R_f}$ = 0.48 (SiO_2, cyclohexane/*t*BME = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.23 (t, $^3J_{1,2}$ = 7.2 Hz, 3H, H-1), 2.58 (t, $^3J_{4,5}$ = 8.0 Hz, 2H, H-4), 2.89 (t, $^3J_{5,4}$ = 8.0 Hz, 2H, H-5), 3.78 (s, 3H, H-10), 4.12 (q, $^3J_{2,1}$ = 7.2 Hz, 2H, H-2), 6.83 (m, 2H, H-7), 7.12 (m_c, 2H, H-8) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 30.1 (C-5), 36.2 (C-4), 55.2 (C-10), 60.3 (C-2), 113.9 (C-7), 129.2 (C-8), 132.6 (C-6), 158.0 (C-9), 172.9 (C-3) ppm. **HRMS (EI)** clacd. for $C_{12}H_{16}O_3^+$ [(M^+)]: 208.1094, found: 208.1100.

The spectroscopic data is in agreement with literature.[22]

7.5.4 Ethyl 3-(4-(benzyloxy)phenyl)propanoate (10d)



10d

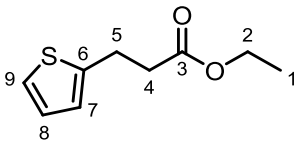
$C_{18}H_{20}O_3$

M_W = 284.36 g/mol

Prepared from **9d** (80.0 mg, 0.28 mmol, 1.00 equiv.), [IPrCuOH] (6.70 mg, 14.2 µmol, 5.00 mol%) and a solution of ammonia borane (26.0 mg, 0.85 mmol, 3.00 equiv.) in THF (6 mL) following **GP4**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 20:1) afforded **10d** (70.0 mg, 0.25 mmol, 87%) as a yellow oil. $\mathbf{R_f}$ = 0.64 (SiO_2, cyclohexane/*t*BME = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.24 (t, $^3J_{1,2}$ = 7.2 Hz, 3H, H-1), 2.59 (t, $^3J_{4,5}$ = 7.8 Hz, 2H, H-4), 2.89 (t, $^3J_{5,4}$ = 7.8 Hz, 2H, H-5), 4.12 (q, $^3J_{2,1}$ = 7.2 Hz, 2H, H-2), 5.05 (s, 2H, H-10), 6.91 (m_c, 2H, H-8), 7.12 (m_c, 2H, H-7), 7.31-7.33 (m, 1H, H-14), 7.38 (m_c, 2H, H-13), 7.42-7.44 (m, 2H, H-12) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 30.1 (C-5), 36.2 (C-4), 60.3 (C-2), 70.0 (C-10), 114.8 (C-8), 127.5 (C-12), 127.9 (C-14), 128.5 (C-13), 129.3 (C-7), 133.0 (C-6), 137.1 (C-11), 157.3 (C-9), 173.0 (C-3) ppm. **HRMS (EI)** calcd. for $C_{18}H_{20}O_3^+$ [(M^+)]: 284.1407, found: 284.1406.

The spectroscopic data is in agreement with literature.[23]

7.5.5 Ethyl 3-(thiophen-2-yl)propanoate (10f)



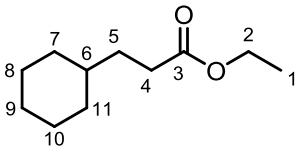
10f

$C_9H_{12}O_2S$

M_W = 184.25 g/mol

Prepared from **9f** (75.0 mg, 0.41 mmol, 1.00 equiv.), [IPrCuOH] (10.0 mg, 22.0 µmol, 5.00 mol%) and a solution of ammonia borane (41.0 mg, 1.32 mmol, 3.00 equiv.) in THF (7 mL) following **GP4**. The reaction mixture was stirred at 50 °C for 16 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 20:1) afforded **10f** (50.0 mg, 0.27 mmol, 66%) as a colorless oil. $\mathbf{R_f}$ = 0.63 (SiO_2, cyclohexane/*t*BME = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.25 (t, $^3J_{1,2}$ = 7.2 Hz, 3H, H-1), 2.68 (m_c, 2H, H-4), 3.17 (m_c, 2H, H-5), 4.15 (q, $^3J_{2,1}$ = 7.2 Hz, 2H, H-2), 6.82-6.83 (m, 1H, H-7), 6.91 (m_c, 1H, H-8), 7.13 (m_c, 1H, H-9) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 25-2 (C-5), 36.2 (C-4), 60.5 (C-2), 123.5 (C-9), 124.6 (C-7), 126.8 (C-8), 143.1 (C-6), 172.4 (C-3) ppm. **IR** (ATR) ν = 2978.5 (w), 1730.0 (s), 1617.0 (w, br), 1373.1 (w), 1162.4 (s, br), 1035.6 (m, br), 850.9 (m), 692.8 (s) cm^{-1}. **HRMS (EI)** calcd. for $C_9H_{12}O_2S$ [(M^+)]: 184.0553, found: 184.0558.

7.5.6 Ethyl 3-cyclohexylpropanoate (10g)

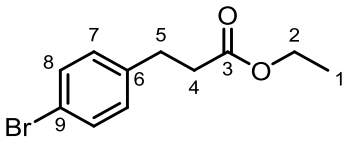


10g
$C_{11}H_{20}O_2$
M_W = 184.28 g/mol

Prepared from **9g** (76.0 mg, 0.42 mmol, 1.00 equiv.), [IPrCuOH] (10.0 mg, 21.6 µmol, 5.00 mol%) and a solution of ammonia borane (27.0 mg, 0.88 mmol, 2.00 equiv.) in THF (6 mL) following **GP4**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 11 cm, cyclohexane/*t*BME = 20:1) afforded **10g** (68.0 mg, 0.37 mmol, 88%) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.85-0.93 (m, 2H, H-9), 1.12-1.23 (m, 4H, H-7, H-11)*, 1.25 (t, $^3J_{1,2}$ = 7.2 Hz, 3H, H-1), 1.52 (m_c, 2H, H-5), 1.63-1.65 (m, 1H, H-6), 1.68-1.70 (m, 4H, H-8, H-10)*, 2.29 (m_c, 2H, H-4), 4.12 (q, $^3J_{2,1}$ = 7.2 Hz, 2H, H-2) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 26.2 (C-6), 26.5 (C-7, C-11)*, 32.0 (C-4), 32.4 (C-5), 33.0 (C-9), 37.2 (C-8, C-10)*, 60.1 (C-2), 174.2 (C-3) ppm. **HRMS (EI)** calcd. for $C_{11}H_{20}O_2^+$ [(M^+)]: calculated: 184.1458, found: 184.1460.

The spectroscopic data is in agreement with literature.[24]

7.5.7 Ethyl 3-(4-bromophenyl)propanoate (10h)

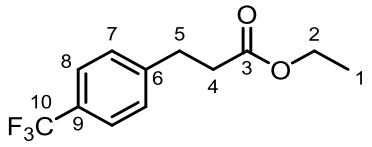


10h
$C_{11}H_{13}BrO_2$
M_W = 257.13 g/mol

Prepared from **9h** (0.10 g, 0.39 mmol, 1.00 equiv.), [IPrCuOH] (9.20 mg, 19.6 µmol, 5.00 mol%) and a solution of ammonia borane (36.0 mg, 1.18 mmol, 3.00 equiv.) in THF (7 mL) following **GP4**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 20:1) afforded **10h** (82.0 mg, 0.32 mmol, 82%) as a yellow oil. $\mathbf{R_f}$ = 0.70 (SiO_2, cyclohexane/*t*BME = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.23 (t, $^3J_{1,2}$ = 7.2 Hz, 3H, H-1), 2.59 (m_c, 2H, H-4), 2.90 (t, $^3J_{5,4}$ = 7.7 Hz, 2H, H-5), 4.12 (q, $^3J_{2,1}$ = 7.2 Hz, 2H, H-2), 7.08 (m_c, 2H, H-7), 7.40 (m_c, 2H, H-8) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 30.3 (C-5), 35.6 (C-4), 60.5 (C-2), 120.0 (C-9), 130.1 (C-7), 131.5 (C-8), 139.5 (C-6), 172.5 (C-3) ppm. **HRMS (EI)** calcd. for $C_{11}H_{13}BrO_2^+$ [(M^+)]: calculated: 256.0093, found: 256.0087.

The spectroscopic data is in agreement with literature.[23]

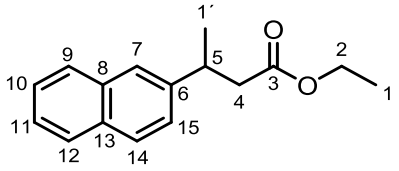
7.5.8 Ethyl 3-(4-(trifluoromethyl)phenyl)propanoate (10i)



10i
$C_{12}H_{13}F_3O_2$
M_W = 246.23 g/mol

Prepared from **9i** (0.10 g, 0.41 mmol, 1.00 equiv.), [IPrCuOH] (9.60 mg, 20.5 µmol, 5.00 mol%) and a solution of ammonia borane (38.0 mg, 1.23 mmol, 3.00 equiv.) in THF (7 mL) following **GP4**. The reaction mixture was stirred at 50 °C for 18 h. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 20:1) afforded **10i** (90.0 mg, 0.37 mmol, 89%) as a yellow oil. $\mathbf{R_f}$ = 0.54 (SiO_2, cyclohexane/*t*BME = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.23 (t, $^3J_{1,2}$ = 7.2 Hz, 3H, H-1), 2.64 (t, $^3J_{4,5}$ = 7.7 Hz, 2H, H-4), 3.01 (t, $^3J_{5,4}$ = 7.7 Hz, 2H, H-5), 4.12 (q, $^3J_{2,1}$ = 7.2 Hz, 2H, H-2), 7.32 (m_c, 2H, H-7), 7.54 (m_c, 2H, H-8) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 30.7 (C-5), 35.4 (C-4), 60.6 (C-2), 124.4 (q, $^1J_{10,F}$ = 276.9 Hz, C-10), 125.4 (q, $^3J_{8,F}$ = 3.8 Hz, C-8). 128.6 (q, $^2J_{9,F}$ = 32.7 Hz, C-9), 128.7 (C-7), 144.7 (C-6), 172.5 (C-3) ppm. **^{19}F-NMR** (470 MHz, $CDCl_3$): δ = -62.4 ppm. **IR** (ATR) ν = 2983.3 (w, br), 1732.7 (m), 1322.4 (s), 1159.5 (s), 1106.9 (s, br), 1066.9 (s), 826.8 (m, br), 596.9 (w, br) cm^{-1}. **HRMS (EI)** calcd. for $C_{12}H_{13}F_3O_2^+$ [(M^+)]: calculated: 246.0862, found: 246.0873.

7.5.9 Ethyl 3-(naphthalen-2-yl)butanoate (10j)

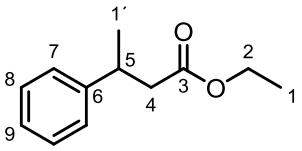


10j
$C_{16}H_{18}O_2$
M_W = 242.32 g/mol

According to **GP4**, first ammonia borane solution (31.0 mg, 1.00 mmol, 3.00 equiv. in 6 mL THF) was added to the solution of **9j** (80.0 g, 0.33 mmol, 1.00 equiv.) and [IPrCuOH] (7.80 mg, 16.6 µmol, 5.00 mol%), after 16 h reaction time at 50 °C, 90% conversion of starting material was detected. Afterwards [IPrCuOH] (7.80 mg, 16.6 µmol, 5.00 mol% in 0.5 mL THF) and ammonia borane (31.0 mg, 1.00 mmol, 3.00 equiv. in 6 mL THF) were added and the reaction mixture was stirred for another 16 h at 50 °C. Purification by flash column chromatography on silica gel (2 × 10 cm, cyclohexane/*t*BME = 20:1) afforded **10j** (74.0 mg, 0.31 mmol, 93%) as colorless oil. $\mathbf{R_f}$ = 0.67 (SiO_2, cyclohexane/*t*BME = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{1,2}$ = 7.0 Hz, 3H, H-1), 1.31 (d, $^3J_{1´,5}$ = 7.0 Hz, 3H, H-1´), 2.68 (m_c, 2H, H-4), 3.45 (m_c, 1H, H-5), 4.08 (m_c, 2H, H-2), 7.38 (m_c, 1H, H-Ar), 7.44 (m_c, 2H, H-Ar), 7.66 (m_c, 1H, H-Ar), 7.79-7.81 (m, 3H, H-Ar) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.1 (C-1), 21.8 (C-1´), 36.6 (C-5), 42.9 (C-4), 60.3 (C-2), 124.9 (C-Ar), 125.3 (C-Ar), 125.5 (C-Ar), 125.9 (C-Ar), 127.5 (C-Ar), 127.6 (C-Ar), 128.1 (C-Ar),

132.3 (C-8), 133.5 (C-13), 143.2 (C-6), 172.3 (C-3) ppm. **IR (**ATR) ν = 2926.0 (m), 1732.7 (s), 1456.5 (w, br), 1274.7 (w, br), 1154.2 (s, nr), 1030.3 (m), 816.2 (s), 744.9 (s), 475.8 (s) cm^{-1}. **HRMS (EI)** calcd. for $C_{16}H_{18}O_2^+$ [(M^+)]: 242.1301, found: 242.1308.

7.5.10 Ethyl 3-phenylbutanoate (10k)

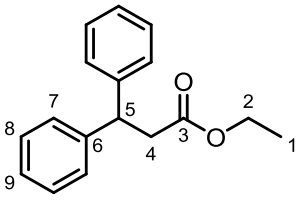


10k
$C_{12}H_{16}O_2$
M_W = 192.26 g/mol

According to **GP4**, first ammonia borane solution (39.0 mg, 1.26 mmol, 3.00 equiv. in 7 mL THF) was added to the solution of **9k** (80.0 g, 0.42 mmol, 1.00 equiv.) and [IPrCuOH] (10.0 mg, 21.0 µmol, 5.00 mol%), after 3.5 h reaction time at 50 °C, 96% conversion of starting material was detected. Afterwards [IPrCuOH] (10.0 mg, 21.0 µmol, 5.00 mol% in 0.5 mL THF) and ammonia borane (39.0 mg, 1.26 mmol, 3.00 equiv. in 7 mL THF) were added and the reaction mixture was stirred for another 16 h at 50 °C. Purification by flash column chromatography on silica gel (2 × 13 cm, cyclohexane/*t*BME = 20:1) afforded **10k** (61.0 mg, 0.32 mmol, 76%) as colorless oil. $\mathbf{R_f}$ = 0.59 (SiO_2, cyclohexane/*t*BME = 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{1,2}$ = 7.2 Hz, 3H, H-1), 1.31 (d, $^3J_{1´,5}$ = 7.0 Hz, 3H, H-1´), 2.58 (m_c, 2H, H-4), 3.28 (m_c, 1H, H-5), 4.08 (q, $^3J_{2,1}$ = 7.2 Hz, 2H, H-2), 7.18-7.23 (m, 3H, H-7, H-9), 7.38-7.31 (m, 2H, H-8) ppm. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.1 (C-1), 21.8 (C-1´), 36.5 (C-5), 43.2 (C-4), 60.2 (C-2), 126.3 (C-9), 126.7 (C-7), 128.4 (C-8), 145.7 (C-6), 172.4 (C-3) ppm. **HRMS (EI)** calcd. for $C_{12}H_{16}O_2^+$ [(M^+)]: 192.1145, found: 192.1143.

The spectroscopic data is in agreement with literature.[25]

7.5.11 Ethyl 3,3-diphenylpropanoate (10l)



10l
$C_{17}H_{18}O_2$
M_W = 254.33 g/mol

According to **GP4**, first ammonia borane solution (36.7 mg, 1.19 mmol, 3.00 equiv. in 7 mL THF) was added to the solution of **9l** (0.10 g, 0.40 mmol, 1.00 equiv.) and [IPrCuOH] (9.30 mg, 19.8 µmol, 5.00 mol%), after 18 h reaction time at 50 °C, 86% conversion of starting material was detected. Afterwards [IPrCuOH] (9.30 mg, 19.8 µmol, 5.00 mol% in

0.5 mL THF) and ammonia borane (24.5 mg, 0.79 mmol, 2.00 equiv. in 6 mL THF) were added and the reaction mixture was stirred for another 16 h at 50 °C. Purification by flash column chromatography on silica gel (2 × 12 cm, cyclohexane/*t*BME = 50:1) afforded **10l** (74.0 mg, 0.29 mmol, 73%) as colorless oil containing 14% of starting material. $\mathbf{R_f}$ = 0.46 (SiO_2, cyclohexane/*t*BME = 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.03 (t, $^3J_{1,2}$ = 7.0 Hz, 3H, H-1), 1.31 (d, $^3J_{4,5}$ = 8.0 Hz, 2H, H-4), 4.00 (m_c, 2H, H-2), 4.47 (t, $^3J_{5,4}$ = 8.0 Hz, 1H, H-5), 7.10 (m_c, 2H, H-9), 7.16-7.24 (m, 8H, H-7, H-8) ppm. The ^{1}H NMR spectra contains 14% of starting material. **^{13}C-NMR** (126 MHz, $CDCl_3$): δ = 14.0 (C-1), 40.8 (C-4), 47.1 (C-5), 60.3 (C-2), 126.5 (C-9), 127.7 (C-7)*, 128.5 (C-8)*, 143.5 (C-6), 171.8 (C-3) ppm. **HRMS (APCI)** calcd. for $C_{17}H_{18}O_2^+$ [(M^+)]: 254.1307, found: 254.1255.

The spectroscopic data is in agreement with literature.[25]

7.6 Synthesis of ammonia borane

$H_3N{\bullet}BH_3$

NBH_6
M_w = 30.87 g/mol

According to a modified literature procedure,[26] in a 500 mL round bottom flask with a condenser, sodium borohydride (4.58 g, 0.12 mol, 1.01 equiv.) was suspended in THF (165 mL) and heated to 35 °C und nitrogen atmosphere. Ammonium carbonate (11.5 g, 0.12 mol, 1.00 equiv.) was added to the reaction mixture over 1 h at 35 °C under vigorous stirring. After complete addition the reaction mixture was slowly heated to 60 °C (10 °C/h). After the reaction mixture reached 60 °C, it was stirred for 12 h to give a white suspension. The reaction mixture was cooled to rt and the solid byproduct was filtered to give a clear solution. The mother liquor was heated to 35 °C and aq. NaOH (32 g, 18.5% w/w) was added and stirred for 10 min. The layers were separated and THF was removed under reduced pressure until 5 mL of solution were left. After addition of *n*-pentane (100 mL) ammonia borane precipitated, was filtered, washed with *n*-pentane (3 x 25 mL), dried under reduced pressure to give ammonia borane (1.96 g, 0.06 mol, 53%) as white crystalline solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.41 (m_c, 3H, B-H), 3.98 (m_c, 3H, N-H) ppm. **^{11}B NMR** (500 MHz, $CDCl_3$): δ = -22.2 ppm.

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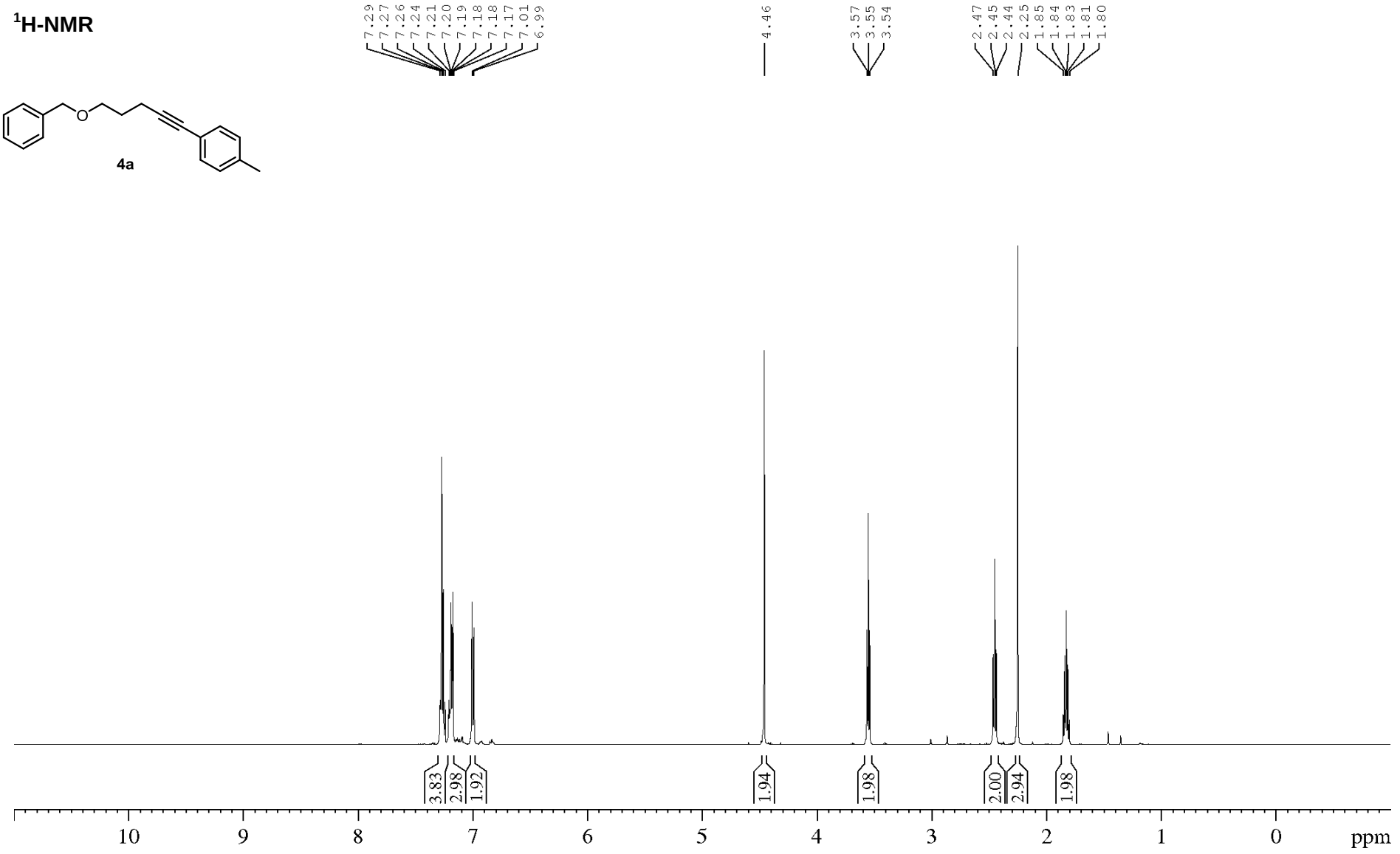
9 Spectra

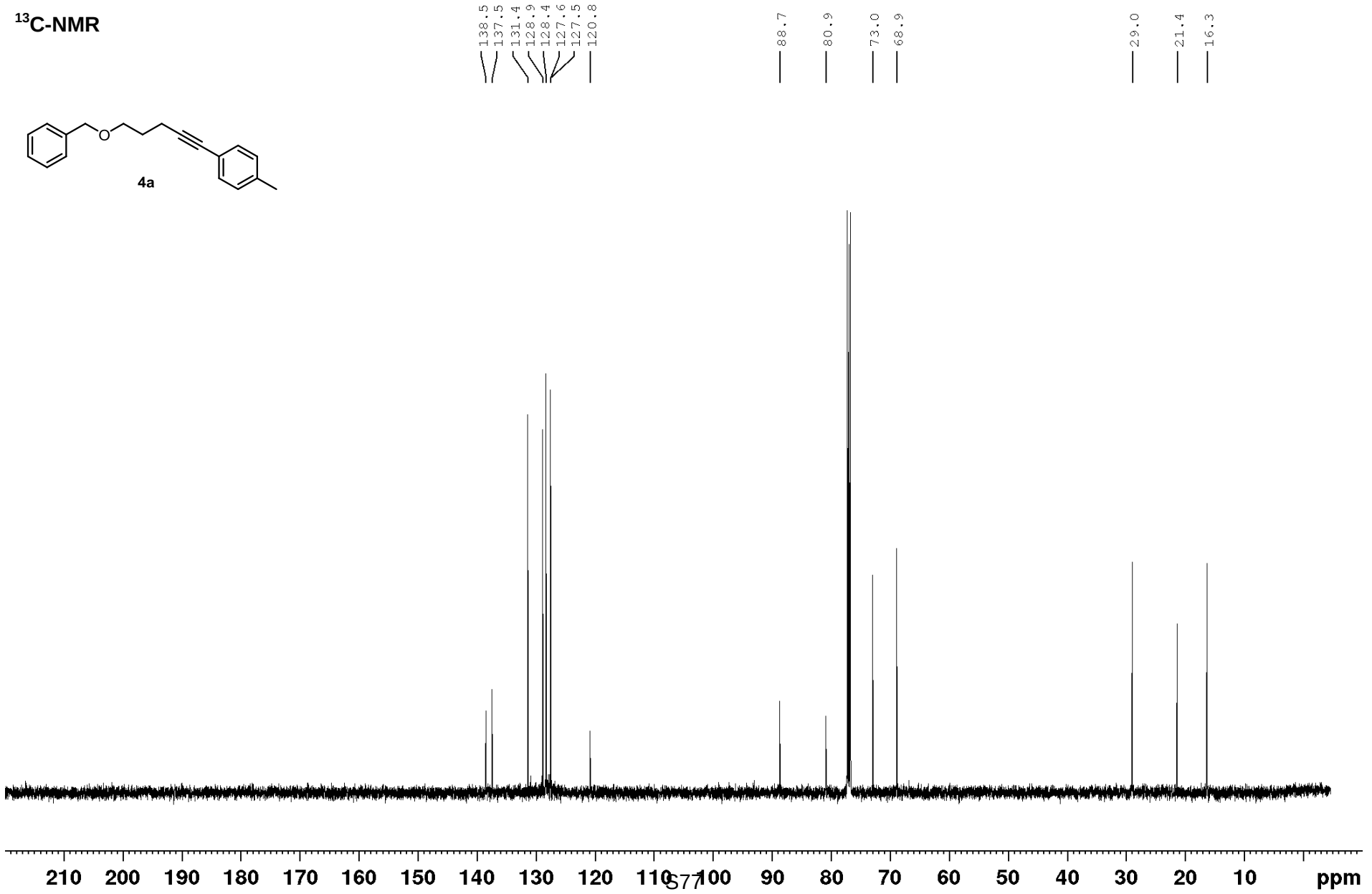
^{1}H-NMR

4a


7.29
7.27
7.26
7.24
7.21
7.20
7.19
7.18
7.18
7.17
7.01
6.99
4.46
3.57
3.55
3.54
2.47
2.45
2.44
2.25
1.85
1.84
1.83
1.81
1.80
3.83
2.98
1.92
1.94
1.98
2.00
2.94
1.98
10
9
8
7
6
5
4
3
2
1
0
ppm

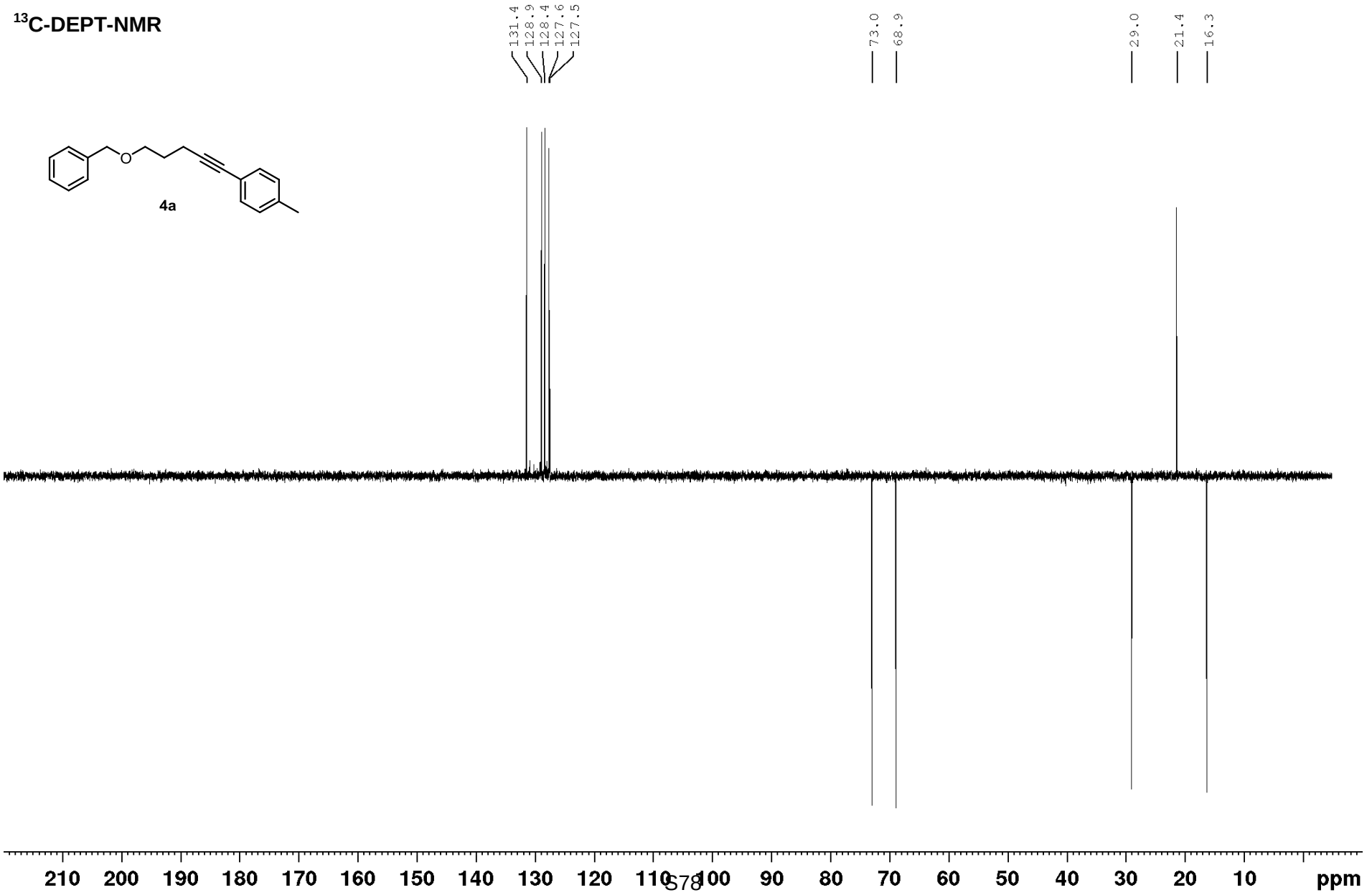
^{13}C-NMR

4a

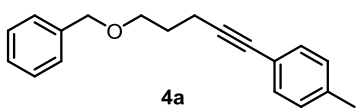

138.5
137.5
131.4
128.9
128.4
127.6
127.5
120.8
88.7
80.9
73.0
68.9
29.0
21.4
16.3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{13}C-DEPT-NMR

4a



^{1}H, ^{1}H COSY



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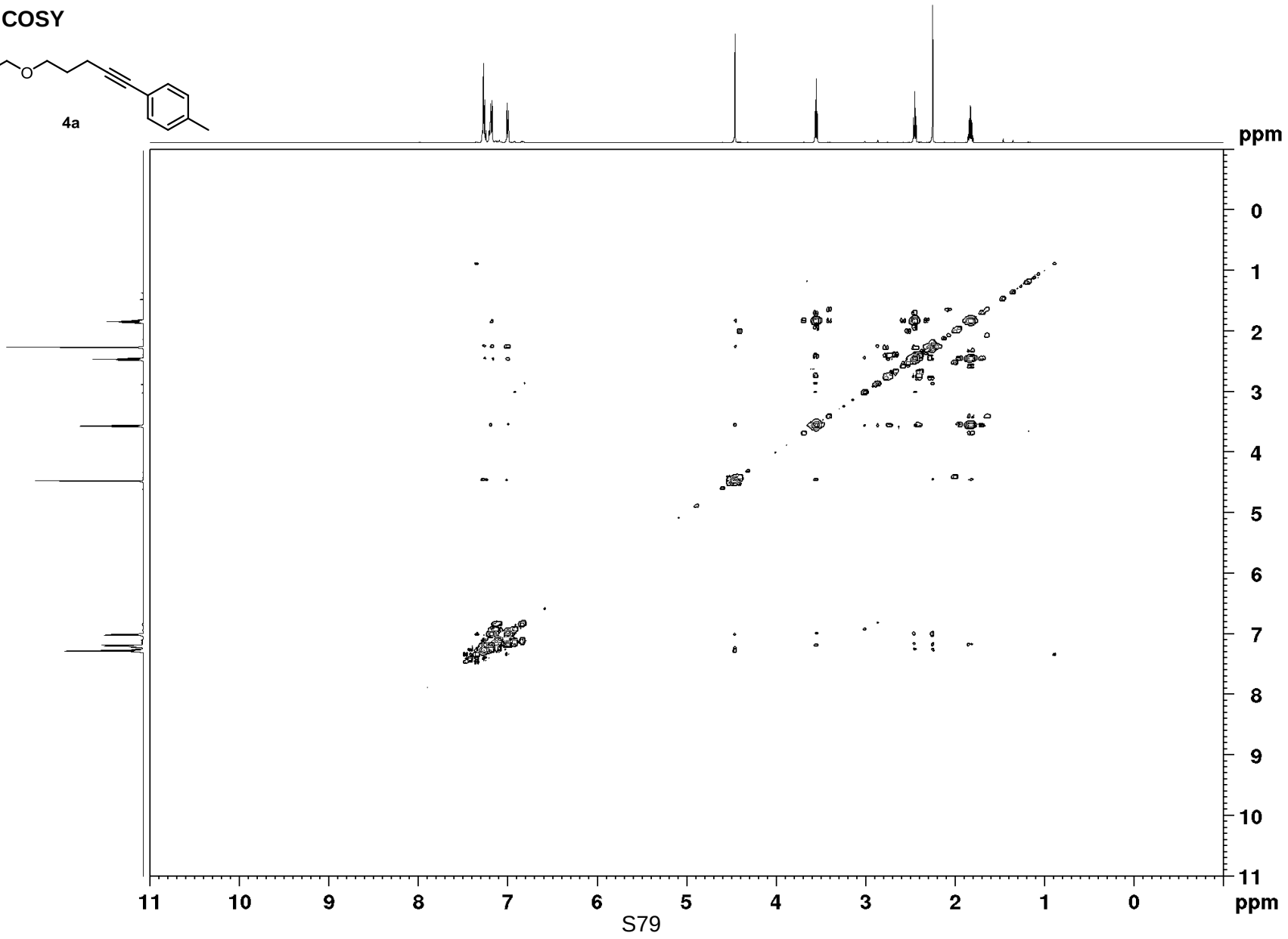
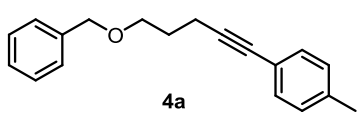
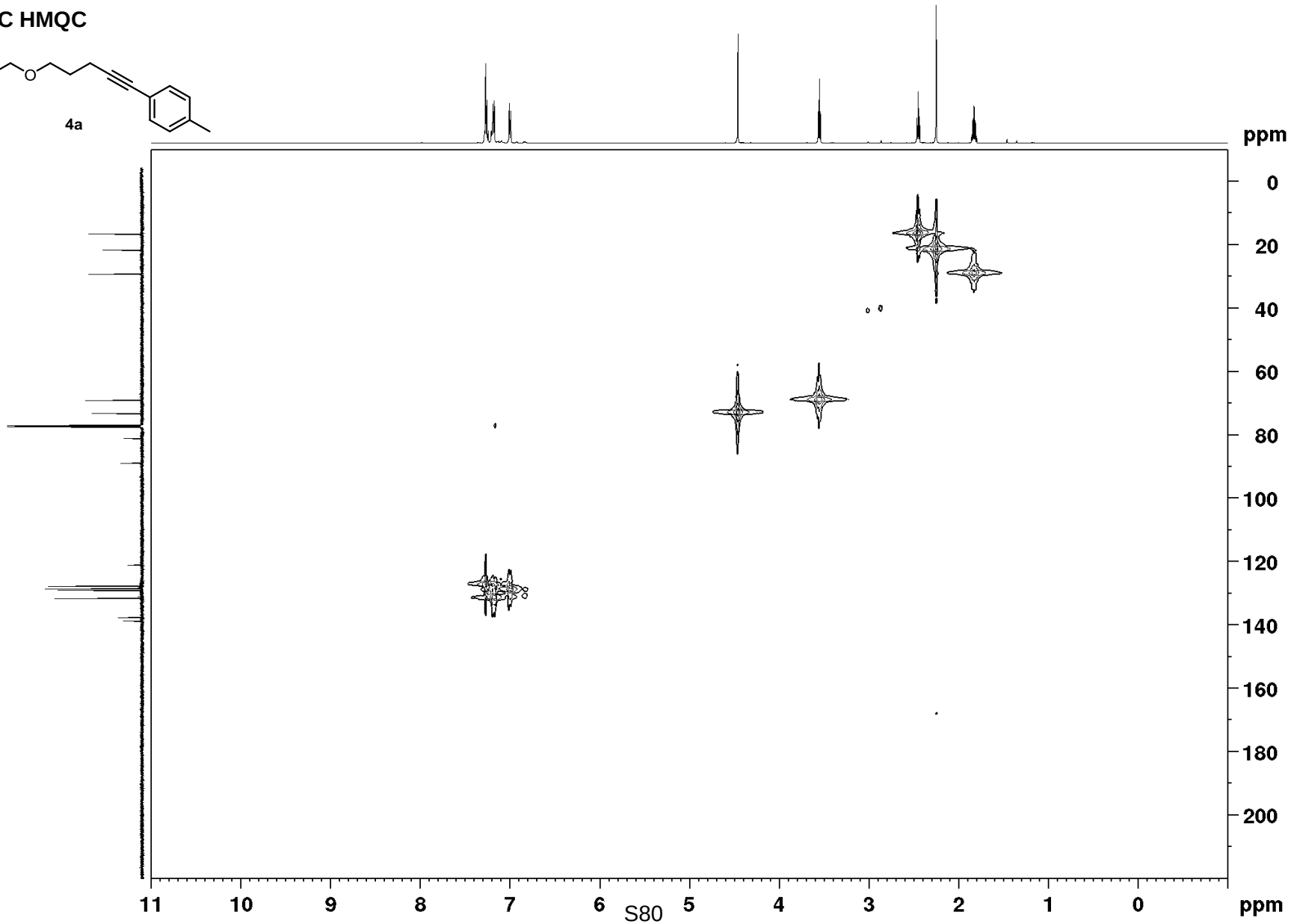


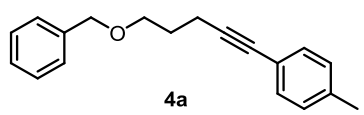
^{1}H, ^{13}C HMQC



4a



^{1}H, ^{13}C HMBC



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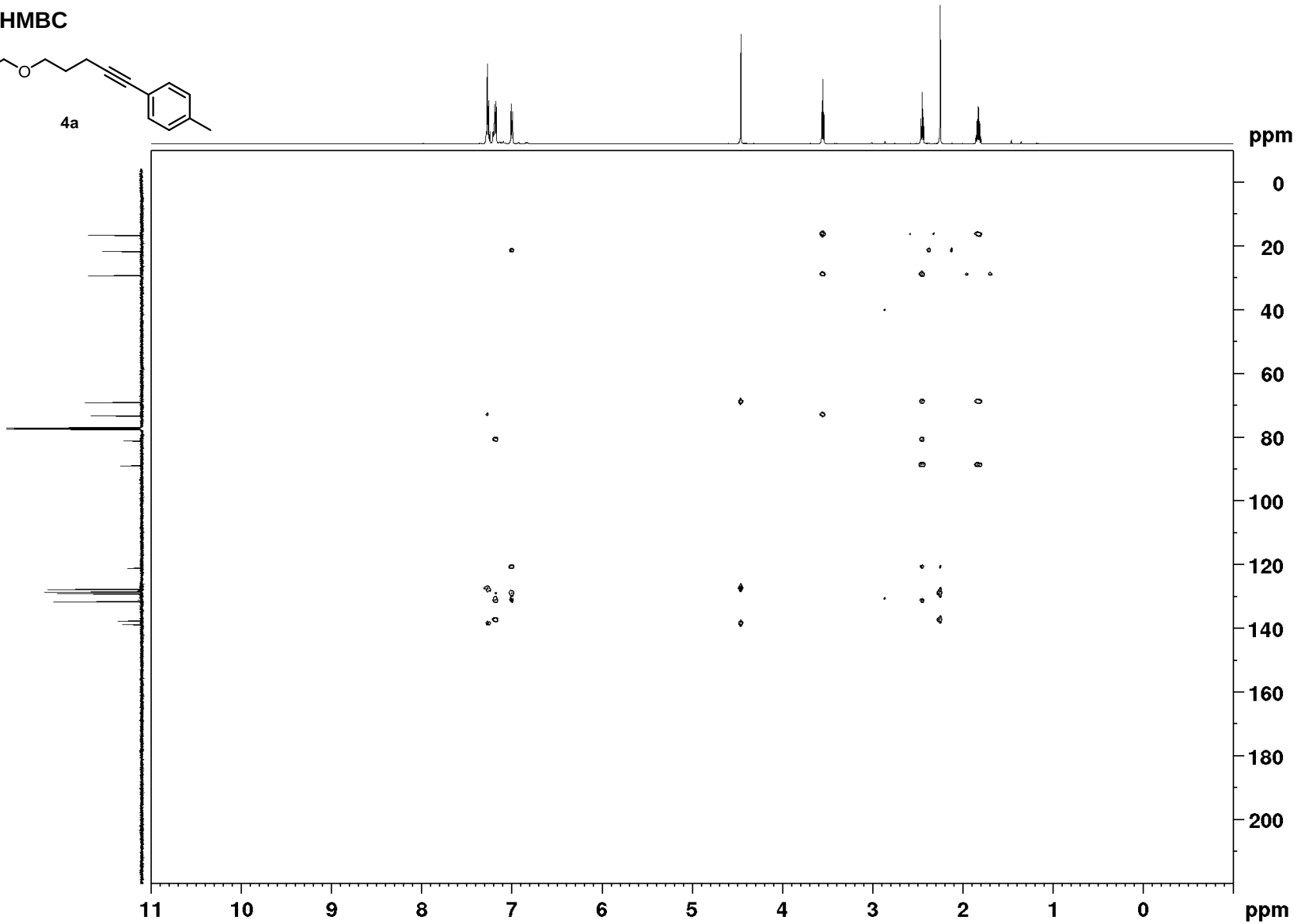
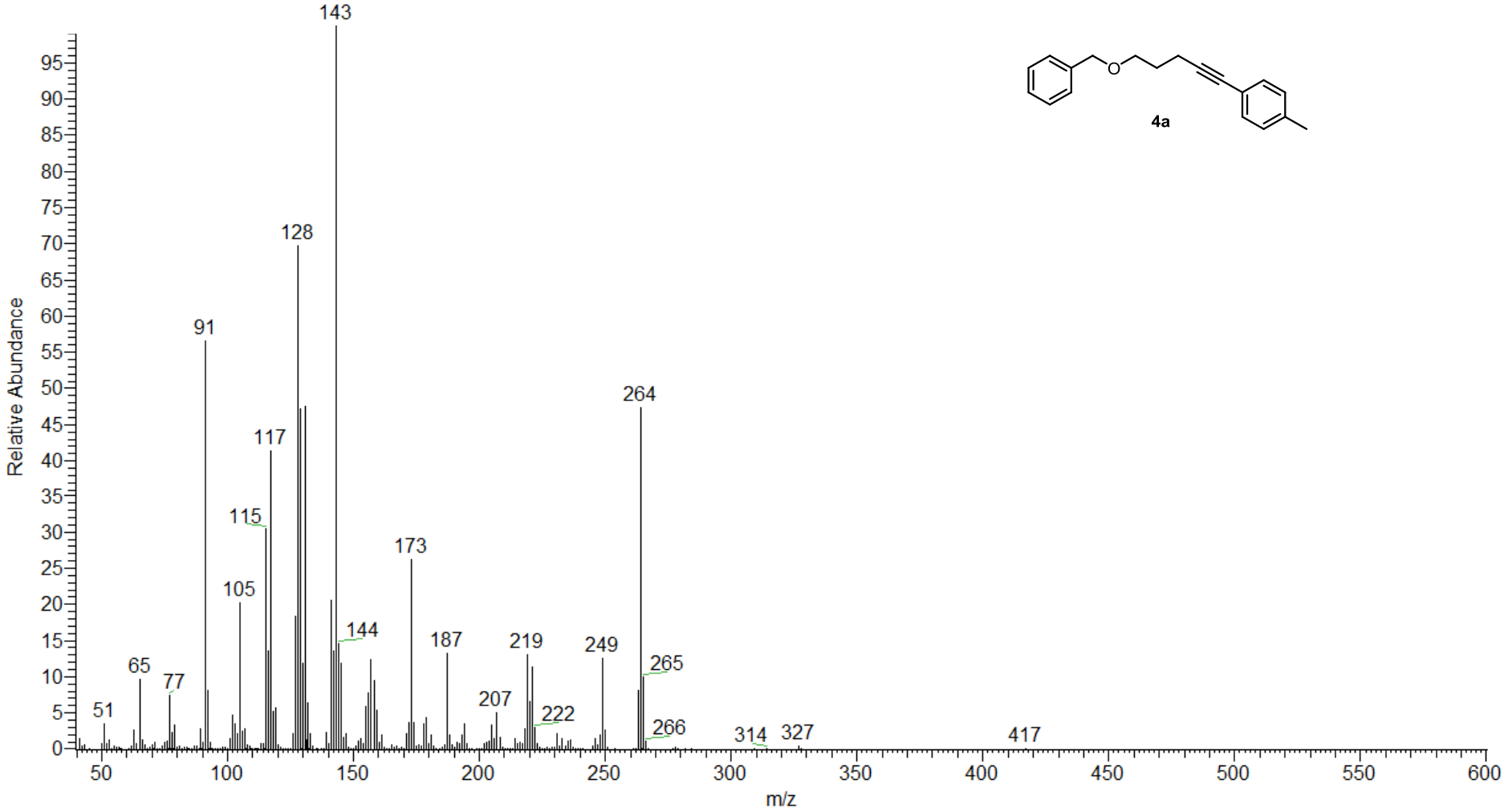
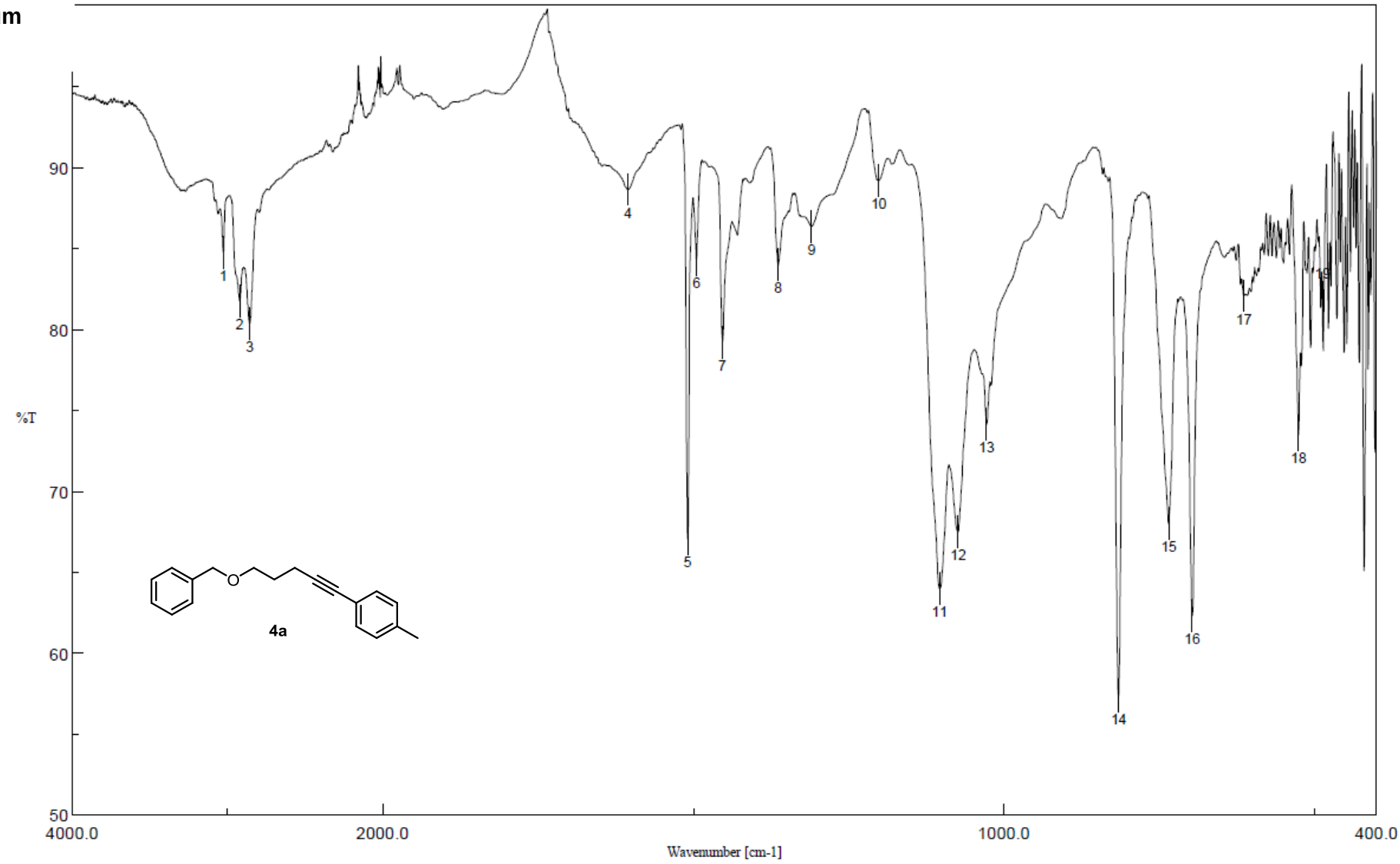


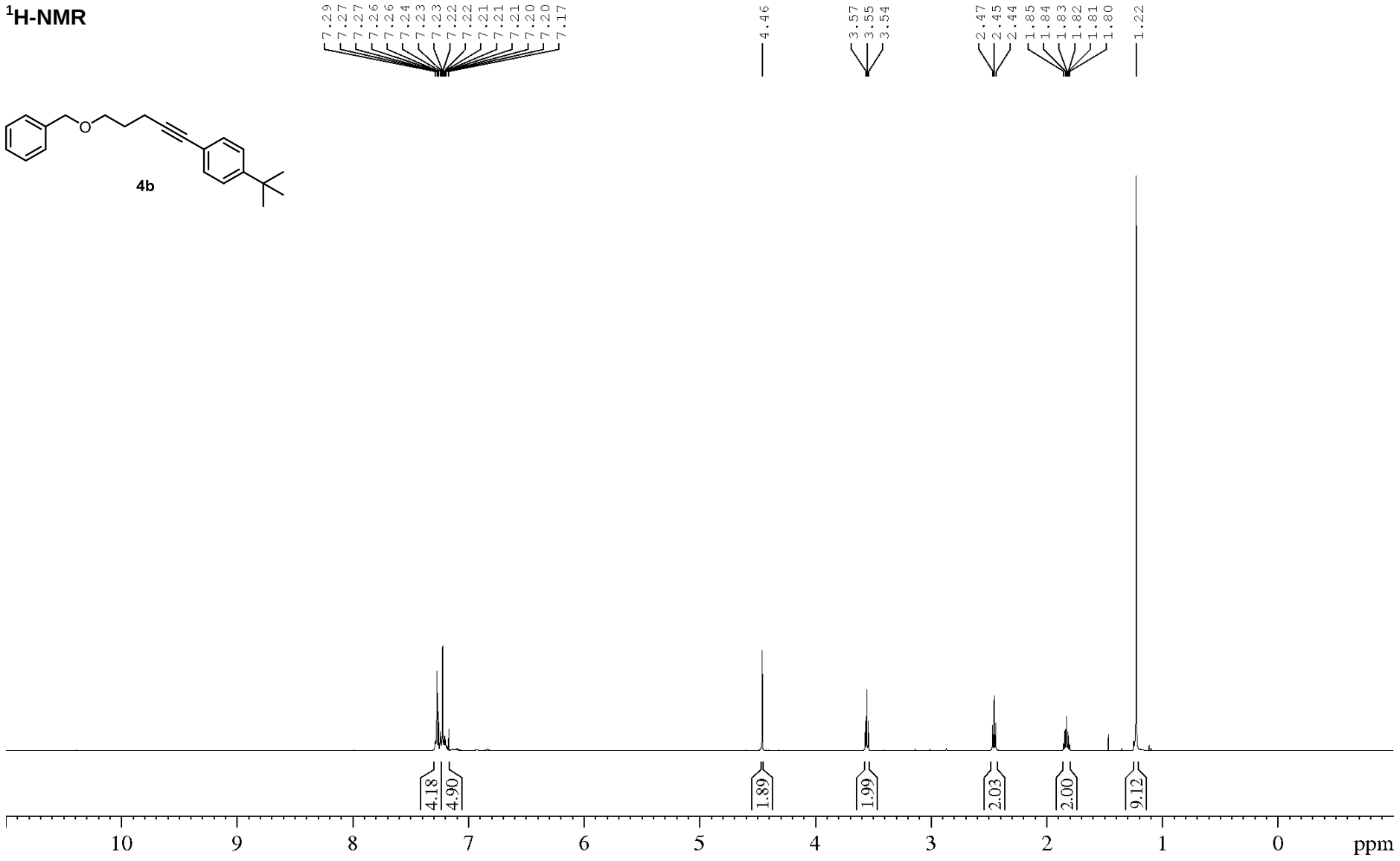
mass spectrum



IR spectrum

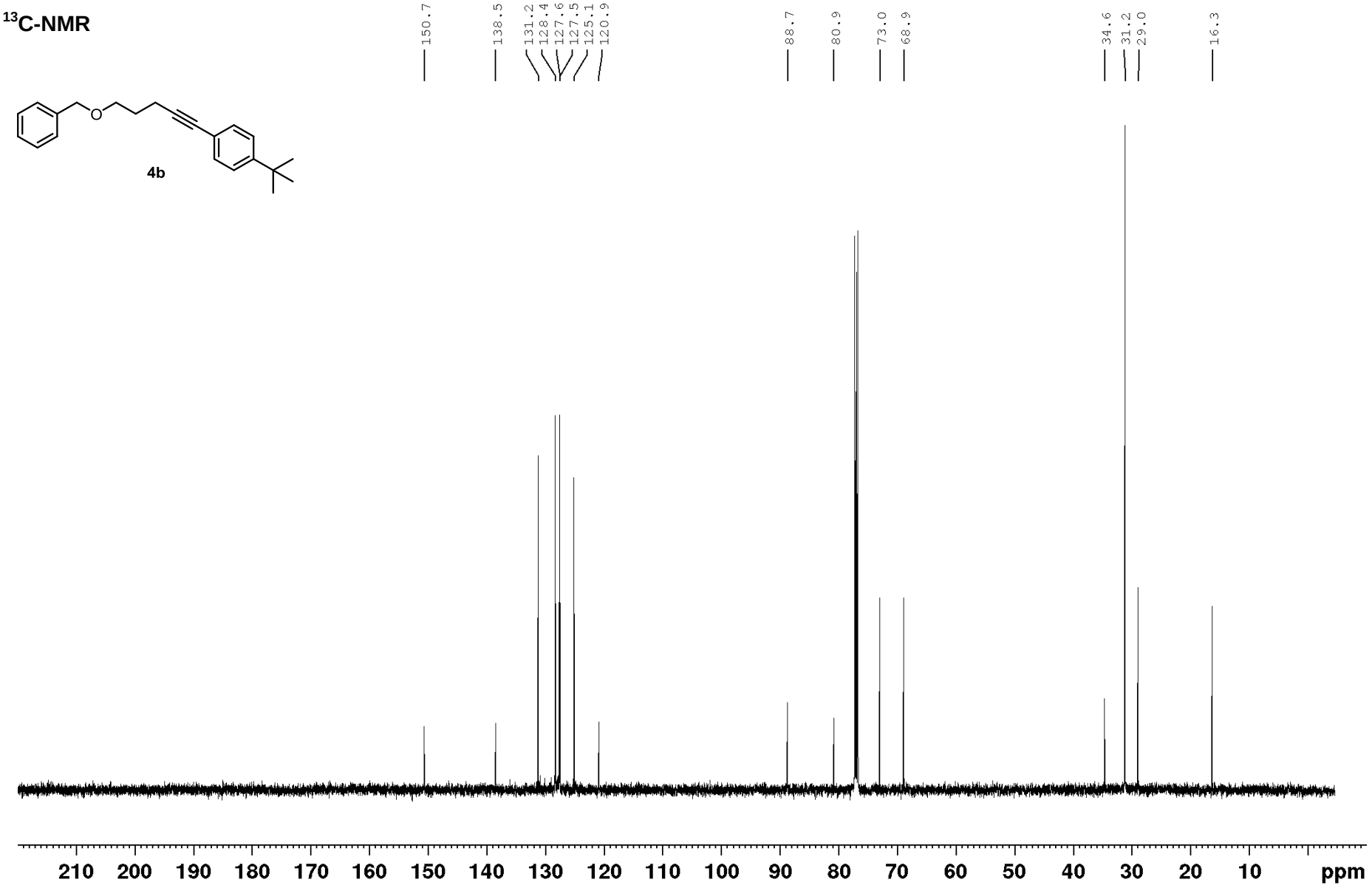

%T
90
80
70
60
50
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
O
4a

[1]H-NMR

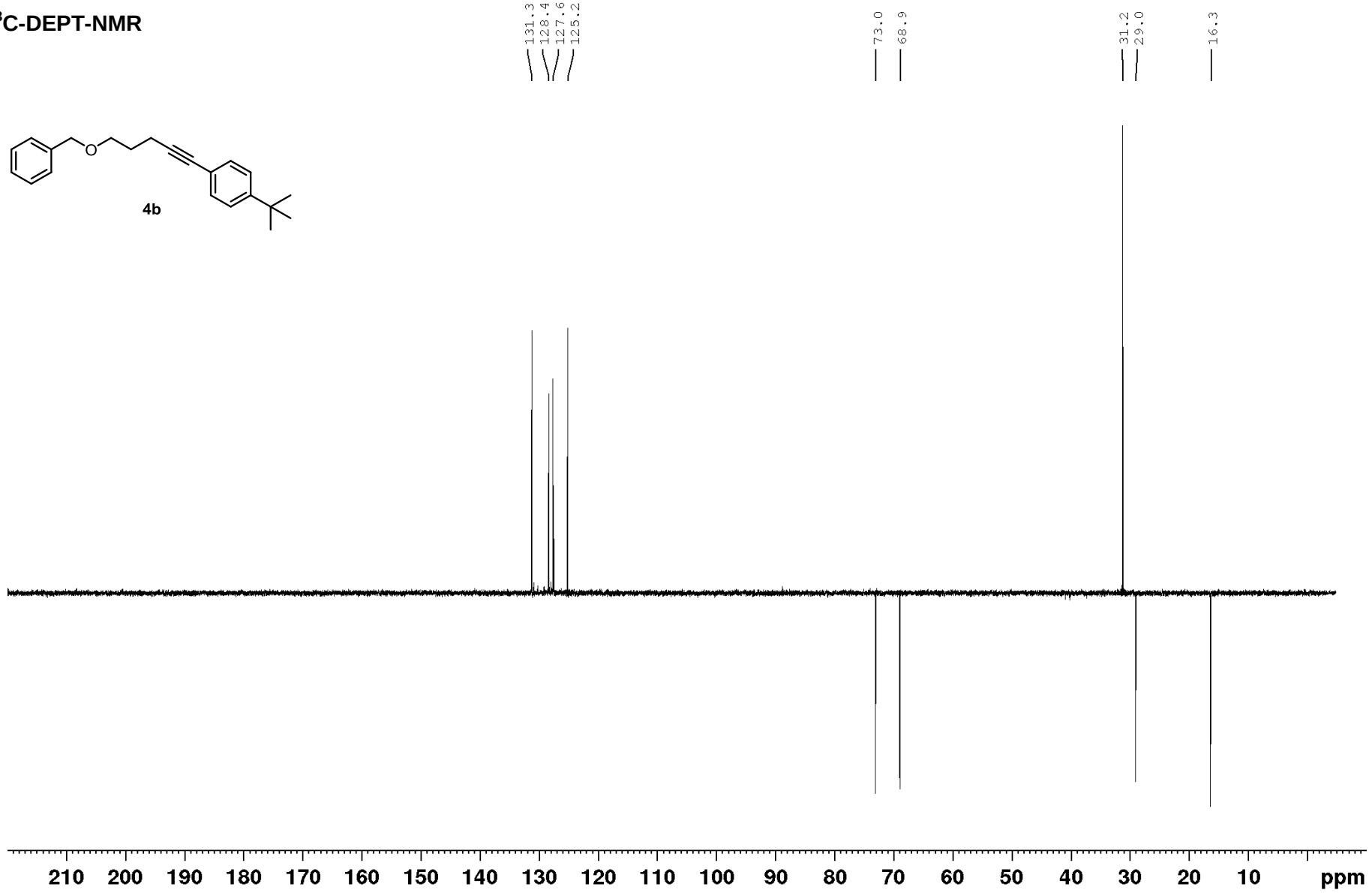

7.29
7.27
7.27
7.26
7.26
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.17
4.46
3.57
3.55
3.54
2.47
2.45
2.44
1.85
1.84
1.83
1.82
1.81
1.80
1.22
O
4b
4.18
4.90
1.89
1.99
2.03
2.00
9.12
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C-NMR

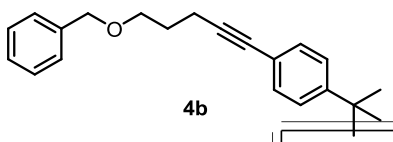
4b


150.7
138.5
131.2
128.4
127.6
127.5
125.1
120.9
88.7
80.9
73.0
68.9
34.6
31.2
29.0
16.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

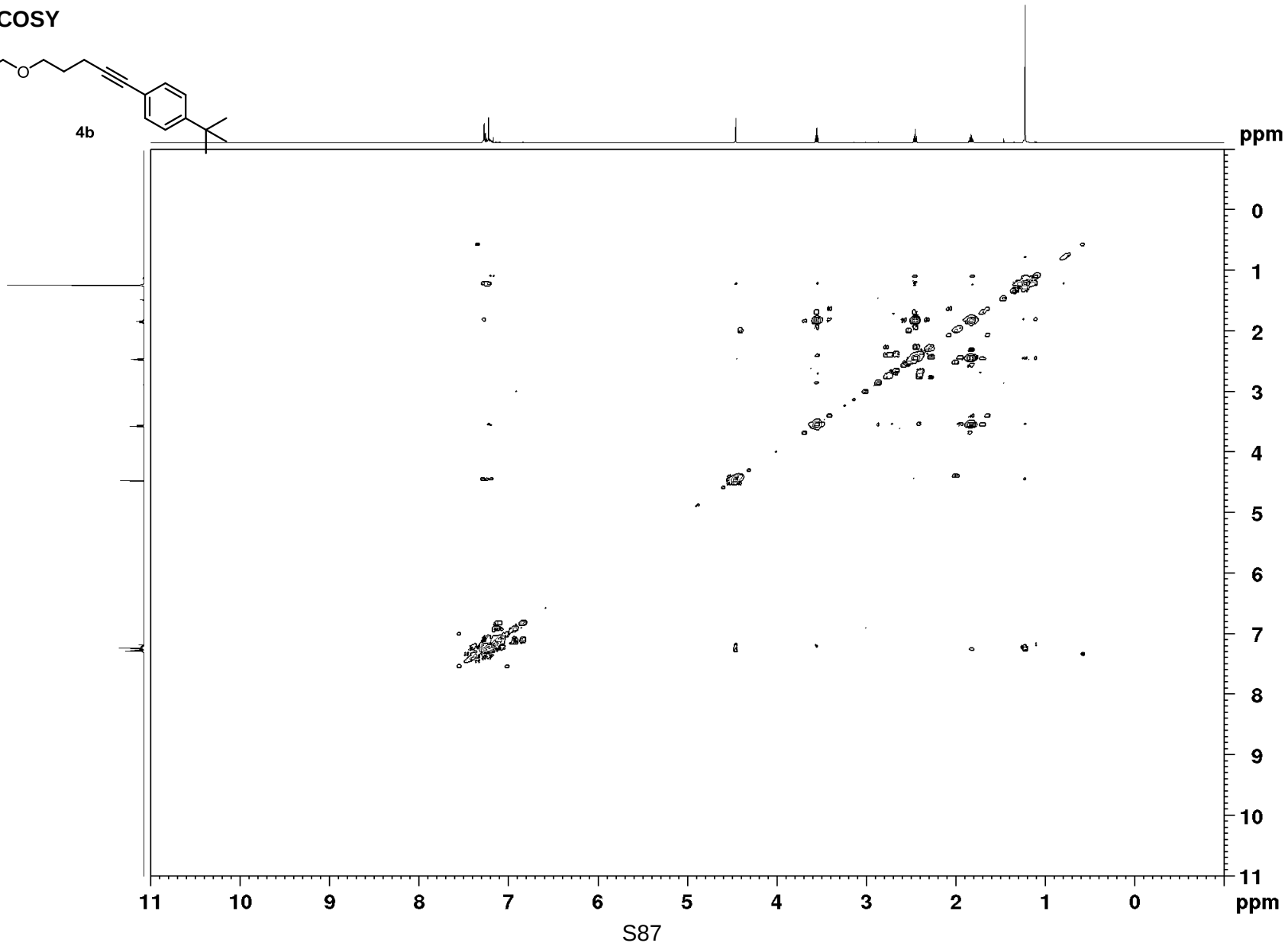
^{13}C-DEPT-NMR


131.3
128.4
127.6
125.2
73.0
68.9
31.2
29.0
16.3
O
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

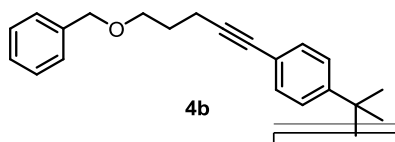
^{1}H, ^{1}H COSY



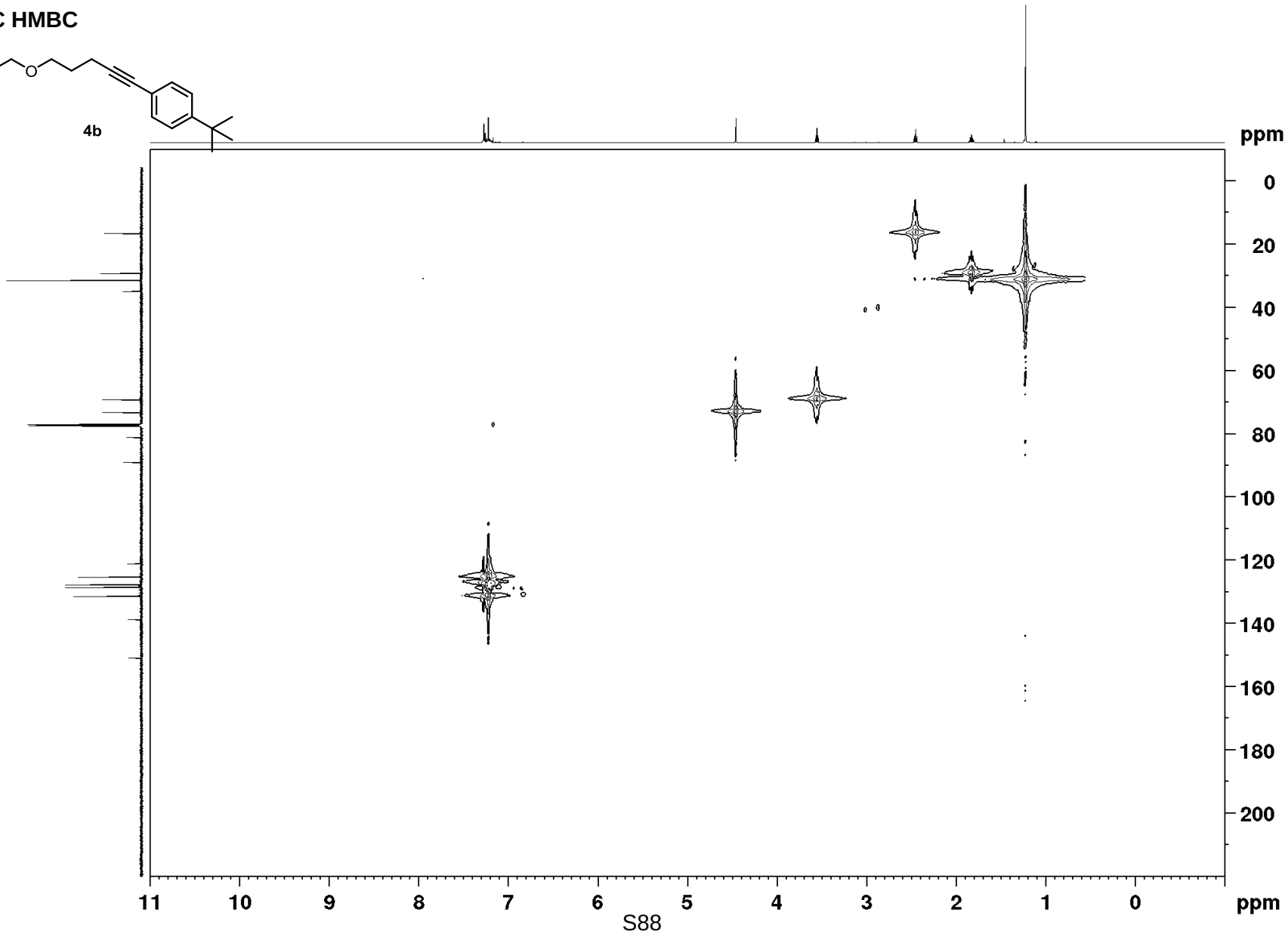
4b



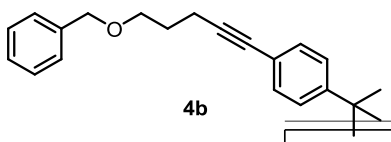
^{1}H, ^{13}C HMBC



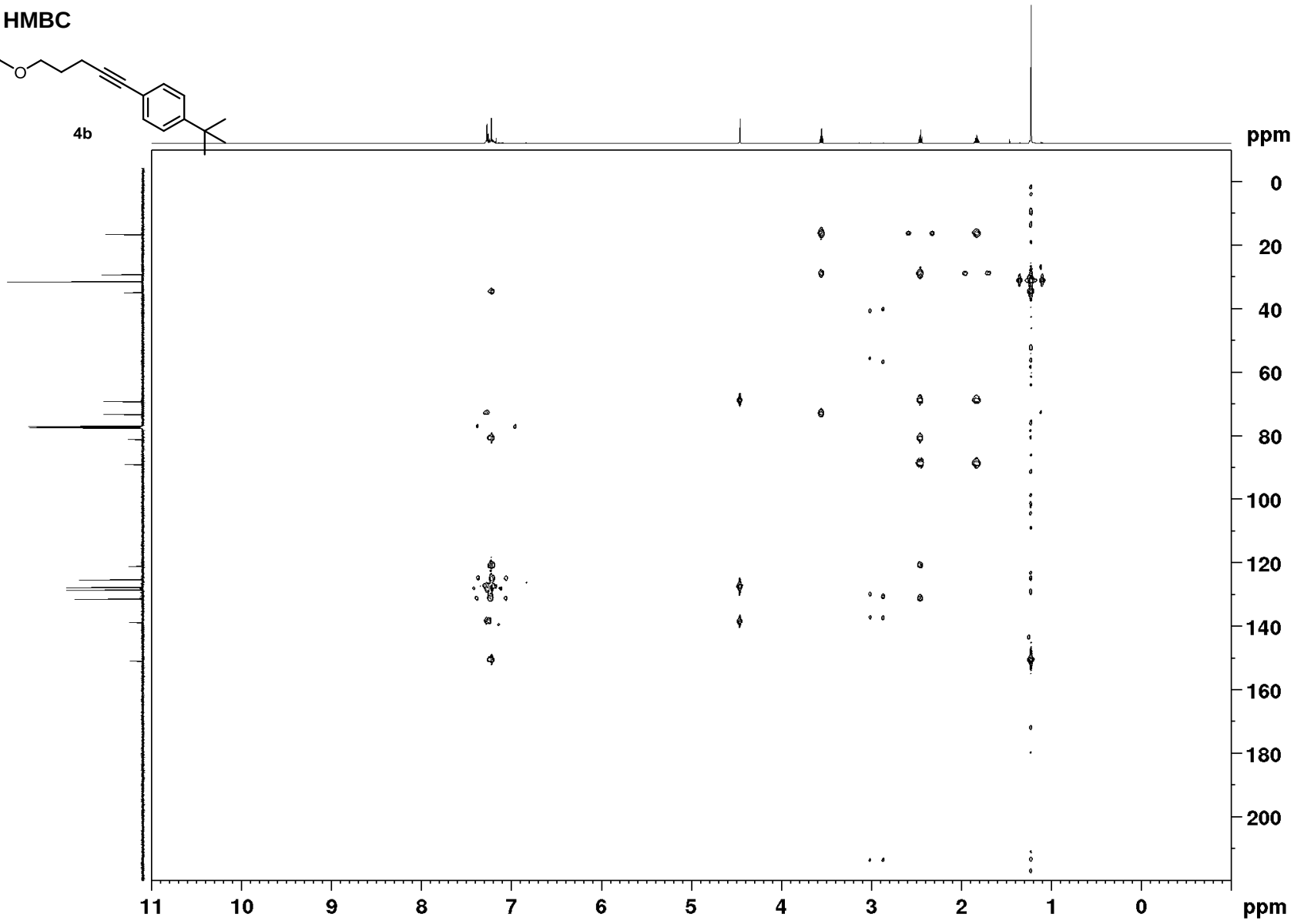
4b



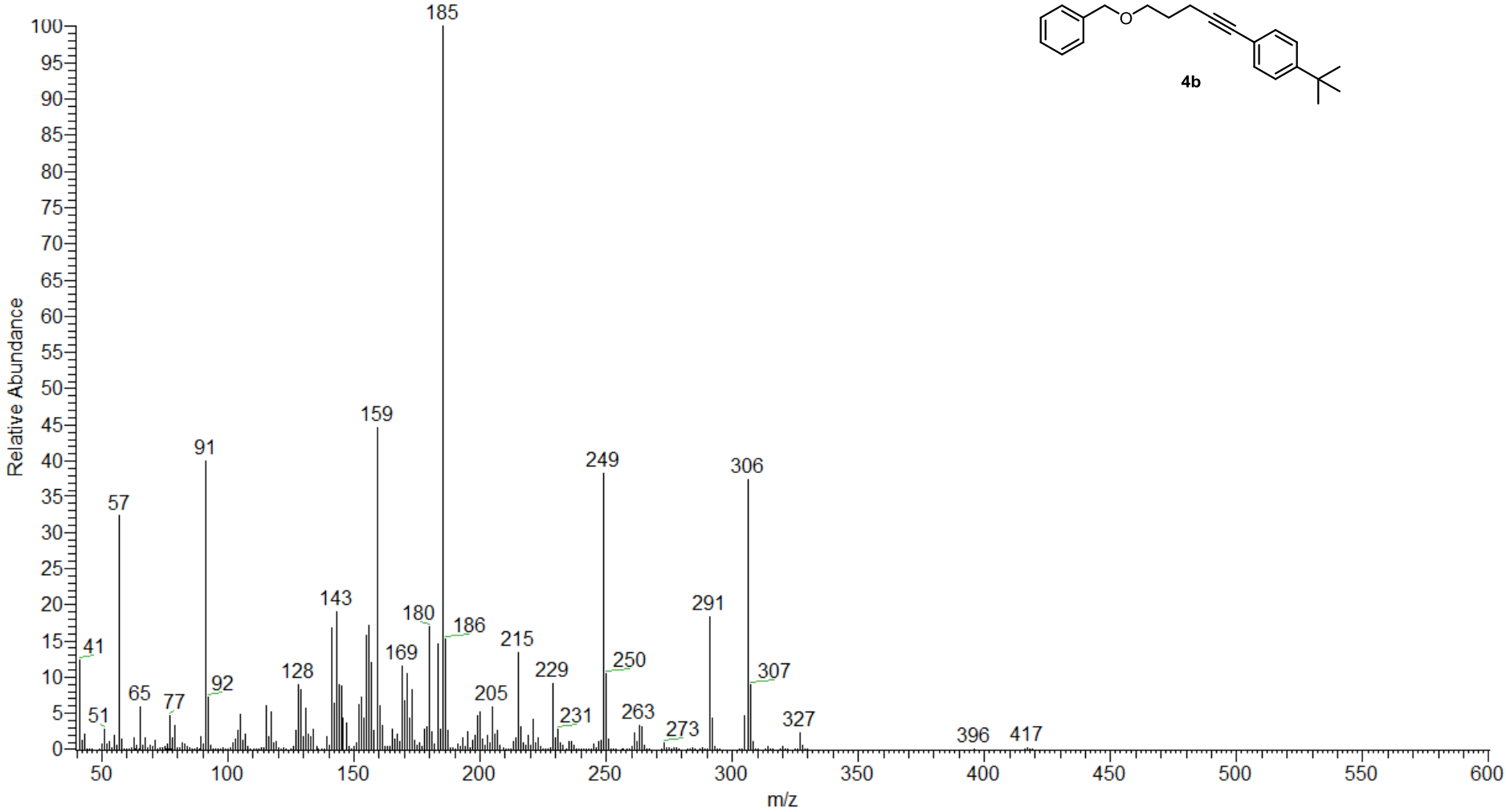
^{1}H, ^{13}C HMBC



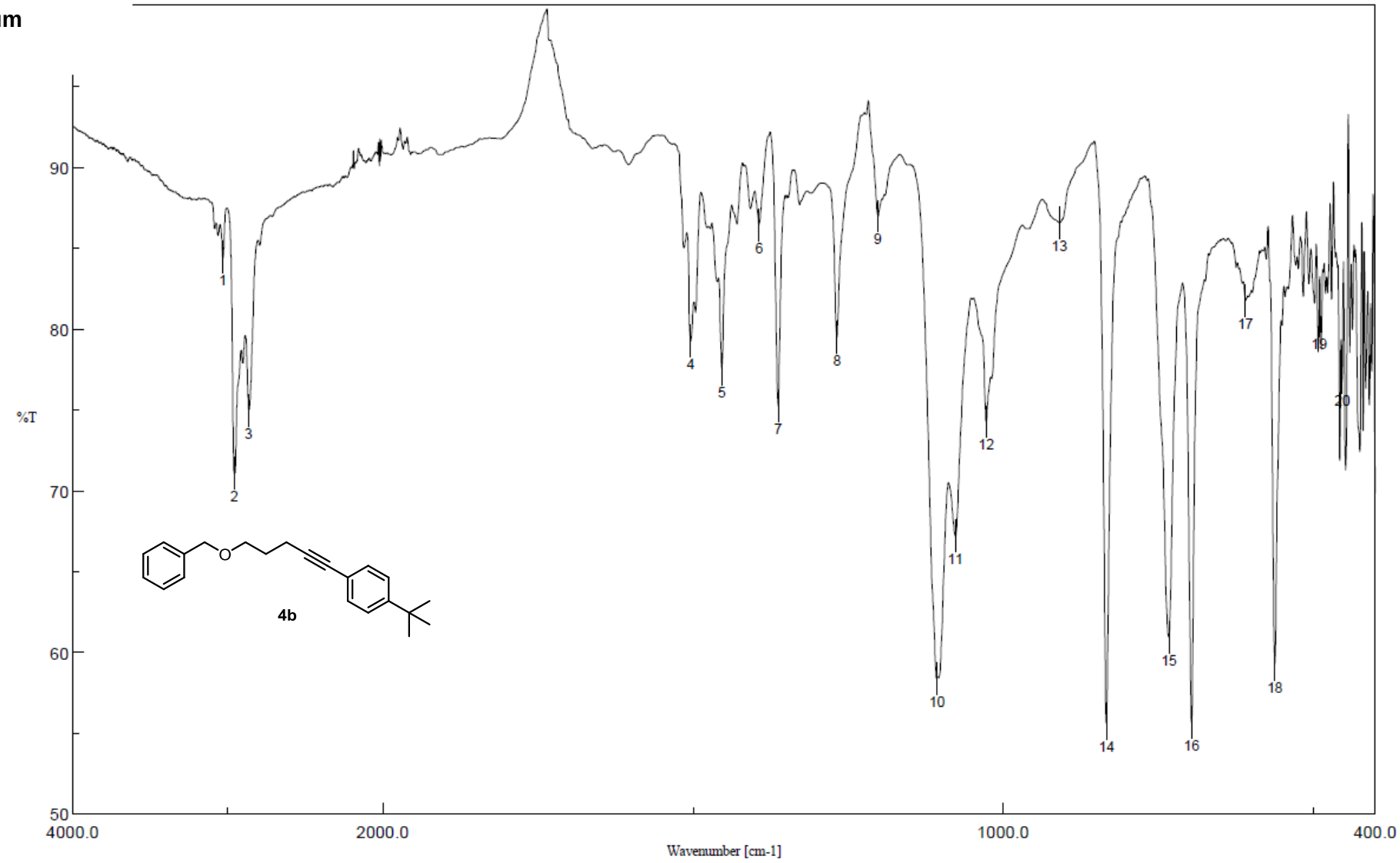
4b



mass spectrum

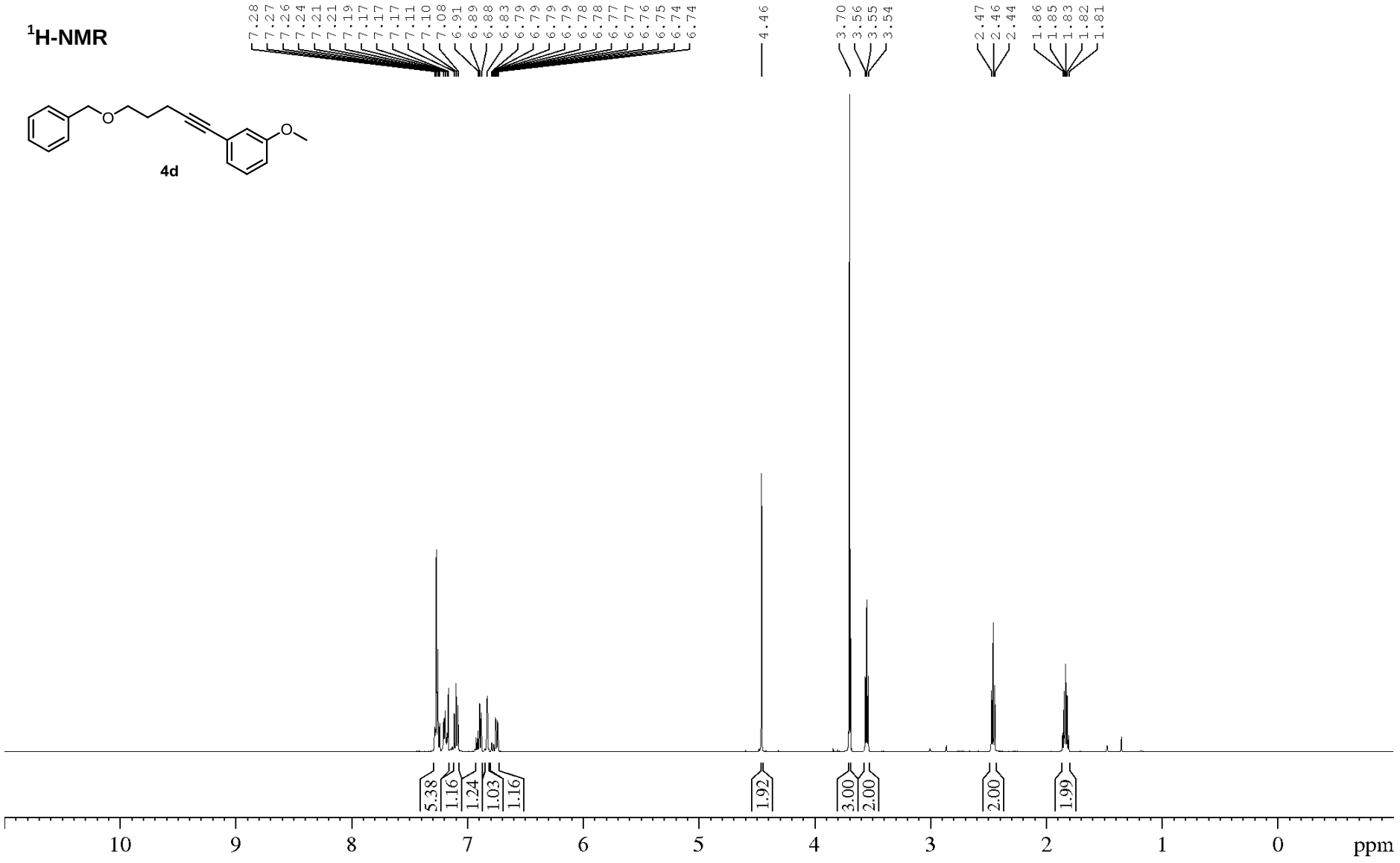


IR spectrum

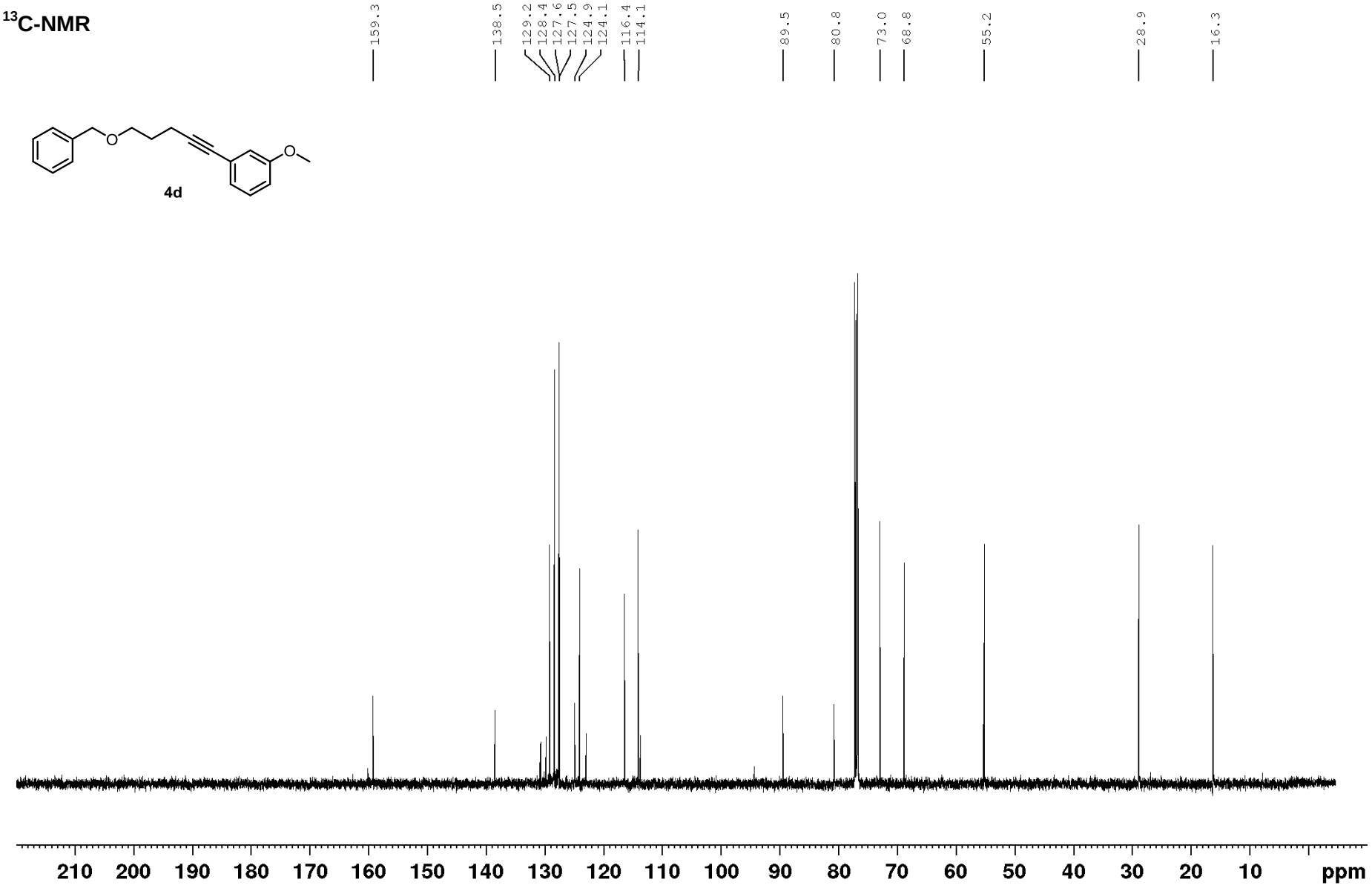

%T
90
80
70
60
50
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
O
4b

^{1}H-NMR

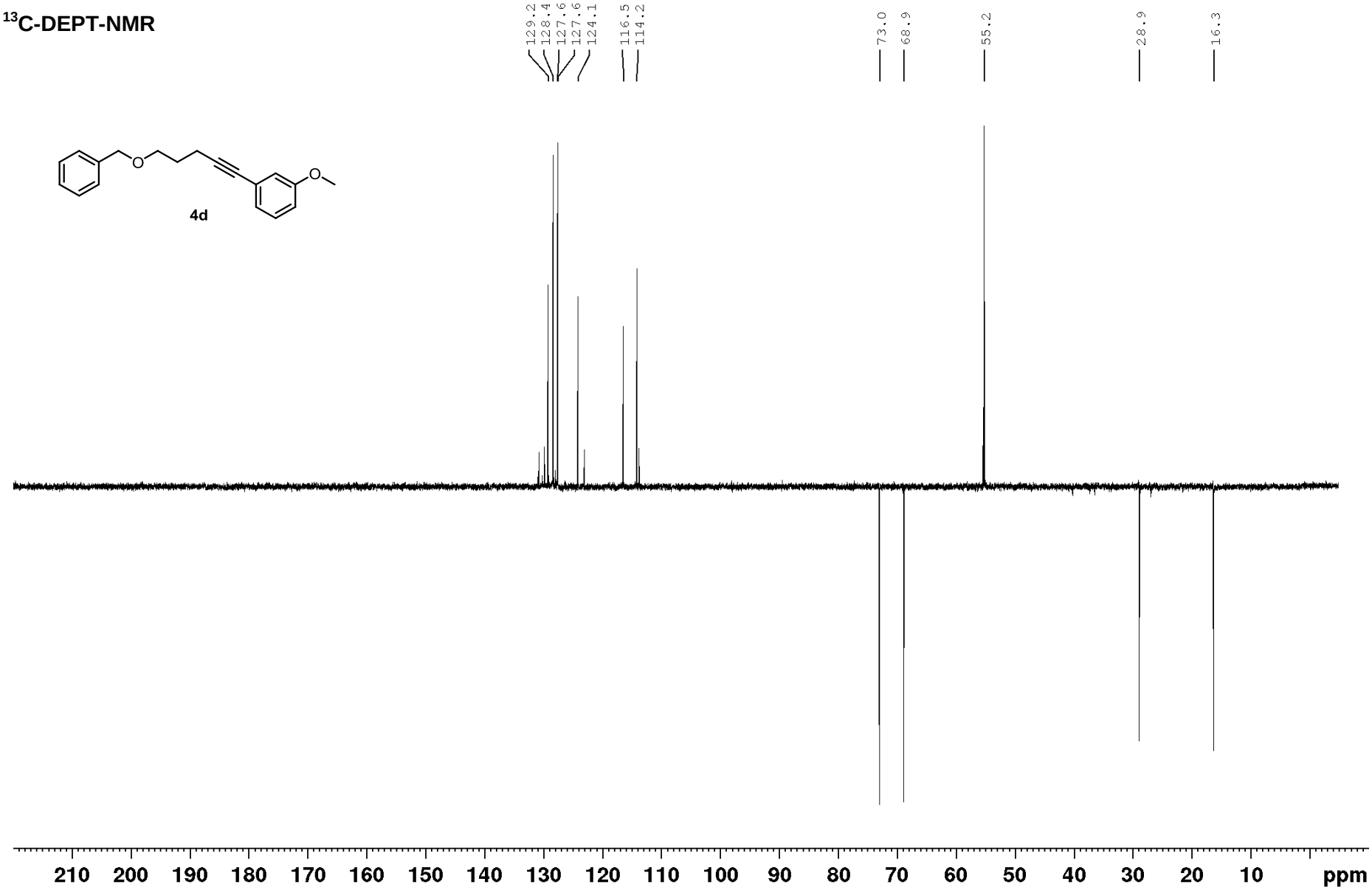
4d


7.28
7.27
7.26
7.24
7.21
7.21
7.19
7.17
7.17
7.17
7.11
7.10
7.08
6.91
6.89
6.88
6.83
6.79
6.79
6.79
6.79
6.78
6.78
6.77
6.77
6.76
6.75
6.74
6.74
4.46
3.70
3.56
3.55
3.54
2.47
2.46
2.44
1.86
1.85
1.83
1.82
1.81
5.38
1.16
1.24
1.03
1.16
1.92
3.00
2.00
2.00
1.99
10
9
8
7
6
5
4
3
2
1
0
ppm

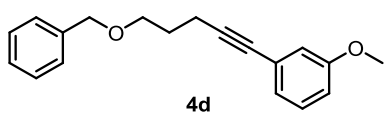
^{13}C-NMR


159.3
138.5
129.2
128.4
127.6
127.5
124.9
124.1
116.4
114.1
89.5
80.8
73.0
68.8
55.2
28.9
16.3
O
O
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

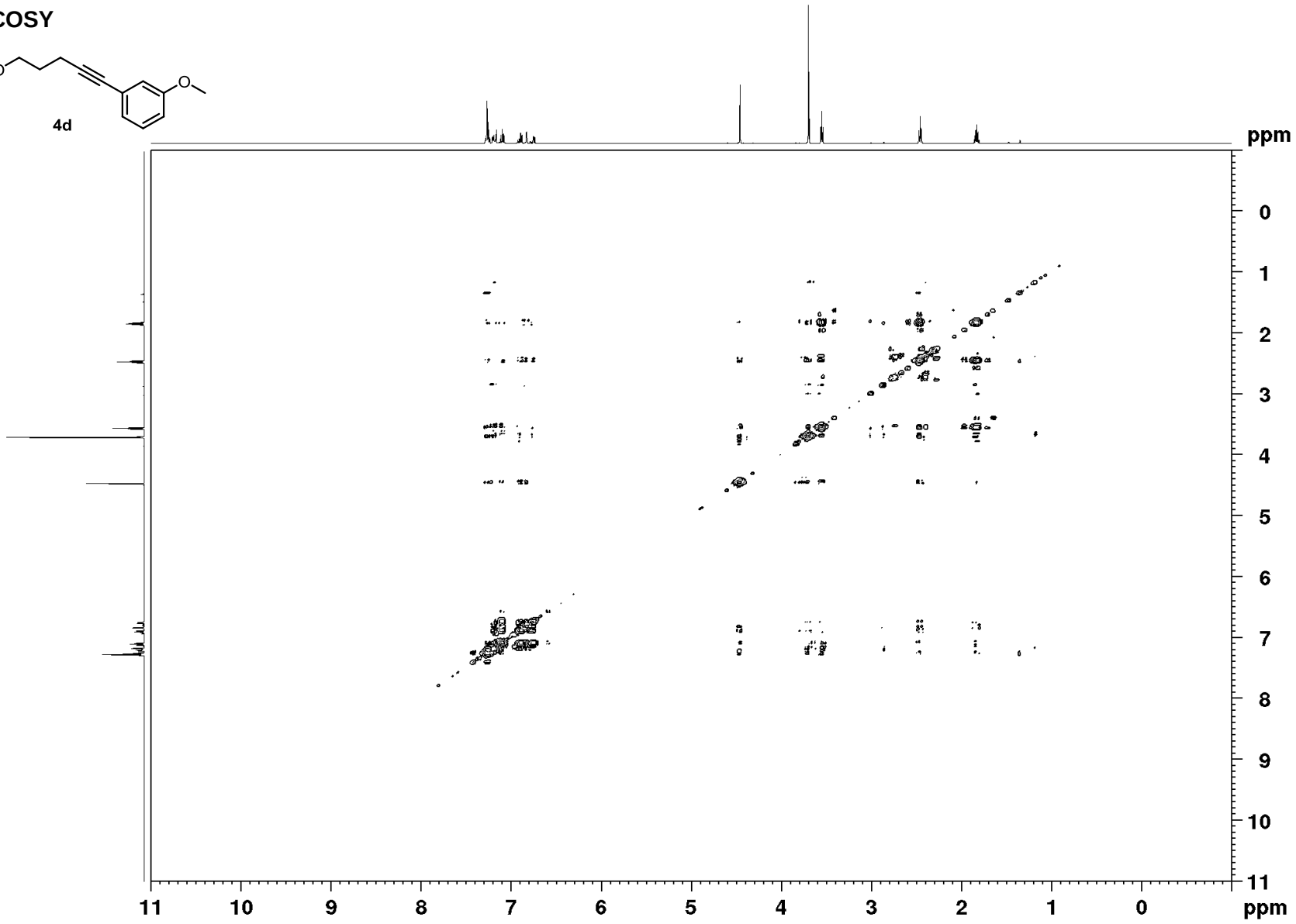
^{13}C-DEPT-NMR


129.2
128.4
127.6
127.6
124.1
116.5
114.2
73.0
68.9
55.2
28.9
16.3
O
O
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

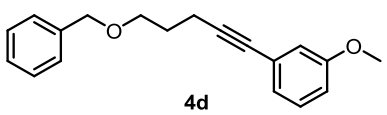
^{1}H, ^{1}H COSY



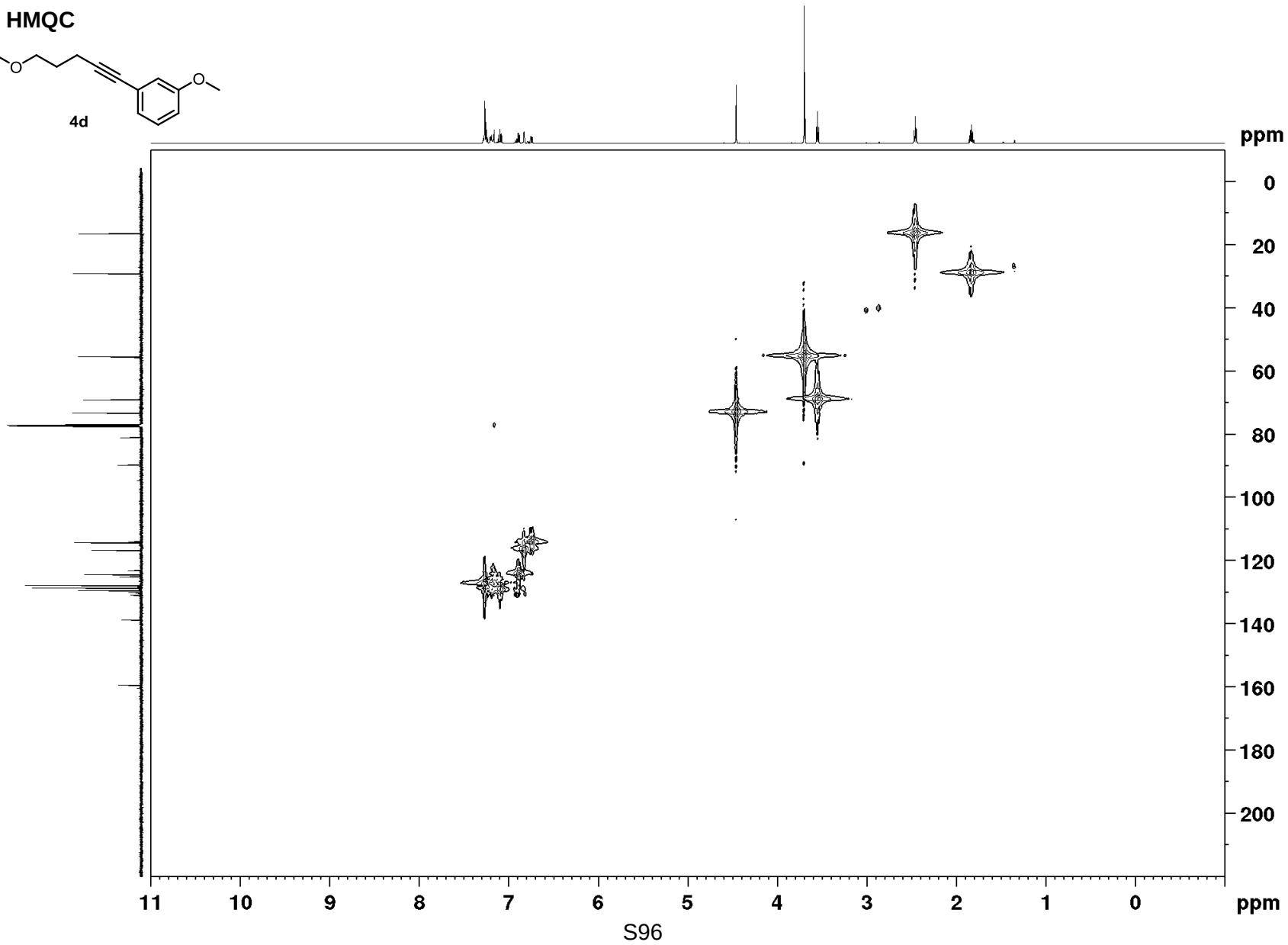
4d



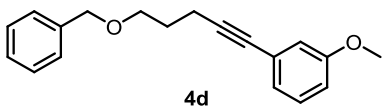
^{1}H, ^{13}C HMQC



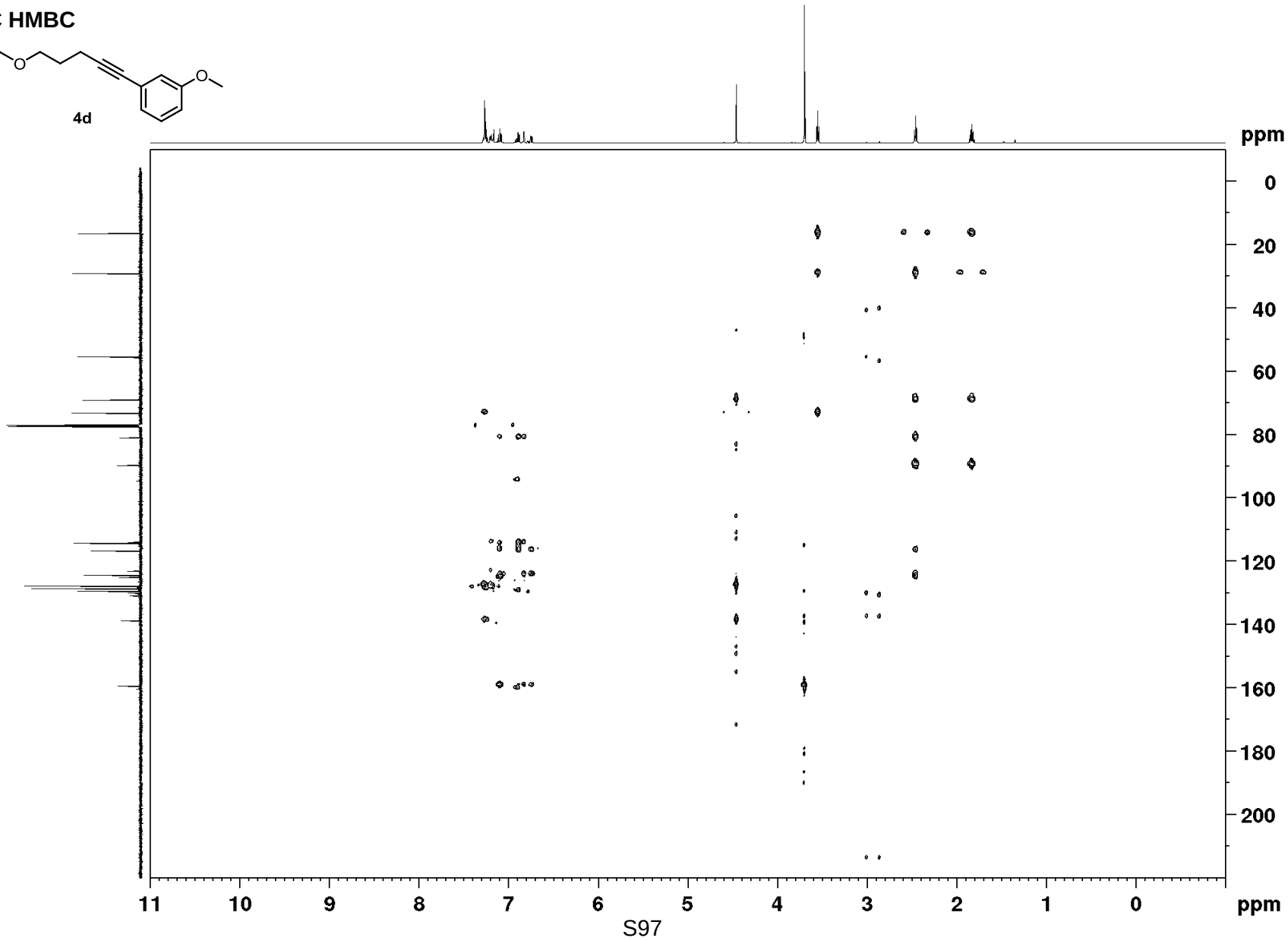
4d



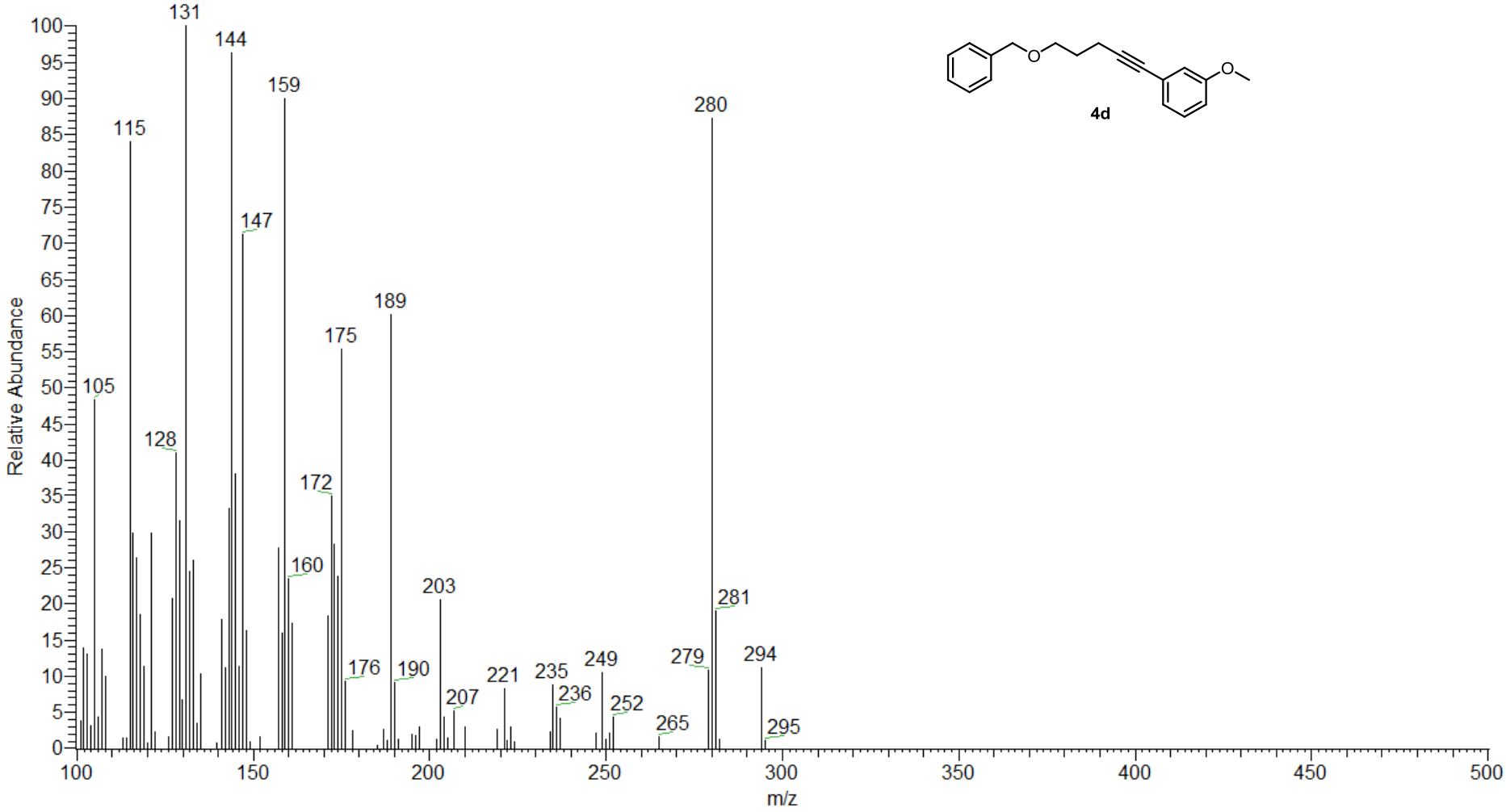
^{1}H, ^{13}C HMBC



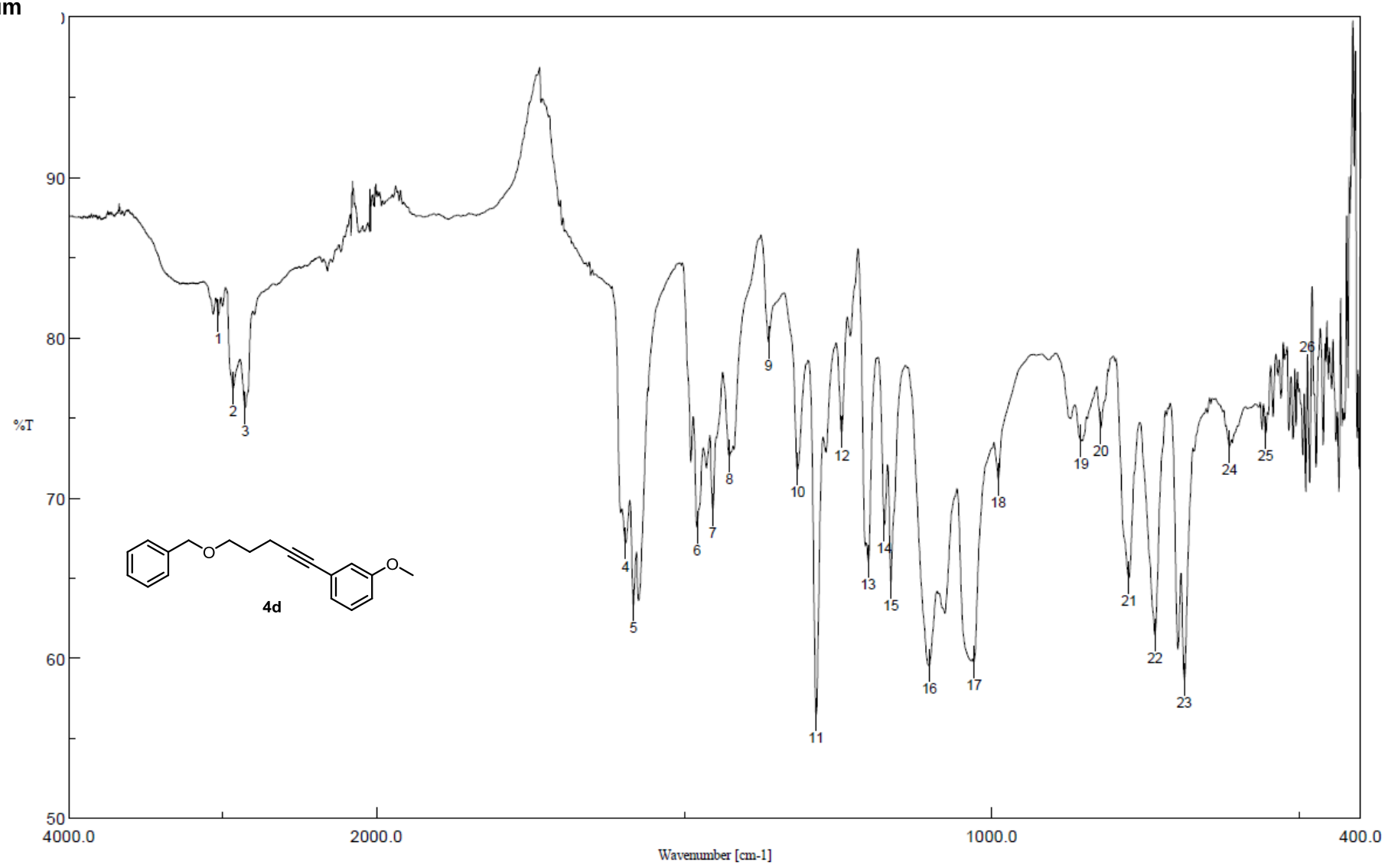
4d



mass spectra

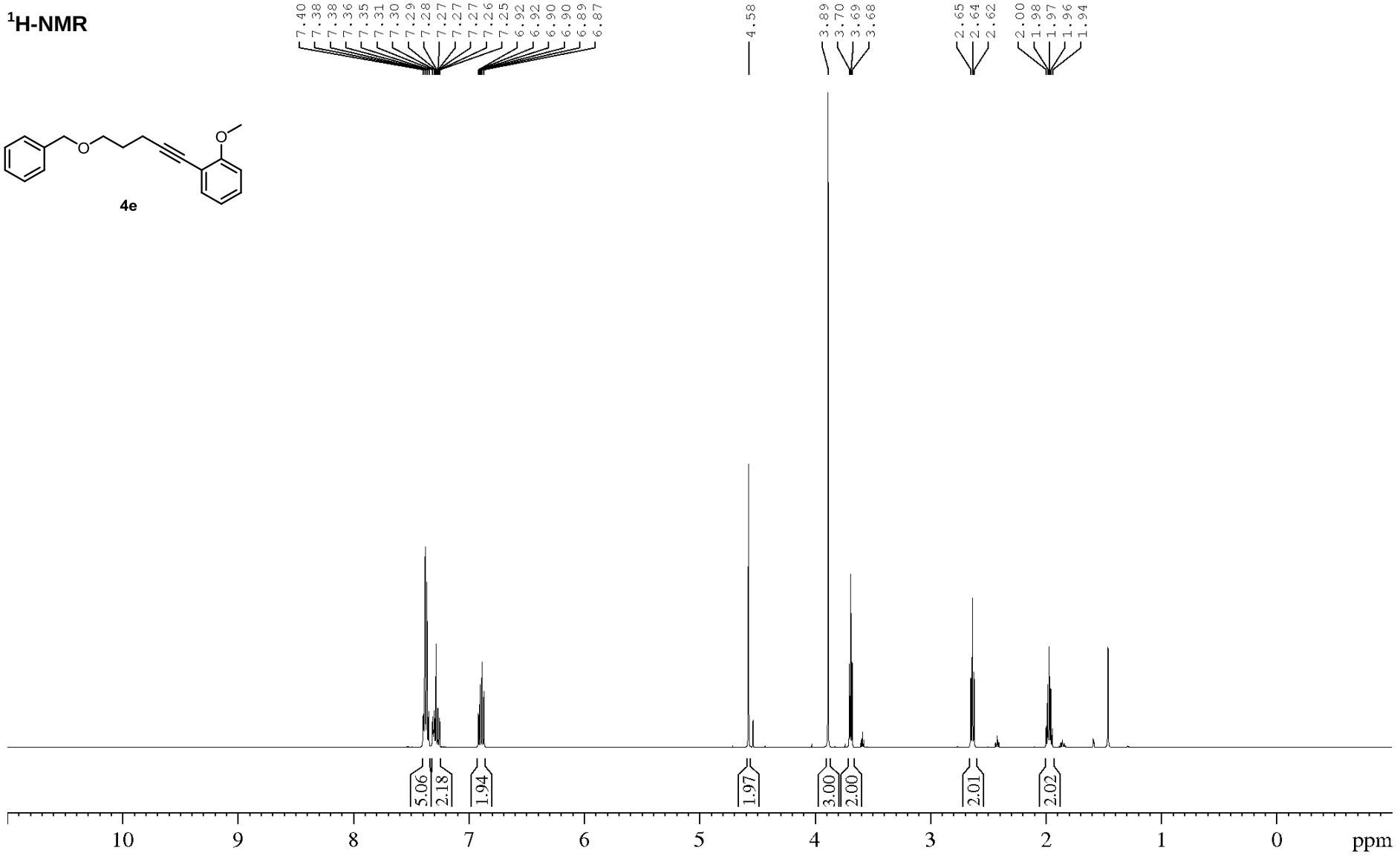

Relative Abundance
m/z
131
144
159
115
280
147
189
175
105
128
172
160
203
281
294
176
190
279
249
221
235
236
207
252
265
295
4d

IR-spectrum

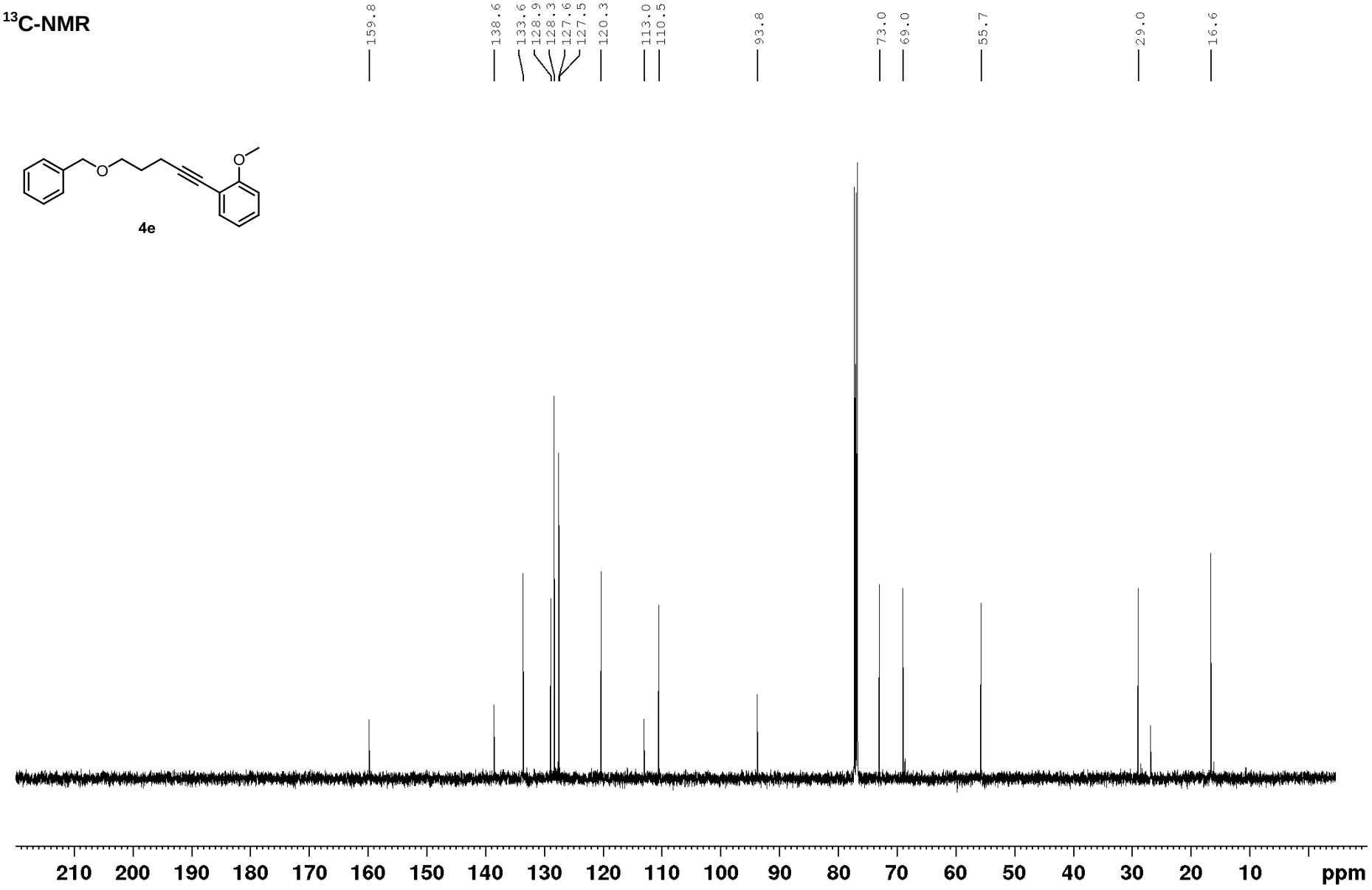

%T
90
80
70
60
50
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
O
O
4d

^{1}H-NMR

4e

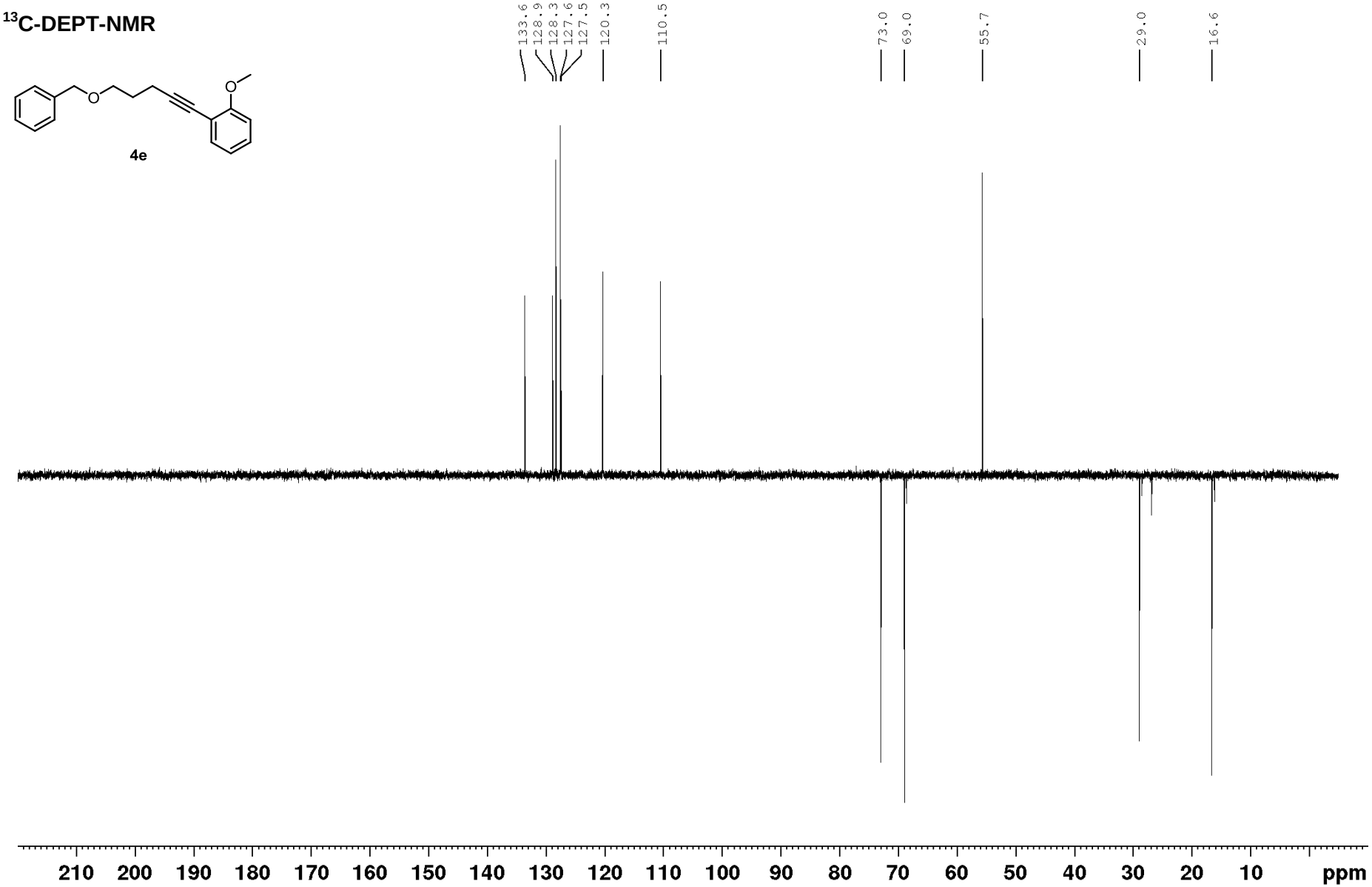

7.40
7.38
7.38
7.36
7.35
7.31
7.30
7.29
7.28
7.27
7.27
7.27
7.26
7.25
6.92
6.92
6.90
6.90
6.89
6.87
4.58
3.89
3.70
3.69
3.68
2.65
2.64
2.62
2.00
1.98
1.97
1.96
1.94
5.06
2.18
1.94
1.97
3.00
2.00
2.01
2.02
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C-NMR

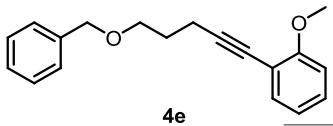

159.8
138.6
133.6
128.9
128.3
127.6
127.5
120.3
113.0
110.5
93.8
73.0
69.0
55.7
29.0
16.6
O
O
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C-DEPT-NMR

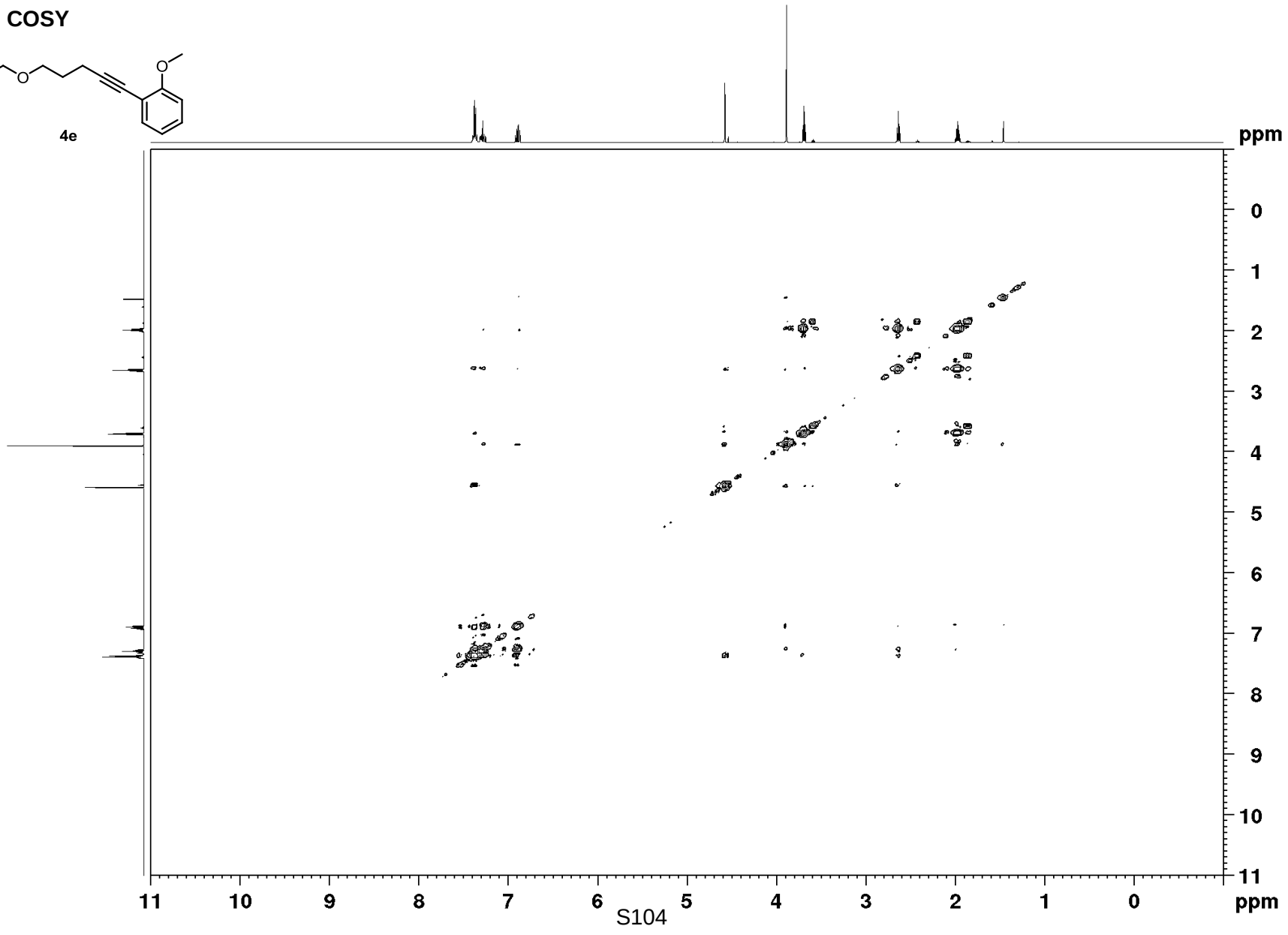
4e



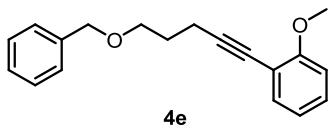
^{1}H, ^{1}H COSY



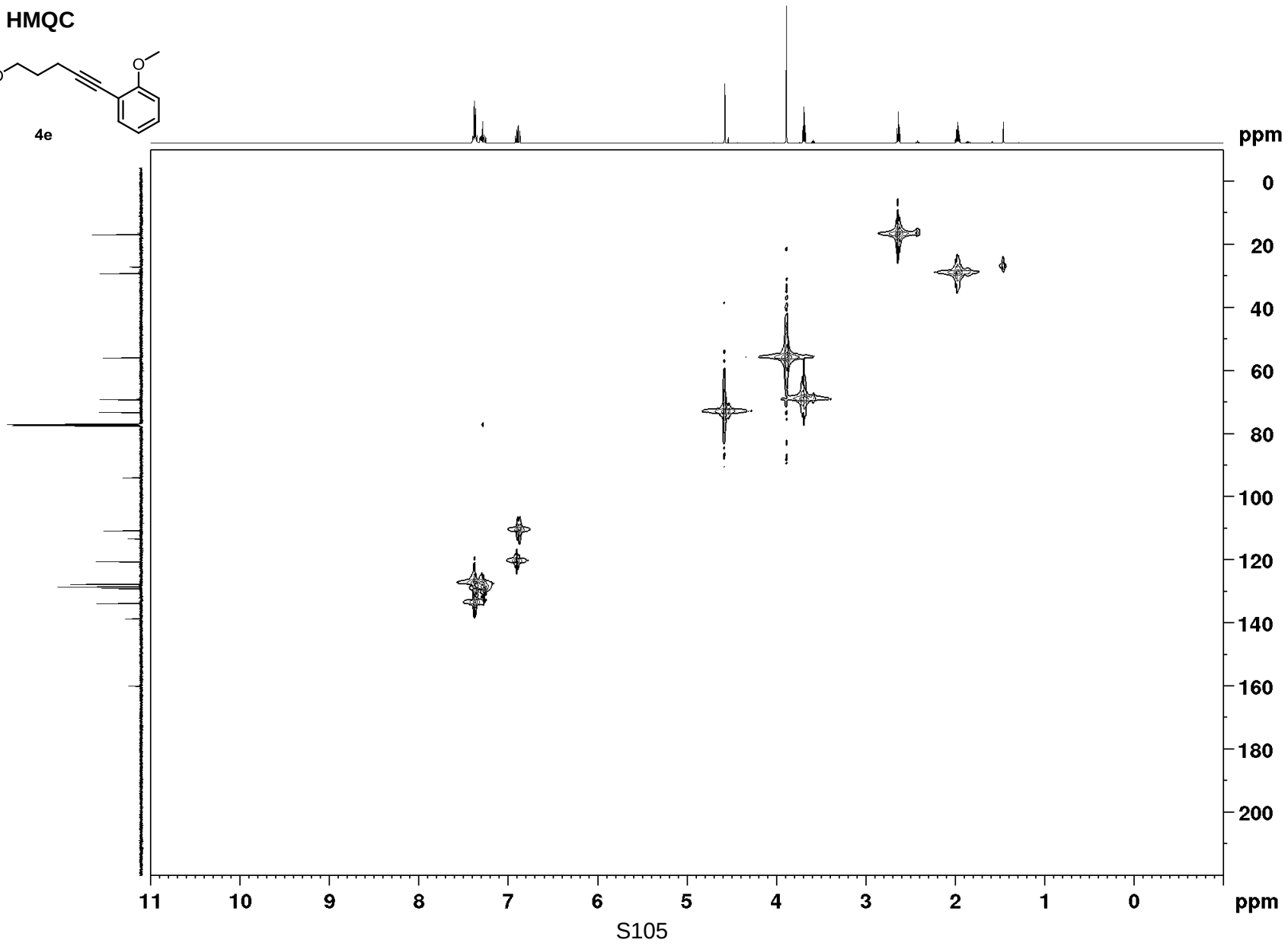
4e



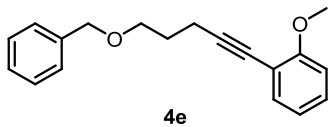
^{1}H, ^{13}C HMQC



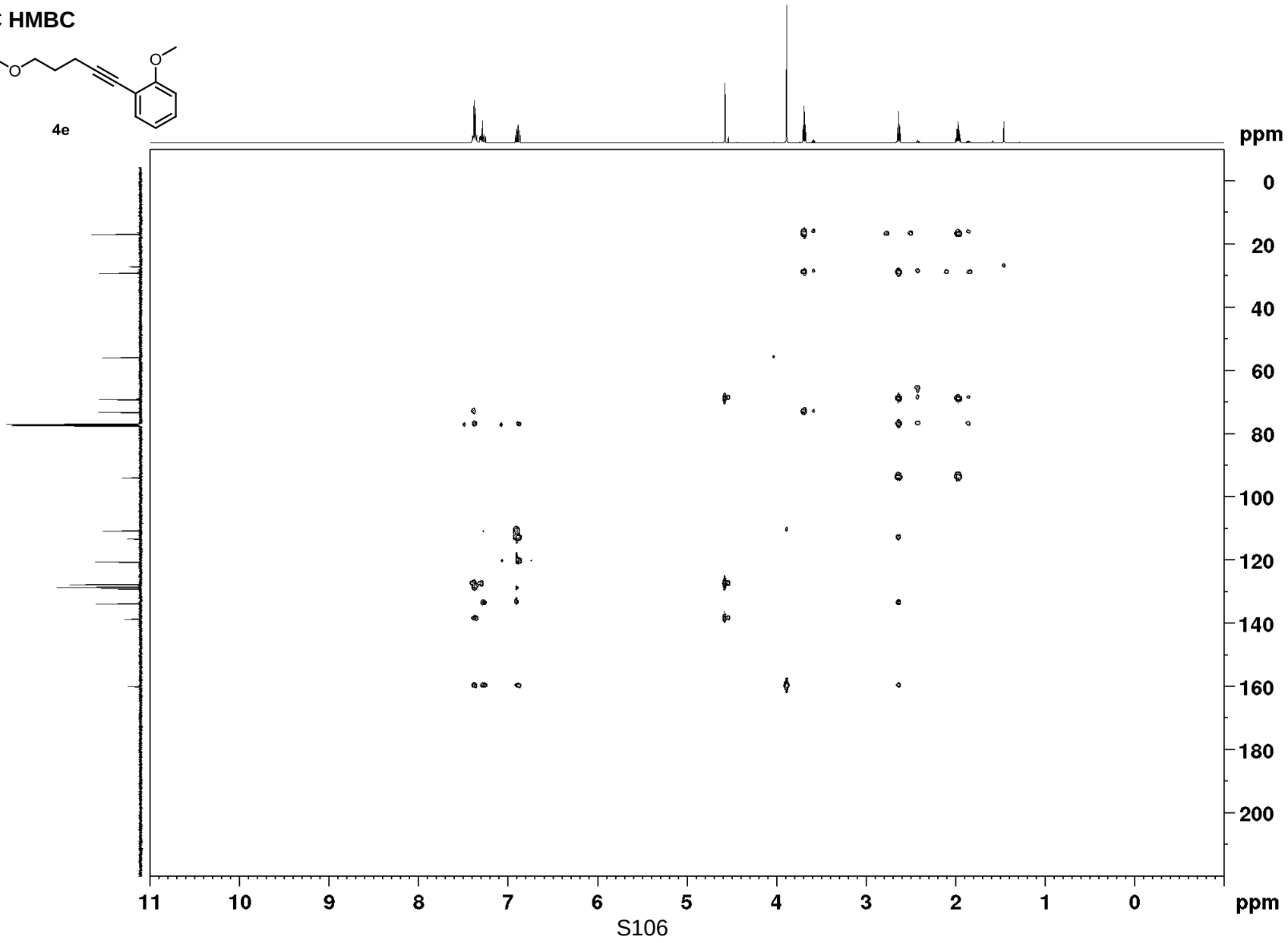
4e



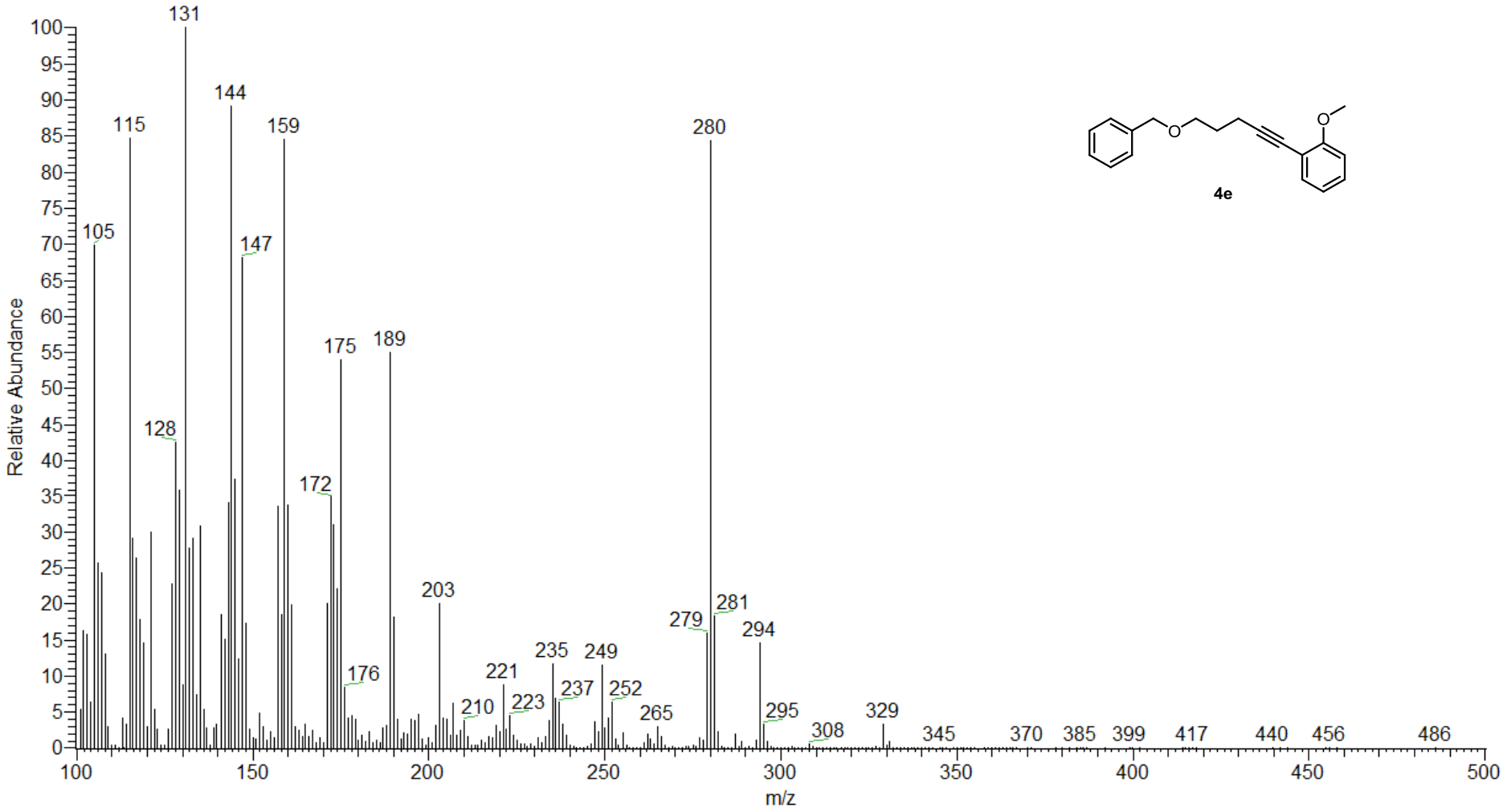
^{1}H, ^{13}C HMBC



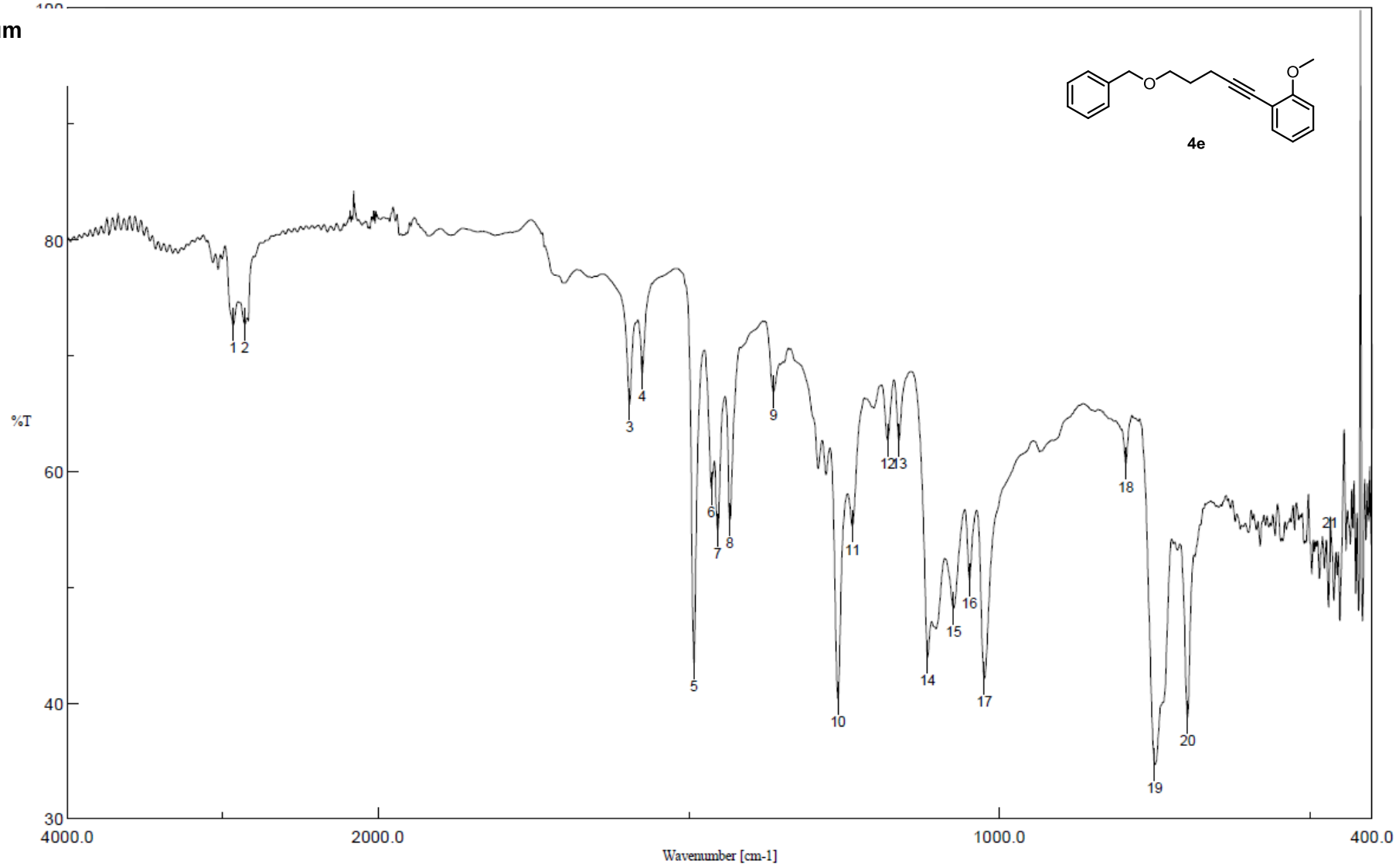
4e



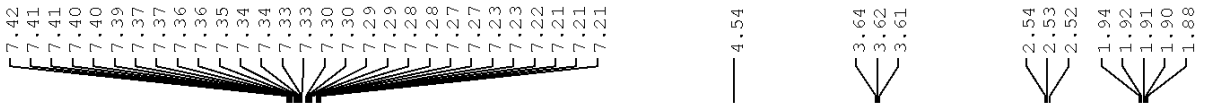
mass spectrum

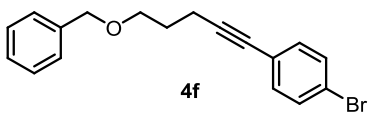


IR-spectrum

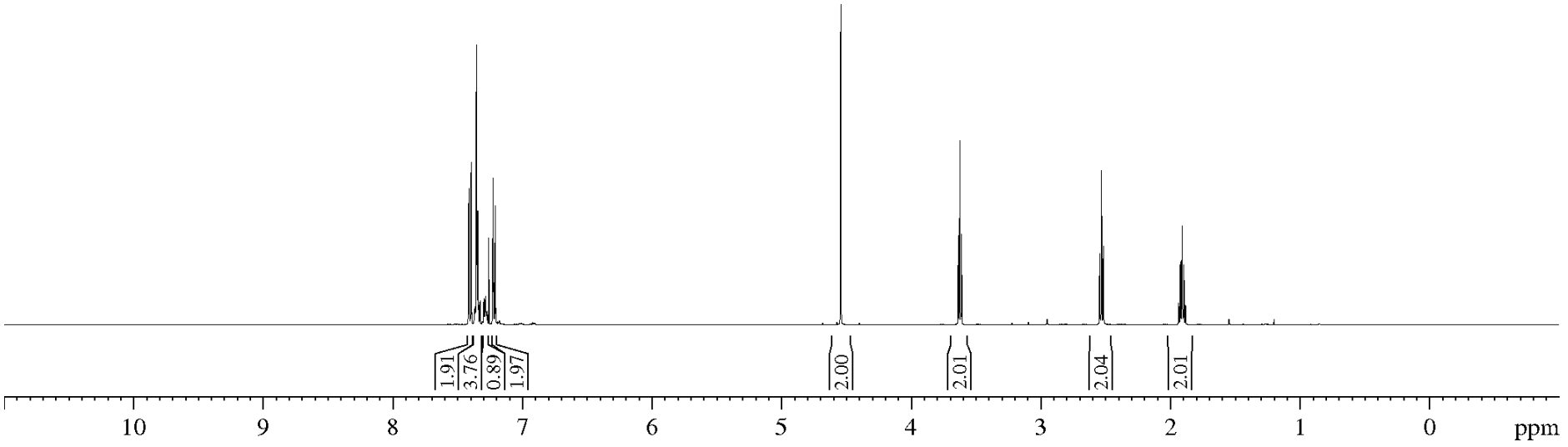

4e
%T
80
60
40
30
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21

^{1}H-NMR

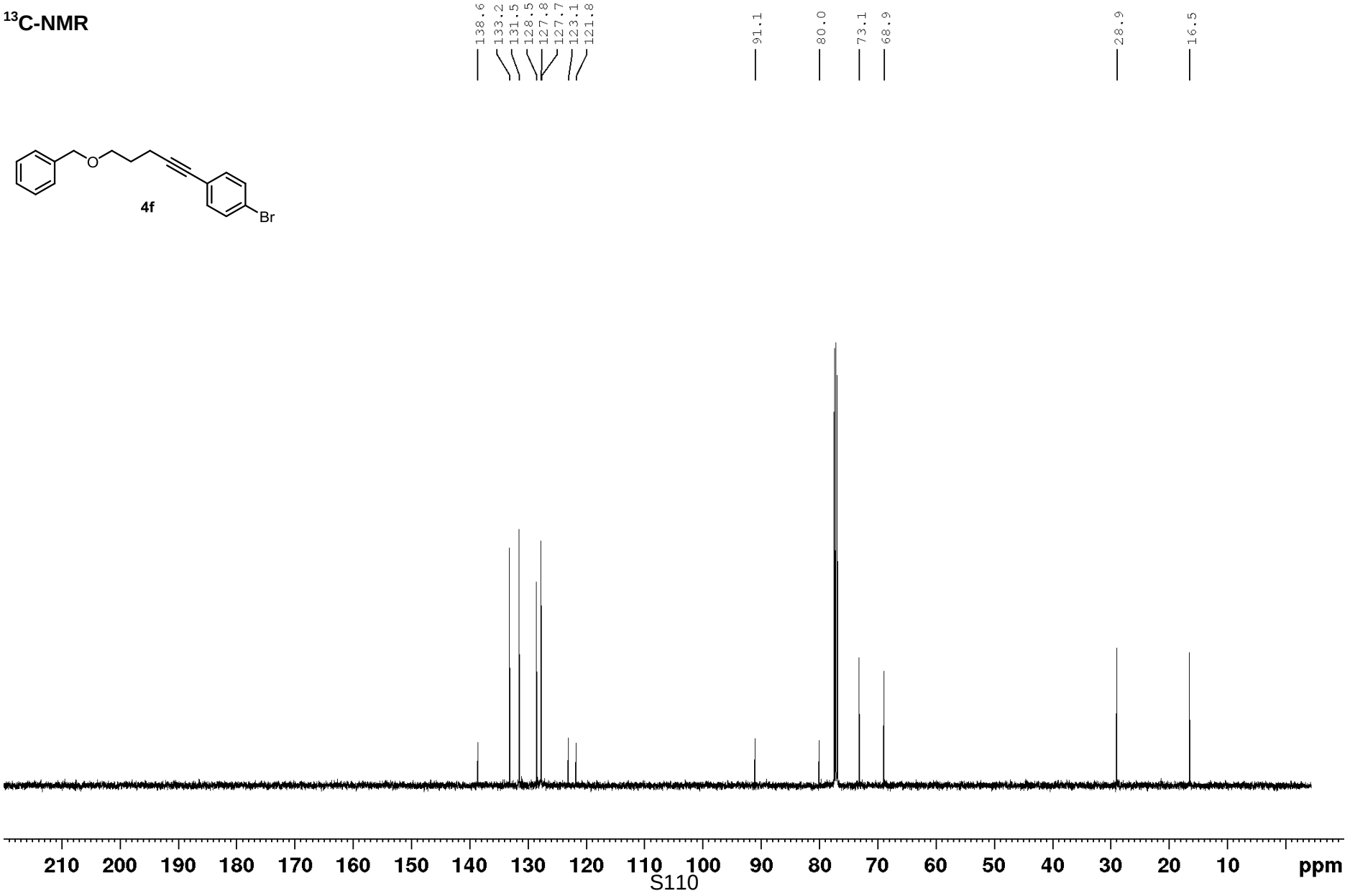

7.42
7.41
7.41
7.40
7.40
7.39
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.23
7.22
7.21
7.21
7.21
4.54
3.64
3.62
3.61
2.54
2.53
2.52
1.94
1.92
1.91
1.90
1.88


O
Br

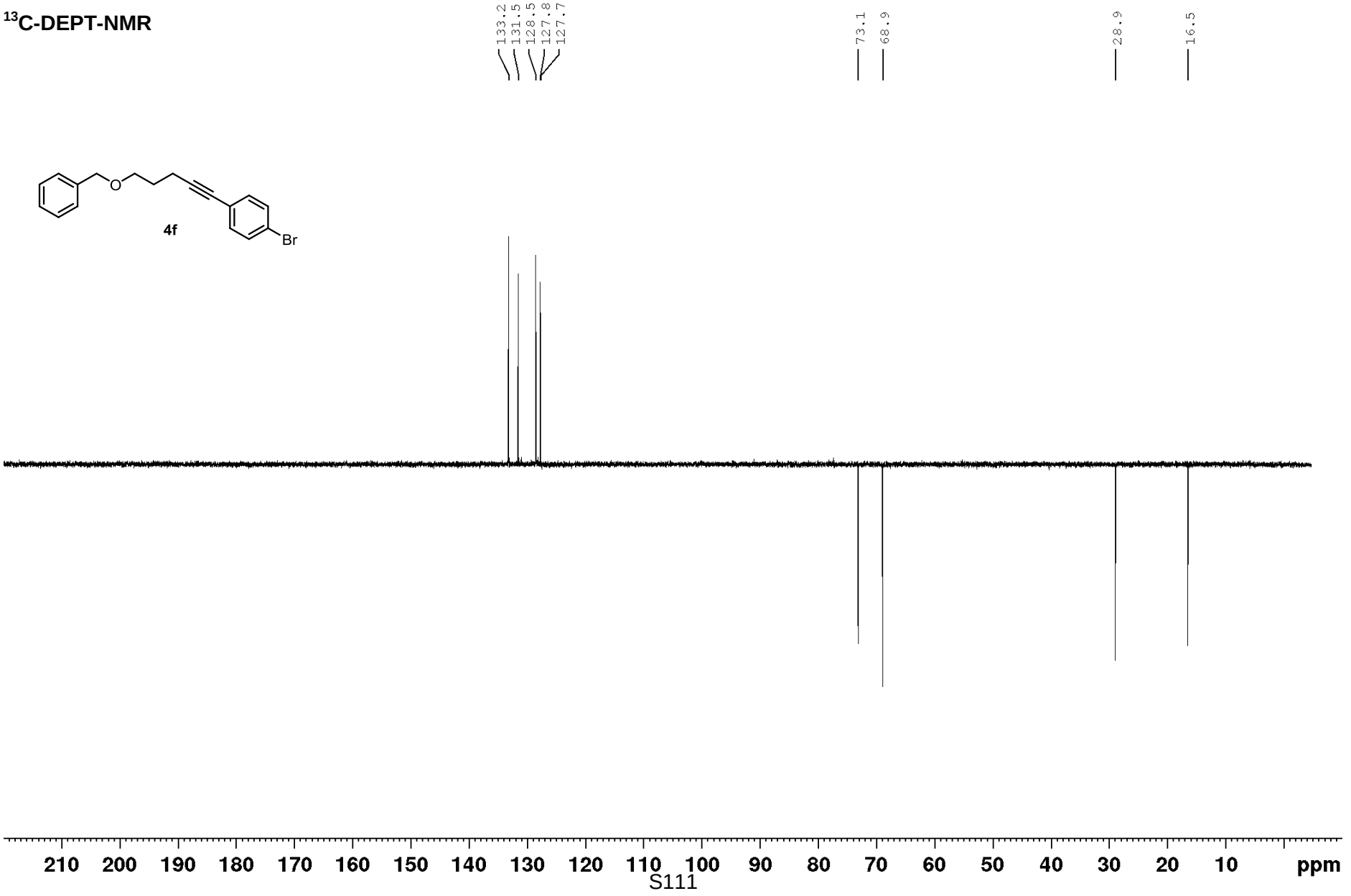
4f


1.91
3.76
0.89
1.97
2.00
2.01
2.04
2.01
10
9
8
7
6
5
4
3
2
1
0
ppm

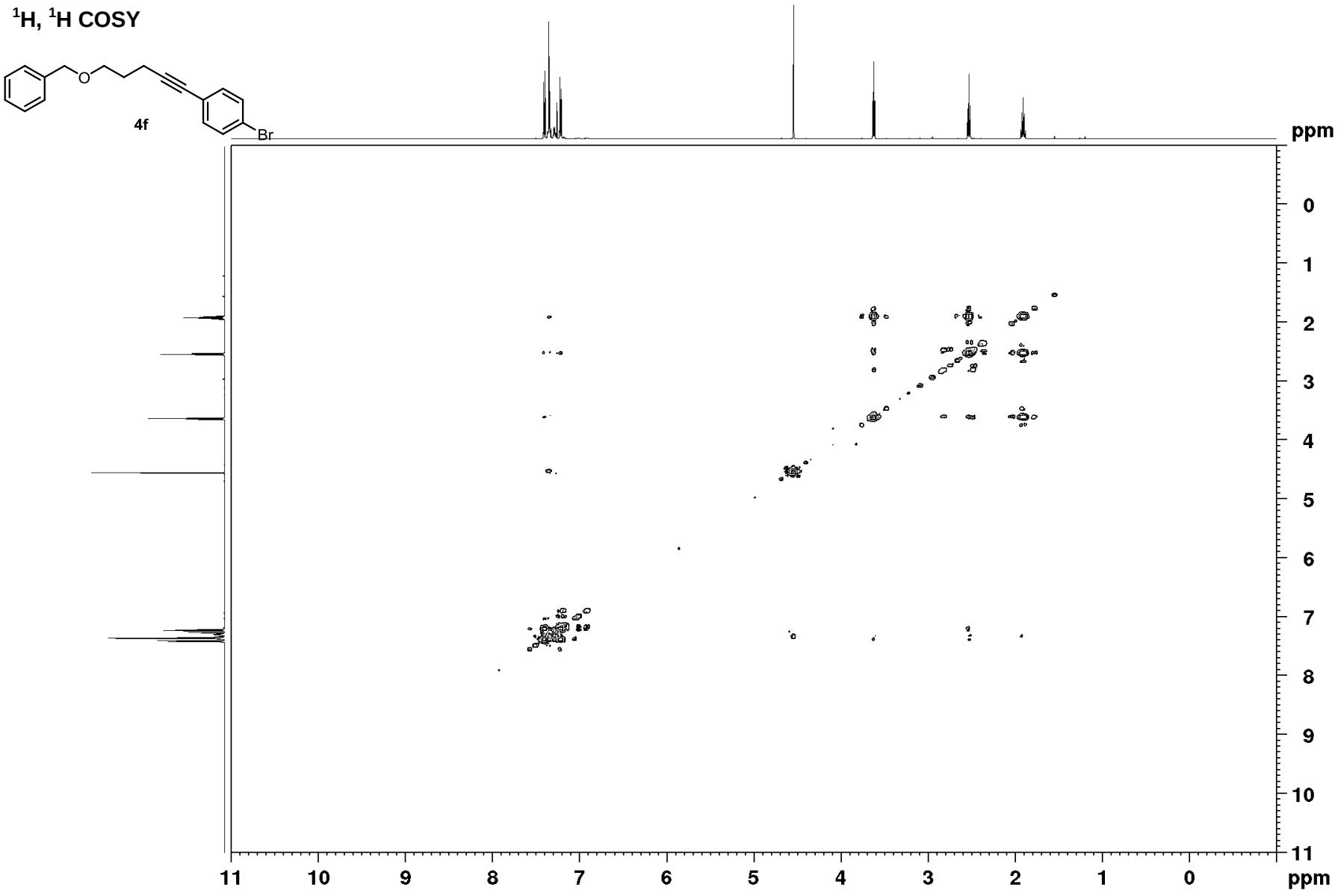
^{13}C-NMR


138.6
133.2
131.5
128.5
127.8
127.7
123.1
121.8
91.1
80.0
73.1
68.9
28.9
16.5
O
Br
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

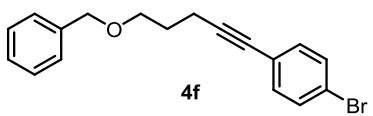
^{13}C-DEPT-NMR


133.2
131.5
128.5
127.8
127.7
73.1
68.9
28.9
16.5
O
Br
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

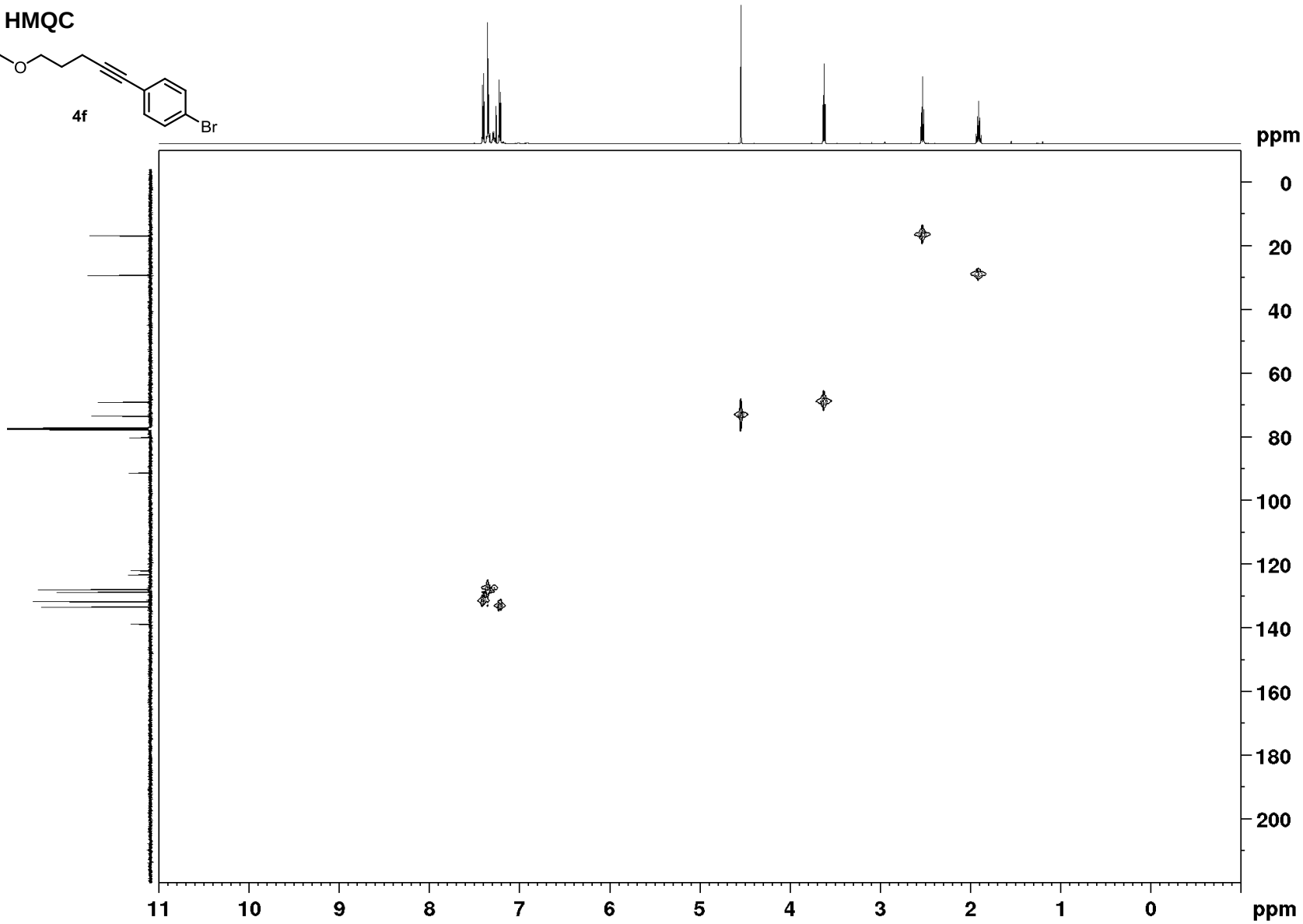
^{1}H, ^{1}H COSY



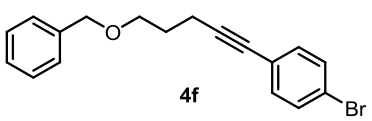
^{1}H, ^{13}C HMQC



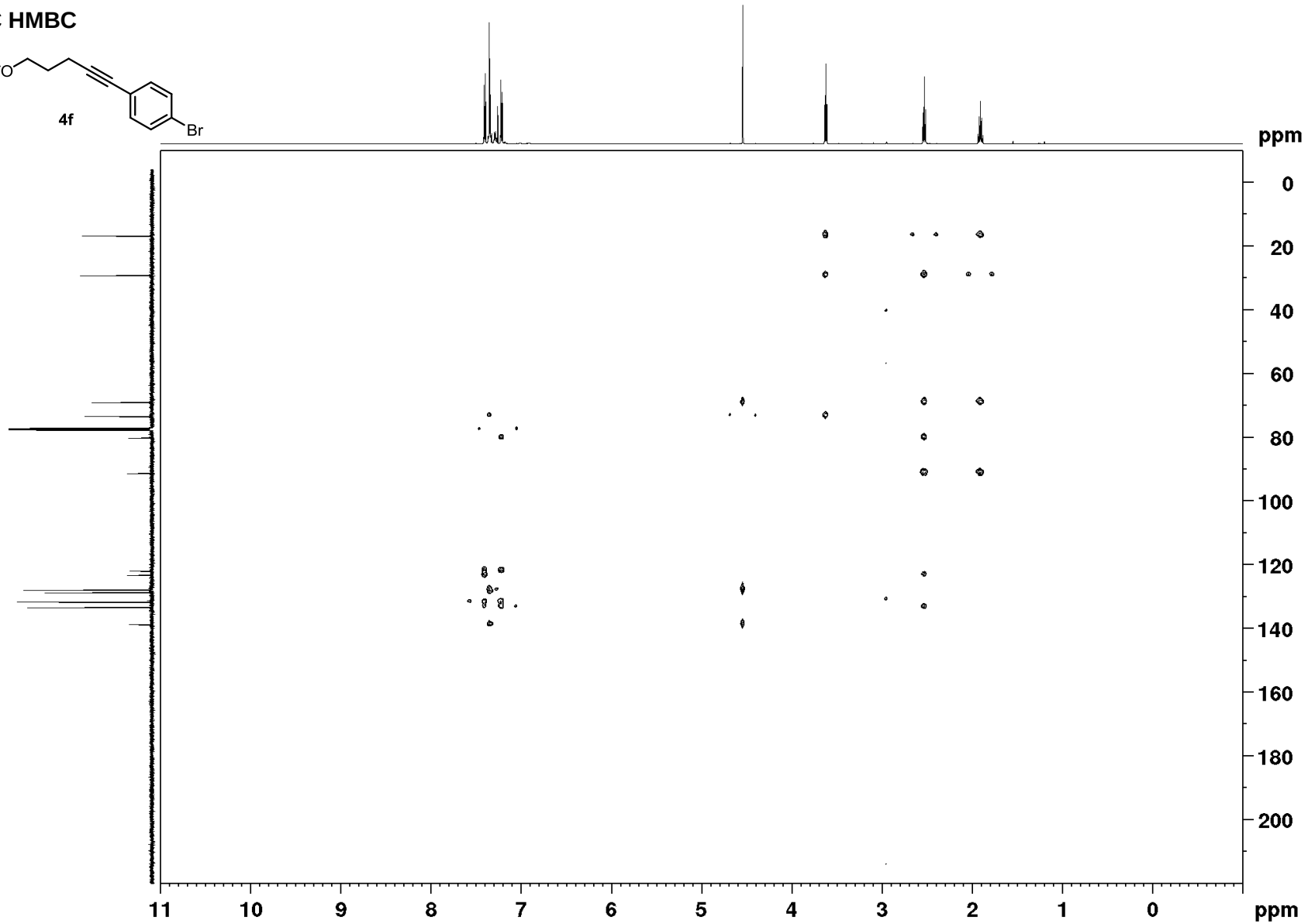
4f



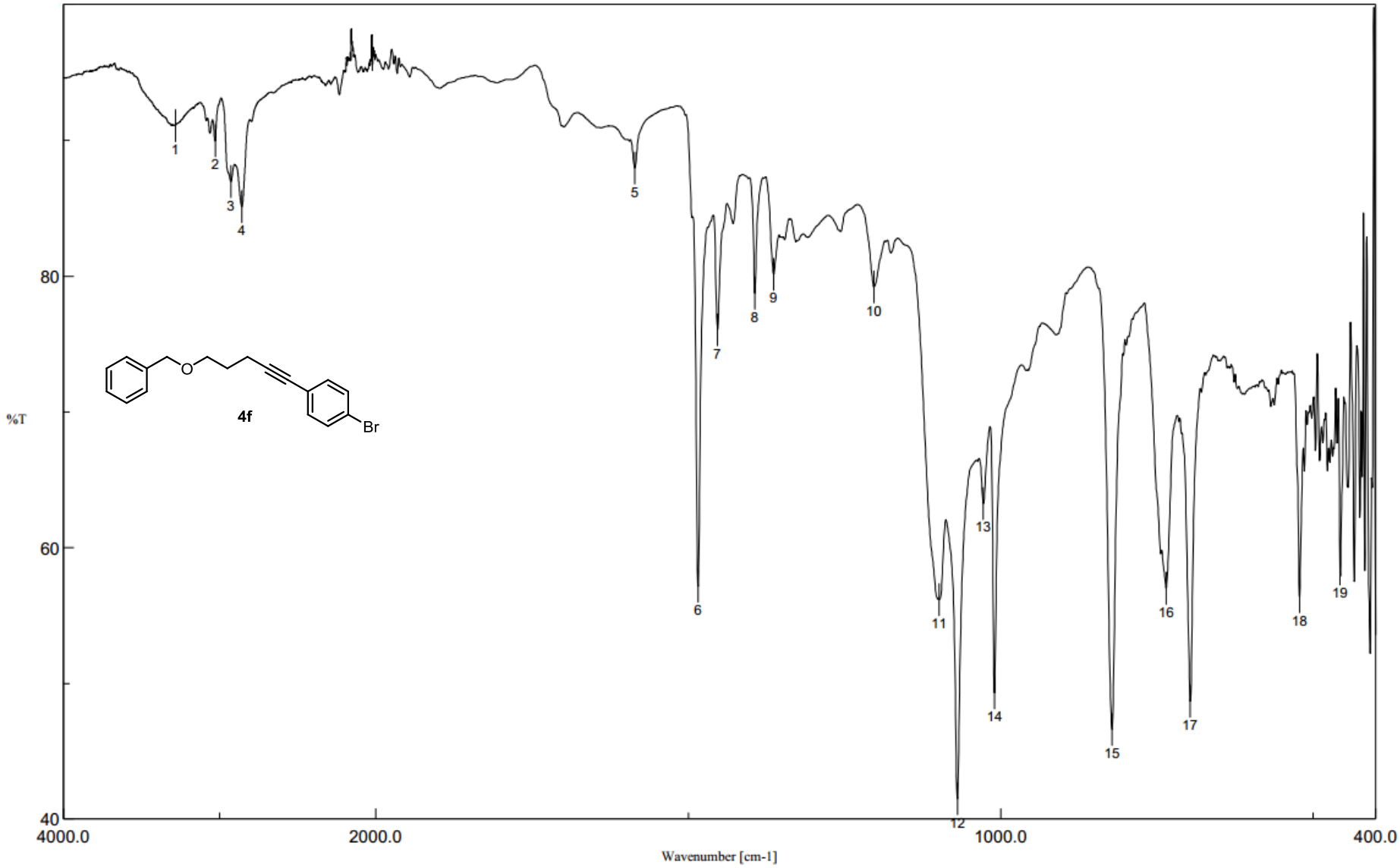
^{1}H, ^{13}C HMBC



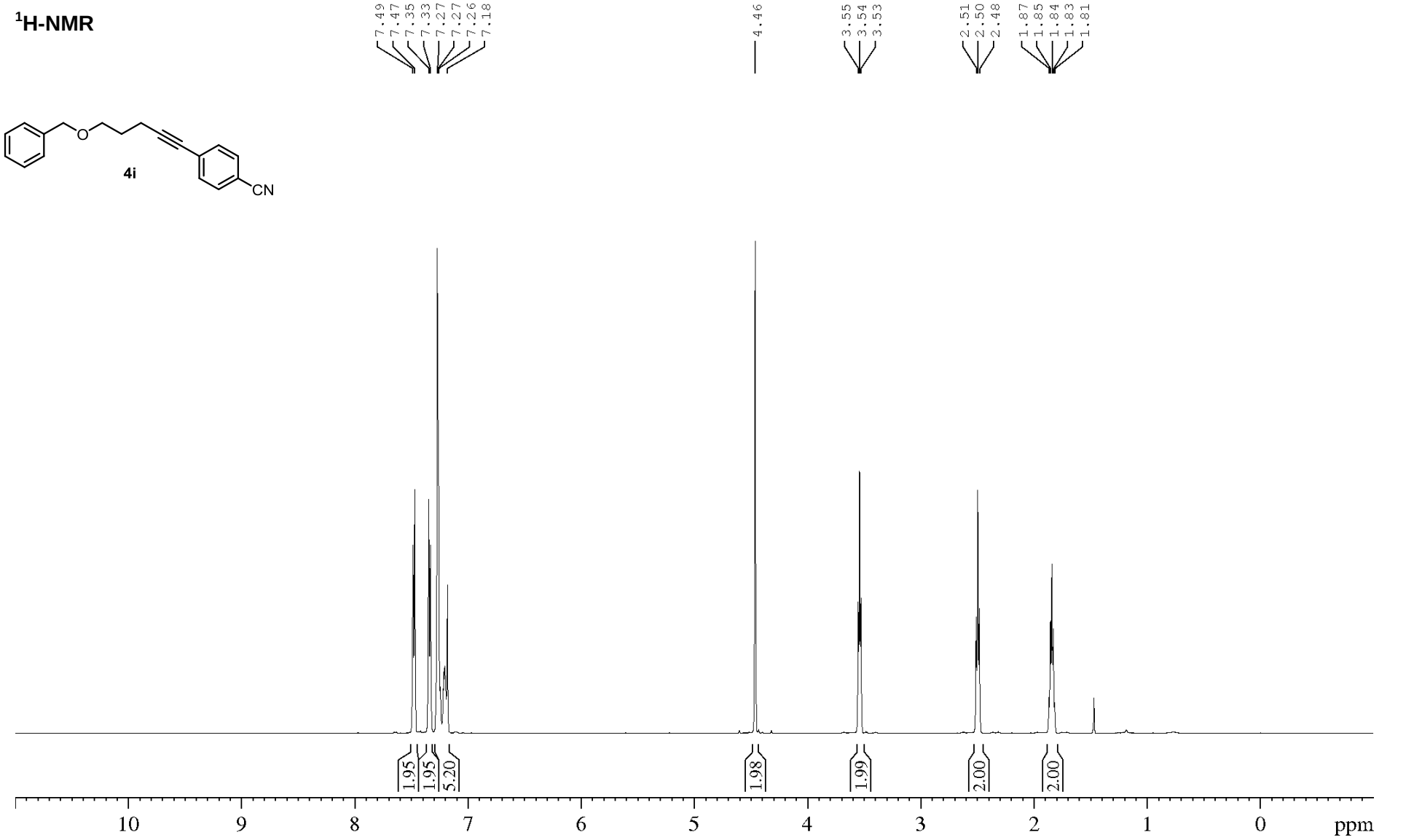
4f



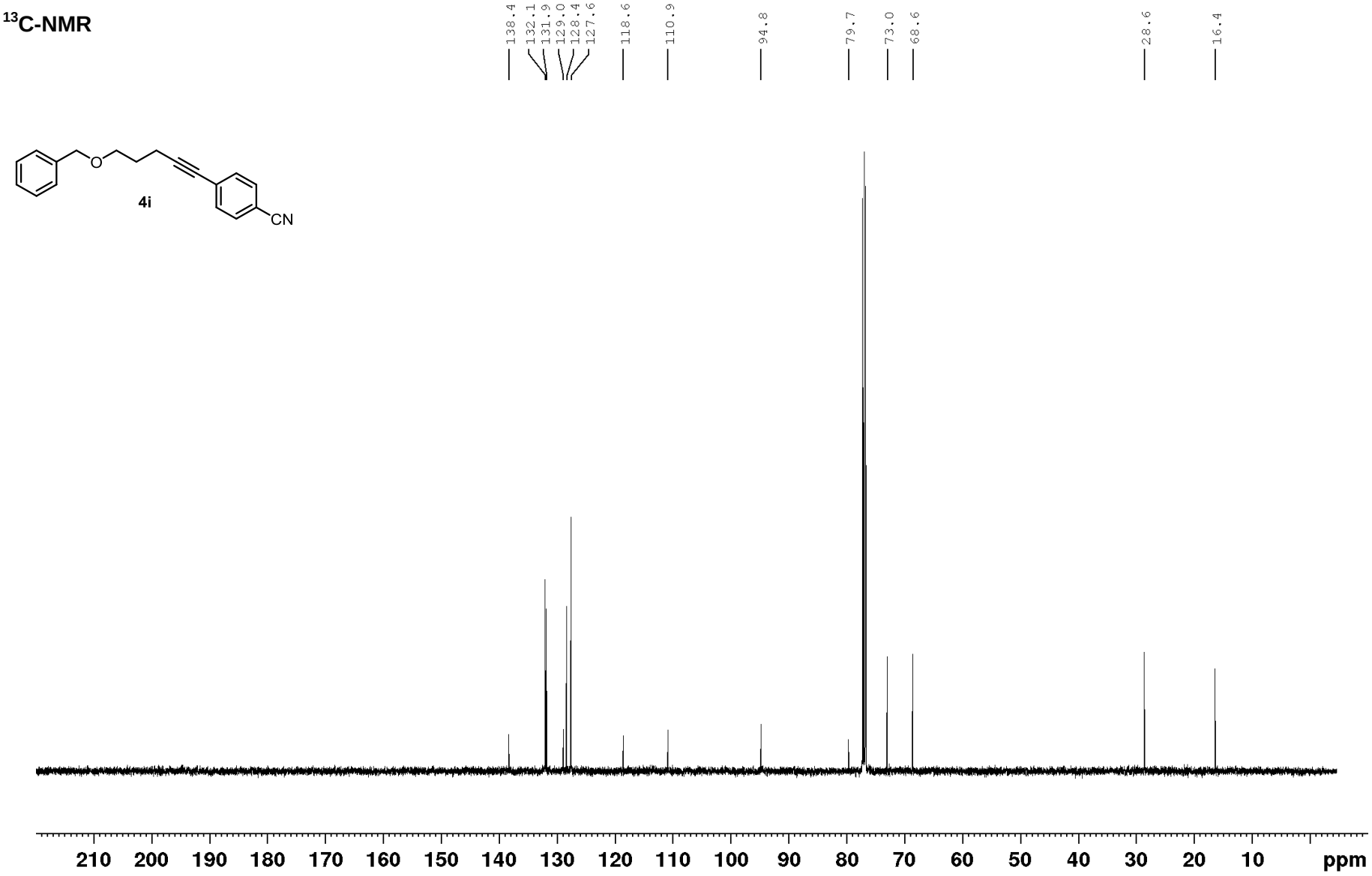
IR spectrum


%T
80
60
40
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
O
Br
4f

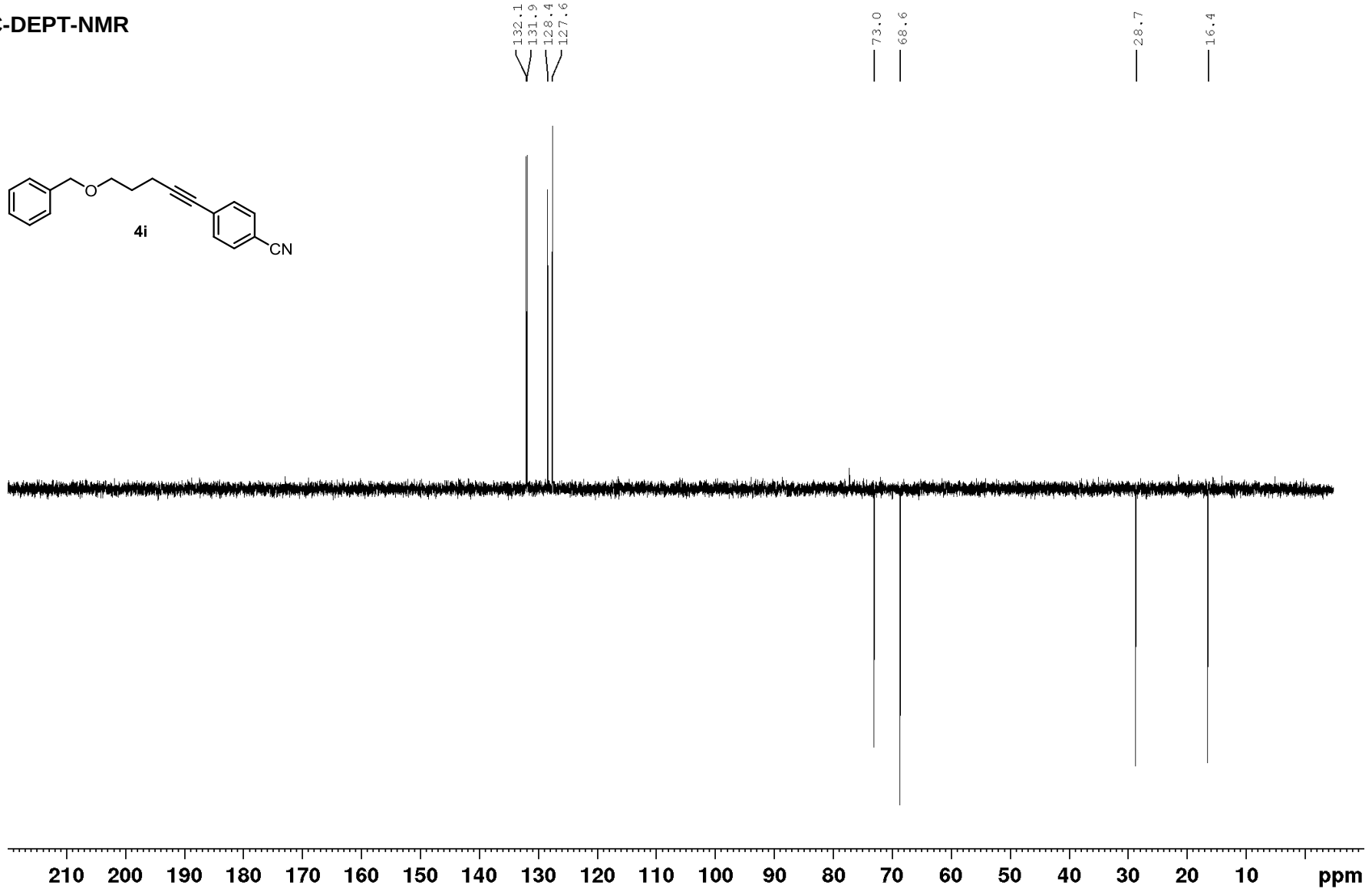
^{1}H-NMR


7.49
7.47
7.35
7.33
7.27
7.27
7.26
7.18
4.46
3.55
3.54
3.53
2.51
2.50
2.48
1.87
1.85
1.84
1.83
1.81
O
CN
4i
1.95
1.95
5.20
1.98
1.99
2.00
2.00
10
9
8
7
6
5
4
3
2
1
0
ppm

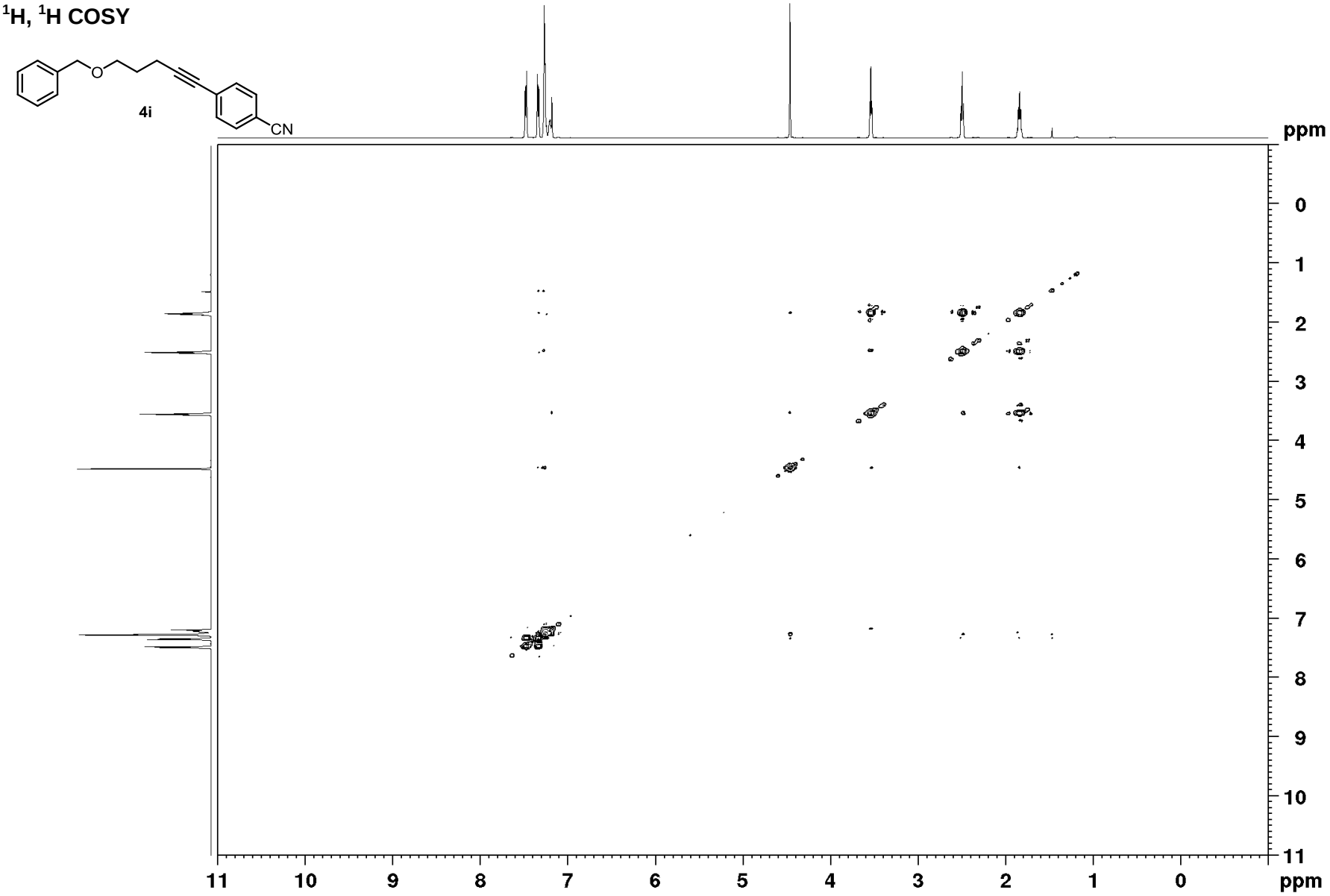
^{13}C-NMR


138.4
132.1
131.9
129.0
128.4
127.6
118.6
110.9
94.8
79.7
73.0
68.6
28.6
16.4
O
CN
4i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

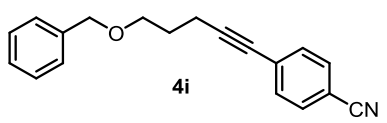
^{13}C-DEPT-NMR


132.1
131.9
128.4
127.6
73.0
68.6
28.7
16.4
O
CN
4i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

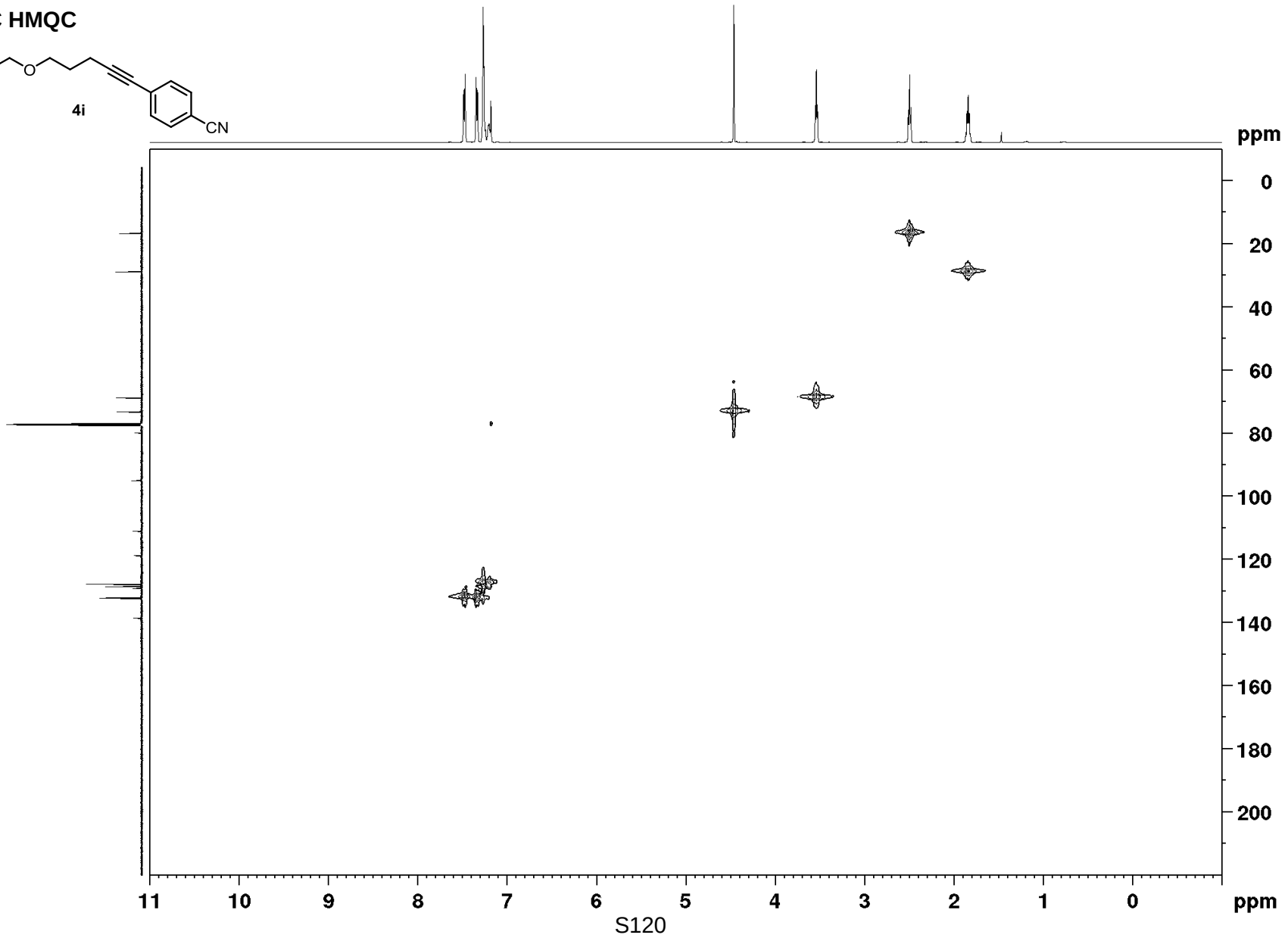
^{1}H, ^{1}H COSY



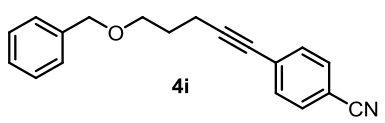
^{1}H, ^{13}C HMQC



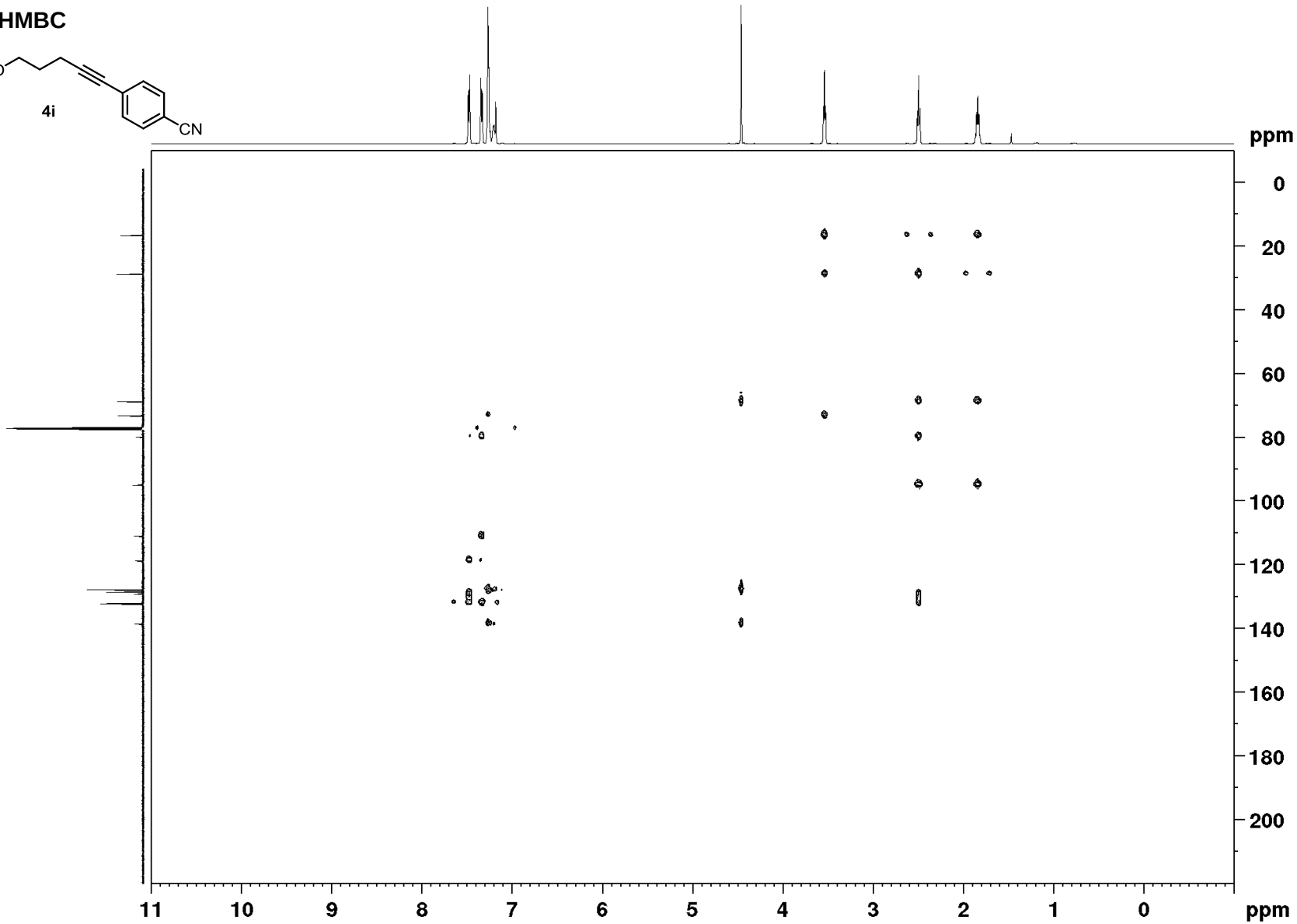
4i

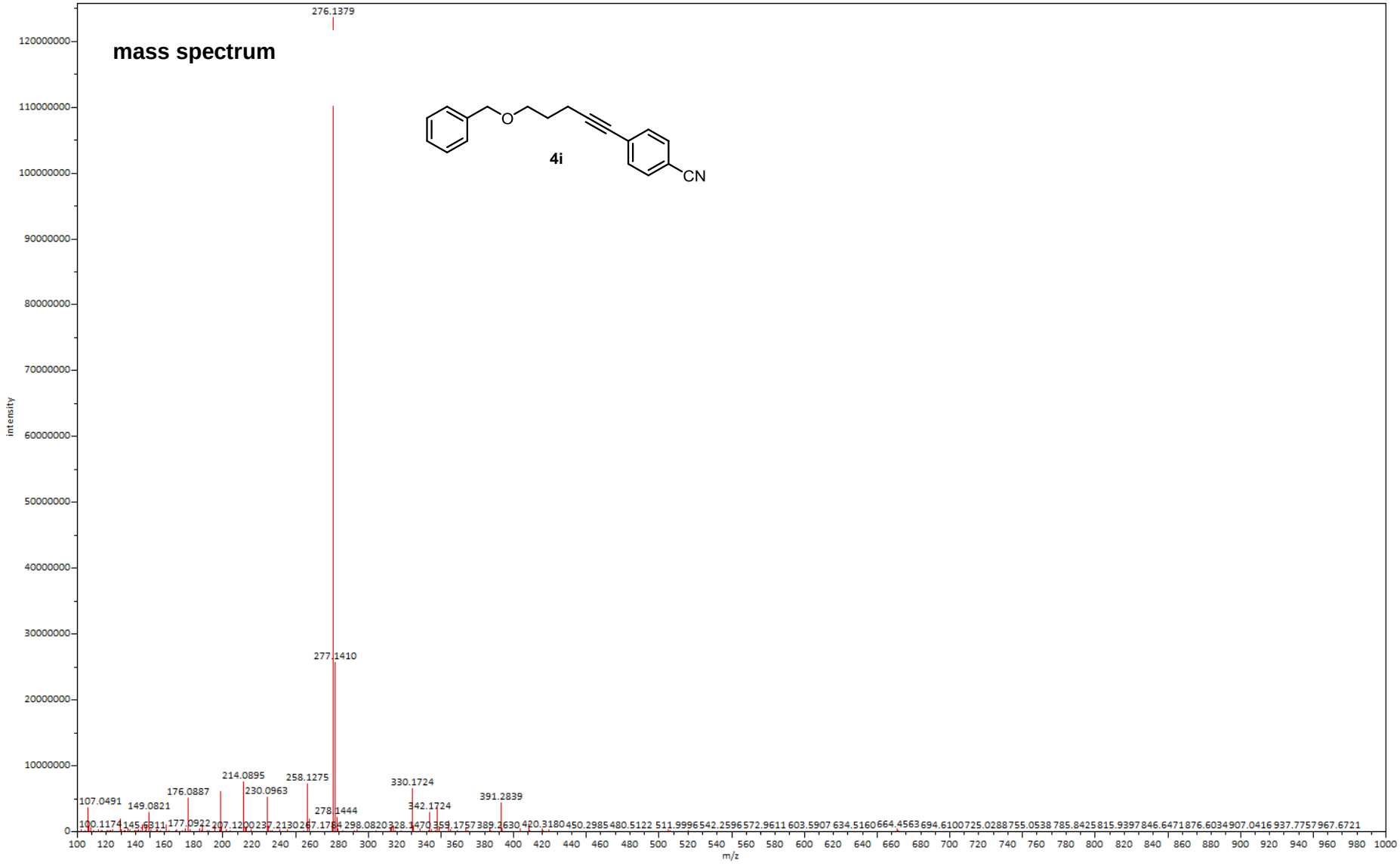


^{1}H, ^{13}C HMBC

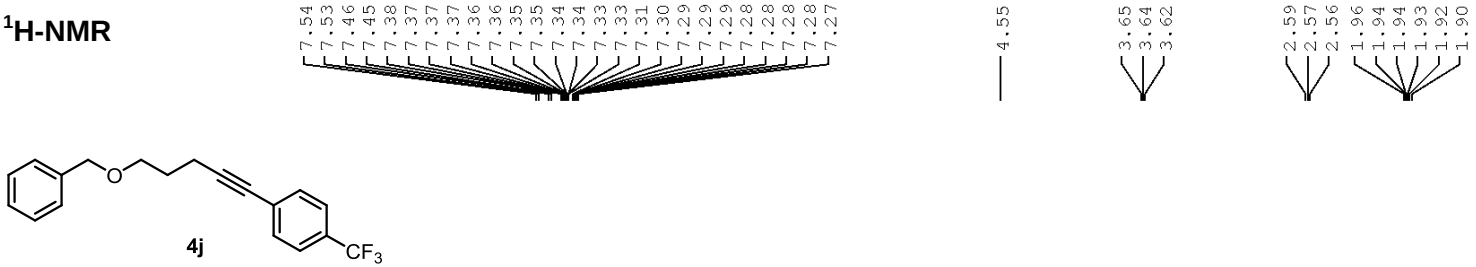


4i

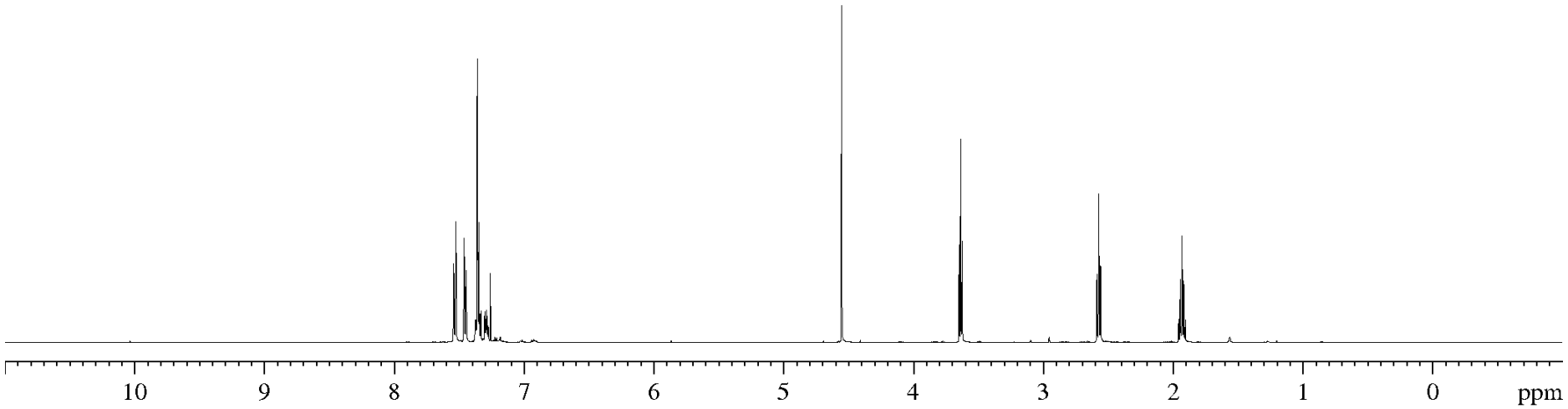



mass spectrum
4i
CN
O
276.1379
277.1410
intensity
m/z

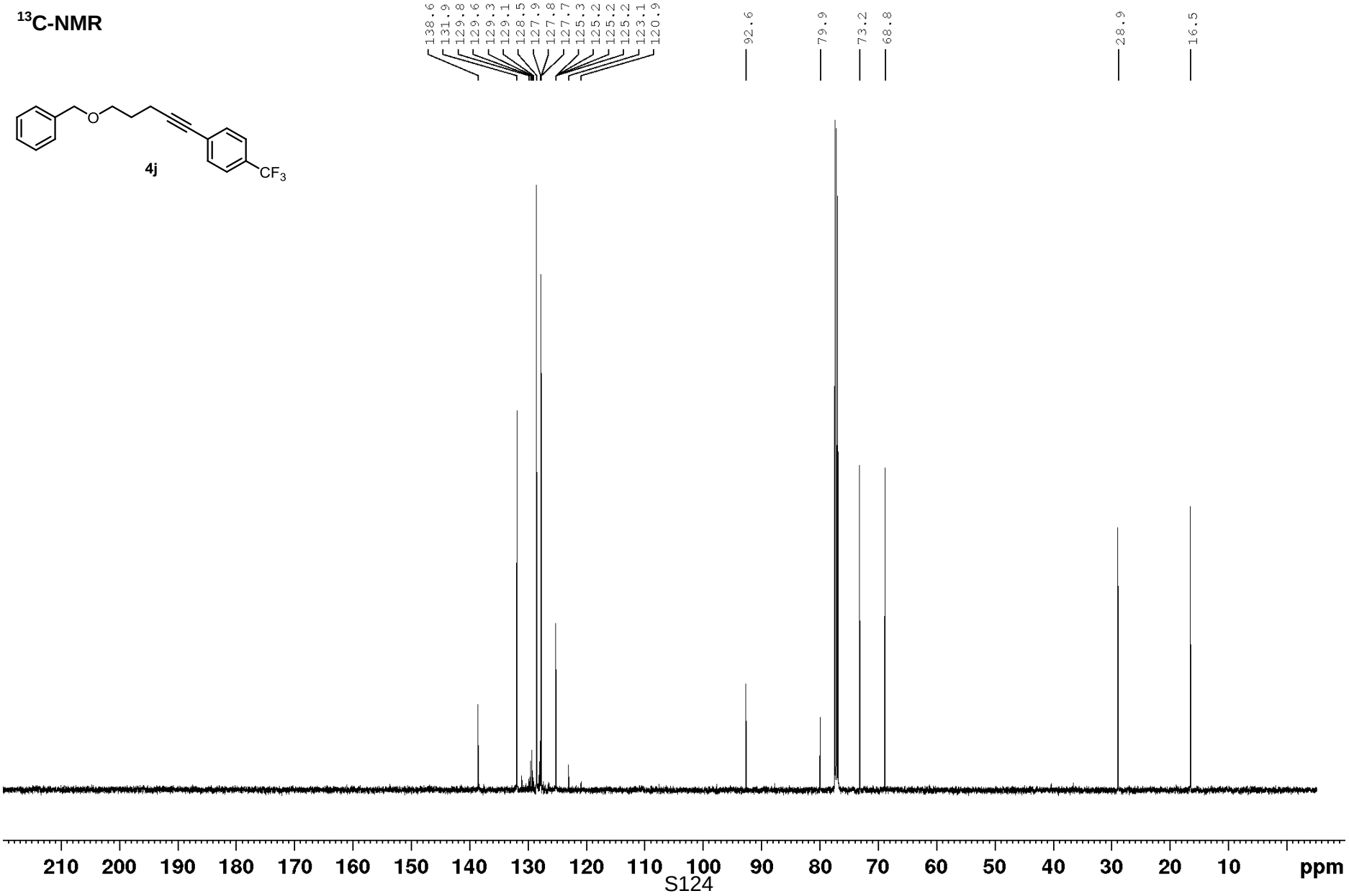
^{1}H-NMR


7.54
7.53
7.46
7.45
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.31
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.28
7.27
4.55
3.65
3.64
3.62
2.59
2.57
2.56
1.96
1.94
1.94
1.93
1.92
1.90
O
CF3

4j

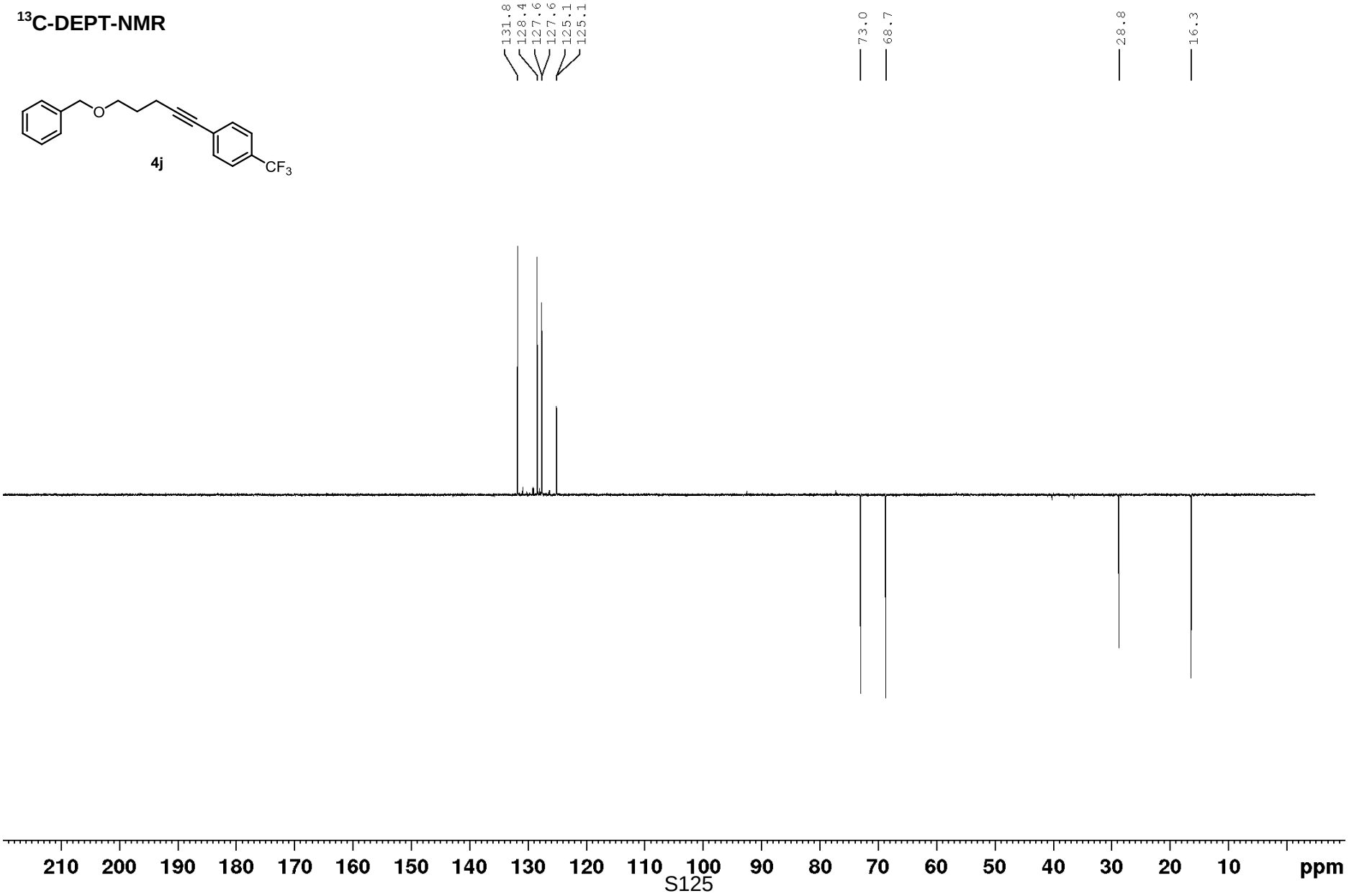

10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C-NMR

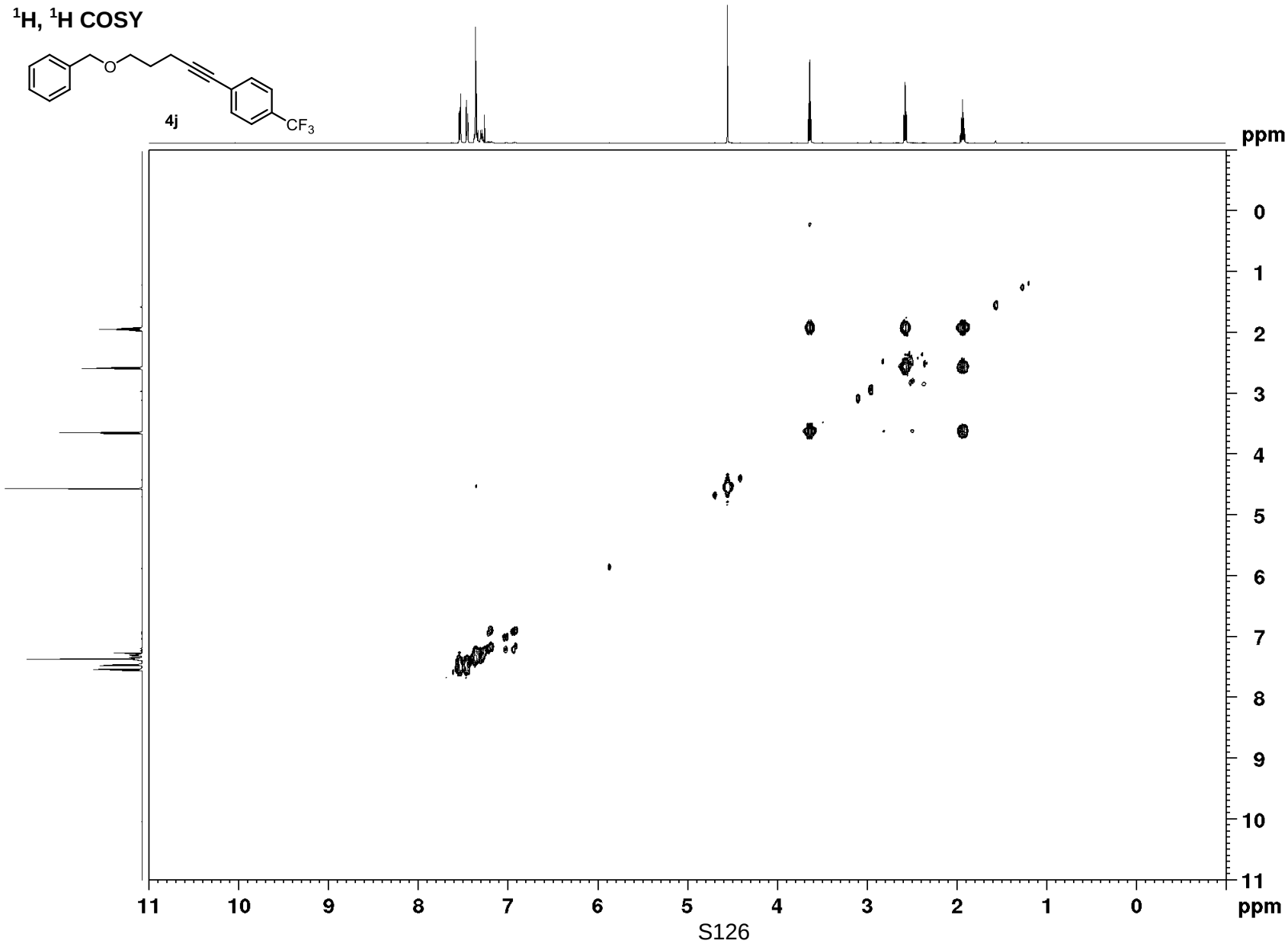

138.6
131.9
129.8
129.6
129.3
129.1
128.5
127.9
127.8
127.7
125.3
125.2
125.2
125.2
123.1
120.9
92.6
79.9
73.2
68.8
28.9
16.5
O
CF3
4j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{13}C-DEPT-NMR

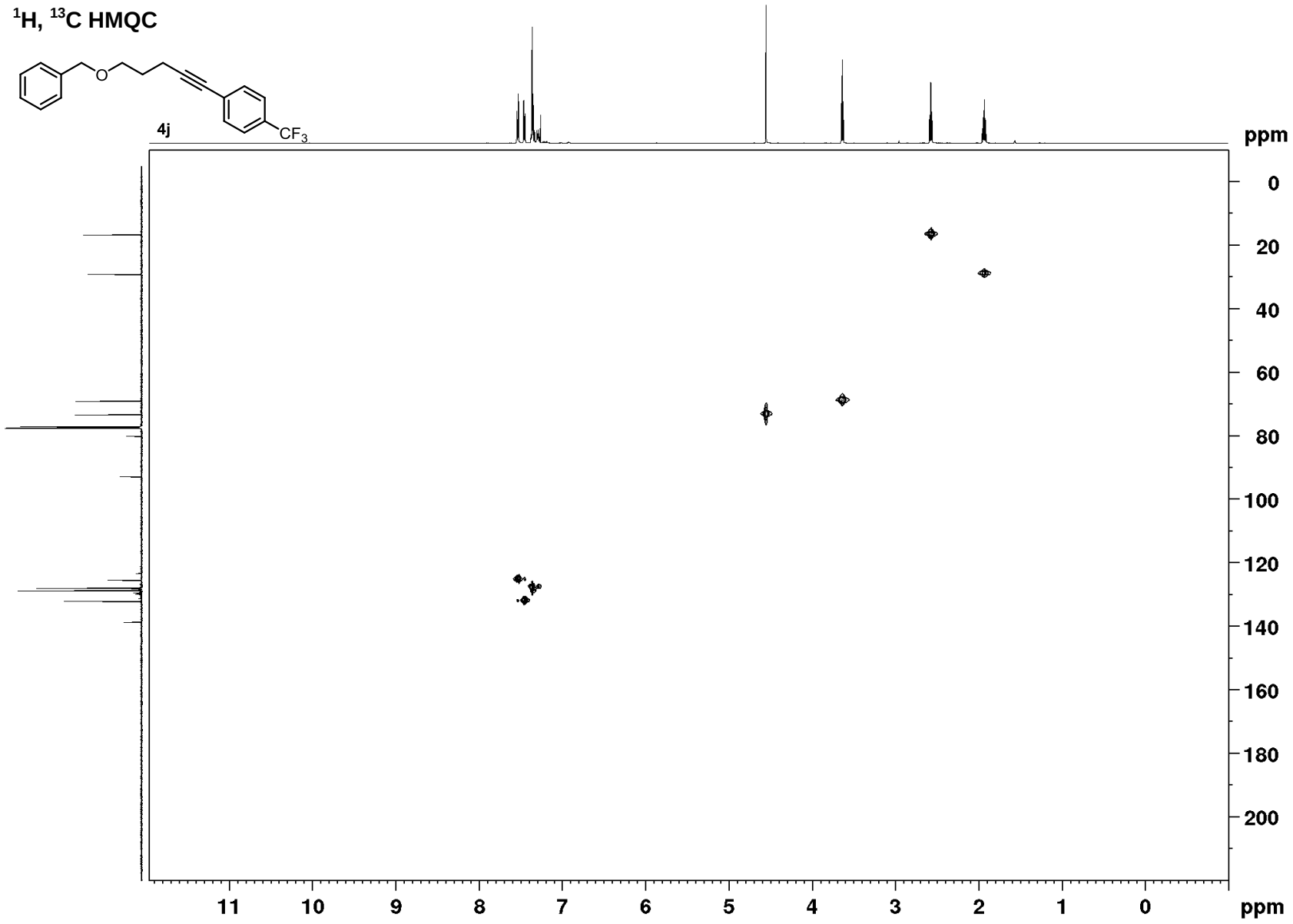
4j



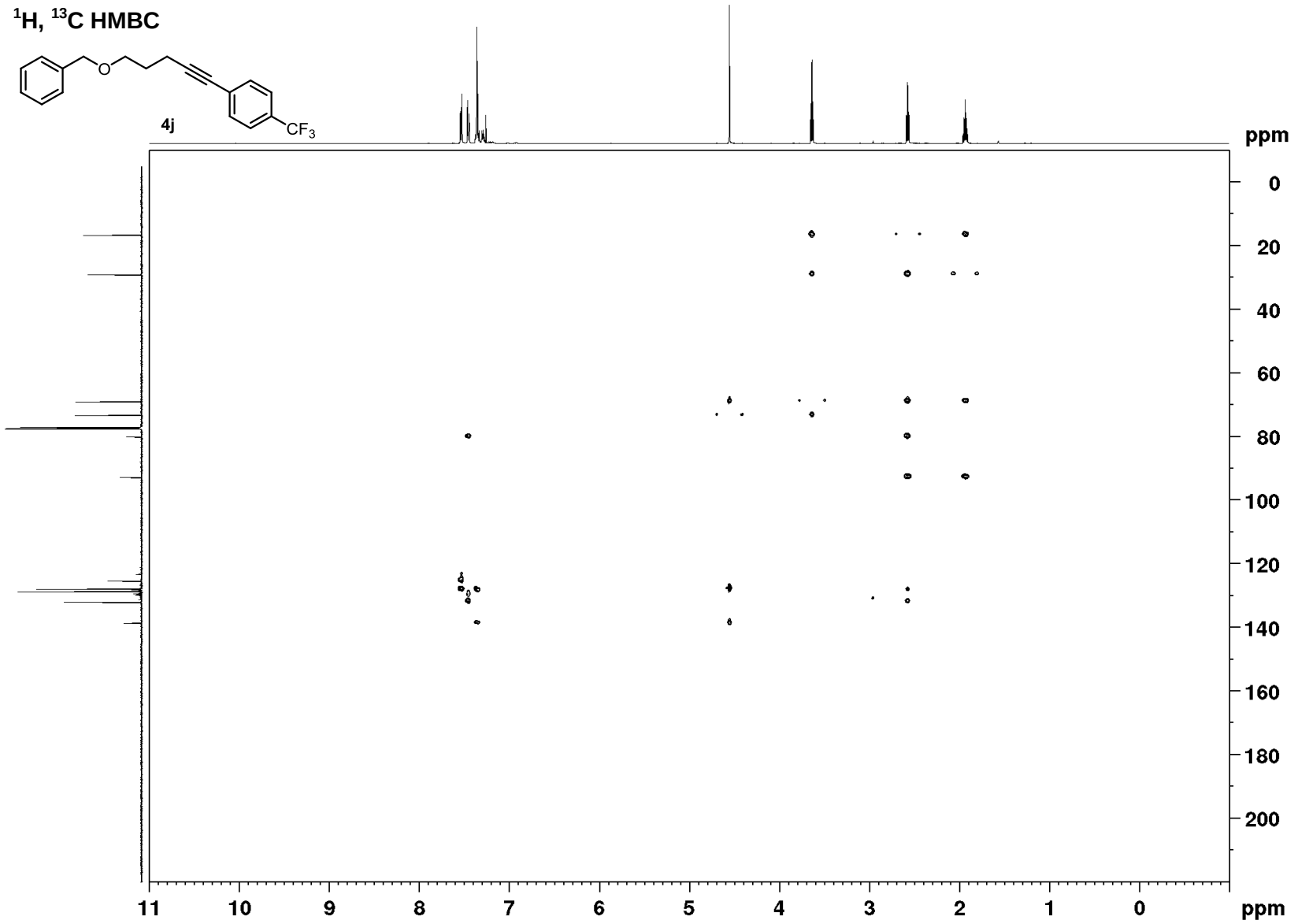
^{1}H, ^{1}H COSY



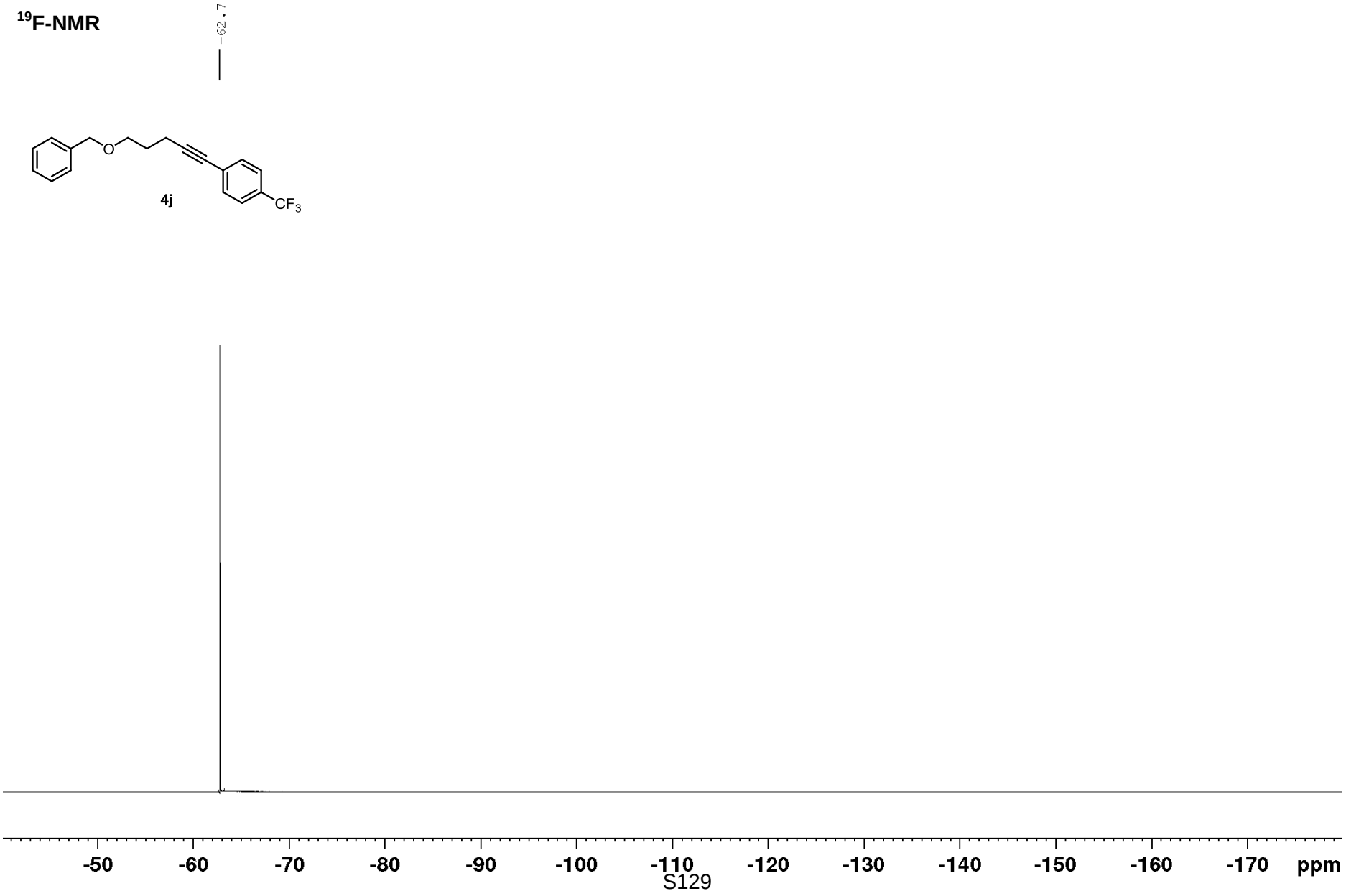
^{1}H, ^{13}C HMQC


O
CF3
4j
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

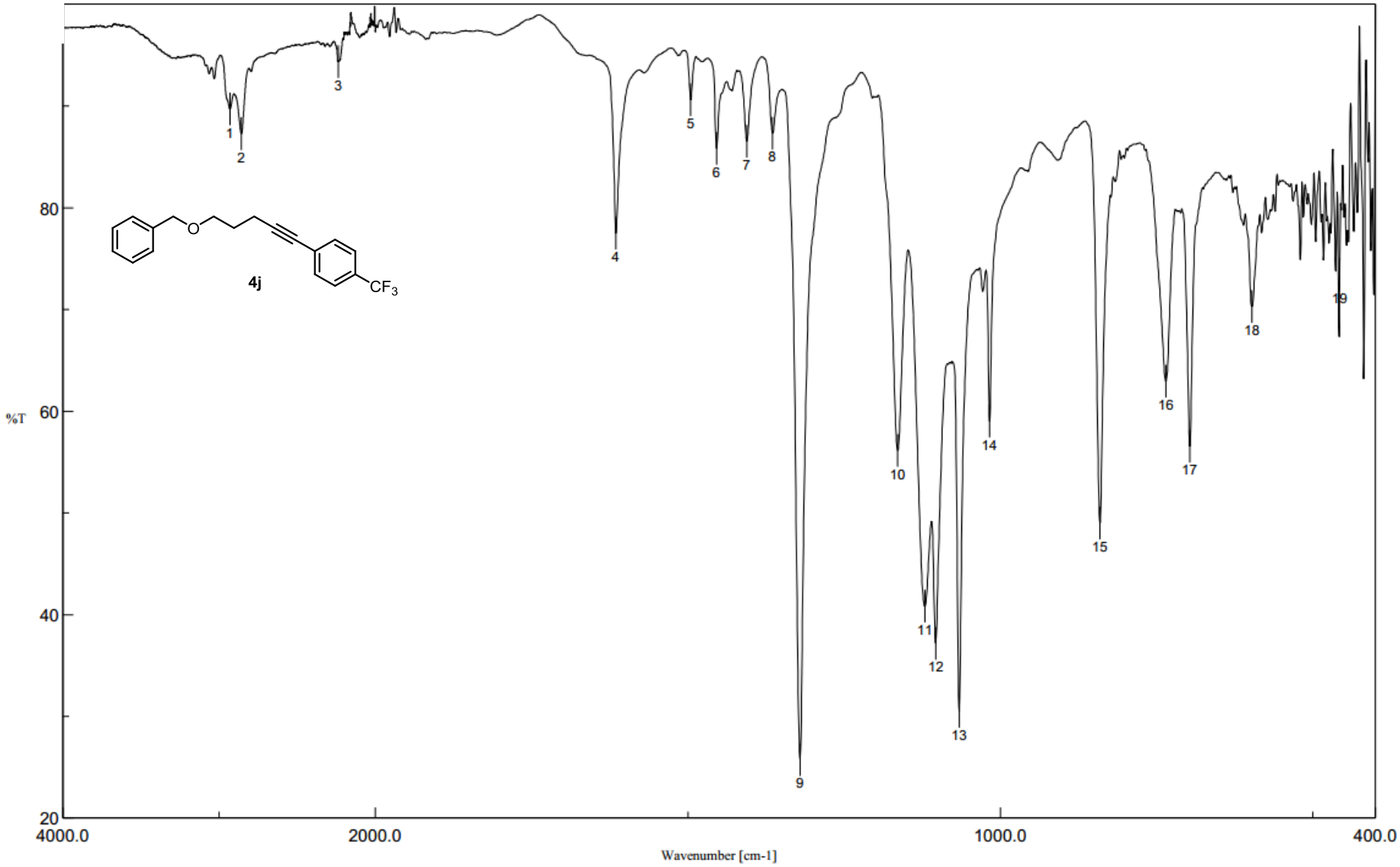
^{1}H, ^{13}C HMBC


O
CF3
4j
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

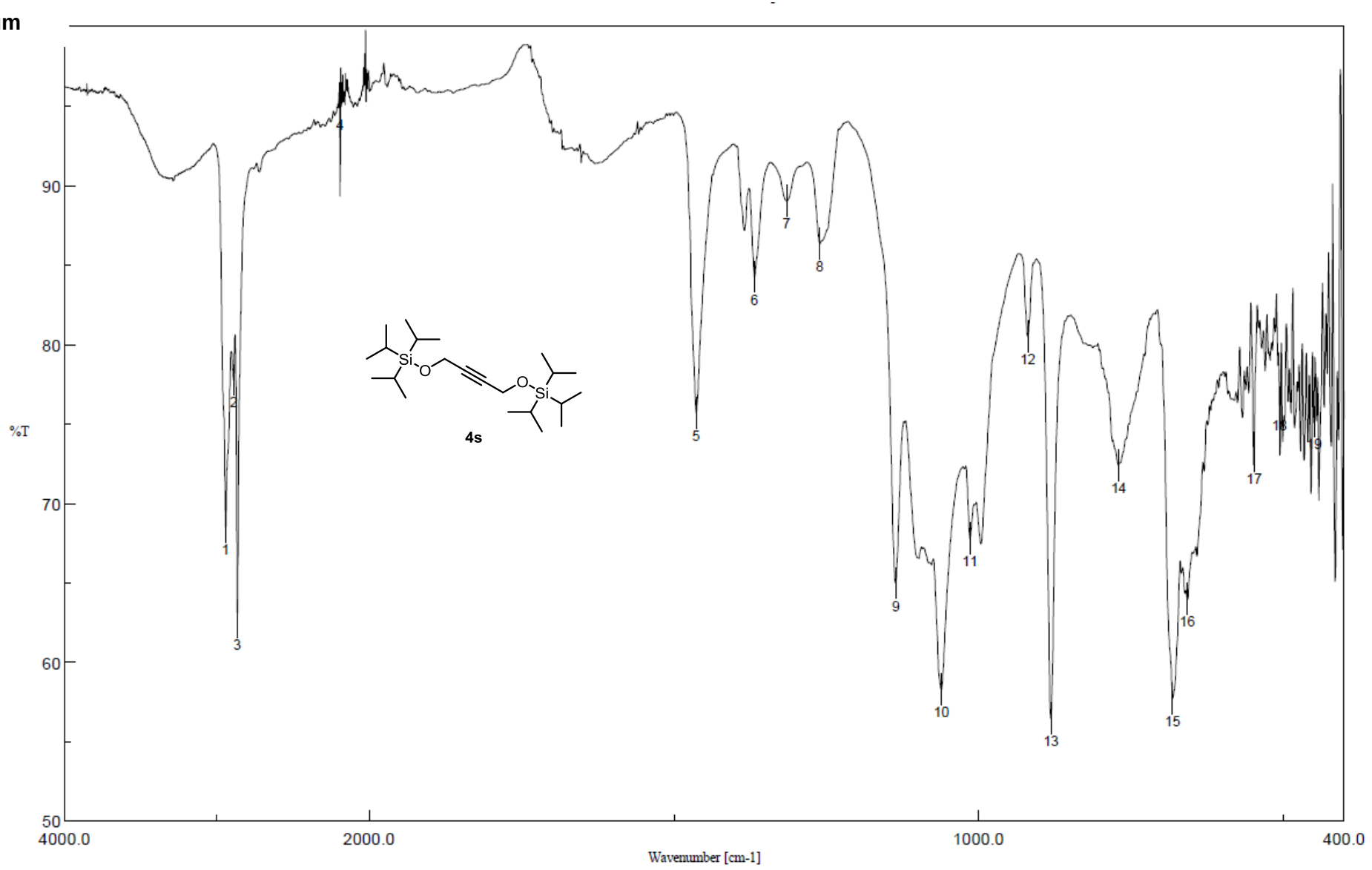
^{19}F-NMR



IR spectrum

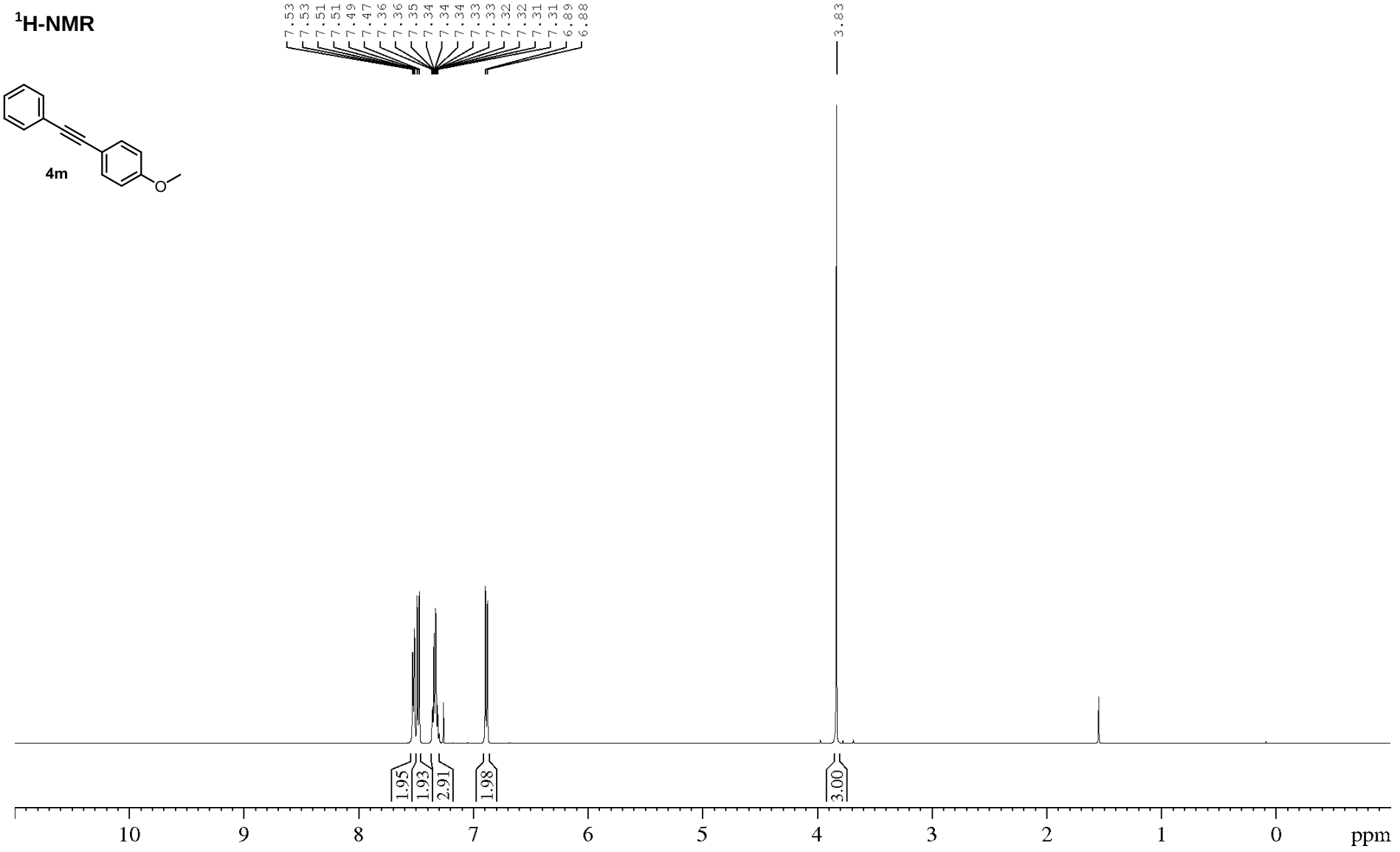

4j
CF3
O
%T
80
60
40
20
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

IR spectrum

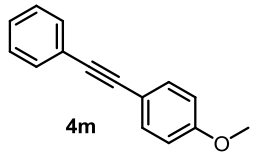

%T
90
80
70
60
50
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
Si
O
O
Si
4s

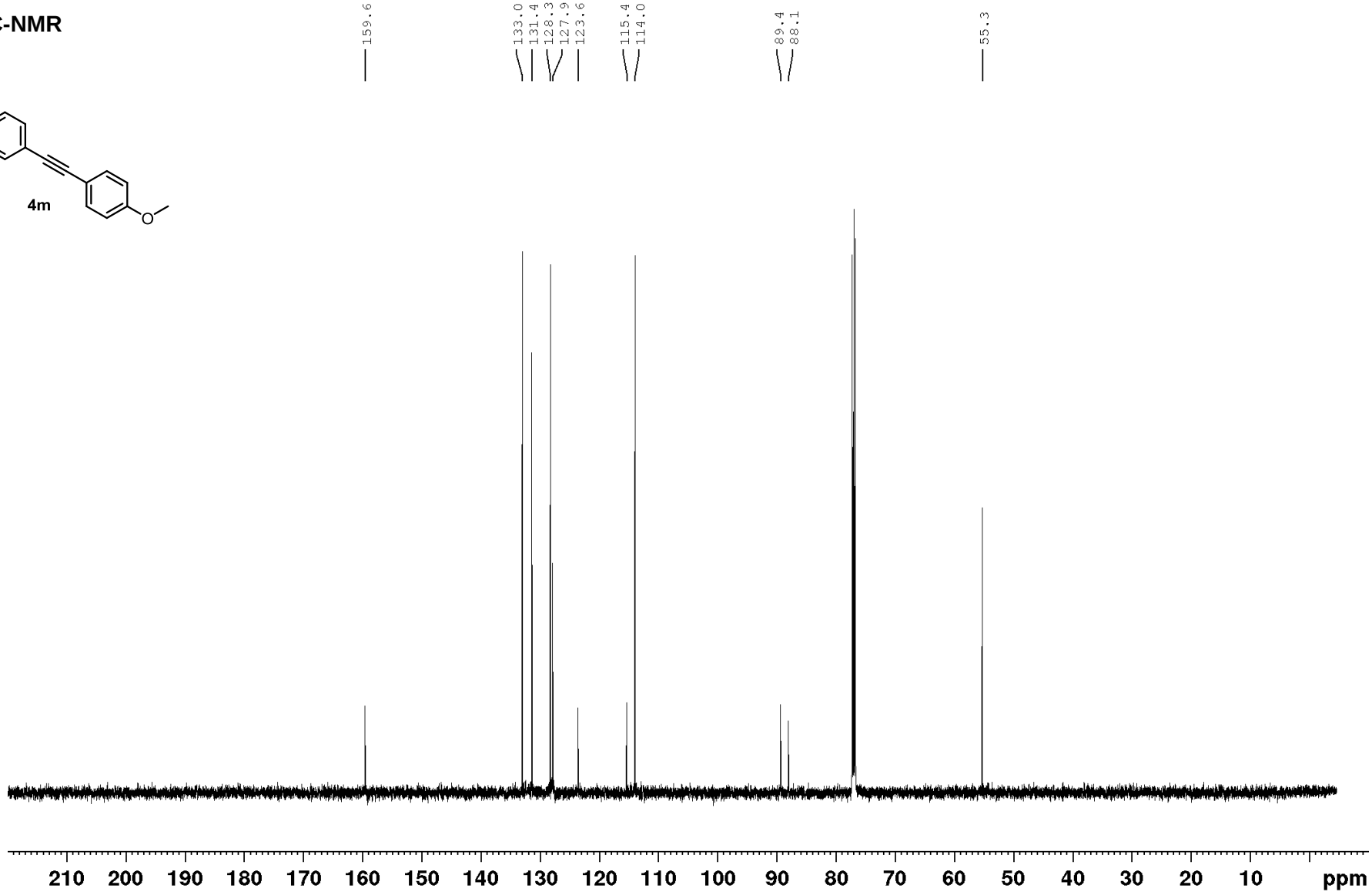
^{1}H-NMR

4m
O

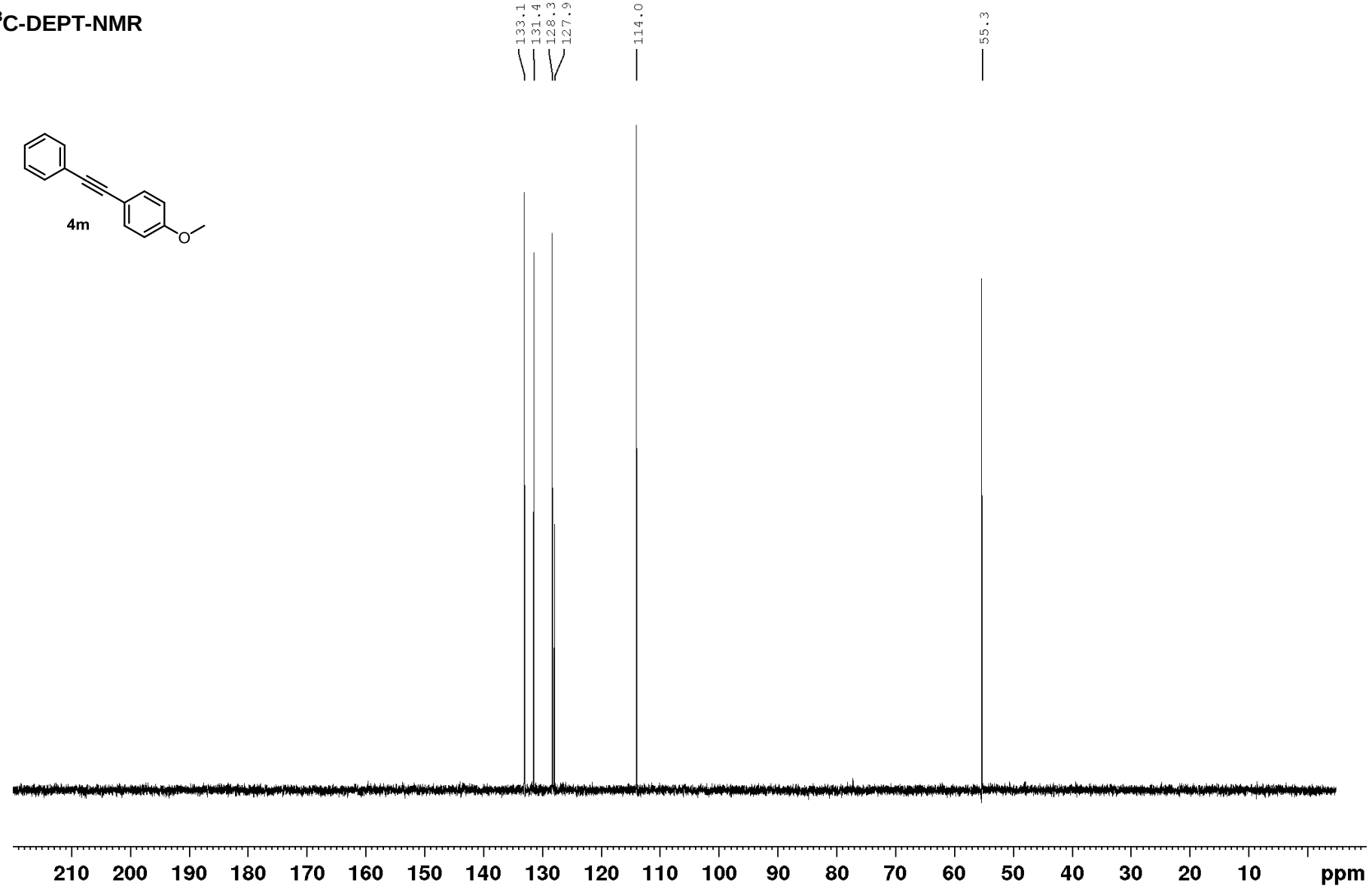

7.53
7.53
7.51
7.51
7.49
7.47
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
6.89
6.88
3.83
1.95
1.93
2.91
1.98
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C-NMR

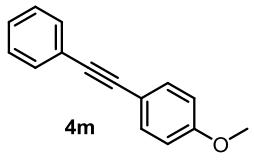

4m
O

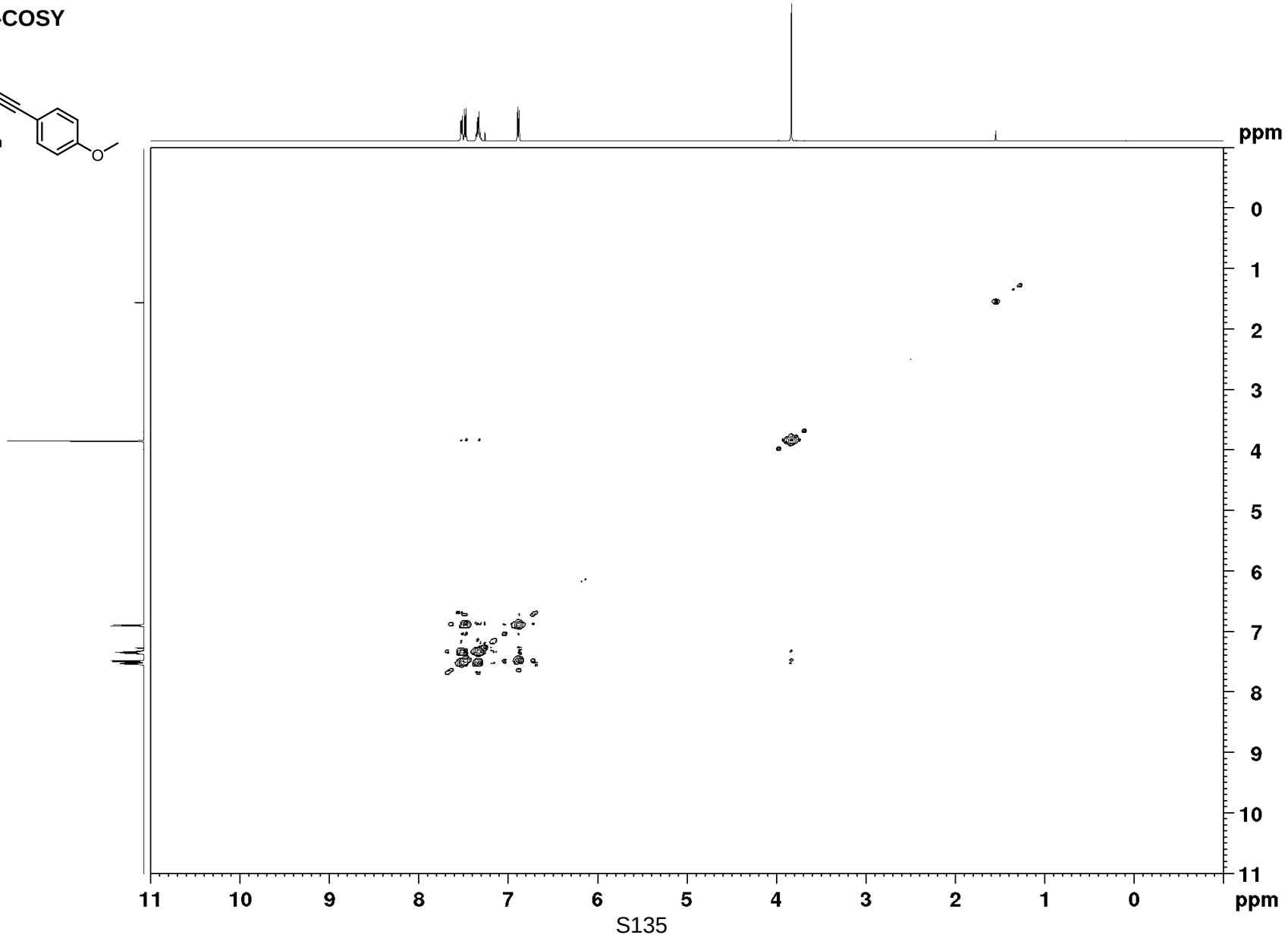

159.6
133.0
131.4
128.3
127.9
123.6
115.4
114.0
89.4
88.1
55.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C-DEPT-NMR

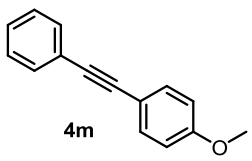

133.1
131.4
128.3
127.9
114.0
55.3
4m
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

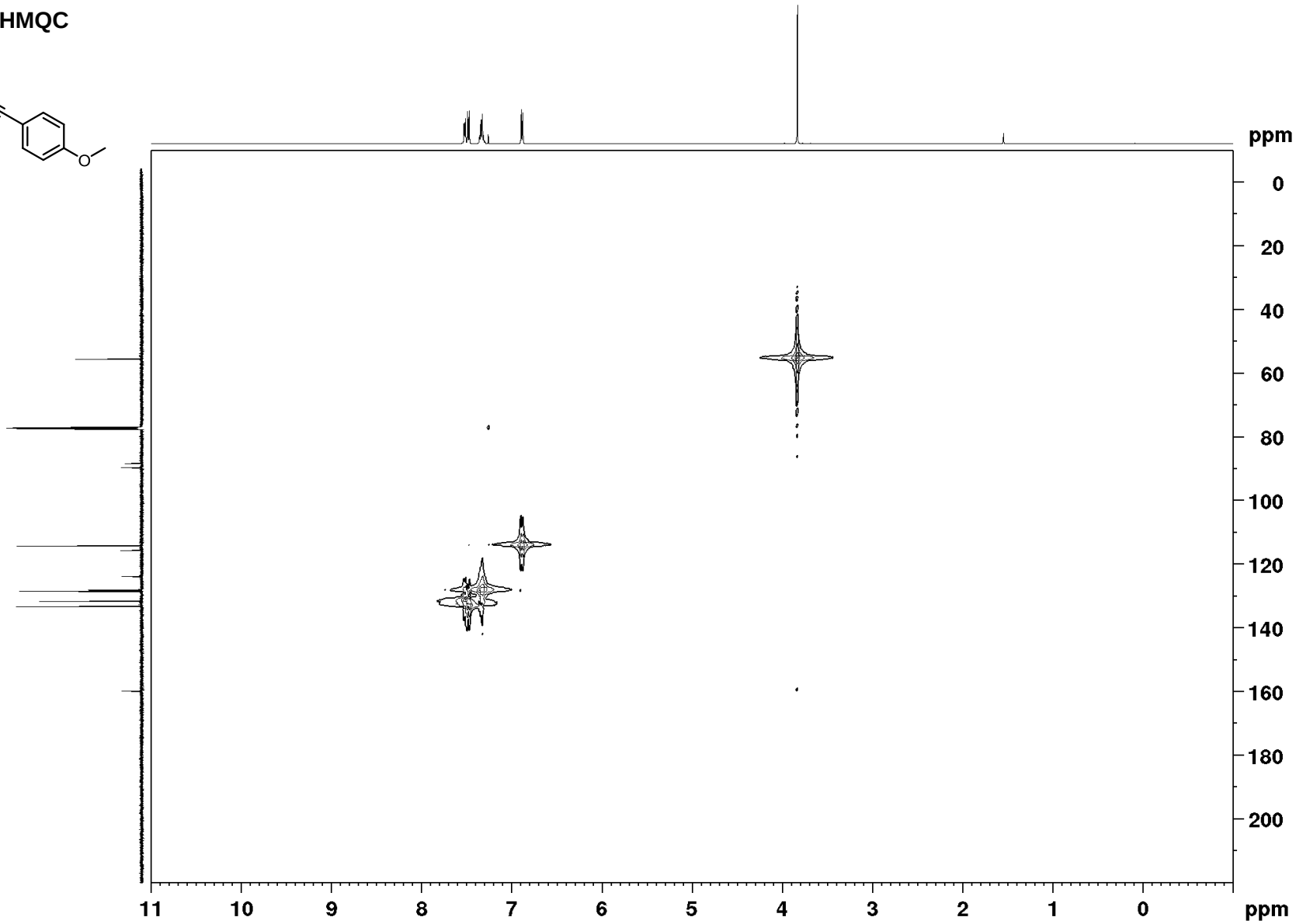
^{1}H, ^{1}H-COSY



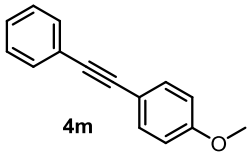


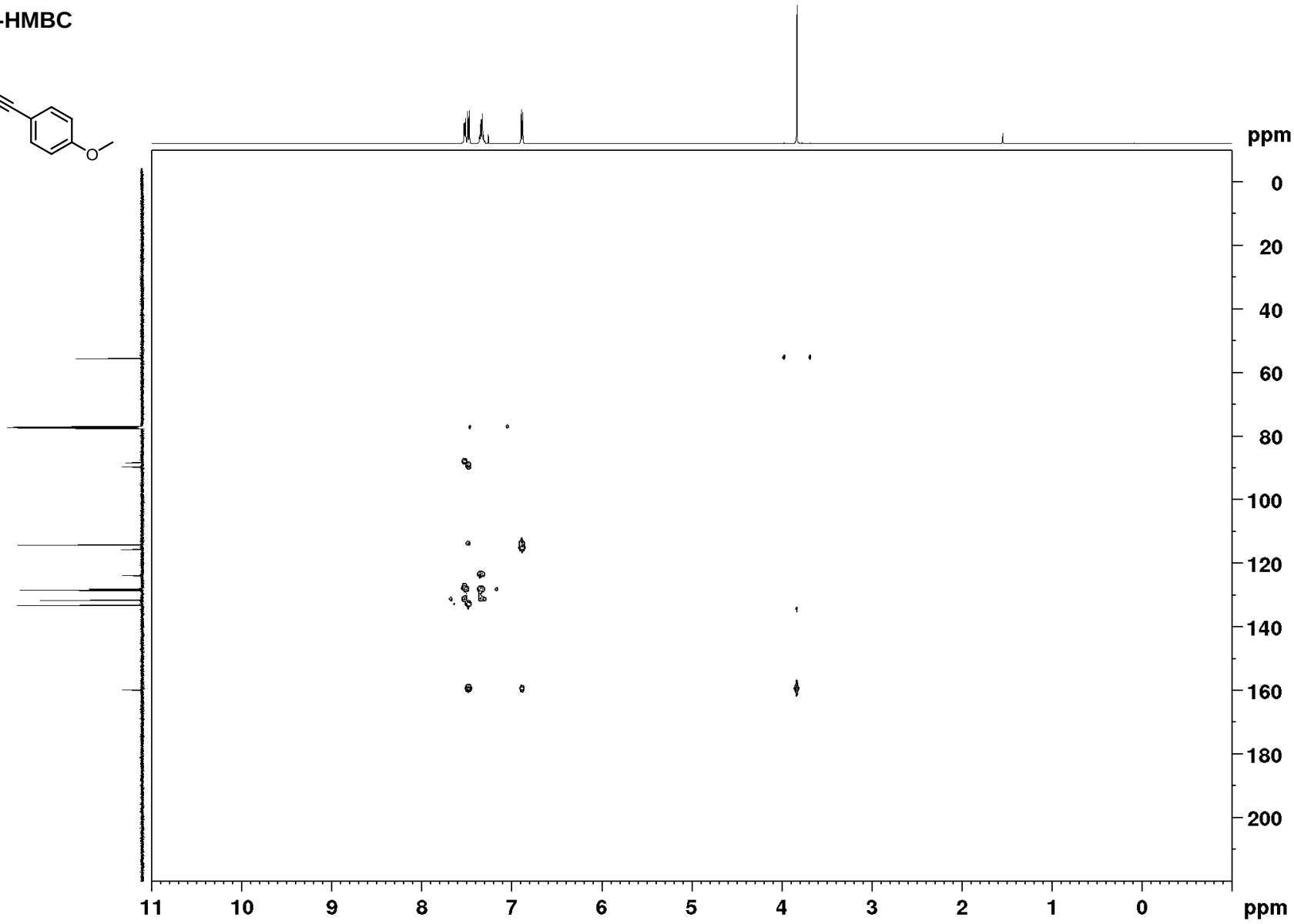
^{1}H, ^{13}C-HMQC


4m
O

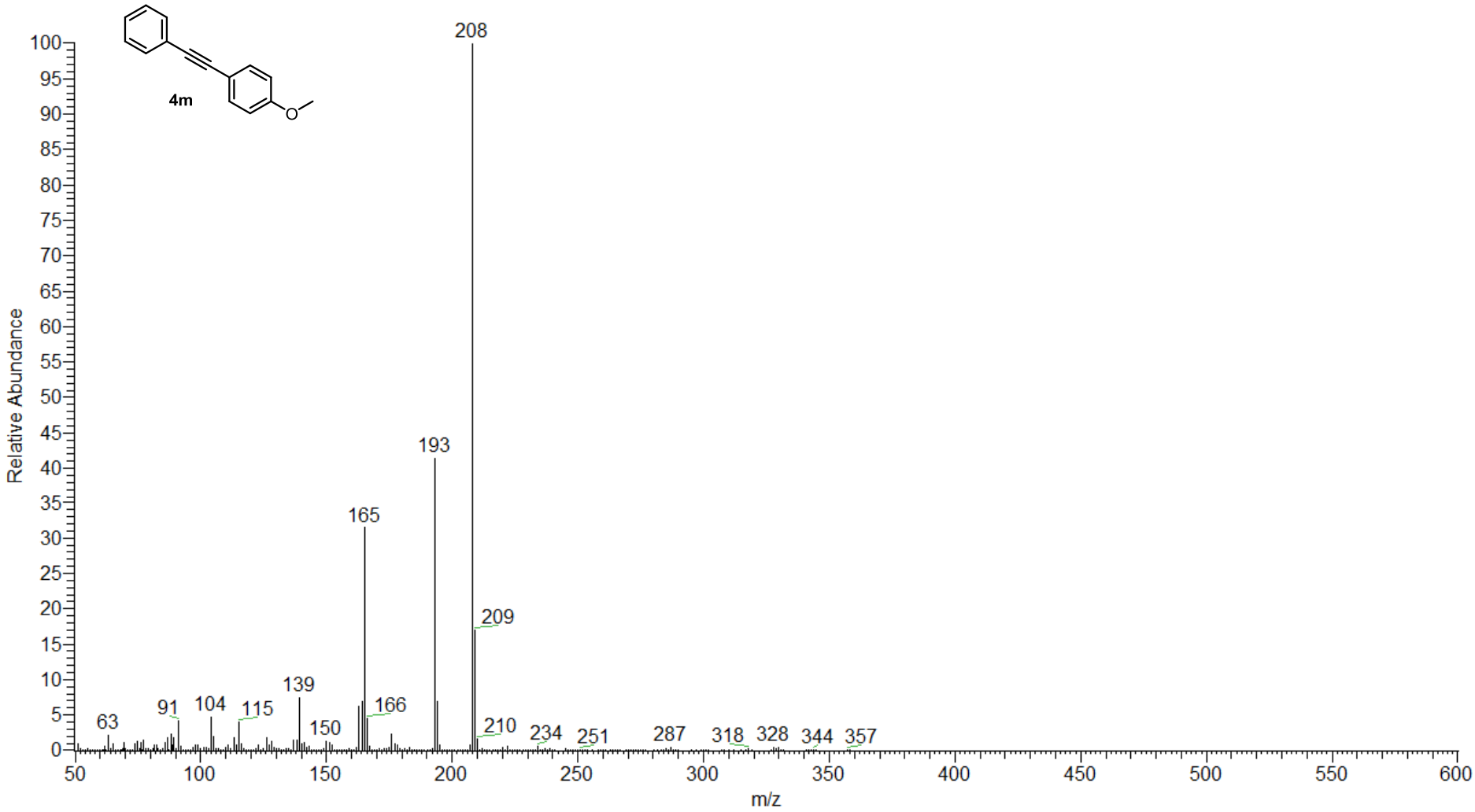

ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H, ^{13}C-HMBC

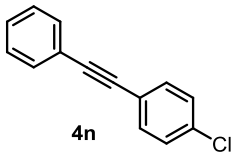

4m
O

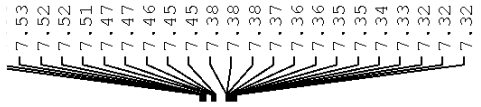

ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

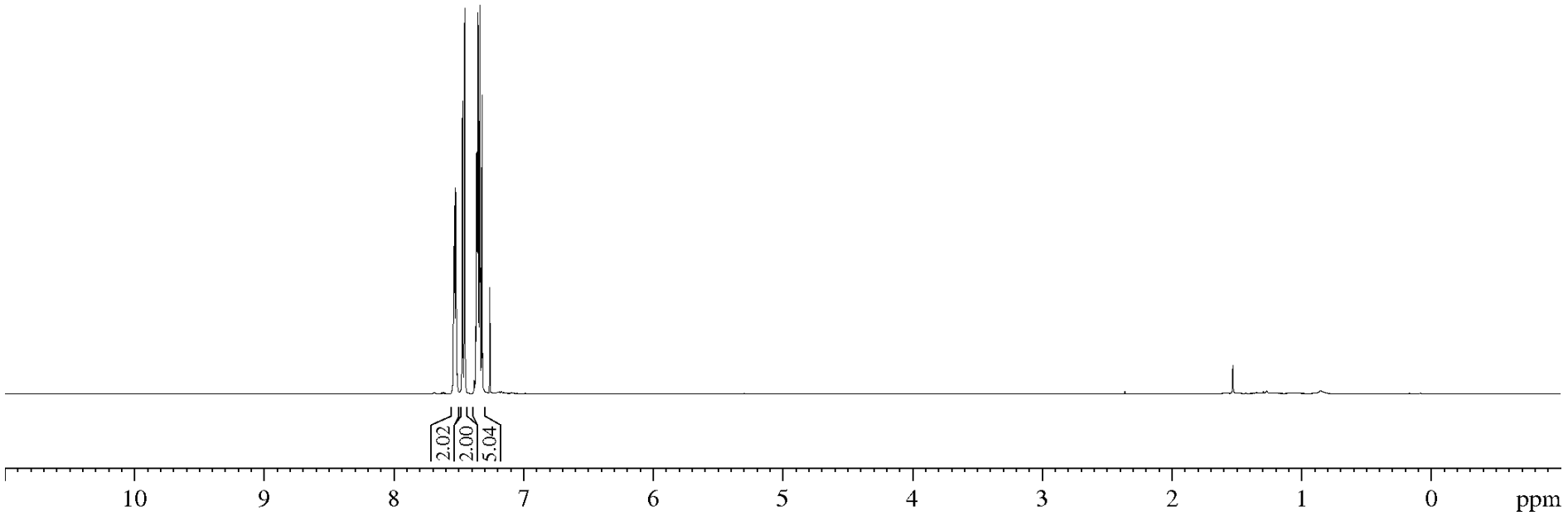
mass spectrum



^{1}H-NMR


4n
Cl

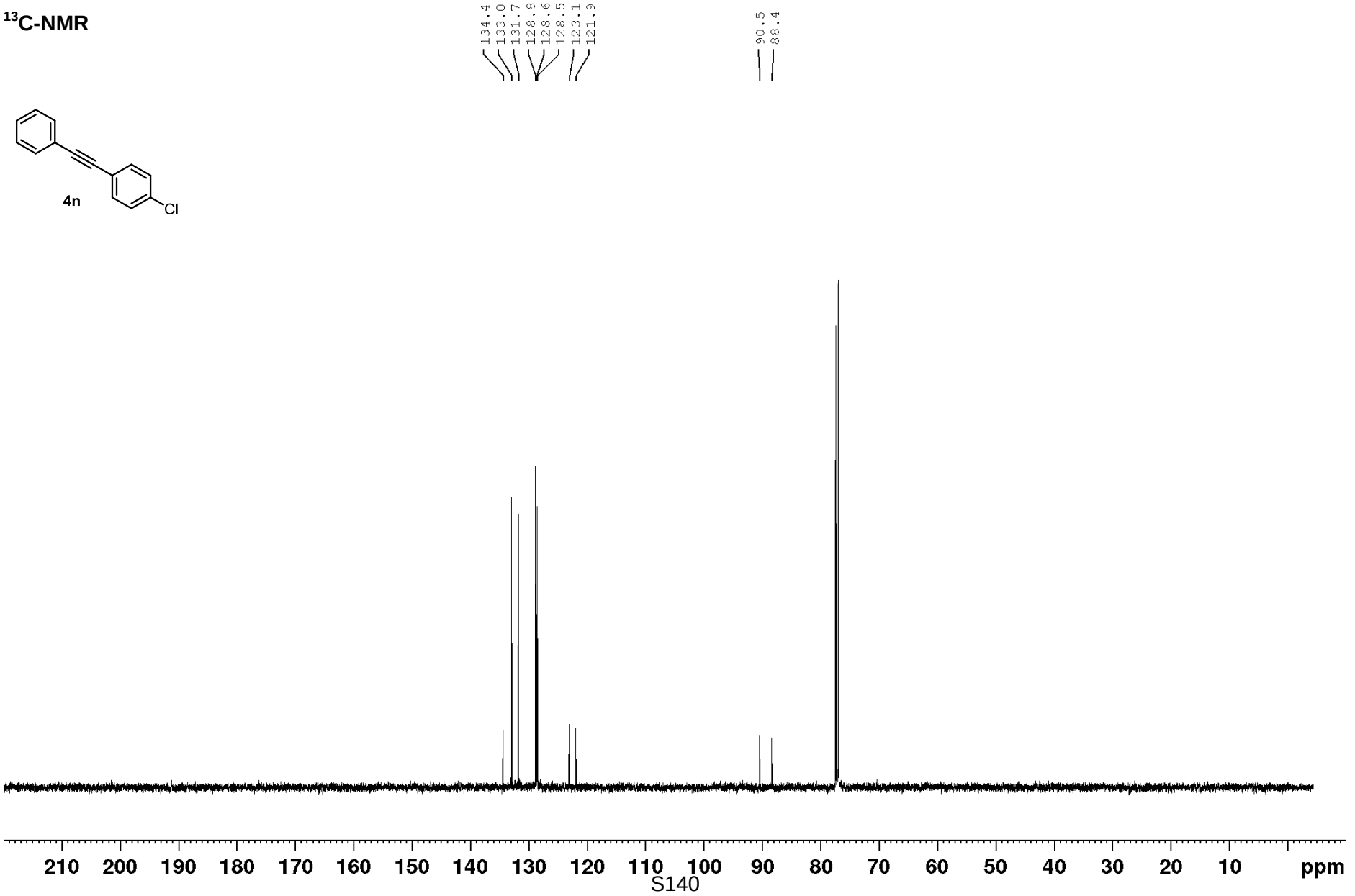

7.53
7.52
7.52
7.51
7.47
7.47
7.46
7.45
7.45
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.32


2.02
2.00
5.04
10
9
8
7
6
5
4
3
2
1
0
ppm

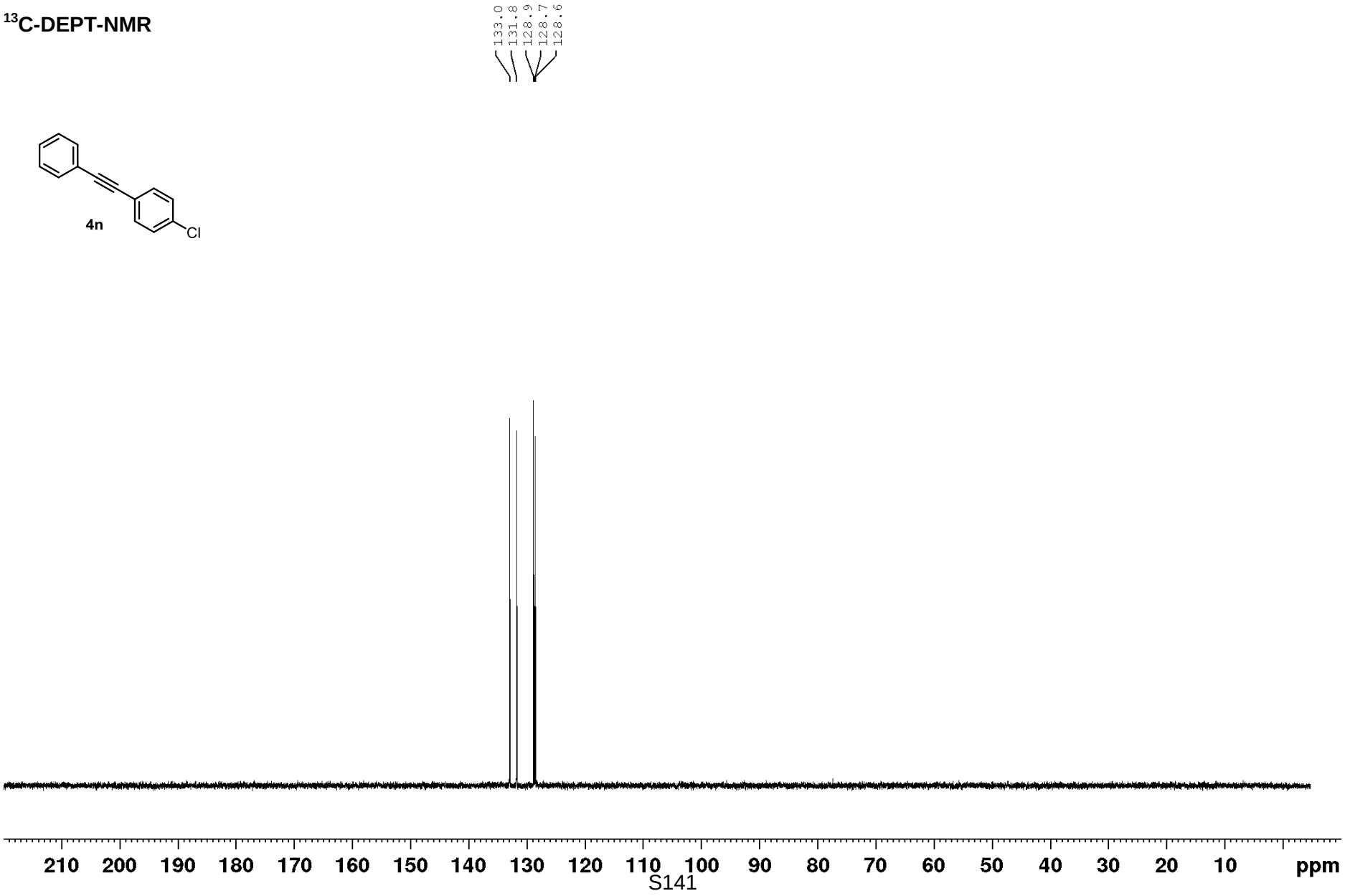
^{13}C-NMR

Cl

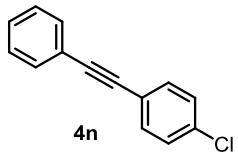
4n

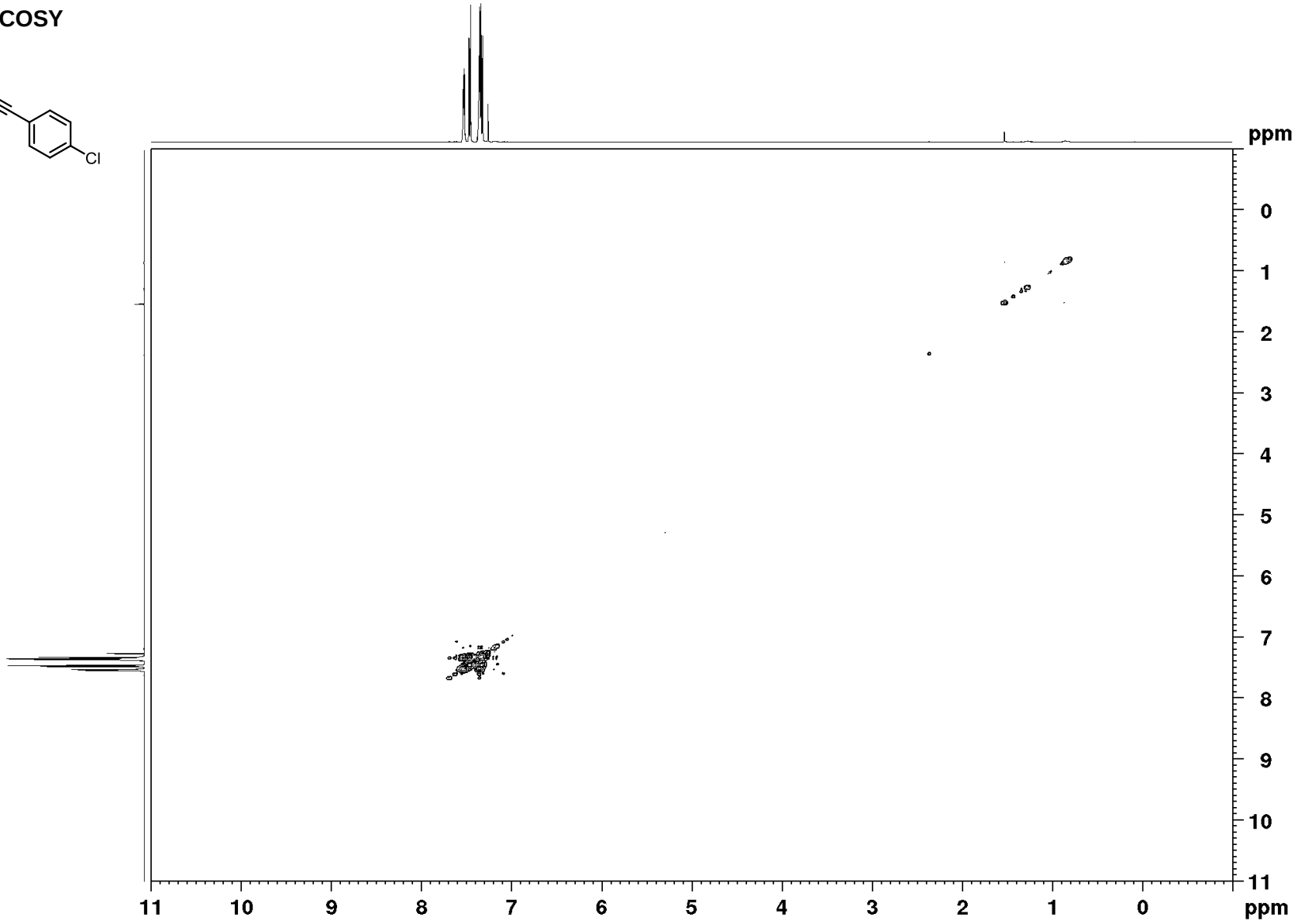

134.4
133.0
131.7
128.8
128.6
128.5
123.1
121.9
90.5
88.4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{13}C-DEPT-NMR

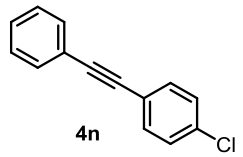

133.0
131.8
128.9
128.7
128.6
Cl
4n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

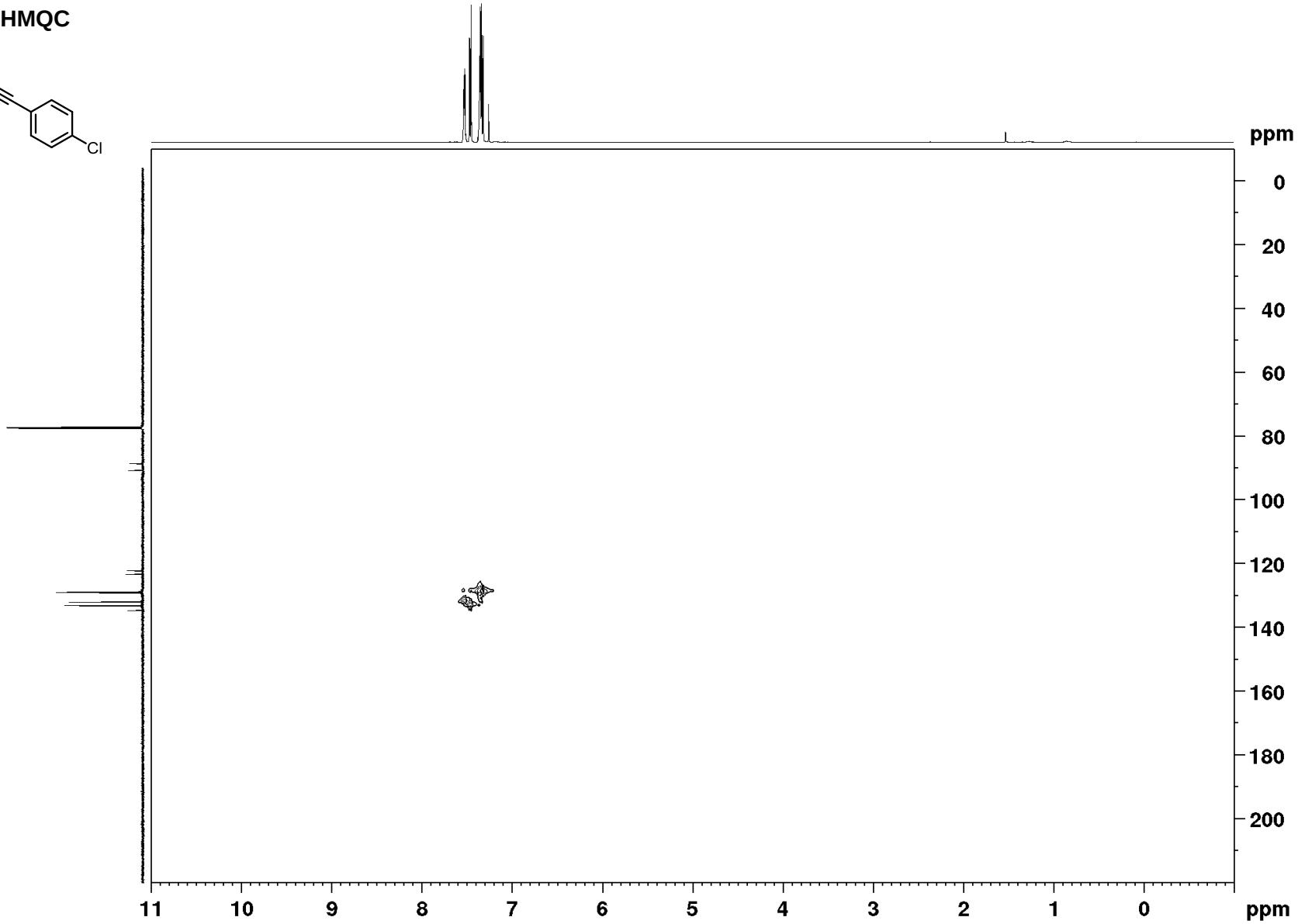
^{1}H, ^{1}H -COSY



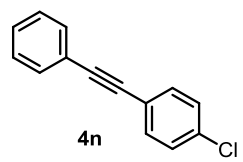


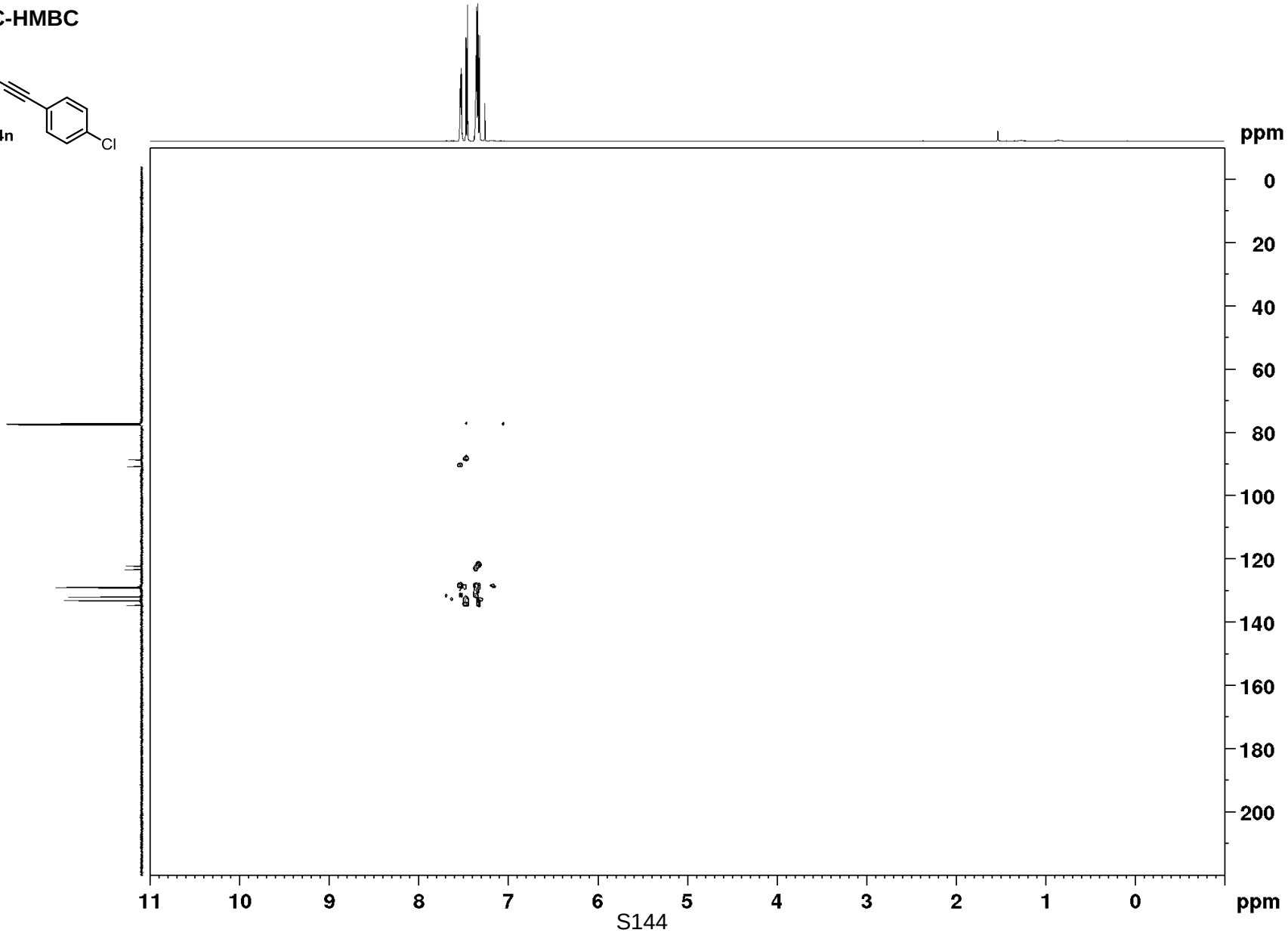
^{1}H, ^{13}C-HMQC


4n
Cl

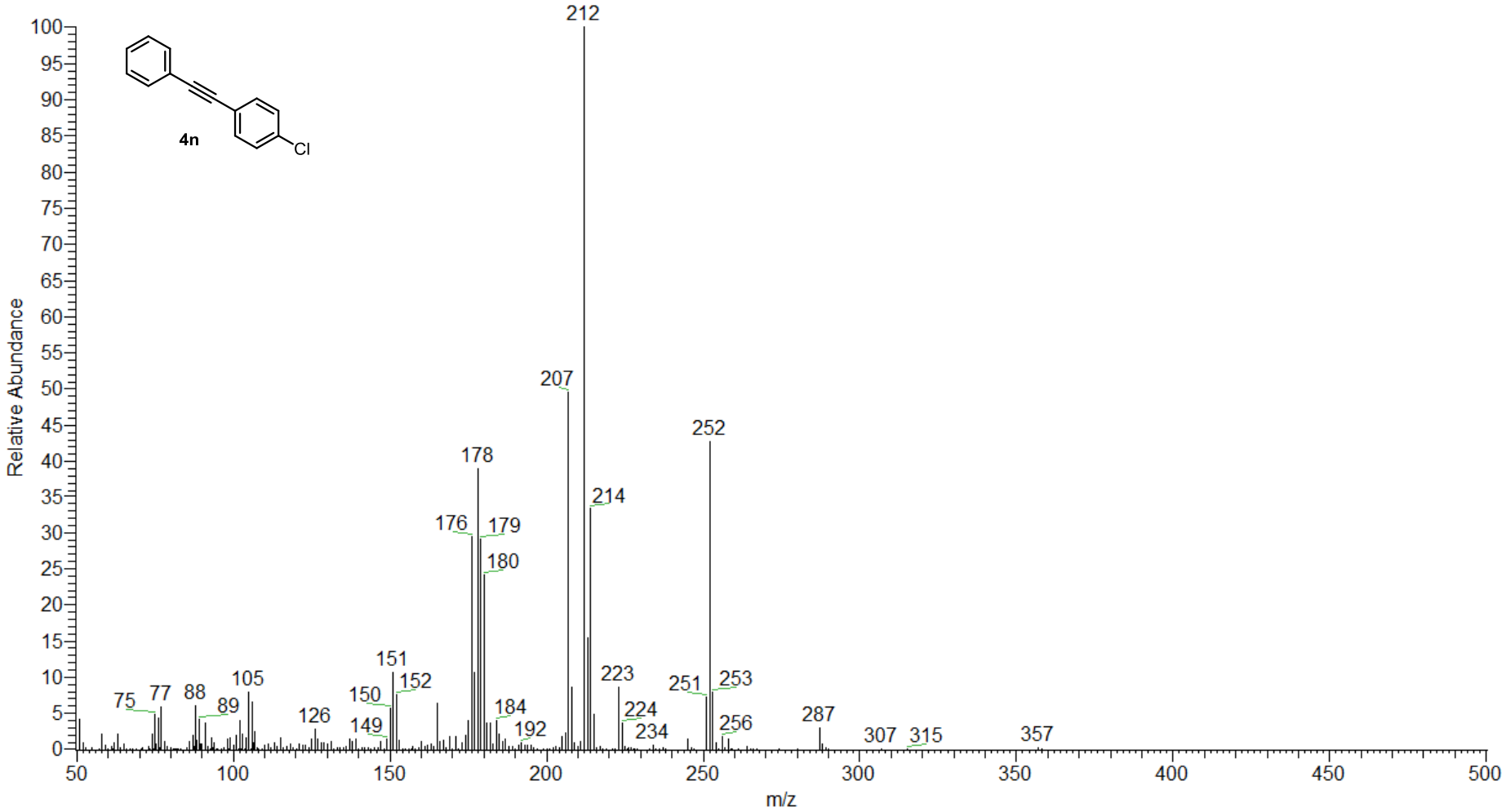

ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H, ^{13}C-HMBC

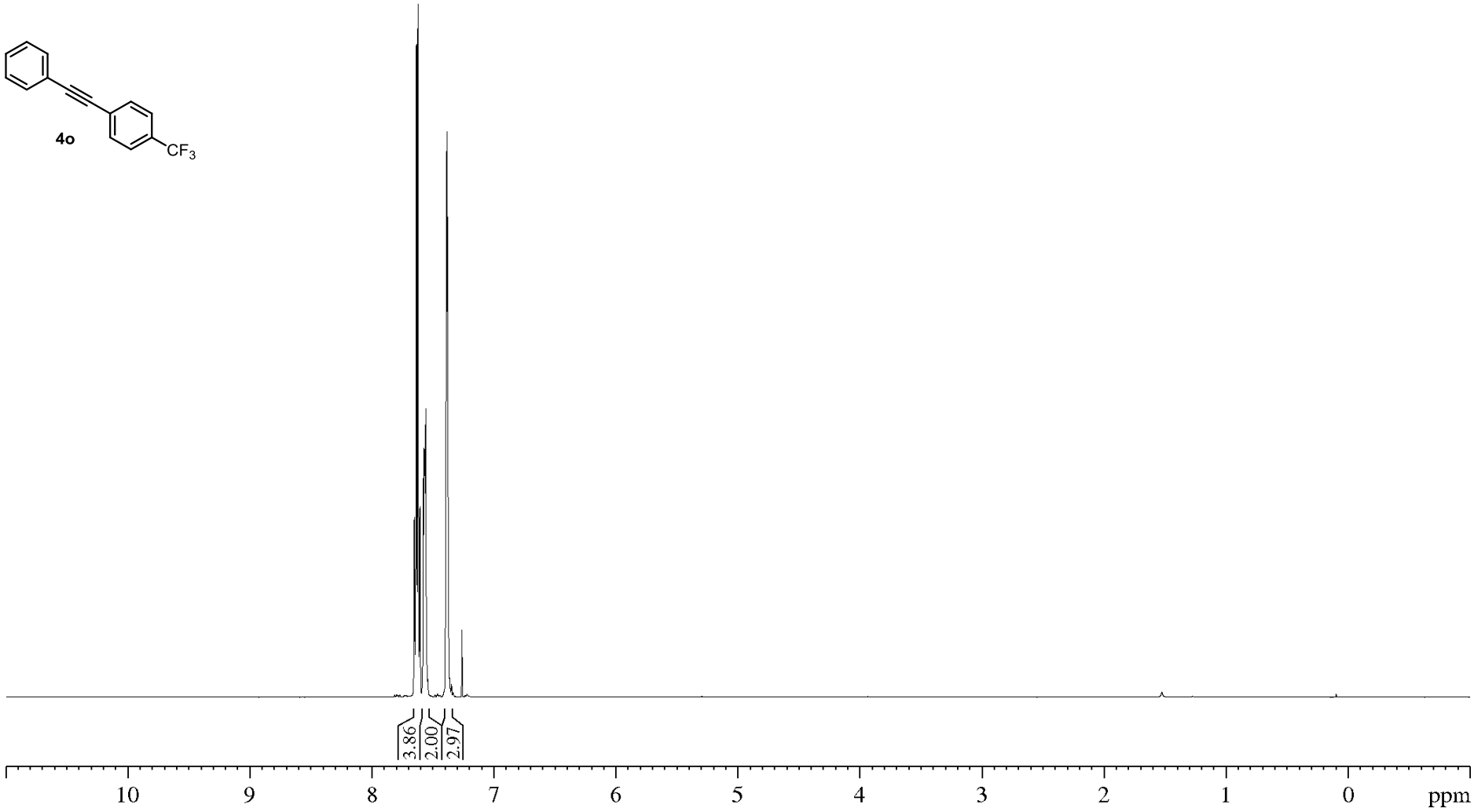

4n
Cl


ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

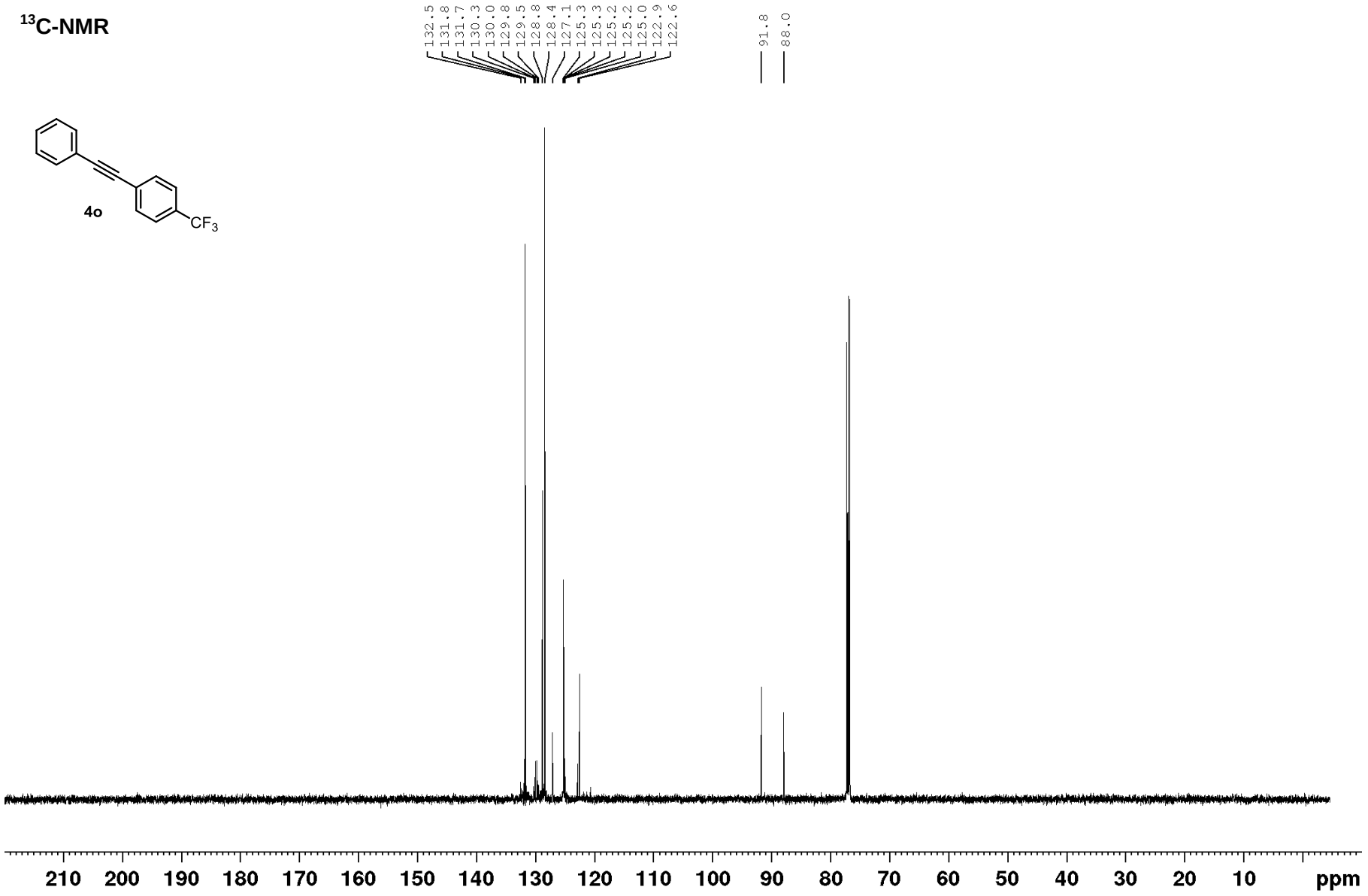
mass spectrum



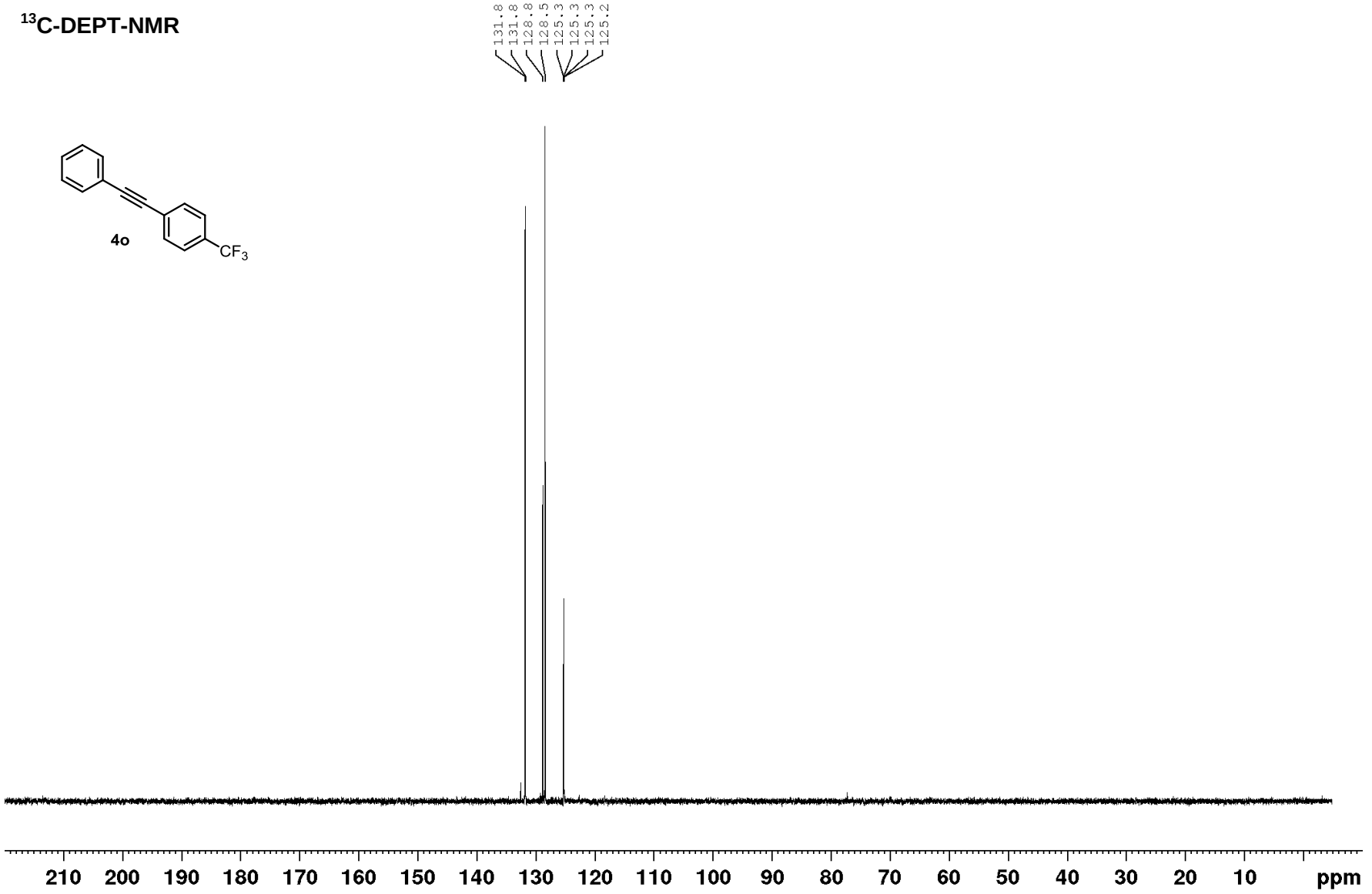
^{1}H-NMR

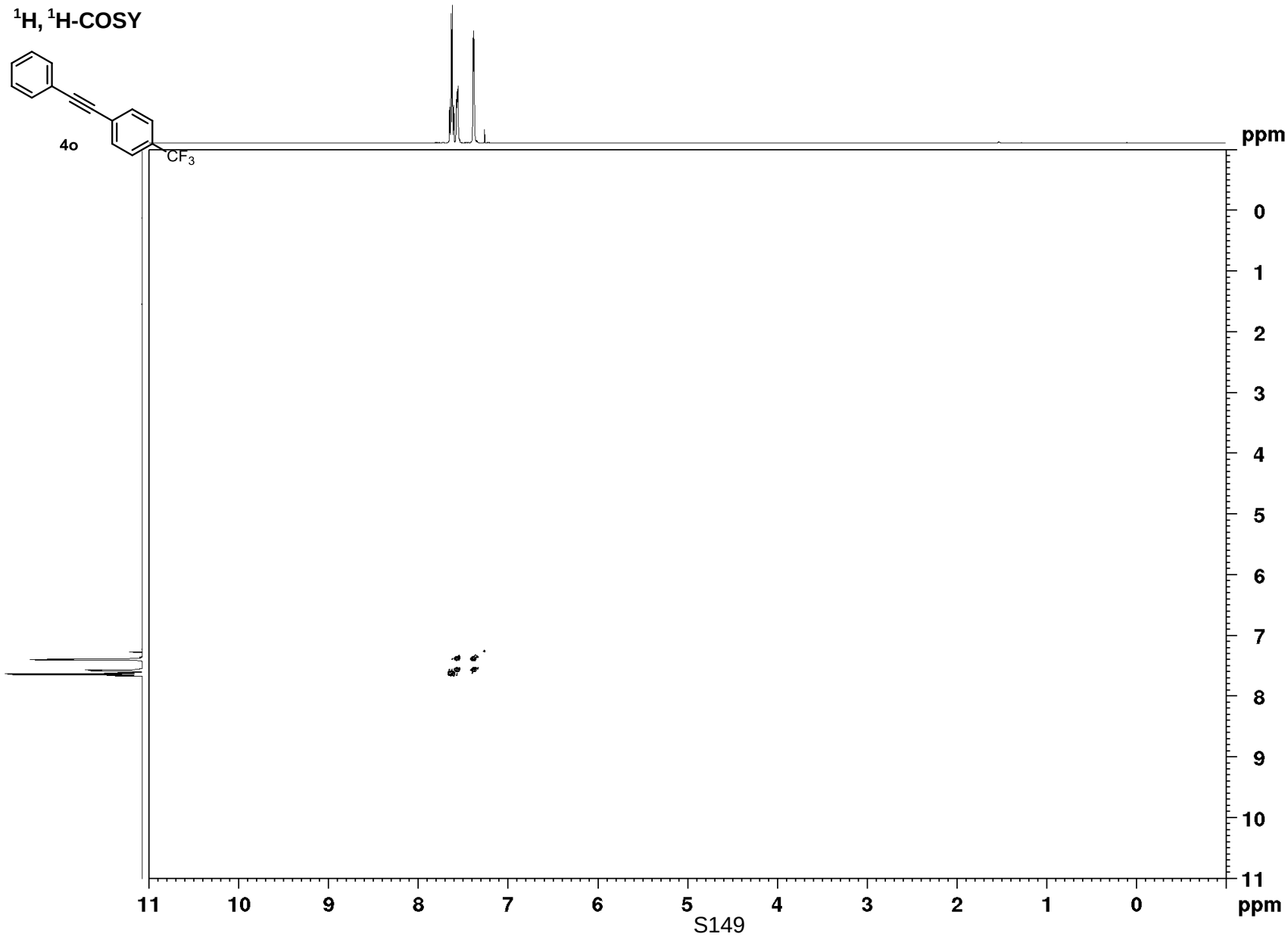


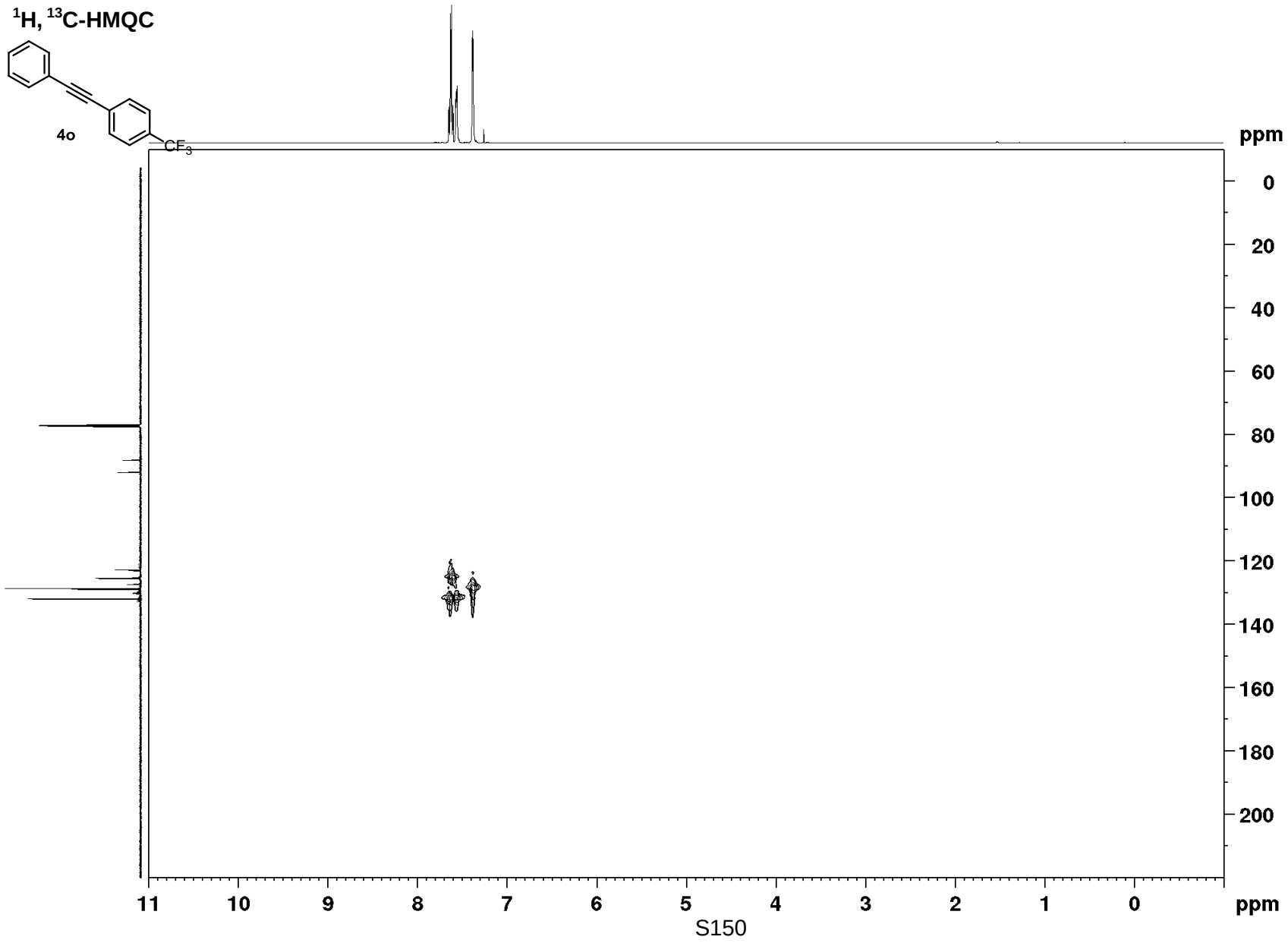
^{13}C-NMR


132.5
131.8
131.7
130.3
130.0
129.8
129.5
128.8
128.4
127.1
125.3
125.3
125.2
125.2
125.0
122.9
122.6
91.8
88.0
4o
CF3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{13}C-DEPT-NMR

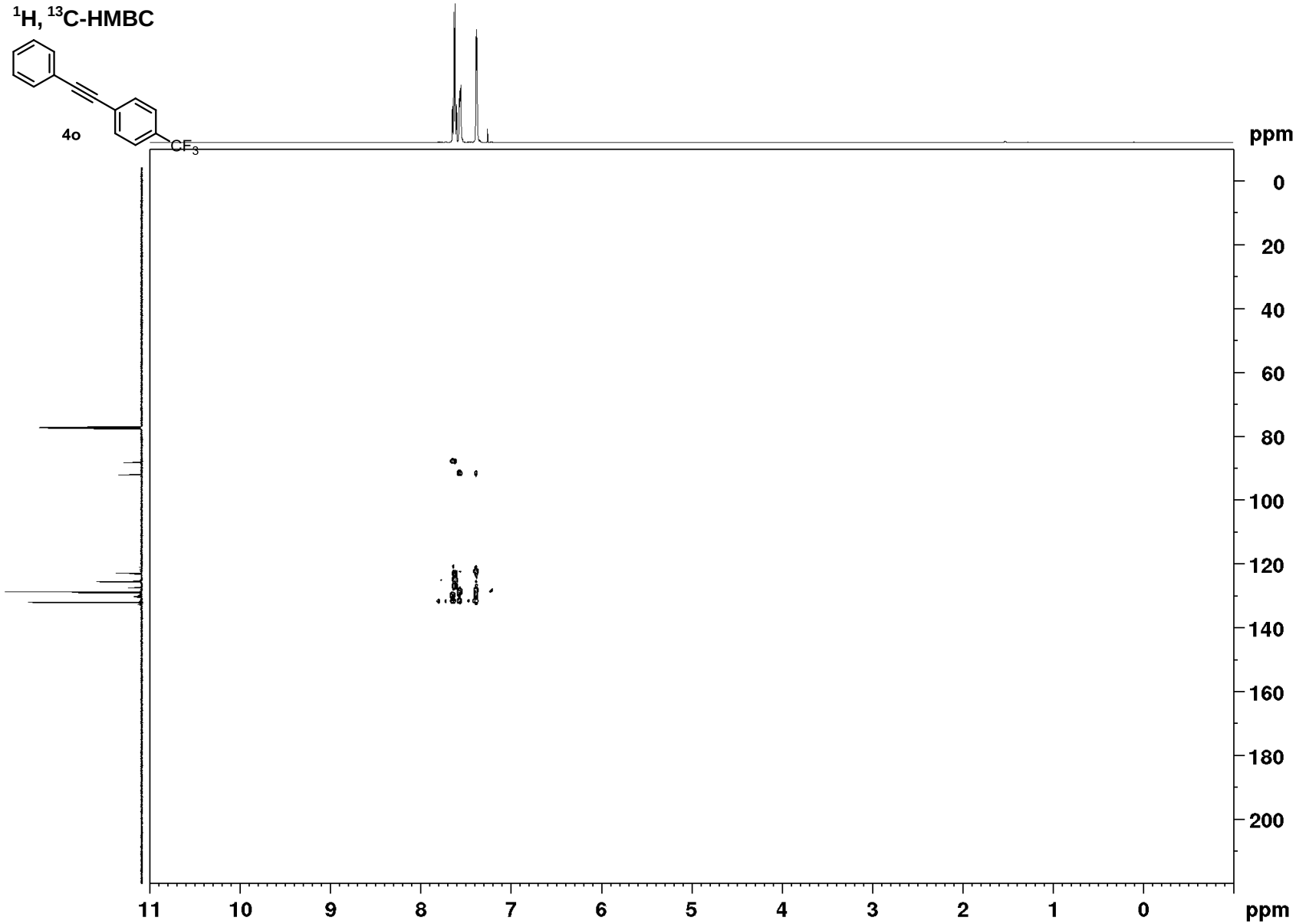

131.8
131.8
128.8
128.5
125.3
125.3
125.2
4o
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{1}H, ^{1}H-COSY
4o
CF_3
ppm
0
1
2
3
4
5
6
7
8
9
10
11
11
10
9
8
7
6
5
4
3
2
1
0
ppm

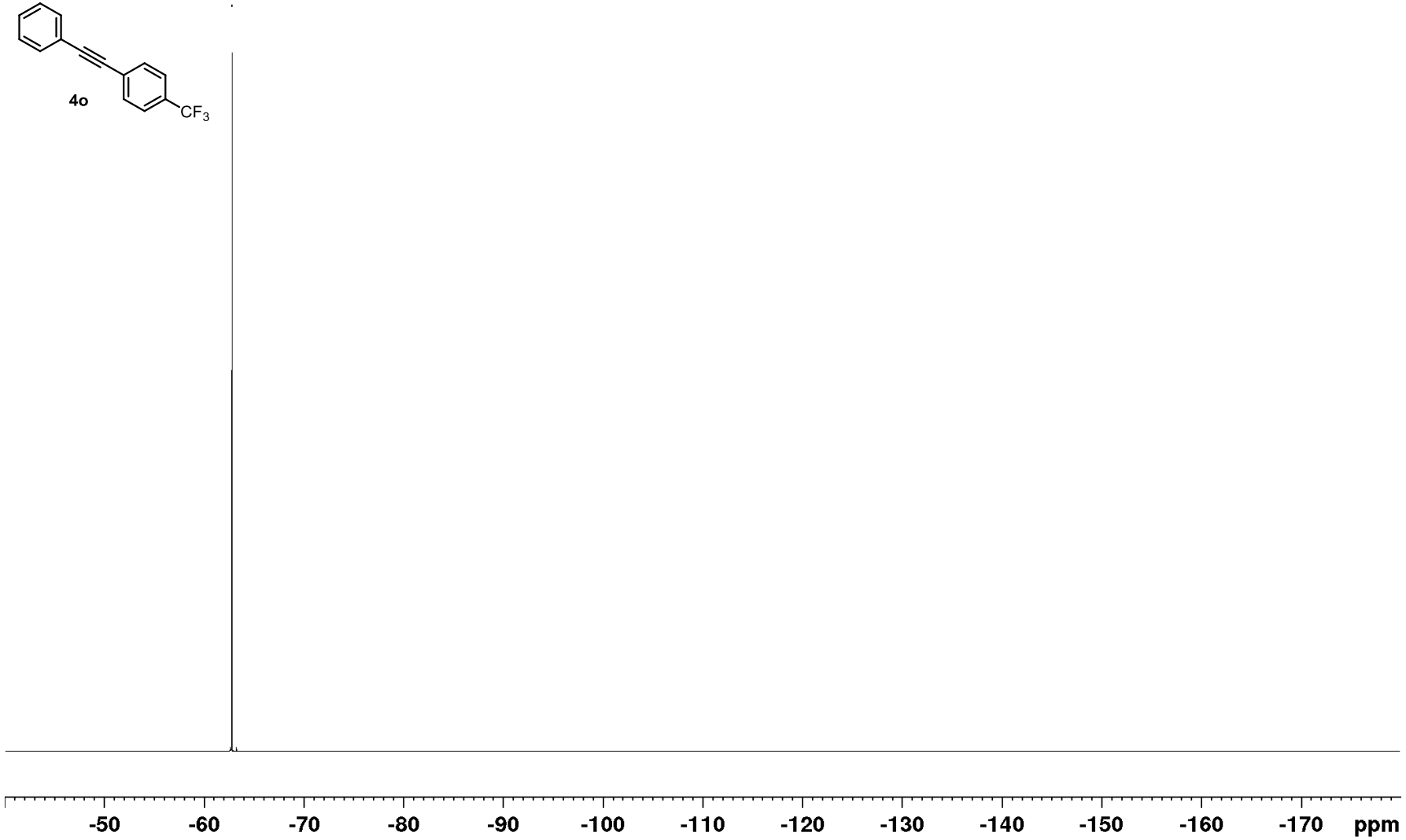

^{1}H, ^{13}C-HMQC
4o
CF_3
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H, ^{13}C-HMBC

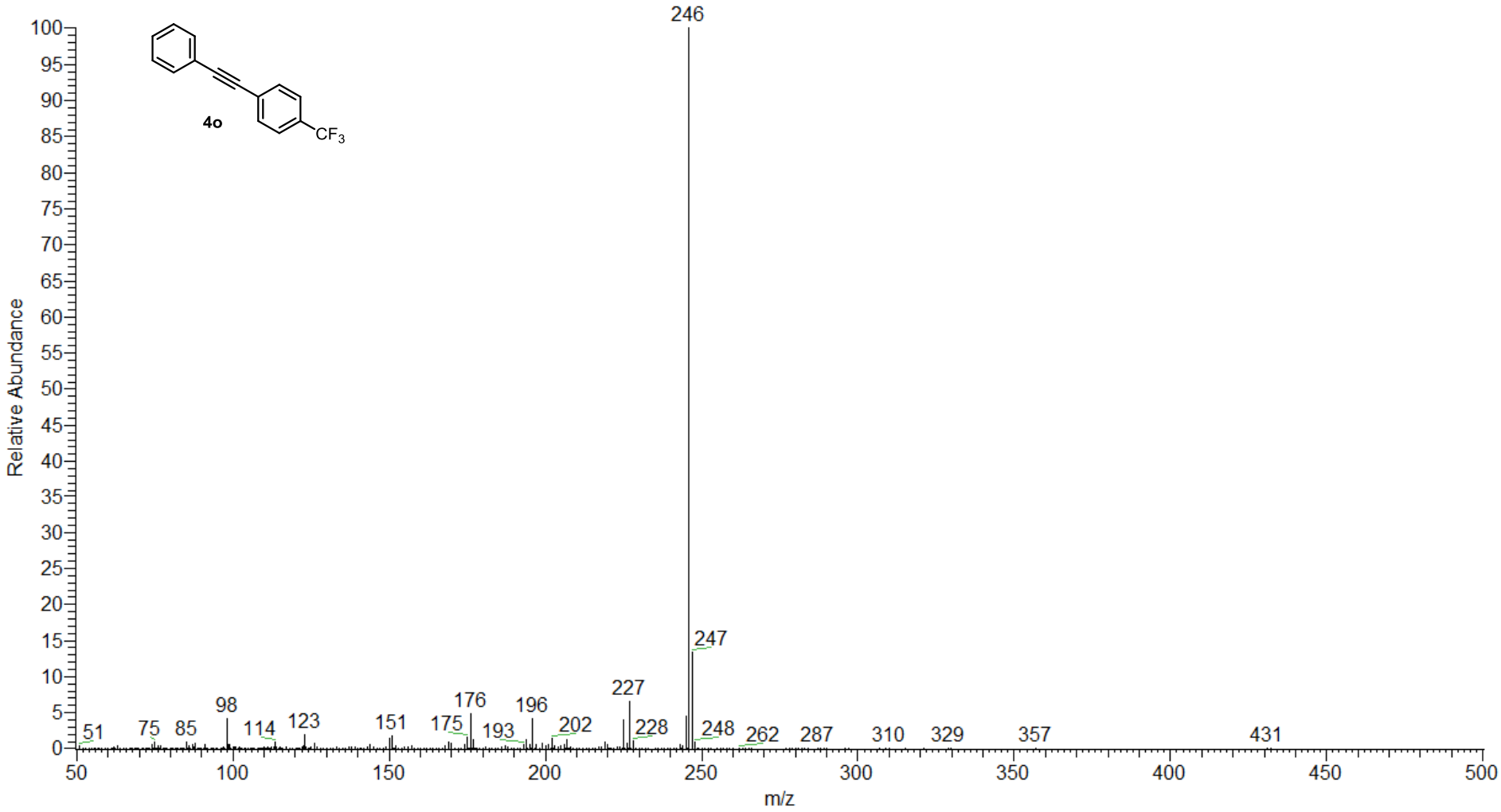
4o
CF3


ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{19}F-NMR

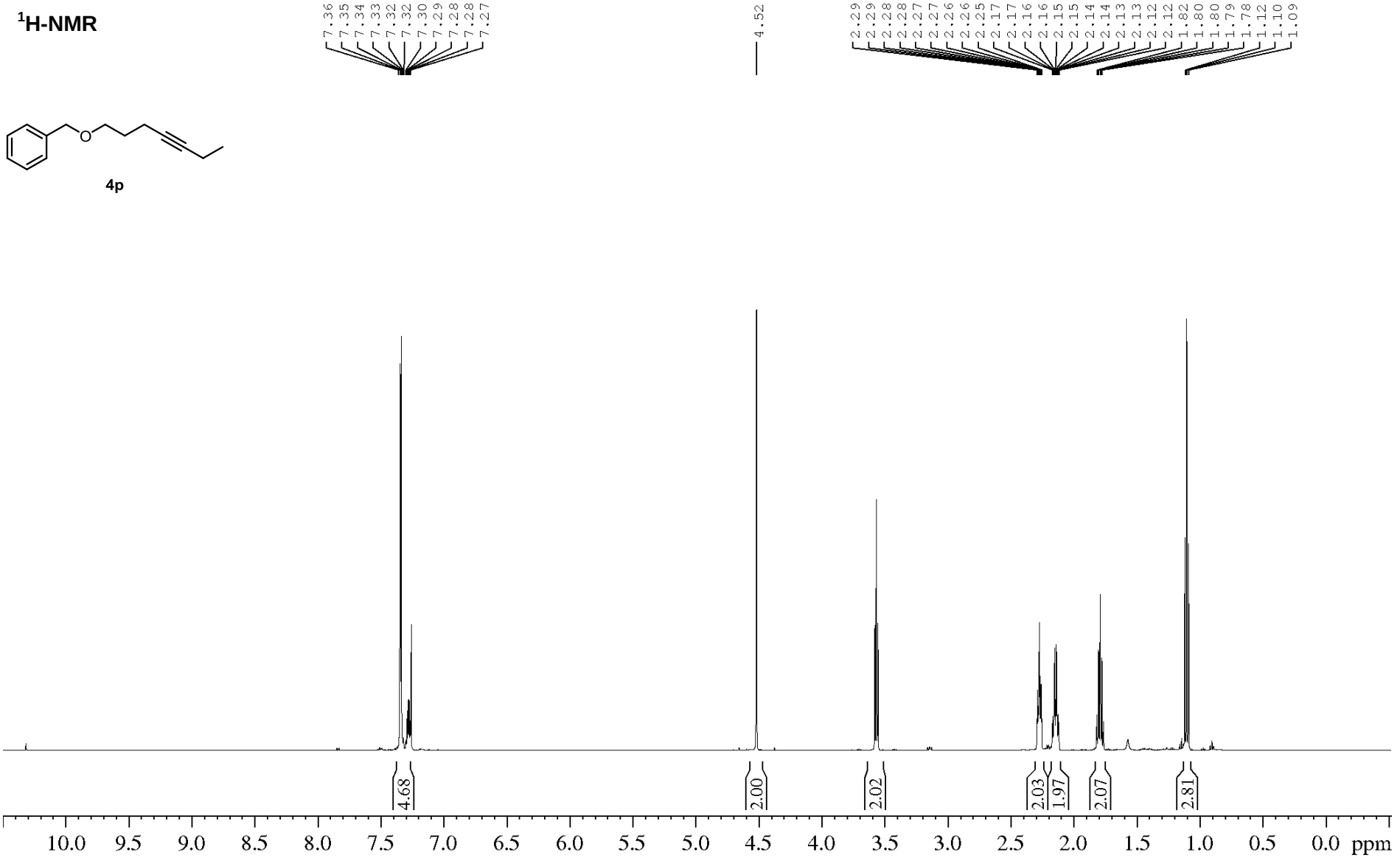


mass spectrum



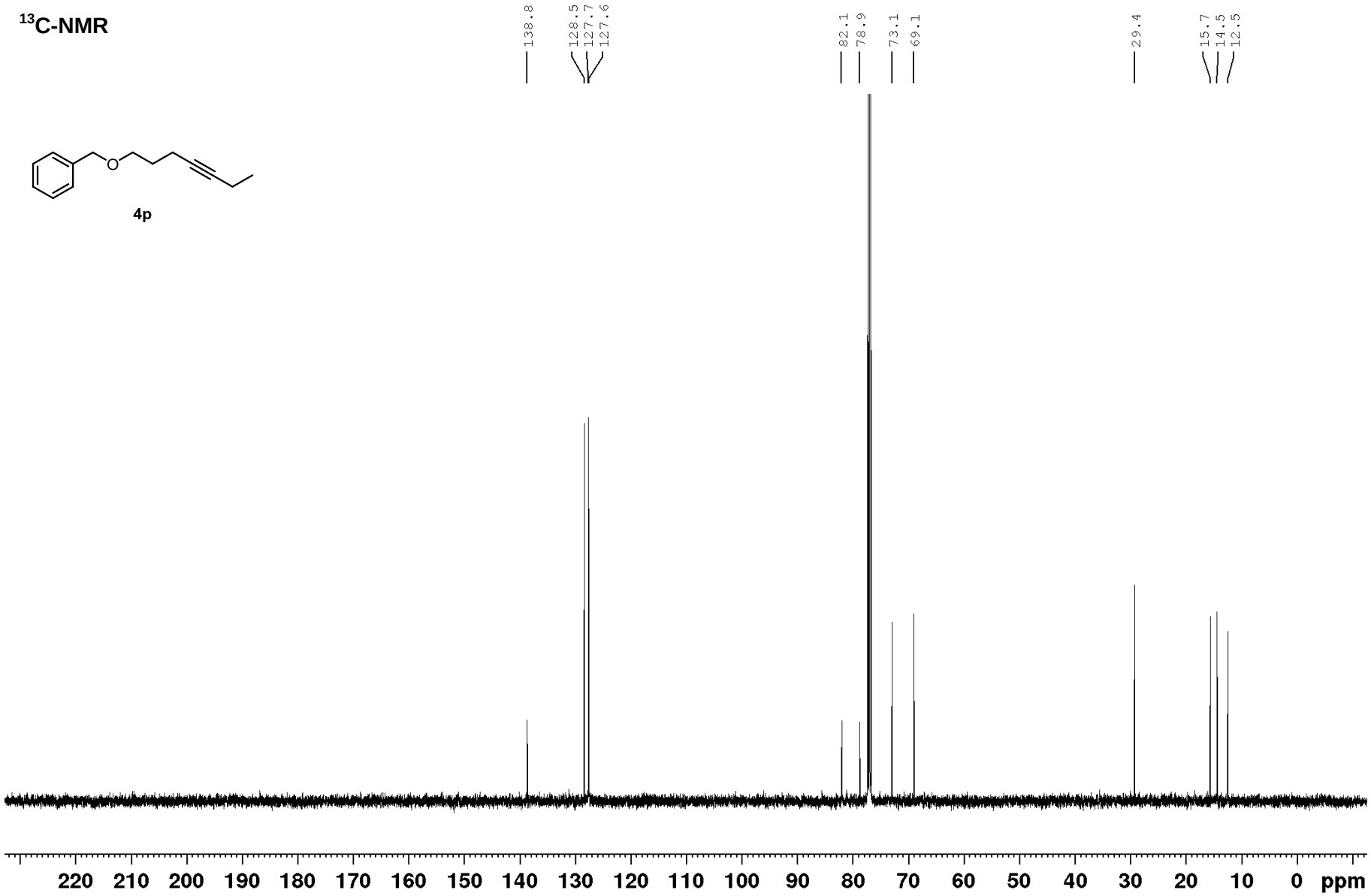
^{1}H-NMR

4p

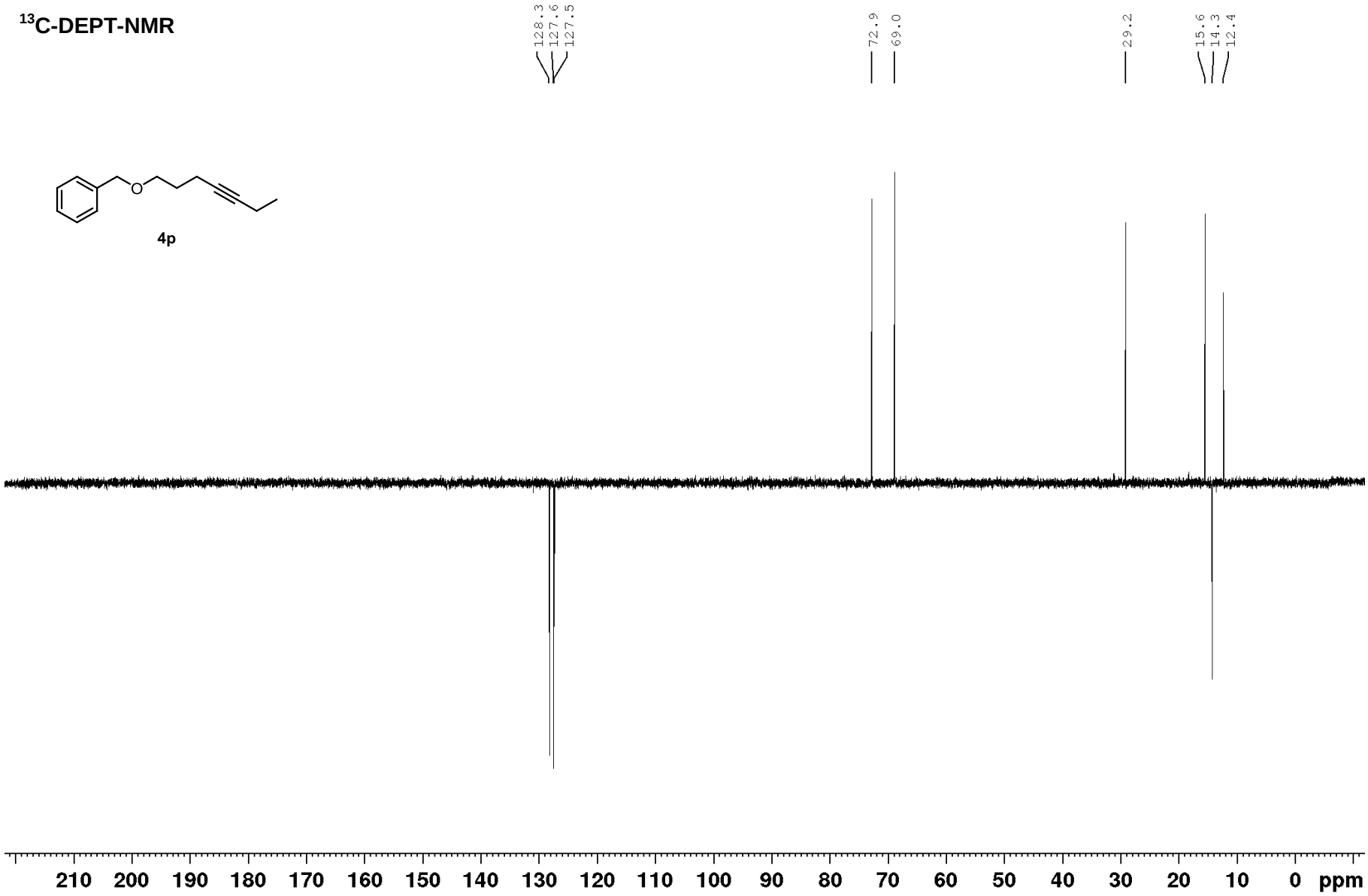

7.36
7.35
7.34
7.33
7.32
7.32
7.30
7.29
7.28
7.28
7.27
4.52
2.29
2.29
2.28
2.28
2.27
2.27
2.26
2.26
2.25
2.17
2.17
2.16
2.16
2.15
2.15
2.14
2.14
2.13
2.13
2.12
2.12
1.82
1.80
1.80
1.79
1.78
1.12
1.10
1.09
4.68
2.00
2.02
2.03
1.97
2.07
2.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

^{13}C-NMR

4p

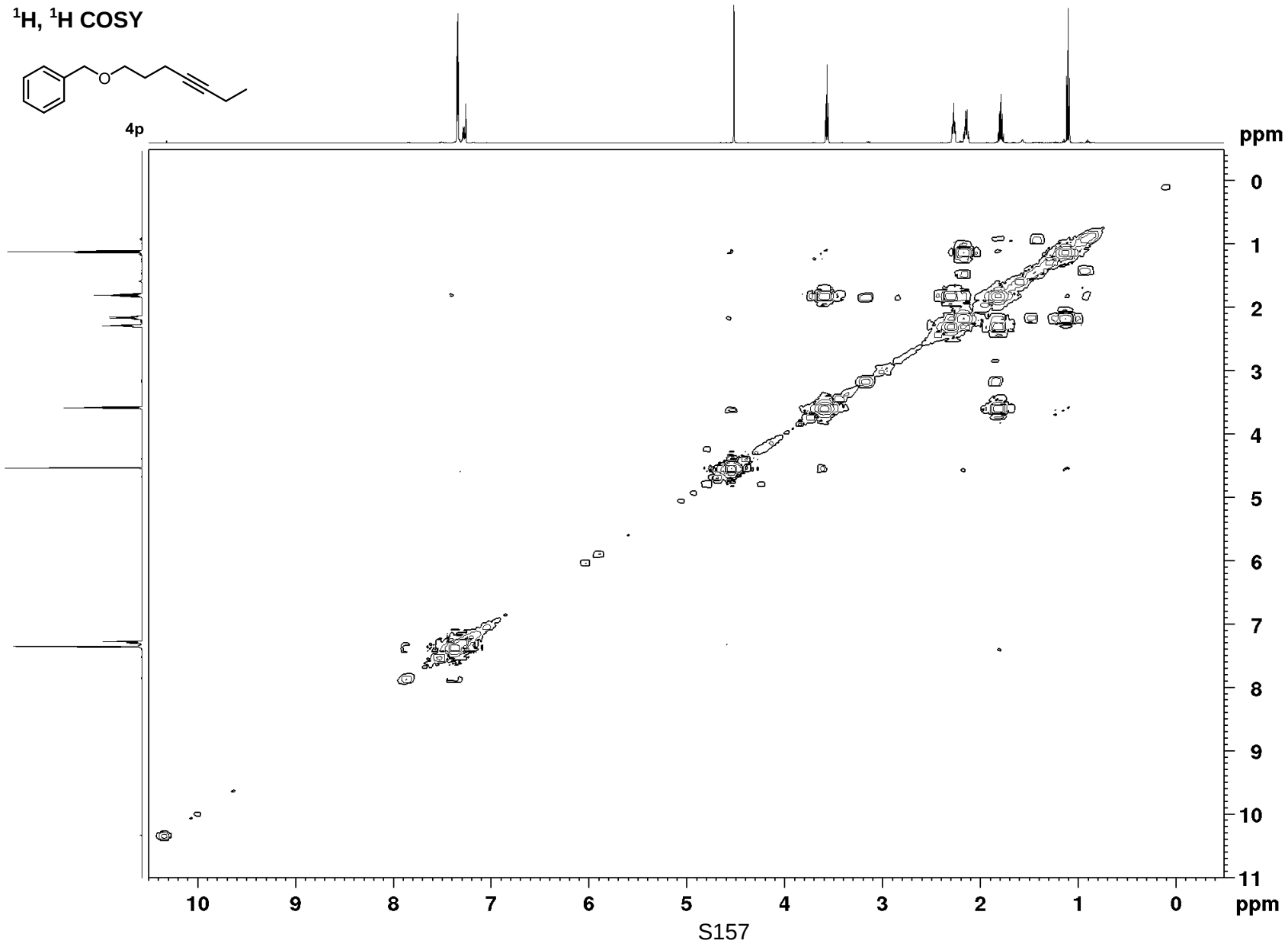

138.8
128.5
127.7
127.6
82.1
78.9
73.1
69.1
29.4
15.7
14.5
12.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

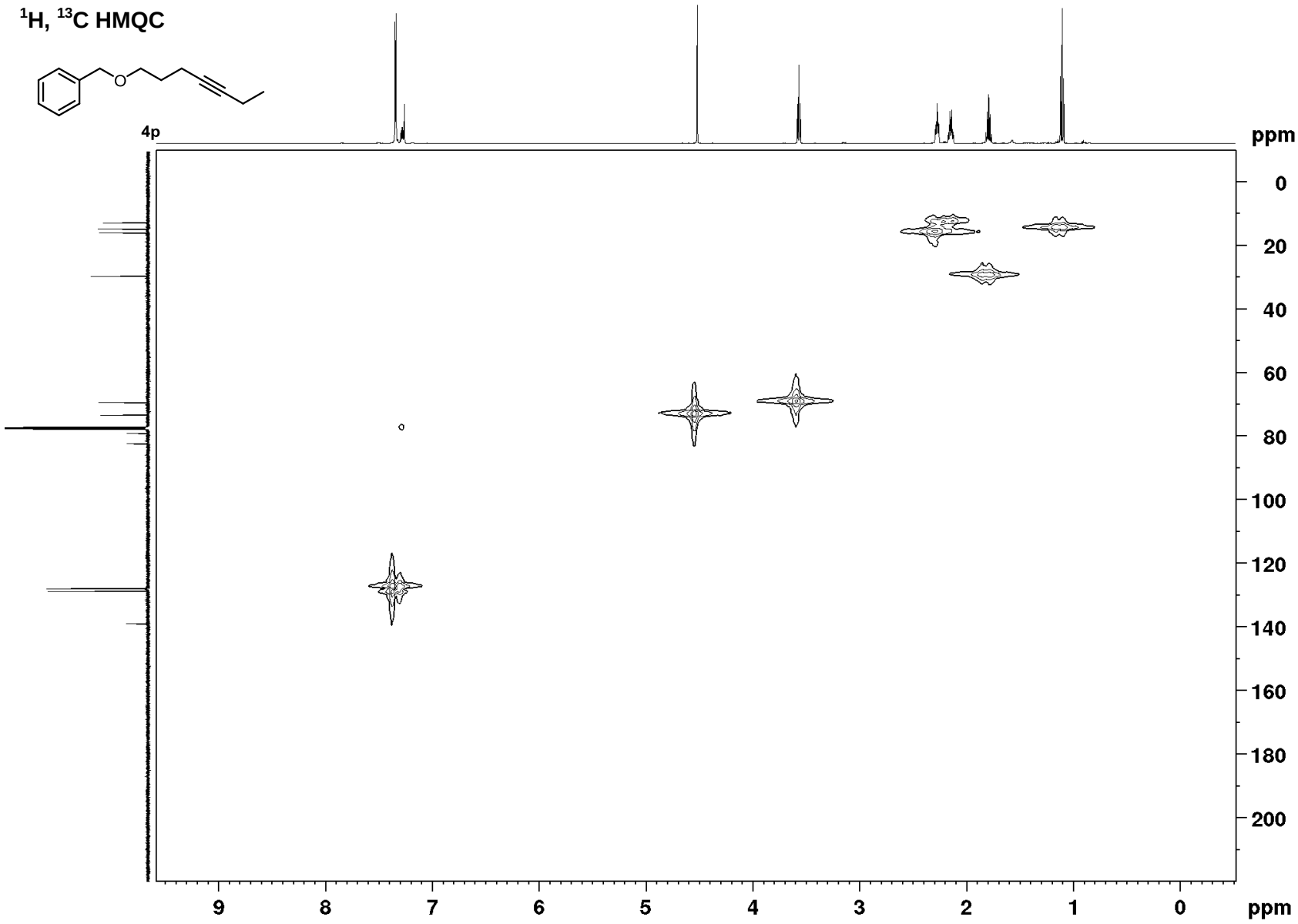
^{13}C-DEPT-NMR


128.3
127.6
127.5
72.9
69.0
29.2
15.6
14.3
12.4
O
4p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

^{1}H, ^{1}H COSY

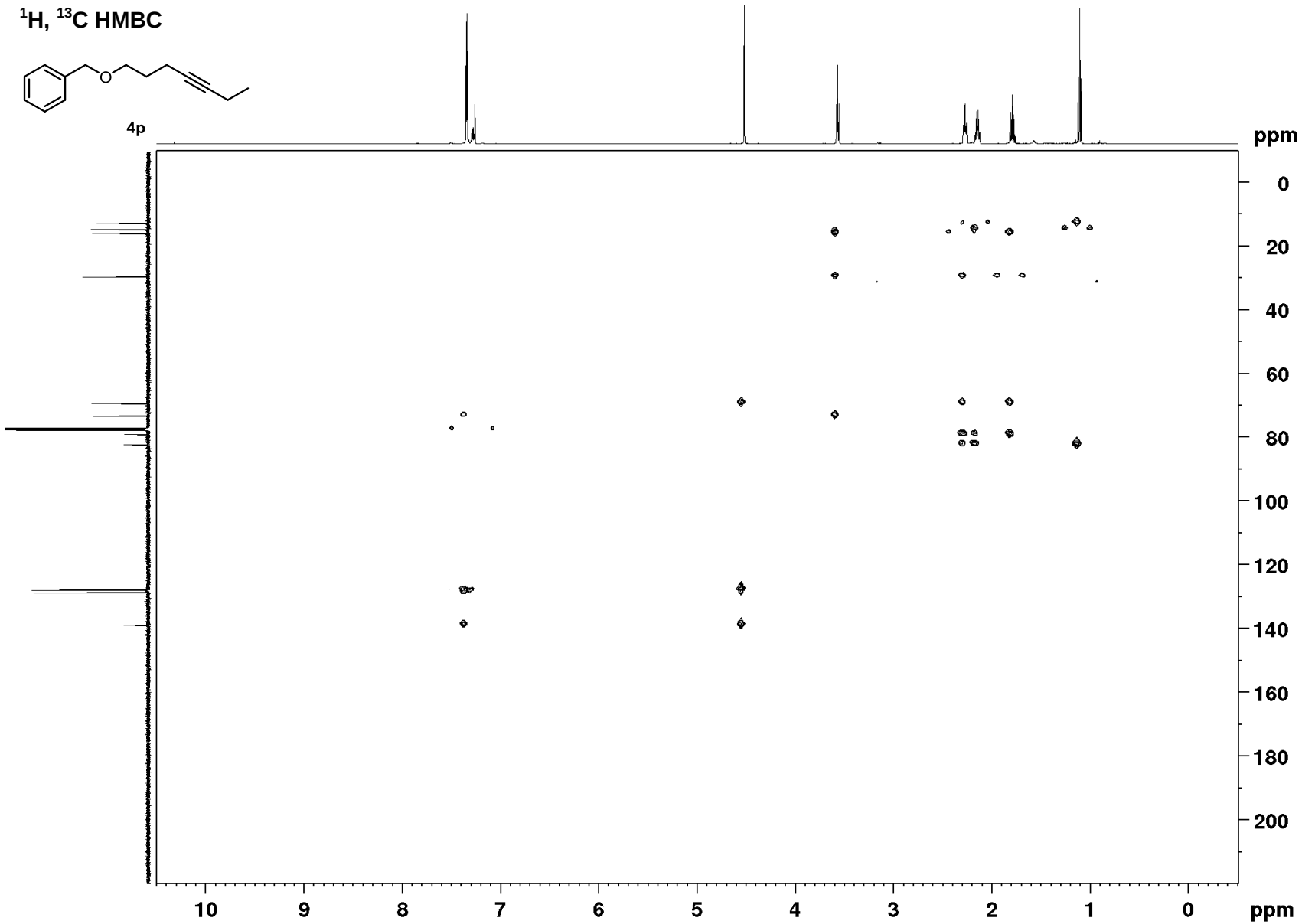
4p

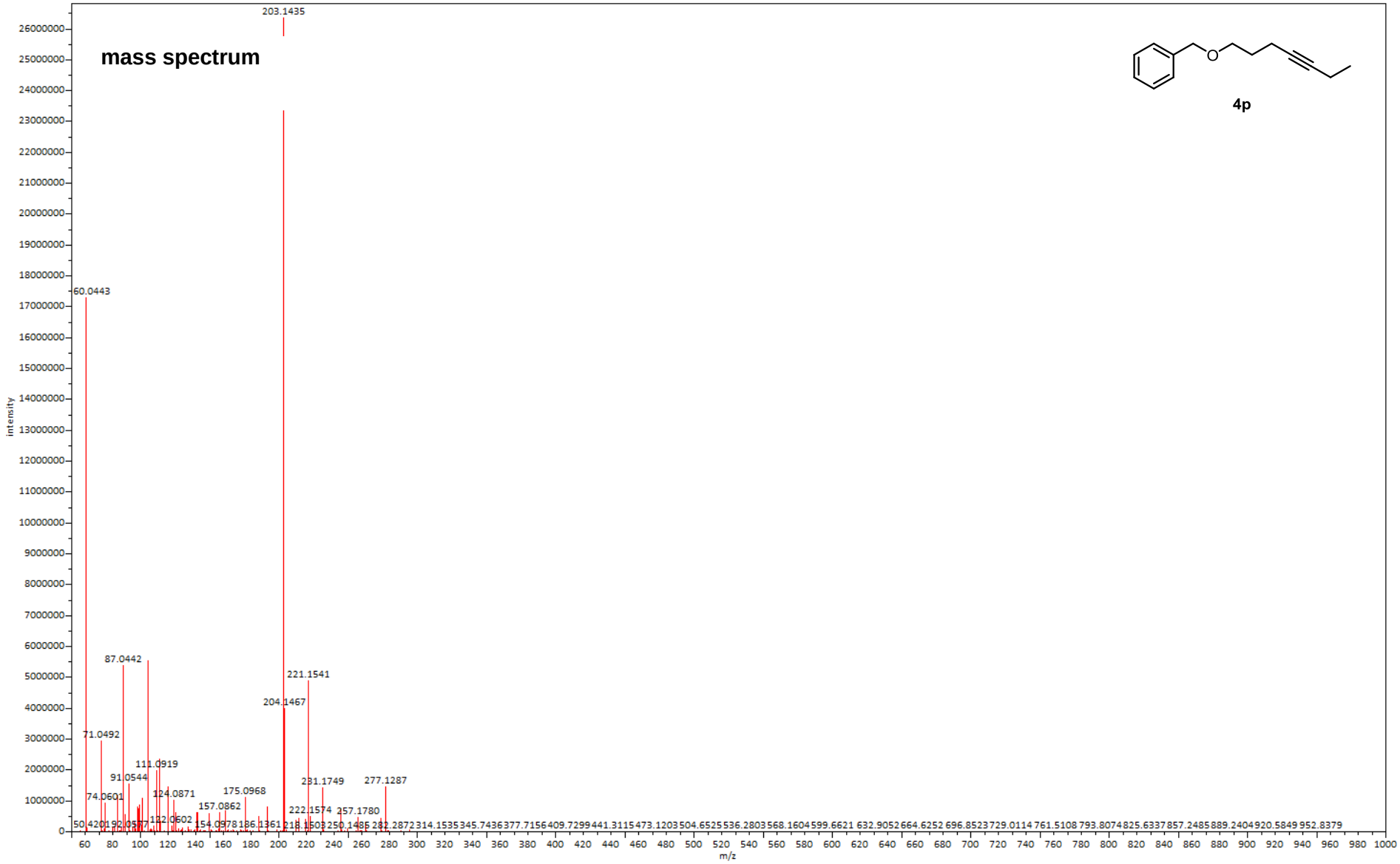



^{1}H, ^{13}C HMQC
4p
ppm
0
20
40
60
80
100
120
140
160
180
200
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H, ^{13}C HMBC

4p

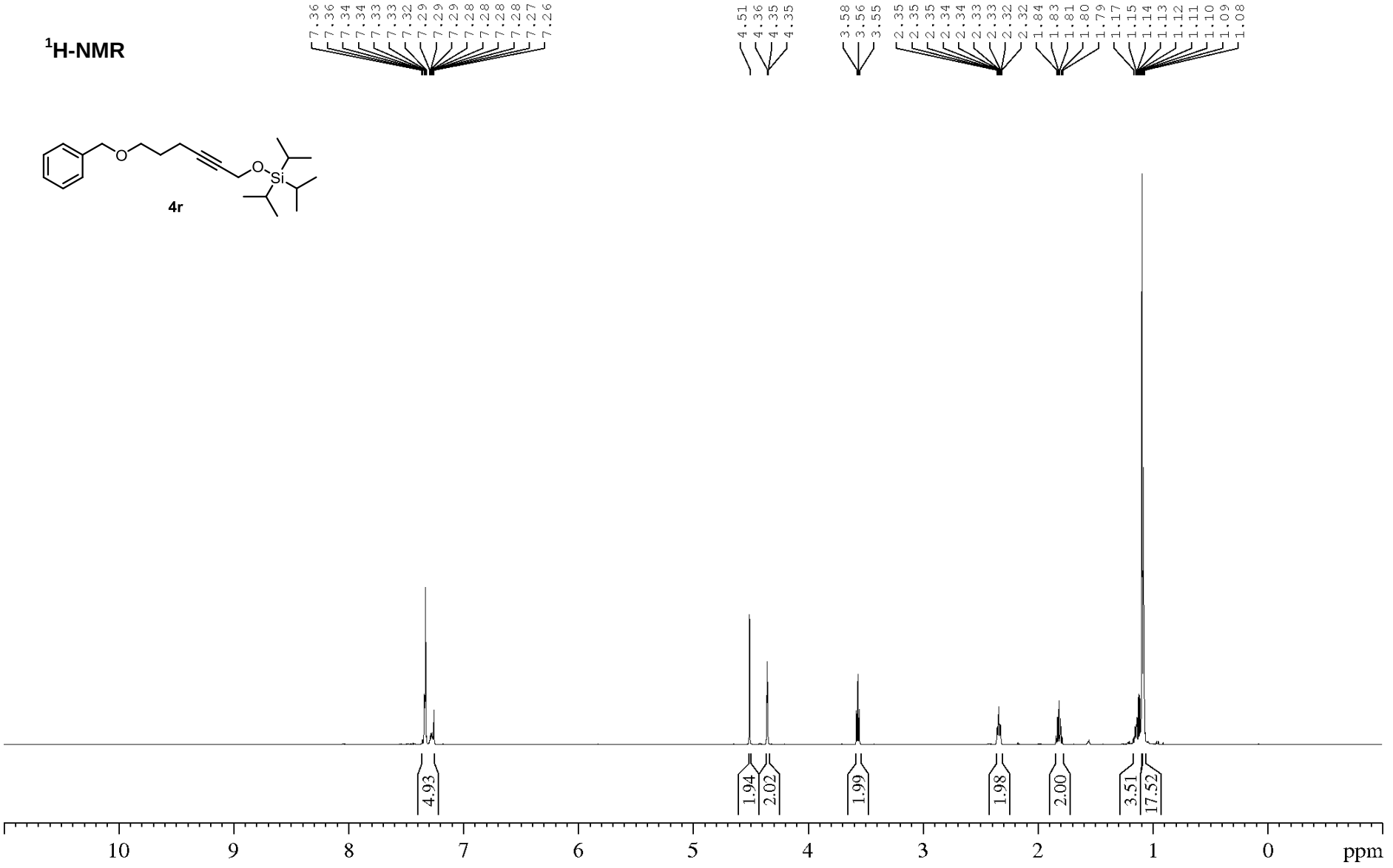



mass spectrum
4p
intensity
m/z
203.1435
60.0443
87.0442
221.1541
204.1467
71.0492
111.0919
91.0544
231.1749
277.1287
74.0601
124.0871
175.0968
157.0862
222.1574
257.1780
132.0602

^{1}H-NMR

O
O
Si

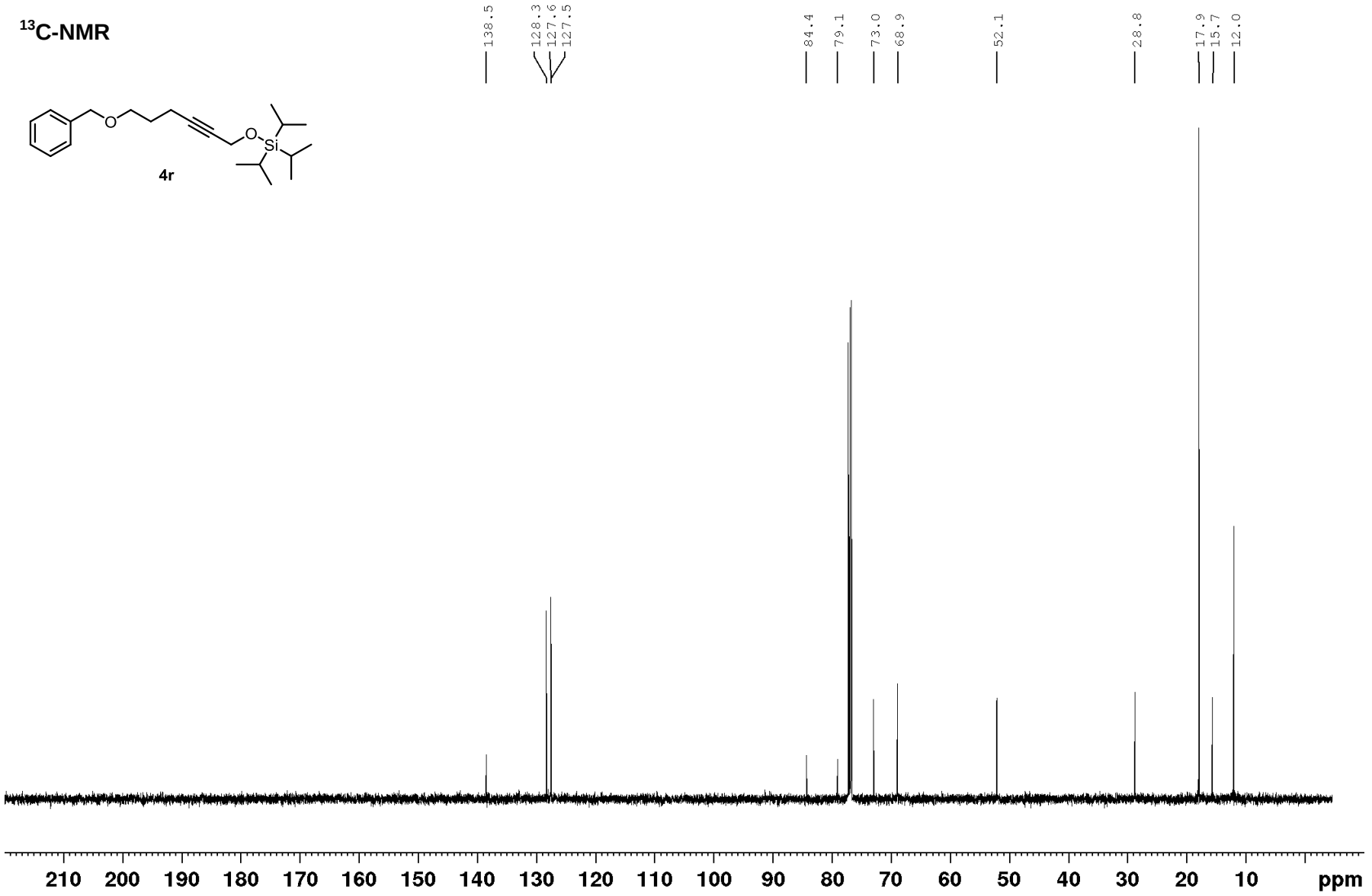
4r


7.36
7.36
7.34
7.34
7.33
7.33
7.32
7.29
7.29
7.29
7.28
7.28
7.28
7.28
7.27
7.26
4.51
4.36
4.35
4.35
3.58
3.56
3.55
2.35
2.35
2.35
2.34
2.34
2.33
2.33
2.32
2.32
1.84
1.83
1.81
1.80
1.79
1.17
1.15
1.14
1.13
1.12
1.11
1.10
1.09
1.08
4.93
1.94
2.02
1.99
1.98
2.00
3.51
17.52
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C-NMR

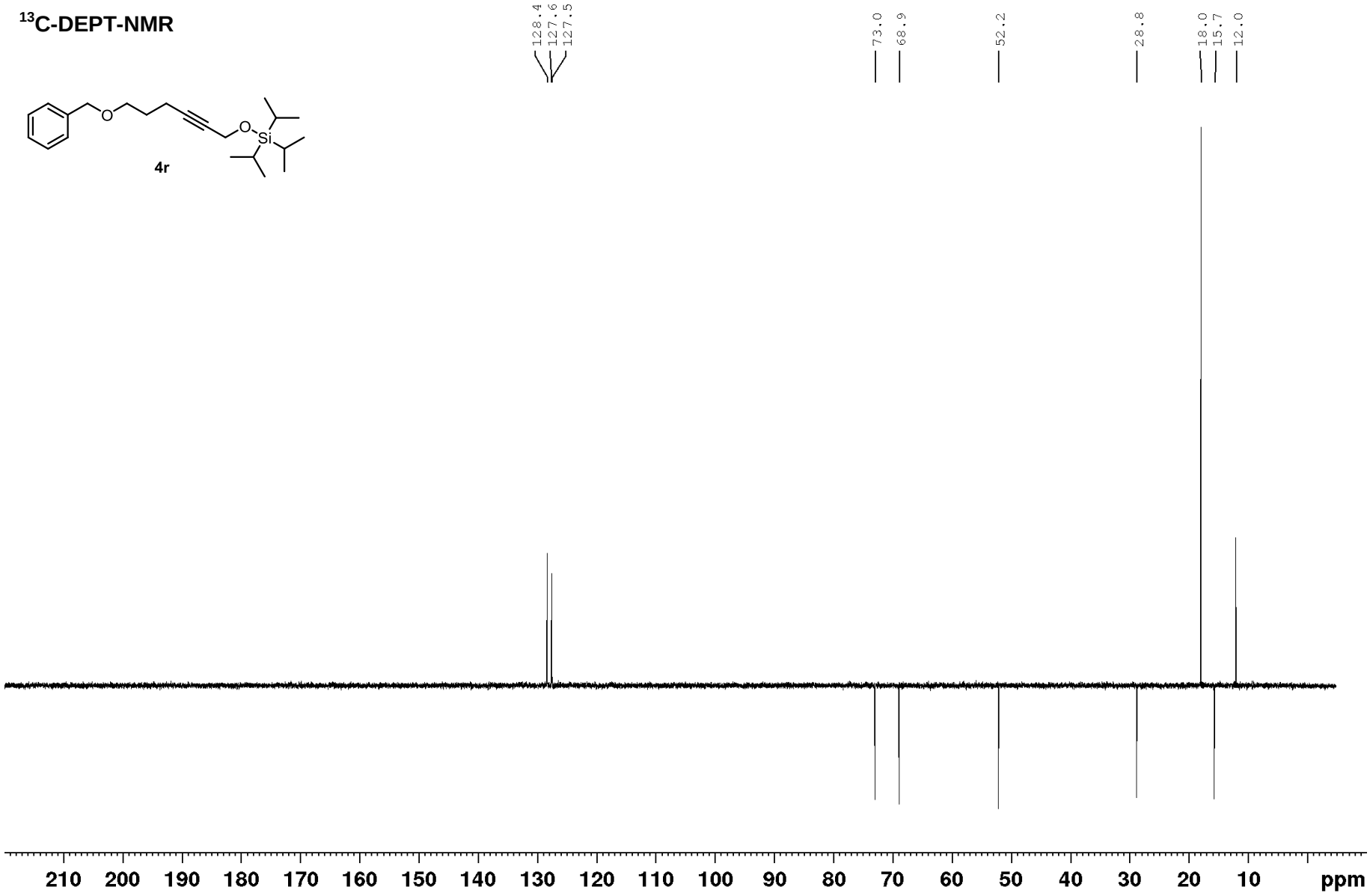
O
O
Si

4r


138.5
128.3
127.6
127.5
84.4
79.1
73.0
68.9
52.1
28.8
17.9
15.7
12.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

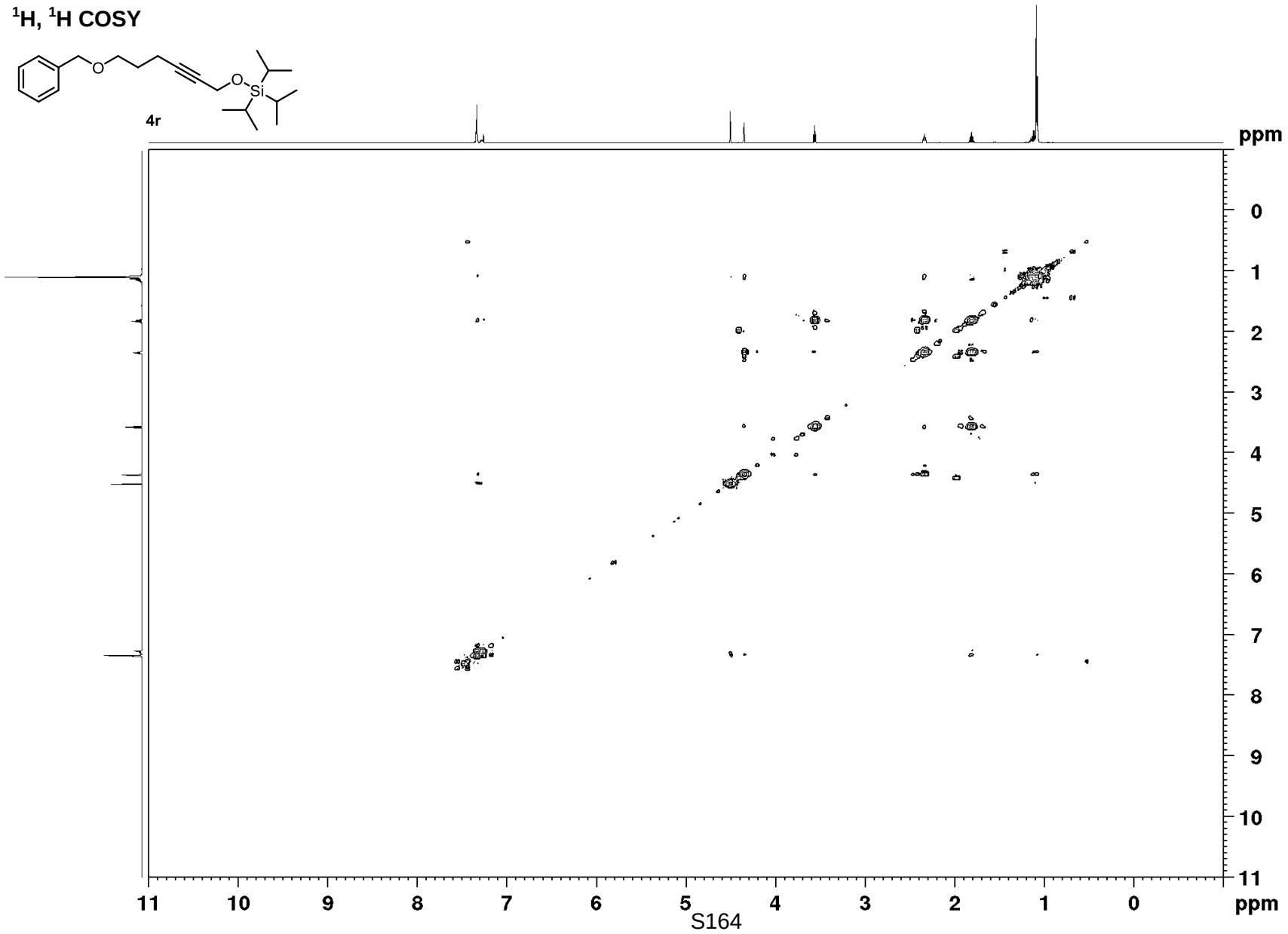
^{13}C-DEPT-NMR

4r



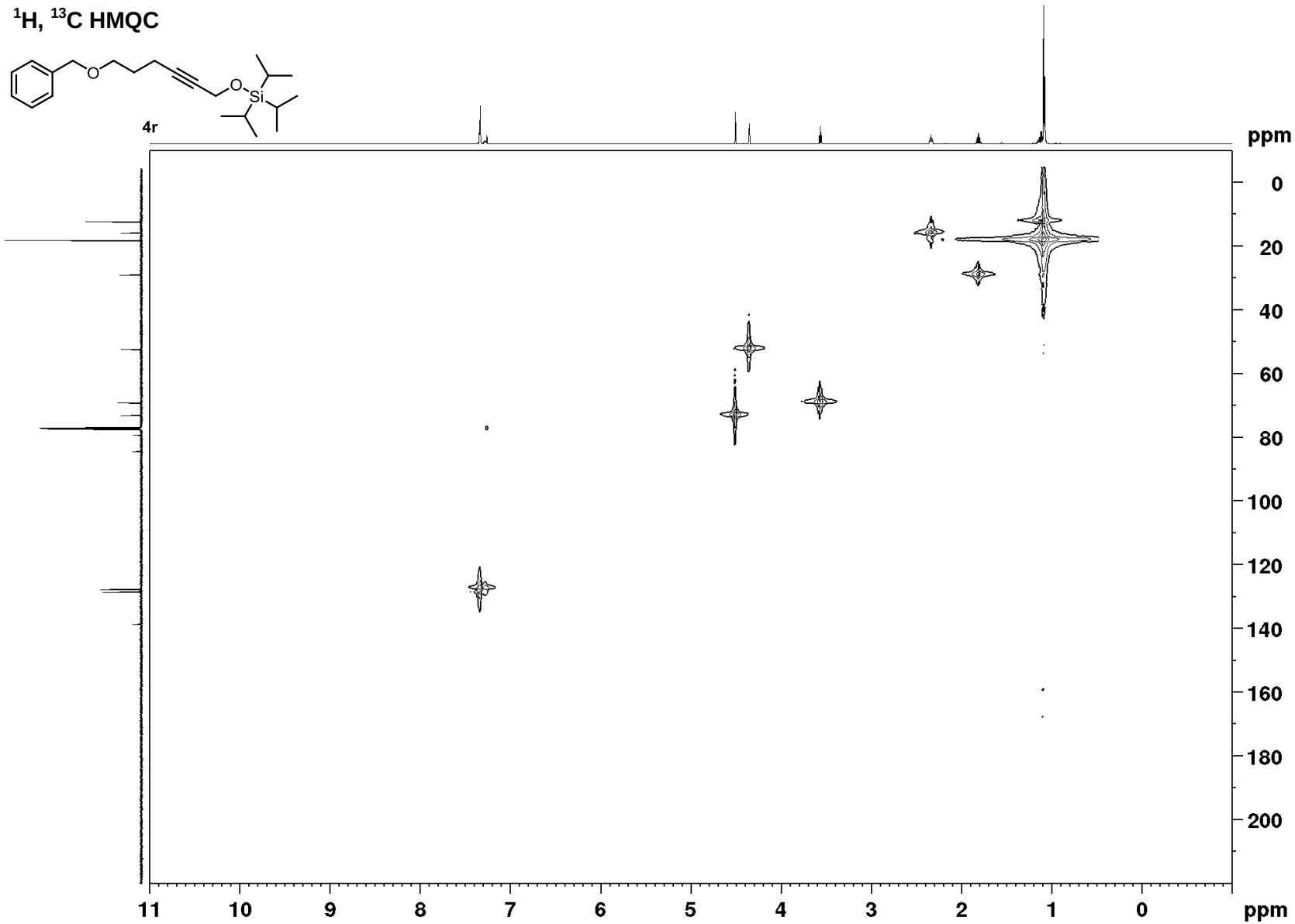
^{1}H, ^{1}H COSY

4r



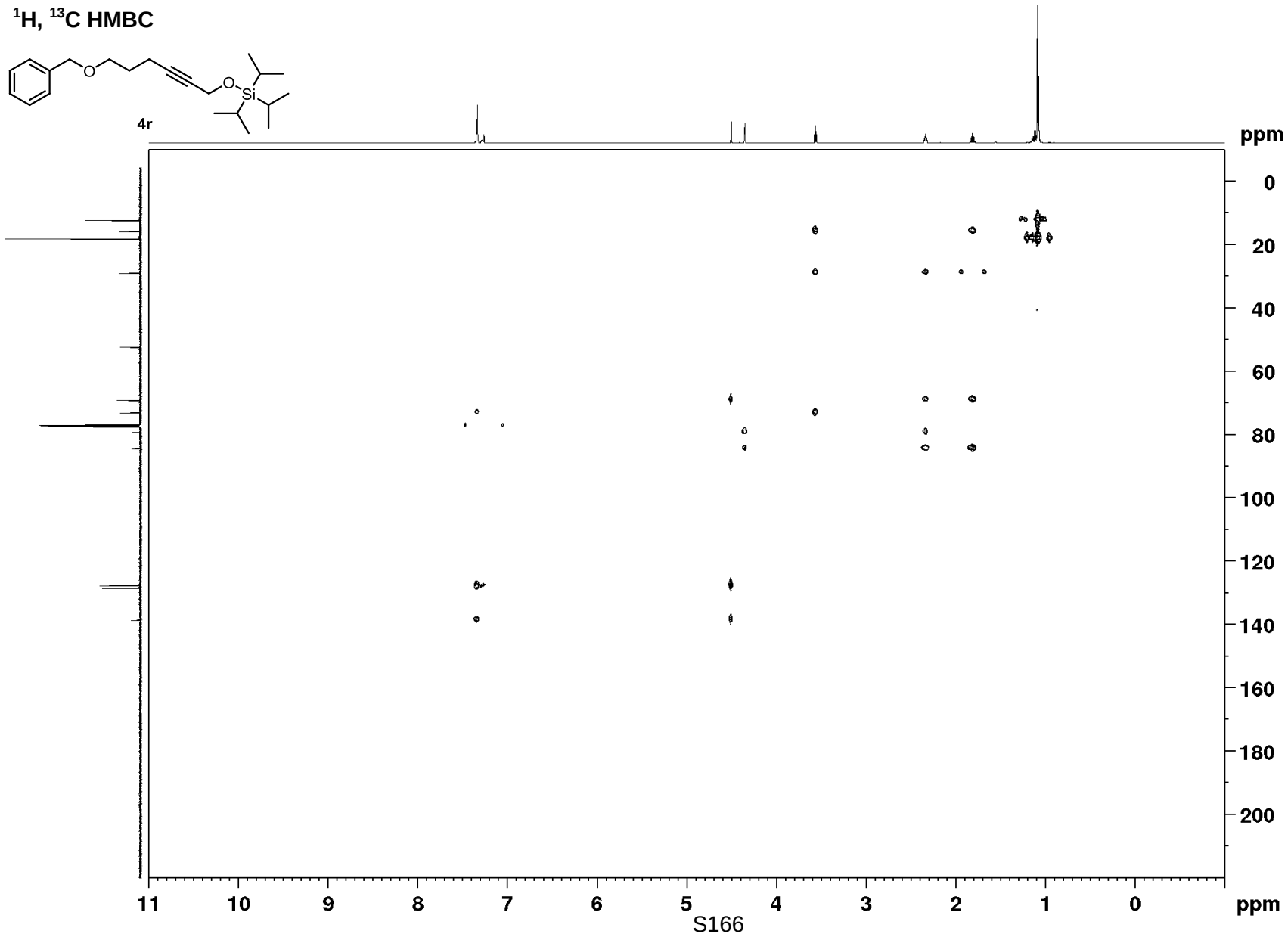
^{1}H, ^{13}C HMQC

4r



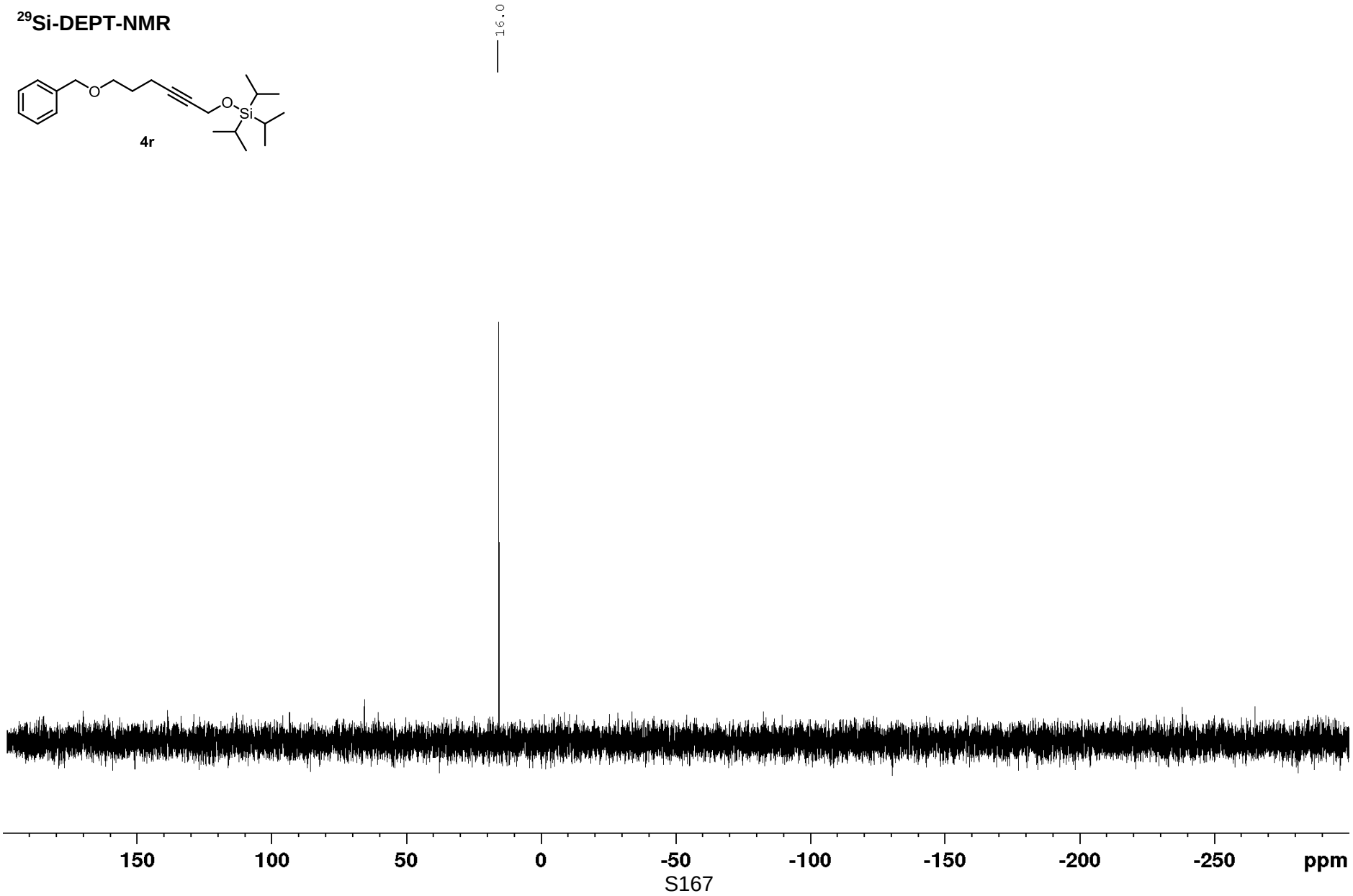
^{1}H, ^{13}C HMBC

4r

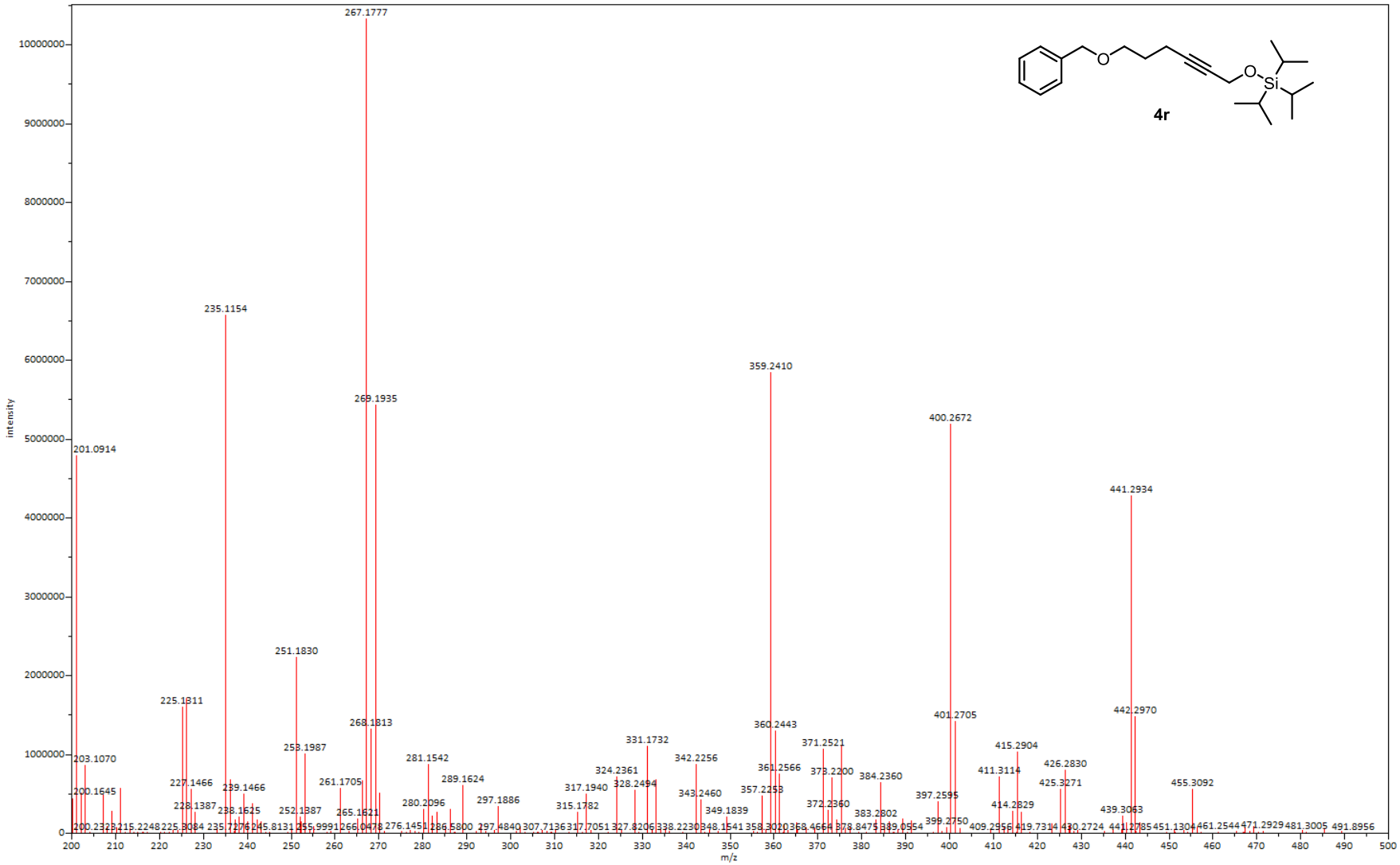


^{29}Si-DEPT-NMR

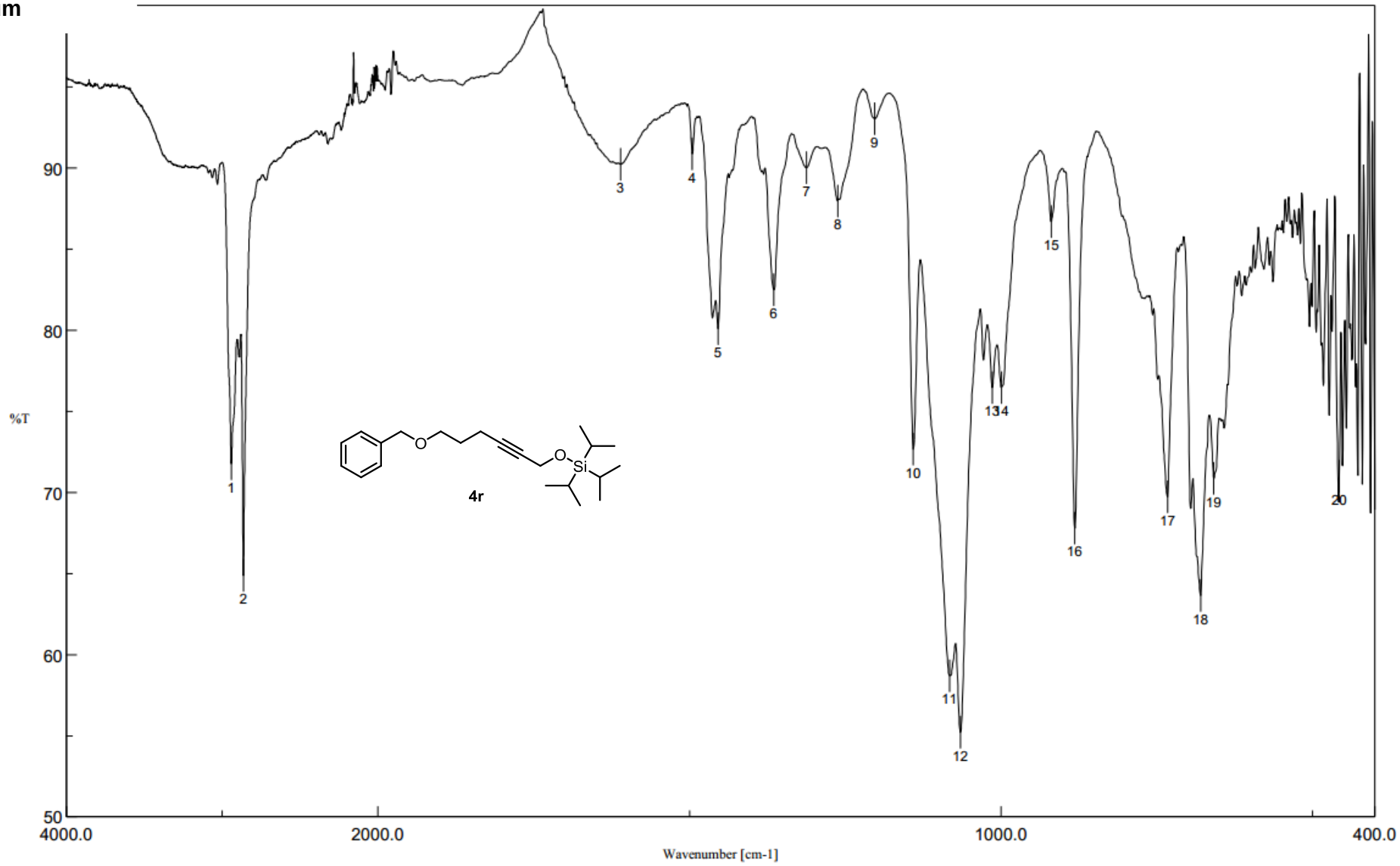
4r



mass spectrum



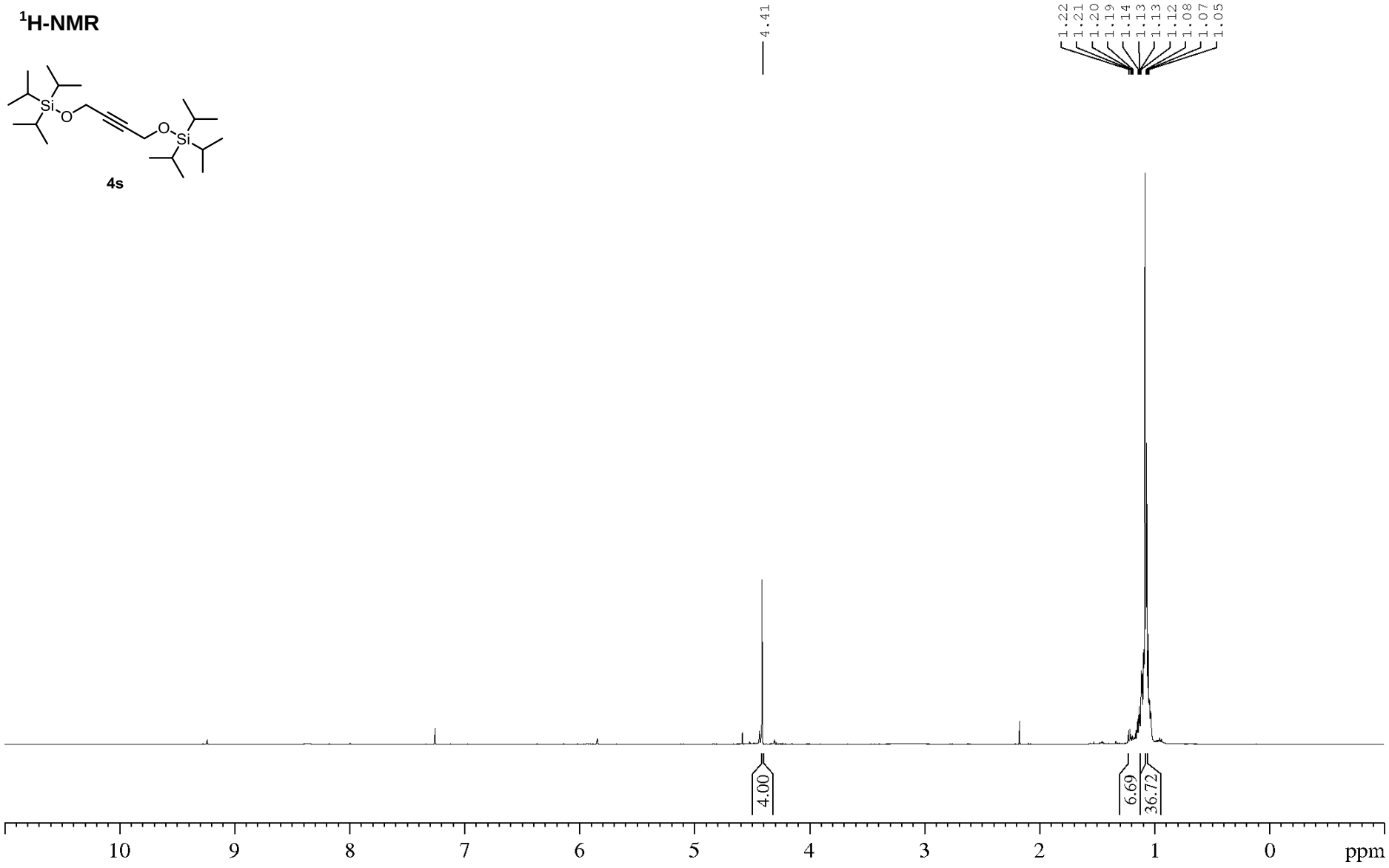
IR spectrum


%T
90
80
70
60
50
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
O
O
Si
4r

^{1}H-NMR

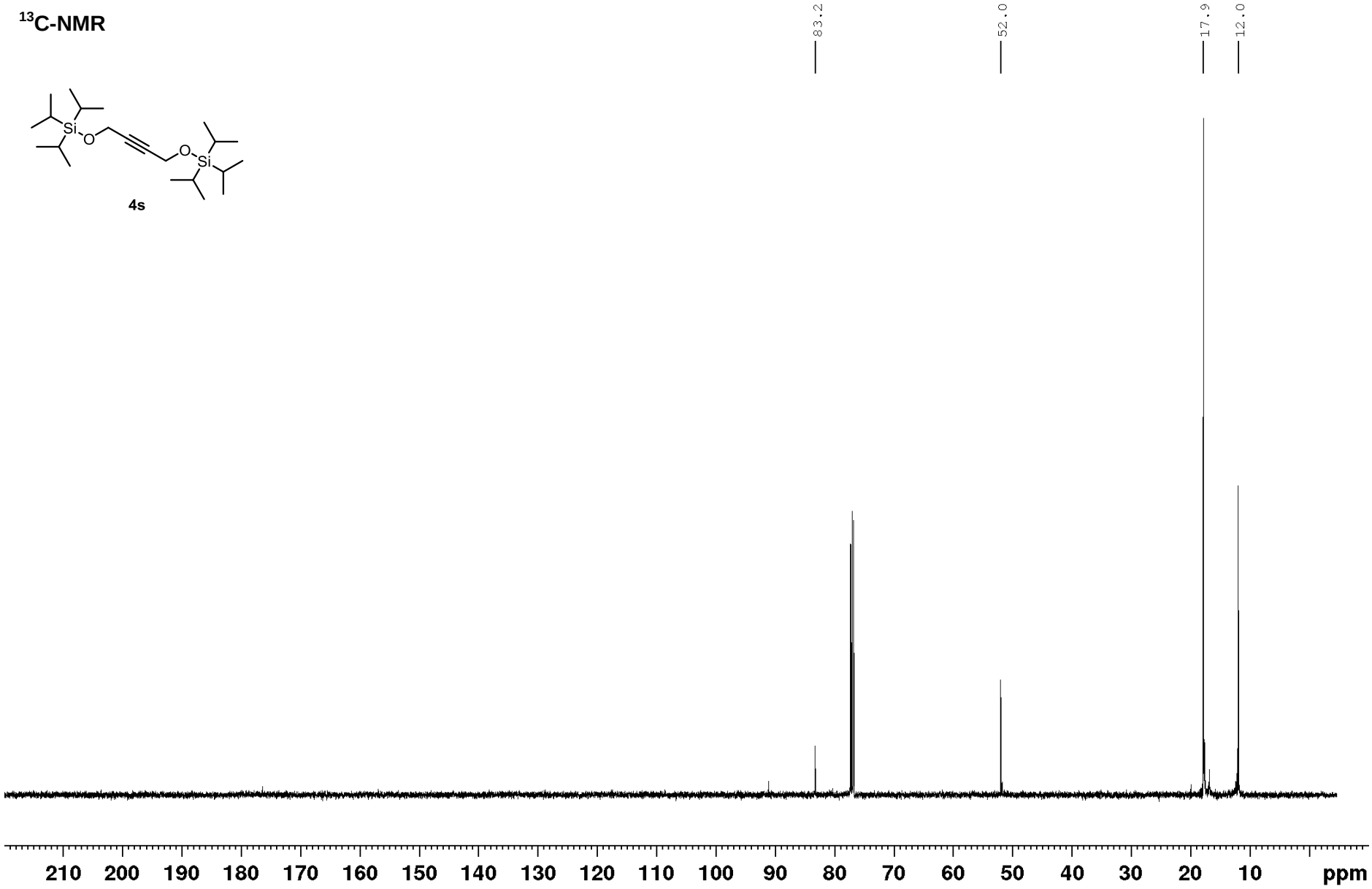
Si
O
O
Si

4s


4.41
1.22
1.21
1.20
1.19
1.14
1.13
1.13
1.12
1.08
1.07
1.05
4.00
6.69
36.72
10
9
8
7
6
5
4
3
2
1
0
ppm

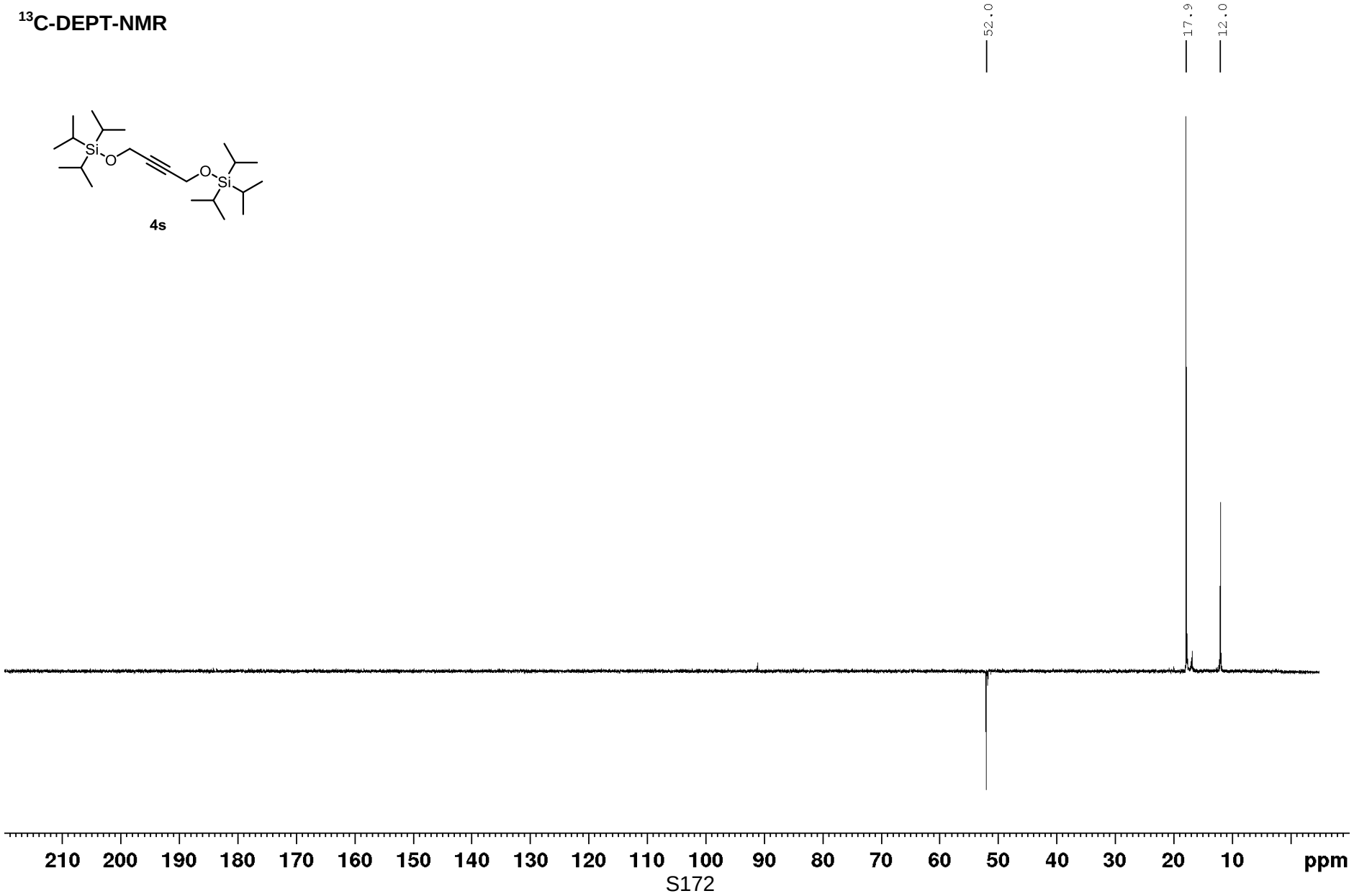
^{13}C-NMR

4s

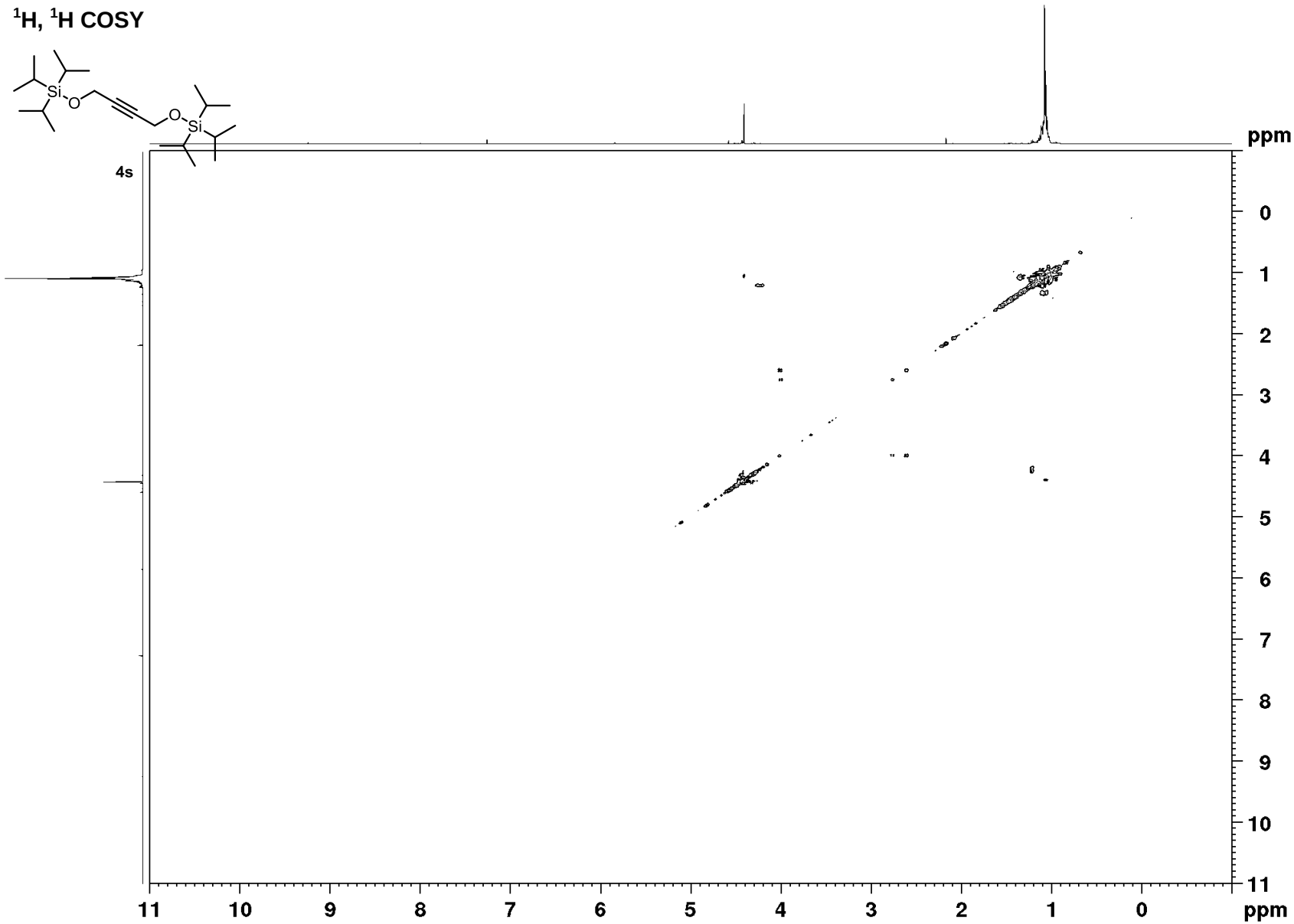

83.2
52.0
17.9
12.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

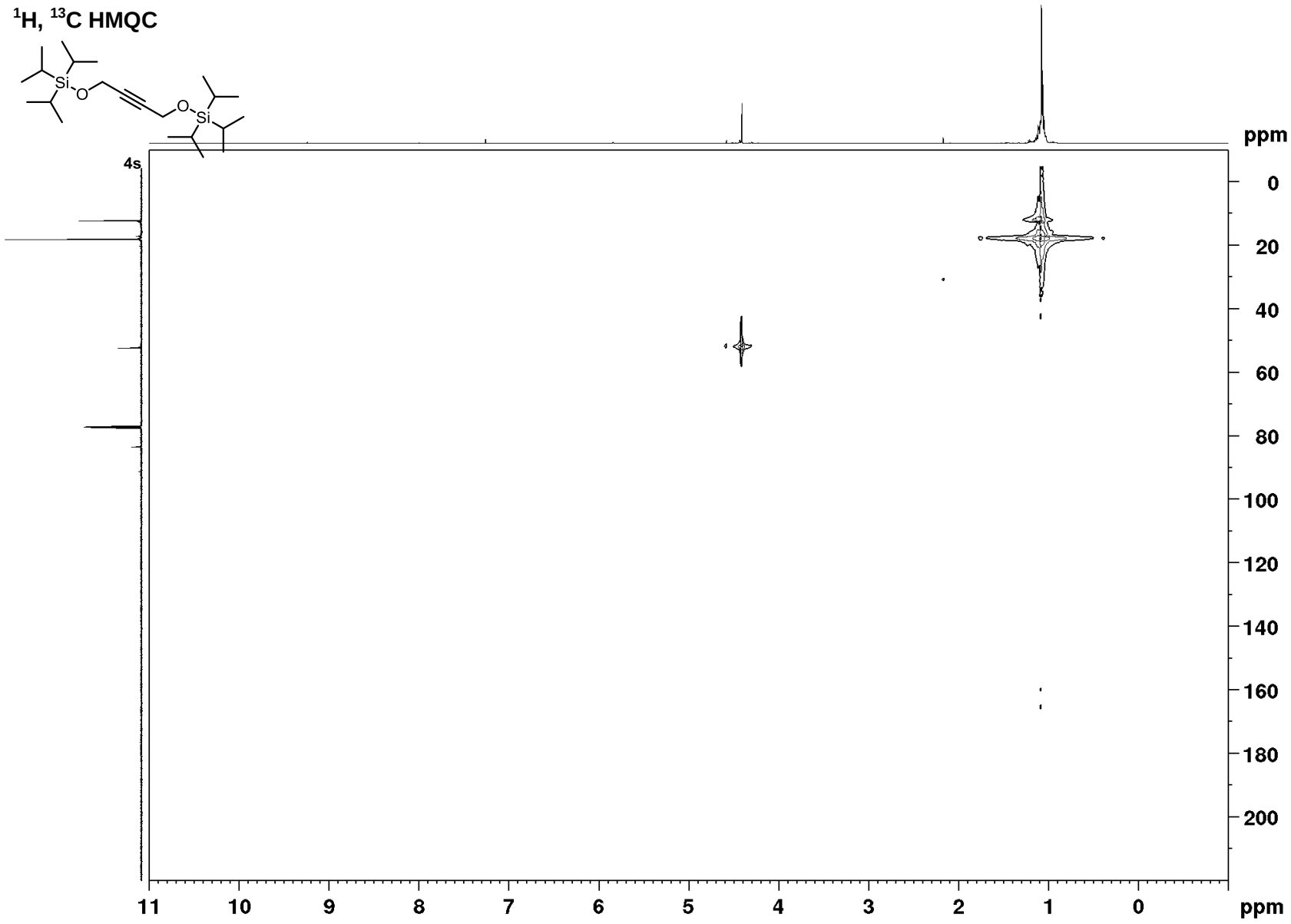
^{13}C-DEPT-NMR

4s



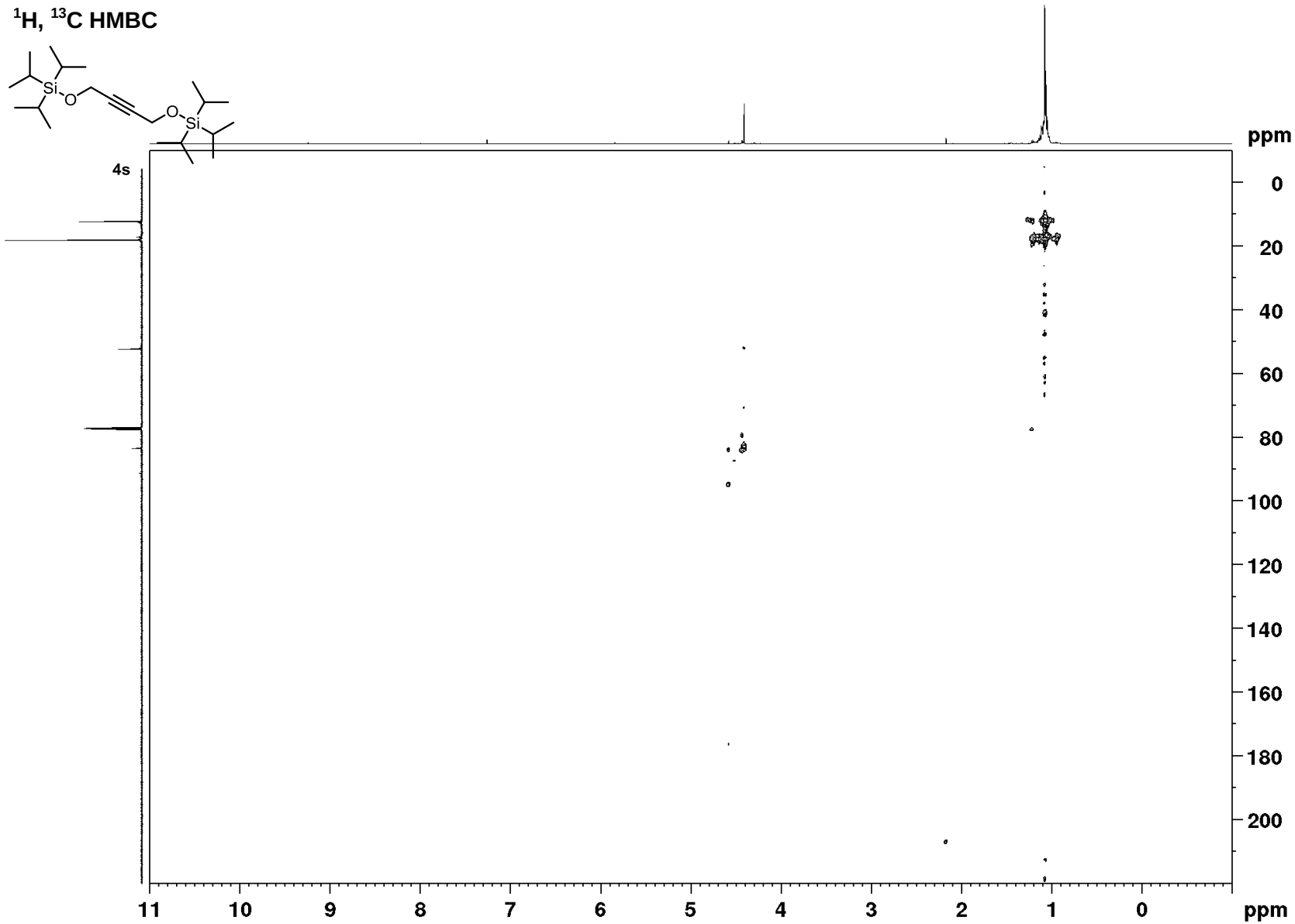
^{1}H, ^{1}H COSY




^{1}H, ^{13}C HMQC
4s
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

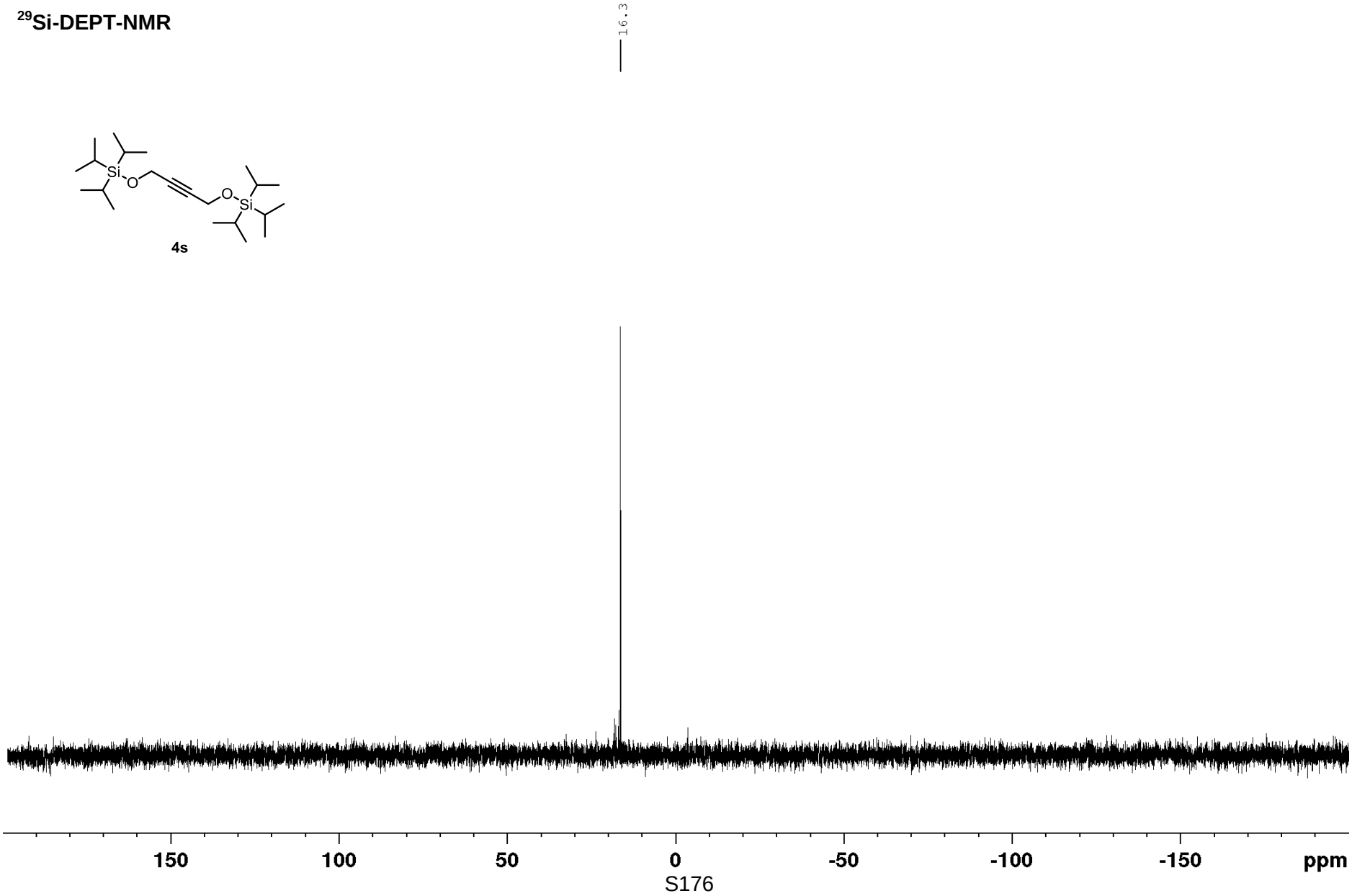
^{1}H, ^{13}C HMBC

Si
O
O
Si

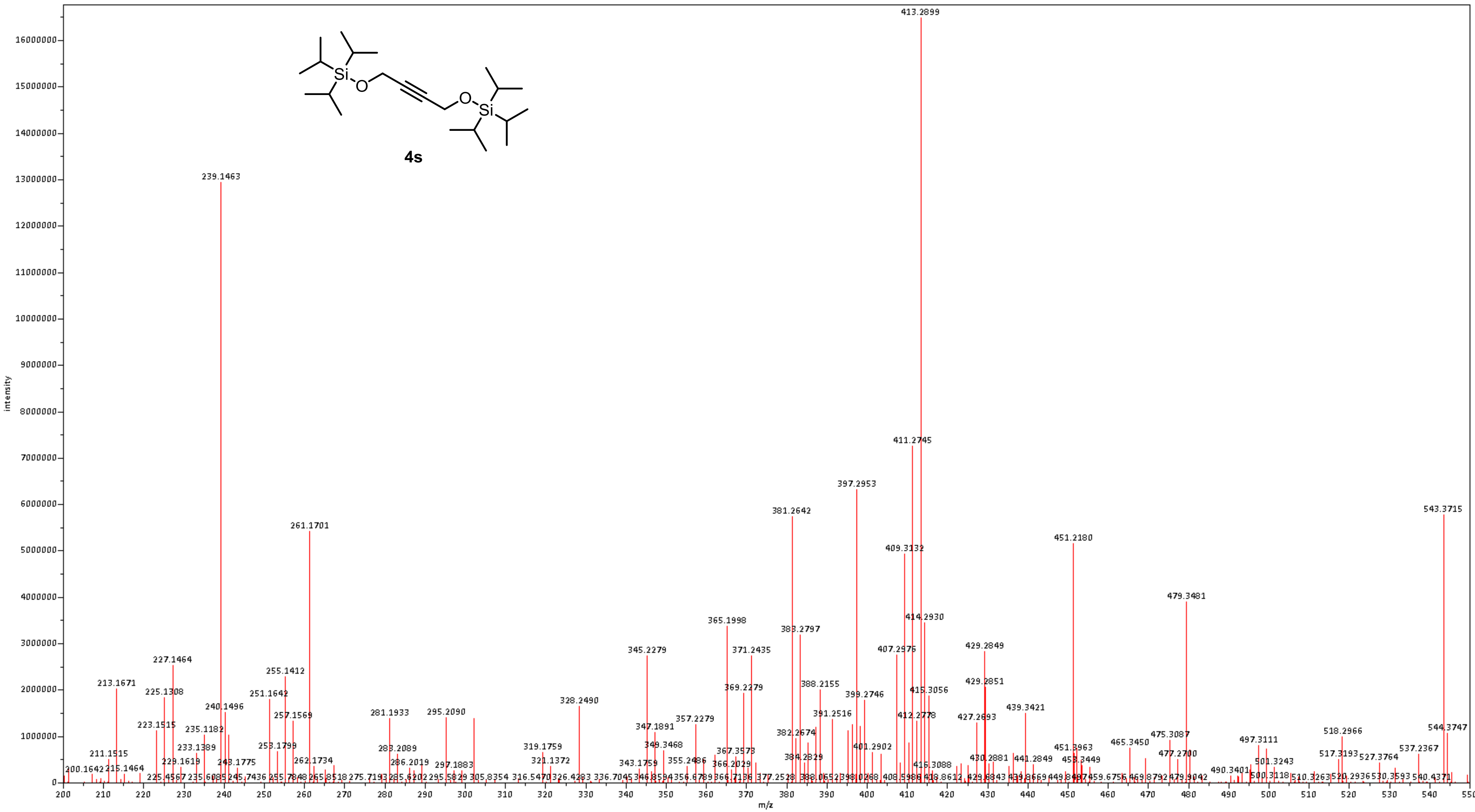

4s
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{29}Si-DEPT-NMR

4s

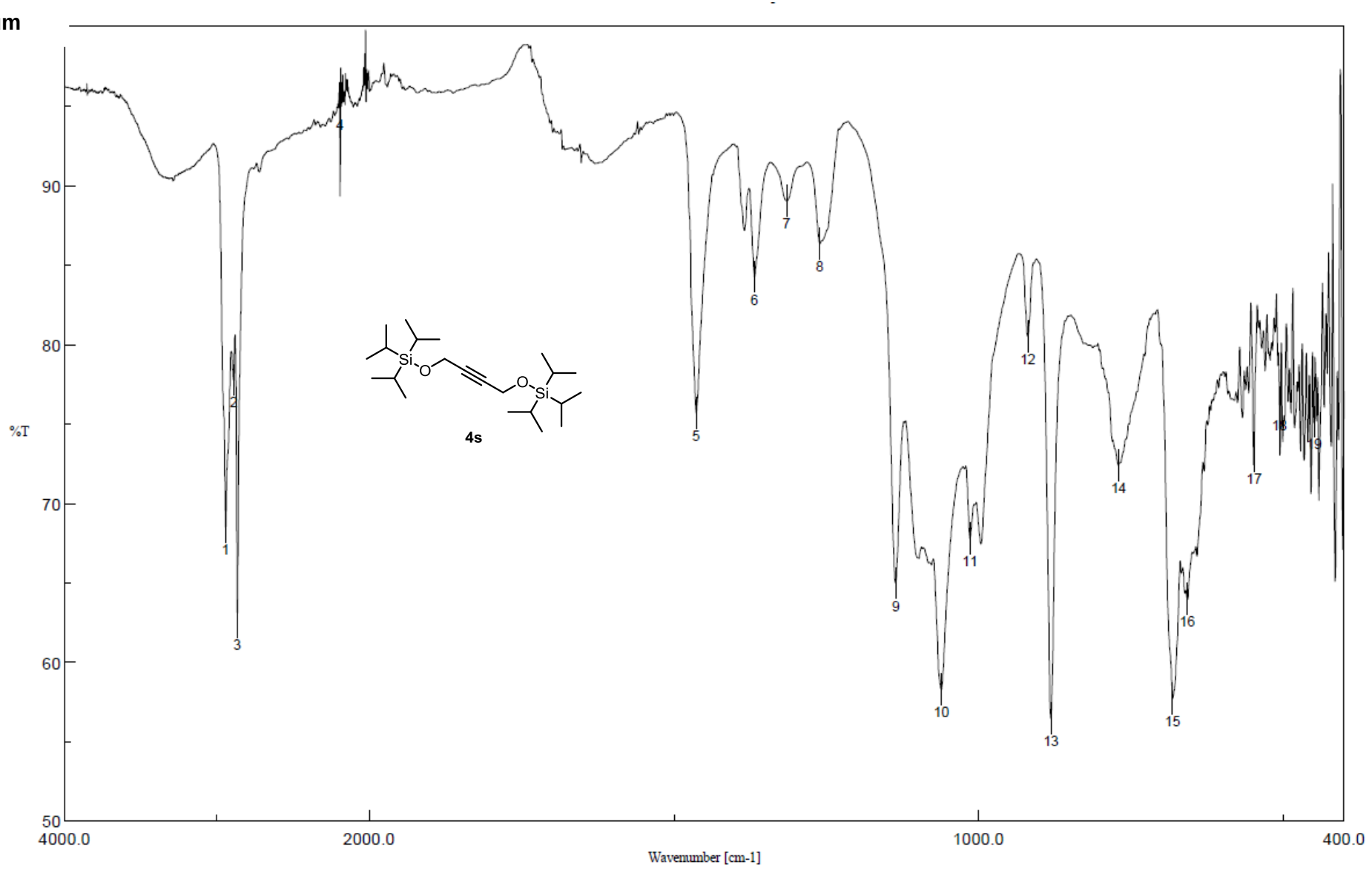


mass spectrum

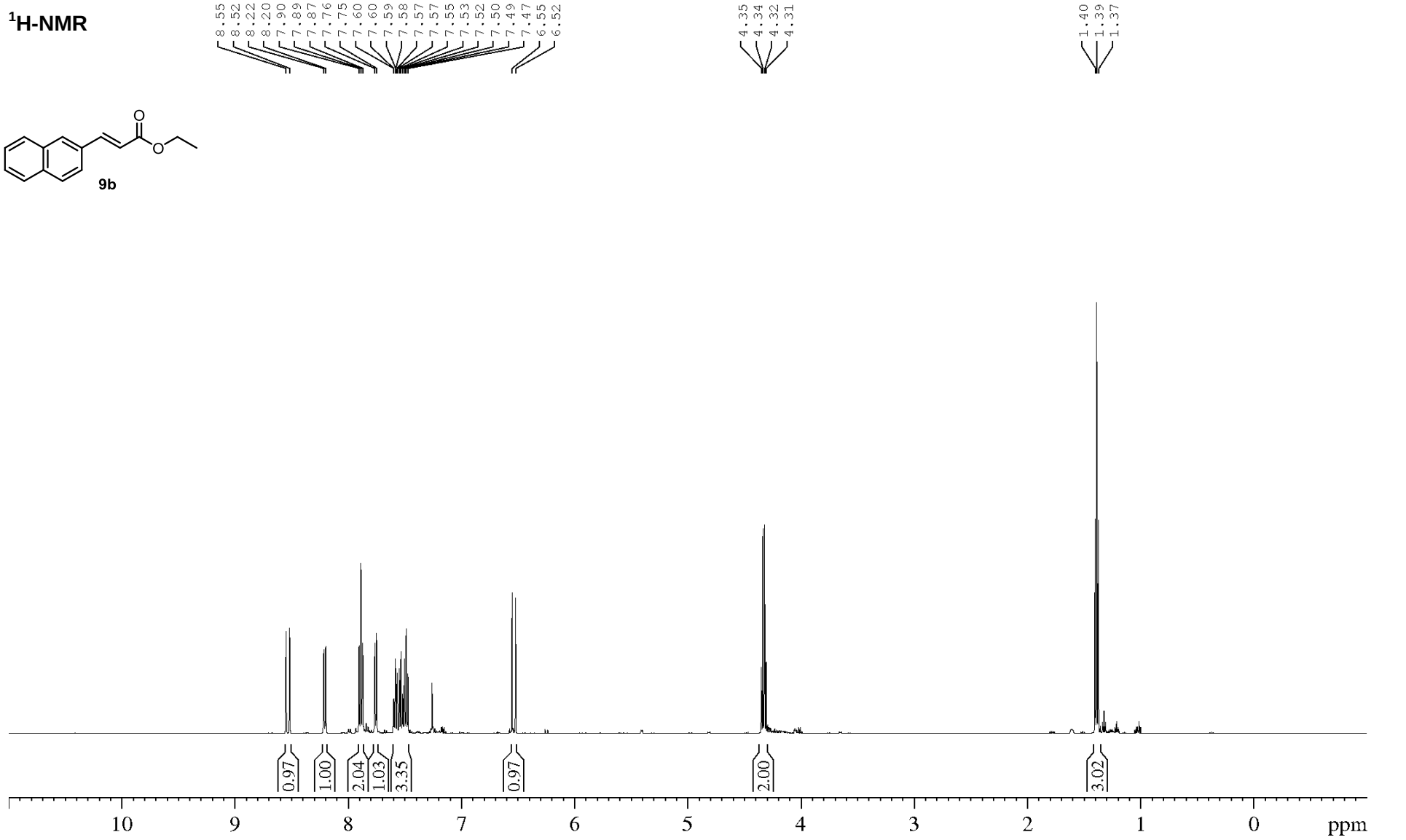


Si
O
4s
intensity
m/z
413.2899
239.1463
411.2745
397.2953
381.2642
543.3715
261.1701
451.2180
409.3132
479.3481

IR spectrum

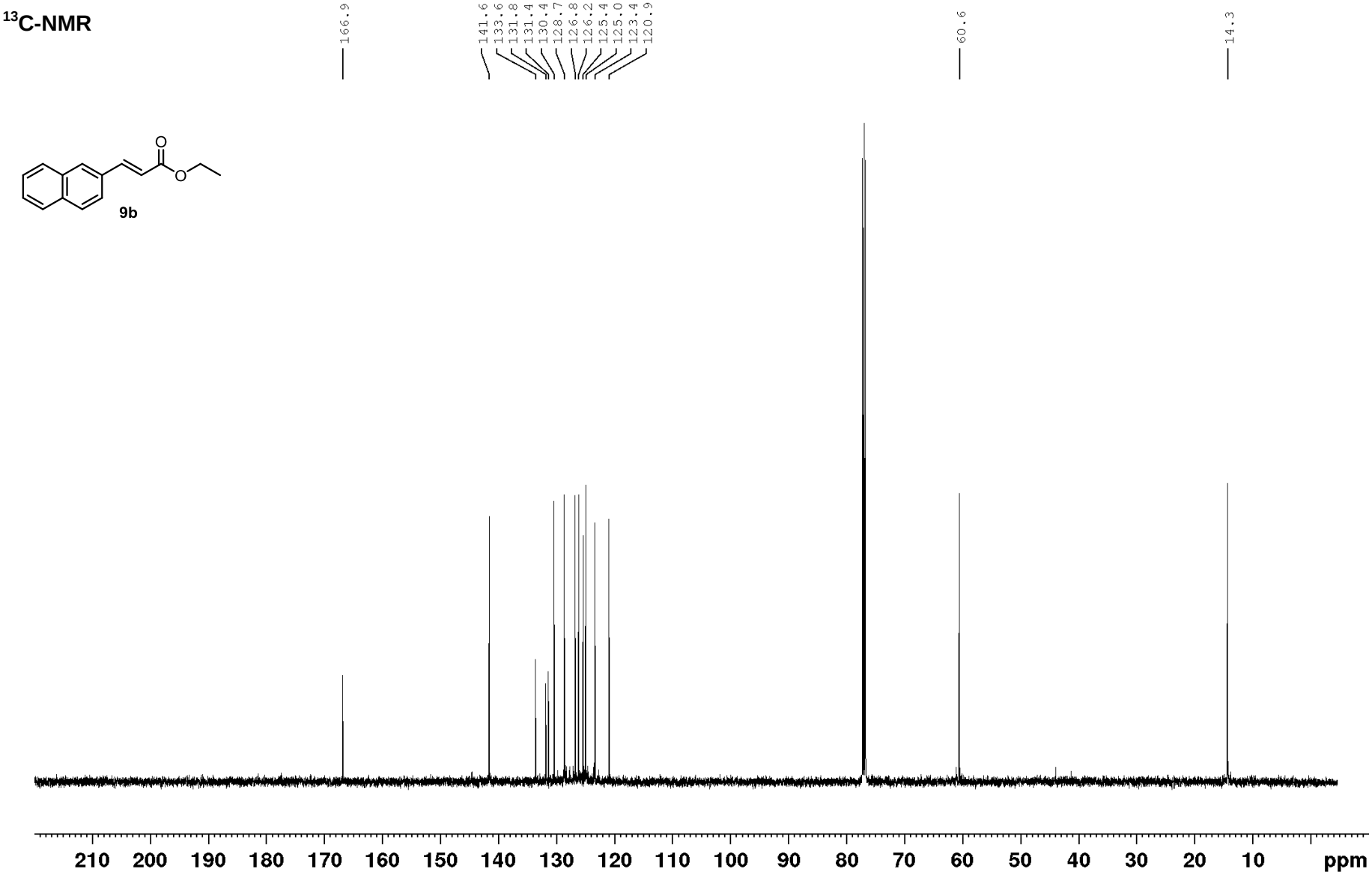

%T
90
80
70
60
50
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
4s

^{1}H-NMR

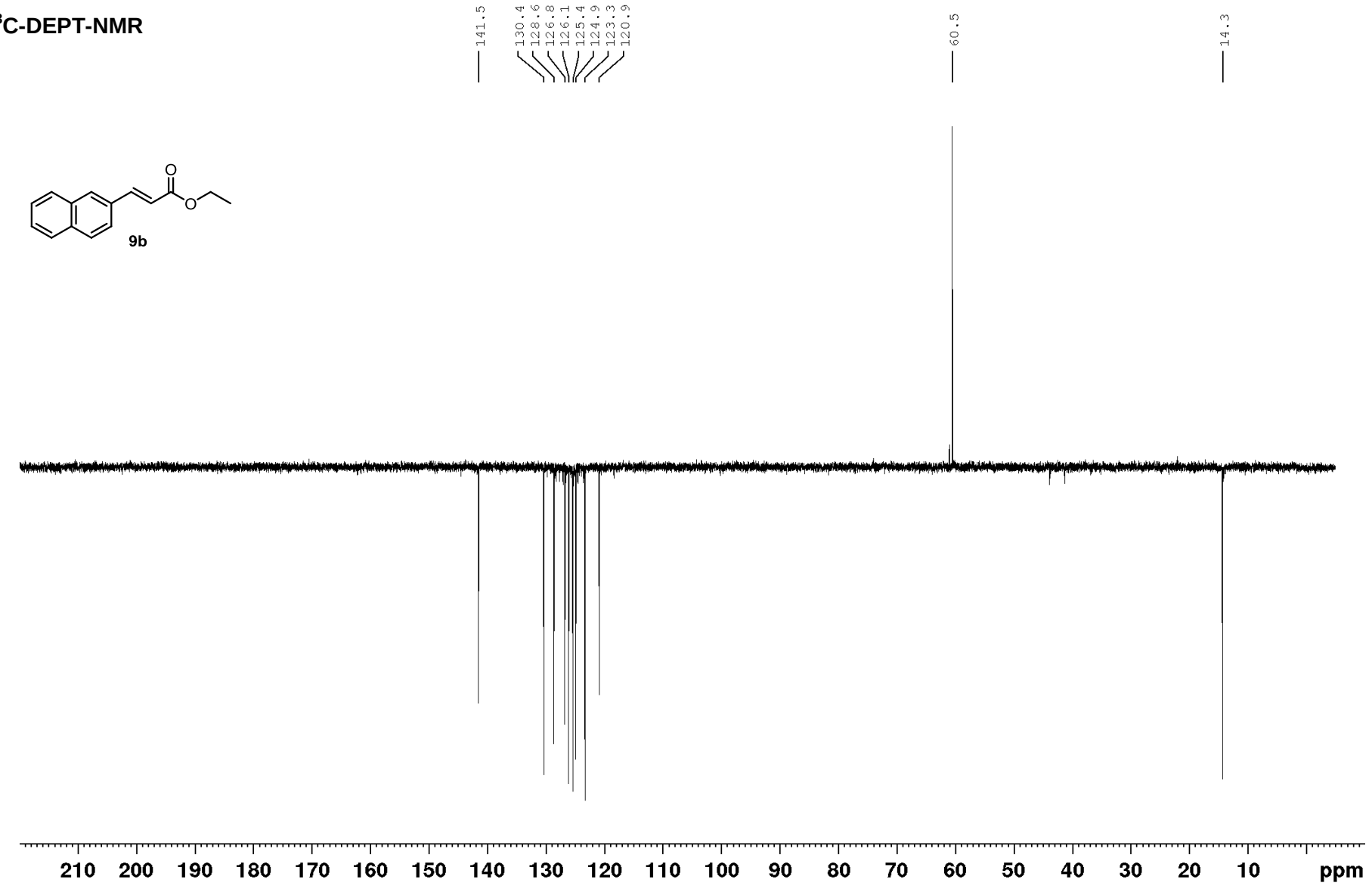

8.55
8.52
8.22
8.20
7.90
7.89
7.87
7.76
7.75
7.60
7.60
7.59
7.58
7.57
7.57
7.55
7.53
7.52
7.50
7.49
7.47
6.55
6.52
4.35
4.34
4.32
4.31
1.40
1.39
1.37
O
O
0.97
1.00
2.04
1.03
3.35
0.97
2.00
3.02
10
9
8
7
6
5
4
3
2
1
0
ppm

9b

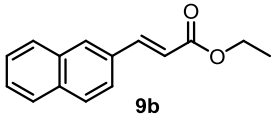
^{13}C-NMR


166.9
141.6
133.6
131.8
131.4
130.4
128.7
126.8
126.2
125.4
125.0
123.4
120.9
60.6
14.3
O
O
9b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

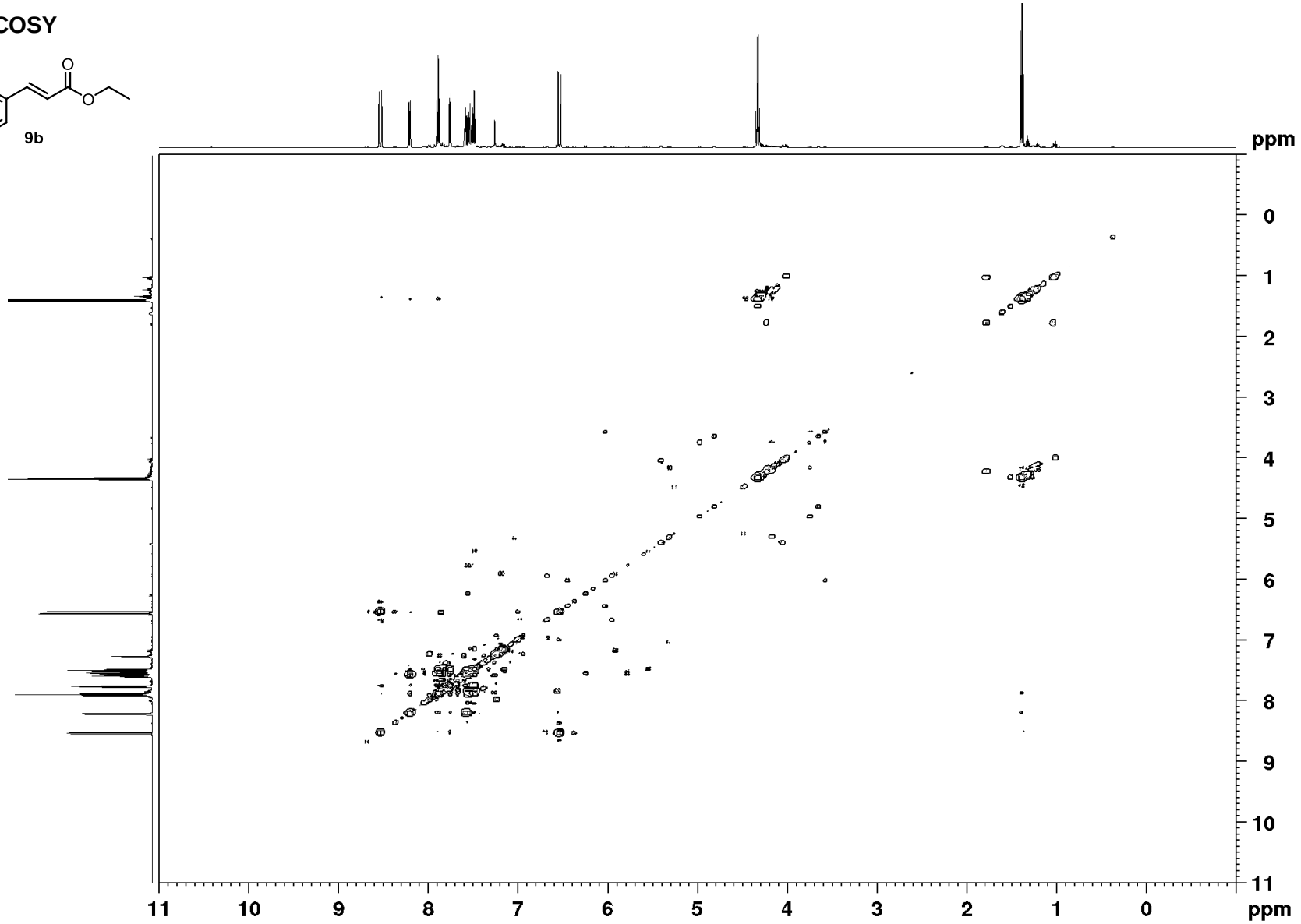
^{13}C-DEPT-NMR


141.5
130.4
128.6
126.8
126.1
125.4
124.9
123.3
120.9
60.5
14.3
O
O
9b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

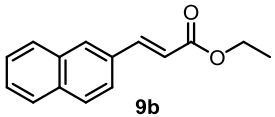
^{1}H, ^{1}H-COSY



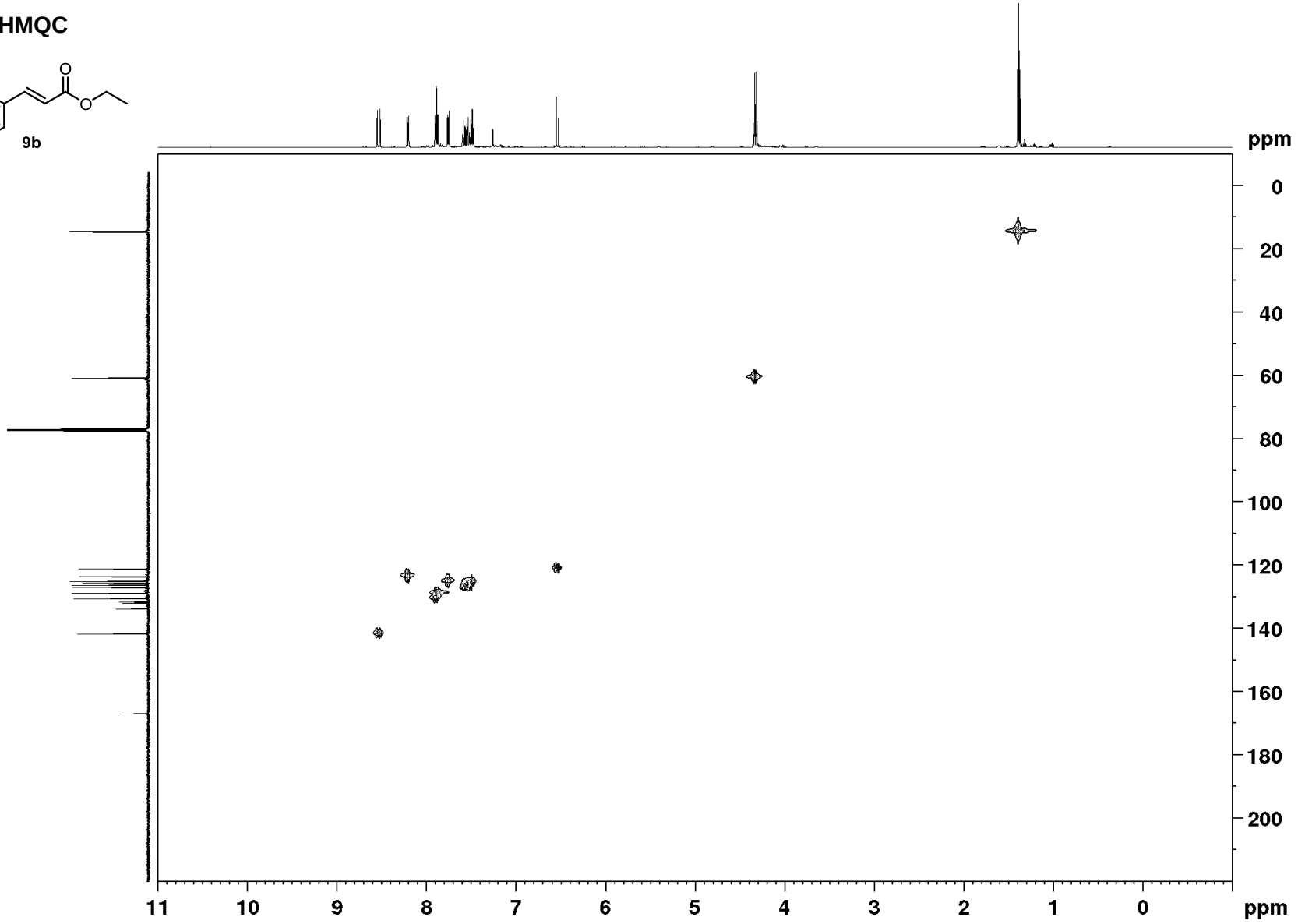
9b



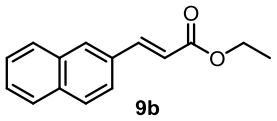
^{1}H, ^{13}C-HMQC



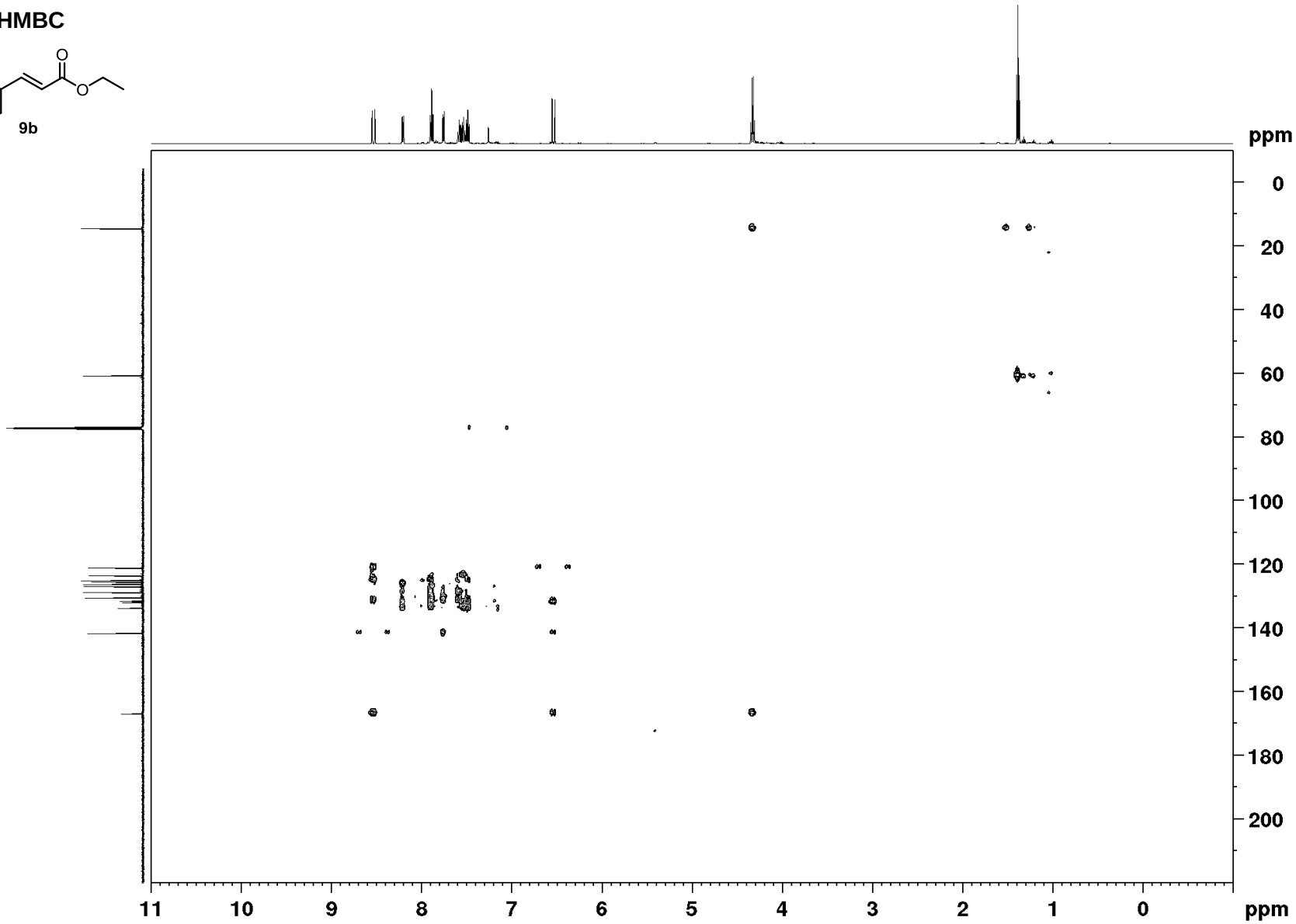
9b



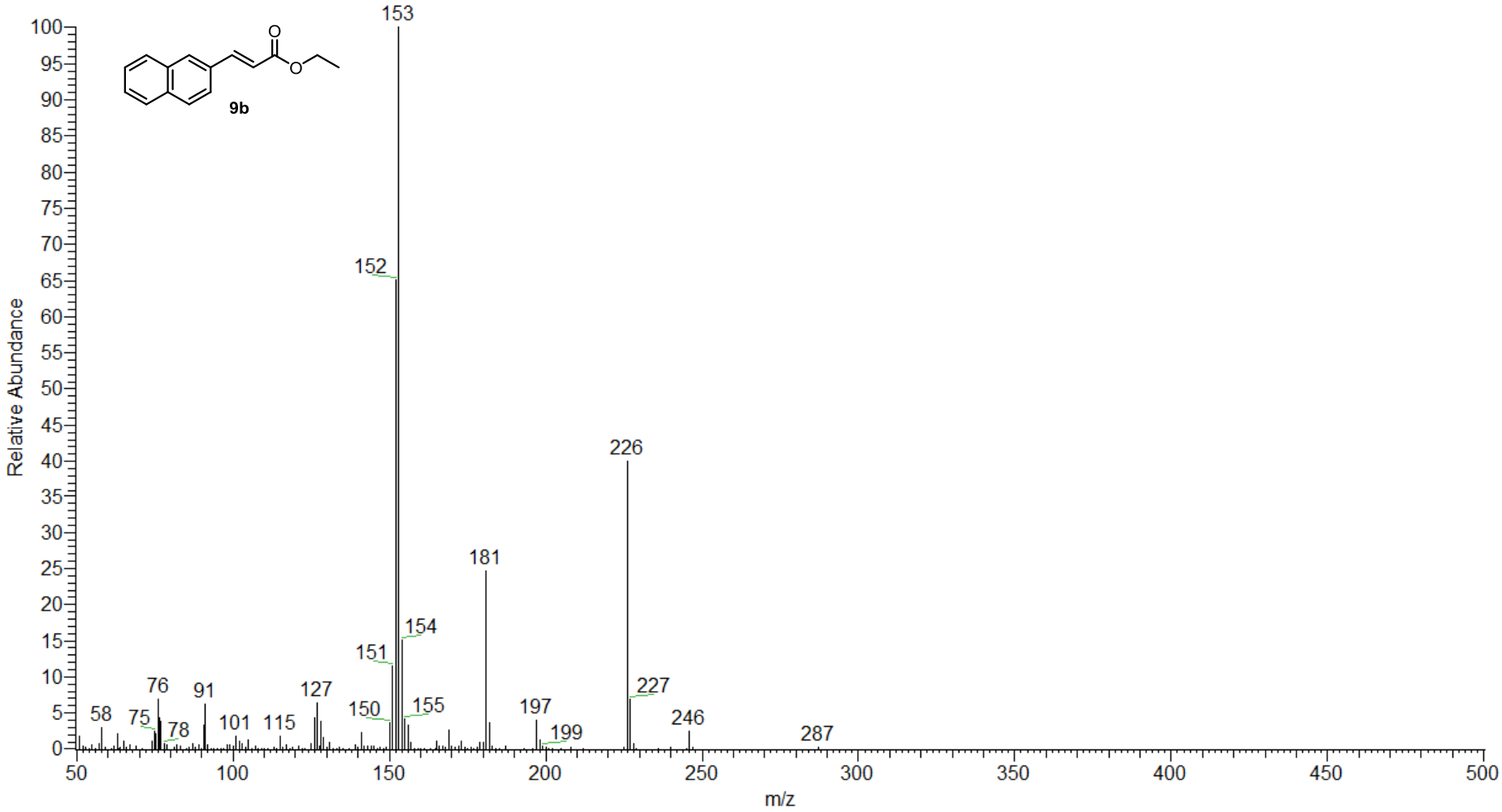
^{1}H, ^{13}C-HMBC



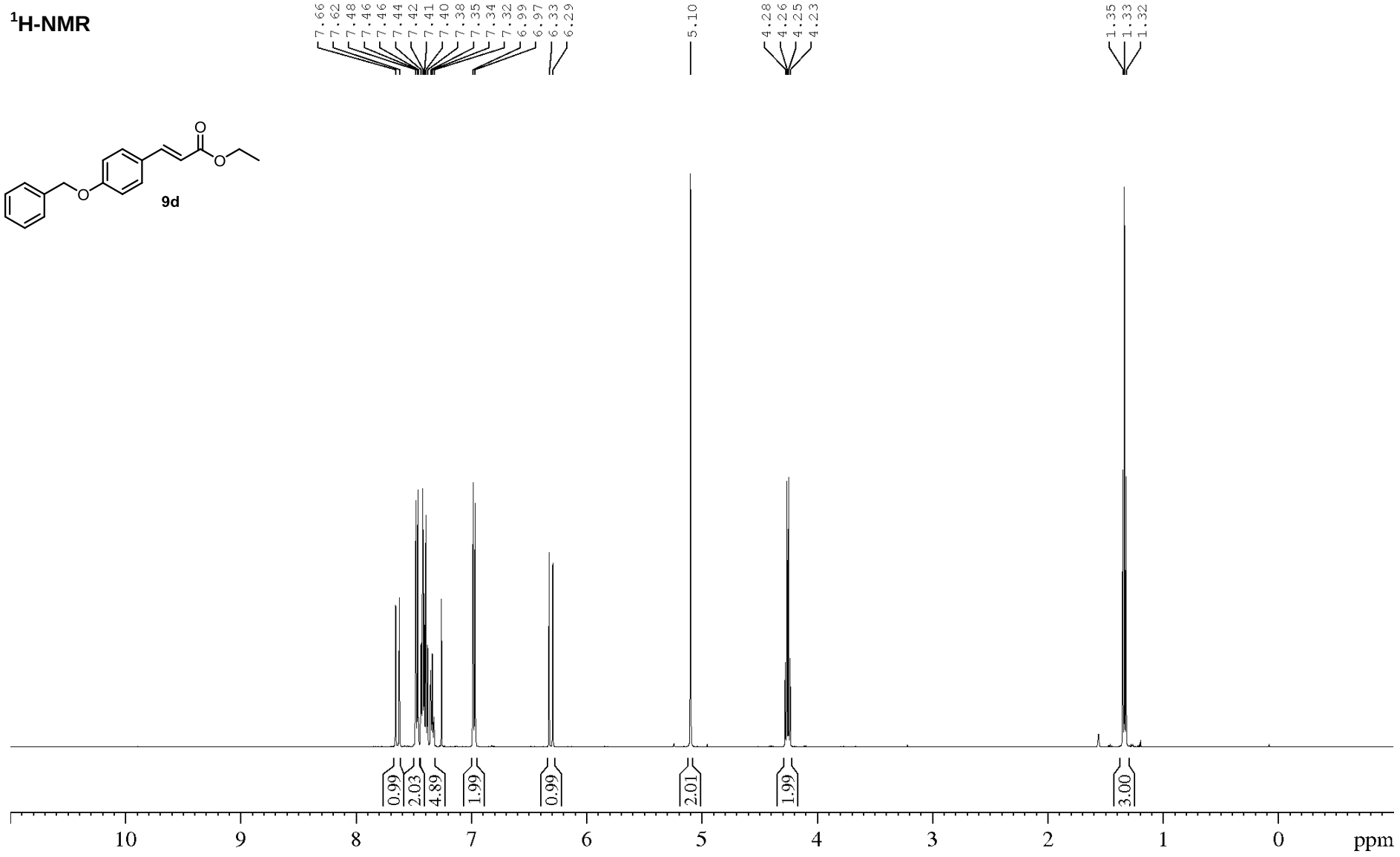
9b



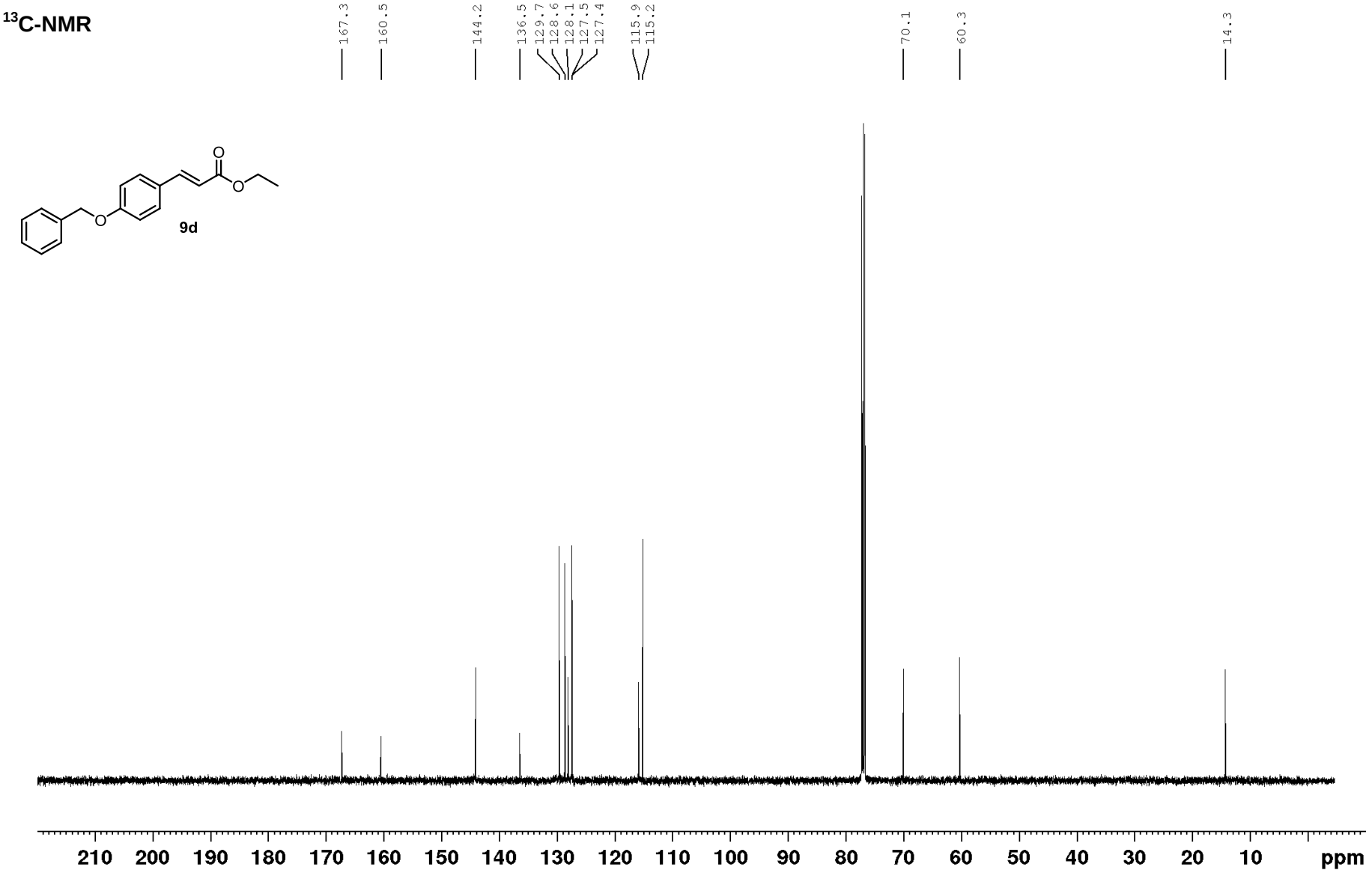
mass spectrum



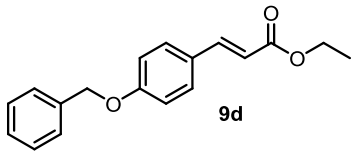
^{1}H-NMR


7.66
7.62
7.48
7.46
7.46
7.44
7.42
7.41
7.40
7.38
7.35
7.34
7.32
6.99
6.97
6.33
6.29
5.10
4.28
4.26
4.25
4.23
1.35
1.33
1.32
O
O
O
9d
0.99
2.03
4.89
1.99
0.99
2.01
1.99
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

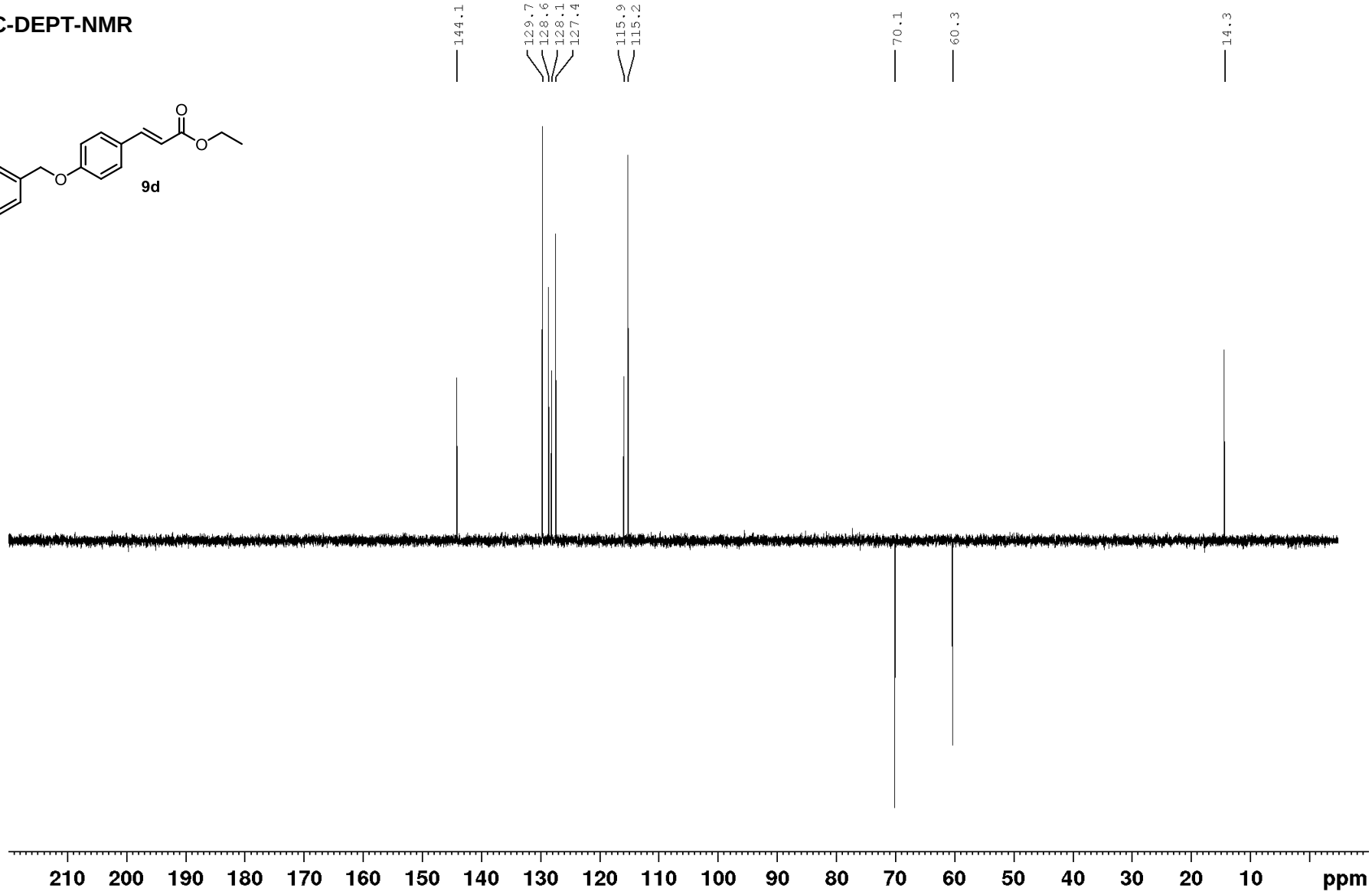
^{13}C-NMR


167.3
160.5
144.2
136.5
129.7
128.6
128.1
127.5
127.4
115.9
115.2
70.1
60.3
14.3
O
O
O
9d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

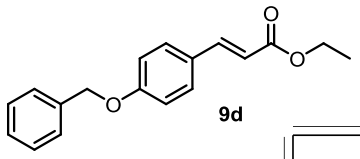
^{13}C-DEPT-NMR



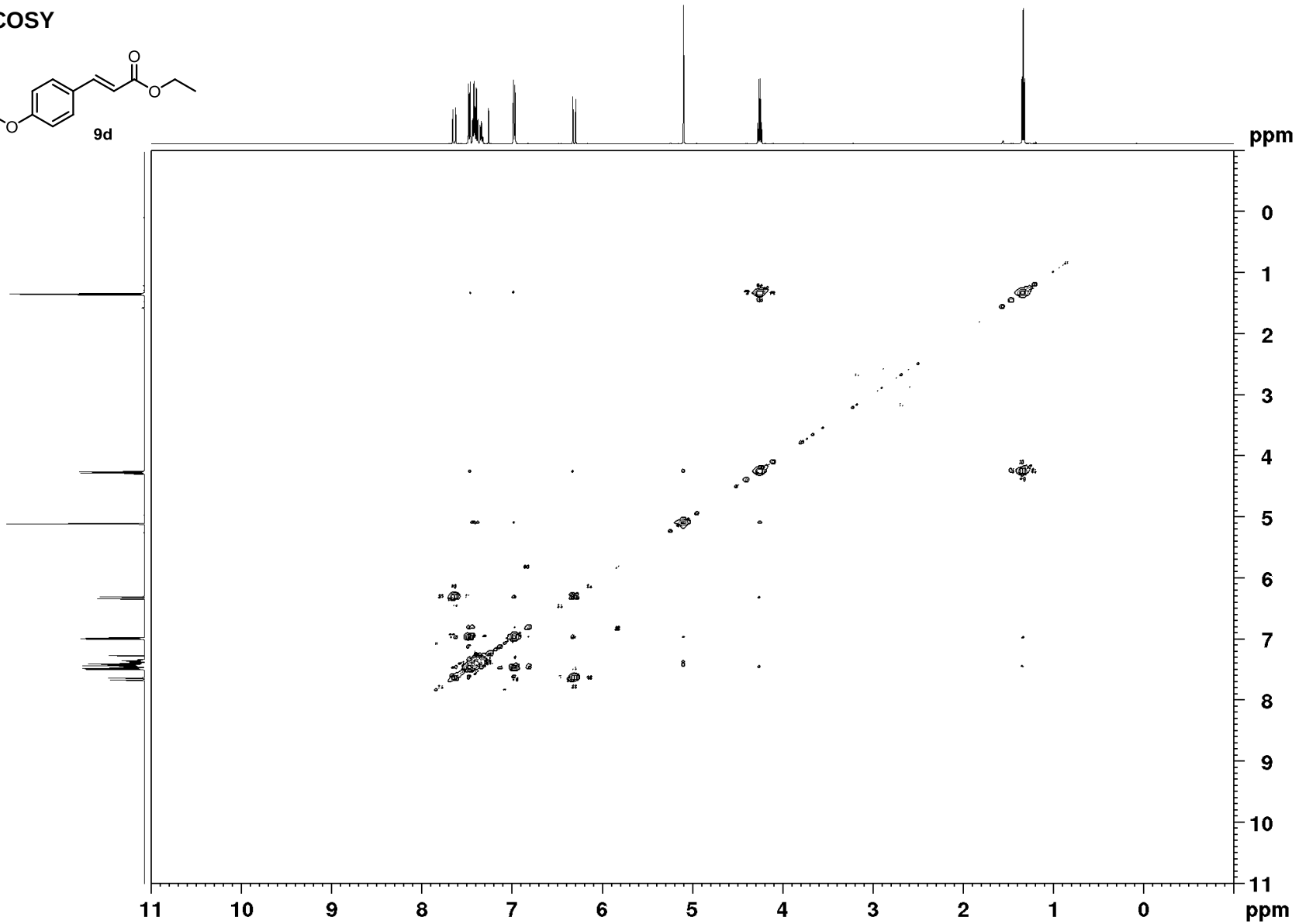
9d



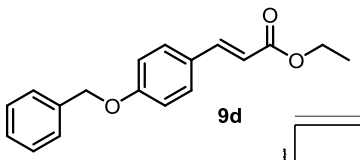
^{1}H, ^{1}H-COSY



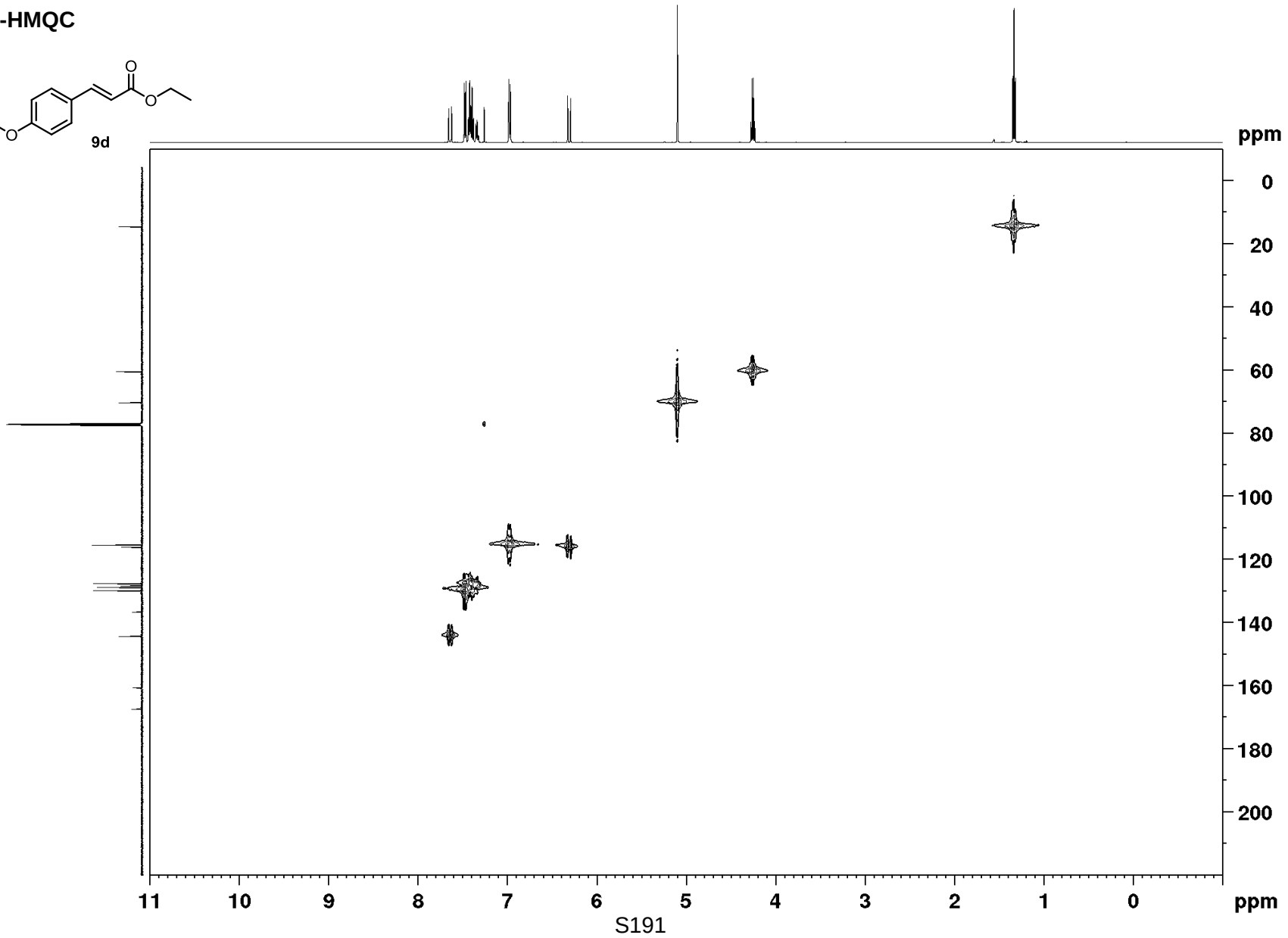
9d



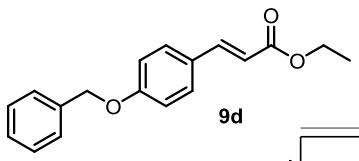
^{1}H, ^{13}C-HMQC



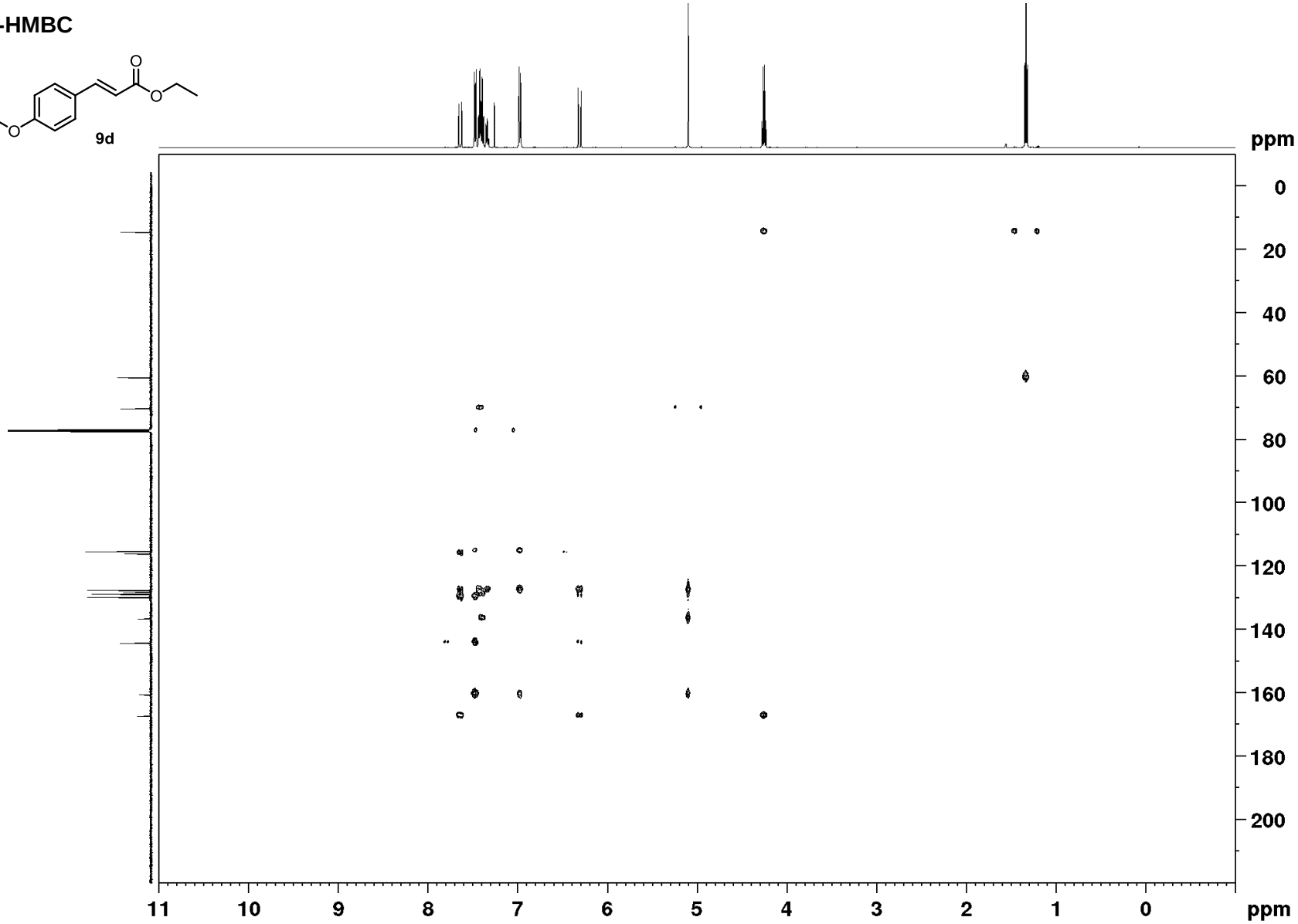
9d



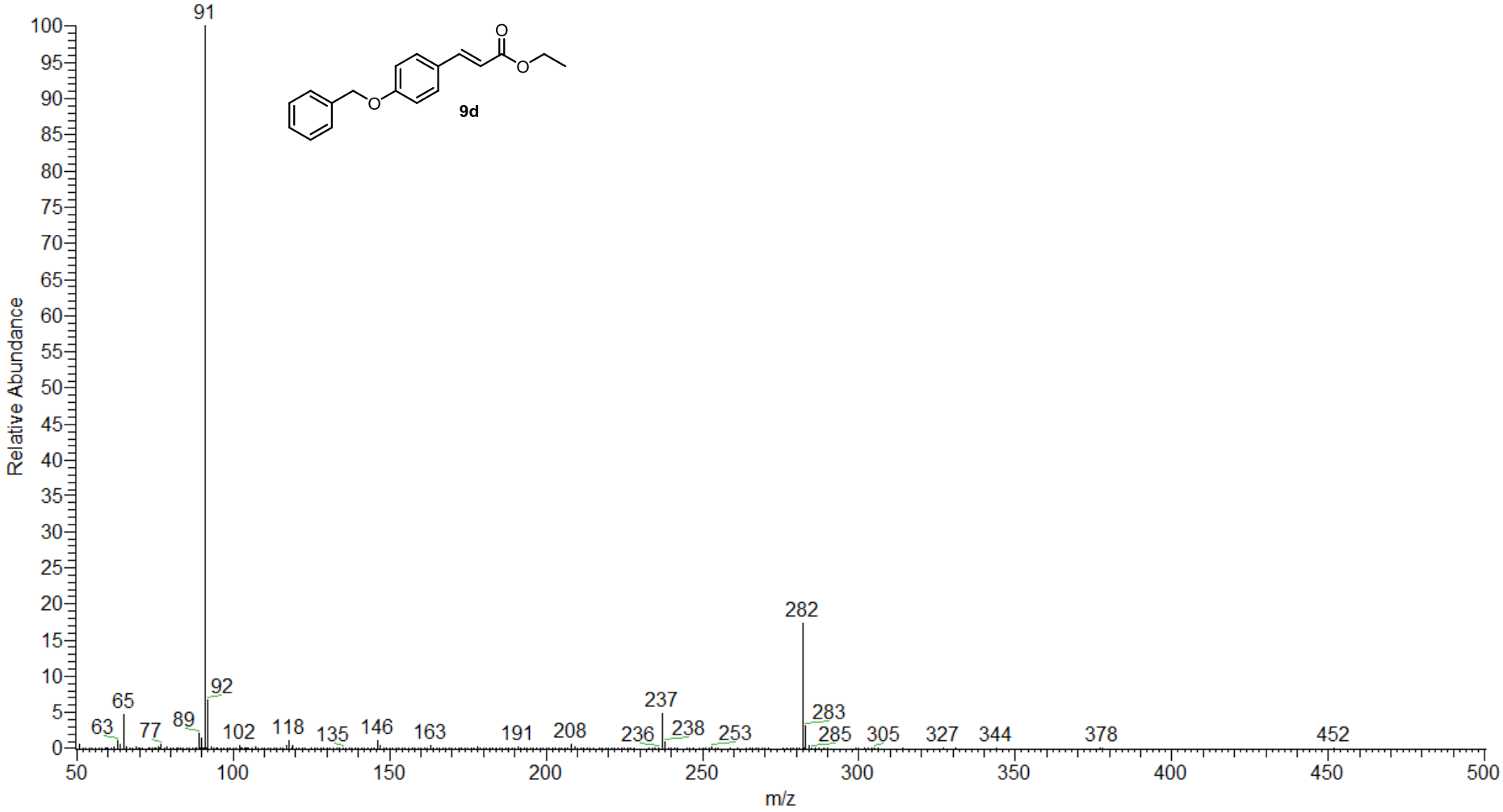
^{1}H, ^{13}C-HMBC



9d



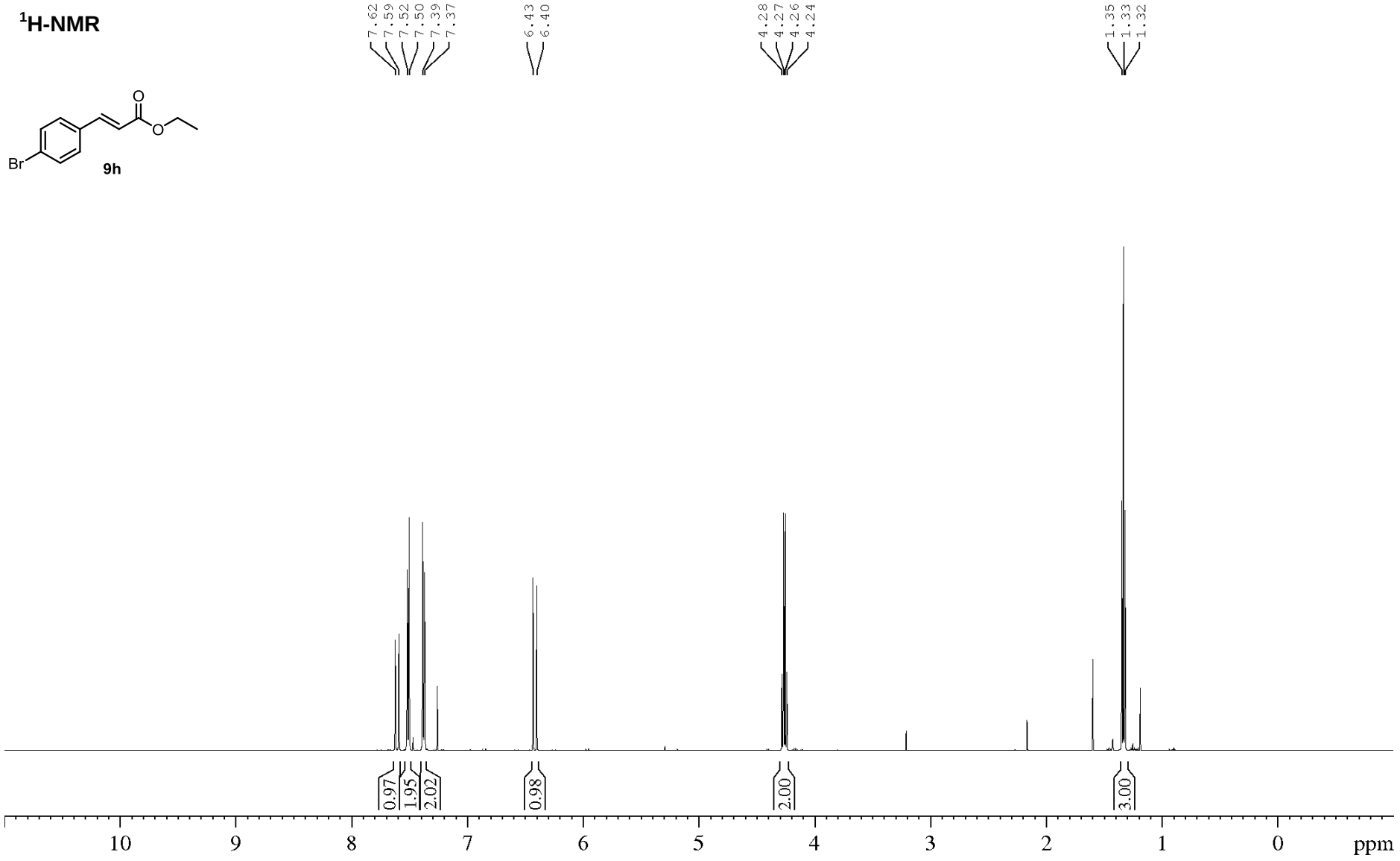
mass spectrum



^{1}H-NMR

O
O
Br

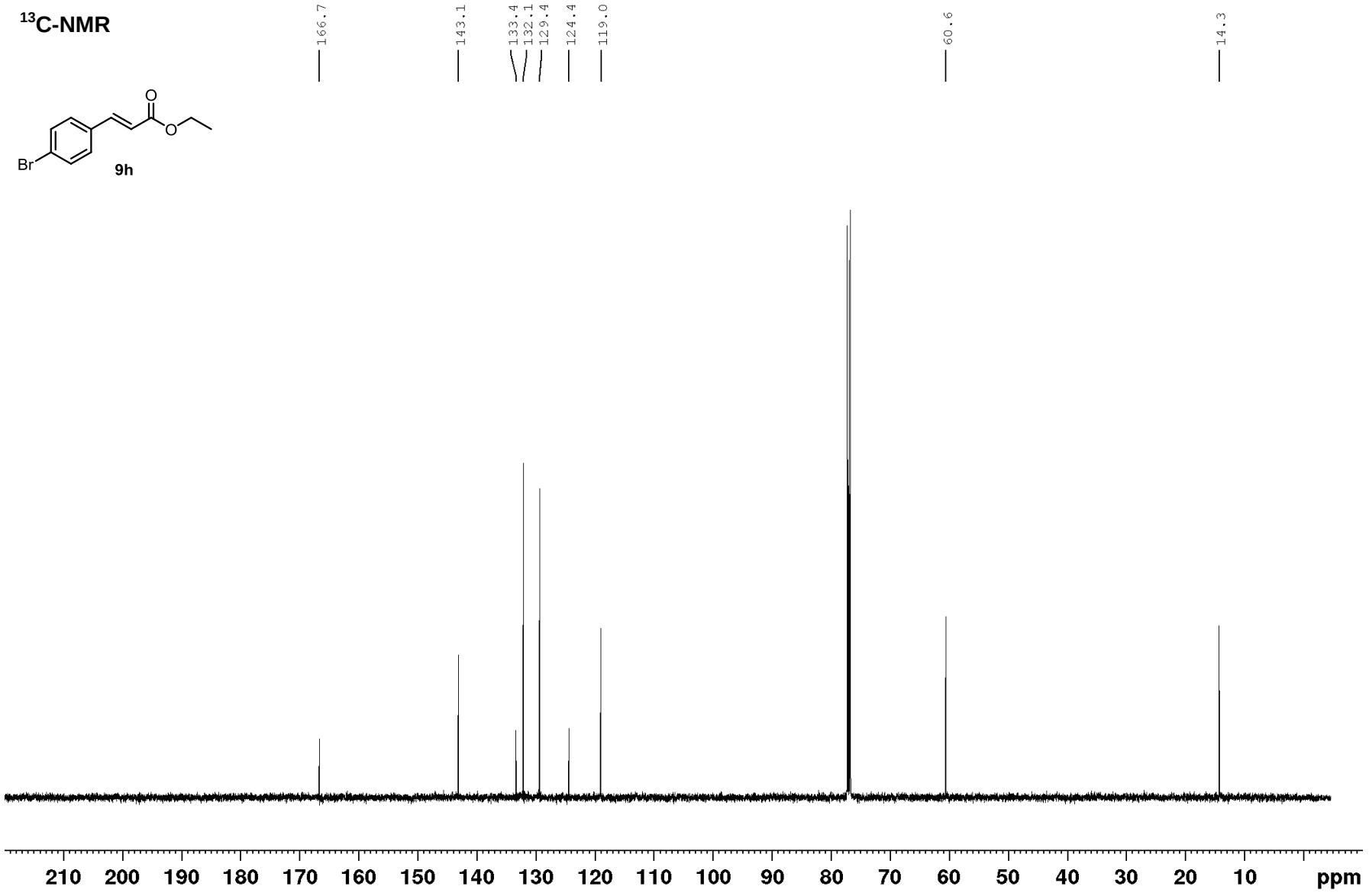
9h


7.62
7.59
7.52
7.50
7.39
7.37
6.43
6.40
4.28
4.27
4.26
4.24
1.35
1.33
1.32
0.97
1.95
2.02
0.98
2.00
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C-NMR

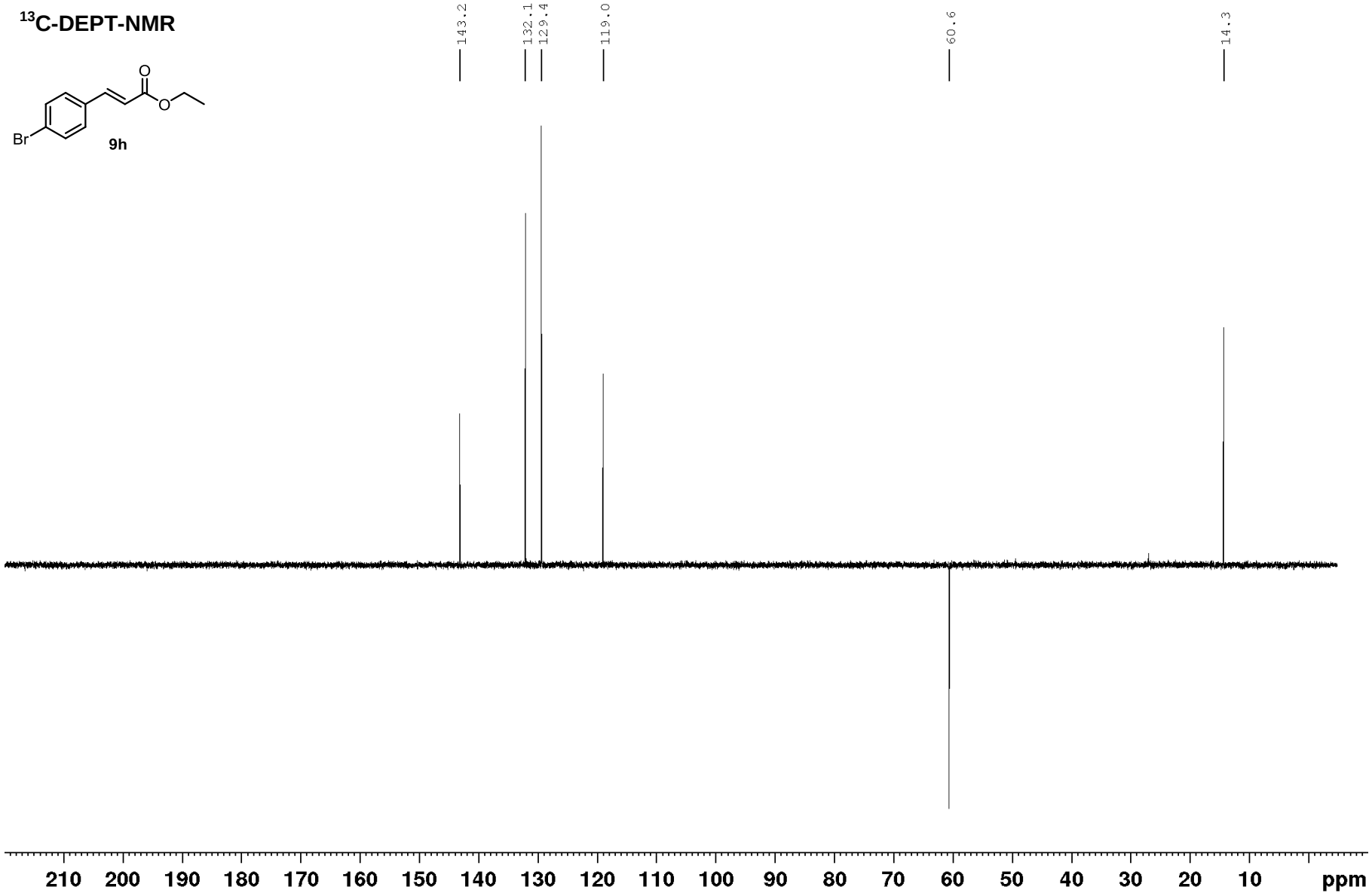
O
O
Br

9h


166.7
143.1
133.4
132.1
129.4
124.4
119.0
60.6
14.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

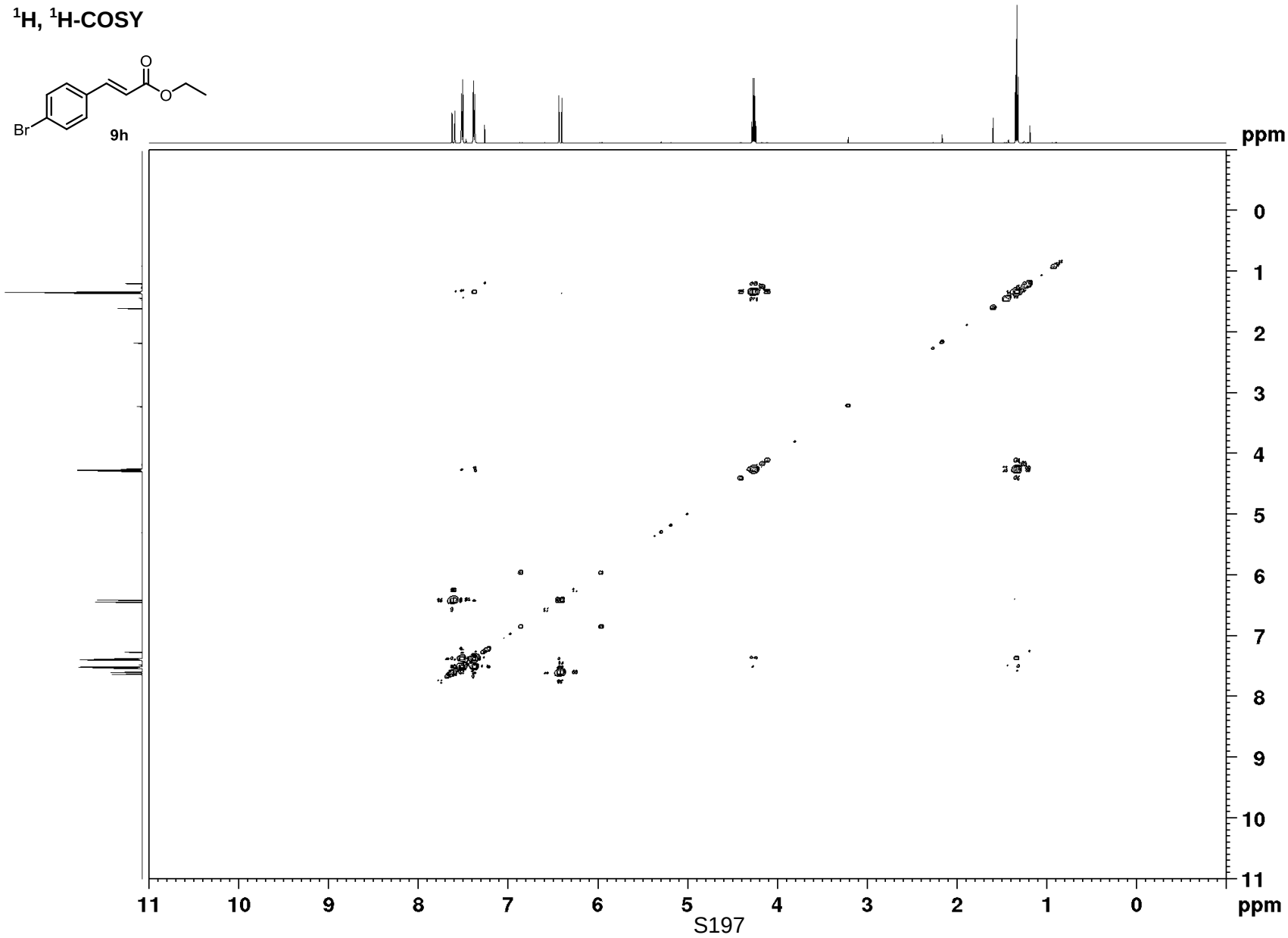
^{13}C-DEPT-NMR

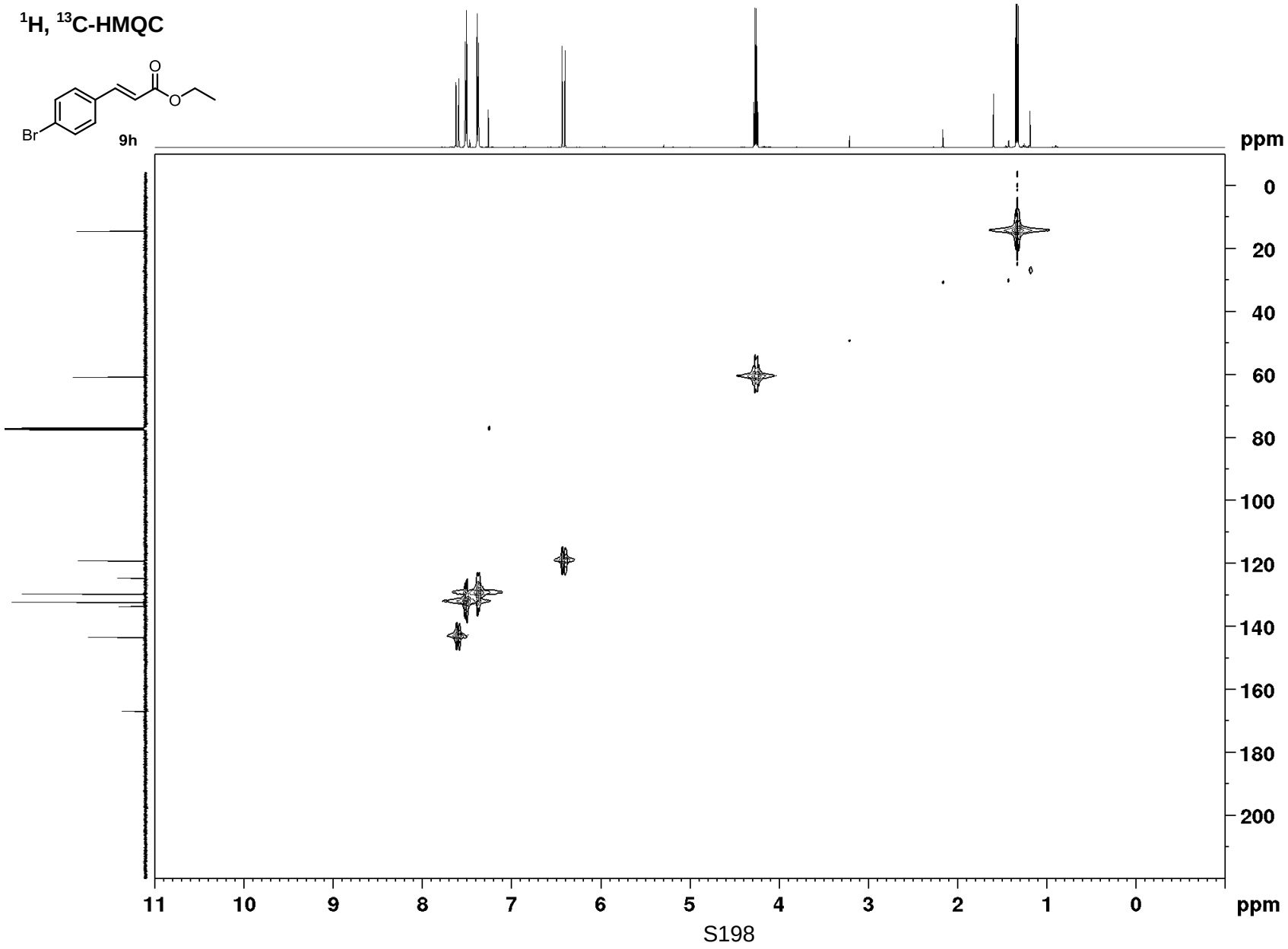
9h

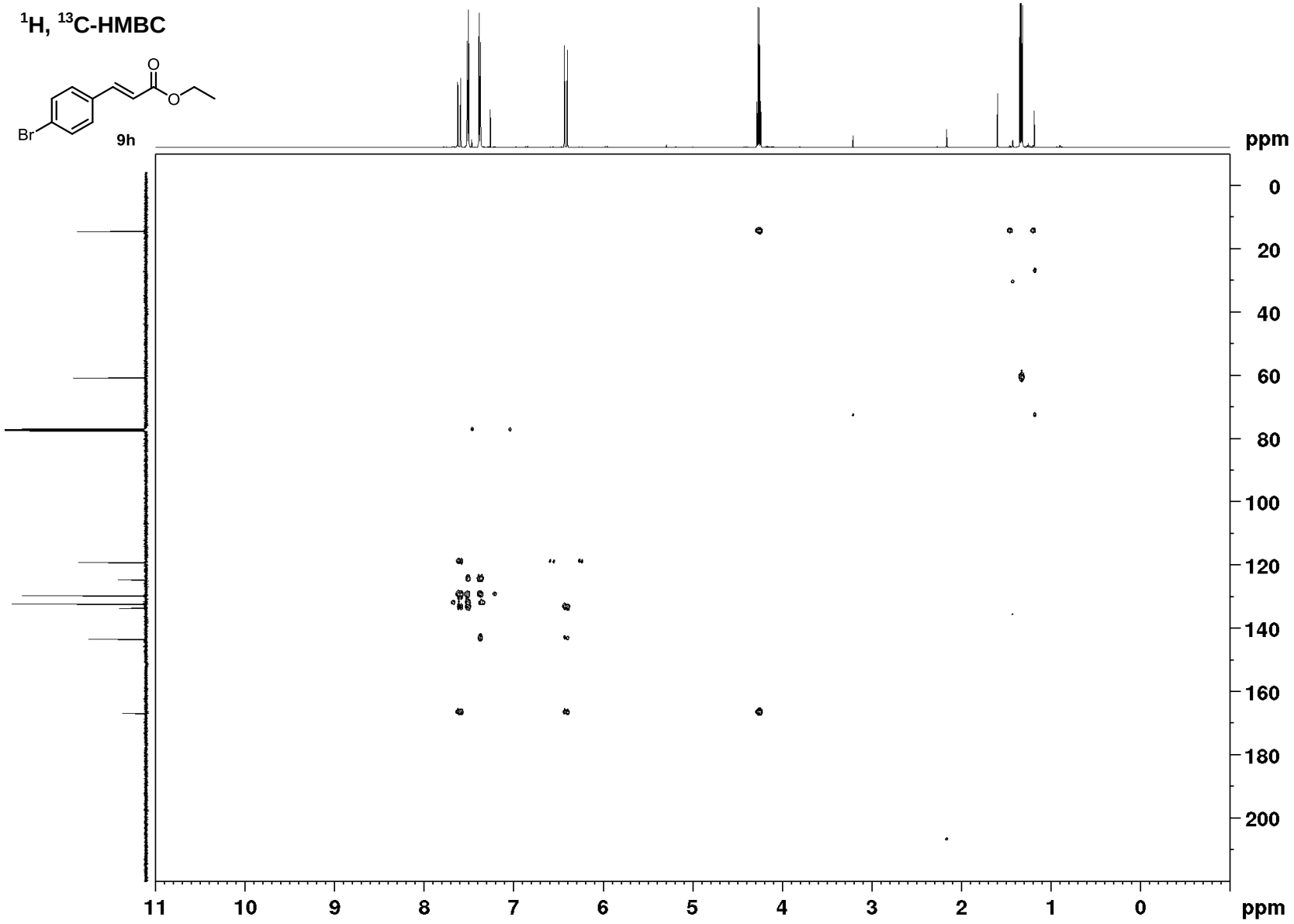


^{1}H, ^{1}H-COSY

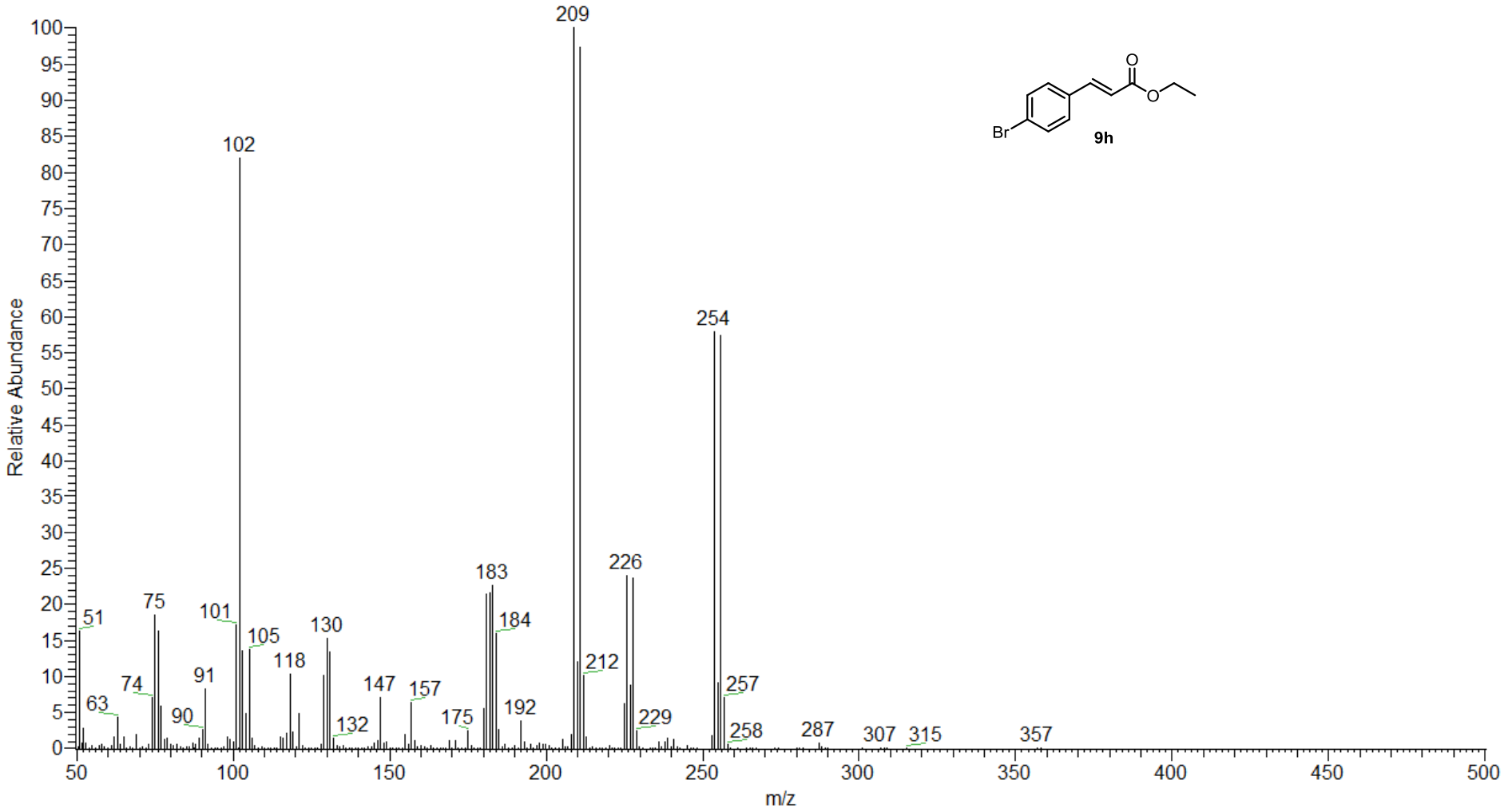
9h




^{1}H, ^{13}C-HMQC
O
O
Br
9h
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

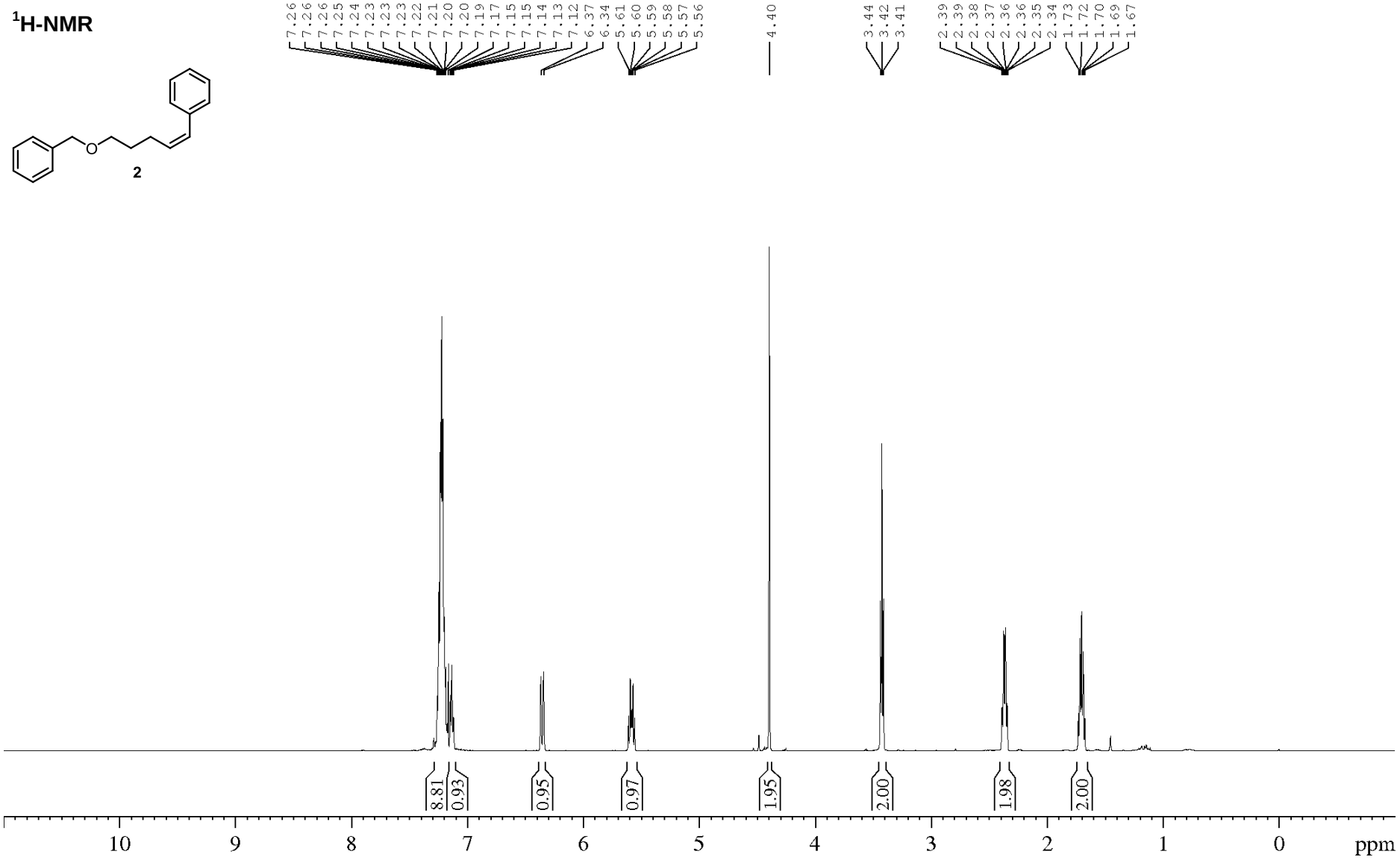

^{1}H, ^{13}C-HMBC
O
O
Br
9h
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

mass spectrum



^{1}H-NMR

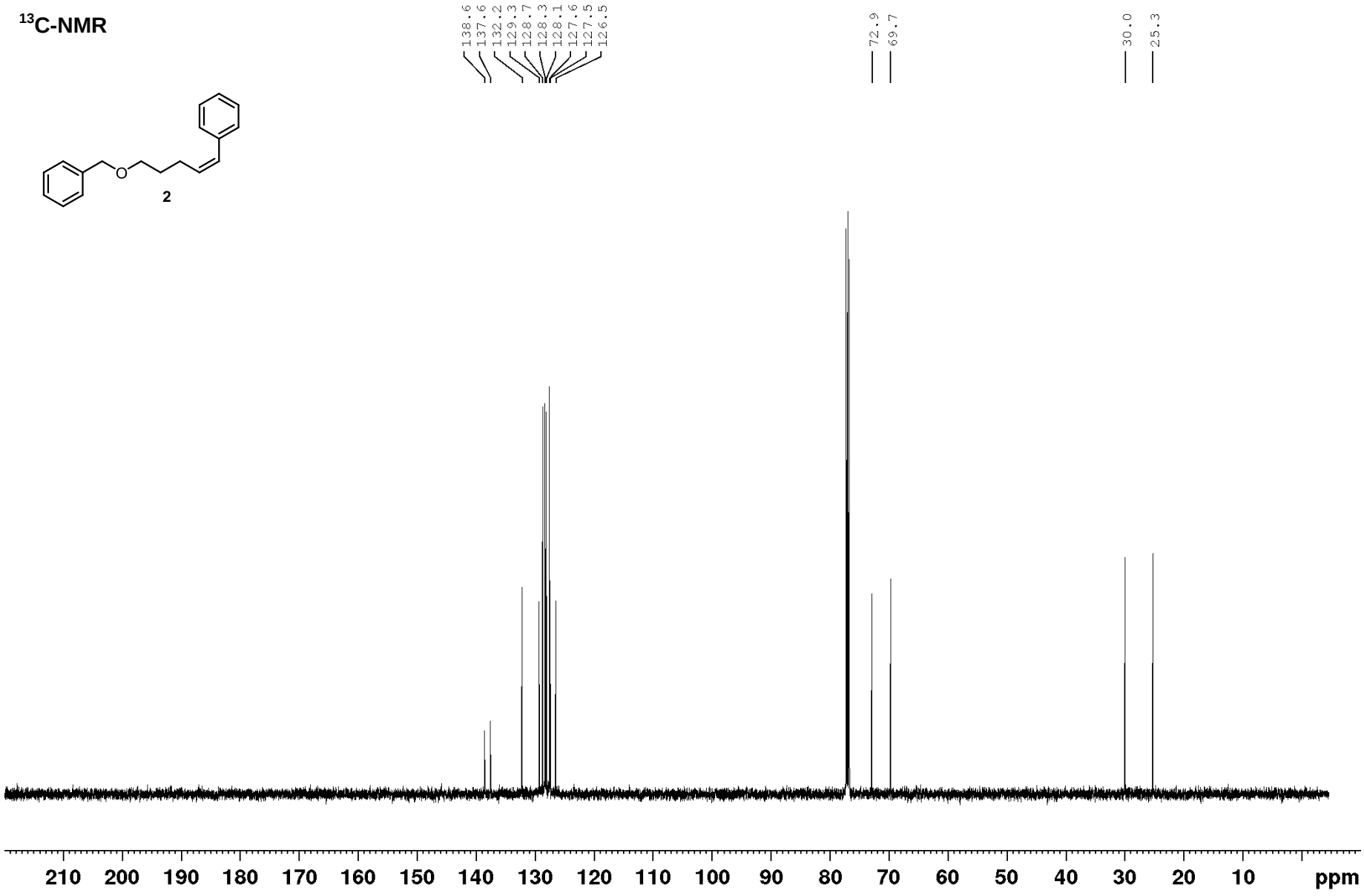
O
2


7.26
7.26
7.26
7.25
7.24
7.23
7.23
7.23
7.22
7.21
7.20
7.20
7.19
7.17
7.15
7.15
7.14
7.13
7.12
6.37
6.34
5.61
5.60
5.59
5.58
5.57
5.56
4.40
3.44
3.42
3.41
2.39
2.39
2.38
2.37
2.36
2.36
2.35
2.34
1.73
1.72
1.70
1.69
1.67
8.81
0.93
0.95
0.97
1.95
2.00
1.98
2.00
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C-NMR

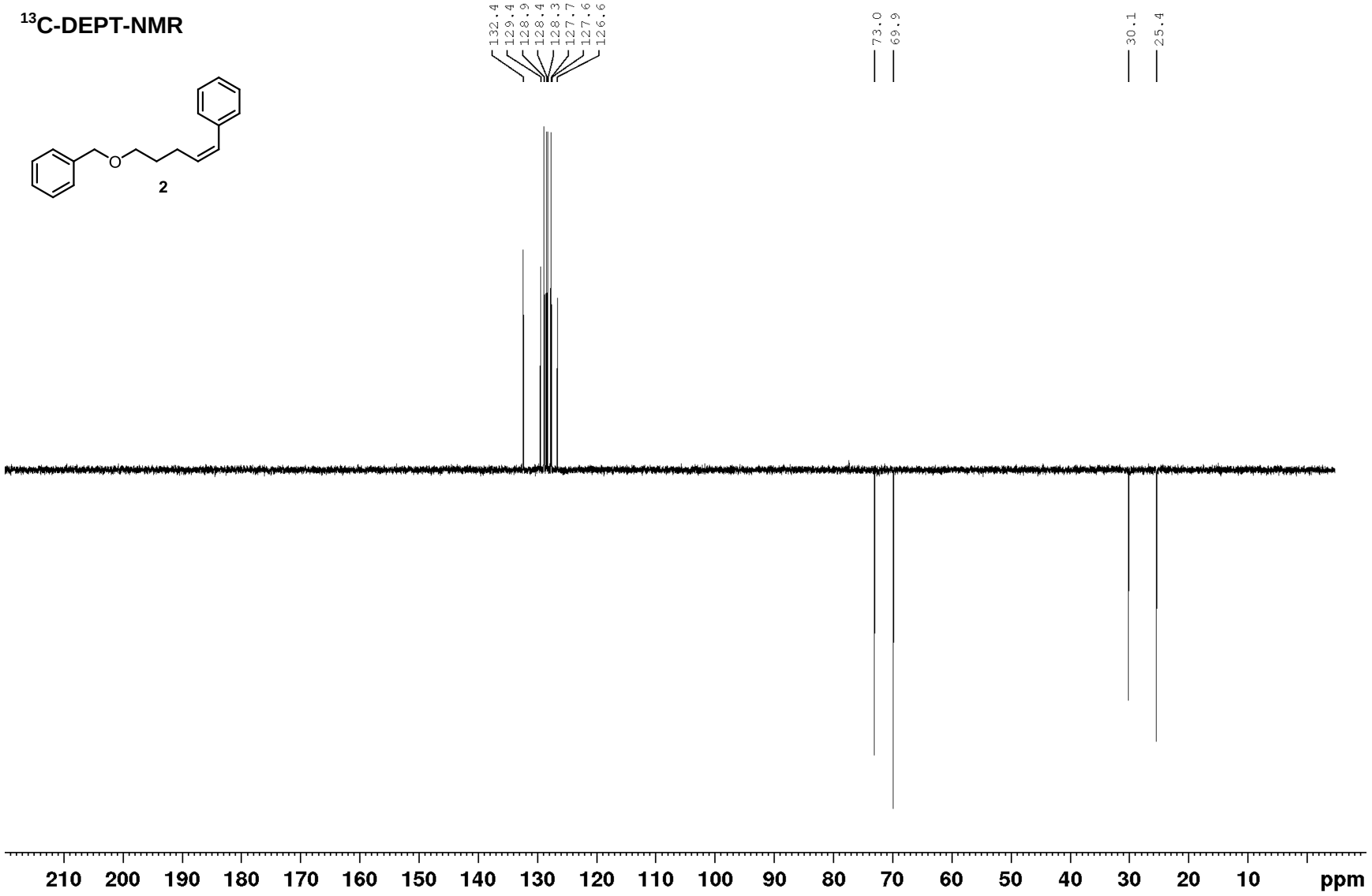
O

2

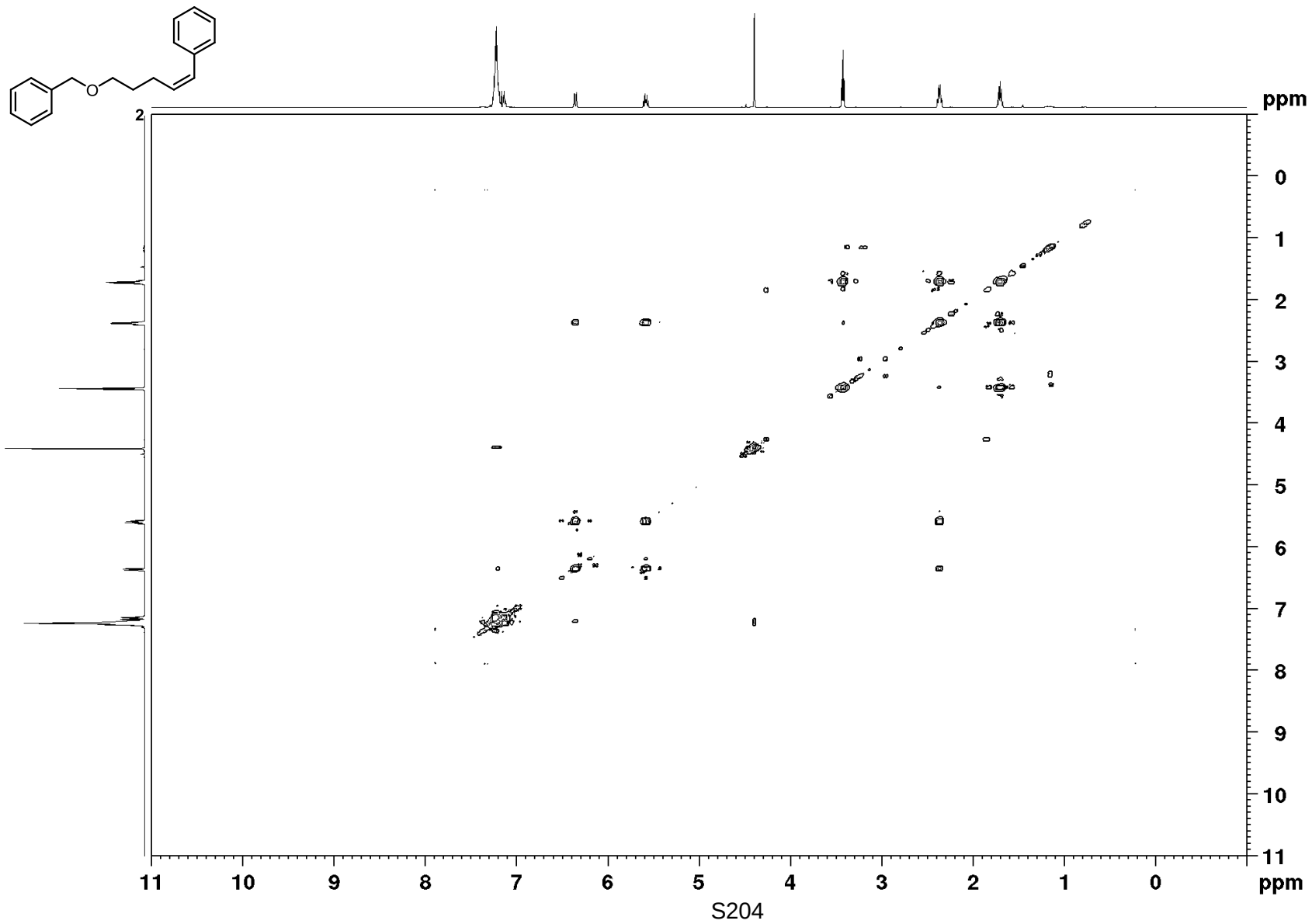

138.6
137.6
132.2
129.3
128.7
128.3
128.1
127.6
127.5
126.5
72.9
69.7
30.0
25.3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{13}C-DEPT-NMR

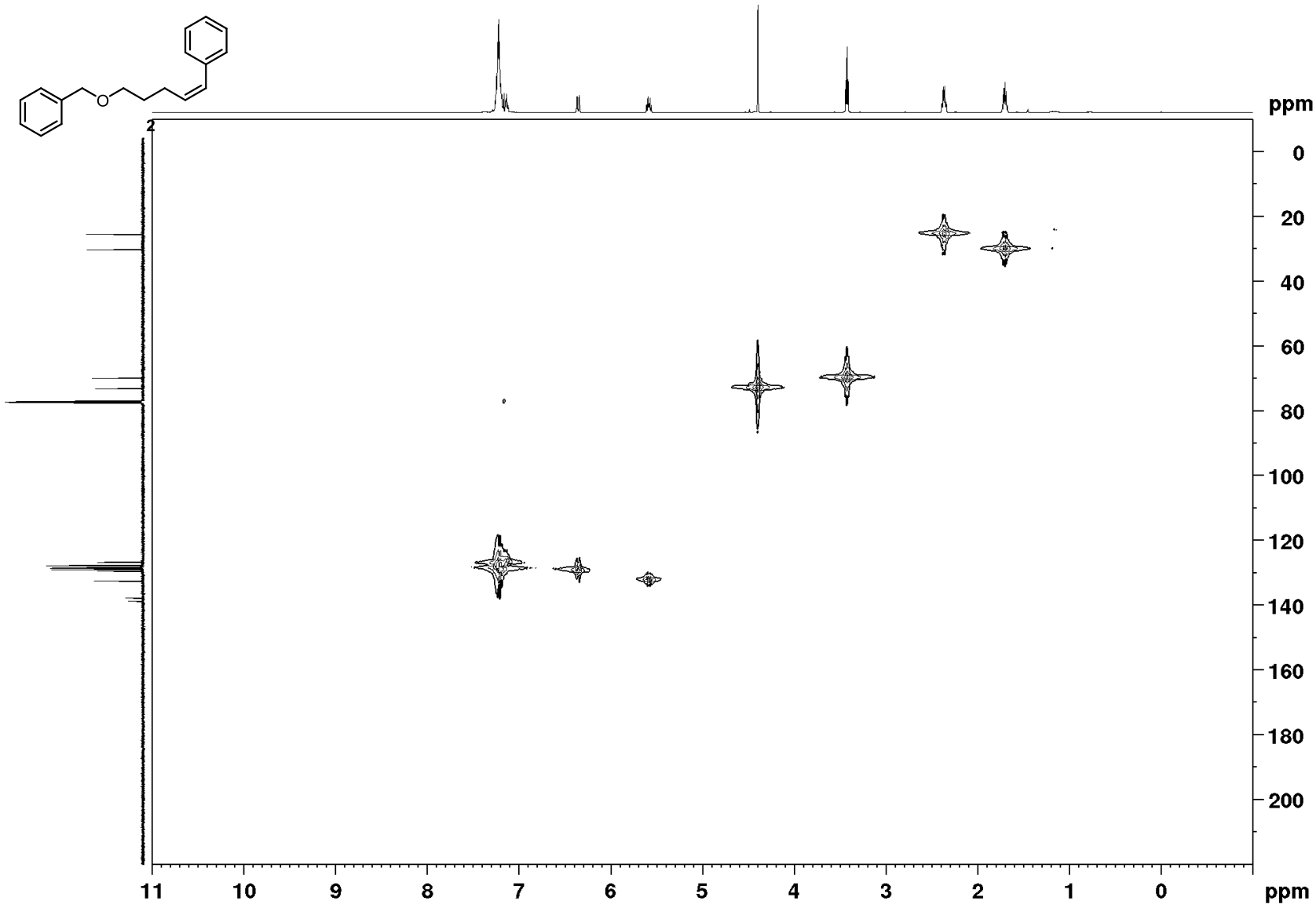
2

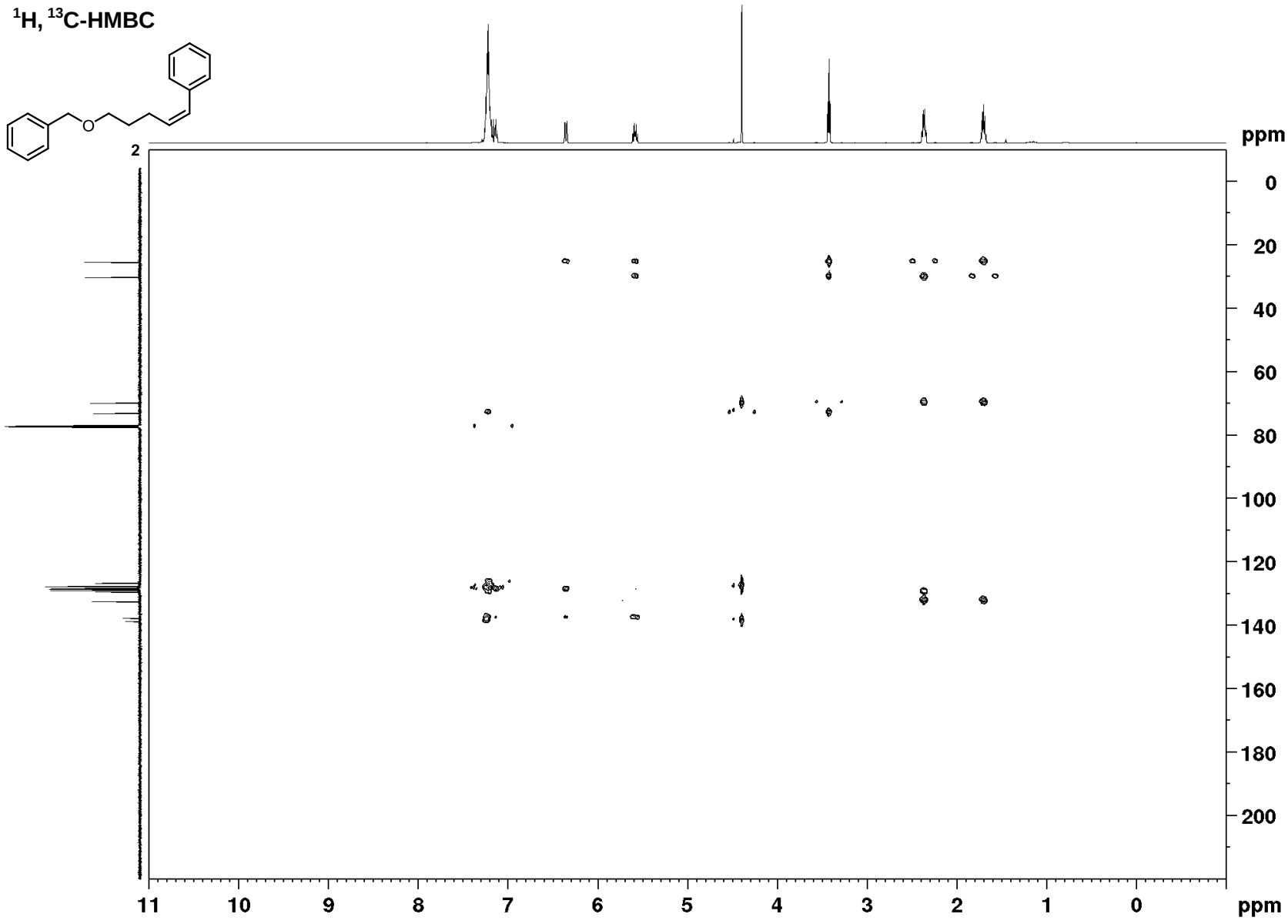


^{1}H, ^{1}H-COSY

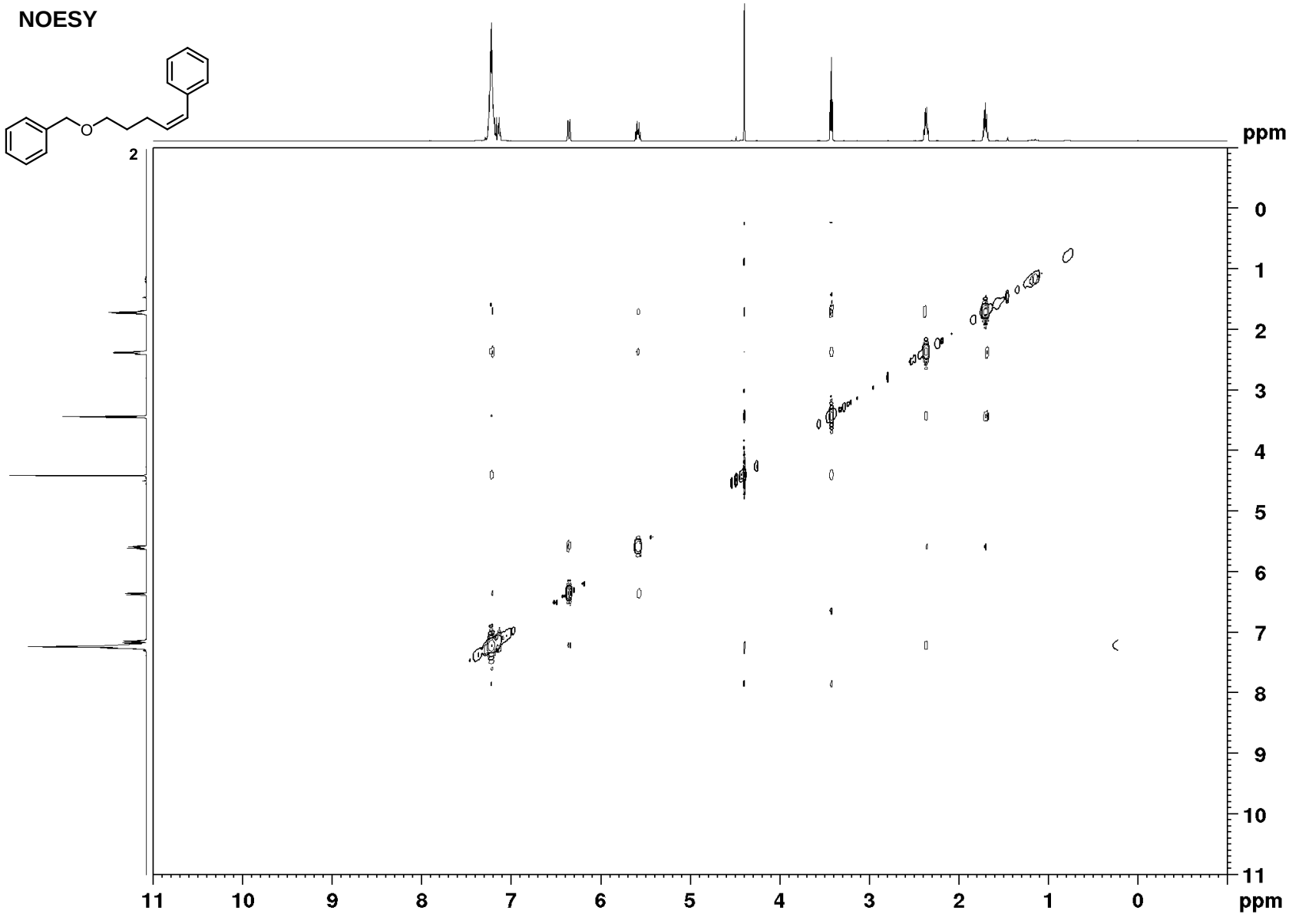


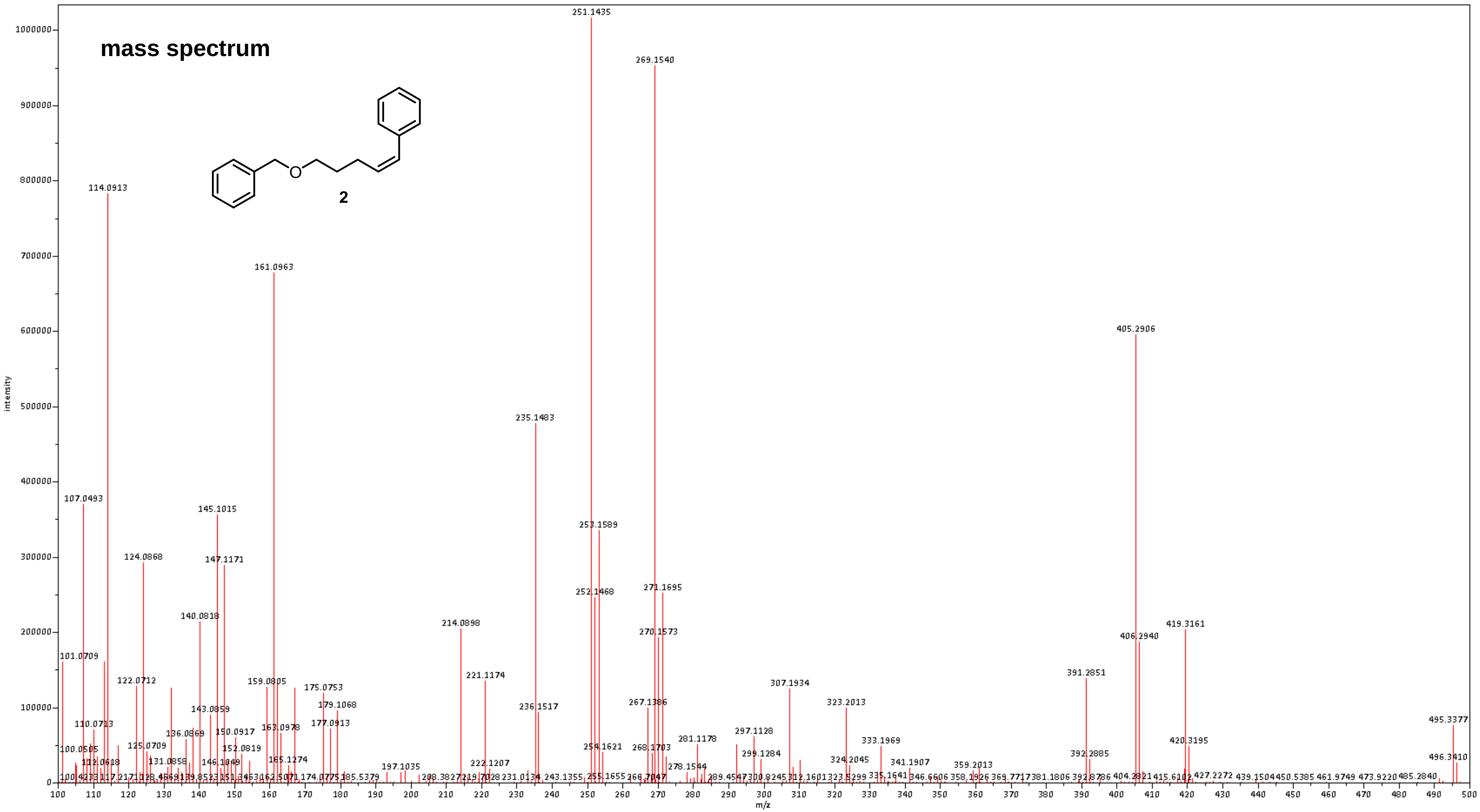
^{1}H, ^{13}C-HMQC



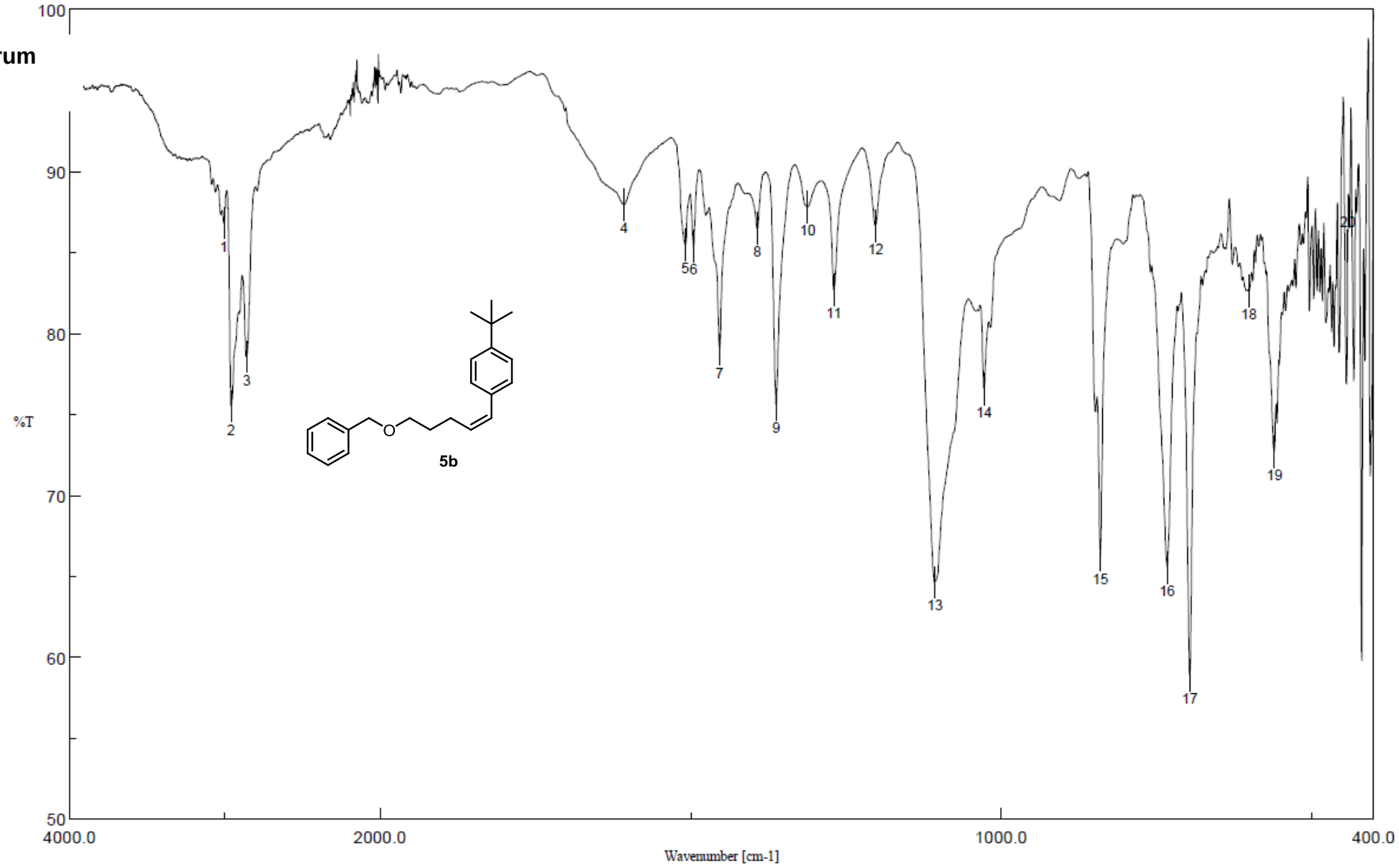

^{1}H, ^{13}C-HMBC
O
2
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

NOESY



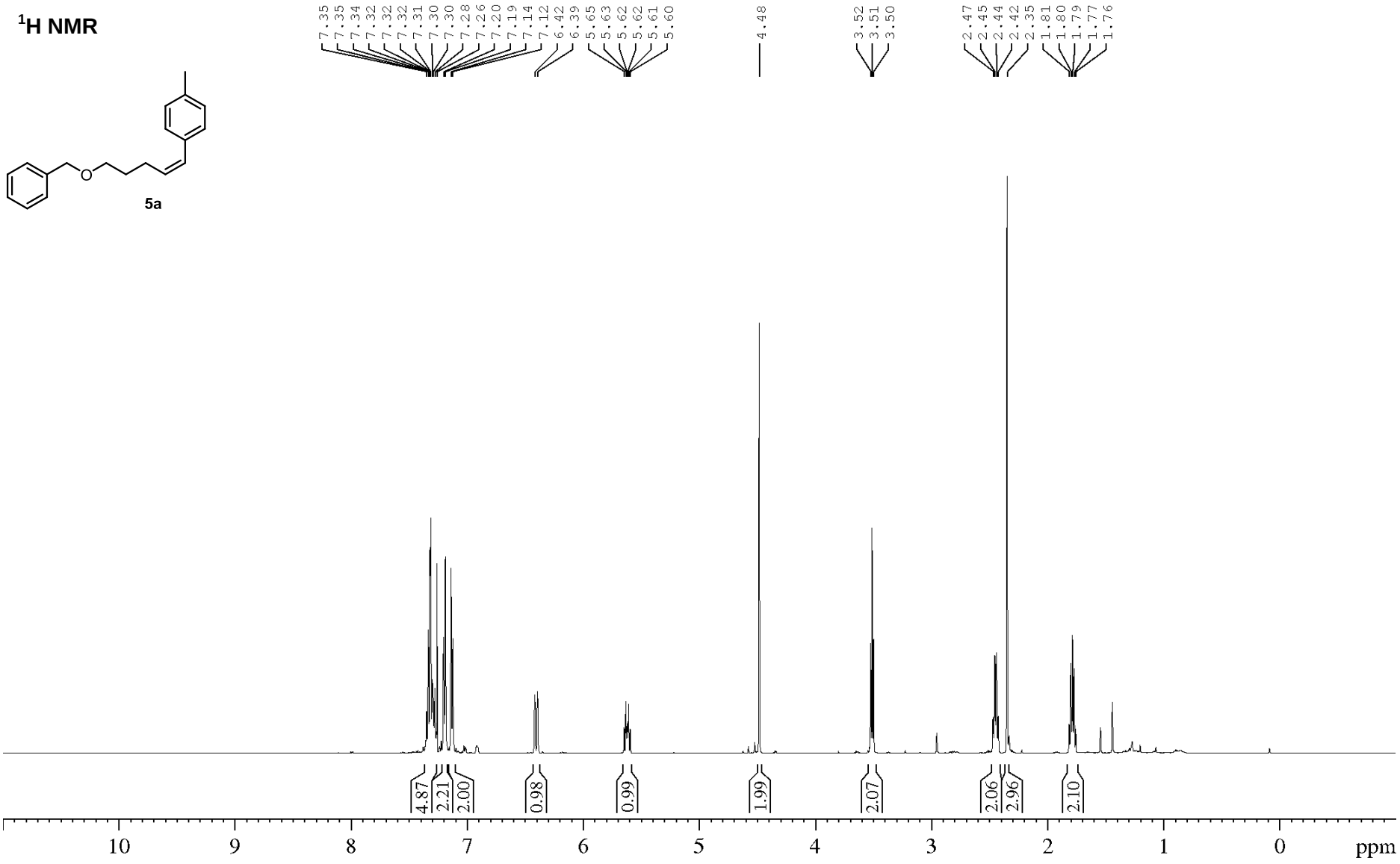

mass spectrum
2
intensity
m/z
251.1435
269.1540
114.0913
161.0963
405.2906
235.1483
107.0493
145.1015
253.1589
124.0868
147.1171
252.1468
271.1695
214.0898
140.0818
419.3161
406.2940
270.1573
101.0709
122.0712
159.0805
175.0753
221.1174
307.1934
391.2851
179.1068
143.0859
236.1517
267.1386
323.2013
495.3377
110.0713
177.0913
163.0978
150.0917
297.1128
136.0869
281.1178
333.1969
420.3195
100.0505
125.0709
254.1621
268.1703
152.0819
392.2885
299.1284
496.3410
131.0858
165.1274
146.1049
112.0618
222.1207
341.1907
324.2045
359.2013
197.1035
278.1544

IR spectrum


100
90
80
70
60
50
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
O
5b

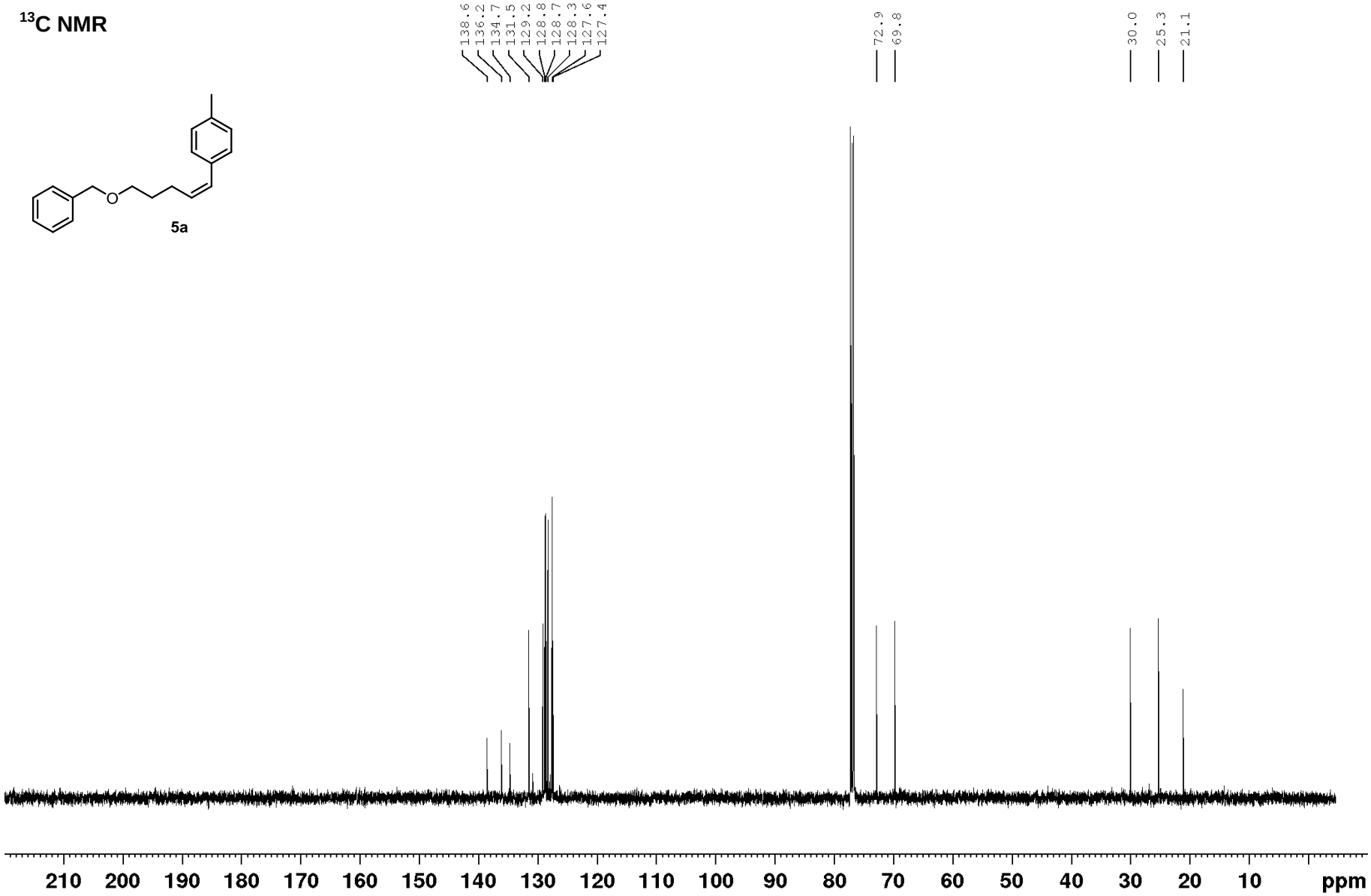
^{1}H NMR

5a

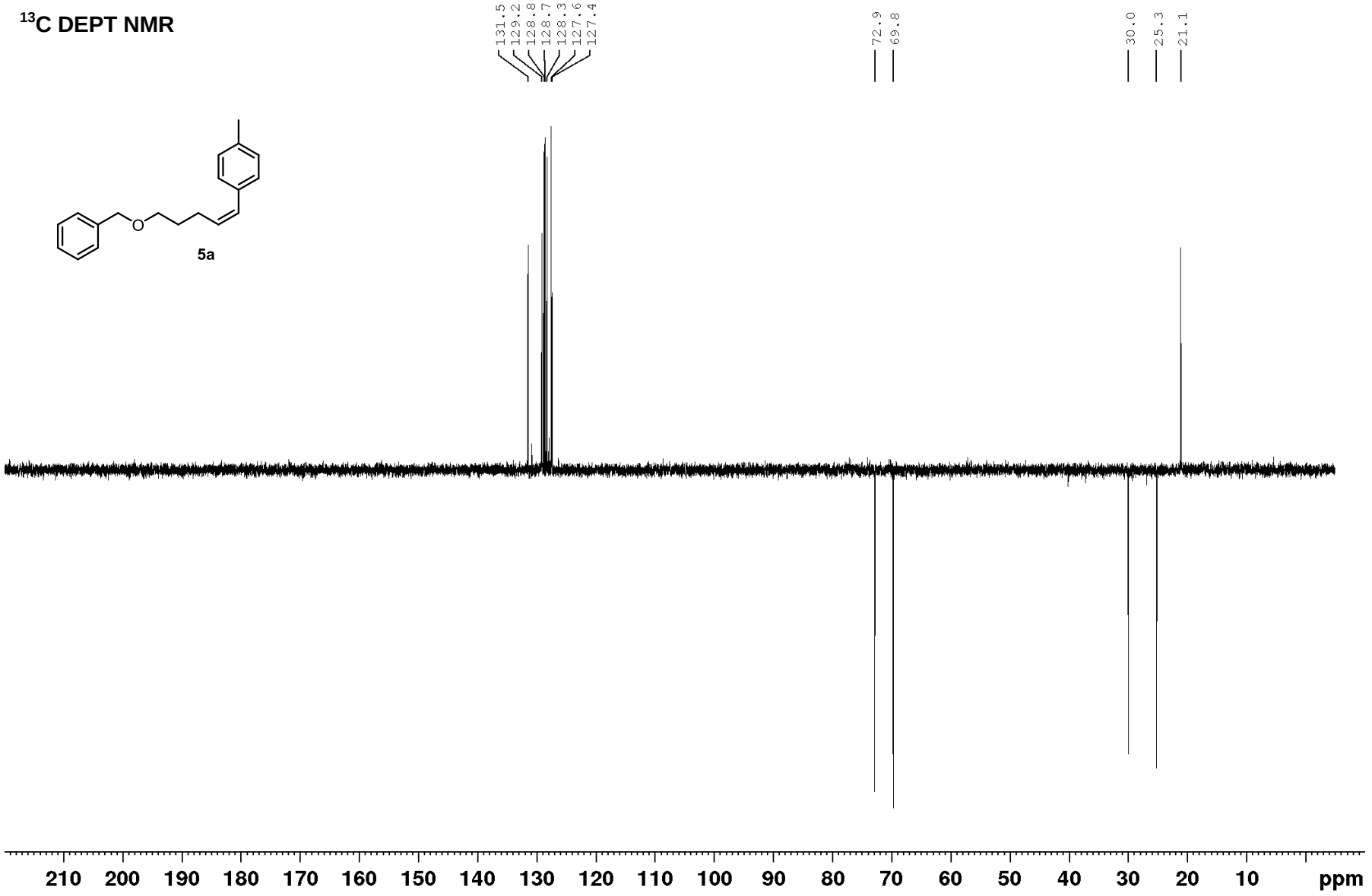

7.35
7.35
7.34
7.32
7.32
7.32
7.31
7.30
7.30
7.28
7.26
7.20
7.19
7.14
7.12
6.42
6.39
5.65
5.63
5.62
5.62
5.61
5.60
4.48
3.52
3.51
3.50
2.47
2.45
2.44
2.42
2.35
1.81
1.80
1.79
1.77
1.76
4.87
2.21
2.00
0.98
0.99
1.99
2.07
2.06
2.96
2.10
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

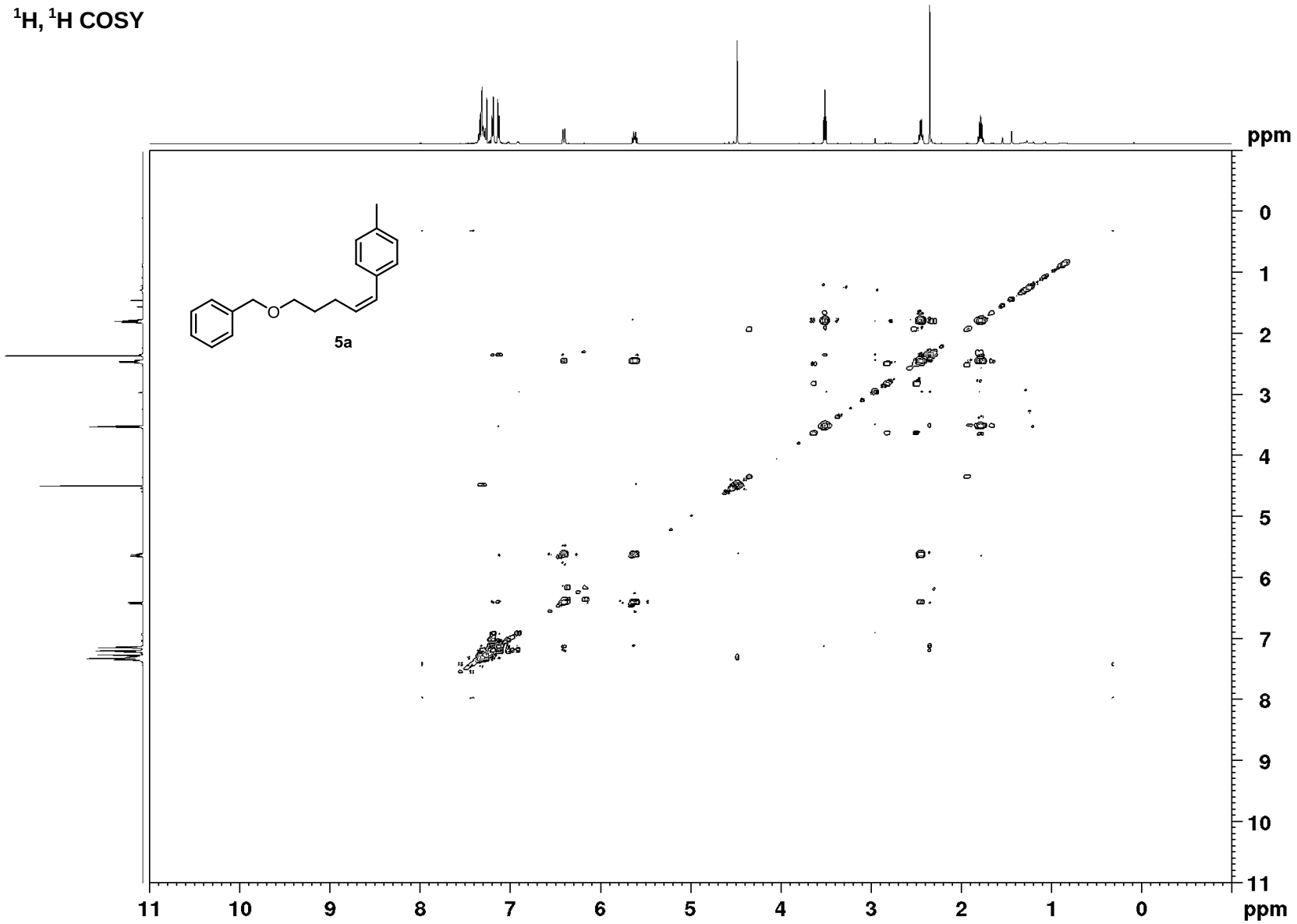
5a


138.6
136.2
134.7
131.5
129.2
128.8
128.7
128.3
127.6
127.4
72.9
69.8
30.0
25.3
21.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

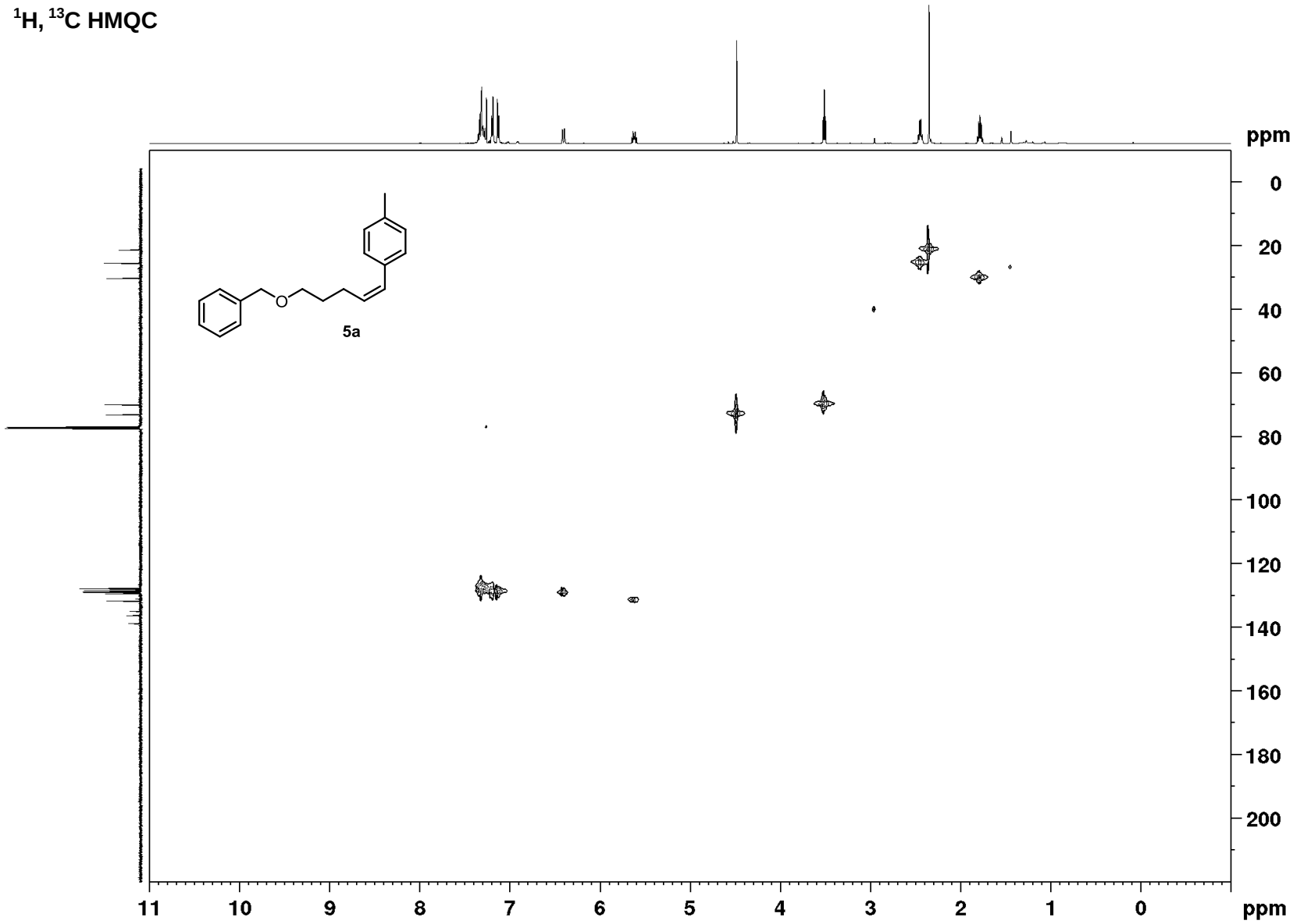
^{13}C DEPT NMR


131.5
129.2
128.8
128.7
128.3
127.6
127.4
72.9
69.8
30.0
25.3
21.1
O
5a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

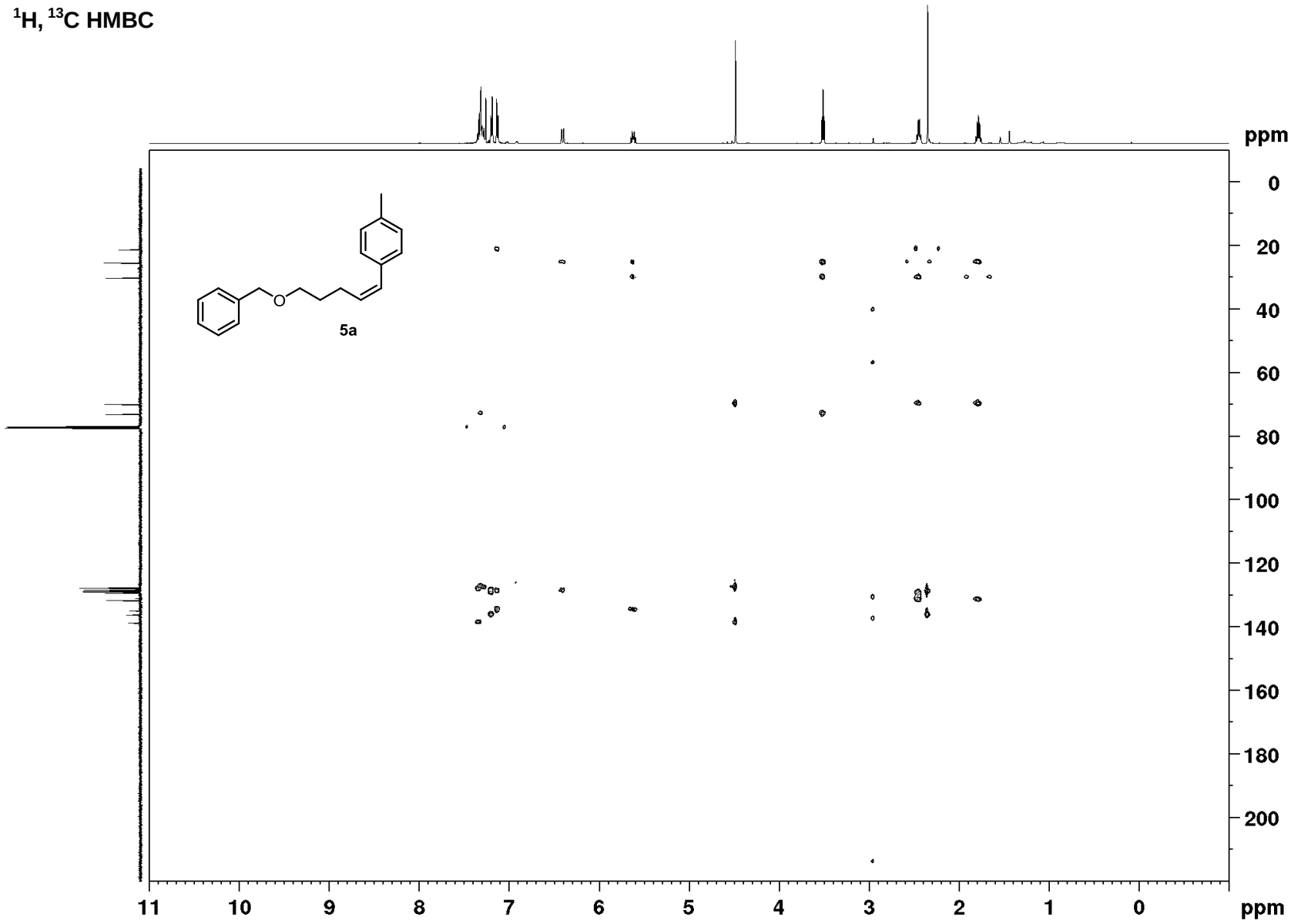
^{1}H, ^{1}H COSY



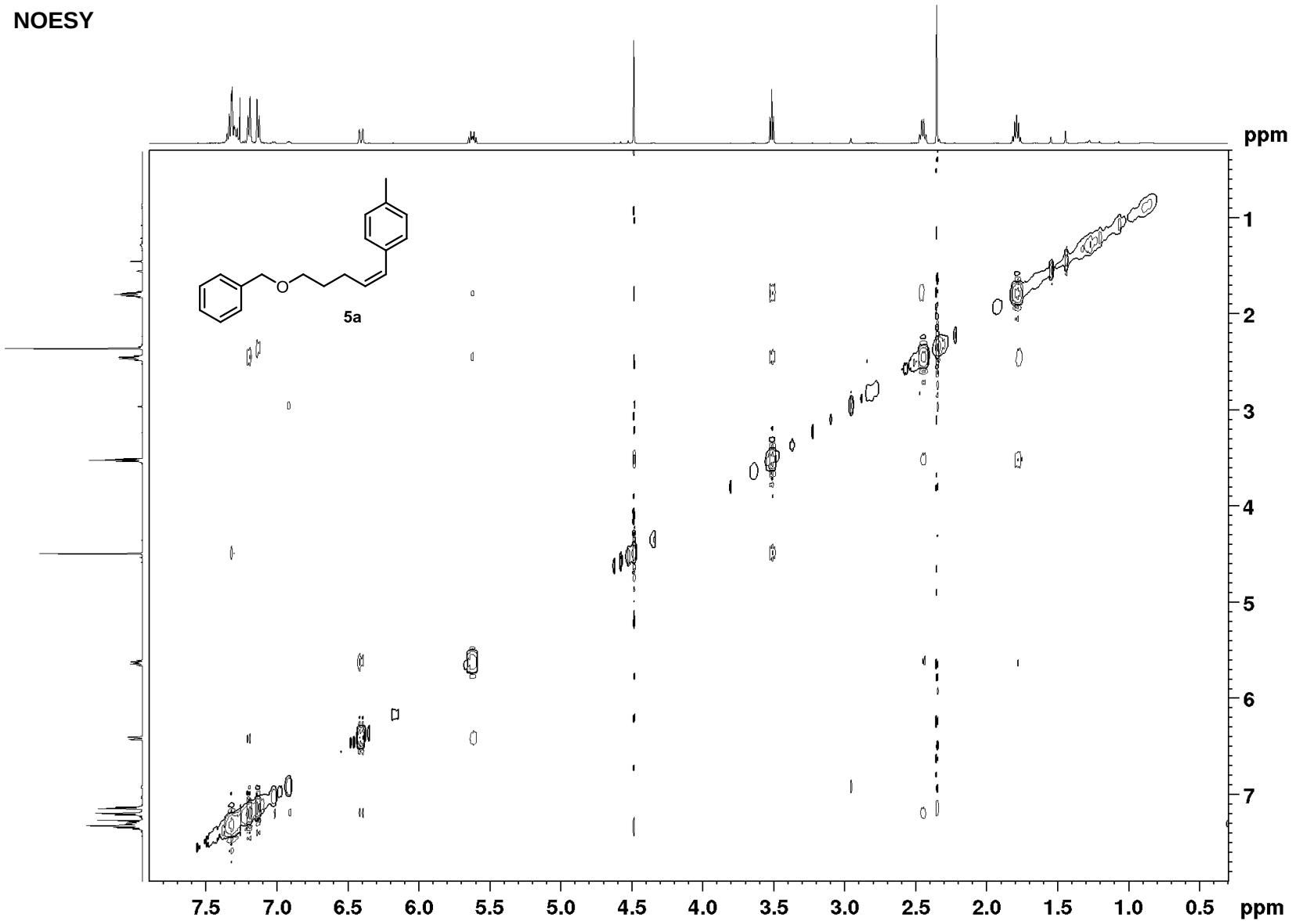
^{1}H, ^{13}C HMQC



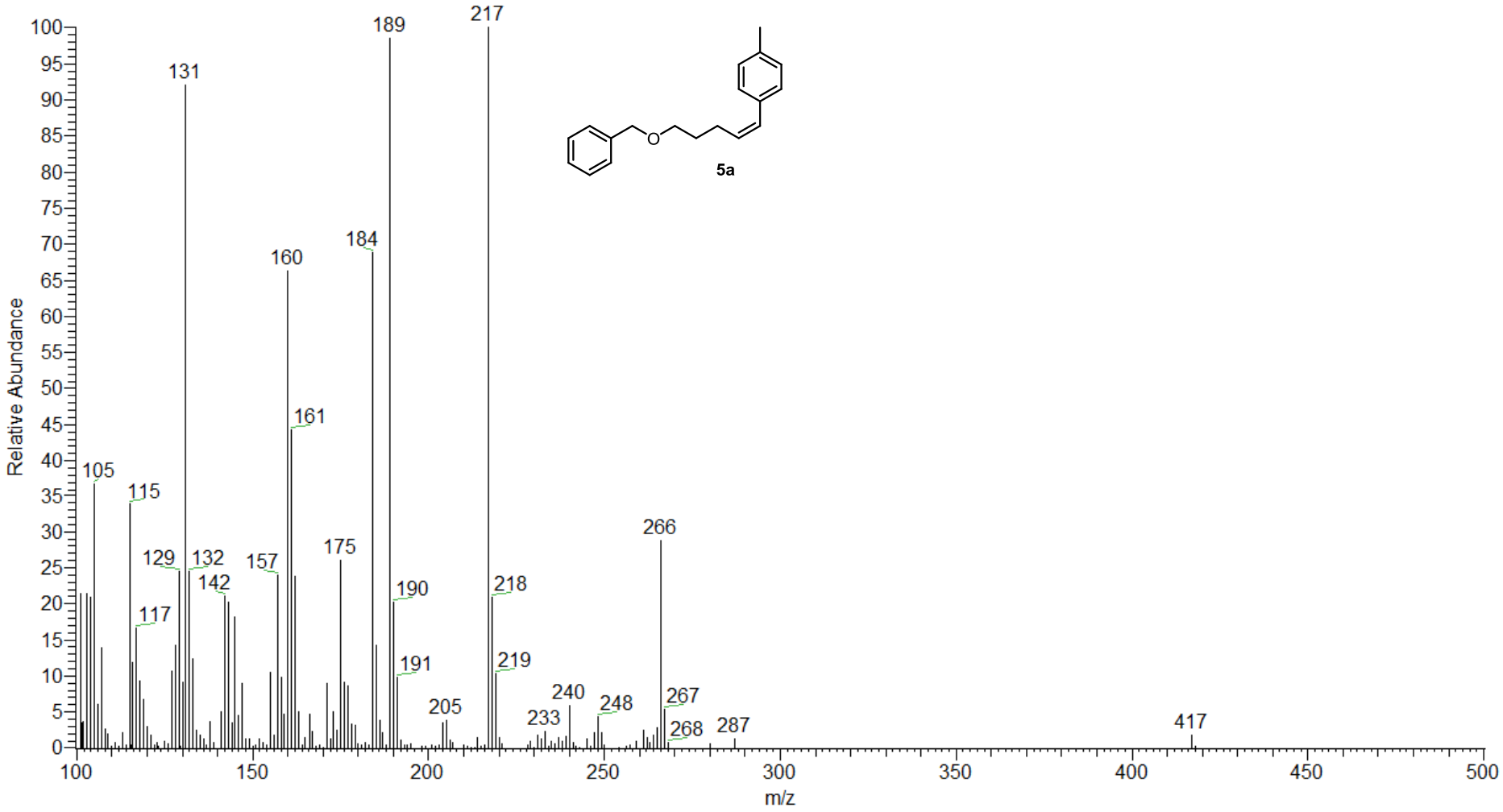
$^{1}H, ^{13}C$ HMBC



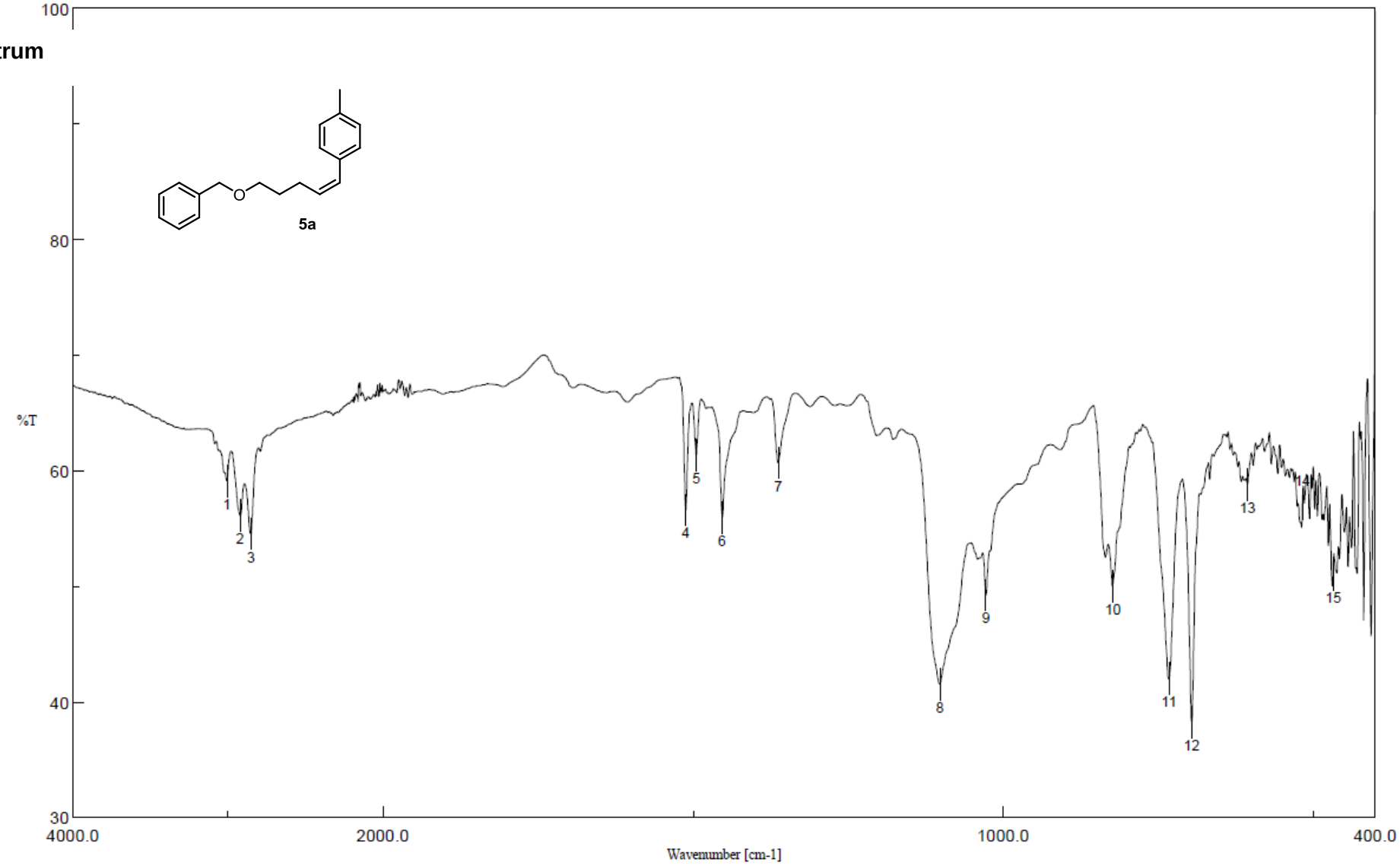
NOESY



mass spectrum

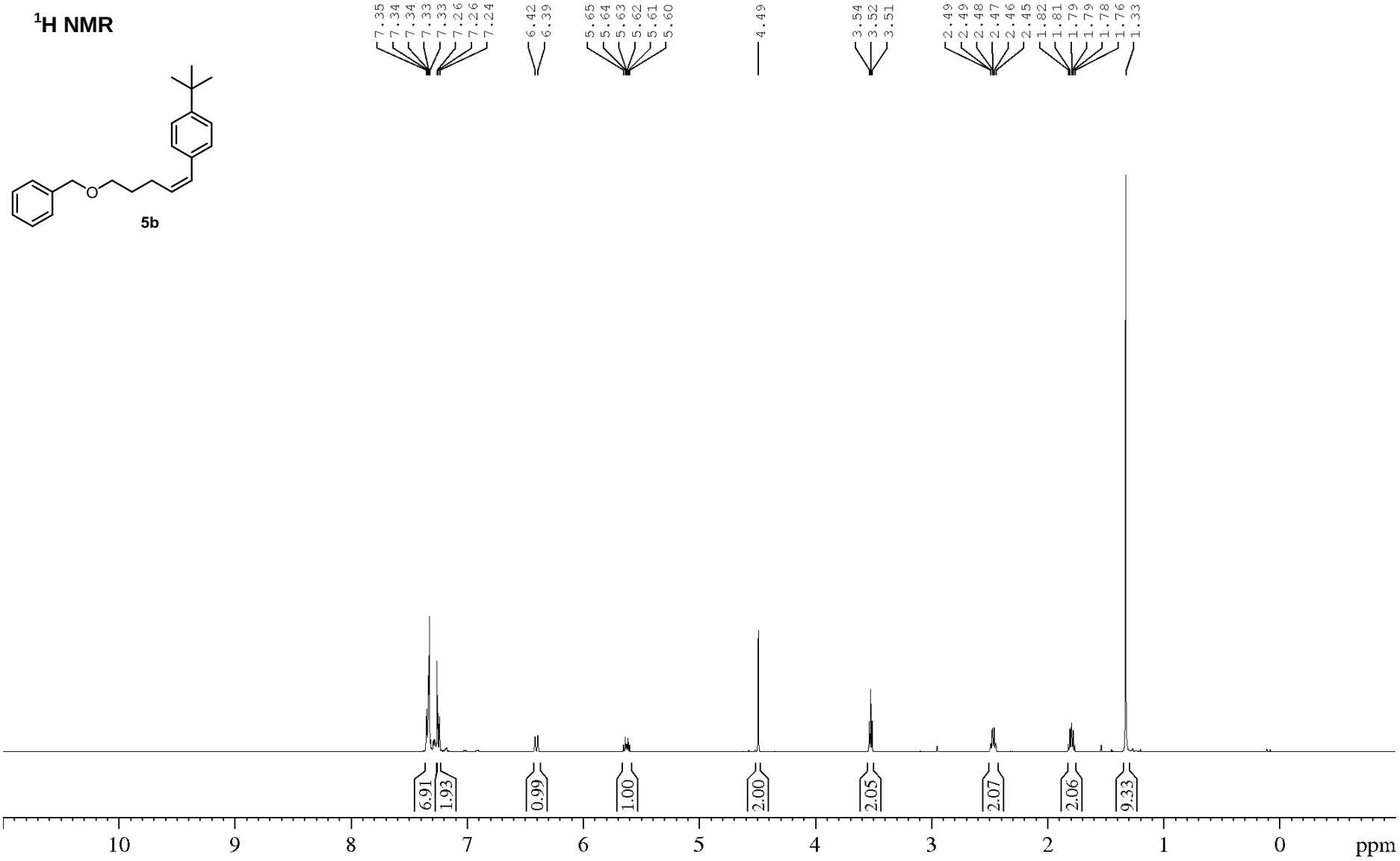


IR spectrum

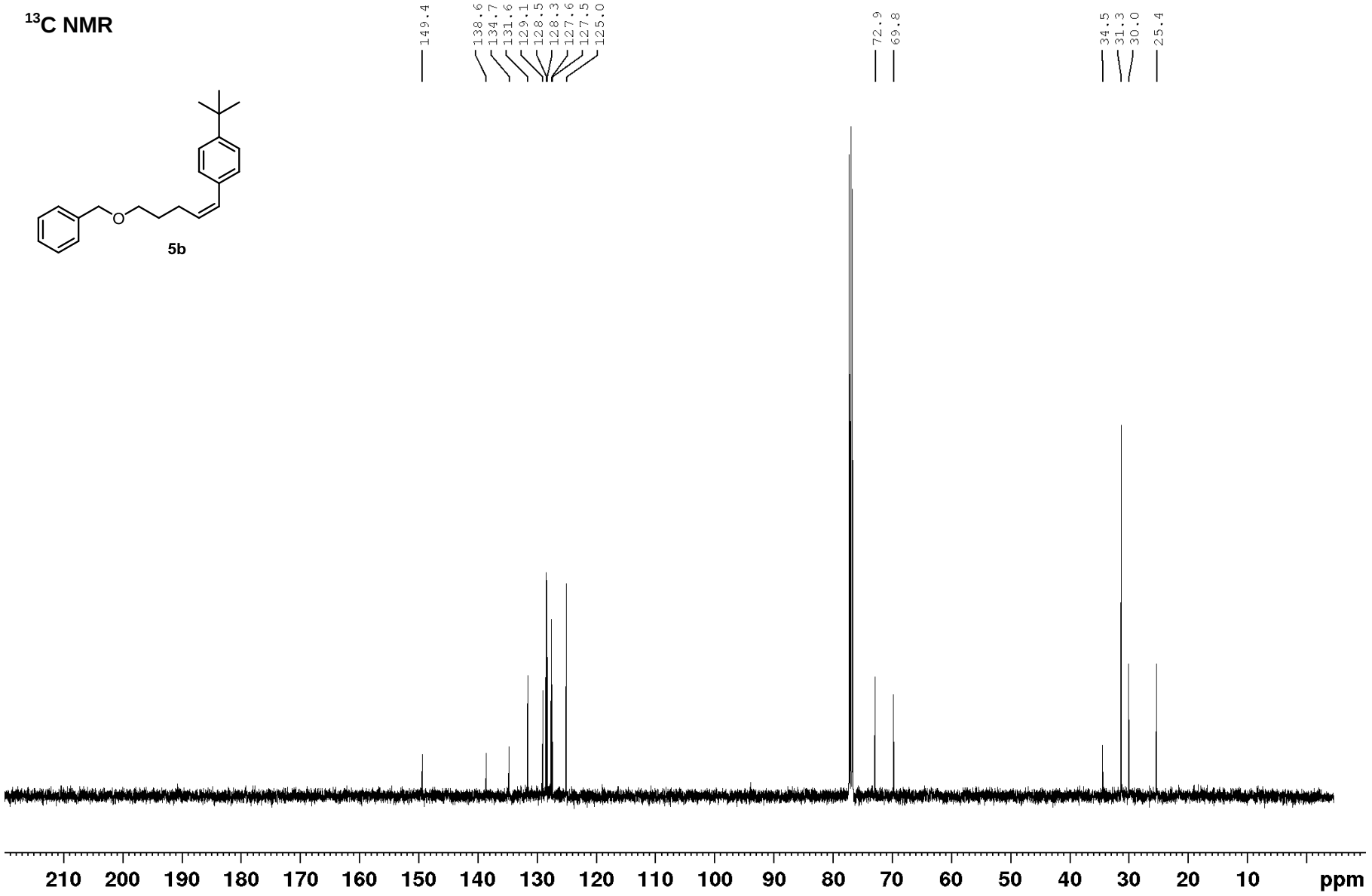

100
80
60
40
30
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
15
O
5a

^{1}H NMR

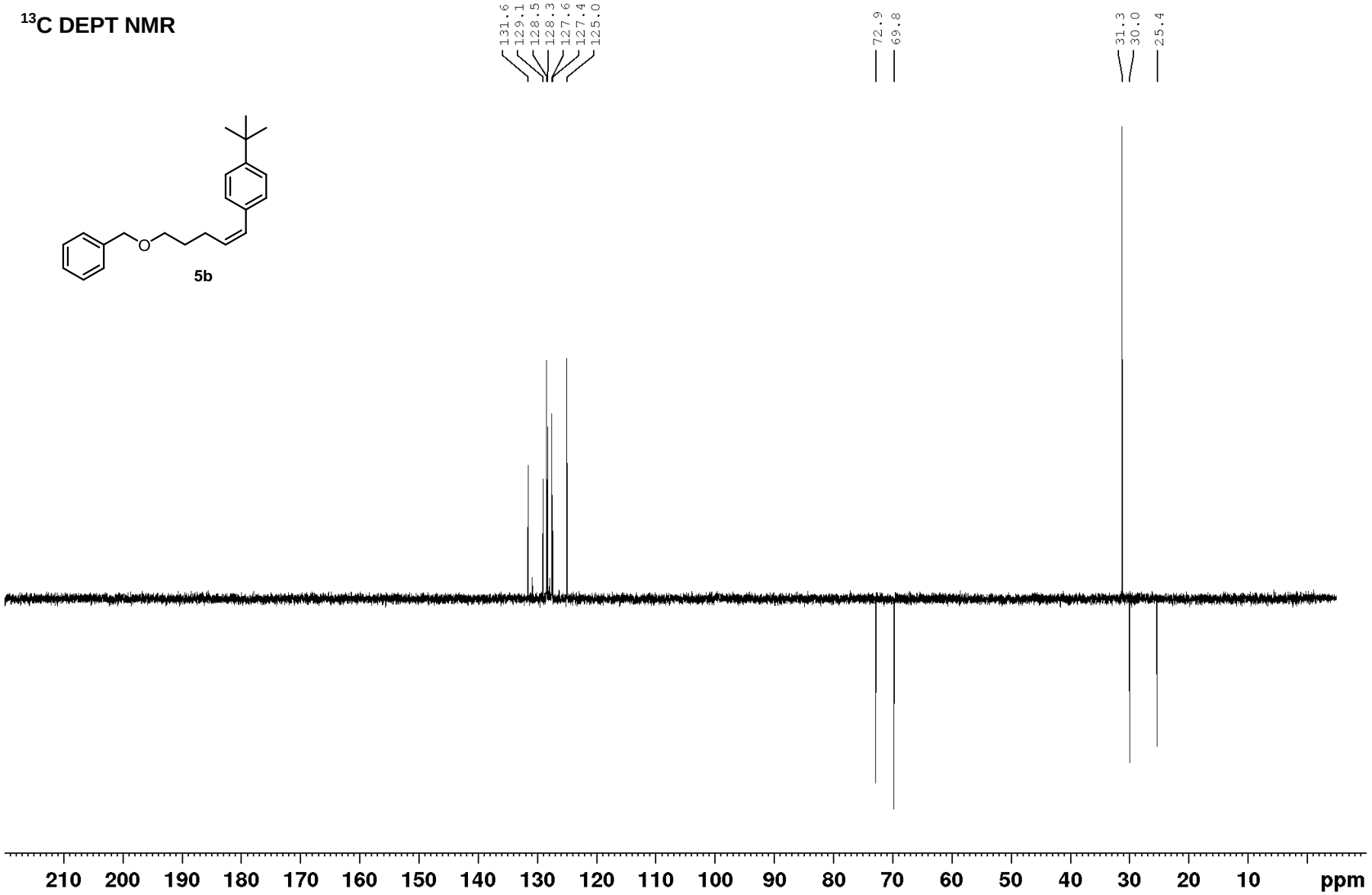
5b


7.35
7.34
7.34
7.33
7.33
7.26
7.26
7.24
6.42
6.39
5.65
5.64
5.63
5.62
5.61
5.60
4.49
3.54
3.52
3.51
2.49
2.49
2.48
2.47
2.46
2.45
1.82
1.81
1.79
1.79
1.78
1.76
1.33
6.91
1.93
0.99
1.00
2.00
2.05
2.07
2.06
9.33
10
9
8
7
6
5
4
3
2
1
0
ppm

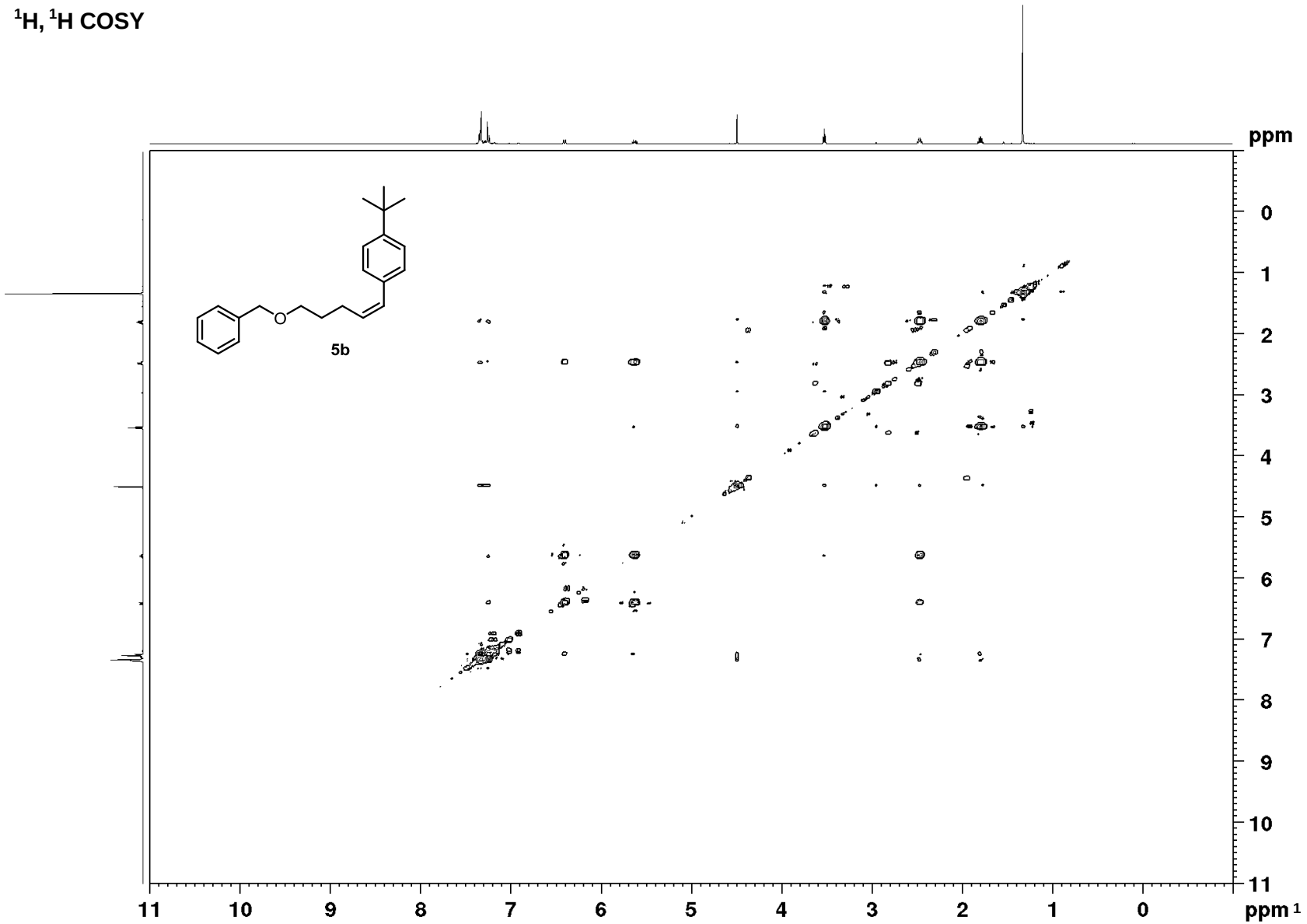
^{13}C NMR


149.4
138.6
134.7
131.6
129.1
128.5
128.3
127.6
127.5
125.0
72.9
69.8
34.5
31.3
30.0
25.4
O
5b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

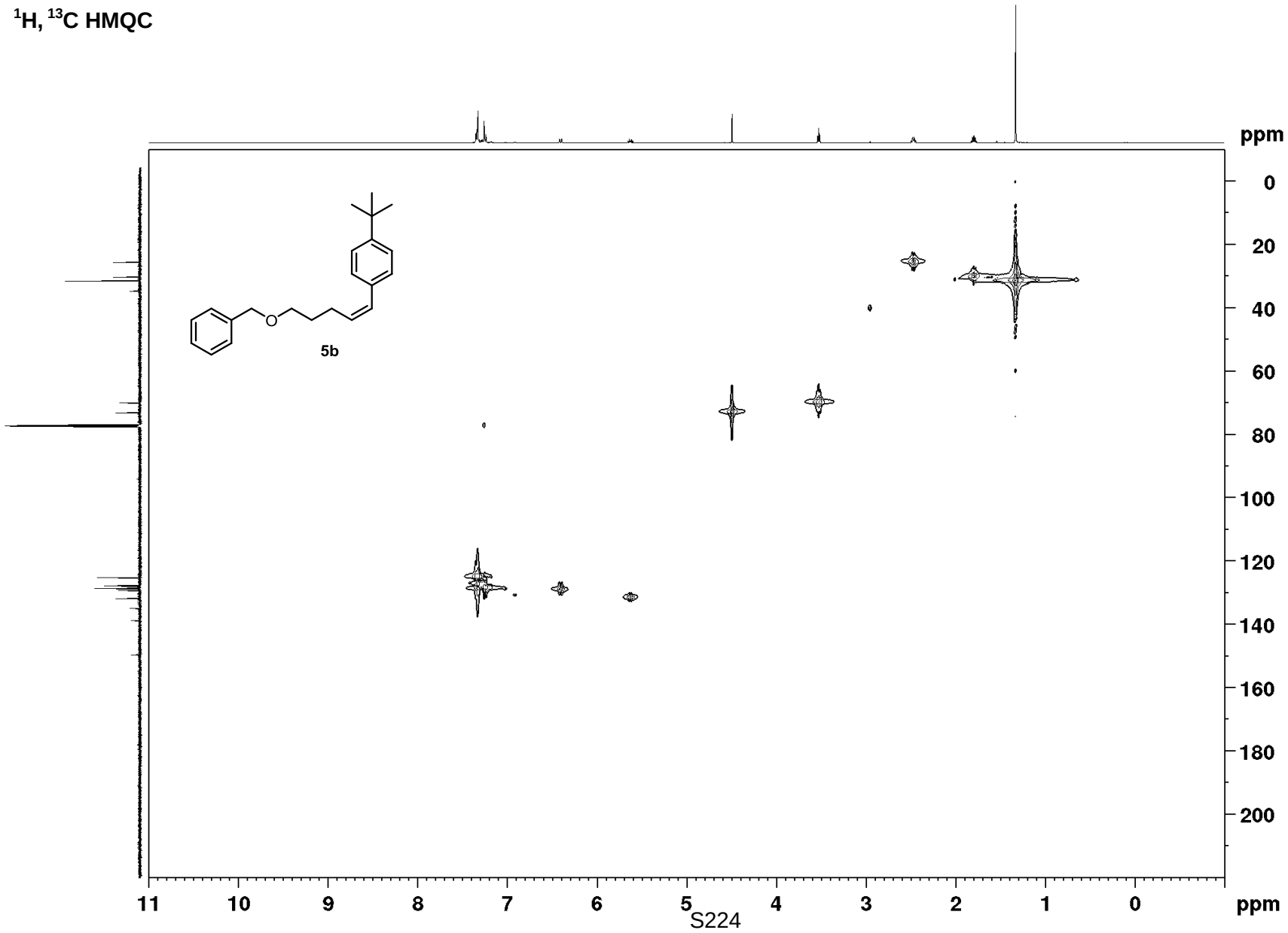
^{13}C DEPT NMR


131.6
129.1
128.5
128.3
127.6
127.4
125.0
72.9
69.8
31.3
30.0
25.4
O
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

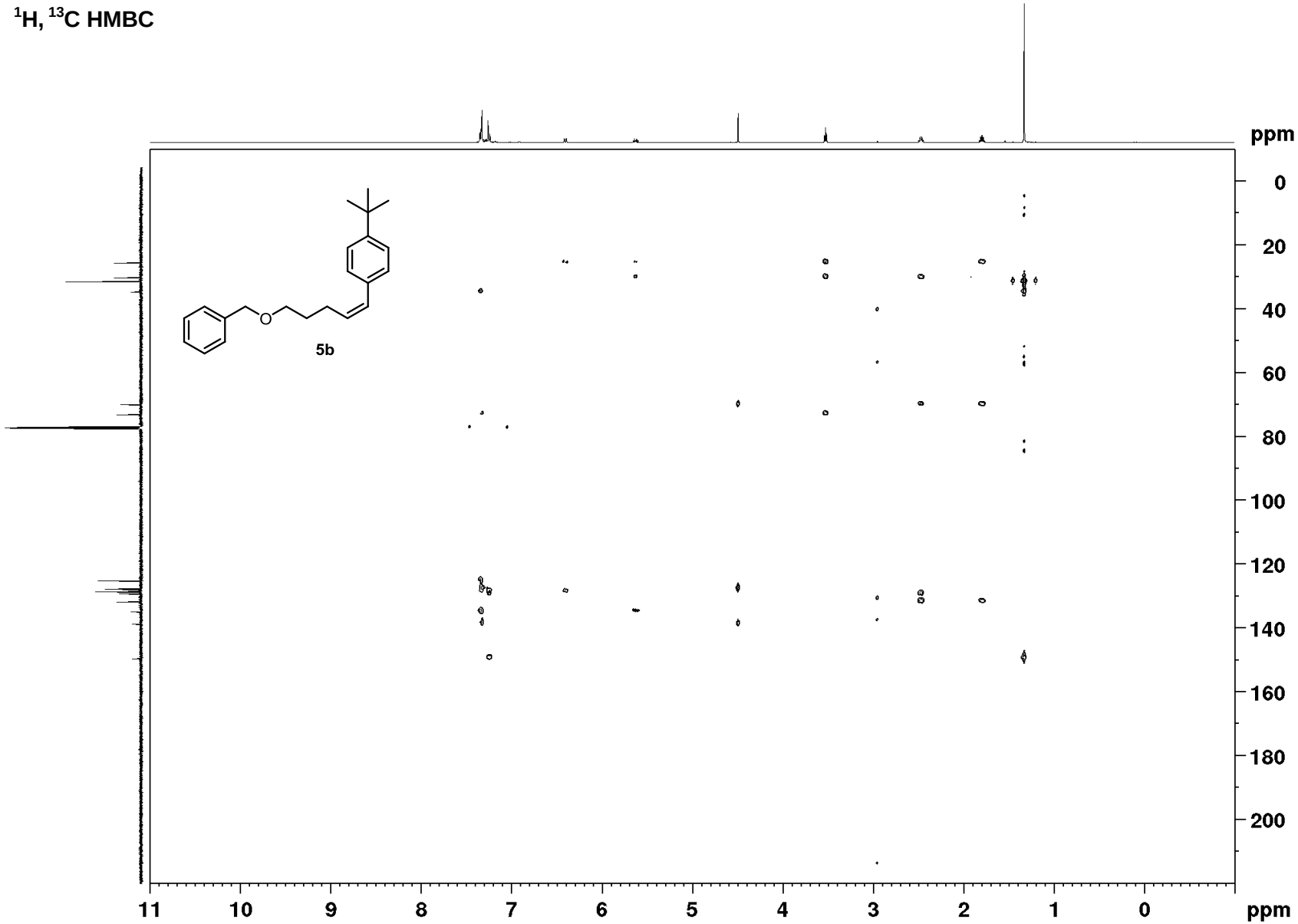
^{1}H, ^{1}H COSY



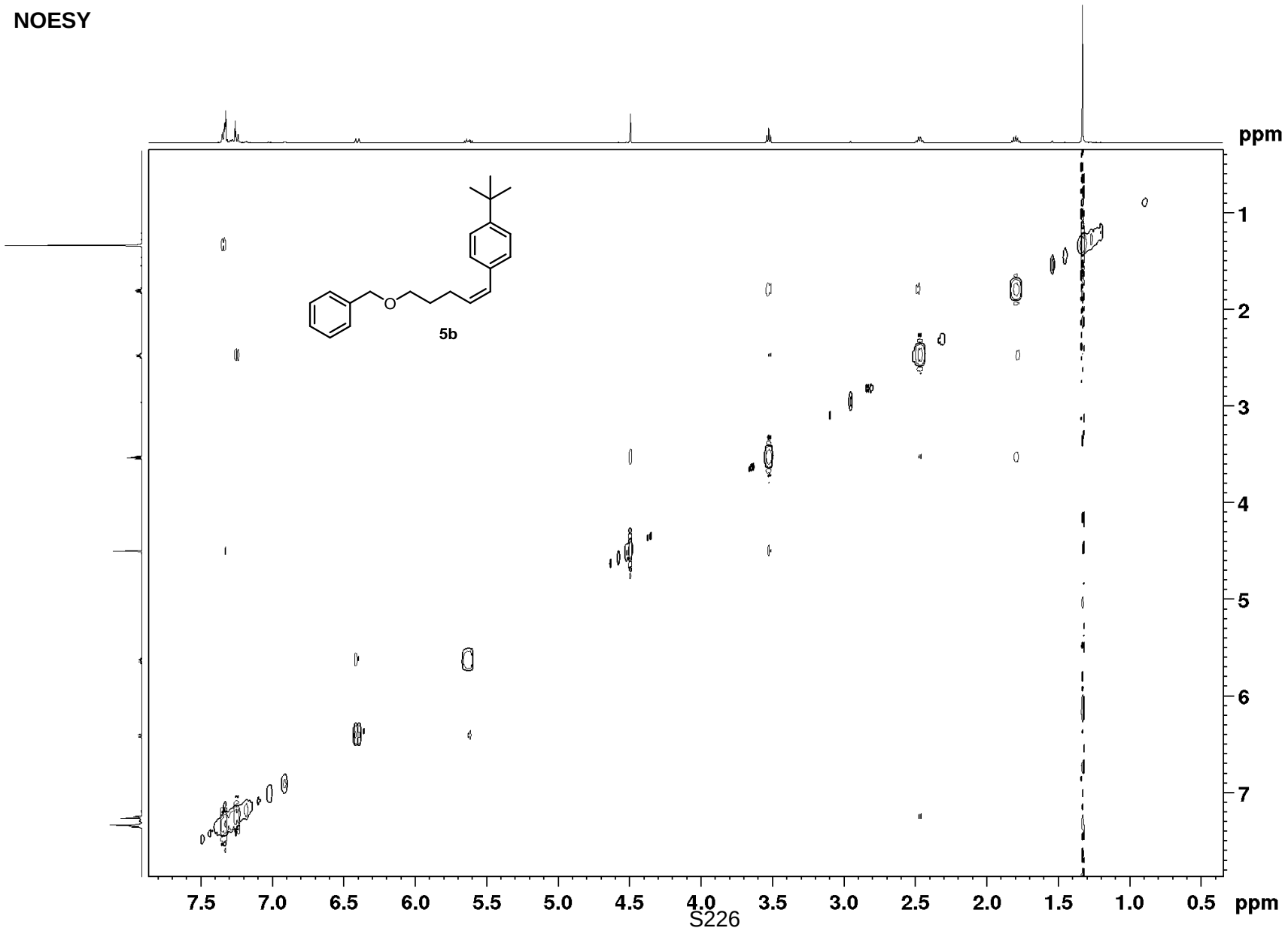
^{1}H, ^{13}C HMQC


ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm
H
O
5b

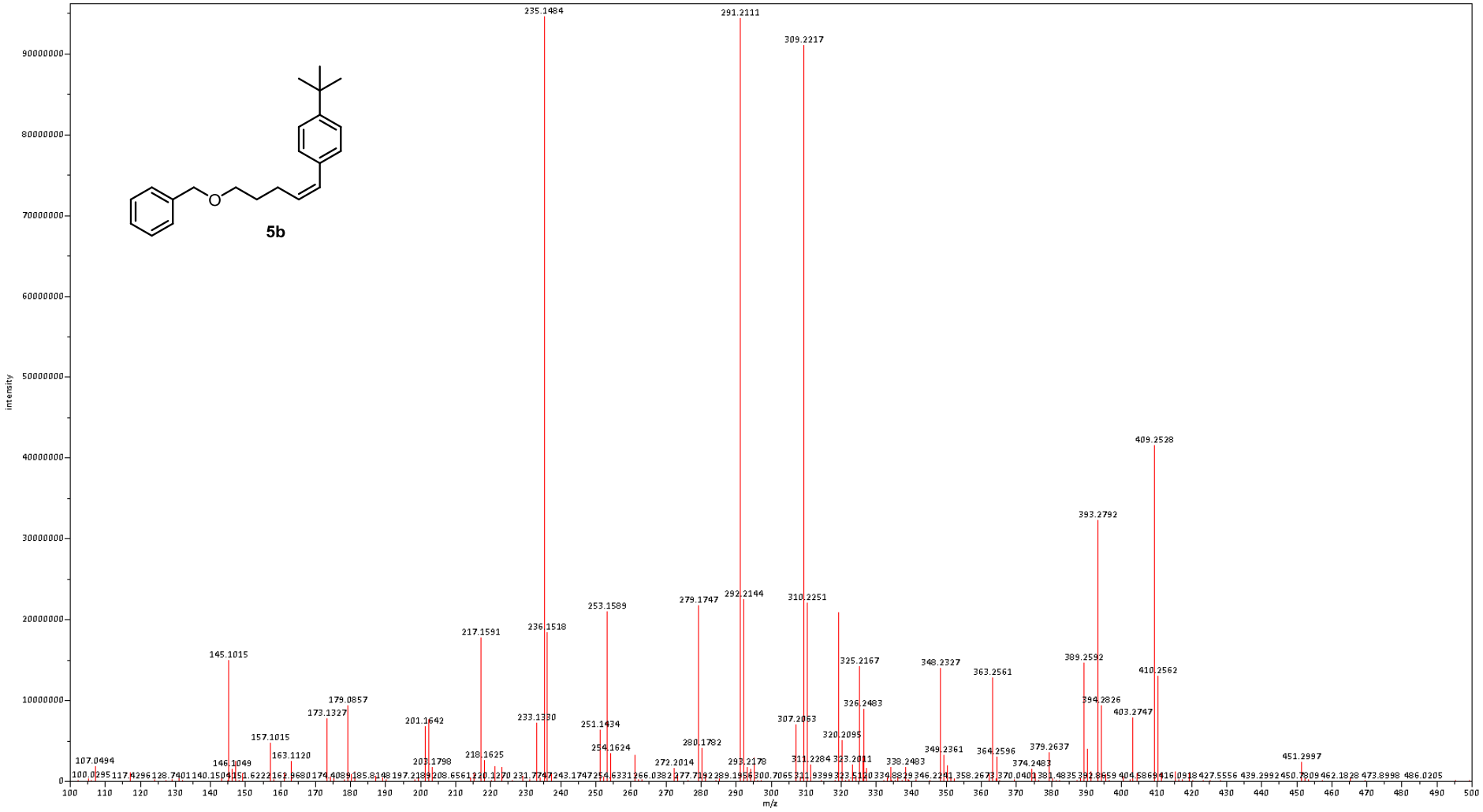
^{1}H, ^{13}C HMBC


ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm
O
5b

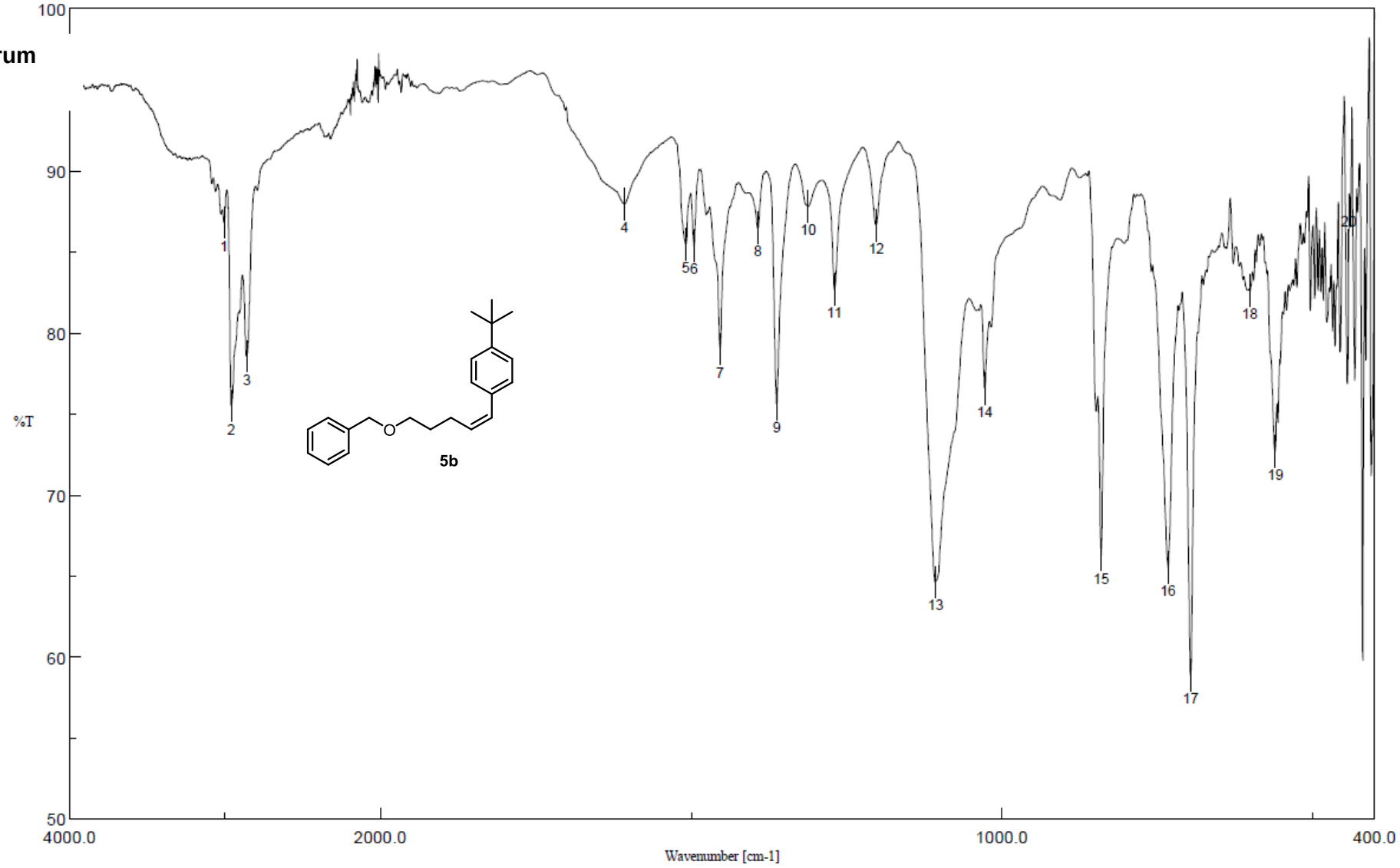
NOESY

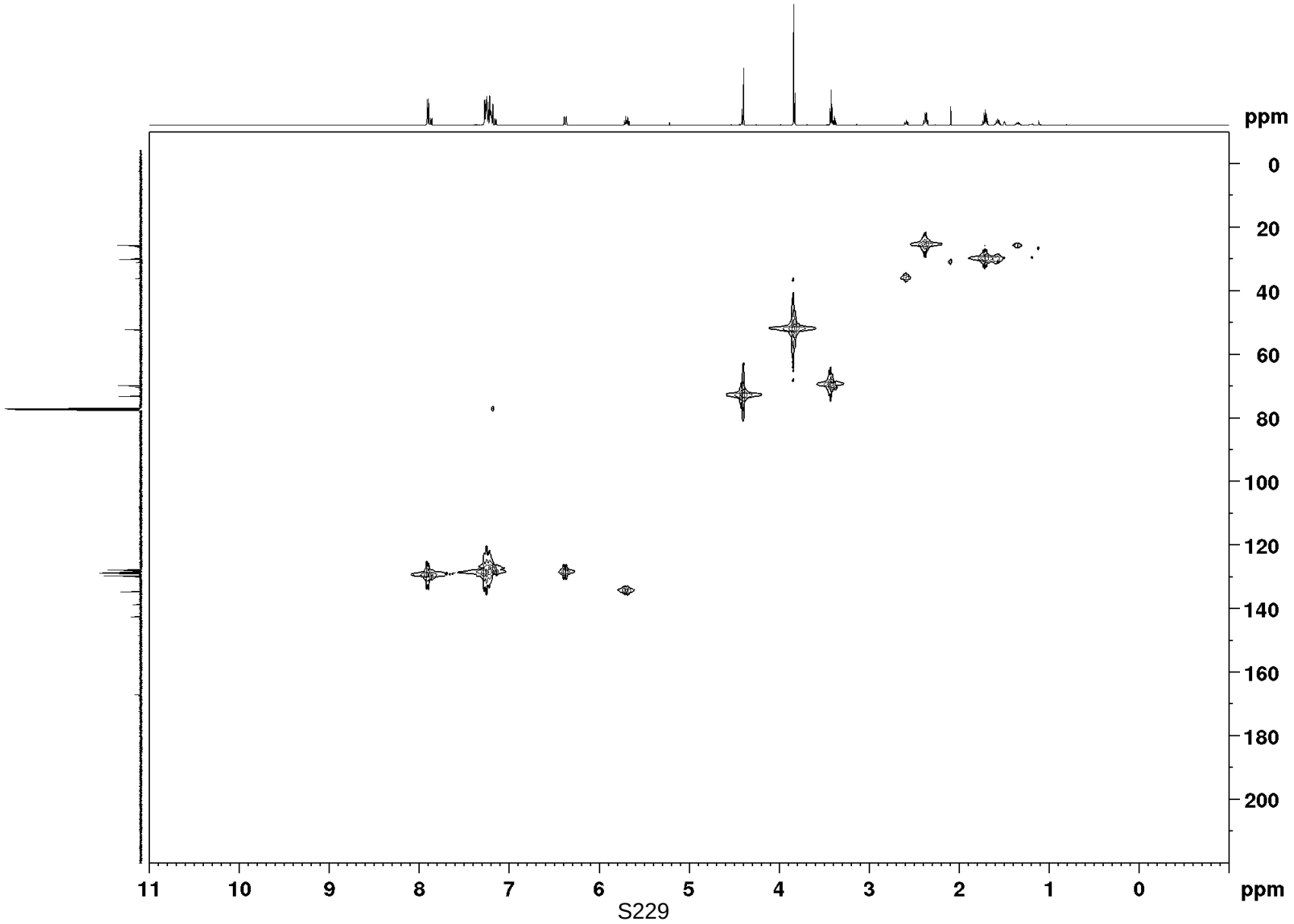


mass spectrum

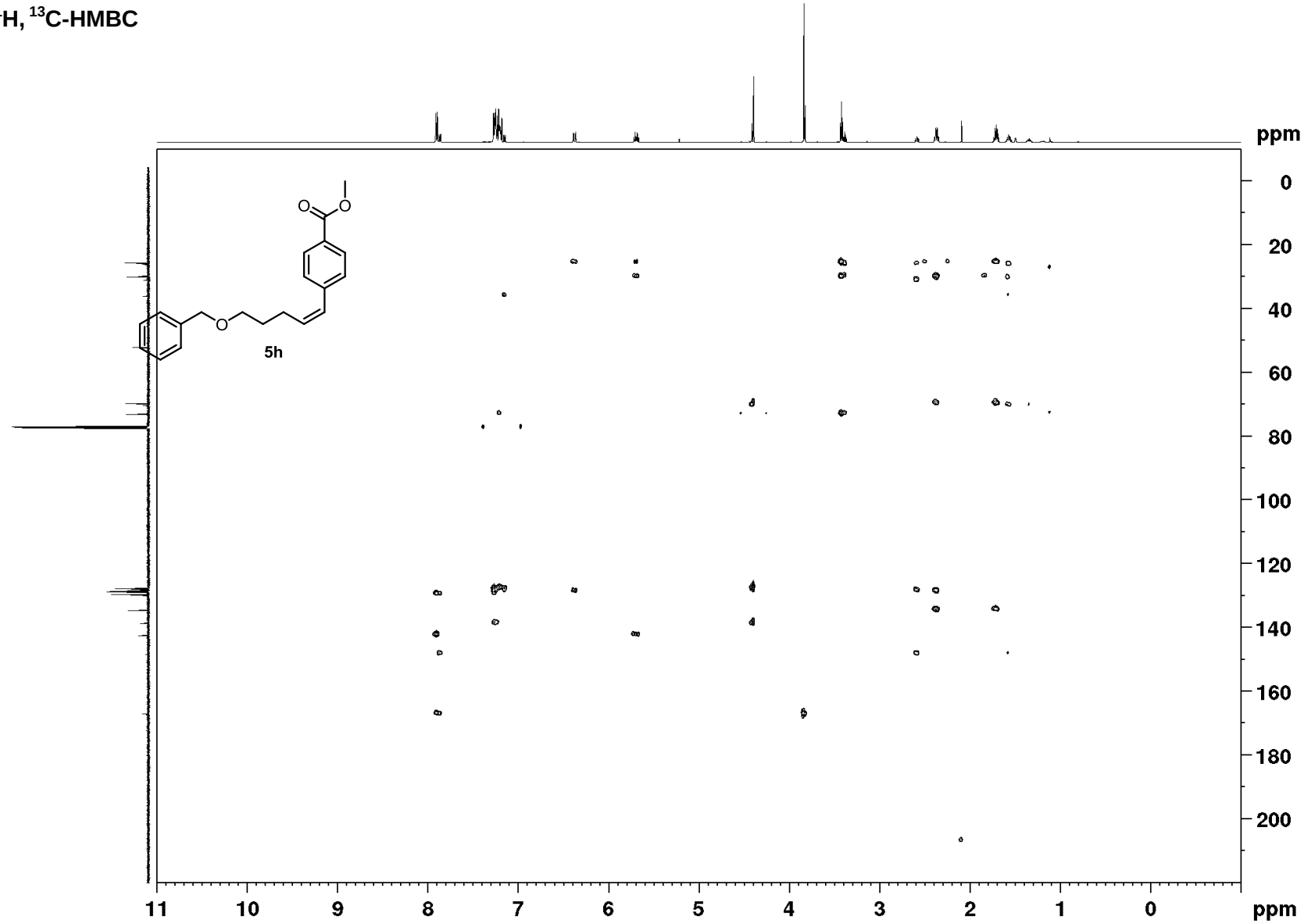


IR spectrum

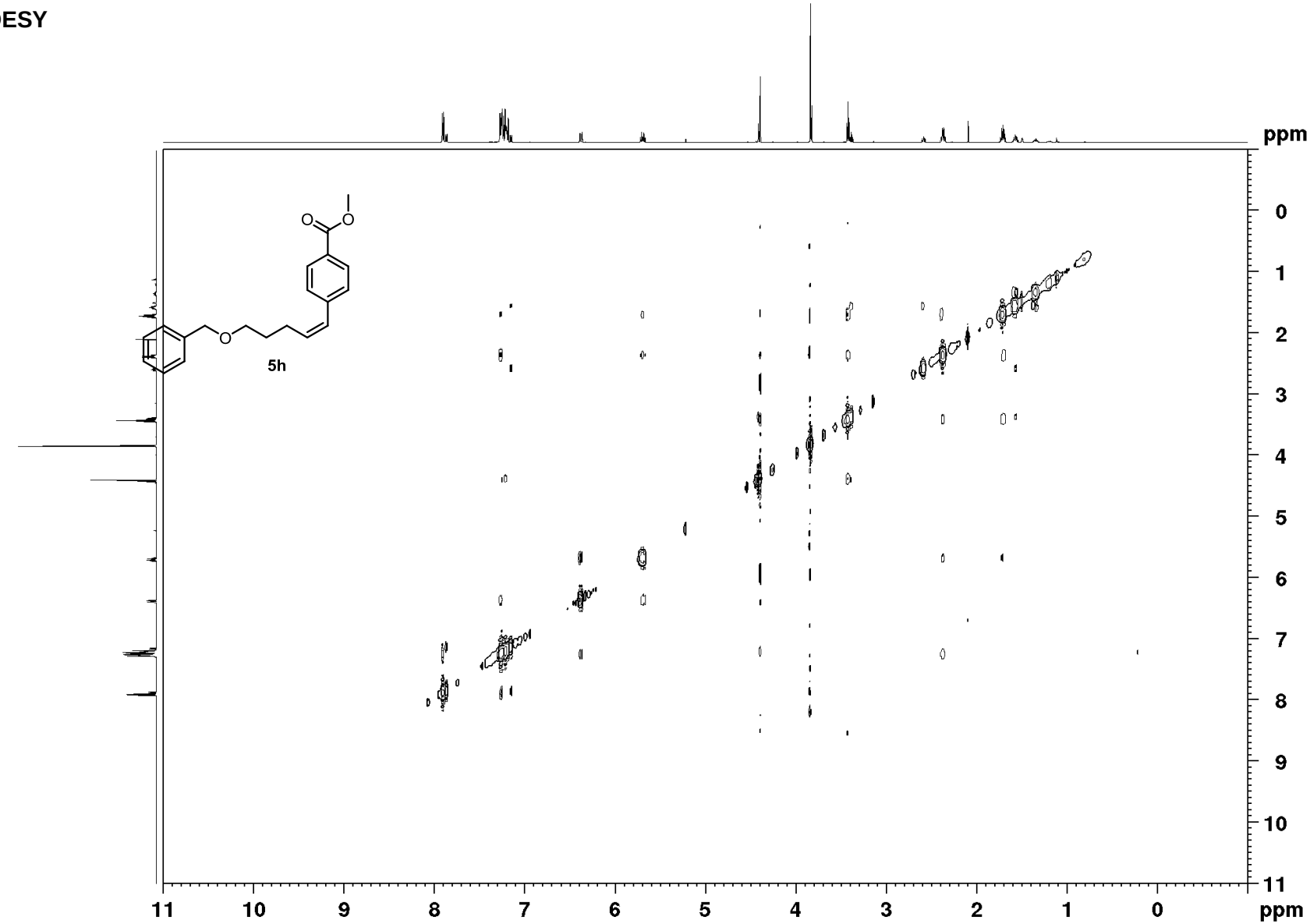

100
90
80
70
60
50
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
O
5b

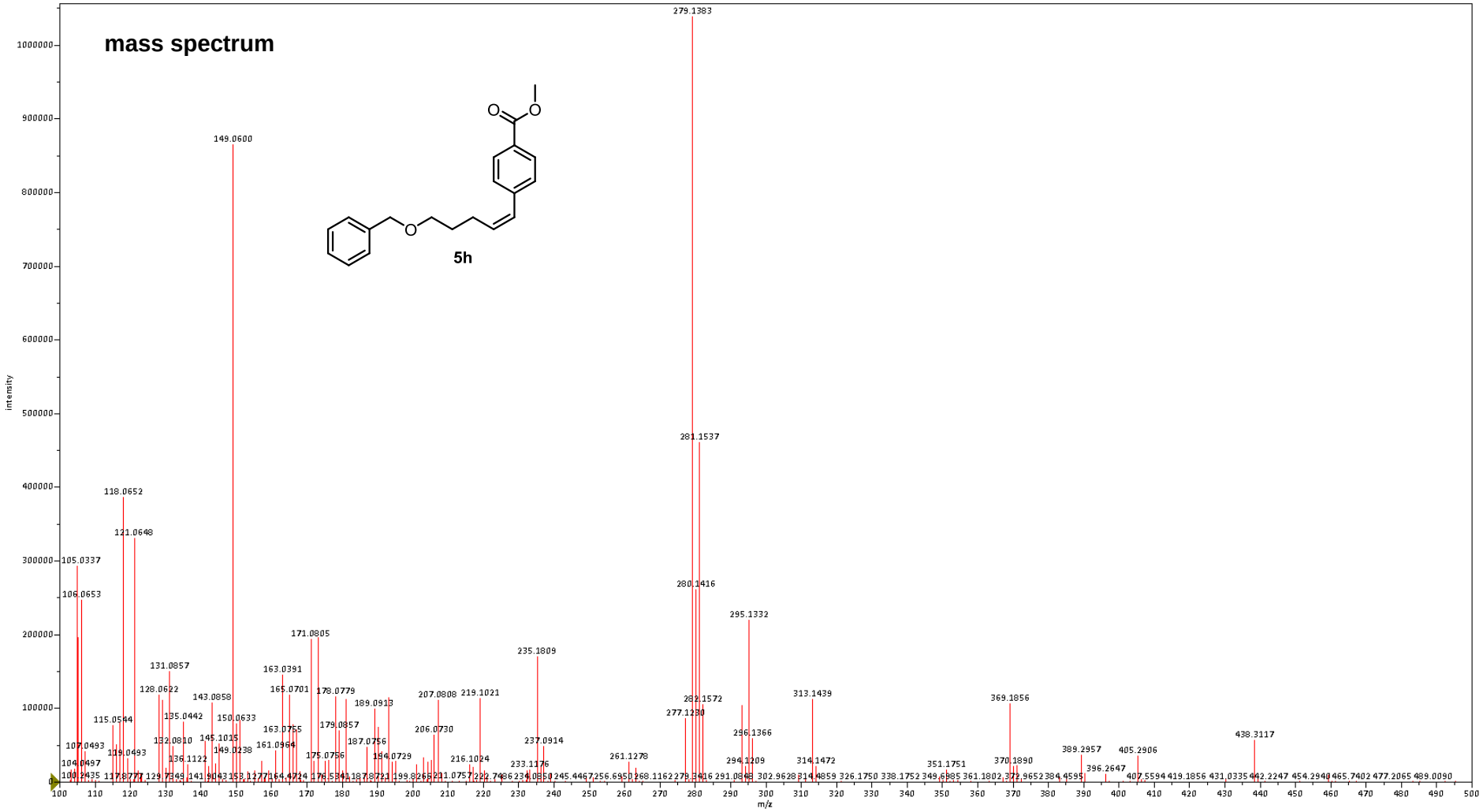

ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

$^{1}H, ^{13}C$-HMBC

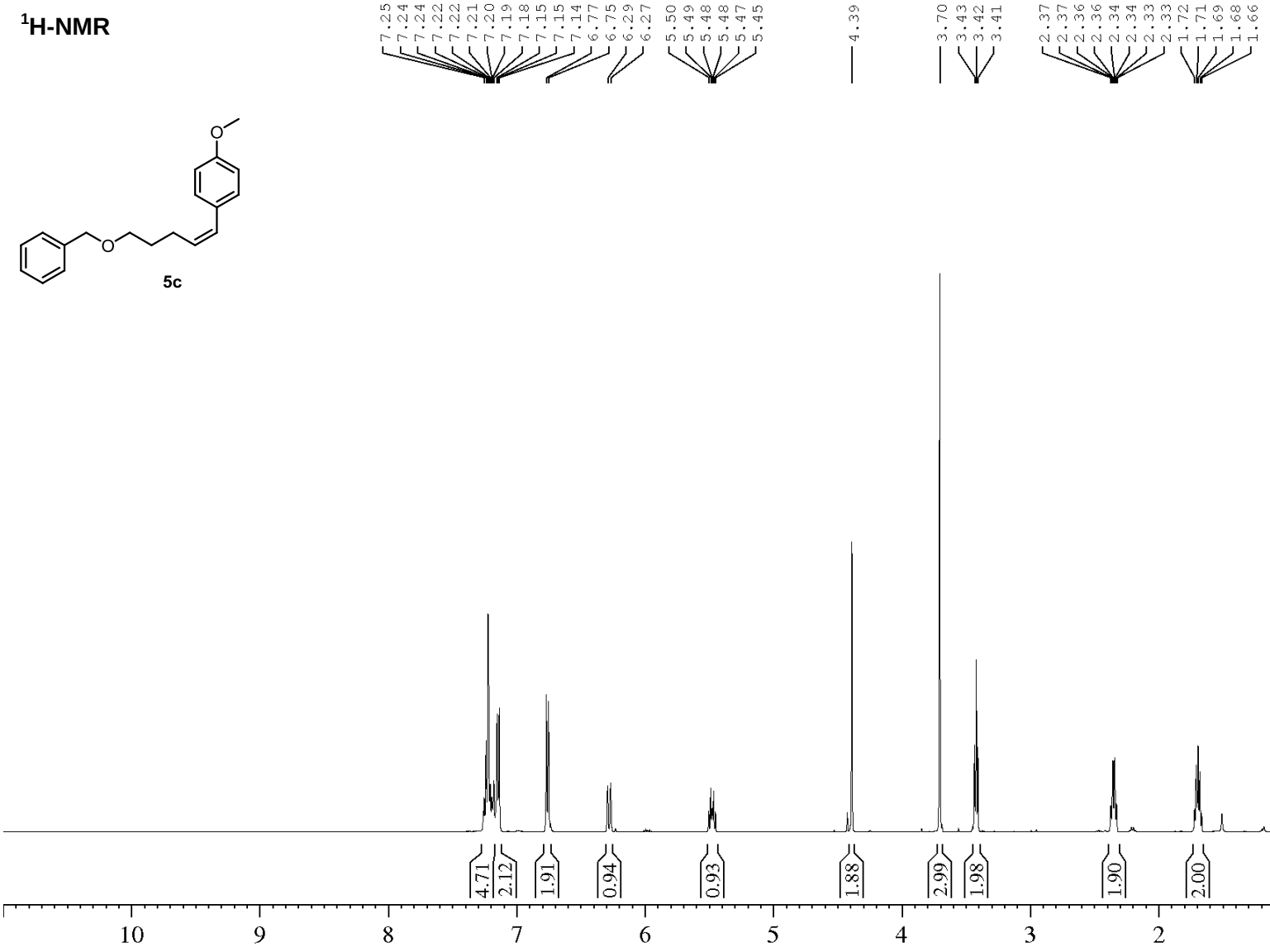


NOESY

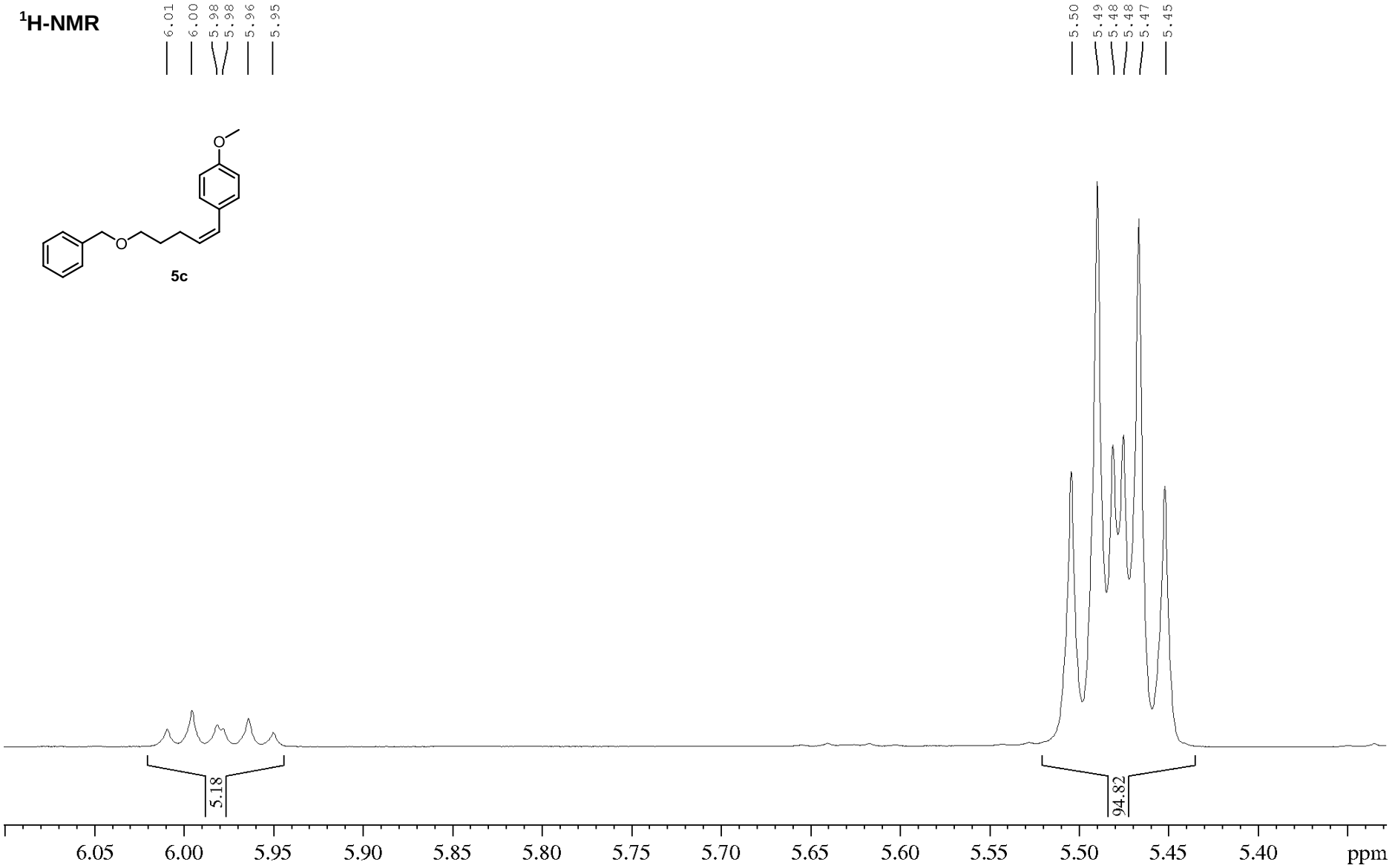



mass spectrum
5h
intensity
m/z
279.1383
149.0600
281.1537
118.0652
121.0648
105.0337
106.0653
280.1416
295.1332
171.0805
235.1809
131.0857
163.0391
165.0701
178.0779
189.0913
207.0808
219.1021
313.1439
369.1856
438.3117
277.1230
282.1572
256.1366
294.1209
314.1472
370.1890
389.2957
405.2906
396.2647
351.1751
261.1278
237.0914
233.1176
216.1024
206.0730
179.0857
187.0756
184.0729
175.0756
161.0964
163.0755
150.0633
143.0858
135.0442
128.0622
115.0544
107.0493
104.0497
119.0493
132.0810
136.1122
145.1015
149.0238

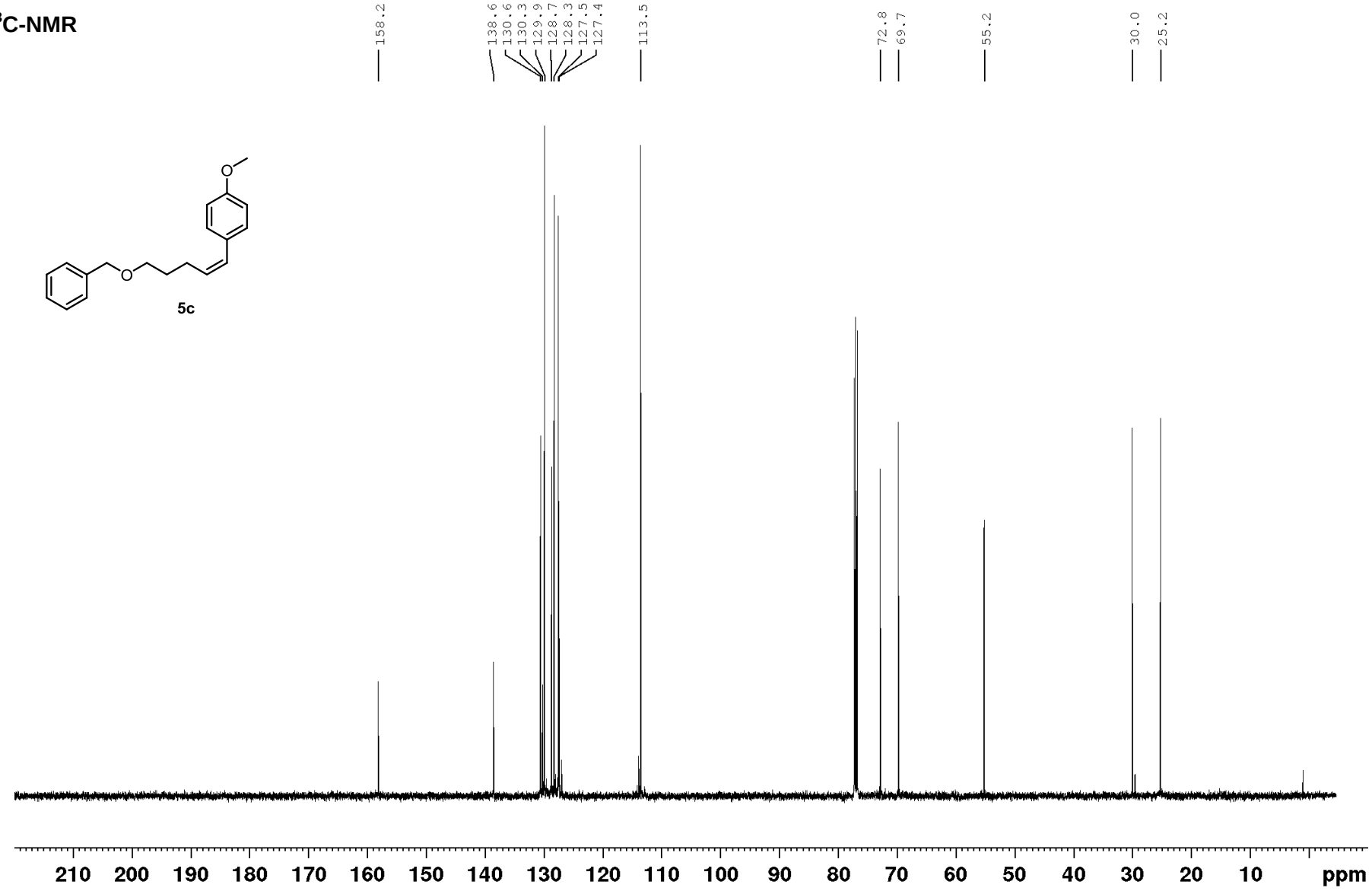
^{1}H-NMR


7.25
7.24
7.24
7.22
7.22
7.21
7.20
7.19
7.18
7.15
7.15
7.14
6.77
6.75
6.29
6.27
5.50
5.49
5.48
5.48
5.47
5.45
4.39
3.70
3.43
3.42
3.41
2.37
2.37
2.36
2.36
2.34
2.34
2.33
2.33
1.72
1.71
1.69
1.68
1.66
O
O
5c
4.71
2.12
1.91
0.94
0.93
1.88
2.99
1.98
1.90
2.00
10
9
8
7
6
5
4
3
2
1
0
ppm

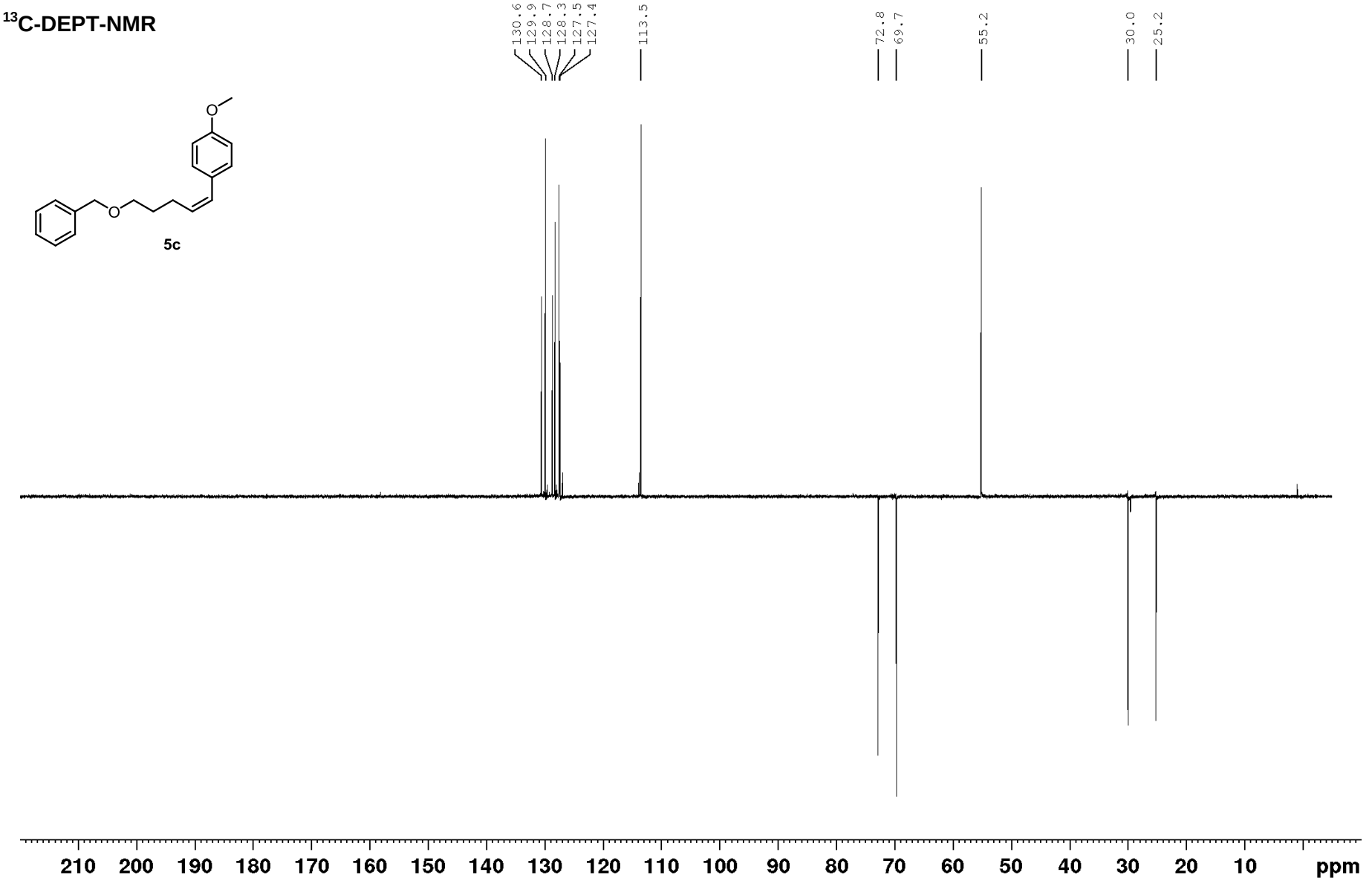
^{1}H-NMR


6.01
6.00
5.98
5.98
5.96
5.95
5.50
5.49
5.48
5.48
5.47
5.45
O
O
5c
5.18
94.82
6.05
6.00
5.95
5.90
5.85
5.80
5.75
5.70
5.65
5.60
5.55
5.50
5.45
5.40
ppm

^{13}C-NMR

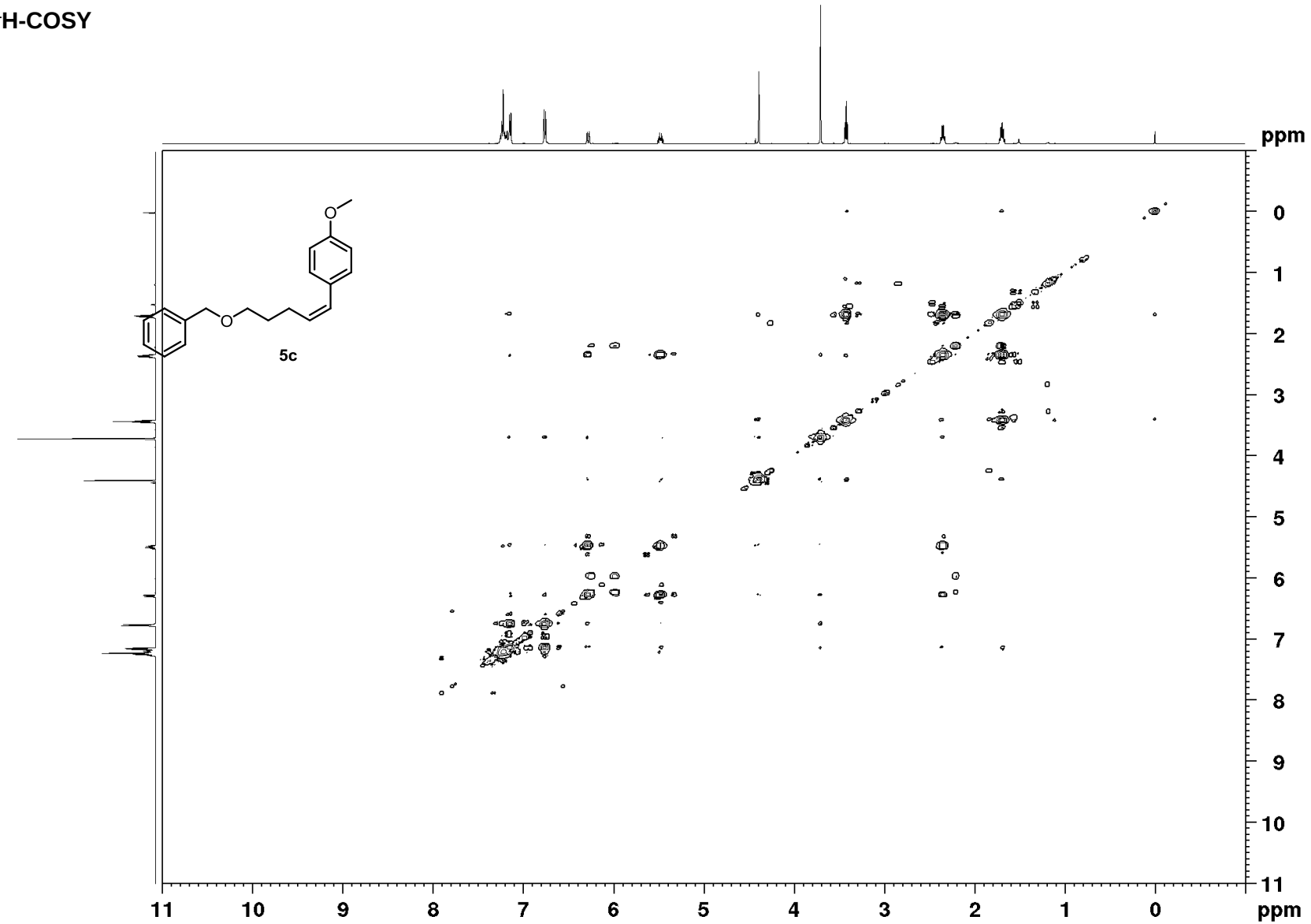

158.2
138.6
130.6
130.3
129.9
128.7
128.3
127.5
127.4
113.5
72.8
69.7
55.2
30.0
25.2
O
O
5c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C-DEPT-NMR

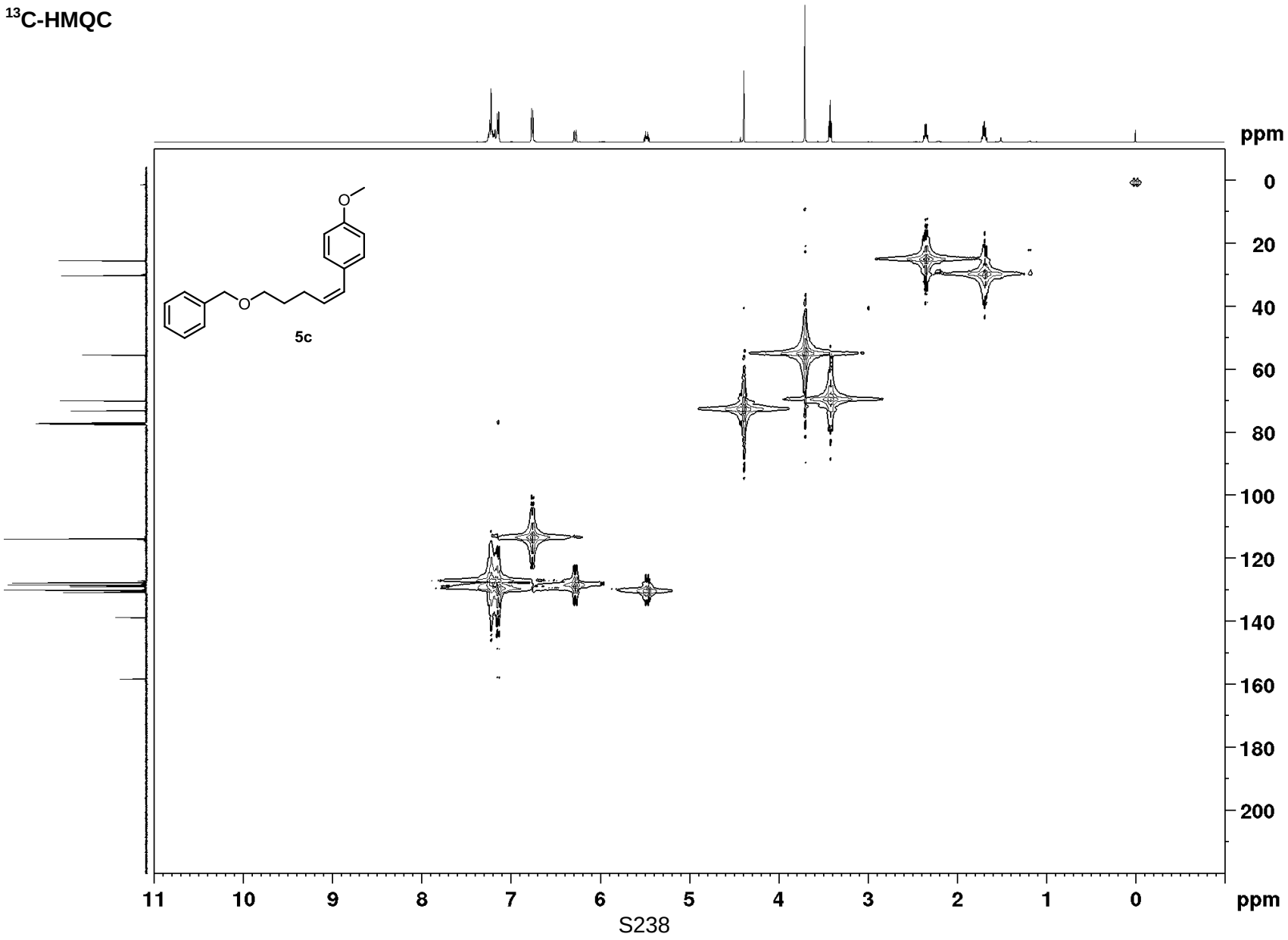


5c

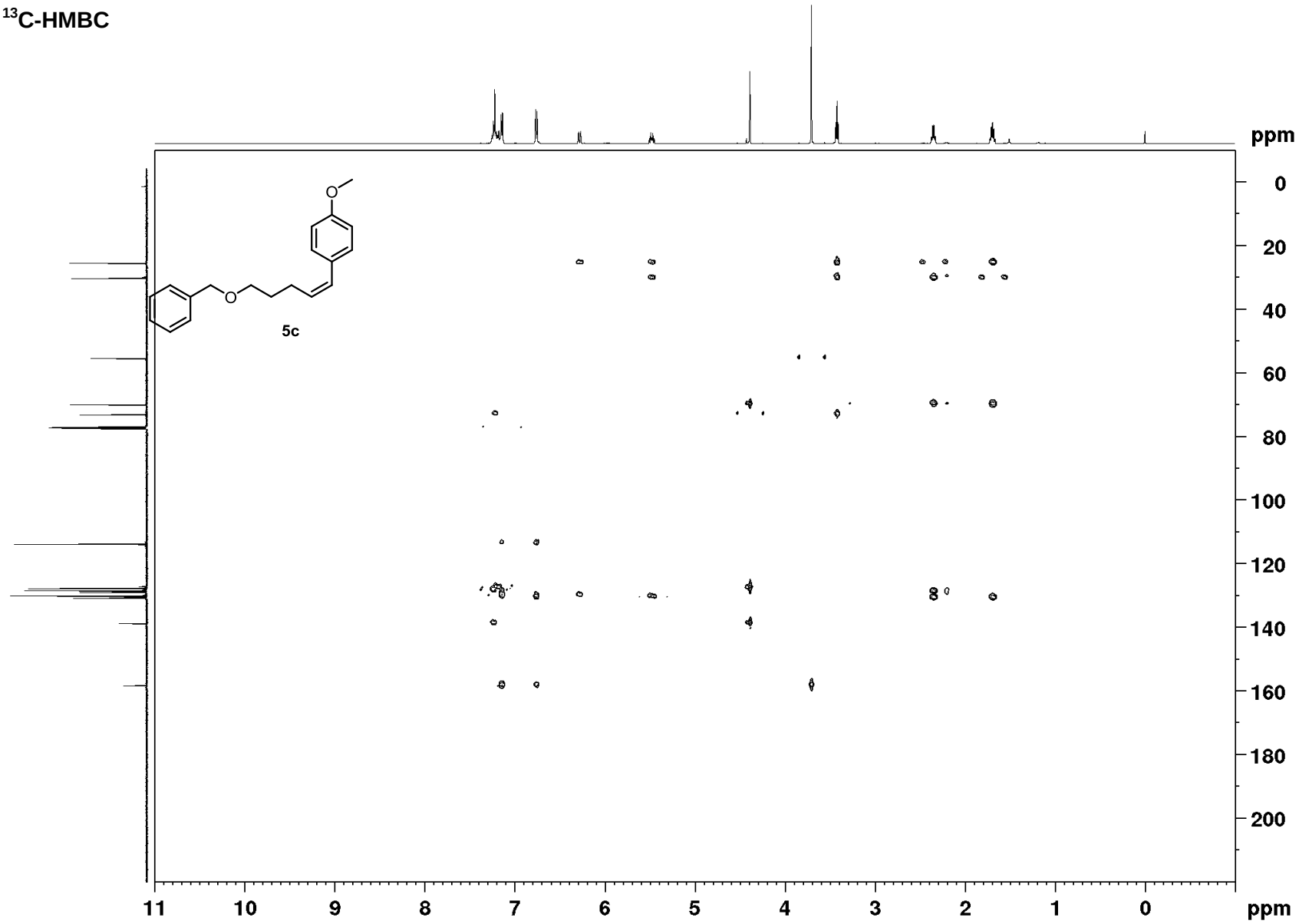
^{1}H, ^{1}H-COSY



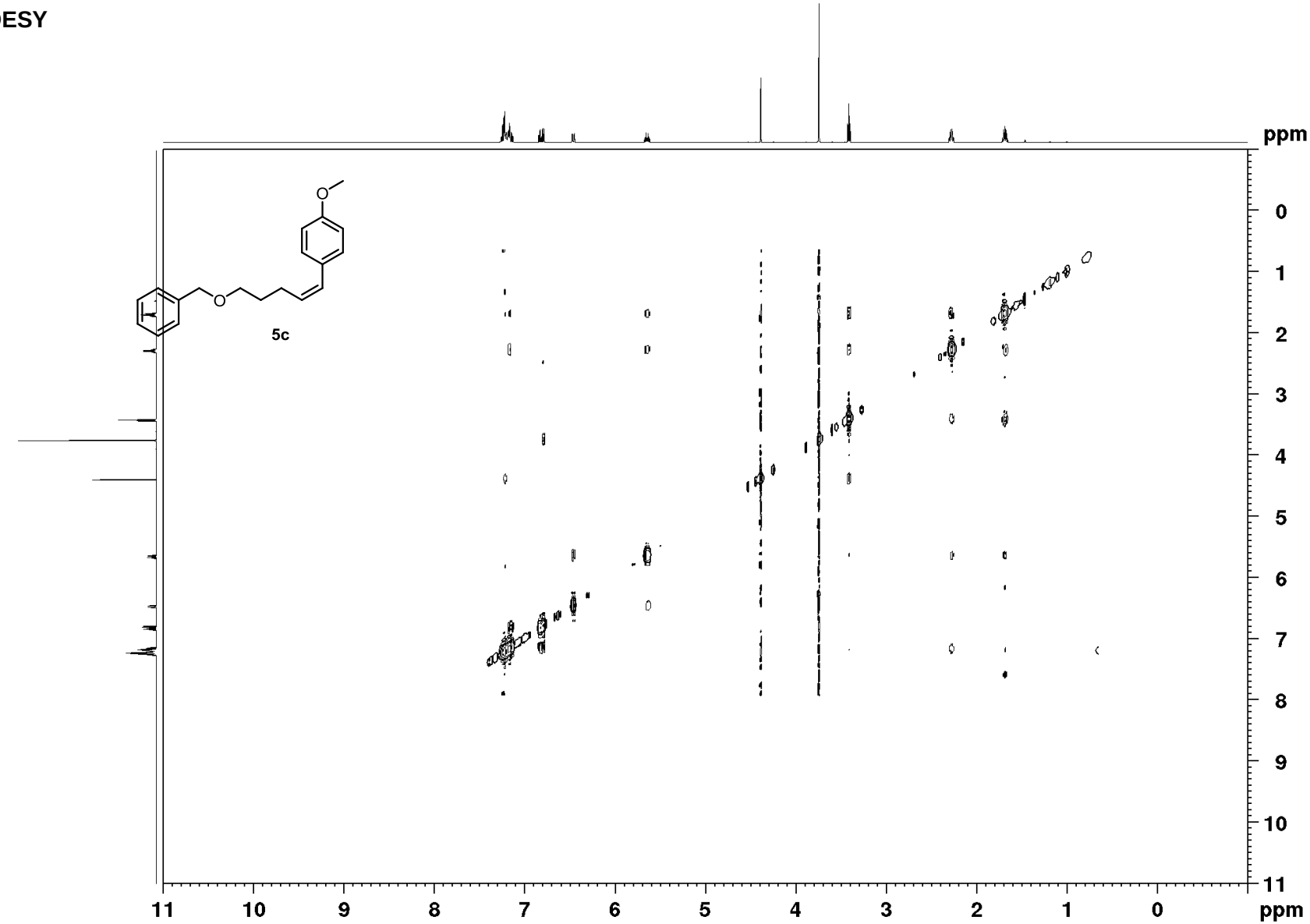
^{1}H, ^{13}C-HMQC



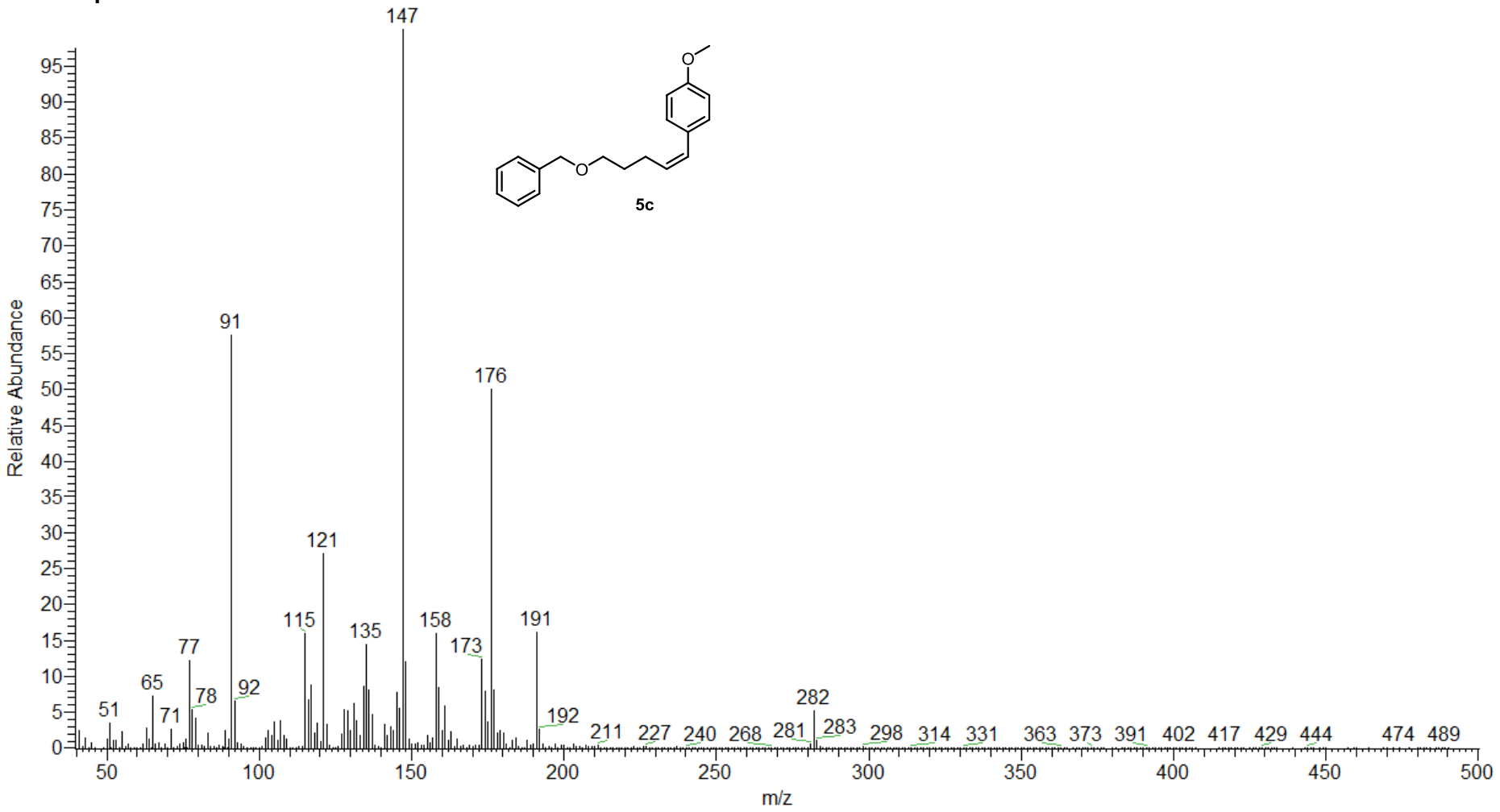
^{1}H, ^{13}C-HMBC

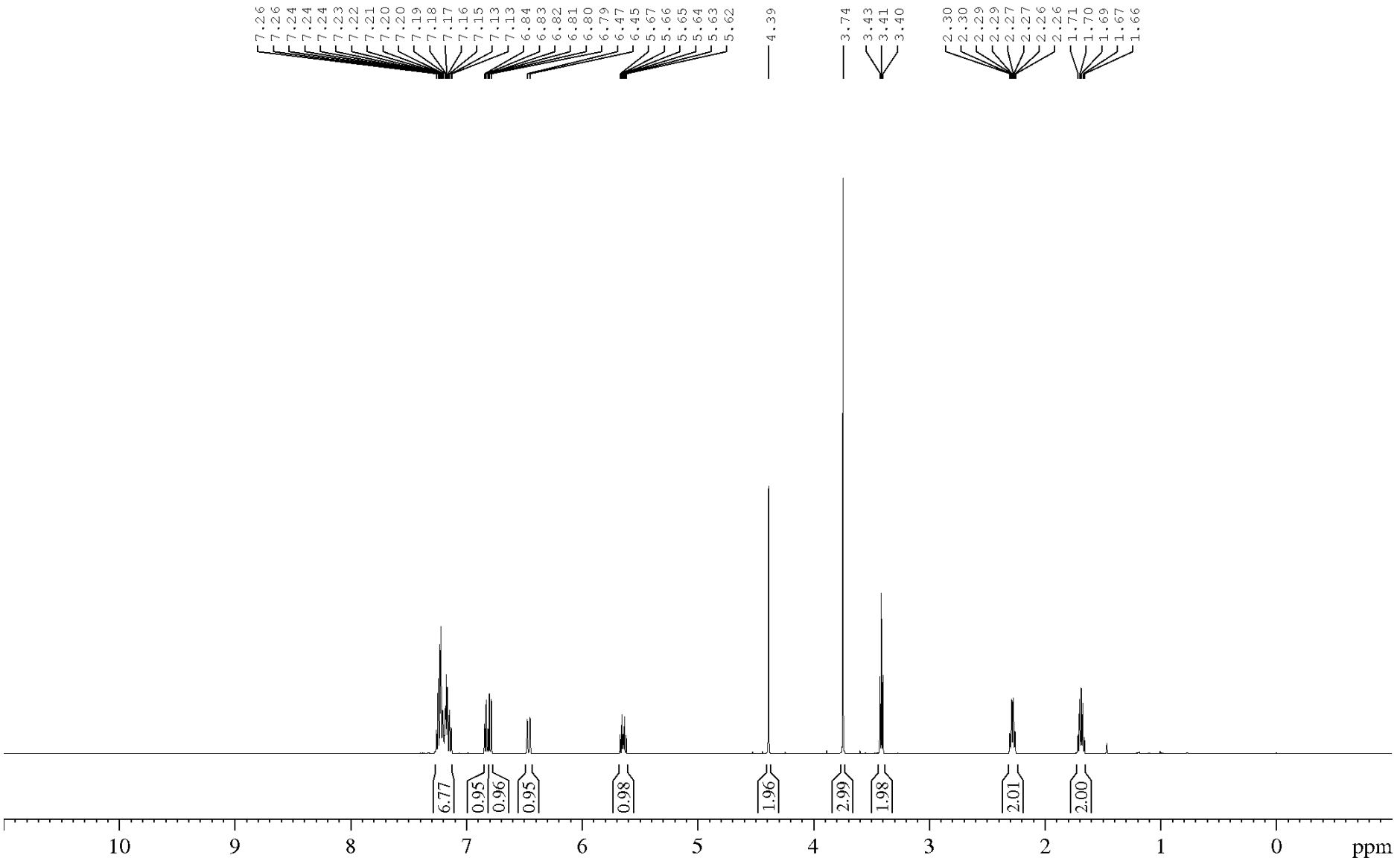


NOESY

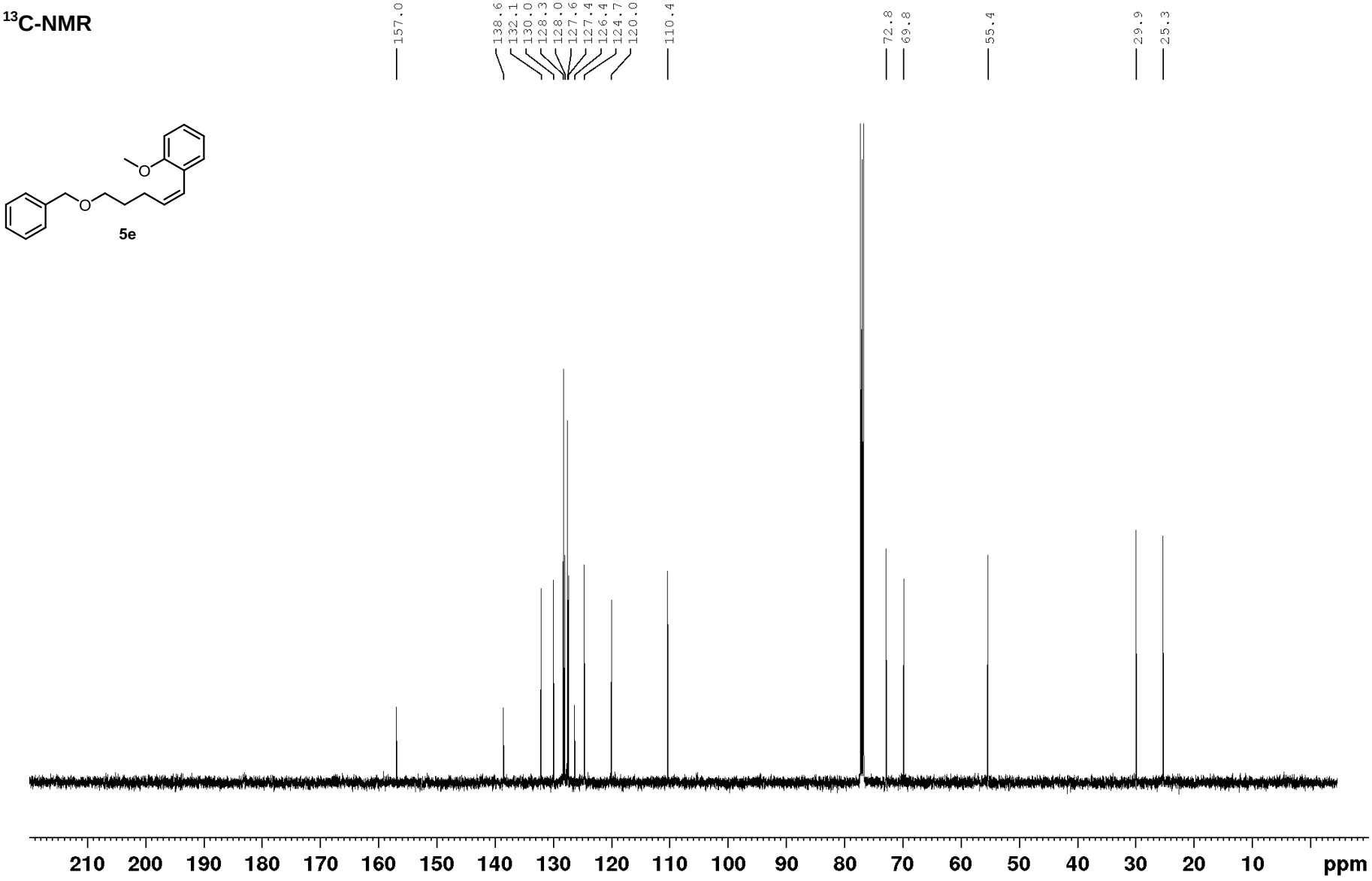


mass spectrum

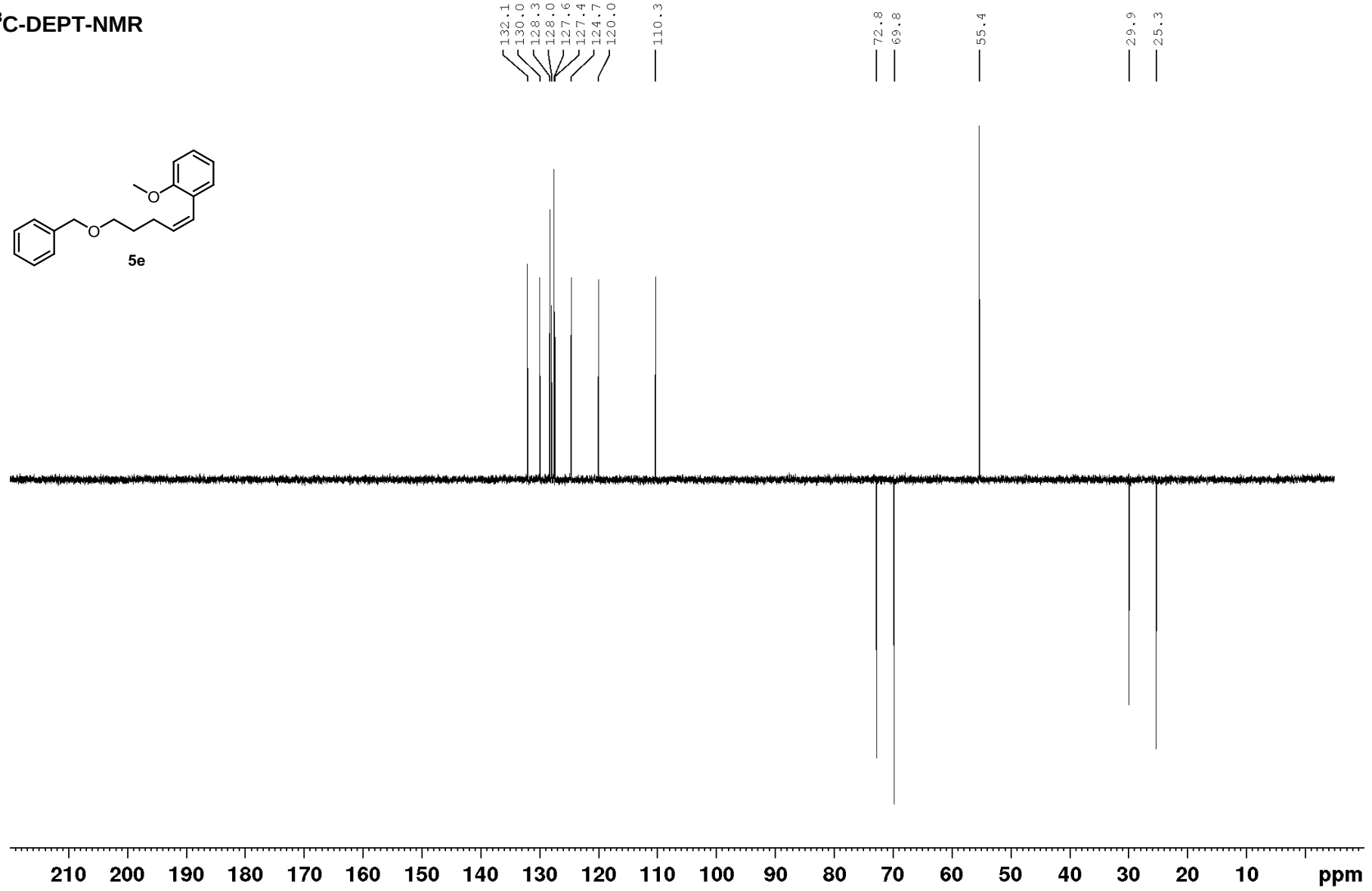



7.26
7.26
7.24
7.24
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.15
7.13
7.13
6.84
6.83
6.82
6.81
6.80
6.79
6.47
6.45
5.67
5.66
5.65
5.64
5.63
5.62
4.39
3.74
3.43
3.41
3.40
2.30
2.30
2.29
2.29
2.27
2.27
2.26
2.26
1.71
1.70
1.69
1.67
1.66
6.77
0.95
0.96
0.95
0.98
1.96
2.99
1.98
2.01
2.00
10
9
8
7
6
5
4
3
2
1
0
ppm

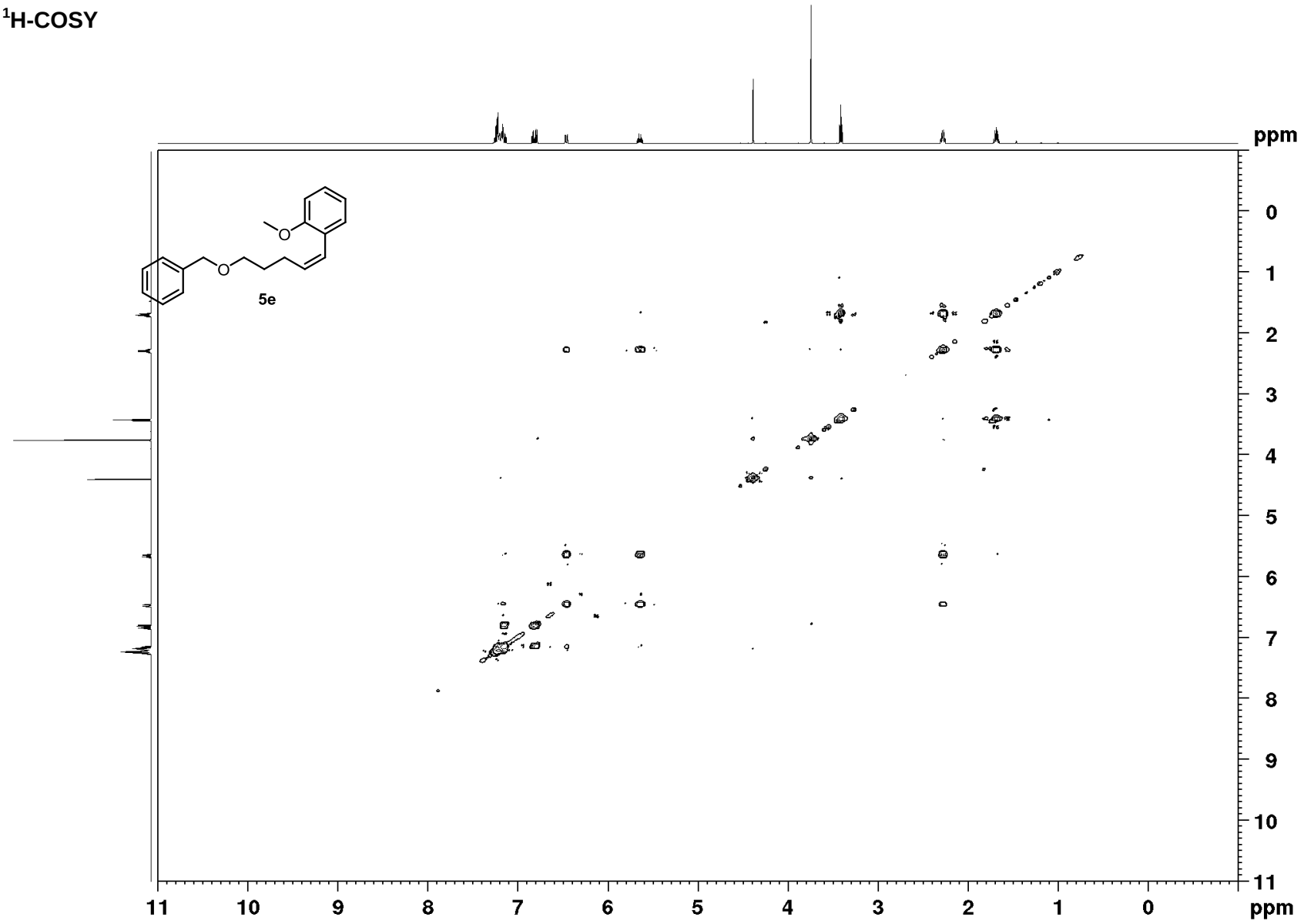
^{13}C-NMR


157.0
138.6
132.1
130.0
128.3
128.0
127.6
127.4
126.4
124.7
120.0
110.4
72.8
69.8
55.4
29.9
25.3
O
O
5e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

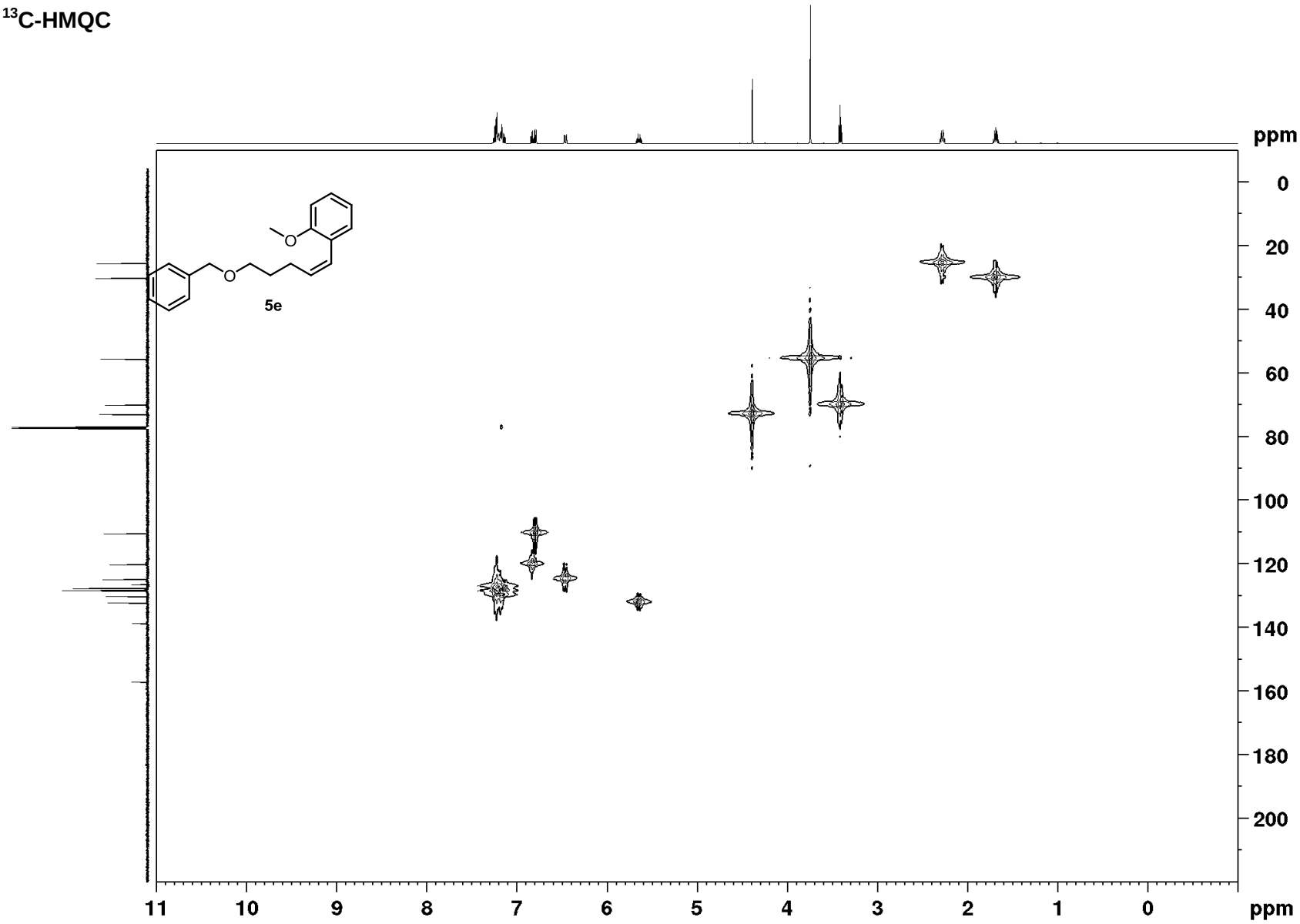
^{13}C-DEPT-NMR


132.1
130.0
128.3
128.0
127.6
127.4
124.7
120.0
110.3
72.8
69.8
55.4
29.9
25.3
O
O
5e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

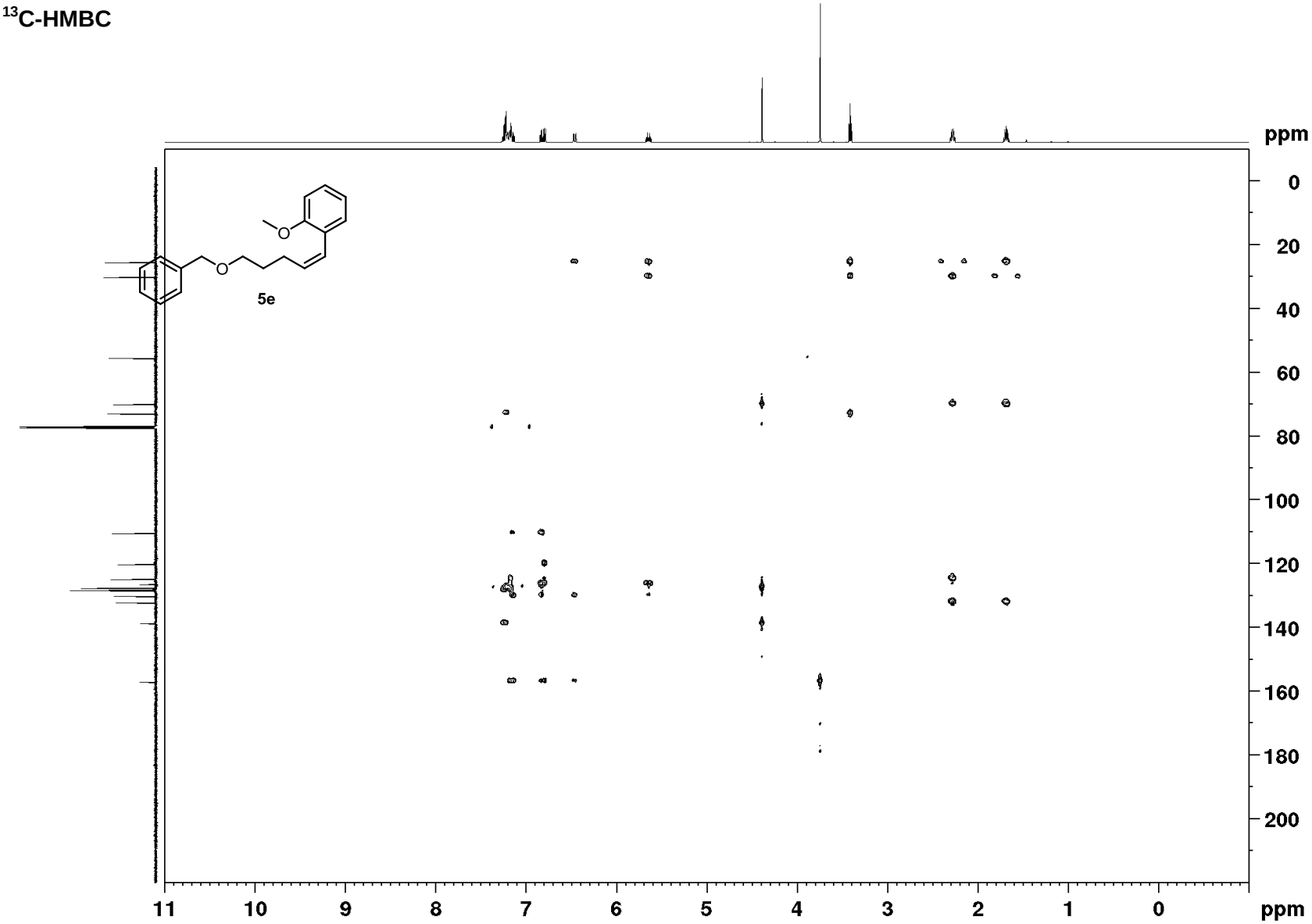
^{1}H, ^{1}H-COSY



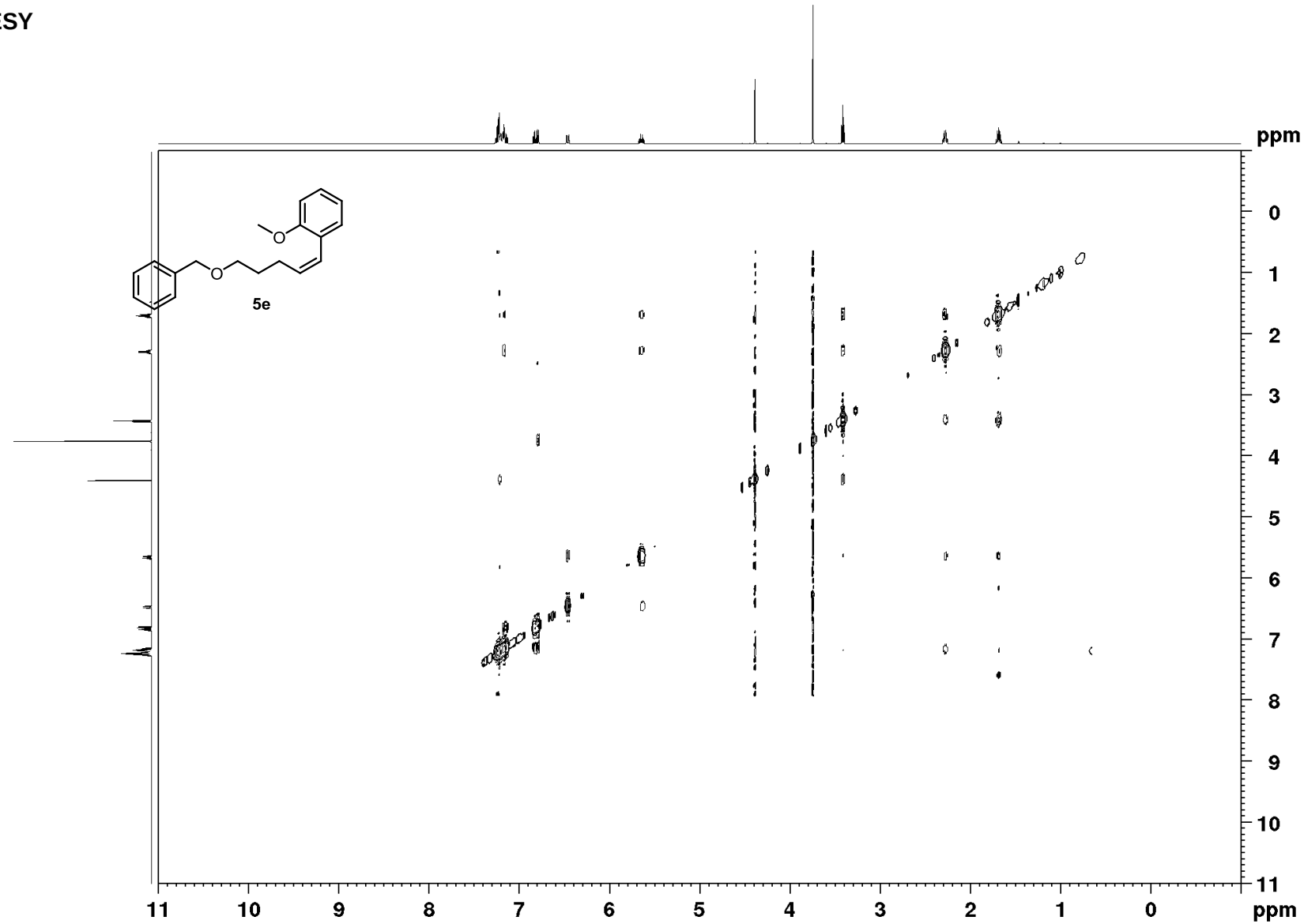
^{1}H, ^{13}C-HMQC



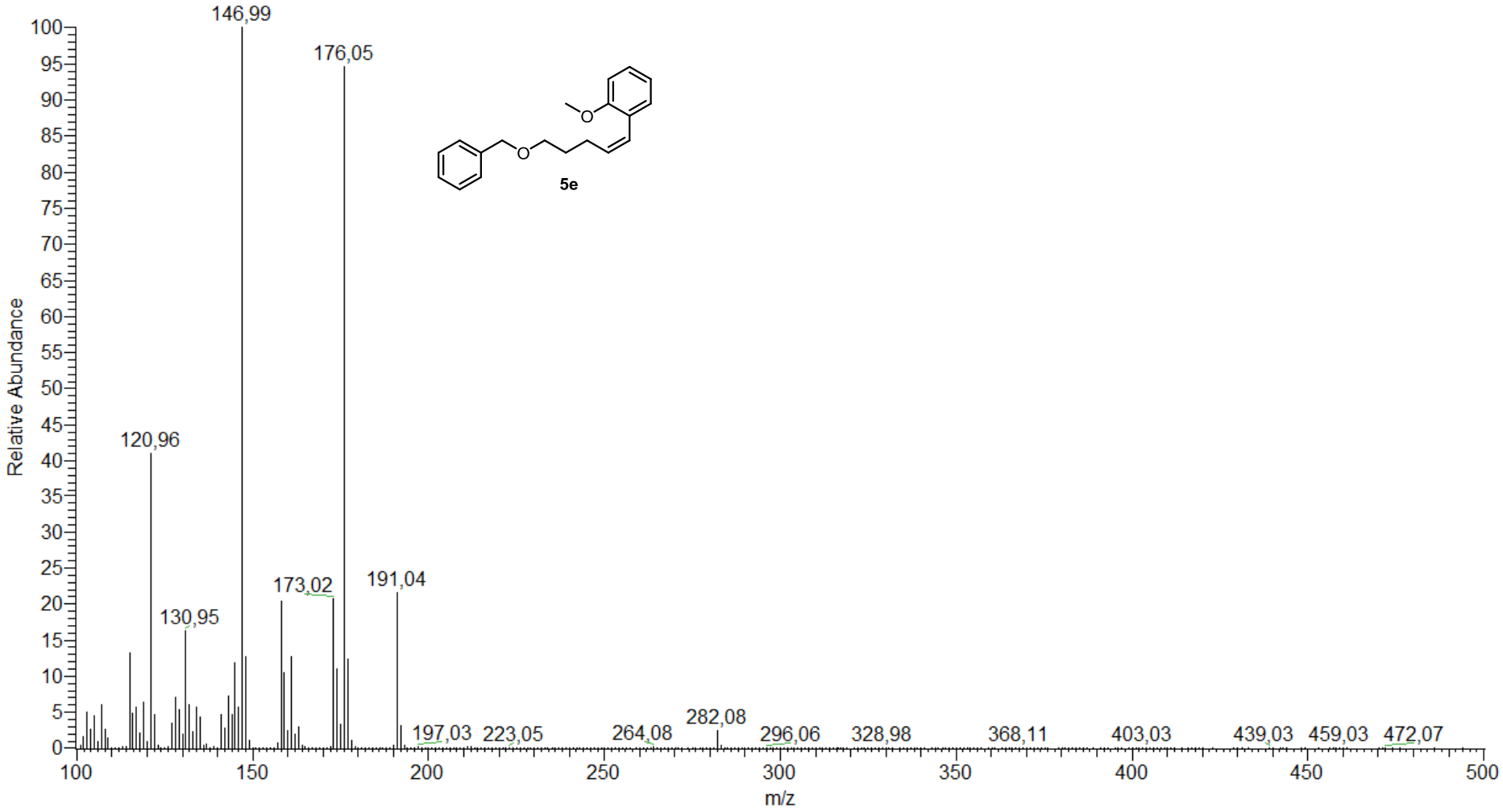
^{1}H, ^{13}C-HMBC


ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm
O
O
5e

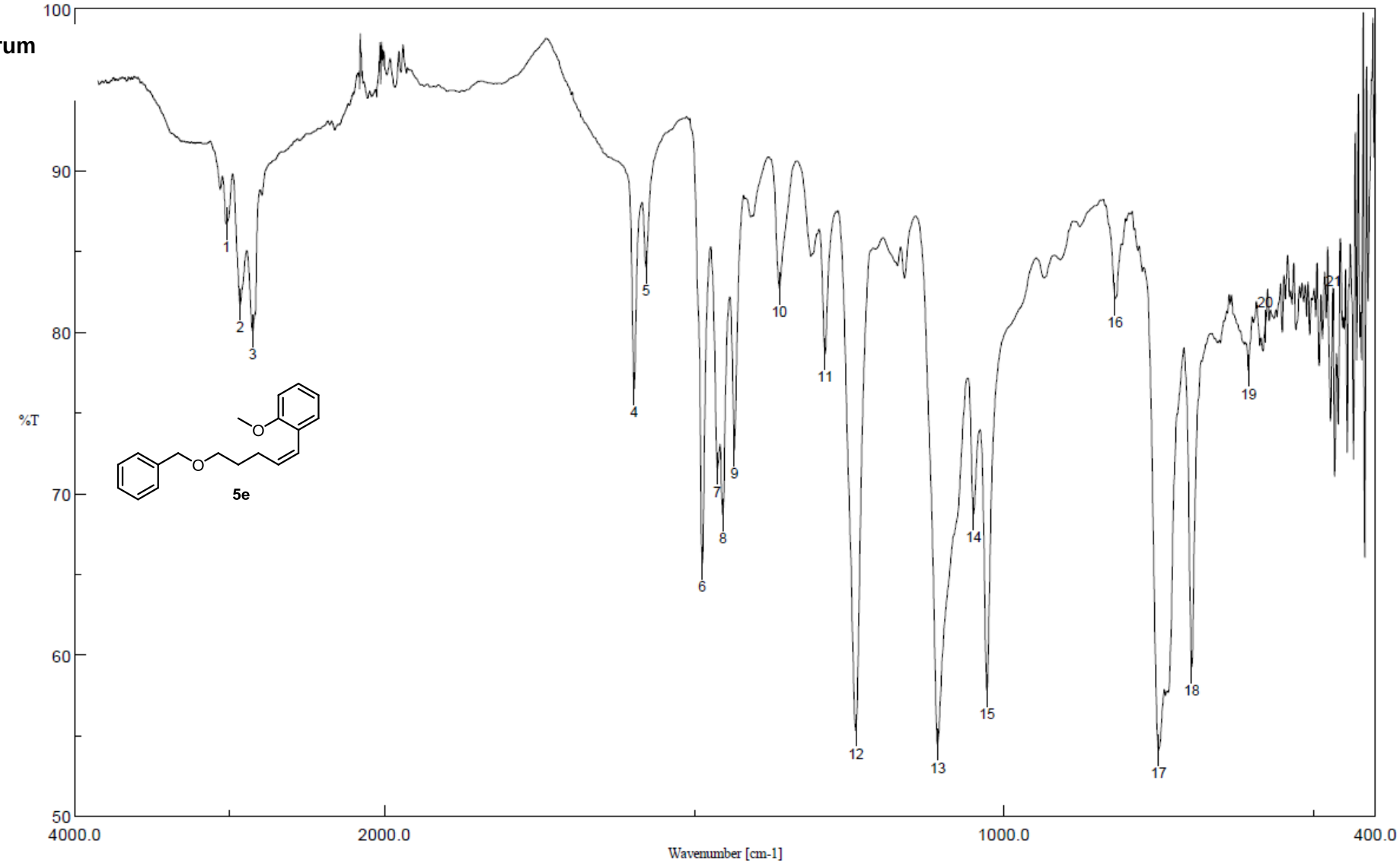
NOESY



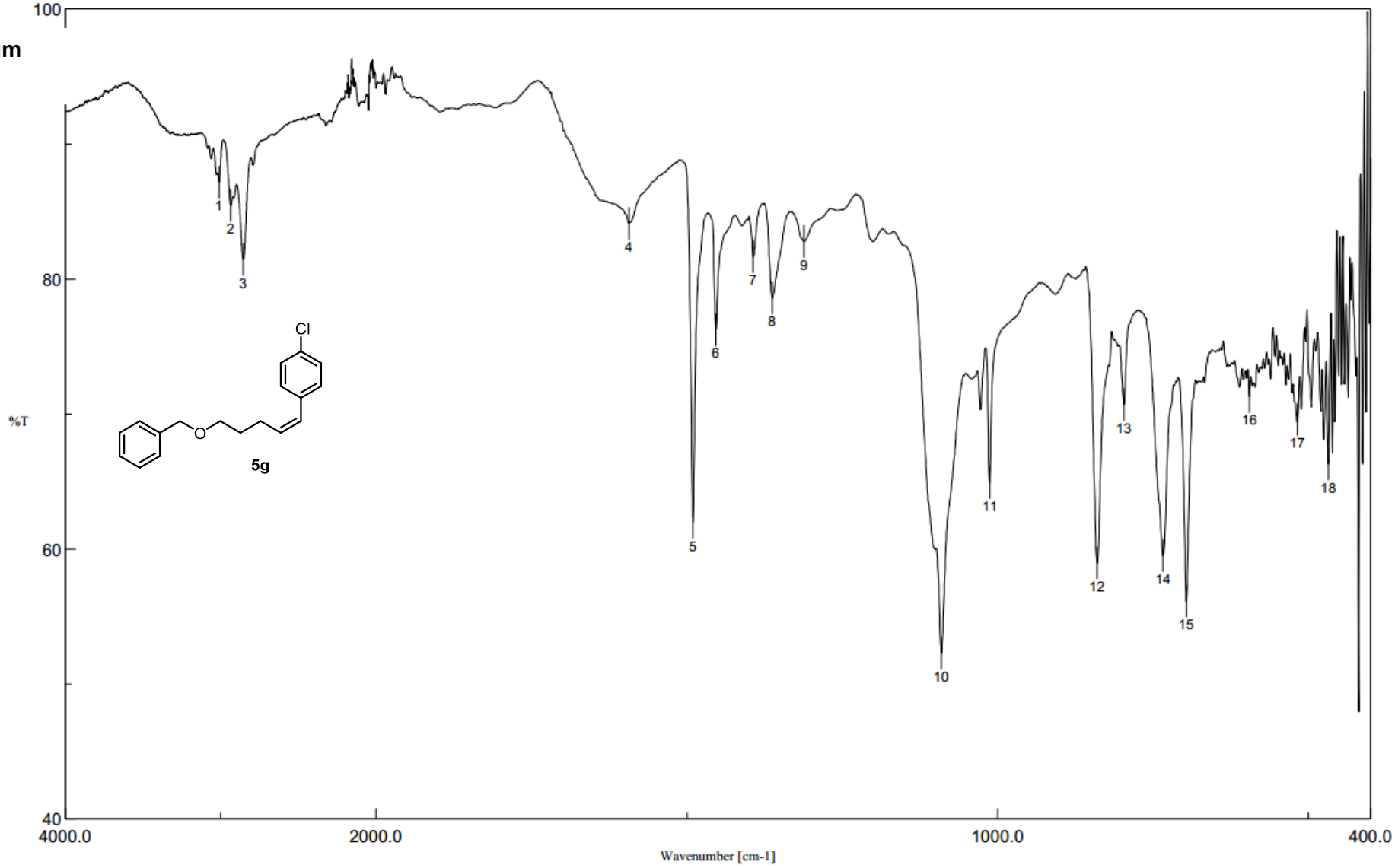
mass spectrum



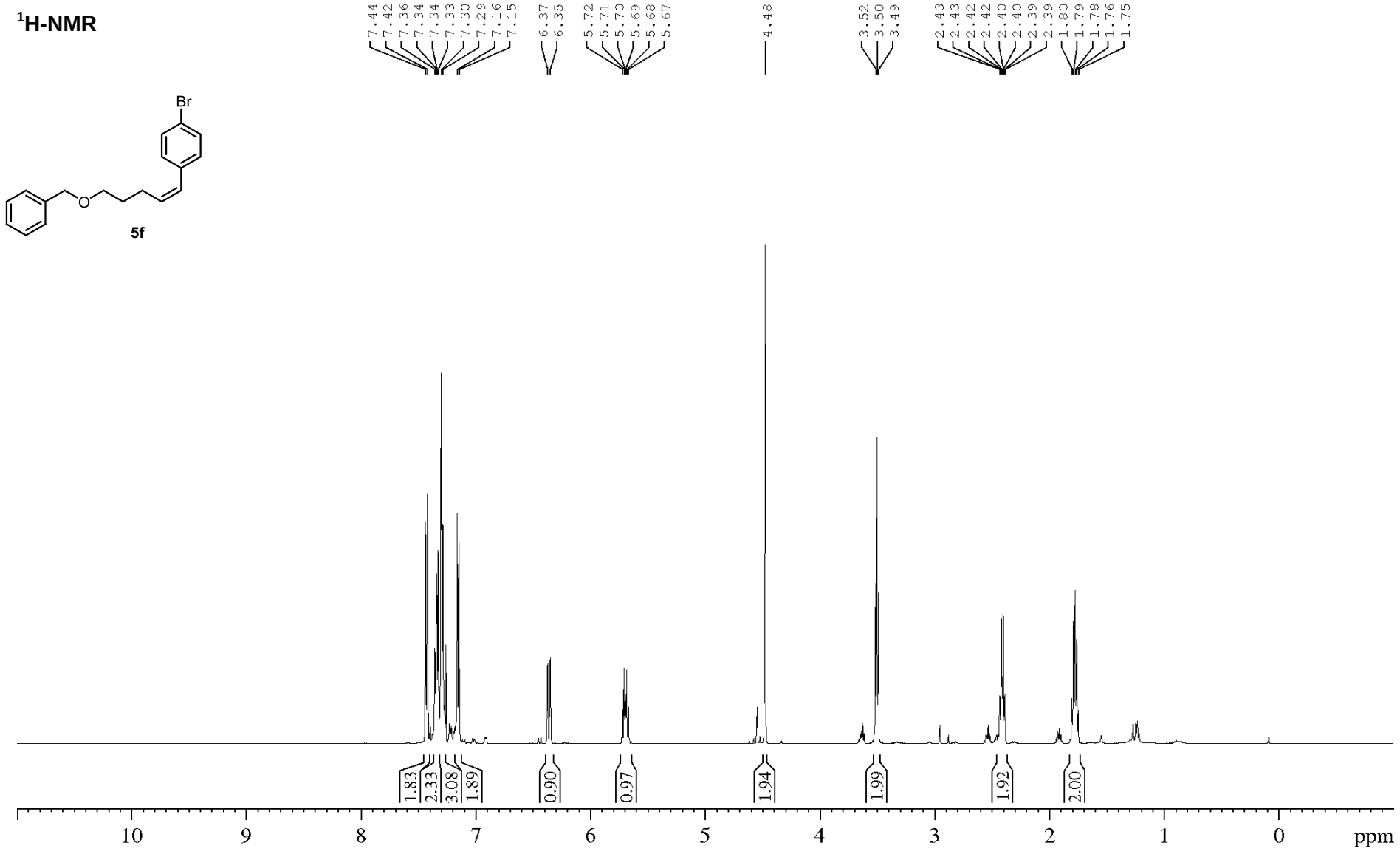
IR spectrum


100
90
80
70
60
50
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
O
O
5e

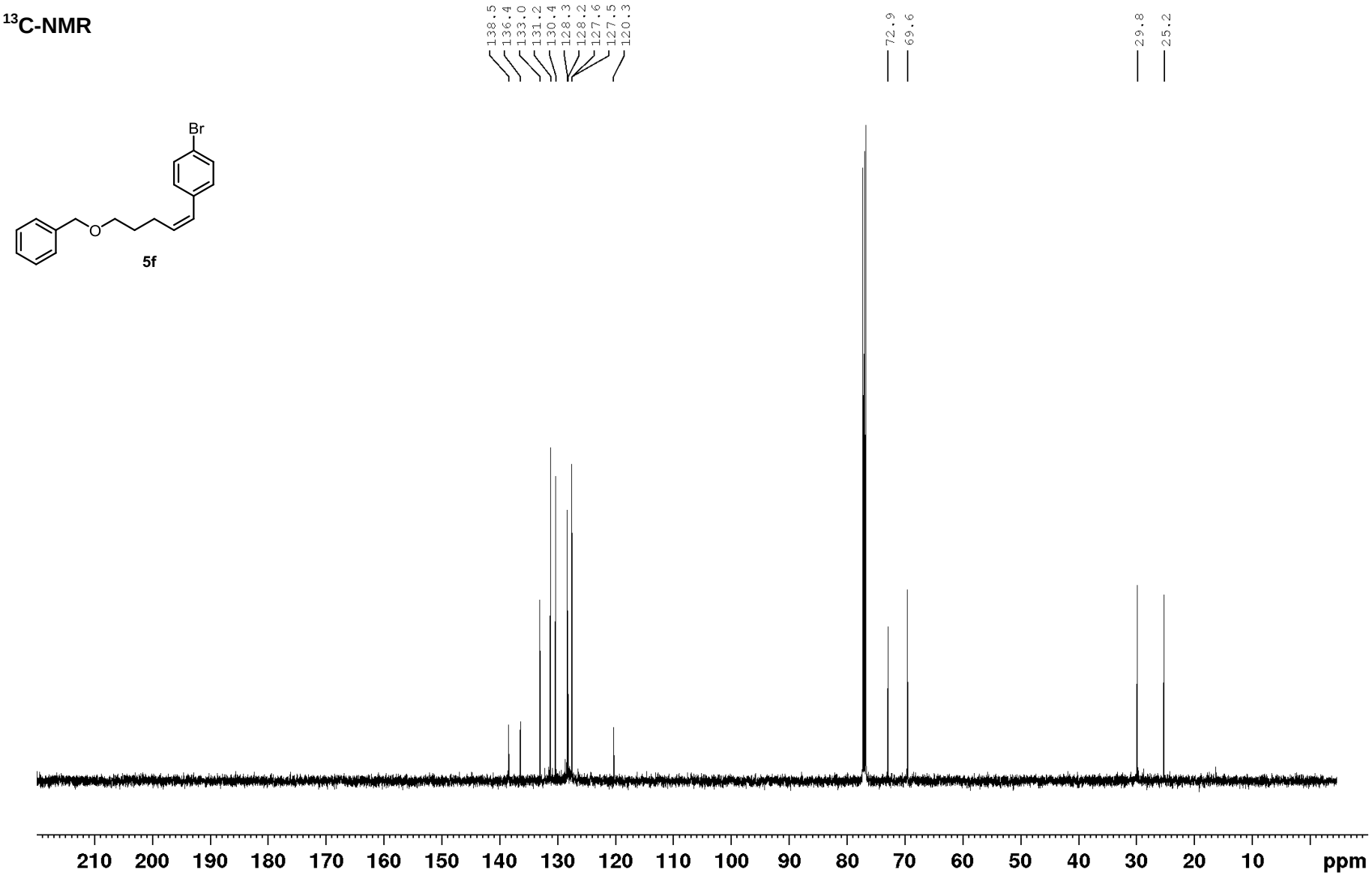
IR spectrum


100
80
60
40
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Cl
O
5g

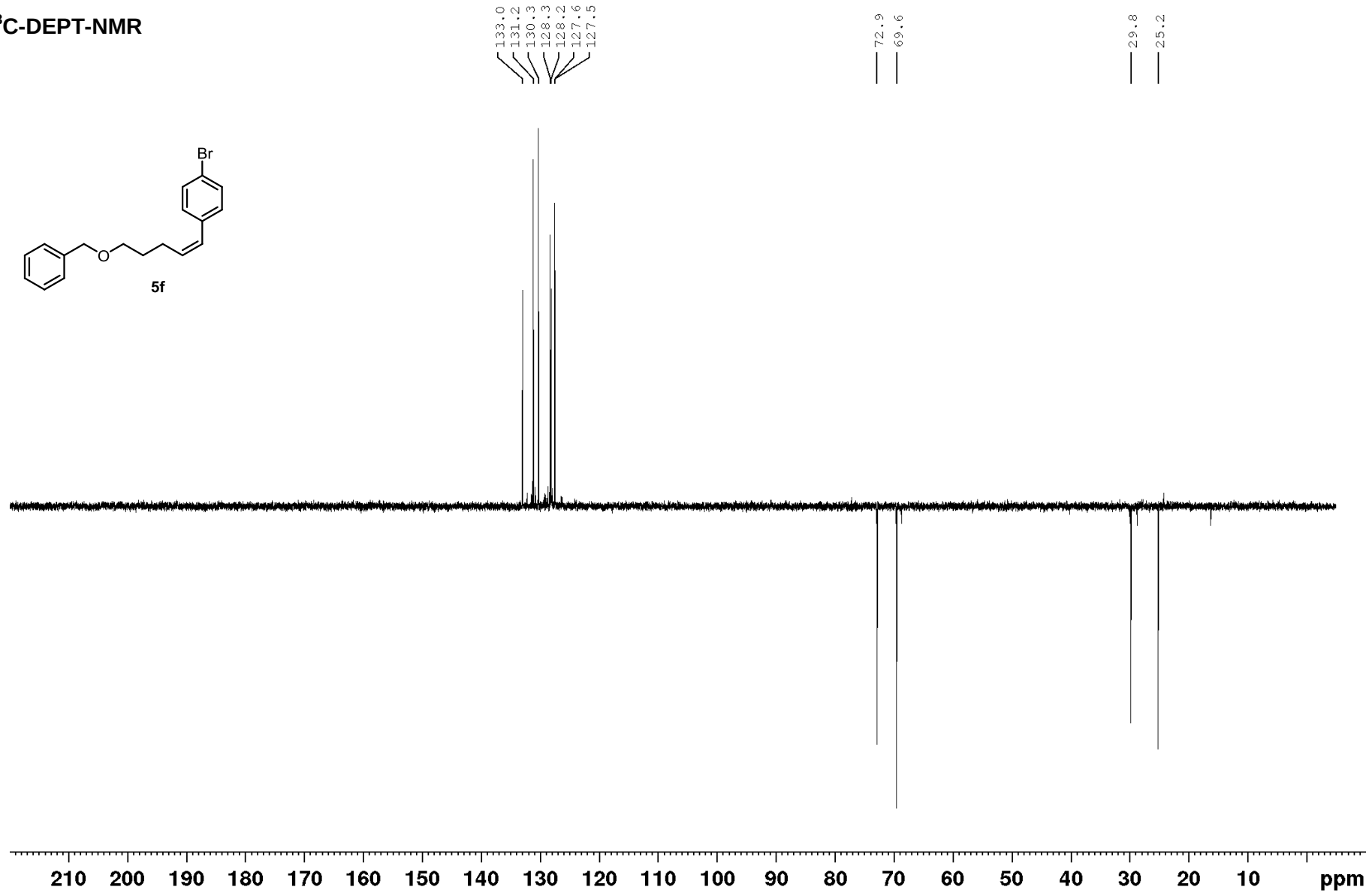
^{1}H-NMR


7.44
7.42
7.36
7.34
7.34
7.33
7.30
7.29
7.16
7.15
6.37
6.35
5.72
5.71
5.70
5.69
5.68
5.67
4.48
3.52
3.50
3.49
2.43
2.43
2.42
2.42
2.40
2.40
2.39
2.39
1.80
1.79
1.78
1.76
1.75
Br
O
5f
1.83
2.33
3.08
1.89
0.90
0.97
1.94
1.99
1.92
2.00
10
9
8
7
6
5
4
3
2
1
0
ppm

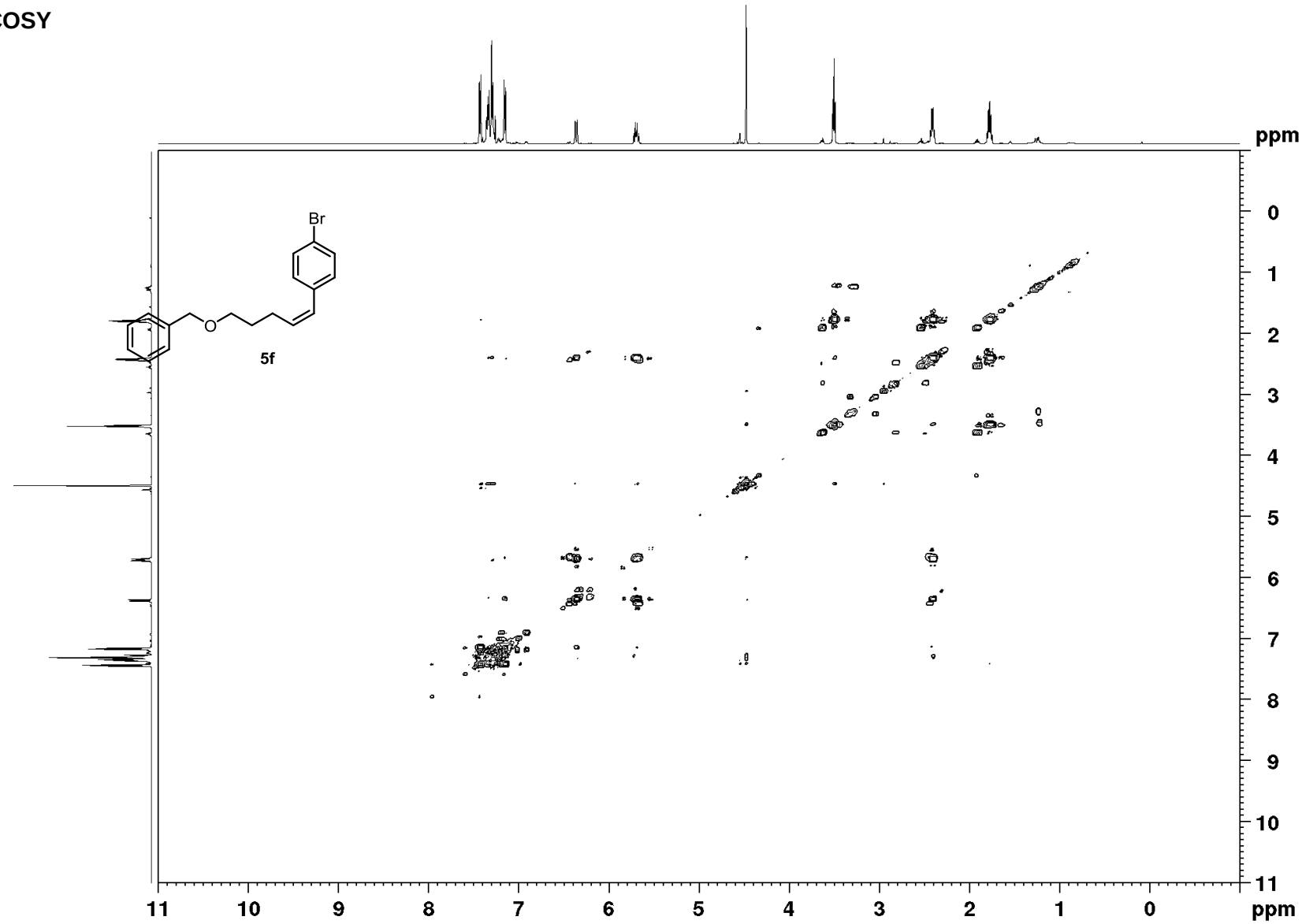
^{13}C-NMR


138.5
136.4
133.0
131.2
130.4
128.3
128.2
127.6
127.5
120.3
72.9
69.6
29.8
25.2
Br
O
5f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

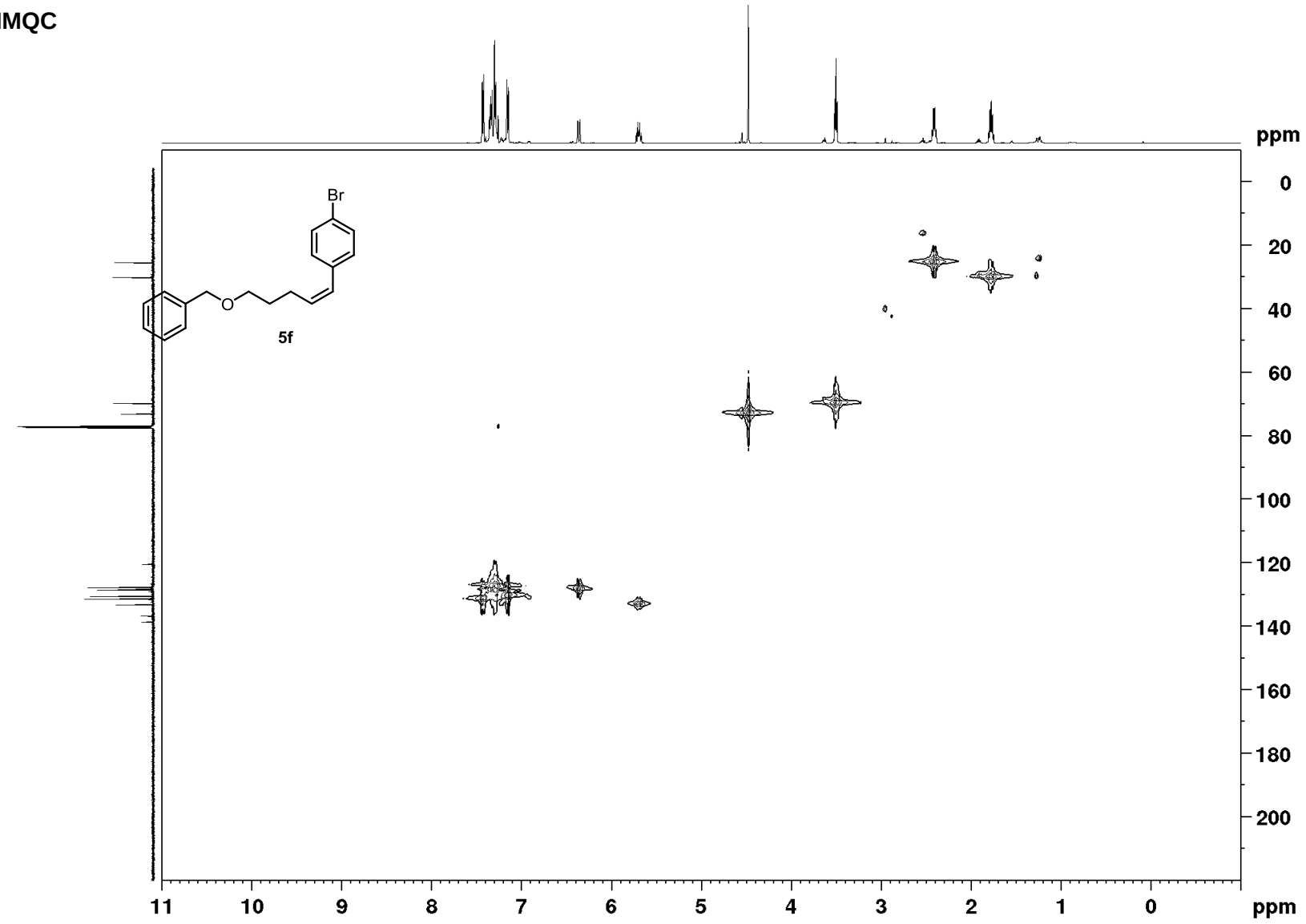
^{13}C-DEPT-NMR


133.0
131.2
130.3
128.3
128.2
127.6
127.5
72.9
69.6
29.8
25.2
Br
O
5f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

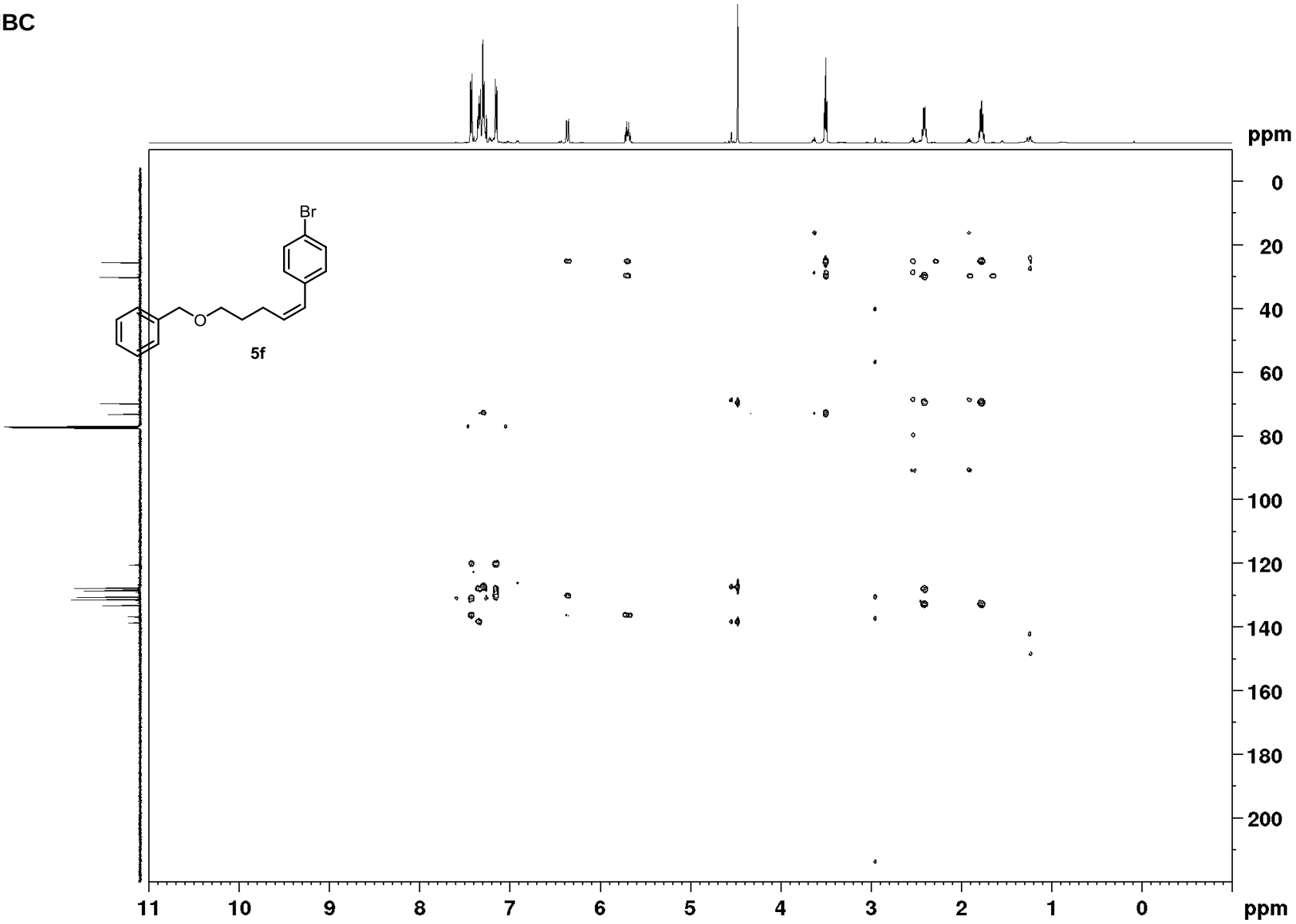
^{1}H, ^{1}H-COSY



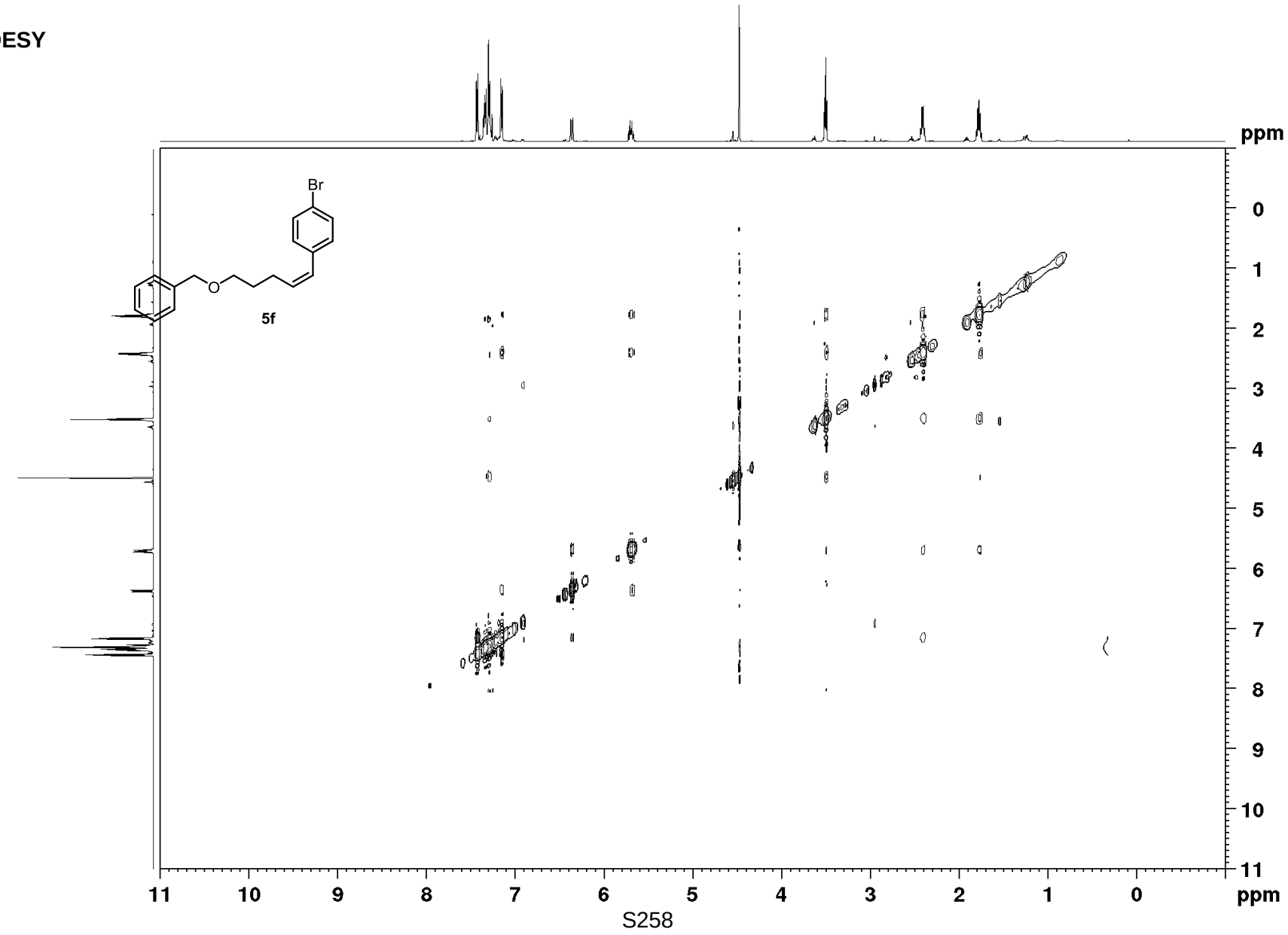
^{1}H, ^{13}C-HMQC

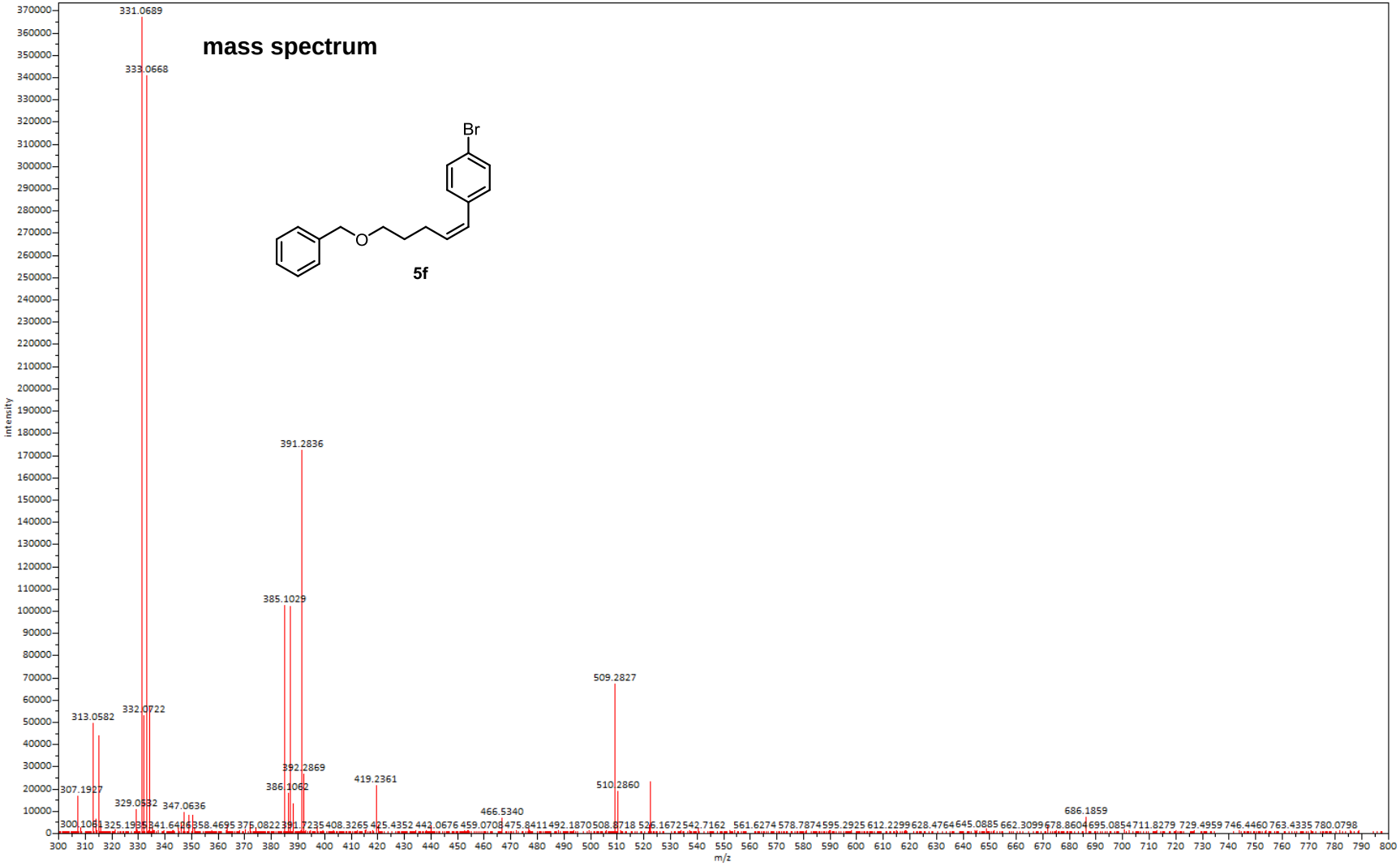

Br
O
5f
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H, ^{13}C-HMBC

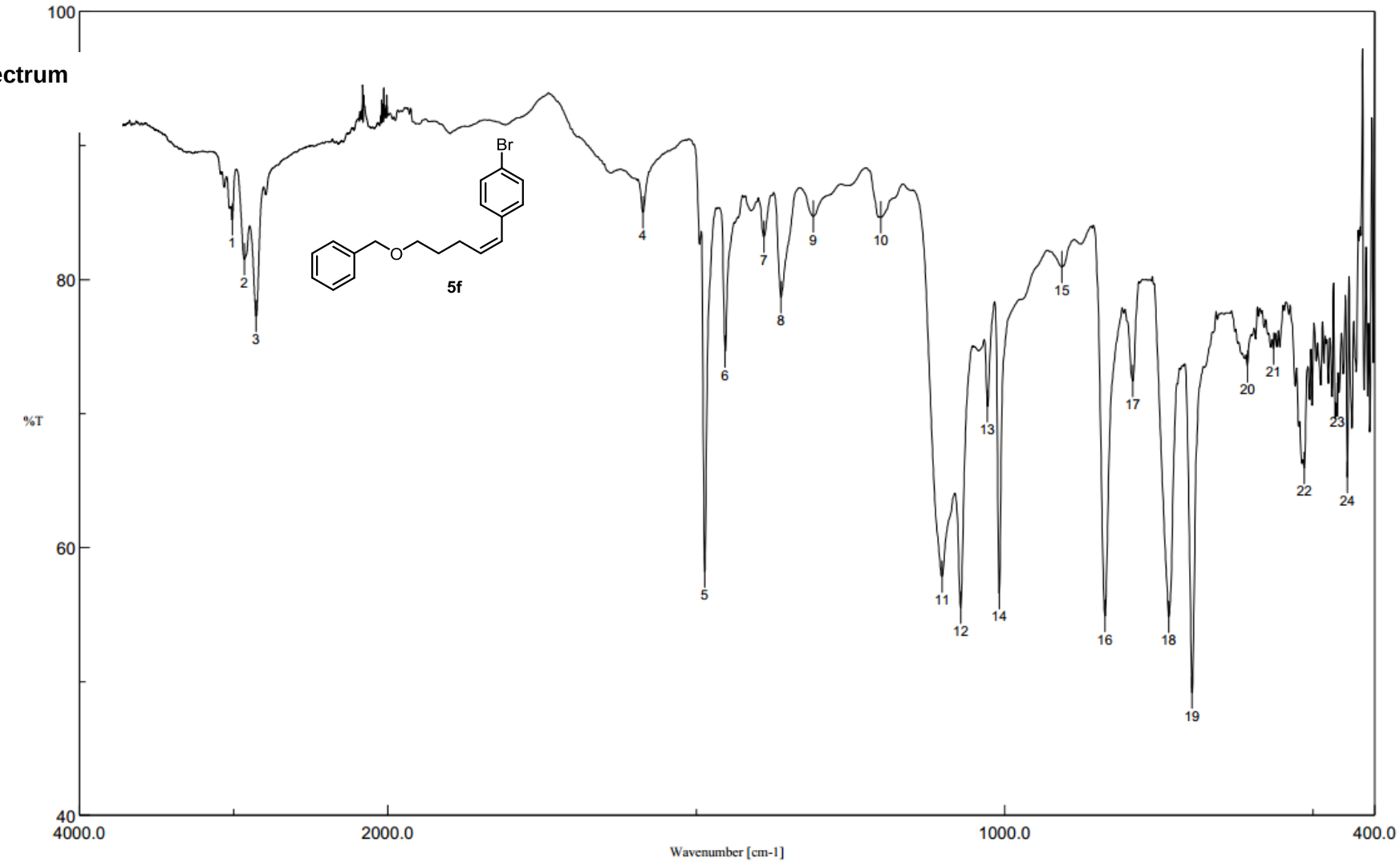

Br
O
5f
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

NOESY




mass spectrum
Br
O
5f
intensity
m/z
331.0689
333.0668
391.2836
385.1029
509.2827
313.0582
332.0722
392.2869
386.1062
419.2361
510.2860
307.1927
329.0532
347.0636
466.5340
686.1859

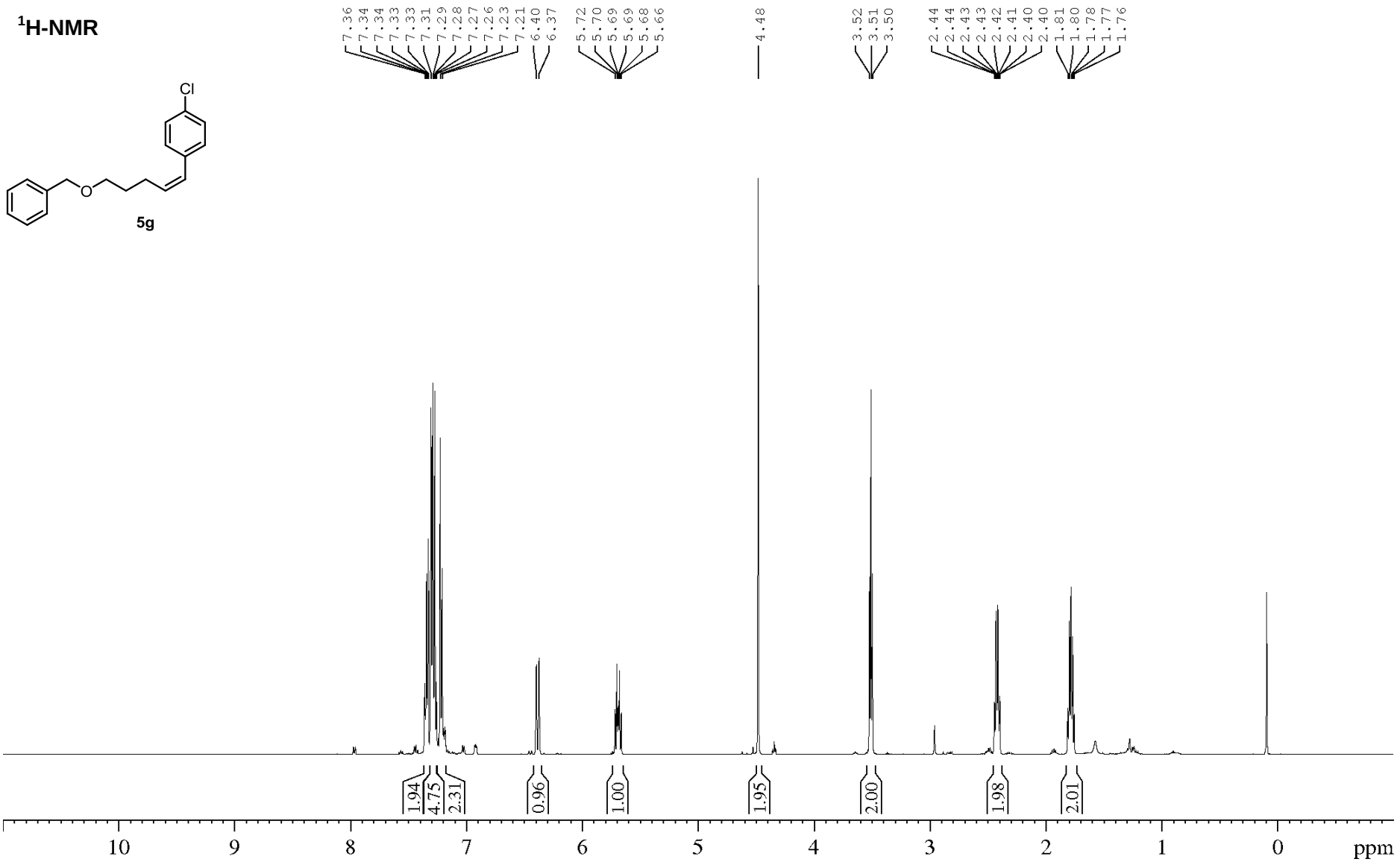
IR spectrum


100
80
60
40
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
Br
O
5f
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

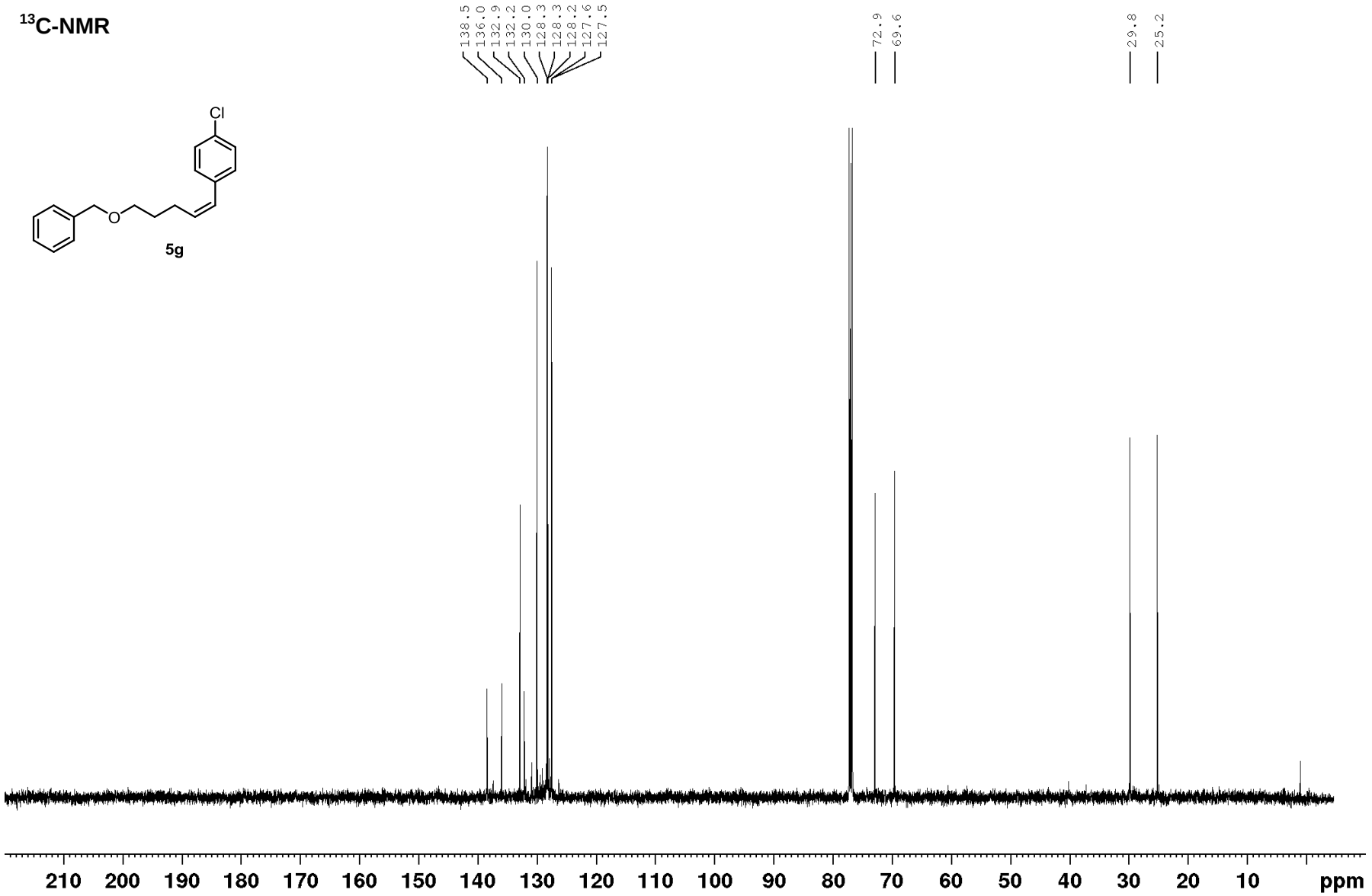
^{1}H-NMR

Cl
O

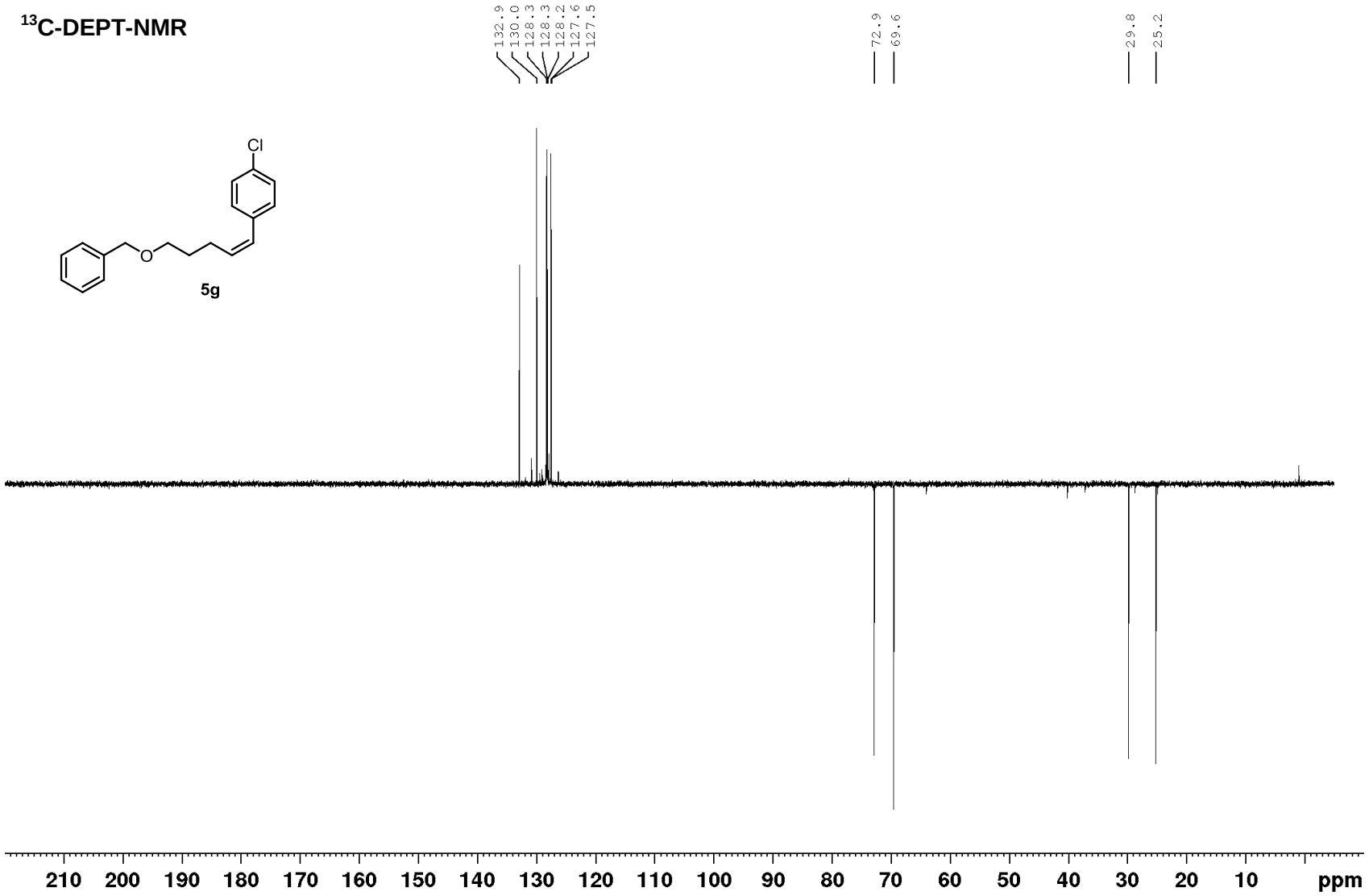
5g


7.36
7.34
7.34
7.33
7.33
7.31
7.29
7.28
7.27
7.26
7.23
7.21
6.40
6.37
5.72
5.70
5.69
5.69
5.68
5.66
4.48
3.52
3.51
3.50
2.44
2.44
2.43
2.43
2.42
2.41
2.40
2.40
1.81
1.80
1.78
1.77
1.76
1.94
4.75
2.31
0.96
1.00
1.95
2.00
1.98
2.01
10
9
8
7
6
5
4
3
2
1
0
ppm

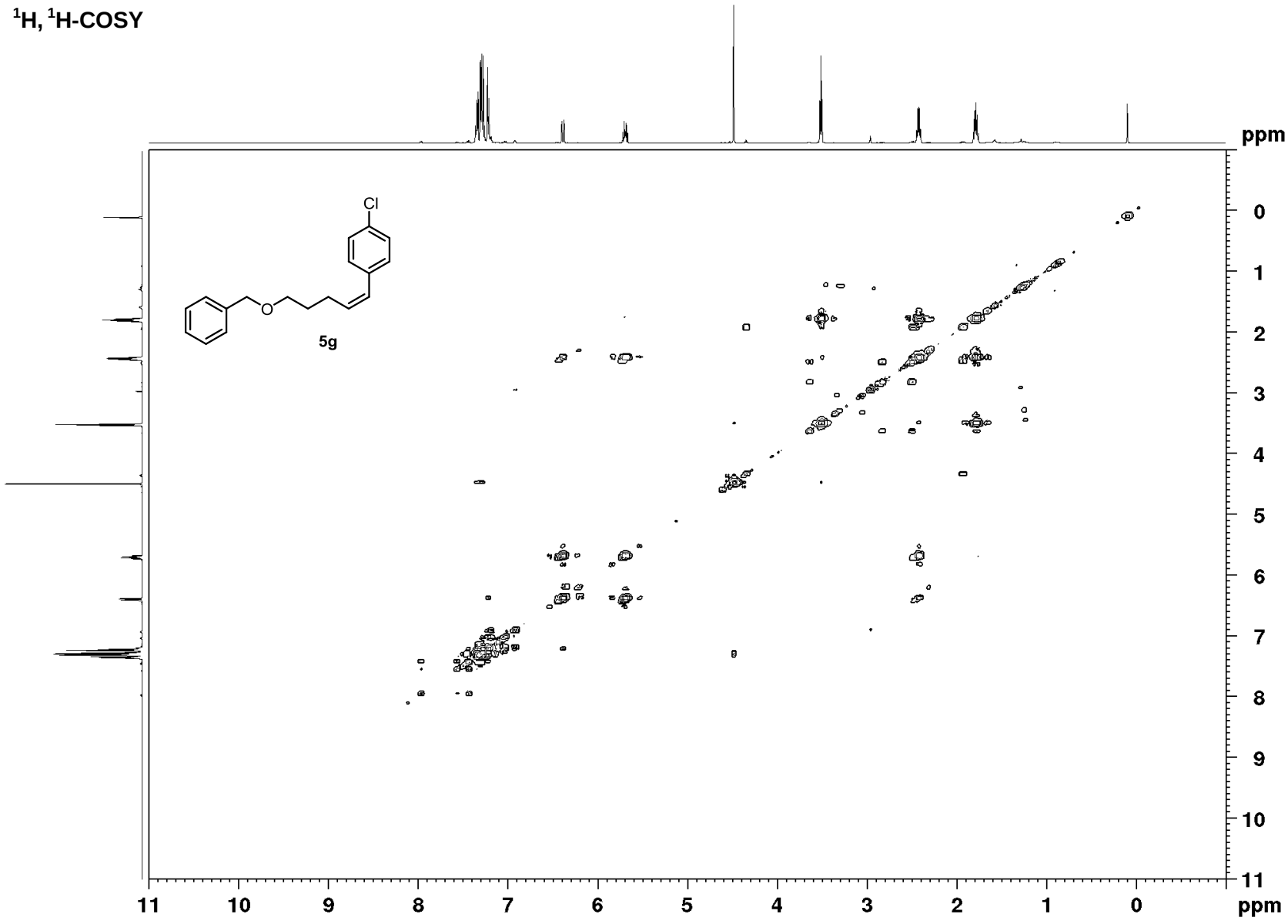
^{13}C-NMR


138.5
136.0
132.9
132.2
130.0
128.3
128.2
127.6
127.5
72.9
69.6
29.8
25.2
Cl
O
5g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

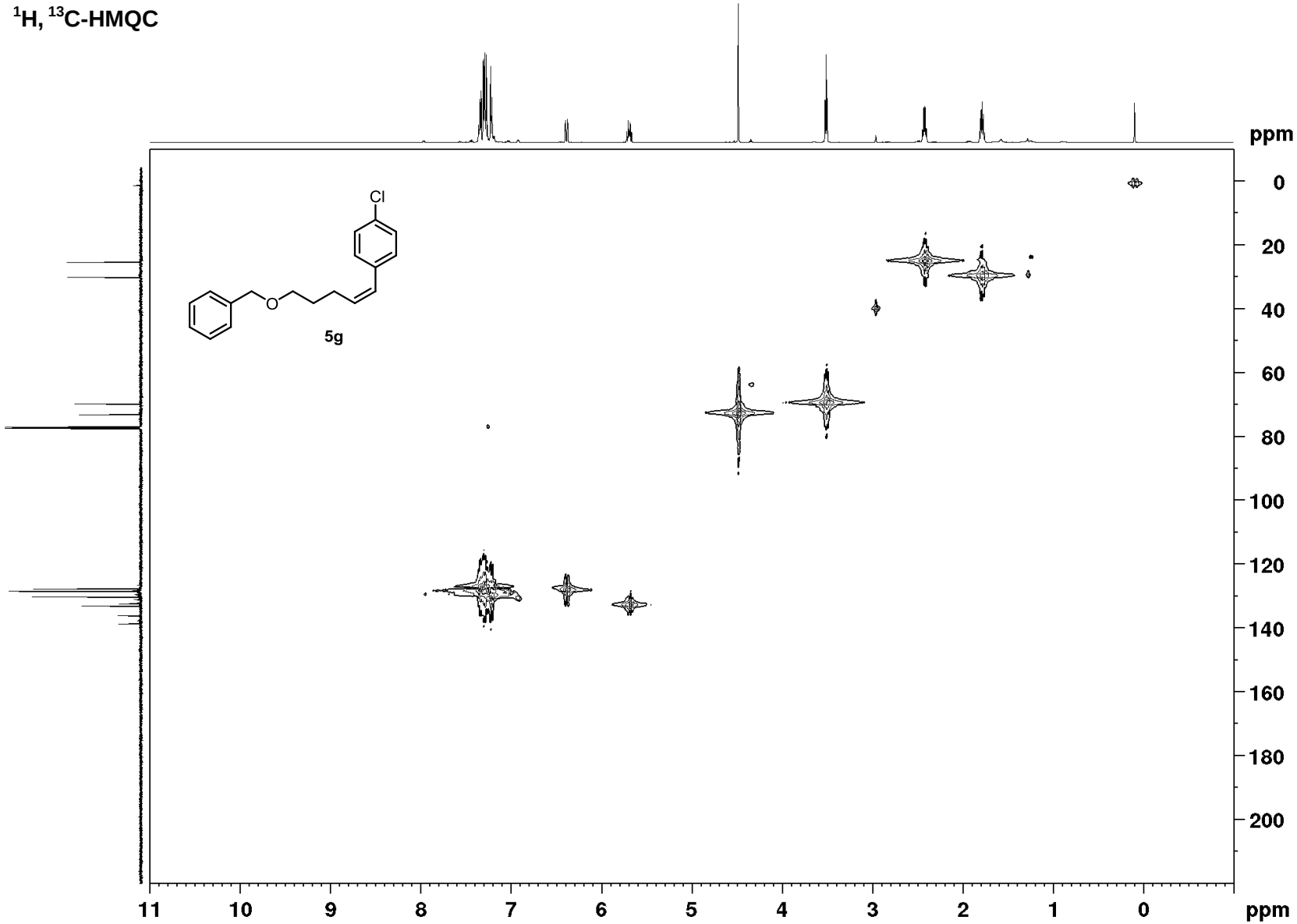
^{13}C-DEPT-NMR


132.9
130.0
128.3
128.3
128.2
127.6
127.5
72.9
69.6
29.8
25.2
Cl
O
5g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

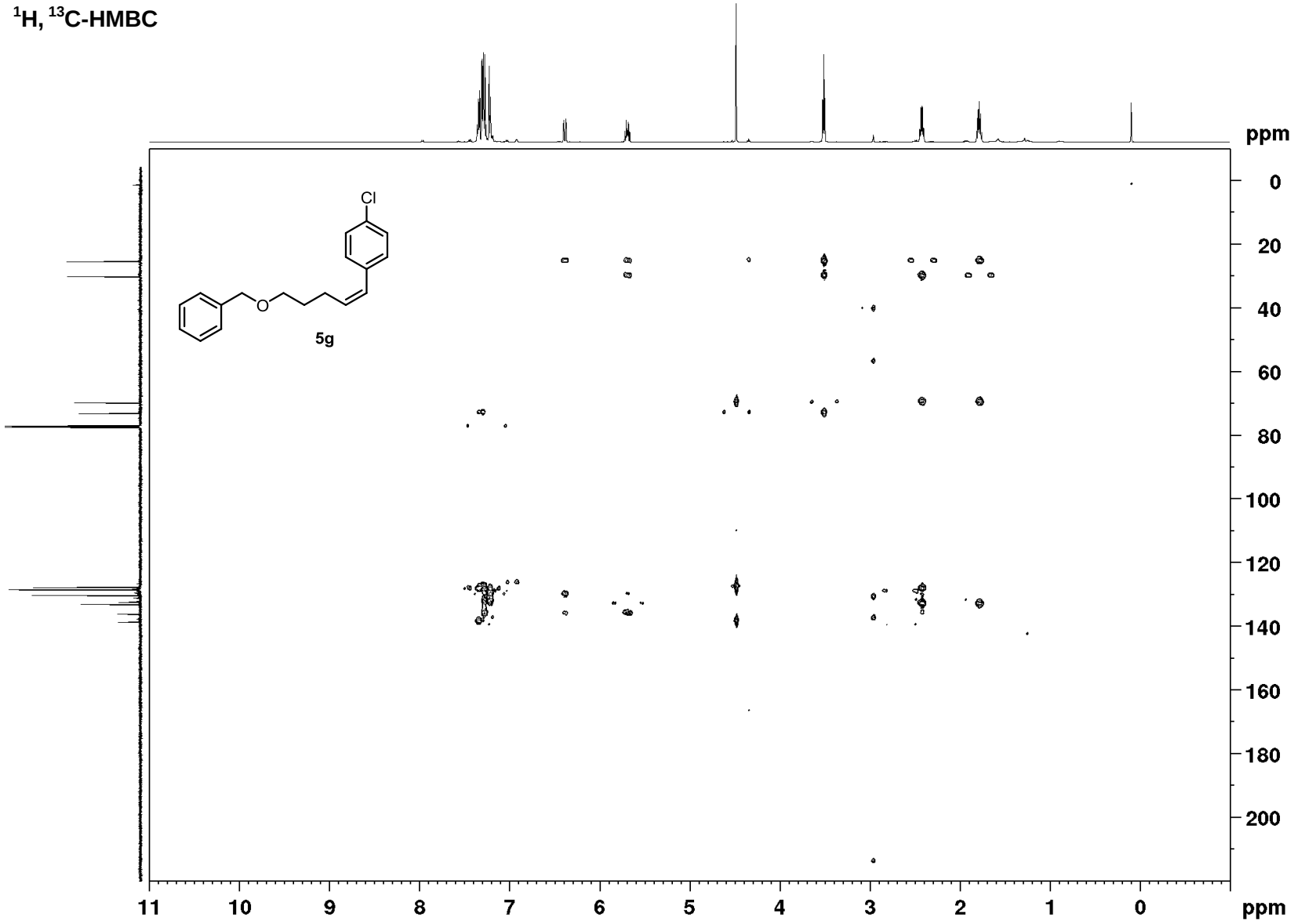
^{1}H, ^{1}H-COSY



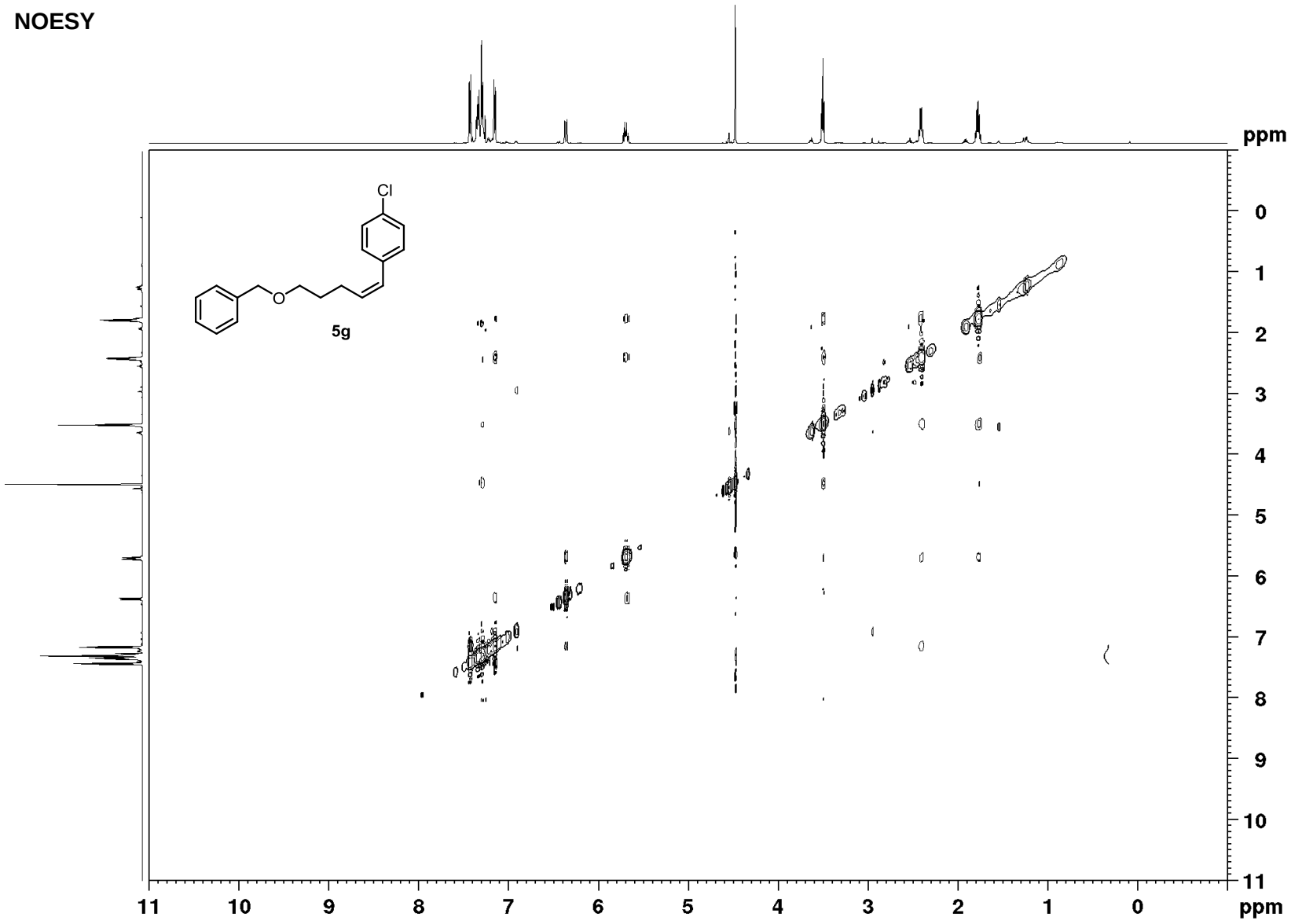
^{1}H, ^{13}C-HMQC


Cl
O
5g
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

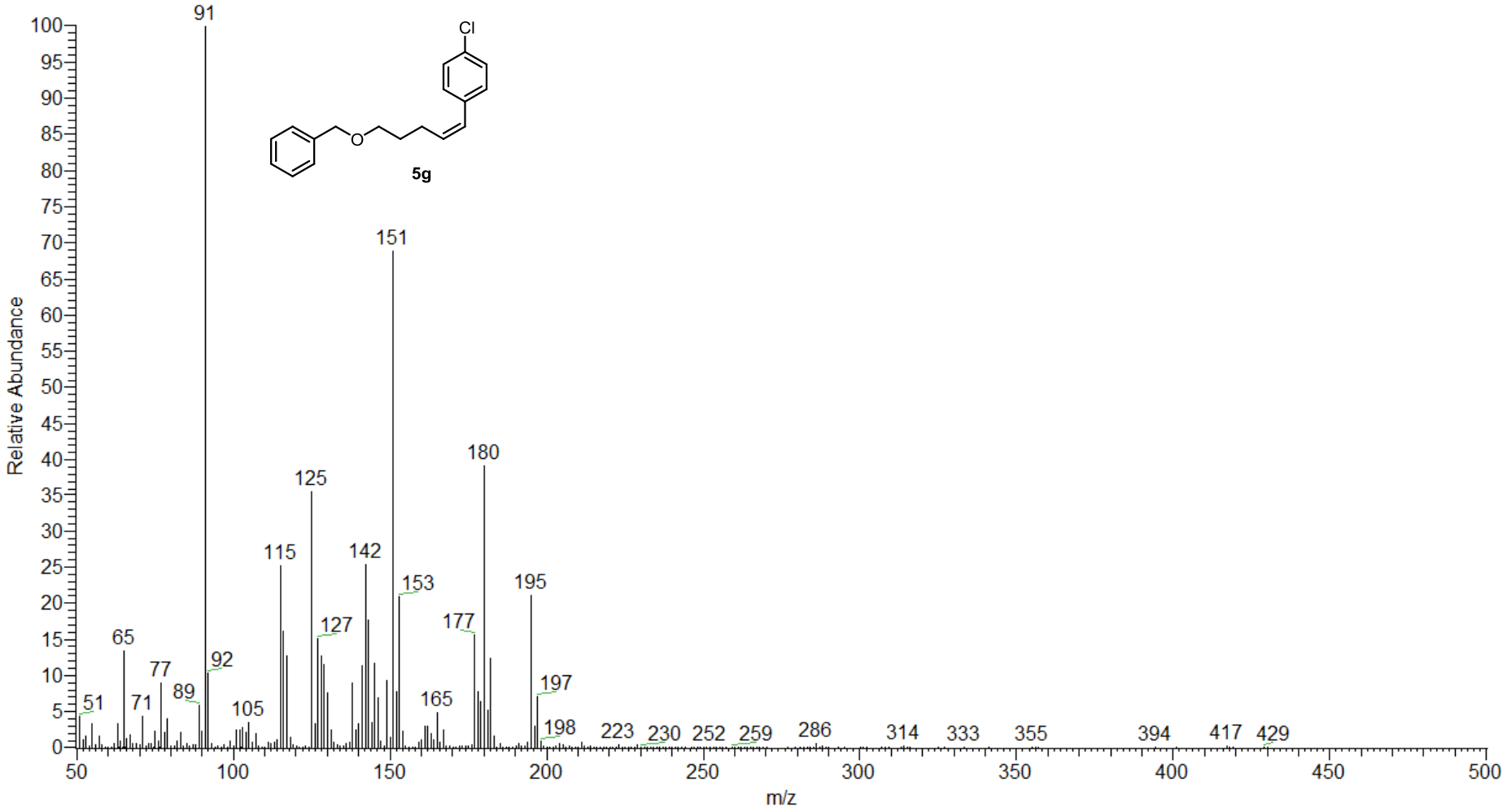
^{1}H, ^{13}C-HMBC


Cl
O
5g
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

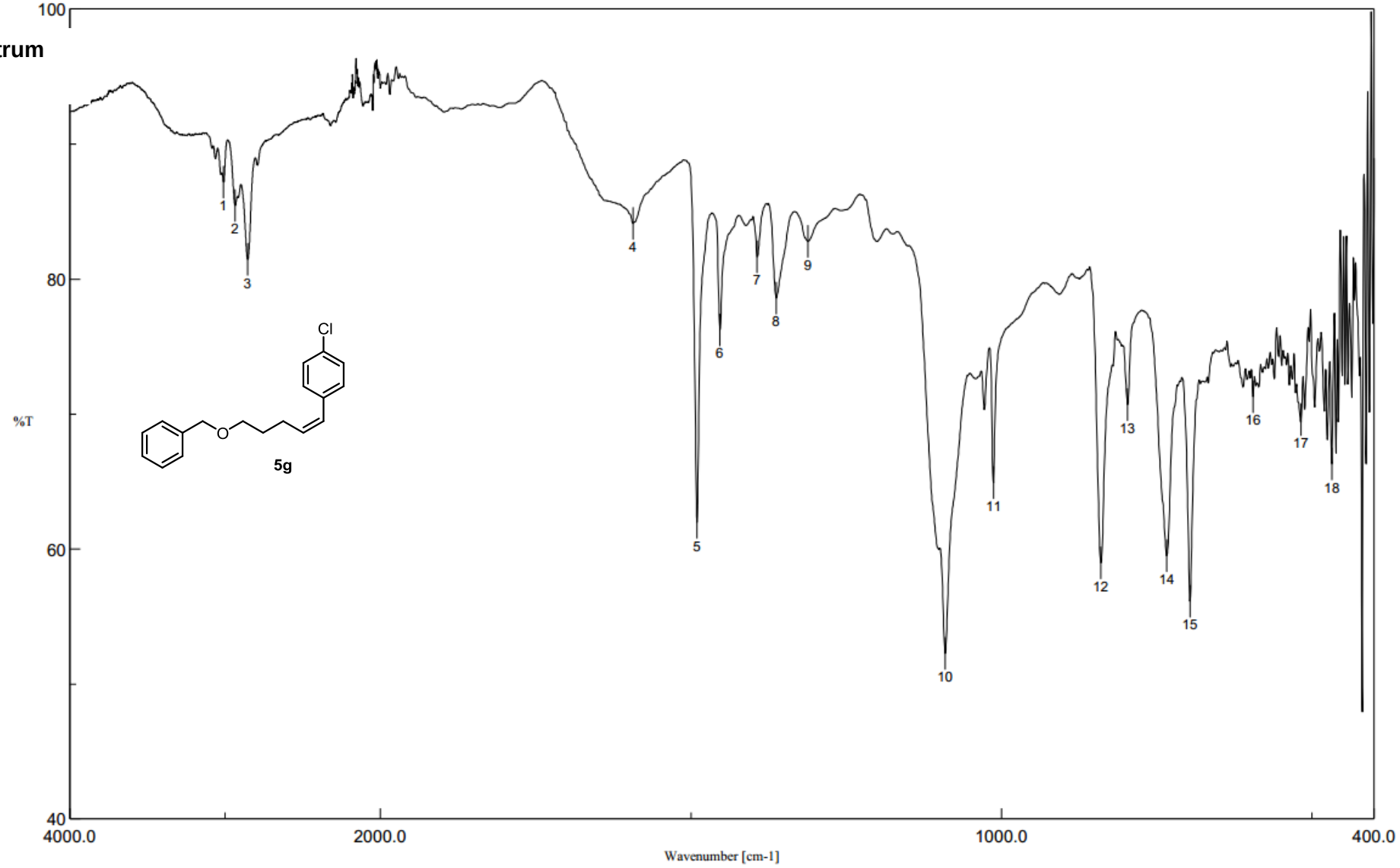
NOESY



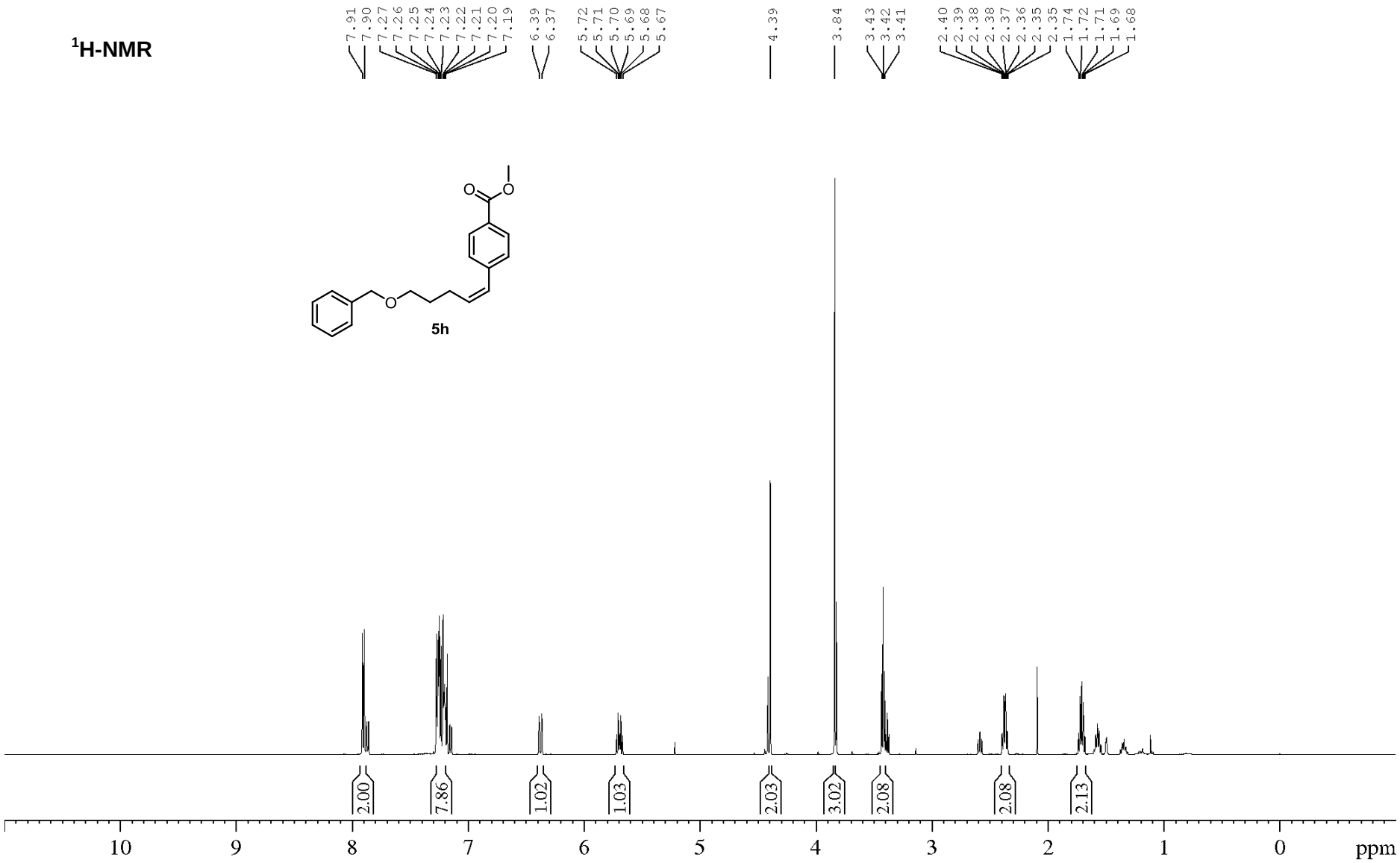
mass spectrum



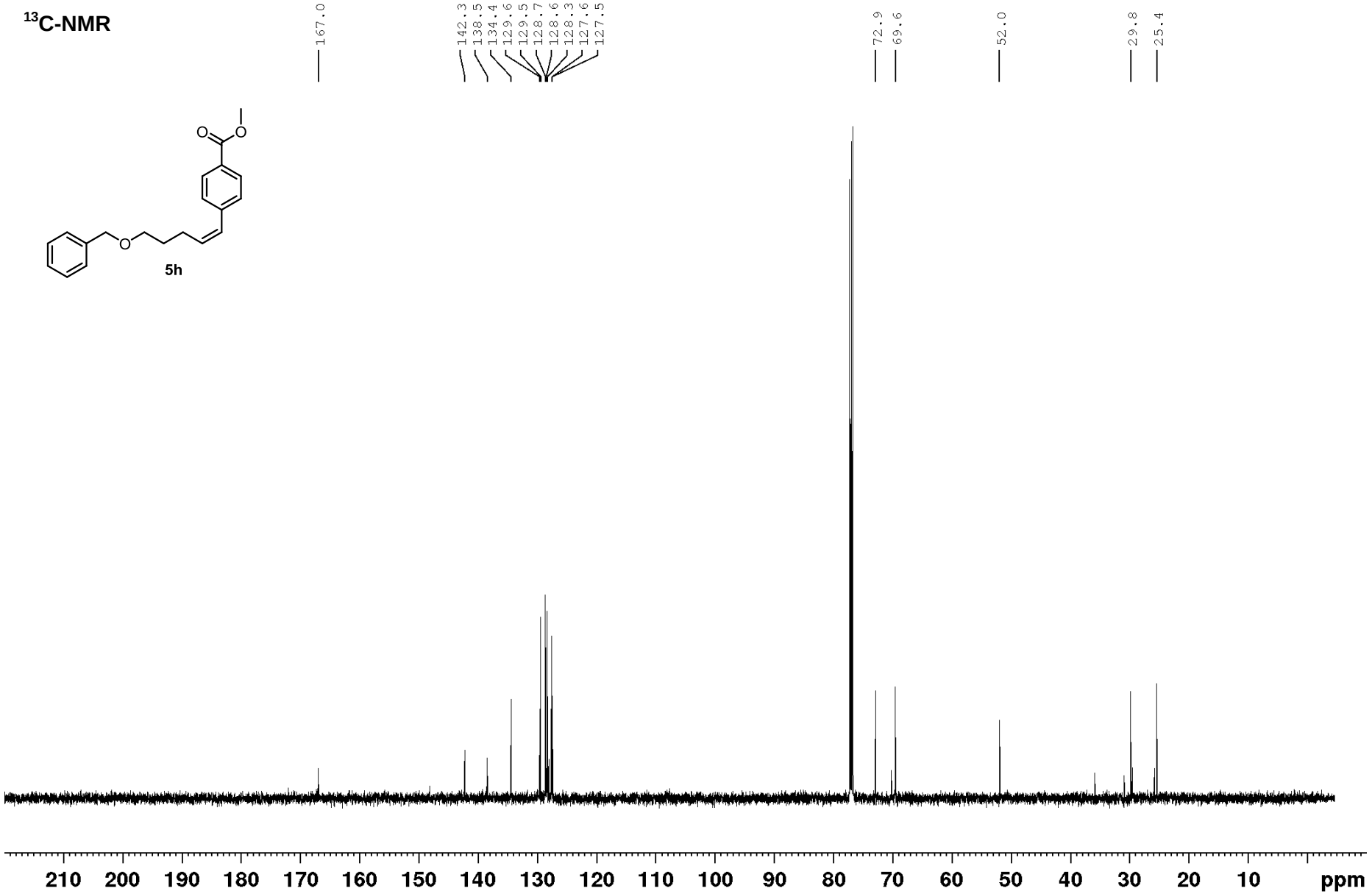
IR spectrum


100
80
60
40
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
Cl
O
5g

^{1}H-NMR

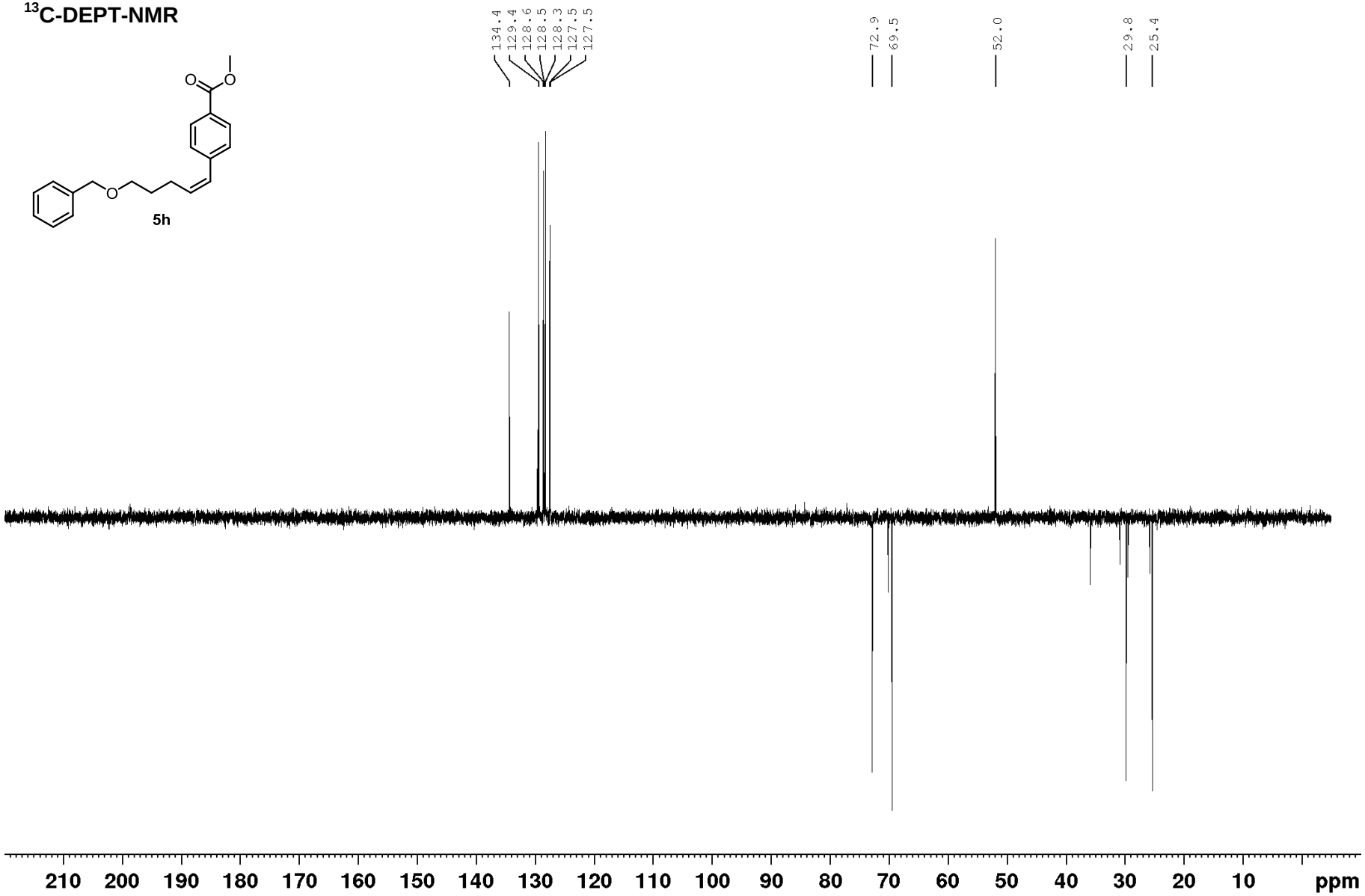

7.91
7.90
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
6.39
6.37
5.72
5.71
5.70
5.69
5.68
5.67
4.39
3.84
3.43
3.42
3.41
2.40
2.39
2.38
2.38
2.37
2.36
2.35
2.35
1.74
1.72
1.71
1.69
1.68
5h
2.00
7.86
1.02
1.03
2.03
3.02
2.08
2.08
2.13
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C-NMR

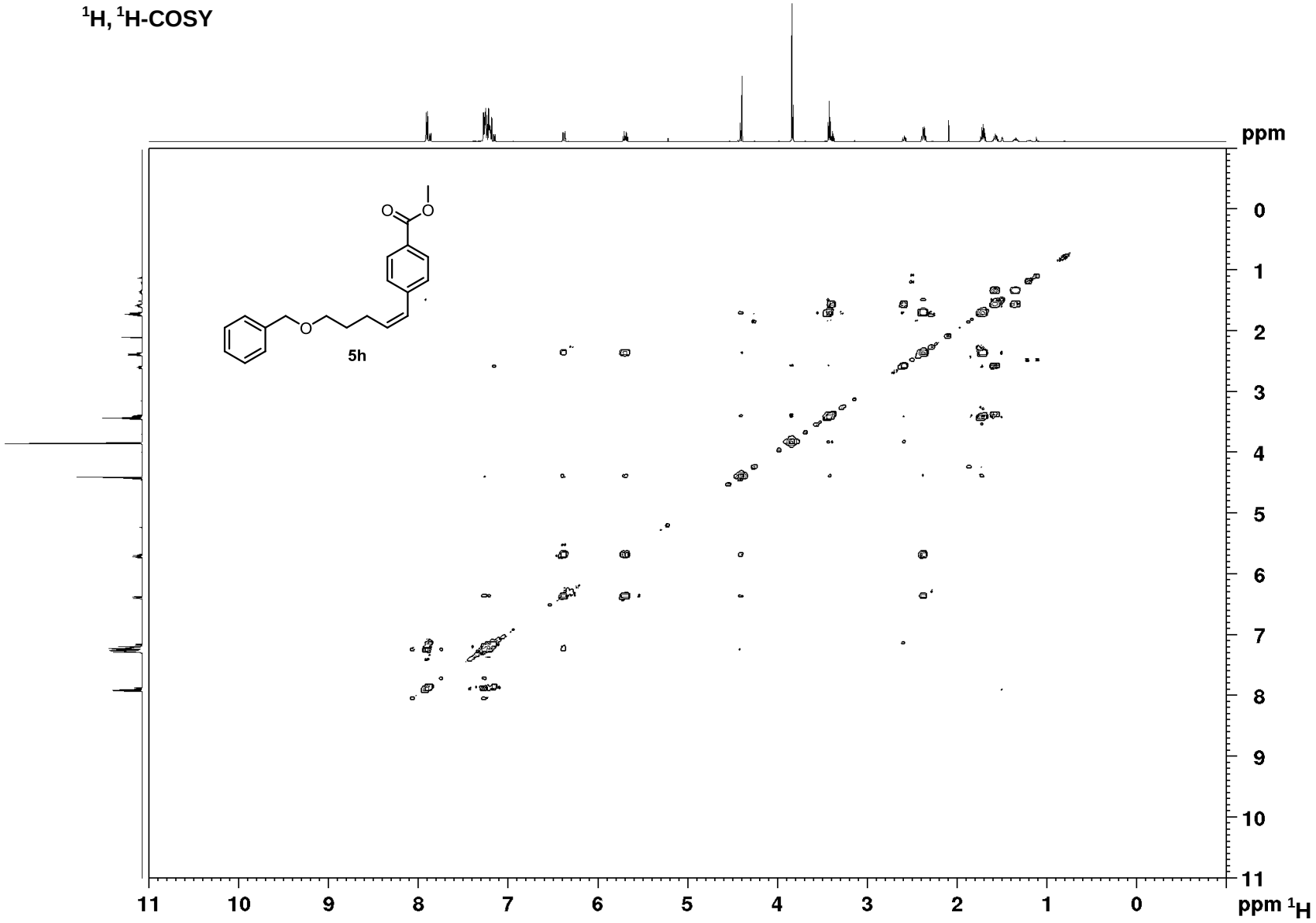

167.0
142.3
138.5
134.4
129.6
129.5
128.7
128.6
128.3
127.6
127.5
72.9
69.6
52.0
29.8
25.4
O
O
O
5h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

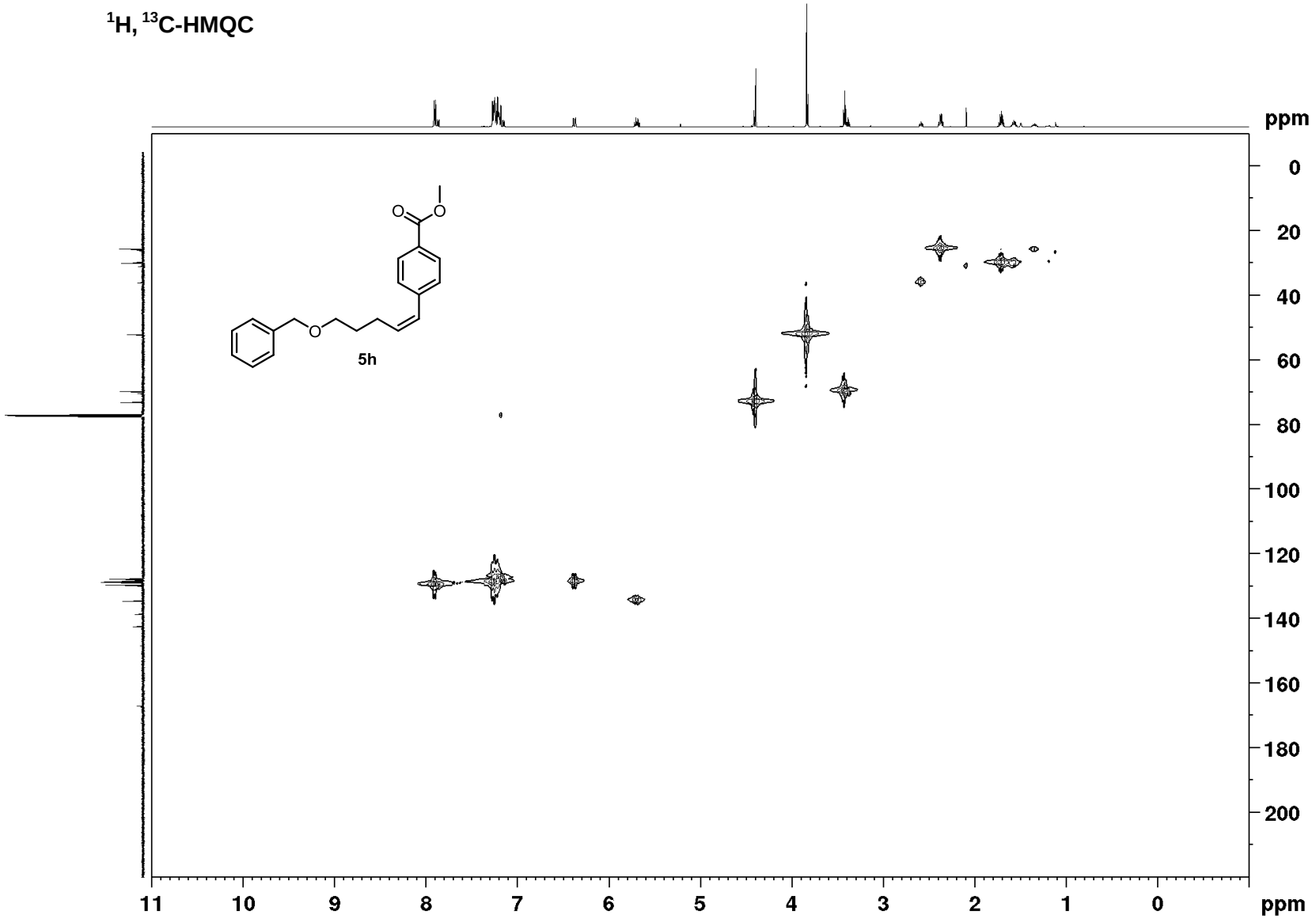
^{13}C-DEPT-NMR

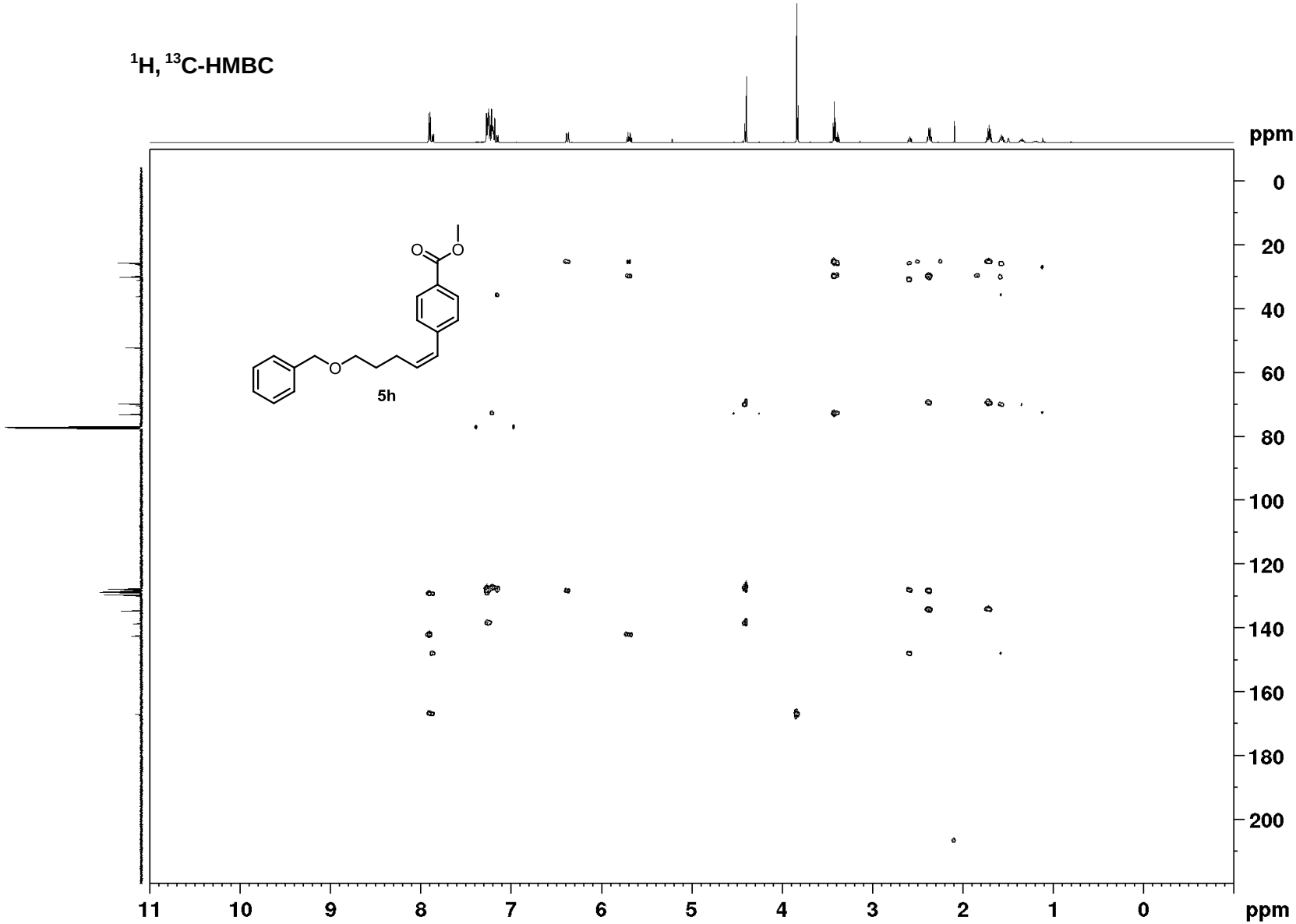
5h



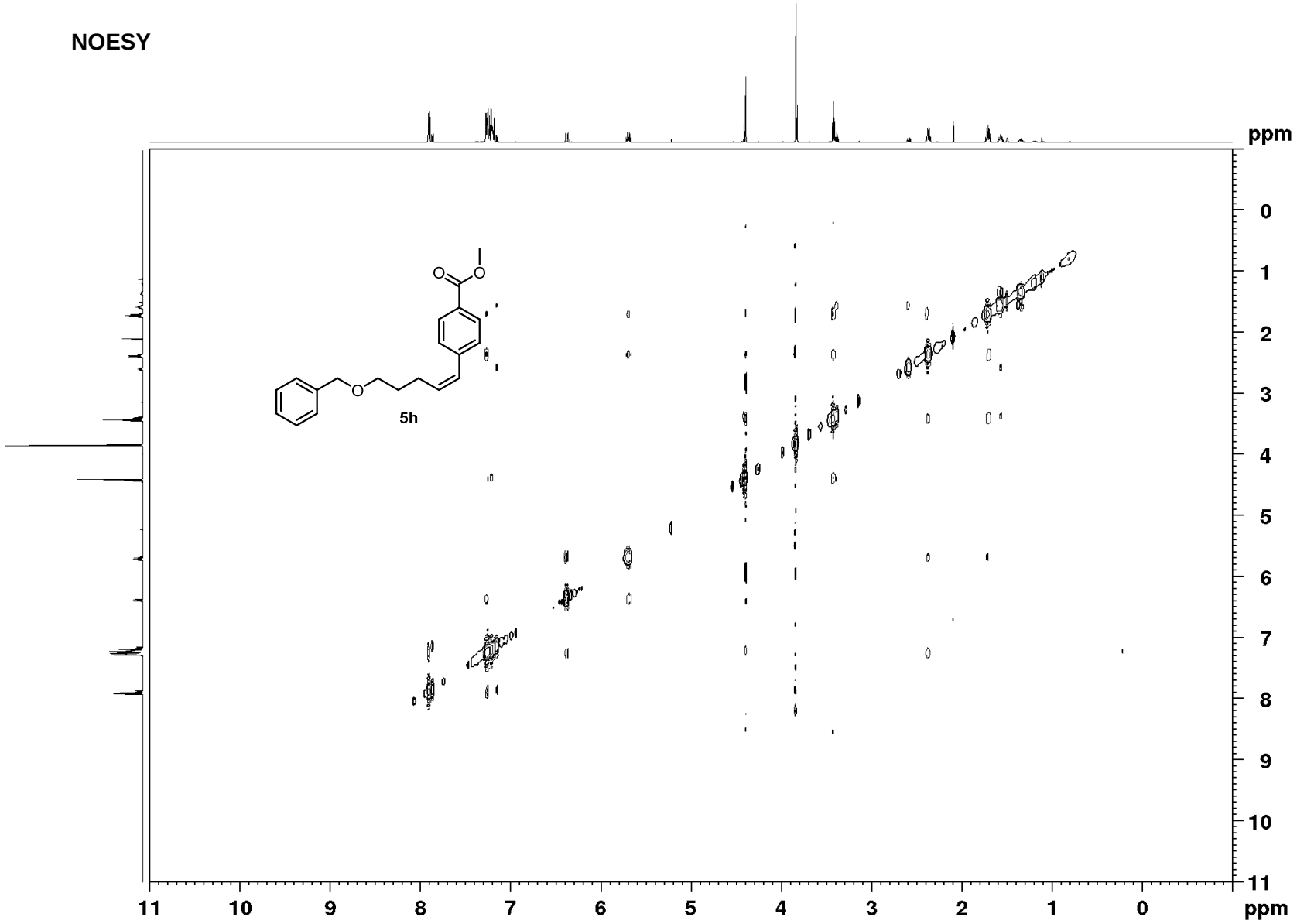
^{1}H, ^{1}H-COSY

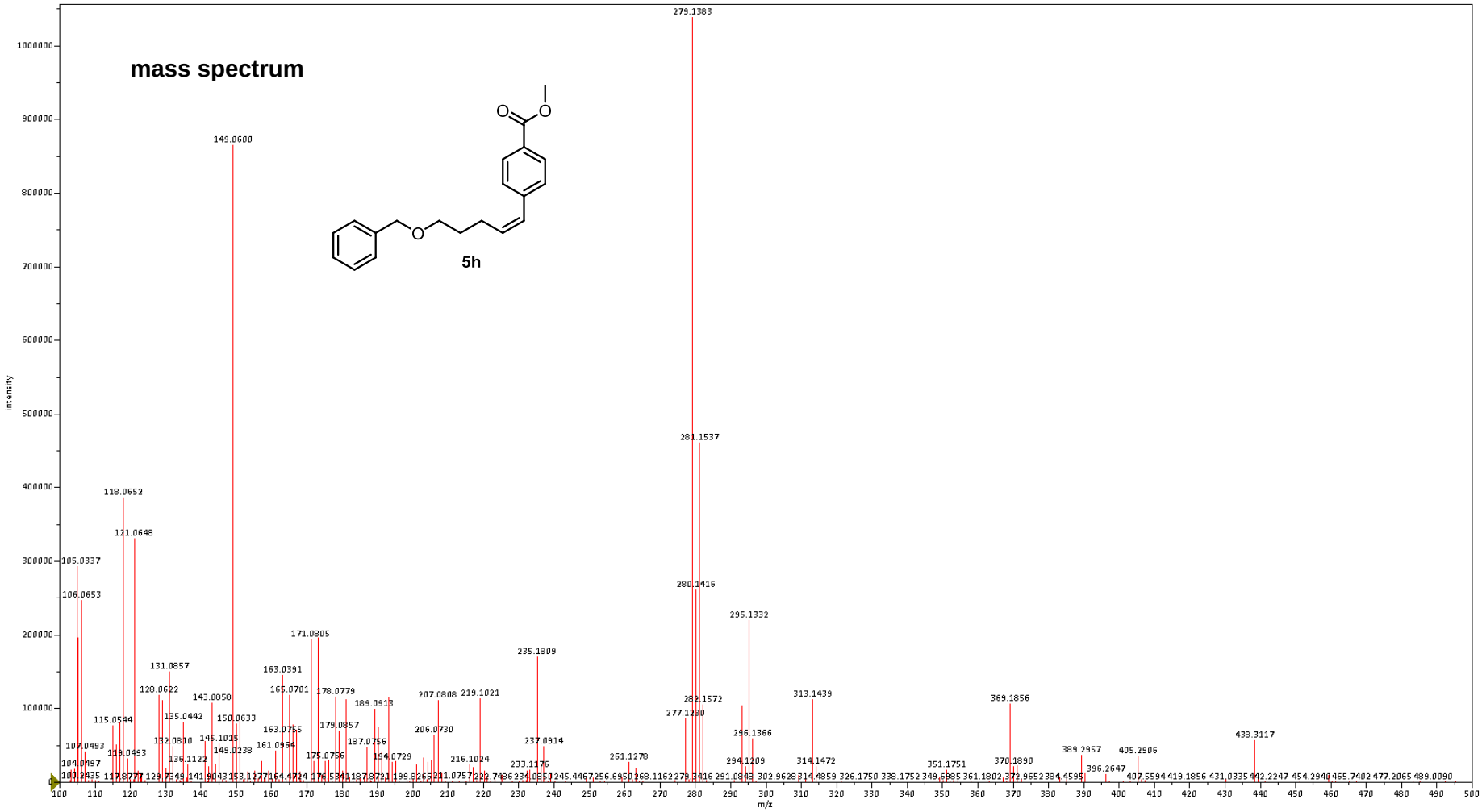



^{1}H, ^{13}C-HMQC
ppm
0
20
40
60
80
100
120
140
160
180
200
O
O
O
5h
11
10
9
8
7
6
5
4
3
2
1
0
ppm

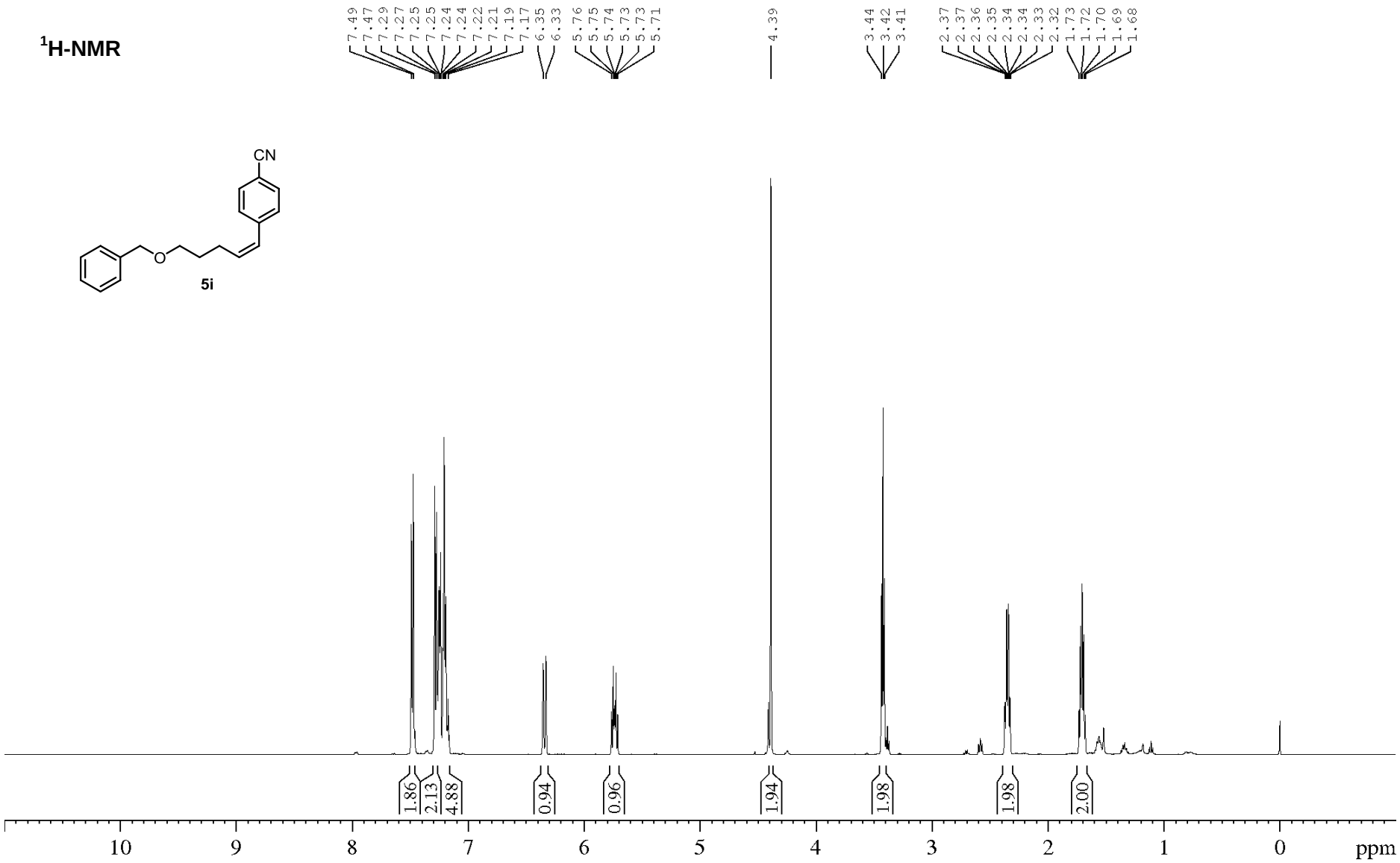

^{1}H, ^{13}C-HMBC
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm
5h

NOESY

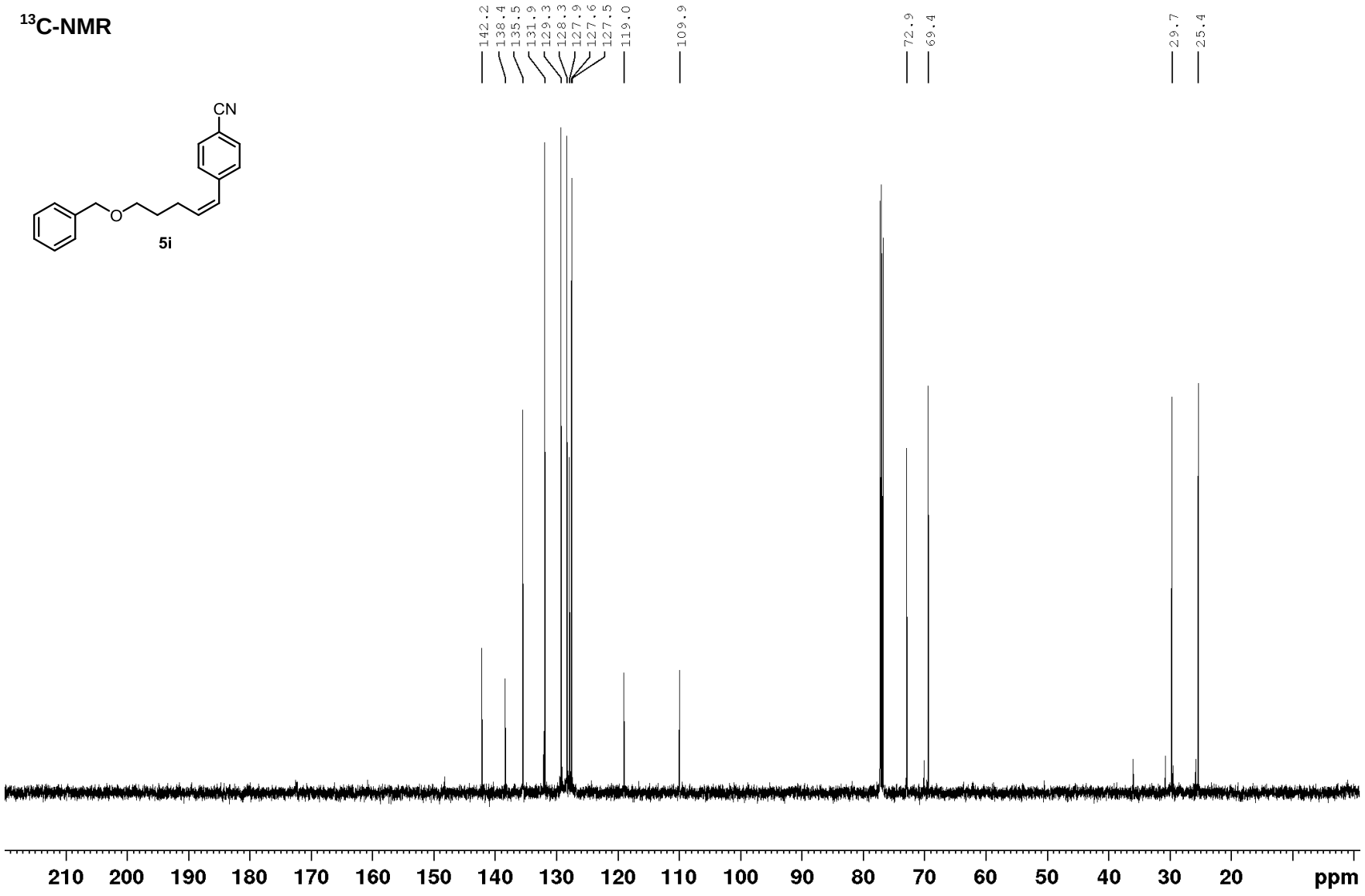



mass spectrum
5h
intensity
m/z
279.1383
149.0600
281.1537
118.0652
121.0648
105.0337
106.0653
280.1416
295.1332
171.0805
235.1809
131.0857
163.0391
165.0701
178.0779
207.0808
219.1021
313.1439
369.1856
438.3117
389.2957
405.2906

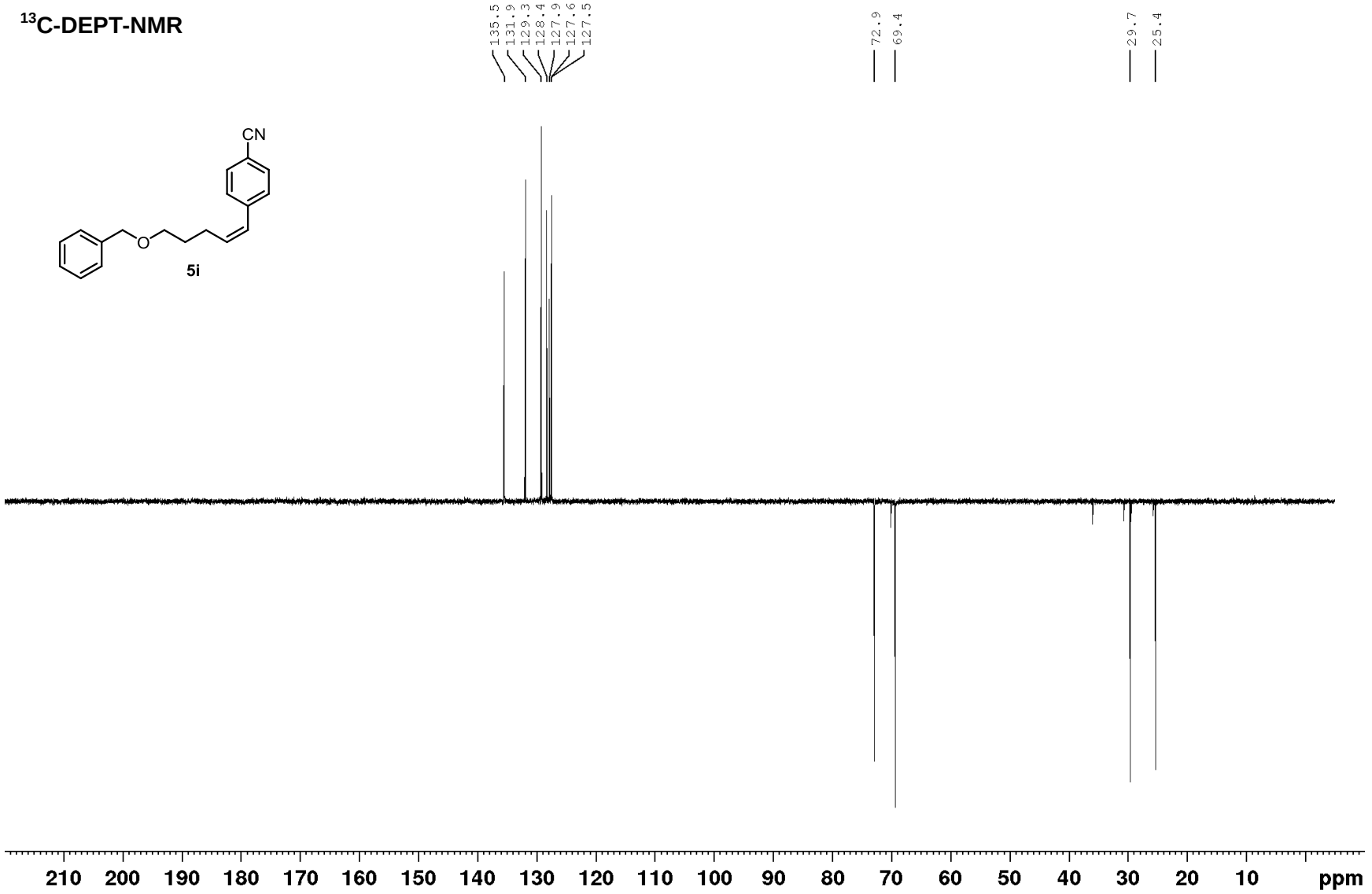
^{1}H-NMR


7.49
7.47
7.29
7.27
7.25
7.25
7.24
7.24
7.22
7.21
7.19
7.17
6.35
6.33
5.76
5.75
5.74
5.73
5.73
5.71
4.39
3.44
3.42
3.41
2.37
2.37
2.36
2.35
2.34
2.34
2.33
2.32
1.73
1.72
1.70
1.69
1.68
CN
O
5i
1.86
2.13
4.88
0.94
0.96
1.94
1.98
1.98
2.00
10
9
8
7
6
5
4
3
2
1
0
ppm

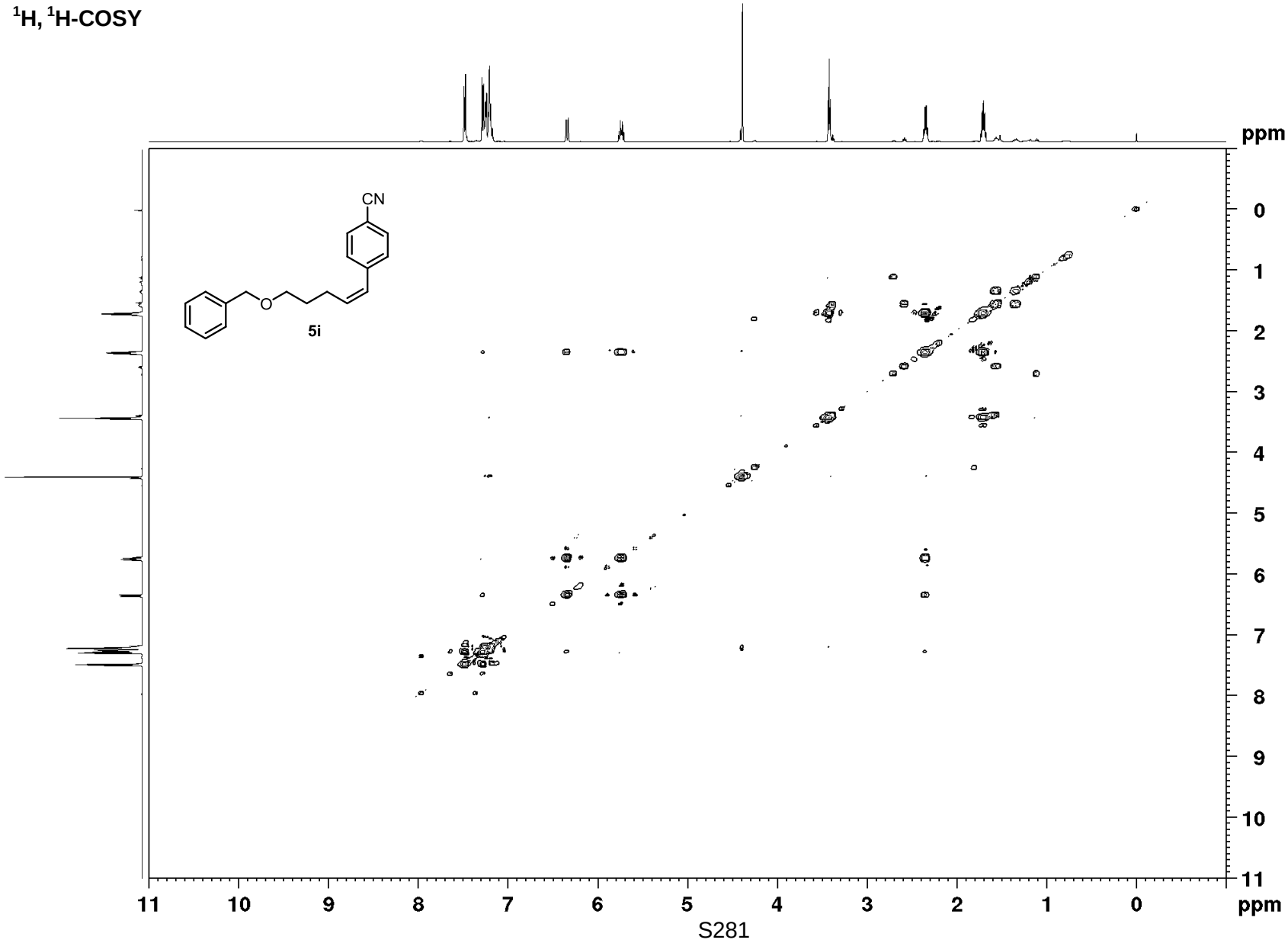
^{13}C-NMR


142.2
138.4
135.5
131.9
129.3
128.3
127.9
127.6
127.5
119.0
109.9
72.9
69.4
29.7
25.4
CN
O
5i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

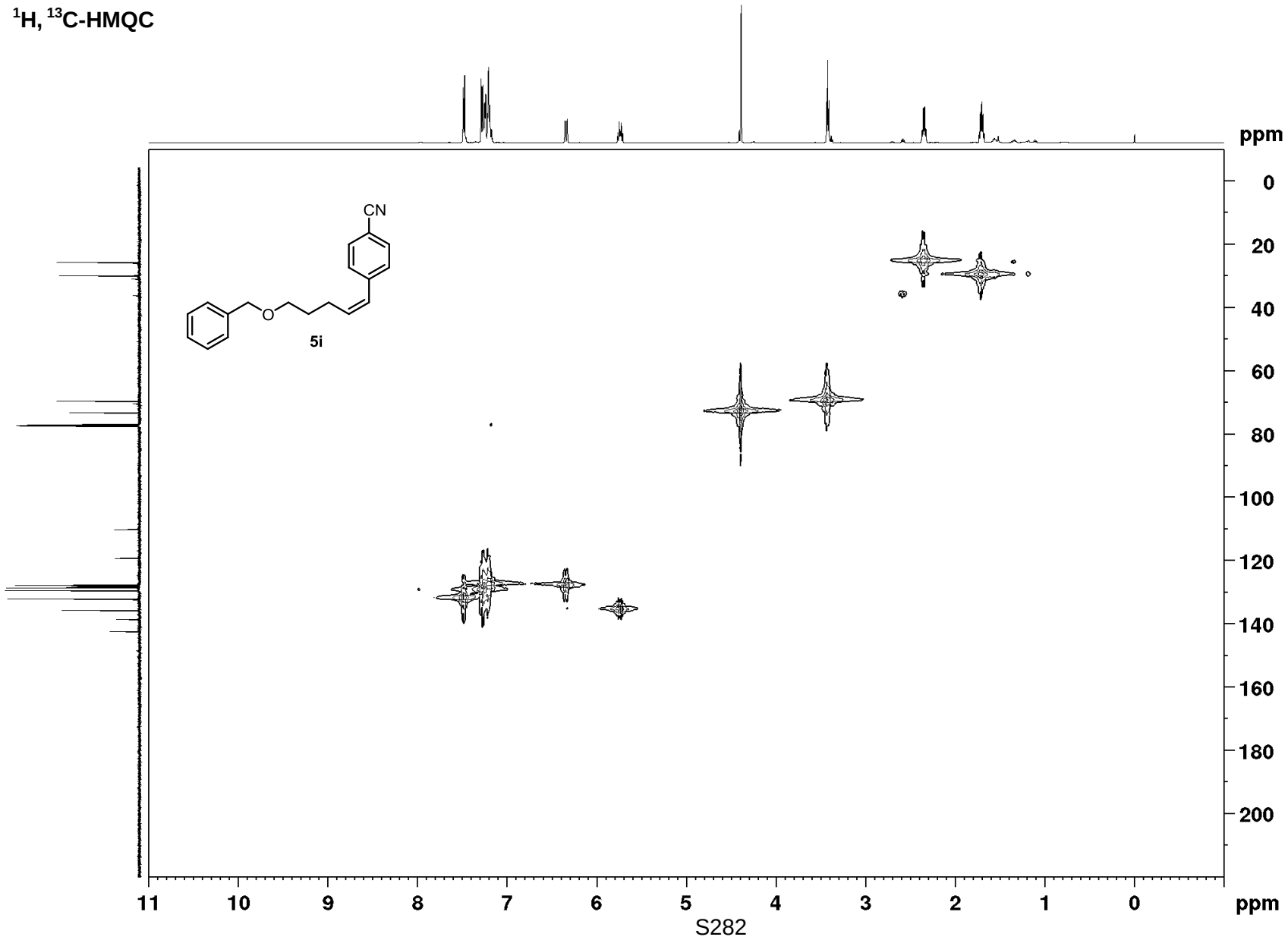
^{13}C-DEPT-NMR


135.5
131.9
129.3
128.4
127.9
127.6
127.5
72.9
69.4
29.7
25.4
CN
O
5i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

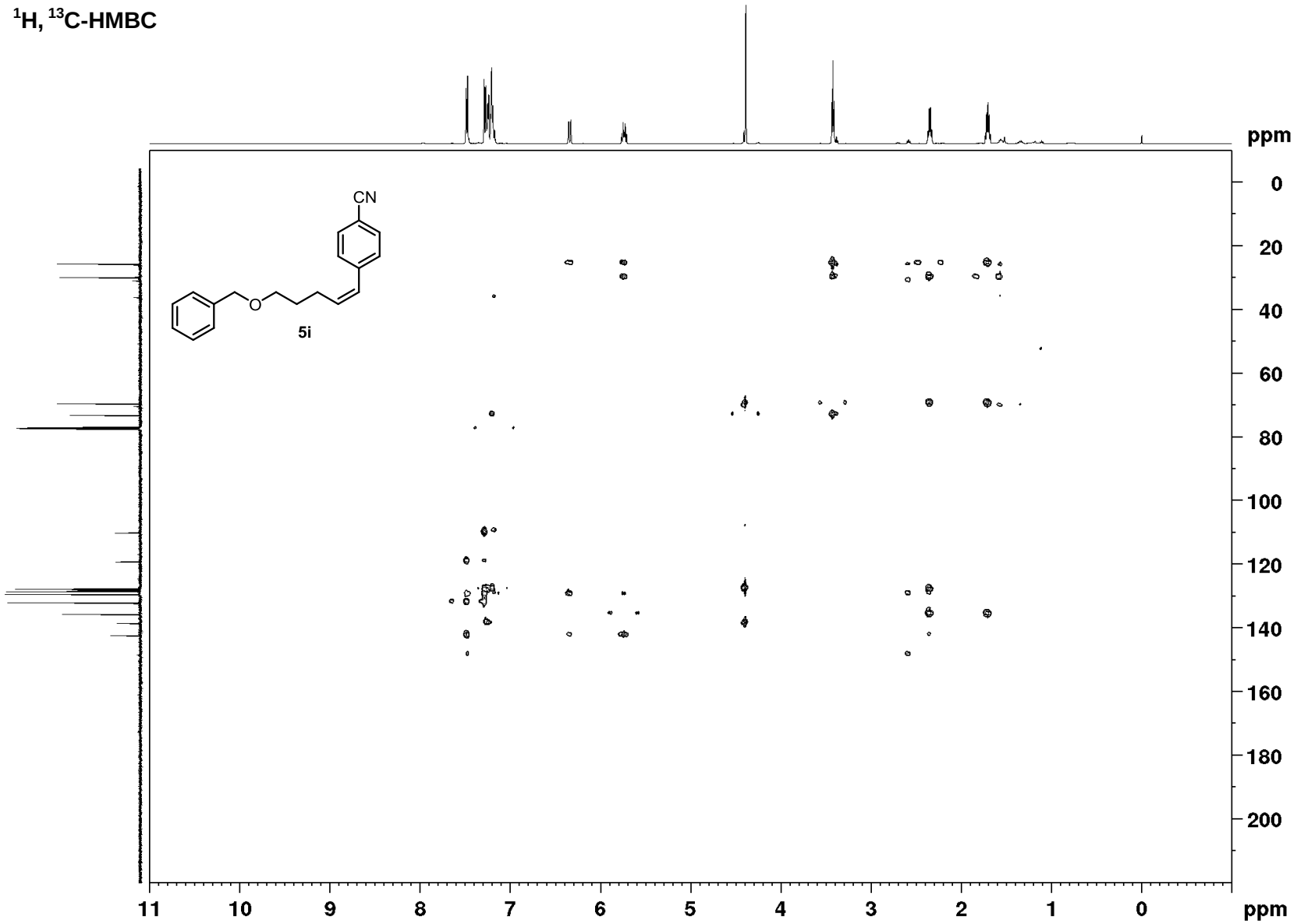
^{1}H, ^{1}H-COSY



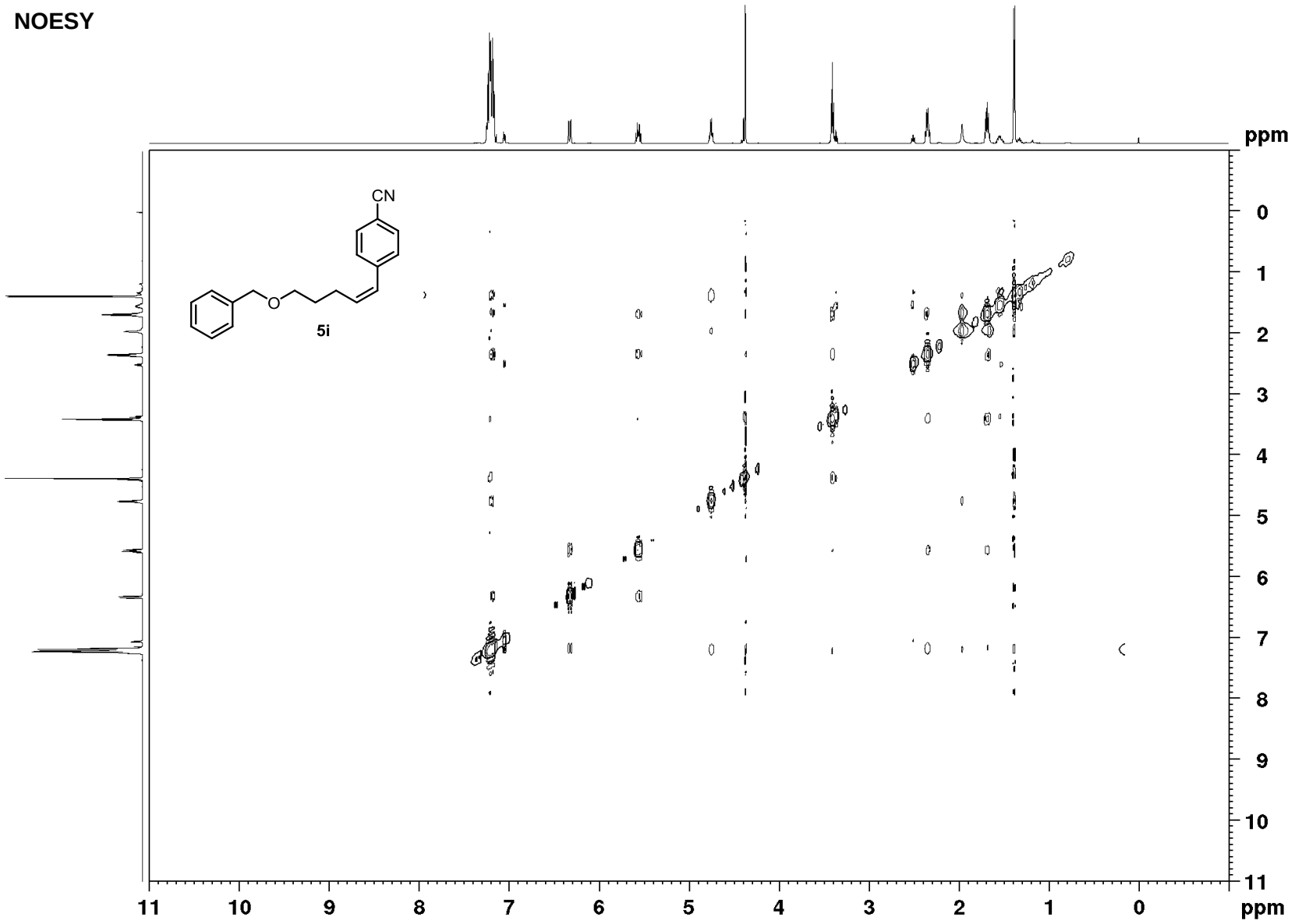
^{1}H, ^{13}C-HMQC


CN
O
5i
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

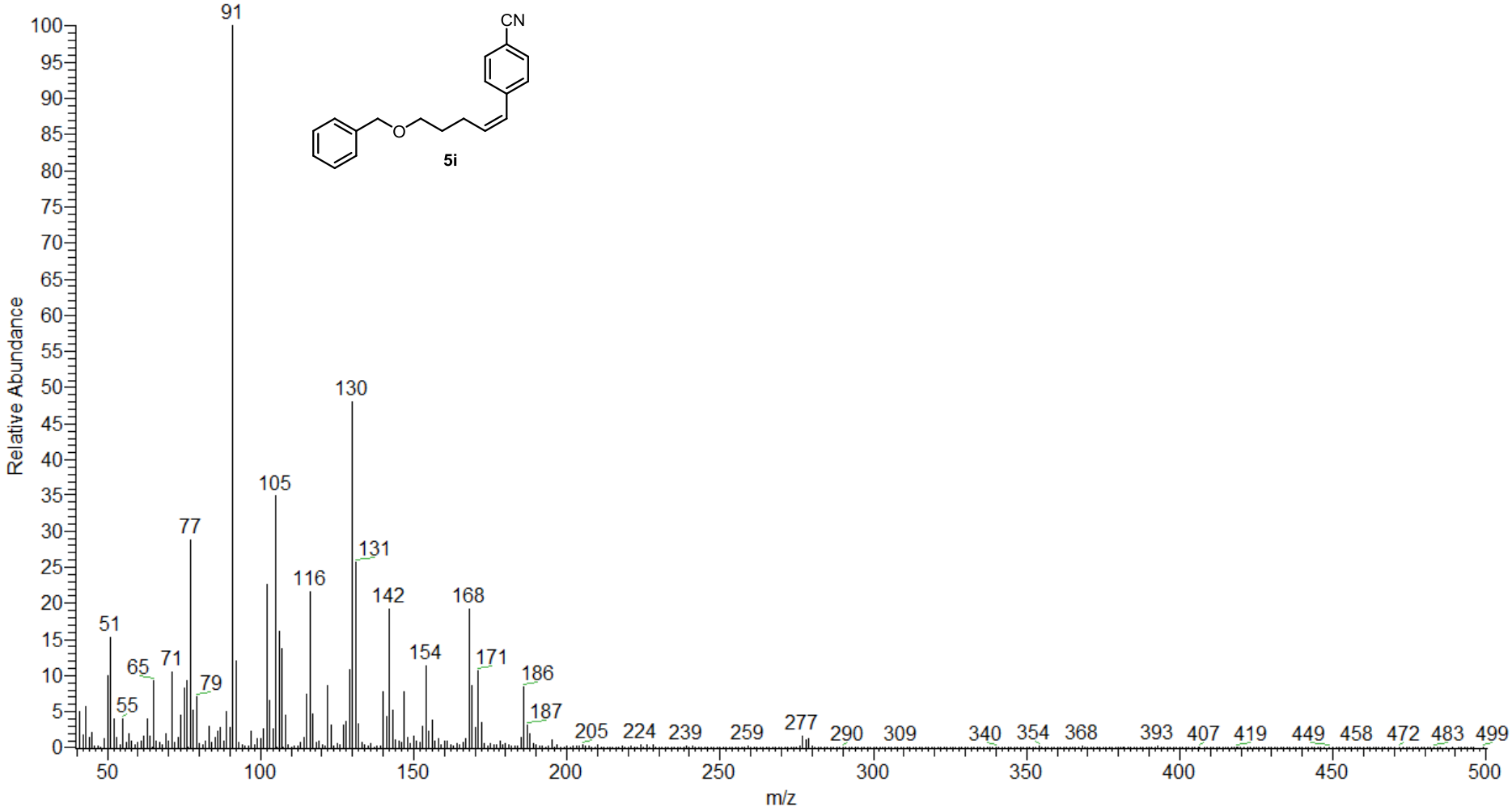
^{1}H, ^{13}C-HMBC


CN
O
5i
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

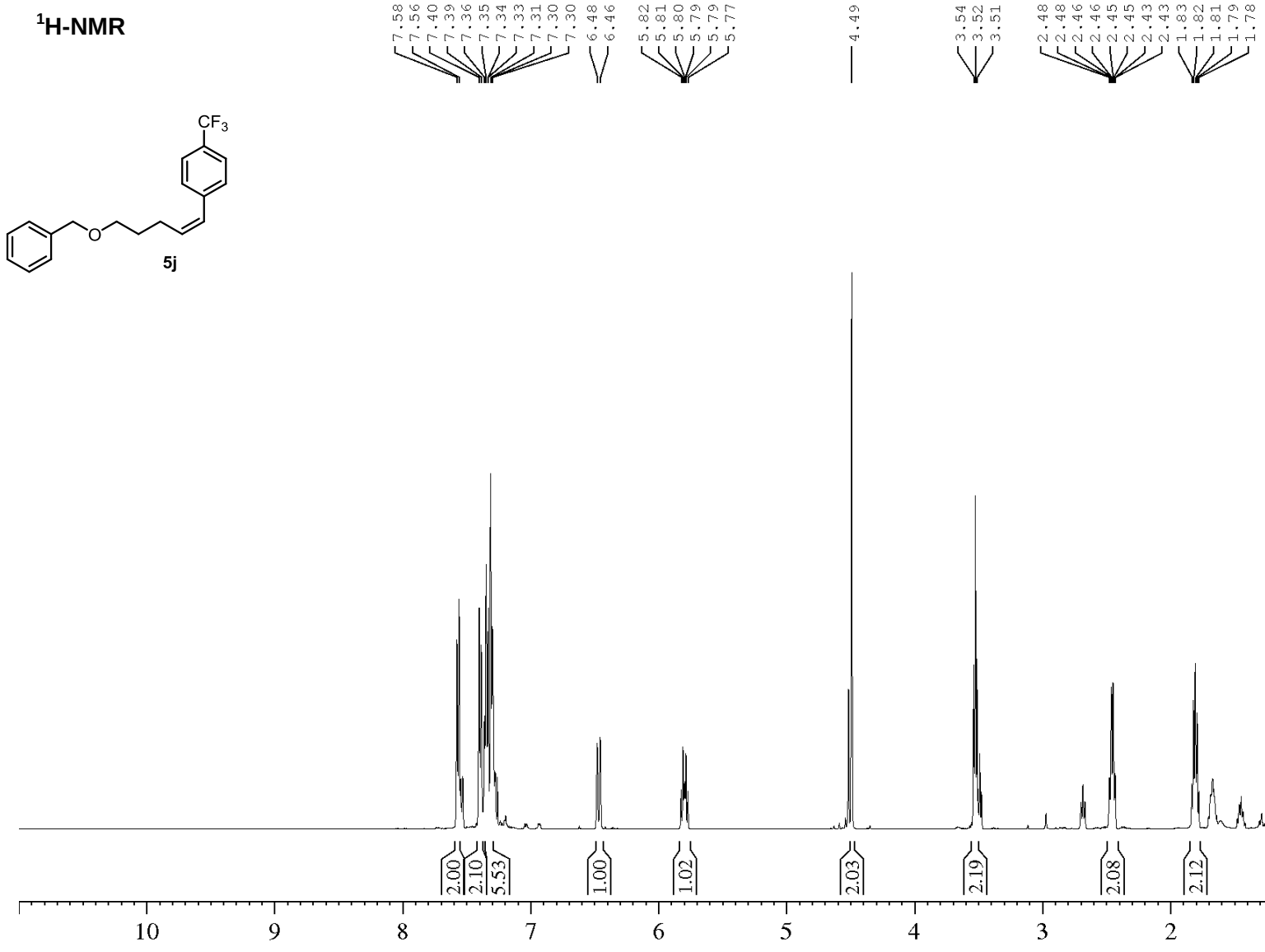
NOESY



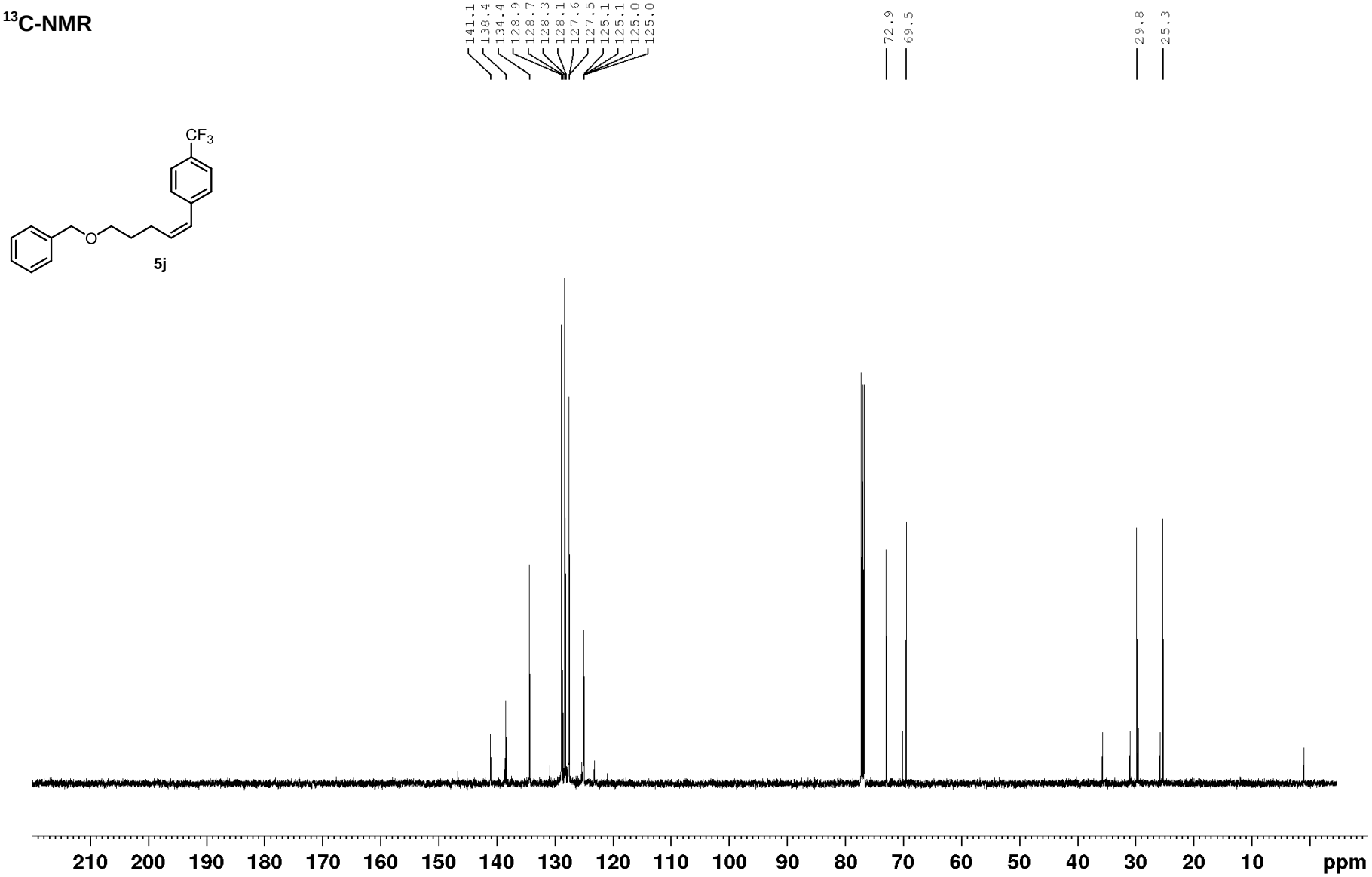
mass spectrum



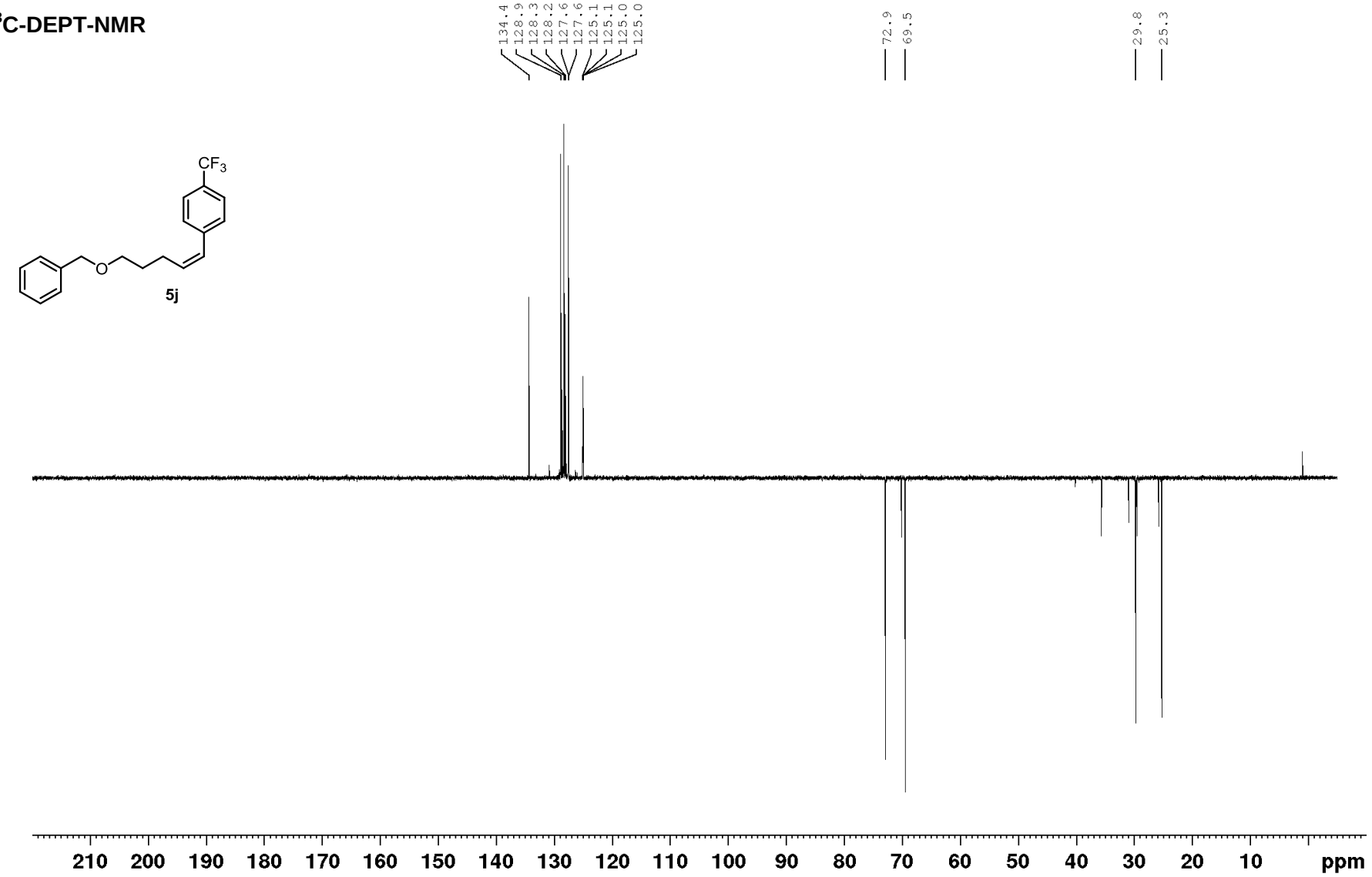
^{1}H-NMR


7.58
7.56
7.40
7.39
7.36
7.35
7.34
7.33
7.31
7.30
7.30
6.48
6.46
5.82
5.81
5.80
5.79
5.79
5.77
4.49
3.54
3.52
3.51
2.48
2.48
2.46
2.46
2.45
2.45
2.43
2.43
1.83
1.82
1.81
1.79
1.78
CF3
O
5j
2.00
2.10
5.53
1.00
1.02
2.03
2.19
2.08
2.12
10
9
8
7
6
5
4
3
2
1
0
ppm

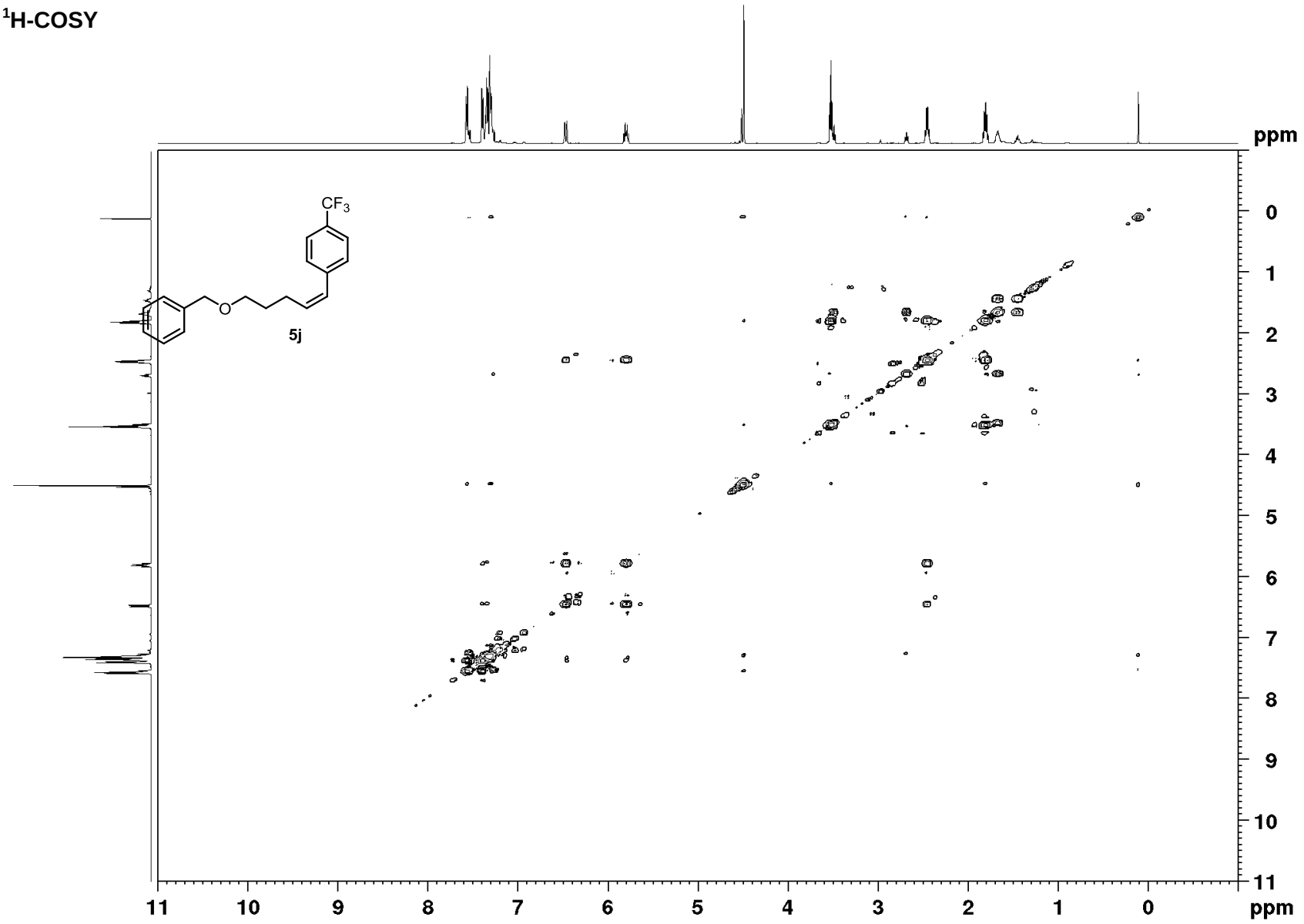
^{13}C-NMR


141.1
138.4
134.4
128.9
128.7
128.3
128.1
127.6
127.5
125.1
125.1
125.0
125.0
72.9
69.5
29.8
25.3
CF3
O
5j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

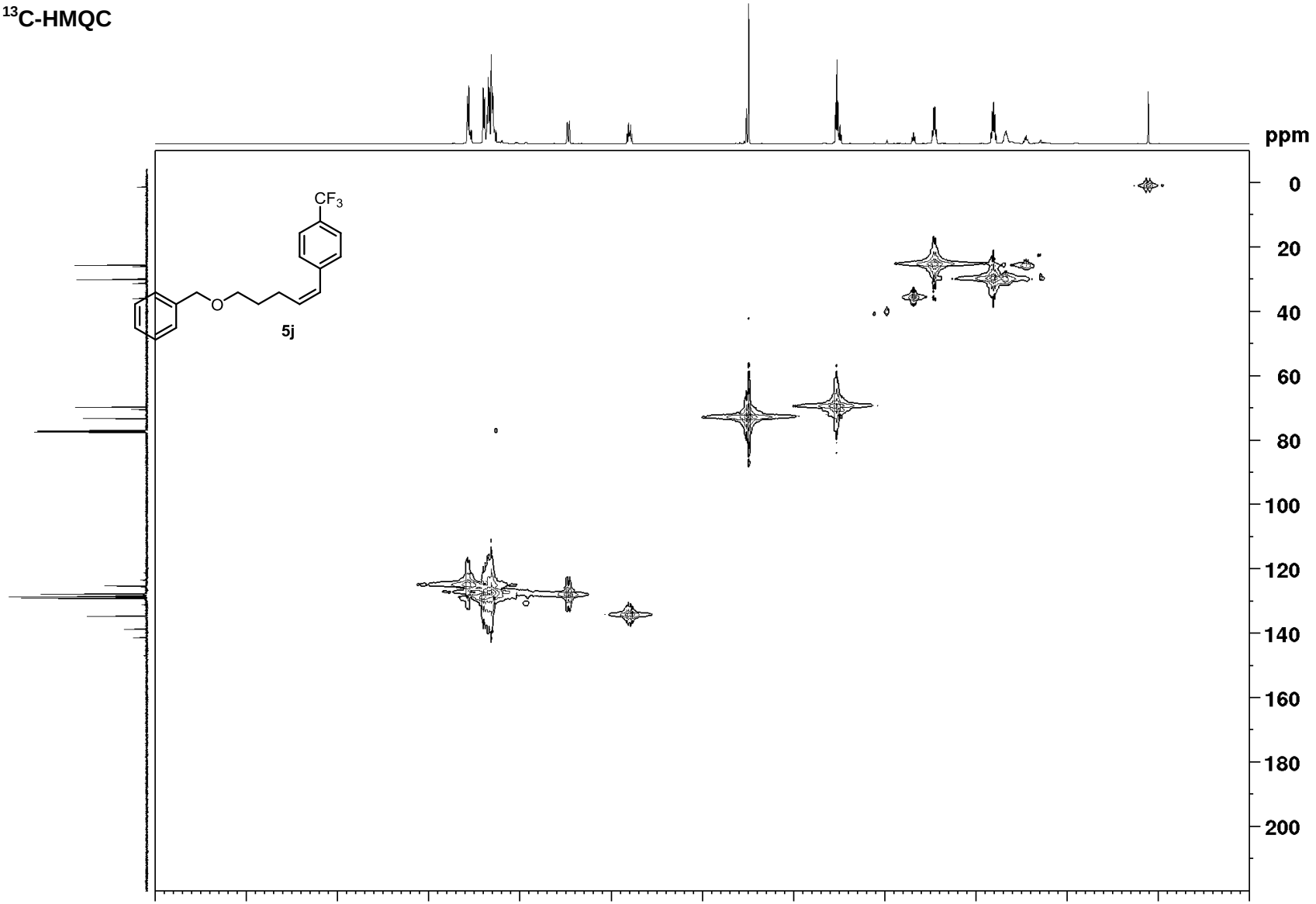
^{13}C-DEPT-NMR


134.4
128.9
128.3
128.2
127.6
127.6
125.1
125.1
125.0
125.0
72.9
69.5
29.8
25.3
CF3
O
5j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

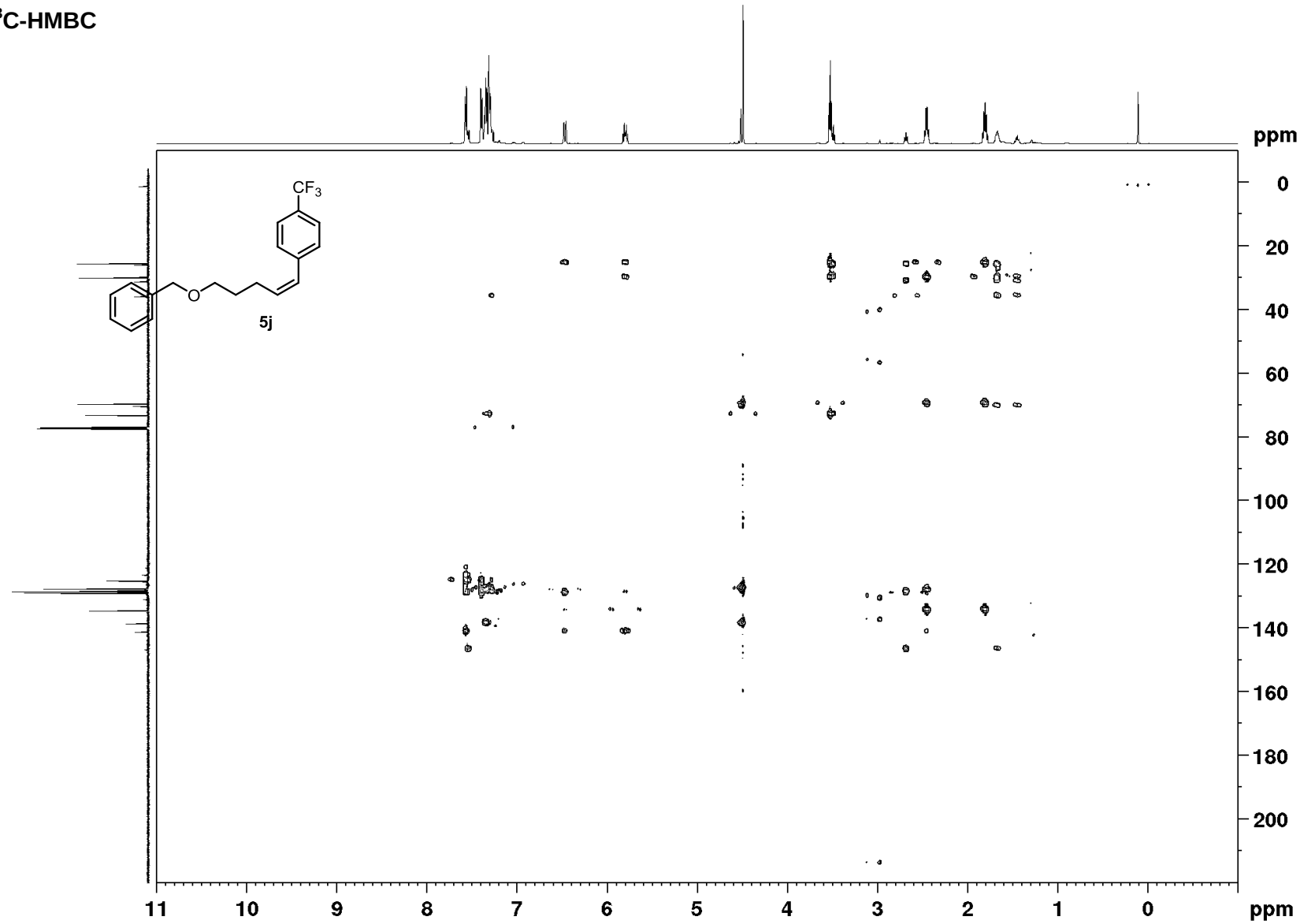
^{1}H, ^{1}H-COSY



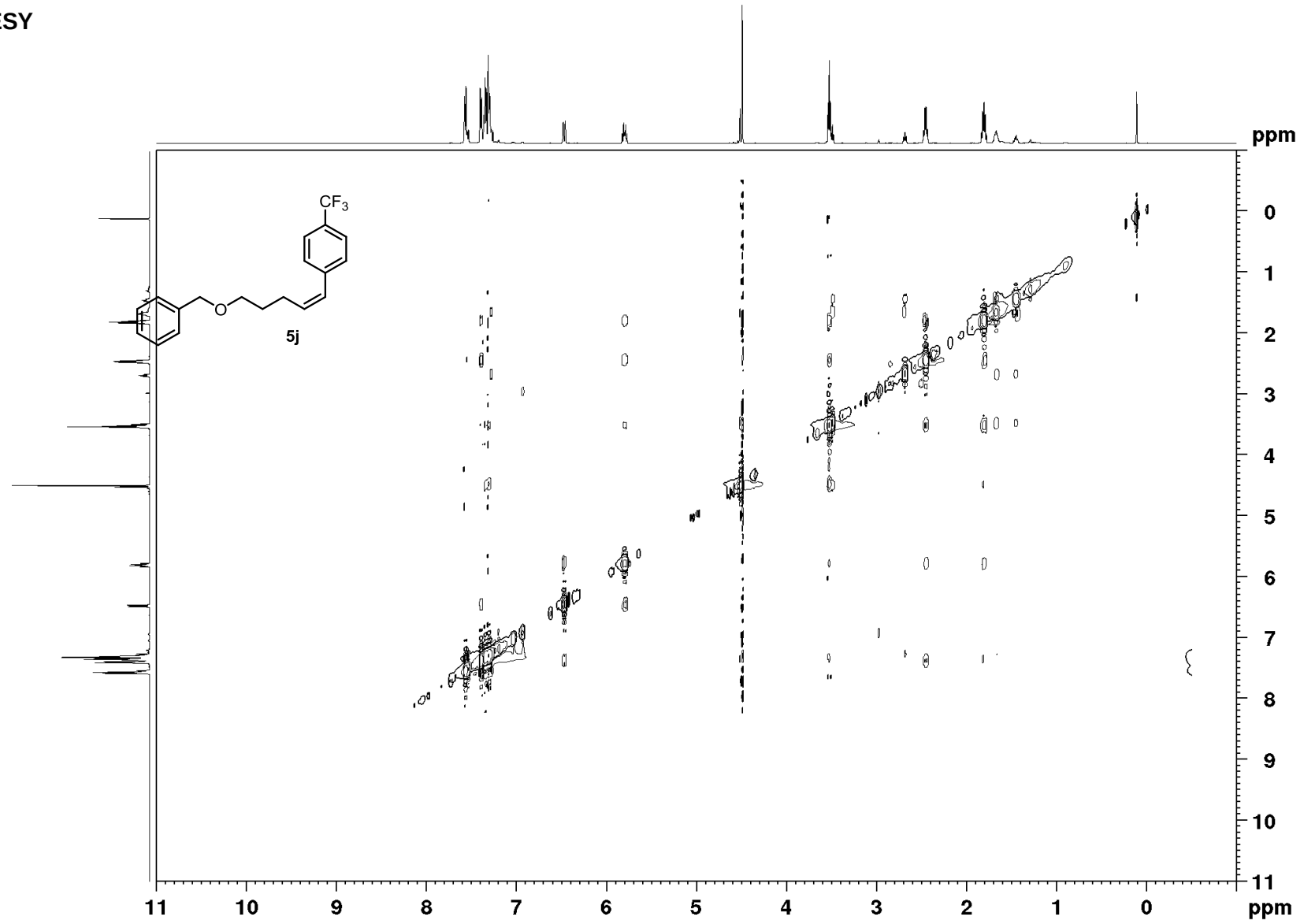
^{1}H, ^{13}C-HMQC


CF3
O
5j
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

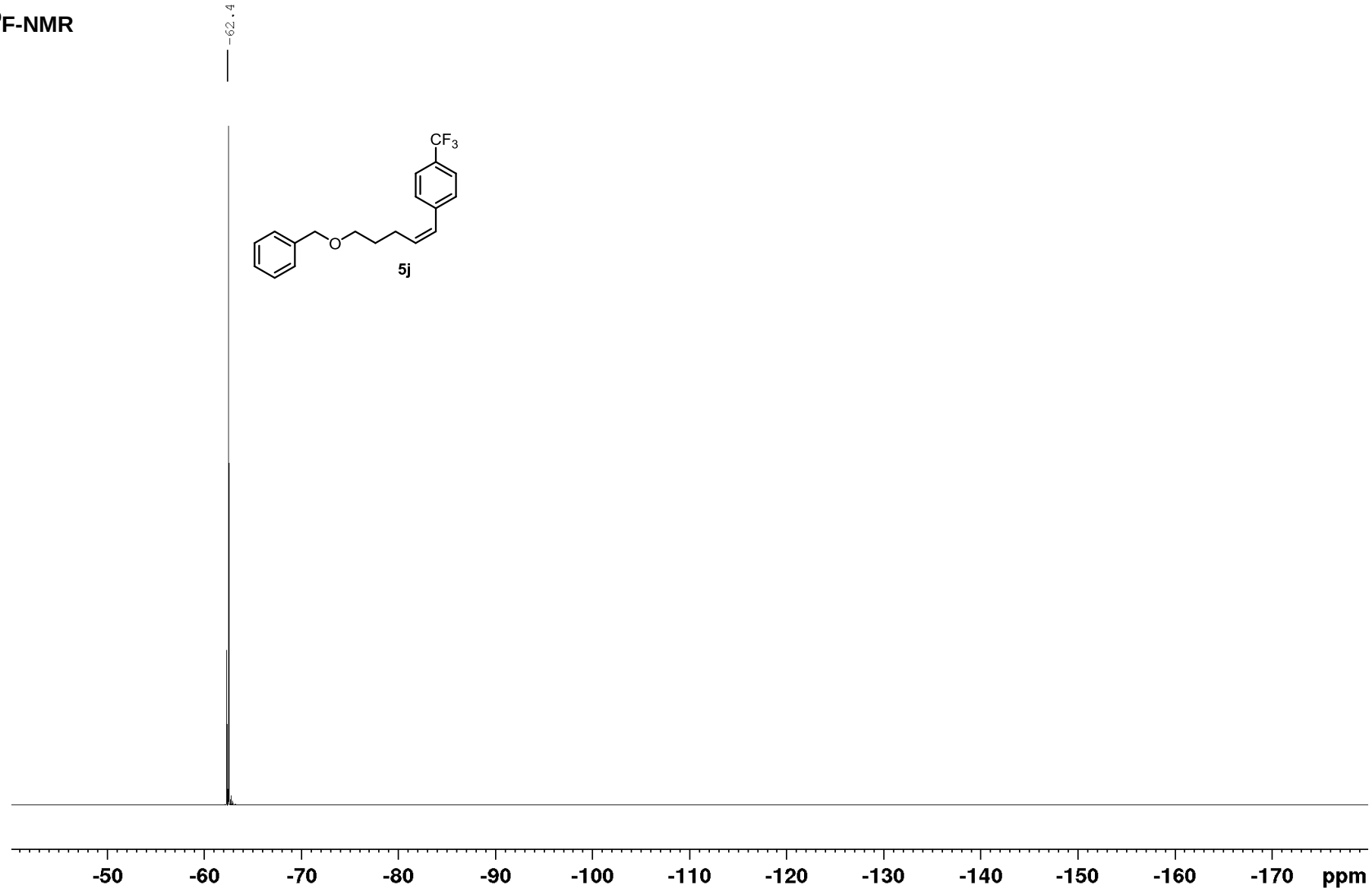
^{1}H, ^{13}C-HMBC


CF3
O
5j
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

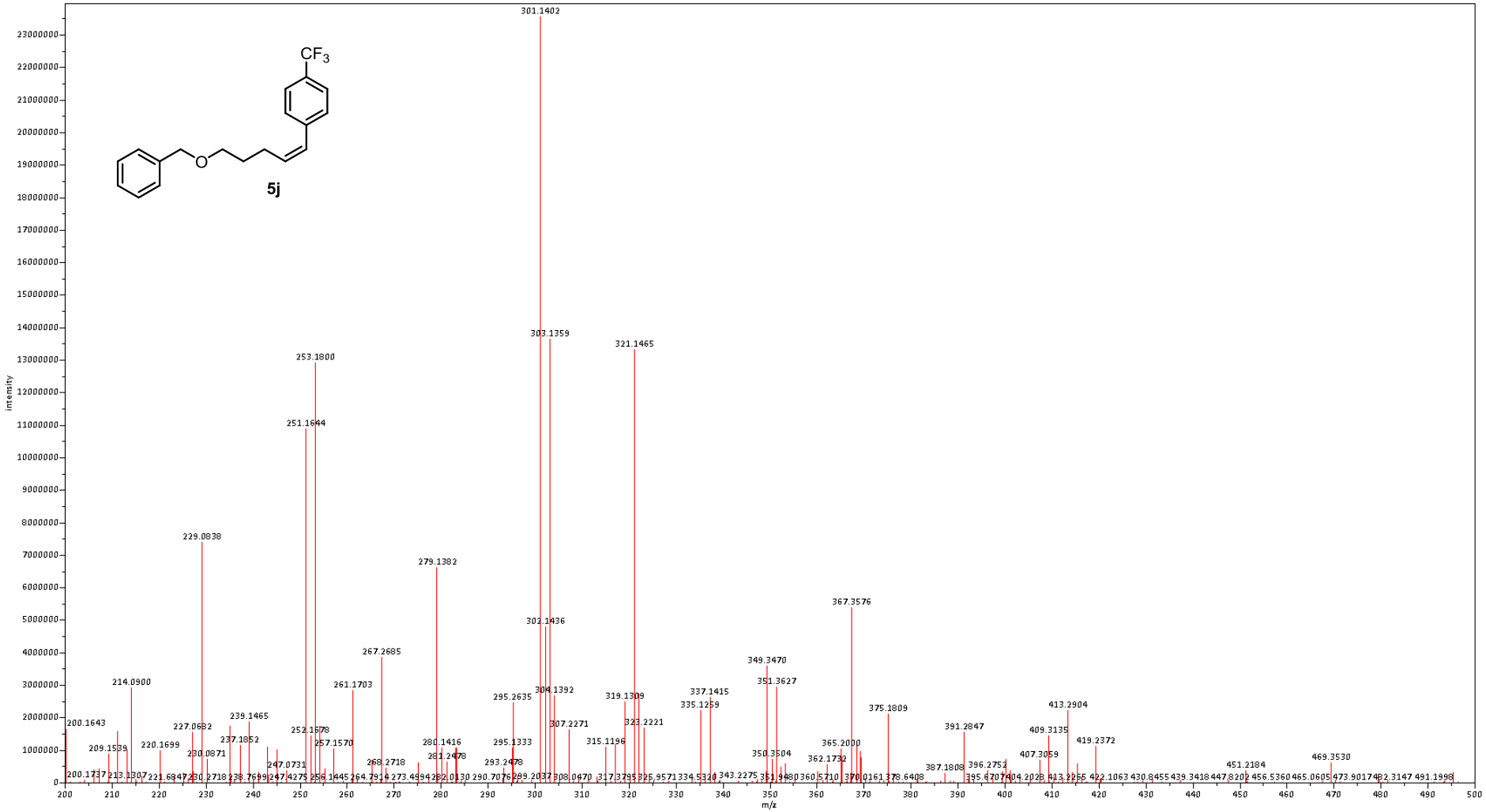
NOESY



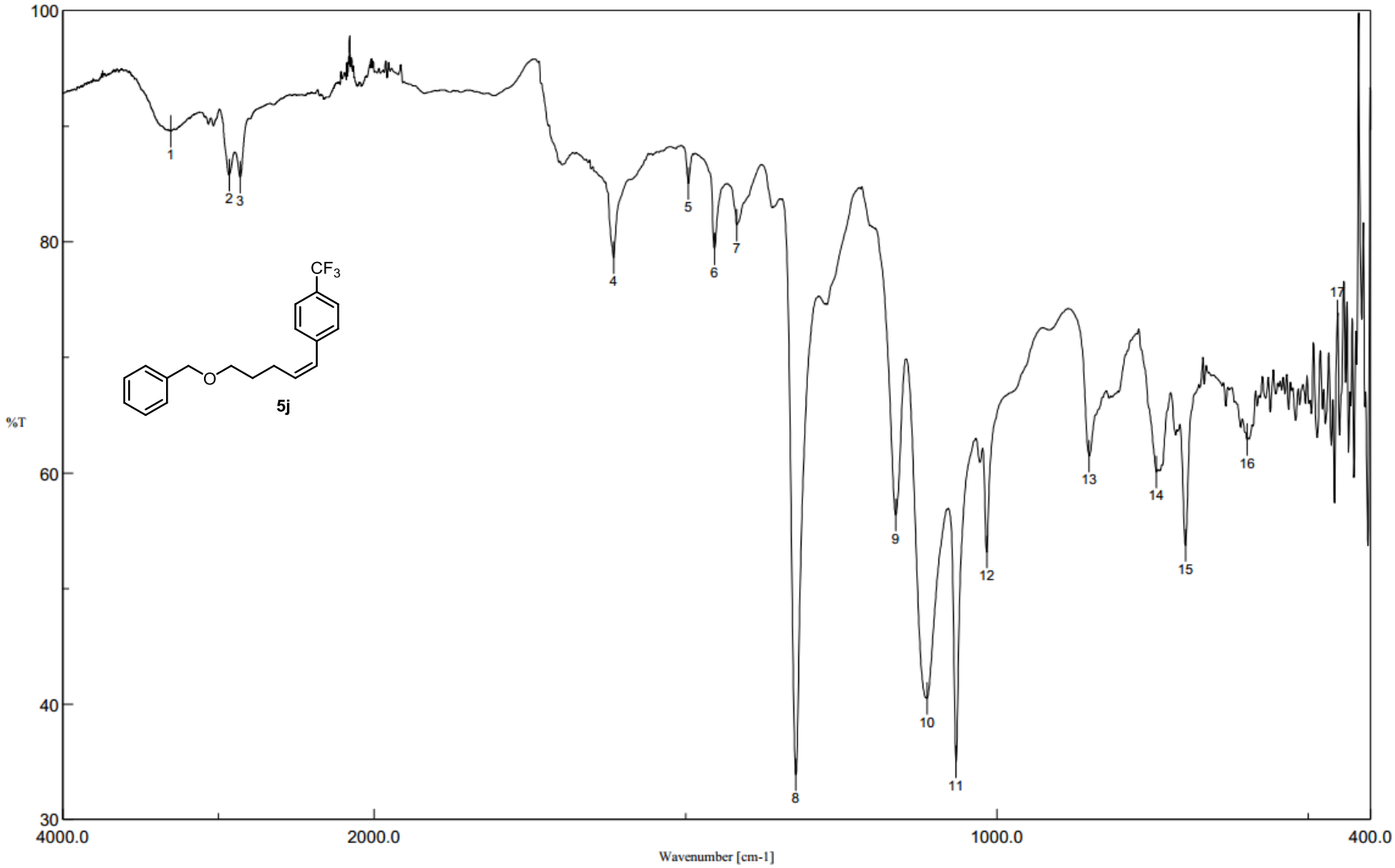
^{19}F-NMR



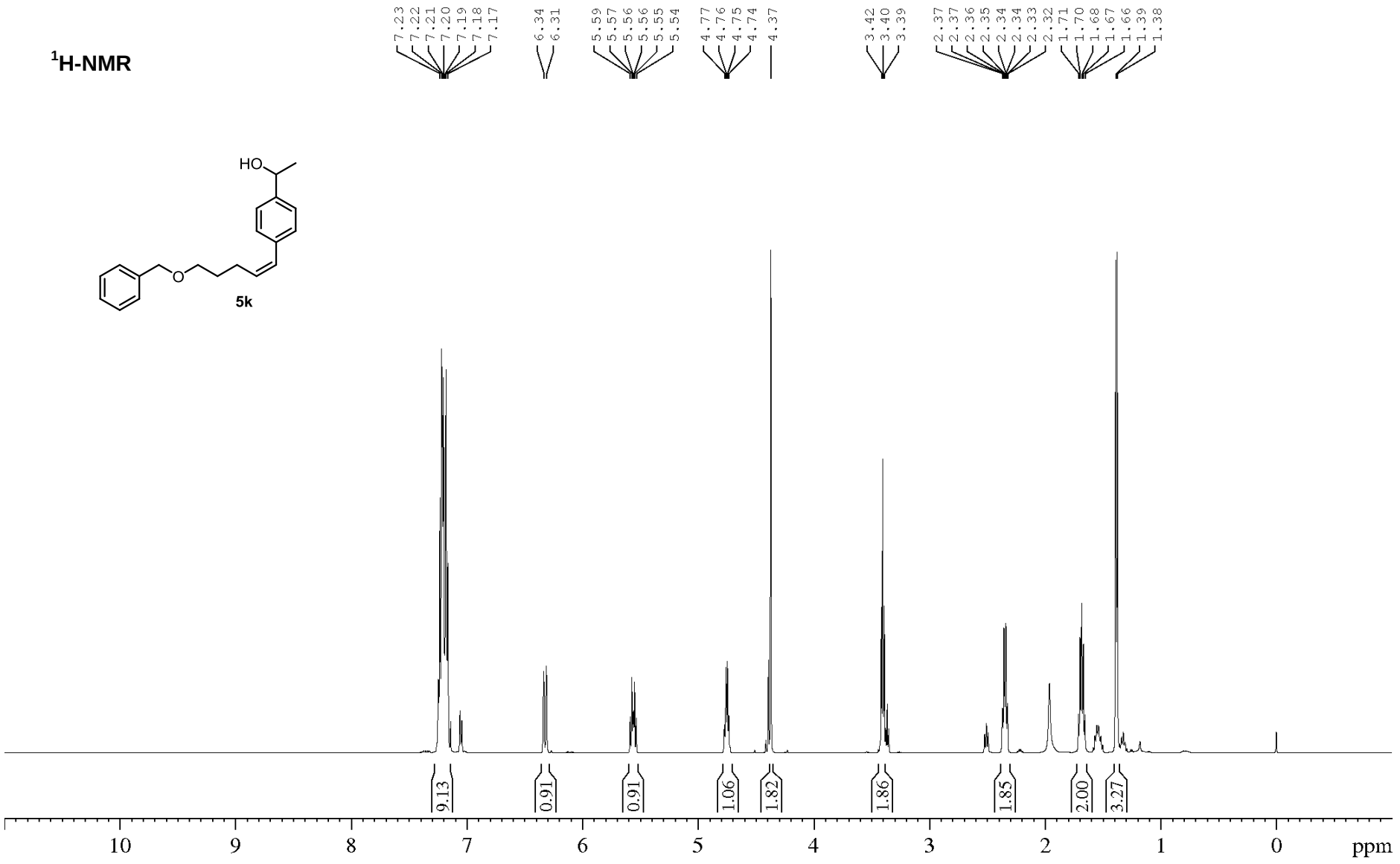
mass spectrum



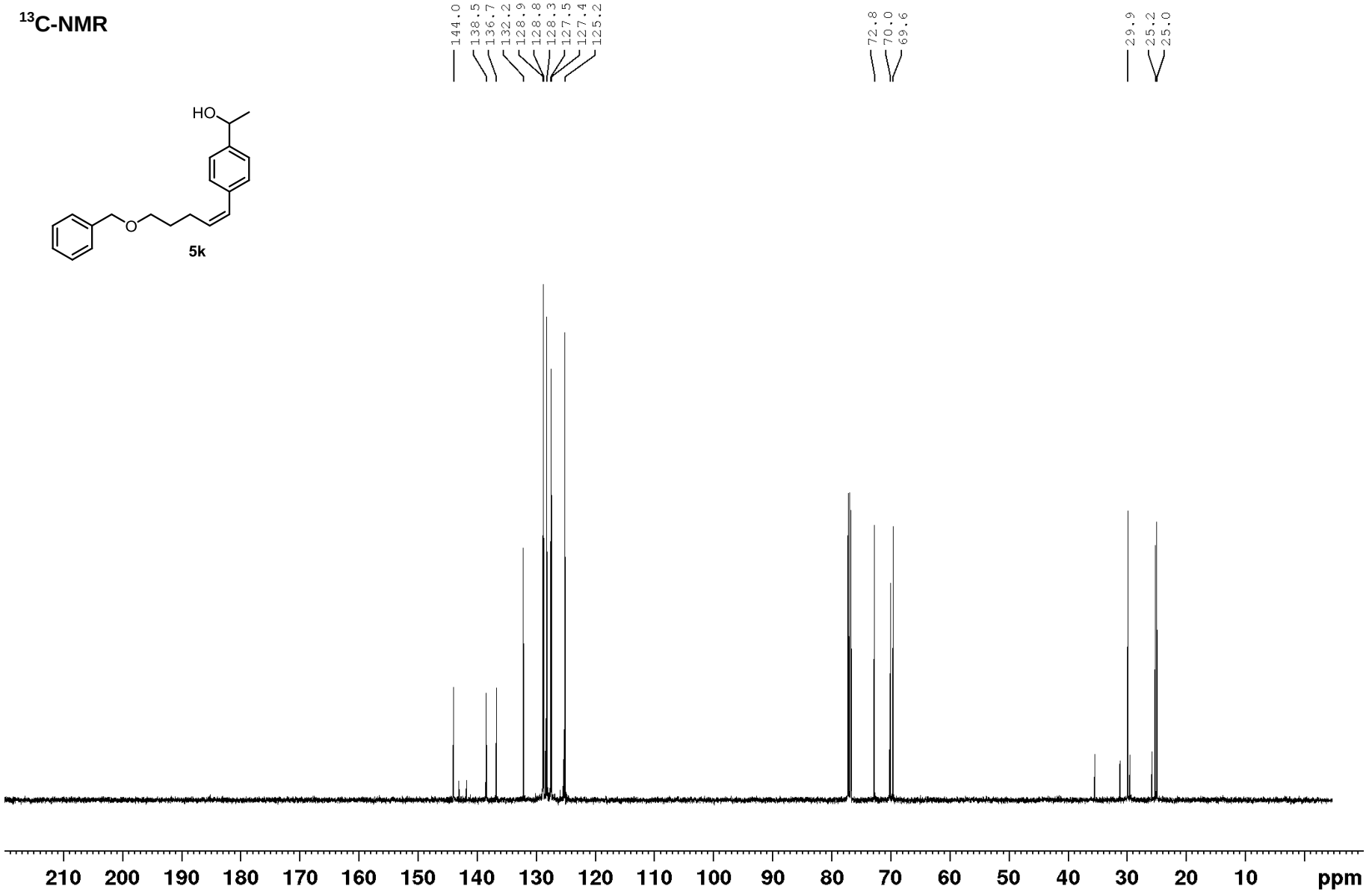
IR spectrum


100
80
60
40
30
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
CF3
O
5j

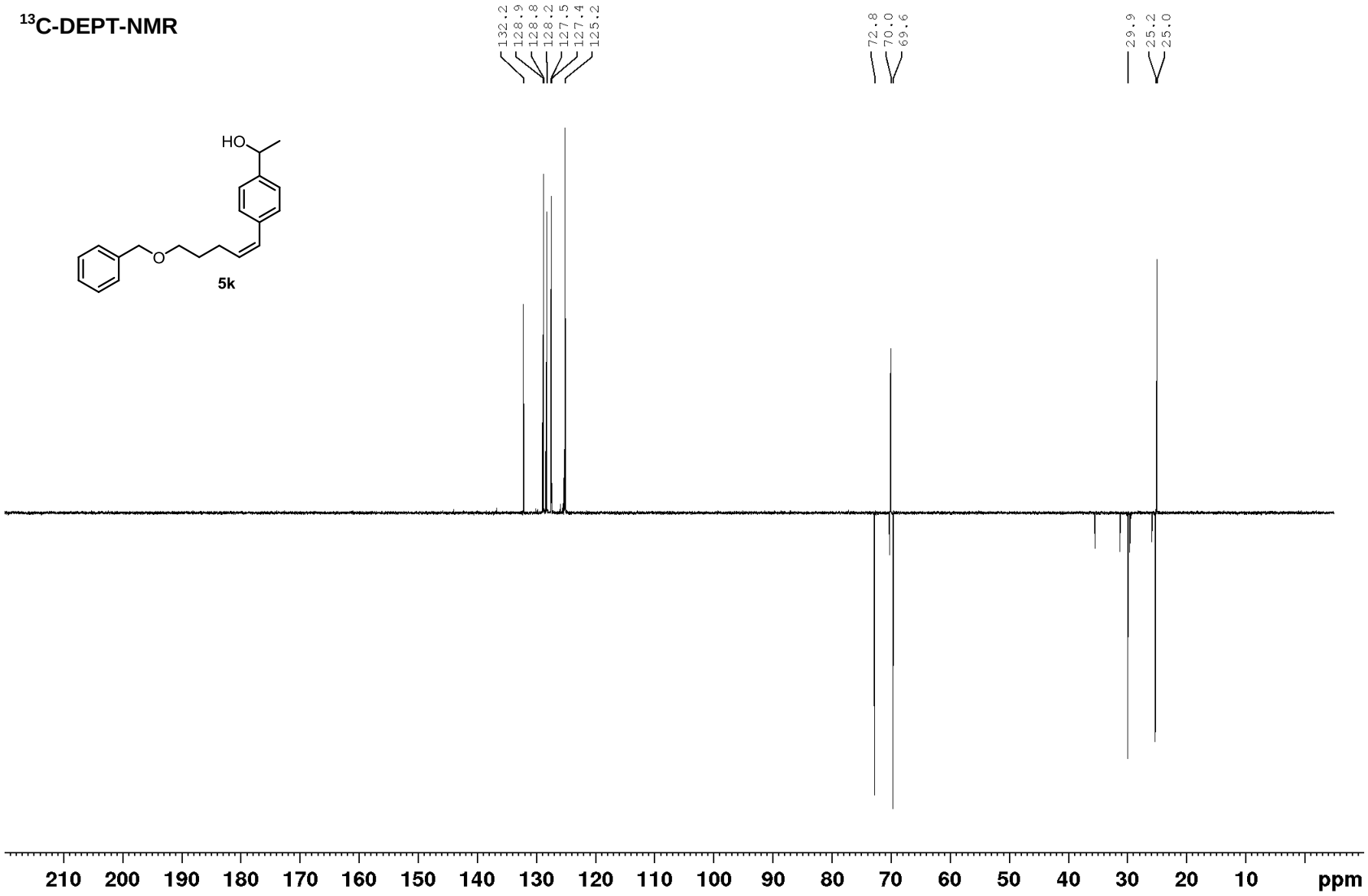
^{1}H-NMR


7.23
7.22
7.21
7.20
7.19
7.18
7.17
6.34
6.31
5.59
5.57
5.56
5.56
5.55
5.54
4.77
4.76
4.75
4.74
4.37
3.42
3.40
3.39
2.37
2.37
2.36
2.35
2.34
2.34
2.33
2.32
1.71
1.70
1.68
1.67
1.66
1.39
1.38
HO
O
5k
9.13
0.91
0.91
1.06
1.82
1.86
1.85
2.00
3.27
10
9
8
7
6
5
4
3
2
1
0
ppm

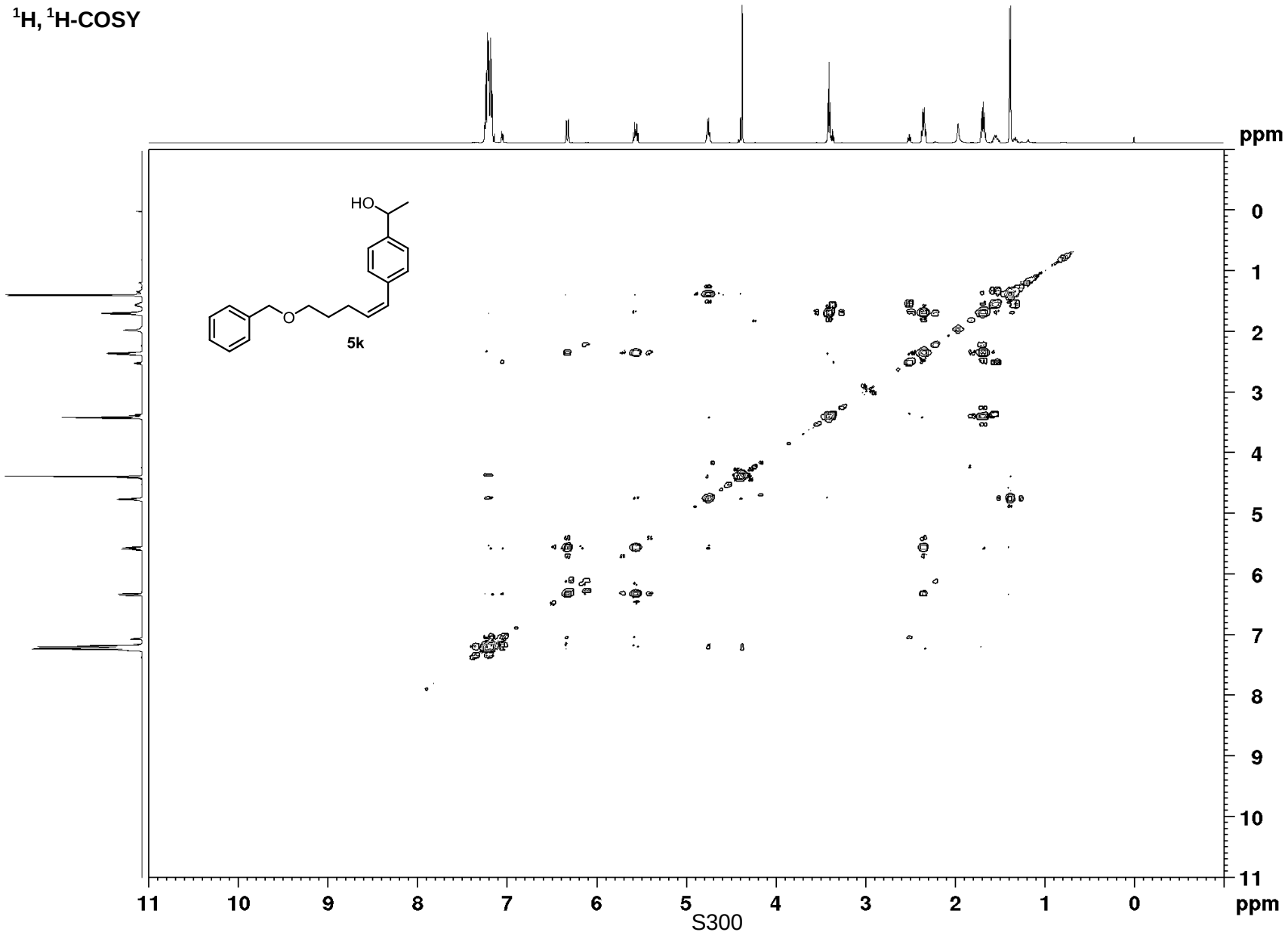
^{13}C-NMR


144.0
138.5
136.7
132.2
128.9
128.8
128.3
127.5
127.4
125.2
72.8
70.0
69.6
29.9
25.2
25.0
HO
O
5k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

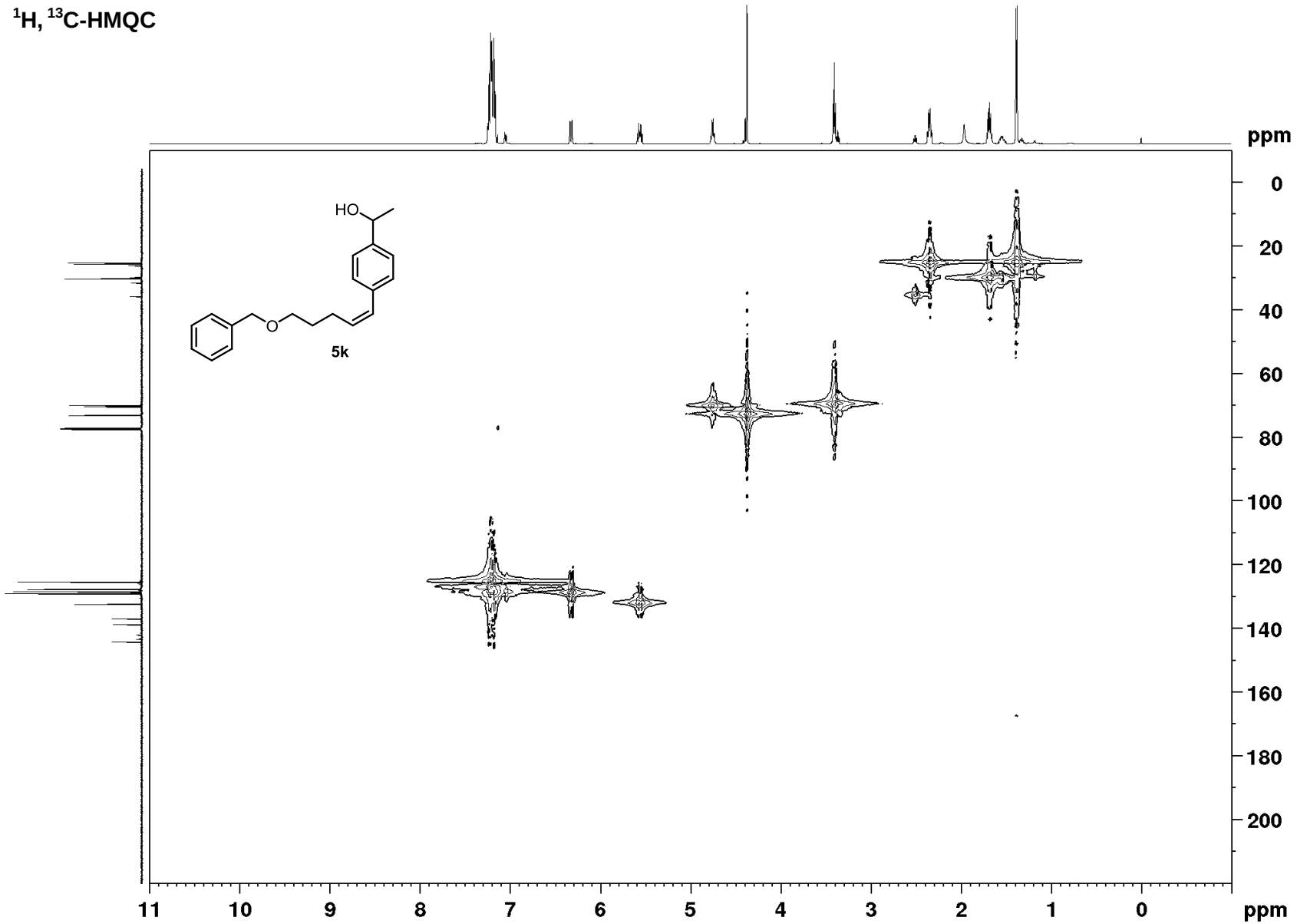
^{13}C-DEPT-NMR


132.2
128.9
128.8
128.2
127.5
127.4
125.2
72.8
70.0
69.6
29.9
25.2
25.0
HO
O
5k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

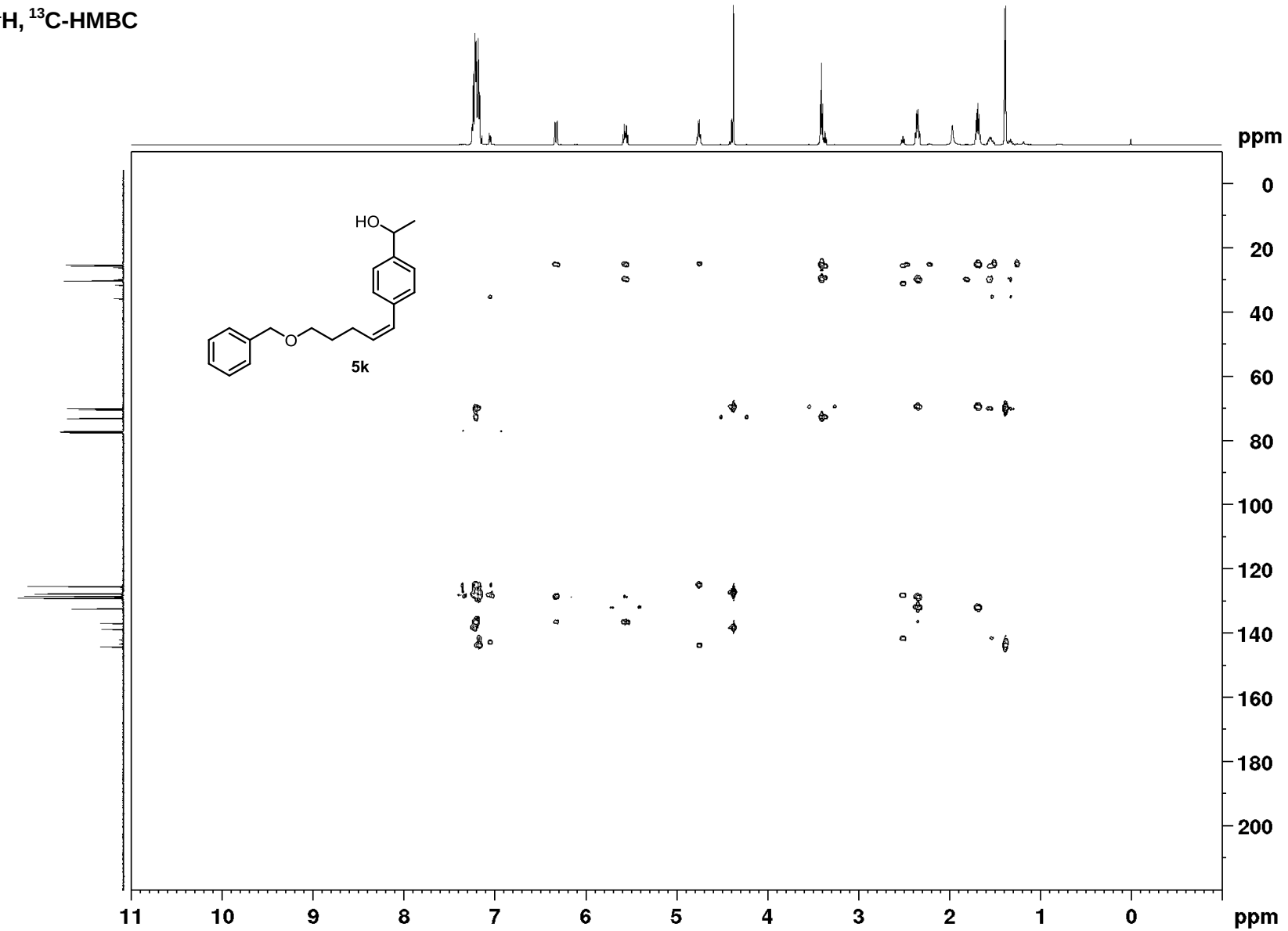
^{1}H, ^{1}H-COSY



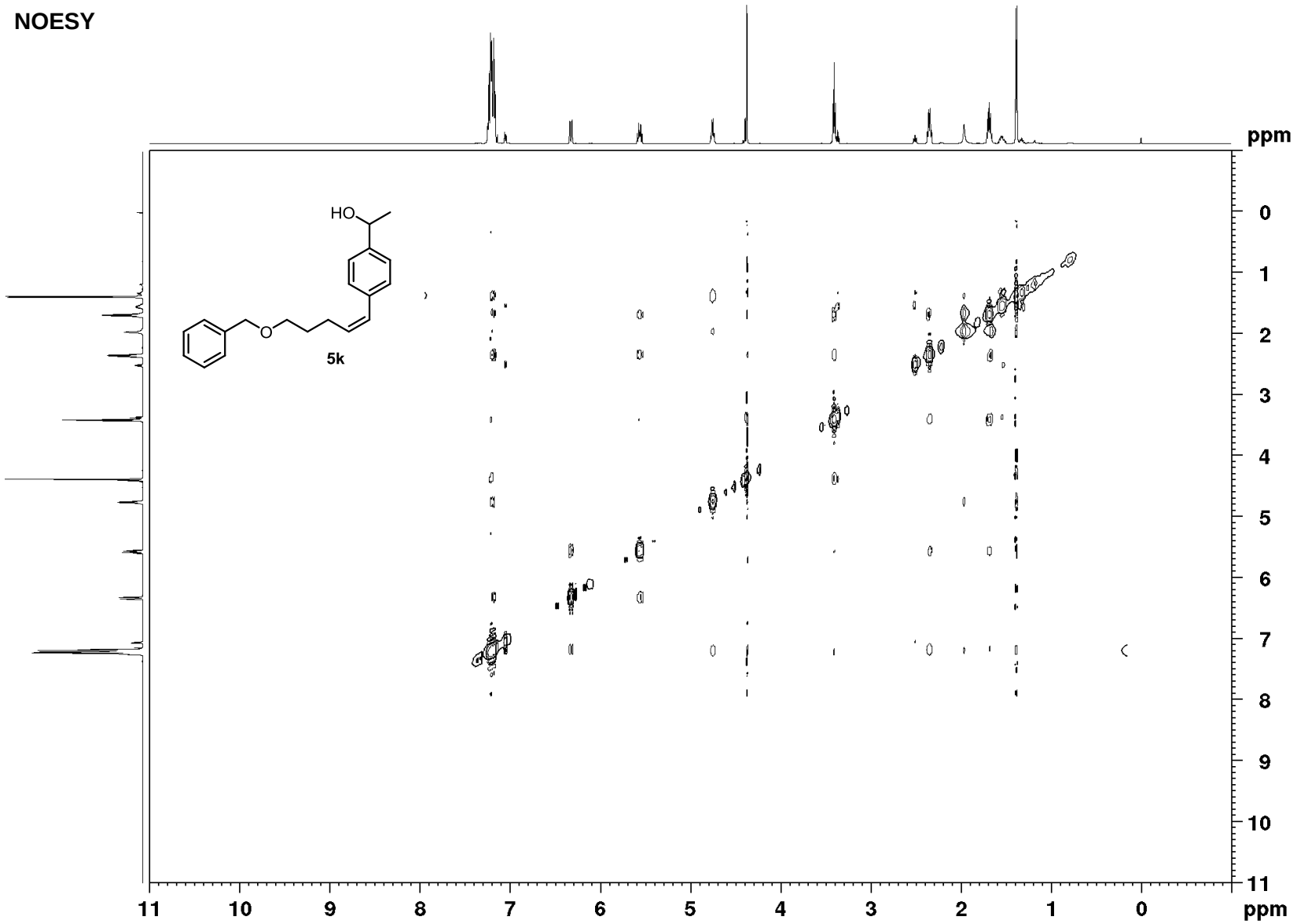
^{1}H, ^{13}C-HMQC


HO
O
5k
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

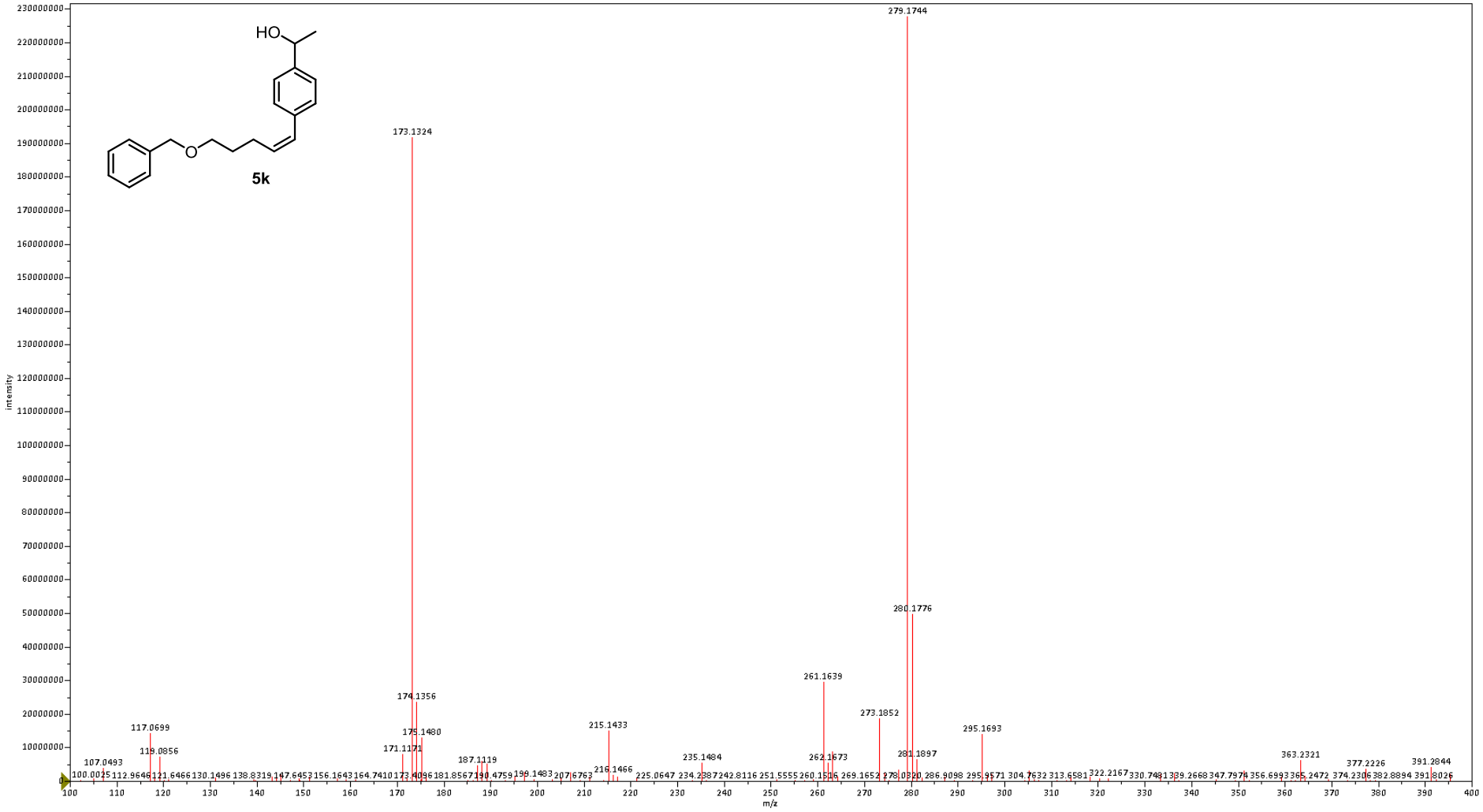
^{1}H, ^{13}C-HMBC


HO
O
5k
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

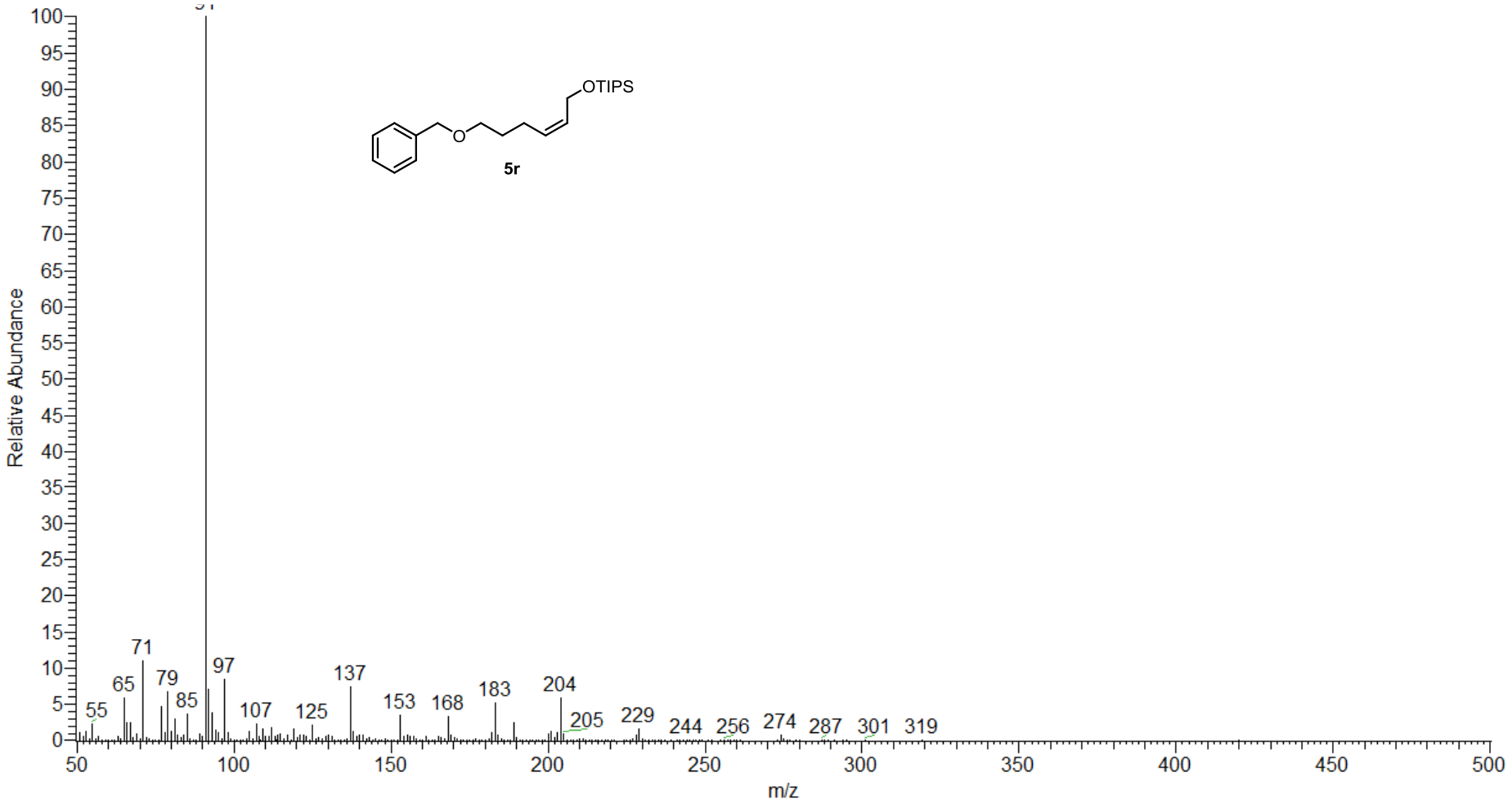
NOESY



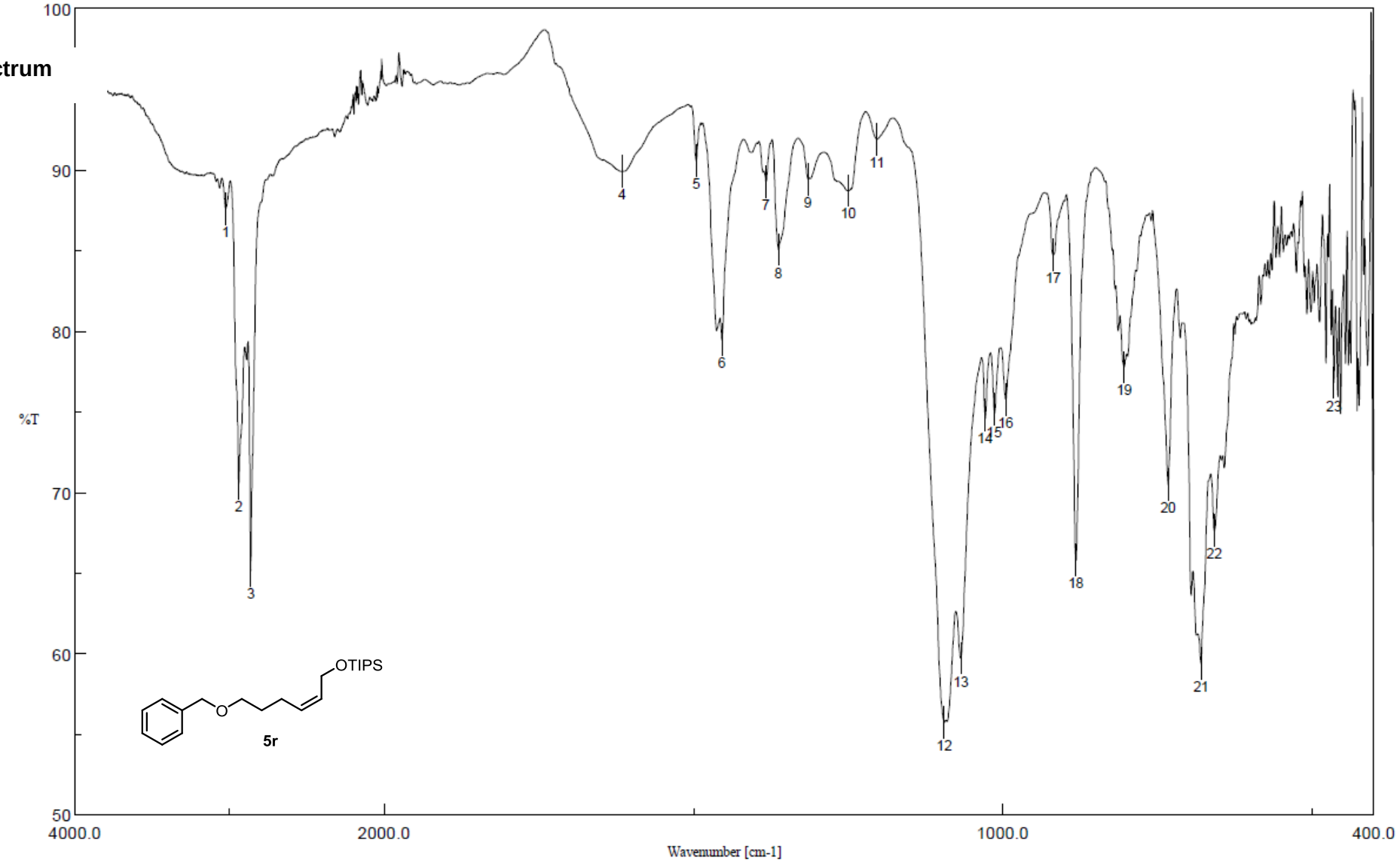
mass spectrum



mass spectrum



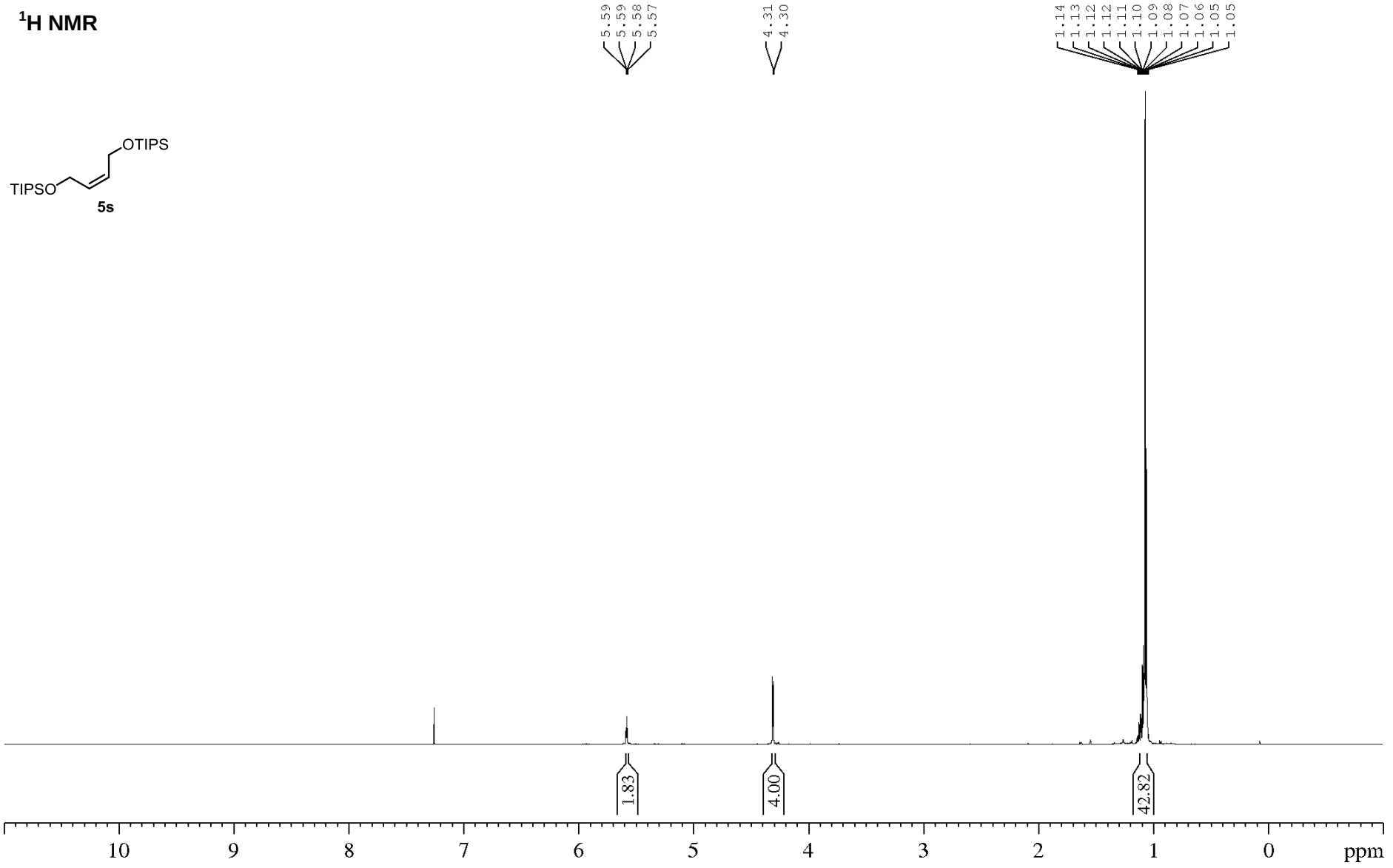
IR spectrum


100
90
80
70
60
50
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
OTIPS
O
5r

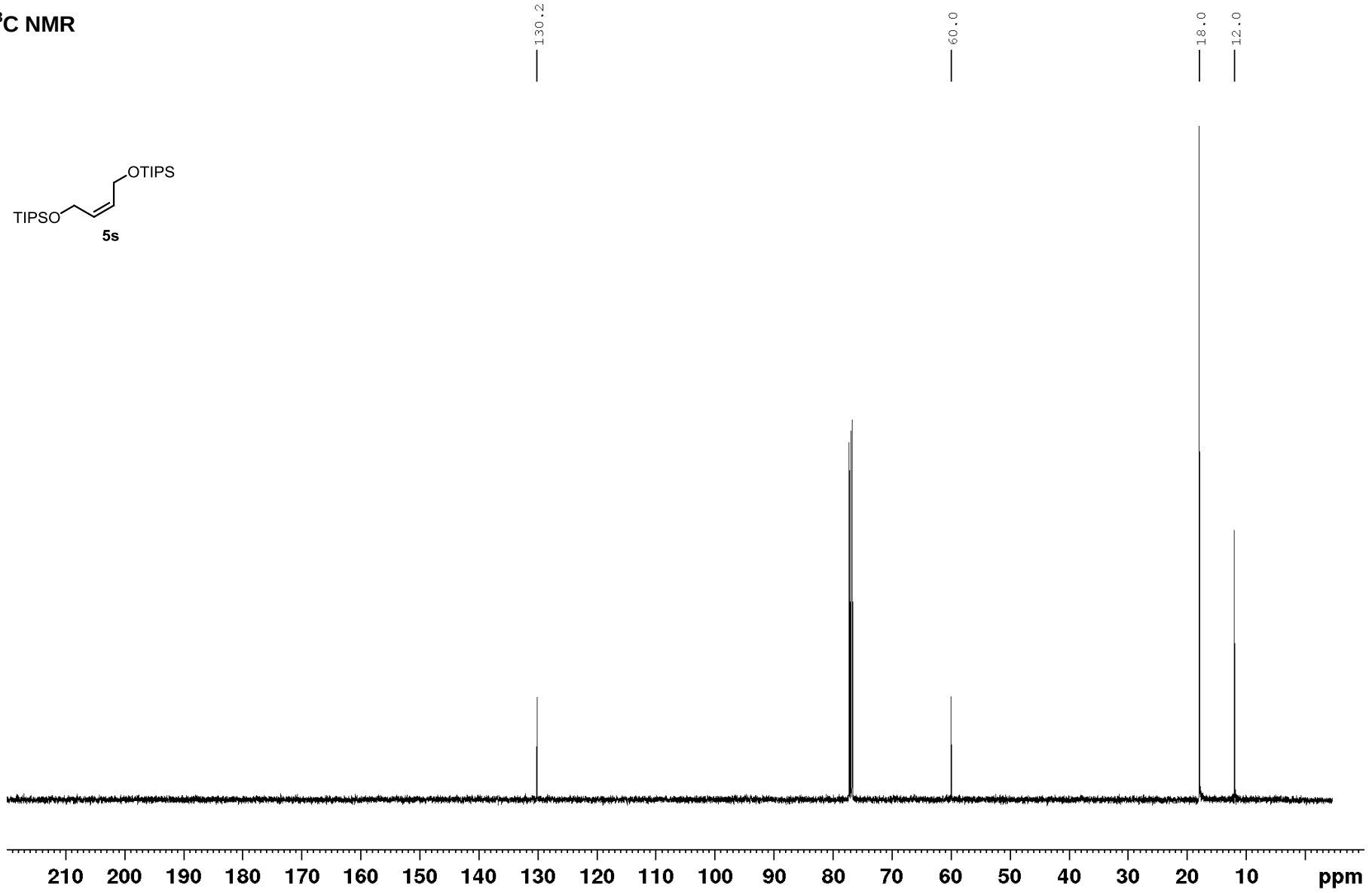
^{1}H NMR

OTIPS
TIPSO

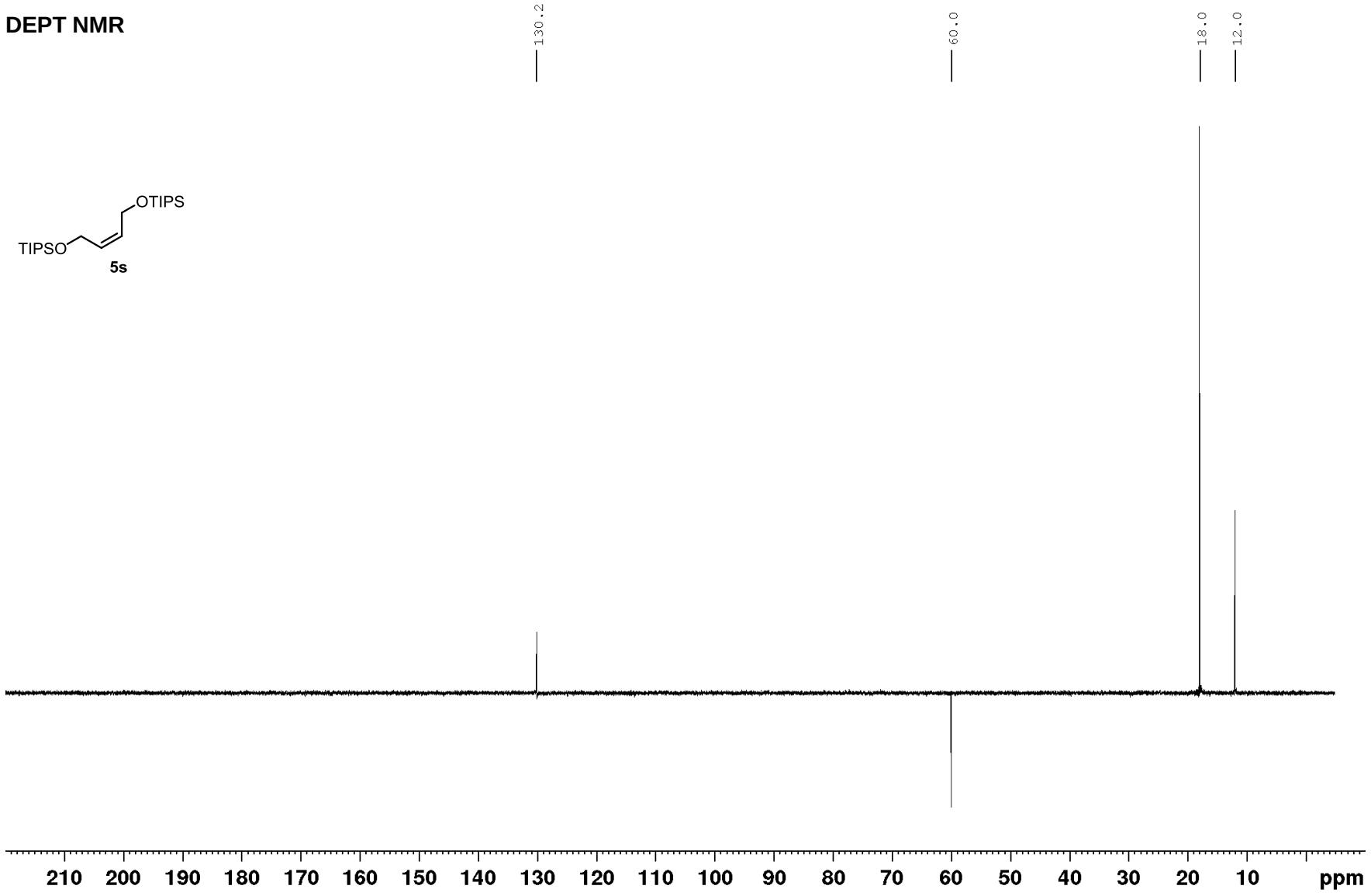
5s


5.59
5.59
5.58
5.57
4.31
4.30
1.14
1.13
1.12
1.12
1.11
1.10
1.09
1.08
1.07
1.06
1.05
1.05
1.83
4.00
42.82
10
9
8
7
6
5
4
3
2
1
0
ppm

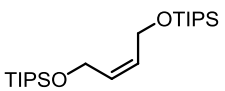
^{13}C NMR


130.2
60.0
18.0
12.0
OTIPS
TIPSO
5s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

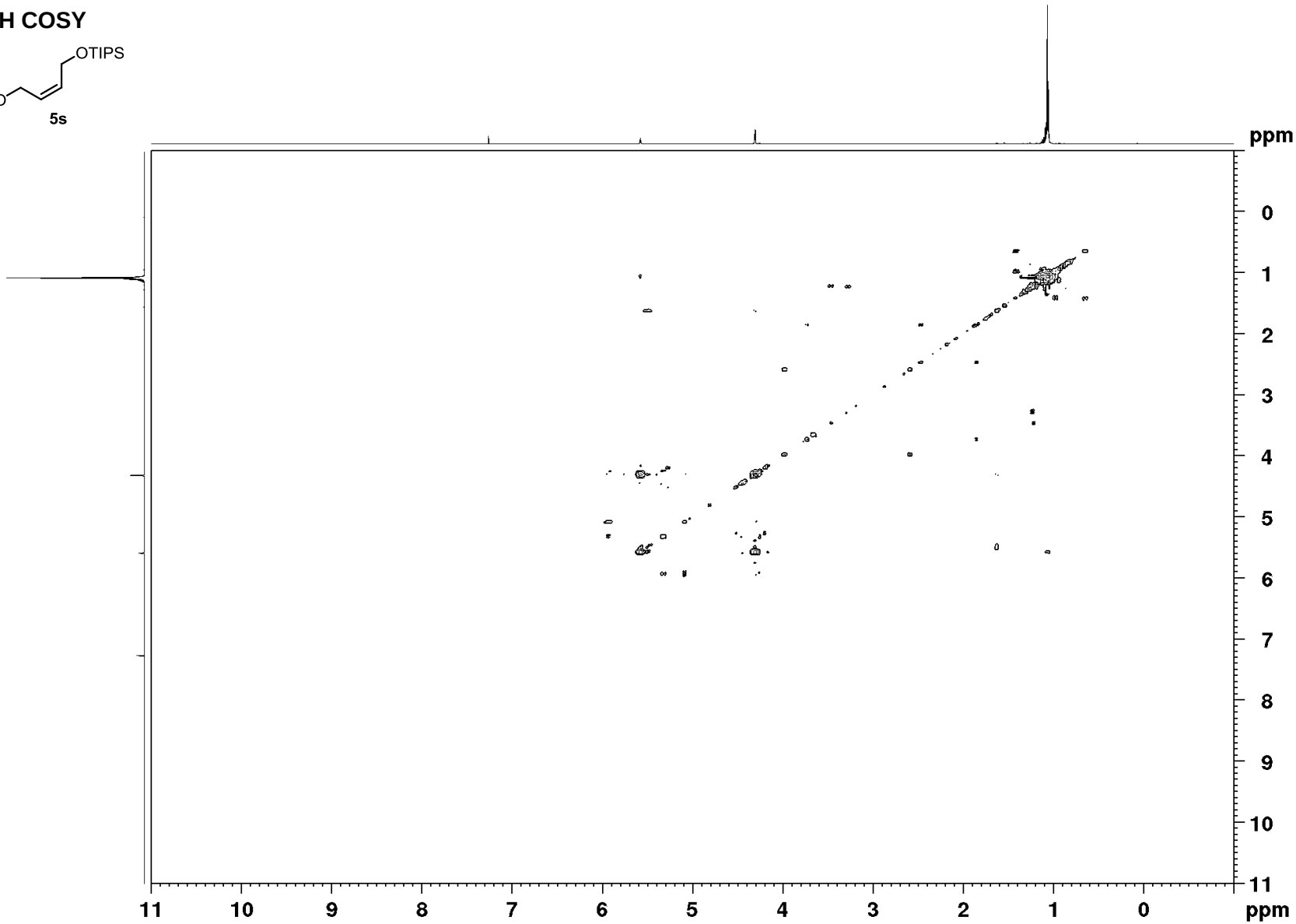
^{13}C DEPT NMR


130.2
60.0
18.0
12.0
OTIPS
TIPSO
5s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

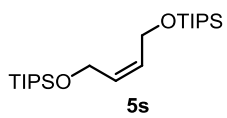
^{1}H, ^{1}H COSY



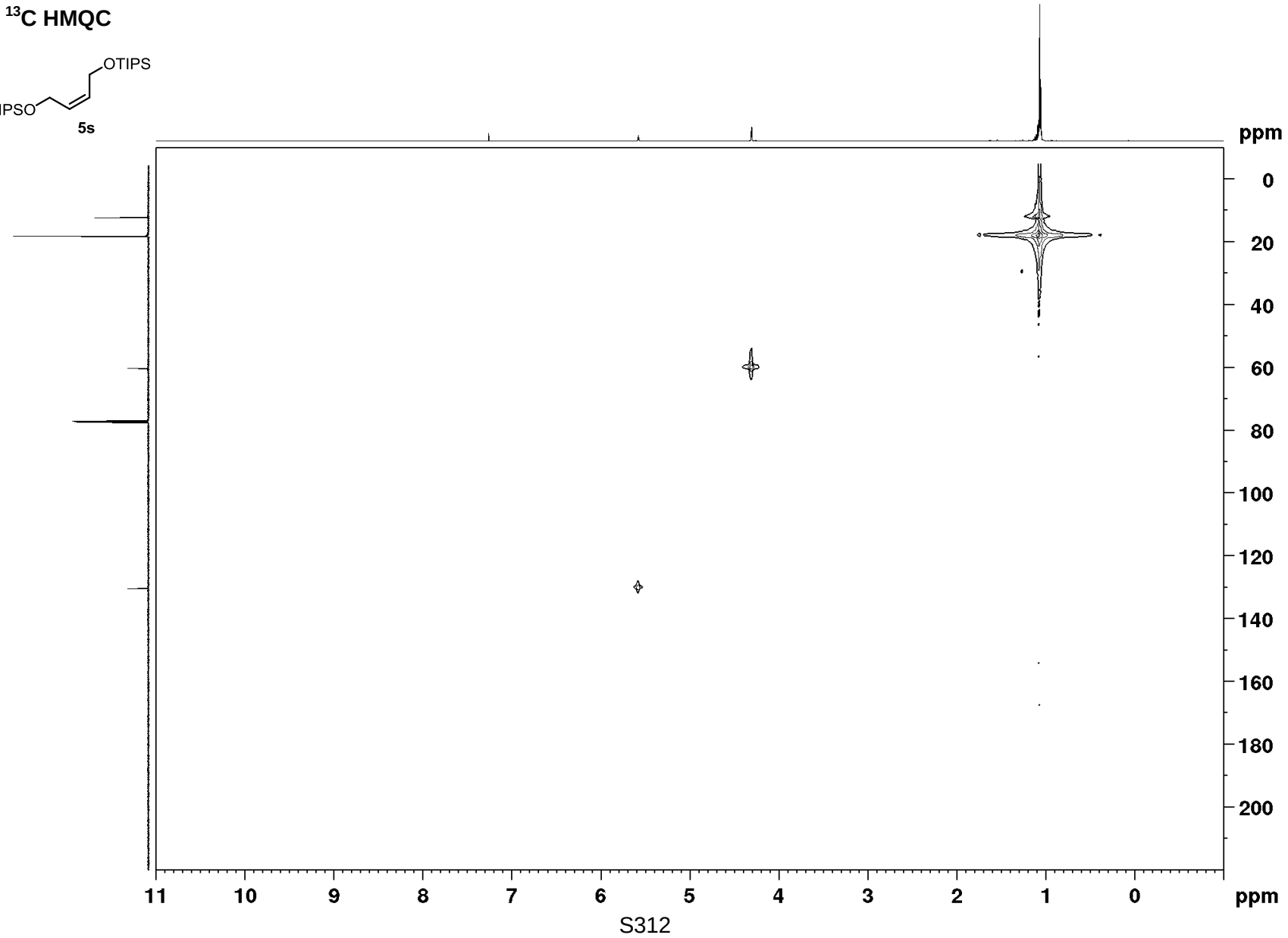
5s



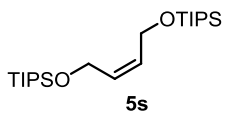
^{1}H, ^{13}C HMQC



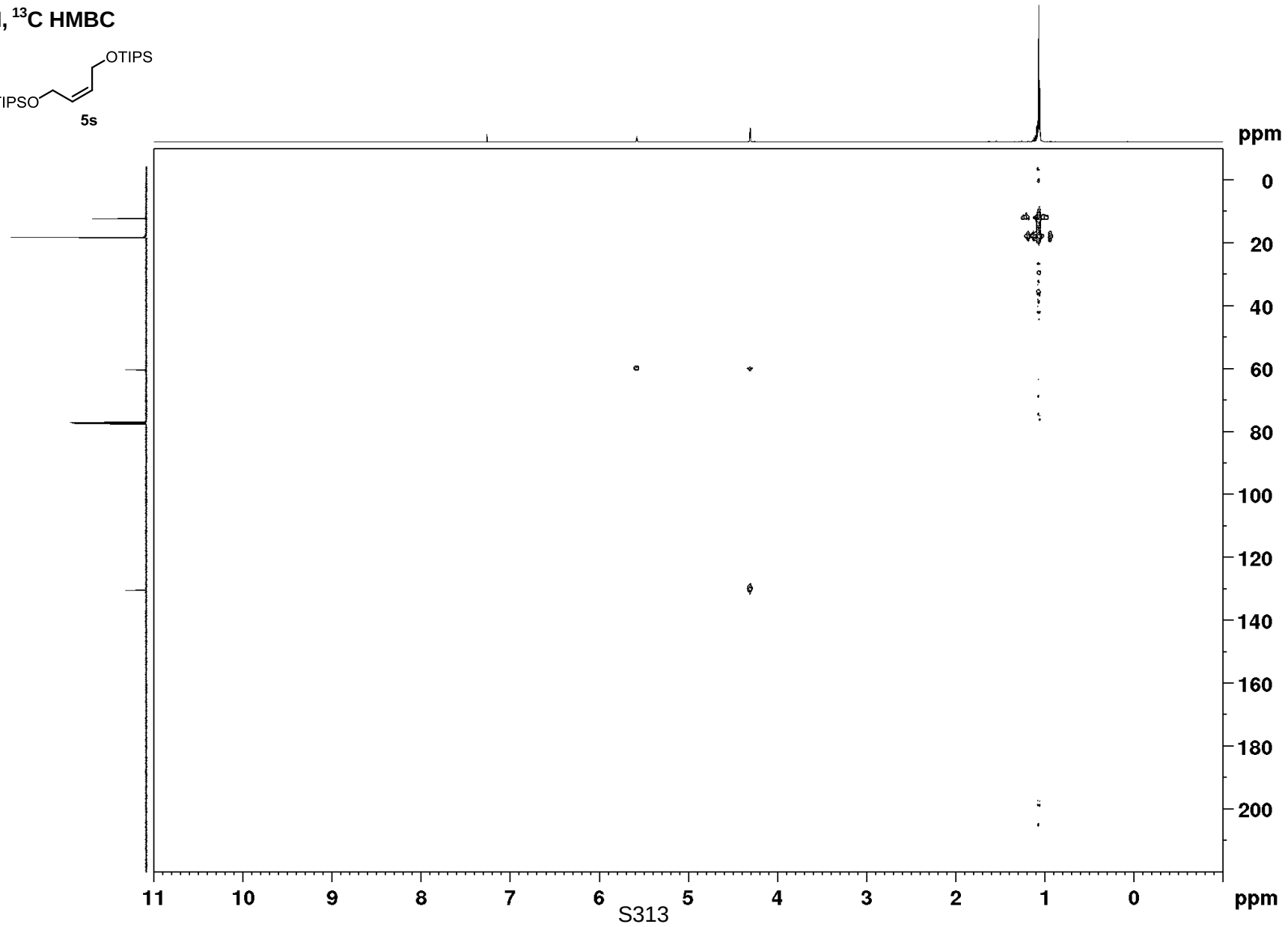
5s



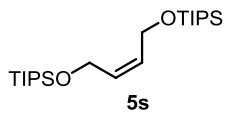
^{1}H, ^{13}C HMBC



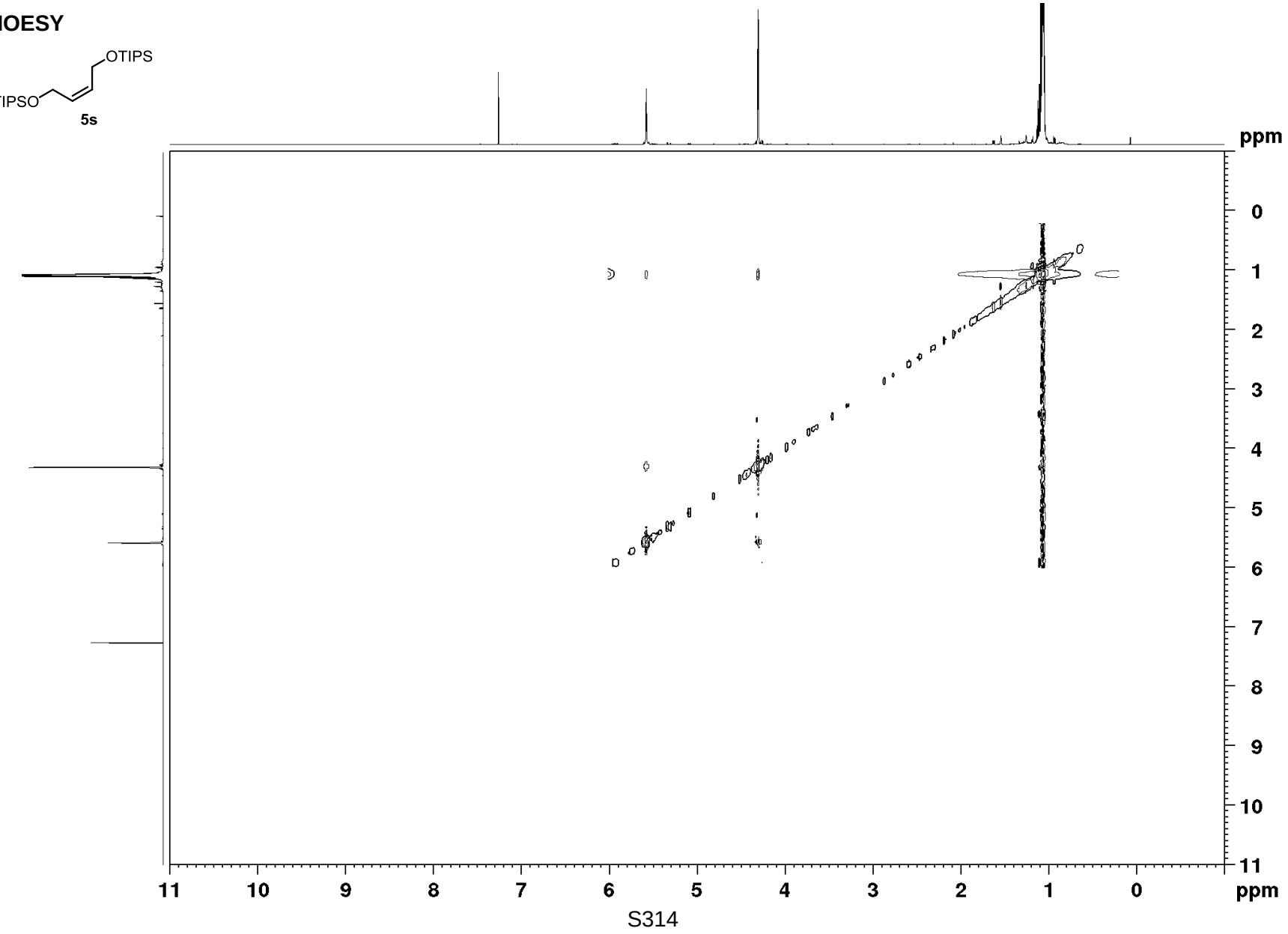
5s



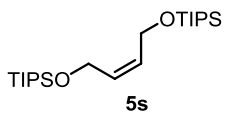
NOESY



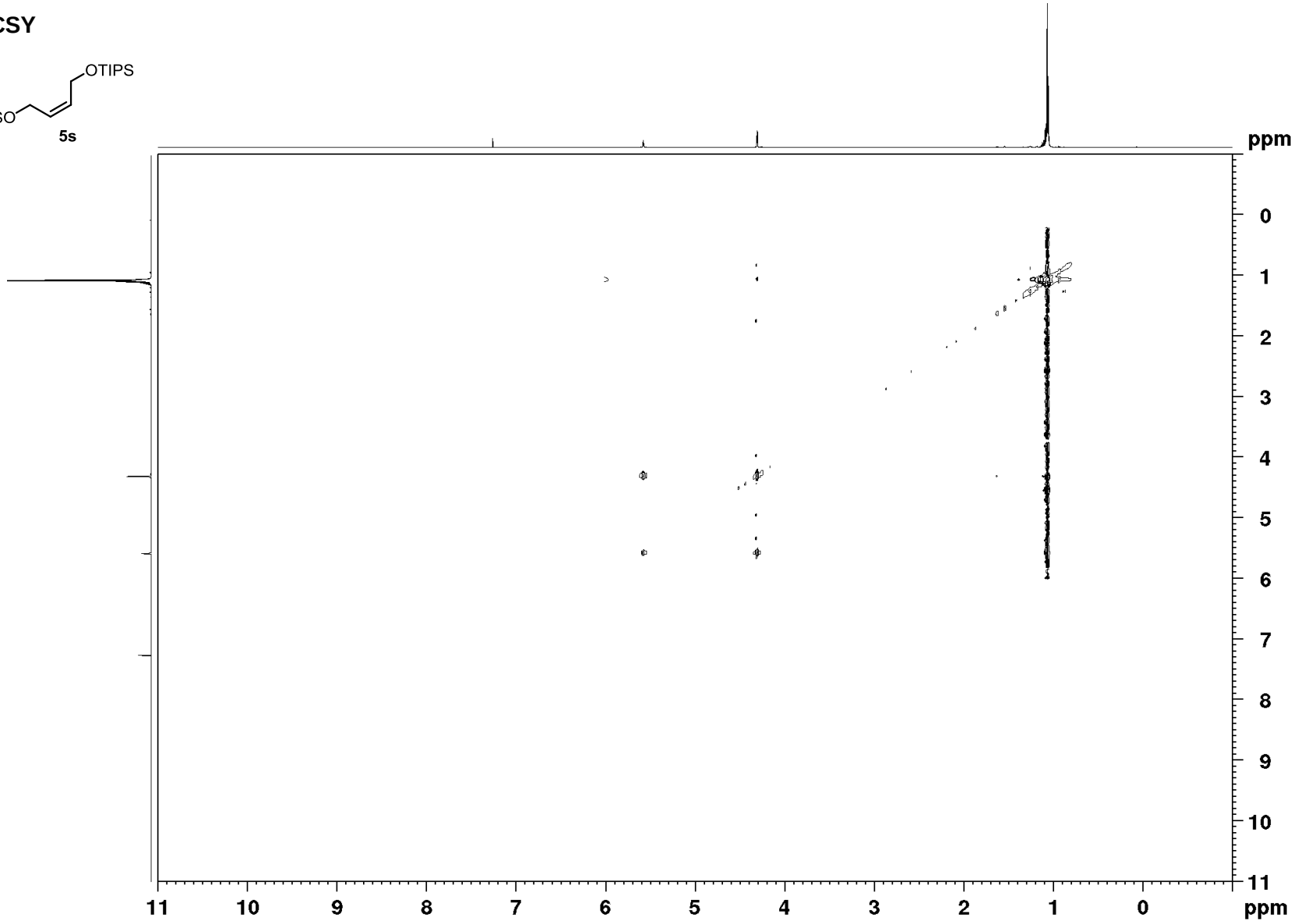
5s



TOCSY

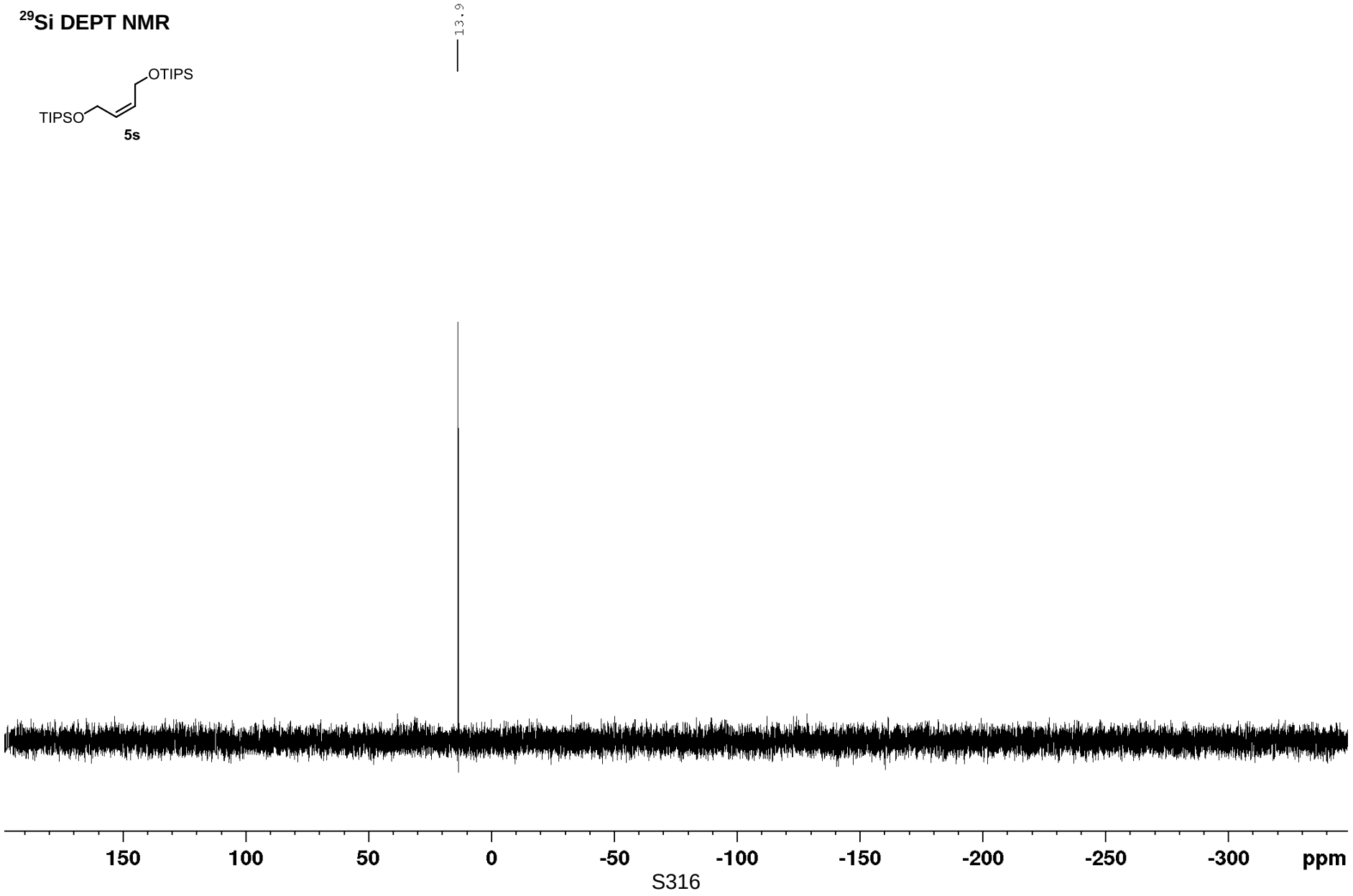


5s

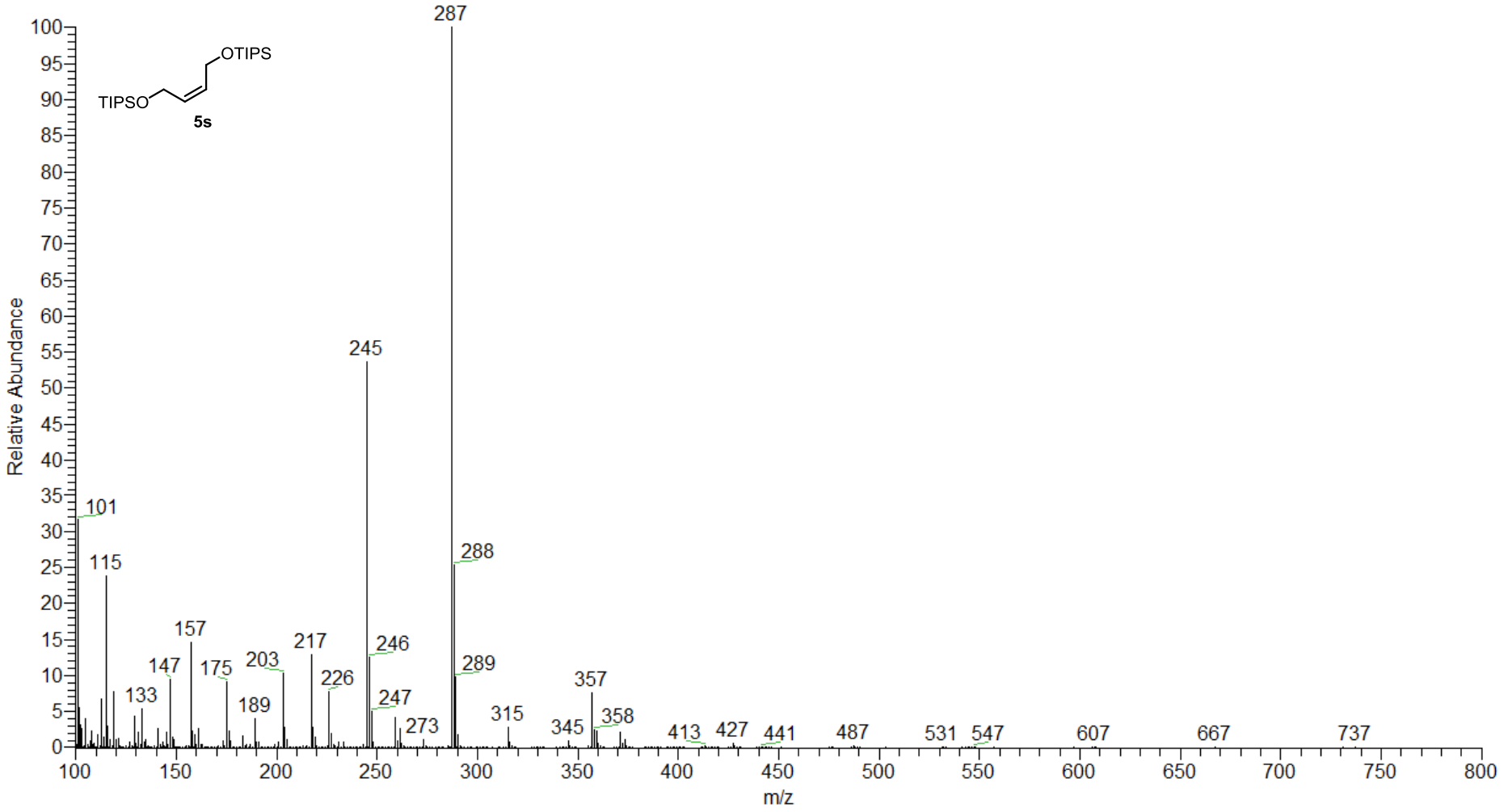


^{29}Si DEPT NMR

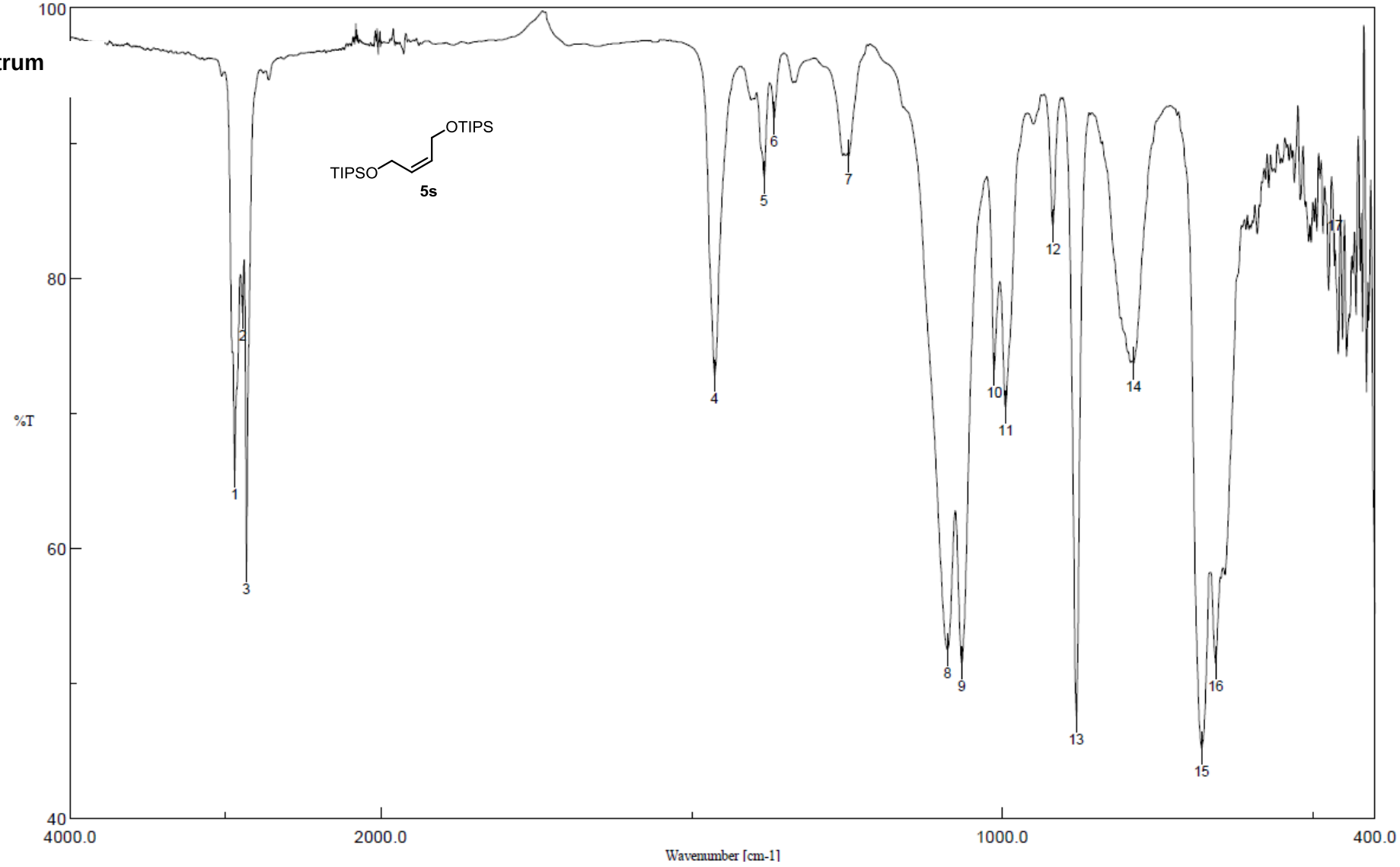
5s



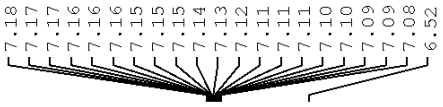
mass spectrum

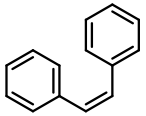


IR spectrum

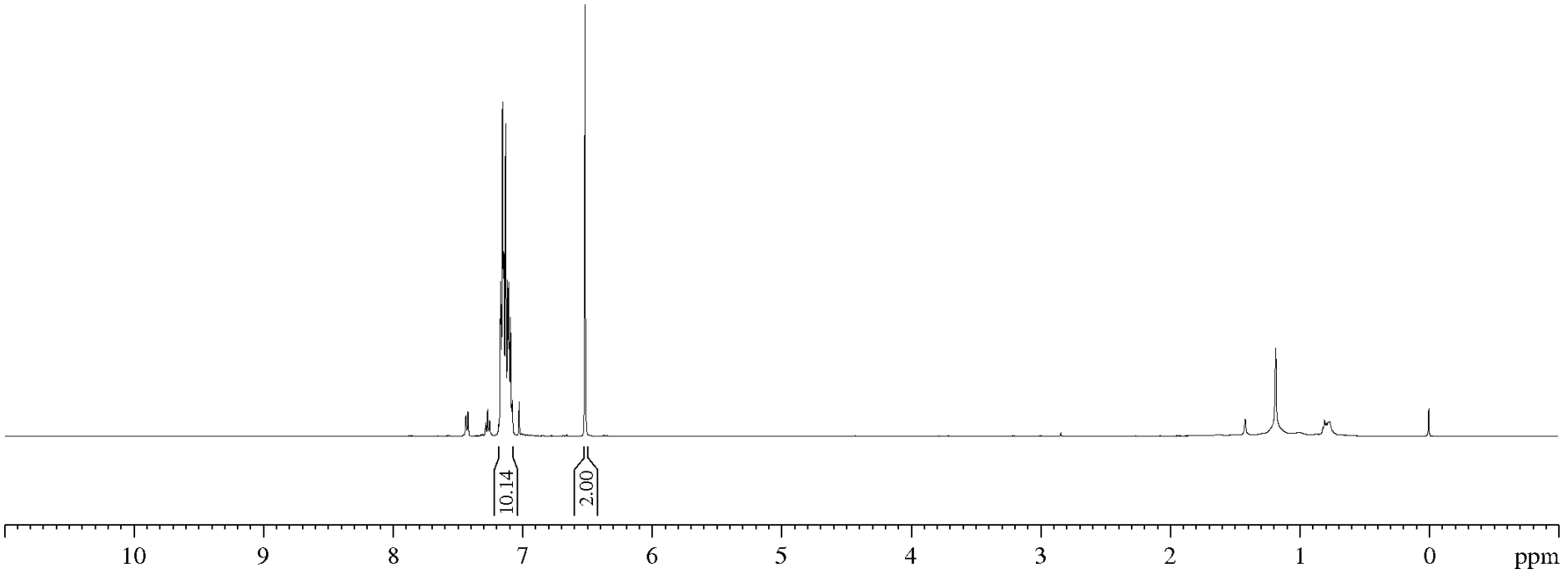

100
80
60
40
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
OTIPS
TIPSO
5s
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

^{1}H NMR


7.18
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.15
7.14
7.13
7.12
7.11
7.11
7.11
7.10
7.10
7.09
7.09
7.08
6.52

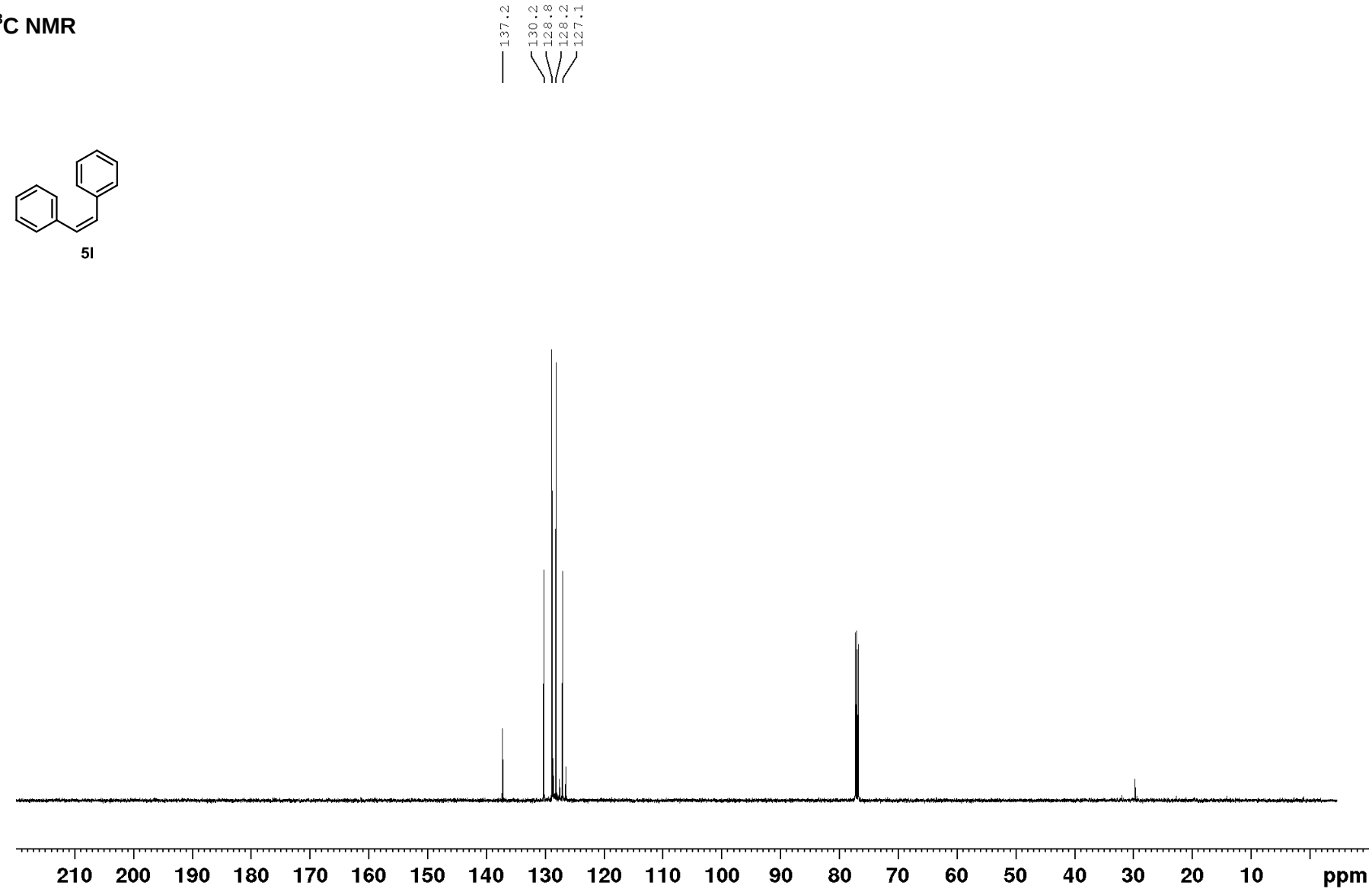


5l


10.14
2.00
10
9
8
7
6
5
4
3
2
1
0
ppm

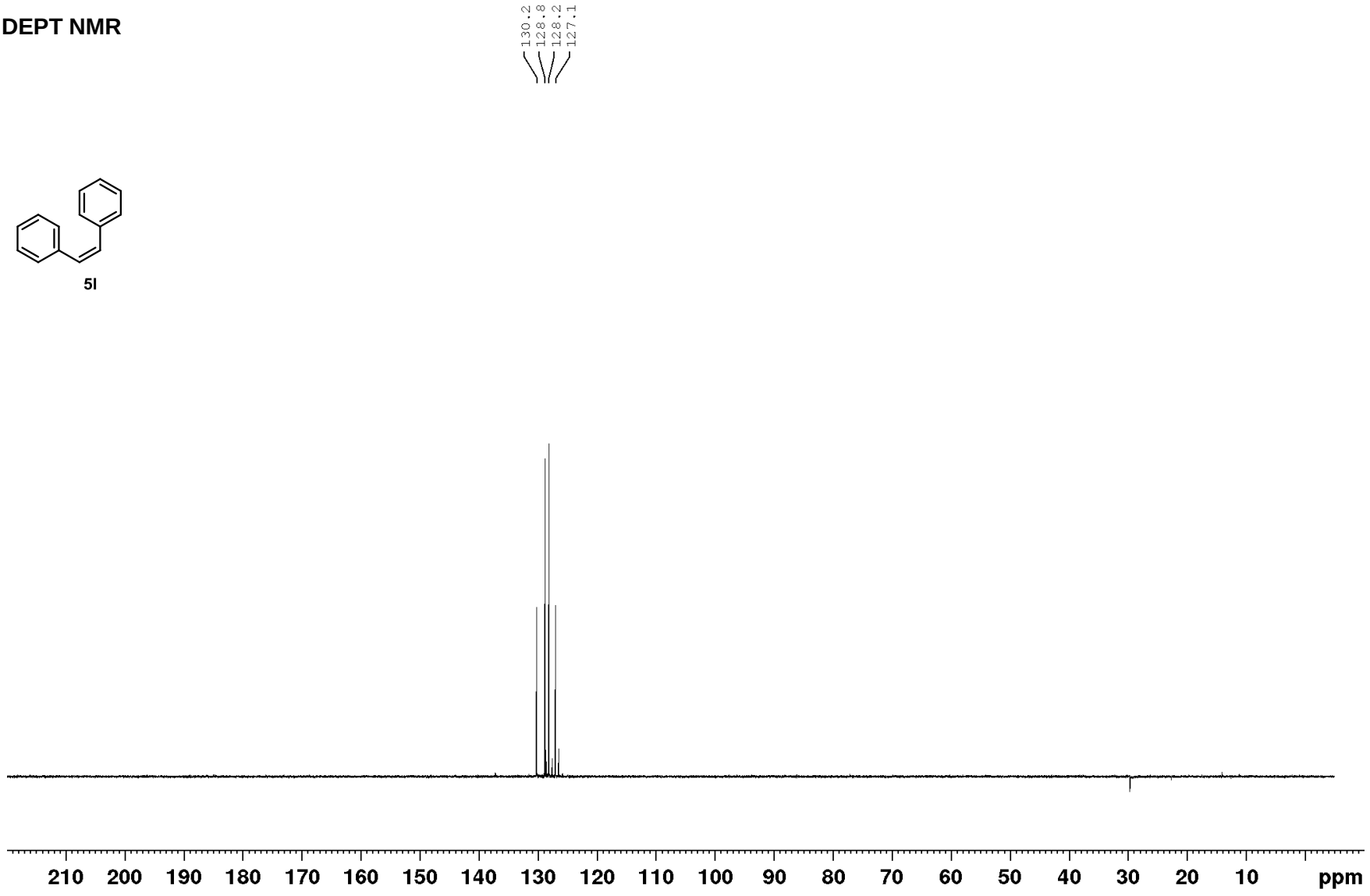
^{13}C NMR

5l

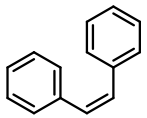

137.2
130.2
128.8
128.2
127.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

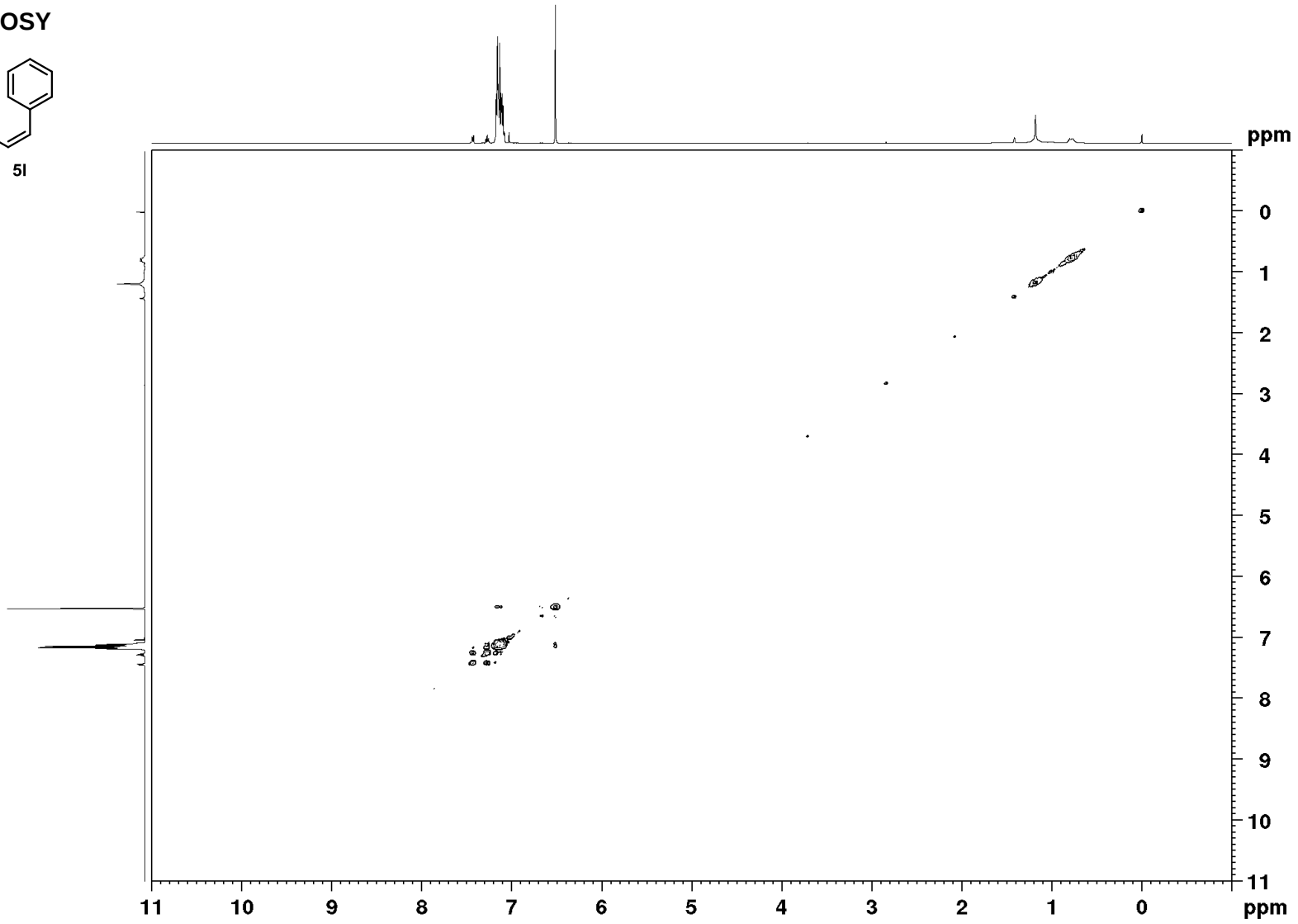
5l



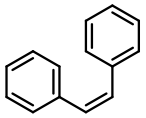
^{1}H, ^{1}H COSY



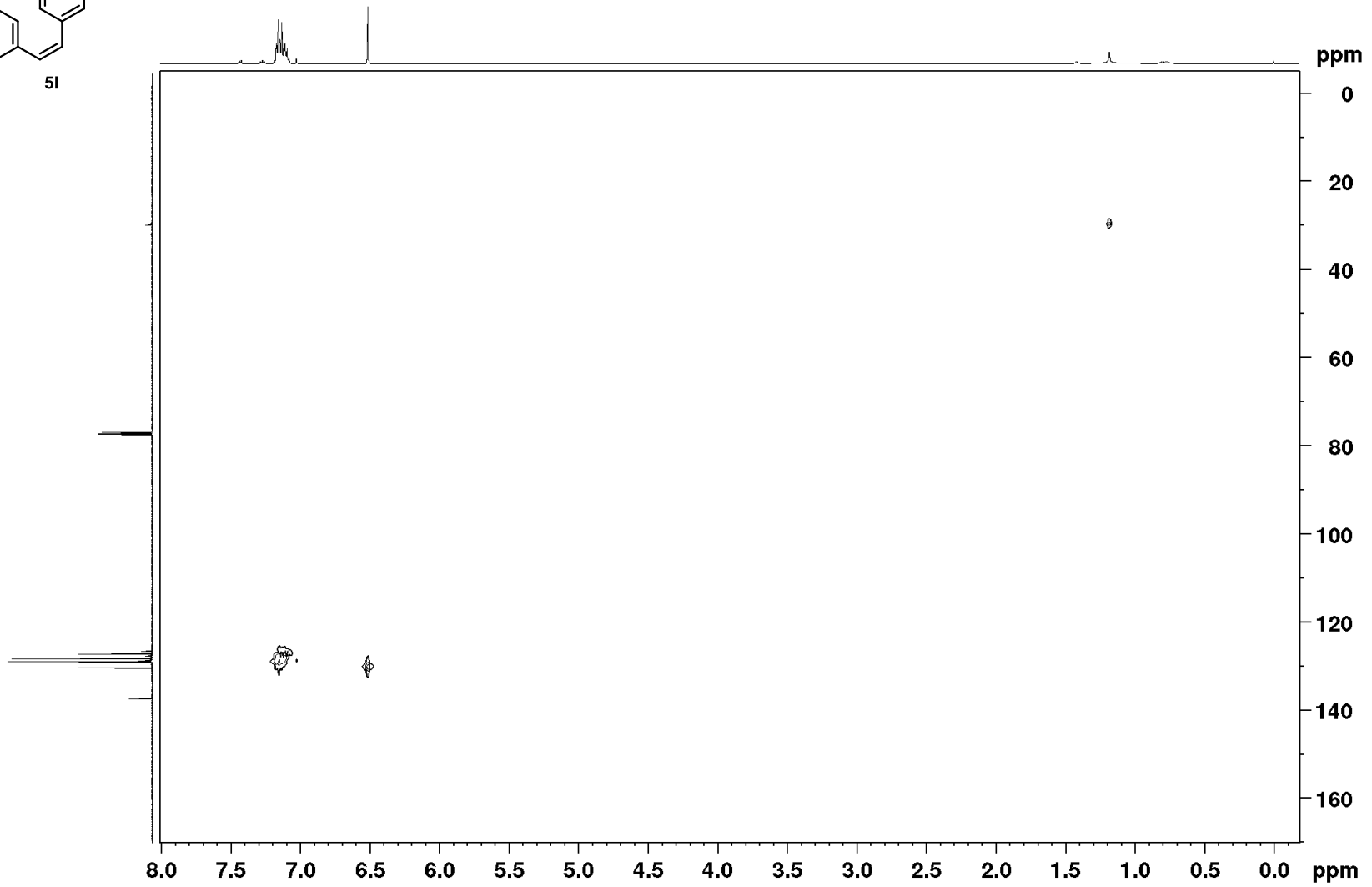
5l



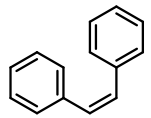
^{1}H, ^{13}C HMQC



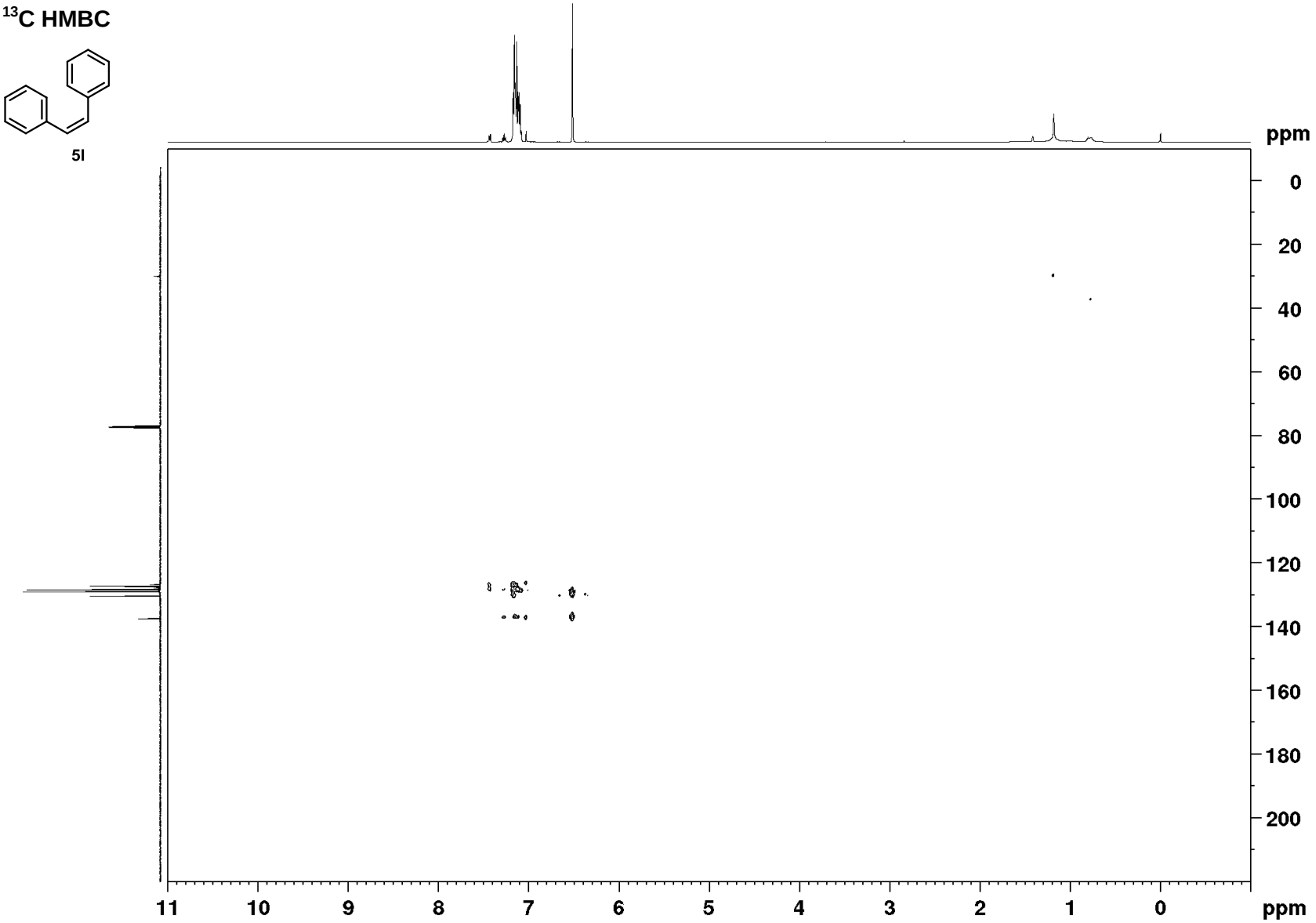
5l



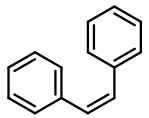
^{1}H, ^{13}C HMBC



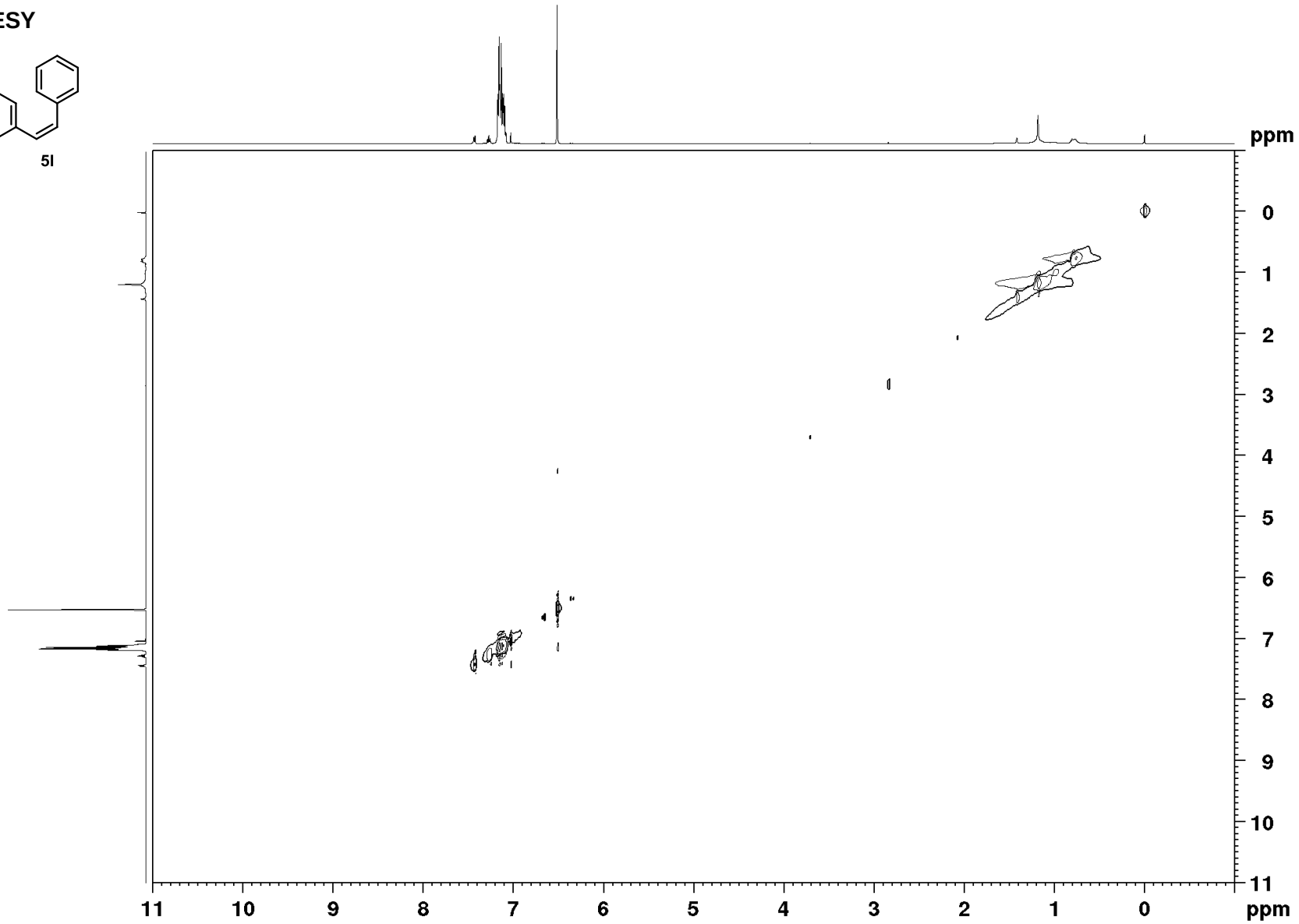
5l



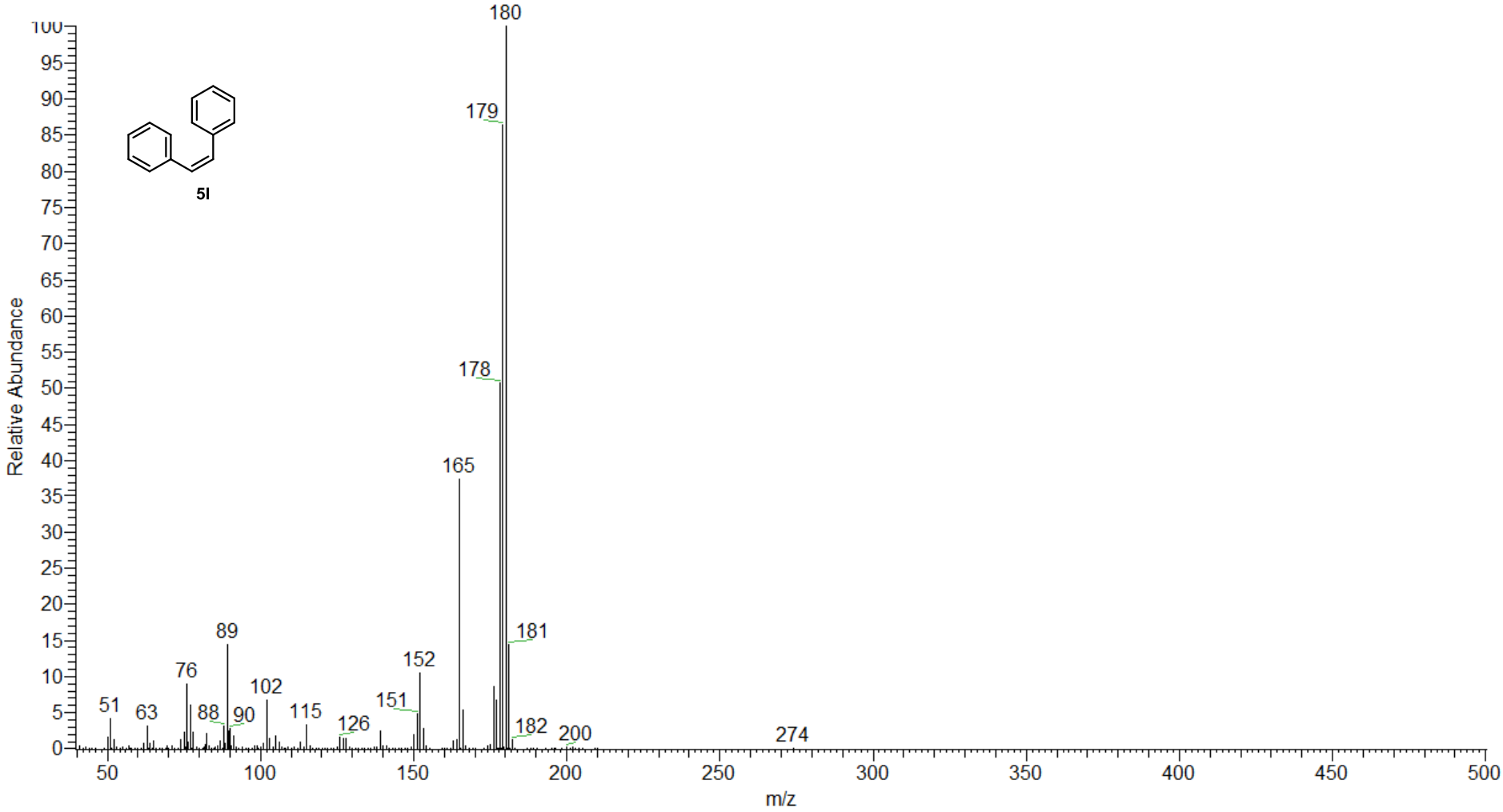
NOESY



5l

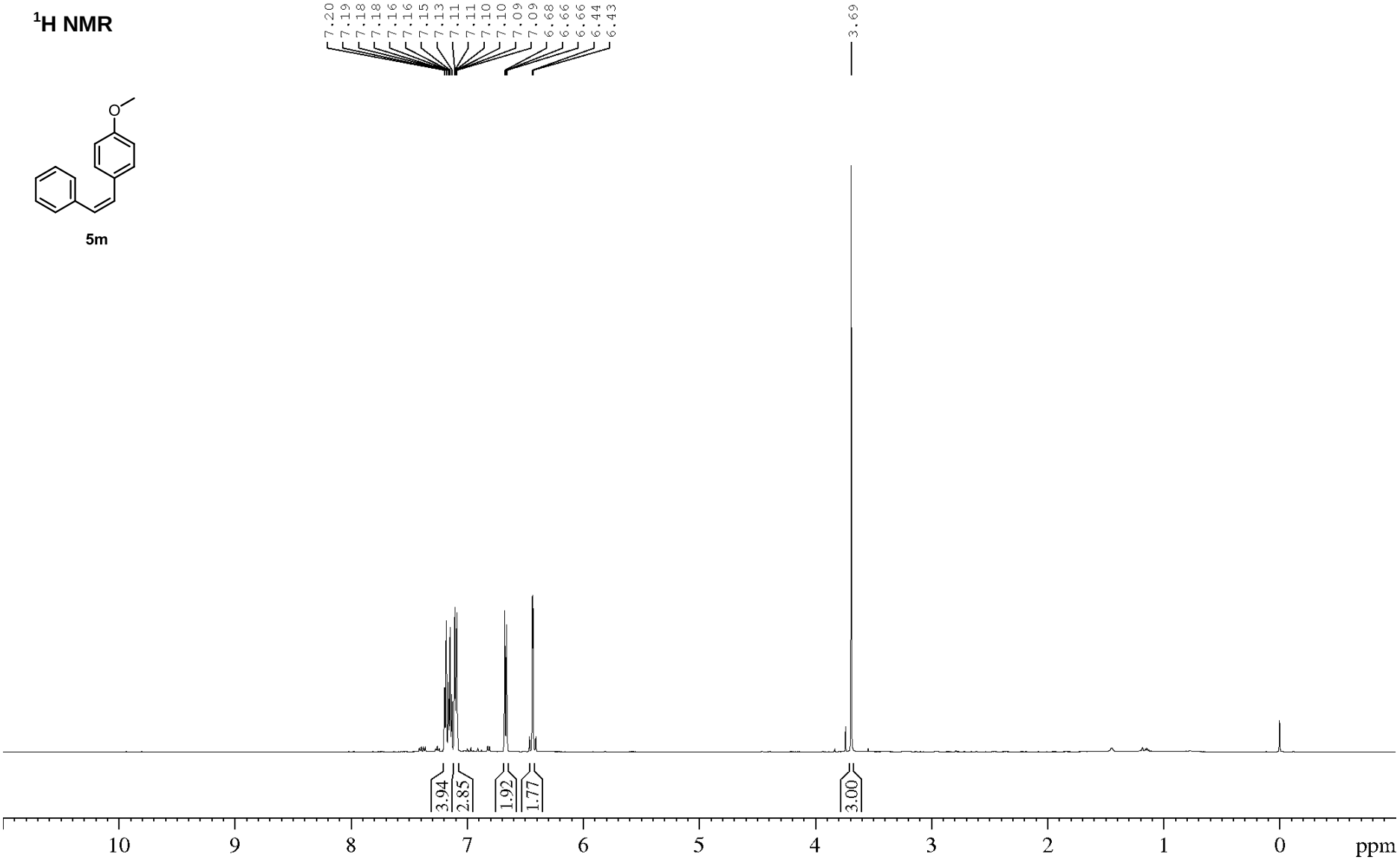


mass spectrum

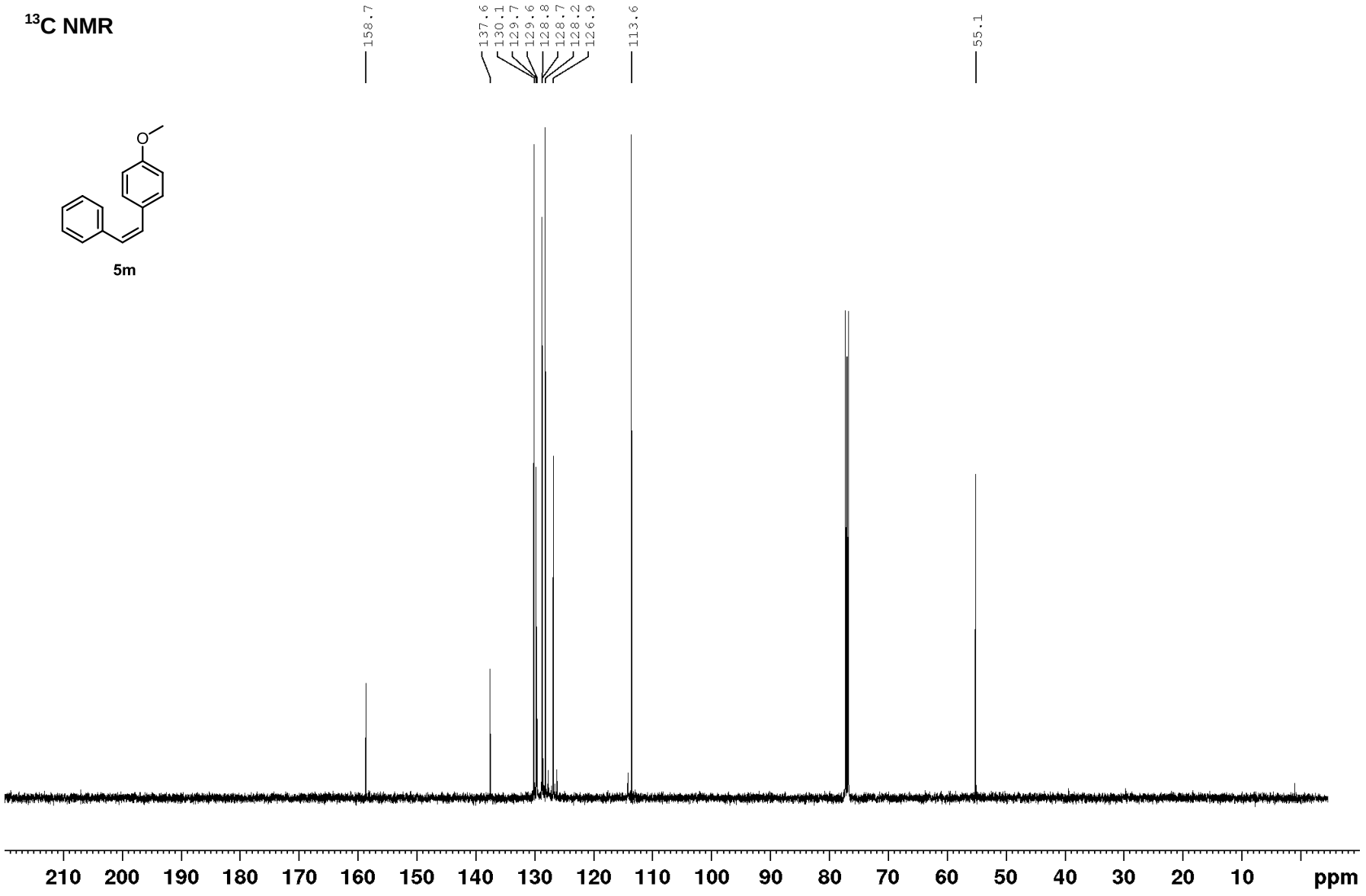


^{1}H NMR

5m

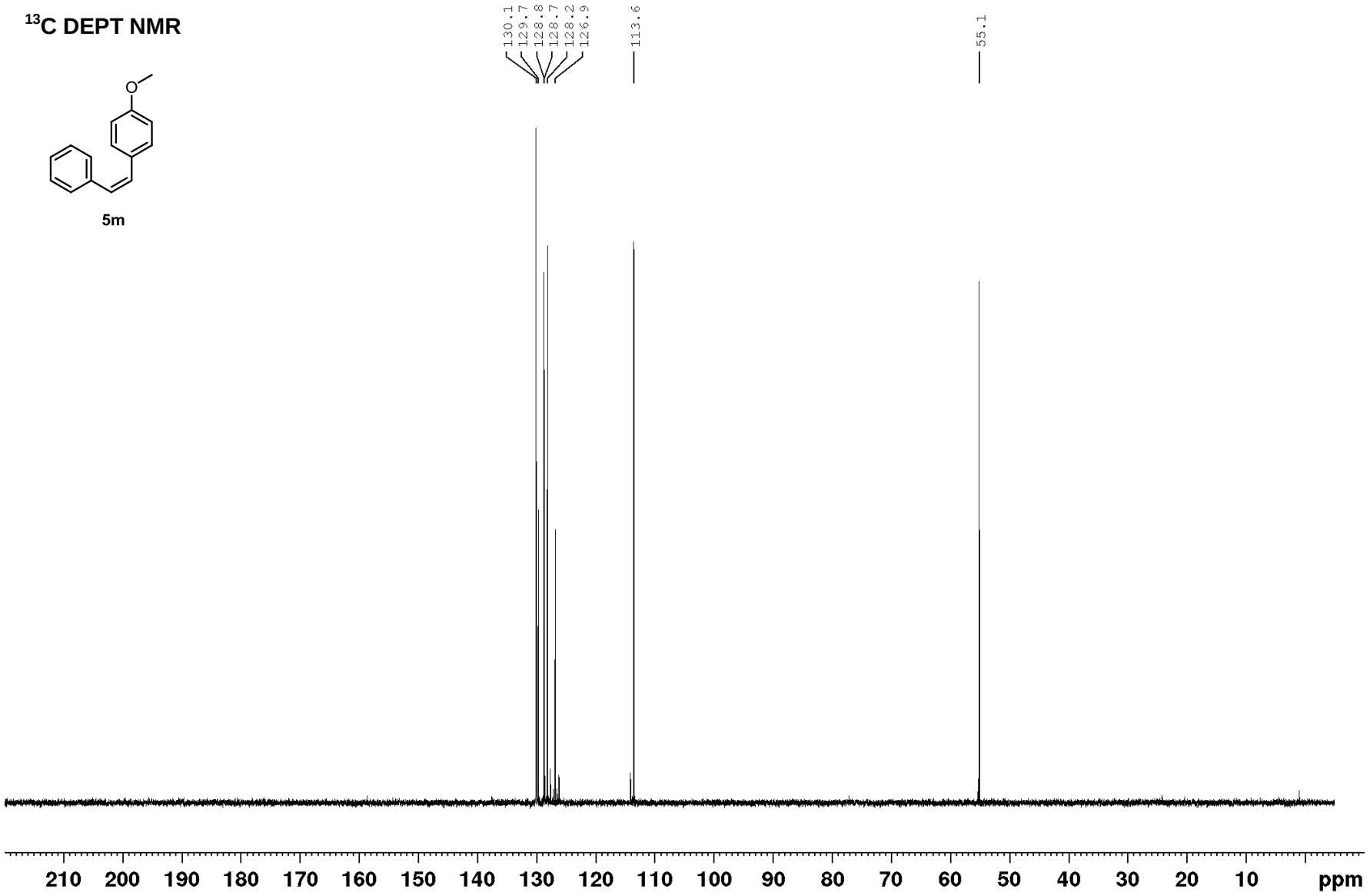

7.20
7.19
7.18
7.18
7.16
7.16
7.15
7.13
7.11
7.11
7.10
7.10
7.09
7.09
6.68
6.66
6.66
6.44
6.43
3.69
3.94
2.85
1.92
1.77
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

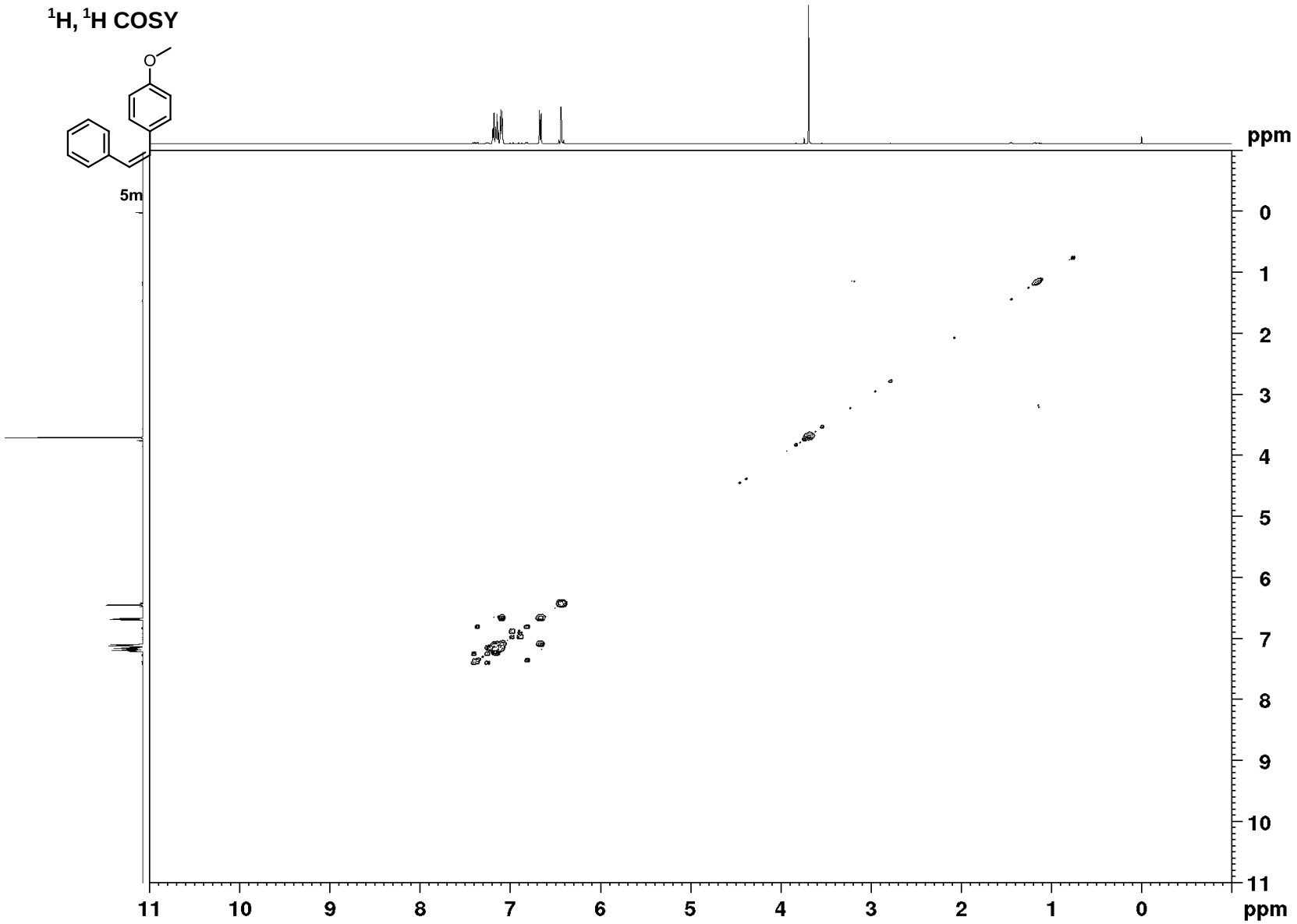
^{13}C NMR

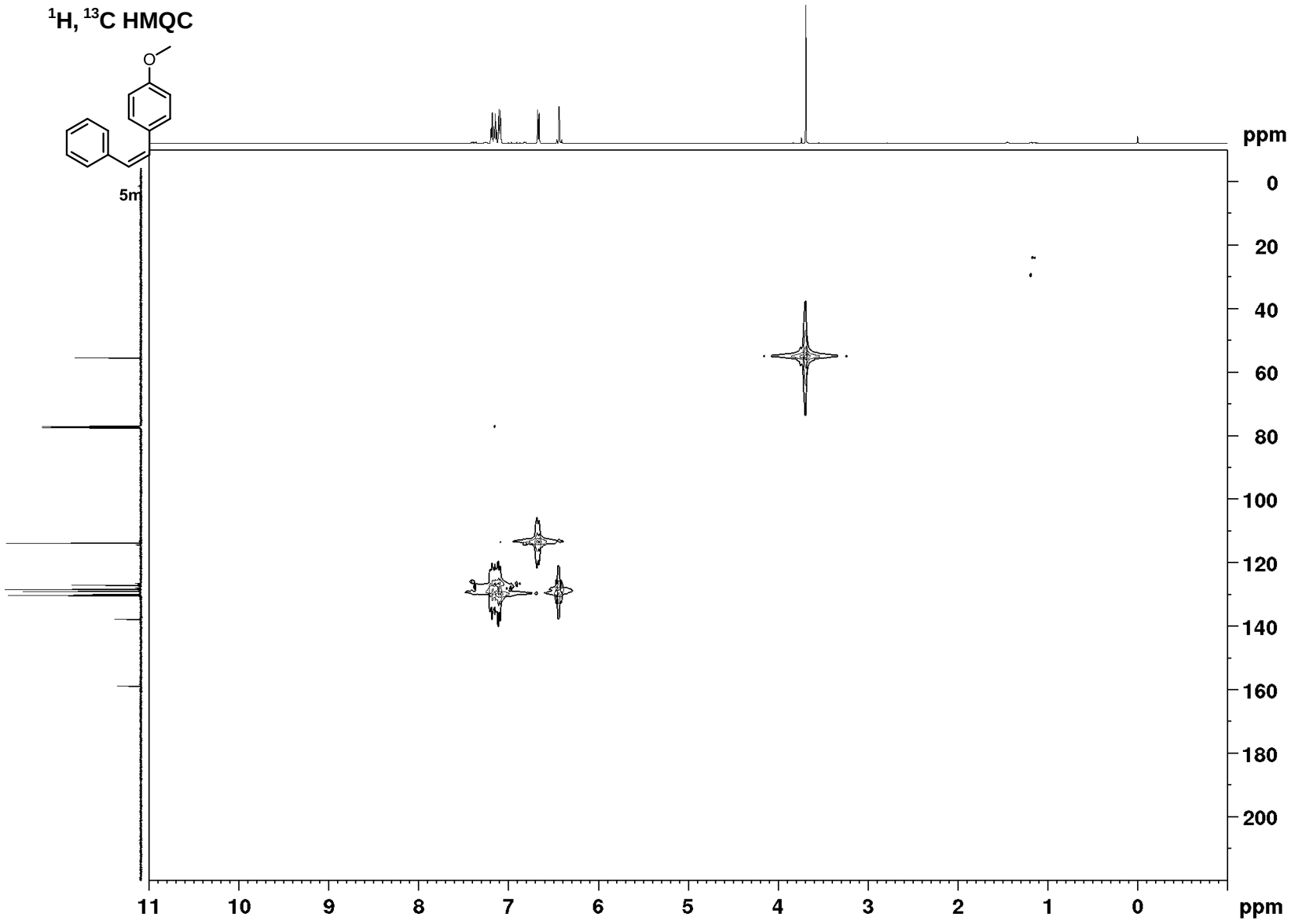

158.7
137.6
130.1
129.7
129.6
128.8
128.7
128.2
126.9
113.6
55.1
O
5m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

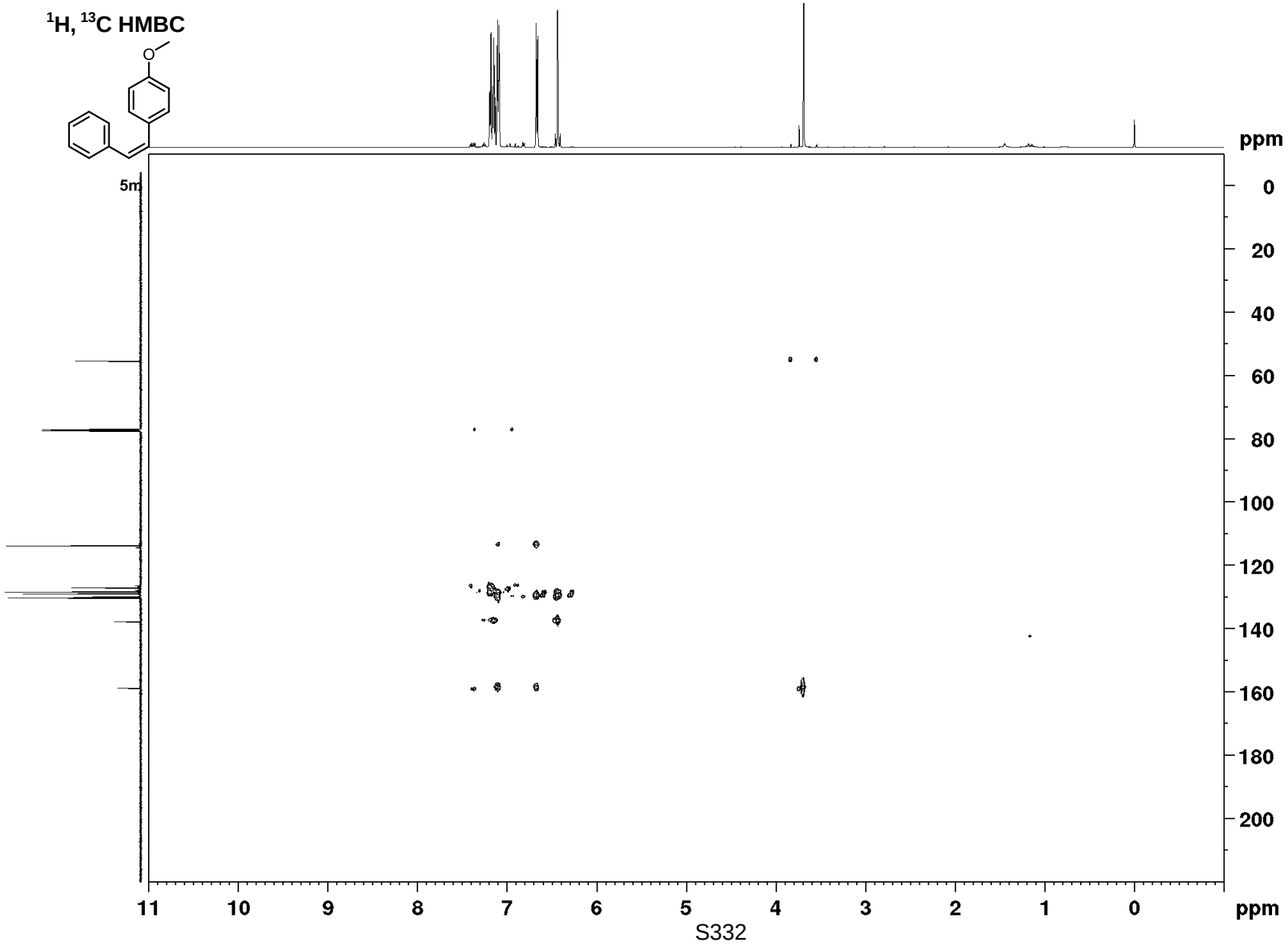
^{13}C DEPT NMR

5m

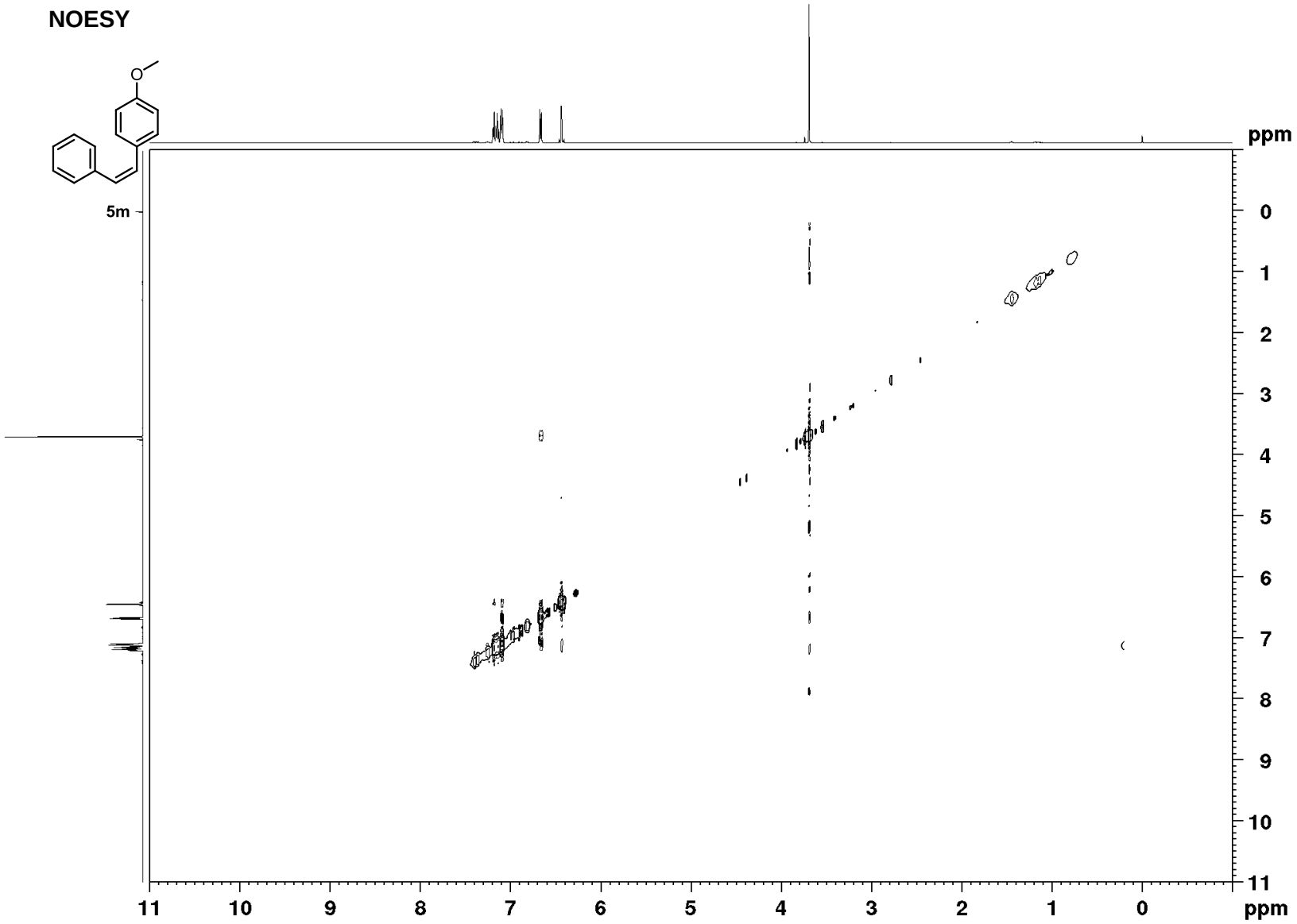



^{1}H, ^{1}H COSY
O
5m
ppm
0
1
2
3
4
5
6
7
8
9
10
11
11
10
9
8
7
6
5
4
3
2
1
0
ppm

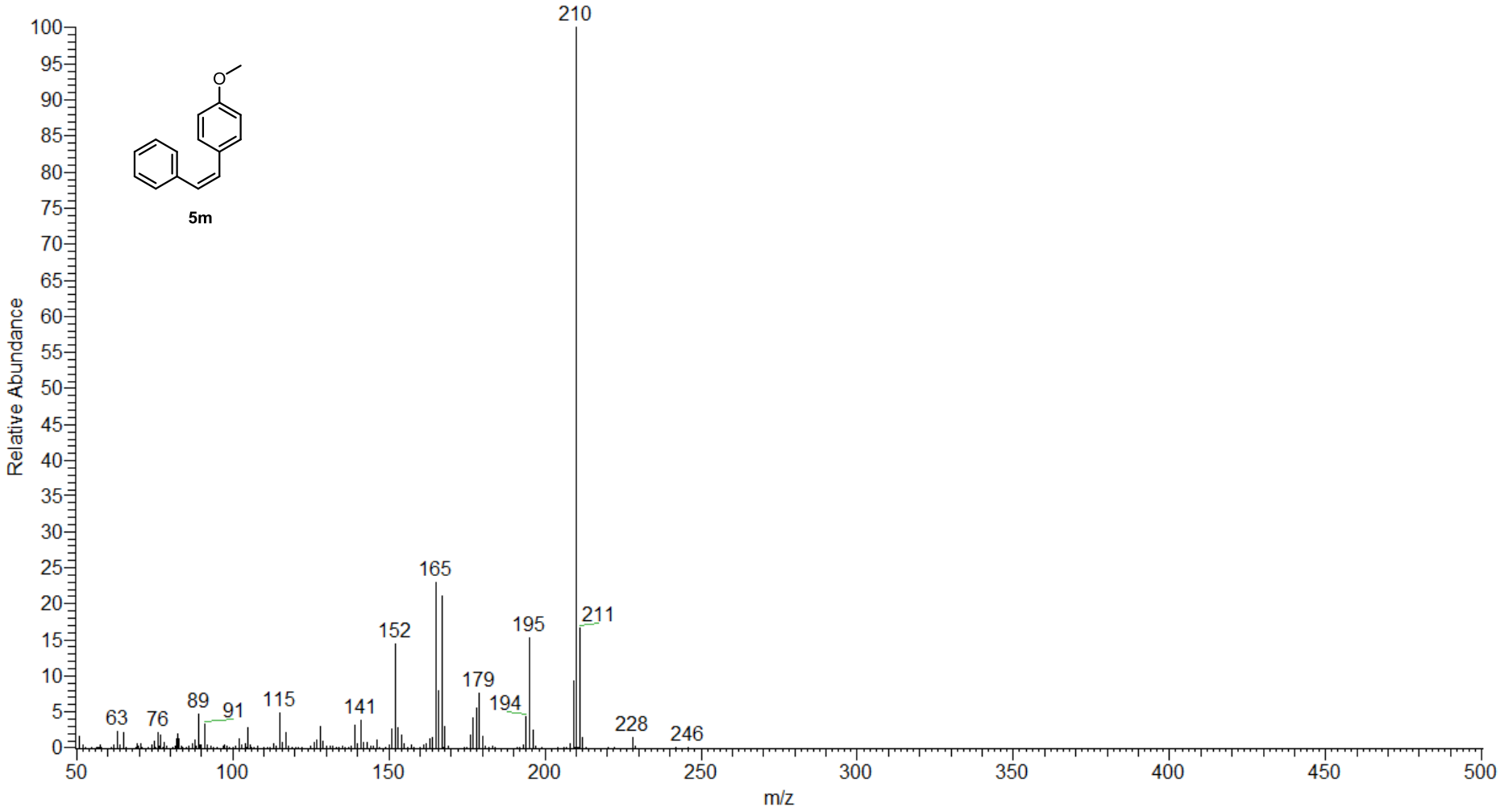

^{1}H, ^{13}C HMQC
O
5m
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm


^{1}H, ^{13}C HMBC
O
5m
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

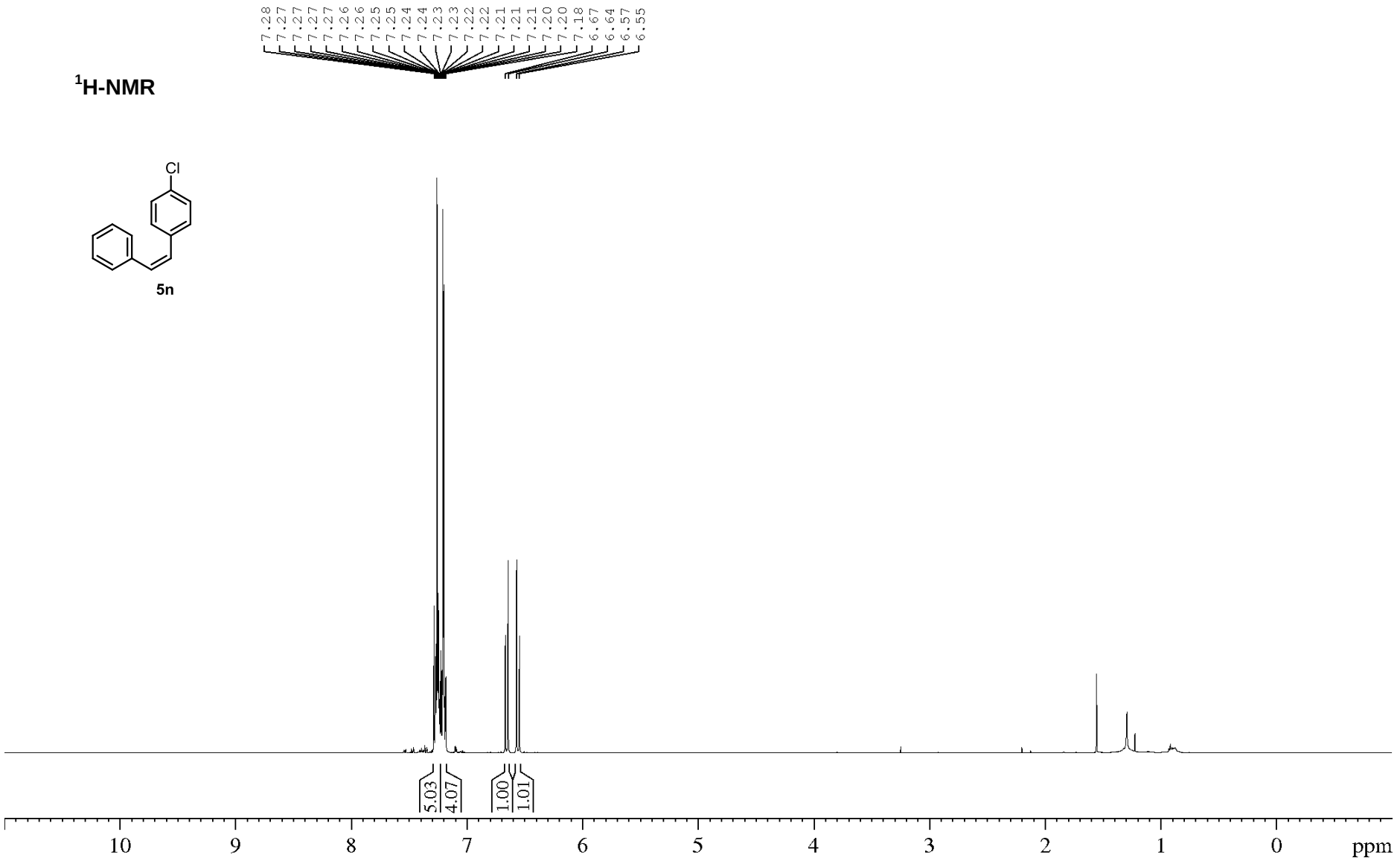
NOESY



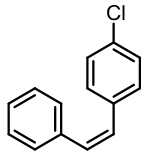
mass spectrum



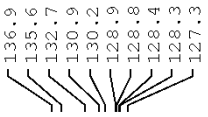
^{1}H-NMR

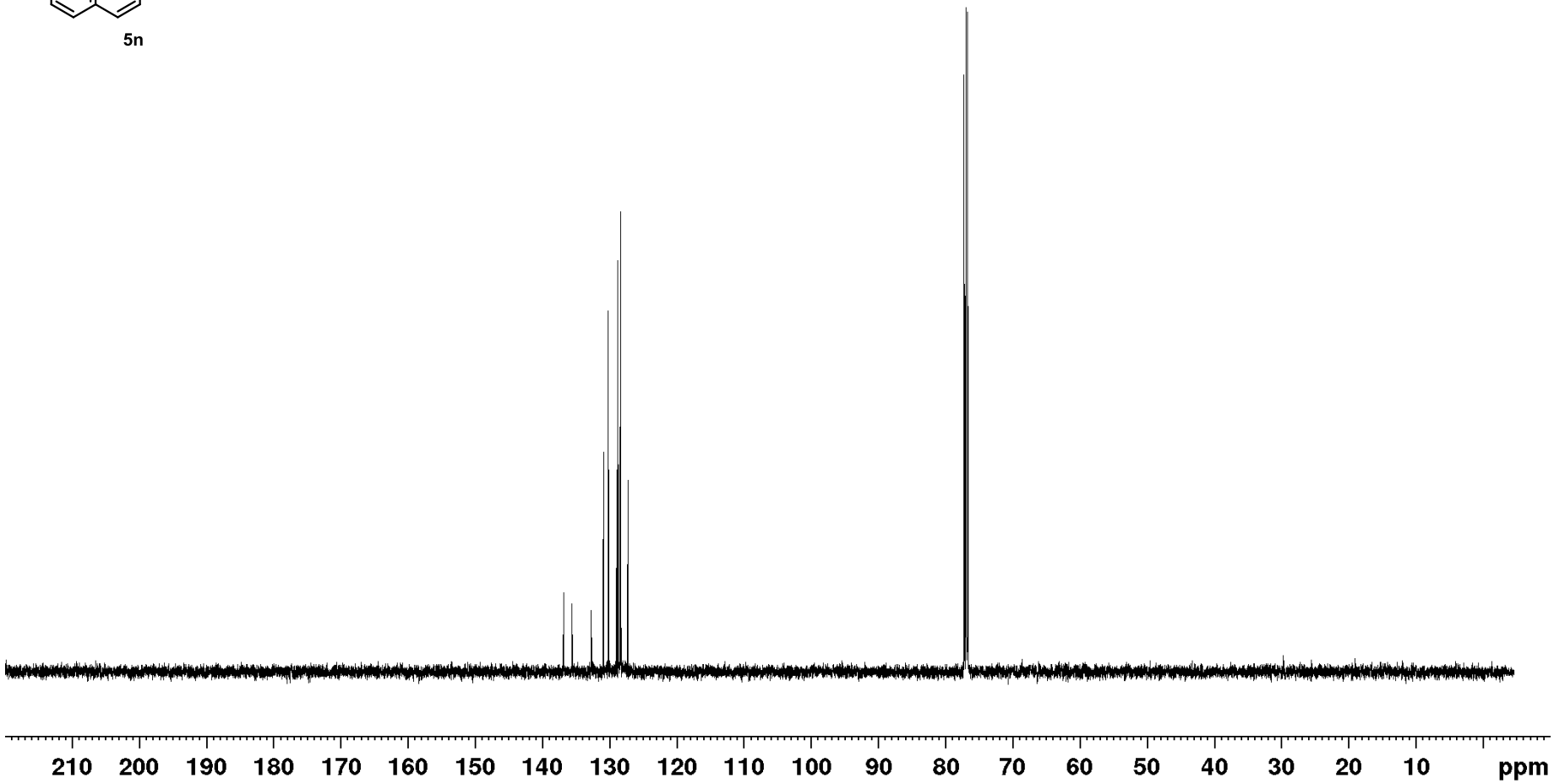

7.28
7.27
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.18
6.67
6.64
6.57
6.55
Cl
5n
5.03
4.07
1.00
1.01
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

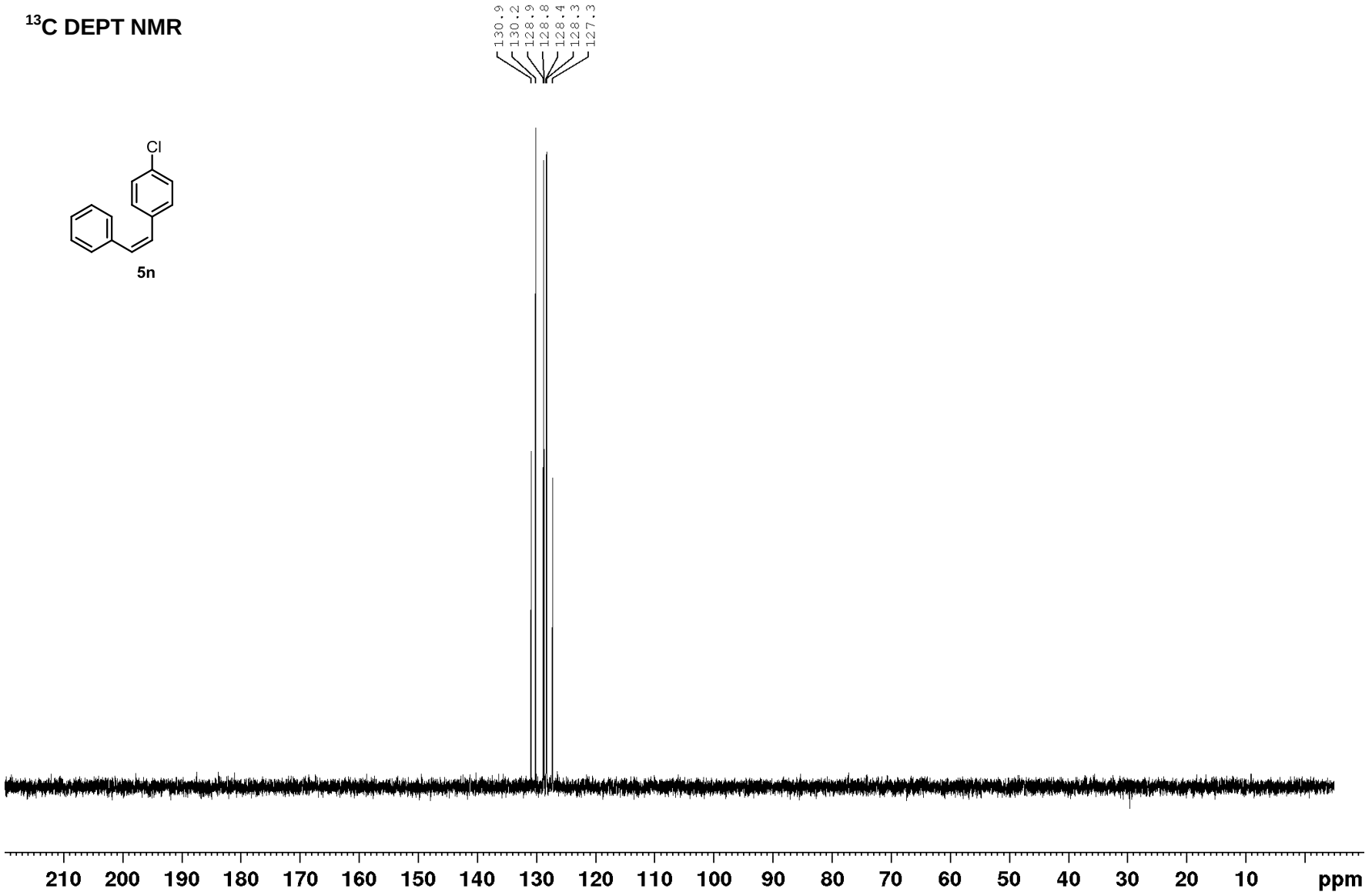

Cl

5n


136.9
135.6
132.7
130.9
130.2
128.9
128.8
128.4
128.3
127.3

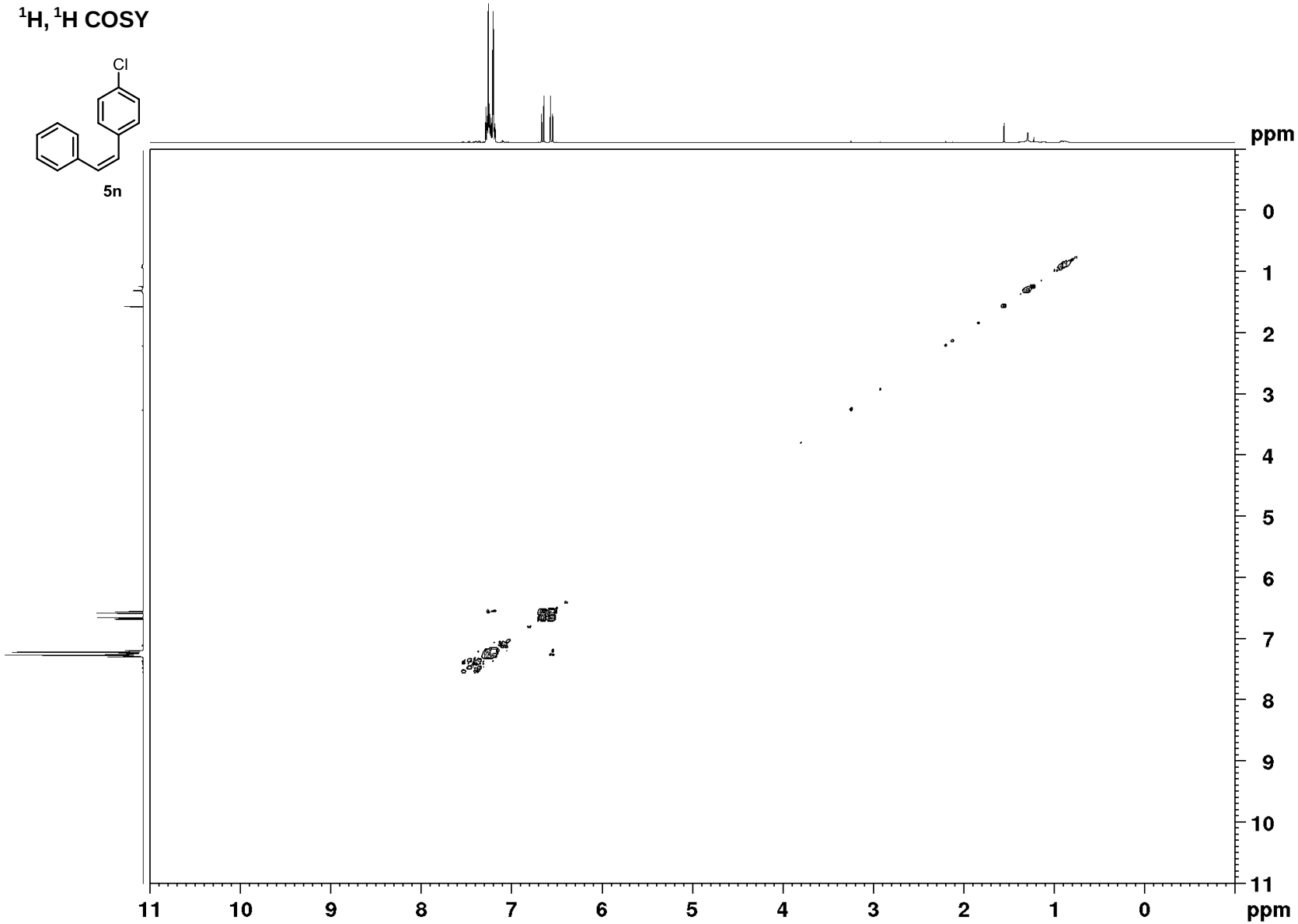

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

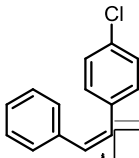

130.9
130.2
128.9
128.8
128.4
128.3
127.3
Cl
5n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H, ^{1}H COSY

5n



^{1}H, ^{13}C HMQC



5n

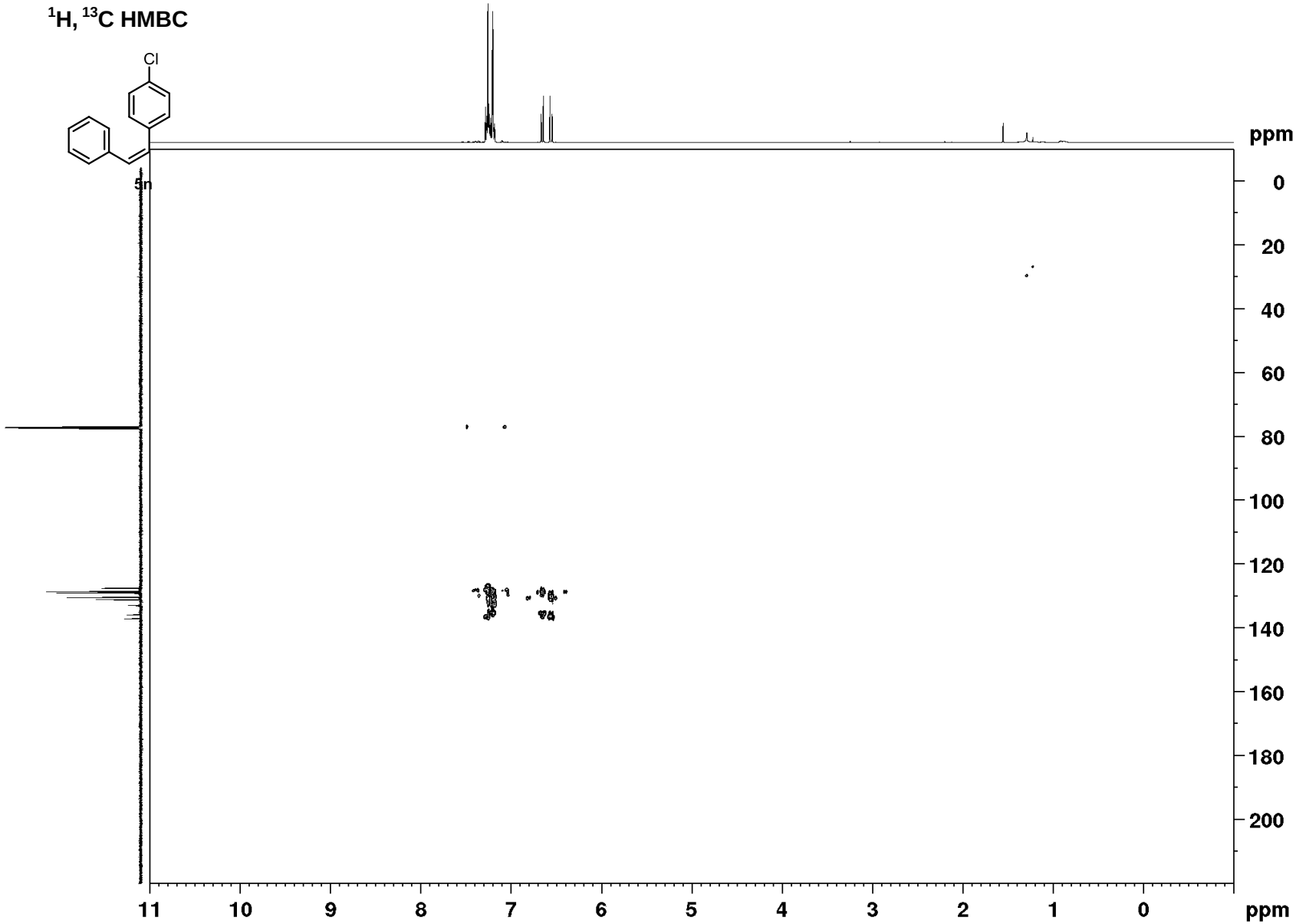
ppm

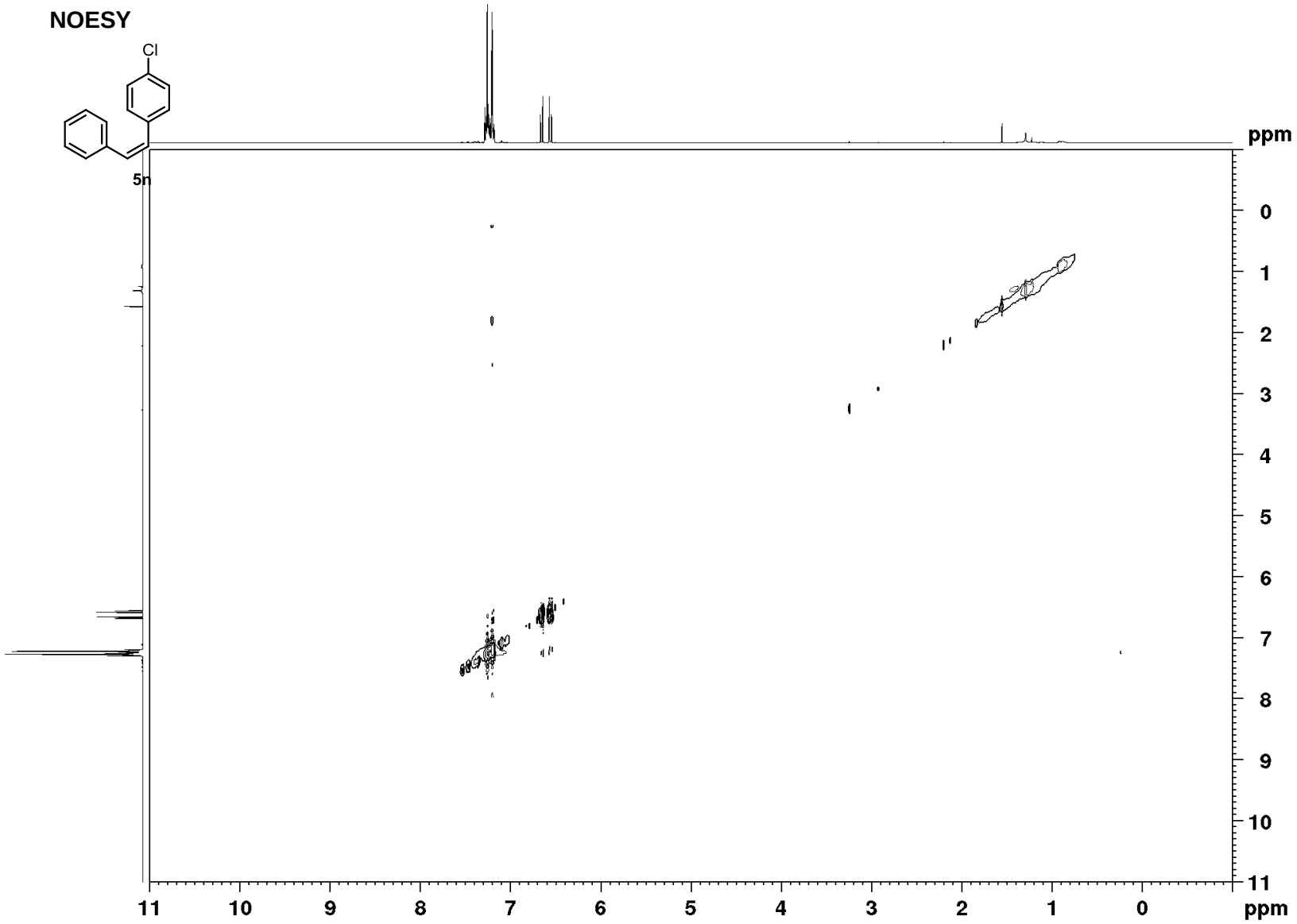
0
20
40
60
80
100
120
140
160
180
200

11 10 9 8 7 6 5 4 3 2 1 0 ppm

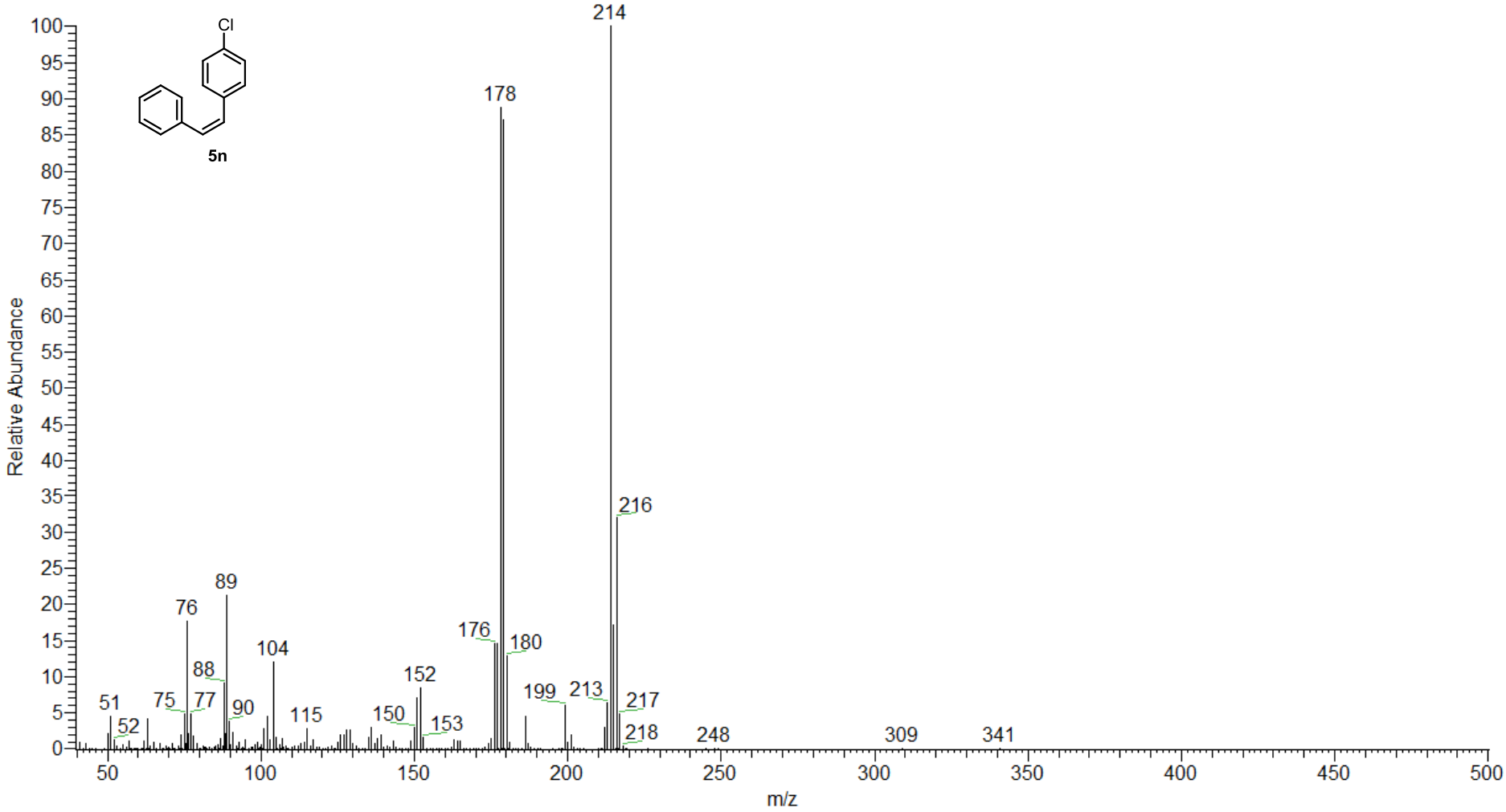
^{1}H, ^{13}C HMBC

5n




NOESY
Cl
5n
ppm
0
1
2
3
4
5
6
7
8
9
10
11
11
10
9
8
7
6
5
4
3
2
1
0
ppm

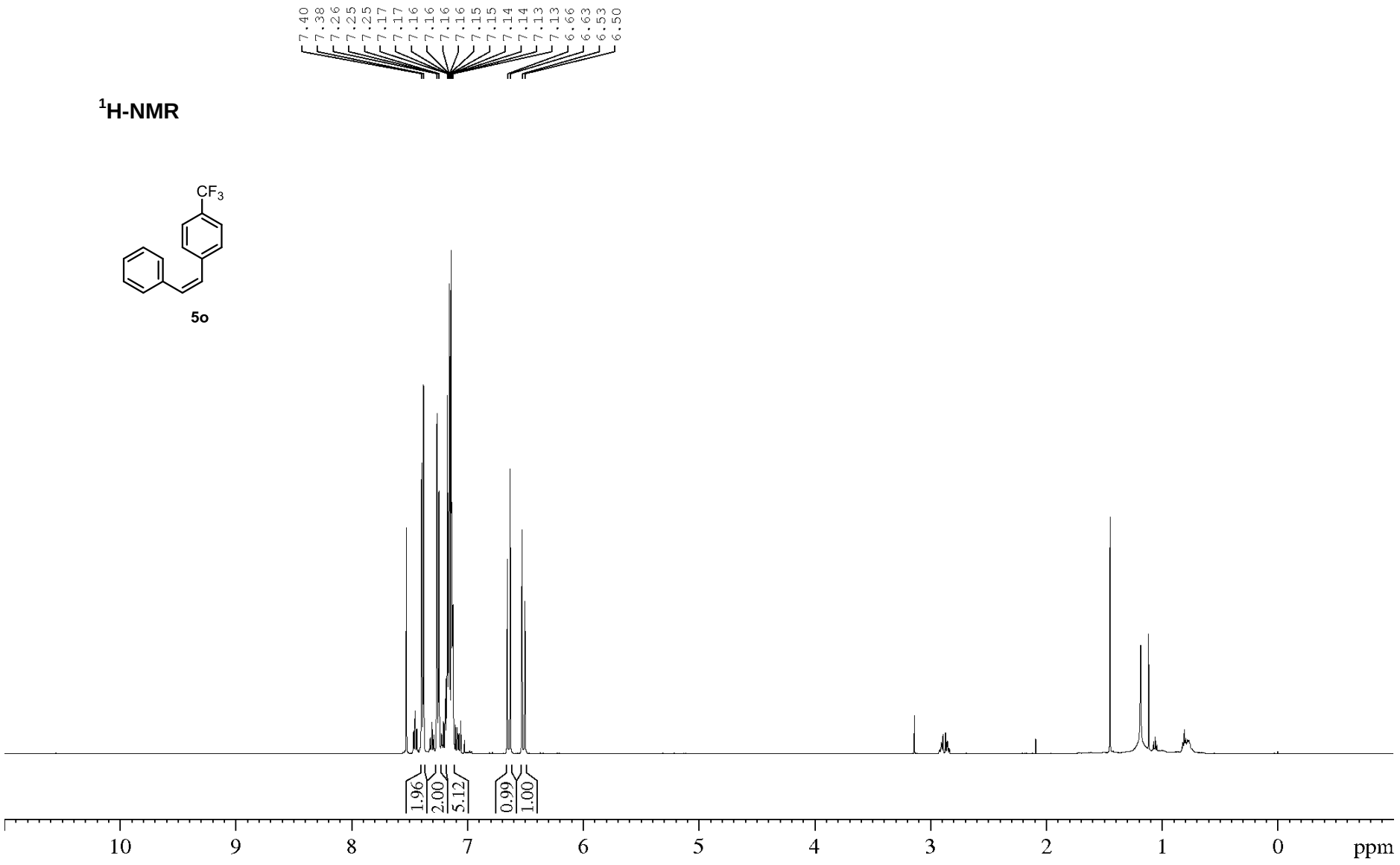
^{1}H NMR


Cl
5n
Relative Abundance
m/z
214
178
216
89
76
176
180
104
88
152
199
213
217
51
75
77
90
115
150
153
218
248
309
341
52

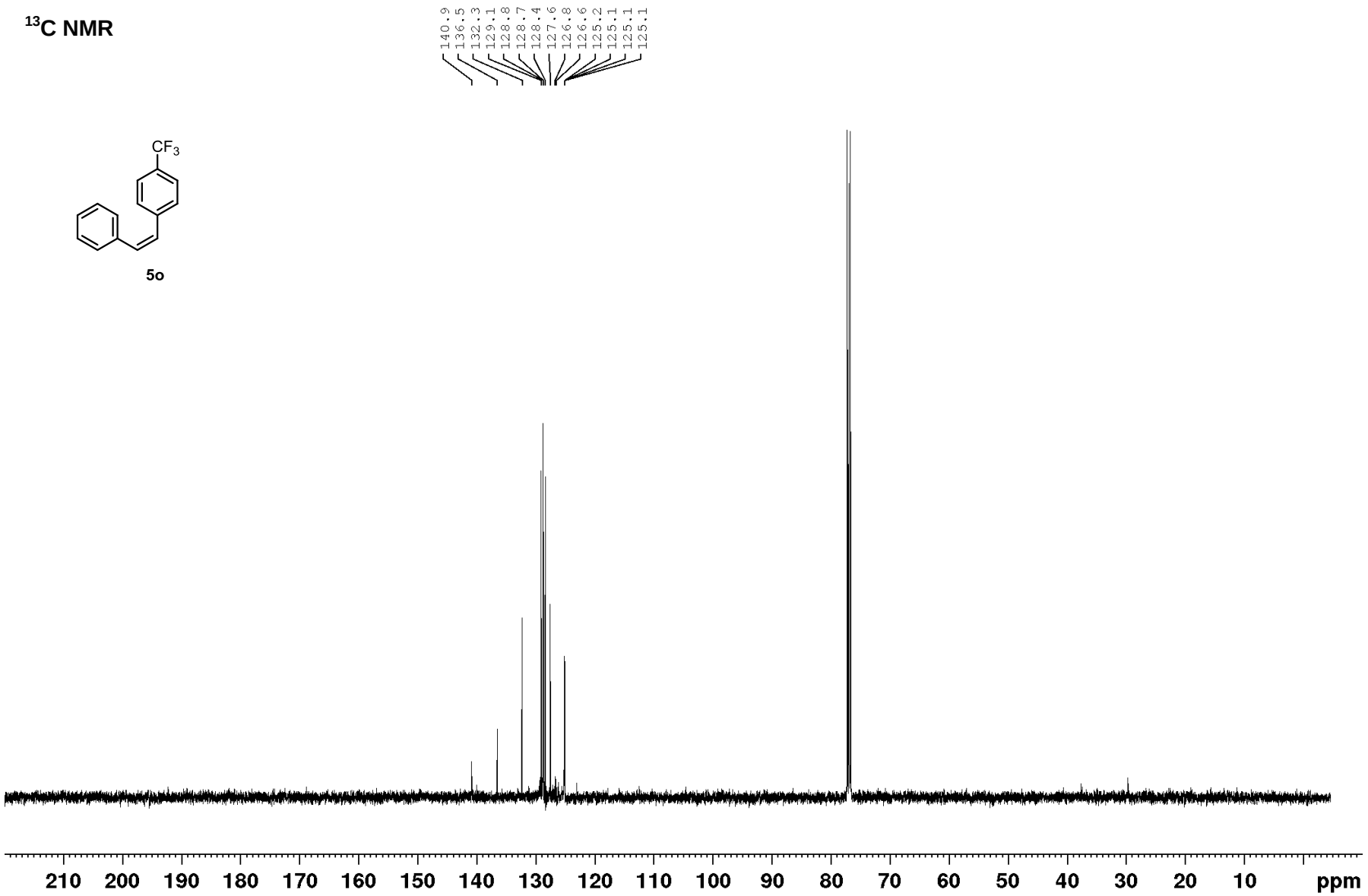
^{1}H-NMR

CF3

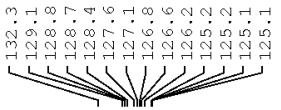
5o

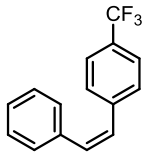

7.40
7.38
7.26
7.25
7.25
7.17
7.17
7.16
7.16
7.16
7.16
7.15
7.15
7.14
7.14
7.13
7.13
6.66
6.63
6.53
6.50
1.96
2.00
5.12
0.99
1.00
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

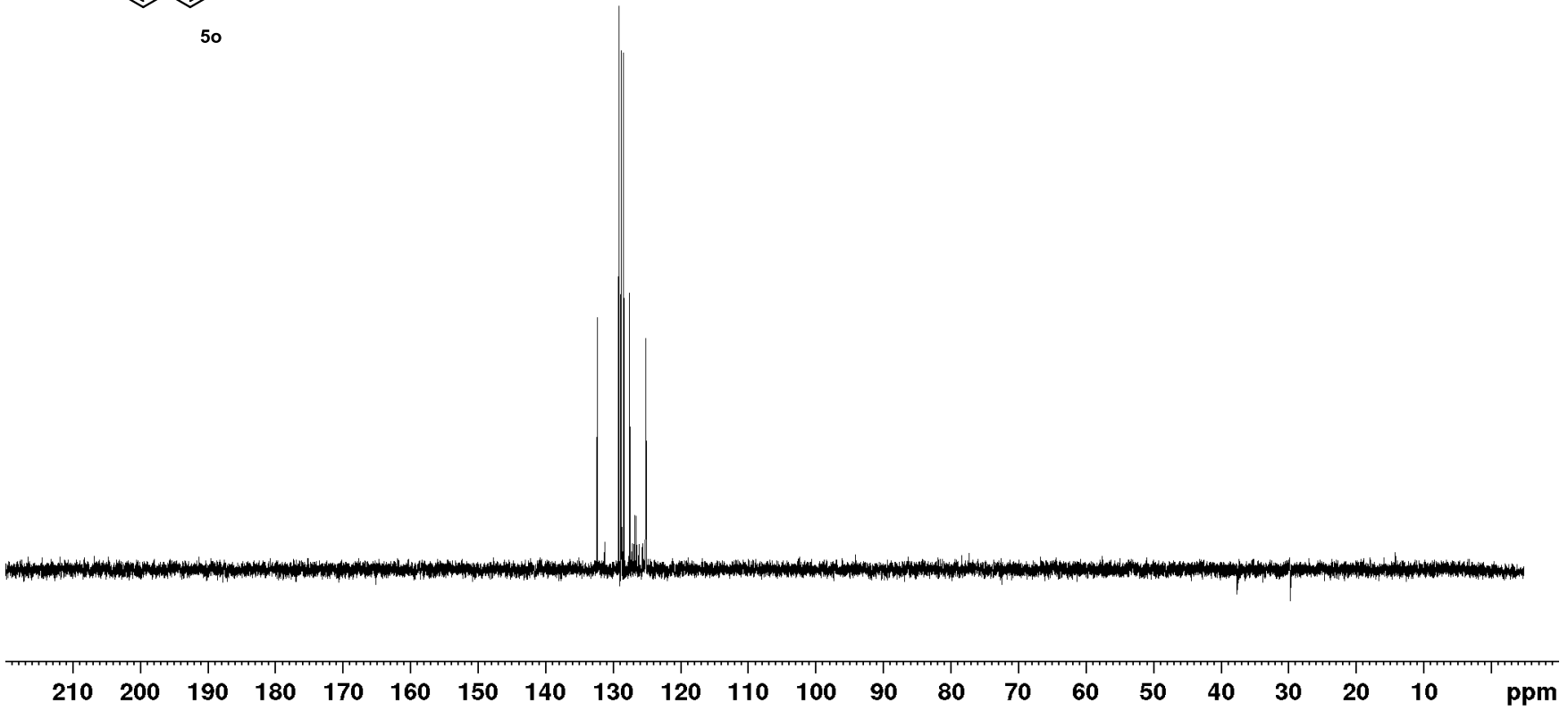

140.9
136.5
132.3
129.1
128.8
128.7
128.4
127.6
126.8
126.6
125.2
125.1
125.1
125.1
CF3
5o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

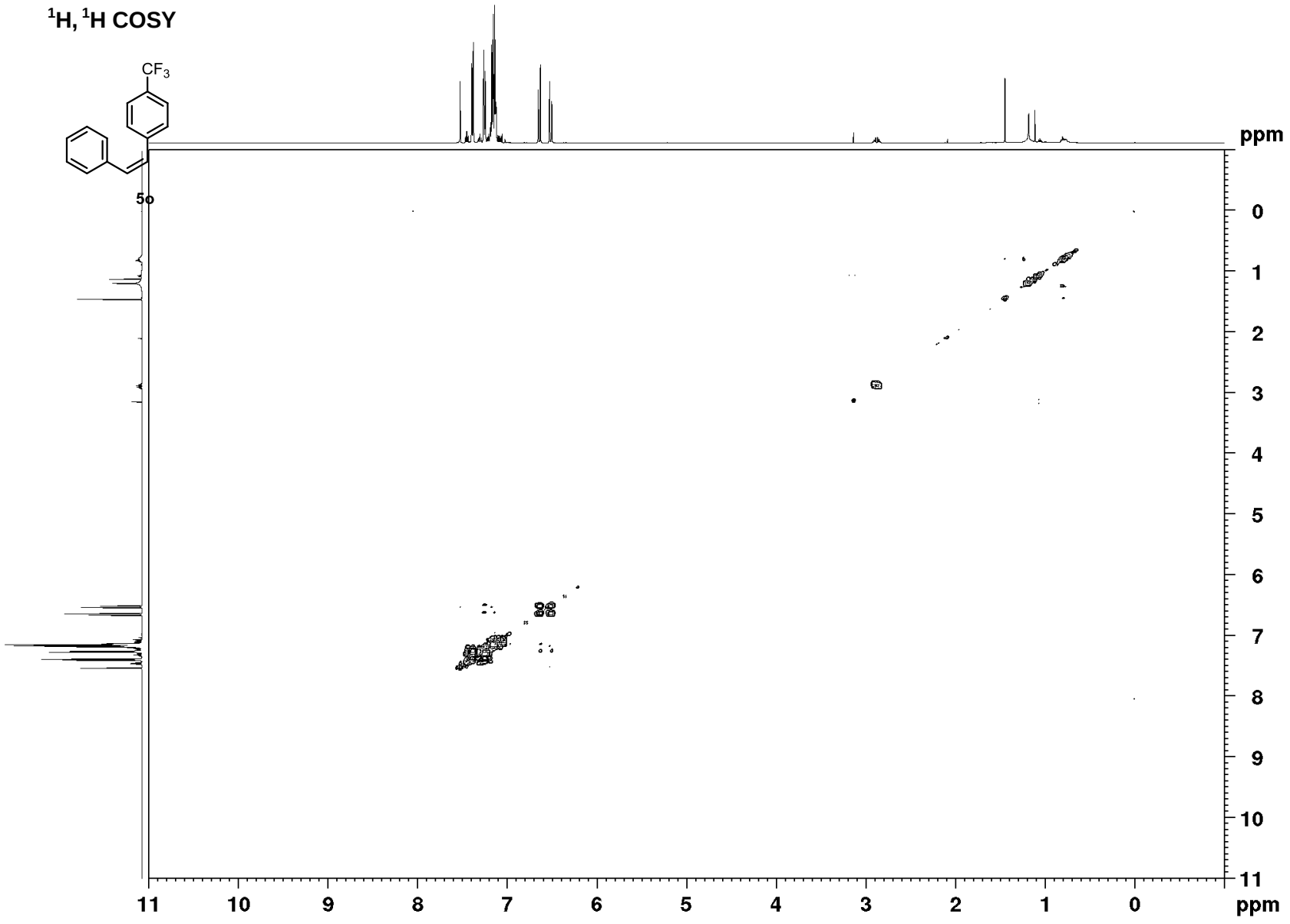


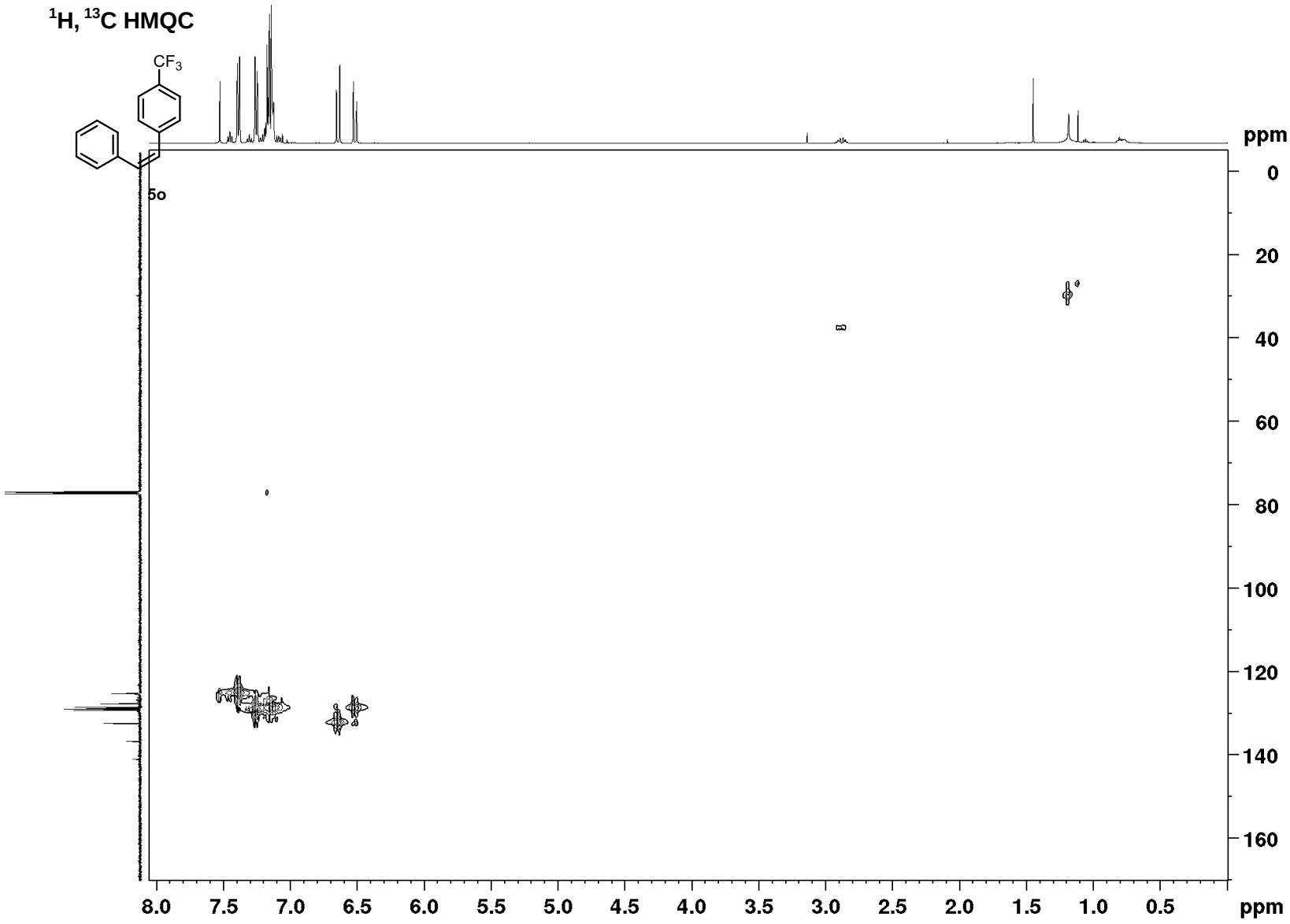


5o

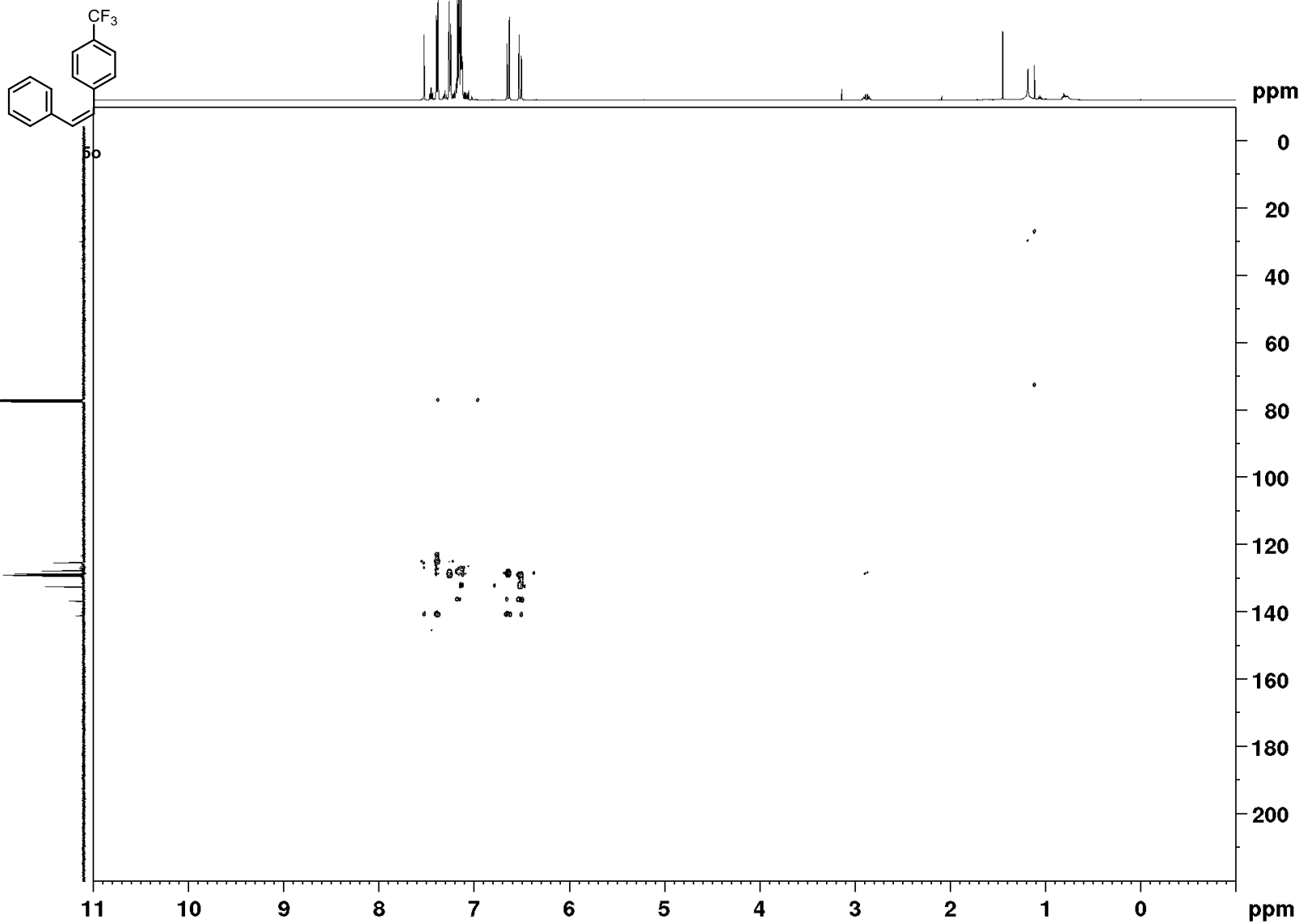


^{1}H, ^{1}H COSY

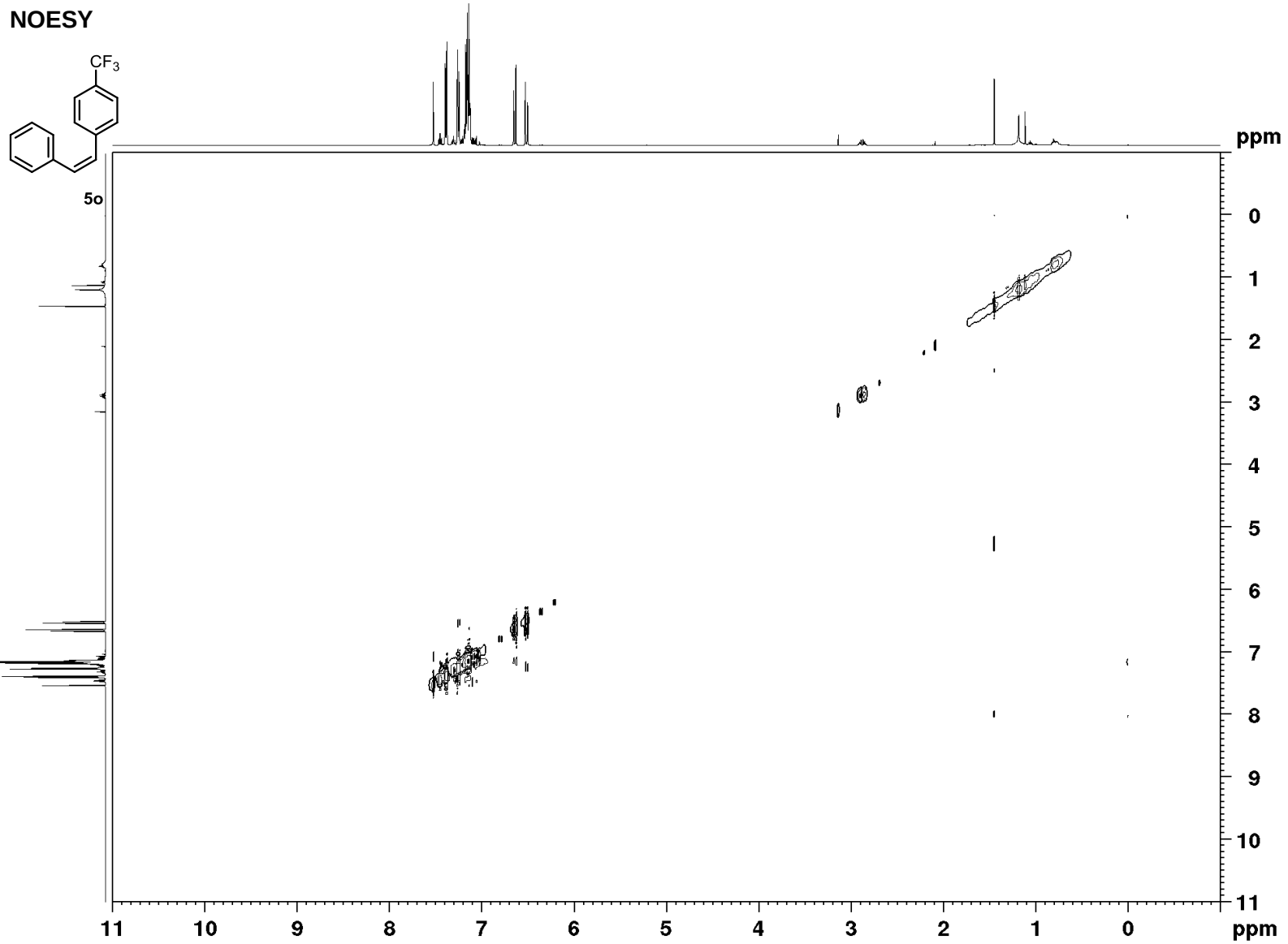



^{1}H, ^{13}C HMQC
CF$_3$
5o
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H, ^{13}C HMBC

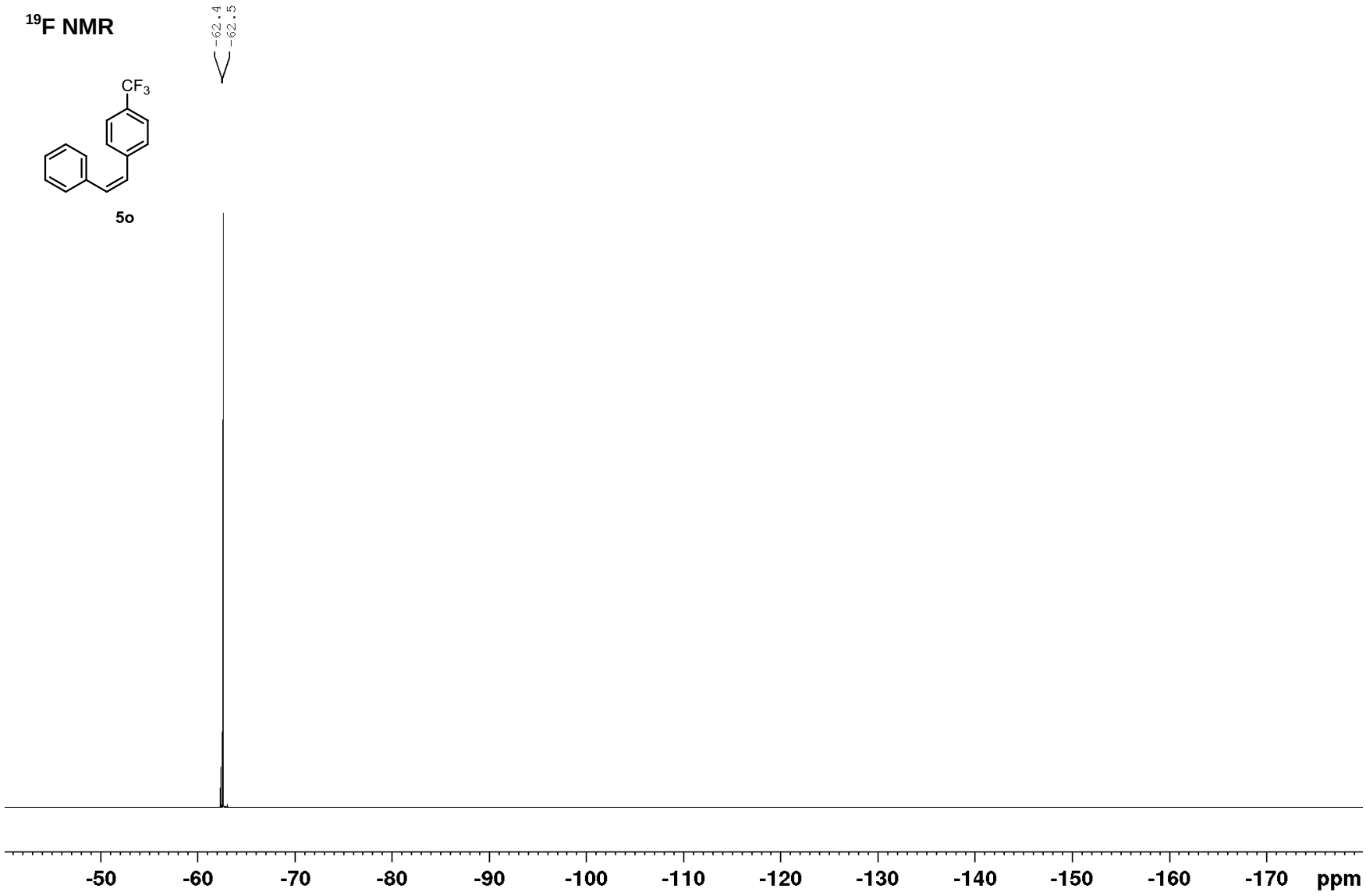

CF3
5o
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

NOESY

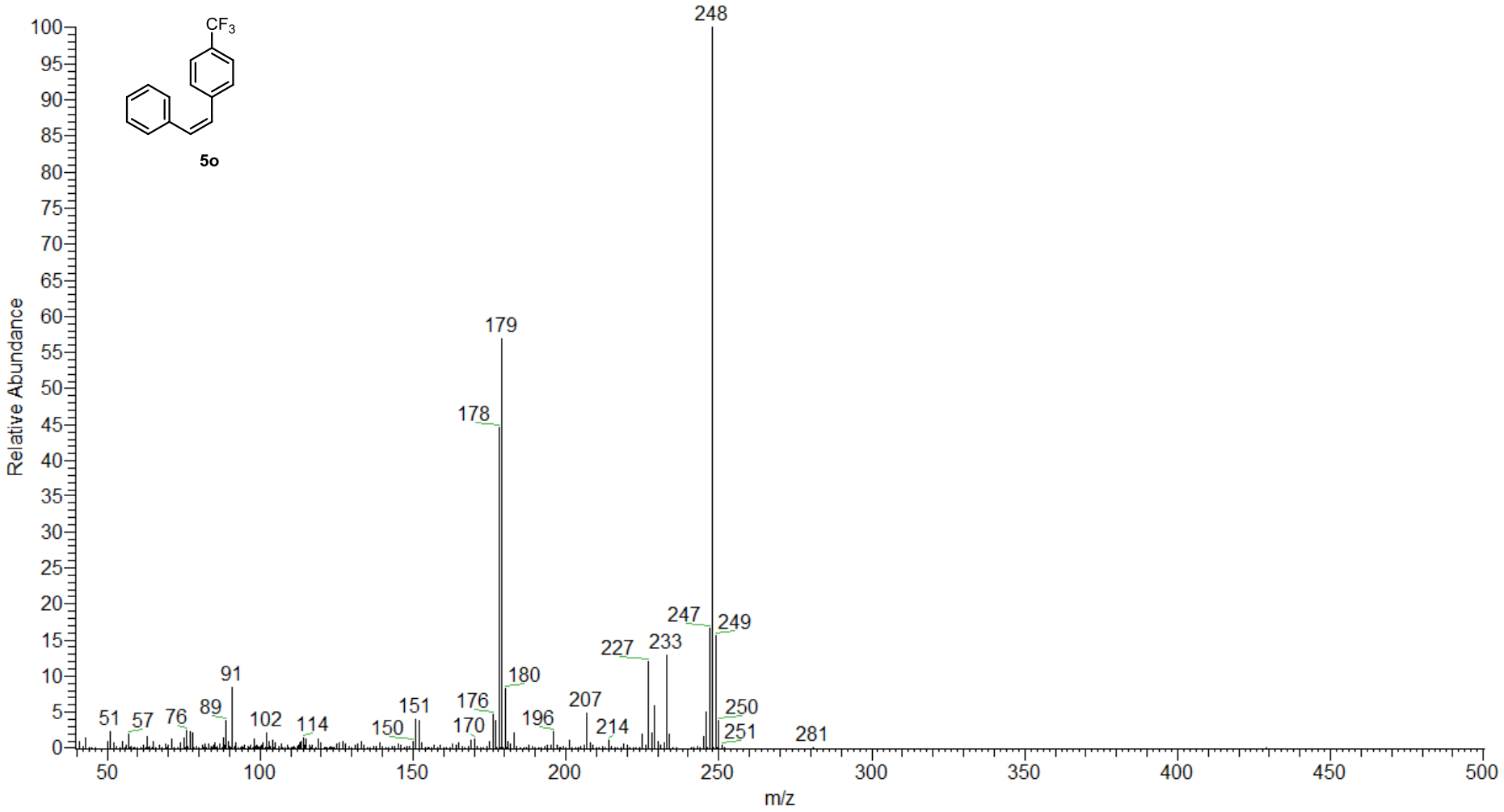


^{19}F NMR

5o

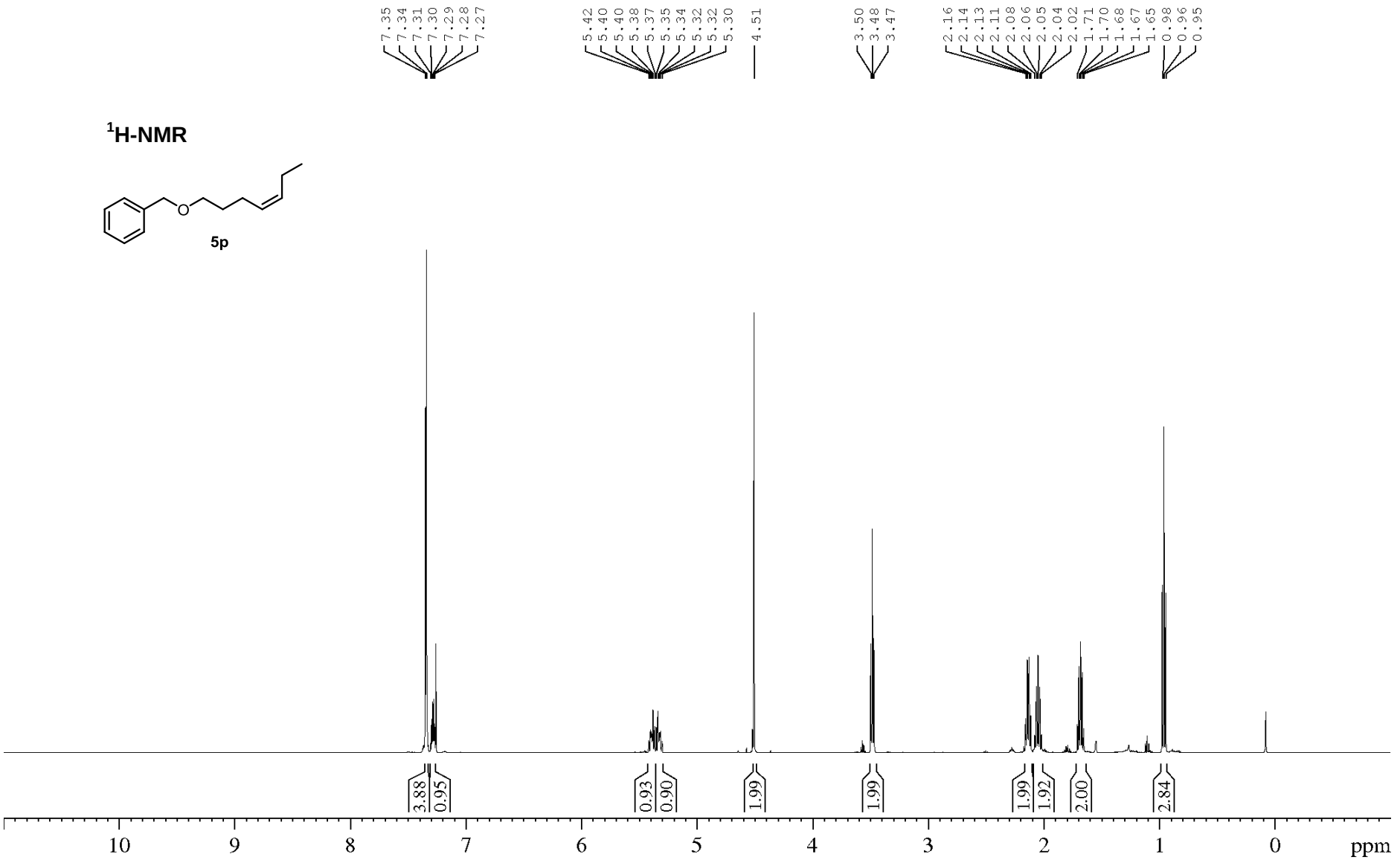


mass spectrum

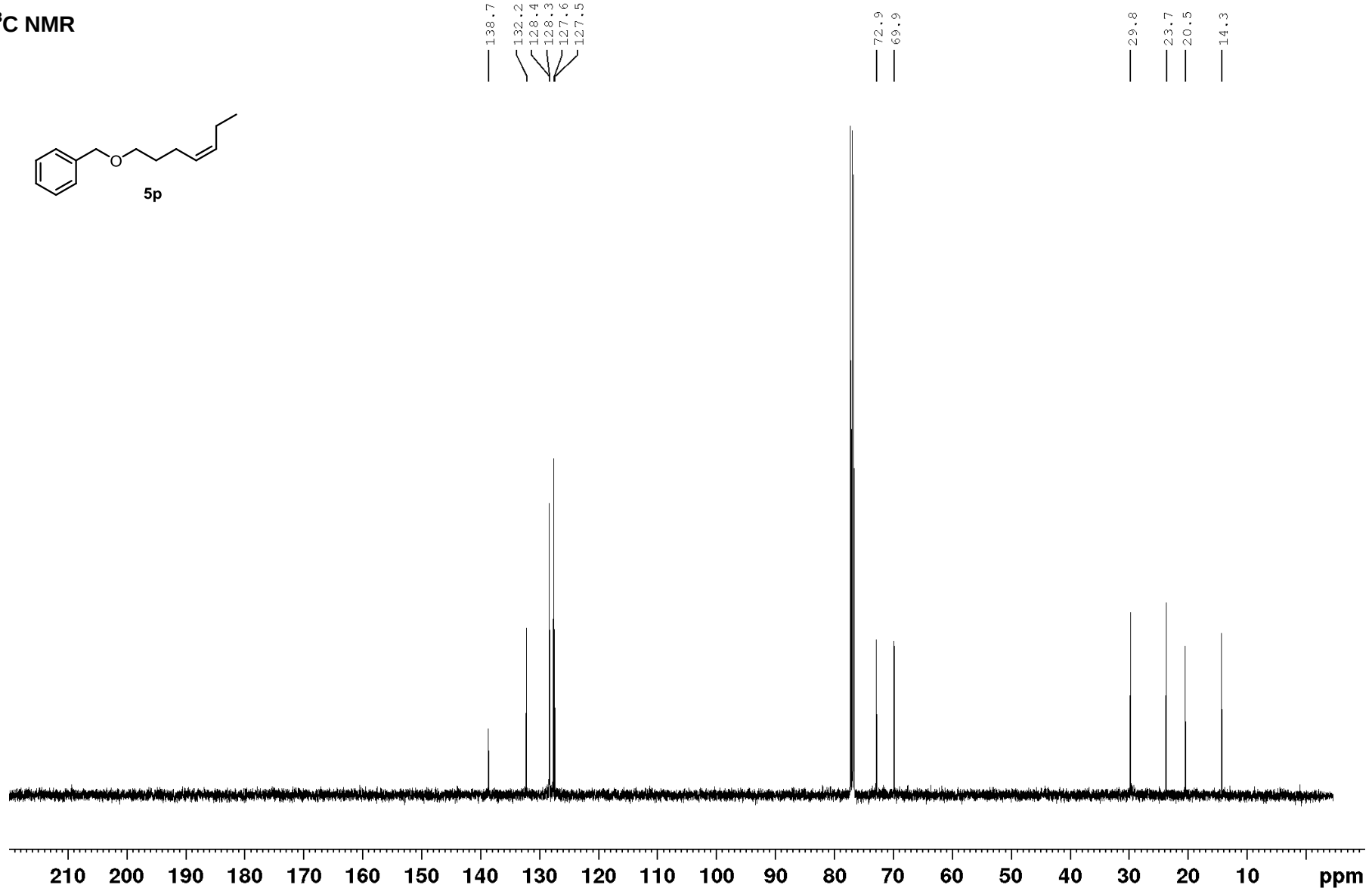


^{1}H-NMR

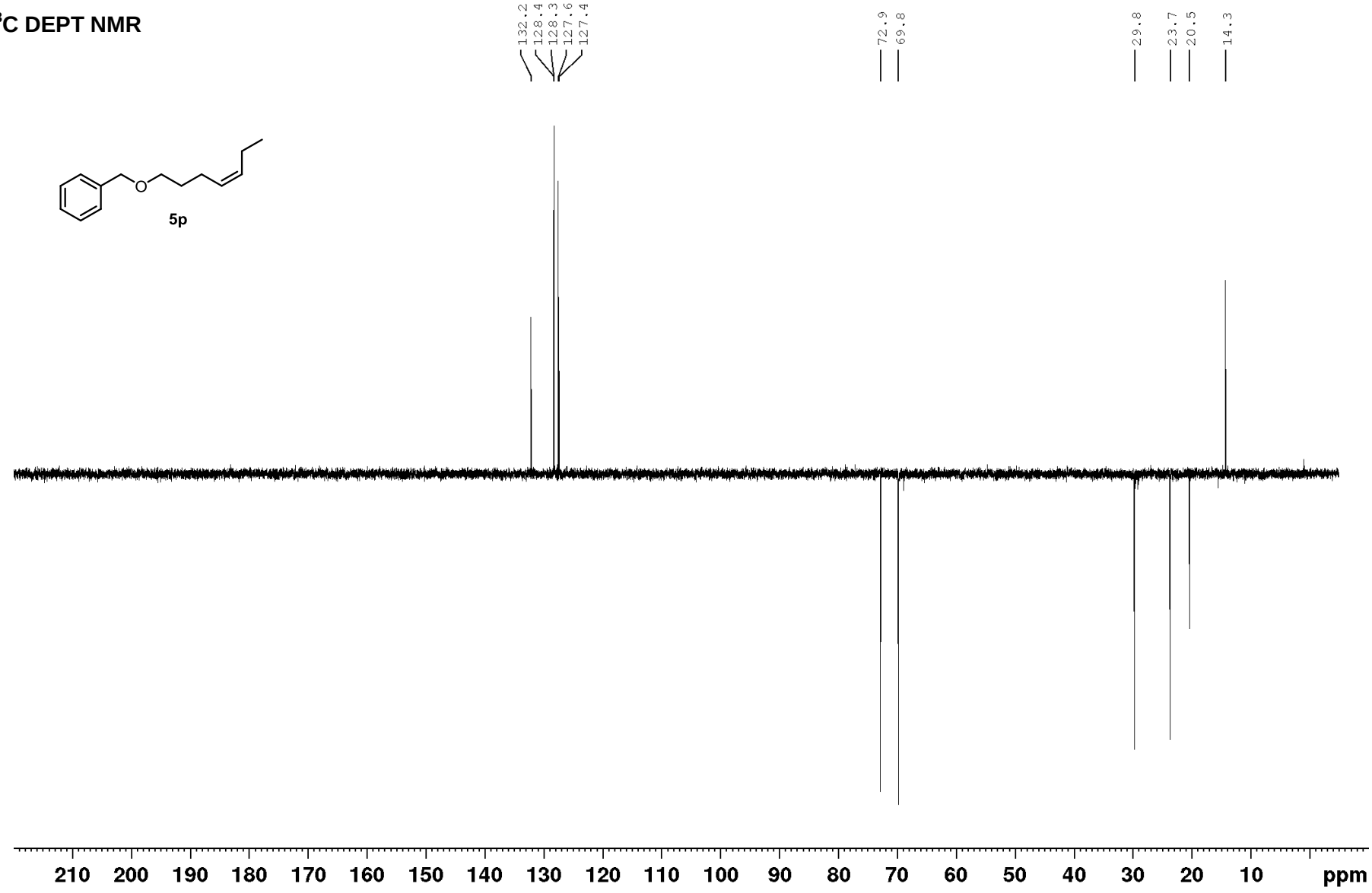
5p


7.35
7.34
7.31
7.30
7.29
7.28
7.27
5.42
5.40
5.40
5.38
5.37
5.35
5.34
5.32
5.32
5.30
4.51
3.50
3.48
3.47
2.16
2.14
2.13
2.11
2.08
2.06
2.05
2.04
2.02
1.71
1.70
1.68
1.67
1.65
0.98
0.96
0.95
3.88
0.95
0.93
0.90
1.99
1.99
1.99
1.92
2.00
2.84
10
9
8
7
6
5
4
3
2
1
0
ppm

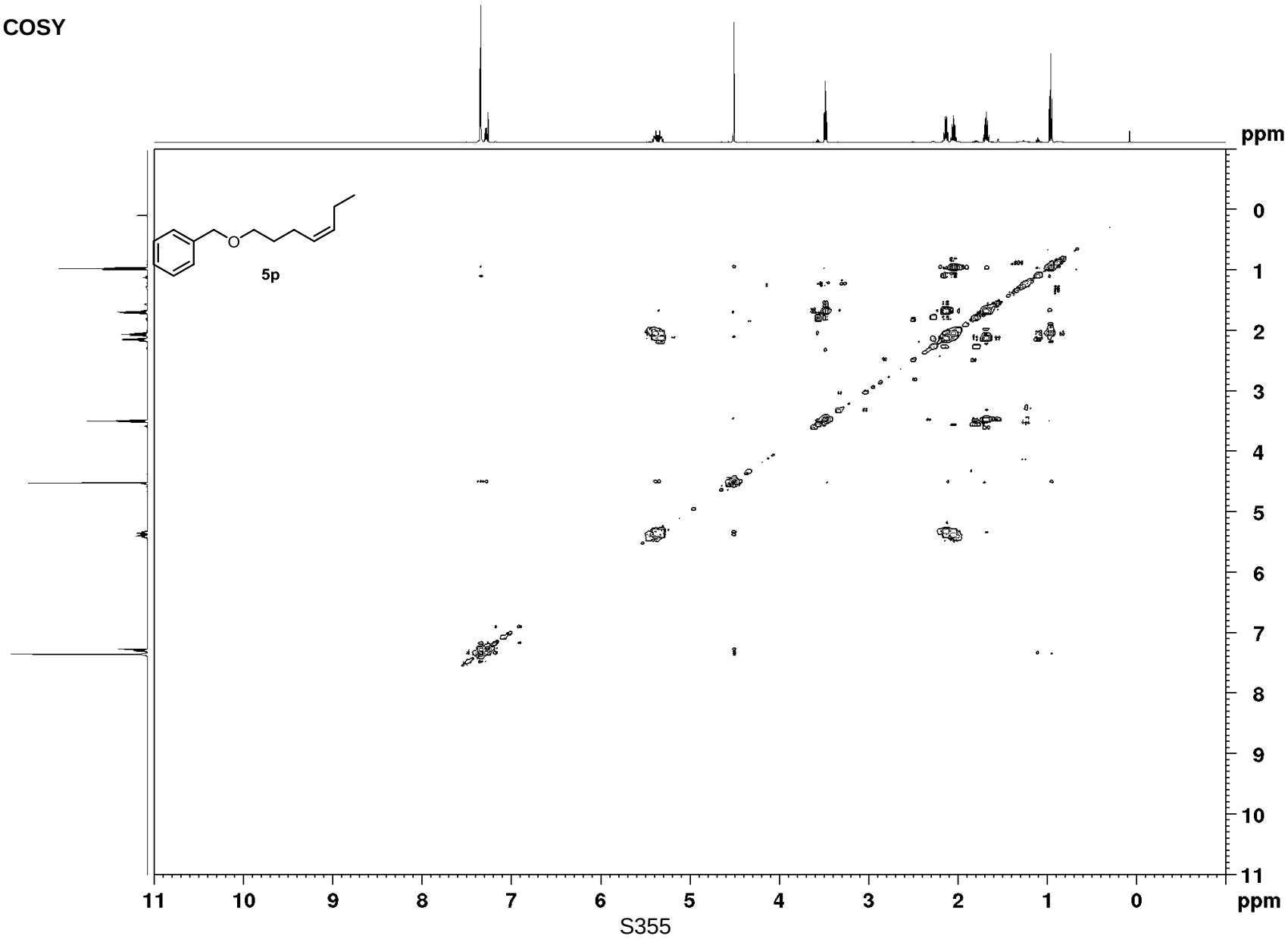
^{13}C NMR


138.7
132.2
128.4
128.3
127.6
127.5
72.9
69.9
29.8
23.7
20.5
14.3
O
5p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

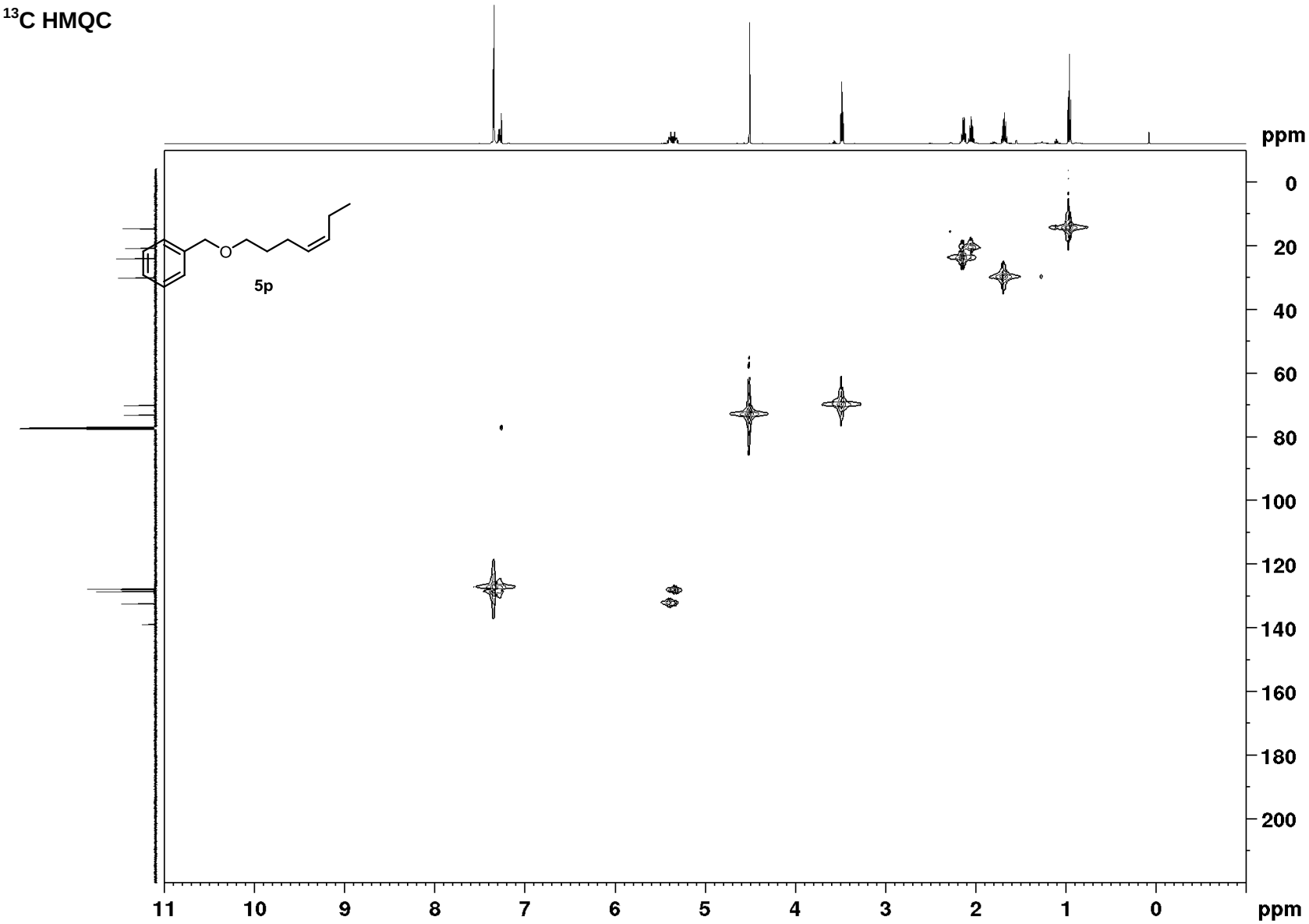
^{13}C DEPT NMR


132.2
128.4
128.3
127.6
127.4
72.9
69.8
29.8
23.7
20.5
14.3
5p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

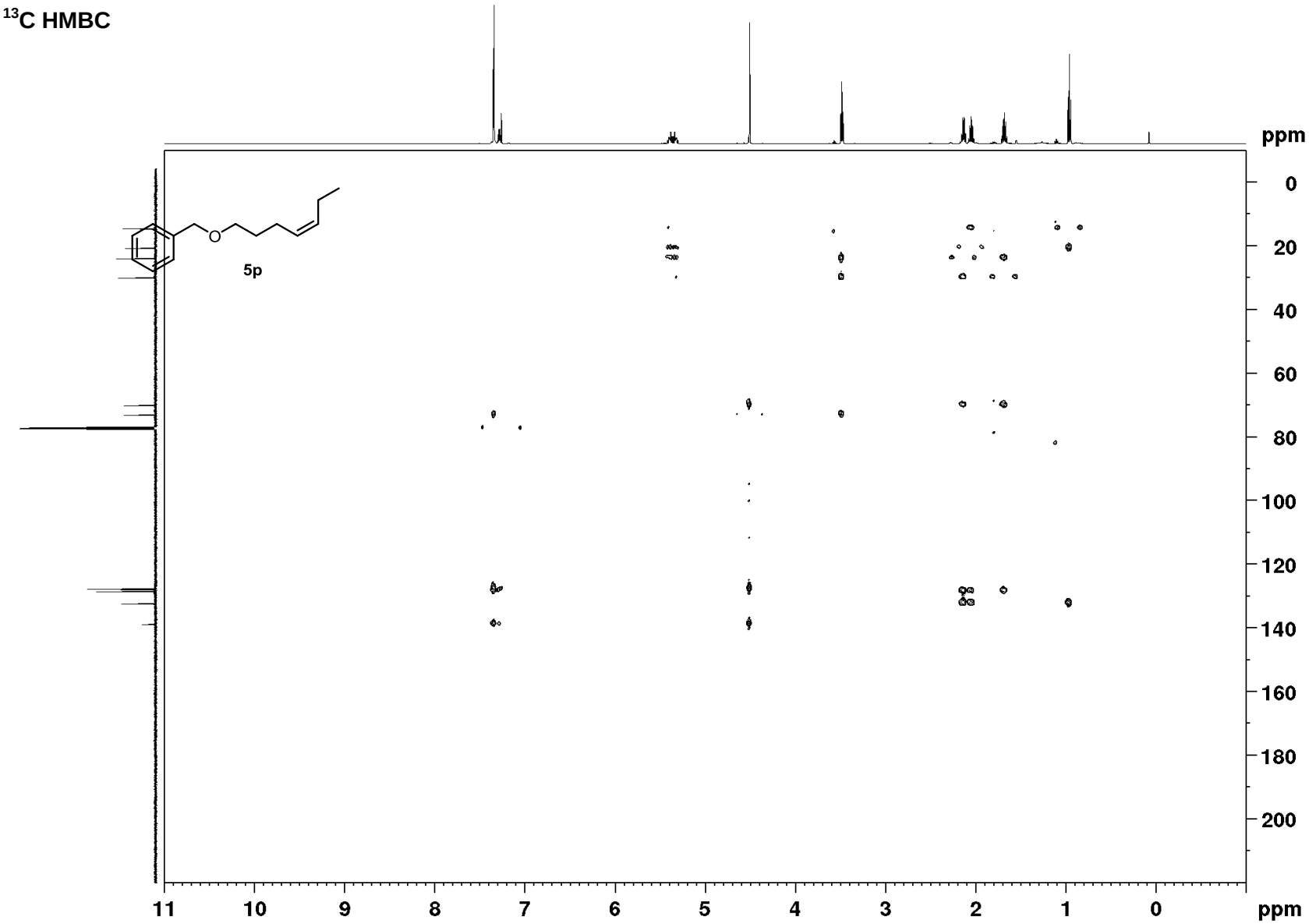
^{1}H, ^{1}H COSY



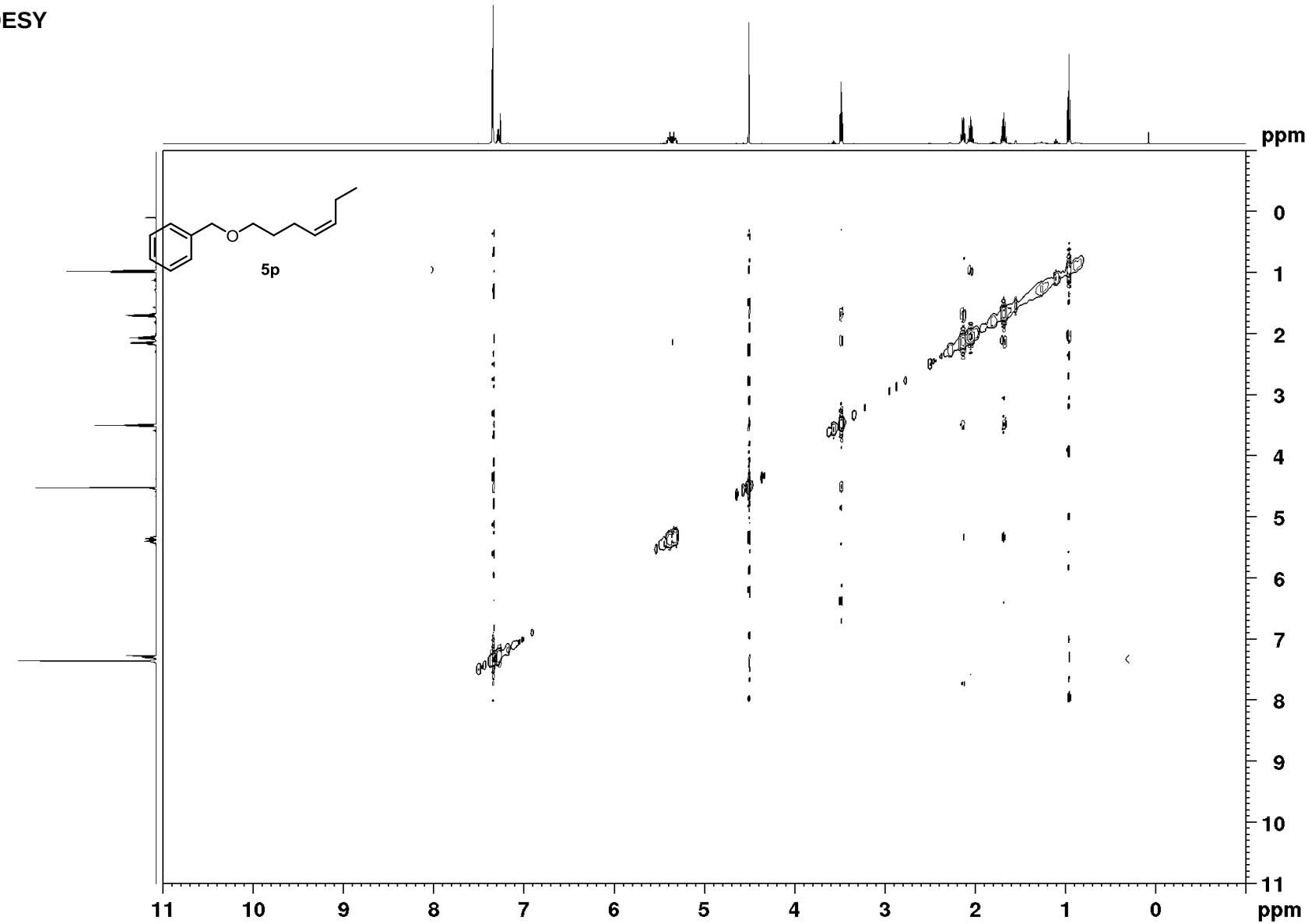
^{1}H, ^{13}C HMQC

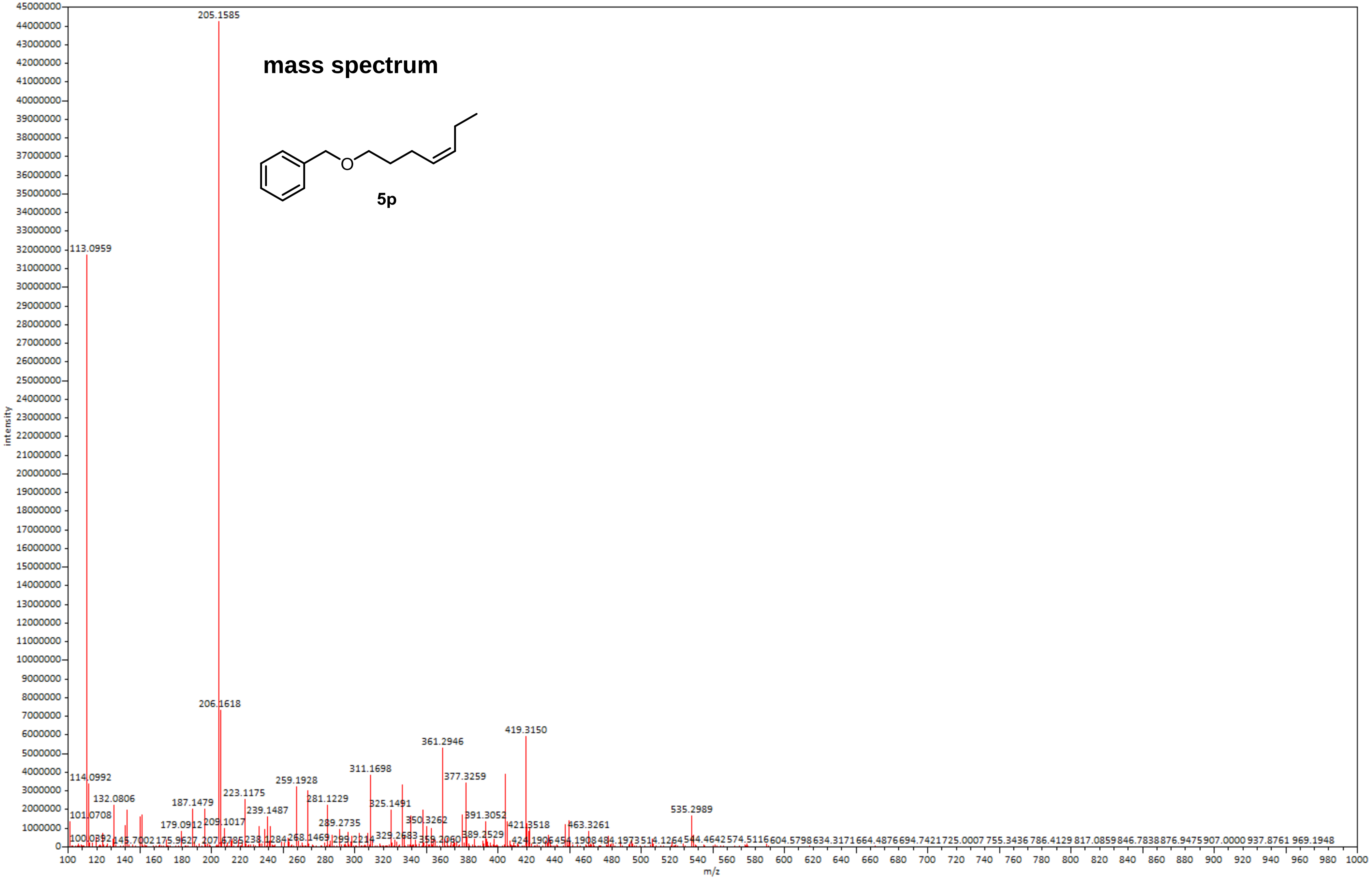


^{1}H, ^{13}C HMBC

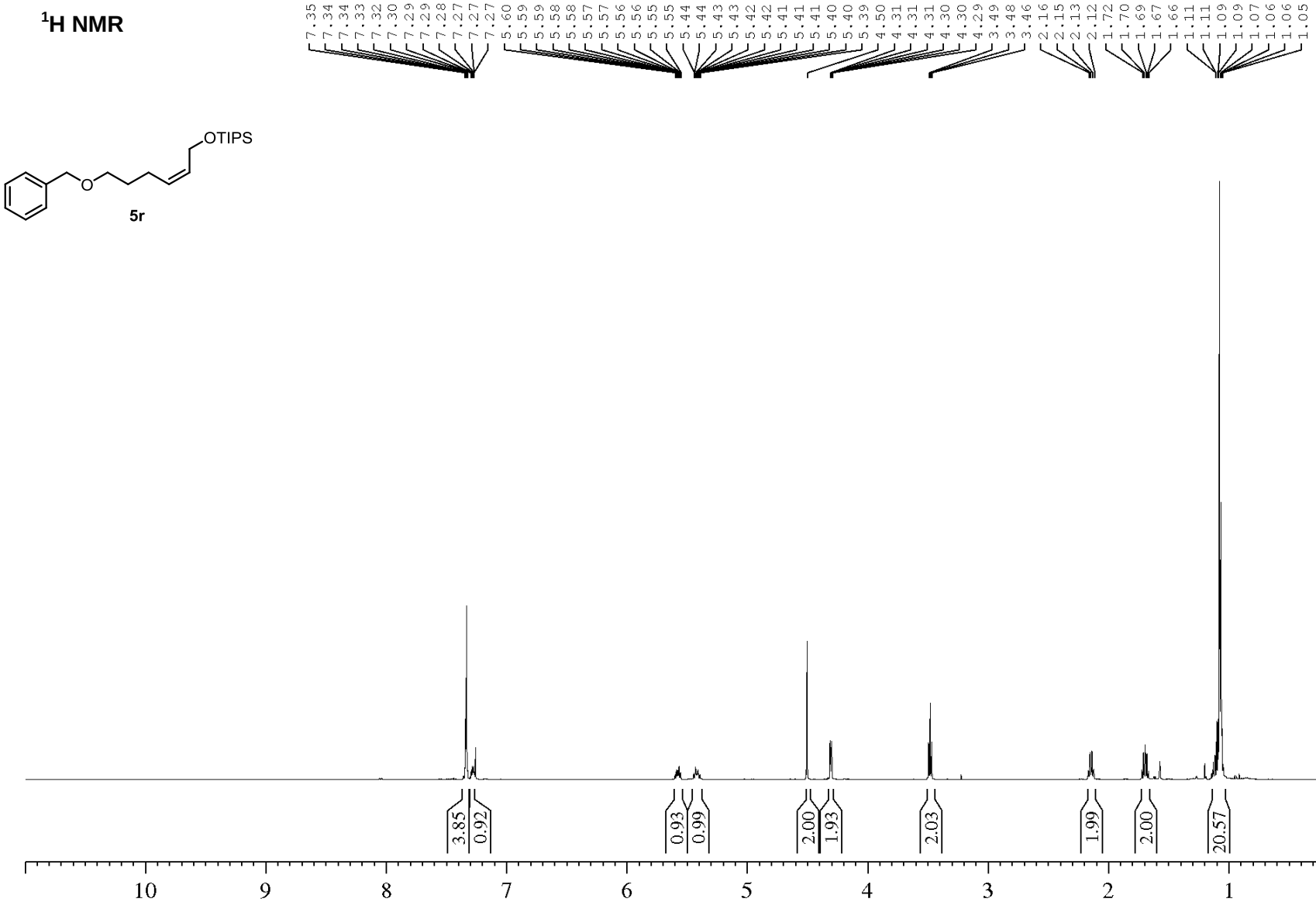


NOESY

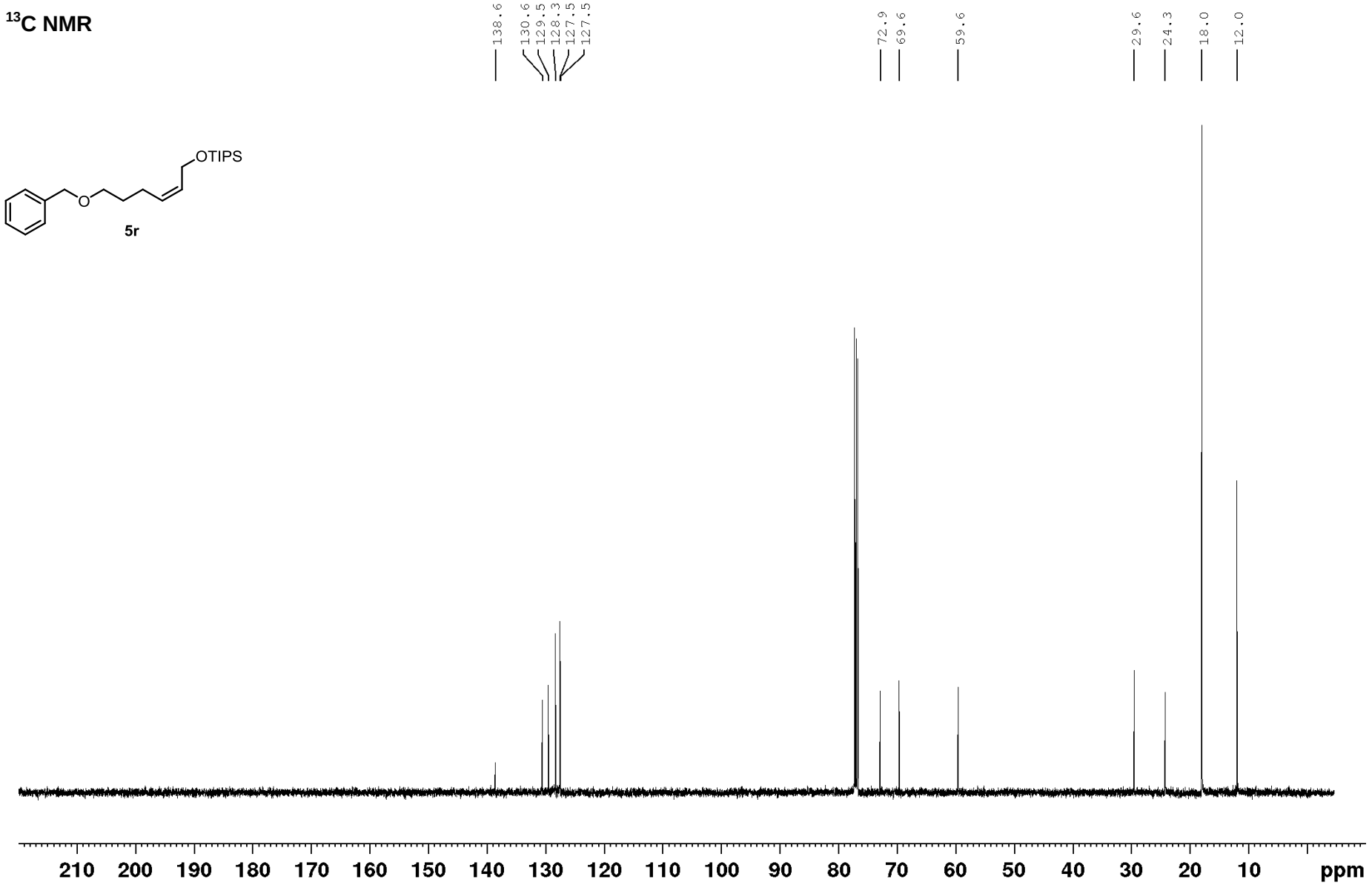



mass spectrum
5p
205.1585
113.0959
206.1618
419.3150
361.2946
377.3259
311.1698
259.1928
114.0992
223.1175
281.1229
132.0806
187.1479
325.1491
535.2989
239.1487
101.0708
391.3052
350.3262
209.1017
179.0912
289.2735
421.3518
463.3261
intensity
m/z

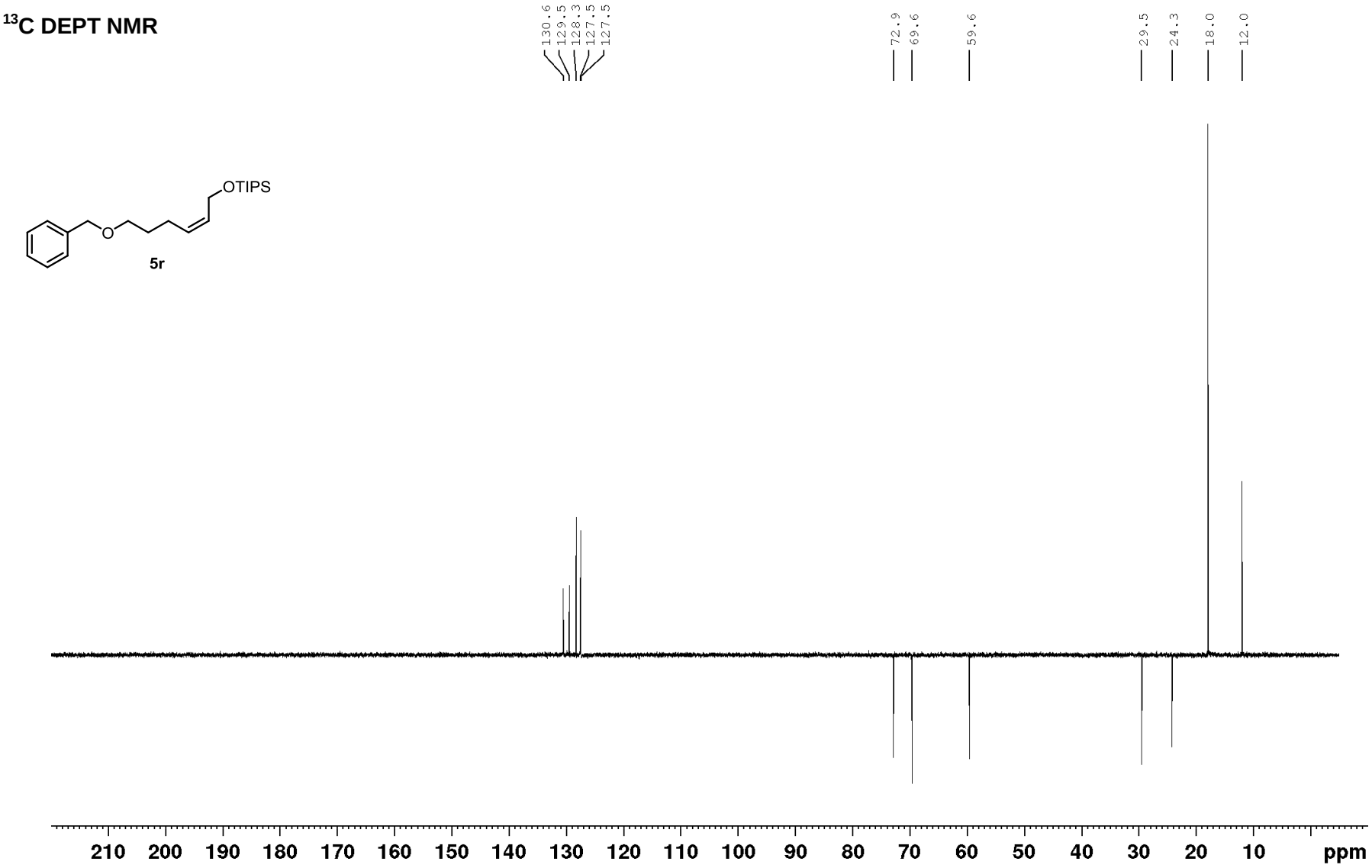
^{1}H NMR


7.35 7.34 7.34 7.33 7.32 7.30 7.29 7.29 7.28 7.27 7.27 7.27
5.60 5.59 5.59 5.58 5.58 5.57 5.57 5.56 5.56 5.55 5.55 5.44 5.44 5.43 5.43 5.42 5.42 5.41 5.41 5.41 5.40 5.40 5.39
4.50 4.31 4.31 4.31 4.30 4.30 4.29 3.49 3.48 3.46
2.16 2.15 2.13 2.12
1.72 1.70 1.69 1.67 1.66
1.11 1.11 1.09 1.09 1.07 1.06 1.06 1.05
OTIPS
O
5r
3.85
0.92
0.93
0.99
2.00
1.93
2.03
1.99
2.00
20.57
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

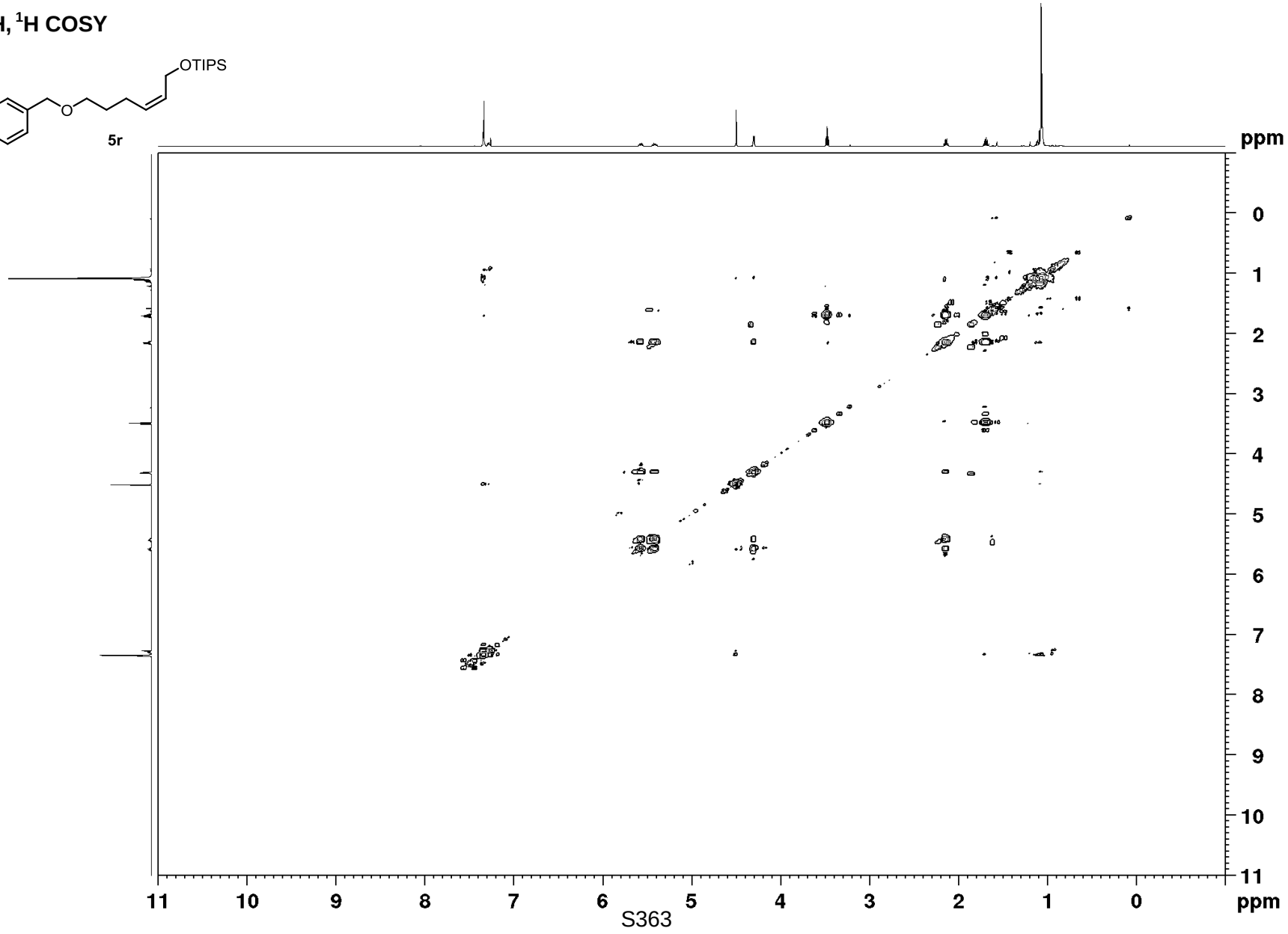

138.6
130.6
129.5
128.3
127.5
127.5
72.9
69.6
59.6
29.6
24.3
18.0
12.0
OTIPS
O
5r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{13}C DEPT NMR

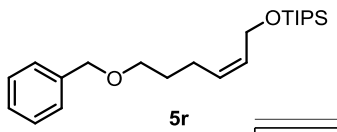

130.6
129.5
128.3
127.5
127.5
72.9
69.6
59.6
29.5
24.3
18.0
12.0
OTIPS
O
5r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H, ^{1}H COSY

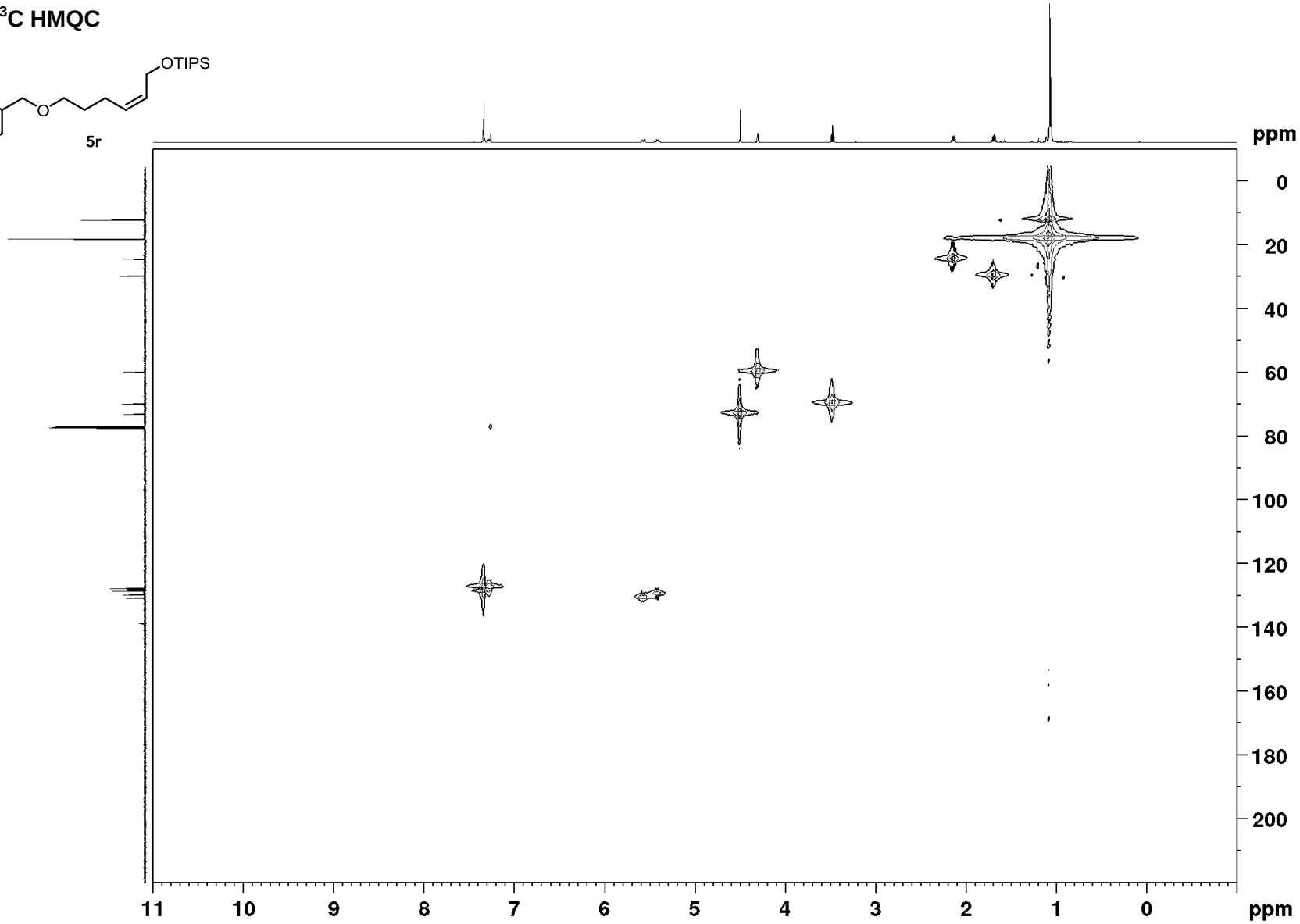
5r



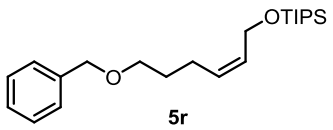
^{1}H, ^{13}C HMQC



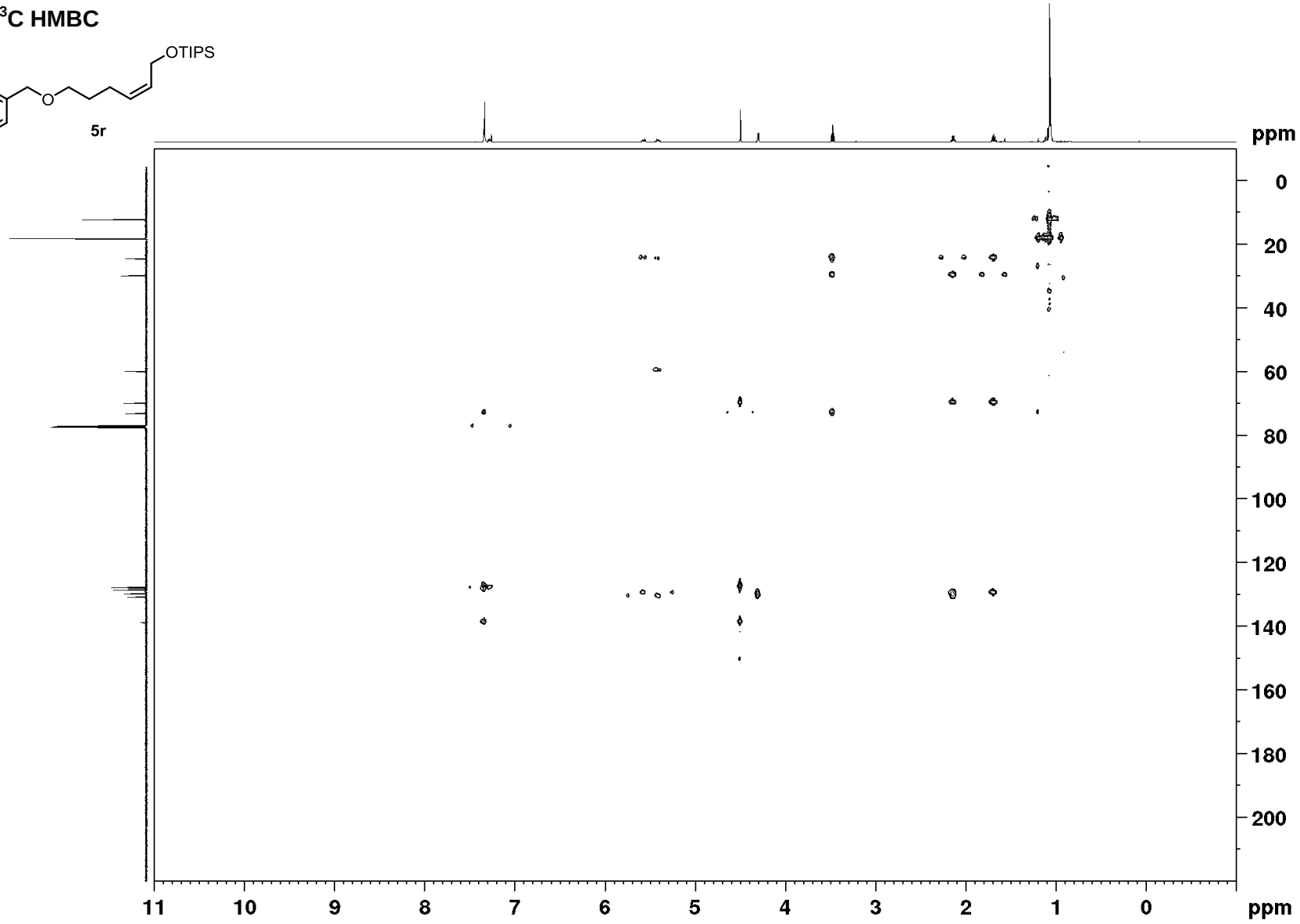
5r



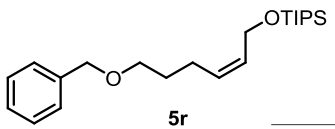
^{1}H, ^{13}C HMBC



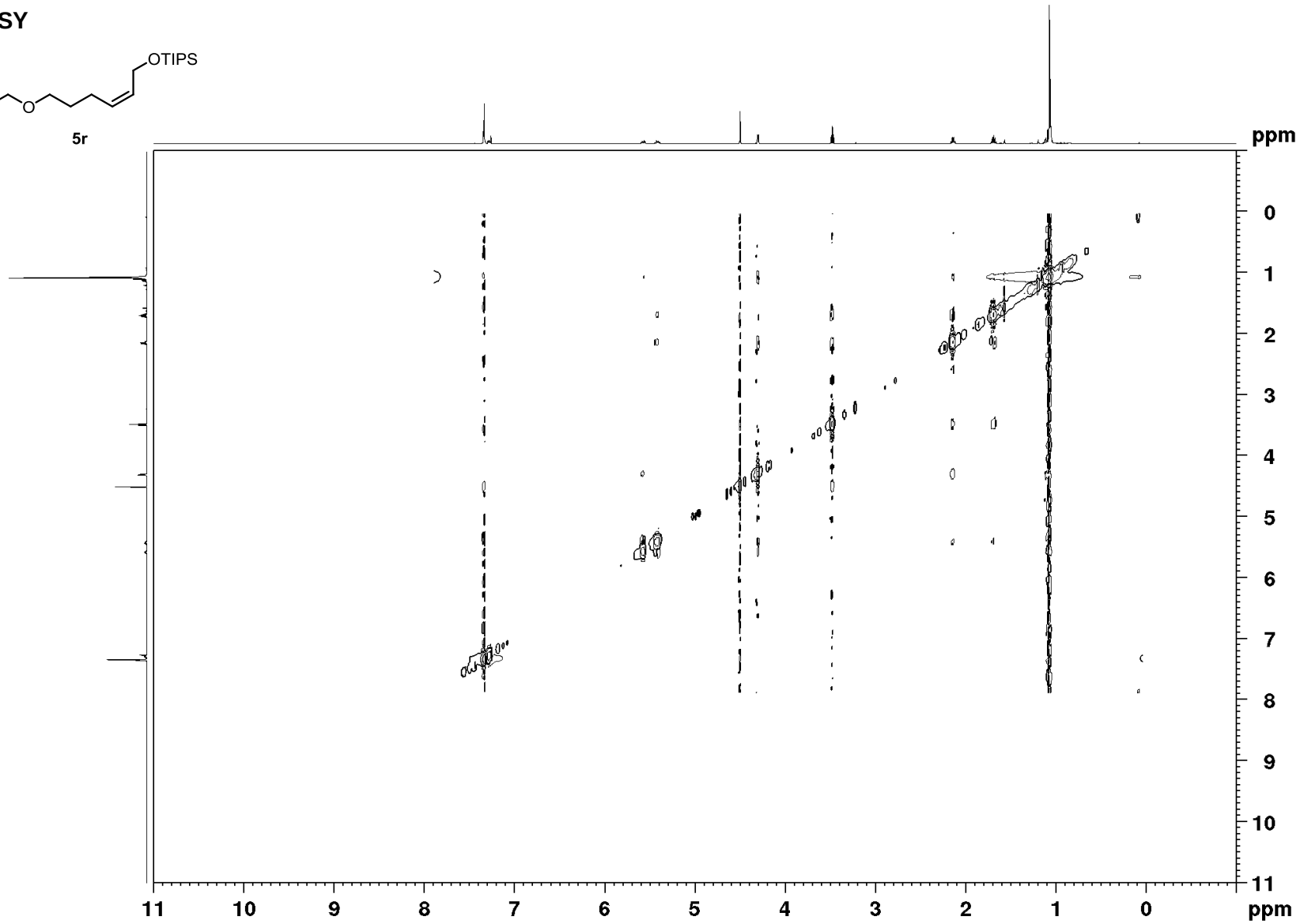
5r



NOESY

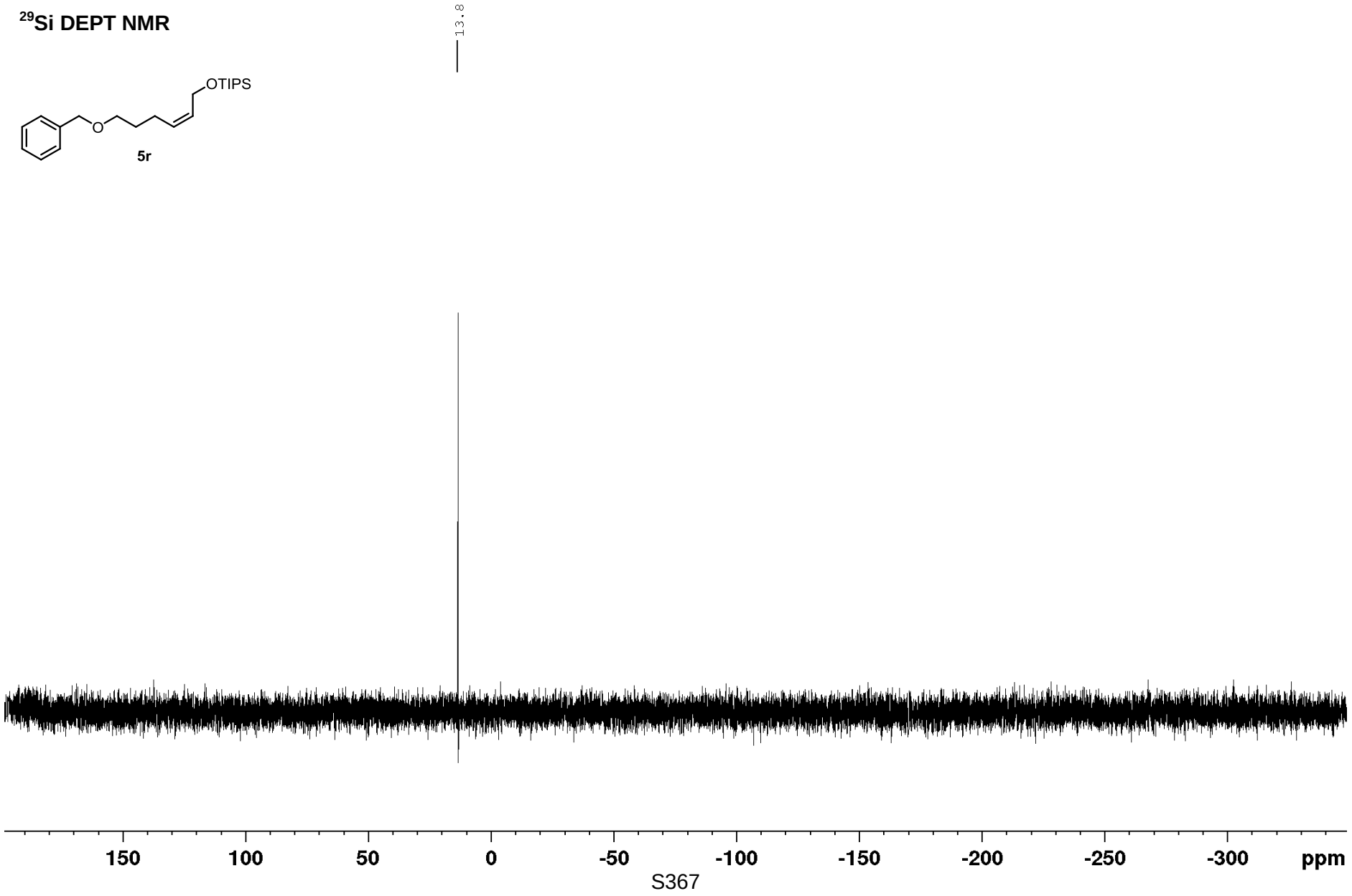


5r

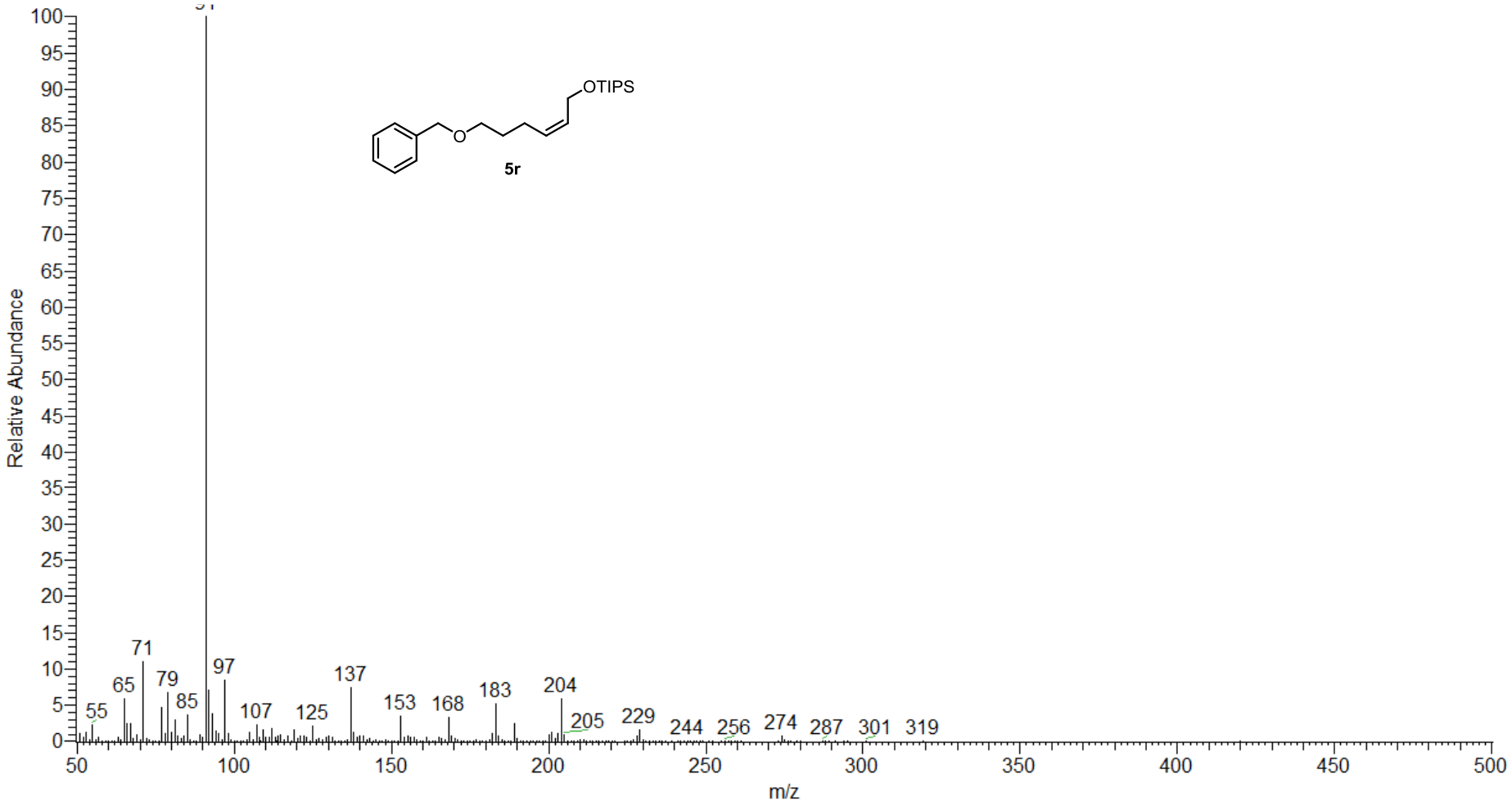


^{29}Si DEPT NMR

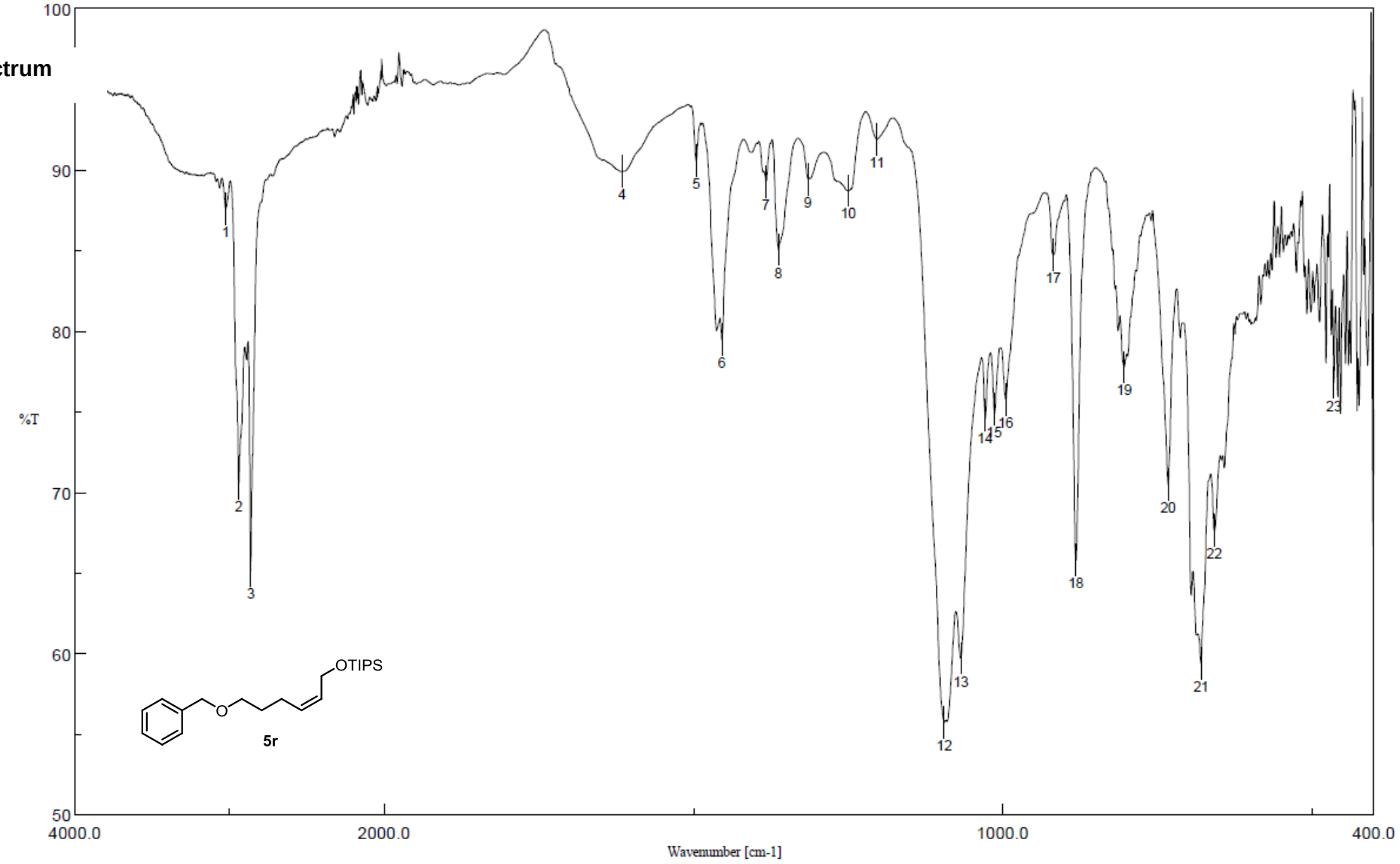
5r



mass spectrum



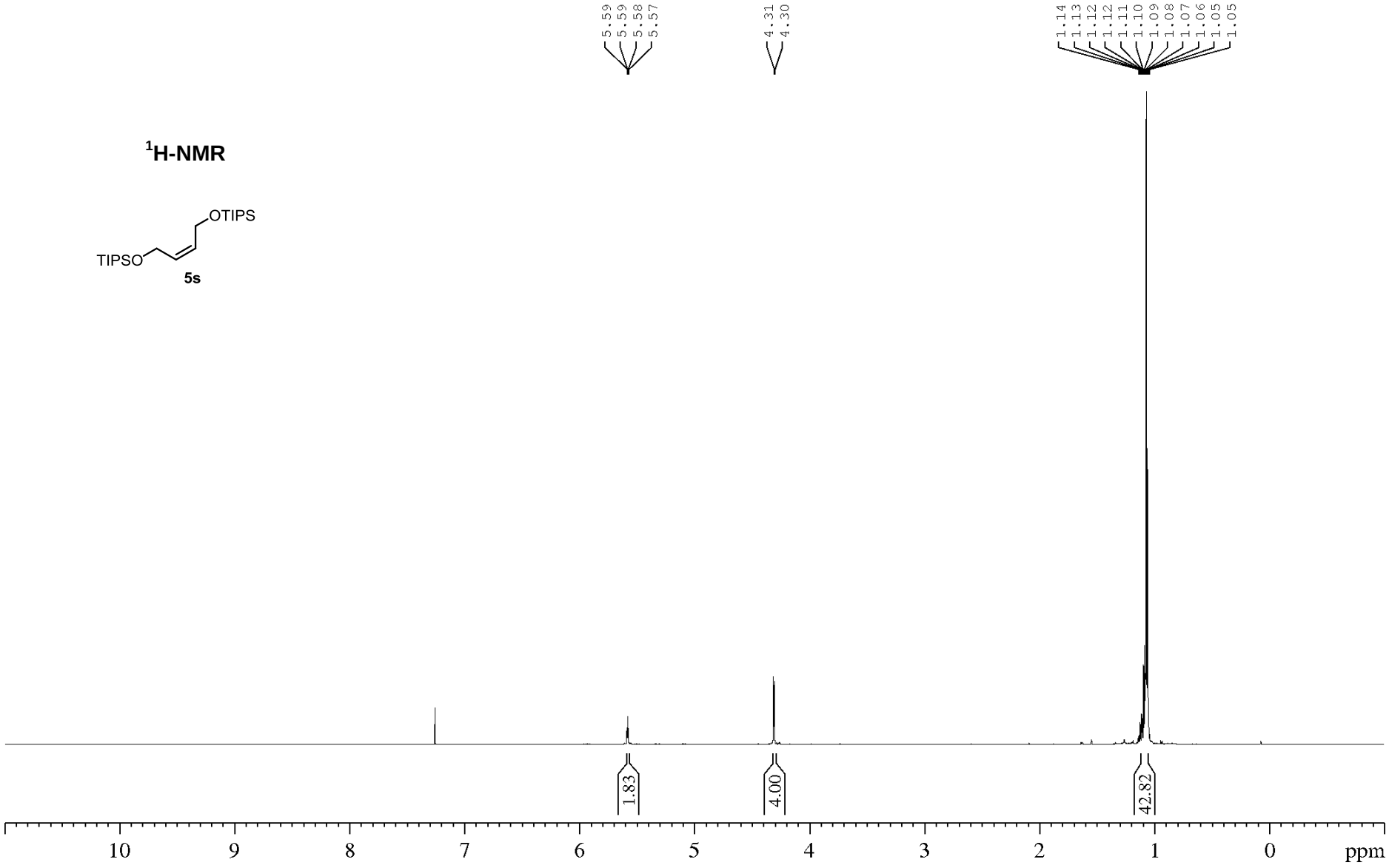
IR spectrum


100
90
80
70
60
50
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
OTIPS
O
5r

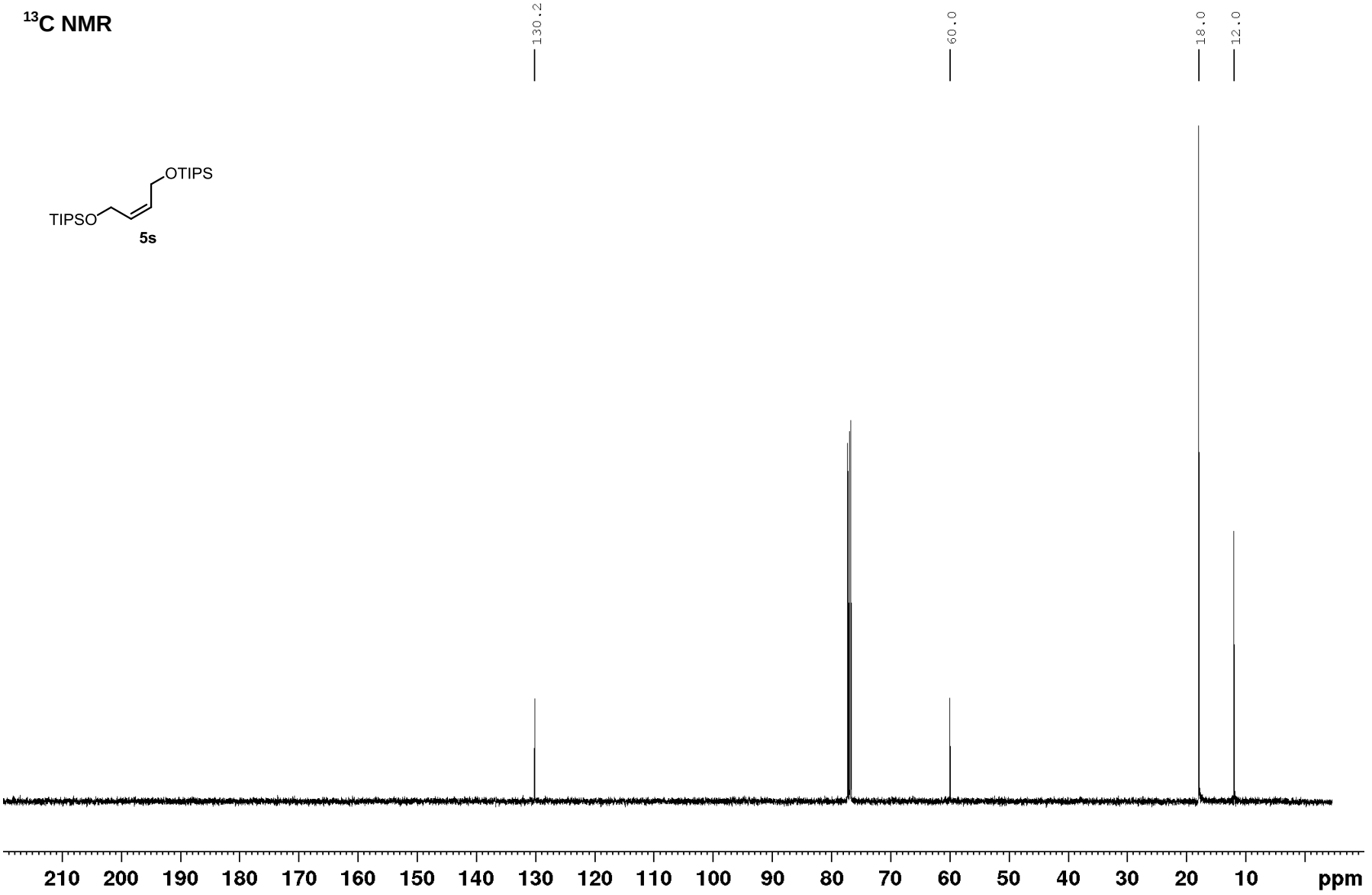
^{1}H-NMR

OTIPS
TIPSO

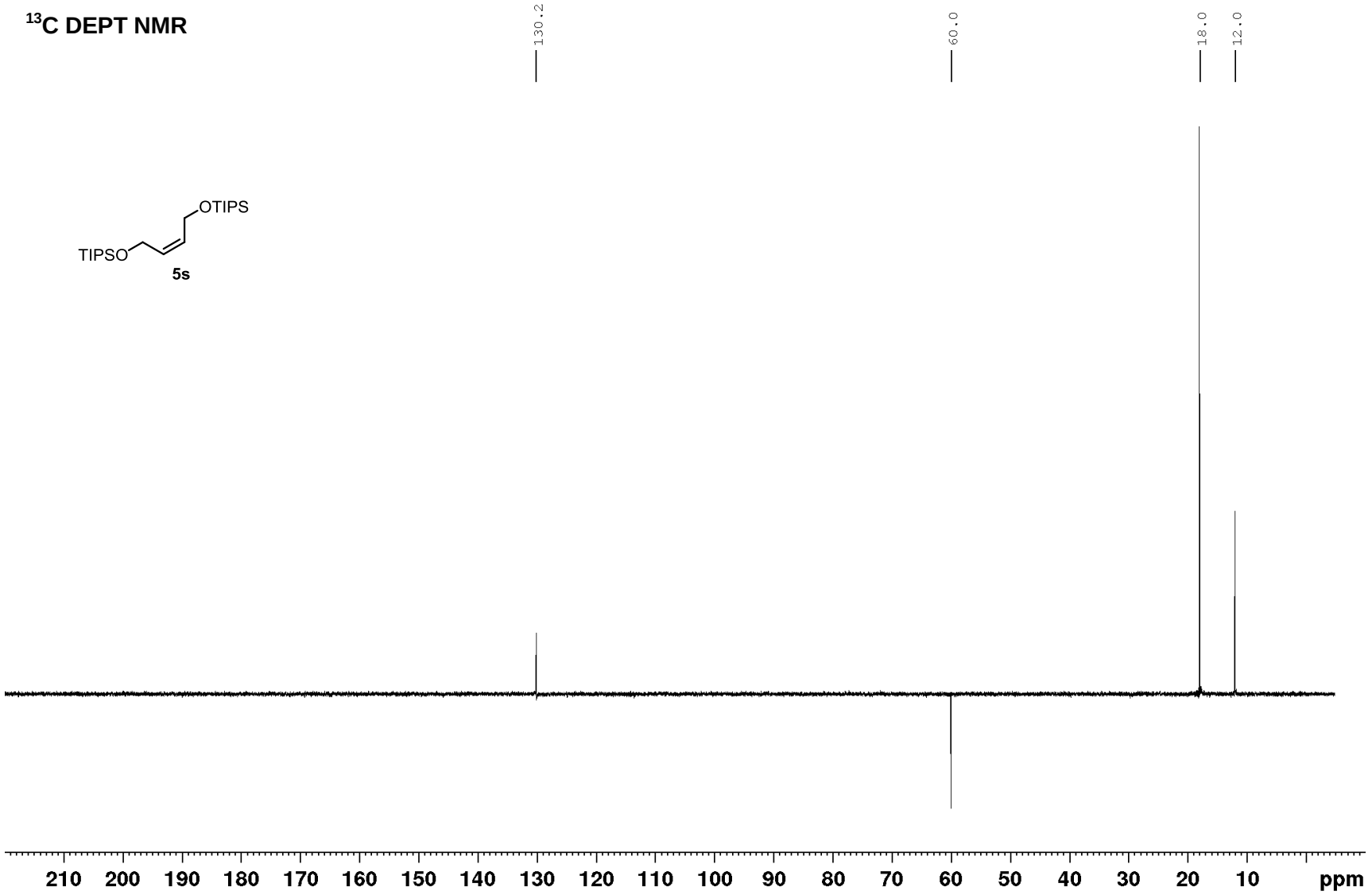
5s


5.59
5.59
5.58
5.57
4.31
4.30
1.14
1.13
1.12
1.12
1.11
1.10
1.09
1.08
1.07
1.06
1.05
1.05
1.83
4.00
42.82
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

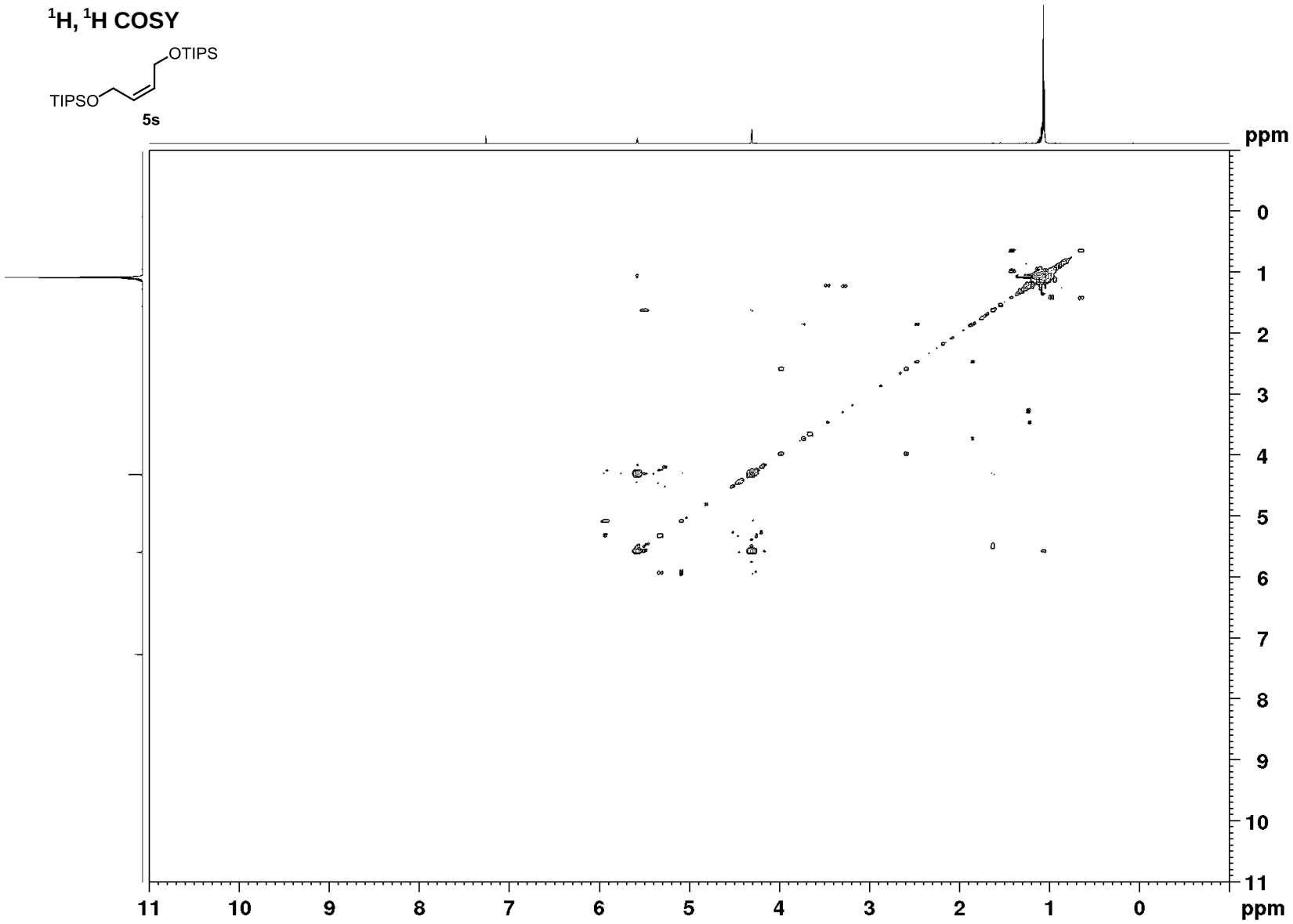

130.2
60.0
18.0
12.0
OTIPS
TIPSO
5s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

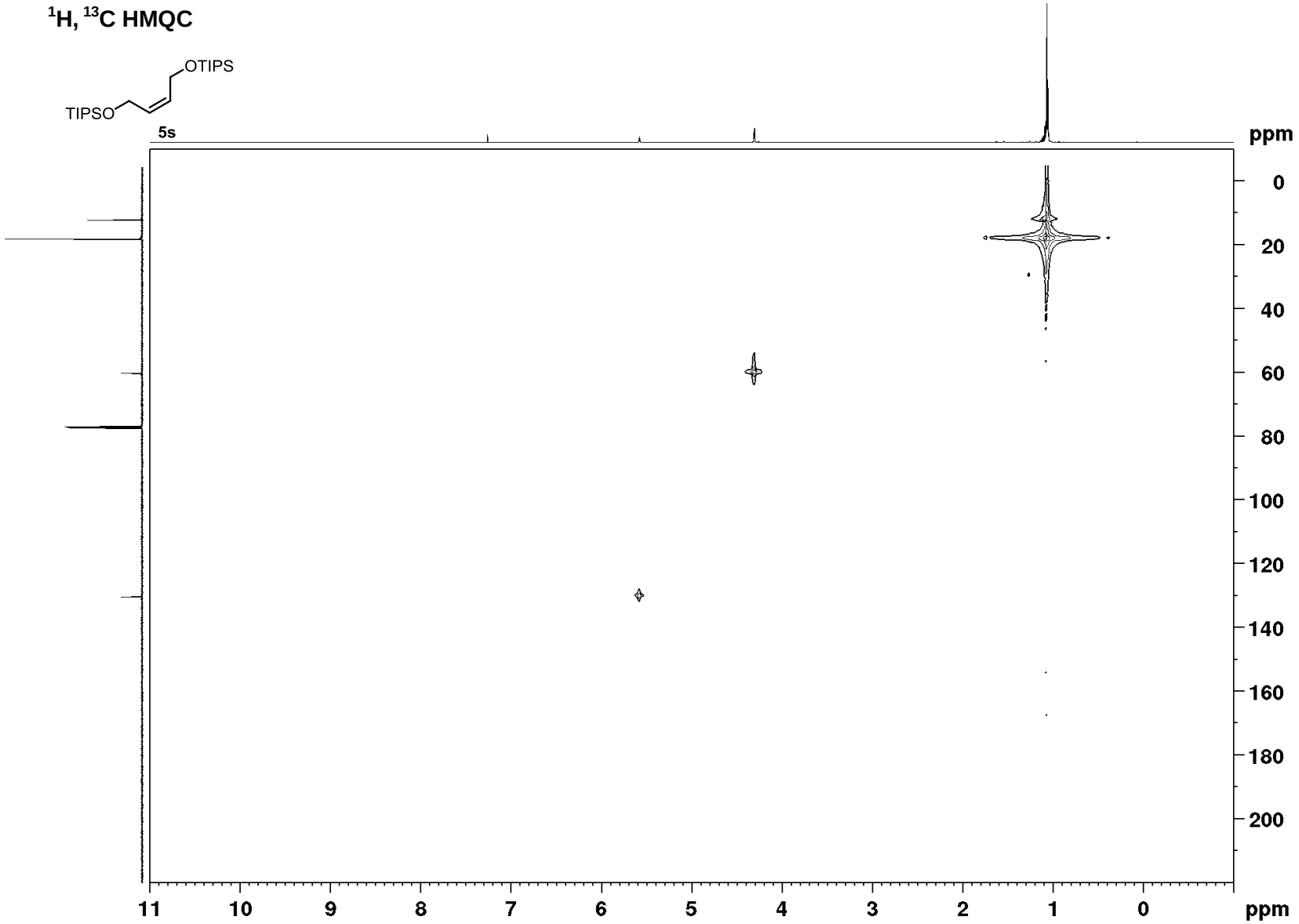

130.2
60.0
18.0
12.0
OTIPS
TIPSO
5s
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H, ^{1}H COSY

5s

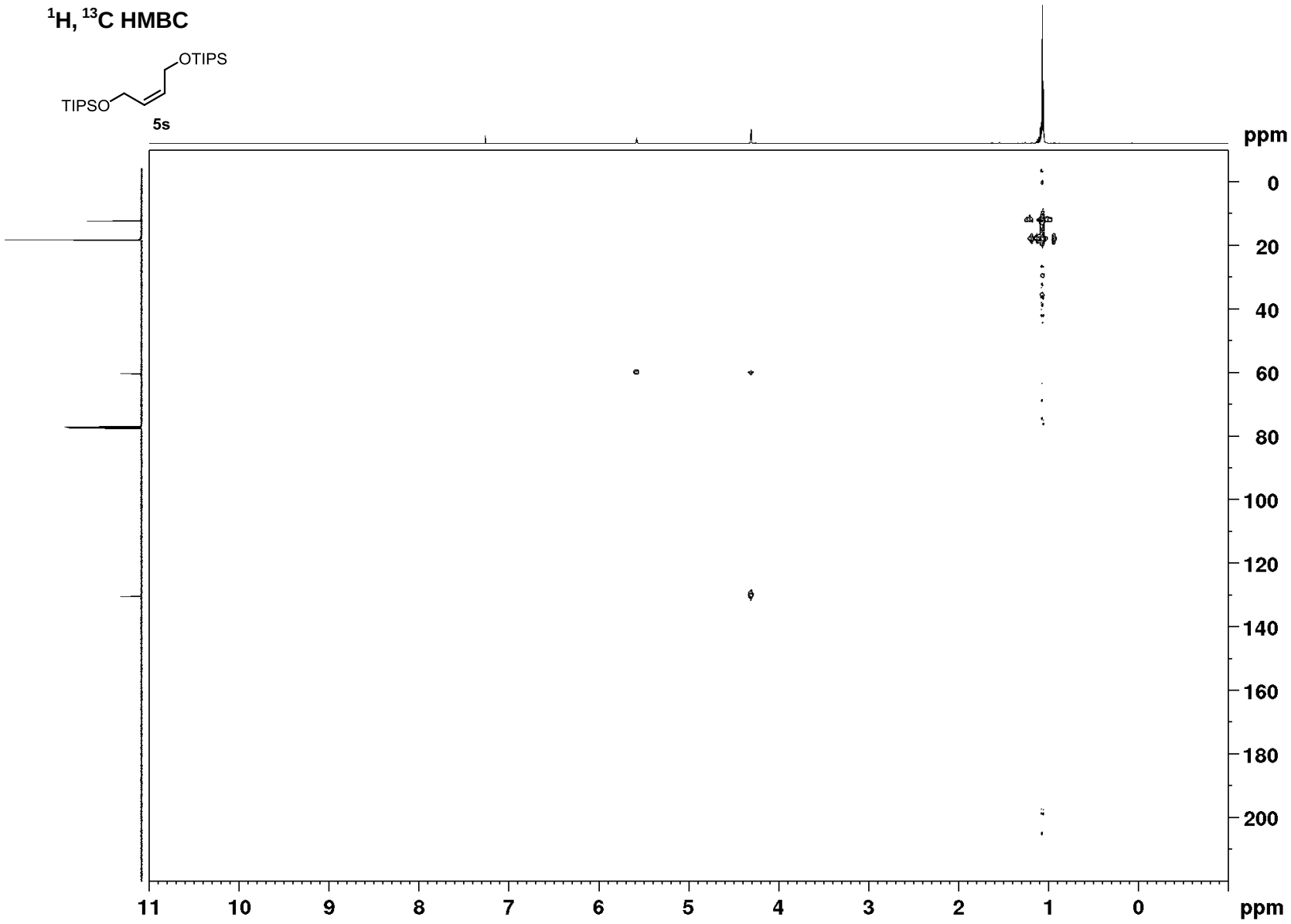


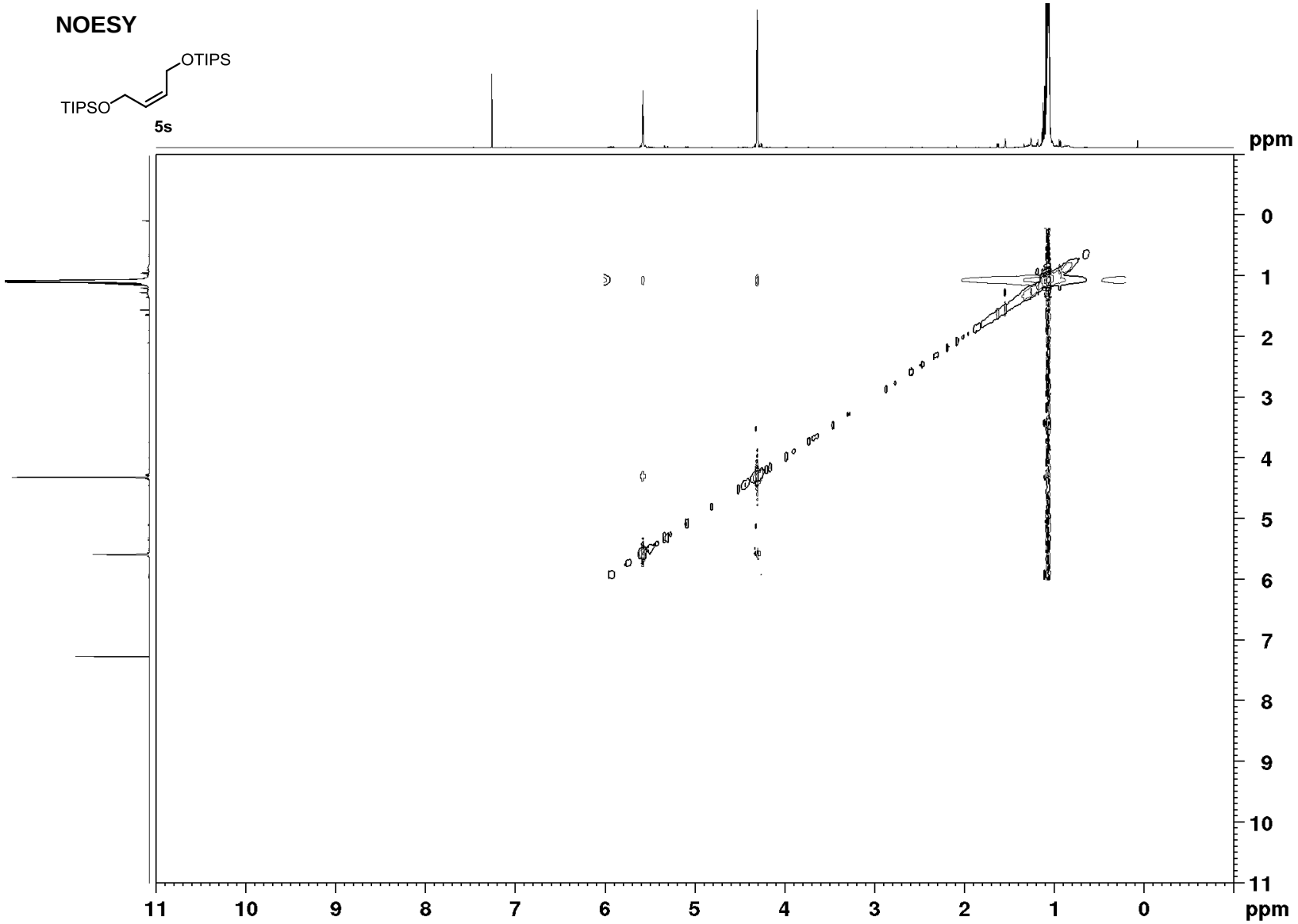
^{1}H, ^{13}C HMQC


OTIPS
TIPSO
5s
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

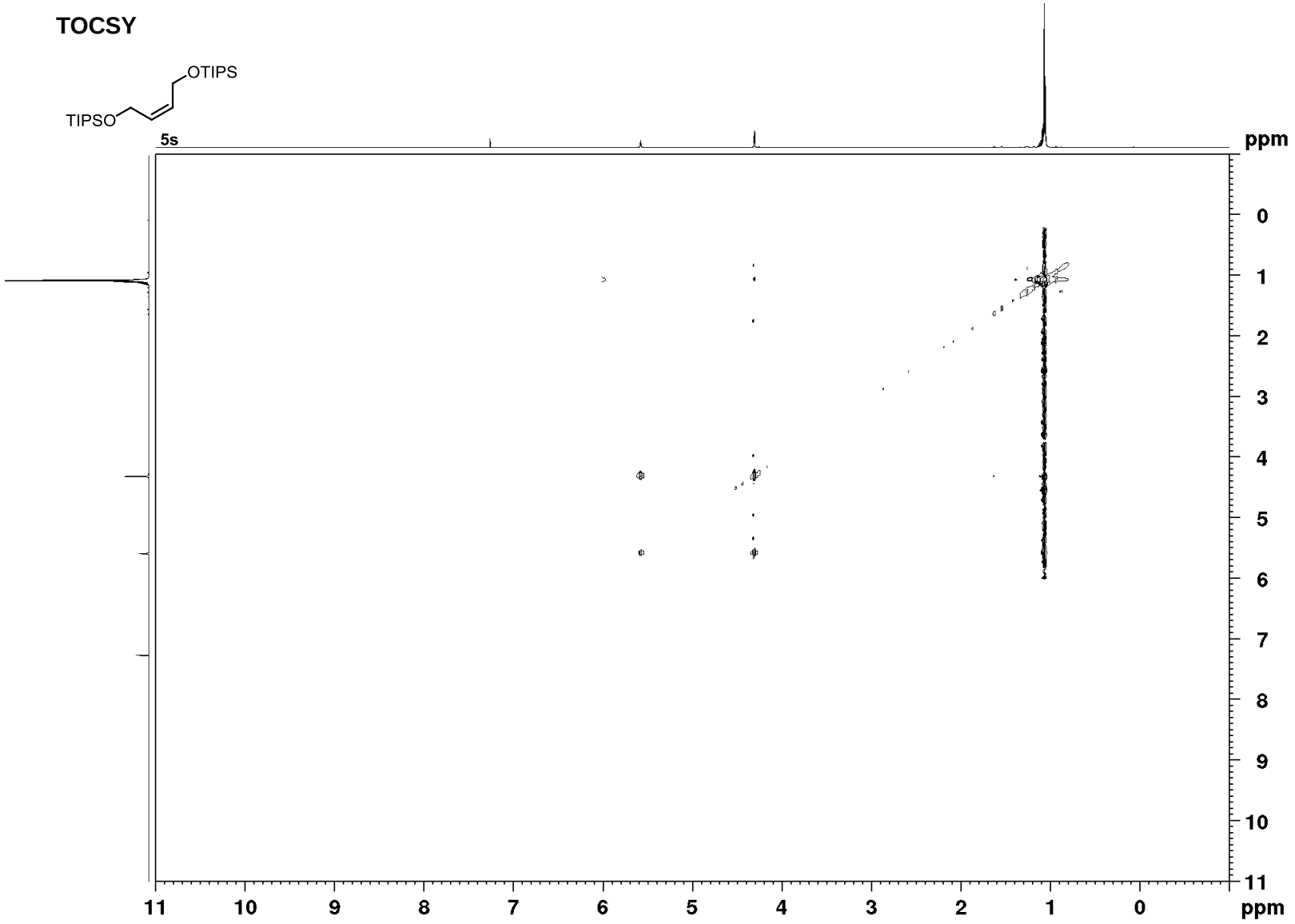
^{1}H, ^{13}C HMBC

5s



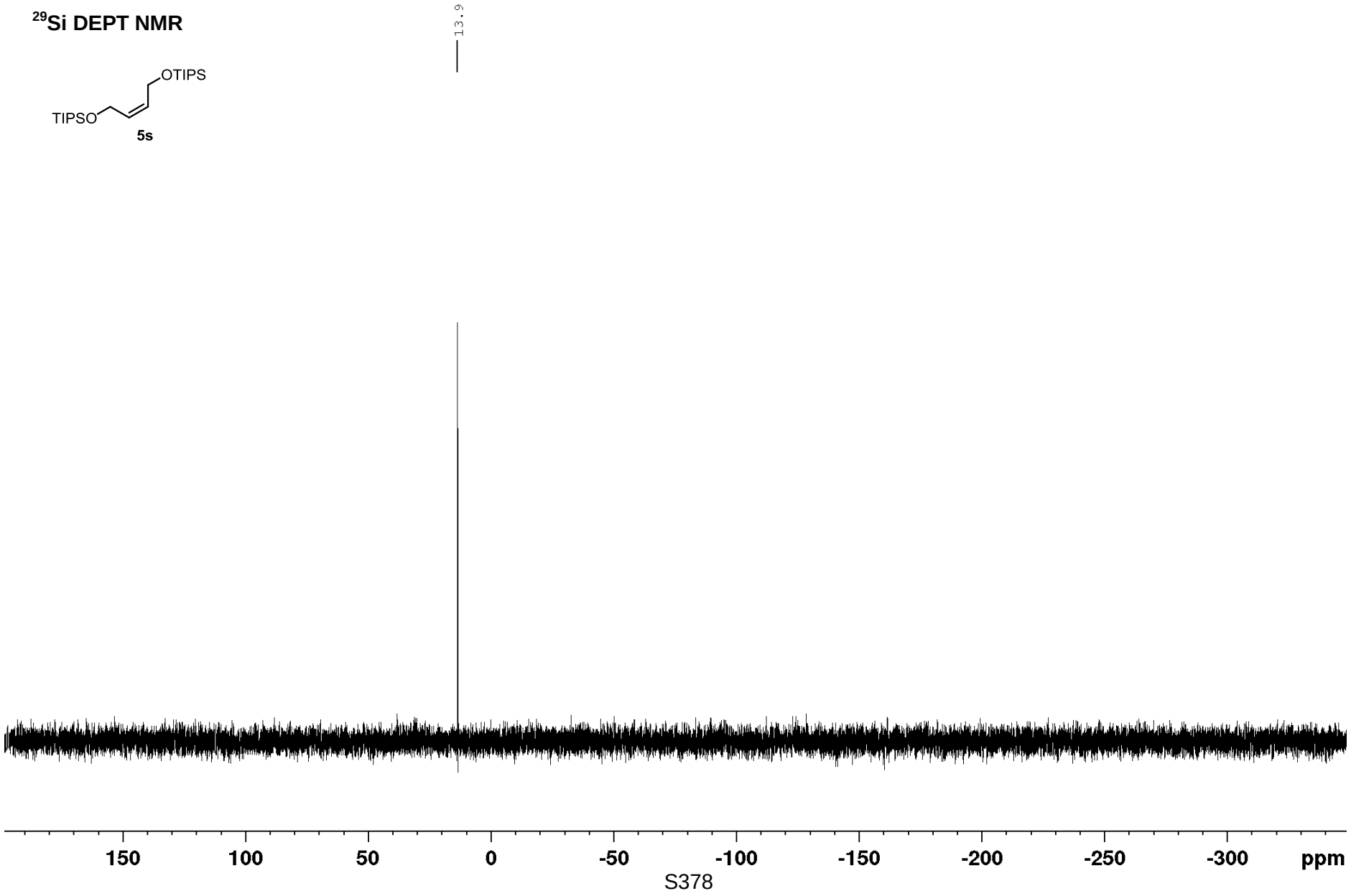

NOESY
OTIPS
TIPSO
5s
ppm
0
1
2
3
4
5
6
7
8
9
10
11
11
10
9
8
7
6
5
4
3
2
1
0
ppm

TOCSY

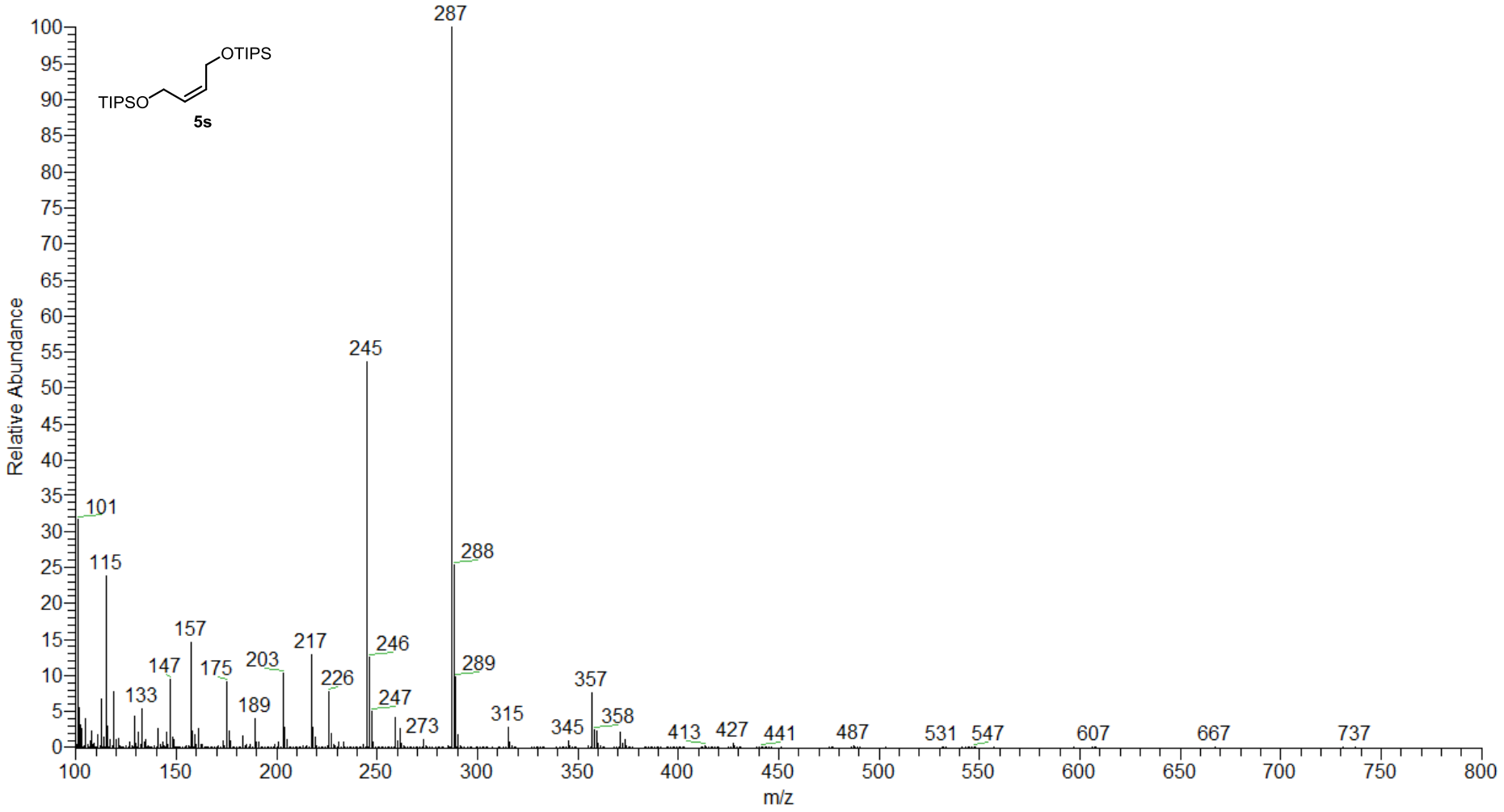


^{29}Si DEPT NMR

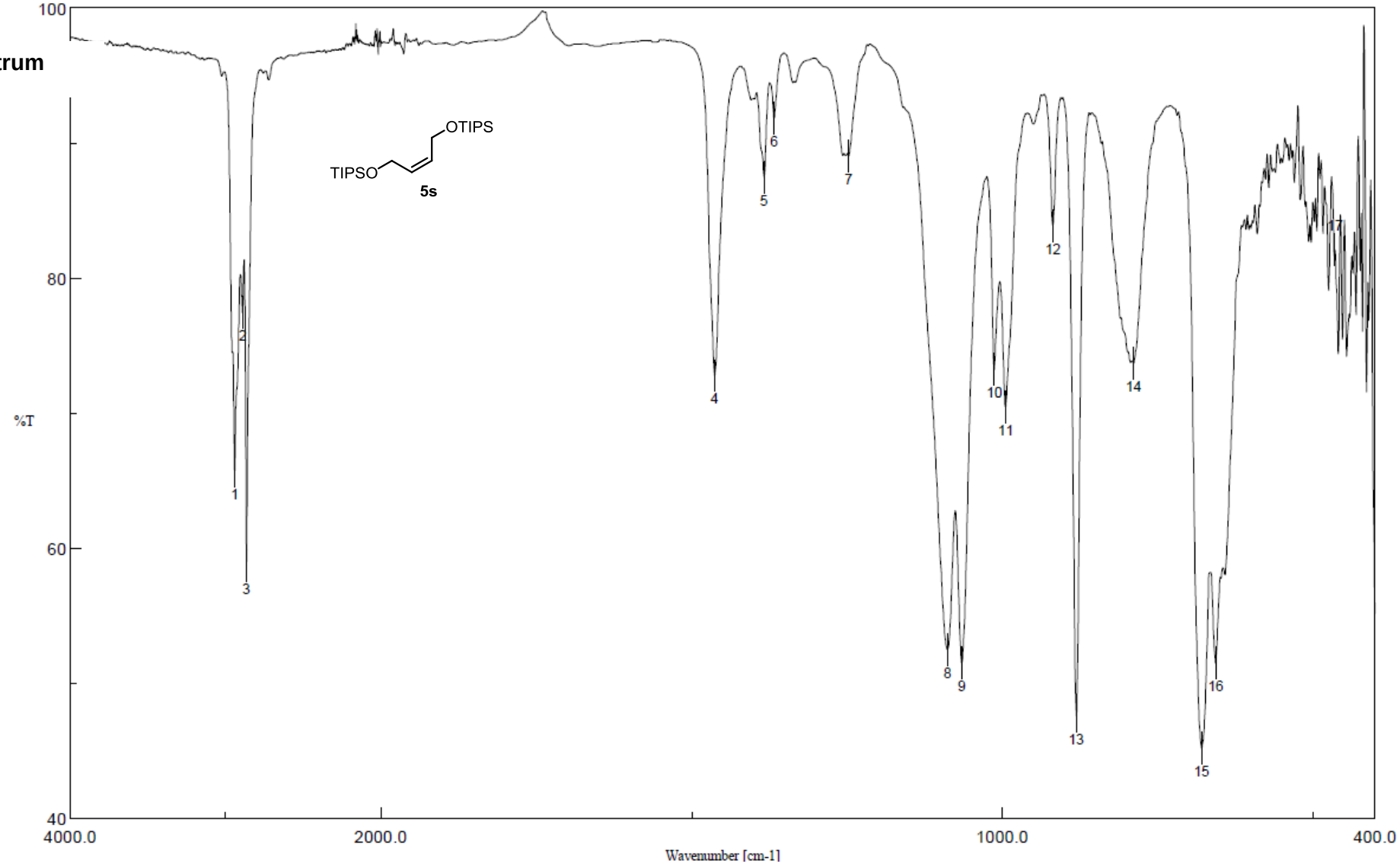
5s



mass spectrum

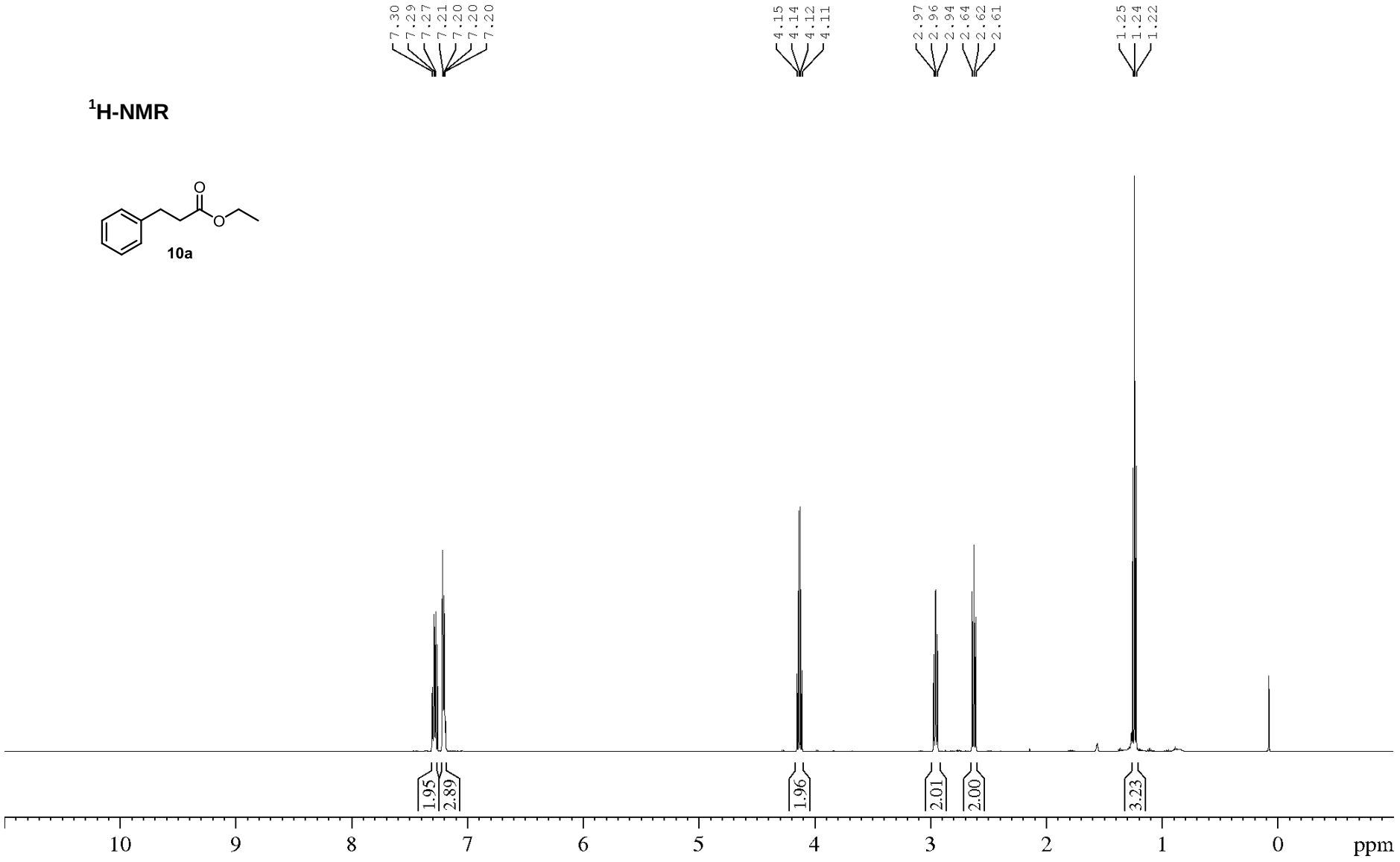


IR spectrum

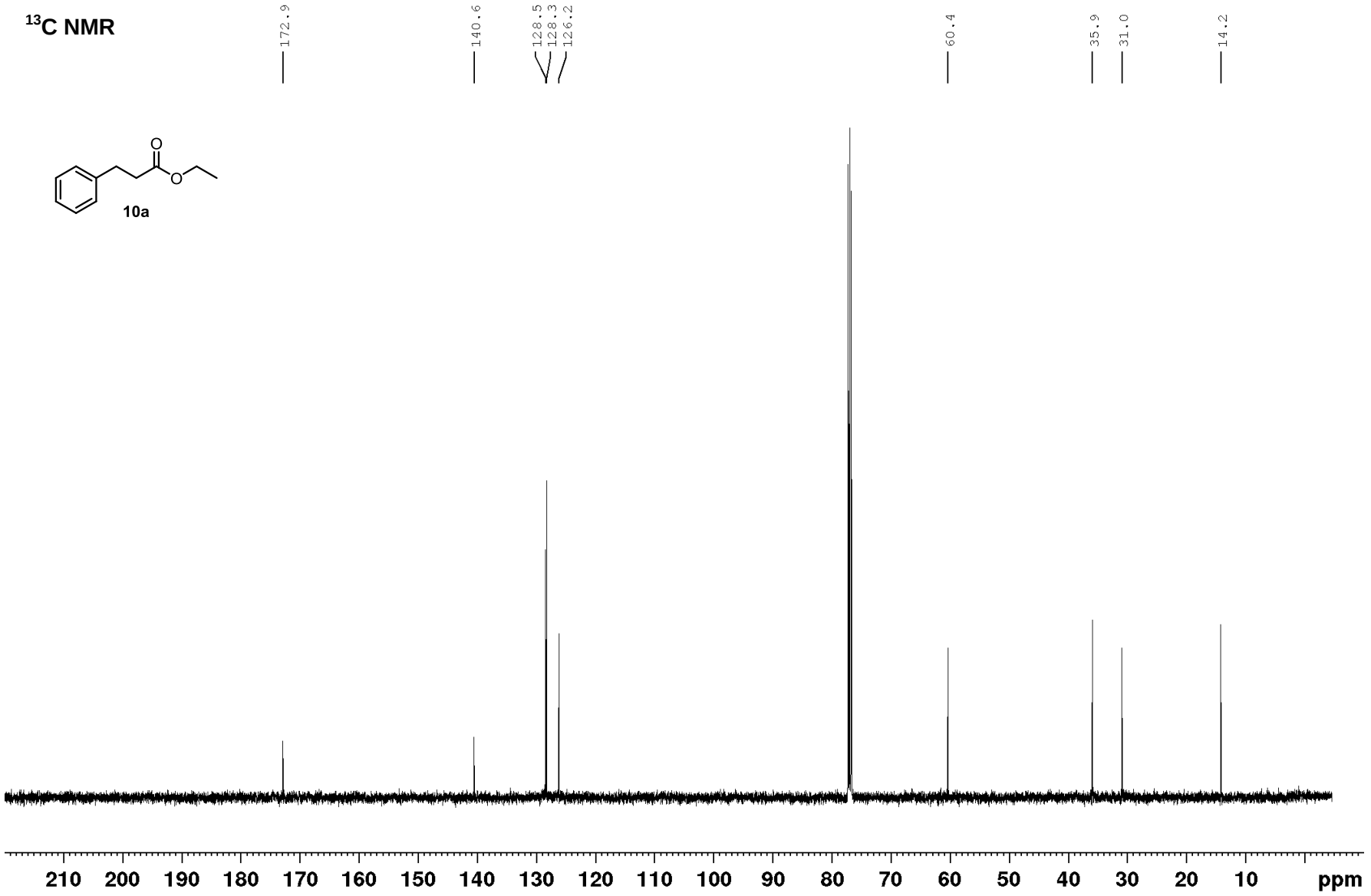

100
80
60
40
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
OTIPS
TIPSO
5s
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

^{1}H-NMR

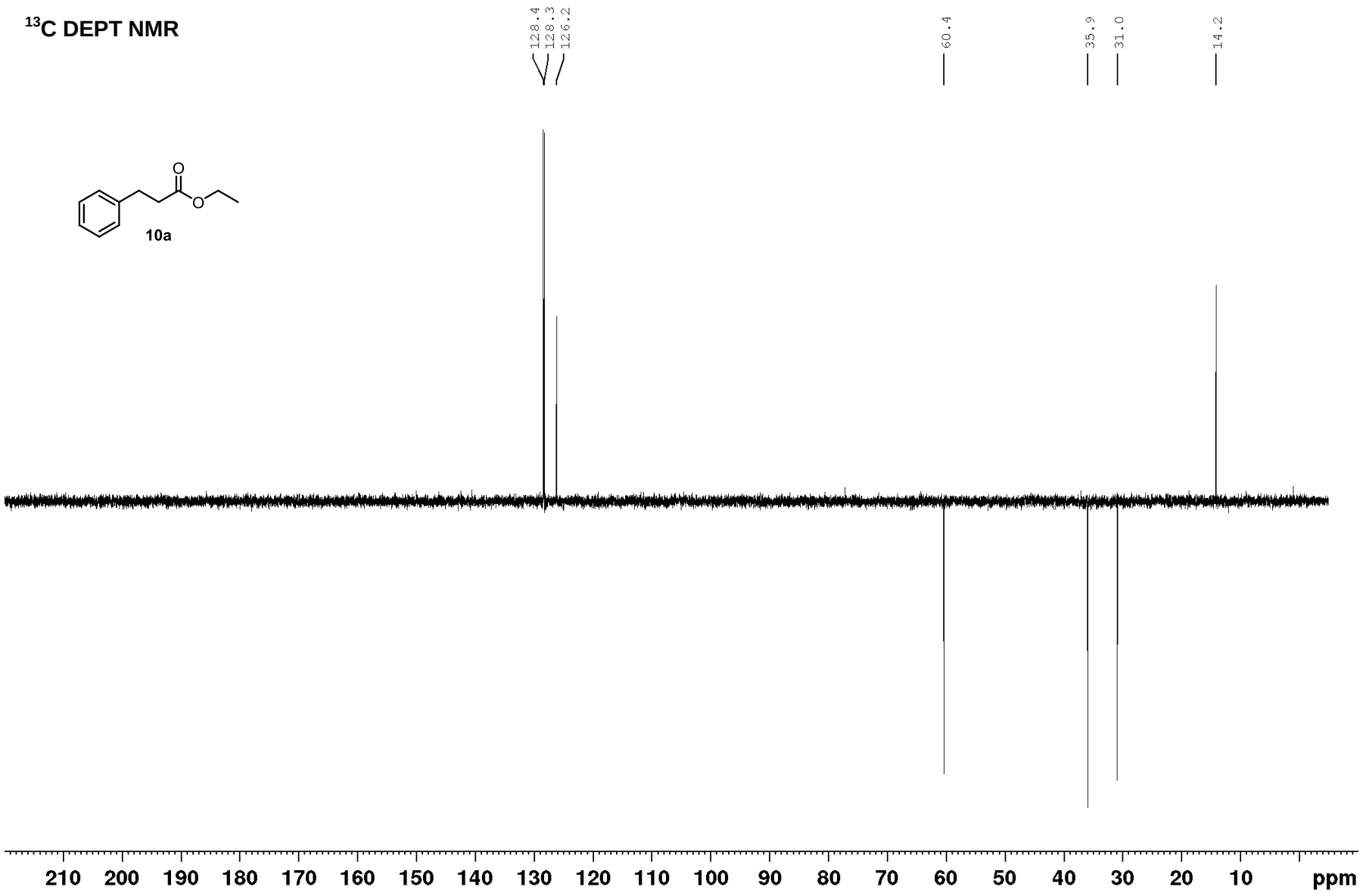
10a


7.30
7.29
7.27
7.21
7.20
7.20
7.20
4.15
4.14
4.12
4.11
2.97
2.96
2.94
2.64
2.62
2.61
1.25
1.24
1.22
1.95
2.89
1.96
2.01
2.00
3.23
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

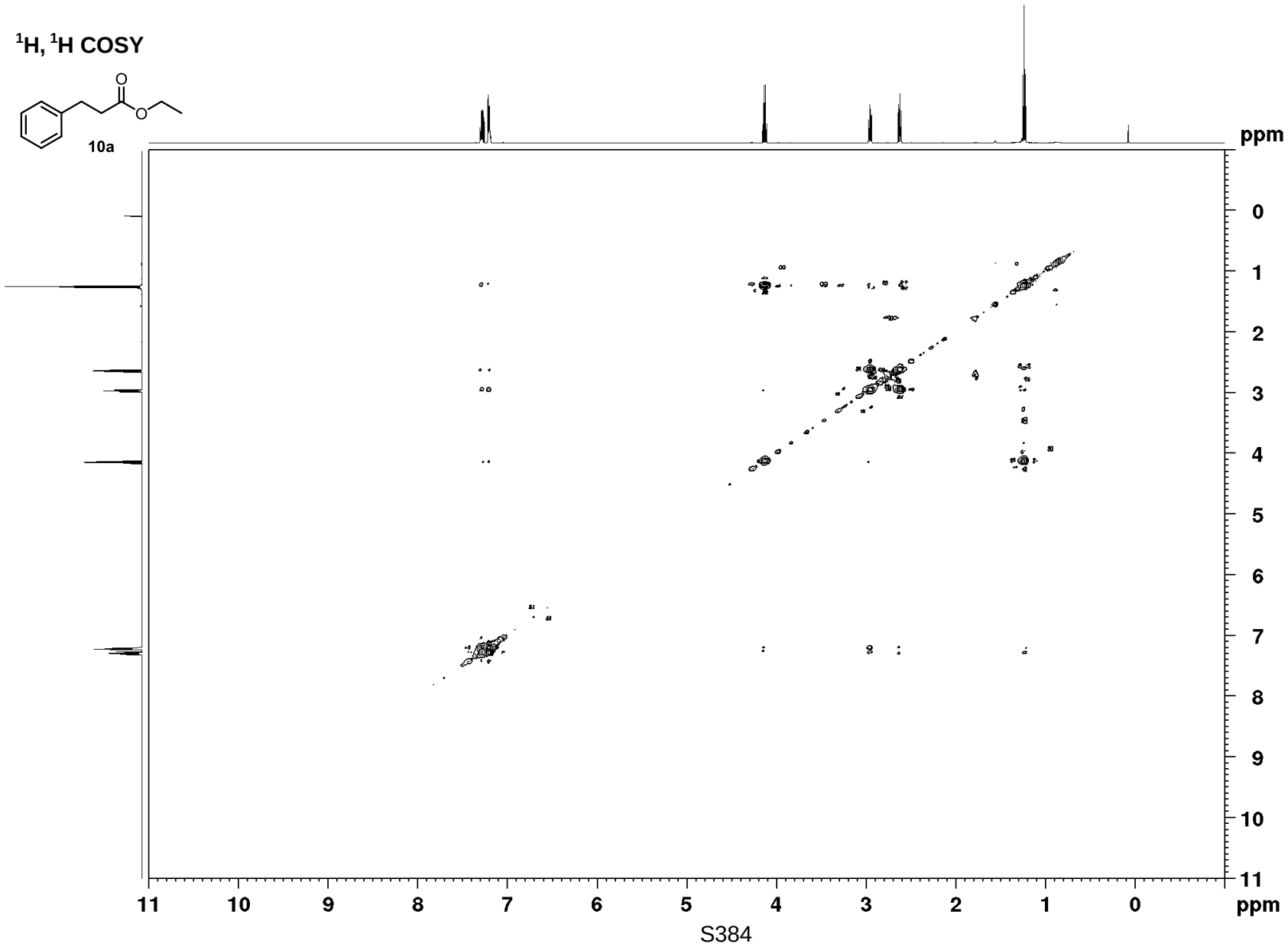

172.9
140.6
128.5
128.3
126.2
60.4
35.9
31.0
14.2
O
O
10a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR


128.4
128.3
126.2
60.4
35.9
31.0
14.2
O
O
10a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

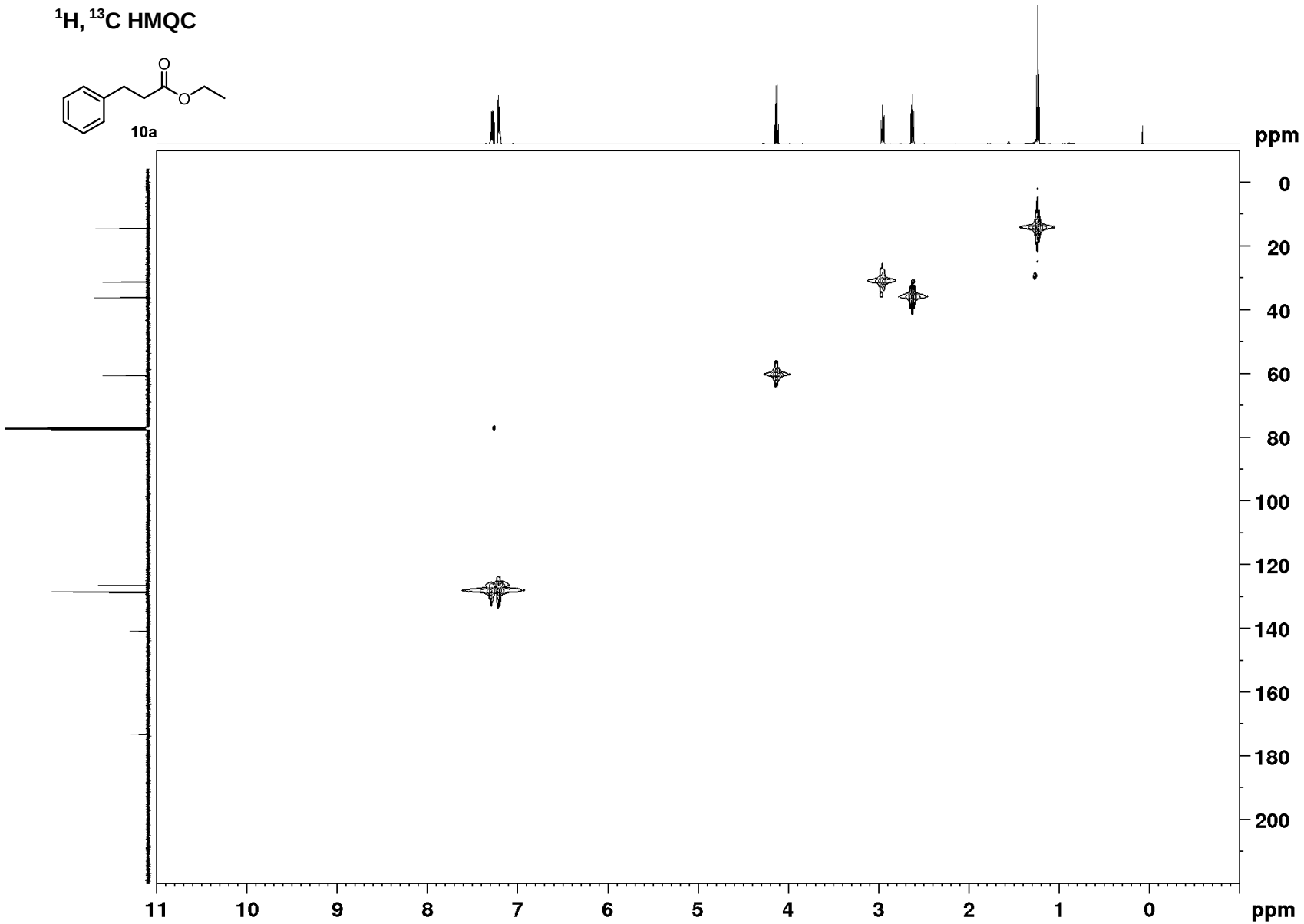
^{1}H, ^{1}H COSY

10a



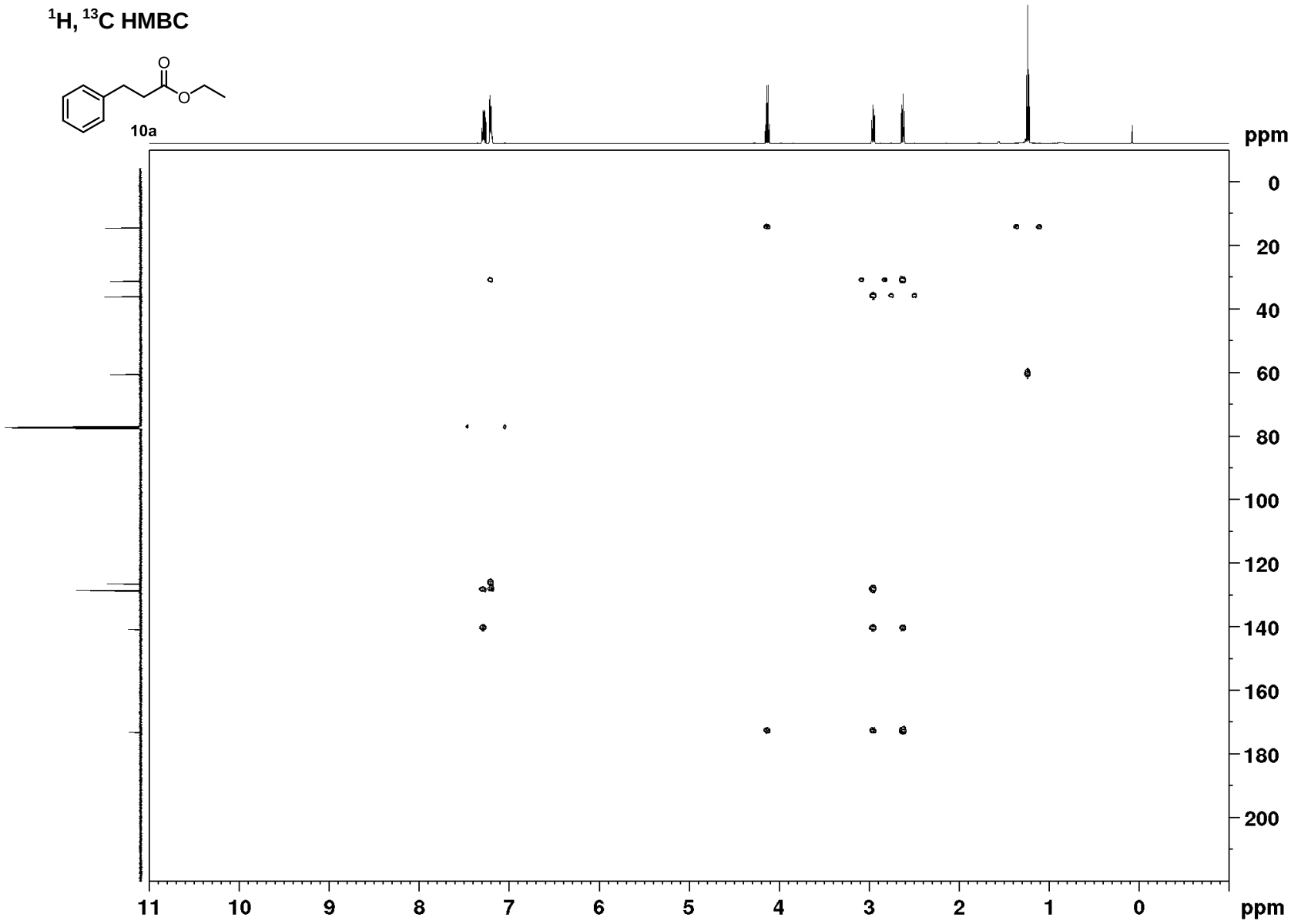
^{1}H, ^{13}C HMQC

10a

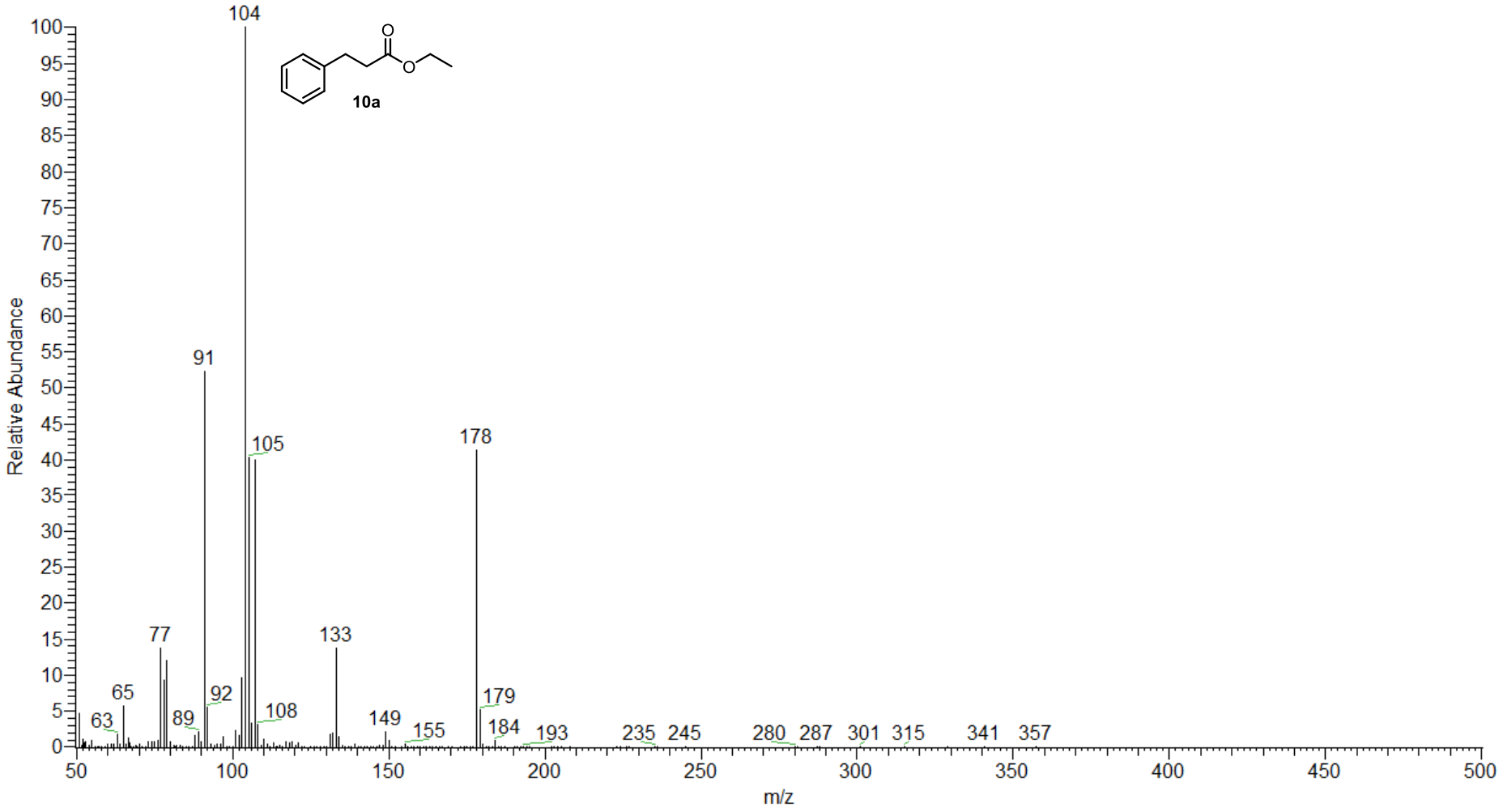


^{1}H, ^{13}C HMBC

10a

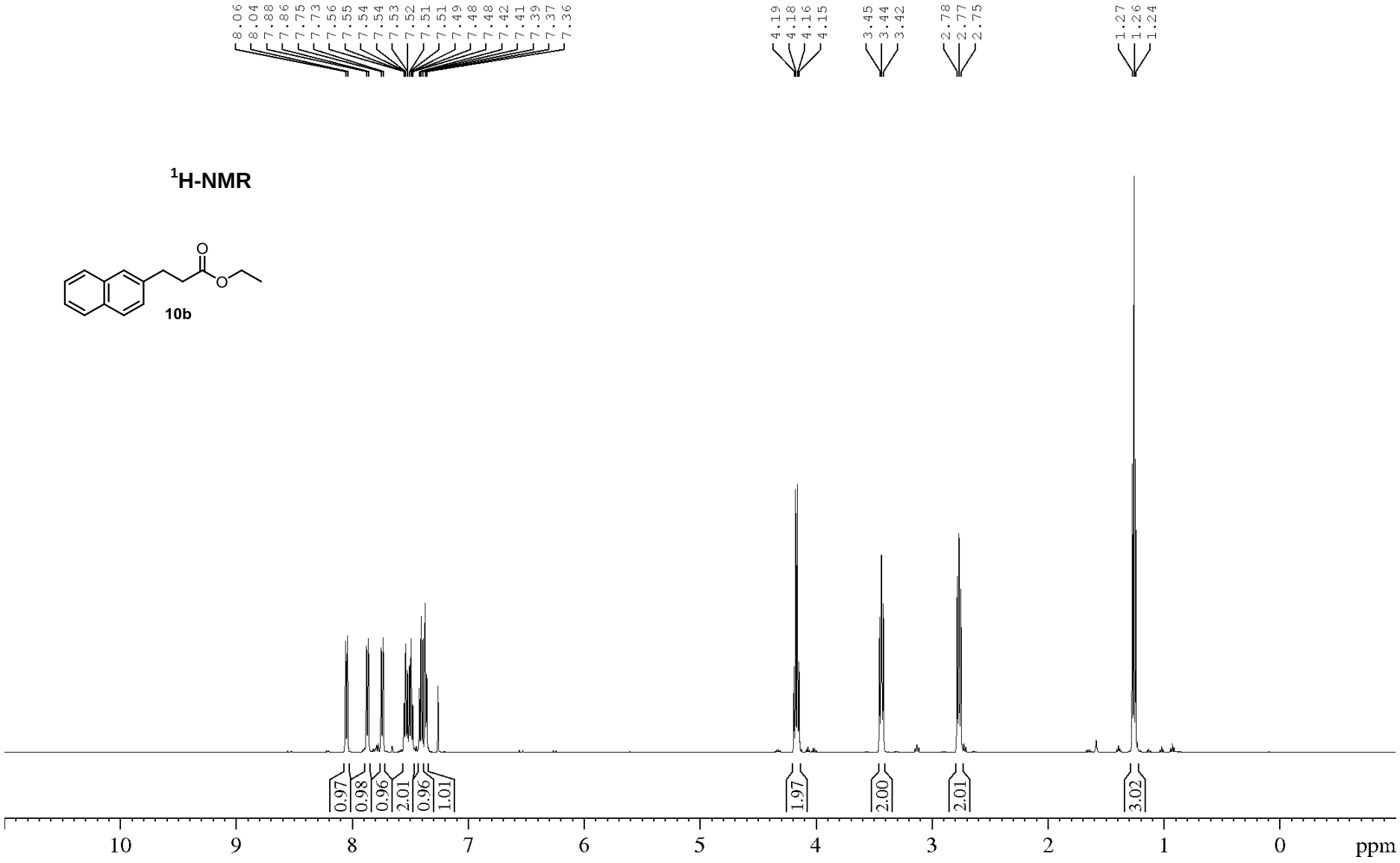


mass spectrum



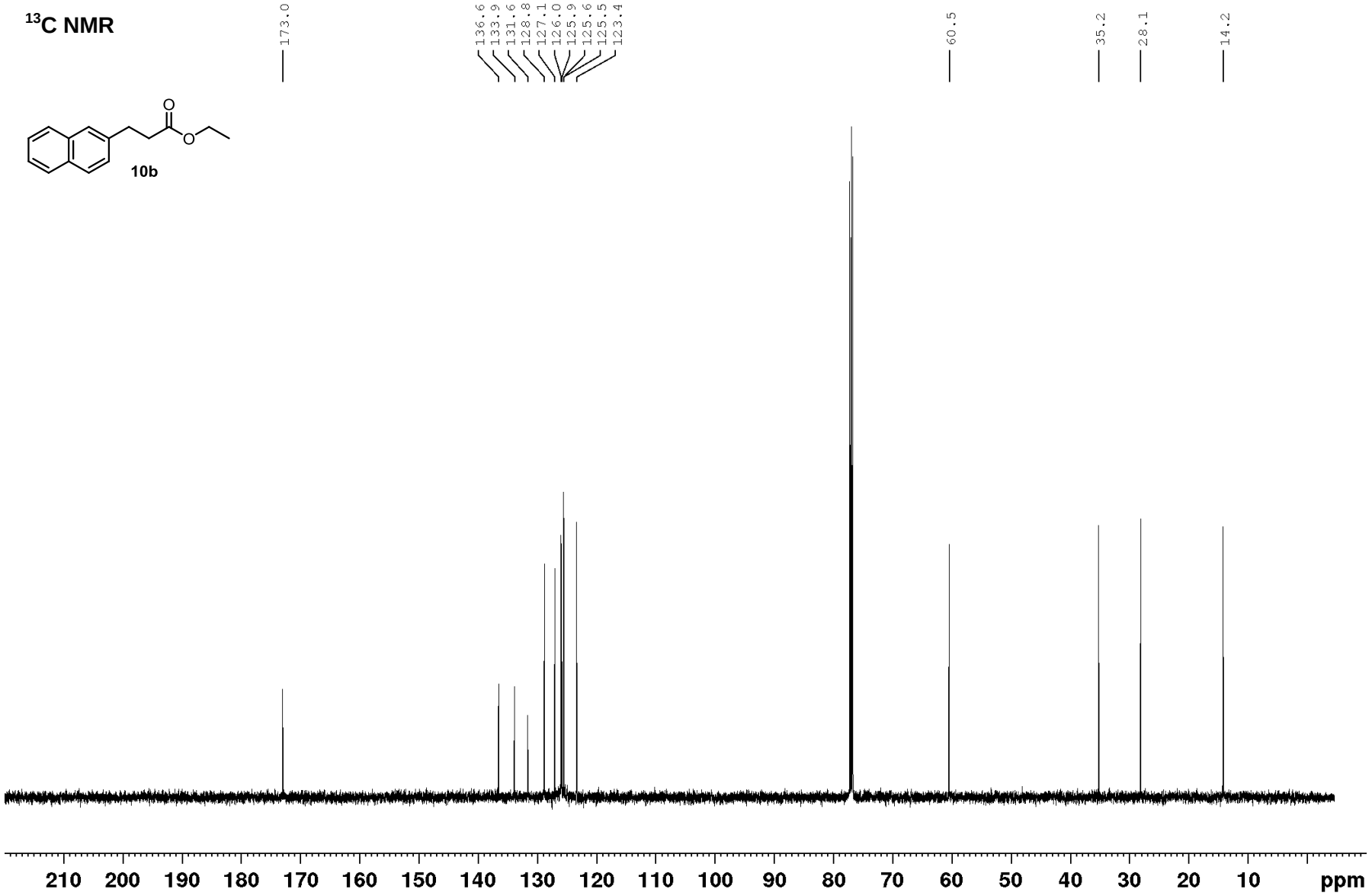
^{1}H-NMR

10b


8.06
8.04
7.88
7.86
7.75
7.73
7.56
7.55
7.54
7.54
7.53
7.52
7.51
7.51
7.49
7.48
7.48
7.42
7.41
7.39
7.37
7.36
4.19
4.18
4.16
4.15
3.45
3.44
3.42
2.78
2.77
2.75
1.27
1.26
1.24
0.97
0.98
0.96
2.01
0.96
1.01
1.97
2.00
2.01
3.02
10
9
8
7
6
5
4
3
2
1
0
ppm

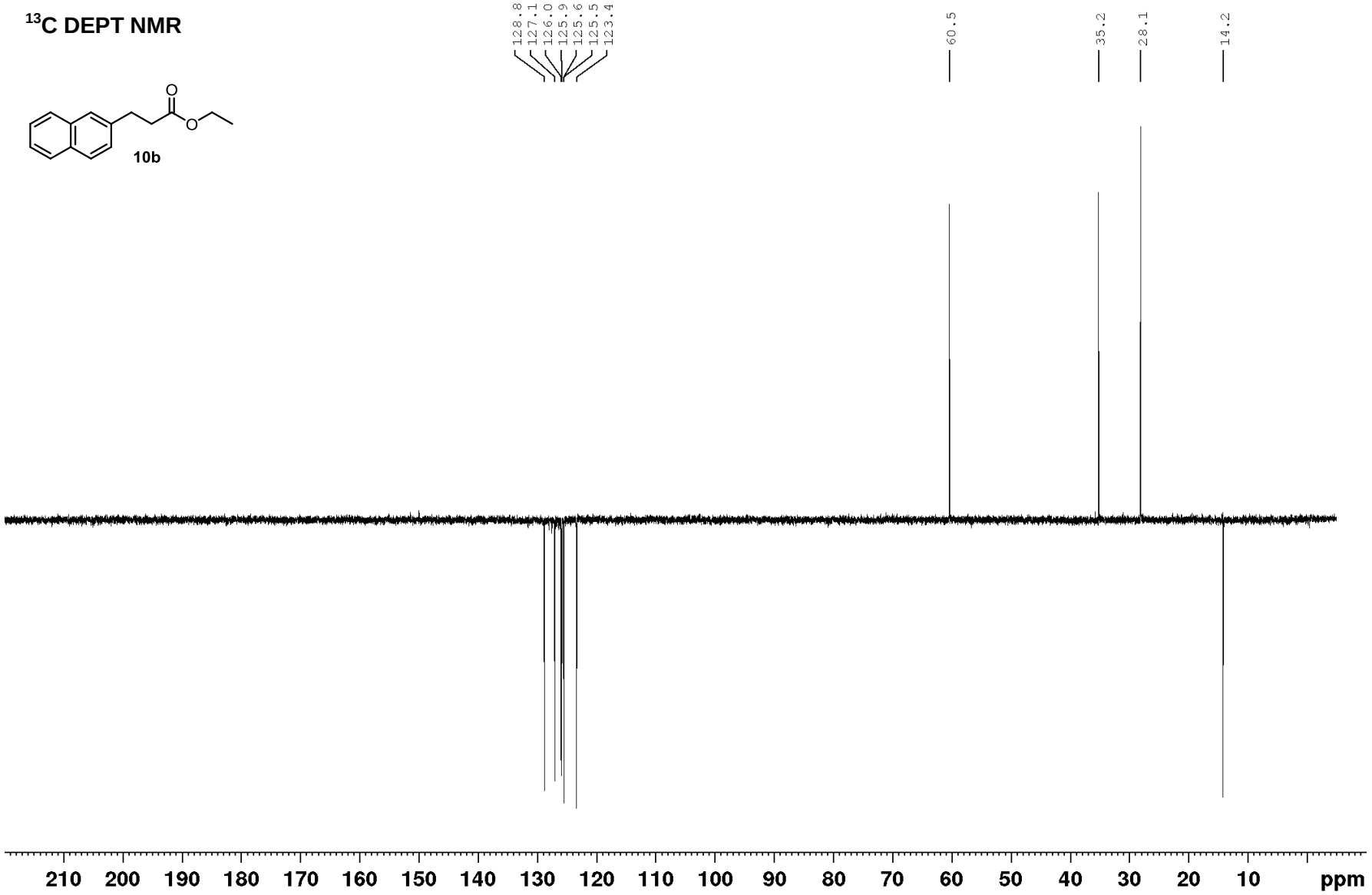
^{13}C NMR

10b

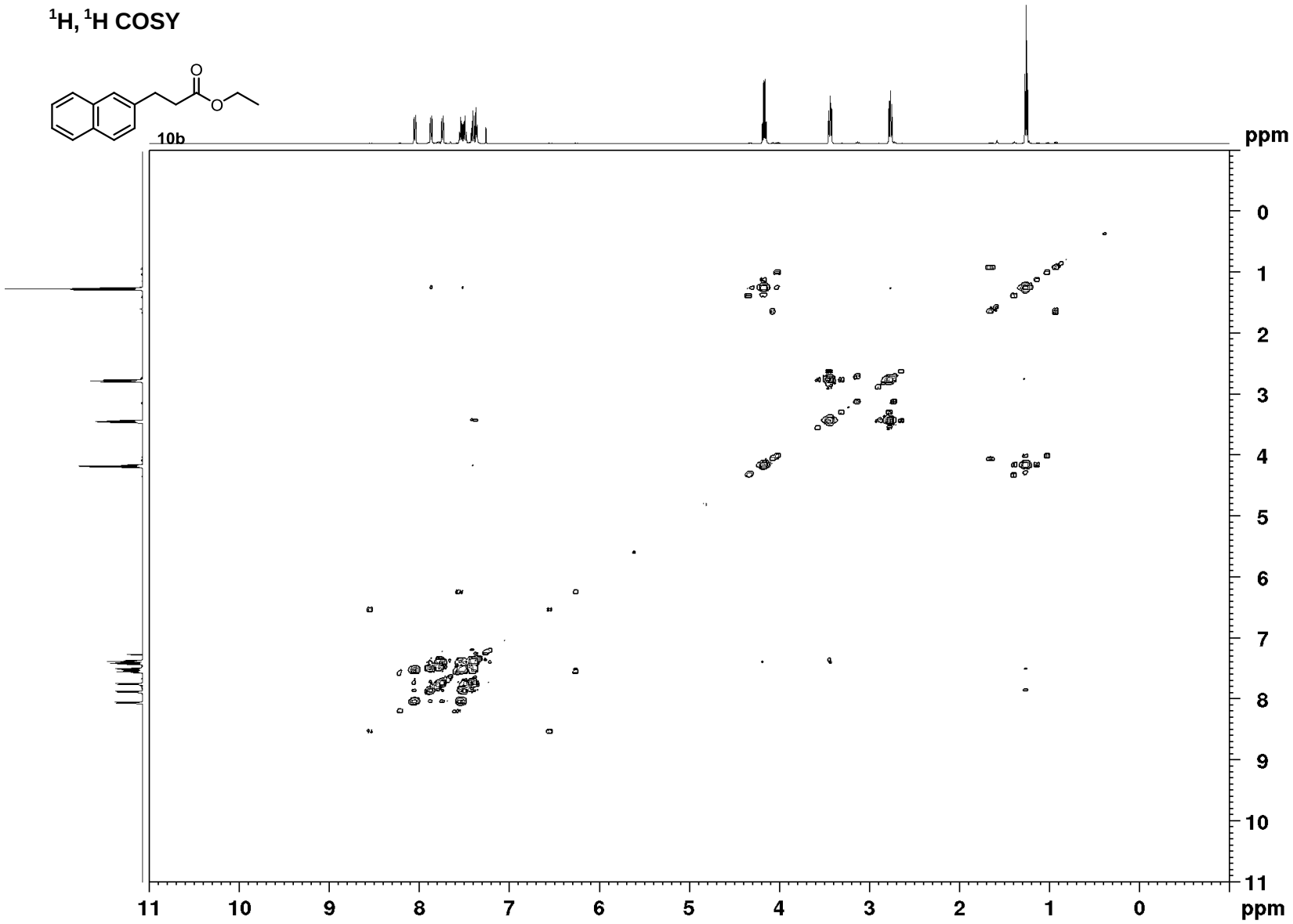

173.0
136.6
133.9
131.6
128.8
127.1
126.0
125.9
125.6
125.5
123.4
60.5
35.2
28.1
14.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

10b

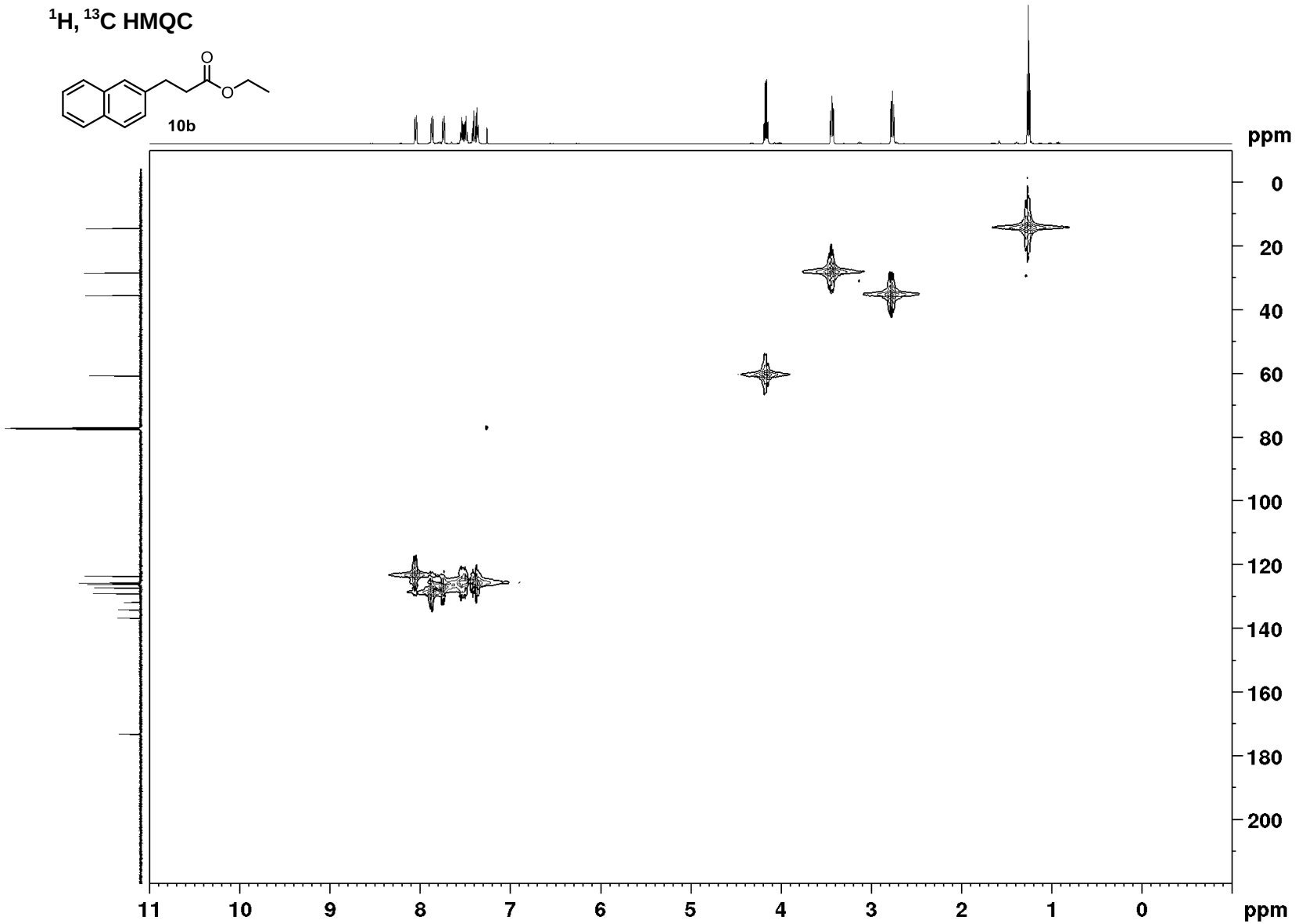


^{1}H, ^{1}H COSY



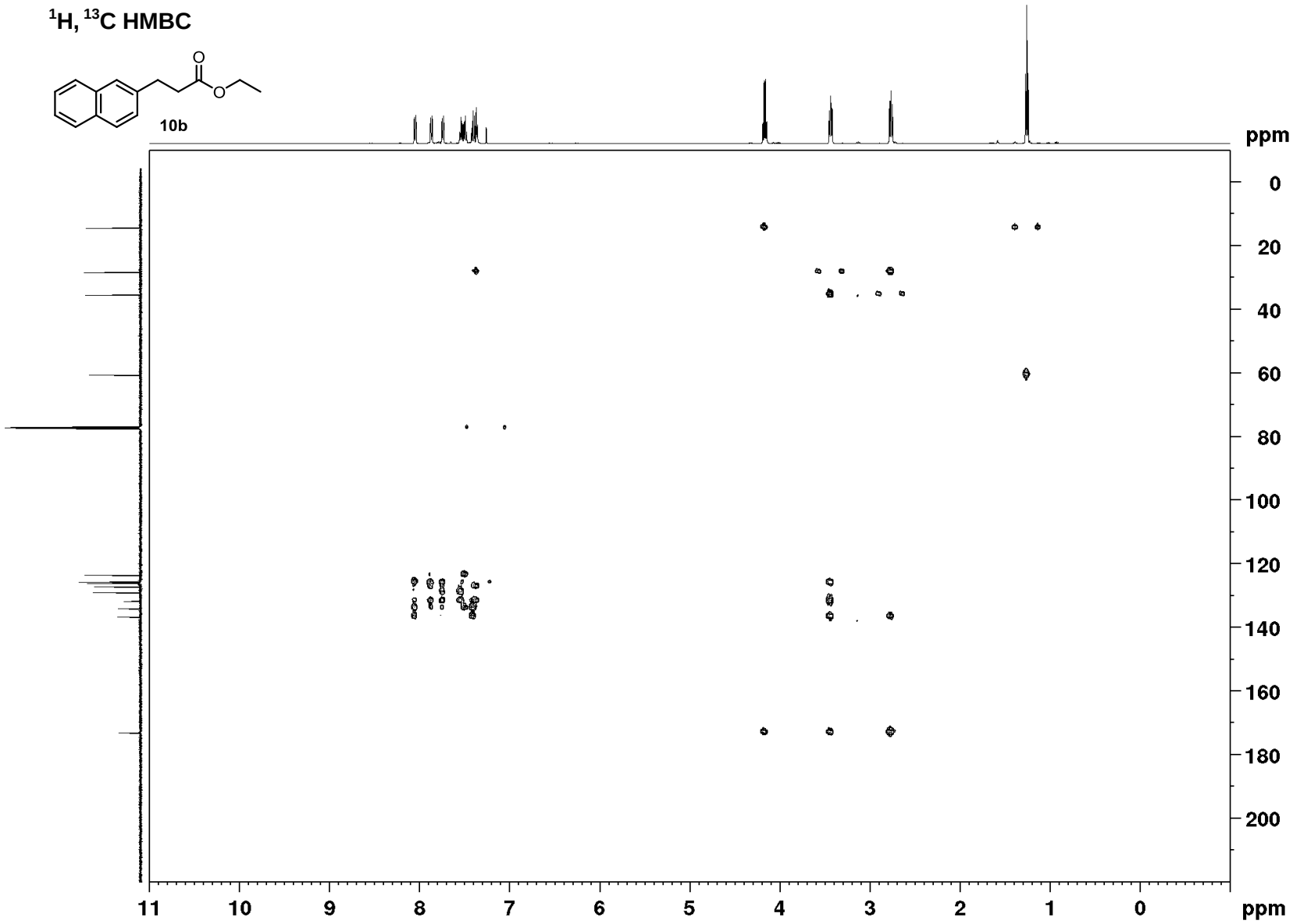
^{1}H, ^{13}C HMQC

10b

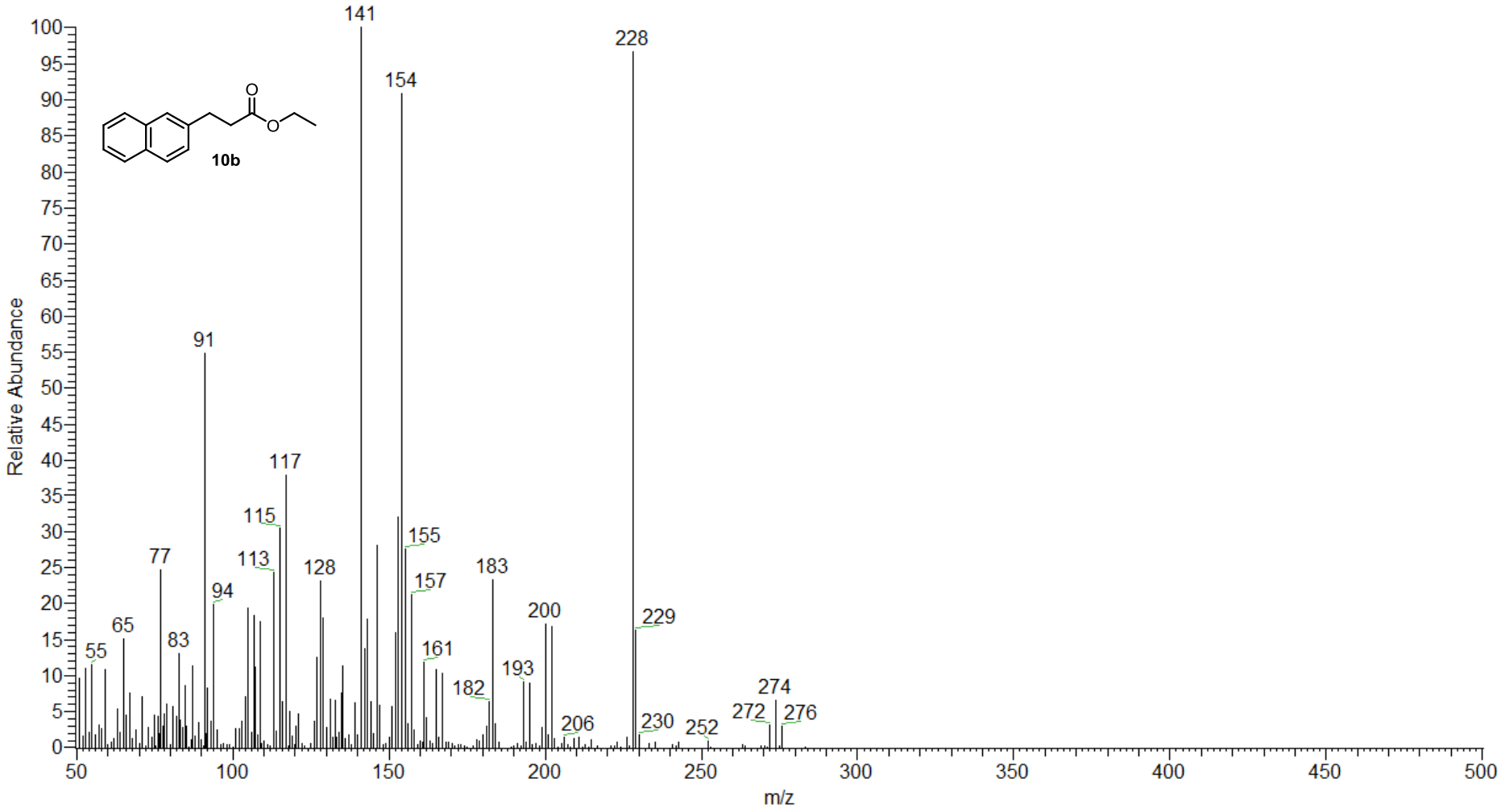


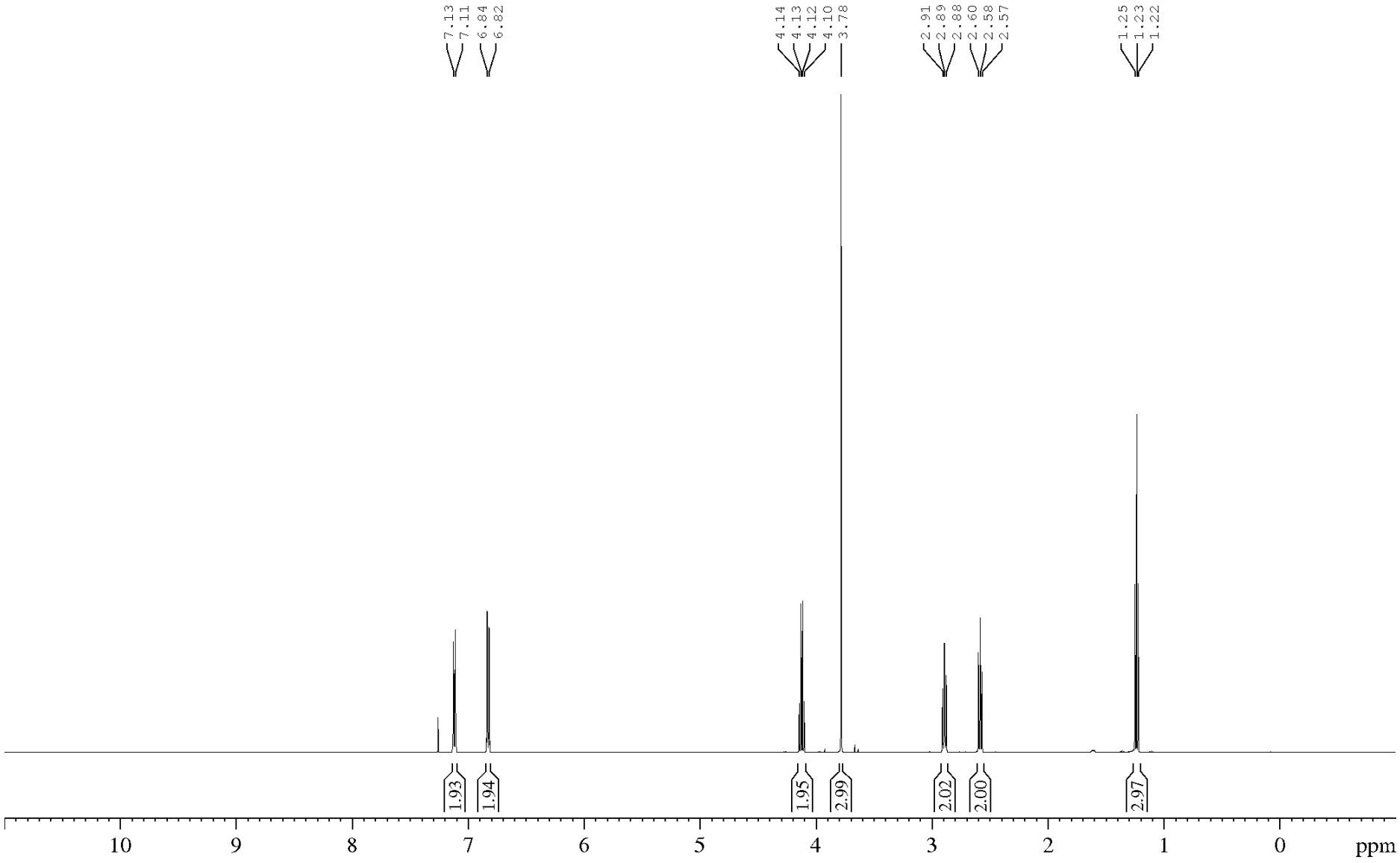
^{1}H, ^{13}C HMBC

10b

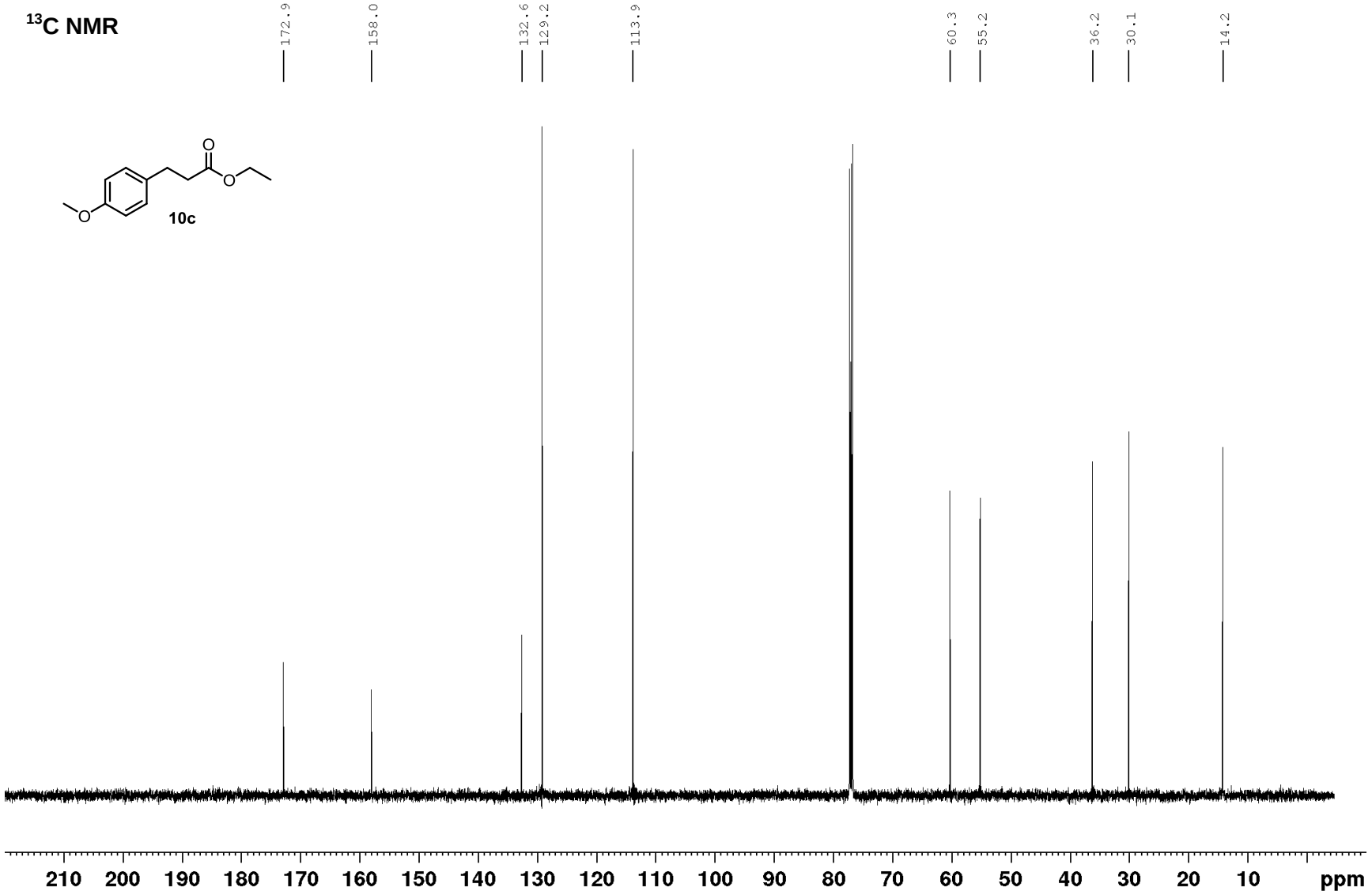


mass spectrum

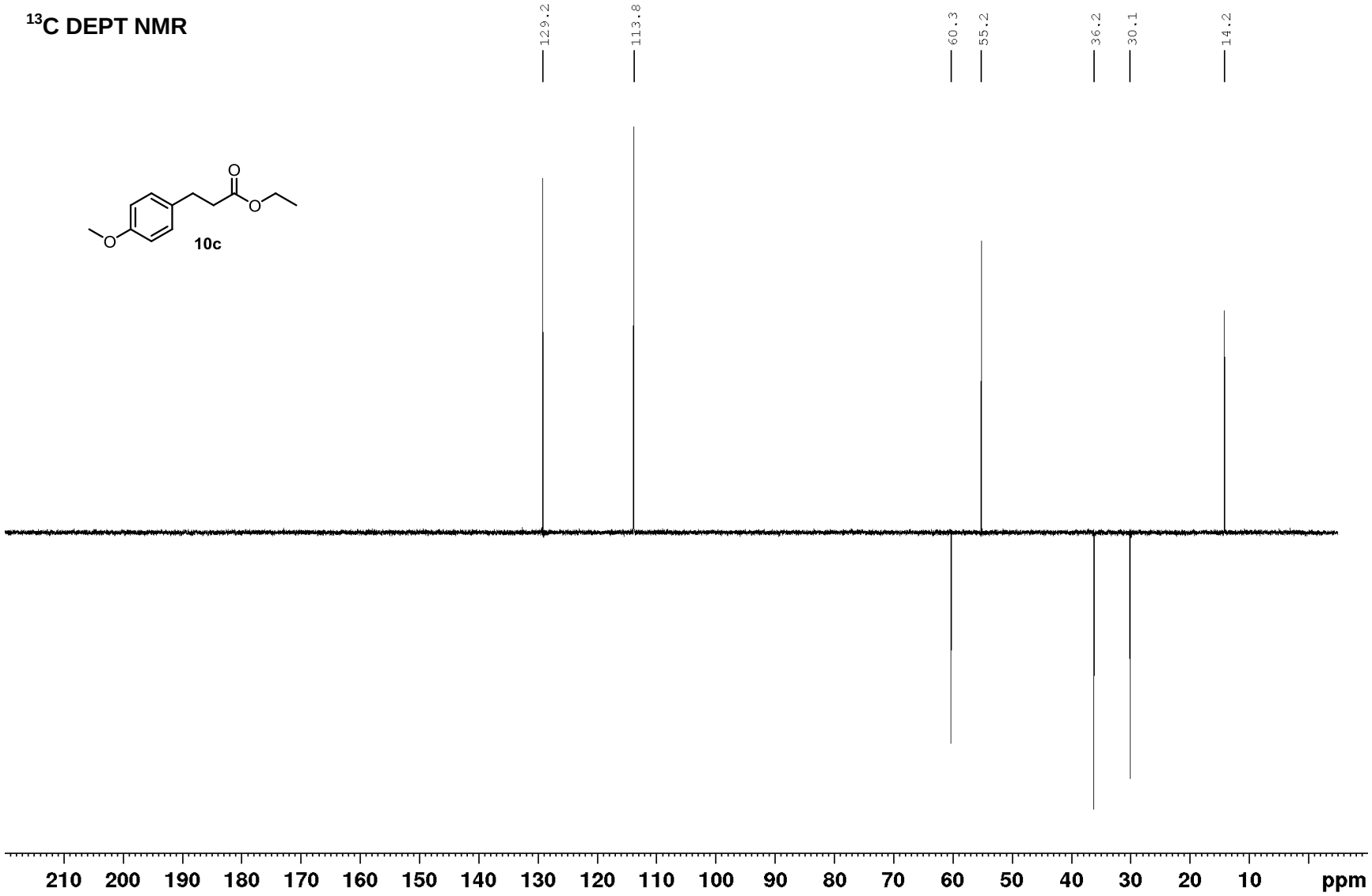



7.13
7.11
6.84
6.82
4.14
4.13
4.12
4.10
3.78
2.91
2.89
2.88
2.60
2.58
2.57
1.25
1.23
1.22
1.93
1.94
1.95
2.99
2.02
2.00
2.97
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

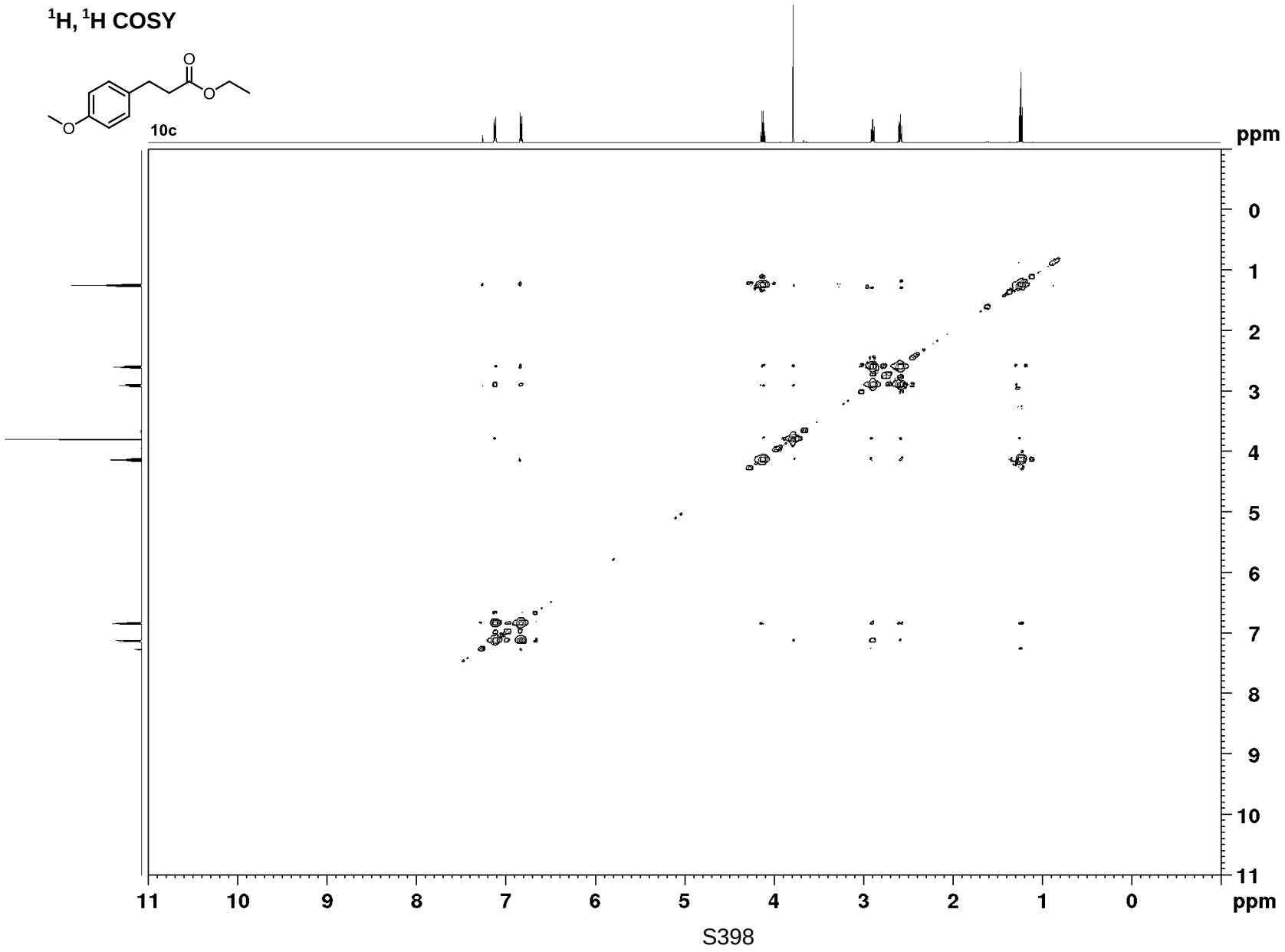

172.9
158.0
132.6
129.2
113.9
60.3
55.2
36.2
30.1
14.2
O
O
O
10c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

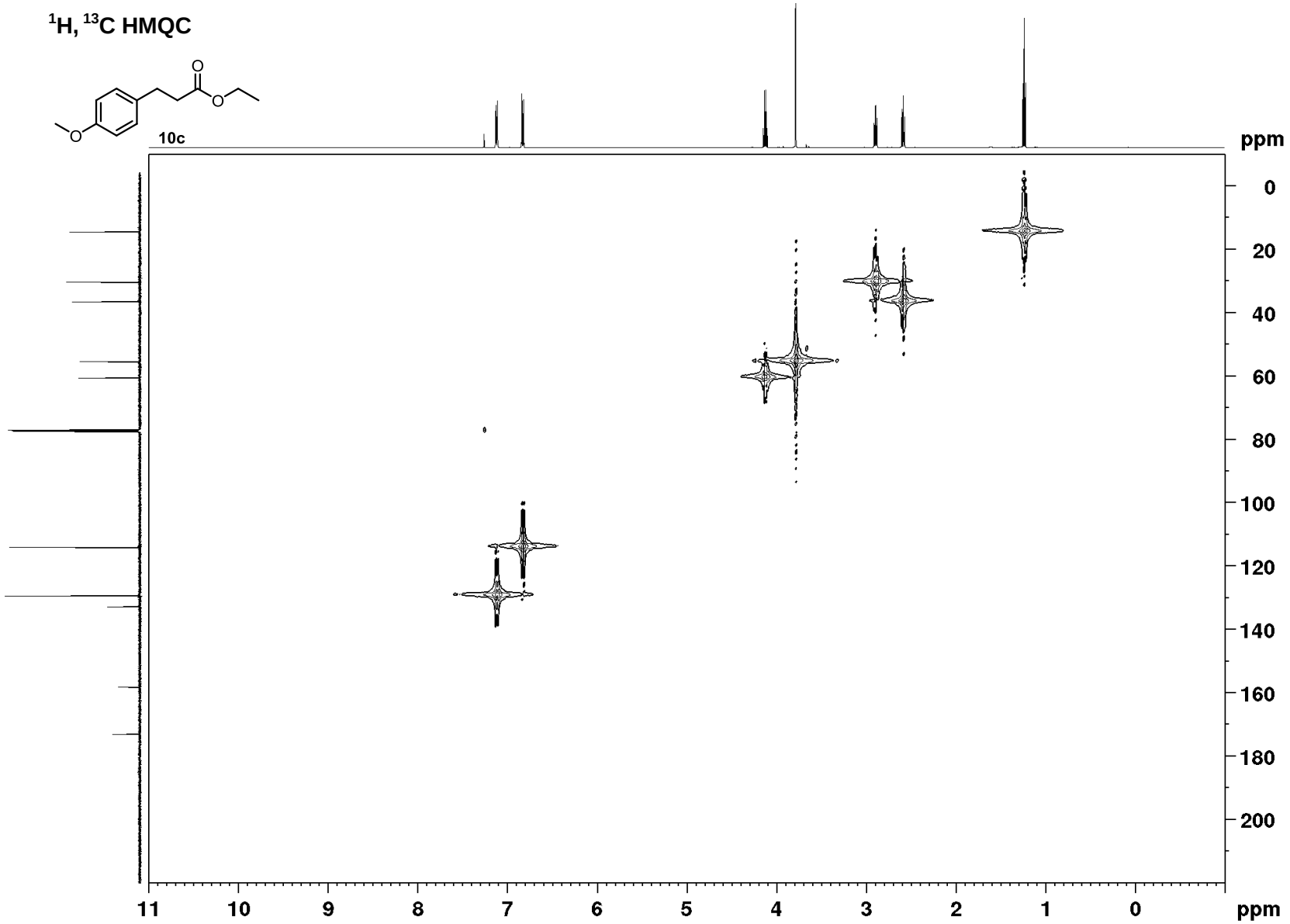
^{13}C DEPT NMR

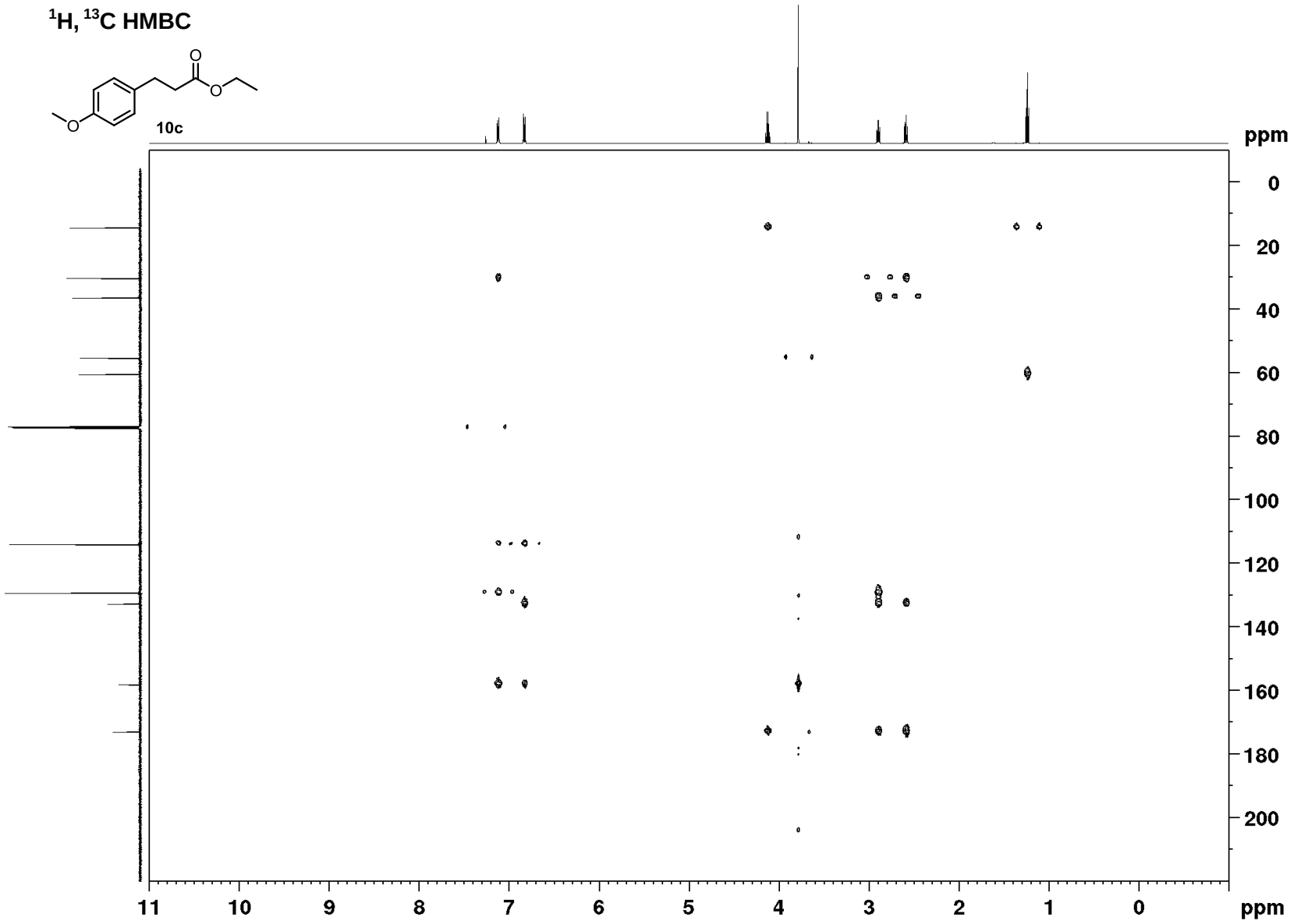

129.2
113.8
60.3
55.2
36.2
30.1
14.2
O
O
O
10c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H, ^{1}H COSY

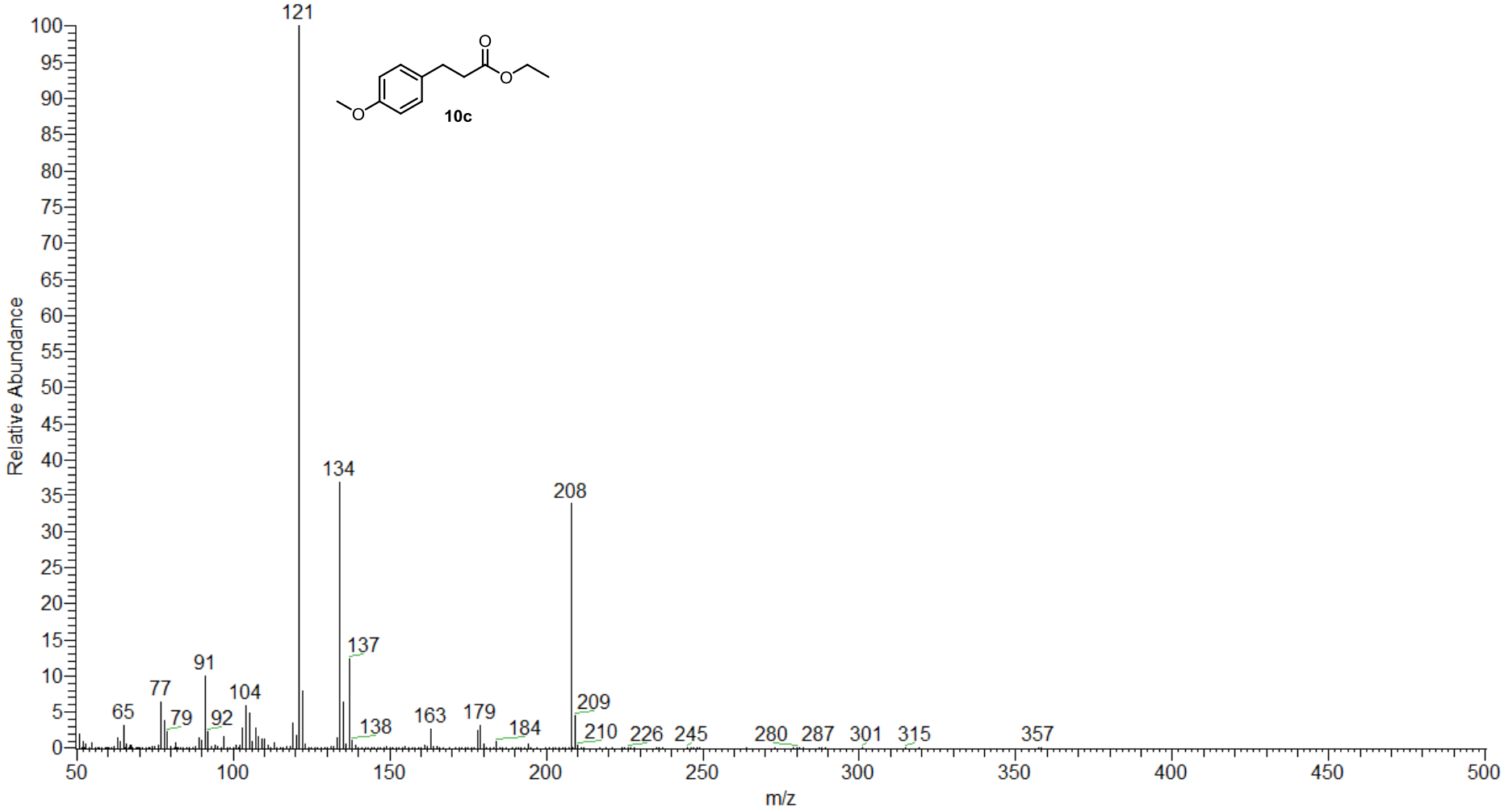
10c




^{1}H, ^{13}C HMQC
10c
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm


^{1}H, ^{13}C HMBC
10c
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

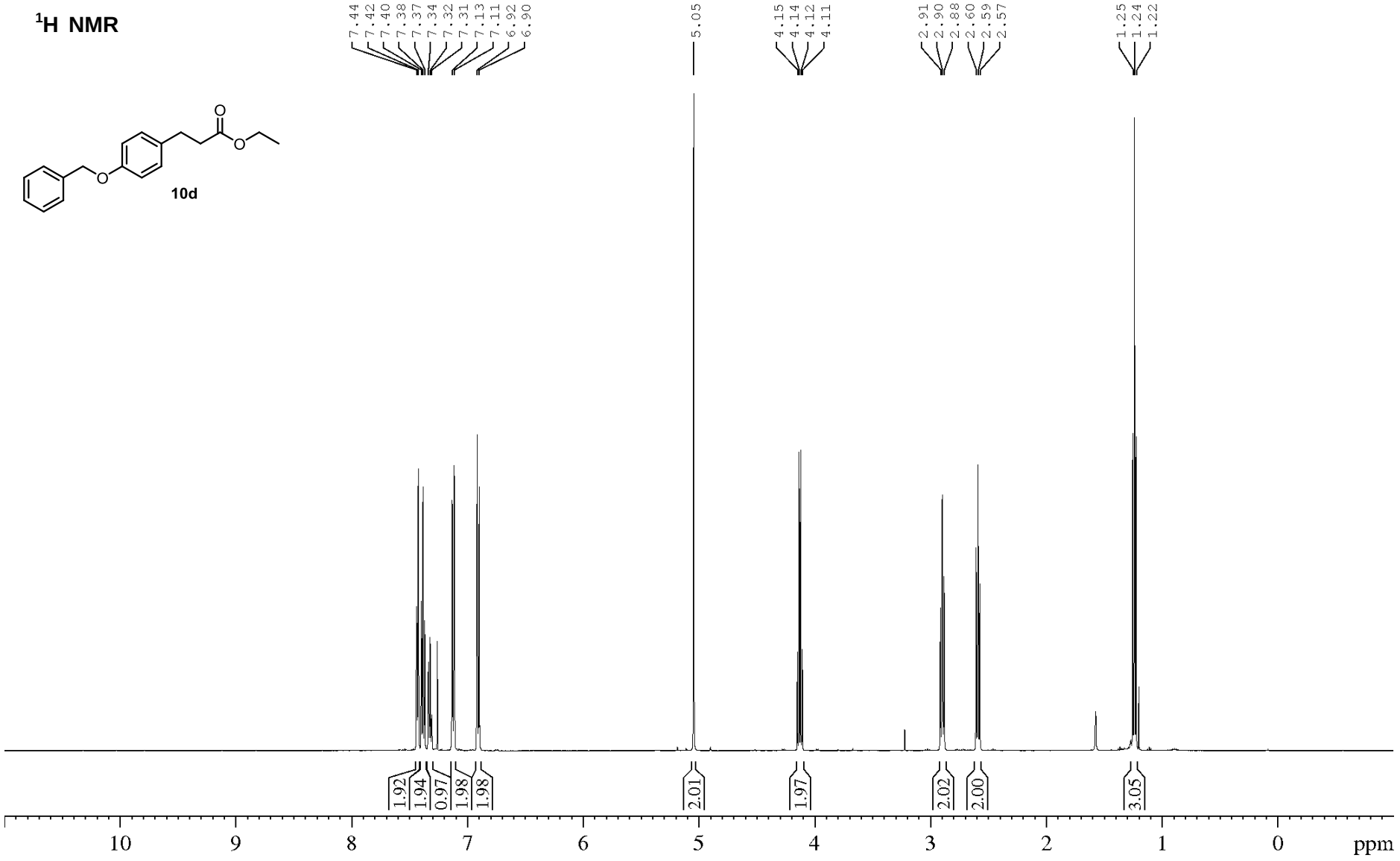
mass spectrum



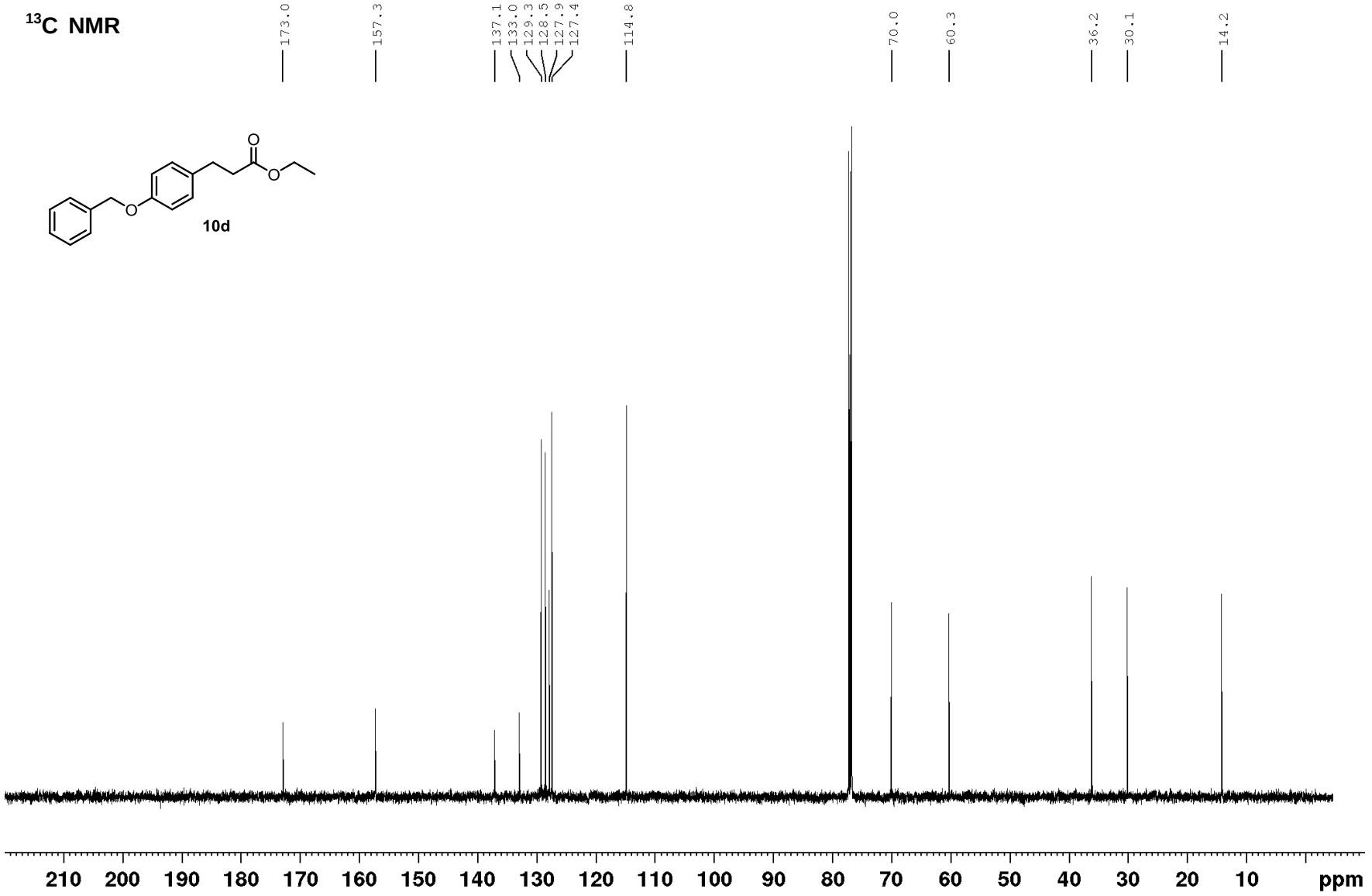
^{1}H NMR

O
O
O

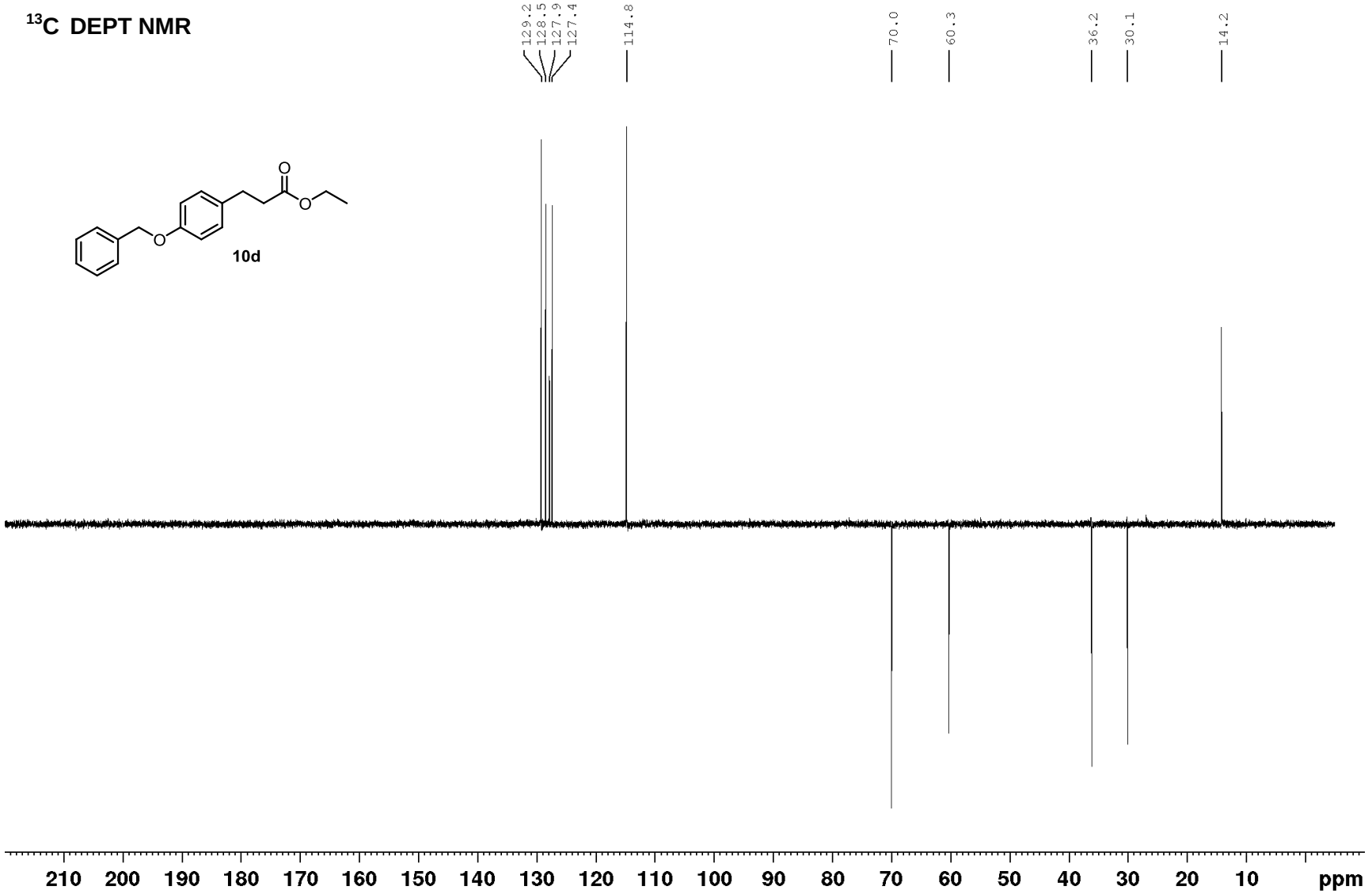
10d

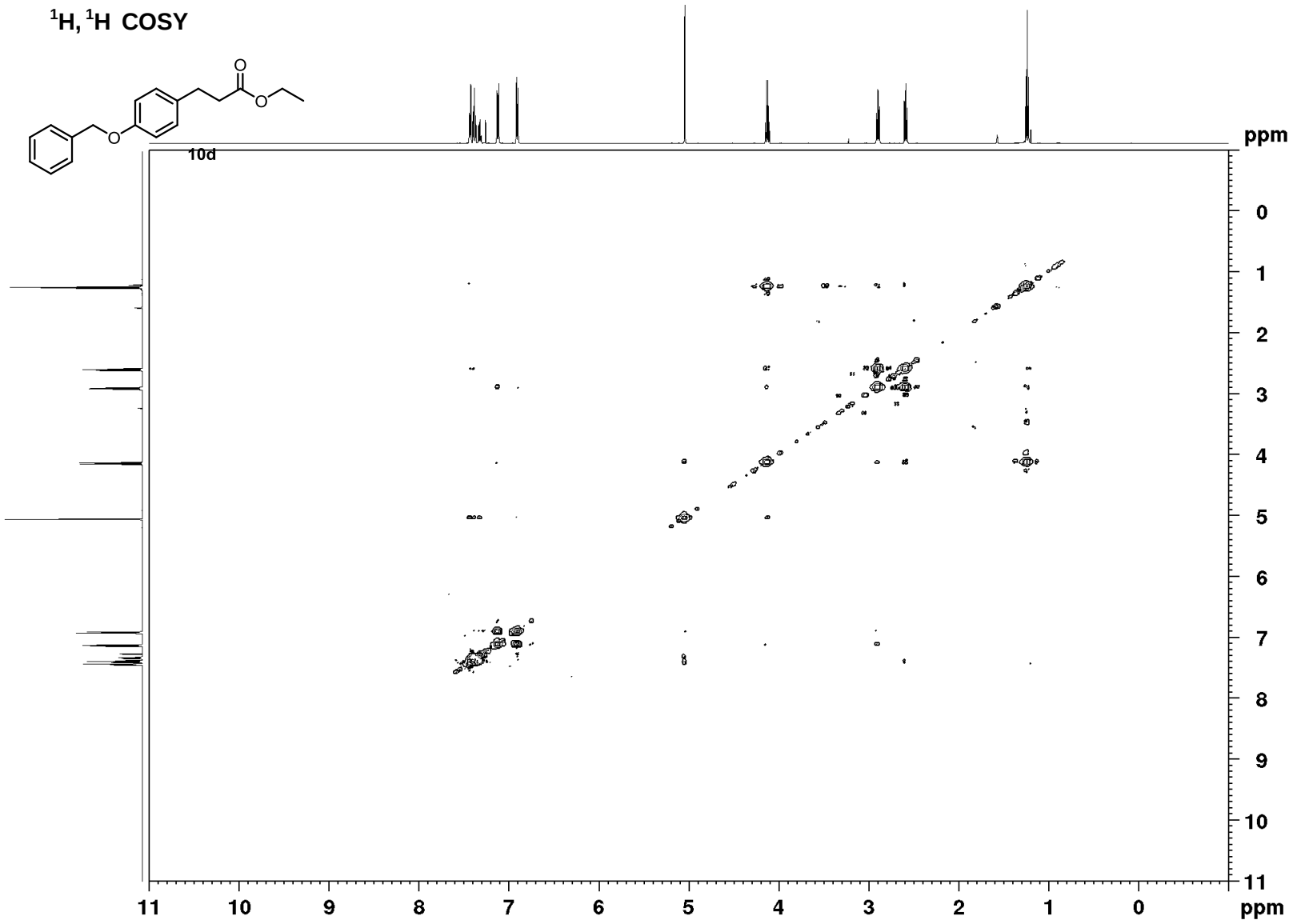

7.44
7.42
7.40
7.38
7.37
7.34
7.32
7.31
7.13
7.11
6.92
6.90
5.05
4.15
4.14
4.12
4.11
2.91
2.90
2.88
2.60
2.59
2.57
1.25
1.24
1.22
1.92
1.94
0.97
1.98
1.98
2.01
1.97
2.02
2.00
3.05
10
9
8
7
6
5
4
3
2
1
0
ppm

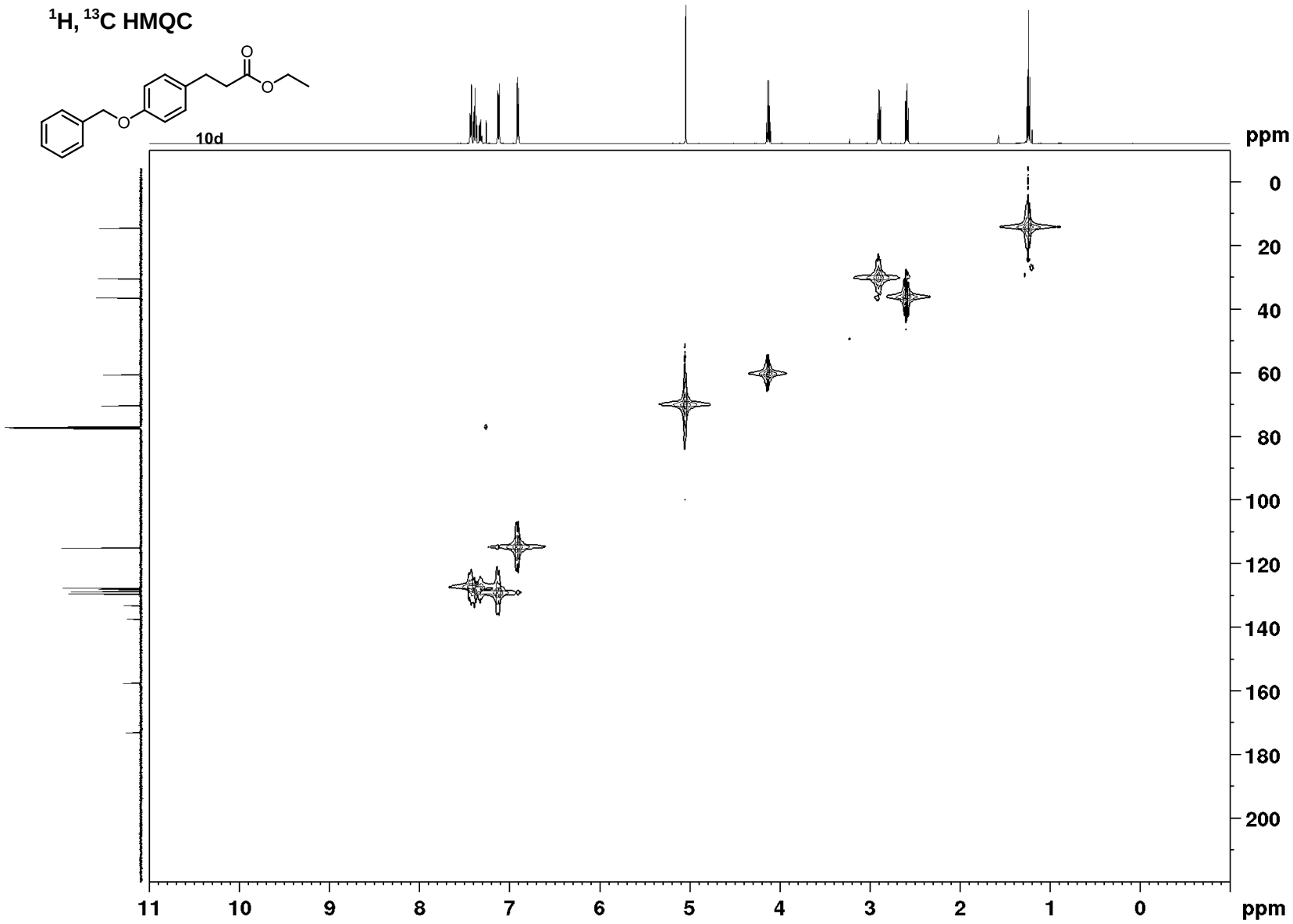
^{13}C NMR

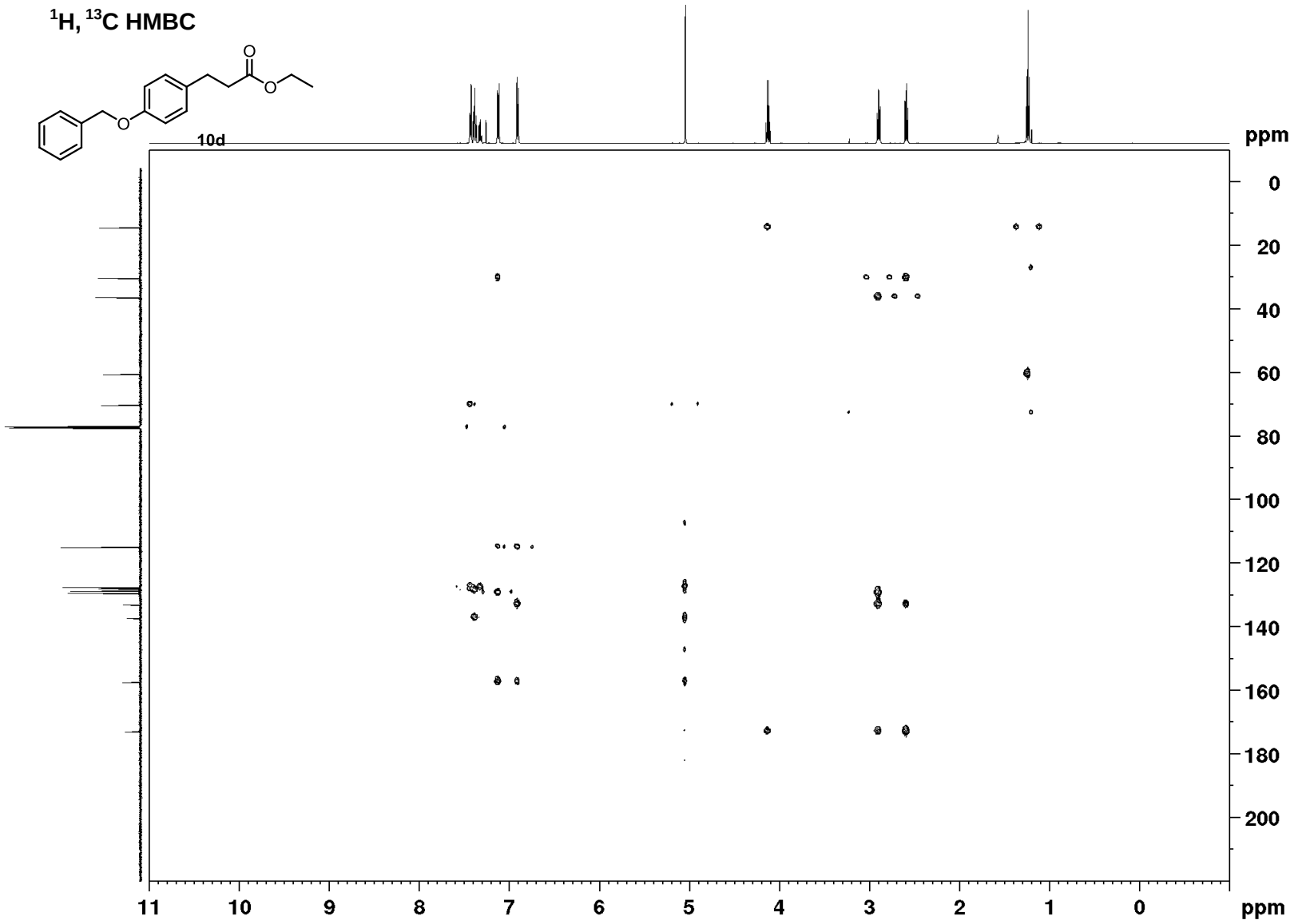

173.0
157.3
137.1
133.0
129.3
128.5
127.9
127.4
114.8
70.0
60.3
36.2
30.1
14.2
O
O
O
10d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

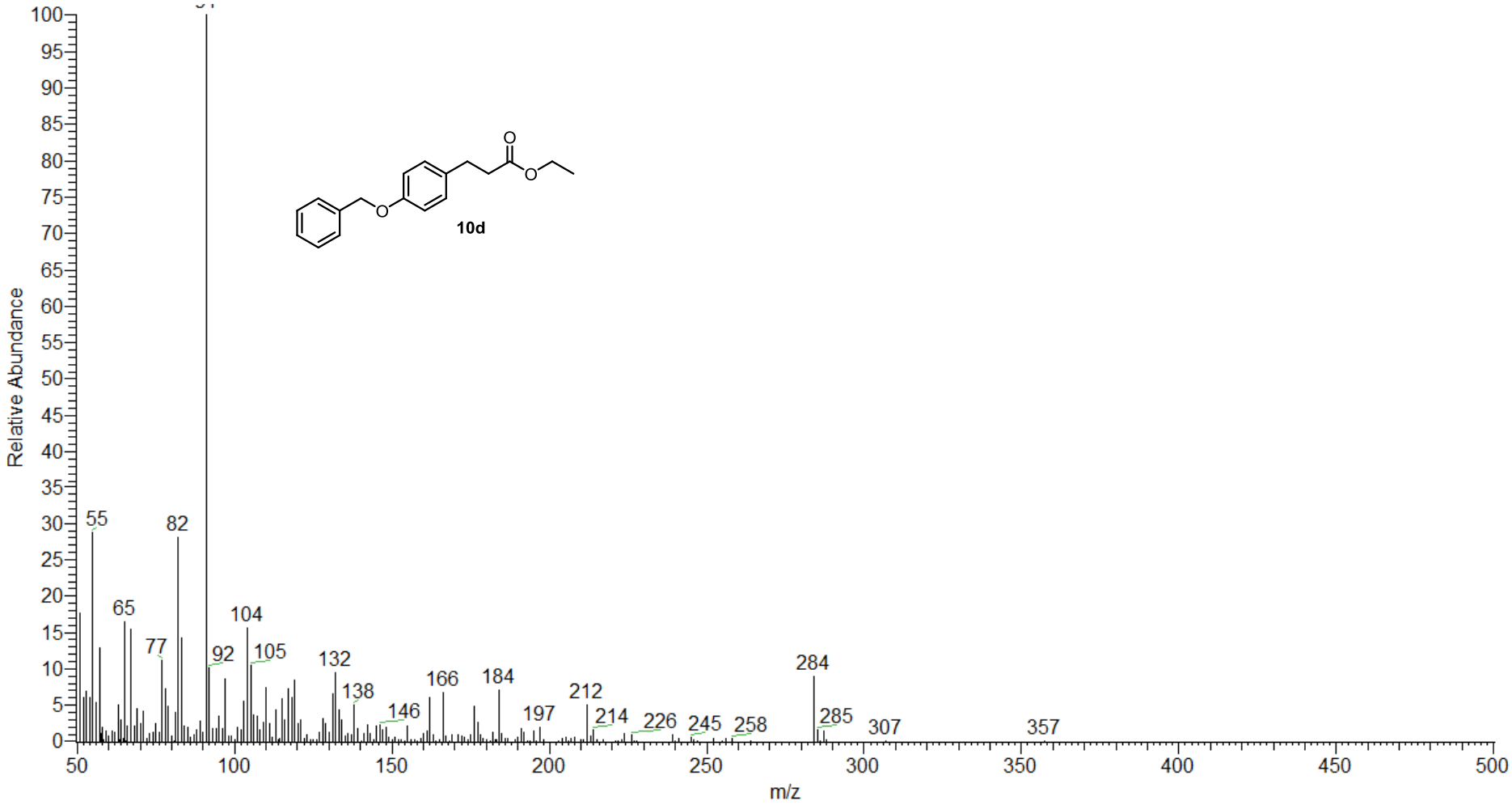

129.2
128.5
127.9
127.4
114.8
70.0
60.3
36.2
30.1
14.2
O
O
O
10d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{1}H, ^{1}H COSY
10d
ppm
0
1
2
3
4
5
6
7
8
9
10
11
11
10
9
8
7
6
5
4
3
2
1
0
ppm


^{1}H, ^{13}C HMQC
10d
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

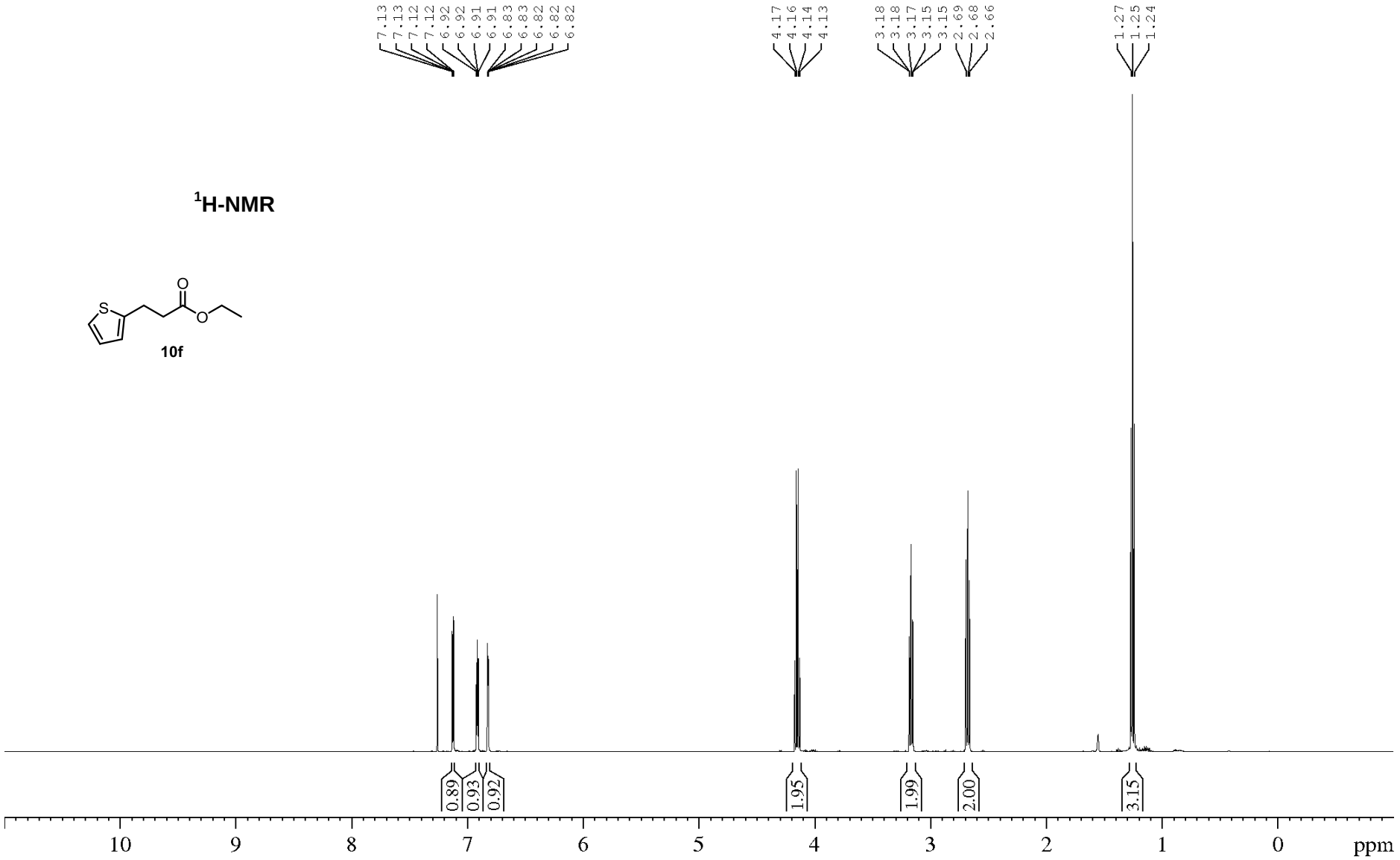

^{1}H, ^{13}C HMBC
10d
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

mass spectrum

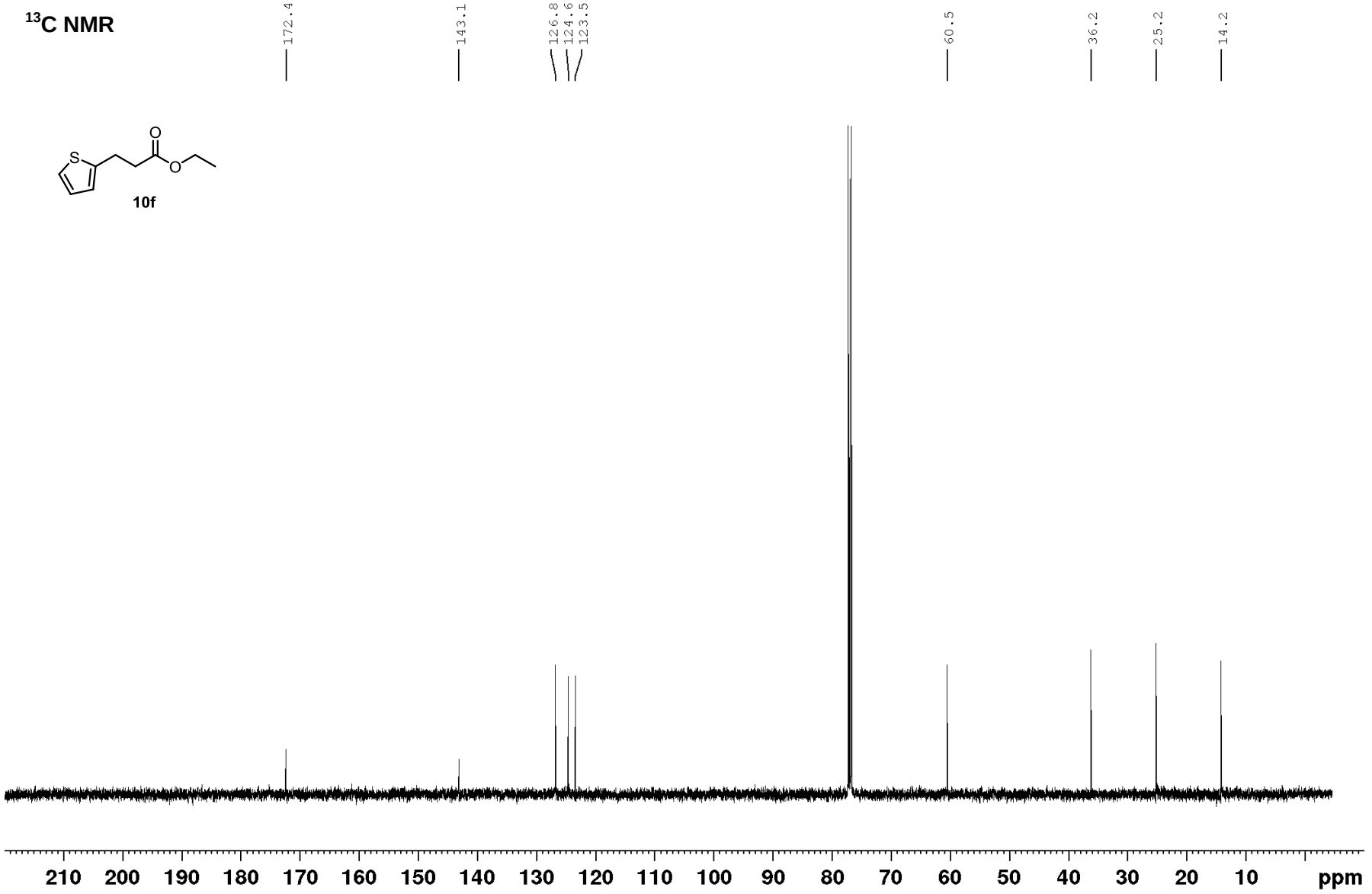


^{1}H-NMR

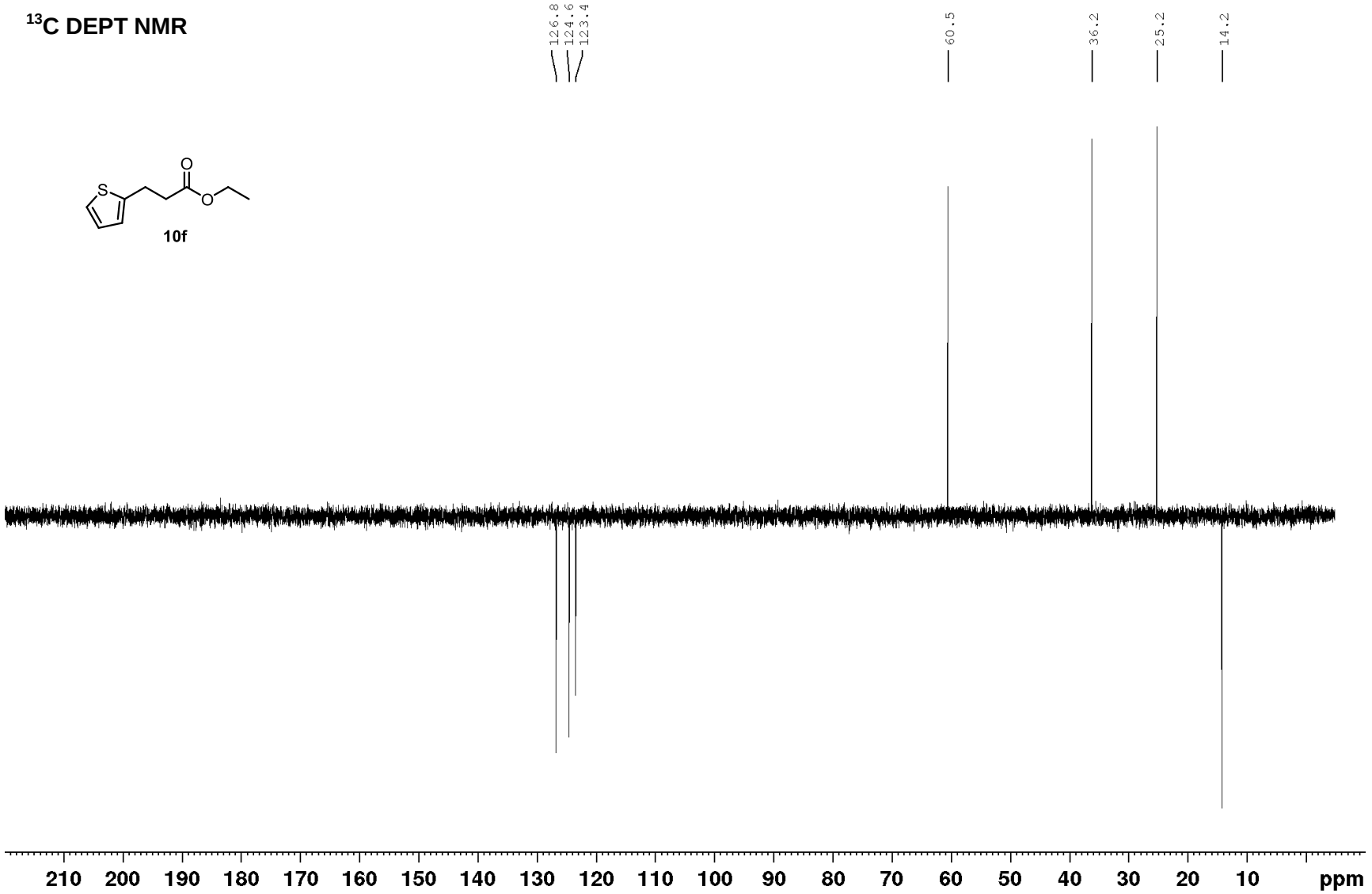
10f


7.13
7.13
7.12
7.12
6.92
6.92
6.91
6.91
6.83
6.82
6.82
6.82
4.17
4.16
4.14
4.13
3.18
3.18
3.17
3.15
3.15
2.69
2.68
2.66
1.27
1.25
1.24
0.89
0.93
0.92
1.95
1.99
2.00
3.15
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

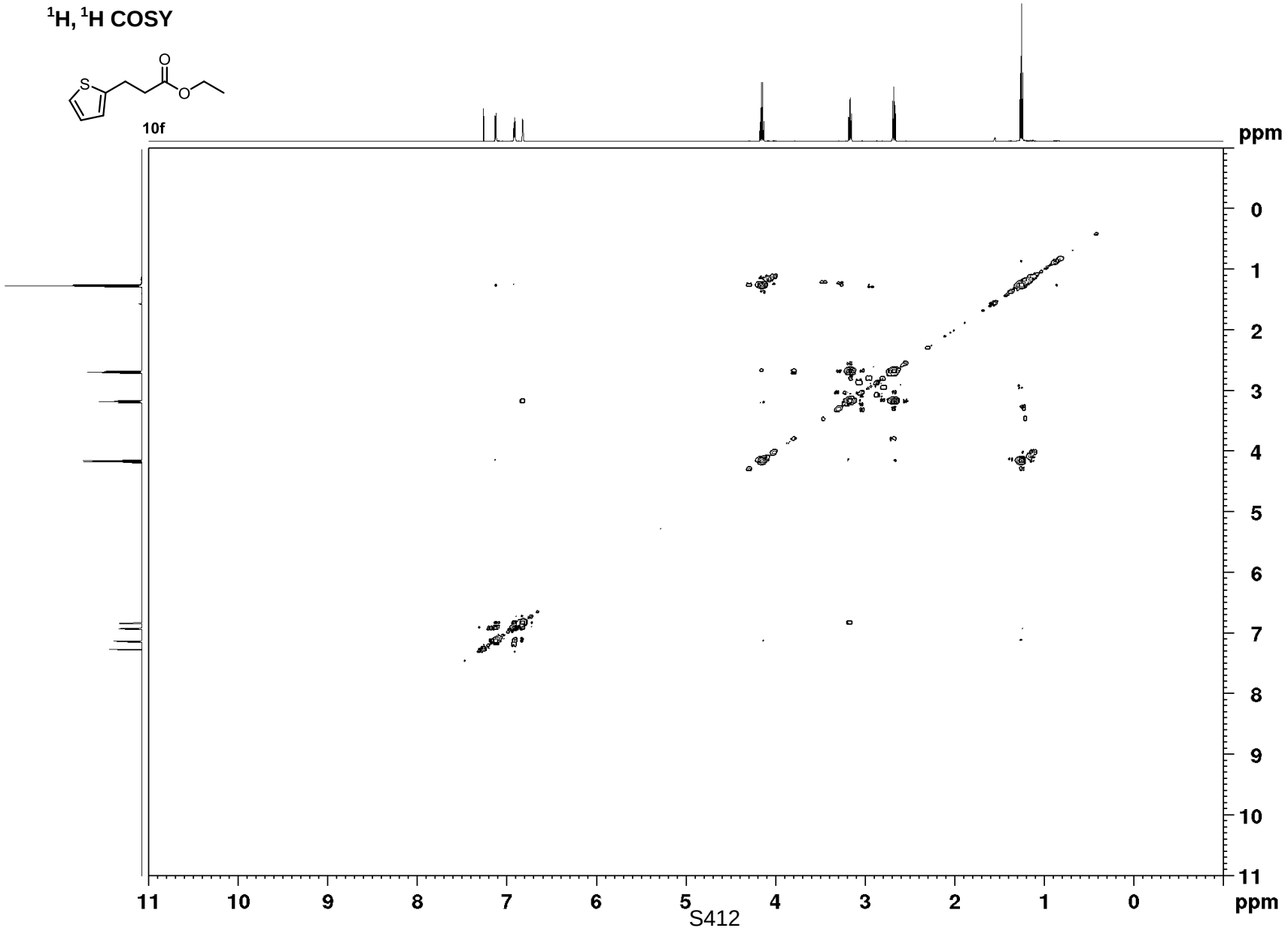

172.4
143.1
126.8
124.6
123.5
60.5
36.2
25.2
14.2
S
O
O
10f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

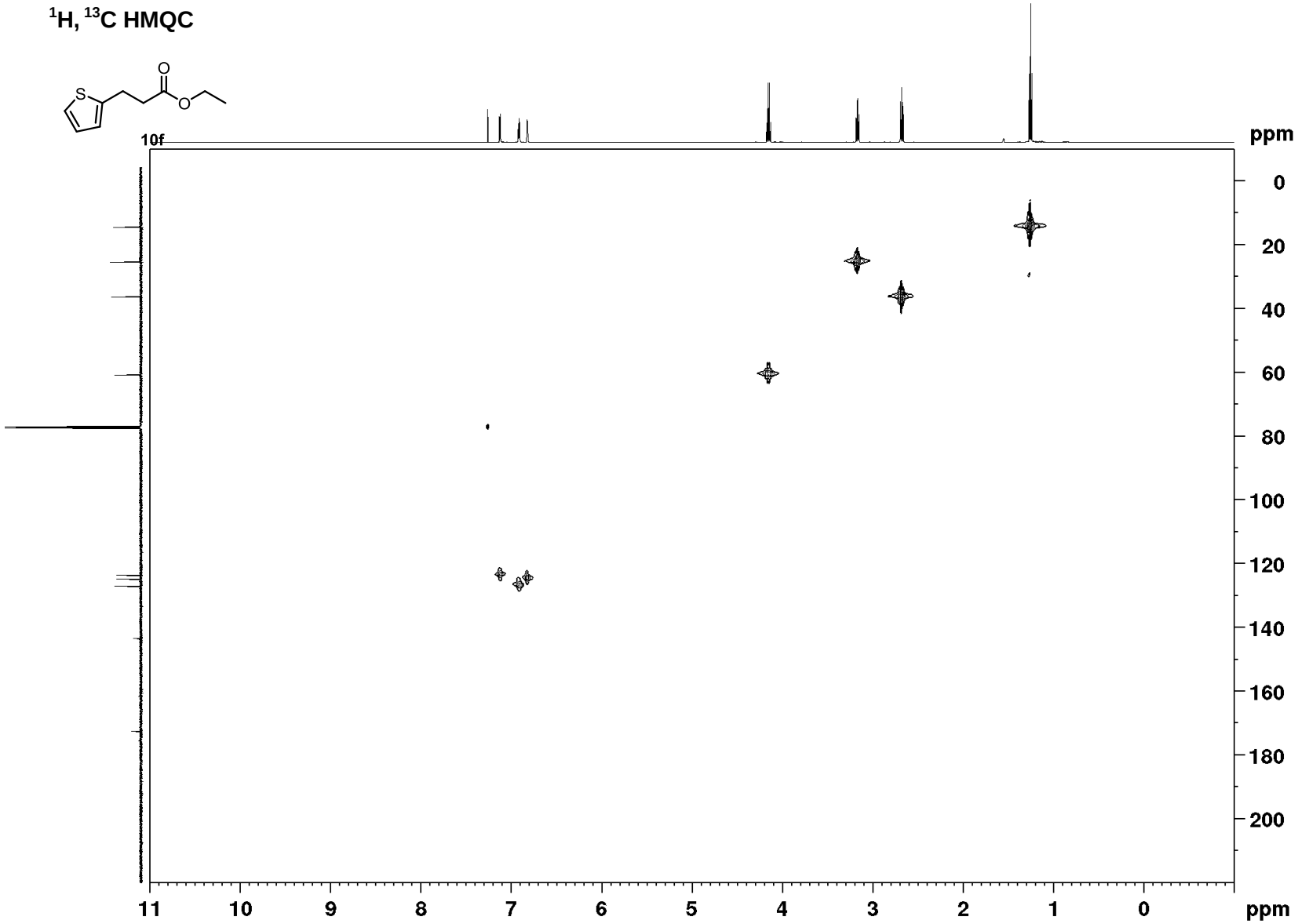

126.8
124.6
123.4
60.5
36.2
25.2
14.2
O
S
O
10f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H, ^{1}H COSY

10f

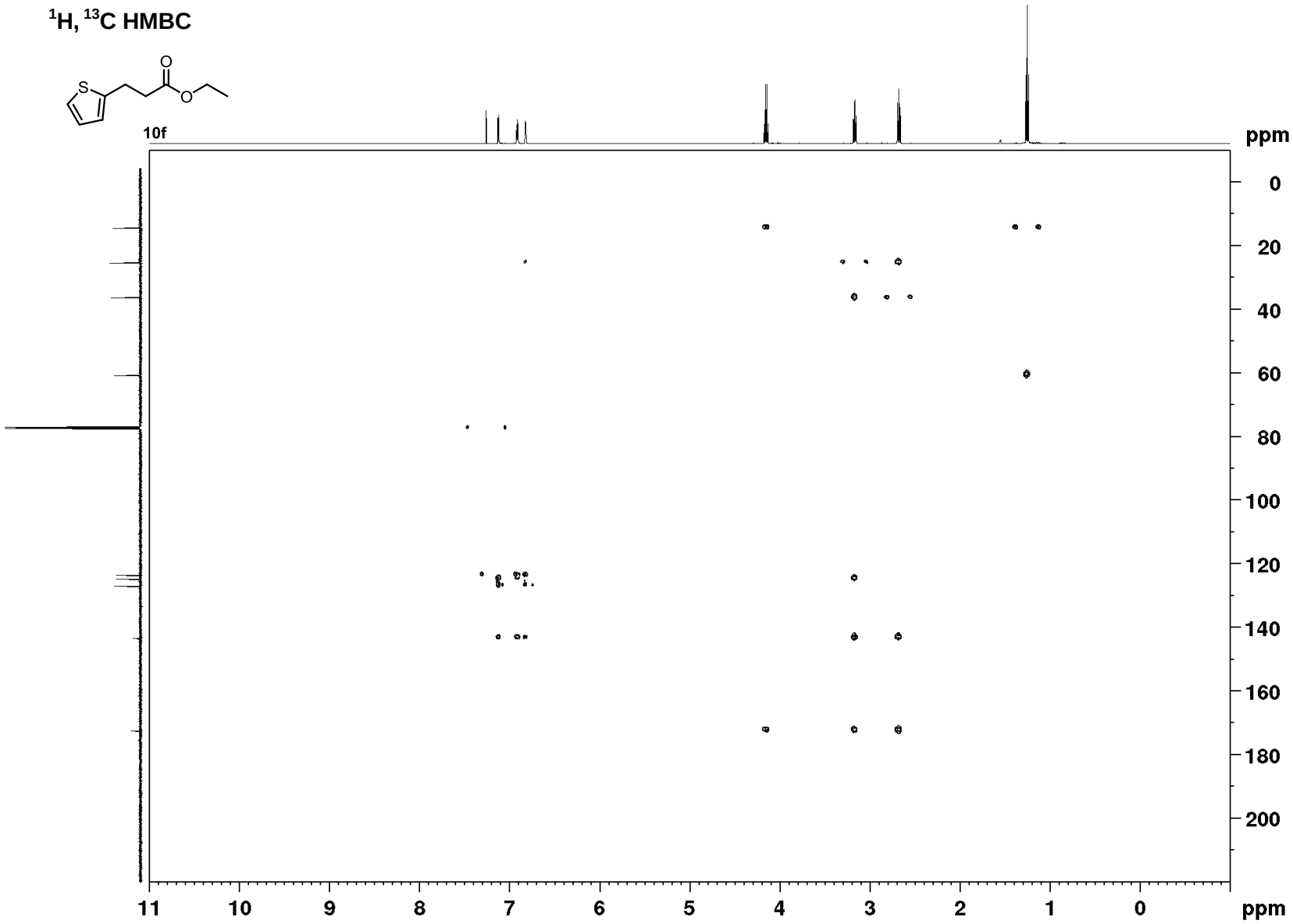


^{1}H, ^{13}C HMQC

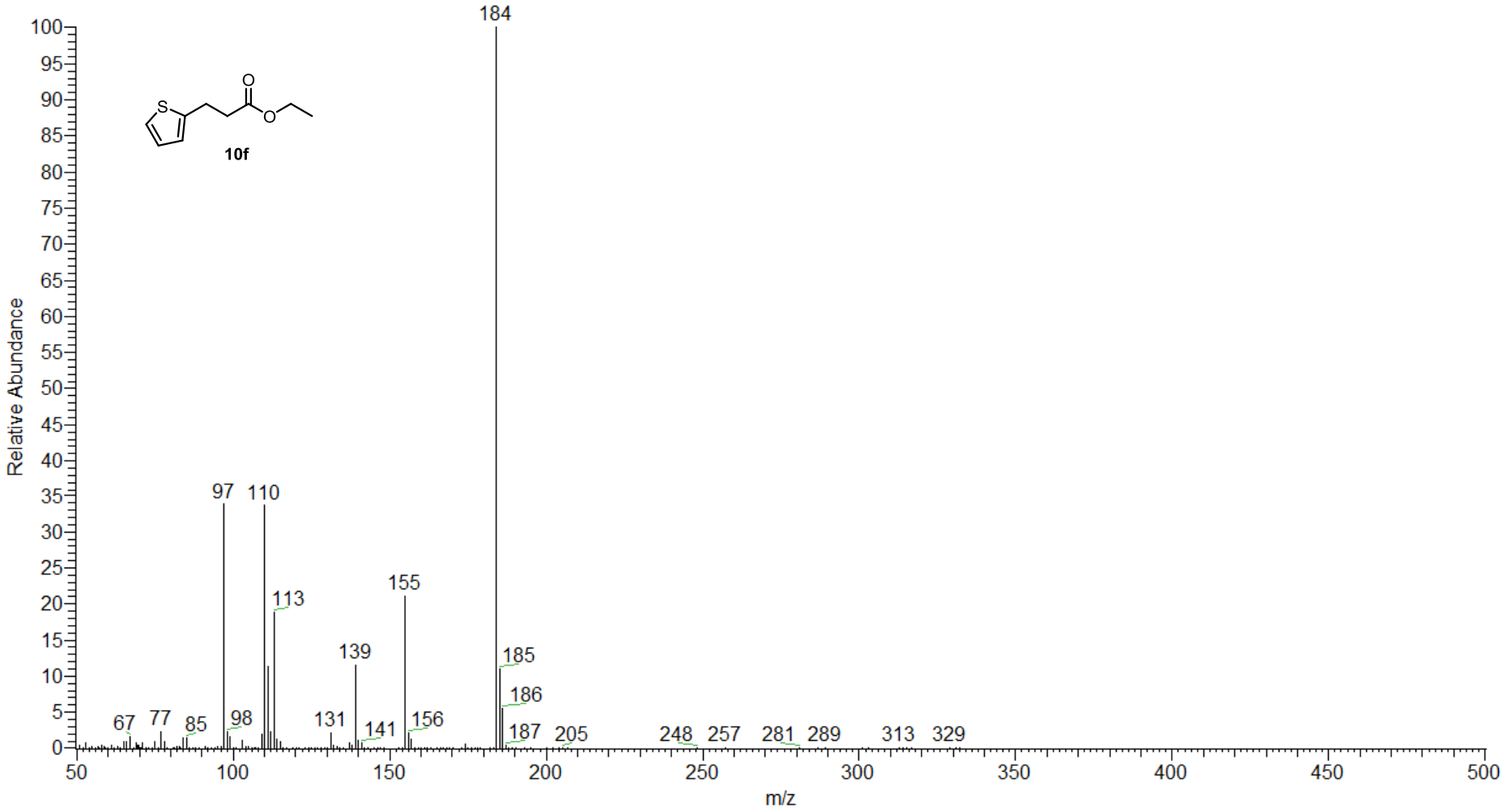

10f
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H, ^{13}C HMBC

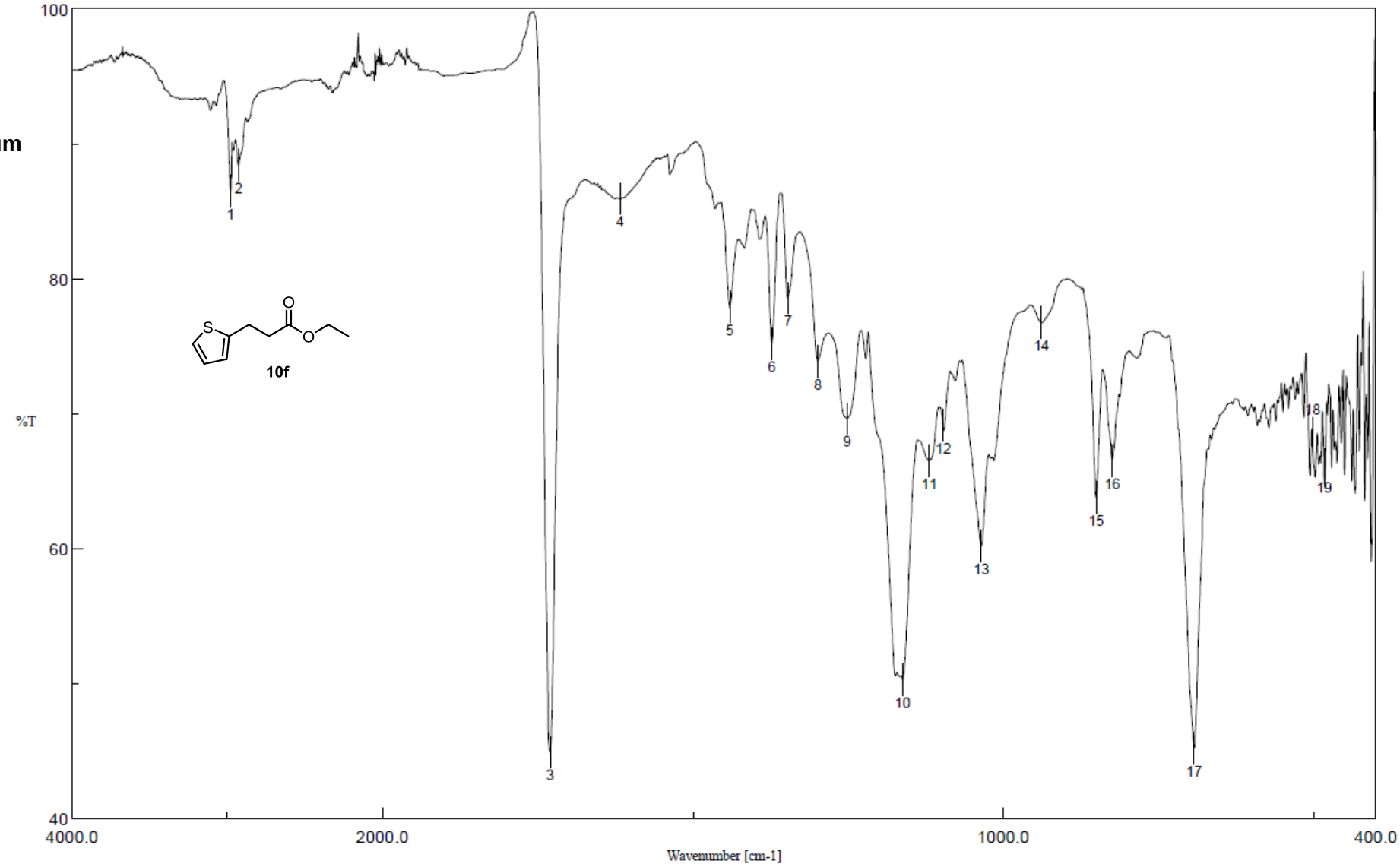
10f



mass spectrum



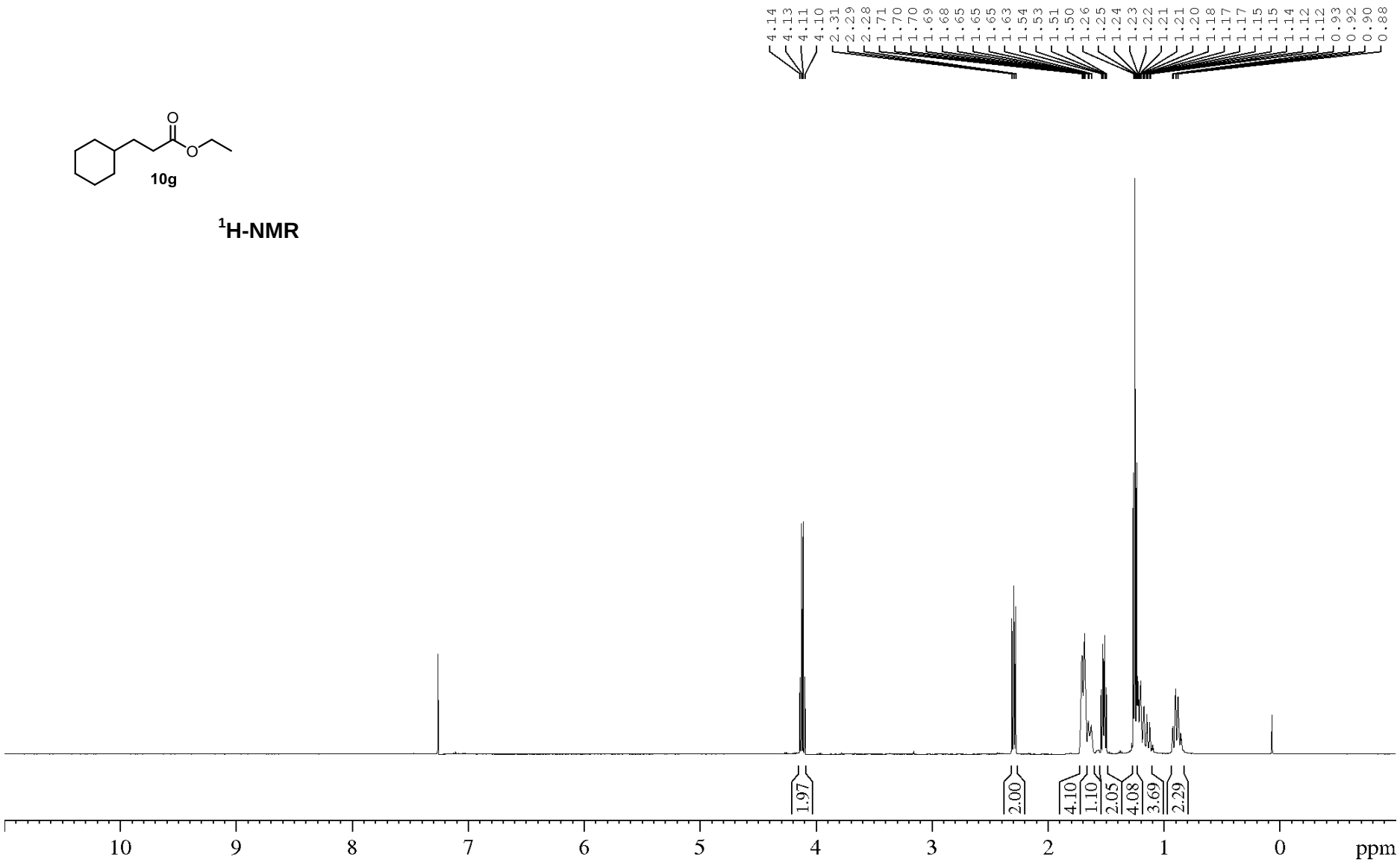
IR spectrum


100
80
60
40
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
O
S
O
10f

O
O

10g

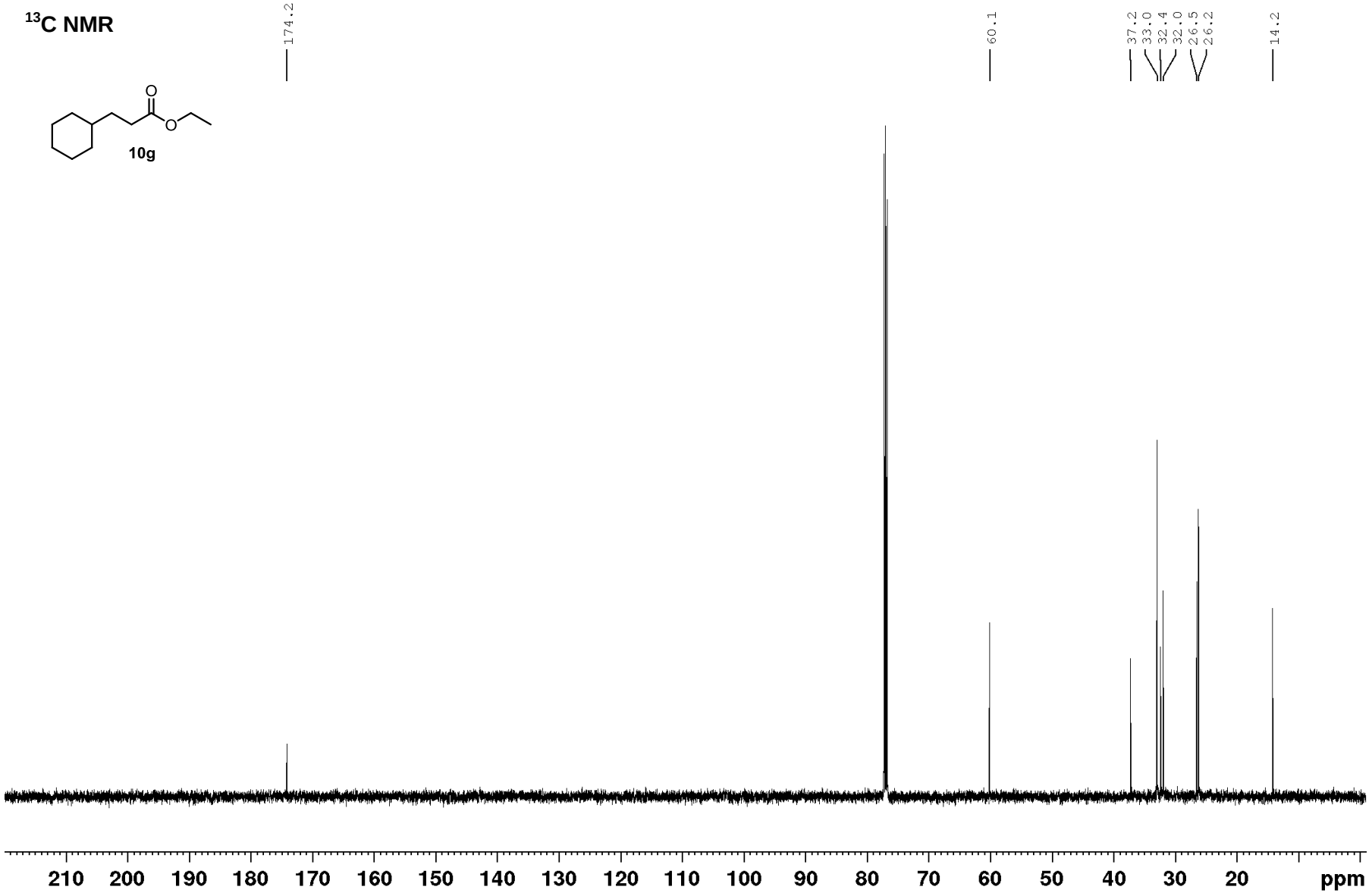
^{1}H-NMR


4.14
4.13
4.11
4.10
2.31
2.29
2.28
1.71
1.70
1.70
1.69
1.68
1.65
1.65
1.65
1.63
1.54
1.53
1.51
1.50
1.26
1.25
1.24
1.23
1.22
1.21
1.21
1.20
1.18
1.17
1.17
1.15
1.15
1.14
1.12
1.12
0.93
0.92
0.90
0.88
1.97
2.00
4.10
1.10
2.05
4.08
3.69
2.29
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

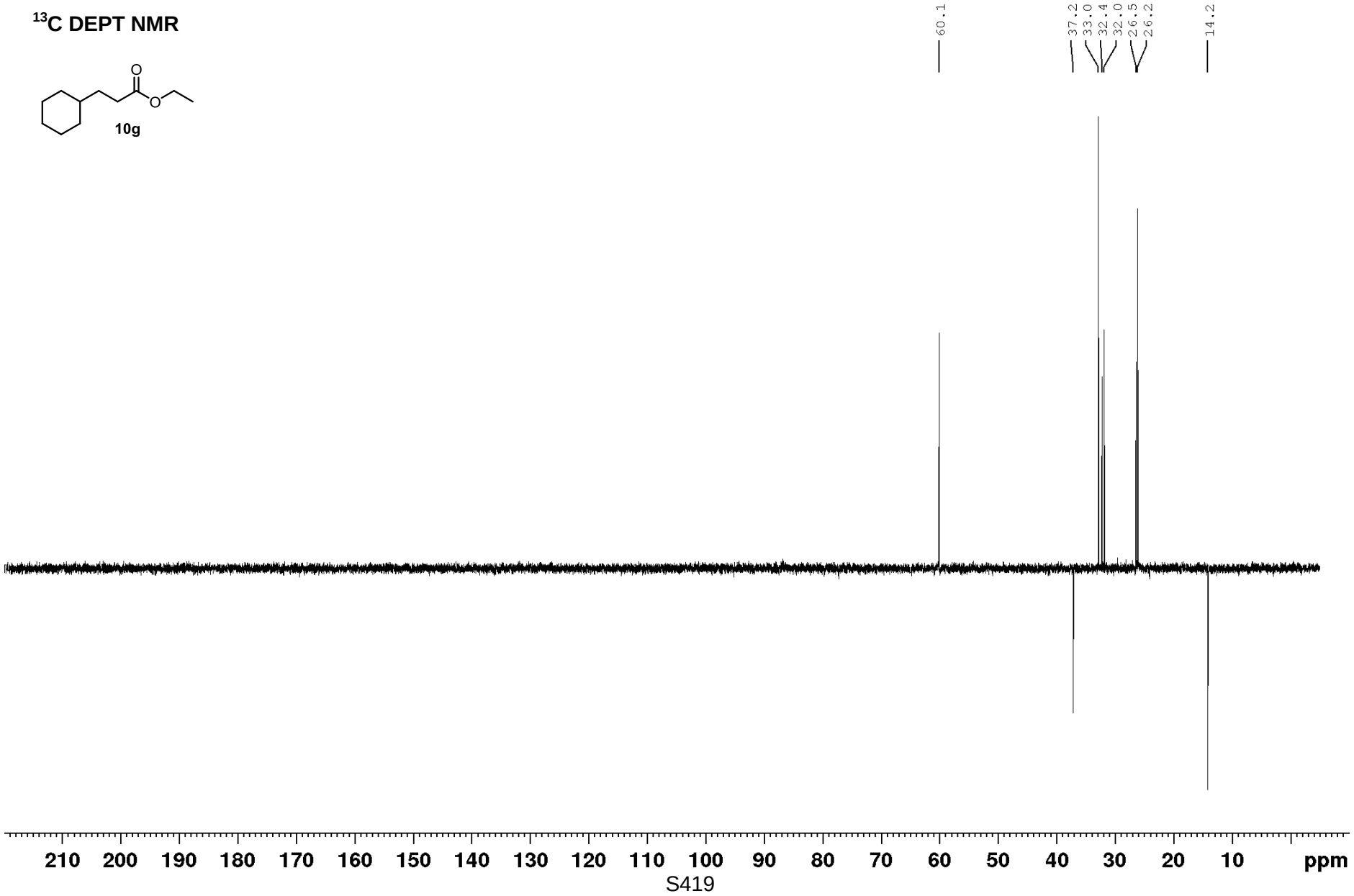
O
O

10g


174.2
60.1
37.2
33.0
32.4
32.0
26.5
26.2
14.2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

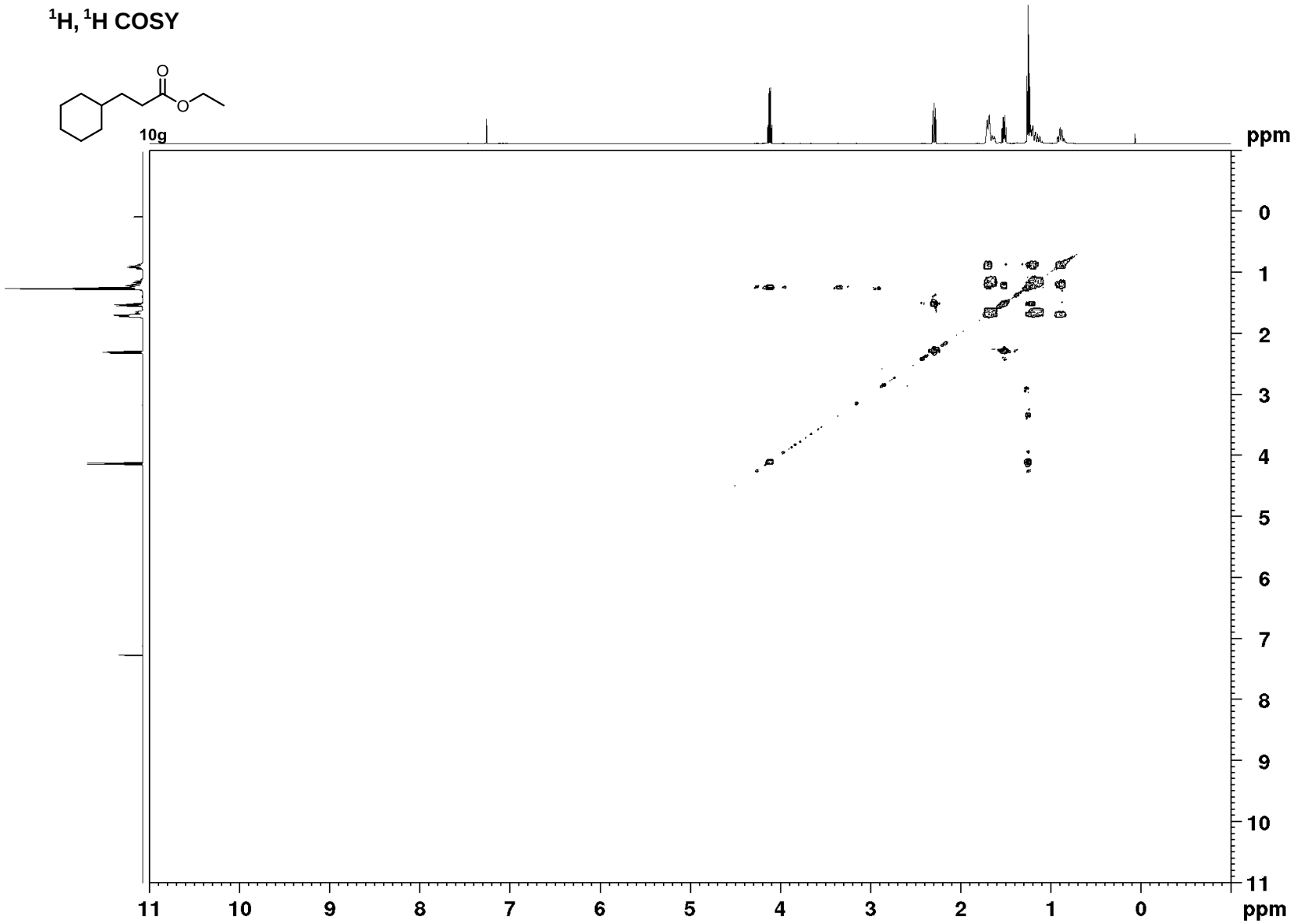
^{13}C DEPT NMR

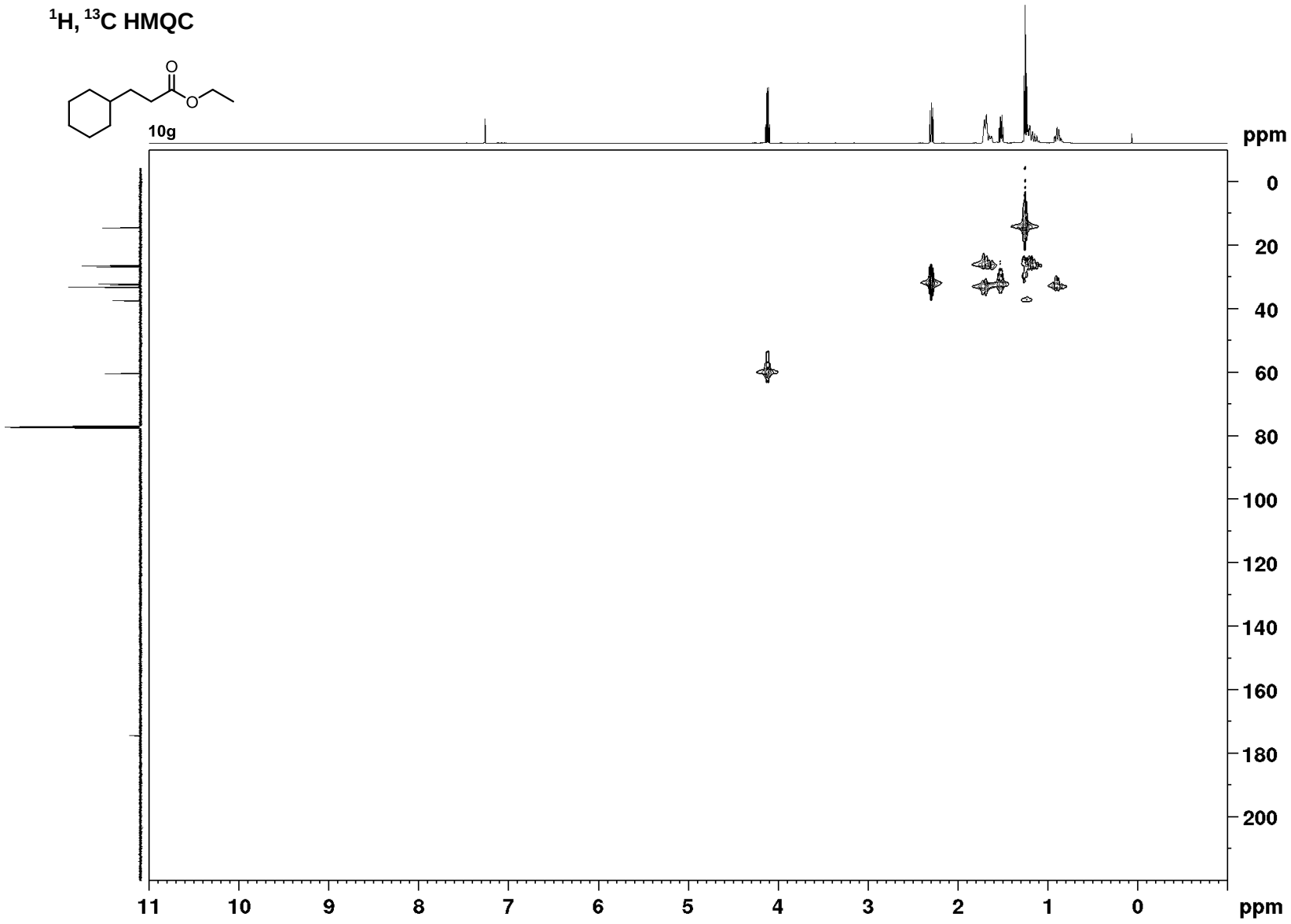
10g



^{1}H, ^{1}H COSY

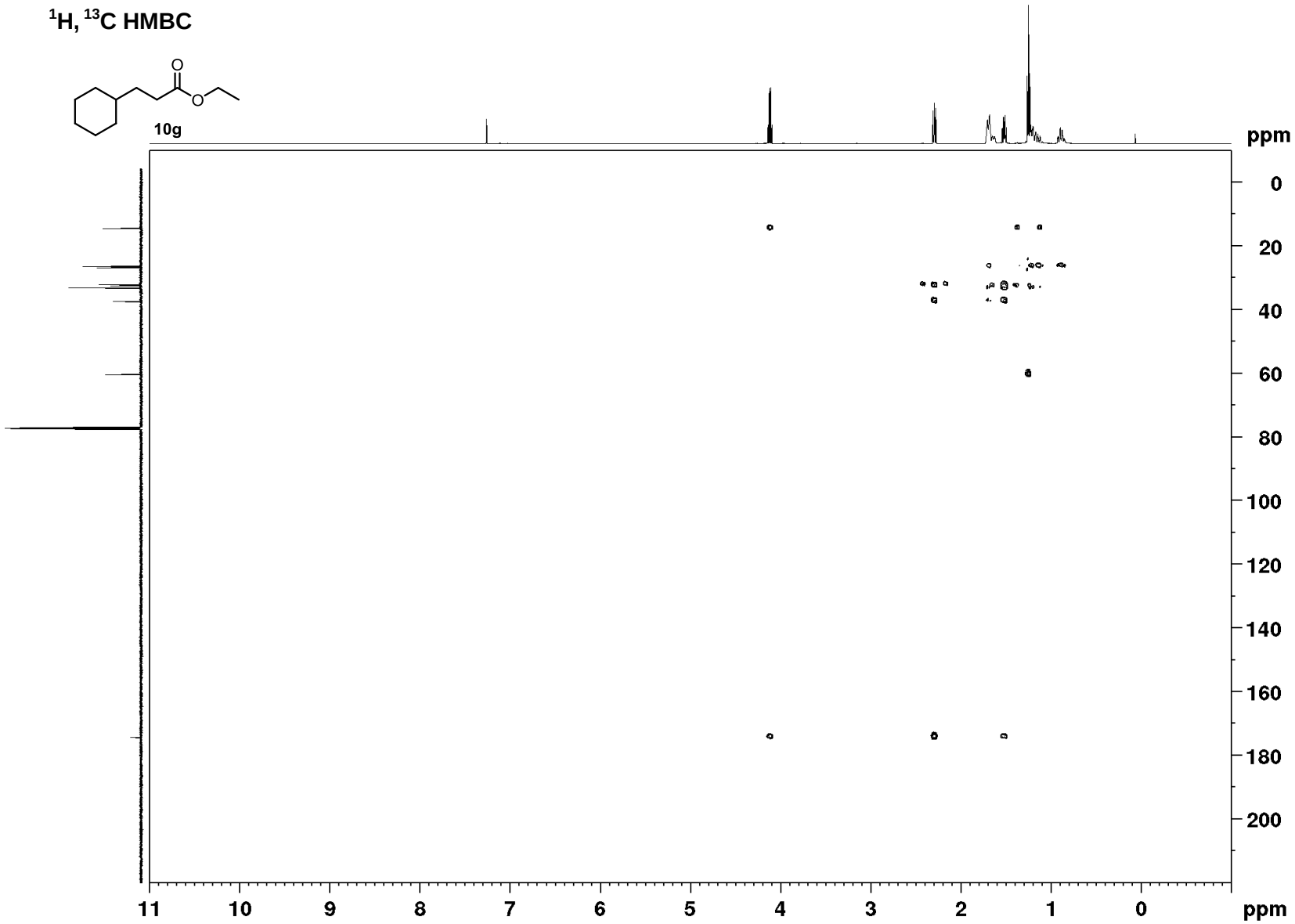
10g



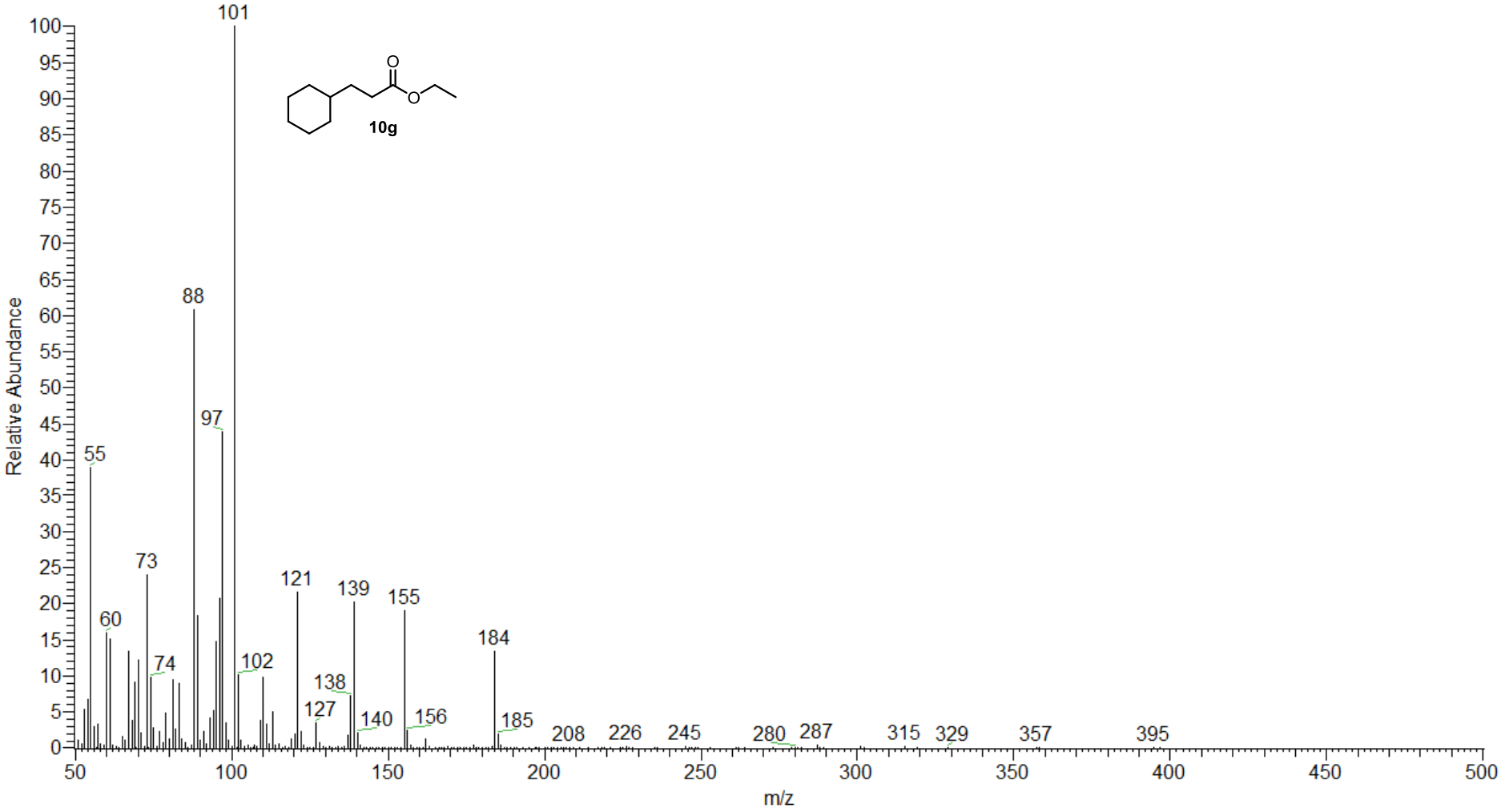

^{1}H, ^{13}C HMQC
10g
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H, ^{13}C HMBC

10g



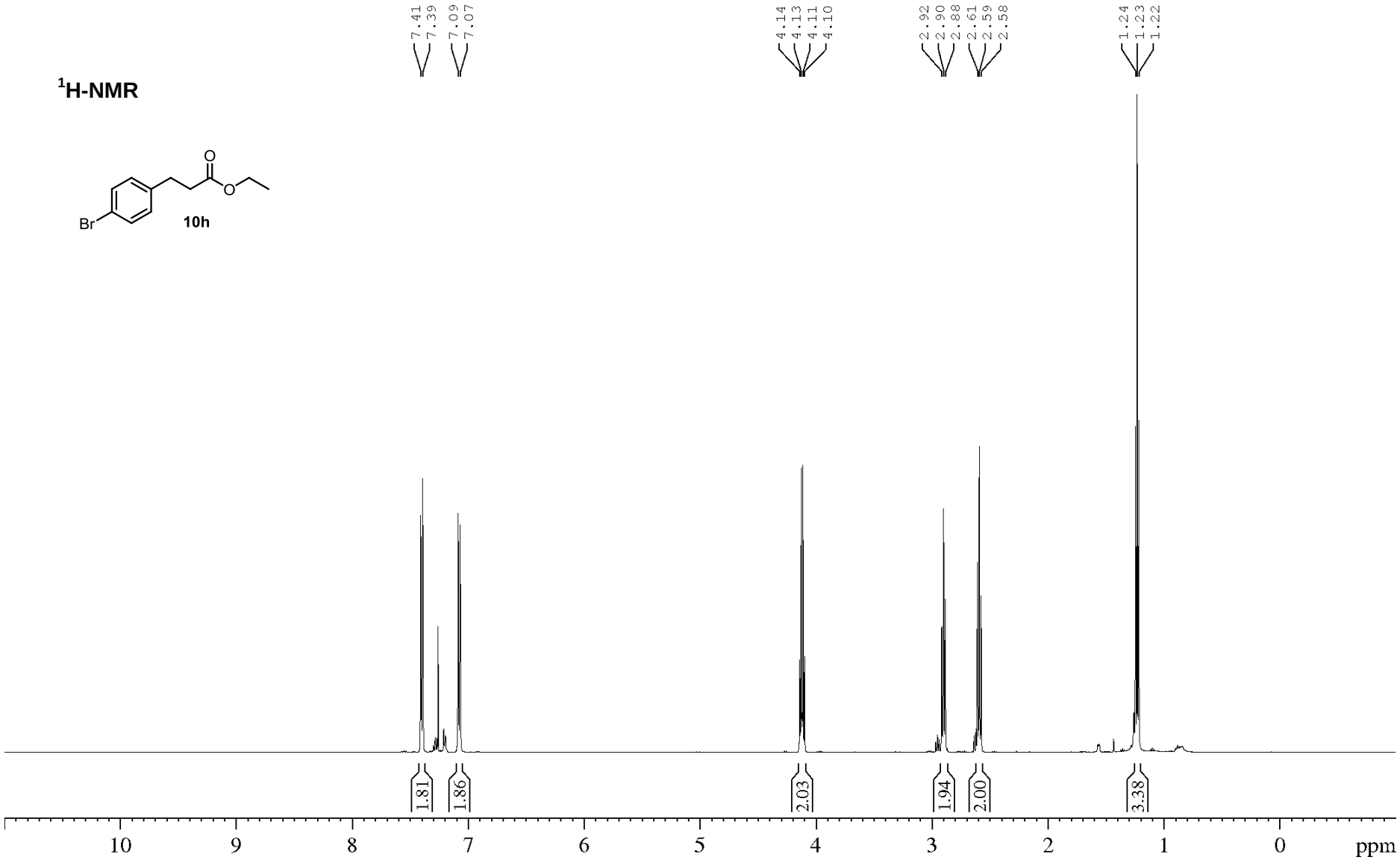
mass spectrum



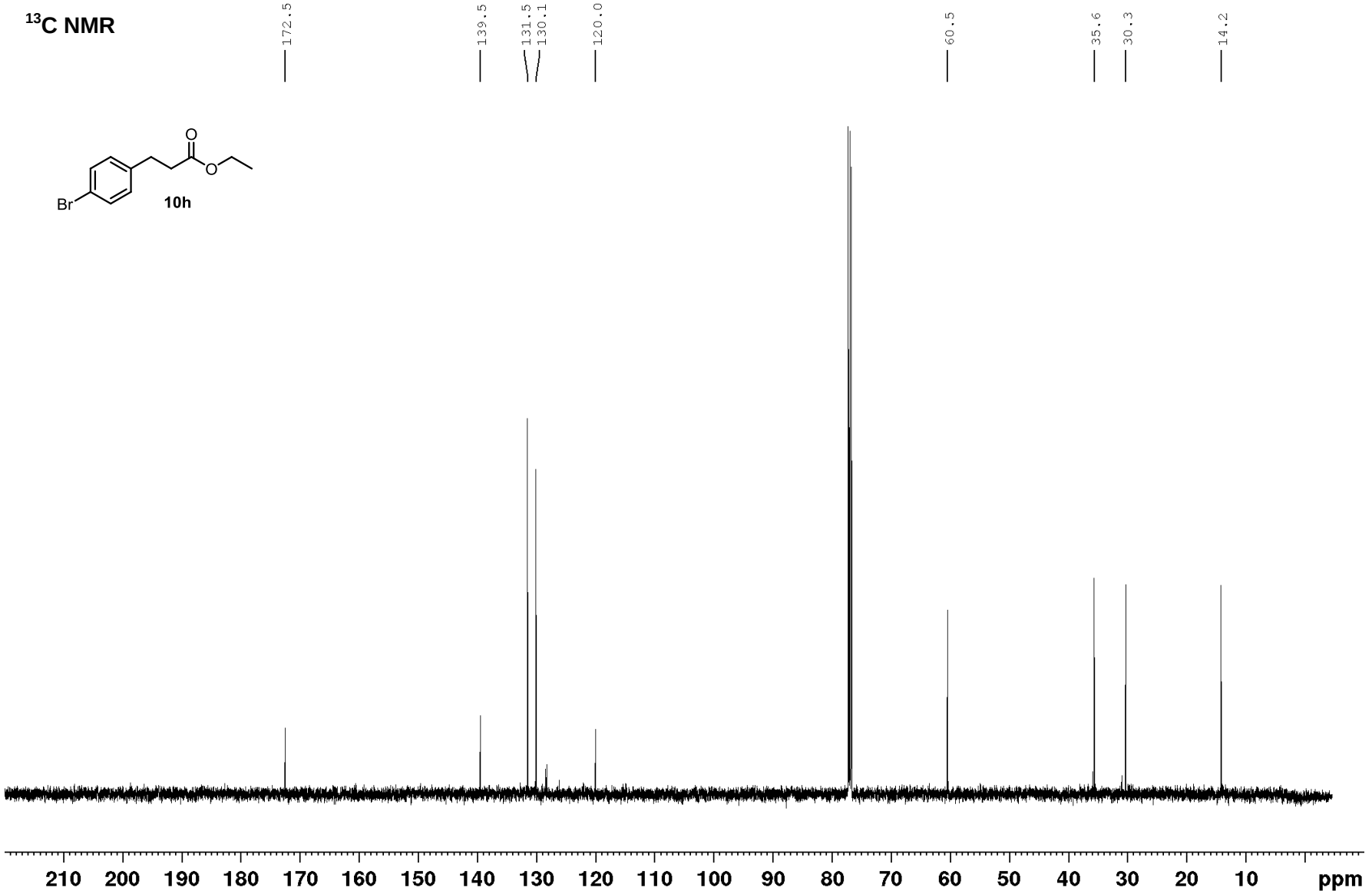
^{1}H-NMR

O
O
Br

10h

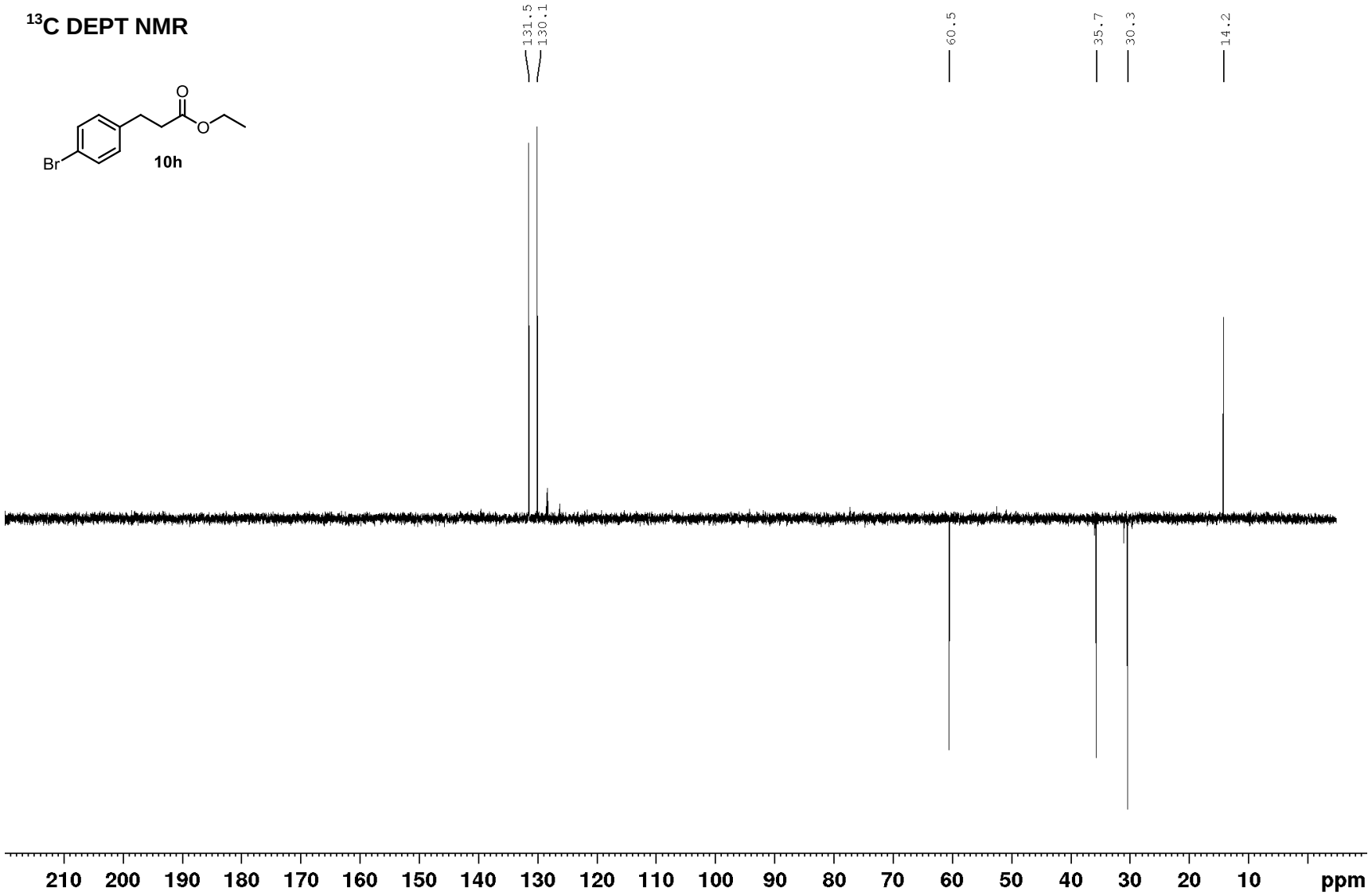

7.41
7.39
7.09
7.07
4.14
4.13
4.11
4.10
2.92
2.90
2.88
2.61
2.59
2.58
1.24
1.23
1.22
1.81
1.86
2.03
1.94
2.00
3.38
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR


172.5
139.5
131.5
130.1
120.0
60.5
35.6
30.3
14.2
O
O
Br
10h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

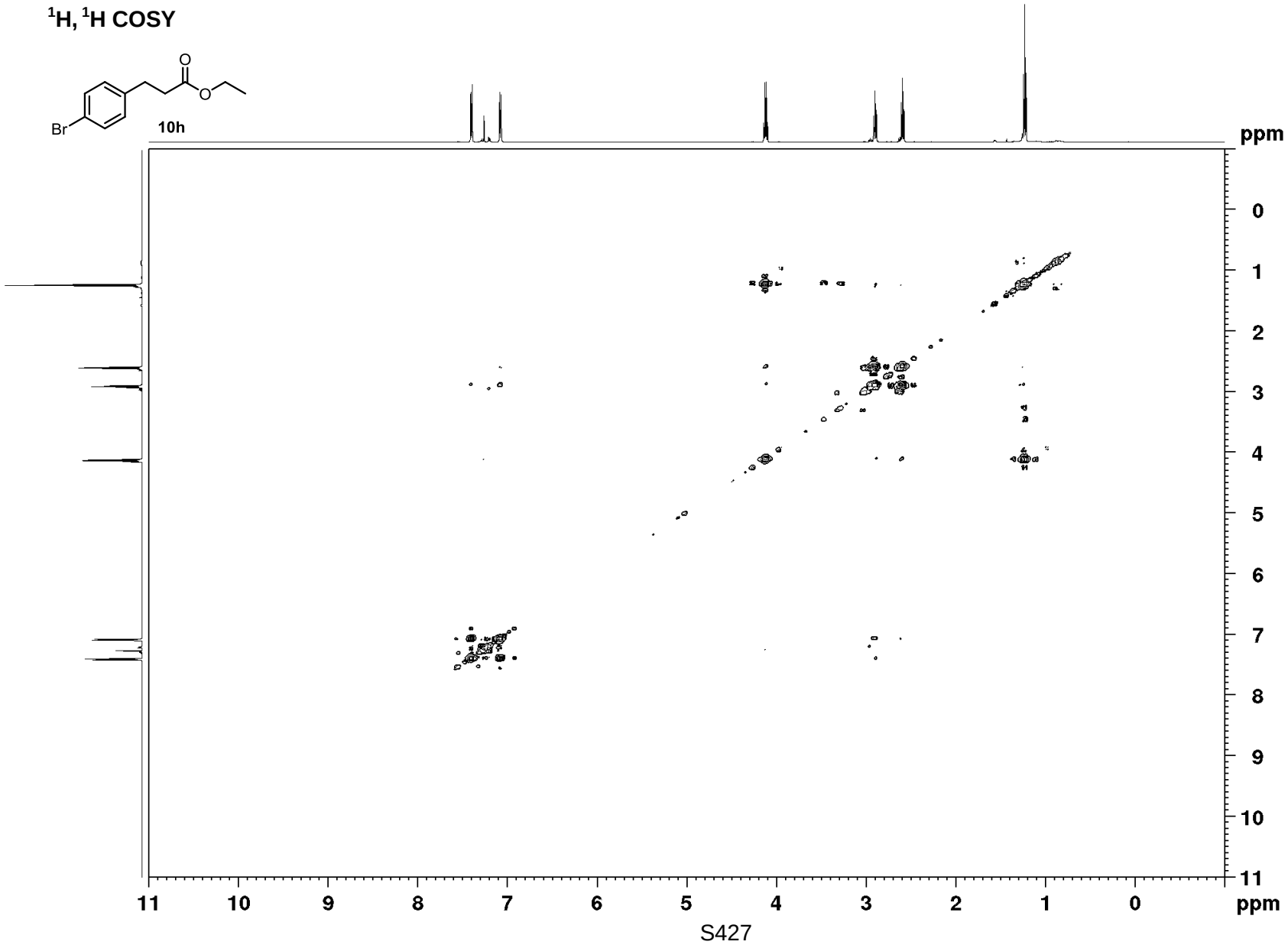
^{13}C DEPT NMR

10h



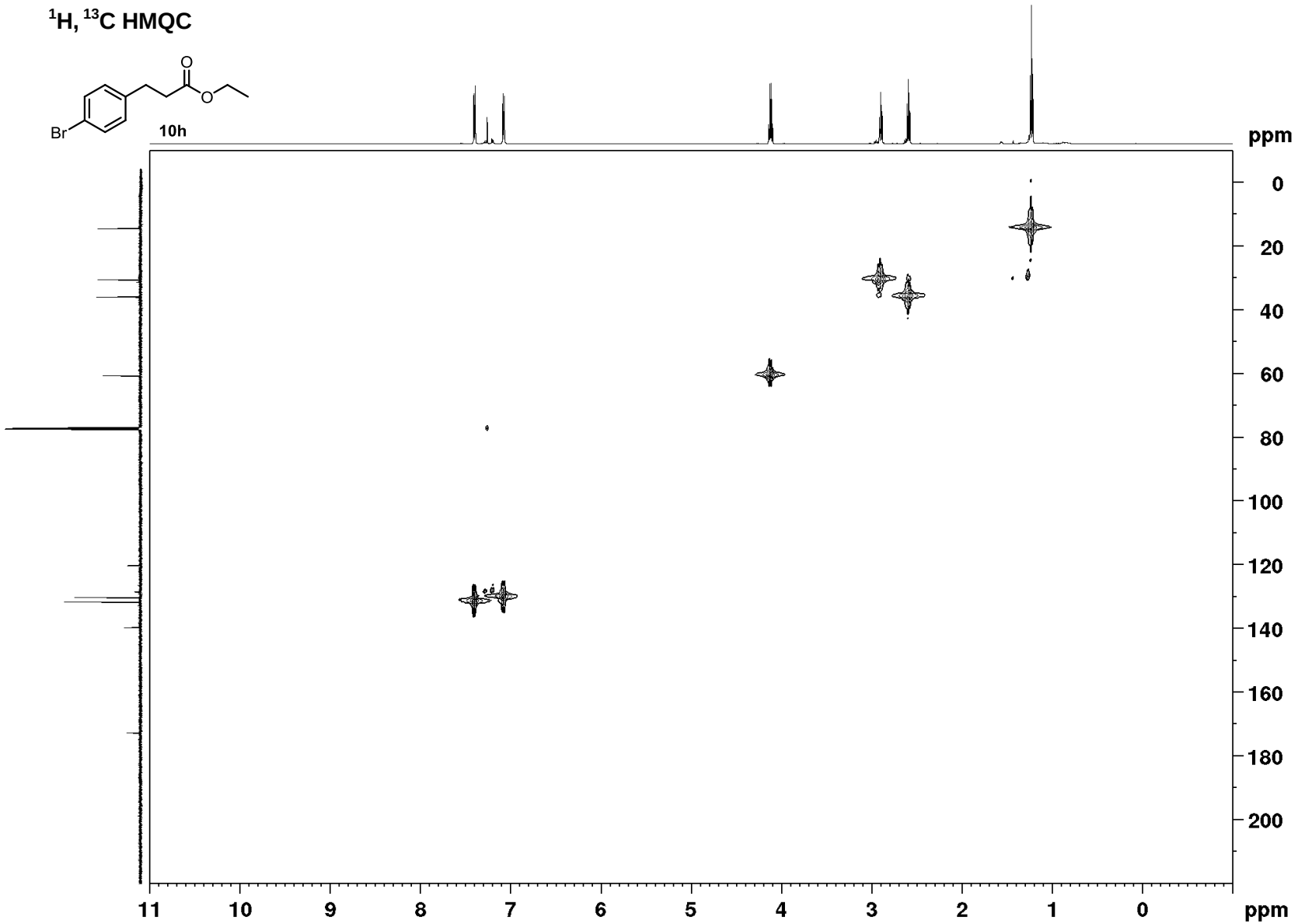
^{1}H, ^{1}H COSY

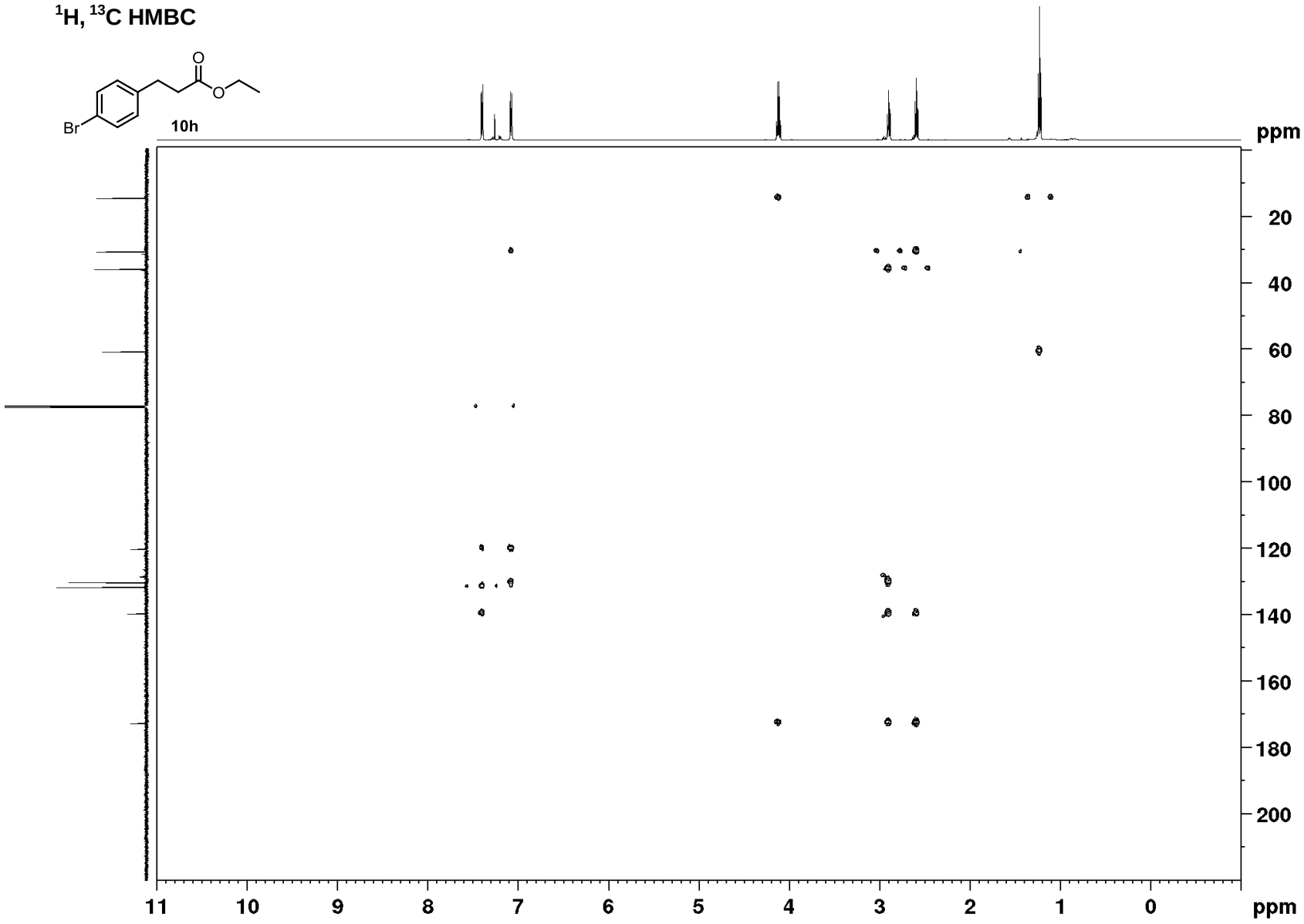
10h



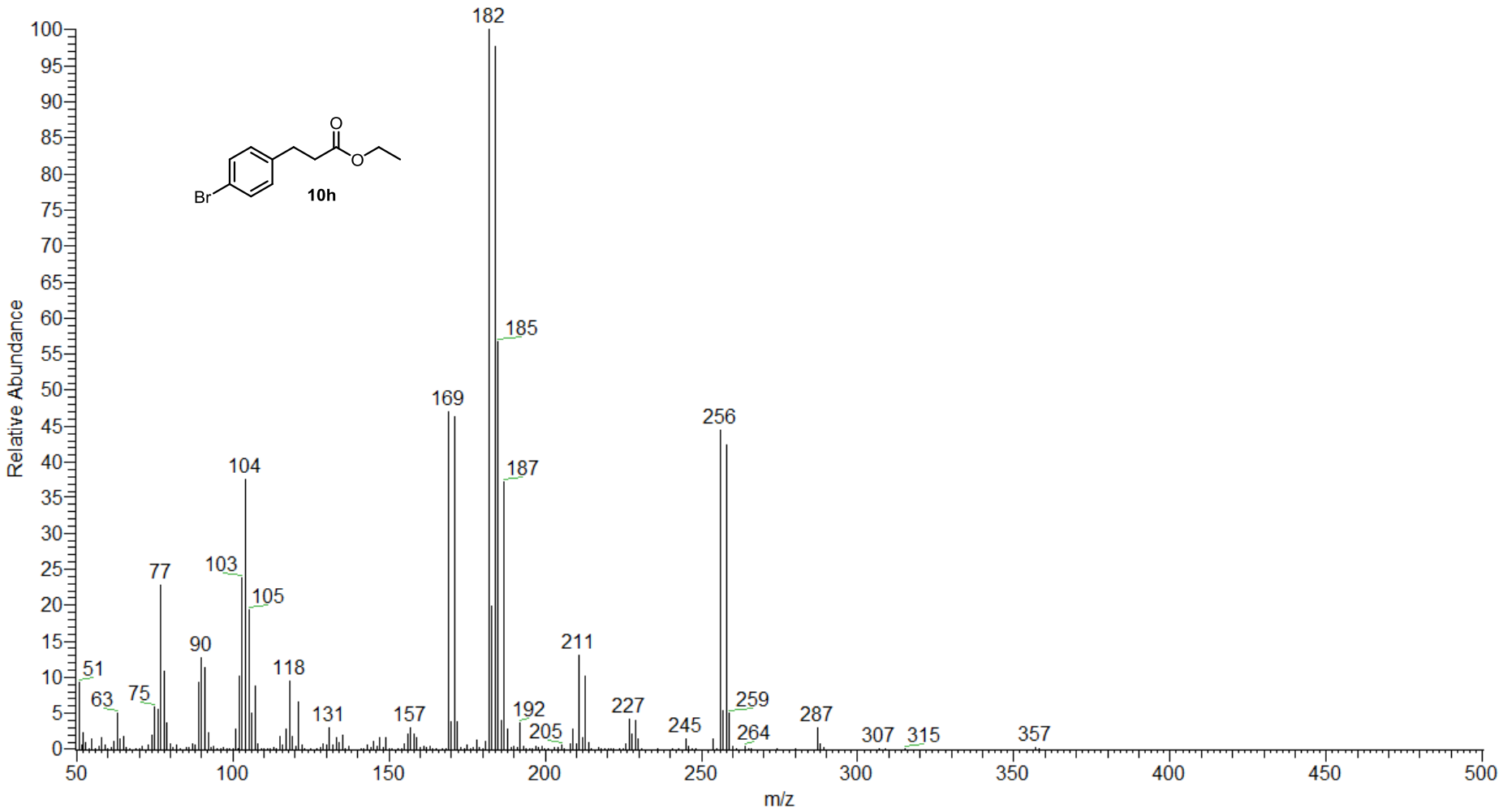
^{1}H, ^{13}C HMQC

10h




^{1}H, ^{13}C HMBC
10h
Br
O
O
ppm
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm

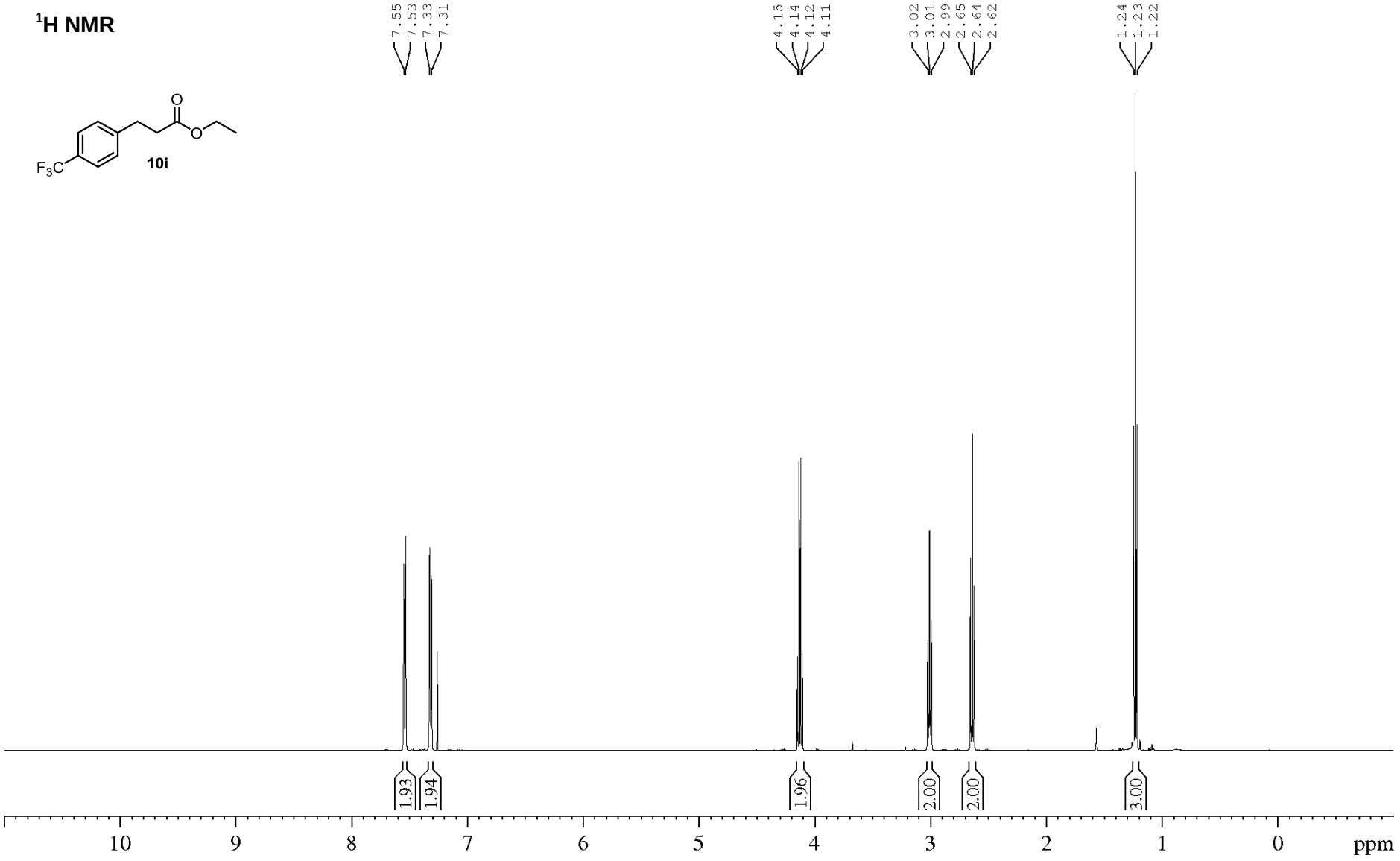
mass spectrum



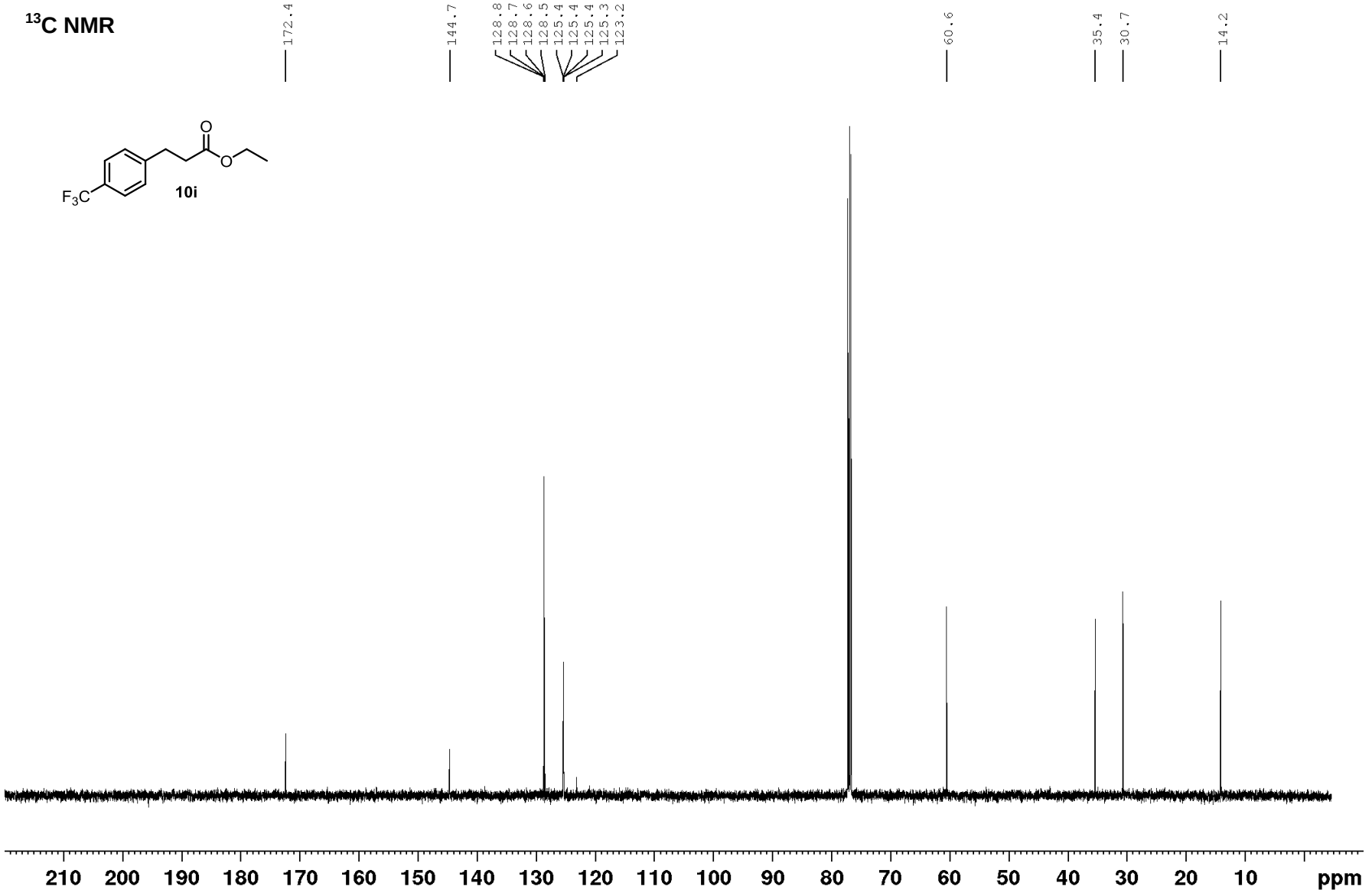
^{1}H NMR

O
O
F3C

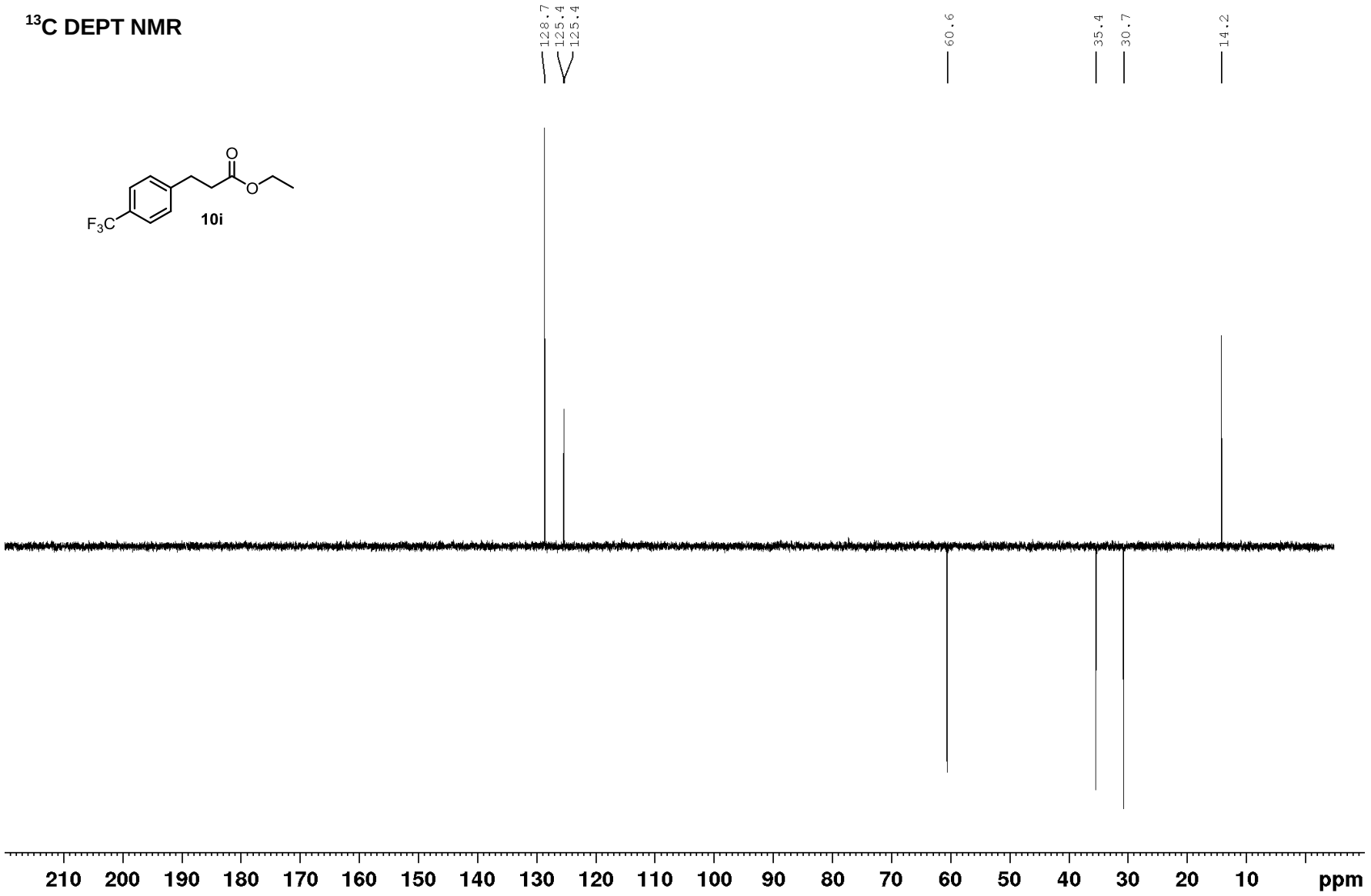
10i


7.55
7.53
7.33
7.31
4.15
4.14
4.12
4.11
3.02
3.01
2.99
2.65
2.64
2.62
1.24
1.23
1.22
1.93
1.94
1.96
2.00
2.00
3.00
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR

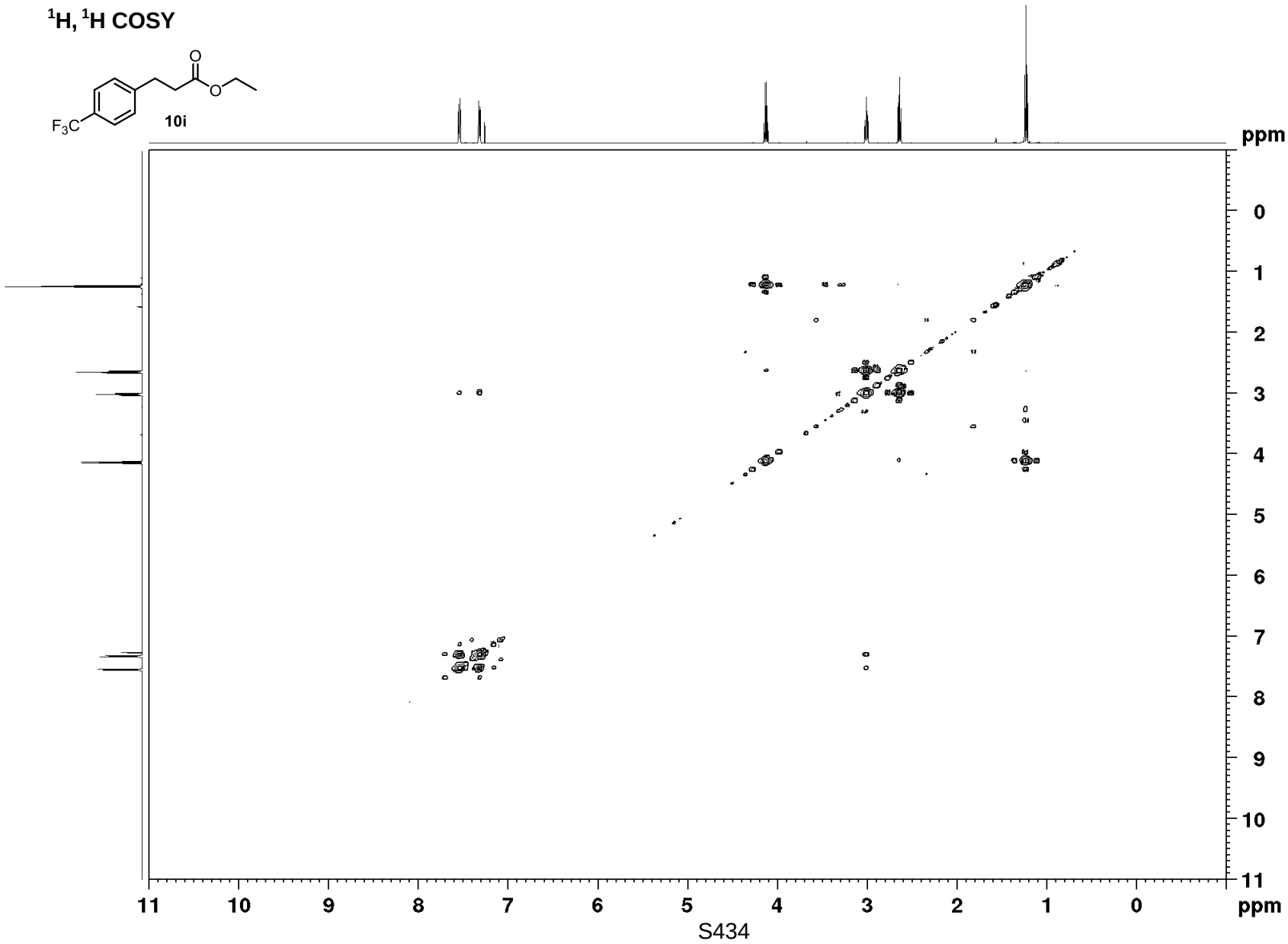

172.4
144.7
128.8
128.7
128.6
128.5
125.4
125.4
125.4
125.3
123.2
60.6
35.4
30.7
14.2
O
O
F3C
10i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR


128.7
125.4
125.4
60.6
35.4
30.7
14.2
O
O
F3C
10i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

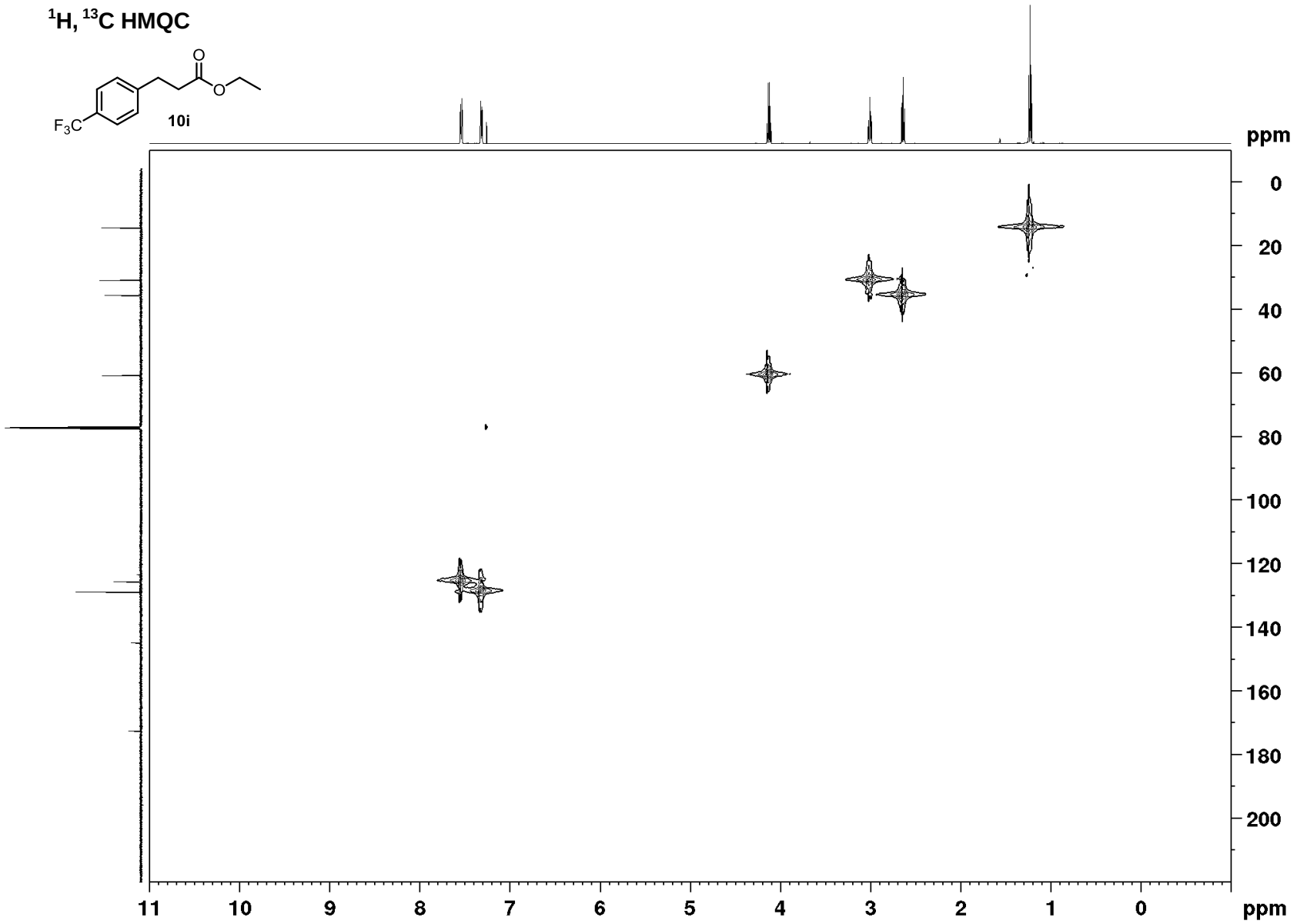
^{1}H, ^{1}H COSY

10i



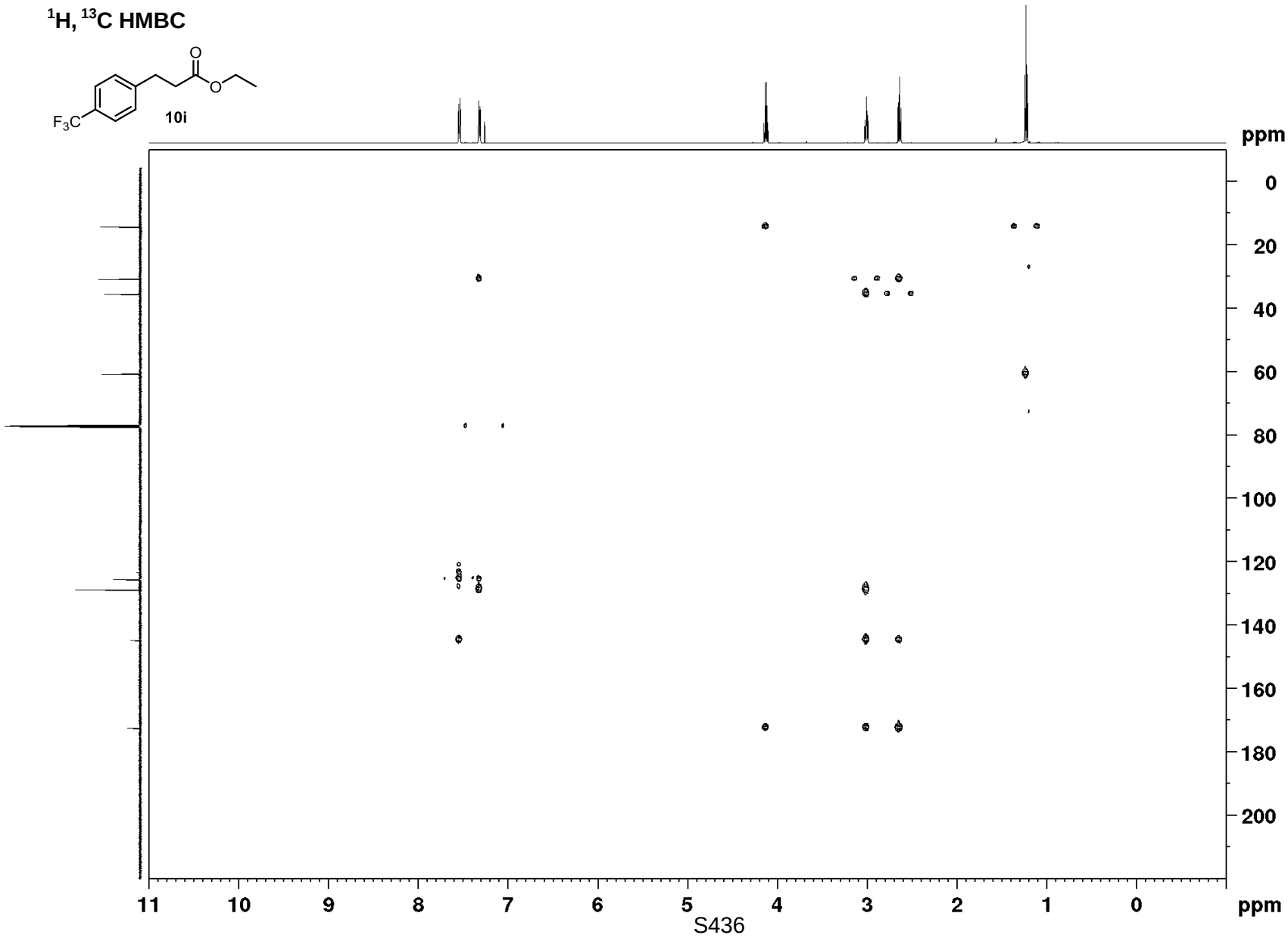
^{1}H, ^{13}C HMQC

10i

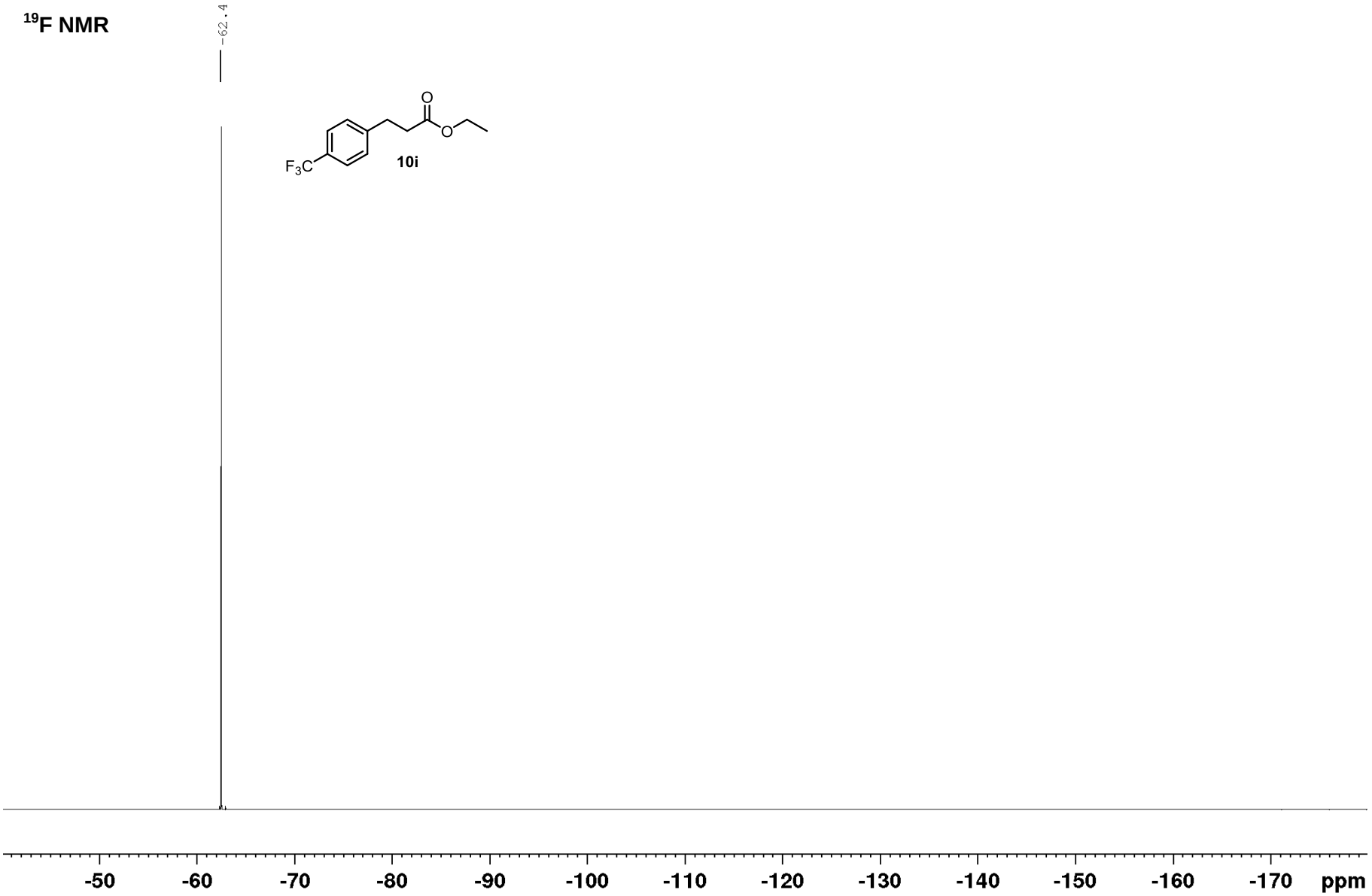


^{1}H, ^{13}C HMBC

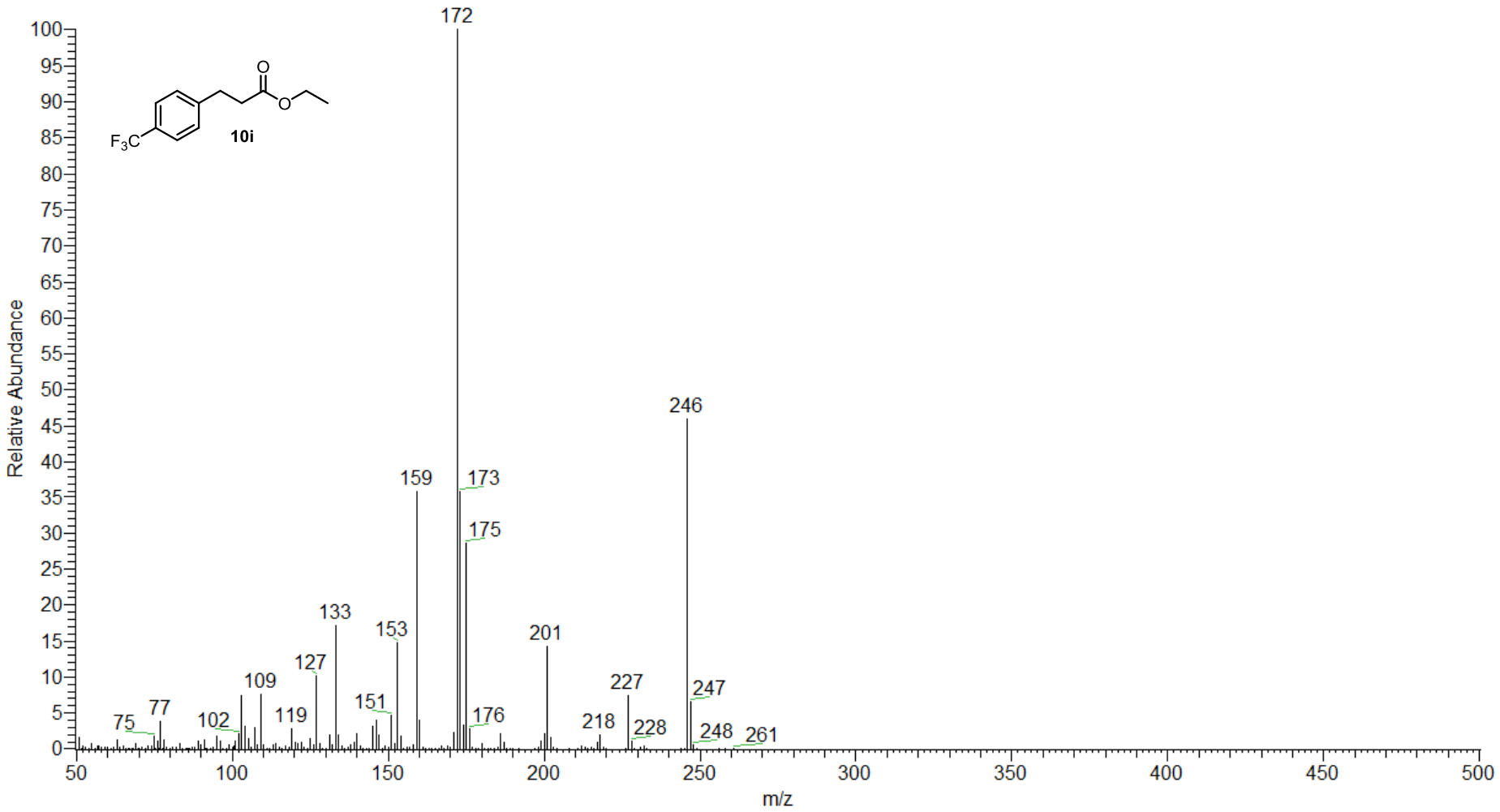
10i



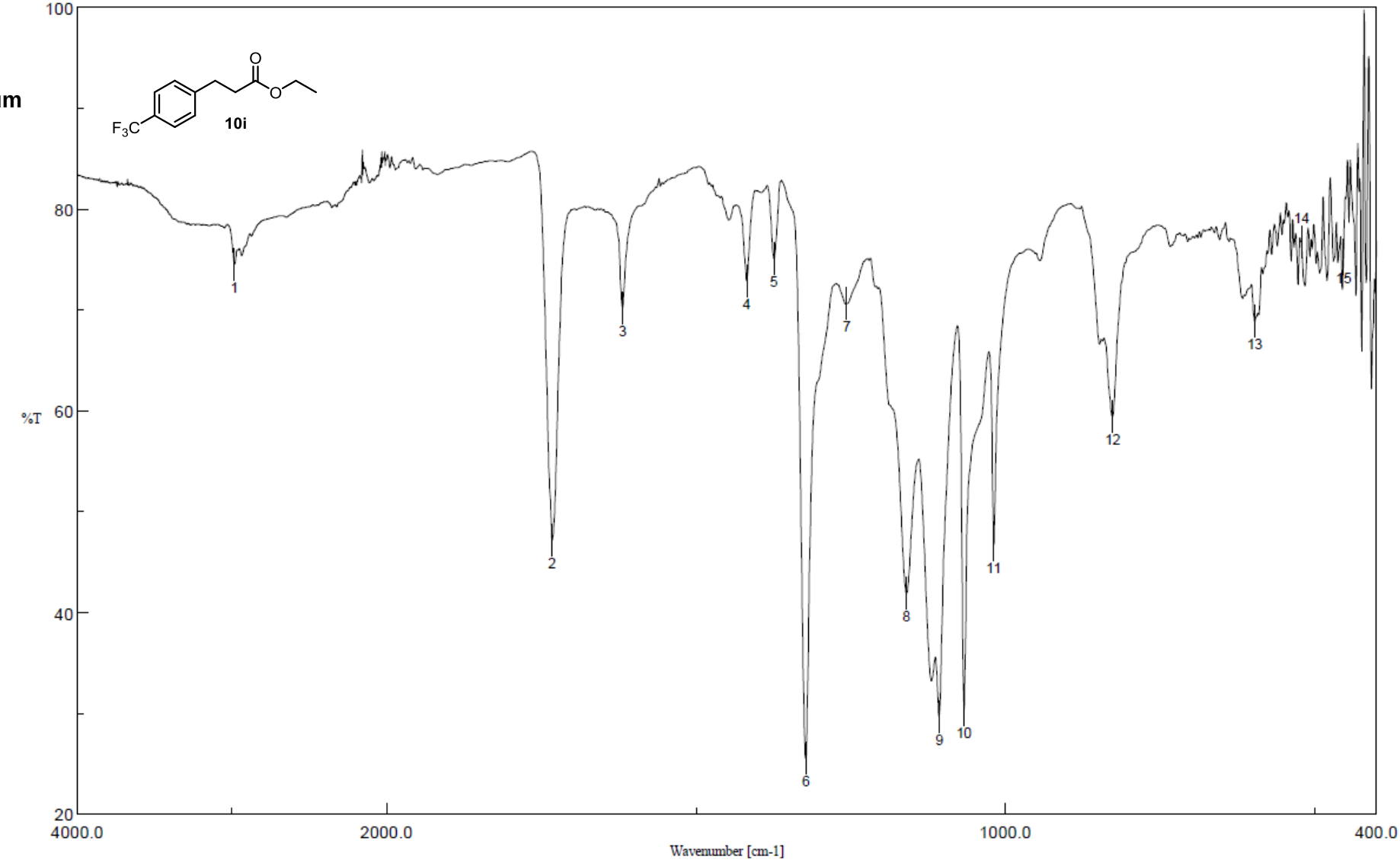
^{19}F NMR



mass spectrum

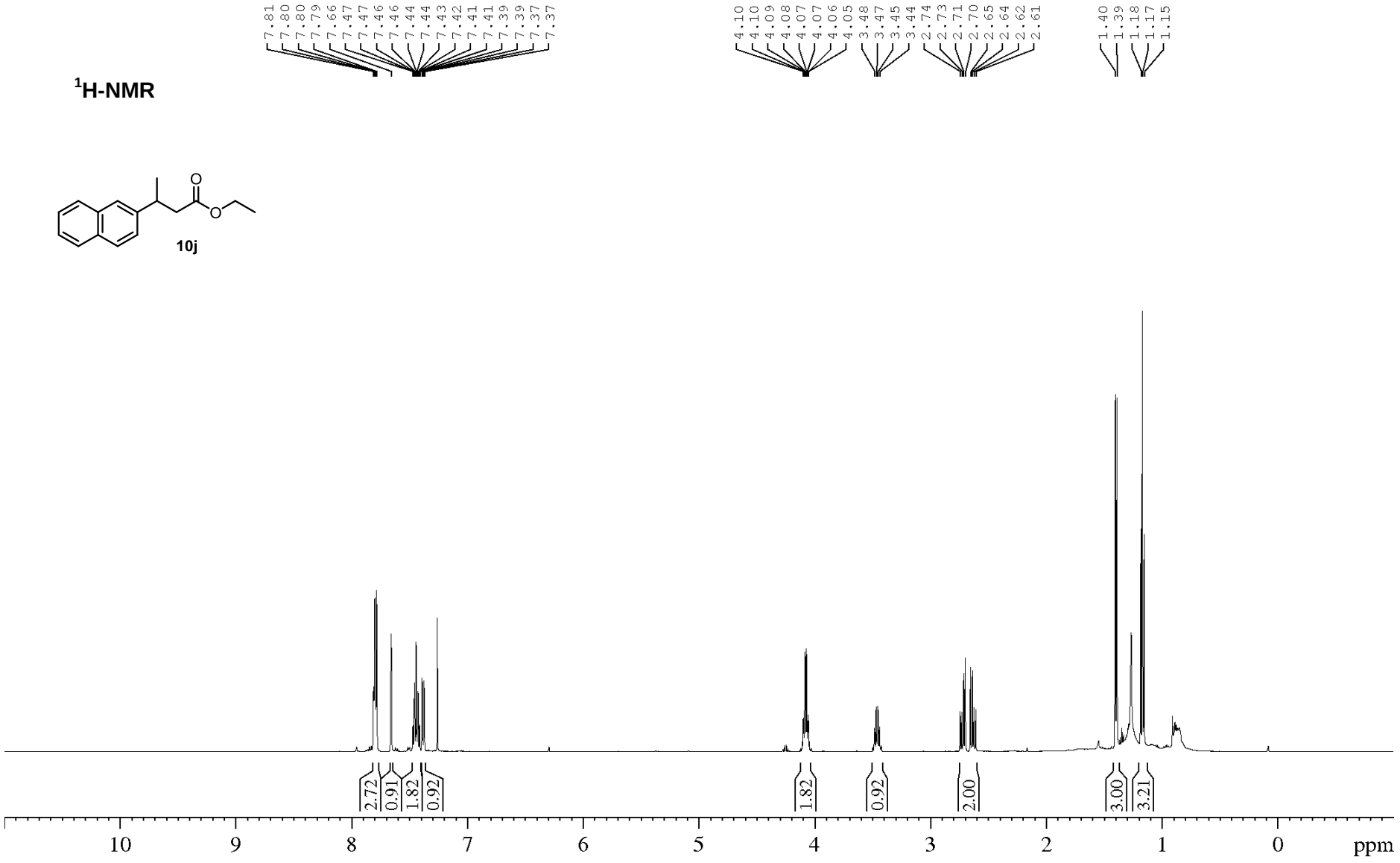


IR spectrum


10i
F3C
O
O
100
80
60
40
20
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

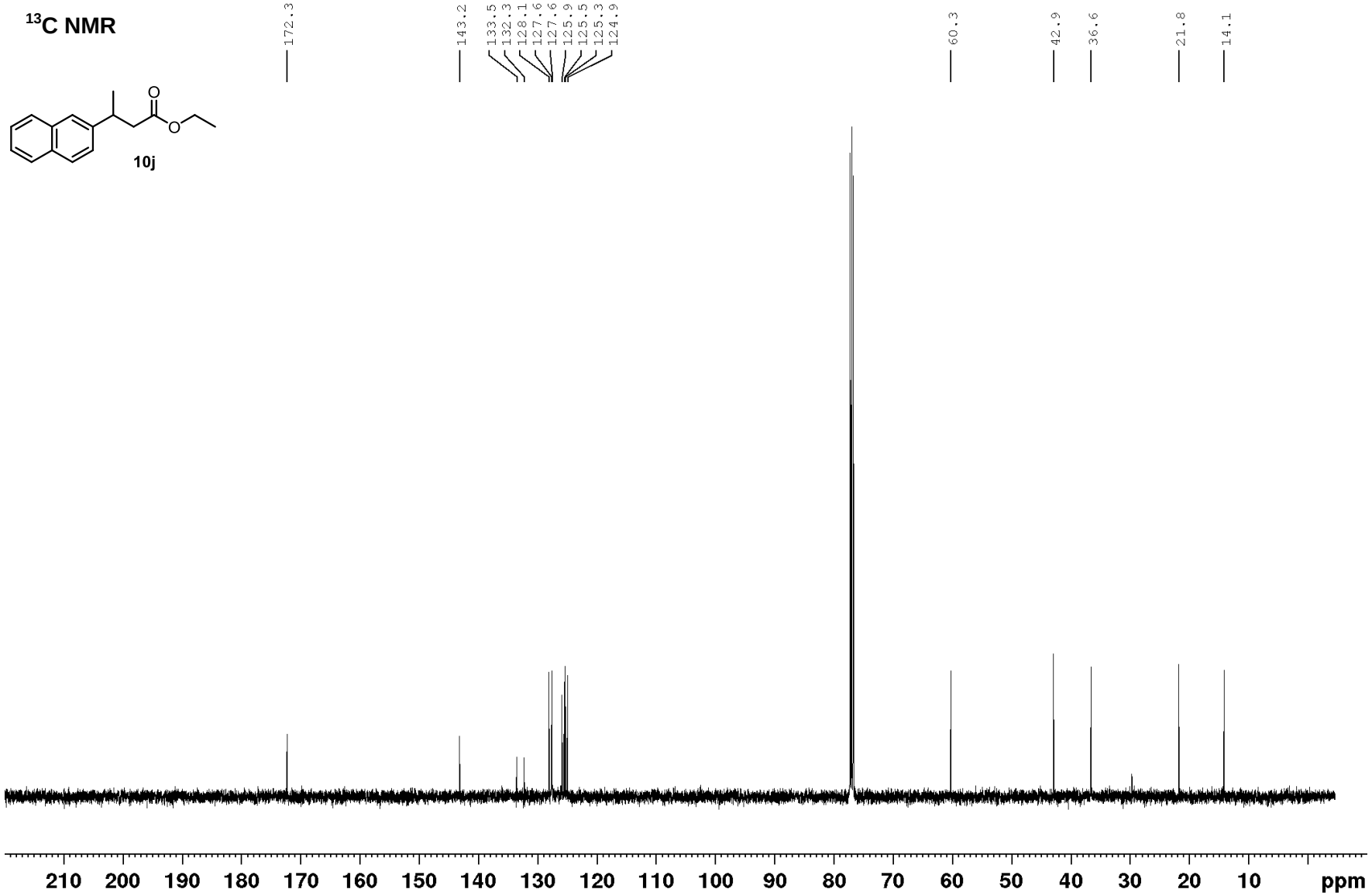
^{1}H-NMR

10j


7.81
7.80
7.80
7.79
7.66
7.47
7.47
7.46
7.46
7.44
7.44
7.43
7.42
7.41
7.41
7.39
7.37
7.37
4.10
4.10
4.09
4.08
4.07
4.07
4.06
4.05
3.48
3.47
3.45
3.44
2.74
2.73
2.71
2.70
2.65
2.64
2.62
2.61
1.40
1.39
1.18
1.17
1.15
2.72
0.91
1.82
0.92
1.82
0.92
2.00
3.00
3.21
10
9
8
7
6
5
4
3
2
1
0
ppm

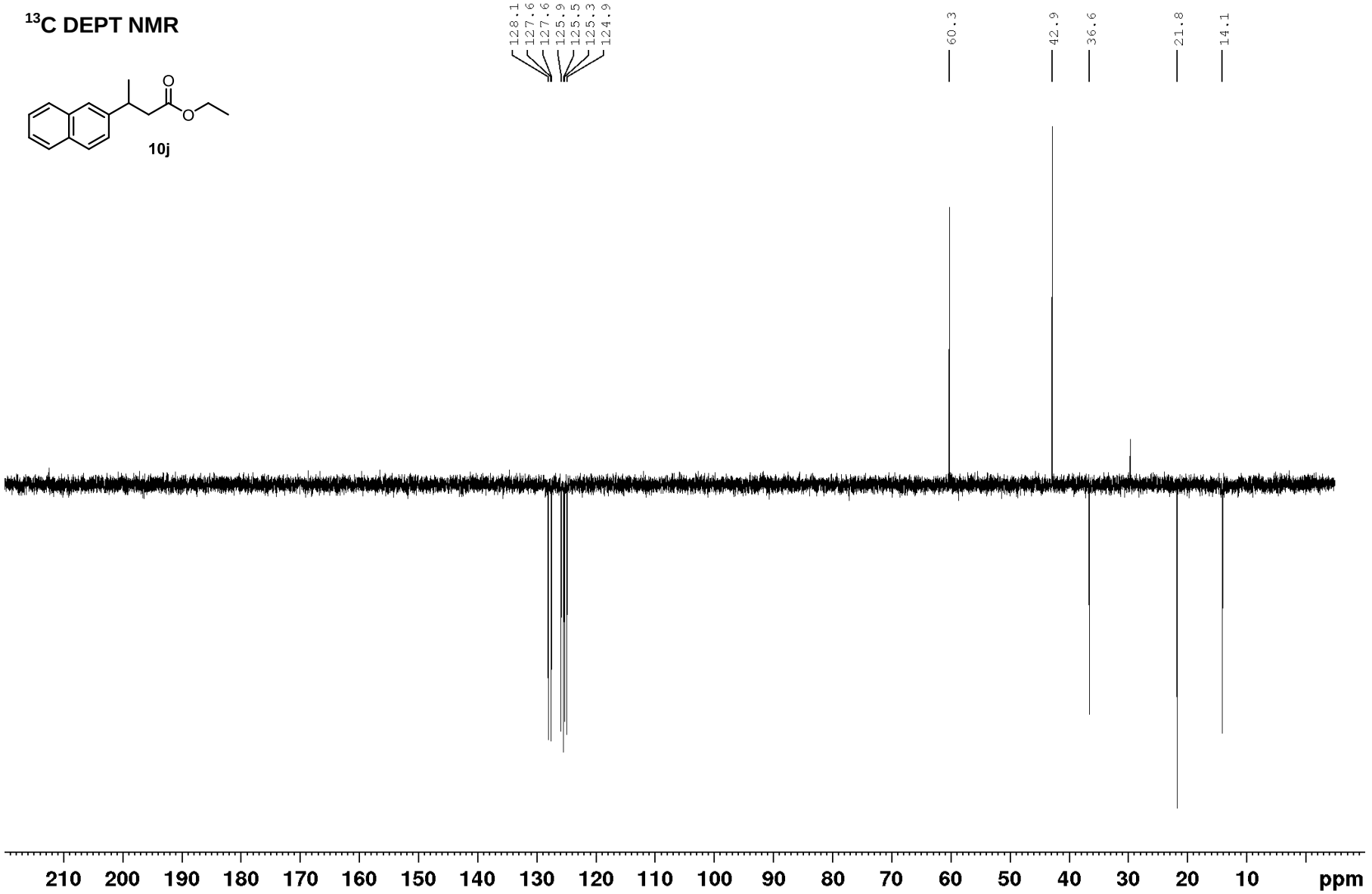
^{13}C NMR

10j


172.3
143.2
133.5
132.3
128.1
127.6
127.6
125.9
125.5
125.3
124.9
60.3
42.9
36.6
21.8
14.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

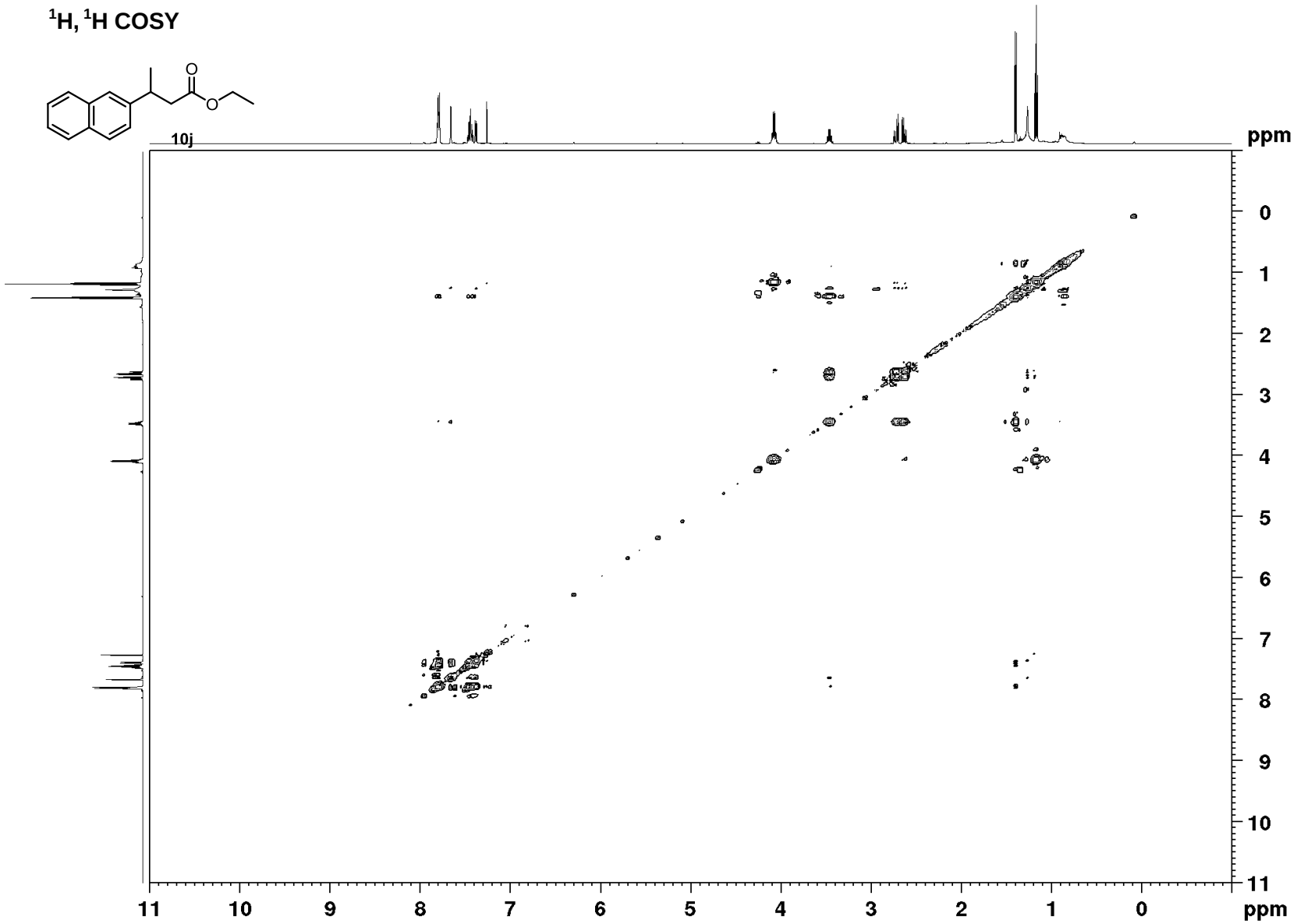
^{13}C DEPT NMR

10j



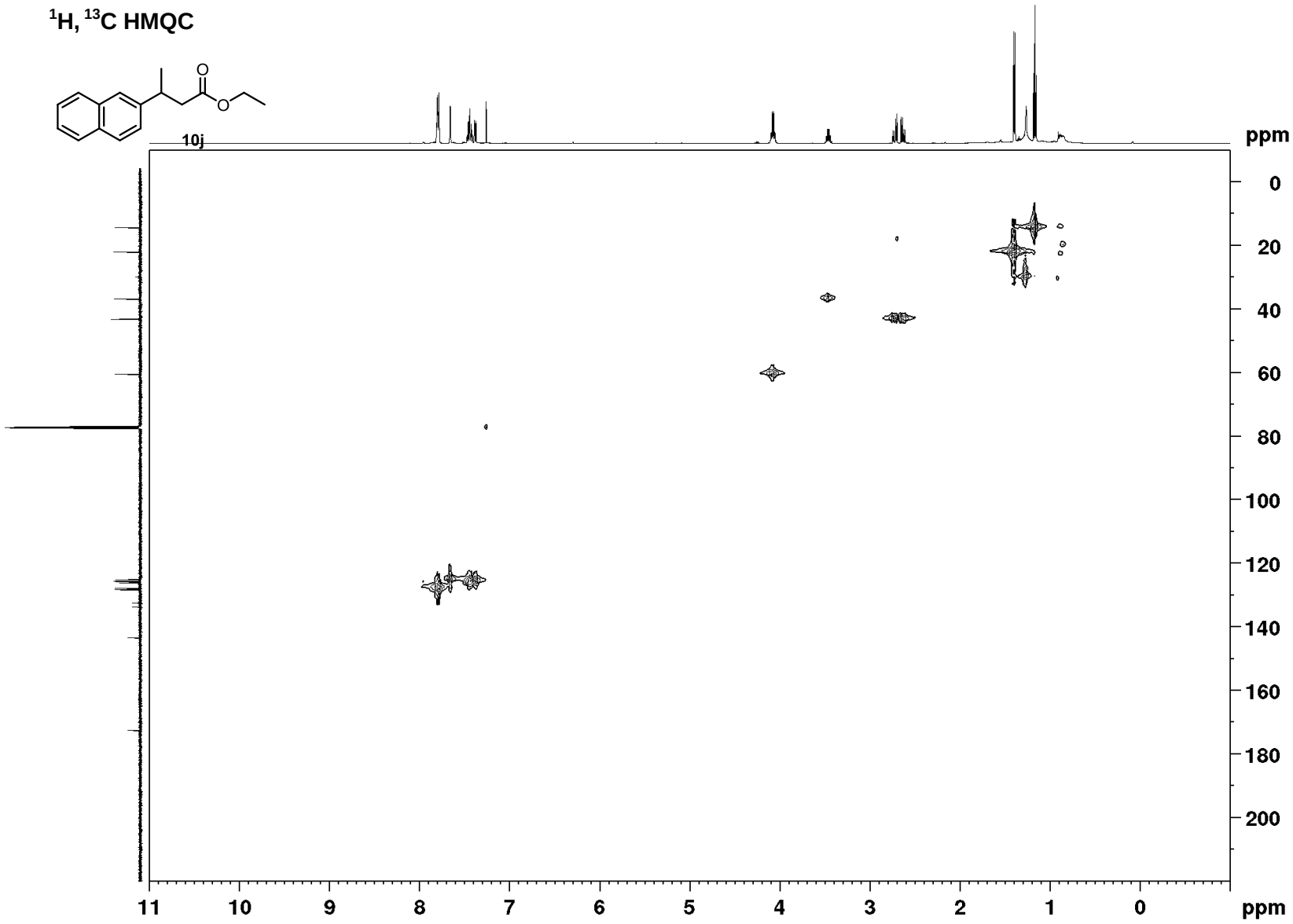
^{1}H, ^{1}H COSY

10j



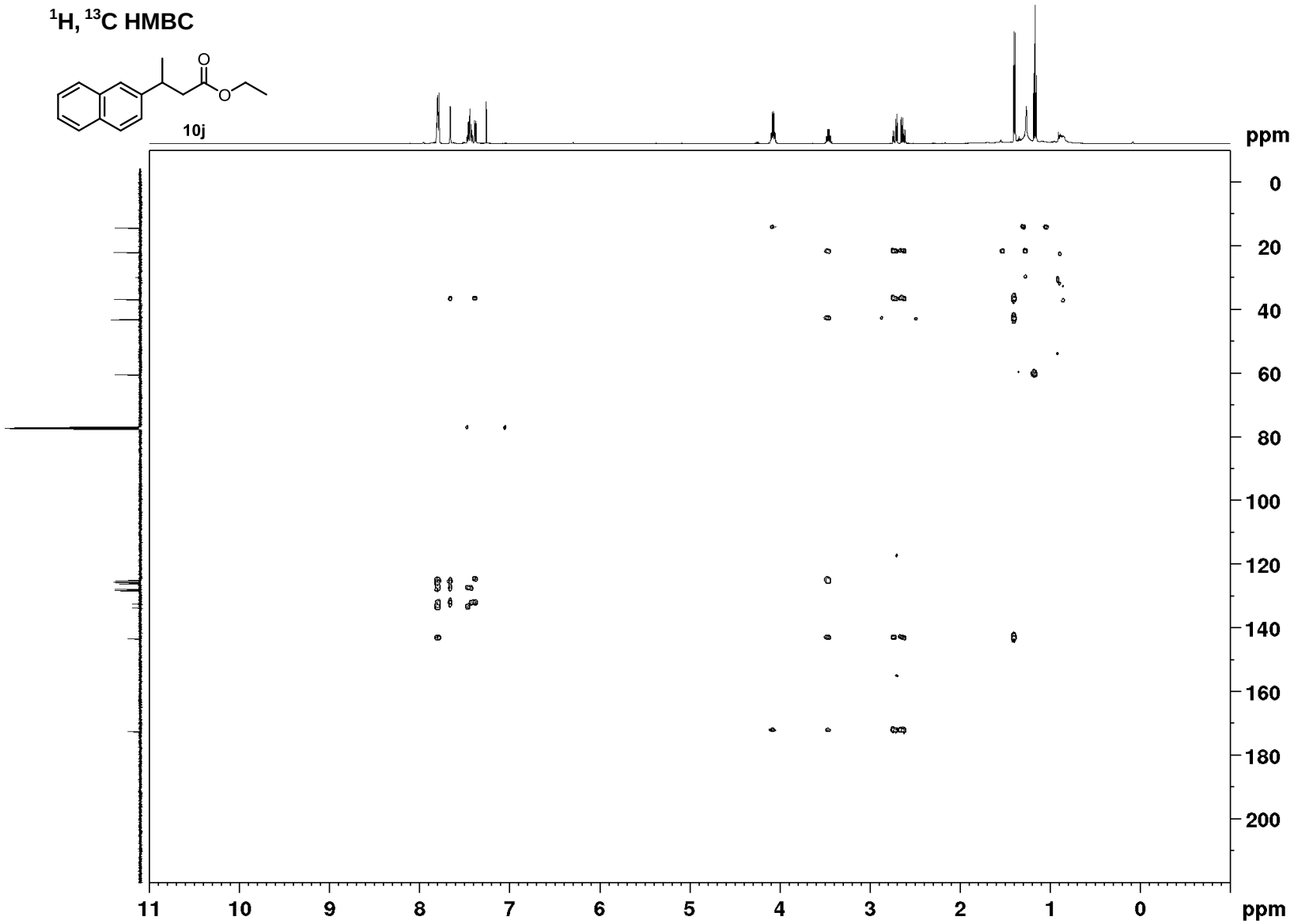
^{1}H, ^{13}C HMQC

10j

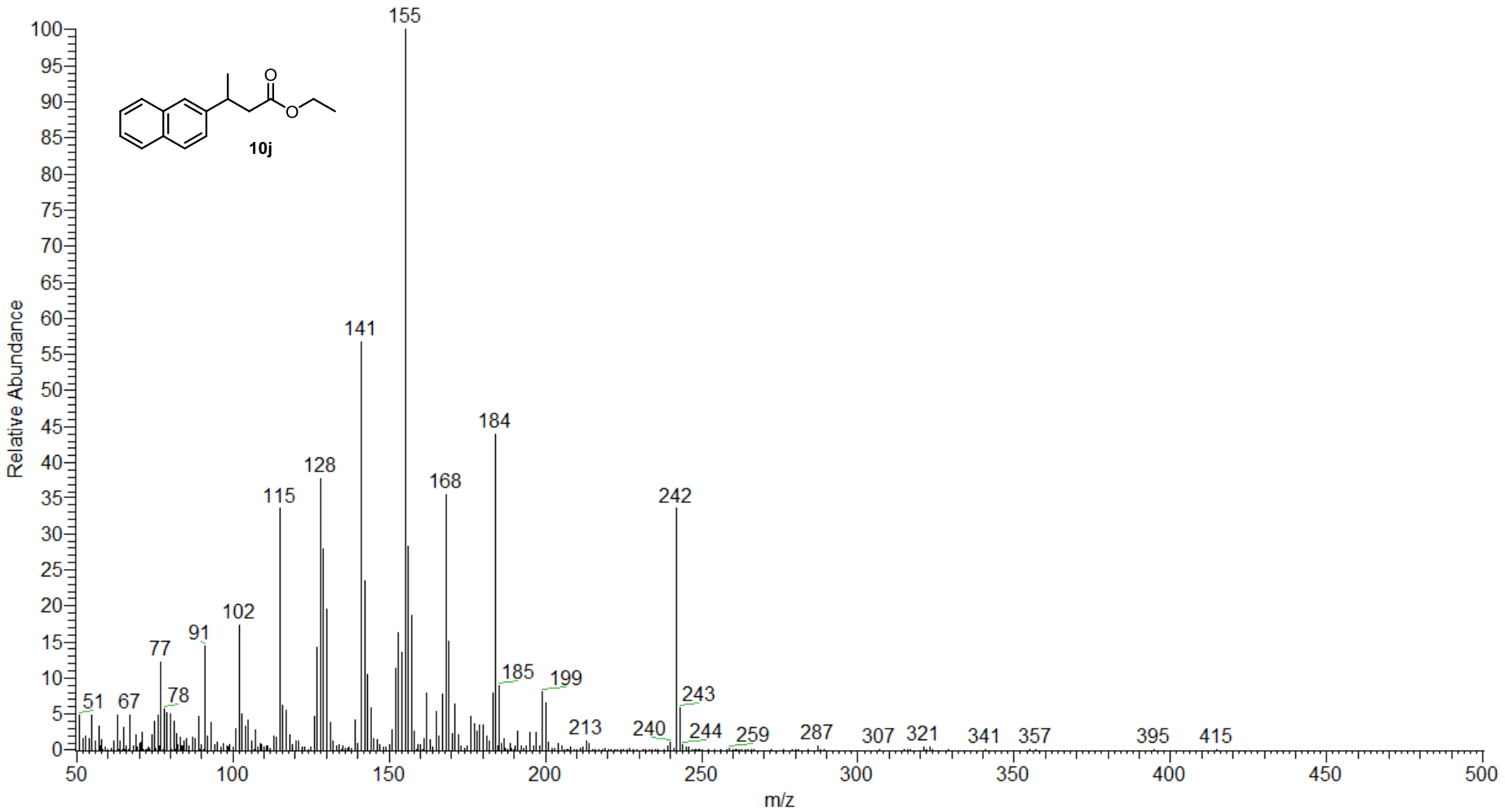


^{1}H, ^{13}C HMBC

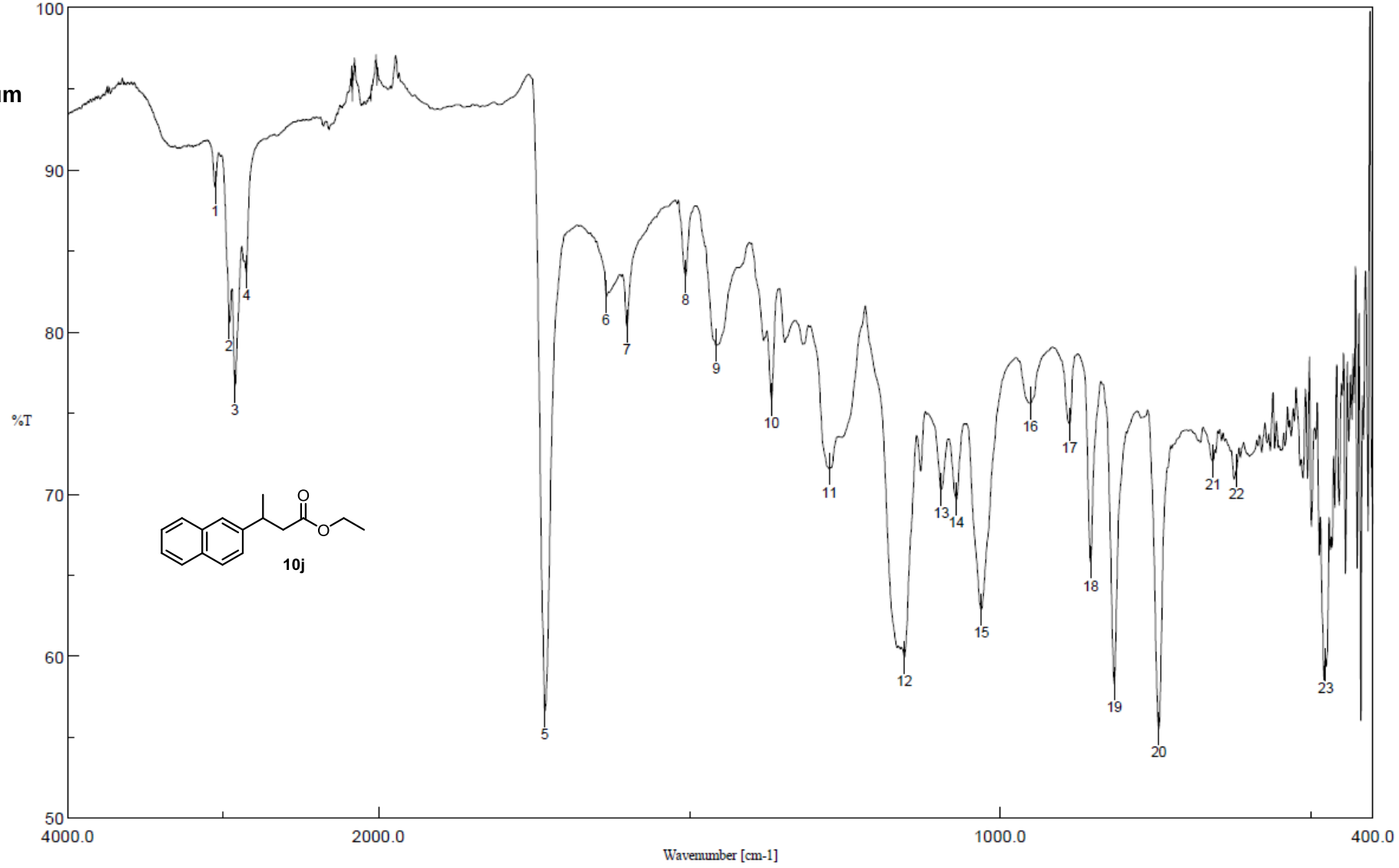
10j



mass spectrum

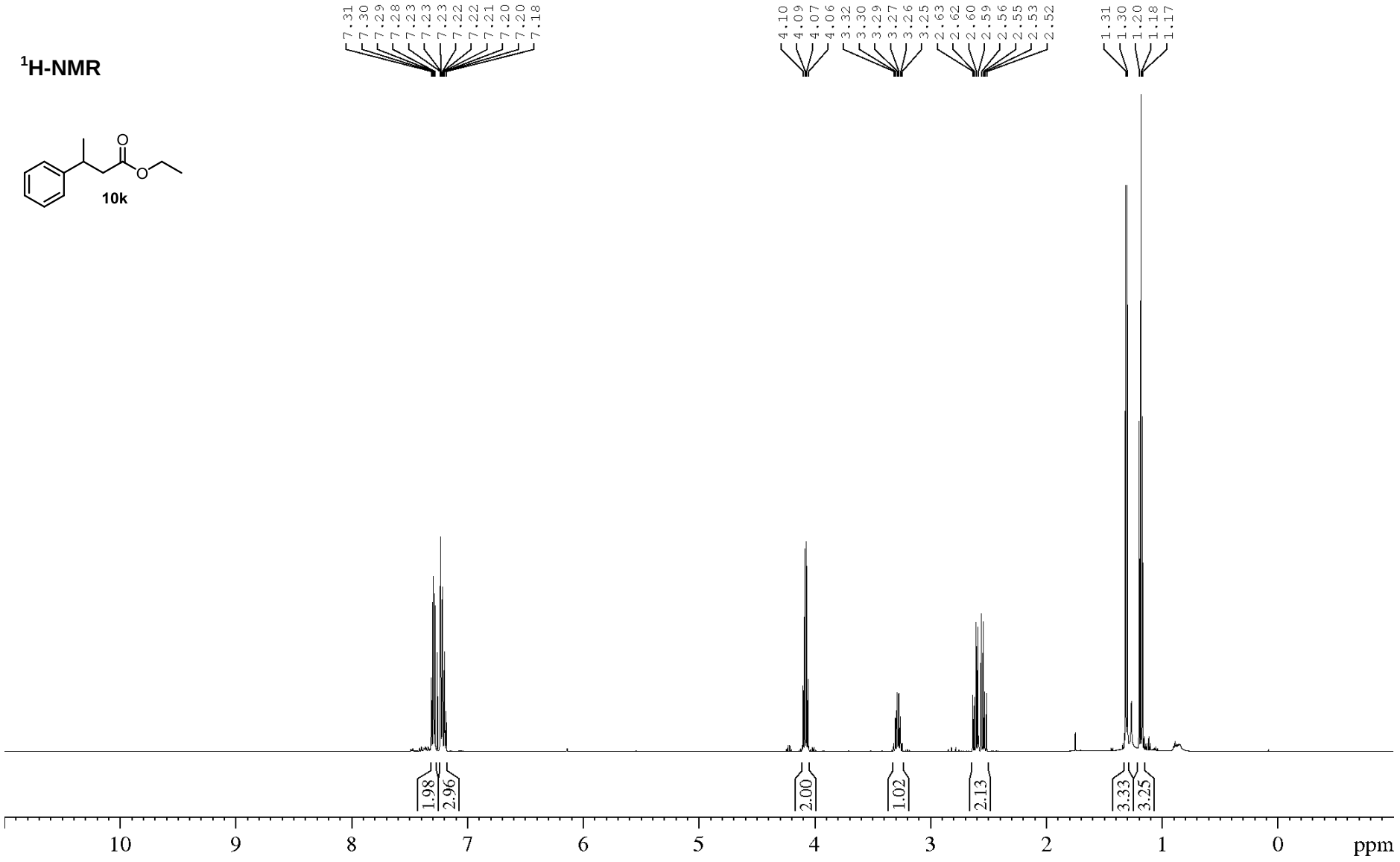


IR spectrum

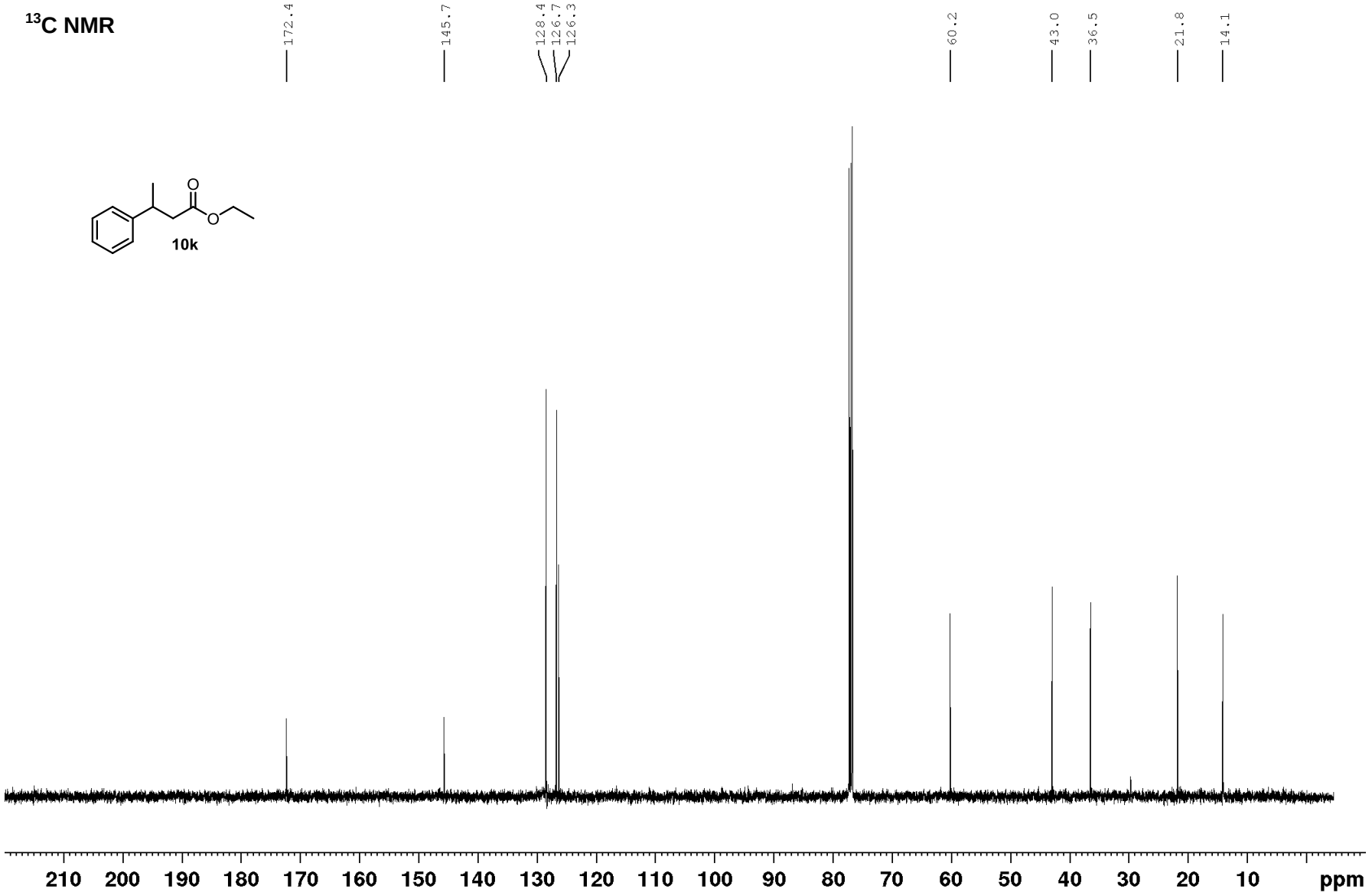

100
90
80
70
60
50
%T
4000.0
2000.0
1000.0
400.0
Wavenumber [cm-1]
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
O
O
10j

^{1}H-NMR

10k

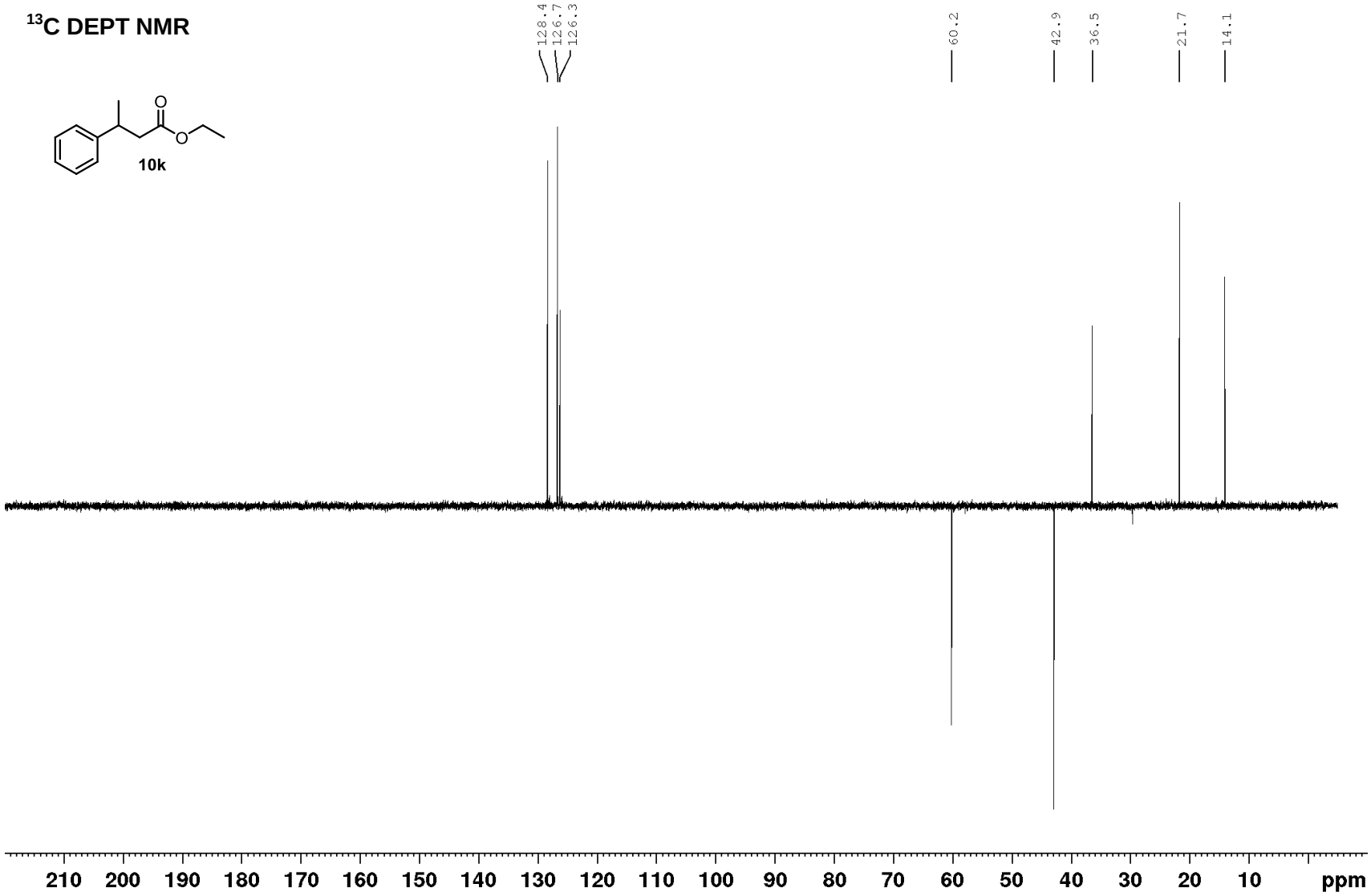

7.31
7.30
7.29
7.28
7.23
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.18
4.10
4.09
4.07
4.06
3.32
3.30
3.29
3.27
3.26
3.25
2.63
2.62
2.60
2.59
2.56
2.55
2.53
2.52
1.31
1.30
1.20
1.18
1.17
1.98
2.96
2.00
1.02
2.13
3.33
3.25
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR


172.4
145.7
128.4
126.7
126.3
60.2
43.0
36.5
21.8
14.1
10k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

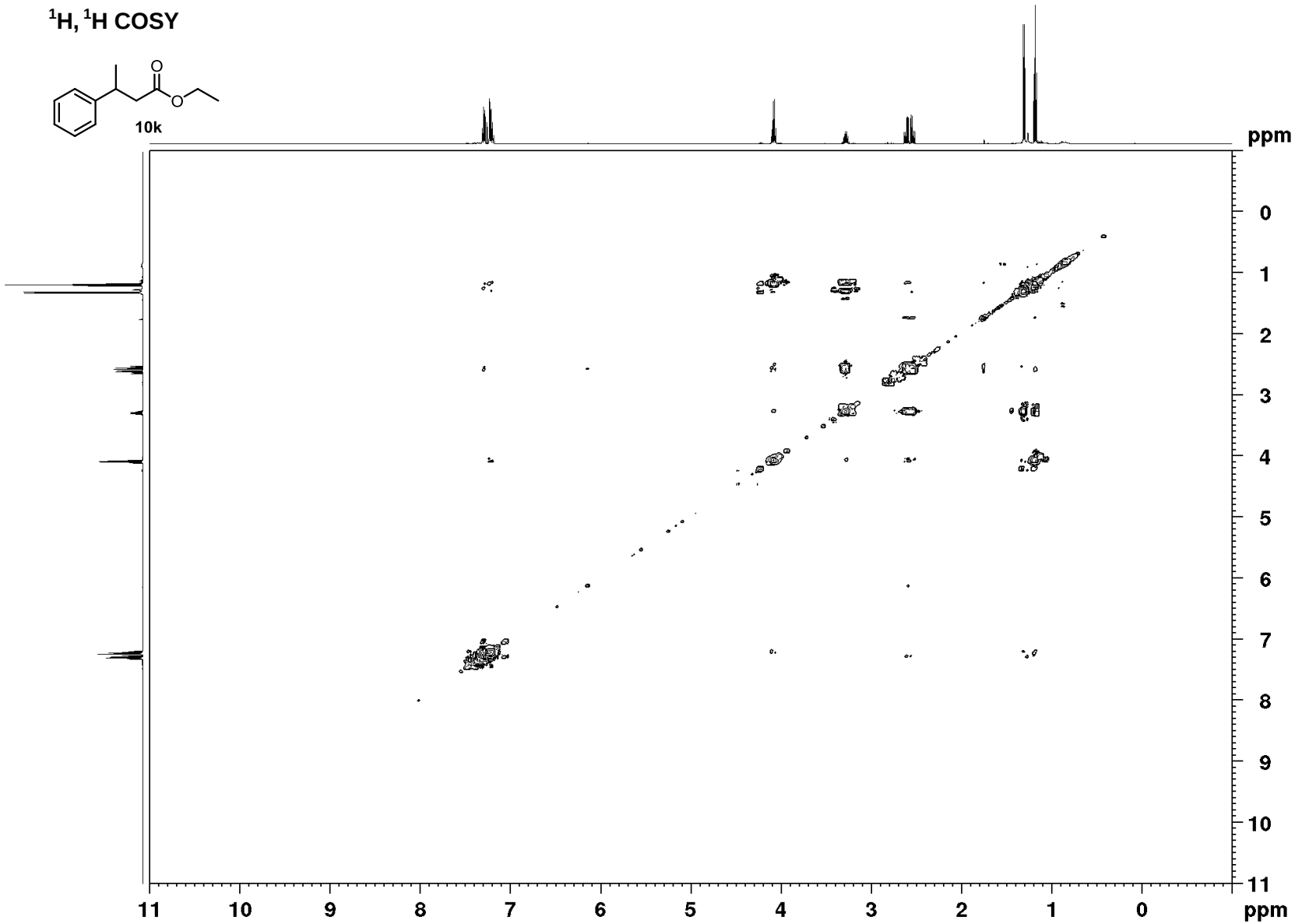
^{13}C DEPT NMR

10k



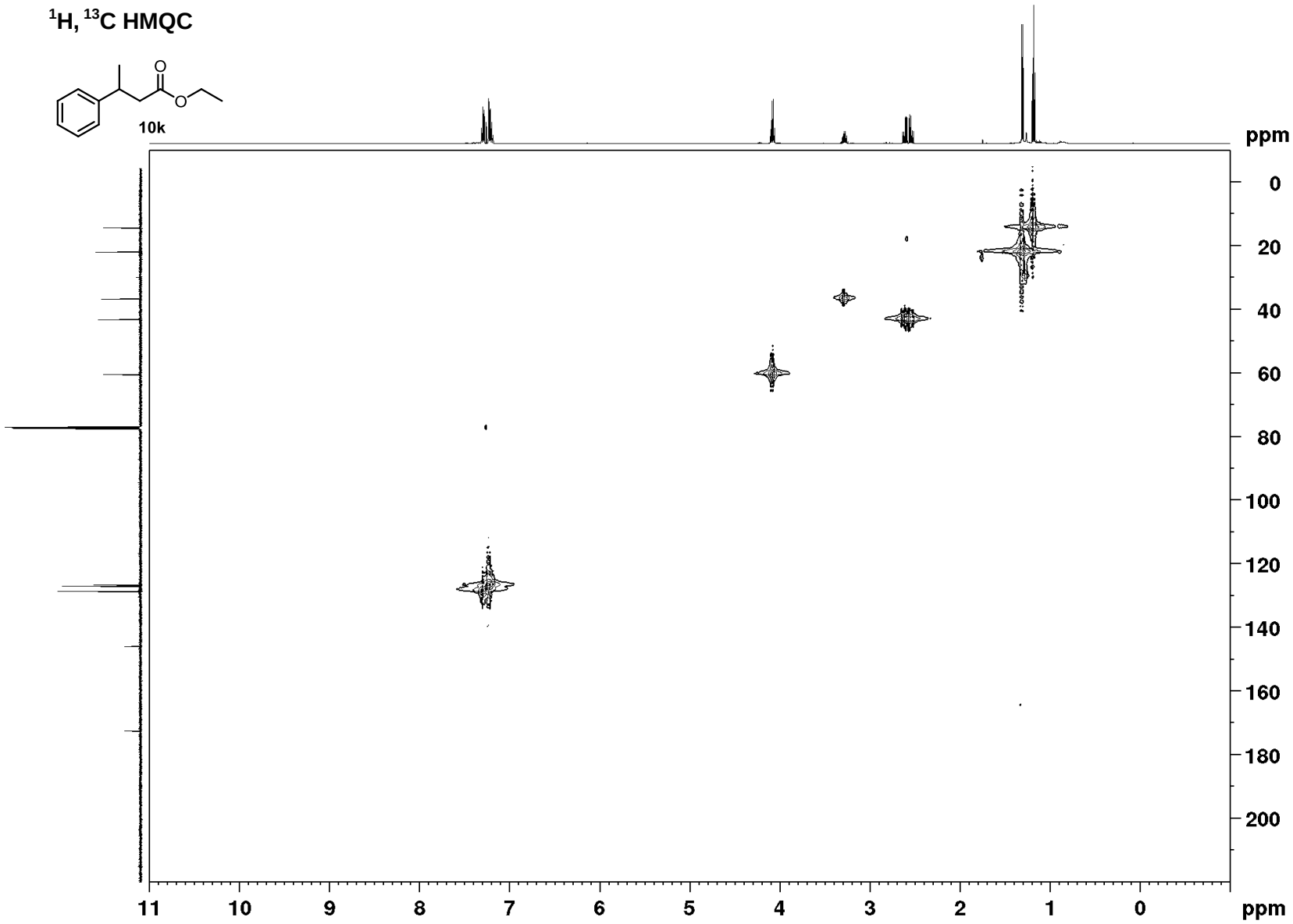
^{1}H, ^{1}H COSY

10k



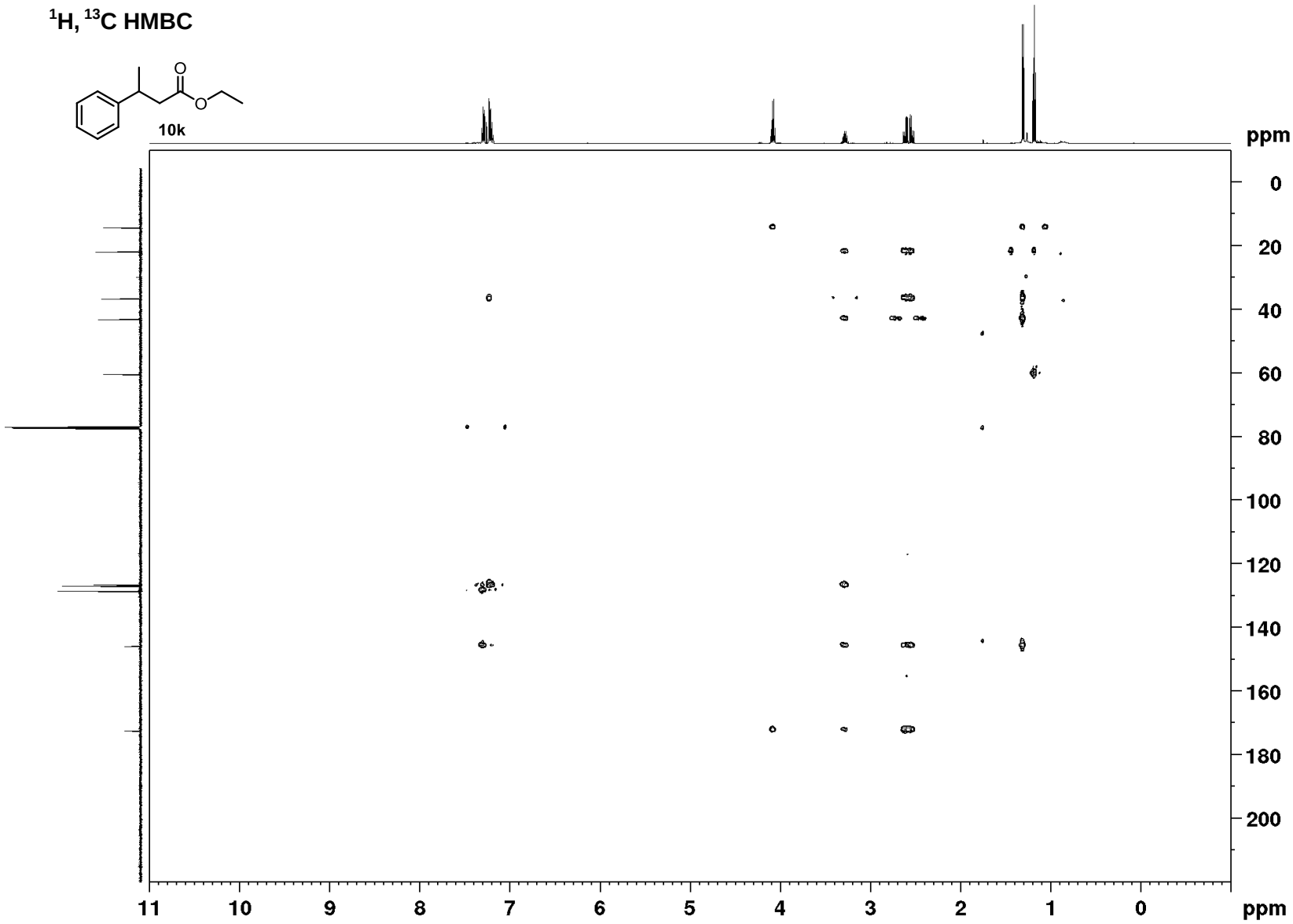
^{1}H, ^{13}C HMQC

10k

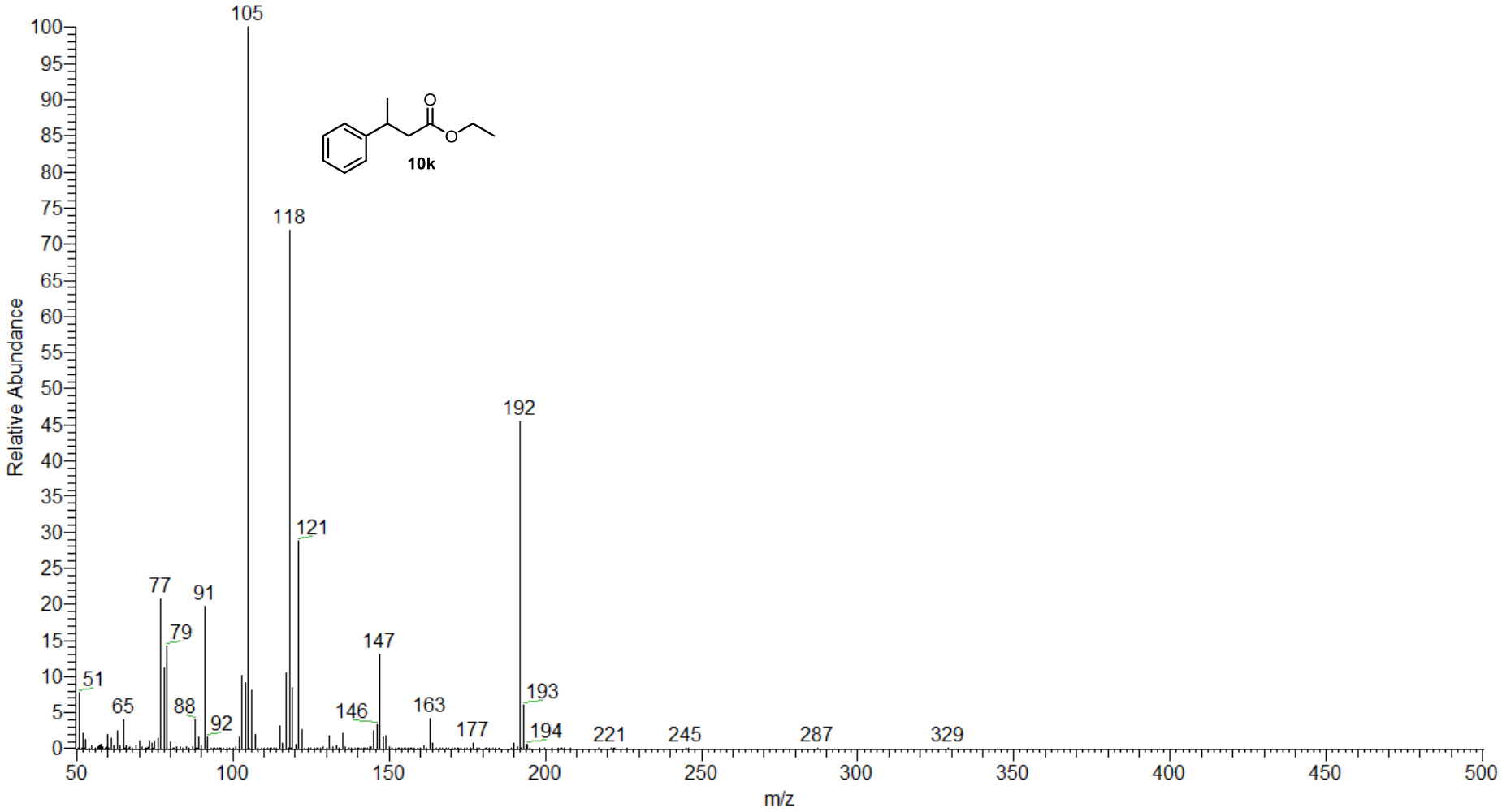


^{1}H, ^{13}C HMBC

10k



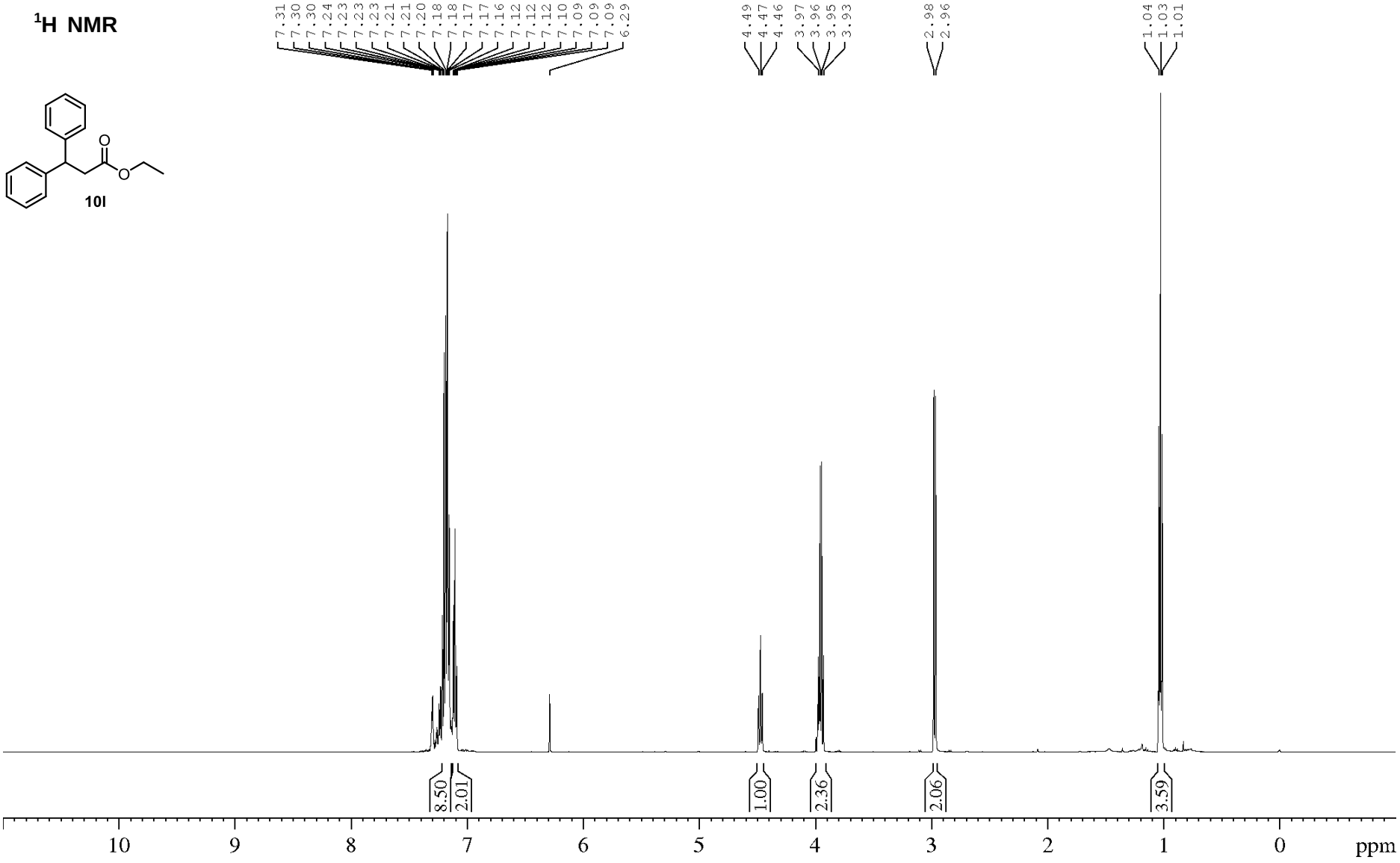
mass spectrum



^{1}H NMR

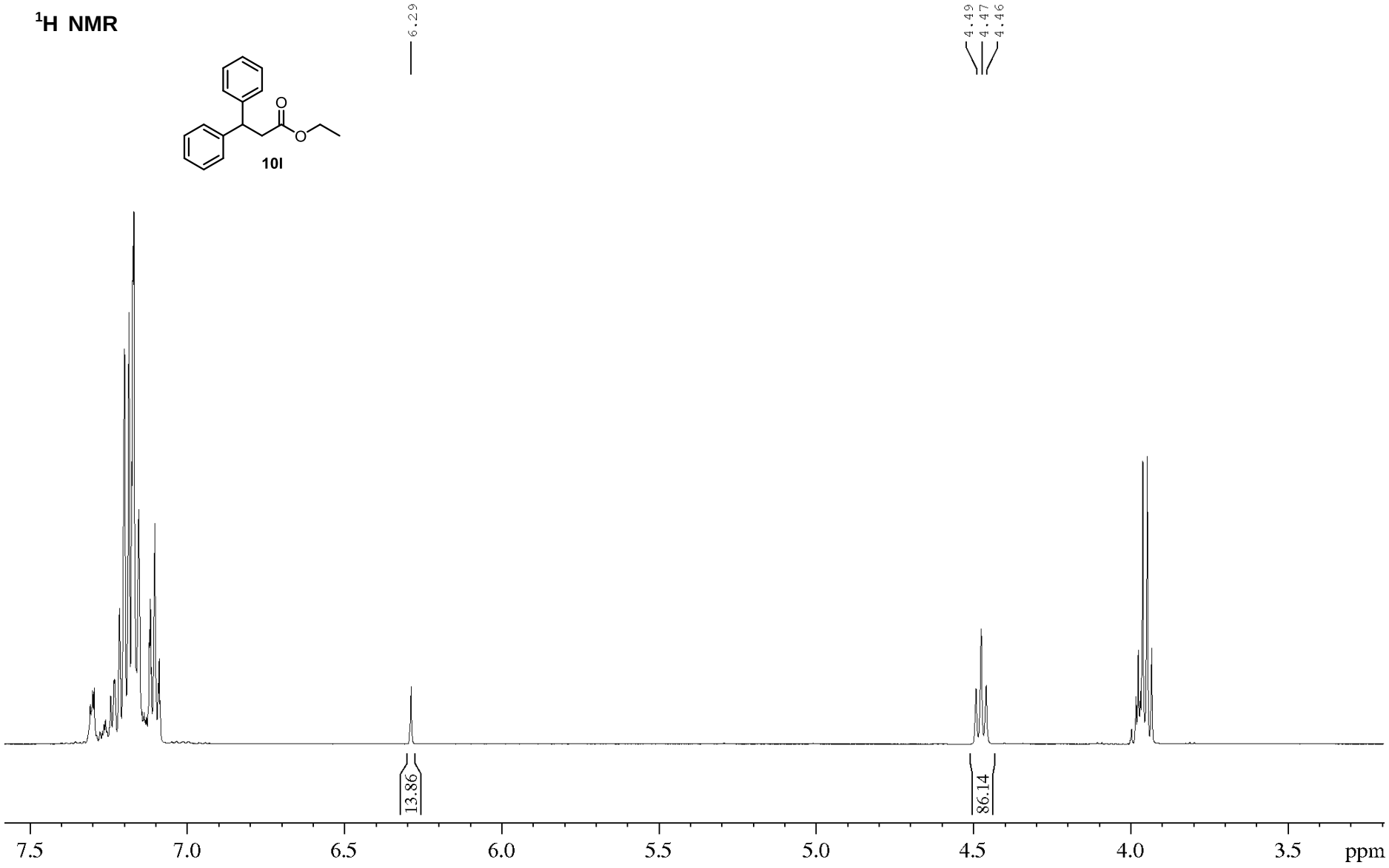
O
O

10l


7.31
7.30
7.30
7.24
7.23
7.23
7.23
7.21
7.21
7.20
7.18
7.18
7.17
7.17
7.16
7.12
7.12
7.12
7.10
7.09
7.09
7.09
6.29
4.49
4.47
4.46
3.97
3.96
3.95
3.93
2.98
2.96
1.04
1.03
1.01
8.50
2.01
1.00
2.36
2.06
3.59
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H NMR

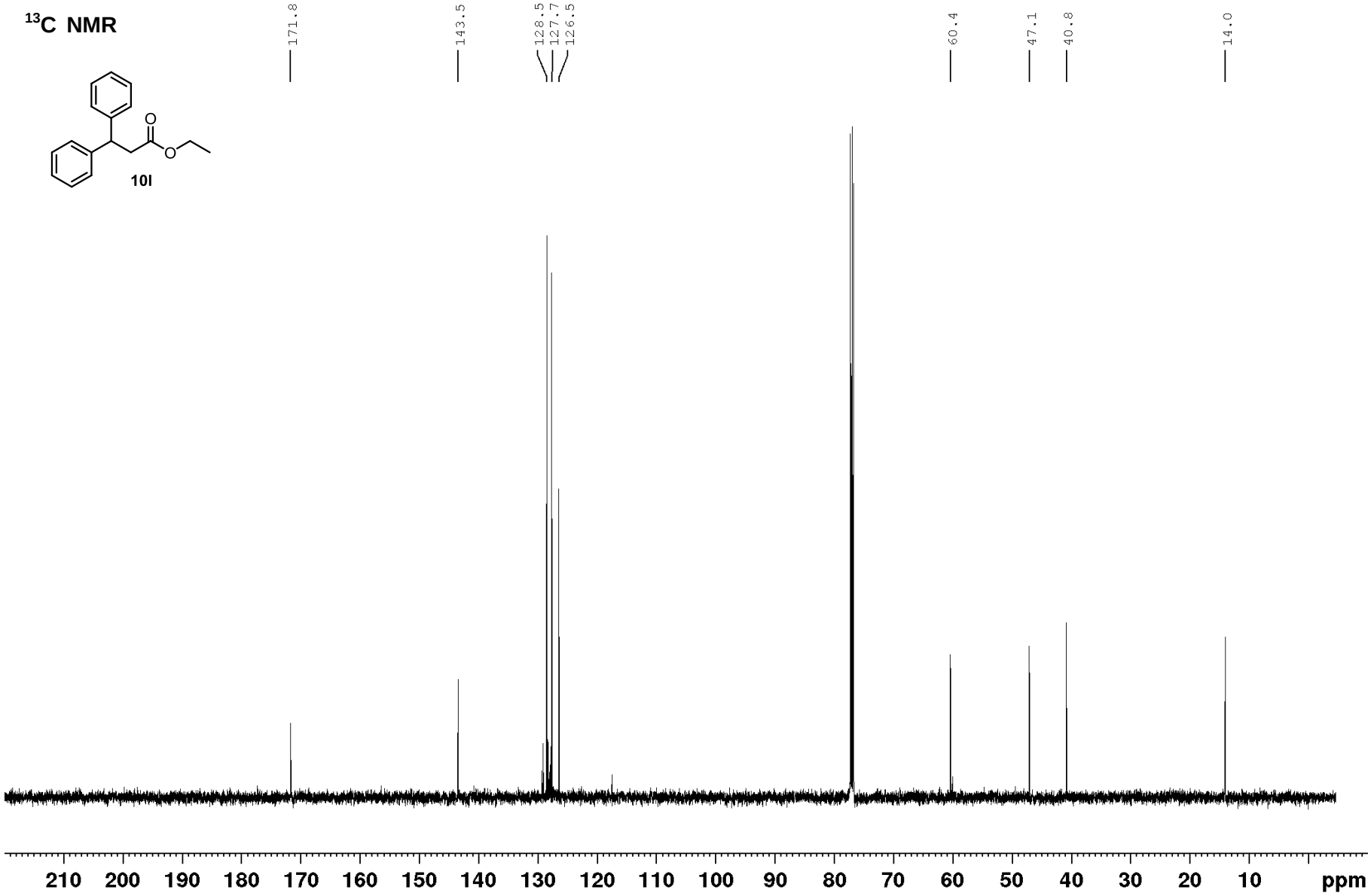
10l



^{13}C NMR

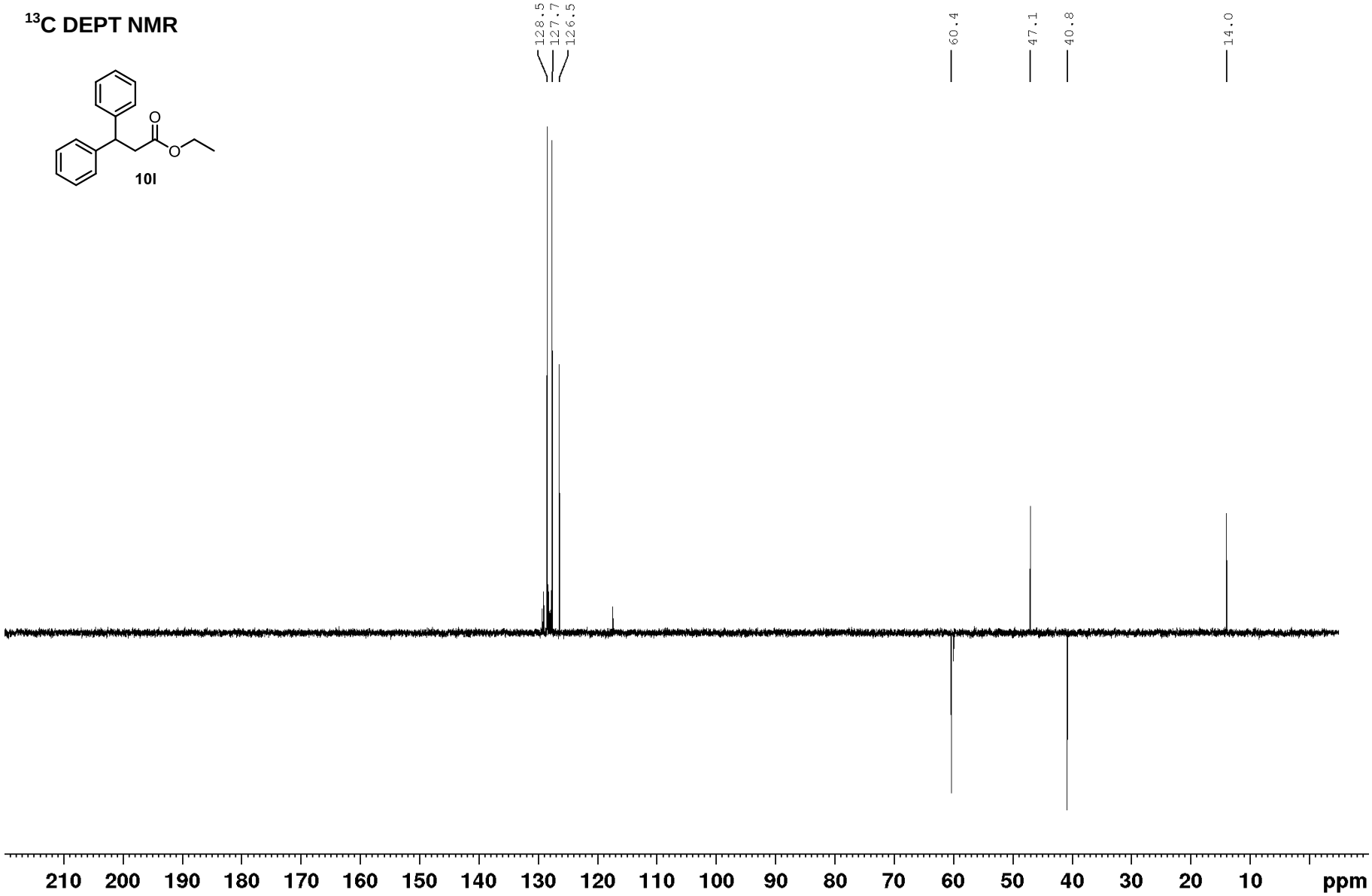
O
O

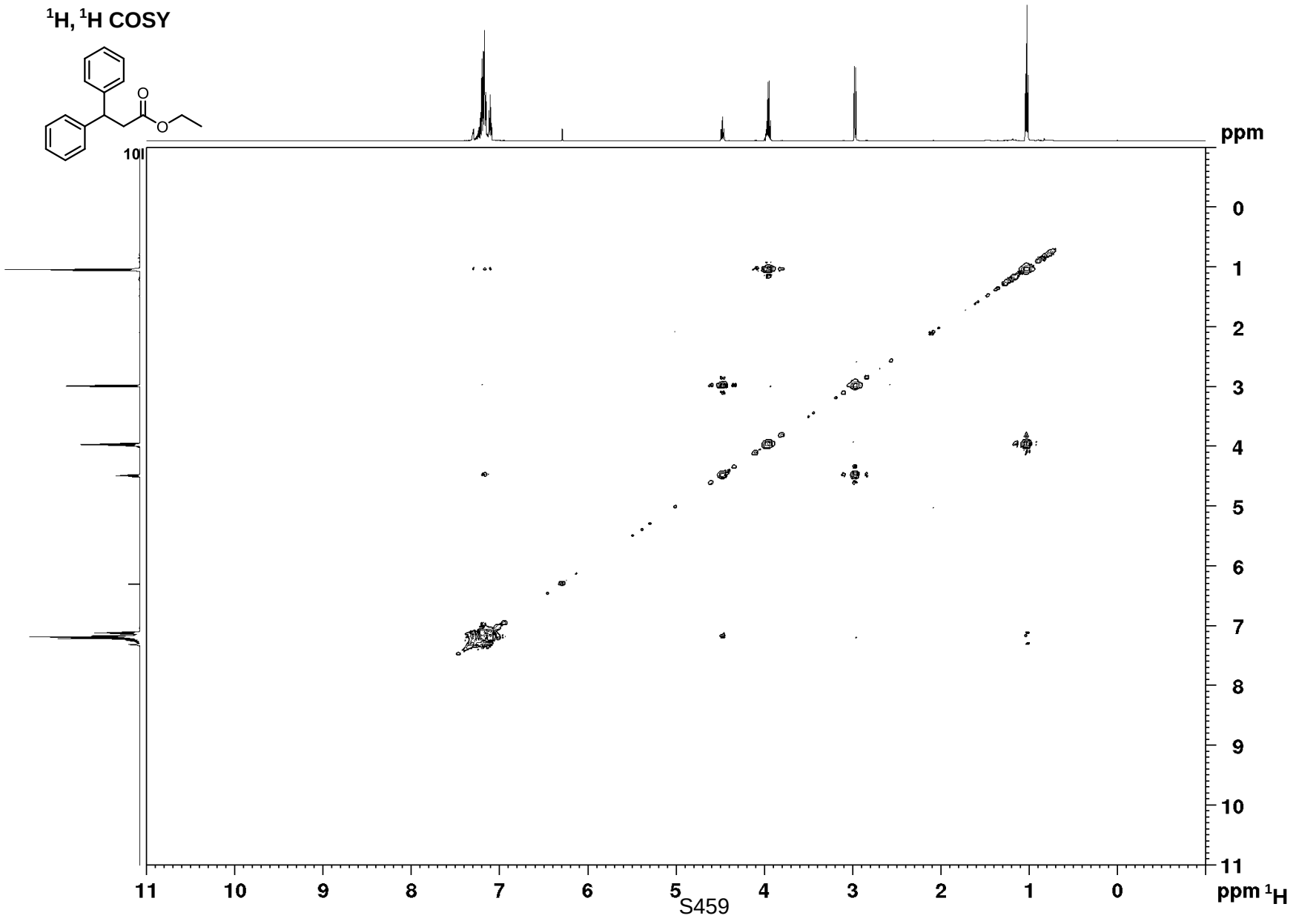
10l

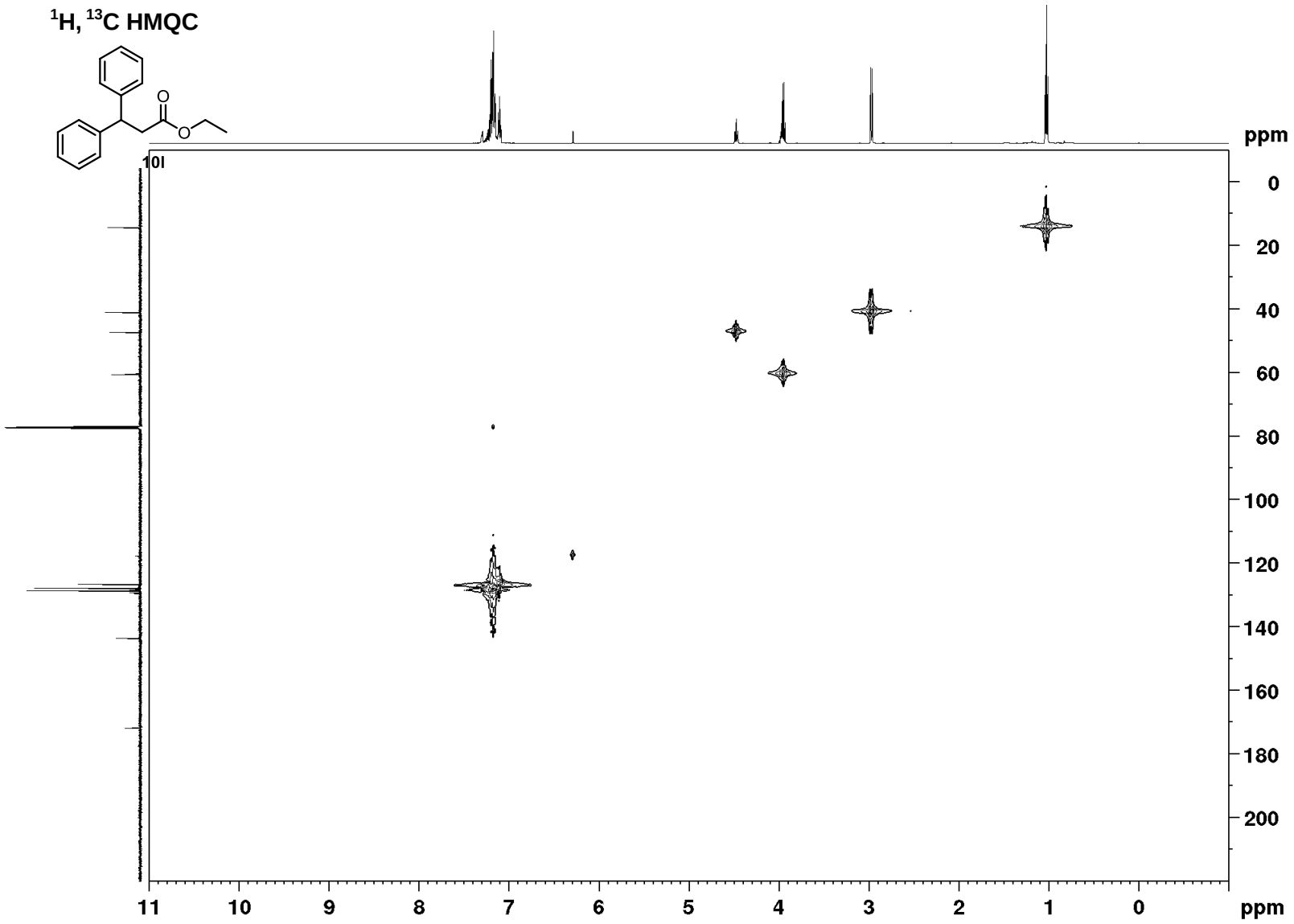

171.8
143.5
128.5
127.7
126.5
60.4
47.1
40.8
14.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

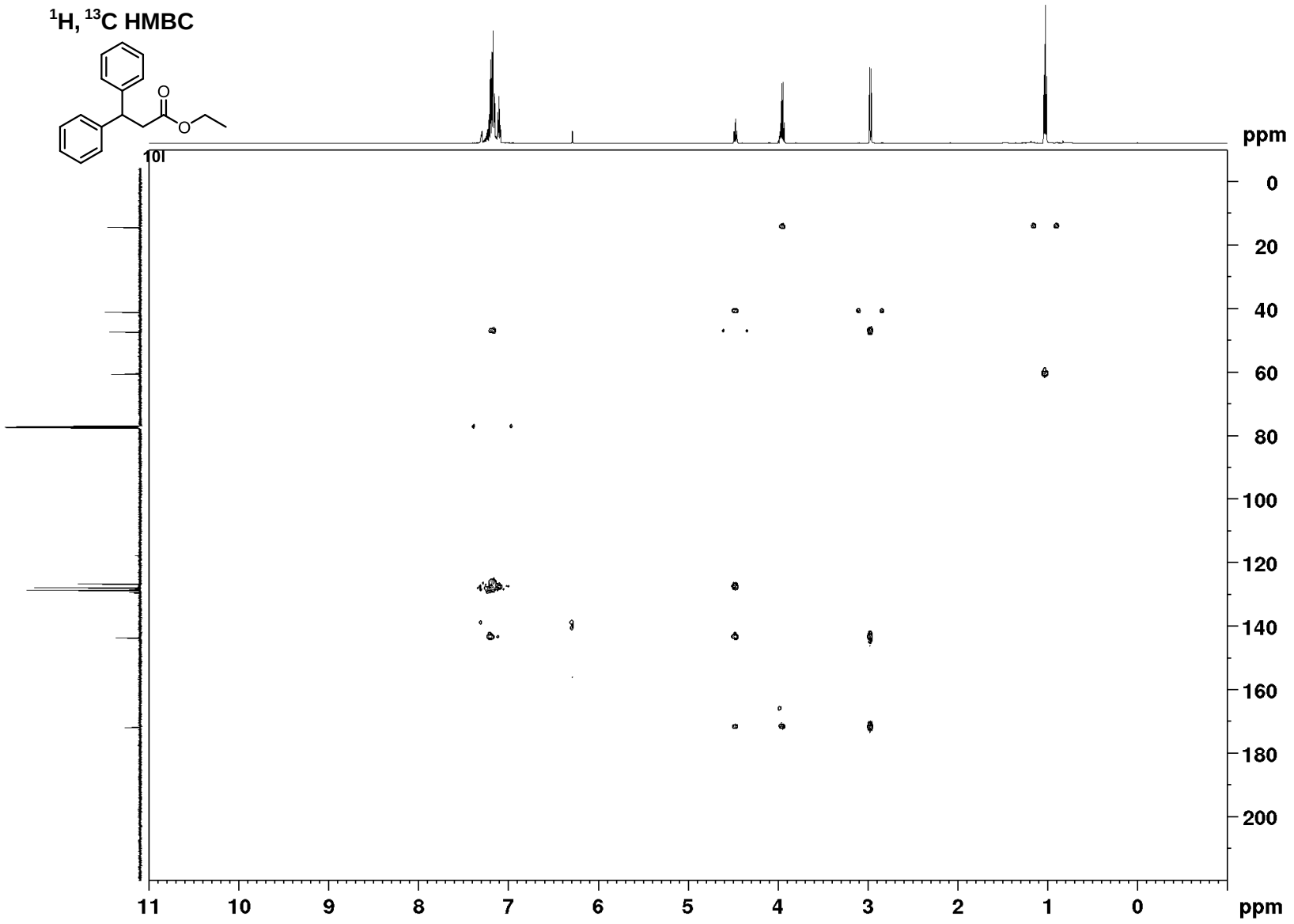
^{13}C DEPT NMR

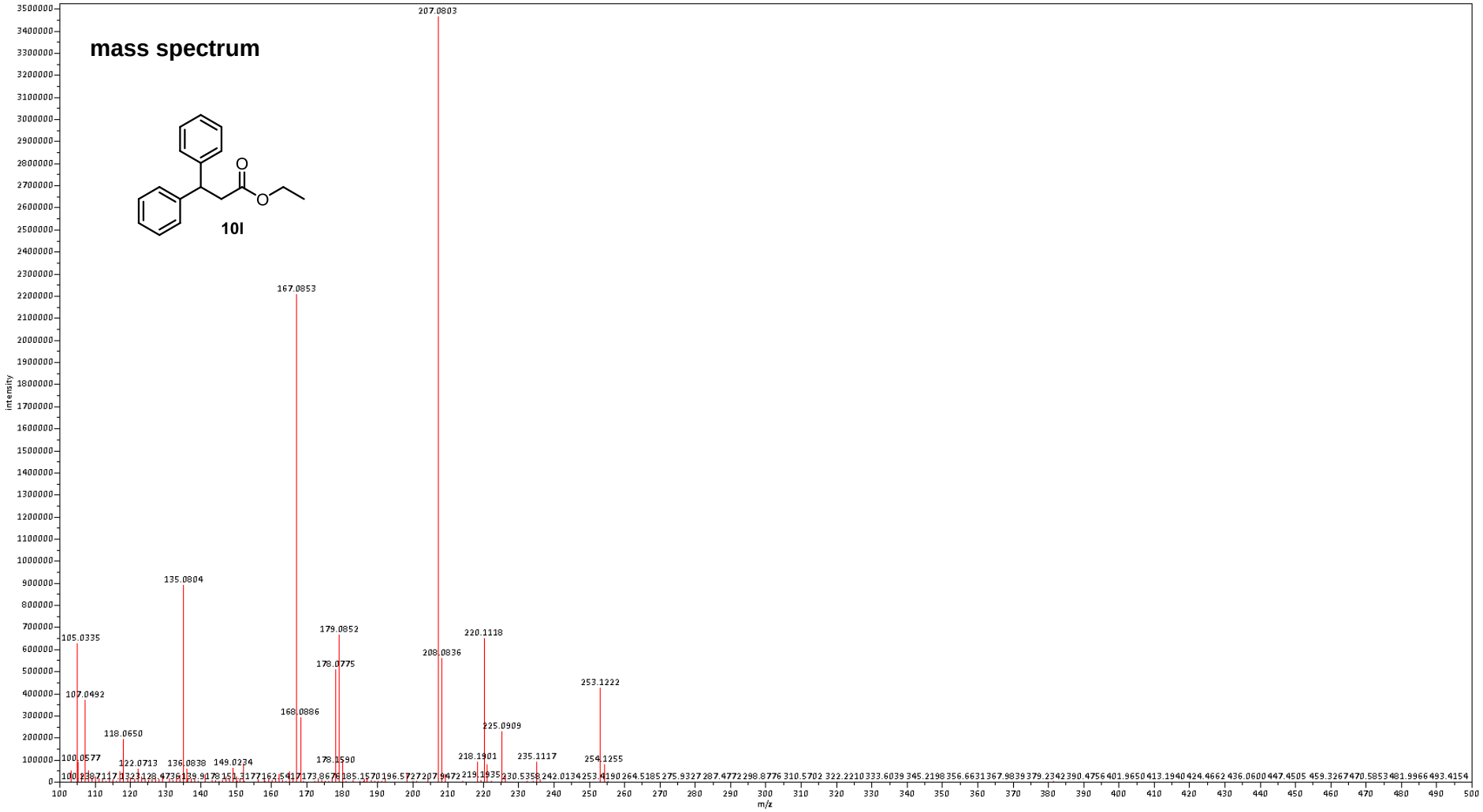
10l




^{1}H, ^{1}H COSY
O
O
ppm
0
1
2
3
4
5
6
7
8
9
10
11
11
10
9
8
7
6
5
4
3
2
1
0
ppm ^{1}H


^{1}H, ^{13}C HMQC
O
O
101
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm


^{1}H, ^{13}C HMBC
O
O
101
ppm
0
20
40
60
80
100
120
140
160
180
200
11
10
9
8
7
6
5
4
3
2
1
0
ppm


mass spectrum
10l
intensity
m/z
207.0803
167.0853
135.0804
105.0335
179.0852
178.0775
220.1118
208.0836
253.1222
107.0492
168.0886
225.0909
118.0650
235.1117
254.1255
100.0577
122.0713
136.0838
149.0234
178.1590
218.1901