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Photo induced oxidative carbon boron bond cleavage

Thesis for acquiring the degree Bachelor of Science (B.Sc.)

From

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Plagiarism Declaration in Accordance with Examination Rules

I herewith declare that I have worked on this thesis independently. Furthermore, it was not submitted to any other examining committee. All sources and aids used in this thesis, including literal and analogous citations, have been identified.

Nürnberg, 12.03.2015

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Signature

Acknowledgments

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Abstract

In the following work, boronic acids, which contain the carbon boron bond in benzylic position have been synthesized. These boronic acids were reacted in the presence of catalytic amounts of a bromine source under irradiation with a xenon lamp. This generated benzyl radicals which were subsequently oxidized by air or oxygen. Primary boronic acid yielded benzoic acids, their secondary counterparts the corresponding ketones. Investigations on the effect of the solvent the bromine source and the structure of the boronic acids have been carried out. This showed that the yield depends highly on the solvent and structure of the boronic acids. Benzyl boronic acids showed the best reactivity, followed by 1-phenylethyl boronic acids and at last diphenylmethyl boronic acids which showed a notable reactivity in oxygen atmosphere only. In each of these three classes of boronic acids it was noticed that electron donating substituents in the aryl moiety contribute to an increased yield.

Keywords

Boronic acid

Photo induced cleavage

HBr as catalyst

Single electron transfer

Green oxidation

Contents

List of abbreviations and symbols

Ac	acetyl
AN	acetonitrile
Ar	aryl
atm	atmosphere
DCM	dichloromethane
DMSO-d_6	deuterated dimethyl sulfoxide
E_b	bond energy
E_D	bond dissociation energy
EtAc	ethyl acetate
Hz	hertz
IR	infra-red
J	spin coupling constant (NMR) [Hz]
Me	methyl
MHz	mega hertz
MeO	methoxy
MeOH	methanol
MS	mass spectroscopy
n-BuLi	n-butyllithium
NEt_3	triethylamine
NHE	normal hydrogen electrode
NMR	nuclear magnetic resonance
Nu	nucleophile
PE	petrol ether
Ph	phenyl
ppm	parts per million
R_f	retardation factor
rt	room temperature
SET	single electron transfer
TFA	trifluoroacetic acid
THF	tetrahydrofuran
tlc	thin layer chromatography

TMS	tetramethylsilane
V	volt
W	watt
δ	chemical shift (NMR) [ppm]
°C	degree Celsius
hν	light energy/photon

1. Introduction

The majority of industrial chemical processes which were developed in the last century for the production of bulk chemicals, are using harsh conditions (e.g. elevated temperature and high pressure) and therefore consume a high amount of energy which is either supplied by burning coal, gas, fossil fuels or nuclear power. The results such as the greenhouse effect and the loss of not renewable resources are well investigated and known to the public. An also important fact to mention here is that in the synthesis of complex molecules in the fine chemical industry or just reactions at laboratory scale the used synthetic methods require often highly specialized reagents, expensive transition metals as catalyst, very low temperatures or difficult work up processes. In conclusion the search for efficient, mild and green methods is a very fast growing field in chemical research. Herein the formation of new bonds and functionality with the aid of photons is one of the most promising concepts. Which can be seen by the vast growing number of publications containing the keyword photocatlysis in the last 15 years. (Figure 1).

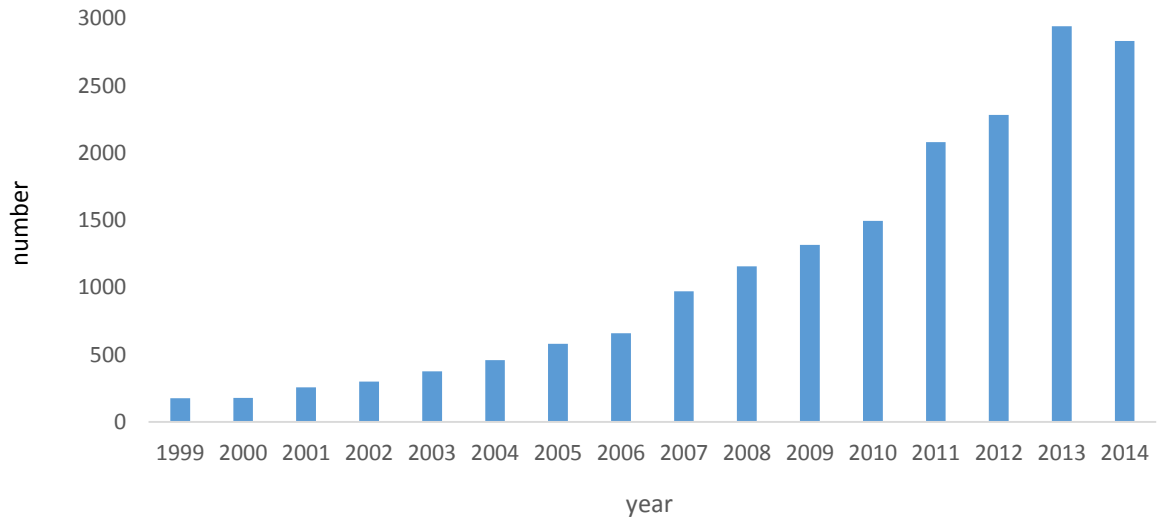
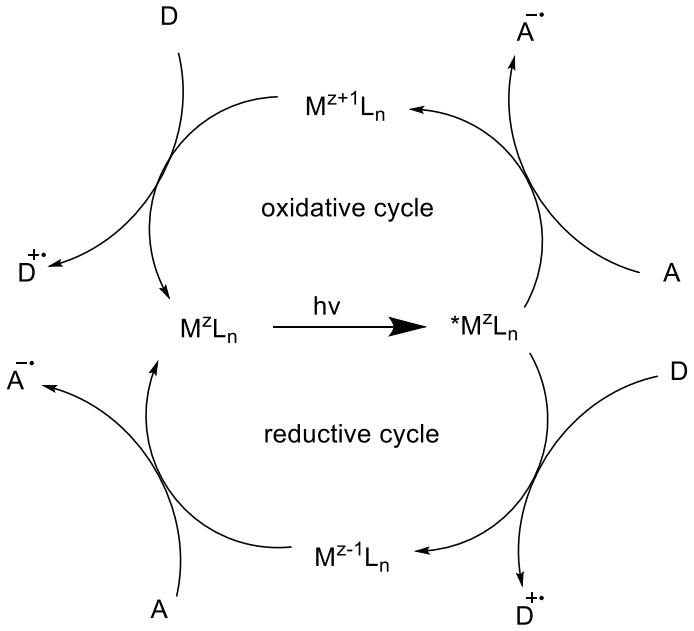


Figure 1: Number of publications containing the keyword "photocatlysis" per year

Although they suffer from drawbacks, photochemical processes offer a lot of advantages. These include the selective activation of individual reactants which, can suppress the formation of byproducts. Unique properties and specific reactivity's of excited molecules can be used. Another big advantage is the low thermal energy that need to be transferred into the reaction system. Since light sources can in most cases just switched off to terminate a reaction, photochemistry offers an accurate control of time and energy.

1.1 Photocatalysis

The majority of the publications in figure 1 focuses on new ways for the activation of small molecules. One well investigated approach is the catalytic activation via single-electron transfers (SET) to or from the organic substrate, conducted by polypyridine complexes of ruthenium and iridium [1]. In the fundamental catalytic cycle an electron the metal centers orbitals is promoted due to photo irradiation in the ligands π-orbitals. This leads to a triplet state which can be more reductive or oxidative than the ground state of the metal complex and can subsequently react with a given substrate in oxidative or reductive manner by donating or accepting an electron [2,3]. This generates a radical anion or cation which can undergo a desired reaction. (Scheme 1).

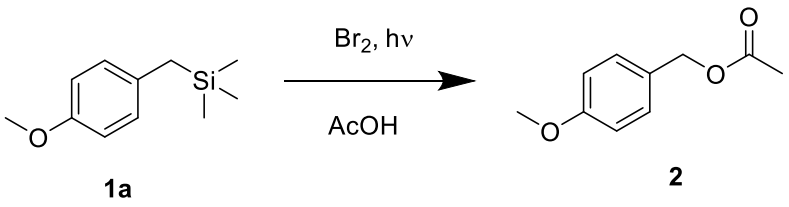


Scheme 1: Example of oxidative and reductive catalytic cycle of transition metal photo redox catalyst (A=Acceptor, D=Donator)

Examples for the successful application of this strategy are the reduction of olefins, the dimerization of benzyl bromides, the reduction of nitro groups or 2+2 cycloadditions and reactions with far more substrates[1]. However it is also known that radicals which are formed by photolysis are able to participate in SET reactions. The bromine radical can be produced from the photolysis of HBr and is a good electron acceptor and oxidant. Its oxidation potential is with 2.0 V vs NHE[4] relatively high. Therefore, Br_2 and HBr, could be a cheap green alternative for the catalytic oxidation of small molecules. This subject was investigated over the last decades with benzyl silanes as possible substrates.

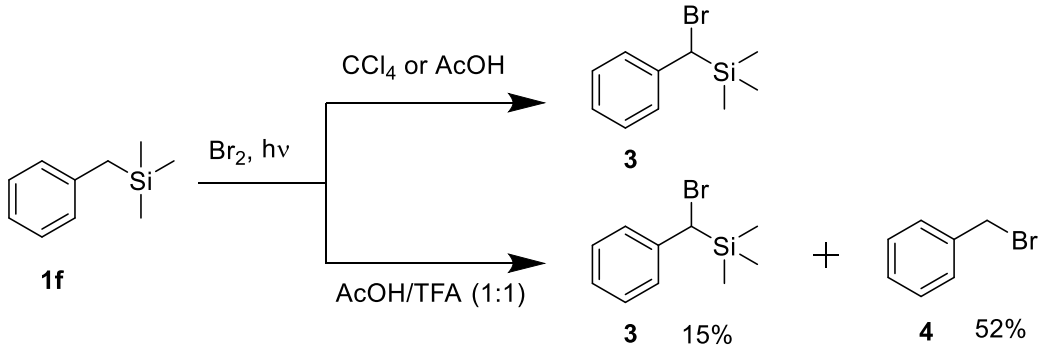
1.2 Photo induced oxidative cleavage of C-Si bonds

In 1990, a study by Baciocchi and Crescenci showed that the bromine radical not only has the well-known ability to abstract benzylic hydrogens, but also can convert 4-methoxybenzyltrimehtylsilane (**1a**) in the corresponding acetyl ester **2**. (Scheme 2) [4].



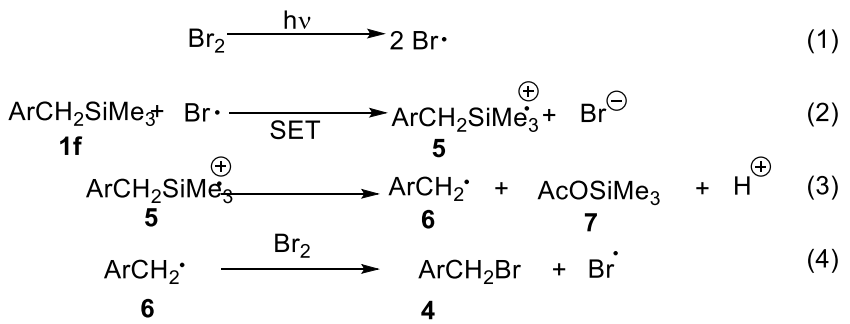
Scheme 2: Conversion of 4-methoxybenzyltrimehtylsilane (**1a**) to the acetyl ester

In their experiments they also observed that the reaction of benzyltrimethylsilane (**1f**) afforded different bromination products in different solvents. (Scheme 3)

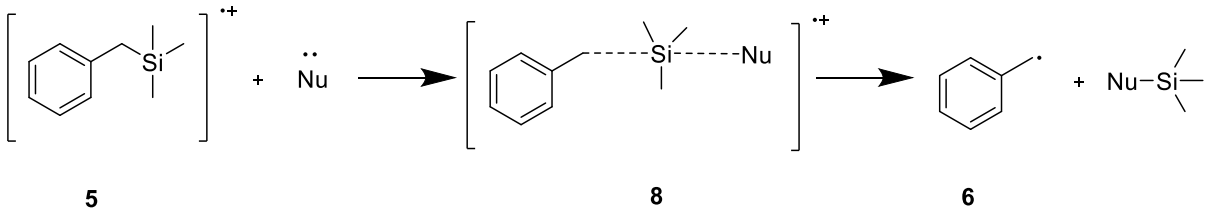


Scheme 3: Solvent effects on the reactions of benzyltrimethylsilane

If they used CCl4 as solvent they obtained only product **3**. In contrast if a mixture of acetic acid and trifluoroacetic acid was used, **3** and **4** were obtained. Henceforth, they concluded that in AcOH/TFA the silane **1f** underwent a rapid desilylation, via the radical cation **5** to form a benzyl radical. This radical reacted with a bromine molecule to form benzyl bromide (**4)** (Eq. 1-4).



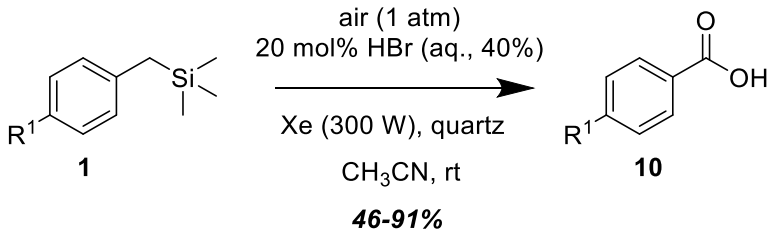
This shows that in nucleophilic solvent systems cleavage of the carbon silicon bond is the main reaction pathway. The reason is that with increased nucleophilicity of the solvent the C-Si σ-bond in the transition state **8** becomes "weaker" due to interaction of the nucleophile with the antibonding σ^*-molecular orbital which leads to a faster cleavage of the C-Si bond [5,6]. (Scheme 4)



Scheme 4: Nucleophile assisted cleavage of a carbon-silicon bond

So it is easy understandable that the major key factors for the formation of benzyl radicals from tribenzyl silanes should be the electron density in the compound and solvent.

These findings found recently application in an published method for photochemical cleavage of the C-Si bond of benzyl silanes with the subsequent chemoselective oxidation of the benzyl radicals to benzoic acids, developed by Jing Sun et al [7]. (Scheme 5)



Scheme 5: Photo induced oxidative cleavage of carbon-silicon bonds

In this method a bromine radical is generated in situ by photo irradiation. This bromine radical acts as electron acceptor and forms a radical cation in situ by abstracting an electron from **1**. This cation yields the mentioned intermediate benzyl radical via nucleophile assisted cleavage by the solvent acetonitrile. After that atmospheric oxygen oxidizes that radical to the corresponding aldehyde, which is further oxidized to the benzoic acid **10**.

1.3 Photo induced oxidative cleavage of C-B bonds

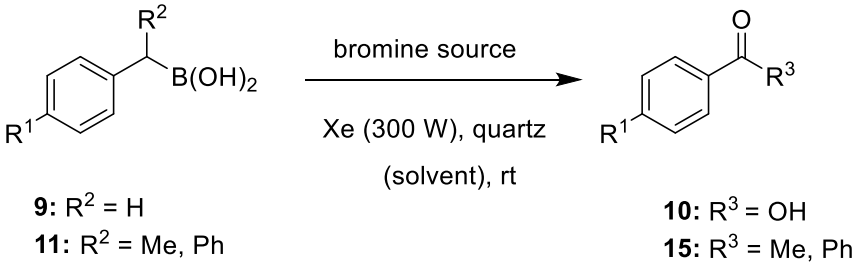
Carbon boron bonds frequently occur in synthetic routs. Boronic esters and acids found their application as substrates for the famous Suzuki-Miyaura cross-coupling reaction[8]. The hydroboration of alkene or alkyne functionalities is a very effective way to convert them in the corresponding alcohols or aldehydes/ketones [9,10]. In contrast to their importance and frequent appearance in the synthetic chemist's toolkit, the photochemistry of carbon boron bonds received only poor attention in the past. Furthermore in the existing studies aryl boronic acids play the major role [11,12]. Only one study in the year of 1976 investigated the light promoted cleavage of the C-B bond in tribenzyl borane and its ammonia complex. The results showed that the electron richer environment of the boron atom in the ammonia complex yields to higher reactions rates and yields. Also it was concluded that solvents which are known to coordinate on the vacant p-orbital of boron (THF, diethyl ether, alcohols) may assist cleavage of carbon boron bonds [13].

Since the bonding energies of C-B and C-Si bonds only differ by 5 kJ/mol (Table 1), it could be expected that they might behave similar in the mentioned nucleophile assisted cleavage.

Table 1: Bonding energies of selected carbon bonds

Bond	E_b [kJ/mol]	Reference
C-C	358	[14]
C-B	323	[14]
C-Si	318	[15]
C-O	383	[14]

On the basis of the previous it should be possible that benzyl boronic acids may undergo the same bromine catalyzed light induced oxidative cleavage like benzyl silanes to yield benzoic acids. Based on the mechanism, which was showed in the previous section, it can be assumed that secondary derivatives should yield ketones.



Scheme 6: Possible cleavage of carbon boron bonds with subsequent oxidation

In the following in work investigations will be made if boronic acids resemble benzyl silanes in photo induced bond cleavage reactions. In addition this will also give more understandment whether boron functionalities in molecules could be stable when other photochemical methods are employed to one complex compound.

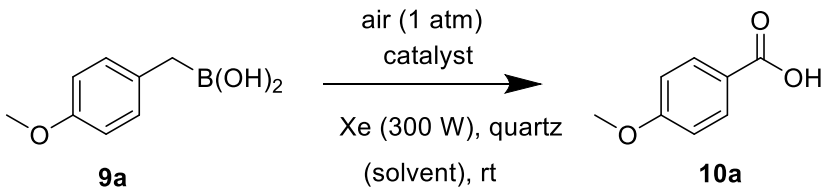
2. Approach

2.1 Objective

The aim of this work is to answer the question how far benzyl boronic acids under light irradiation as well as in the presence of bromine compounds behave analogous to their silicon counterparts. A logical starting point therefore is the orientation on the parameters used in the previous mentioned method for the oxidation of benzyl silanes [7].

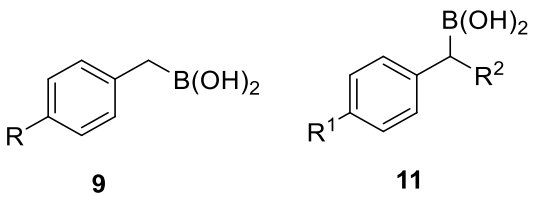
2.2 Plan

In the beginning the electron rich boronic acid (4-methoxybenzyl)-boronic acid (**9**) is used as model substrate to test the feasibility of the reaction. In the first place the effect of the solvent will be studied. Next the bromine source should be varied and at last the amount of catalyst, to find the optimal conditions for the reaction (Scheme 7).



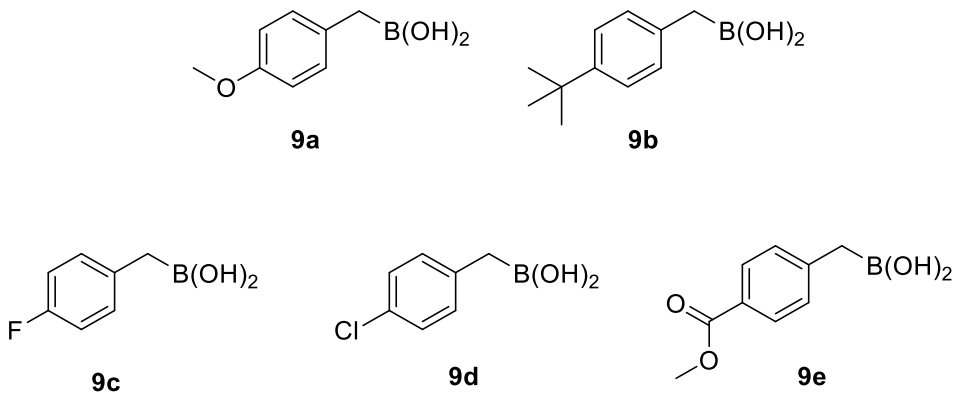
Scheme 7: Photo induced oxidation of boronic Acids

After that, to study electronic effects a diversity of two types of boronic acids are planned to be synthesized. (Scheme 8)

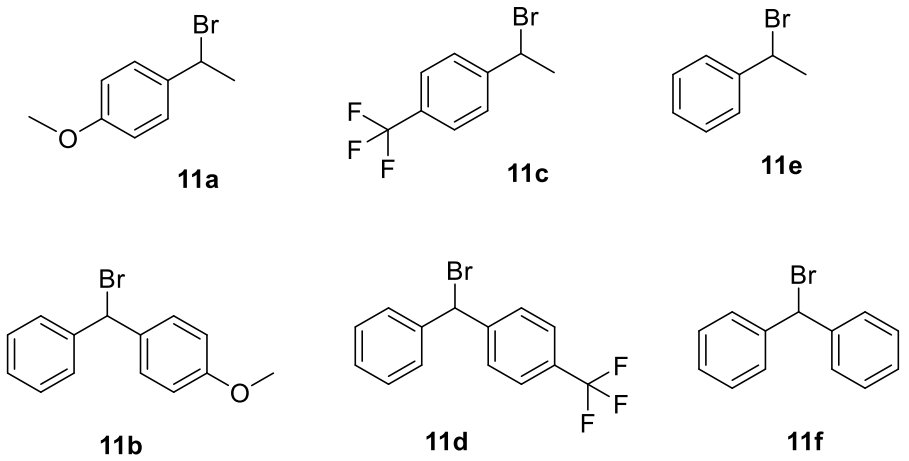


Scheme 8: "Primary" and "secondary" boronic acids

Note: This part of the work is splitted up. The “primary” benzyl boronic acids **9** were synthesized by Yawei Li, Zhengzhou University and Sheng Liuwang, Fudan University. Also the photoreactions of these compounds will be carried out by them. The “secondary” boronic acids **11** will be synthesized by Bernhard Stadler, Nuremberg Institute of Technology. (Scheme 9 and 10)



Scheme 9: Primary boronic acids



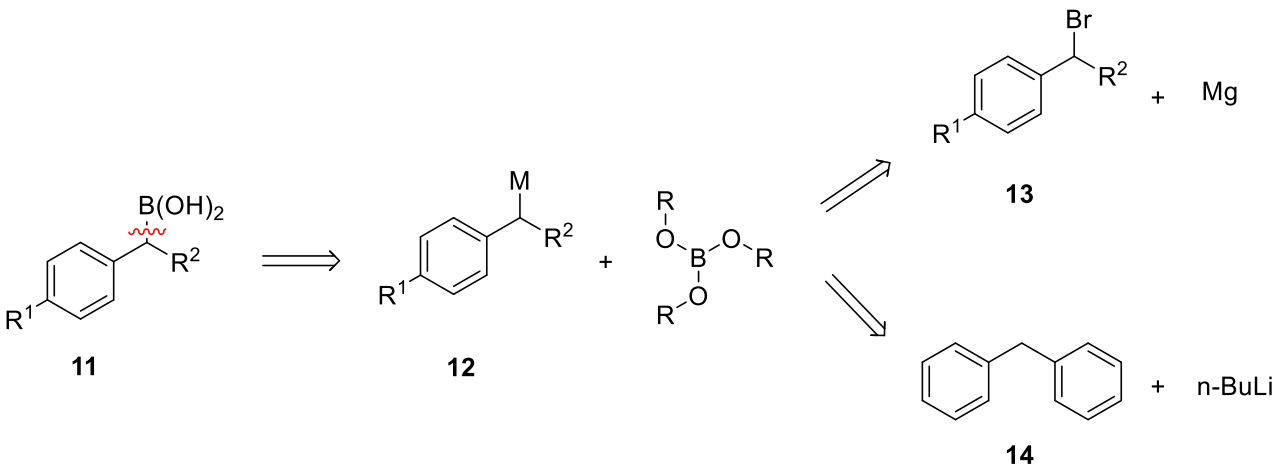
Scheme 10: Secondary boronic acids

3. Synthesis of the boronic acids

In the following section the approach to the synthesis of the starting materials **11a-11f** is explained. The detailed and substance specific synthetic procedures are described in the experimental section.

3.1 General synthetic considerations

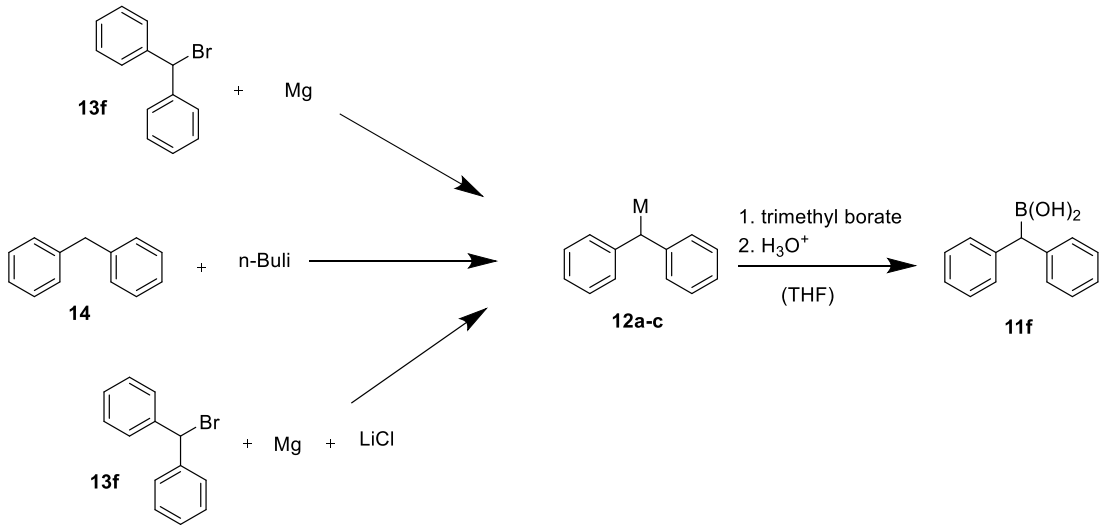
The structures of **11a-11f** are very similar. The trifluoromehtyl and methoxy group are relatively inert functionalities in a lot reaction conditions, so a converged synthesis should be practical. However unlike the wide variety of synthetic methods for aryl boronic acids the amount of publications on the synthesis of alkyl boronic acids, especially secondary ones like **11a-f** is very limited. In the present literature alkyl carbon-boron bonds have often been formed by hydroboration of alkene functionalities using substituted boranes [16,17]. However in this way only "Anti-Markovnikow-Products" can be obtained, so by employing this strategy it would be impossible to form the desired carbon-boron bond in benzyl position (**11a, 11c, 11e**). Another possible way is trapping an organometalic reagent with a trialkyl borate as electrophile [18,19]. Lithium or Grignard compounds can employed here. Organolithium compounds could be obtained by reacting a diphenylmethane derivate with n-BuLi. The Grignard compounds by reacting a benzyl bromide **13** with elemental magnesium. Standard acidic workup should hydrolyze the intermediate borate and yield the boronic acids. Commercial unavailable benzyl bromides might be accessible by bromination of the corresponding alcohols. (Scheme 11)



Scheme 11: Retro synthesis of the boronic acids. R=Alkyl, M=Li,Mg

3.2 Comparison between organolithium compounds and Grignard reagents

To establish a method for the carbon-boron bond formation a couple of test reactions were carried out with different nucleophiles. Trimethyl borate was chosen as the borylation reagent and electrophile. To suppress the formation of borinic acid and boranes, which can occur by multiple substitution, the borate was used in excess. As first attempt it was tried to employ an organolithium reagent as nucleophile to obtain the boronic acid **11a**. This lithium reagent was prepared by reacting diphenylmethane (**14)** with n-butyl lithium. (Scheme 12). To ensure that the desired deprotonation by n-BuLi as taken place almost completely a small amount of the reaction solution was quenched which iodine. Analysis by tlc showed the formation of a product which a lesser R_f value than that of diphenylmethane (**14)**.



Scheme 12: Different ways to obtain a nucleophile for the reaction conditions see Table, **12a** M= Li, **12b** M=MgBr, **12c** M=MgBr·LiCl

It was surprising that the application of the organolithium reagent didn't yield the desired product even when different temperatures were applied (Table 3, Entry 1-3). After that it was tried to obtain the desired product with Grignard reagents. Since LiCl is known for its ability to break up the oligomeric and polymeric forms of Grignard Reagents in solution [20], it was also tried whether it can enhance the reactivity of the organomagnesium compound against the electrophile trimethyl borate. See also scheme 12. When trimethyl borate was added to the "classic" Grignard reagent **12b** only a yield of 30% was obtained. If the reaction was carried out in the presence of anhydrous LiCl, the yield rose up to 45%. See table 2. Steric effects are maybe the key factor here since the metal organyl with its two bulky phenyl groups may not attack the boron atom so easily, the previous mentioned polymeric structure of Grignard

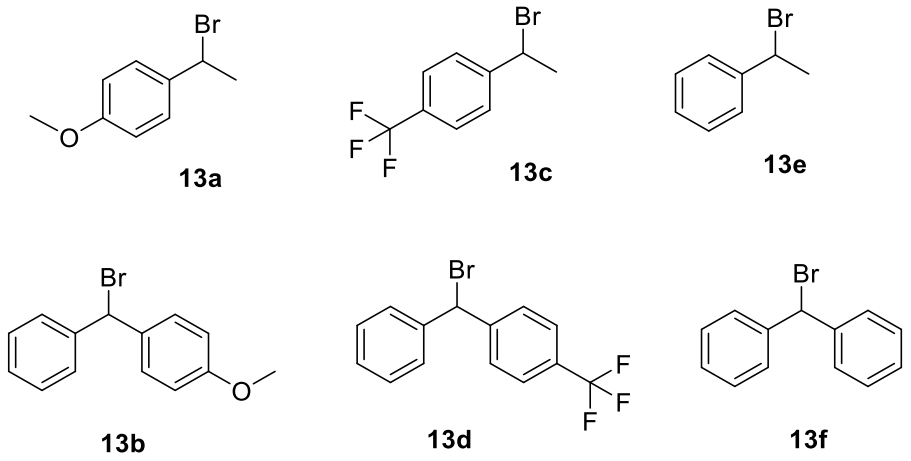
reagents may contribute to a lower reactivity in the absence of LiCl. However since the focus of this work is not on the synthesis of the boronic acids, no attempts were made to optimize this method any further.

Table 2: Synthesis of **11f** with different organometallic reagents.

Entry	**12**	**M**	**eq. trimethyl borate***	**T [°C]**	**Solvent**	**Yield 11f#** **[%]**
1	12a	Li	3.0	-78	THF	-
2	12a	Li	3.0	-40	THF	-
3	12a	Li	3.0	0	THF	-
4	12b	MgBr	3.0	RT	THF	30
6	12c	MgBr·LiCl	3.0	RT	THF	45

*based on 13 or 14, #isolated yield

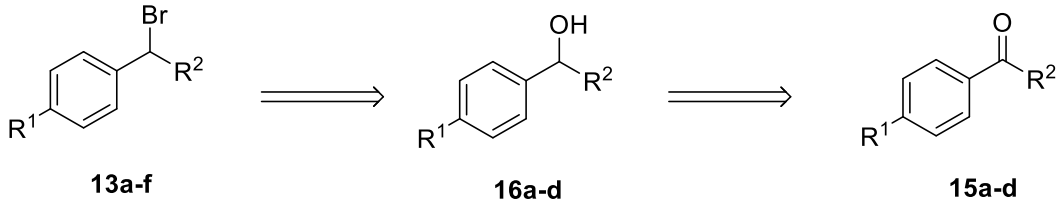
With that conditions in hands it was decided to prepare the boronic acids **11a-e** in a similar way from the bromides **13a-e.** Scheme 13 summarizes the halogen precursors.



Scheme 13: Halogen precursors

3.3 Synthesis of the bromine precursors

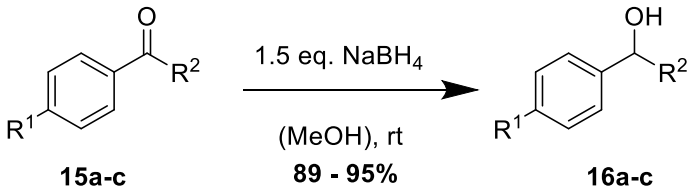
While the bromides **13e** and **13f** could be obtained by suppliers, the bromides **13a-13d** were not commercial available at the time of this work, so it was decided to obtain them from the corresponding alcohols. These alcohols should be easy to transfer in bromide compounds by the use of common halogenation reagents. The alcohols should be conveniently prepared by the reduction of the benzophenones and acetophenones **15a-d**. (Scheme 14)



Scheme 14: Retrosynthesis of the bromides

3.1.1 Preparation of the alcohols 16a-d

The benzyl alcohols **16a-c** were prepared by reducing the corresponding ketones **15a-c** with $NaBH_4$ on the basis of a procedure which is described in literature for **16a**.[21]



Scheme 15: Reduction of ketones

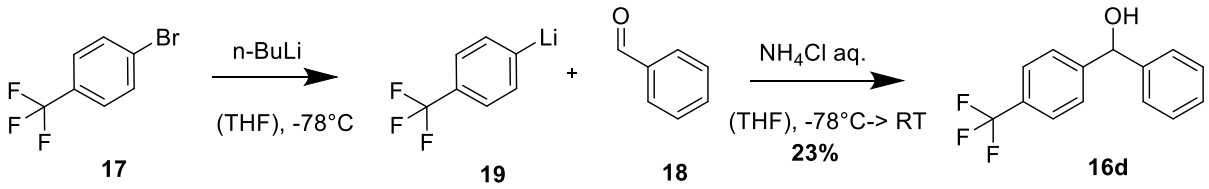
Table 3 summarizes the results. In the case of benzophenone **15b,** ethyl acetate was added to enhance its solubility. The alcohols **16a-c** were obtained in excellent yield. Analysis of the reaction mixture via tlc confirmed that **15a-15c** were completely consumed and no by product formation occurred.

Table 3: Results of the reduction of 15a-c

Entry	15	R^1	R^2	16	Yield [%]
1	15a	MeO	Me	16a	92
2	15b*	MeO	Ph	16b	95
3	15c	CF_3	Me	16c	89

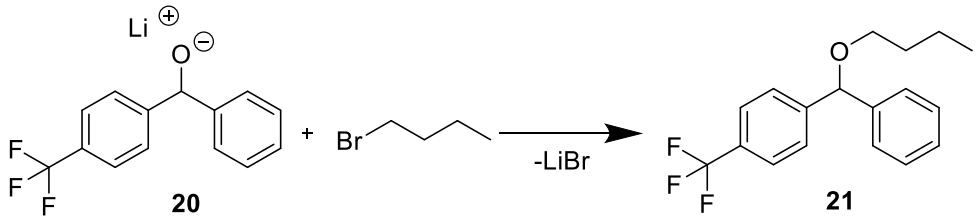
*Carried out in a 2:1 (V/V) mixture of MeOH and EtAc

At the time of this work the precursor benzophenone for alcohol **16d** was commercially difficult to access, so it was decided, to prepare the alcohol **16d** from 1-Bromo-4-(trifluoromethyl)benzene (**17)** by coupling an organometallic intermediate of it with benzaldehyde (**18)**. (Scheme 16). Since **17** is a very electron poor compound it seemed difficult to prepare the Grignard reagent with elemental magnesium. Therefore n-BuLi was chosen to generate the organolithium compound **19** by an lithium-bromine exchange. The organolithium reagent **19** should also show a better nucleophilicity, towards benzaldehyde **18,** than the Grignard compound[22]. This should contribute to a high yield of alcohol **16d.**



Scheme 16: Preparation of phenyl-(4-trifluoromethyl)phenyl)-methanol (**16d)**

The tlc analysis of the crude reaction mixture showed the formation of multiple side products and only 23% of the theoretical yield could be isolated via column chromatography. The reason might lie in the reactivity of the lithium alcoholate **20** which might attack the formed n-butyl bromide by a nucleophilic attack. See scheme 17.

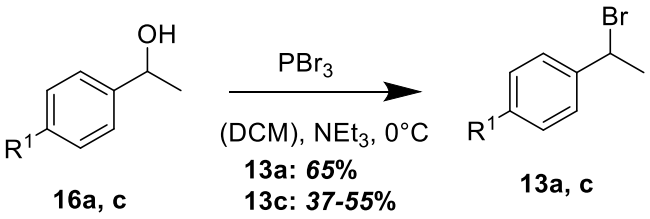


Scheme 17: Possible side reaction in the preparation of **16d**

But however since the obtained amount of **16d** was enough and the time of this work was limited no further investigations were carried out.

3.1.2 Preparation of the bromides 13a-d

Because of its simplicity it was decided to use phosphorus tribromide as the brominating reagent. Triethylamine was added to suppress a possible dehydration of the benzylic alcohols by scavenging the hydrogen bromide which was evolved during the reaction. Dichloromethane was chosen as the solvent because its relatively medium polar character should support an S_N2 reaction of the intermediate phosphites. (Scheme 18)



Scheme 18: Brominatinon of the benzyl alcohols using PBr_3

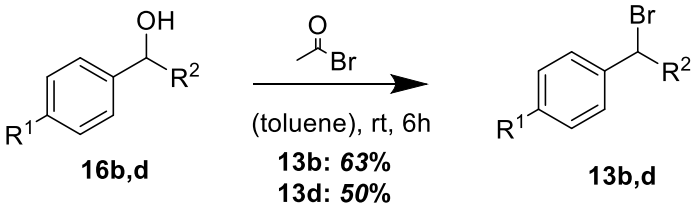
In theory one equivalent of phosphorus tribromide should be sufficient to brominate three times the amount of an alcohol. However when only 0.5 equivalents of PBr_3, with respect to the alcohol were employed the obtained yields were very different. Showing an acceptable yield of **13a** but only 37% of **13c** was obtained. If the reaction was carried out again using 3.0 equivalents, a yield of 55% was collected. (Table 4). It seemed that the strong electron withdrawing trifluoromethyl group significantly reduces the nucleophilicity of the alcohol **16c** towards the PBr_3. It should be also noted that in all cases the product, which was obtained after a simple basic aqueous work up, was pure enough to be used in the next steps.

Table 4: Yields of 13a-c:

Entry	**16**	**R^1**	**eq. PBr_3**	**13**	**Isolated yield**
1	16a	MeO	0.5	13a	65
2	16c	CF_3	0.5	13c	37
3	16c	CF_3	3.0	13c	55

In contrast, the reaction of alcohol **16b** with phosphorus tribromide led to many side products which were very difficult to separate from the product by column chromatography. Therefore **13b** and **13d** were prepared by bromination with acetyl bromide, as described in scheme 19.

The reaction was carried out according to known procedures [23,24]. The only change was to use toluene instead of the more dangerous and cancerogenic benzene.



Scheme 19: Halogenation with acetyl bromide

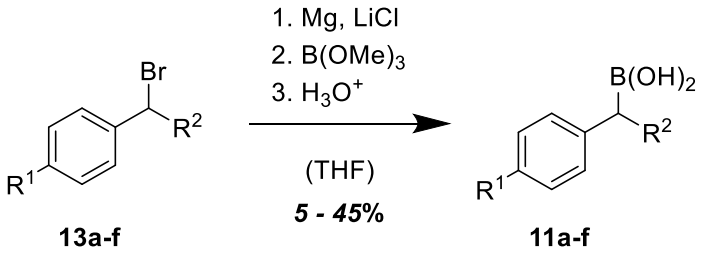
Table 5 summarizes the obtained yields together. The yields 63% and 50% fall or are close to the range of 58 - 74%[23,24] reported for similar compounds which were obtained by the original method in benzene. The yield for **13b** turned out to be 11% lower than the reported yields in benzene [24]. **13d** has not been reported to be synthesized using this procedure. Likewise to the preparation of **13a** and **13d** the obtained products were pure enough to be used in the next step.

Table 5: Reported yields in literature

Entry	13	R^1	R^2	Solvent	Yield 13	Reference
1	13b	MeO	Ph	Toluene/Benzene	65%/74%	this work/[24]
2	13d	CF3	Ph	Toluene	50%	this work
3	13g	Me	4Me-Ph	Benzene	58%	[23]
4	13h	MeO	4MeO-Ph	Benzene	77%	[24]

3.3.3 Attempts to synthesis of the boronic acids 11a-11f

With the bromides **13a-13f** in hand the procedure from Section 3.2 (Table 3, Entry 6) was applied with various success. The benzyhdryl bromid **13b** and **13f** compounds gave higher yields than their counterparts with only one phenyl group. No boronic acid could be obtained when **13d** was employed.



Scheme 20: Borylation of compounds **13a-f**

Table 6: Yields of the boronic acids **11a-f**

Entry	13	R1	R2	11	Yield [%]
1	13a	MeO	Me	11a	10
2	13b	MeO	Ph	11b	38
3	13c	CF3	Me	11c	24*
4	13d	CF3	Ph	11d	-
5	13e	H	Me	11e	5
6	13f	H	Ph	11f	45

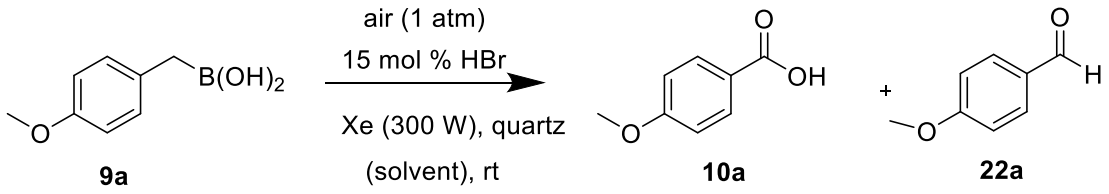
*Not able to characterize via NMR spectroscopy

It can be seen that there is a huge difference if there are two or just one phenyl group present. In the case when R^2 is a methyl group the yield is only 5-10% otherwise 38-45% (Table 7, Entries 1, 2 and 5, 6). In the case of **13c** a solid is obtained which shows similar characteristics in solubility to the other compounds. Also the IR-Spectra looked quite similar. But even when large amounts of substance analyzed, the obtained ^{1}H-NMR spectra looked as if only an insufficient amount of substance was dissolved. Therefore, it can be assumed that the obtained compound is not stable in contact with air. This is supported by the fact that in the NMR-Tubes the formation of a white precipitate was observed after a few hours. **11c** was not used. The obtained compounds **11a**+**11b** and **11e**+**11f** could be obtained pure, so that they could be used in the photoreactions.

4. Photoreactions of the boronic acids

4.1 Reaction conditions

As mentioned in section 2 to find the optimal condition for the photo oxidation of the boronic acids the effect of the solvent was studied. For this first attempts the amount of HBr was set to 15 mol%. The electron rich boronic acid **9a** was chosen as model substrate, since it should relatively easy to oxidize via single electron transfer. Thus a couple of test reactions were carried out using the conditions described in scheme 21. The yield of the aldehyde **22a** and benzoic acid **10a** was determined by ^{1}H-NMR spectroscopy using CH_2Br_2 as internal standard.



Scheme 21: Reactions to investigate the solvent effect

Table 7: Solvent effects on the oxidation of the boronic acids

Entry	Solvent	Time [h]	Yield of 10a* [%]	Yield of 22a* [%]	Ratio 10a:22a
1	Dichloromethane	18	20	18	53:47
2	Ethanol	18	53	6	90:10
3	Acetonitrile	18	62	14	82:18
4	Ethylacetate	10	72	n.d.	>99:1
5	Water	6	NR		n.a.
6	Tetrahydrofurane	18	comp.		n.a.
7	Acetone	5	86	n.d.	>99:1

*Determined by ^{1}H-NMR, NR: no reaction, comp.: the ^{1}H-NMR was too complicated, n.d.: the yield was below the detection limit

As seen in table 8, entry 6, if **9a** was irradiated in THF the reaction mixture turned out to be very complicated. The reason might be that THF can also react in this conditions, since it is also known to form highly reactive ether peroxides when just exposed to air. The irradiation might accelerate this process. The fact that boronic acids can be stabilized with water or moisture[25] may contribute that no reaction could be observed in water. When dichloromethane or ethanol are used as solvent the overall yield is only 38% respectively 59% with poor chemo selectivity. When the reaction was carried out in acetonitrile the overall yield rose up to 76%. This is consistent with the previously mentioned fact in section 1.2. that acetonitrile can assist the bonding cleavage due to its higher nucleophilicity [4,5]. The same might be said about

acetone and ethyl acetate with the additional fact that it seems the also to promote the oxidation of the intermediate aldehyde **22a** to 4-methoxybenzoic acid (**10a**). Since the highest yield of benzoic acid **10a** was obtained in acetone, it was used as solvent for the further investigations on the amount of the catalyst. Table 8.

Table 8: The effect of the amount of HBr on the yield of aldehyde 22a and benzoic acid 10a

Entry	Catalyst	Time [h]	Yield of 10a* [%]	Yield of 22a* [%]	Ratio 10a:22a
1	HBr (1 mol %)	12	25	Trace	n.a.
2	HBr (5 mol %)	12	32	Trace	n.a.
3	HBr (10 mol %)	12	78	n.d.	>99:1
4	HBr (15 mol %)	5	86	n.d	>99:1
5	No catalyst	5	NR		n.a.

*Determined by ^{1}H-NMR, NR.: no reaction, n.d.: the yield was below the detection limit

Entry 1 in Table 8 shows clearly that HBr catalyzes the oxidation, since only 1 mol % already afforded a yield of 25%. Also the selectivity was good. The reaction without hydrogen bromide was stopped after 5 hours since the tlc analysis of the reaction mixture showed still only the spot of the starting material.

However since the hydrogen bromide can evaporate during long reaction times it was checked if alkali bromides can show similar performance and therefore might be a more reliable bromine source.

Table 9: Reactions with different bromine sources

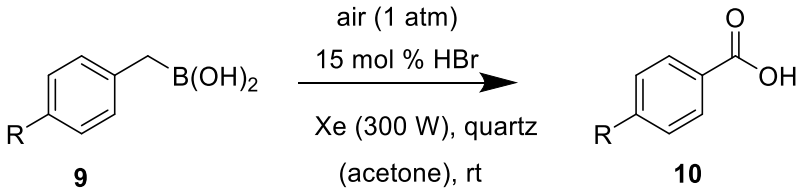
Entry	Catalyst	Time [h]	Yield of 10a* [%]	Yield of 22a* [%]	Ratio 10a:22a
1	LiBr (15 mol %)	12	trace	trace	n.a.
2	NaBr (15 mol %)	12	26	14	35:65
3	KBr (15 mol %)	12	55	12	82:18

*Determined by ^{1}H-NMR

Here lithium bromide showed only a little effect. Although the overall yield was 67% in case of KBr, table 9 entry 3, there was still an amount of aldehyde left. This suggests that an acidic environment is important for the oxidation of the aldehyde **22a.**

4.2 Photoreactions of primary boronic acid which different substituents

To determine electronic effects in this oxidation procedure, the primary boronic acids were reacted according to the most effective conditions in the previous section. Table 10 summarizes the yields of benzoic acid **10**. Scheme 22 illustrates the conditions.



Scheme 22: Oxidation of primary boronic acids

Table 10: Effect of the substitution

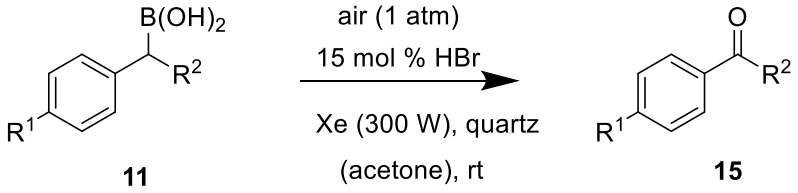
Entry	9	R	10	Time (h)	Yield (%)*
1	9a	MeO	10a	5	87
4	9b	*tert*-Butyl	10b	9	69
2	9c	F	10c	8	54
3	9d	Cl	10d	18	77
6	9e	COOMe	10e	10	60

*Isolated yield after preparative tlc

If the boronic acid contains the strong electron donating methoxy-group in para position, the reaction was completed in only 5 hours and afforded the highest yield. If the weak electron donating t-Butyl was added to the aromatic ring the yield went down to 69%. In contrast (1-(4-chlorophenyl) ethyl)-boronic acid (**9d)** which contains the weak electron withdrawing chlorine reacted to 77% of **10d**. When the strong electron withdrawing acyl group was attached to the phenyl group the yield broke down to 60%. However when fluorine was part of the aryl group only a yield of 54% was collected. This might be due to a competitive fast photodecomposition of the intermediate aldehyde [26].

4.3 Photoreactions of the secondary boronic acids

When the secondary boronic acids were reacted under the same conditions the results were quite different. (Table 11 and scheme 23)



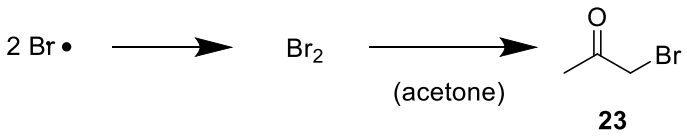
Scheme 23: Photoreactions of secoundary boronic acids

Table 11: Reactions using the condition of the previous section

Entry	11	R1	R2	15	Time [h]	Yield [%]
1	11a	MeO	Me	15a	9	53[#]
2	11b	MeO	Ph	15b	9	NR
3	11e	H	Me	15e	7	22[*]
4	11e	H	Me	15e	9	28[*]
5	11e	H	Me	15e	14	27[*]
6	11f	H	Ph	15f	12	NR
7	11f	Ph	Ph	15f	16	NR
8	11f	Ph	Ph	15f	20	NR

*Yield calculated from the ^{1}H-NMR of the crude mixture, NR: no reaction, [#]after preparative tlc

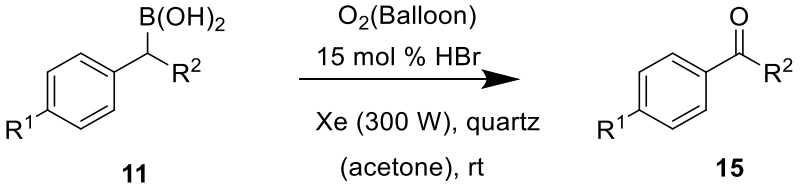
Only in the case of boronic acid **11a** a acceptable yield of **15a** could be isolated. Benzhydrylboronic acid (**11f**) and ((4-methoxyphenyl)(phenyl)-methyl)boronic (**11b**) acid were almost inert under the conditions from section 4.2. If R^2 was exchanged with the methyl some acetophenone (22-28 % yield) was formed according to the ^{1}H-NMR spectra (**N1-N3**) of the crude reaction mixture, but some starting material was still present. Since the yield was almost the same if the mixture was irradiated for 8.5 or 14 hours it was clearly that longer irradiation time would not lead to a full conversion of the starting material. The cause could have been a loss of bromine via bromination of the solvent acetone. This might be possible in case of the combination of two bromine radicals to molecular bromine. The later one is known to react easy with acetone to bromo acetone **23.** See scheme 23



Scheme 24: Bromination of acetone

4.4 Photoreactions in oxygen atmosphere or in acetonitrile

To further investigate this issue and whether **11f** and **11b** are reactive at all, reactions were carried out under oxygen atmosphere. (Scheme 25 and Table 12).



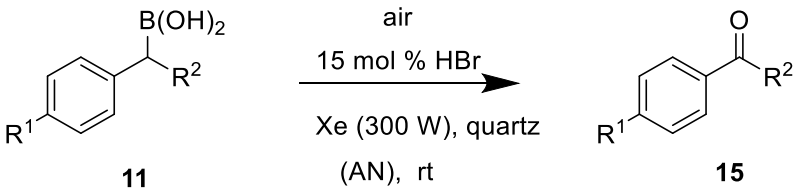
Scheme 25: Reaction in oxygen

Table 12: Yields of the reactions in oxygen

Entry	11	R1	R2	15	Time [h]	Yield*
1	11b	MeO	Ph	15b	9	45
2	11e	H	Me	15e	8.5	58-67
3	11e	H	Me	15e	14	66-69
4	11f	Ph	Ph	15f	12	23

*Yield calculated from the ^{1}H-NMR of the crude mixture,

As expected the yield of **11f** increased. Also a notable conversion of **11f** to benzophenone occurred (**15f)** but this yielded only 23% of the ketone. The boronic acid **11b** which contains the methoxy group in para position in one of the two phenyl moieties yielded 45% of the corresponding ketone **15b**. This shows once more that electronic enrichment is a key factor for the oxidation. However since the use of an oxygen atmosphere might restrict the employability of this transformation it was tried whether the boronic acids can be oxidized in an appropriate time and yield with air. Taken into account that also the nucleophilicity of the solvent might be important for an effective cleavage of the carbon boron bond, acetonitrile was reviewed as potential solvent to assist the cleavage better than acetone. Thus the boronic acids **11a**, **11e** and **11f** were reacted again in the open the air but with acetonitrile as the solvent (Scheme 26)



Scheme 26: Reactions in air and acetonitrile

Table 13: Reactions in acetonitrile

Entry	11	R1	R2	15	Time [h]	Yield*
1	11a	MeO	Me	15a	9	80
2	11e	H	Me	15e	12	62
3	11f	H	Ph	15e	12	NR

*Isolated yield after preparative tlc.

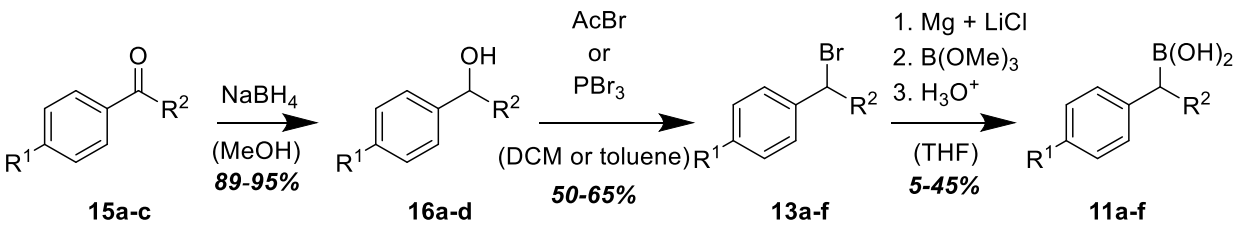
Boronic acid **11f** still showed no reactivity. In the cases of the boronic acids which contain only one phenyl moiety the yield rose up in comparison to the reactions in acetone and air atmosphere.

5. Results and Discussion

In this work secondary benzyl boronic of the general structures **11** and **9** should have been synthesized and investigated if they can undergo a photo induced cleavage of carbon boron bond with subsequent oxidation to benzoic acids or ketones.

5.1 Synthesis of the boronic acids

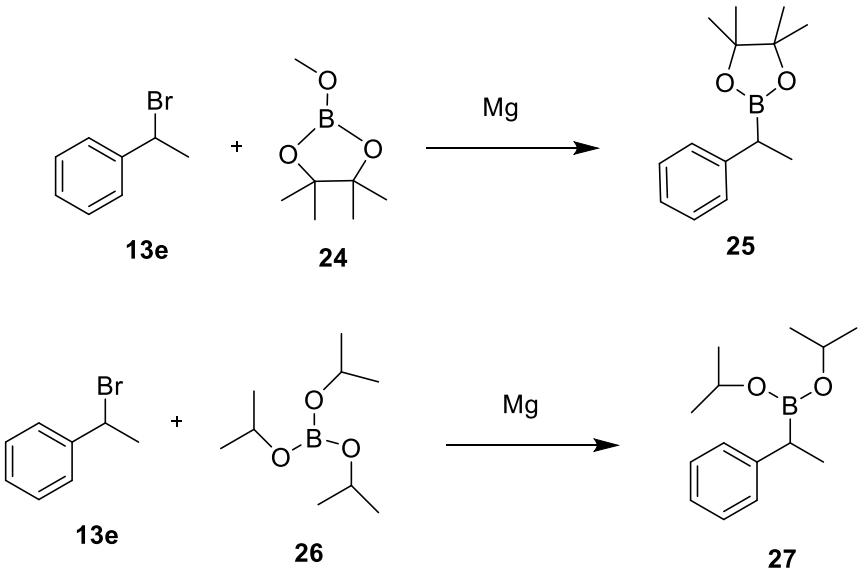
While reactions of trimehtyl borate and organolithium reagents could not yield the desired boronic acids. Grignard reagents and trimethyl borate afforded the desired products in amounts that could be used in the photo reactions. It was noticed that lithium chloride could increase the reactivity of the organomagnesium compounds towards trimethyl borate. Not available bromine precursors were obtained by reducing the corresponding ketones followed by brominating of the alcohols **16** with phosphorus tribromide or acetyl bromide. It was notable that the reaction with PBr_3 only yielded the bromine in case R^2 was a methyl group. Scheme 27 summarizes the results.



Scheme 27: Synthetic path way to obtain the boronic acids

However the obtained yields were still very poor. This is consistent with other reported synthesis to obtain similar boronic acids which also reported low yields [27]. A starting point for

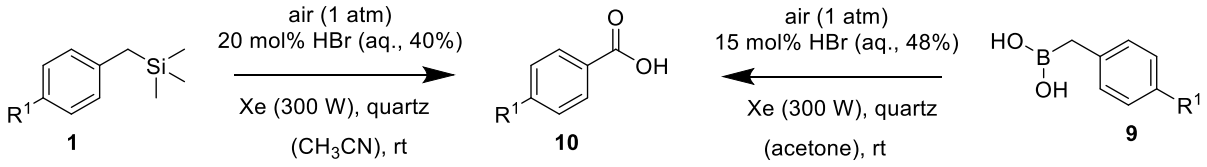
further optimization of the last step could be an exchange of the borates. Derivatives of pinacolborate **(24)** for example should be able to suppress the formation of side products like borinic acid and boranes more effective due to increased steric hindrance. But it should be taken in consideration that the ester intermediate maybe more difficult to hydrolyze due to the same steric interference. The hydrolysis of the resulting borates often requires refluxing the compound for several days in aqueous acids. [28] A suitable compromise could be the employment of triisopropyl borate (**26)** as borylation reagent. Scheme 28 illuminates these alternative ways.



Scheme 28: Possible alternative borylation reagents

5.2 Photoreactions

The highest yields and selectivity (with respect to benzoic acid **10**) were obtained by using acetone as solvent. The effect of the amount of the catalyst HBr was investigated in the range of 1 mol% to 15 mol%. It turned out that the minimum quantity required for a complete oxidation of boronic acid and intermediate aldehyde below a reaction time of 12 hours is 15 mol%, respectively. When alkali metal halides were used as bromine source the reaction proceeded (expect with LiBr) but the mixture still contained a relative high amount of aldehyde. This suggests that an acidic environment plays a key role for the oxidation of the intermediate aldehyde. Comparing the yields of benzoic acid obtained from boronic acids which those afforded by their silane counterparts, there is only a slight difference. On the other hand an overall increase of reaction time was noted. Whether the properties of the carbon boron bond or the solvent (acetonitrile was exchanged with acetone) contributes more could not by determined. (See table 14)



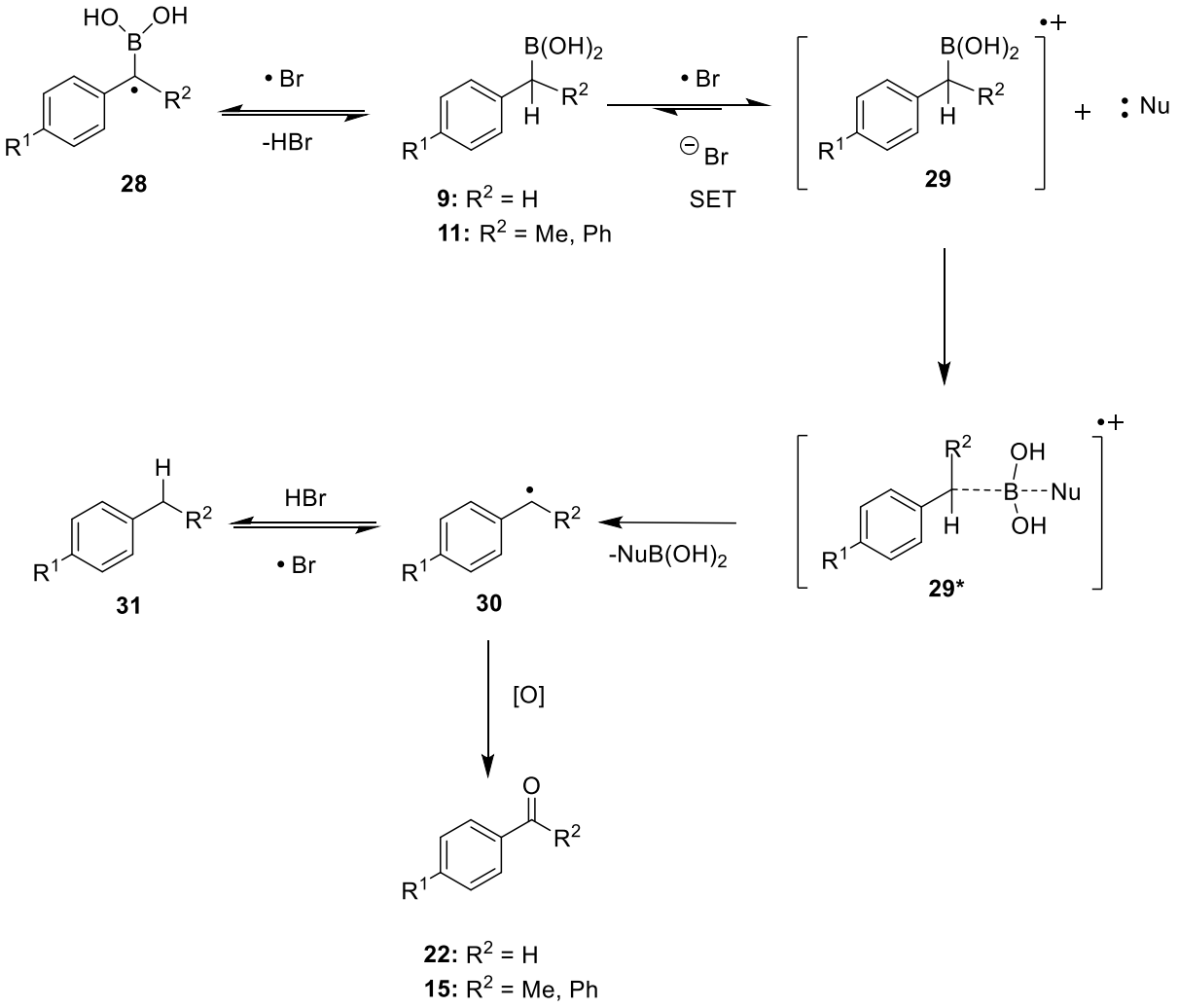
Scheme 29: Cleavage of carbon boron and carbon silica bonds

Table 14: Yields of 10 compared with selected values from literature[7]

Entry	10	R^1	yield C-Si cleavage [%][7]	time [h]	yield C-B cleavage [%]	time [h]
1	10a	MeO	91	3.5	87	5
2	10b	*tert*-Butyl	66	3	69	9
3	10c	F	82	9	54	8
4	10d	Cl	70	5.5	77	18
5	10e	COOMe	66	9	60	10

The increase of reaction time and decrease of the yield correlates for each substance positively with the electronic effect of the substituent of the aryl group. Strong electron donating substituents affect high yields and shorter reaction times and vice versa. And outliner of this trend is the fluorine containing boronic acid which yielded the least amount of carboxylic acid (Table 14, entry 3).

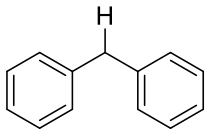
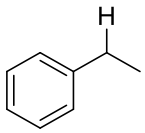
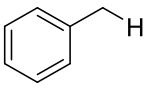
On the other side the secondary boronic acids only (1-(4-methoxyphenyl)ethyl)-boronic (**11a)** acid exhibits similar reactivity in acetone. Boronic acid **11e** showed only little reactivity. In this case the methoxy group showed big influence on the yield, which is increased. (29% vs 53%). The boronic acids with two phenyl groups **11b** and **11f** only showed significant reactivity when additional oxygen was supplied. When the solvent acetone is exchanged with acetonitrile the yield of 4-methoxyactophenone (**15a)** and actophenone (**15f)** rose up. It seems to be clearly that acetonitrile is more capable to assist the cleavage of the carbon boron bond. In the initial solvent screening the reaction time in acetonitrile was quite high but it also need to be considered that this time also included the oxidation from the aldehyde intermediate to the carboxylic acid.
Assuming that the properties of the carbon boron bond might in every boronic acid be the same and taken the literature mentioned in section 1.2 into account, the following overall reaction mechanism might be possible.



Scheme 30: Plausible reaction mechanism

At first, when the reaction mixture is irradiated a bromine radical is formed by photolysis of HBr. This bromine radical could now react with a boronic acid **9** or **11** in two different ways. First hydrogen abstraction may occur which leads to radical **28** [4]. The formation of **28** should depend on its thermodynamic stability. For example if the C-H dissociation energies of the corresponding hydrocarbons **31** are compared (Table 15), it can be concluded that a boronic acid where R^2=Ph should be more likewise to underwent hydrogen abstraction than one where R^2=Me followed by R^2=H. However this radical can be quenched by some hydrogen donor e.g. HBr or water which returns the starting material.

Table 15: Bond dissociation energies (E_D) for selected hydrocarbons [29]

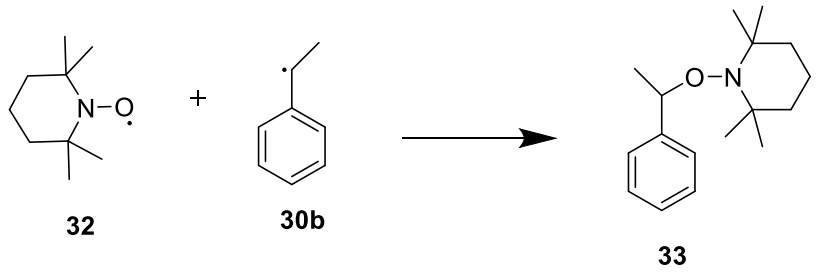
31	**E_D [kJ/mol]**
 **31a**	356
 **31b**	364
 **31c**	374

The other way is the desired singe electron transfer, which forms the radical cation **29** that undergoes a fast carbon boron bond cleavage to yield a benzyl, phenylehtyl or diphenylmehtyl radical **30**. This might be also an equilibrium since a higher oxygen concentration can accelerate the reaction rate. The radical cation will be subsequently oxidized to an aldehyde or ketone. The oxidation of the aldehyde is also light mediated and are discussed elsewhere [30]. All in all the previous work showed that boronic acids could be useful precursors to obtain benzoic acids or ketones just by oxidation with air. Benzyl boronic acids showed good reactivity. Diphenylmehtyl boronic acids found to be reactive only in oxygen atmosphere. Phenylethyl boronic acids are placed in the middle and their reactivity depends very much on the solvent.

6. Outlook

Although it could be showed that boronic acid functionalities have great potential to be used as substrates in green and mild reaction condition, the different reactivity of phenylethyl and benzyl boronic acids in acetone and acetonitrile might be some draw back. In addition the high reaction times can be seen as disadvantage. Since it seems that the ability of the solvent to assist the cleavage of the carbon boron bond is quite necessary in the most cases, in the further optimization of this oxidation procedure it should be focused on the reaction medium. To improve this issue it should be investigated if Lewis bases might be added to improve the bond cleavage in acetone, acetonitrile and the other solvents. One promising compound herein might be triehtylamine since it should be able to coordinate on the vacant p-orbtial of the boron center. On the other hand the usage of simple ammonia bromides may more consist with the notion of green chemistry. So further investigations should be carried out employing ammonia bromides (e.g. NH_4Br, Et_3NHBr) and their mixtures with HBr as additives.

The proposed mechanism of the reaction the possible mechanism should be proved to gain further knowledge about this reaction. This could be done by trapping the proposed radical species **30** and **28** with a radical scavenger. For example 2,2,6,6-Tetramethylpiperidinyloxyl (TEMPO) (**32**) could be sufficient for this purpose. The formed compounds 30 can then be isolated and characterized [31]. (Scheme 31)

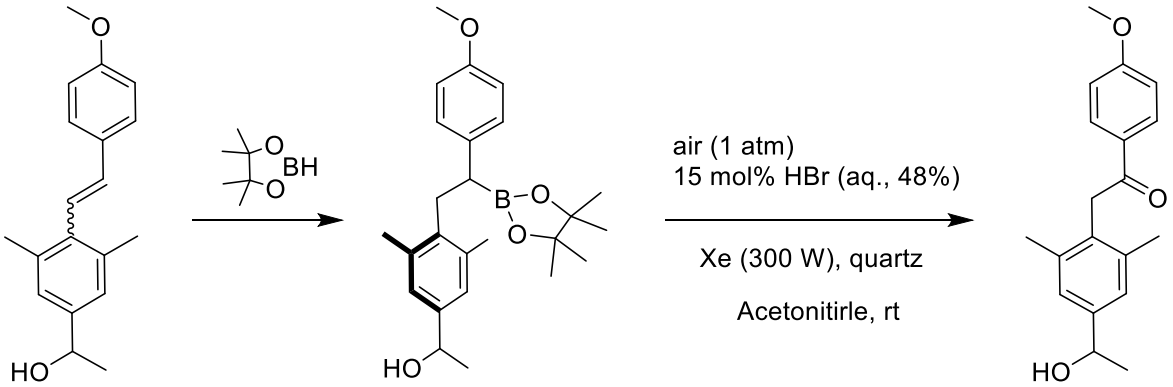


Scheme 31: Example for probing the reaction mechanism with TEMPO (**32**)

This insight in the reaction mechanism might provide the knowledge of intermediates which can be used as starting point to develop new synthetic methods.

All in all if the developed method is further optimized it can be an alternative to hydroboration processes with subsequent oxidation. An example therefore might be the synthesis of a diphenylethanone moiety **34** which contains a hydroxyl group from a stilbene derivate **36**. In

that case **37** can underwent hydroboration with pinacolborane. The resulting boronic ester can then be directly oxidized to the ketone. The hydroxyl group should be hardly affect. (Scheme 32)



36 **37** **34**

Scheme 32: Exemplary application of the developed photochemical procedure in a synthesis sequence.

Because of such application possibilities the question arises to what extent sensitive functional groups can be tolerated. If this should be the case, the light-induced oxidative cleavage of carbon boron bonds might represent a green and efficient method for the synthesis of ketones and carboxylic acids.

7. Experimental section

7.1 General information

All reactions involving air- or moisture-sensitive reagents were involved were carried out under an argon atmosphere using standard Schlenk techniques.

7.1.1 Reagents and solvents

4-Methoxyacetophenone, 4-(trifluoromethyl)-acetophenone, (4-methoxyphenyl)-(phenyl)-methanone, 1-bromo-4-(trifluoromethyl)-benzene, trimethyl borate, and acetyl bromide were purchased from Energy Chemical and used as received.

1-Bromo-1-phenylethane, bromo diphenylmethane, and diphenylmethane were purchased from Tokyo Chemical Industry Co, Ltd and used without purification. Hydrogen bromide (48 wt. in H_2O), phosphorus dibromide and n-butyl lithium (1.6 mol/l in Hexane) were bought from Alfa Sear and used as received. TETRAHYDROFURAN was distilled over potassium/benzophenone under Argon right before use. Dichloromethane and Toluene, were dried over fused $CaCl_2$ according to Literature [32]. LiBr, NaBr and KBr solutions were obtained by dissolving a suitable amount to get a solution with c= 8.9 mol/l

7.1.2 Photoreactions

All photoreactions were carried out in dry quartz reaction tubes. As light source a 300 W Xenon lamp system PLS XE300 from Perfect Light was used. A typical setup is shown in figure 2.

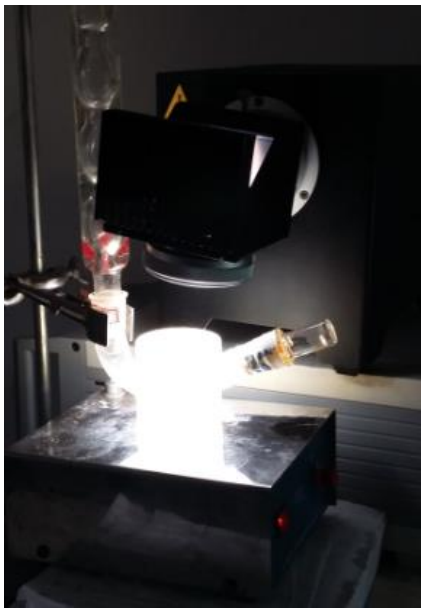


Figure 2: A typical setup for the photoreactions

7.1.3 IR-Spectroscopy

IR Spectra of the boronic acids in a KBr matrix were obtained with a Perkin Elmer FT-IR Spectrometer “Spectrum Two”.

7.1.4 NMR-Spectroscopy

^{1}H-NMR und ^{13}C-NMR-Spectra were recorded with an AVANCE III 400 spectrometer. The chemical shifts are given in ppm and refer to tetramethylsilane or the residue proton signal of the solvent in the ^{1}H spectra. Coupling constants are given in Hertz. The multiplicities are abbreviated as followed: s: singlet, d: doublet, dd: doublet of doublets, t: triplet, q: quartet, m: multiplet, br: broad

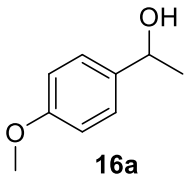
7.1.5 MS-Spectroscopy

Mass spectra were obtained with electron ionization (EI) using an Agilent Technologies 5937-N spectrometer.

7.2 Synthesis of the starting materials

7.2.1 Preparation of alcohols 16a-d

1-(4-Methoxyphenyl)-ethanol



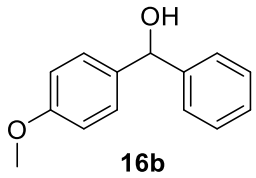
16a

To a solution of 27 mmol (4.00 g) of 4-methoxyacetophenone (**15a**) in 20 ml Methanol in a round bottom flask, 40 mmol (1.47 g) $NaBH_4$ was added portion wise. Then the reaction mixture was stirred till no more hydrogen evolution was observed and the tlc analysis showed that there was no starting material left. After that time the reaction mixture was poured into a separation funnel containing 20 ml H_2O and 30 ml of ethyl acetate. The organic layer was separated and the aqueous layer was extracted wit EtAc (3x20 ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent yielded the product as a colorless liquid. 3.74 g (92% of Theory).

This was used in the next step without further purification. The ^{1}H-NMR spectrum is in agreement with previous in literature reported spectral data [33].

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 8.44 Hz, 2 H, 2 x Ar*H*) 6.87 (d, *J* = 8.62 Hz, 2 H, 2 x Ar*H*) 4.80 (q, *J* = 5.93 Hz, 1 H, C*H*CH) 3.79 (s, 3 H) 2.61 - 3.00 (m, 1 H, O*H*) 1.45 (dd, *J* = 6.42, 0.73 Hz, 3 H, C*H*CH_3)

(4-methoxyphenyl)(phenyl)-methanol

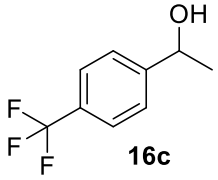


16b

To a solution of 30 mmol (6.36 g) of (4-Methoxyphenyl)(phenyl)-methanone (**15b**) in a mixture of 20 ml Methanol and 10 ml EtAc in a round bottom flask, 40 mmol (1.47 g) $NaBH_4$ was added portion wise. Then the reaction mixture was stirred till no more hydrogen evolution was observed and tlc analysis showed that there was no starting material left. After that time the reaction mixture was poured into a separation funnel containing 20 ml H_2O and 30 ml of Ethyl acetate. The organic layer was separated and the aqueous layer was extracted wit EtAc (3x20 ml) and dried over anhydrous Sodium sulfate. Evaporation of the solvent yielded the product as white solid 6.12 g (95% of Theory), which was used without purification in the next step. The ^{1}H-NMR Spectrum is in agreement with previous literature [34].

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 - 7.56 (m, 7 H, 7 x Ar*H*) 6.85 (d, *J* = 8.62 Hz, 2 H, 2 x Ar*H*) 5.78 (s, 1 H, C*H*OH) 3.77 (s, 3 H OCH_3)

1-(4-(trifluoromethyl)phenyl)-ethanol



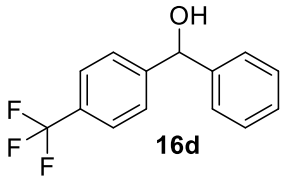
16c

To a solution of 30 mmol (5.69 g) of 4-(trifluoromehtyl)-acetophenone (**15c**) in 30 ml in Methanol a round bottom flask, 45 mmol (1.70 g) $NaBH_4$ was added portion wise. Then the

reaction mixture is stirred till no more hydrogen evolution occurred. After that time the reaction mixture was poured into a separation funnel containing 20 ml H_2O and 30 ml of ethyl acetate. The organic layer was separated and the aqueous layer was extracted wit EtAc (3x20 ml) and dried over anhydrous Sodium sulfate. Evaporation of the solvent yielded the product as an orange liquid. 5.11 g (89% of Theory). The ^{1}H-NMR Spectrum is in agreement with previous literature [35].

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.07 Hz, 2 H, 2 x Ar*H*) 7.48 (d, *J* = 8.44 Hz, 2 H, Ar*H*) 4.95 (q, *J* = 6.42 Hz, 1 H, C*H*CH_3) 2.34 (br. s., 1 H) 1.50 (d, *J* = 6.42 Hz, 3 H, CHC*H*$_3$)

Phenyl-(4-(trifluoromethyl)phenyl)-methanol



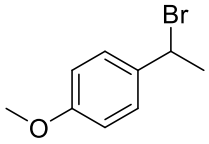
16d

A dry round bottom flask under argon was charged with 30 ml anhydrous tetrahydrofuran and 20 mmol (2.8 ml) of 1-bromo-(4-trifluoromethyl)benzene and cooled down to -78°C. At this temperature 20 mmol (1.6 mmol/l in hexane) of n-buthyl lithium was added in 20 min. The mixture was stirred for one hour. After that 20 mmol of (2.6 ml) of benzaldehyde was added. Saturated NH_4Cl-Solution was added to quench the reaction. After that the reaction mixture was allowed to reach room temperature. The organic layer was separated and the aqueous layer extracted with ethyl acetate (3x20 ml). The combined organic layers are washed with 20 ml brine and dried over anhydrous sodium sulfate. Evaporation of the solvent yielded an orange oil. Further purification by column chromatography on silica (Eluent 8:1 PE/EtAc) yielded the final product as 1.16 g of a white solid (23% of Theory). ^{1}H-NMR Spectra is consent with previous reported data [34].

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (s, 1 H, Ar*H*) 7.38 - 7.64 (m, 8 H, 8 x Ar*H*) 5.87 (s, 1 H, C*H*) 3.94 (br. s, 1 H, CHO*H*)

7.2.2 Preparation of bromides 13a-d

1-(1-bromoethyl)-4-methoxy-benzene

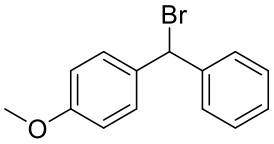


13a

A dry round bottom flask witch was equipped with a magnetic stirrer under argon was charged with 16 mmol (2.4g) of 1-(4-methoxyphenyl)-ethanol (**16a**). Then 50 ml anhydrous dichloromethane and 2.5 mmol (0.4 ml) anhydrous trimethylamine were added. The mixture was cooled to 0°C. At this temperature 8 mmol (1 ml) of phosphorus tribromide was added slowly with a syringe. The reaction was stirred till all the starting material was consumed (ca. 30-60 min), as showed by tlc (Eluent: PE/EtAc 10:1, R_f(**13a**)=0,85). After that the reaction mixture is poured into a separation funnel containing 20 ml of a saturated $NaHCO_3$-solution. The organic layer was separated. And the aqueous layer was extracted 3 times with 30 ml of DCM. Afterwards the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed, yielding a yellow sluggish residue which was diluted with diethyl ether (ca. 10 mL) and passed through a syringe filter. Evaporation of the diethyl ether yielded the product **13a** as slightly orange oil, 2.22 g (65% of theory). The ^{1}H-NMR is consistent with literature [36].

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 8.80 Hz, 2 H, Ar*H*) 6.90 (d, *J* = 8.80 Hz, 3 H, Ar*H*) 5.29 (q, *J* = 6.72 Hz, 1 H, C*H*CH_3) 3.83 (s, 3 H, OC*H*$_3$) 2.08 (d, *J* = 6.97 Hz, 3 H, CHC*H*$_3$)

1-(bromophenylmethyl)-4-methoxy-benzene

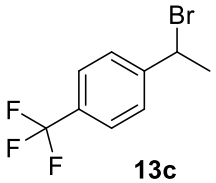


13b

A dry round bottom flask which was equipped with a magnetic stirrer was charged subsequently with 28 mmol (6.0 g) of (4-methoxyphenyl)(phenyl)-methanol (**16c**) and 50 ml of anhydrous toluene. After that 100 mmol (7.4 ml) of acetyl bromide was added slowly via syringe and the reaction was stirred for 6 hours. Toluene and the excess acetyl bromide were remove under reduce pressure, yielding a dark green sluggish residue. This residue is diluted with ca. 50 ml of diethyl ether and washed subsequently with $NaHCO_3$-solution till the pH was neutral. After that the organic layer was washed with brine (2x25 ml). The organic layer was dried over $MgSO_4$. Evaporation of the solvent yields the product as a dark green oil which crystallized spontaneously to a green solid. (5.17 g, 63% of theory). ^{1}H-NMR is consistent with literature [24].

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 - 7.67 (m, 2 H, Ar*H*) 7.17 - 7.41 (m, 5 H Ar*H*) 6.88 (d, *J* = 8.80 Hz, 2 H, Ar*H*) 6.33 (s, 1 H, C*H*) 3.82 (s, 3 H, OCH_3)

1-(1-bromoethyl)-4-(trifluoromethyl)-benzene



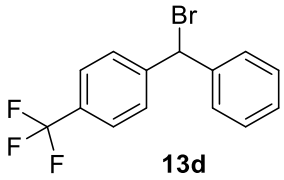
13c

A dry round bottom flask which was equipped with a magnetic stirrer under argon was charged with 15 mmol (2.4 g) of 1-(4-(trifluoromethyl)phenyl)-ethanol (**16c**). Then 50 ml anhydrous dichloromethane and 2.5 mmol (0.4 ml) anhydrous trimethylamine were added. 45 mmol (4.4 ml) of phosphorus tribromide were added slowly with a syringe. The reaction is stirred till all the starting material is consumed (ca. 30-60 min), as monitored by tlc. After that the reaction mixture was poured into a separation funnel containing 20 ml of a saturated $NaHCO_3$-solution. The organic layer was separated. And the aqueous layer was extracted 3 times with 30 ml of

DCM. Afterwards organic layers were dried over anhydrous $MgSO_4$. The solvent was removed, yielding a yellow sluggish residue which was diluted whit diethyl ether (ca. 10 mL) and passed through a syringe filter. Evaporation of the diethyl ether yielded the product **13c** as orange oil, 2.10 g (55% of theory). The ^{1}H-NMR is consistent with literature [35].

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 - 7.67 (m, 2 H, 2 x Ar*H*) 7.55 - 7.61 (m, 2 H, 2 x Ar*H*) 5.23 (q, *J* = 6.91 Hz, 1 H, C*H*CH_3) 2.07 (d, *J* = 6.79 Hz, 3 H, C*H*CH_3)

1-(bromo(phenyl)methyl)-4-(trifluoromethyl)-benzene



13d

A dry round bottom flask equipped with a magnetic stirrer was charged with 4.6 mmol (1.16 g) of Phenyl-(4-(trifluoromethyl)-phenyl)-methanol (**16d)** and 20 ml of anhydrous toluene. After that 25 mmol (1.8 ml) of acetyl bromide was added slowly via syringe. After that the reaction was stirred for 6 hours. Toluene and the excess acetyl bromide were remove under reduce pressure, yielding a dark green sluggish residue. This residue was diluted with ca. 50 ml of diethyl ether and washed subsequently with $NaHCO_3$-solution till the pH was neutral. After that the organic layer was washed with brine (2x25 ml). The organic layer was dried over $MgSO_4$. Evaporation of the solvent yielded the product as a dark green oil which was crystallized by adding PE to a green solid. (5.17 g, 63% of theory). ^{1}H-NMR is consistent with literature [37].

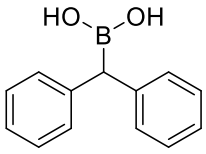
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 - 7.80 (m, 9 H, 9 x Ar*H*) 6.28 (s, 1 H, C*H*)

7.2.3 Synthesis of the boronic Acids

Attempts to the synthesis with organolithium reagents

A three neck round bottom flask containing a solution of 20 mmol (3.1 ml) diphenylmethane **11** was cooled to 0°C. At this temperature 12.5 ml of n-BuLi (c=1.6 mol/l in hexane) was added drop wise via a dropping funnel in 30 minutes. During this time the color of the solution turned into a bright red which confirmed the formation of the lithium reagent. The solution was allowed to reach room temperature and was stirred for 15 minutes. The reaction mixture was cooled to -78°C (respectively -40°C or 0°C). After that trimehtyl borate 60 mmol (6.7 ml) was added and the mixture was stirred for another hour, after that the reaction was quenched with water and allowed to reach room temperature. At this temperature 20 ml of HCl a.q. (c=1 mol/l) was added. The organic layer was separated and the aqueous layer was extracted with EtAc. Removal of EtAc under reduced pressure leaded a yellow suspension. This was diluted with DCM and the precipitated boric acid $B(OH)_3$ was removed by filtration. DCM was removed again under reduced pressure yielding a brown oil. No solid could be precipitated by adding PE and the NMR of this crude product also showed no evidence for the formation of the desired compound.

Benzhydrylboronic acid – Procedure 1



11f

An apparatus consisting of a 3 neck round bottom flask, magnetic stirrer, dropping funnel and condenser was charged with 16 mmol of magnesium shavings (389 mg). Next, 20 ml of anhydrous tetrahydrofuran and one granular of iodine were added. After that 16 mmol (3,96g) of benzhydryl bromide (**13f**) dissolved in 10 ml anhydrous tetrahydrofuran were added drop wise in half an hour. Subsequently the reaction mixture was refluxed for 1 hour. After the solution turned to a dark black it was cooled back to room temperature. At this temperature 48 mmol (5.4 ml) of trimethyl borate was added. The reaction was stirred for one hour, cooled back to RT and subsequently quenched with 20 ml of HCl a.q. (c=1.0 mol/l). The organic layer was separated and the aqueous layer was extracted three times with 25 ml of EtAc. The

combined organic layers were dried over anhydrous sodium sulfate. Evaporation of the solvent afforded a yellow oil. This oil was diluted with dichloromethane, causing the inorganic boric acid $B(OH)_3$ to precipice which was then filtered off. Evaporation of DCM yielded a green crystalline solid which was then suspended in PE and filtered of. This solid was washed with water and PE several times till it turned white. 1.00 g (30 % of Theory) of 11a was obtained.

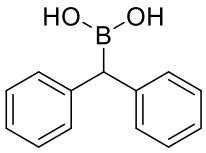
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.17 - 7.22 (m, 2 H, 2 x Ar*H*) 7.10 - 7.16 (m, 2 H, 2 x Ar*H*) 7.01 - 7.07 (m, 2 H, 2 x Ar*H*) 4.80 (s, 1 H, C*H*)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.14 (s, 2 C, C_{Ar}) 128.19 (s, 4 C, 4 x C_{Ar}) 127.80 (s, 4 C, 4 x C_{Ar}) 125.50 (s, 2 C, 2 x C_{Ar}) 56.02 (s, 1 C, *C*H)

IR (KBr) $\tilde{\nu}$ [cm^{-1}]: 3419 (m, b) [O-H], 3061 (s), 3024 (s), 2892 (s), 1598 (m), 1493 (s), 1449 (s), 1031 (s) [B-O], 1003 (w)

MS, *m/z* (%): 167 (100) [M^+ - $B(OH)_2$]

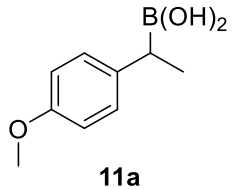
Benzhydrylboronic acid – Procedure 2



11f

Magnesium shavings, 5 mmol (122 mg), and anhydrous lithium chloride, 2.5 mmol (494 mg) were put in in a dry Schlenk tube which was equipped with a magnetic stirrer. Followed by 5 ml of anhydrous THF and one granular of iodine. After that 2 mmol (494 mg) of benzhydryl bromide **13f** is added as solution in 2 ml of anhydrous THF. The reaction is stirred for 20 min till all LiCl is dissolved. Followed by the addition of 6 mmol (0.7 ml) of $B(OMe)_3$. The same workup procedure as in synthesis procedure 1 was applied. Yielding 156 mg (37 % of theory). The analytical data was consisted with the product obtained by procedure 1.

(1-(4-methoxyphenyl)ethyl)-boronic acid



11a

(1-(4-methoxyphenyl)ethyl)-boronic acid (**11a)** was prepared by reacting 10 mmol (2.15g) of 1-(1-bromoethyl)-4-methoxy-benzene (**13a**), 12 mmol magnesium shavings (291 mg), 12.5 mmol anhydrous LiCl (530 mg) and 30 mmol of trimethyl borate (3.3 ml) in 20 ml THF, likewise to the procedure 2 for **11a.** Instead of a Schlenk tube a Schlenk flask was used. 180 mg (10 % of theory) of the pure product as slightly yellow crystalline solid was obtained.

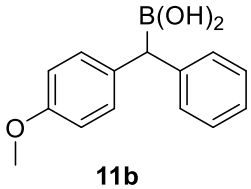
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14 (d, *J* = 8.80 Hz, 2 H, 2 x Ar*H*) 6.88 (d, *J* = 8.80 Hz, 2 H, Ar*H*) 3.83 (s, 3 H, OCH_3) 2.74 (dd, *J* = 4.22, 2.20 Hz, 1 H, C*H*CH_3) 1.03 (d, *J* = 6.60 Hz, 3 H, CHCH_3)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.78 (s, 1 C, C_{Ar}) 138.60 (s, 1 C, C_{Ar}) 128.41 (s, 2 C, C_{Ar}) 113.55 (s, 2 C, C_{Ar}) 55.20 (s, 1 C) 46.48 (s, 1 C) 20.95 (s, 1 C, C*C*H_3)

IR (KBr) $\tilde{\nu}$ [cm^{-1}]: 3429 (b, m) [O-H], 3033 (m), 2980 (m), 2952 (m), 1646 (m), 1613 (s), 1583 (m), 1510 (s), 1445 (s), 1258 (s), 1176 (s), 1036 [B-O] (s), 835 (s)

MS, *m/z* (%): 197 (100) [M^+ - $B(OH)_2$]

((4-methoxyphenyl)(phenyl)methyl)boronic acid



11b

(1-(4-methoxyphenyl)methyl)-boronic acid (**11b)** was prepared by reacting 5 mmol (1.38) of 1-(bromophenyl methyl)-4-methoxy-benzene (**13b**), 10 mmol of magnesium shavings (243mg), 12.5 mmol anhydrous LiCl (530 mg) and 15 mmol of trimethyl borate (1.7 ml) in 20 ml tetrahydrofuran, likewise to the procedure 2 for **11a.** Instead of a Schlenk tube a Schlenk flask was used. 436 mg (38 % of theory) of the pure product as slightly red crystalline solid was obtained.

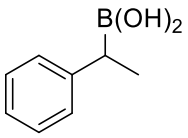
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 - 7.16 (m, 4 H, 4 x Ar*H*) 6.97 - 7.07 (m, 3 H, Ar*H*) 6.63 (d, *J* = 8.80 Hz, 2 H, 2 x Ar*H*) 4.67 (s, 1 H, Ar_2CH) 3.65 (s, 3 H, OCH_3)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.46 (s, 1 C, C_{Ar}) 145.80 (s, 1 C, C_{Ar}) 135 (s, 1 C, C_{Ar}) 129.36 (s, 2 C, 2 x C_{Ar}) 128.42 (s, 2 C, 2 x C_{Ar}) 128.13 (s, 2 C, 2 x C_{Ar}) 125.69 (s, 1 C, C_{Ar}) 113.50 (s, 2 C, 2 x C_{Ar}) 55.61 (s, 1 C) 55.03 (s, 1 C)

IR (KBr) $\tilde{\nu}$ [cm^{-1}]: 3435 (b, m) [O-H], 3030 (m), 2980 (m), 2952 (m), 2926 (m), 1613 (m), 1583 (m), 1511 (s), 1445 (s), 1304 [B-O], 1251 (s), 1176 (s), 1060 (s) 1035 (s)

MS, *m/z* (%): 197 (100) [M^+ - $B(OH)_2$]

(1-phenylethyl)-boronic acid



11e

An apparatus consisting of a 3 neck round bottom flask, magnetic stirrer, dropping funnel and condenser was charged with 30 mmol of magnesium shavings (389 mg). Next, 20 ml of anhydrous THF and one granular of iodine were added. After that 20 mmol (4.1 ml) (1-bromoethyl)-benzene (**13e**) which was dissolved in 10 ml anhydrous THF, was added drop wise in half an hour. Subsequently the reaction mixture was refluxed for 1 hour. After the solution turned to a dark black it was cooled back to rt. The Grignard reagent precipitated at rt. At this temperature 60 mmol (6.7 ml) of trimethyl borate was added. The reaction was stirred for one hour and subsequently quenched with 20 ml of HCl a.q. (c=1.0 mol/l). The organic layer was separated and the aqueous layer was extracted three times with 25 ml of EtAc. The combined organic layers were dried over anhydrous sodium sulfate. Evaporation of the solvent afforded a yellow oil. This oil was diluted with dichloromethane, causing the inorganic boric acid $B(OH)_3$ to precipitate, which was then filtered off. Evaporation of DCM yielded a brown-orange oil from which the target product was precipitated with PE and subsequently filtered of. This solid was washed with water and ice cold PE several times till it turned white. Yielding 235 mg (5% of theory) of **11e.**

^{1}H NMR (400 MHz, CD_3COCD_3) δ = 7.29 - 7.39 (m, 4 H, 4 x Ar*H*) 7.17 - 7.27 (m, 1 H, Ar*H*) 2.88 (dd, *J* = 4.40, 2.20 Hz, 1 H, C*H*CH_3) 1.00 (d, *J* = 6.60 Hz, 3 H, CHC*H*$_3$)

^{13}C NMR (101 MHz, CD_3COCD_3) δ = 146.64 (s, 1 C, C_{Ar}) 128.27 (s, 2 C, 2 x C_{Ar}) 127.52 (s, 2 C, 2 x C_{Ar}) 126.00 (s, 1 C, C_{Ar}) 46.98 (s, 1 C, B*C*HCH_3) 20.69 (s, 1 C, CH*C*H_3)

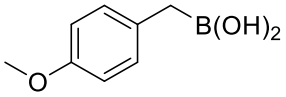
IR (KBr) $\tilde{\nu}$ [cm^{-1}]: 3429 (b, m) [O-H], 3100 (m), 3061 (s), 3023 (s), 3002 (m), 1600 (m), 1492 (s), 1448 (s), 1370 (m) [B-O], 1082 [B-O] (m), 1003 (s), 1258 (s), 774 (s), 1060 (s) 515 (s)

MS, *m/z* (%): 105 (100) [M^+ - $B(OH)_2$]

Boronic acids 9a-9e

These boronic acids were synthesized similar to procedure 1 for **11f** by Yawei Lee B.Sc. and Sheng Liuwang B.Sc. the exact synthetic procedures will be puplished in the near future.

(4-methoxybenzyl)boronic acid

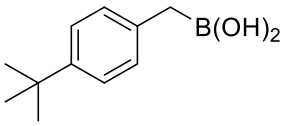


9a

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (d, *J* = 8.0 Hz, 2 H, 2 x Ar*H*) 6.87 (d, *J* = 8.4 Hz, 2 H, 2 x Ar*H*) 3.82 (s, 3 H, OC*H*$_3$) 2.88 (s, 2 H, C*H*$_2$)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.88 (s, 1 C, C_{Ar}), 134.02 (s, 1 C, C_{Ar}), 129.43 (s, 2 C, C_{Ar}) 133.78 (s, 2 C, C_{Ar}) 55.28 (s, 1 C, O*C*H$_3$) 37.32 (s, 1 C, *C*H$_2$)

(4-(tert-butyl)benzyl)boronic acid

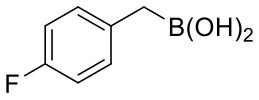


9b

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 6.8 Hz, 2 H, 2 x Ar*H*) 7.17 (d, *J* = 8.0 Hz, 2 H, 2 x Ar*H*) 2.89 (s, 2 H, C*H*$_2$) 1.32 (s, 9 H, C(C*H*$_3$)$_3$)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.67 (s, 1 C, C_{Ar}), 139.02 (s, 1 C, C_{Ar}), 128.11 (s, 2 C, C_{Ar}) 125.47 (s, 2 C, C_{Ar}) 37.33 (s, 1 C, *C*H$_2$) 34.33 (s 1 C, *C*(CH$_3$)$_3$) 31.38 (s 3 C, C(*C*H$_3$)$_3$)

(4-fluorobenzyl)boronic acid



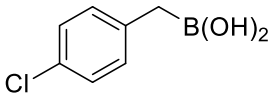
9c

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 – 6.98 (m, 4 H, 4 x Ar*H*) 2.89 (s, 2 H, CH_2)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 129.84 (s, 2 C, C_{Ar}) 129.76 (s, 1 C, C_{Ar}) 115.13 (s, 2 C, C_{Ar}) 114.92 (s, 1 C, C_{Ar}) 37.11 (s, 1 C, CH$_2$)

^{19}F NMR (376 MHz, $CDCL_3$) δ = –117.44 (s, 1 F, Ar*F*)

(4-chlorobenzyl)boronic acid

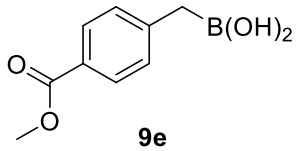


9d

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.4 Hz, 2 H, 2 x Ar*H*) 7.04 (d, *J* = 8.4 Hz, 2 H, 2 x Ar*H*) 2.85 (s, 2 H, CH_2)

^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.61 (s, 1 C, C_{Ar}) 131.75 (s, 1 C, C_{Ar}) 129.84 (s, 2 C, C_{Ar}) 128.45 (s, 2 C, C_{Ar}) 37.00 (s, 1 C, CH$_2$)

(4-(methoxycarbonyl)benzyl)boronic acid



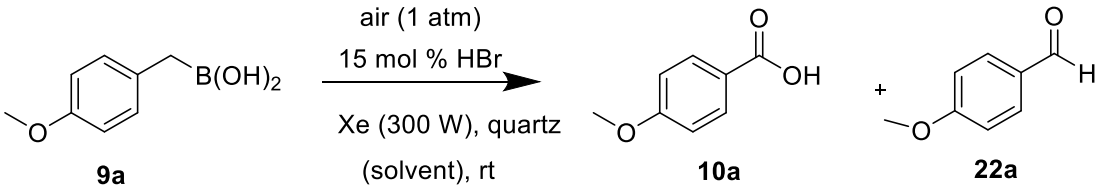
9e

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 8.0 Hz, 2 H, 2 x Ar*H*) 7.48 (d, *J* = 8.0 Hz, 2 H, 2 x Ar*H*) 4.52 (s, 2 H, C*H*$_2$) 3.94 (s, 3 H, C*H*$_3$)

7.3 Photoreactions

7.3.1 Investigations of the solvent effect

Boronic acid **9a** (0.2 mmol, 33 mg), solvent (10 mL), and HBr (aq., 48%) (3.4 µL, 0.03 mmol) were added to a dry quartz reaction flask which was equipped with a magnetic stirrer and a condenser. The mixture was exposed to the irradiation of a Xe lamp (300 W) at rt in the open air. The photoreactions were monitored by tlc (PE:EtAc 20:1). The reactions were stopped after the spot of **9a** and **22a** had disappeared. The maximum time was set to 18 hours. The solvent was removed under reduced pressure. The residue was solved in DMSO-d_6 and 0.2 mmol (14 µl) of CH_2Br_2 (DMSO-d_6, δ=5.38 ppm) was added as internal standard. The yield was calculated from the integral values of the signals of the aldehydic proton (δ=9.8 ppm, Lit.: 9.89 [38]) of **22a**, respectively the two aromatic protons of **10a** (δ=6.9 ppm,)



Scheme 33: Reactions on the solvent effect

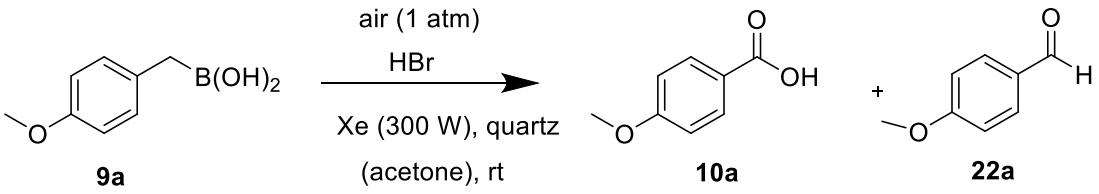
Table 16: Yields by ^{1}H-NMR

Entry	Solvent	Time [h]	Yield of 10a [%]	Yield of 22a [%]	Spectrum
1	Dichloromethane	18	20	18	**A**
2	Ethanol	18	53	6	**B**
3	Acetonitrile	18	62	14	**C**
4	Ethyl acetate	10	72	n.d.	**D**
5	Water*	6	NR		**E**
6	Tetrahydrofurane	18	comp.		**F**
7	Acetone	5	86	n.d.	**G**

*****the reaction solution was extracted with EtAc in the presence of HCl a.q., NR.: no reaction, comp.: the ^{1}H-NMR was too complicated, n.d.: the yield was below the detection limit

7.3.2 Experiments on the bromine content

Five quartz reaction flasks were each charged with boronic acid **9a** (0.2 mmol, 33 mg), and acetone (10 mL). To four of them HBr (aq., 48%) 0.03 mmol (3.4 µl), 0.02 mmol (2.3 µl), 0.01 mmol (1.1 µl) respectively 0.002 mmol (0.2 µl) were added. The reaction mixture was irradiated by a Xe lamp (300 W) at rt in the open air. The Photoreactions were monitored by tlc (PE:EtAc 20:1). The reactions were stopped after the spot of **9a** and **22a** had disappeared or 12 hours were reached. The solvent was removed under reduced pressure. The residue was dissolved in DMSO-d_6 and 0.2 mmol (14 µl) of CH_2Br_2 (DMSO-d_6, δ=5.38 ppm) was added as internal standard. The yields were calculated from the integral values of the signals of the aldehydic proton (δ=9.8 ppm) of **22a** [38], respectively the two aromatic protons of **10a** (δ=6.9 ppm) [39].



Scheme 34: Experiments on the bromine content

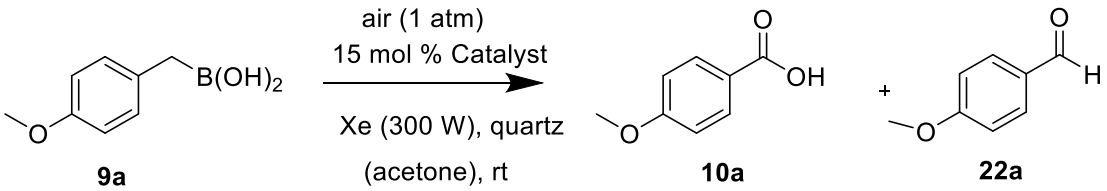
Table 17: The effect of the amount of HBr on the yield of aldehyde 22a and benzoic acid 10a

Entry	Catalyst	Time [h]	Yield of 10a* [%]	Yield of 22a* [%]	Spectrun
1	HBr (1 mol %)	12	25	Trace	**H**
2	HBr (5 mol %)	12	32	Trace	**I1**
3	HBr (10 mol %)	12	78	n.d.	**I2**
4	HBr (15 mol %)	5	86	n.d	**G**
5	No catalyst	5	NR		**M**

NR.: no reaction, n.d.: the yield was below the detection limit

7.3.3 Experiments on the bromine source

Three quartz reaction flasks were each charged with boronic acid **9a** (0.2 mmol, 33 mg), and acetone (10 mL). To which LiBr (aq. c=8.9 mol/l) 0.03 mmol (3.4 µl), NaBr (aq. c=8.9 mol/l) 0.03 mmol (3.4 µl) respectively KBr (aq. c=8.9 mol/l) 0.03 mmol (3.4 µl) were added. The reaction mixture was irradiated by a Xe lamp (300 W) at rt in the open air. The photoreactions were monitored by TLC (PE:EtAc 20:1). The reactions were stopped after the spot of **9a** and **22a** had disappeared or 12 hours were reached. The solvent was removed under reduced pressure. The residue was dissolved in DMSO-d_6 and 0.2 mmol (14 µl) of CH_2Br_2 (DMSO-d_6, δ=5.38 ppm) was added as internal standard. The yields were calculated from the integral values of the signals of the aldehydic proton (δ=9.8 ppm) [38] of **22a**, respectively the two aromatic protons of **10a** (δ=6.9 ppm) [39]



Scheme 35: Reaction with different catalysts

Table 18: Different bromine sources

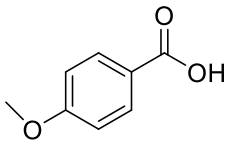
Entry	Catalyst	Time [h]	Yield of 10a [%]	Yield of 22a [%]	Spectrum
1	LiBr (15 mol %)	12	trace	trace	**J**
2	NaBr (15 mol %)	12	26	14	**K**
3	KBr (15 mol %)	12	55	12	**L**

7.3.4 Photoreactions of the boronic acids 9a-9f

Genral procedure for oxidation of the boronic acids

Boronic acid **9** (0.2 mmol), acetone (10 mL), and HBr (aq., 48%) (3.4 µL, 0.03 mmol) were added to a dry quartz reaction flask which was equipped with a magnetic stirrer and a condenser. The mixture was exposed to the irradiation of a Xe lamp (300 W) at rt in the open air. Then the reaction was stirred for an indicated time. The solvent was removed under reduced pressure. The obtained residue purified by preparative tlc (PE:EtAc 10:1, R_f=0)

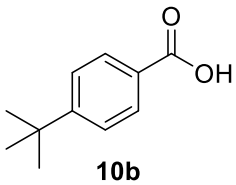
4-methoxybenzoic acid



10a

Boronic acid **9a** (33 mg, 0.2 mmol) was irradiated 5 hours and treated according to the general procedure. This yielded 26 mg (8/% of theory) of **10a**

4-(tert-butyl)benzoic acid

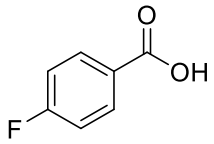


10b

(4-(tert-butyl)benzyl)boronic acid **(9b)** (38 mg, 0.2 mmol) was irradiated for 9 hours and treated according to the general procedure. This yielded 25 mg (69 % of theory) of **10b** as a white solid.

Spectrum P1: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.03 (d, *J* = 8.4 Hz, 2 H, 2 x Ar*H*) 7.50 (d, *J* = 8.4 Hz, 2 H, 2 x Ar*H*) 4.52 (s, 2 H, CH_2) 1.29 (s, 9 H, C(CH_3)$_3$)

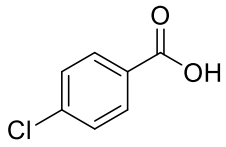
4-fluorobenzoic acid



10c

(4-fluorobenzyl)boronic acid **(9c)** (31 mg, 0.2 mmol) was irradiated for 8 hours and treated according to the general procedure. This yielded 15 mg (54 % of theory) of **10c** as a white solid.

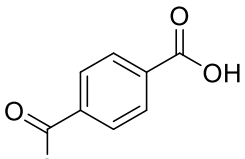
4-chlorobenzoic acid



10d

4-chlorobenzoic acid **(10d)** (34 mg, 0.2 mmol) was prepared by irradiating **9d** for 18 hours and treated according to the general procedure. This yielded 24 mg (77 % of theory) of **10d** as a white solid.

4-(methoxycarbonyl)benzoic acid



10e

When boronic acid **9e (**39 mg, 0.2 mmol was reacted for 10 hours according the general procedure 22 mg (60% of theory) of **10e** was collected.

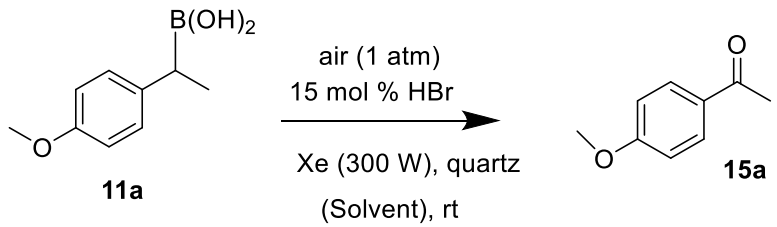
Spectrum P2: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.06 (s, 4 H, 4 x Ar*H*) 3.88 (s, 3 H, COOCH_3)

7.3.5 Photo reactions of the boronic acids 11a, 11b, 11e and 11f

General procedure

Boronic acid **11** (0.2 mmol), solvent (10 mL), and HBr (aq., 48%) (3.4 µL, 0.03 mmol) were added to a dry quartz reaction flask which was equipped with a magnetic stirrer and a condenser. The mixture was exposed to the irradiation of a Xe lamp (300 W) at rt in the open air. Then the reaction was stirred for an indicated time. The solvent was removed under reduced pressure. The residue was solved in $CDCl_3$ and 0.2 mmol (14 µl) of CH_2Br_2 ($CDCL_3$-*d*, δ=4.92 ppm) was added as internal standard. If the yield was above 50% in the reactions without oxygen the product was isolated by preparative tlc with PE/EtAc 10:1. The petrol ether was distilled before used in the chromatographic procedures.

Boronic acid 11a



Scheme 36: Reactions 11ap

Reacting **11a** (0.2 mmol, 36 mg) and HBr (aq., 48%) (3.4 µL, 0.03 mmol) for 6 hours in acetonitrile afforded 24 mg (80% of Theory) as white solid **15a** after preparative tlc (R_f=0.4)

Spectrum P3: ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ = 7.96 (d, *J* = 8.99 Hz, 2 H, 2 x Ar-*H*) 6.95 (d, *J* = 8.80 Hz, 2 H, 2 x Ar-*H*) 3.89 (s, 3 H, O-CH_3) 2.58 (s, 3 H, CH_3)

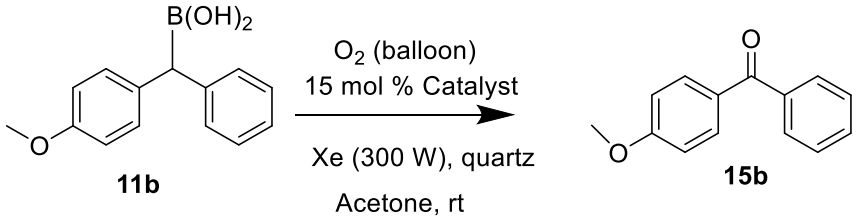
Reacting **11a** (0.2 mmol, 36 mg) and HBr (aq., 48%) (3.4 µL, 0.03 mmol) for 9 hours in actone afforded 16 mg (53% of Theory) **15a** after preparative tlc (R_f=0.4)

Spectrum P4: ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ = 7.96 (d, *J* = 8.99 Hz, 2 H, 2 x Ar*H*) 6.95 (d, *J* = 8.80 Hz, 2 H, 2 x Ar-*H*) 3.89 (s, 3 H, O-CH_3) 2.58 (s, 3 H, CH_3)

This data is in accordance with literature [40]

Boronic acid 11b

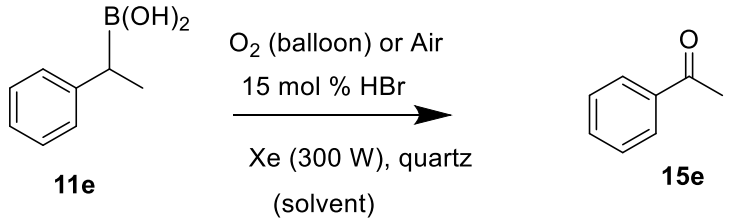
Reacting **11b** (0.2 mmol, 48 mg) and HBr (aq., 48%) (3.4 μL, 0.03 mmol) for 9 hours in acetone afforded no product.



Scheme 37: Reaction of 11b

Reacting **11b** (0.2 mmol, 48 mg) and HBr (aq., 48%) (3.4 μL, 0.03 mmol) for 9 hours in with connection to an oxygen balloon or acetone afforded **15b** in 45% yield according to spectrum **O2**. The yield was calculated from the integral of the signal of the methoxy group of **15b** [41].

Boronic acid 11e



Scheme 38: Photoreactions of 11e

Reacting **11e** (0.2 mmol, 30 mg) and HBr (aq., 48%) (3.4 μL, 0.03 mmol) for 6.5 hours in acetone (10 ml) showed a yield determined by ^{1}H-NMR of 22 %. For 8.5 hours 28% and for 14 hours 27%. Spectra **N1-N3.**

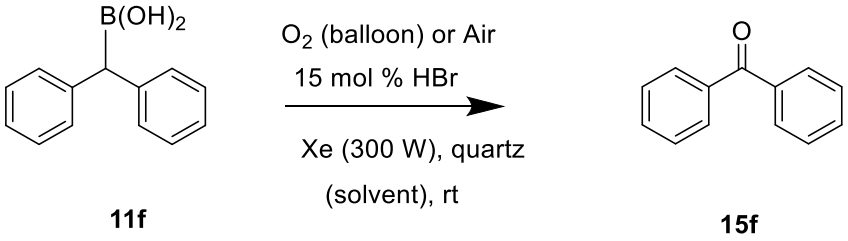
When **11e** (0.2 mmol, 30 mg) and HBr (aq., 48%) (3.4 μL, 0.03 mmol) are irradiated in acetone in an oxygen atmosphere provided by a balloon. 58-67% are produced by irritating the solution for 8.5 hour. Spectrum **O4**. Further irradiation did not increase the yield (66-69%). Spectrum **O3**.

From the reaction of **11e** (0.2 mmol, 30 mg) and HBr (aq., 48%) (3.4 μL, 0.03 mmol) in 10 ml acetonitrile open to the air 15 mg 62% of **15e** was obtained with preparative tlc (R_f=0.8) as oil. Note: The yield may not exact since some by product co-elutes.

Spectrum **P5**: ^{1}H NMR (400 MHz, $CDCL_3$) δ = 7.88 - 8.09 (m, 2 H, 2 x Ar*H*) 7.54 - 7.66 (m, 1 H, Ar*H*) 7.40 - 7.54 (m, 2 H, 2 x Ar*H*) 2.63 (s, 3 H, CH_3)

This data is in accordance with literature [42].

Boronic acid 11f



11f **15f**

Reacting **11b** (0.2 mmol, 48 mg) and HBr (aq., 48%) (3.4 µL, 0.03 mmol) for 12, 16 or 20 hours in acetone or acetonitrile with connection to the air afforded no product.

Reacting **11b** (0.2 mmol, 48 mg) and HBr (aq., 48%) (3.4 µL, 0.03 mmol) for 12 hours in aceton with connection to an oxygen balloon afforded **15f** in 23% yield according to spectrum **O1**.[41]

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9. Spectral data

9.1 Alcohols 16a-d

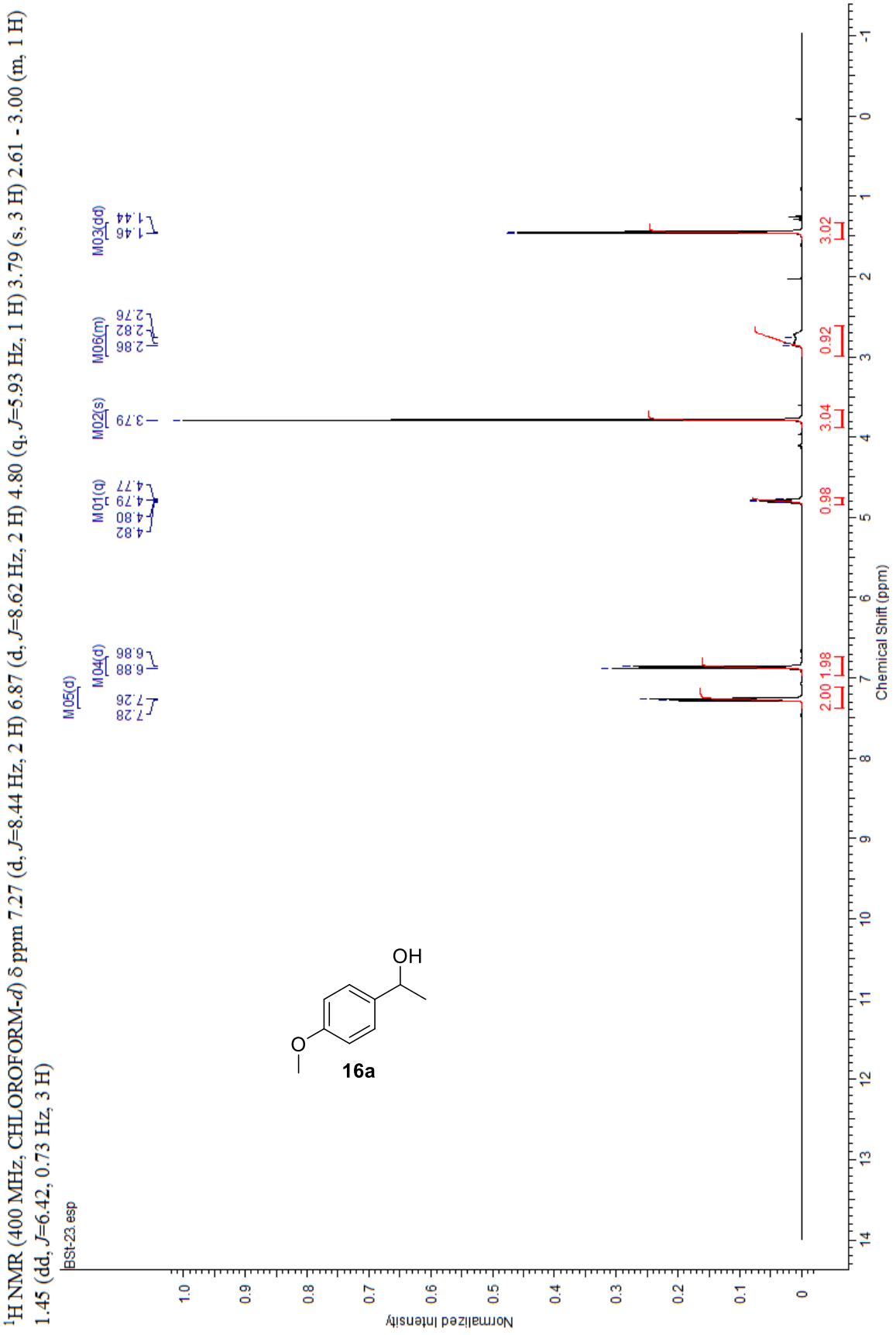

Figure 3:^{1}H-NMR Spectrum of 16a

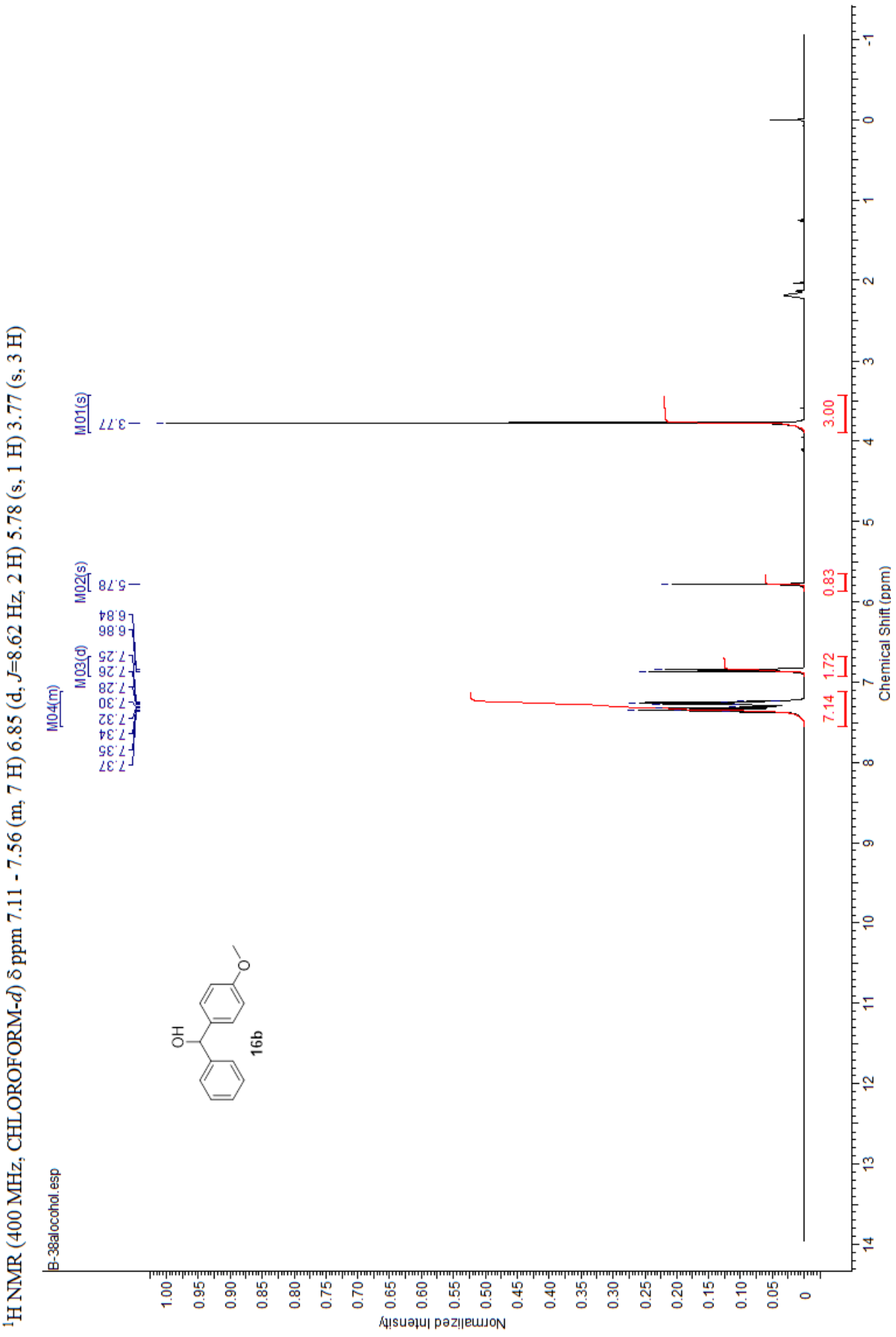

Figure 4: ^{1}H-NMR Spectrum of 16b

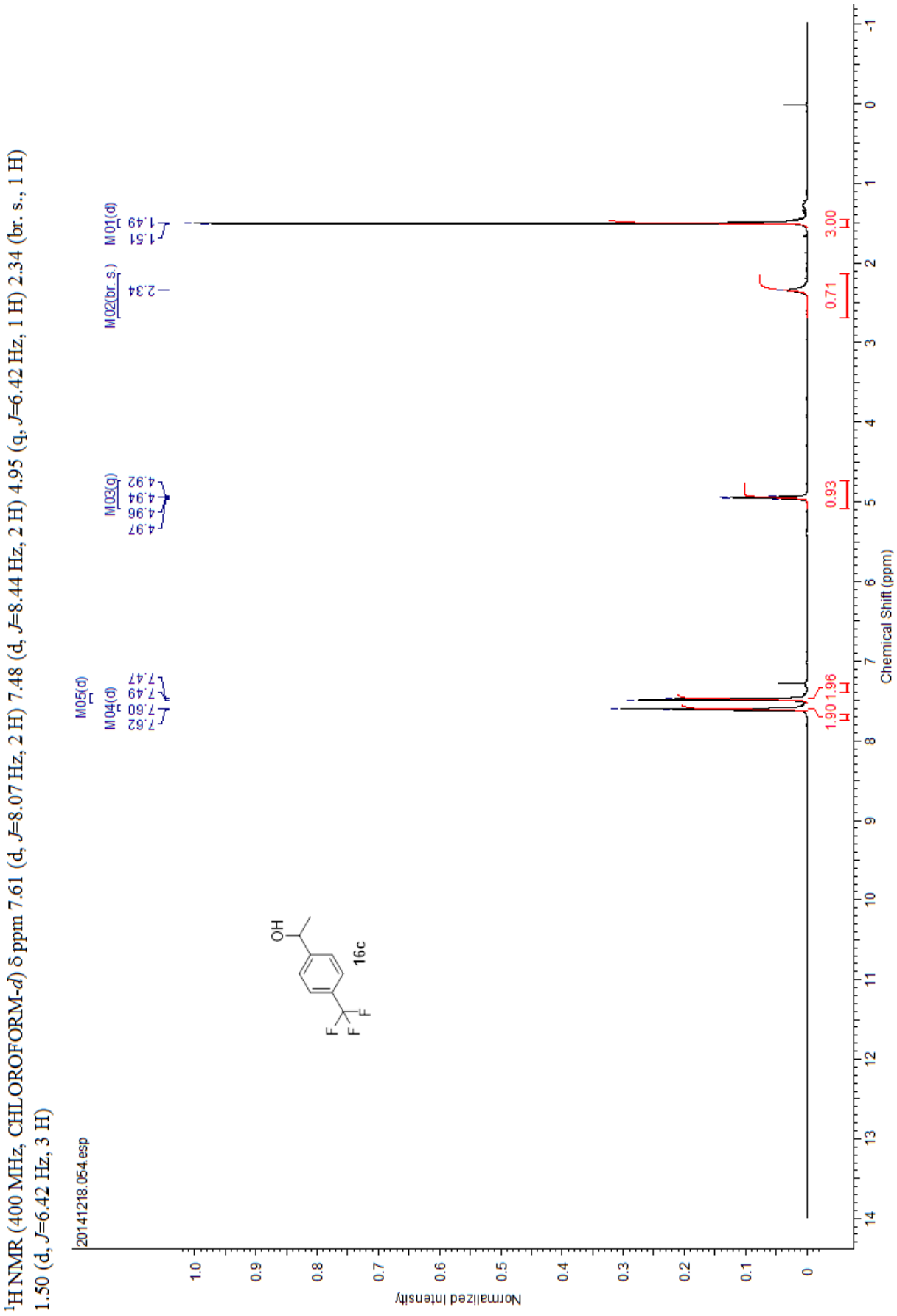

Figure 5: ^{1}H-NMR Spectrum of 16c

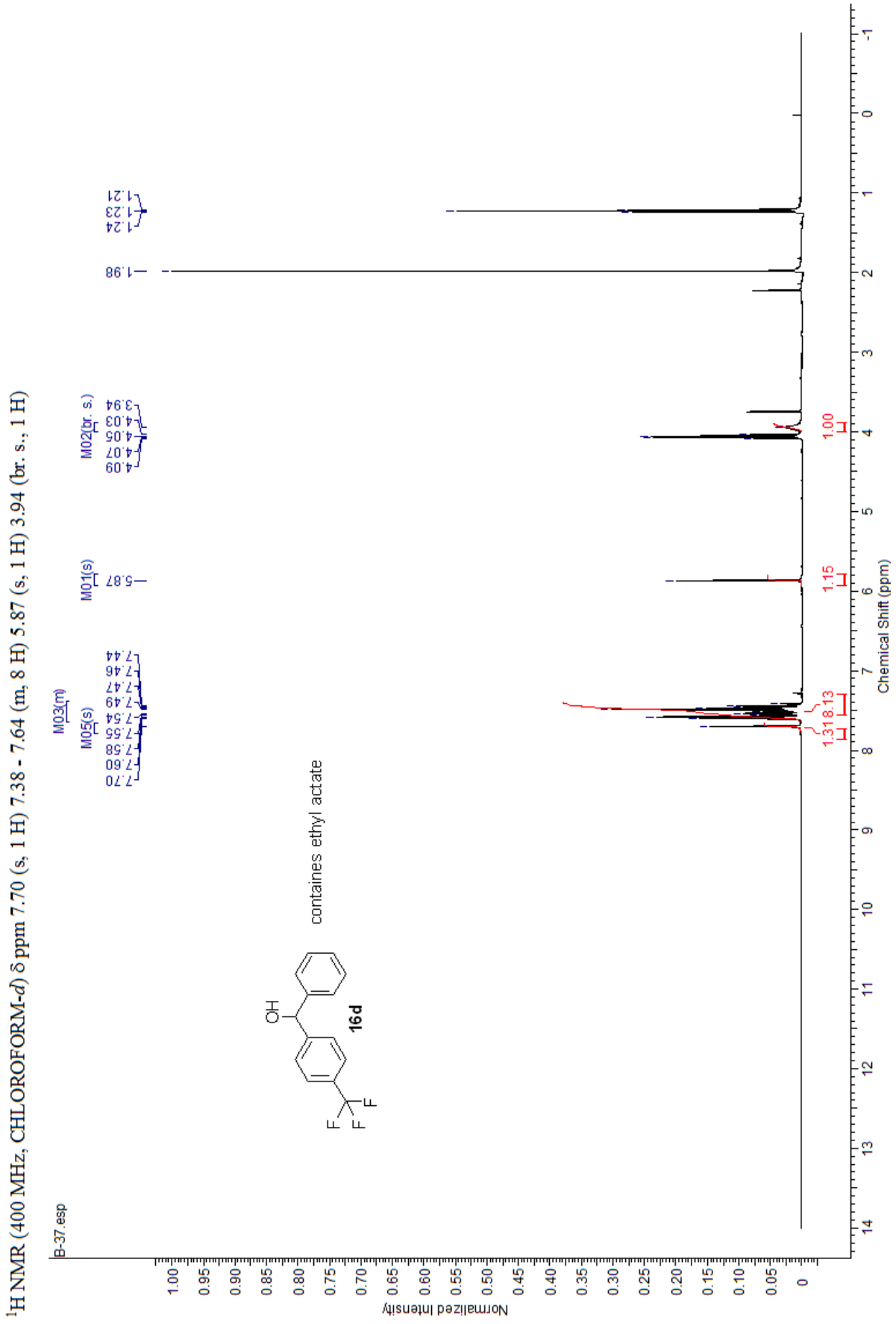

Figure 6: ^{1}H-NMR Spectrum of 16d

9.2 Bromides 13a-d

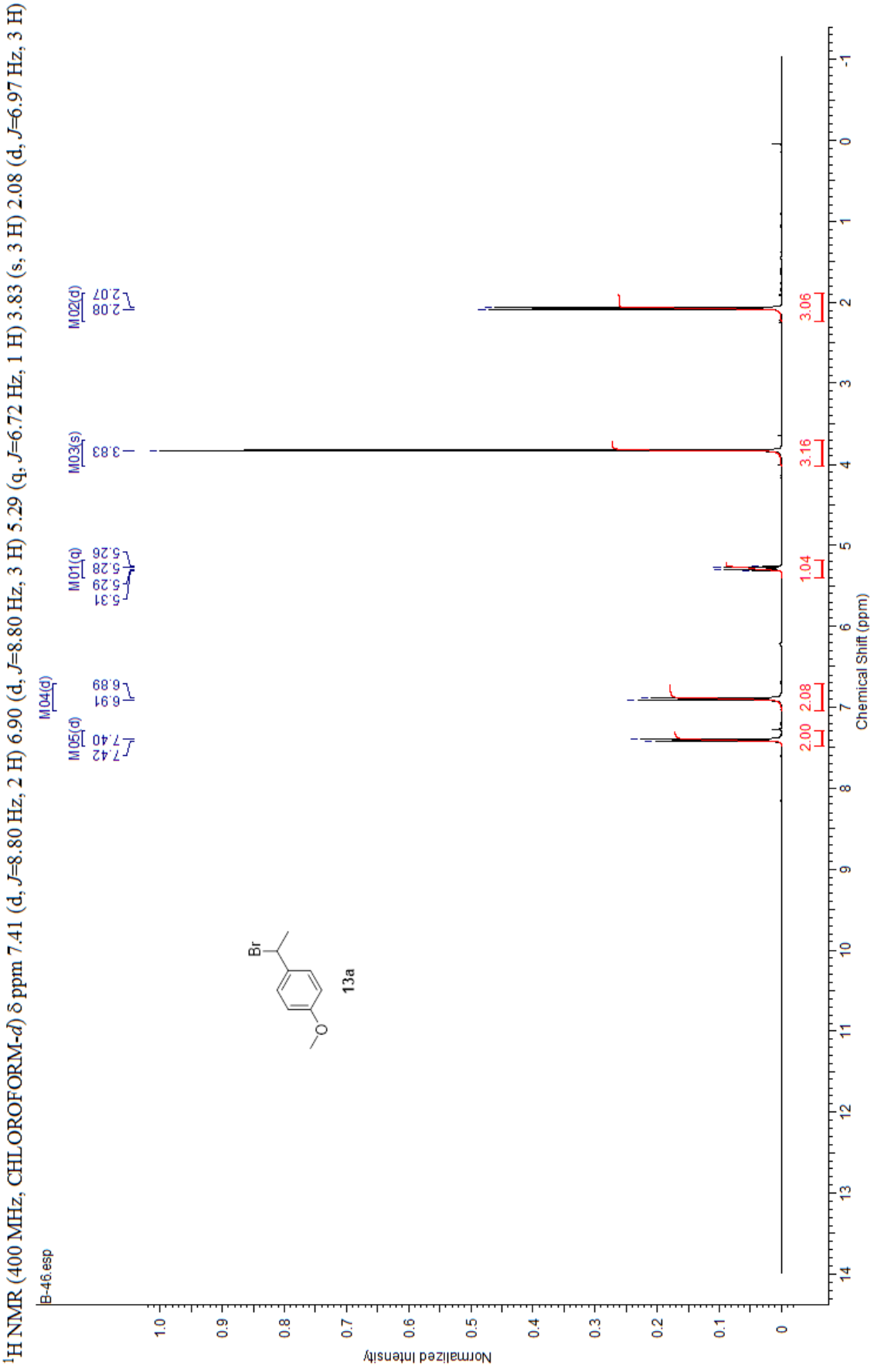

Figure 7: ^{1}H-NMR Spectrum of 13a

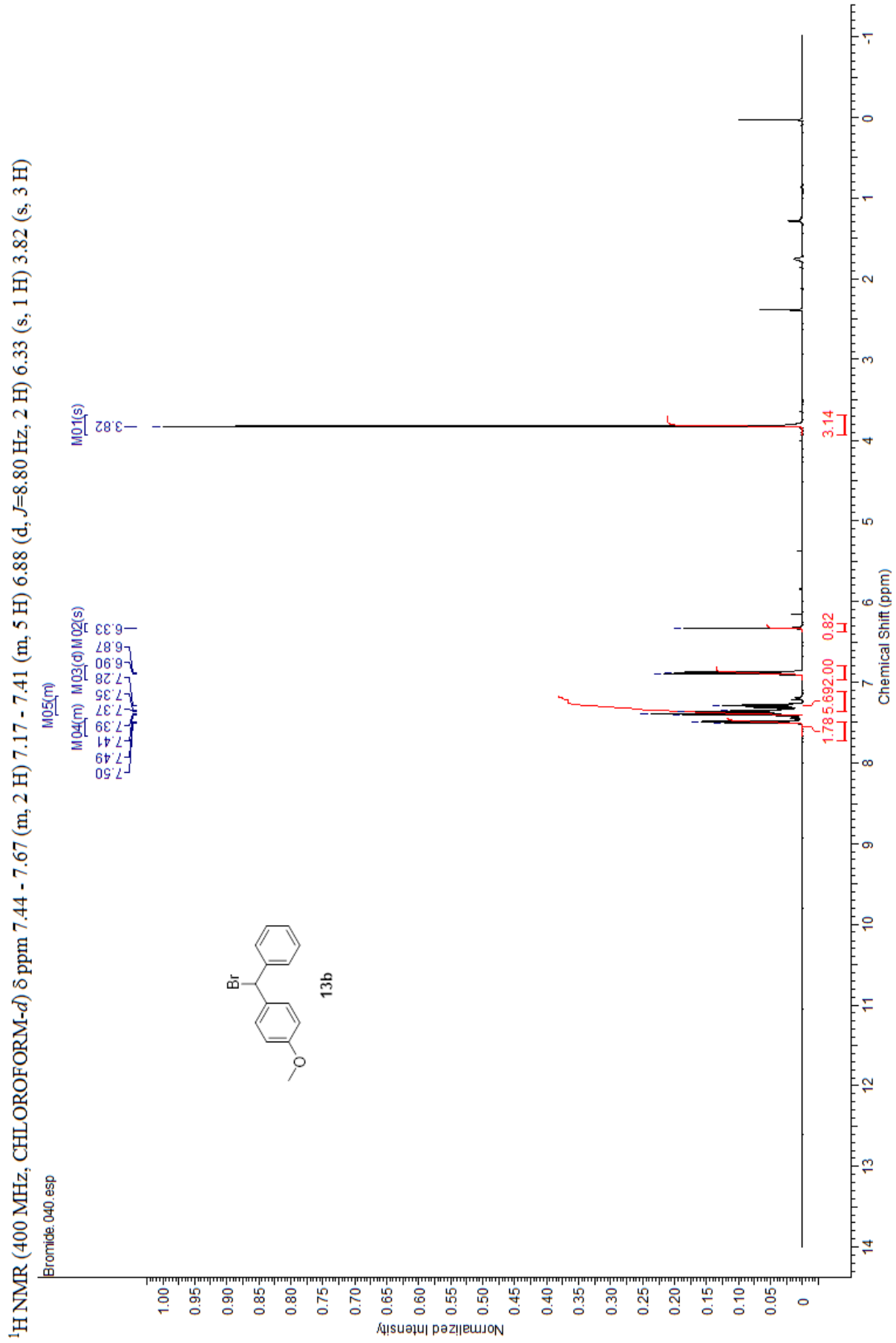

Figure 8: ^{1}H-NMR Spectrum of 13b

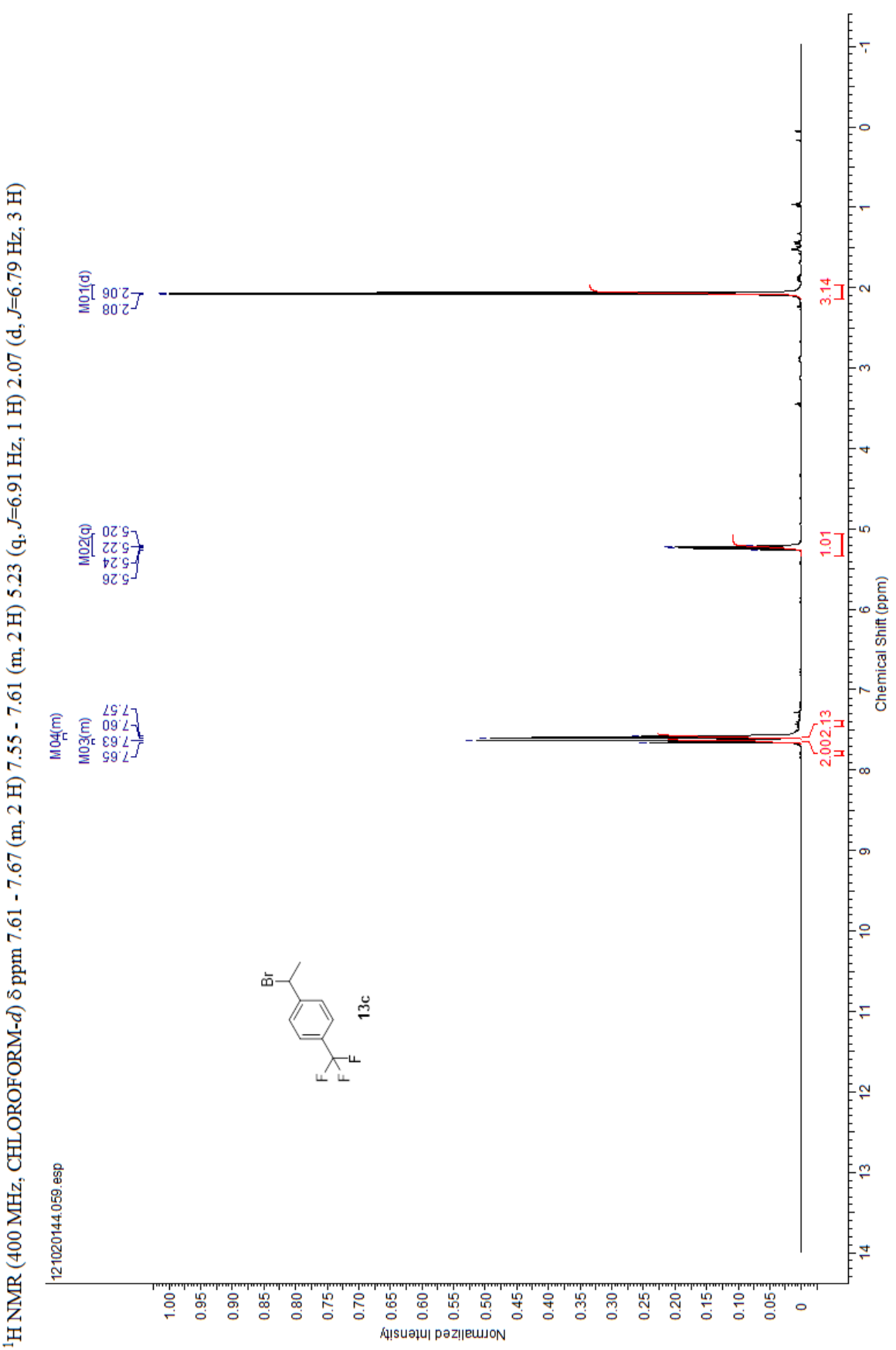

Figure 9: ^{1}H-NMR Spectrum of 13c

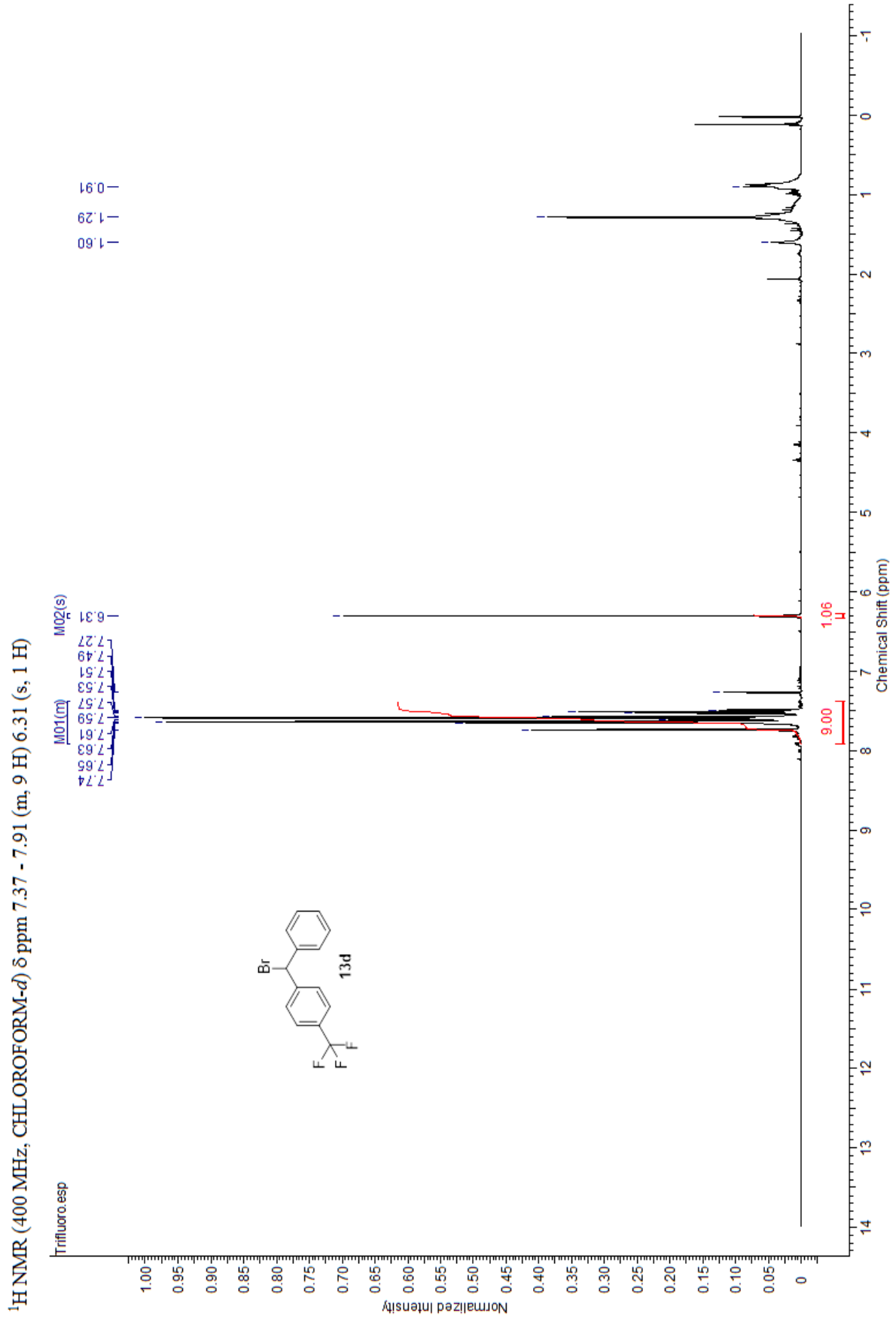

Figure 10: ^{1}H-NMR Spectrum of 13d

9.3 Boronic acids 9a-9e

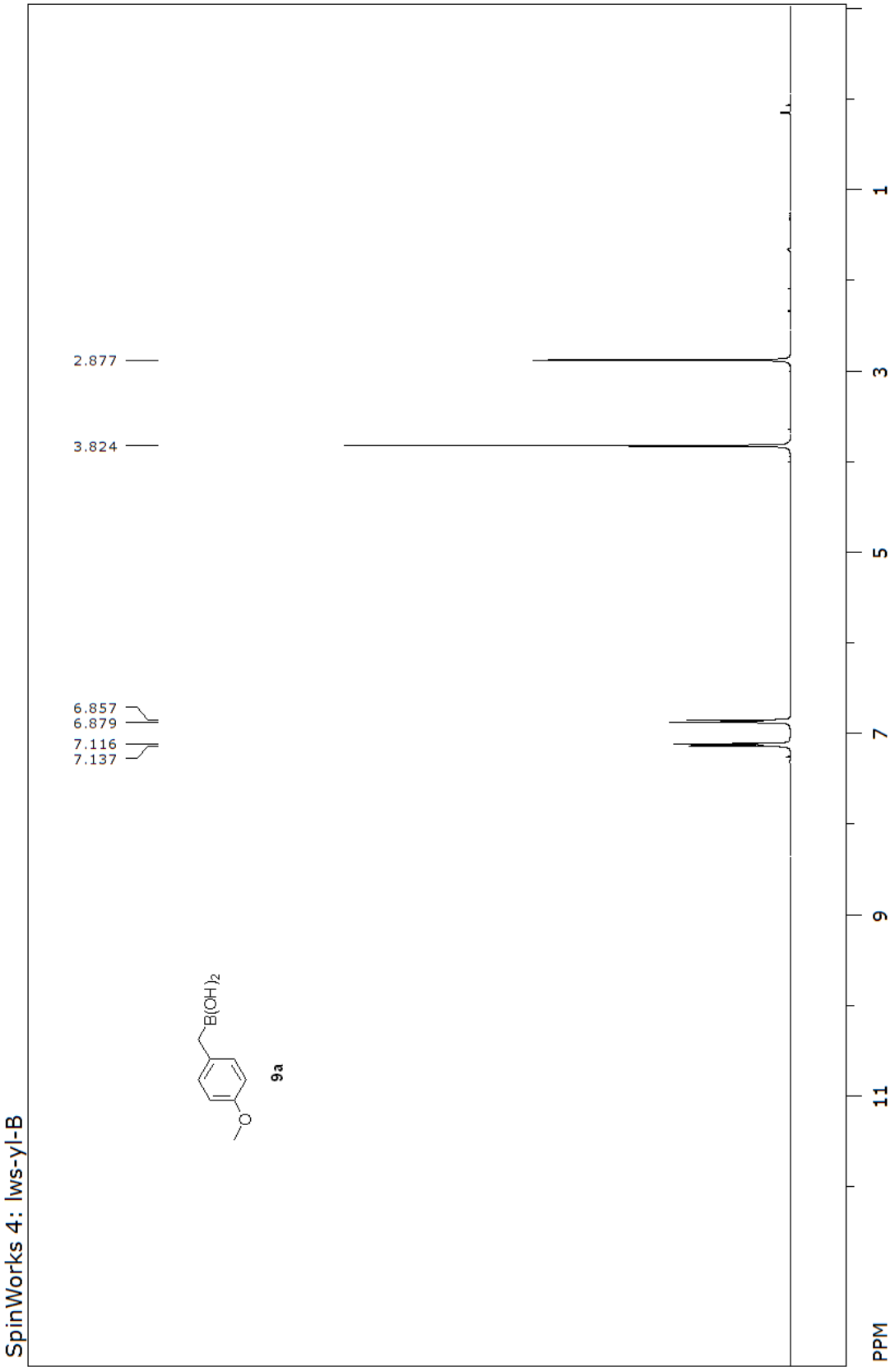

Figure 11: ^{1}H-NMR spectrum of 9a

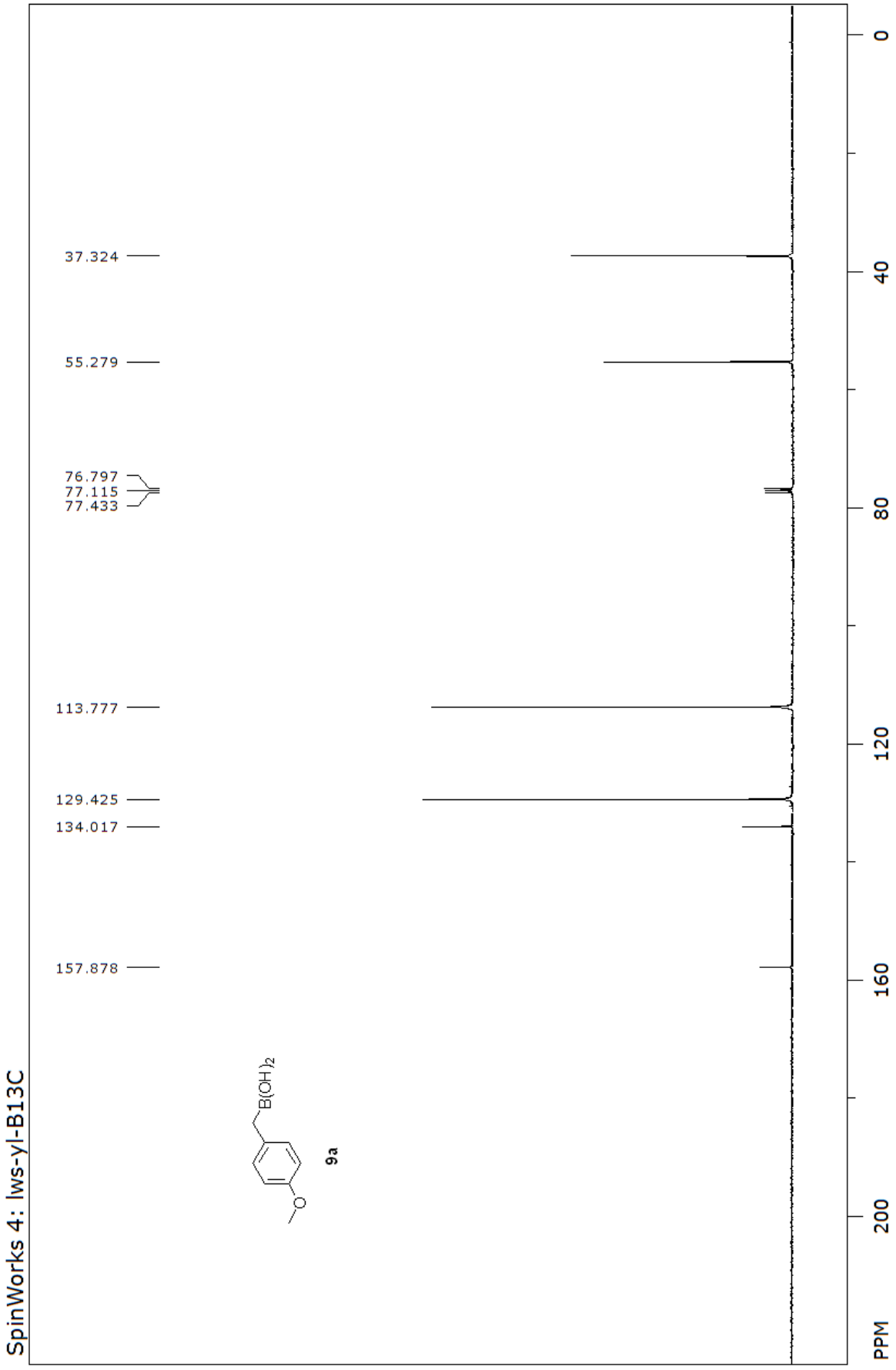

Figure 12: ^{13}C-NMR of 9a

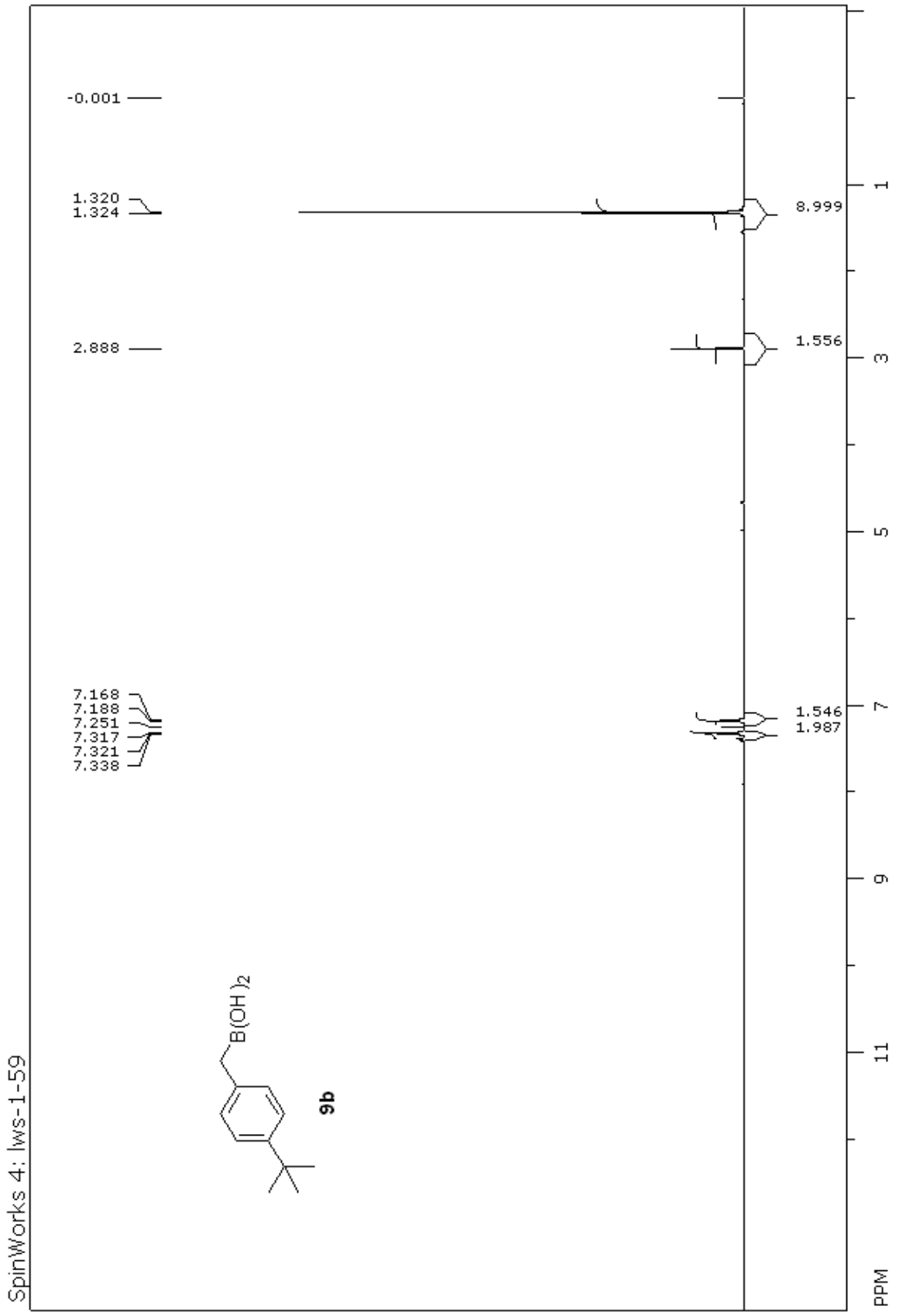

Figure 13: ^{1}H-NMR spectrum of 9b

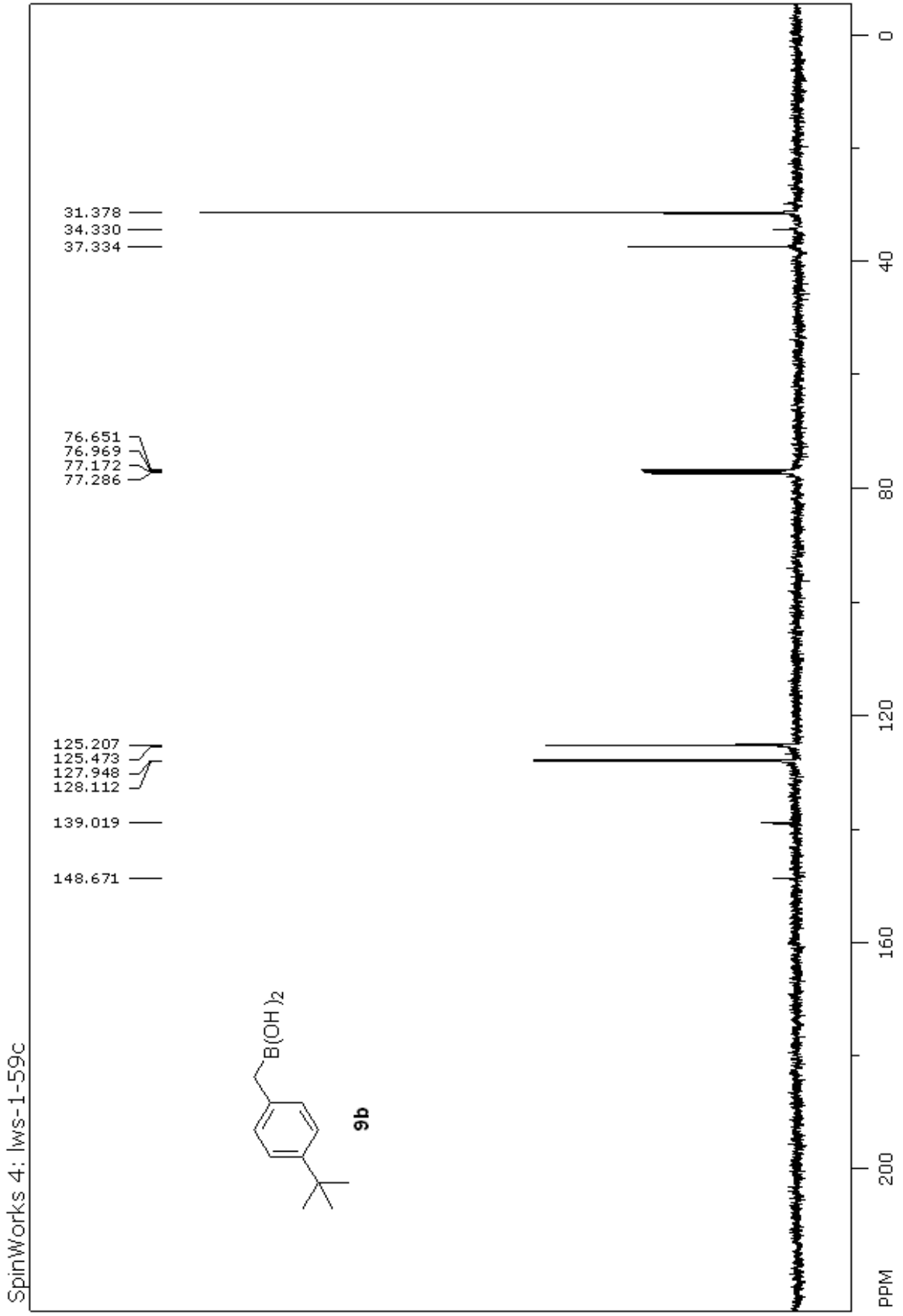

Figure 14: ^{13}C-NMR of 9b

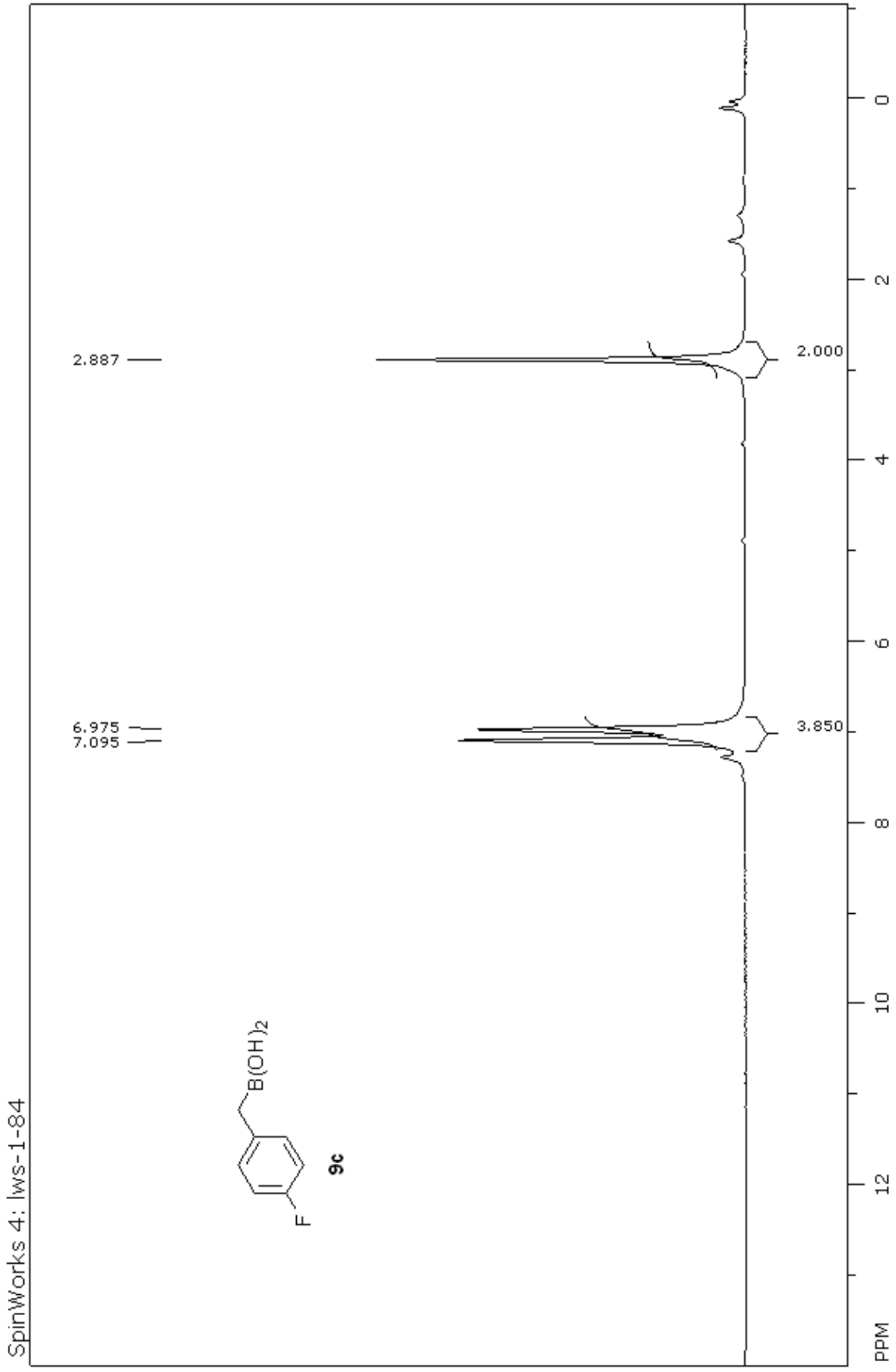

Figure 15: ^{1}H-NMR of 9c

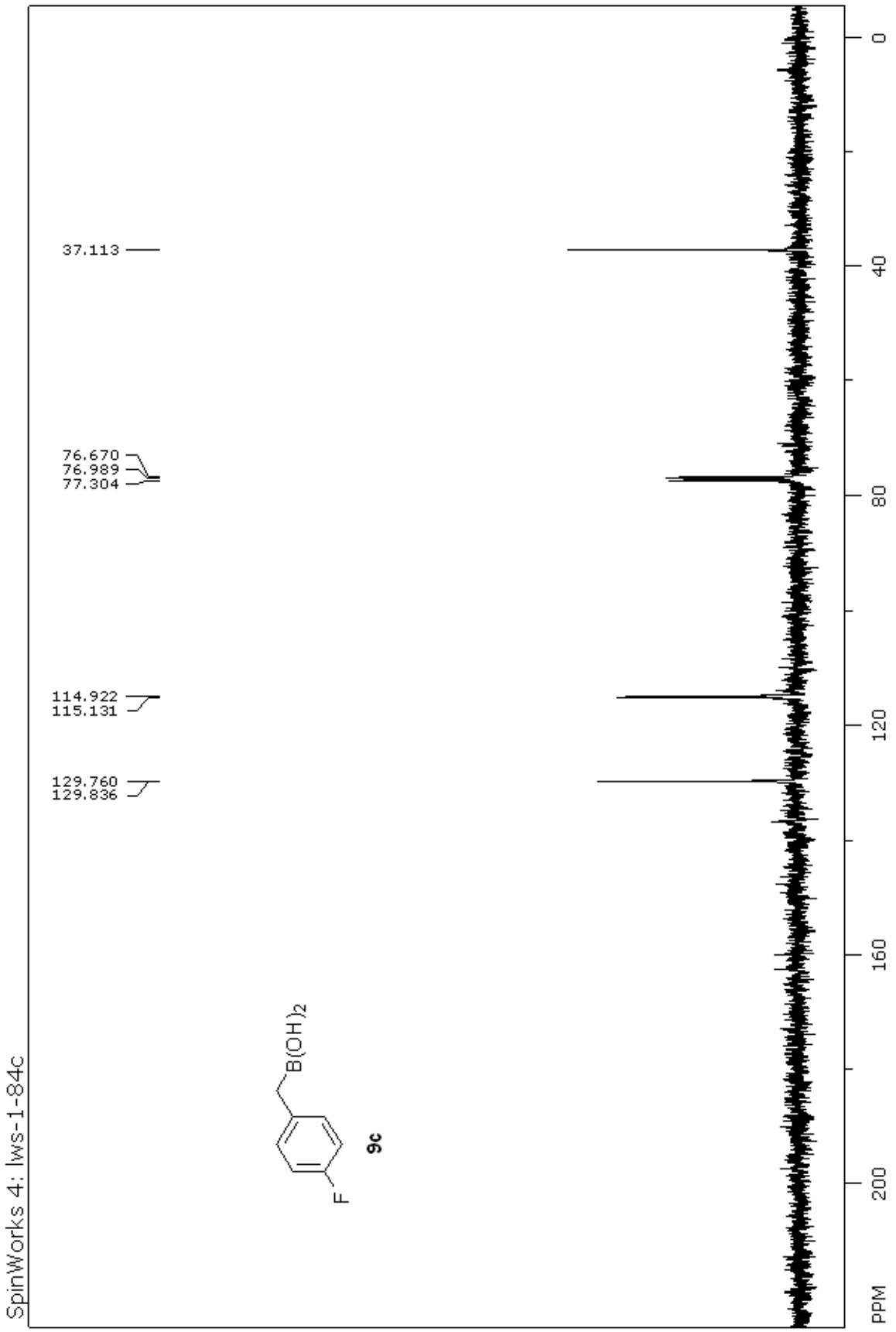

Figure 16: 13C-NMR of 9c

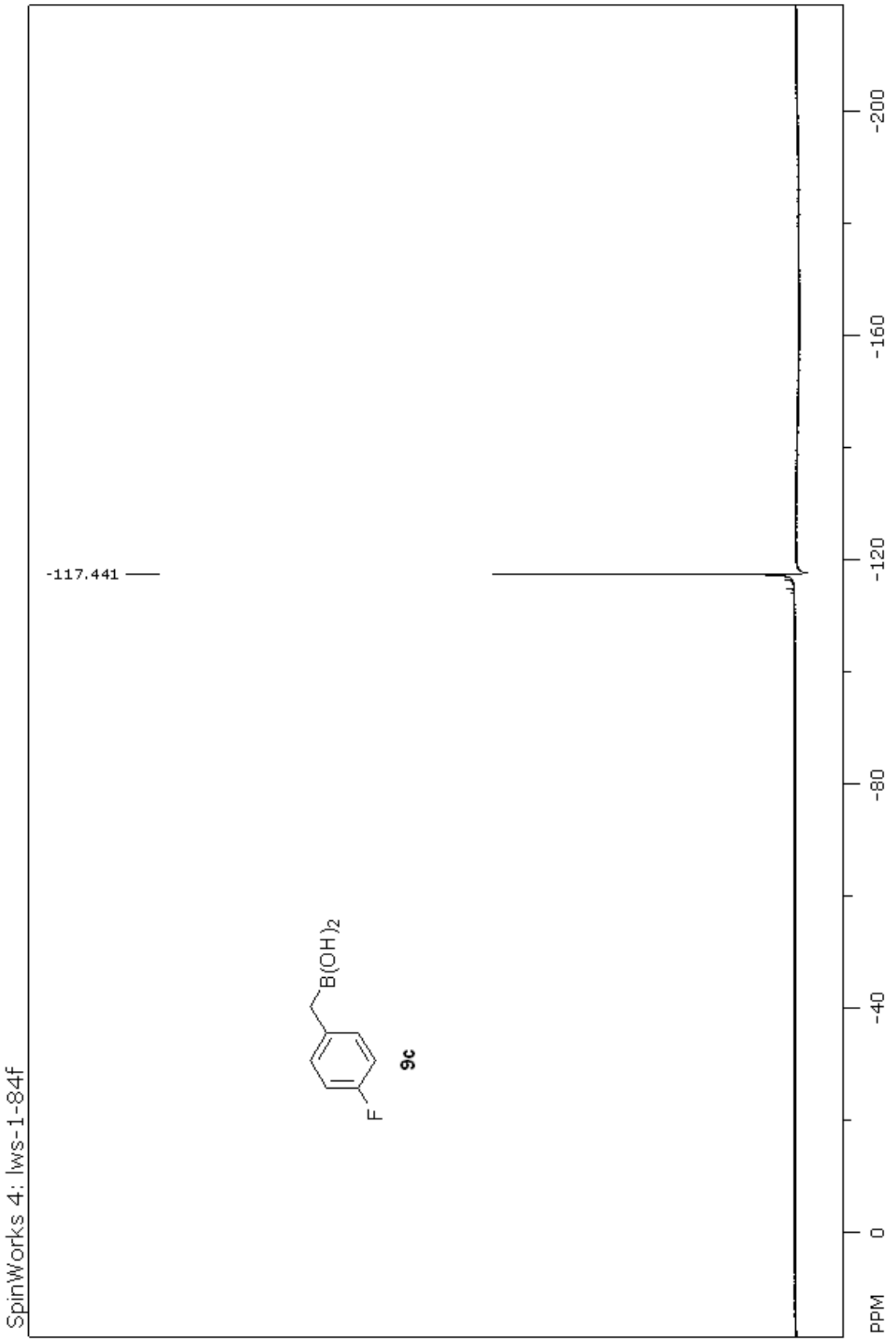

Figure 17: ^{19}F-NMR of 9c

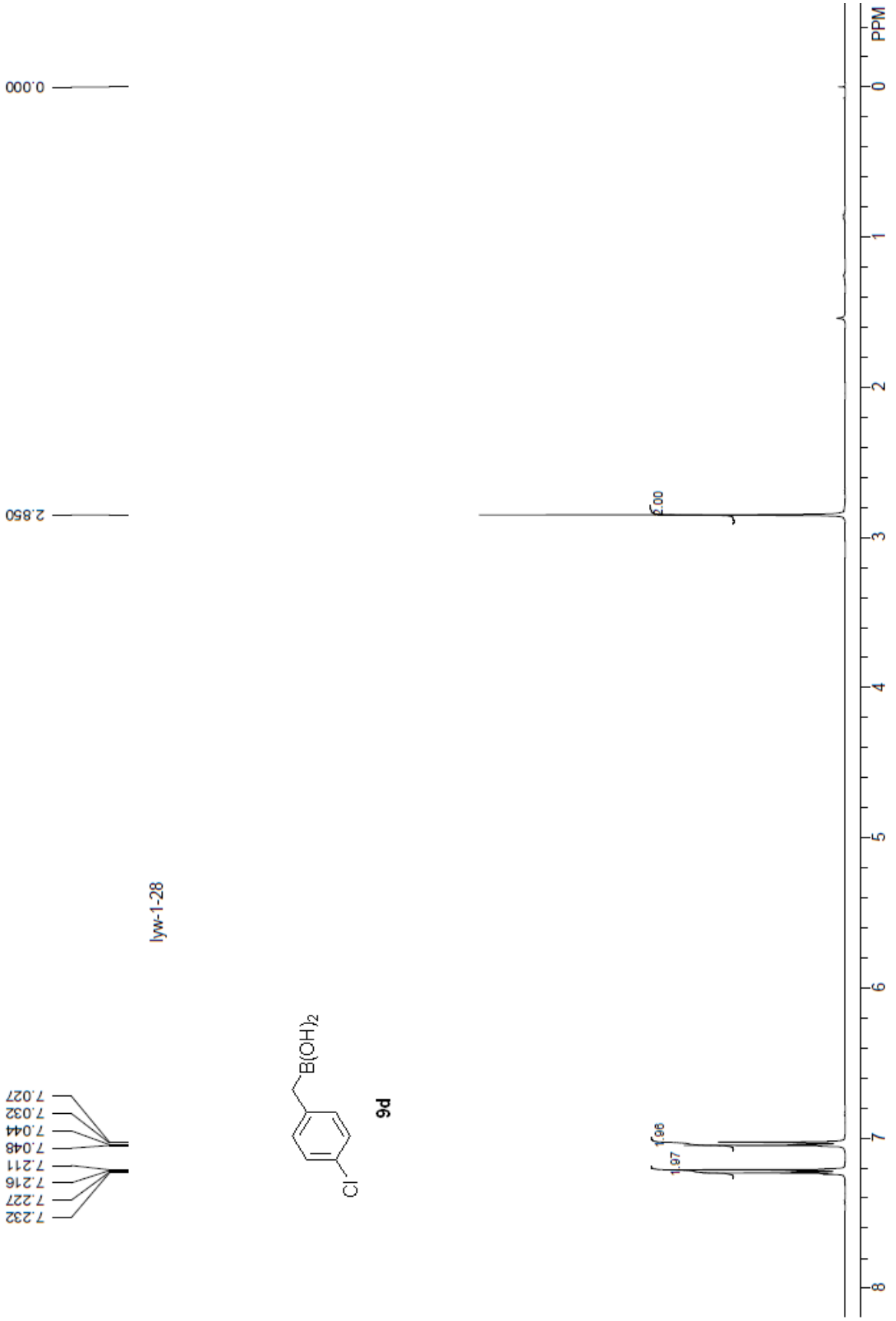

Figure 18: ^{1}H-NMR spectrum of 9d

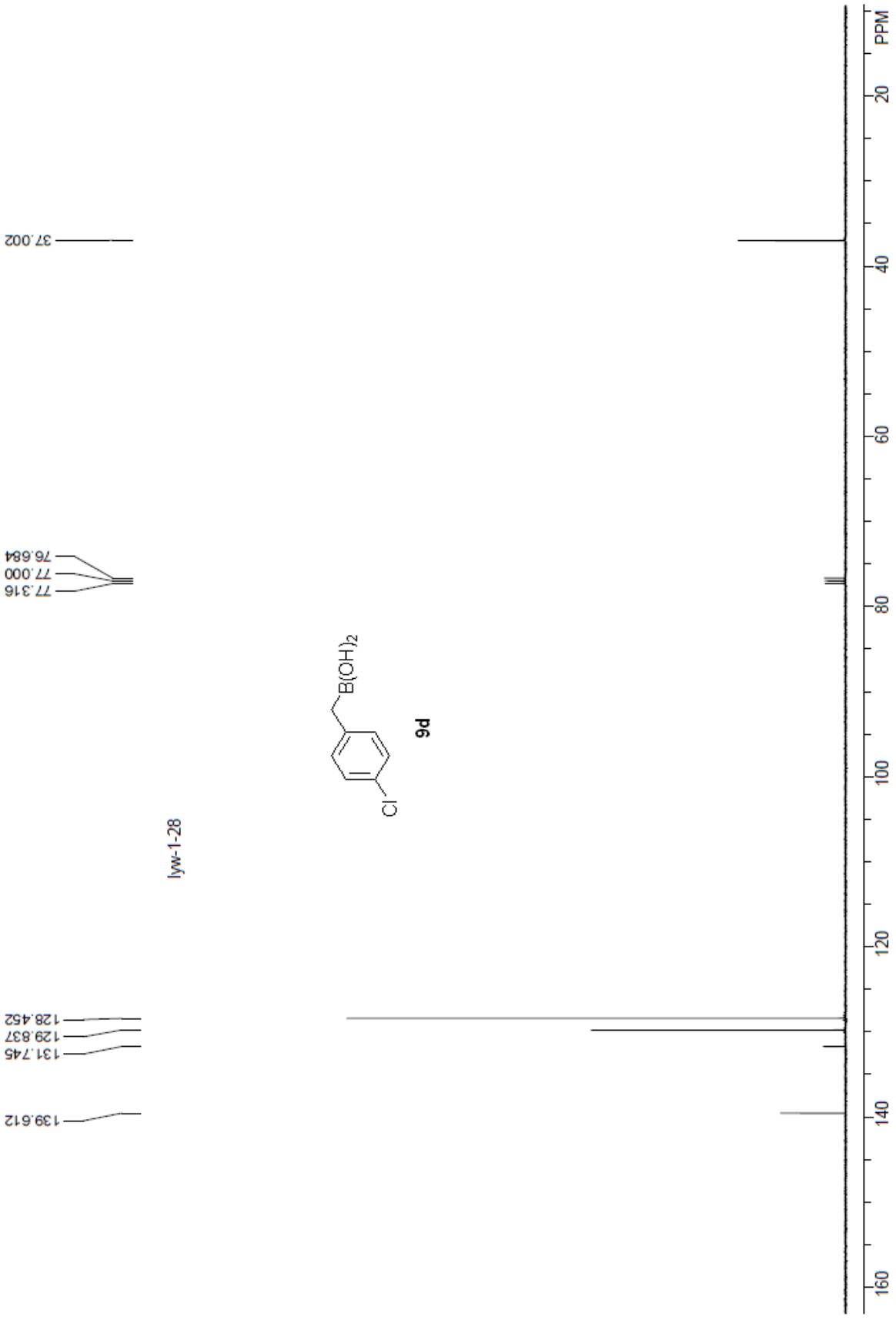

Figure 19:13C-NMR spectrum of 9d

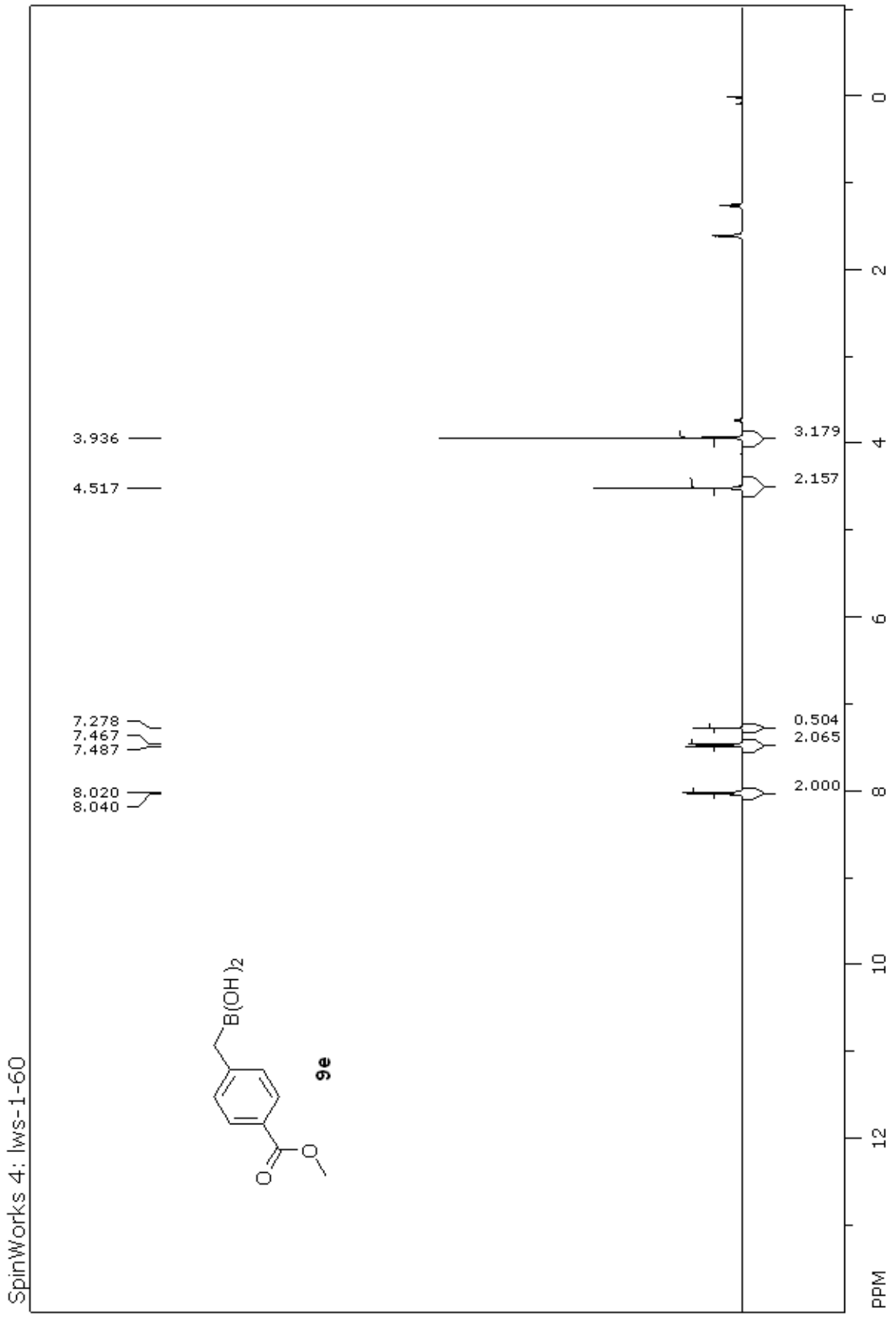

Figure 20: 1H-NMR of 9e

9.4 Boronic acids 11a-11b and11e-f

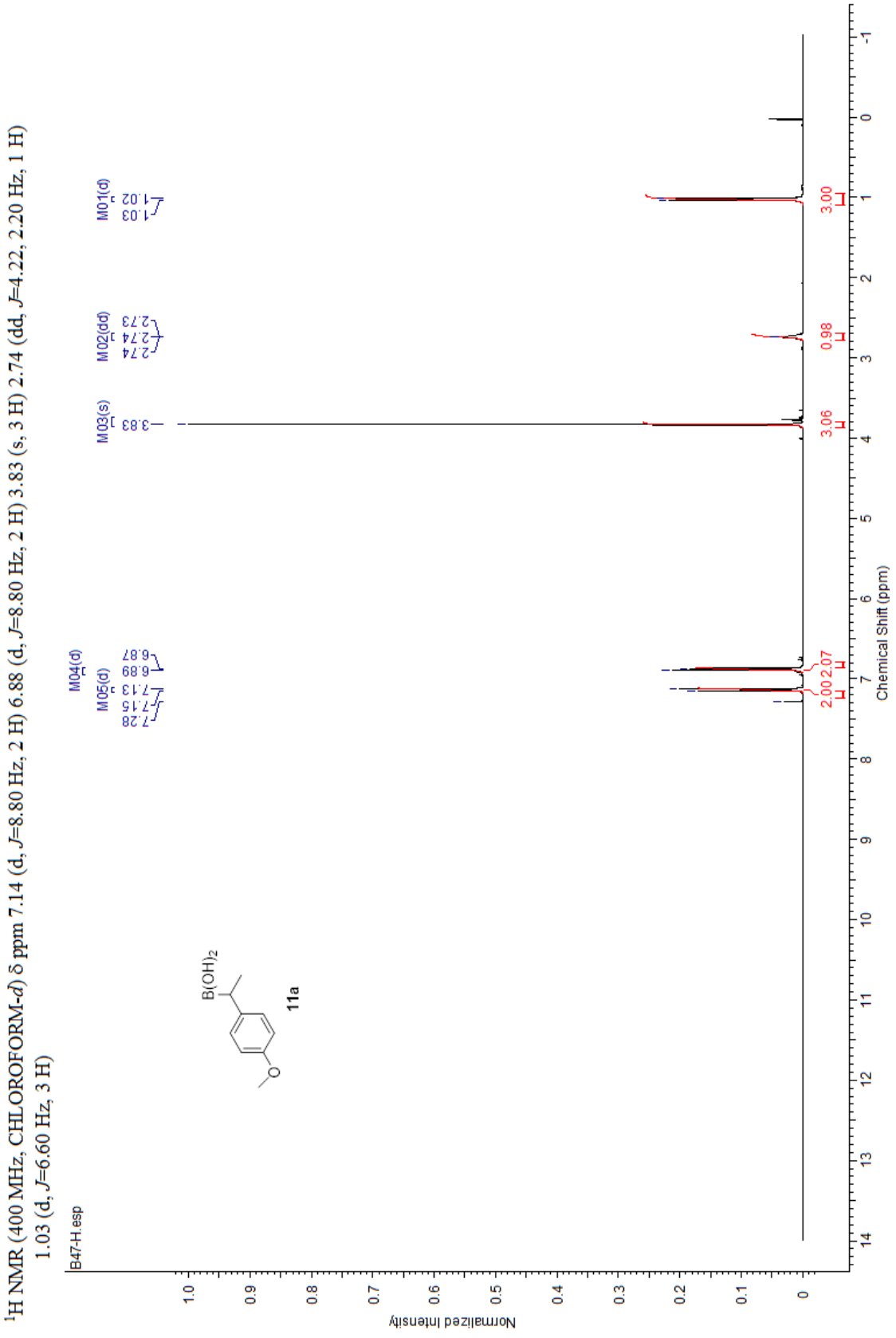

Figure 21: ^{1}H-NMR spetrum of 11a

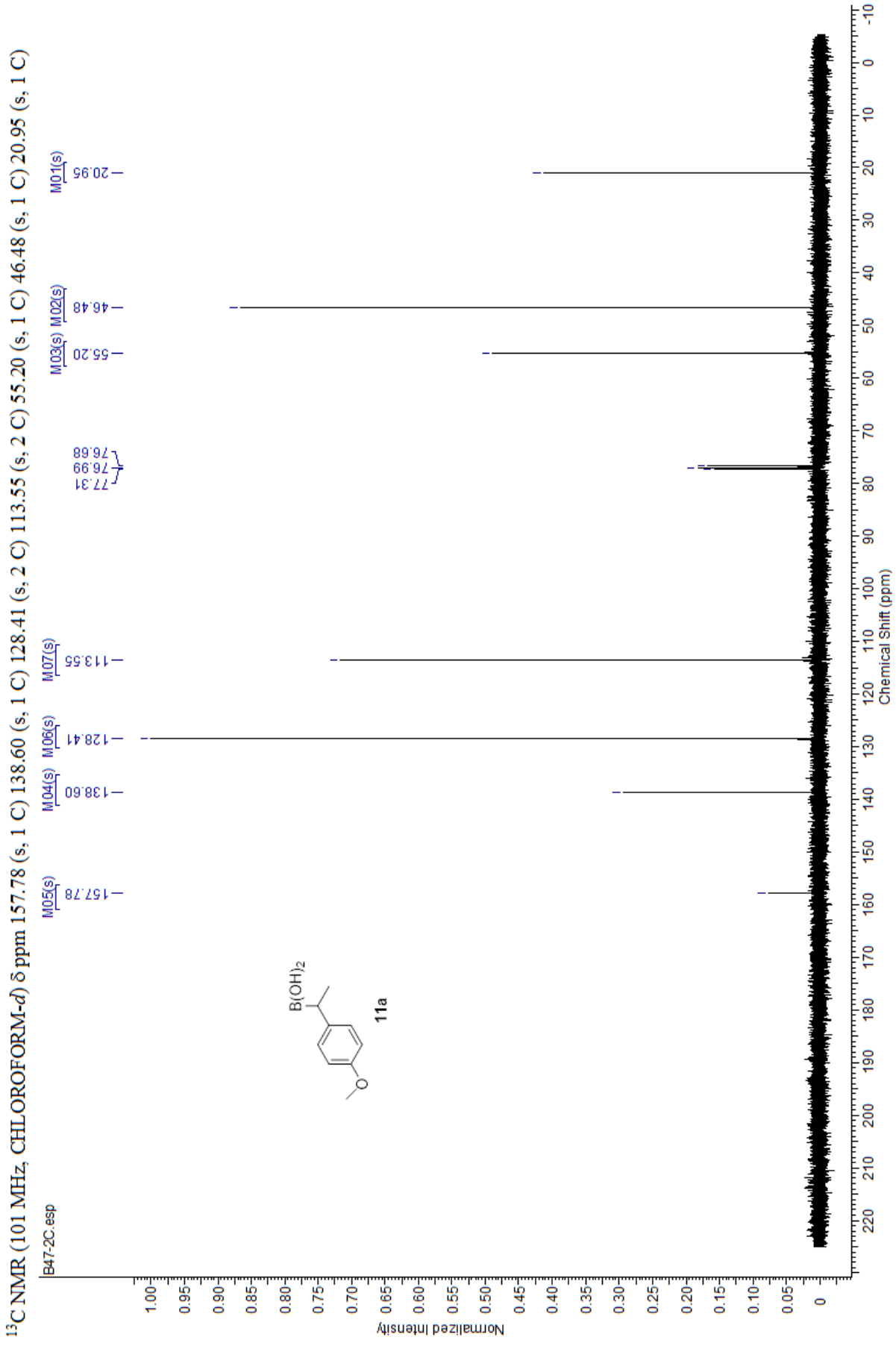

Figure 22: ^{13}C-NMR spetrum of 11a

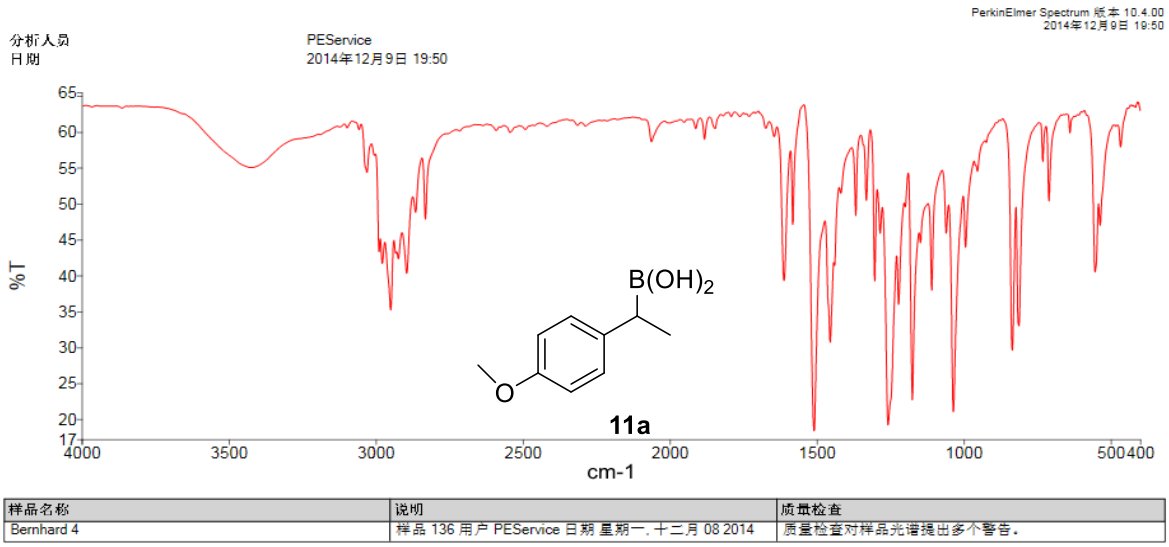

Figure 23: IR-Spectrum of 11a

Table 19: Nominated IR-Transmission values

$[\tilde{\nu}\,cm^{-1}]$	transmittance	$[\tilde{\nu}\,cm^{-1}]$	transmittance
3429	0.8692	731	0.8827
3033	0.8582	711	0.7969
2980	0.6583	553	0.6398
2952	0.5556	467	0.9146
2926	0.6681		
2897	0.6361		
2867	0.7704		
2834	0.7559		
2064	0.9259		
1883	0.9316		
1646	0.9371		
1613	0.6203		
1583	0.7447		
1510	0.2892		
1455	0.485		
1368	0.7635		
1332	0.7972		
1304	0.6196		
1285	0.7245		
1258	0.3024		
1222	0.568		
1176	0.3589		
1110	0.6003		
1060	0.7247		
1036	0.3313		
995	0.6944		
835	0.4675		
813	0.5204		

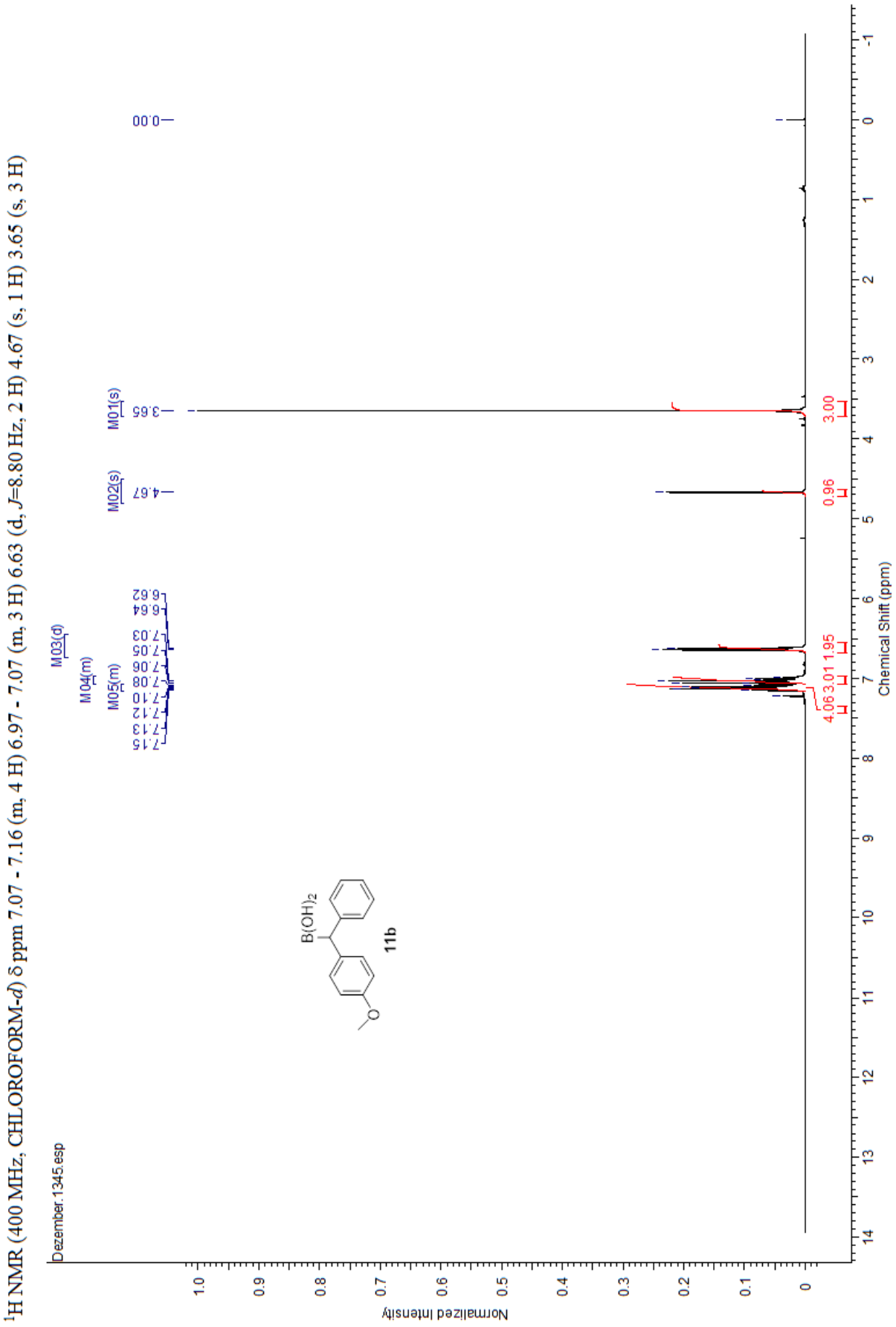

Figure 24: 1H-NMR spectrum of 11b

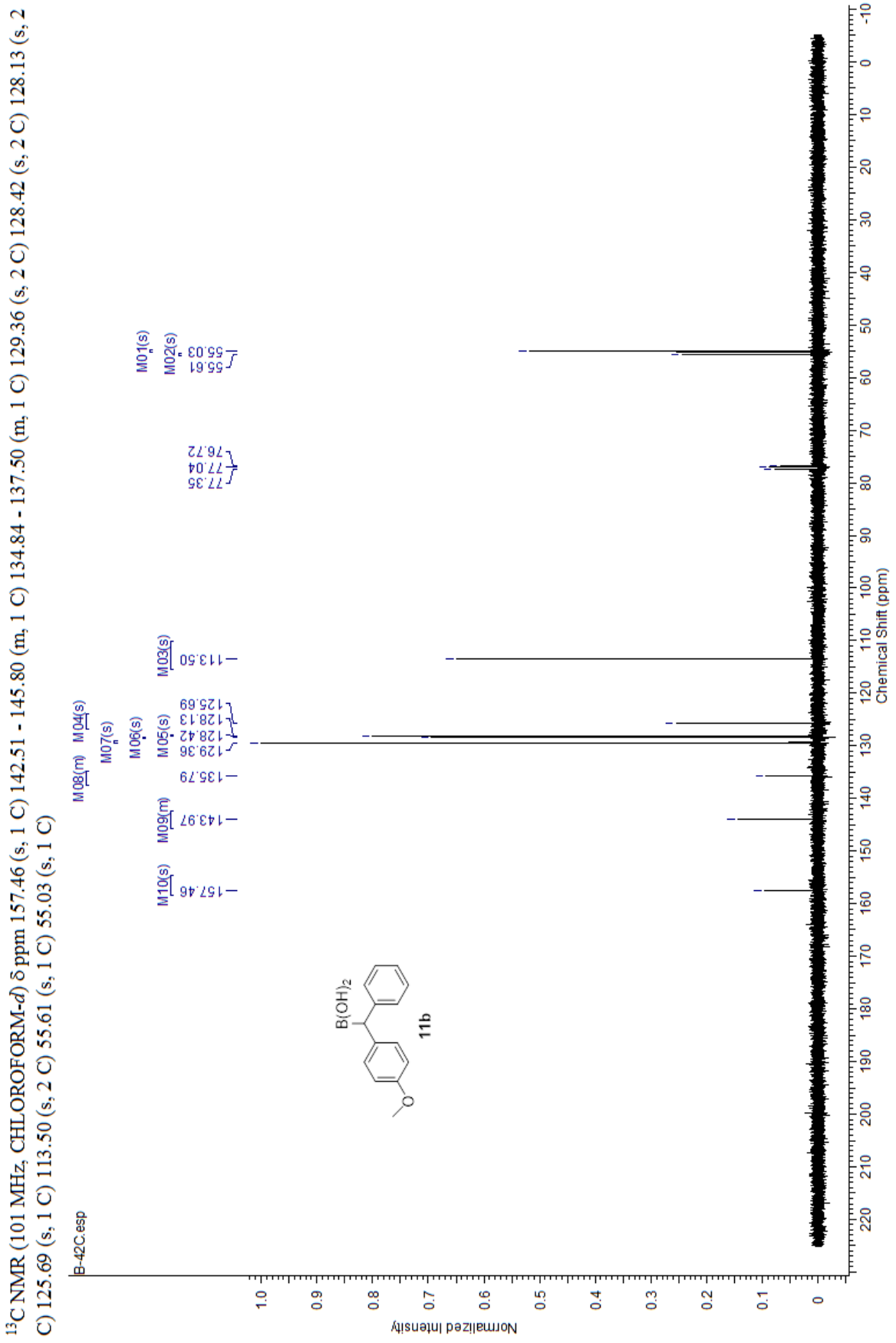

Figure 25: ^{13}C-NMR spectrum of 11b

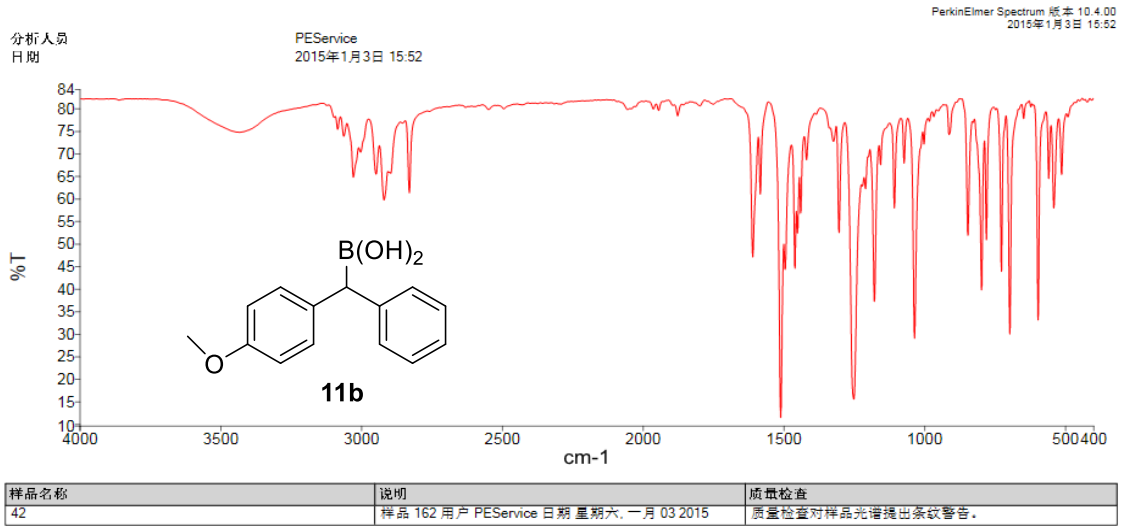

Figure 26: IR-Spectra of 11b

Table 20: Nominated IR-Transmission values

[$\tilde{\nu}$cm^{-1}]	transmittance	[$\tilde{\nu}$cm^{-1}]	transmittance	[$\tilde{\nu}$cm^{-1}]	Transmittance
3435	0.7493	2291	0.812	1178	0.3728
3167	0.8102	2249	0.8178	1156	0.677
3086	0.756	2208	0.819	1107	0.5809
3065	0.7407	2152	0.8209	1072	0.6813
3030	0.6498	2138	0.8213	1035	0.2922
3005	0.7052	2123	0.8214	983	0.774
2950	0.656	2055	0.7999	967	0.7841
2921	0.5988	1998	0.8175	950	0.7968
2898	0.6581	1964	0.8012	912	0.7445
2856	0.7701	1945	0.7983	846	0.5204
2831	0.6156	1877	0.7862	797	0.3984
2760	0.7958	1798	0.8084	780	0.5101
2690	0.8061	1751	0.812	726	0.4431
2631	0.8049	1702	0.8232	696	0.3028
2603	0.8067	1611	0.4728	647	0.7802
2549	0.8	1584	0.6138	622	0.8057
2495	0.8018	1511	0.1148	596	0.3321
2430	0.8107	1461	0.4483	558	0.6471
2401	0.8139	1419	0.6884	540	0.5809
2374	0.8133	1324	0.7293	512	0.656
2357	0.8139	1304	0.5262	422	0.817
2335	0.8145	1251	0.1554	1072	0.6813
2316	0.8126	1210	0.6238	1035	0.2922

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: National Center for Organic Mass Spectrometry in Shanghai, Shanghai Institute of Organic Chemistry

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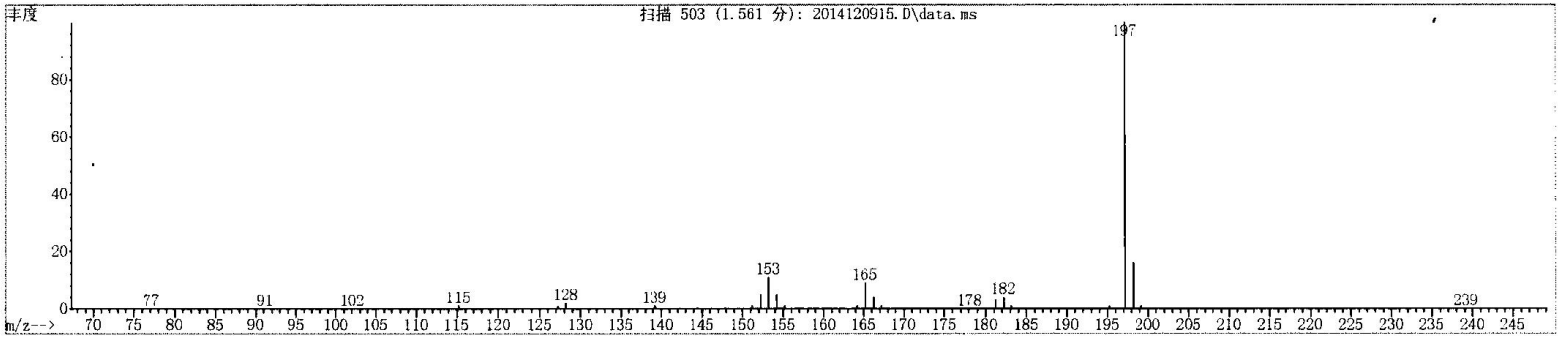
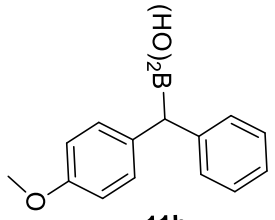


m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%
77	0.39	91	0.44	102	0.48	115	0.94	126	0.32	127	0.65	128	1.66	129	0.28	139	0.53
141	0.49	151	1.03	152	5.35	153	11.11	154	5.13	155	0.79	163	0.28	164	0.82	165	9.37
166	4.25	167	1.26	178	0.33	179	0.29	181	3.17	182	4.24	183	0.56	195	0.68	197	100
198	15.84	199	1.36	239	0.28												

8 Peak Value:

197	100	198	15.84	153	11.11	165	9.37	152	5.35	154	5.13	166	4.25	182	4.24



11b

Figure 27: Mass spectrum of 11b

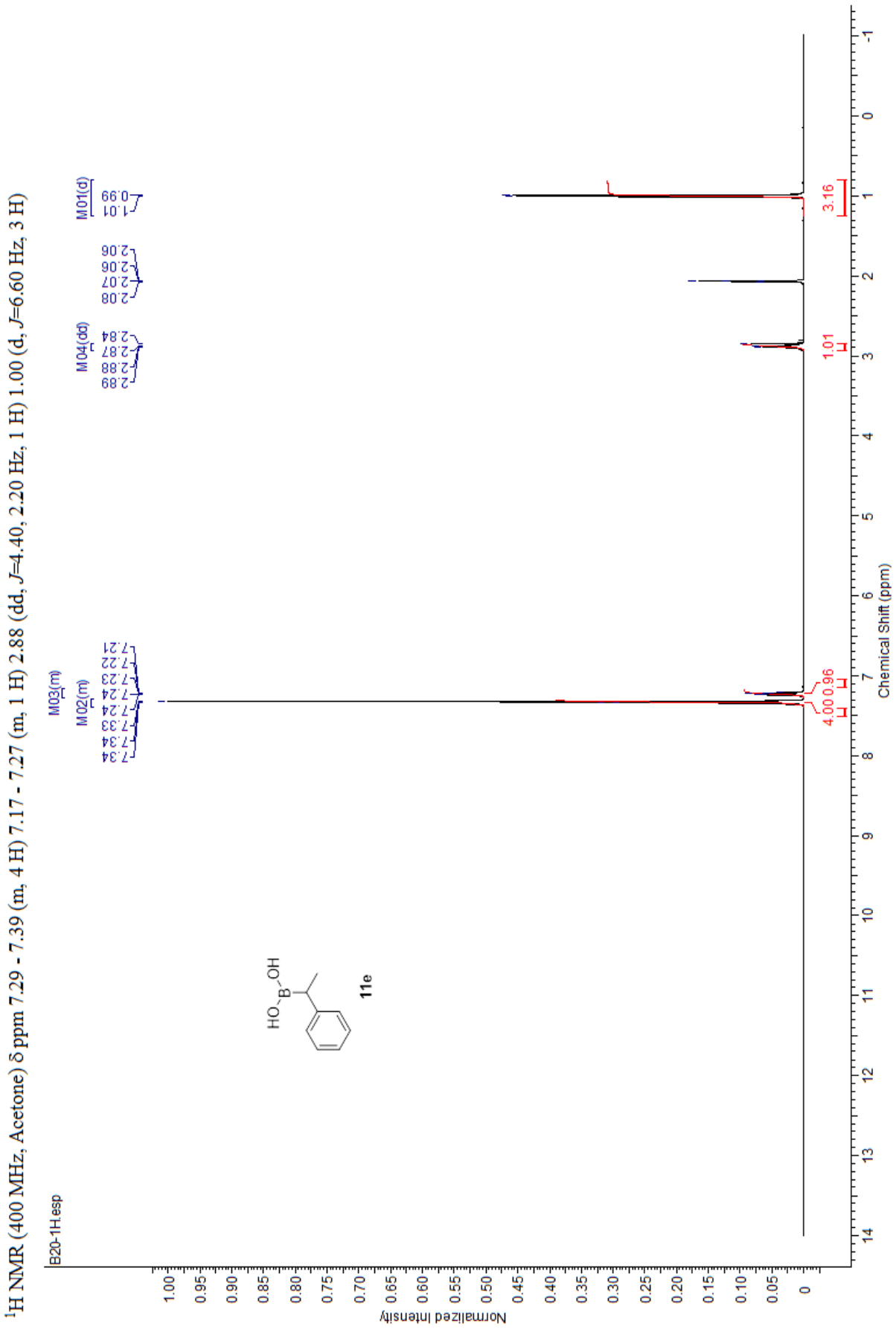


Figure 28: ^{1}H-NMR spectrum of 11e

F

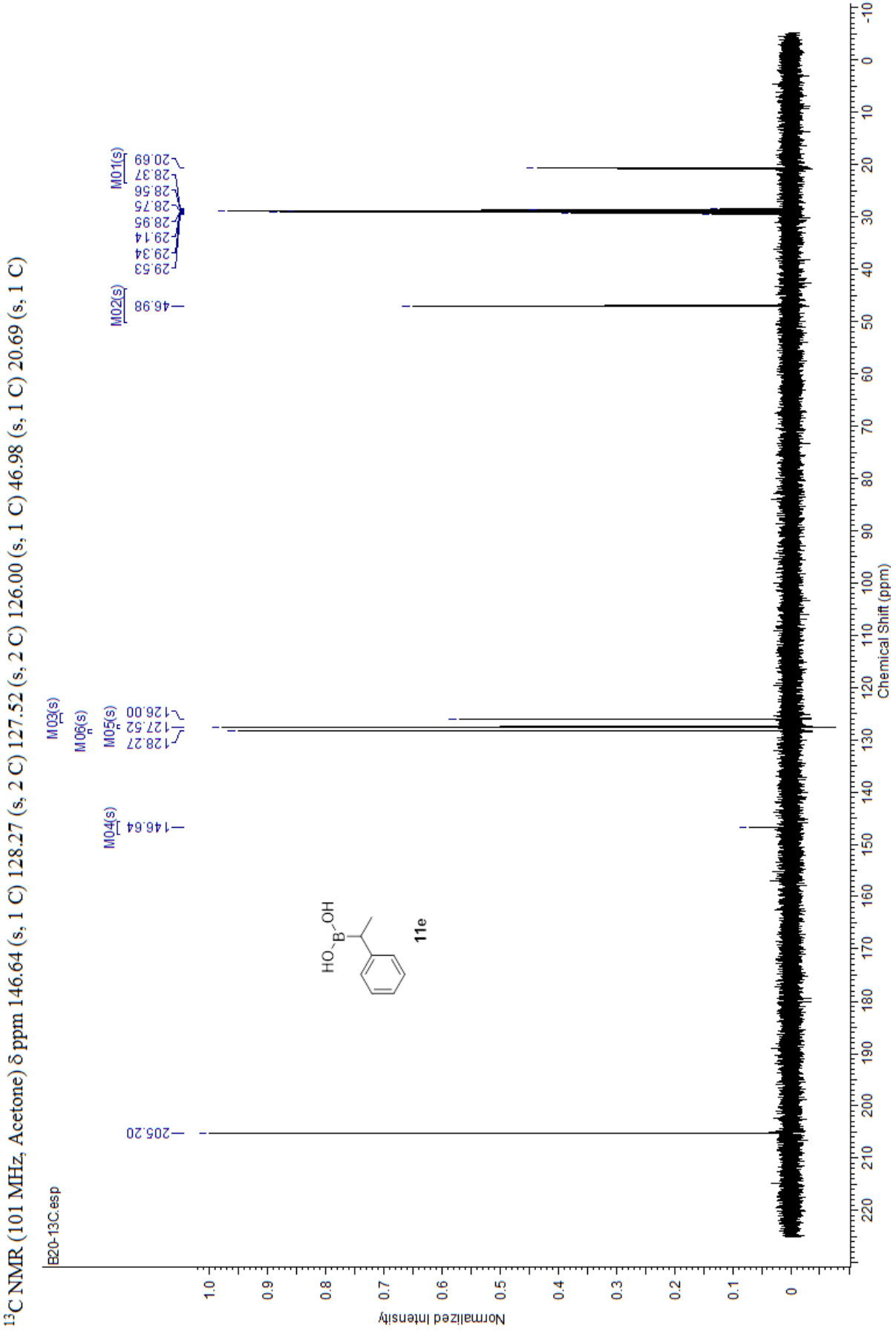


Figure 29:^{13}C-NMR of 11e

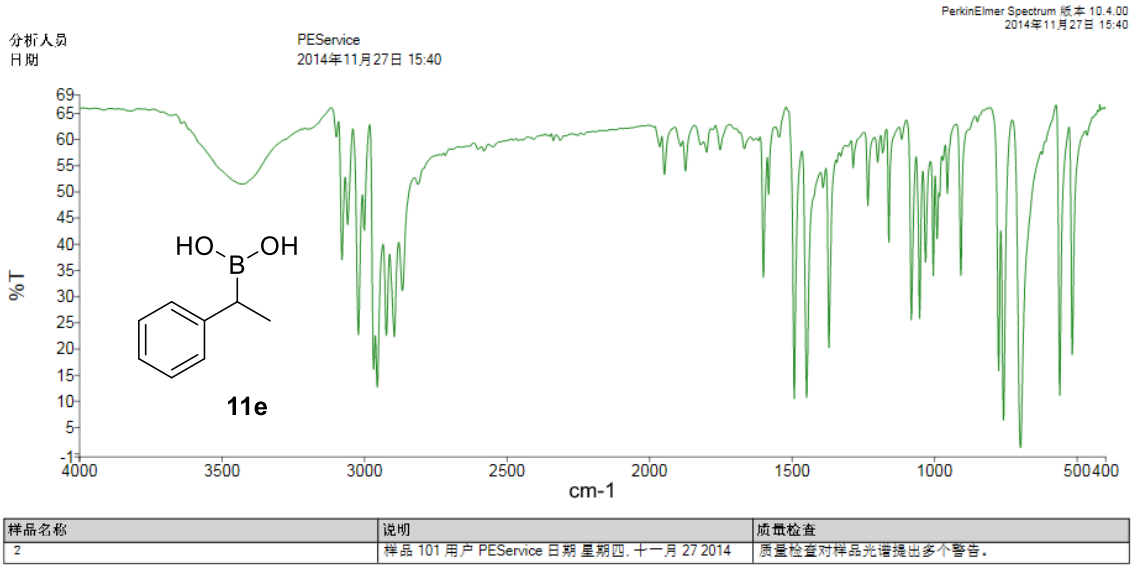


Figure 30: IR-Spectrum of 11e

Table 21: Nominated IR-Transmittance

[$\tilde{\nu}$cm^{-1}]	transmittance	[$\tilde{\nu}$cm^{-1}]	transmittance	[$\tilde{\nu}$cm^{-1}]	transmittance
3429	0.5159	2162	0.5997	1370	0.2023
3198	0.6212	2118	0.6005	1303	0.5881
3100	0.6062	2094	0.6017	1285	0.5471
3081	0.3717	2078	0.6088	1233	0.4752
3061	0.4387	2015	0.5993	1199	0.5577
3023	0.2273	1964	0.5999	1182	0.5754
3002	0.427	1948	0.6094	1160	0.4049
2956	0.1278	1891	0.6105	1115	0.6017
2925	0.2262	1874	0.6157	1081	0.2582
2897	0.2232	1821	0.6182	1051	0.2607
2868	0.3116	1799	0.6198	1031	0.3668
2814	0.5152	1752	0.622	1003	0.3434
2731	0.5716	1667	0.6225	990	0.4107
2718	0.5707	1635	0.6272	954	0.4981
2696	0.5821	1600	0.5872	907	0.3422
2664	0.5862	1582	0.5341	849	0.6355
2631	0.5881	1546	0.5887	774	0.158
2603	0.5825	1492	0.541	757	0.0635
2582	0.5794	1448	0.5911	697	0.0107
2548	0.5874	1391	0.5771	559	0.1114
2479	0.6003	1370	0.5817	515	0.1899

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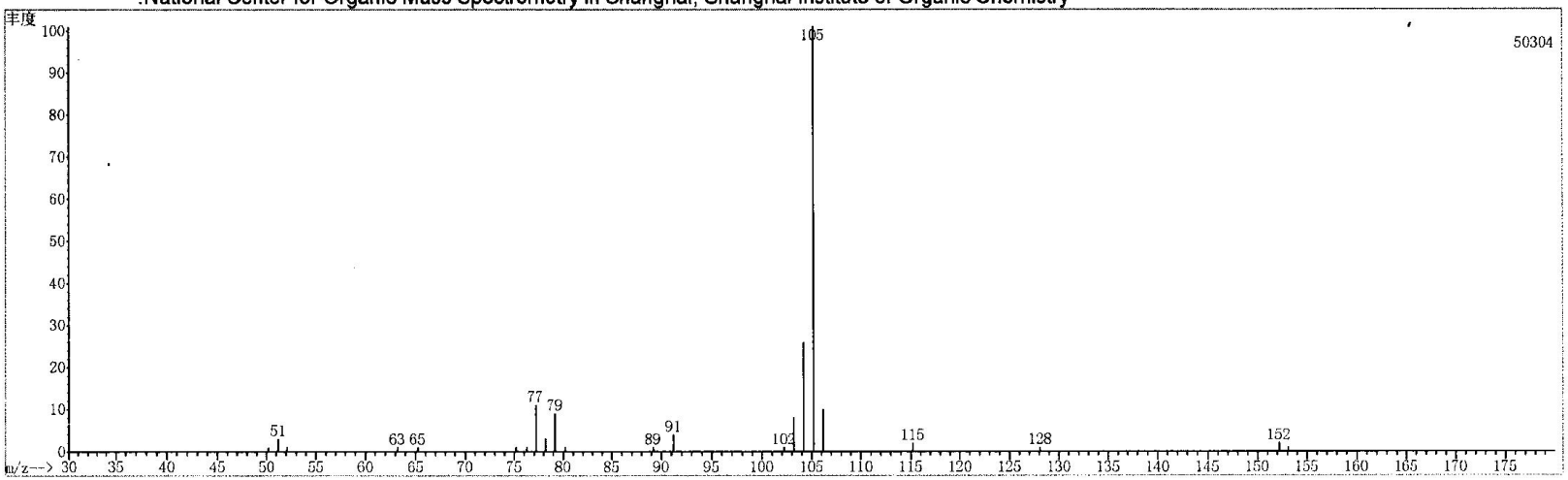
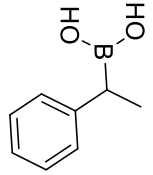


m/z	%RA	m/z	%RA	m/z	%RA
50	0.78	83	0.39	127	0.37
51	2.51	89	1.38	128	0.55
52	0.52	90	0.44	139	0.34
53	0.48	91	4.30	151	0.43
63	1.03	92	0.38	152	1.76
65	1.46	102	1.20	153	0.91
74	0.35	103	7.99		
75	0.51	104	25.36		
76	1.19	105	100.00		
77	11.09	106	9.46		
78	3.45	107	0.45		
79	8.93	115	2.29		
80	0.61	116	0.48		
82	0.35	117	0.46		

8 Peak Value:

105	100.00	104	25.36	77	11.09	106	9.46	79	8.93	103	7.99	91	4.30	78	3.45



11e

Figure 31: Mass spectra of 11e

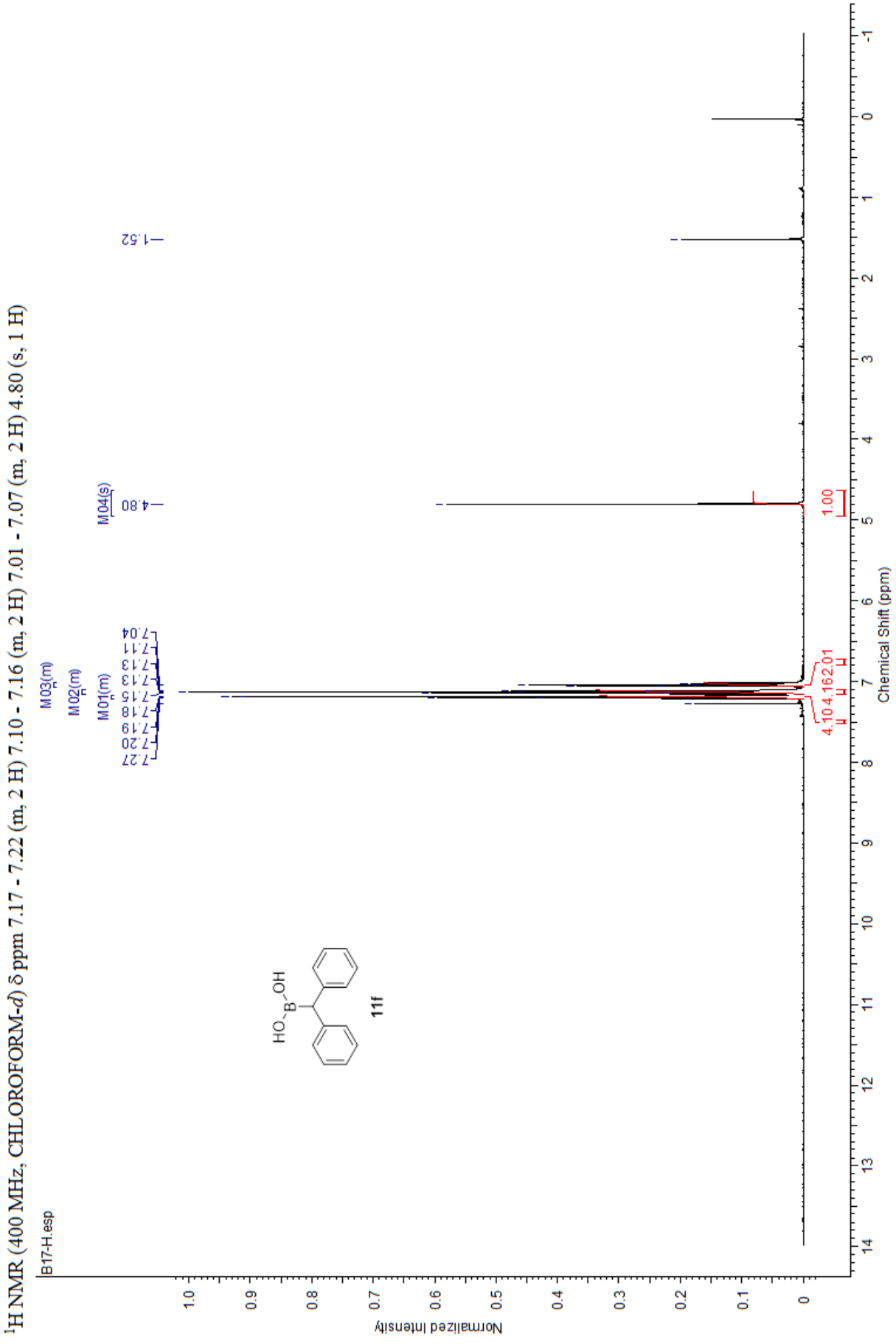


Figure 32: ^{1}H-NMR of 11f

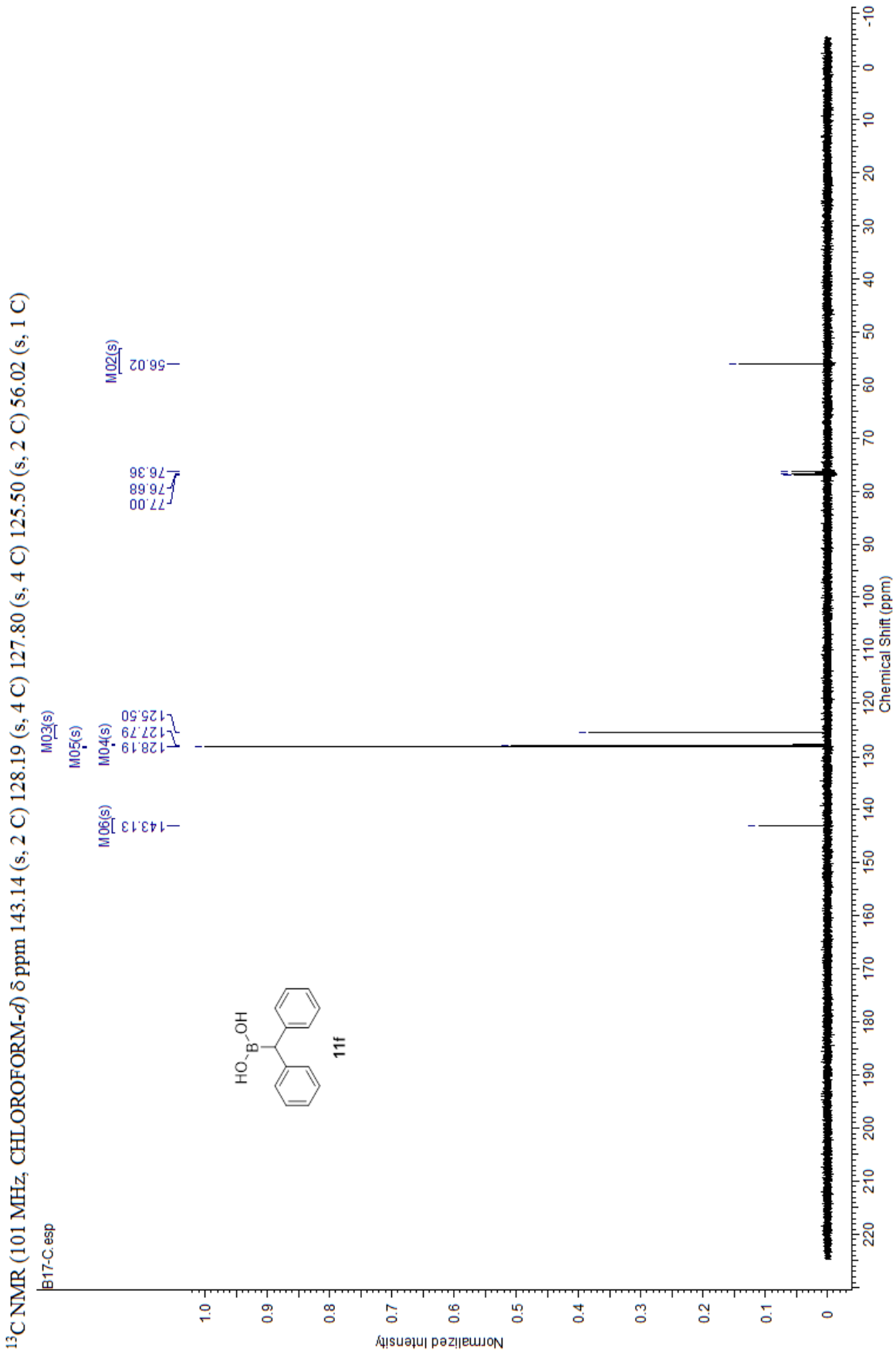


Figure 33: ^{13}C-NMR of 11f

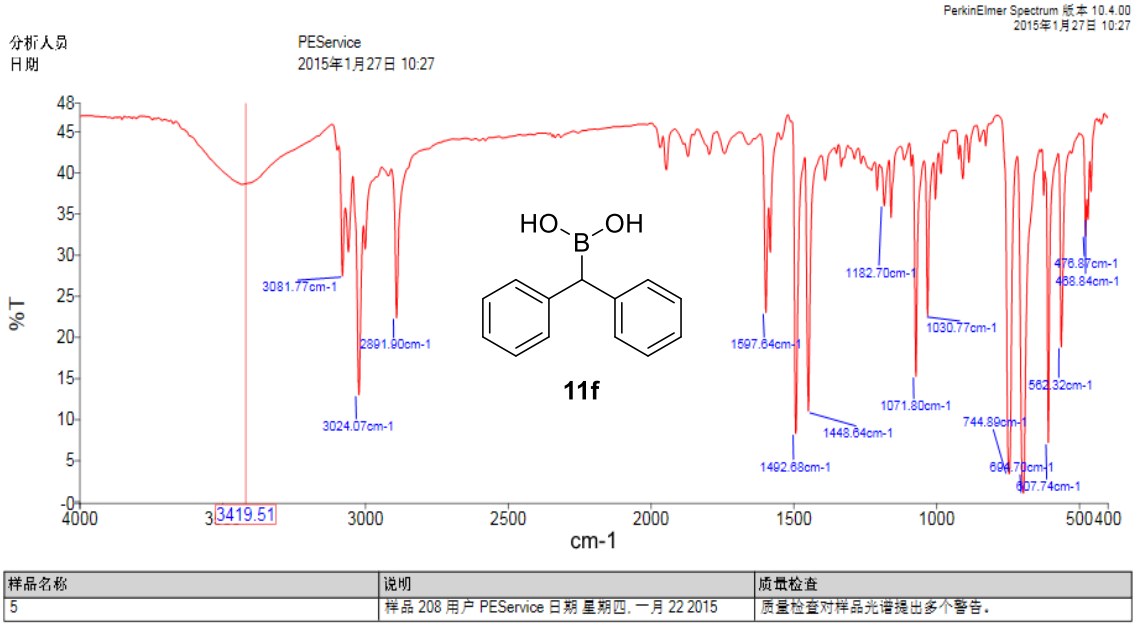


Figure 34: IR-Spectra of 11f

Table 22: Nominated *IR*-transmittance values

[$\tilde{\nu}$cm^{-1}]	transmittance
3082	0.5875
3061	0.65
3024	0.2772
3002	0.6571
2892	0.4777
1598	0.4927
1582	0.6503
1493	0.1776
1449	0.2369
1208	0.8111
1183	0.7704
1159	0.7397
1072	0.3265
1031	0.4845
1003	0.7877
745	0.0711
695	0.0209
624	0.7986
608	0.1552
562	0.4031
477	0.6912

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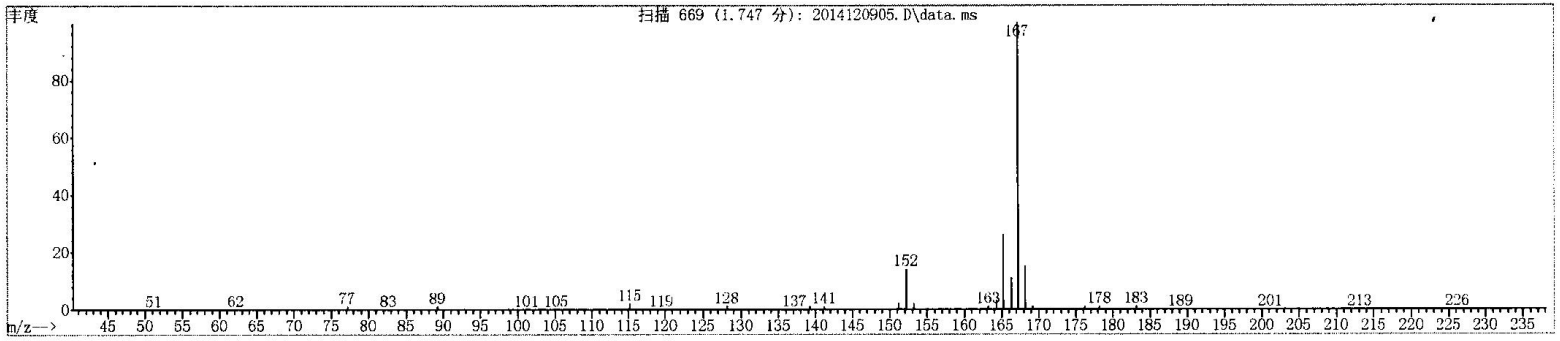
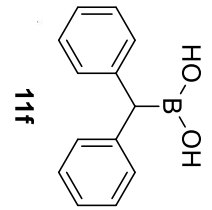


m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%
50	0.11	51	0.42	52	0.09	62	0.09	63	0.37	64	0.07	65	0.35	74	0.08	75	0.15
76	0.22	77	0.65	78	0.17	83	0.18	86	0.05	87	0.12	88	0.1	89	0.54	90	0.08
91	0.46	92	0.12	101	0.11	102	0.36	103	0.05	105	0.37	113	0.26	114	0.16	115	1.82
116	0.18	120	0.05	120	0.04	125	0.09	126	0.4	127	0.4	128	1.41	129	0.16	137	0.1
138	0.15	139	1.28	140	0.19	141	0.78	142	0.09	144	0.05	149	0.06	150	0.34	151	1.76
152	14.41	153	2.03	154	0.29	162	0.12	163	1.16	164	2.53	165	26.23	166	11.37	167	100
168	15.37	169	1.07	175	0.04	176	0.51	177	0.32	178	1.02	179	0.37	180	0.11	183	0.81
184	0.11	187	0.05	188	0.05	189	0.14	200	0.1	201	0.07	202	0.16	213	0.11	215	0.15
224	0.09	225	0.07	226	0.23	227	0.09	228	0.08								

8 Peak Value:

167	100	165	26.23	168	15.37	152	14.41	166	11.37	164	2.53	153	2.03	115	1.82



11f

Figure 35: MS of 11f

9.5 Photoreactions - Solvent screening (Spectra A-M)

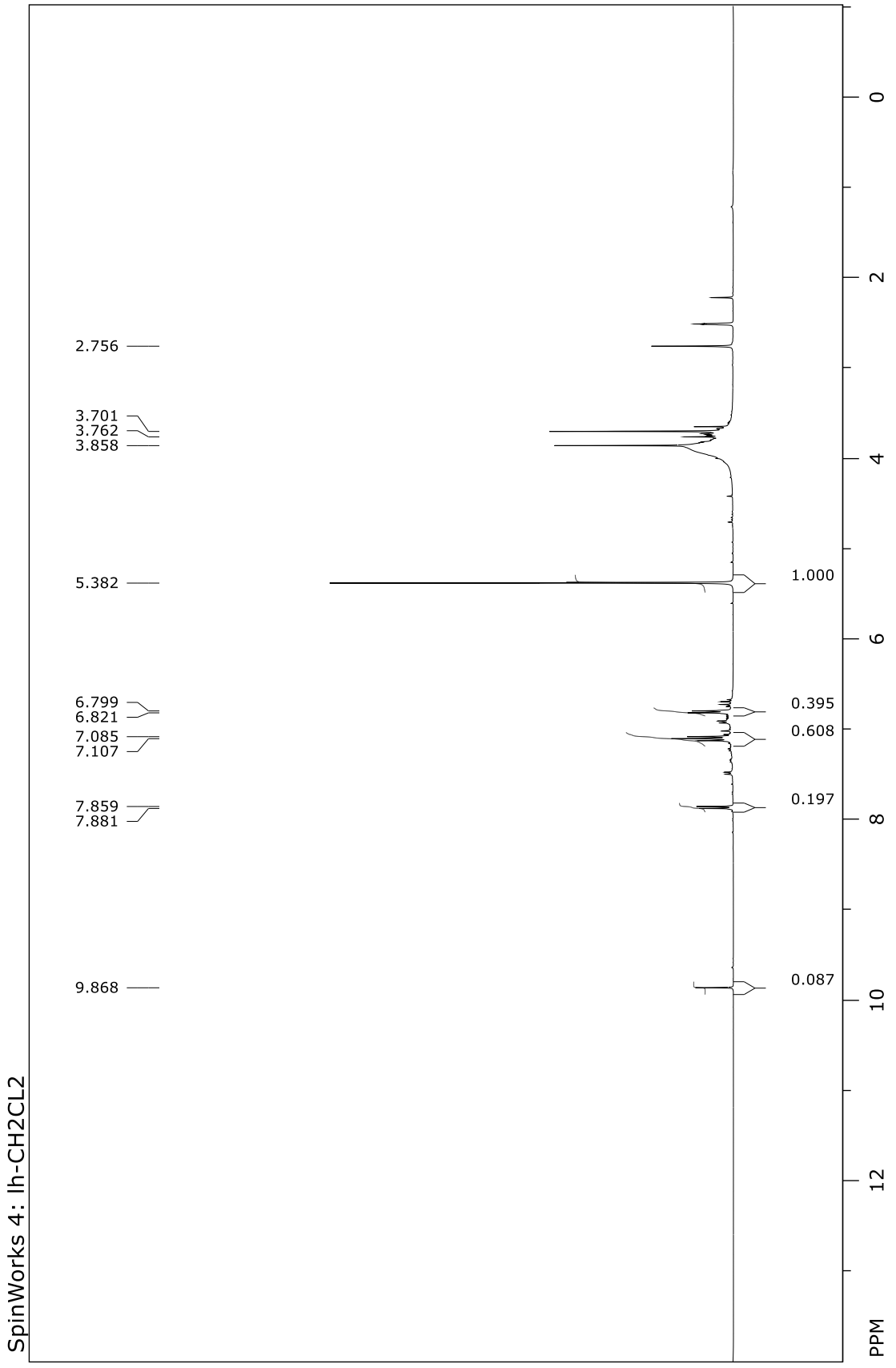


Figure 36: Spectrum **A** - Reaction in DCM

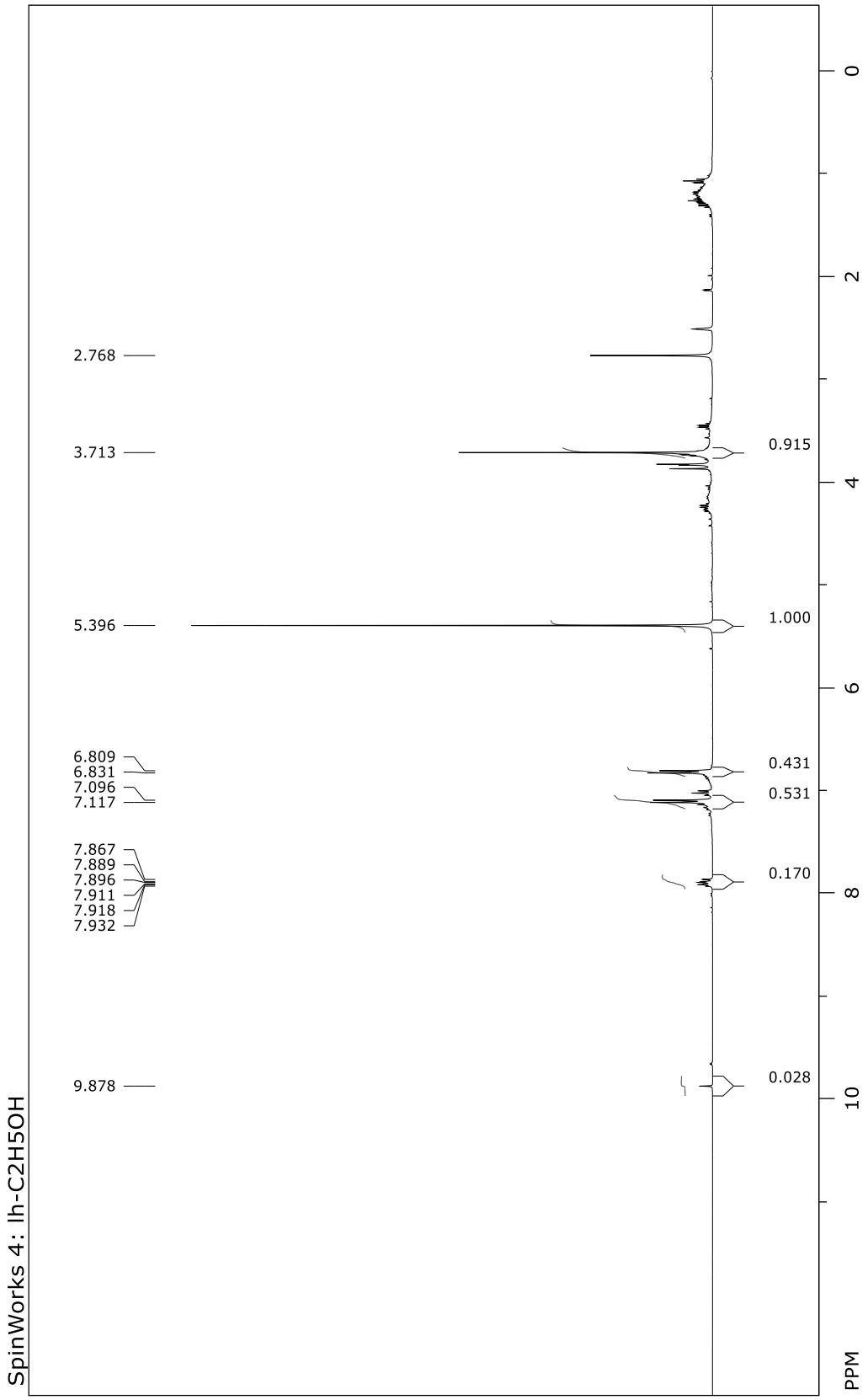


Figure 37: Spectrum **B** - Reaction in ethanol

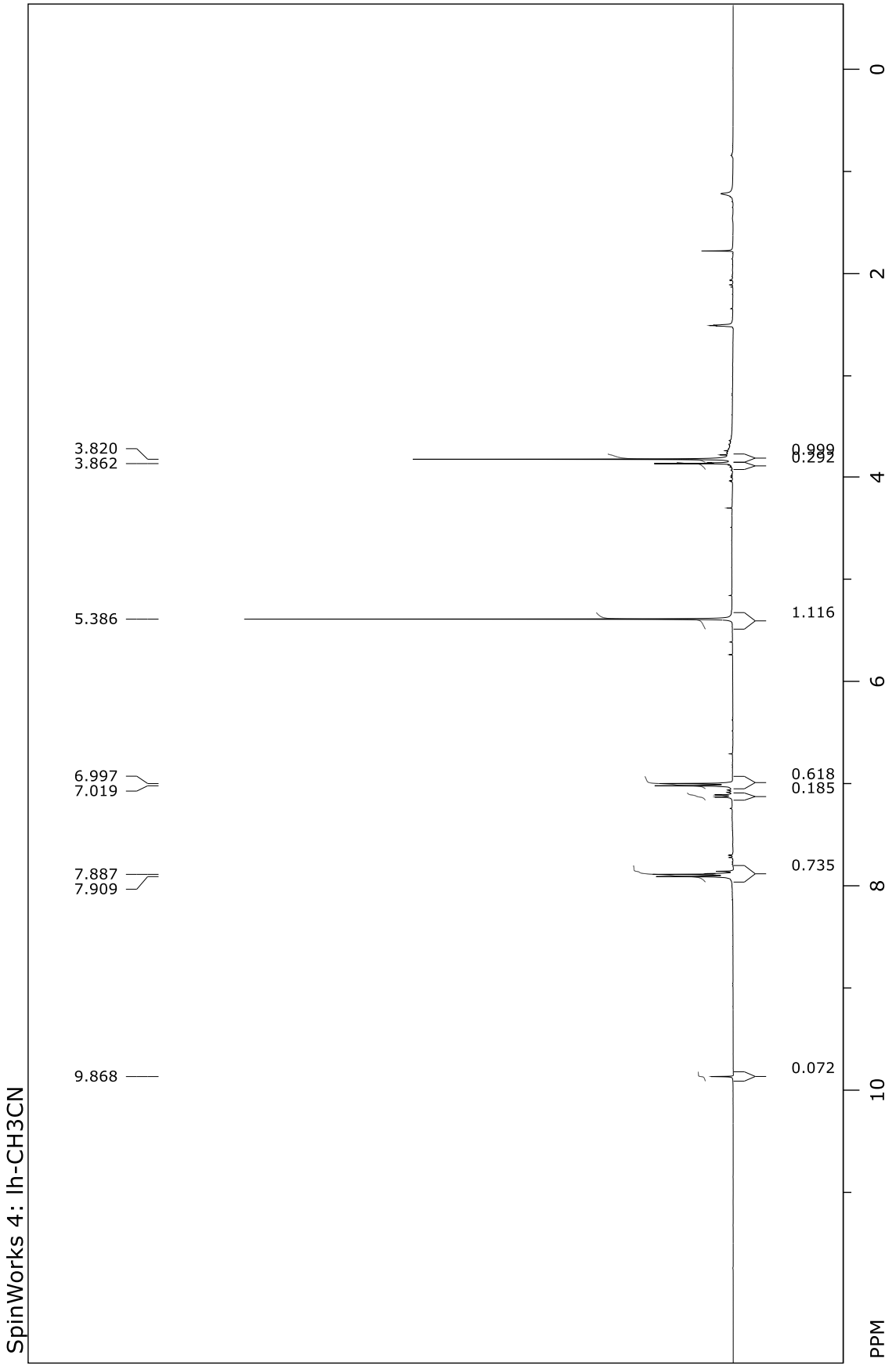


Figure 38: Spectrum **C** – Reaction in Acetonitrile

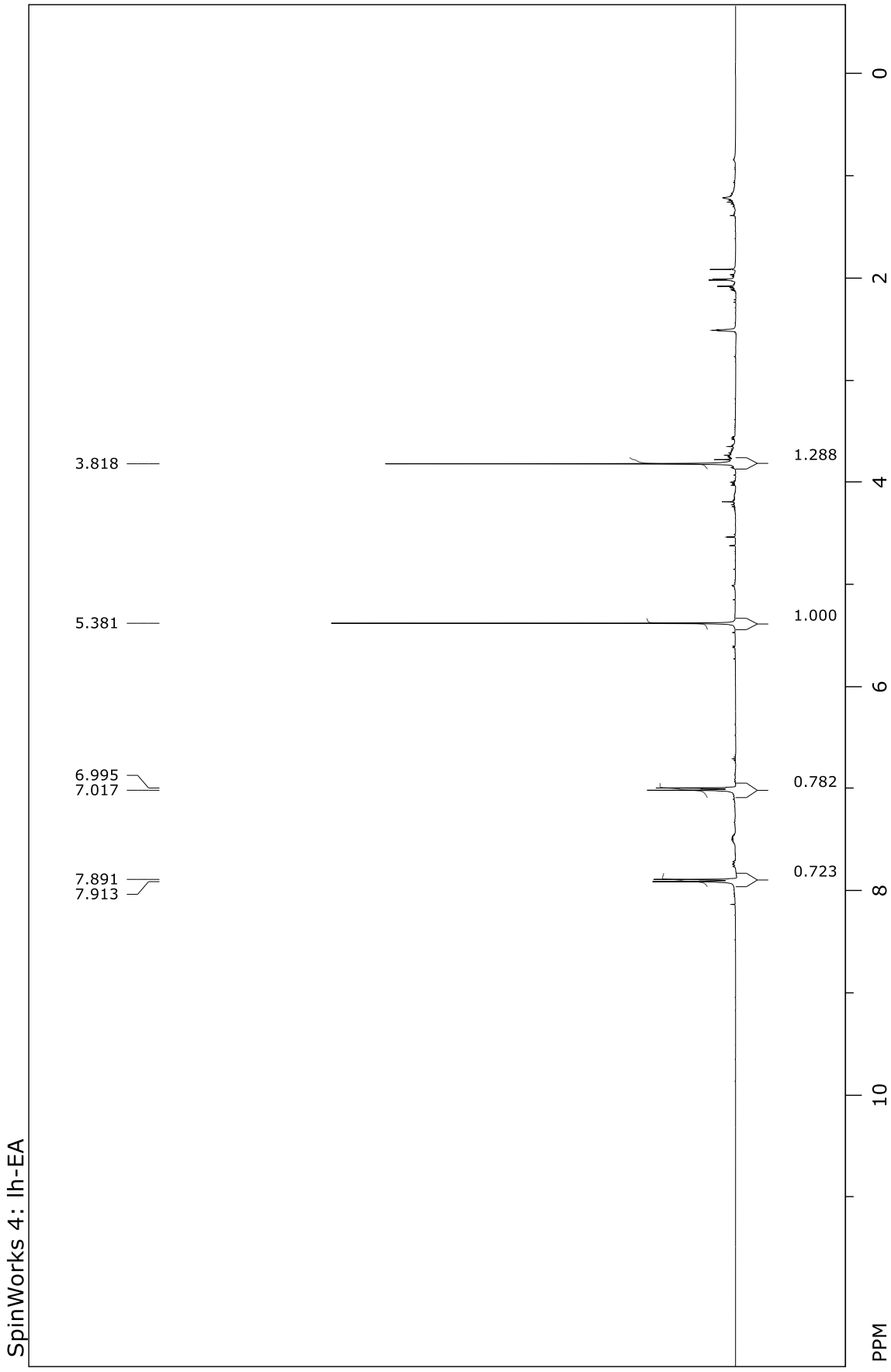


Figure 39: Spectrum **D** – Reaction in ethyl acetate

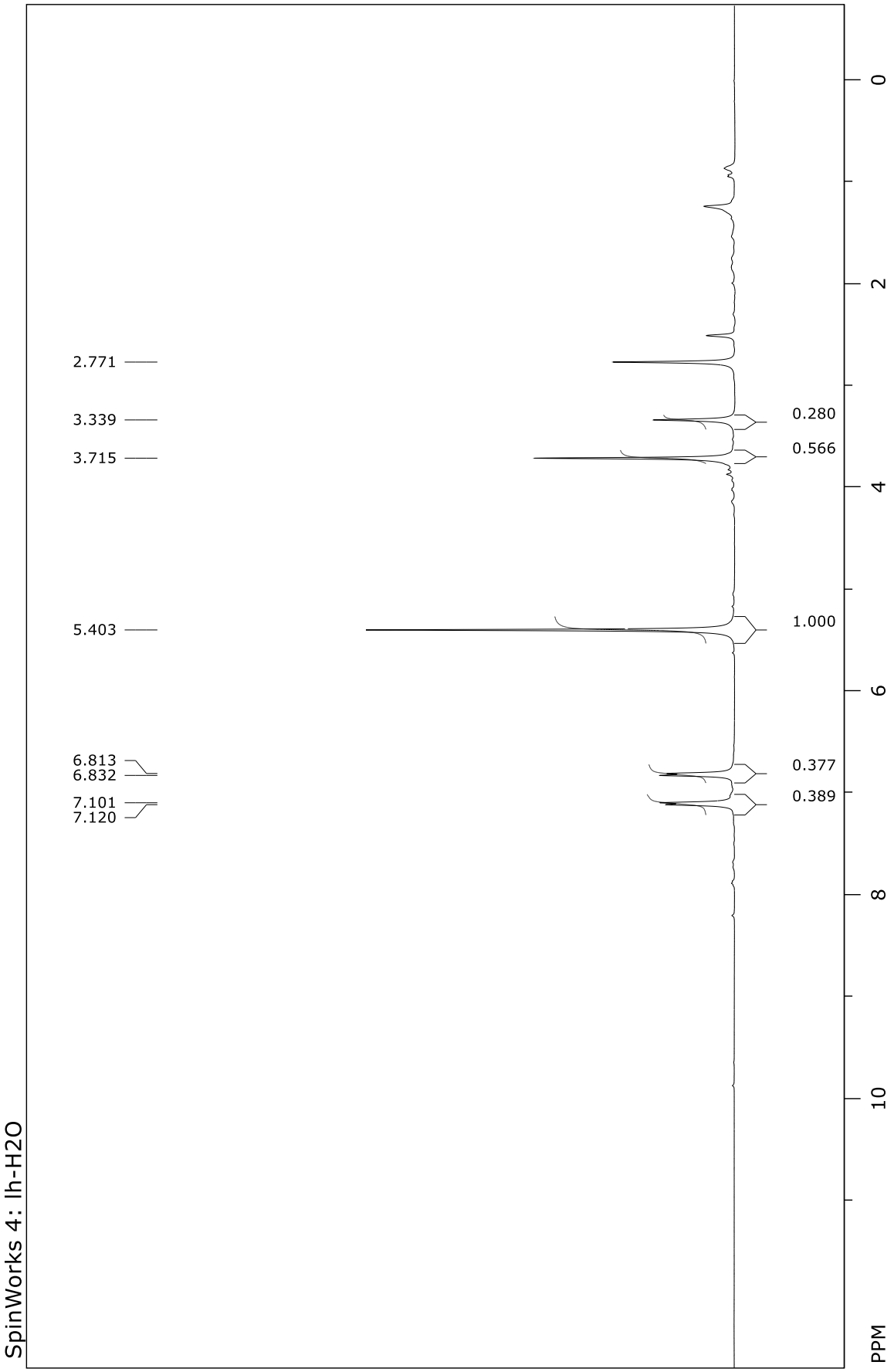


Figure 40: Spectrum **E** - Reaction in H_2O

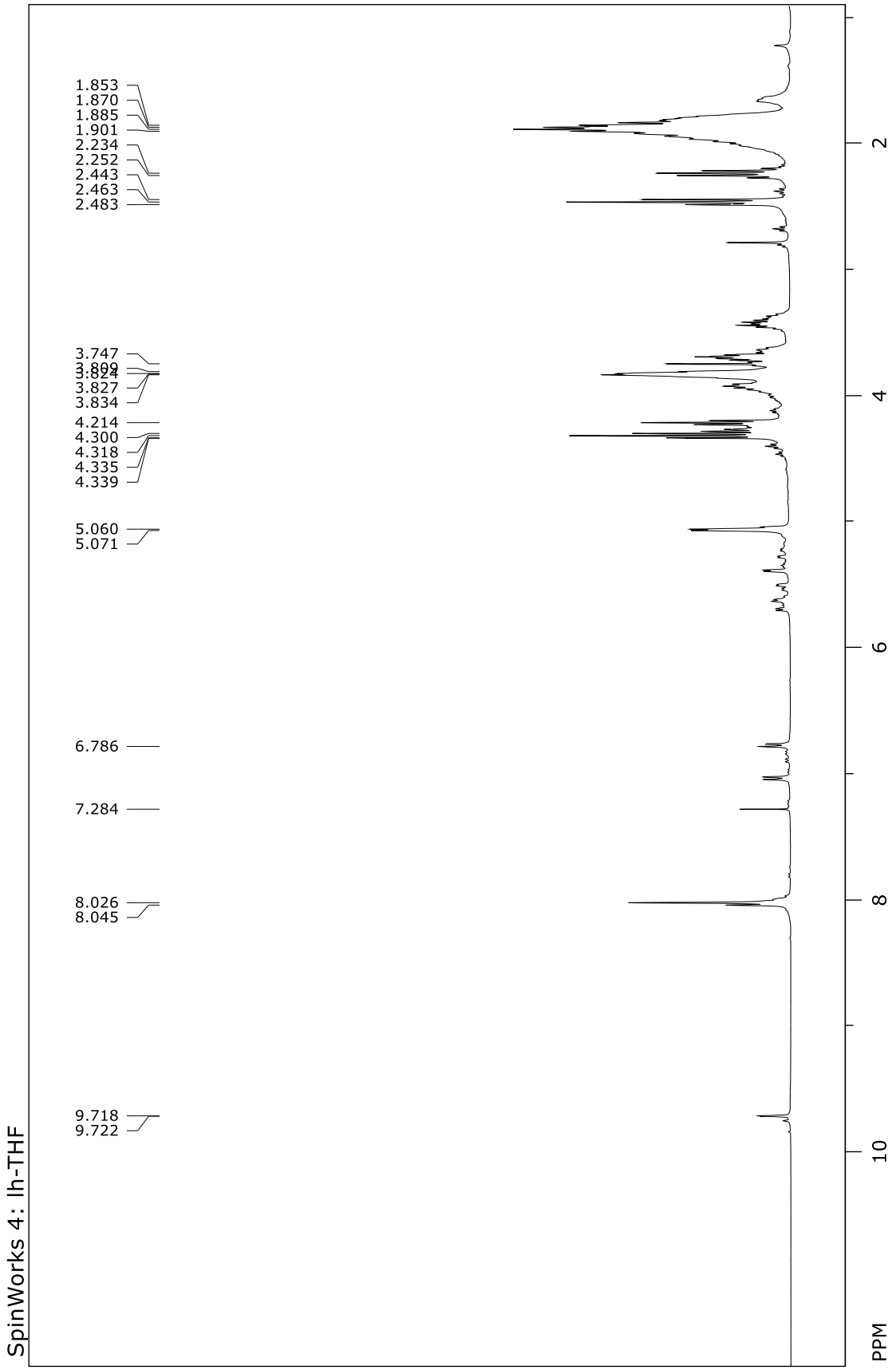


Figure 41: Spectrum **F** - Reaction of **9a** in THF

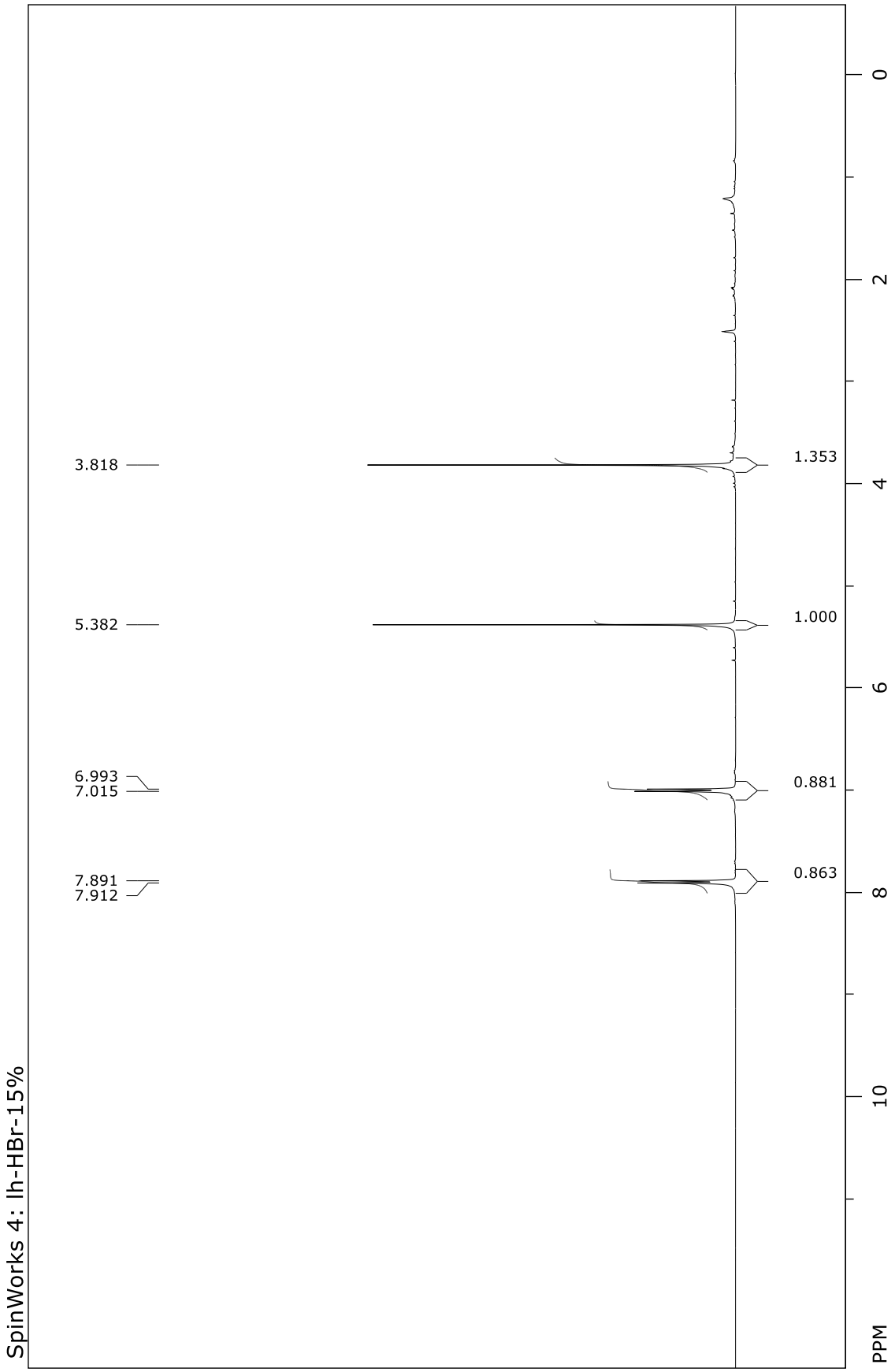


Figure 42: Spectrum **G** - Reaction Acetone with 15 mol % HBr

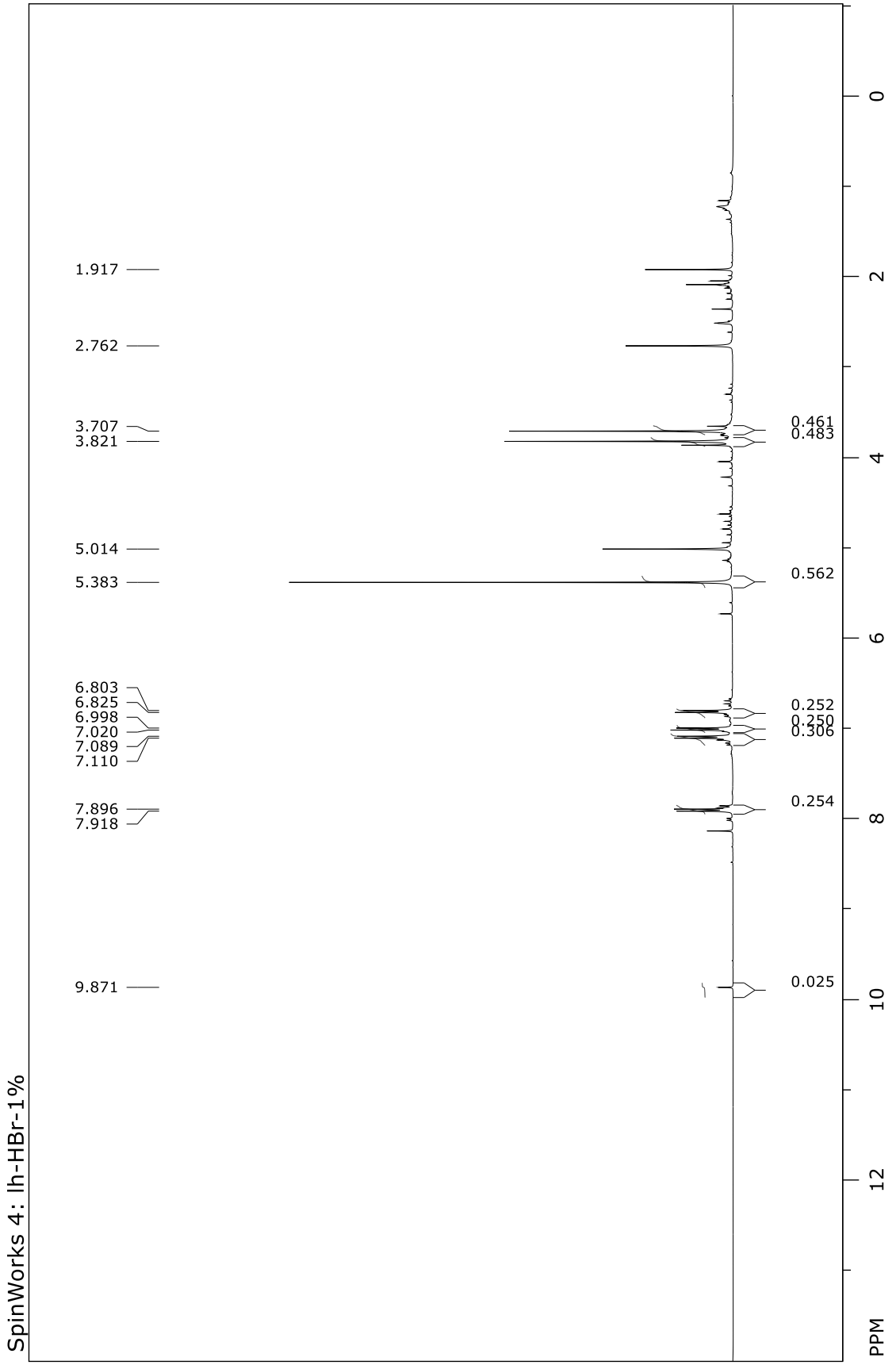


Figure 43: Spectrum **H** - Reaction Acetone with 1 mol % HBr

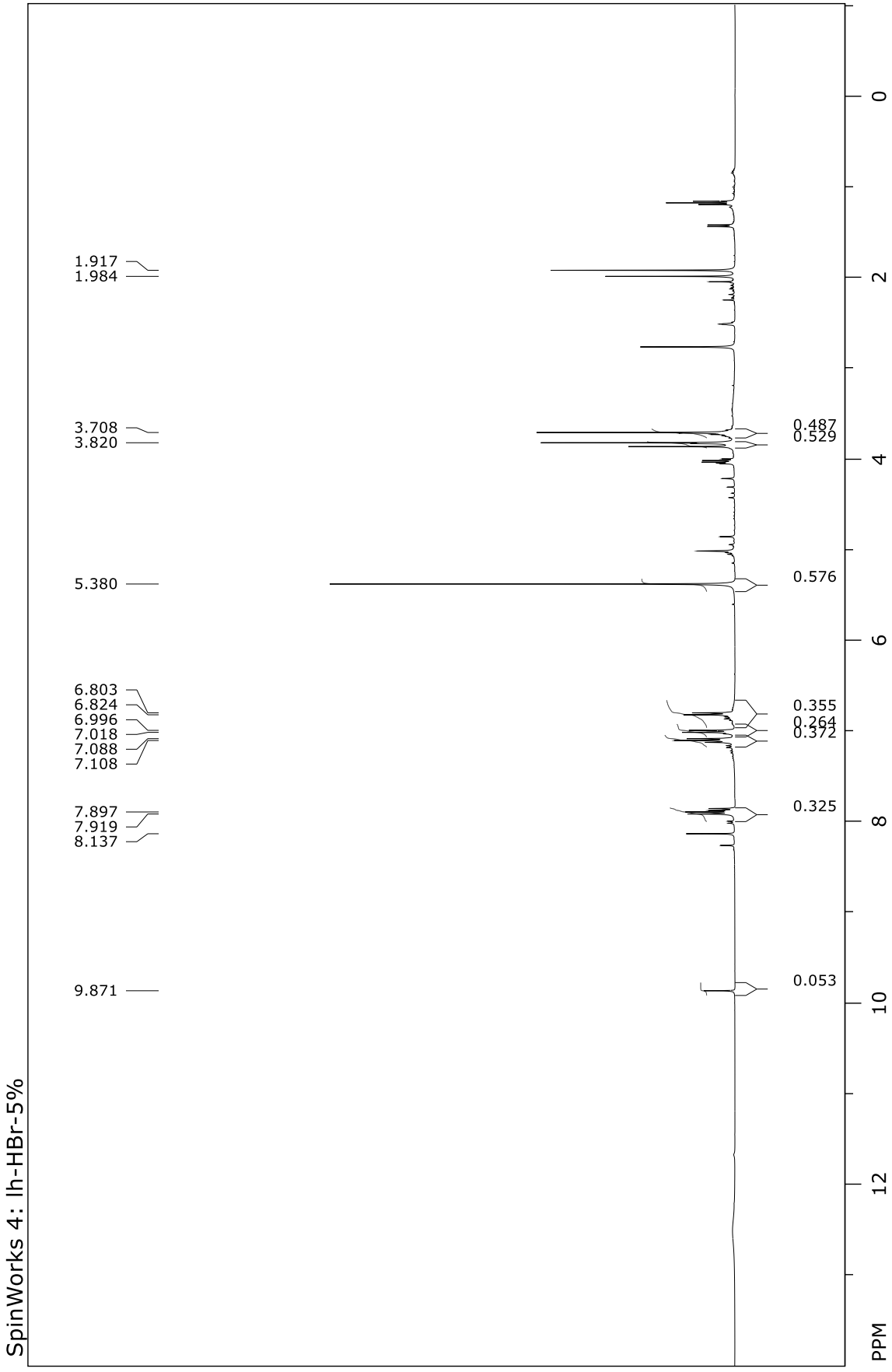


Figure 44: Spectrum **I1** - Reaction Acetone with 5 mol % HBr

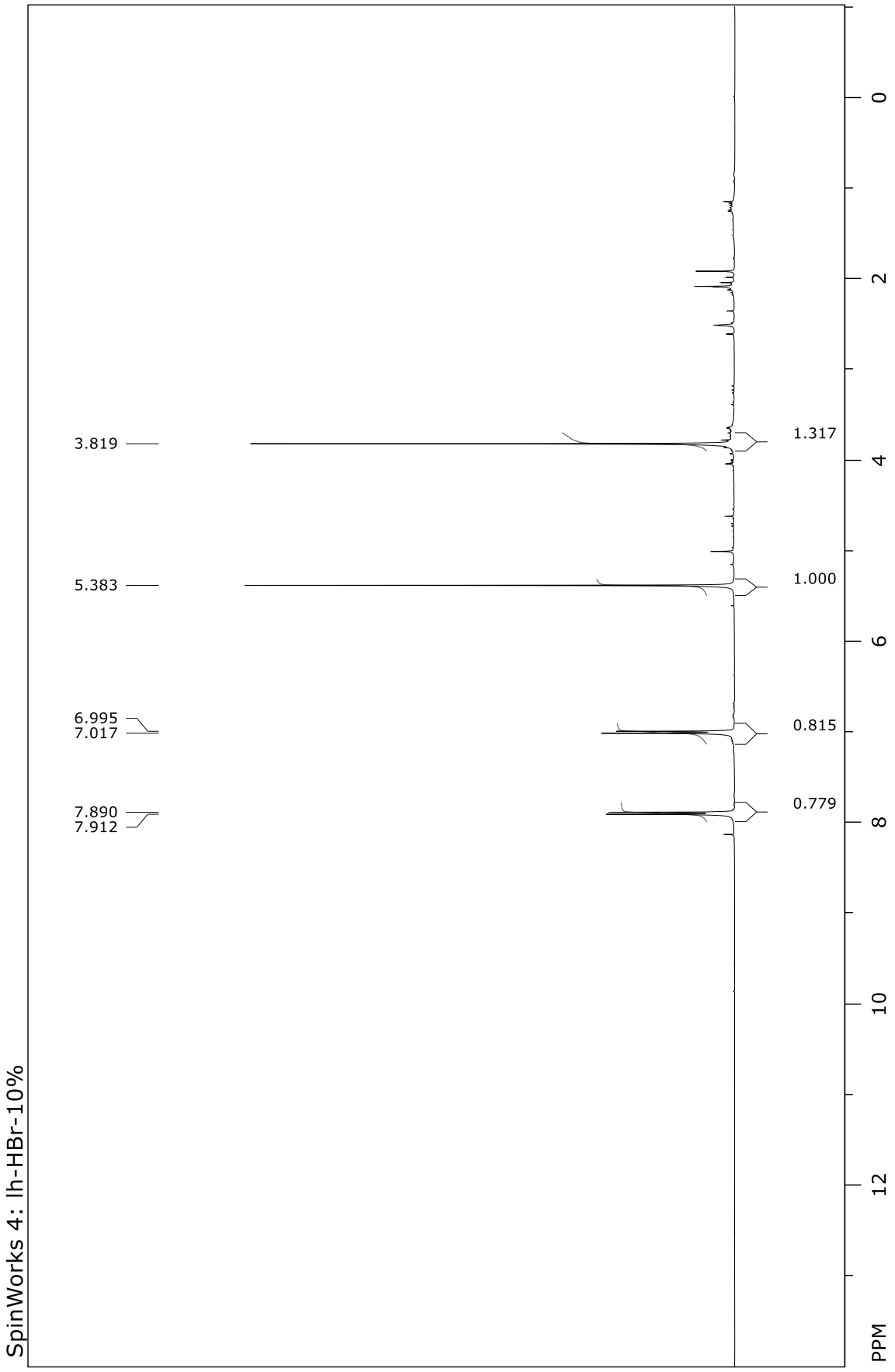


Figure 45: Spectrum **I2** – Reaction in Acetone with 10 mol % HBr

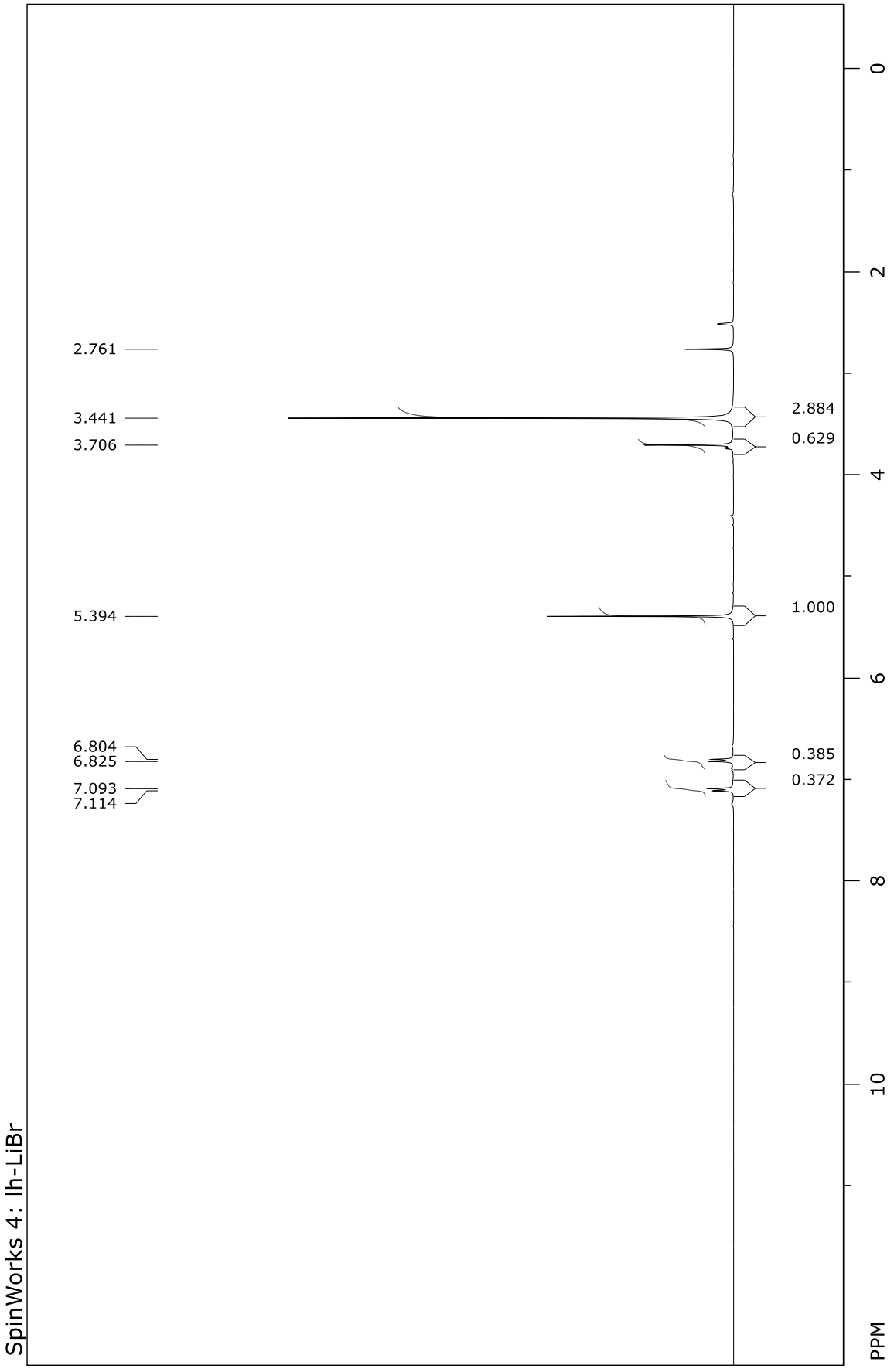


Figure 46: Spectrum **J** - Reaction in the persence of **15** mol % LiBr

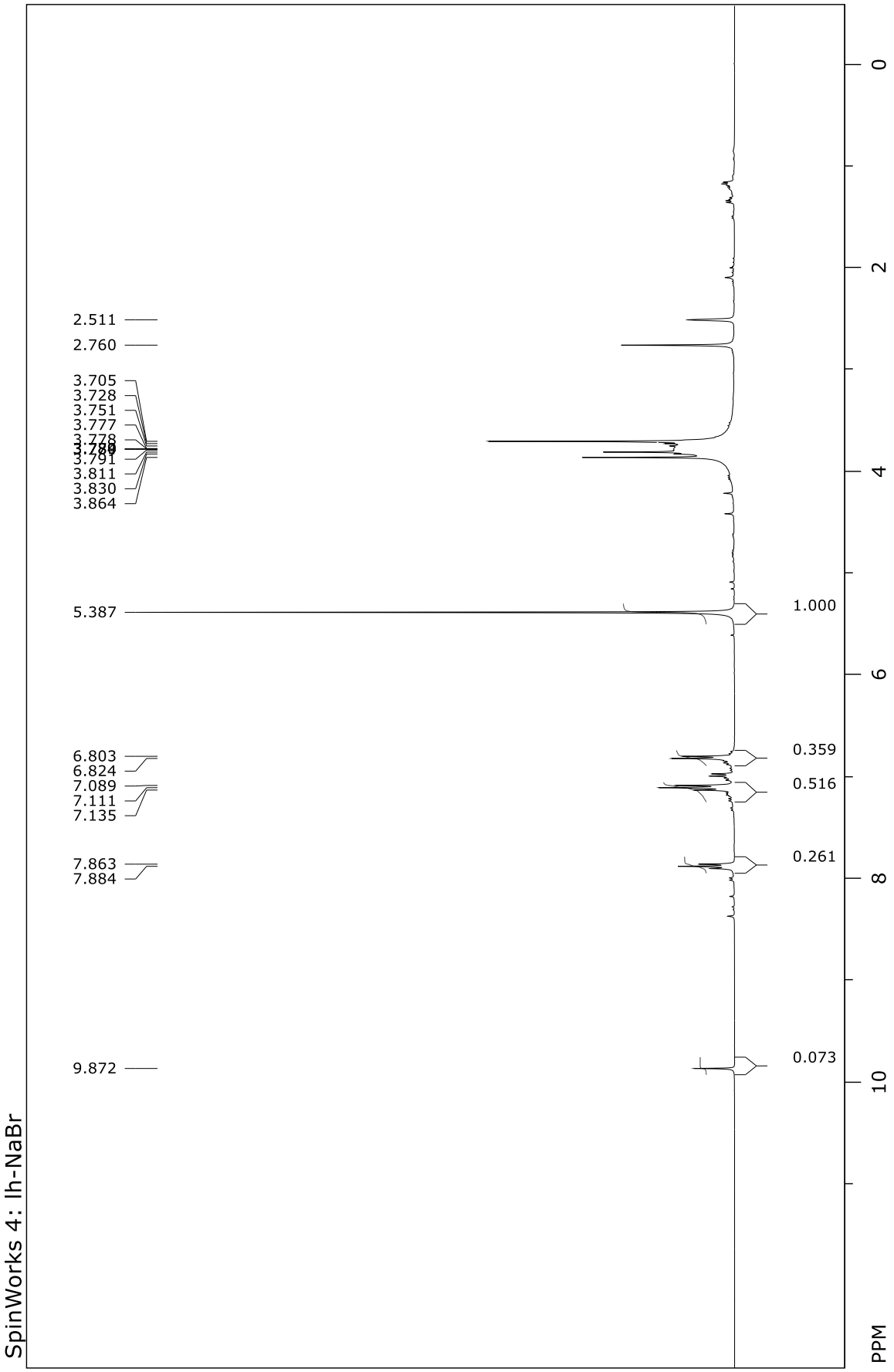


Figure 47: Spectrum **K –** Reaction in the presence of 15 mol % NaBr

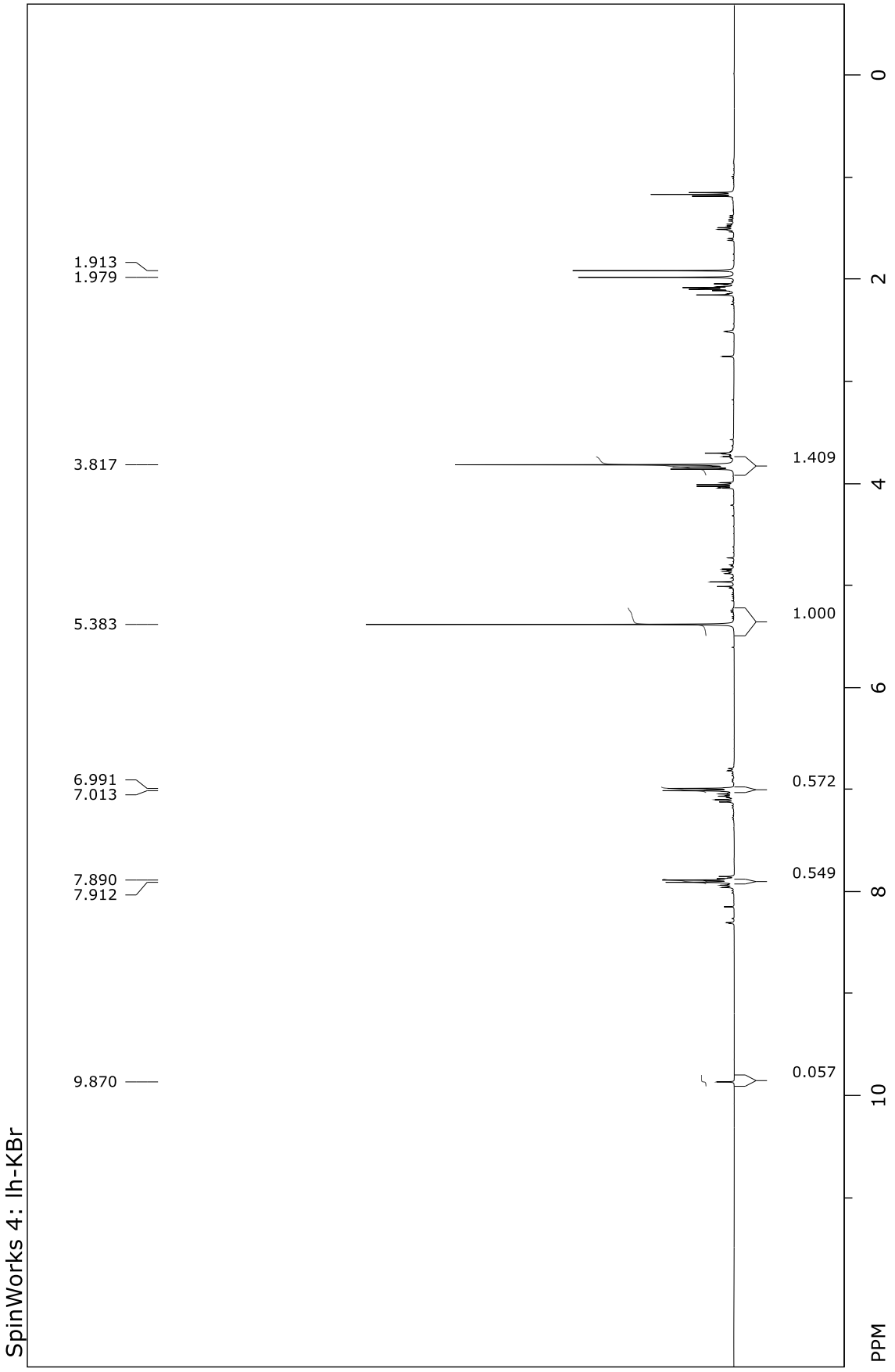


Figure 48: Spectrum **L** – Reaction in the presence of 15 mol % KBr

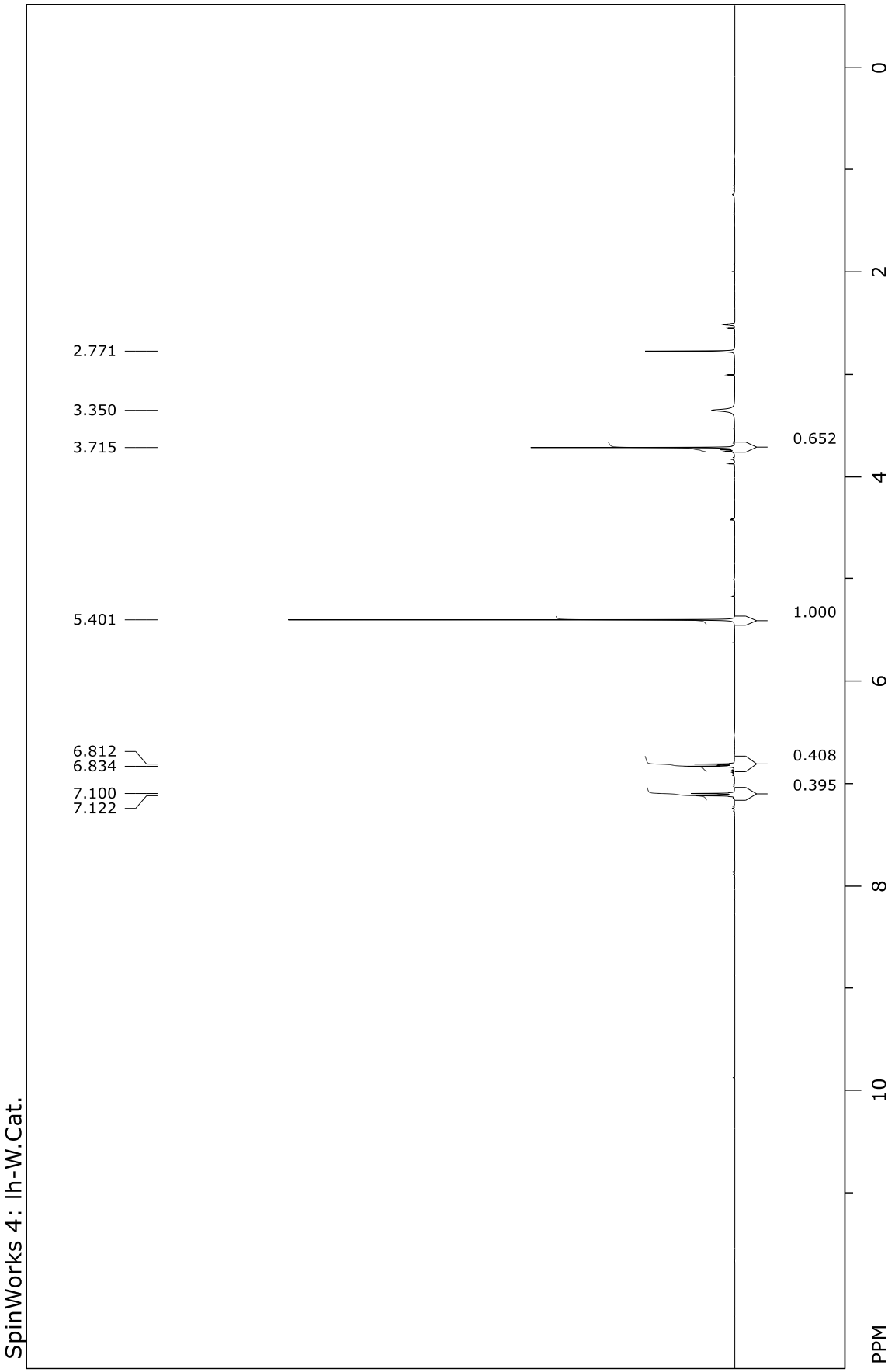


Figure 49: Spectrum **M** – In absence of the catalyst

9.6 Photoreactions of the boronic acids (Spectra N-P)

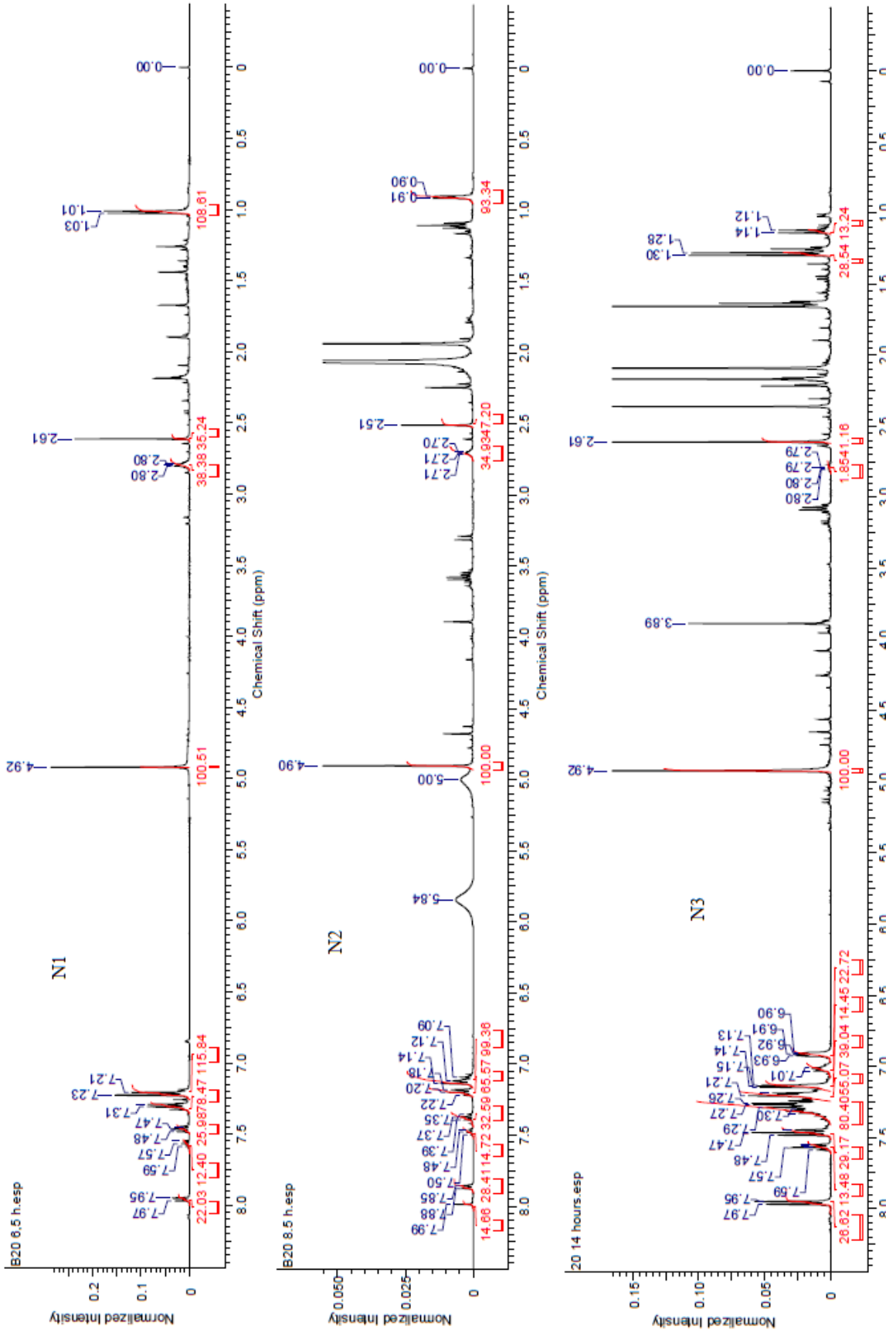


Figure 50: Reaction of 11e in Acetone and Air (N1: 6.5 hours, N2: 8.5 hours, N3: 14 hours)

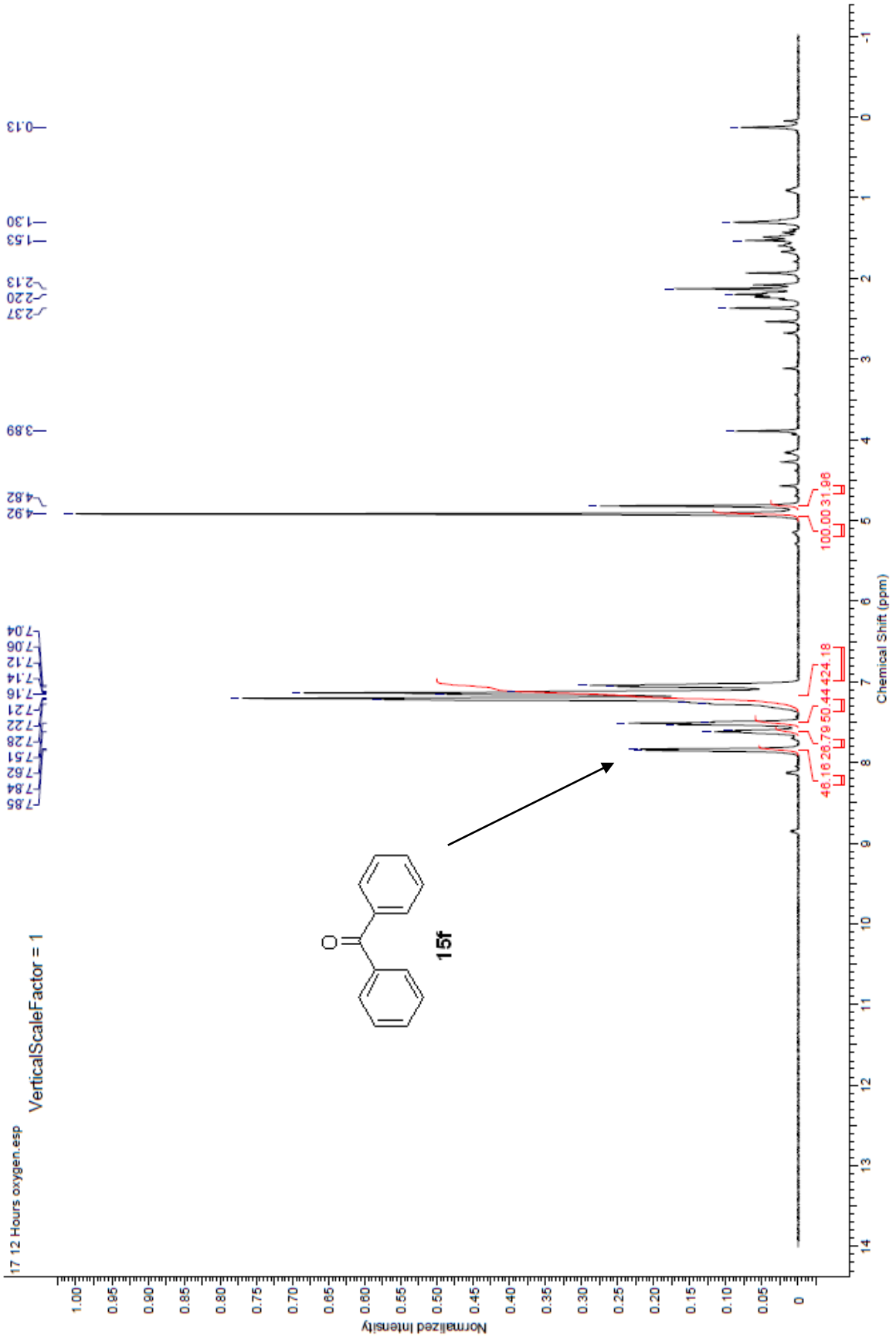


Figure 51: Spectrum O1: Photoreaction of 11f in acetone and oxygen atmosphere

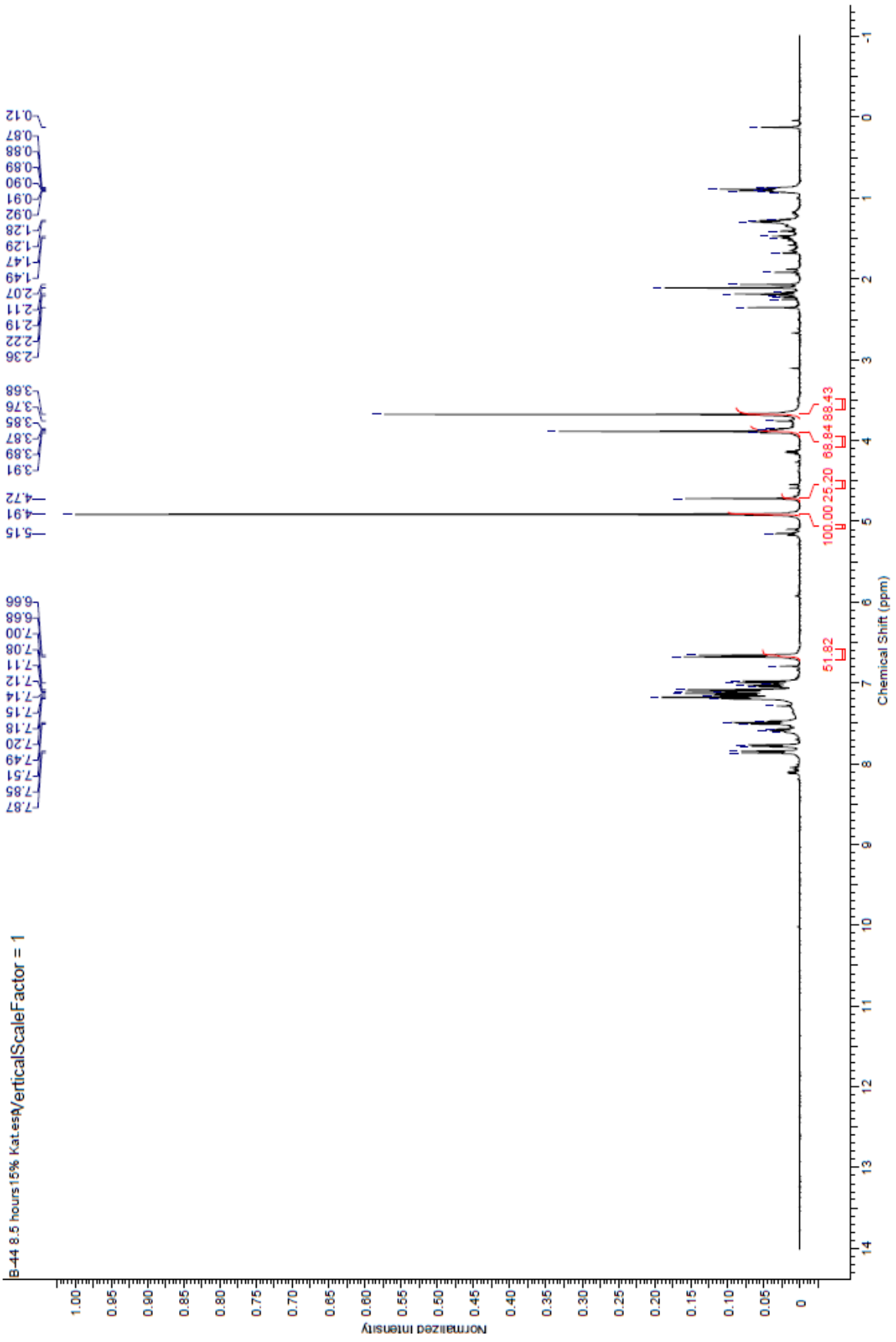


Figure 52: Spectrum O2: Photoreaction of 11b in acetone and oxygen atmosphere

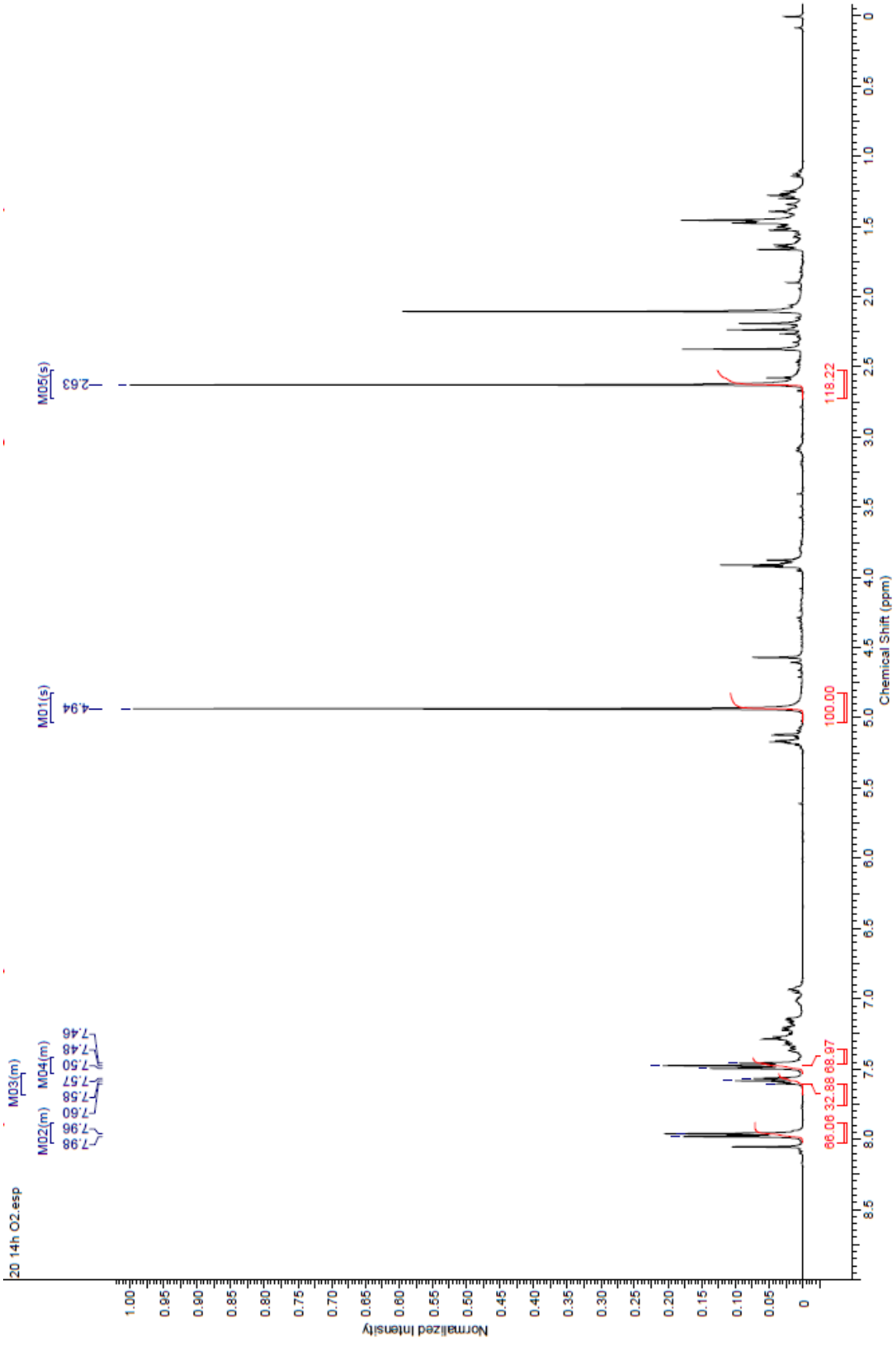


Figure 53: O3 - Reaction of 11e in acetone and oxygen atmosphere 14 hours

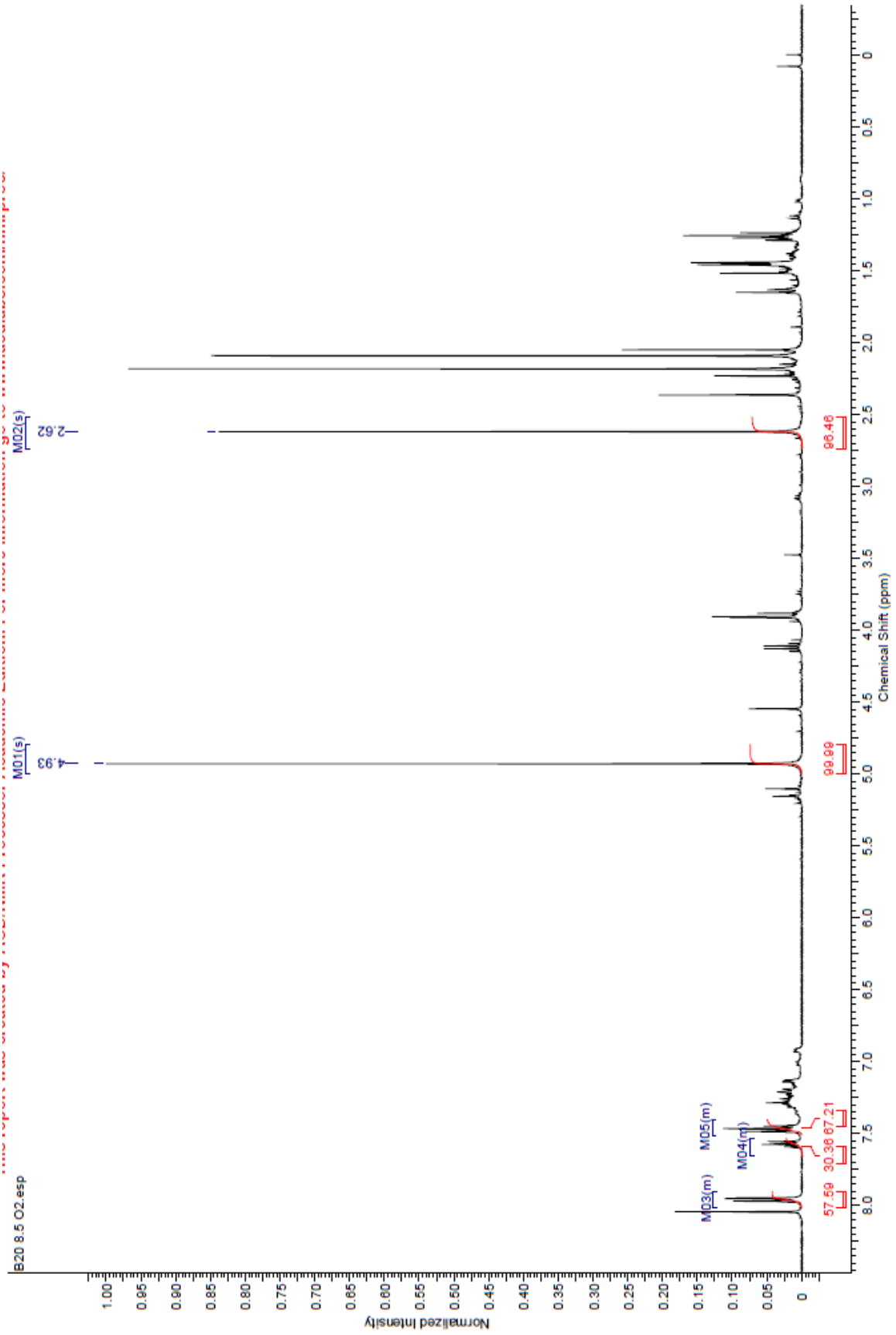


Figure 54: O4 - Reaction of 11e in acetone and oxygen atmosphere 8.5 hours

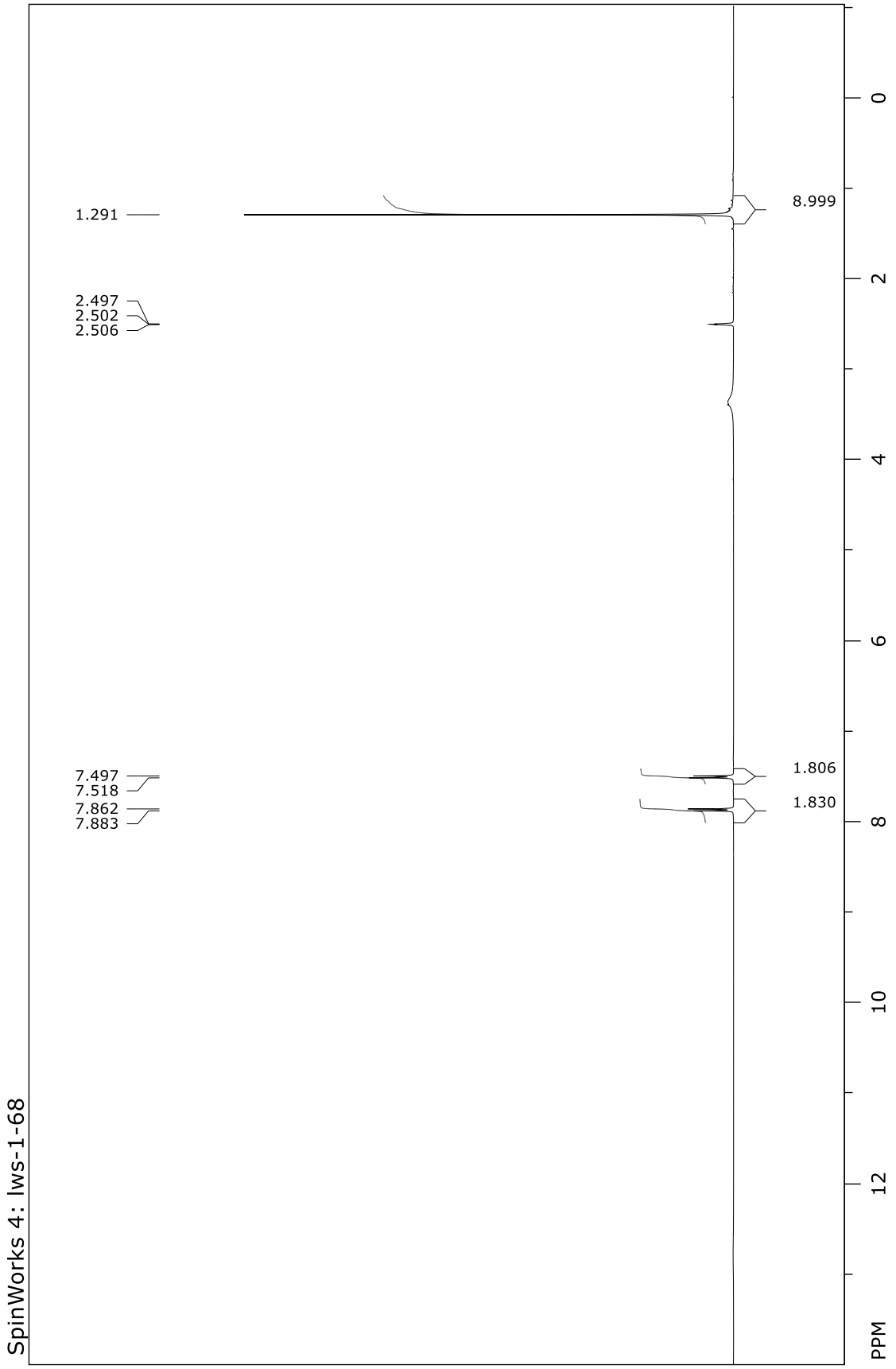


Figure 55: Spectrum P1 - (4-tert-butyl)benzoic acid **9b**

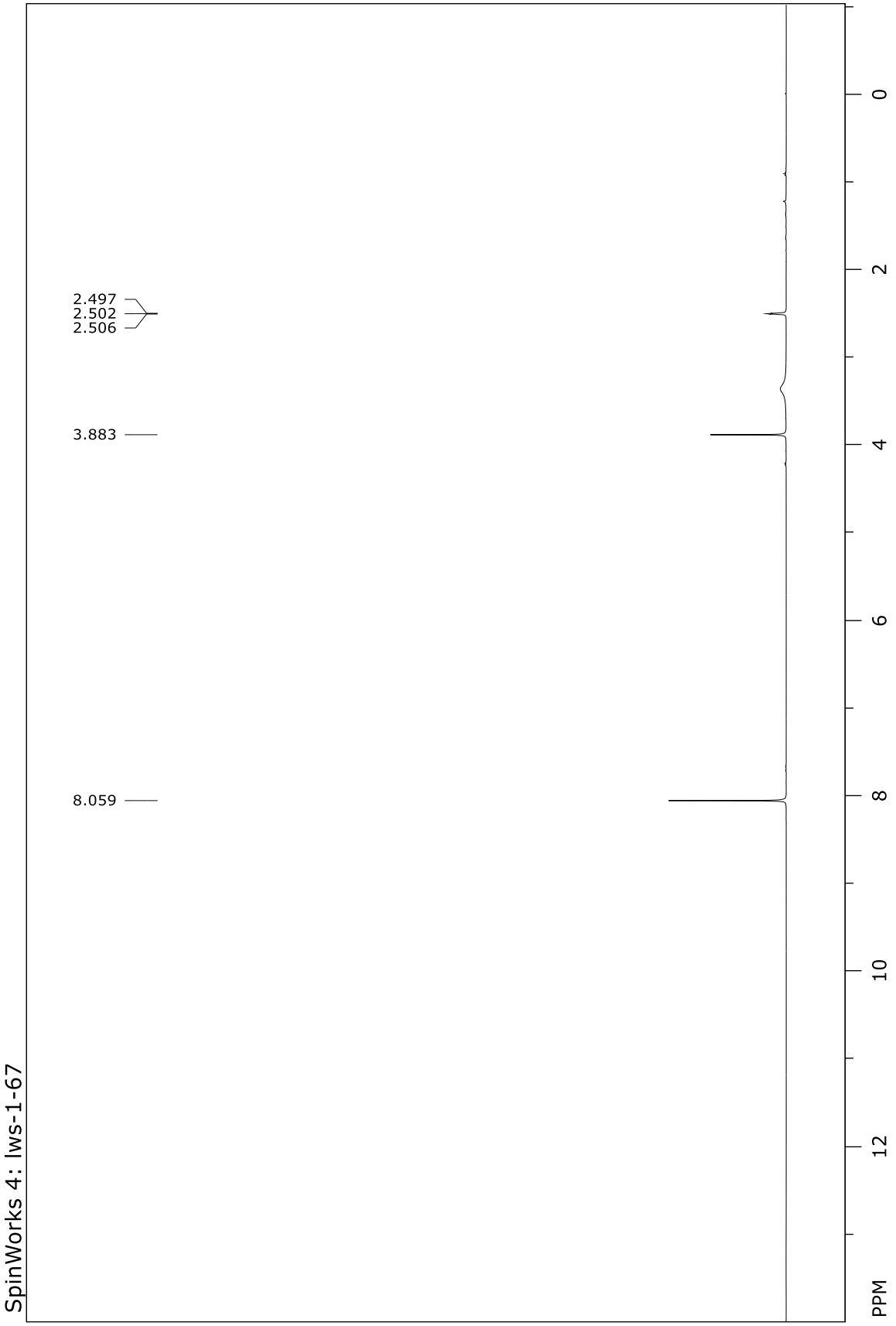


Figure 56: Spectra P2 - Benzoic acid 9e

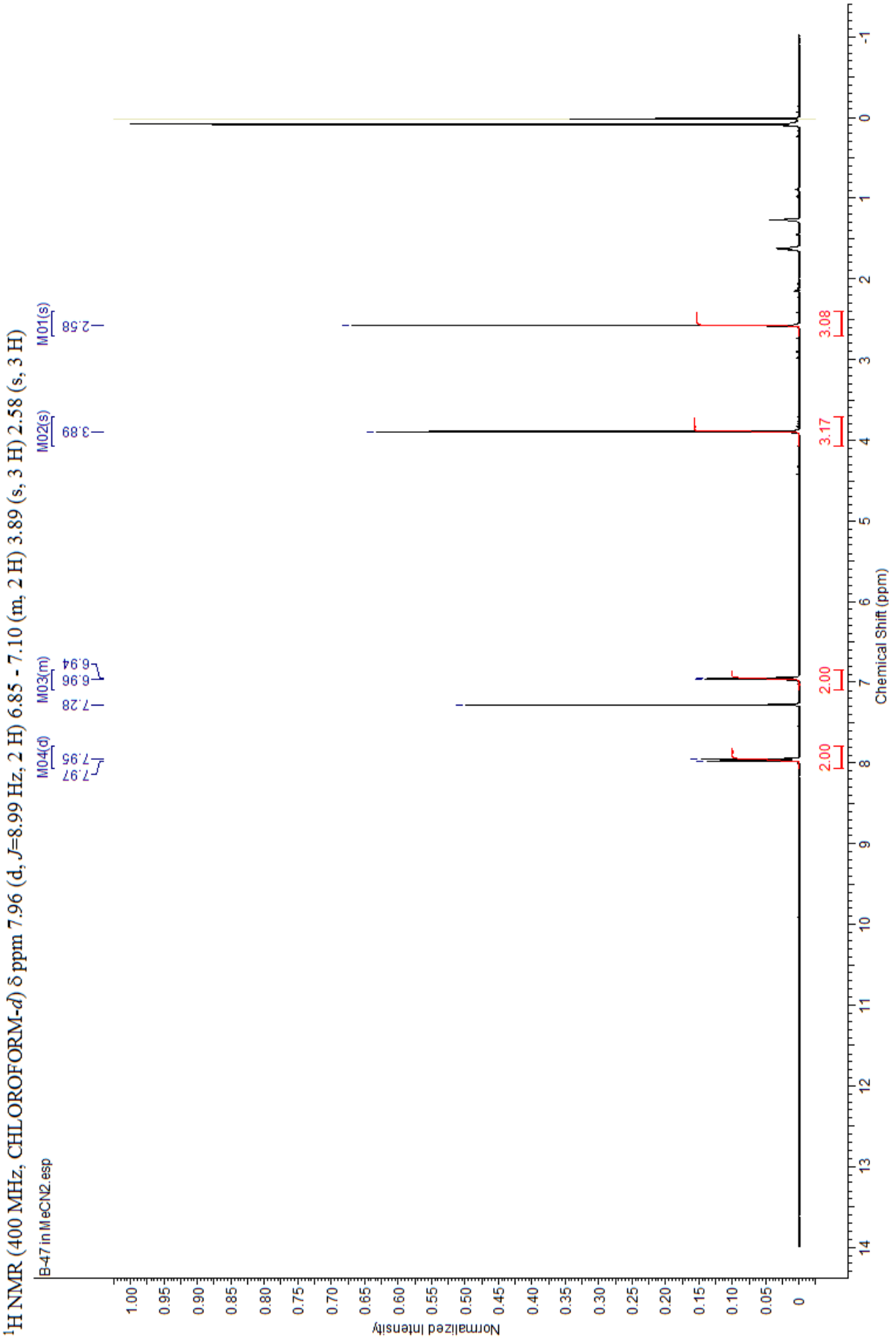


Figure 57: Spectrum P2: Reaction of 11a in acetonitrile in air

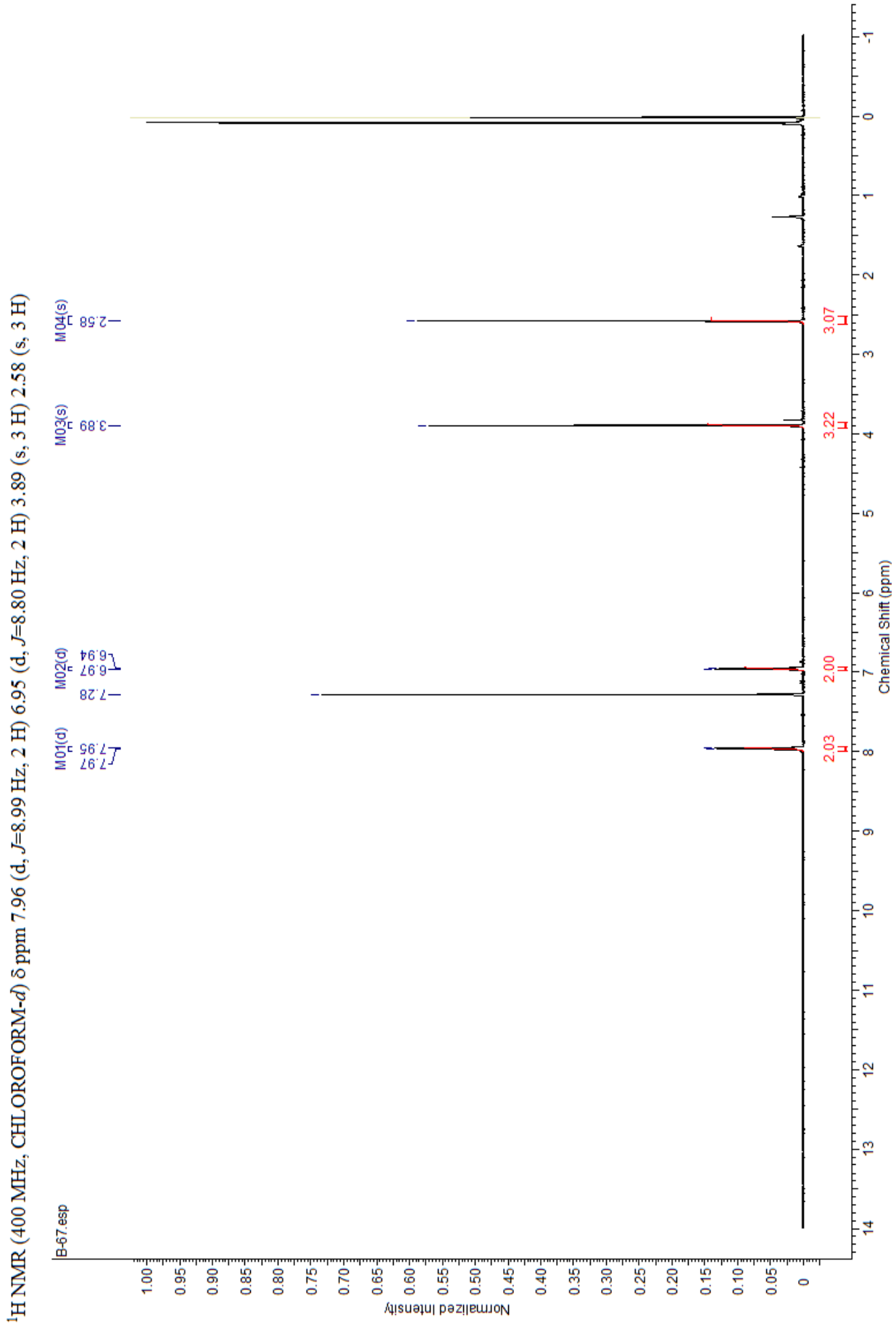


Figure 58: Spectrum P3: Product of the Photoreaction of 11a in Acetone and Air

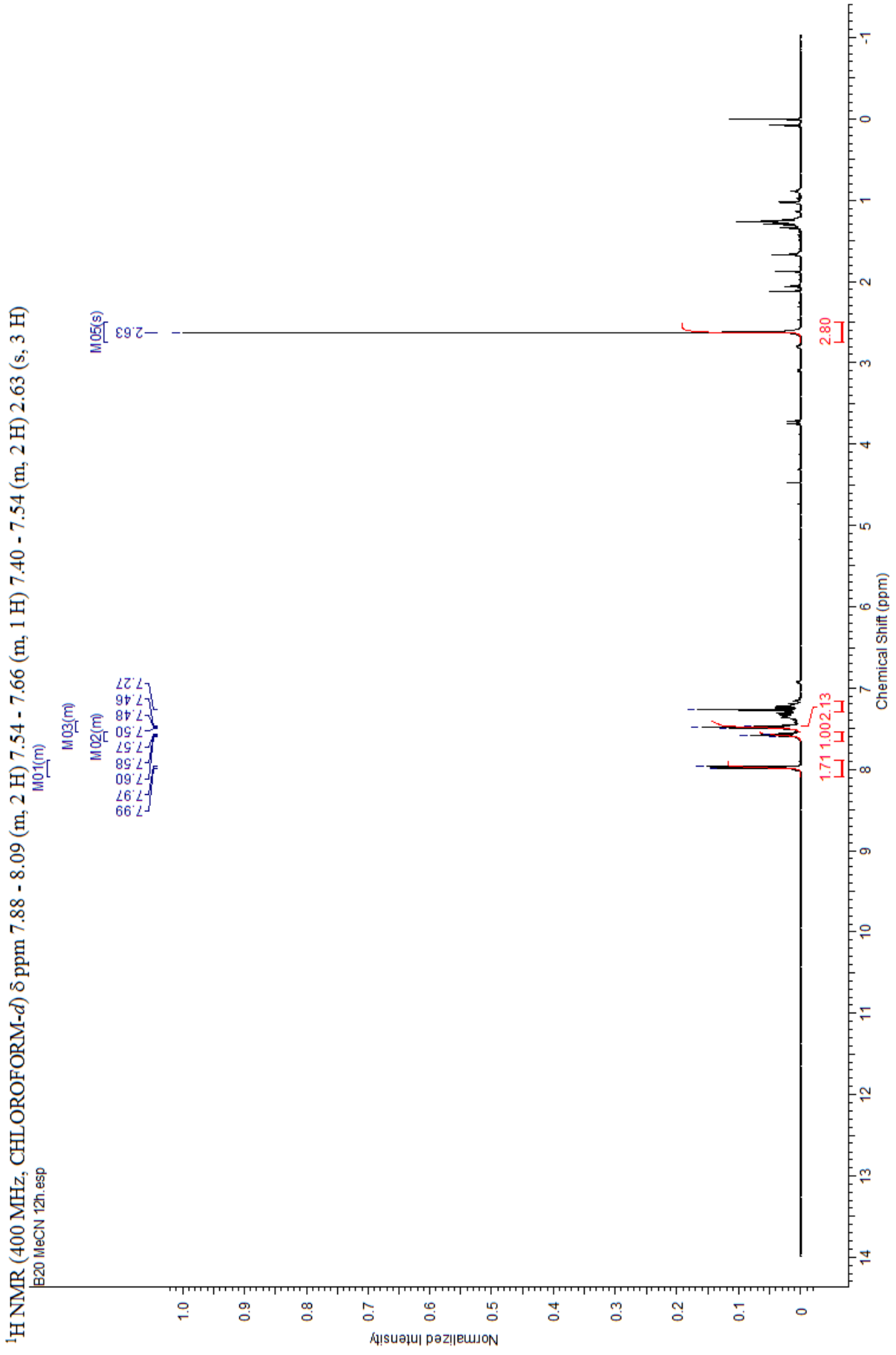


Figure 59: Spectrum P4: Photoreaction of 11e in MeCN