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Direct Azidation of Allylic/Benzylic Alcohols and Ethers Followed by the Click Reaction: One-Pot Synthesis of 1,2,3-Triazoles and 1,2,3-Triazole Moiety Embedded Macrocycles

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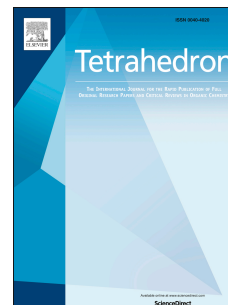
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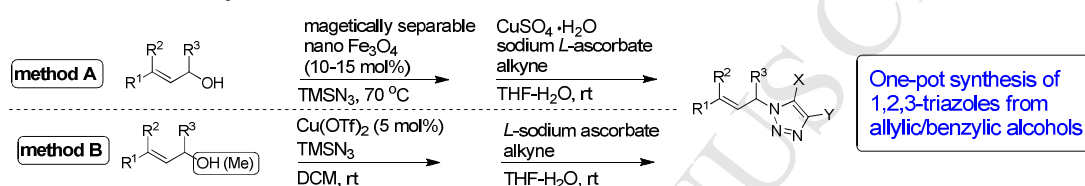
## Graphical Abstract

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## Direct Azidation of Allylic/Benzylic Alcohols and Ethers Followed by the Click Reaction: One-Pot Synthesis of 1,2,3-Triazoles and 1,2,3-Triazole Moiety Embedded Macrocycles

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### ABSTRACT

Investigations on the one-pot direct azidation of allylic/benzylic alcohols or their methyl ethers followed by the click reaction are reported. Two methods involving sequential reactions were developed for synthesizing substituted 1,2,3 triazoles starting from allylic/benzylic alcohols. The first method involves magnetically separable nano Fe<sub>3</sub>O<sub>4</sub>-catalyzed direct azidation of various allylic/benzylic alcohols with TMSN<sub>3</sub> as the first step followed by the Cu-catalyzed click reaction of azides with alkynes as the second step. The second method involves Cu(OTf)<sub>2</sub>-catalyzed direct azidation of allylic/benzylic alcohols and their methyl ethers with TMSN<sub>3</sub> as the first step followed by the click reaction of azides with alkynes as the second step. In this method, Cu(OTf)<sub>2</sub> served as a single catalyst for both the azidation of alcohol and click reaction steps. Utility of this protocol has been revealed by synthesizing new classes of polyether systems and macrocycles embedded with the 1,2,3-triazole and 1,3-diyne units.

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Catalytic direct nucleophilic substitution of free OH group of allylic/benzylic alcohols by nucleophiles is an important process in organic chemistry.<sup>1-3</sup> In spite of the two known limitations, such as the poor ability of the OH group as a leaving group and the formation water as the by-product which requires the use of a water tolerant catalyst, several procedures involving a range of catalysts (e.g., transition metal, Brønsted acid, Lewis acid catalysts) were developed for the direct nucleophilic substitution of allylic/benzylic alcohols by various carbon-based or nitrogen-based nucleophiles. Consequently, the formation of carbon-nitrogen bonds via the direct catalytic substitution of OH group of alcohols with nitrogen-based nucleophiles is a simple synthetic procedure for obtaining allylic/benzylic amines and azides and other related nitrogenous compounds.<sup>4-11</sup> Several allylic/benzylic amines and azides are versatile synthetic building blocks for synthesizing heterocyclic compounds, natural products and biologically active molecules.<sup>4-11</sup> Notably, the azide moiety is reported to be a key component of the HIV/AIDS drug, zidovudine.<sup>12</sup>

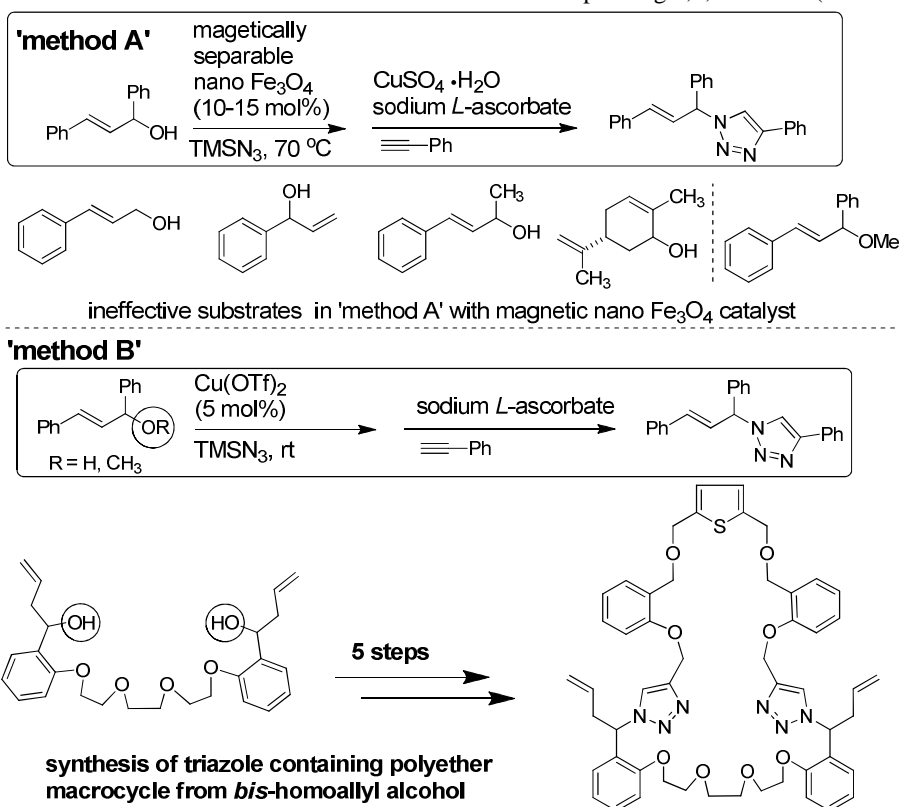
Conversion of readily accessible alcohols to azides is a straightforward method for the synthesis of a variety of organic azides. Usually, this transformation has been carried out in two steps; first an alcohol is converted in to the respective halide or sulfonate and then, the corresponding halide/sulfonate is converted into an azide *via* the nucleophilic substitution reaction.<sup>13</sup> Consequently, the direct azidation of allylic/benzylic alcohols with an azide reagent is considered as one of the easy ways for synthesizing allylic/benzylic azides. The direct

conversion of alcohols into azides has been accomplished using the well-established Mitsunobu reaction pathway and modified Mitsunobu-type procedures.<sup>14,15</sup> Along this line, there have been other methods for the direct conversion of alcohols into azides, which include, NaN<sub>3</sub>/BF<sub>3</sub>·OEt<sub>2</sub>,<sup>5c</sup> NaN<sub>3</sub>/CCl<sub>4</sub>-DMF,<sup>16a</sup> TsIm/TBAI/NaN<sub>3</sub>,<sup>16b</sup> 2,4,6-trichloro[1,3,5]triazine/*n*-Bu<sub>4</sub>NN<sub>3</sub>,<sup>16c</sup> 2-azido-1,3 dimethylimidazolium hexafluorophosphate (2-ADMP)/DBU<sup>6a</sup> and NaN<sub>3</sub>/ionic liquid [H-NMP]HSO<sub>4</sub>,<sup>16d</sup> NaN<sub>3</sub>/amphiphilic resin-supported palladium phosphine complex<sup>16e</sup> and NaN<sub>3</sub>/triphosgene.<sup>6b</sup> On the other hand, the direct azidation of allylic and benzylic alcohols with TMSN<sub>3</sub> as an azide reagent has been accomplished in the presence of various catalysts/promoters, e.g., AgOTf,<sup>6c</sup> Mo(IV) complex,<sup>17a</sup> Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O,<sup>17b</sup> Cu(OTf)<sub>2</sub>,<sup>17c</sup> and BF<sub>3</sub>·OEt<sub>2</sub>.<sup>4c</sup> Further, the conversion of allyl esters into azides has been carried out in the presence of Pd(0) catalyst.<sup>18</sup>

The synthesis of 1,2,3-triazoles *via* the [3+2] cycloaddition of organic azides and alkynes (click reaction) has gained significant attention in the fields of chemistry, biology, medicine, and materials science.<sup>10,11</sup> Generally, the required organic azide molecules are prepared by the substitution reaction of the organic halides/pseudo halides by sodium azide. It is worth to mention that some of the organic azide molecules can be explosive and it is essential to handle the organic azides with care. Hence, a one-pot synthesis of organic azide followed by the click reaction procedure without isolating the corresponding azide would be very convenient.<sup>19,20</sup> Accordingly, the one-pot synthesis of 1,2,3-triazoles involving sequential reactions starting from organic

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halide/pseudo halide, azide reagent and alkyne have been reported.<sup>19-21</sup> Others did not react with  $\text{TMSN}_3$  in the presence of nano  $\text{Fe}_3\text{O}_4$  and subsequently, the click reaction also failed to afford the corresponding 1,2,3-triazole (Scheme 1).



**Scheme 1:** Theme of this work. One-pot direct azidation of allylic/benzylic alcohols and ethers followed by the click reaction.

In this one-pot process, if we can use readily accessible starting materials, e.g., alcohols instead of organic halides/pseudo halides or protected alcohols, then the synthetic procedure will be simple to work out. Although, methods for the direct conversion of alcohols into azides are well-known; however, to the best of our knowledge, one-pot sequential processes comprising, the direct azidation of allylic/benzylic alcohols followed by the Cu-catalyzed click reaction of the corresponding azides with alkynes are limited and not been well explored. Wang *et al.*<sup>20</sup> revealed a one-pot multistep synthesis of triazolyglycosides from unprotected monosaccharides. Sreedhar *et al.*<sup>4d</sup> revealed a one-pot sequential reaction procedure for the synthesis of 1,2,3-triazoles from homoallyl alcohols *via* the Pd-catalyzed azidation followed by the Cu(I)-catalyzed click reaction. Apart from this work, Fukuzawa,<sup>21a</sup> Chandrasekhar,<sup>21b</sup> Sreedhar,<sup>21c</sup> have revealed the one-pot sequential reaction procedures for the synthesis of 1,2,3-triazoles starting from benzyl acetates or Baylis-Hillman acetates. Yadav *et al.*<sup>22</sup> reported a four-component reaction of aldehyde, alcohol, azide, and alkyne *via* Cu(OTf)<sub>2</sub>-catalyzed acetal formation followed by Cu(0)-mediated click reaction. Recently, we also reported our preliminary work<sup>23</sup> encompassing the direct azidation of allylic/benzylic alcohols catalyzed by magnetic nano  $\text{Fe}_3\text{O}_4$ <sup>24</sup> followed by the Cu-catalyzed click reaction of the corresponding azides with alkynes for the synthesis of 1,2,3-triazoles (Scheme 1). This method involves magnetically separable nano  $\text{Fe}_3\text{O}_4$ -catalyzed direct azidation of various allylic/benzylic alcohols with  $\text{TMSN}_3$  as the first step followed by the Cu-catalyzed click reaction of the corresponding azides with alkynes as the second step. Further, we found some limitations with this method that some of the alcohols/methyl

We envisaged to overcome this limitation and simplify the reaction procedure using a single catalyst to perform the direct azidation of allylic/benzylic alcohols with  $\text{TMSN}_3$  followed by the click reaction of the corresponding azides with alkynes. In view of developing synthetic procedures which are simple to work out and for achieving the chemical diversity, we envisioned to improve our method<sup>23</sup> and use of  $\text{Cu}(\text{OTf})_2$  a single catalyst for performing the one-pot direct azidation of allylic/benzylic alcohols with  $\text{TMSN}_3$  and click reaction of the corresponding azides with alkynes (Scheme 1). Herein, we report our comprehensive works on the synthesis of several substituted 1,2,3-triazole *via* the one-pot direct azidation of allylic alcohols/ethers followed by the click reaction. Further, this protocol has been applied for the synthesis of acyclic and macrocyclic crown ethers/polyethers embedded with *bis*-triazole moieties and a 1,3-diyne unit, starting from *bis*-homoallylic alcohols and involving the Glaser-Eglinton-Hay coupling reaction.

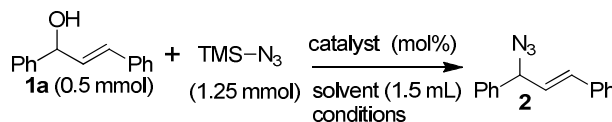
Scheme 1 illustrates the two different methods (method A and method B) presented in this paper for synthesizing several substituted 1,2,3 triazole derivatives starting from allylic and benzylic alcohols without isolating the corresponding azides. To accomplish the method A, initially, we performed various optimization reactions to find out the suitable reaction condition for the direct azidation of allylic alcohol **1a** with  $\text{TMSN}_3$  in the presence of magnetically separable nano  $\text{Fe}_3\text{O}_4$  catalyst<sup>24-26</sup> (particle size = < 50 nm). We found two best reaction conditions for the effective conversion of alcohol **1a** into the corresponding azide substrate **2**. We obtained the azide substrate **2** in 89% yield when the azidation of **1a** (1 equiv) was carried out with  $\text{TMSN}_3$

(2.5 equiv) in the presence of 15 mol% of nano Fe<sub>3</sub>O<sub>4</sub> in 1,2-DCE at rt (entry 2, Table 1). The azide substrate **2** was obtained in 98% yield when the azidation of **1a** (1 equiv) was carried out with TMSN<sub>3</sub> (2.5 equiv) in the presence of nano Fe<sub>3</sub>O<sub>4</sub> (15 mol%) in 1,2-DCE at 70 °C (entry 5, Table 1). As shown in the Table 1, the conversion of alcohol **1a** into the corresponding azide substrate **2** was not effective when the reaction was carried out in solvents, such as 1,4-dioxane, MeCN, MeOH, acetone, THF and toluene and in the presence of other catalysts, e.g. nano Fe<sub>2</sub>O<sub>3</sub> or powder Fe<sub>3</sub>O<sub>4</sub>. We have also checked the recyclability of the magnetic nano Fe<sub>3</sub>O<sub>4</sub> catalyst and accordingly, the direct azidation of allylic alcohol **1a** with TMSN<sub>3</sub> afforded the product **2** in 95% yield in the 7<sup>th</sup> run (Table 1). The recovered nano Fe<sub>3</sub>O<sub>4</sub> catalyst after the usage at different runs was analyzed by FT-IR and HRTEM. The FT-IR spectra of the fresh and recovered magnetic nano Fe<sub>3</sub>O<sub>4</sub> catalyst showed no characteristic changes and the HRTEM analysis of the recovered magnetic nano Fe<sub>3</sub>O<sub>4</sub> catalyst revealed that there was no significant change in the morphology of the nanoparticles.<sup>23</sup>

Next, we focused our attention to execute the one-pot method A and method B to synthesize substituted 1,2,3 triazole derivatives starting from allylic and benzylic alcohols. Having the best reaction condition for the direct azidation of **1a** with TMSN<sub>3</sub> in the presence of nano Fe<sub>3</sub>O<sub>4</sub> catalyst (entry 5, Table 1), then, we decided to perform the Cu-catalyzed click reaction of the product **2** in the same RB without isolating the azide substrate **2**. Accordingly, at first, we carried out the method A procedure, in which the direct azidation of allylic alcohol **1a** was performed followed by the copper-catalyzed click reaction of the azide **2** ((*E*)-(3-azidoprop-1-ene-1,3-diyl)dibenzene) with ethyl propiolate which gave the substituted 1,2,3-triazole derivative **4a** in 86% yield (entry 1, method A, Table 2). Successively, we performed the one-pot direct azidation of substrate **1a** followed by the copper-catalyzed click reaction of the product **2** with various alkynes **3b-e**, **3g-j**, which gave the corresponding substituted 1,2,3-triazole derivatives **4b-e**, **4g-j** in 75-93% yields (method A, Table 2).

Method A involves nano Fe<sub>3</sub>O<sub>4</sub>-catalyzed direct azidation of **1a** with TMSN<sub>3</sub> as the first step followed by the Cu-catalyzed click reaction of the corresponding azides with alkynes as the second step. We envisaged simplifying the reaction procedure of the method A and using a single catalyst to perform the direct azidation of **1a** with TMSN<sub>3</sub> followed by the click reaction of the corresponding azides with alkynes. Accordingly, we used the method B procedure, in which the direct azidation of substrate **1a** with TMSN<sub>3</sub> was carried out in the presence of 5 mol% of Cu(OTf)<sub>2</sub> followed by the click reaction of the product **2** in the same RB with various alkynes. In this regard, initially, we performed the optimization of the reactions to find out the best reaction conditions for the method B. The direct azidation of the substrate **1a** with TMSN<sub>3</sub> in the presence of 5 mol% of Cu(OTf)<sub>2</sub> followed by the click reaction of the azide **2** with **3a** and without any additive in the click reaction step did not give the expected 1,2,3-triazole **4a** (entry 1, method B, Table 2). When we used DIPEA or *L*-ascorbic acid as an additive, the 1,2,3-triazole **4a** was obtained in 10 and 20% yields, respectively (entry 1, method B, Table 2). The use of sodium *L*-ascorbate as an additive in the click reaction step gave the 1,2,3-triazole **4a** in 87% yield (entry 1, method B, Table 2). Then, using the same reaction conditions, we performed the direct azidation of substrate **1a** followed by the click reaction of the product **2** with various alkynes **3b-i**, which gave the corresponding substituted 1,2,3-triazole derivatives **4b-i** in 72-98% yields (method B, Table 2).

**Table 1.** Nano Fe<sub>3</sub>O<sub>4</sub>-catalyzed reaction **1a** with TMSN<sub>3</sub>.



Entry	Catalyst (mol %)	Solvent (1.5 mL)	Reaction Condition	Yield of azide <b>2</b> (%)
1	nil	1,2-DCE	70 °C, 40 h	0
2	nano Fe <sub>3</sub> O <sub>4</sub> (15)	1,2-DCE	rt, 15 h	89
3	nano Fe <sub>3</sub> O <sub>4</sub> (15)	1,2-DCE	rt, 15 h	80 <sup>a</sup>
4	nano Fe <sub>3</sub> O <sub>4</sub> (15)	1,2-DCE	rt, 15 h	83 <sup>b</sup>
5	nano Fe <sub>3</sub> O <sub>4</sub> (15)	1,2-DCE	70 °C, 6 h	98
6	nano Fe <sub>3</sub> O <sub>4</sub> (15)	1,2-DCE	70 °C, 6 h	85 <sup>a</sup>
7	nano Fe <sub>3</sub> O <sub>4</sub> (15)	1,2-DCE	70 °C, 6 h	89 <sup>b</sup>
8	nano Fe <sub>3</sub> O <sub>4</sub> (15)	DCM	rt, 10 h	85
9	nano Fe <sub>3</sub> O <sub>4</sub> (15)	DCM	reflux, 8 h	92
10	nano Fe <sub>3</sub> O <sub>4</sub> (15)	1,4-dioxane	rt, 30 h	0
11	nano Fe <sub>3</sub> O <sub>4</sub> (15)	MeCN	rt, 30 h	0
12	nano Fe <sub>3</sub> O <sub>4</sub> (15)	MeOH	rt, 30 h	0
13	nano Fe <sub>3</sub> O <sub>4</sub> (15)	acetone	rt, 30 h	23
14	nano Fe <sub>3</sub> O <sub>4</sub> (15)	THF	rt, 30 h	20
15	nano Fe <sub>3</sub> O <sub>4</sub> (15)	toluene	rt, 30 h	55
16	nano Fe <sub>3</sub> O <sub>4</sub> (10)	1,2-DCE	70 °C, 16 h	92
17	nano Fe <sub>2</sub> O <sub>3</sub> (15)	1,2-DCE	70 °C, 30 h	<5
18	powder Fe <sub>3</sub> O <sub>4</sub> (15)	1,2-DCE	70 °C, 48 h	35

#### Recycling of nano Fe<sub>3</sub>O<sub>4</sub><sup>c</sup>

Run	1	2	3	4	5	6	7
Time (h)	6	6	8	10	12	15	20
Yield of <b>2</b> (%)	98	97	97	97	97	96	95

<sup>a</sup> In this case, 0.55 mmol of TMSN<sub>3</sub> was used. <sup>b</sup> In this case, 0.75 mmol of TMSN<sub>3</sub> was used. <sup>c</sup> The reaction was carried out using **1a** (0.5 mmol), TMSN<sub>3</sub> (1.25 mmol) and nano Fe<sub>3</sub>O<sub>4</sub> (15 mol%) in 1,2-DCE (1.5 mL) at 70 °C.

Next, we decided to explore the direct conversion of various allylic alcohols **1b-g** (Table 3) into the corresponding substituted 1,2,3-triazole derivatives in one-pot using either method A or method B procedure. The substituted 1,2,3-triazole derivatives **4k** (75%) and **4l** (60%) were synthesized from **1b** using the method B procedure involving Cu(OTf)<sub>2</sub> as the single catalyst (entries 1 and 2, Table 3). The substituted 1,2,3-triazole derivatives **4m-o** and **4oA** were synthesized from the corresponding alcohols **1b-d** and **1dA** using the method A or B procedures (entries 3-6, Table 3). The products **4n,o** and **4oA** were obtained as a mixture of regioisomers since the corresponding allylic alcohols **1c,d** and **1dA** underwent an allylic rearrangement under the experimental condition, thereby led to the formation of the corresponding regioisomers. The allylic alcohols **1e-g** failed to afford corresponding substituted 1,2,3-triazole derivatives **4p** and **4q** when the direct azidation of allylic alcohols **1e-g** followed by the click reaction was performed using method A procedure. This is because the nano Fe<sub>3</sub>O<sub>4</sub>-catalyzed conversion of allylic alcohols **1e-g** into the corresponding azides did not occur in the first step as a result the subsequent click reaction failed to afford the 1,2,3-triazole derivatives **4p** and **4q** under the method A procedure (entries 6-8, method A, Table 3). However, the allylic alcohols **1e-g** successfully afforded the corresponding substituted 1,2,3-triazole derivatives **4p** (70-80%) and **4q** (76%) when the direct azidation of allylic alcohols **1e-g** followed by the click reaction was performed using the method B procedure (entries 7-10, method B, Table 3). Similarly, the substituted 1,2,3-triazole derivatives **4r** was obtained in 85% yield from the corresponding alcohols **1g** using the method B procedure (entry 9, method B Table 3).

**Table 2.** One-Pot direct azidation of allylic alcohol **1a** followed by the click reaction with **4a-j**. Synthesis of substituted 1,2,3-triazoles **4a-j**.<sup>a</sup>

method A:		method B:		
Entry	Alkyne	Triazole	Yield (%) Method A	Yield (%) Method B
1			86	(0), <sup>b</sup> (10), <sup>c</sup> (20), <sup>d</sup> (60), <sup>e</sup> (81), <sup>f</sup> (87) <sup>g</sup>
2			82	75
2			90	97
3			93	96
4			86	72
5			- <sup>h</sup>	98
6			85	97
7			92	93
8			85	89
9			75	- <sup>h</sup>

<sup>a</sup> In method A, 0.5 mmol of **1a** and 1.5 mmol of TMSN<sub>3</sub> were used. In method B, 0.5 mmol of **1a** and 0.75 mmol of TMSN<sub>3</sub> were used. In both the methods, initially, the azidation of **1a** was carried out with TMSN<sub>3</sub> and after the reaction period the solvent was evaporated. Then, the click reaction was carried out.

<sup>b</sup> The reaction was carried out without sodium *L*-ascorbate.

<sup>c</sup> DIPEA (50 mol%) was used instead of sodium *L*-ascorbate.

<sup>d</sup> *L*-Ascorbic acid (50 mol%) was used instead of sodium *L*-ascorbate.

<sup>e</sup> CuCl (60 mol%) was used instead of sodium *L*-ascorbate.

<sup>f</sup> Sodium *L*-ascorbate (30 mol%) was used.

<sup>g</sup> Sodium *L*-ascorbate (50 mol%) was used.

<sup>h</sup> The reaction was not performed.

**Table 3.** One-Pot direct azidation of various allylic alcohols **1b-g** followed by the click reaction with alkynes. Synthesis of substituted 1,2,3-triazoles **4k-r** and **4oA**.<sup>a</sup>

method A:		magetically separable nano Fe <sub>3</sub> O <sub>4</sub> (15 mol%)	CuSO <sub>4</sub> ·5H <sub>2</sub> O (30 mol%) sodium L-ascorbate (30 mol%)		
alcohol + TMSN <sub>3</sub>	1,2-DCE (3 mL) t (h), 70 °C	alkyne (2 mmol) THF / H <sub>2</sub> O (3 mL / 3 mL), rt, 12 h			
method B:		Cu(OTf) <sub>2</sub> (5 mol%)	sodium L-ascorbate (50 mol%)		
alcohol + TMSN <sub>3</sub>	DCM (3 mL) 3 h, rt	alkyne (1.25 mmol) THF / H <sub>2</sub> O (2 mL / 2 mL), rt, 20 h			
Entry	Alcohol	Alkyne	Triazole	Yield (%) Method A	Yield (%) Method B <sup>b</sup>
1				- <sup>c</sup>	75
2	<b>1b</b>			- <sup>c</sup>	60
3	<b>1b</b>			52 (14 h) <sup>d</sup>	50
4				82 (12 h) <sup>d</sup> (50:50) <sup>e</sup>	70 (50:50) <sup>e</sup>
5				72 (15 h) <sup>d</sup> (50:50) <sup>e</sup>	64 (50:50) <sup>e</sup>
6				- <sup>c</sup>	68 (50:50) <sup>e</sup>
7				0	70
8				0	80
9				0	76
10	<b>1g</b>			- <sup>c</sup>	85

<sup>a</sup> In both the methods, initially, the azidation of **1a** was carried out with TMSN<sub>3</sub> and after the reaction period the solvent was evaporated. Then, the click reaction was carried out.

<sup>b</sup> In method B, for all the reactions, 0.5 mmol of **1a** and 0.75 mmol of TMSN<sub>3</sub> were used.

<sup>c</sup> The reaction was not performed.

<sup>d</sup> In this reaction, 1 mmol of alcohol and 3 mmol of TMSN<sub>3</sub> were used and the reaction time indicated in the parenthesis corresponds to azidation reaction.

<sup>e</sup> Products were obtained as a mixture of regioisomers due to an allylic rearrangement under the experimental condition.

**Table 4.** One-Pot direct azidation of conjugated and cyclic allylic alcohols **1h-k** followed by the click reaction with alkynes. Synthesis of substituted 1,2,3-triazoles **4s-y**.

method A:		method B:			
alcohol +	magetically separable nano Fe <sub>3</sub> O <sub>4</sub> (15 mol%)	alcohol +	Cu(OTf) <sub>2</sub> (5 mol%)		
TMSN <sub>3</sub>	1,2-DCE (3 mL)	TMSN <sub>3</sub>	DCM (3 mL)		
	t (h), 70 °C		3 h, rt		
	CuSO <sub>4</sub> ·5H <sub>2</sub> O (30 mol%) sodium L-ascorbate (30 mol%) alkyne (2 mmol) THF / H <sub>2</sub> O (3 mL / 3 mL), rt, 12 h		sodium L-ascorbate (50 mol%) alkyne (1.25 mmol) THF / H <sub>2</sub> O (2 mL / 2 mL), rt, 20 h		
Entry	Alcohol	Alkyne	Triazole	Yield (%) Method A	Yield (%) Method B <sup>b</sup>
1				62 (18 h) <sup>c</sup>	68
2	<b>1h</b>			<sup>d</sup>	73
3	<b>1h</b>			57 (18 h) <sup>c</sup>	42
4				62 (30 h) <sup>c</sup> (76:24) <sup>e</sup>	<5 <sup>f</sup>
5				45 (24 h) <sup>c</sup> (88:12) <sup>e</sup>	<5 <sup>f</sup>
6				0 (24 h) <sup>c</sup>	80 (86:14) <sup>g</sup>
7	<b>1k (60:40)</b>			<sup>d</sup>	87 (86:14) <sup>g</sup>

<sup>a</sup> In both the methods, initially, the azidation of **1a** was carried out with TMSN<sub>3</sub> and after the reaction period the solvent was evaporated. Then, the click reaction was carried out.

<sup>b</sup> In method B, for all the reactions, 0.5 mmol of **1a** and 0.75 mmol of TMSN<sub>3</sub> were used.

<sup>c</sup> In this reaction, 1 mmol of alcohol and 3 mmol of TMSN<sub>3</sub> were used and the reaction time indicated in the parenthesis corresponds to azidation reaction.

<sup>d</sup> The reaction was not performed.


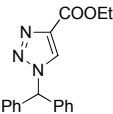


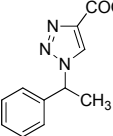


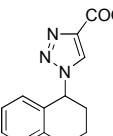


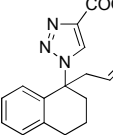

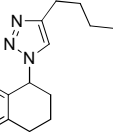

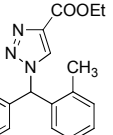

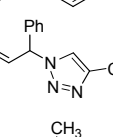

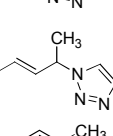

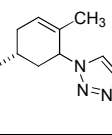
<sup>e</sup> Products were obtained as a mixture of regioisomers due to an allylic rearrangement under the experimental condition.

<sup>f</sup> In this case, the reaction gave a mixture of compounds and the expected product could not be isolated in pure form.

<sup>g</sup> The products **4x,y** were obtained as a mixture of diastereomers as the starting material **1k** was used as diastereomers



**Table 5.** One-pot synthesis of 1,2,3-triazoles **6a-f** and **4a,q,x** from allylic and benzylic ethers **5a-k**.

Entry	Ether Substrate	Triazole	Yield (%) Method A	Yield (%) Method B
1	 <b>5a</b>	 <b>6a</b>	71	- <sup>d</sup>
2	 <b>5b</b>	<b>6a</b>	0	75
3	 <b>5c</b>	 <b>6b</b>	35	- <sup>d</sup>
4	 <b>5d</b>	<b>6b</b>	- <sup>d</sup>	50
5	 <b>5e</b>	 <b>6c</b>	70	- <sup>d</sup>
6	 <b>5f</b>	<b>6c</b>	- <sup>d</sup>	70
7	 <b>5g</b>	 <b>6d</b>	52	- <sup>d</sup>
8 <sup>c</sup>	 <b>5e</b>	 <b>6e</b>	70	- <sup>d</sup>
9	 <b>5h</b>	 <b>6f</b>	- <sup>d</sup>	87
10	 <b>5i</b>	 <b>4a</b>	0	80
11	 <b>5j</b>	 <b>4q</b>	- <sup>d</sup>	72
12	 <b>5k</b> (60:40)	 <b>4x</b>	- <sup>d</sup>	70 (84:16) <sup>e</sup>

<sup>a</sup> Reaction condition for method A: The reaction was performed using **5** (1 mmol), TMSN<sub>3</sub> (3 mmol) and nano Fe<sub>3</sub>O<sub>4</sub> (15 mol%) in 1,2-DCE (3 mL) at 70 °C for 14-20 h and the solvent was evaporated and then, the click reaction was carried out using ethyl propiolate (**3a**, 2 mmol) in THF (3 mL) and water (3 mL) in the presence of CuSO<sub>4</sub>·5H<sub>2</sub>O (30 mol%) and sodium *L*-ascorbate (30 mol%) at rt for 12 h.

<sup>b</sup> Reaction condition for method B: The reaction was performed using **5** (0.5 mmol), TMSN<sub>3</sub> (0.75 mmol) and Cu(OTf)<sub>2</sub> (5 mol%) in DCM (3 mL) at rt for 3 h and the solvent was evaporated and then, the click reaction was carried out using ethyl propiolate (**3a**, 1.25 mmol) in THF (2 mL) and water (2 mL) in the presence sodium *L*-ascorbate (50 mol%) at rt for 20 h.

<sup>c</sup> In this case, alkyne **3g** was used instead of **3a**.

<sup>d</sup> The reaction was not performed.

<sup>e</sup> Product was obtained as a mixture of diastereomers as the starting material **5k** was used as diastereomers.

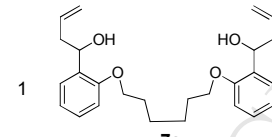
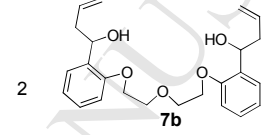
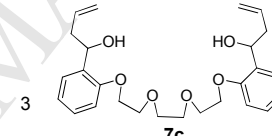
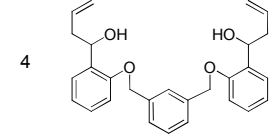
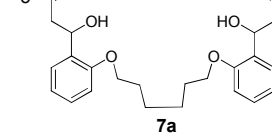
Next, we performed the conversion of the conjugated and cyclic allylic alcohols **1h-k** (Table 4) into the corresponding substituted 1,2,3-triazole derivatives using the reaction conditions of either method A or method B. The direct azidation of the allylic alcohol **1h** followed by the click reaction with **3c** using the method A and method B procedures afforded the substituted 1,2,3-triazole derivative **4s** in 62 and 68% yields, respectively. The azidation of the allylic alcohol **1h** followed by the click reaction with different alkynes **3a** and **3i** afforded the corresponding 1,2,3-triazole derivatives **4t** (73% yield in method B) and **4u** (57% yield in method A). Then, the substituted 1,2,3-triazole derivatives **4v** (62%), and **4w** (45%) were synthesized from the corresponding cyclic allylic alcohols **1i** and **1j** using the method A procedure (entries 4 and 5, Table 4). The products **4v** and **4w** were obtained as a mixture of regioisomers since the corresponding cyclic allylic alcohols **1i** and **1j** underwent an allylic rearrangement under the experimental condition, thereby led to the formation of their regioisomers, respectively.

The cyclic allylic alcohol **1k** failed to afford corresponding substituted 1,2,3-triazole derivative **4x** when the direct azidation of allylic alcohol **1k** followed by the click reaction with **3a** was performed using the method A procedure. This is perhaps, because the nano  $\text{Fe}_3\text{O}_4$ -catalyzed conversion of allylic alcohol **1k** into the corresponding azides did not occur in the first step and as a result, the subsequent click reaction failed to afford the 1,2,3-triazole derivative **4x** (entry 6, method A, Table 4). However, the cyclic allylic alcohol **1k** successfully afforded the corresponding substituted 1,2,3-triazole derivatives **4x** (80%) when the direct azidation of allylic alcohol **1k** followed by the click reaction was performed using the method B procedure (entry 6, method B, Table 4). Similarly, the substituted 1,2,3-triazole derivatives **4y** (87%) was obtained from the alcohol **1k** using the method B procedure (entry 7, method B Table 4). Since, we used the alcohol **1k** as a mixture of diastereomers (dr 60:40), the corresponding substituted 1,2,3-triazole derivatives **4x** and **4y** were obtained as diastereomers with improved diastereoselectivity (dr 86:14) under the experimental condition. Our efforts to isolate the respective major isomers of **4x** and **4y** were failed and the stereochemistry of the major/minor diastereomers was not determined.

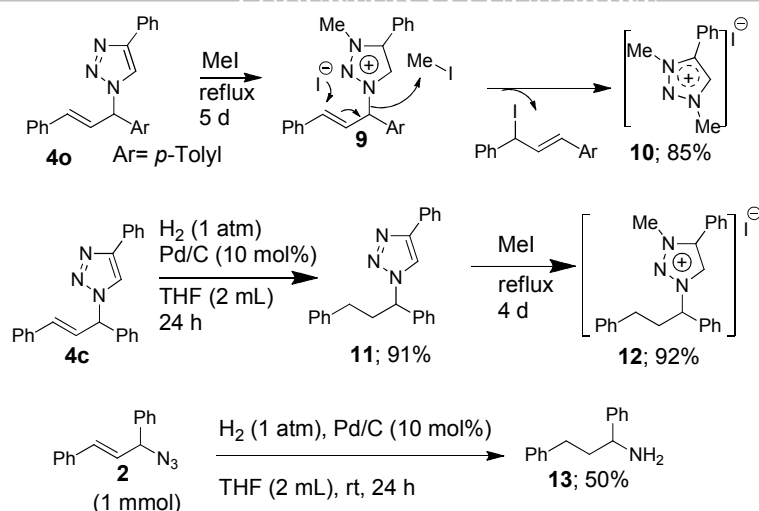
Next, we studied the direct conversion of the benzylic alcohols **5a,c,e,g** and methyl ethers **5b,d,f,h** prepared from their corresponding alcohols (Table 5) into the corresponding substituted 1,2,3-triazole derivatives using the reaction conditions of either method A or method B. The direct azidation of the benzylic alcohol **5a** followed by the click reaction with **3a** using the method A procedure afforded the substituted 1,2,3-triazole derivative **6a** in 71% yield (entry 1, method A, Table 5). On the other hand, the direct azidation of the ether **5b** followed by the click reaction with **3a** using the method A procedure failed to afford the substituted 1,2,3-triazole derivative **6a** (entry 2, method A, Table 5). However, the direct azidation of the substrate **5b** followed by the click reaction with **3a** using the method B procedure successfully afforded the product **6a** in 75% yield (entry 2, method B, Table 5). Similarly, various substituted 1,2,3-triazole derivatives **6b-f** were synthesized in 35-87% yields starting from the corresponding benzylic alcohols or their corresponding methyl ethers **5b-h** by using the method A and method B procedures, respectively (entries 3-9, Table 5). Additionally, the azidation of methyl ethers **5i-k** prepared from of their corresponding allyl alcohols followed by the click reaction with ethyl propiolate under the method B procedure successfully afforded the corresponding 1,2,3-triazole derivatives

**4a** (80%), **4q** (72%), and **4x** (70%, dr 84:16, entries 10-12, Table 5).

**Table 6.**  $\text{Cu}(\text{OTf})_2$ -catalyzed one-pot synthesis of bis-1,2,3-triazoles **8a-e** from bis-homoallyl alcohols.

Entry	Bis-Homoallyl Alcohol	Alkyne	Triazole System <b>8</b> : Yield (%)
1		<b>3a</b>	<b>8a</b> ; 72
2		<b>3a</b>	<b>8b</b> ; 84
3		<b>3a</b>	<b>8c</b> ; 82
4		<b>3a</b>	<b>8d</b> ; 87
5		<b>3i</b>	<b>8e</b> ; 68

<sup>a</sup> Reagents and Conditions: The direct azidation of substrate **7** was carried out using  $\text{Cu}(\text{OTf})_2$  (10 mol%),  $\text{TMSN}_3$  (3 equiv) in DCM (3 mL) at rt for 3 h and the solvent was evaporated in vacuum. Then, the click reaction was carried out using alkyne (5 equiv) in THF (2 mL) and water (2 mL) in the presence of *L*-sodium ascorbate (100 mol%) at rt for 20 h.



**Scheme 2.** Synthetic transformations of 1,2,3-triazole derivative **4c** and conversion of azide **2** into **13**.

**Table 7.** Assembling of *bis*-1,2,3-triazole incorporated polyether systems **8**, **14** and **15**.<sup>a</sup>

The reaction scheme shows the one-pot sequential synthesis of bis-1,2,3-triazole systems **8**, **14**, and **15** from bis-homoallyl alcohols **7**.   
 Step 1: **7** reacts with Cu(OTf)<sub>2</sub> and TMSN<sub>3</sub> to form the triazole system **8**.   
 Step 2: **8** is reduced with NaBH<sub>4</sub> (a) to form the diol system **14**.   
 Step 3: **14** is treated with NaH and propargyl bromide (b) to form the bis-alkyne system **15**.

Entry	Bis-Homoallyl Alcohol <b>7</b>	Triazole System <b>8</b> : Yield (%)	Triazole System <b>14</b> : Yield (%)	Triazole System <b>15</b> : Yield (%)
1	<b>7b</b>	<b>8f</b> ; 78	<b>14a</b> ; 96	<b>15a</b> ; 60
2	<b>7c</b>	<b>8g</b> ; 81	<b>14b</b> ; 95	<b>15b</b> ; 85
3	<b>7d</b>	<b>8h</b> ; 78	<b>14c</b> ; 92	<b>15c</b> ; 80

<sup>a</sup> Reagents and Conditions: The direct azidation of substrate **7** was carried out using Cu(OTf)<sub>2</sub> (10 mol%), TMSN<sub>3</sub> (3 equiv) in DCM (3 mL) at rt for 3 h and the solvent was evaporated in vacuum. Then, the click reaction was carried out using alkyne (5 equiv) in THF (2 mL) and water (2 mL) in the presence of *L*-sodium ascorbate (100 mol%) at rt for 20 h. (a) NaBH<sub>4</sub> (4 equiv), THF (3 mL) and EtOH (7 mL), 1 h, r.t. (b) NaH (4 equiv), propargyl bromide (5 equiv), THF (3 mL), 20 h, r.t.

**Table 8.** Synthesis of new class of *bis*-1,2,3-triazole incorporated polyether macrocycles **16** and **17**.

Entry	Triazole System <b>15</b>	Macrocycle <b>16</b> : Yield (%)	Macrocycle <b>17</b> : Yield (%)
1			
2			
3			

Further, we aimed to elaborate the scope of this work by synthesizing polyethers embedded with *bis*-triazole moieties<sup>27</sup> (**8** Table 6). Towards this end, at first, we prepared the *bis*-homoallylic alcohols **7a-d** from the Zn-mediated allylation of the corresponding *bis*-aldehydes, which were assembled from salicylaldehyde and a suitable linker (aliphatic linker or polyether linker or aromatic linker).<sup>27</sup> Then, the *bis*-homoallylic alcohols having aliphatic linker (**7a**), polyether linker (**7b,c**) and aromatic linkers (**7d**) were treated with TMSN<sub>3</sub> (3 equiv) in the presence of Cu(OTf)<sub>2</sub> (10 mol%) at rt in DCM for 3 h and after this period, the solvent was evaporated and subsequently, we performed the click reaction of the corresponding azides obtained in the azidation step with ethyl propiolate, which gave the corresponding compounds **8a-d** with *bis*-triazole moieties linked through suitable linkers in 72-87% yields, (entries 1-4, Table 6). Similarly, the compound **8e** with *bis*-triazole moieties linked through suitable linkers was obtained in 68% yield from the direct azidation of the corresponding *bis*-homoallylic alcohols **7a** followed by the click reaction with **3i** (entries 5, Table 6).

We also explored the synthetic utility of representative 1,2,3-triazoles and in this regard, initially we carried out the reaction of MeI with the 1,2,3-triazole **4o** in which we observed the formation of an ionic liquid-type product **10**.<sup>30</sup> Presumably, in the reaction of MeI with **4o**, the product **10** formed *via* the loss of the allylic moiety present in the 1,2,3-triazole derivative **4o** (Scheme 2). To avoid the elimination of the allylic moiety present in the 1,2,3-triazole system, in a succeeding reaction, at first we carried out the hydrogenation of the olefin moiety present in the 1,2,3-triazole system **4c**, which gave the 1,2,3-triazole system **11**. Then, the reaction of the 1,2,3-triazole system **11** with MeI gave an ionic liquid-type product **12** (Scheme 2). We also carried out the hydrogenation of a representative azide compound **2**, which gave the benzylamine substrate **13** (1,3-diphenylpropan-1-amine) in 50% yield (Scheme 2).

There have been various reports on the synthesis of polyethers embedded with *bis*-triazole moieties<sup>27</sup> and 1,2,3-triazole moiety incorporated macrocyclic systems.<sup>28</sup> For example, recently, Beer *et al.* reported the synthesis of Ferrocene-based triazole moiety

incorporated macrocycles.<sup>28c</sup> Along this line and in continuation of our interest on the synthesis of macrocyclic polyethers/crown ethers,<sup>29</sup> we also intended to prepare the 1,2,3-triazole moiety incorporated macrocyclic polyether involving the direct azidation of alcohol as one of the steps. In this regard, the compounds **8f-h** with *bis*-triazole moieties linked through a polyether linker were treated with NaBH<sub>4</sub> to afford the compounds **14a-c** (Table 7). Then, the compounds **14a-c** were treated with propargyl bromide in the presence of NaH to give the products **15a-c** having two terminal alkyne units. Next, the Glaser–Eglinton–Hay-type cyclization<sup>29b</sup> of substrate **15a-c** in the presence of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O in DMSO at 110 °C under an open-air atmosphere gave a new class of polyether macrocyclic systems **16a-c** (Table 8) embedded with 1,2,3-triazole moieties and the 1,3-diyne unit. Consequently, we planned to convert the 1,2-diyne unit present in the compounds **16a-c** into a thiophene ring.<sup>29b</sup> Accordingly, the reaction of macrocycles **16a-c** with Na<sub>2</sub>S·xH<sub>2</sub>O in the presence of catalytic amount of 1,10-phenanthroline and CuI in DMF at 90 °C under an open-air atmosphere gave a new class of polyether macrocyclic system **17a-c** embedded with 1,2,3-triazole moieties and a thiophene ring (Table 8).

In summary, we have shown our investigations on the one-pot direct azidation of allylic alcohols/ethers followed by click reaction. Two methods were successfully developed for synthesizing various substituted 1,2,3 triazole derivatives directly from various allylic/benzylic alcohols without isolating the corresponding azides. The first method (Method A) involved magnetic nano Fe<sub>3</sub>O<sub>4</sub>-catalyzed direct azidation of various allylic/benzylic alcohols with TMSN<sub>3</sub> as the first step followed by the Cu-catalyzed click reaction of the corresponding azides with alkynes as the second step. The second method (Method B) involved the Cu(OTf)<sub>2</sub>-catalyzed direct azidation of various allylic/benzylic alcohols and methyl ethers of allylic/benzylic alcohols with TMSN<sub>3</sub> as the first step followed by the click reaction of the corresponding azides with alkynes as the second step. In this method, Cu(OTf)<sub>2</sub> served as a single catalyst for both the azidation of alcohol and click reaction steps. We have also shown the utility of this protocol by synthesizing new class of polyethers embedded with triazole moiety and a 1,3-diyne unit.

## Experimental Section

**General.** Melting points are uncorrected. FT-IR spectra of compounds were recorded as thin films or KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds were recorded on 400 MHz and 100 MHz spectrometers (using TMS as an internal standard), respectively. Column chromatography was carried out on silica gel (100-200 mesh). Thin layer chromatography (TLC analysis) was performed on silica gel plates or neutral Al<sub>2</sub>O<sub>3</sub> plates and components were visualized by observation under iodine. Solvents were dried by following the standard drying methods. Reactions were carried out in anhydrous solvent under a nitrogen atmosphere wherever required. Solutions were dried using anhydrous Na<sub>2</sub>SO<sub>4</sub>. Isolated yields of all the products were reported and yields were not optimized and total yield (all the isomers wherever applicable) is reported. Ratios of isomers were determined from the NMR spectra of crude reaction mixtures or after isolation. In some of the reactions, only the major product isomer was isolated in pure form (in some cases, the product was isolated as mixture of isomer). The particle size of Fe<sub>3</sub>O<sub>4</sub> nanoparticles (before and after usage in the reaction) was determined from HRTEM analysis.<sup>23</sup> Compounds **1b-d**,<sup>31a</sup> **1e**,<sup>31b</sup> **1g**,<sup>31a</sup> **1h**,<sup>31c</sup> **1i,j**,<sup>31d,e</sup> **4r**,<sup>31f</sup> **4p**,<sup>31g</sup> **5b**,<sup>31h,i</sup> **5d**,<sup>31h</sup> **5f**,<sup>31i</sup> **5h**,<sup>31j</sup> **5i**,<sup>31i</sup> **5j**,<sup>31k</sup> **5k**.<sup>31l</sup> Though the compounds **7**, **8** and **14-17** have two remote stereocenters and due to the molecular symmetry, the

molecules **7**, **8** and **14-17** were isolated as a mixture of diastereomers (*dr* = 50:50) and we could not separate the diastereomers and characterization data given for both isomers.

**General procedure for the magnetic nano Fe<sub>3</sub>O<sub>4</sub>-catalyzed direct azidation of allylic/benzylic alcohol, Step '1'.** A round-bottom flask containing a mixture of the corresponding allylic/benzylic alcohol **1** (0.5 mmol, 1 equiv), trimethylsilyl azide (1.25-1.5 mmol, 2.5-3 equiv) and magnetic nano Fe<sub>3</sub>O<sub>4</sub> (particle size < 50 nm, 15 mol% and the Fe<sub>3</sub>O<sub>4</sub> nanoparticles can be handled using a Teflon spatula) in 1,2-dichloroethane (1.5-3 mL) was stirred at 70 °C for 6 h. The purification of the corresponding azide product **2** and recovery of the catalyst (Fe<sub>3</sub>O<sub>4</sub> nanoparticles) were performed as stated in Step '2'. **Step '2'.** After the reaction time, a magnet was externally appended to the RB flask, the magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were gathered at the walls of the RB flask and the resulting clear solution of the reaction mixture was transferred in to an another RB flask with the help of a dropper. Then, the catalyst (Fe<sub>3</sub>O<sub>4</sub> nanoparticles) was washed again using EtOAc (2 mL). The RB flask containing Fe<sub>3</sub>O<sub>4</sub> nanoparticles was heated in an oven (at 100-110 °C, overnight) and the catalyst was reused in the next cycle. The combined organic layers were evaporated under vacuum and purified by column chromatography to give the corresponding azide product **2**.

**General procedure (Method A) for the one-pot magnetic nano Fe<sub>3</sub>O<sub>4</sub>-catalyzed direct azidation of allylic alcohols and click reaction, Step '3'.** The direct azidation of the corresponding allylic/benzylic alcohol **1** (0.5 mmol, 1 equiv) was carried out using the step '1' procedure. Next, the catalyst (Fe<sub>3</sub>O<sub>4</sub> nanoparticles) was removed using an external magnet and the solvent was evaporated. Then, to the crude reaction mixture obtained in the step '1' procedure, THF (3 mL), water (3 mL), alkyne (1-1.2 mmol), CuSO<sub>4</sub>·5H<sub>2</sub>O (30 mol%) and sodium *L*-ascorbate (30 mol%) were sequentially added. Then, the reaction mixture was stirred at rt for 12 h, then, was extracted using EtOAc and the combined organic layers were concentrated and the resulting crude reaction mixture was purified by column chromatography (50% EtOAc/Hexanes), to afford the corresponding 1,2,3-triazole product **4/6** (see the corresponding Tables/Schemes for specific entries).

**General procedure for the copper(II) triflate-catalyzed one-pot direct azidation of alcohol followed by click reaction (Method B):** A solution of allylic alcohol **1** (0.5 mmol) and TMSN<sub>3</sub> (0.75 mmol, 1.5 equiv) and copper(II) triflate (5 mol%) in DCM (3 mL) was stirred at rt for 3 h under an inert atmosphere. Then, DCM was removed under reduced pressure. After this, to the resulting crude reaction mixture THF (2-3 mL), water (2-3 mL), alkyne (1-1.25 mmol) and sodium *L*-ascorbate (50 mol%) were added and the reaction mixture was stirred at rt for 20 h. Then, the reaction mixture was extracted using EtOAc and the combined organic layers were evaporated and the resulting reaction mixture was purified by silica gel column chromatography to afford the triazole product **4/6** (See the corresponding Tables/Schemes for specific entries).

**General procedure for the copper(II) triflate-catalyzed one-pot direct azidation of allylic and benzylic methyl ethers followed by click reaction (Method B):** A solution of allyl methyl ether **5** (0.5 mmol) and TMSN<sub>3</sub> (0.75 mmol, 1.5 equiv) and copper(II) triflate (5 mol%) in DCM (3 mL) was stirred at rt for 3 h under an inert atmosphere. After this period, the solvent was evaporated. Then, to the resulting reaction mixture THF (2 mL), water (2 mL), alkyne (1.25 mmol, 2.5 equiv) and sodium *L*-ascorbate (50 mol%) were added and the reaction mixture was stirred at rt for 20 h. Then, the reaction mixture was extracted by using ethyl acetate (3 X 10 mL). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the organic phase was

concentrated and the resulting crude reaction mixture was purified by silica gel column chromatography (EtOAc/Hexanes) to give the desired 1,2,3-triazole product **4/6** (see the corresponding Tables/Schemes for specific entries).

**(E)-Ethyl 1-(1,3-diphenylallyl)-1H-1,2,3-triazole-4-carboxylate (4a).** Following the general procedure, **4a** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a brown solid (286 mg, 86%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 123-125 °C; IR (thin film):  $\nu_{max}$  2982, 1727, 1449, 1202 and 1038  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  8.12 (1 H, s), 7.42-7.29 (10 H, m), 6.70 (1 H, dd,  $J_1 = 15.7$  Hz,  $J_2 = 6.8$  Hz), 6.58 (1 H, d,  $J = 6.8$  Hz), 6.50 (1 H, d,  $J = 15.7$  Hz), 4.42 (2 H, q,  $J = 7.1$  Hz), 1.40 (3 H, t,  $J = 7.1$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  160.8, 140.3, 137.1, 135.3, 135.2, 129.3, 129.1, 128.8, 127.5, 126.9, 124.9, 66.7, 61.4, 14.3 ppm; HRMS (ESI):  $MNa^+$ , found 356.1385.  $C_{20}H_{19}N_3NaO_2$  requires 356.1375.

**(E)-(1-(1,3-Diphenylallyl)-1H-1,2,3-triazol-4-yl)methanol (4b).** Following the general procedure, **4b** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (238 mg, 82%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{max}$  3375, 2954, 1731, 1450, 1223 and 1091  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.57 (1 H, s), 7.41-7.28 (10 H, m), 6.70 (1 H, dd,  $J_1 = 15.6$  Hz,  $J_2 = 7.2$  Hz), 6.52-6.47 (2 H, m), 4.79 (2 H, s), 3.36 (1 H, br. s);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  147.8, 137.7, 135.5, 134.7, 129.2, 128.8, 128.7, 128.6, 127.5, 126.9, 125.5, 121.2, 66.5, 56.4; HRMS (ESI):  $MNa^+$ , found 314.1254.  $C_{18}H_{17}N_3ONa$  requires 314.1269.

**(E)-1-(1,3-Diphenylallyl)-4-phenyl-1H-1,2,3-triazole (4c).** Following the general procedure, **4c** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (303 mg, 90%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 178-179 °C; IR (thin film)  $\nu_{max}$  2925, 1724, 1450, 1226 and 970  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.86 (2 H, d,  $J = 7.1$  Hz), 7.79 (1 H, s), 7.45-7.31 (13 H, m), 6.77 (1 H, dd,  $J_1 = 15.8$  Hz,  $J_2 = 6.7$  Hz), 6.59-6.53 (2 H, m) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  147.9, 137.9, 135.6, 134.7, 130.5, 129.2, 128.8, 128.8, 128.6, 128.2, 127.5, 126.9, 125.8, 125.6, 118.9, 66.4 ppm; HRMS (ESI):  $MH^+$ , found 338.1642.  $C_{23}H_{20}N_3$  requires 338.1657.

**(E)-(1-(1,3-Diphenylallyl)-1H-1,2,3-triazol-4-yl)methyl acrylate (4d).** Following the general procedure, **4d** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (321 mg, 93%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 112-114 °C; IR (thin film)  $\nu_{max}$  2926, 1495, 1454 and 1045  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.66 (1 H, s), 7.43-7.29 (10 H, m), 6.72 (1 H, dd,  $J_1 = 15.6$  Hz,  $J_2 = 7.2$  Hz), 6.54-6.42 (3 H, m), 6.15 (1 H, dd,  $J_1 = 17.3$  Hz,  $J_2 = 10.4$  Hz), 5.87 (1 H, d,  $J = 10.4$  Hz), 5.33 (2 H, s) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  166.0, 142.8, 137.7, 135.5, 134.9, 131.6, 129.2, 128.9, 128.7, 128.6, 128.0, 127.4, 126.9, 125.5, 123.1, 66.6, 57.8 ppm; HRMS (ESI):  $MH^+$ , found 346.1555.  $C_{21}H_{20}N_3O_2$  requires 346.1556.

**(E)-Dimethyl 1-(1,3-diphenylallyl)-1H-1,2,3-triazole-4,5-dicarboxylate (4e).** Following the general procedure, **4e** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as yellow liquid (324 mg, 86%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{max}$  2950, 1735, 1485, 1210 and 1020  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.45-7.28 (10 H, m), 6.96 (1 H, dd,  $J_1 = 15.7$  Hz,  $J_2 = 8.0$  Hz), 6.81 (1 H, d,  $J = 8.0$  Hz), 6.64 (1 H, d,  $J = 15.7$  Hz), 3.97 (3 H, s), 3.85 (3 H, s) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  160.6, 159.3, 139.8, 137.3, 135.5, 135.1, 130.2, 129.0, 128.8, 128.7, 128.6, 127.4, 127.0, 125.1, 67.1, 53.4, 52.7 ppm; HRMS (ESI):  $MNa^+$ , found 400.1285.  $C_{21}H_{19}N_3NaO_4$  requires 400.1273.

**(E)-4-Butyl-1-(1,3-diphenylallyl)-1H-1,2,3-triazole (4f).** Following the general procedure, **4f** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (154 mg, 98%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $CH_2Cl_2$ ):  $\nu_{max}$  2927, 1495, 1451, 1215 and 747  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta_H$  7.43-7.28 (11 H, m), 6.72 (1 H, dd,  $J_1 = 16.1$  Hz,  $J_2 = 6.6$  Hz), 6.51 (1 H, d,  $J = 4.58$  Hz), 6.48 (1 H, d,  $J = 2.8$  Hz), 2.74 (2 H, t,  $J = 7.6$  Hz), 1.71-1.63 (2 H, m), 1.42-1.35 (2 H, m), 0.94 (3 H, t,  $J = 7.3$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta_C$  138.2, 135.6, 134.4, 129.1, 128.7, 128.6, 128.5, 127.4, 126.8, 125.9, 119.8, 66.2, 31.6, 25.5, 22.4, 13.9 ppm; HRMS (ESI):  $MNa^+$ , found 340.1773.  $C_{21}H_{23}N_3Na$  requires 340.1790.

**(E)-1-(1,3-Diphenylallyl)-4-hexyl-1H-1,2,3-triazole (4g).** Following the general procedure, **4g** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (293 mg, 85%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 98-100 °C; IR (thin film)  $\nu_{max}$  2928, 1495, 1454 and 1044  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.42-7.28 (11 H, m), 6.73 (1 H, dd,  $J_1 = 16.1$  Hz,  $J_2 = 6.5$  Hz), 6.51-6.48 (2 H, m), 2.74 (2 H, t,  $J = 7.6$  Hz), 1.72-1.67 (2 H, m), 1.39-1.29 (6 H, m), 0.89 (3 H, t,  $J = 6.1$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  148.6, 138.2, 135.7, 134.4, 129.1, 128.7, 128.6, 128.5, 127.4, 126.8, 126.0, 119.9, 66.2, 31.6, 29.4, 29.0, 25.9, 22.6, 14.1 ppm; HRMS (ESI):  $MH^+$ , found 346.2294.  $C_{23}H_{28}N_3$  requires 346.2283.

**(E)-1-(1,3-Diphenylallyl)-4-octyl-1H-1,2,3-triazole (4h).** Following the general procedure, **4h** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (343 mg, 92%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 99-101 °C; IR (thin film)  $\nu_{max}$  2926, 1495, 1454 and 967  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.43-7.28 (11 H, m), 6.72 (1 H, dd,  $J_1 = 16.1$  Hz,  $J_2 = 6.6$  Hz), 6.49 (2 H, dd,  $J_1 = 12.0$  Hz,  $J_2 = 4.4$  Hz), 2.73 (2 H, t,  $J = 7.7$  Hz), 1.71-1.64 (2 H, m), 1.38-1.27 (10 H, m), 0.89 (3 H, t,  $J = 6.6$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  148.6, 138.2, 135.7, 134.4, 129.1, 128.7, 128.6, 128.5, 127.4, 126.8, 126.0, 119.8, 66.2, 31.9, 29.5, 29.3, 29.2, 25.8, 22.7, 14.1 ppm; HRMS (ESI):  $MH^+$ , found 374.2591.  $C_{25}H_{32}N_3$  requires 374.2596.

**(E)-2-((1-(1,3-Diphenylallyl)-1H-1,2,3-triazol-4-yl)methoxy)benzaldehyde (4i).** Following the general procedure, **4i** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 27:73) as a red colored solid (336 mg, 85%);  $R_f$  (30% EtOAc/Hexanes) 0.55; mp 111-113 °C; IR (thin film)  $\nu_{max}$  3030, 1663, 1598, 1456 and 1236  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  10.44 (1 H, s), 7.82 (1 H, d,  $J = 7.6$  Hz), 7.75 (1 H, br. s), 7.54 (1 H, t,  $J = 7.4$  Hz), 7.42-7.27 (10 H, m), 7.17 (1 H, d,  $J = 8.5$  Hz), 7.03 (1 H, t,  $J = 7.6$  Hz), 6.74 (1 H, dd,  $J_1 = 16.1$  Hz,  $J_2 = 6.8$  Hz), 6.51 (2 H, dd,  $J_1 = 12.0$  Hz,  $J_2 = 4.4$  Hz), 5.33 (2 H, s) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  189.7, 160.5, 143.3, 137.7, 136.1, 135.4, 134.9, 129.2, 128.9, 128.8, 128.7, 128.6, 127.4, 126.9, 125.4, 125.0, 122.5, 121.3, 113.1, 66.7, 62.6 ppm; HRMS (ESI):  $MH^+$ , found 396.1702.  $C_{25}H_{22}N_3O_2$  requires 396.1712.

**1,12-Bis(1-((E)-1,3-diphenylallyl)-1H-1,2,3-triazol-4-yl)-2,5,8,11-tetraoxadodecane (4j).** Following the general procedure, **4j** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as colorless liquid (522 mg, 75%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{max}$  2869, 1495, 1450 and 1097  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.60 (2 H, s), 7.41-7.28 (20 H, m), 6.71 (2 H, dd,  $J_1 = 15.6$  Hz,  $J_2 = 7.2$  Hz), 6.52-6.47 (4 H, m), 4.69 (4 H, s), 3.70-3.62 (8 H, m), 3.60 (4 H, s) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  145.2, 137.9, 135.5, 134.7, 129.1, 128.8, 128.7, 128.5, 127.5, 126.8, 125.7, 121.9, 70.5, 70.5, 69.8, 66.4, 64.8 ppm; HRMS (ESI):  $MH^+$ , found 697.3505.  $C_{42}H_{45}N_6O_4$  requires 697.3502.

**(E)-1-(1,3-Bis(4-chlorophenyl)allyl)-4-phenyl-1H-1,2,3-triazole (4k).** Following the general procedure, **4k** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless solid (151 mg, 75%);  $R_f$  (30% EtOAc/Hexanes) 0.52; mp: 88-90 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2928, 1595, 1491, 1407 and 764 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.85 (2 H, dd,  $J_1 = 7.1$  Hz,  $J_2 = 1.4$  Hz), 7.79 (1 H, s), 7.45-7.25 (11 H, m), 6.71 (1 H, dd,  $J_1 = 15.8$  Hz,  $J_2 = 6.8$  Hz), 6.50-6.45 (2 H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  148.0, 136.2, 134.9, 134.4, 133.8, 133.8, 130.3, 129.4, 129.0, 128.9, 128.8, 128.4, 128.1, 125.8, 125.7, 118.9, 65.7 ppm; HRMS (ESI): MNa<sup>+</sup>, found 428.0672. C<sub>23</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>Na requires 428.0697.

**(E)-Ethyl 1-(1,3-bis(4-chlorophenyl)allyl)-1H-1,2,3-triazole-4-carboxylate (4l).** Following the general procedure, **4l** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (120 mg, 60%);  $R_f$  (30% EtOAc/Hexanes) 0.48; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2983, 1731, 1594, 1492, 1093 and 737 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  8.10 (1 H, s), 7.39 (2 H, d,  $J = 8.5$  Hz), 7.32 (4 H, s), 7.23 (2 H, d,  $J = 8.4$  Hz), 6.65 (1 H, dd,  $J_1 = 15.8$  Hz,  $J_2 = 6.5$  Hz), 6.54 (1 H, d,  $J = 6.9$  Hz), 6.46 (1 H, dd,  $J_1 = 15.8$  Hz,  $J_2 = 1.1$  Hz), 4.42 (2H, q,  $J = 7.1$  Hz), 1.40 (3 H, t,  $J = 7.1$  Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  160.6, 140.4, 135.4, 135.3, 134.7, 134.4, 133.5, 129.6, 129.0, 128.8, 128.1, 126.8, 125.0, 66.0, 61.5, 14.3 ppm; HRMS (ESI): MNa<sup>+</sup>, found 424.0578. C<sub>20</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>2</sub> requires 424.0596.

**(E)-Dimethyl 1-(1,3-bis(4-chlorophenyl)allyl)-1H-1,2,3-triazole-4,5-dicarboxylate (4m).** Following the general procedure, **4m** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a yellow liquid (232 mg, 52%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film):  $\nu_{max}$  2954, 1732, 1491, 1224 and 1092 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.37-7.26 (8 H, m), 6.88 (1 H, dd,  $J_1 = 15.6$  Hz,  $J_2 = 7.7$  Hz), 6.80 (1 H, d,  $J = 7.8$  Hz), 6.56 (1 H, d,  $J = 15.6$  Hz), 3.98 (3 H, s), 3.90 (3 H, s) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  160.5, 159.2, 140.1, 135.6, 135.0, 134.5, 134.1, 133.8, 129.6, 129.3, 129.0, 128.9, 128.2, 125.4, 66.1, 53.5, 52.8 ppm; HRMS (ESI): MNa<sup>+</sup>, found 468.0487. C<sub>21</sub>H<sub>17</sub>Cl<sub>2</sub>N<sub>3</sub>NaO<sub>4</sub> requires 468.0494.

**(E)-1-(3-(4-Bromophenyl)-1-phenylallyl)-4-hexyl-1H-1,2,3-triazole (4n).** Following the general procedure, **4n** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as colorless liquid (346 mg, 82%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{max}$  2927, 2857, 1588, 1488 and 1071 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.53-7.13 (10 H, m), 6.75-6.64 (1 H, m), 6.51-6.38 (2 H, m), 2.75-2.70 (2 H, m), 1.69-1.65 (2 H, m), 1.38-1.28 (6 H, m), 0.88 (3 H, t,  $J = 6.8$  Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  148.8, 148.7, 137.9, 137.3, 135.4, 134.9, 134.6, 133.1, 132.2, 131.8, 129.1, 129.1, 128.8, 128.7, 128.3, 127.4, 126.9, 126.9, 125.3, 122.7, 122.3, 119.9, 119.8, 66.1, 65.6, 31.5, 29.4, 29.0, 25.8, 22.6, 14.1 ppm; HRMS (ESI): MH<sup>+</sup>, found 424.1386. C<sub>23</sub>H<sub>27</sub>BrN<sub>3</sub> requires 424.1388. Isolated as a mixture of regioisomers and NMR values given for both isomers.

**(E)-4-Phenyl-1-(3-phenyl-1-(p-tolyl)allyl)-1H-1,2,3-triazole (4o).** Following the general procedure, **4o** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as colorless solid (253 mg, 72%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 134-136 °C; IR (thin film)  $\nu_{max}$  2930, 1482, 1456, 1224 and 970 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.87 (2 H, d,  $J = 7.5$  Hz), 7.82 (1 H, s), 7.55-7.19 (12 H, m), 6.85-6.33 (3 H, m), 2.32 (3 H, s) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  147.9, 147.6, 138.1, 136.7, 136.0, 135.7, 135.6, 134.8, 133.8, 132.8, 131.3, 130.6, 130.5, 129.2, 128.9, 128.5, 128.2, 127.4, 127.3, 127.0, 126.8, 126.8, 126.3, 126.0, 125.8, 125.7, 119.2, 118.8, 66.6, 63.0, 19.8, 19.2 ppm; HRMS (ESI):

MH<sup>+</sup>, found 352.1807. C<sub>24</sub>H<sub>22</sub>N<sub>3</sub> requires 352.1814. Isolated as a mixture of regioisomers and NMR values given for both isomers.

**(E)-Ethyl 1-(1-(4-nitrophenyl)-3-phenylallyl)-1H-1,2,3-triazole-4-carboxylate (4oA).** Following the general procedure, **4oA** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as light yellow colour liquid (128 mg, 68%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{max}$  2979, 1731, 1519, 1344 and 733 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  8.28-8.19 (2 H, m), 8.06 (1 H, s), 7.57-7.28 (7 H, m), 6.92 (1 H, dd,  $J_1 = 15.9$  Hz,  $J_2 = 6.5$  Hz), 6.66-6.48 (2 H, m), 4.43 (2 H, q,  $J = 7.1$  Hz), 1.40 (3 H, t,  $J = 7.1$  Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  160.7, 147.6, 141.6, 140.4, 137.1, 136.1, 132.5, 129.8, 129.6, 129.6, 129.3, 128.9, 128.2, 127.7, 127.7, 127.5, 127.0, 127.0, 126.9, 124.4, 124.1, 123.0, 66.5, 66.0, 61.6, 61.5, 14.3 ppm; HRMS (ESI): MNa<sup>+</sup>, found 401.1239. C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>NaO<sub>4</sub> requires 401.1226. Isolated as a mixture of regioisomers and NMR values given for both isomers.

**Ethyl 1-cinnamyl-1H-1,2,3-triazole-4-carboxylate (4p).** Following the general procedure, **4p** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless solid (89 mg, 70%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp: 87-89 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  3139, 2983, 1731, 1450 and 759 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  8.16 (1 H, s), 7.39-7.28 (5 H, m), 6.69 (1 H, d,  $J = 15.8$  Hz), 6.36-6.29 (1 H, m), 5.18 (2 H, d,  $J = 6.7$  Hz), 4.39 (2 H, q,  $J = 7.1$  Hz), 1.38 (3 H, t,  $J = 7.1$  Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  160.7, 140.7, 136.2, 135.2, 128.8, 127.3, 126.8, 120.9, 61.3, 52.6, 14.3 ppm; HRMS (ESI): MNa<sup>+</sup>, found 280.1059. C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>NaO<sub>2</sub> requires 280.1062.

**(E)-Ethyl 1-(4-phenylbut-3-en-2-yl)-1H-1,2,3-triazole-4-carboxylate (4q).** Following the general procedure, **4q** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless solid (102 mg, 76%);  $R_f$  (30% EtOAc/Hexanes) 0.50; mp: 77-79 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2984, 1738, 1494, 1376 and 754 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  8.16 (1 H, s), 7.37-7.24 (5 H, m), 6.59 (1 H, d,  $J = 15.9$  Hz), 6.35 (1 H, dd,  $J_1 = 15.9$  Hz,  $J_2 = 6.9$  Hz), 5.49-5.44 (1 H, m), 4.39 (2 H, q,  $J = 7.1$  Hz), 1.80 (3 H, d,  $J = 6.9$  Hz), 1.37 (3 H, t,  $J = 7.1$  Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  160.8, 140.1, 135.3, 133.5, 128.7, 128.6, 126.8, 126.7, 125.9, 61.2, 59.0, 20.9, 14.3 ppm; HRMS (ESI): MNa<sup>+</sup>, found 294.1208. C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>NaO<sub>2</sub> requires 294.1218.

**(E)-4-Hexyl-1-(4-phenylbut-3-en-2-yl)-1H-1,2,3-triazole (4r).** Following the general procedure, **4r** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (120 mg, 85%);  $R_f$  (30% EtOAc/Hexanes) 0.45; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  3028, 1482, 1448, 1178 and 764 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.36-7.20 (6 H, m), 6.52 (1 H, d,  $J = 16.0$  Hz), 6.35 (1 H, dd,  $J_1 = 15.9$  Hz,  $J_2 = 6.6$  Hz), 5.38-5.31 (1 H, m), 2.70 (2 H, t,  $J = 7.9$  Hz), 1.75 (3 H, d,  $J = 6.9$  Hz), 1.69-1.62 (2 H, m), 1.36-1.22 (6 H, m), 0.86 (3 H, t,  $J = 7.0$  Hz) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  148.4, 135.7, 132.4, 128.7, 128.3, 128.1, 126.6, 118.9, 58.2, 31.6, 29.5, 29.0, 25.8, 22.6, 20.8, 14.1 ppm; HRMS (ESI): MH<sup>+</sup>, found 284.2115. C<sub>18</sub>H<sub>26</sub>N<sub>3</sub> requires 284.2127.

**1-((2E,4E)-1,5-Diphenylpenta-2,4-dien-1-yl)-4-phenyl-1H-1,2,3-triazole (4s).** Following the general procedure, **4s** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (225 mg, 62%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 131-133 °C; IR (thin film)  $\nu_{max}$  3028, 1494, 1449 and 990 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.87 (2 H, d,  $J = 8.4$  Hz), 7.77 (1 H, s), 7.47-7.26 (13 H, m), 6.88 (1 H, dd,  $J_1 = 15.6$  Hz,  $J_2 = 8.4$  Hz), 6.60 (1 H, d,  $J = 15.6$  Hz), 6.52 (1 H, d,  $J = 5.6$  Hz), 6.40-6.28 (2 H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  147.8, 137.8, 136.6, 135.1, 134.9, 130.6, 129.2,

129.1, 128.9, 128.8, 128.8, 128.7, 128.2, 128.1, 127.5, 127.0, 126.6, 125.8, 118.9, 66.2 ppm; HRMS (ESI):  $MNa^+$ , found 386.1622.  $C_{25}H_{21}N_3Na$  requires 386.1633.

**Ethyl 1-((2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-1*H*-1,2,3-triazole-4-carboxylate (4t).** Following the general procedure, **4t** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (131 mg, 73%);  $R_f$  (30% EtOAc/Hexanes) 0.32; IR ( $CH_2Cl_2$ )  $\nu_{max}$  2983, 1731, 1449, 1377 and 736  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  8.10 (1 H, s), 7.41-7.38 (5 H, m), 7.33 (2 H, t,  $J = 7.5$  Hz), 7.29-7.26 (3 H, m), 6.87-6.81 (1 H, m), 6.59 (1 H, d,  $J = 15.7$  Hz), 6.51 (1 H, d,  $J = 5.3$  Hz), 6.29-6.26 (2 H, m), 4.42 (2 H, q,  $J = 7.2$  Hz), 1.40 (3 H, t,  $J = 7.0$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  160.8, 140.2, 137.1, 136.5, 135.5, 135.4, 129.3, 129.1, 128.7, 128.2, 128.2, 127.5, 126.9, 126.7, 126.6, 66.5, 61.4, 14.4 ppm; HRMS (ESI):  $MNa^+$ , found 382.1522.  $C_{22}H_{21}N_3NaO_2$  requires 382.1531.

**2-(((2*E*,4*E*)-1,5-Diphenylpenta-2,4-dien-1-yl)-1*H*-1,2,3-triazol-4-yl)methoxy)benzaldehyde (4u).** Following the general procedure, **4u** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as yellow liquid (240 mg, 57%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{max}$  3030, 1663, 1598, 1456 and 1236  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  10.46 (1 H, s), 7.85 (1 H, d,  $J = 7.5$  Hz), 7.67 (1 H, s), 7.57 (1 H, t,  $J = 8.5$  Hz), 7.42-7.26 (10 H, m), 7.19 (1 H, d,  $J = 8.4$  Hz), 7.08 (1 H, t,  $J = 7.5$  Hz), 6.86 (1 H, dd,  $J_1 = 15.6$  Hz,  $J_2 = 9.4$  Hz), 6.57 (1 H, d,  $J = 15.6$  Hz), 6.46 (1 H, d,  $J = 5.7$  Hz), 6.36-6.24 (2 H, m), 5.36 (2 H, s) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  189.7, 160.5, 143.4, 137.6, 136.5, 136.1, 135.2, 135.2, 129.2, 128.9, 128.7, 128.7, 128.6, 128.2, 127.4, 126.9, 126.6, 125.1, 122.2, 121.4, 113.1, 66.5, 62.7 ppm; HRMS (ESI):  $MH^+$ , found 422.1858.  $C_{27}H_{24}N_3O_2$  requires 422.1869.

**(*E*)-Ethyl 1-((3-benzylidenecyclohex-1-en-1-yl)(phenyl)methyl)-1*H*-1,2,3-triazole-4-carboxylate (4v).** Following the general procedure, **4v** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (247 mg, 62%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 135-137 °C; IR (thin film)  $\nu_{max}$  2936, 1722, 1447, 1224 and 1038  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  8.01/7.90\* (1 H, s), 7.44-7.20 (9 H, m), 7.04 (1 H, d,  $J = 7.2$  Hz), 6.48/6.35\* (1 H, s), 6.25/6.17\* (1 H, s), 5.74 (1 H, s), 4.44 (2 H, q,  $J = 7.2$  Hz), 2.68-2.65/2.48-2.45\* (2 H, m), 2.12 (2 H, t,  $J = 5.8$  Hz), 1.88-1.85\*/1.80-1.73 (2 H, m), 1.42 (3 H, t,  $J = 7.2$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  160.9, 139.9, 138.5, 137.2, 136.6, 135.7, 135.6, 134.3, 131.4, 129.4, 129.3, 129.3, 129.2, 129.1, 128.9, 128.3, 128.2, 128.2, 128.1, 127.5, 127.1, 126.7, 126.6, 125.3, 70.1, 70.0, 61.4, 61.3, 31.9, 28.0, 27.6, 26.4, 22.9, 22.5, 14.4 ppm; HRMS (ESI):  $MNa^+$ , found 422.1844.  $C_{25}H_{25}N_3NaO_2$  requires 422.1844. Isolated as a mixture of regioisomers and the characterization data given correspond to both isomers and \*corresponds to the minor isomer in the  $^1H$  NMR.

**(*E*)-Ethyl 1-((3-benzylidenecyclopent-1-en-1-yl)(phenyl)methyl)-1*H*-1,2,3-triazole-4-carboxylate (4w).** Following the general procedure, **4w** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (173 mg, 45%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 153-155 °C; IR (thin film)  $\nu_{max}$  2926, 1724, 1448, 1202 and 1039  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  8.05/8.00\* (1 H, s), 7.45-7.43 (3 H, m), 7.34 (5 H, d,  $J = 4.4$  Hz), 7.22-7.17 (1 H, m), 6.61 (1 H, s), 6.35 (1 H, s), 5.90 (1 H, s), 4.44 (2 H, q,  $J = 7.1$  Hz), 3.02-2.99 (2 H, m), 2.63-2.60 (2 H, m), 1.42 (3 H, t,  $J = 7.1$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  160.8, 160.8, 150.7, 147.0, 145.8, 146.4, 140.1, 140.0, 138.1, 137.9, 136.7, 135.6, 135.4, 130.6, 129.4, 128.5, 128.1, 128.0, 128.0, 127.8, 127.0, 126.3, 126.3, 122.3, 120.7, 66.4, 66.2,

61.4, 34.0, 31.9, 31.5, 29.5, 14.4 ppm; HRMS (ESI):  $MNa^+$ , found 408.1696.  $C_{24}H_{23}N_3NaO_2$  requires 408.1688. Isolated as a mixture of regioisomers and the characterization data given correspond to both isomers and \*corresponds to the minor isomer in the  $^1H$  NMR.

**Ethyl 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)-1*H*-1,2,3-triazole-4-carboxylate (4x).** Following the general procedure, **4x** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (110 mg, 80%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $CH_2Cl_2$ )  $\nu_{max}$  3132, 2977, 1731, 1645, 1538 and 735  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  8.02\*/8.01 (1 H, s), 5.92 (1 H, br. s), 5.12 (1 H, br. s), 4.64 (1 H, s), 4.57 (1 H, s), 4.34 (2 H, q,  $J = 7.0$  Hz), 2.29-1.89 (5 H, m), 1.58 (6 H, s), 1.32 (3 H, t,  $J = 7.1$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  160.9, 160.8, 147.2, 147.0, 140.2, 139.6, 130.4, 130.0, 128.2, 127.7, 126.7, 126.0, 109.9, 109.9, 62.5, 61.2, 61.2, 60.0, 40.4, 36.5, 34.8, 34.6, 30.5, 30.3, 20.8, 20.7, 20.6, 20.5, 18.8, 14.3 ppm; HRMS (ESI):  $MNa^+$ , found 298.1519.  $C_{15}H_{21}N_3NaO_2$  requires 298.1531. Isolated as a mixture of diastereomers and the characterization data given correspond to both isomers and \*corresponds to the minor isomer in the  $^1H$  NMR.

**4-Hexyl-1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-yl)-1*H*-1,2,3-triazole (4y).** Following the general procedure, **4y** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (124 mg, 87%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $CH_2Cl_2$ ):  $\nu_{max}$  3131, 2926, 2857, 1548, 1377 and 809  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta_H$  7.25 (1 H, s), 5.90 (1 H, br. s), 5.08 (1 H, br. s), 4.72 (1 H, s), 4.65 (1 H, s), 2.70 (2 H, t,  $J = 7.8$  Hz), 2.34-1.90 (5 H, m), 1.66-1.62 (8 H, m), 1.35-1.25 (6 H, m), 0.86 (3 H, t,  $J = 6.8$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta_C$  148.6, 147.8, 147.7, 147.5, 131.2, 129.1, 128.9, 127.1, 119.7, 118.8, 109.7, 61.8, 59.2, 40.7, 36.5, 35.3, 34.9, 31.5, 30.6, 30.4, 29.4, 28.9, 25.8, 25.7, 22.5, 20.8, 20.7, 20.5, 18.9, 14.0 ppm; HRMS (ESI):  $MH^+$ , found 288.2436.  $C_{18}H_{30}N_3$  requires 288.2440. Isolated as a mixture of diastereomers and the characterization data given correspond to both isomers.

**Ethyl 1-benzhydryl-1*H*-1,2,3-triazole-4-carboxylate (6a).** Following the general procedure, **6a** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (218 mg, 71%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 146-148 °C; IR (thin film)  $\nu_{max}$  2983, 1722, 1453, 1207 and 1041  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.94 (1 H, s), 7.39-7.37 (6 H, m), 7.18 (1 H, s), 7.12-7.10 (4 H, m), 4.40 (2 H, q,  $J = 7.1$  Hz), 1.39 (3 H, t,  $J = 7.1$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  160.8, 140.0, 137.4, 129.1, 128.9, 128.0, 127.7, 68.4, 61.4, 14.3 ppm; HRMS (ESI):  $MH^+$ , found 308.1398.  $C_{18}H_{18}N_3O_2$  requires 308.1399.

**Ethyl 1-(1-phenylethyl)-1*H*-1,2,3-triazole-4-carboxylate (6b).** Following the general procedure, **6b** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as yellow liquid (87 mg, 35%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{max}$  2926, 1731, 1375, 1220 and 1095  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta_H$  7.97 (1 H, s), 7.43-7.37 (3 H, m), 7.31-7.29 (2 H, m), 5.90 (1 H, q,  $J = 7.1$  Hz), 4.41 (2 H, q,  $J = 7.1$  Hz), 2.02 (3 H, d,  $J = 7.1$  Hz), 1.40 (3 H, t,  $J = 7.1$  Hz) ppm;  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta_C$  160.9, 140.2, 138.9, 129.2, 129.0, 126.6, 126.2, 61.3, 60.7, 21.2, 14.3 ppm; HRMS (ESI):  $MH^+$ , found 246.1252.  $C_{13}H_{16}N_3O_2$  requires 246.1243.

**Ethyl 1-(1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-1,2,3-triazole-4-carboxylate (6c).** Following the general procedure, **6c** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless solid (190 mg, 70%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 86-88 °C; IR



(thin film)  $\nu_{\max}$  2939, 1721, 1452, 1198 and 1038  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.69 (1 H, s), 7.26-7.10 (3 H, m), 6.89 (1 H, d,  $J = 7.6$  Hz), 5.95 (1 H, t,  $J = 5.1$  Hz), 4.31 (2 H, q,  $J = 7.1$  Hz), 2.93-2.78 (2 H, m), 2.31-2.26 (2 H, m), 1.89-1.81 (1 H, m), 1.74-1.68 (1 H, m), 1.32 (3 H, t,  $J = 7.1$  Hz) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  160.8, 139.7, 137.9, 131.6, 129.8, 129.1, 128.9, 127.1, 126.8, 61.2, 59.4, 30.9, 28.6, 18.9, 14.3 ppm; HRMS (ESI):  $\text{MH}^+$ , found 272.1390.  $\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_2$  requires 272.1399.

**Ethyl 1-(1-allyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1H-1,2,3-triazole-4-carboxylate (6d).** Following the general procedure, **6d** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as a colorless liquid (162 mg, 52%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{\max}$  2939, 1739, 1319, 1221 and 773  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.52 (1 H, s), 7.34-7.21 (4 H, m), 5.59-5.48 (1 H, m), 5.24-5.07 (2 H, m), 4.36 (2 H, q,  $J = 7.1$  Hz), 3.52 (1 H, dd,  $J_1 = 14.4$  Hz,  $J_2 = 8.4$  Hz), 3.24-3.19 (1 H, m), 2.84-2.80 (2 H, m), 2.56-2.51 (1 H, m), 2.32-2.24 (1 H, m), 1.85-1.78 (1 H, m), 1.35 (3 H, t,  $J = 7.1$  Hz), 1.38-1.34 (1 H, m) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  161.1, 138.7, 138.6, 134.0, 132.5, 130.2, 129.0, 128.3, 127.8, 127.0, 120.0, 66.1, 61.2, 45.0, 35.1, 29.5, 18.2, 14.3 ppm; HRMS (ESI):  $\text{MH}^+$ , found 312.1704.  $\text{C}_{18}\text{H}_{22}\text{N}_3\text{O}_2$  requires 312.1712.

**4-Hexyl-1-(1,2,3,4-tetrahydronaphthalen-1-yl)-1H-1,2,3-triazole (6e).** Following the general procedure, **6e** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 30:70) as yellow liquid (198 mg, 70%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{\max}$  2928, 1454, 1219 and 1042  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.28 (1 H, t,  $J = 7.7$  Hz), 7.21 (1 H, d,  $J = 6.1$  Hz), 7.15 (1 H, t,  $J = 7.7$  Hz), 6.95 (1 H, s), 6.91 (1 H, d,  $J = 7.7$  Hz), 5.93 (1 H, t,  $J = 6.1$  Hz), 3.00-2.83 (2 H, m), 2.67 (2 H, t,  $J = 7.5$  Hz), 2.35-2.24 (2 H, m), 1.92-1.84 (2 H, m), 1.66-1.59 (2 H, m), 1.35-1.27 (6 H, m), 0.87 (3 H, t,  $J = 6.8$  Hz) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  148.2, 137.7, 133.1, 129.5, 128.9, 128.3, 126.6, 119.8, 58.9, 31.5, 31.3, 29.4, 28.9, 25.8, 22.5, 19.7, 14.0 ppm; HRMS (ESI):  $\text{MH}^+$ , found 284.2118.  $\text{C}_{18}\text{H}_{26}\text{N}_3$  requires 284.2127.

**Ethyl 1-(phenyl(o-tolyl)methyl)-1H-1,2,3-triazole-4-carboxylate (6f).** Following the general procedure, **6f** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (139 mg, 87%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\max}$  2985, 1738, 1491, 1375 and 754  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.83 (1 H, s), 7.35-7.25 (3 H, m), 7.30 (1 H, s), 7.23-7.13 (3 H, m), 7.03-7.02 (2 H, m), 6.66 (1 H, d,  $J = 7.7$  Hz), 4.37 (2 H, q,  $J = 7.0$  Hz), 2.16 (3 H, s), 1.33 (3 H, t,  $J = 7.1$  Hz) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  160.8, 139.7, 136.8, 136.3, 135.7, 131.2, 129.2, 128.9, 128.9, 128.0, 128.0, 127.3, 126.6, 65.6, 61.3, 19.2, 14.3 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 344.1366.  $\text{C}_{19}\text{H}_{19}\text{N}_3\text{NaO}_2$  requires 344.1375.

**General procedure for the synthesis of bis-alcohols 7a-d.**<sup>29</sup> To a mixture of corresponding bis-aldehyde (3 mmol), allyl bromide (7 equiv) in THF (7 mL) were sequentially added sat.  $\text{NH}_4\text{Cl}$  (18 mL) and Zn metal (5 equiv) at rt. The resulting mixture was stirred at rt for 30 h. After this period, the reaction mixture was extracted by using ethyl acetate (3 X 7 mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the organic phase was concentrated, and the resulting crude reaction mixture was purified by silica gel column chromatography (EtOAc/hexanes) to give the desired products **7a-d**.<sup>29</sup>

**Compound 7a.** Following the general procedure, **7a** as a colorless liquid (885 mg, 72%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\max}$  3413, 2937, 1600, 1453 and 751  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.32 (2 H, d,  $J = 7.2$  Hz), 7.19 (2 H, t,  $J = 7.4$  Hz), 6.92 (2 H, t,  $J = 7.4$  Hz), 6.82 (2 H, d,  $J = 8.1$  Hz), 5.87-5.77 (2 H, m), 5.11-5.04 (4 H, m) 4.95 (2 H, br. s), 3.98-3.96 (4

H, m), 2.86 (2 H, s), 2.57-2.42 (4 H, m), 1.83-1.81 (4 H, m), 1.56-1.54 (4 H, m) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  155.7, 135.4, 132.1, 128.2, 126.8, 120.6, 117.4, 111.2, 69.6, 67.6, 42.1, 29.3, 26.0 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 433.2357.  $\text{C}_{26}\text{H}_{34}\text{NaO}_4$  requires 433.2355. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**General procedure for the one-pot synthesis of 1,2,3-triazoles 8a-h directly from bis-homoallylic alcohols 7a-d.** A solution of the corresponding bis-homoallylic alcohol **7** (0.5 mmol) and  $\text{TMSN}_3$  (1.5 mmol, 3 equiv) and copper(II) triflate (10 mol%) in DCM (5.0 mL) was stirred at rt for 3 h under an inert atmosphere. After this period, the solvent was evaporated. Then, to the resulting reaction mixture THF (2-3 mL), water (2-3 mL), alkyne (2.5 mmol, 5 equiv) and sodium *L*-ascorbate (100 mol%) were added and stirred at rt for 20 h. Then, the reaction mixture was extracted by using ethyl acetate (3 X 10 mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the organic phase was concentrated, and the resulting crude reaction mixture was purified by silica gel column chromatography (EtOAc/Hexanes) to give the desired 1,2,3-bis-triazole product **8** (see the corresponding Tables/Schemes for specific entries).

**Diethyl 1,1'-(((hexane-1,6-diylbis(oxy))bis(2,1-phenylene))bis(but-3-ene-1,1-diyl))bis(1H-1,2,3-triazole-4-carboxylate) (8a).** Following the general procedure, **8a** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a red color liquid (117 mg, 72%);  $R_f$  (50% EtOAc/Hexanes) 0.45; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\max}$  2939, 1738, 1602, 1542, 1494 and 754  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  8.04 (2 H, s), 7.34-7.28 (4 H, m), 6.97 (2 H, t,  $J = 7.5$  Hz), 6.91 (2 H, d,  $J = 8.6$  Hz), 6.14 (2 H, t,  $J = 7.1$  Hz), 5.74-5.70 (2 H, m), 5.14-5.02 (4 H, m), 4.38 (4 H, q,  $J = 7.2$  Hz), 4.02-3.93 (4 H, m), 3.24-3.18 (2 H, m), 3.06-3.02 (2 H, m), 1.82-1.79 (4 H, m), 1.47-1.44 (4 H, m), 1.37 (6 H, t,  $J = 7.1$  Hz) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  161.0, 156.1, 139.5, 132.9, 130.2, 127.5, 127.2, 127.2, 125.4, 120.7, 118.9, 111.7, 67.9, 61.2, 59.2, 59.2, 38.1, 29.0, 25.8, 14.3 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 679.3224.  $\text{C}_{36}\text{H}_{44}\text{N}_6\text{NaO}_6$  requires 679.3220. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**Diethyl 1,1'-(((oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(but-3-ene-1,1-diyl))bis(1H-1,2,3-triazole-4-carboxylate) (8b).** Following the general procedure, **8b** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (135 mg, 84%);  $R_f$  (50% EtOAc/Hexanes) 0.45; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\max}$  2939, 1731, 1642, 1542, and 754  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  8.18 (2 H, s), 7.36-7.28 (4 H, m), 6.97 (2 H, t,  $J = 7.5$  Hz), 6.92 (2 H, d,  $J = 8.2$  Hz), 6.12-6.07 (2 H, m), 5.67-5.60 (2 H, m), 5.08-4.97 (4 H, m), 4.34 (4 H, q,  $J = 7.1$  Hz), 4.21-4.09 (4 H, m), 3.89 (4 H, t,  $J = 4.6$  Hz), 3.26-3.19 (2 H, m), 3.08-3.01 (2 H, m), 1.34 (6 H, t,  $J = 7.1$  Hz) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  161.0, 156.0, 139.5, 132.9, 130.3, 127.8, 127.6, 127.5, 125.6, 125.6, 121.2, 118.9, 112.0, 69.7, 69.7, 67.6, 61.2, 59.5, 59.5, 37.7, 14.3 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 667.2863.  $\text{C}_{34}\text{H}_{40}\text{N}_6\text{NaO}_7$  requires 667.2856. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**Diethyl 1,1'-((((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(but-3-ene-1,1-diyl))bis(1H-1,2,3-triazole-4-carboxylate) (8c).** Following the general procedure, **8c** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (141 mg, 82%);  $R_f$  (50% EtOAc/Hexanes) 0.45; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\max}$  2933, 1737, 1602, 1494, and 754  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  8.22 (2 H, s), 7.33 (2 H, d,  $J = 7.5$  Hz), 7.28 (2 H, t,  $J = 7.8$  Hz), 6.96 (2 H, t,  $J = 7.5$  Hz), 6.85 (2 H, d,  $J$

= 8.2 Hz), 6.10 (2 H, t,  $J = 7.7$  Hz), 5.70-5.63 (2 H, m), 5.11-4.97 (4 H, m), 4.37 (4 H, q,  $J = 7.1$  Hz), 4.14-4.05 (4 H, m), 3.84 (4 H, t,  $J = 5.5$  Hz), 3.77 (4 H, br. s), 3.29-3.21 (2 H, m), 3.09-3.02 (2 H, m), 1.36 (6 H, t,  $J = 7.1$  Hz) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  161.0, 155.9, 139.4, 133.0, 130.2, 127.8, 127.8, 125.9, 121.2, 118.9, 112.0, 70.7, 69.4, 67.5, 61.1, 59.6, 37.7, 14.3 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 711.3135.  $\text{C}_{36}\text{H}_{44}\text{N}_6\text{NaO}_8$  requires 711.3118. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**Diethyl 1,1'-(((1,3-phenylenebis(methylene))bis(oxy))bis(2,1-phenylene))bis(but-3-ene-1,1-diyl))bis(1H-1,2,3-triazole-4-carboxylate) (8d).** Following the general procedure, **8d** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (147 mg, 87%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$  2982, 1732, 1493, 1227, 1041 and 754  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.90 (2 H, s), 7.44 (4 H, s), 7.37-7.28 (4 H, m), 7.04-6.91 (4 H, m), 6.10-6.05 (2 H, m), 5.65-5.58 (2 H, m), 5.06-4.95 (8 H, m), 4.41-4.35 (4 H, m), 3.21-3.12 (2 H, m), 3.10-2.95 (2 H, m), 1.40-1.38 (6 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  160.9, 155.7, 155.7, 139.5, 134.5, 134.4, 132.6, 132.6, 130.4, 129.8, 129.7, 129.1, 127.7, 127.6, 127.2, 127.2, 125.7, 125.6, 121.5, 121.5, 119.1, 119.1, 112.3, 112.2, 68.2, 68.1, 61.2, 59.0, 58.8, 38.1, 14.3 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 699.2918.  $\text{C}_{38}\text{H}_{40}\text{N}_6\text{NaO}_6$  requires 699.2907. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**2,2'-(((1,1'-(((Hexane-1,6-diylbis(oxy))bis(2,1-phenylene))bis(but-3-ene-1,1-diyl))bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene))bis(oxy))dibenzaldehyde (8e).** Following the general procedure, **8e** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (131 mg, 68%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$  2940, 1687, 1599, 1456 and 752  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  10.42 (2 H, s), 7.80 (2 H, dd,  $J_1 = 5.8$  Hz,  $J_2 = 1.8$  Hz), 7.65 (2 H, s), 7.52 (2 H, t,  $J = 8.8$  Hz), 7.31-7.26 (4 H, m), 7.13 (2 H, d,  $J = 8.4$  Hz), 7.02 (2 H, t,  $J = 7.4$  Hz), 6.95 (2 H, t,  $J = 8.2$  Hz), 6.89 (2 H, d,  $J = 8.0$  Hz), 6.11 (2 H, t,  $J = 8.7$  Hz), 5.75-5.65 (2 H, m), 5.29 (4 H, s), 5.10-4.99 (4 H, m), 4.00-3.93 (4 H, m), 3.25-3.18 (2 H, m), 3.06-2.99 (2 H, m), 1.80-1.77 (4 H, m), 1.49-1.47 (4 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  189.6, 160.6, 156.0, 142.5, 136.0, 133.3, 129.9, 128.5, 127.4, 126.2, 125.0, 122.8, 121.2, 120.7, 118.5, 113.1, 111.6, 67.9, 62.7, 59.0, 38.3, 29.1, 25.8 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 803.3548.  $\text{C}_{46}\text{H}_{48}\text{N}_6\text{NaO}_6$  requires 803.3533. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**2,2'-(((1,1'-(((Oxybis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(but-3-ene-1,1-diyl))bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene))bis(oxy))dibenzaldehyde (8f).** Following the general procedure, **8f** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (299 mg, 78%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$  2976, 1686, 1599, 1483 and 756  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  10.41 (2 H, s), 7.79 (2 H, dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.1$  Hz), 7.73 (2 H, s), 7.52 (2 H, td,  $J_1 = 7.8$  Hz,  $J_2 = 1.2$  Hz), 7.30-7.24 (4 H, m), 7.10 (2 H, d,  $J = 8.4$  Hz), 7.02 (2 H, t,  $J = 7.6$  Hz), 6.96 (2 H, t,  $J = 7.5$  Hz), 6.85 (2 H, d,  $J = 8.2$  Hz), 6.10-6.06 (2 H, m), 5.69-5.62 (2 H, m), 5.22 (4 H, d,  $J = 3.9$  Hz), 5.05 (2 H, d,  $J = 17.1$  Hz), 4.96 (2 H, d,  $J = 10.2$  Hz), 4.17-4.06 (4 H, m), 3.88-3.84 (4 H, m), 3.25-3.17 (2 H, m), 3.07-3.02 (2 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  189.7, 160.5, 155.8, 142.5, 136.0, 133.3, 130.0, 128.5, 127.7, 126.5, 125.0, 122.9, 121.3, 121.2, 118.5, 113.1, 112.0, 69.7, 67.7, 62.7, 59.1, 59.0, 38.0 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 791.3150.  $\text{C}_{44}\text{H}_{44}\text{N}_6\text{NaO}_7$  requires 791.3169. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**2,2'-(((1,1'-(((Ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(but-3-ene-1,1-diyl))bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene))bis(oxy))dibenzaldehyde (8g).** Following the general procedure, **8g** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (163 mg, 81%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$  2875, 1687, 1599, 1493 and 756  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  10.39 (2 H, s), 7.82 (2 H, s), 7.77-7.75 (2 H, m), 7.50-7.46 (2 H, m), 7.28-7.21 (4 H, m), 7.12 (2 H, d,  $J = 8.4$  Hz), 7.00-6.90 (4 H, m), 6.81 (2 H, d,  $J = 8.1$  Hz), 6.06 (2 H, t,  $J = 6.8$  Hz), 5.69-5.62 (2 H, m), 5.25 (4 H, s), 5.07-4.93 (4 H, m), 4.10-4.00 (4 H, m), 3.78-3.76 (4 H, m), 3.69 (4 H, br. s), 3.25-3.18 (2 H, m), 3.04-3.00 (2 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  189.7, 160.6, 155.7, 142.4, 136.0, 133.4, 129.9, 128.4, 127.7, 126.6, 125.0, 123.3, 121.2, 121.2, 118.5, 113.2, 112.0, 70.6, 69.5, 67.6, 62.6, 59.2, 37.9 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 835.3456.  $\text{C}_{46}\text{H}_{48}\text{N}_6\text{NaO}_8$  requires 835.3431. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**2,2'-(((1,1'-(((1,3-Phenylenebis(methylene))bis(oxy))bis(2,1-phenylene))bis(but-3-ene-1,1-diyl))bis(1H-1,2,3-triazole-4,1-diyl))bis(methylene))bis(oxy))dibenzaldehyde (8h).** Following the general procedure, **8h** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (312 mg, 78%);  $R_f$  (50% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$  2976, 1686, 1462, 1194 and 751  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  10.37 (2 H, s), 7.79 (2 H, dd,  $J_1 = 7.4$  Hz,  $J_2 = 0.9$  Hz), 7.62 (2 H, s), 7.51 (2 H, td,  $J_1 = 7.8$  Hz,  $J_2 = 1.7$  Hz), 7.37-7.26 (8 H, m), 7.10 (2 H, d,  $J = 8.4$  Hz), 7.03-6.96 (6 H, m), 6.16-6.12 (2 H, m), 5.73-5.62 (2 H, m), 5.24 (4 H, s), 5.12-4.97 (8 H, m), 3.26-3.18 (2 H, m), 3.07-3.00 (2 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  189.6, 160.5, 155.6, 142.5, 137.0, 136.0, 133.2, 130.0, 129.1, 128.5, 127.6, 127.1, 126.5, 126.2, 125.0, 123.0, 121.3, 121.2, 118.7, 113.1, 112.2, 70.0, 62.6, 58.9, 38.3 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 823.3250.  $\text{C}_{48}\text{H}_{44}\text{N}_6\text{NaO}_6$  requires 823.3220. Isolated as a mixture of diastereomers ( $dr = 50:50$ ) and NMR values given for both isomers.

**Preparation of the compound 10.**<sup>30</sup> A solution of (*E*)-4-phenyl-1-(3-phenyl-1-(*p*-tolyl)allyl)-1H-1,2,3-triazole (**4o**) in MeI (5 mL) was refluxed for 5 d. After this period, excess of MeI was removed under vacuum and the resulting crude reaction mixture was washed with Hexanes and ether which gave the compound **10**.

**1-(1,3-Diphenylpropyl)-4-phenyl-1H-1,2,3-triazole (11).** To the solution of (*E*)-1-(1,3-diphenylallyl)-4-phenyl-1H-1,2,3-triazole (**4c**, 1 mmol) in THF (2 mL) was added Pd/C (10 mol%). The reaction mixture was stirred at room temperature for 24 h, under  $\text{H}_2$  atm (1 atm). After completion of the reaction, the reaction mixture was filtered by using a layer of celite pad and the filtrate was evaporated under vacuum and the resulting crude reaction mixture was purified by silica gel column chromatography (EtOAc : Hexanes = 30 : 70) which gave the compound **11** as a colorless solid (311 mg, 91%);  $R_f$  (30% EtOAc/Hexanes) 0.42; mp 110-112 °C; IR (thin film)  $\nu_{\text{max}}$  3062, 3028, 1603, 1454 and 767  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.84 (2 H, d,  $J = 7.1$  Hz), 7.71 (1 H, s), 7.45-7.22 (11 H, m), 7.19 (2 H, d,  $J = 7.1$  Hz), 5.61 (1 H, dd,  $J_1 = 9.2$  Hz,  $J_2 = 6.2$  Hz), 2.95-2.88 (1 H, m), 2.70-2.66 (3 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  147.8, 140.3, 138.8, 130.6, 129.1, 128.8, 128.7, 128.7, 128.5, 128.2, 127.0, 126.4, 125.7, 118.8, 64.4, 36.6, 32.3 ppm; HRMS (ESI):  $\text{MH}^+$ , found 340.1806.  $\text{C}_{23}\text{H}_{22}\text{N}_3$  requires 340.1814.

**Preparation of the compound 12.** A solution of (1-(1,3-diphenylpropyl)-4-phenyl-1H-1,2,3-triazole (**11**, 0.25 mmol) in MeI (5 mL) was refluxed for 4 d. After this period, excess of MeI

was removed under vacuum and the resulting crude reaction mixture was washed with Hexanes and ether which gave the compound **12** as a semi solid (110 mg, 92%);  $R_f$  (30% EtOAc/Hexanes) 0.42; IR (thin film)  $\nu_{max}$  2928, 1603, 1494, 1454, 1384 and 770  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_H$  9.45 (1 H, s), 7.72 (2 H, d,  $J = 8.0$  Hz), 7.61 (2 H, d,  $J = 8.0$  Hz), 7.53-7.45 (3 H, m), 7.42-7.37 (3 H, m), 7.18 (4 H, d,  $J = 4.3$  Hz), 7.13-7.08 (1 H, m), 6.54 (1 H, t,  $J = 7.6$  Hz), 4.20 (3 H, s), 3.12-3.03 (1 H, m), 2.81-2.69 (3 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_C$  142.8, 139.7, 135.5, 132.0, 130.0, 129.7, 129.5, 129.5, 128.9, 128.6, 128.4, 128.2, 126.3, 121.5, 68.9, 39.7, 35.6, 32.3 ppm; HRMS (ESI):  $\text{M-IH}^+$ , found 355.1996.  $\text{C}_{24}\text{H}_{25}\text{N}_3$  requires 355.2048.

**Preparation of the compound 13.** To a solution of (*E*)-(3-azidoprop-1-ene-1,3-diyl)dibenzene (**2**, 1 mmol) in THF (2 mL) was added Pd/C (10 mol%). The reaction mixture was stirred at room temperature for 24 h under  $\text{H}_2$  atm (1 atm). After completion of the reaction, the reaction mixture was filtered by using a layer of celite pad and the filtrate was evaporated under vacuum and the resulting crude reaction mixture was transferred into a separating funnel with DCM and extracted twice with 1 N HCl (4 mL). The acidic aqueous layer was washed 2 times with EtOAc (5 mL). The aqueous phase was then made basic (pH: 10-11) with 2 N NaOH and extracted with DCM (5 mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the organic phase was concentrated to afford the compound **13** as colorless liquid (105 mg, 50%); IR (Thin film)  $\nu_{max}$  3026, 1602, 1453 and 1029  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_H$  7.39-7.18 (10 H, m), 3.93 (1 H, t,  $J = 6.8$  Hz), 2.70-2.55 (2 H, m), 2.07-2.01 (2 H, m), 1.73 (2 H, s) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_C$  146.2, 141.9, 128.6, 128.4, 127.1, 126.4, 125.8, 55.8, 41.0, 32.8 ppm; HRMS (ESI):  $\text{MH}^+$ , found 212.1441.  $\text{C}_{15}\text{H}_{18}\text{N}$  requires 212.1439.

**Procedure for the synthesis of bis-alcohol 14.**  $\text{NaBH}_4$  (4 mmol) was added to a mixture of bis-aldehyde **8** (1 mmol) in THF (3 mL) and ethanol (7 mL) at room temperature. The resulting mixture was stirred at room temperature for 1 h. After this period, the reaction mixture was poured on to cold water (5 mL). Then, extracted by using ethyl acetate (3 X 10 mL) and the combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the organic phase was concentrated and the resulting crude reaction mixture was purified by silica gel column chromatography (EtOAc : Hexanes) to give the desired compound **14**.

**Compound 14a:** Following the general procedure, **14a** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 60:40) as a colorless liquid (741 mg, 96%);  $R_f$  (60% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{max}$  3402, 2936, 1601, 1455 and 754  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_H$  7.65 (2 H, s), 7.31-7.20 (8 H, m), 6.99-6.89 (6 H, m), 6.84 (2 H, d,  $J = 8.2$  Hz), 6.05-6.01 (2 H, m), 5.69-5.62 (2 H, m), 5.10-4.96 (8 H, m), 4.62 (4 H, s), 4.15-4.03 (4 H, m), 3.85-3.80 (4 H, m), 3.23-3.19 (2 H, m), 3.05-3.02 (2 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_C$  156.1, 155.9, 155.8, 143.2, 143.2, 133.3, 133.3, 130.0, 129.9, 129.0, 129.0, 128.8, 127.8, 127.8, 126.4, 126.4, 122.7, 122.6, 121.3, 121.3, 118.5, 112.0, 69.8, 67.7, 62.3, 61.3, 59.1, 37.9, 37.8 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 795.3467.  $\text{C}_{44}\text{H}_{48}\text{N}_6\text{NaO}_7$  requires 795.3482. The OH protons could not be detected.

**Compound 14b:** Following the general procedure, **14b** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 50:50) as a colorless liquid (709 mg, 95%);  $R_f$  (60% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{max}$  3412, 2876, 1589, 1602, 1454 and 754  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_H$  7.75 (2 H, s), 7.32-7.19 (8 H, m), 6.98-6.91 (6 H, m), 6.83 (2 H, d,  $J = 8.2$  Hz), 6.05 (2 H, t,  $J = 7.7$  Hz), 5.71-5.64 (2 H, m), 5.16 (4 H, s), 5.10-4.97 (4 H, m), 4.63 (4 H, s), 4.08-3.98 (4 H, m), 3.75 (4

H, t,  $J = 4.8$  Hz), 3.69 (4 H, br. s), 3.25-3.19 (2 H, m), 3.08-3.03 (2 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_C$  156.1, 155.8, 143.1, 133.4, 130.0, 129.9, 128.9, 128.7, 127.9, 126.5, 122.9, 121.3, 121.2, 118.5, 112.0, 112.0, 70.6, 69.5, 67.5, 62.4, 61.1, 59.2, 37.9 ppm; HRMS (ESI):  $\text{MNa}^+$ , found 839.3761.  $\text{C}_{46}\text{H}_{52}\text{N}_6\text{NaO}_8$  requires 839.3744. The OH protons could not be detected.

**Compound 14c:** Following the general procedure, **14c** was obtained after purification by silica gel column chromatography (EtOAc:Hexanes = 60:40) as a colorless liquid (739 mg, 92%);  $R_f$  (60% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{max}$  3345, 1601, 1492, 1243 and 755  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_H$  7.52 (2 H, s), 7.41 (2 H, t,  $J = 8.2$  Hz), 7.30 (8 H, m), 7.22 (2 H, t,  $J = 8.0$  Hz), 7.01-6.92 (8 H, m), 6.13-6.09 (2 H, m), 5.72-5.62 (2 H, m), 5.15-4.98 (12 H, m), 4.62 (4 H, s), 3.25-3.18 (2 H, m), 3.07-3.00 (2 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_C$  156.1, 155.6, 143.2, 137.0, 133.2, 130.0, 129.9, 129.1, 128.9, 128.8, 127.6, 127.1, 127.1, 126.6, 126.6, 126.3, 126.3, 122.6, 122.6, 121.4, 118.6, 112.2, 112.0, 70.0, 62.4, 61.4, 58.9, 58.9, 38.2 ppm; HRMS (ESI):  $\text{MH}^+$ , found 805.3755.  $\text{C}_{48}\text{H}_{49}\text{N}_6\text{O}_6$  requires 805.3714. The OH protons could not be detected.

**Procedure for the syntheses of compounds 15.** To a mixture of the diol compound **14** (0.5 mmol) in dry THF (3 mL) was added NaH (4 mmol, 55-60 % suspension in mineral oil) at rt. The mixture was stirred at room temperature for 10 min and then, propargyl bromide (5 mmol, 80 wt% in toluene) was added. The resulting mixture was stirred for 20 h at rt. After this period, few drops of EtOH was added and stirred for 10 min and then, the resulting mixture was poured on to water (20 mL) and was extracted by using ethyl acetate (3 X 10 mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the organic phase was concentrated, and the resulting crude reaction mixture was purified by silica gel column chromatography (EtOAc/Hexanes) to give the desired product **15**.

**Compound 15a:** Following the general procedure, **15a** was obtained after purification by silica gel column chromatography as colorless liquid (254 mg, 60%);  $R_f$  (40% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{max}$  3288, 2976, 1602, 1455 and 755  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_H$  7.68 (2 H, s), 7.36 (2 H, dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.4$  Hz), 7.29-7.24 (6 H, m), 6.99-6.95 (6 H, m), 6.86 (2 H, d,  $J = 8.6$  Hz), 6.11-6.06 (2 H, m), 5.71-5.64 (2 H, m), 5.18 (4 H, s), 5.07 (2 H, d,  $J = 17.1$  Hz), 4.99 (2 H, d,  $J = 10.1$  Hz), 4.61 (4 H, s), 4.16-4.08 (8 H, m), 3.88-3.84 (4 H, m), 3.22-3.17 (2 H, m), 3.07-2.99 (2 H, m), 2.37 (2 H, m) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_C$  156.1, 155.7, 143.6, 133.4, 129.9, 129.8, 129.2, 127.6, 126.7, 126.1, 122.6, 122.6, 121.2, 121.1, 118.4, 112.1, 112.0, 80.0, 74.5, 69.8, 67.8, 66.7, 62.6, 58.9, 57.4, 38.1 ppm; HRMS (ESI):  $\text{MH}^+$ , found 849.3996.  $\text{C}_{50}\text{H}_{53}\text{N}_6\text{O}_7$  requires 849.3976.

**Compound 15b:** Following the general procedure, **15b** was obtained after purification by silica gel column chromatography as colorless liquid (379 mg, 85%);  $R_f$  (40% EtOAc/Hexanes) 0.42; IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu_{max}$  2875, 1602, 1493, 1454, 1247 and 755  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_H$  7.73 (2 H, s), 7.37 (2 H, dd,  $J_1 = 7.4$  Hz,  $J_2 = 1.5$  Hz), 7.29-7.24 (6 H, m), 7.00-6.94 (6 H, m), 6.85 (2 H, d,  $J = 8.2$  Hz), 6.11-6.07 (2 H, m), 5.73-5.67 (2 H, m), 5.21 (4 H, s), 5.11-5.98 (4 H, m), 4.61 (4 H, s), 4.14-4.03 (8 H, m), 3.79 (4 H, t,  $J = 4.8$  Hz), 3.71 (4 H, s), 3.24-3.19 (2 H, m), 3.07-2.99 (2 H, m), 2.38 (2 H, t,  $J = 2.4$  Hz) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_C$  156.1, 155.7, 143.5, 133.5, 129.8, 129.7, 129.2, 127.6, 126.9, 126.1, 122.9, 121.2, 121.1, 118.4, 112.1, 112.0, 80.0, 74.5, 70.7, 69.6, 67.6, 66.7, 62.6, 59.0, 57.4, 38.1 ppm; HRMS (ESI):  $\text{MH}^+$ , found 893.4271.  $\text{C}_{52}\text{H}_{57}\text{N}_6\text{O}_8$  requires 893.4238.

**Compound 15c:** Following the general procedure, **15c** was obtained after purification by silica gel column chromatography as colorless liquid (352 mg, 80%);  $R_f$  (40% EtOAc/Hexanes)

0.42; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2973, 1603, 1461, 1249 and 669 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.58 (2 H, s), 7.43-7.23 (12 H, m), 7.01-6.95 (8 H, m), 6.14 (2 H, t, *J* = 7.1 Hz), 5.74-5.64 (2 H, m), 5.20 (4 H, m), 5.13-4.99 (8 H, m), 4.60 (4 H, s), 4.12-4.10 (4 H, m), 3.26-3.18 (2 H, m), 3.07-3.00 (2 H, m), 2.31 (2 H, t, *J* = 2.3) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  156.1, 155.5, 143.6, 137.0, 133.3, 129.9, 129.8, 129.2, 129.1, 127.5, 127.1, 126.8, 126.2, 126.1, 122.6, 121.3, 121.1, 118.6, 112.2, 112.1, 80.0, 74.5, 70.0, 66.7, 62.7, 58.8, 57.4, 38.4 ppm; HRMS (ESI): MNa<sup>+</sup>, found 903.3871. C<sub>54</sub>H<sub>52</sub>N<sub>6</sub>NaO<sub>6</sub> requires 903.3846.

**Procedure<sup>29b</sup> for the synthesis of macrocyclic bis-triazole polyether 16.** A mixture of **15** (0.5 mmol), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (100 mol%) and DMSO (2 mL) was taken in a 10 ml round bottom flask. The reaction mixture was stirred at 110 °C under open air atmosphere for 12 h. After this period, the resulting mixture was cooled to rt and diluted with water (4 mL). The mixture was filtered through a filtration funnel and then washed with ethyl acetate (4 times, using 5 mL of EtOAc) and extracted using EtOAc (3 X 5 mL) and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (EtOAc/Hexanes) which gave the macrocyclic bis-triazole polyether **16**.

**Compound 16a:** Following the general procedure, **16a** was obtained after purification by silica gel column chromatography as colorless liquid (194 mg, 46%); R<sub>f</sub> (40% EtOAc/Hexanes) 0.42; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2973, 1601, 1459, 1368 and 754 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.79 (2 H, s), 7.38 (2 H, dt, *J*<sub>1</sub> = 7.7 Hz, *J*<sub>2</sub> = 1.9 Hz), 7.33 (2 H, dd, *J*<sub>1</sub> = 7.3 Hz, *J*<sub>2</sub> = 1.6 Hz), 7.29-7.22 (4 H, m), 7.00-6.95 (6 H, m), 6.82-6.79 (2 H, m), 6.04-5.99 (2 H, m), 5.70-5.63 (2 H, m), 5.22-5.15 (4 H, m), 5.07 (2 H, m), 5.00-4.96 (2 H, m), 4.60 (4 H, s), 4.23 (4 H, s), 4.16-4.06 (4 H, m), 3.88-3.81 (4 H, m), 3.31-3.28 (2 H, m), 3.10-3.05 (2 H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  156.0, 155.9, 143.4, 133.4, 130.0, 129.2, 129.2, 128.2, 128.2, 126.5, 125.8, 123.1, 123.0, 121.2, 121.0, 118.4, 112.0, 111.9, 76.0, 70.3, 69.7, 69.7, 67.6, 67.6, 67.1, 62.7, 62.6, 59.3, 58.1, 37.7 ppm; HRMS (ESI): MH<sup>+</sup>, found 847.3850. C<sub>50</sub>H<sub>51</sub>N<sub>6</sub>O<sub>7</sub> requires 847.3819.

**Compound 16b:** Following the general procedure, **16b** was obtained after purification by silica gel column chromatography as colorless liquid (259 mg, 57%); R<sub>f</sub> (40% EtOAc/Hexanes) 0.42; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2926, 1603, 1493, 1454, 1247 and 754 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.88 (2 H, s), 7.38-7.24 (8 H, m), 7.03-6.95 (6 H, m), 6.81 (2 H, d, *J* = 8.2 Hz), 6.05-6.01 (2 H, m), 5.74-5.64 (2 H, m), 5.22 (4 H, t, *J* = 3.6 Hz), 5.11-5.07 (2 H, m), 5.00-4.98 (2 H, m), 4.61 (4 H, s), 4.24 (4 H, s), 4.05-4.00 (4 H, m), 3.75-3.71 (8 H, m), 3.35-3.27 (2 H, m), 3.12-3.05 (2 H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  156.0, 155.8, 143.3, 133.5, 129.8, 129.2, 129.2, 128.1, 128.1, 126.8, 126.8, 125.9, 123.5, 121.2, 121.0, 118.4, 111.9, 111.9, 75.9, 70.6, 70.3, 69.5, 67.5, 67.5, 67.1, 62.6, 59.3, 59.3, 58.1, 37.7 ppm; HRMS (ESI): MH<sup>+</sup>, found 891.4110. C<sub>52</sub>H<sub>55</sub>N<sub>6</sub>O<sub>8</sub> requires 891.4081. This compound contains traces of residual DMSO signal.

**Compound 16c:** Following the general procedure, **16c** was obtained after purification by silica gel column chromatography as colorless liquid (184 mg, 42%); R<sub>f</sub> (40% EtOAc/Hexanes) 0.42; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2975, 1602, 1493, 1244 and 930 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.55 (2 H, s), 7.41-7.26 (12 H, m), 7.02-6.92 (8 H, m), 6.07-6.02 (2 H, m), 5.73-5.65 (2 H, m), 5.23-4.98 (12 H, m), 4.53 (4 H, s), 4.09-4.06 (4 H, m), 3.32-3.25 (2 H, m), 3.09-3.03 (2 H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  156.1, 156.0, 155.7, 155.7, 143.4, 143.4, 137.0, 133.4, 133.4, 129.9, 129.5, 129.3, 129.1, 127.9, 127.4, 127.3, 126.6, 126.6, 125.8, 125.8, 123.1, 123.1, 121.3, 121.1, 118.6, 112.1, 112.1, 111.9, 111.9, 75.8, 75.8, 70.3, 70.1, 70.0, 67.0, 62.7, 62.6, 59.0, 58.9,

57.9, 38.0, 38.0 ppm; HRMS (ESI): MH<sup>+</sup>, found 879.3891. C<sub>54</sub>H<sub>51</sub>N<sub>6</sub>O<sub>6</sub> requires 879.3870.

**Procedure<sup>29b</sup> for the synthesis of macrocycle 17.** A mixture of **16** (0.1 mmol), Na<sub>2</sub>S<sub>x</sub>·H<sub>2</sub>O (70 mg), CuI (10 mol%), 1,10-phen (15 mol%) in DMF (0.5 mL) was stirred at 90 °C for 12 h under open air atmosphere. After this period, the reaction mixture was cooled to room temperature. Then, the resulting mixture was diluted with water (4 mL). The mixture was filtered through a filtration funnel and then washed with ethyl acetate (4 times, using 5 mL of EtOAc) and extracted using ethyl acetate (3 X 5 mL) and the combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography (EtOAc/Hexanes) which gave the desired macrocyclic polyether **17**.

**Compound 17a:** Following the general procedure, **17a** was obtained after purification by silica gel column chromatography as yellow color liquid (39 mg, 45%); R<sub>f</sub> (40% EtOAc/Hexanes) 0.42; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2975, 1721, 1602, 1457 and 755 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.69 (2 H, s), 7.40-7.33 (4 H, m), 7.26-7.20 (4 H, m), 7.00-6.94 (6 H, m), 6.76-6.74 (4 H, m), 5.99-5.93 (2 H, m), 5.69-5.60 (2 H, m), 5.18 (4 H, br. s), 5.08-4.94 (4 H, m), 4.60 (4 H, d, *J* = 4.8 Hz), 4.56 (4 H, d, *J* = 4.7 Hz), 4.06-3.93 (4 H, m), 3.74-3.65 (4 H, m), 3.29-3.23 (2 H, m), 3.08-3.01 (2 H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  156.1, 155.8, 155.8, 143.4, 141.7, 133.5, 129.9, 129.6, 129.0, 128.2, 128.1, 126.5, 126.4, 125.9, 123.0, 121.2, 121.0, 118.4, 111.9, 69.6, 69.5, 67.5, 67.5, 67.0, 67.0, 66.9, 66.9, 62.6, 62.6, 59.5, 59.3, 37.7, 37.7 ppm; HRMS (ESI): MNa<sup>+</sup>, found 903.3545. C<sub>50</sub>H<sub>52</sub>N<sub>6</sub>NaO<sub>7</sub>S requires 903.3516.

**Compound 17b:** Following the general procedure, **17b** was obtained after purification by silica gel column chromatography as yellow color liquid (66 mg, 72%); R<sub>f</sub> (40% EtOAc/Hexanes) 0.42; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2926, 1600, 1493, 1454, 1247 and 754 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.77 (2 H, s), 7.39 (2 H, d, *J* = 7.4 Hz), 7.31 (2 H, dt, *J*<sub>1</sub> = 7.7 Hz, *J*<sub>2</sub> = 1.8 Hz), 7.27-7.23 (4 H, m), 7.01-6.94 (6 H, m), 6.79 (2 H, d, *J* = 8.7 Hz), 6.78 (1 H, s), 6.76 (1 H, s), 5.99 (2 H, t, *J* = 8.2 Hz), 5.70-5.62 (2 H, m), 5.20 (4 H, br. s), 5.08-4.96 (4 H, m), 4.62 (4 H, s), 4.58 (4 H, s), 4.02-3.94 (4 H, m), 3.67-3.64 (4 H, m), 3.59 (4 H, s), 3.29-3.24 (2 H, m), 3.08-3.04 (2 H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  156.1, 155.7, 143.4, 141.7, 133.5, 129.8, 129.5, 128.9, 128.1, 128.0, 126.9, 126.8, 126.7, 125.9, 123.4, 123.4, 121.2, 121.2, 121.0, 118.4, 112.0, 111.9, 70.6, 70.5, 69.4, 67.5, 67.5, 67.0, 66.9, 66.9, 62.6, 59.4, 59.3, 37.7 ppm; HRMS (ESI): MH<sup>+</sup>, found 925.3987. C<sub>52</sub>H<sub>57</sub>N<sub>6</sub>O<sub>8</sub>S requires 925.3959.

**Compound 17c:** Following the general procedure, **17c** was obtained after purification by silica gel column chromatography as yellow color liquid (62 mg, 69%); R<sub>f</sub> (40% EtOAc/Hexanes) 0.42; IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{max}$  2971, 1603, 1495, 1243 and 752 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta_H$  7.47 (2 H, s), 7.38-7.32 (4 H, m), 7.28-7.20 (8 H, m), 7.00-6.95 (6 H, m), 6.90 (2 H, d, *J* = 8.3 Hz), 6.65 (1 H, s), 6.60 (1 H, s), 6.63-5.97 (2 H, m), 5.71-5.62 (2 H, m), 5.23-5.15 (4 H, m), 5.09-4.95 (8 H, m), 4.50-4.67 (8 H, m), 3.28-3.21 (2 H, m), 3.07-2.99 (2 H, m) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta_C$  156.0, 155.6, 155.6, 143.5, 143.4, 141.6, 137.0, 133.4, 129.9, 129.9, 129.5, 129.2, 129.1, 129.0, 127.9, 127.8, 127.2, 126.6, 126.6, 126.6, 126.6, 126.4, 126.3, 125.8, 125.8, 123.1, 123.0, 121.3, 121.3, 121.1, 118.5, 112.1, 111.9, 69.9, 69.9, 66.8, 66.8, 66.7, 62.6, 62.6, 59.2, 58.9, 38.1, 38.0 ppm; HRMS (ESI): MH<sup>+</sup>, found 913.3716. C<sub>54</sub>H<sub>53</sub>N<sub>6</sub>O<sub>6</sub>S requires 913.3747.

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24. Magnetic nano Fe<sub>3</sub>O<sub>4</sub> used in this work was purchased from Sigma-Aldrich and the size of the nano particles was verified through HRTEM analysis (see the Supporting Information) before using the nano Fe<sub>3</sub>O<sub>4</sub>. For selected papers dealing on the preparation and characterization of nano Fe<sub>3</sub>O<sub>4</sub>, see: (a) Wu, S.; Sun, A.; Zhai, F.; Wang, J.; Xu, W.; Zhang, Q.; Volinsky, A. A. *Mater. Lett.* **2011**, *65*, 1882. (b) Yang, T.; Shen, C.; Li, Z.; Zhang, H.; Xiao, C.; Chen, S.; Xu, Z.; Shi, D.; Li, J.; Gao, H. *J. Phys. Chem. B* **2005**, *109*, 23233. (c) Sun, J.; Zhou, S.; Hou, P.; Yang, Y.; Weng, J.; Li, X.; Li, M. *J. Biomed. Mater. Res. A* **2007**, *80A*, 333. (d) Yuanbi, Z.; Zumin, Q.; Jiaying, H. *Chin. J. Chem. Eng.* **2008**, *16*, 451.
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26. (a) Wang, D.; Astruc, D. *Chem. Rev.* **2014**, *114*, 6949. (b) Babu, S. G.; Karvembu, R. *Catal. Surv. Asia* **2013**, *17*, 156. (c) Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J.-M. *Chem. Rev.* **2011**, *111*, 3036. (d) Shylesh, S.; Schünemann, V.; Thiel, W. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 3428. (e) Gawande, M. B.; Branco, P. S.; Varma, R. S. *Chem. Soc. Rev.* **2013**, *42*, 3371.
27. For selected papers dealing on the application of click reaction for the preparation of triazole moiety incorporated polyether systems, see: (a) Astruc, D.; Liang, L.; Rapakousiou, A.; Ruiz, J. *Acc. Chem. Res.* **2012**, *45*, 630. (b) Li, N.; Echeverría, M.; Moya, S.; Ruiz, J.; Astruc, D. *Inorg. Chem.* **2014**, *53*, 6954. (c) Jia, M.; Li, A.; Mu, Y.; Jiang, W.; Wan, X. *Polymer* **2014**, *55*, 1160. (d) Soto-Castro, D.; Magaña-Vergara, N. E.; Farfán, N.; Santillan, R. *Tetrahedron Lett.* **2014**, *55*, 1014. (e) Kantheti, S.; Narayan, P. S. S. R.; Raju, K. V. S. N. *React. Funct. Polym.* **2013**, *73*, 1597.
28. For selected papers dealing on the application of click reaction for the preparation of triazole moiety incorporated macrocycles, see: (a) Bédard, A.-C.; Collins, S. K. *Org. Lett.* **2014**, *16*, 5286. (b) Lepage, M. L.; Meli, A.; Bodlenner, A.; Tarnus, C.; Riccardis, F. D.; Izzo, I.; Compain, P. *Beilstein J. Org. Chem.* **2014**, *10*, 1406. (c) Noor, A.; Lo, W. K. C.; Moratti, S. C.; Crowley, J. D. *Chem. Commun.* **2014**, *50*, 7044. (d) Xu, L.; Li, Y.; Li, Y. *Asian J. Org. Chem.* **2014**, *3*, 582. (e) White, N. G.; Beer, P. D. *Beilstein J. Org. Chem.* **2012**, *8*, 246.
29. (a) Naveen; Parella, R.; Babu, S. A. *Tetrahedron Lett.* **2013**, *54*, 2255. (b) Naveen; Babu, S. A.; Kaur, G.; Aslam, N. A.; Karanam, M. *RSC Adv.* **2014**, *4*, 18904 and references cited therein.
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#### Supplementary data

Supplementary data (copy of <sup>1</sup>H, <sup>13</sup>C NMR Charts of all the compounds) associated with this article can be found, in the online version.

## Supporting Information

### Direct Azidation of Allylic/Benzylic Alcohols and Ethers Followed by the Click Reaction: One-Pot Synthesis of 1,2,3-Triazoles and 1,2,3-Triazole Moiety Embedded Macrocycles

Naveen, Srinivasarao Arulananda Babu,\* Nayyar Ahmad Aslam, Akshey Sandhu, Dharmendra Kumar Singh and Ameet Rana

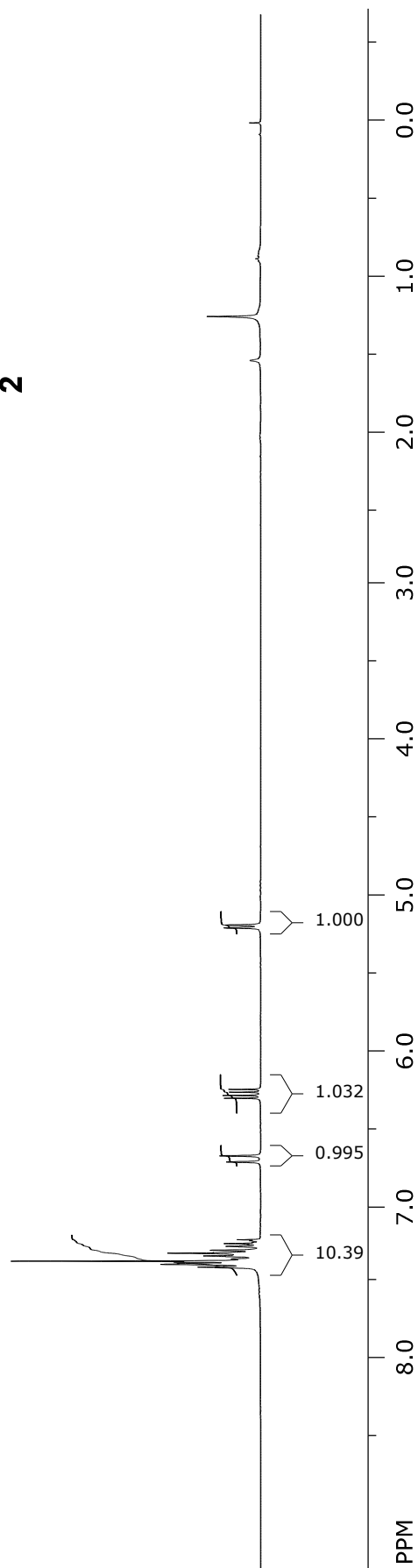
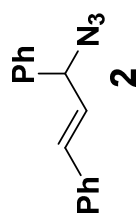
Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Manauli P.O., Sector 81, SAS Nagar, Mohali, Knowledge City, Punjab 140306, India  
E-mail: sababu@iisermohali.ac.in

## Contents

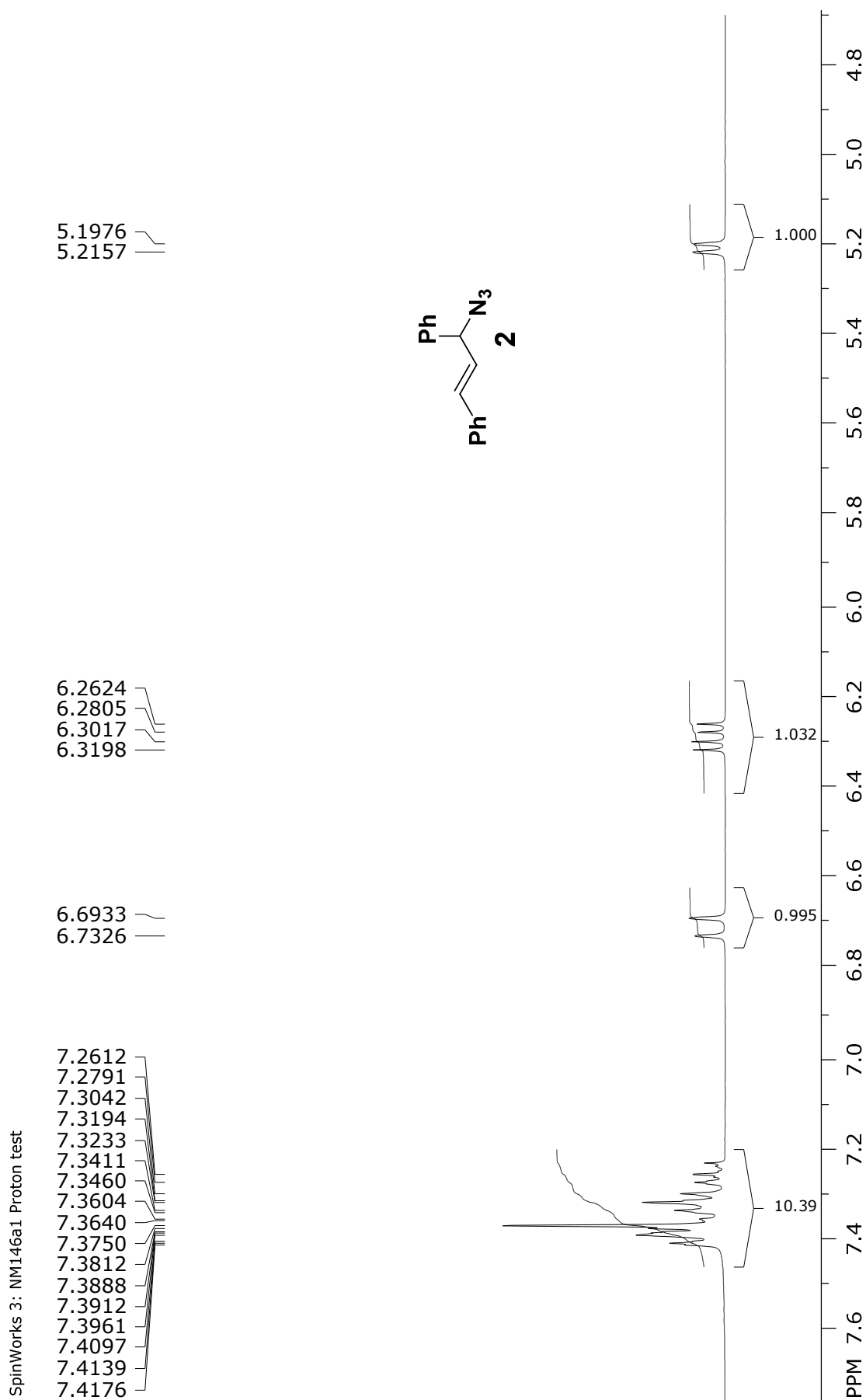
<sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds: Page No. 2-268

SpinWorks 3: NM146a1 Proton test

5.1976  
5.2157  
6.2624  
6.2805  
6.3017  
6.3198  
6.6933  
6.7326  
7.2612  
7.2791  
7.3042  
7.3194  
7.3233  
7.3411  
7.3460  
7.3604  
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7.3961  
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7.4176



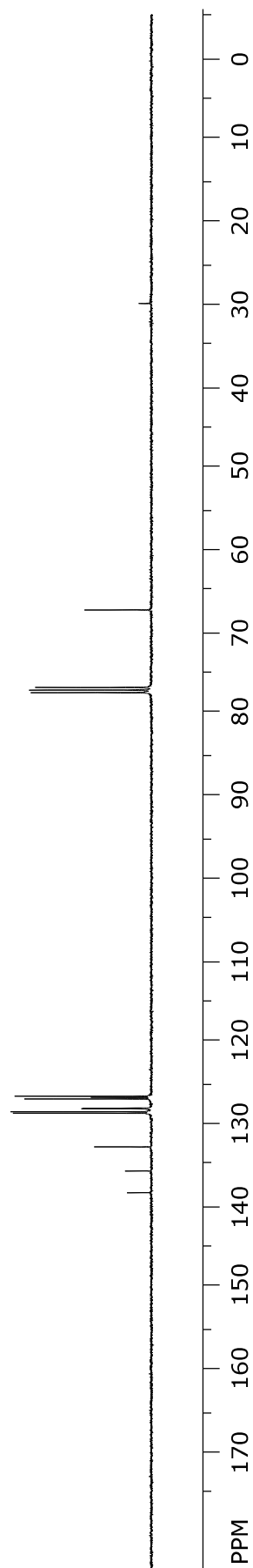
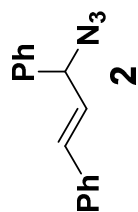


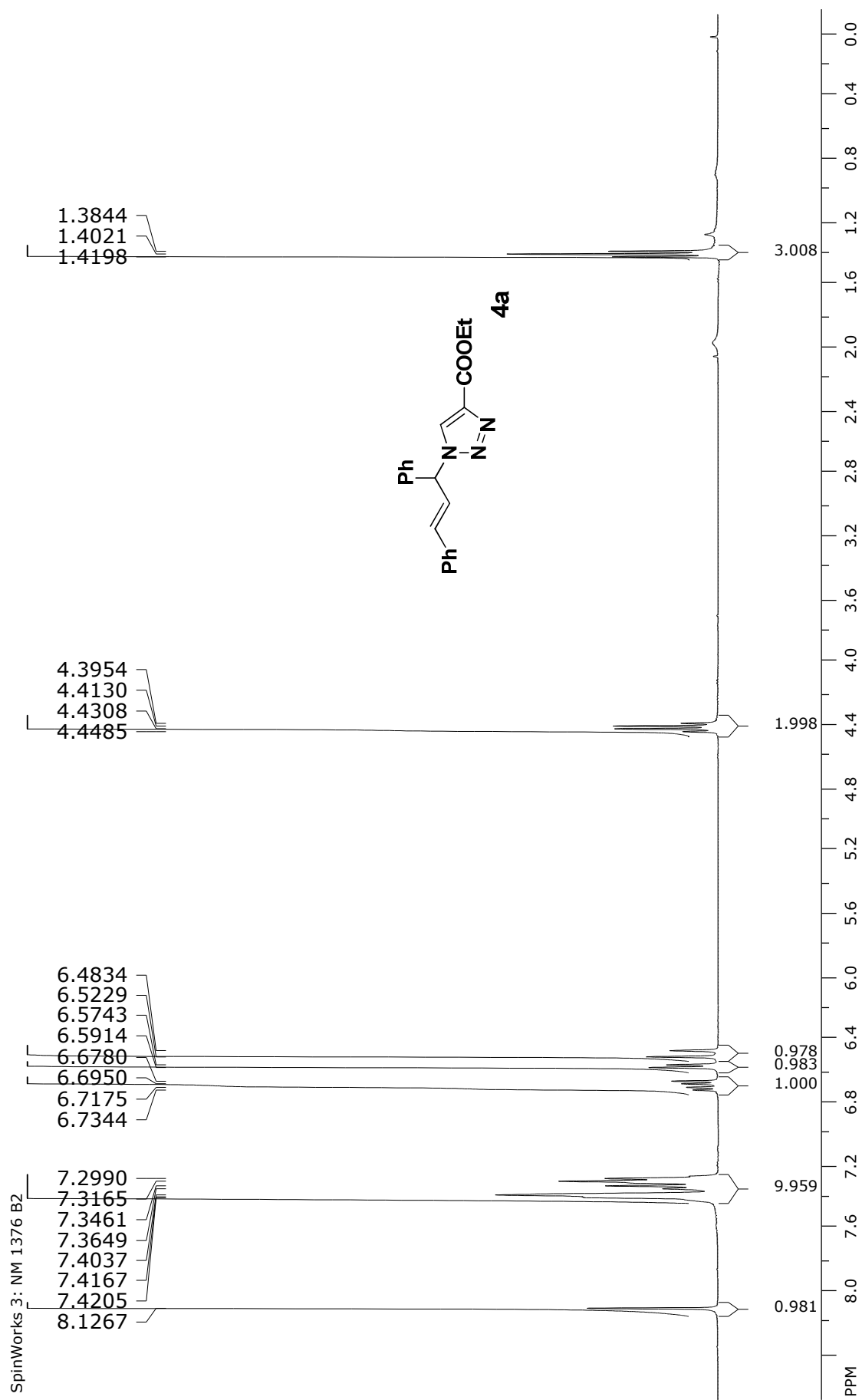


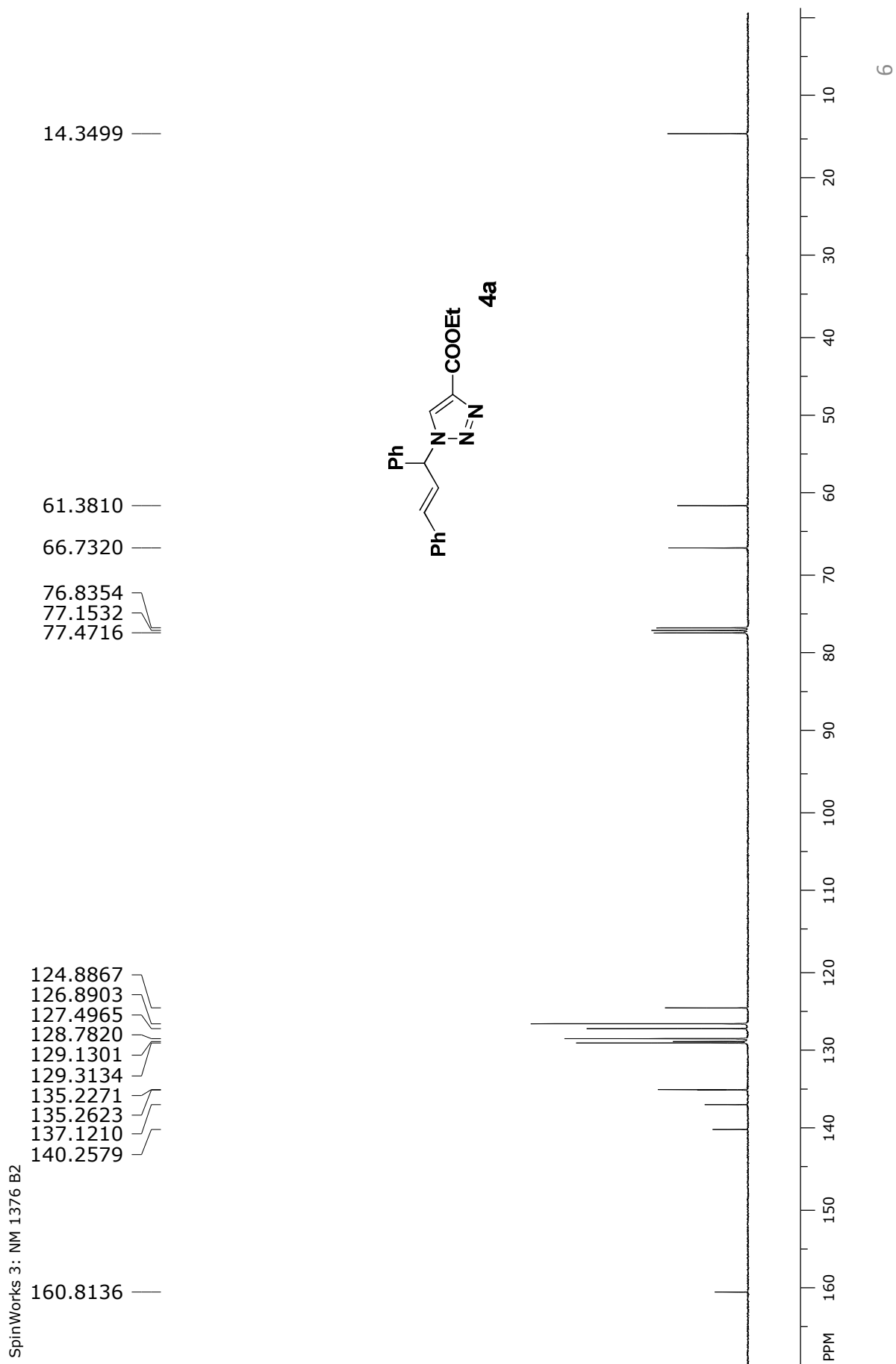
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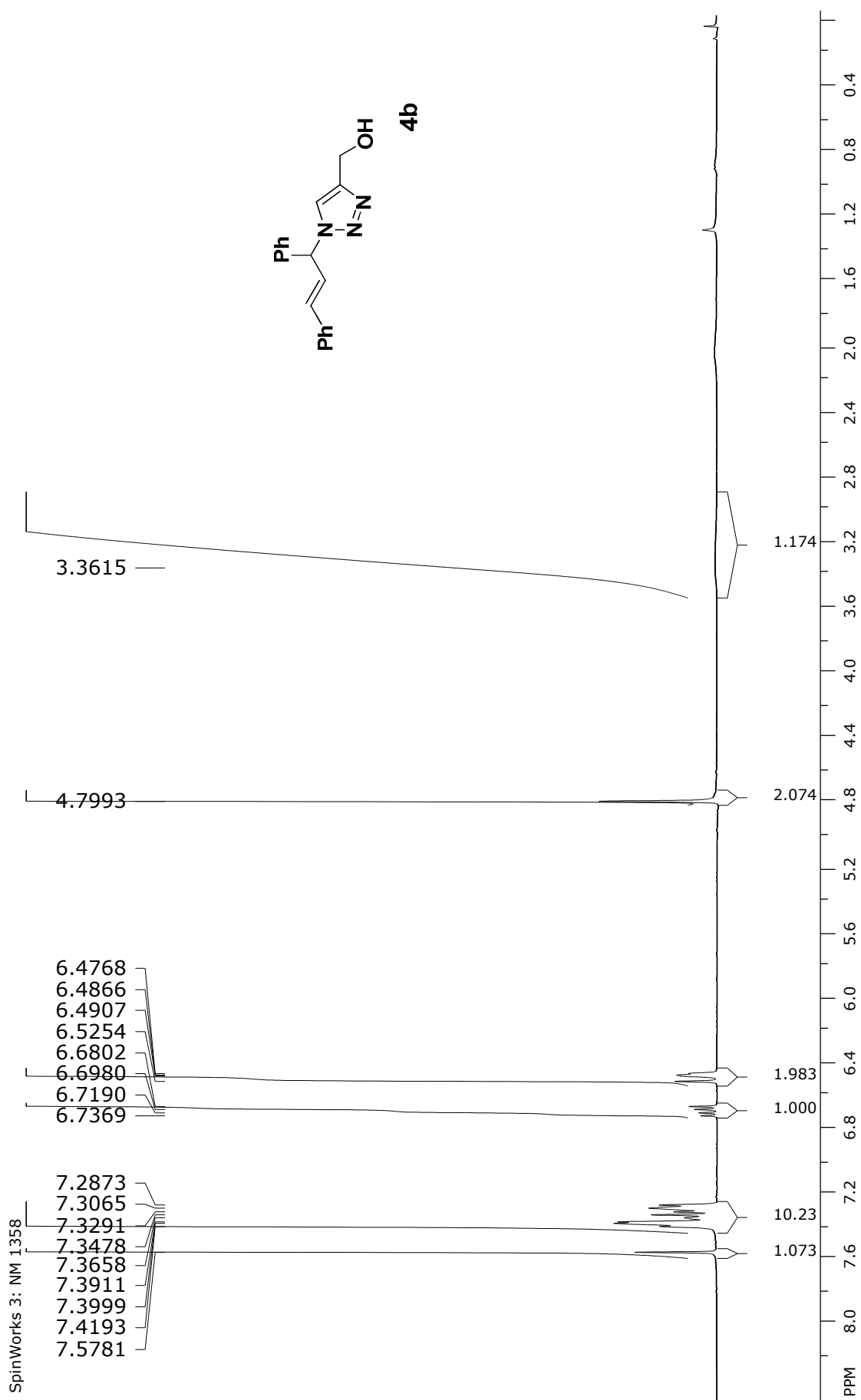
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138.6027

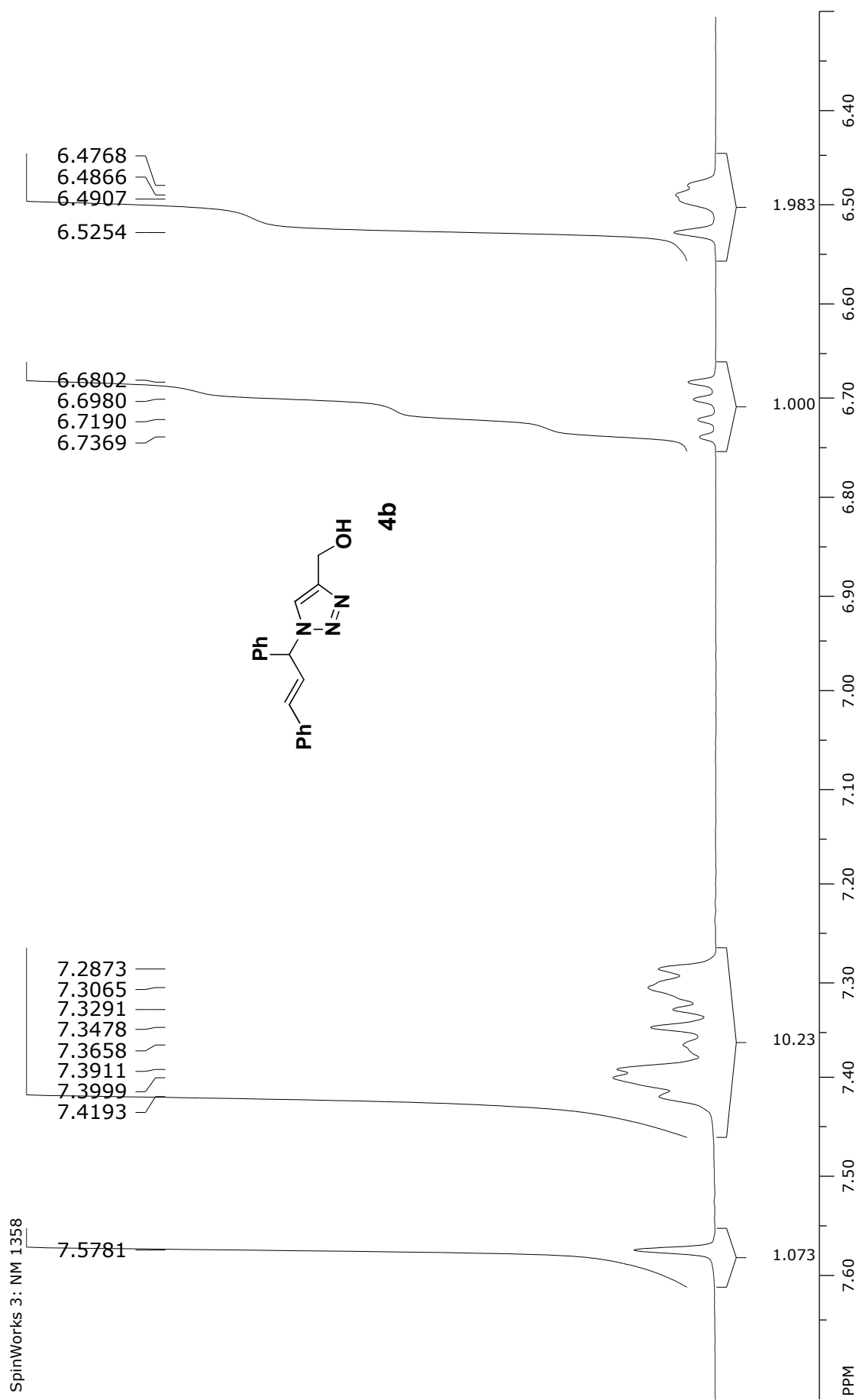
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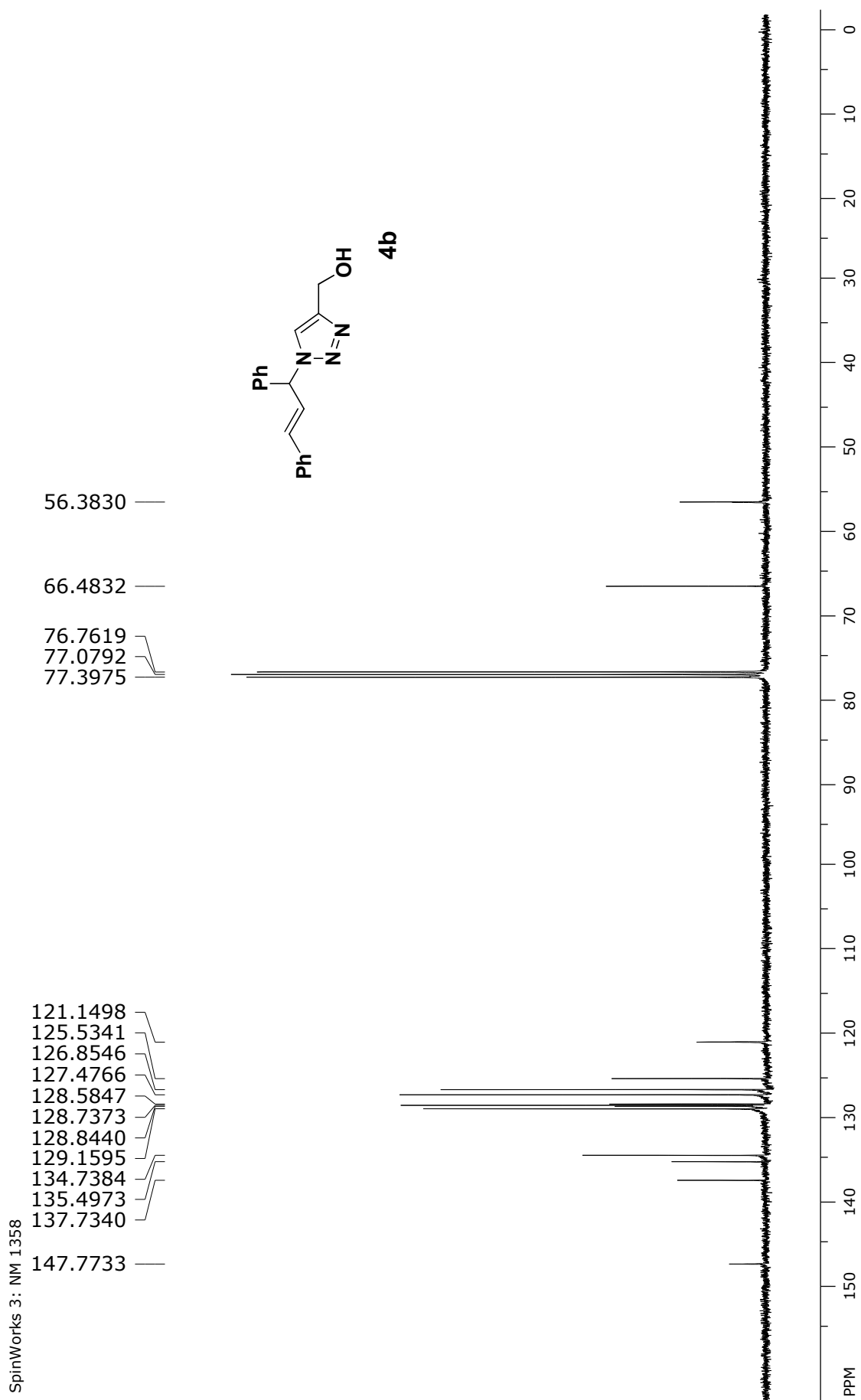


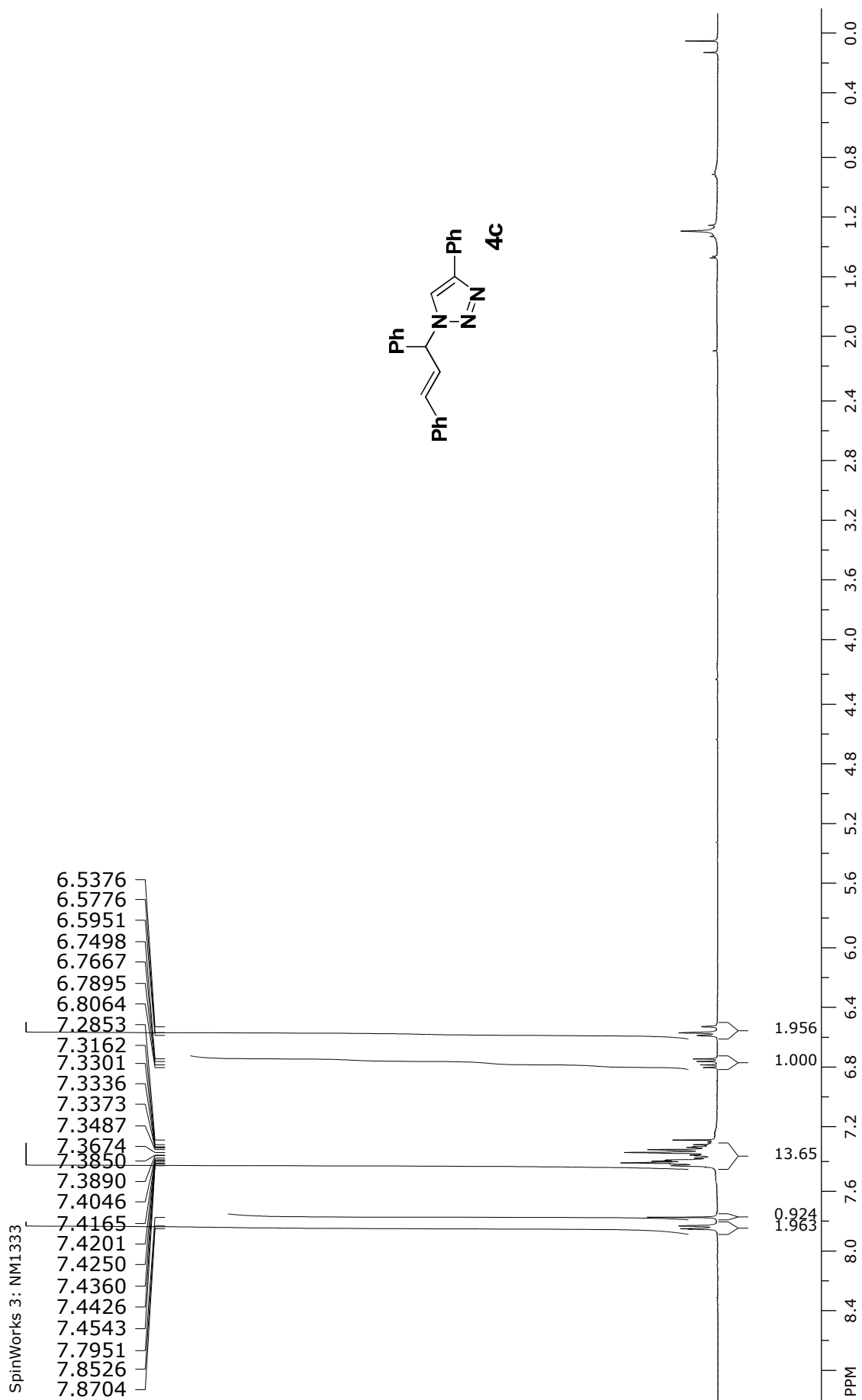




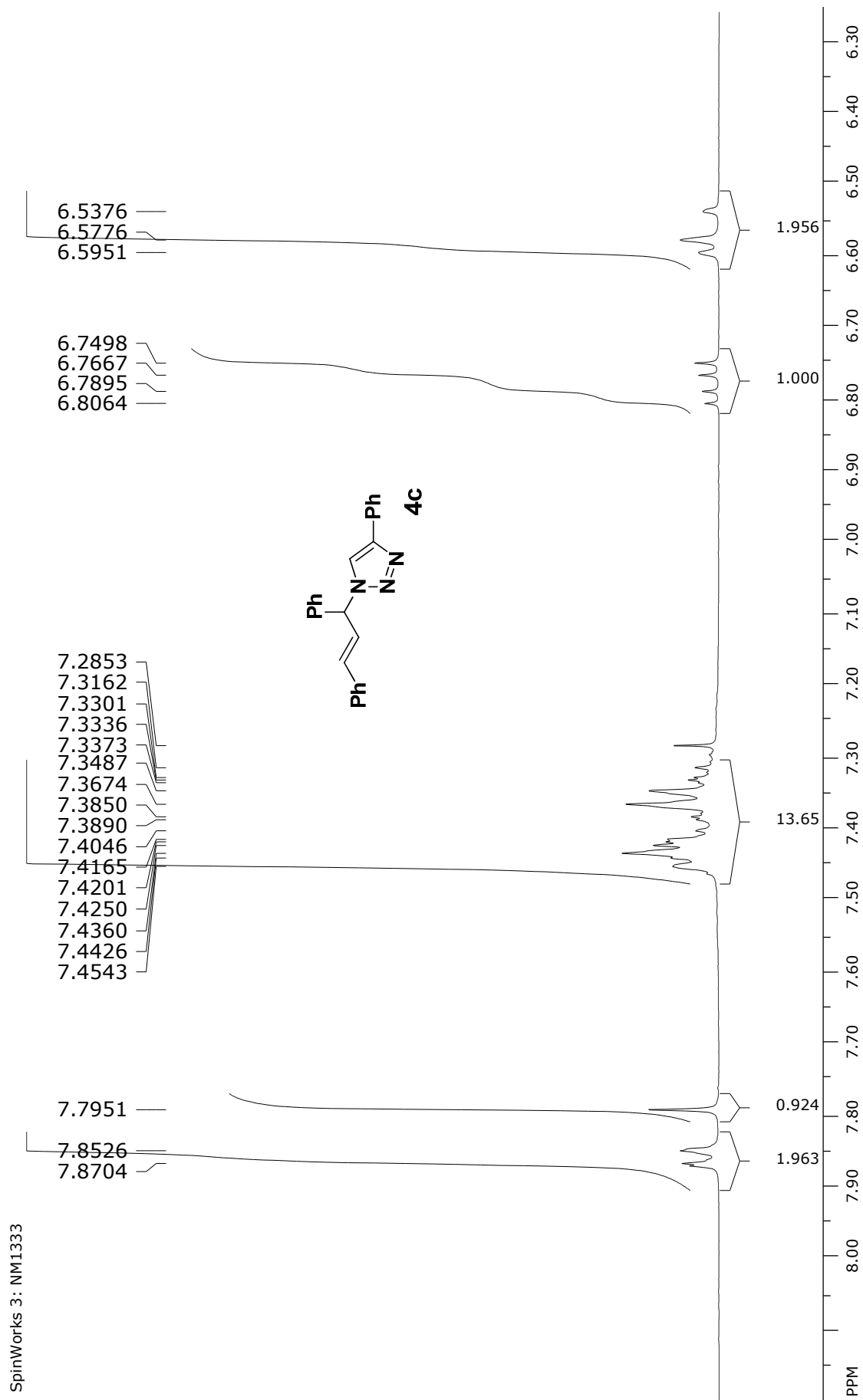


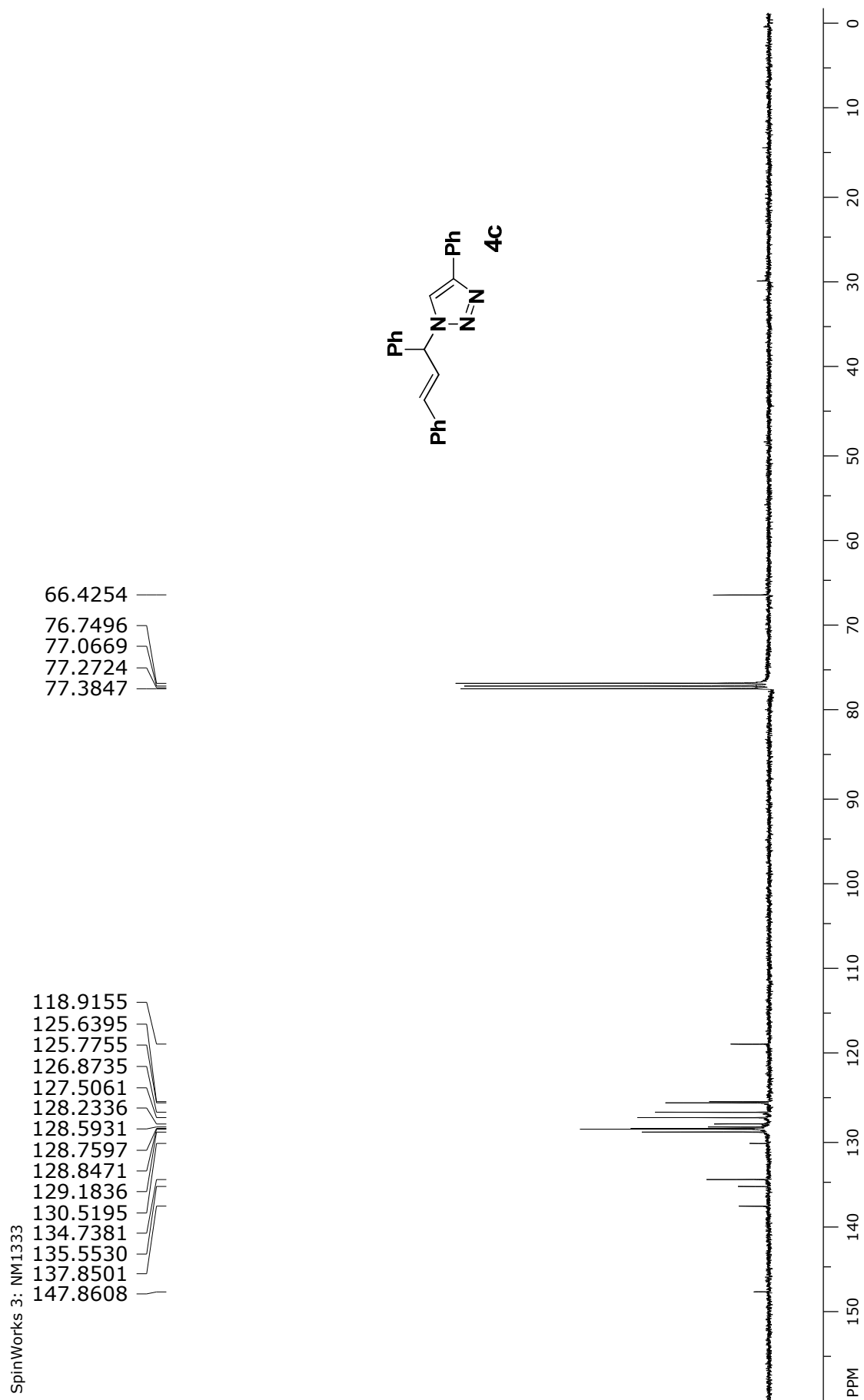


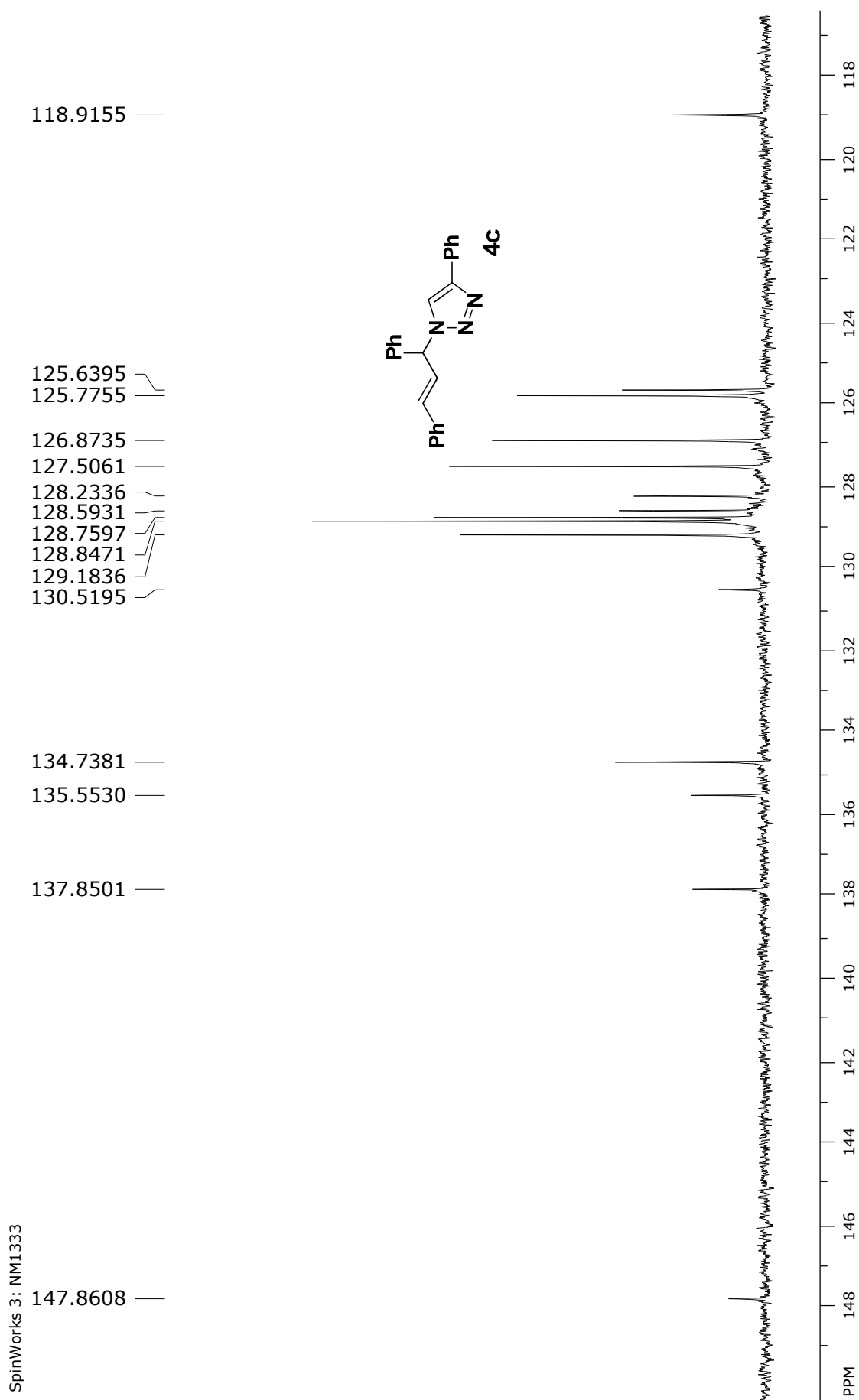


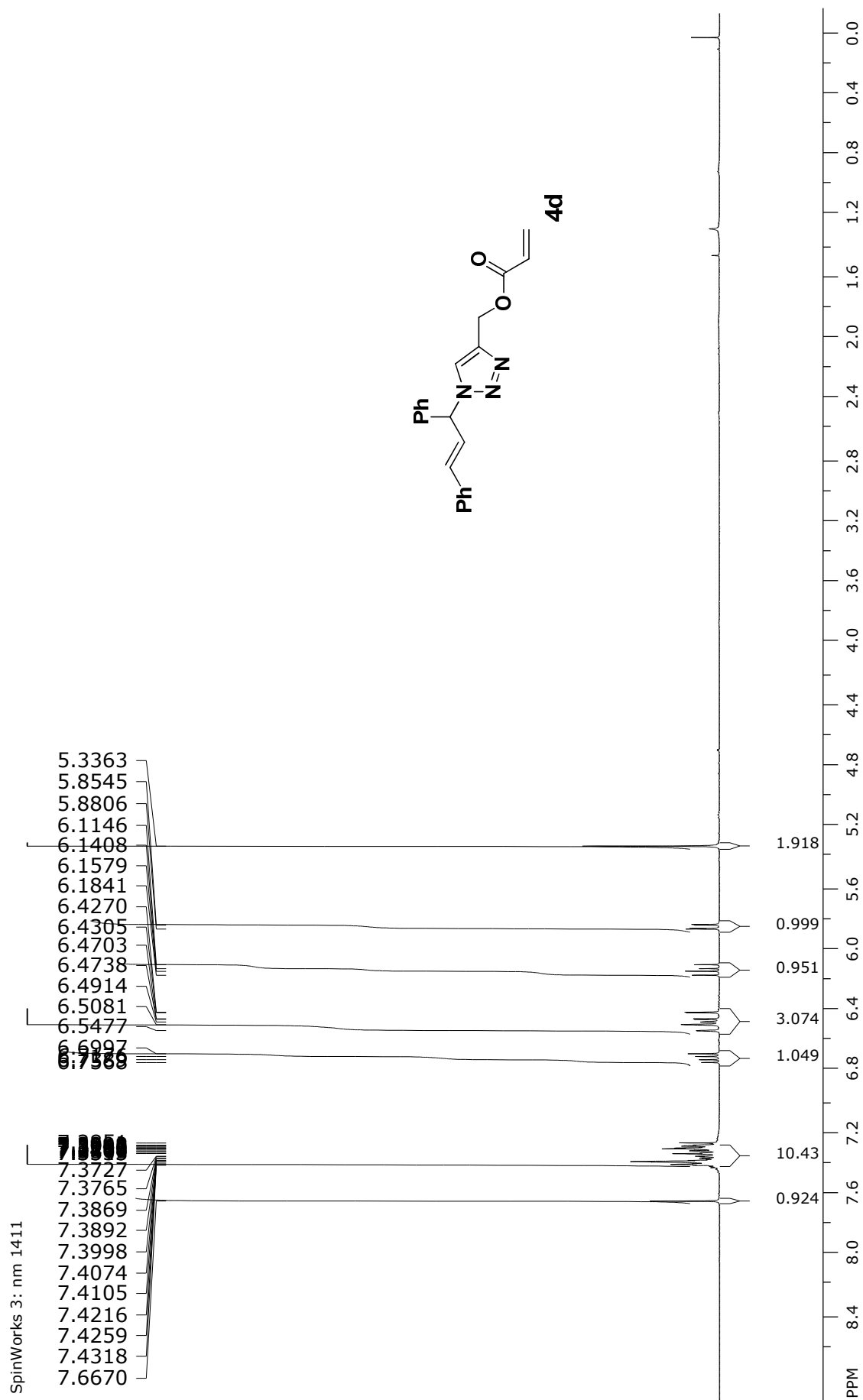


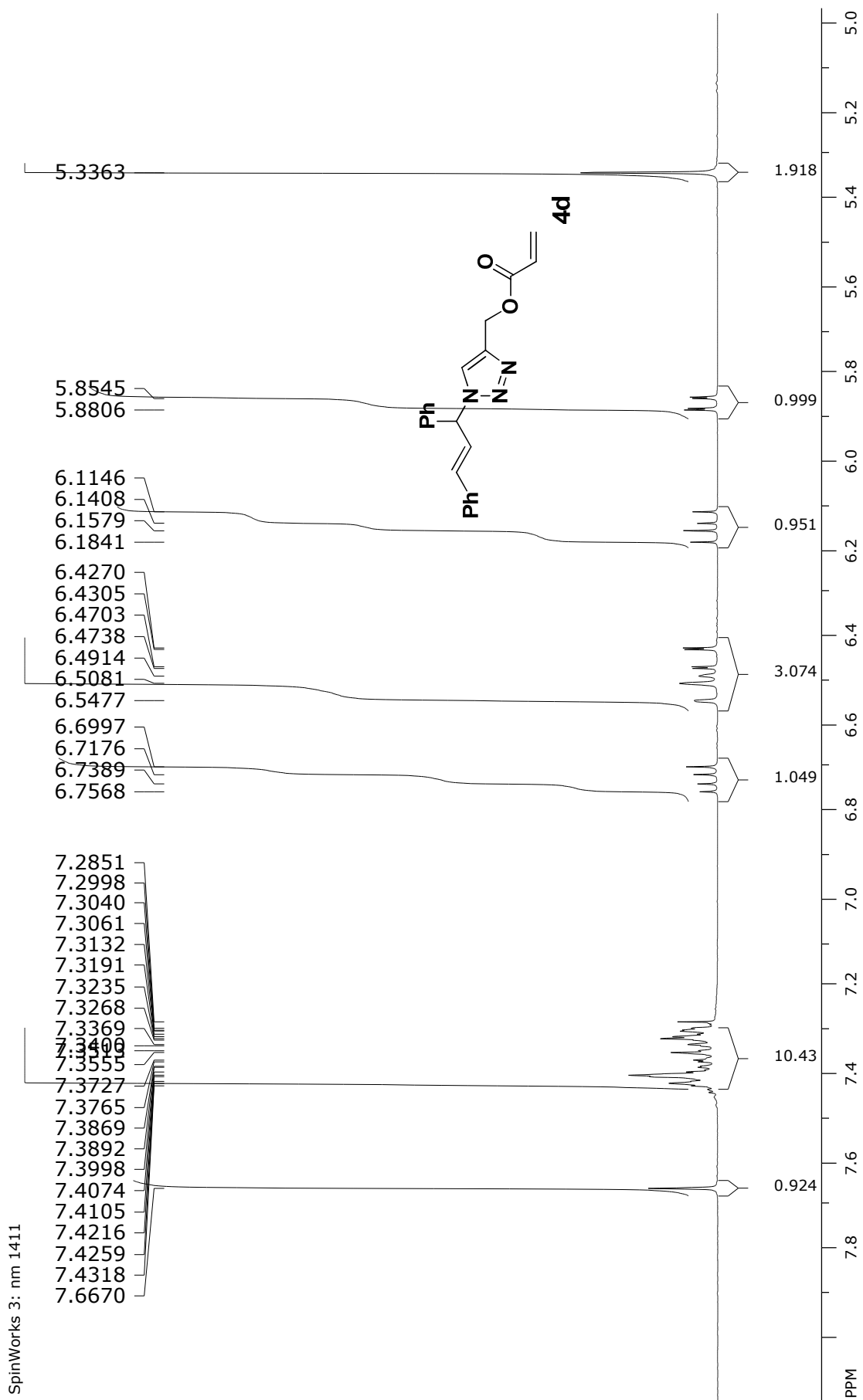


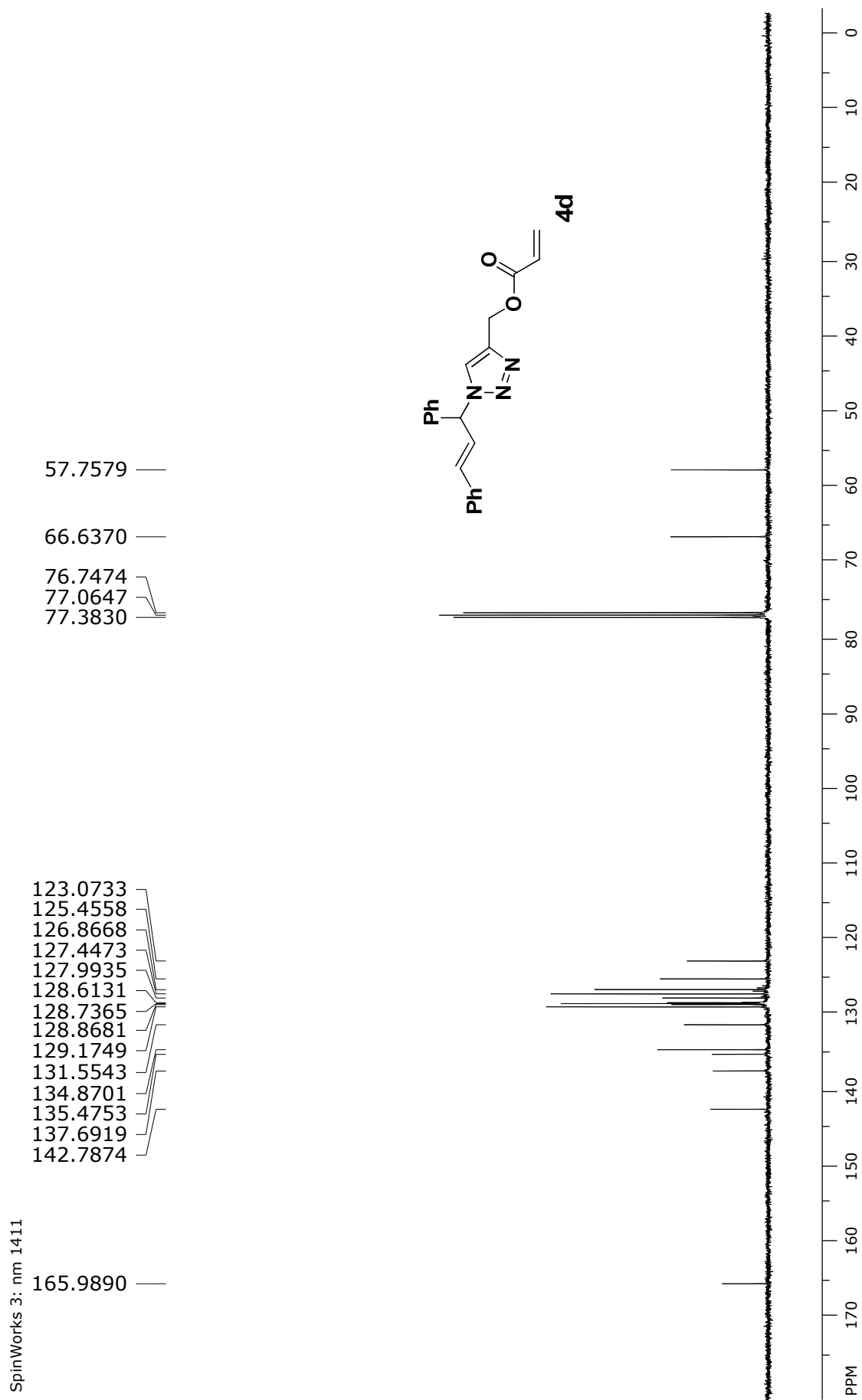


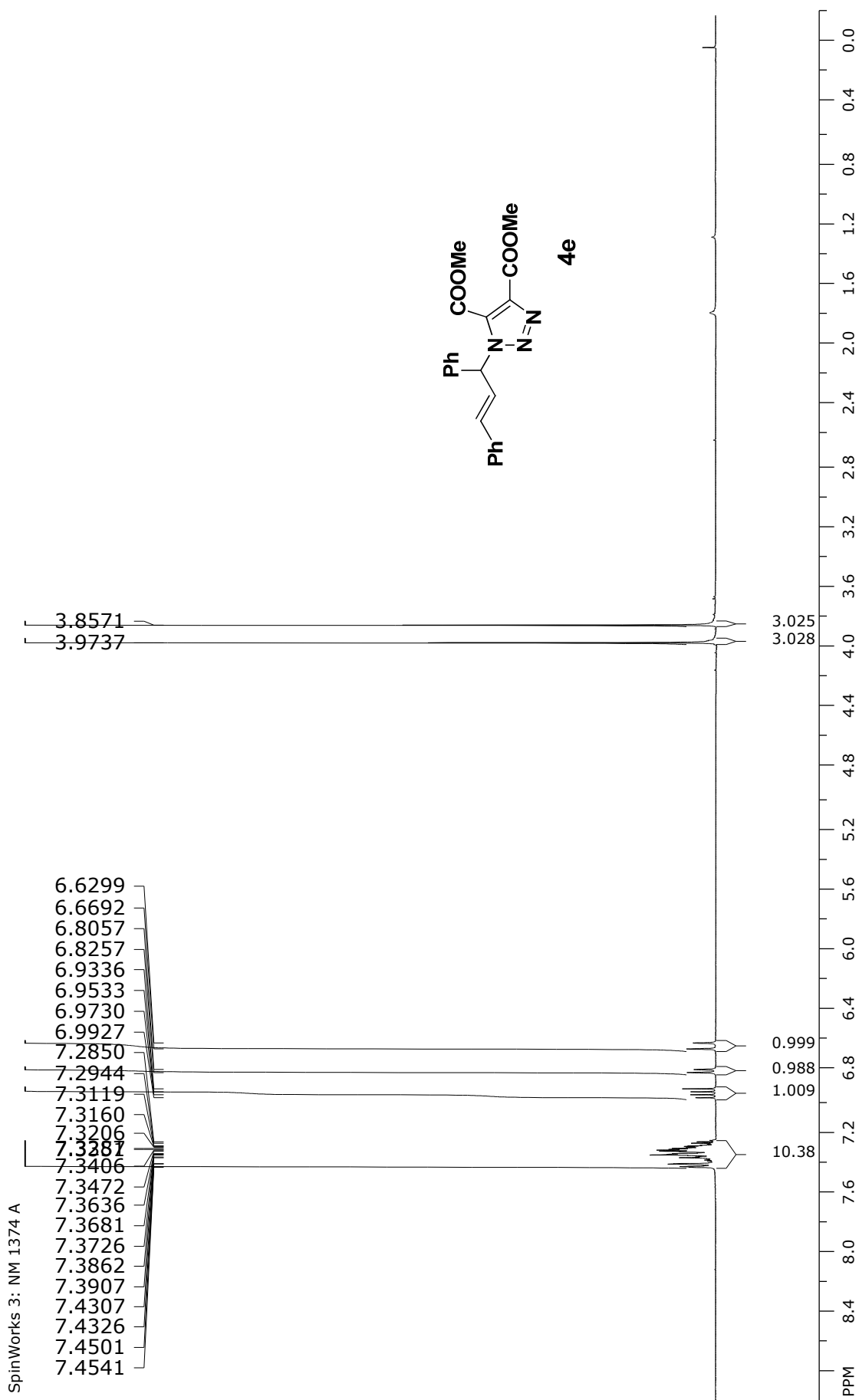


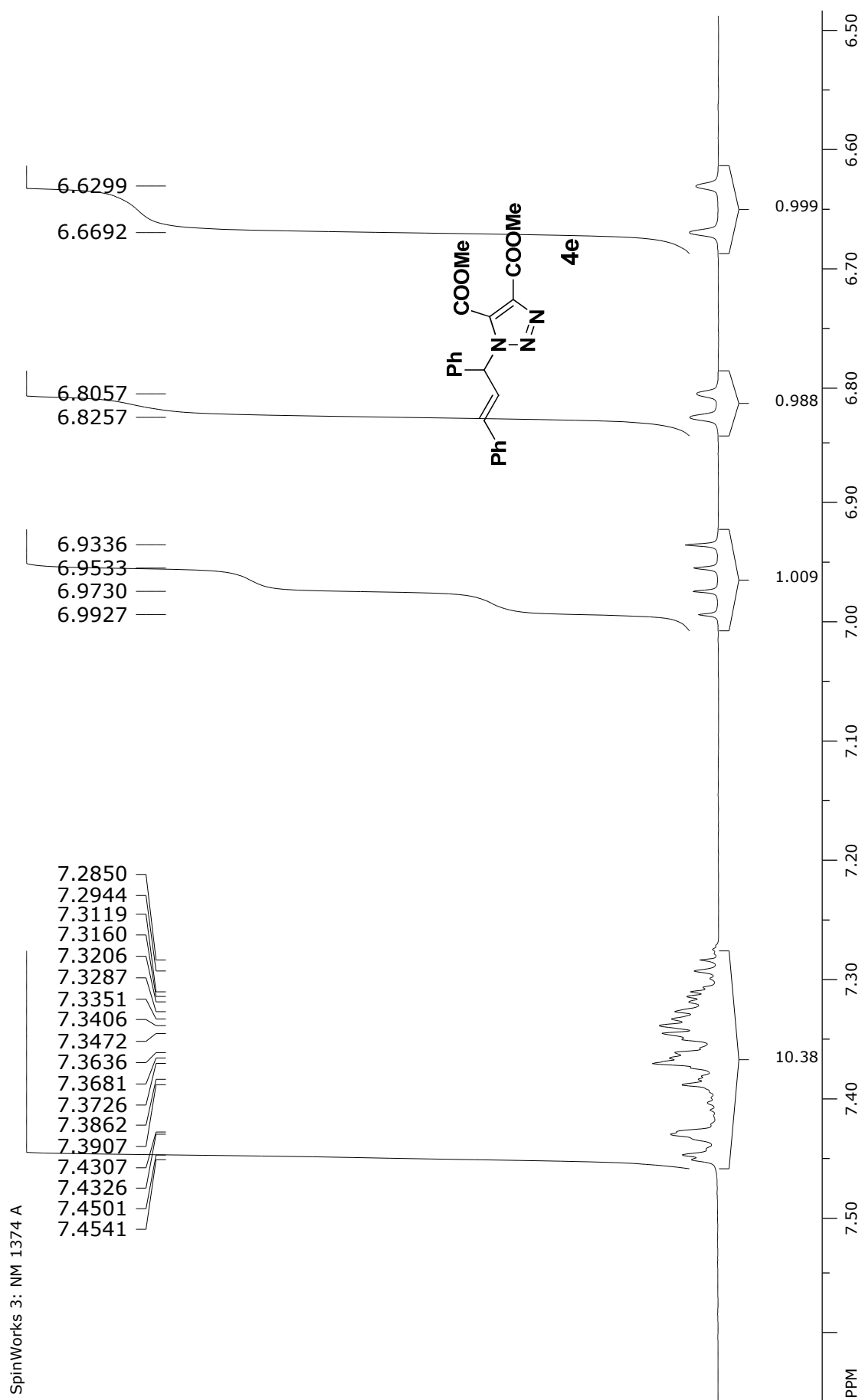




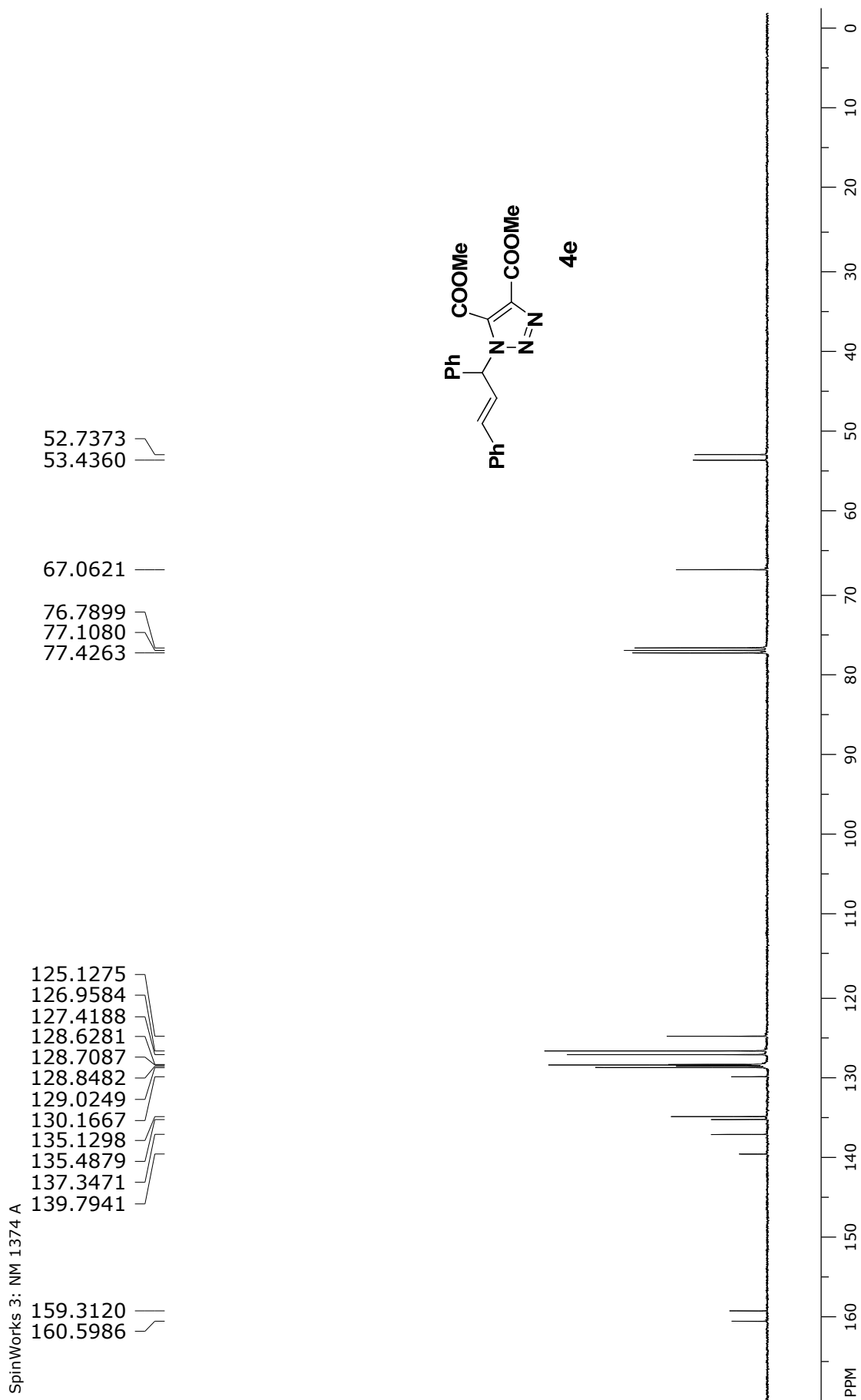


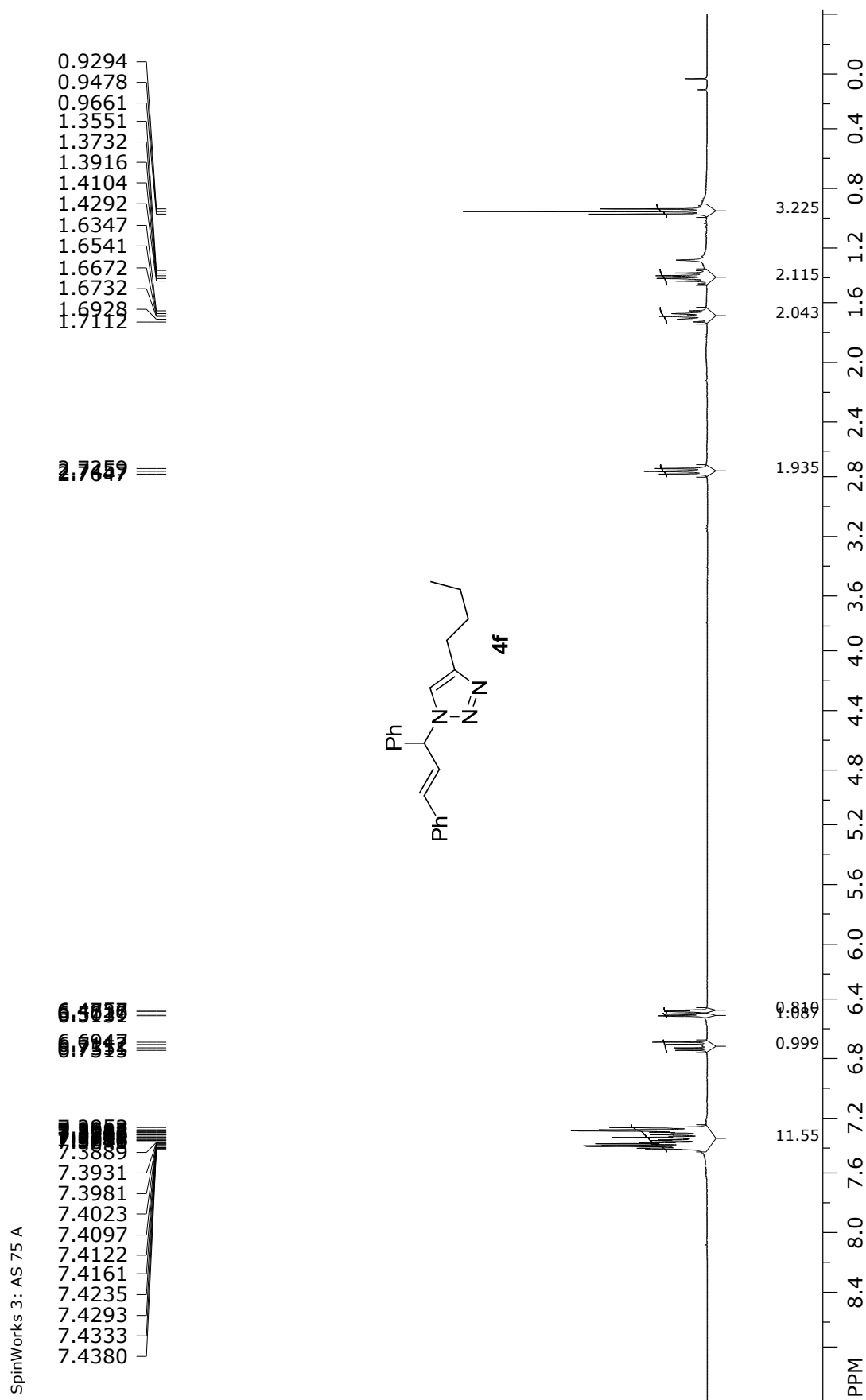












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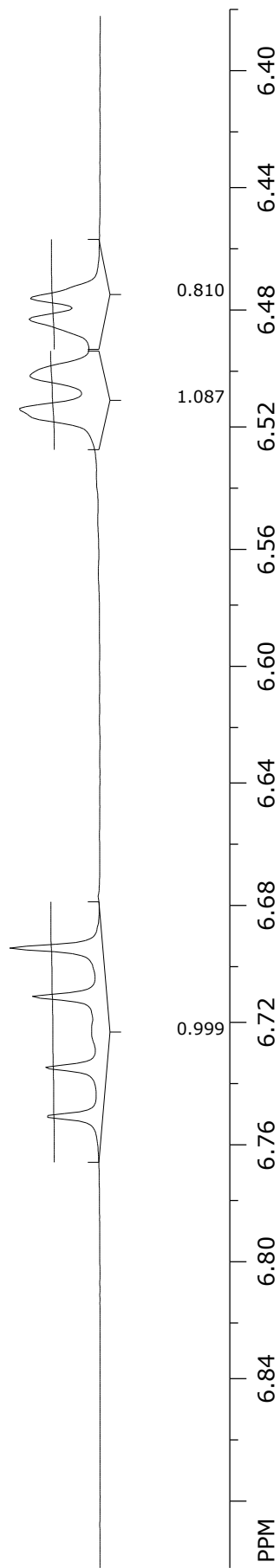
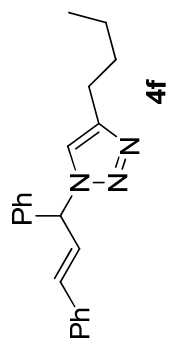
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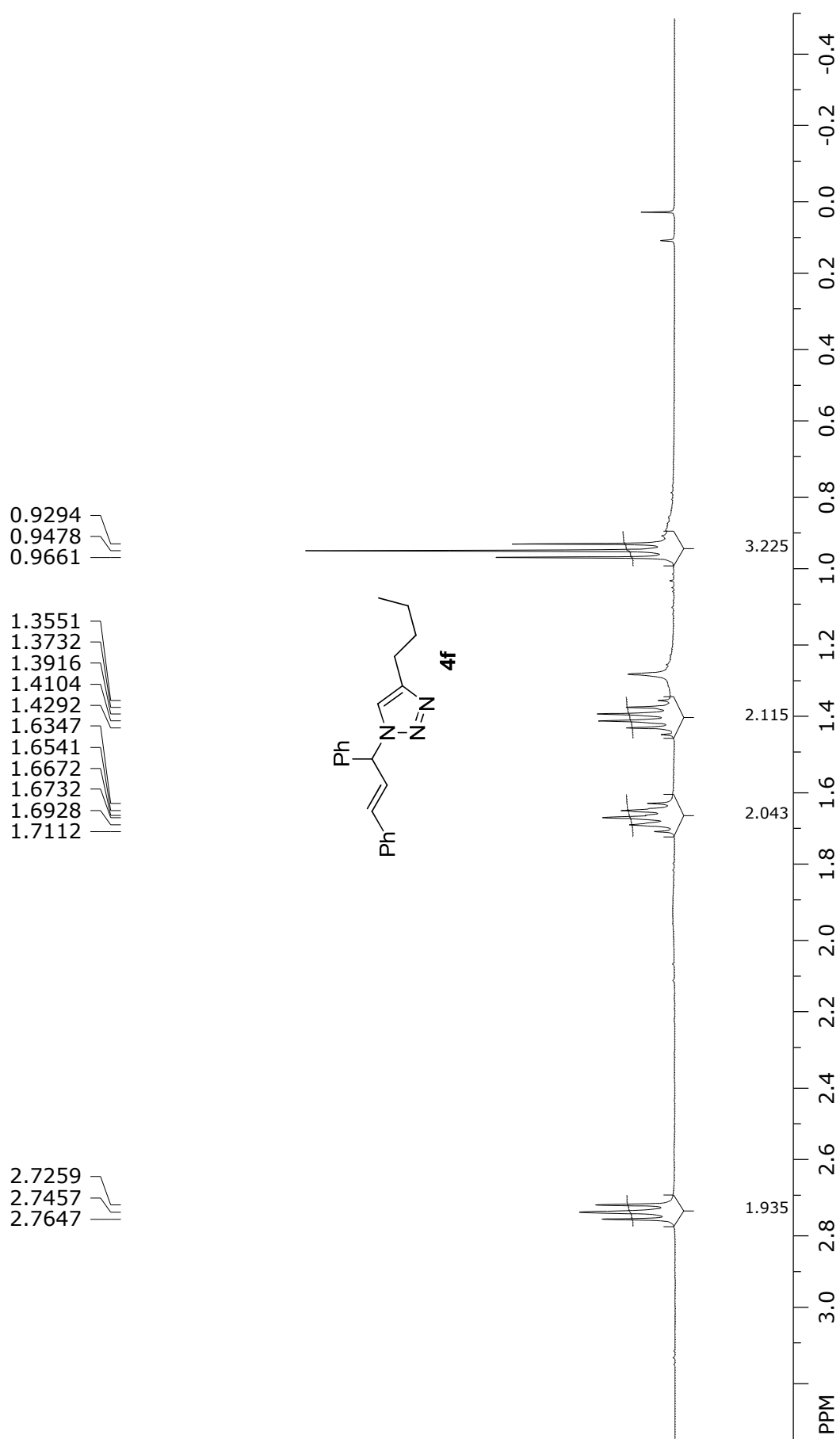
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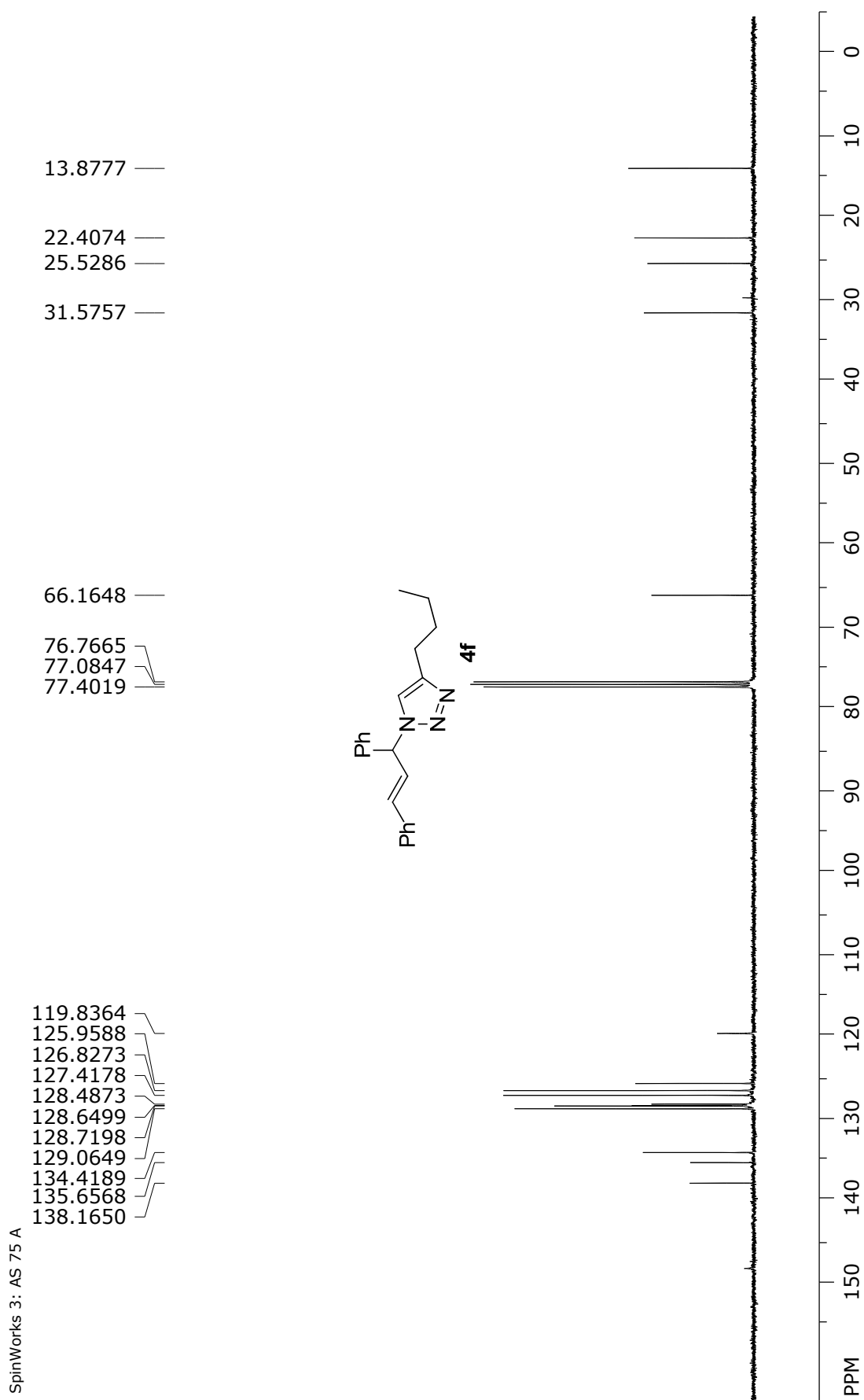
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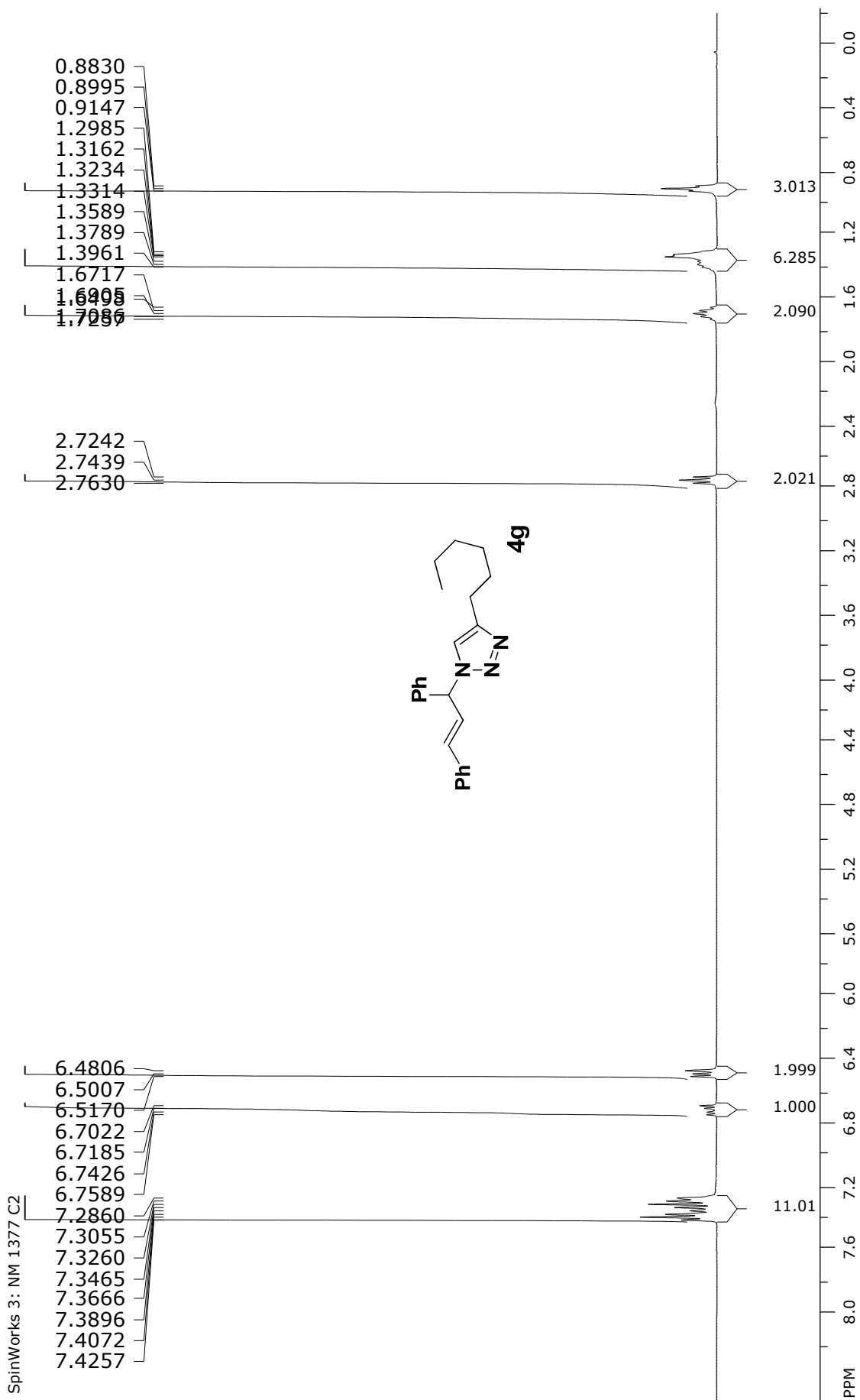
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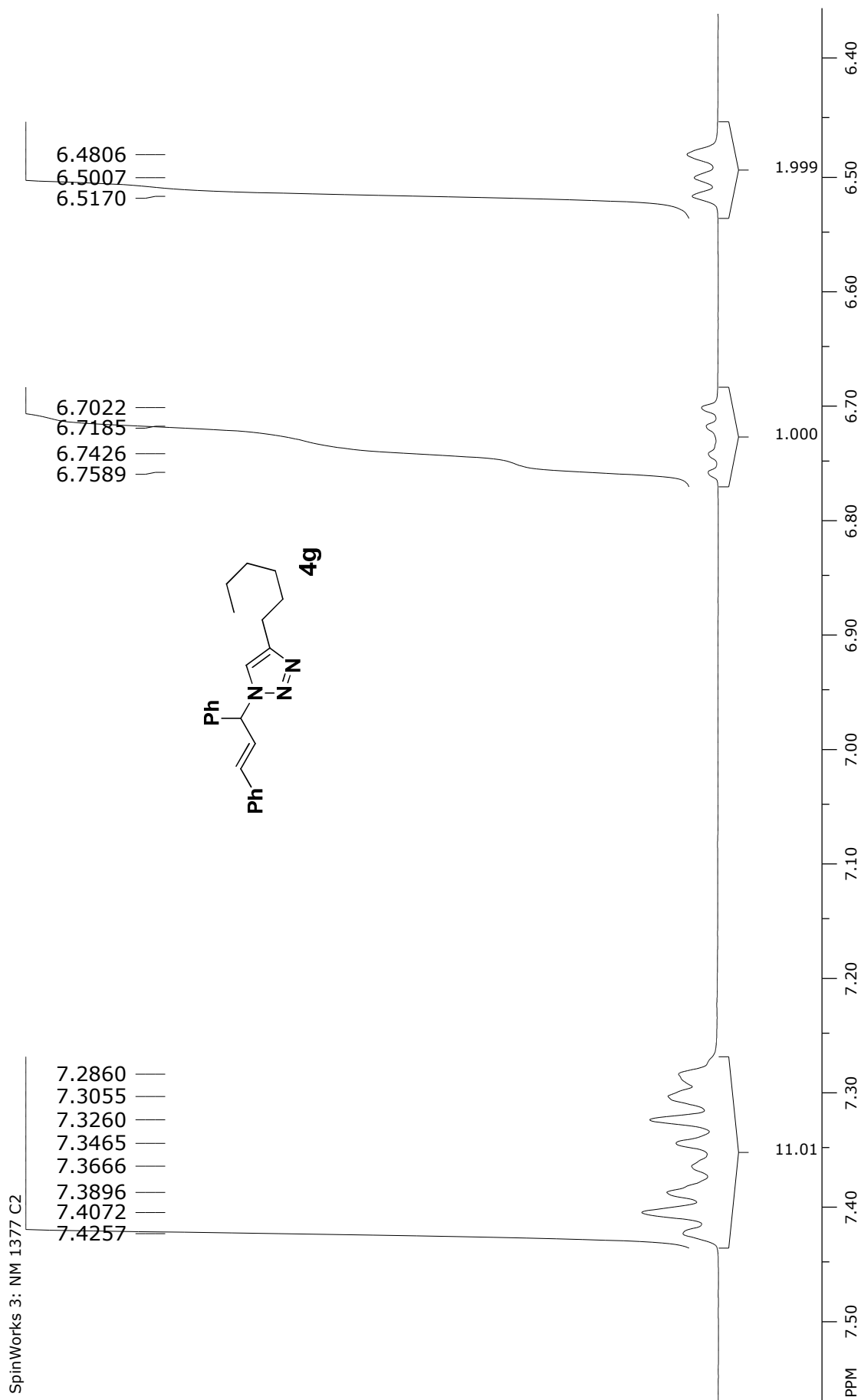


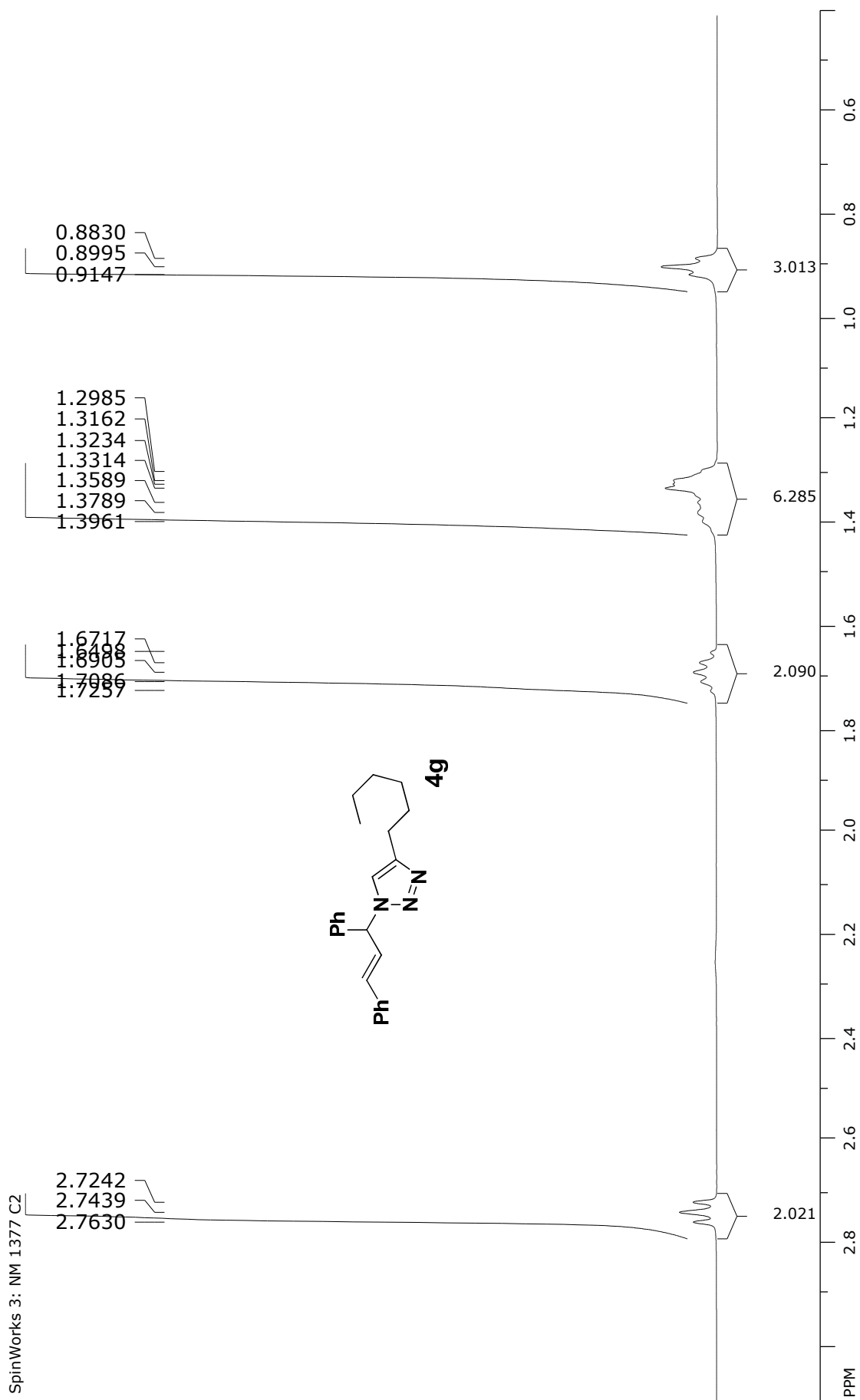
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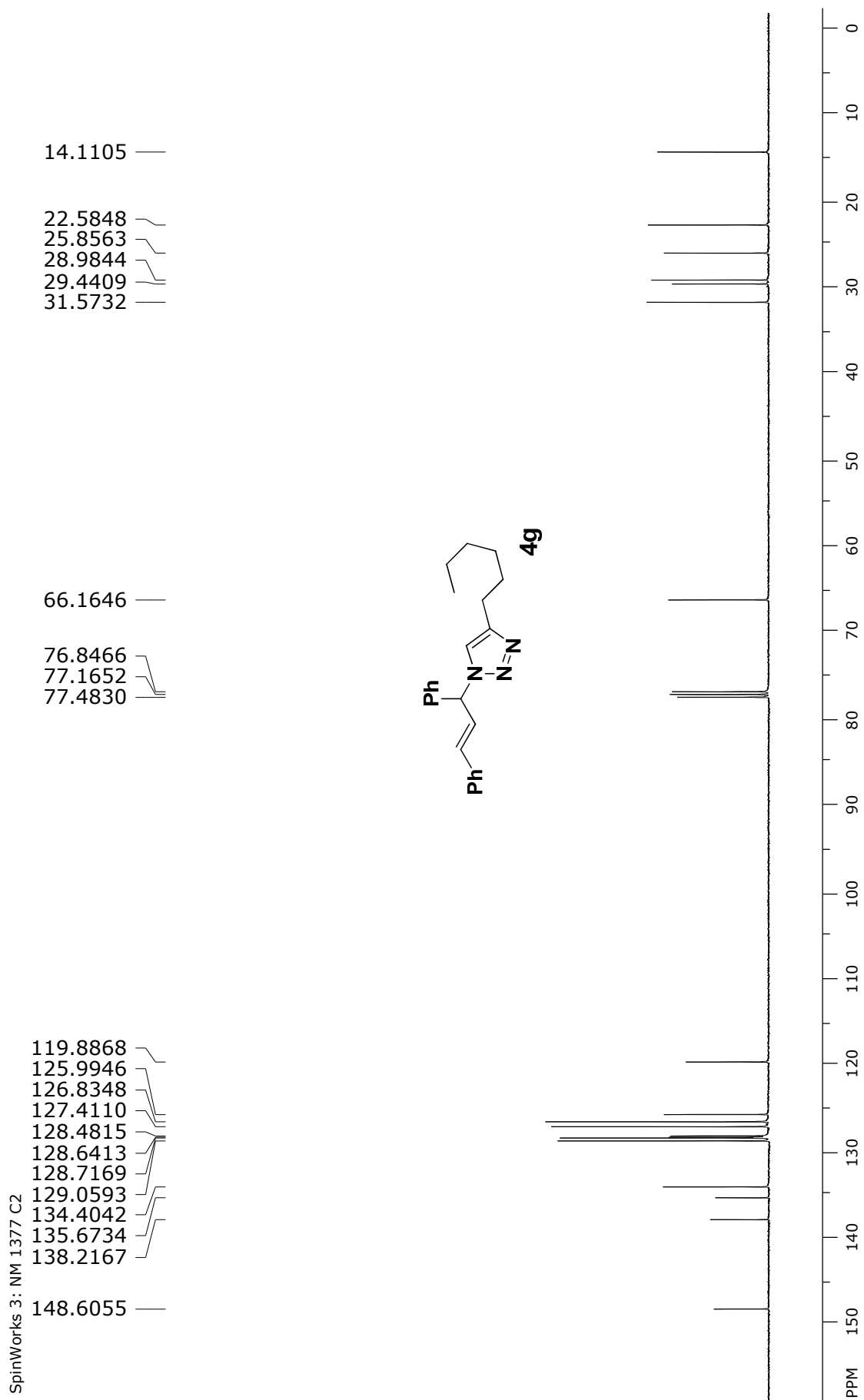


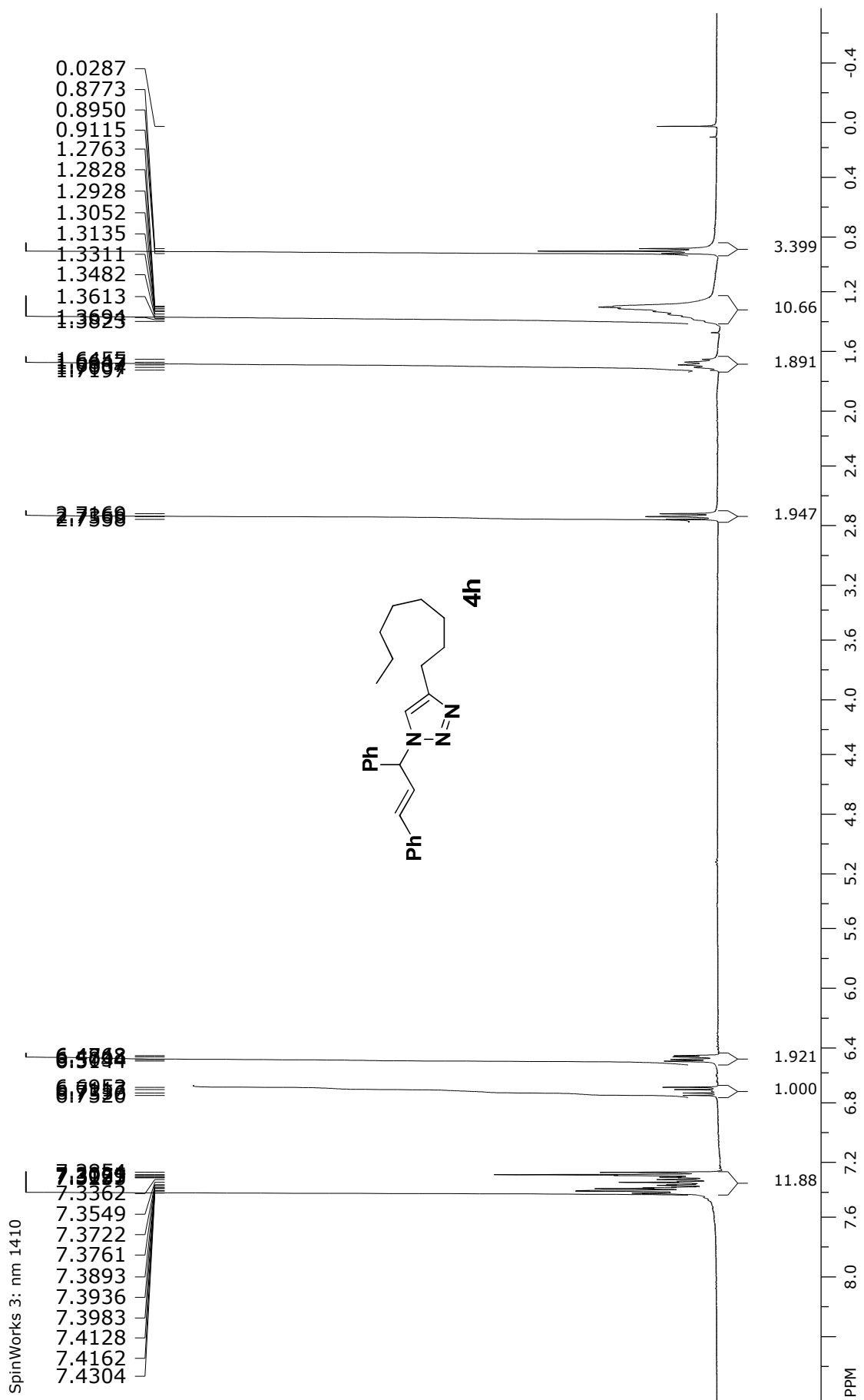


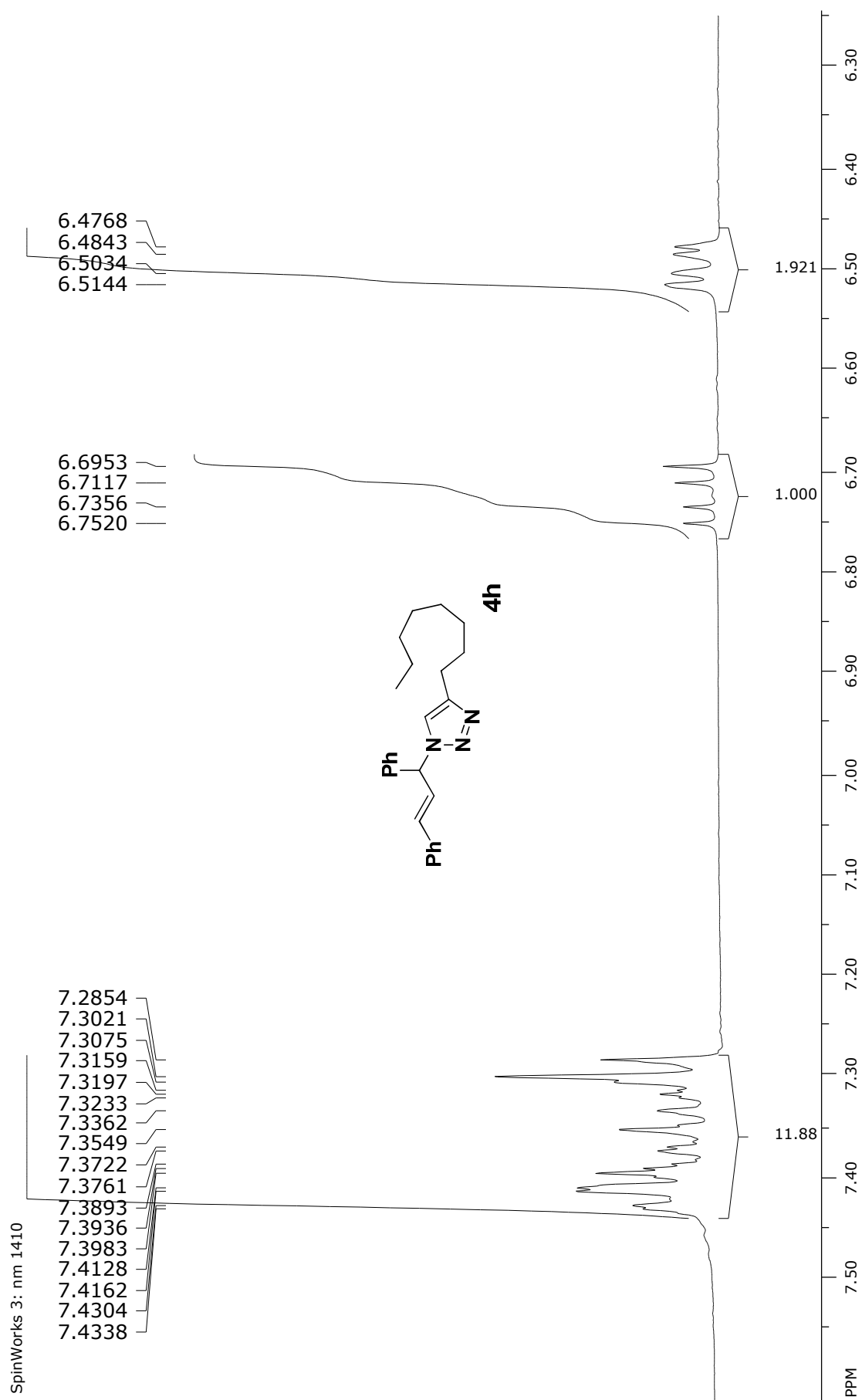


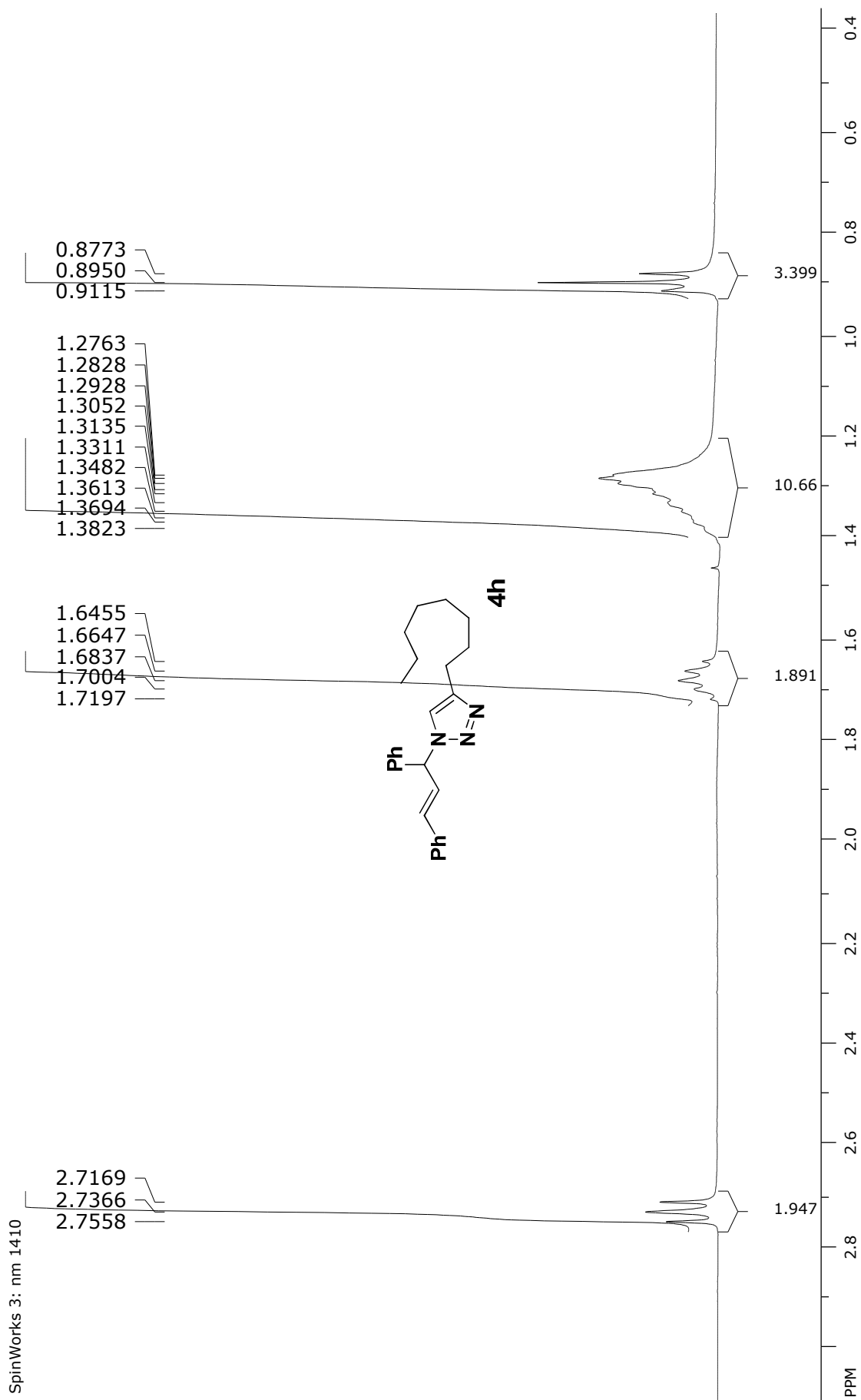


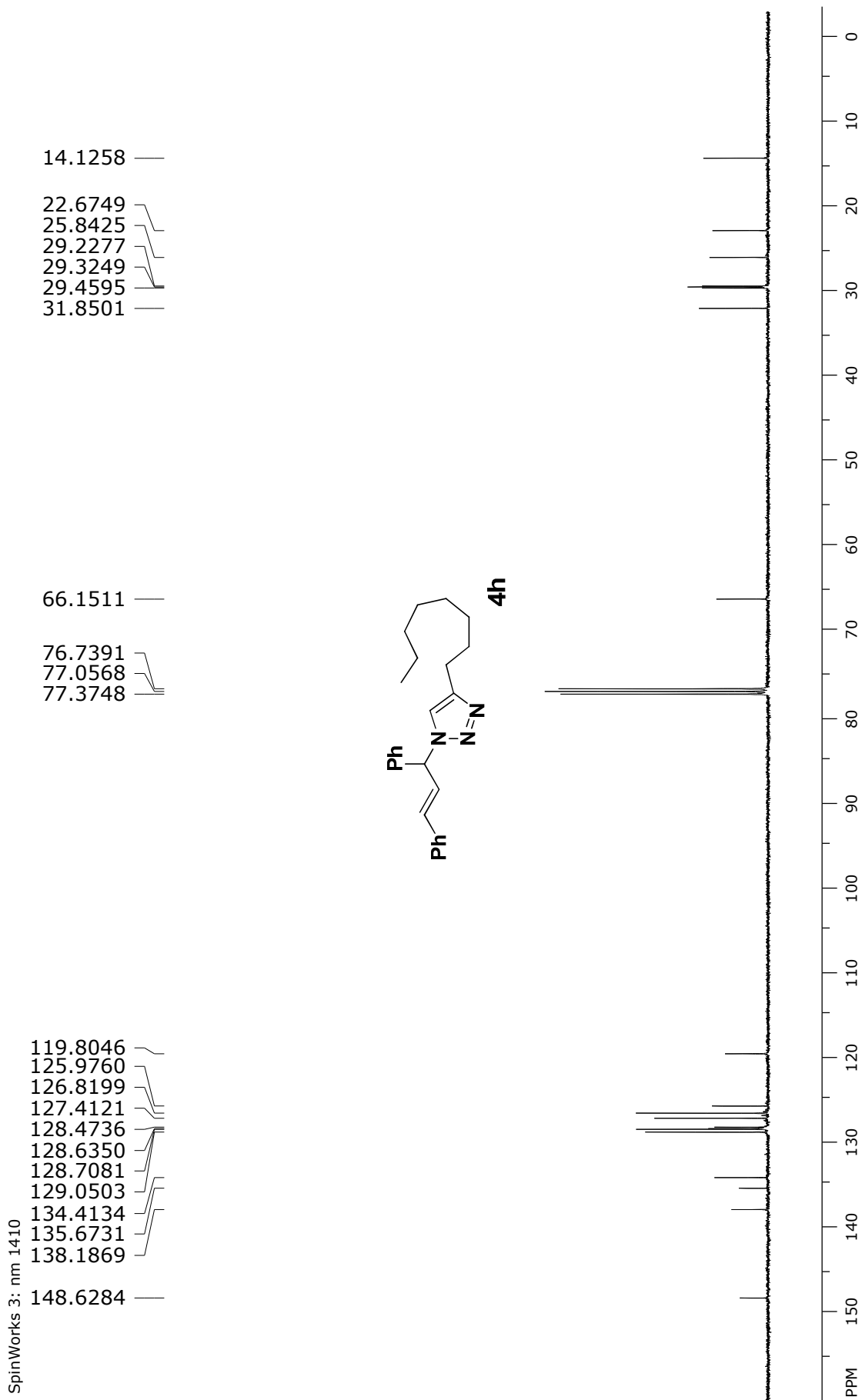


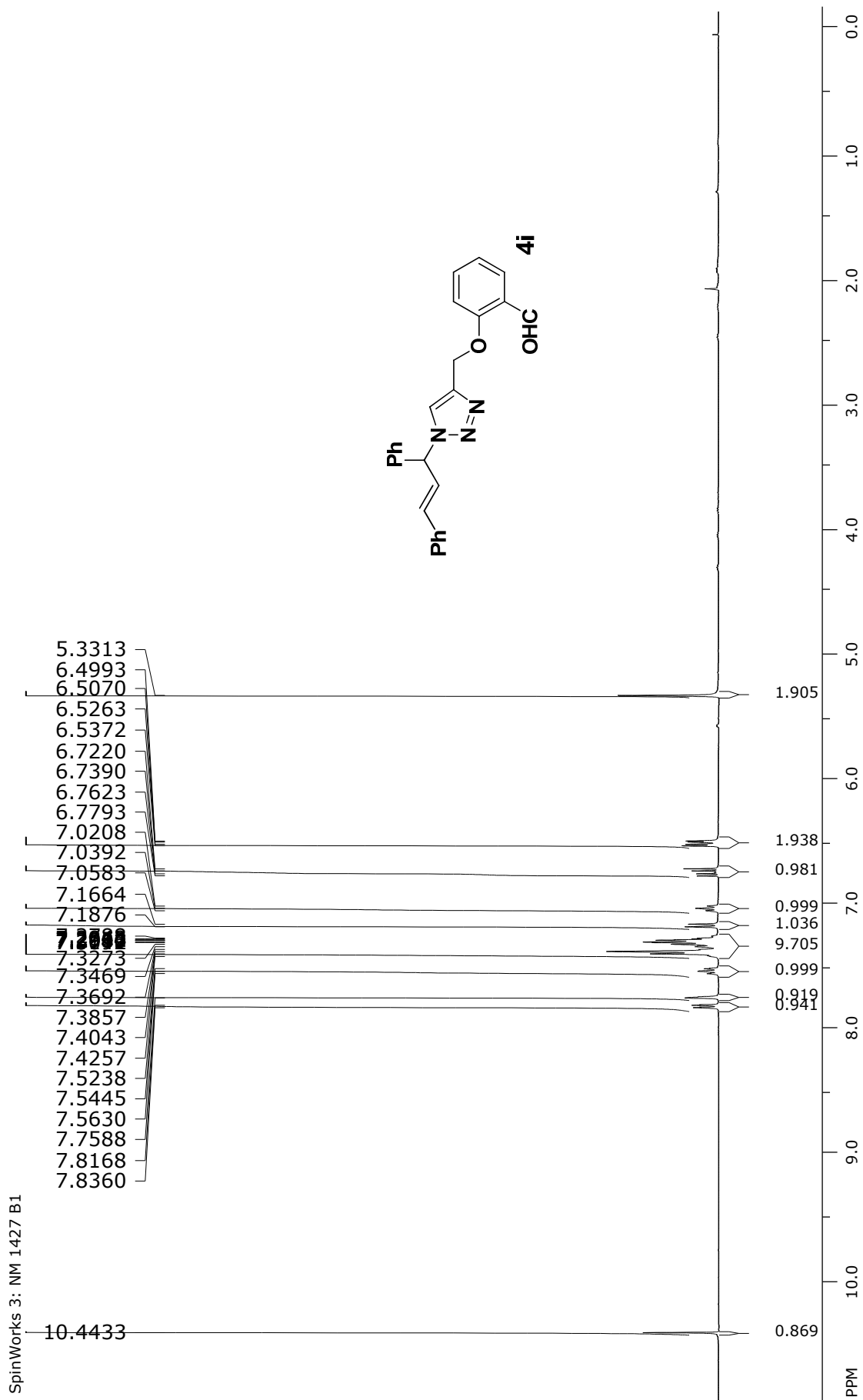


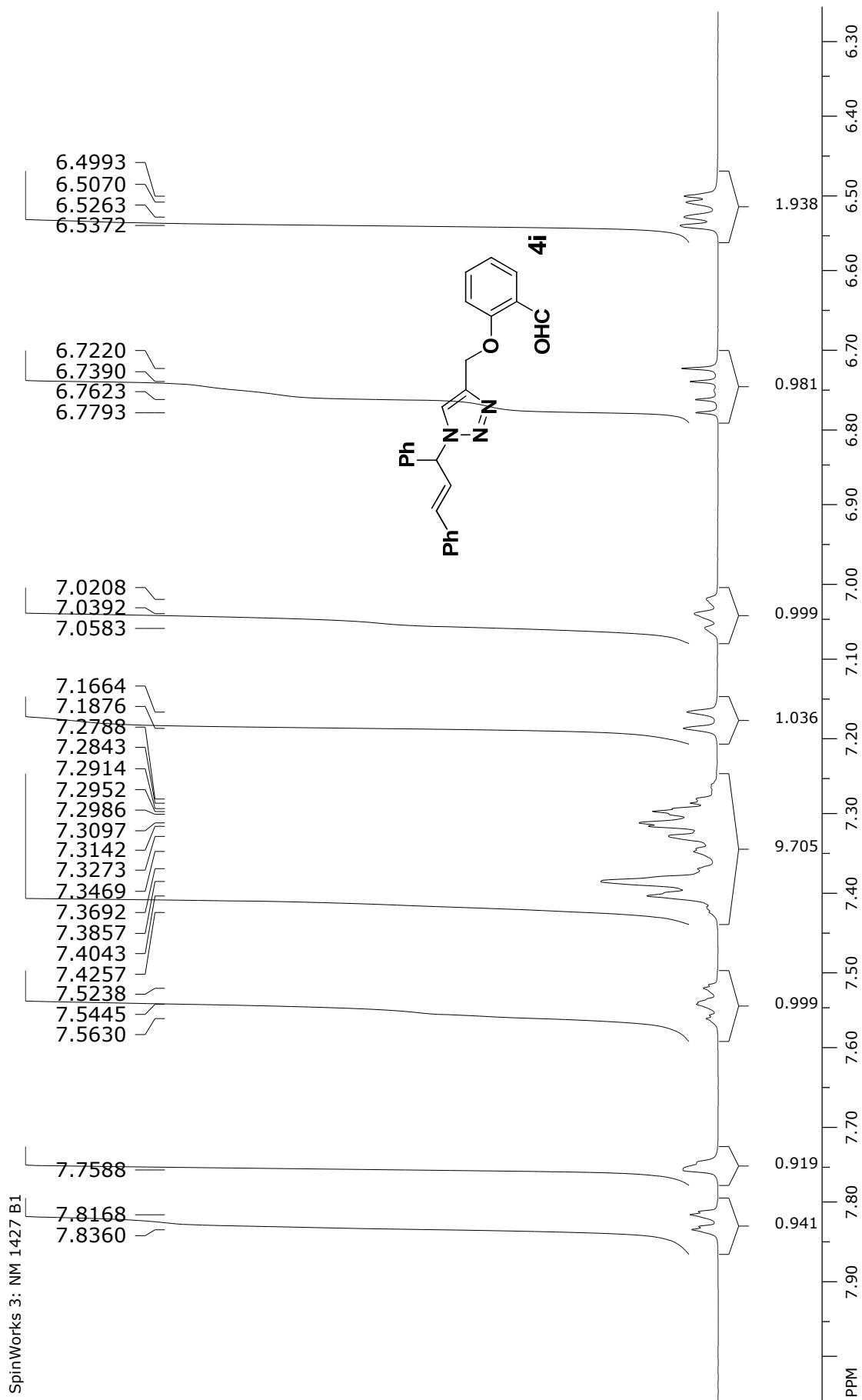


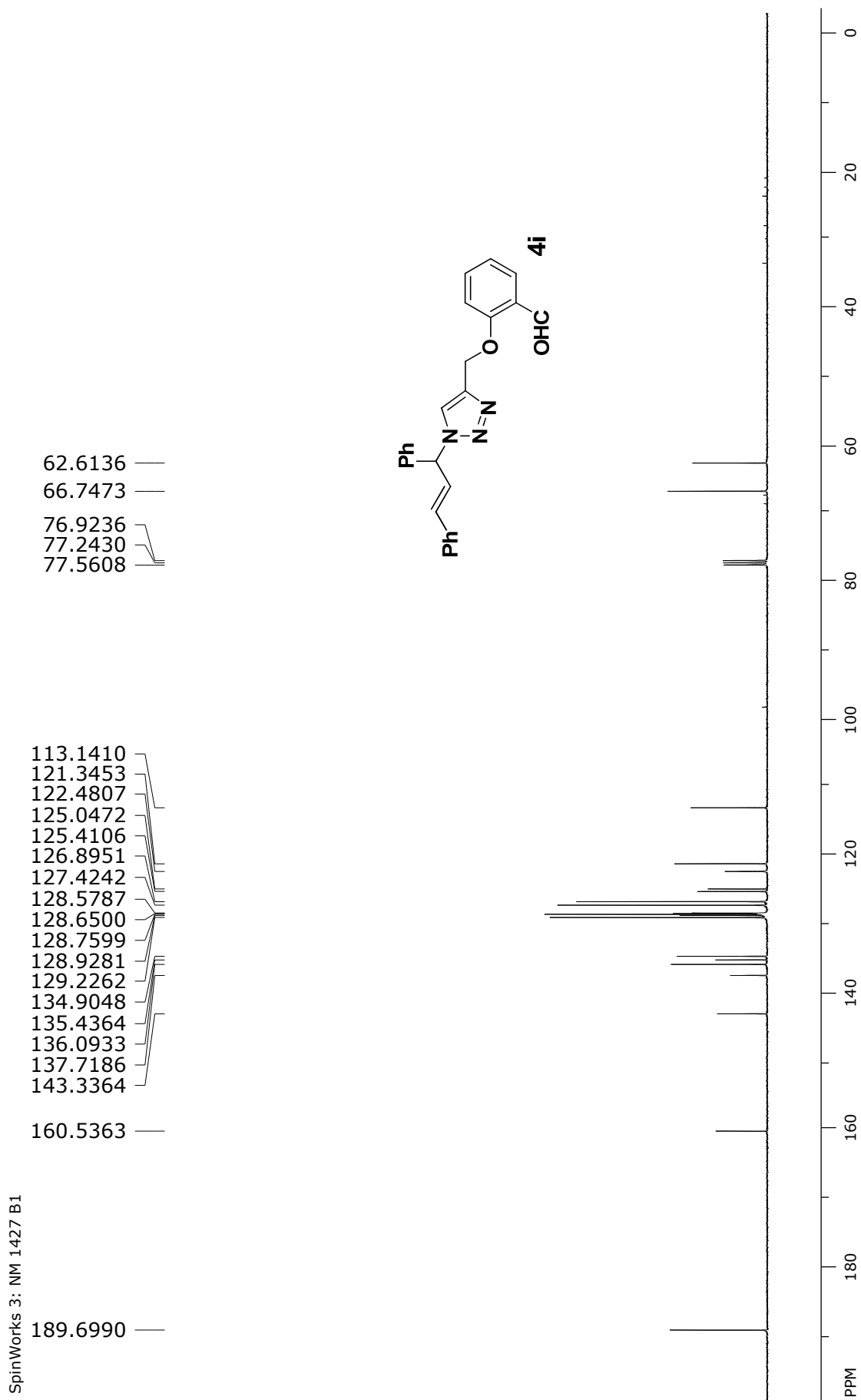




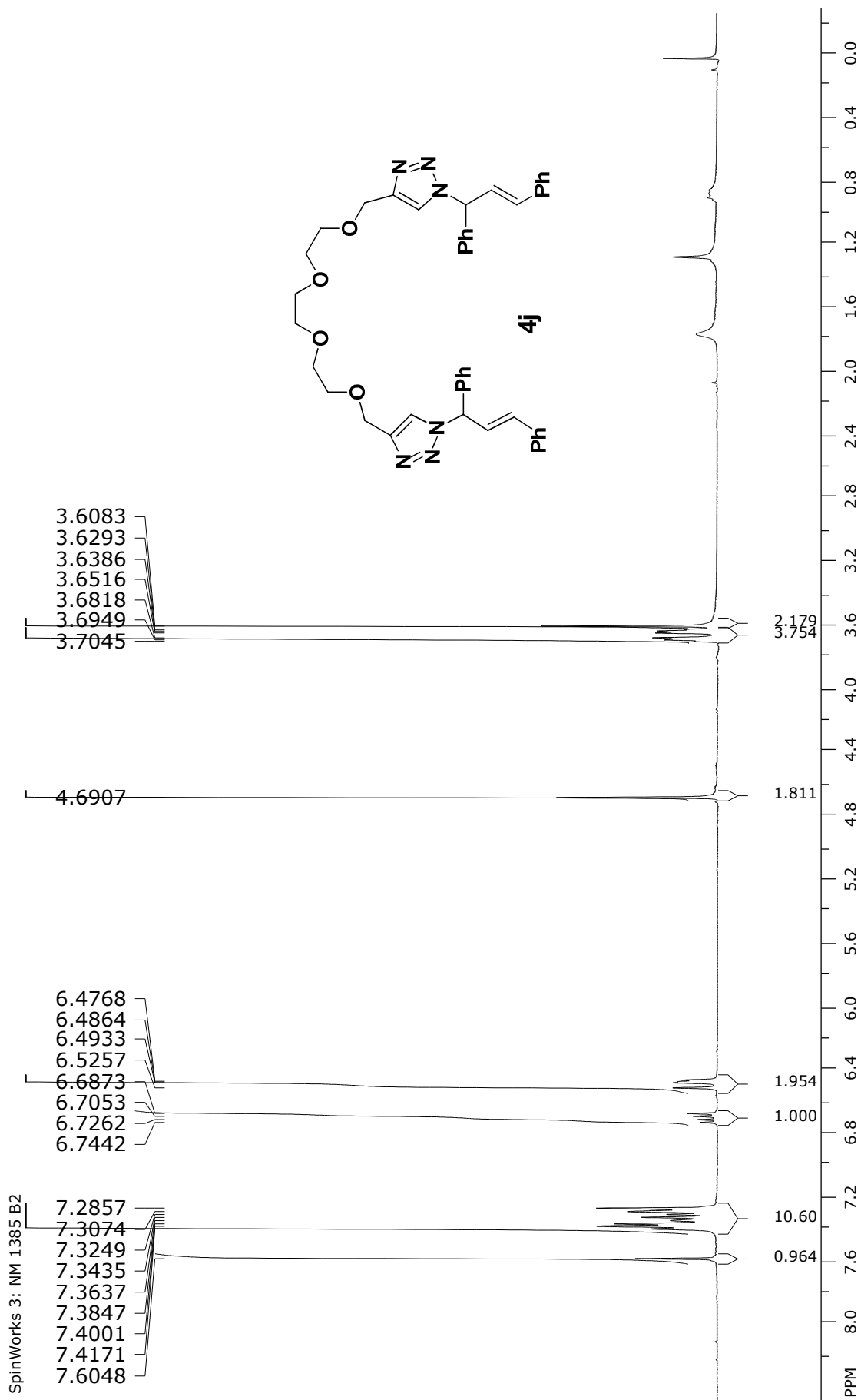


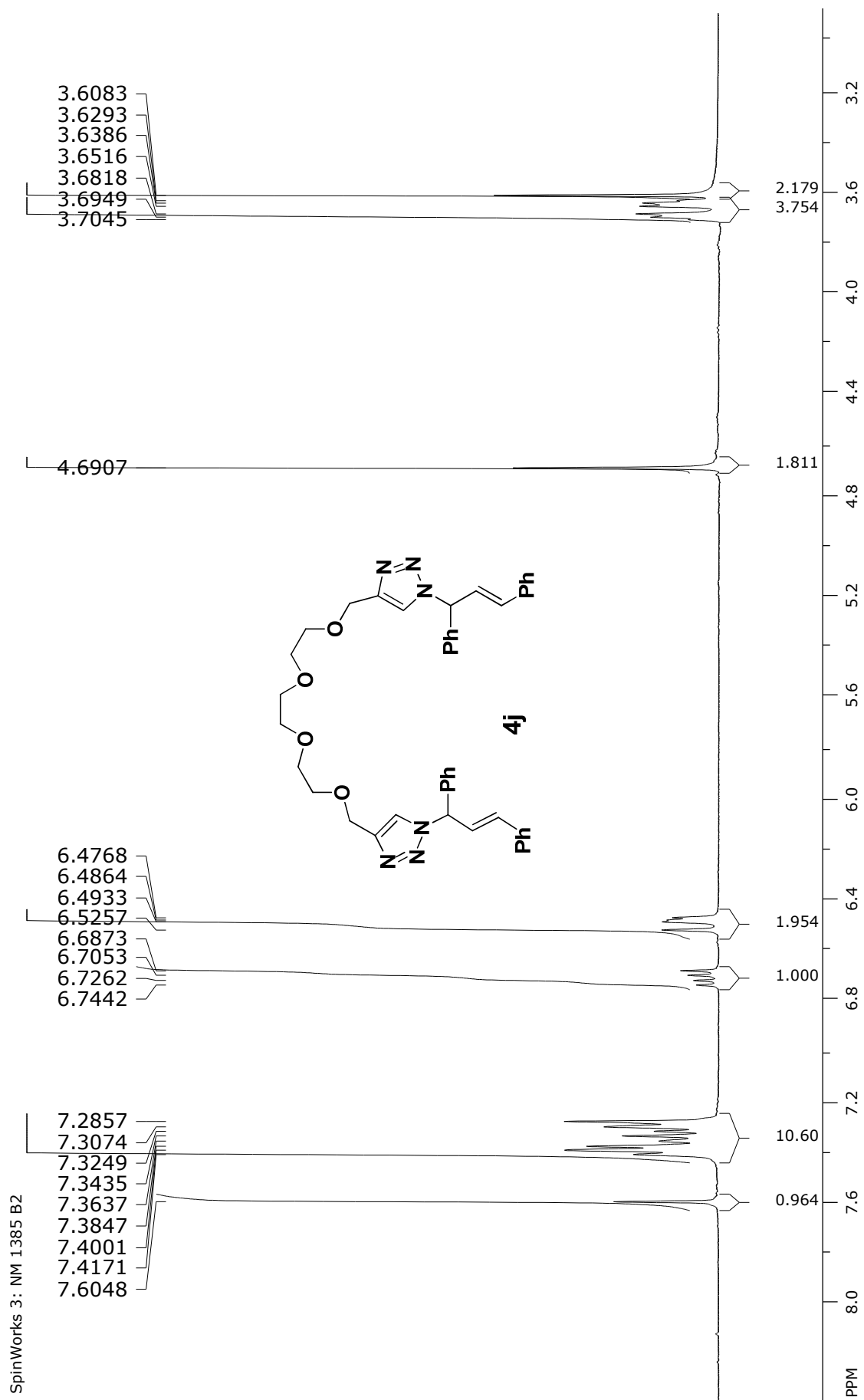








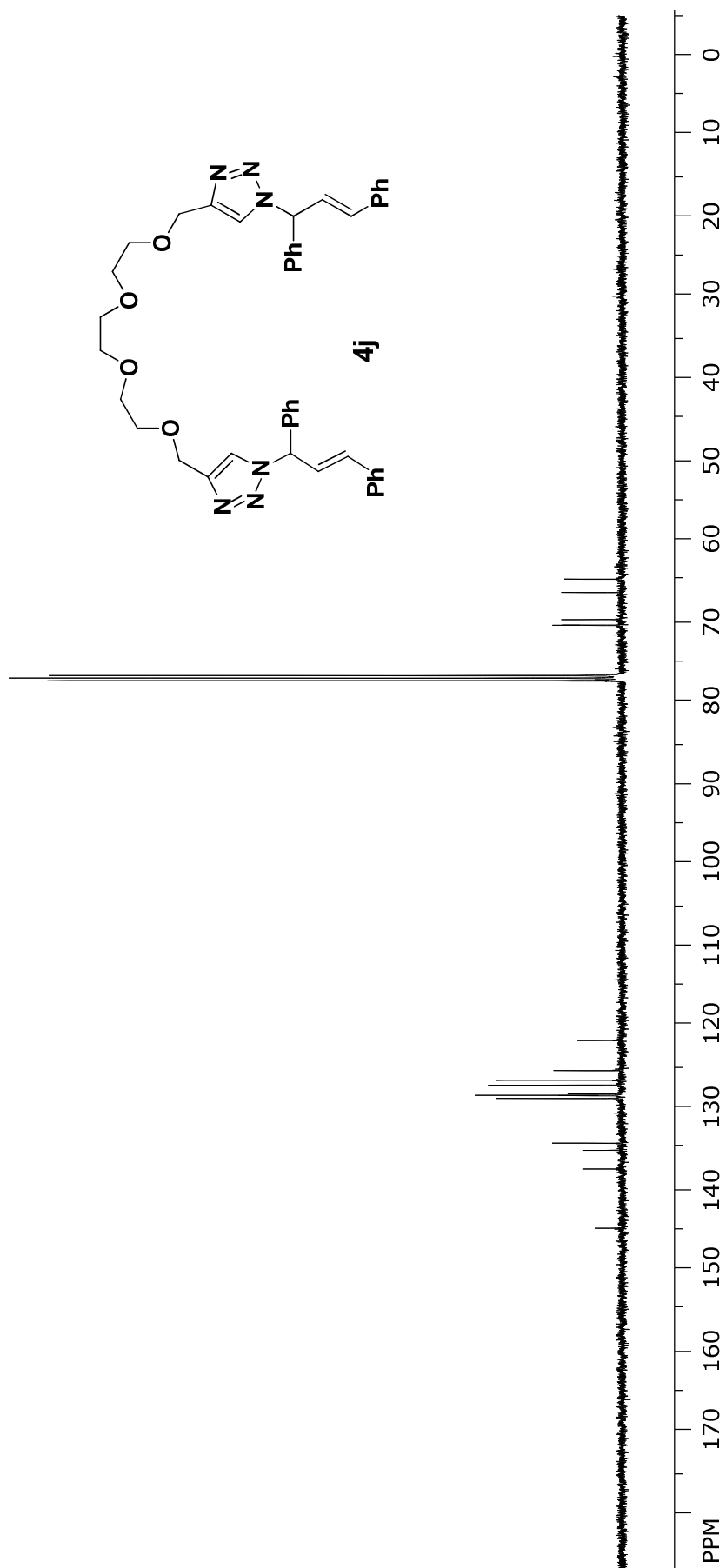


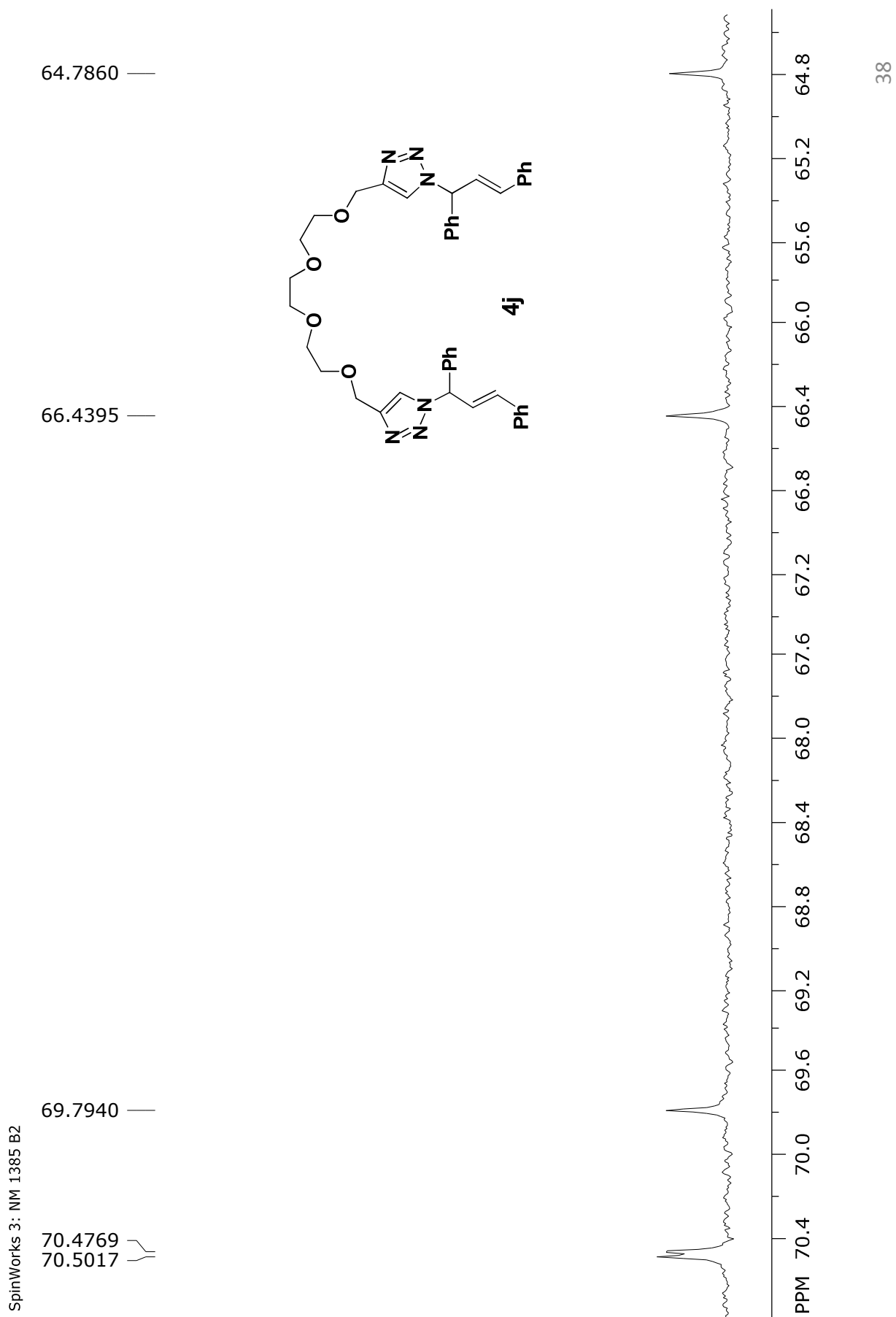


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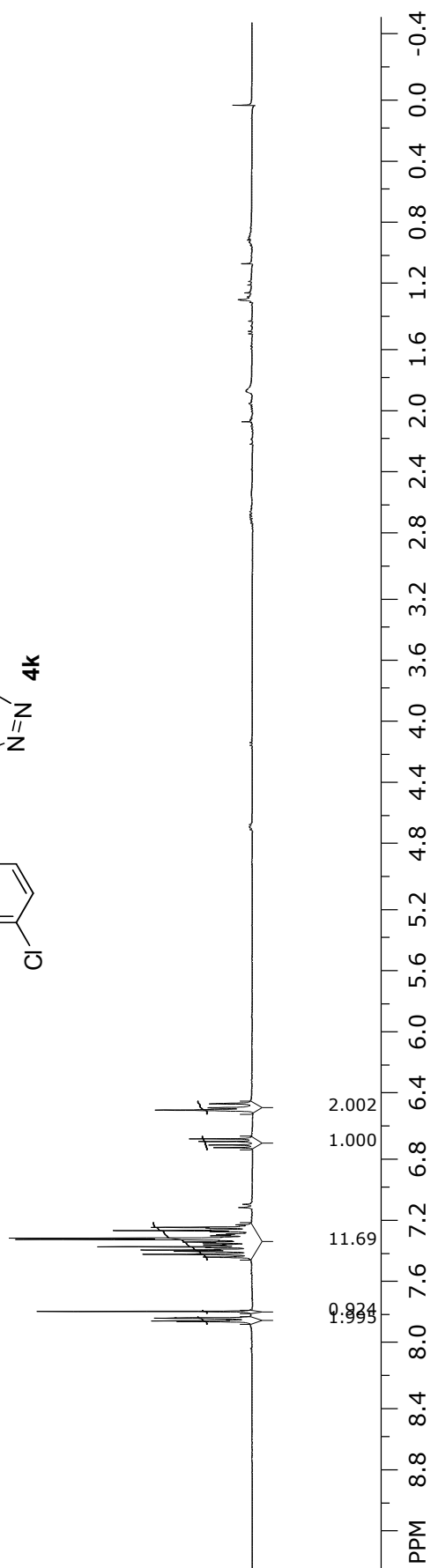
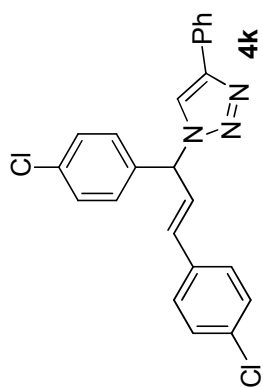
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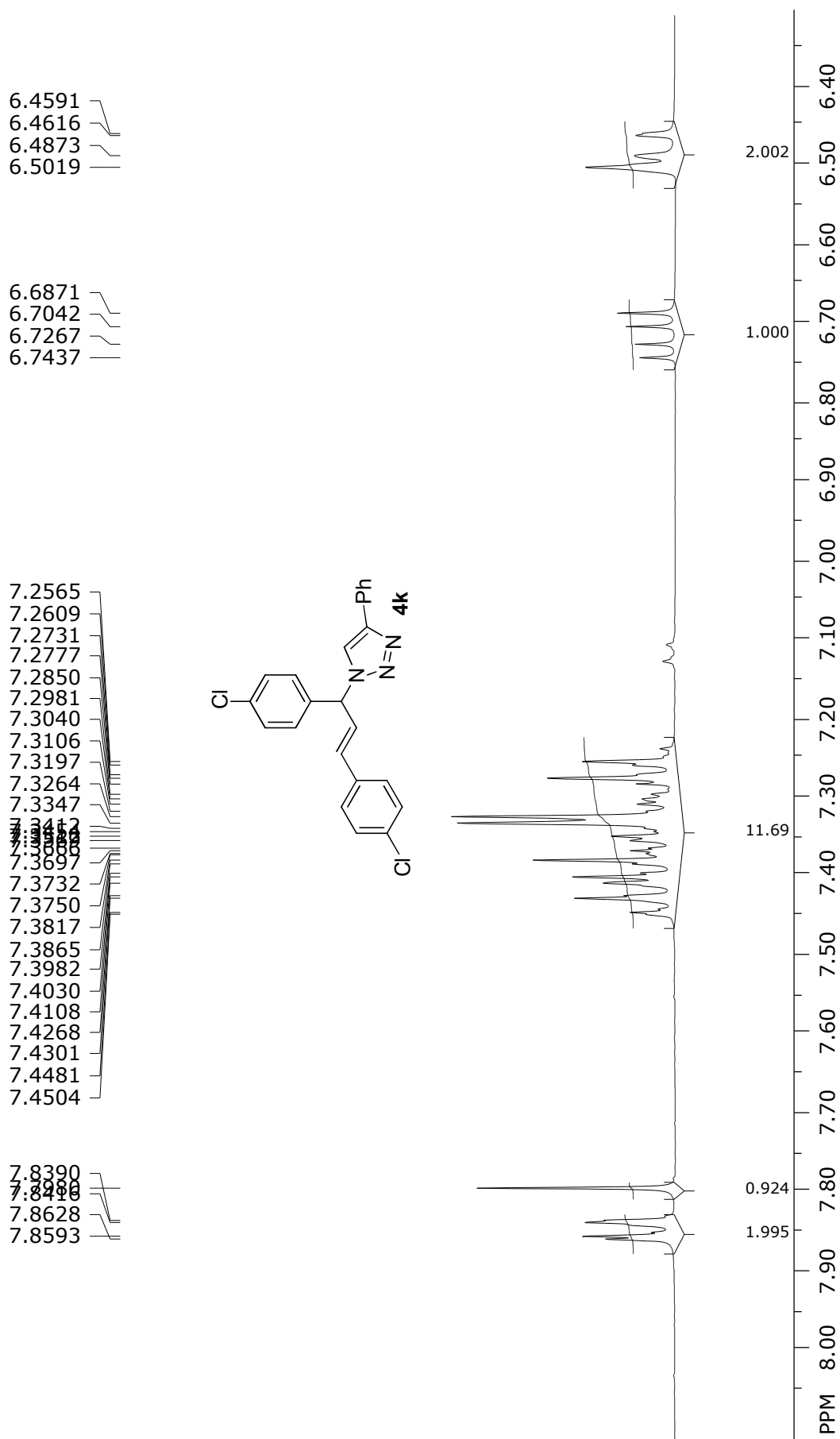


SpinWorks 3: AS 70 RA

6.4591  
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6.7267  
6.7437  
7.2565  
7.2609  
7.2731  
7.2777  
7.2850  
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7.7980



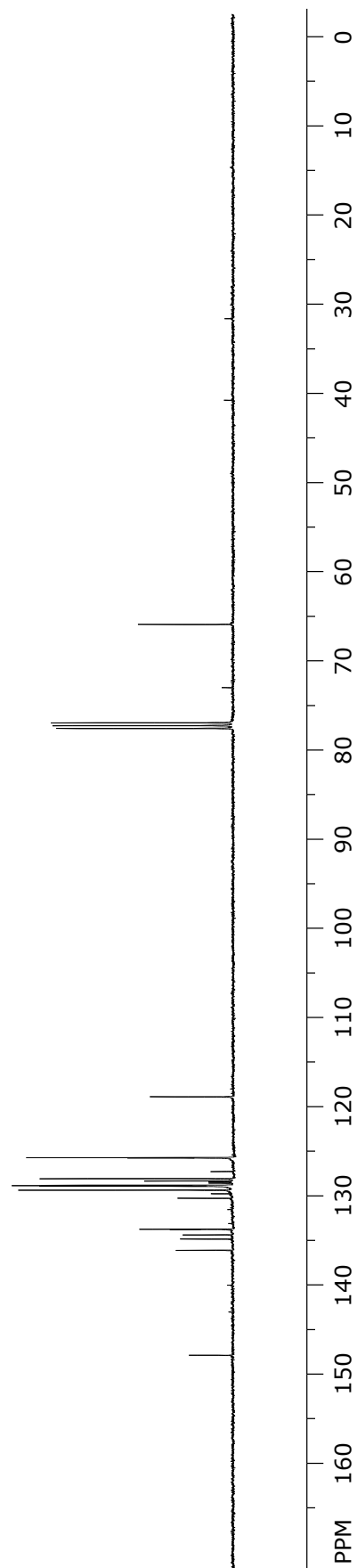
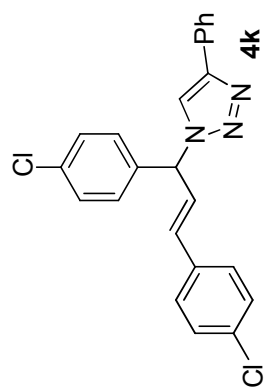
SpinWorks 3: AS 70 RA

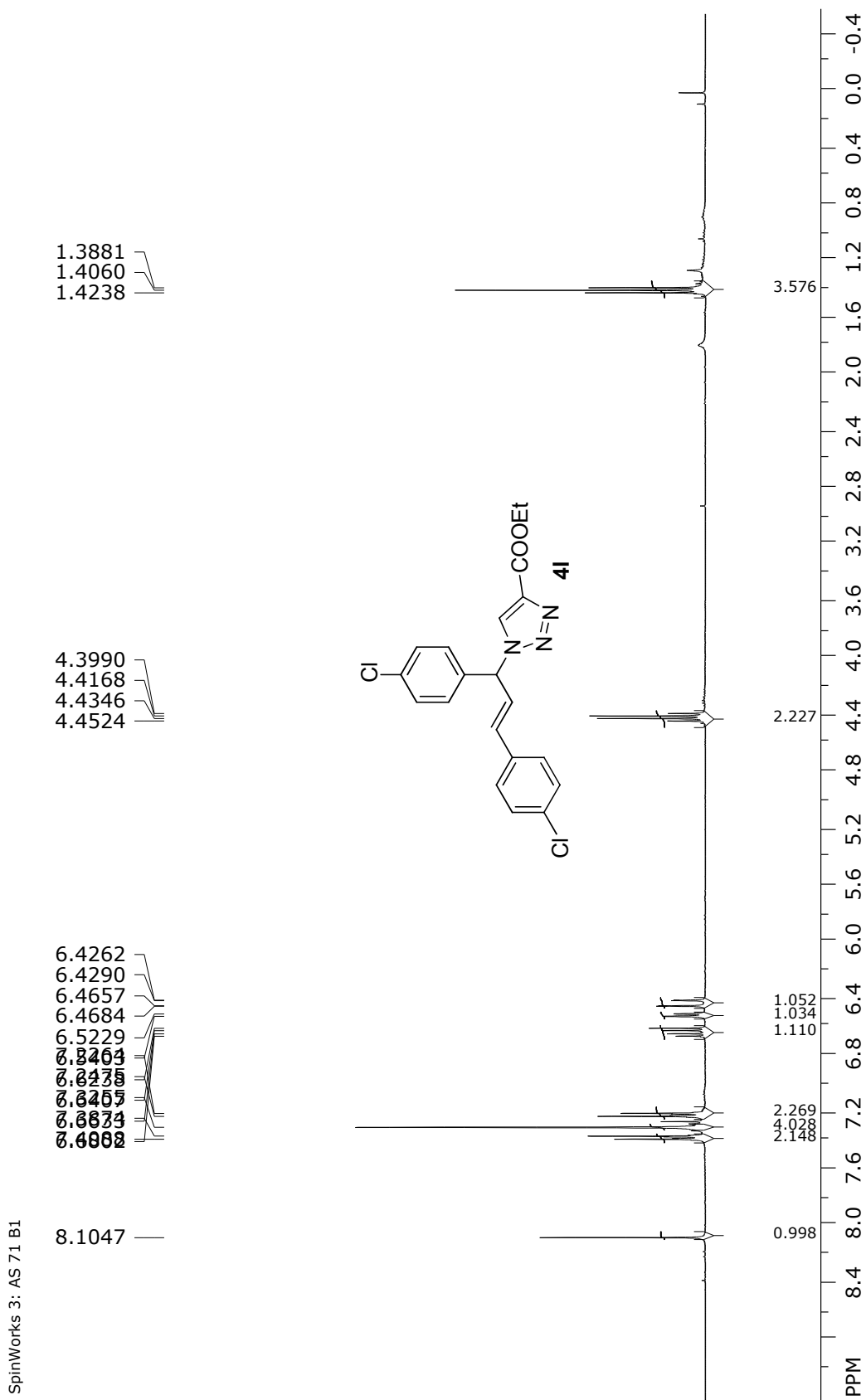


SpinWorks 3: AS 70 RA

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128.8599  
128.9051  
128.9734  
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130.3346  
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133.8393  
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148.0105

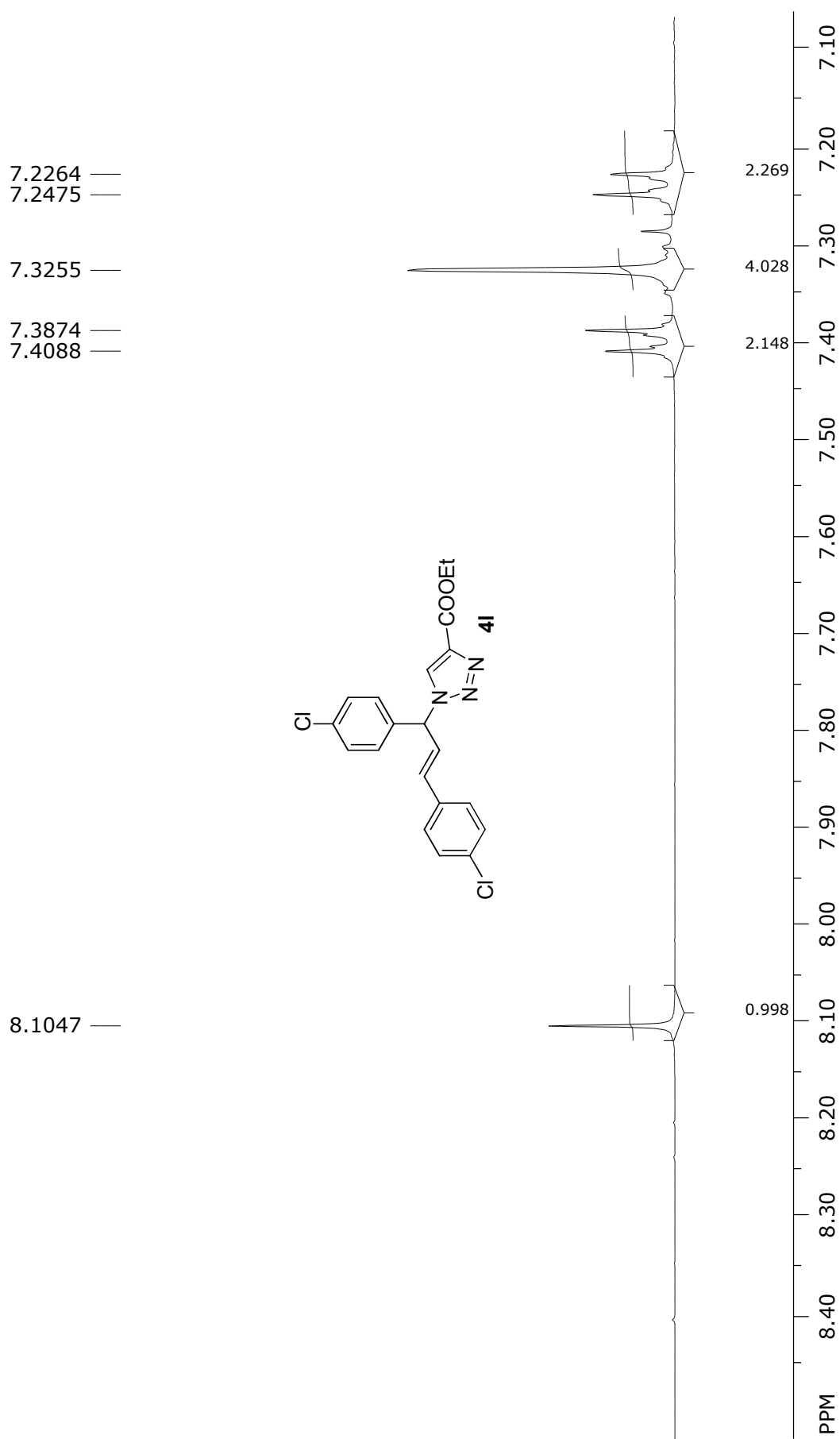
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77.4231



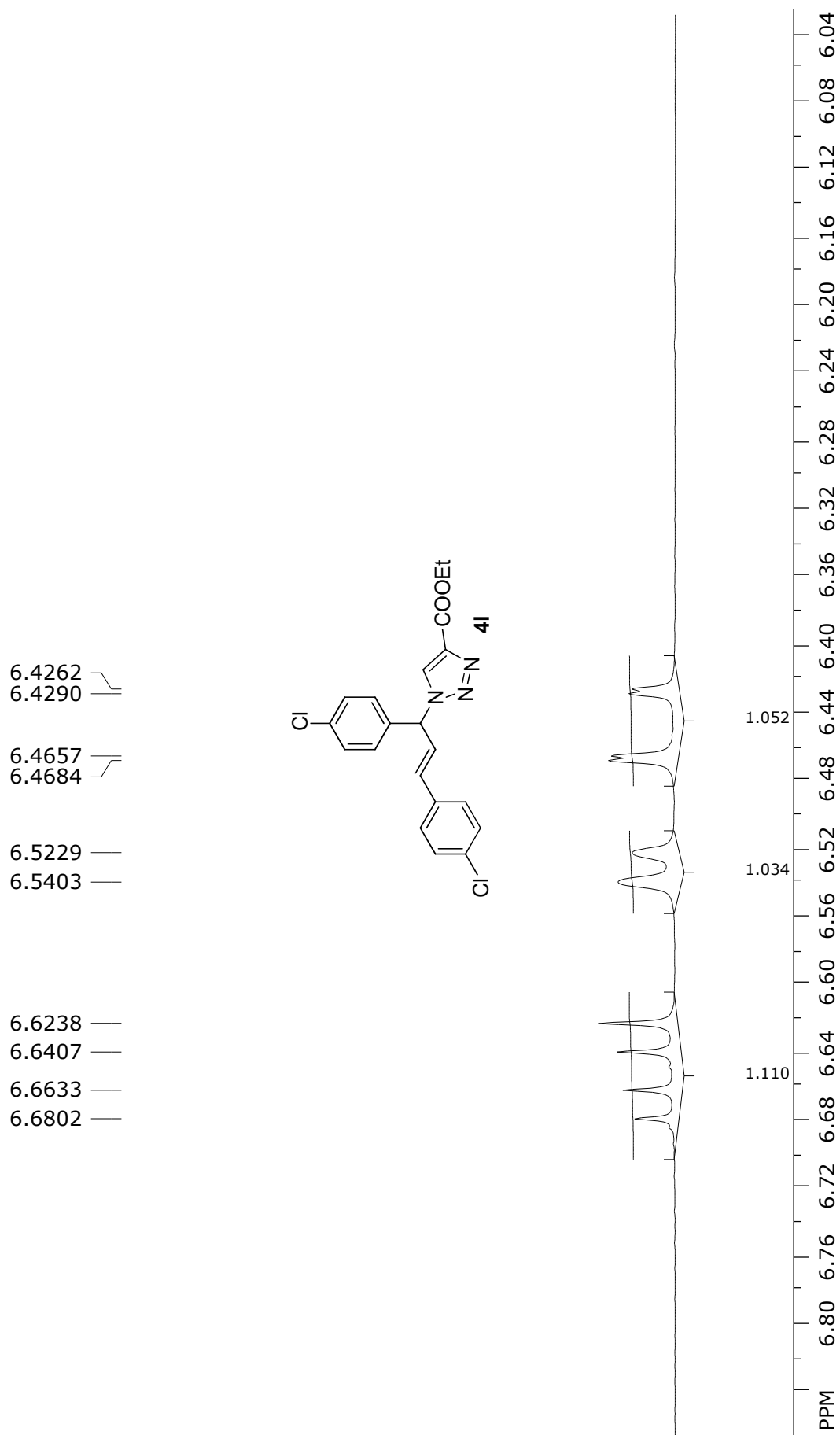




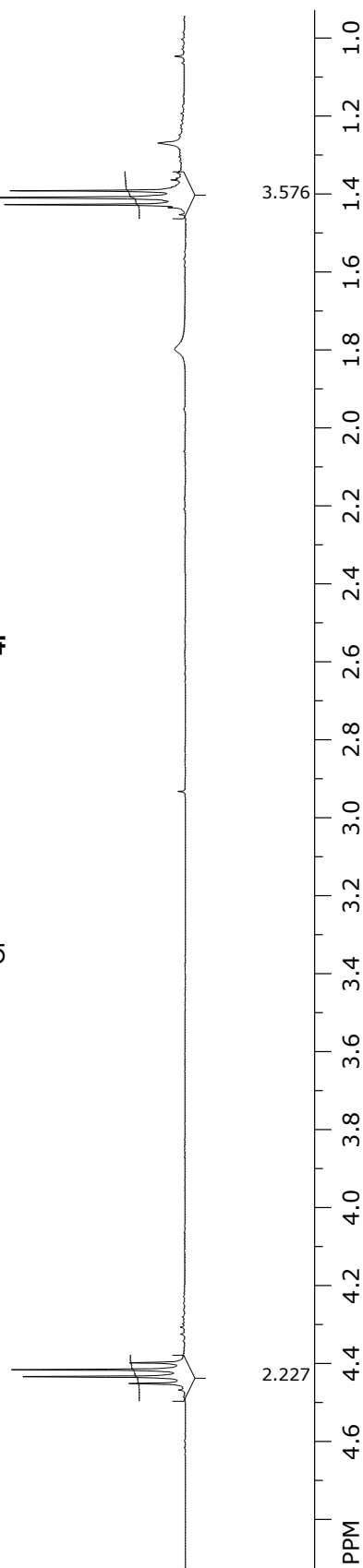
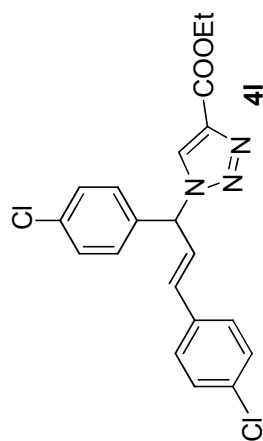
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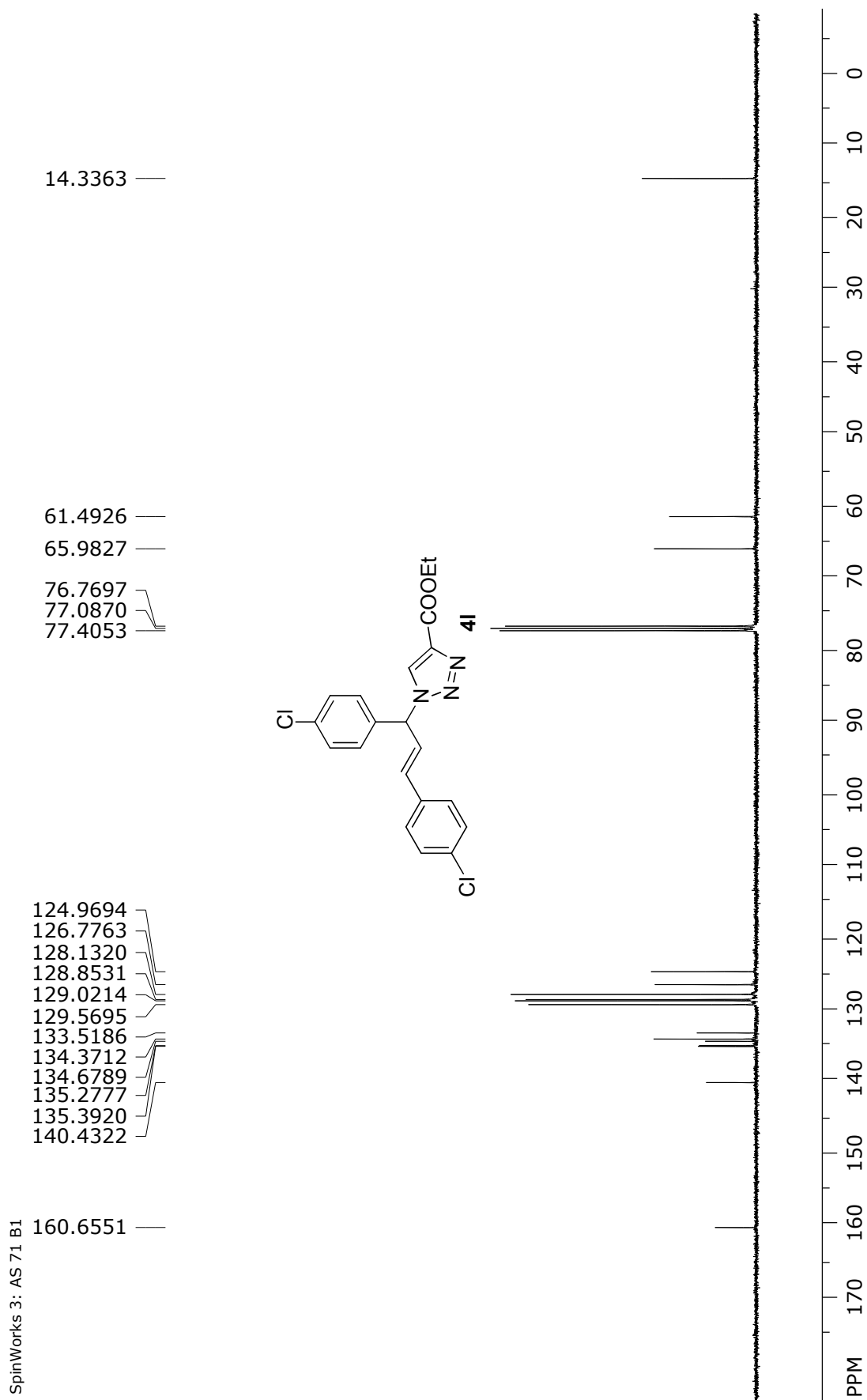


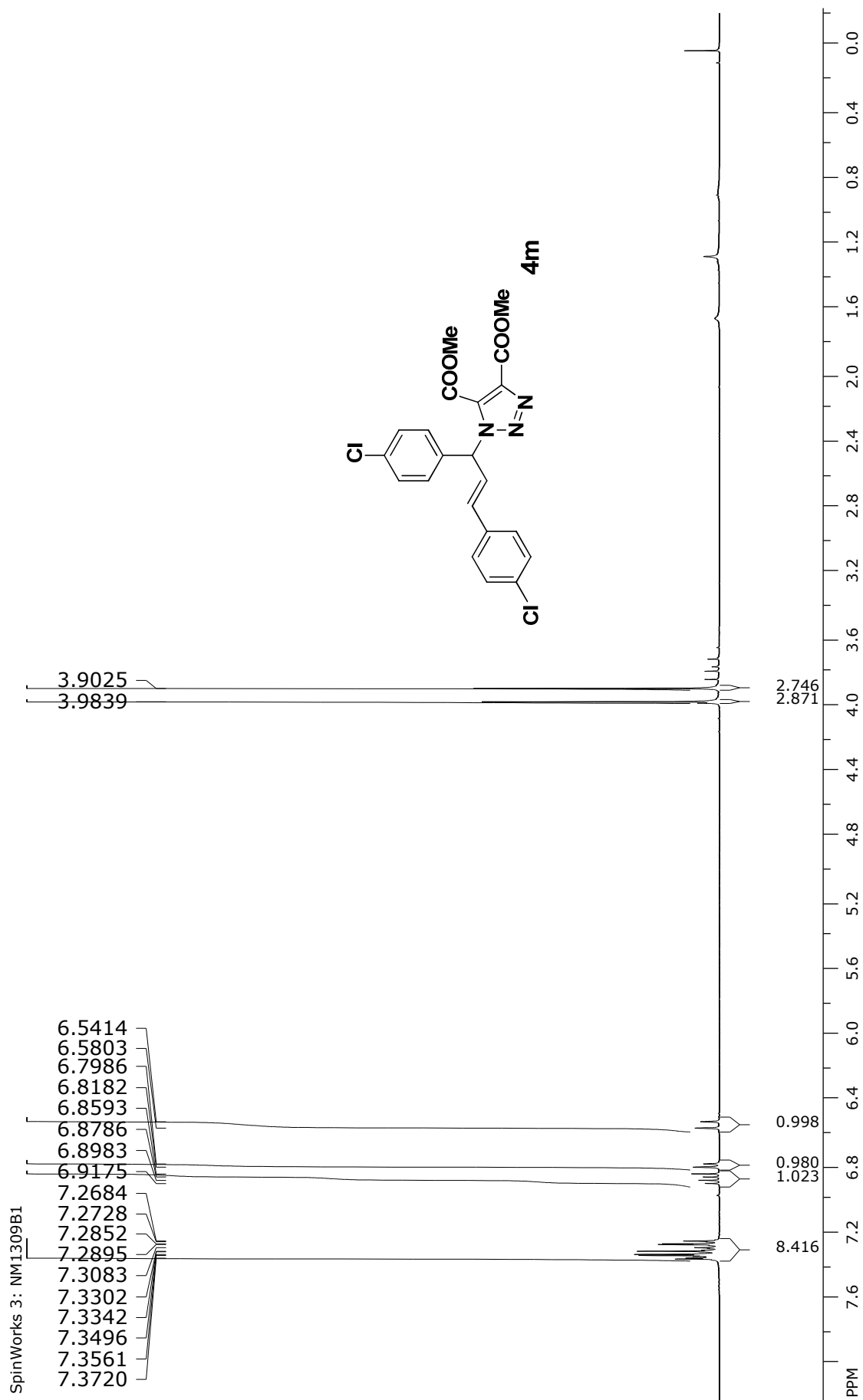
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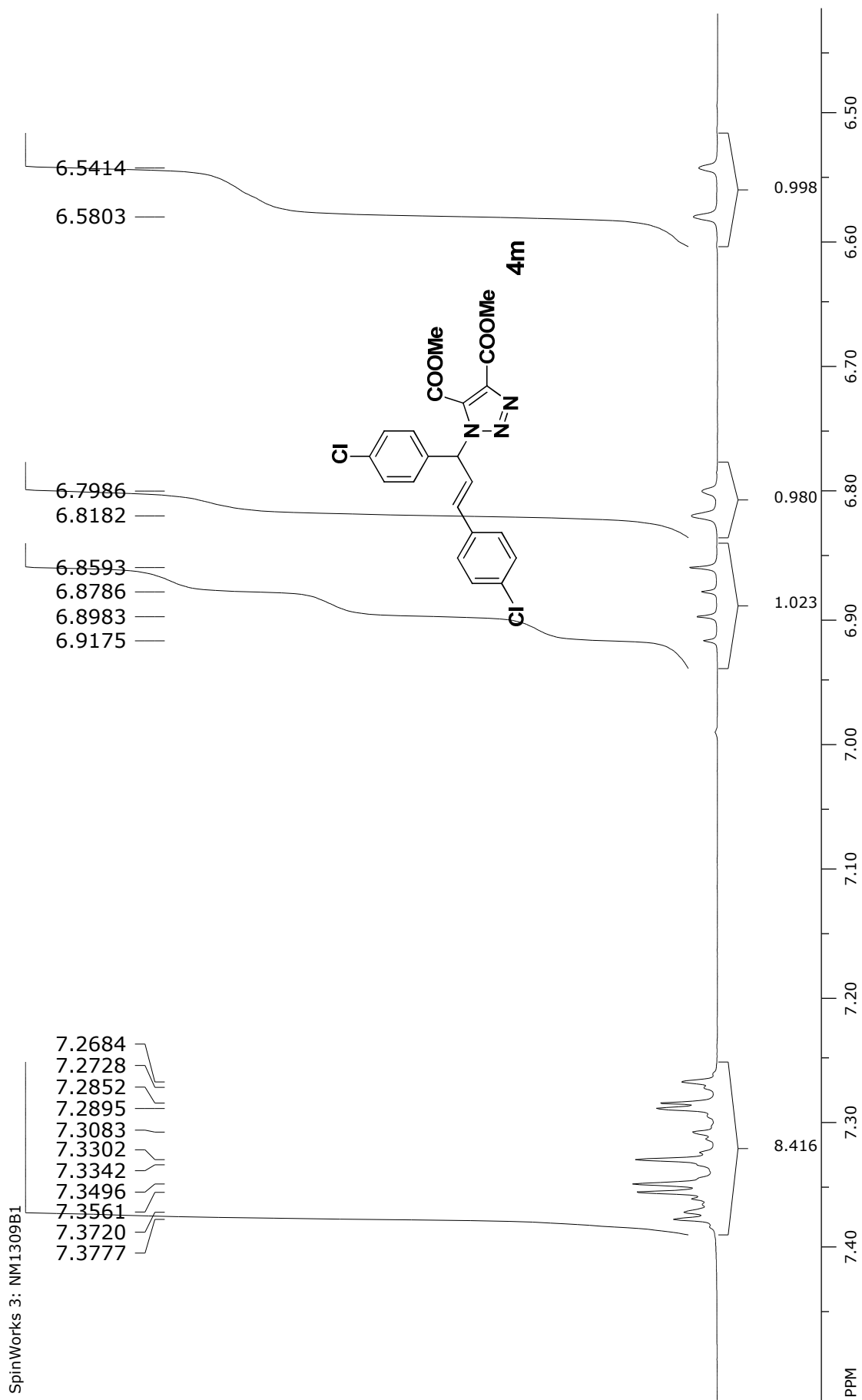


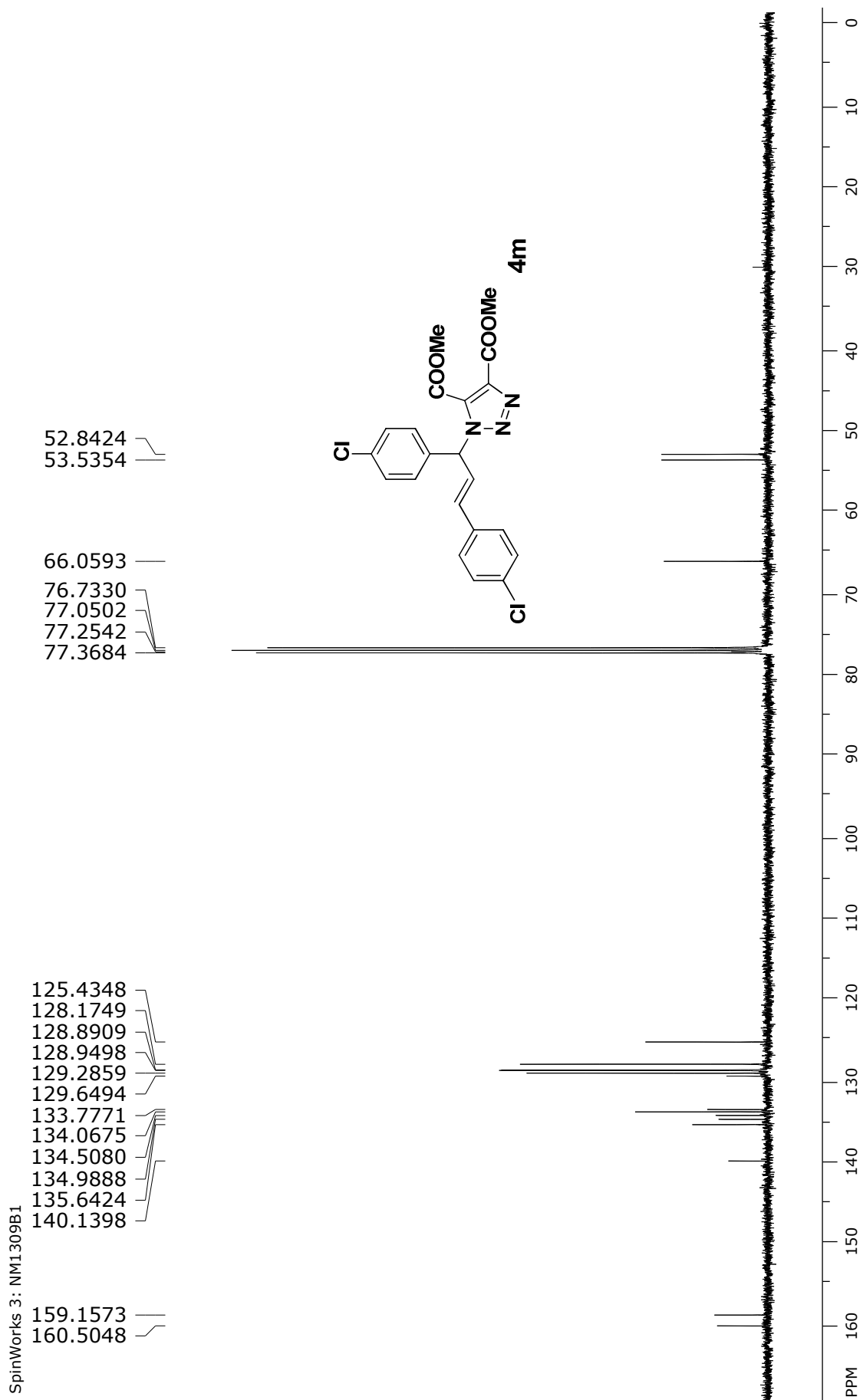
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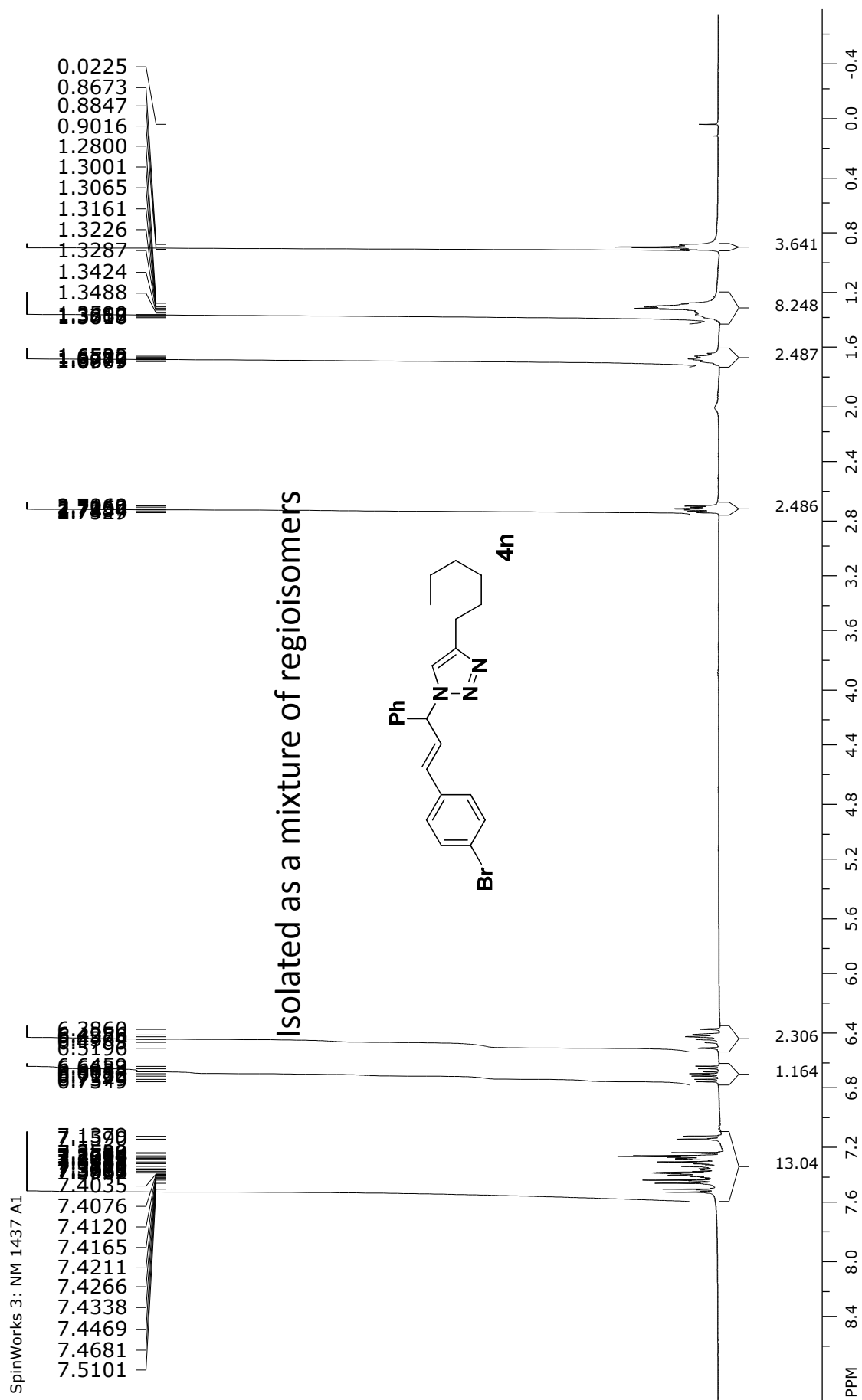
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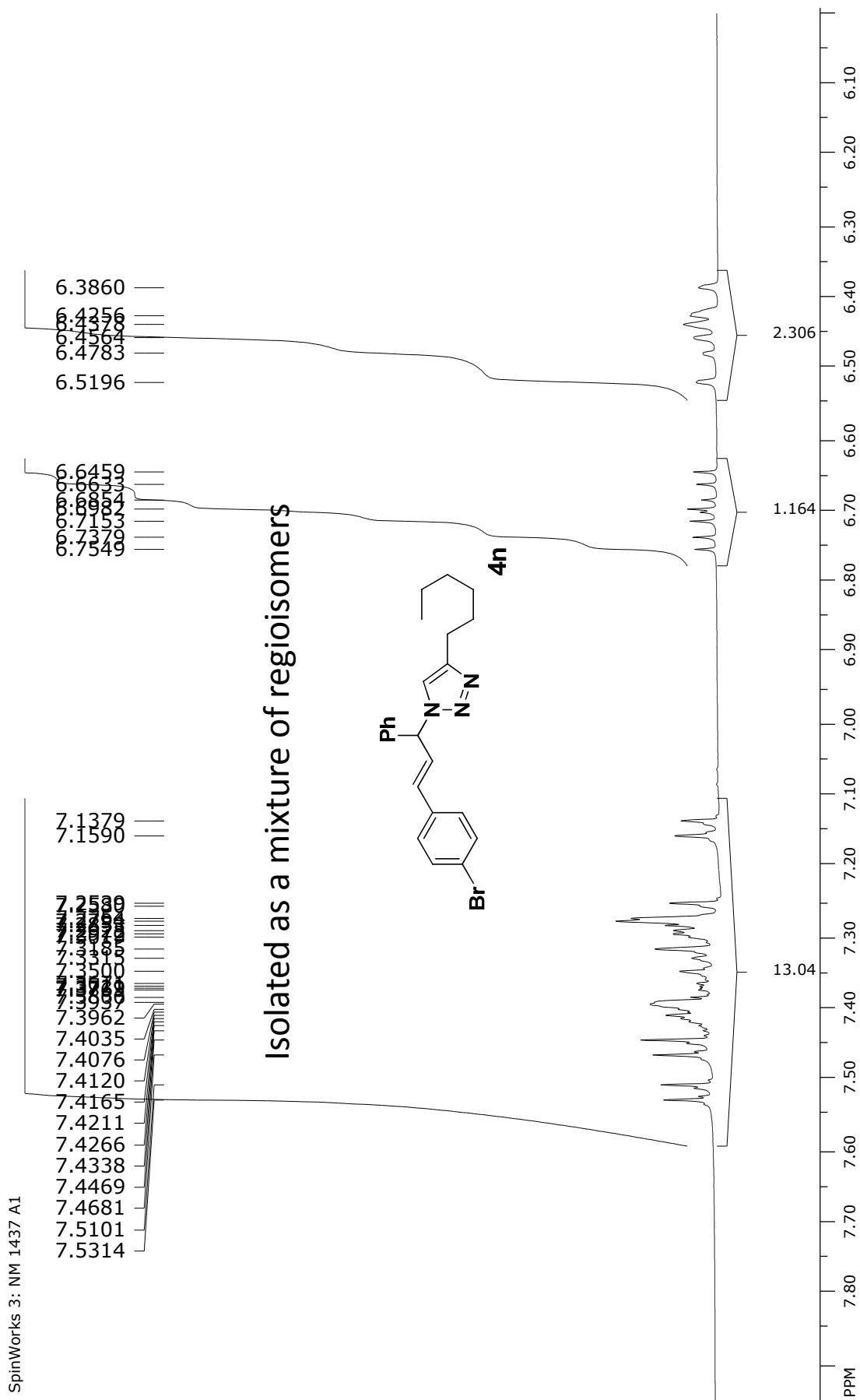


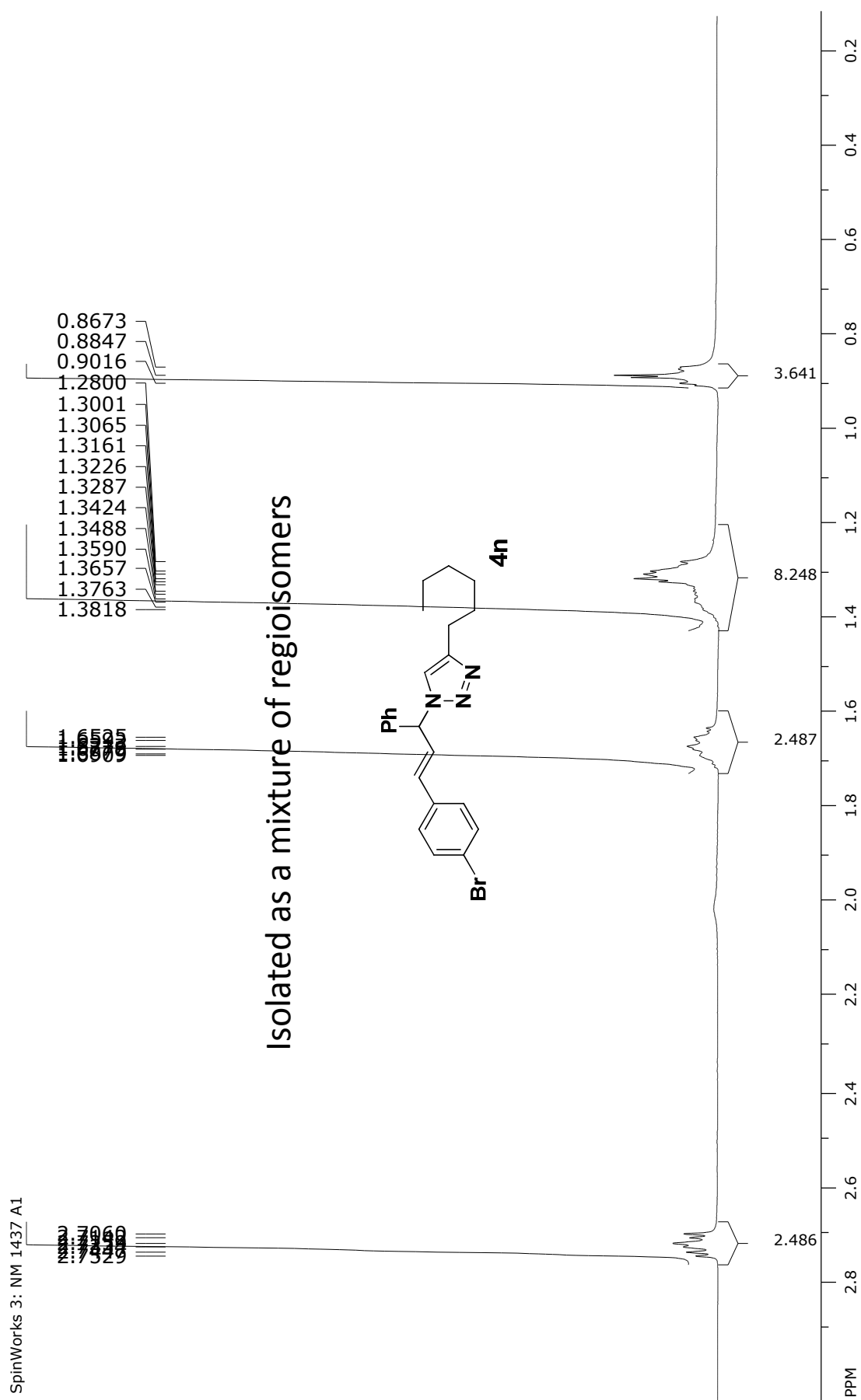


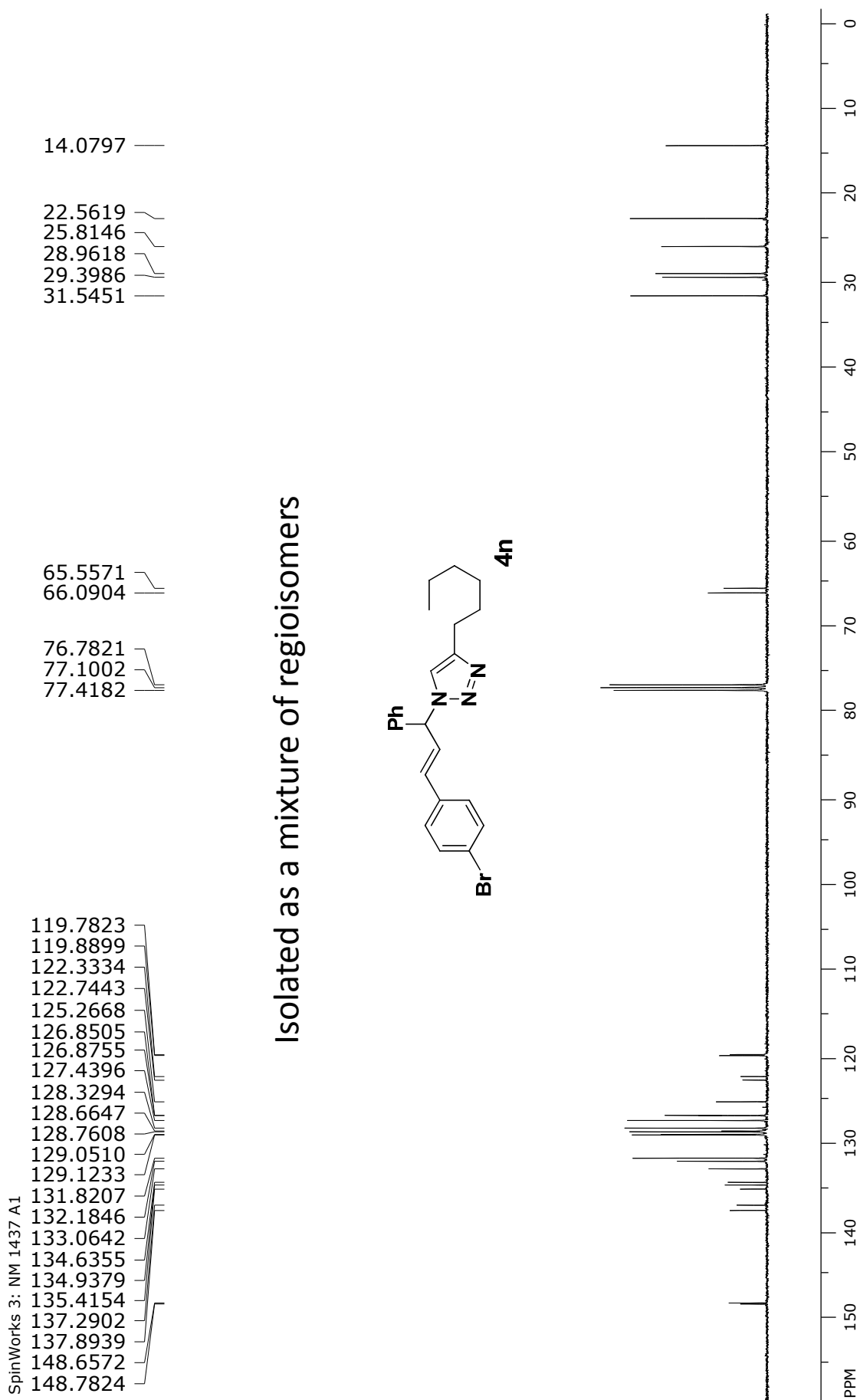


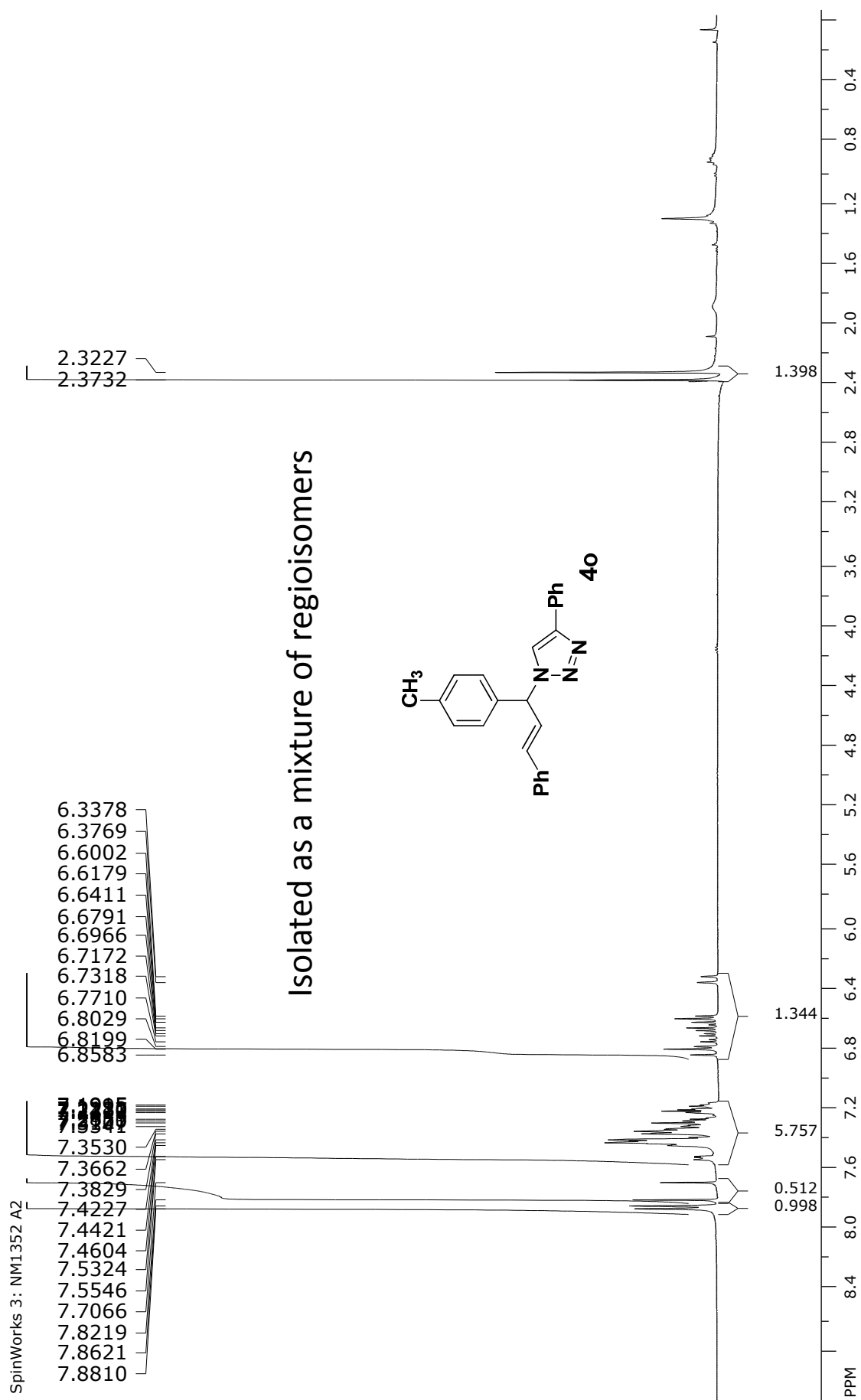


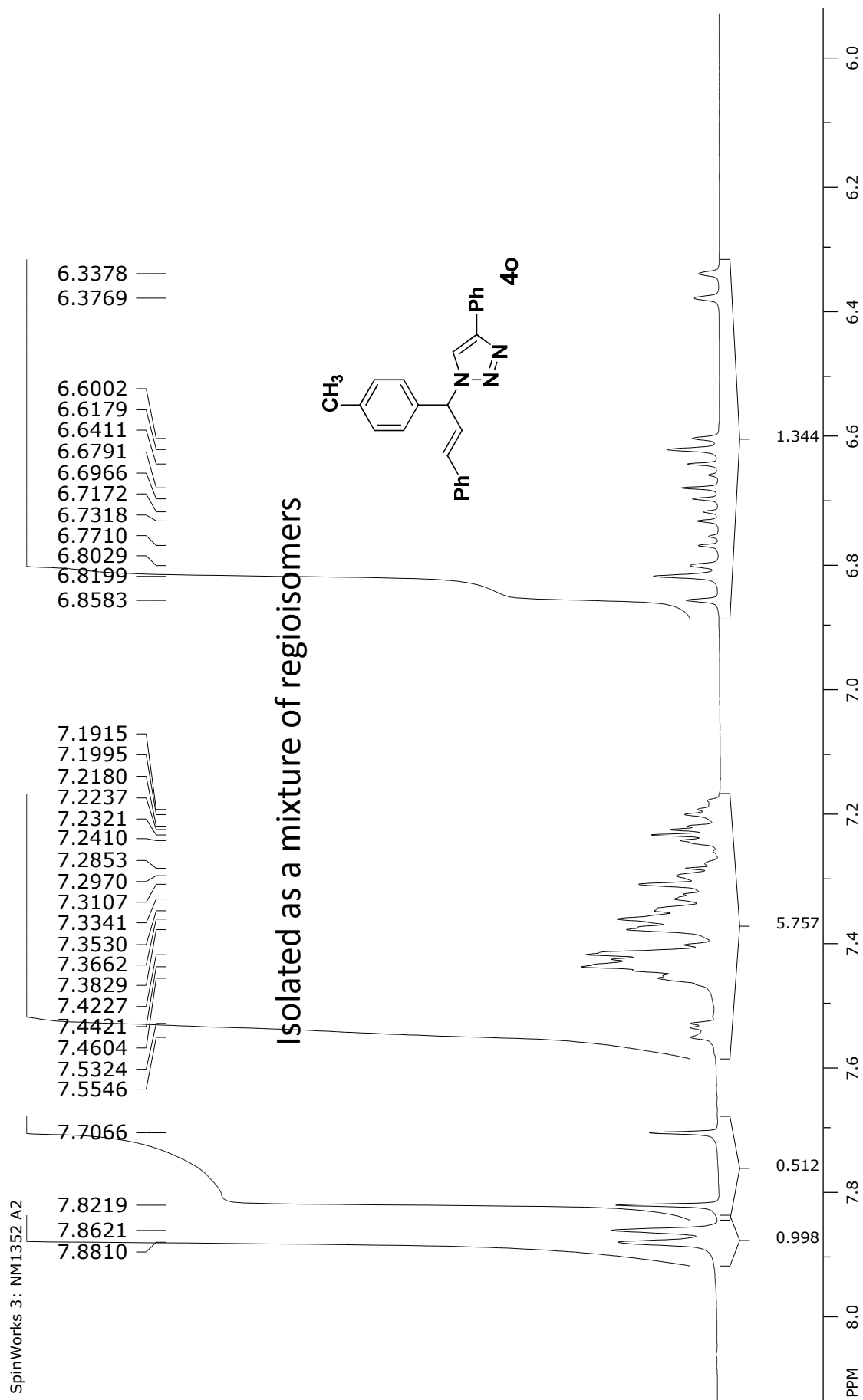


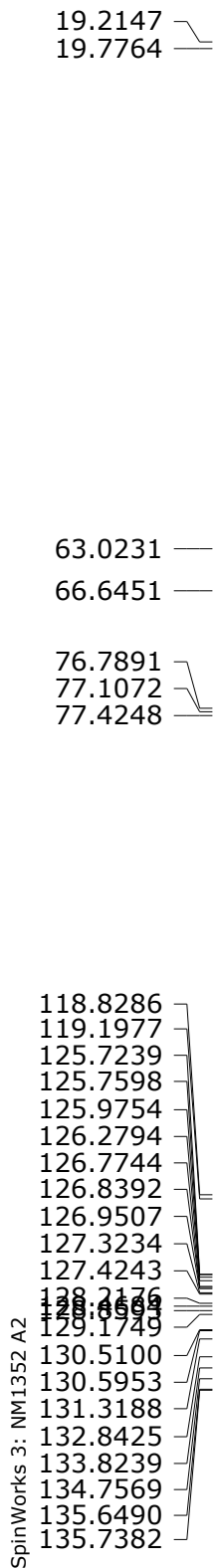










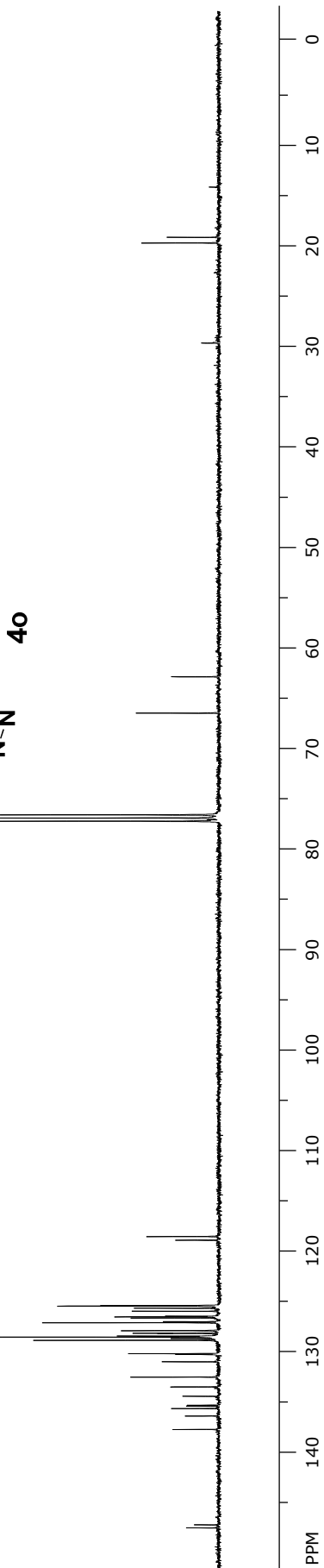
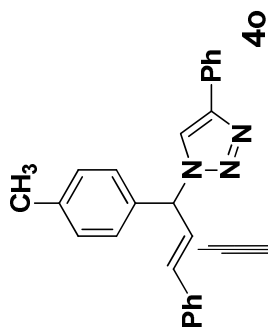


19.2147  
19.7764

63.0231  
66.6451

76.7891  
77.1072  
77.4248

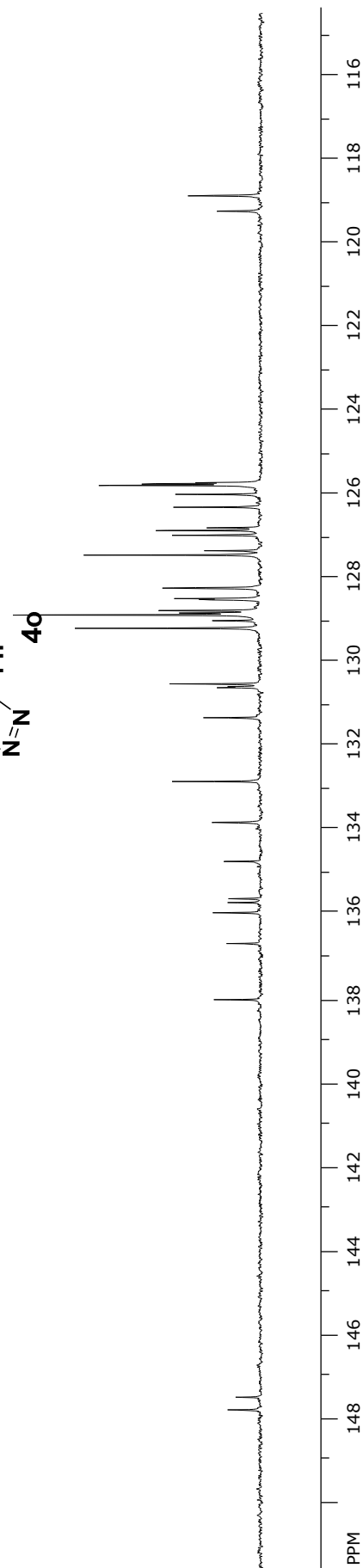
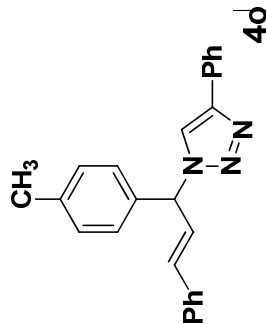
## Isolated as a mixture of regioisomers



SpinWorks 3: NM1352 A2

147.5723  
147.8785118.8286  
119.1977125.7239  
125.7598  
125.9754  
126.2794  
126.7744  
126.8392  
126.9507  
127.3234  
127.4243  
128.2176  
128.4684  
128.8593  
129.1749  
130.5100  
130.5953  
131.3188  
132.8425  
133.8239  
134.7569  
135.6490  
135.7382  
135.9843  
136.7215  
138.0641

## Isolated as a mixture of regioisomers



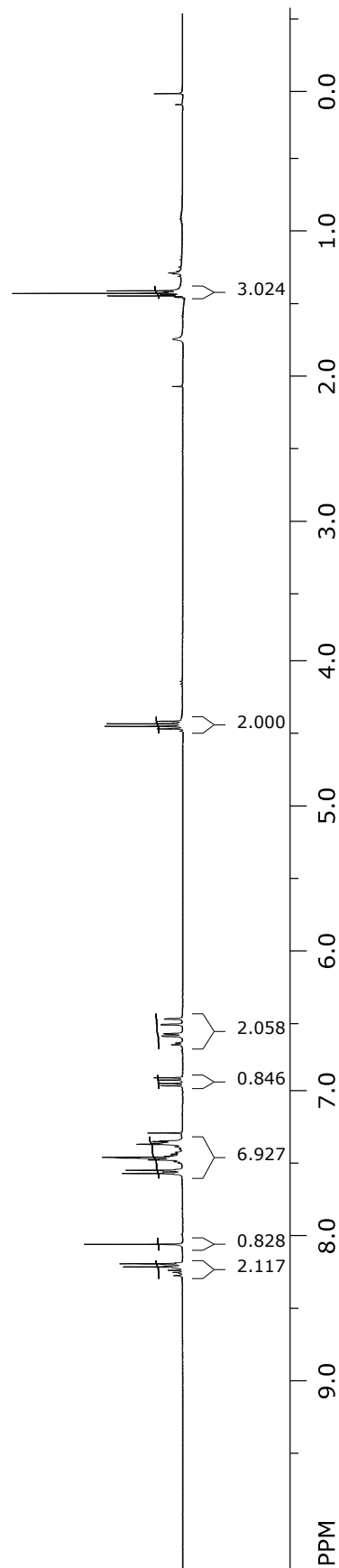
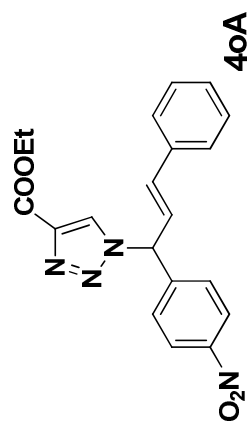
SpinWorks 3: NM 2210 A

1.3920  
1.4098  
1.42764.4041  
4.4219  
4.4398  
4.45766.4855  
6.4882  
6.5254  
6.5281  
6.5901  
6.5928  
6.6063  
6.6089  
6.6552  
6.6660  
6.6686

0.9900

7.3855  
7.3855  
7.5510  
7.5639  
7.5685  
7.5742  
8.0642  
8.1944  
8.2003  
8.2049  
8.2176  
8.2224  
8.2280  
8.2459  
8.2610  
8.2831

Isolated as a mixture of regioisomers

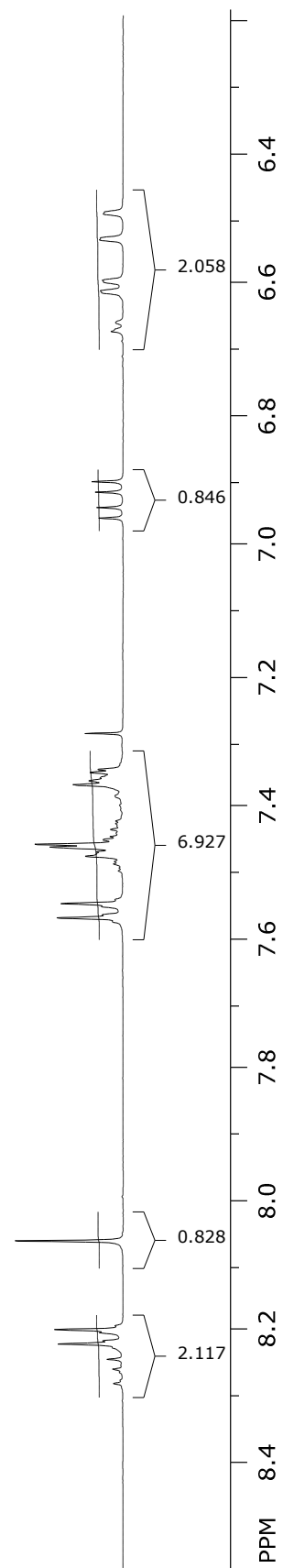
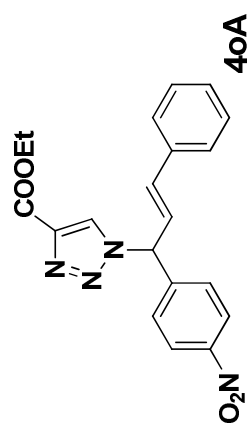




SpinWorks 3: NM 2210 A



## Isolated as a mixture of regioisomers



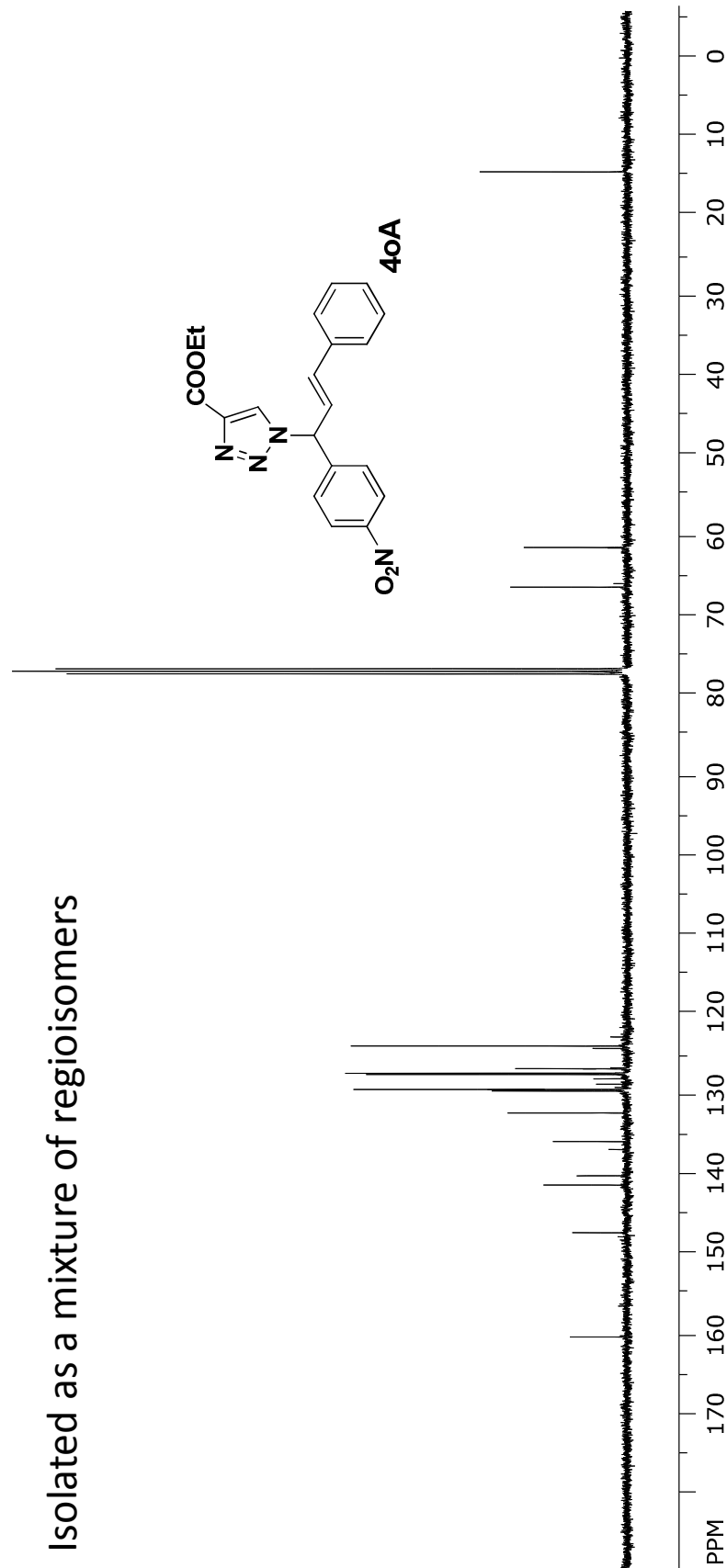
SpinWorks 3: NM 2210 A

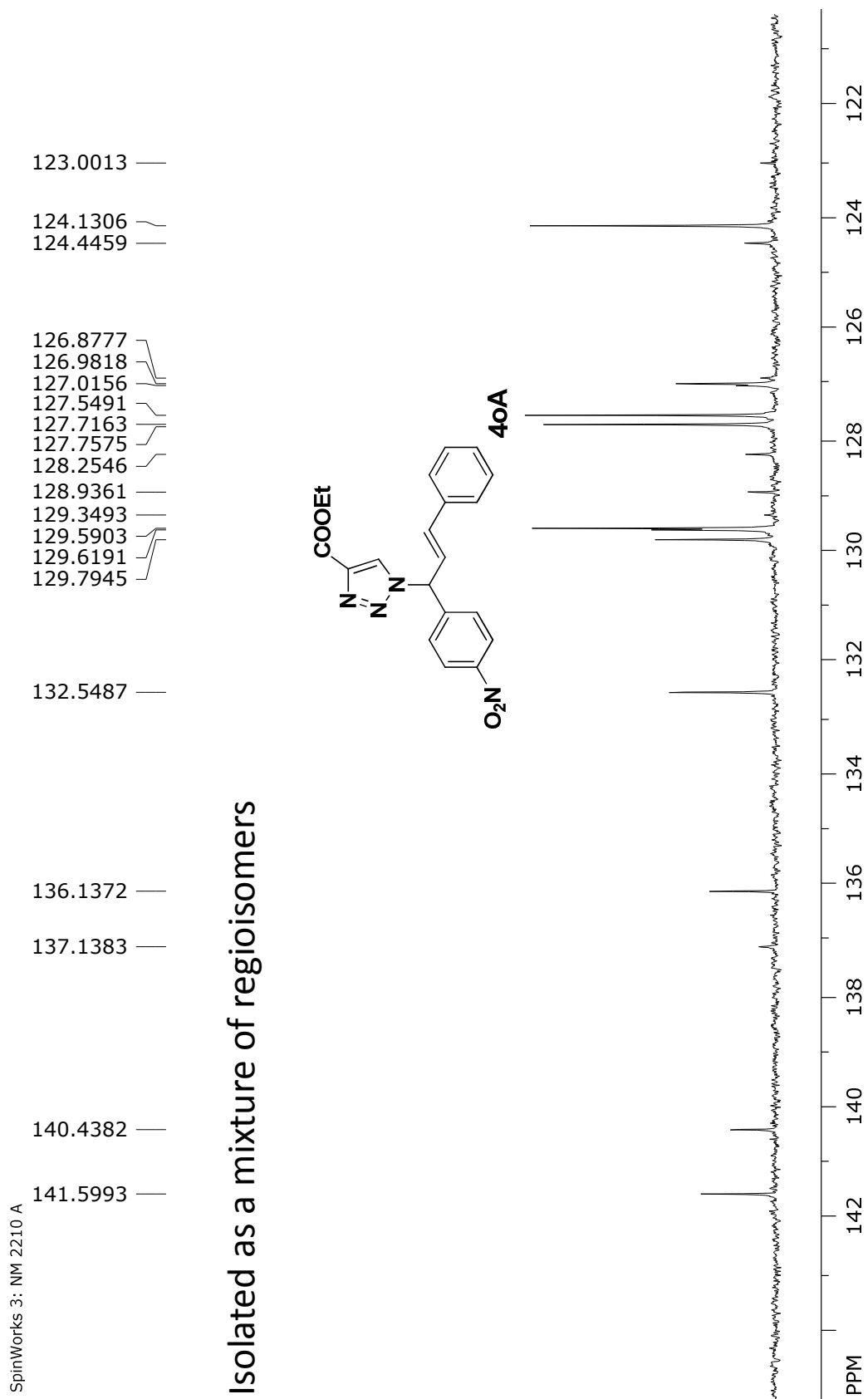
123.0013  
124.1306  
124.4459  
126.8777  
126.9818  
127.0156  
127.5491  
127.7163  
127.7575  
128.2546  
128.9361  
129.3493  
129.5903  
129.6191  
129.7945  
132.5487  
136.1372  
137.1383  
140.4382  
141.5993  
147.5918  
160.6892

14.3313

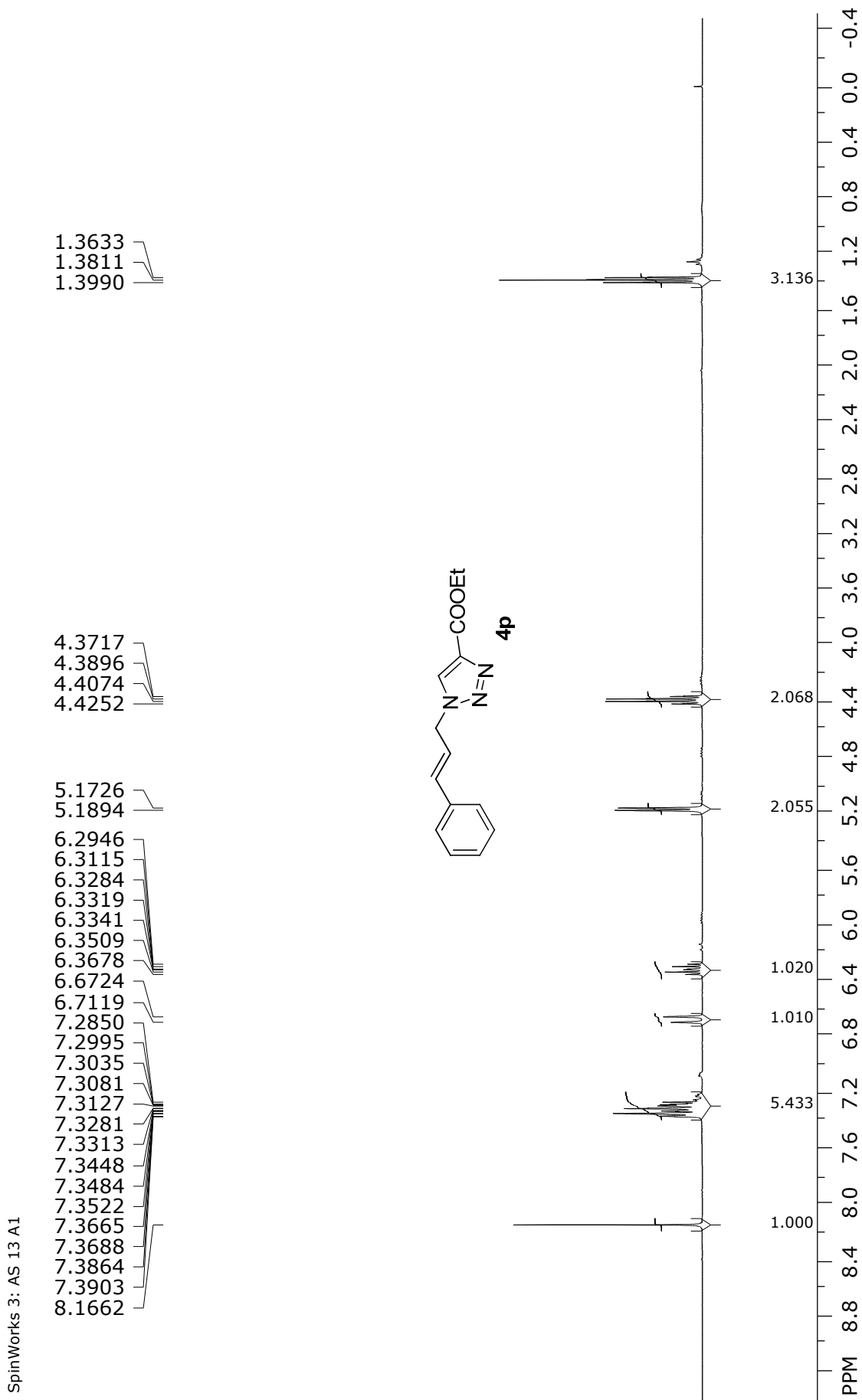
61.5143  
61.5865  
66.0595  
66.5002  
76.7532  
77.0712  
77.3890

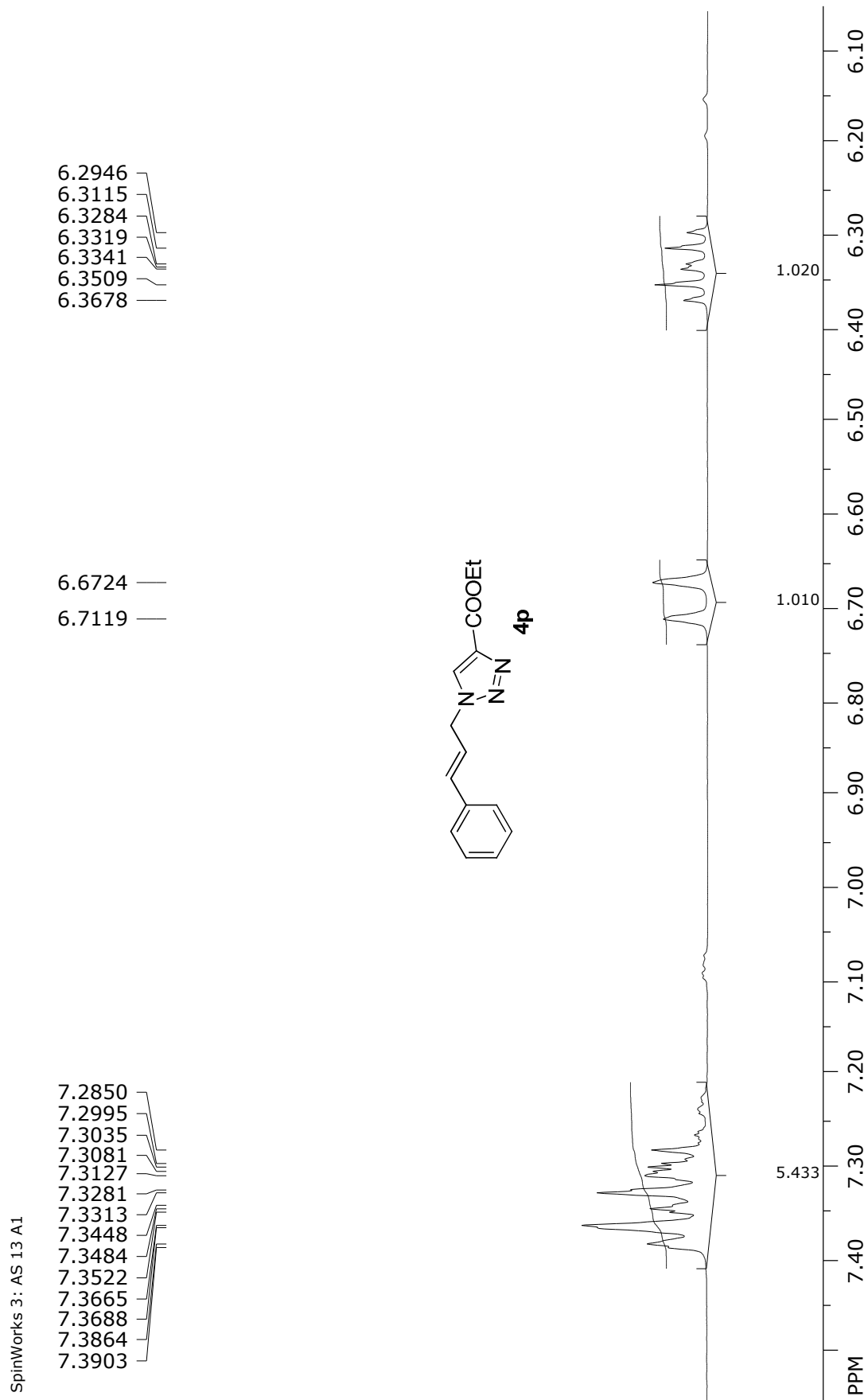
Isolated as a mixture of regioisomers



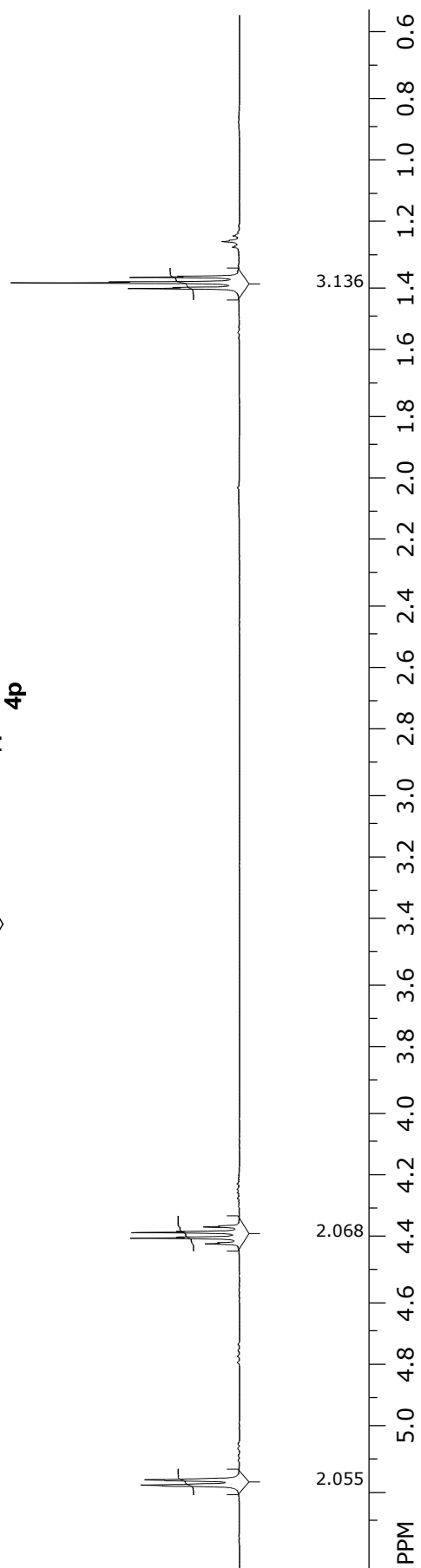
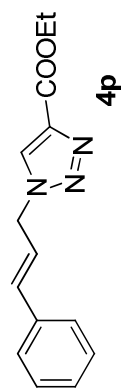


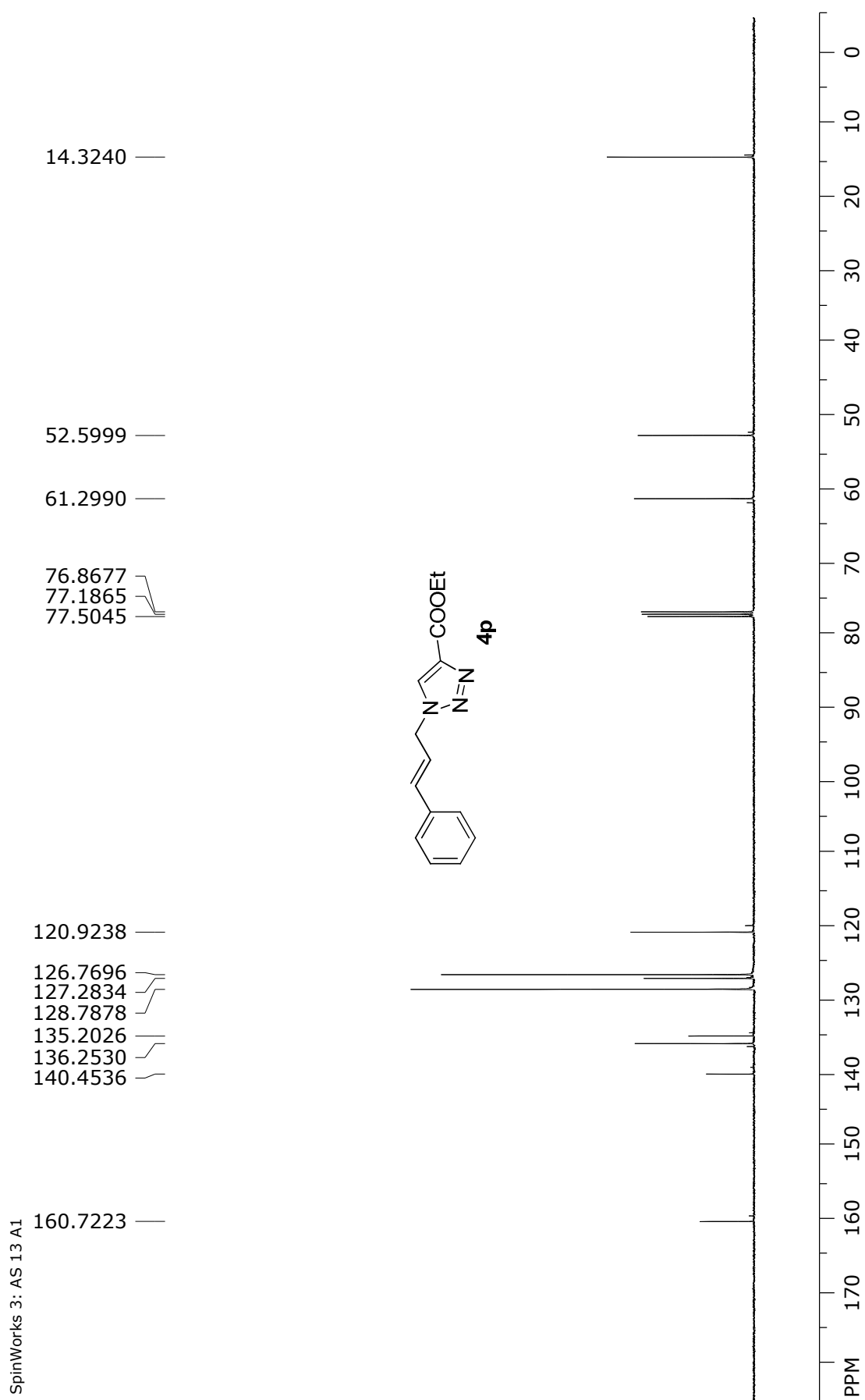
Isolated as a mixture of regioisomers

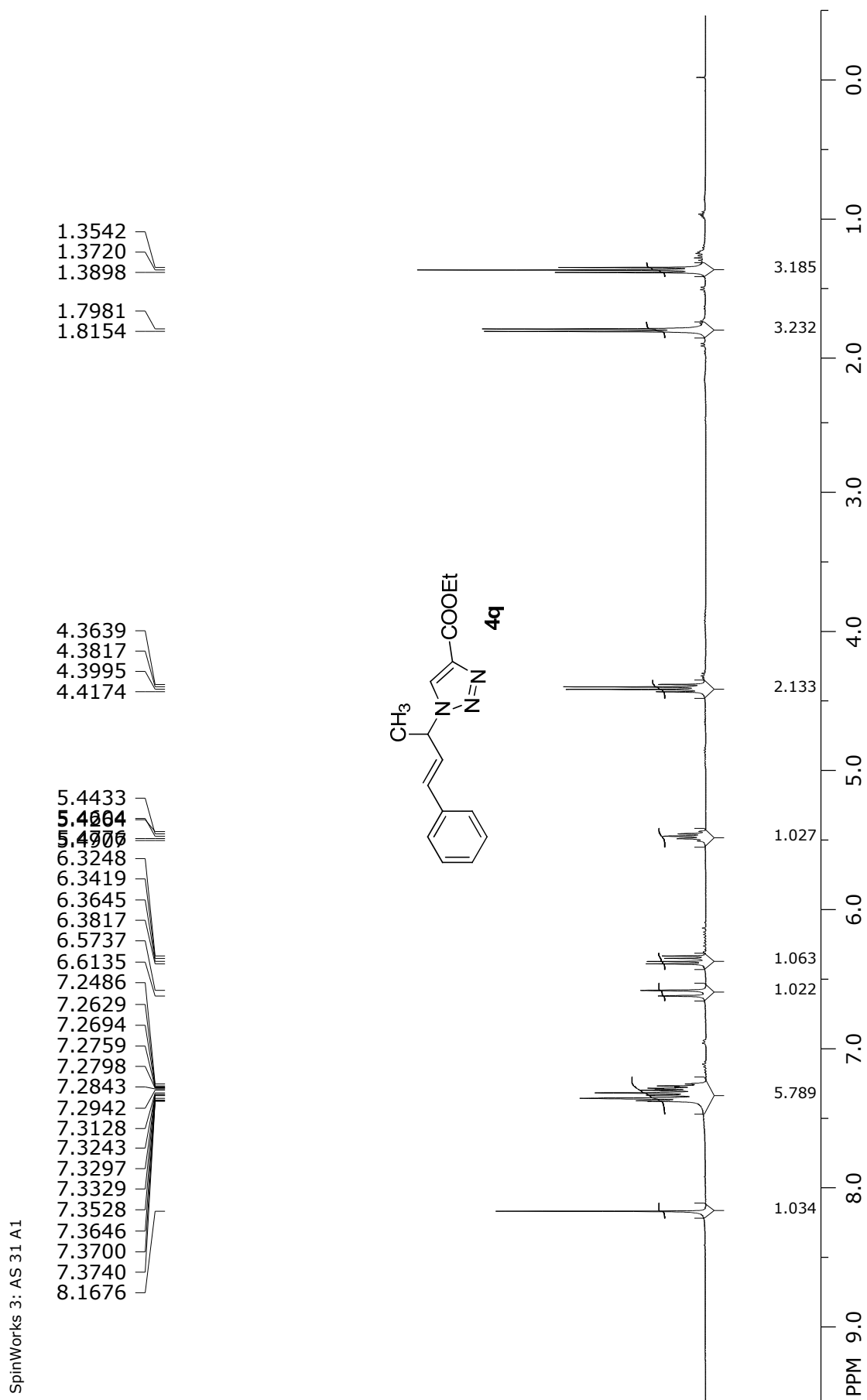




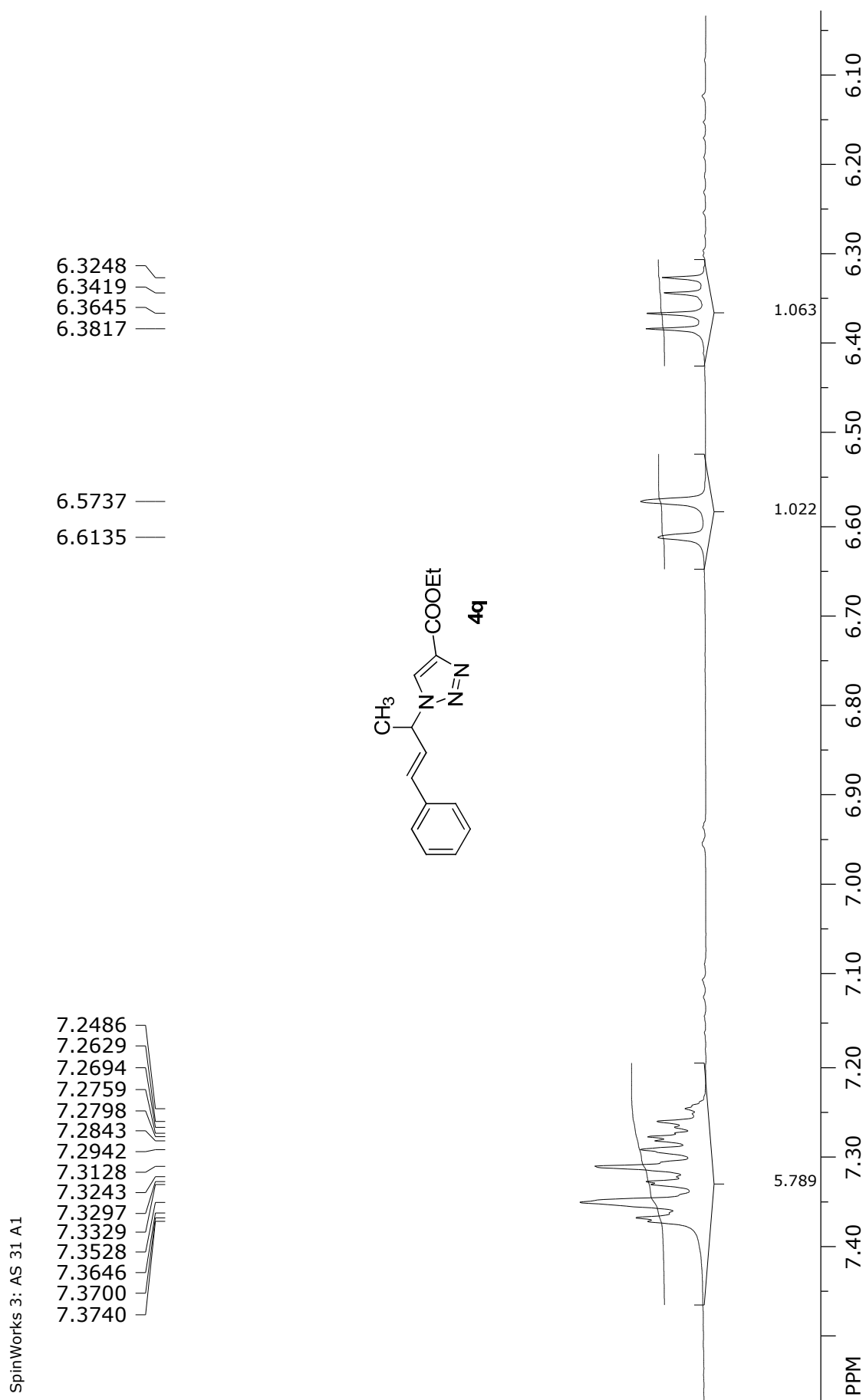
SpinWorks 3: AS 13 A1

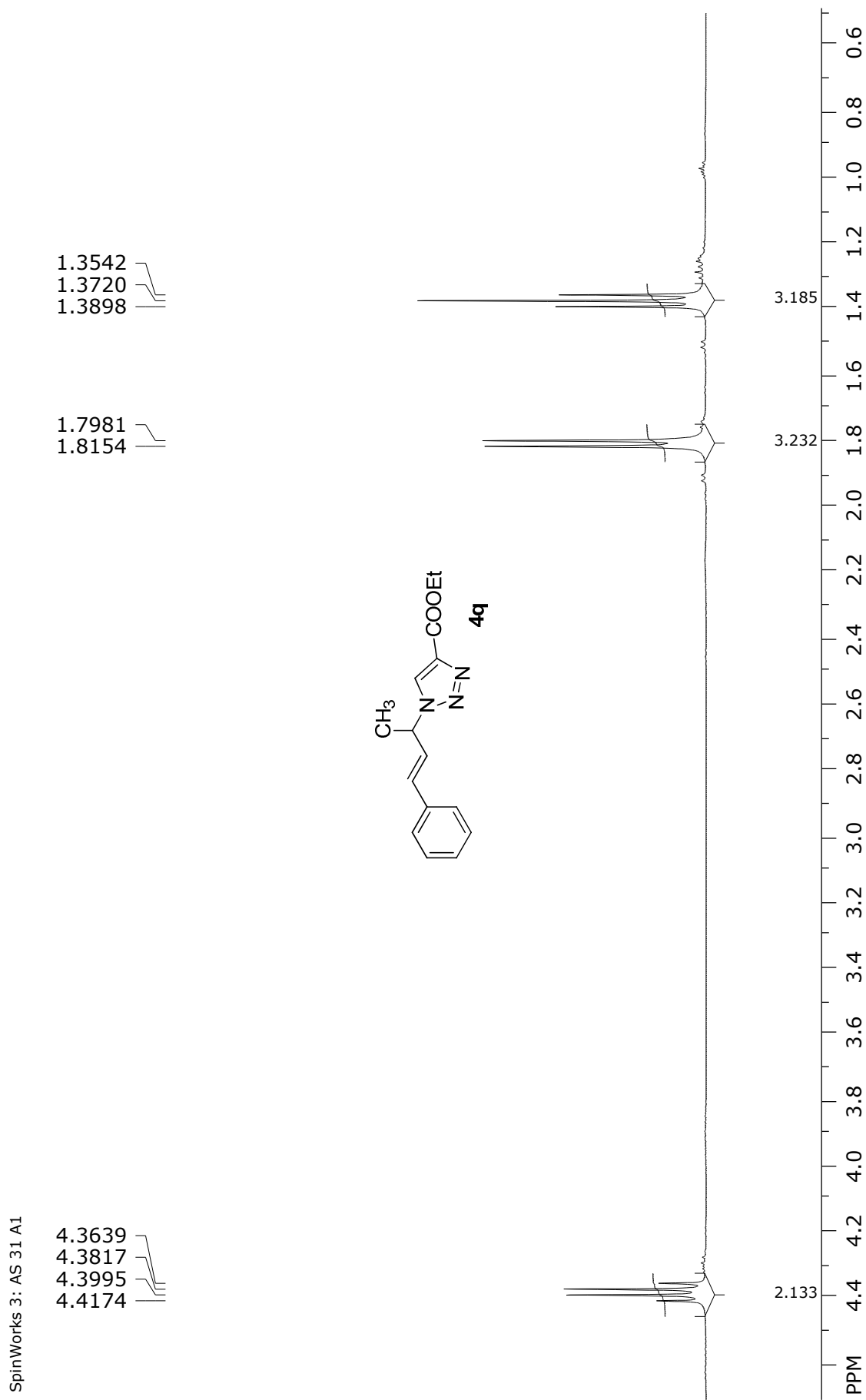
5.1726  
5.18944.3717  
4.3896  
4.4074  
4.42521.3633  
1.3811  
1.3990

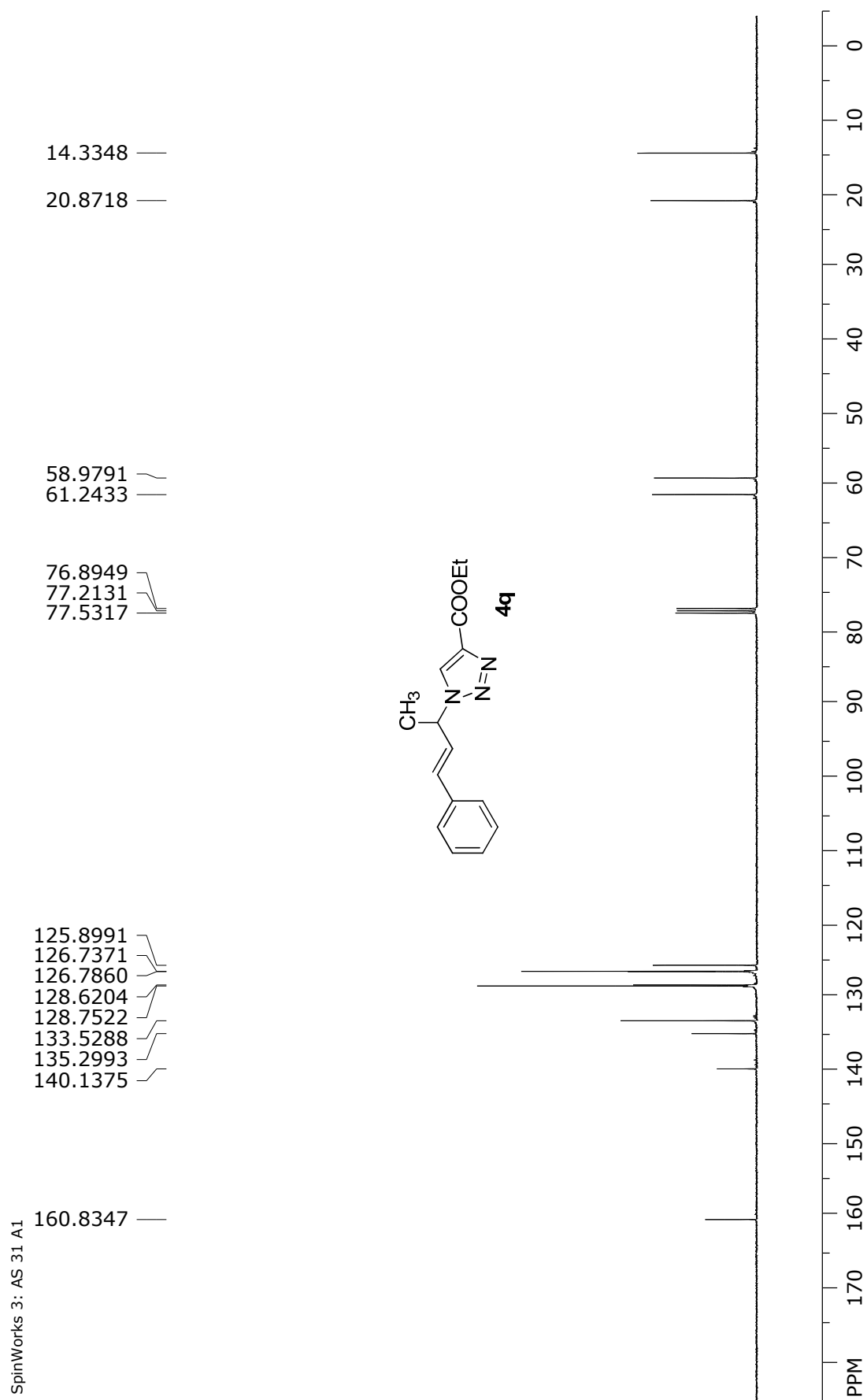




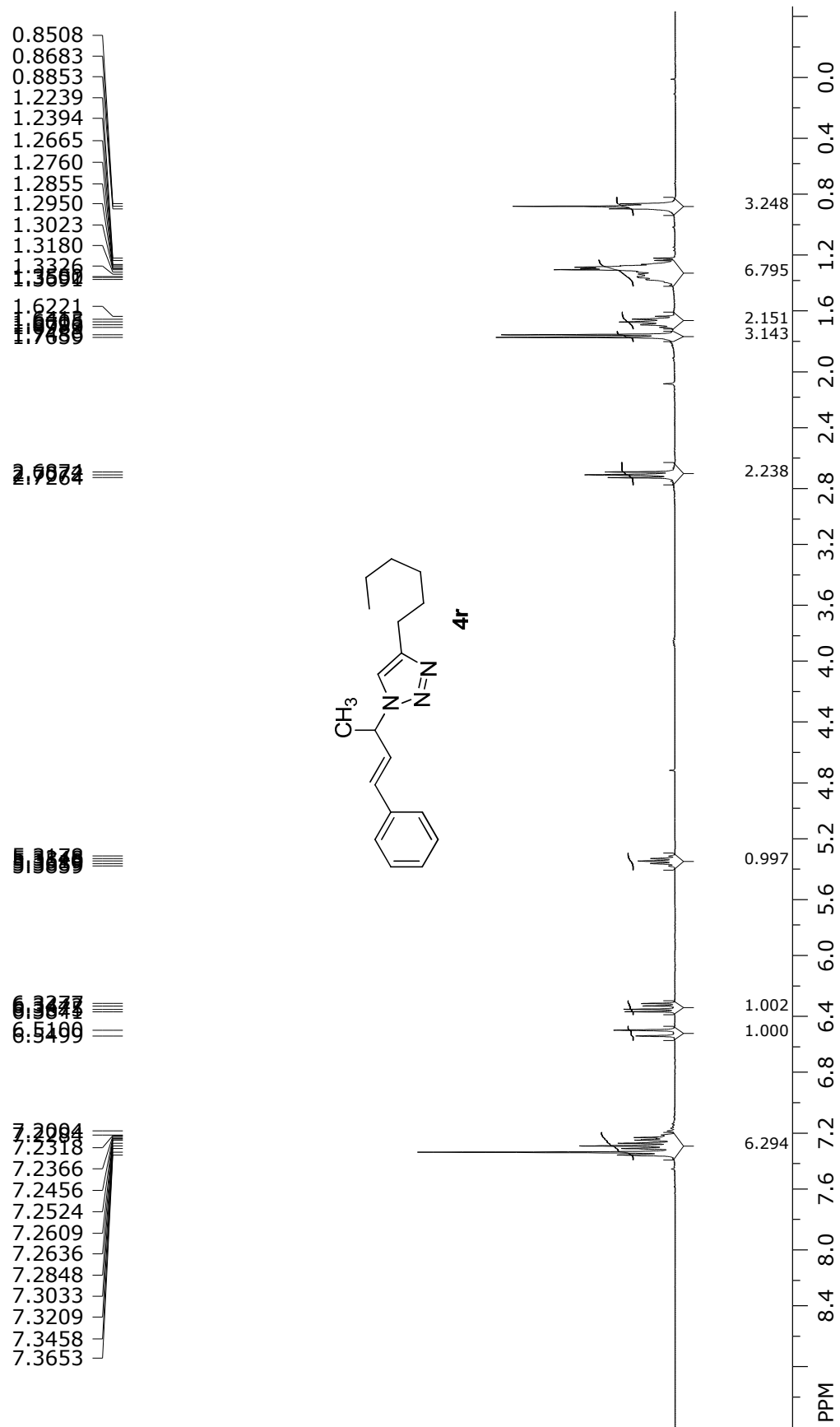


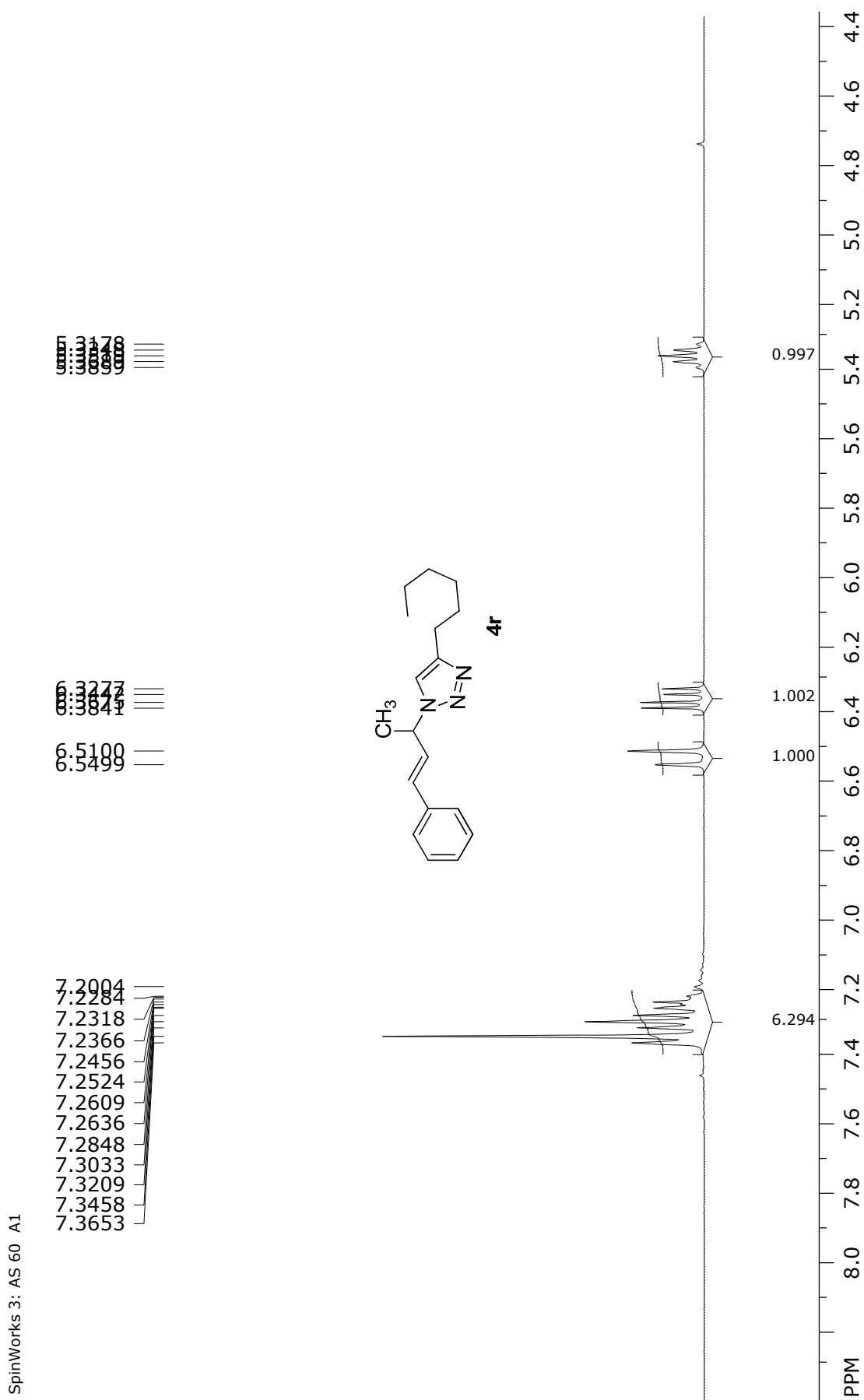




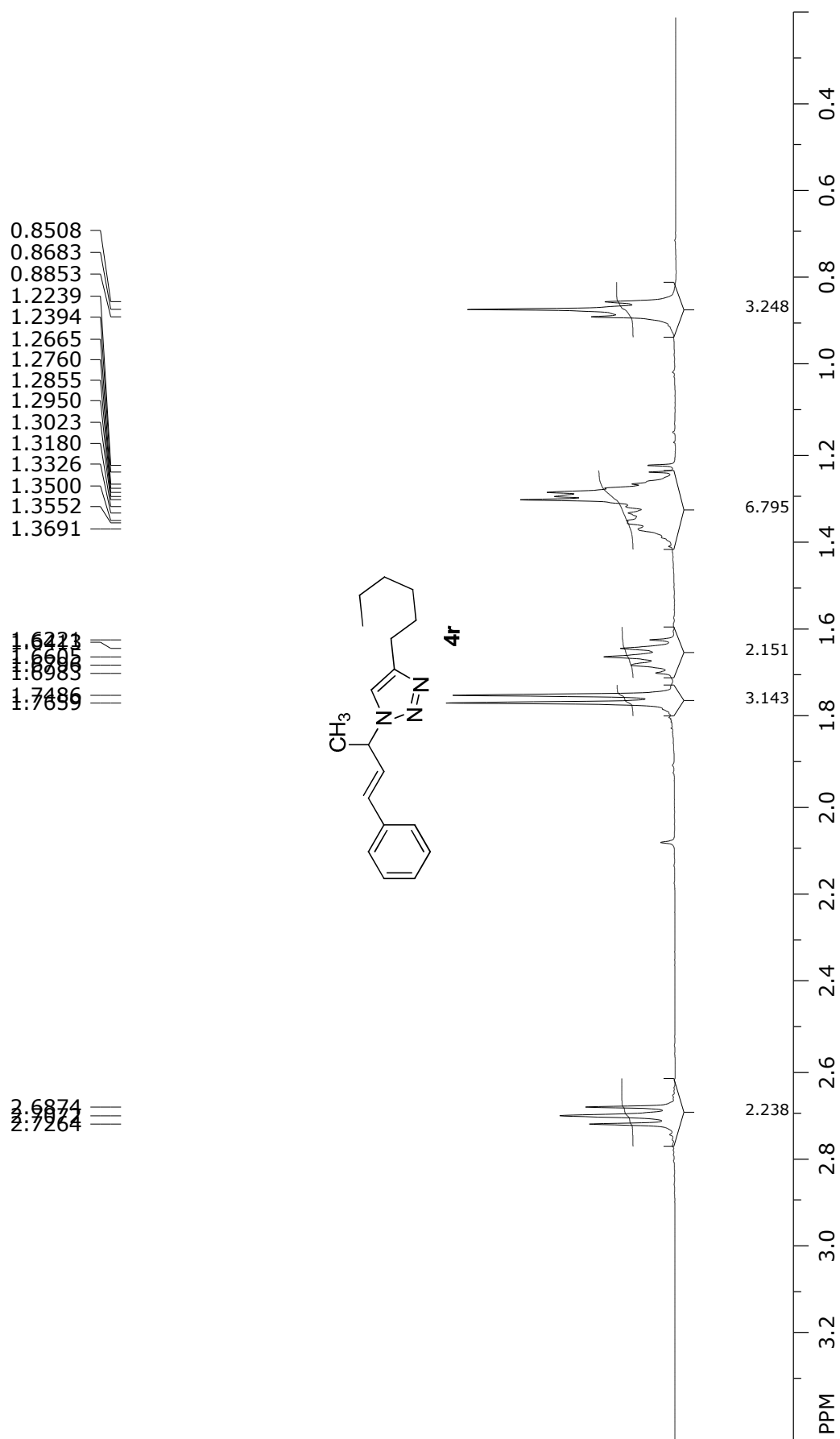


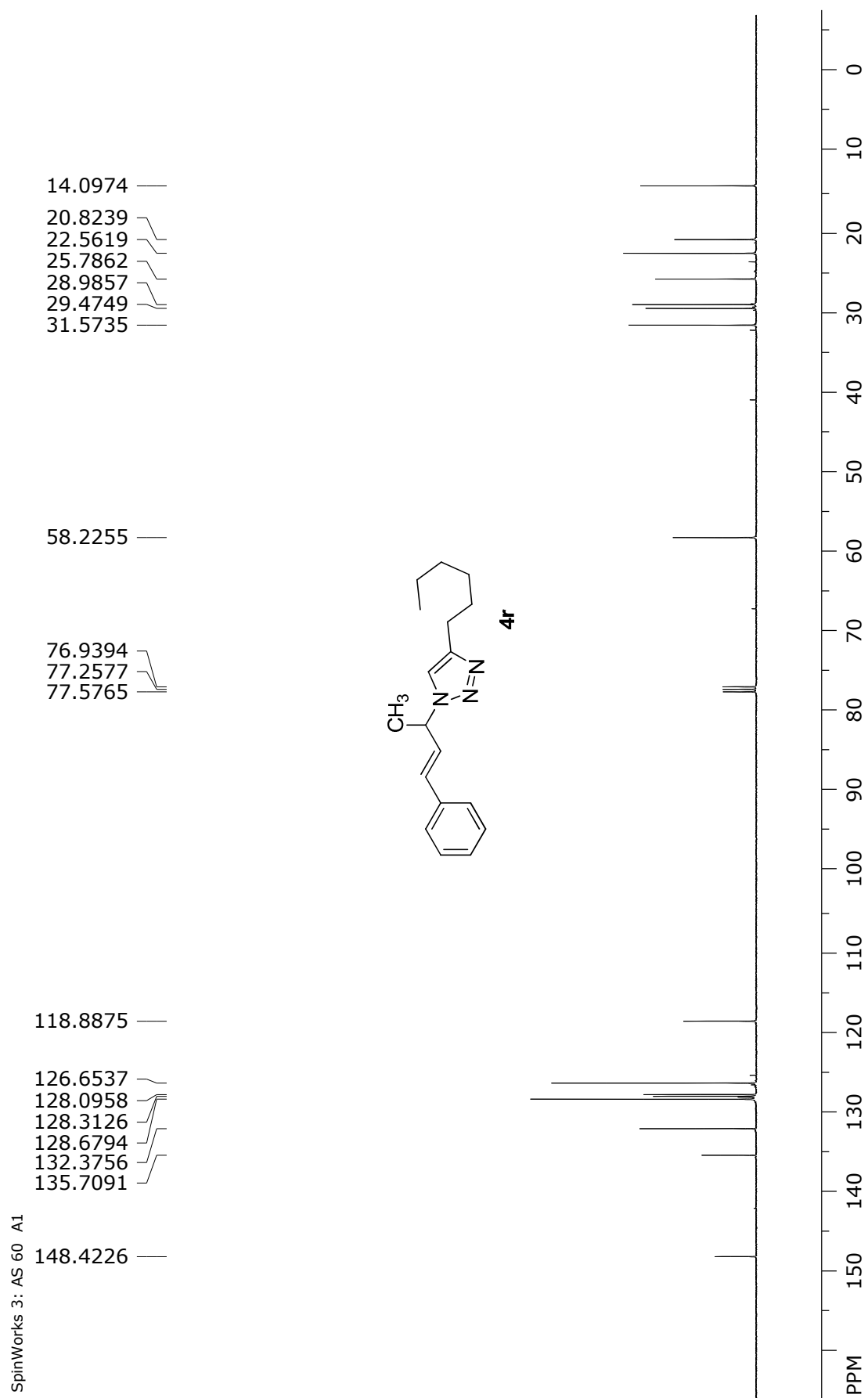
SpinWorks 3: AS 60 A1



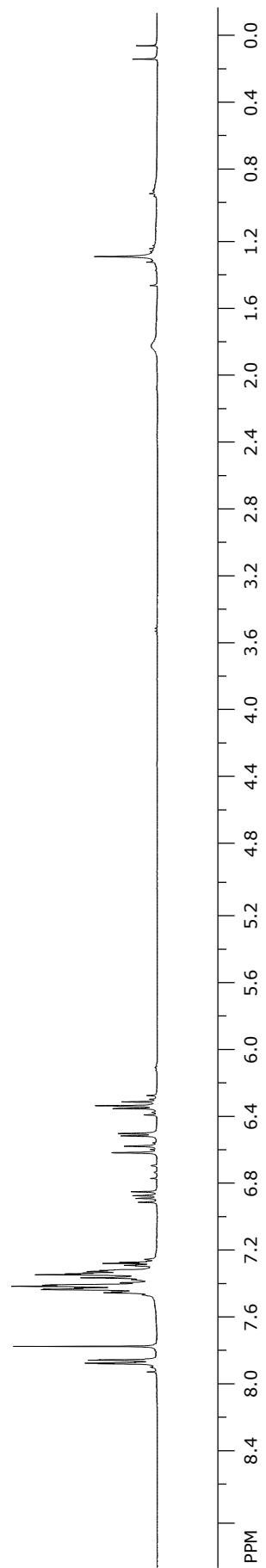
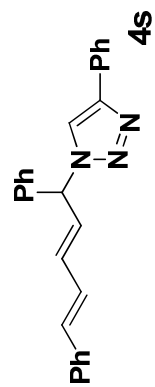
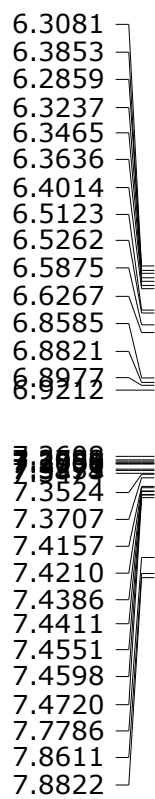


SpinWorks 3: AS 60 A1

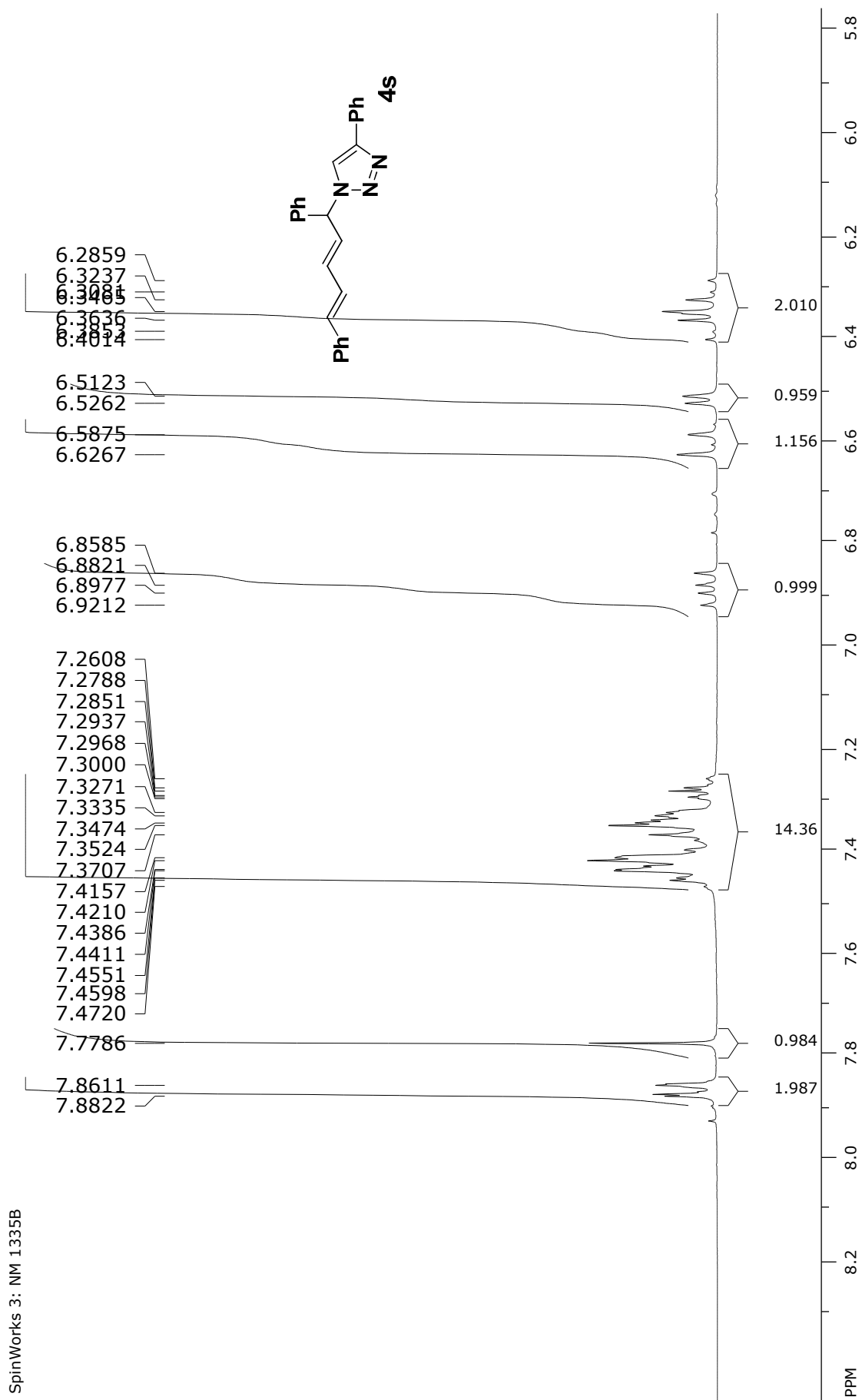


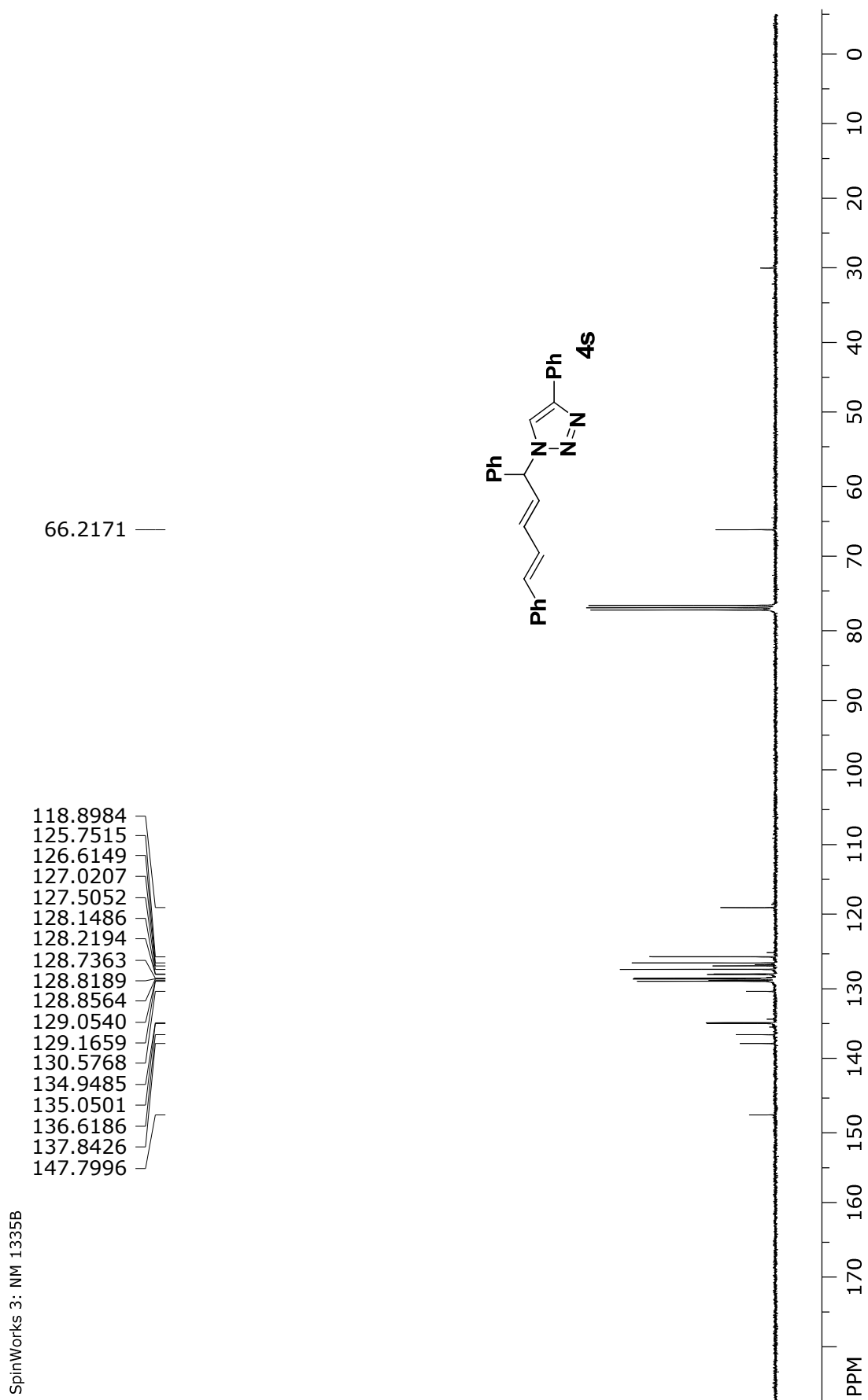


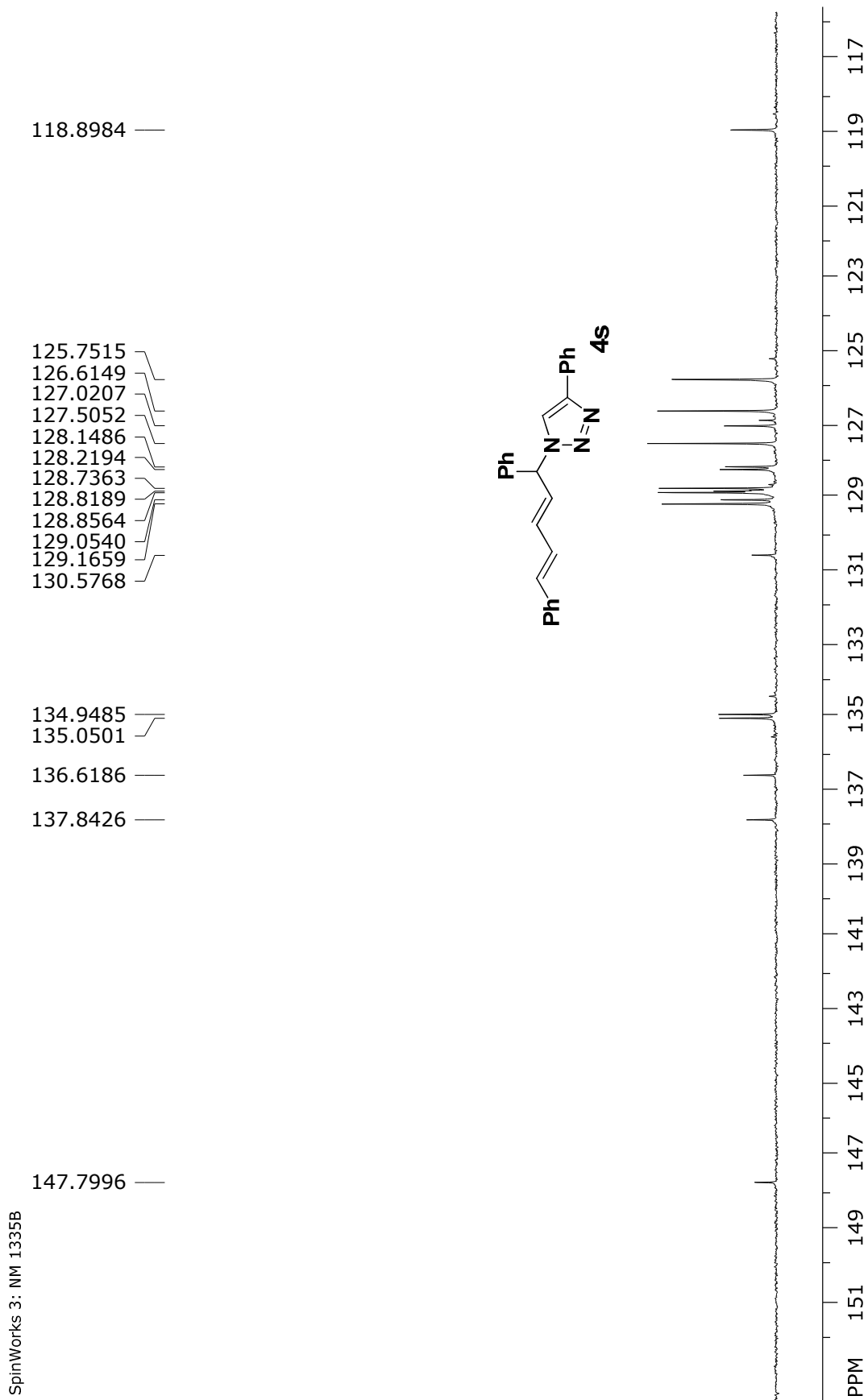
SpinWorks 3: NM 1335B



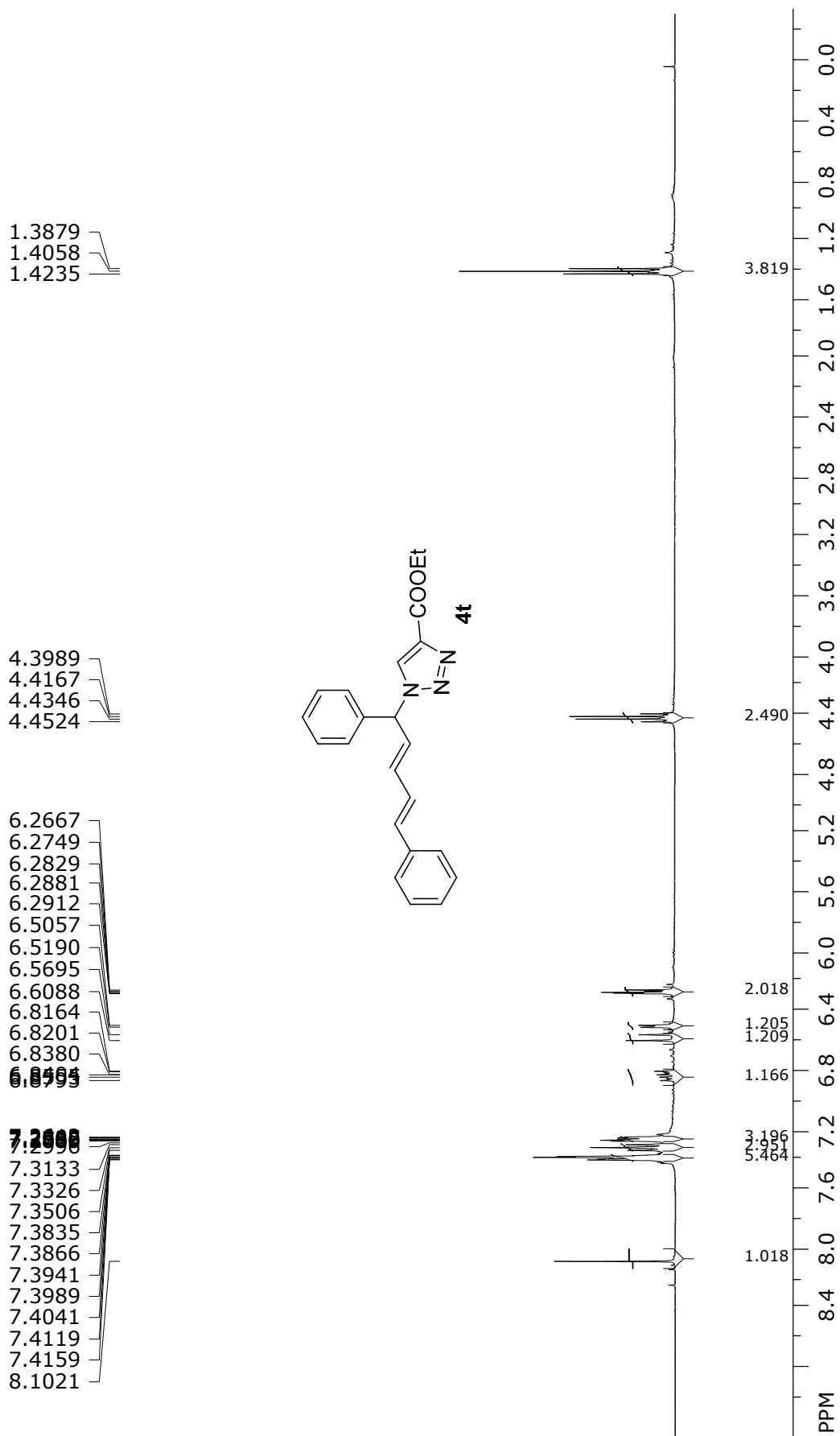


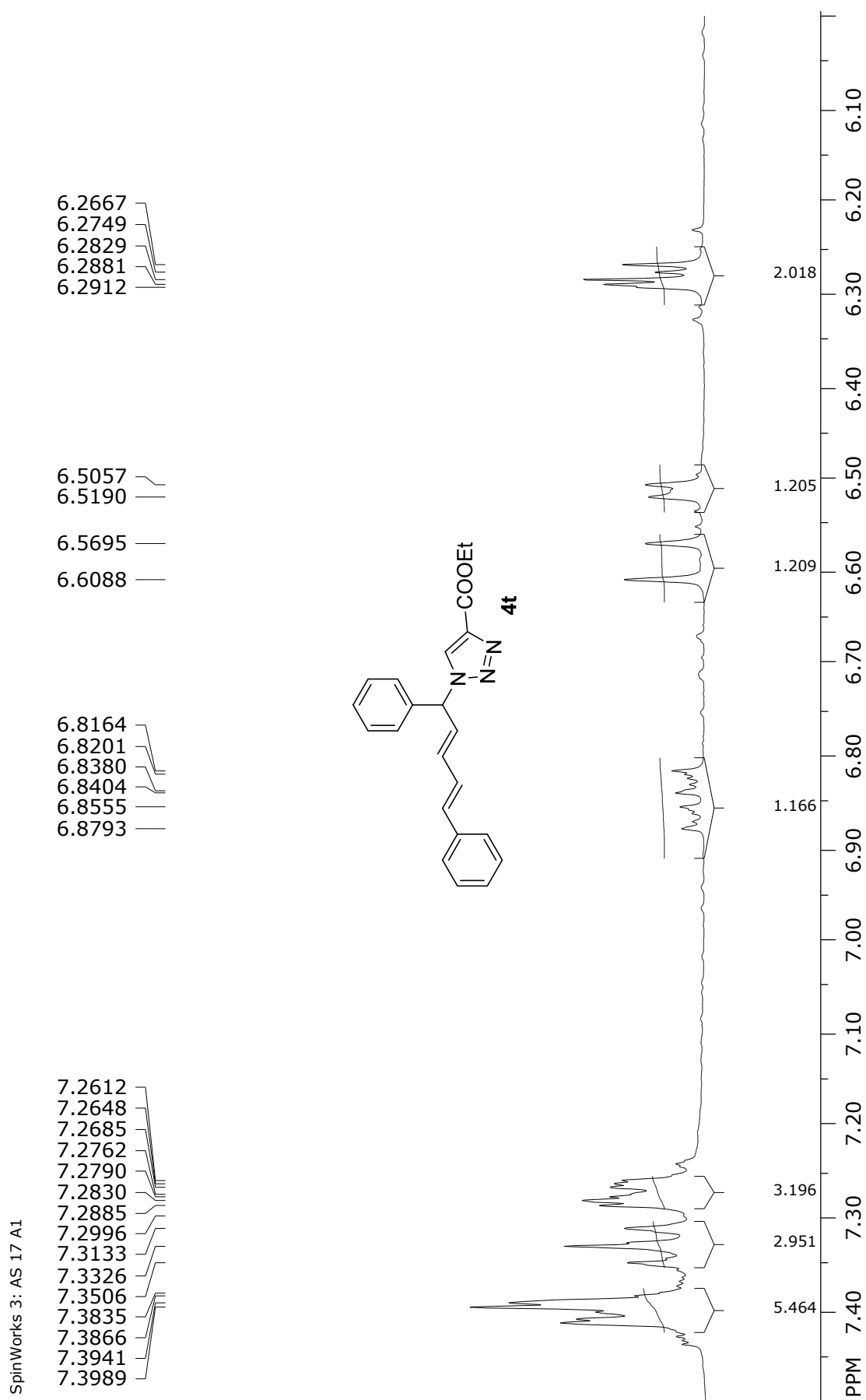


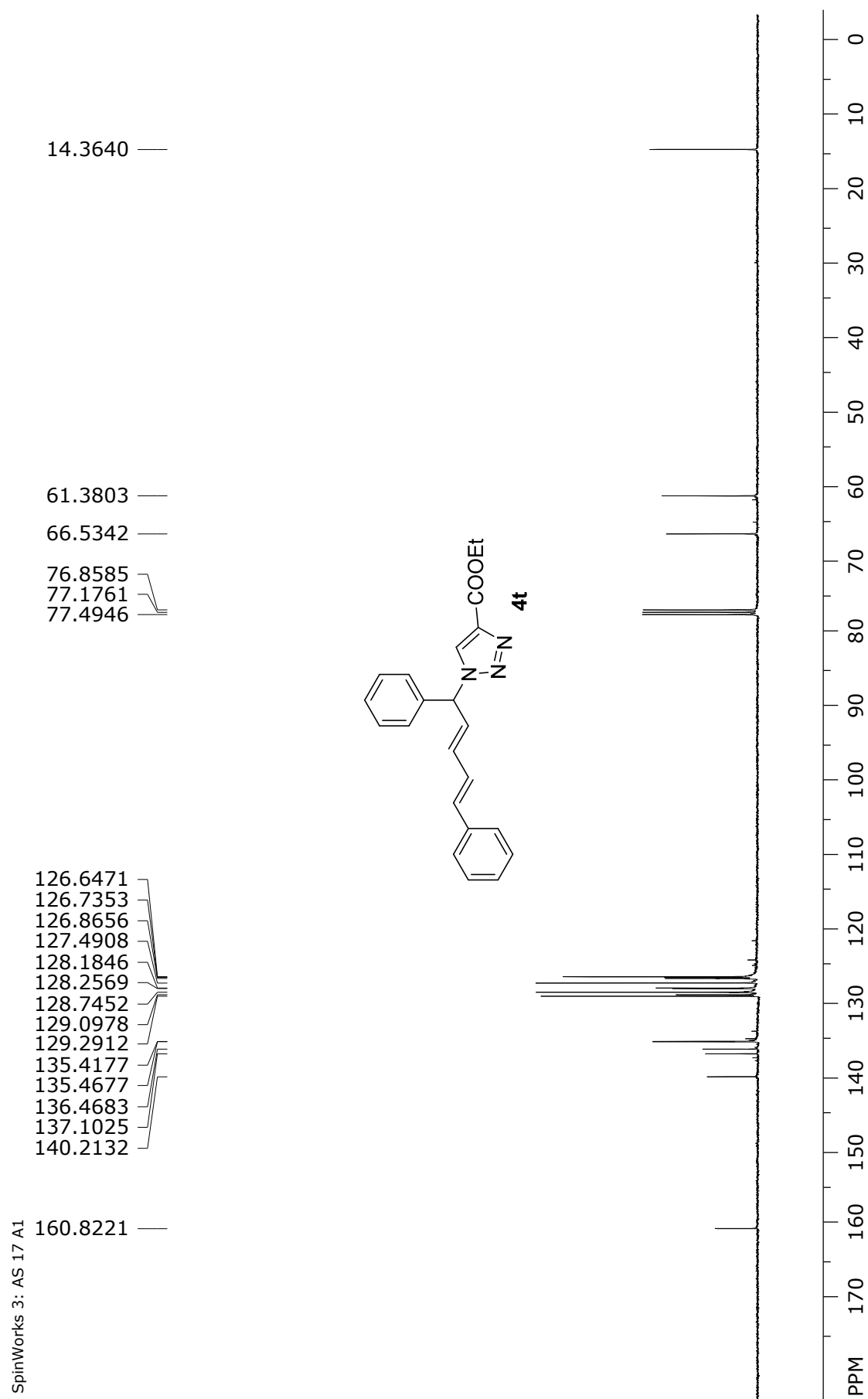


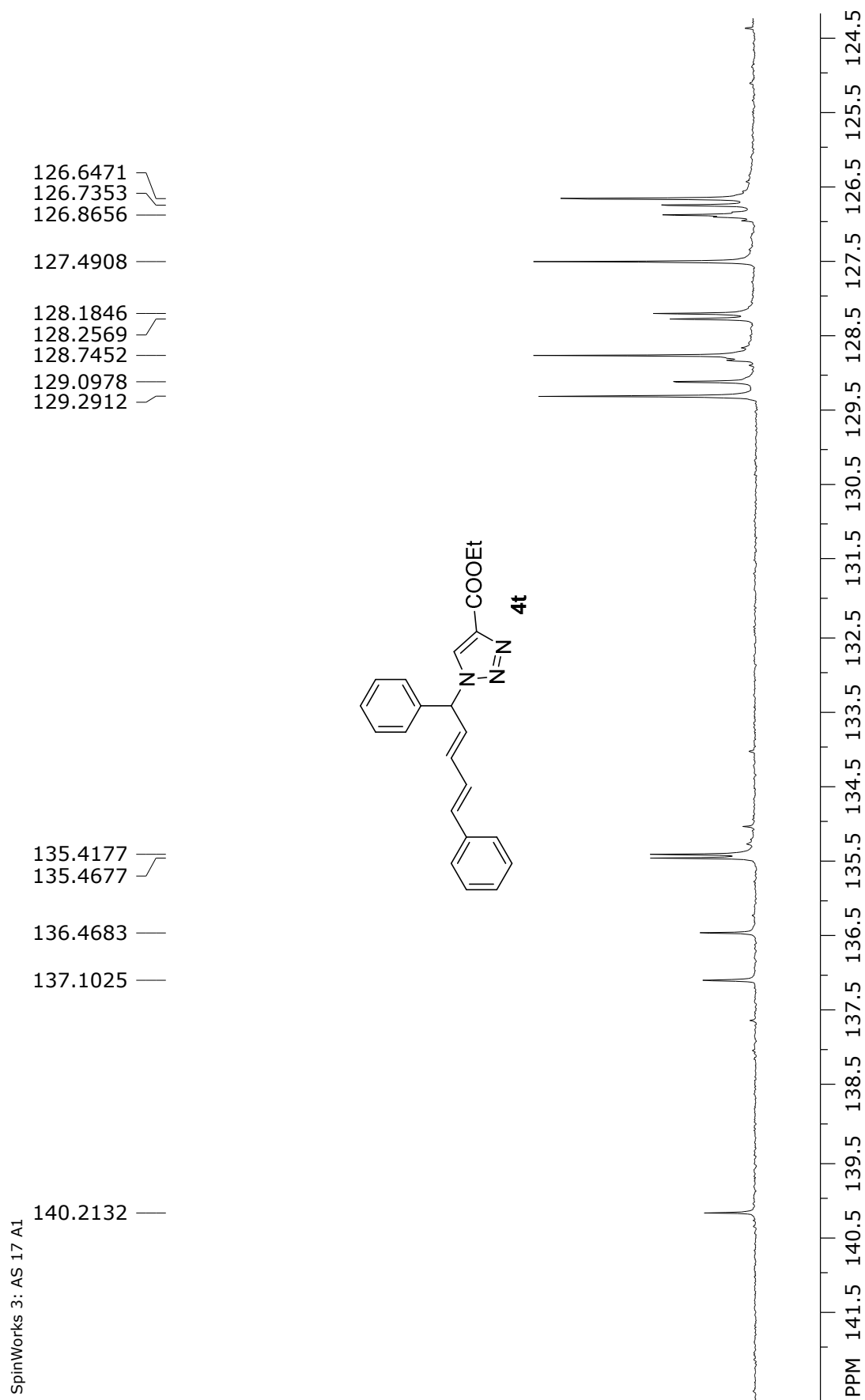


SpinWorks 3: AS 17 A1



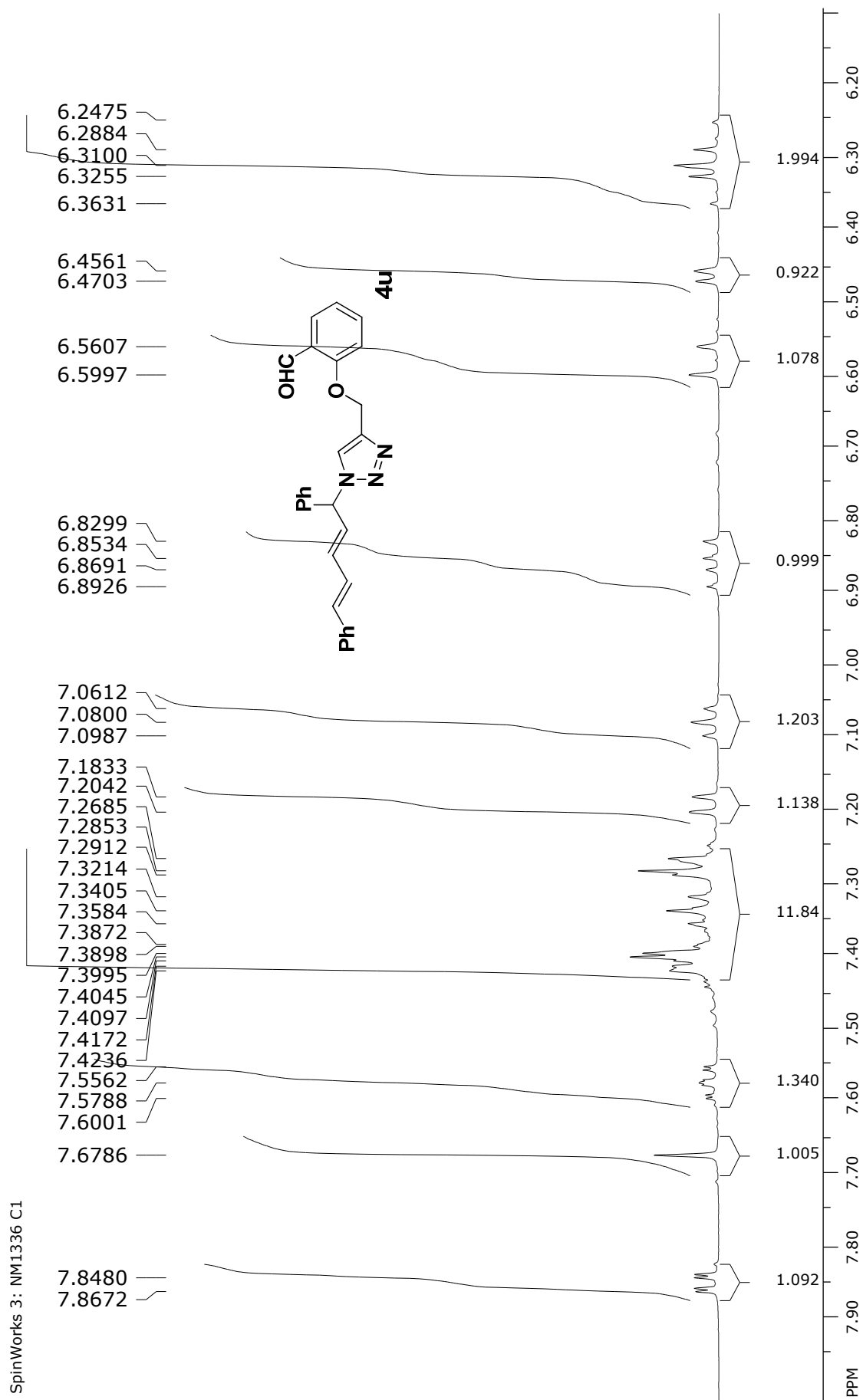


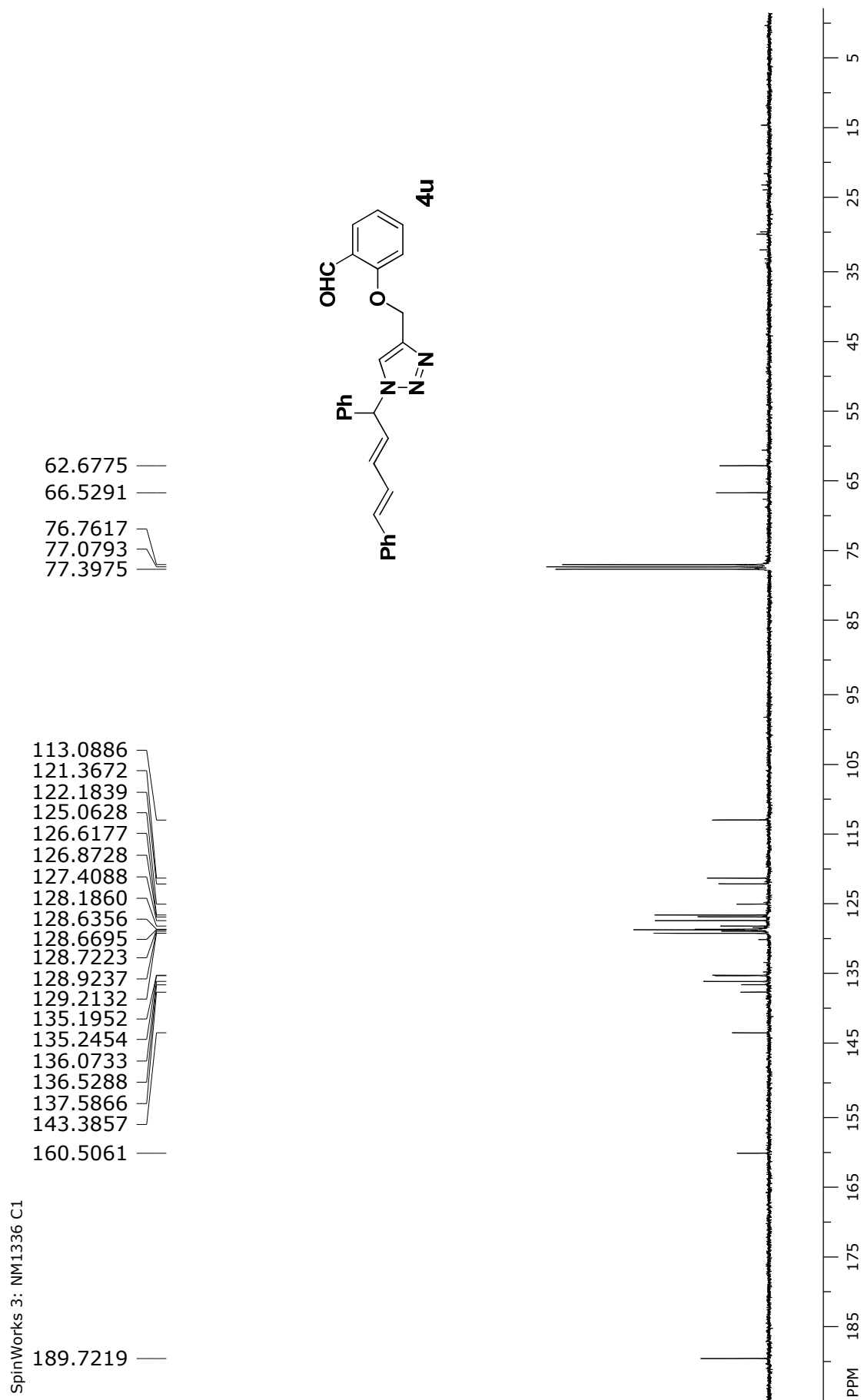


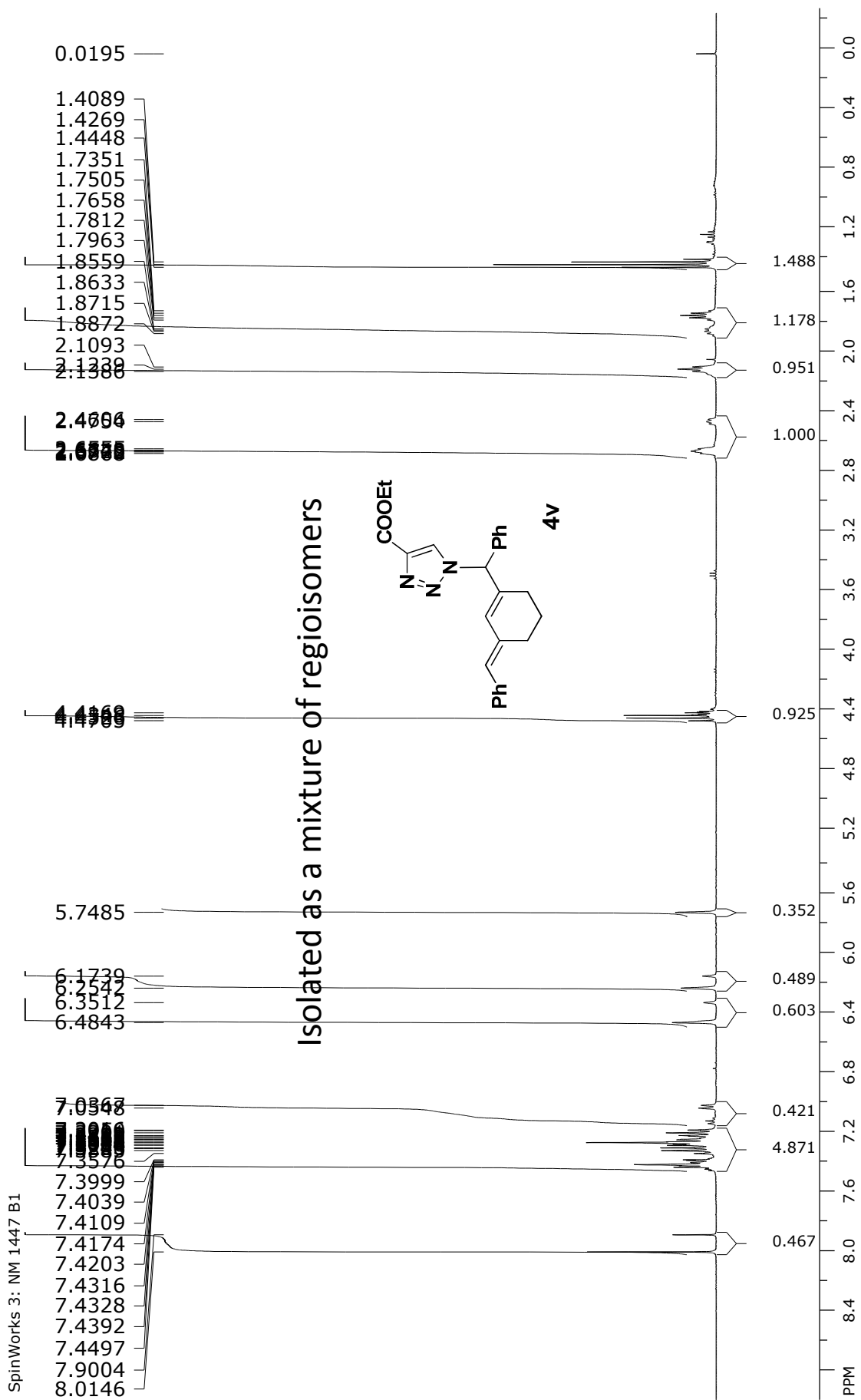


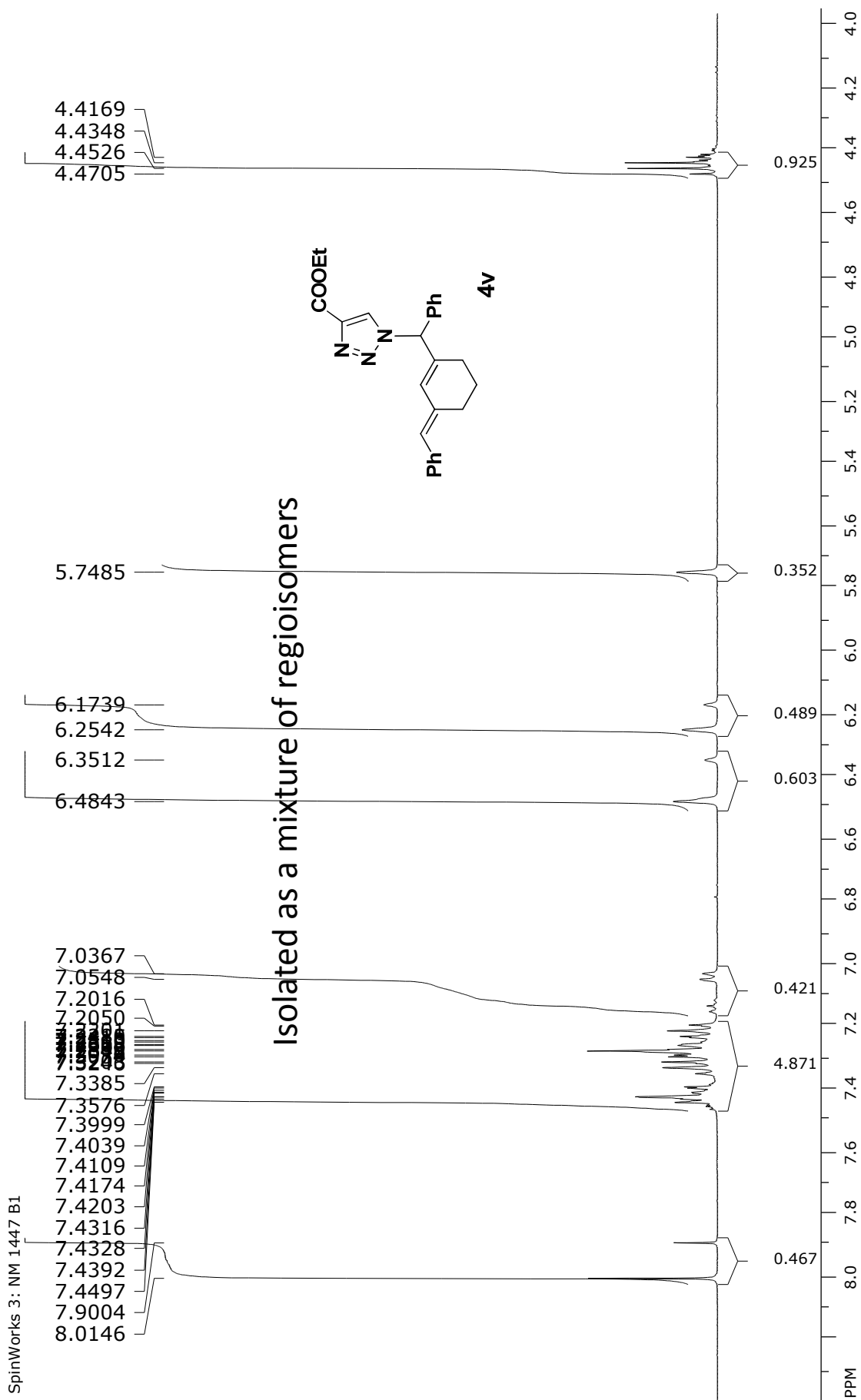


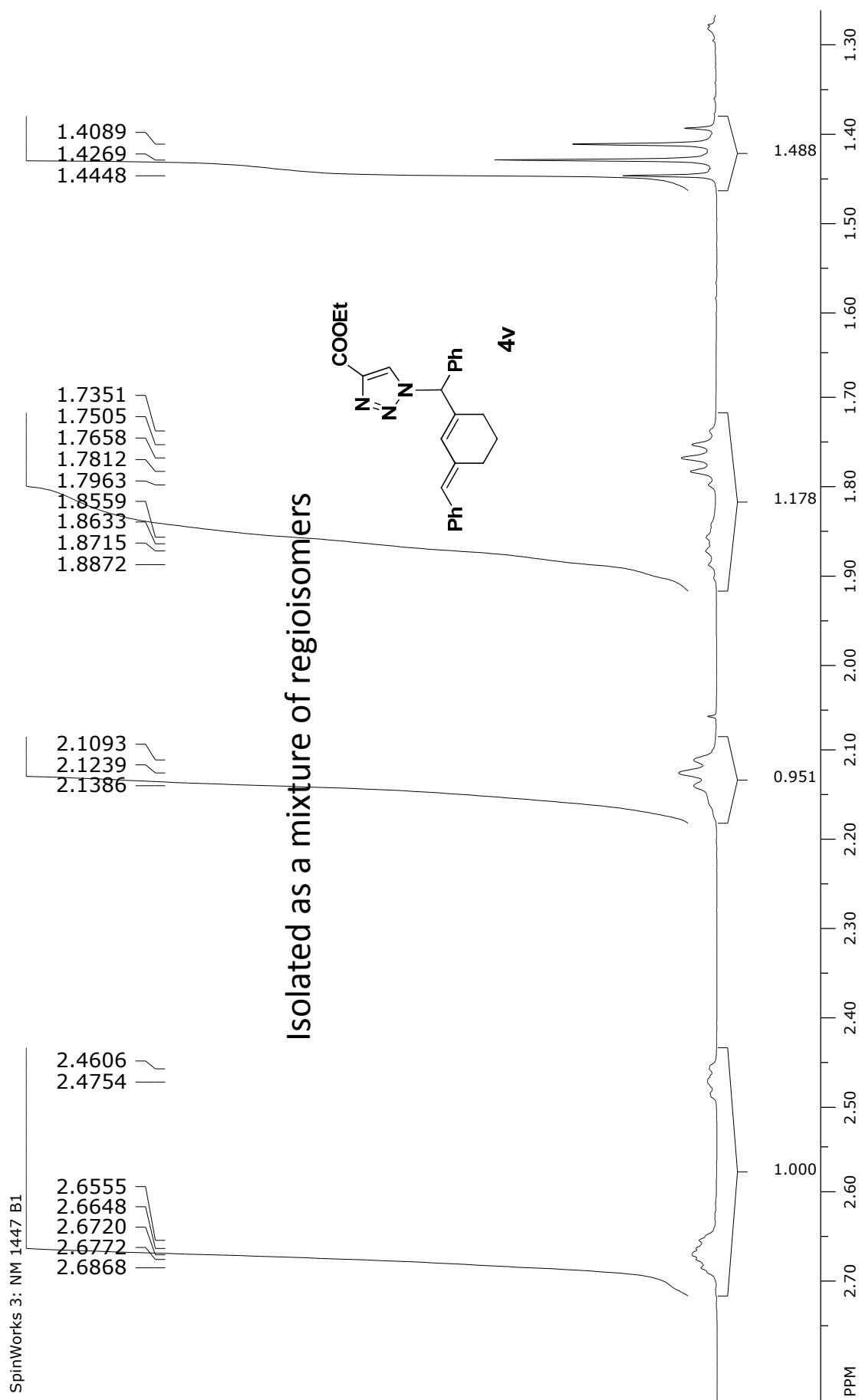


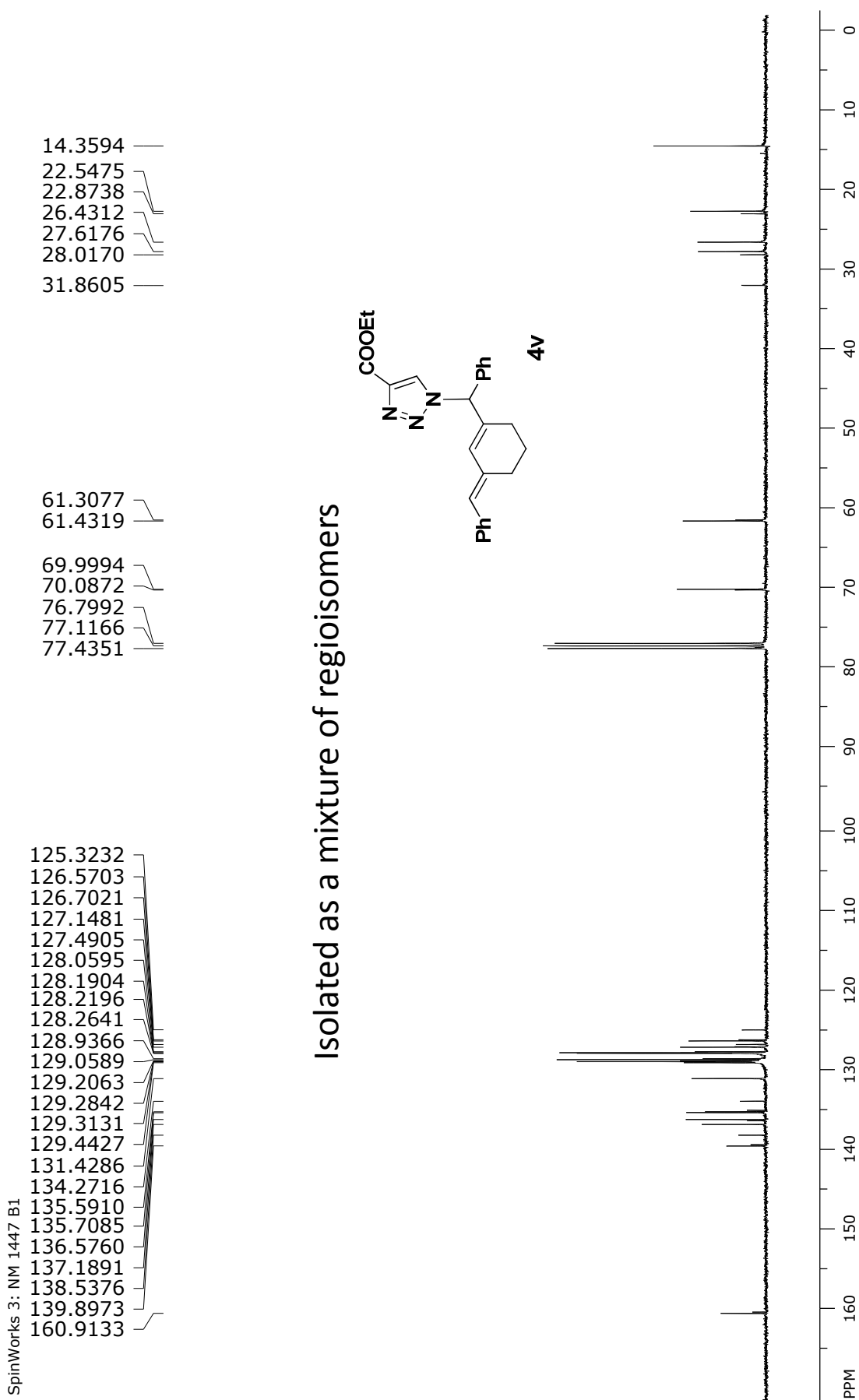


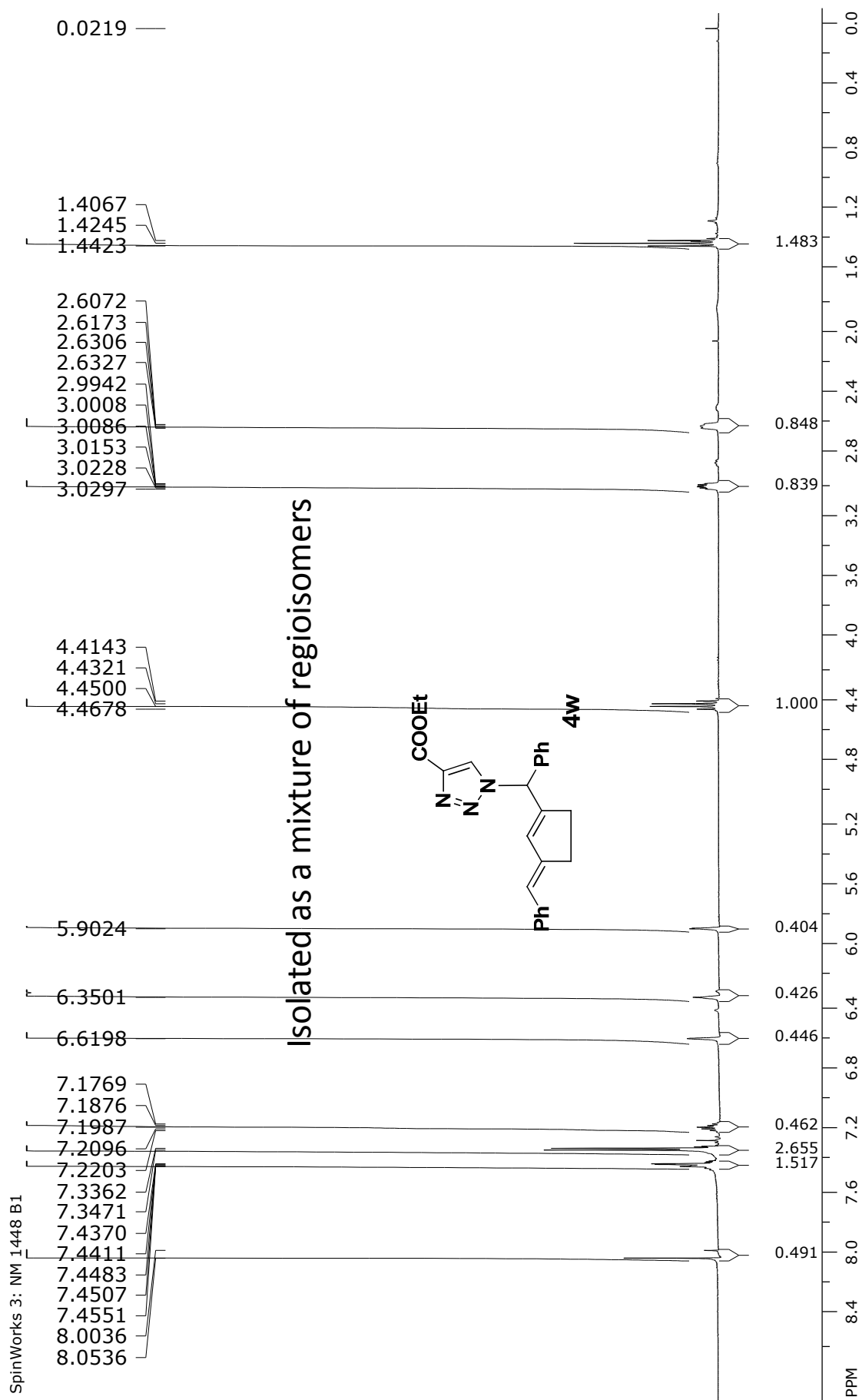


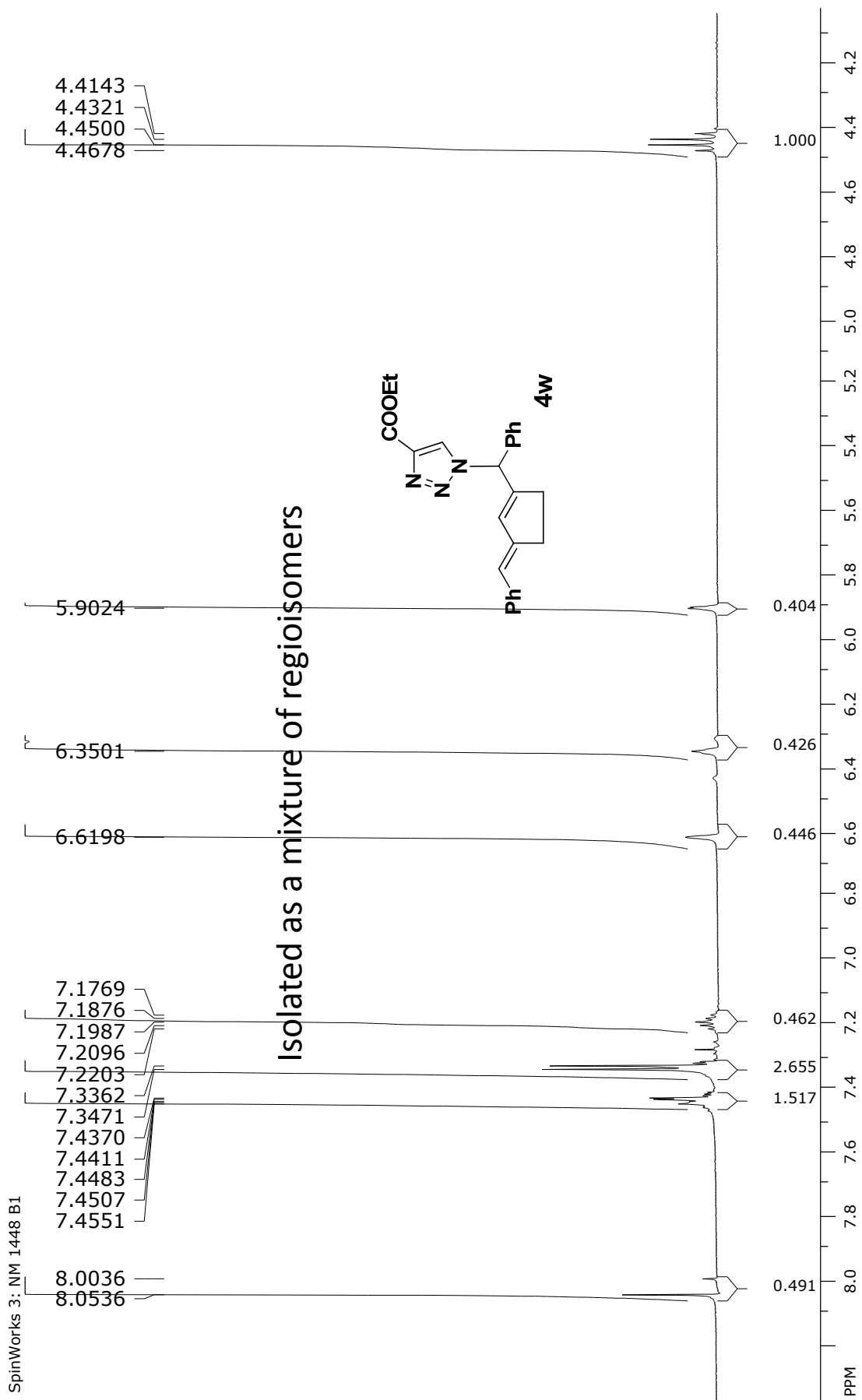




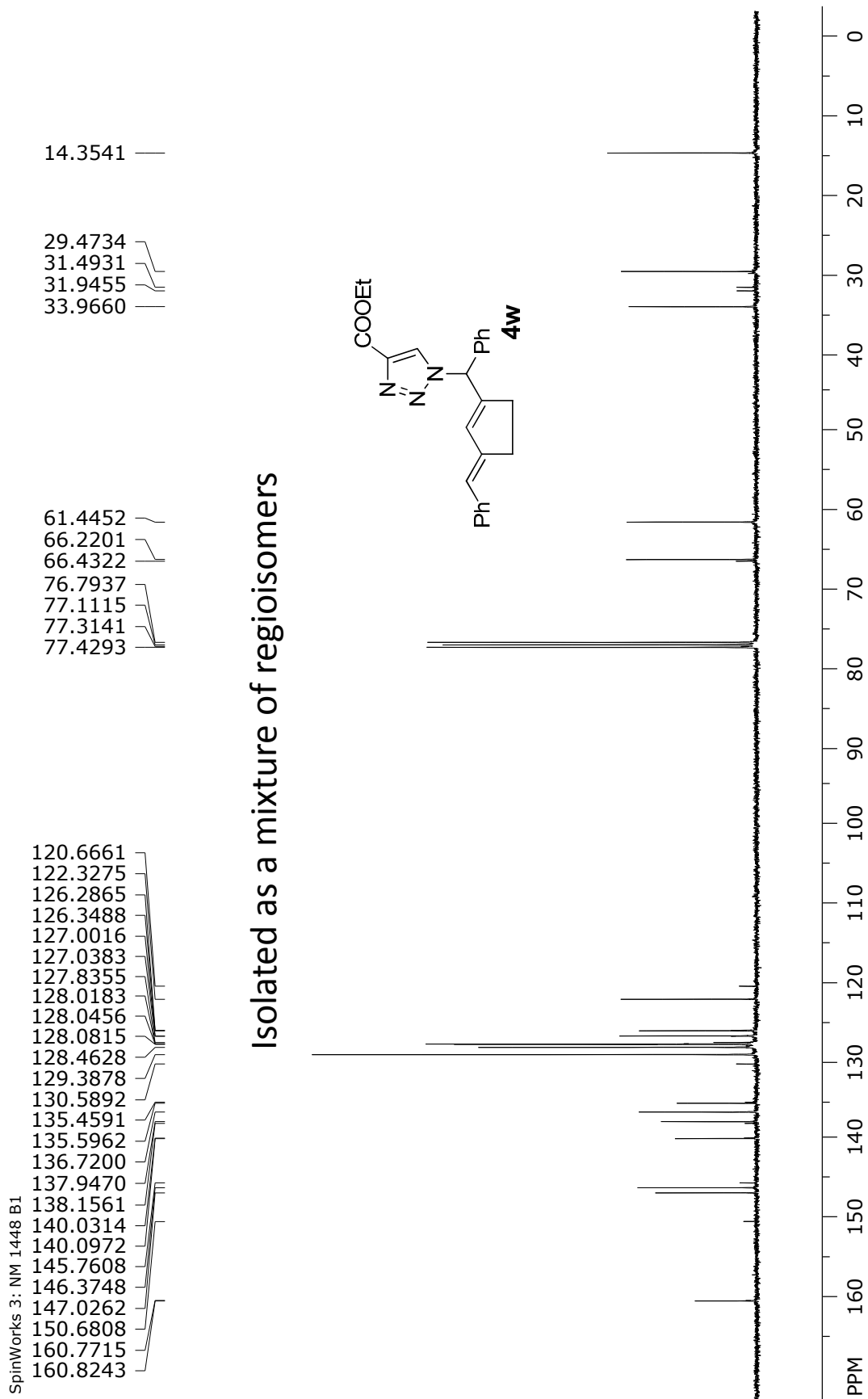




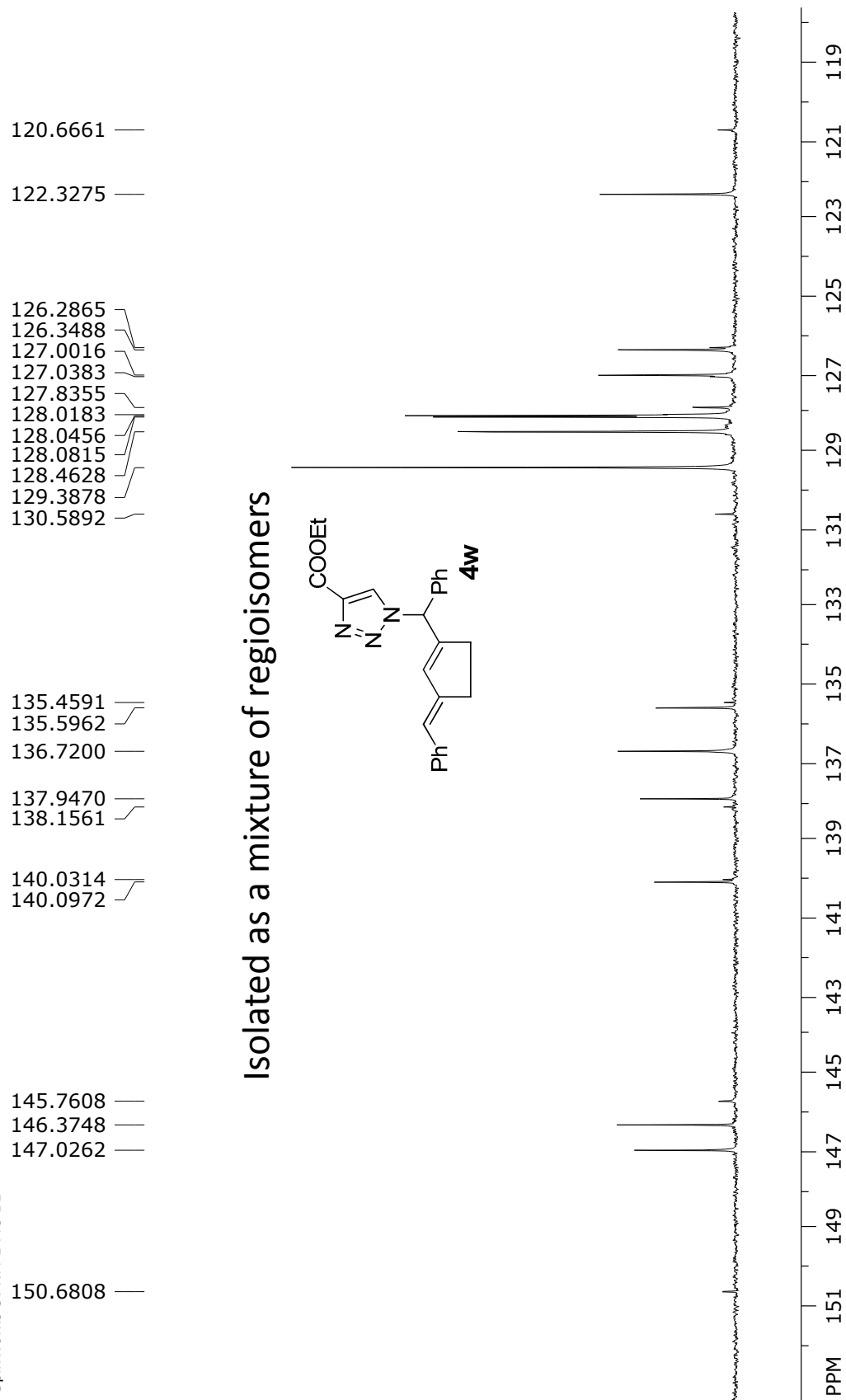








SpinWorks 3: NM 1448 B1

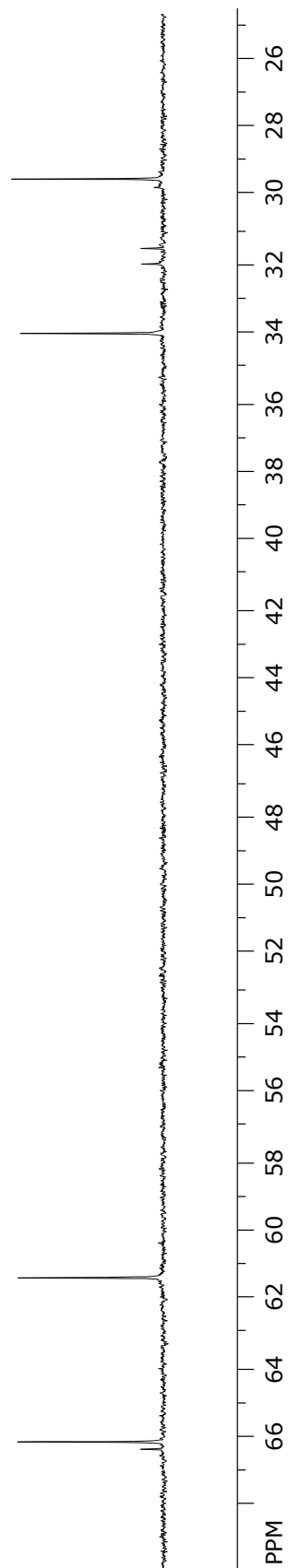
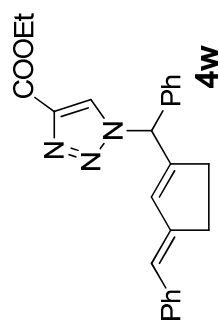


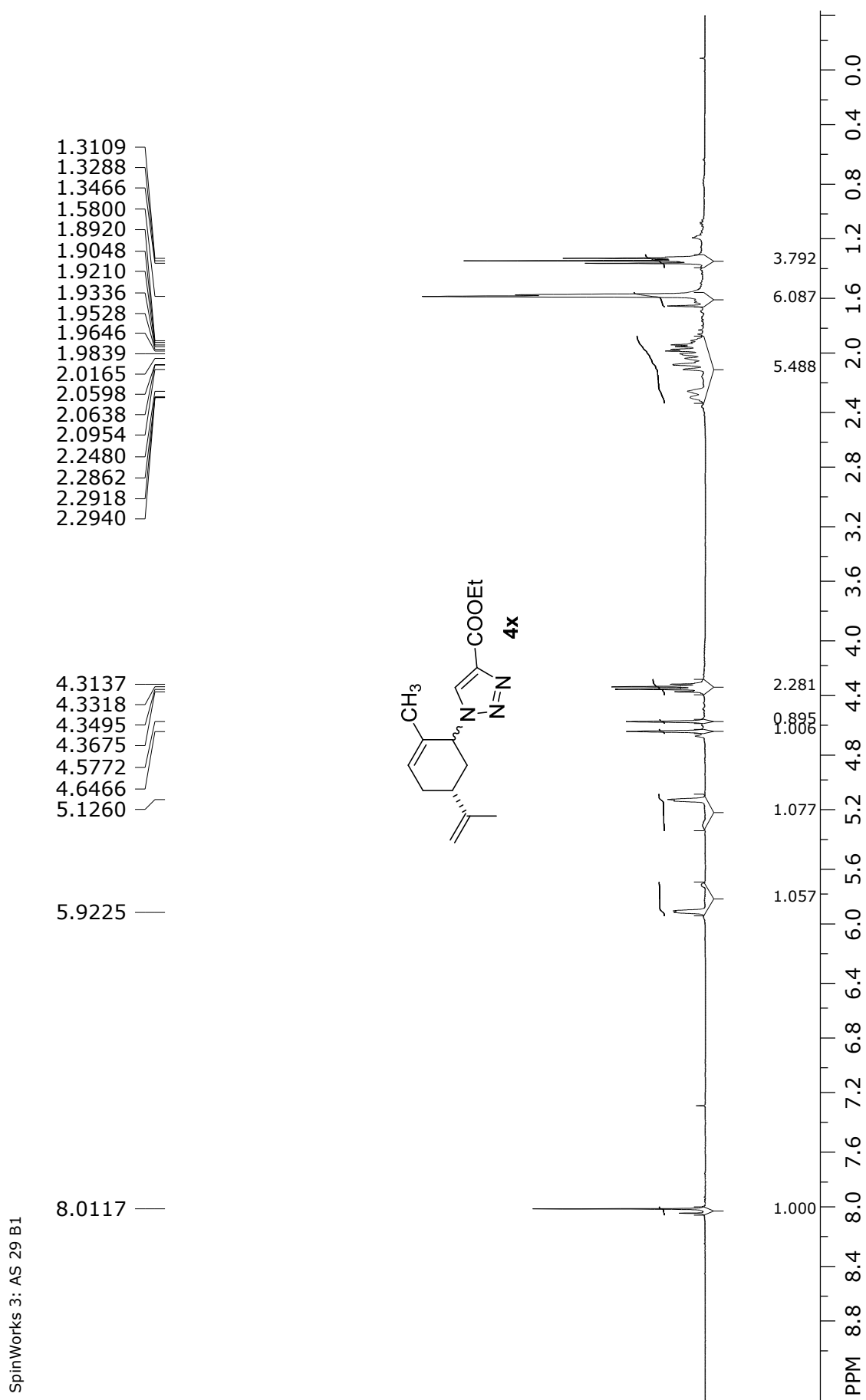
SpinWorks 3: NM 1448 B1

29.4734 —  
31.4931 —  
31.9455 —  
33.9660 —

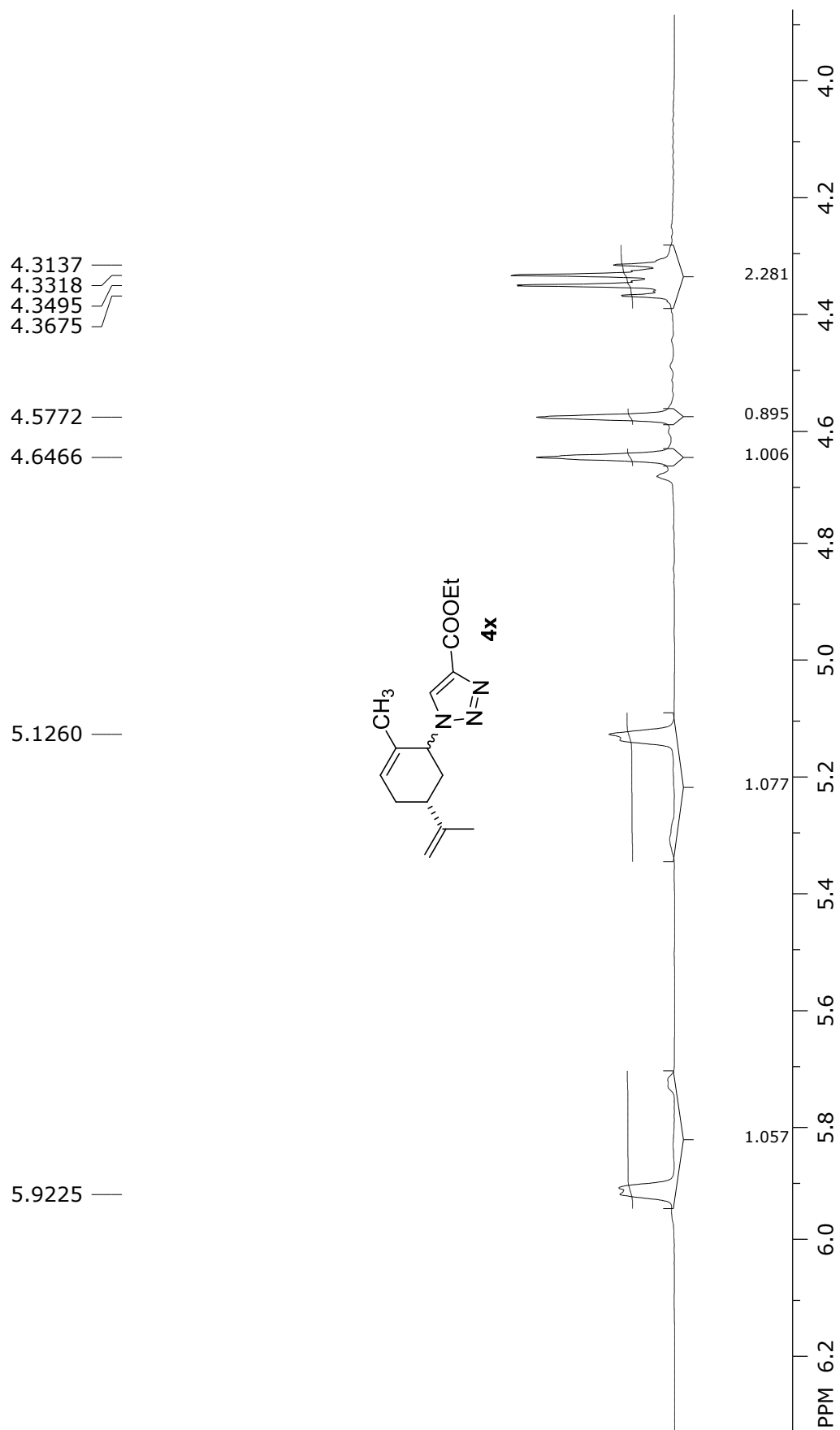
61.4452 —  
66.2201 —  
66.4322 —

Isolated as a mixture of regioisomers

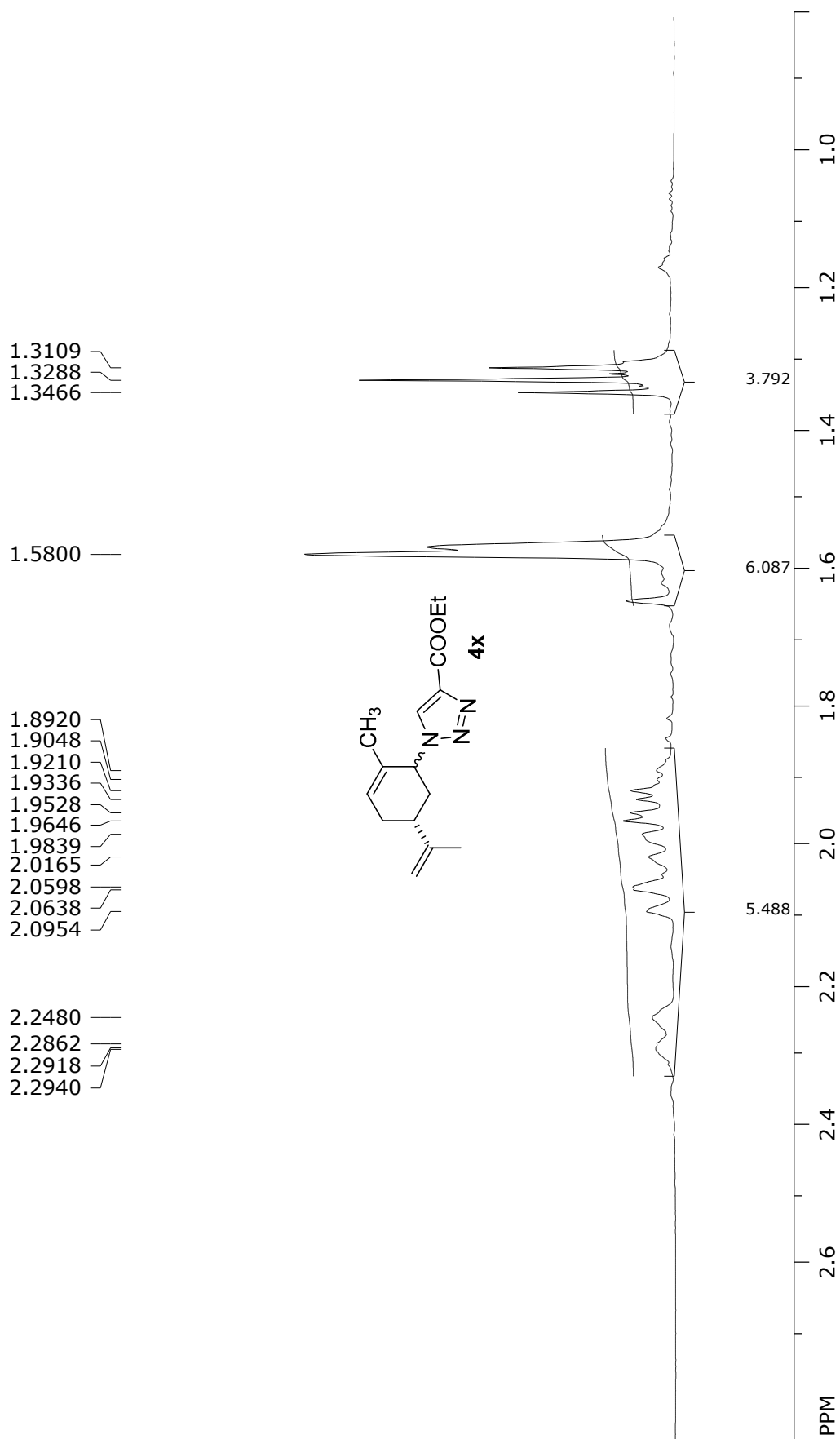


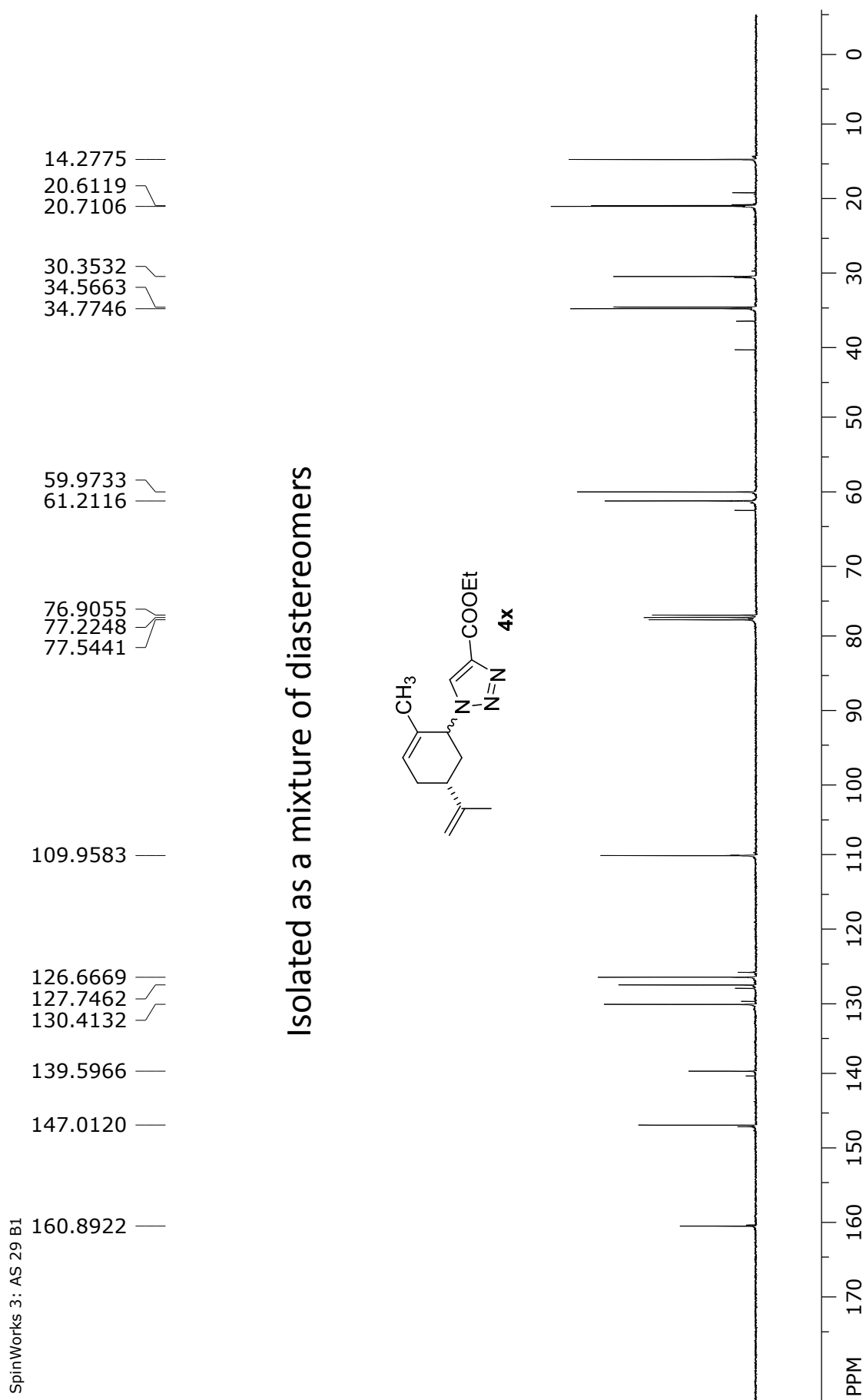


SpinWorks 3 : AS 29 B1

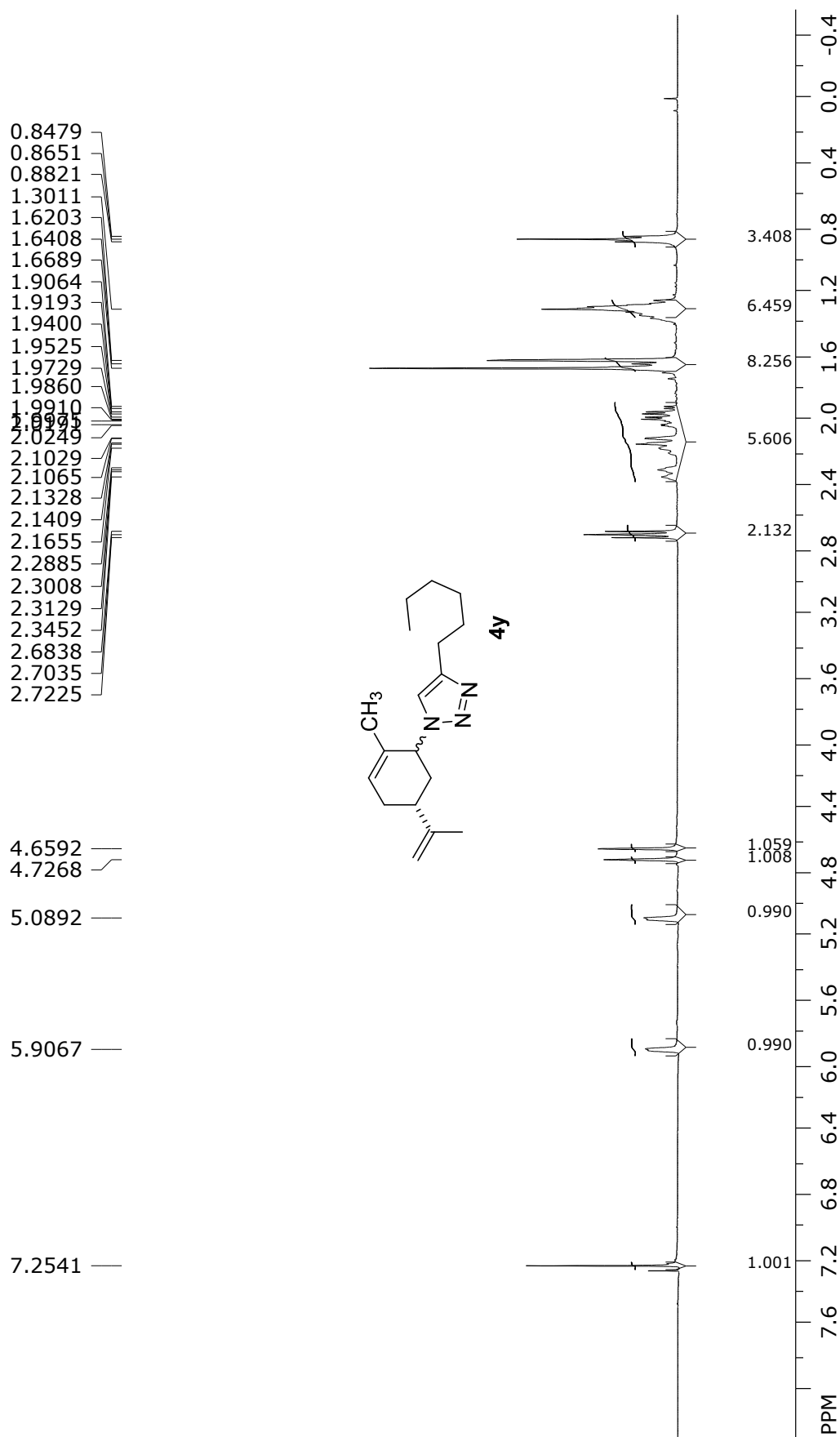


SpinWorks 3 : AS 29 B1



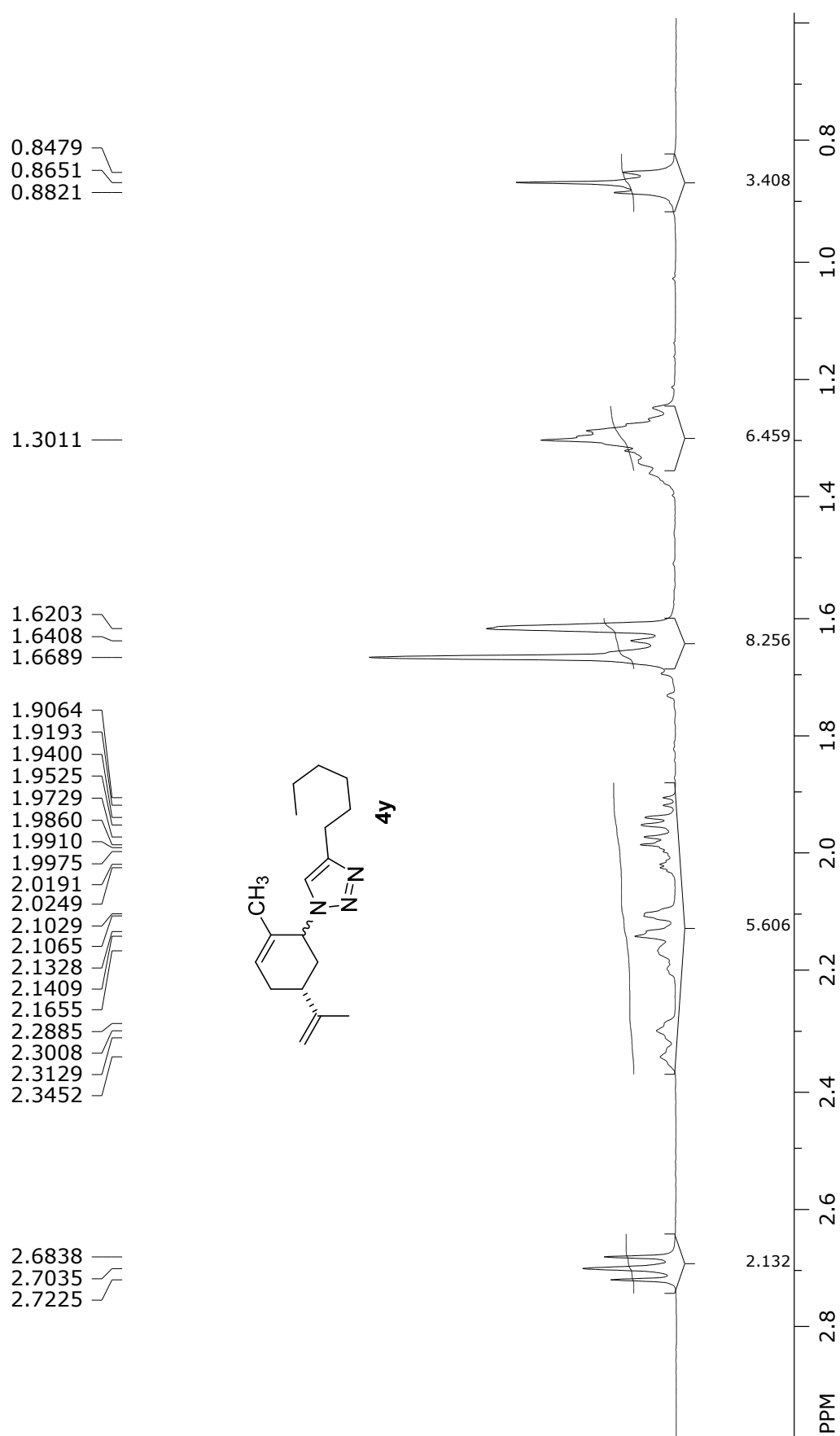


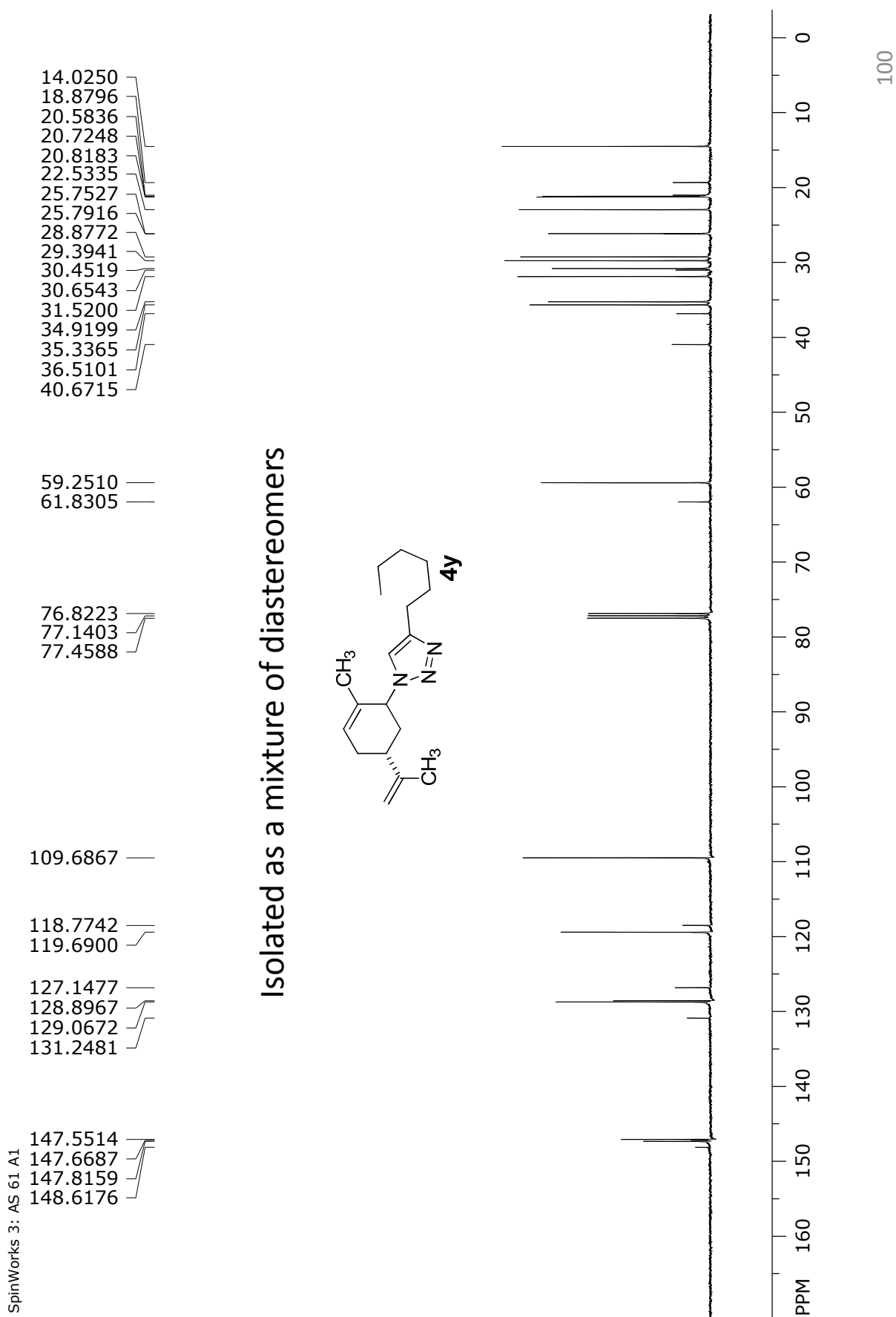
SpinWorks 3: AS 61 A2





SpinWorks 3: AS 61 A2





SpinWorks 3: AS 61 A1

147.5514  
147.6687  
147.8159  
148.6176

131.2481

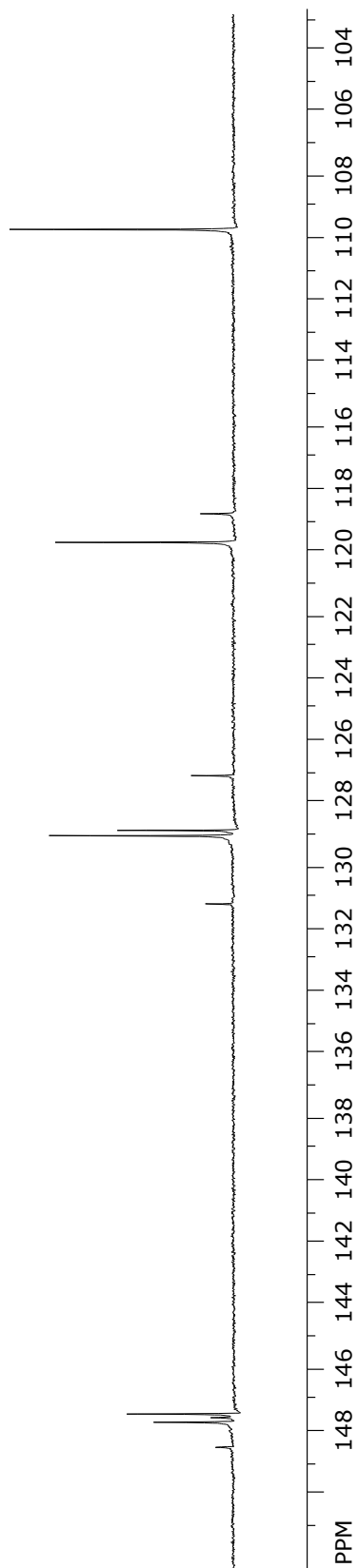
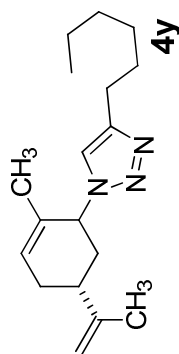
128.8967  
129.0672

127.1477

118.7742  
119.6900

109.6867

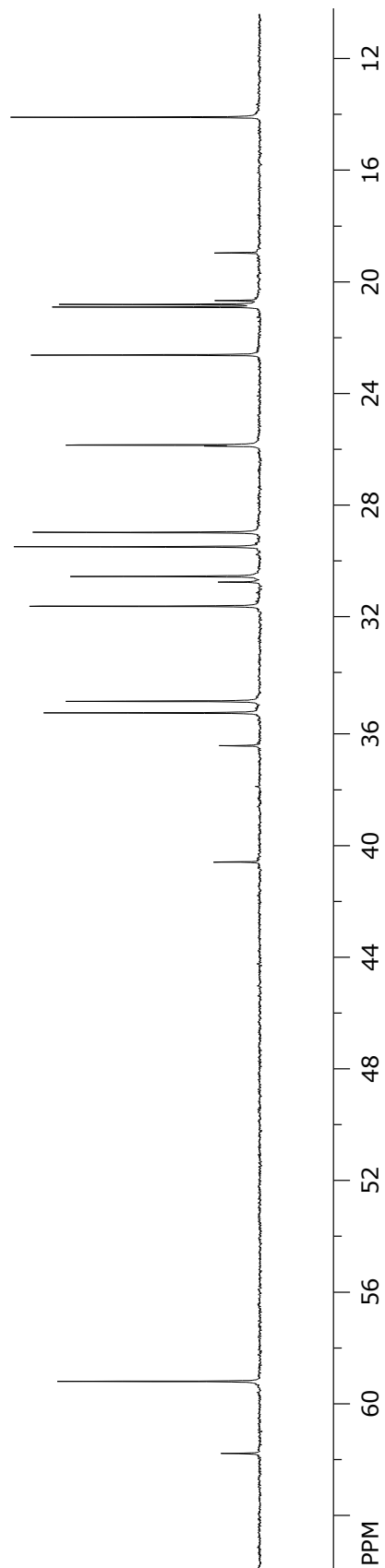
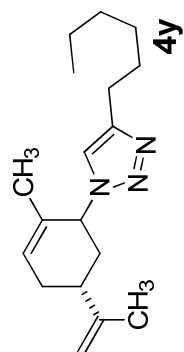
## Isolated as a mixture of diastereomers

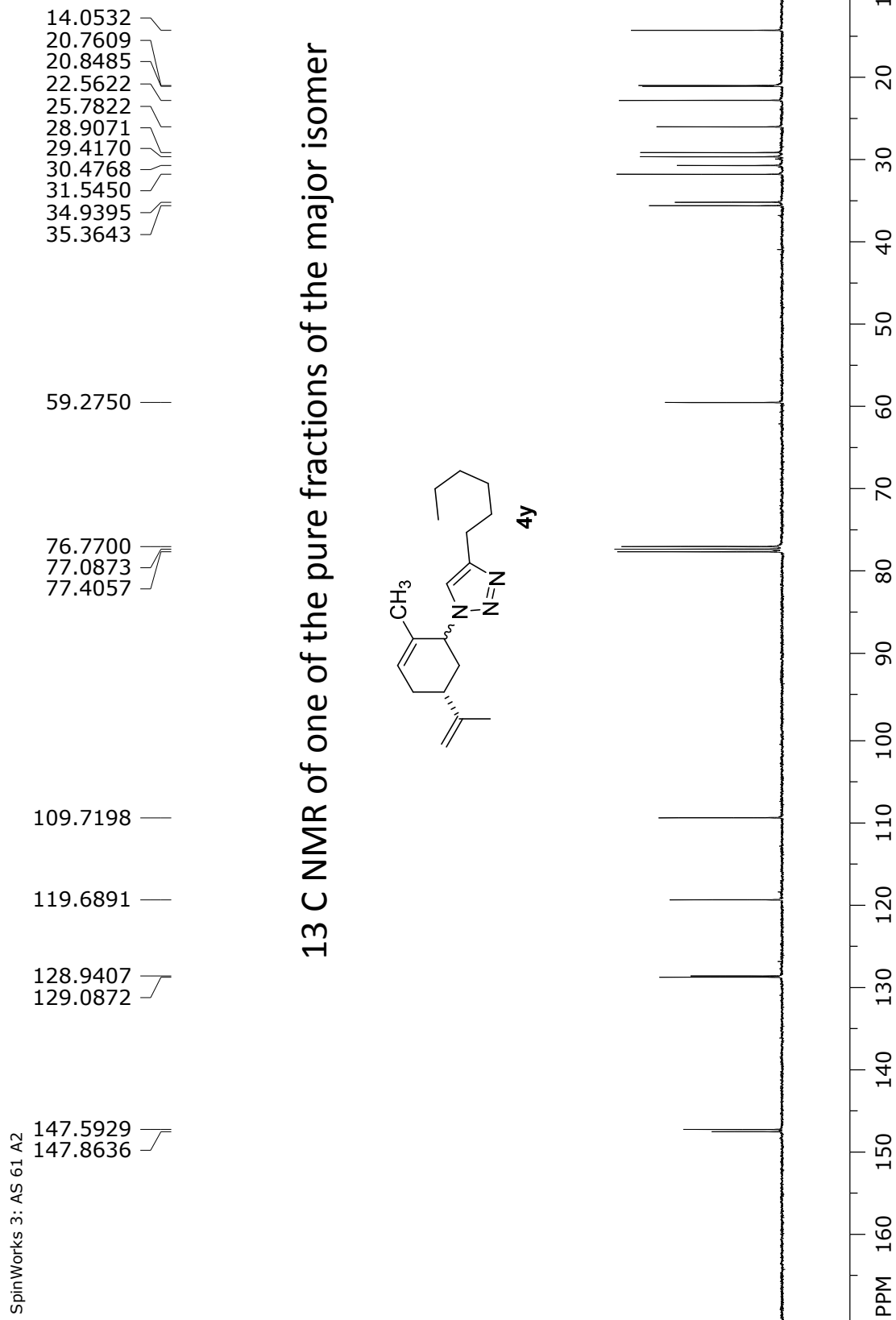


SpinWorks 3: AS 61 A1

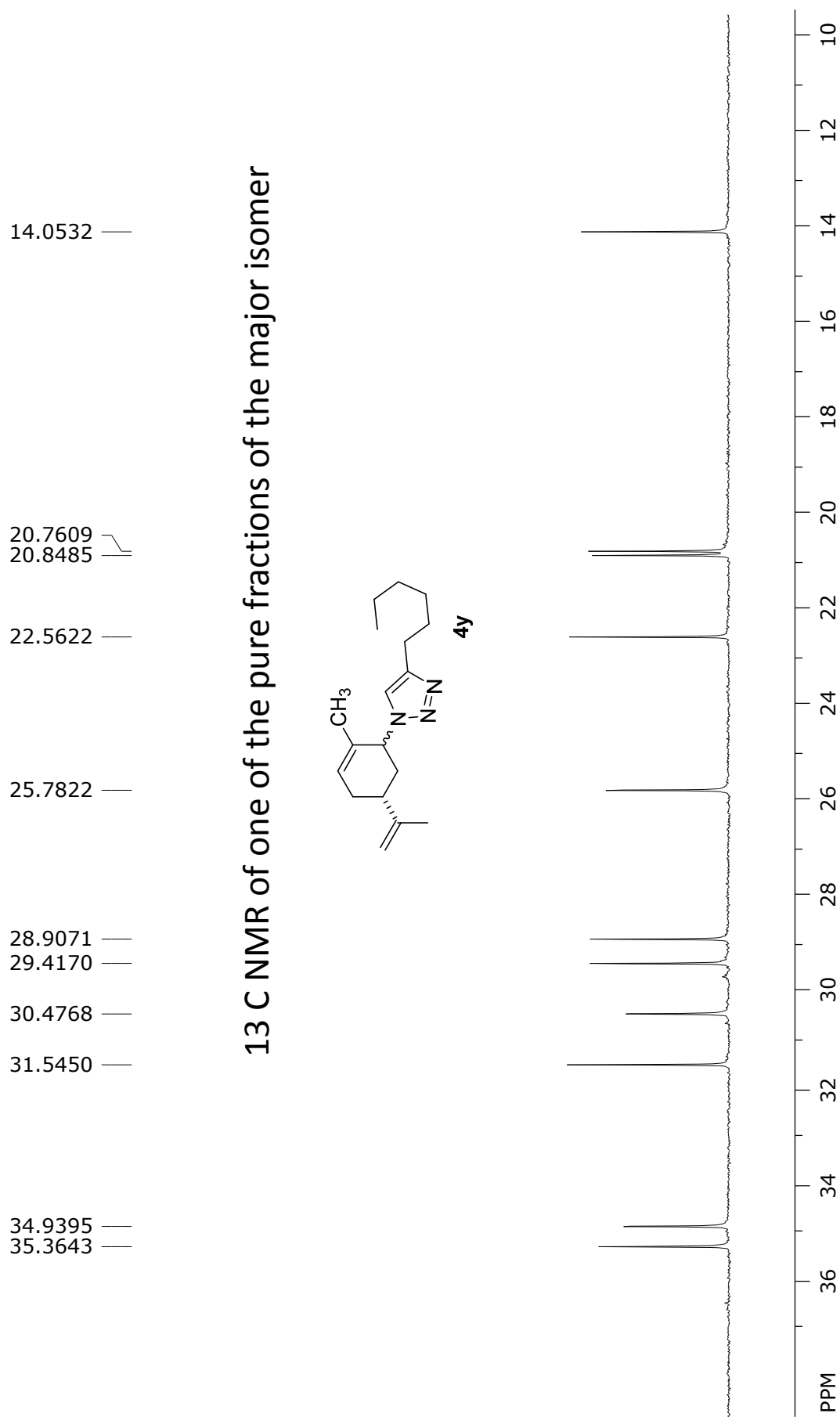
59.2510 —  
61.8305 —  
40.6715 —  
36.5101 —  
35.3365 —  
34.9199 —  
31.5200 —  
30.6543 —  
30.4519 —  
29.3941 —  
28.8772 —  
25.7916 —  
25.7527 —  
22.5335 —  
20.8183 —  
20.7248 —  
20.5836 —  
18.8796 —  
14.0250 —

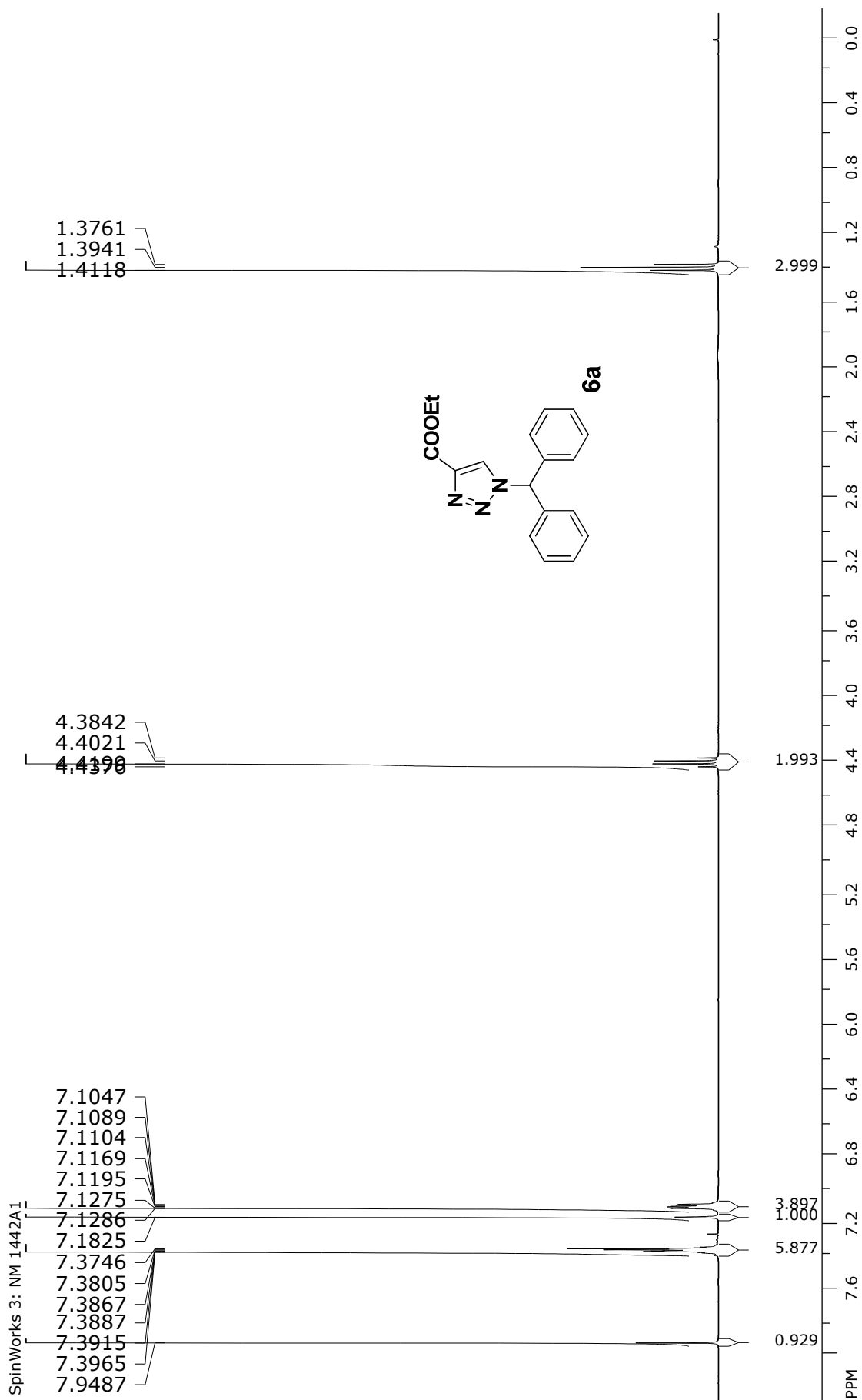
Isolated as a mixture of diastereomers

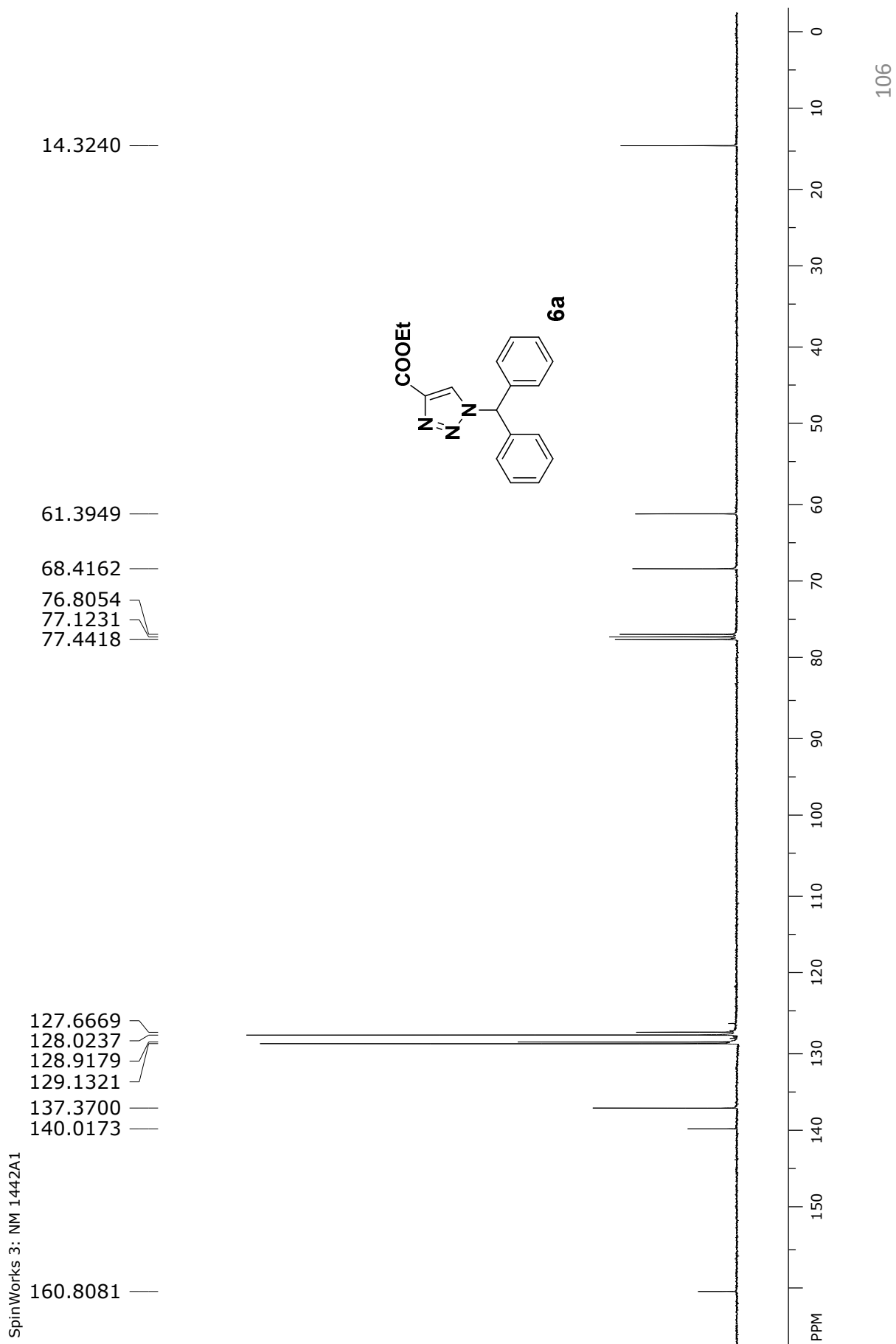




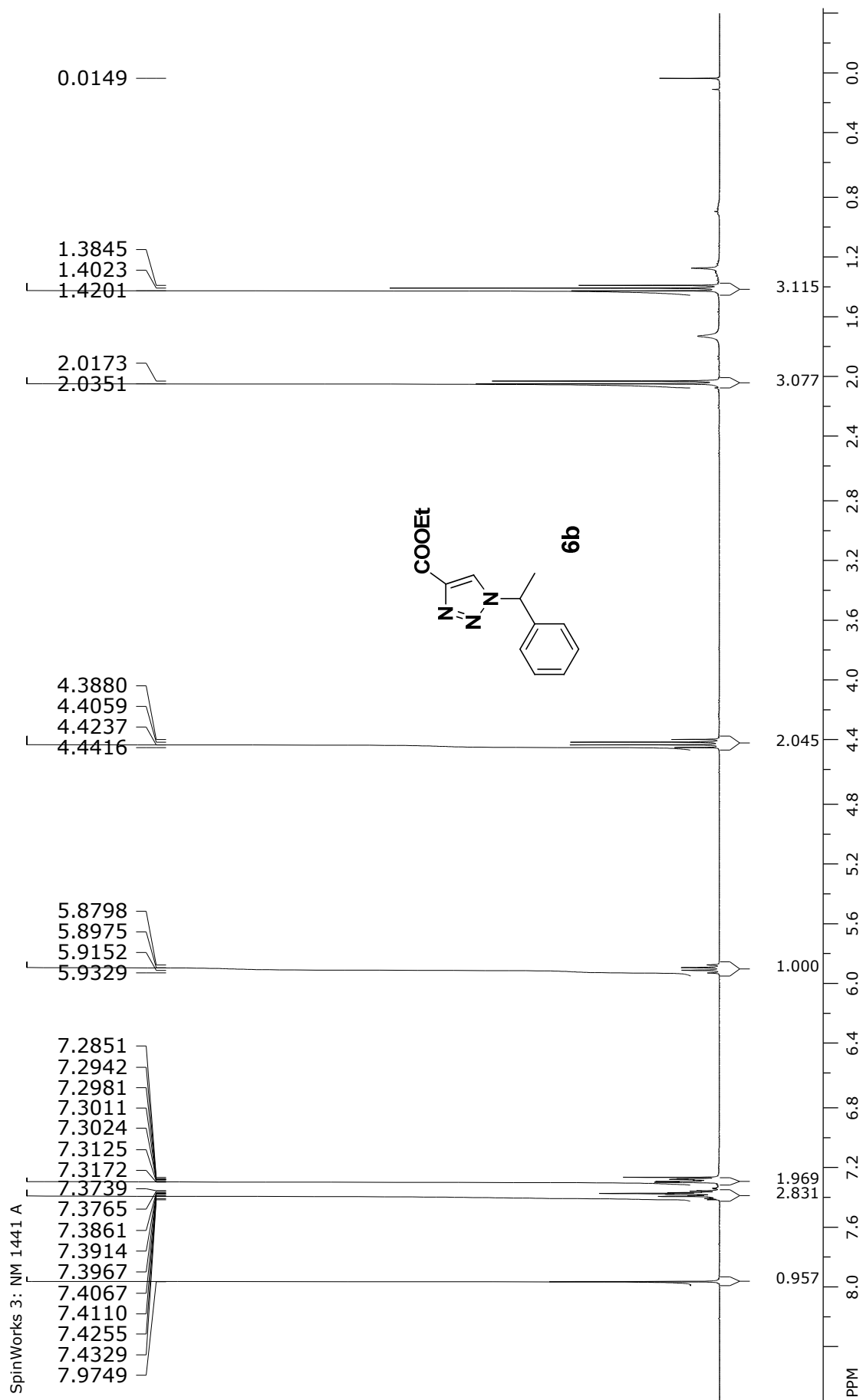
SpinWorks 3: AS 61 A2

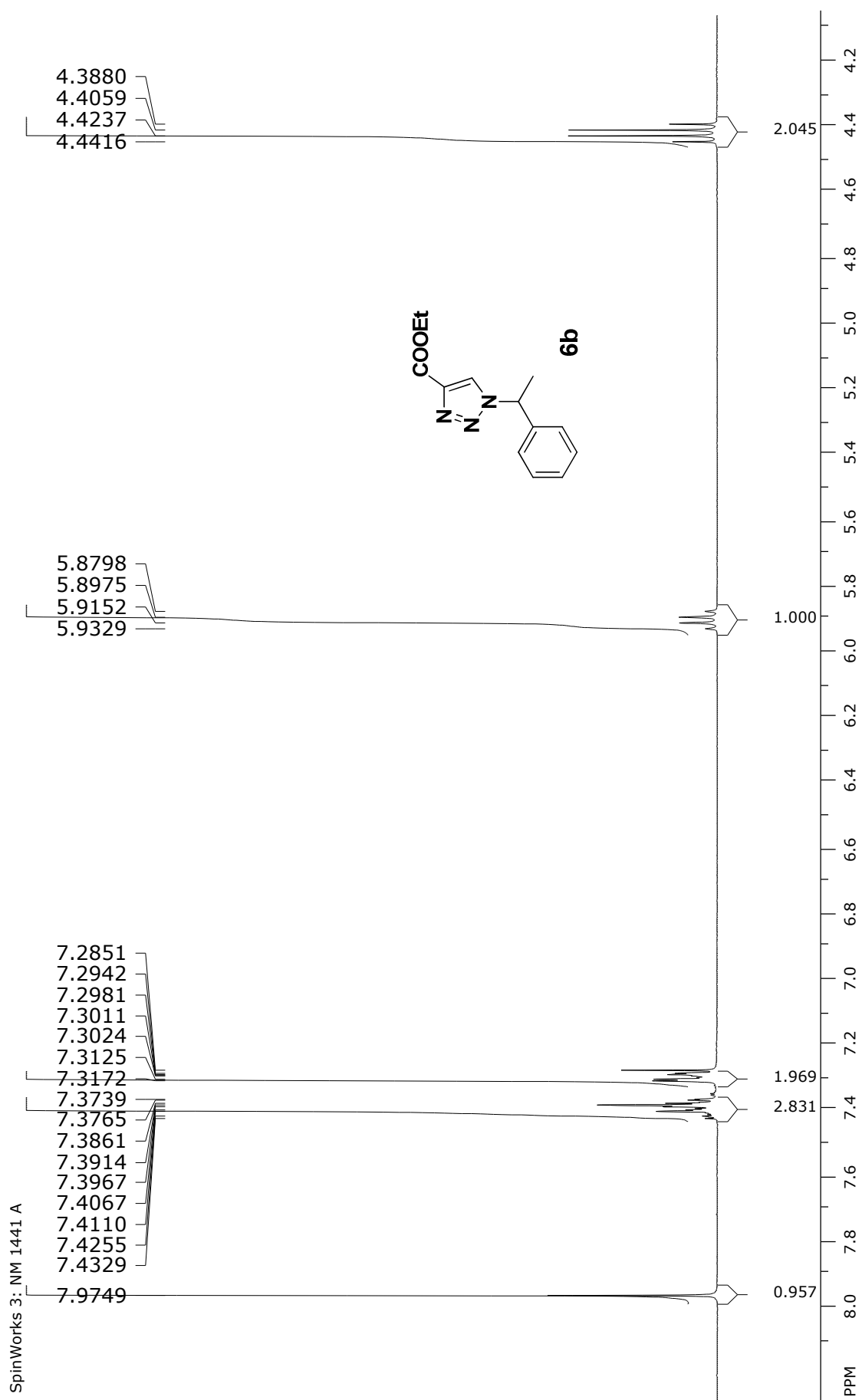


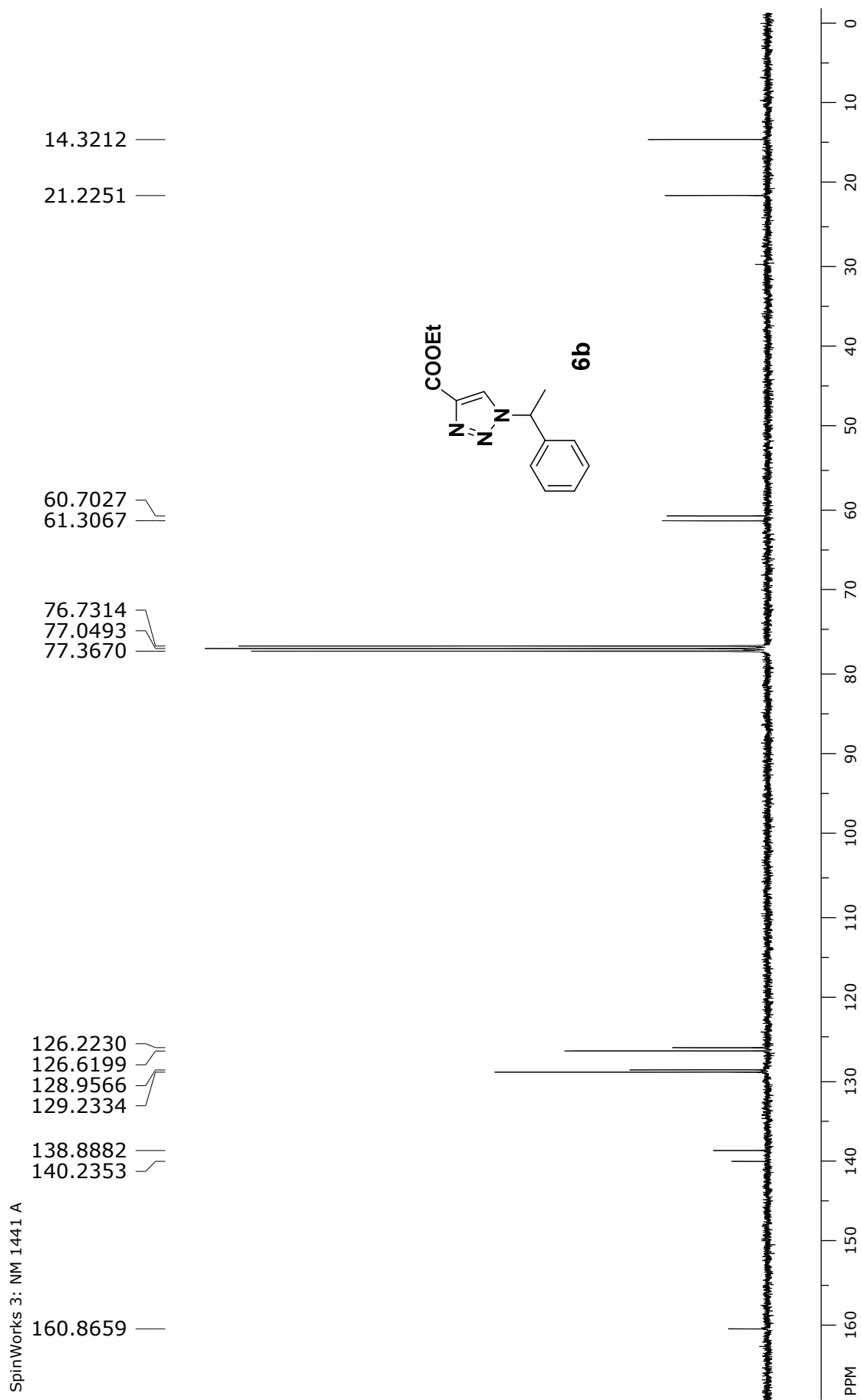


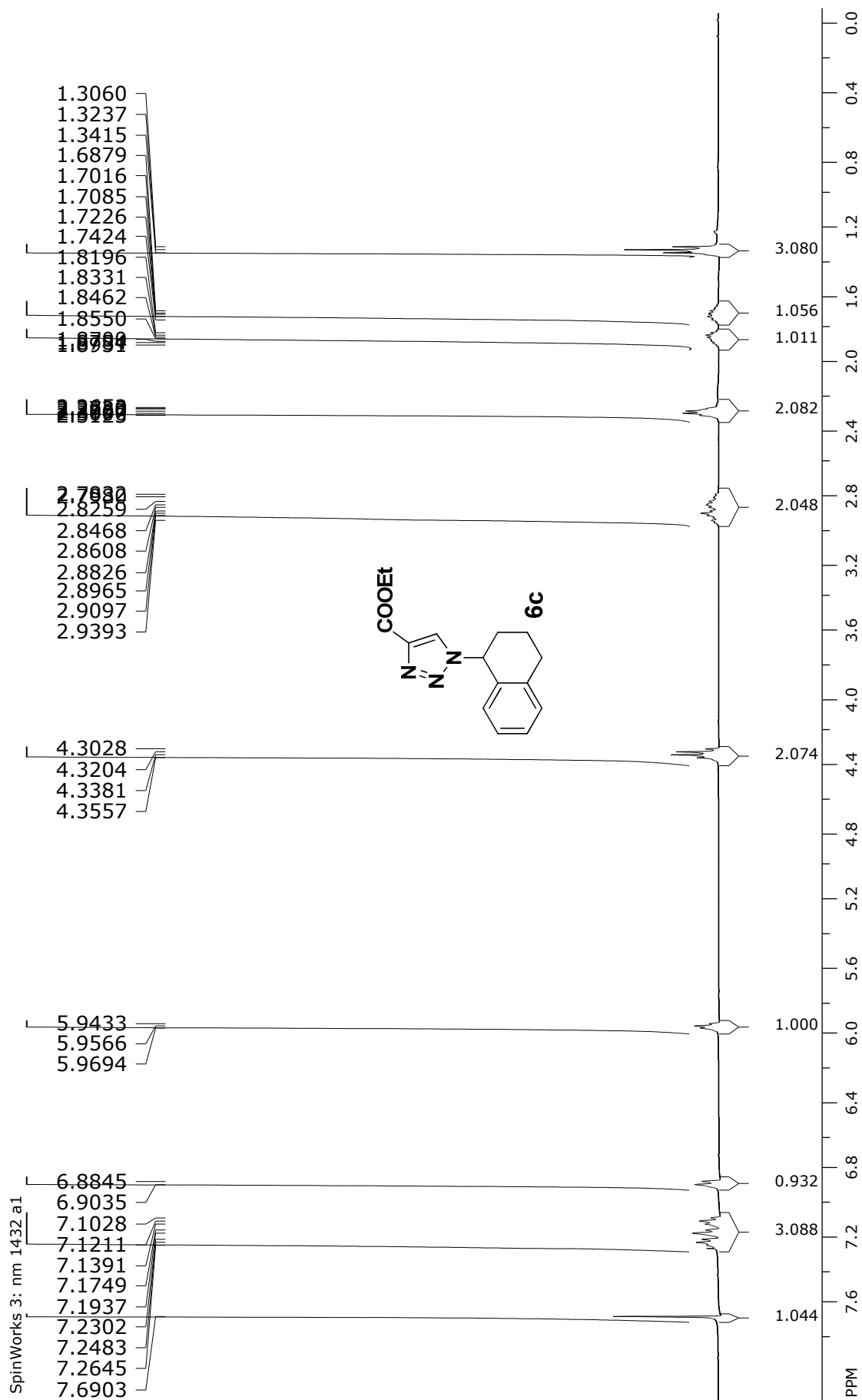


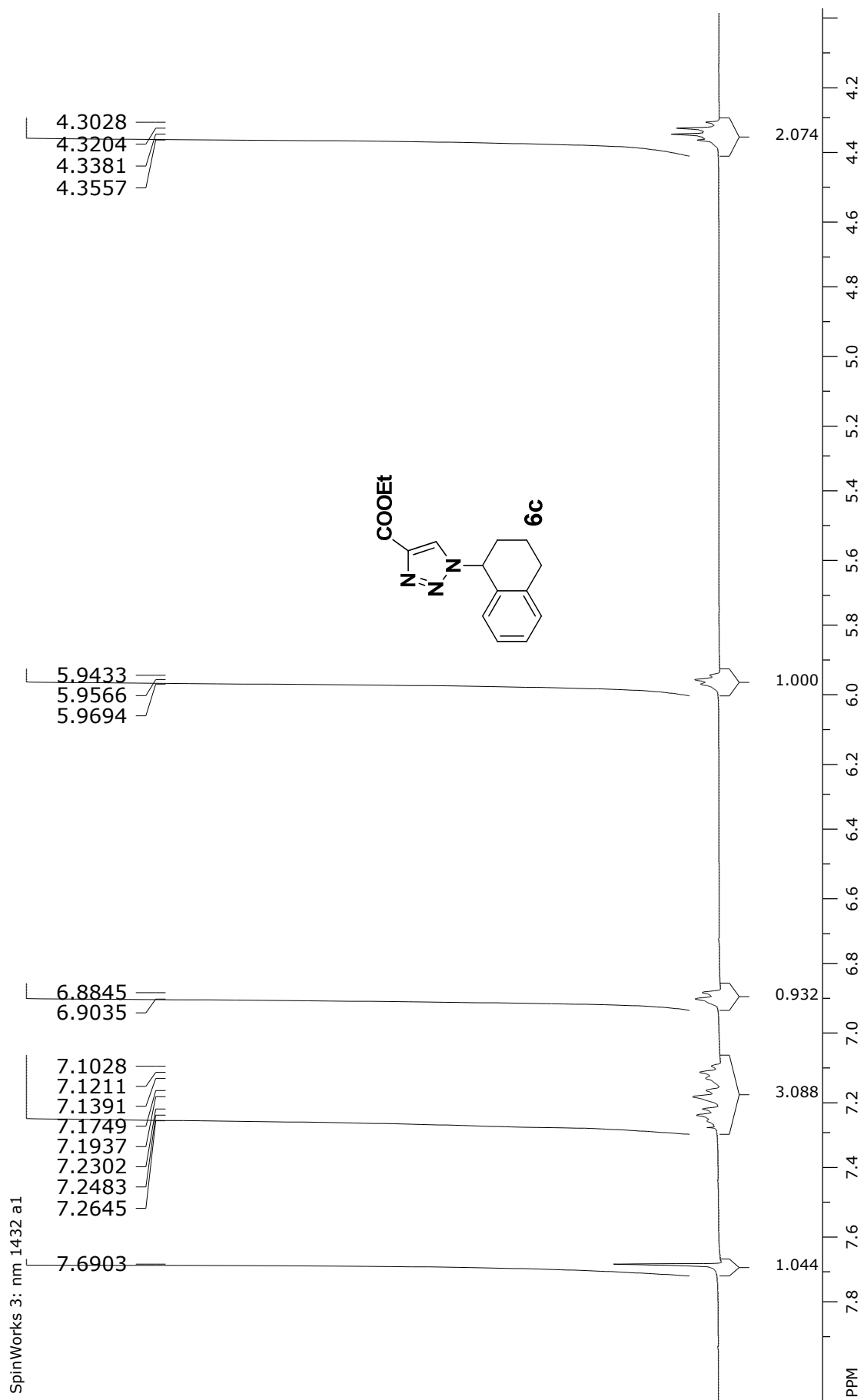


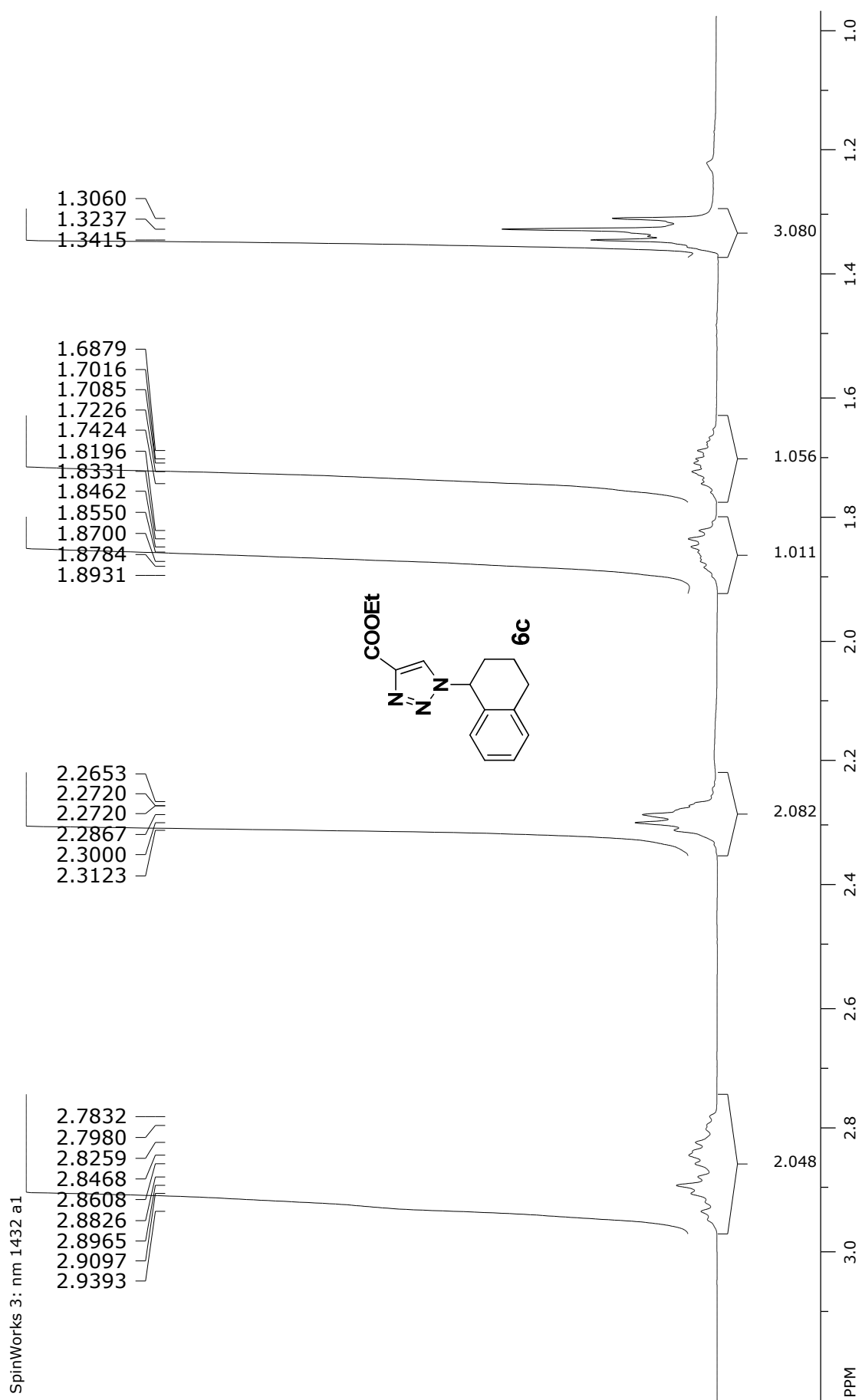


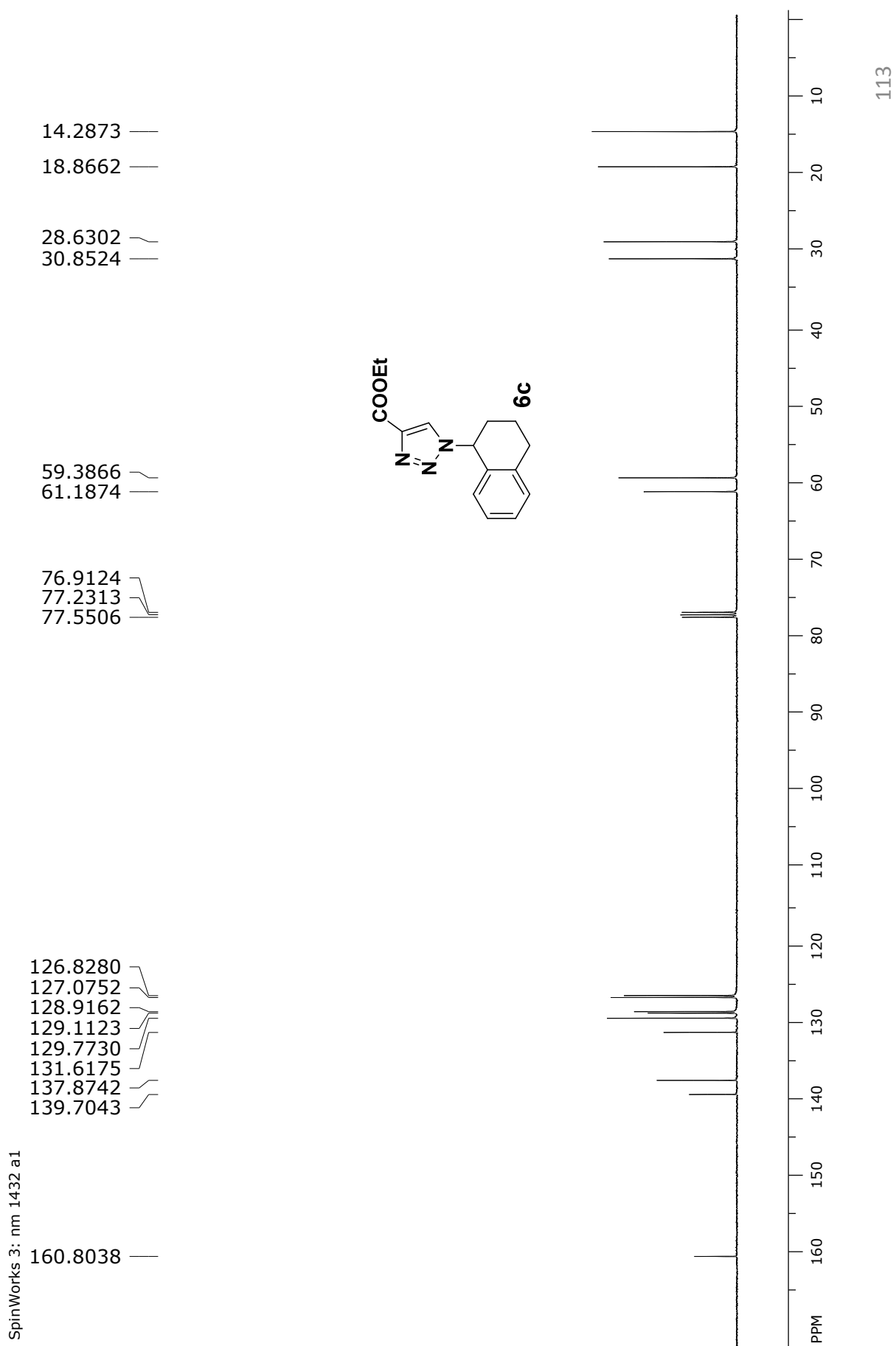


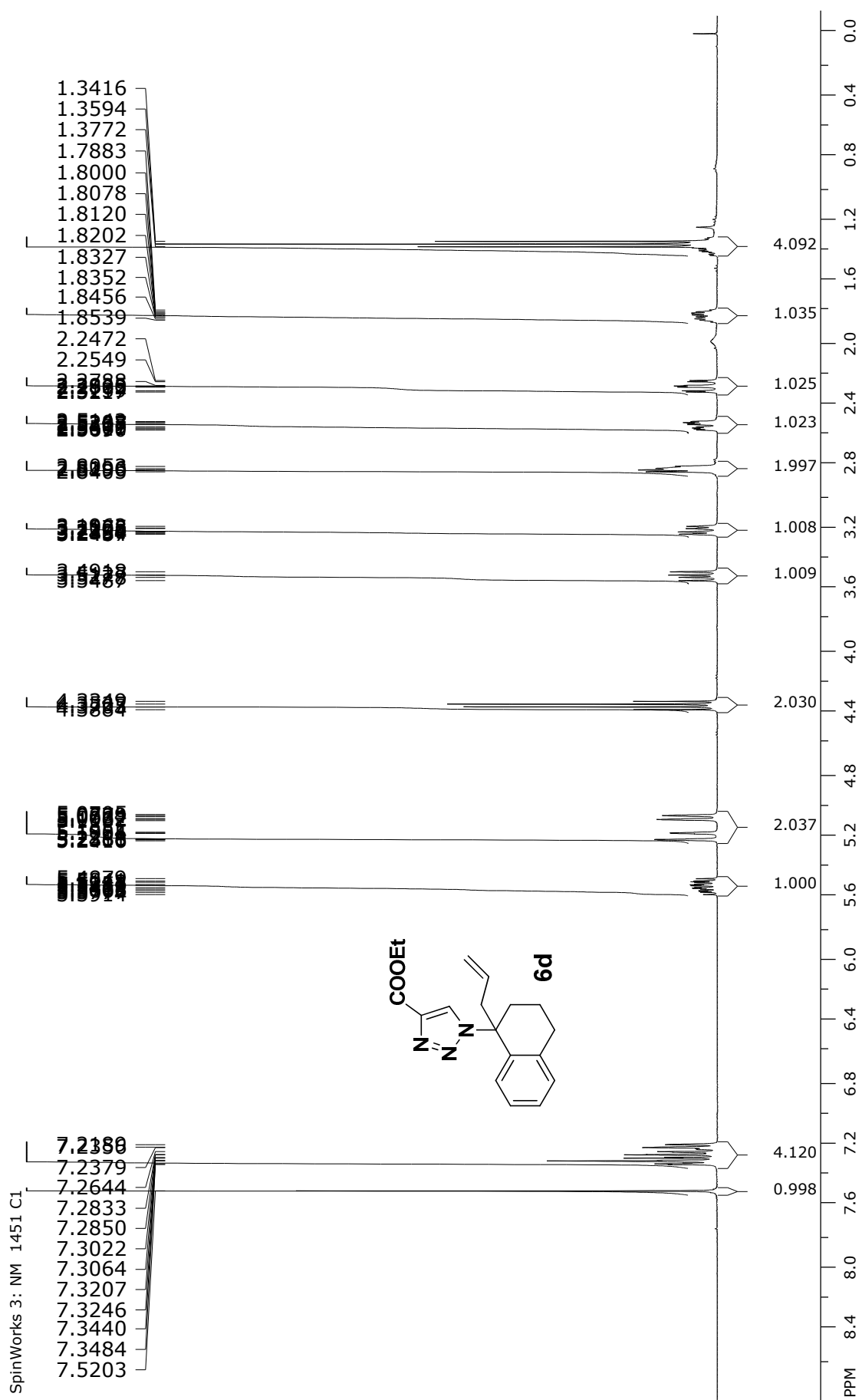




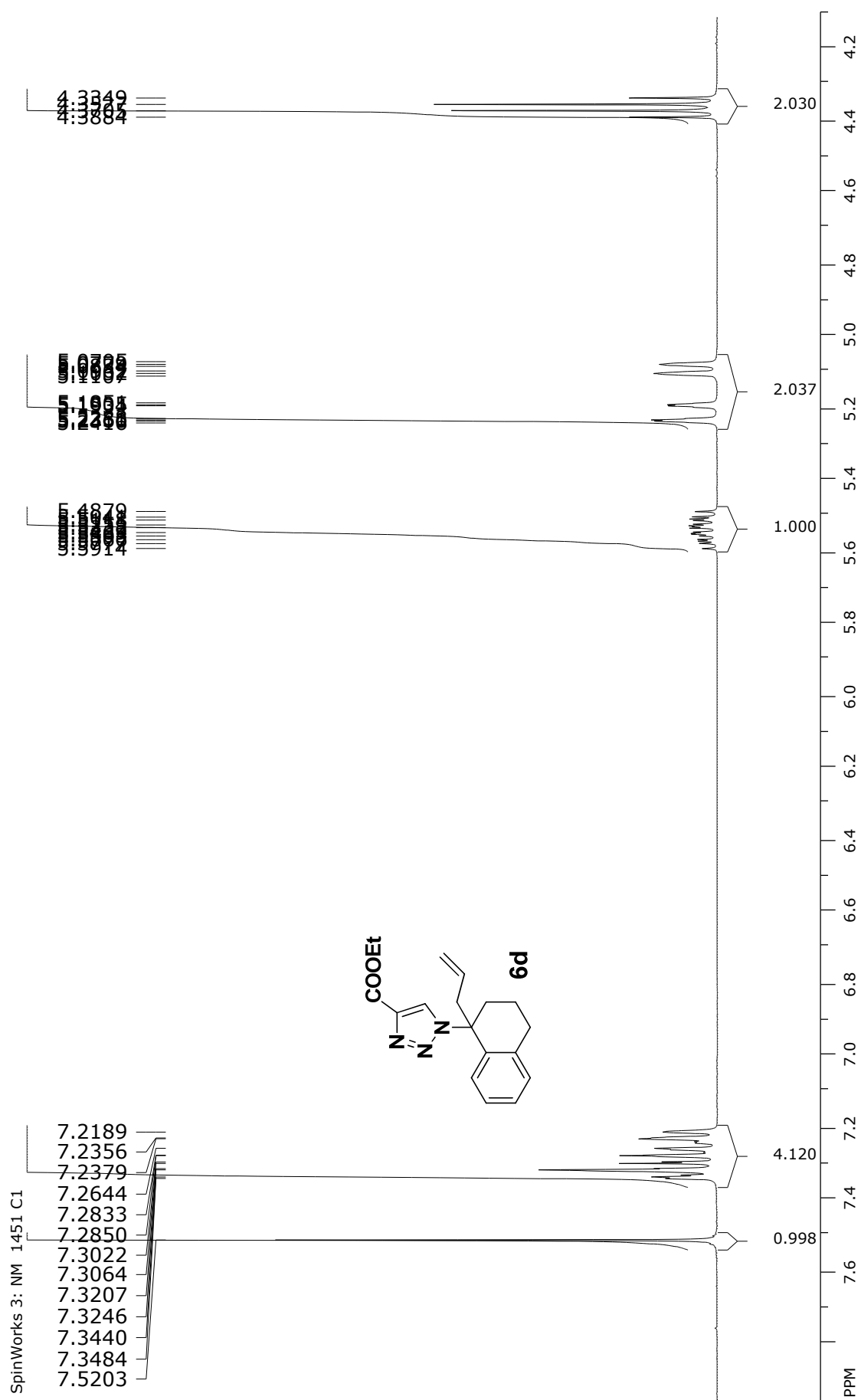


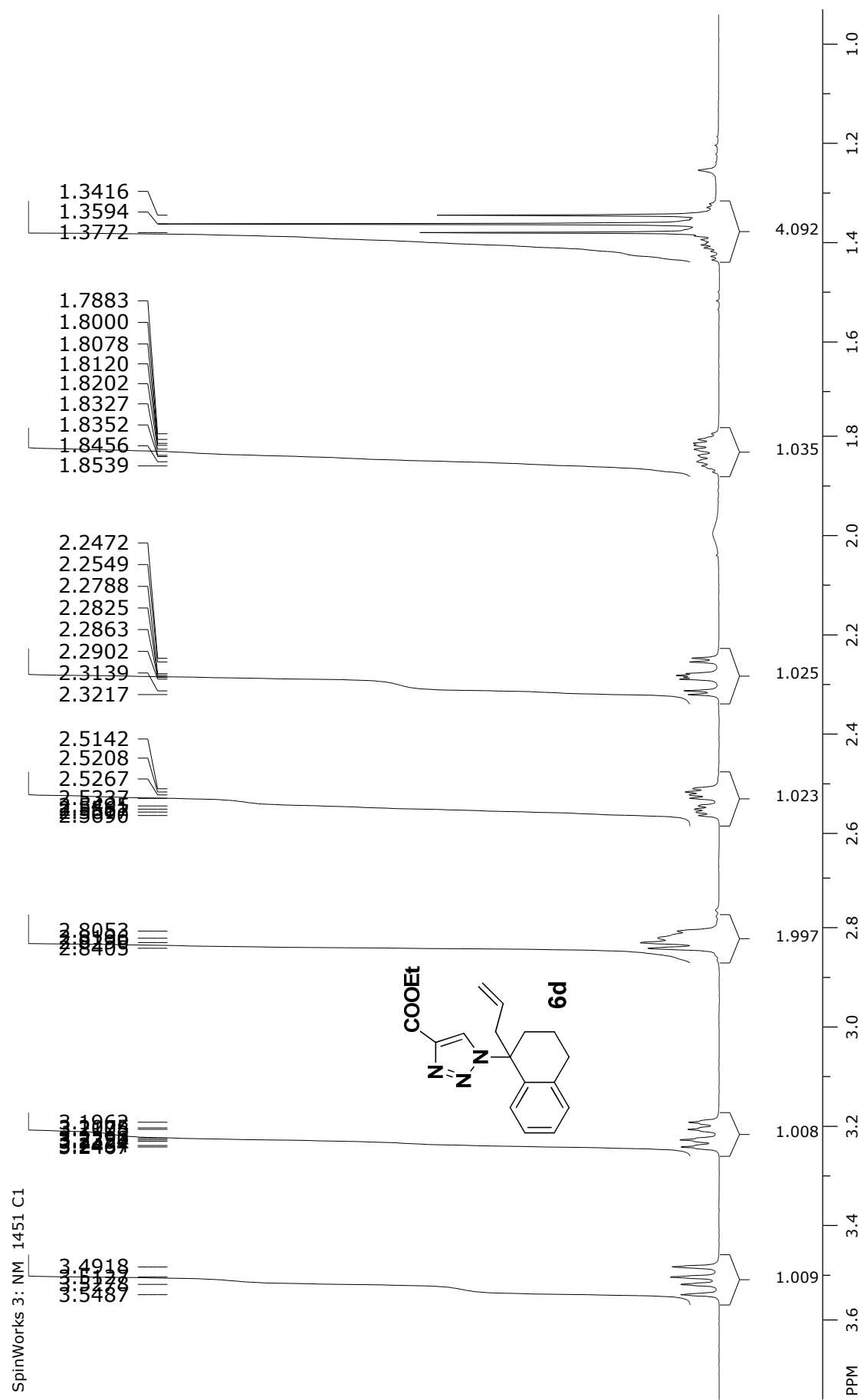


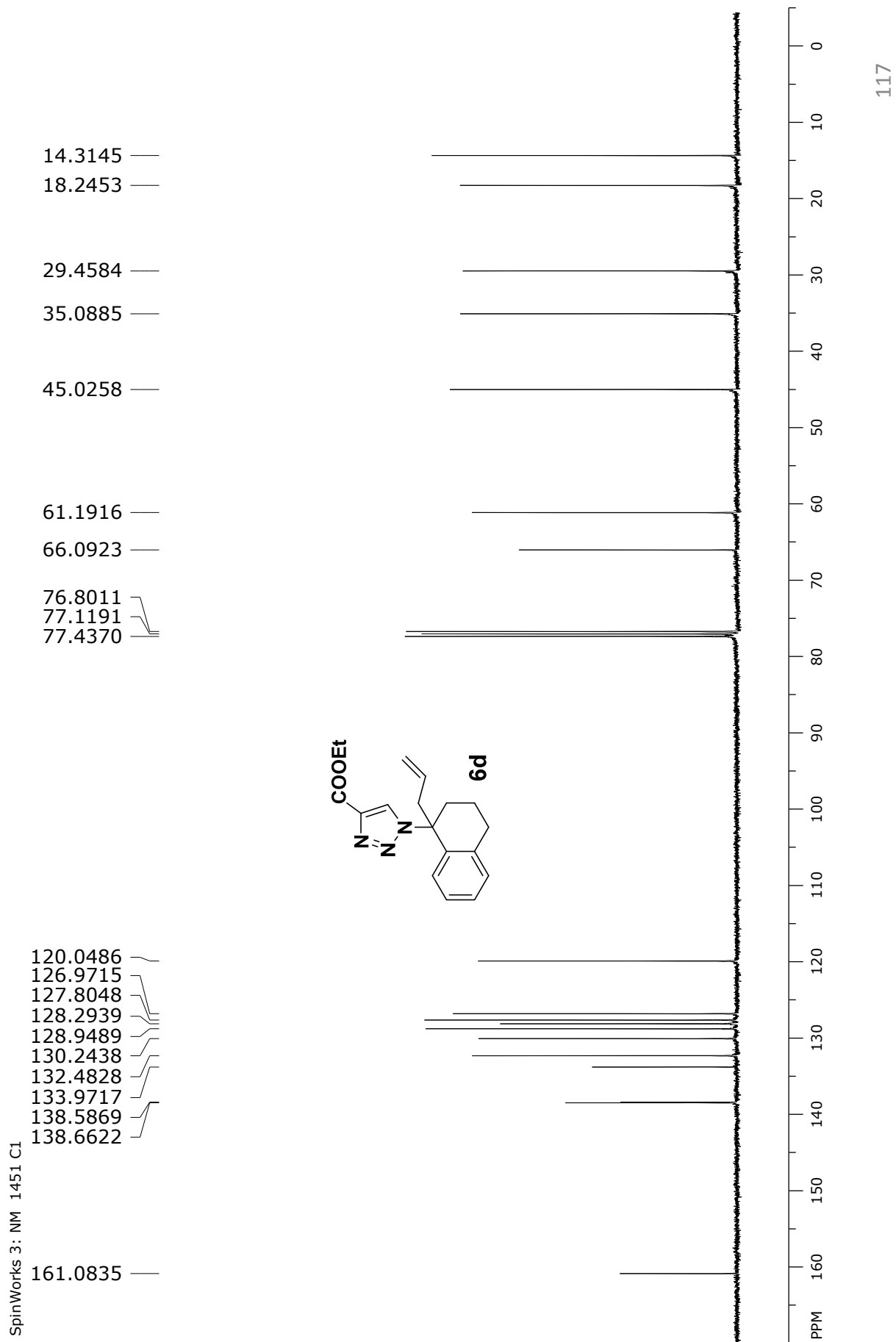


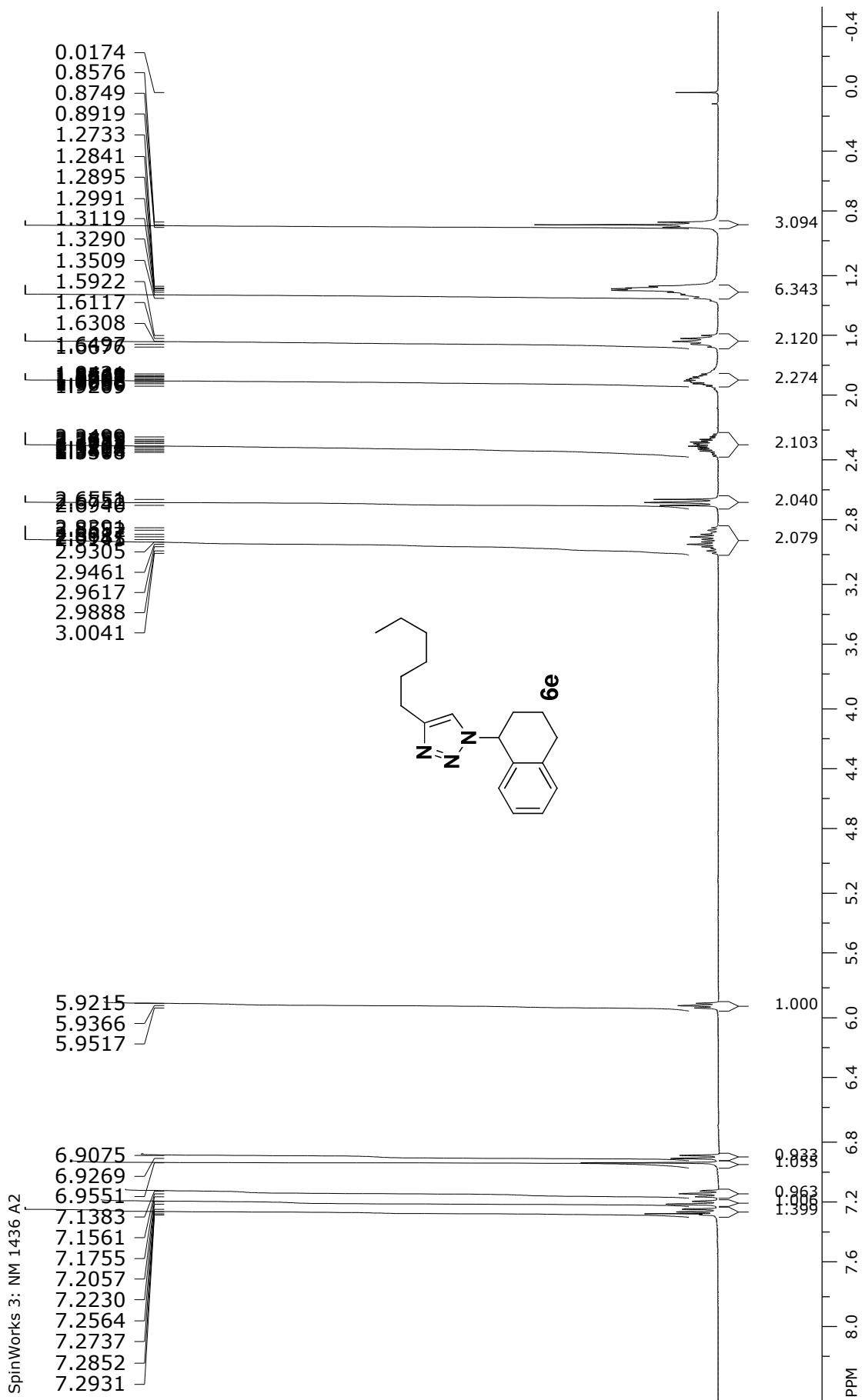


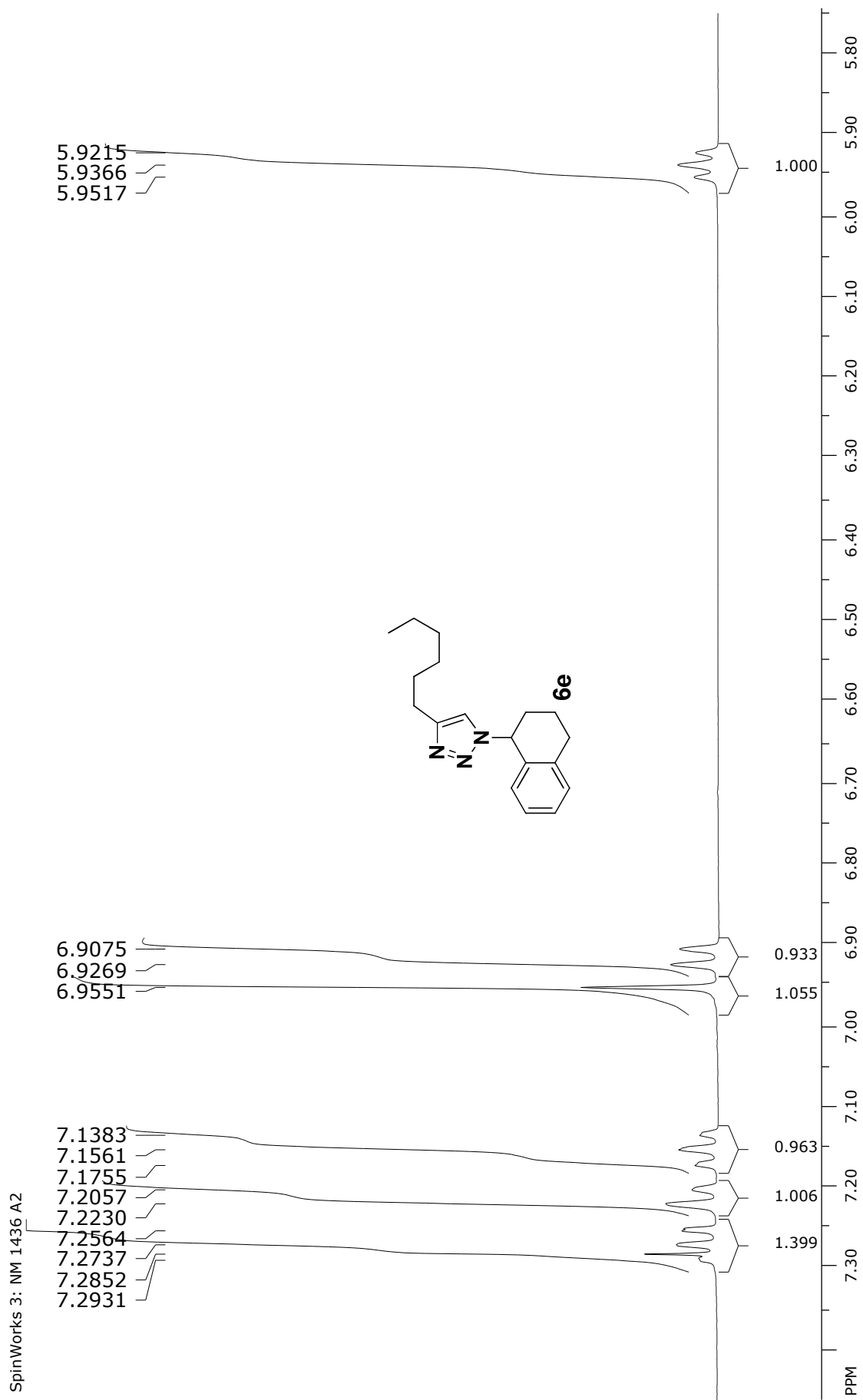


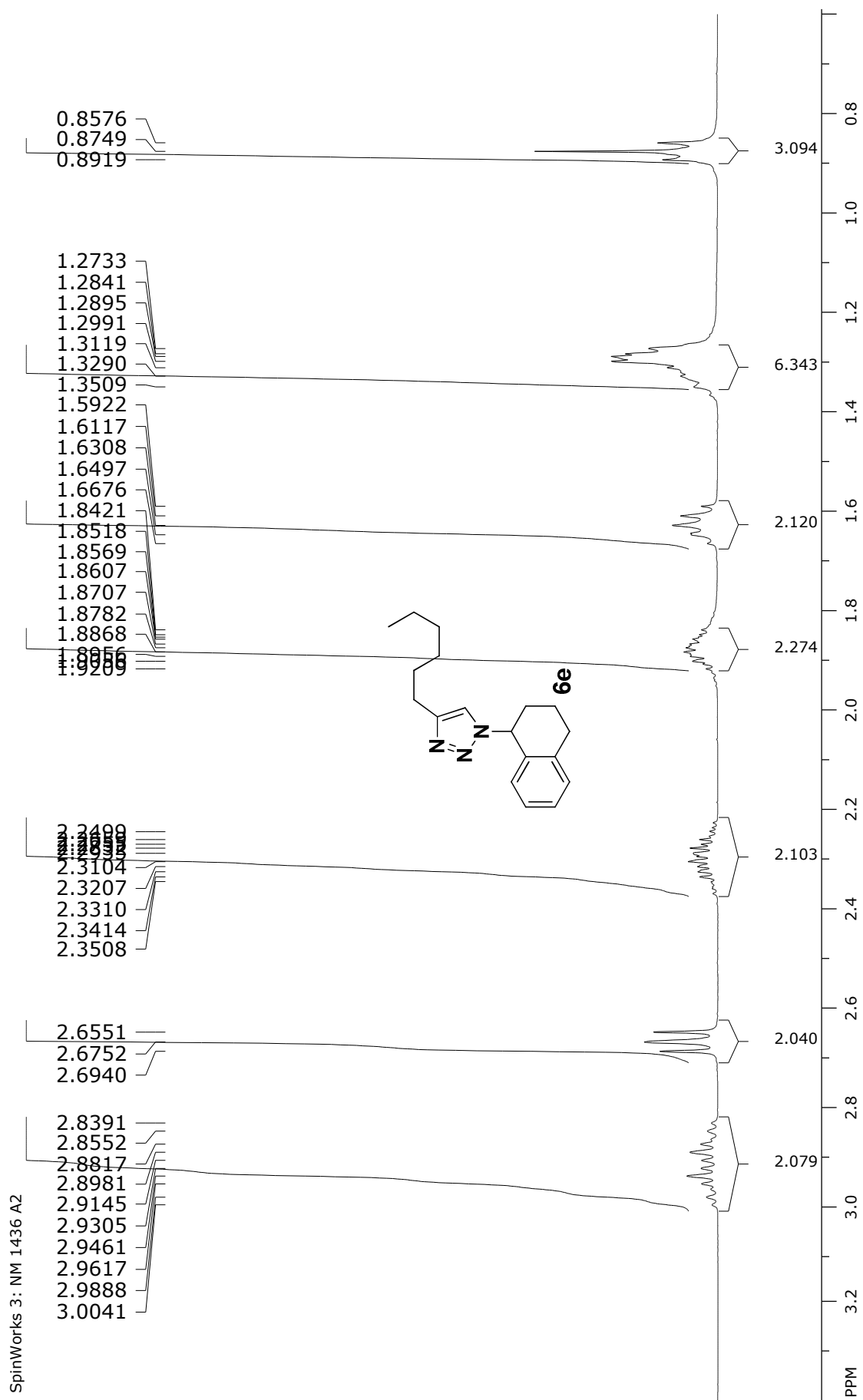


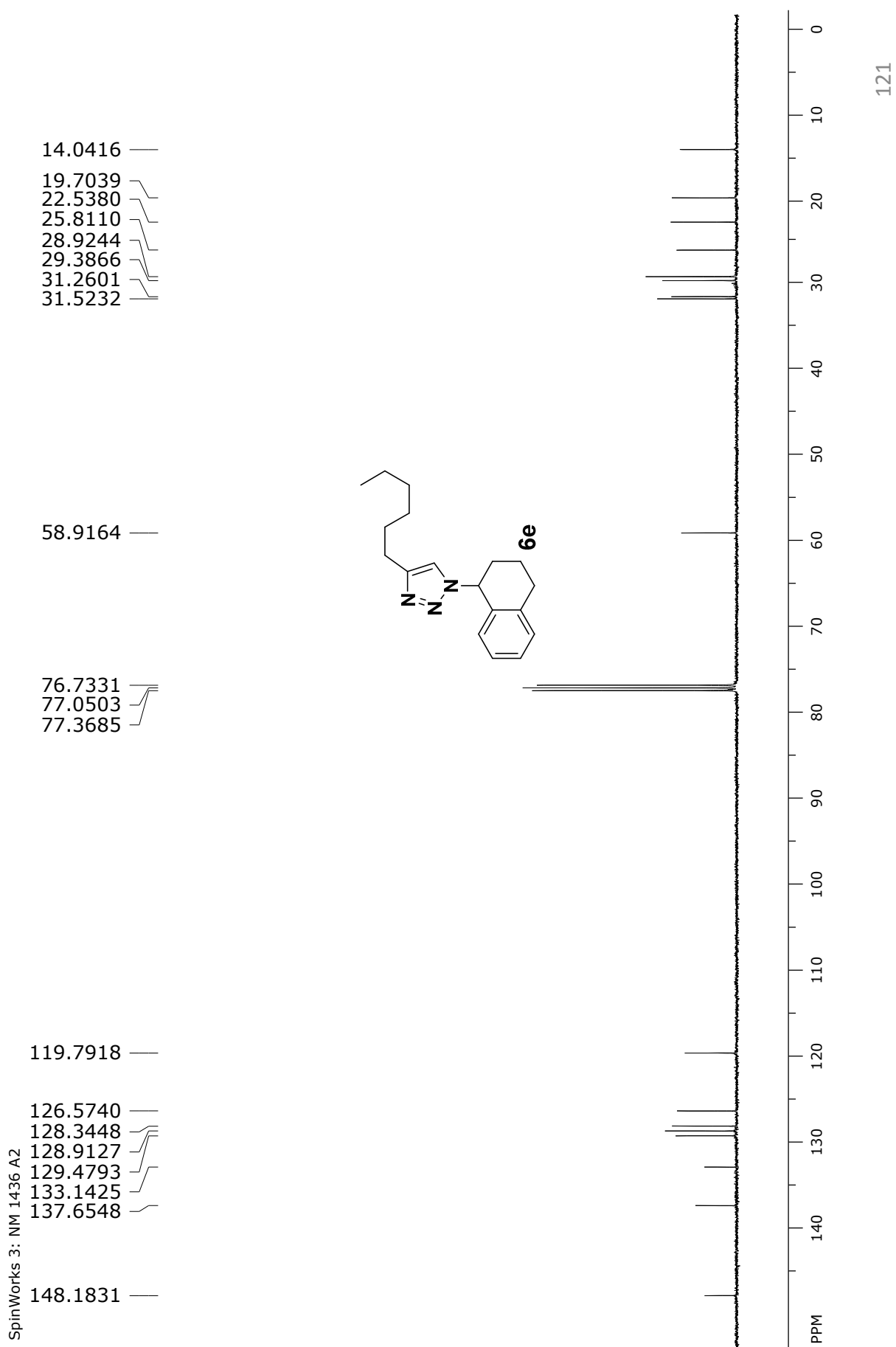




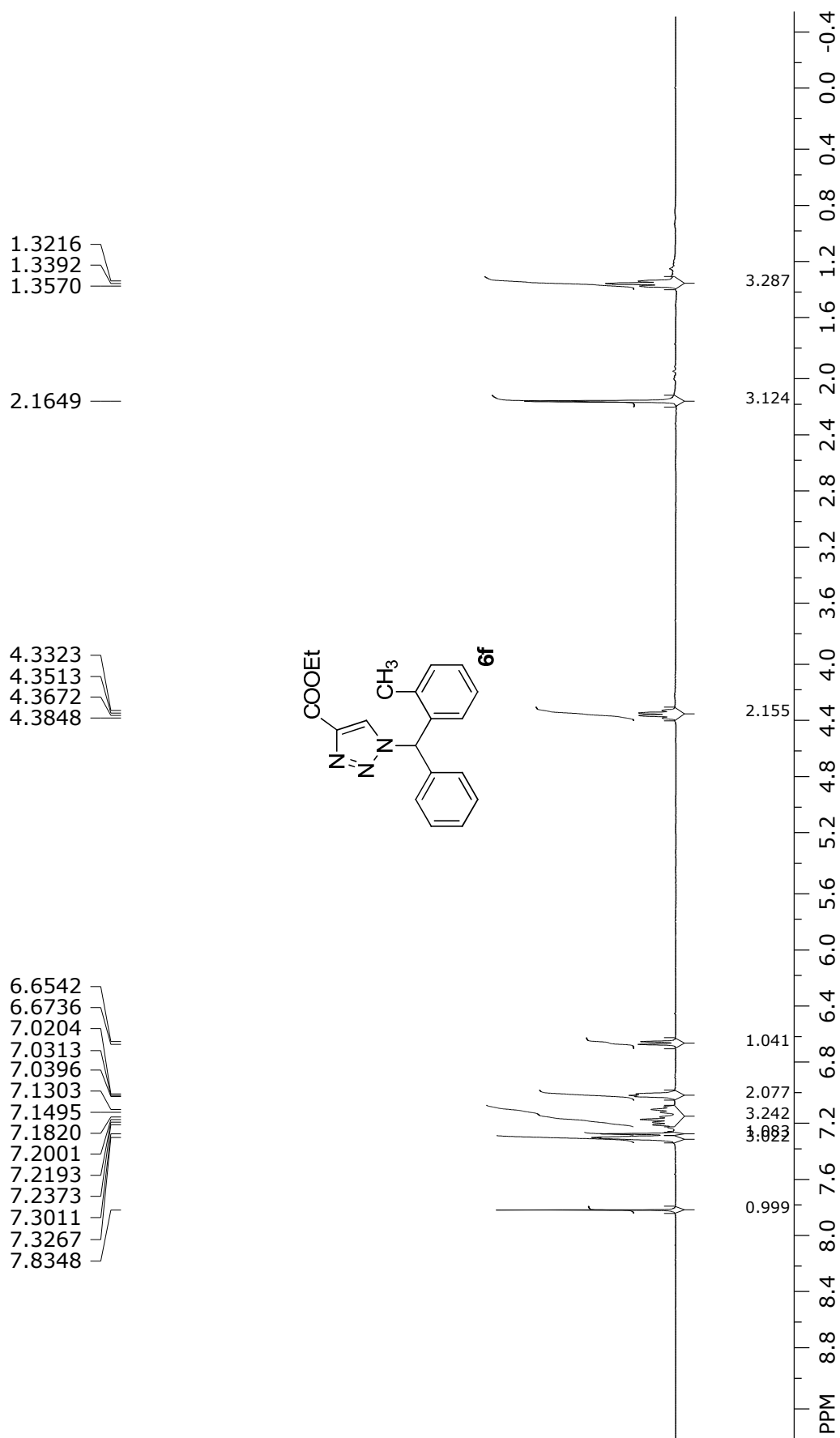




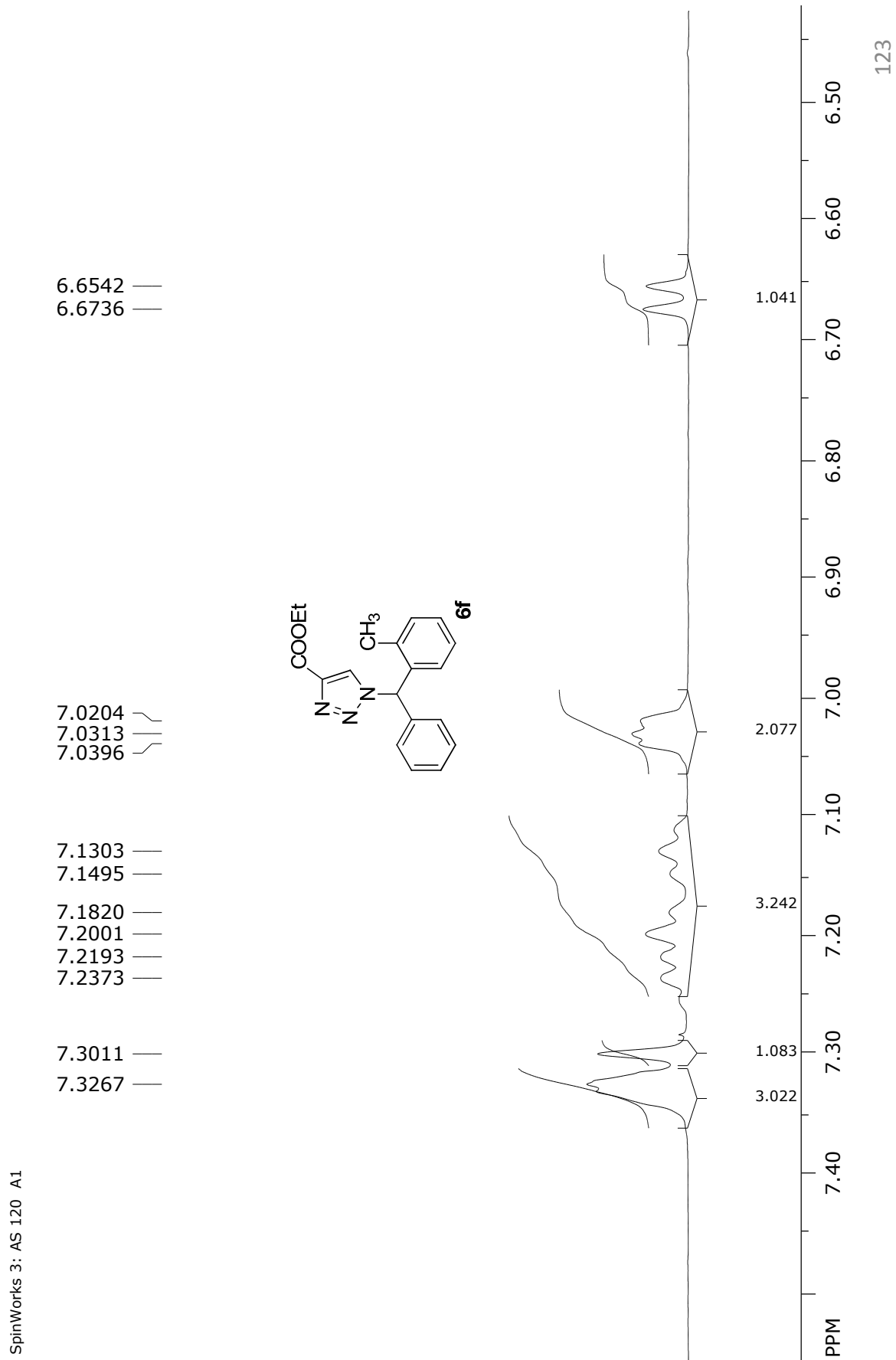




SpinWorks 3: AS 120 A1



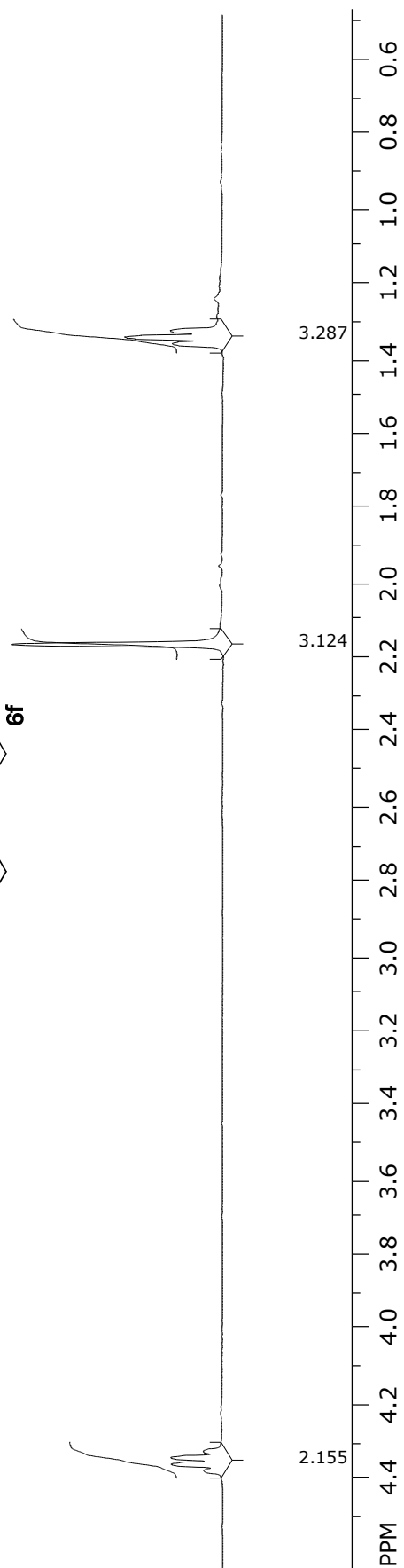
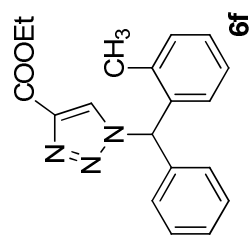


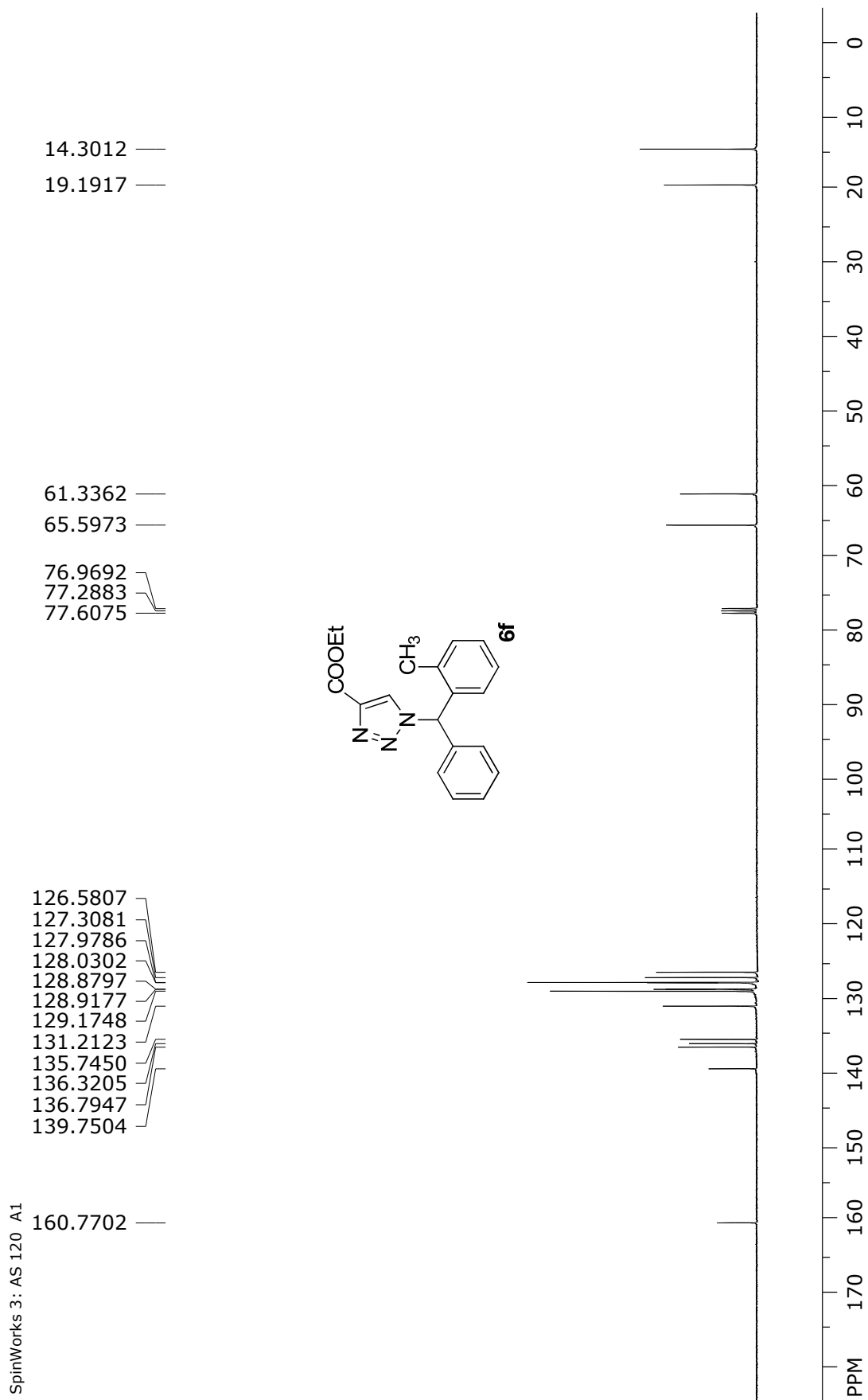


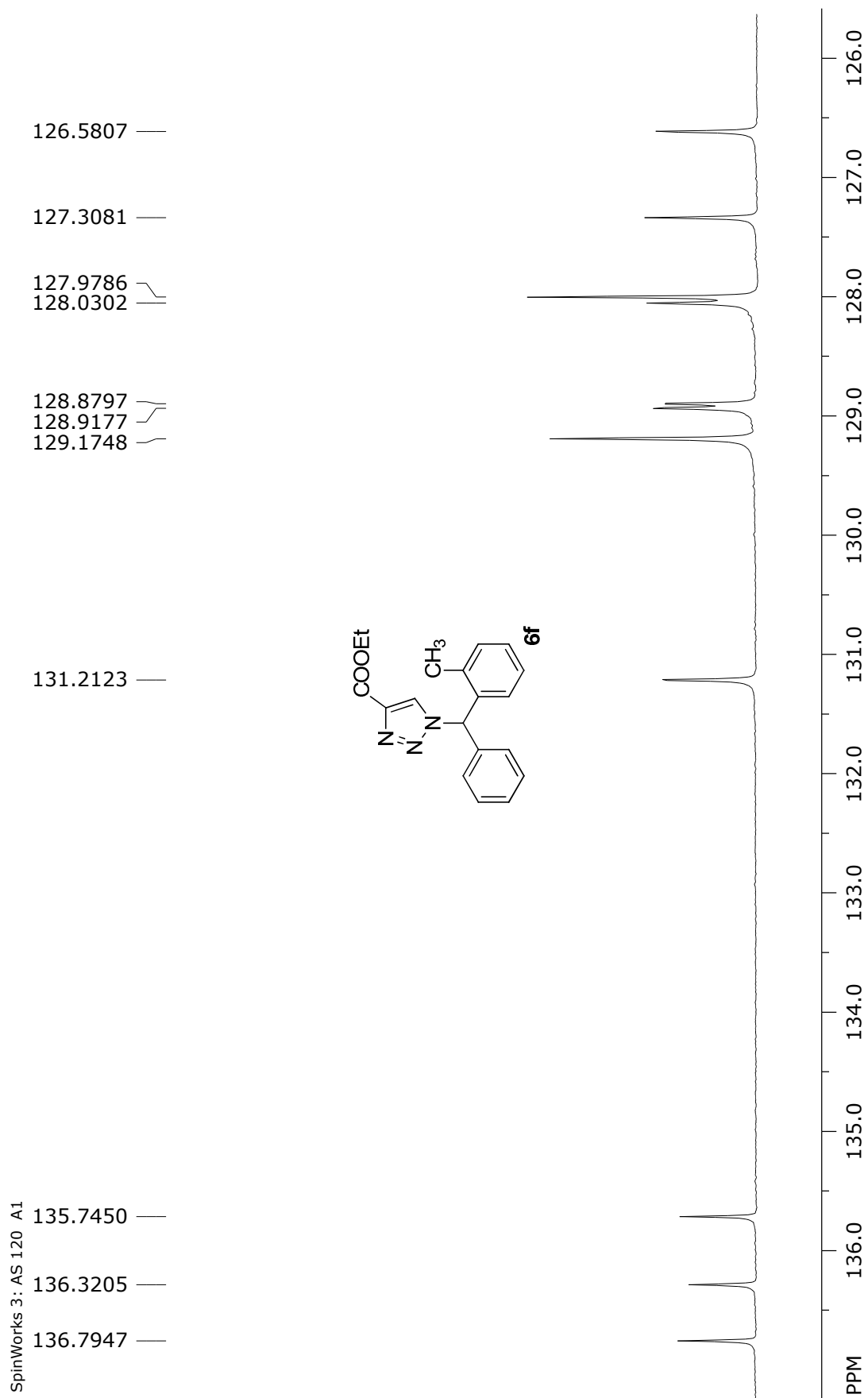
SpinWorks 3: AS 120 A1

4.3323  
4.3513  
4.3672  
4.38481.3216  
1.3392  
1.3570

2.1649

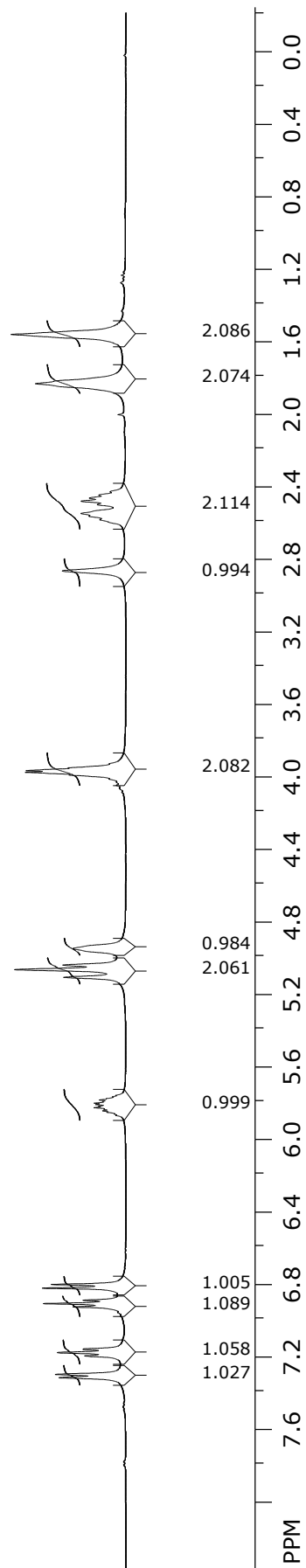
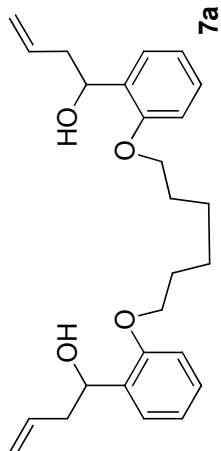


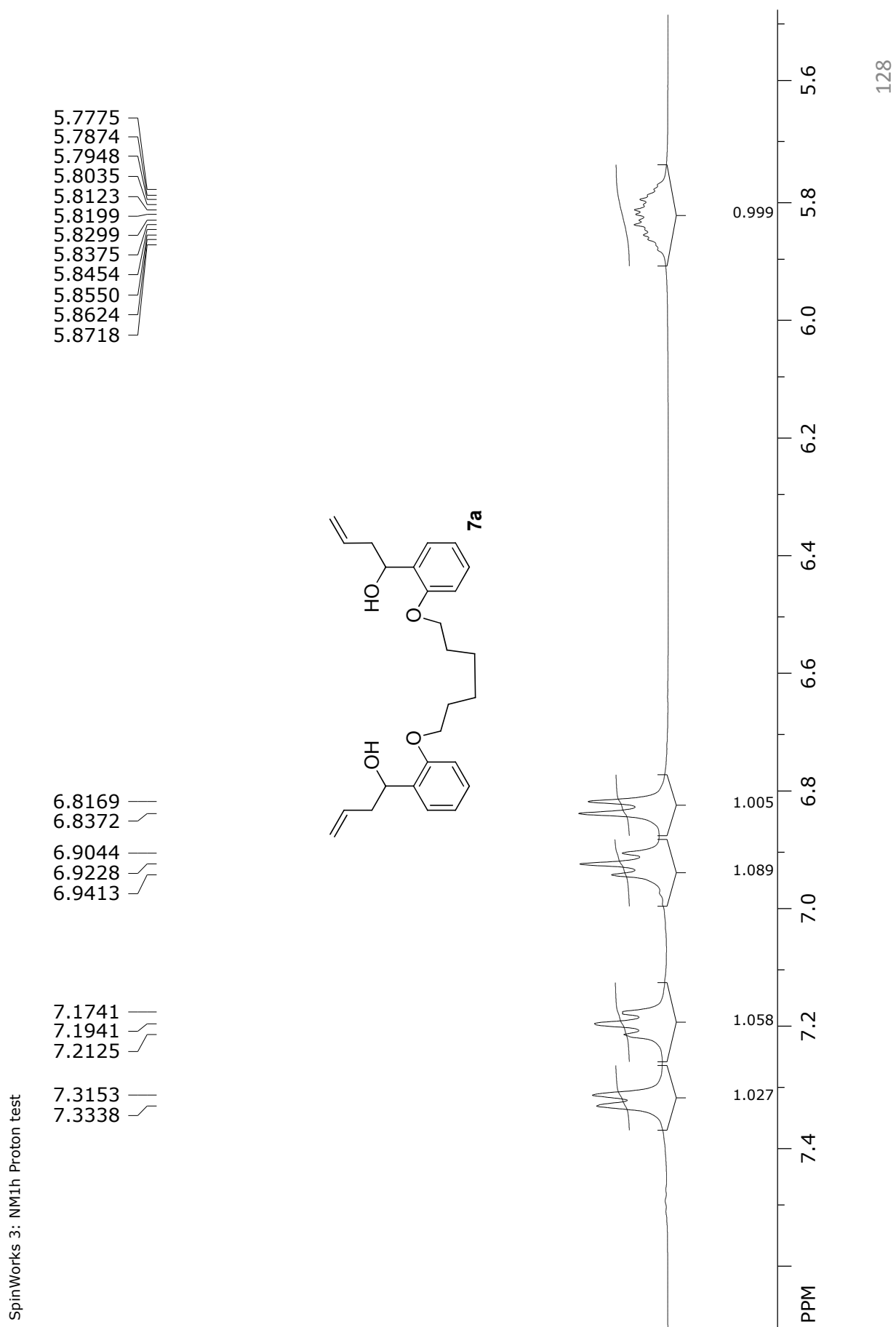


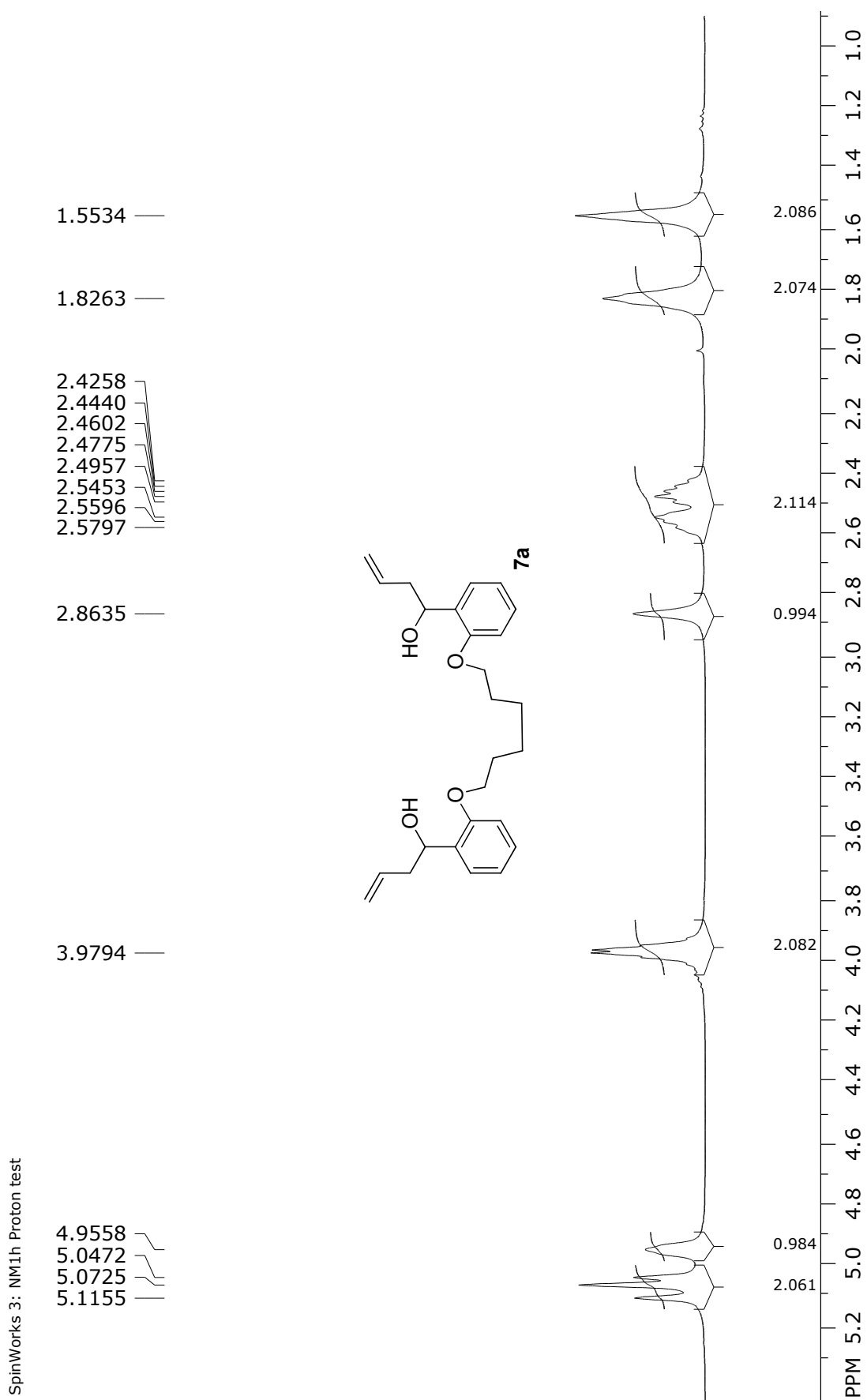


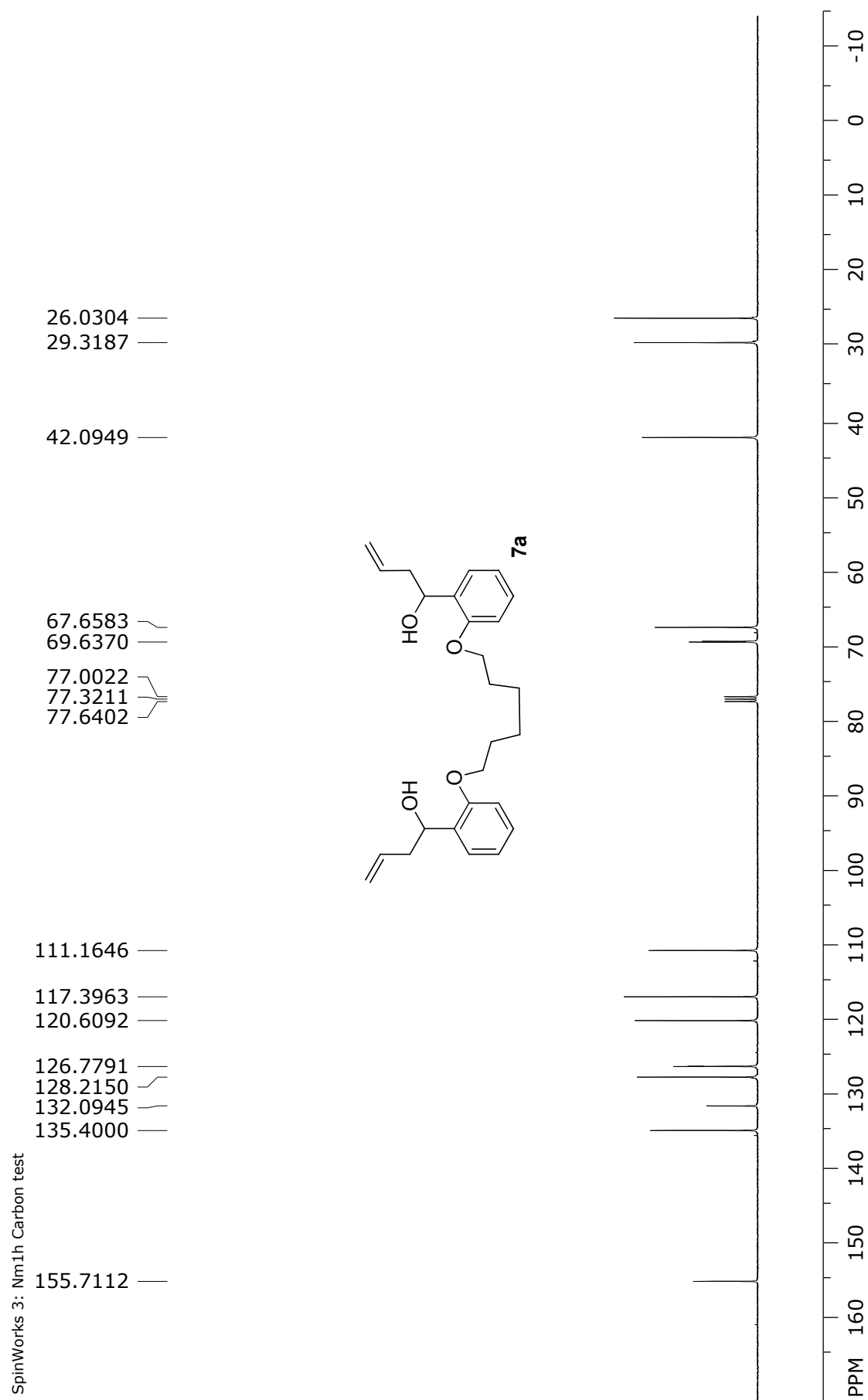
SpinWorks 3: NM1h Proton test

1.5534  
1.8263  
2.4258  
2.4440  
2.4602  
2.4775  
2.4957  
2.5453  
2.5596  
2.5797  
  
2.8635  
  
3.9794  
  
4.9558  
5.0472  
5.0725  
5.1155  
5.7775  
5.7874  
5.7948  
5.8035  
5.8123  
5.8199  
5.8299  
5.8375  
5.8454  
5.8550  
5.8624  
5.8718  
  
6.8169  
6.8372  
6.9044  
6.9228  
6.9413  
7.1741  
7.1941  
7.2125  
7.3153  
7.3338





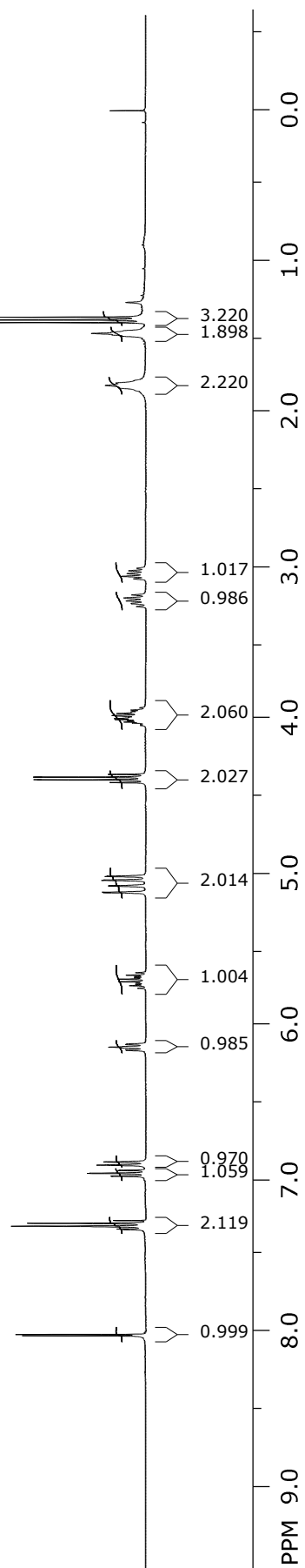
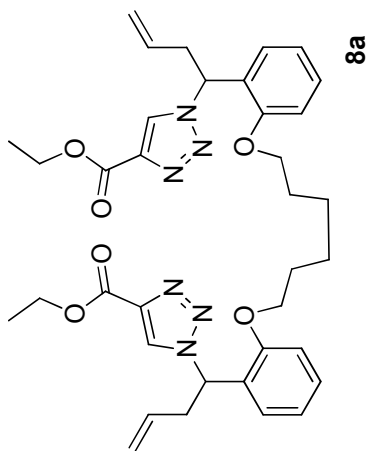


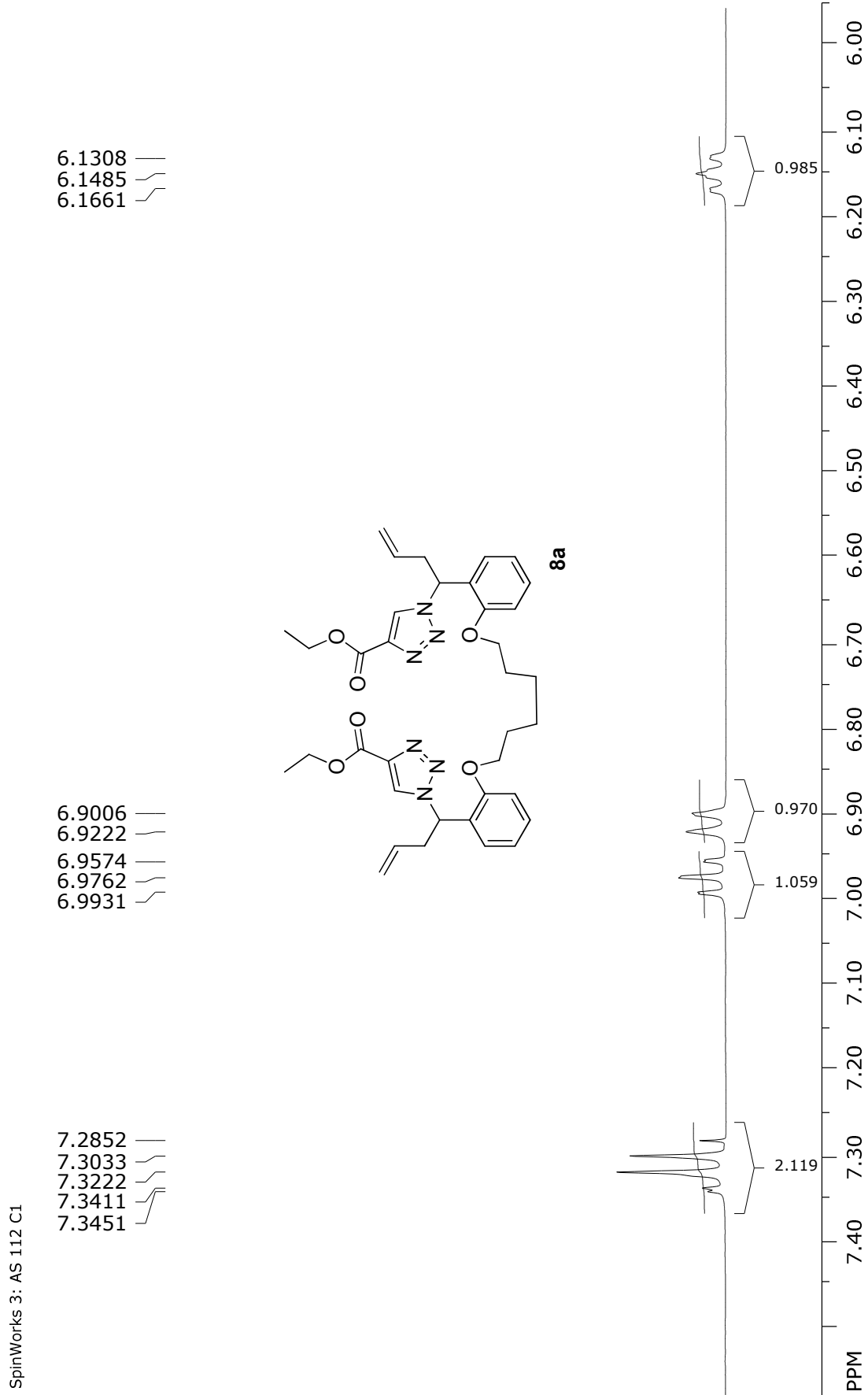




SpinWorks 3: AS 112 C1

1.3619  
1.3797  
1.4875  
1.4885  
  
3.0149  
3.0435  
3.0612  
3.1831  
3.2019  
3.2041  
3.2202  
3.2225  
3.2382  
3.2405  
3.9380  
3.9450  
3.9509  
3.9607  
4.0039  
4.0049  
4.3606  
  
5.0895  
5.0894  
5.0929  
5.1321  
5.1356  
5.6770  
5.7025  
5.7195  
5.7451  
6.1308  
6.1485  
6.1661  
  
6.9006  
6.9222  
6.9574  
6.9762  
6.9931  
7.2852  
7.3033  
7.3222  
7.3411  
7.3451  
8.0327  
8.0404

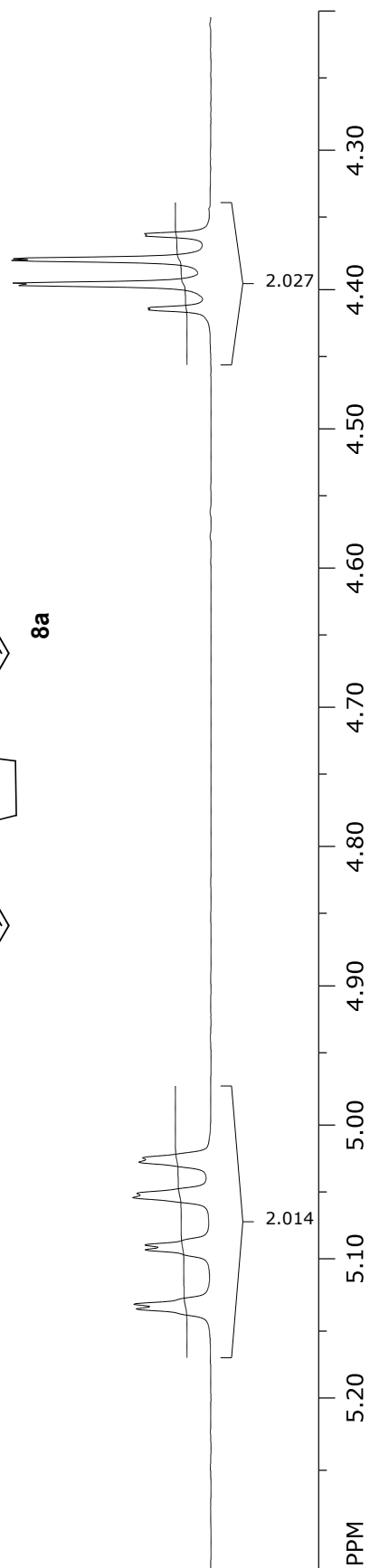
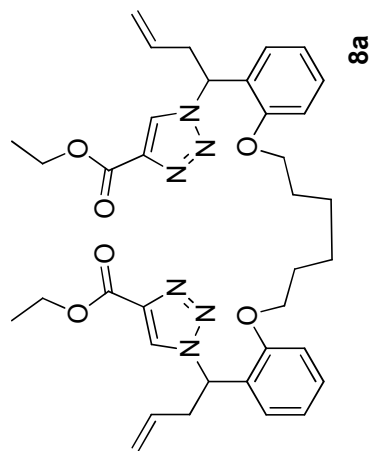




SpinWorks 3: AS 112 C1

4.3606 —  
4.3784 —  
4.3964 —  
4.4140 —

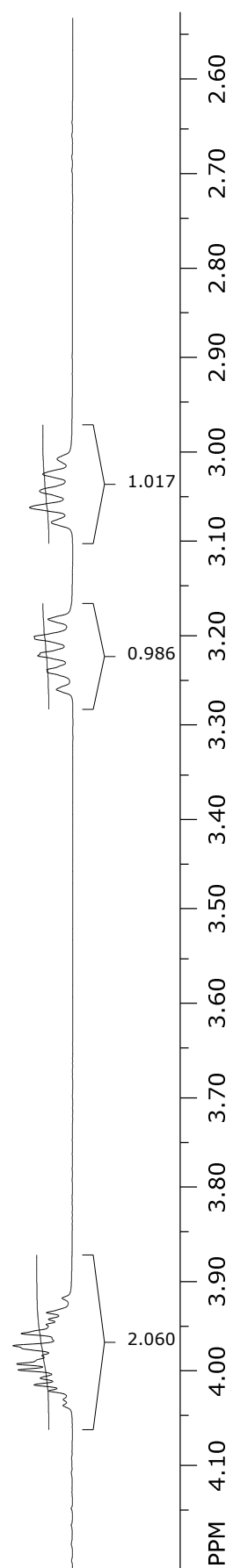
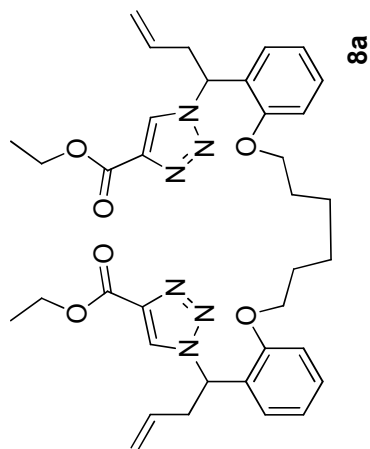
5.0265 —  
5.0295 —  
5.0521 —  
5.0551 —  
5.0894 —  
5.0929 —  
5.1321 —  
5.1356 —



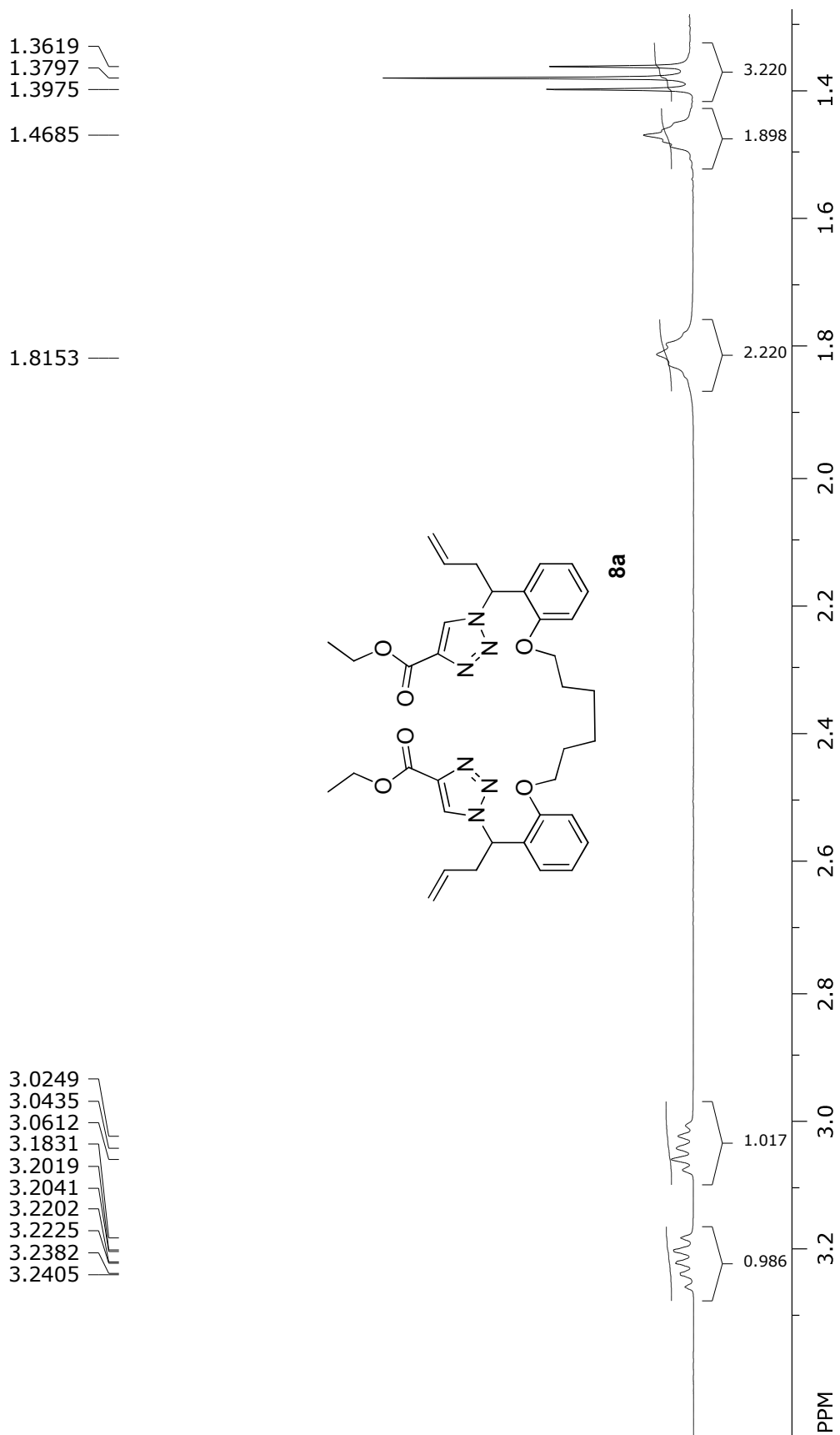
SpinWorks 3: AS 112 C1

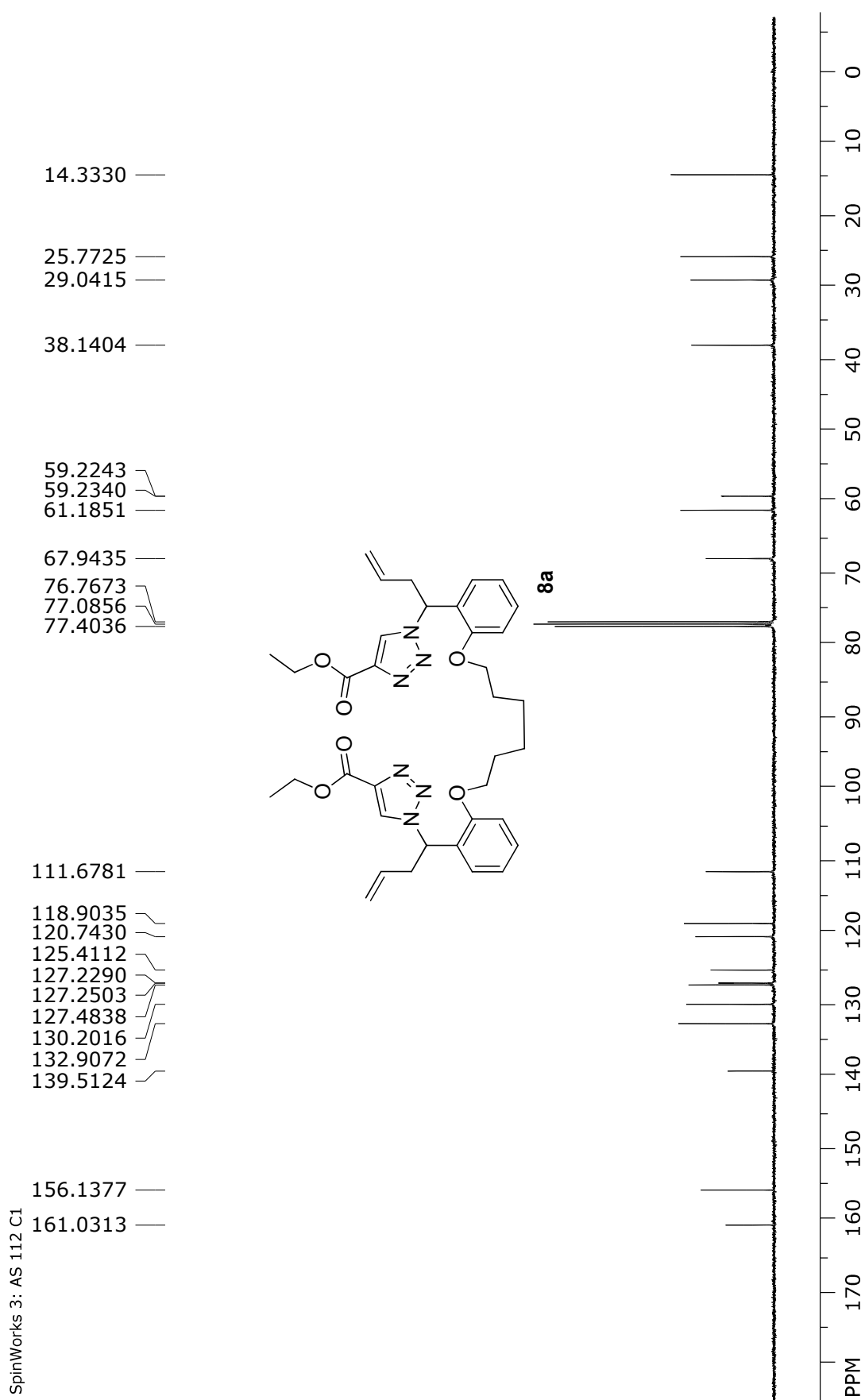
3.0249  
3.0435  
3.0612  
3.1831  
3.2019  
3.2041  
3.2202  
3.2225  
3.2382  
3.2405

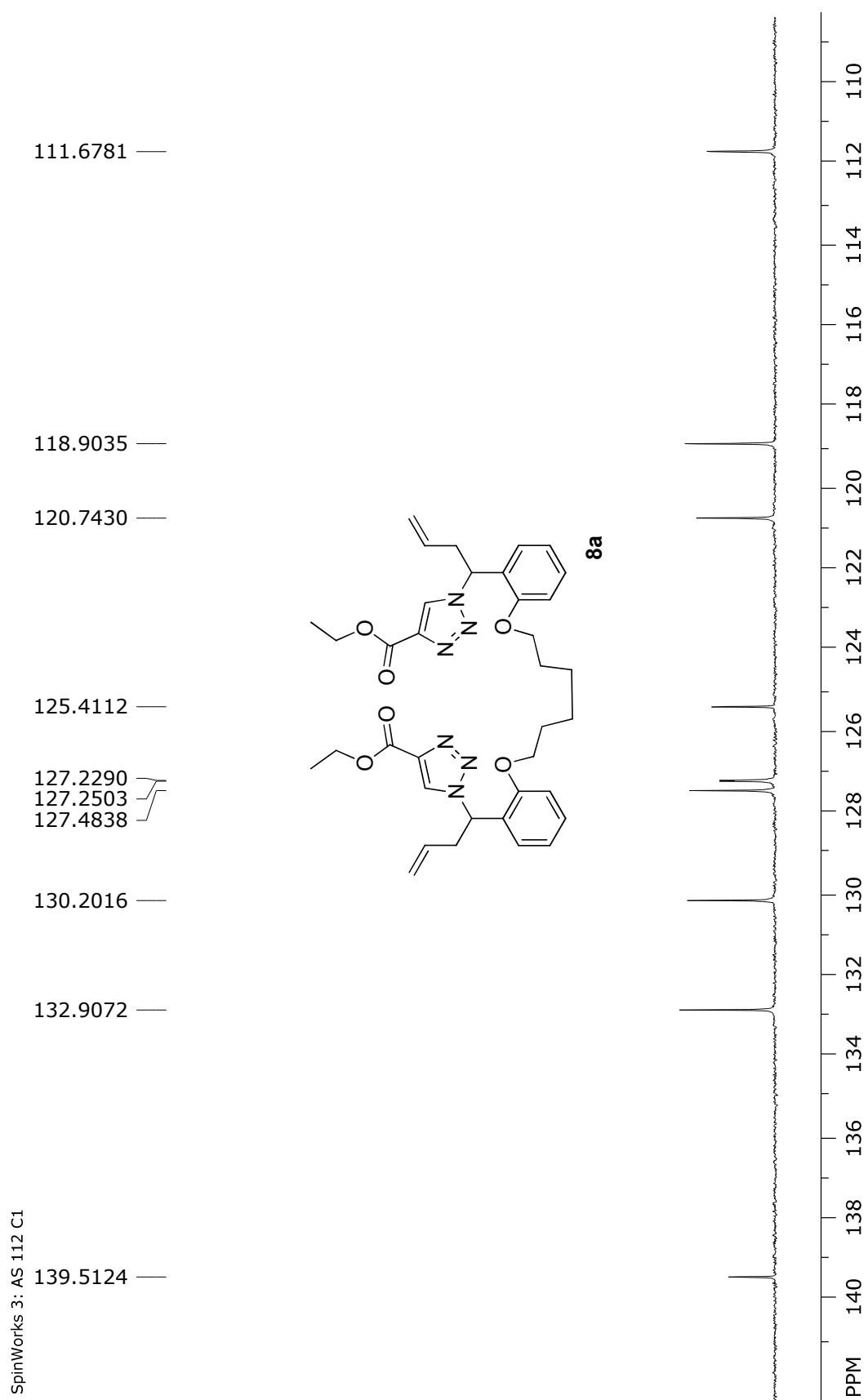
3.9380  
3.9450  
3.9509  
3.9607  
3.9739  
3.9847  
3.9936  
4.0004  
4.0092  
4.0164  
4.0232

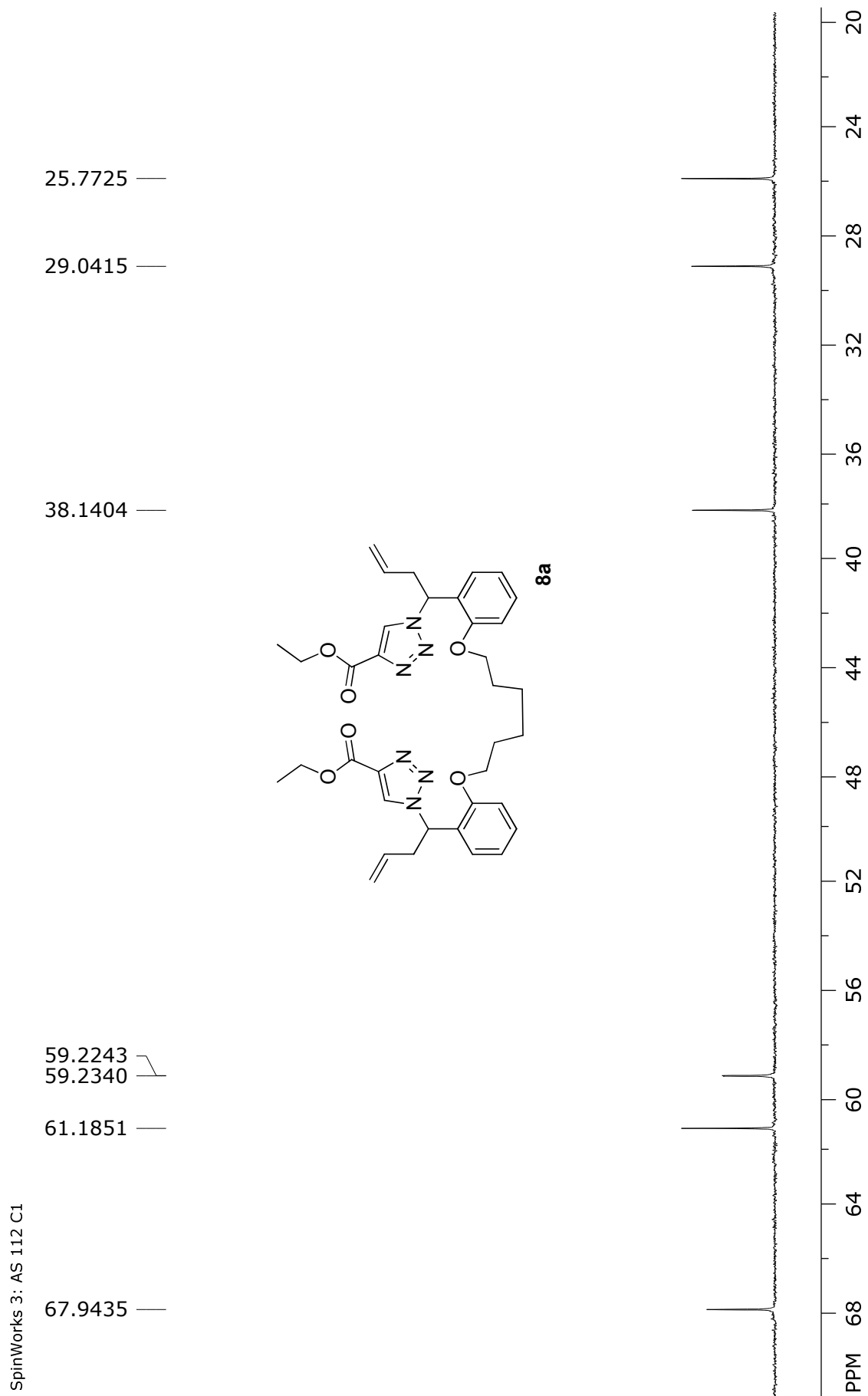


SpinWorks 3: AS 112 C1



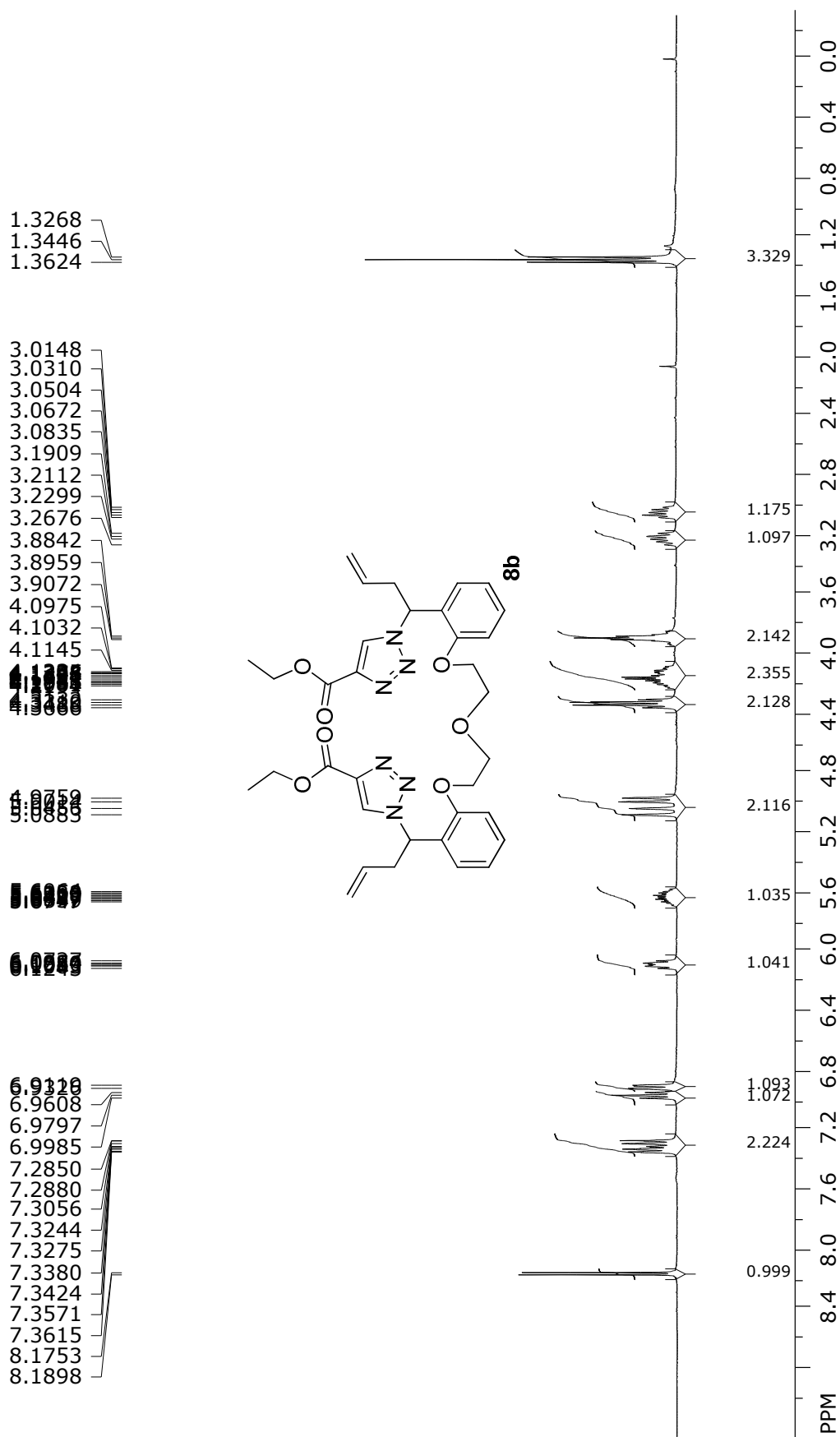


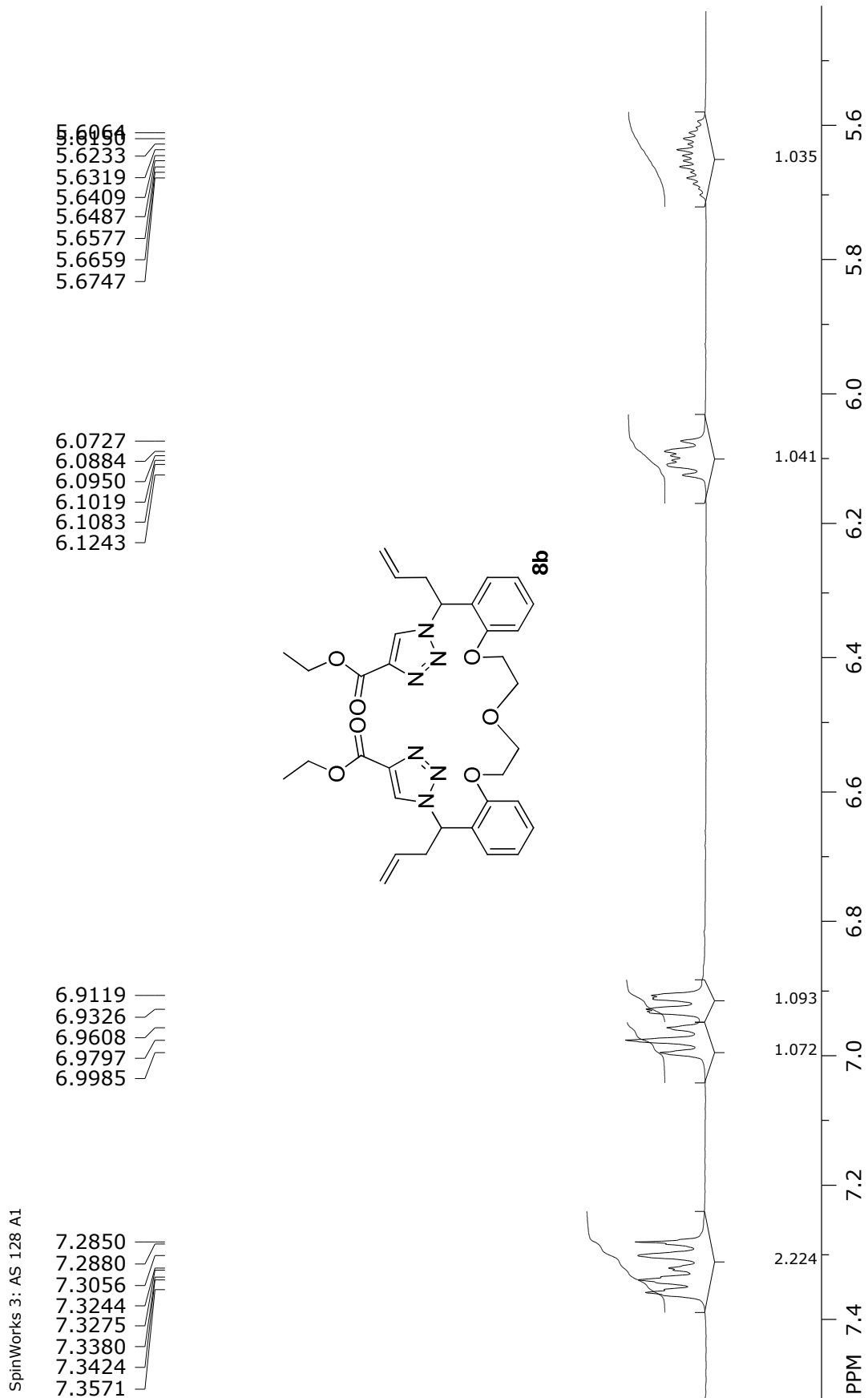






SpinWorks 3: AS 128 A1



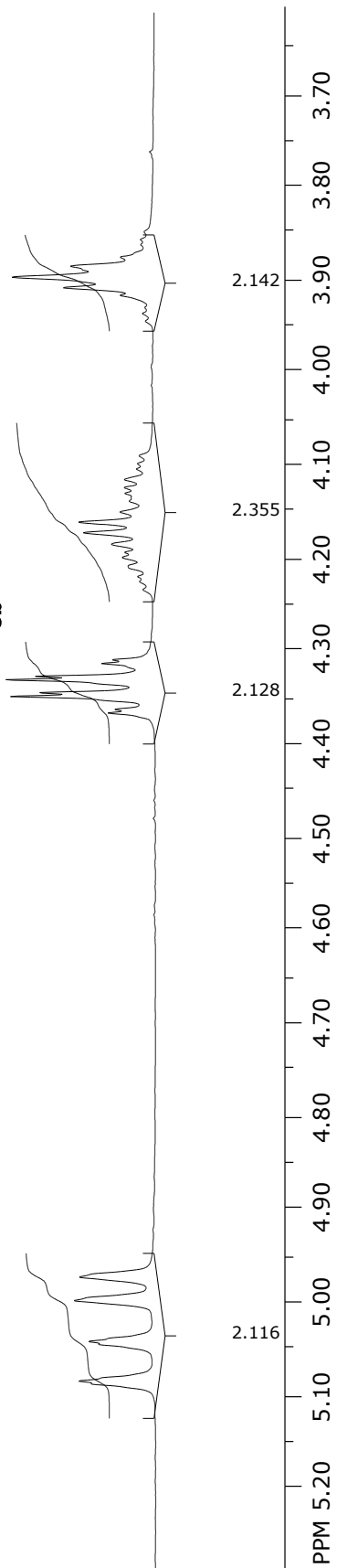
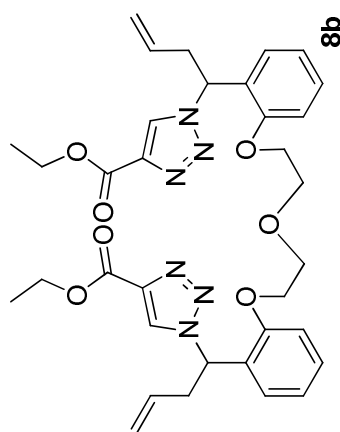


SpinWorks 3: AS 128 A1

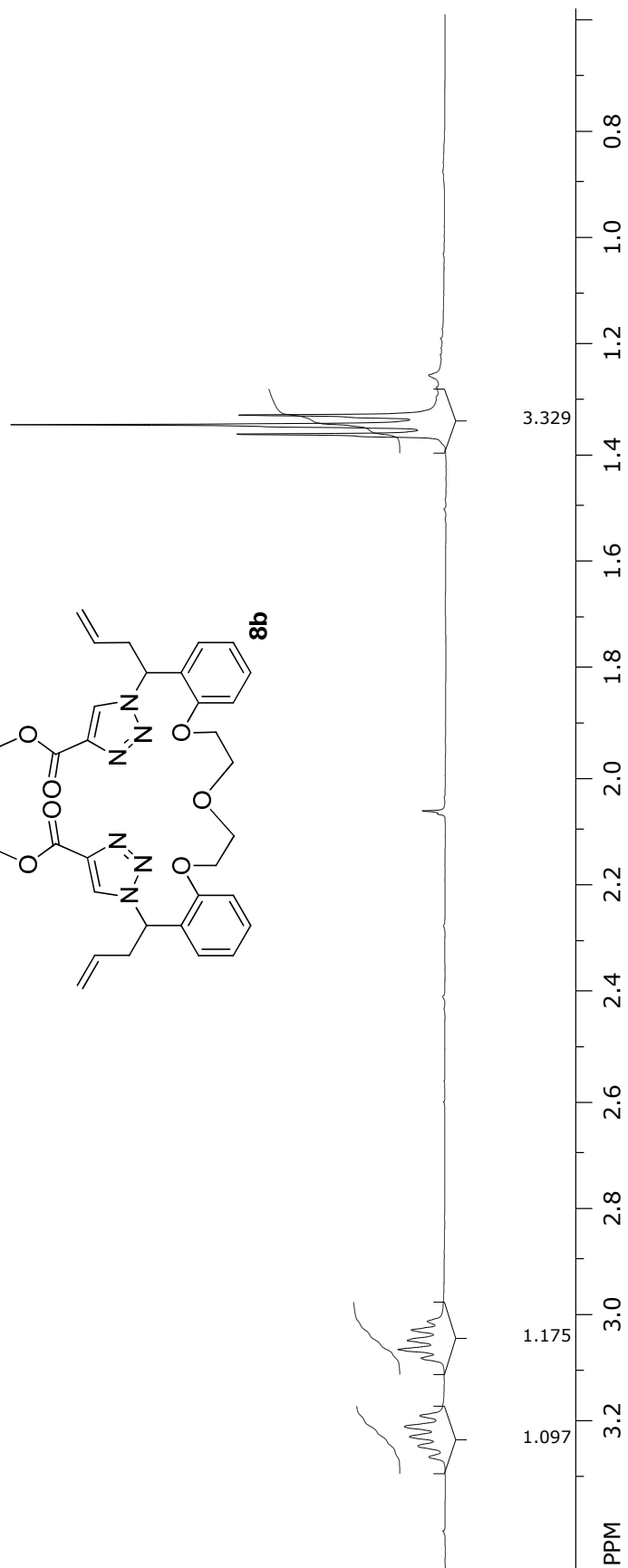
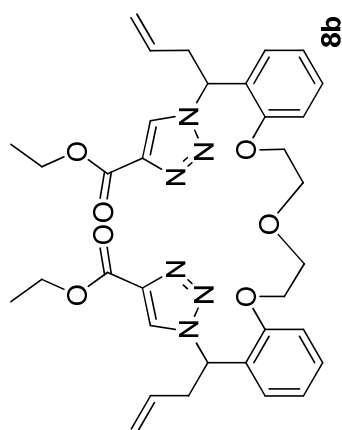
3.8842  
3.8959  
3.9072  
4.0975  
4.1032  
4.1145  
4.1234  
4.1295  
4.1343  
4.1378  
4.1495  
4.1604  
4.1721  
4.1843  
4.1931  
4.2089  
4.2194

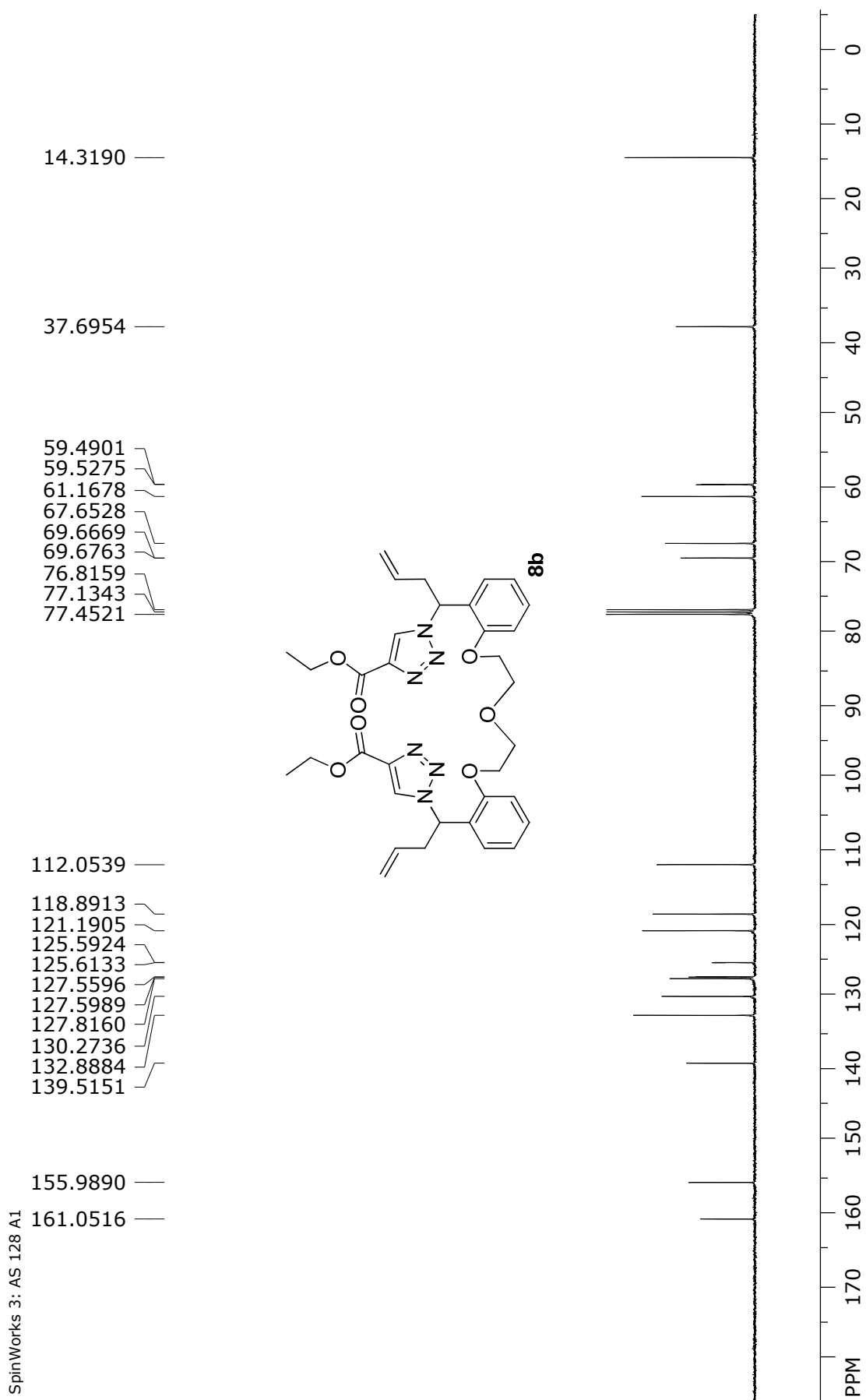
4.3132  
4.3310  
4.3488  
4.3666

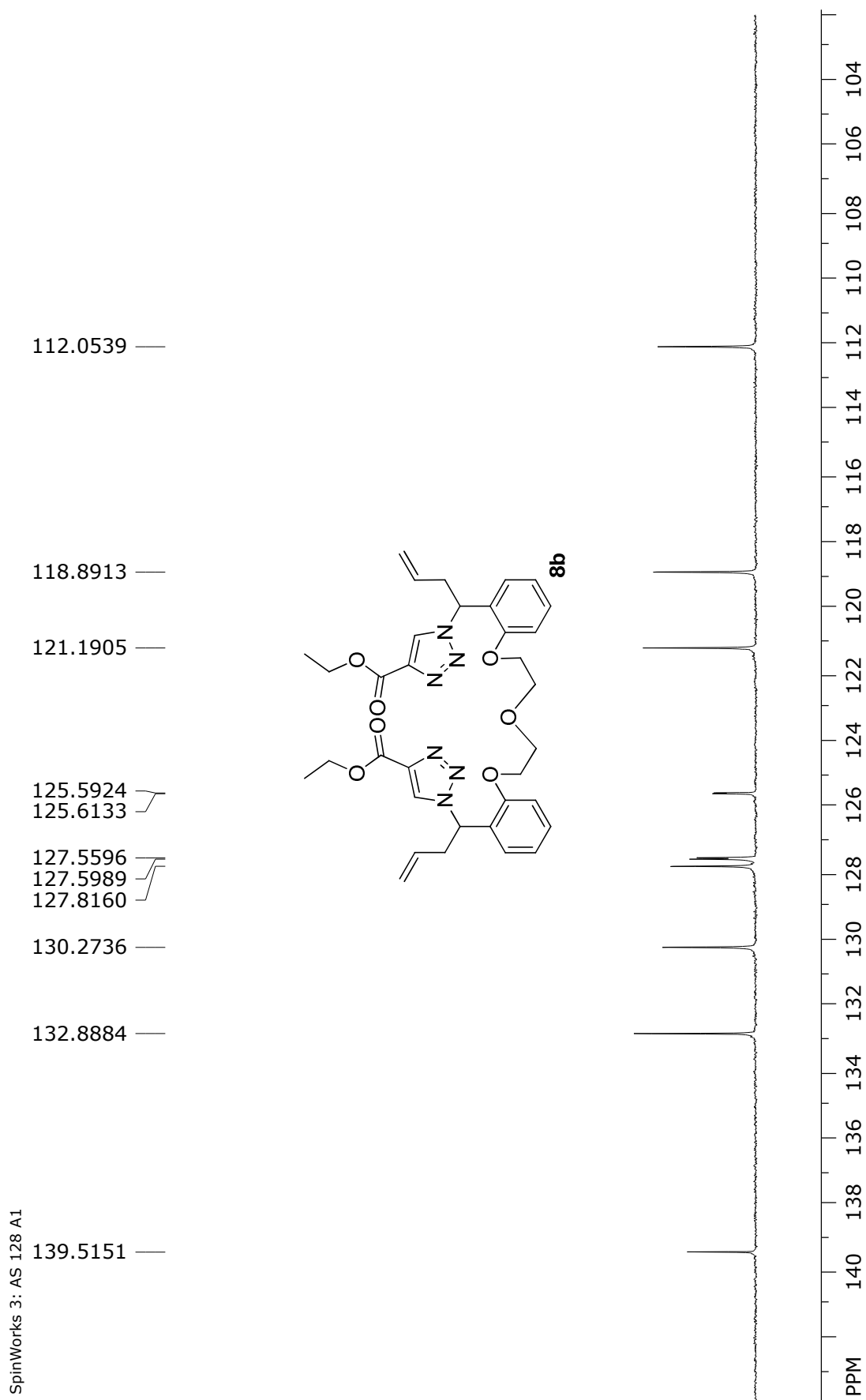
4.9759  
5.0014  
5.0456  
5.0883



SpinWorks 3: AS 128 A1

1.3268  
1.3446  
1.36243.0148  
3.0310  
3.0504  
3.0672  
3.0835  
3.1909  
3.2112  
3.2299  
3.2676



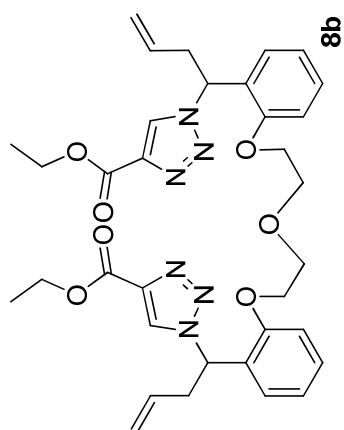


SpinWorks 3: AS 128 A1

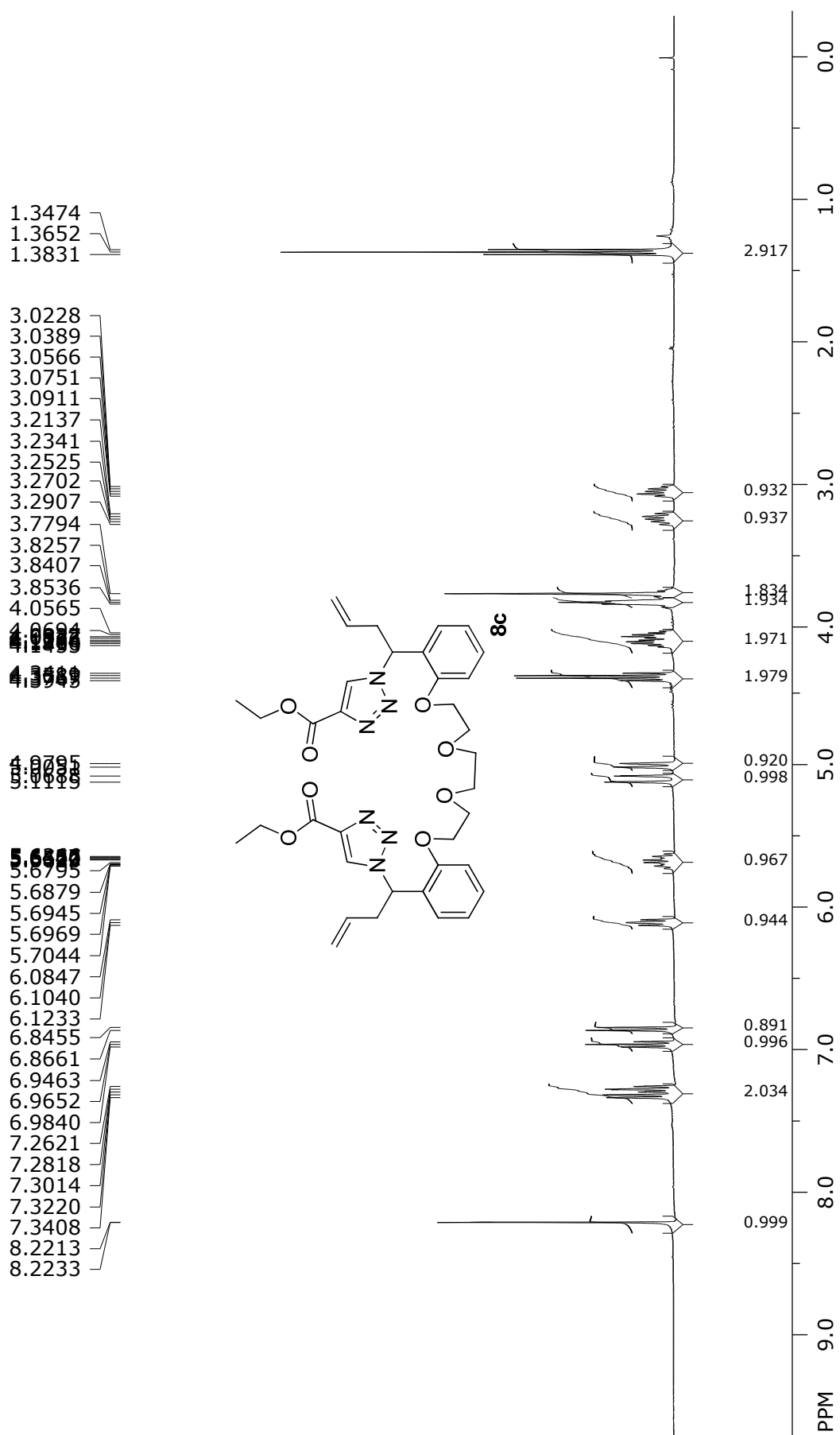
69.6669  
69.6763

67.6528

61.1678

59.4901  
59.5275

SpinWorks 3: AS 129 A1





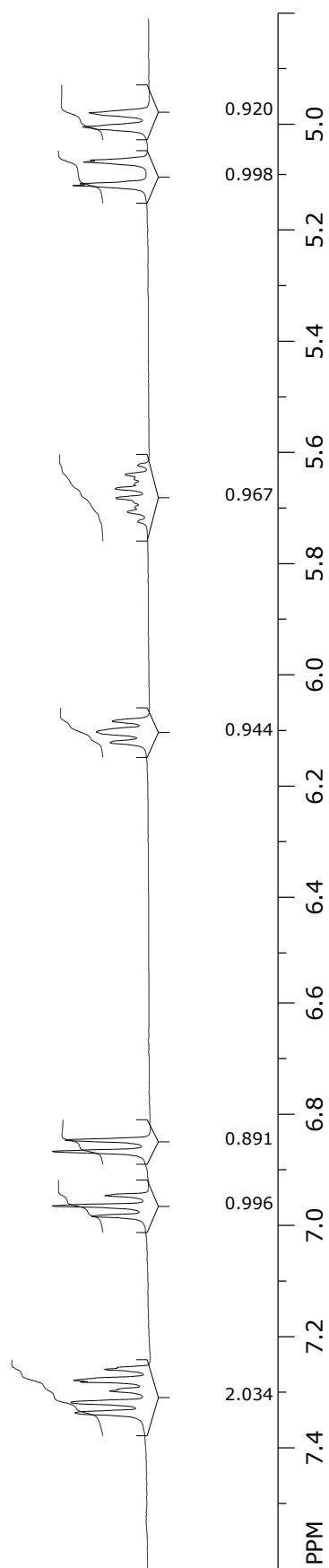
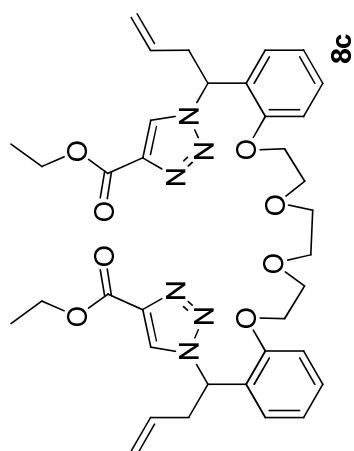
SpinWorks 3: AS 129 A1

4.9795  
5.0051  
5.0688  
5.1115

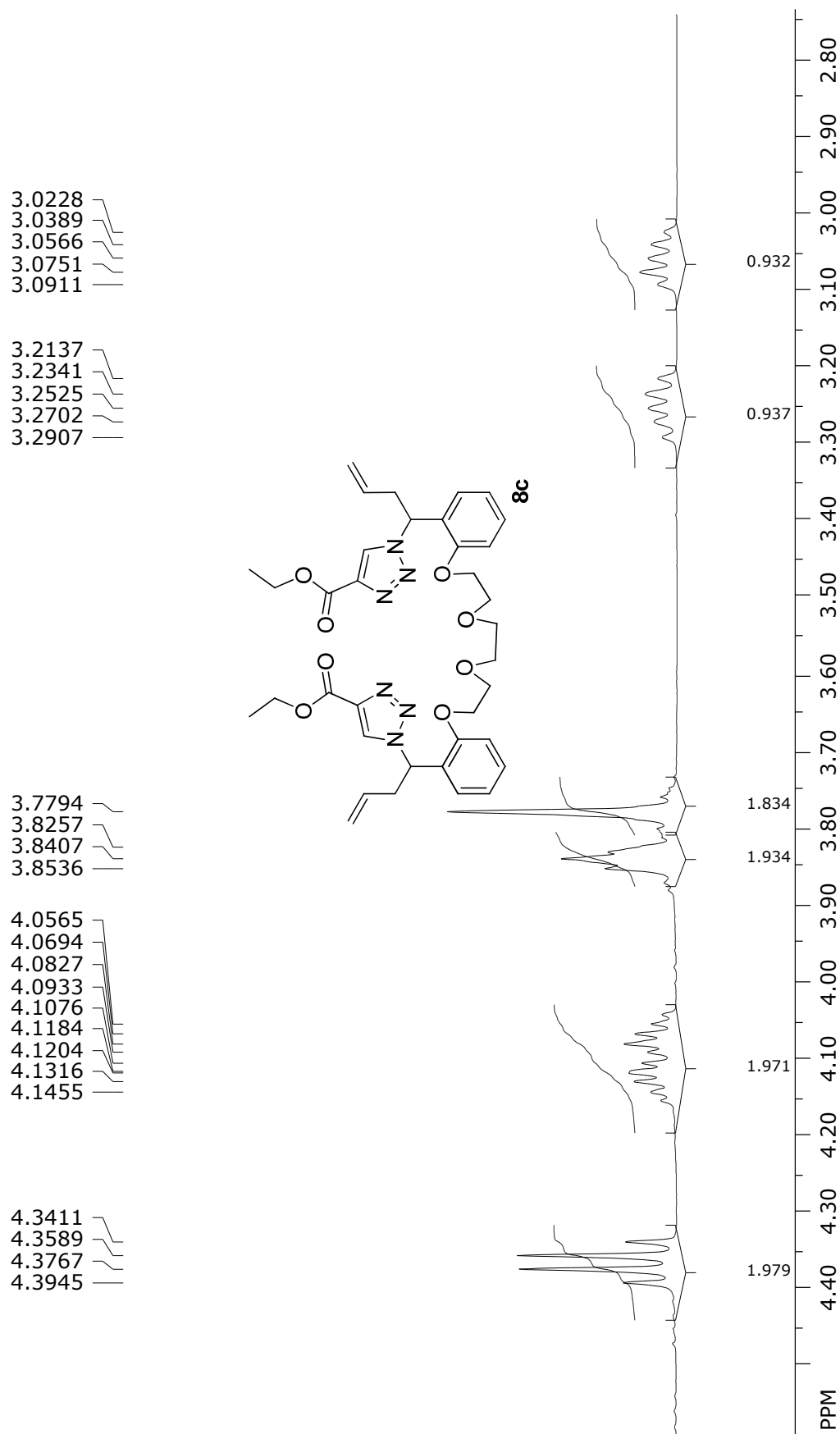
5.6366  
5.6427  
5.6454  
5.6520  
5.6542  
5.6623  
5.6795  
5.6879  
5.6945  
5.6969  
5.7044  
6.0847  
6.1040  
6.1233

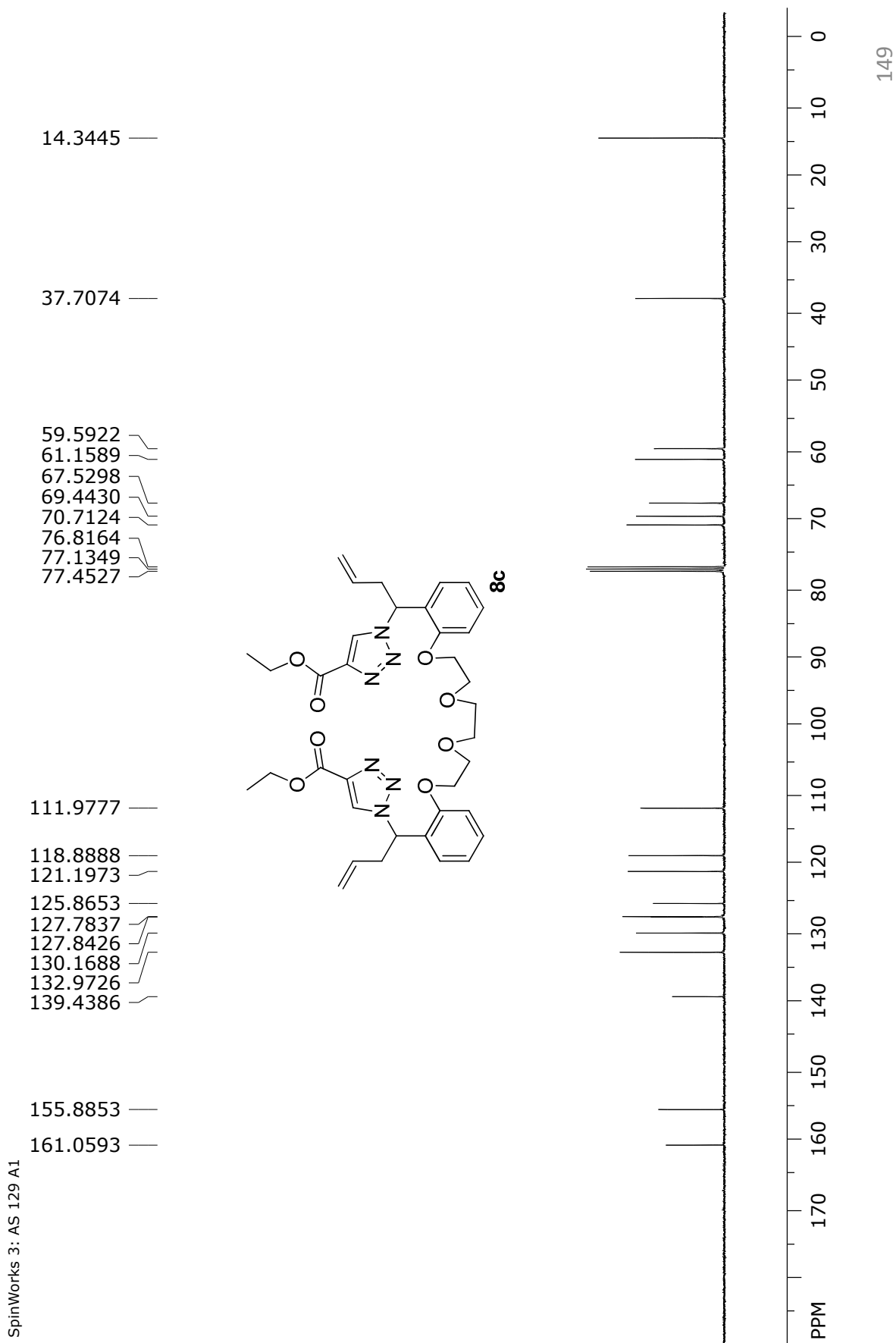
6.8455  
6.8661  
6.9463  
6.9652  
6.9840

7.2621  
7.2818  
7.3014  
7.3220  
7.3408



SpinWorks 3: AS 129 A1





SpinWorks 3: AS 131 A1

1.3608  
1.3670  
1.3786  
1.3848  
1.3965  
1.4027

2.9566  
2.9598  
2.9643  
2.9682  
2.9763  
2.9798  
2.9842  
2.9876  
2.9924  
**3.0058**  
**3.1688**

**4.2598**

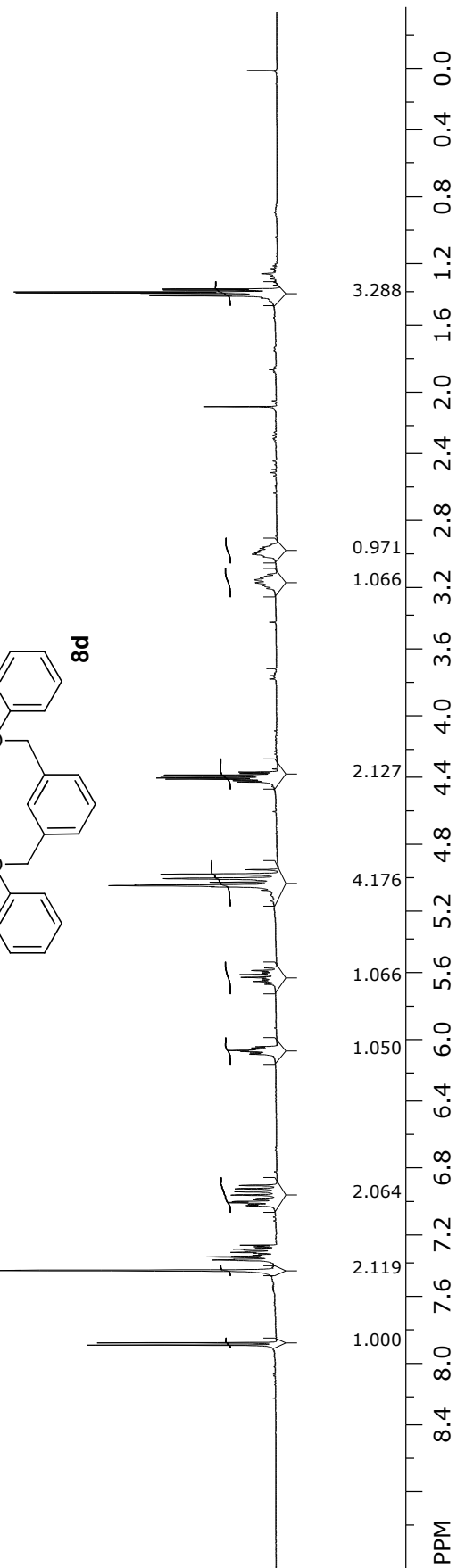
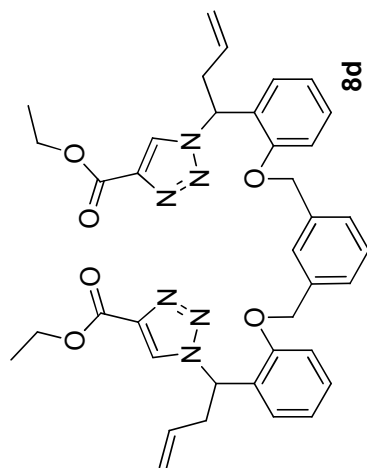
**4.6584**

**5.6932**

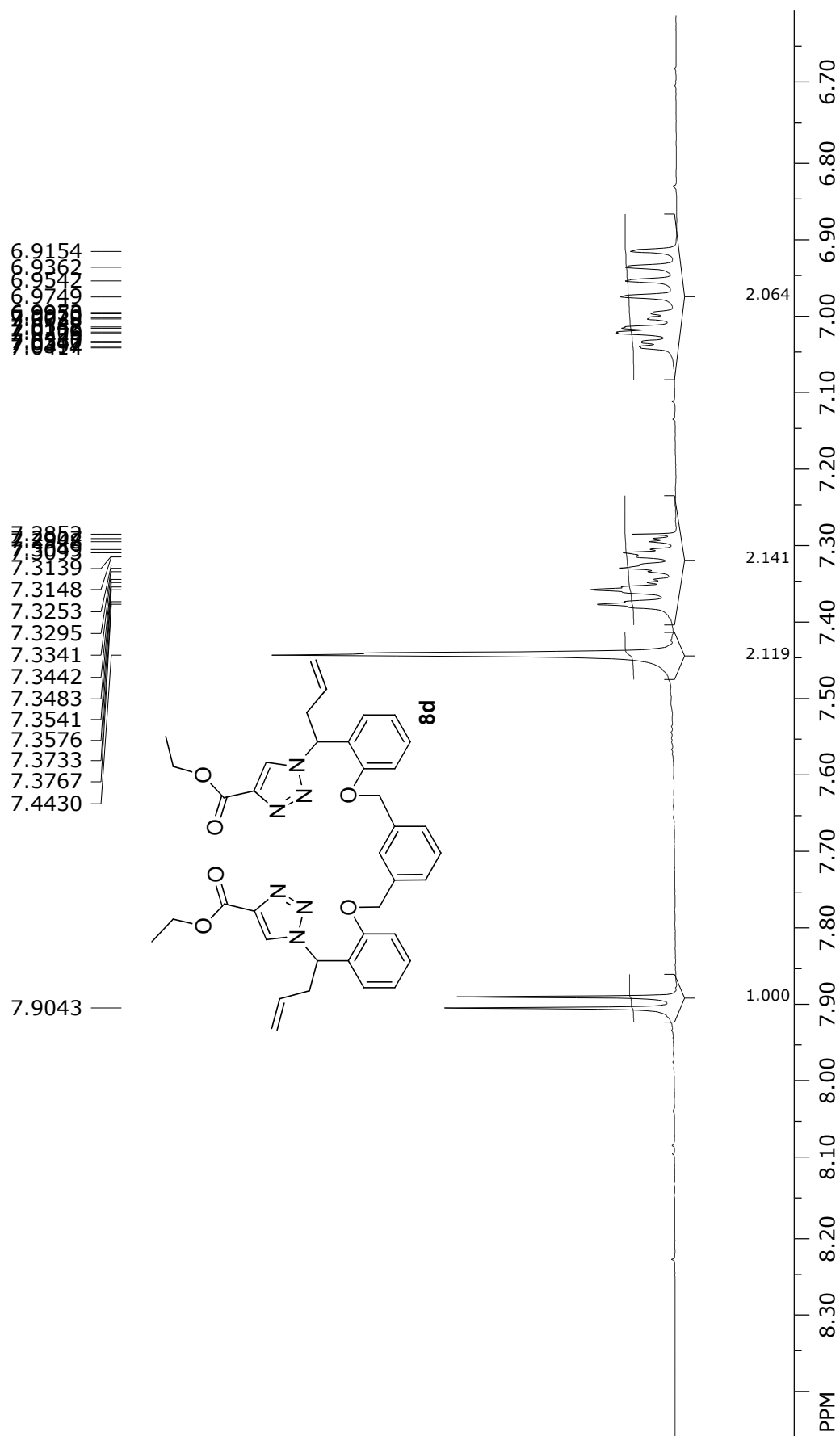
**6.0521**

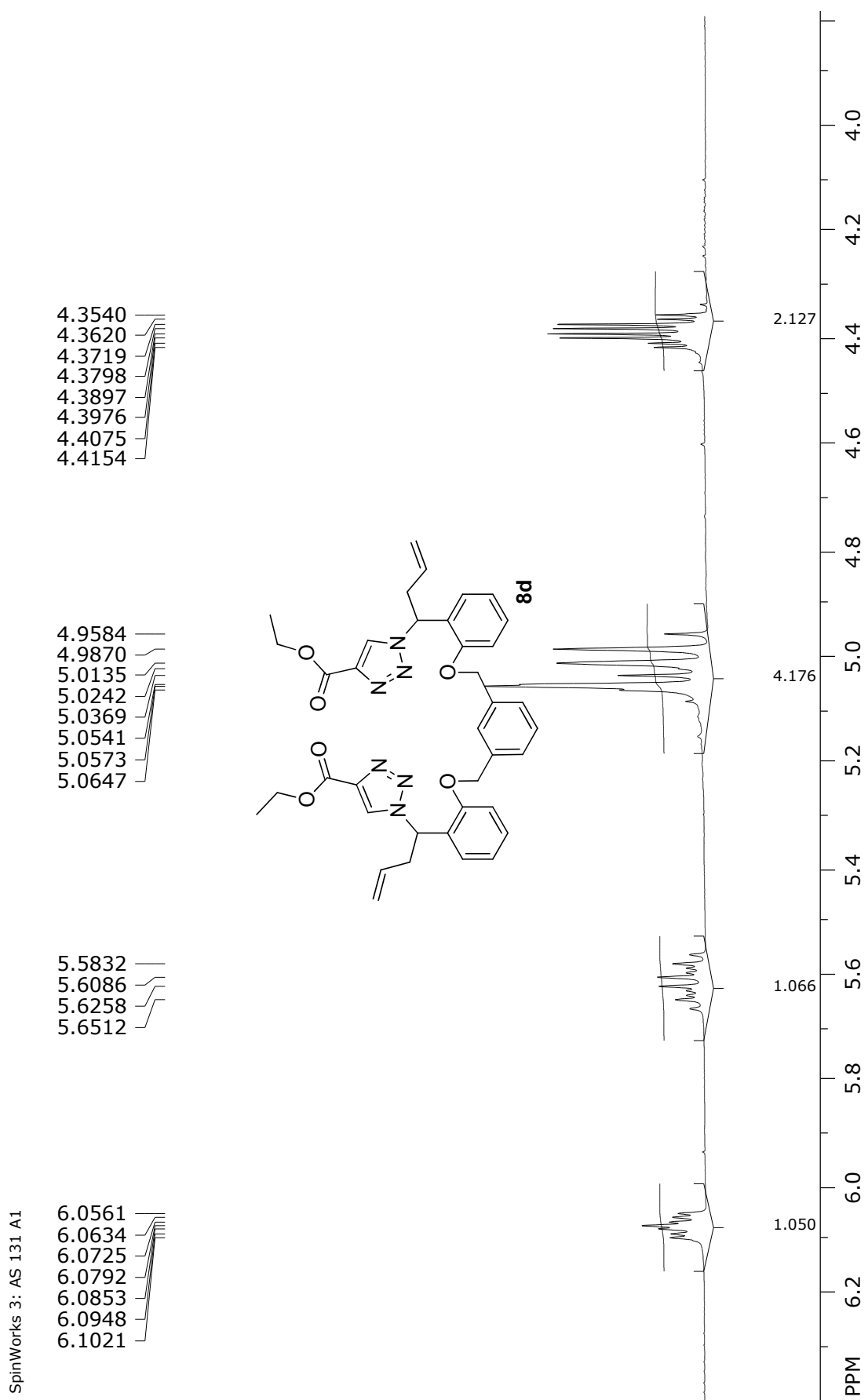
**6.9051**

**7.2008**  
7.3253  
7.3295  
7.3341  
7.3442  
7.3483  
7.3541  
7.3576  
7.3733  
7.3767  
7.4430  
7.9043



SpinWorks 3: AS 131 A1



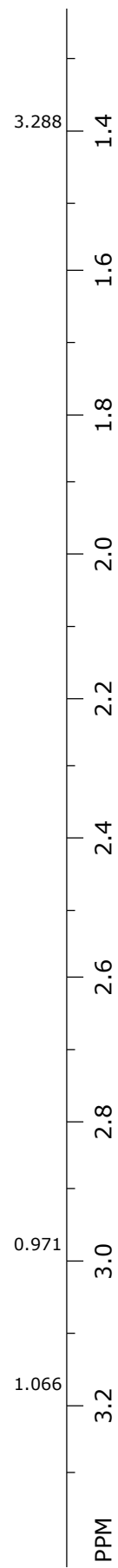
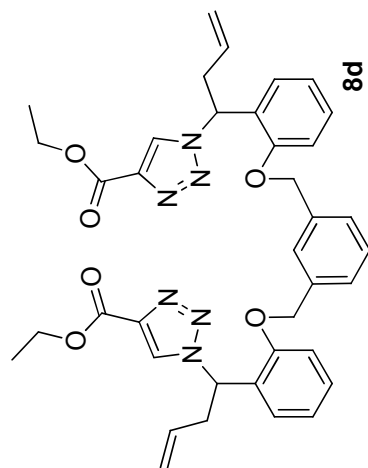


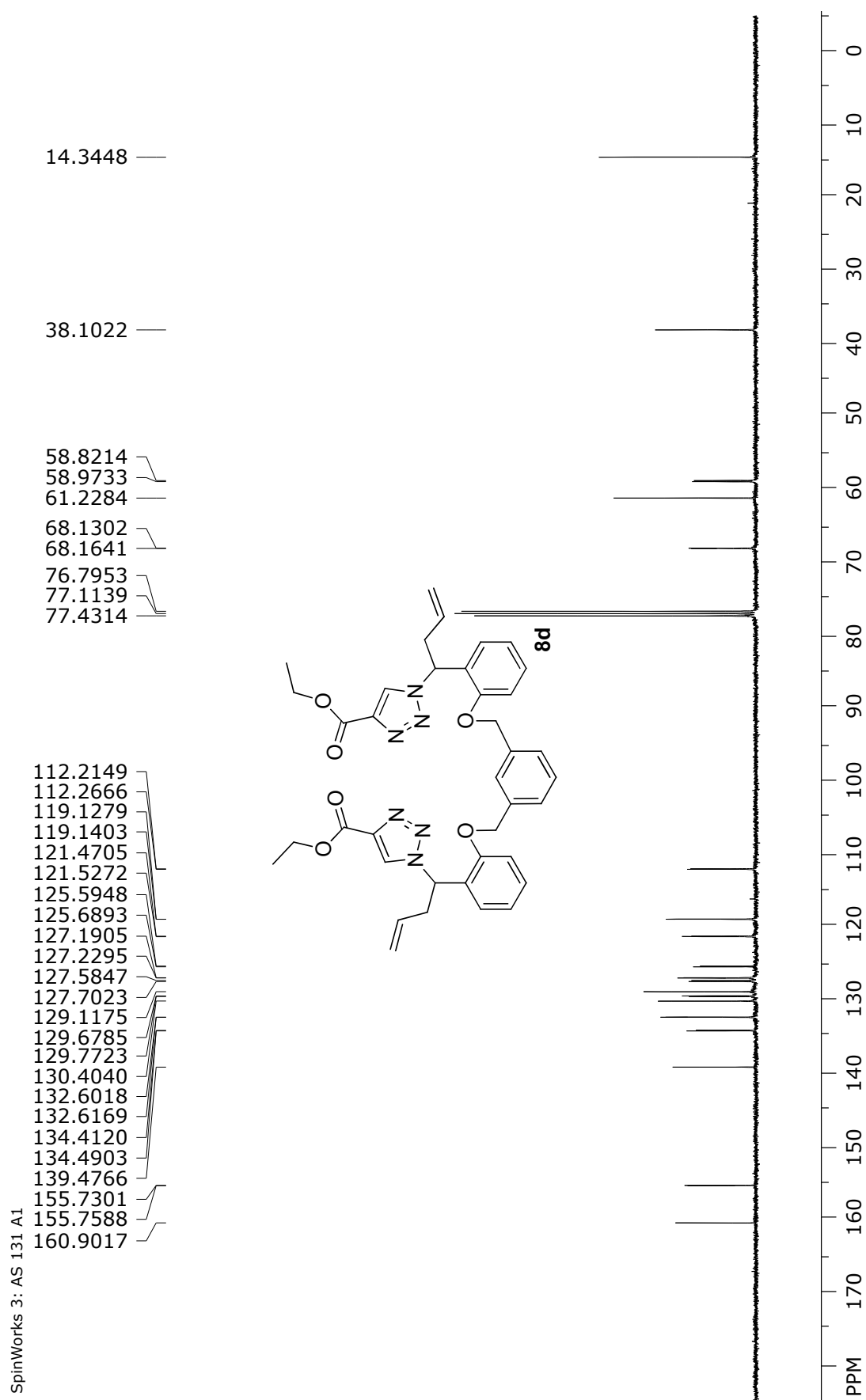
SpinWorks 3: AS 131 A1

1.3670  
1.3786  
1.3848  
1.3965  
1.4027

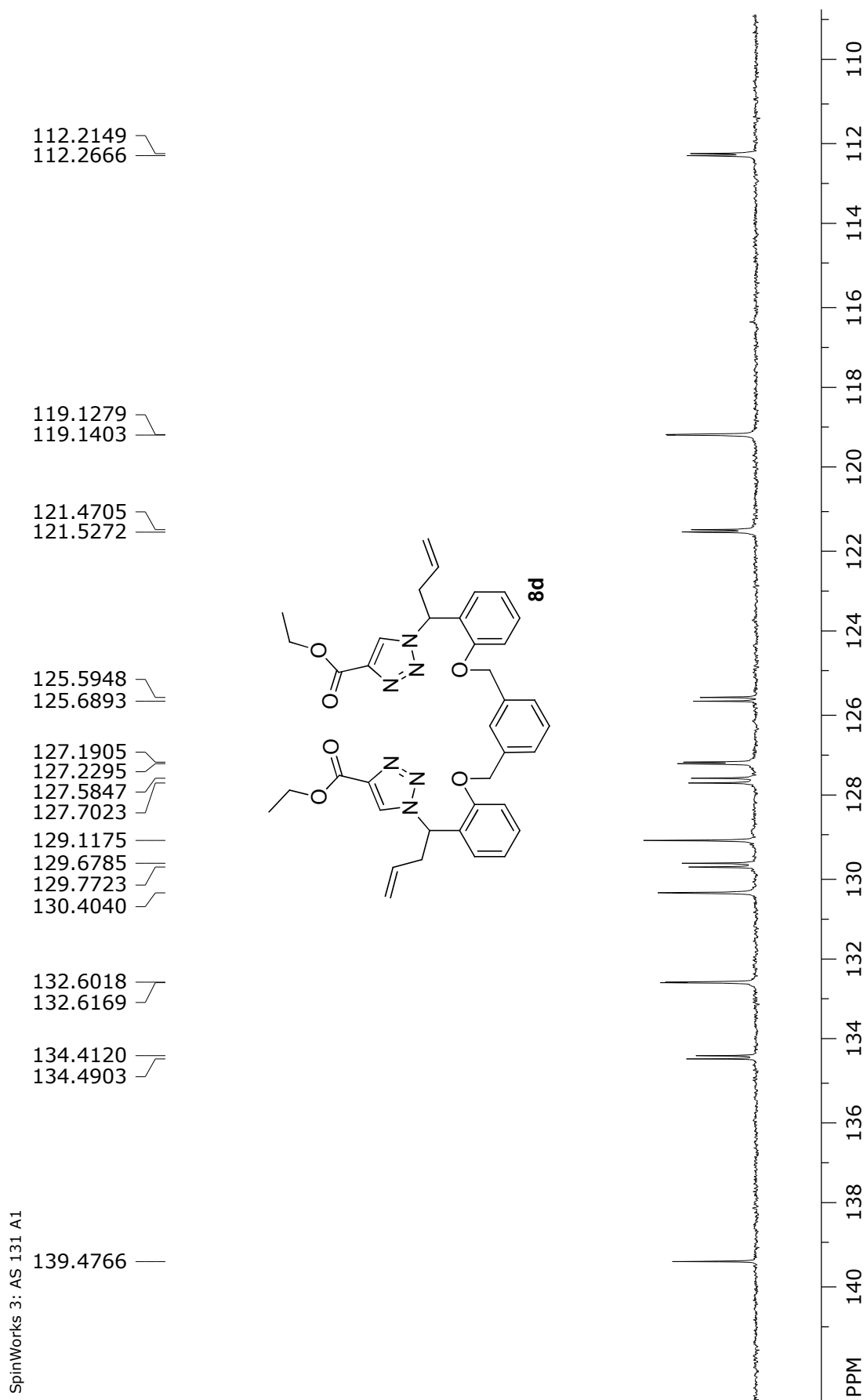
2.9566  
2.9598  
2.9643  
2.9682  
2.9763  
2.9798  
2.9842  
2.9876  
2.9924  
2.9959

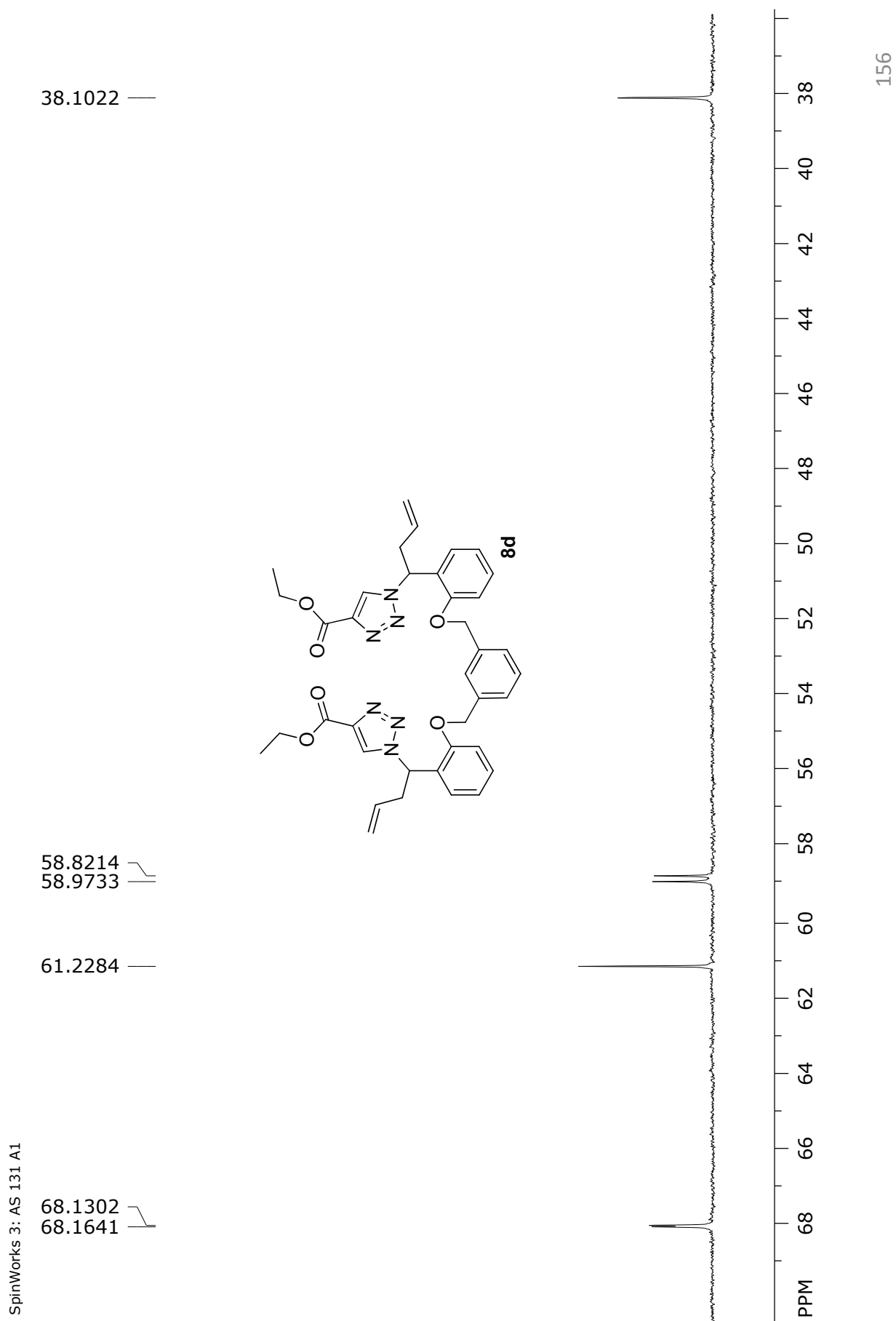
1.3670  
1.3786  
1.3848  
1.3965  
1.4027

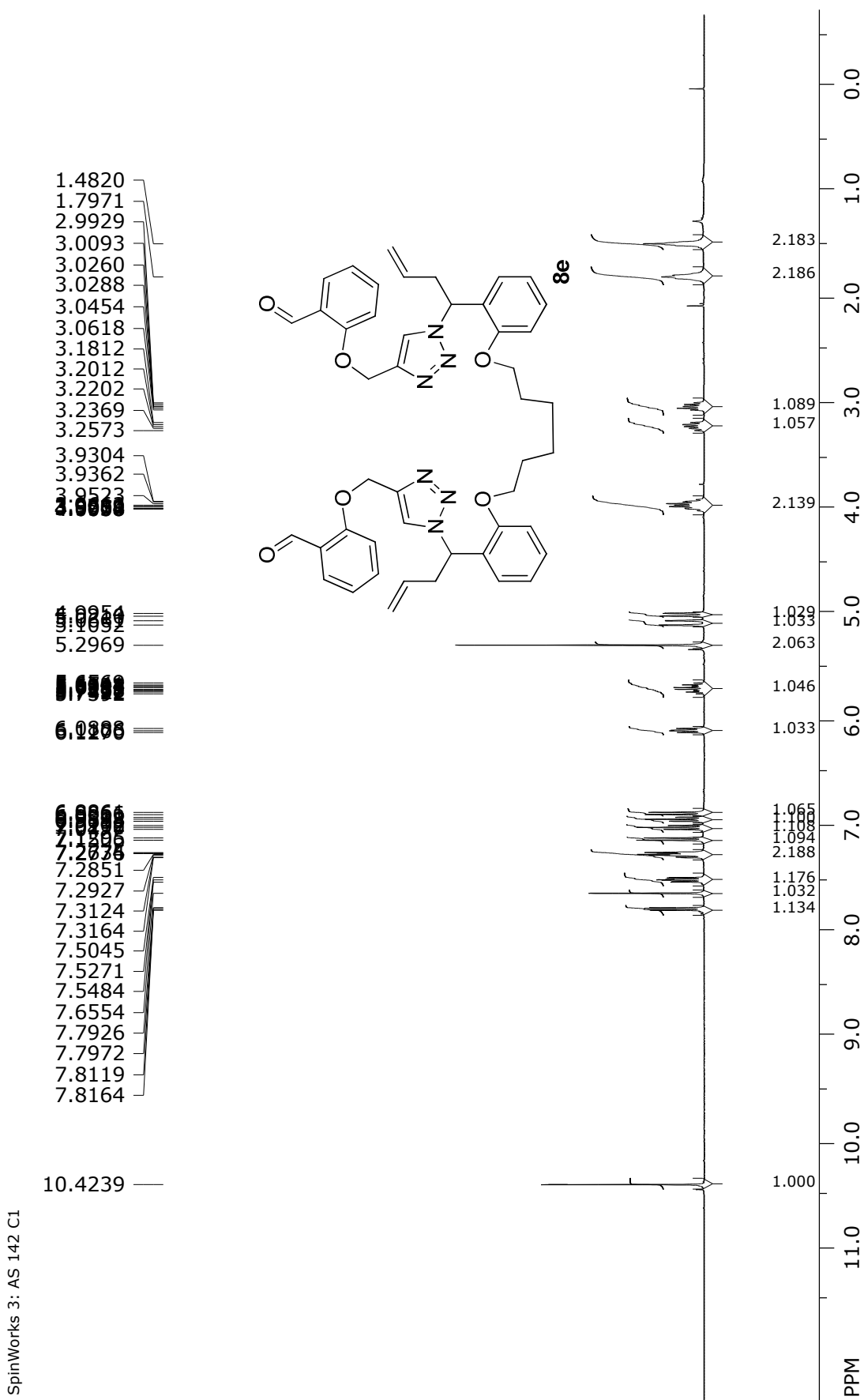


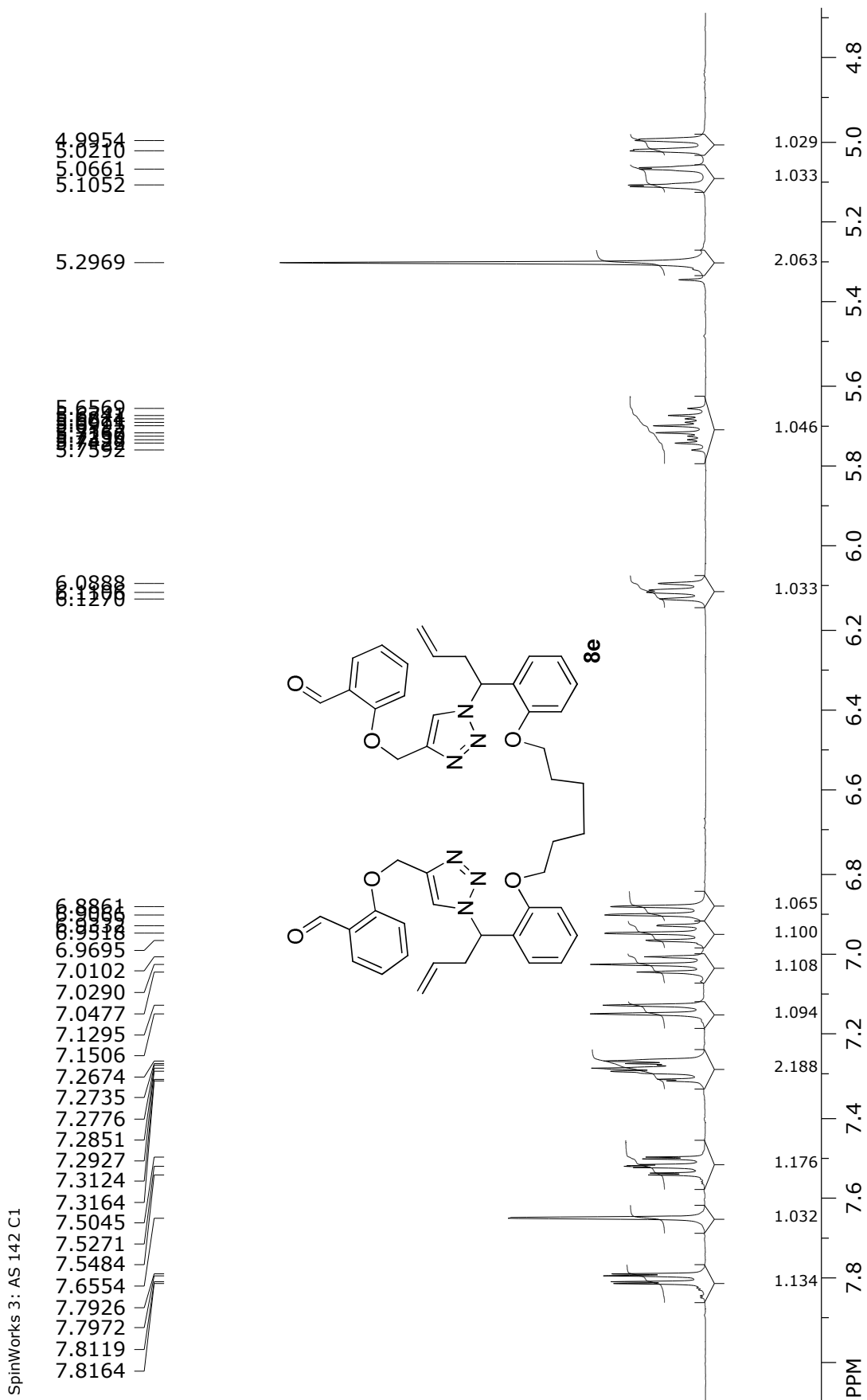




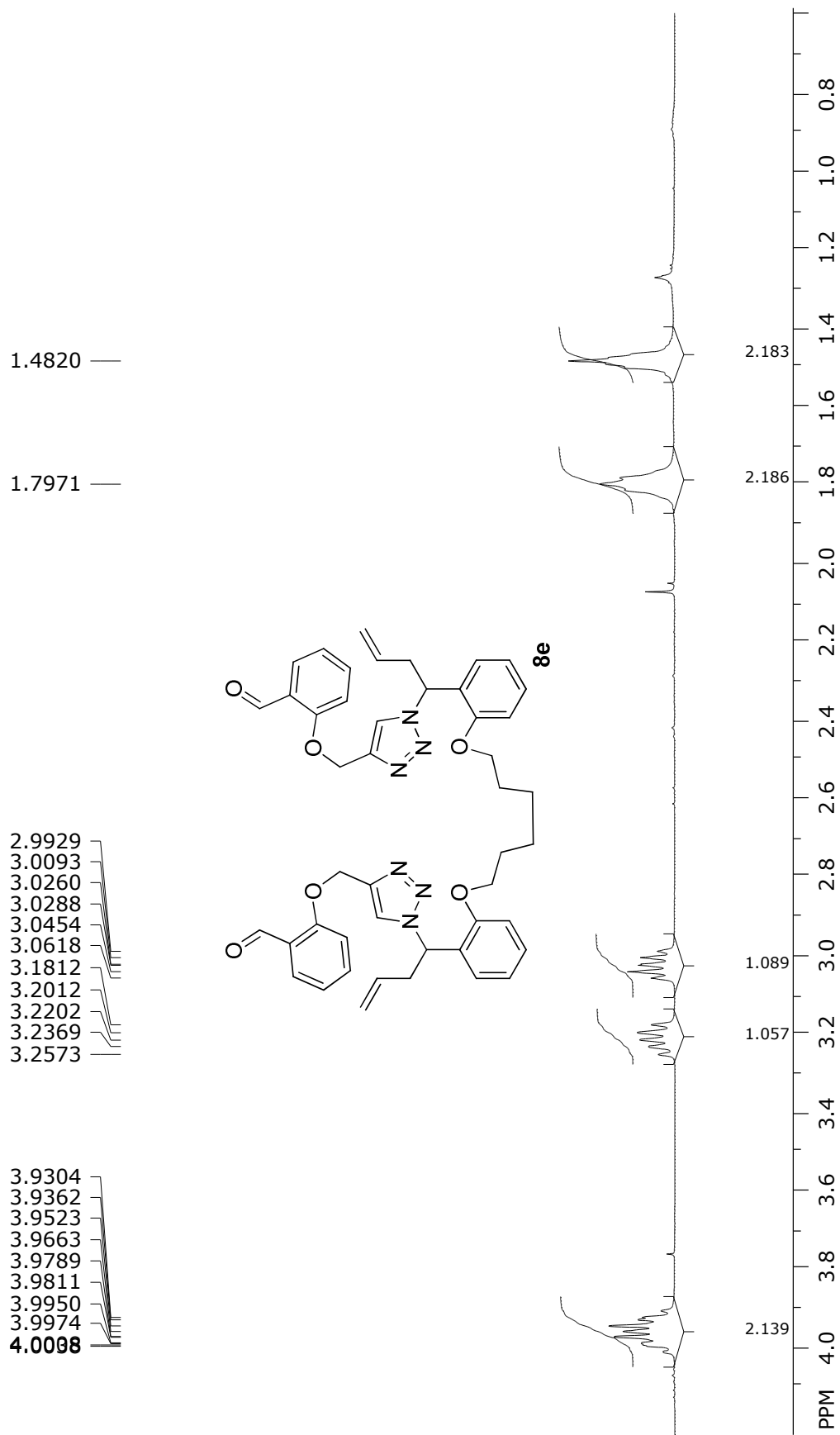


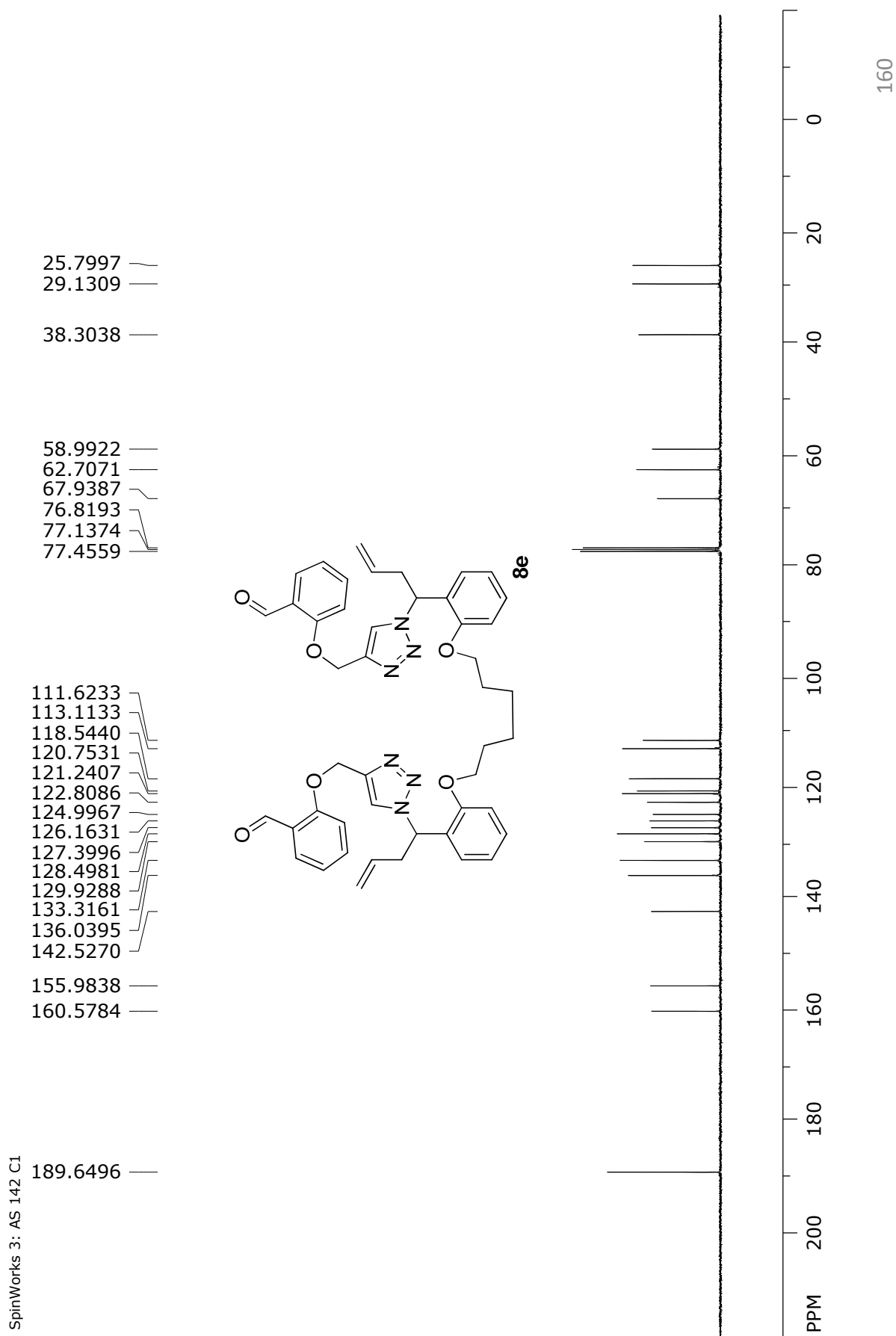




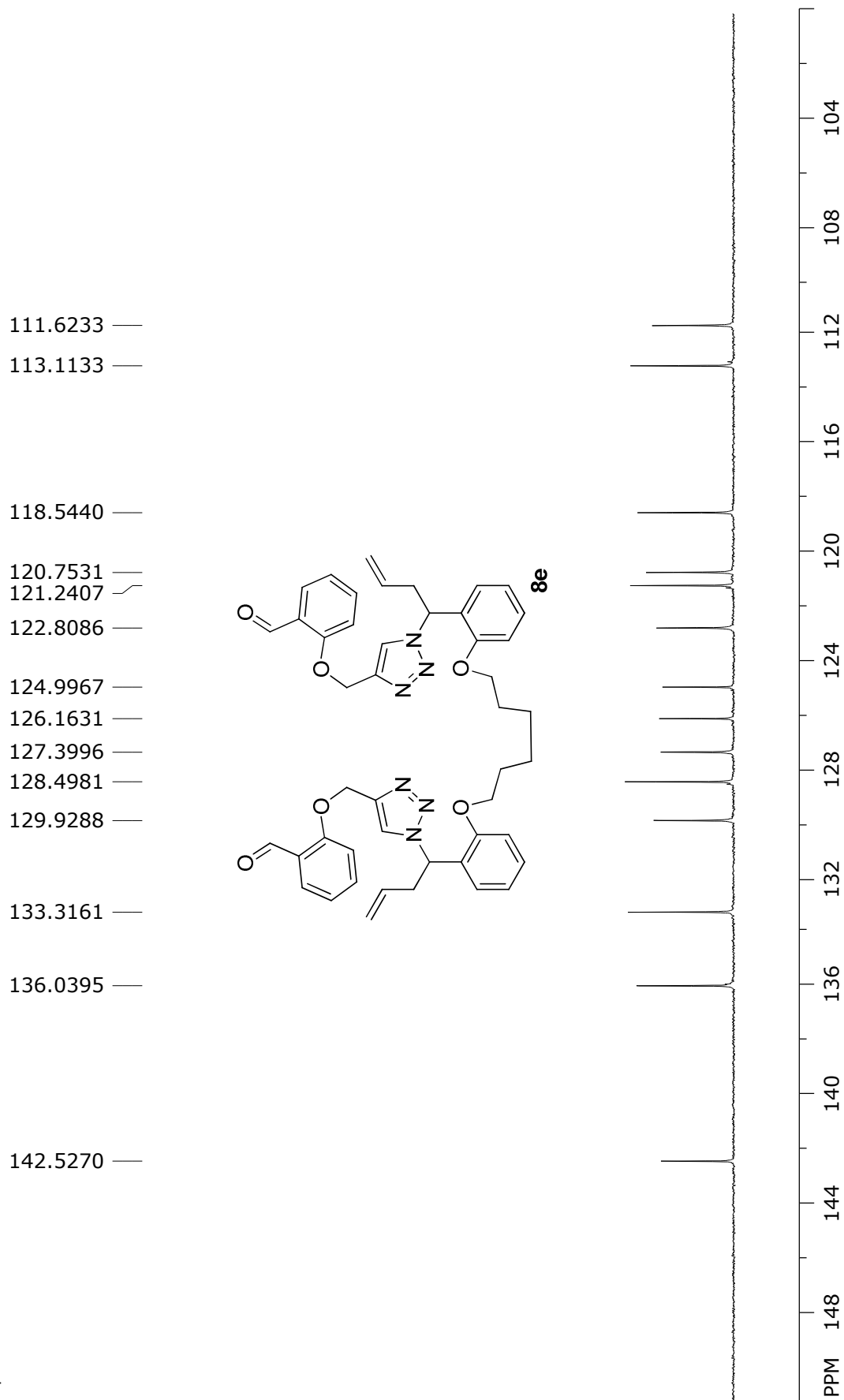


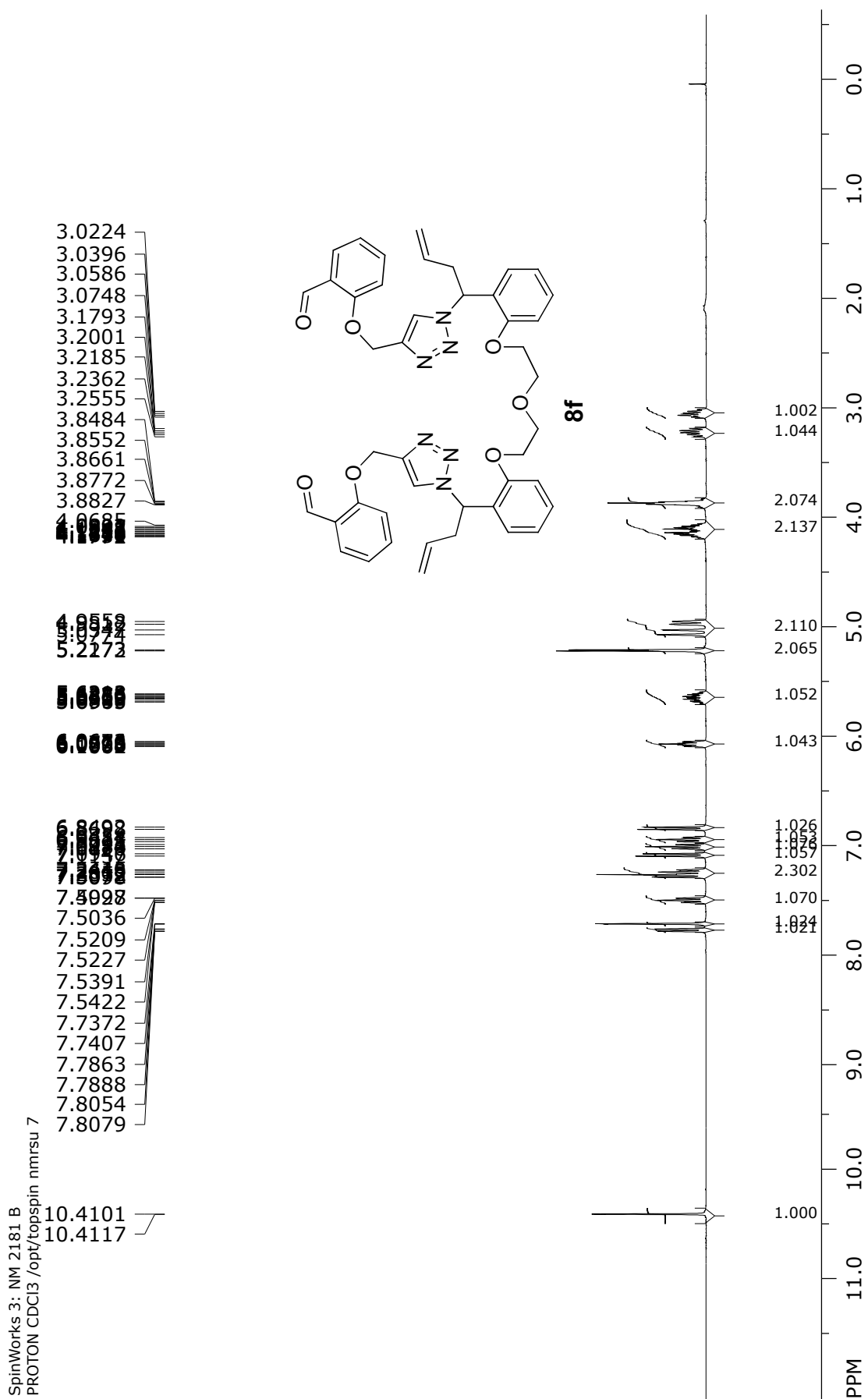
SpinWorks 3: AS 142 C1





SpinWorks 3: AS 142 C1







SpinWorks 3: NM 2181 B  
 PROTON CDCl<sub>3</sub> /opt/topspin nmrsu 7

6.8492 —  
 6.8698 —

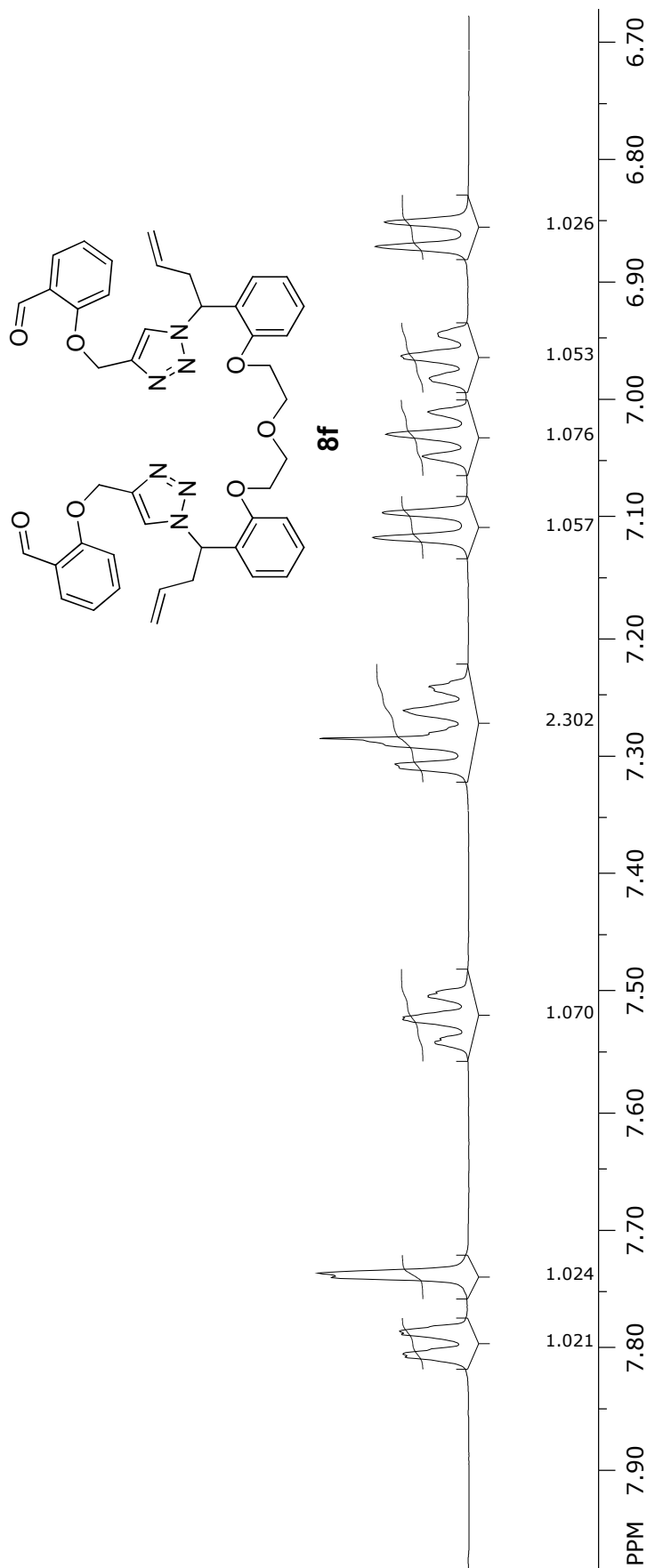
6.9454 —  
 6.9623 —  
 6.9811 —  
 7.0095 —  
 7.0284 —  
 7.0470 —

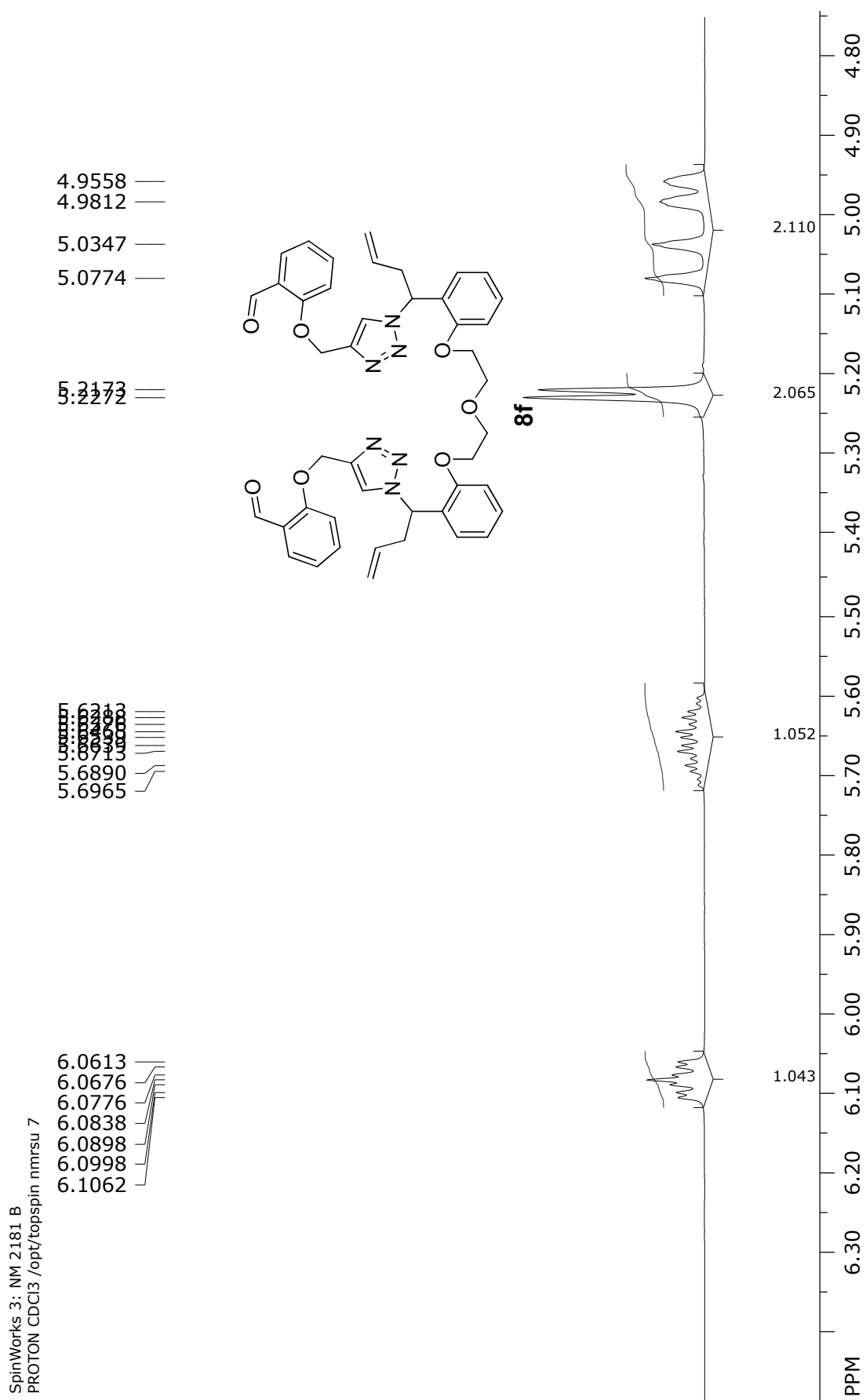
7.0946 —  
 7.1157 —

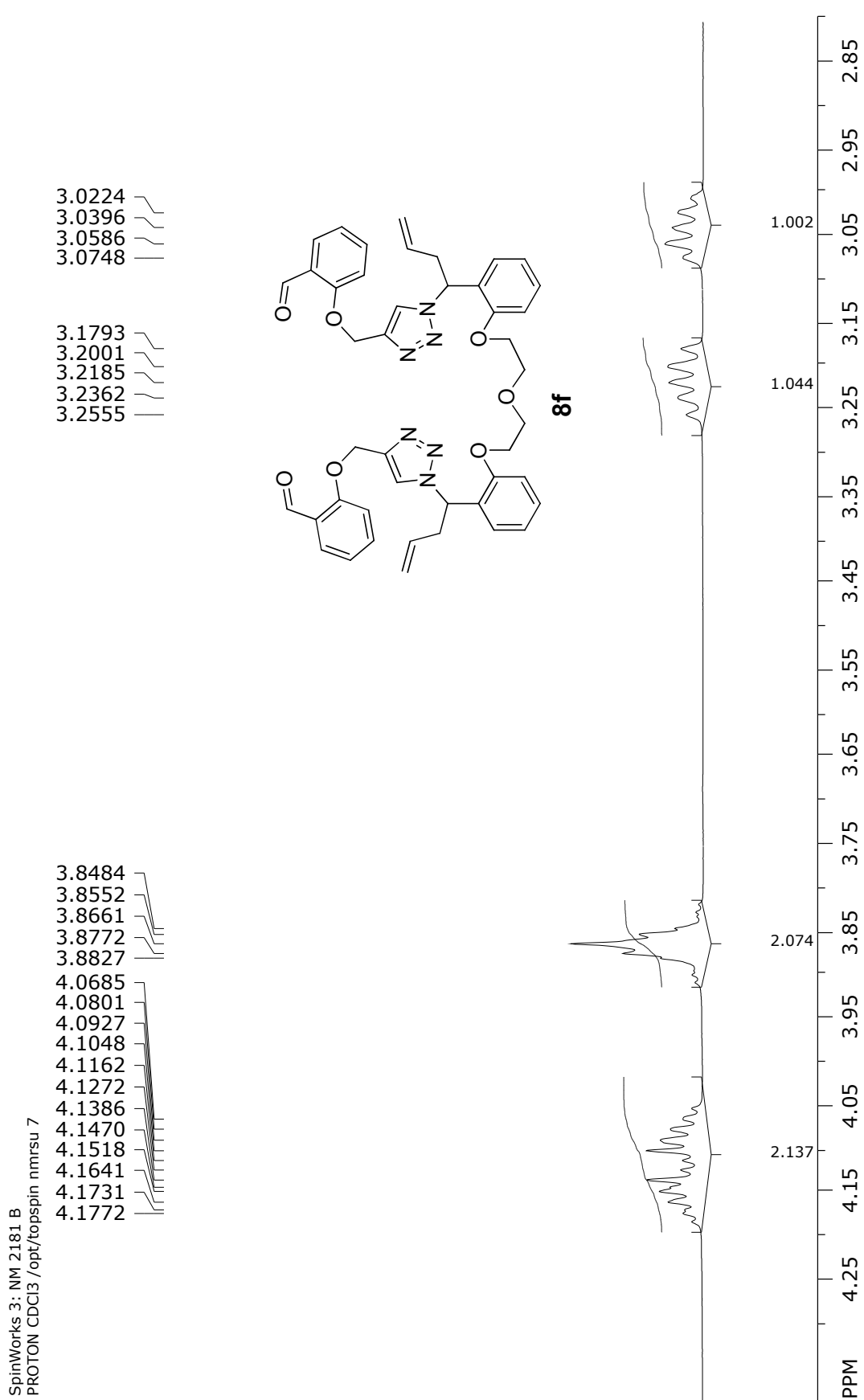
7.2415 —  
 7.2448 —  
 7.2619 —  
 7.2812 —  
 7.2853 —  
 7.3072 —  
 7.3098 —

7.4997 —  
 7.5028 —  
 7.5036 —  
 7.5209 —  
 7.5227 —  
 7.5391 —  
 7.5422 —

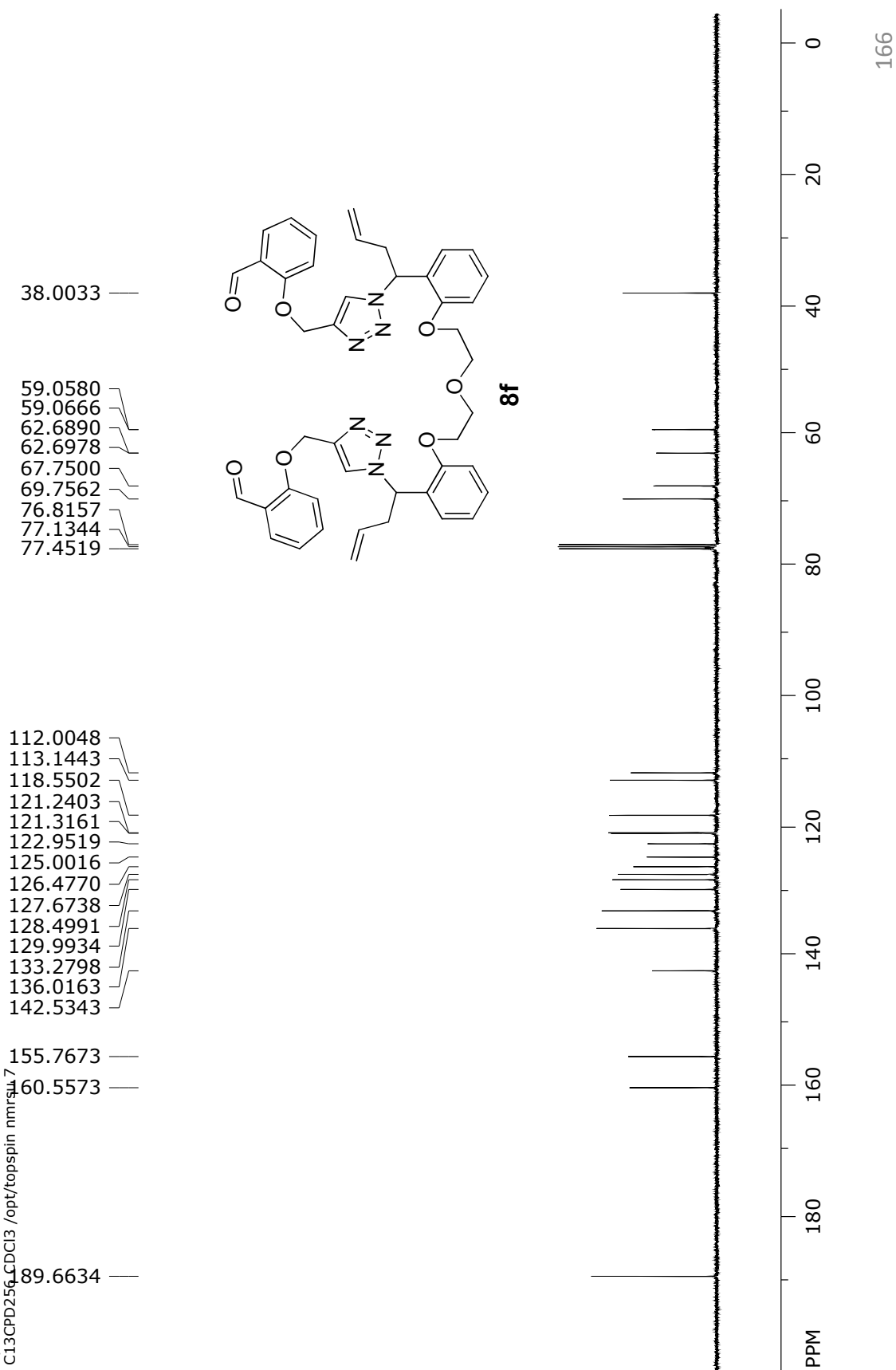
7.7372 —  
 7.7407 —  
 7.7863 —  
 7.7888 —  
 7.8054 —  
 7.8079 —

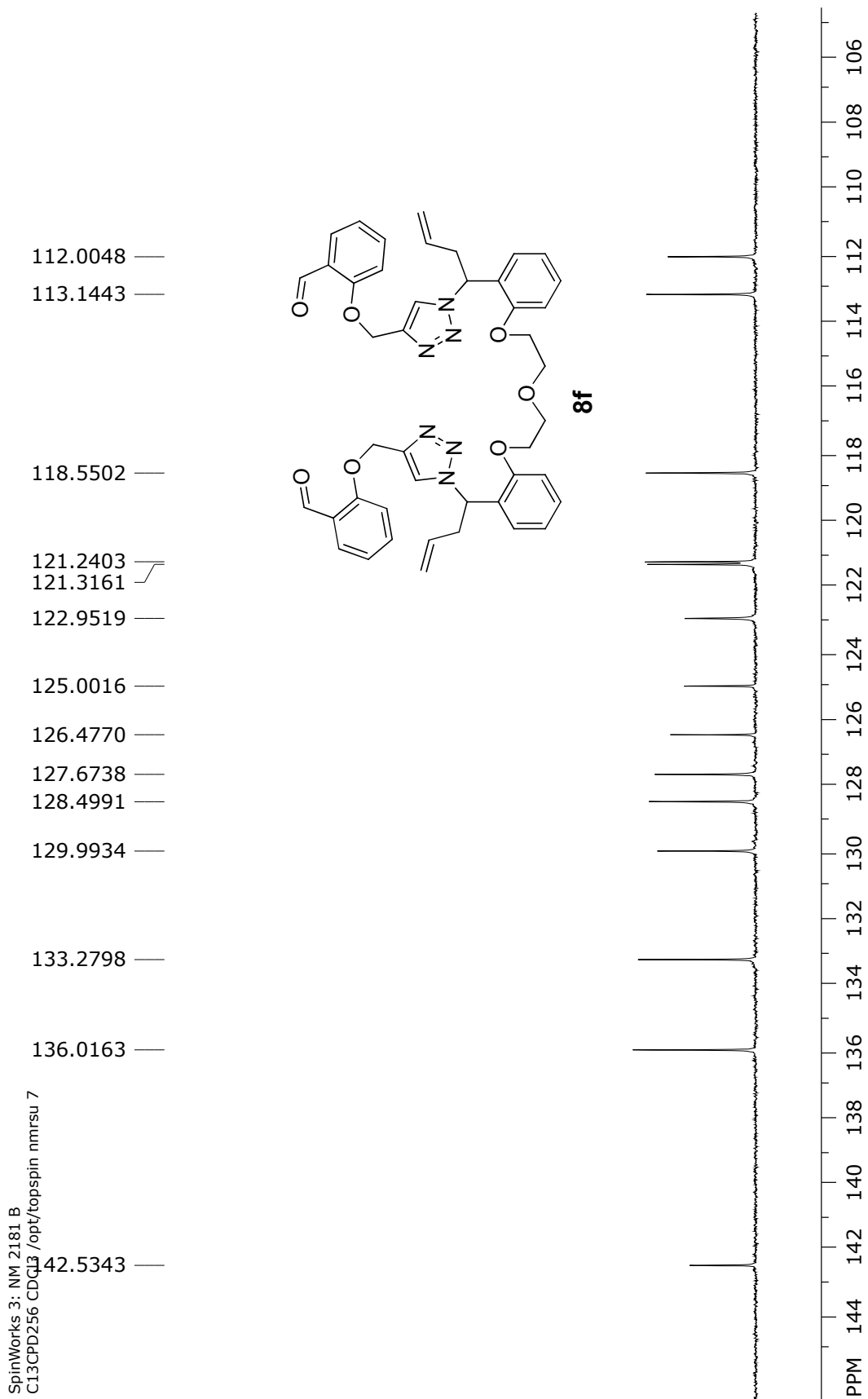


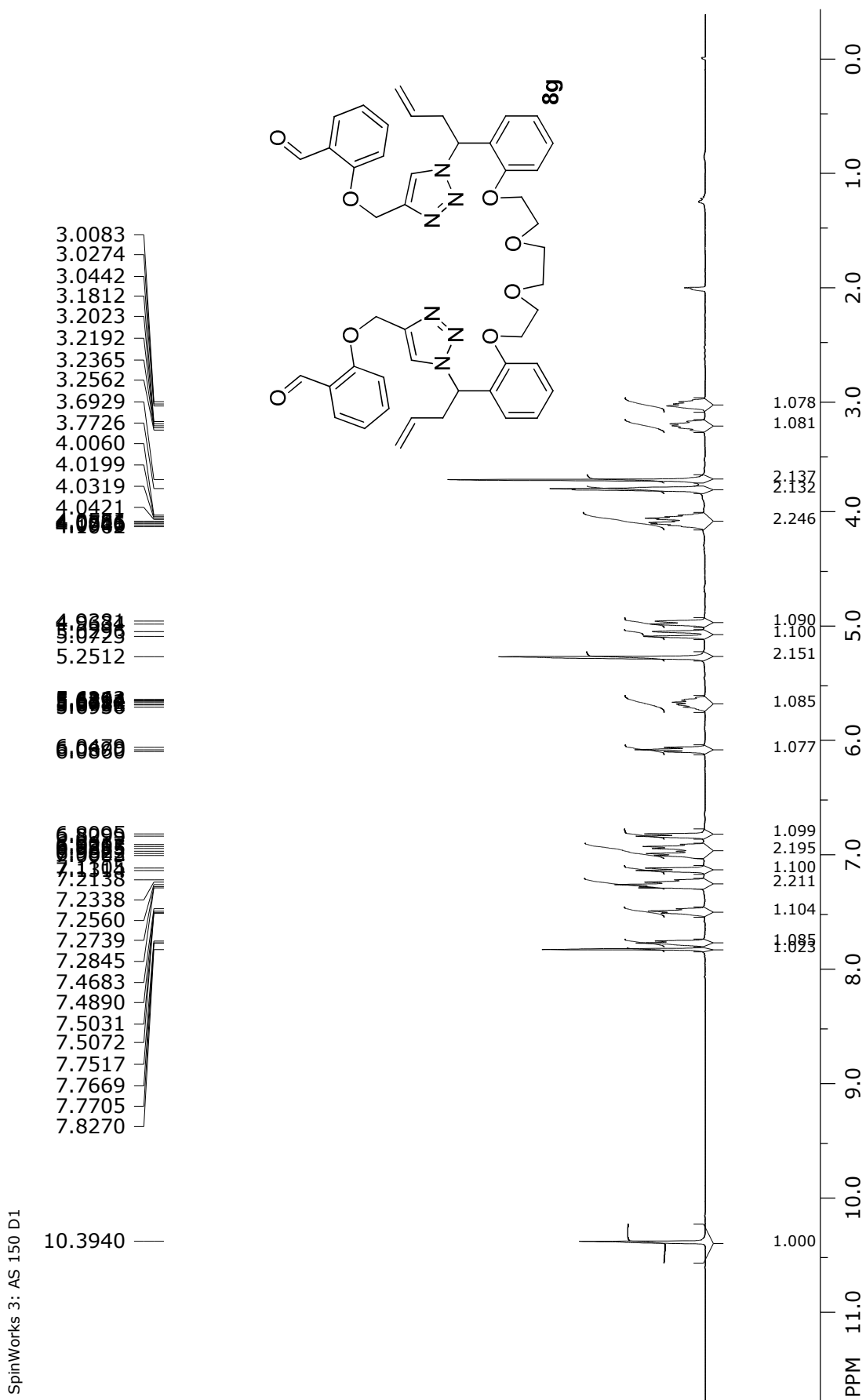


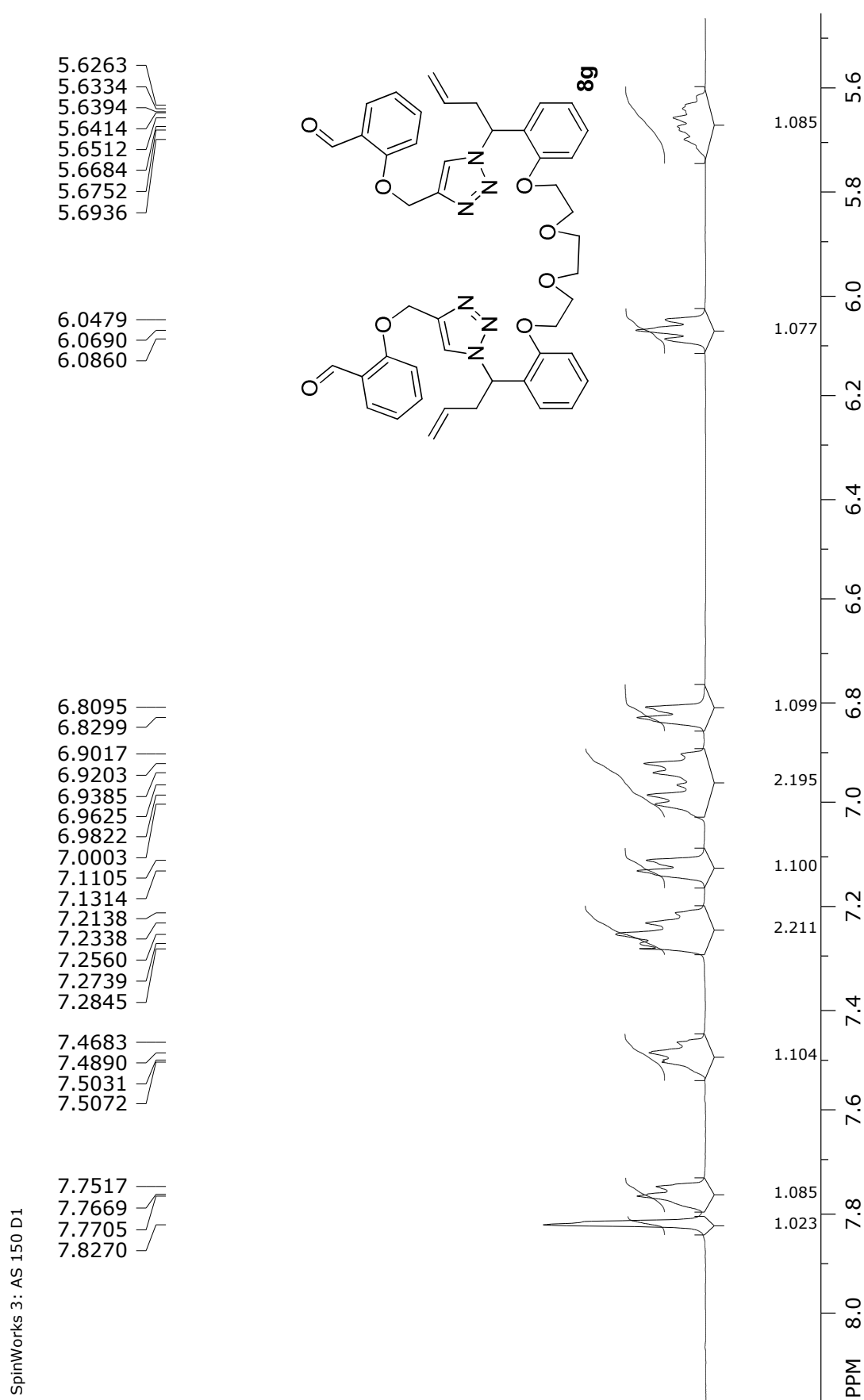


SpinWorks 3: NM 2181 B  
C13CPD256\_CDCI3 /opt/topspin nmrsu7

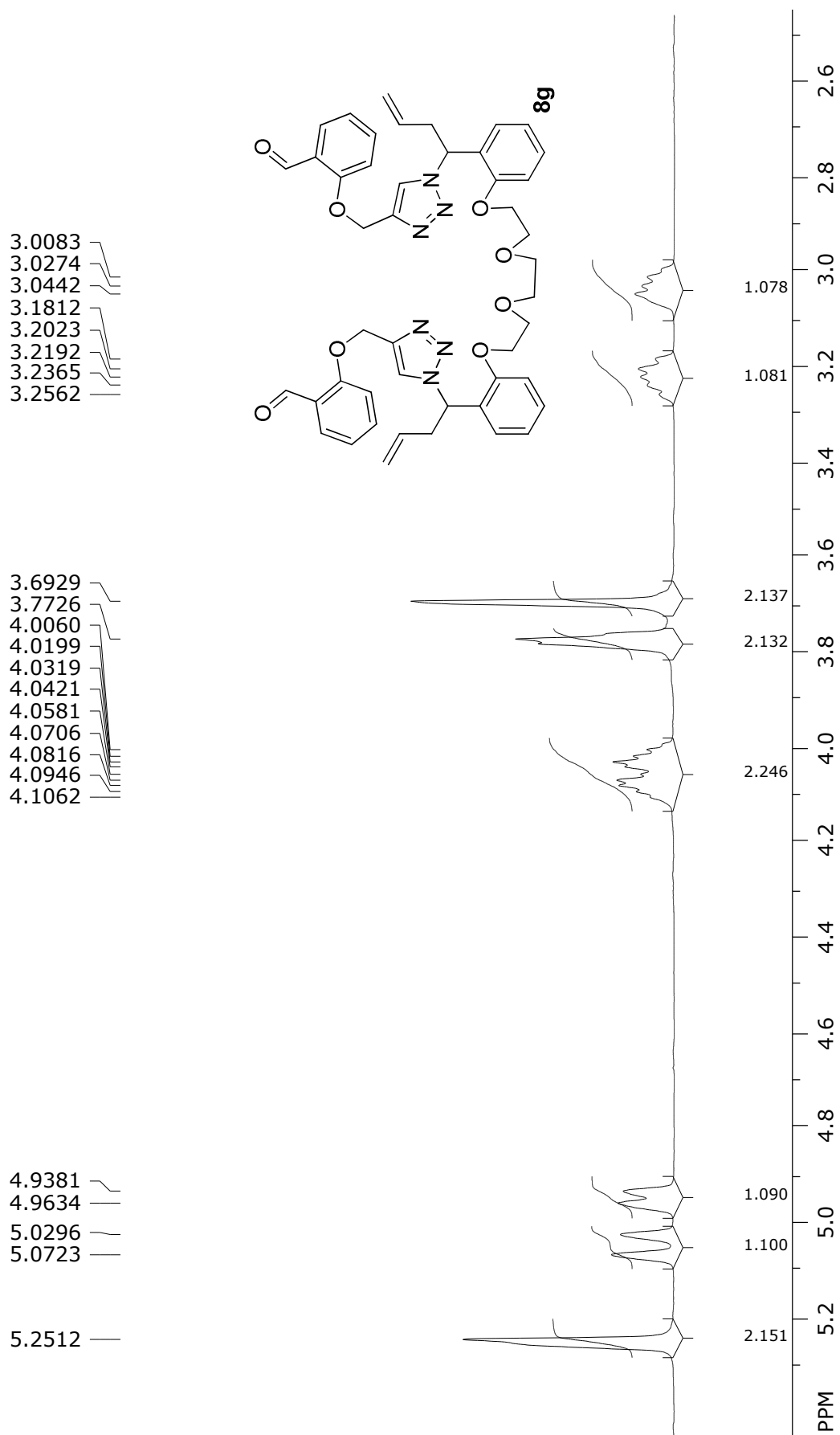




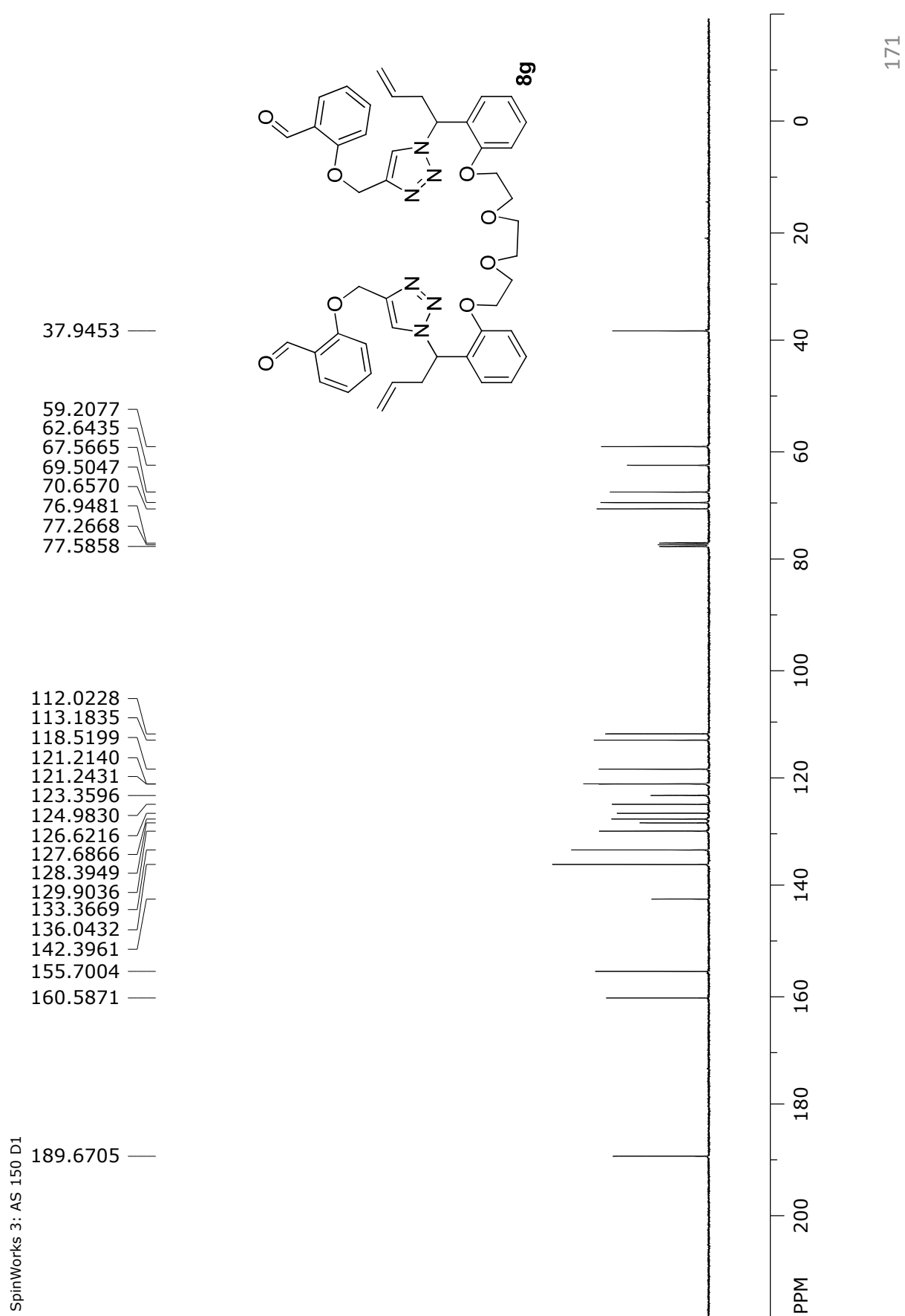


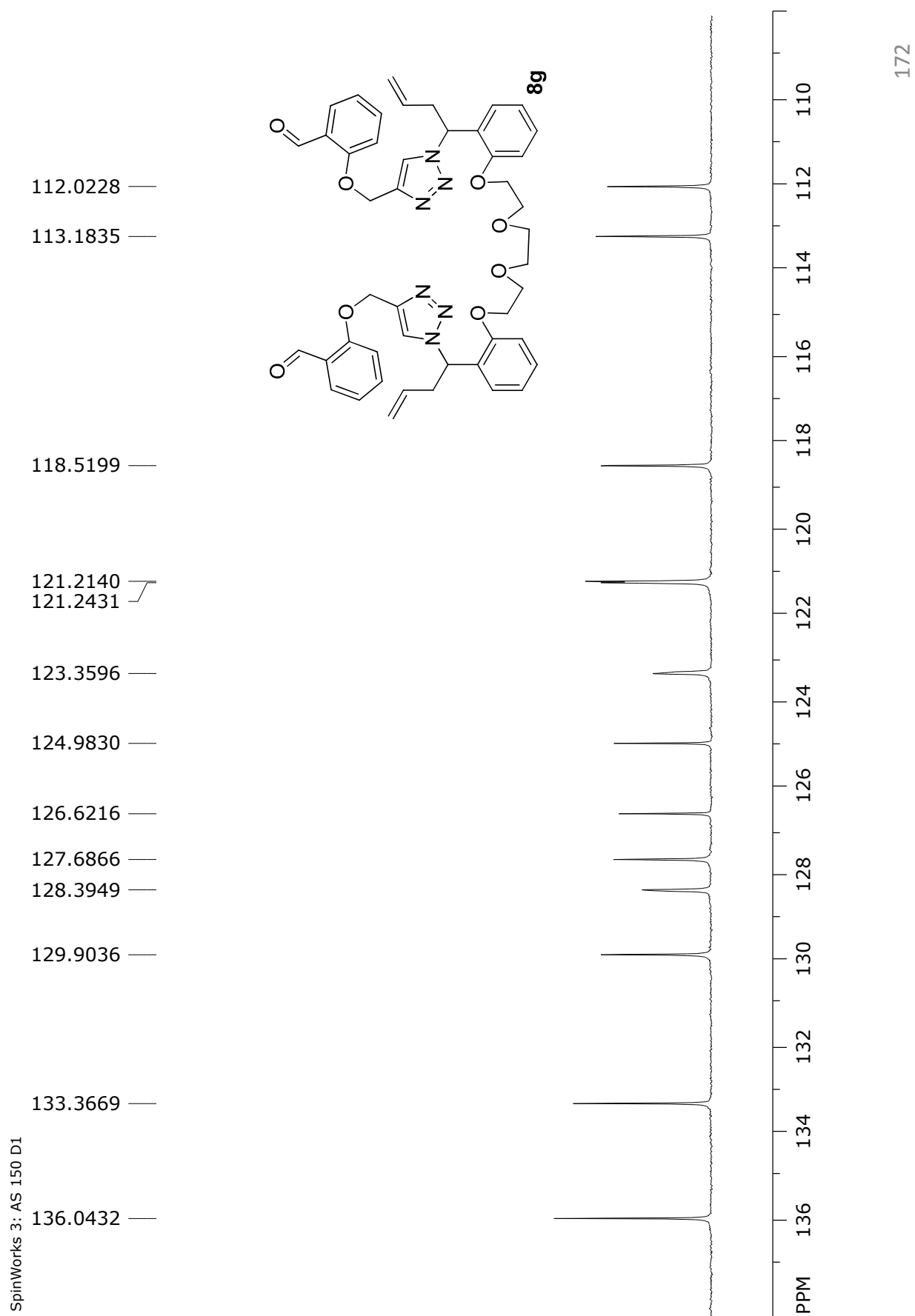


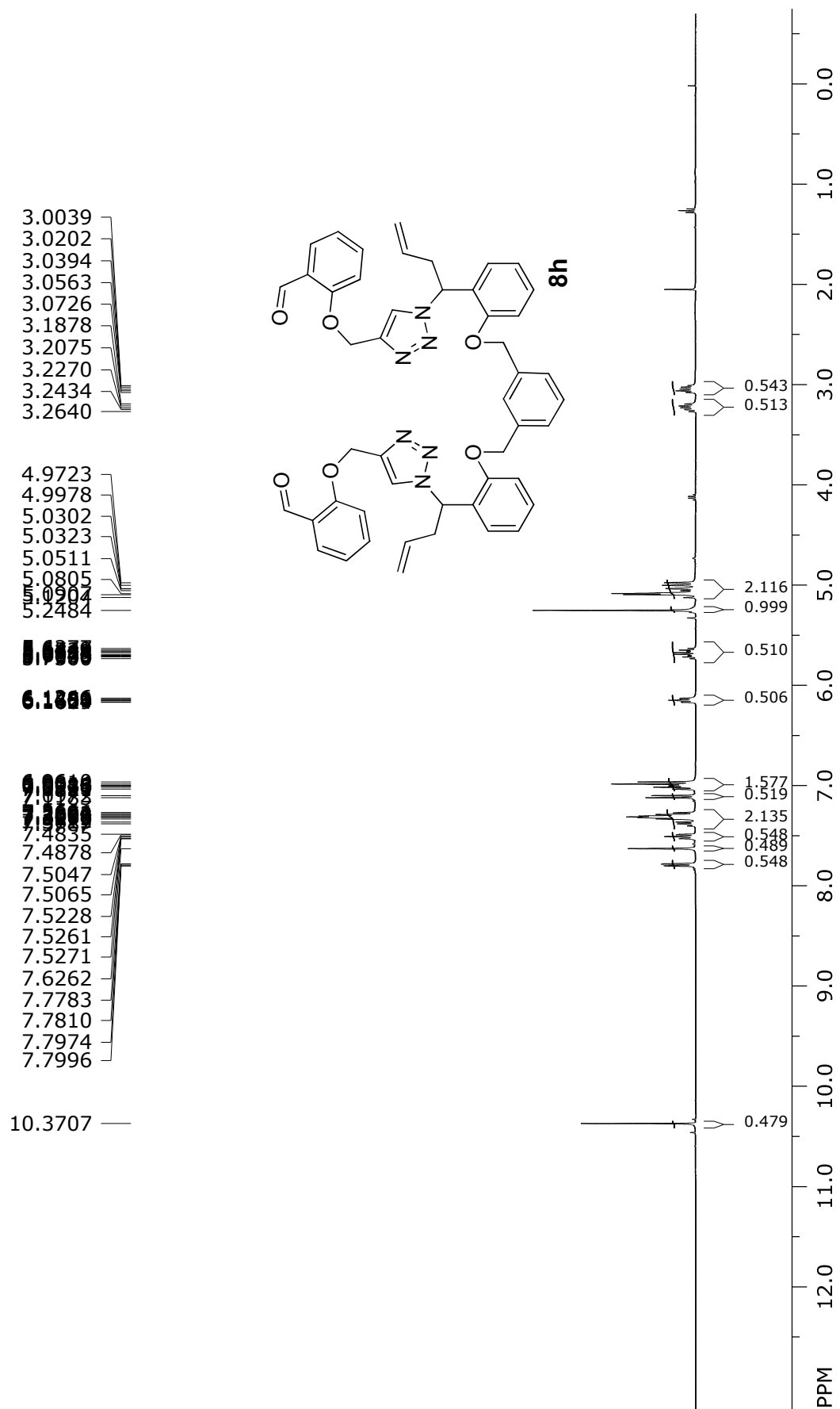
SpinWorks 3: AS 150 D1



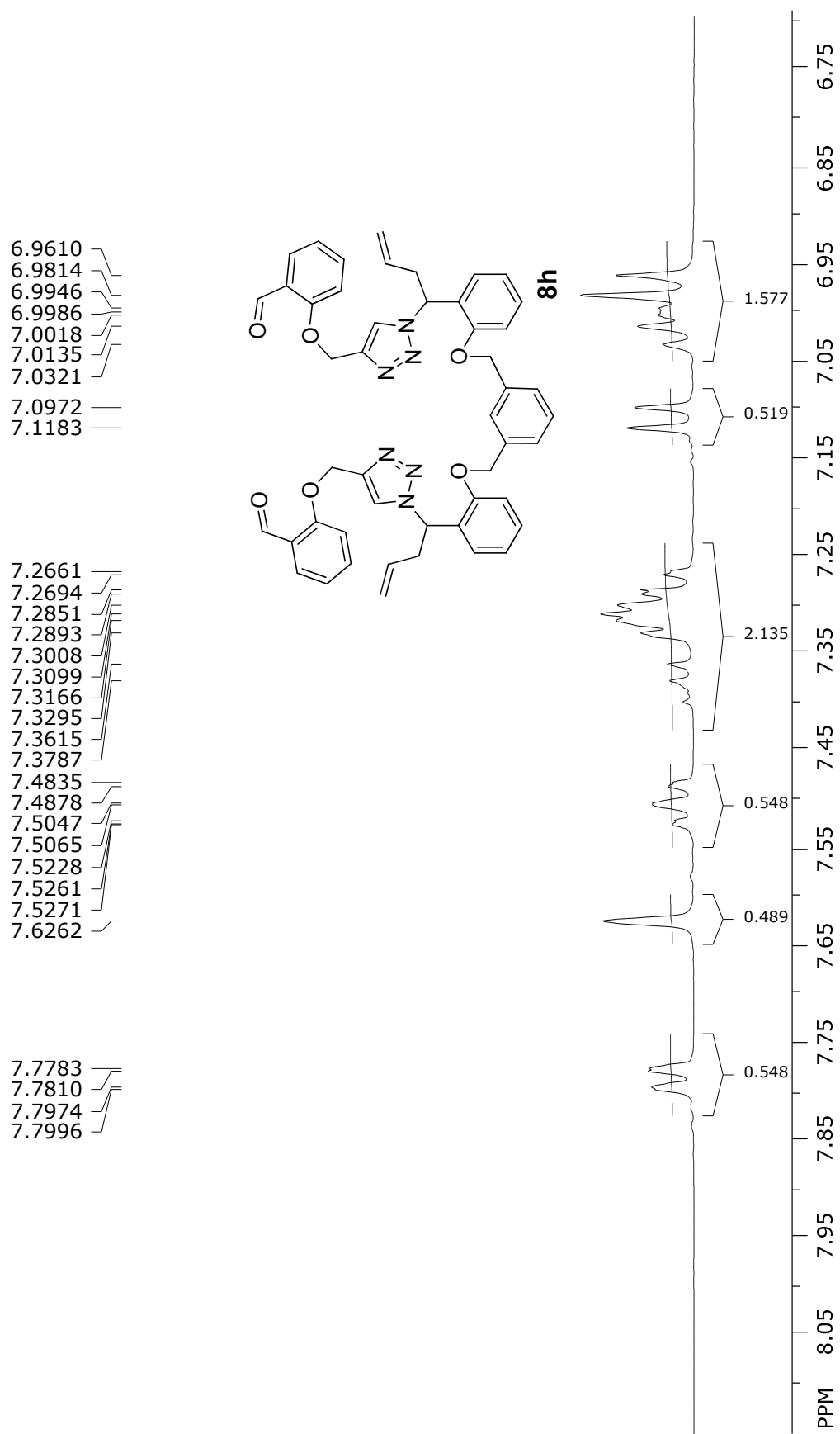


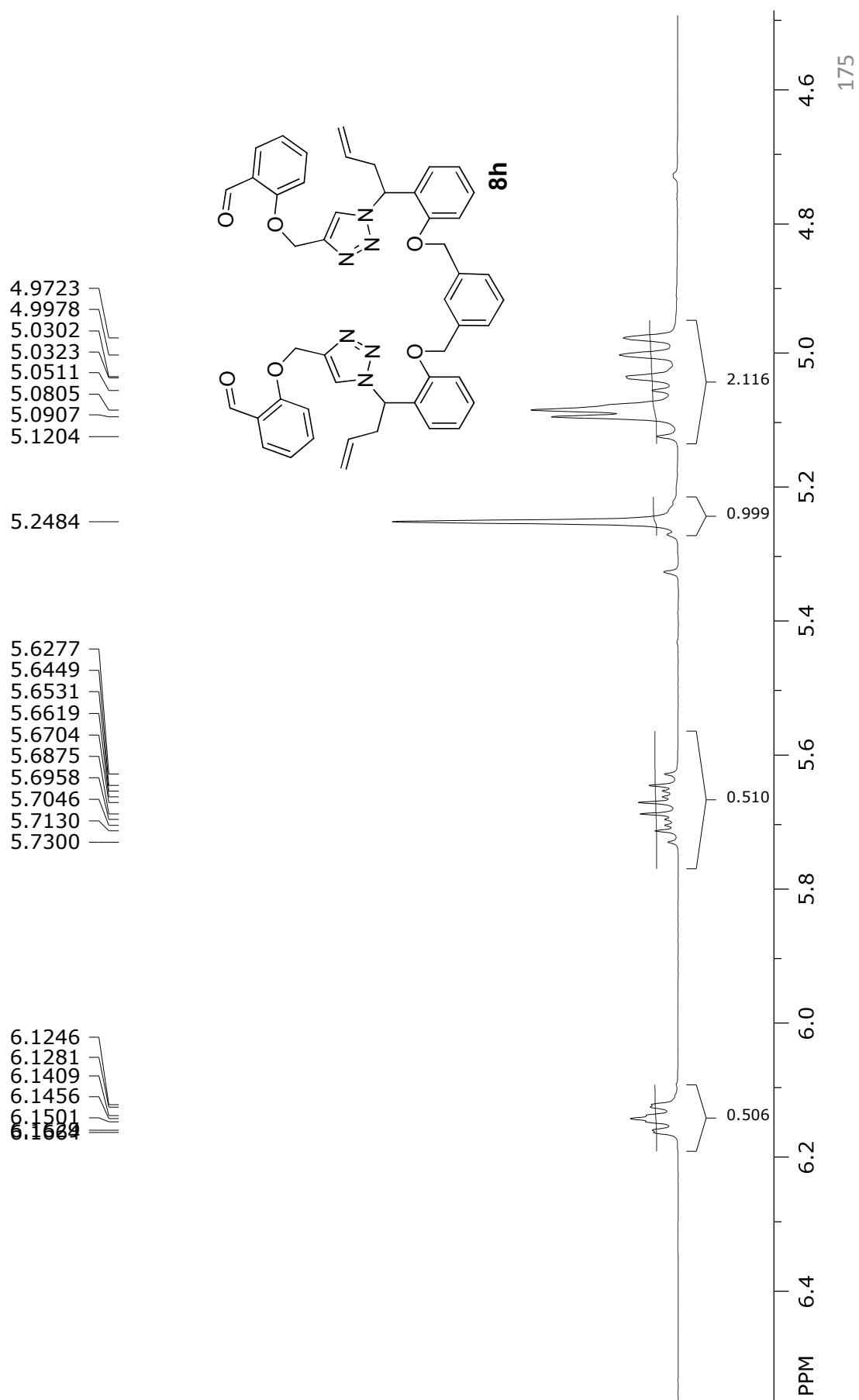


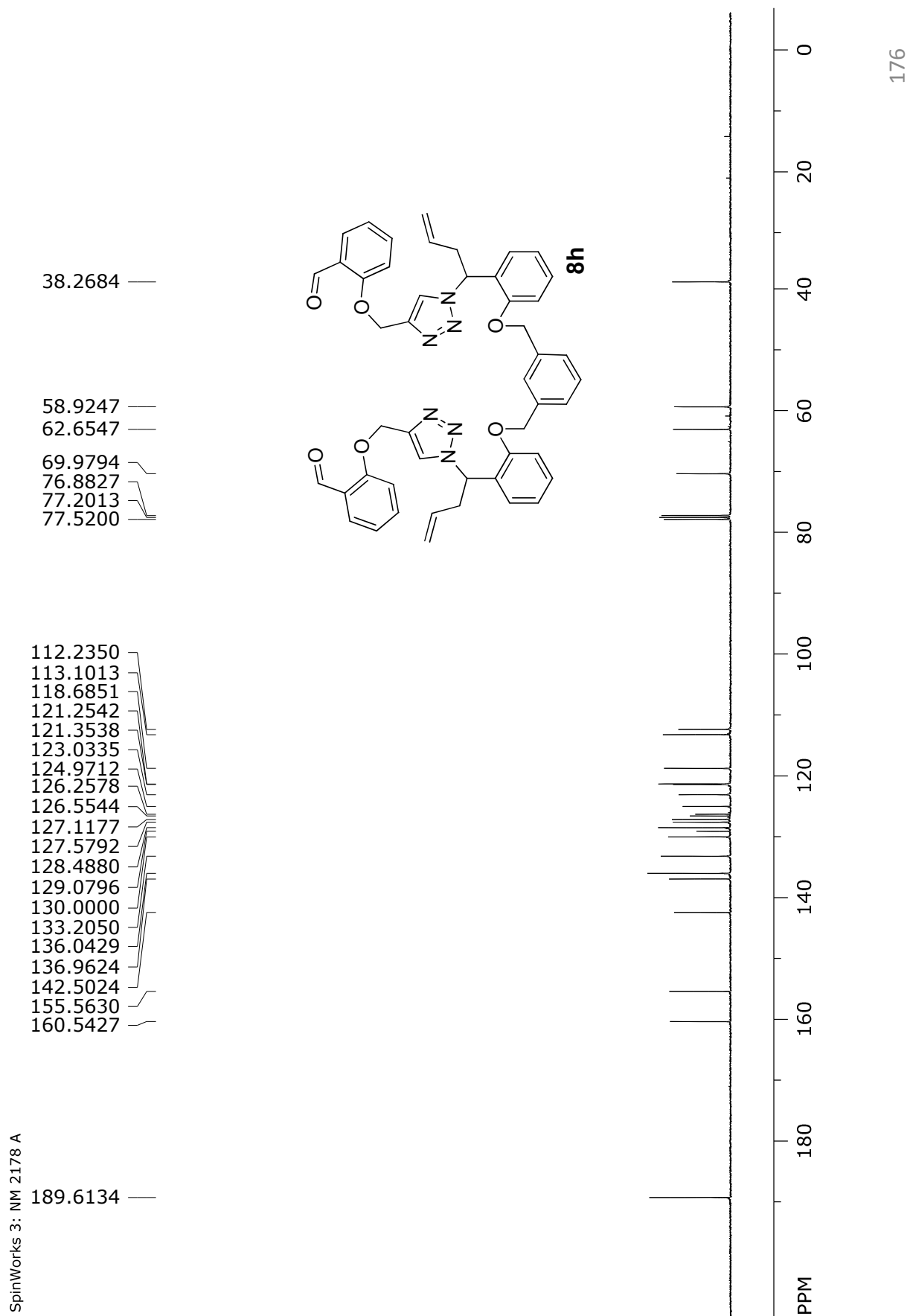


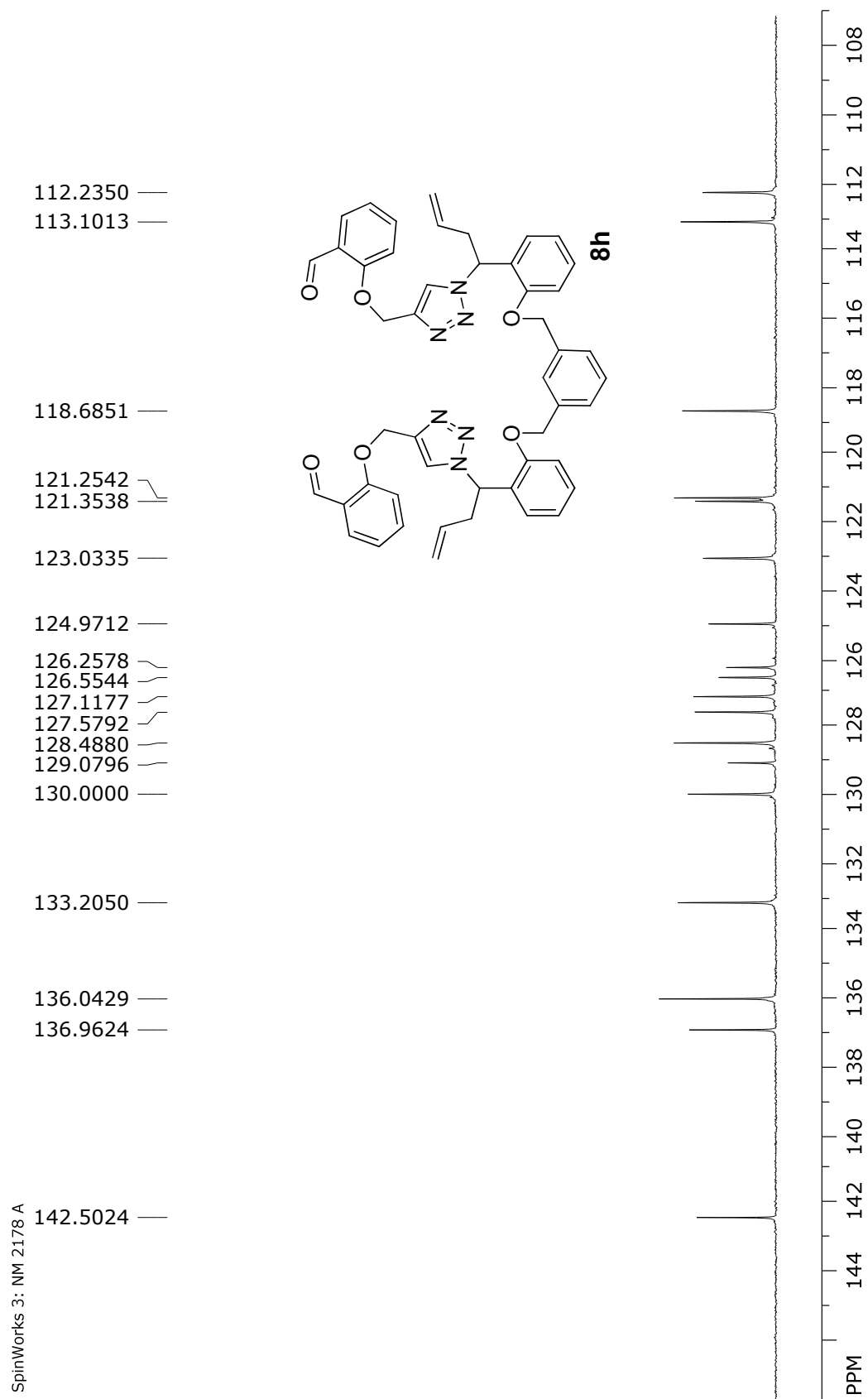


SpinWorks 3: NM 2178 A



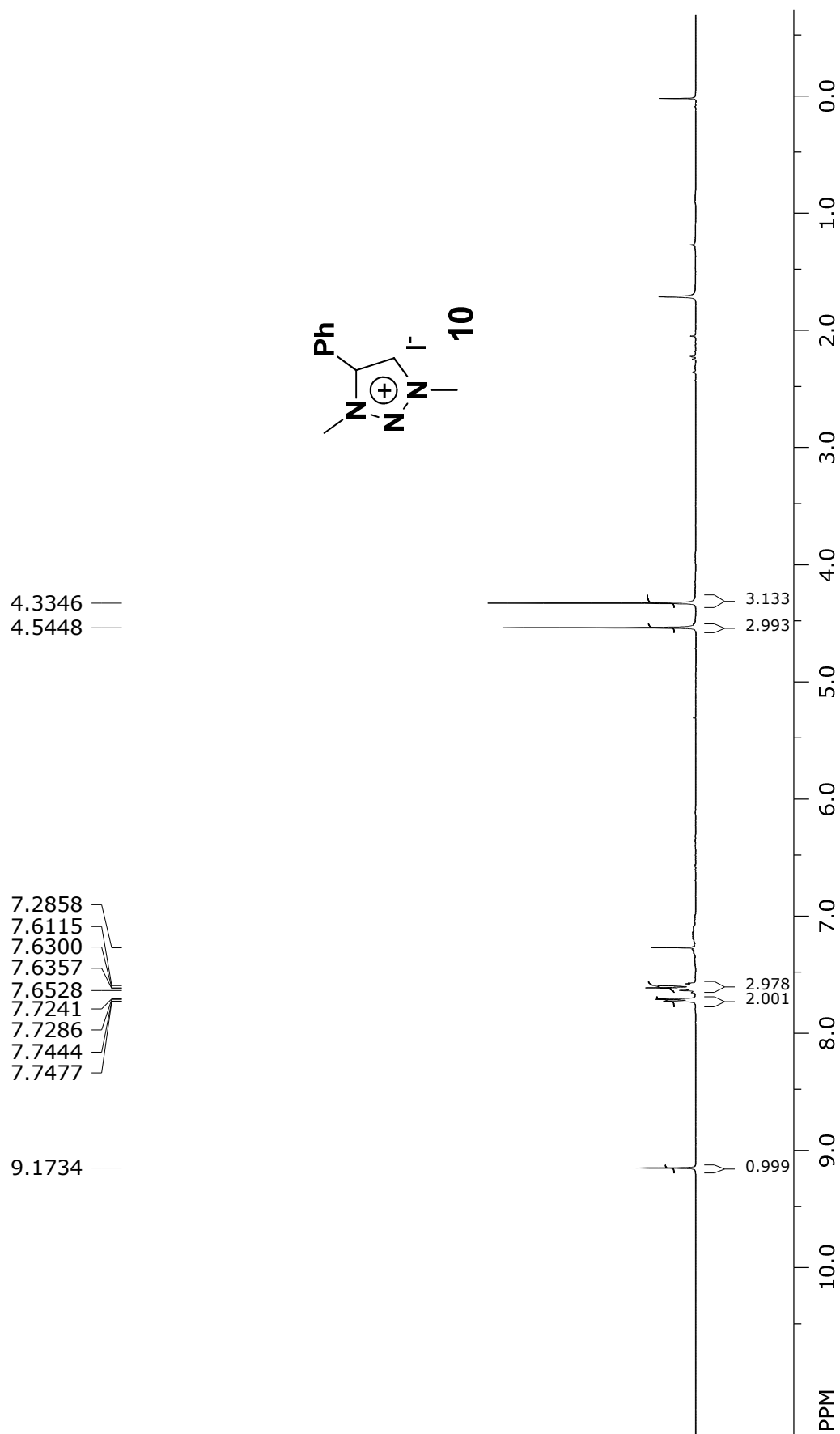






Nm- 1390

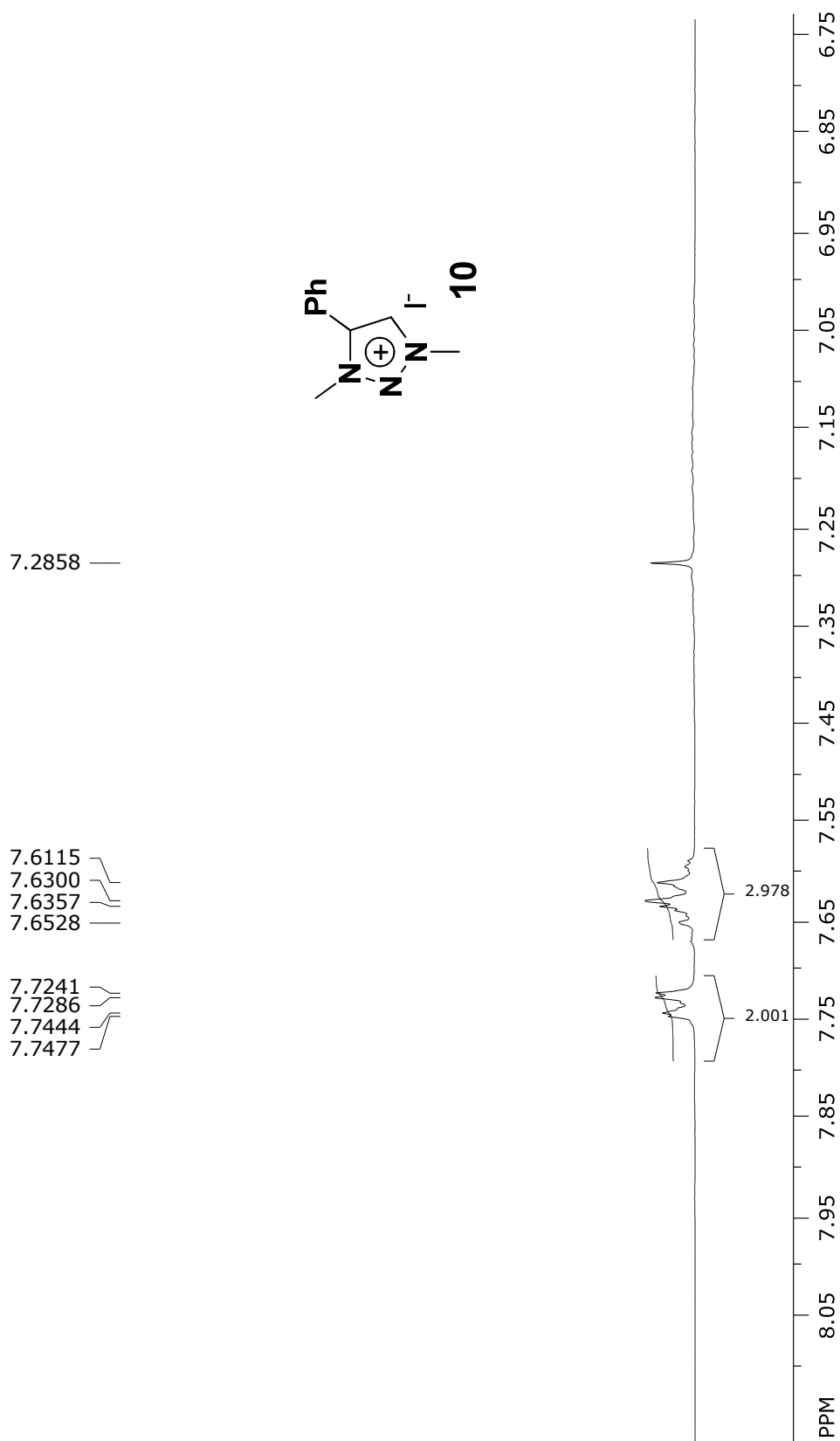
SpinWorks 3: NM Ionic





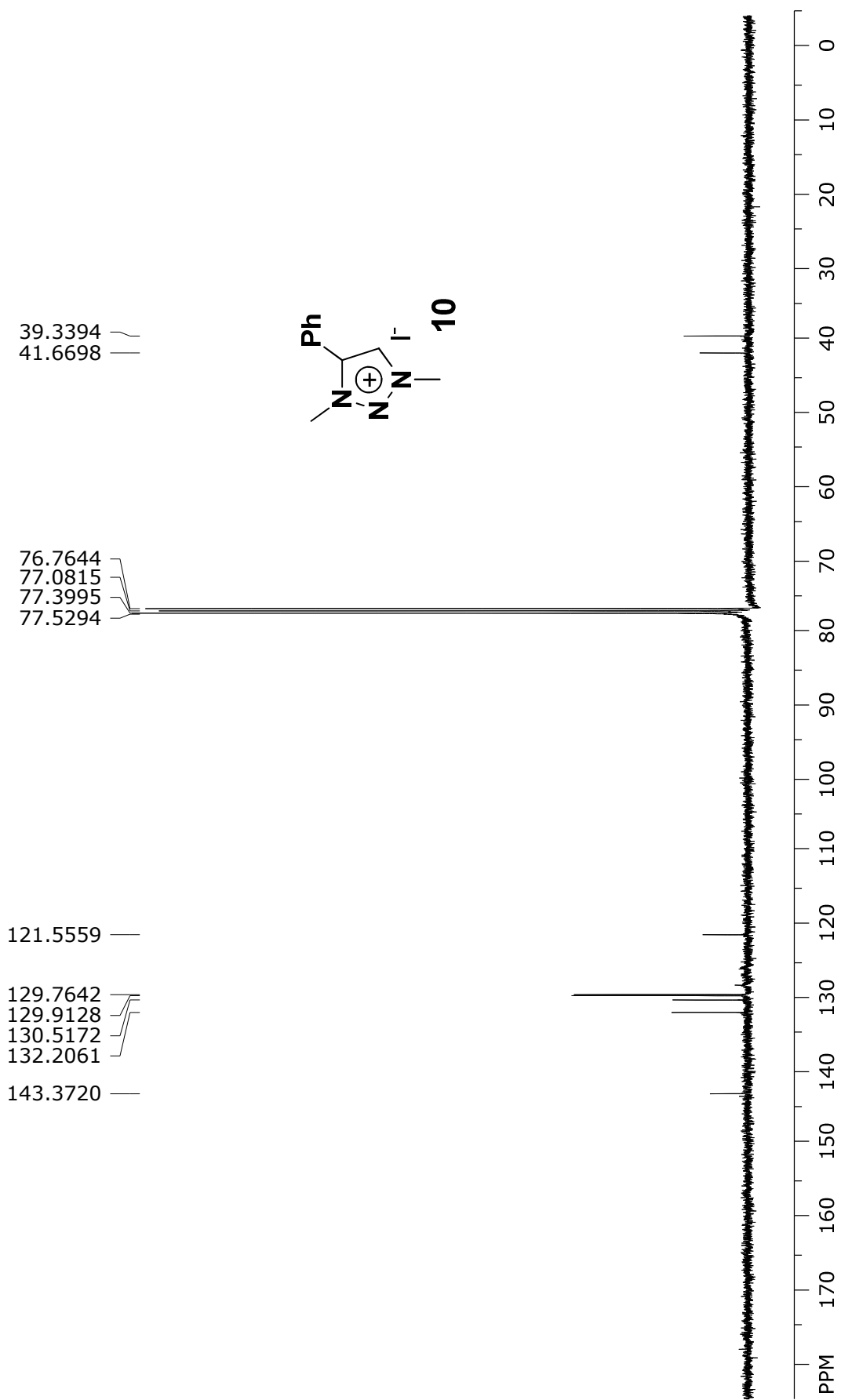
Nm- 1390

SpinWorks 3: NM Ionic



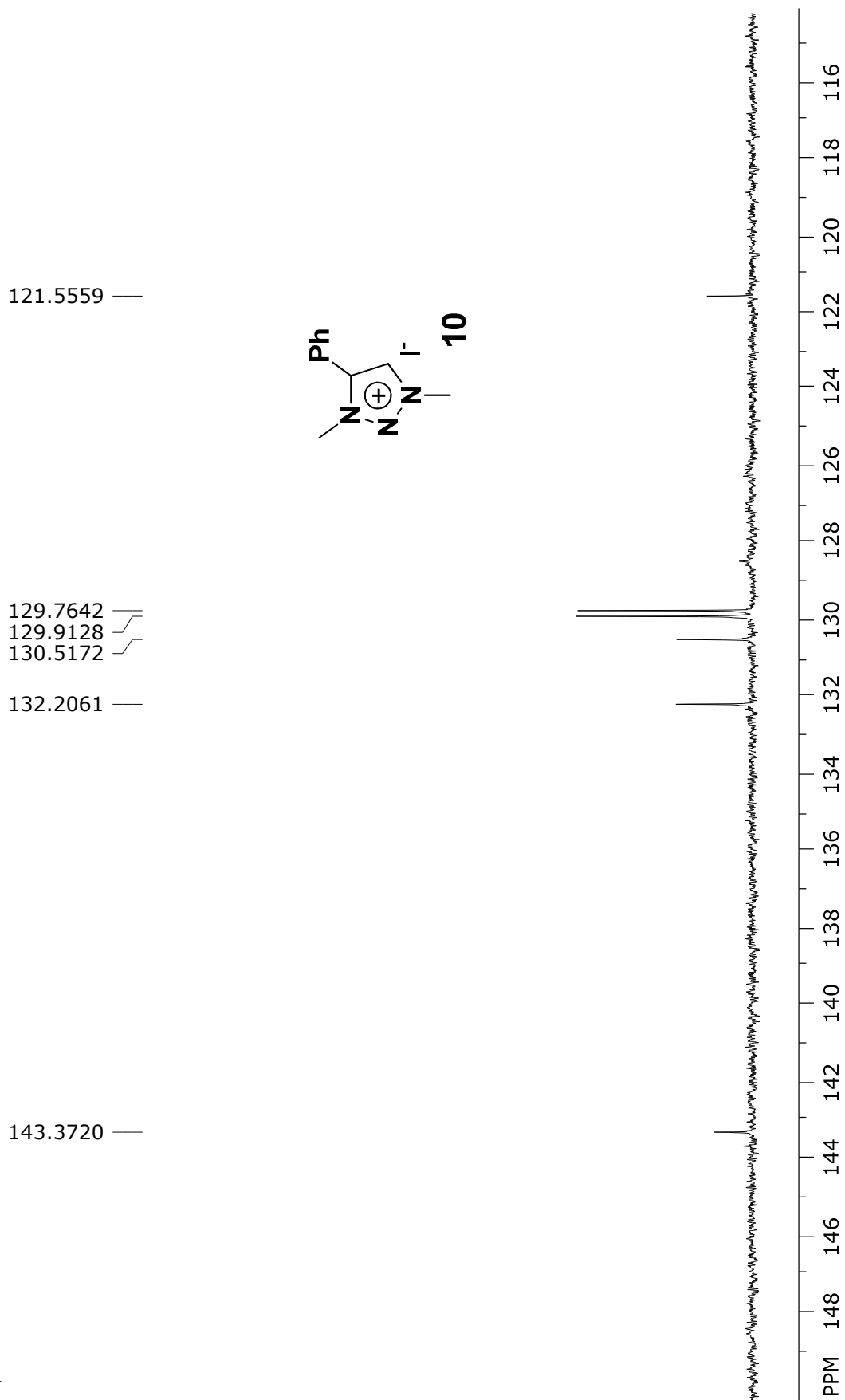
Nm- 1390

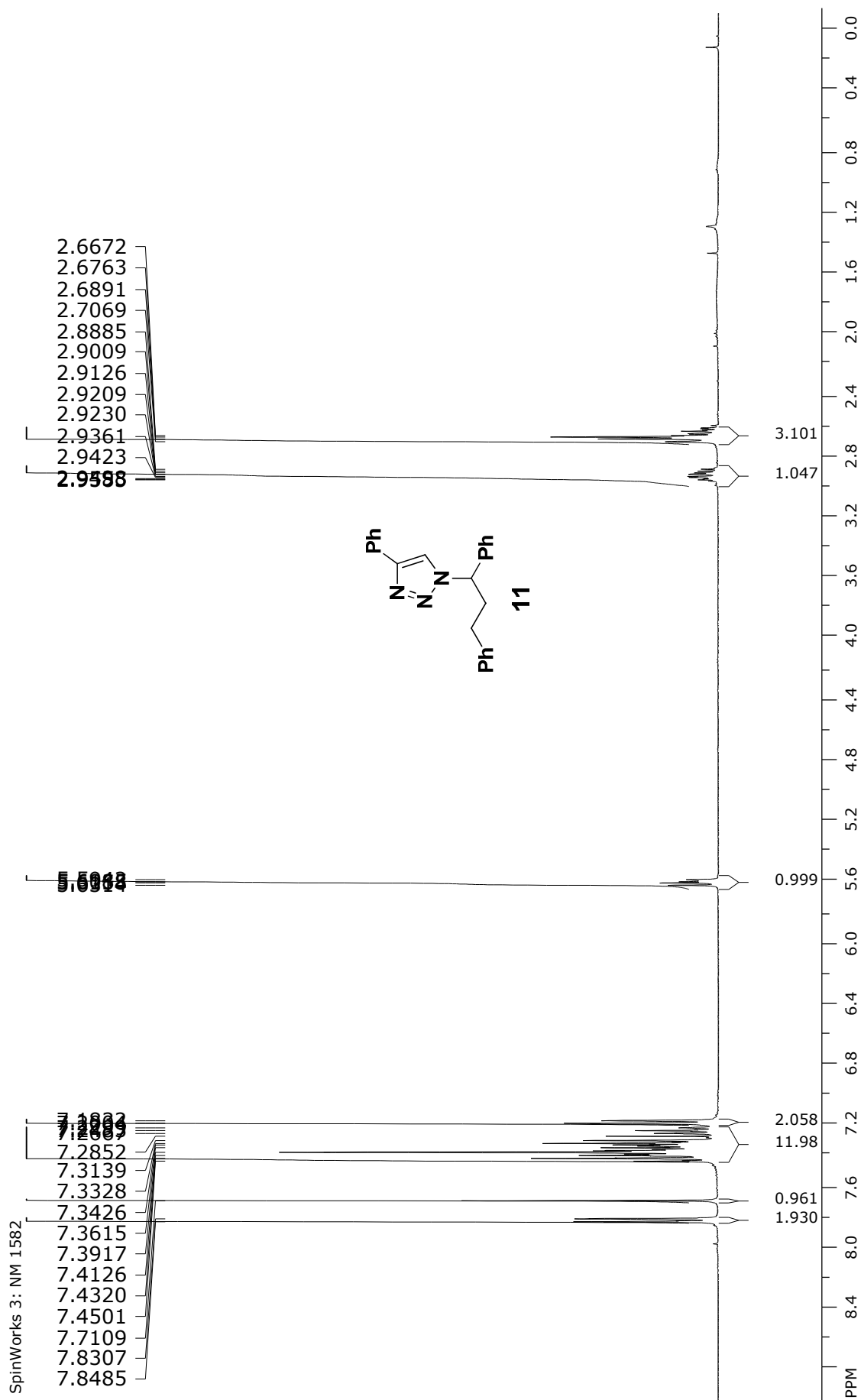
SpinWorks 3: NM Ionic

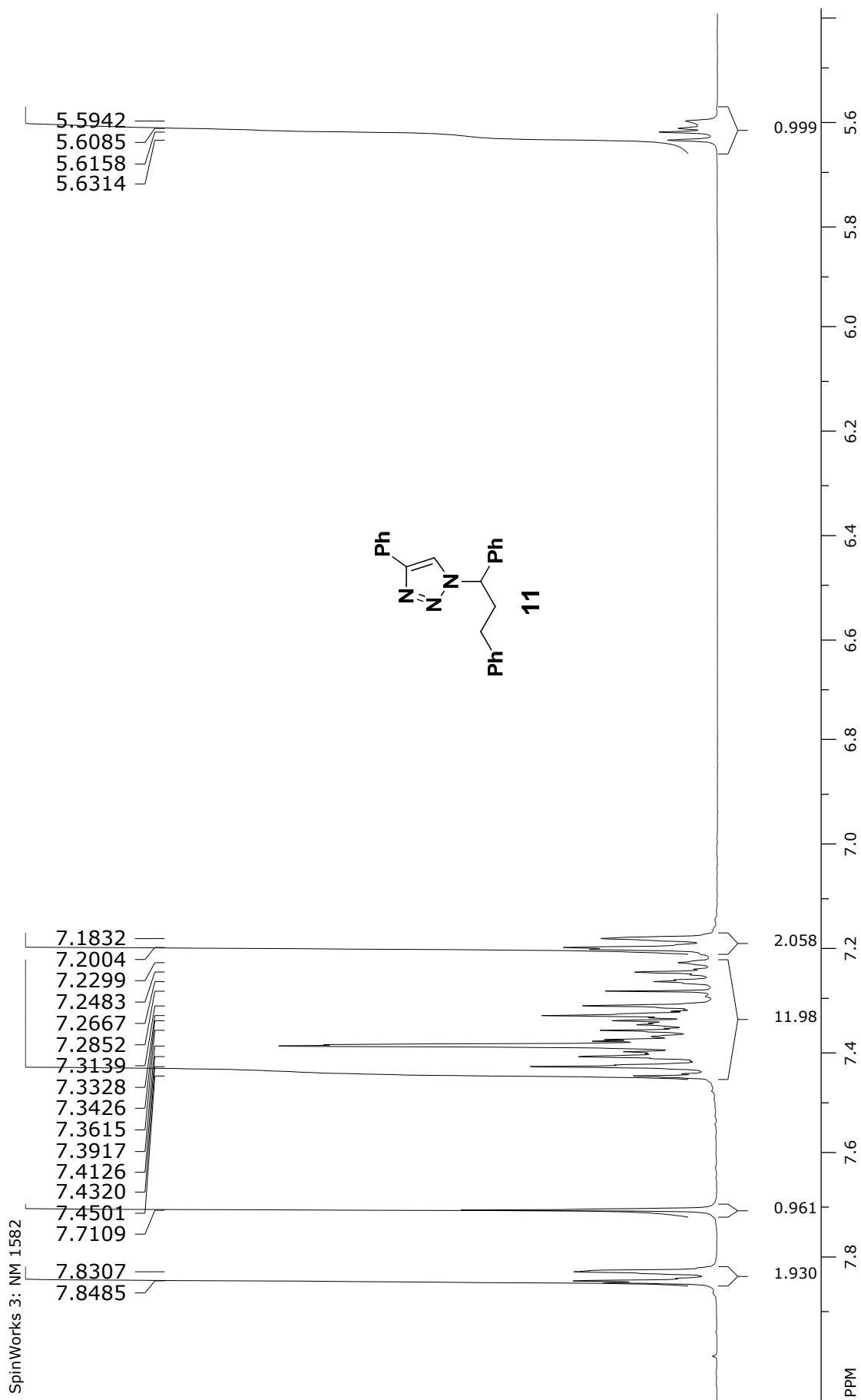


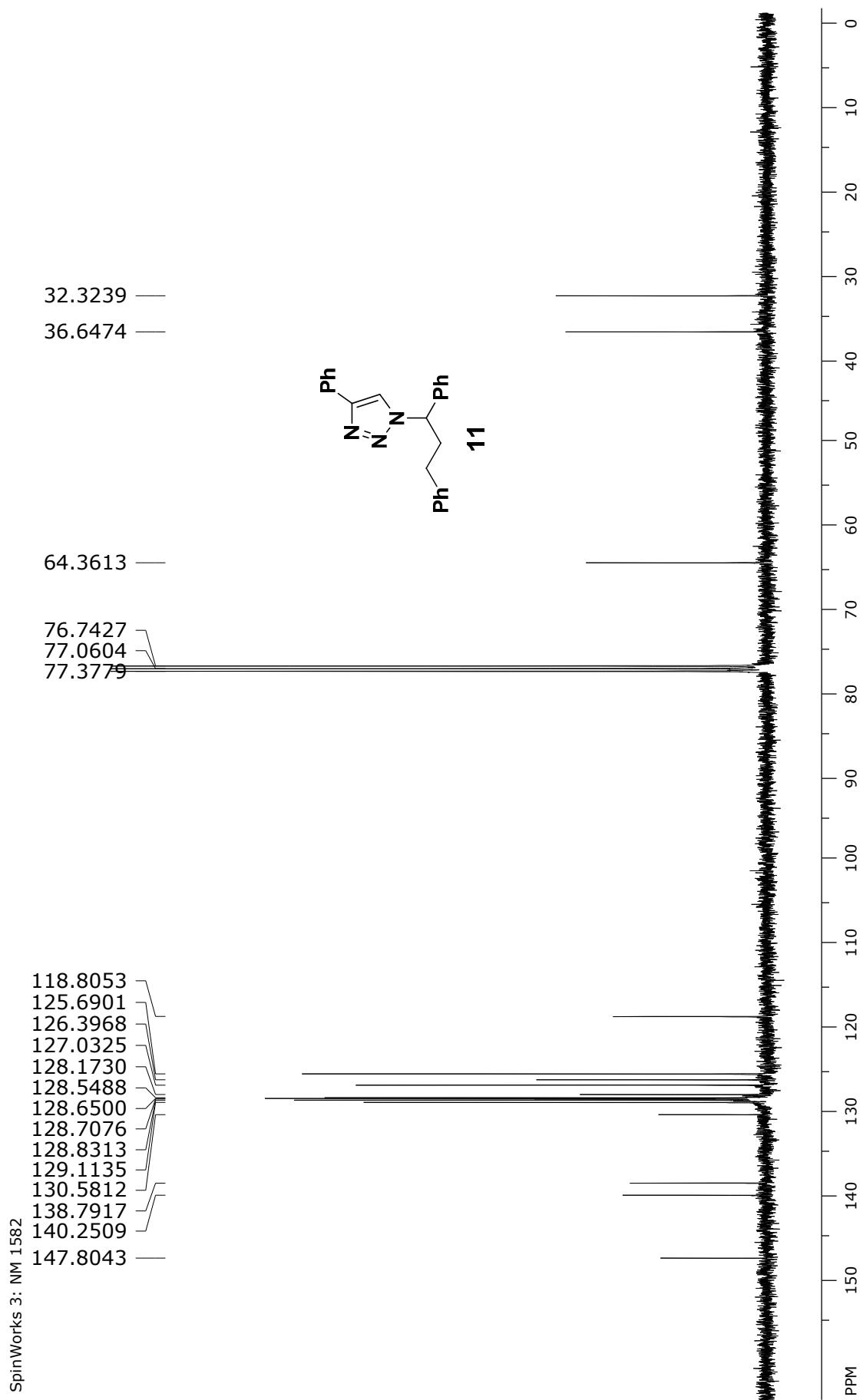
Nm- 1390

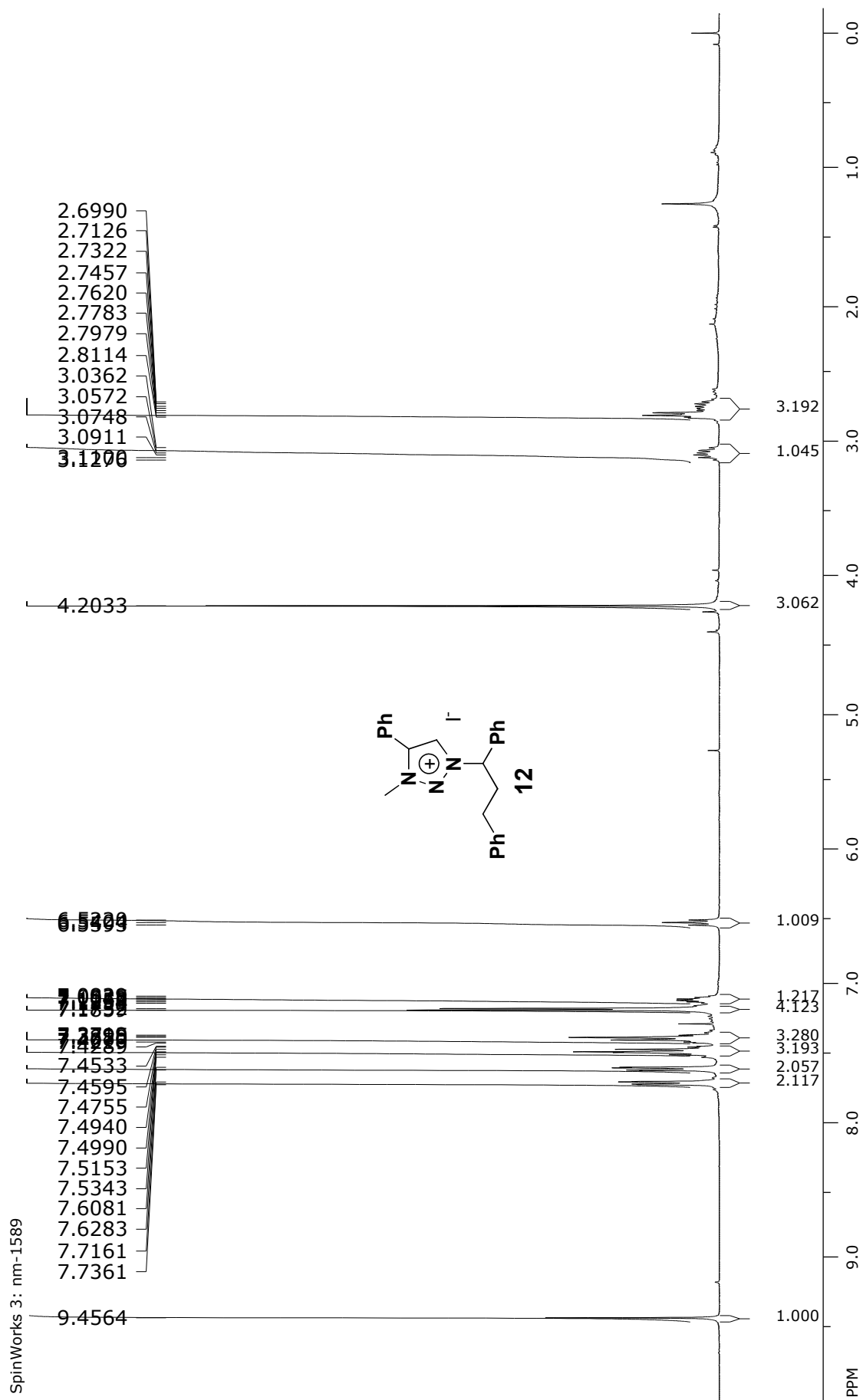
SpinWorks 3: NM Ionic

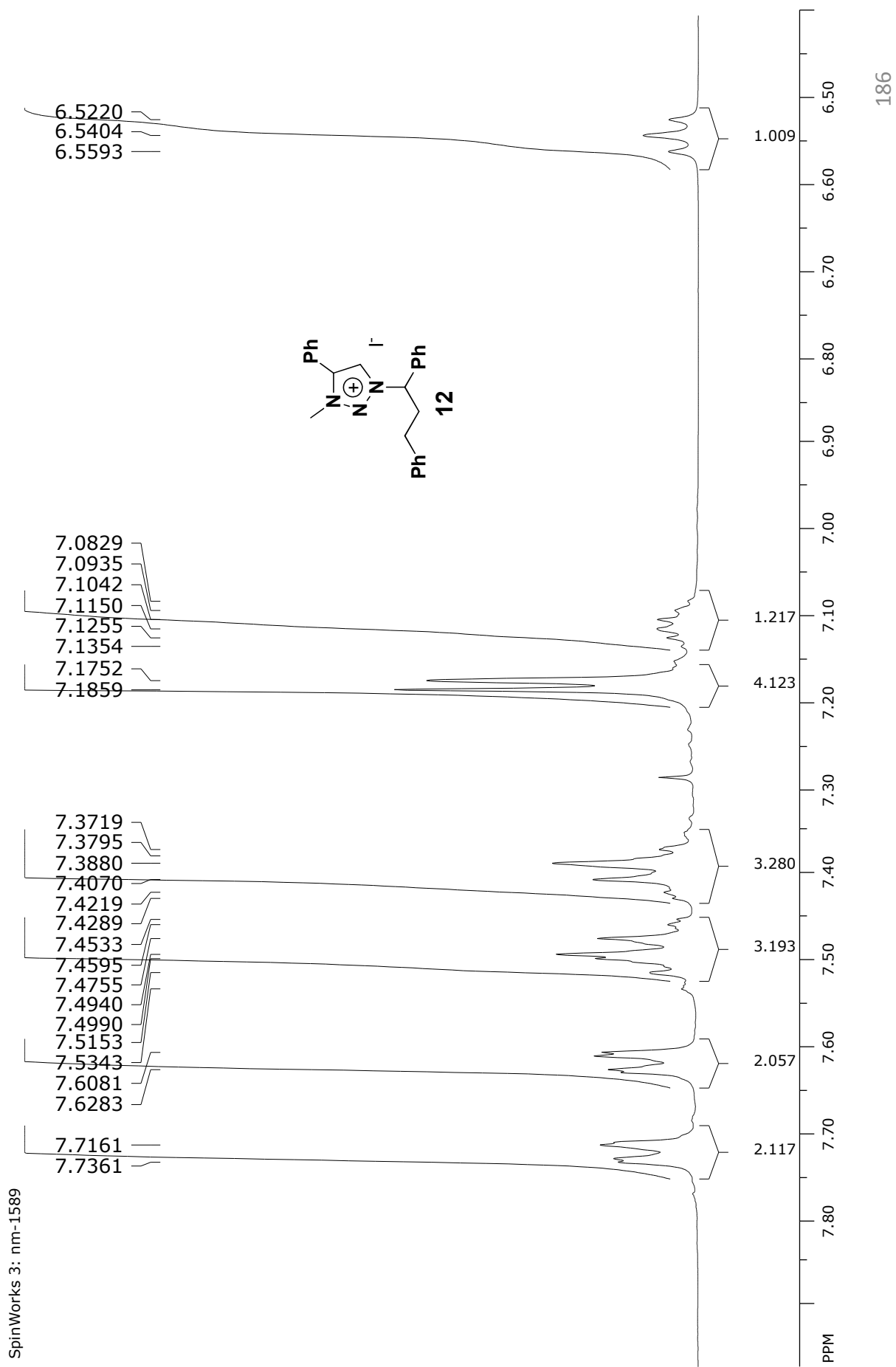




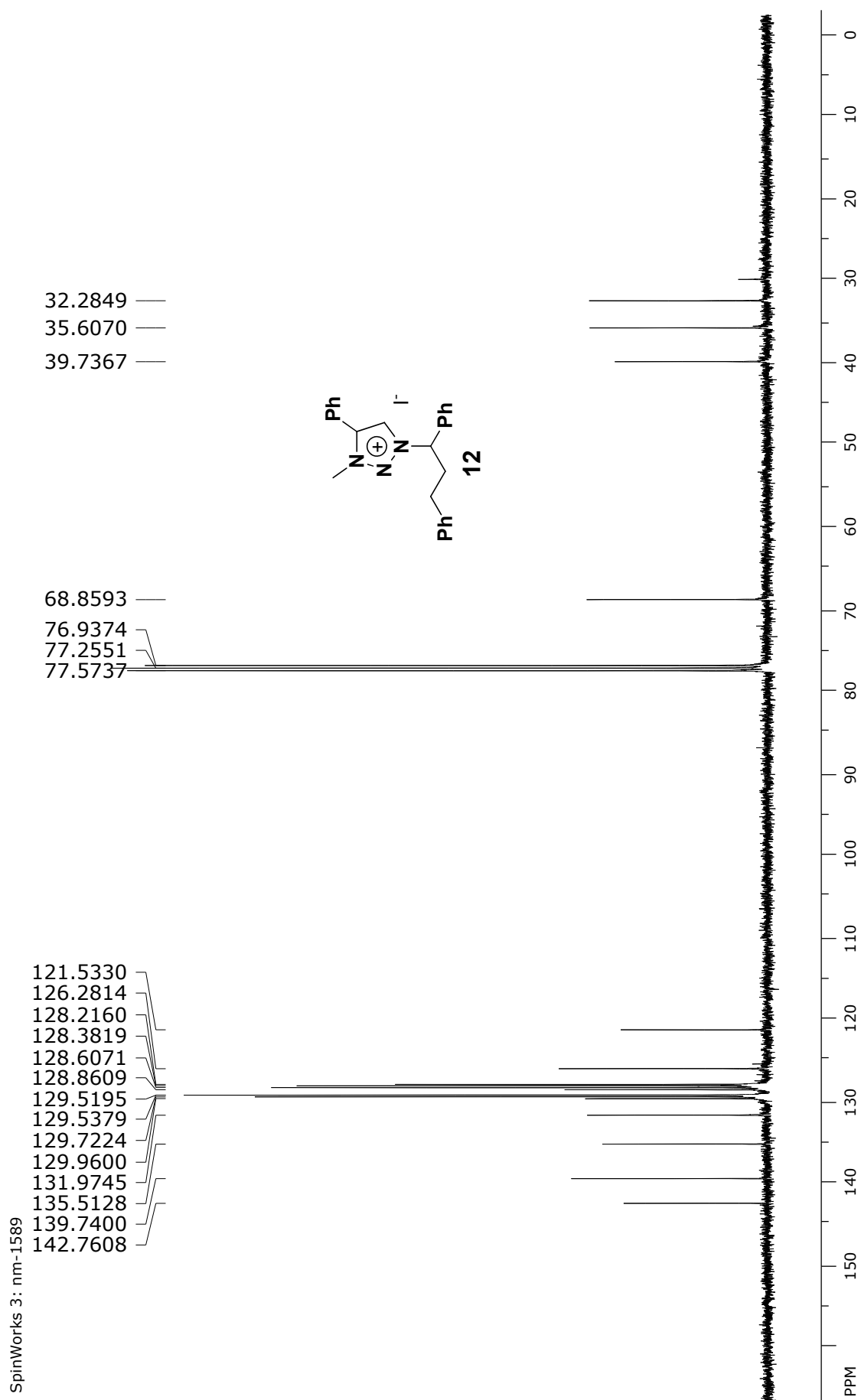


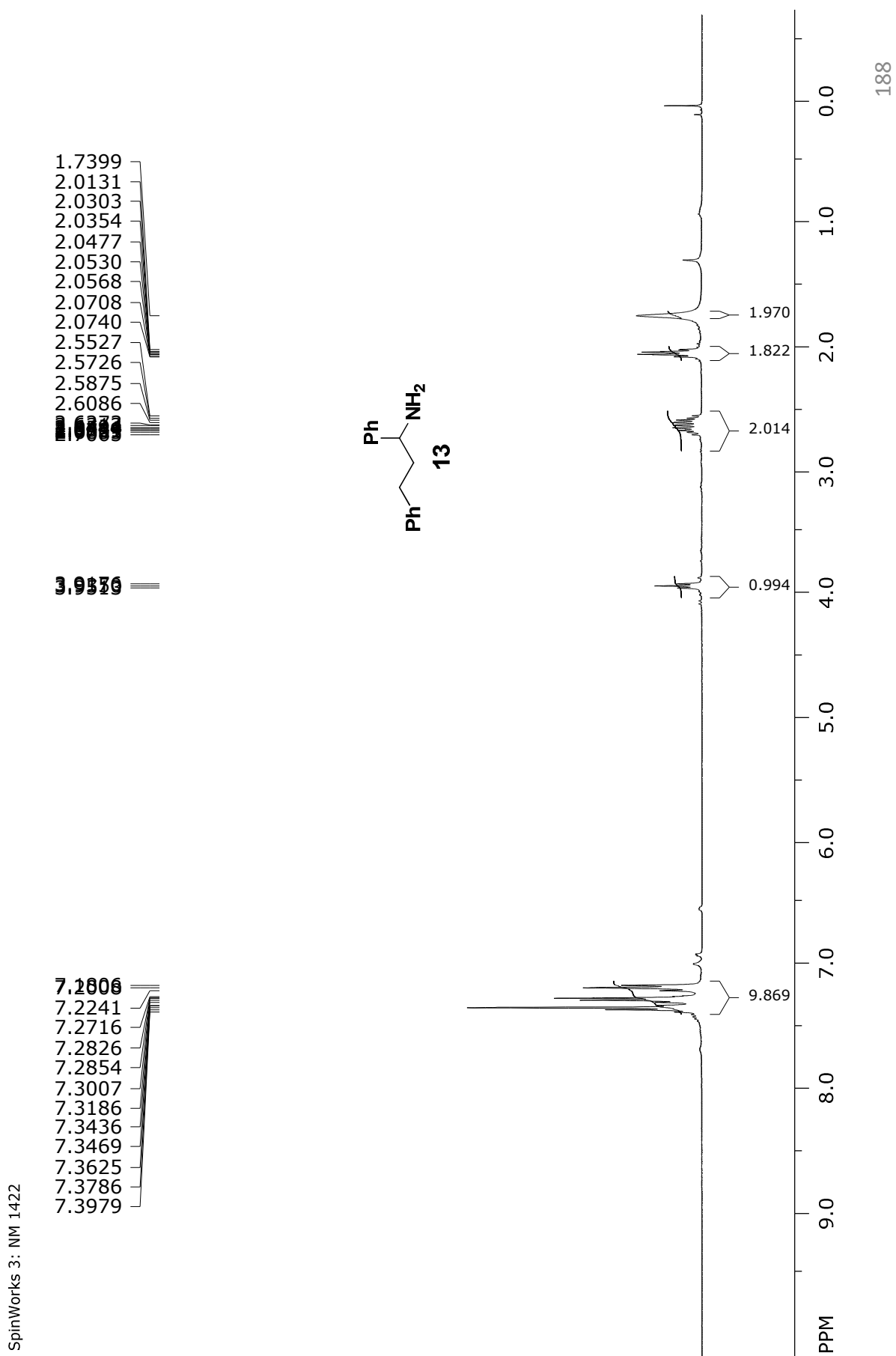


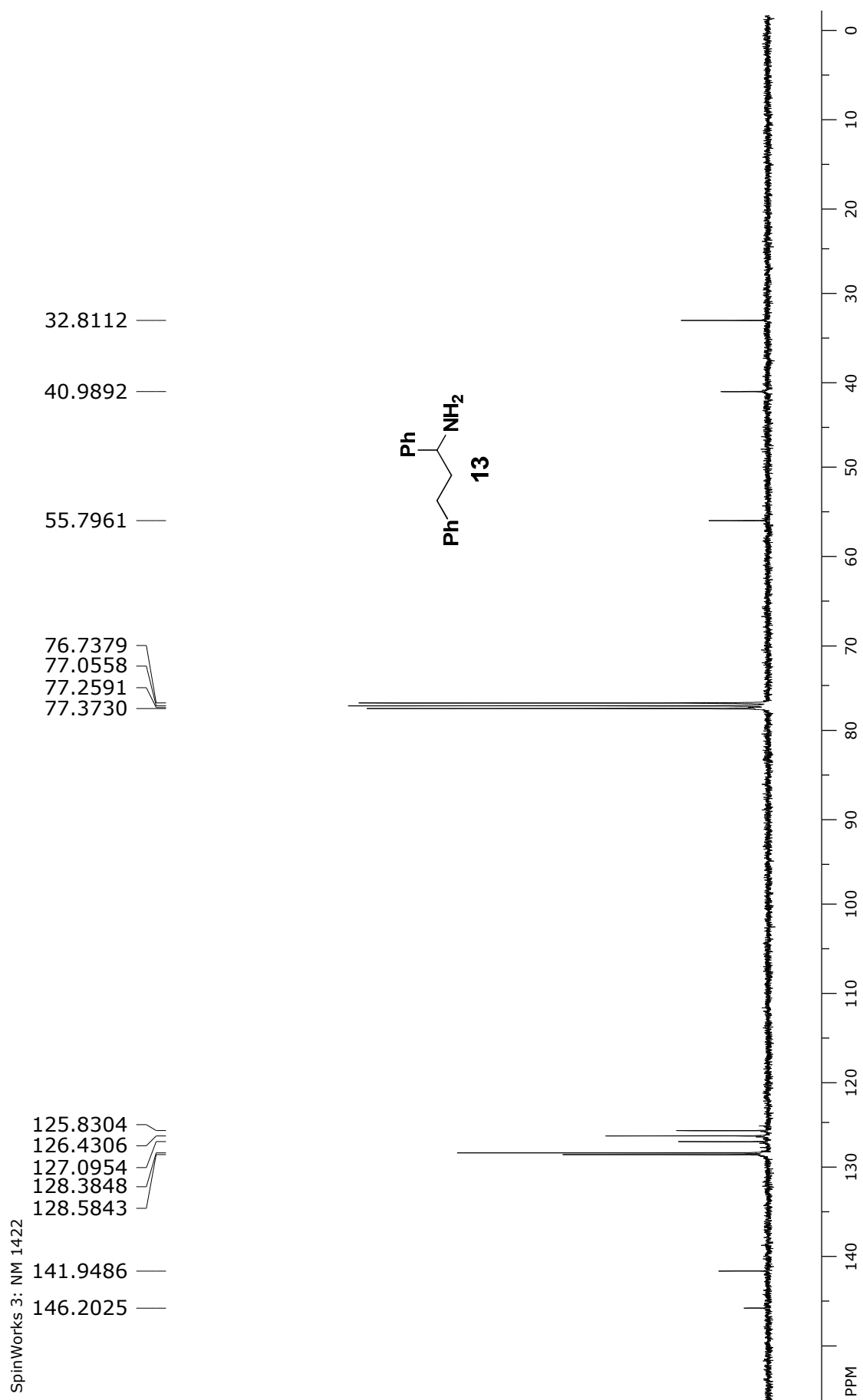




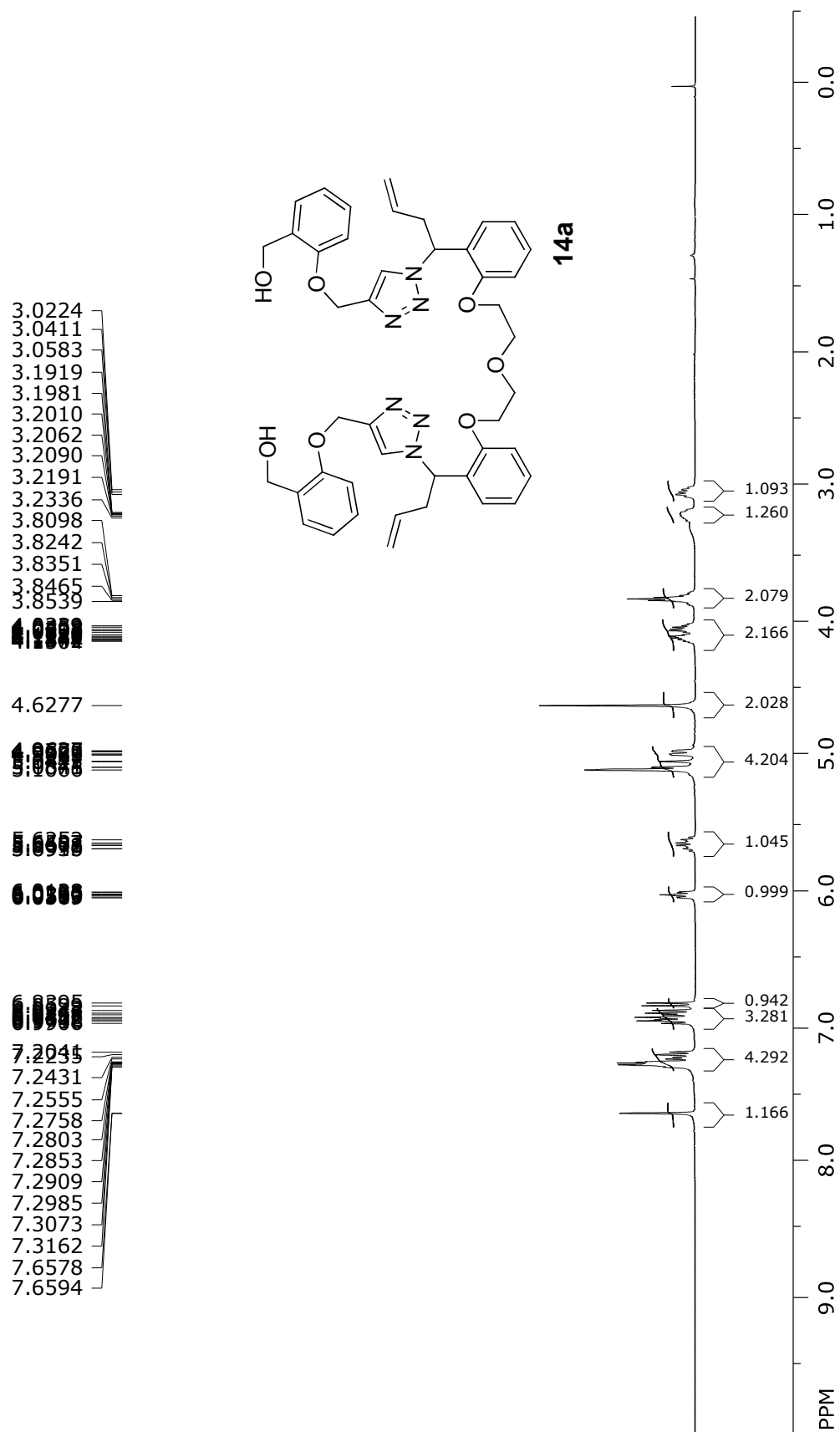




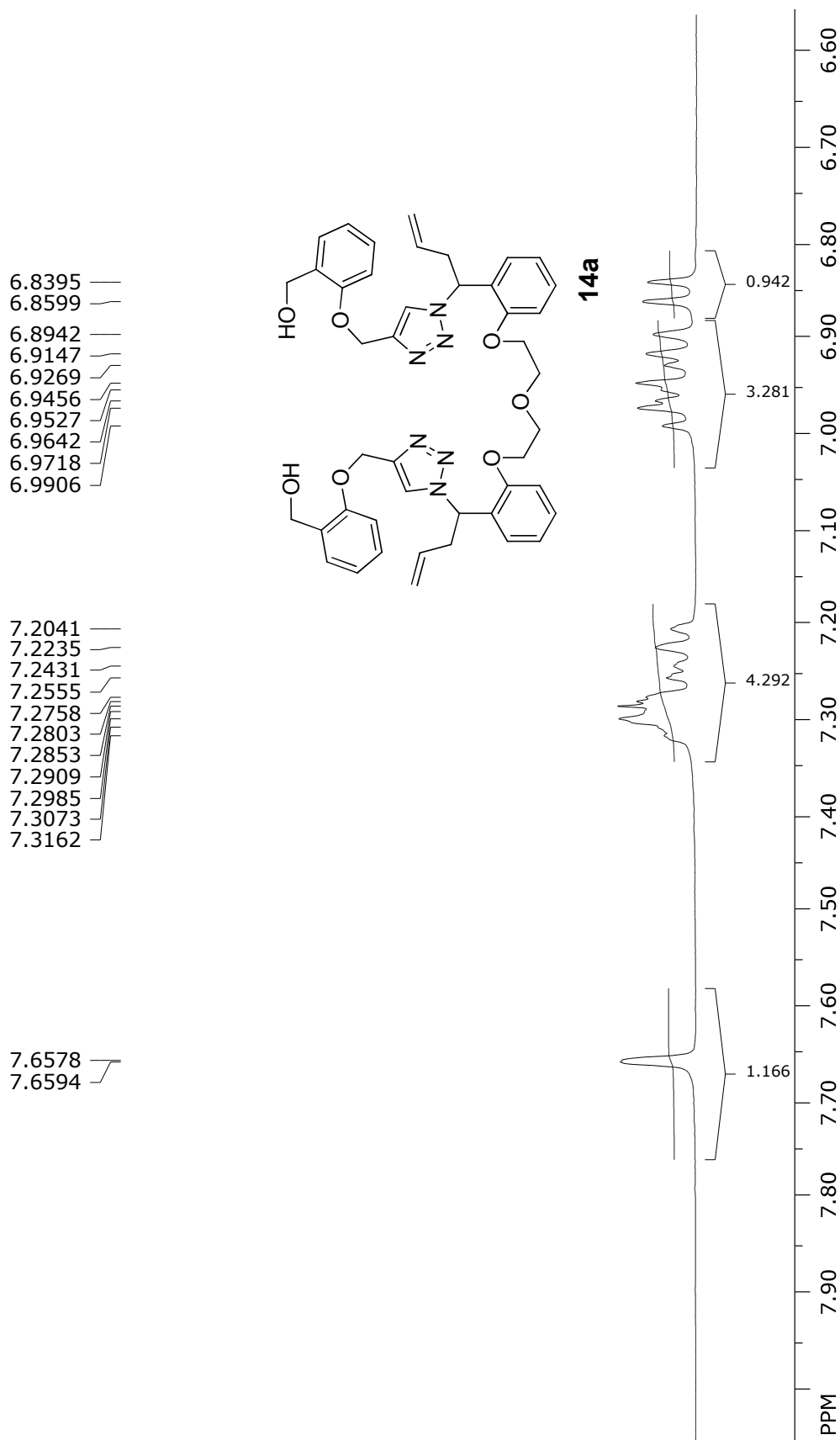




SpinWorks 3: NM-2193



SpinWorks 3: NM-2193

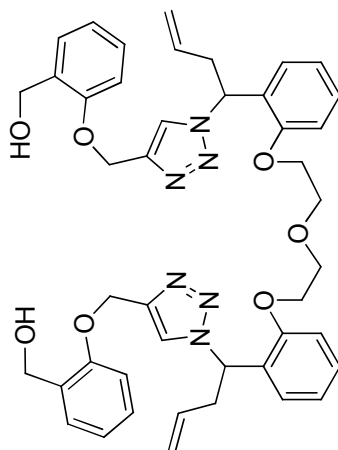
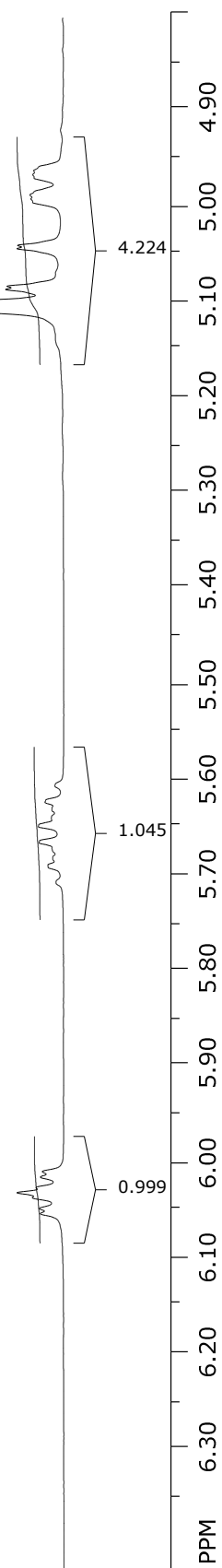


SpinWorks 3: NM-2193

4.9527  
4.9585  
4.9882  
4.9981  
5.0447  
5.0875  
5.1066

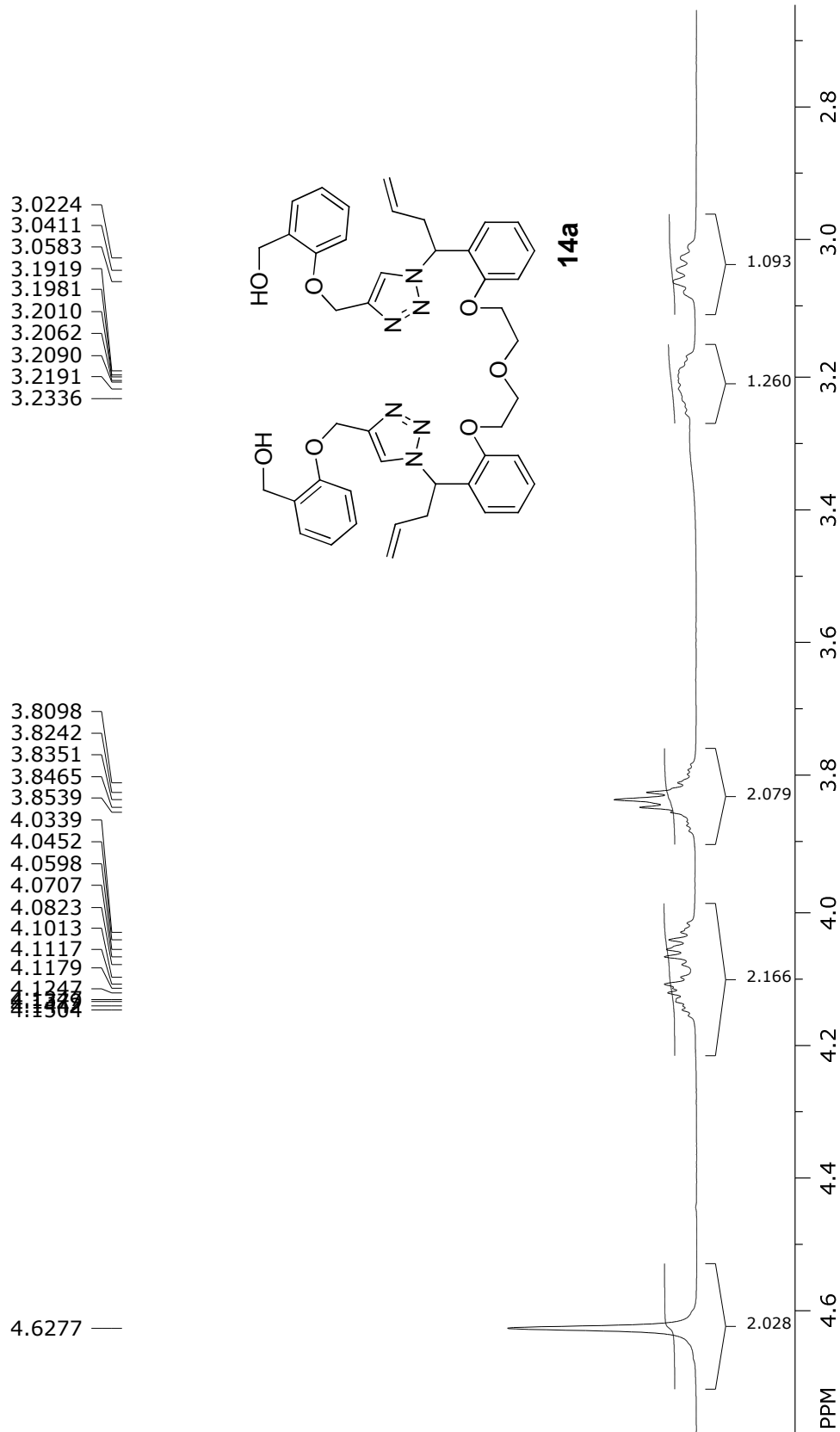
5.6252  
5.6407  
5.6661  
5.6678  
5.6913  
5.6930

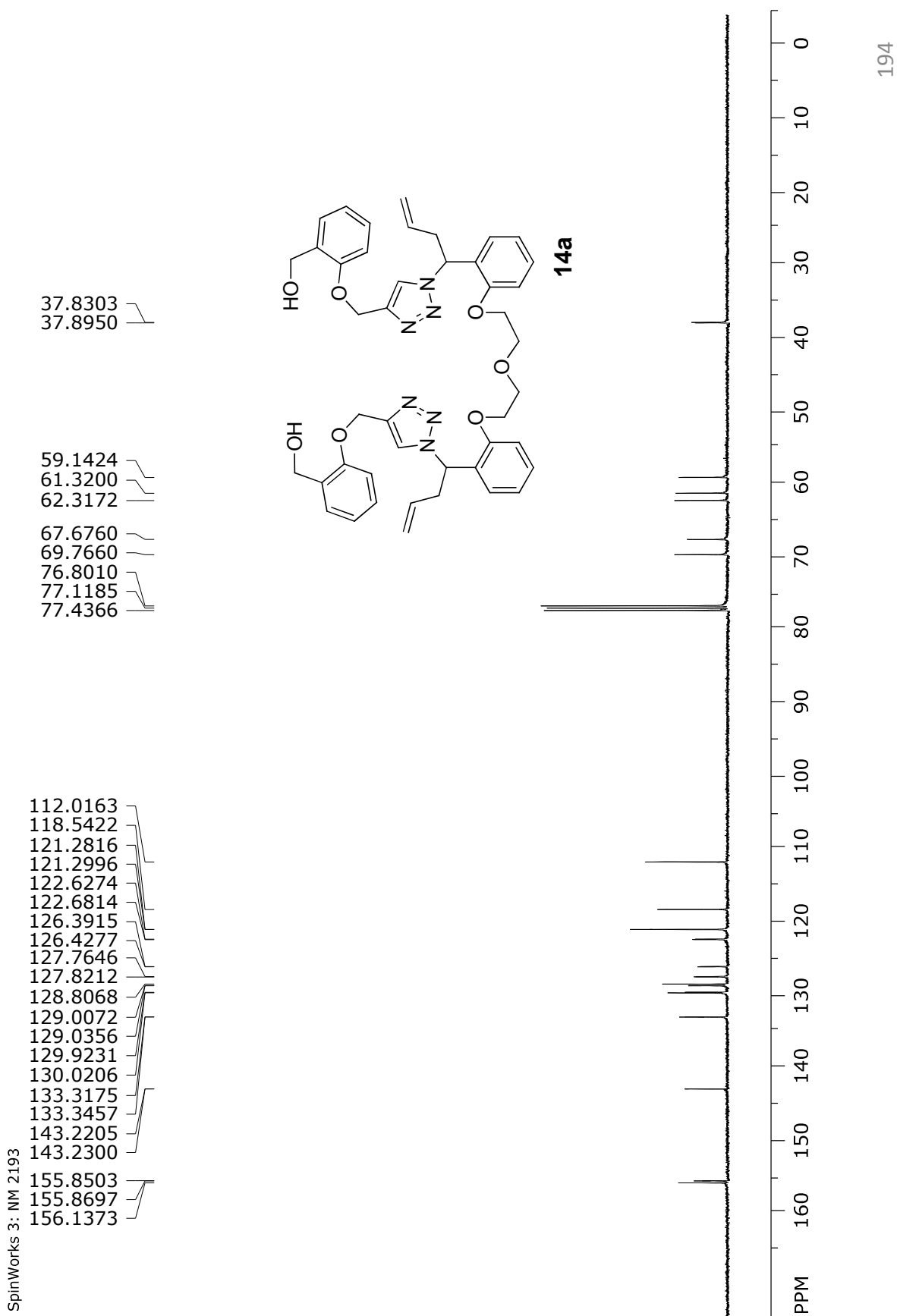
6.0128  
6.0183  
6.0295  
6.0350  
6.0399  
6.0513  
6.0569

**14a**

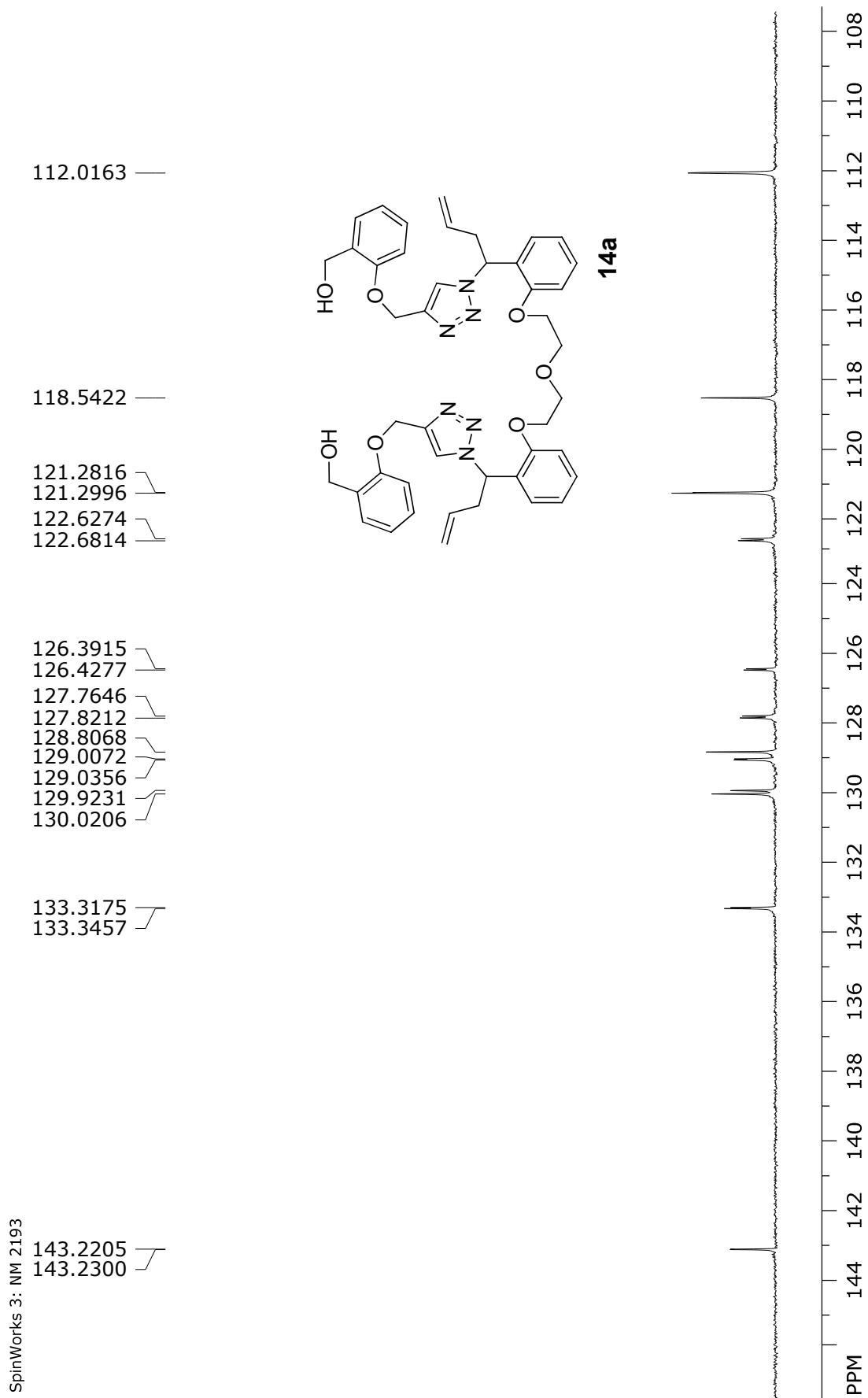
192

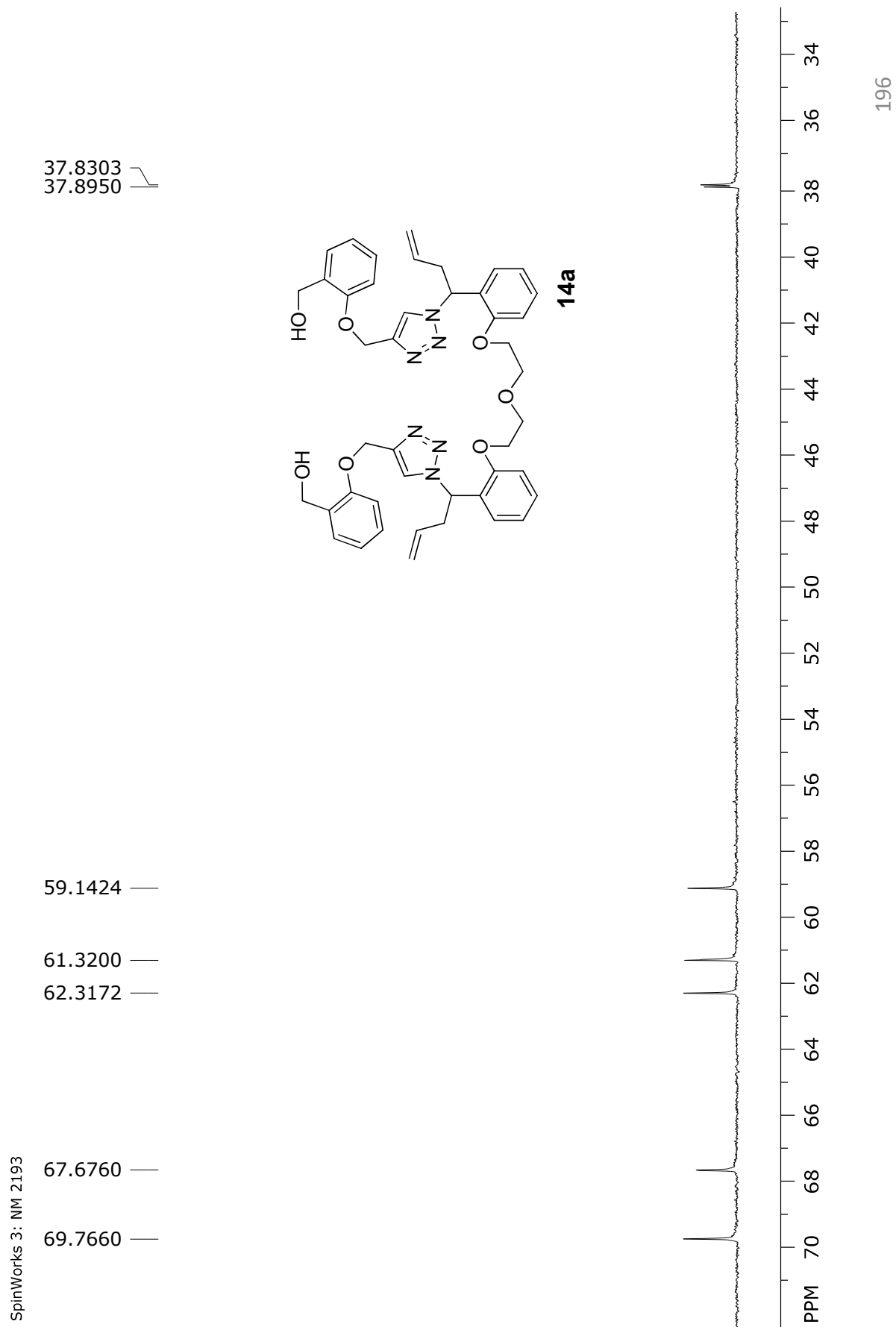
SpinWorks 3: NM-2193



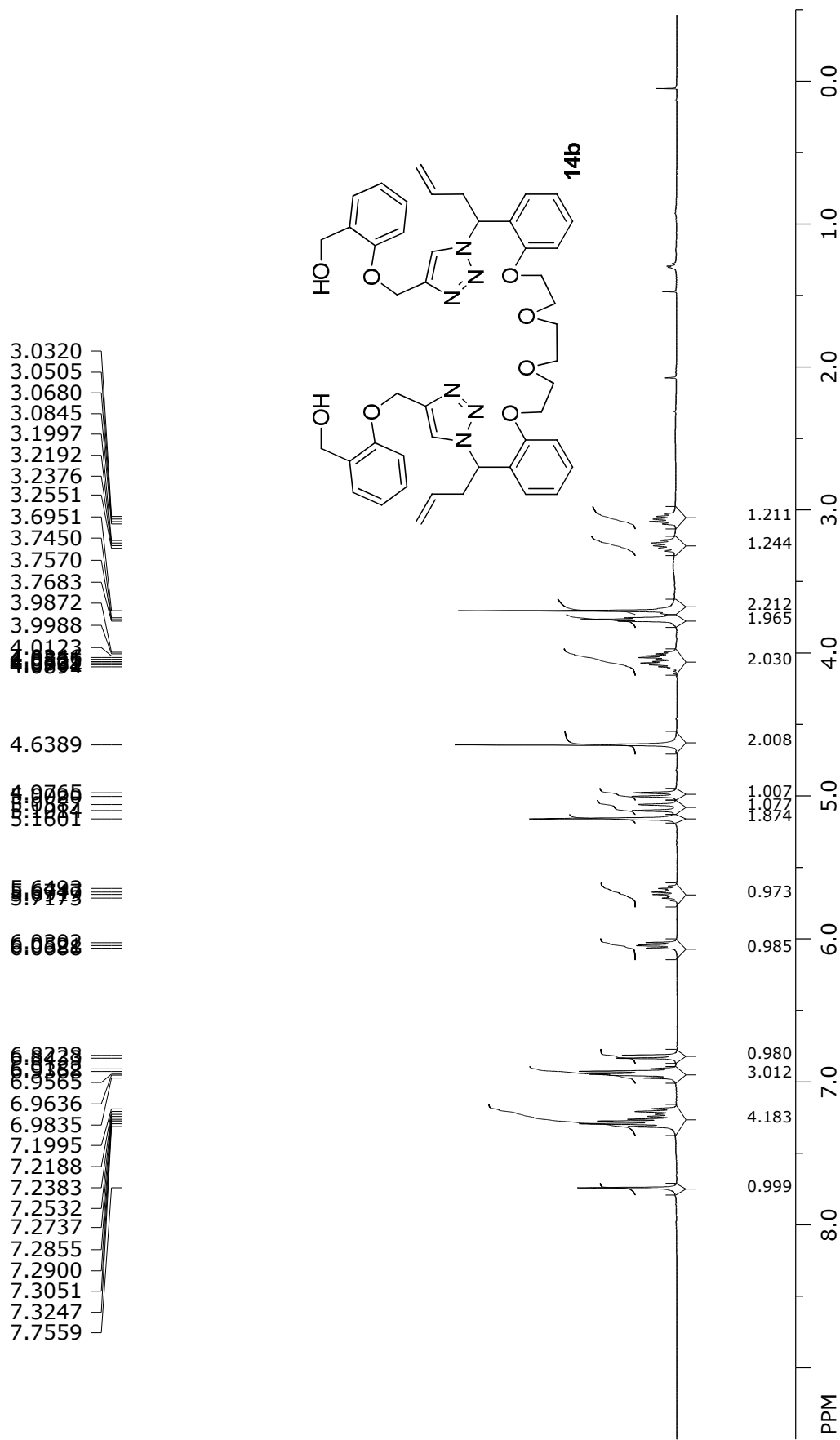


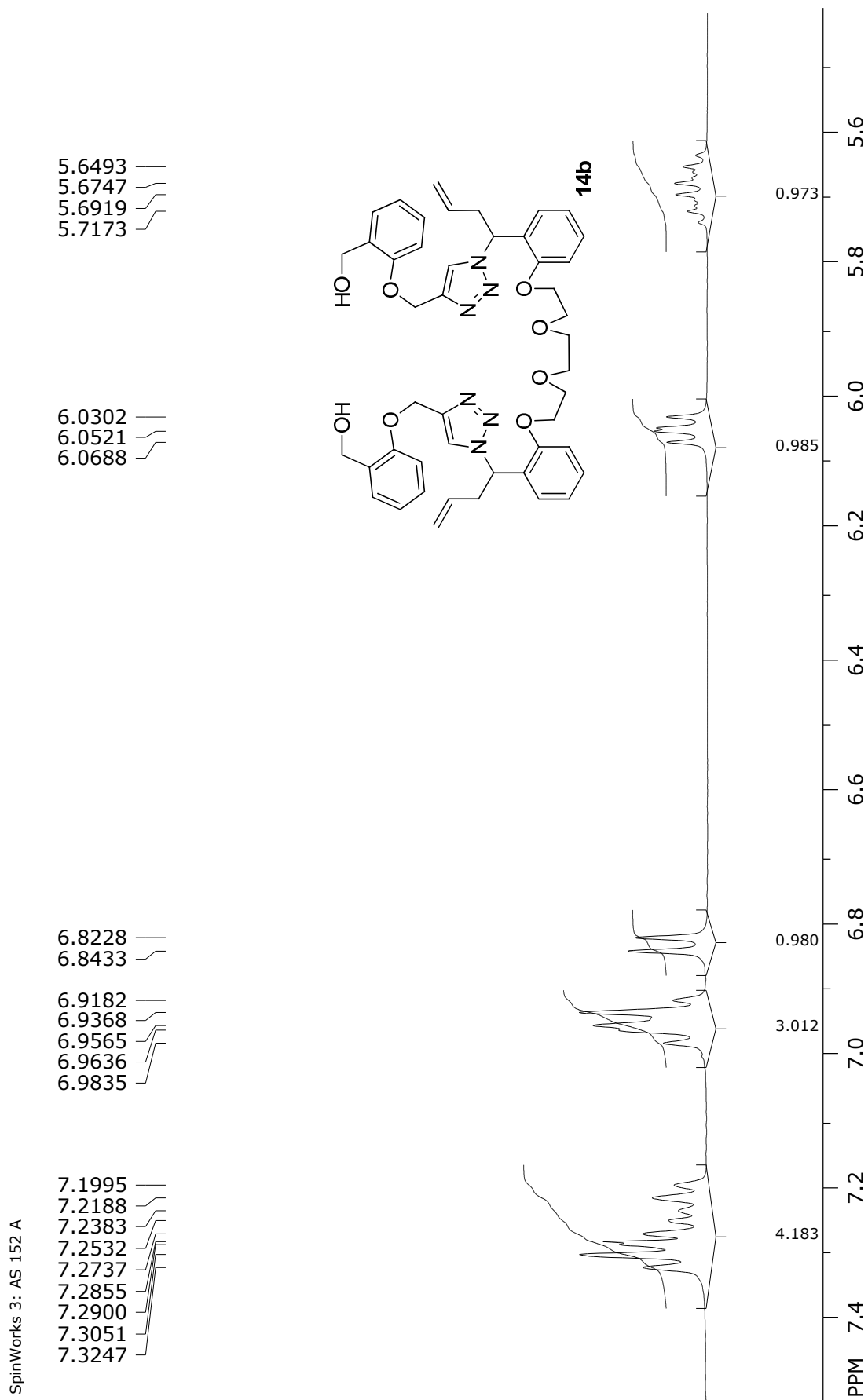


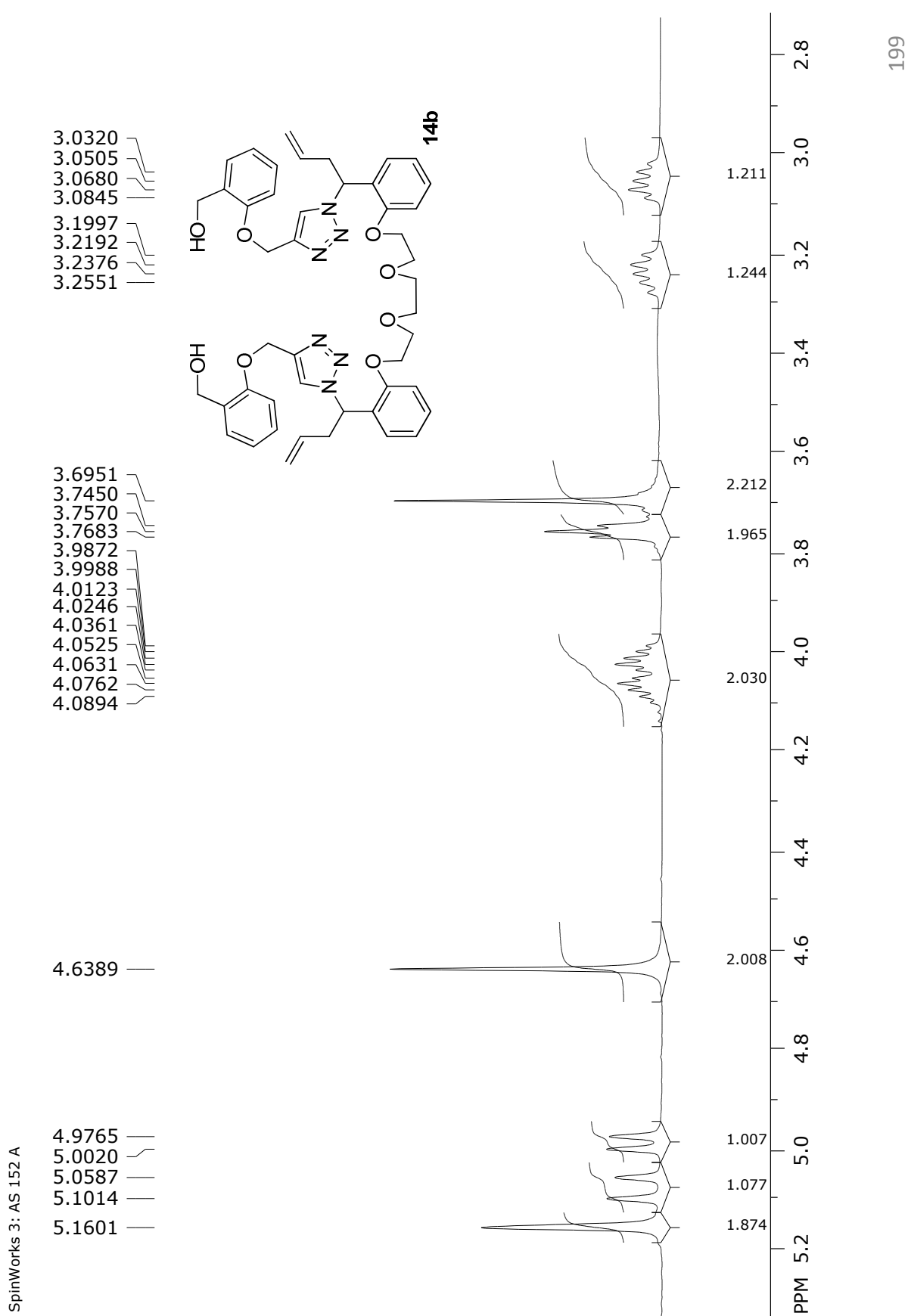


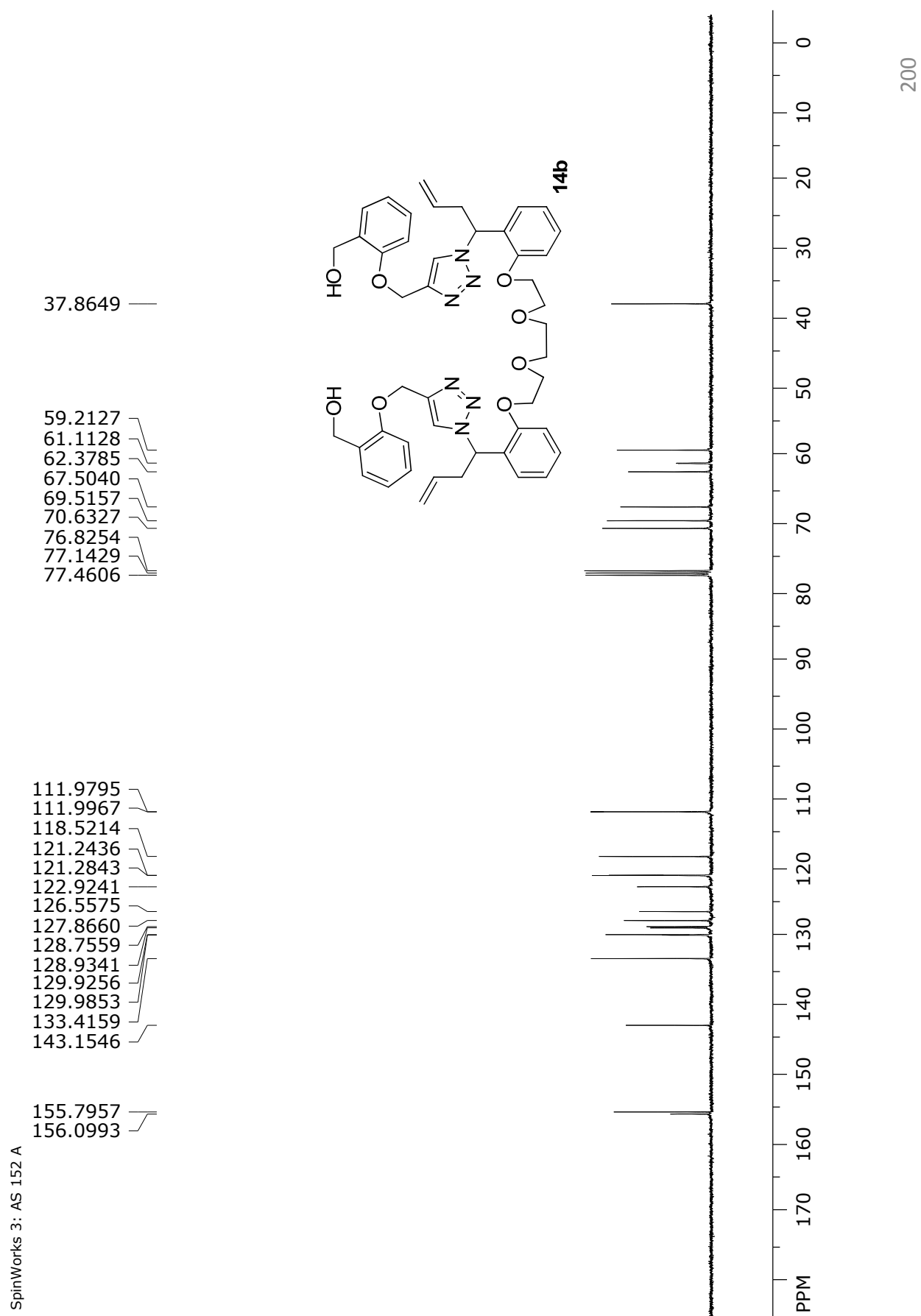


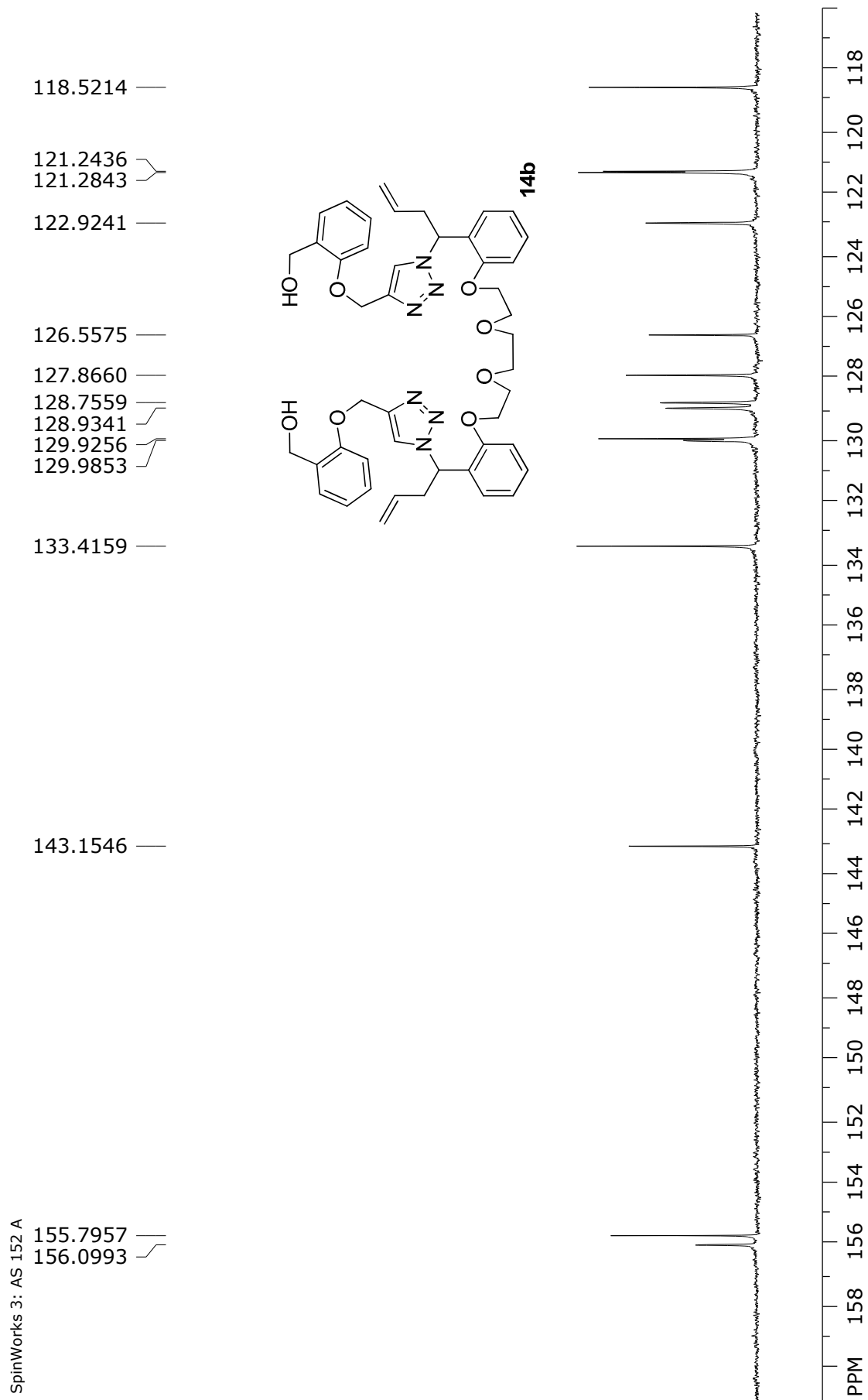
SpinWorks 3: AS 152 A



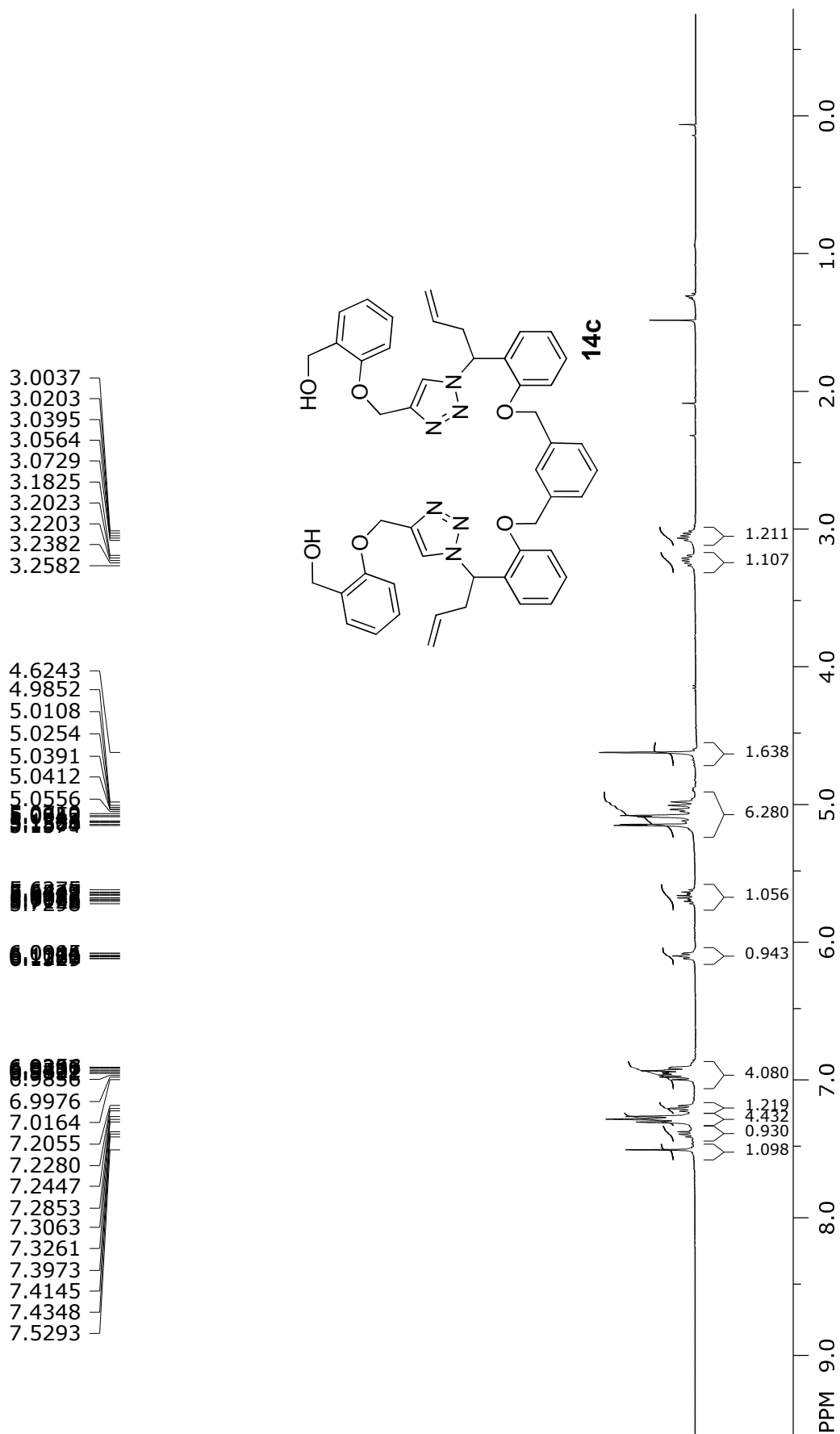








SpinWorks 3: NM 2195





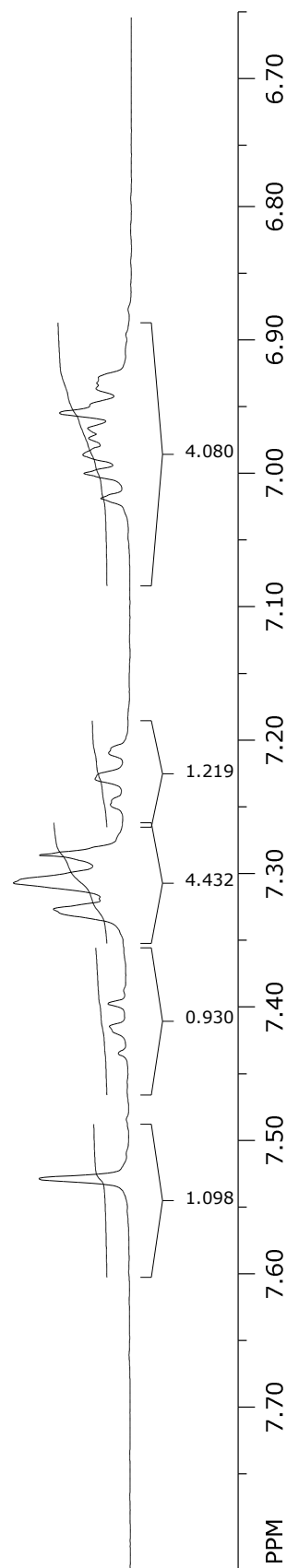
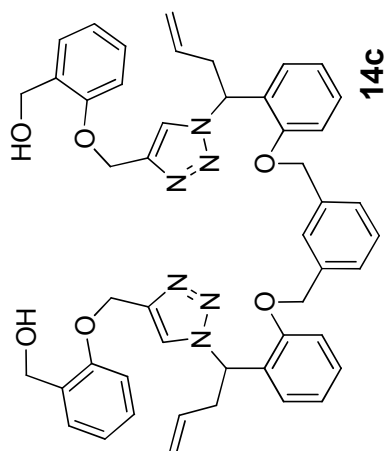
SpinWorks 3: NM 2195

6.9256  
6.9296  
6.9337  
6.9462  
6.9521  
6.9637  
6.9711  
6.9836  
6.9976  
7.0164

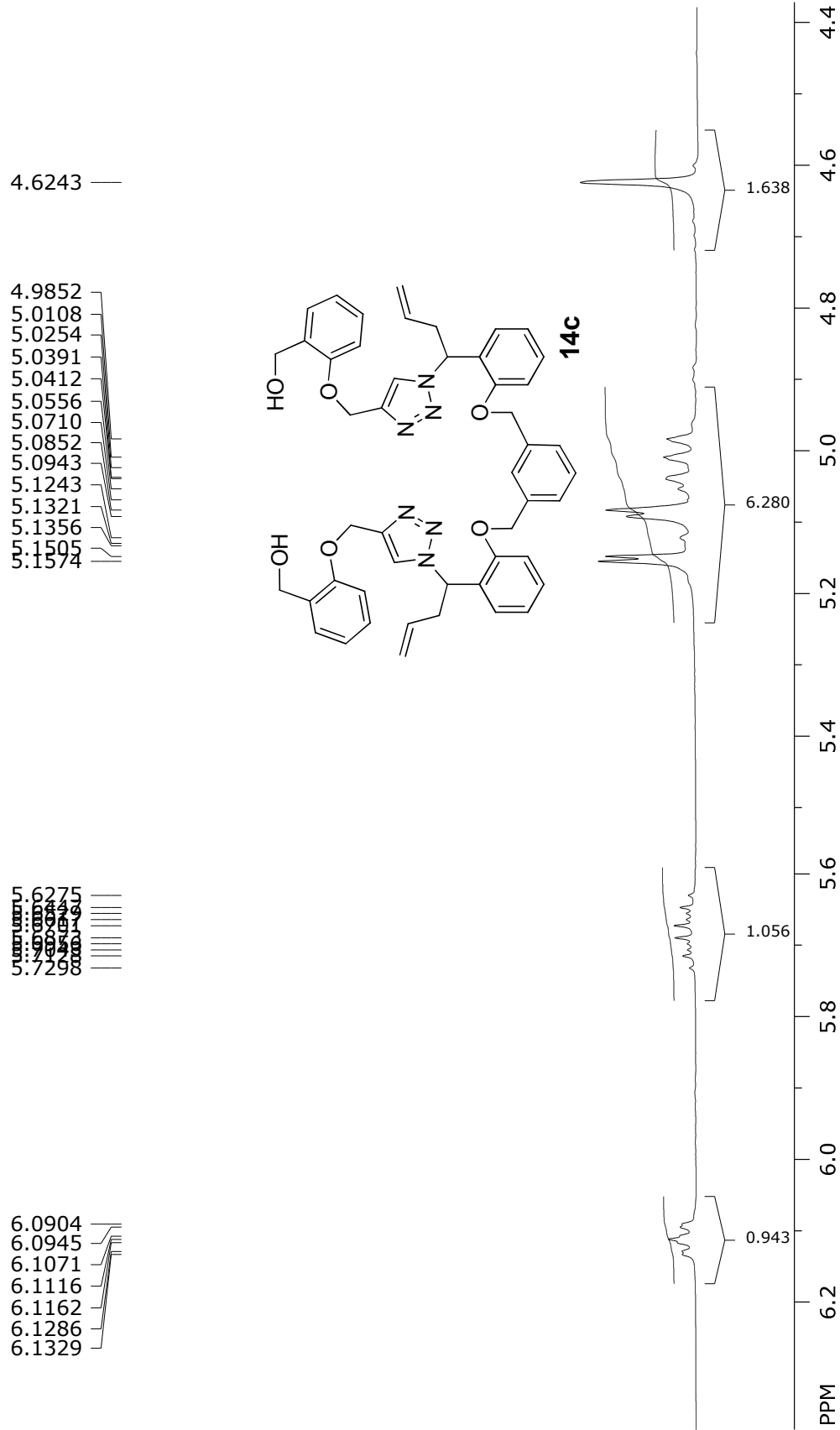
7.2055 —  
7.2280 —  
7.2447 —  
7.2853 —  
7.3063 —  
7.3261 —

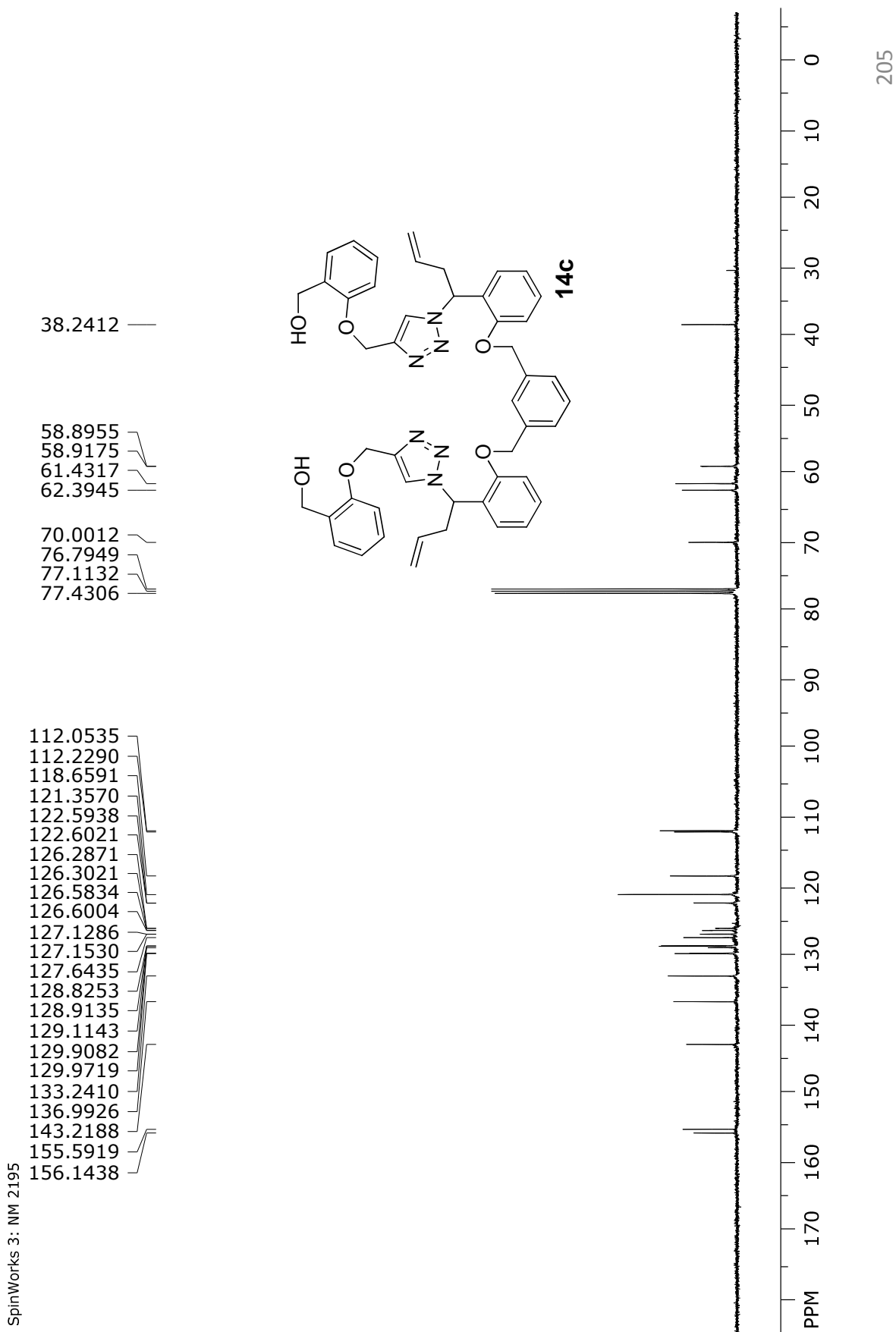
7.3973 —  
7.4145 —  
7.4348 —

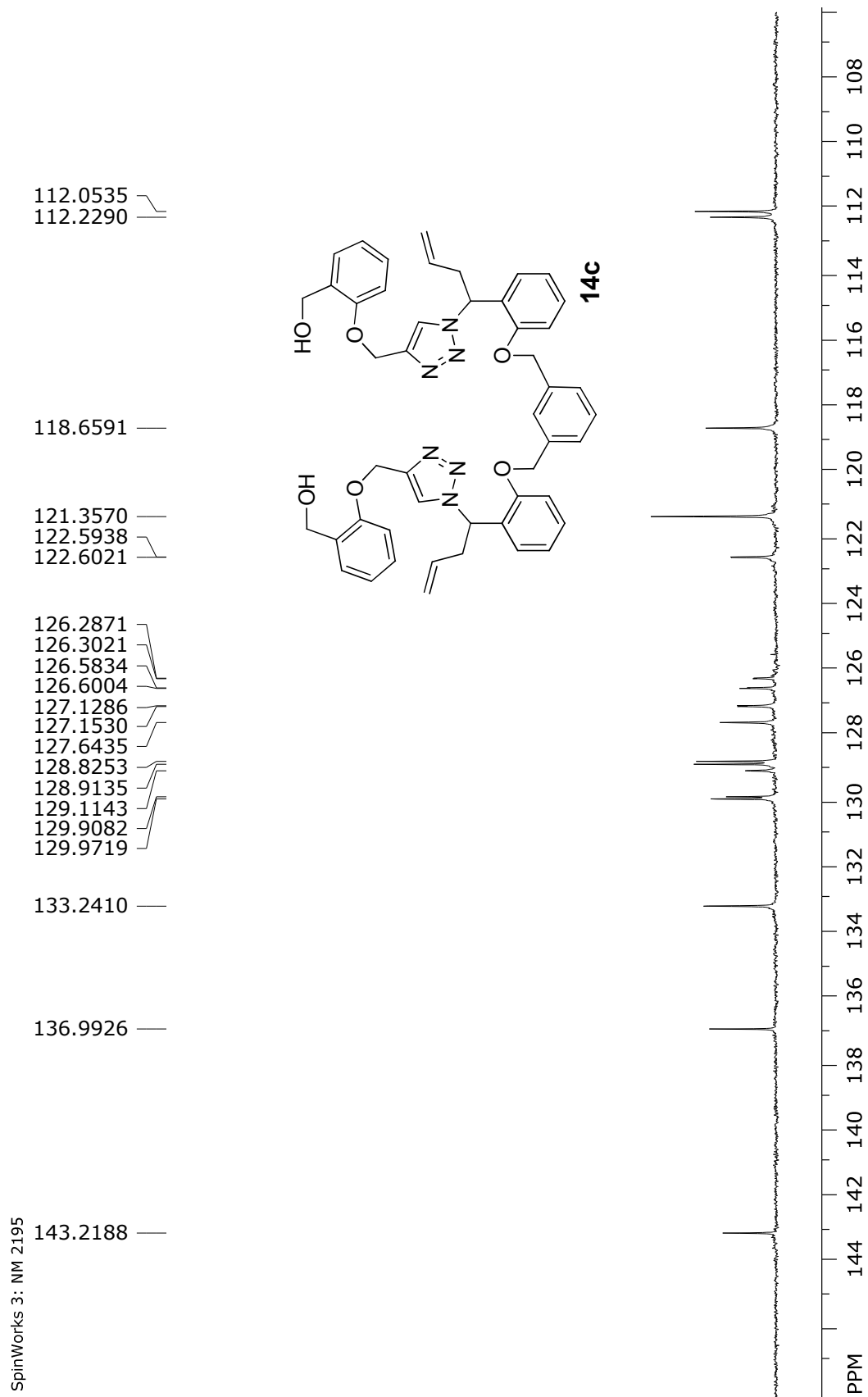
7.5293 —

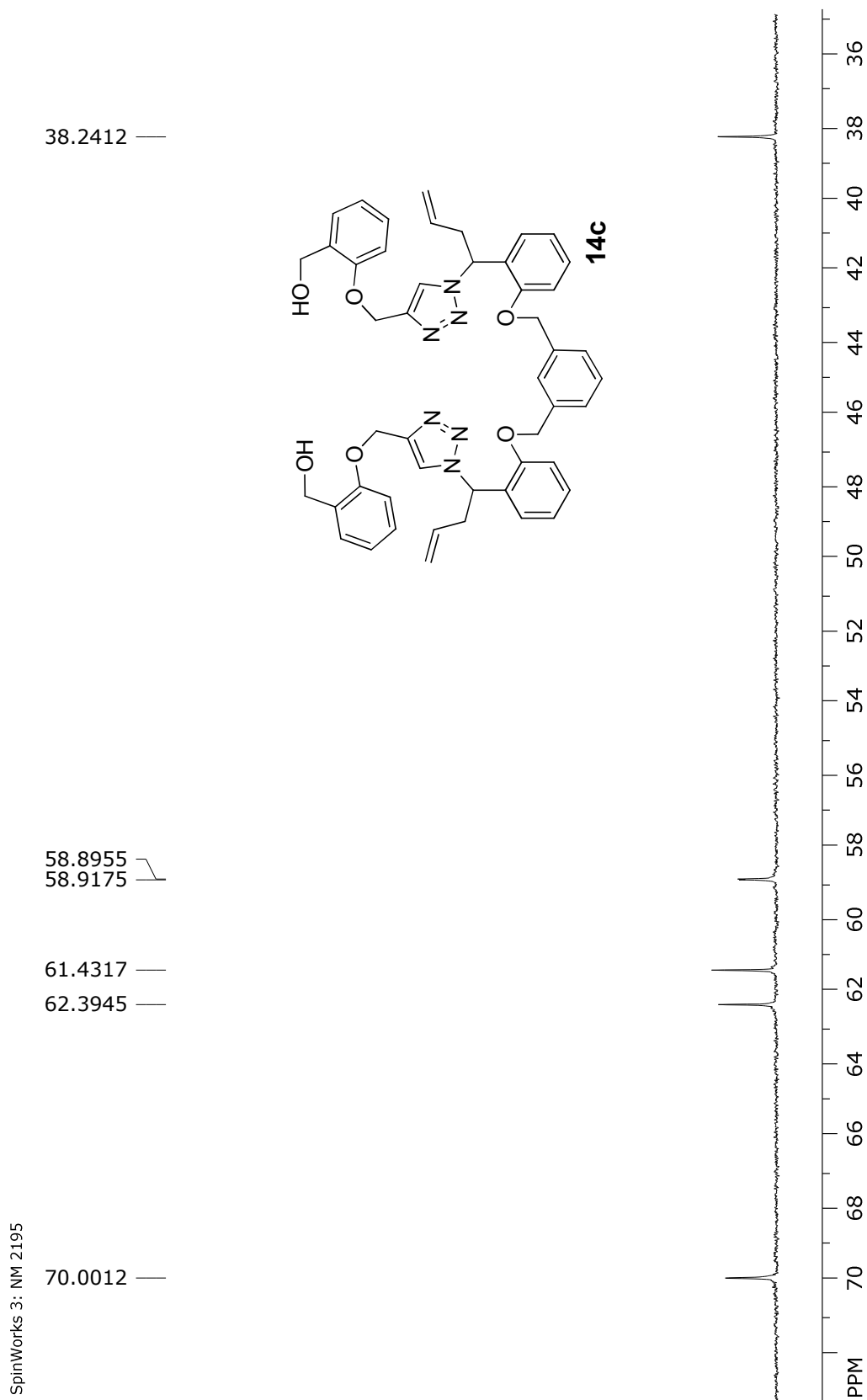


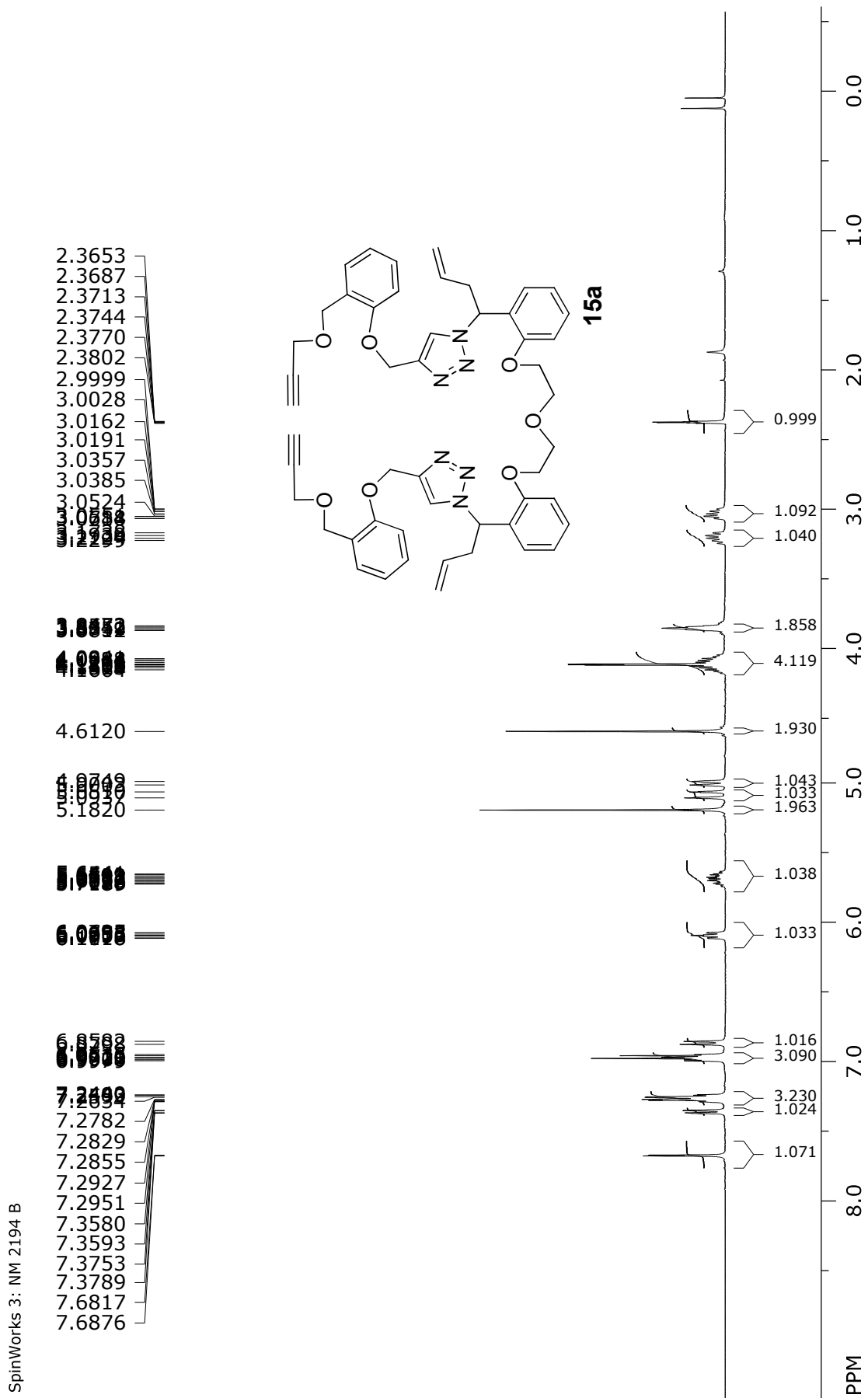
SpinWorks 3: NM Z195

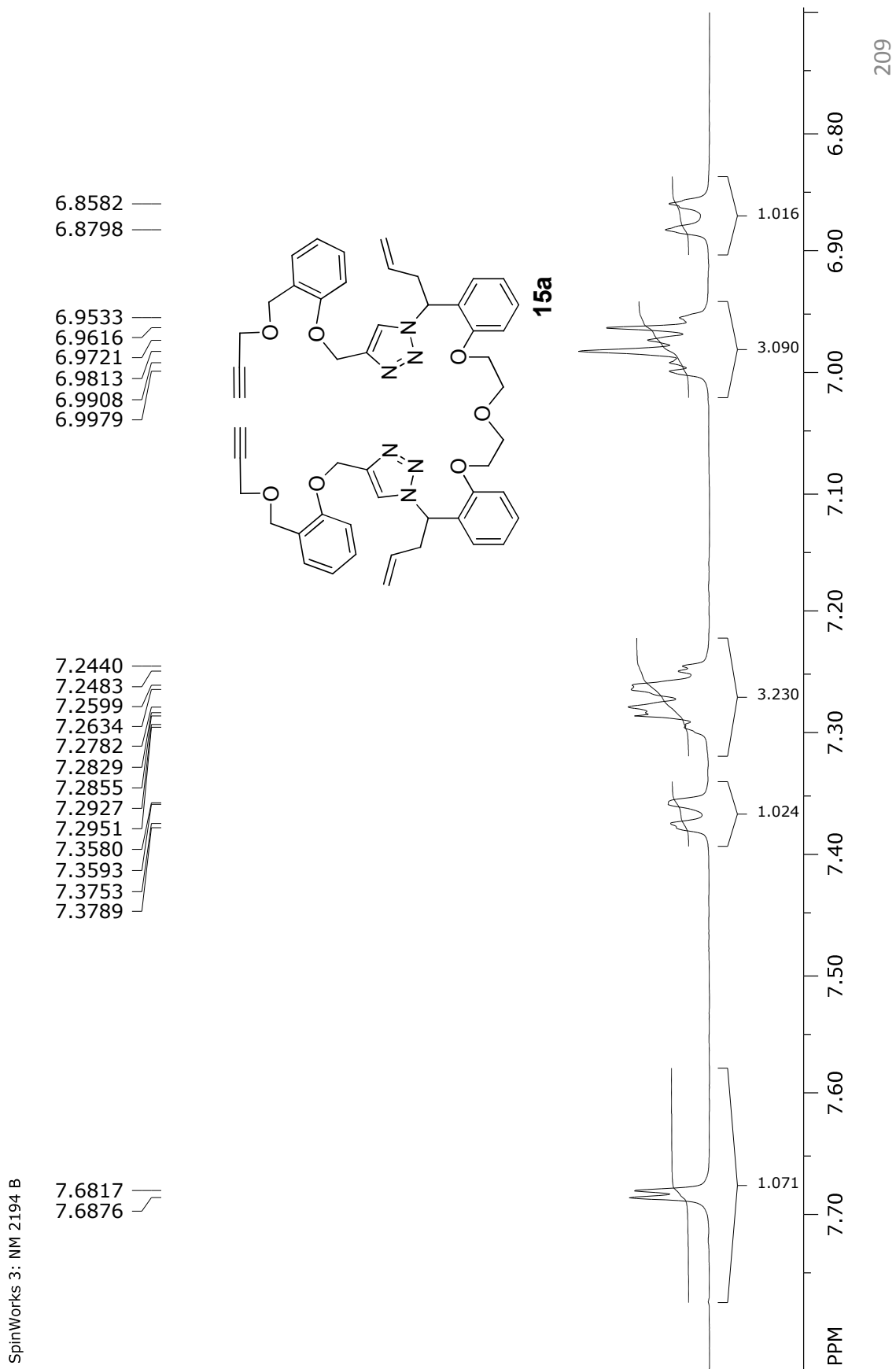












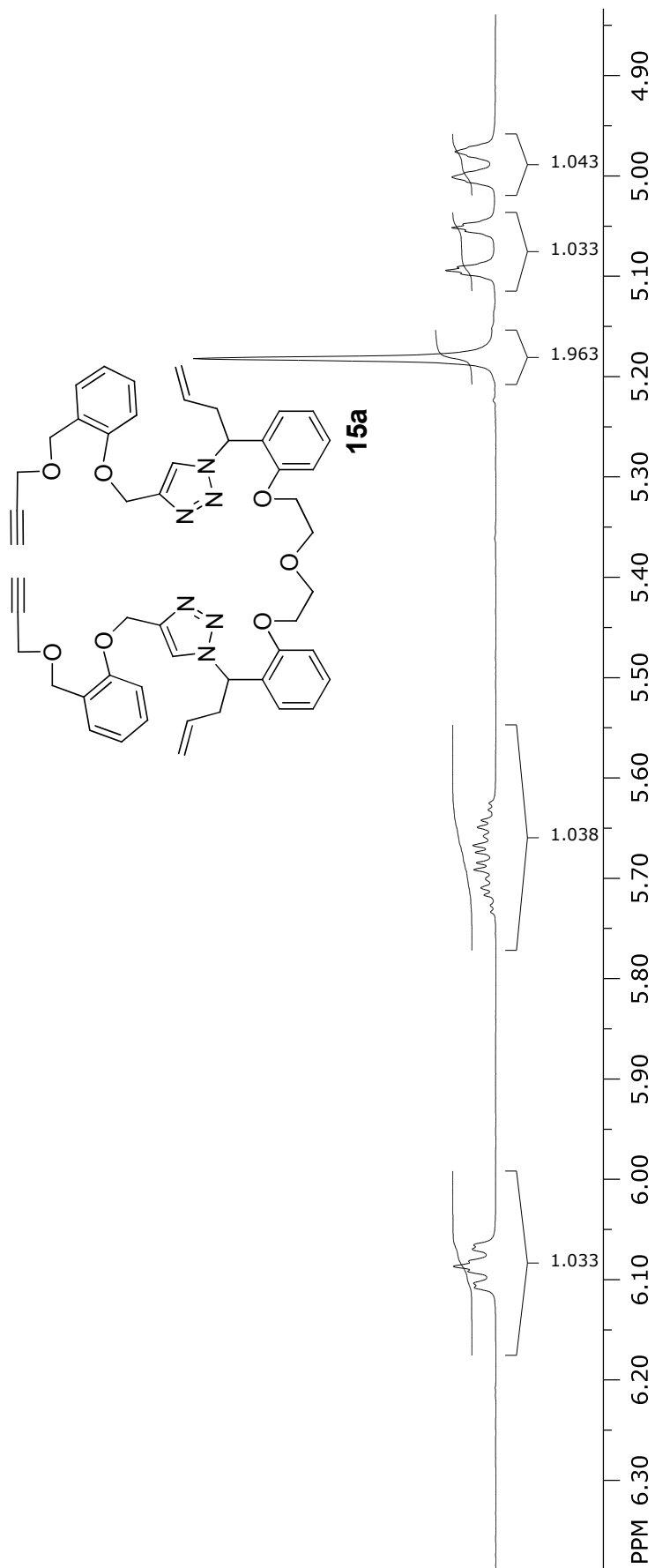







SpinWorks 3: NM 2194 B

6.1076  
6.1118

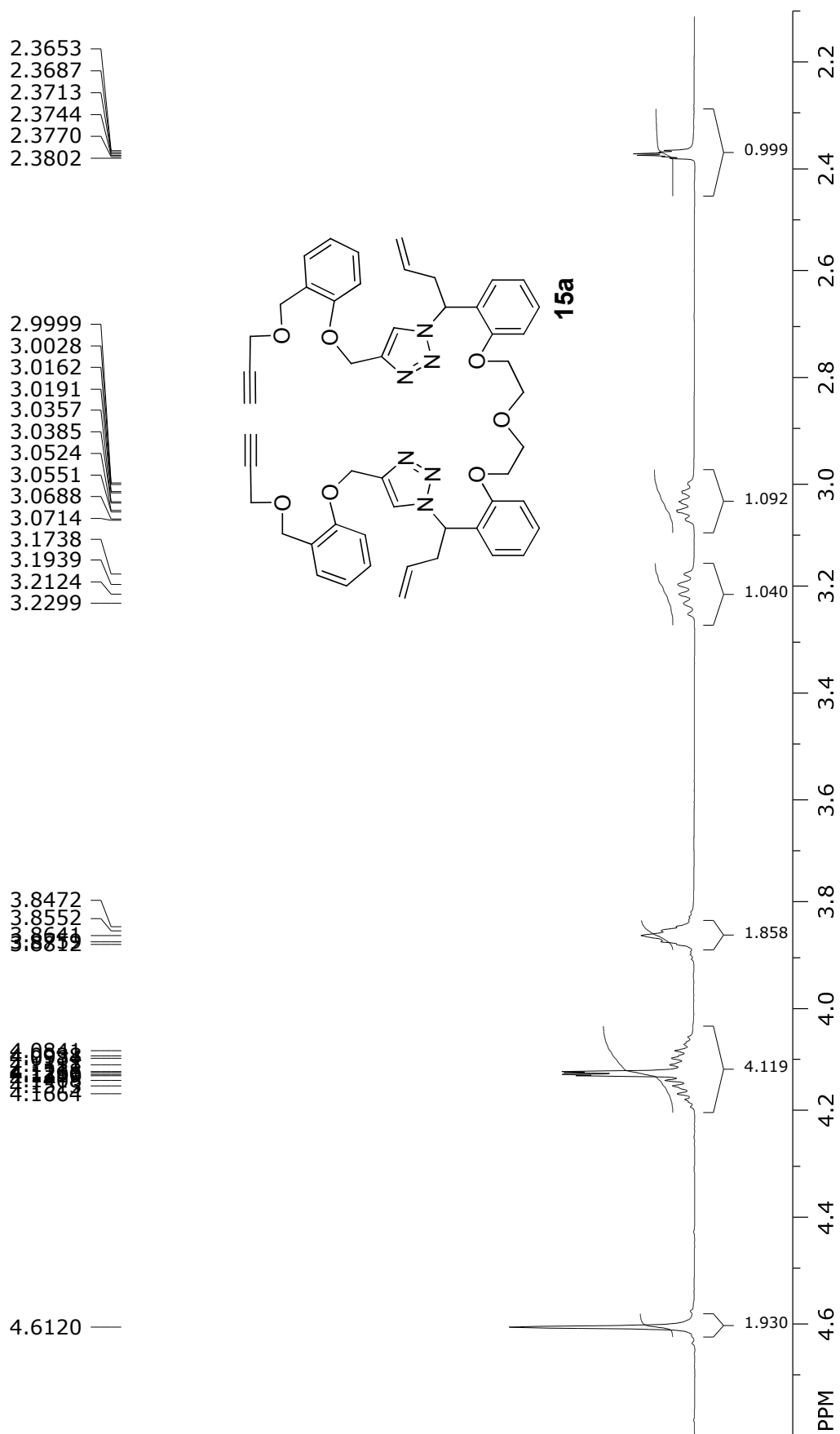


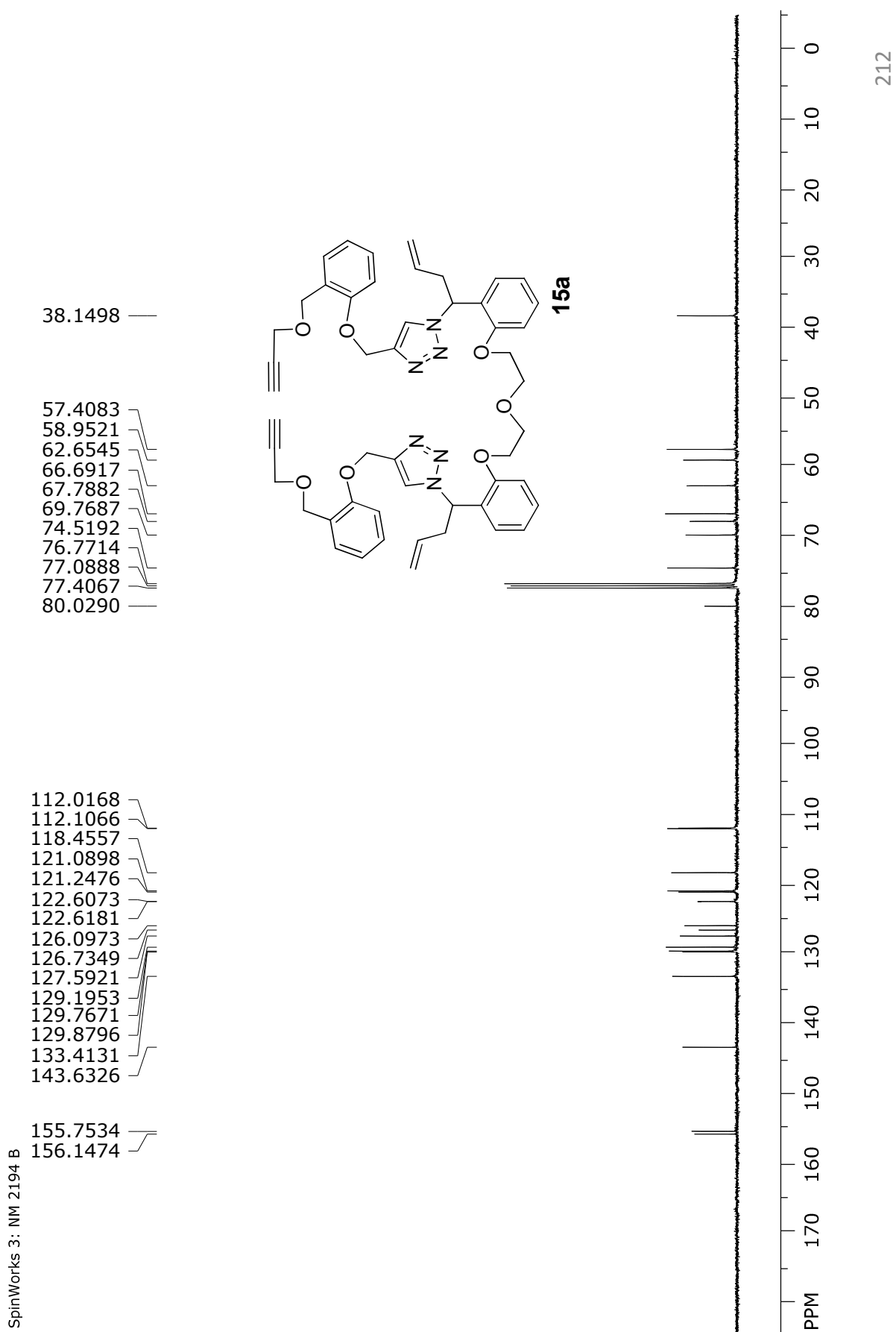
4.9749  
5.0003  
5.0510  
5.0937  
5.1820

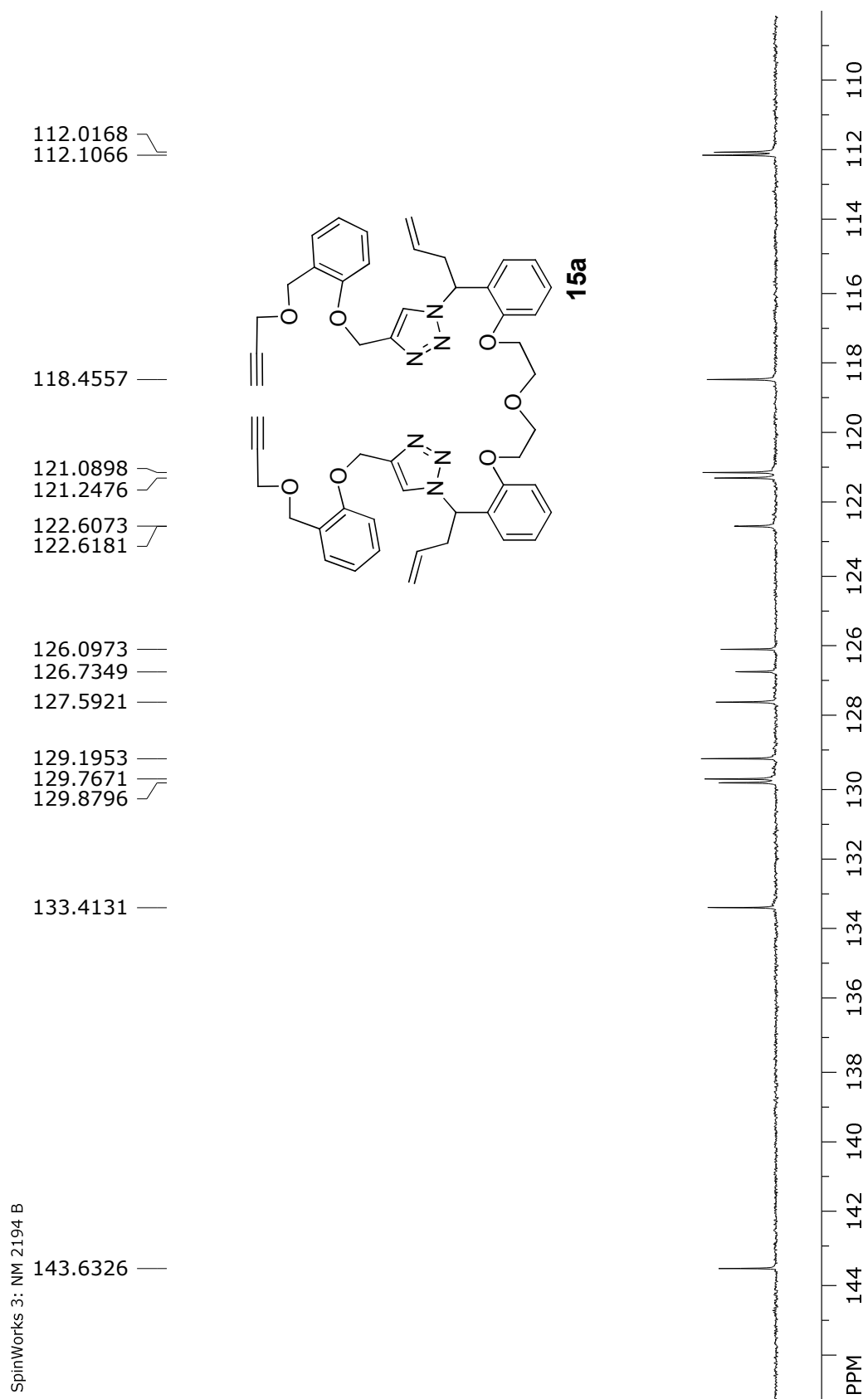




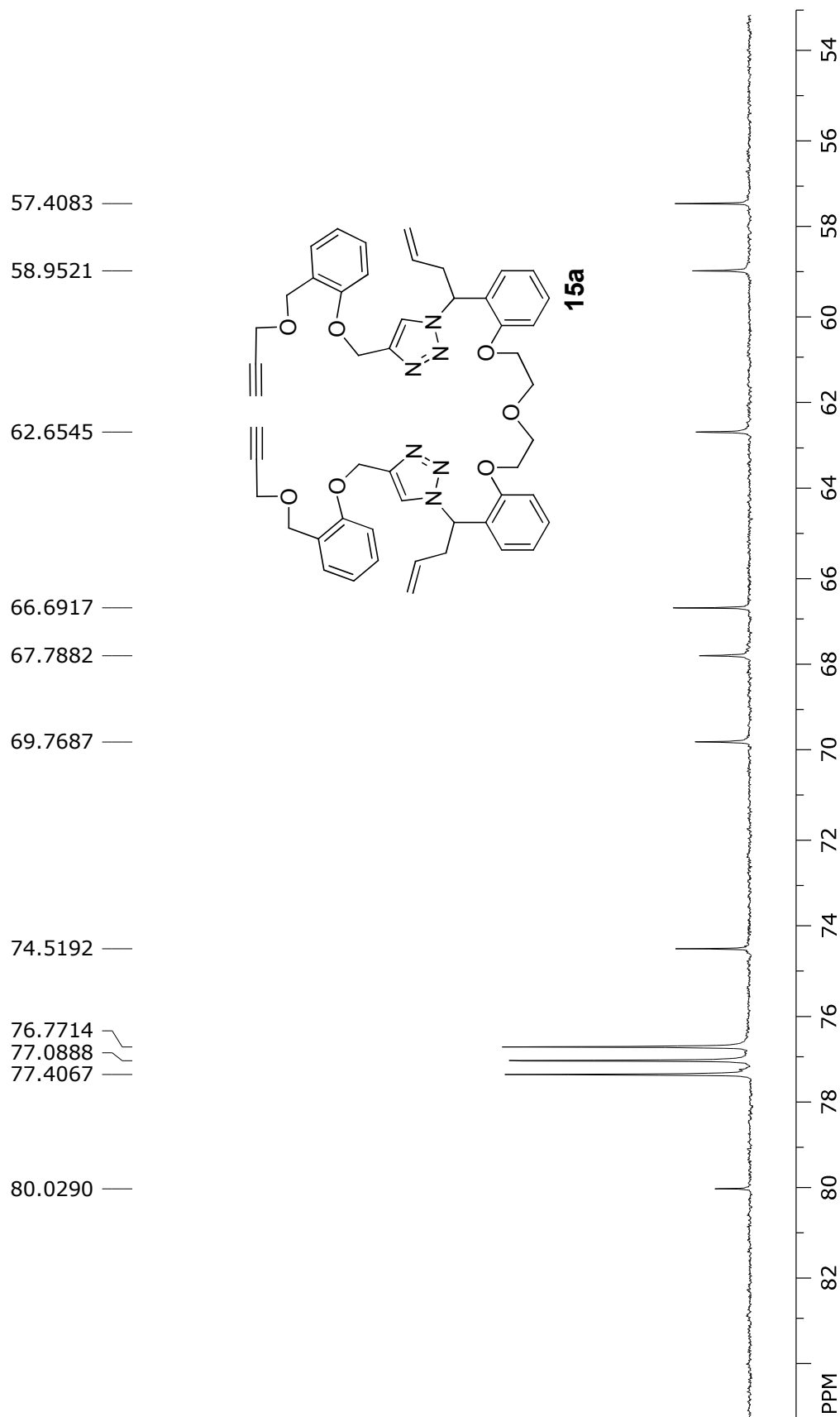
SpinWorks 3: NM 2194 B



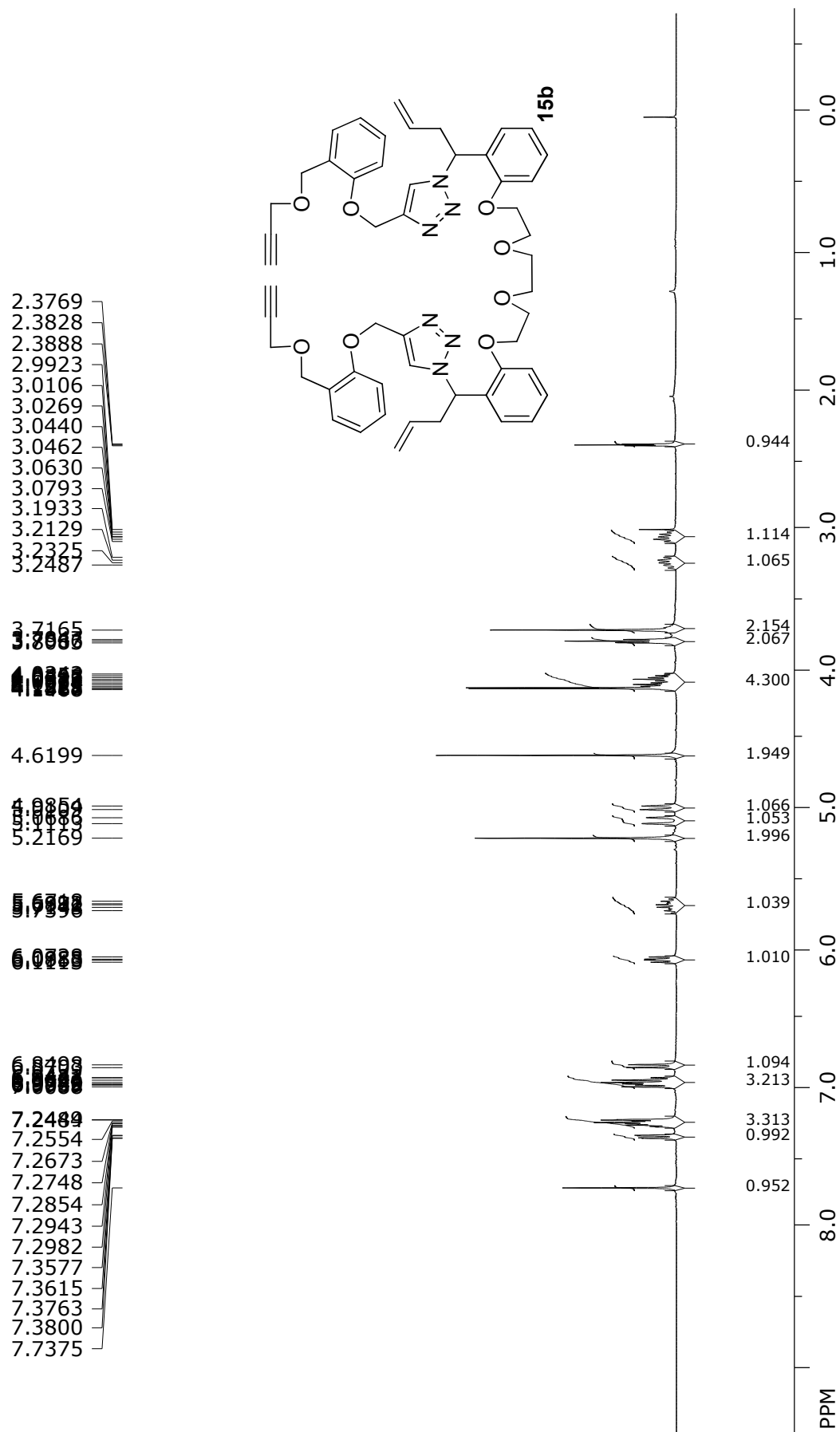




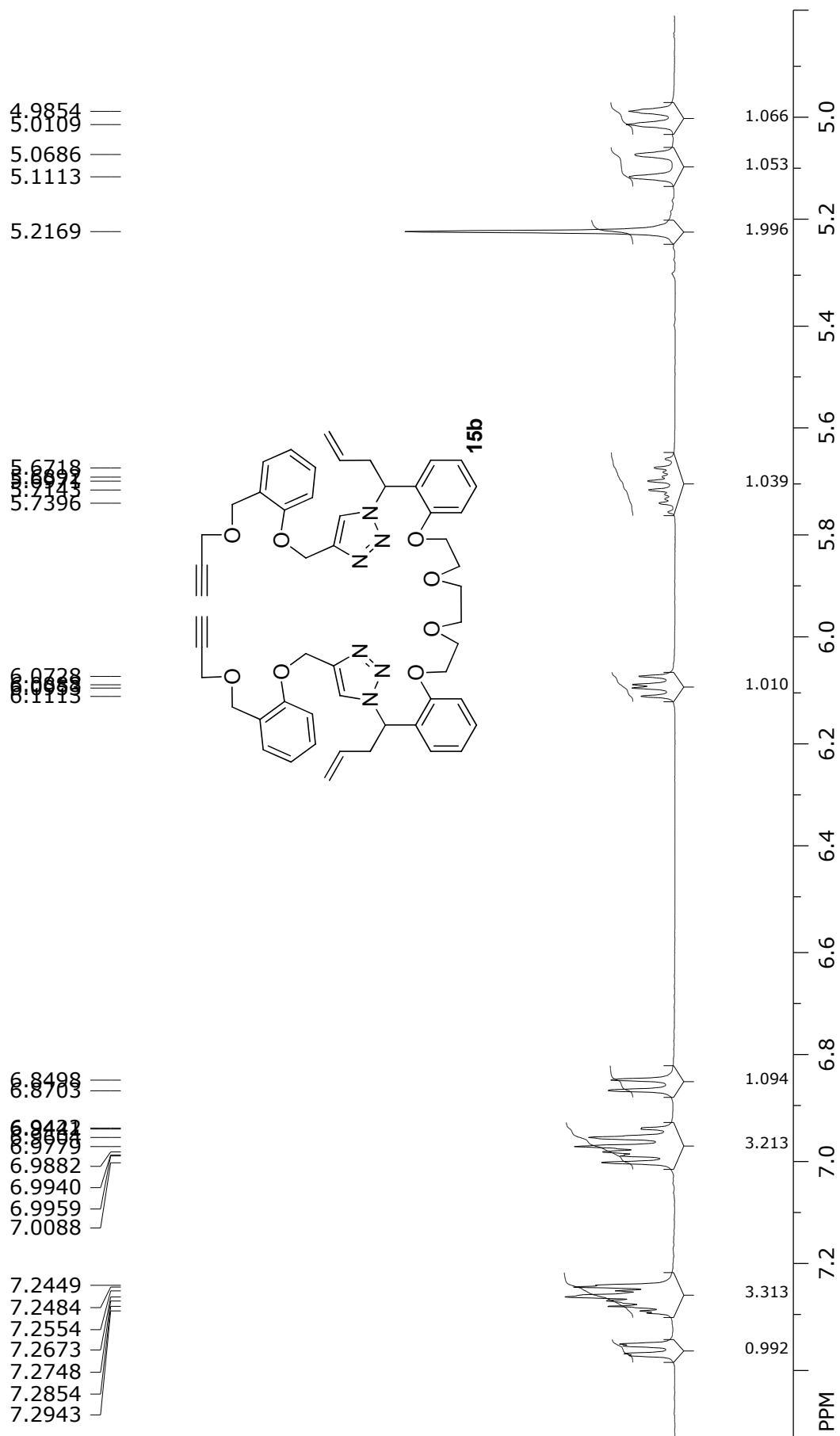
SpinWorks 3: NM 2194 B



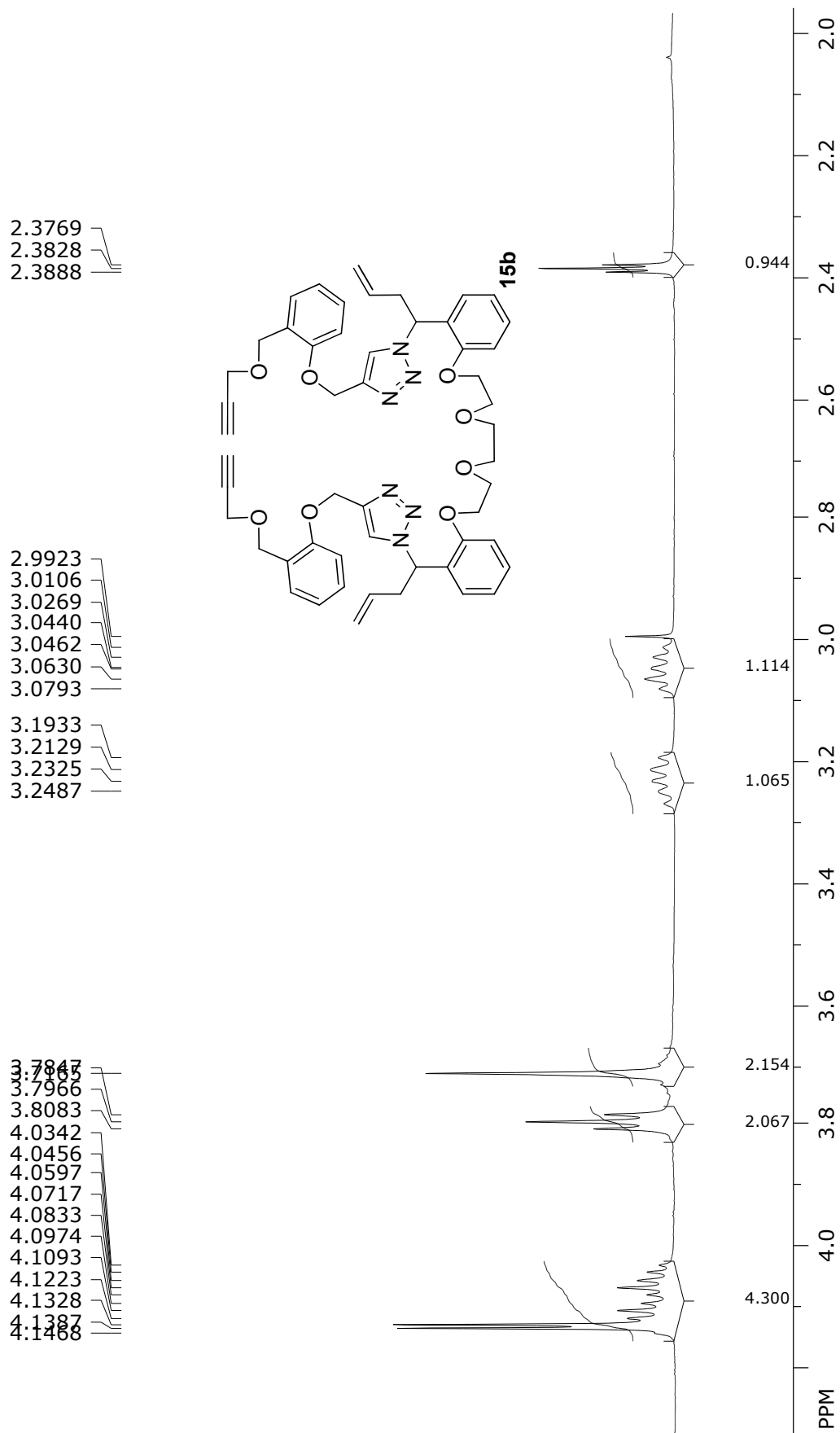
SpinWorks 3: AS 153 A1

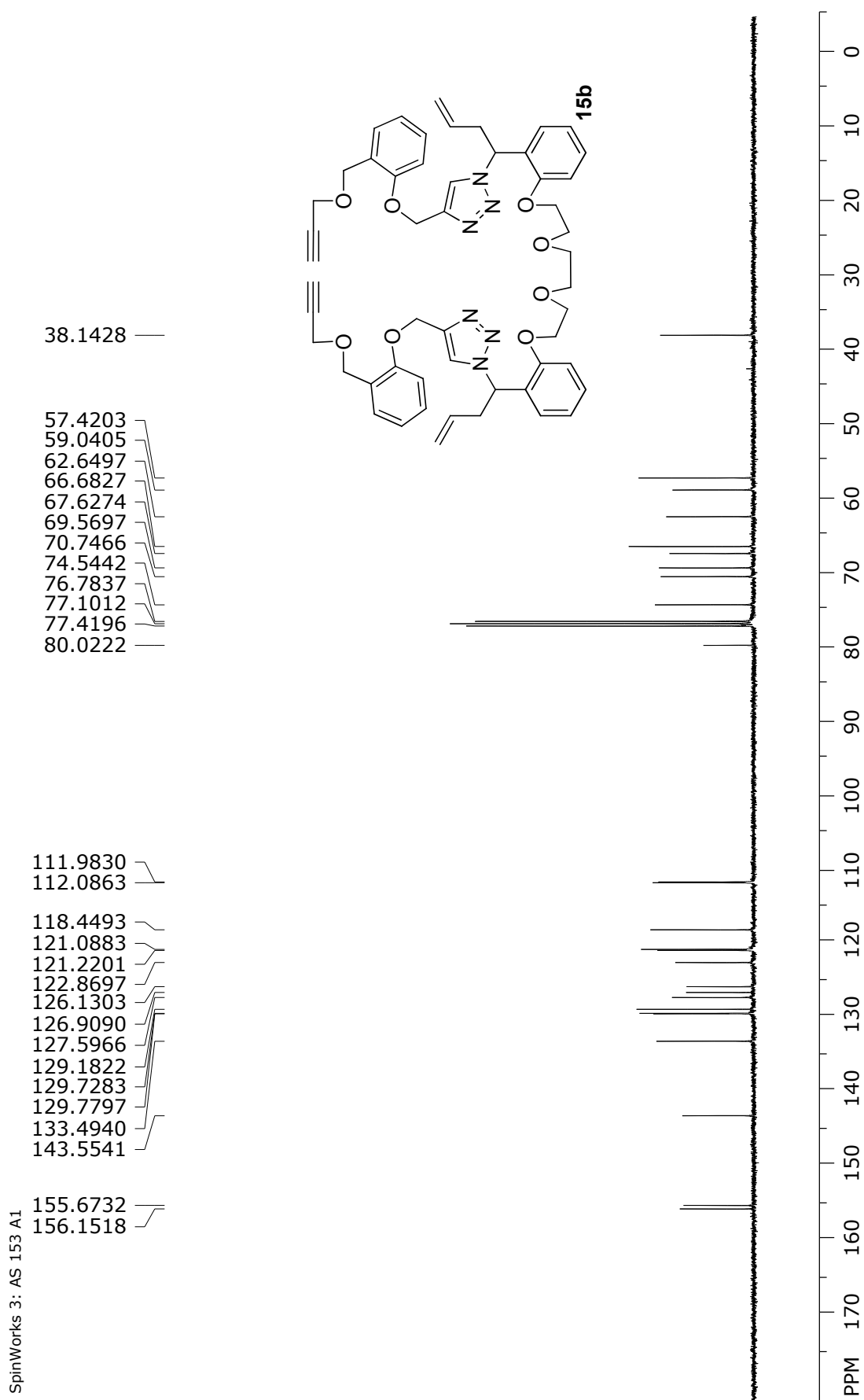


SpinWorks 3: AS 153 A1

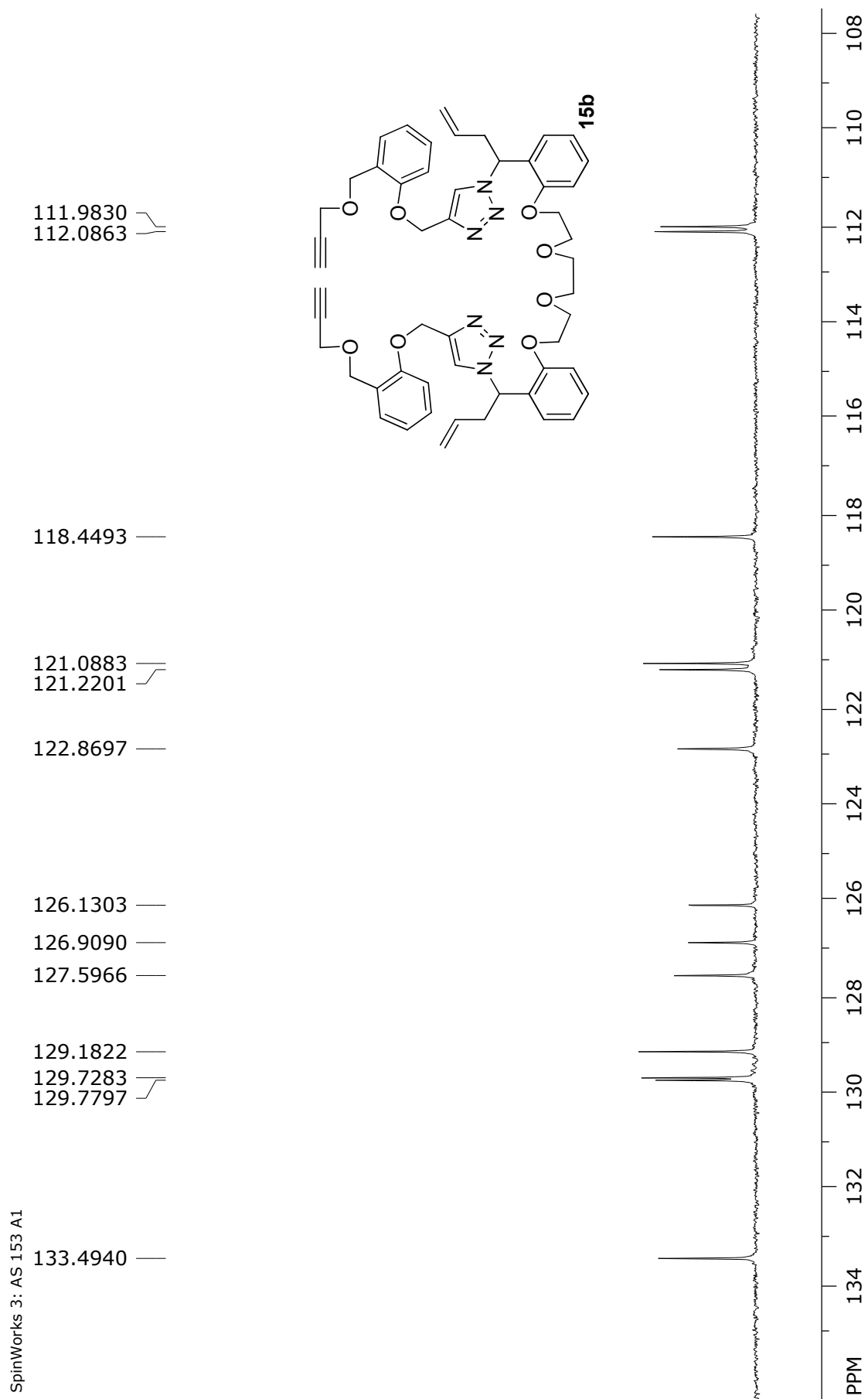


SpinWorks 3: AS\_153 A1

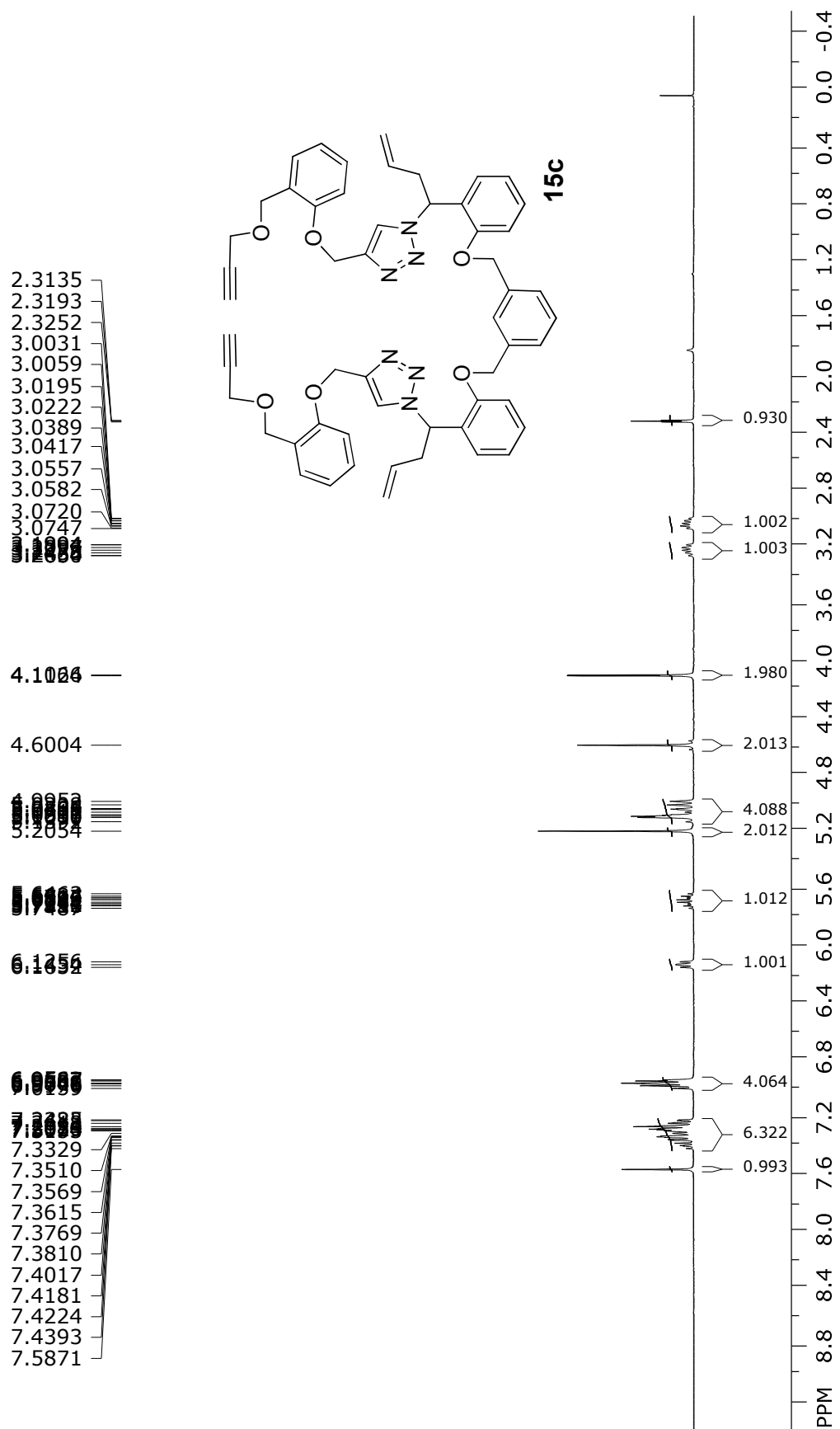








SpinWorks 3: NM 2182 B1

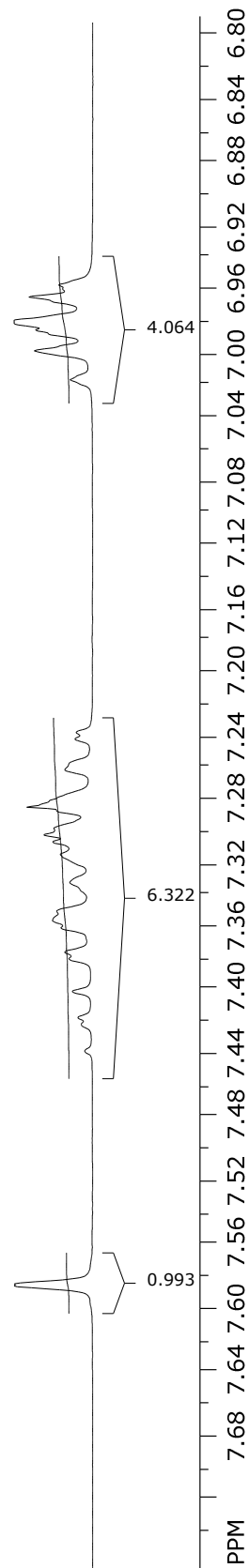
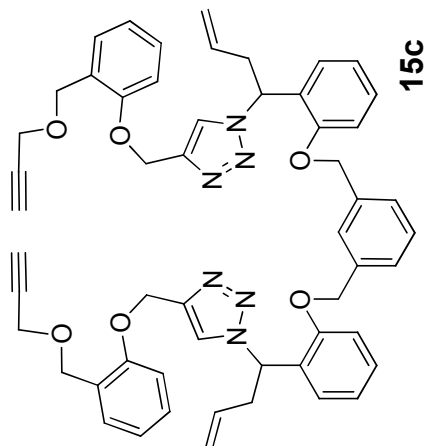


SpinWorks 3: NM 2182 B1

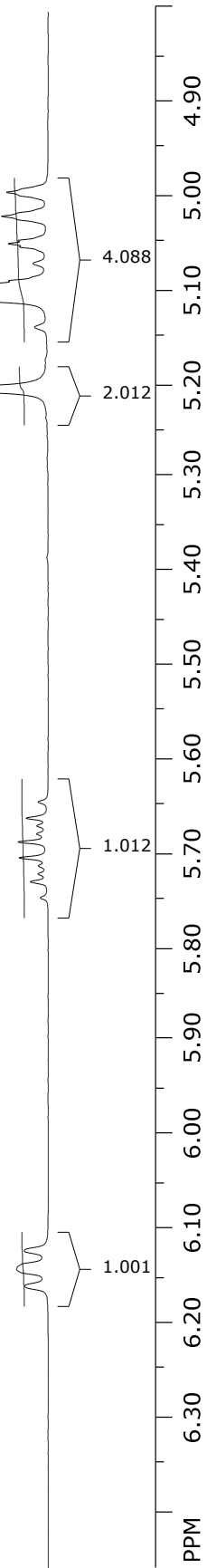
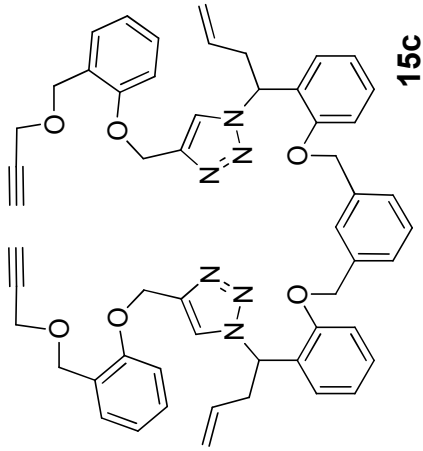
6.9562  
6.9587  
6.9637  
6.9789  
6.9801  
6.9846  
6.9976  
7.0159

7.2383  
7.2425  
7.2618  
7.2854  
7.2988  
7.3029  
7.3074  
7.3153  
7.3329  
7.3510  
7.3569  
7.3615  
7.3769  
7.3810  
7.4017  
7.4181  
7.4224  
7.4393

7.5871



SpinWorks 3: NM 2182 B1

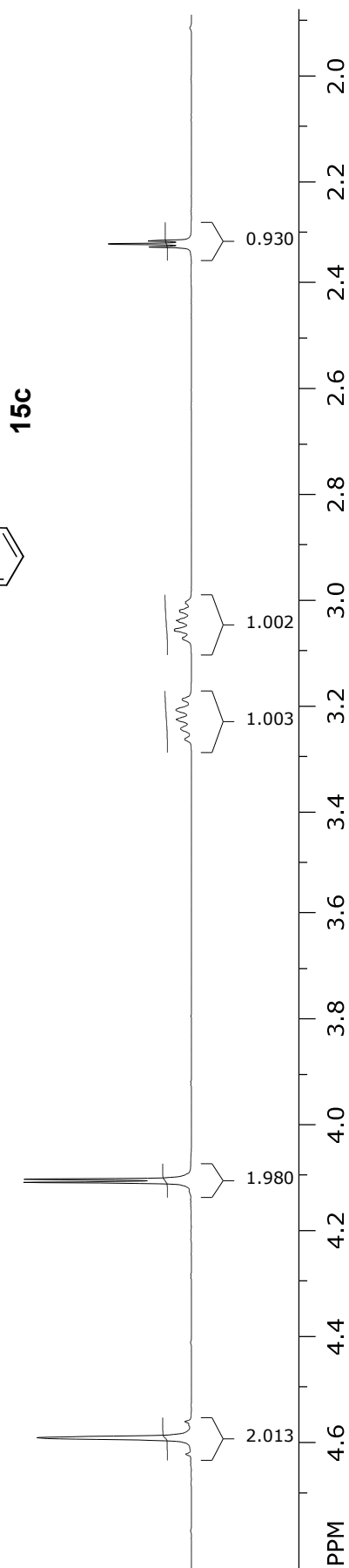
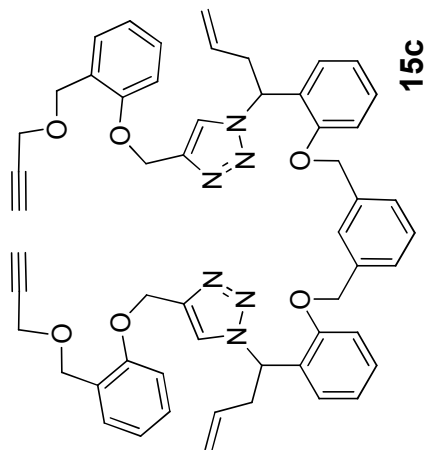
6.1256  
6.1456  
6.16325.7007  
5.7007  
5.7007  
5.7007  
5.7007  
5.7007  
5.7007  
5.7007  
5.7007  
5.7007  
5.70075.2054  
5.1392  
5.0897  
5.0712  
5.0535  
5.0501  
5.0468  
5.0208  
4.9952

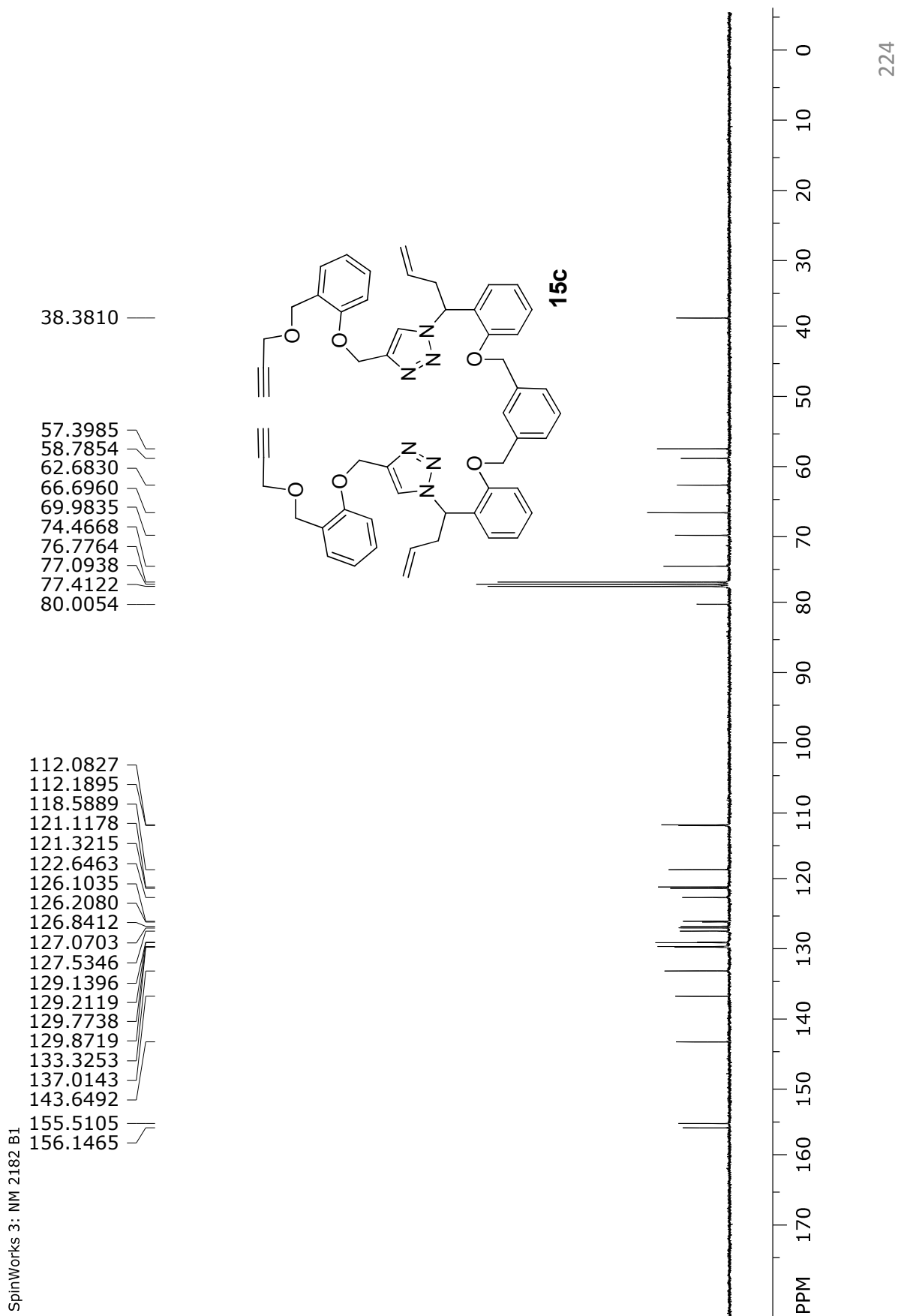
SpinWorks 3: NM 2182 B1

2.3135  
2.3193  
2.32523.0031  
3.0059  
3.0195  
3.0222  
3.0389  
3.0417  
3.0557  
3.0582  
3.0720  
3.0747  
3.1894  
3.1904  
3.2097  
3.2279  
3.2458  
3.2660

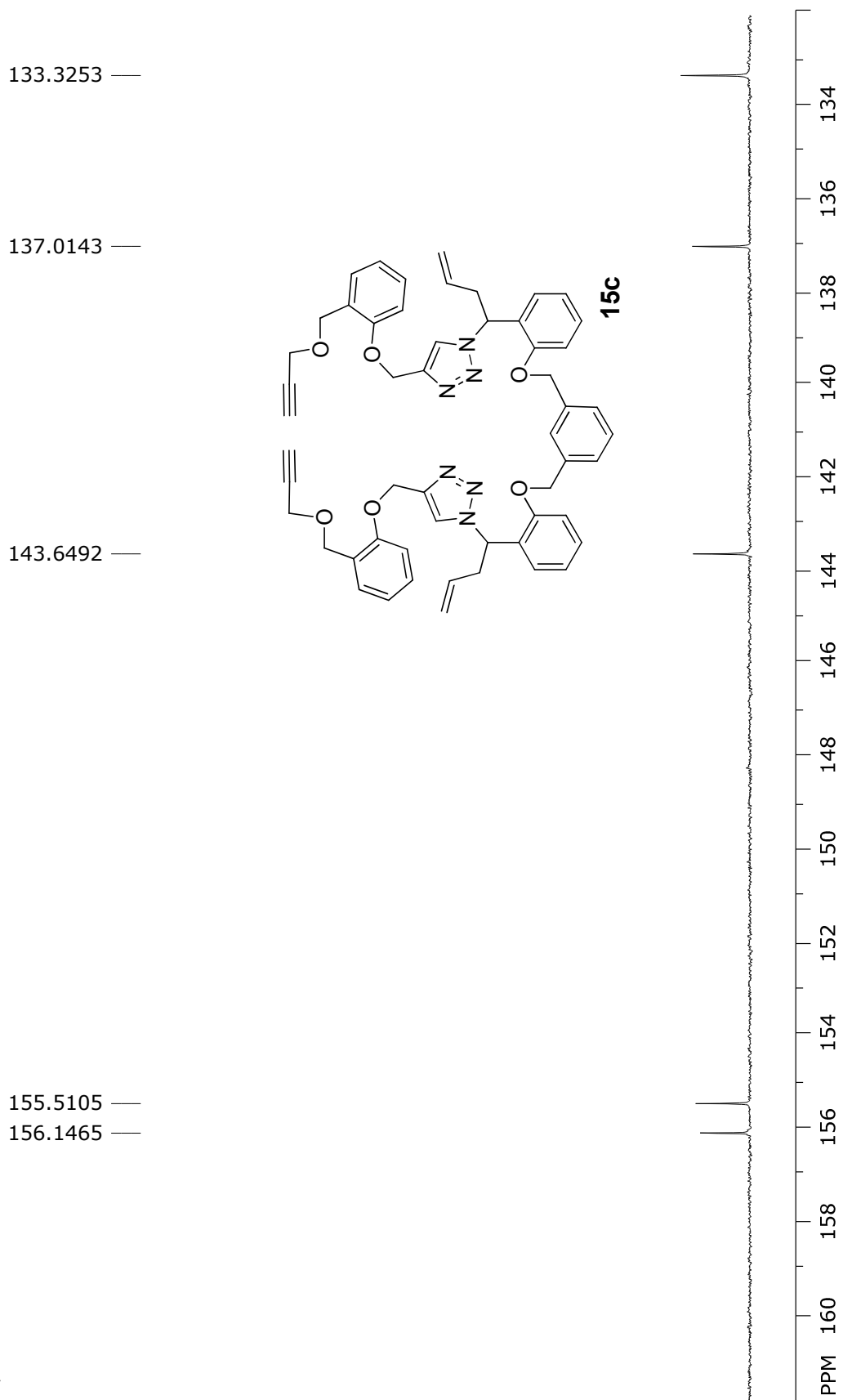
4.1064

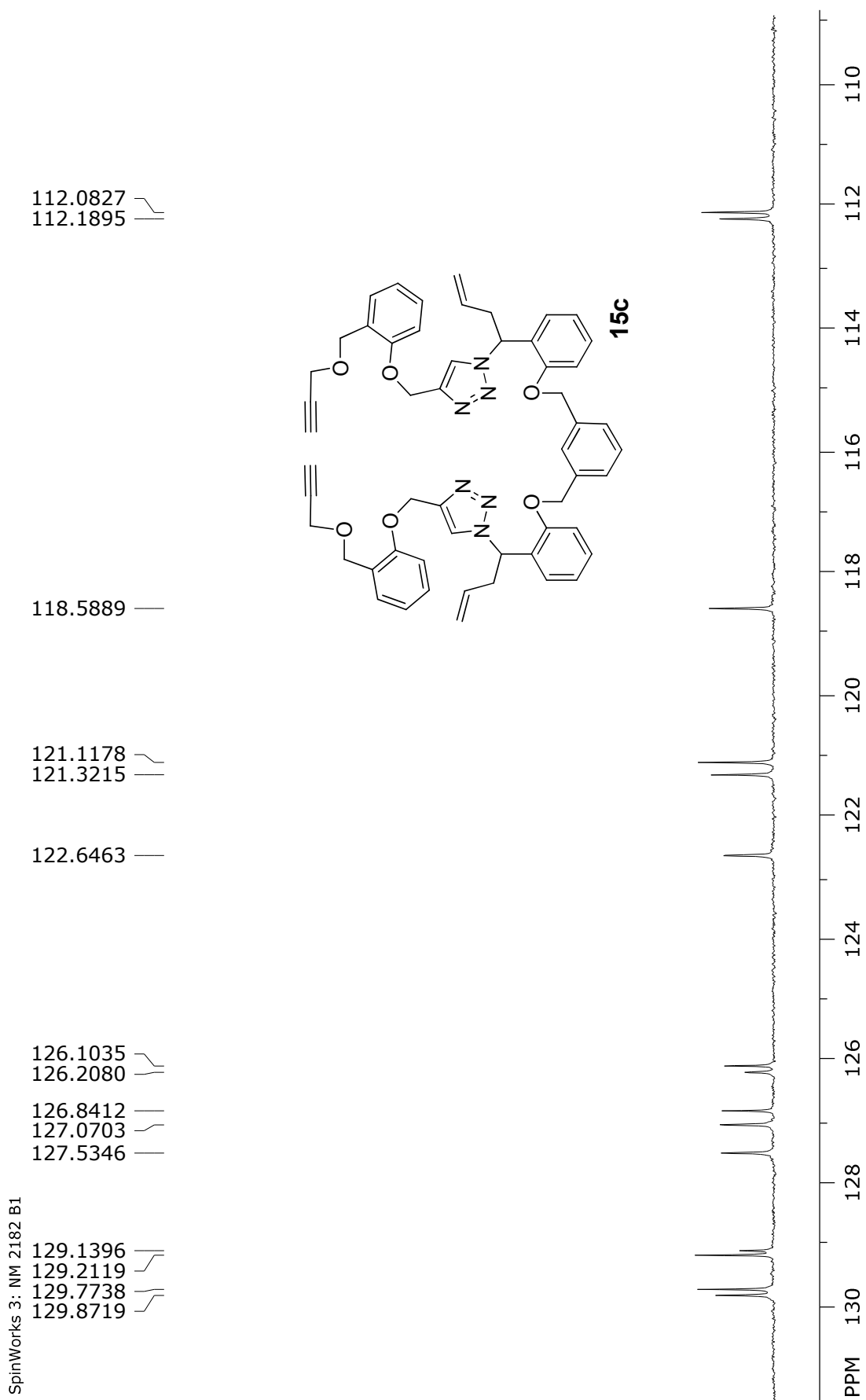
4.6004



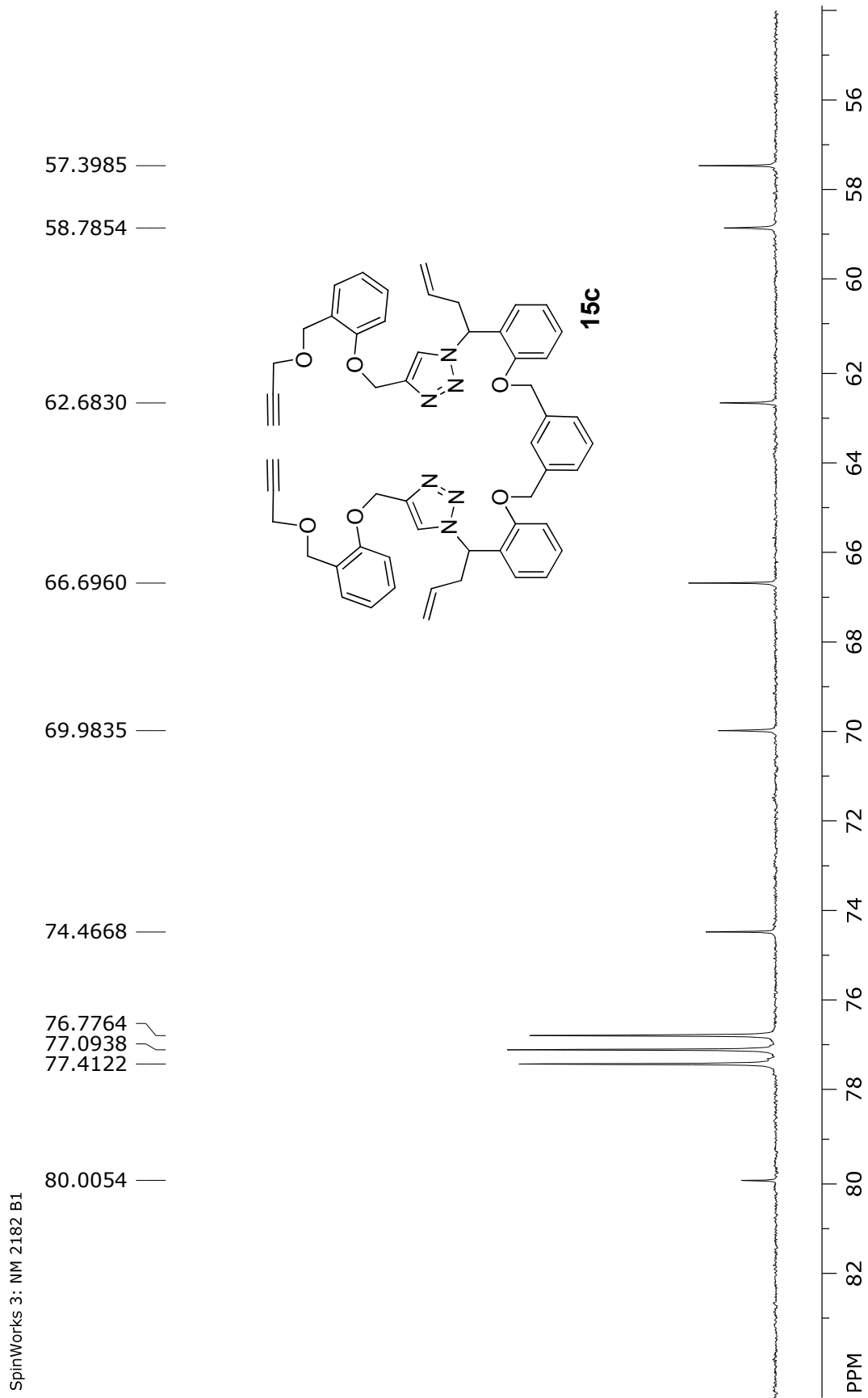


SpinWorks 3: NM 2182 B1

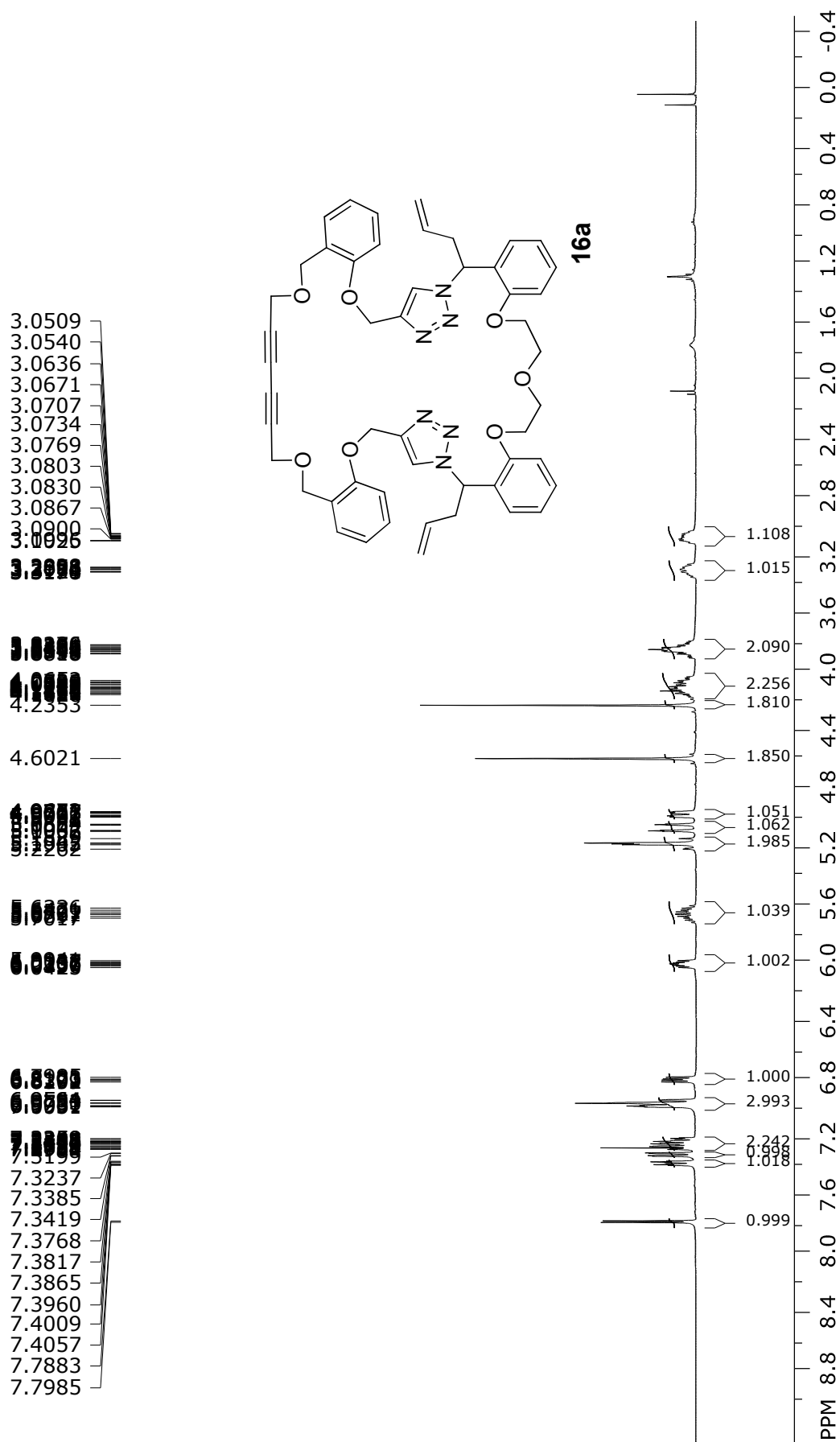








SpinWorks 3: NM 2196 A



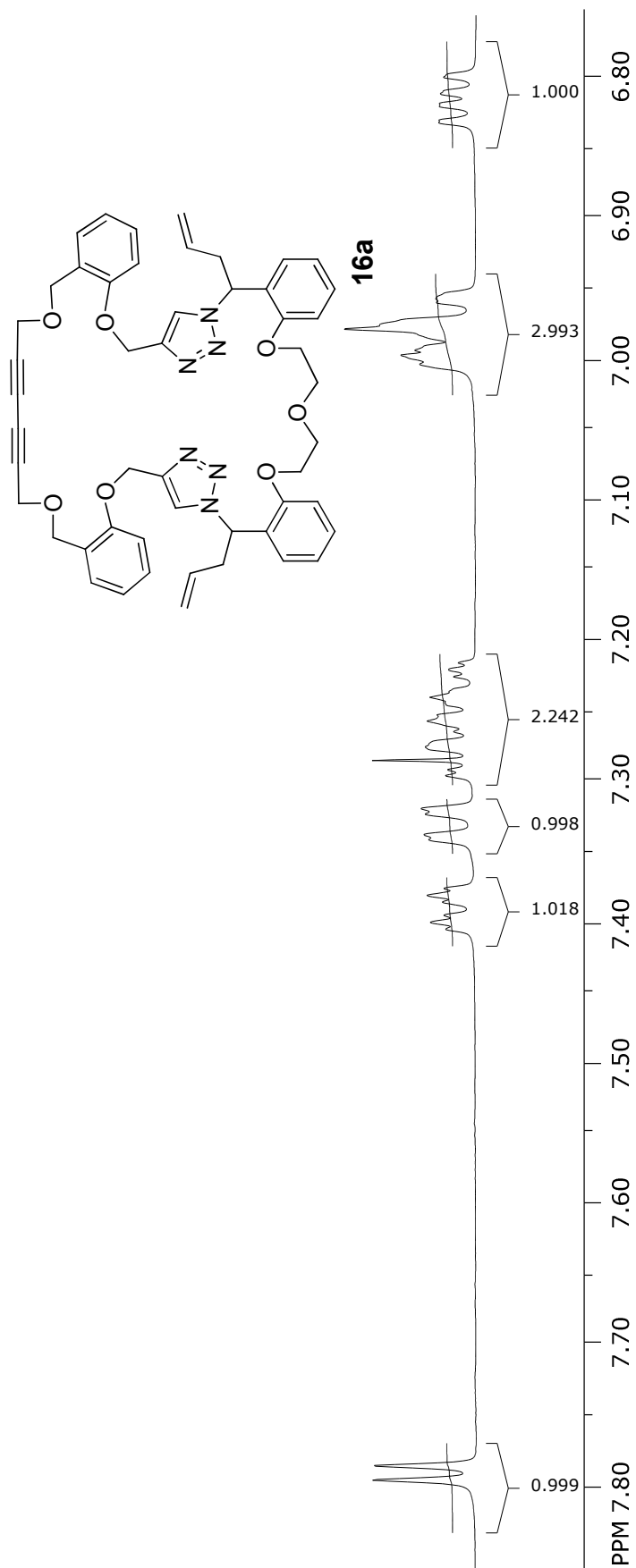
SpinWorks 3: NM 2196 A

6.7985  
6.8103  
6.8193  
6.8209

6.9564  
6.9750  
6.9867

7.2200  
7.2298  
7.2366  
7.2456  
7.2574  
7.2650  
7.2739  
7.2759  
7.2855  
7.2921  
7.2964  
7.3199  
7.3237  
7.3385  
7.3419  
7.3768  
7.3817  
7.3865  
7.3960  
7.4009  
7.4057

7.7883  
7.7985



SpinWorks 3: NM 2196 A

5.1539  
5.1843  
5.2262

5.0539

5.1062

5.1539

5.1843

5.2262

5.6336

5.6647

5.6954

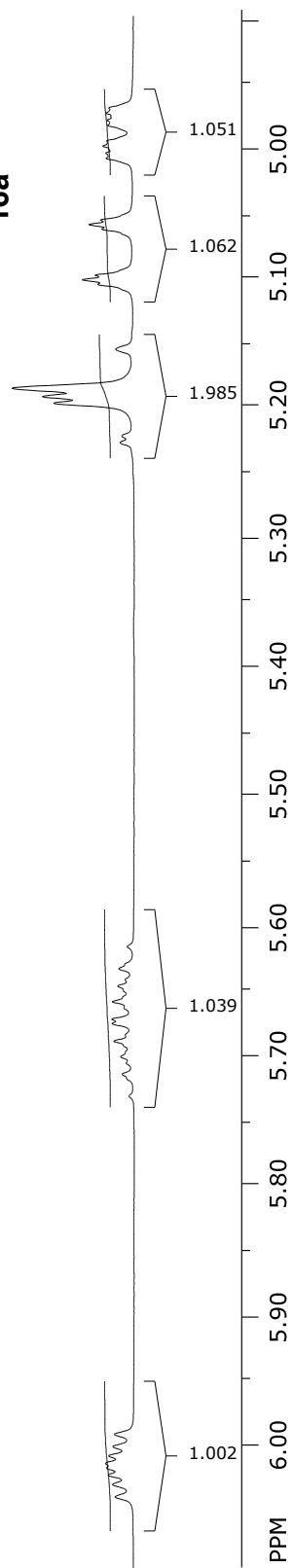
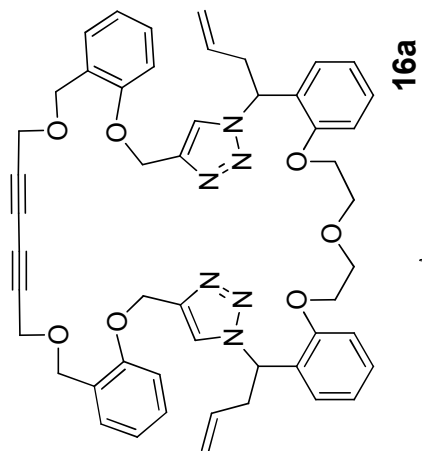
5.7017

5.6336

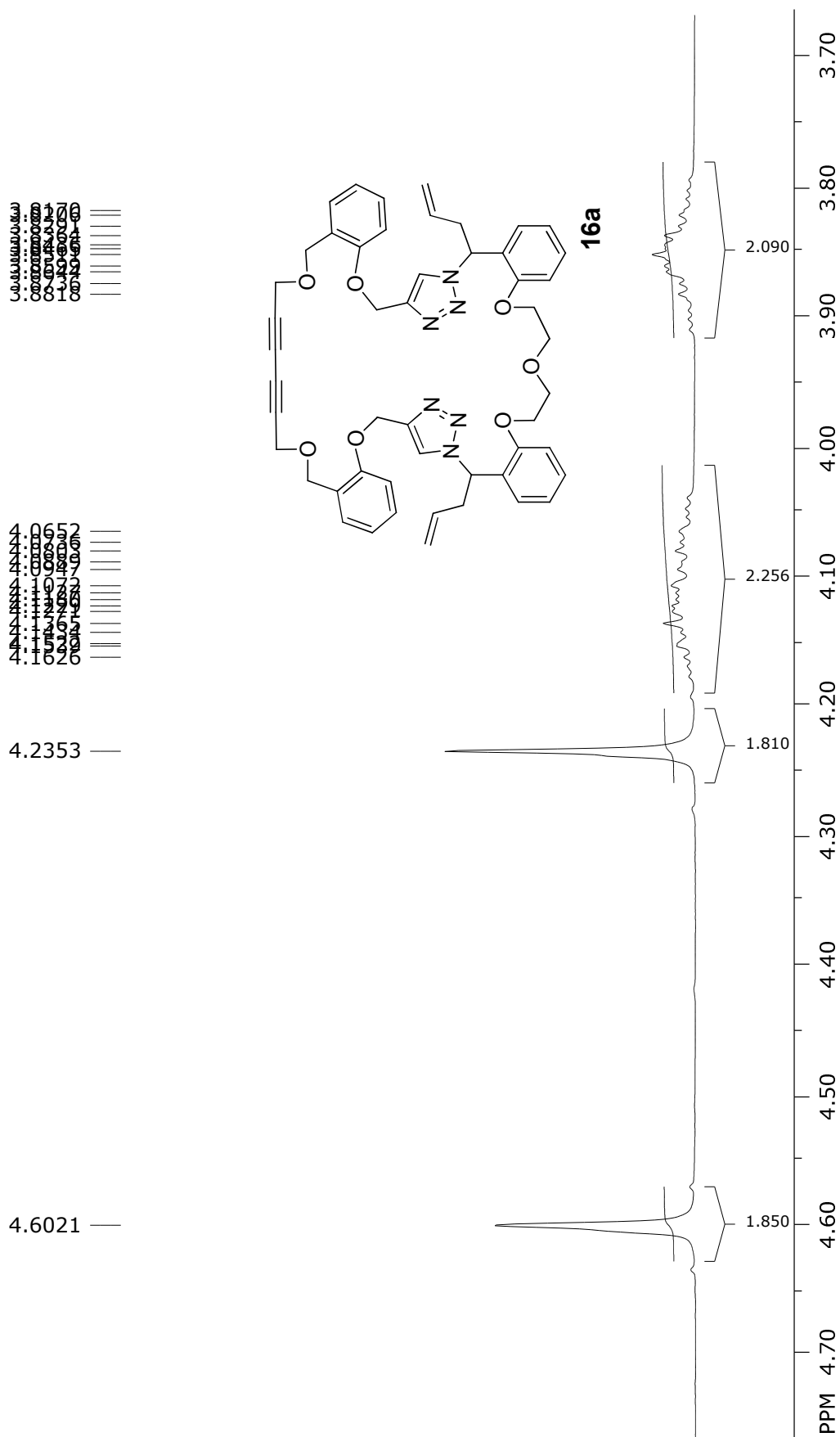
5.6647

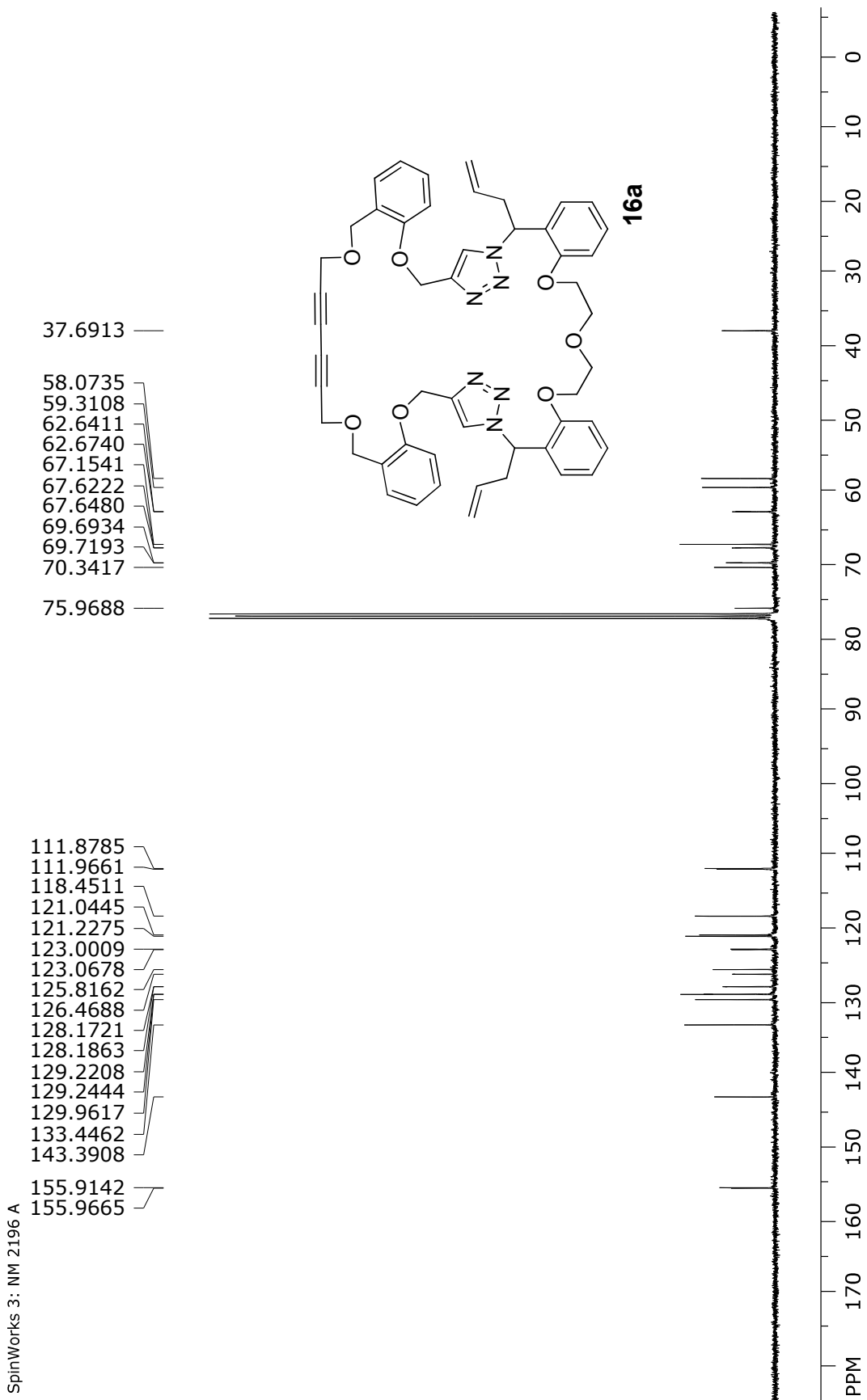
5.6954

5.7017

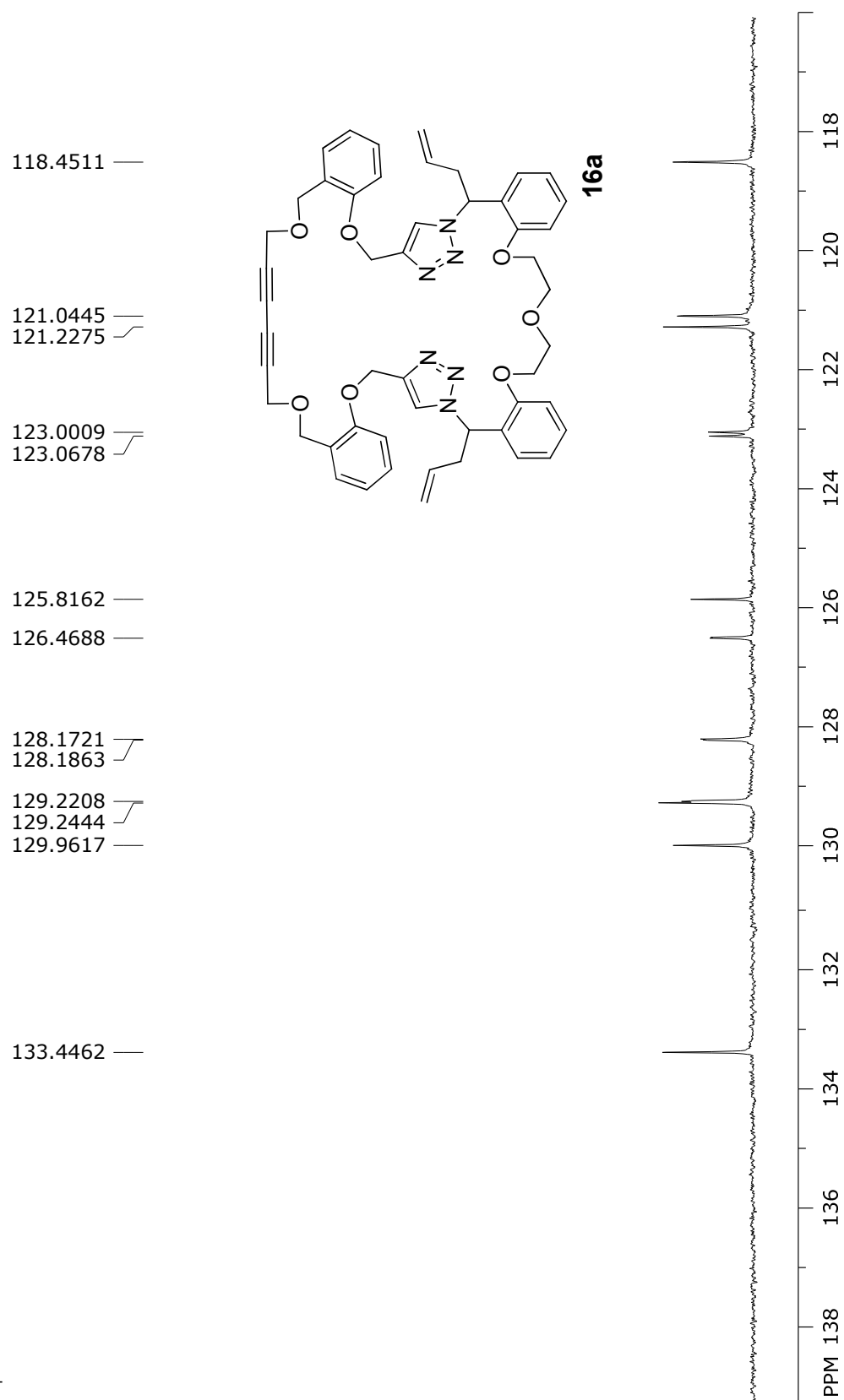


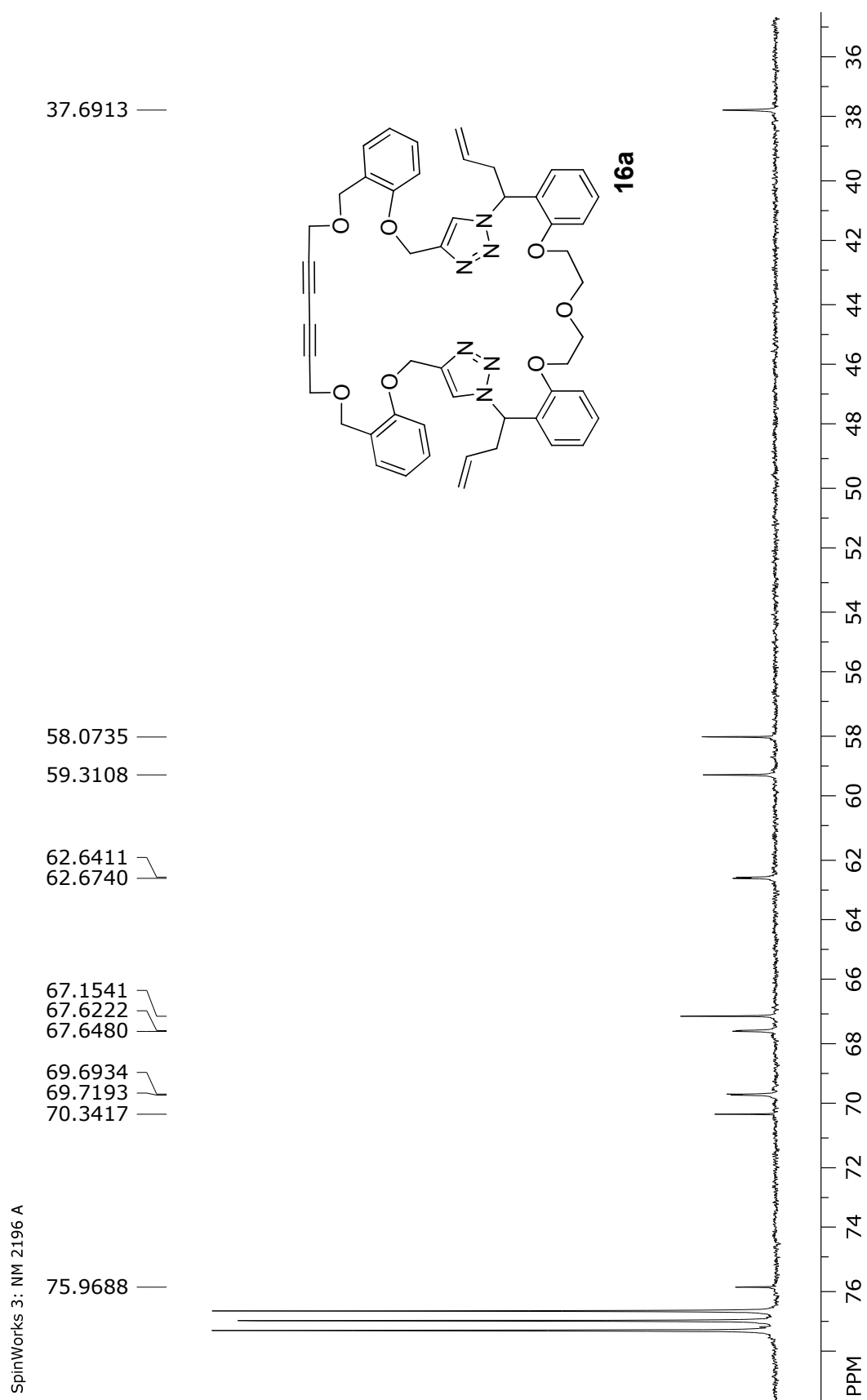
SpinWorks 3: NM 2196 A





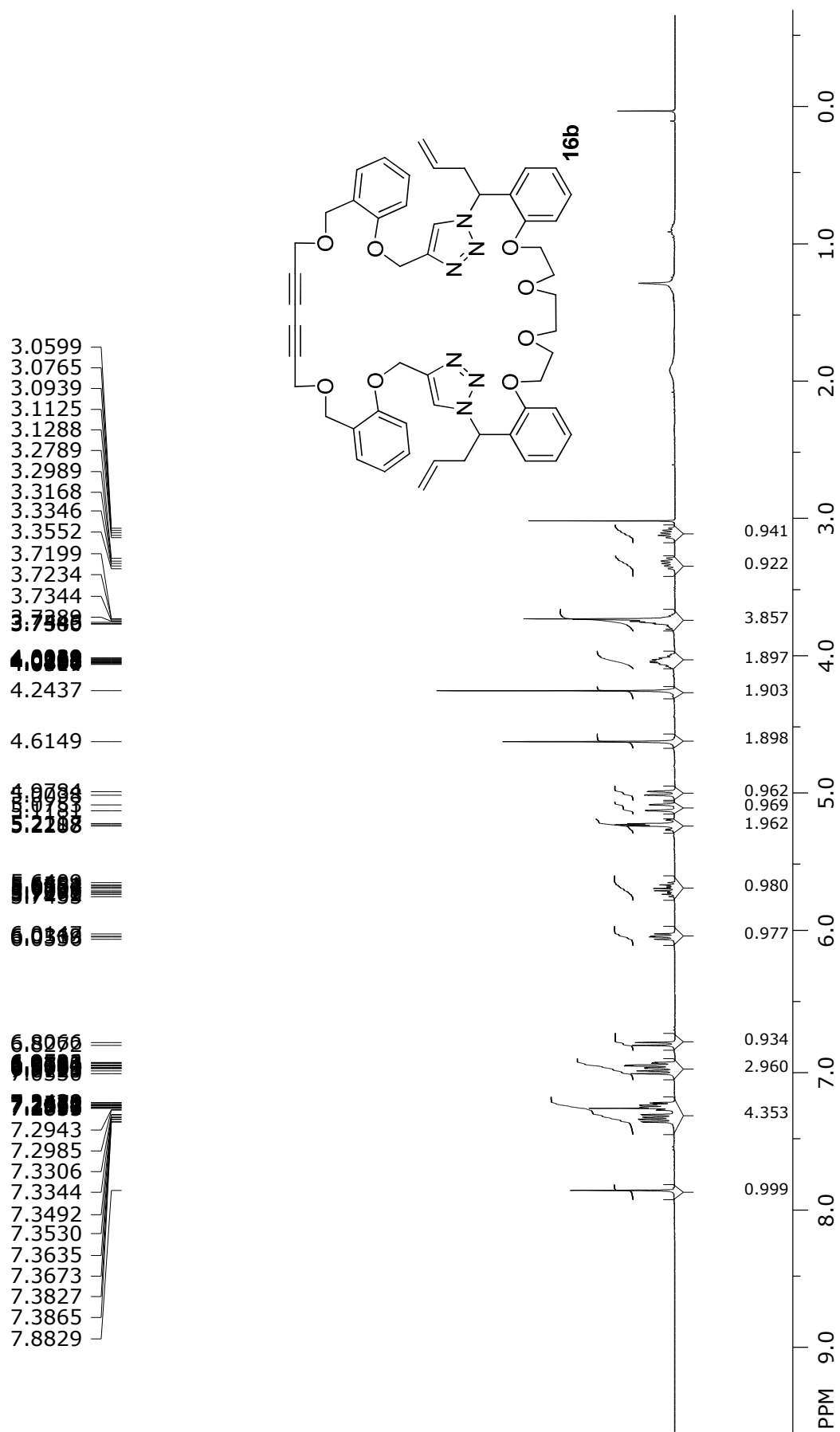
SpinWorks 3: NM 2196 A







SpinWorks 3: AS 156 A1



SpinWorks 3: AS 156 A1

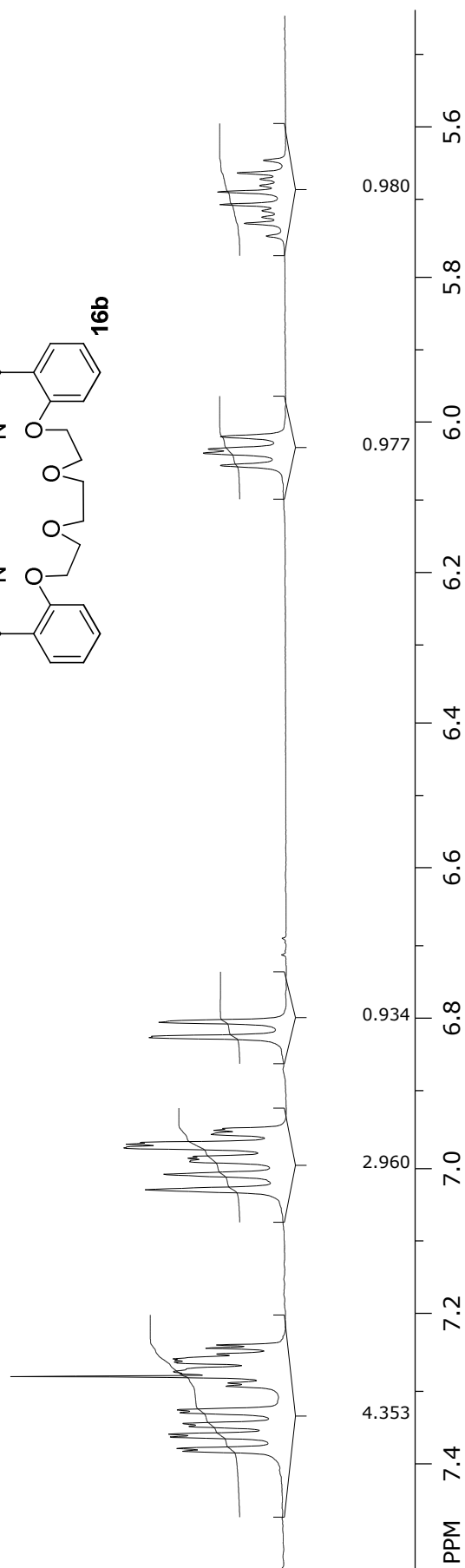
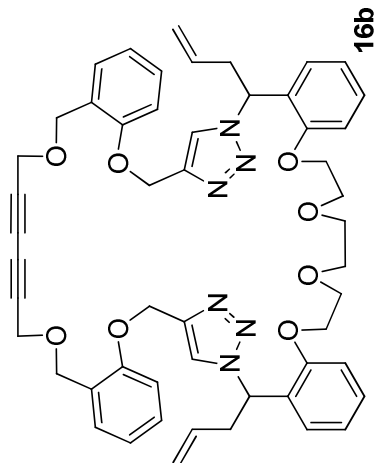
7.2817  
7.2855  
7.2943  
7.2985  
7.3306  
7.3344  
7.3492

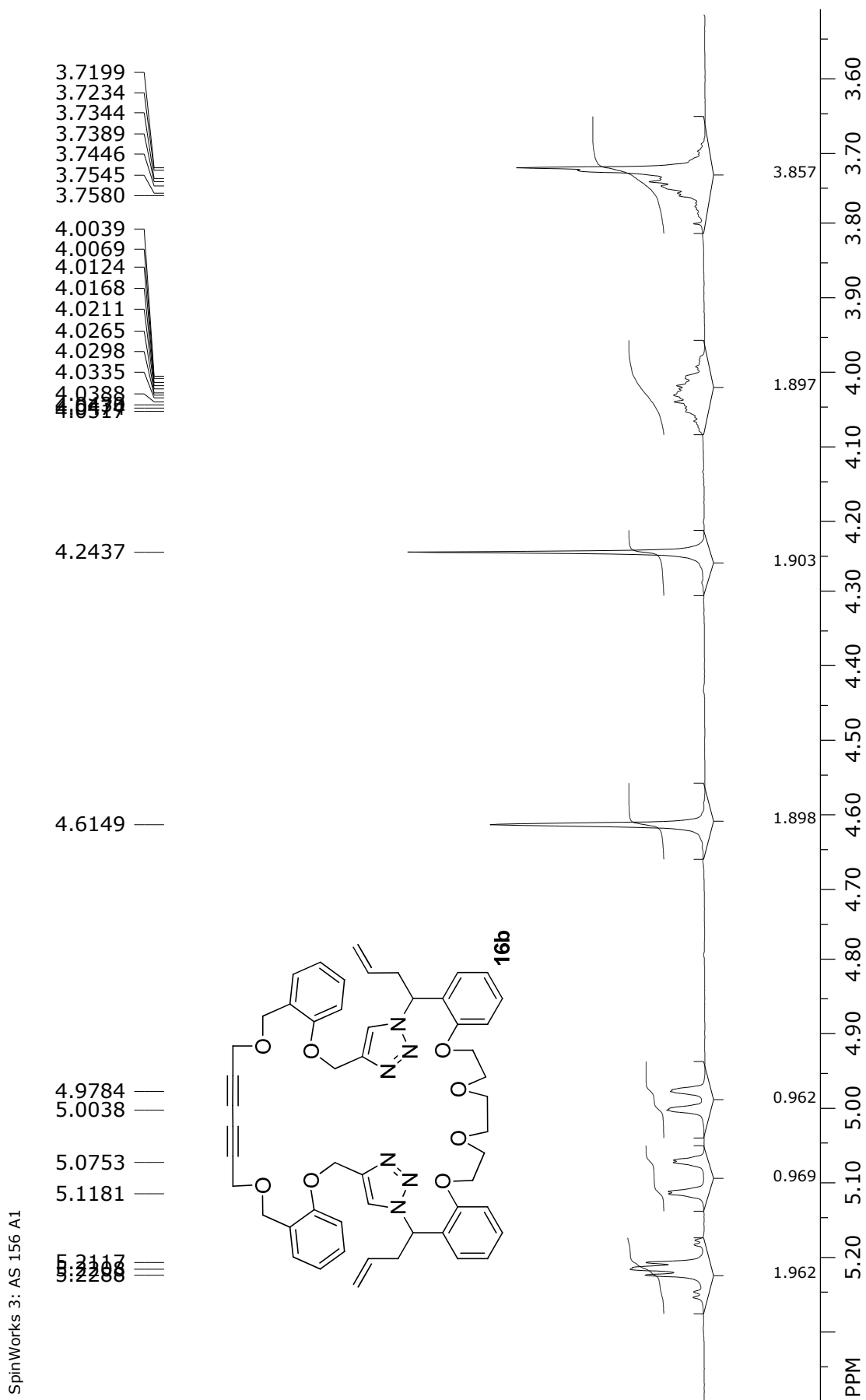
7.0330  
7.0333  
7.0336  
7.0339  
7.0342  
7.0345

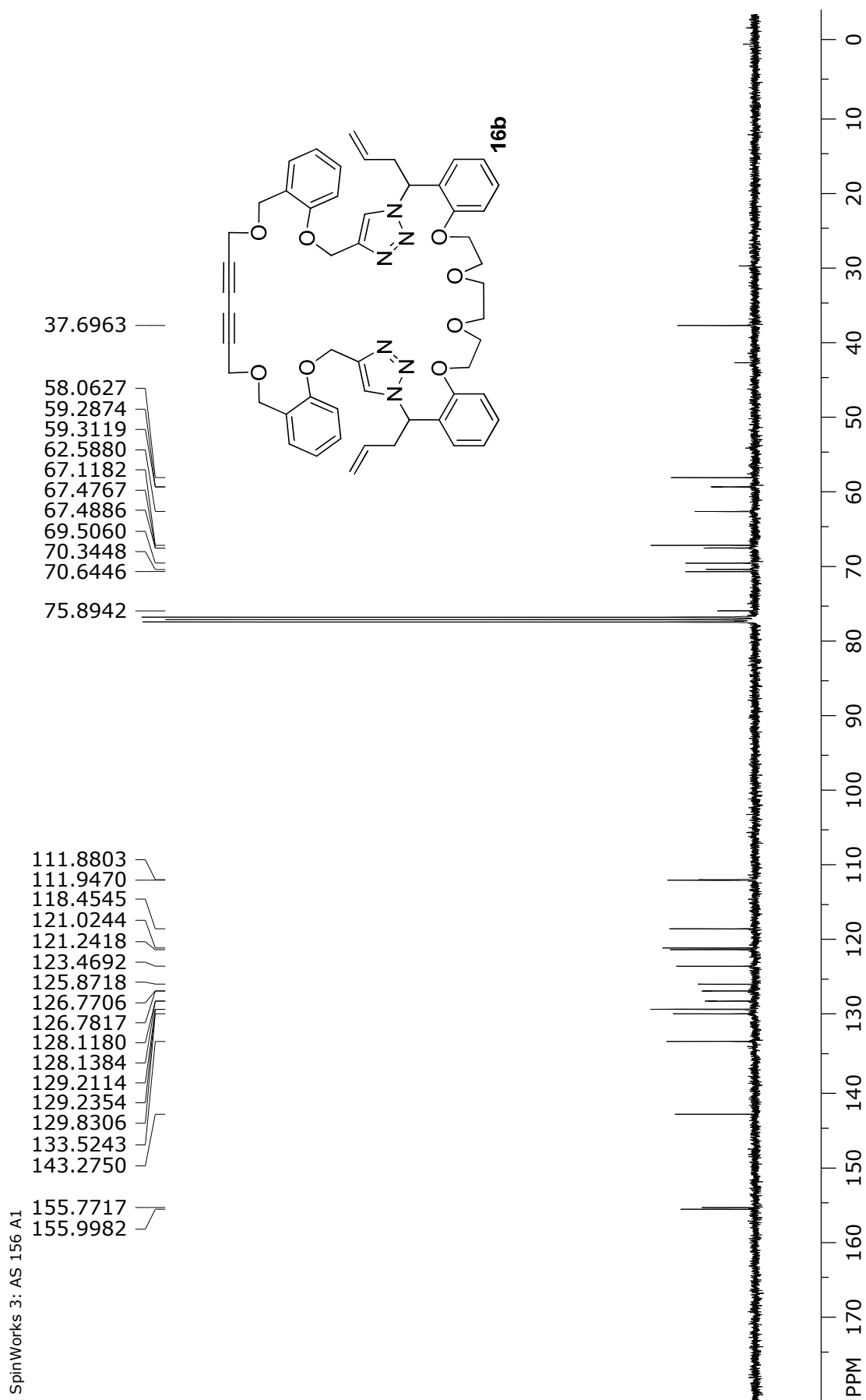
6.8272  
6.8066

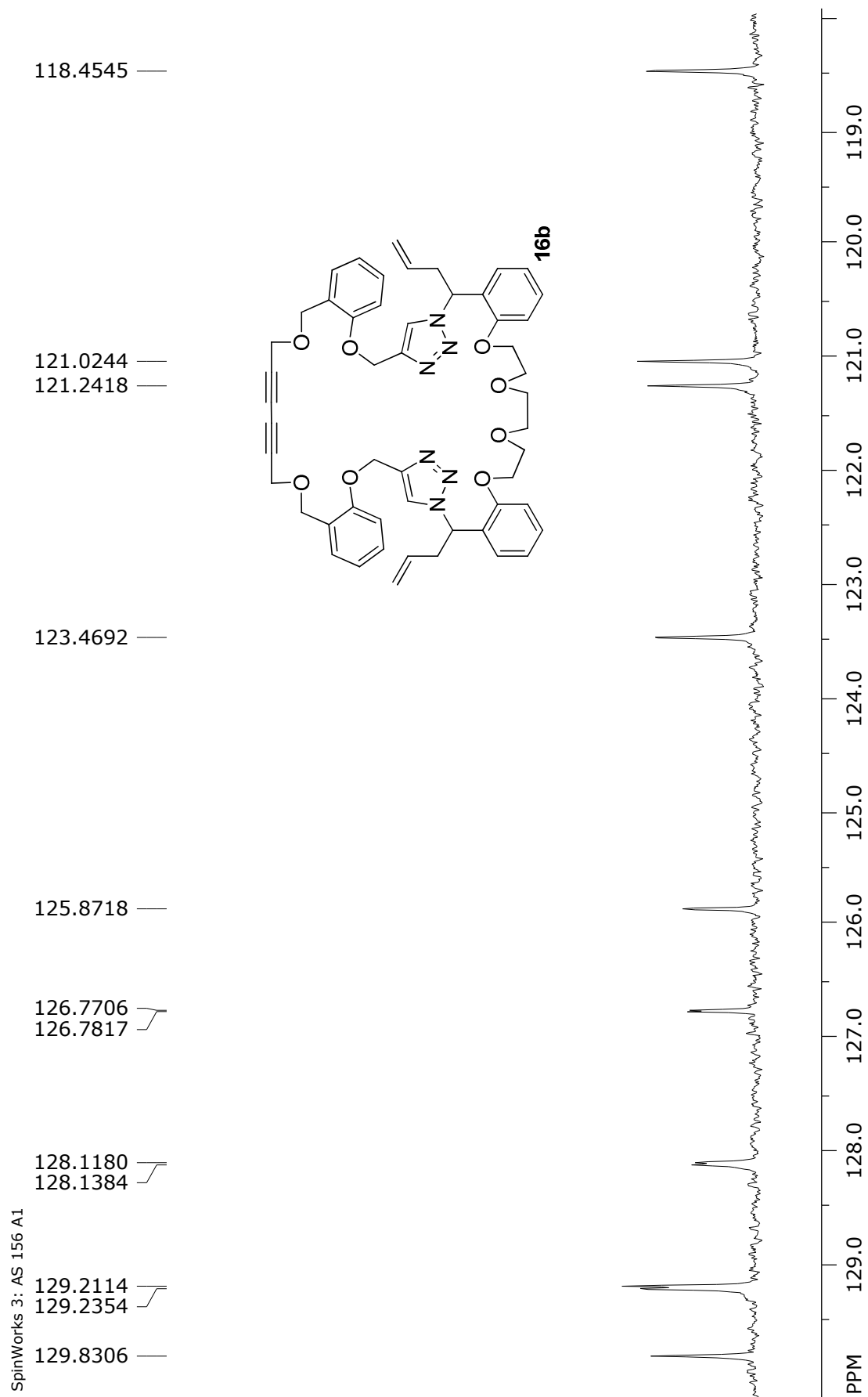
6.0530  
6.0347  
6.0164  
5.9981  
5.9798

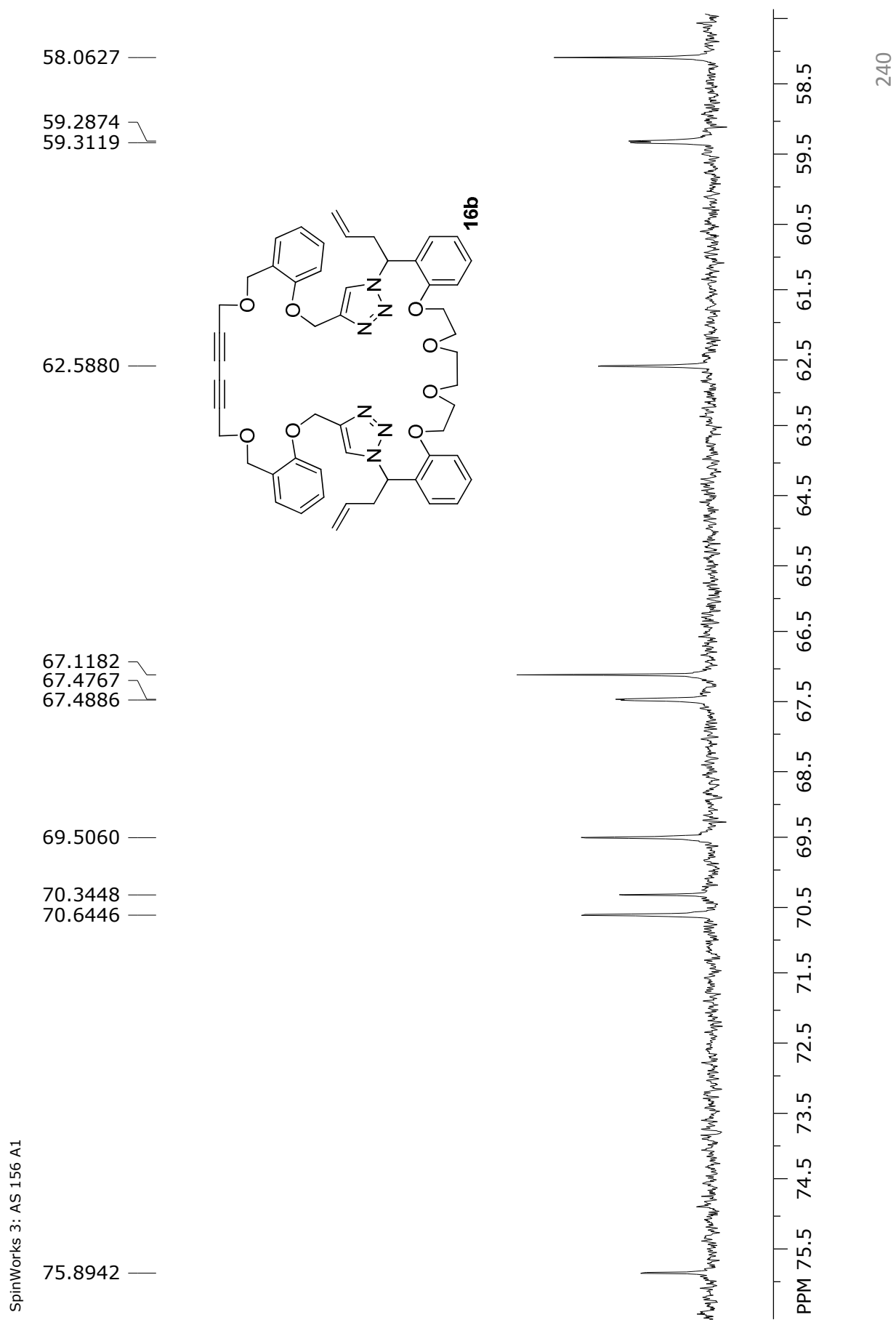
5.7435  
5.7252  
5.7069  
5.6886  
5.6703



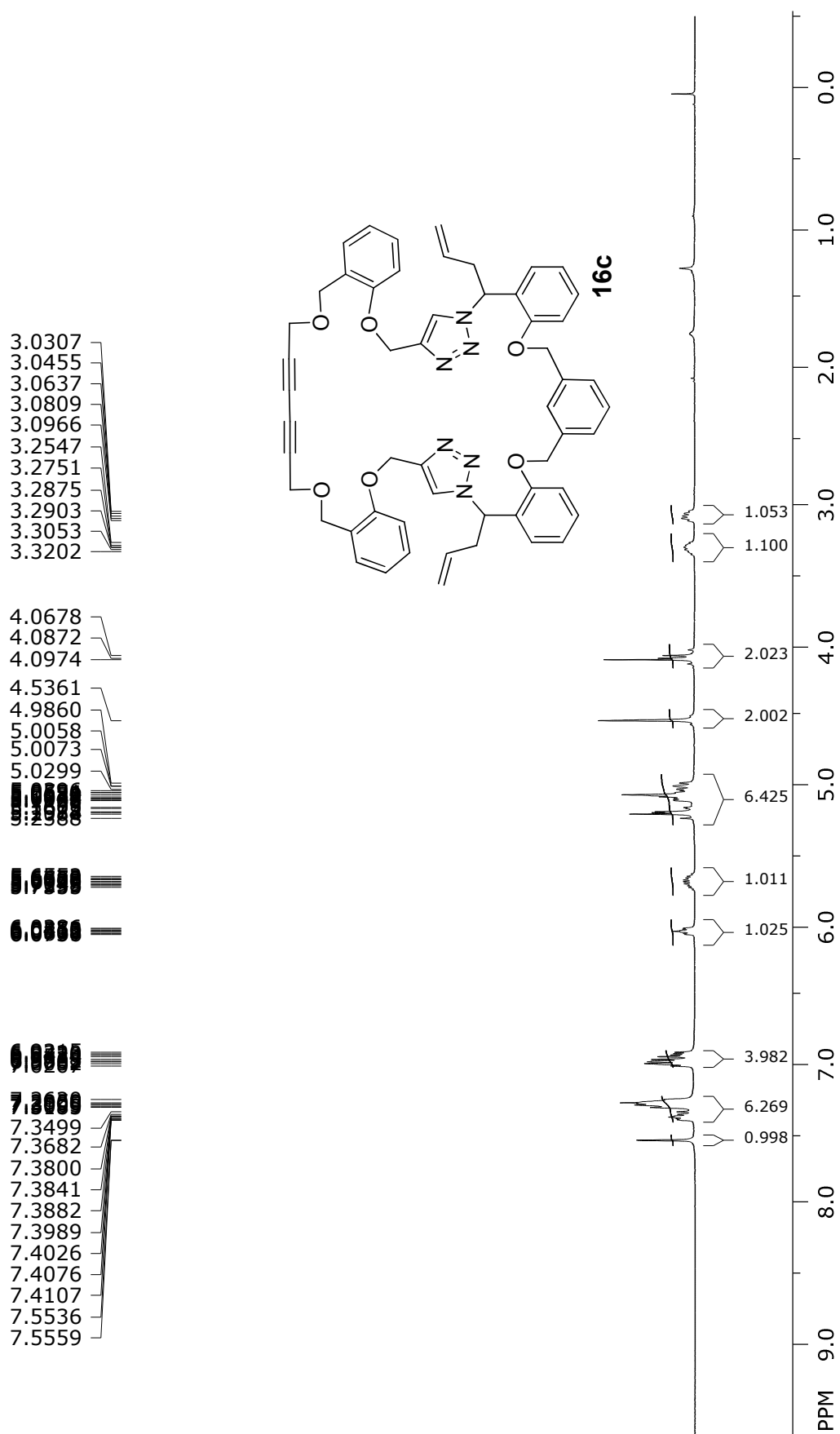






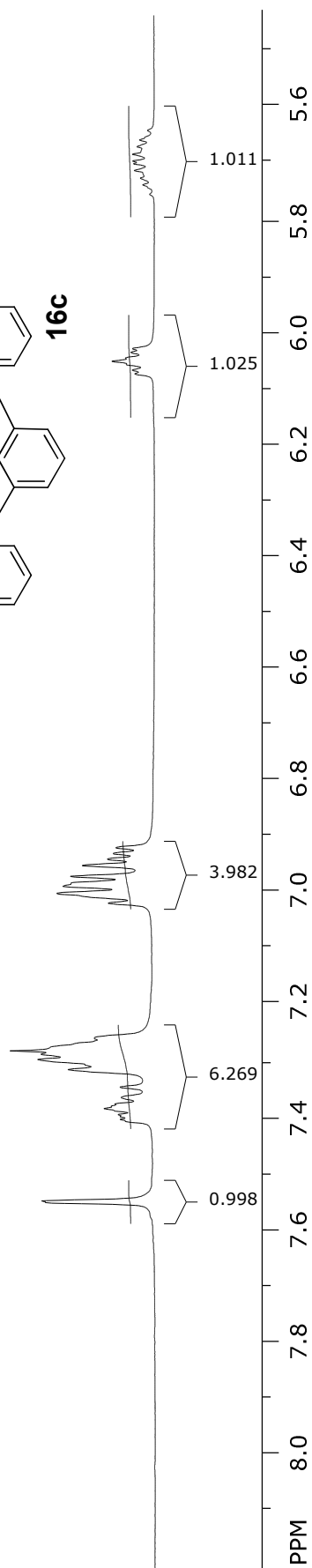
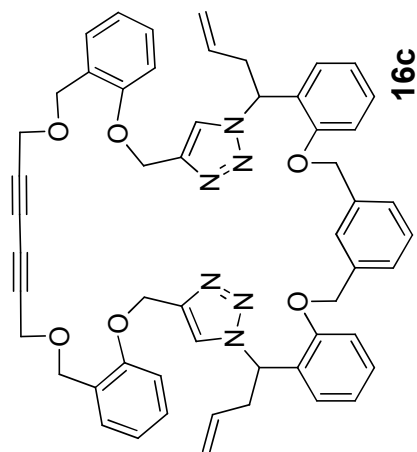
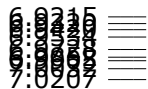


SpinWorks 3: NM-2185 A



SpinWorks 3: NM1-2185 A

7.2620  
7.2620  
7.3099  
7.3185  
7.3499  
7.3682  
7.3800  
7.3841  
7.3882  
7.3989  
7.4026  
7.4076  
7.4107  
7.5536  
7.5559

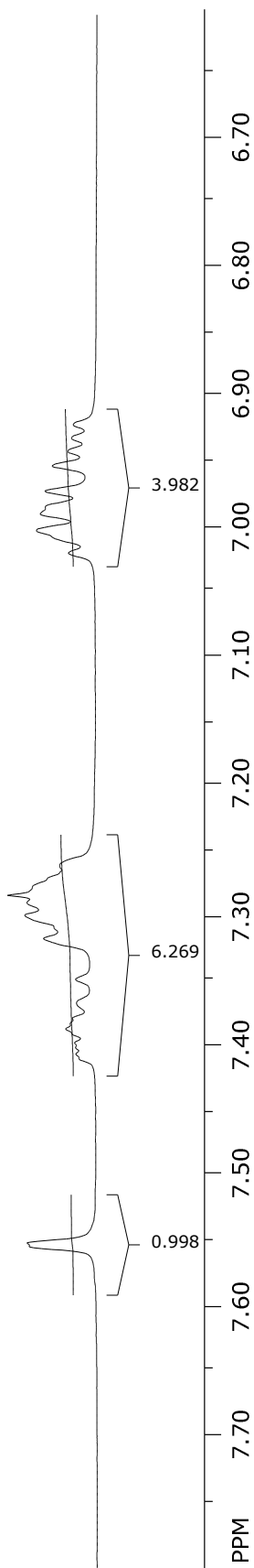
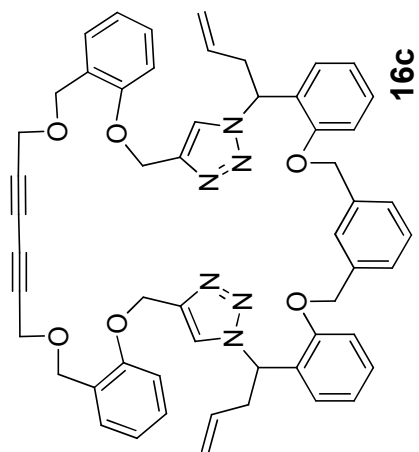


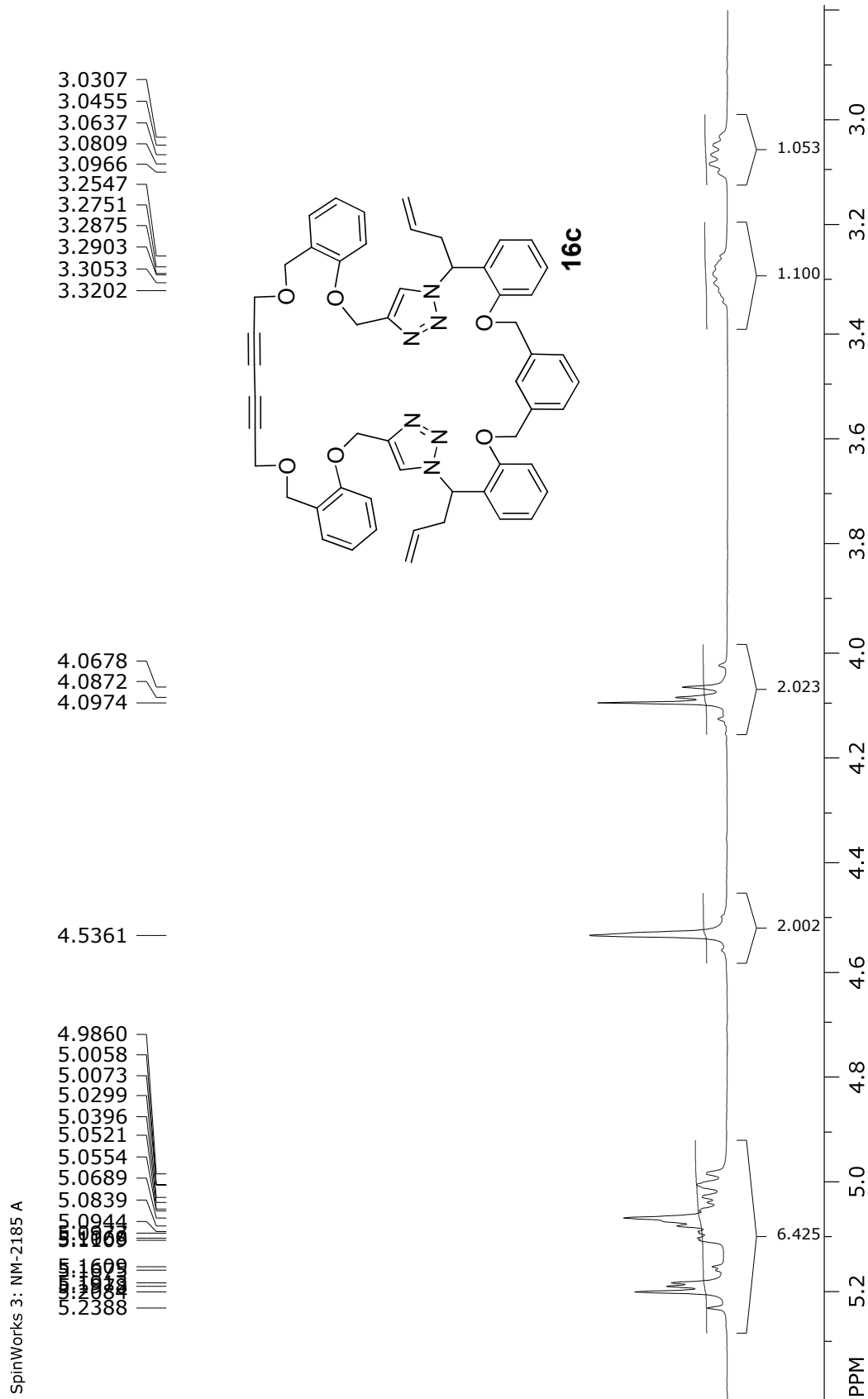


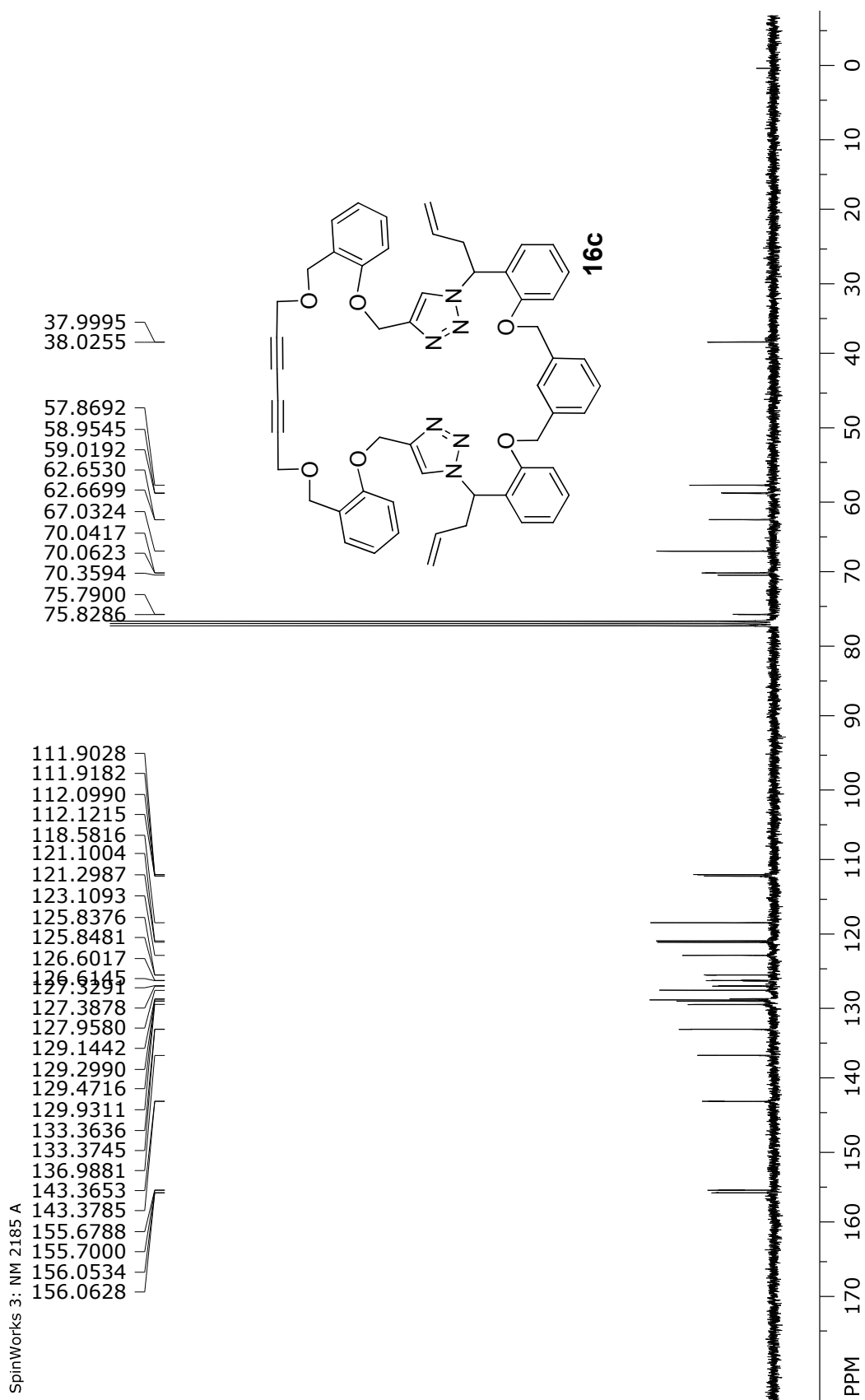
SpinWorks 3: NM-2185 A

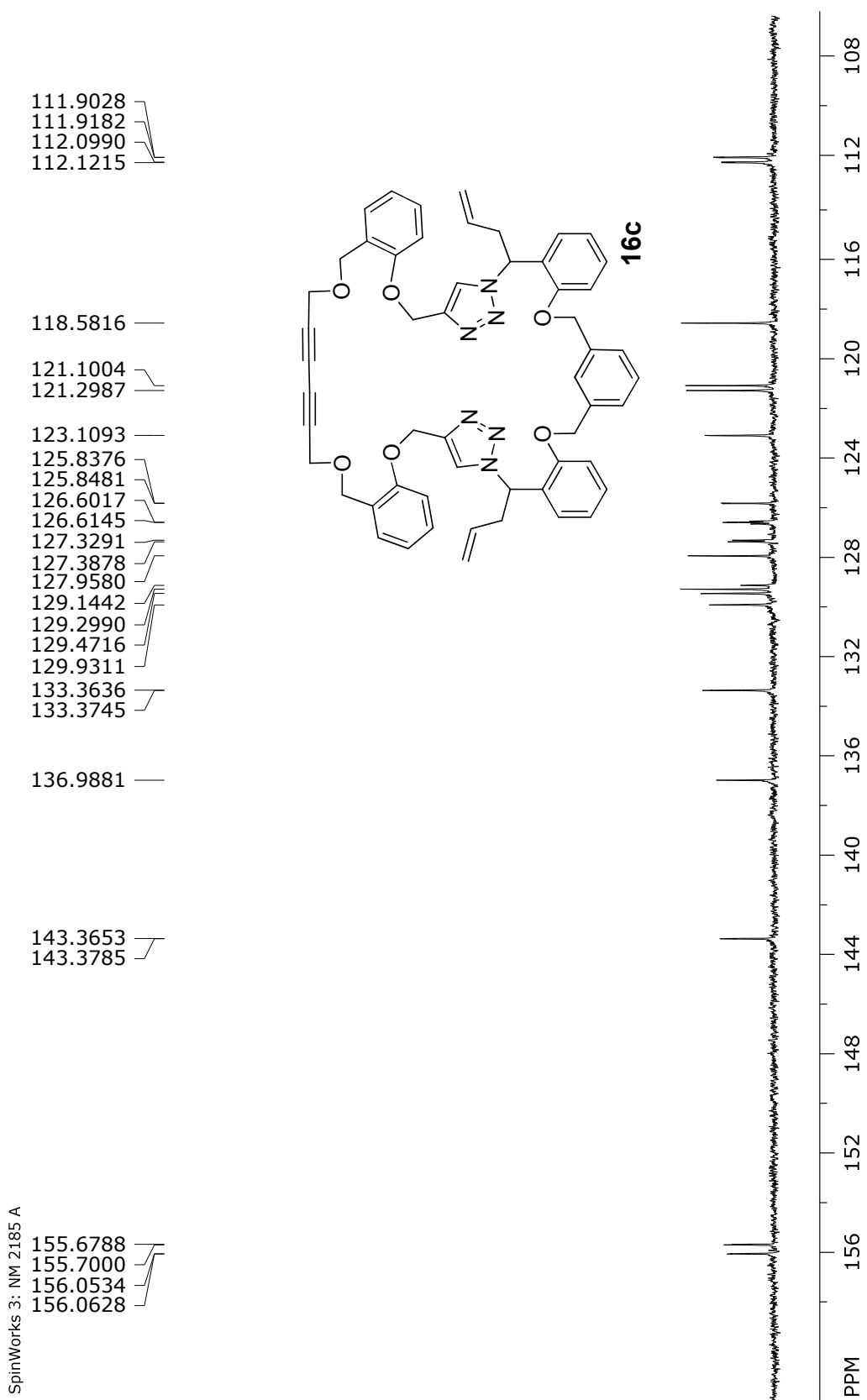
6.9215  
6.9320  
6.9420  
6.9534  
6.9728  
6.9852  
6.9905  
7.0032  
7.0207

7.2620  
7.2850  
7.2908  
7.3005  
7.3099  
7.3185  
7.3499  
7.3682  
7.3800  
7.3841  
7.3882  
7.3989  
7.4026  
7.4076  
7.4107  
  
7.5536  
7.5559





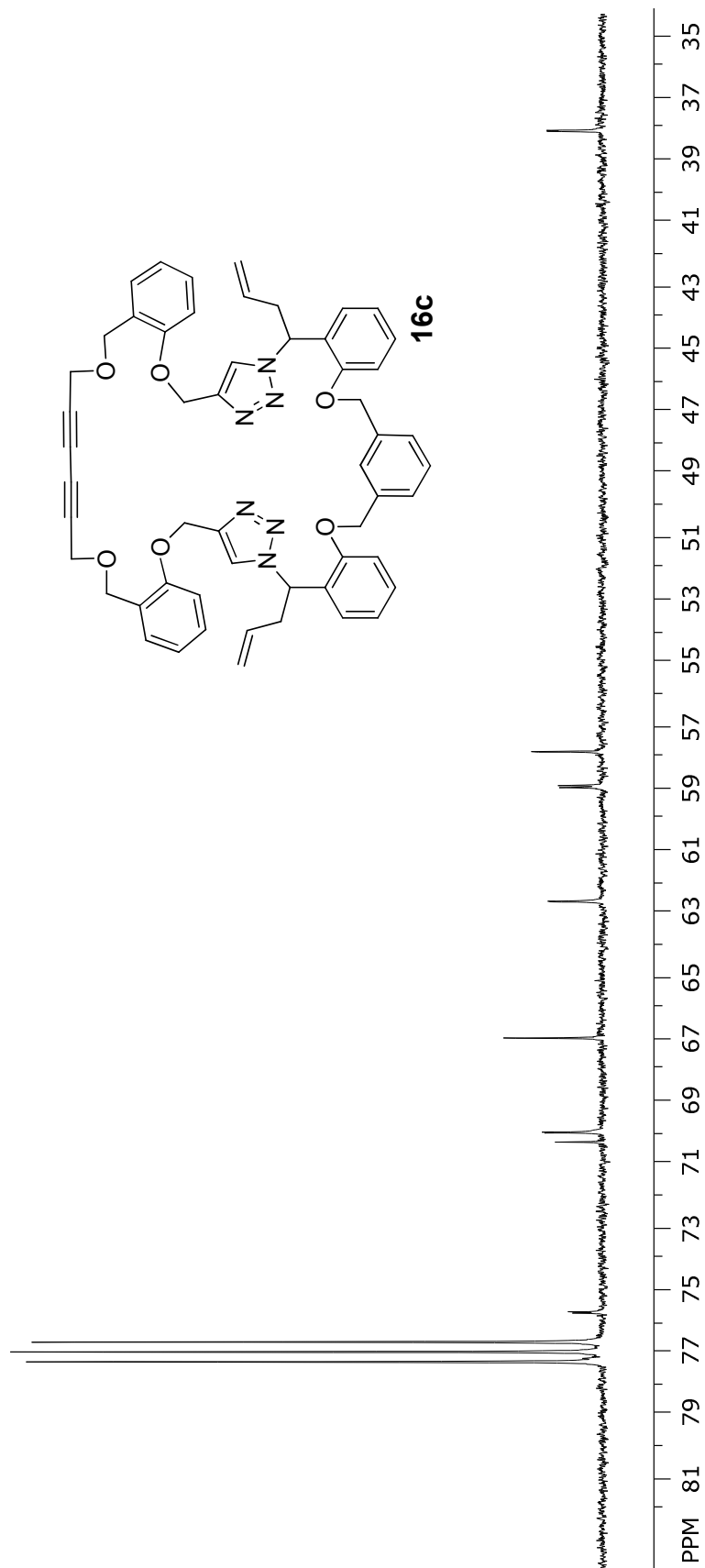




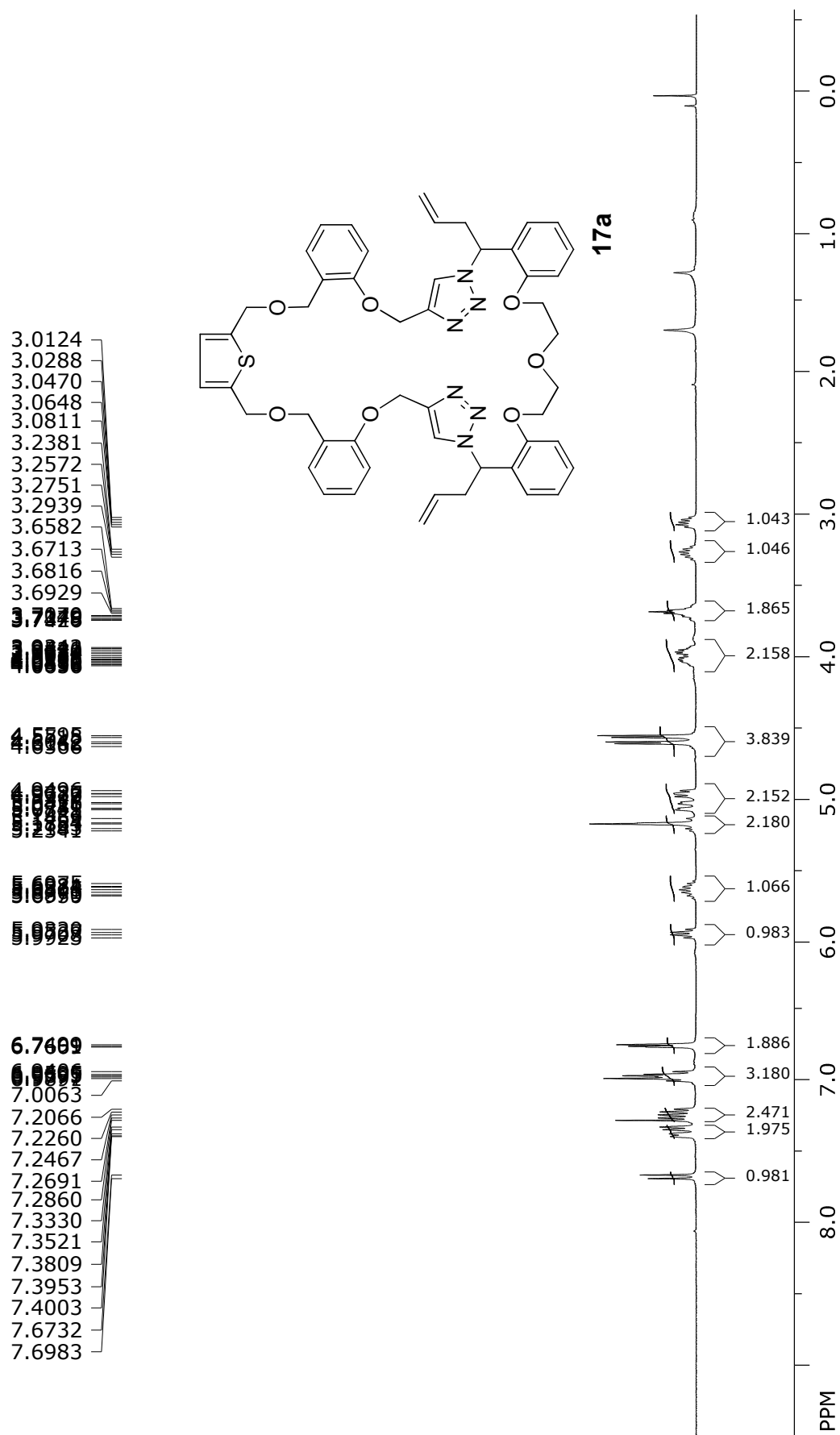
SpinWorks 3: NM 2185 A

37.9995  
38.025557.8692  
58.9545  
59.019262.6530  
62.6699

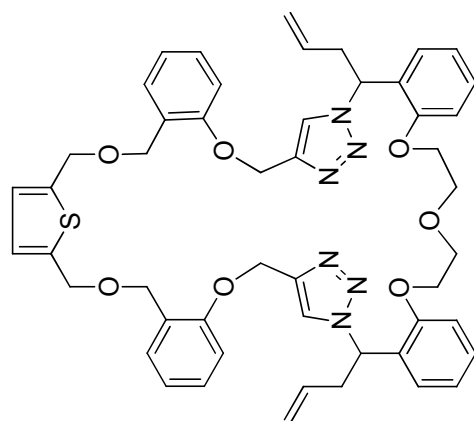
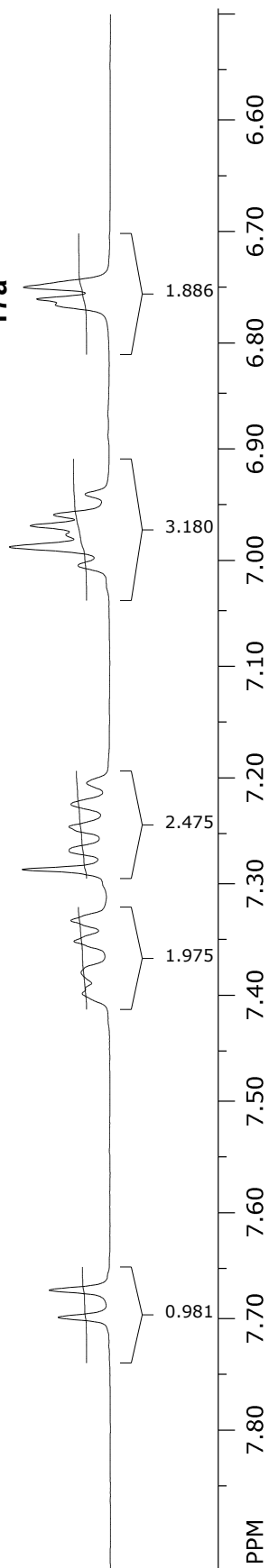
67.0324

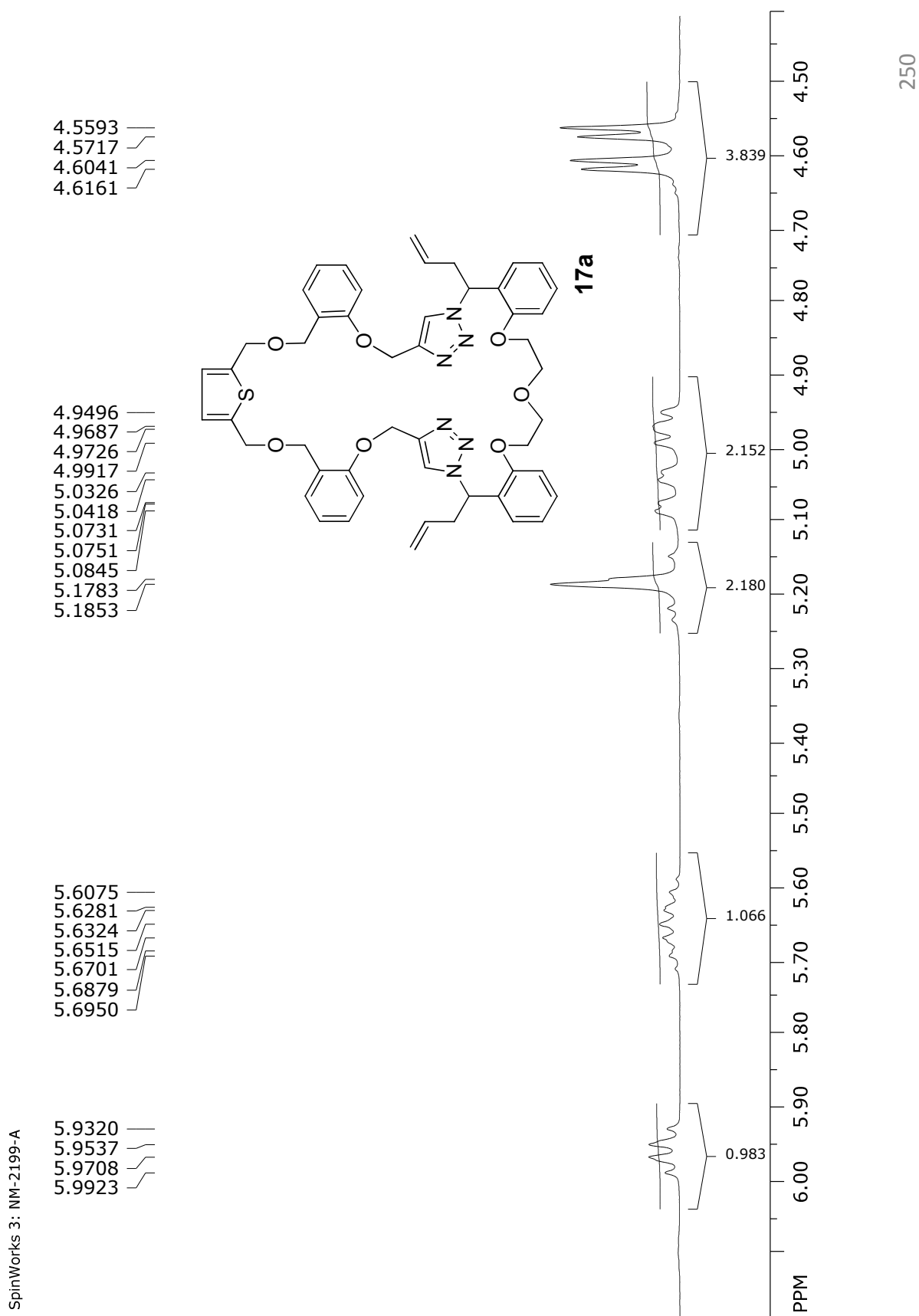
70.0417  
70.0623  
70.359475.7900  
75.8286

SpinWorks 3: NM-2199-A



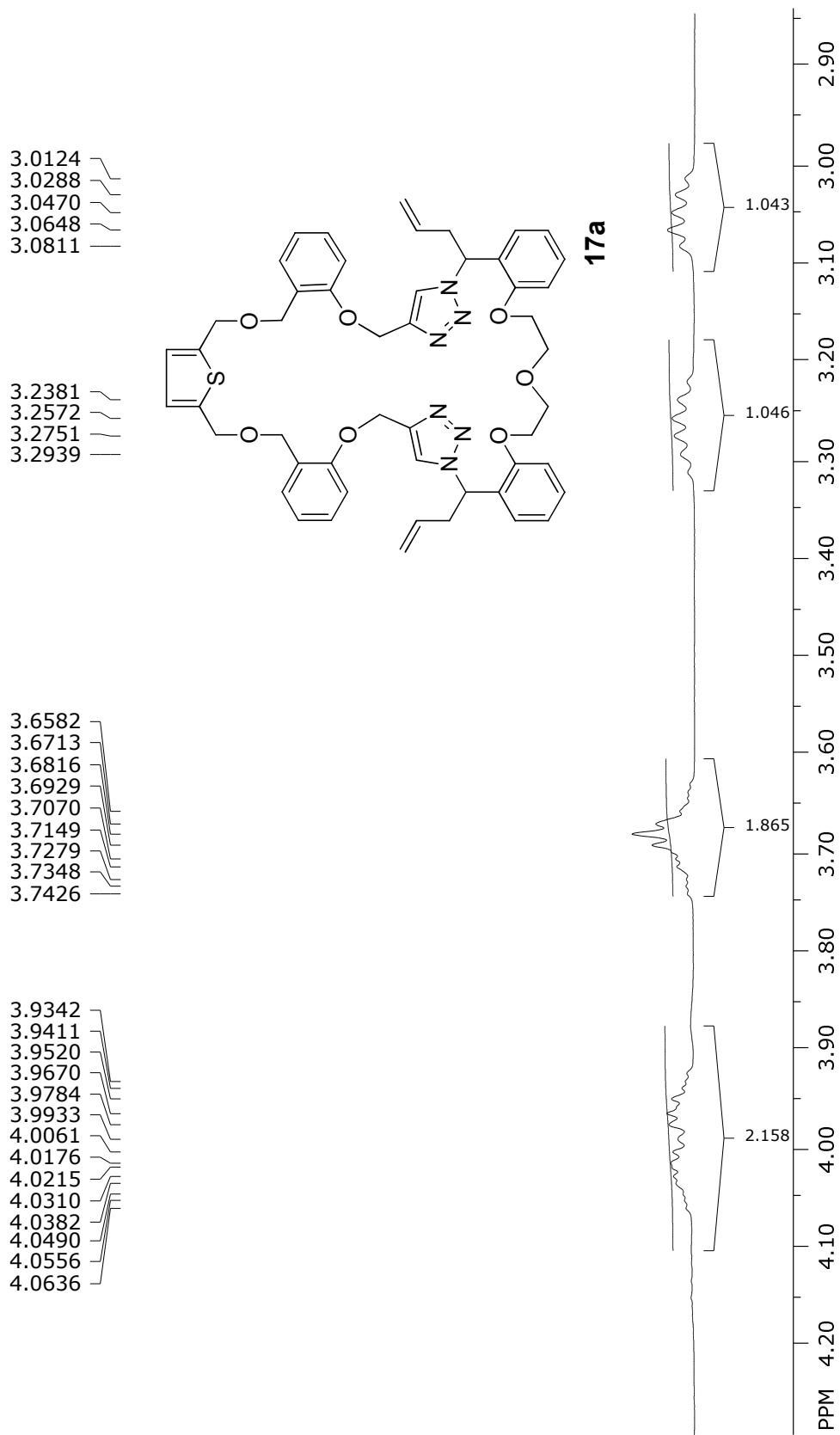
SpinWorks 3: NM-2199-A

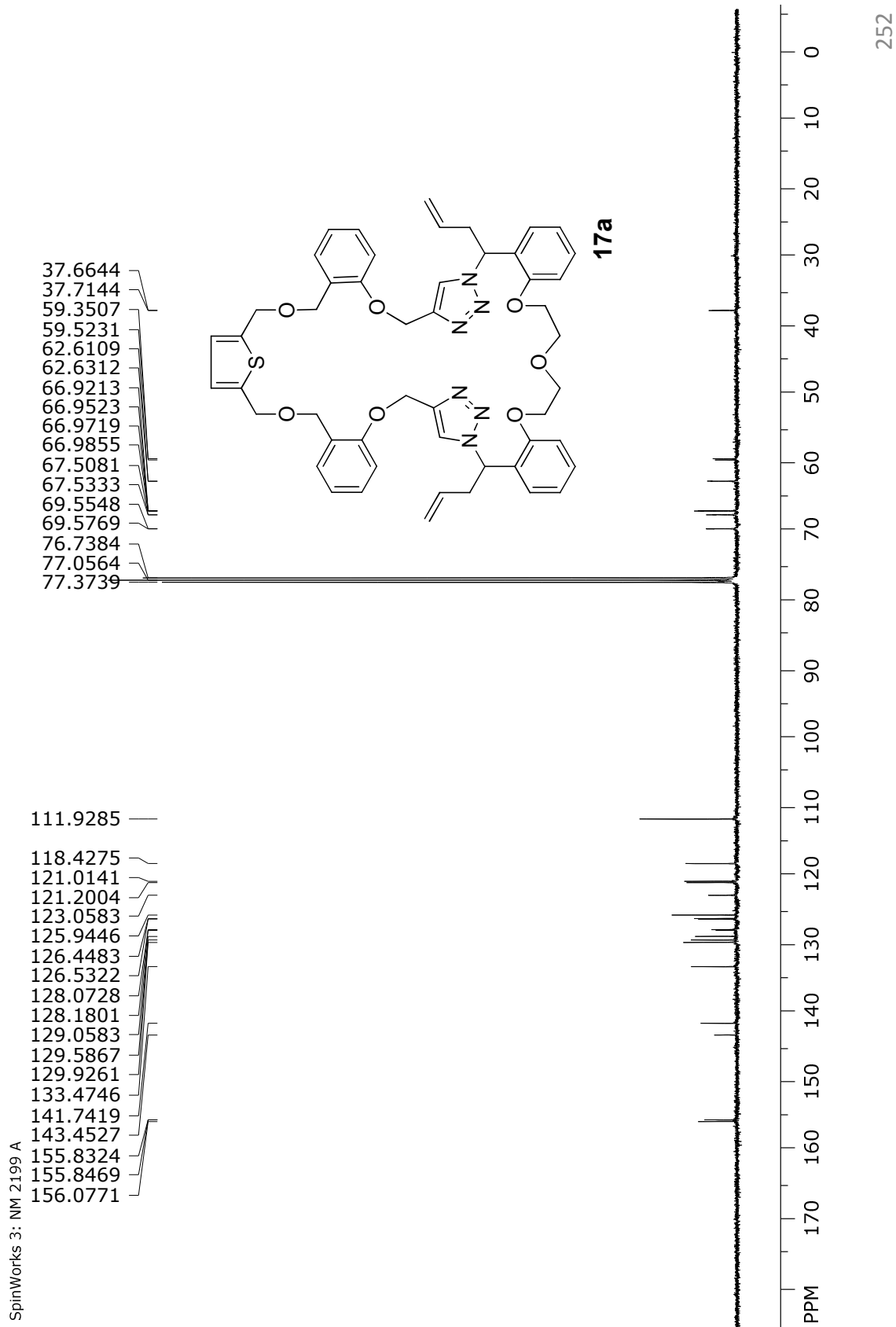
6.7499  
6.7609  
6.76616.9406  
6.9595  
6.9695  
6.9777  
6.9891  
7.00637.2066  
7.2260  
7.2467  
7.2691  
7.28607.3330  
7.3521  
7.3809  
7.3953  
7.40037.6732  
7.6983**17a**

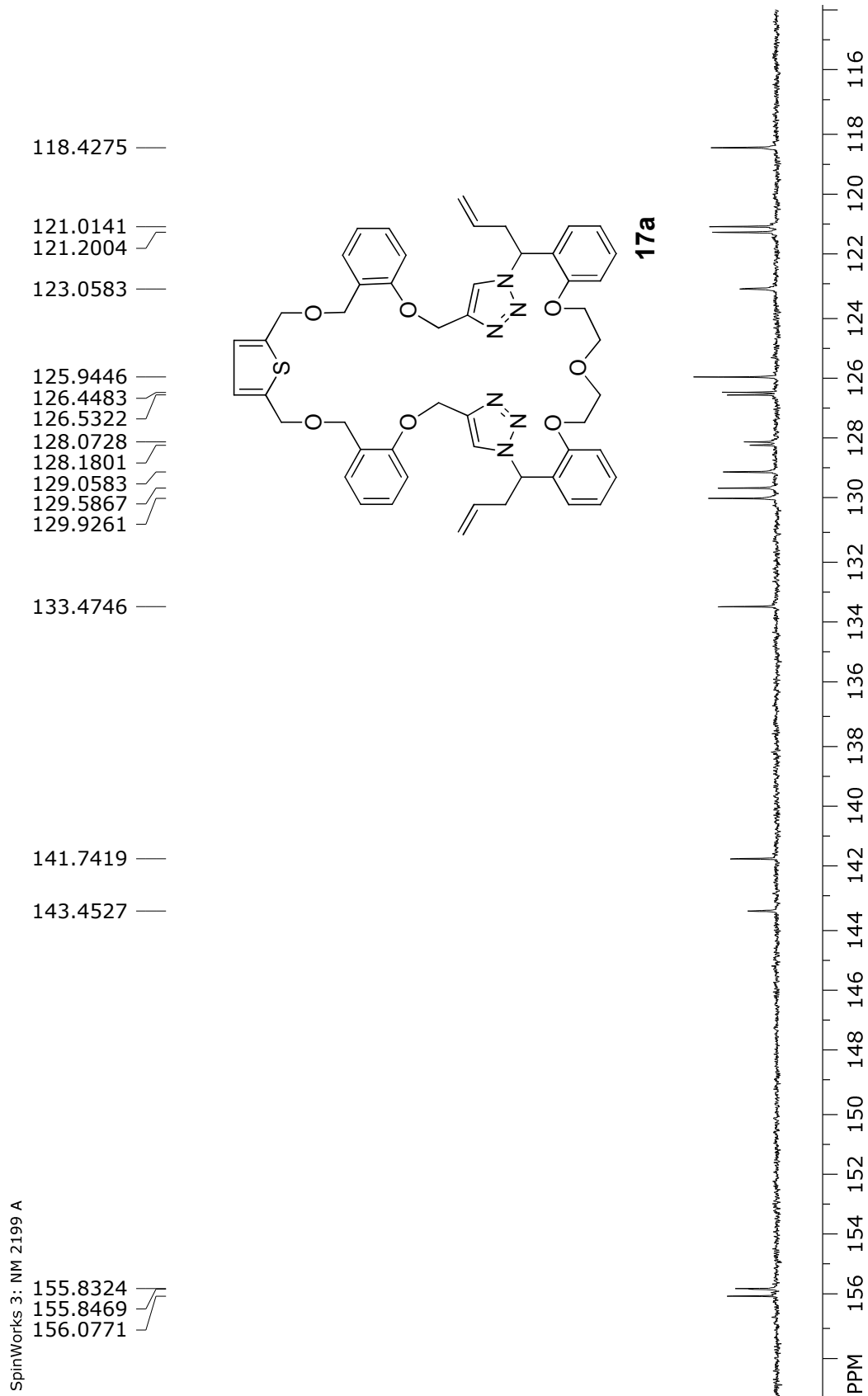




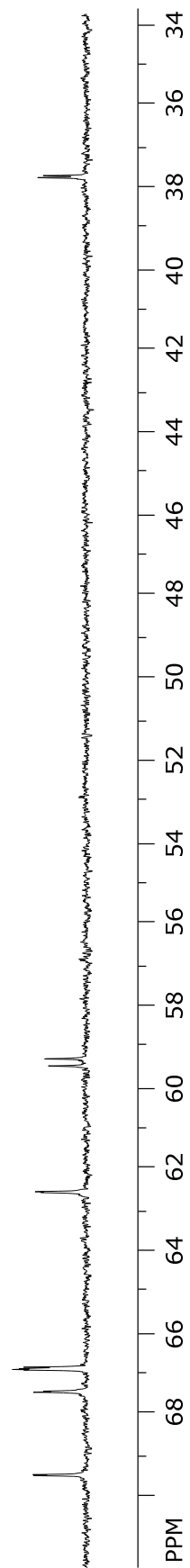
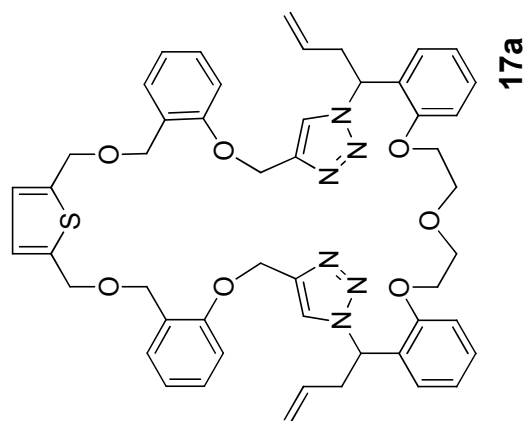
SpinWorks 3: NM-2199-A



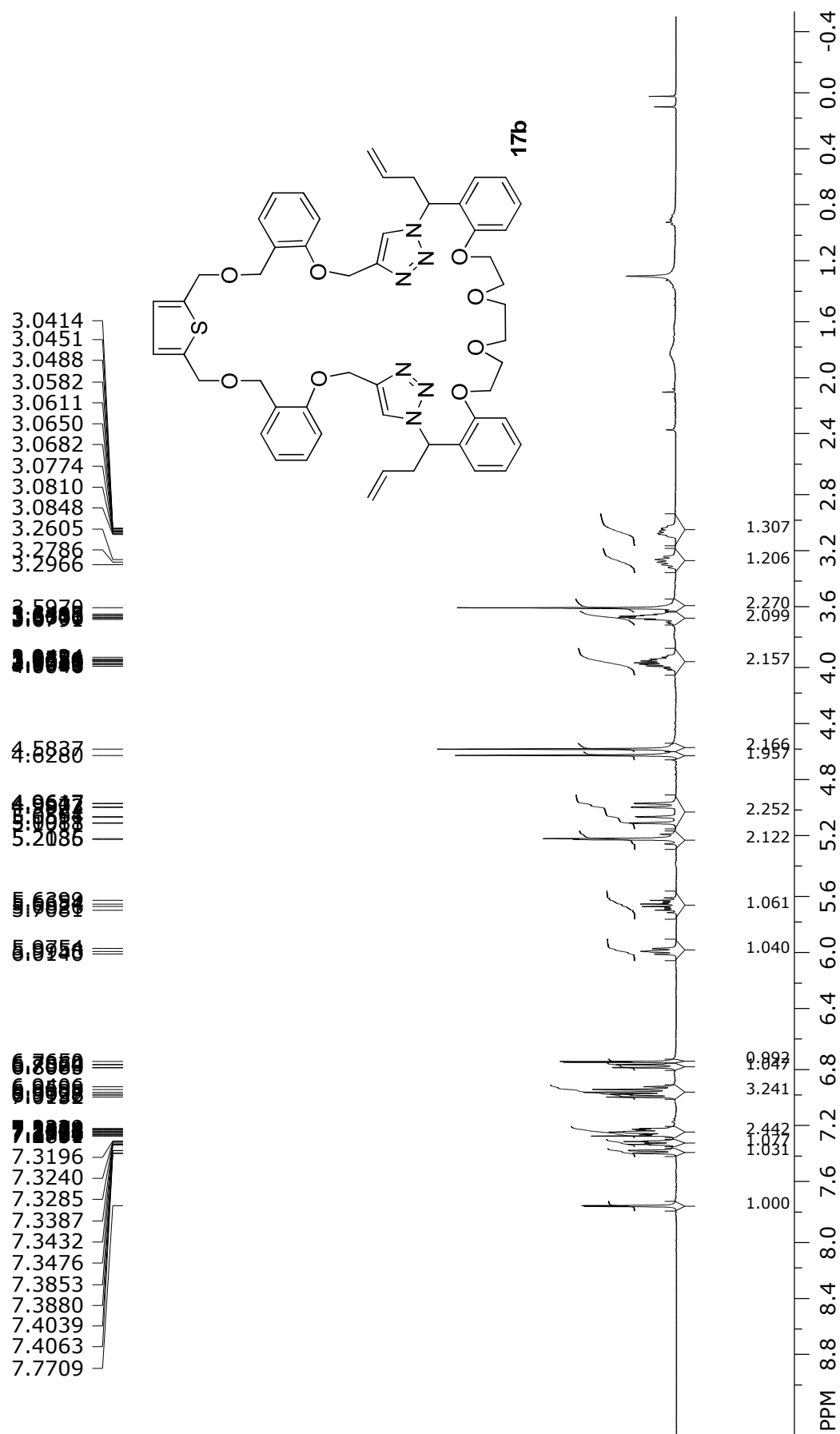




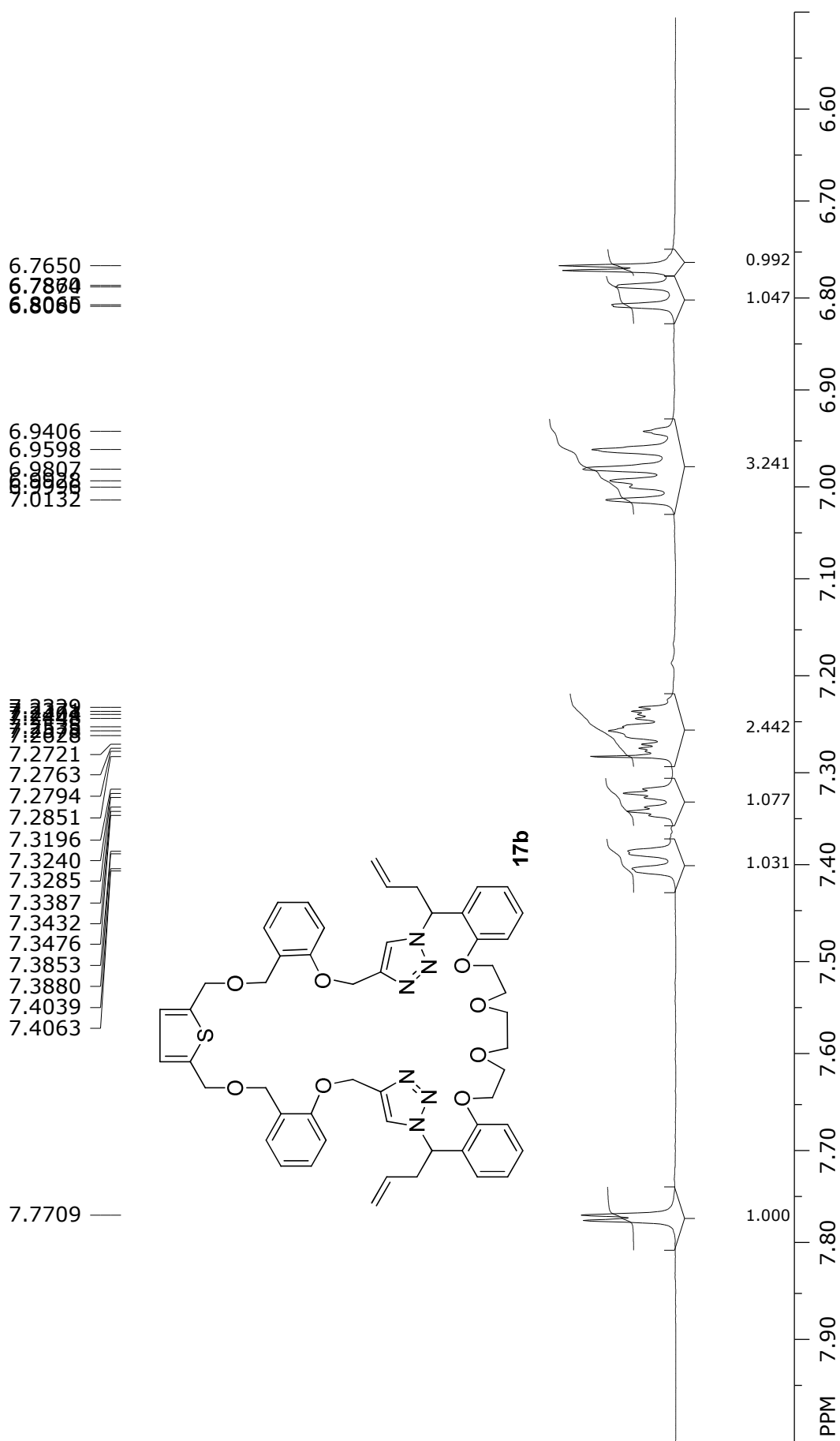
SpinWorks 3: NM 2199 A

37.6644  
37.714459.3507  
59.523162.6109  
62.631266.9213  
66.9523  
66.9719  
66.9855  
67.5081  
67.533369.5548  
69.5769

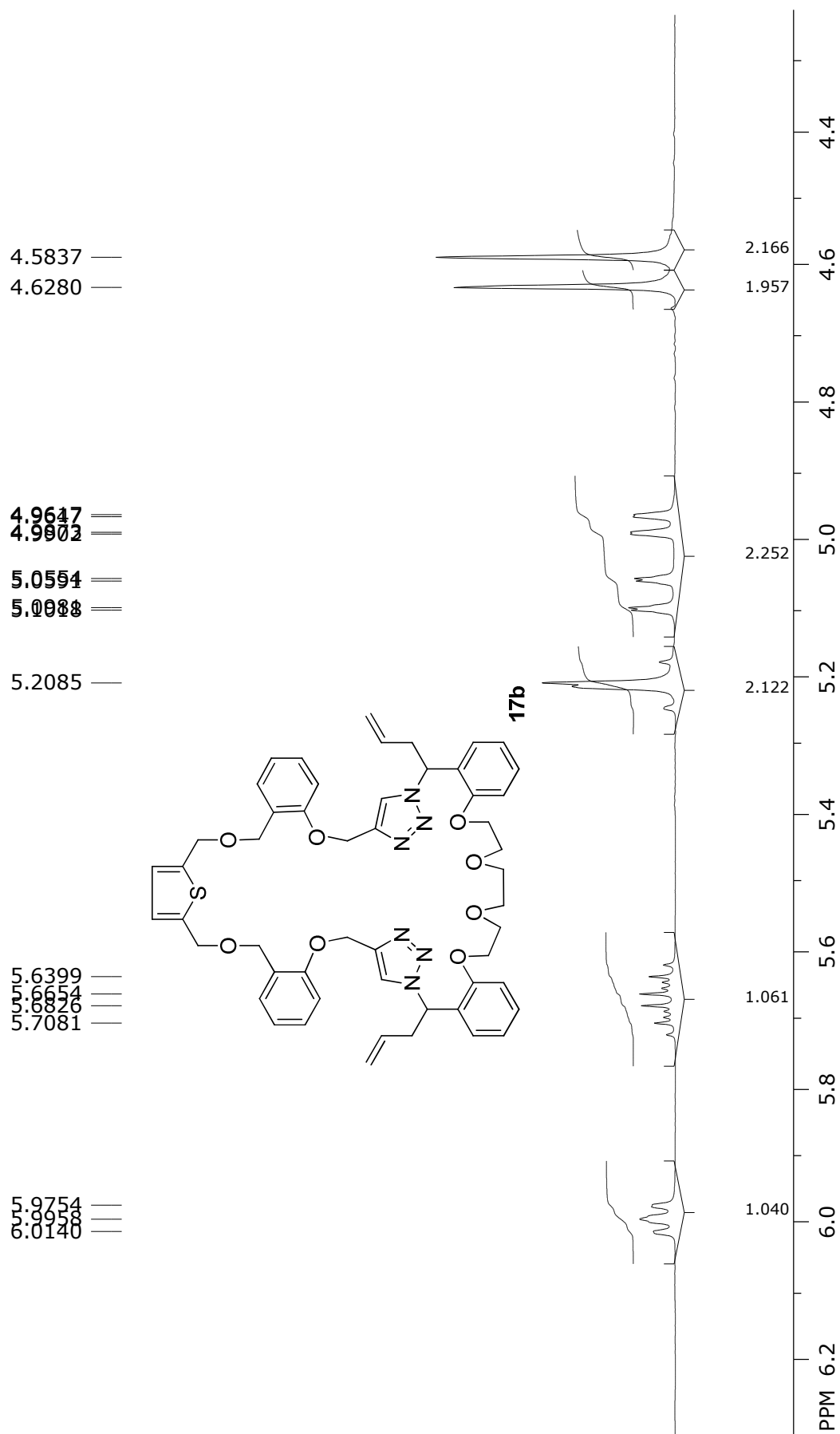
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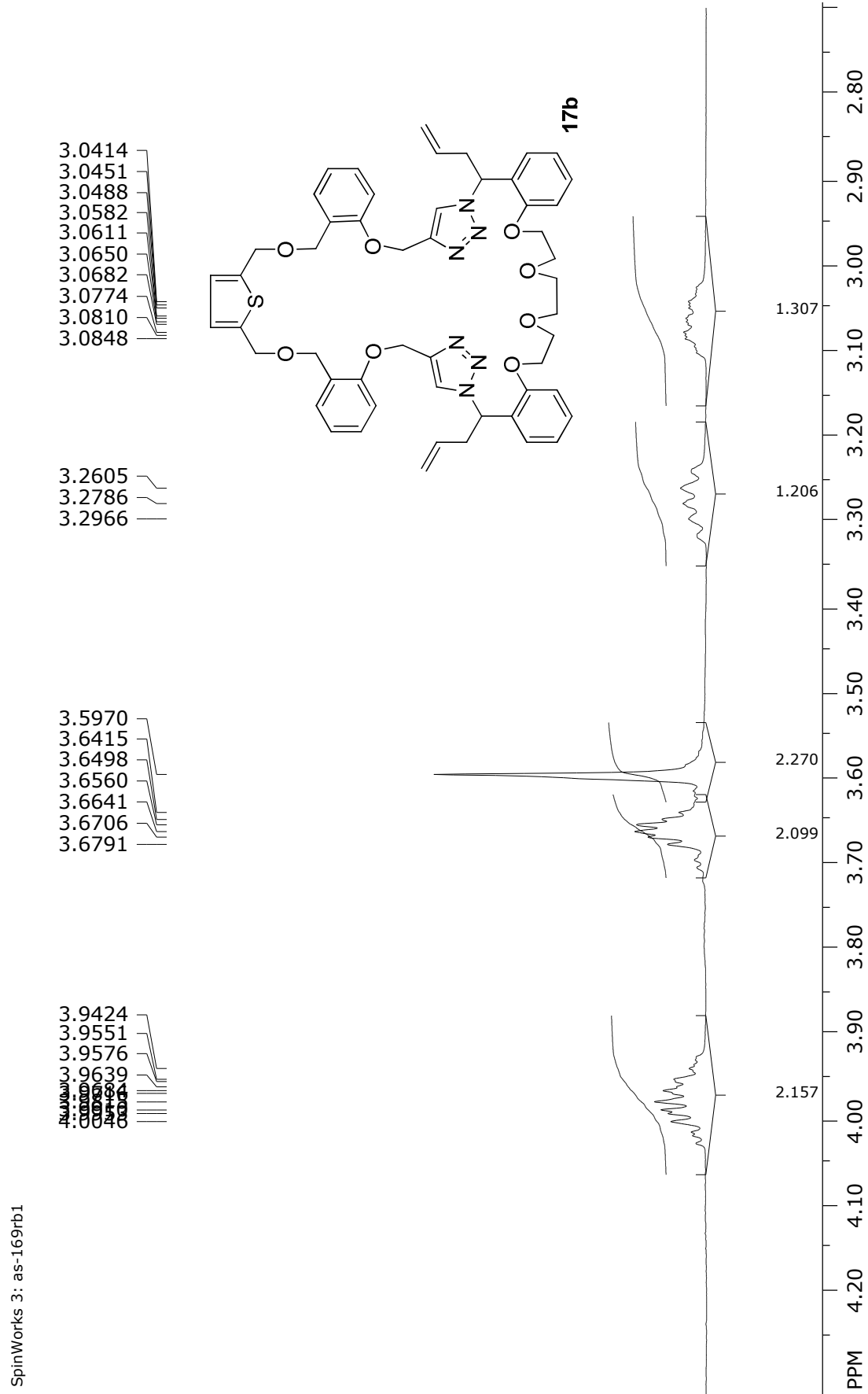


SpinWorks 3: as-169rb1

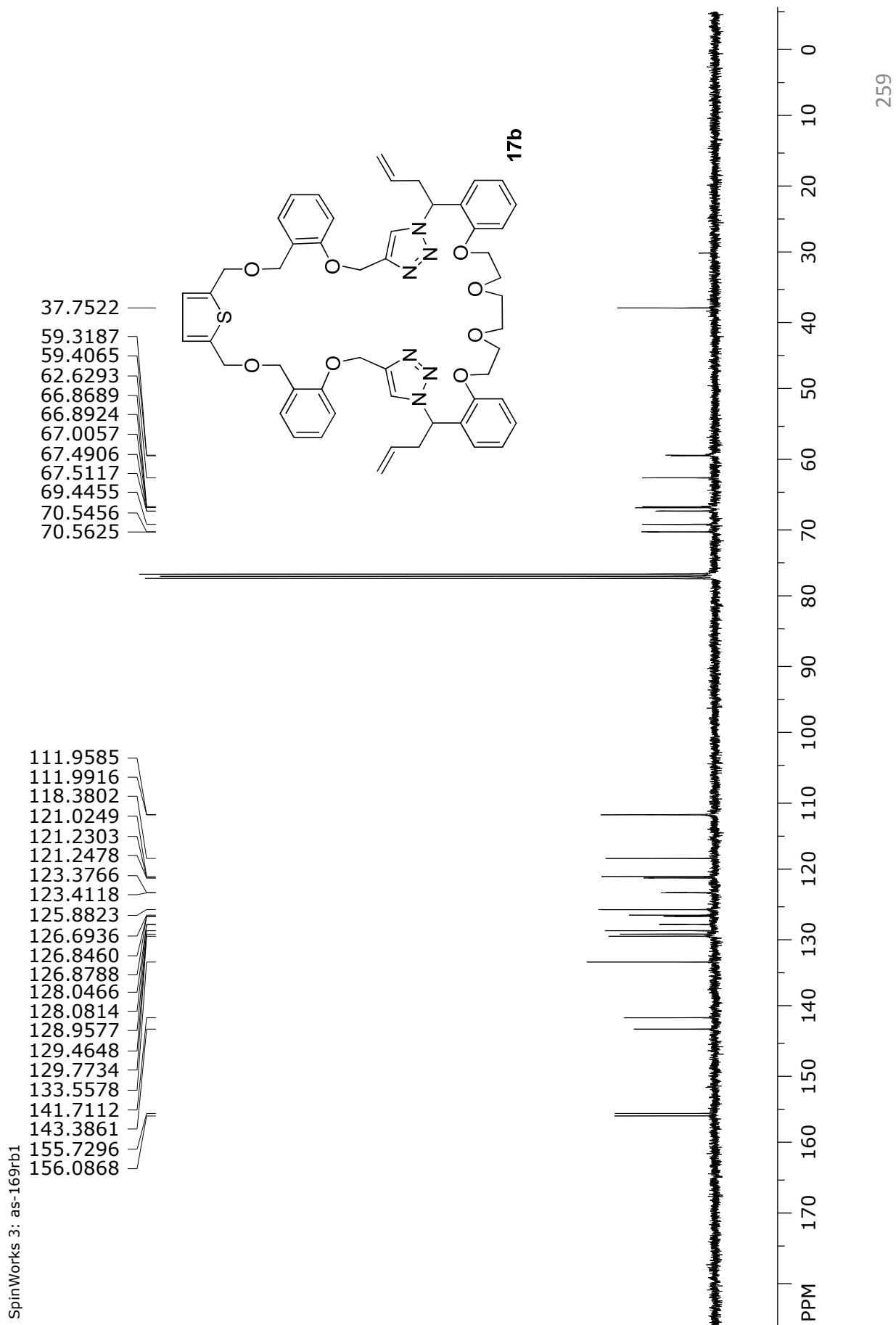


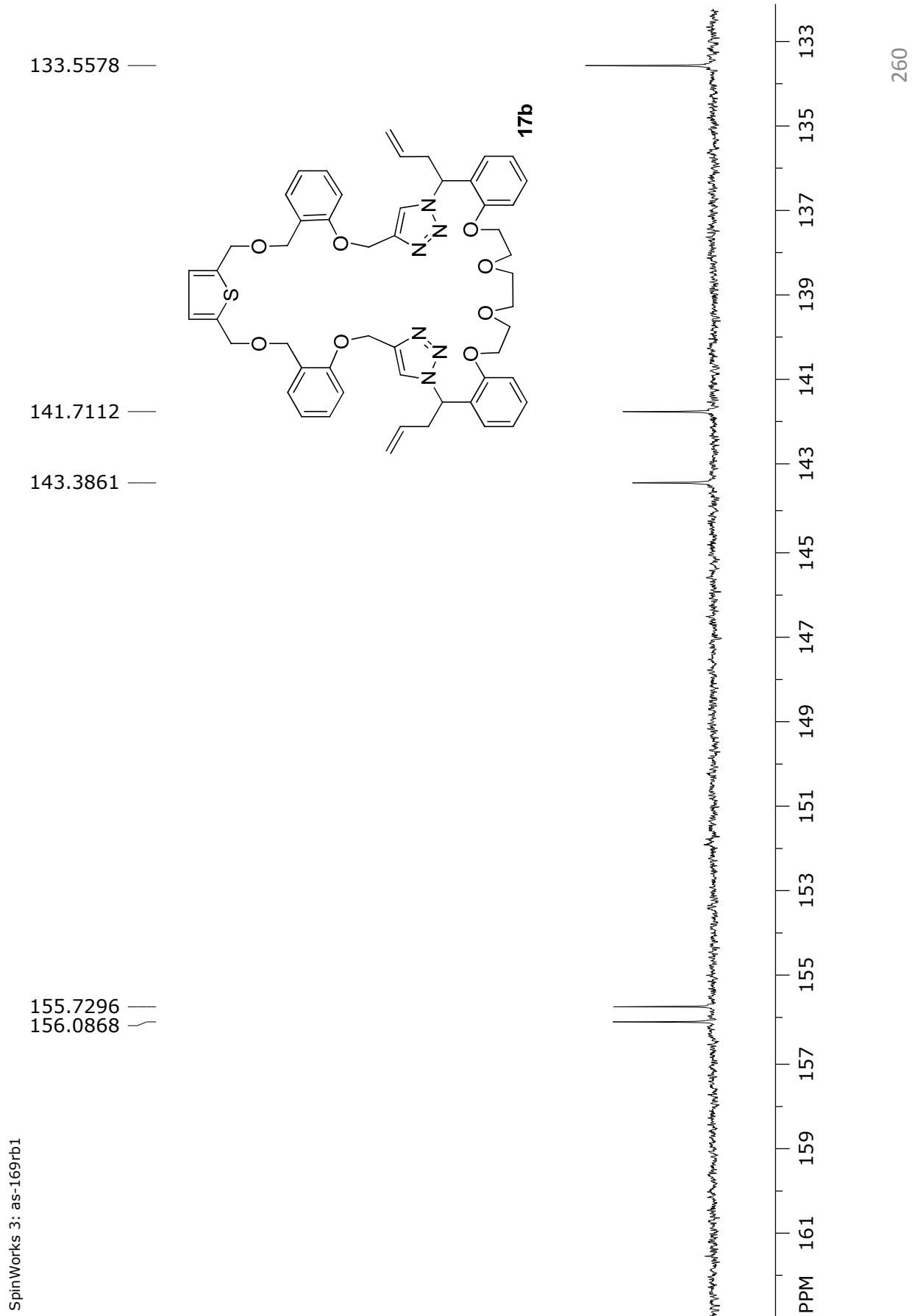
SpinWorks 3: as-169rb1

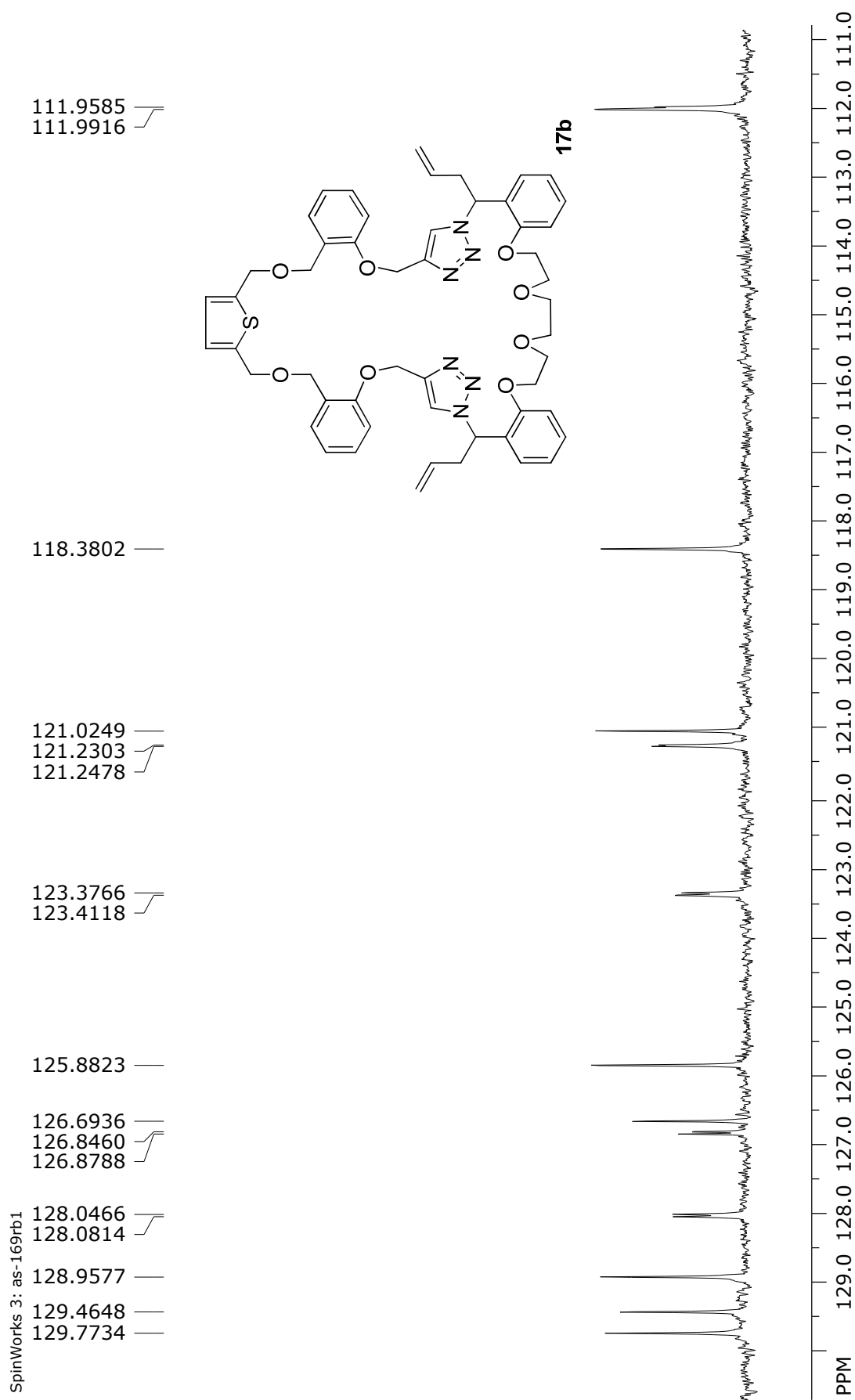


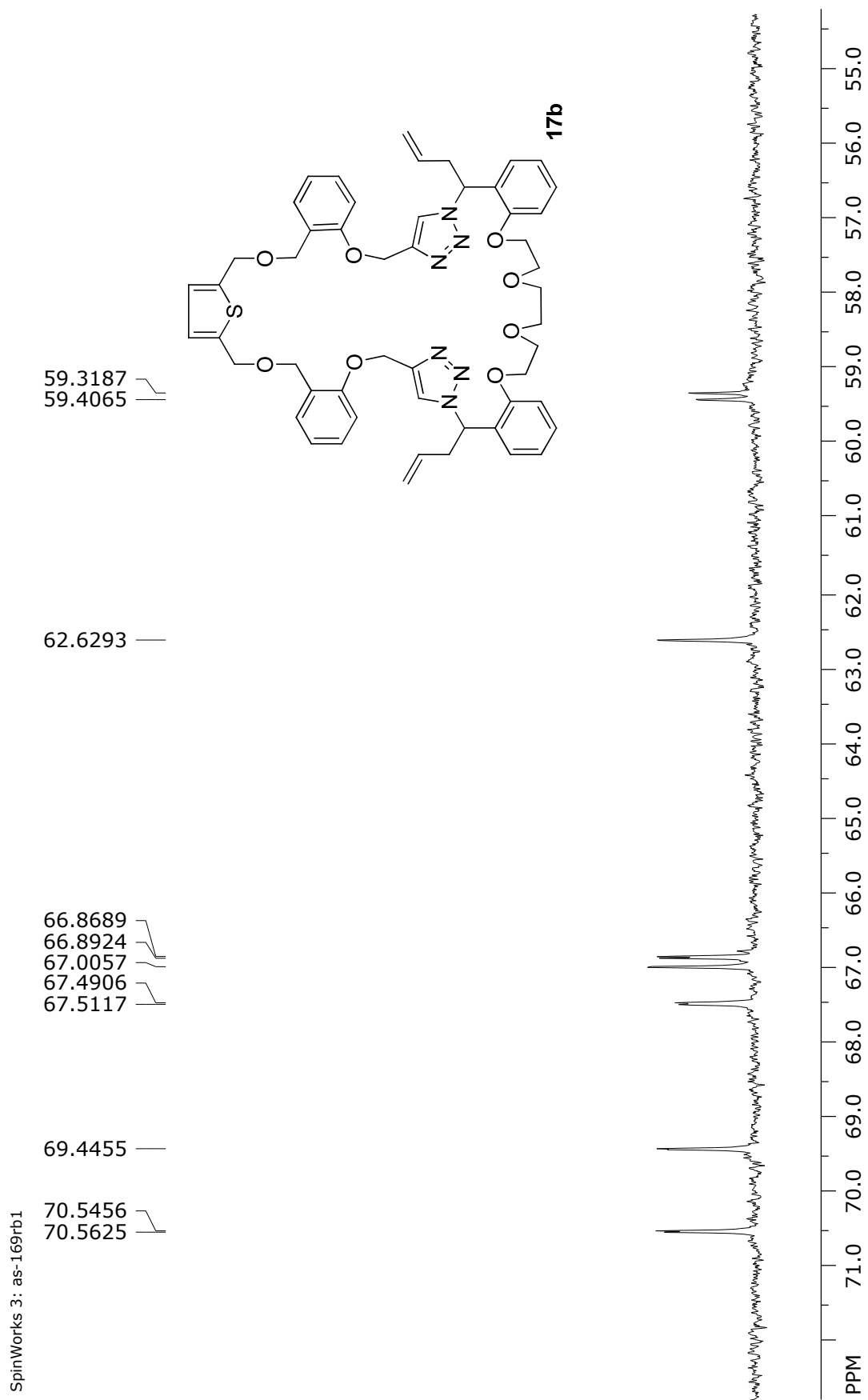




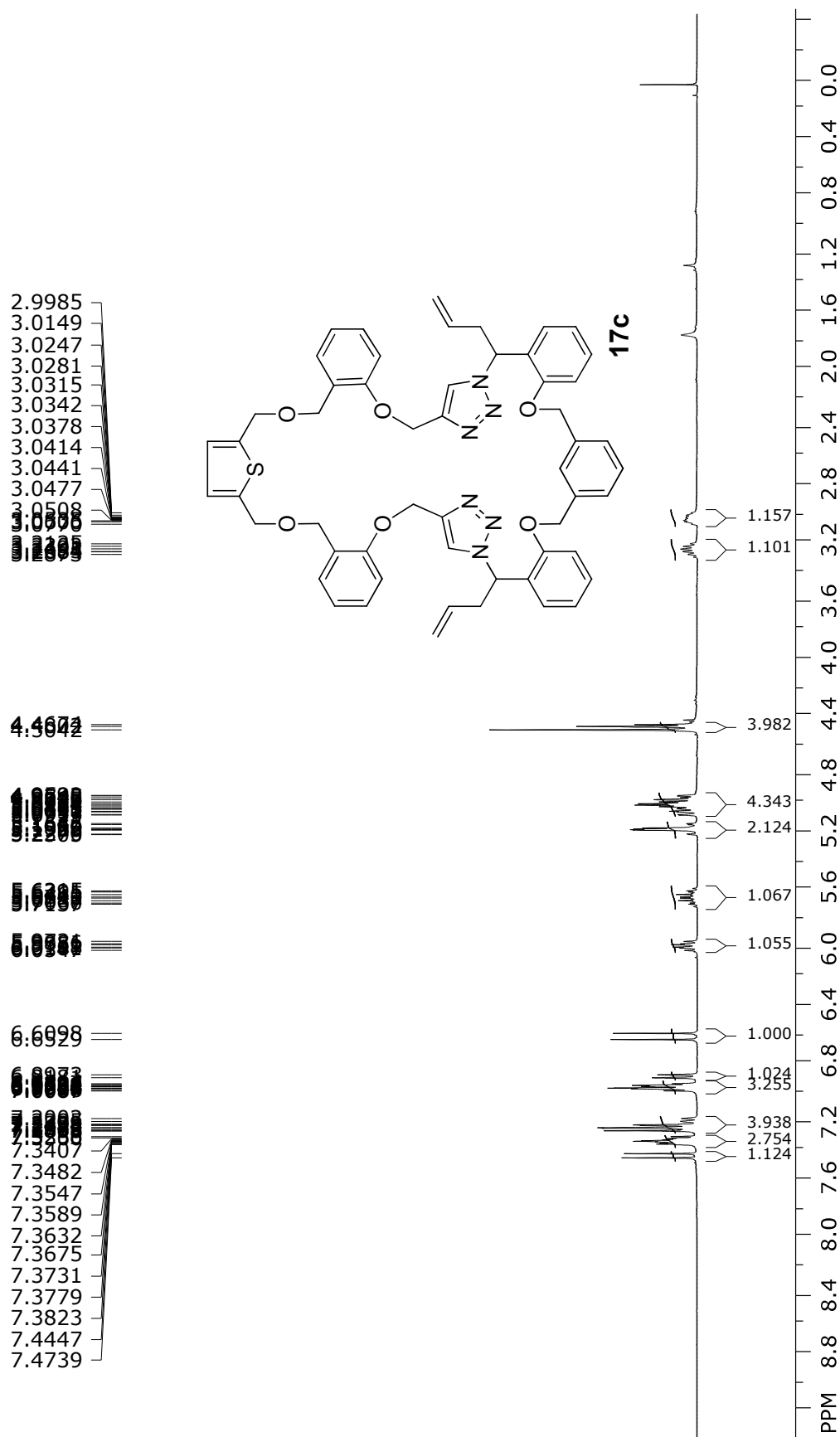


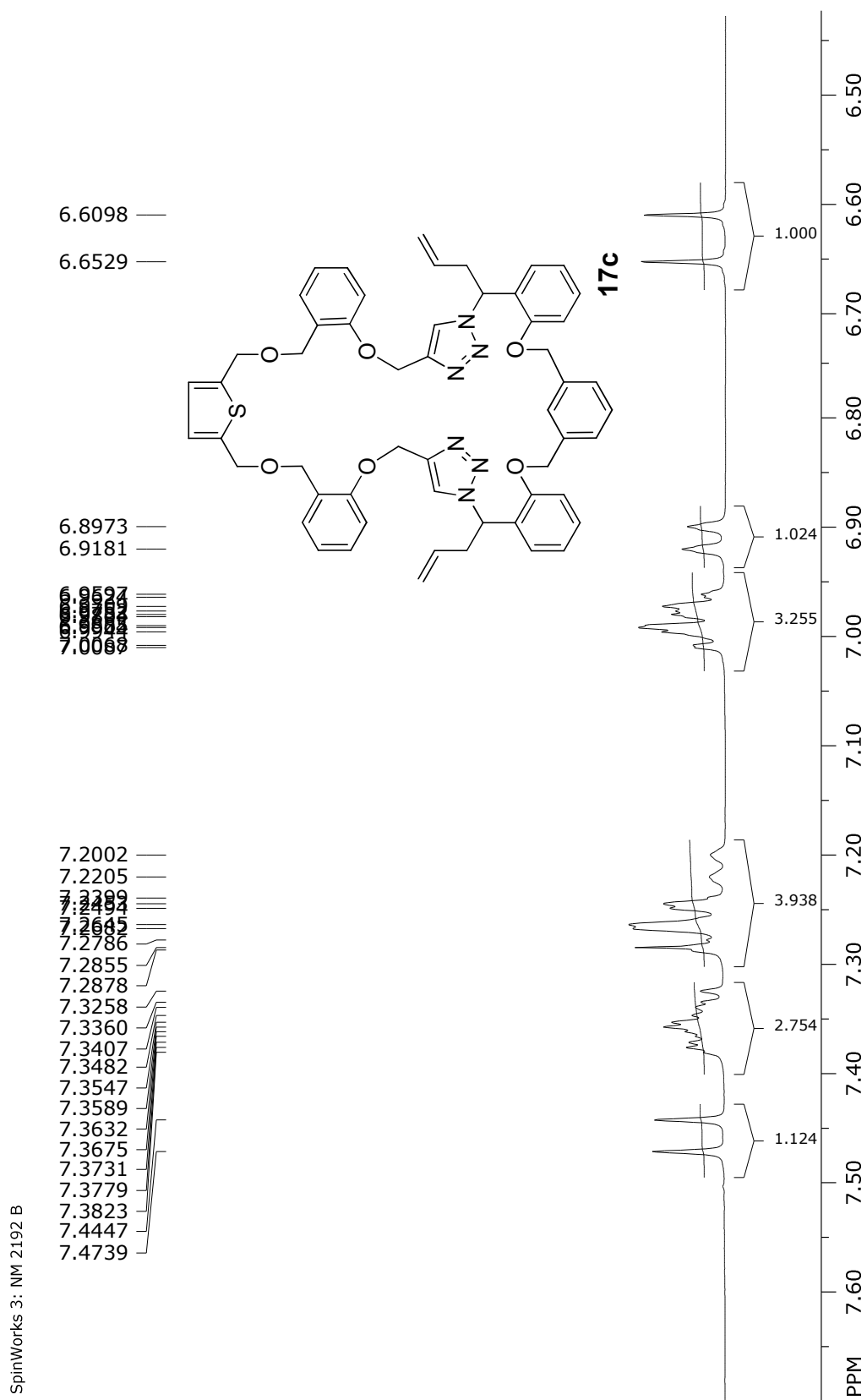




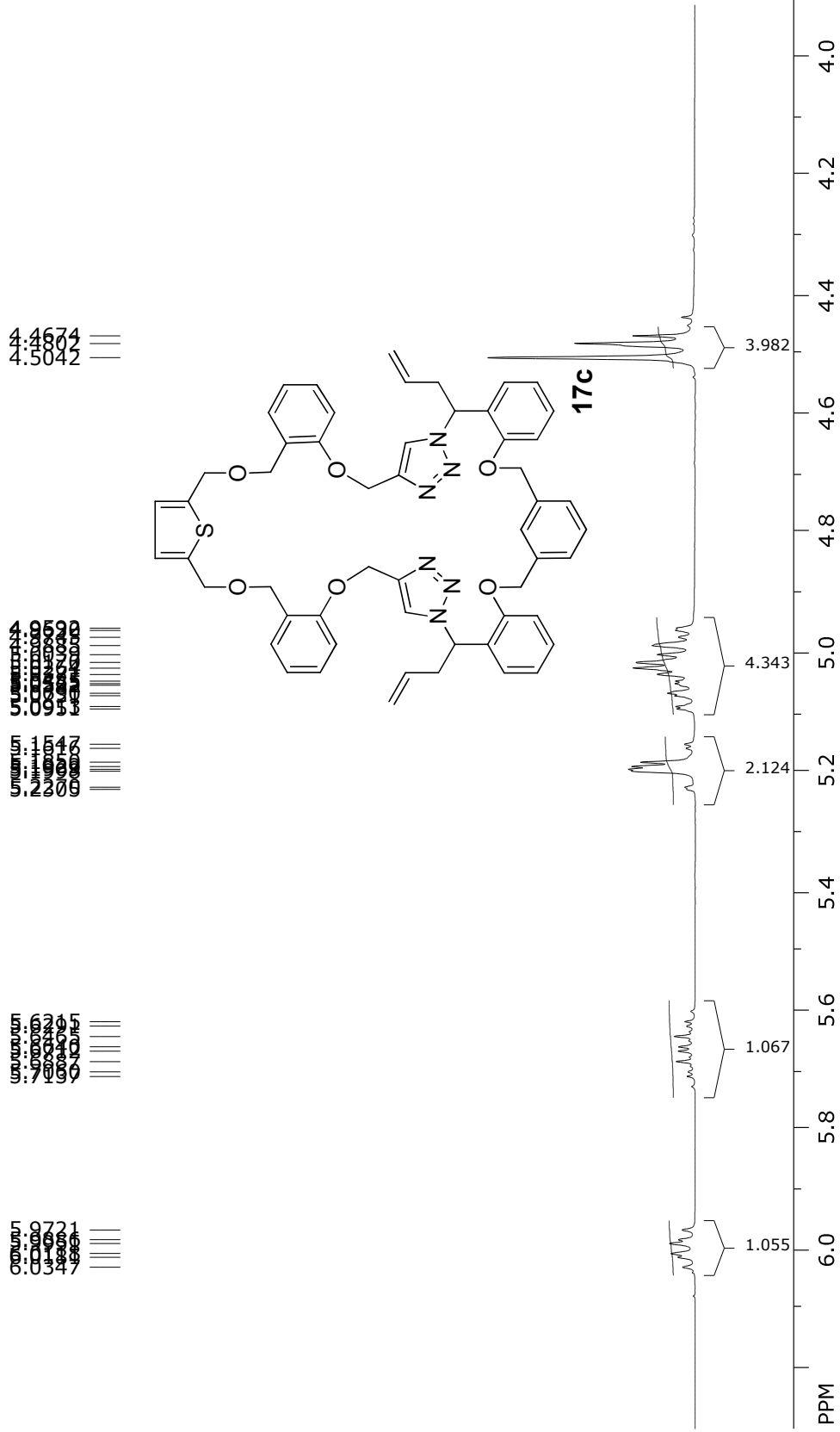


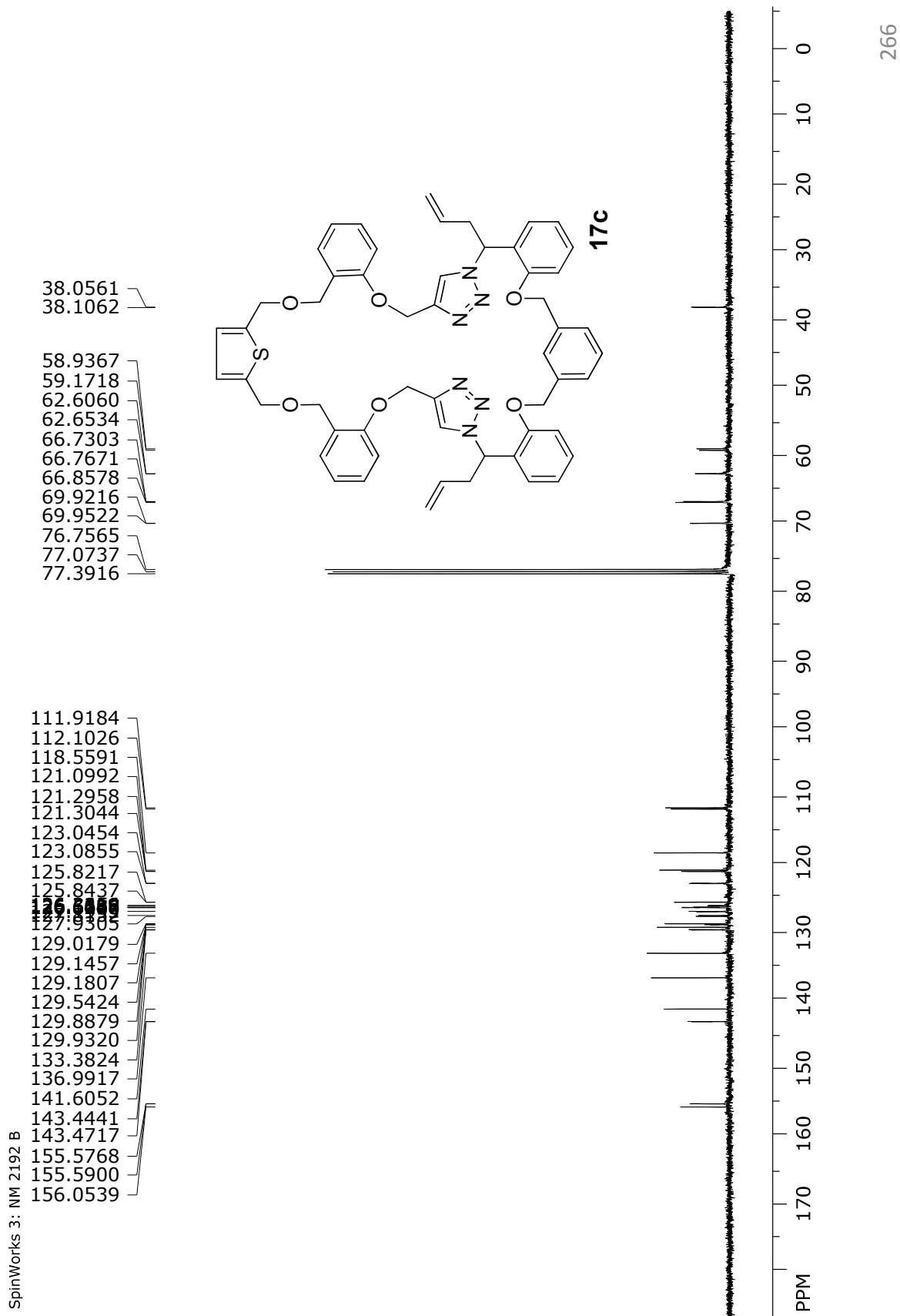
SpinWorks 3: NM 2192 B



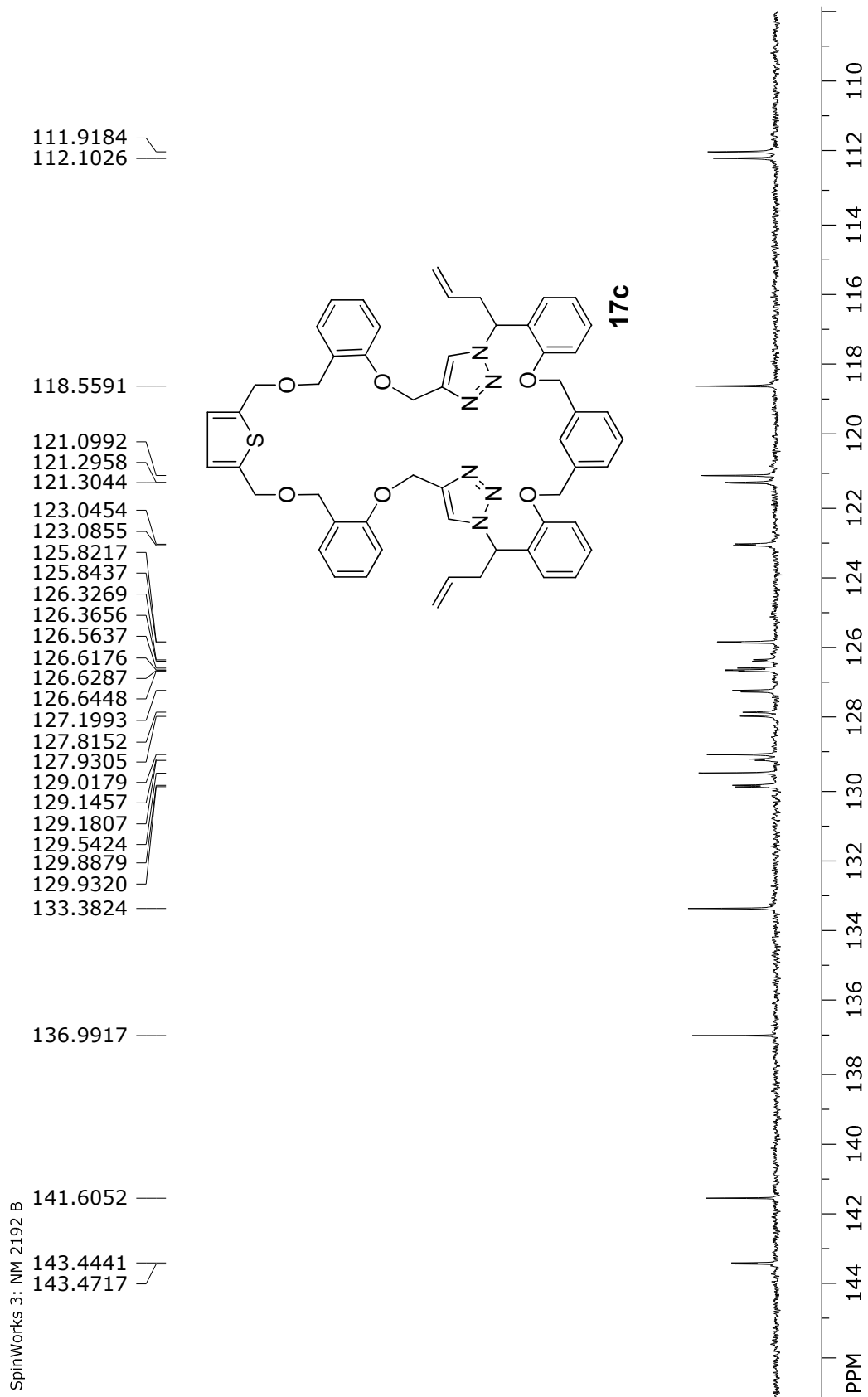


SpinWorks 3: NM 2192 B









SpinWorks 3: NM 2192 B

38.0561  
38.106258.9367  
59.171862.6060  
62.653466.7303  
66.7671  
66.857869.9216  
69.9522