

*Supplementary*

# Zinc- and Copper-Loaded Nanosponges from Cellulose Nanofibers Hydrogels: New Heterogeneous Catalysts for the Synthesis of Aromatic Acetals

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## NMR Spectra

NMR of the crude products are here reported. All the spectra were recorded with a 400 MHz Brüker NMR spectrometer. Products have not been purified. The  $^1\text{H}$ -NMR characterization of all products is in agreement with the literature (see references herein reported). Full NMR characterization of new compound **5** is here reported.

Figure S1: $^1\text{H}$ NMR spectrum of 1-(dimethoxymethyl)-4-fluorobenzene <b>1</b>	p2
Figure S2: $^1\text{H}$ NMR spectrum of 1-(dimethoxymethyl)-4-methylbenzene <b>3a</b>	p2
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Figure S11: $^1\text{H}$ NMR spectrum of 1-(diethoxymethyl)-4-methylbenzene <b>6a</b>	p7
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Figure S20: $^{13}\text{C}$ -APT NMR spectrum of 1-(diethoxymethyl)-4-fluorobenzene <b>5</b>	p11
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Figure S23: HSQC NMR spectrum of 1-(diethoxymethyl)-4-fluorobenzene <b>5</b>	p13

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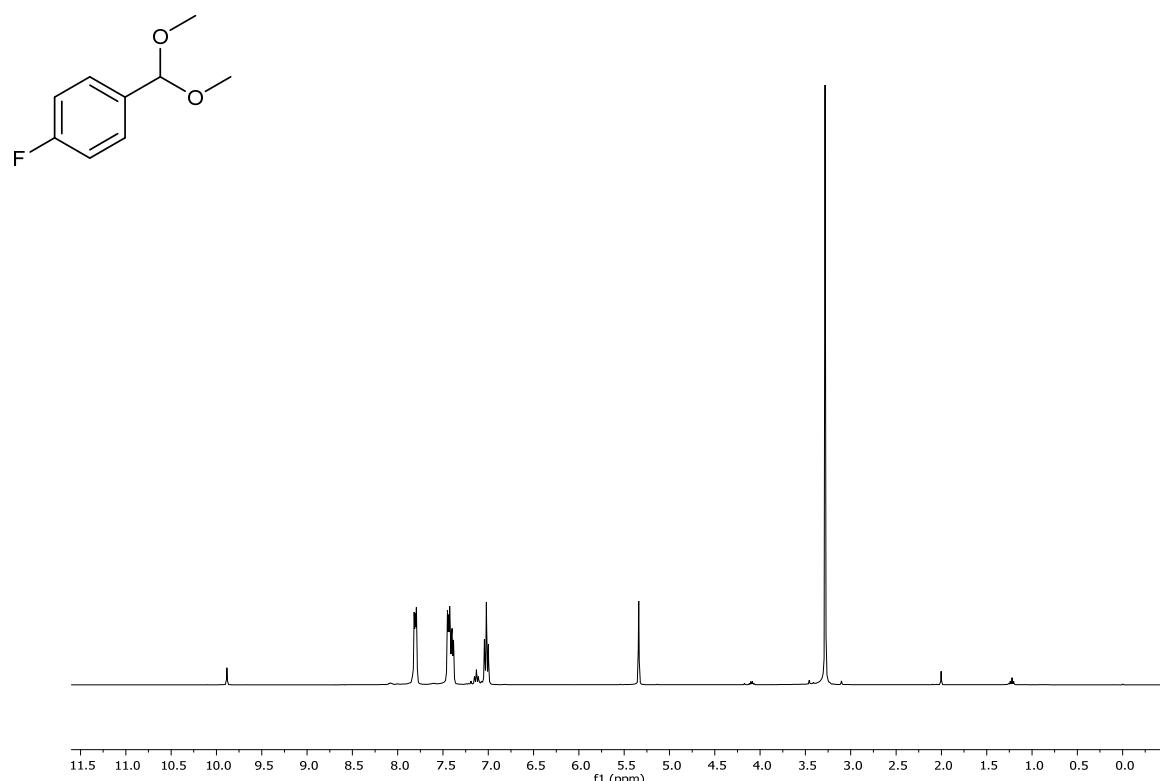
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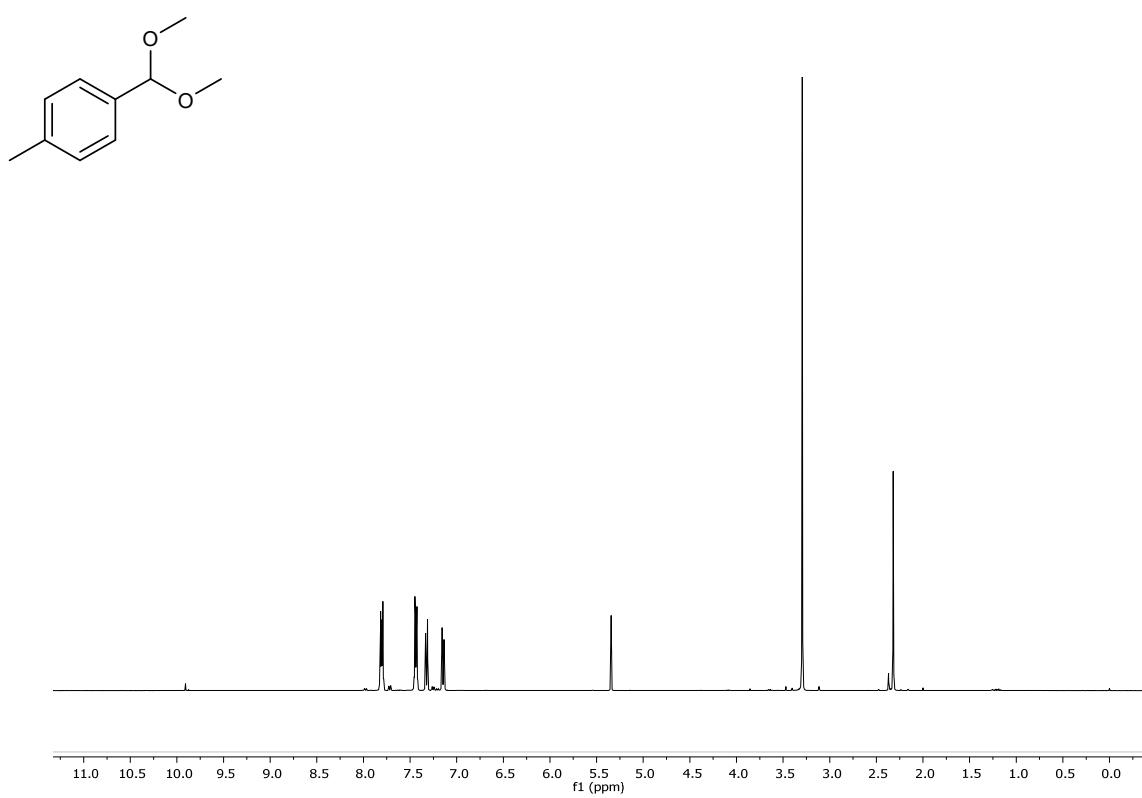
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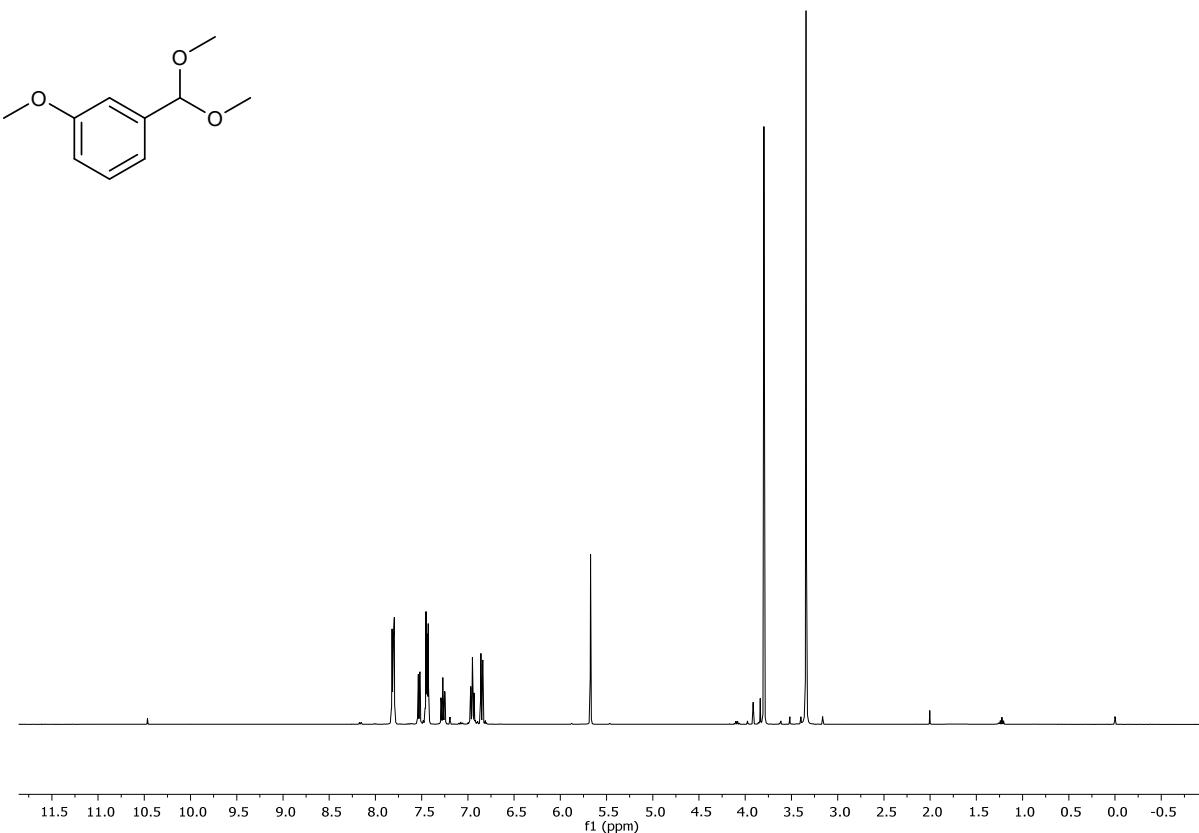
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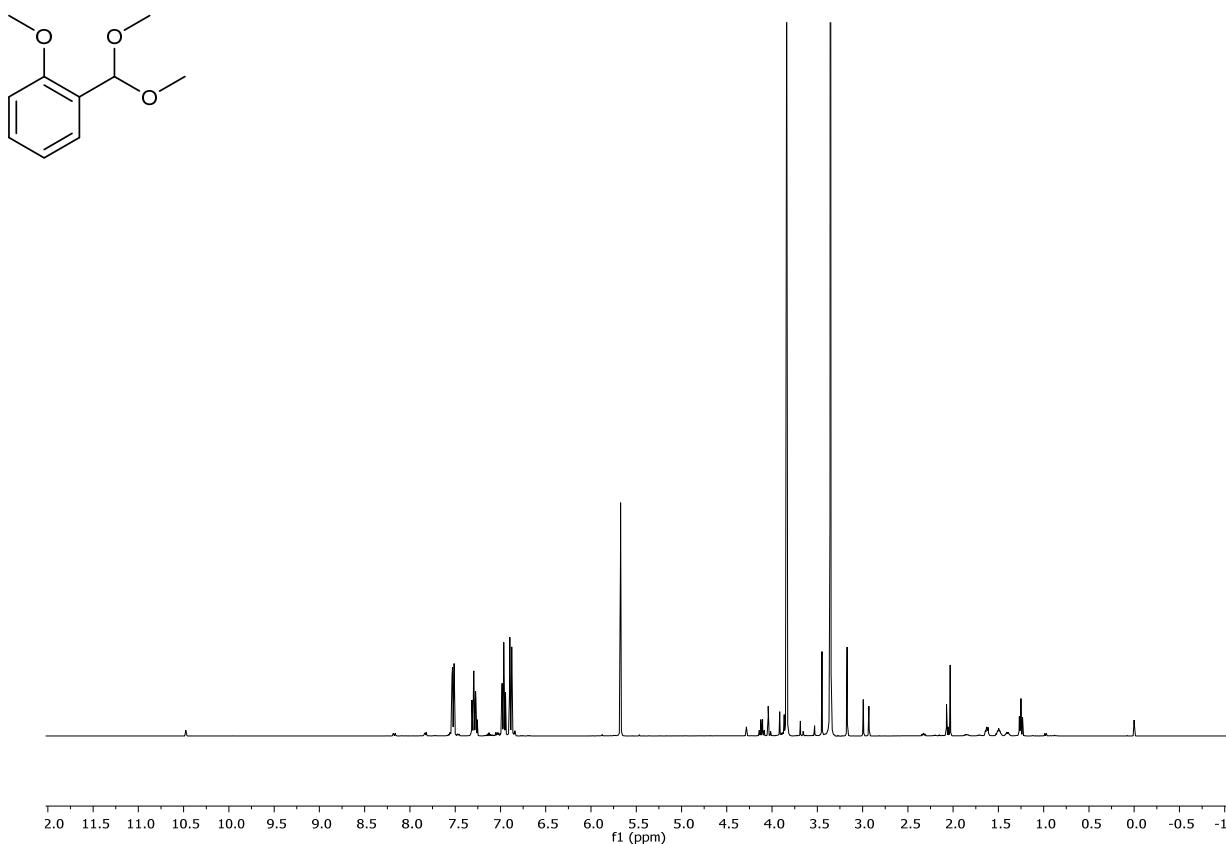
**Figure S1.**  $^1\text{H}$  NMR spectrum of product **1** in  $\text{CDCl}_3$  [1].



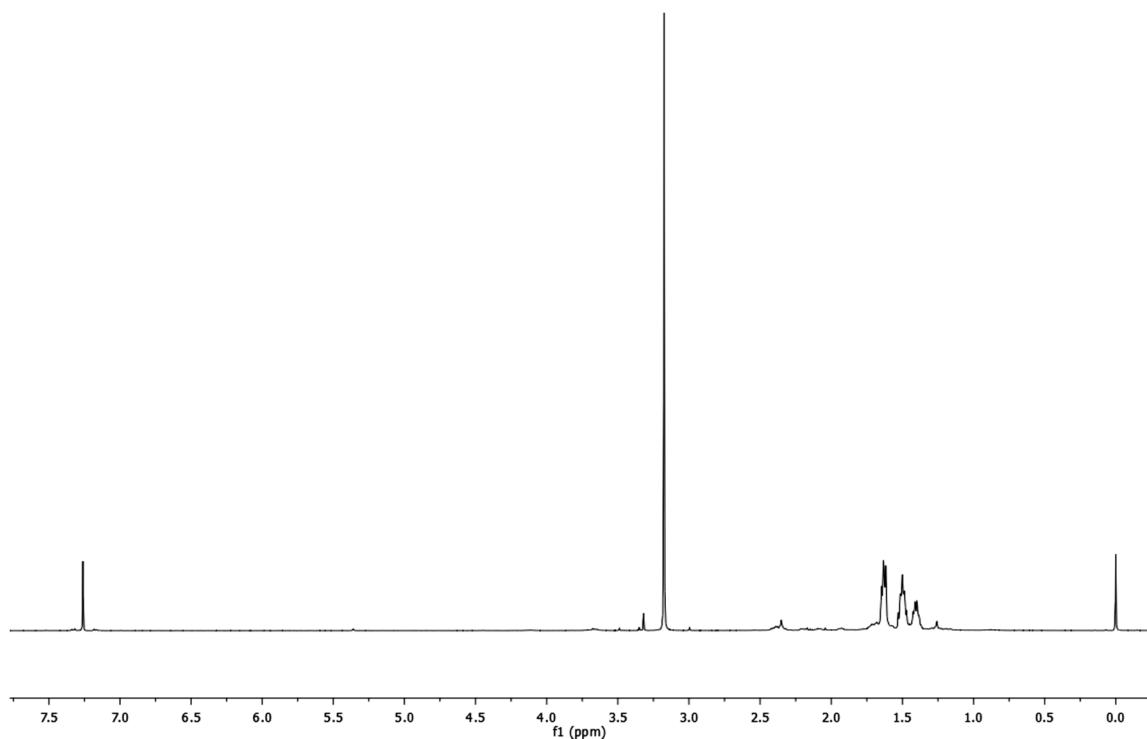
**Figure S2.**  $^1\text{H}$  NMR spectrum of product **3a** in  $\text{CDCl}_3$  [1].



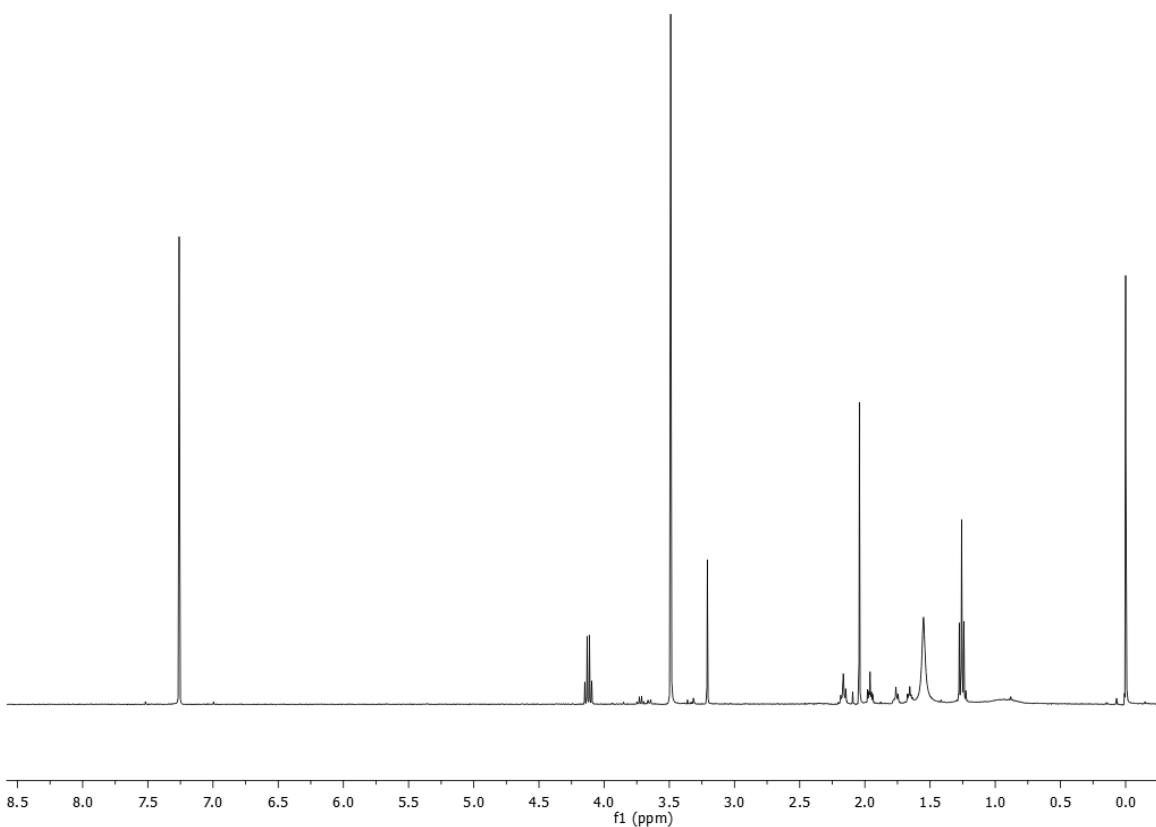
**Figure S3.** <sup>1</sup>H NMR spectrum of product **3b** in CDCl<sub>3</sub> [2].



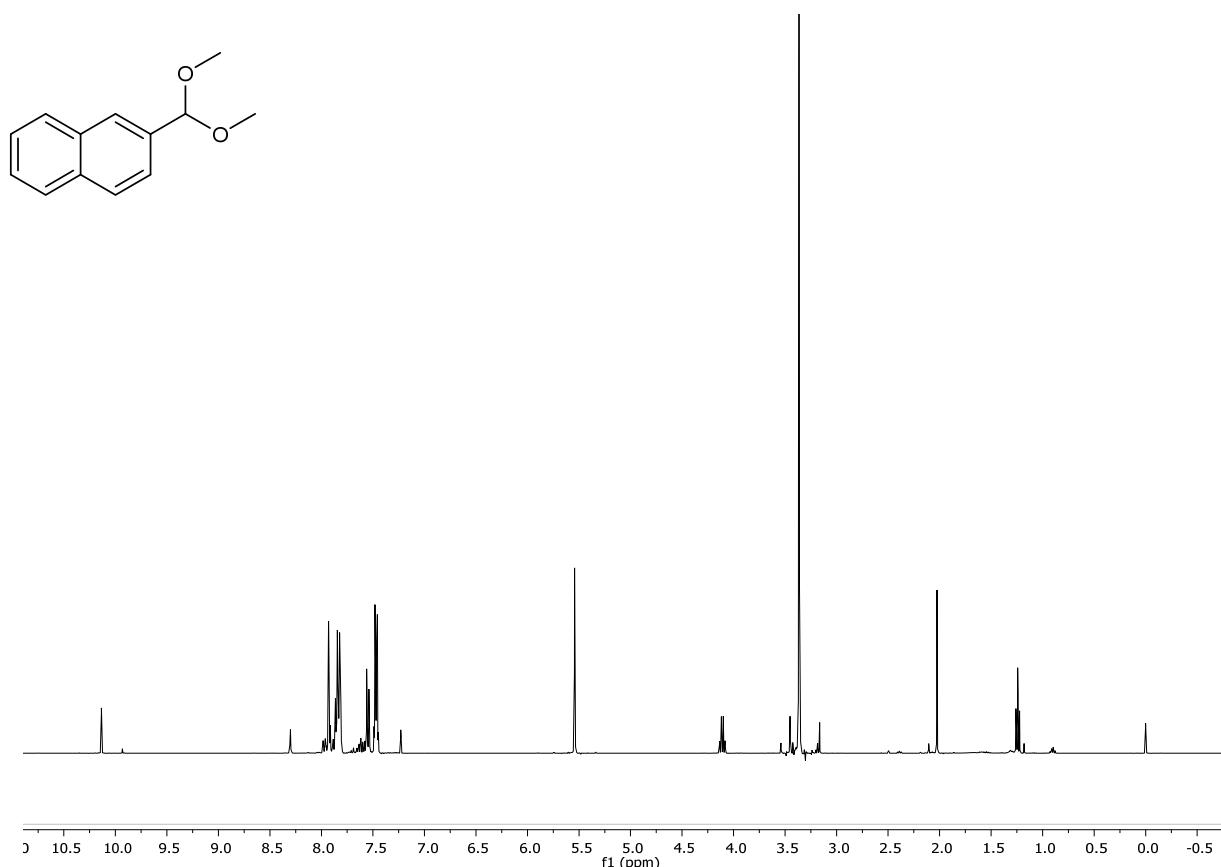
**Figure S4.** <sup>1</sup>H NMR spectrum of product **3c** in CDCl<sub>3</sub> [3].



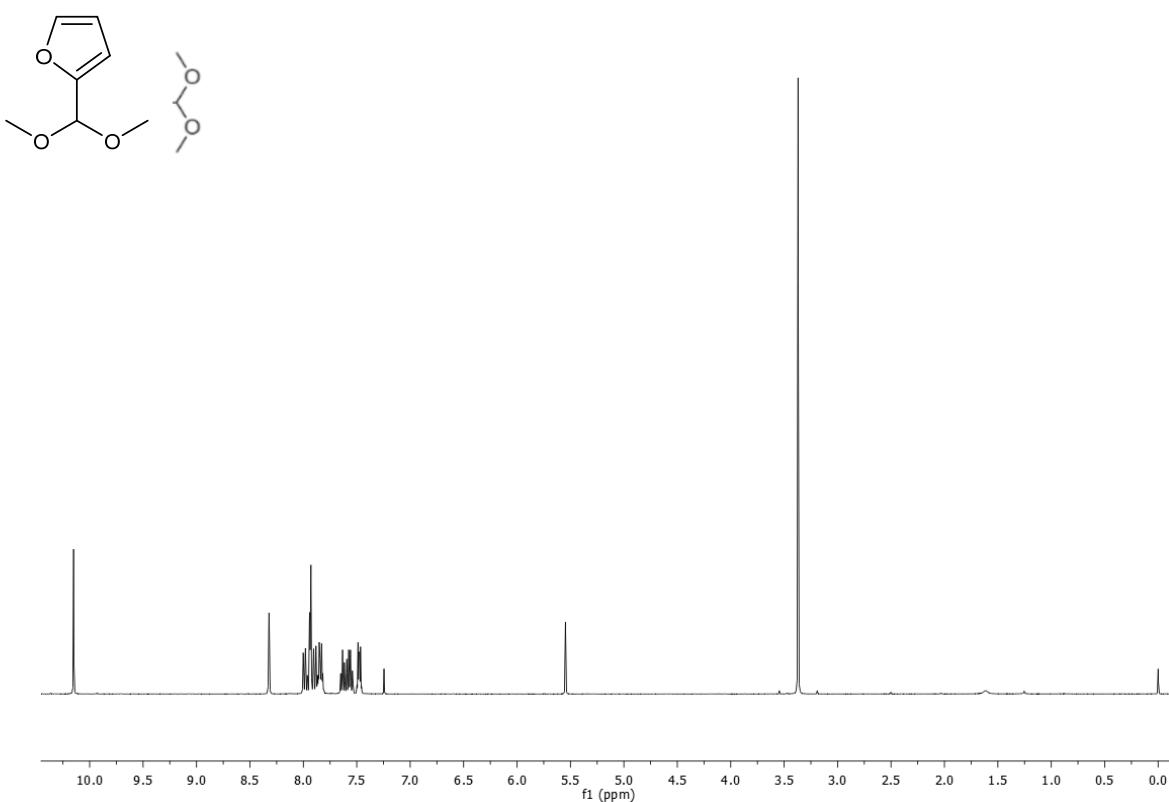
**Figure S5.** <sup>1</sup>H NMR spectrum of product **3d** in  $\text{CDCl}_3$  [4].



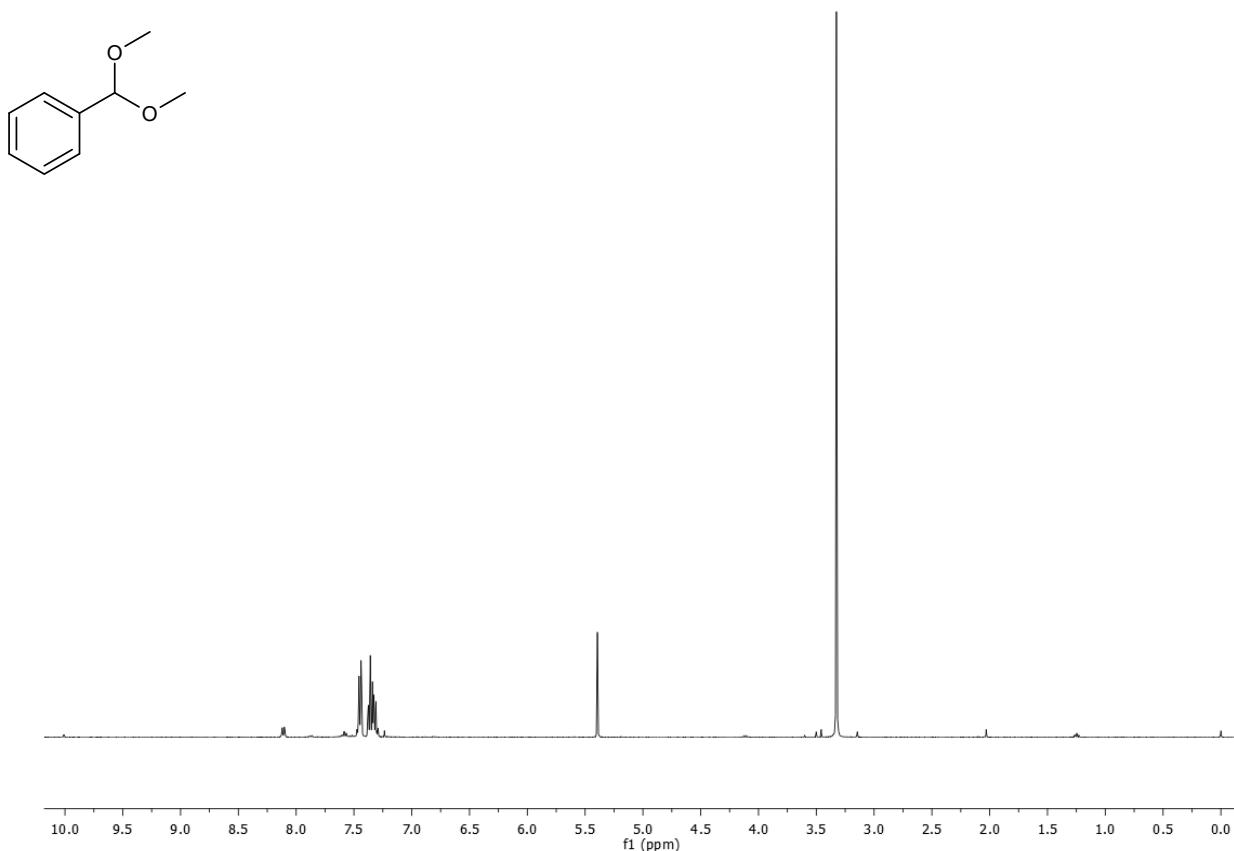
**Figure S6.** <sup>1</sup>H NMR spectrum of product **3e** in  $\text{CDCl}_3$  [5].



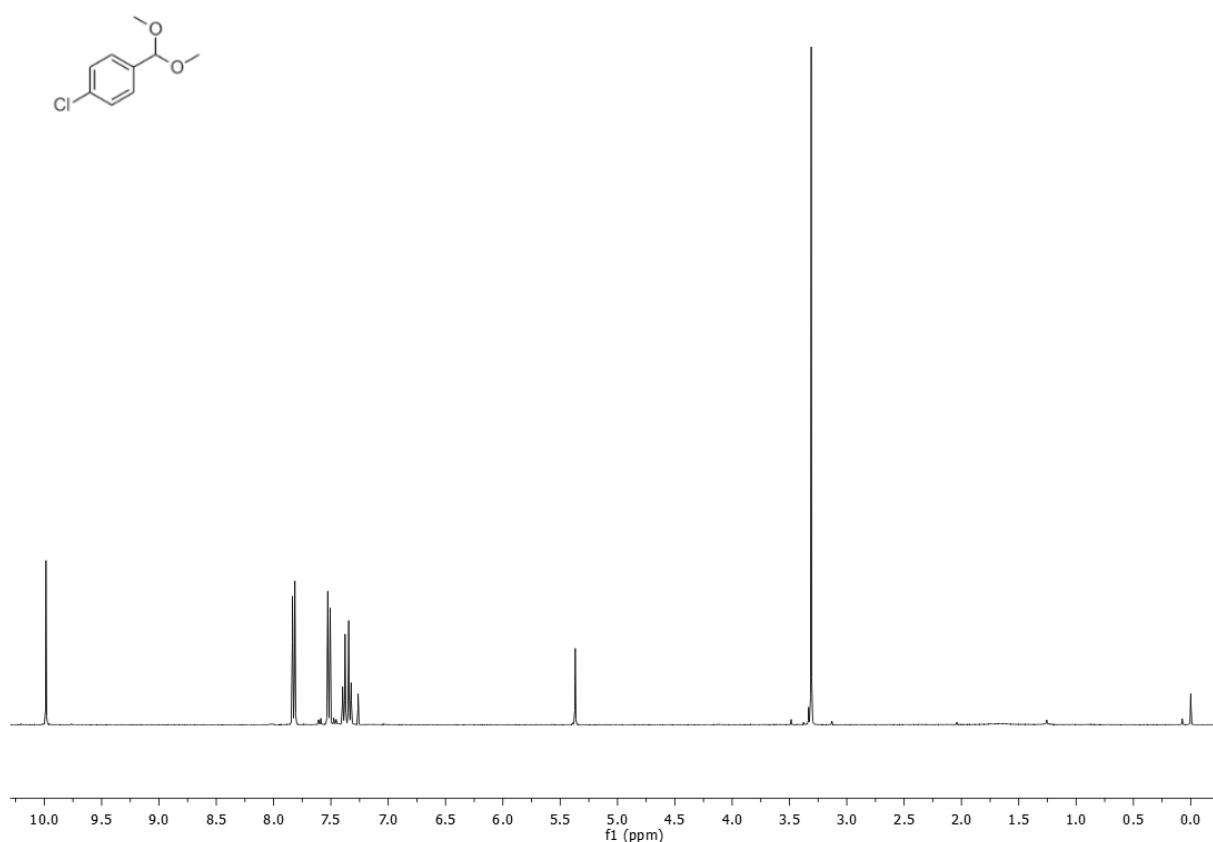
**Figure S7.** <sup>1</sup>H NMR spectrum of product **3f** in CDCl<sub>3</sub> [6].



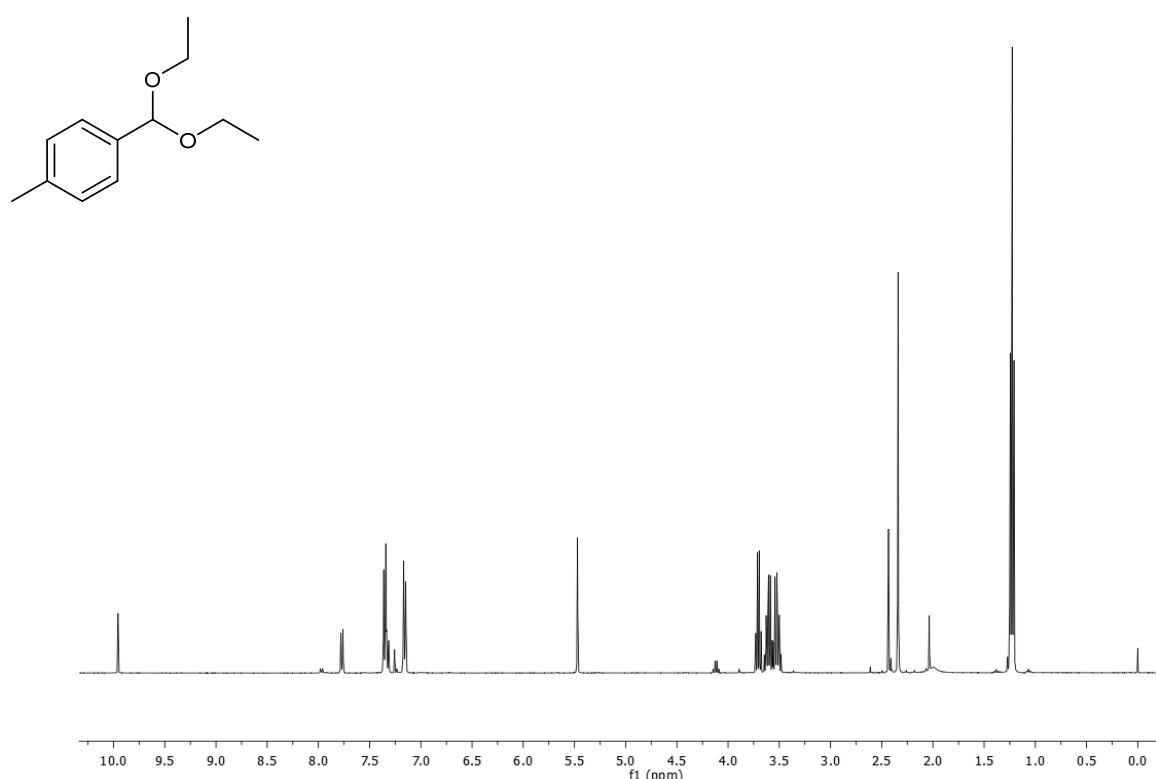
**Figure S8.** <sup>1</sup>H NMR spectrum of product **3g** in CDCl<sub>3</sub> [7].



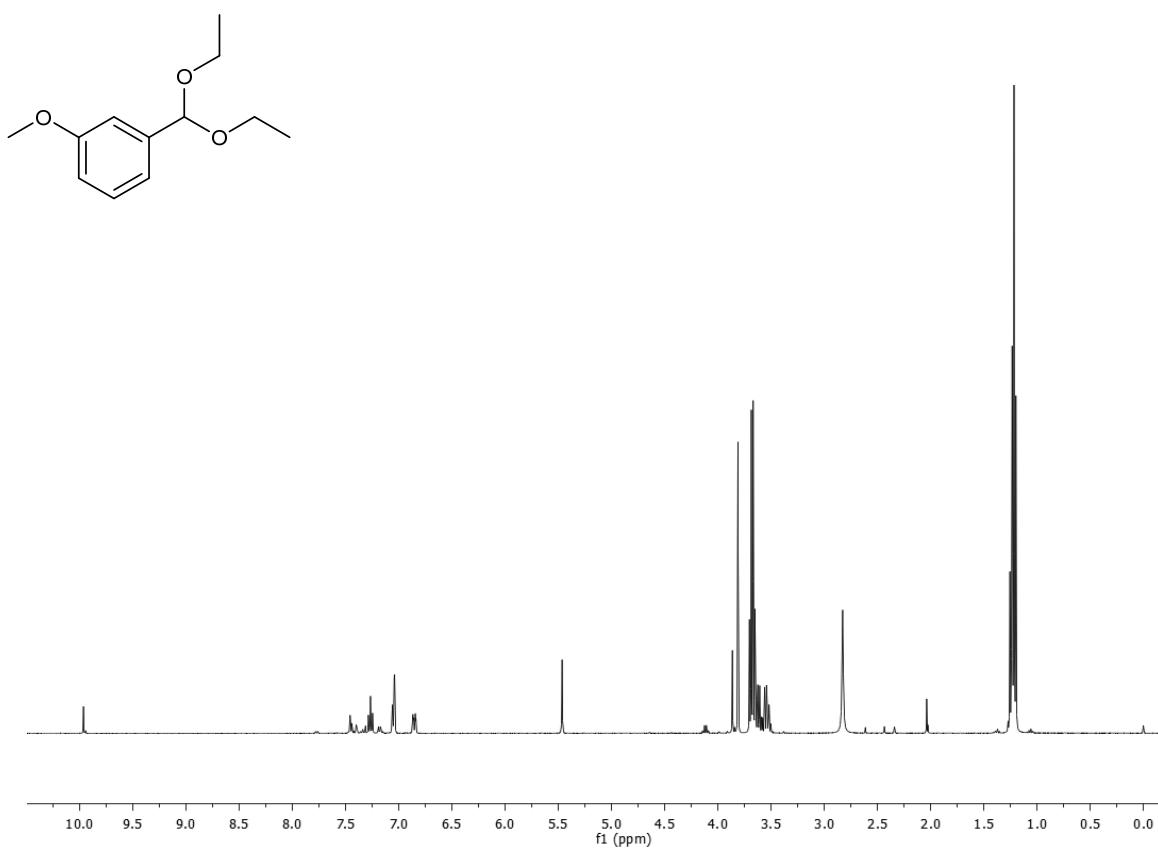
**Figure S9.** <sup>1</sup>H NMR spectrum of product **3h** in CDCl<sub>3</sub> [7].



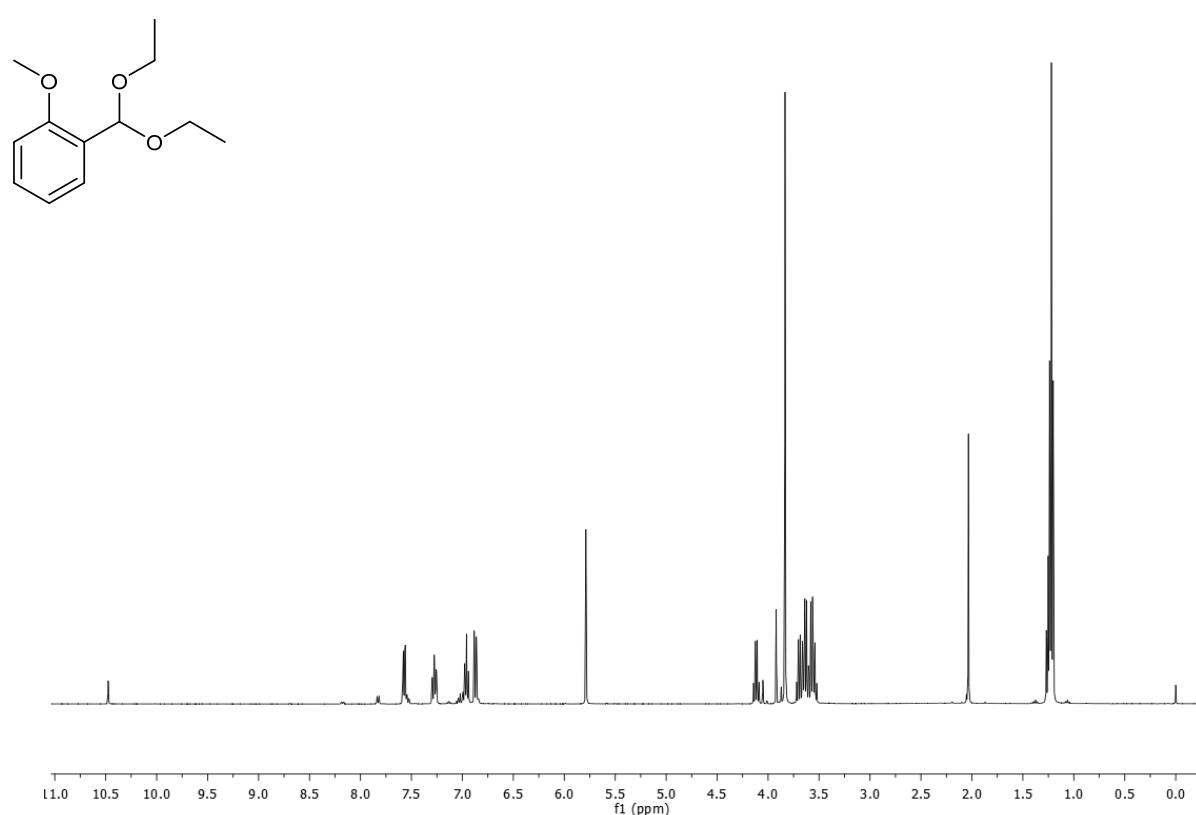
**Figure S10.** <sup>1</sup>H NMR spectrum of product **3i** in CDCl<sub>3</sub> [1].



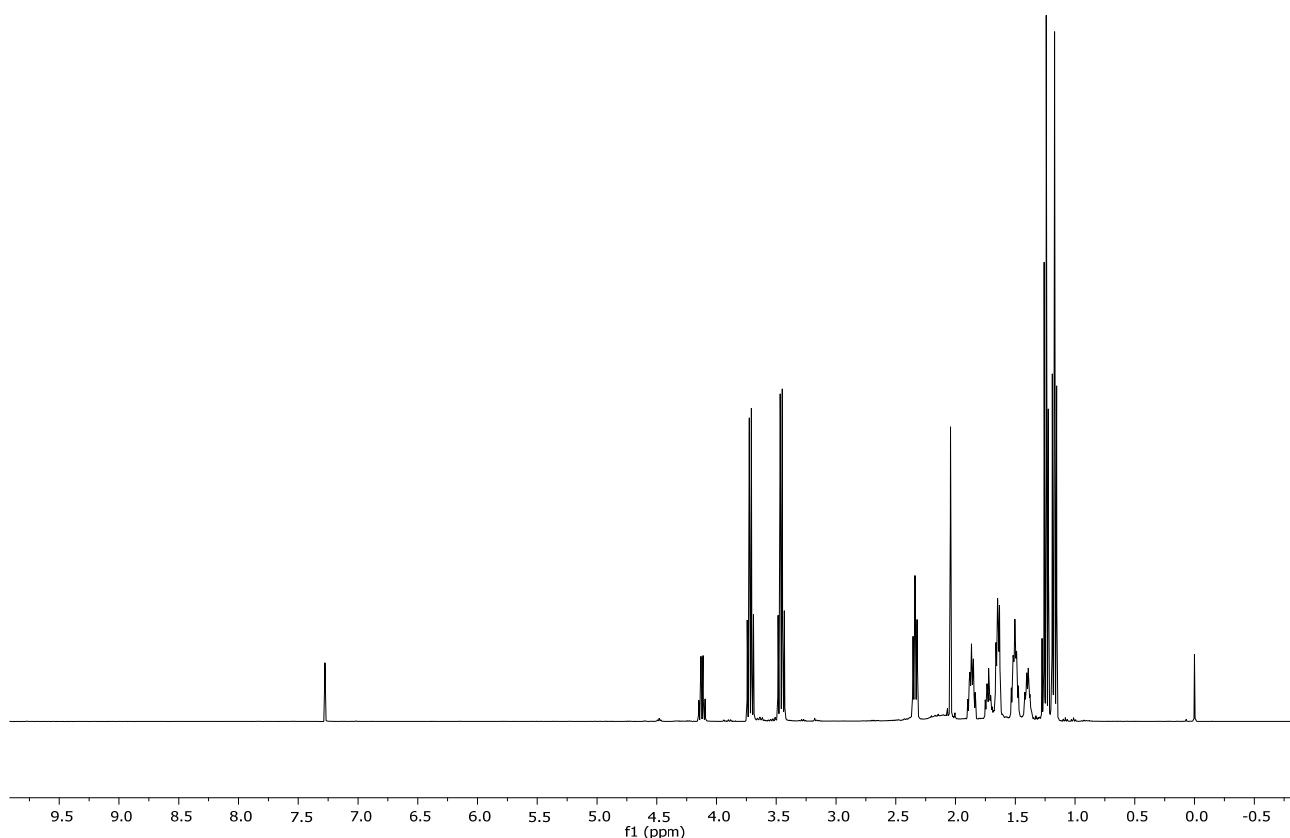
**Figure S11.** <sup>1</sup>H NMR spectrum of product **6a** in CDCl<sub>3</sub> [8].



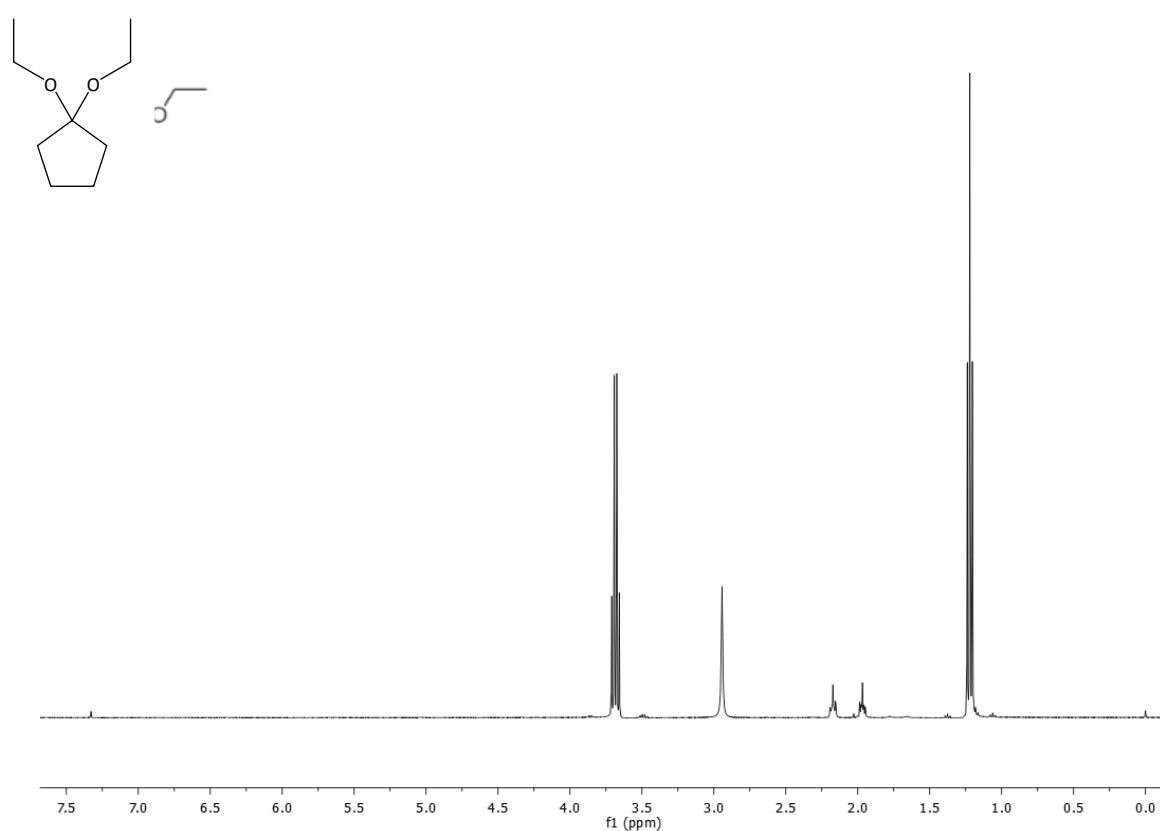
**Figure S12.** <sup>1</sup>H NMR spectrum of product **6b** in CDCl<sub>3</sub> [9].



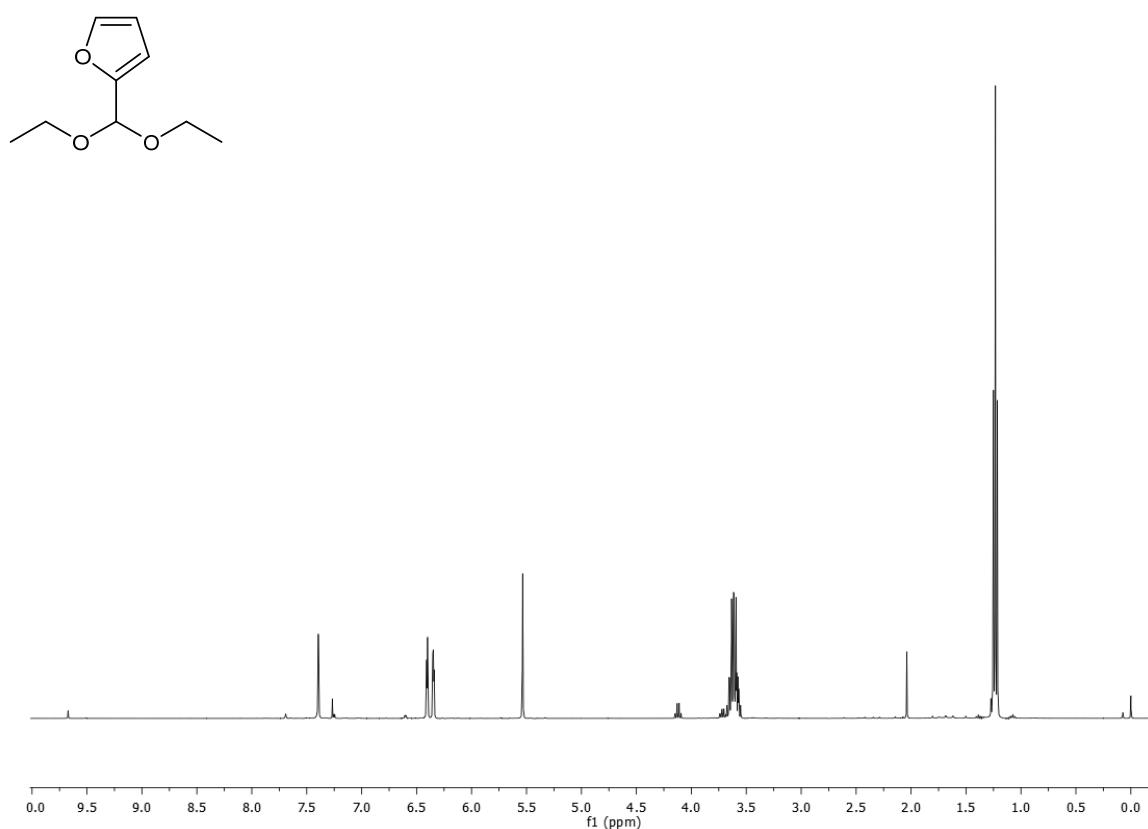
**Figure S13.** <sup>1</sup>H NMR spectrum of product **6c** in CDCl<sub>3</sub> [9].-



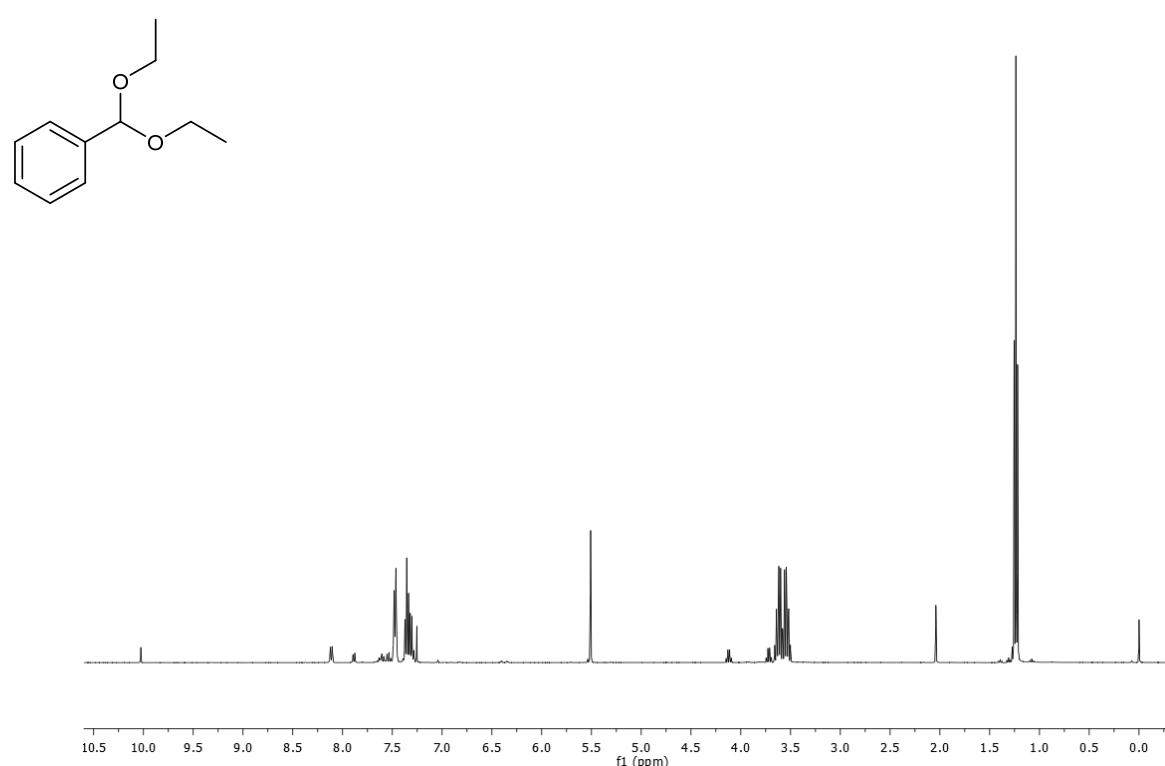
**Figure S14.** <sup>1</sup>H NMR spectrum of product **6d** in CDCl<sub>3</sub> [8].



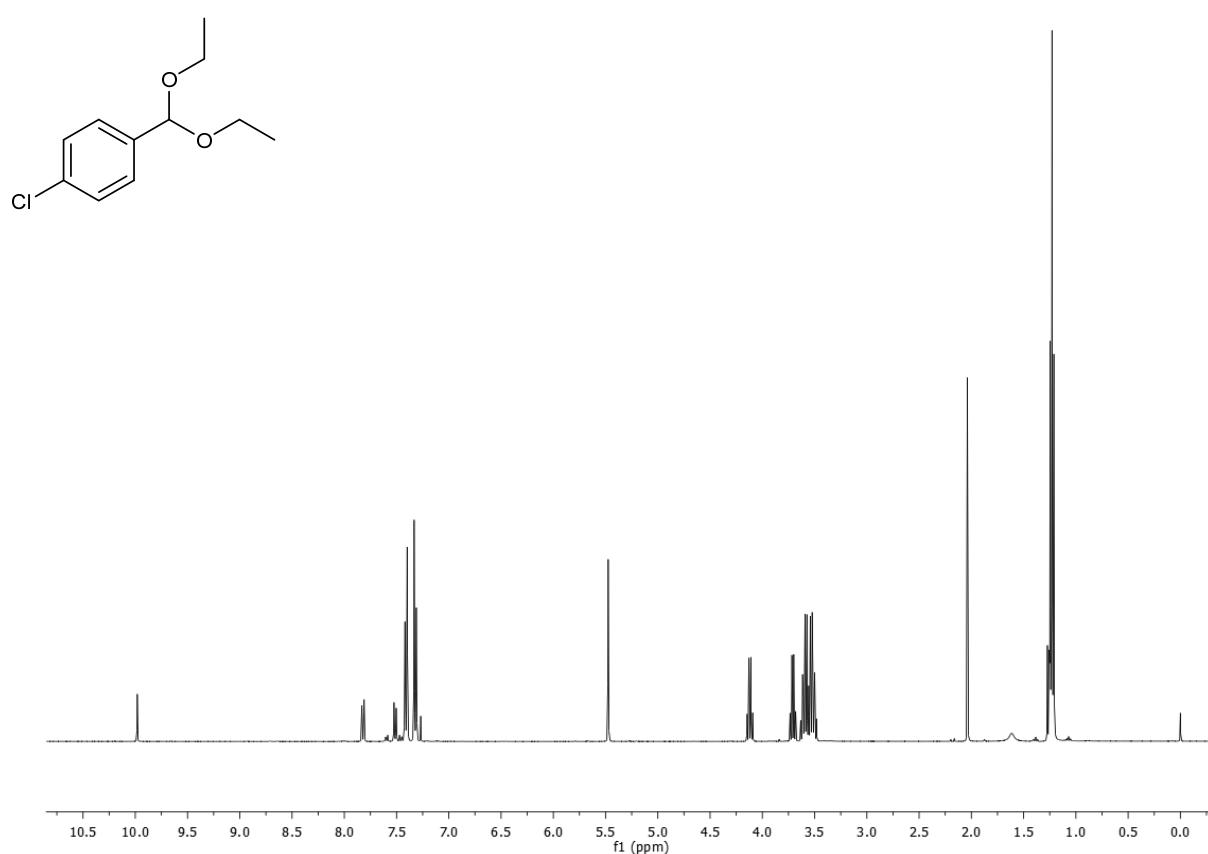
**Figure S15.** <sup>1</sup>H NMR spectrum of product **6e** in CDCl<sub>3</sub> [10].



**Figure S16.** <sup>1</sup>H NMR spectrum of product **6g** in CDCl<sub>3</sub> [11].

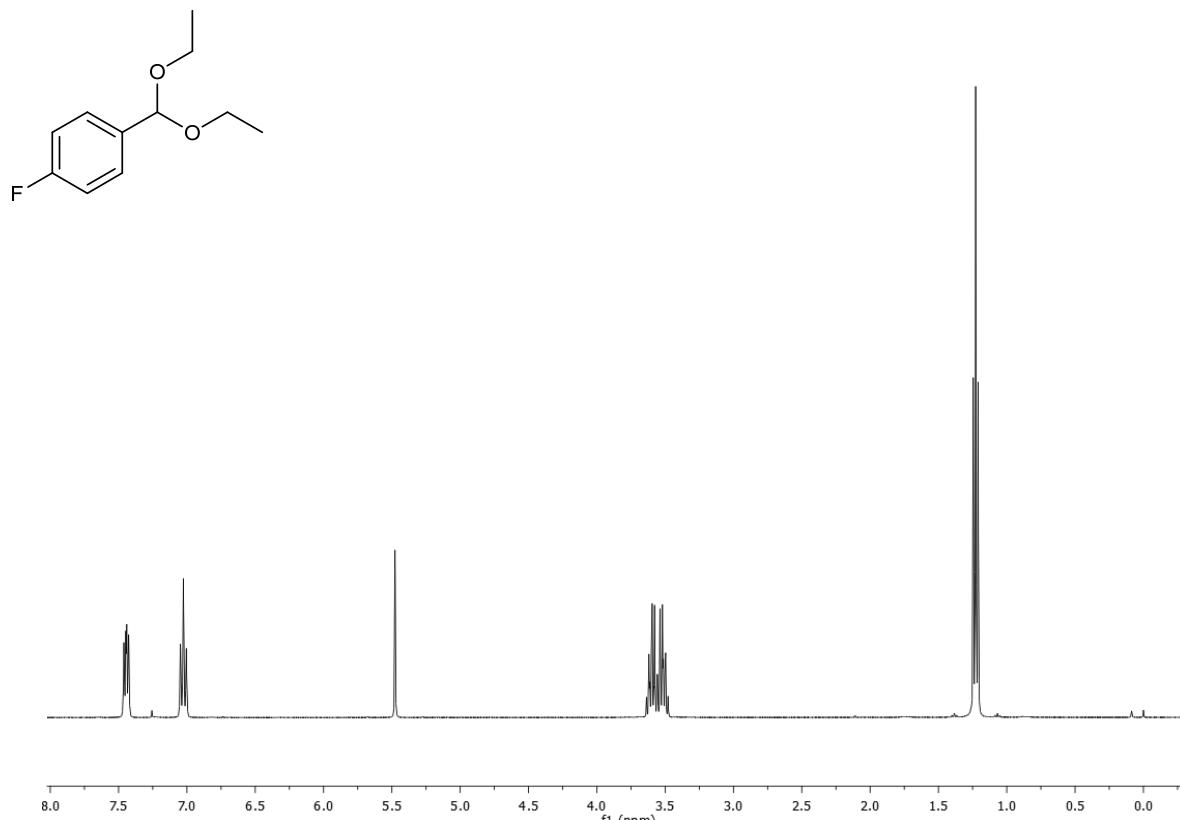


**Figure S17.** <sup>1</sup>H NMR spectrum of product **6h** in CDCl<sub>3</sub> [8].

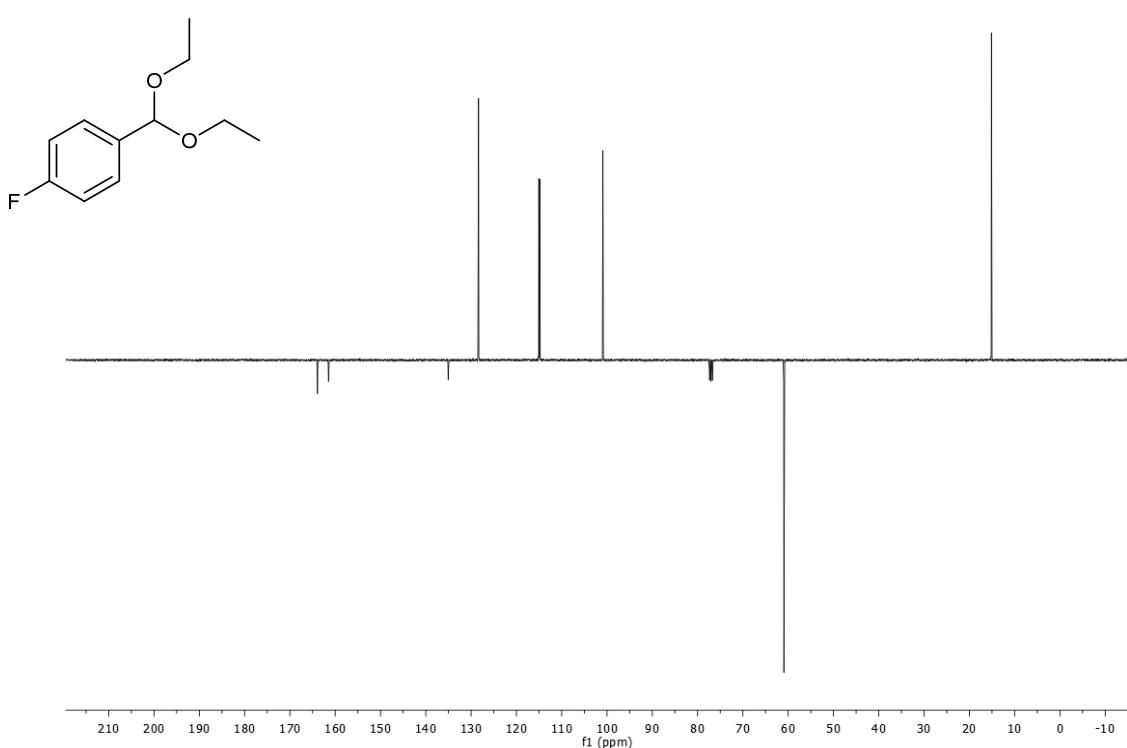


**Figure S18.** <sup>1</sup>H NMR spectrum of product **6i** in CDCl<sub>3</sub> [12].

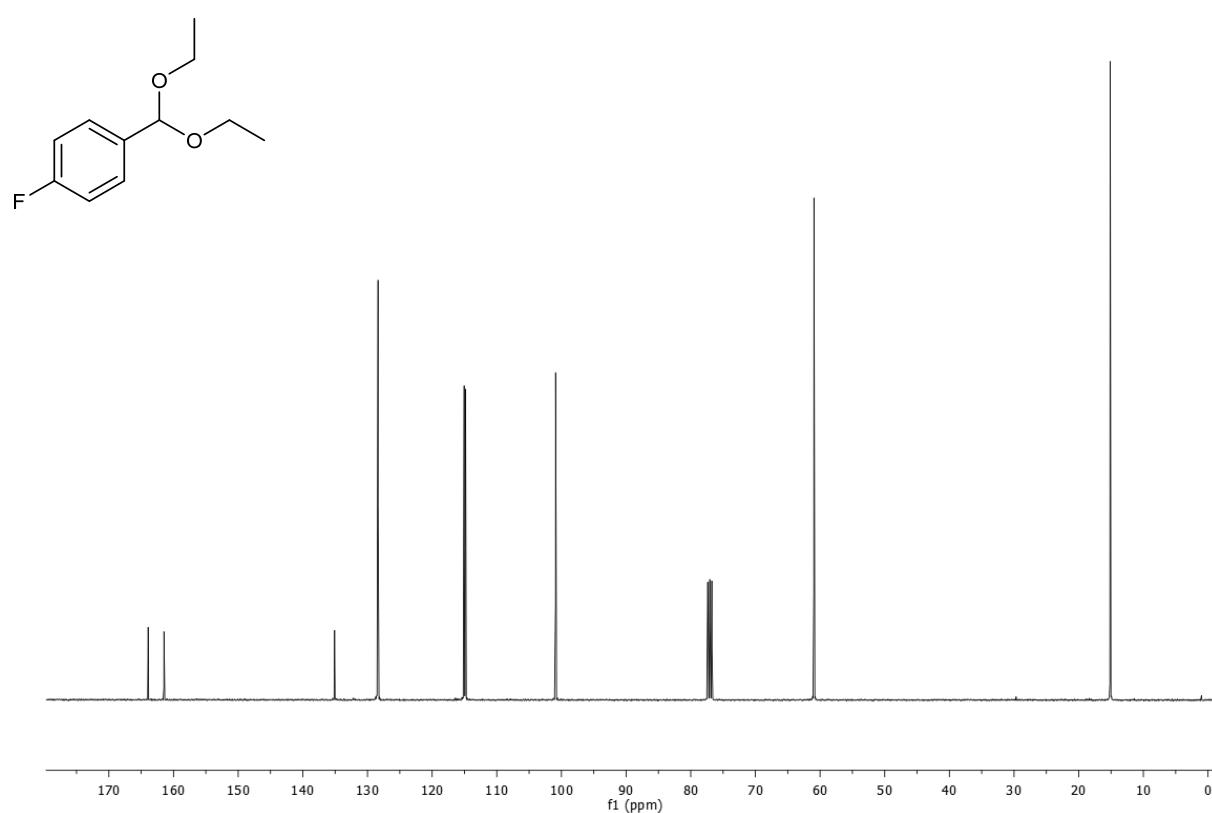
The reaction product obtained reacting *p*-F-Benzaldehyde and ethanol (product **5**) is not characterized in literature. Isolation and complete characterization were carried out through NMR analysis. Below, complete NMR characterization of product **5** is reported.



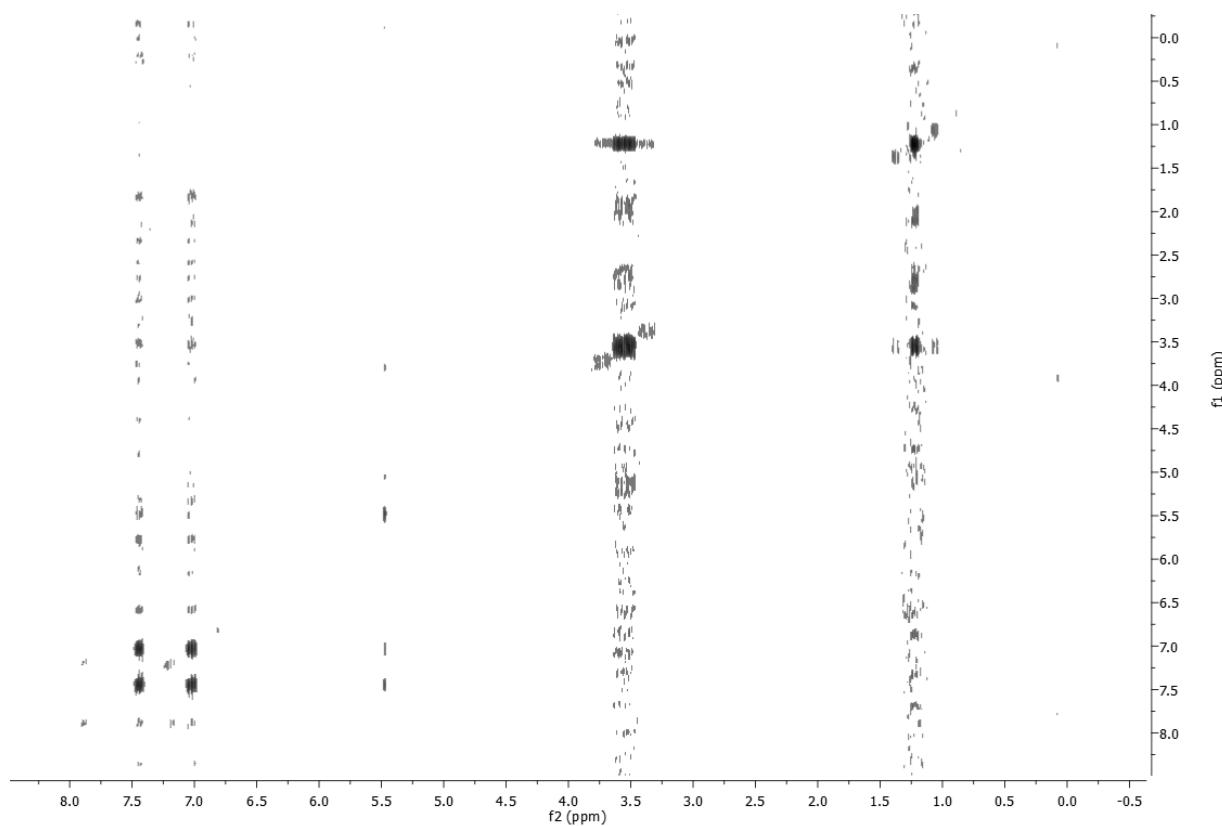
**Figure S19.** <sup>1</sup>H NMR spectrum of product **5** in CDCl<sub>3</sub>.



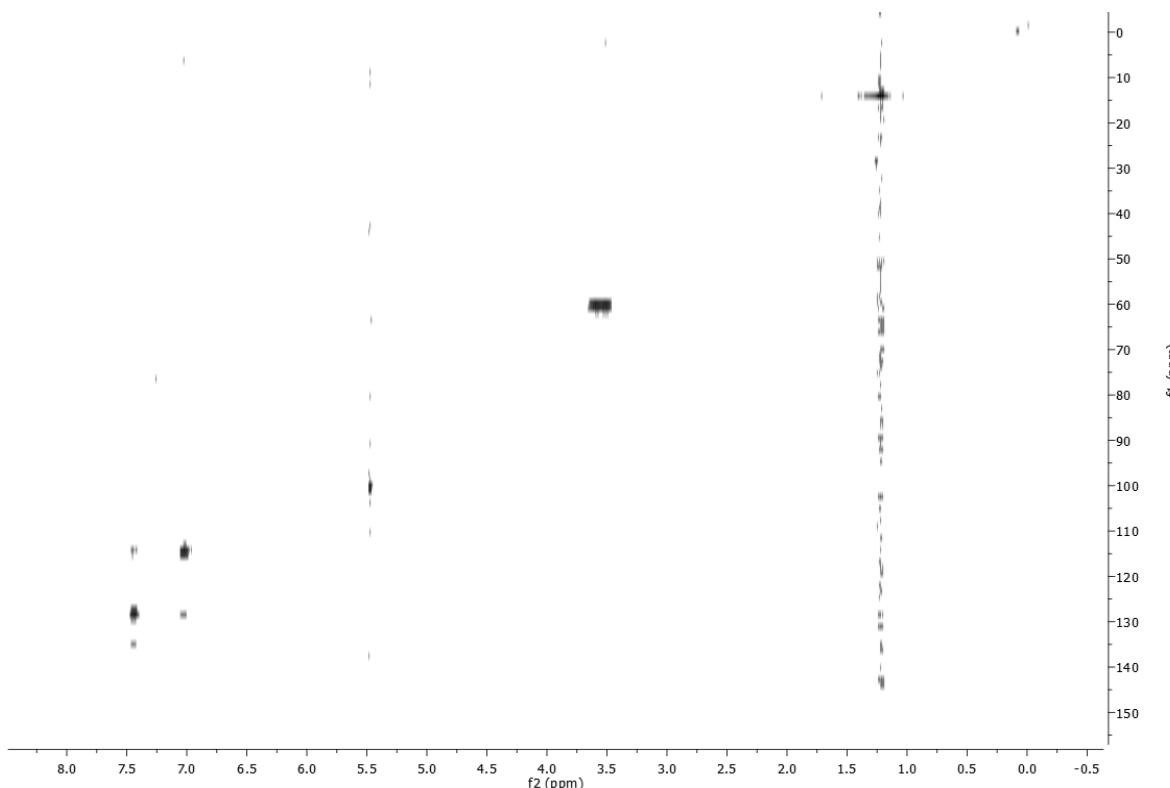
**Figure S20.** <sup>13</sup>C-APT NMR spectrum of product **5** in CDCl<sub>3</sub>.



**Figure S21.**  $^{13}\text{C}$  NMR spectrum of product 5 in  $\text{CDCl}_3$ .



**Figure S22.** COSY NMR spectrum of product 5 in  $\text{CDCl}_3$ .



**Figure S23.** HSQC NMR spectrum of product **5** in  $\text{CDCl}_3$ .

## References

- Wilk, M.; Trzepizur, D.; Koszelewski, D.; Brodzka, A.; Ostaszewski, R. Synthesis of (E)- $\alpha,\beta$ -unsaturated carboxylic esters derivatives from cyanoacetic acid via promiscuous enzyme-promoted cascade esterification/Knoevenagel reaction. *Bioorg. Chem.* **2019**, doi:10.1016/j.bioorg.2019.02.041.
- Emsermann, J.; Opatz, T. Photochemical Approaches to the Bilobalide Core. *European J. Org. Chem.* **2017**, doi:10.1002/ejoc.201700461.
- Xavier, T.; Rayapin, C.; Le Gall, E.; Presset, M. Multicomponent Aromatic and Benzylic Mannich Reactions through C–H Bond Activation. *Chem. - A Eur. J.* **2019**, doi:10.1002/chem.201903414.
- Spiliopoulou, N.; Nikitas, N.F.; Kokotos, C.G. Photochemical synthesis of acetals utilizing Schreiner's thiourea as the catalyst. *Green Chem.* **2020**, doi:10.1039/d0gc01135e.
- Baxter, M.; Bolshan, Y. A General Access to Propargylic Ethers through Brønsted Acid Catalyzed Alkylation of Acetals and Ketals with Trifluoroborates. *Chem. - A Eur. J.* **2015**, doi:10.1002/chem.201502797.
- Lan, J.; Jiang, G.; Yang, J.; Zhu, H.; Le, Z.; Xie, Z.  $\alpha$ -Chymotrypsin-Induced Acetalization of Aldehydes and Ketones with Alcohols. *Synth.* **2020**, doi:10.1055/s-0039-1690883.
- Subaramanian, M.; Landge, V.G.; Mondal, A.; Gupta, V.; Balaraman, E. Nickel-Catalyzed Chemoselective Acetalization of Aldehydes With Alcohols under Neutral Conditions. *Chem. - An Asian J.* **2019**, doi:10.1002/asia.201900908.
- Ugarte, R.A.; Hudnall, T.W. Antimony(v) catalyzed acetalisation of aldehydes: An efficient, solvent-free, and recyclable process. *Green Chem.* **2017**, doi:10.1039/c6gc03629e.
- Maegawa, T.; Otake, K.; Goto, A.; Fujioka, H. Direct conversion of acetals to esters with high regioselectivity via O,P-acetals. *Org. Biomol. Chem.* **2011**, doi:10.1039/c1ob05687e.
- Silverman, R.B.; Ding, C.Z.; Silverman, R.B.; Ding, C.Z. Chemical Model for a Mechanism of Inactivation of Monoamine Oxidase by Heterocyclic Compounds. Electronic Effects on Acetal Hydrolysis. *J. Am. Chem. Soc.* **1993**, doi:10.1021/ja00064a020.
- Mensah, E.A.; Green, S.D.; West, J.; Kindoll, T.; Lazaro-Martinez, B. Formation of Acetals and Ketals from Carbonyl Compounds: A New and Highly Efficient Method Inspired by Cationic Palladium. *Synlett* **2019**, doi:10.1055/s-0039-1690497.
- Du, Y.; Tian, F. Brønsted acidic ionic liquids as efficient and recyclable catalysts for protection of carbonyls to acetals and ketals under mild conditions. *Synth. Commun.* **2005**, doi:10.1080/00397910500214409.