

Supporting Information

Mechanistic Investigation of a Visible Light Mediated Dehalogenation/Cyclisation Reaction using Iron(III), Iridium(III) and Ruthenium(II) Photosensitizers

Akin Aydogan,¹ Rachel E. Bangle,² Simon De Kreijger,¹ John C. Dickenson,² Michael L. Singleton,¹ Emilie Cauët,³ Alejandro Cadranel,⁴ Gerald J. Meyer,² Benjamin Elias¹ Renato N. Sampaio,^{2,5,*} and Ludovic Troian-Gautier^{1,*}

¹Université catholique de Louvain (UCLouvain), Institut de la Matière Condensée et des Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1, bte L4.01.02, 1348 Louvain-la-Neuve, Belgium

²Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, 27599-3290, United States

³Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (CP 160/09), Université libre de Bruxelles, 50 av. F. D. Roosevelt, B-1050 Brussels, Belgium

⁴Department of Chemistry and Pharmacy, Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

⁵Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

*Correspondence to: ludovic.troian.@uclouvain.be, renatons@email.unc.edu

Table of contents

<i>Excited-State Quenching Experiments</i>	2
<i>Dehalogenation Yields Using Green Light Irradiation</i>	6
<i>NMR Characterizations</i>	7

Excited-State Quenching Experiments

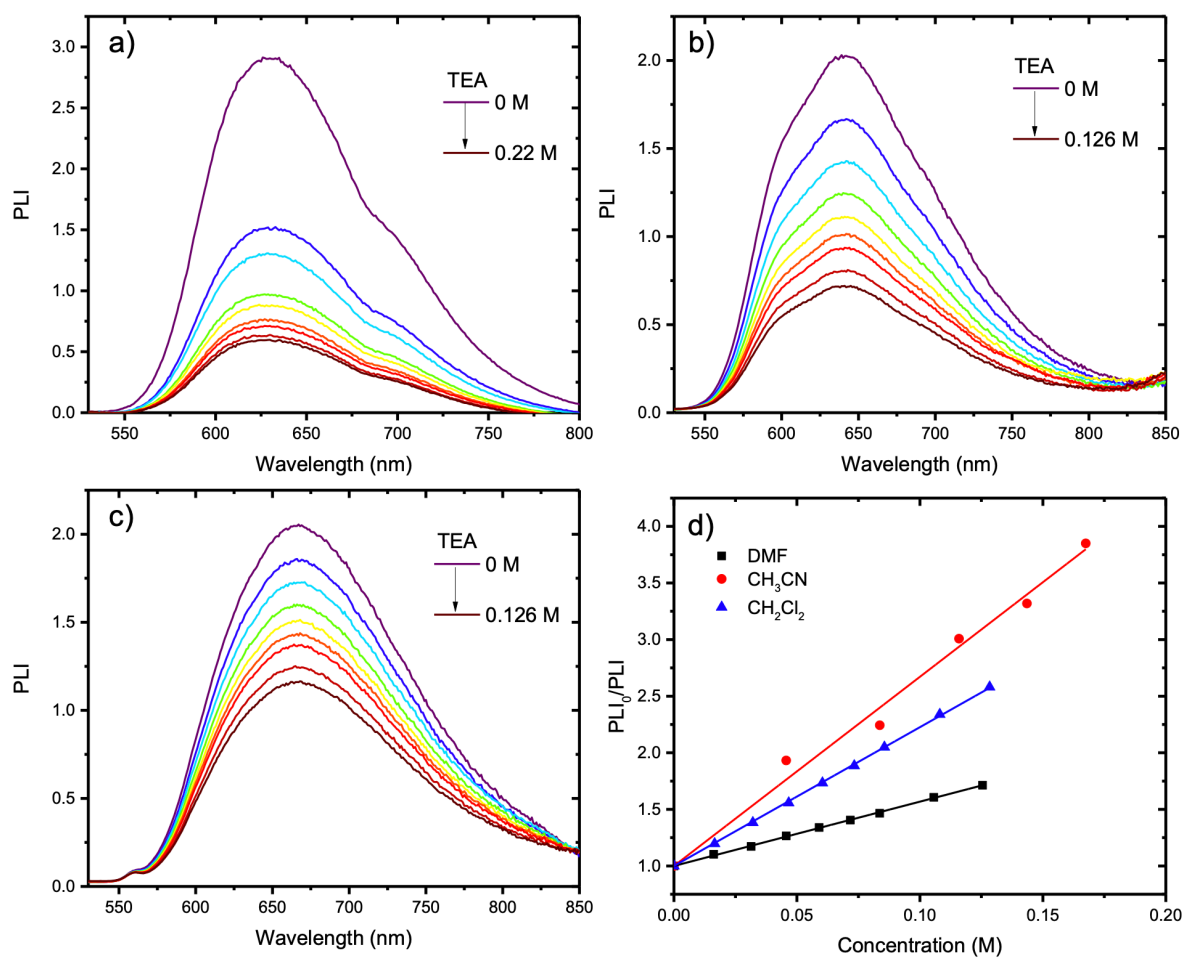


Figure S1: Excited-state quenching of $[\text{Fe}(\text{phtmeimb})_2]^{+*}$ by triethylamine in argon-purged CH_3CN (a), CH_2Cl_2 (b) and DMF (c). The corresponding Stern-Volmer plots are gathered in panel (d).

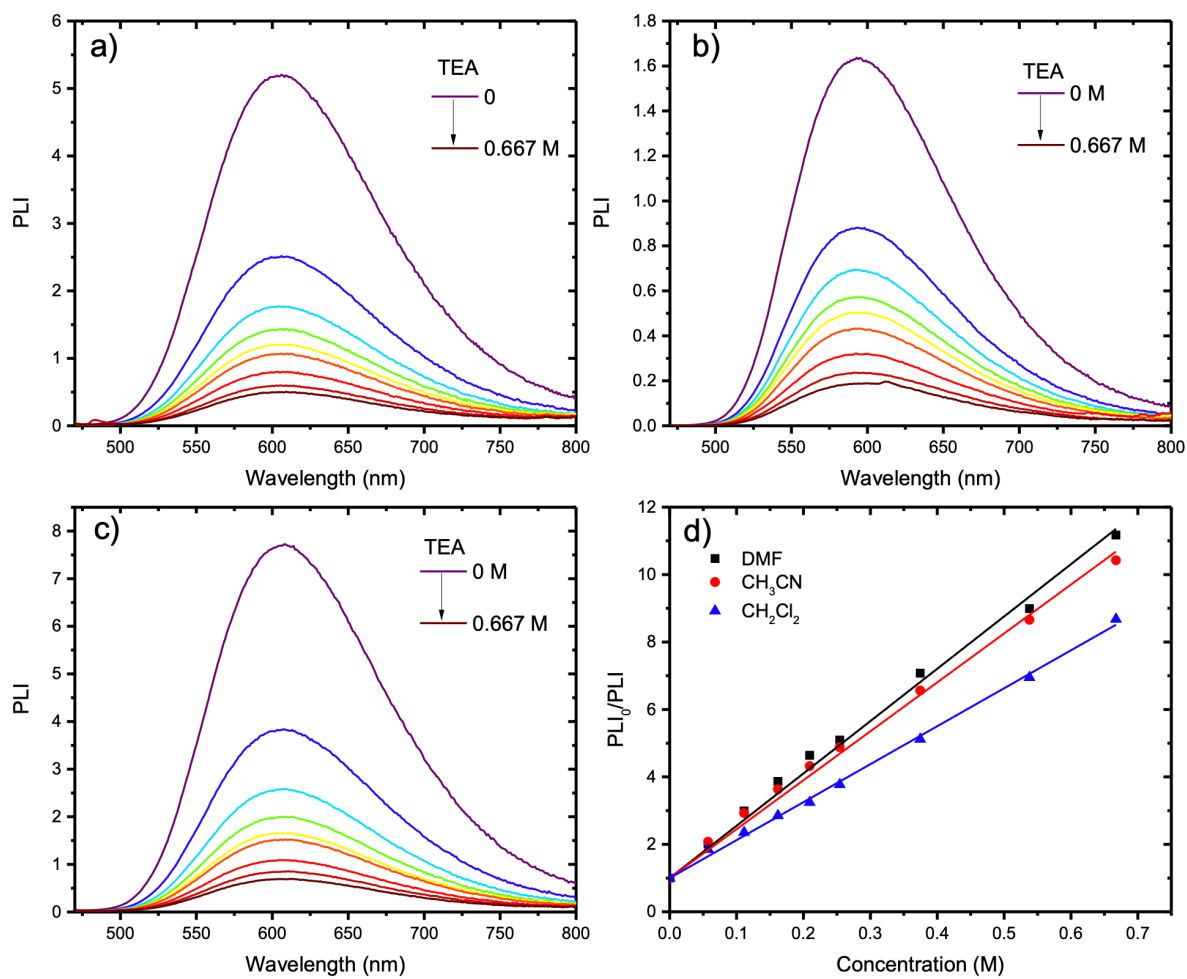


Figure S2: Excited-state quenching of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^{+*}$ by triethylamine in argon-purged CH_3CN (a), CH_2Cl_2 (b) and DMF (c). The corresponding Stern-Volmer plots are gathered in panel (d).

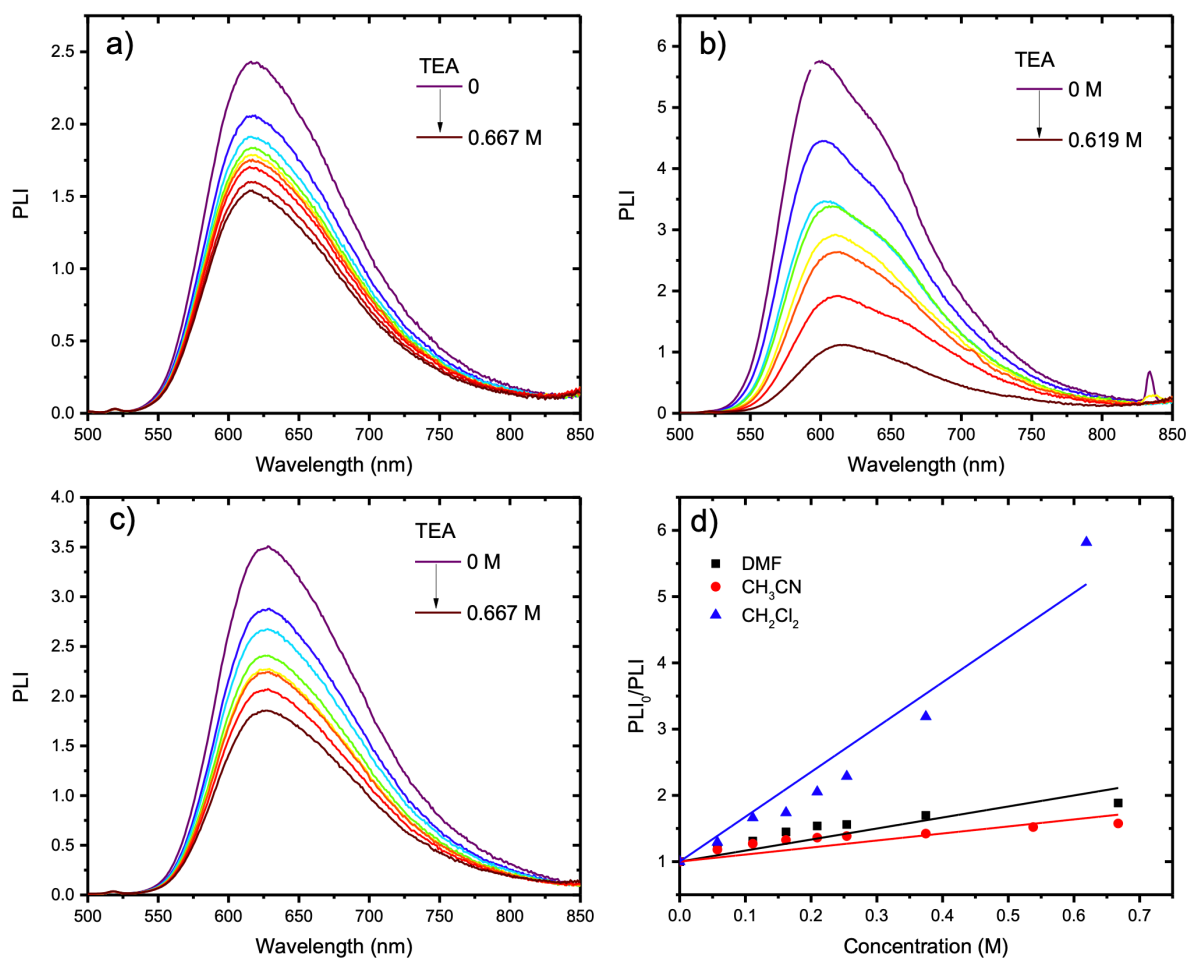


Figure S3: Excited-state quenching of $[\text{Ru}(\text{bpy})_3]^{2+*}$ by triethylamine in argon-purged CH_3CN (a), CH_2Cl_2 (b) and DMF (c). The corresponding Stern-Volmer plots are gathered in panel (d).

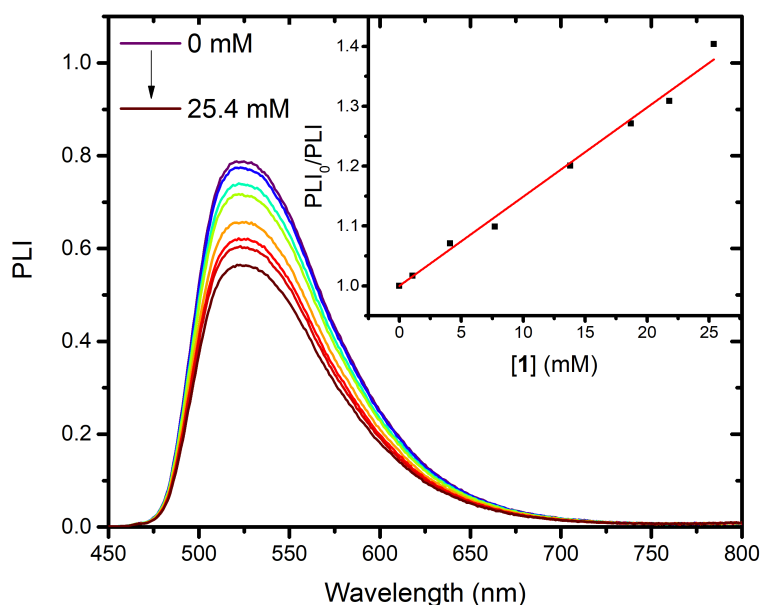


Figure S4. Excited-state quenching of $[\text{Ir}(\text{ppy})_3]^*$ by triethylamine in CH_3CN . The corresponding Stern-Volmer plot is shown in the inset from which $k_q = 7.45 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ was determined.

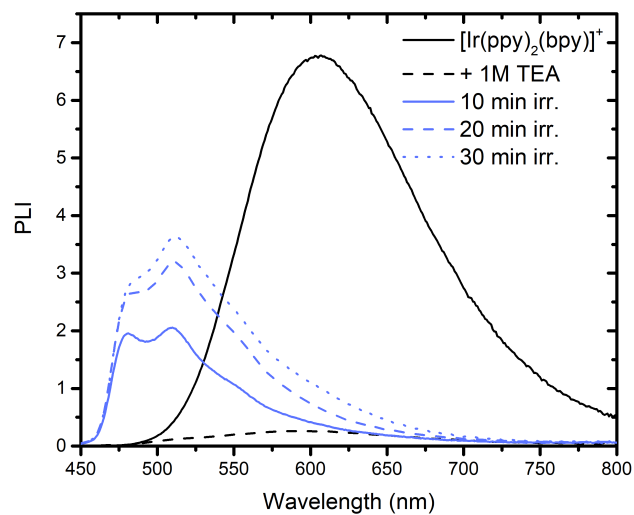


Figure S5. Evolution of the PL spectra of $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ in the presence on 1M TEA (black) and following blue light illumination for the indicated period of time (blue). Experiments were performed in argon purged acetonitrile at room temperature.

Dehalogenation Yields Using Green Light Irradiation

Table S1. Yields of compounds 1-4 obtained with green light irradiation

	CH₂Cl₂ (1/2/3/4) (%)	CH₃CN (1/2/3/4) (%)	DMF (1/2/3/4) (%)
[Ru(bpy)₃]²⁺	0/0/48/25	0/0/47/9	0/0/55/23
[Ir(ppy)₂(bpy)]⁺	0/0/43/18	0/0/49/16	0/0/42/6
[Fe(phtmeimb)₂]⁺	0/29/29/14	72/4/15/2	75/4/1/4

Conditions : PS (1 mol%), TEA (3.5 eq., 0.7 mmol), solvent (2 mL), green light, under inert atmosphere and under irradiation for 24h.

NMR Characterizations

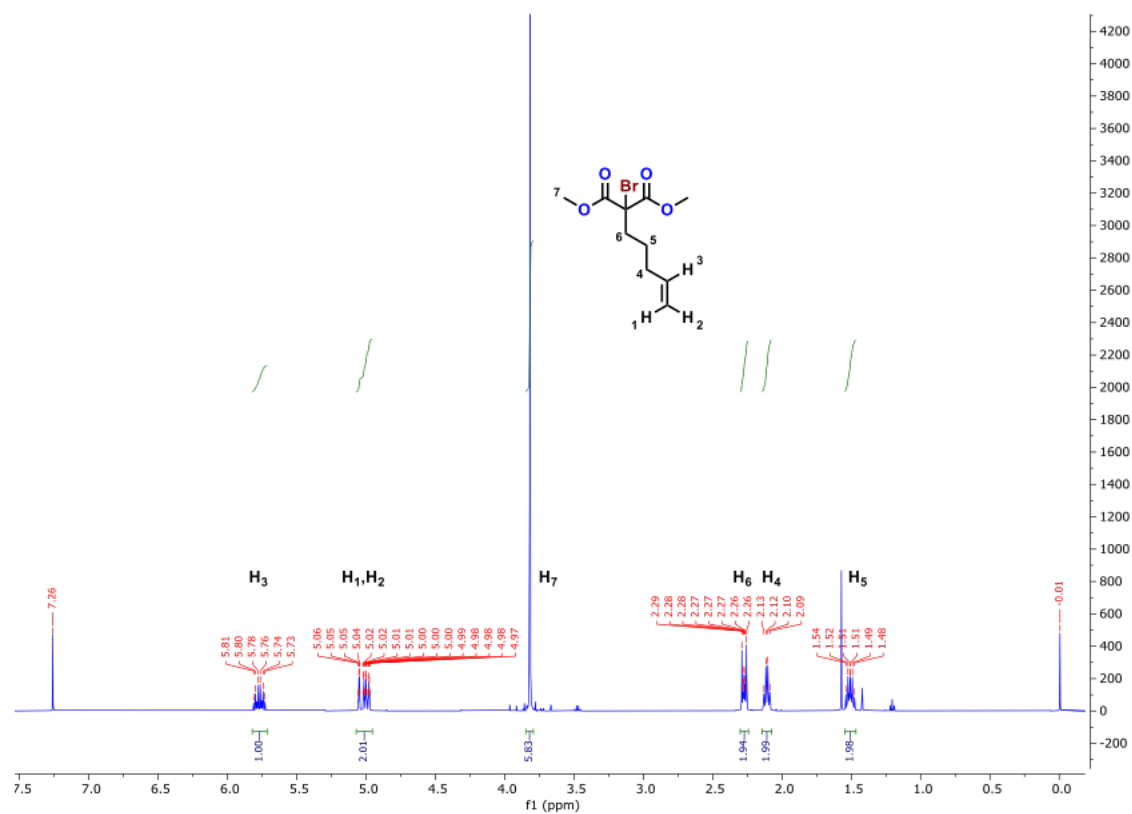


Figure S6: ¹H NMR spectrum of compound **1** recorded in CDCl₃ at 500 MHz and at 298 K.

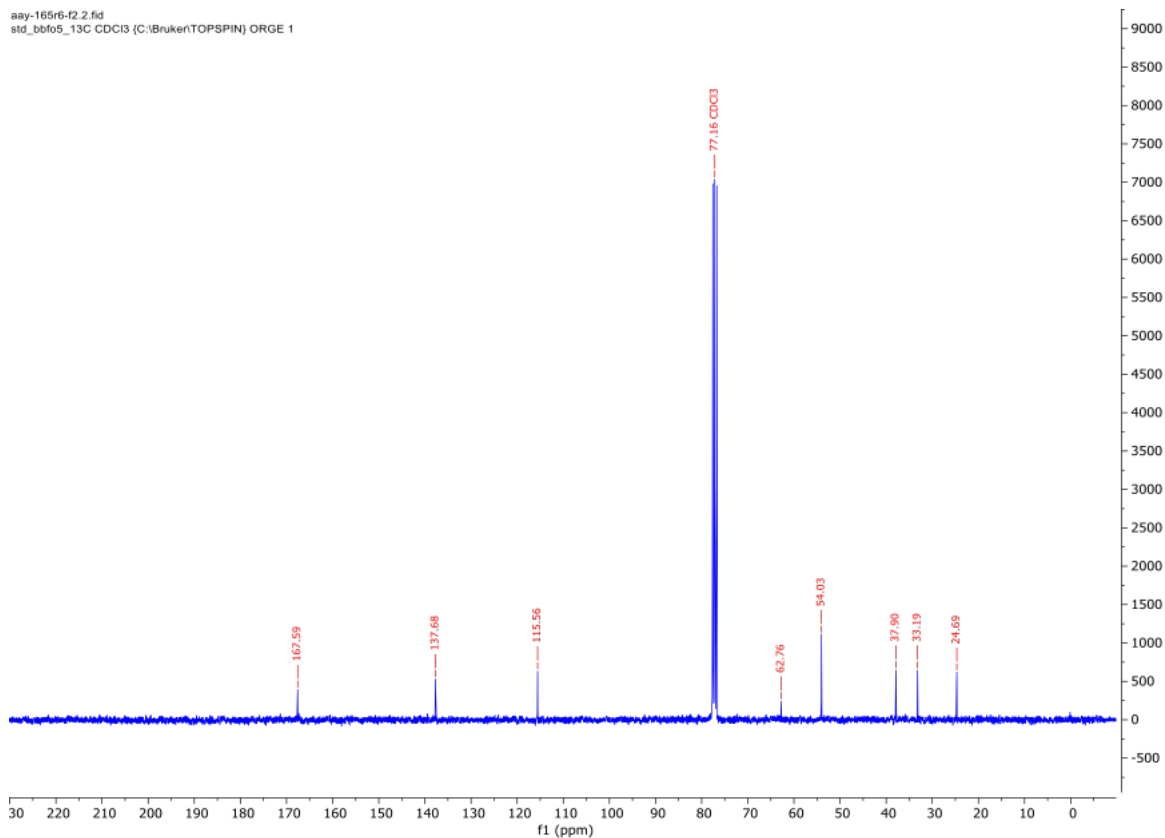


Figure S7: ^{13}C NMR spectrum of compound **1** recorded in CDCl_3 at 75 MHz and at 298 K.

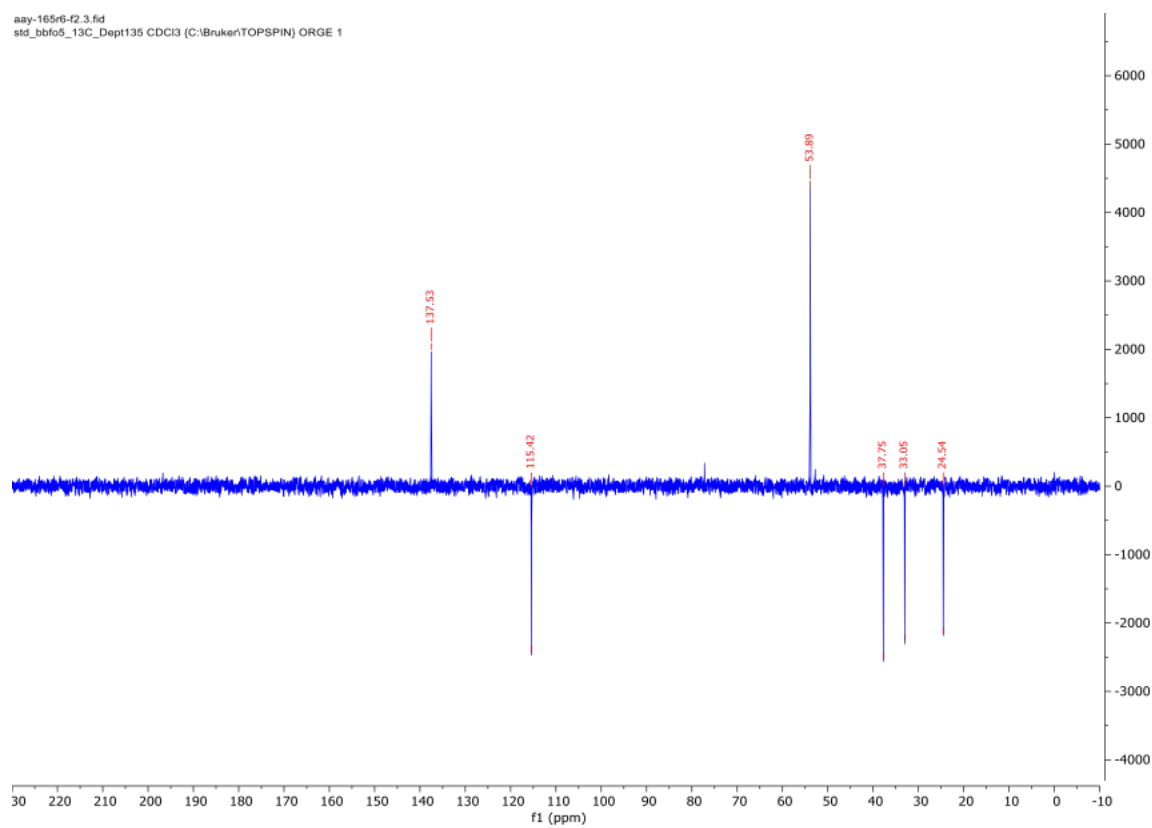


Figure S8: ^{13}C DEPT 135 NMR spectrum of compound **1** recorded in CDCl_3 at 75 MHz and at 298 K.

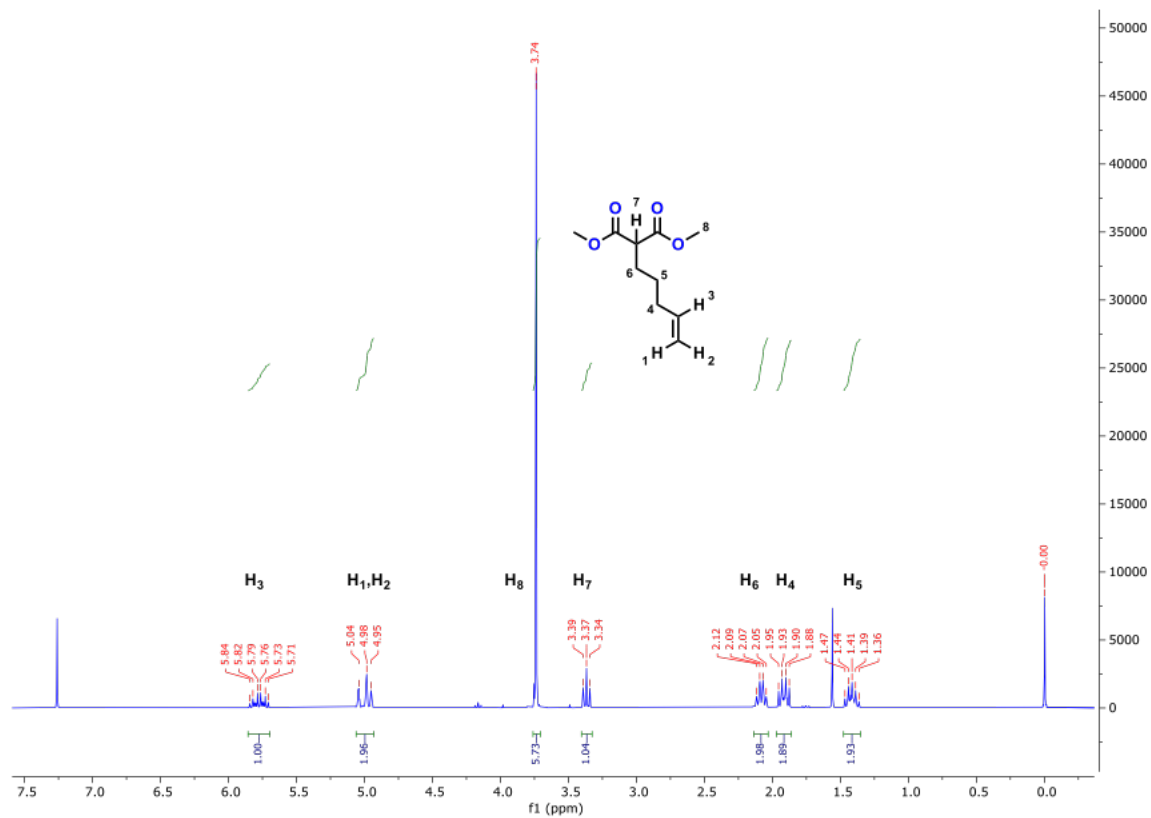


Figure S9: ¹H NMR spectrum of compound **2** recorded in CDCl₃ at 300 MHz and at 298 K.

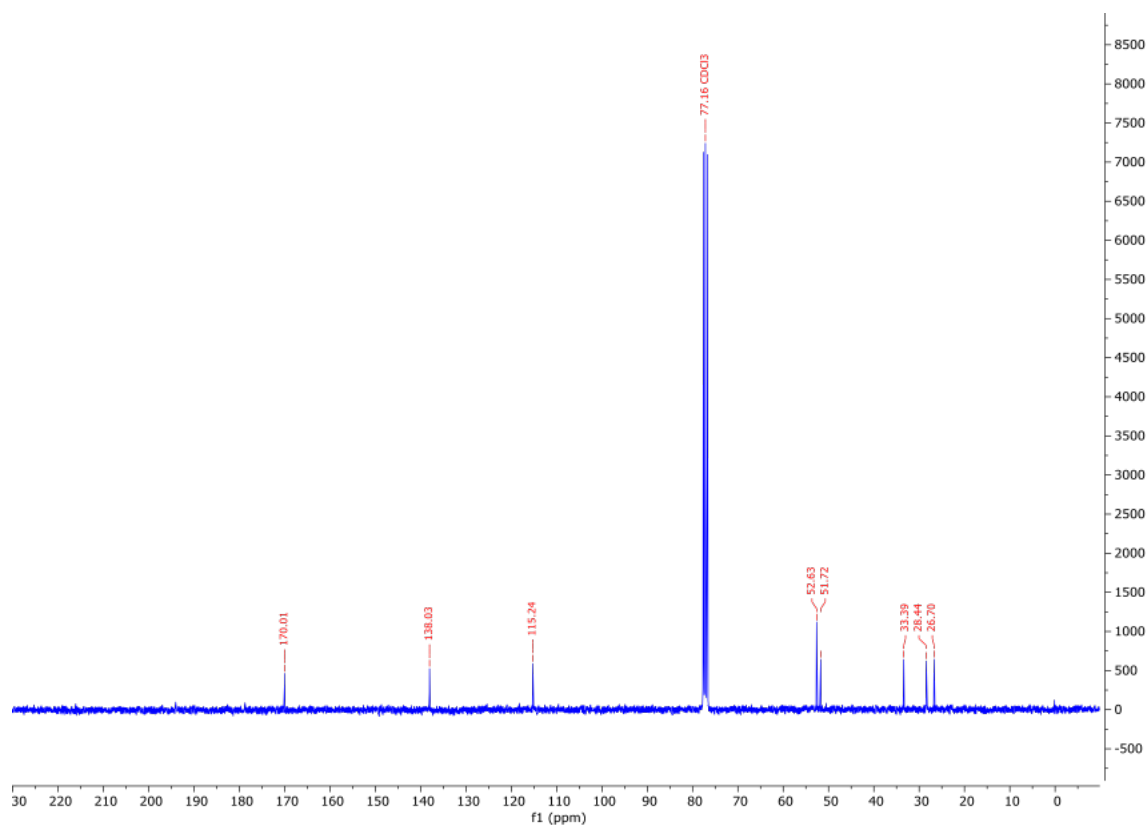


Figure S10: ¹³C NMR spectrum of compound **2** recorded in CDCl₃ at 75 MHz and at 298 K.

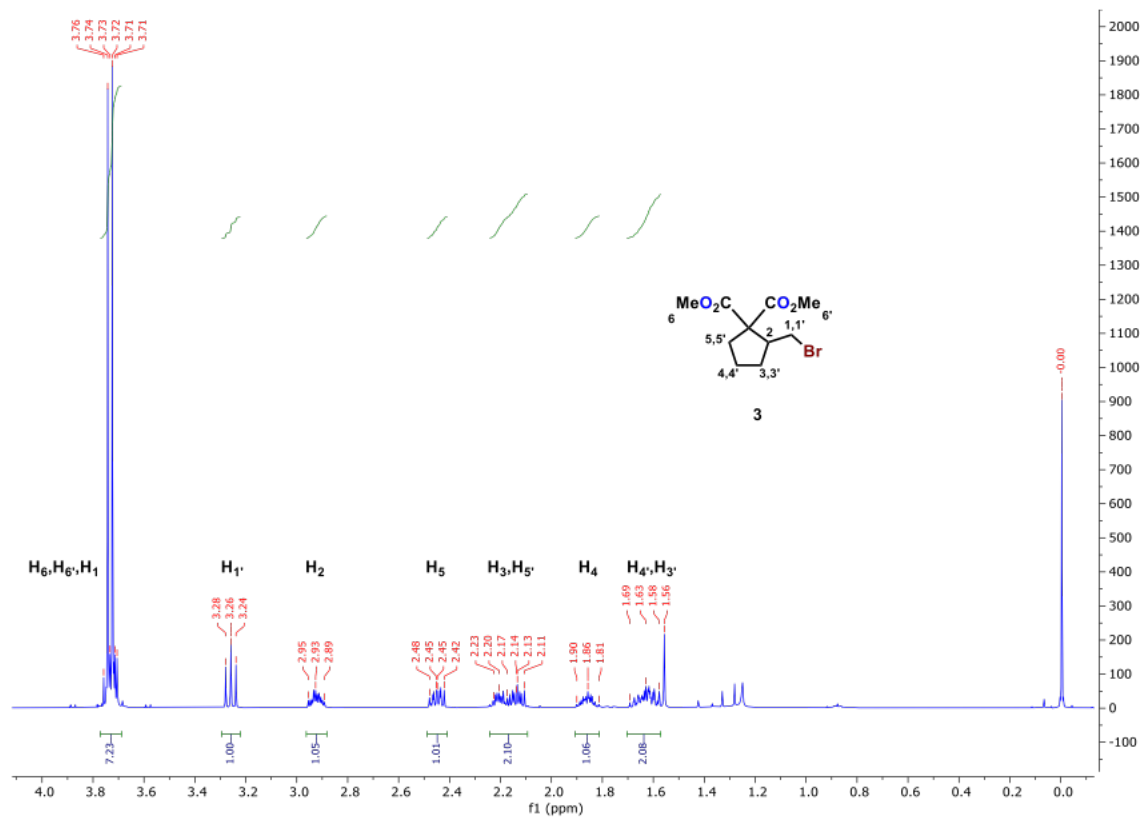


Figure S11: ^1H NMR spectrum of compound **3** recorded in CDCl_3 at 500 MHz and at 298 K.

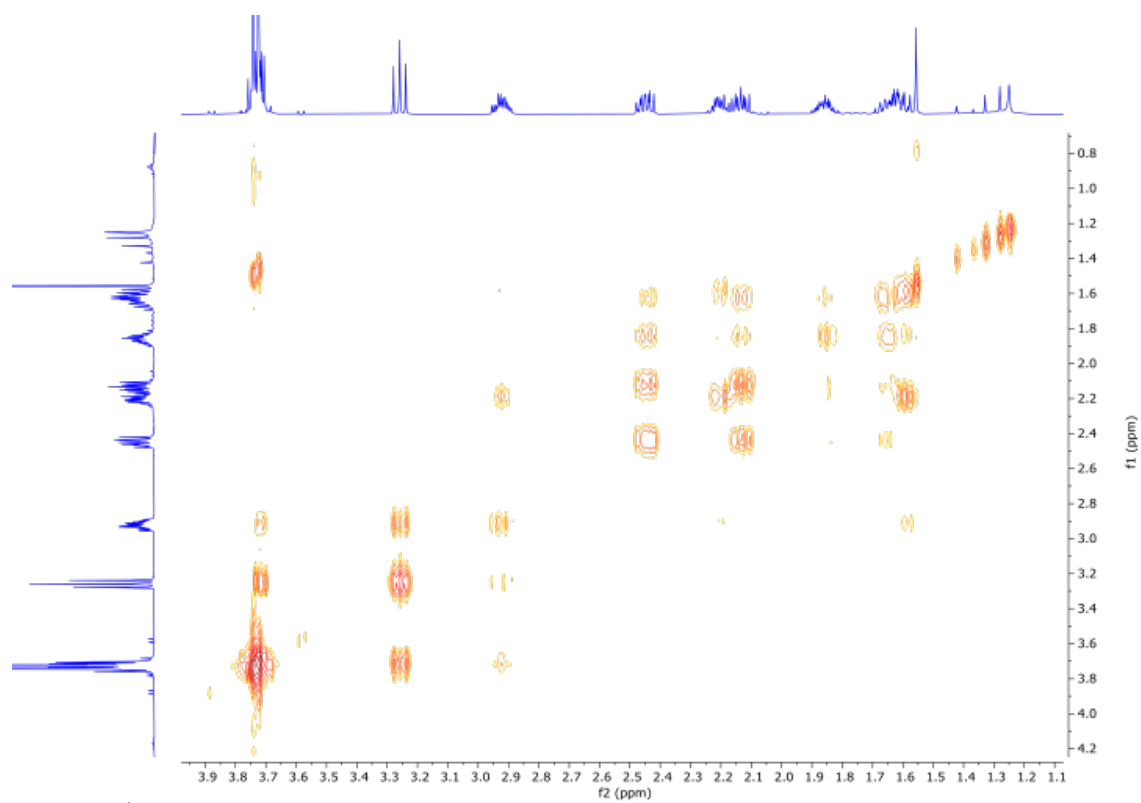


Figure S12: ^1H COSY NMR spectrum of compound **3** recorded in CDCl_3 at 500 MHz and at 298 K.

ay-PR-7-r3.1.fid
purified product
std_bbf05_13C CDCl3 (C:\Bruker\TOPSPIN) ORGE 1

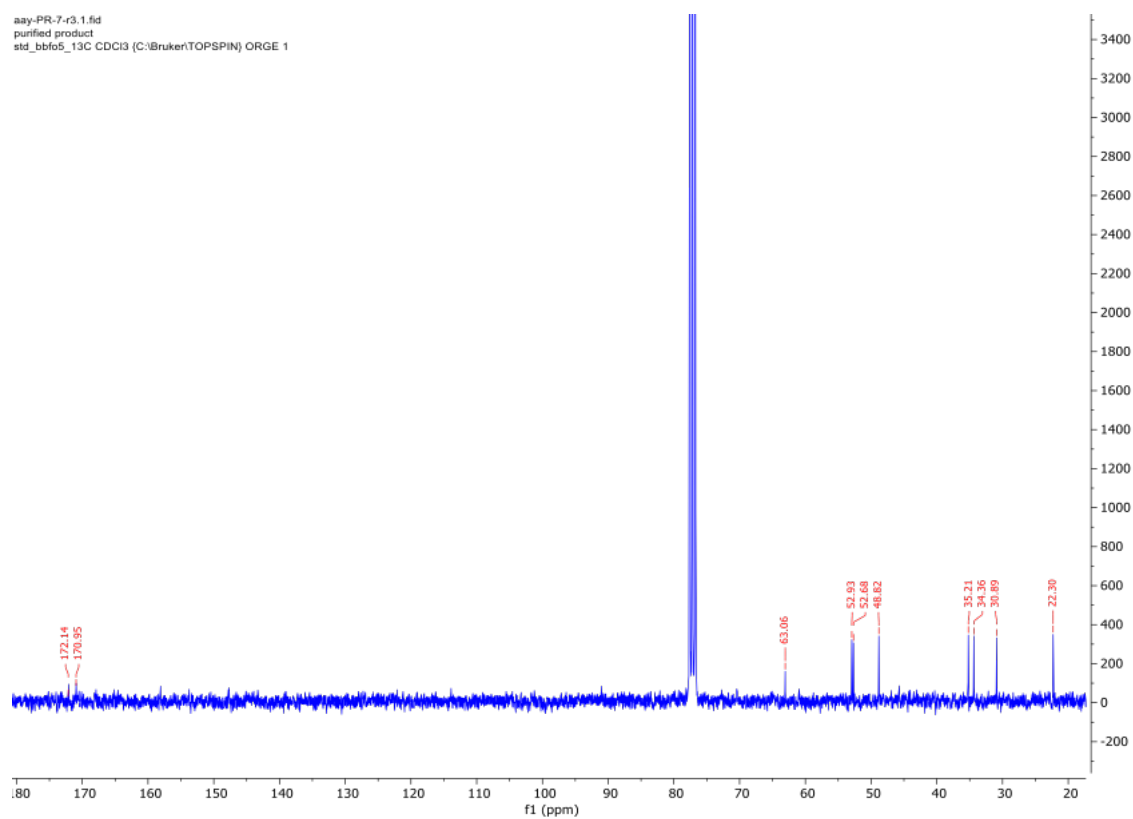


Figure S13: ¹³C NMR spectrum of compound **3** recorded in CDCl₃ at 75 MHz and at 298 K.

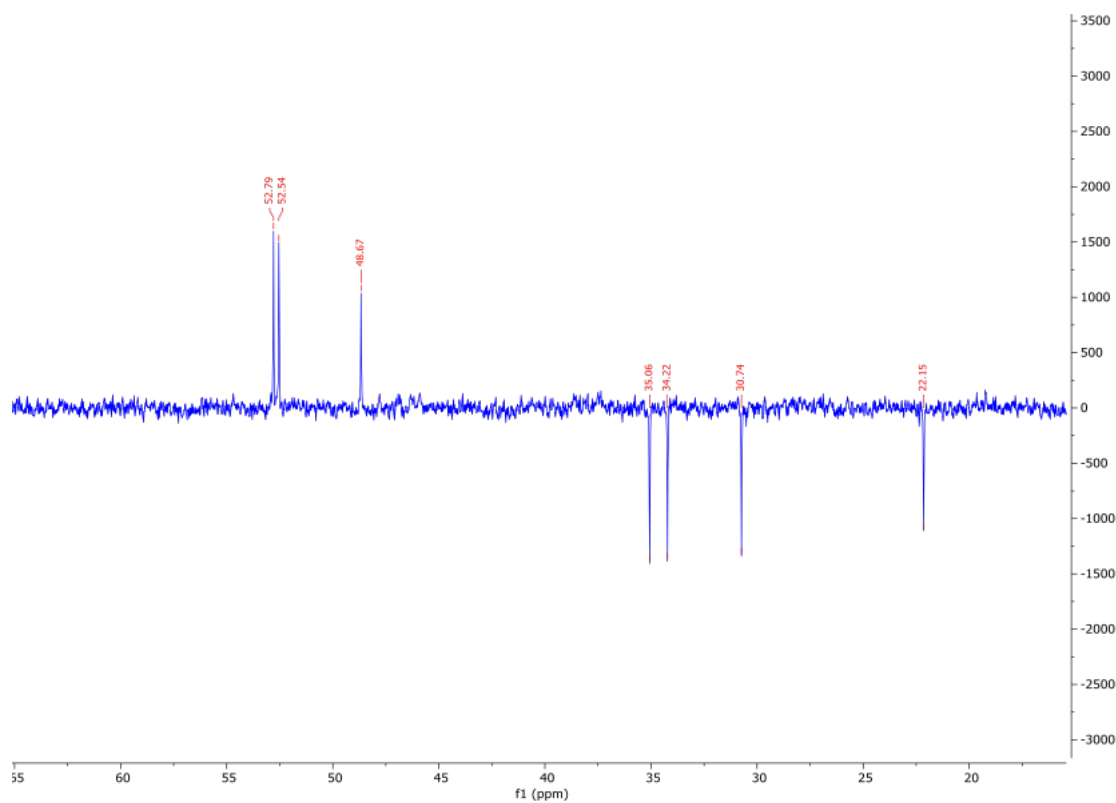


Figure S14: ¹³C DEPT 135 NMR spectrum of compound **3** recorded in CDCl₃ at 75 MHz and at 298 K.

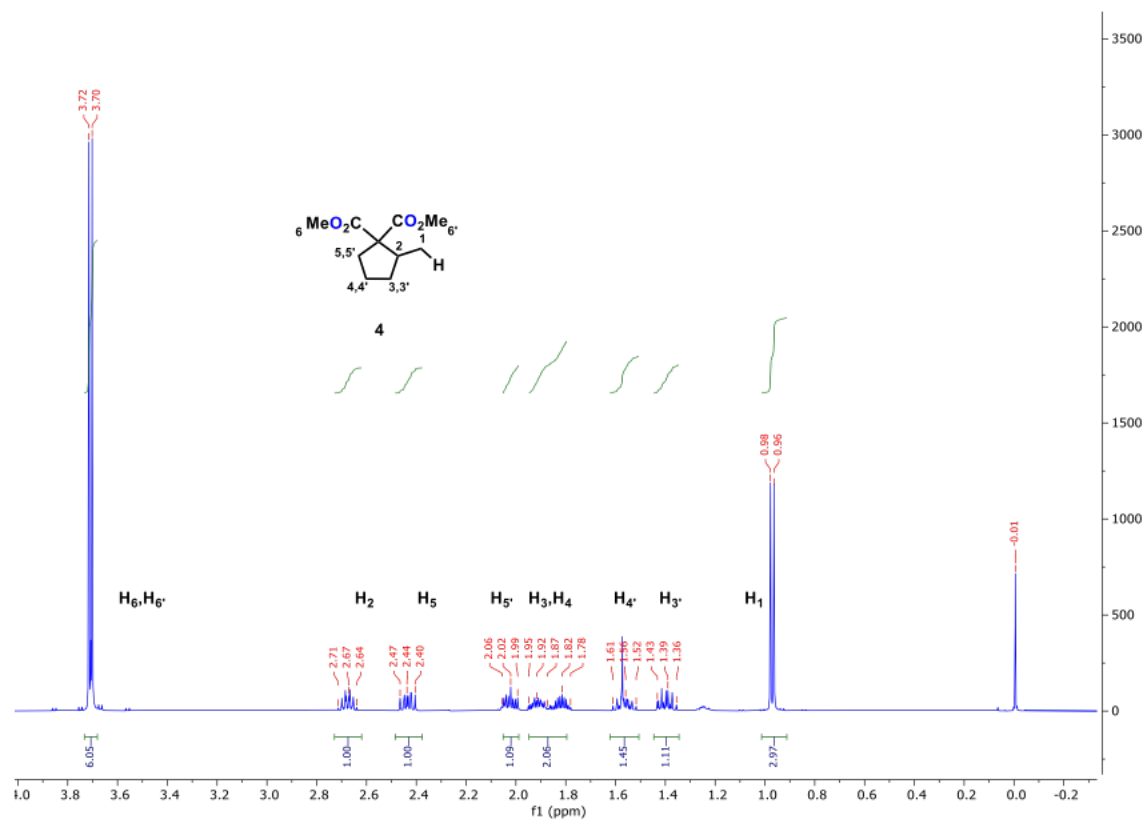


Figure S15: ^1H NMR spectrum of compound **4** recorded in CDCl_3 at 500 MHz and at 298 K.

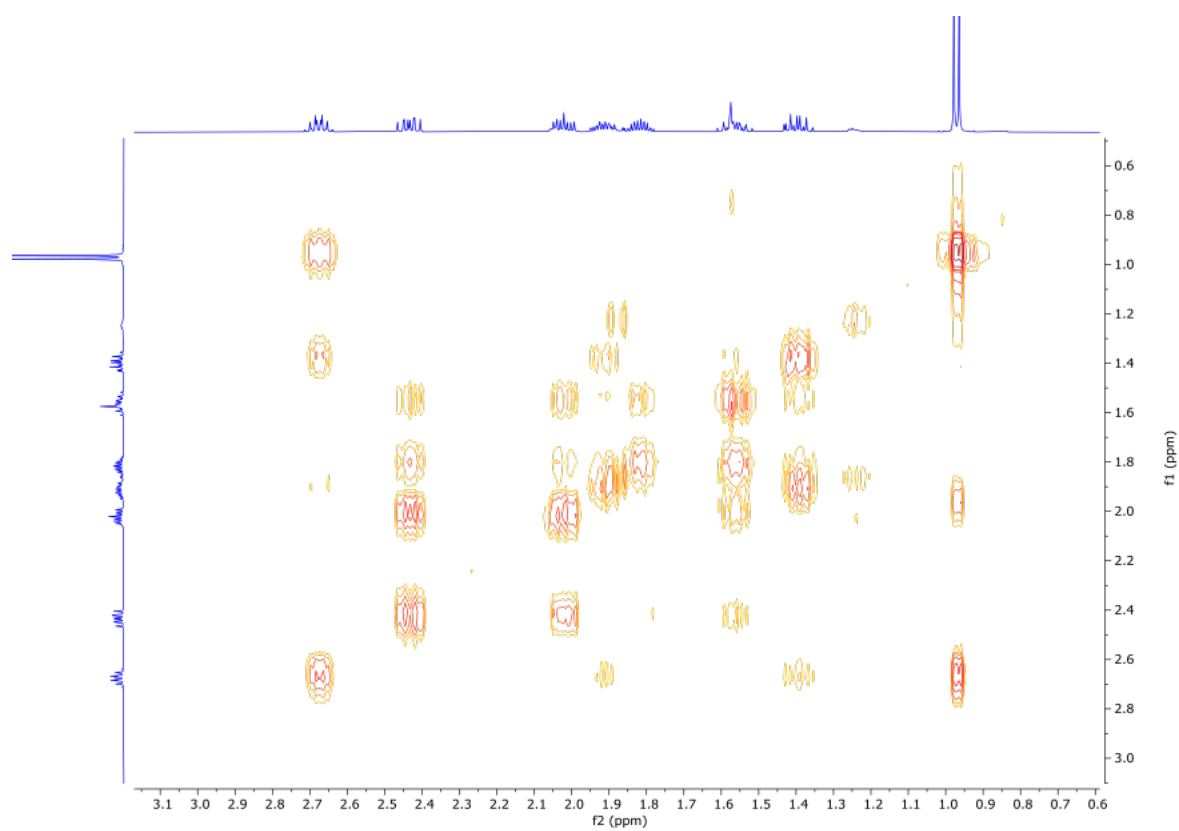


Figure S16: ^1H COSY NMR spectrum of compound **4** recorded in CDCl_3 at 500 MHz and at 298 K.

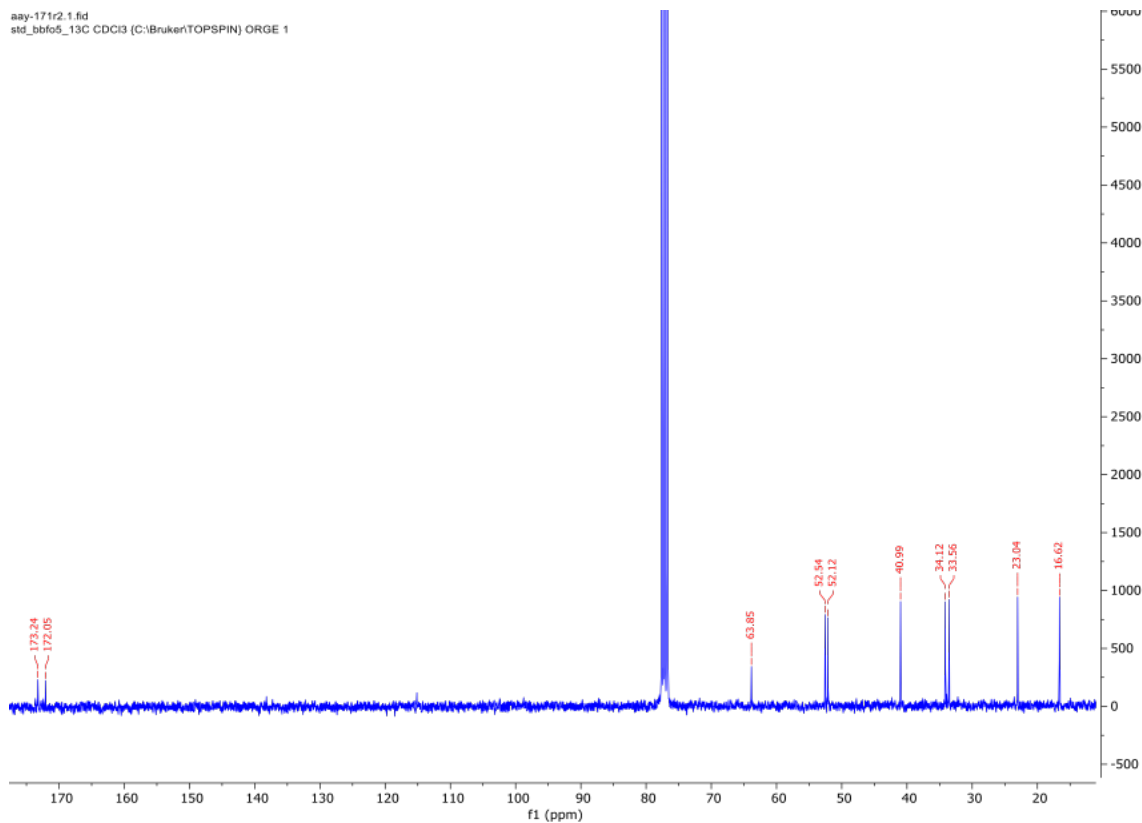


Figure S17: ^{13}C NMR spectrum of compound **4** recorded in CDCl_3 at 75 MHz and at 298 K.

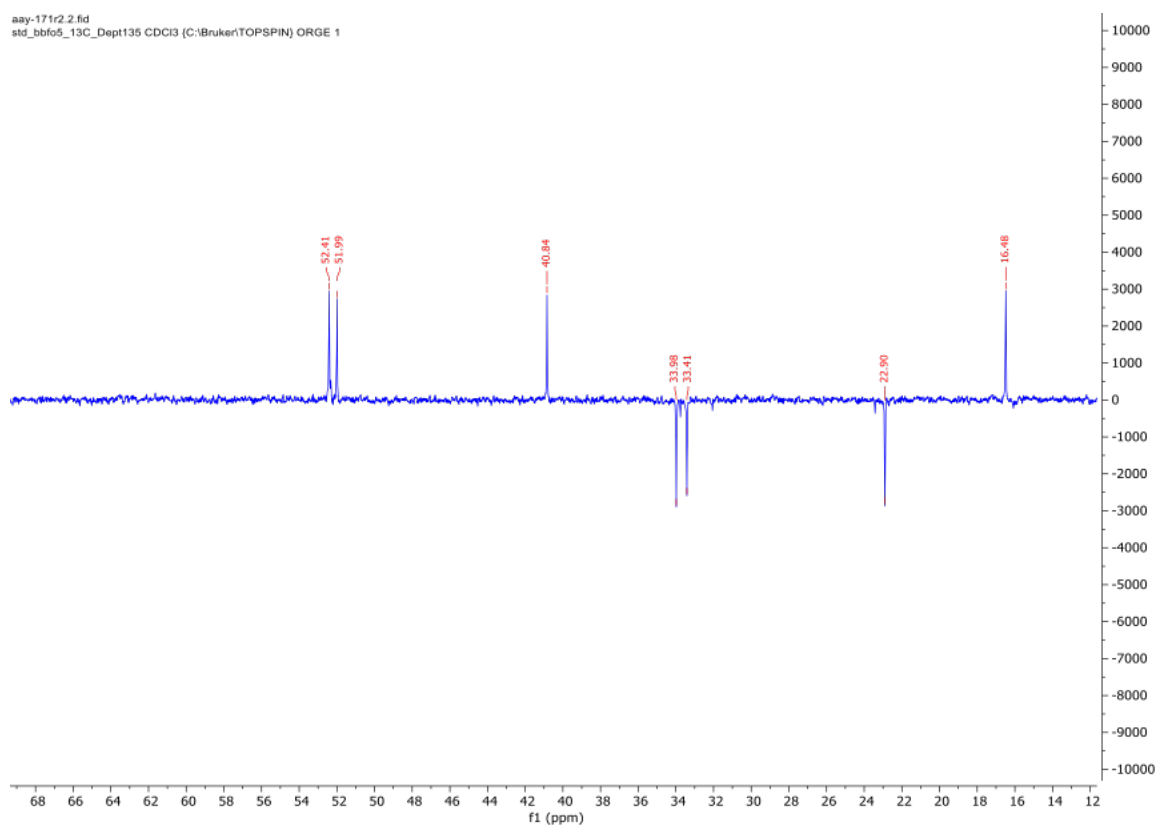


Figure S18: ^{13}C DEPT 135 NMR spectrum of compound **4** recorded in CDCl_3 at 75 MHz and at 298 K.