Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Visible light mediated homo- and heterocoupling of benzyl alcohols and benzyl amines on polycrystalline cadmium sulfide

Tatiana Mitkina,[a] Christoph Stanglmair,[a] Wolfgang Setzer,[a] Michael Gruber,[b] Horst Kisch [c] and Burkhard König[a]*

[a] *Department of Chemistry and Pharmacy, Universität Regensburg Universitätsstraße 31, 93040 Regensburg, Germany; Fax: +499419431717; Tel: +499419434575, E-mail: Burkhard.Koenig@chemie.uni-regensburg.de*

[b] *Department of Anaesthesia, University Hospital Regensburg, 93051 Regensburg, Germany. Fax: +49 941 944 7801; Tel: +49 941 944 7870; E-mail: michael.gruber@klinik.uni-regensburg.de*

[c] *University of Erlangen-Nuremberg, Department of Chemistry and Pharmacy, Egerlandstrasse 1, 91058 Erlangen, Germany*

Supporting Information

1. Materials and methods:

All commercially available chemicals were used as provided without additional purification unless otherwise noted. Compounds **19a-c**[1-3] were synthesized according to published procedures. Compounds: **4**[4], **5**[5-10], **6**[11-14], **7**[15], **11**[16], **13**[17], **17**[18-20], **18**[21], **20a**[22], and **25**[23] are literature known.

Blue light high power LEDs Philips LUXEON® 440±10 nm (3W) were used as a light source for photocatalytic experiments. ^{1}H and ^{13}C NMR spectra were recorded on the Bruker Avance 300 (300.13 MHz), 400 MHz (400.13 MHz) or 600 (600.13 MHz) using the solvent peak as internal reference ($CDCl_3$: δ H 7.26; δC 77.16; CD_3CN: δ H 1.94; δ C 118.26; DMSO-d_6: δ H 2.50; δ C 39.52). The gas chromatography measurements were carried out at the GC 6890 Series Agilent equipped with a J+W Scientific – DB-5MS (30 m x 0.25 μm) capillary column (T(i) = 250 °C, T(d) = 300 °C (FID)) using split injection (40:1 split). Data acquisition and evaluation was done by using the software Agilent ChemStation Rev.A.06.03.(509). The GC oven temperature program adjustment was as follows: The initial temperature was 40 °C, which was kept for 3 min, and then increased constantly at a rate of 15 °C/min for 16 min and the final temperature of 280 °C was kept for 5 min.

The data of the X-ray single crystal analysis of compound ***meso*-17b** were collected on a SuperNova diffractometer at 243K using an Oxford Cryosystems. The structure was solved by direct methods (SIR-97) and refined by full-matrix anisotropic least squares (SHELXL97). The H-atoms were calculated geometrically and a riding model was used during refinement process.

2. Experimental procedures

Preparation of CdS.[24]

Cadmium sulfate ($CdSO_4 \cdot 8/3\ H_2O$, 2.17 g, 10.4 mmol) was dissolved in 75 mL of a 10 % aqueous ammonia. To this solution the solution of sodium sulfide ($Na_2S \cdot x\ H_2O$, 2.33 g, 29.8 mmol) in 25 mL distilled water was dropwise added within 1 hour under vigorous stirring at room temperature by a syringe pump. The resulting yellow precipitate was stirred 20 hours, filtered off under vacuum through porous glass filter (4) and washed with distilled water, until the pH of the washings was neutral. The yellow-orange powder was dried *in vacuo* over P_4O_{10} and stored under nitrogen.

General procedure for photocatalytic experiments:

Cadmium sulfide (CdS, unless otherwise stated, 15 mg, 0.1 mmol), acetonitrile (3 mL), the respective substrate(s) (0.1 mmol; unless otherwise stated) and a magnetic stirring bar were placed into the small glass vial, sealed with a rubber septum and frozen in liquid nitrogen. The mixture was allowed to warm up to room temperature under vacuum (50 mbar) and flushed with dinitrogen gas. The procedure was twice repeated, and then the suspension was irradiated with high power 440 nm LEDs (3W) for 24 h with stirring.

After irradiation the product mixture was filtered off by syringe filter, a standard solution of chlorobenzene in acetonitrile was added to the filtrate and the resulting solution was analyzed by gas chromatography (GC). In the cases, where GC could not provide quantitative information, the solutions were evaporated, ferrocene was added as standard for quantification, the mixture was dissolved in $CDCl_3$, CD_3CN or DMSO-D_6 and analyzed by ^1H NMR spectroscopy. Spectroscopic data were identical to reported values.

Kinetic measurements:

Cadmium sulfide (CdS, 15 mg, 0.1 mmol), acetonitrile (3 mL) and N,N-dibenzylamine (**14c**, 0.1 mmol) were placed into the small glass vial, sealed with a rubber septum and freeze-pumped-thawed two times. The suspension was irradiated with high power 440 nm LEDs (3W) for 24 h under stirring. Every hour a sample (50 μL) from the solution was taken by syringe, mixed with standard chlorobenzene solution in acetonitrile and analyzed by gas chromatography.

3. Crystal data and structure refinement for the compound *meso*-17b

Formula	$C_{34}H_{40}N_2$
FW	476.68
T (K)	243
cryst syst	Monoclinic
space group	P 2_1/c
a (Å)	10.7984(2)
b (Å)	14.4140(3)
c (Å)	18.7238(3)
α (deg)	90
β (deg)	104.7734(19)
γ (deg)	90
V (Å^3)	2817.98(9)
Z	4
D_{calc}(Mg/m^3)	1.124
crystal size (mm^3)	0.1902×0.1489×0.1102
no. of reflections collected	21665
no. of independent reflections	5808 [R(int) = 0.0262]
max. and min. transmission	0.958 and 0.933
GOF on F^2	1.052
final R indices [$I>2\sigma(I)$][a]	R1 = 0.0535, wR2 = 0.1576
R indices (all data)	R1 = 0.0610, wR2 = 0.1659

4. Gas chromatographic analyses of cross-coupling of benzyl alcohol and benzyl amine

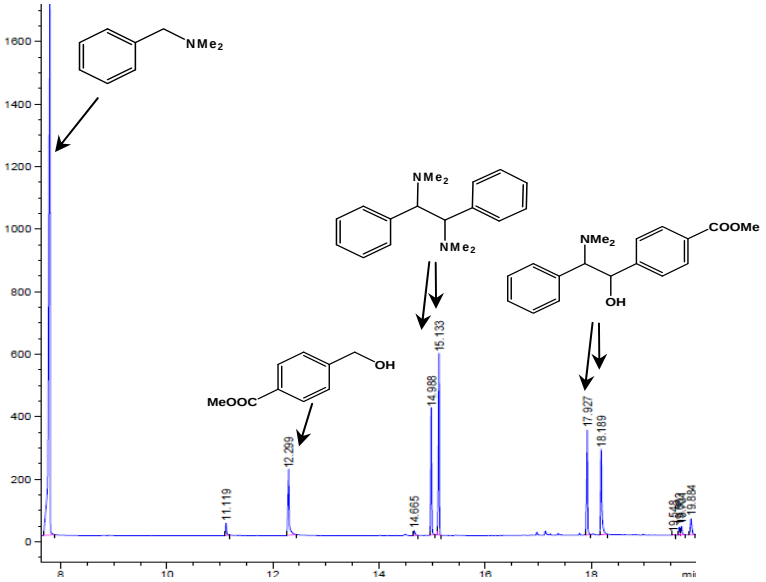

Figure S-1. Raw product mixture of photocatalytic cross coupling of equivmolar amounts of benzyl amine **16a** and benzyl alcohol **3-COOMe** on CdS

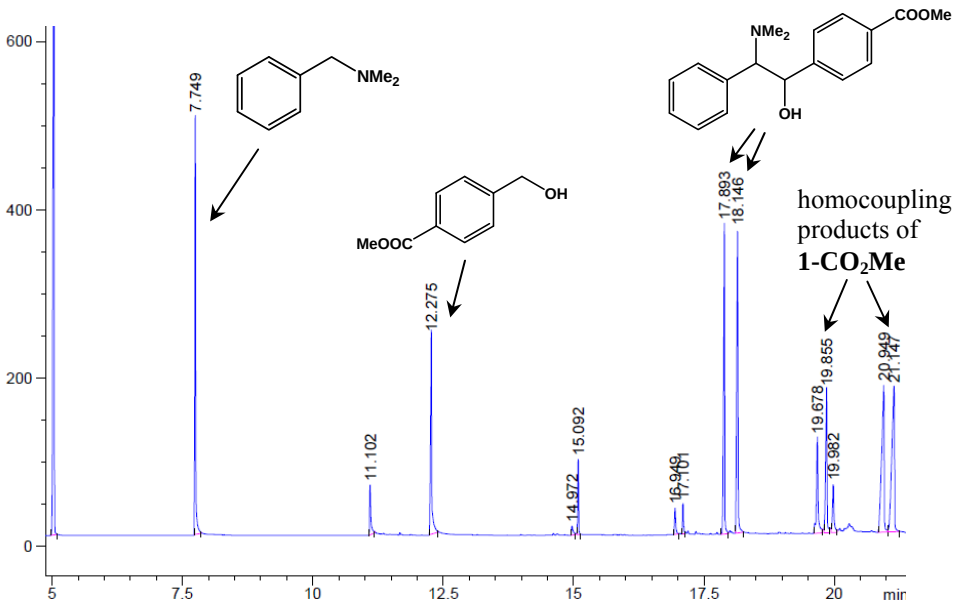

Figure S-2. Raw product mixture of photocatalytic cross-coupling of benzyl amine **16a** and benzyl alcohol **3-COOMe** in a ratio of 1:3 on CdS

5. Spectral data for compounds

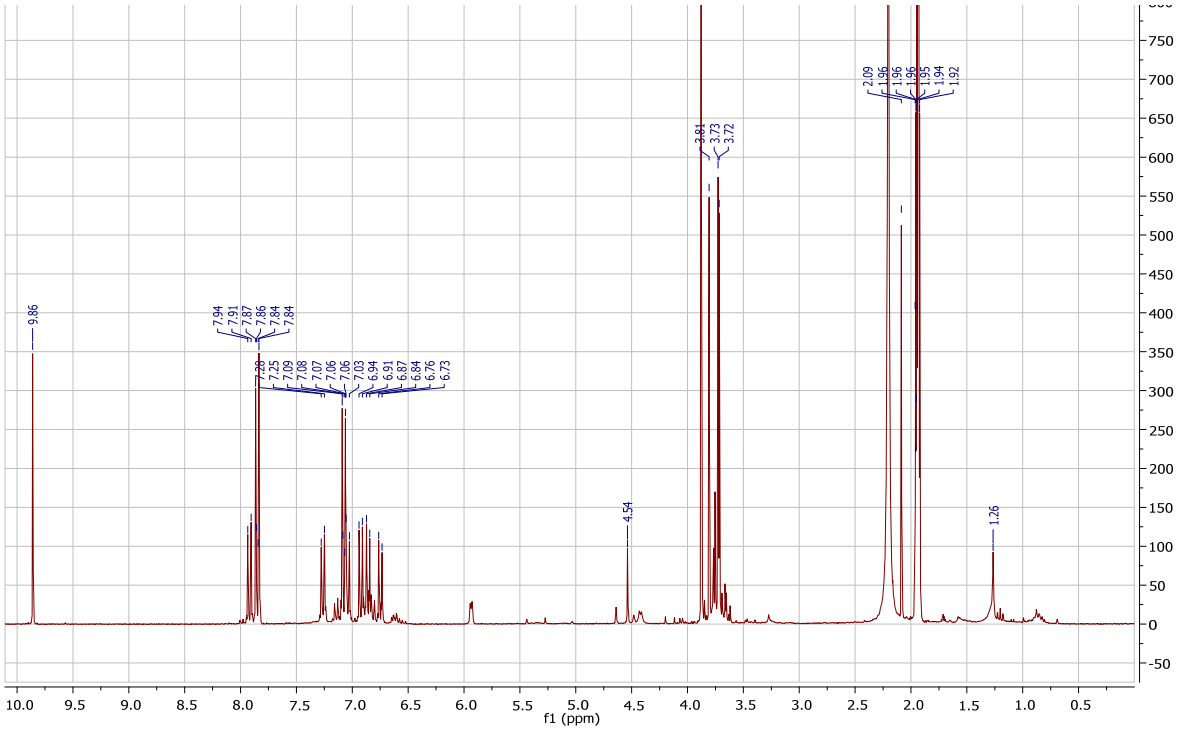

Figure S-3. Proton NMR (300 MHz, CD_3CN) of the reaction products of the photoconversion of compound **3-OMe** yielding **4-OMe, 5-OMe** and **6-OMe**

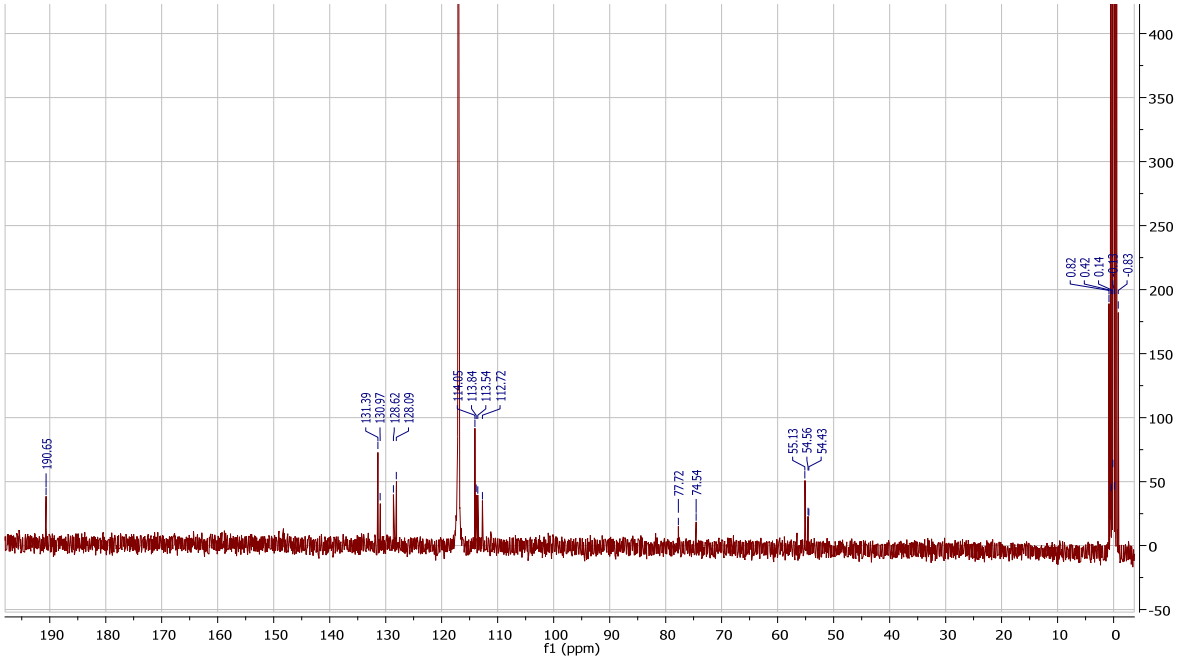

Figure S-4. Carbon NMR (75 MHz, CD_3CN) of the reaction products of the photoconversion of compound **3-OMe** yielding **4-OMe, 5-OMe** and **6-OMe**

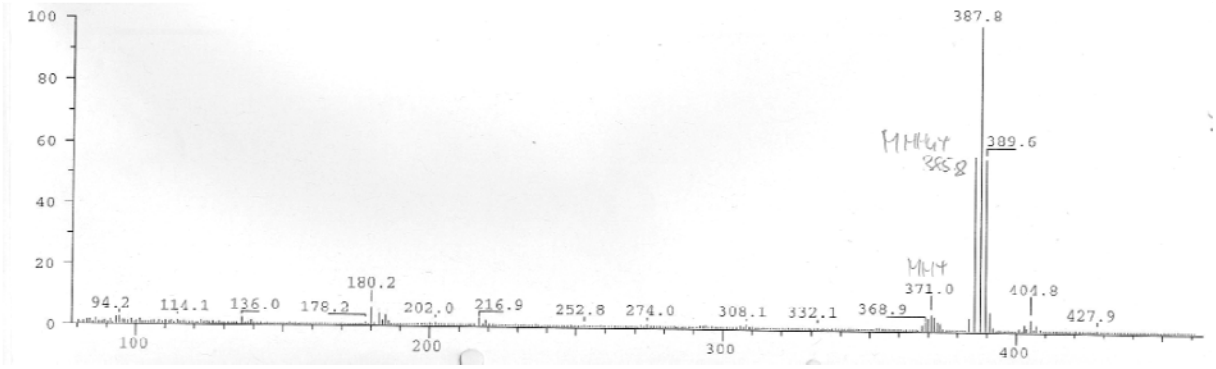

Figure S-5. Mass spectrum (GC-MS, EI) of compound **5-Br** and **6-Br**

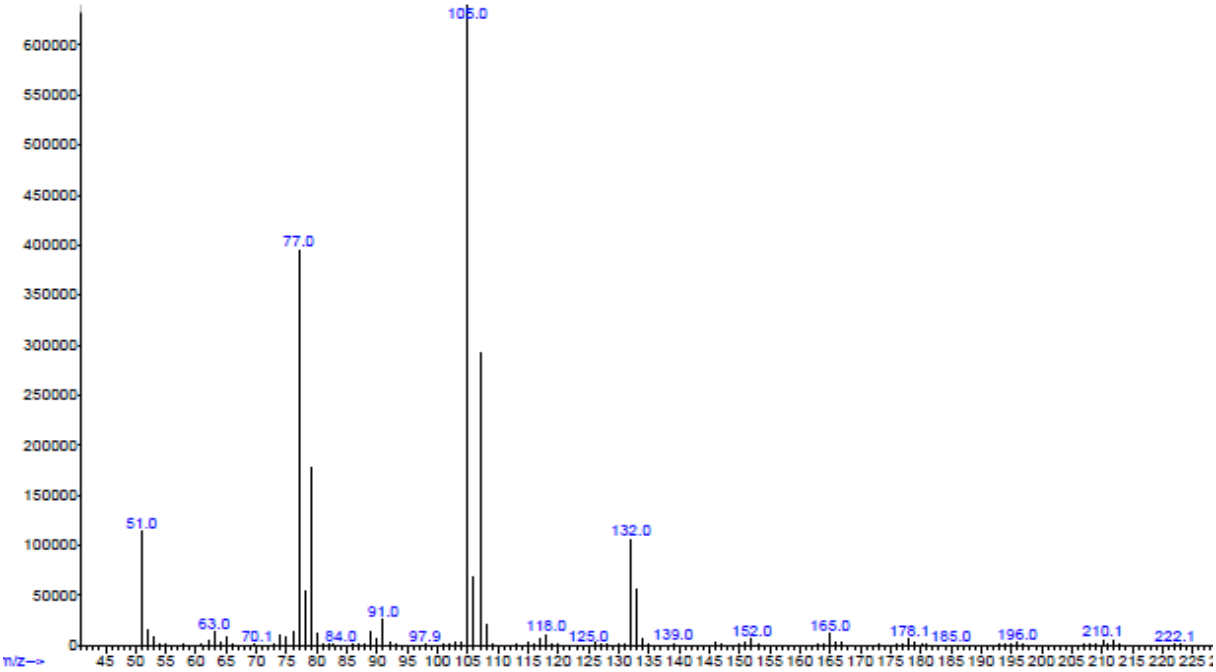

Figure S-6. Mass spectrum (GC-MS, EI) of compound **6-H**[25]

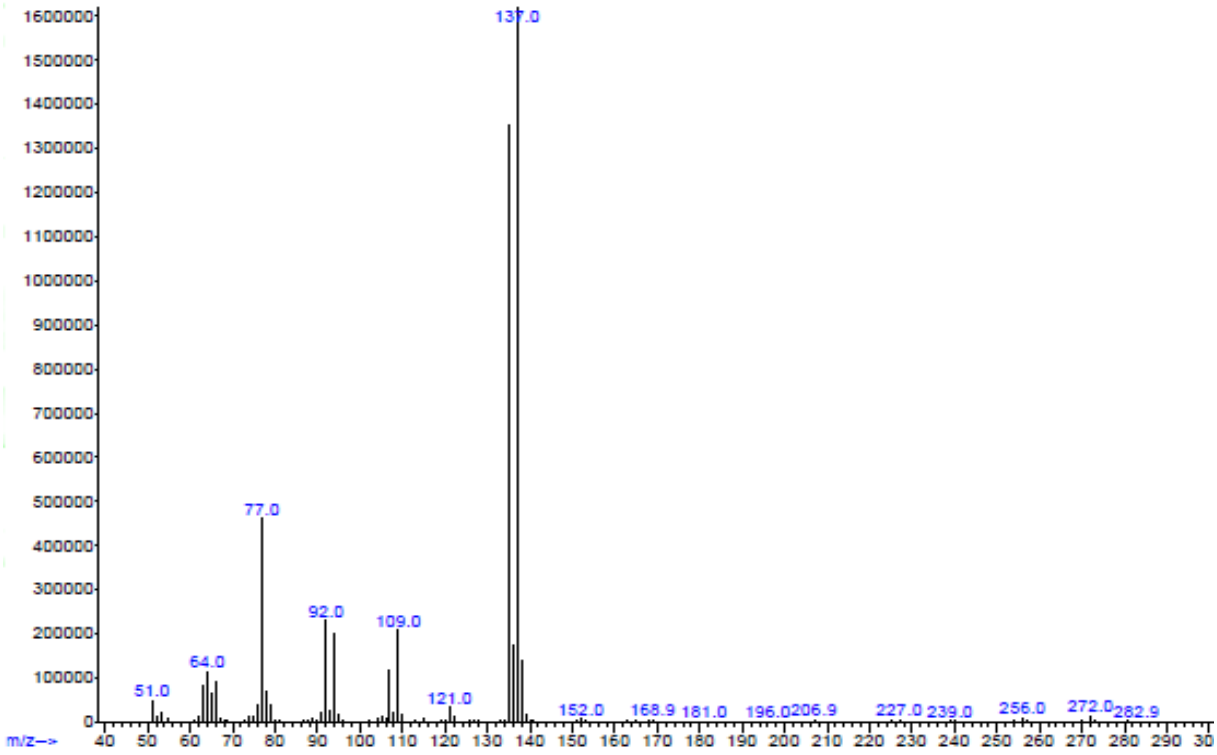

Figure S-7. Mass spectrum (GC-MS, EI) of compound **6-OMe**[25]

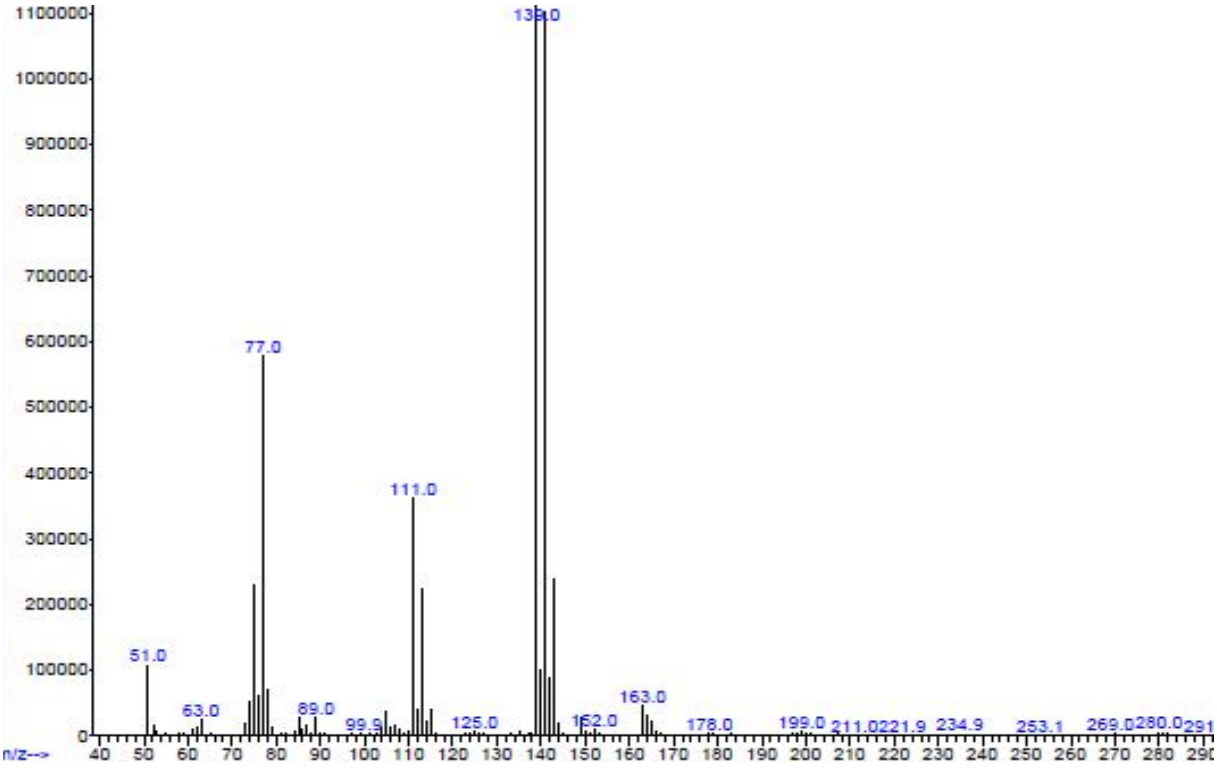

Figure S-8. Mass spectrum (GC-MS, EI) of compound **6-Cl**[25]

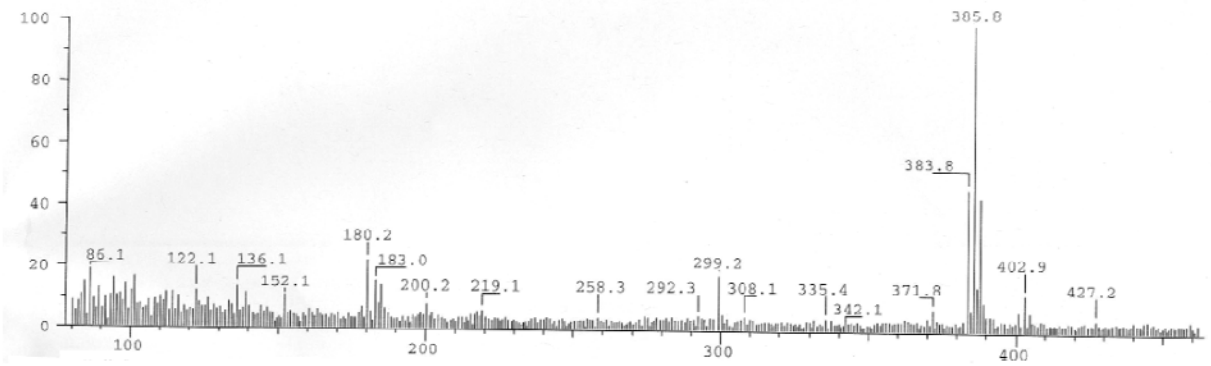

Figure S-9. Mass spectrum (GC-MS, CI) of compound **6-Br**

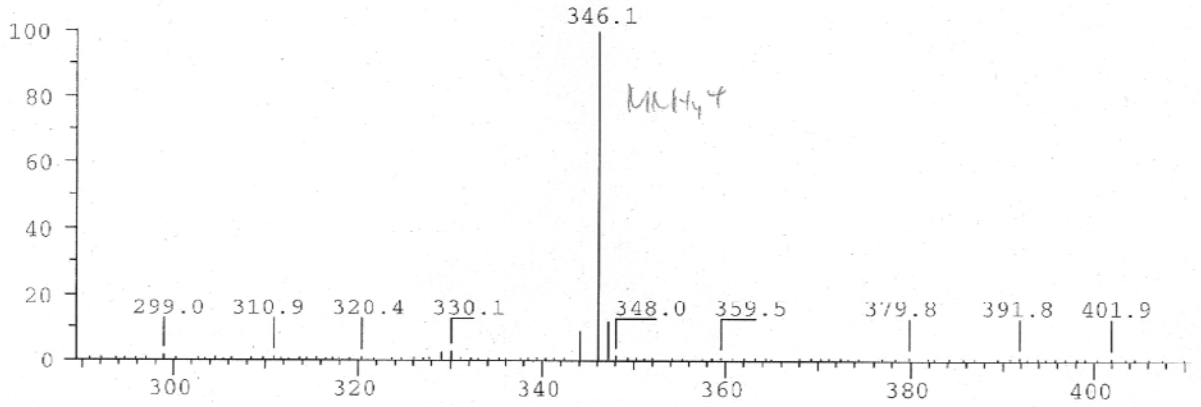

Figure S-10. Mass spectrum (GC-MS, CI) of compound **6-COOMe**

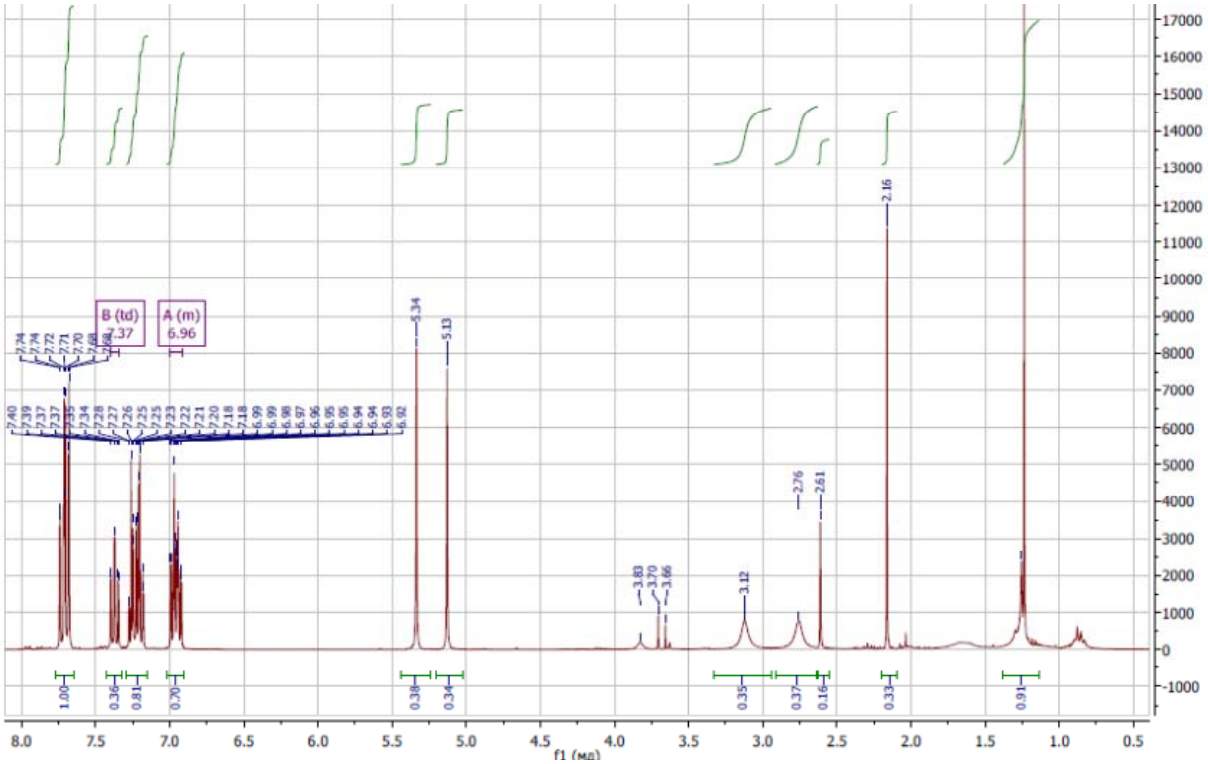

Figure S-11. Proton NMR (300 MHz, $CDCl_3$) of compound **5-I**

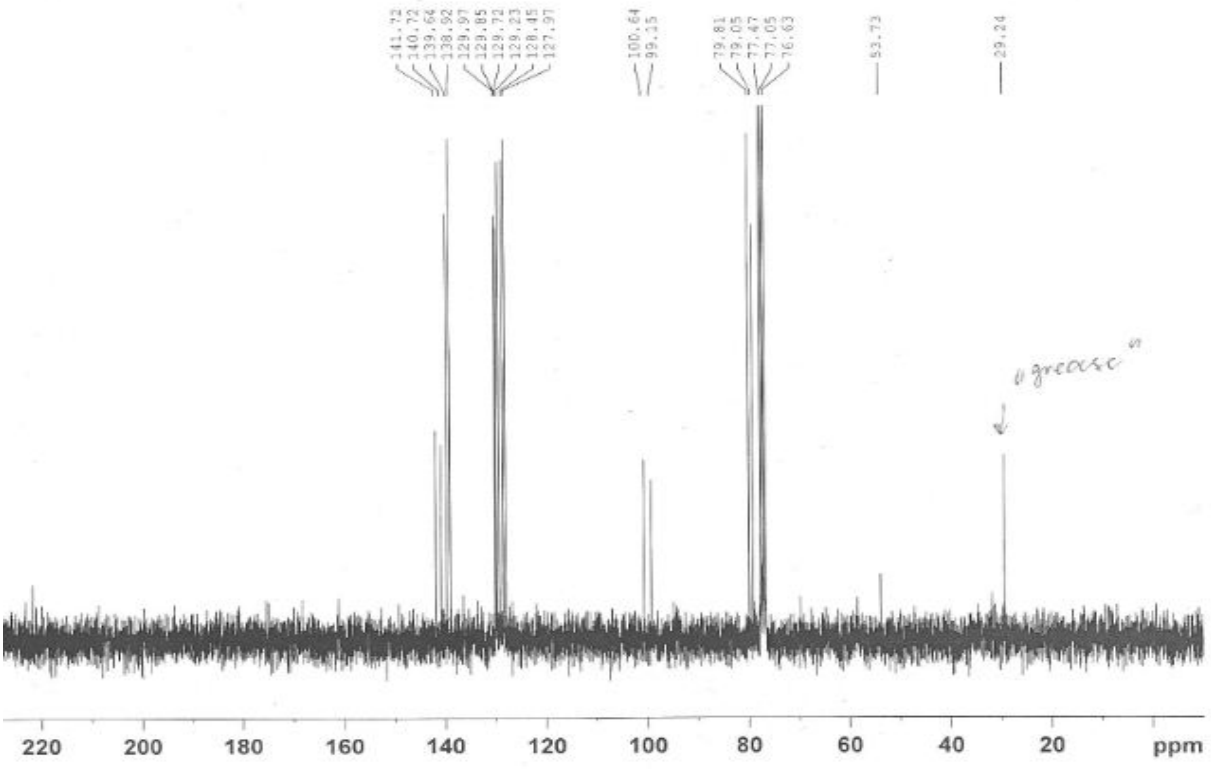

Figure S-12. Carbon NMR (75 MHz, $CDCl_3$) of compound **5-I**

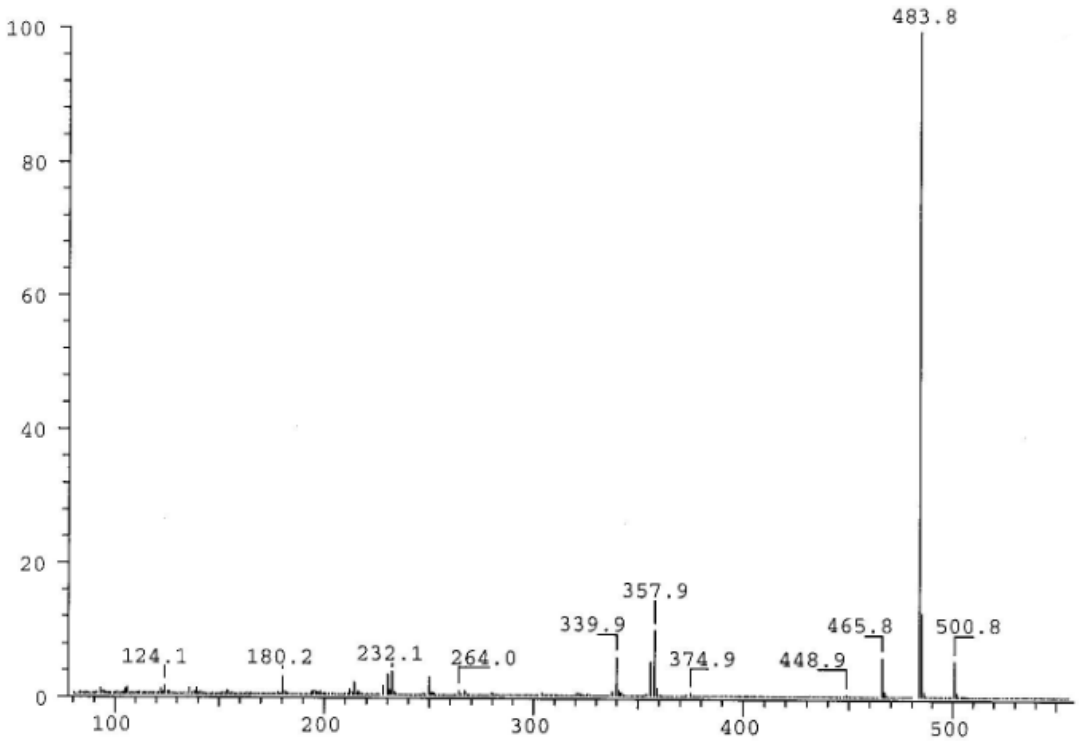

Figure S-13. Mass spectrum of compound **5-I** (GC-MS, CI)

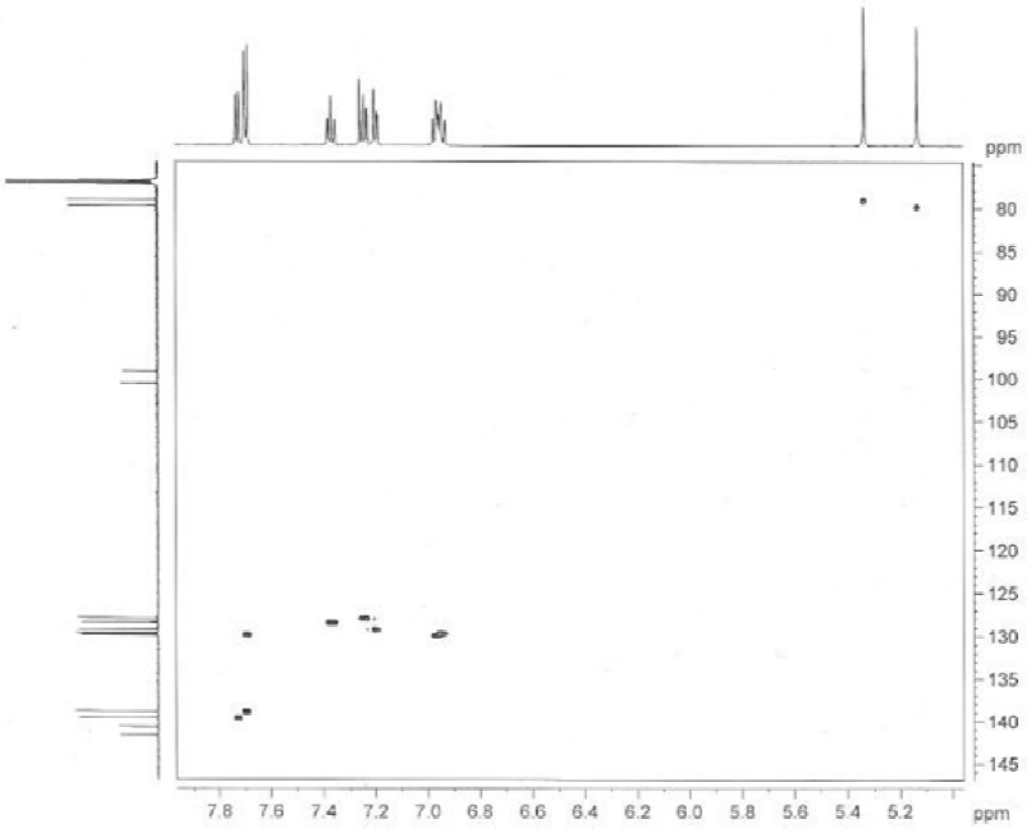

Figure S-14. HSQC NMR (300 / 75 MHz, $CDCl_3$) spectrum of compound **5-I**

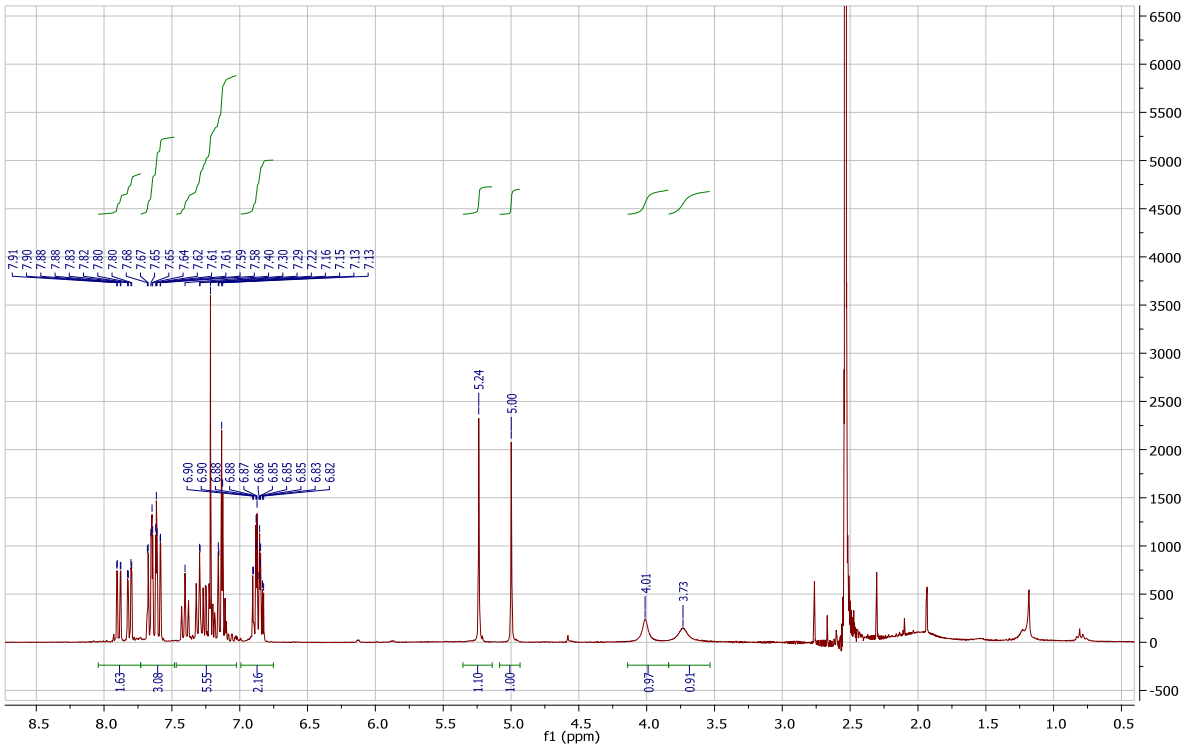

Figure S-15. Proton NMR (300 MHz, $CDCl_3$) of compound **6-I**

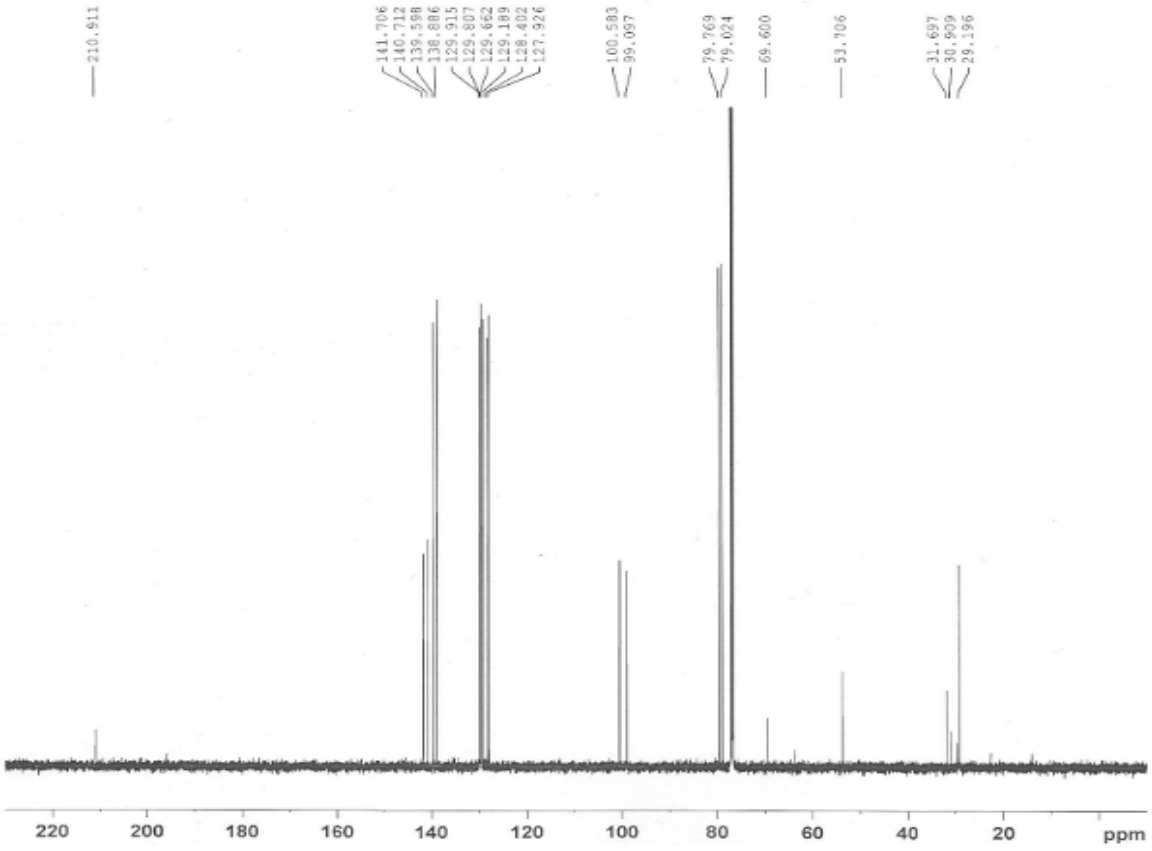

Figure S-16. Carbon NMR (75 MHz, $CDCl_3$) of compound **6-I**

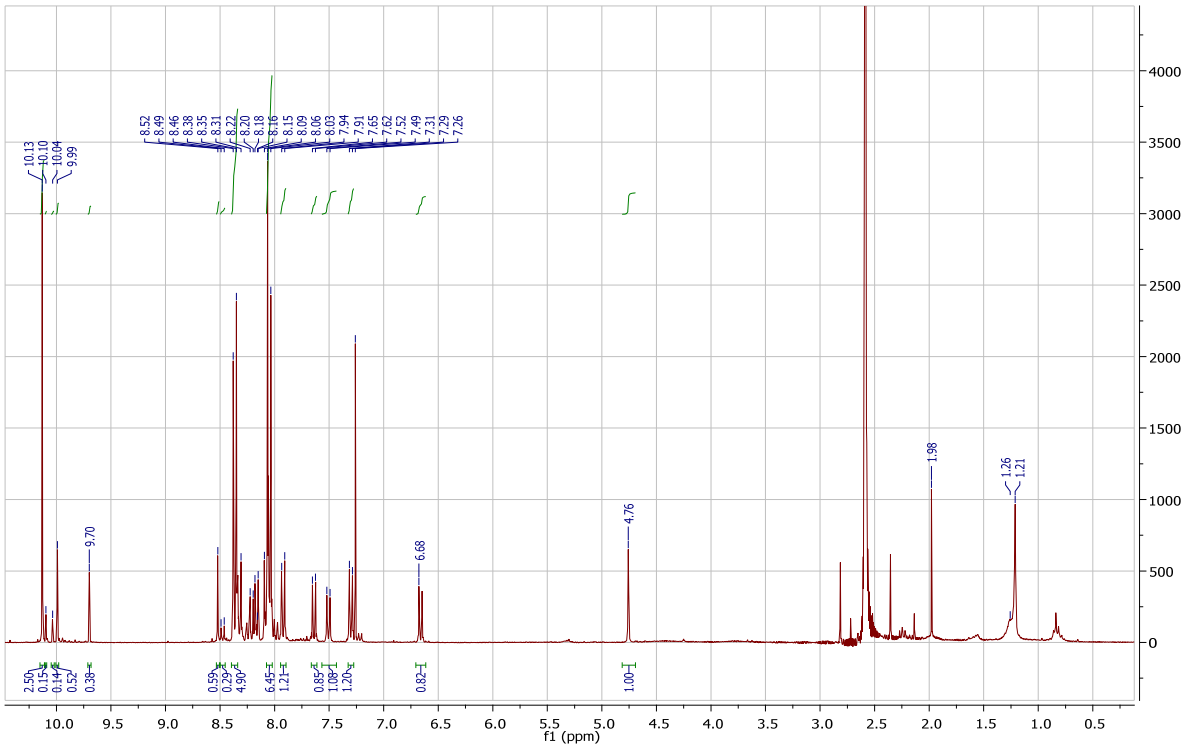

Figure S-17. Proton NMR (300 MHz, $CDCl_3$) of the product mixture of compounds **7** and **4-NO_2** obtained from photocatalytic conversion of **3-NO_2**

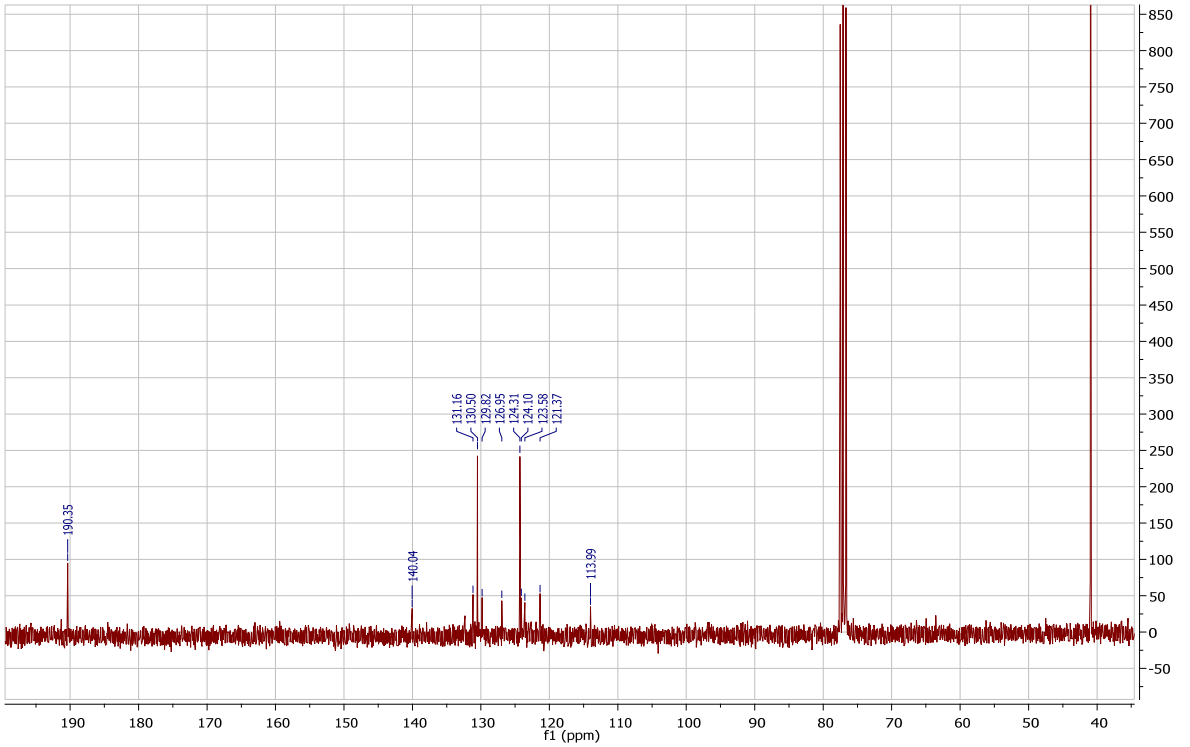

Figure S-18. Carbon NMR (75 MHz, $CDCl_3$) of the product mixture of compounds **7** and **4-NO_2** obtained from photocatalytic conversion of **3-NO_2**

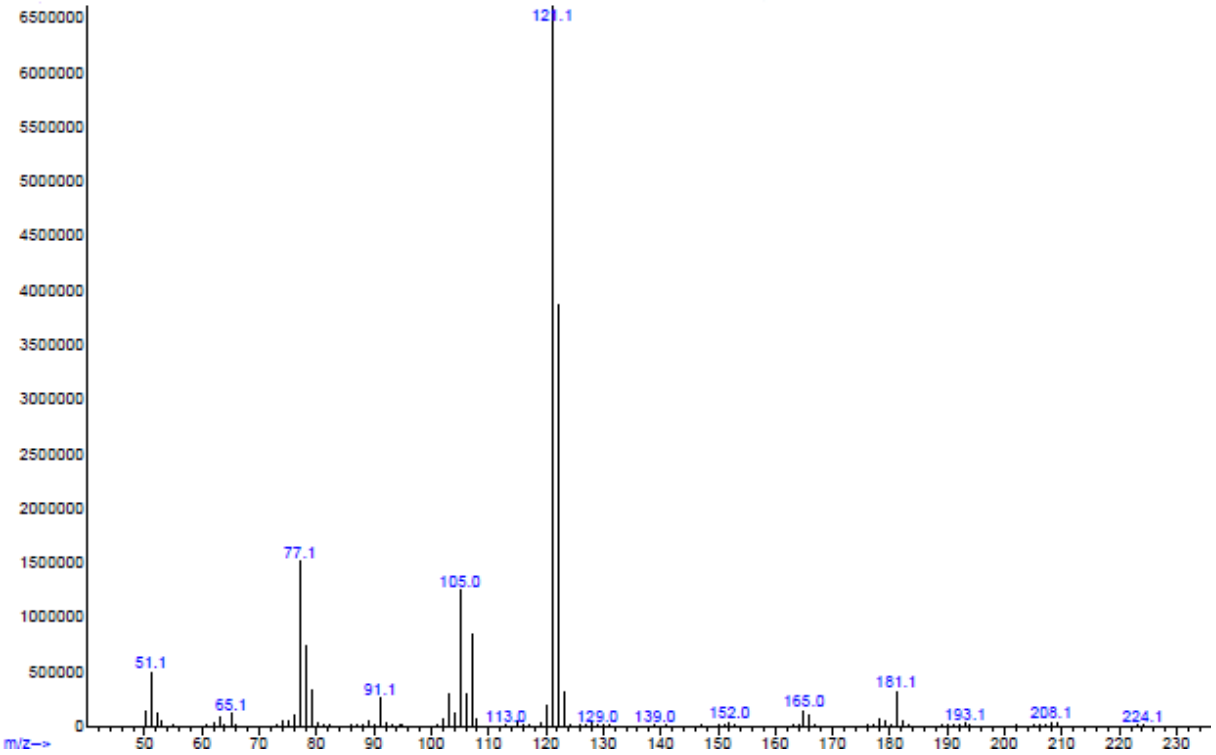

Figure S-19. Mass spectrum (GC-MS, EI) of compound **11**[25]

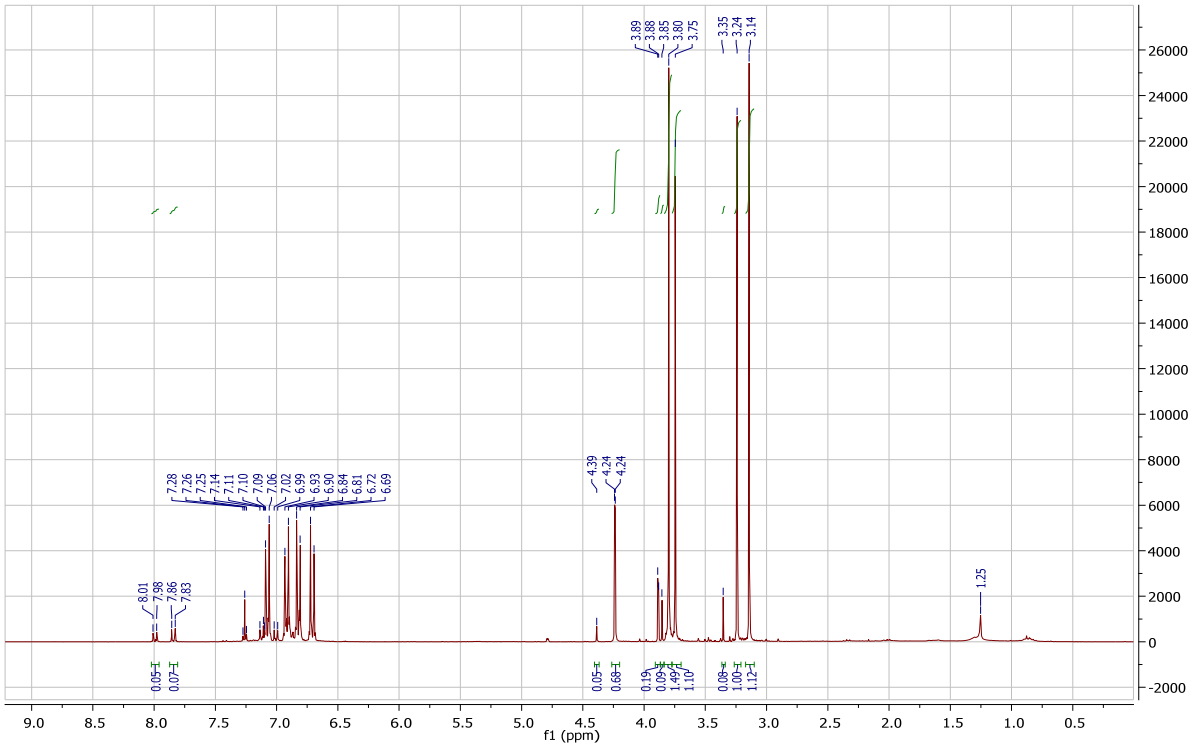

Figure S-20. Proton NMR (300 MHz, $CDCl_3$) of compound **13**

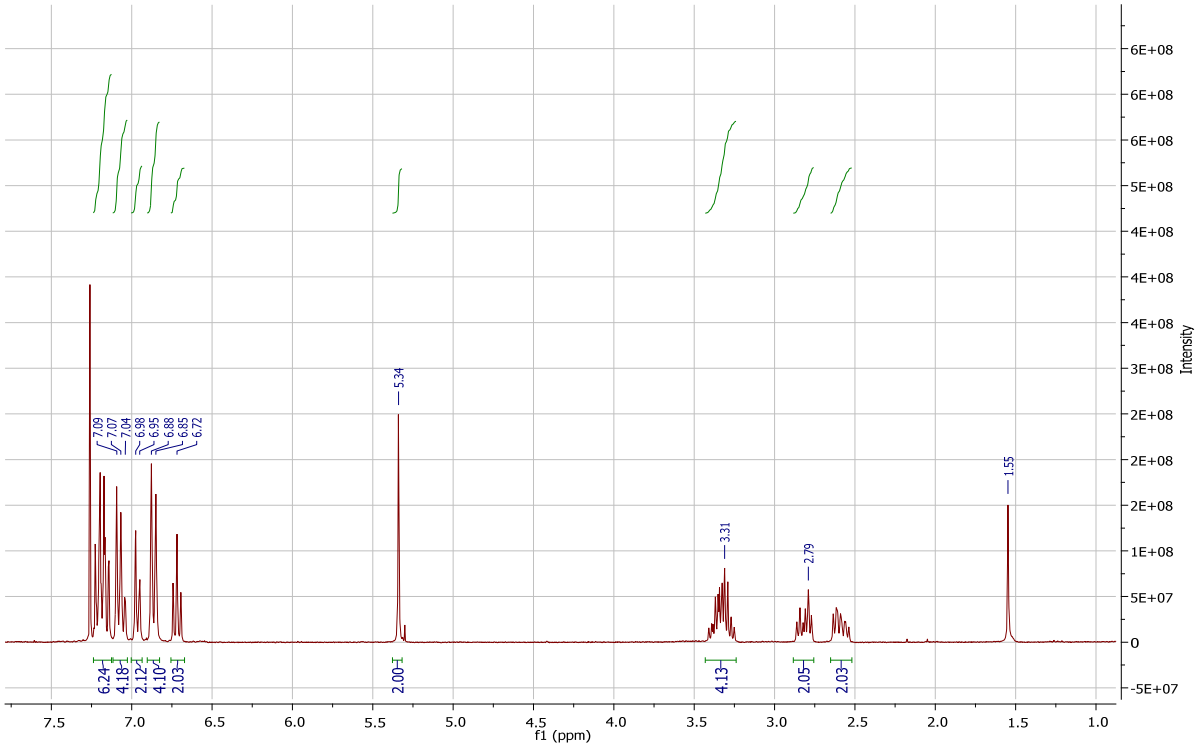

Figure S-21. Proton NMR (300 MHz, $CDCl_3$) spectrum of compound **17a**

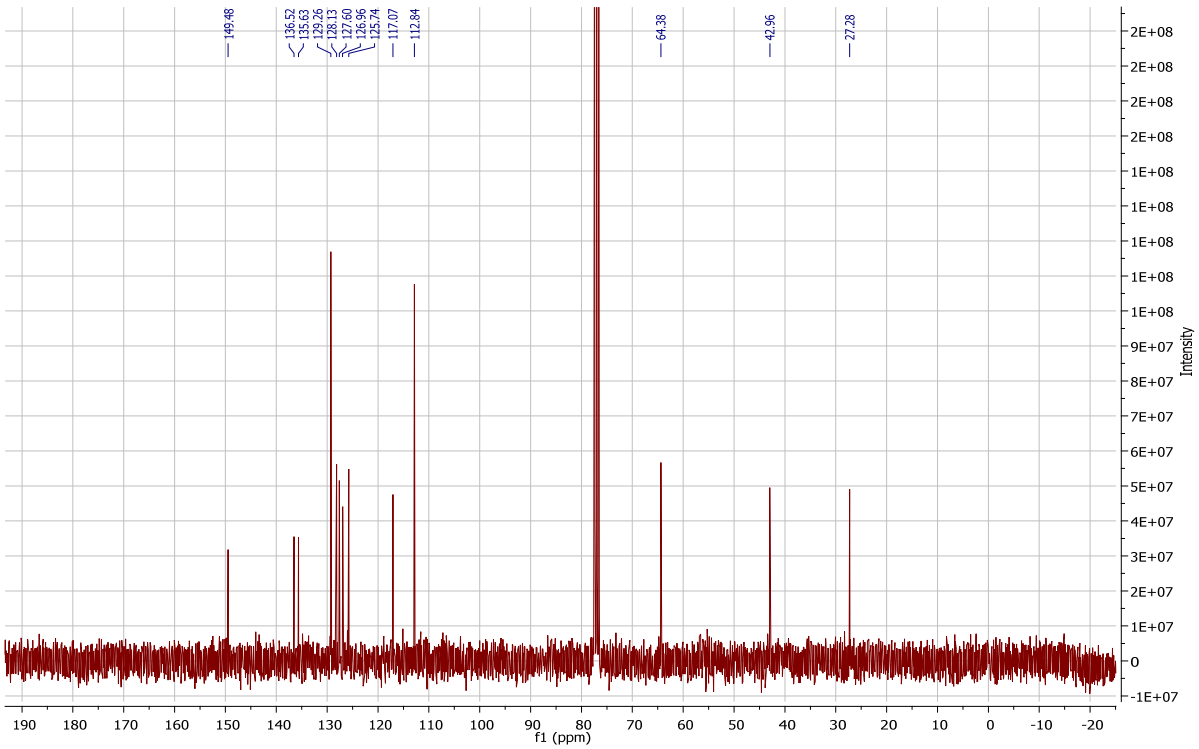

Figure S-22. Carbon NMR (75 MHz, $CDCl_3$) of compound **17a**

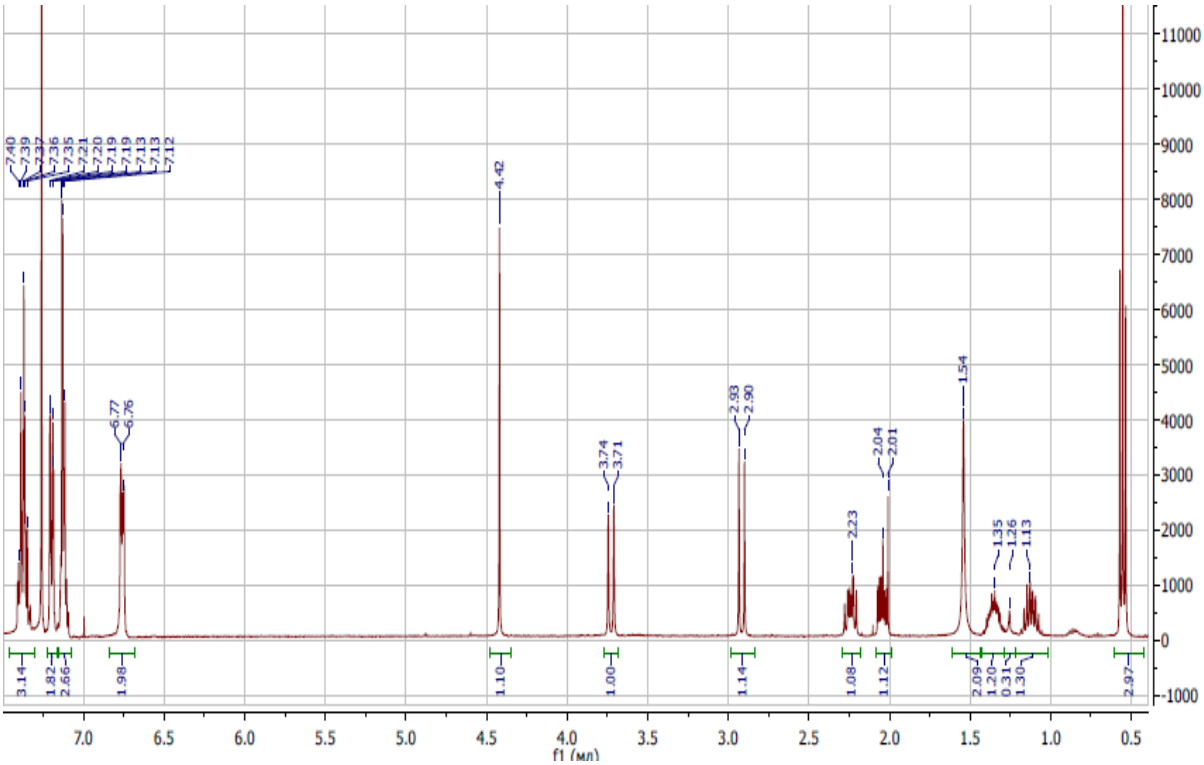

Figure S-23. Proton NMR (300 MHz, $CDCl_3$) of compound **17b**

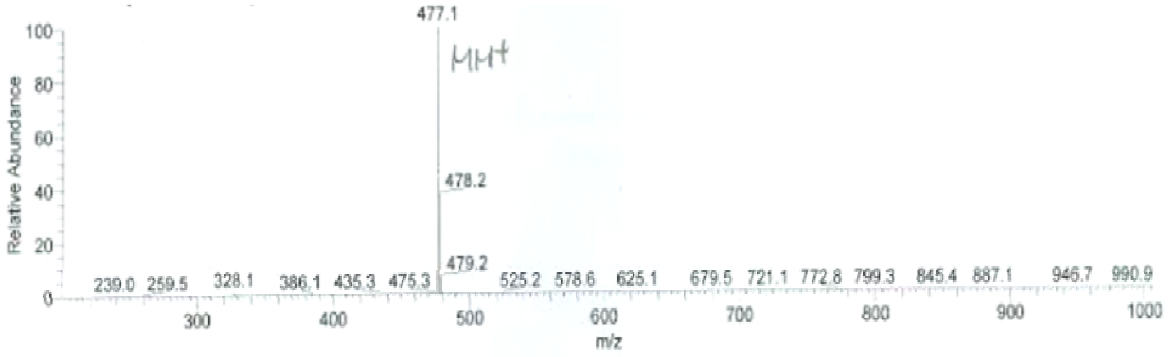

Figure S-24. Mass spectrum (GC-MS, ESI) of compound **17b**

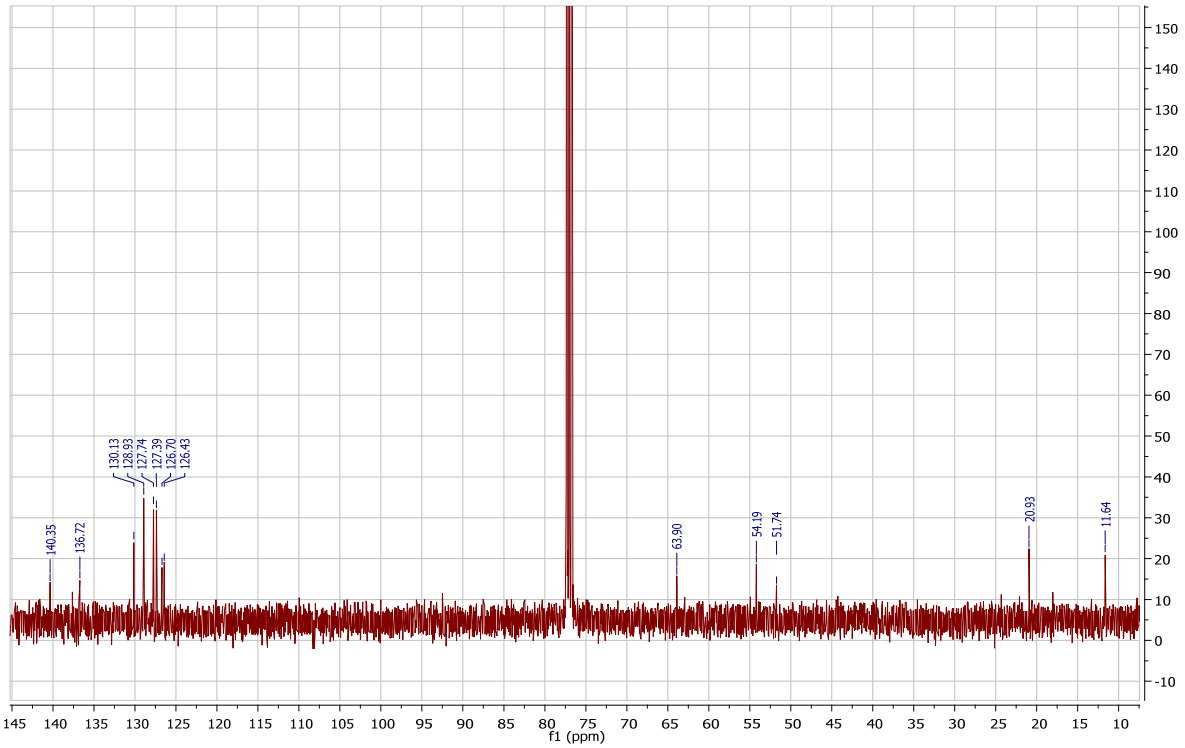

Figure S-25. Carbon NMR (75 MHz, $CDCl_3$) of compound **17b**

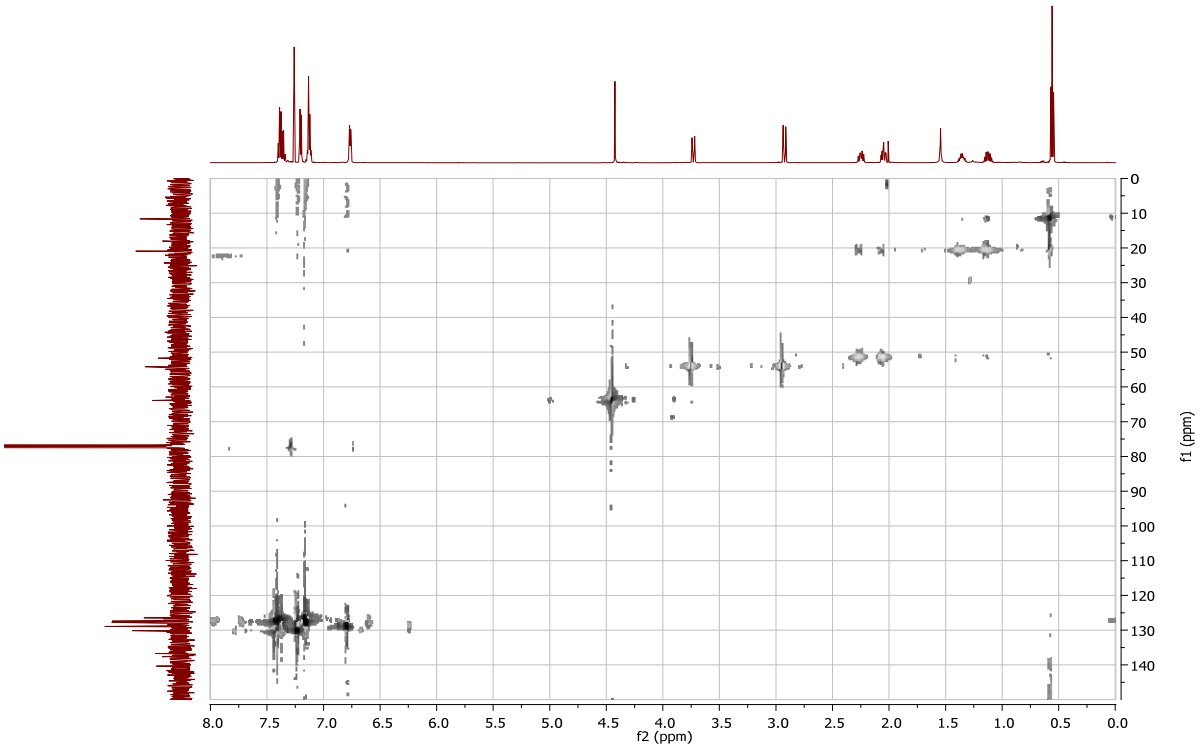

Figure S-26. HSQC NMR (300 / 75 MHz, $CDCl_3$) spectrum of compound **17b**

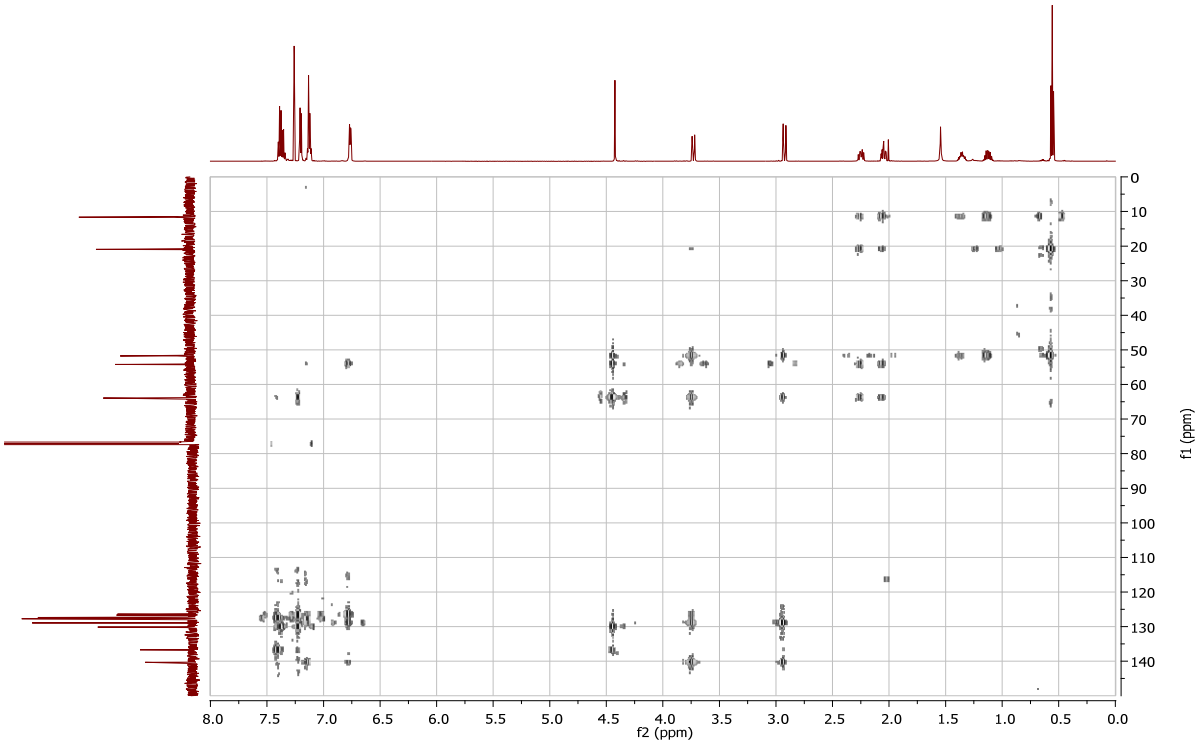

Figure S-27. HMBC NMR (300 / 75 MHz, $CDCl_3$) spectrum of compound **17b**

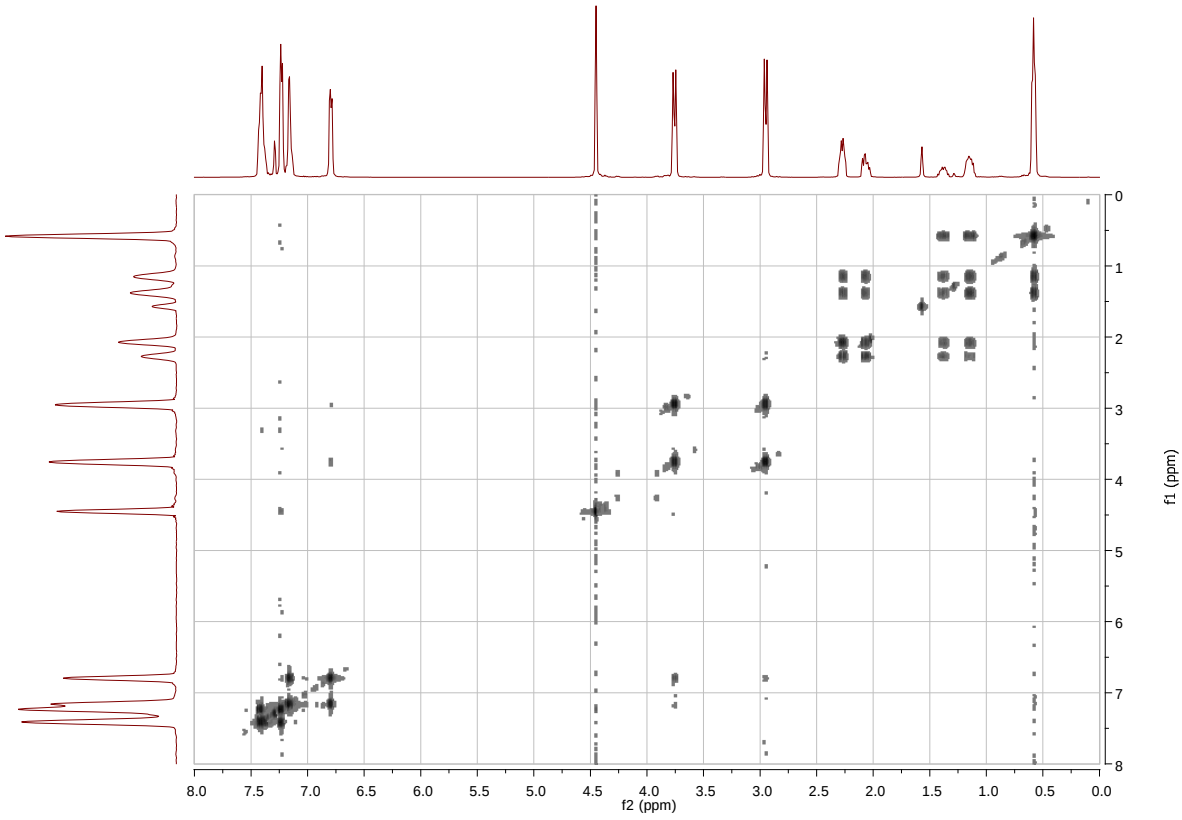

Figure S-28. COSY NMR (300 MHz, $CDCl_3$) spectrum of compound **17b**

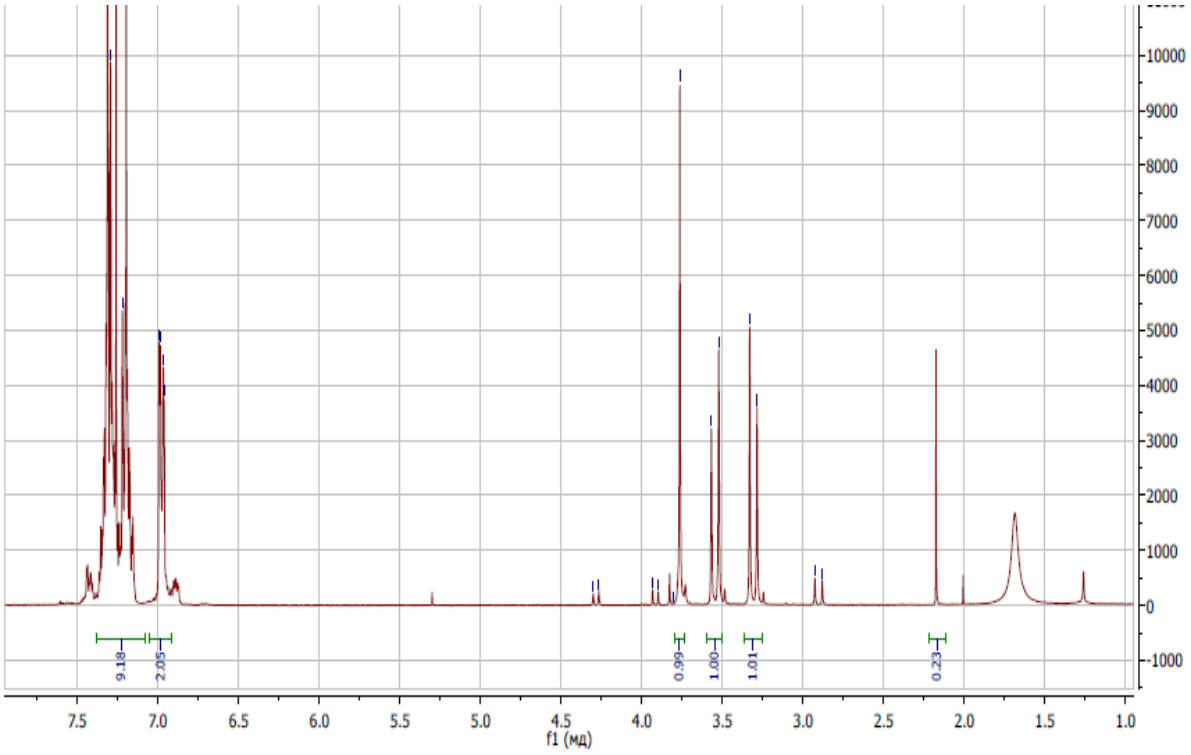

Figure S-29. Proton NMR (300 MHz, $CDCl_3$) of compound **17c**

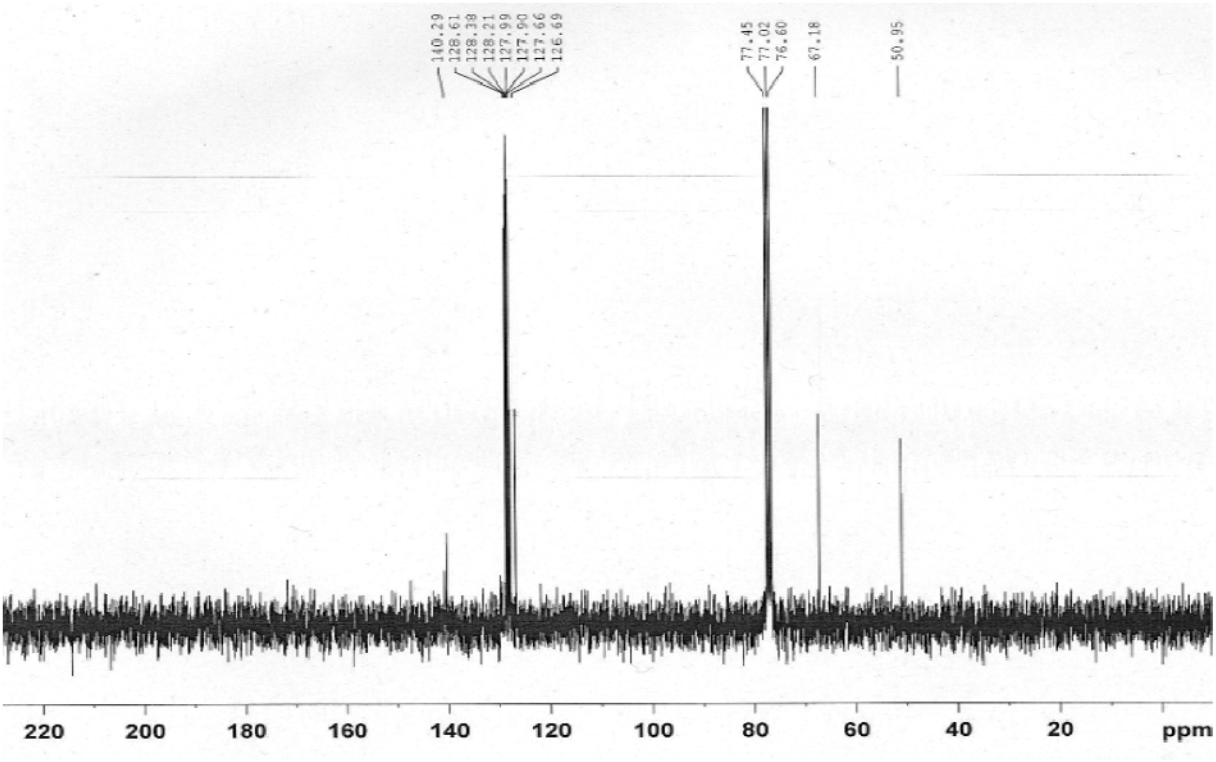

Figure S-30. Carbon NMR (75 MHz, $CDCl_3$) of compound **17c**

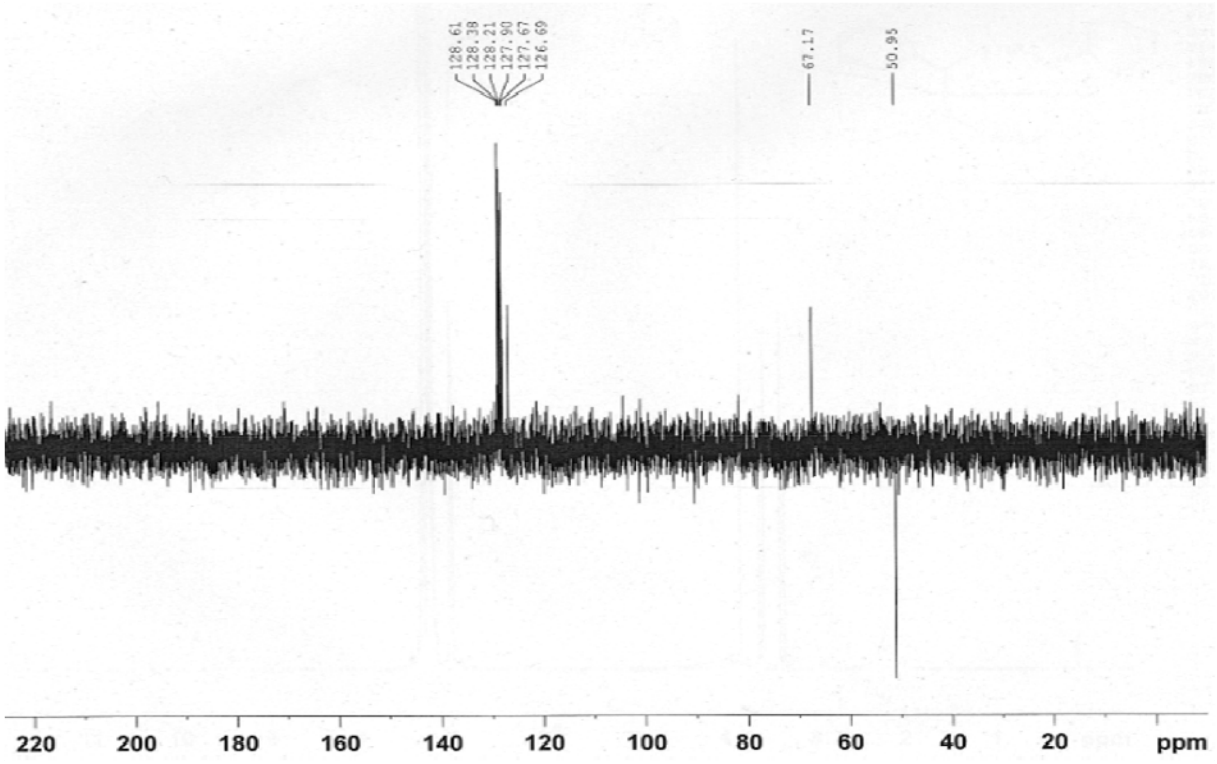

Figure S-31. DEPT (75 MHz, $CDCl_3$) spectrum of compound **17c**

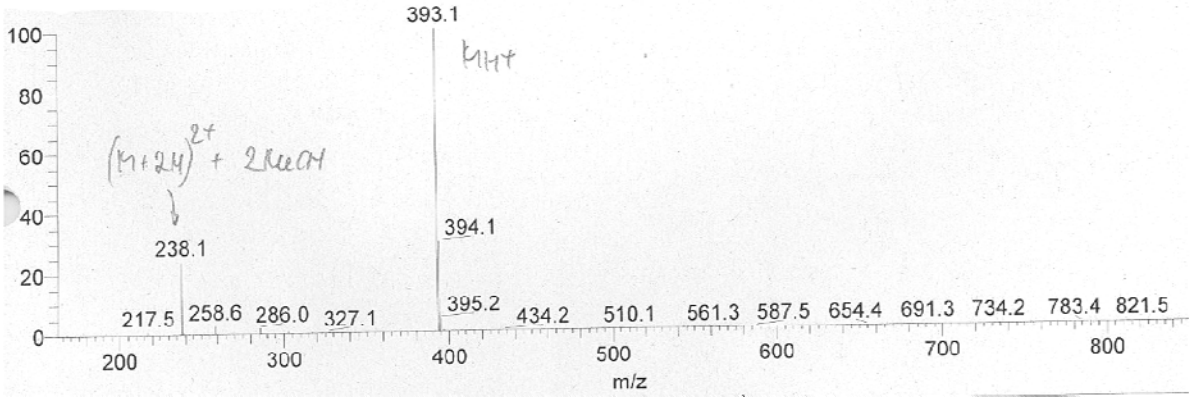

Figure S-32. Mass spectrum (GC-MS, ESI) of compound **17c**

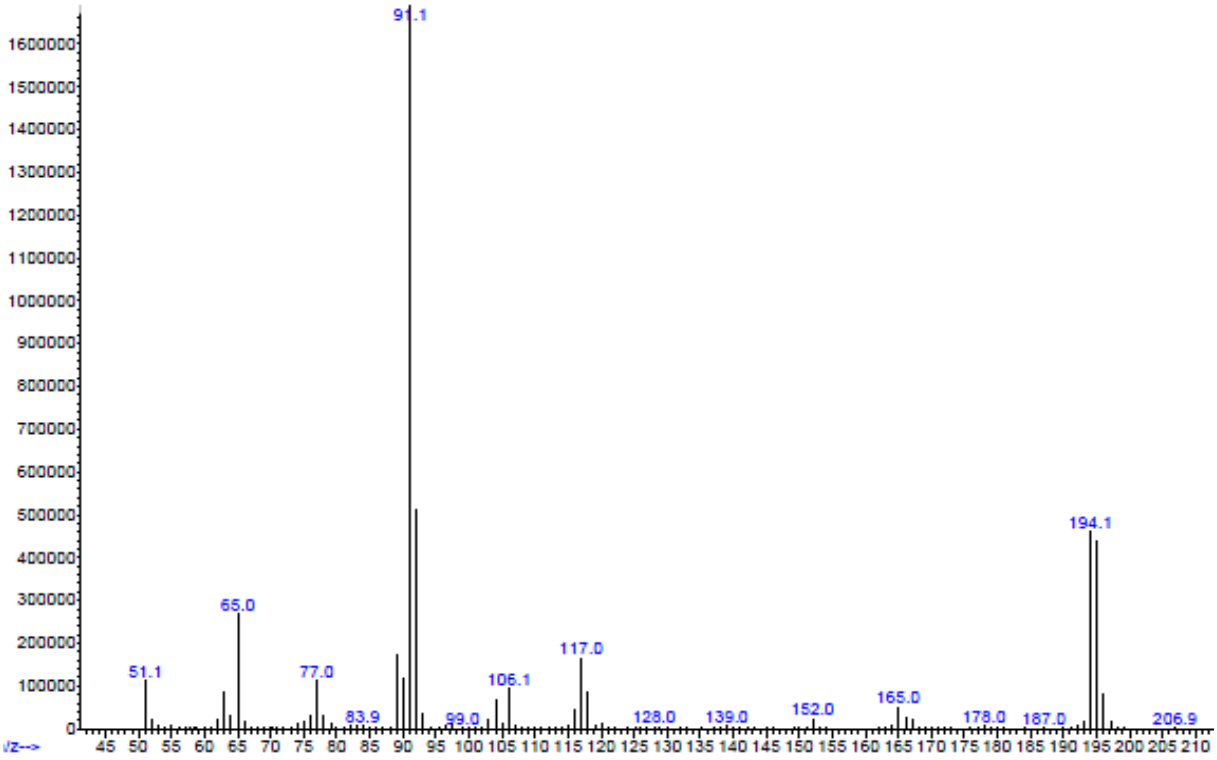

Figure S-33. Mass spectrum (GC-MS, EI) of compound **18c**[25]

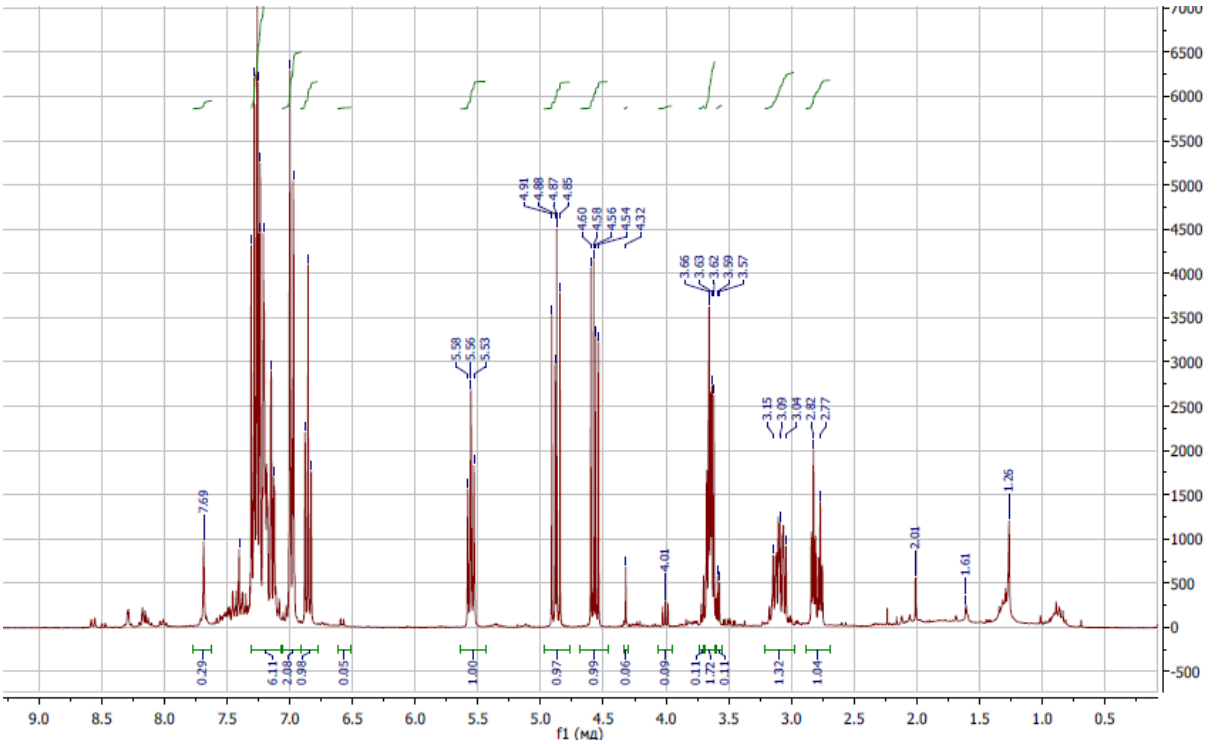

Figure S-34. Proton NMR (300 MHz, DMSO) of the reaction product of the photoconversion of compound **19a** yielding **20a**, as a mixture of diastereomers, and compound **21a** as a 3% byproduct

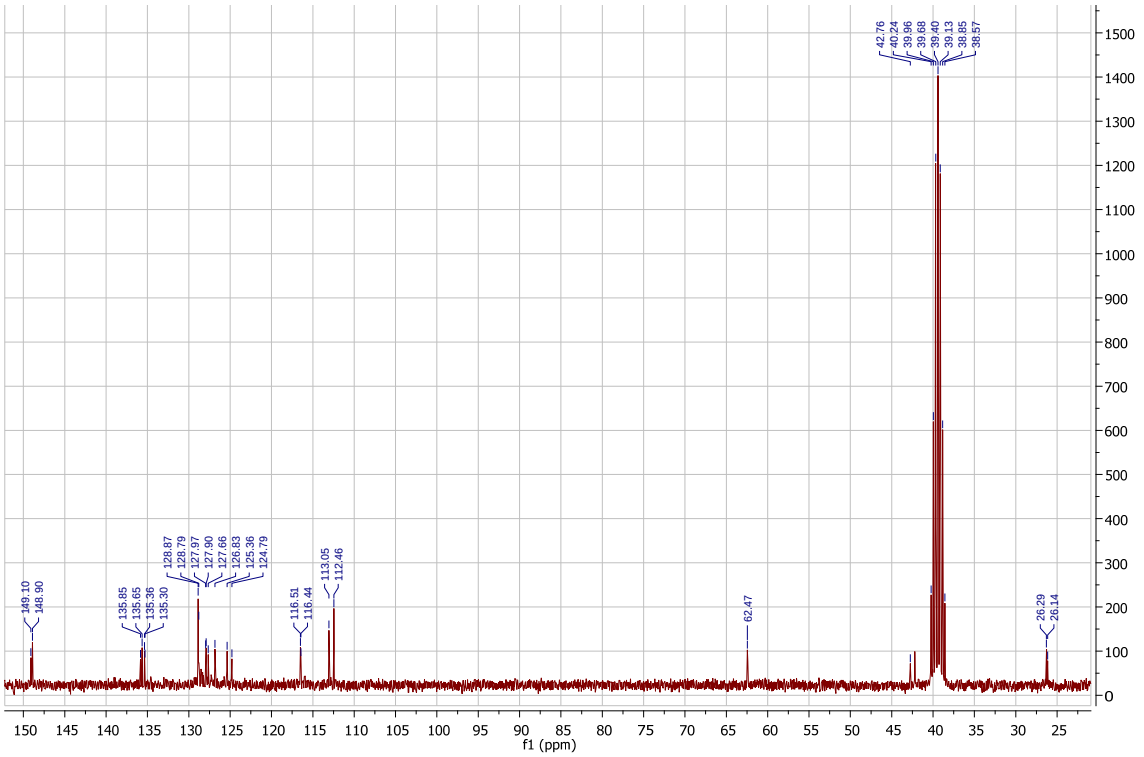

Figure S-35. Carbon NMR (75 MHz, DMSO) of compound **20a** (contains **21a** as a 3% minor byproduct)

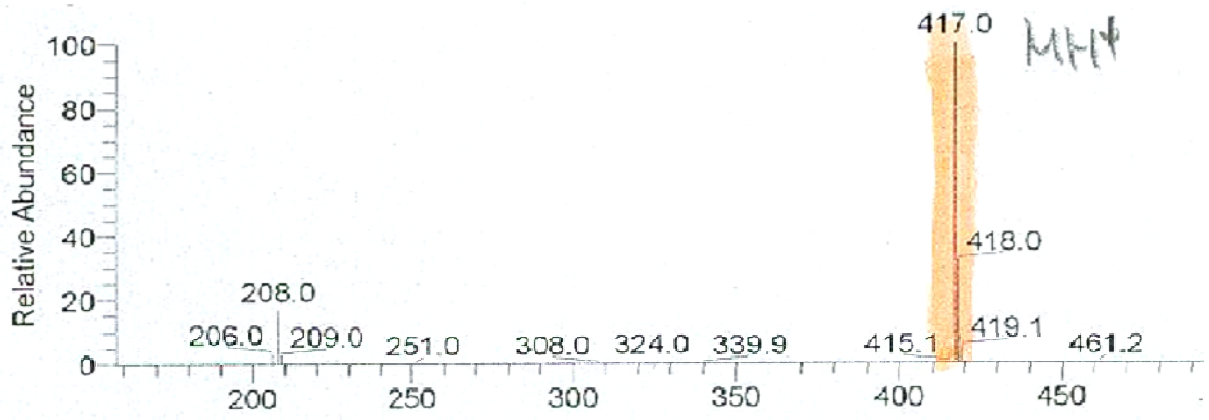

Figure S-36. Mass spectrum (GC-MS, ESI) of compound **20a**

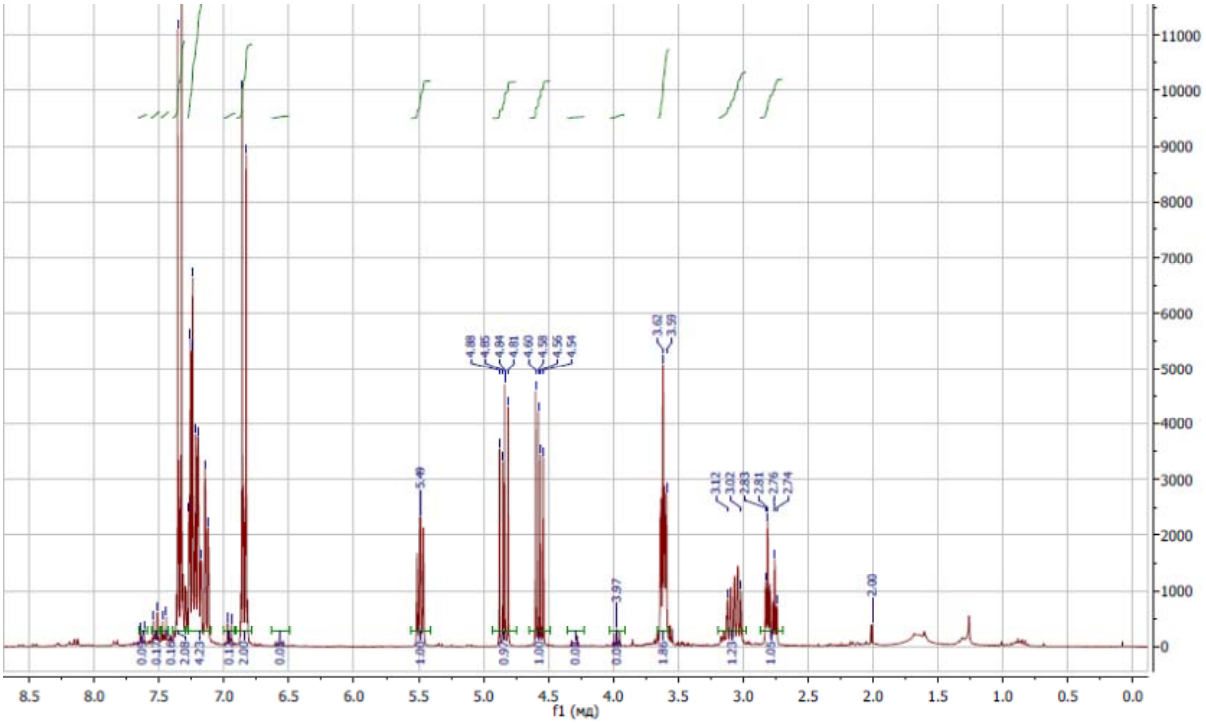

Figure S-37. Proton NMR (300 MHz, $CDCl_3$) of the reaction product of the photoconversion of compound **19b** yielding **20b**, as a mixture of diastereomers, and compound **21b** as a 8% byproduct

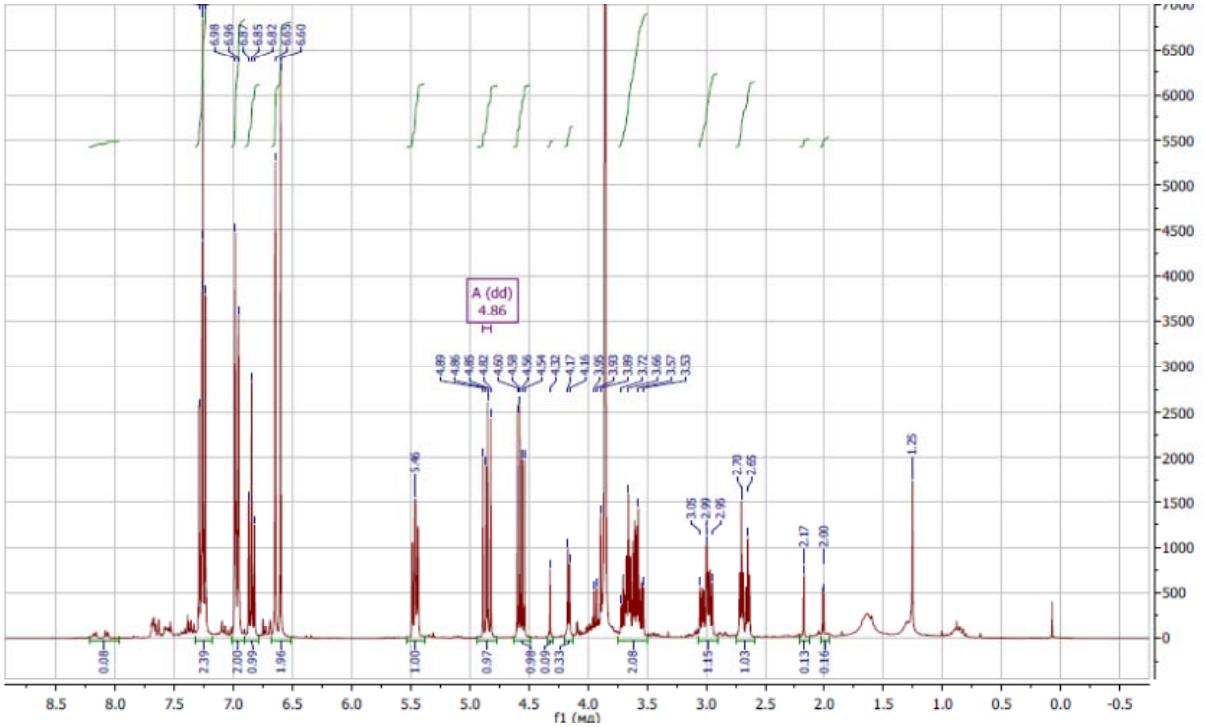

Figure S-38. Proton NMR (300 MHz, $CDCl_3$) of the reaction product of the photoconversion of compound **19c** yielding **20c**, as pure *meso* compound, and compound **21b** as a 10% byproduct

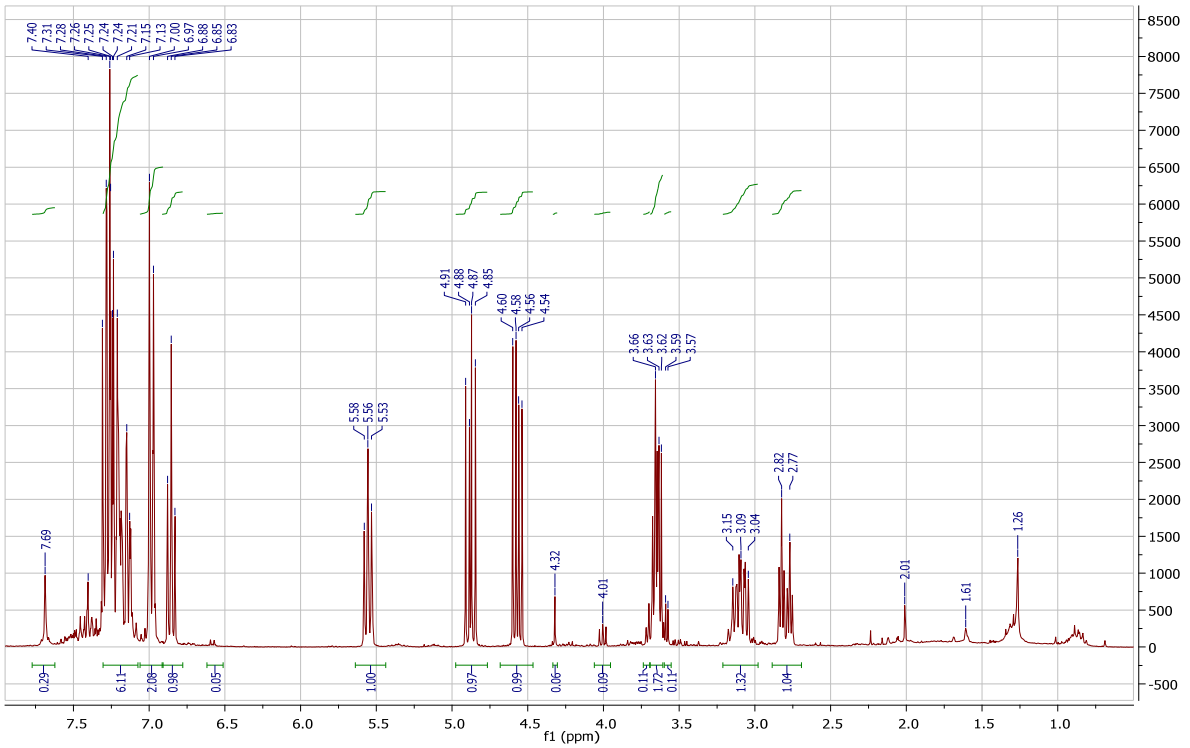

Figure S-39. Proton NMR (300 MHz, $CDCl_3$) of the reaction mixture containing compound **25a**

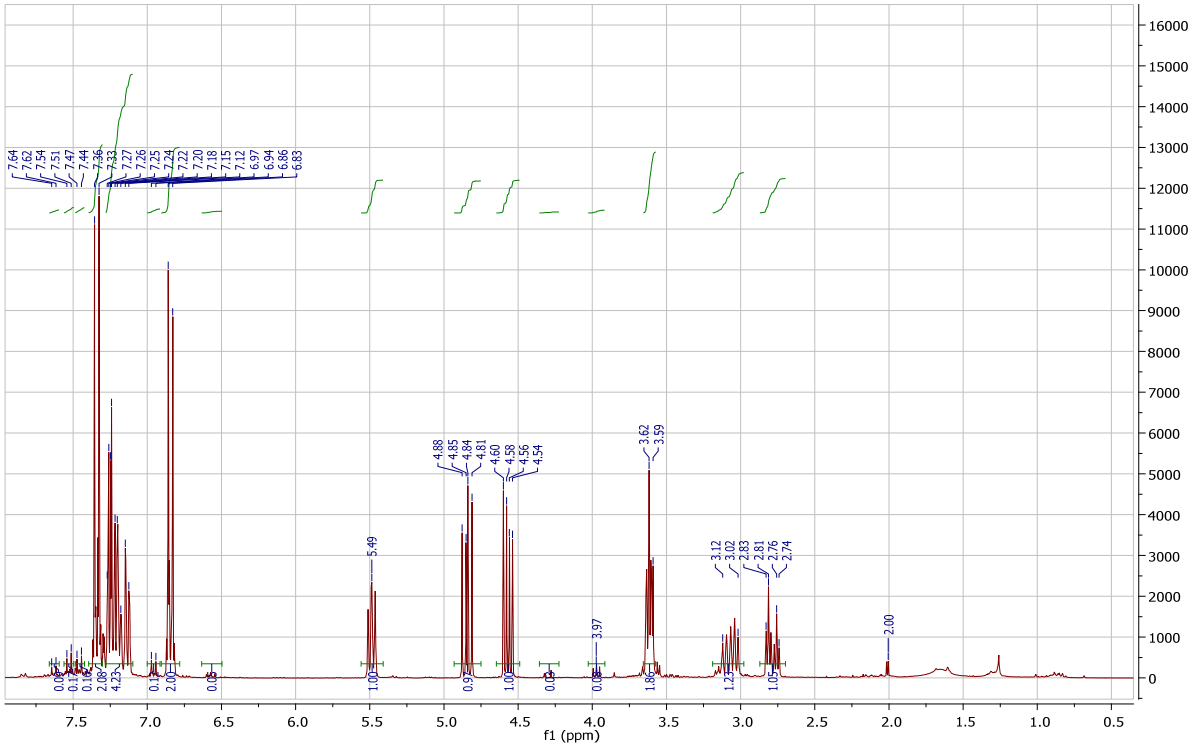

Figure S-40. Proton NMR (300 MHz, $CDCl_3$) of the reaction mixture containing compound **25b**

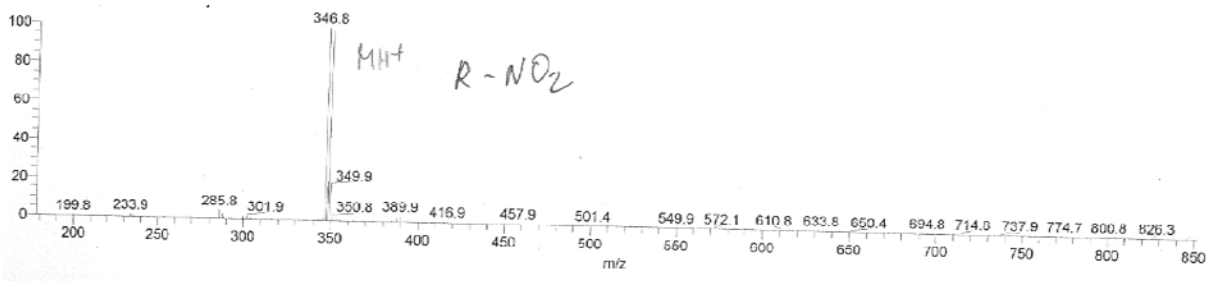

Figure S-41. Mass spectrum (GC-MS, ESI) of compound **25b**

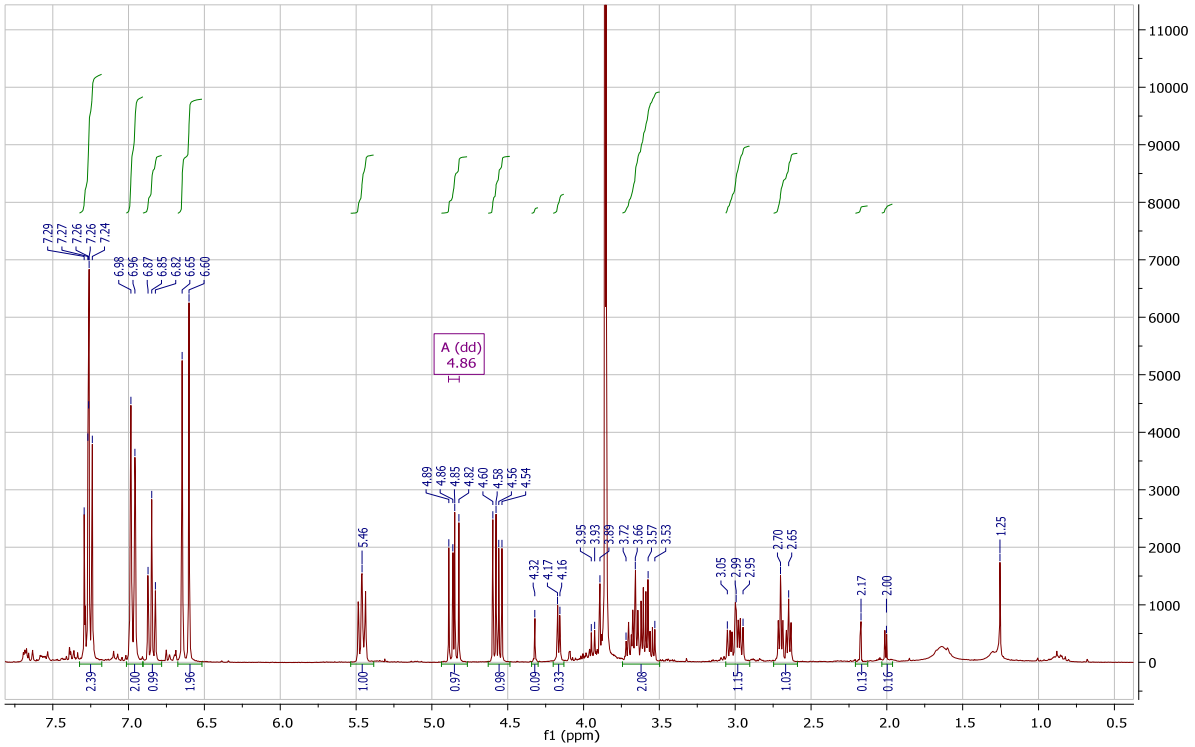

Figure S-42. Proton NMR (300 MHz, $CDCl_3$) of compound **25c**

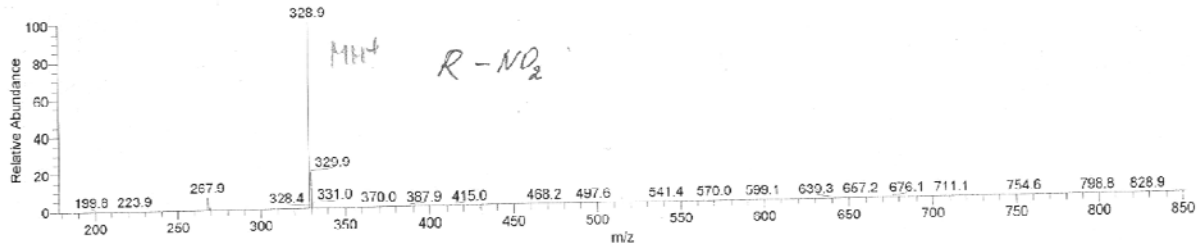

Figure S-43. Mass spectrum (GC-MS, ESI) of compound **25c**

6. References

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25. These spectra were measured at 70 eV ionization energy and the fragmentation footprint analyzed with the NIST/EPA/NIH mass spectral library.