

Supporting Information

Visible Light Mediated [2+2] Cycloaddition Reactions of 1,4-Quinones and Terminal Alkynes

Shaista Sultan,^{a,†} Muneer-ul-Shafi Bhat,^{a,†} Masood Ahmad Rizvi,^{*,‡} and Bhahwal Ali Shah^{*,†}

[†] AcSIR and Natural Product Microbes, CSIR-Indian Institute of Integrative Medicine, Jammu-180001,

[‡]Department of Chemistry, University of Kashmir, Srinagar, 190006

^a Both authors contributed equally

Table of content:

| | |
|---|--------|
| (1) Spectrophotometric Dye-degradation experiment | S2-S3 |
| (2) Cyclic Voltammetry | S3-S4 |
| (3) Spectra | S5-S51 |

Spectrophotometric Dye-degradation experiment:

The generation of sulfate radical anion from the potassium persulfate salt under visible light was explored using spectrophotometric dye degradation studies. In our investigations, the generation of the sulfate radical ion under visible (blue LEDs) was established from the dye degradation study of Eosin, Malachite green and Rose Bengal dyes which are known to degrade under oxidative conditions of radicals.¹ These dyes depicted a sequential decrease in the absorbance at their corresponding λ_{max} with the increasing irradiation time in presence of added potassium persulfate reagent (Figure S1, A-C).

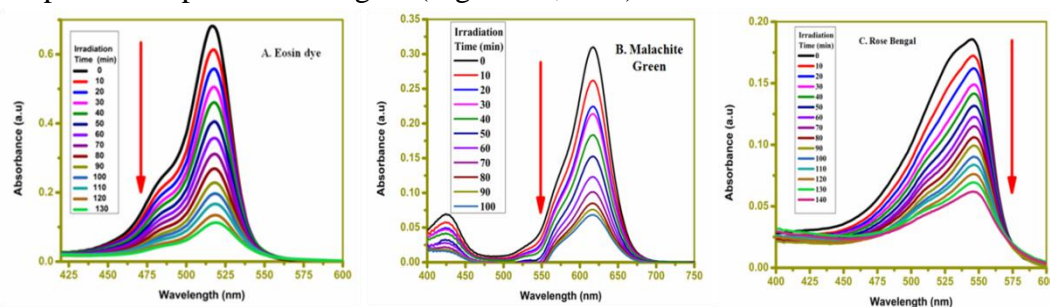


Figure S1. Photocatalytic dye degradation of **A.** Eosin, **B.** Malachite Green, **C.** Rose Bengal by sulfate radical anion.

From Figure S1(A-C), it can be seen that in presence of potassium persulfate under the blue LEDs irradiation, the studied dyes are undergoing a sequential decrease in absorbance /concentration indicating the oxidative degradation by the generated sulfate radical ions. The observed dye degradation data fits the second order reaction kinetics with respect to dye concentration. The comparative kinetic plots depicting the dye degradation under simple blue LEDs irradiation in absence and in presence of added potassium persulfate is as shown in Figure S2.

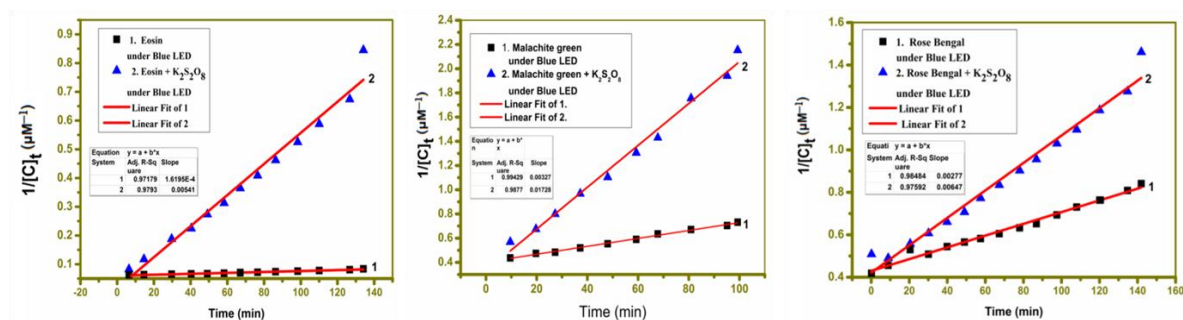


Figure S2. Kinetic plots of photocatalytic dye degradation. (1: dye degradation under only blue LEDs; 2: dye degradation under blue LEDs in presence of potassium persulfate)

Thus, from the dye degradation results it can be proposed that the generation of sulfate radical anion under blue LEDs irradiation is possible even though at a comparatively lower rate than the corresponding UV Illumination. This is in conformity to the earlier report of Xia *et al.*²

Dye Degradation study Procedure:

In a typical experiment, 80 mL of 0.02mM aqueous solution of dye was taken in 100 mL beaker at 25 °C and neutral pH. Prior to the light exposure, 10 mL of 0.4mM aqueous solution

of $K_2S_2O_8$ was added to it and the reaction mixture was magnetically stirred for 1 min. This followed the illumination of reaction mixture with blue LEDs strip (40 mW/cm^2 at 460 nm). The concentration of unreacted dye in the solution after every 10 minutes irradiation was calculated from absorbance values at the corresponding λ_{max} 's of dyes using UV-Vis double beam spectrophotometer PC1650. The time dependent absorbance data was solved for the detailed kinetic studies using Microsoft origin software.

Cyclic Voltammetry studies:

Electrochemical methods are continuing to be used by synthetic organic chemists as tools of mechanistic studies in electro-organic synthesis.³ Cyclic voltammetry (CV) is an important electro-analytical method for investigating the electrochemical behavior of a reaction system. The CV descriptors provide kinetic and thermodynamic information which can be indispensable for mechanistic studies⁴. In the present work, CV studies were used to obtain the redox potentials of the reactants for the thermodynamic feasibility of the proposed reaction steps. For a feasible electron transfer process the E_{cell} should be positive making the overall free energy change (ΔG) negative. E_{cell} is positive when the reduction potential of the oxidizing agent is higher than the reactant. In our proposed mechanism for the reaction, the sulfate radical anion is an oxidizing agent for the phenylacetylene. This requires the reduction potential of sulfate radical anion to be higher than the reduction potential of phenylacetylene. The redox potential of the sulfate radical anion has been reported to be around 2.6 V with a reasonably good life time of near 40 μs .^{2,5} In our CV studies we have observed that phenylacetylene shows an irreversible redox behavior with only single oxidation peak current starting at a potential close to 1.9 V (vs. SCE) and no reduction peak Figure S3.

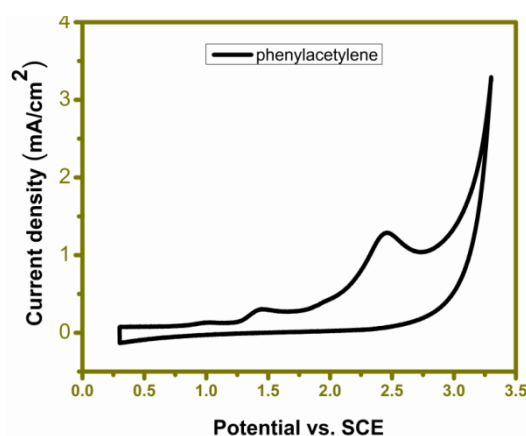


Figure S3: Cyclic Voltammogram depicting phenylacetylene oxidation at glassy carbon electrode { CH_3CN solvent, (0.1M) TBAP supporting electrolyte at a scan rate of 100 mV sec^{-1} }

The onset of oxidation peak is close to 1.9 V and it maximizes around 2.4 V (vs. SCE). The CV plot of phenylacetylene over a changing scan rate study did not produce ideal plots owing to some polymerizing / major structural change in the analyte. Thus CV data indicates a single redox system of irreversible nature in phenylacetylene. The single redox system is suggestive of one electron transfer reaction and the calculated formal potential of phenylacetylene (1.9- 2.4) suggest that it can be oxidized by the persulfate radical anion

having a higher reduction potential of (2.6 V vs SCE), thus supporting our mechanistic hypothesis.

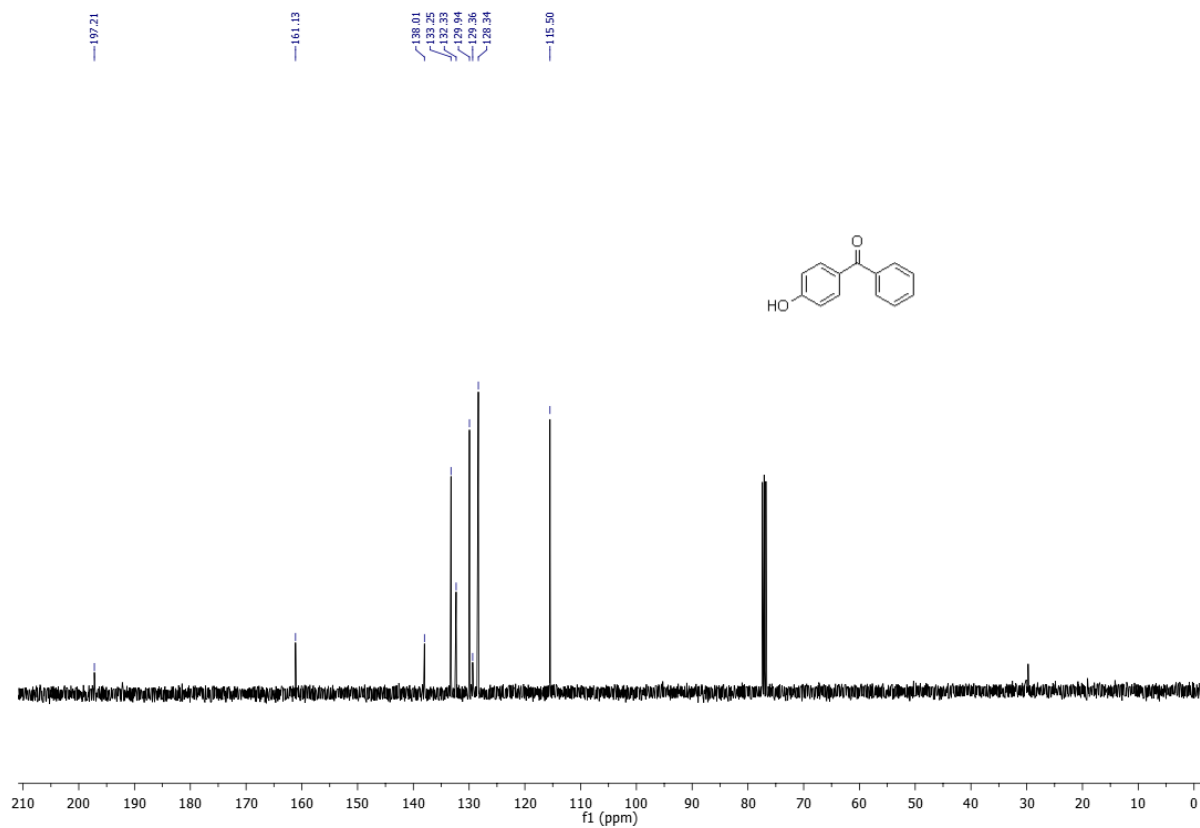
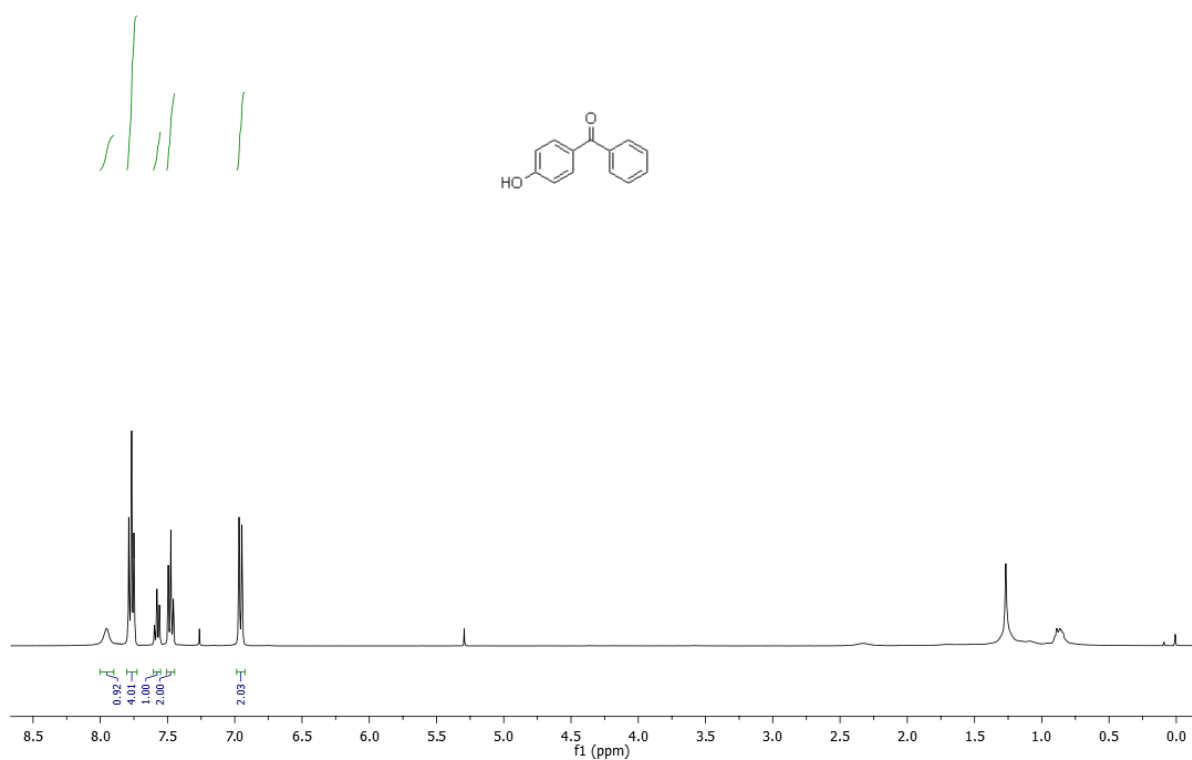
Experimental Procedure:

Cyclic voltammetry studies were carried out with VMP-300 Electrochemical Workstation (Biologic, France) in standard three-electrode setup with glassy carbon (area=0.071cm² diameter) as the working electrode, platinum mesh as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The measurements were done with phenylacetylene (1mM) in acetonitrile solution with tetrabutylammonium perchlorate (0.1M) as supporting electrolyte under different scan rates (2 -100 mv sec)

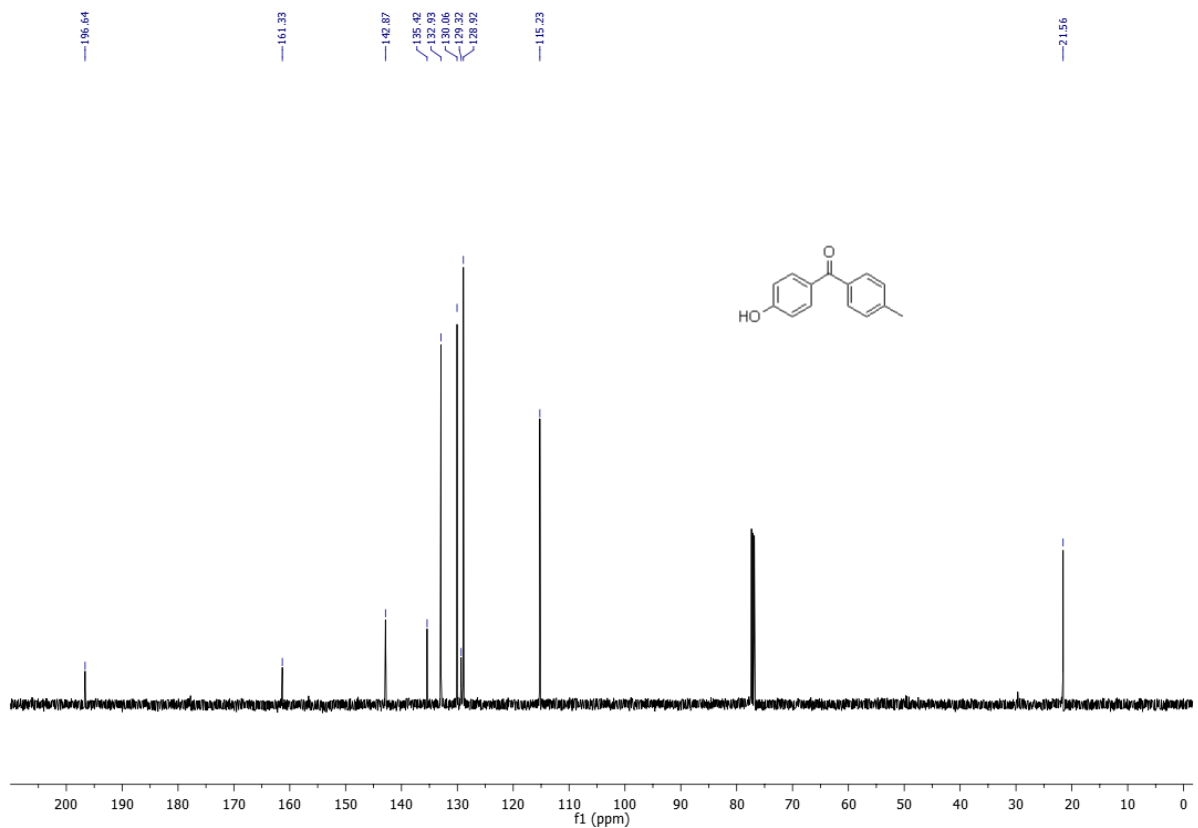
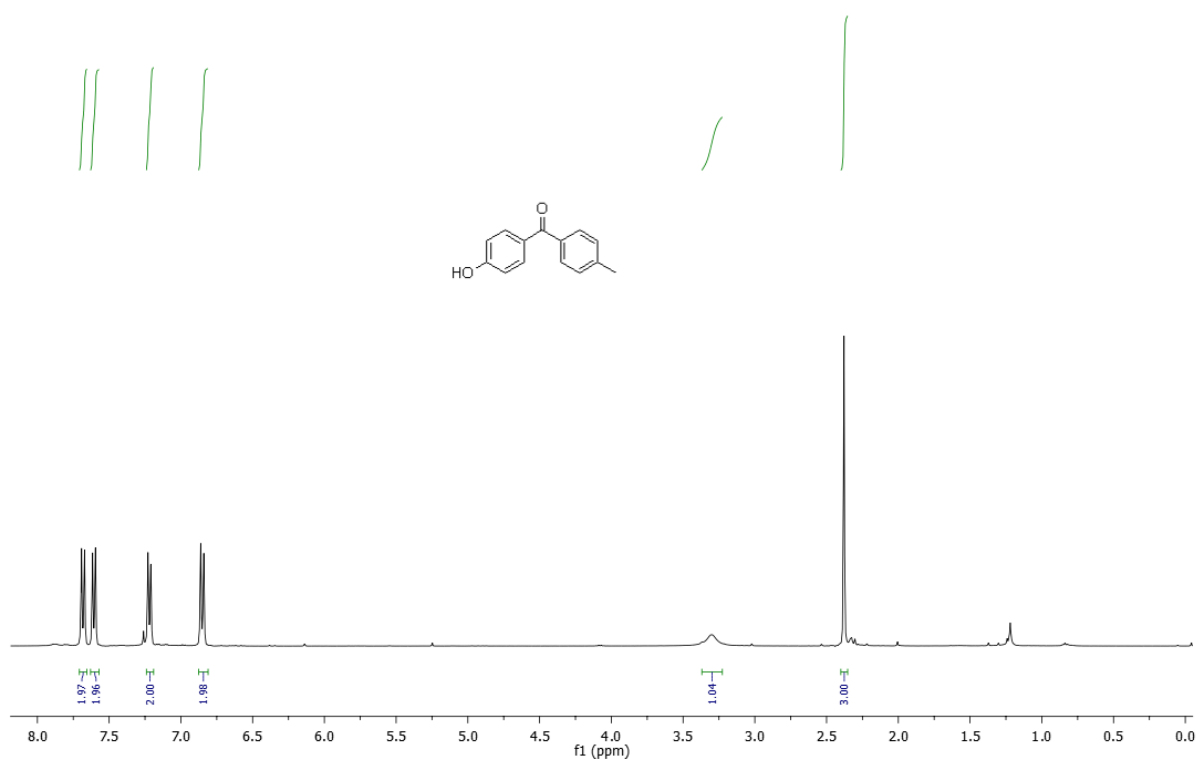
References:

1. (a) Li, X. Z.; Liu, H. L.; Yue, P. T. Photoelectrocatalytic Oxidation of Rose Bengal in Aqueous Solution Using a Ti/TiO₂ Mesh Electrode *Environ. Sci. Technol.* **2000**, *34*, 4401. (b) Chen, F.; Ma, W.; He, J.; Zhao, J. Fenton Degradation of Malachite Green Catalyzed by Aromatic Additives *J. Phys. Chem. A* **2002**, *106*, 9485.
2. Zhao, Y.; Huang, B.; Yang, C.; Xia, W.; Visible-Light-Promoted Direct Amination of Phenols via Oxidative Cross-Dehydrogenative Coupling Reaction *Org. Lett.* **2016**, *18*, 3326.
3. (a) Stork, G.; Davies, J. E.; Meisels, A. The total synthesis of a naturally occurring pentacyclic triterpene system *J. Am. Chem. Soc.* **1959**, *81*, 5516. (b) Shono, T.; Matsumura, Y.; Katoh, S.; Takeuchi, K.; Sasaki, K.; Ramada, T.; Shimizu, R. Electroorganic Chemistry. 120. New Patterns of Anodic Oxidation of Amides. Synthesis of α -Amino Aldehyde Acetals and Pyrrolidines from Amines *J. Am. Chem. Soc.* **1990**, *112*, 2368. (c) Mihelcic J.; Moeller, K. D. Oxidative Cyclizations: The Asymmetric Synthesis of (-)-Alliacol A *J. Am. Chem. Soc.* **2004**, *126*, 9106. (d) T. Morofuji, A. Shimizu, J. Yoshida, Direct C–N Coupling of Imidazoles with Aromatic and Benzylic Compounds via Electrooxidative C–H Functionalization *J. Am. Chem. Soc.* **2014**, *136*, 4496.
4. Rudenko, A. P.; Zarubin, M. J.; Barsheva, N. S. Electrochemical oxidation of organic compounds in fluorosulfuric acid—III. Voltammetric investigation of aromatic carboxylic acids and acylium ions *Electrochimica Acta.* **1983**, *28*, 317.
5. (a) Gau, B. C.; Chen, H.; Zhang, Y.; Gross, M. L. Sulfate Radical Anion as a New Reagent for Fast Photochemical Oxidation of Proteins *Anal. Chem.* **2010**, *82*, 7821. (b) More, N. Y.; Jeganmohan, M. Oxidative Cross-Coupling of Two Different Phenols: An Efficient Route to Unsymmetrical Biphenols *Org. Lett.* **2015**, *17*, 3042. (c) Yi, K.; Lin, A.; Lin, J. T.; Jochems, A. P. Oxidation of amaranth dye by persulfate and peroxymonosulfate activated by ferrocene *J. Chem. Technol. Biotechnol.* **2016**, *92*, 163.

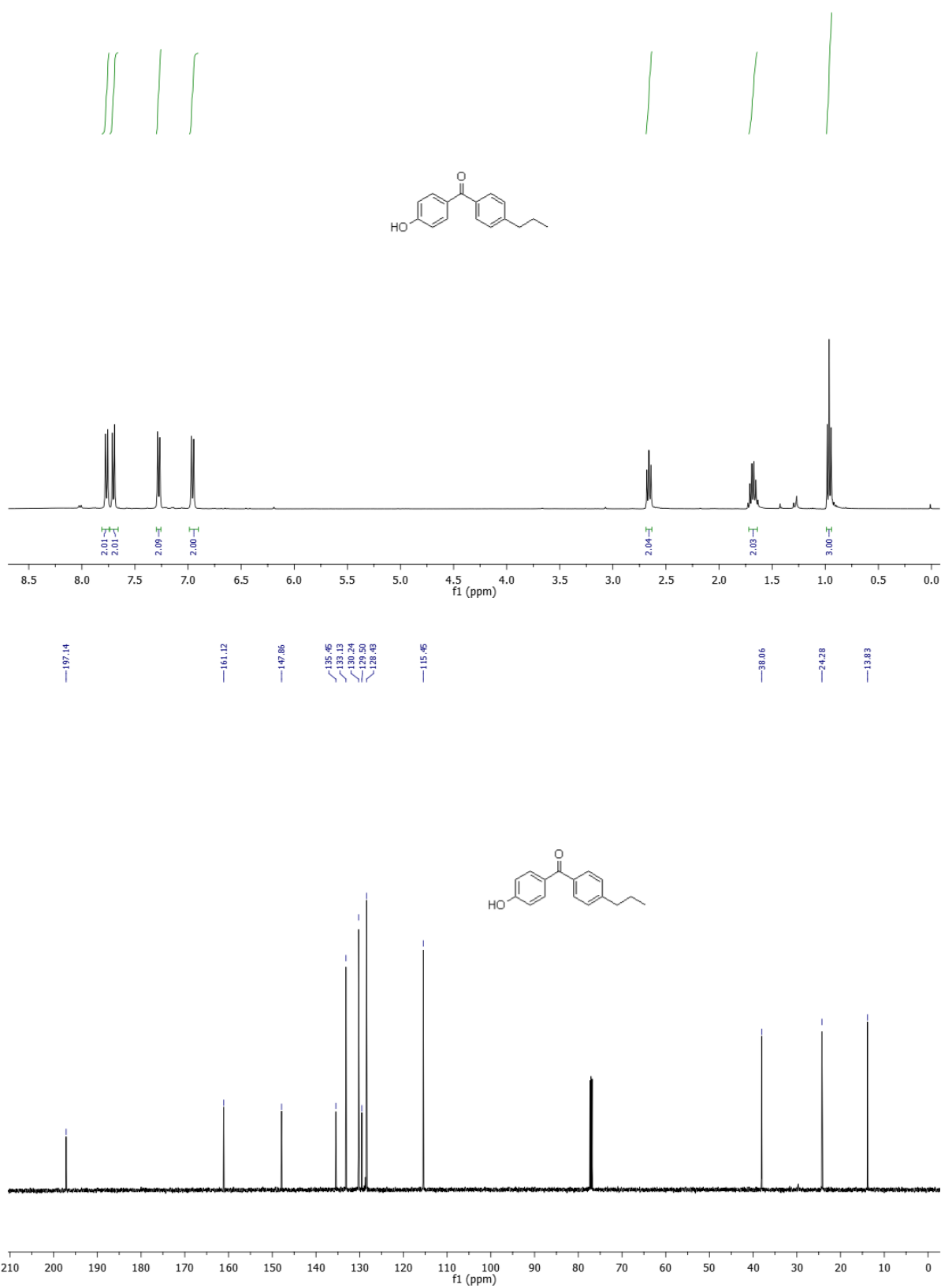
^1H and ^{13}C NMR of 3:



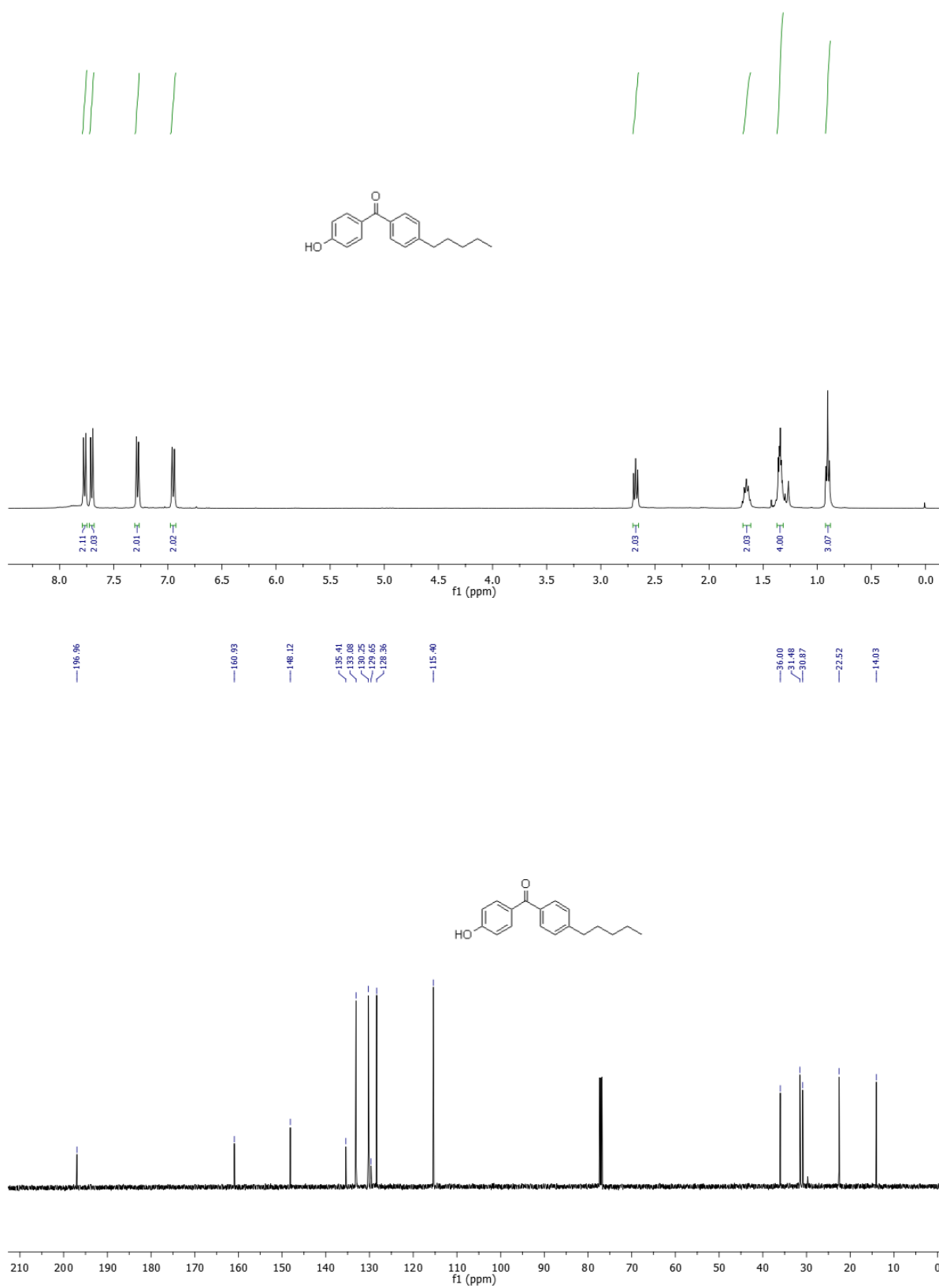
^1H and ^{13}C NMR of 4:



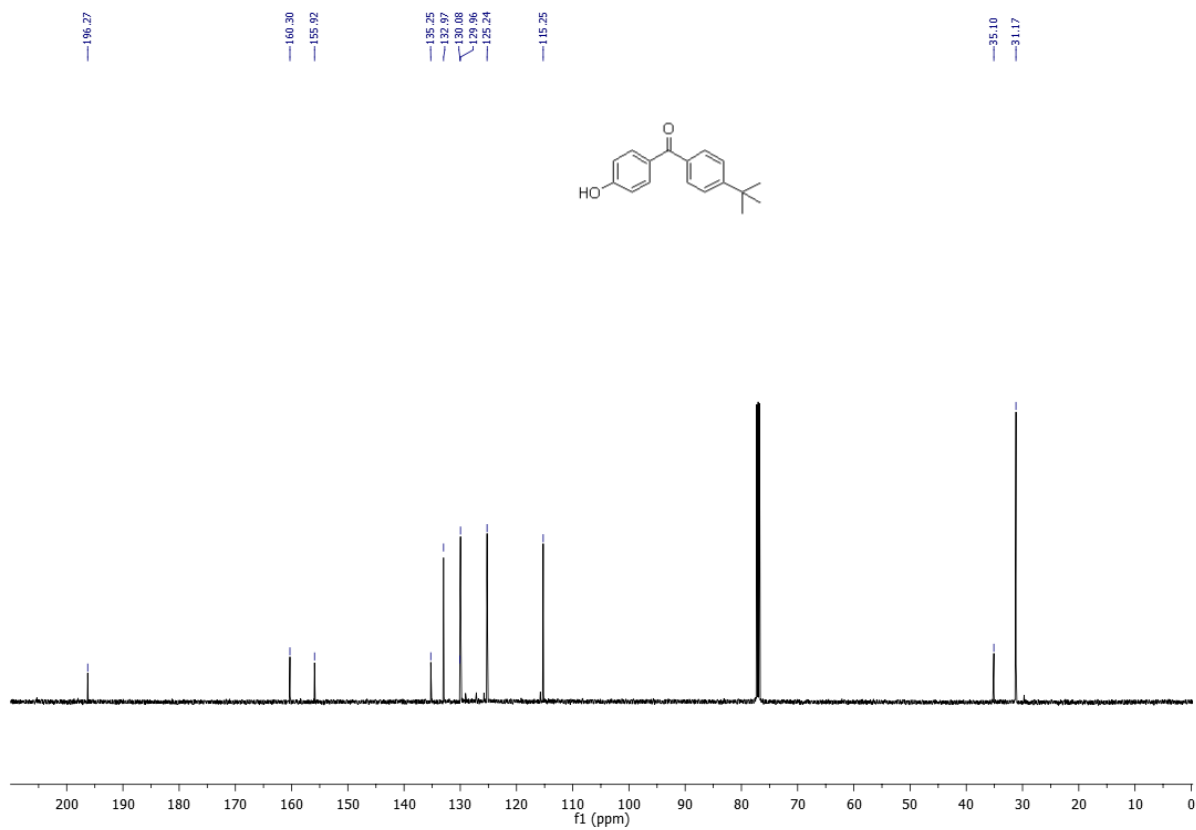
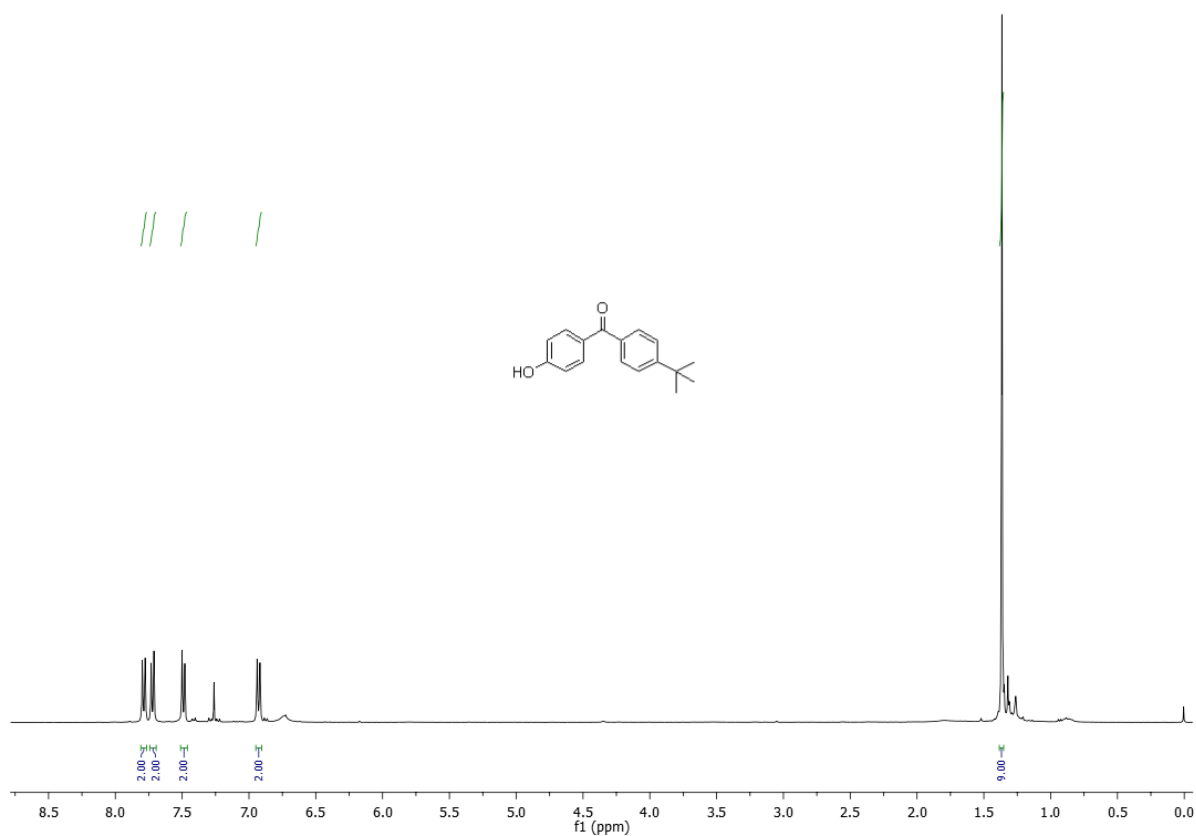
^1H and ^{13}C NMR of 5:



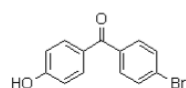
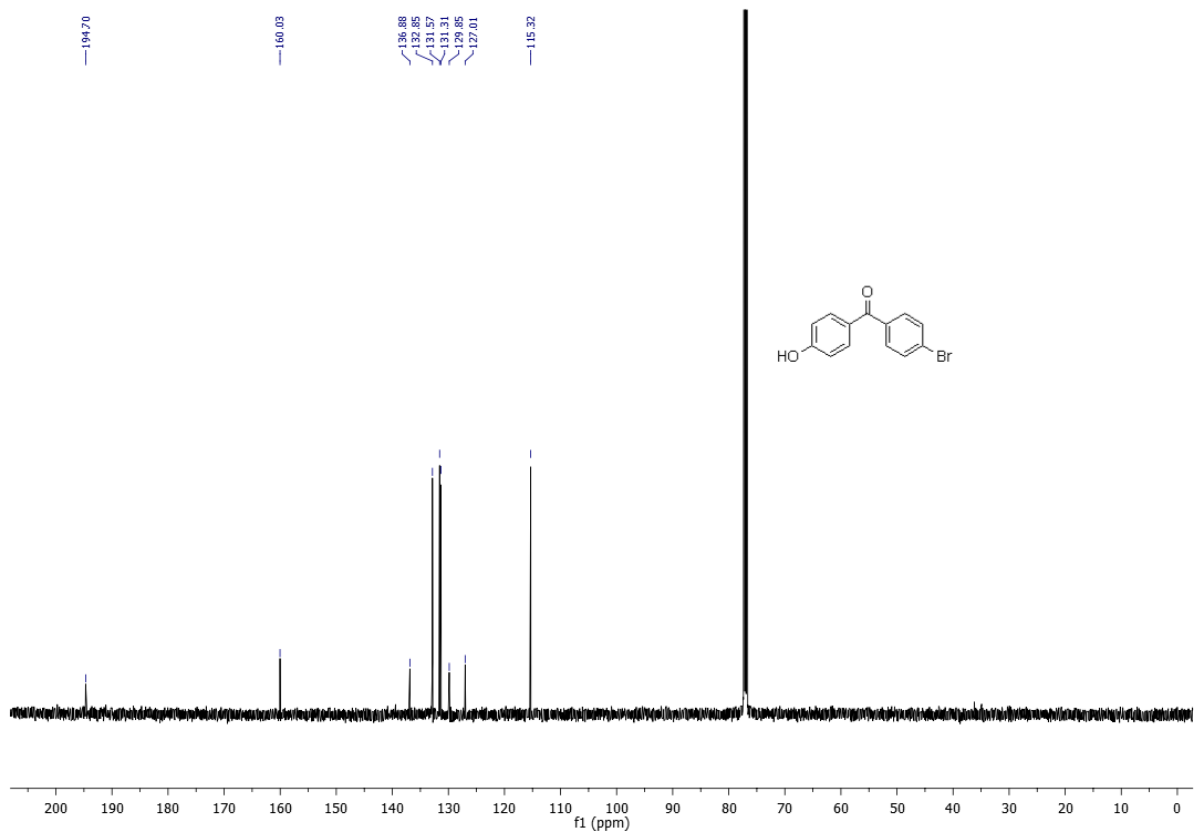
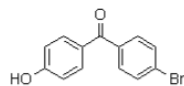
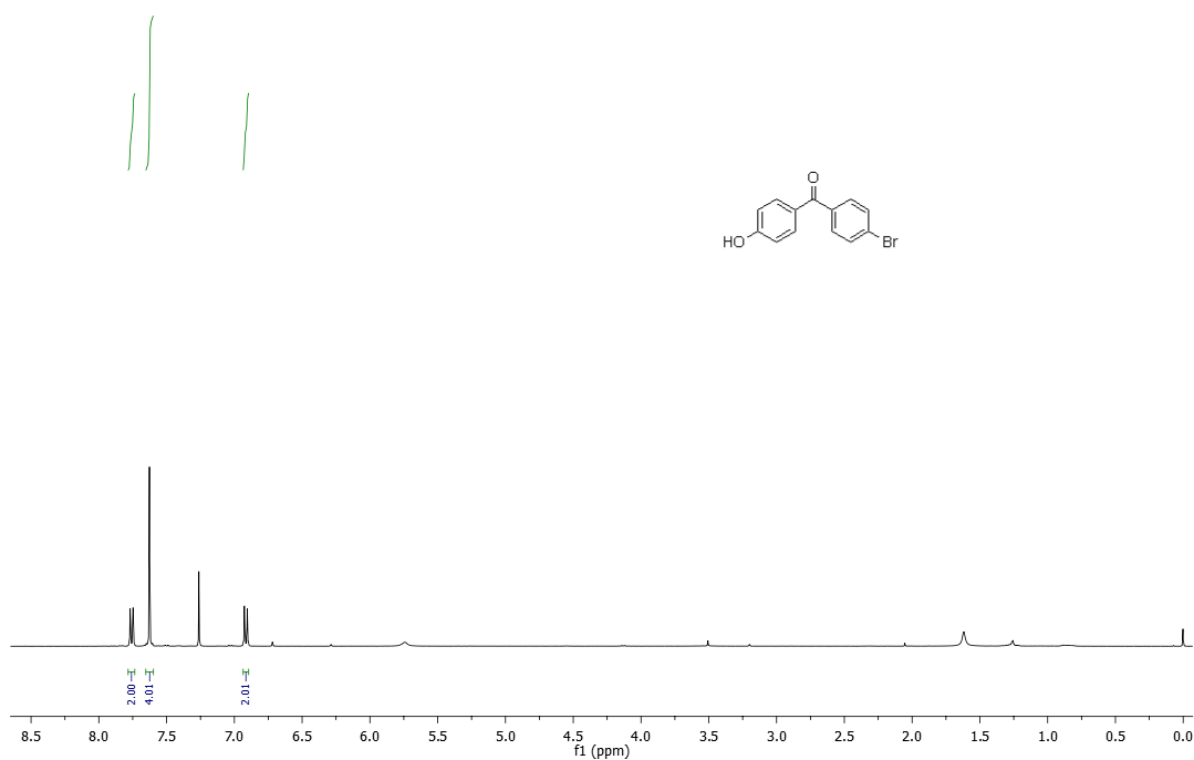
^1H and ^{13}C NMR of 6:



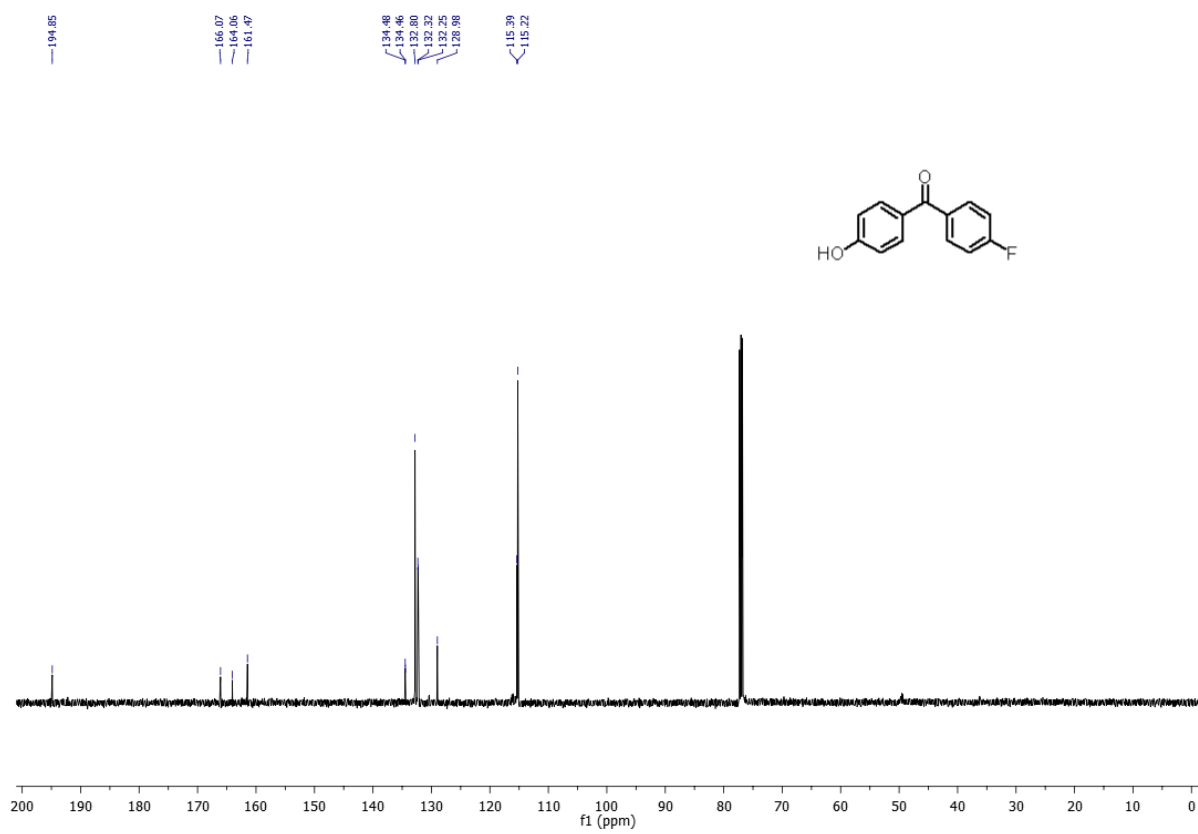
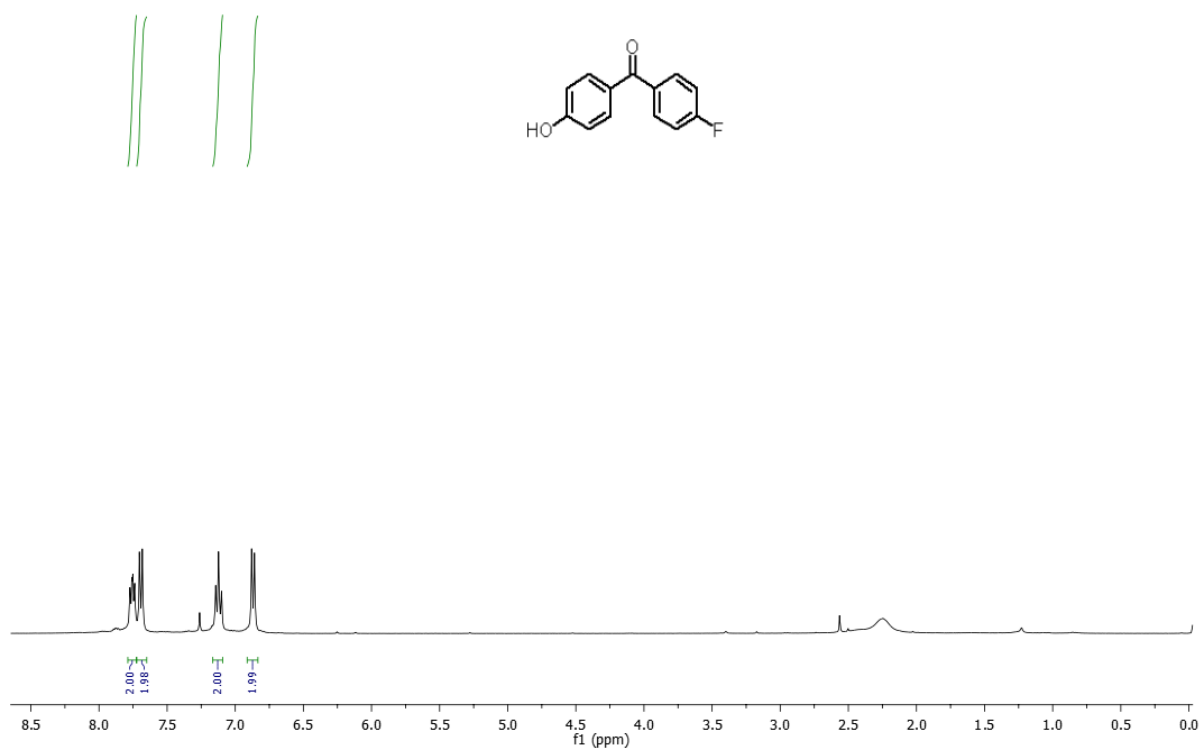
^1H and ^{13}C NMR of 7:



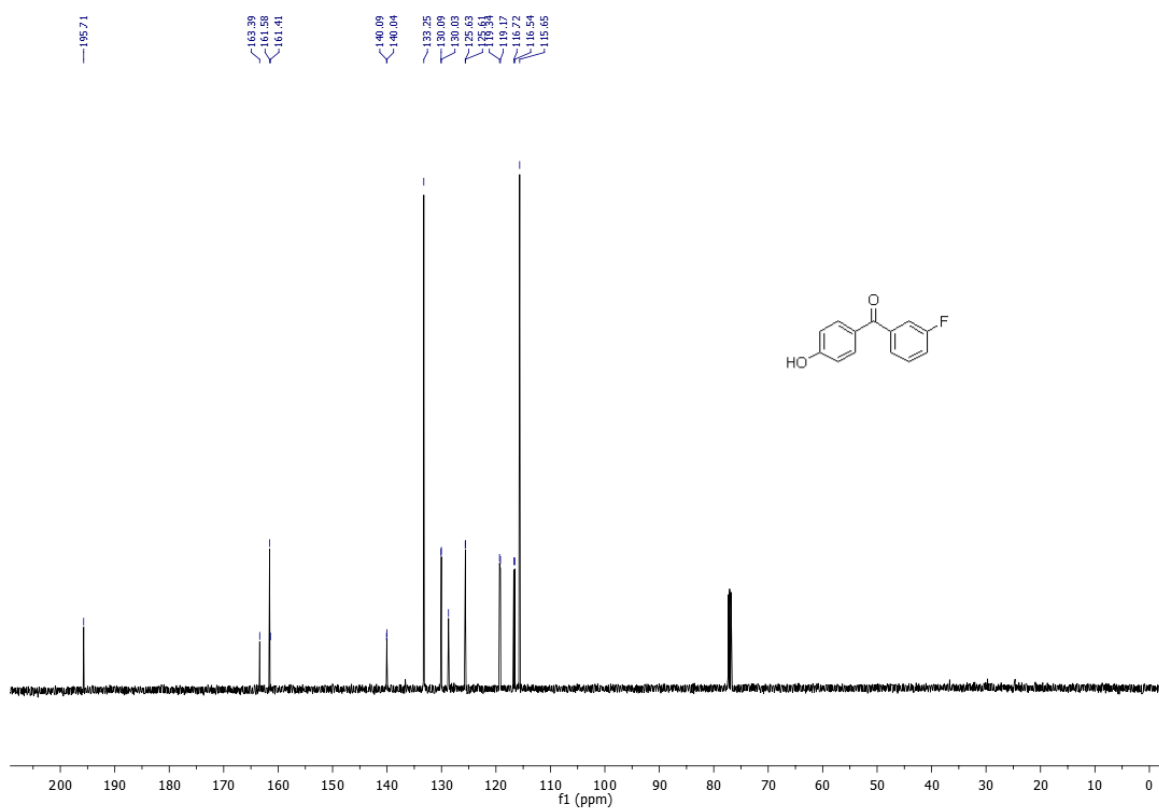
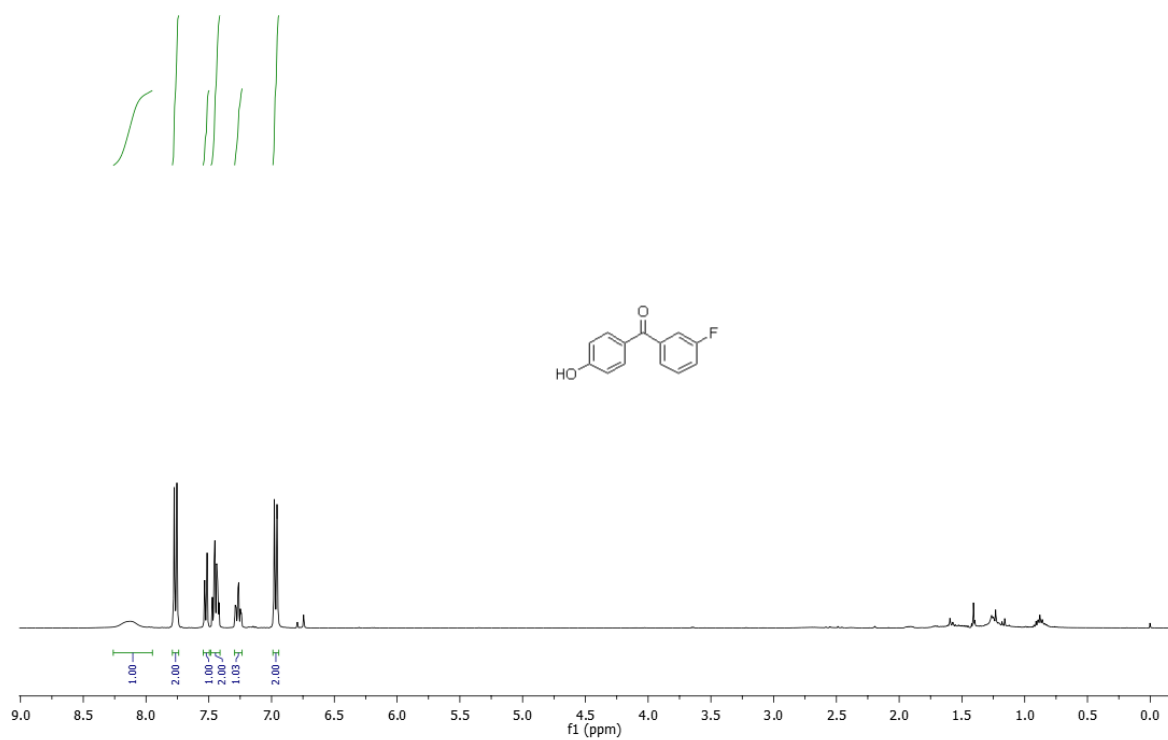
^1H and ^{13}C NMR of 8:



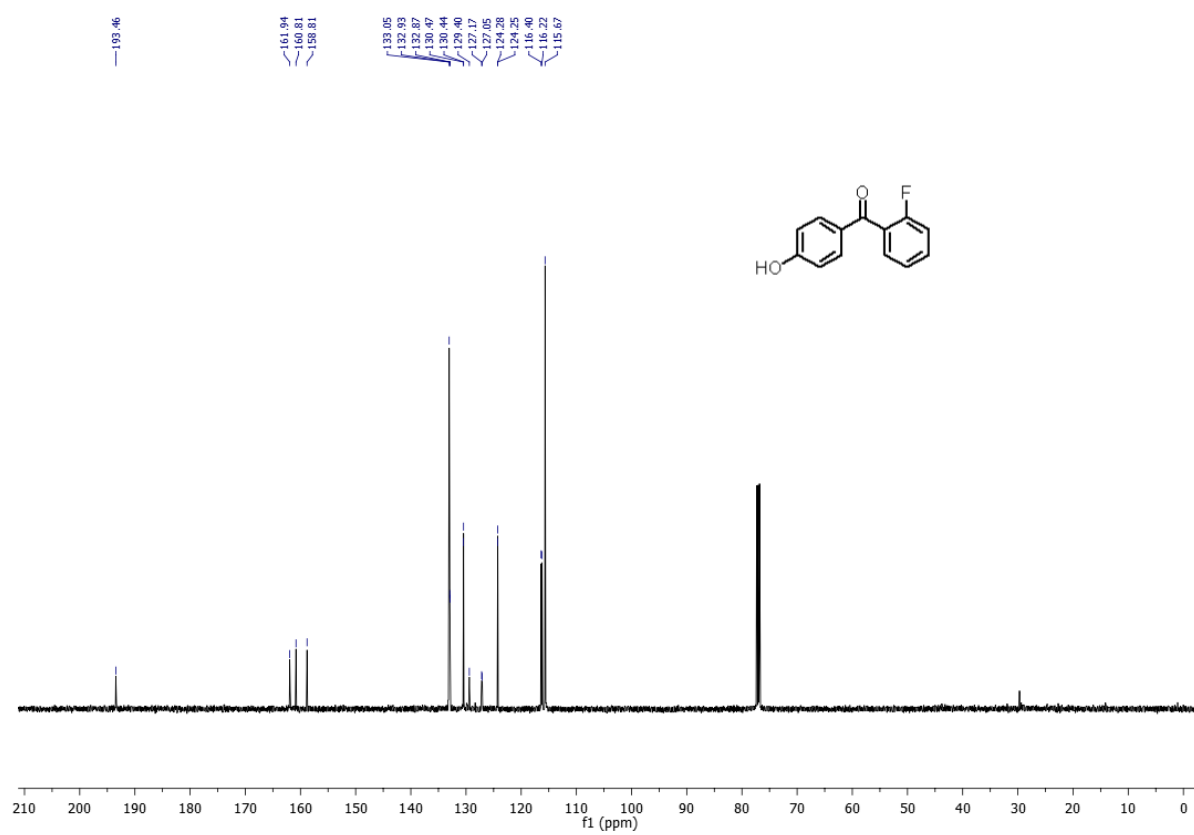
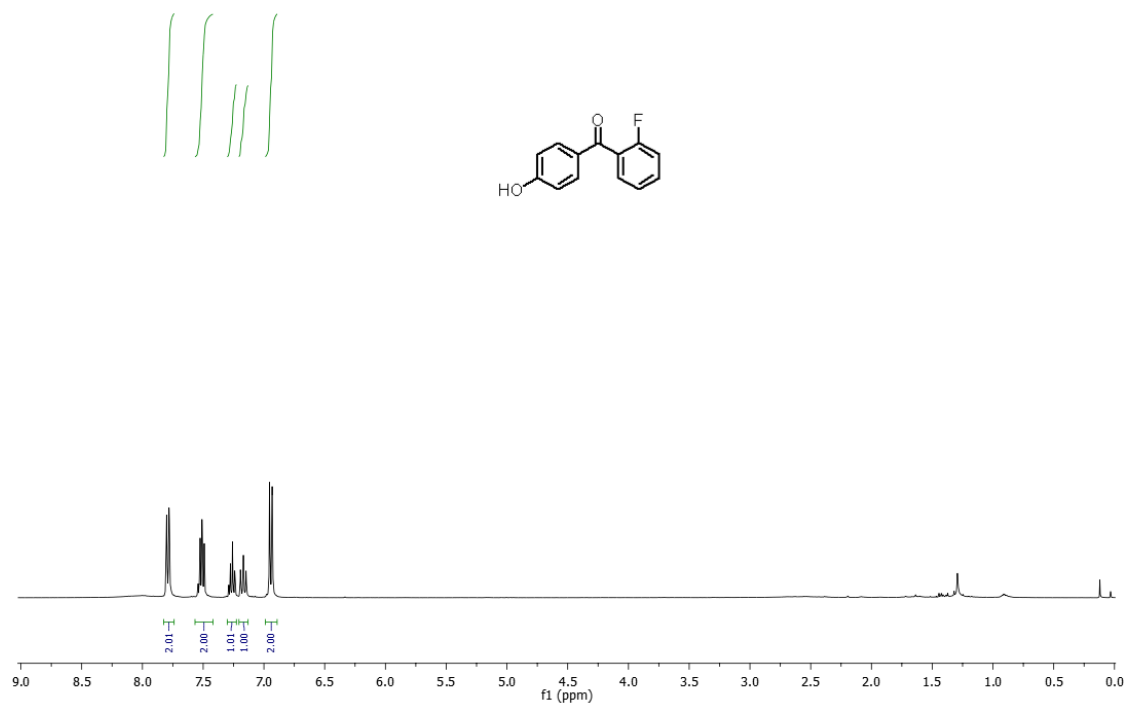
^1H and ^{13}C NMR of 9:



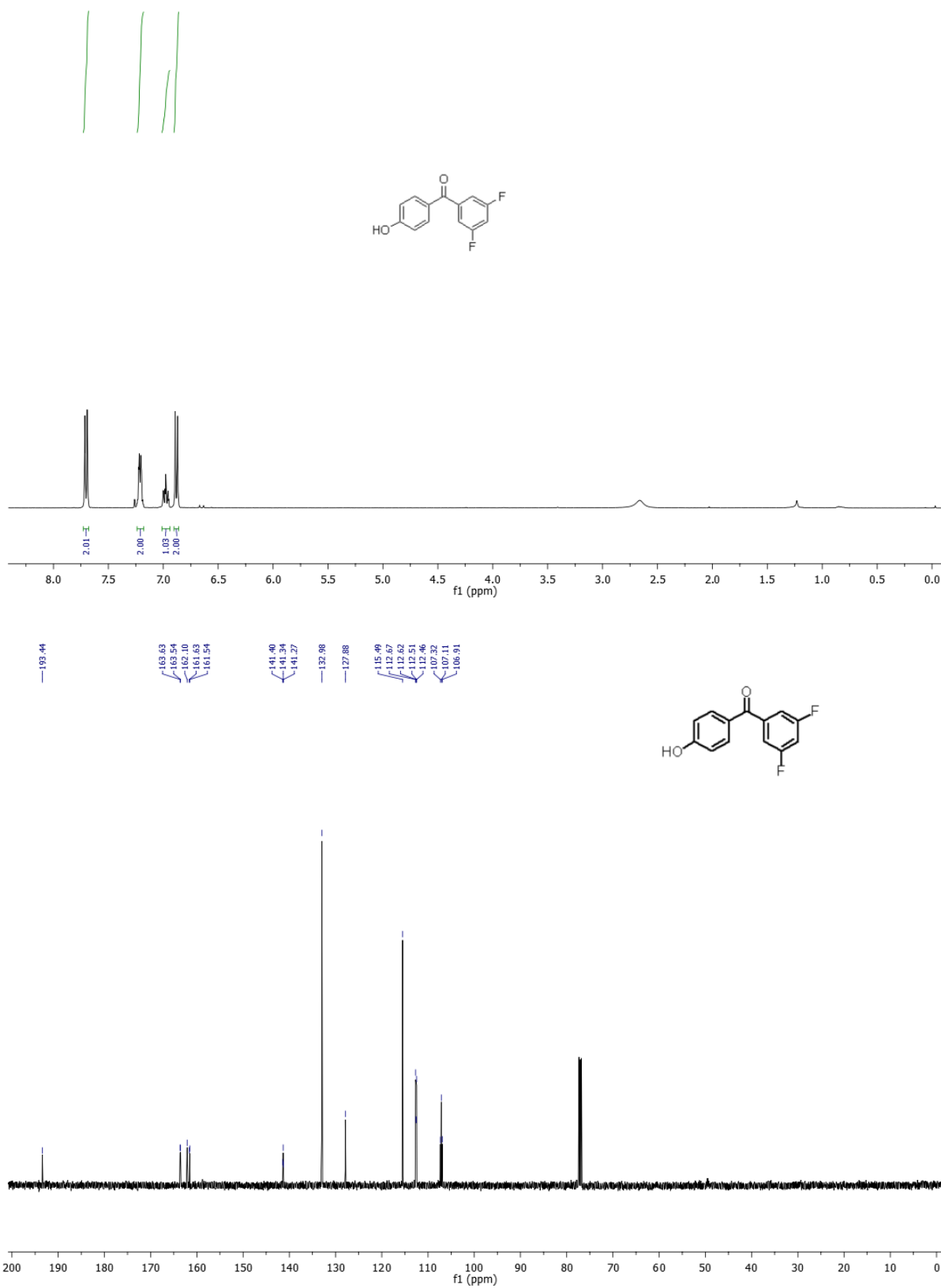
^1H and ^{13}C NMR of 10:



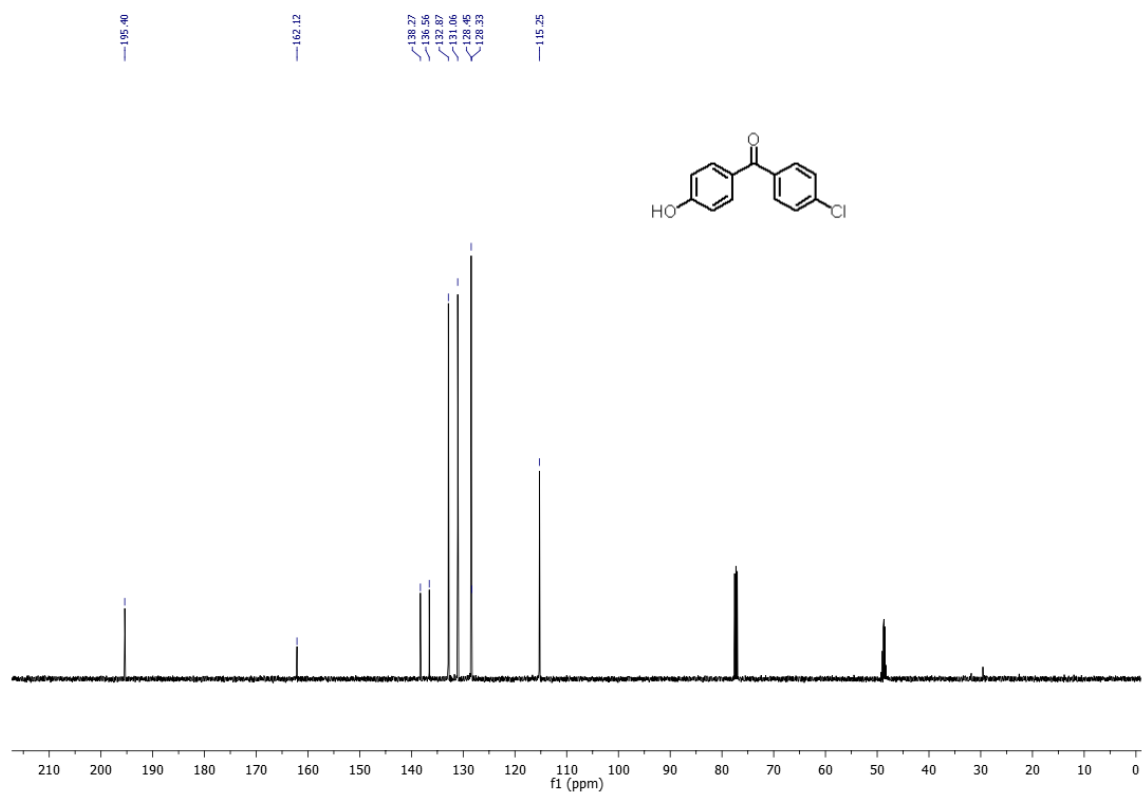
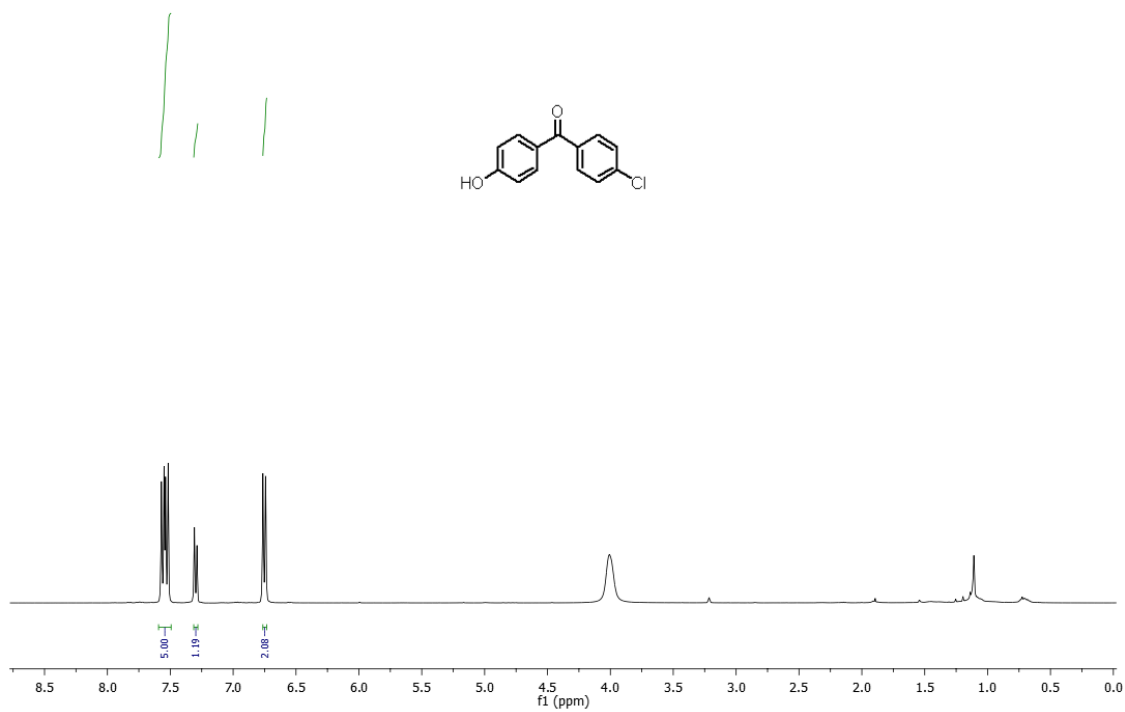
^1H and ^{13}C NMR of 11:



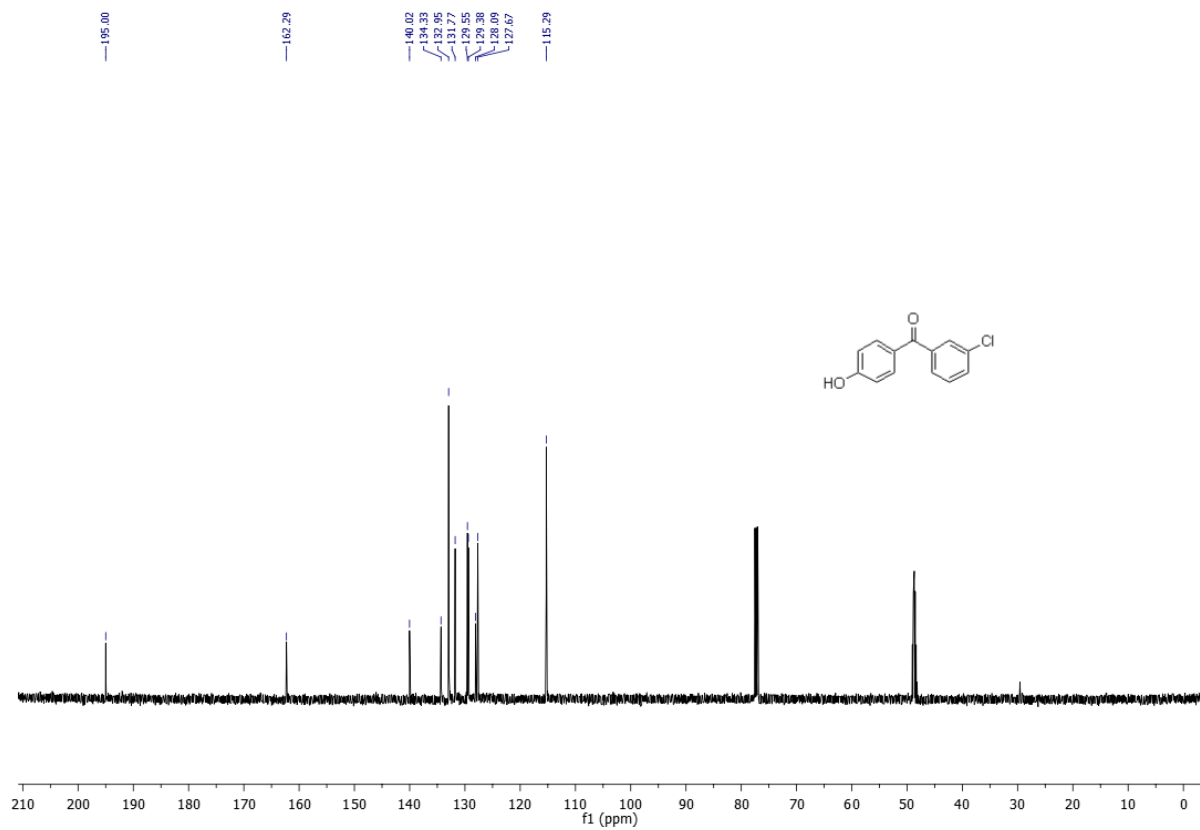
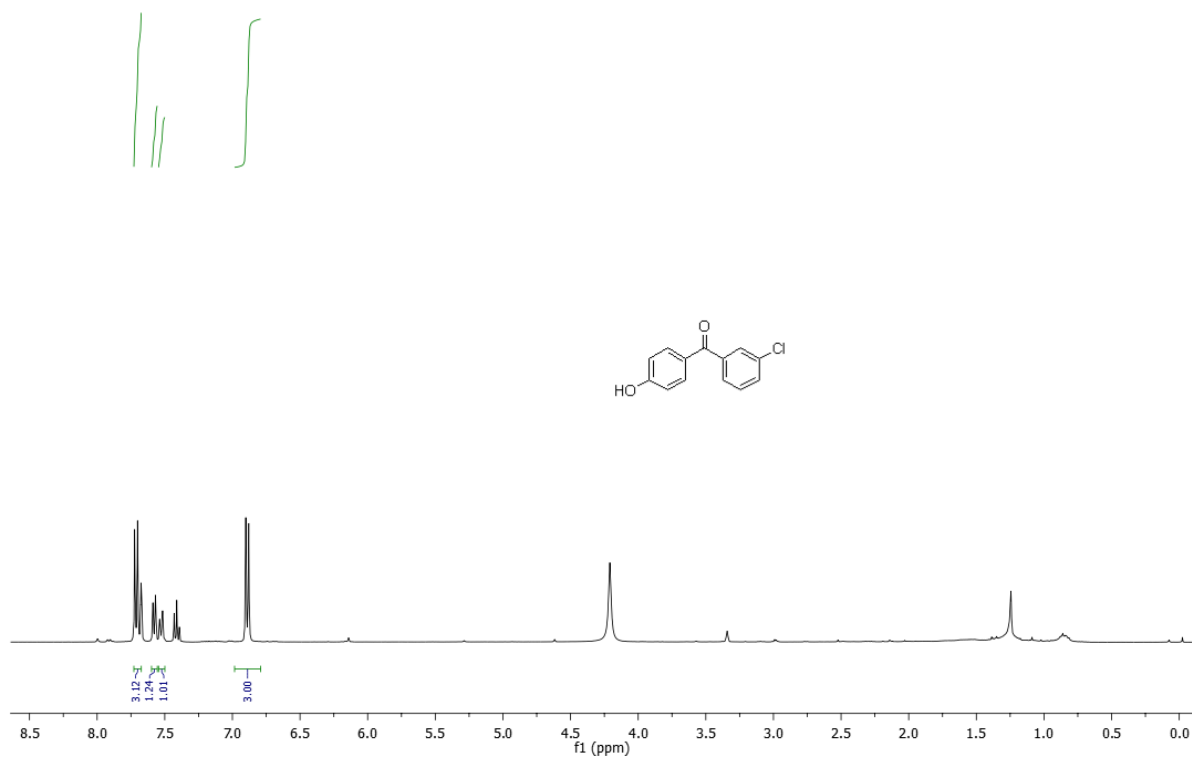
^1H and ^{13}C NMR of 12:



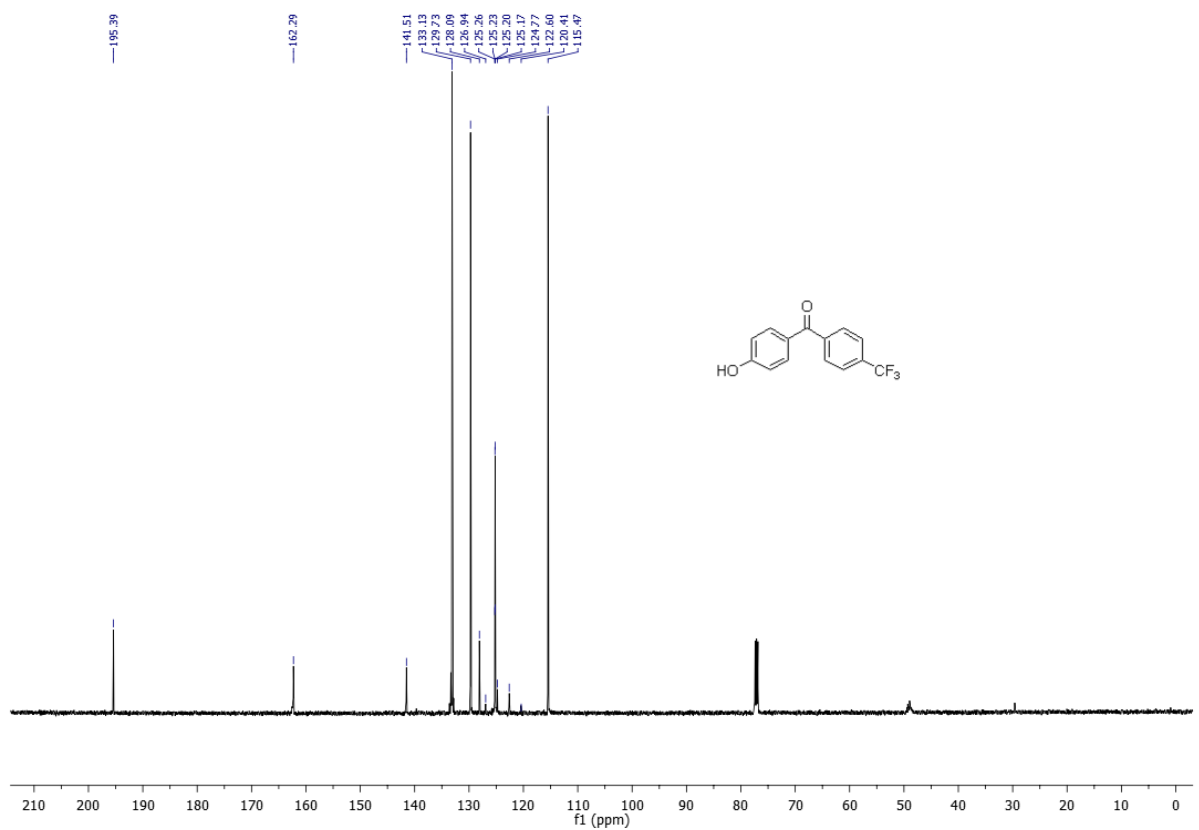
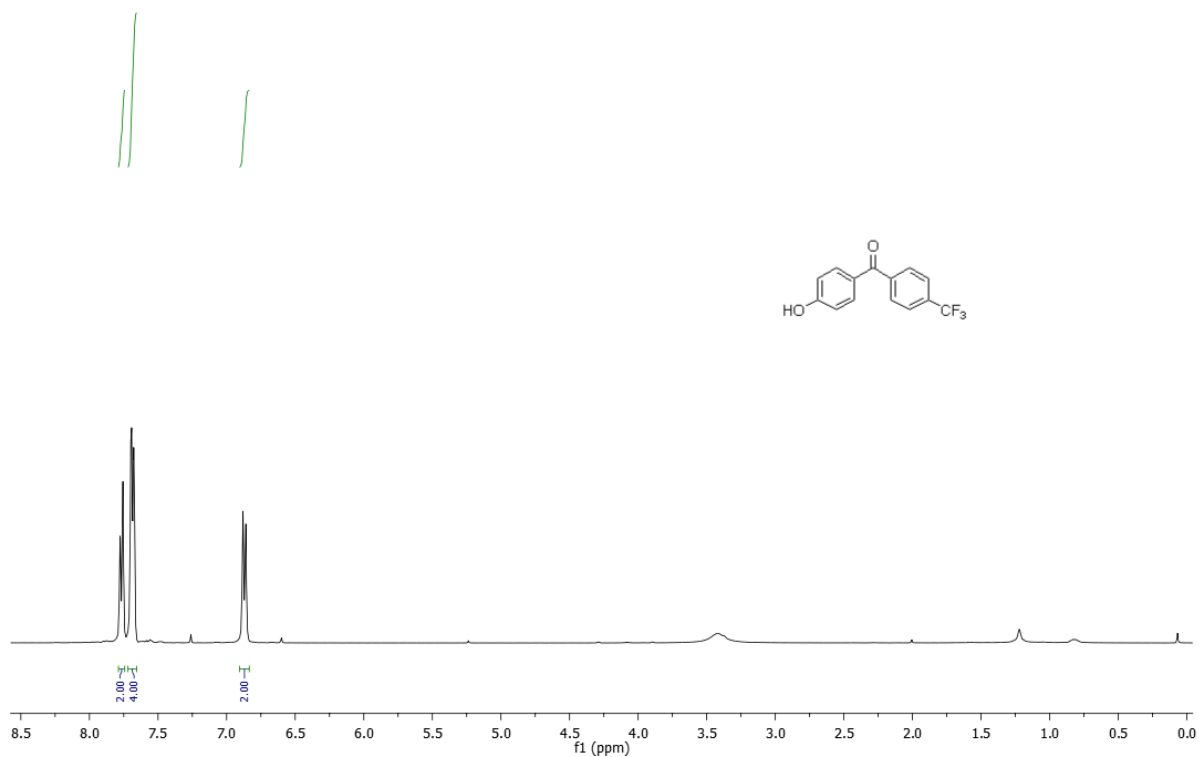
^1H and ^{13}C NMR of 13:



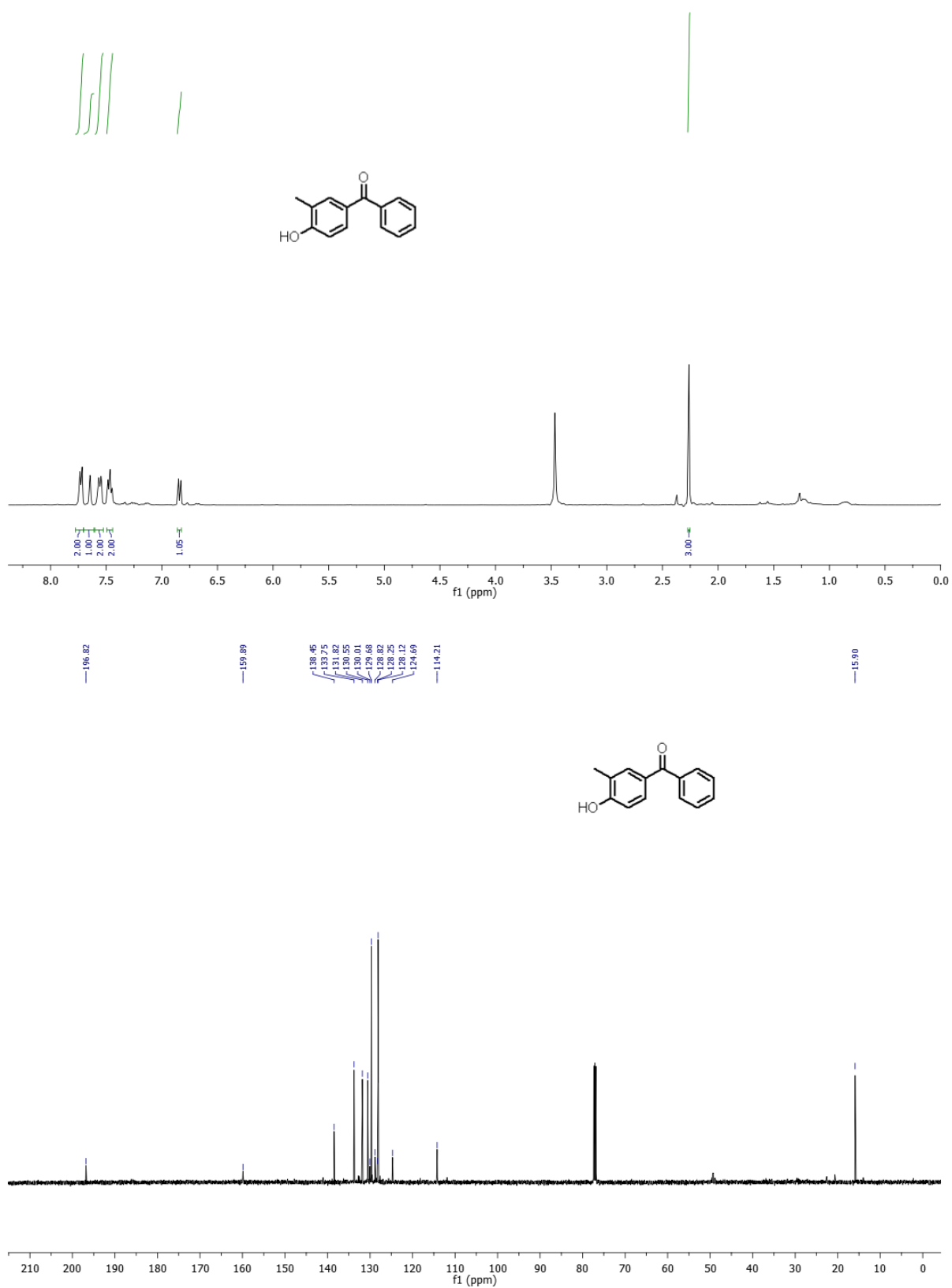
^1H and ^{13}C NMR of 14:



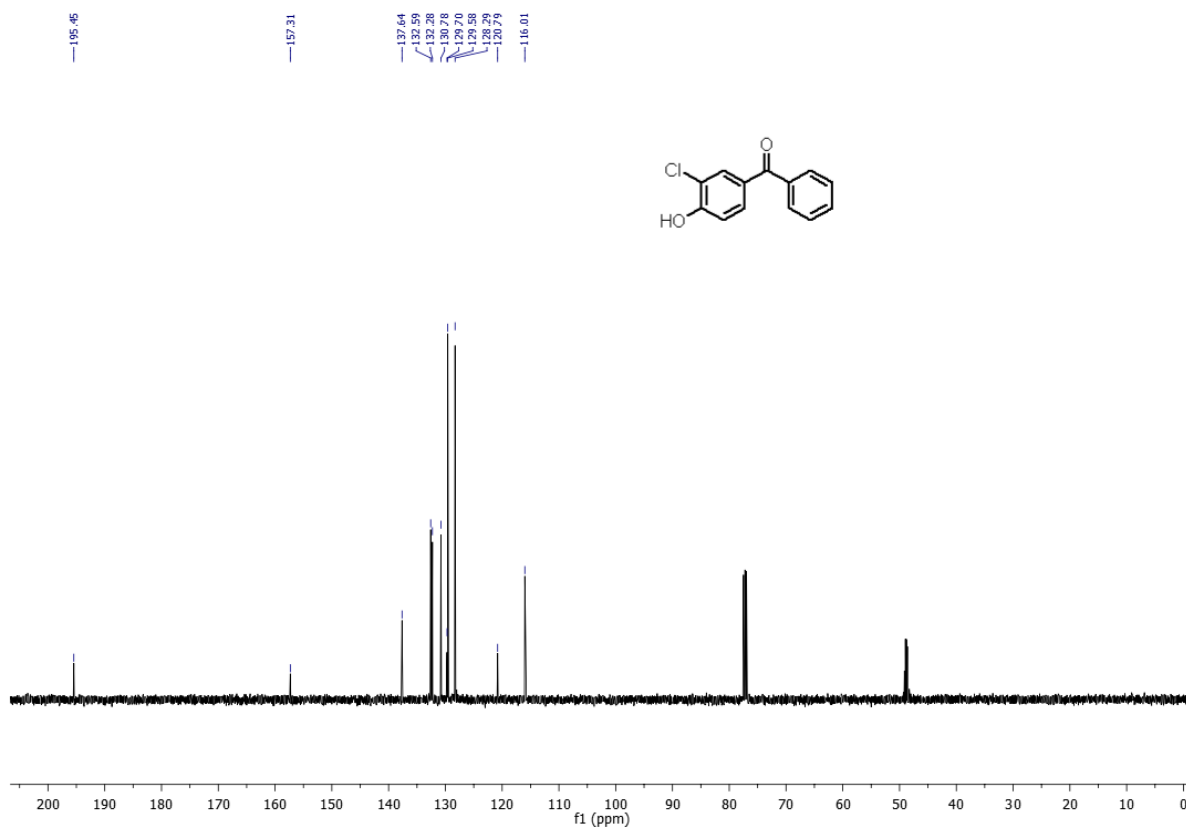
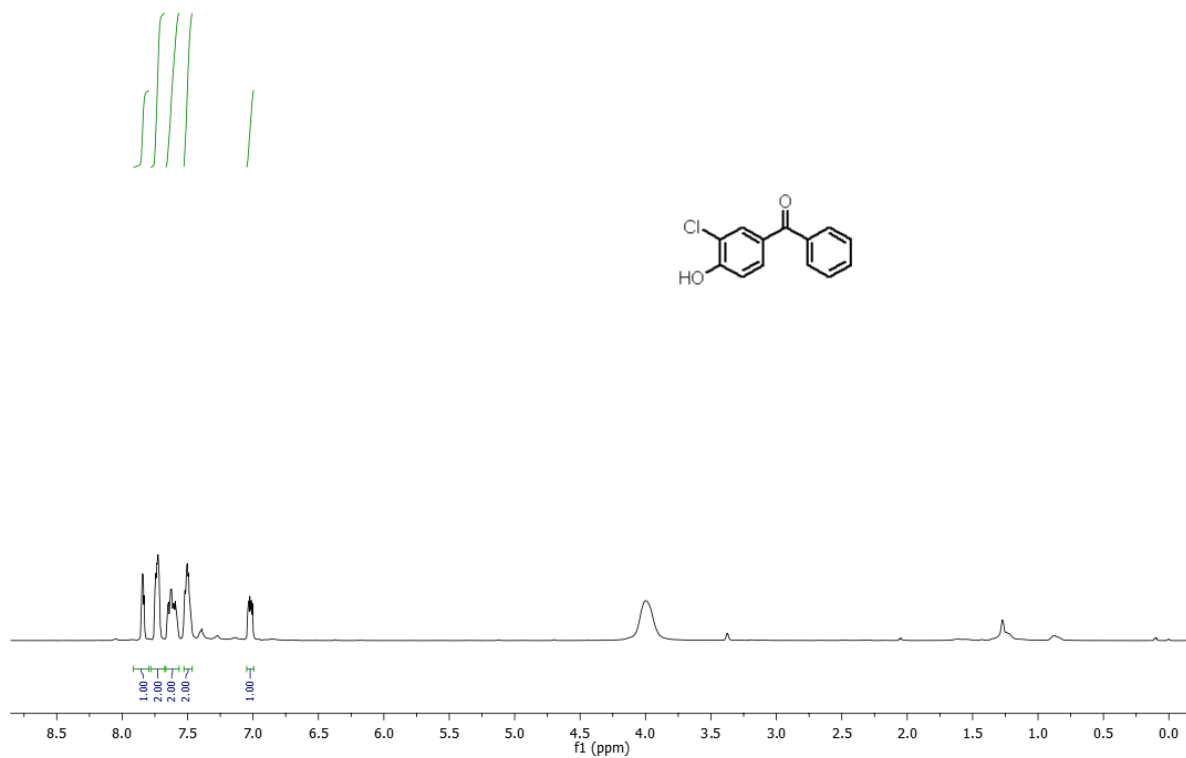
^1H and ^{13}C NMR of 15:



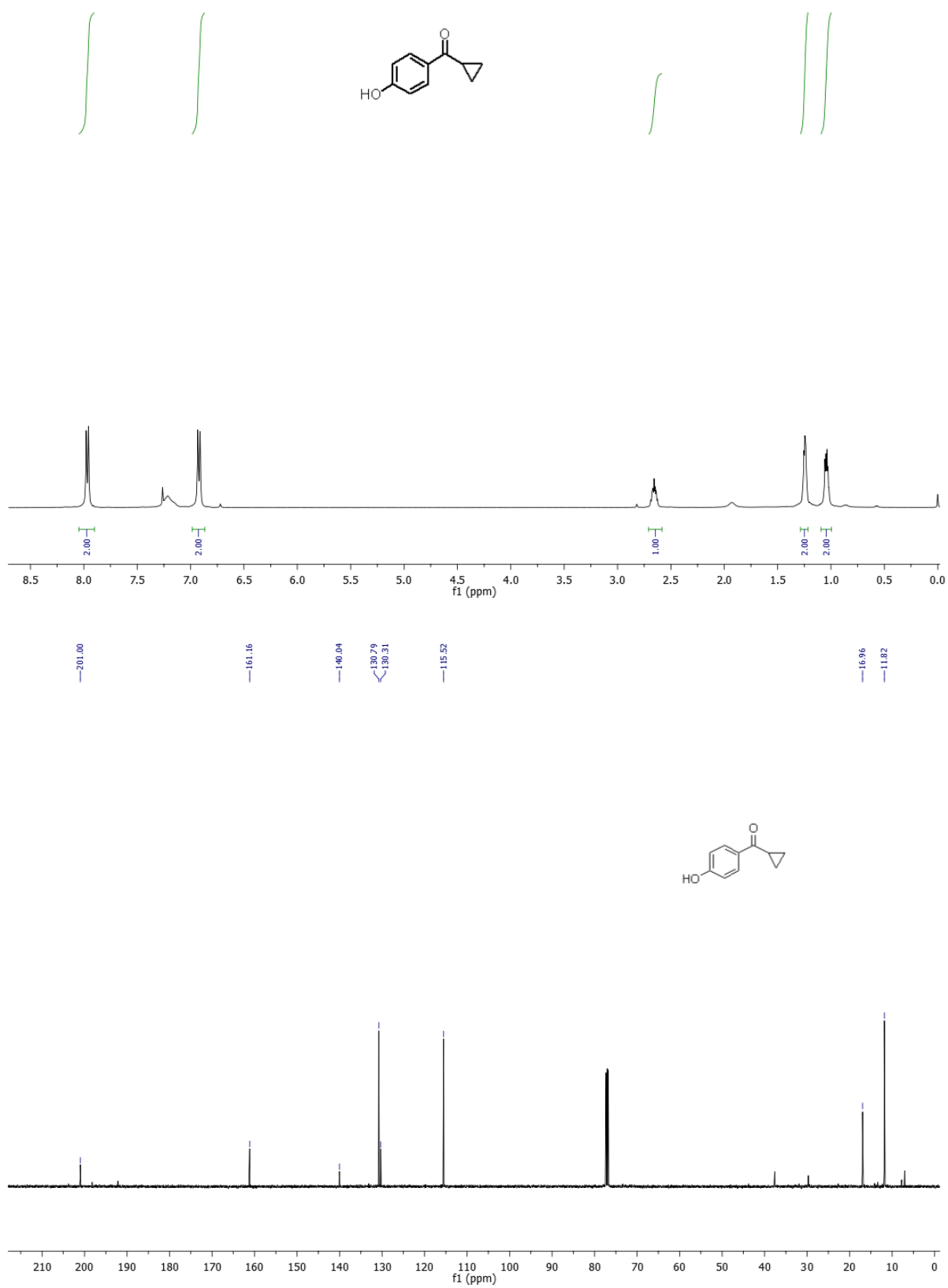
^1H and ^{13}C NMR of 16:



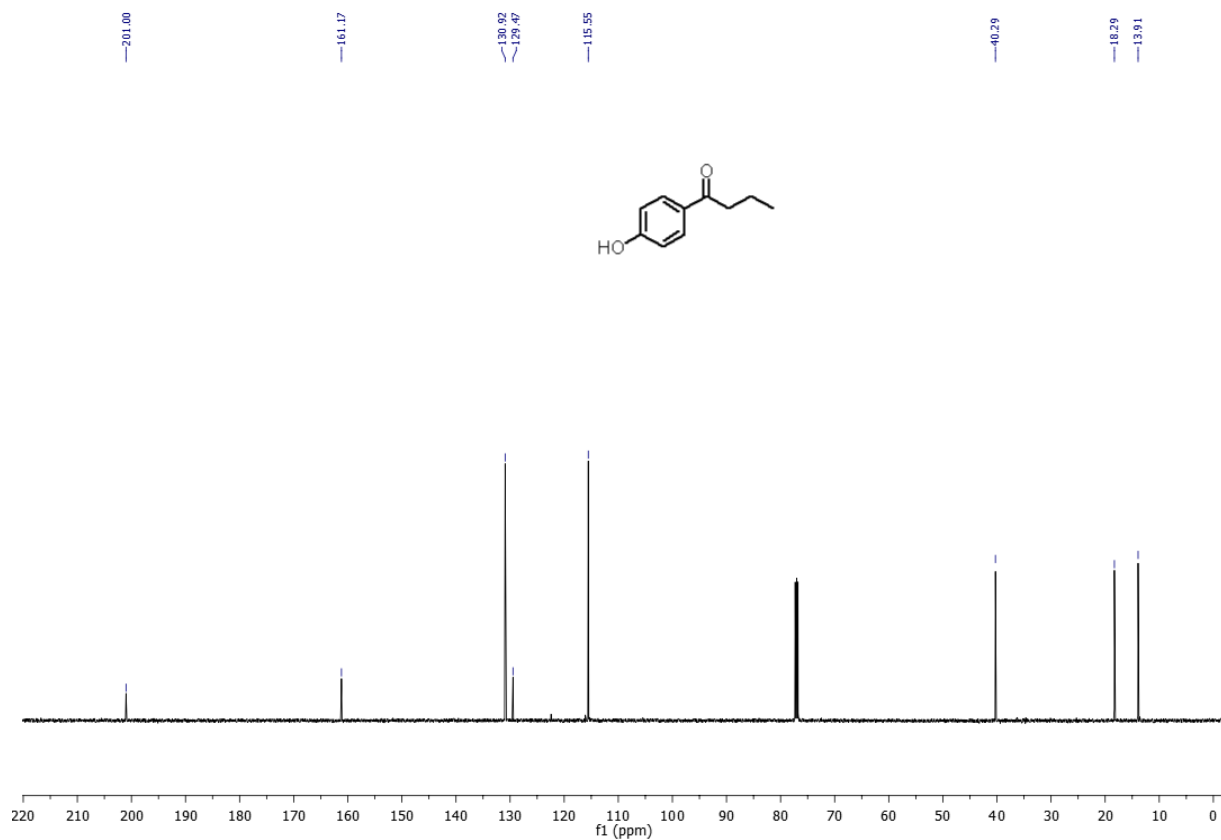
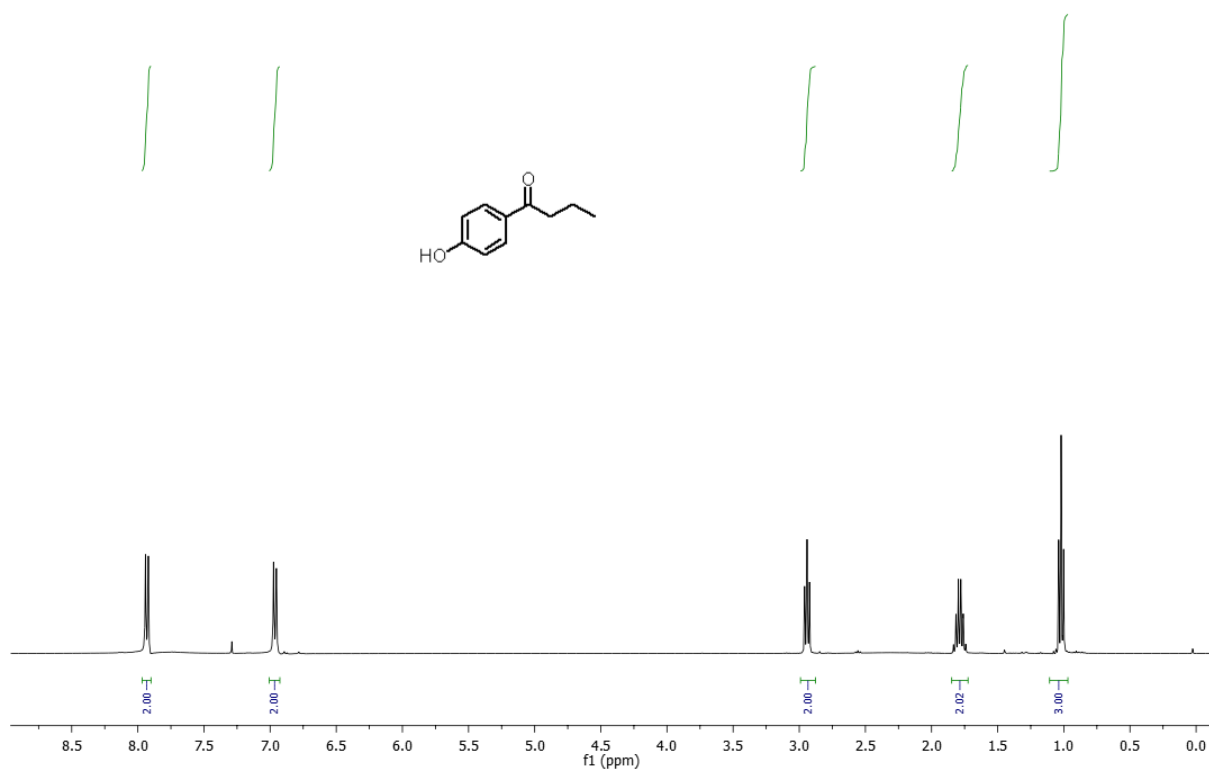
^1H and ^{13}C NMR of 17:



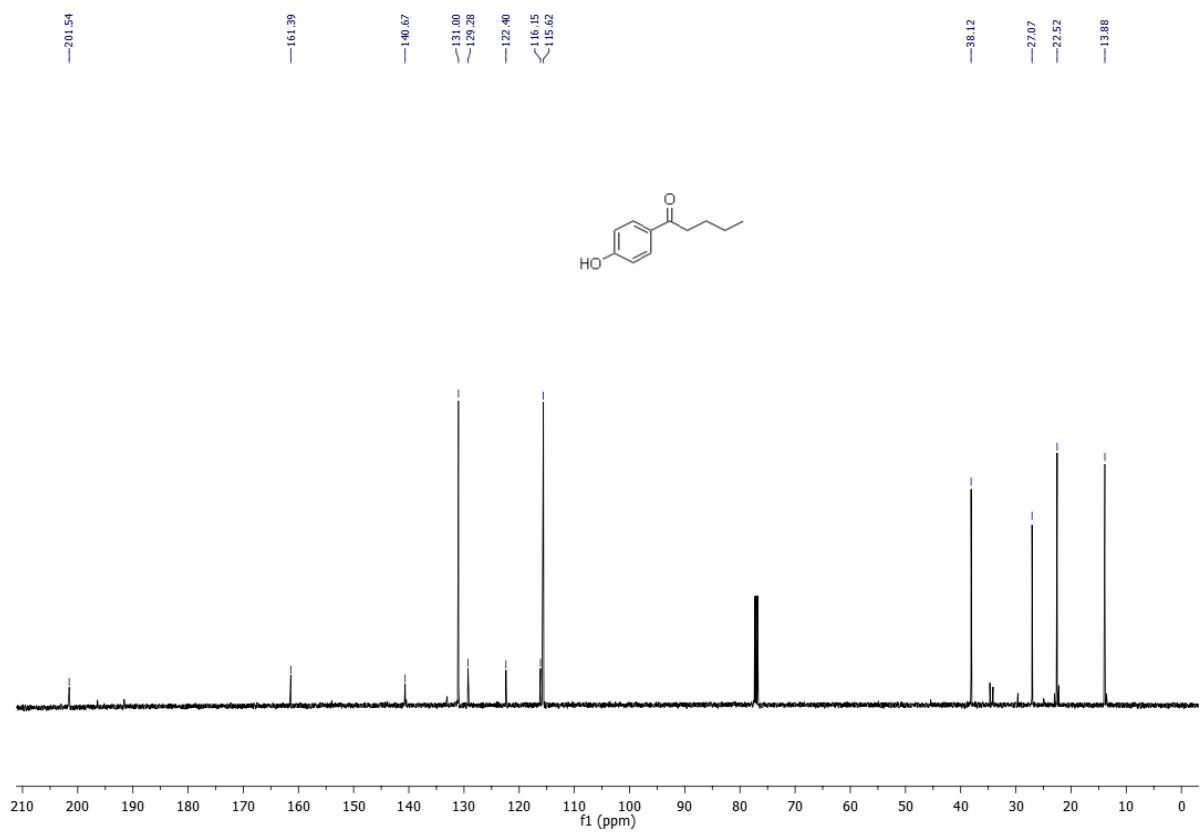
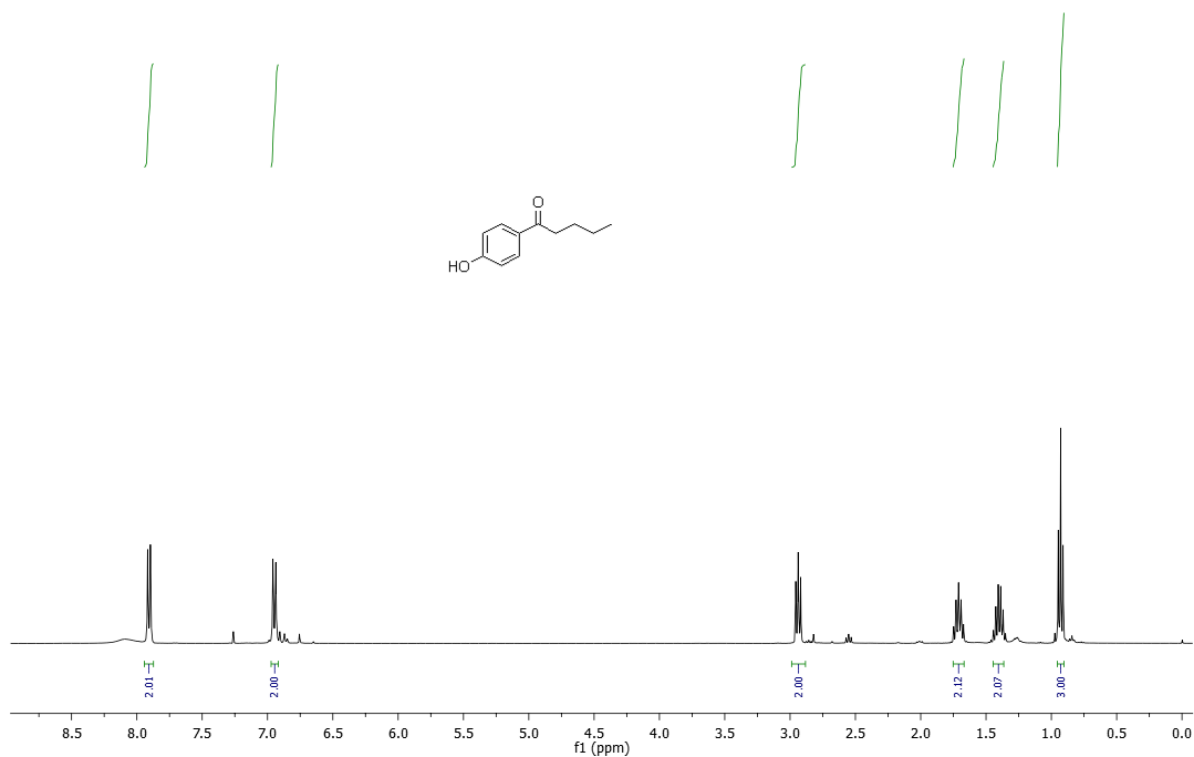
^1H and ^{13}C NMR of 18:



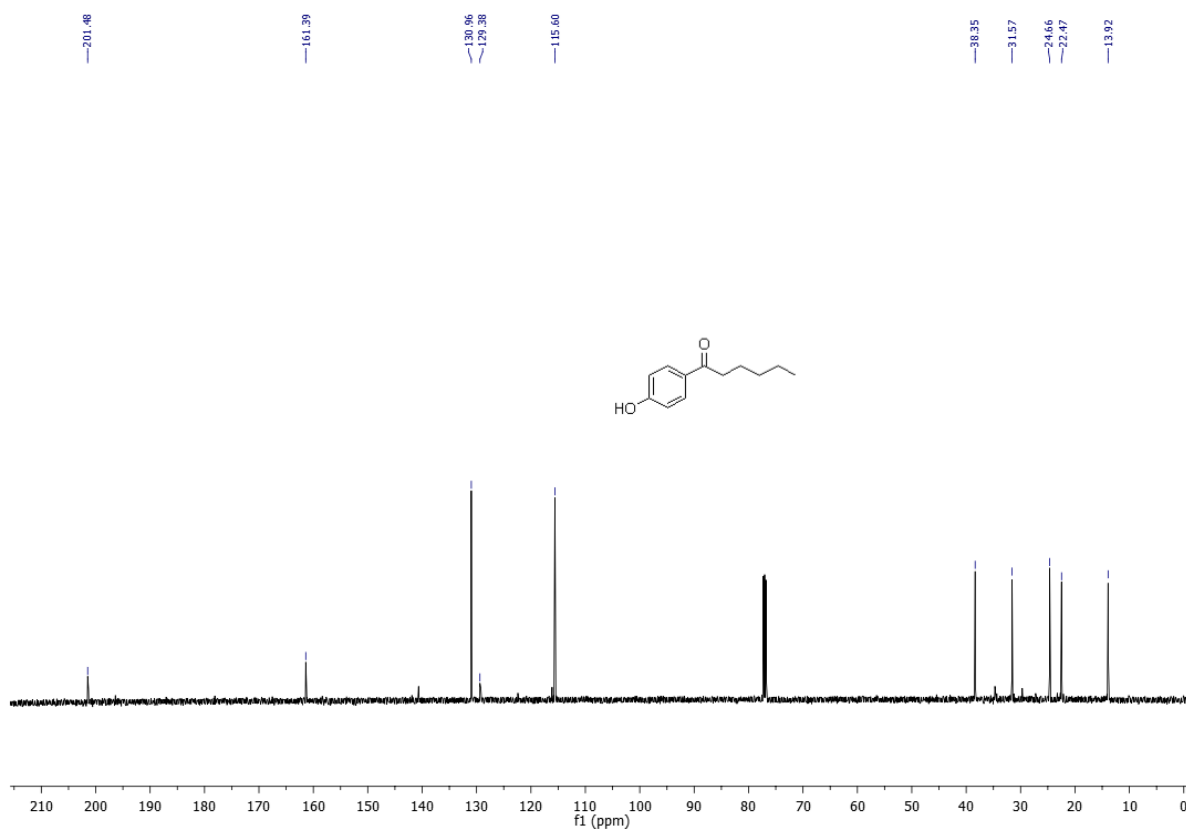
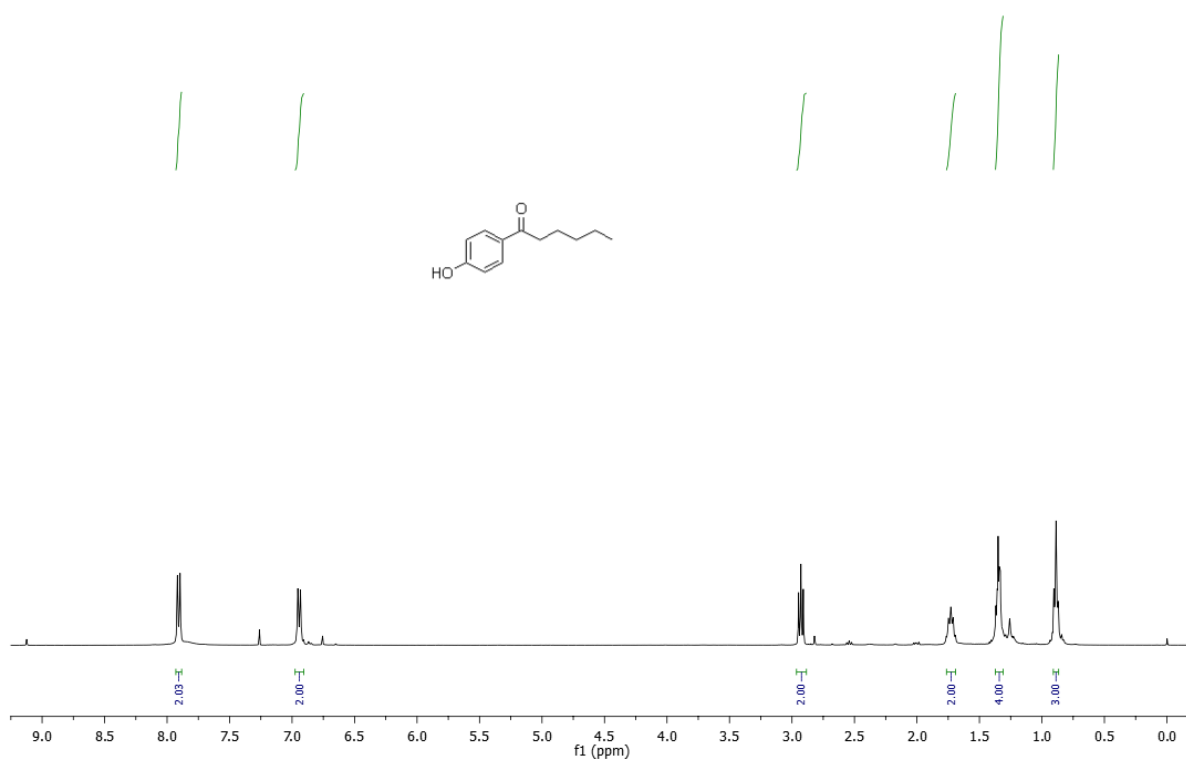
^1H and ^{13}C NMR of 19:



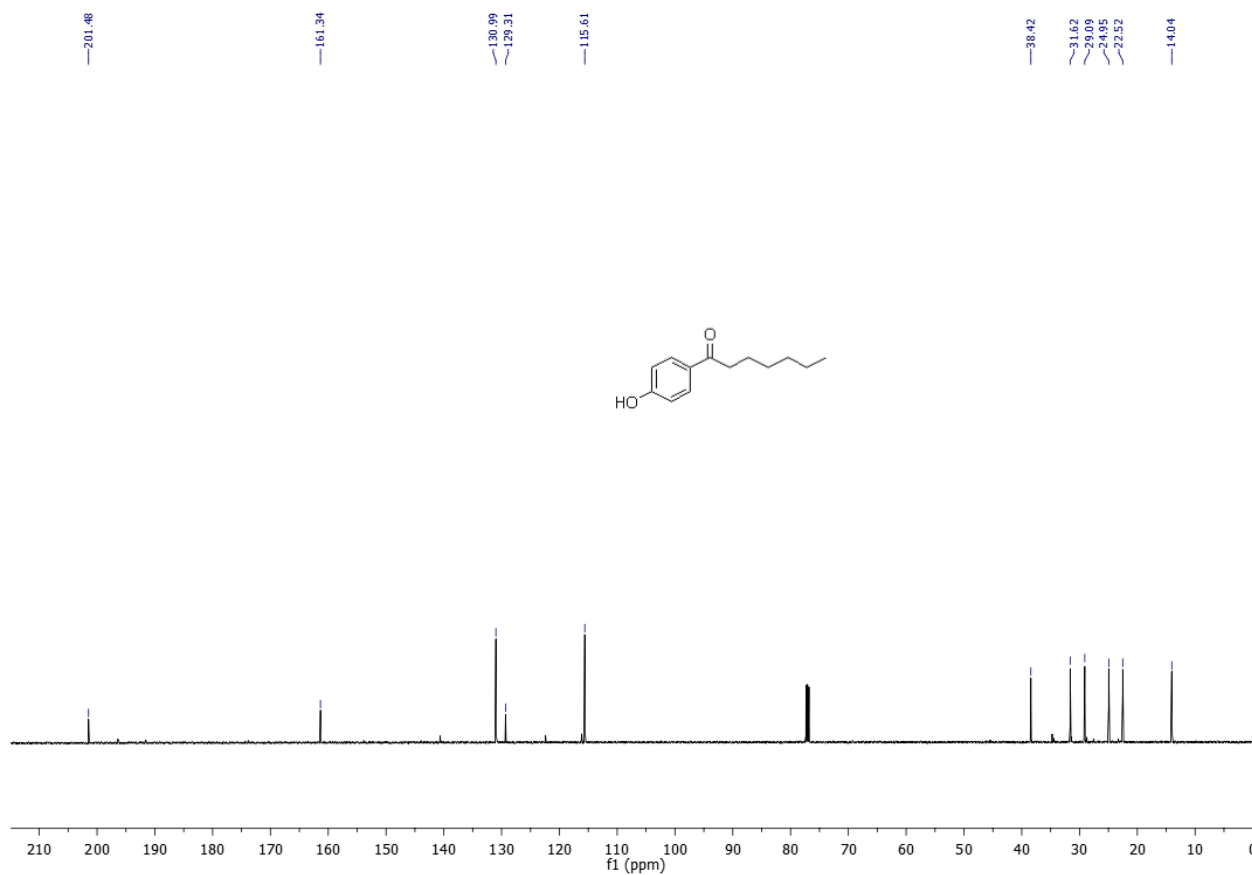
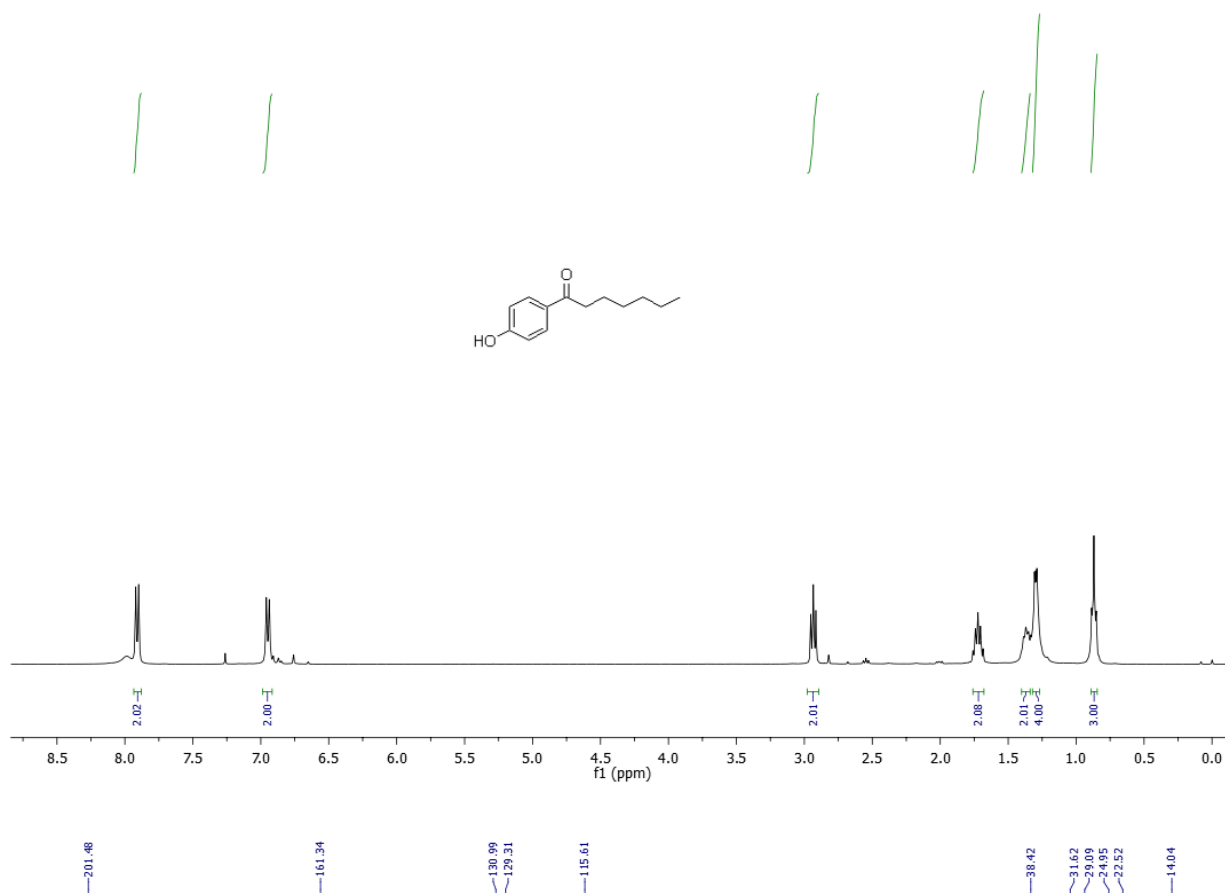
^1H and ^{13}C NMR of 20:



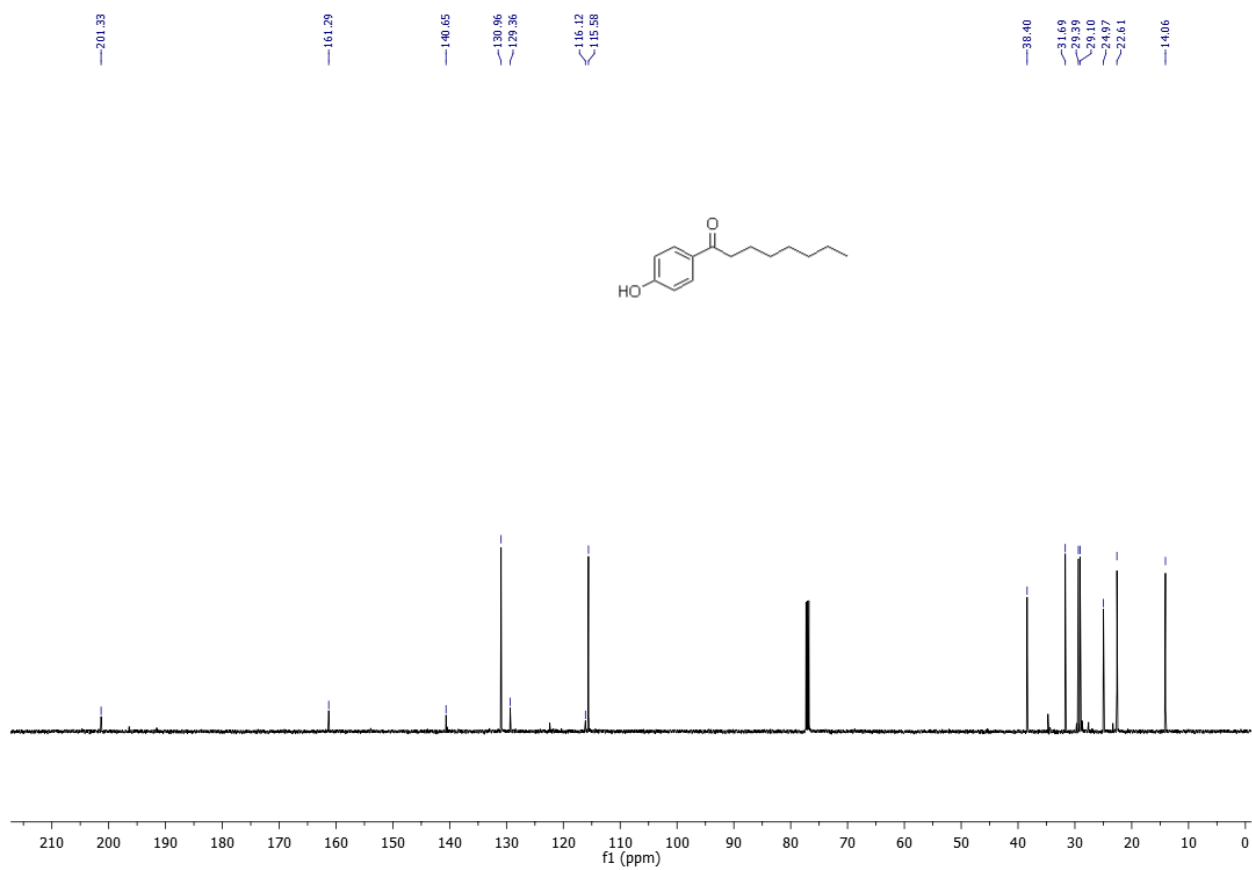
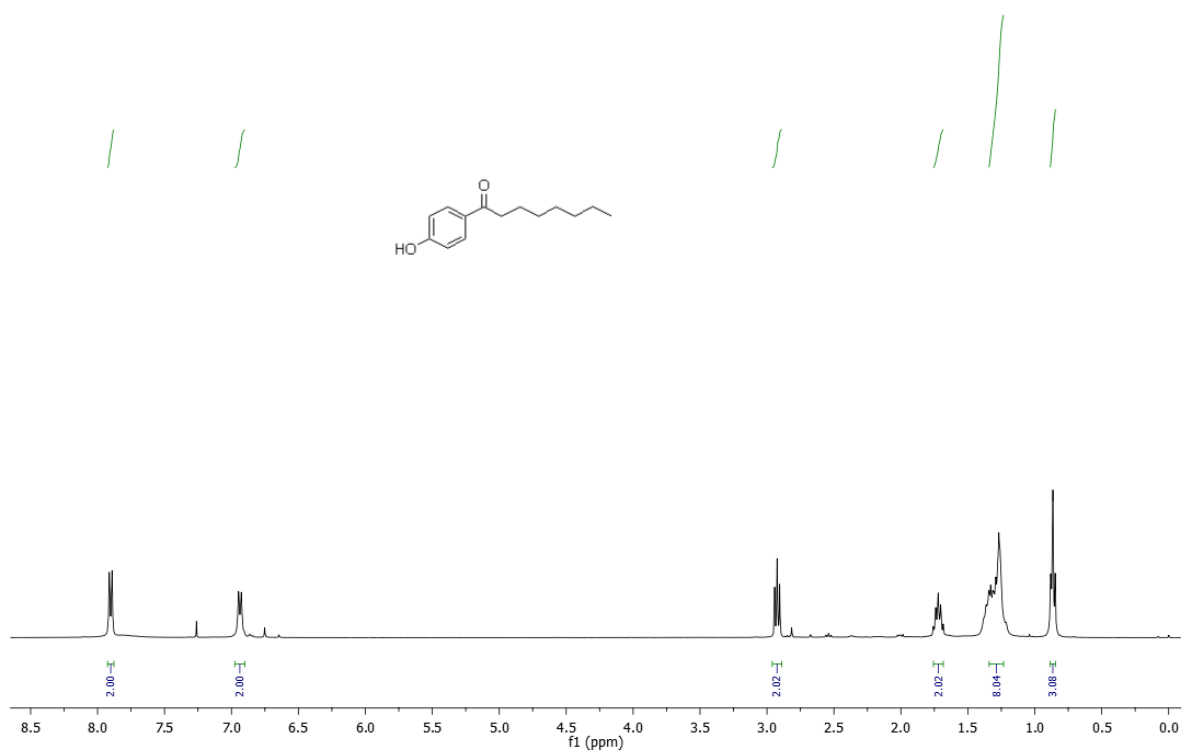
^1H and ^{13}C NMR of 21:



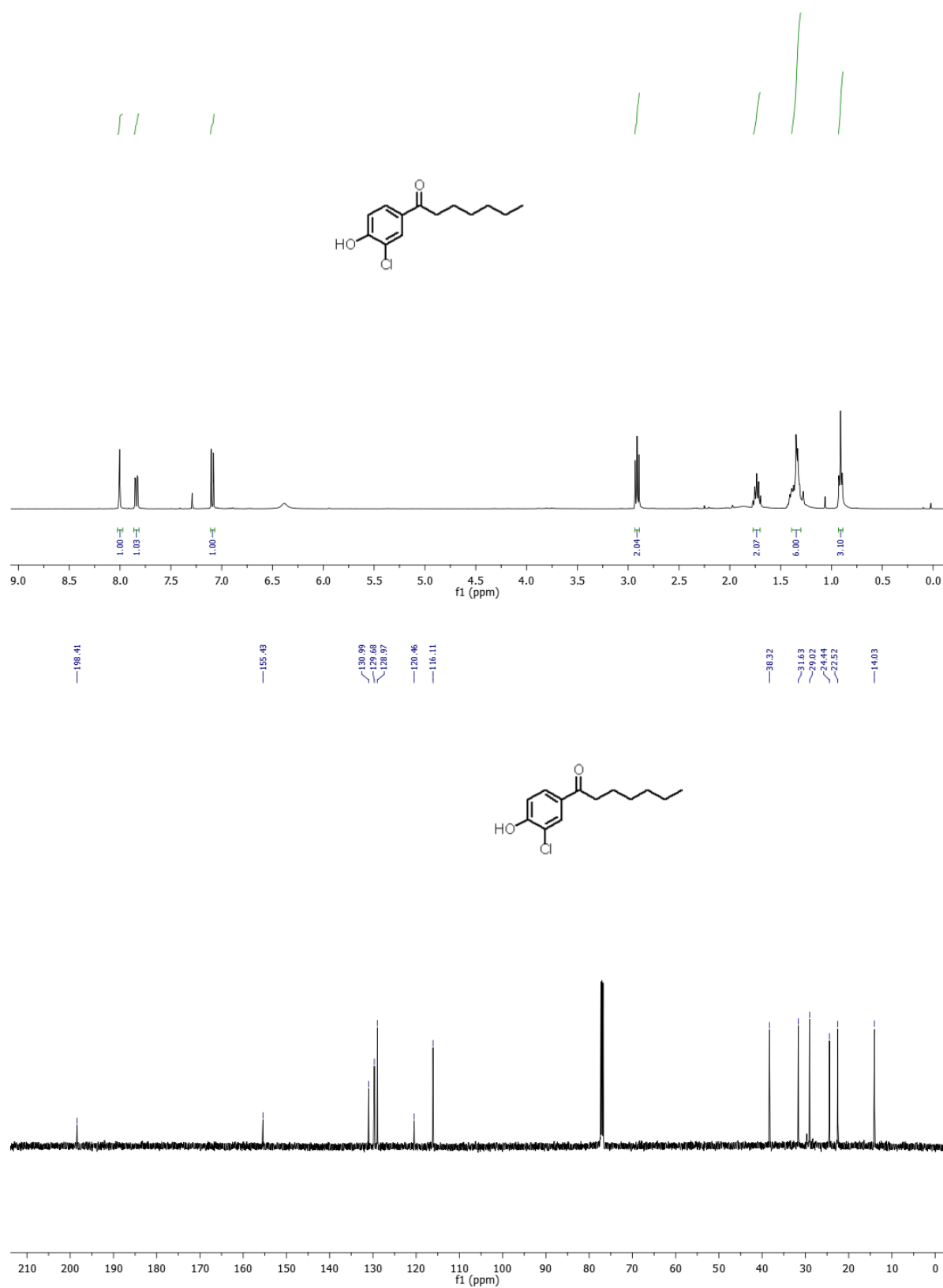
^1H and ^{13}C NMR of 22:



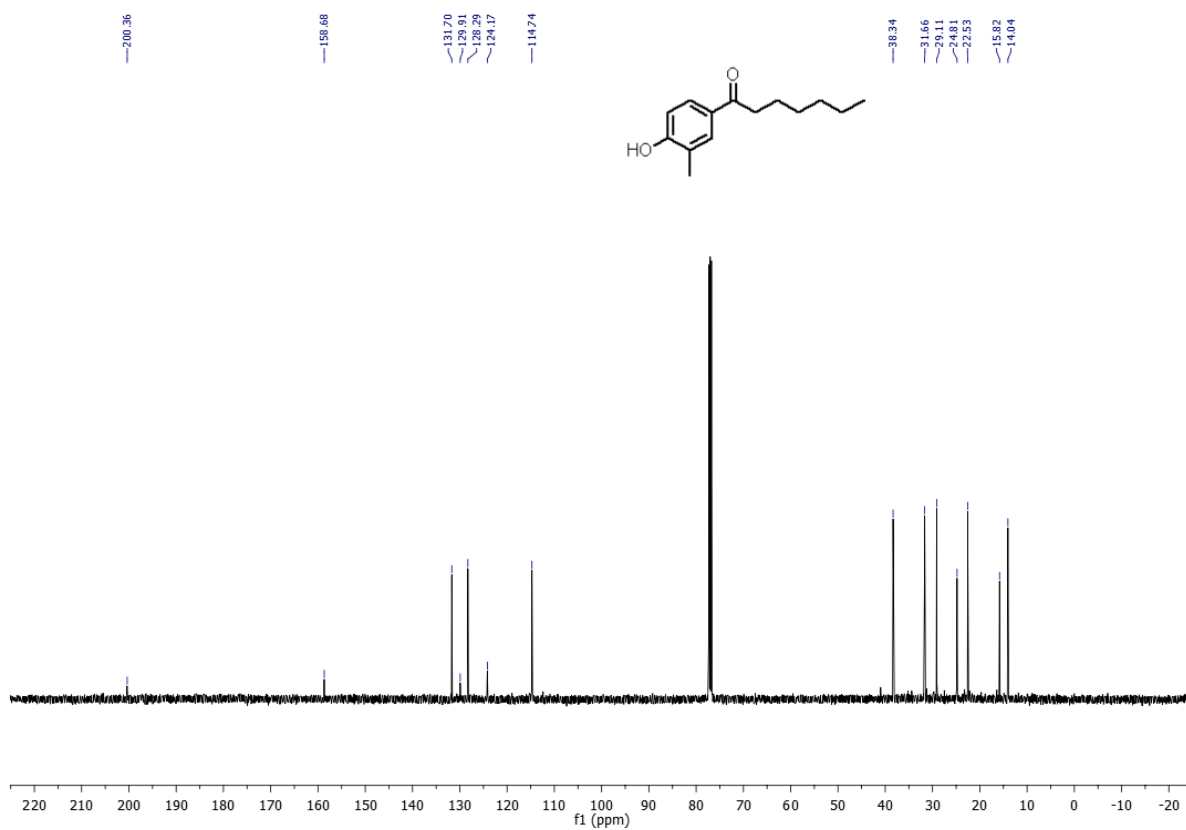
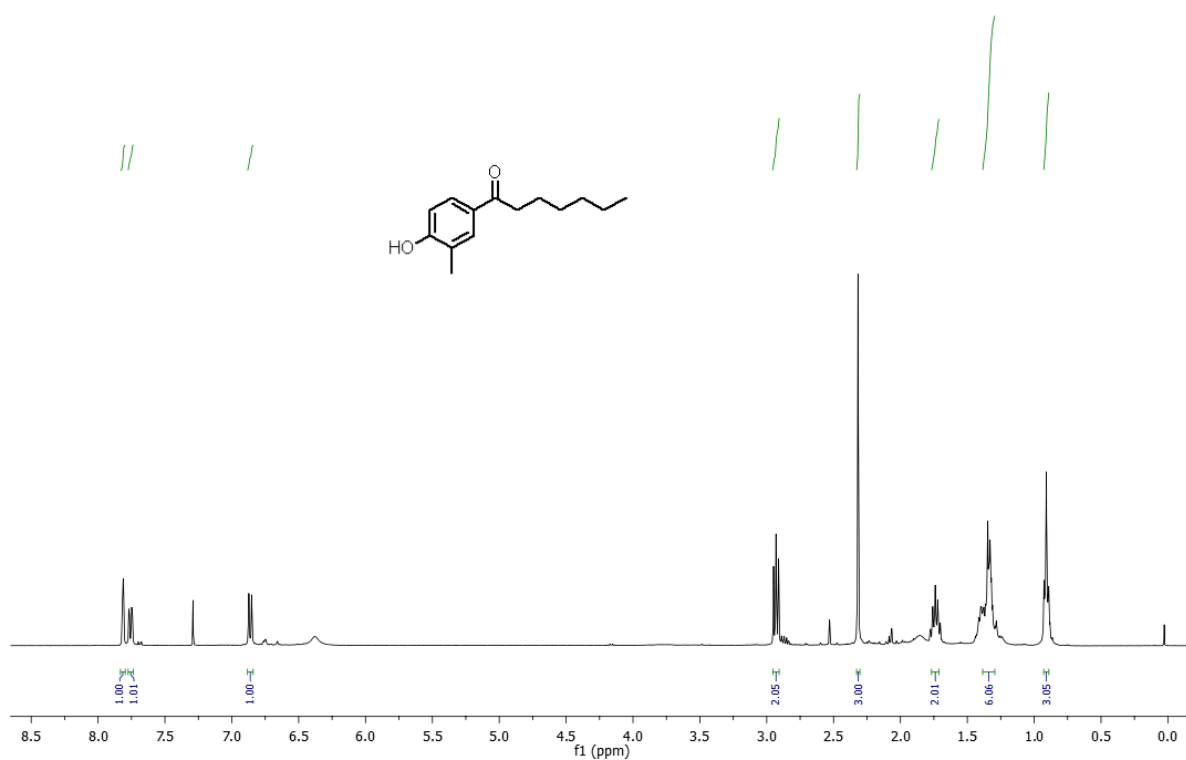
^1H and ^{13}C NMR of 23:



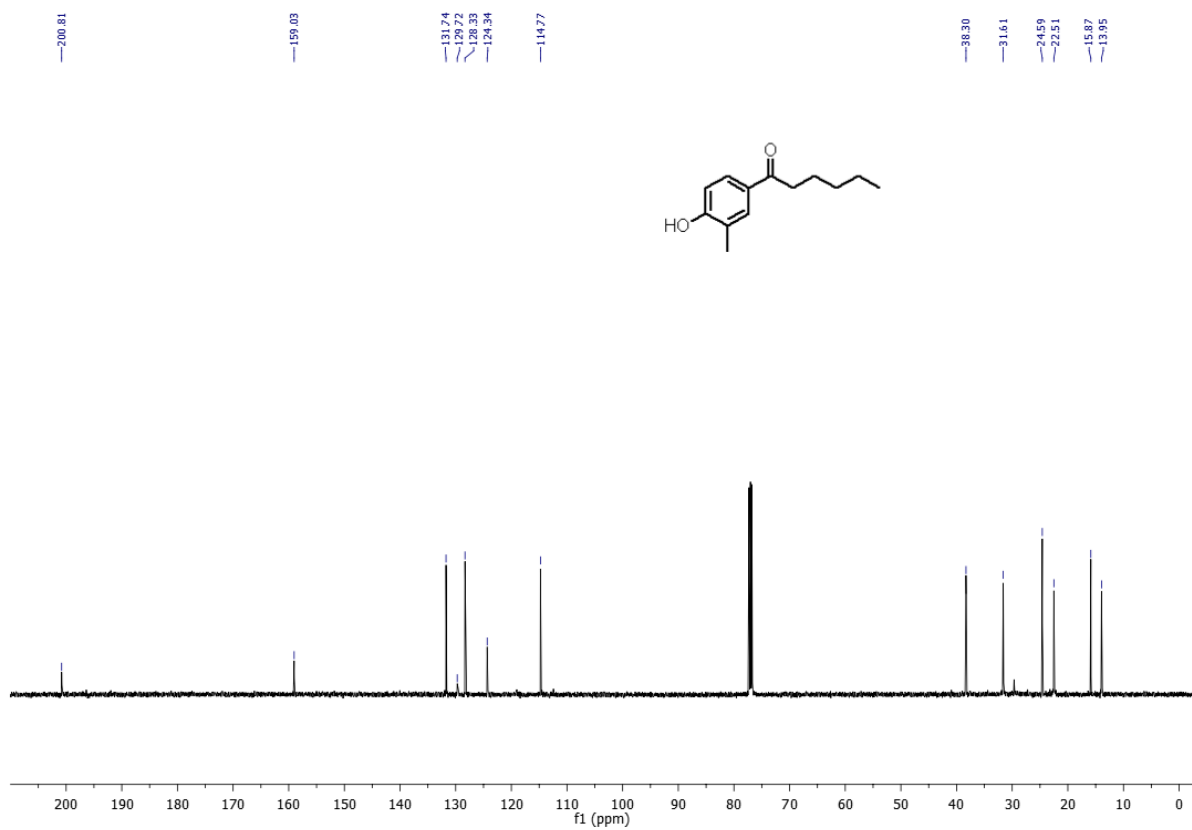
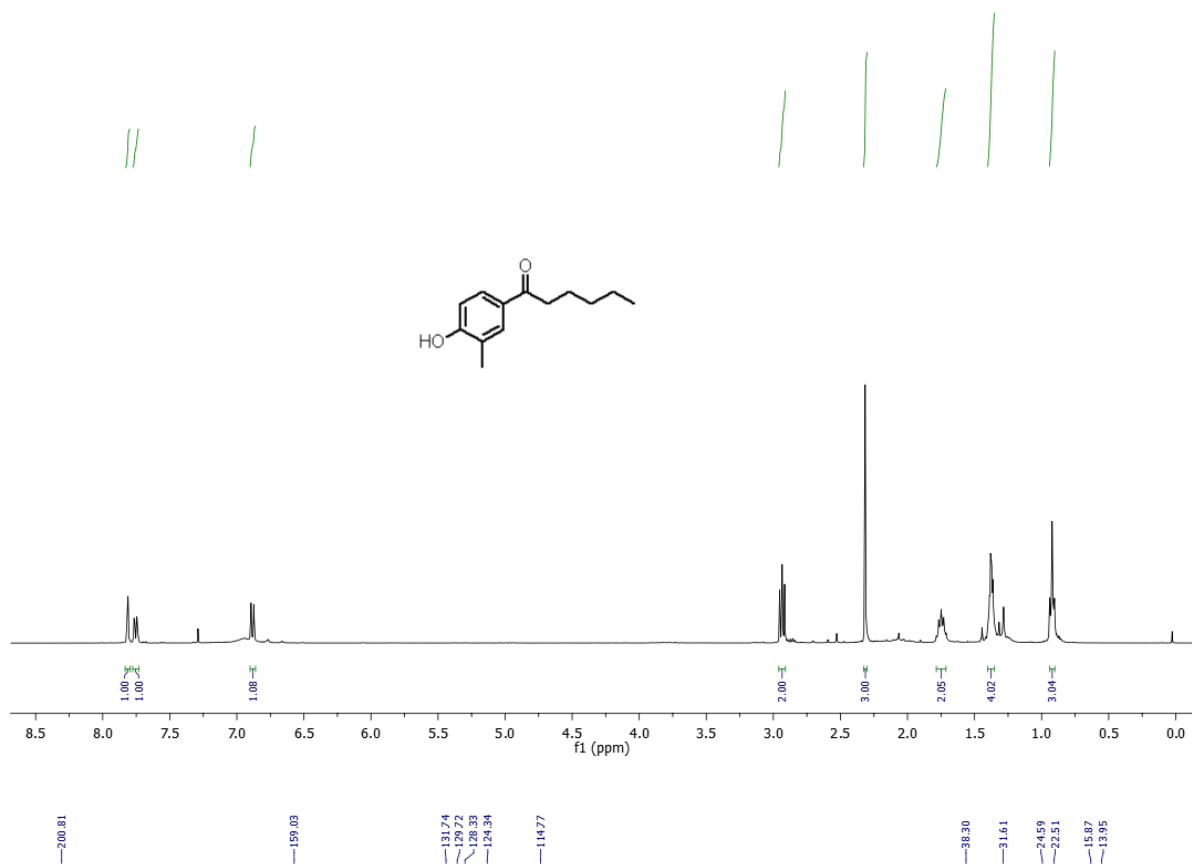
^1H and ^{13}C NMR of 24:



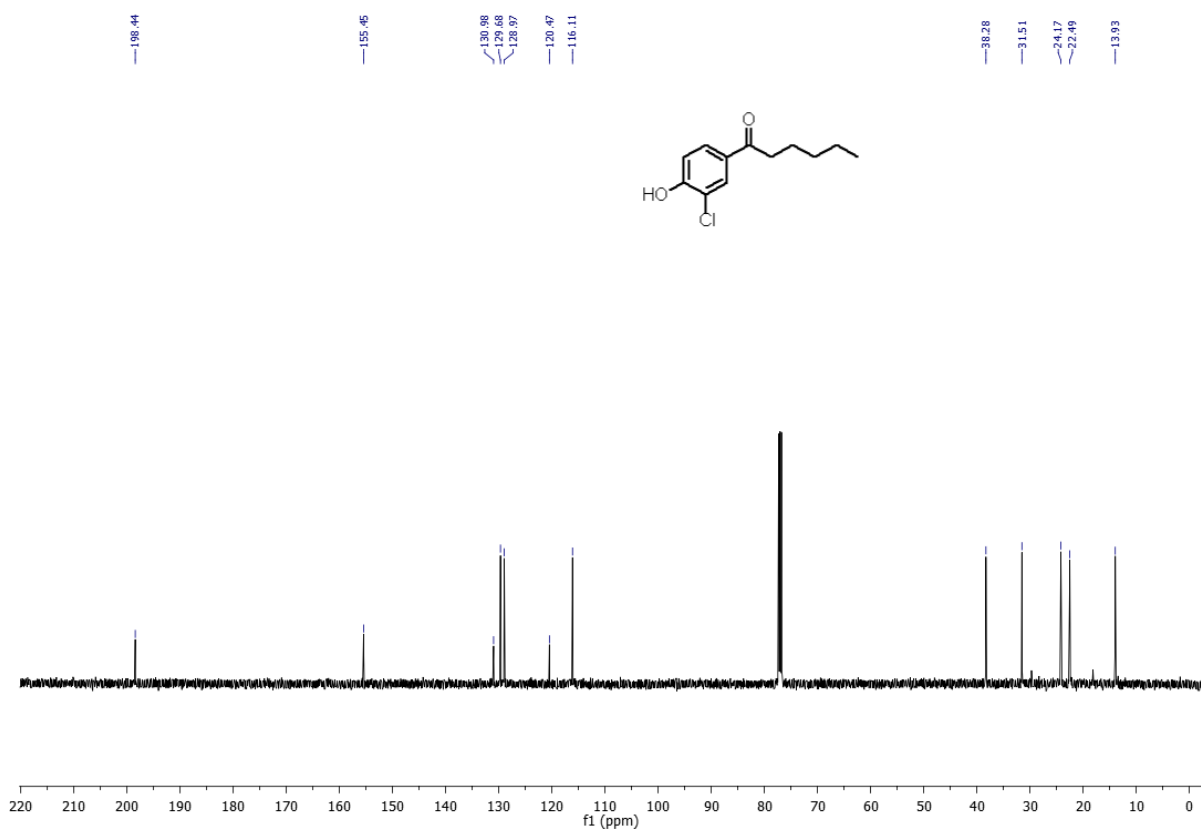
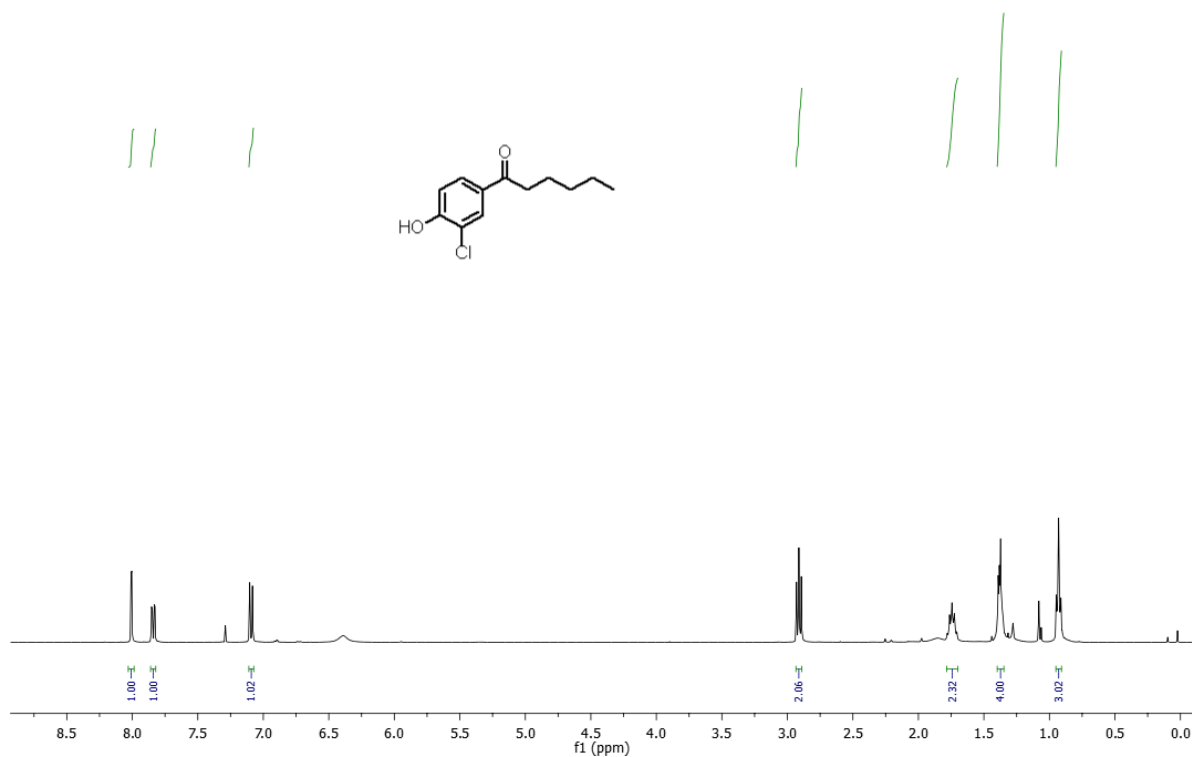
^1H and ^{13}C NMR of 25:



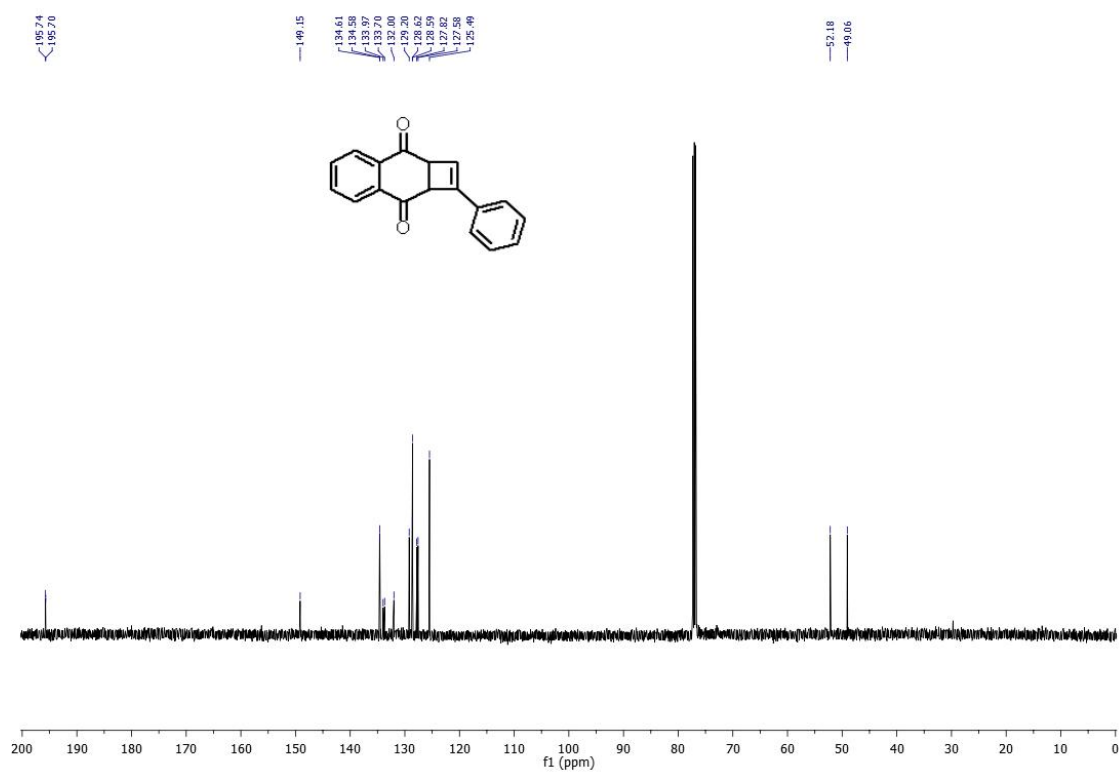
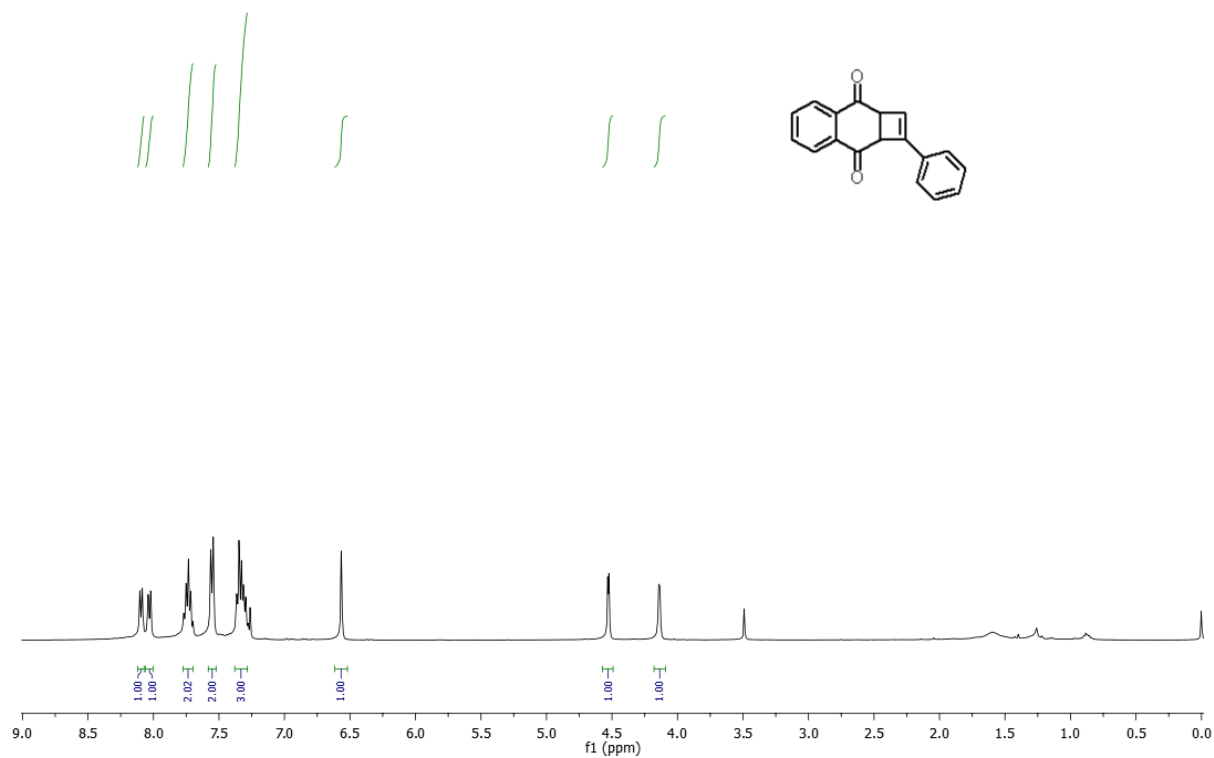
^1H and ^{13}C NMR of 26:



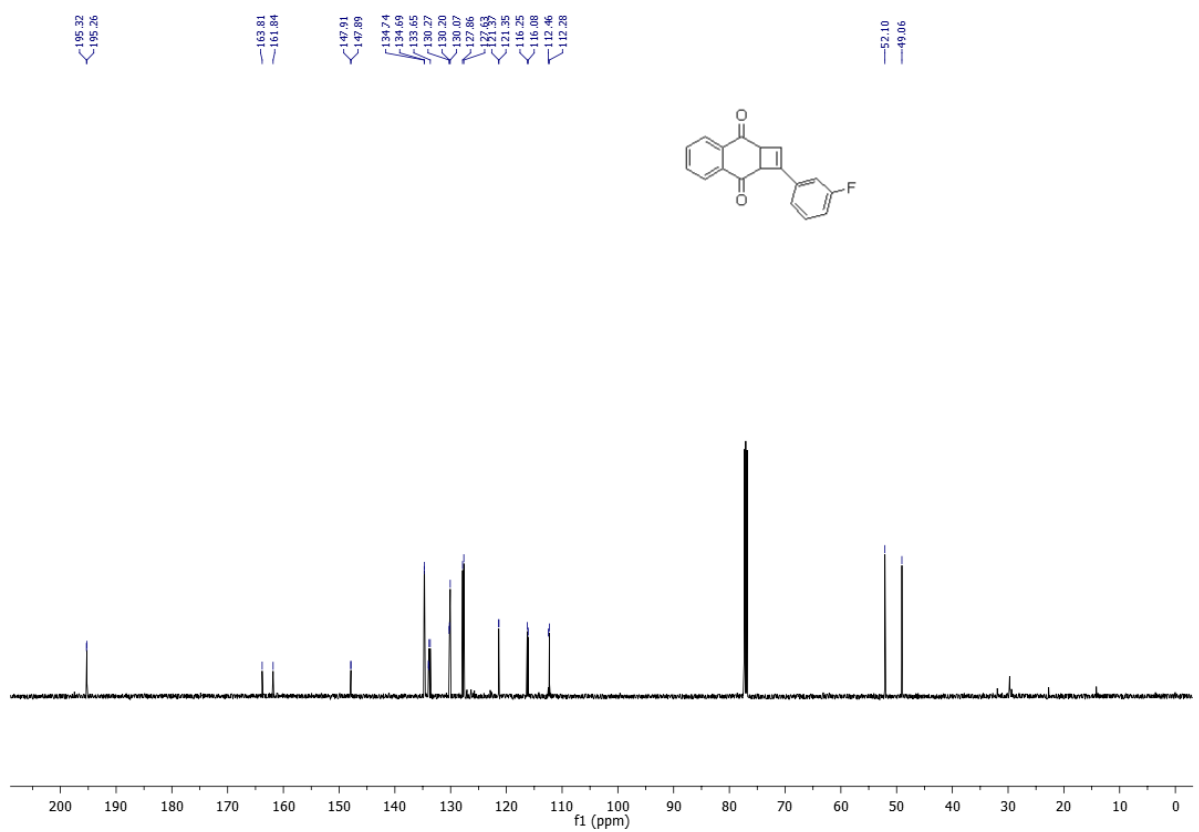
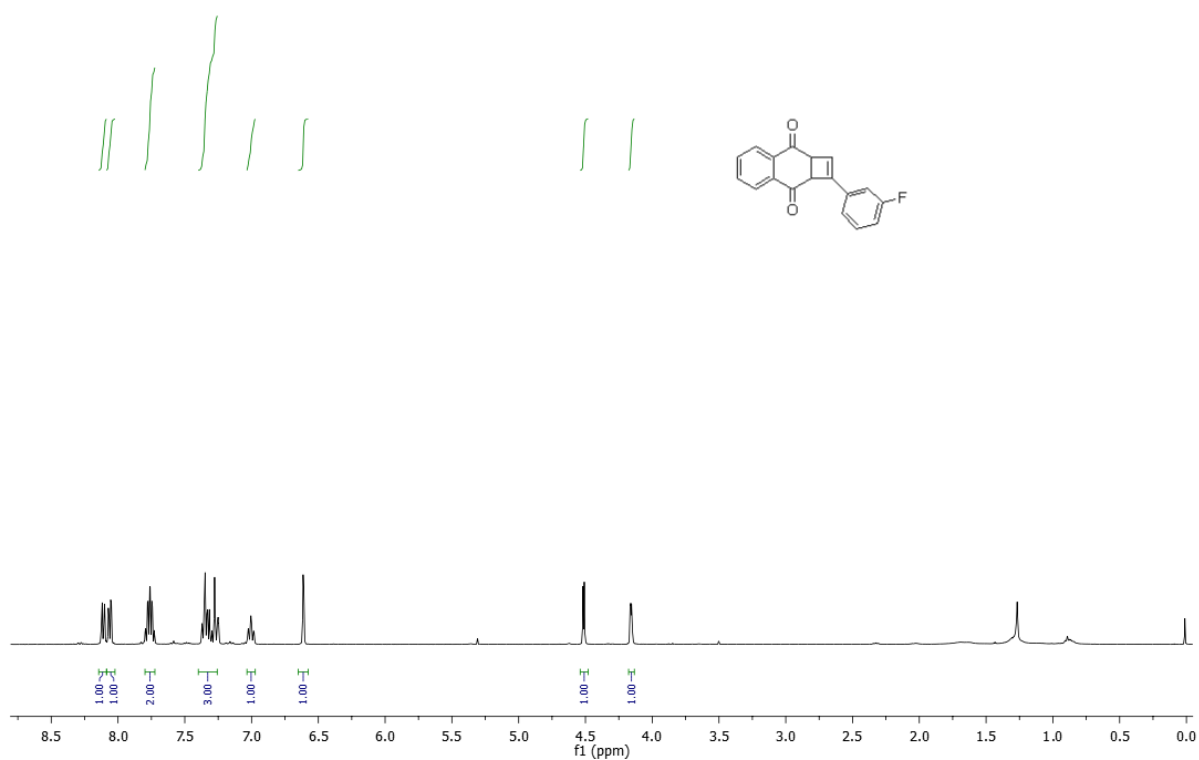
^1H and ^{13}C NMR of 27:



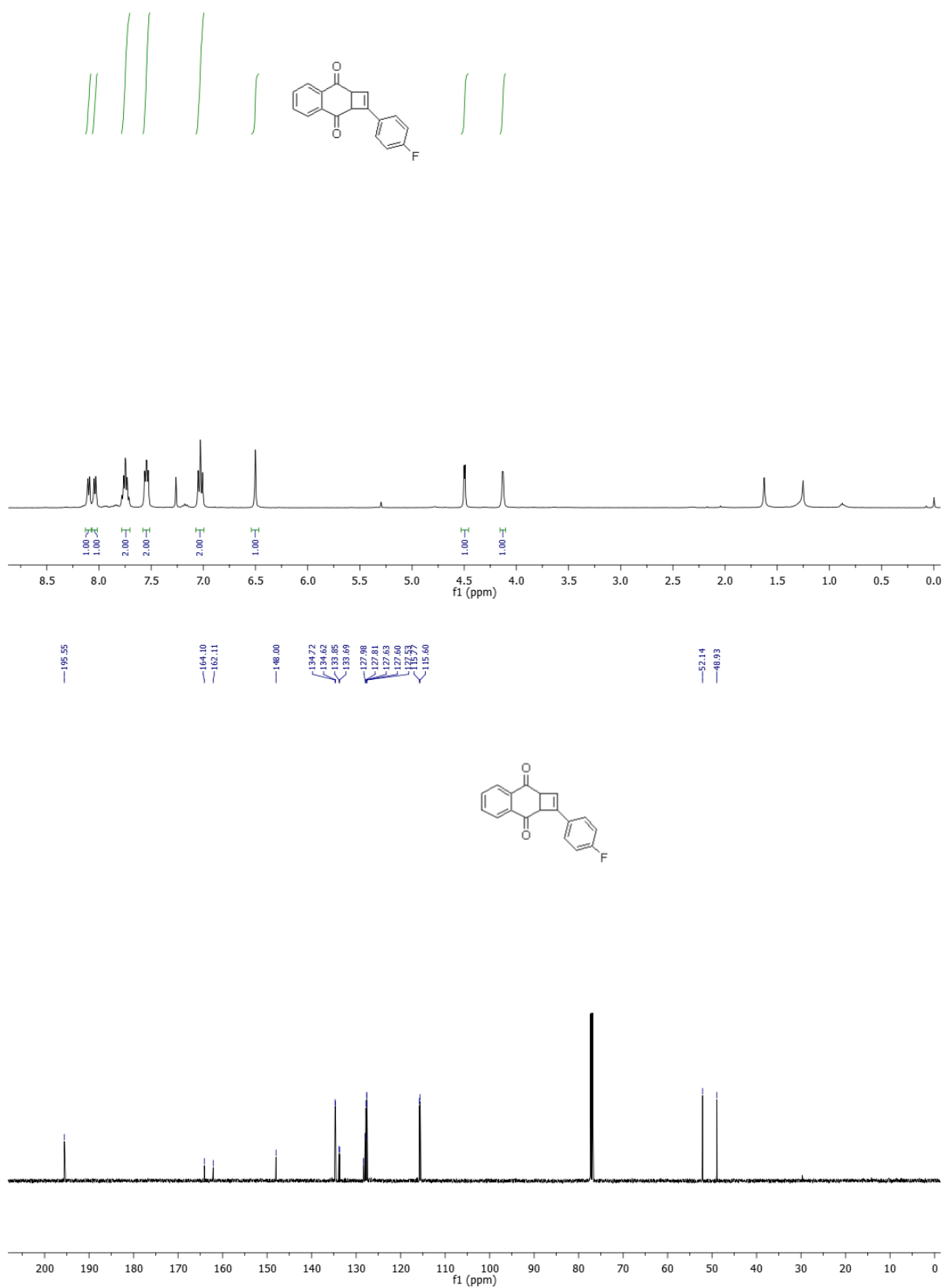
^1H and ^{13}C NMR of 28:



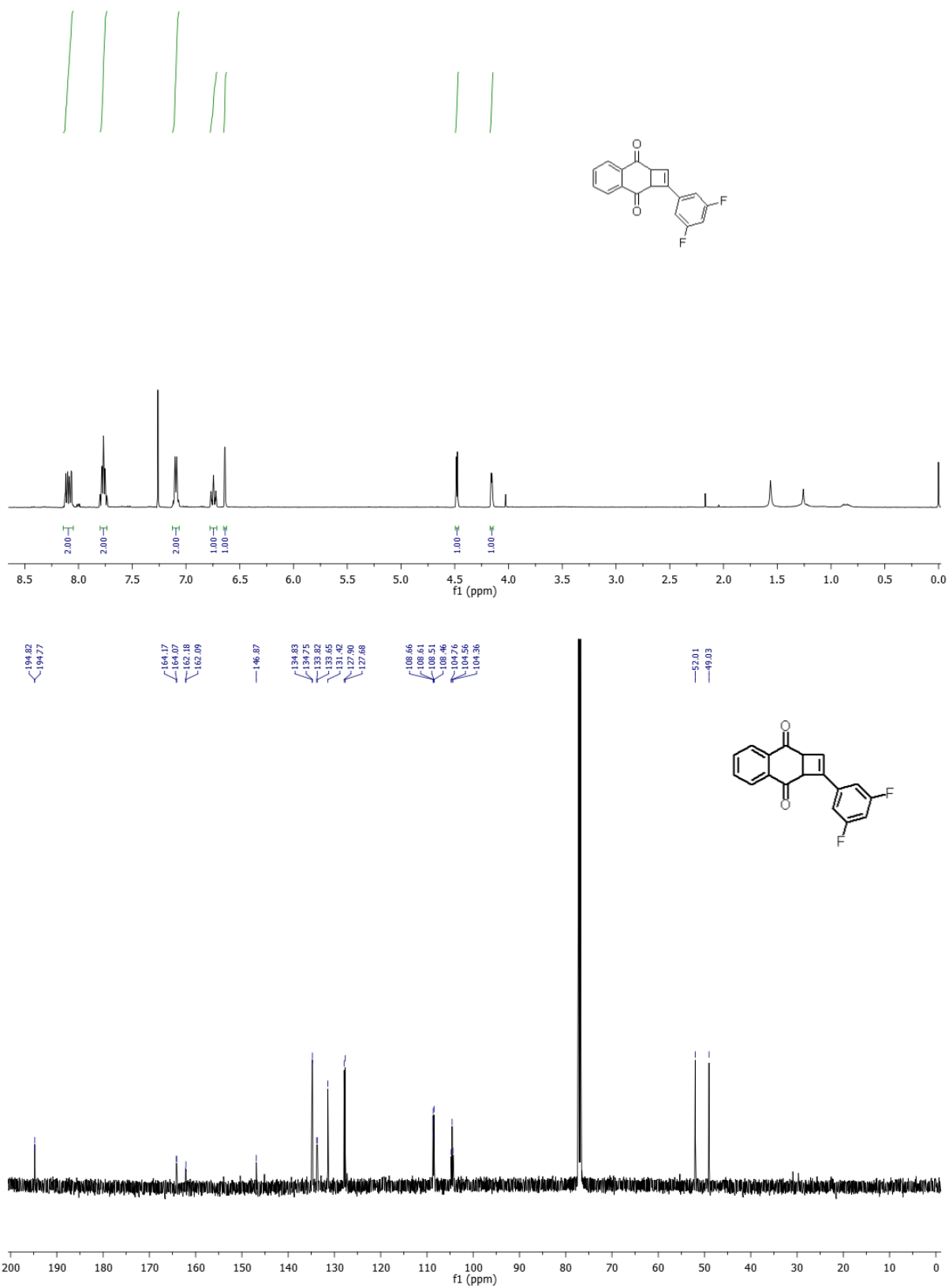
^1H and ^{13}C NMR of 29:



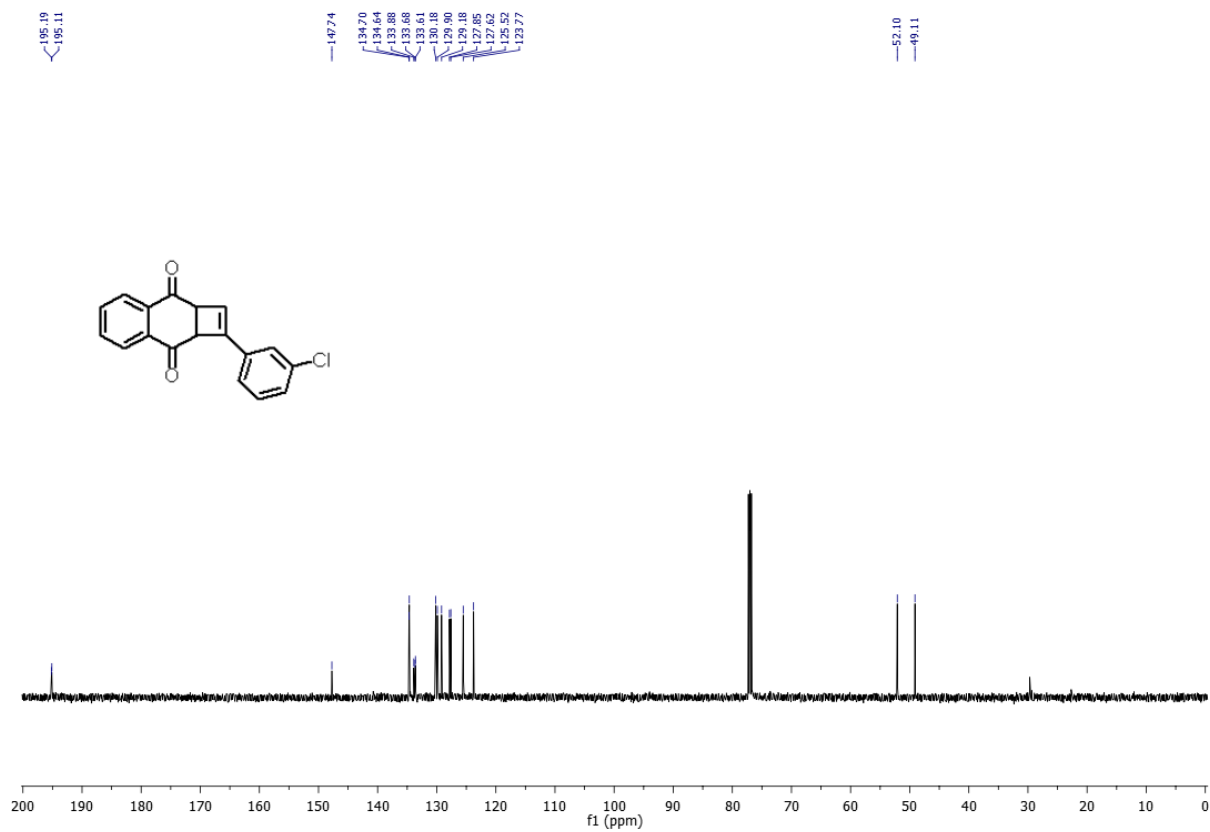
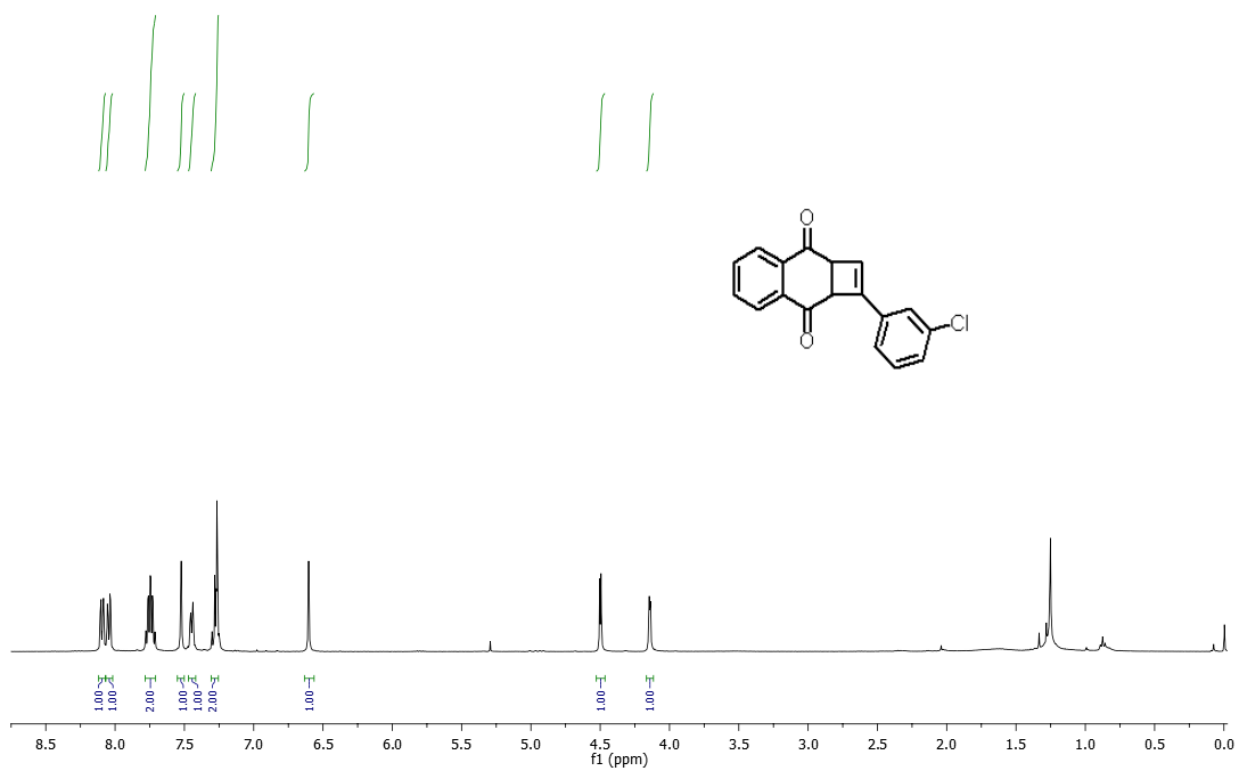
^1H and ^{13}C NMR of 30:



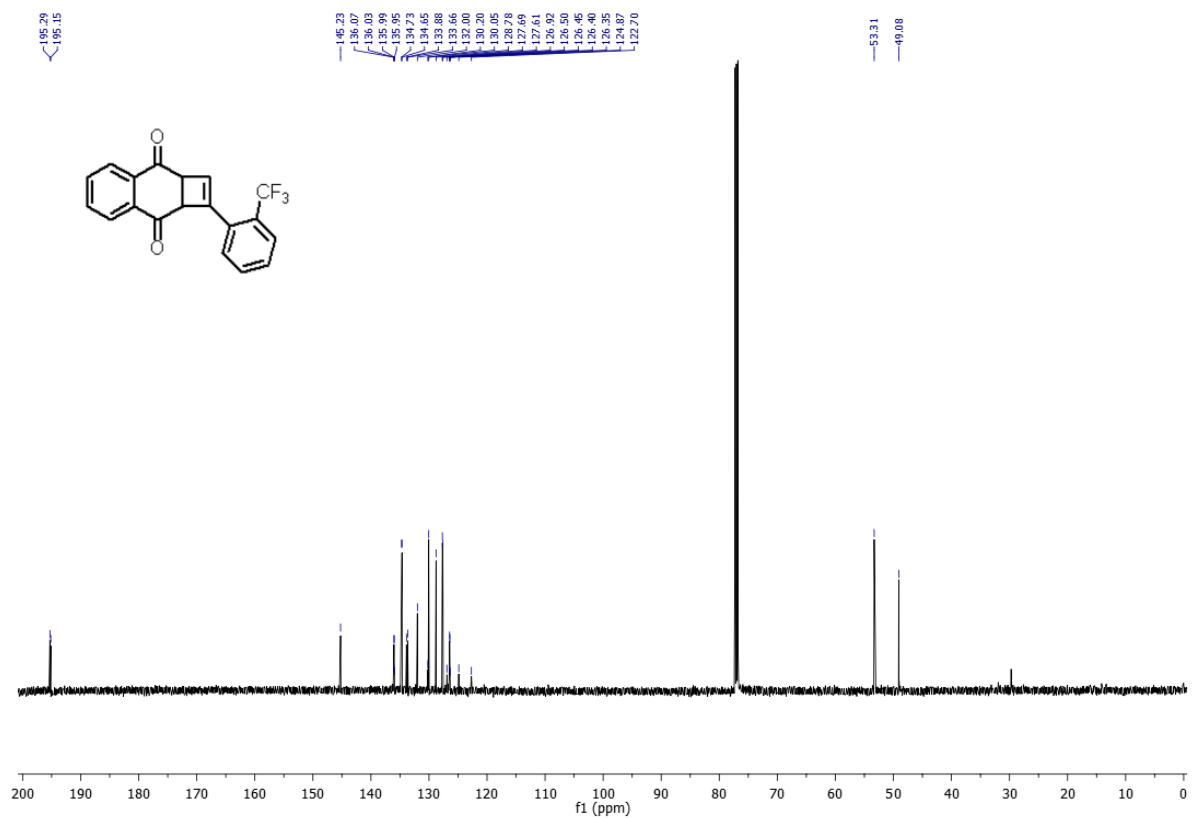
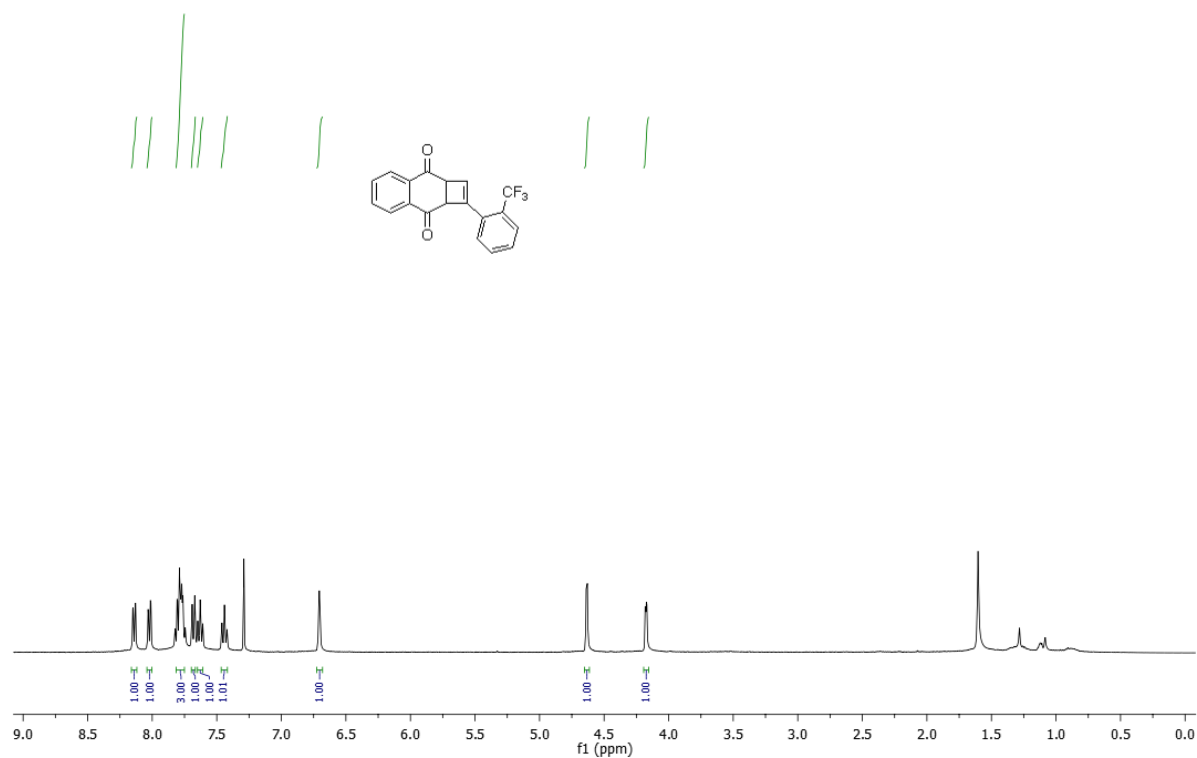
^1H and ^{13}C NMR of 31:



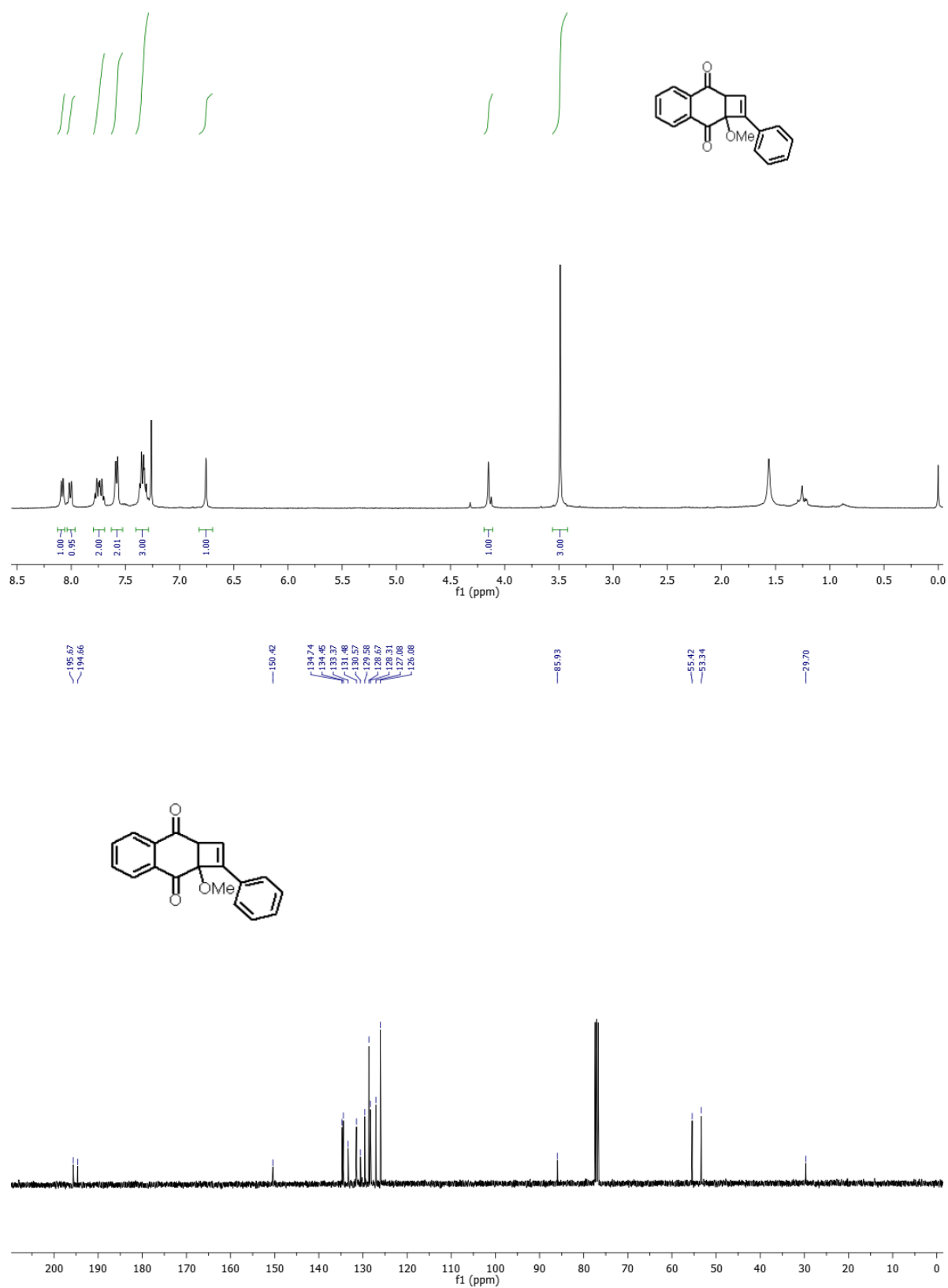
^1H and ^{13}C NMR of 32:



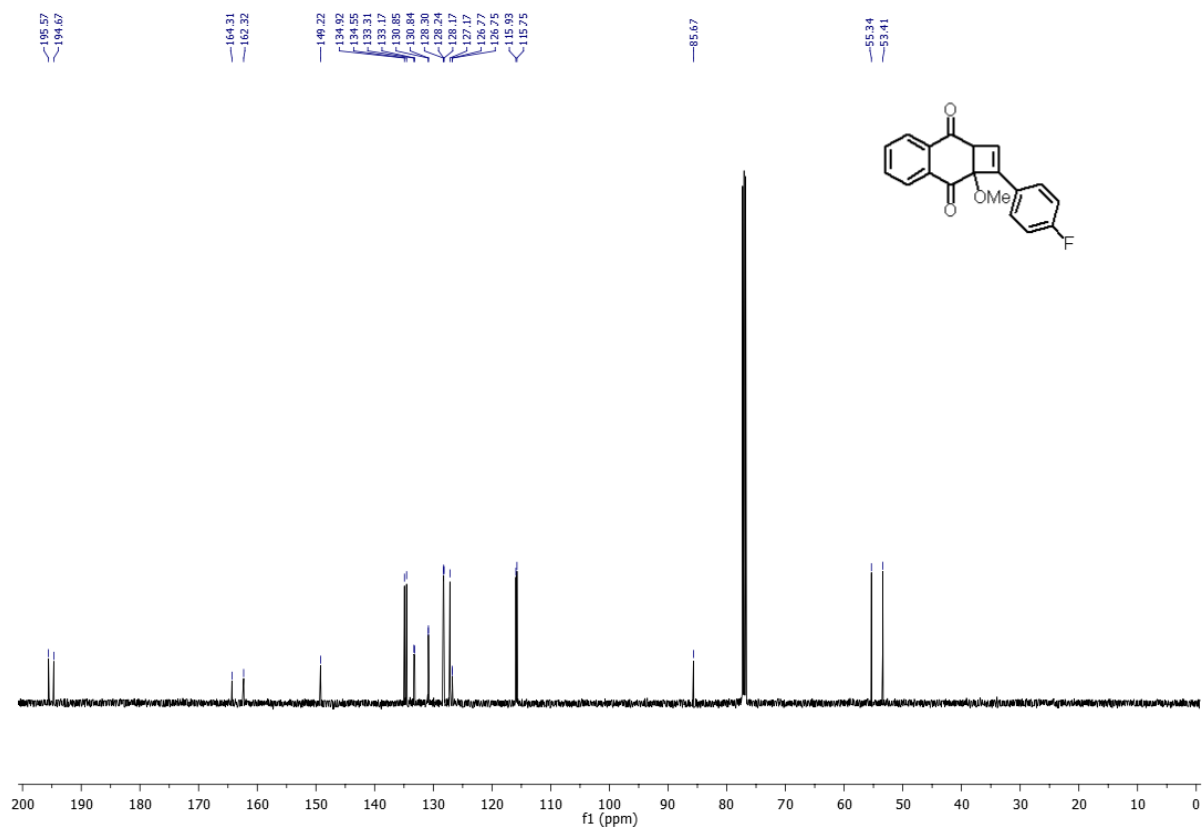
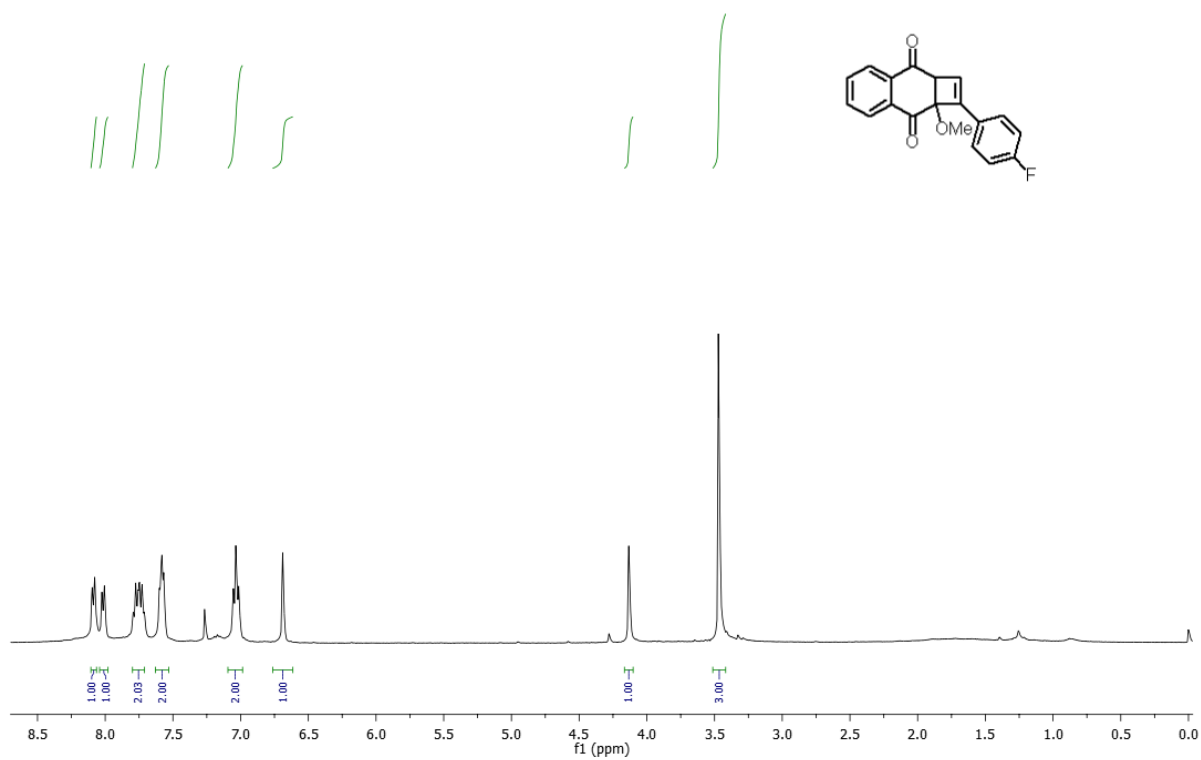
^1H and ^{13}C NMR of 33:



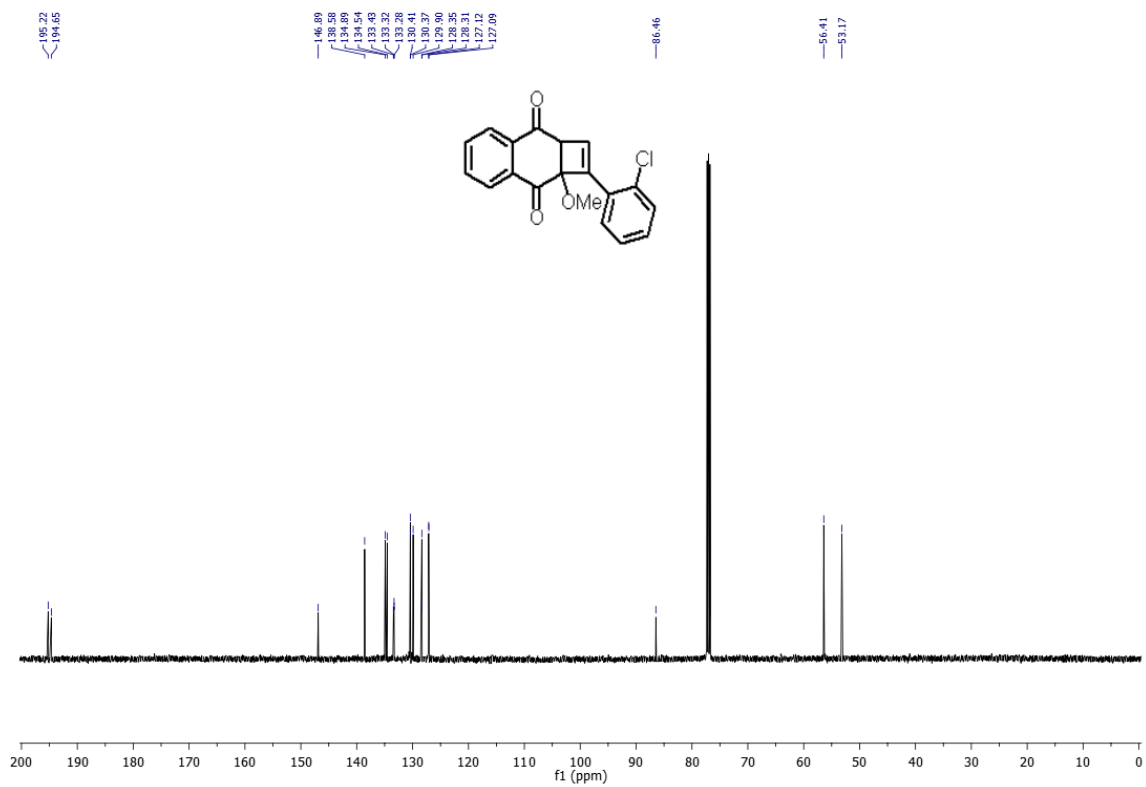
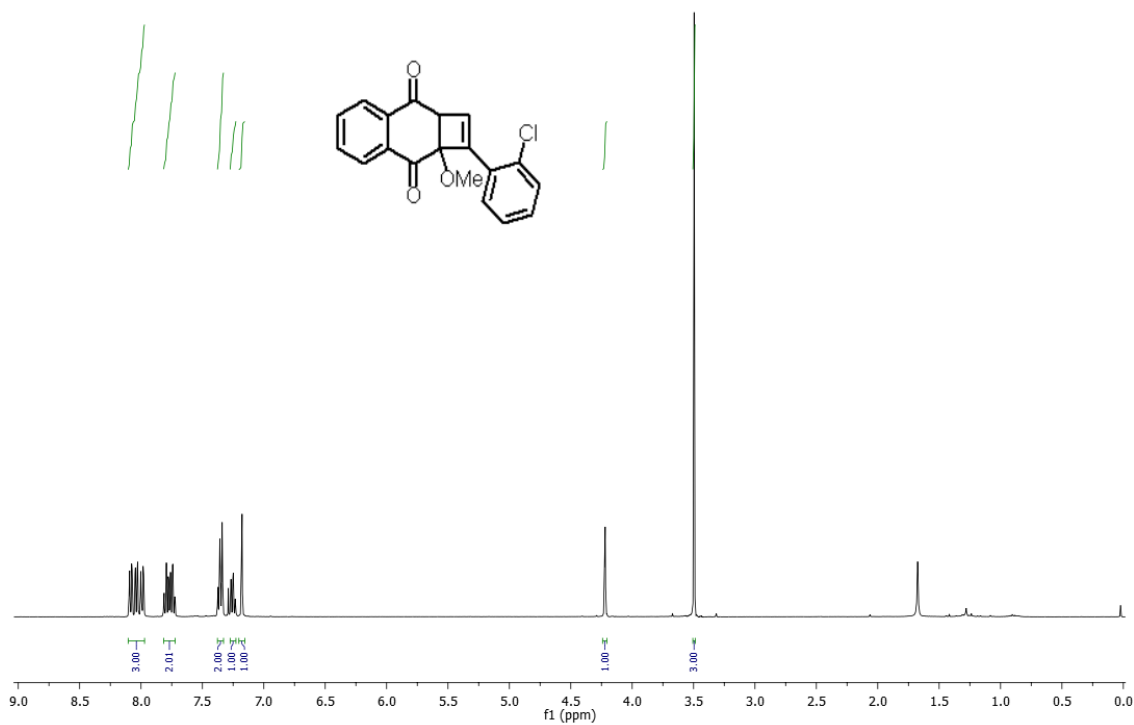
^1H and ^{13}C NMR of 34:



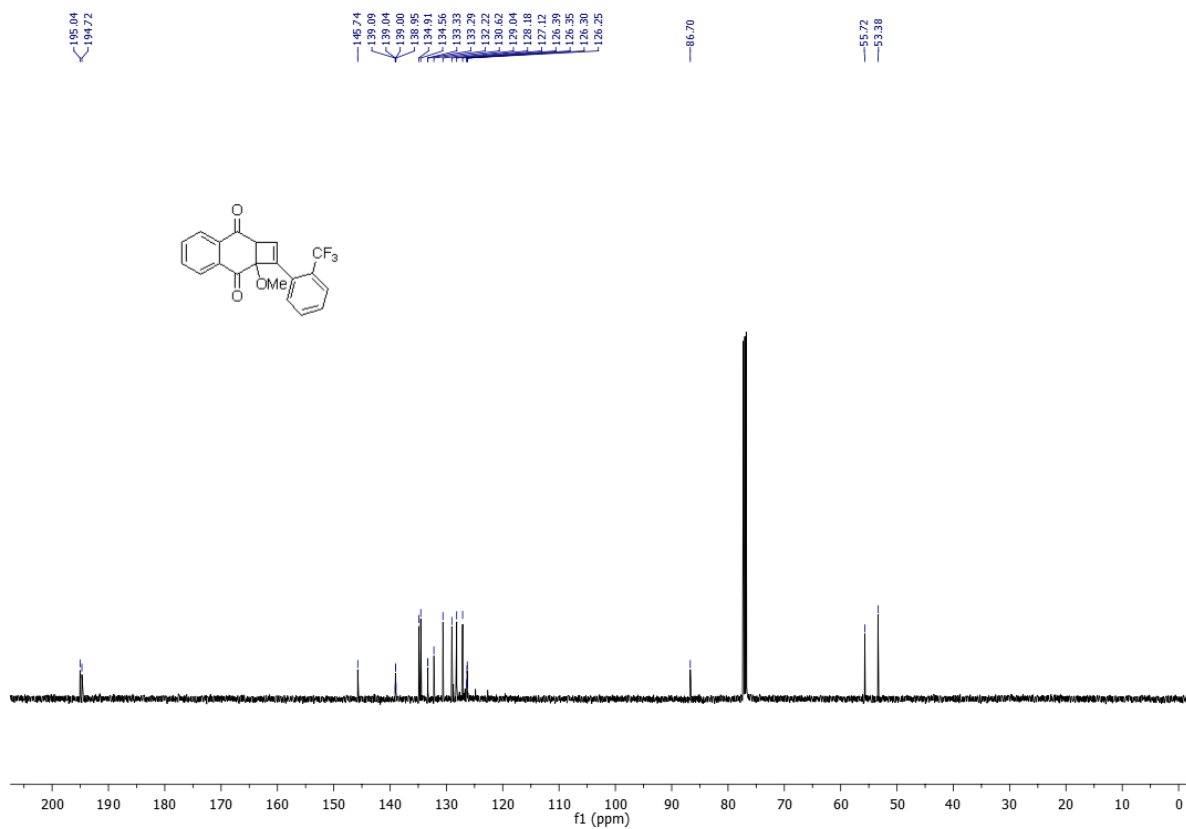
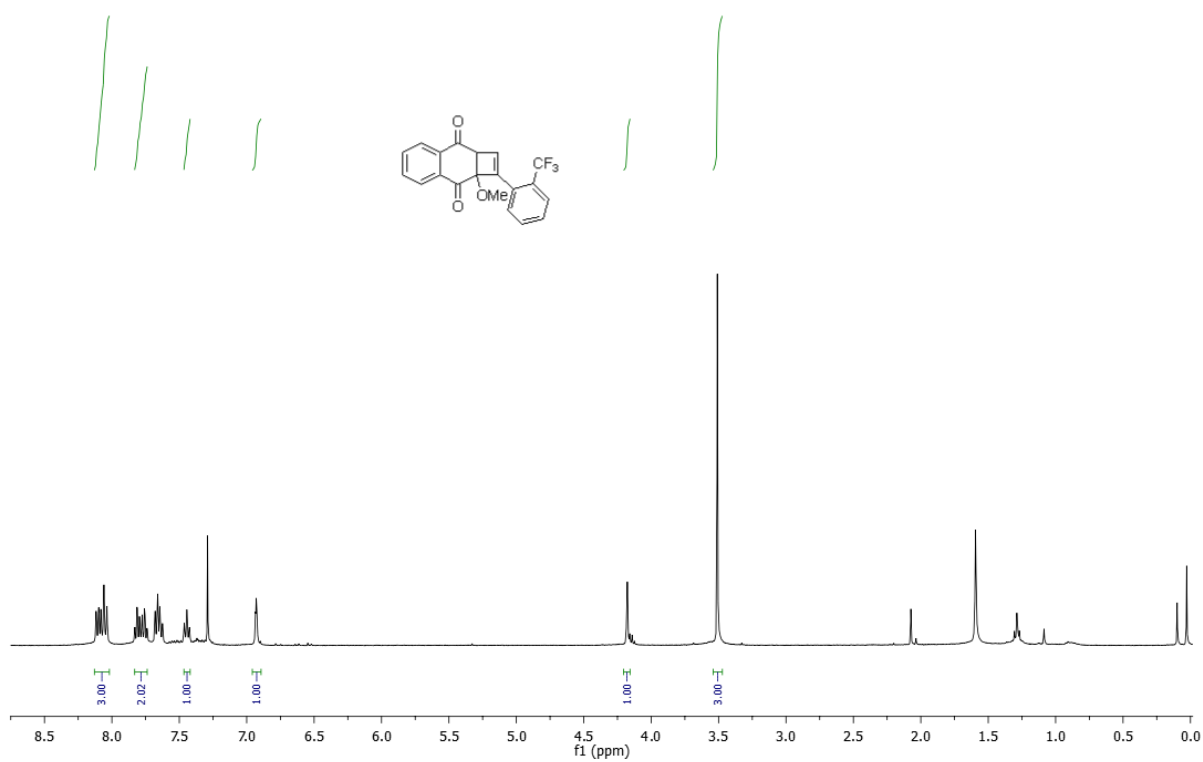
^1H and ^{13}C NMR of 35:



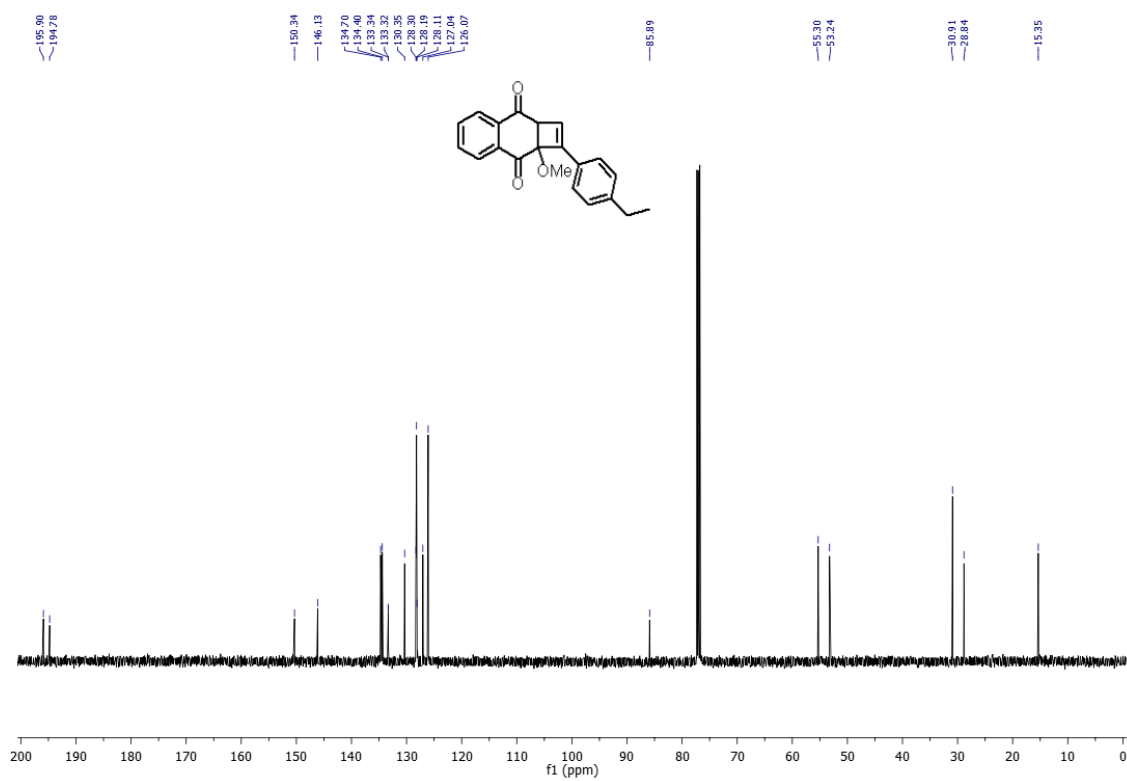
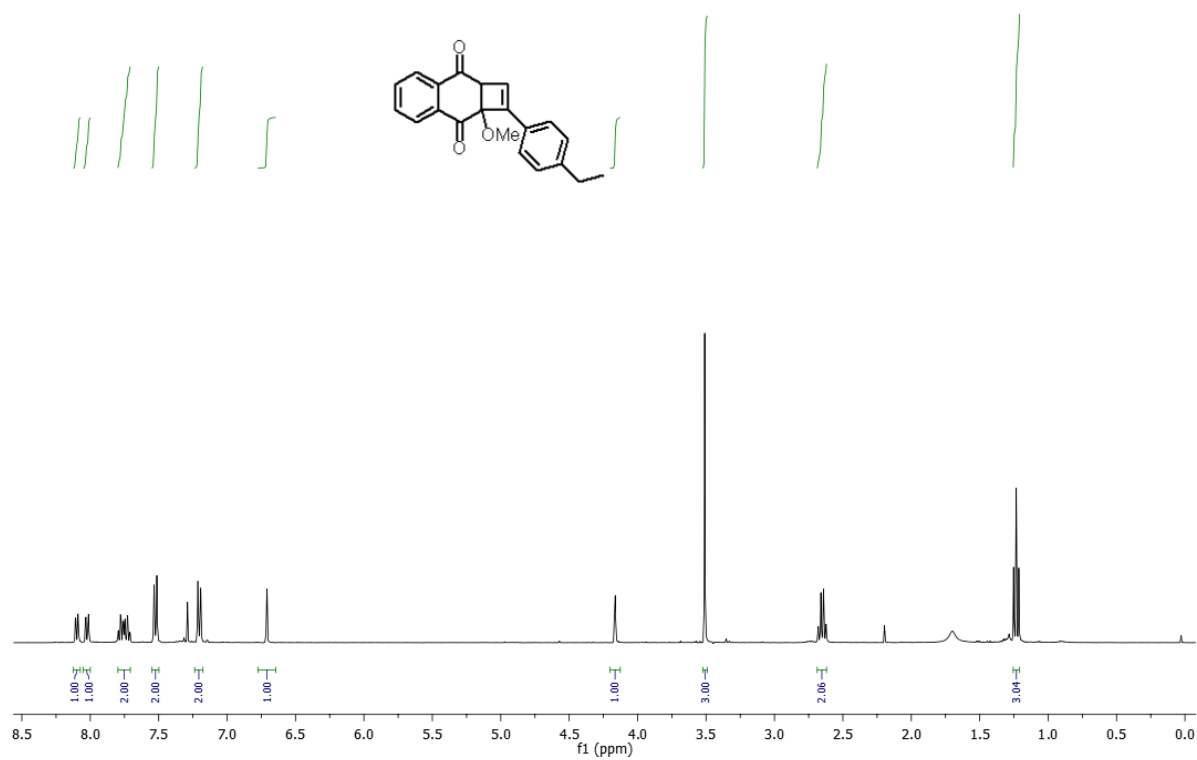
^1H and ^{13}C NMR of 36:



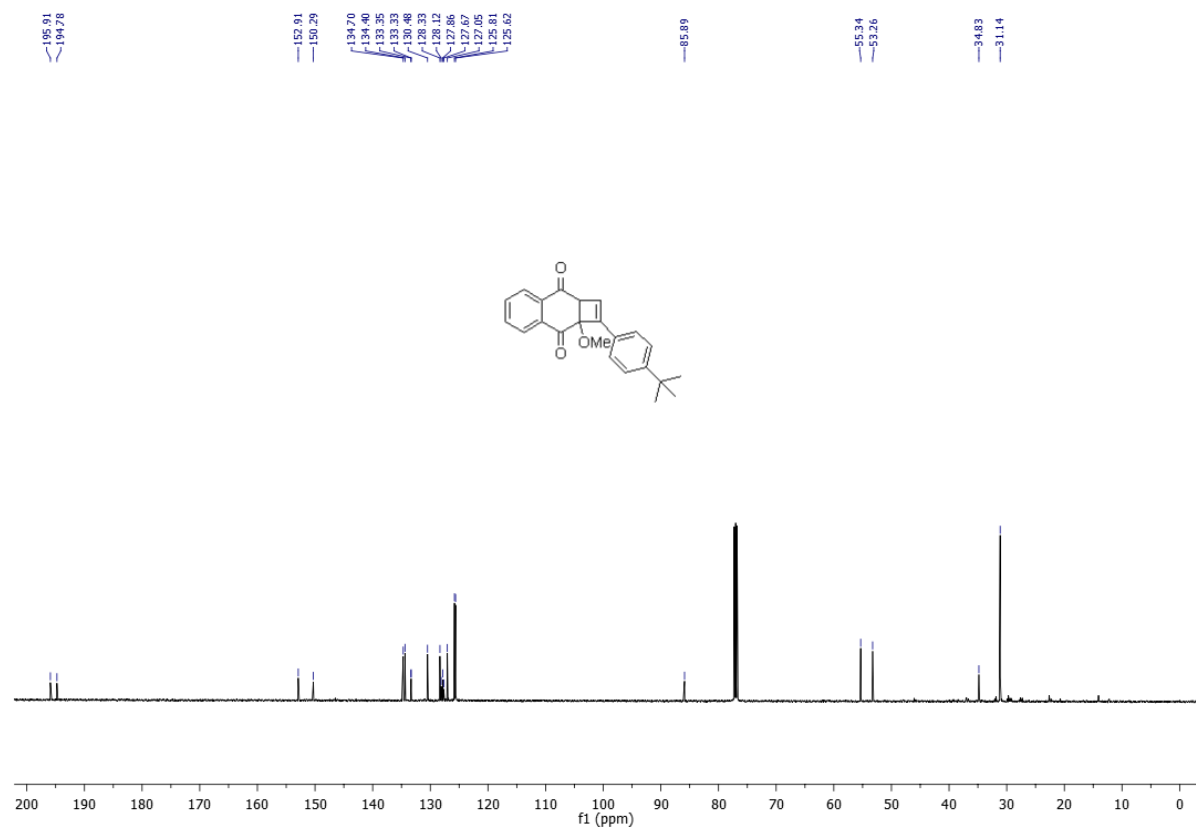
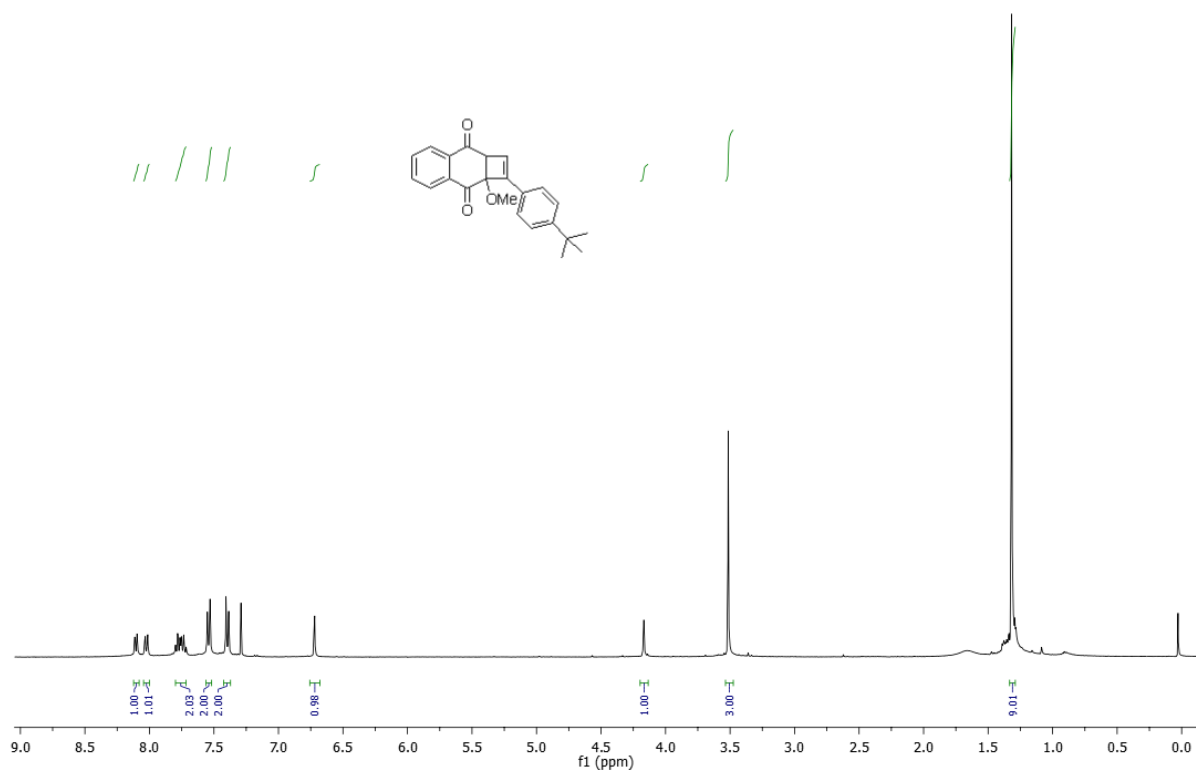
^1H and ^{13}C NMR of 37:



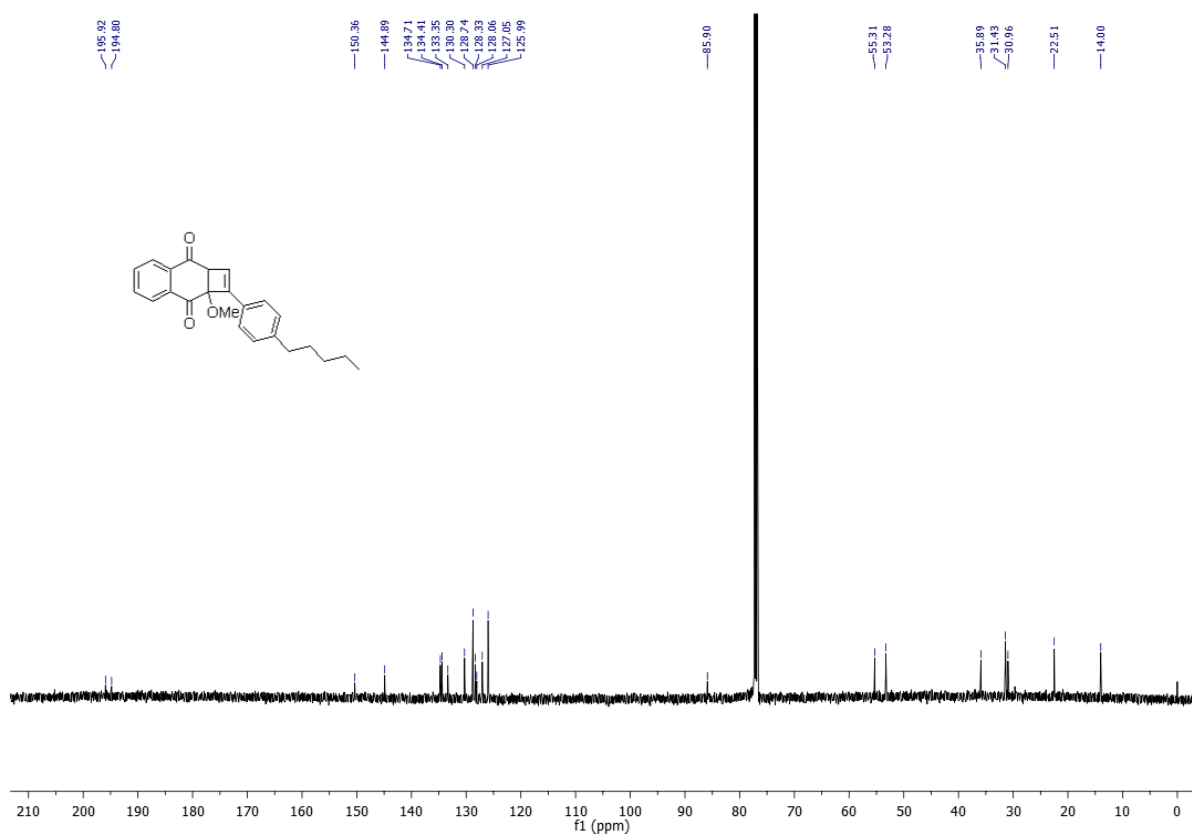
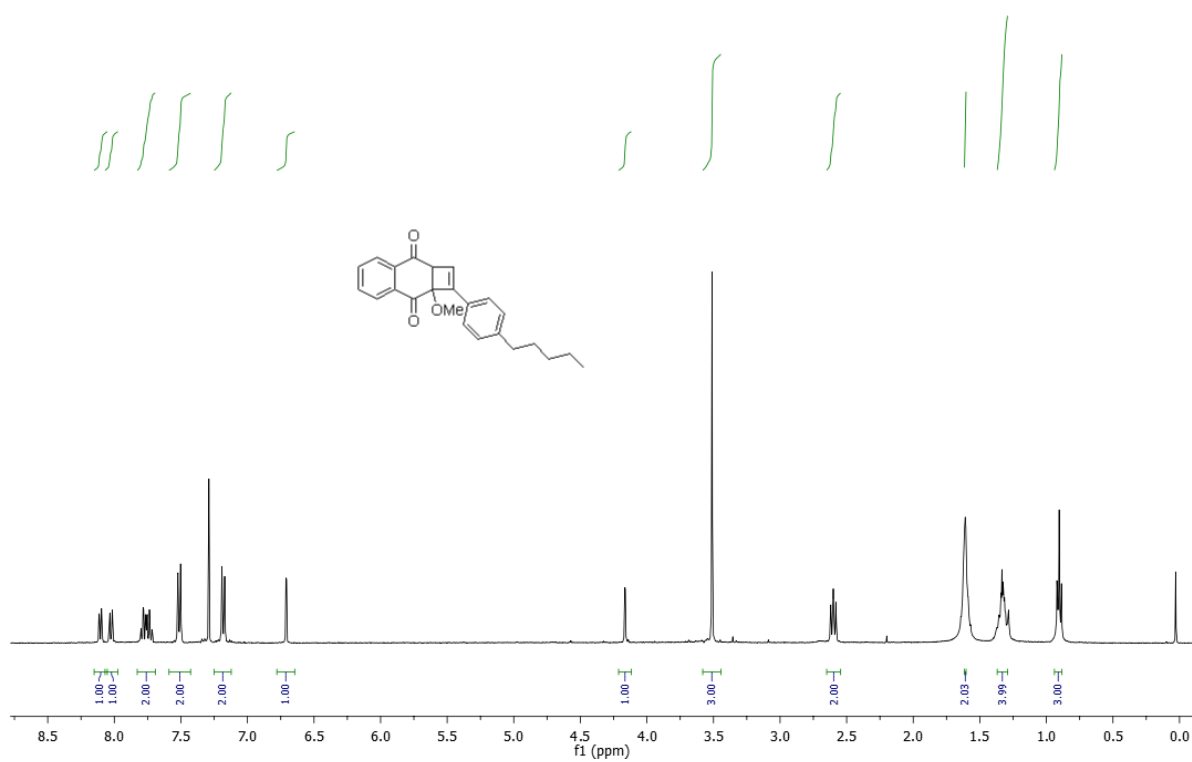
^1H and ^{13}C NMR of 38:



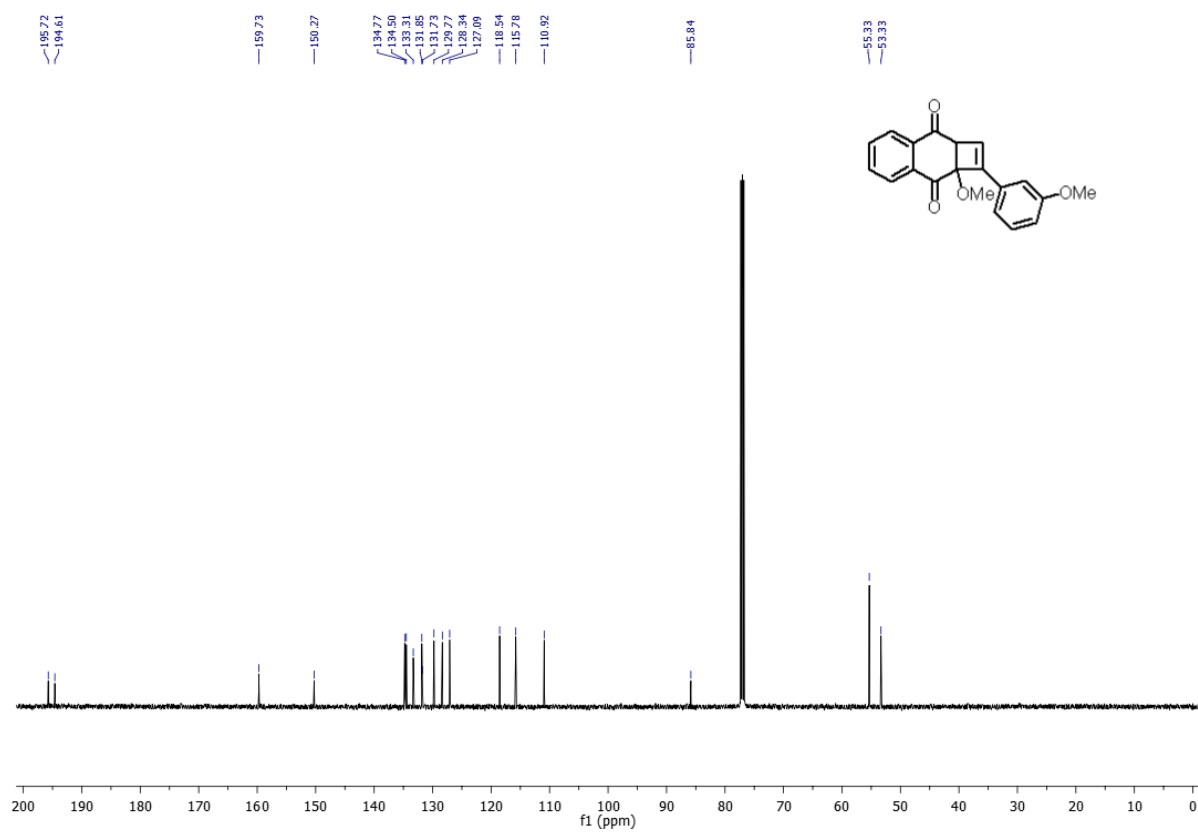
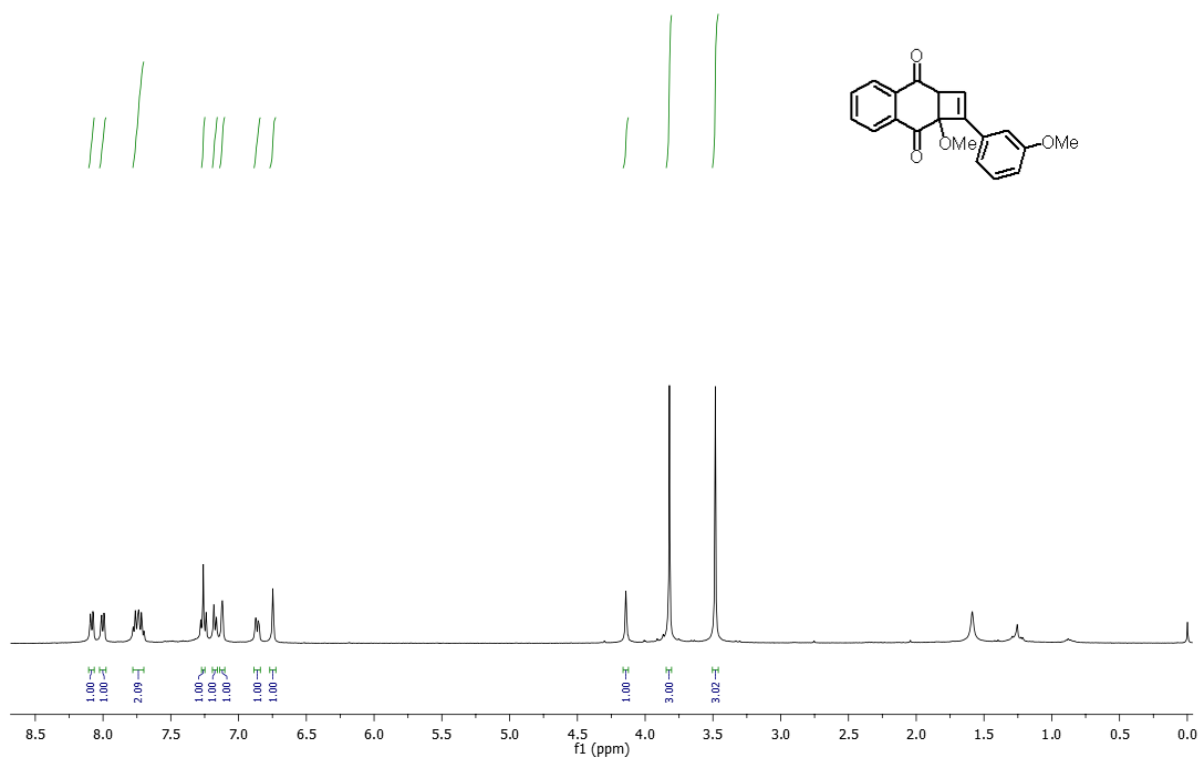
^1H and ^{13}C NMR of 39:



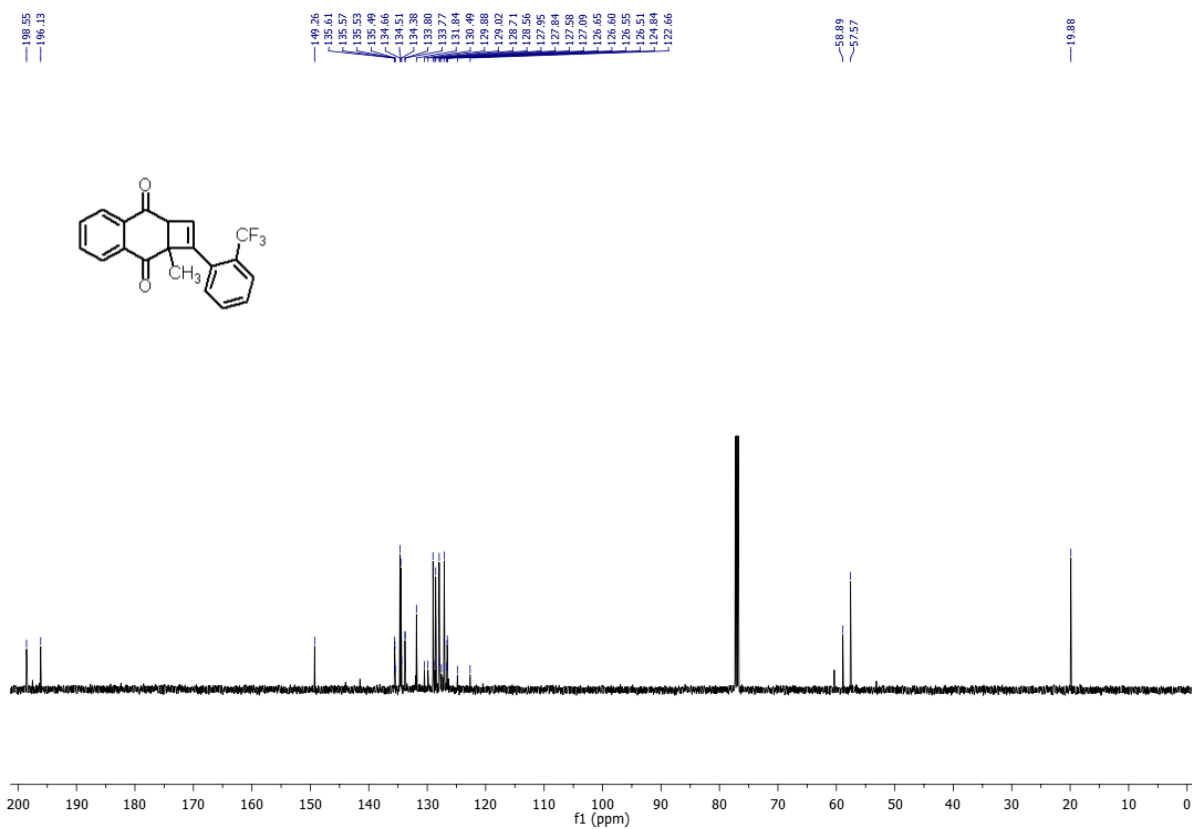
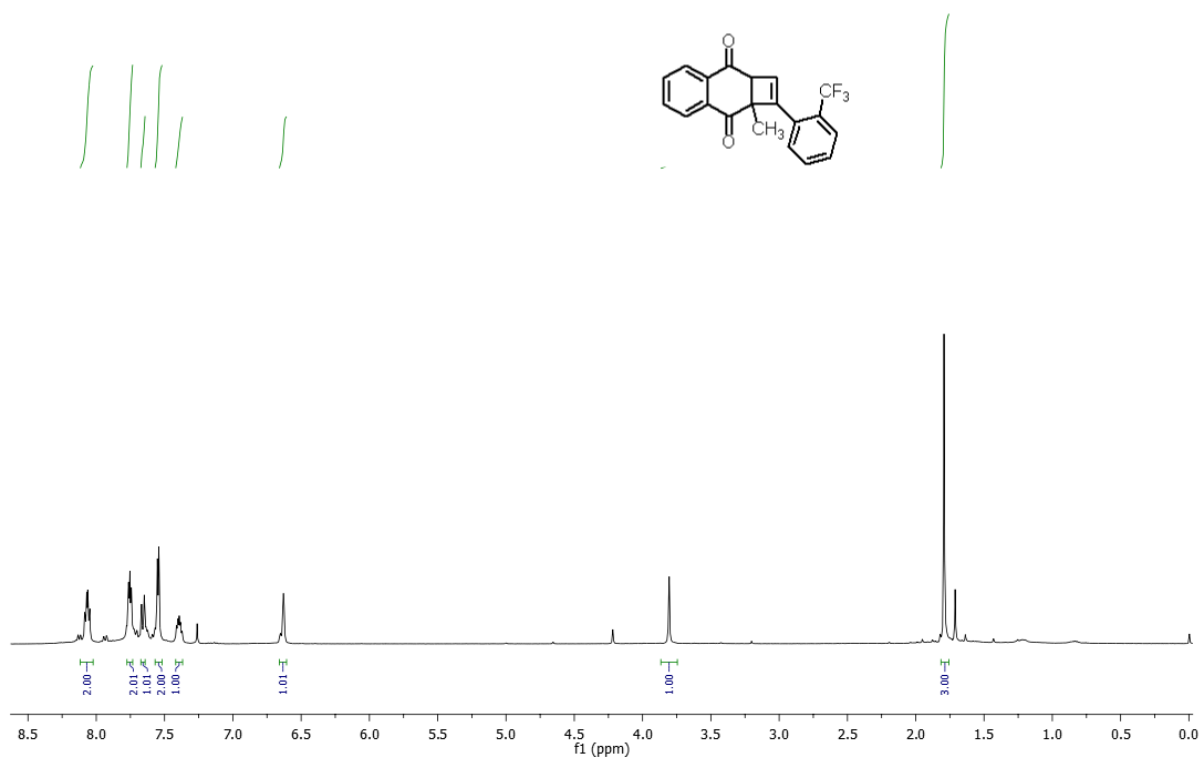
^1H and ^{13}C NMR of 40:



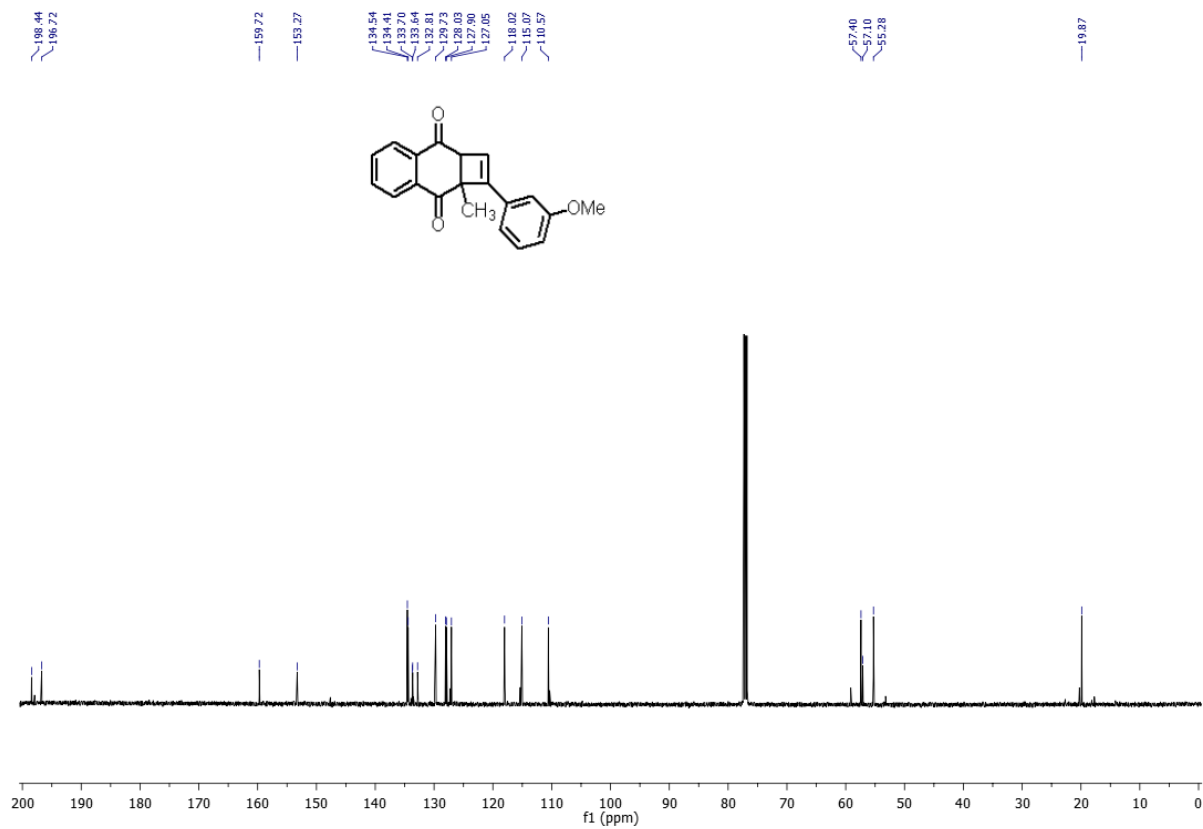
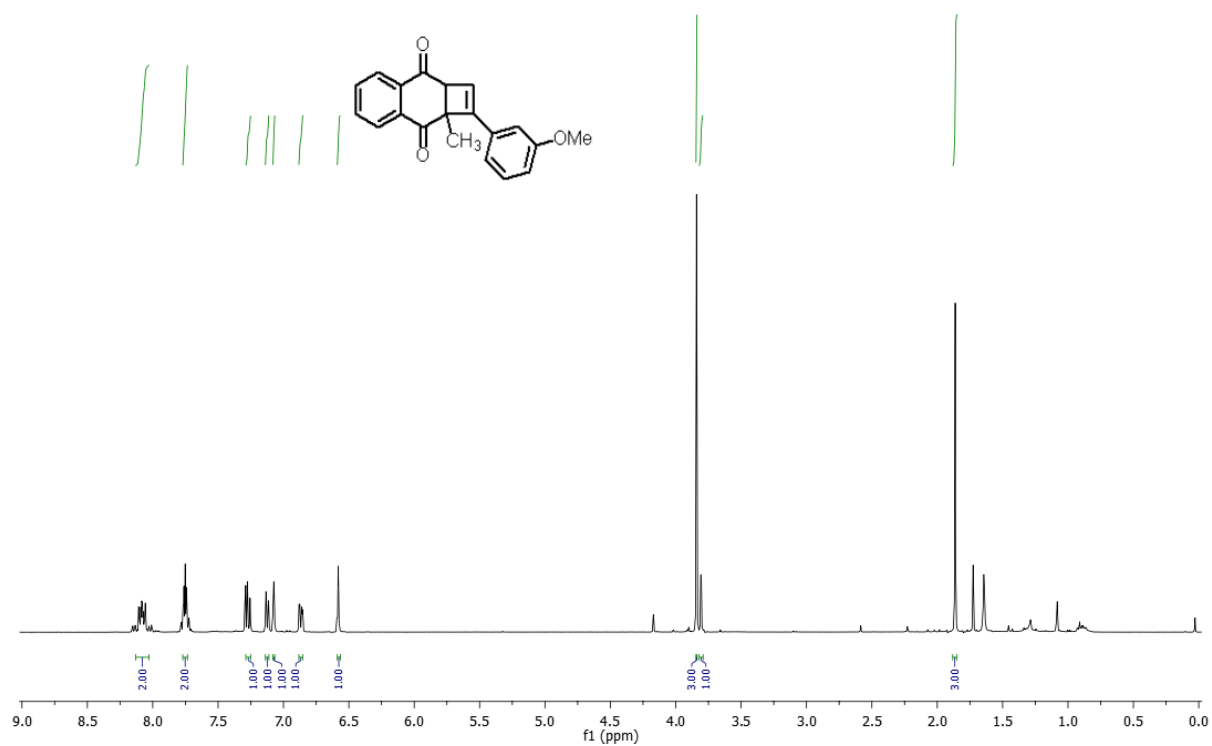
^1H and ^{13}C NMR of 41:



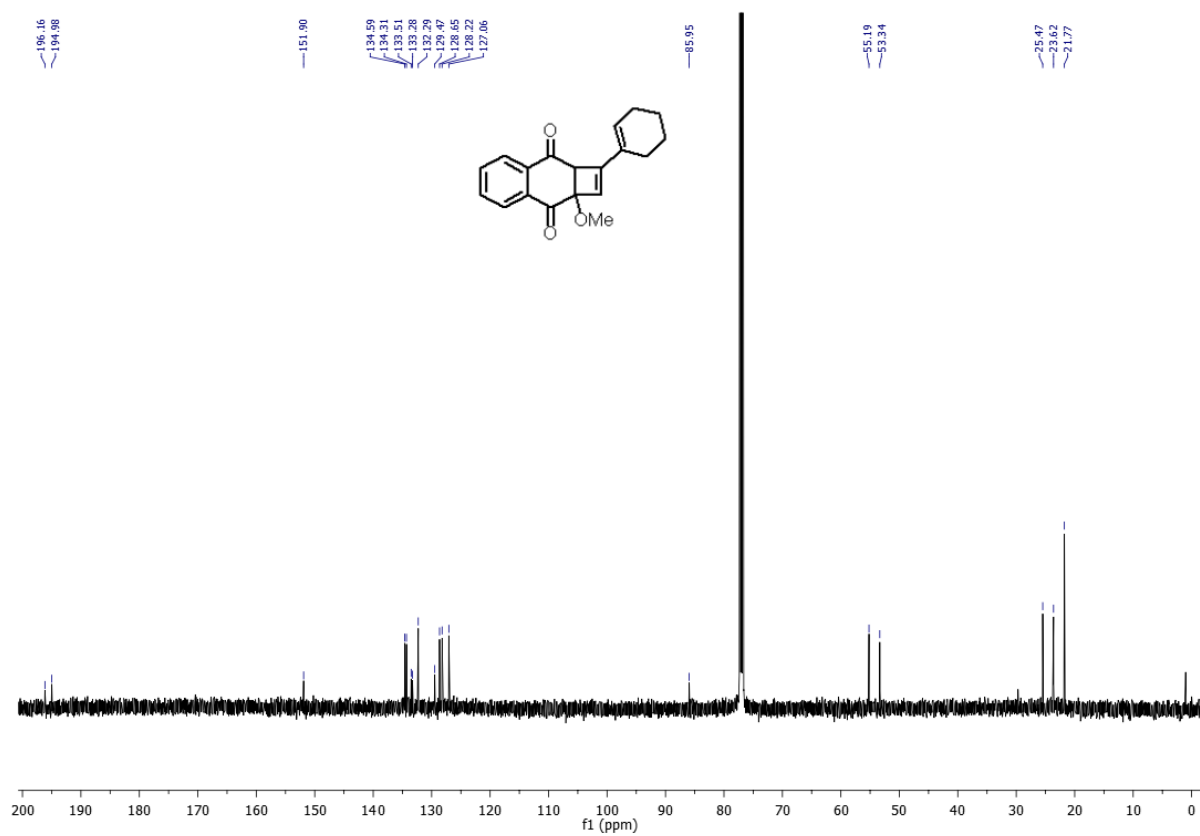
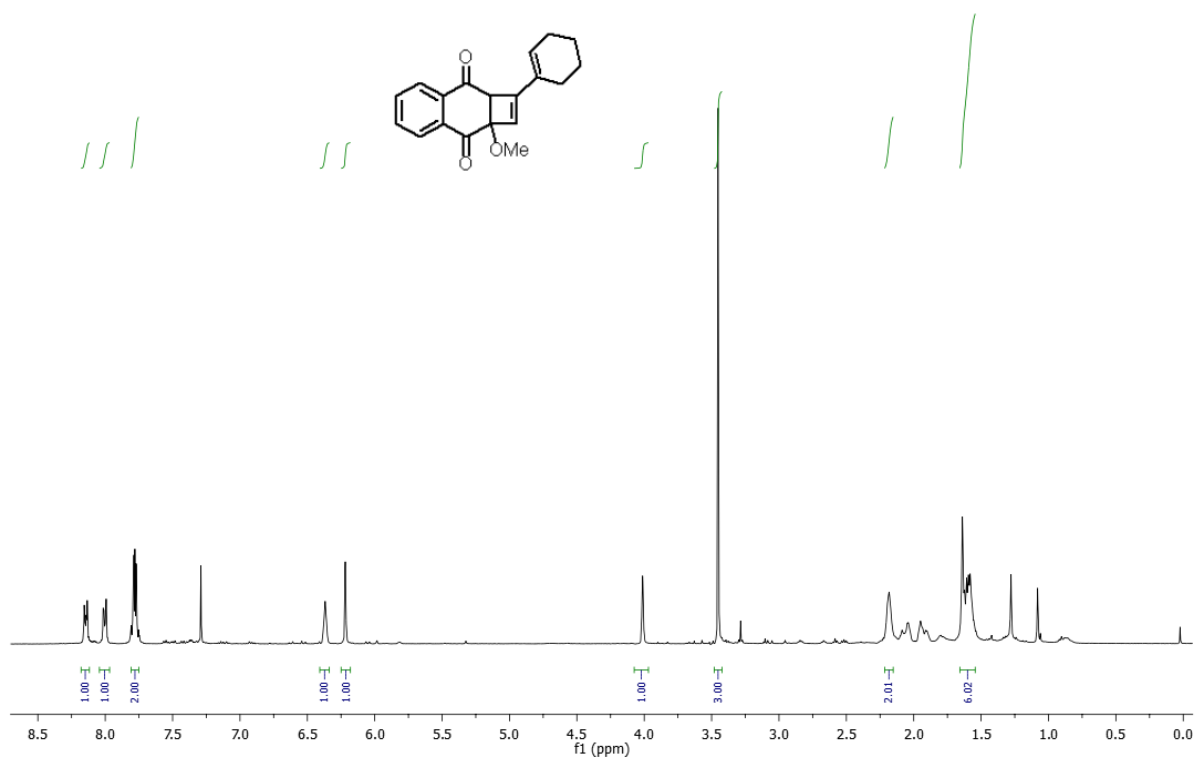
^1H and ^{13}C NMR of 42:



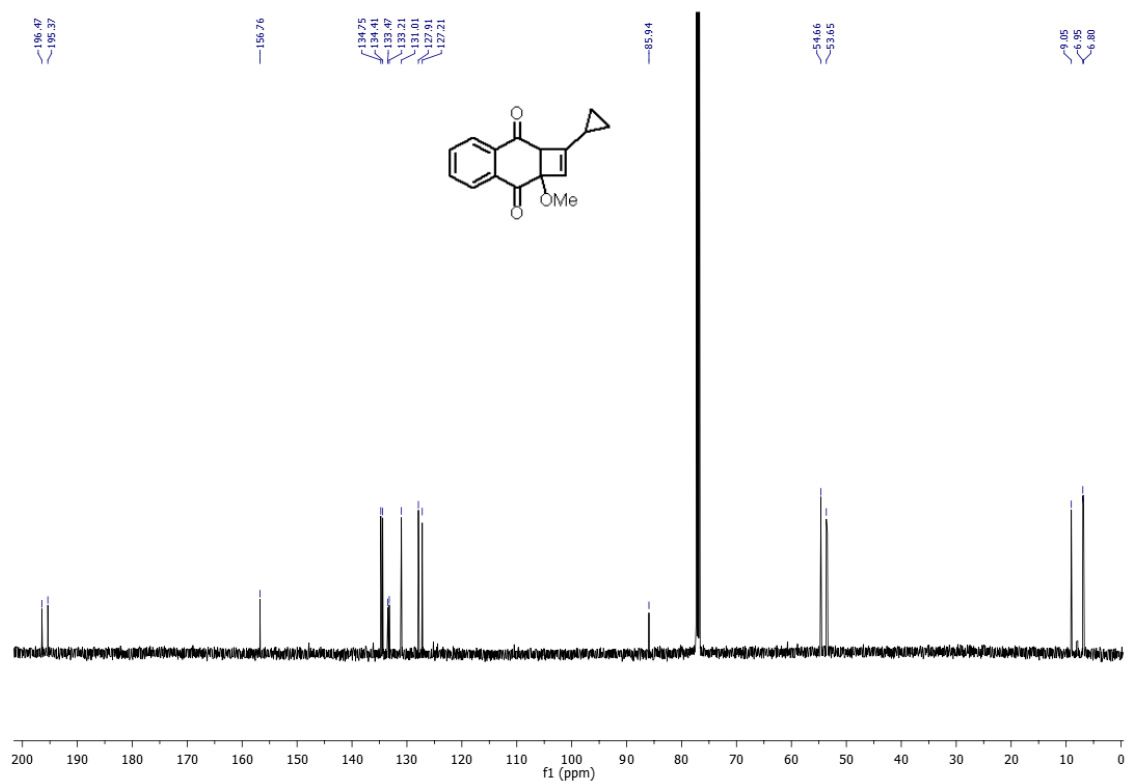
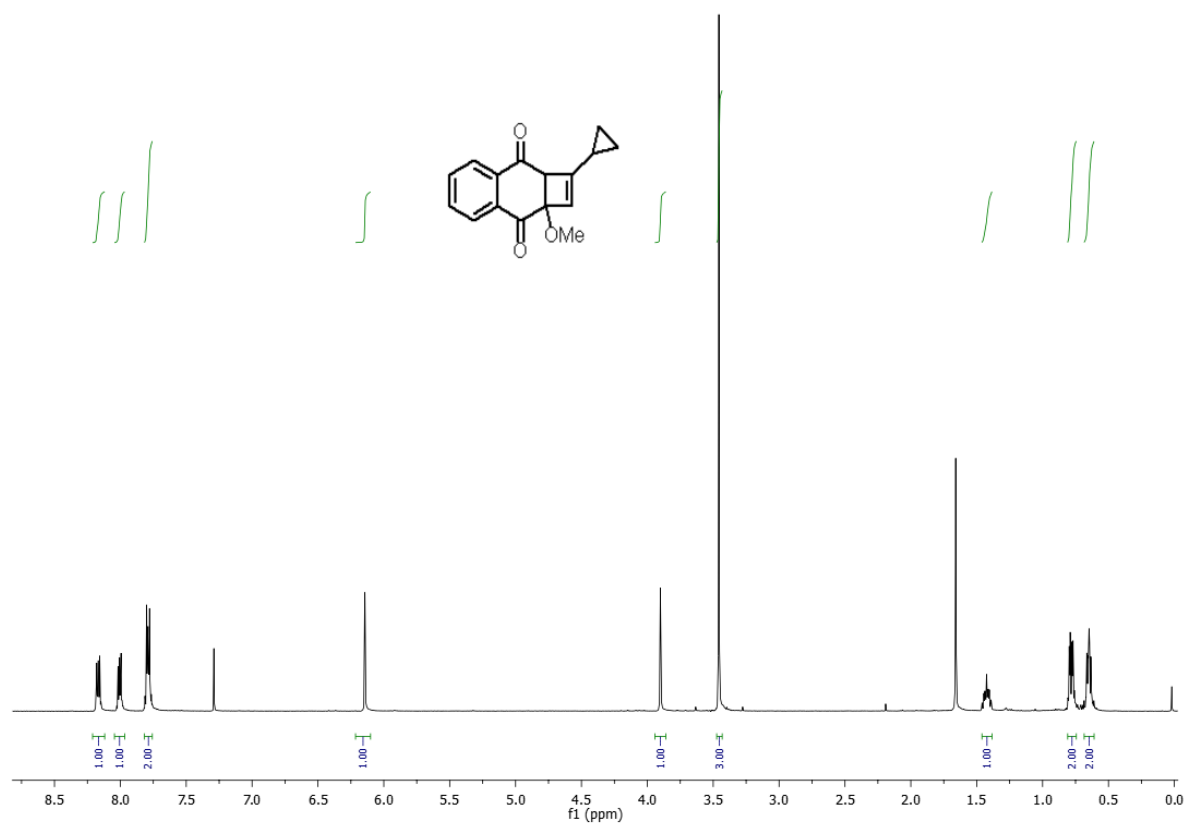
^1H and ^{13}C NMR of 43:



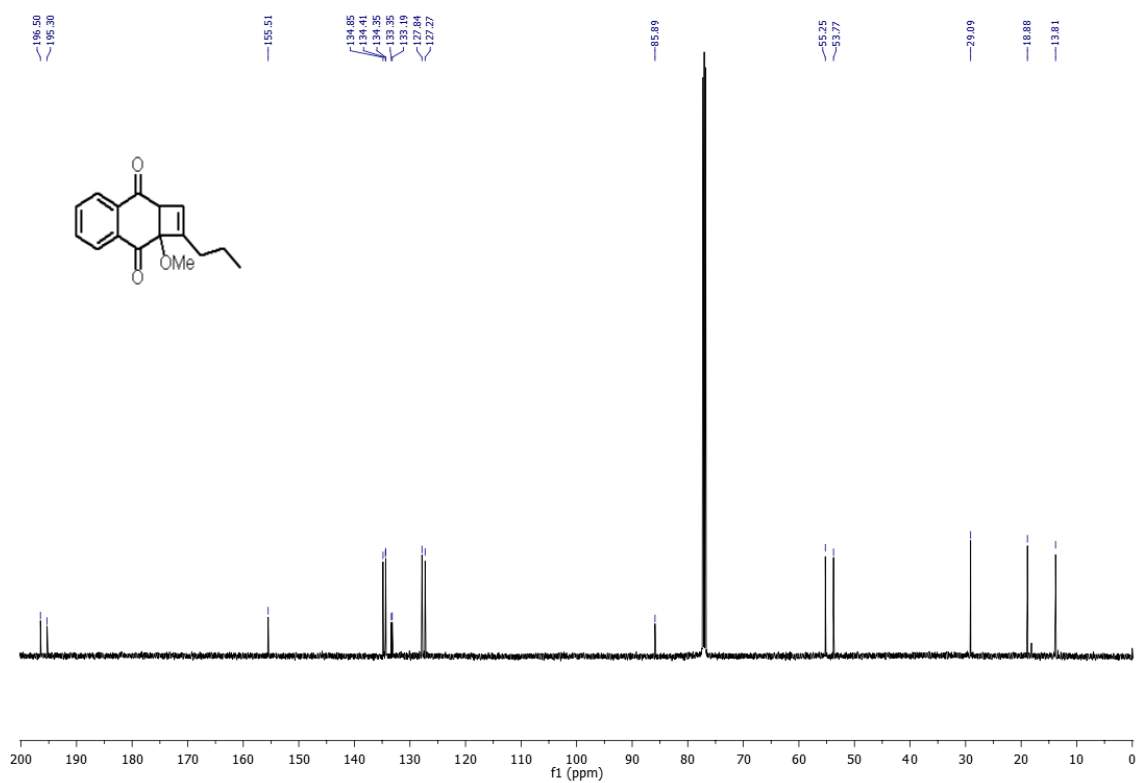
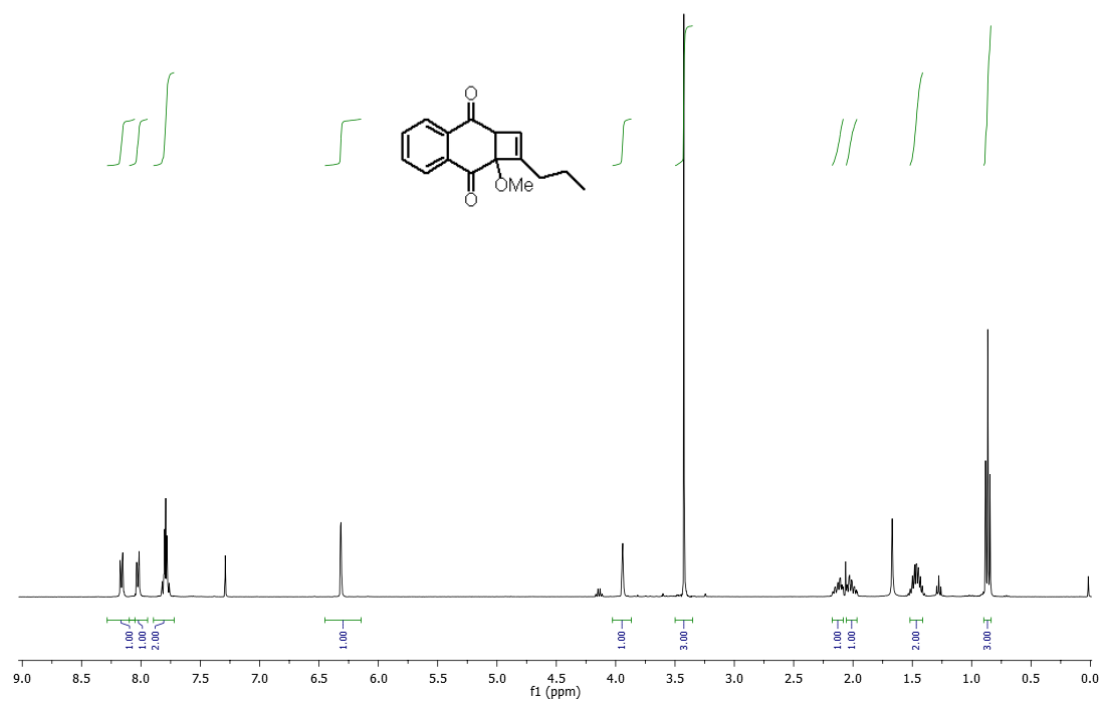
^1H and ^{13}C NMR of 44:



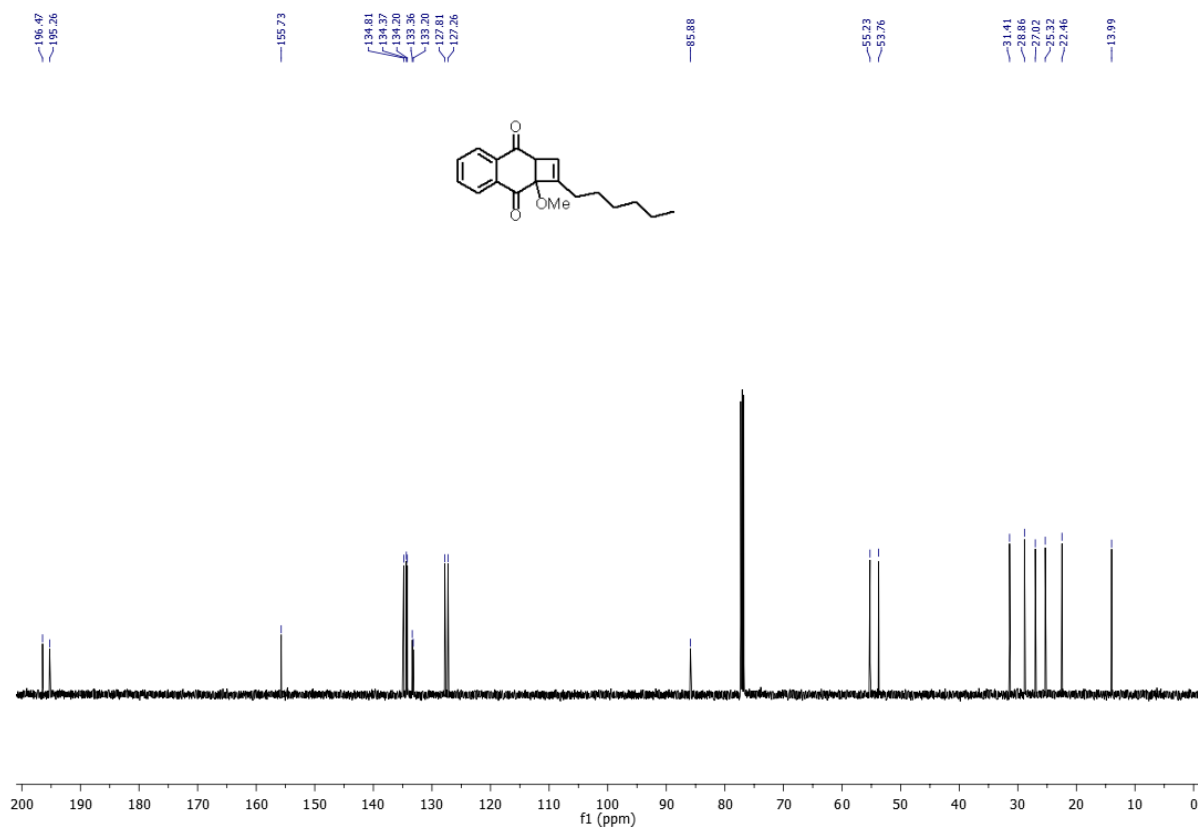
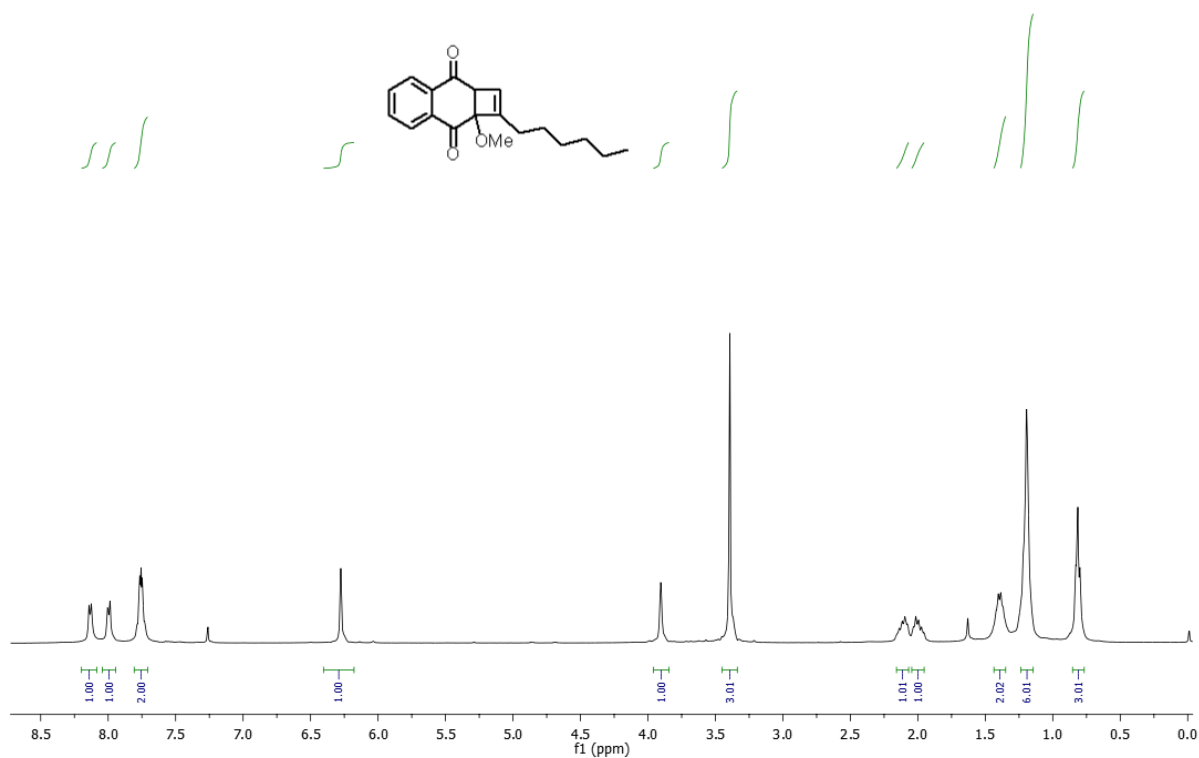
^1H and ^{13}C NMR of 45:



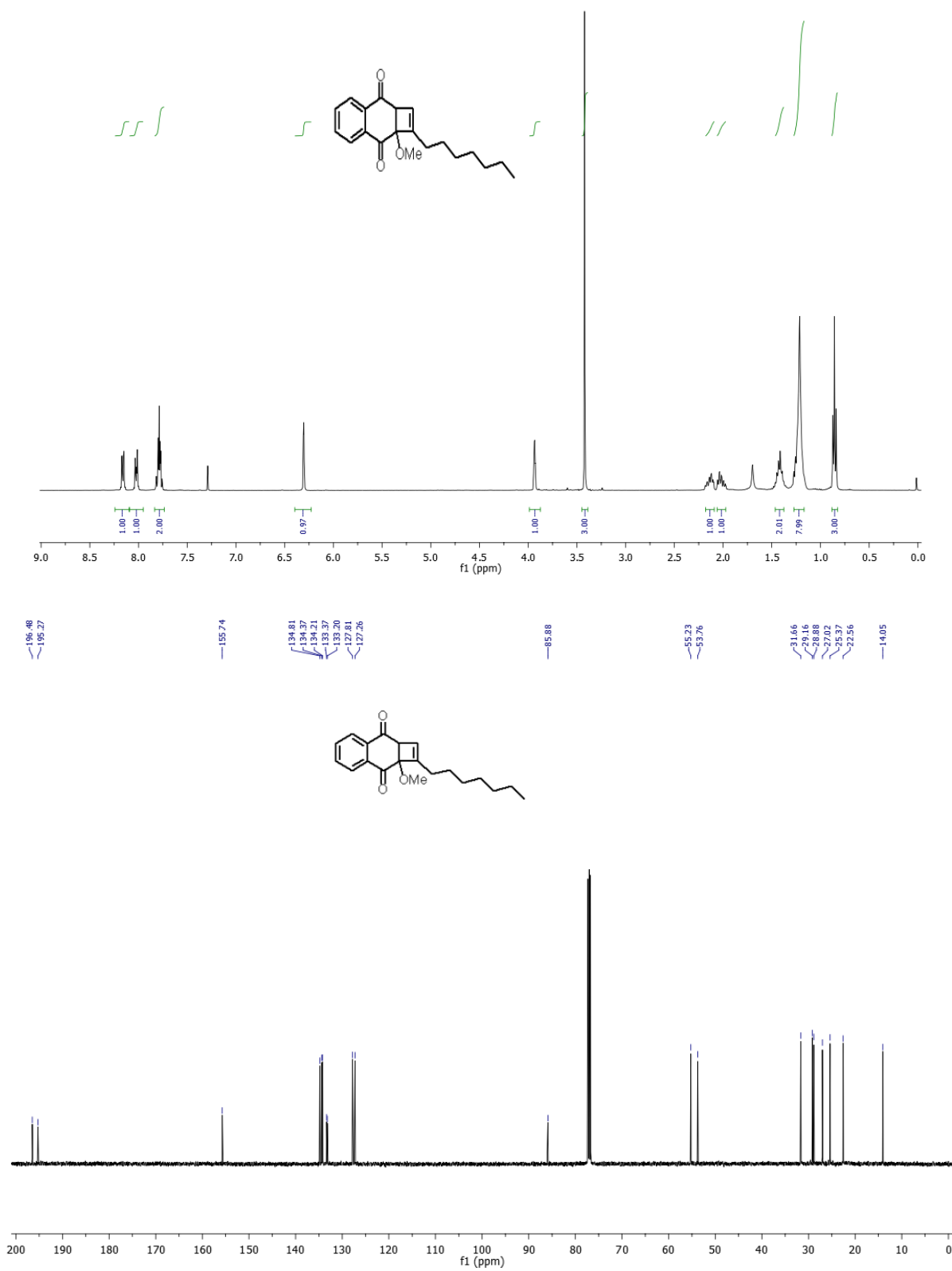
^1H and ^{13}C NMR of 46:



^1H and ^{13}C NMR of 47:



^1H and ^{13}C NMR of 48:



^1H and ^{13}C NMR of 49:

