Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

SUPPORTING INFORMATION I

Access to Chiral α-Bromo and α-H-Substituted Tertiary Allylic Alcohols via Copper(I) Catalyzed 1,2-Addition of Grignard Reagents to Enones

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General Information

Flash chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and Seebach's reagent, a mixture of phosphomolybdic acid (25 g), cerium (IV) sulfate (7.5 g), H_2O (500 mL) and H_2SO_4 (25 mL) or potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). High resolution mass spectra (HRMS) were recorded on a AEI-MS-902 and FTMS orbitrap (Thermo Fisher Scientific) mass spectrometer. ^{1}H- and ^{13}C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian Gemini 200, using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Carbon assignments are based on APT ^{13}C-NMR experiments. Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Enantiomeric excesses were determined by HPLC analysis using a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector or by capillary GC analysis (HP 6890, CP-Chiralsil-Dex-CB column (25 m x 0.25 mm) or Chiraldex B-PM (30 m x 0.25 mm x 0.25 μm)) using a flame ionization detector.

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. *t*BuOMe and dichloromethane were dried and distilled from calcium hydride; toluene, THF and *n*-hexane were dried and distilled from sodium. All copper salts were

purchased from Aldrich, and used without further purification. Starting materials were prepared following literature procedures.[1,2] Grignard reagents were purchased from Aldrich (*i*BuMgBr (2 M in Et_2O), EtMgBr (3 M in Et_2O). Ligands **L1-L6** were purchased from Aldrich. Racemic products were synthesized by reaction of the α,β-unsaturated ketones (**1-3**) and the corresponding Grignard reagent at rt in Et_2O. All Grignard reagents were prepared from the corresponding alkyl bromides and Mg activated with I_2 in Et_2O. Absolute configurations of products were not determined.

Formation of a single copper complex:

The copper based catalyst employed in the reactions was normally prepared in situ by mixing **L5** with CuBr·SMe_2 in 1.1:1 ratio. Formation of a single copper complex was anticipated upon mixing both reagents. This was supported by both ^{1}H and ^{31}P NMR spectroscopy upon mixing **L5** and CuBr·SMe_2 in 1:1 ratio. NMR spectra showed complete disappearance of the signals corresponding to the free ligand **L5** and appearance of a new set of signals corresponding to the copper complex of **L5**.

NMR spectra of all new compounds

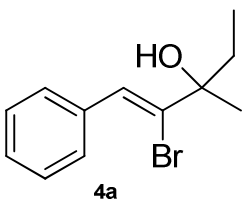
^{1}H NMR

[1] Lu, S-M., Bolm, C. *Angew. Chem., Int. Ed.* **2008,** *47*, 8920.
[2] Moser, R., Boskovic, Z. V., Crowe, C. S., Lipshutz, B. H. *J. Am. Chem Soc.* **2010**, *132*, 7852.

^{13}C NMR

APT

HMQC



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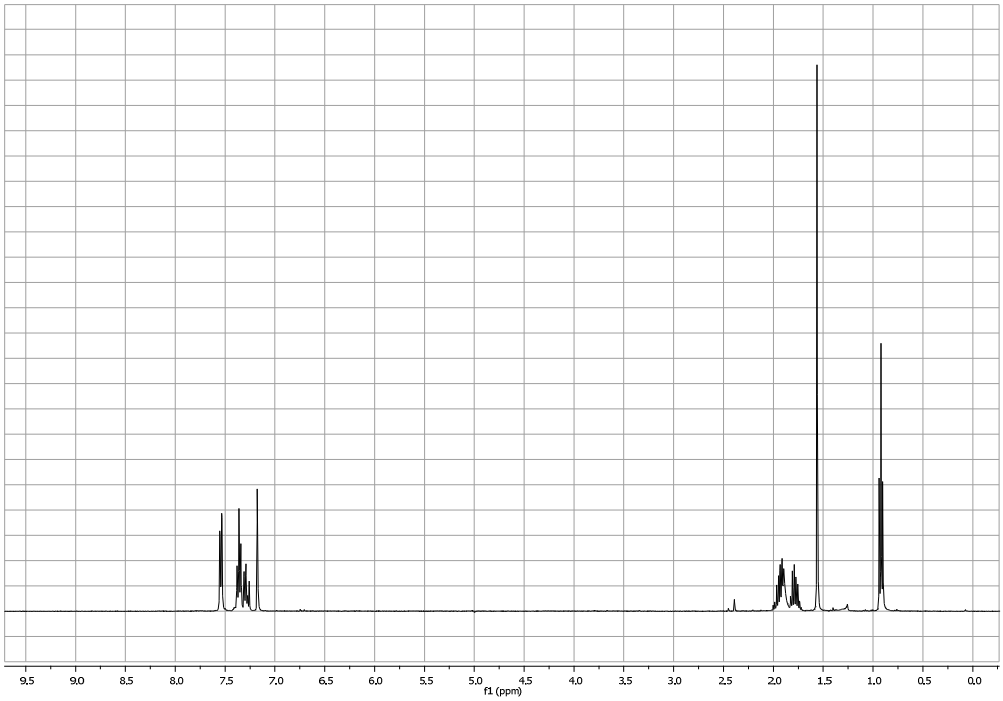

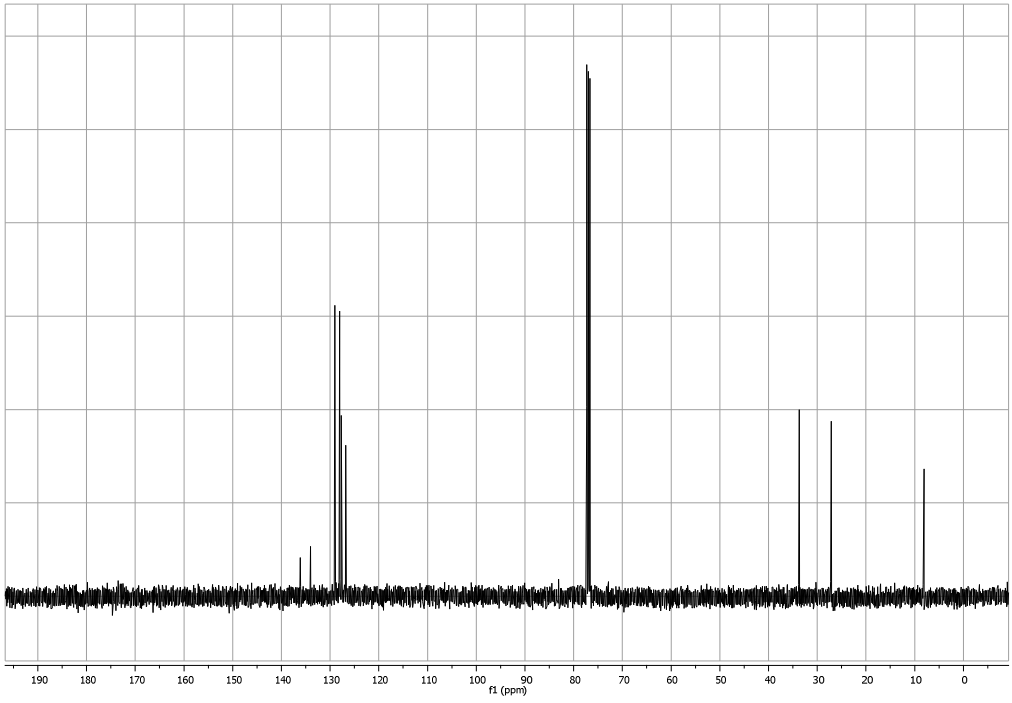

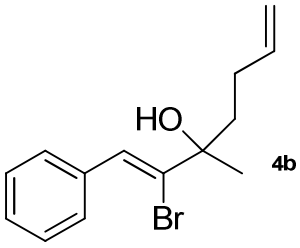

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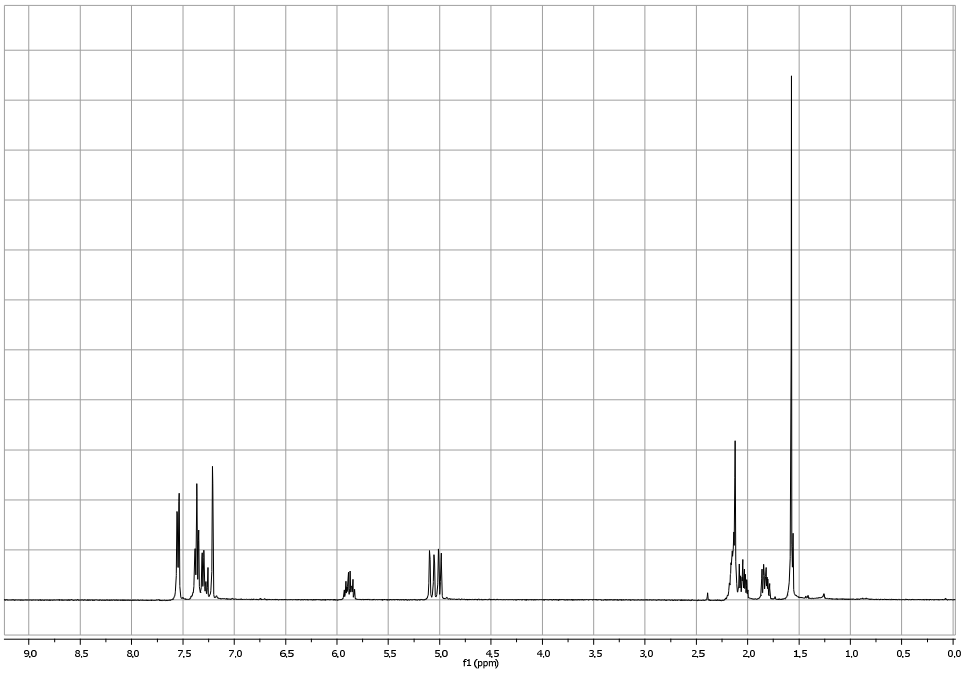

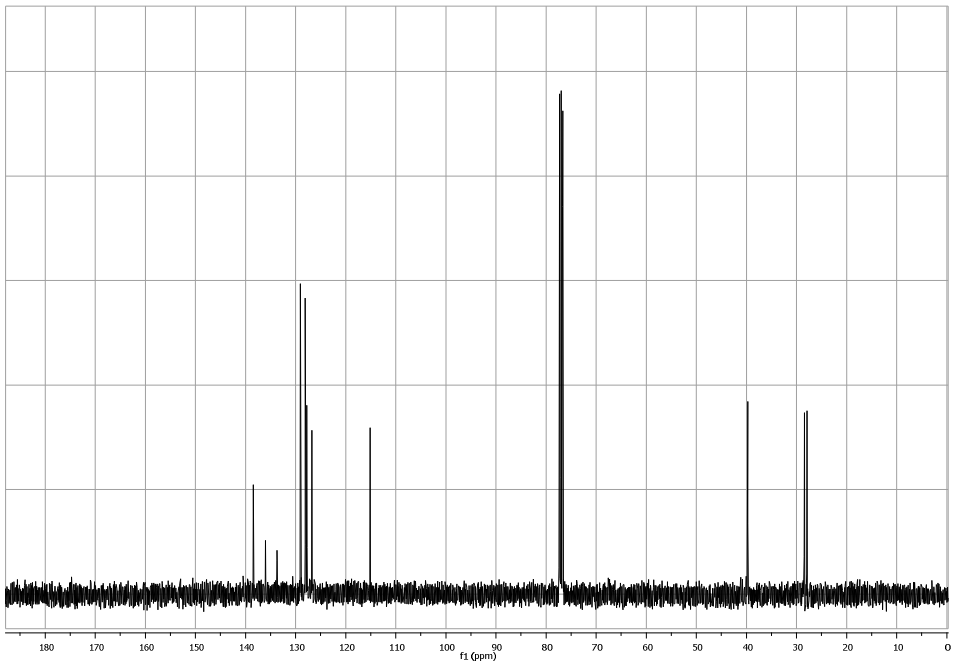

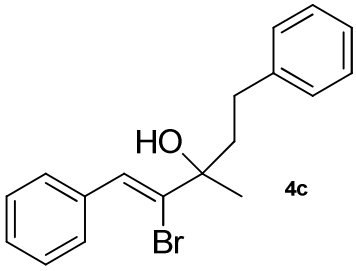

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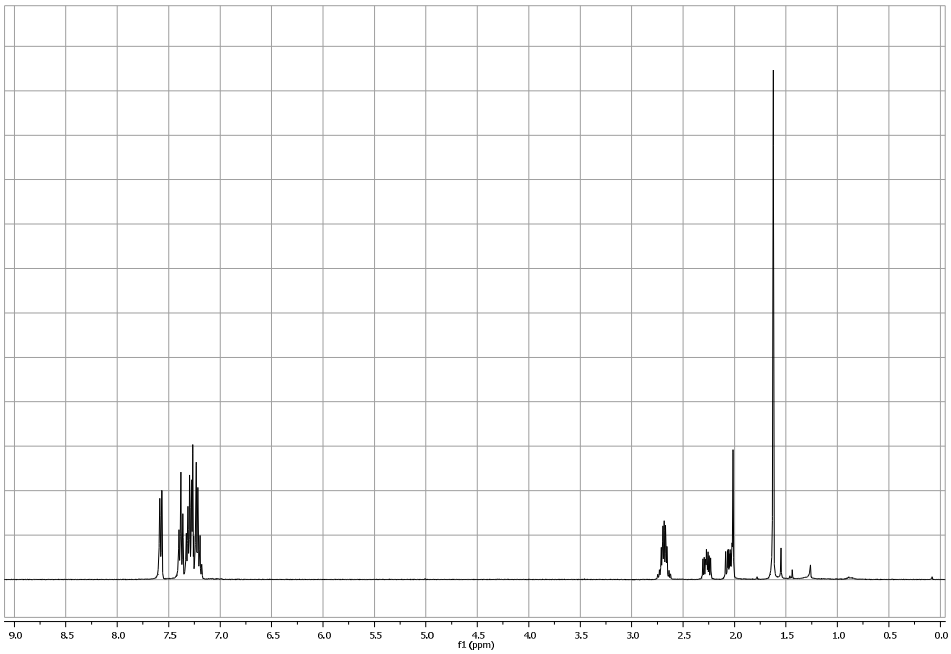

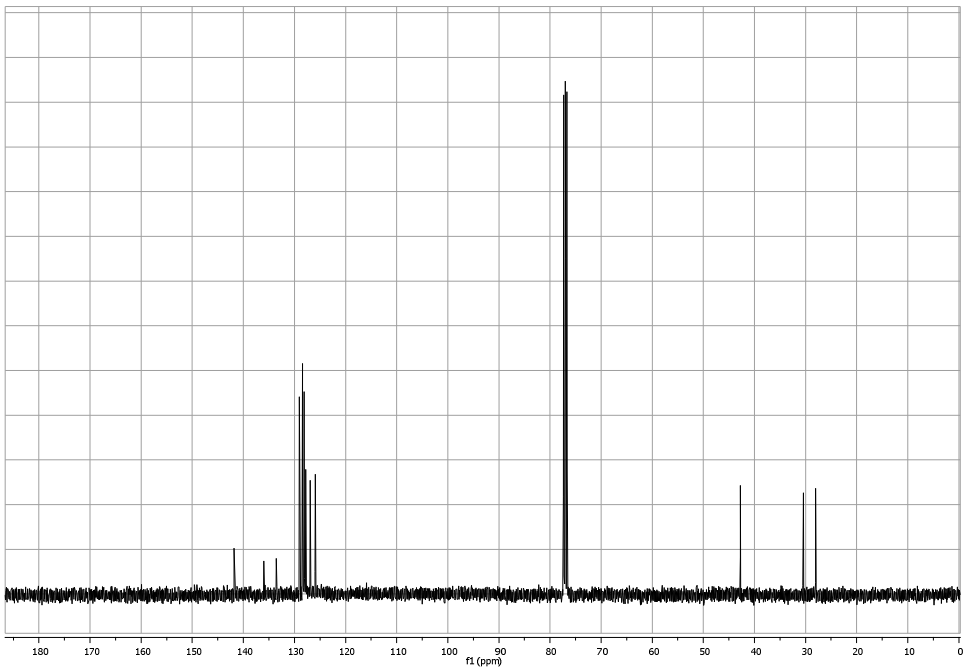

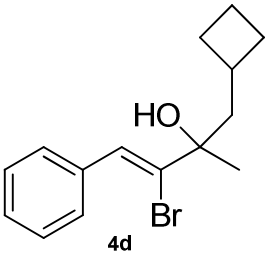

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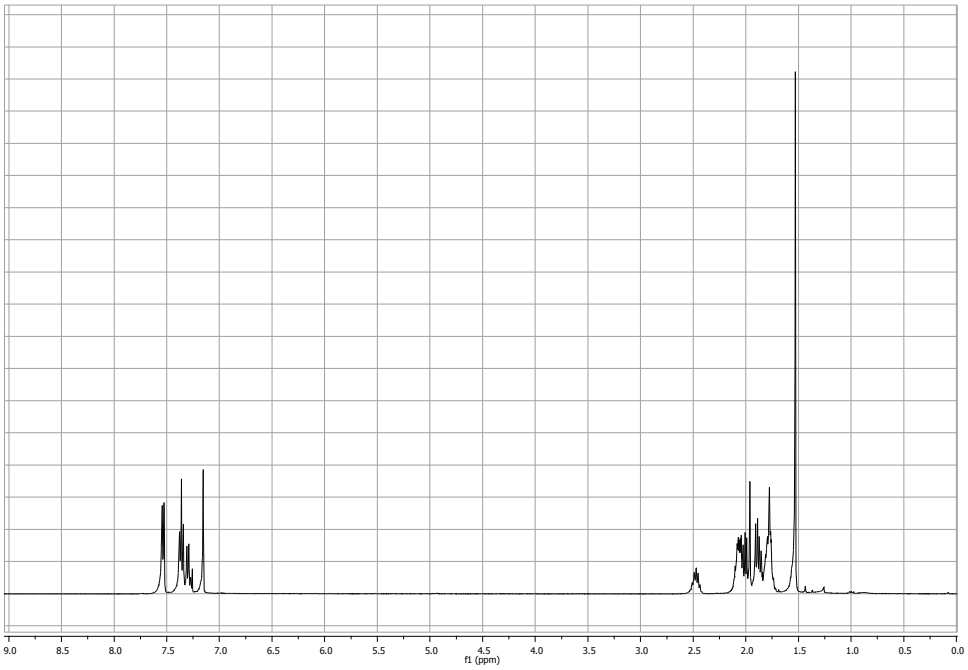

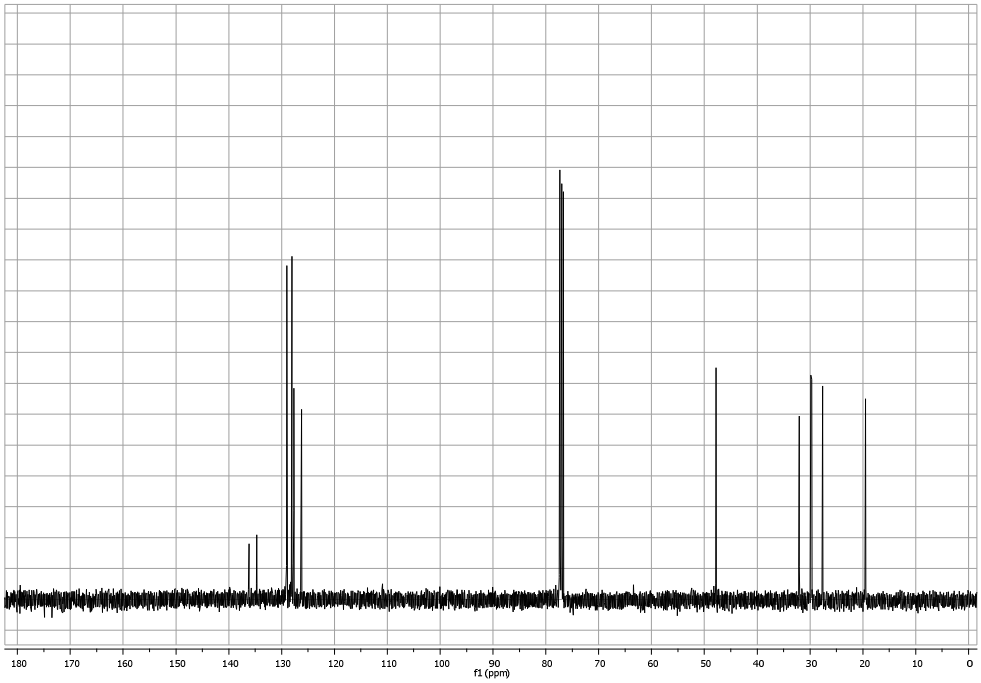

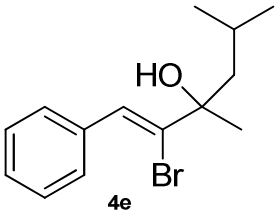

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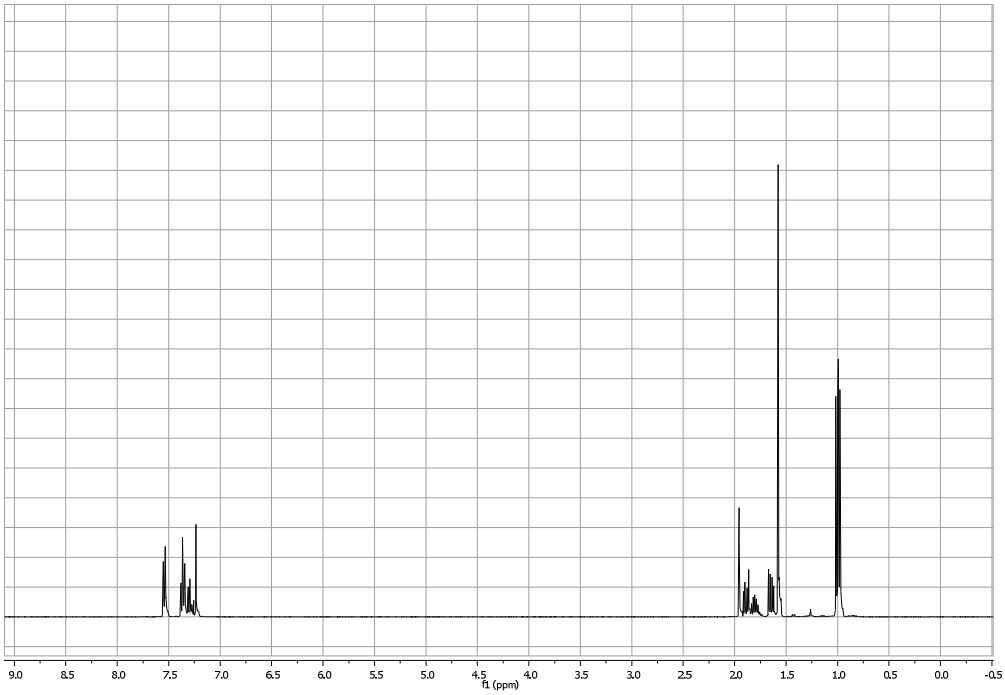

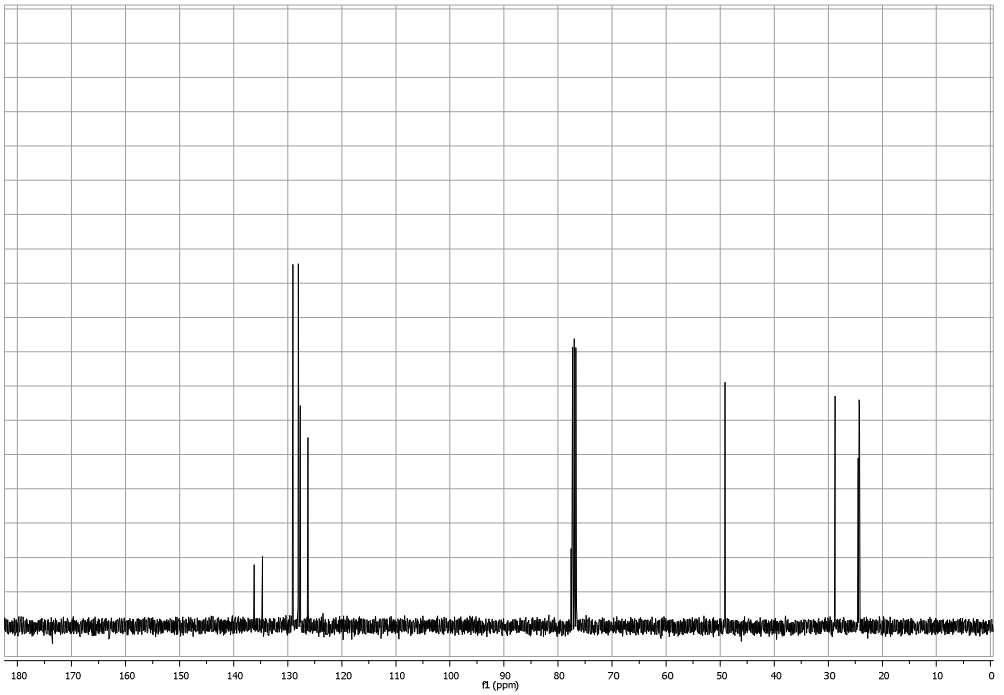

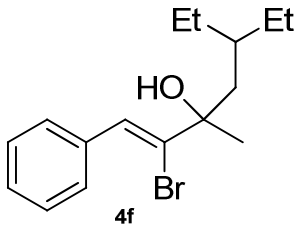

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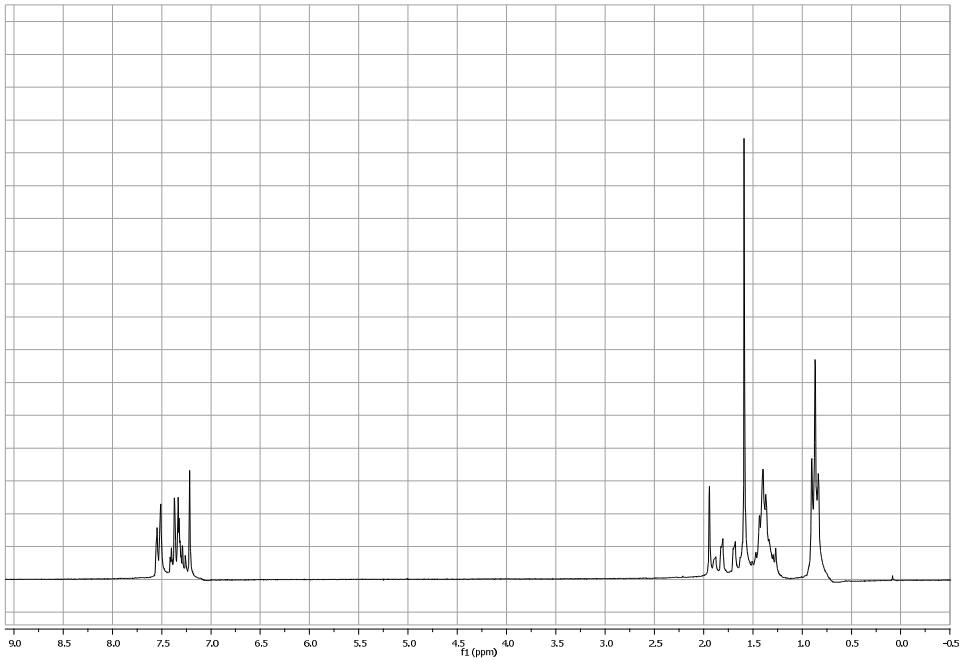

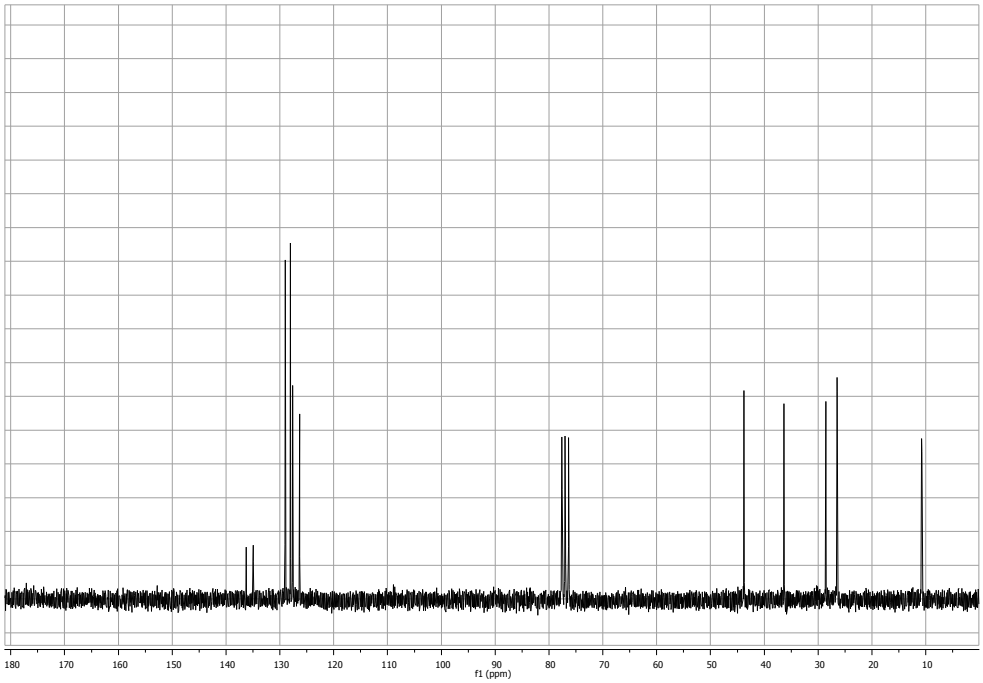

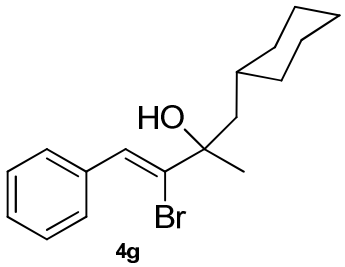

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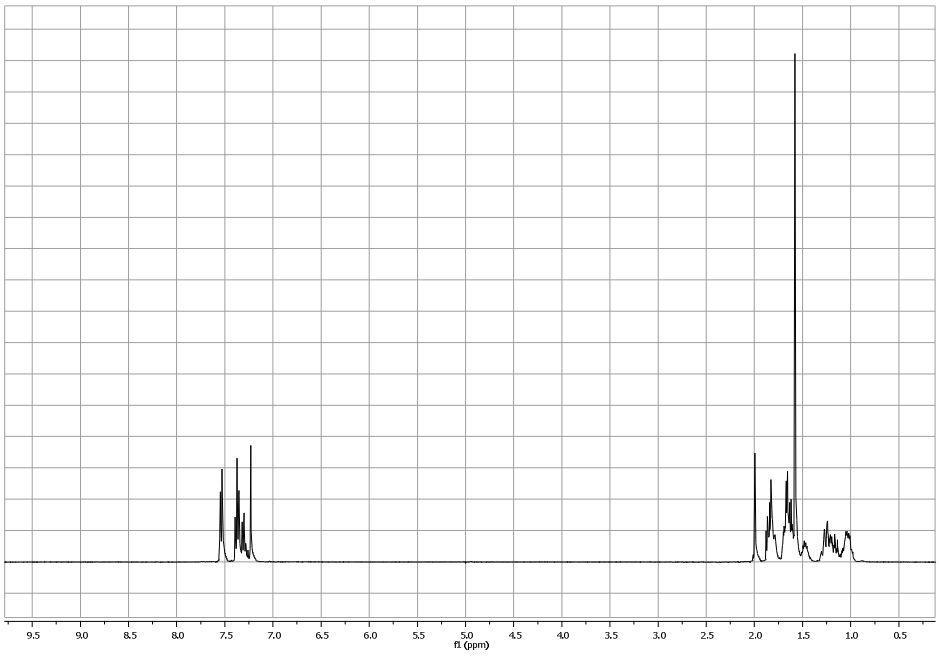

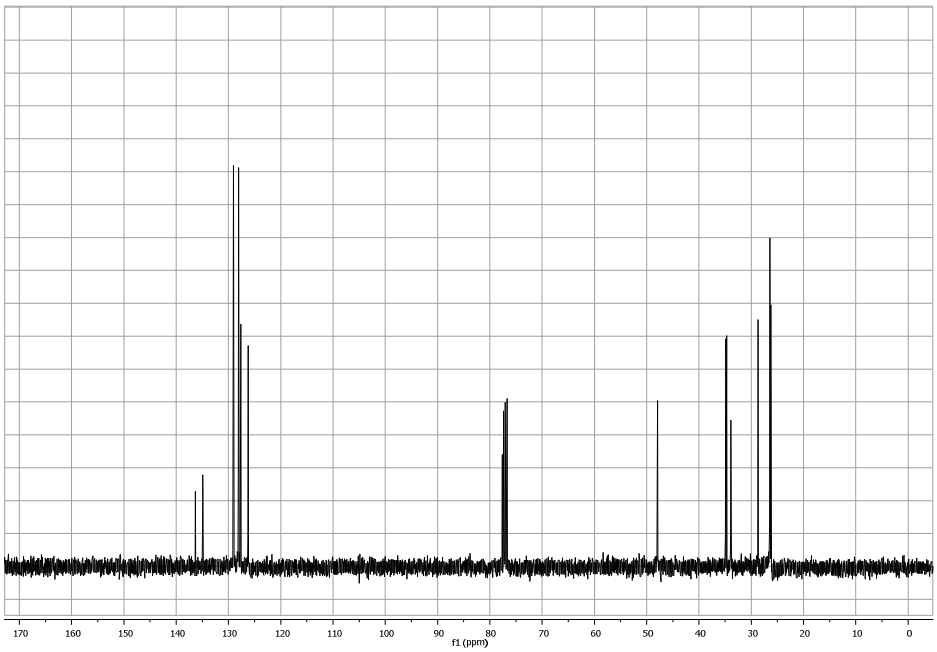

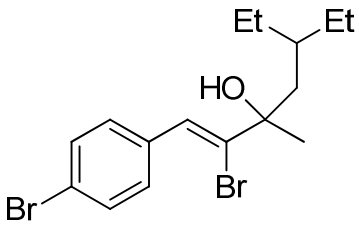

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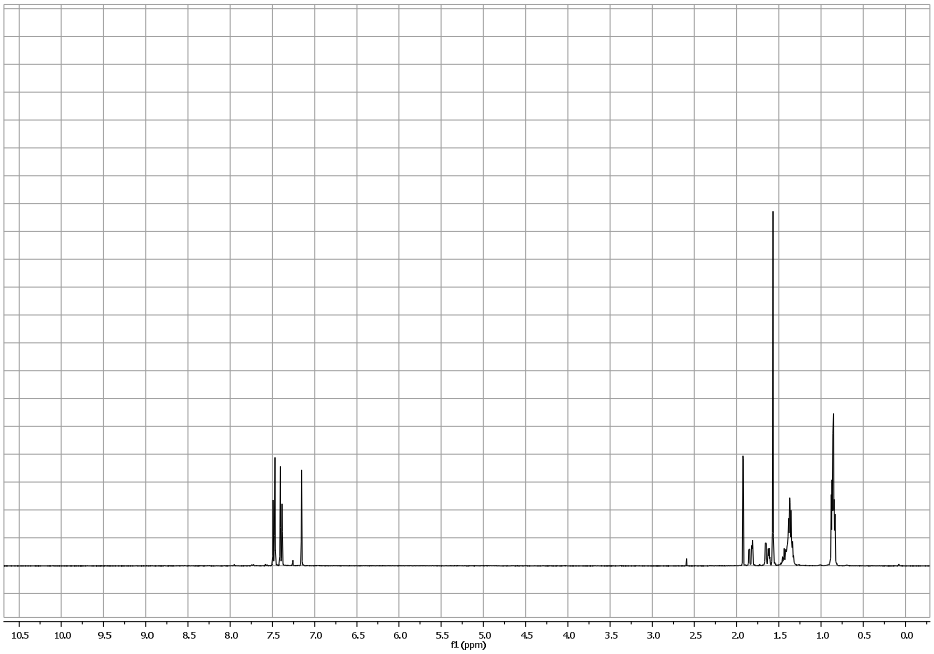

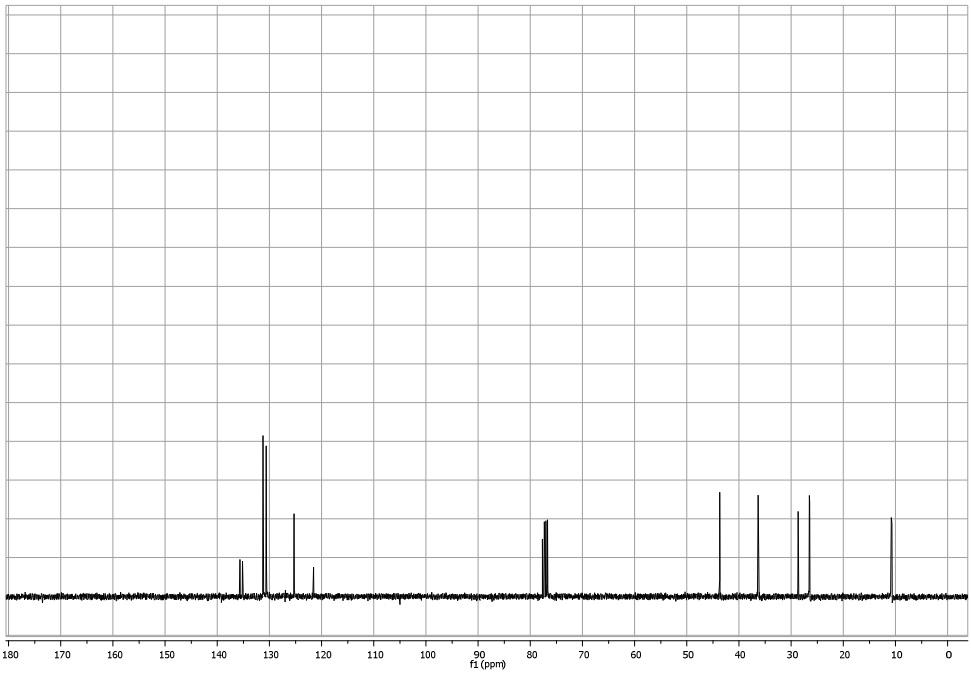

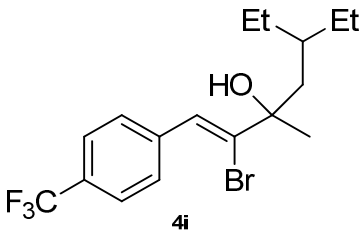

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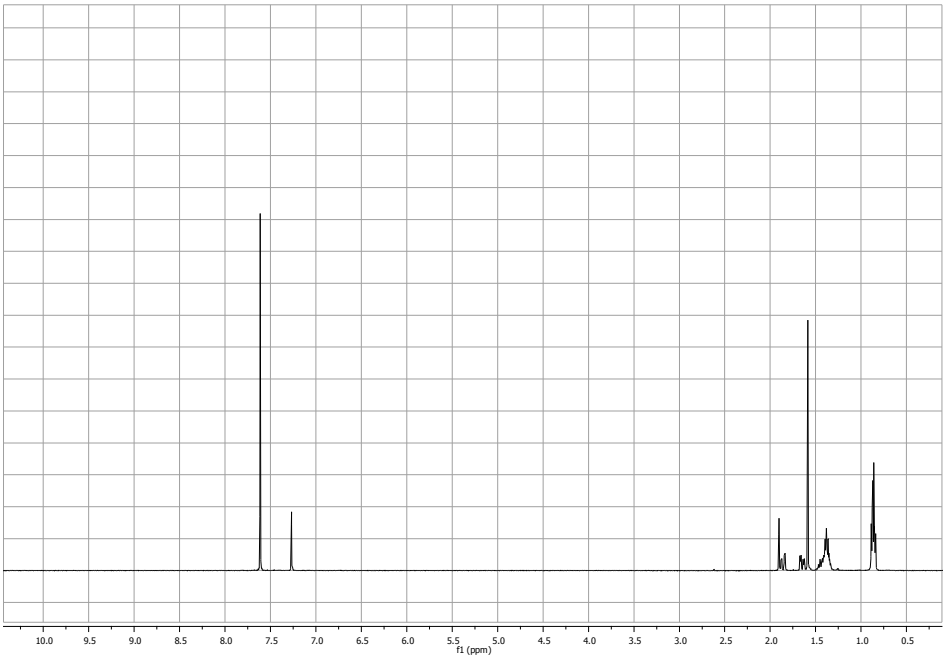

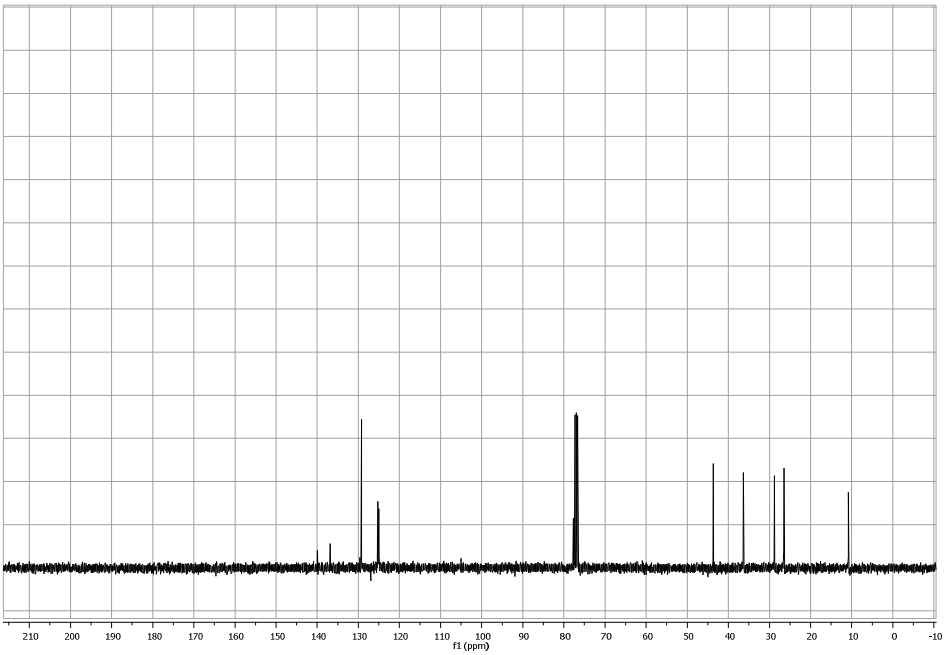

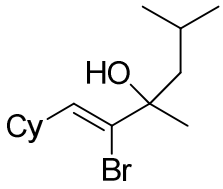

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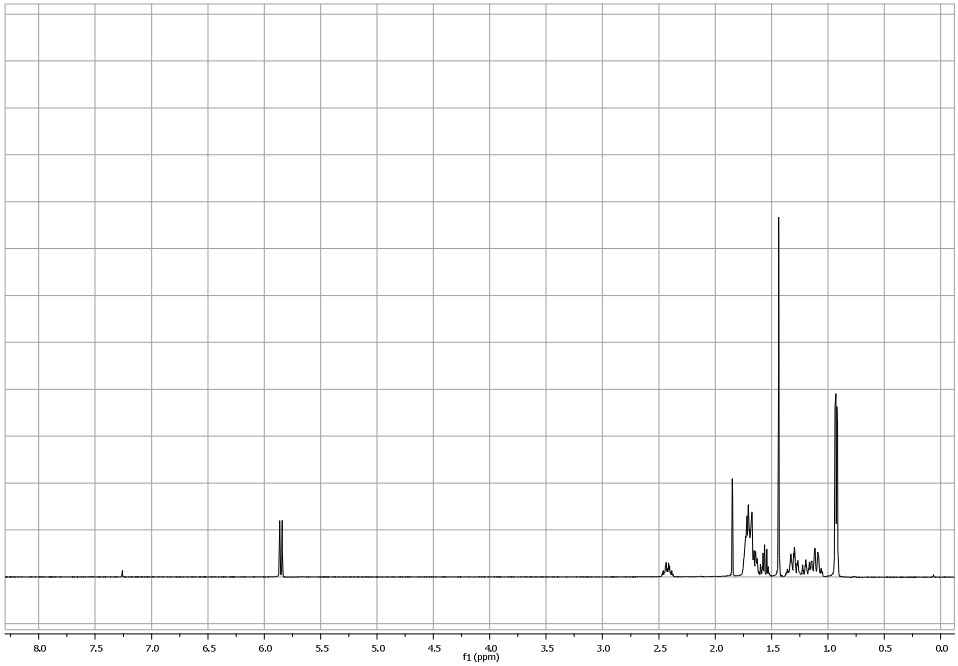

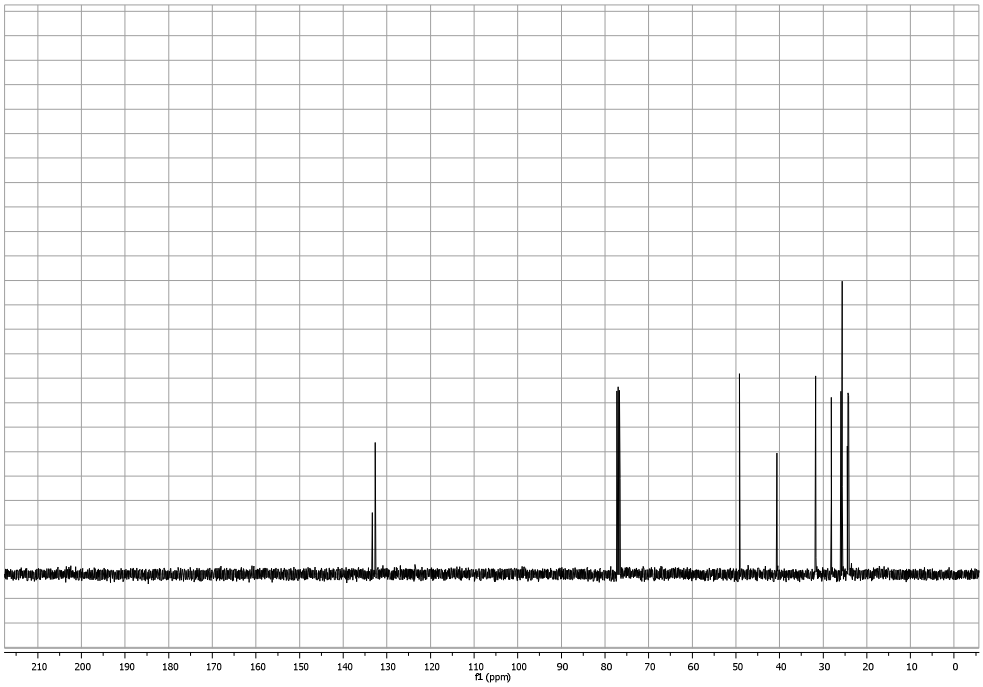

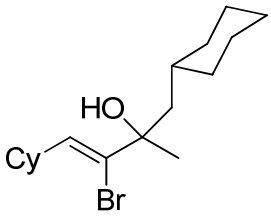

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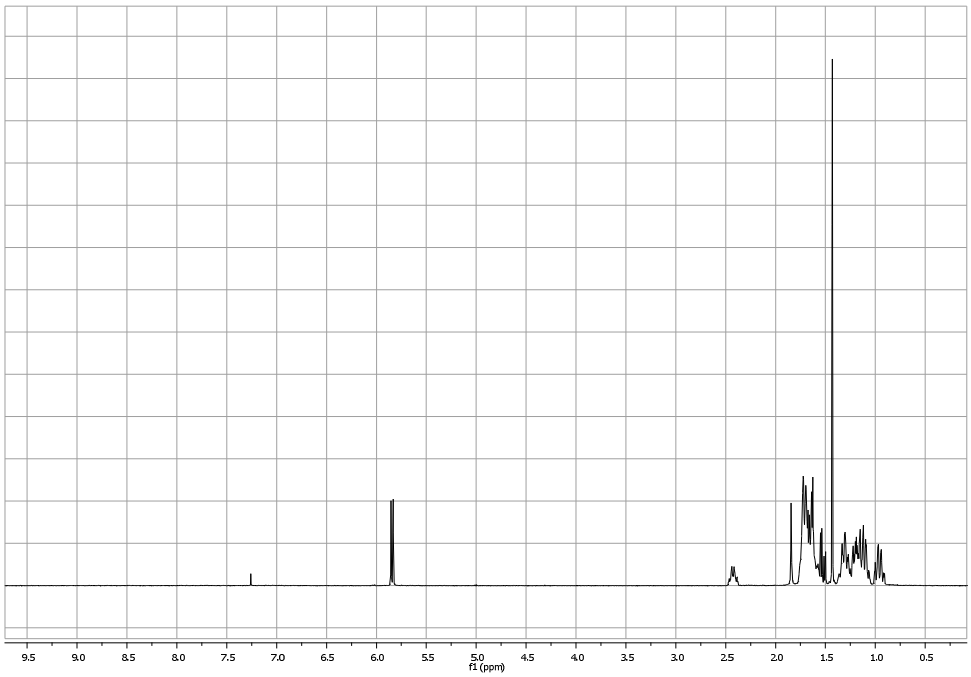

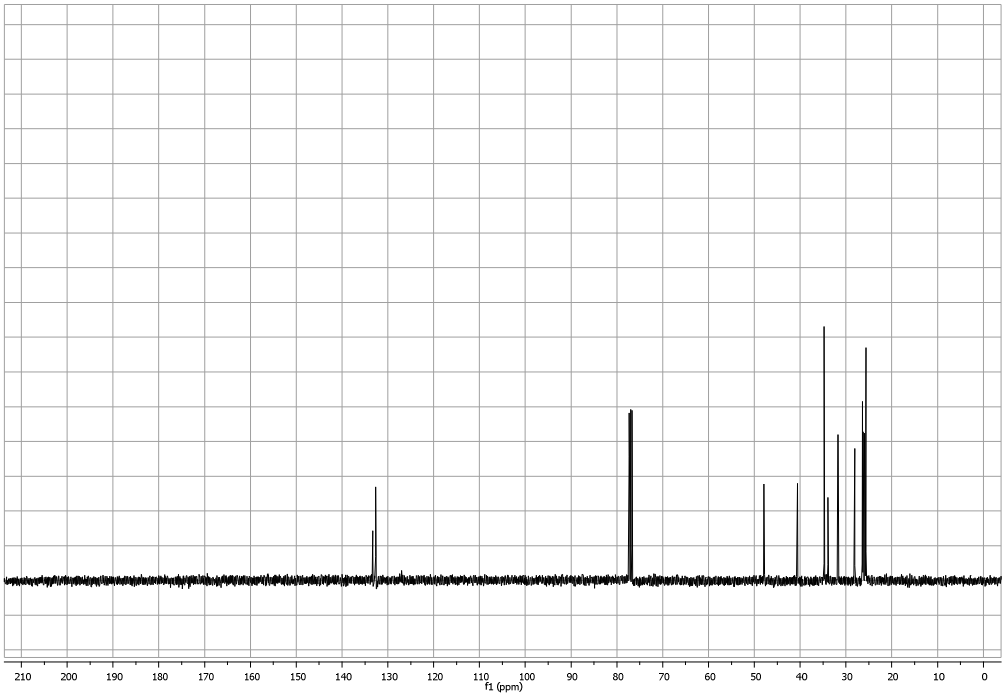

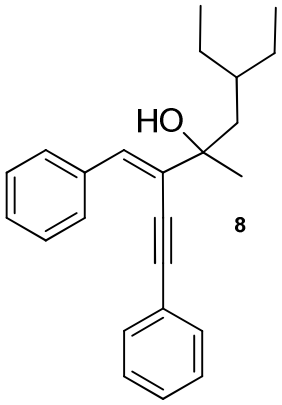

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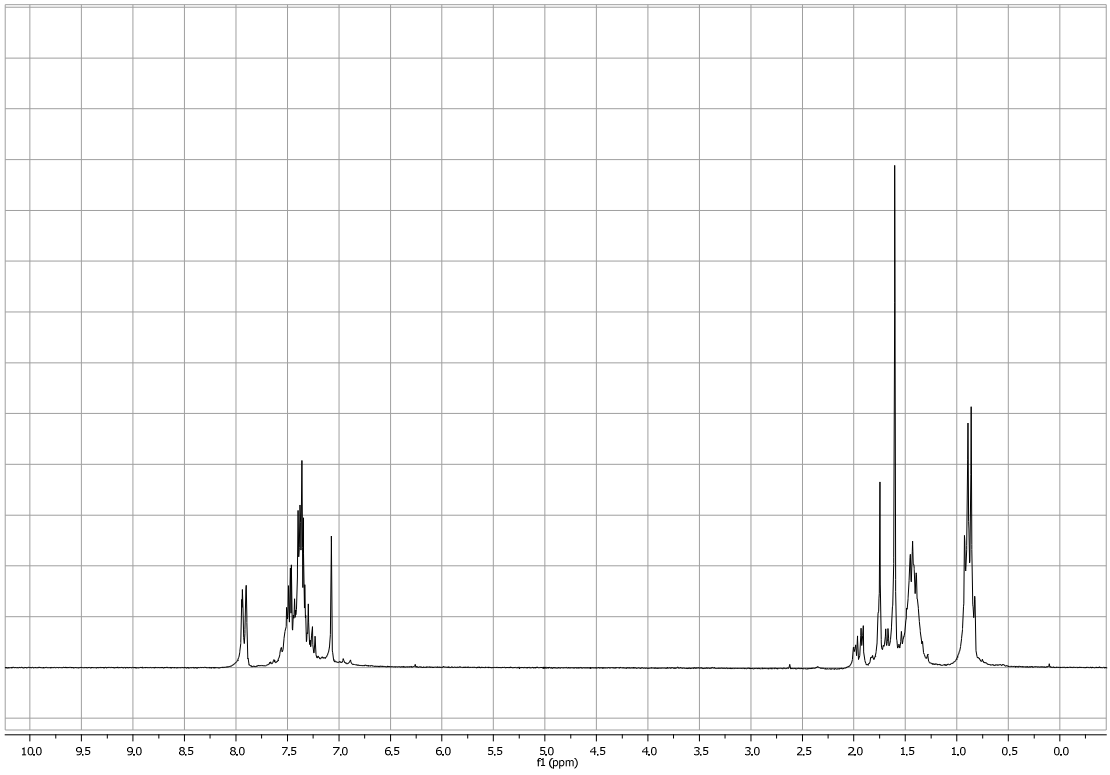

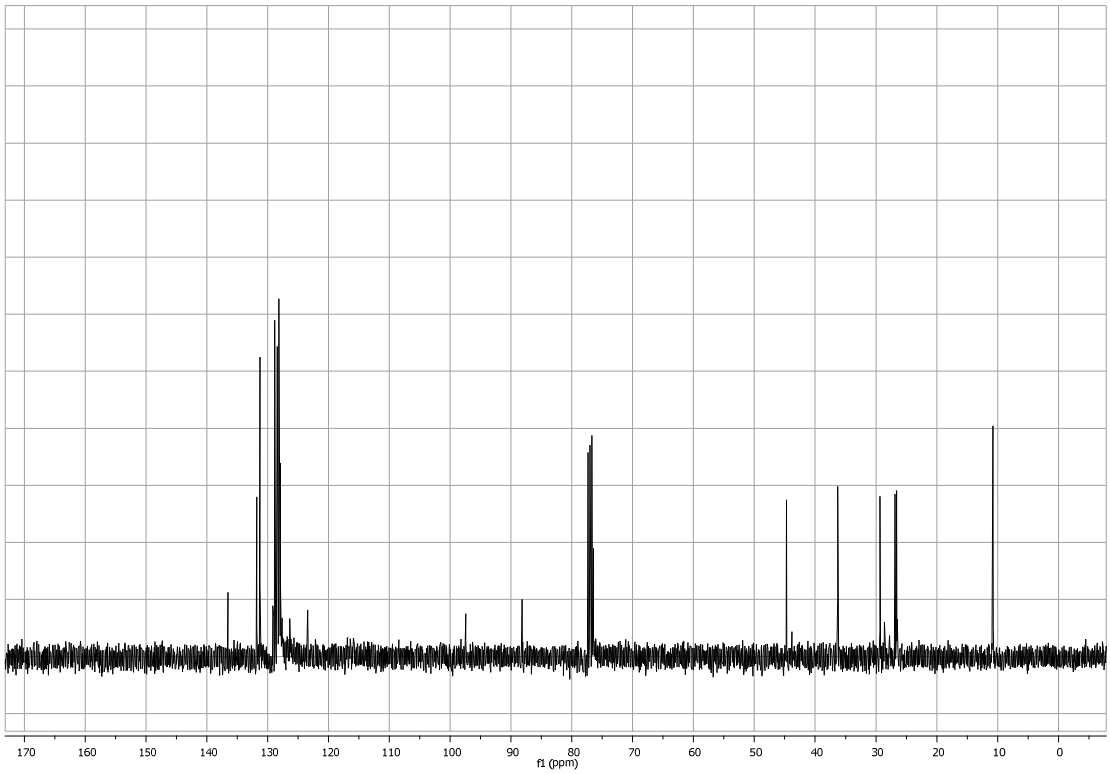

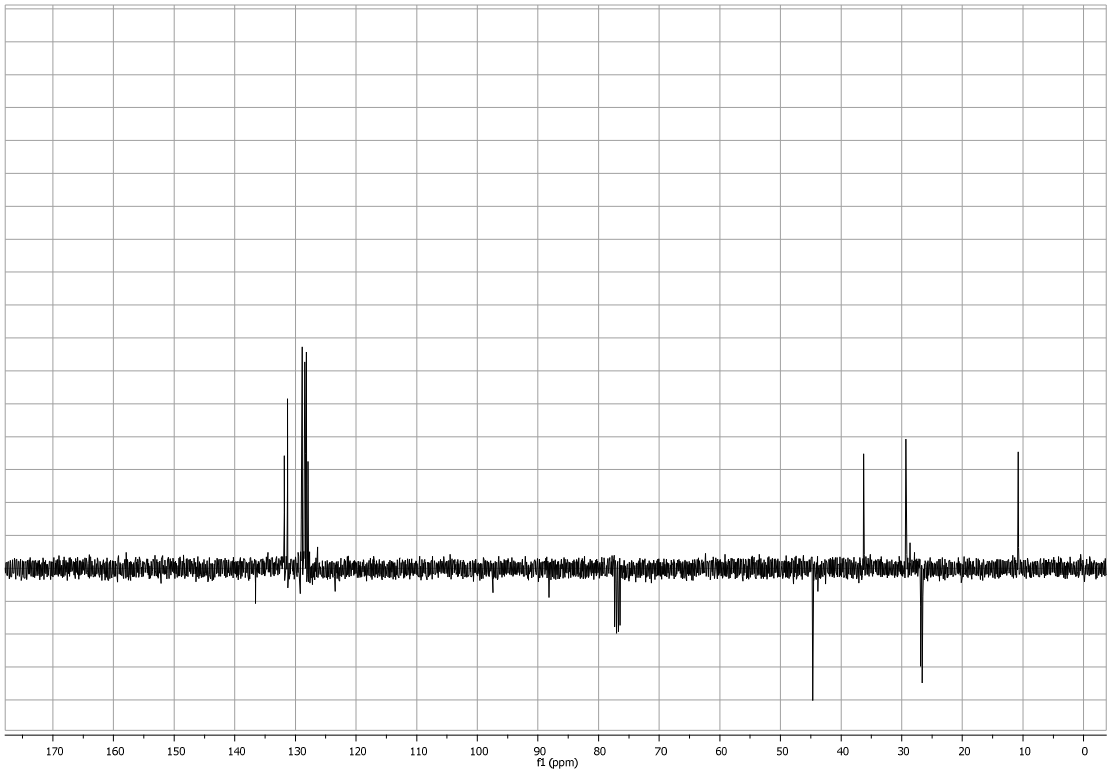

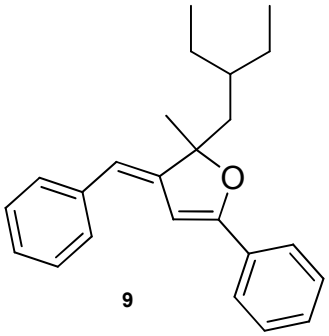

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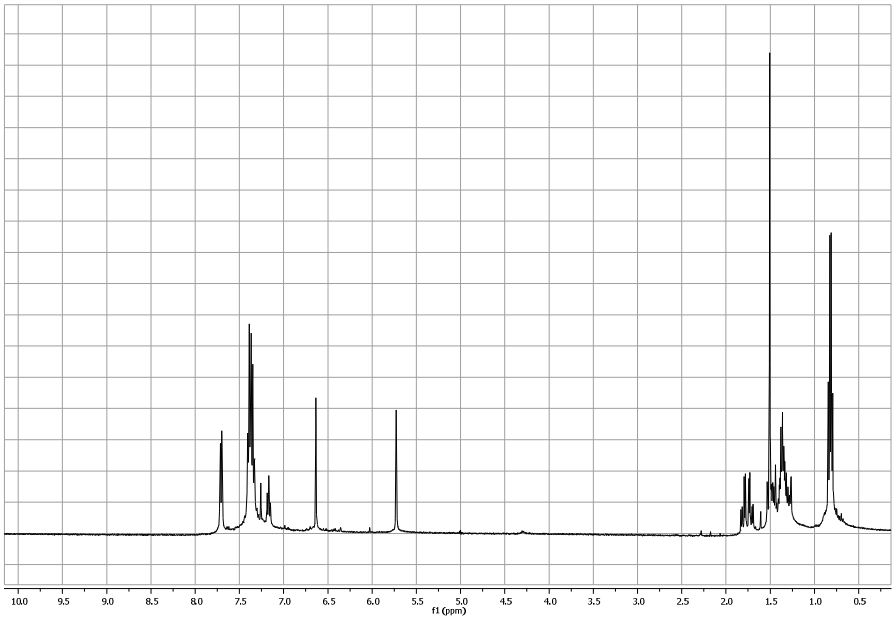

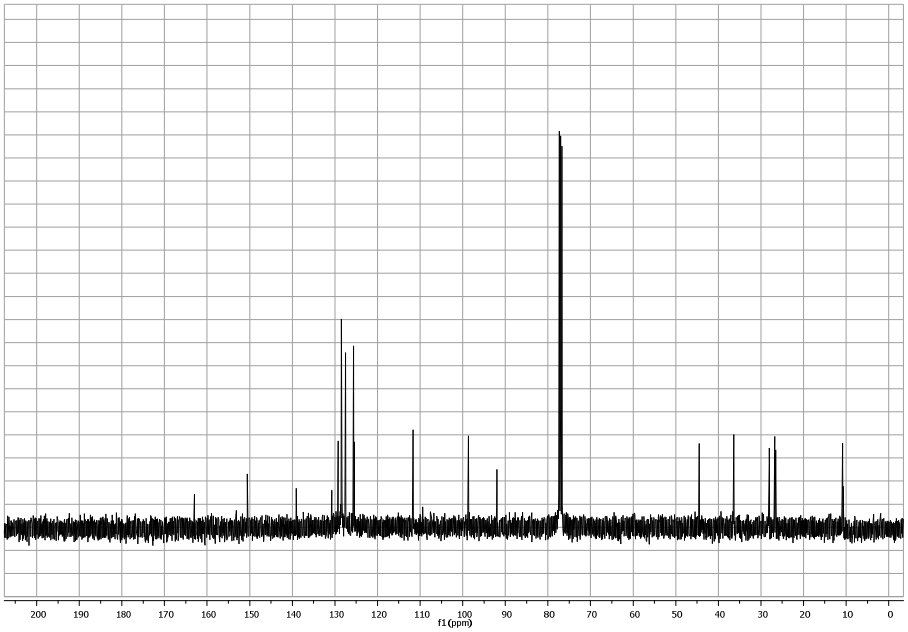

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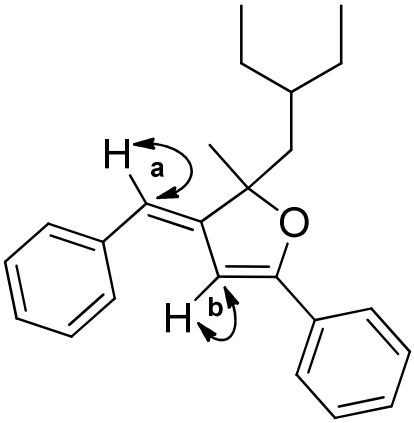
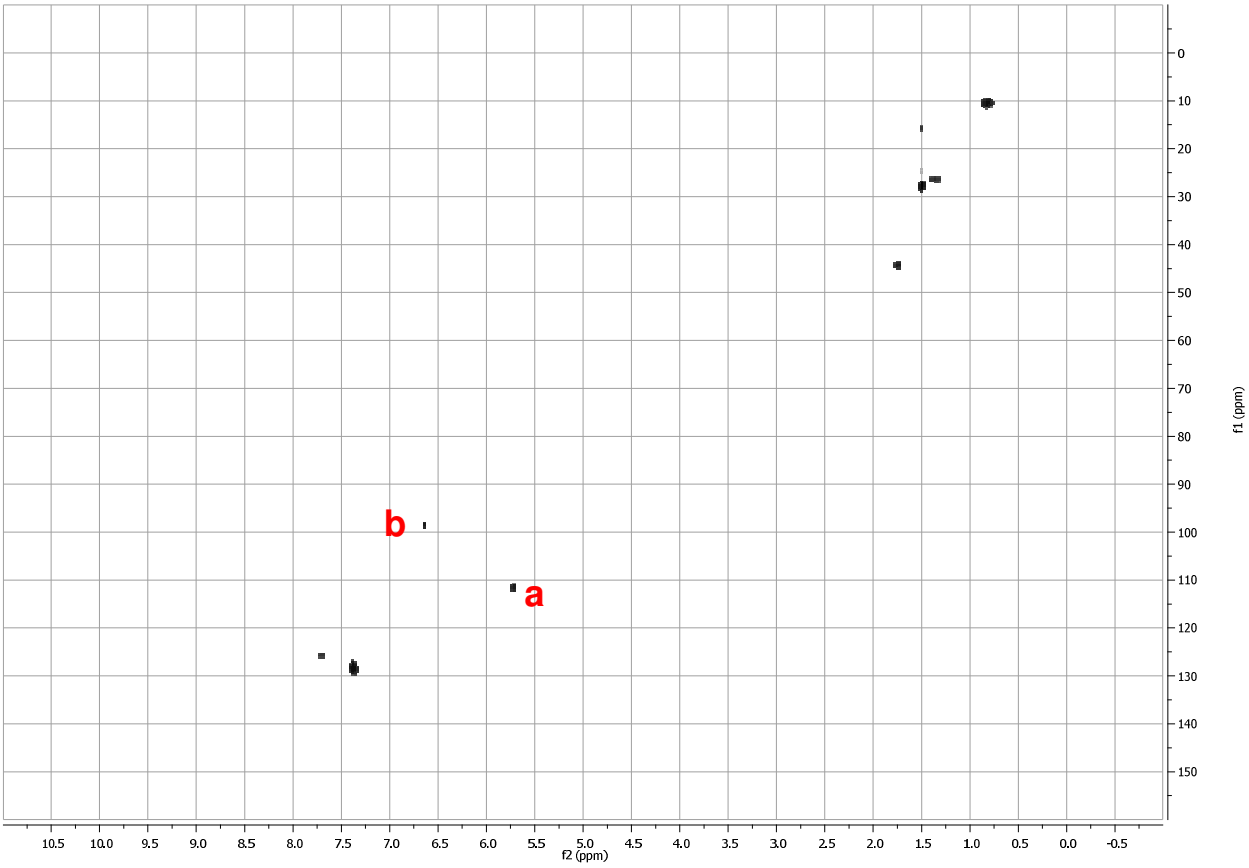
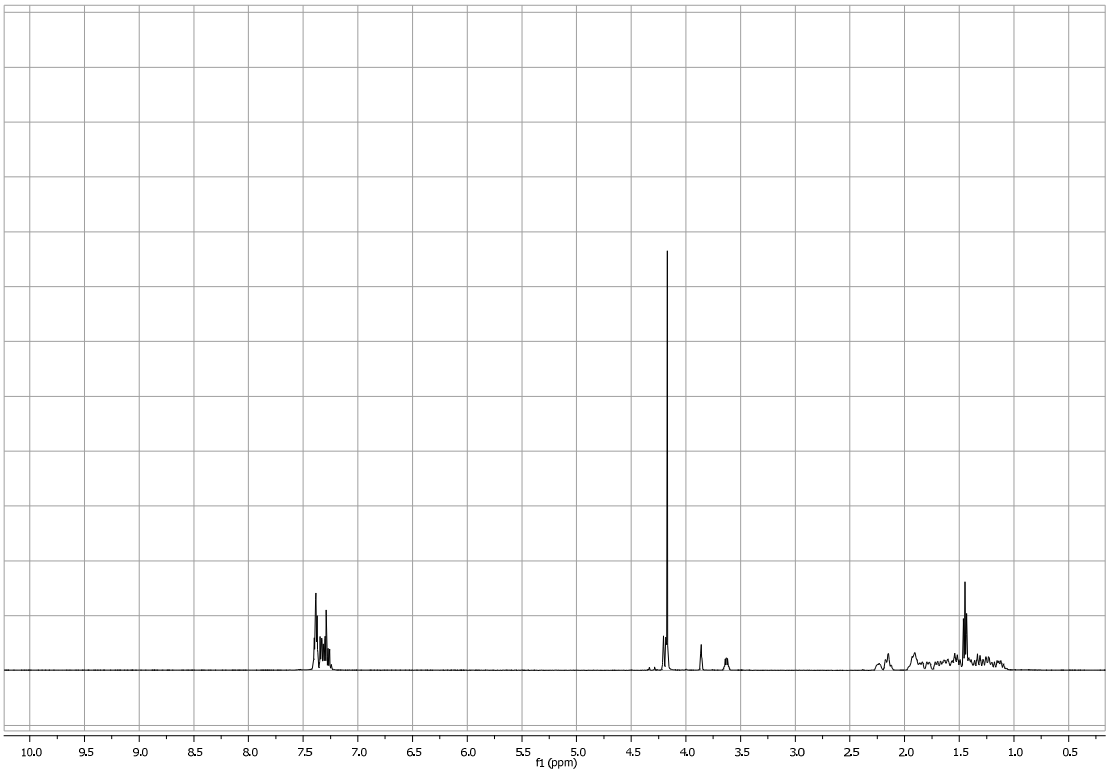
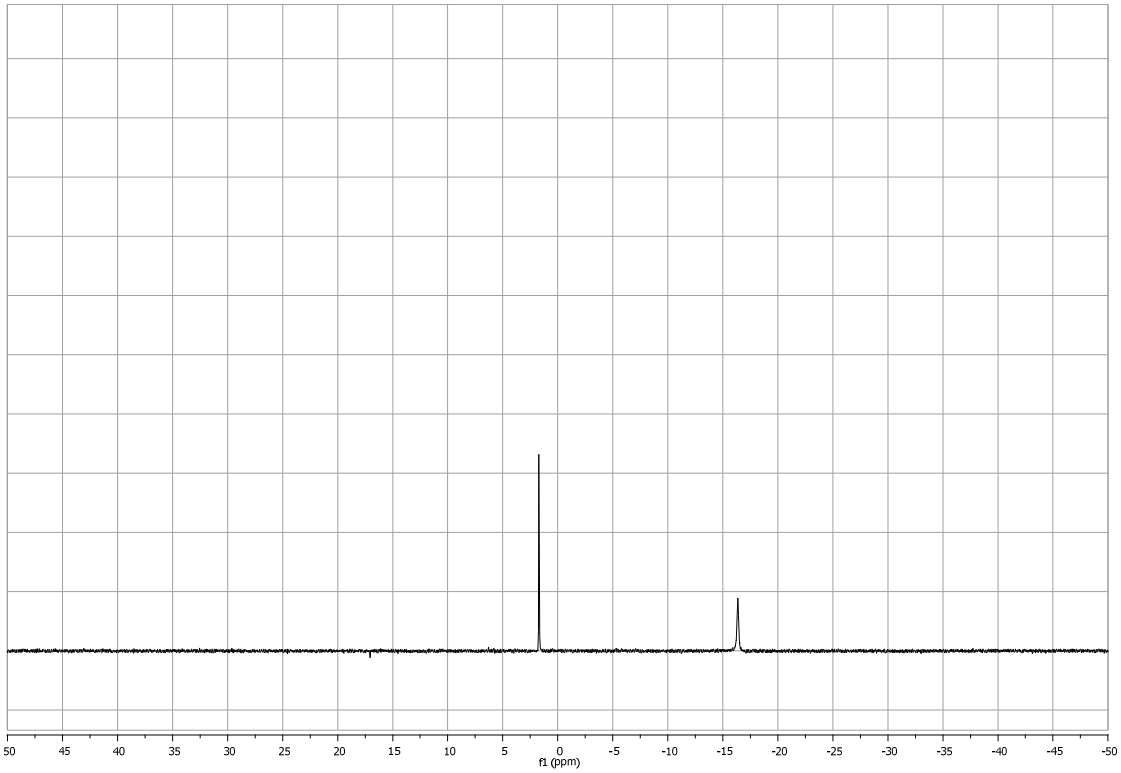




a and **b** are the signals observed for the protons attached to that particular carbon.

^{1}H NMR & ^{31}P NMR specrum of ligand L1 ($CDCl_3$, 500MHz):





^{1}H NMR & ^{31}P NMR specrum of CuBr•SMe_2 complex of L1 ($CDCl_3$, 500MHz):