Supplementary information for

**For Catching-by-Polymerization Oligo Purification: Scalable Synthesis of the Precursors to the Polymerizable Tagging Phosphoramidites**

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**Content**

General experimental information, and images of compound, TLC, NMR and MS.

**General**. All reactions were performed in oven-dried glassware under nitrogen using standard Schlenk techniques. Reagents and solvents from commercial sources were used as received with the following exceptions. DCM, pyridine, diethyl ether and diisopropylamine were distilled over CaH2 under nitrogen. THF was distilled over CaH2 and then Na/benzophenone under nitrogen. Sigma-Aldrich TLC plates, silica gel 60F-254 over glass support, 0.25 µm thickness, were used for TLC. Selecto Scientific silica gel, particle size 32-63 µm, was used for flash column chromatography. 1H amd 13C NMR spectra were measured on a Bruker spectrometer at 500 and 126 MHz, respectively. Chemical shifts (*δ*) were reported in reference to solvent peaks, residue CHCl3 at 7.24 ppm for 1H, CDCl3 at 77.00 ppm for 13C. MS was obtained on a Thermo Finnigan LCQ Advantage Ion Trap Mass Spectrometer.



A glass vase with orange liquid

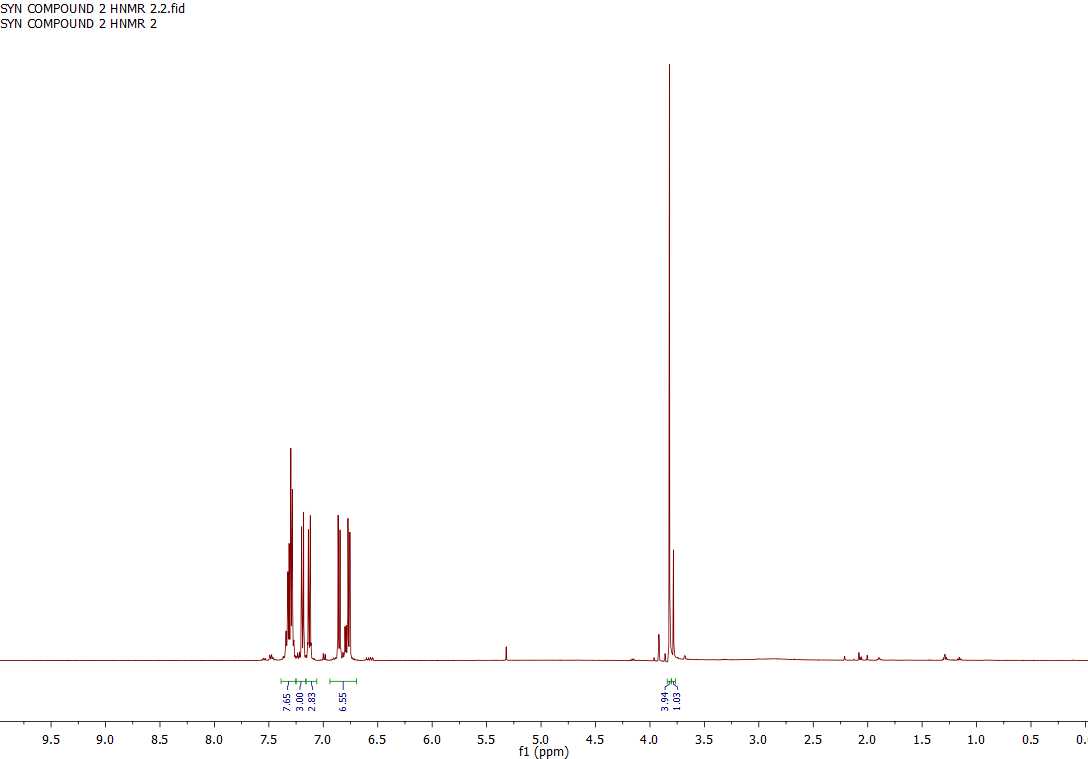
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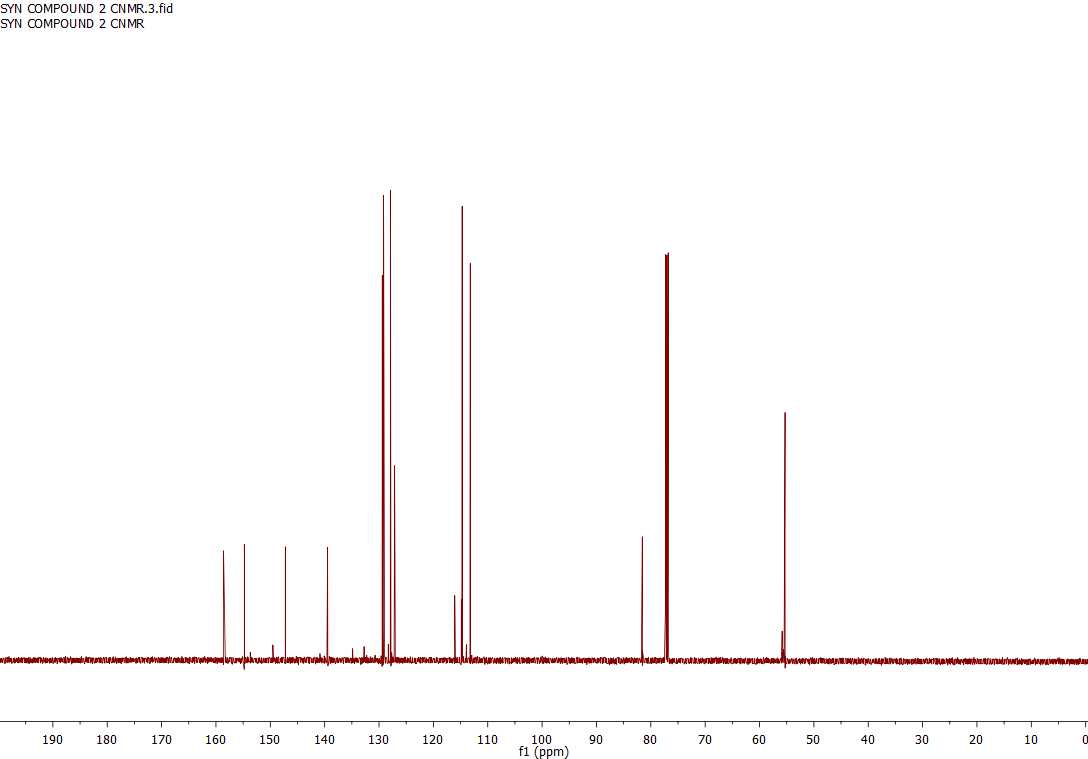
Image of compound **6**.

A green paper with three dots on it

Description automatically generated

TLC (SiO2, 3:1 hexanes/EtOAc) for compound **6**. Left lane: crude reaction mixture before precipitation and partition (bottom spot is the product, top spot is anisole); middle lane: co-spot of samples on left and right lanes; right lane: compound **6** after precipitation of the deprotonated product with Et2O followed by partition.







A glass flask with a liquid inside

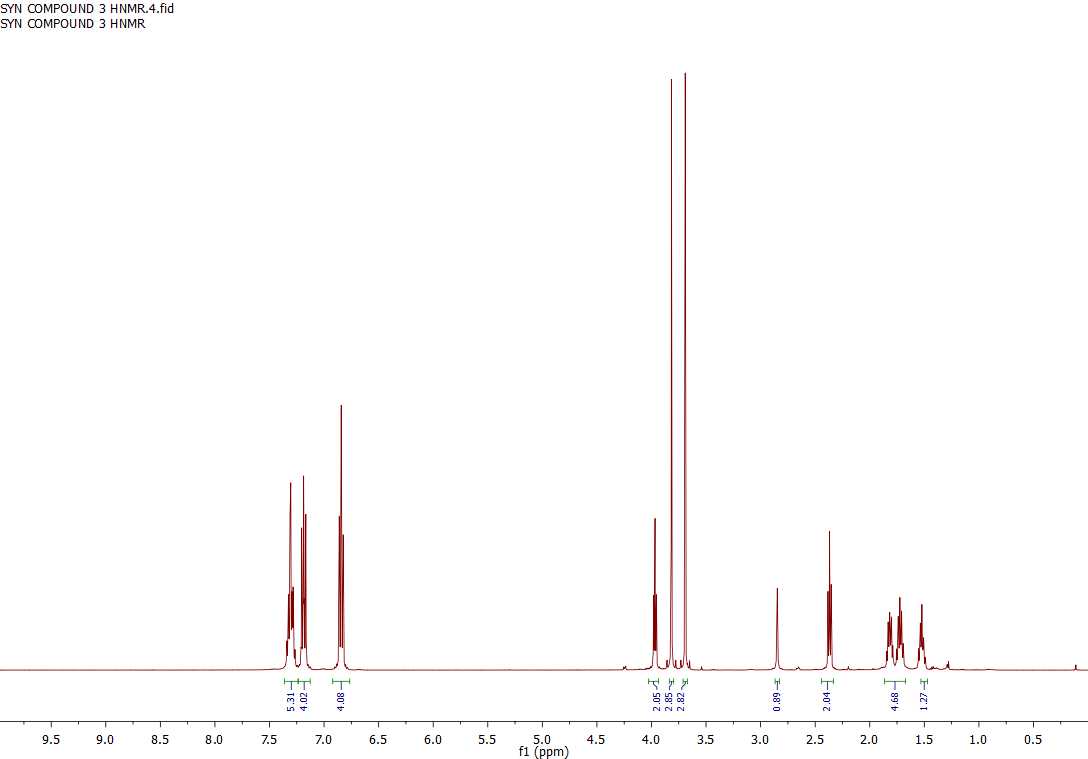
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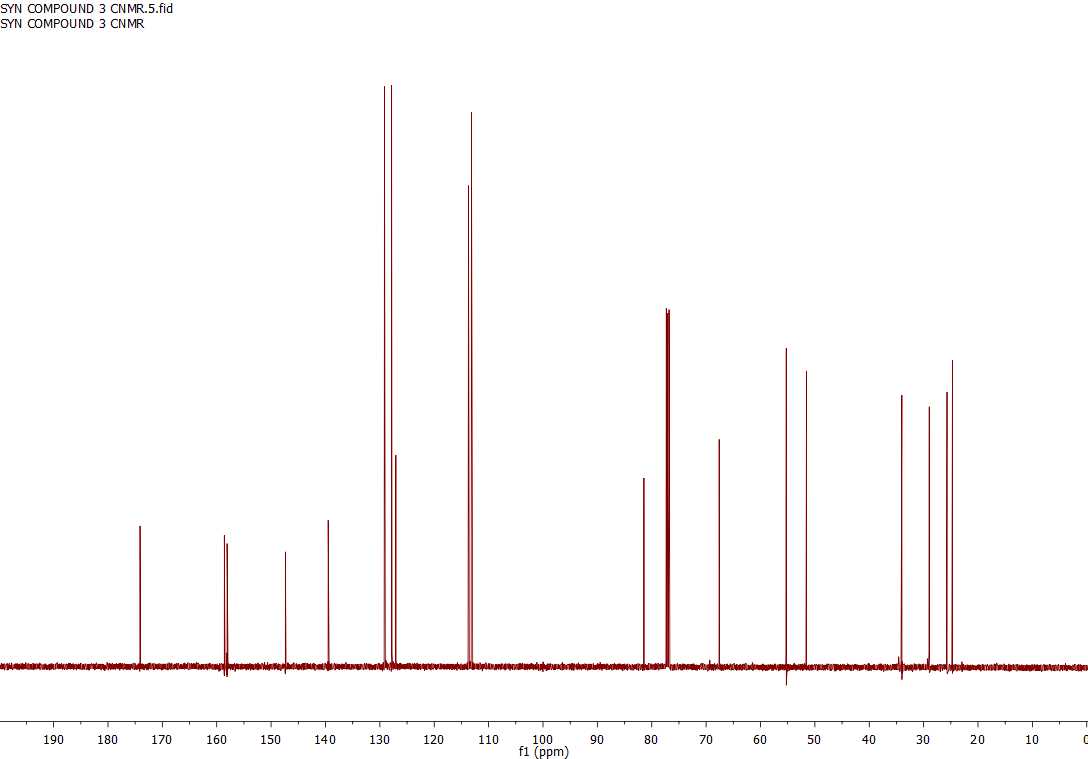
Image of compound **7**.

A green paper with writing on it

Description automatically generated

TLC (SiO2, 3:1 hexanes/EtOAc) for compound **7**. Left lane: **7** after purification by precipitation from DCM with hexanes; middle lane: co-spot of samples on left and right lanes; right lane: authentic **7** purified with chromatography and characterized with NMR.







A clear glass ball with bubbles inside

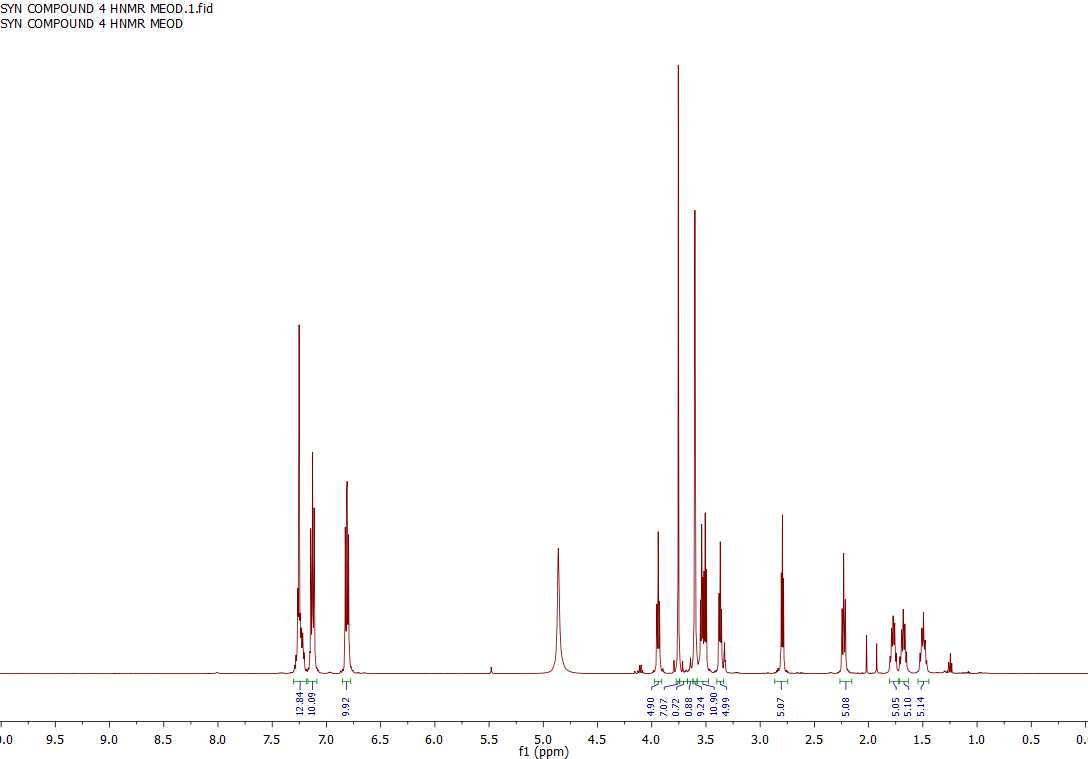
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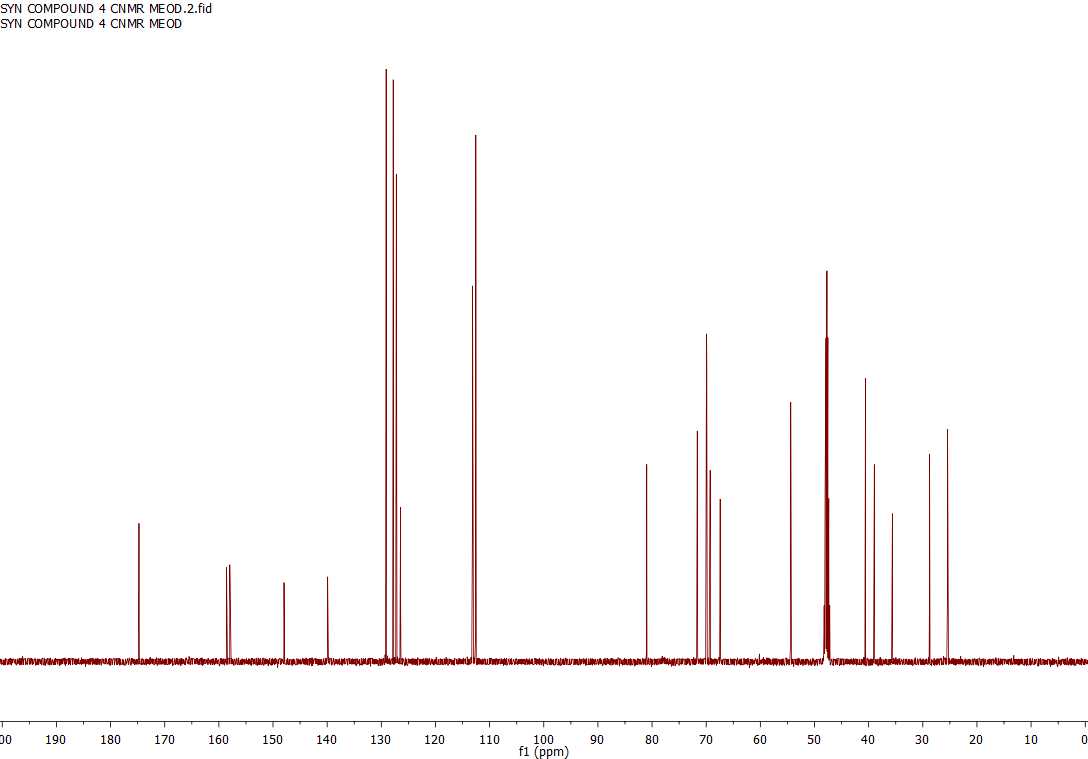
Image of compound **8**.

A green paper with a blurry face

Description automatically generated

TLC (SiO2, 5:2:2:1 Et2O/MeCN/MeOH/Et3N) for compound **8**. Left lane: compound **7**; middle lane: co-spot of samples on left and right lanes; right lane: product **8** purified by partition between DCM and water.







A picture containing indoor, bottle, bell jar, close

Description automatically generated

Image of compound **9**.

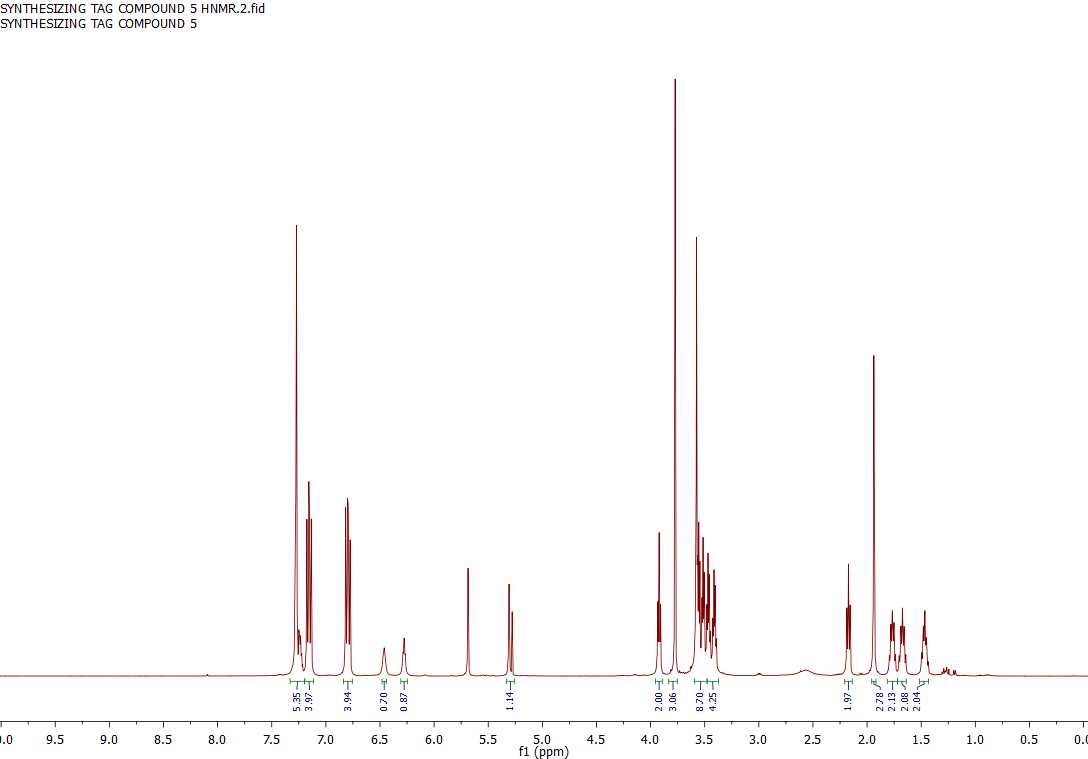
A green paper with black text

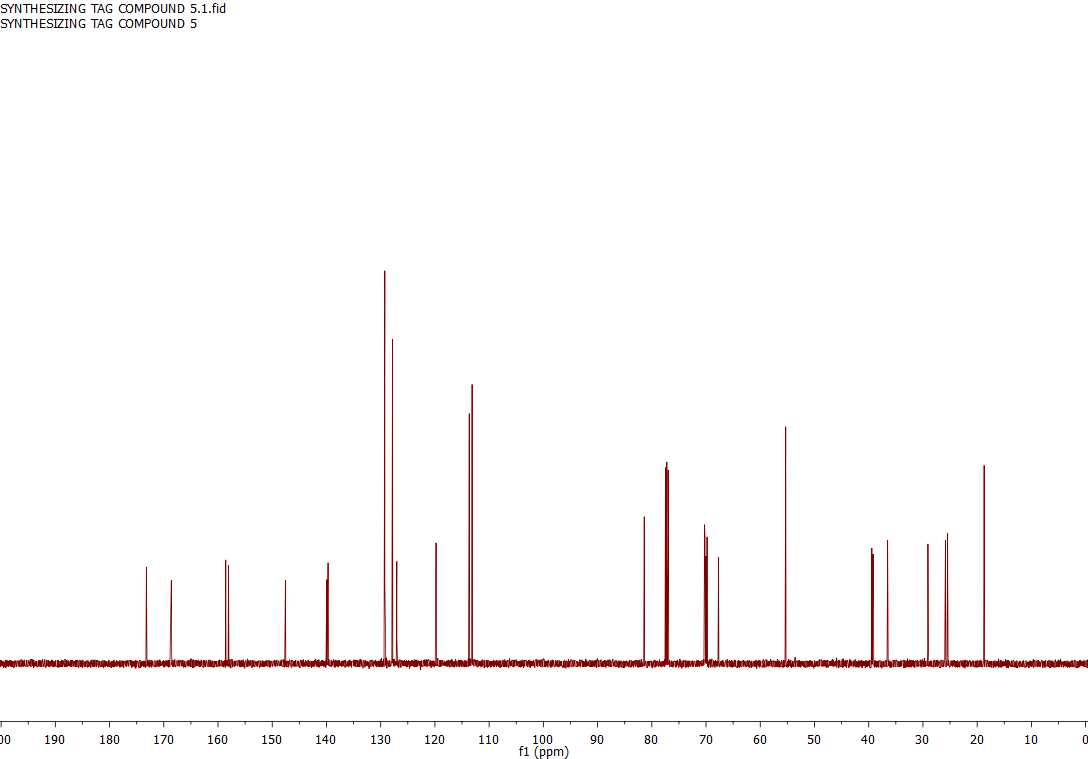
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Left TLC (SiO2, 3:2 acetone/hexanes 5% Et3N) for compound **9**. Left lane: reaction mixture after partition between DCM and K2CO3; middle lane: co-spot of samples on left and right lanes; right lane: authentic **9** purified with chromatography and characterized with NMR.

Right TLC (SiO2, 3:2 acetone/hexanes 5% Et3N) for compound **9**. Left lane: product after purification by partition and precipitation from 1% DIEA in THF with hexanes; middle lane: co-spot of samples on left and right lanes; right lane: authentic **9** purified with chromatography and characterized with NMR.







A glass vase with a white substance inside

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Image of compound **10a**.

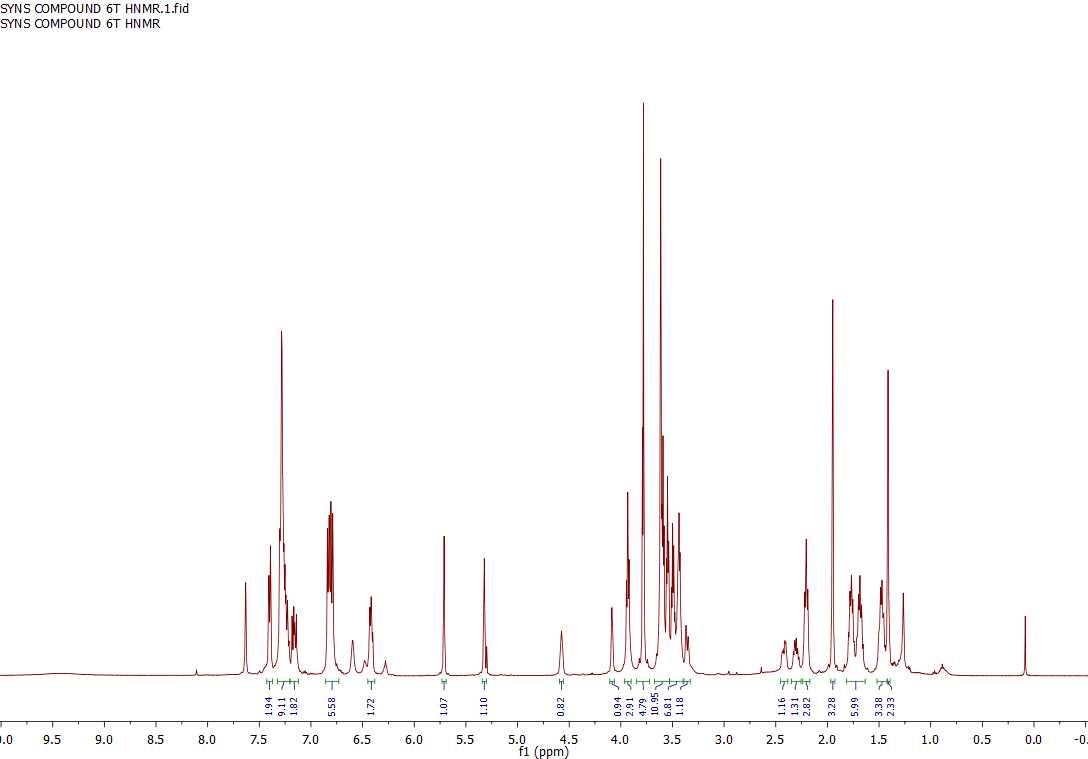
A picture containing colorfulness

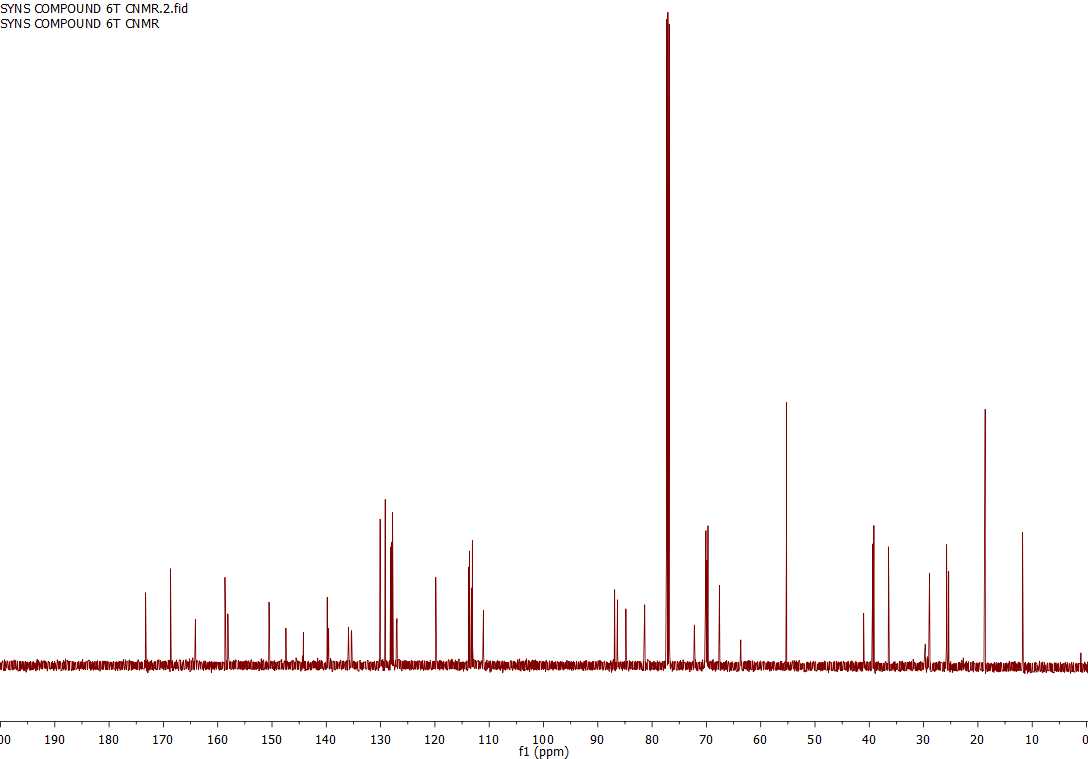
Description automatically generated A picture containing rectangle, colorfulness, screenshot, green

Description automatically generated

Left TLC (SiO2, 3:2 acetone/hexanes 5% Et3N) for compound **10a**. Left lane: compound **9**; middle lane: co-spot of samples on left and right lanes; right lane: crude reaction mixture (upper spot is pyridine, lower spot is the product).

Right TLC (SiO2, 3:2 acetone/hexanes 5% Et3N) for compound **10a**. Left lane: compound **9**; middle lane: co-spot of samples on left and right lanes; right lane: product **10a** after purification by partition and precipitation.





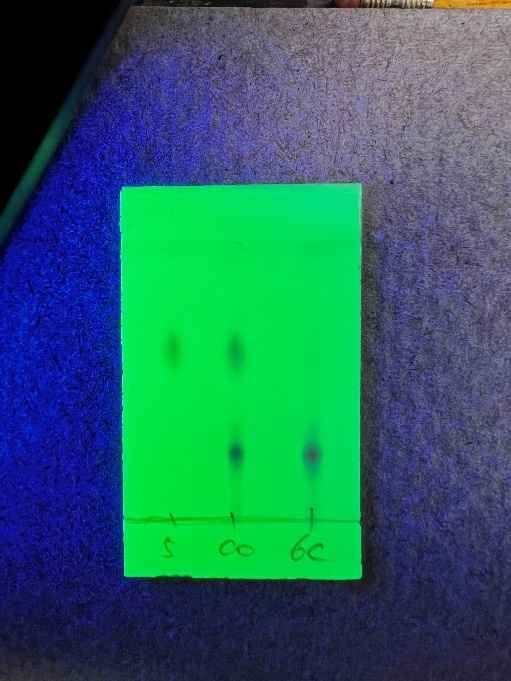




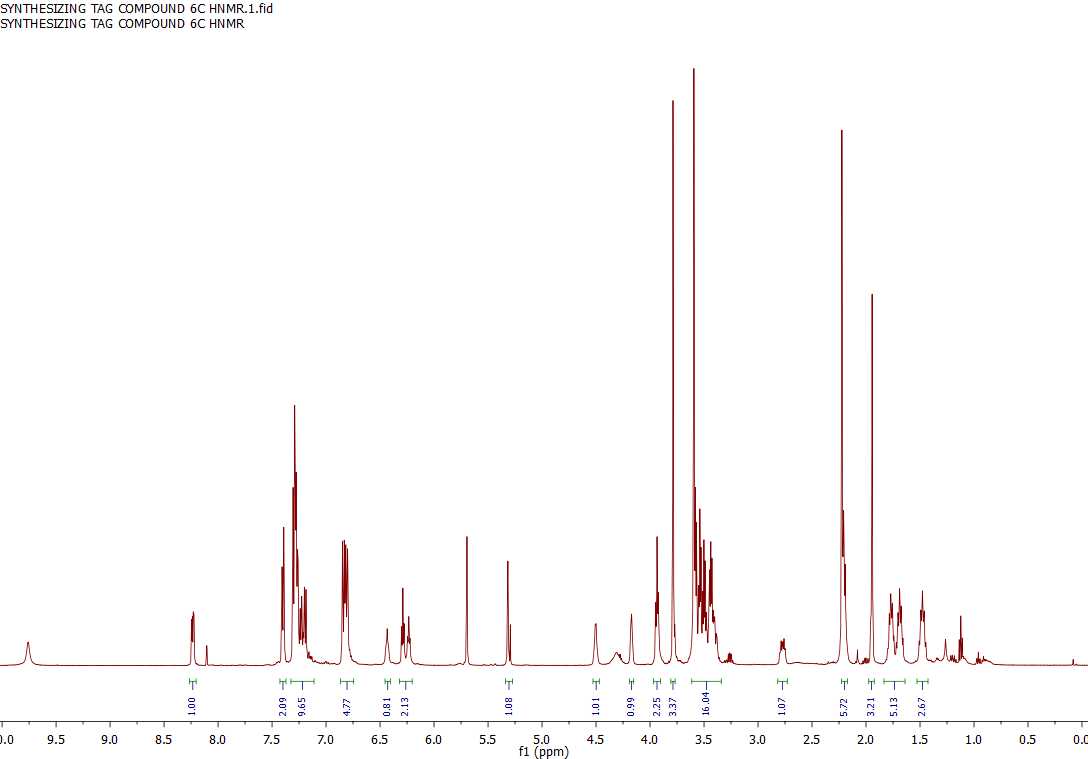
A clear glass flask with sand inside

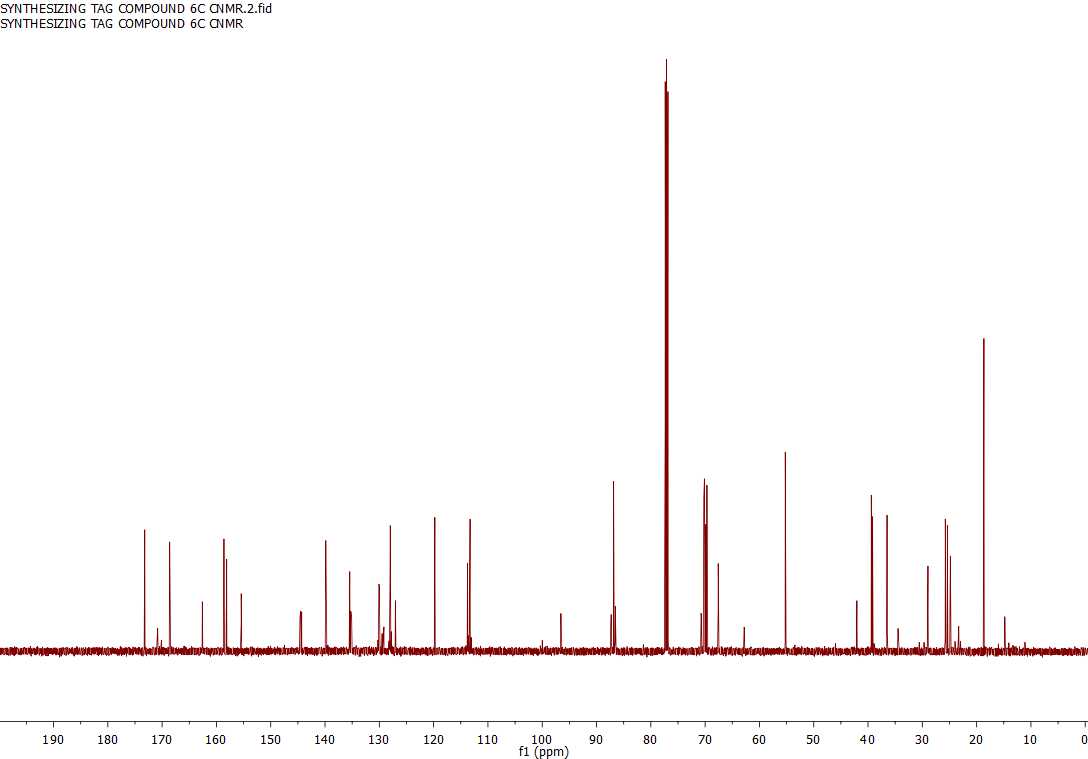
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Image of compound **10b**.



TLC (SiO2, 3:2 acetone/hexanes with 5% Et3N) for compound **10b**. Left lane: compound **9**; middle lane: co-spot of samples on left and right lanes; right lane: product after partition and precipitation.





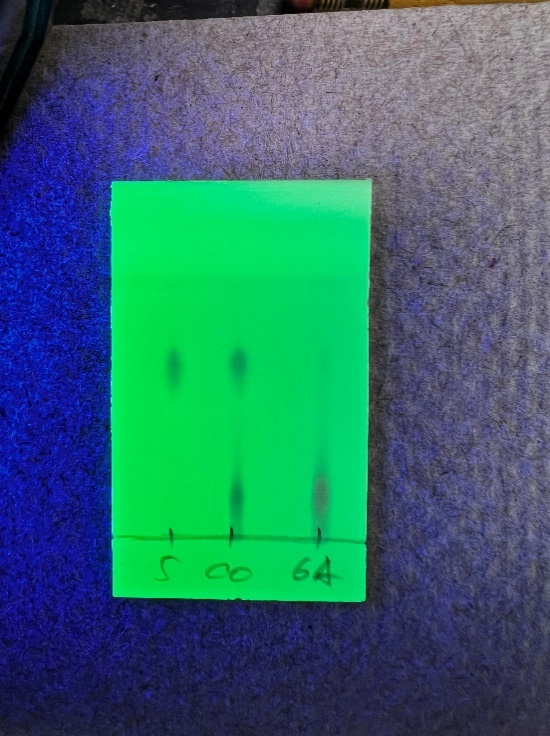




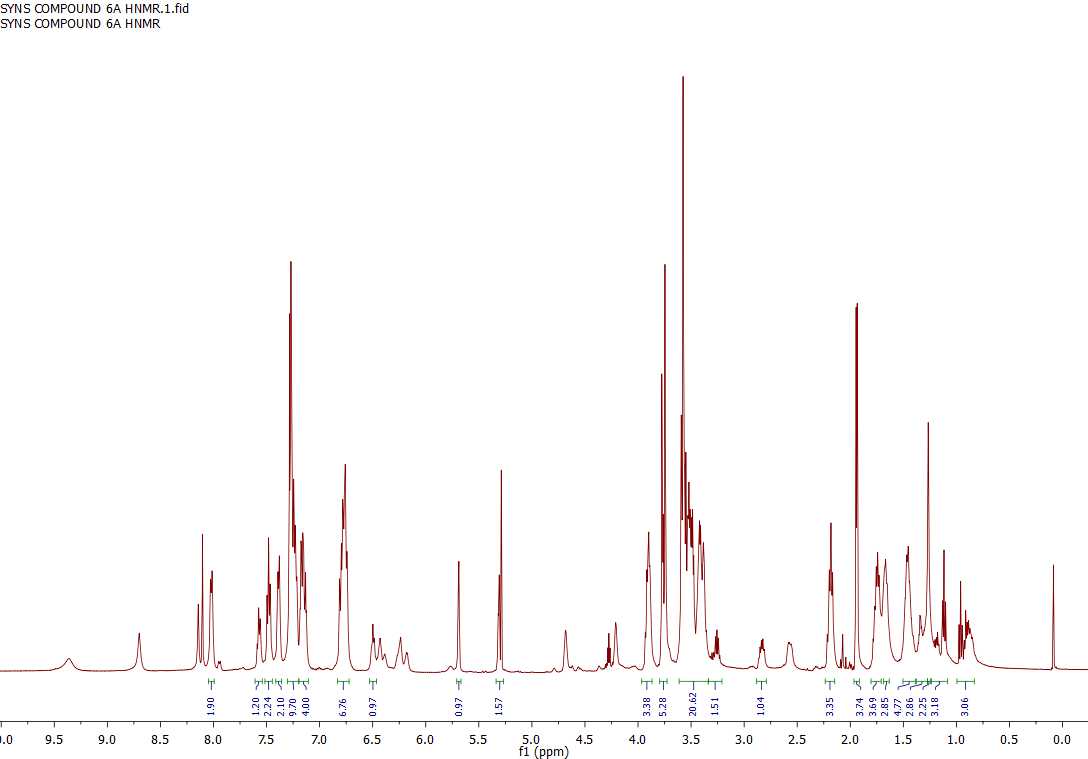
A clear glass ball with sand inside

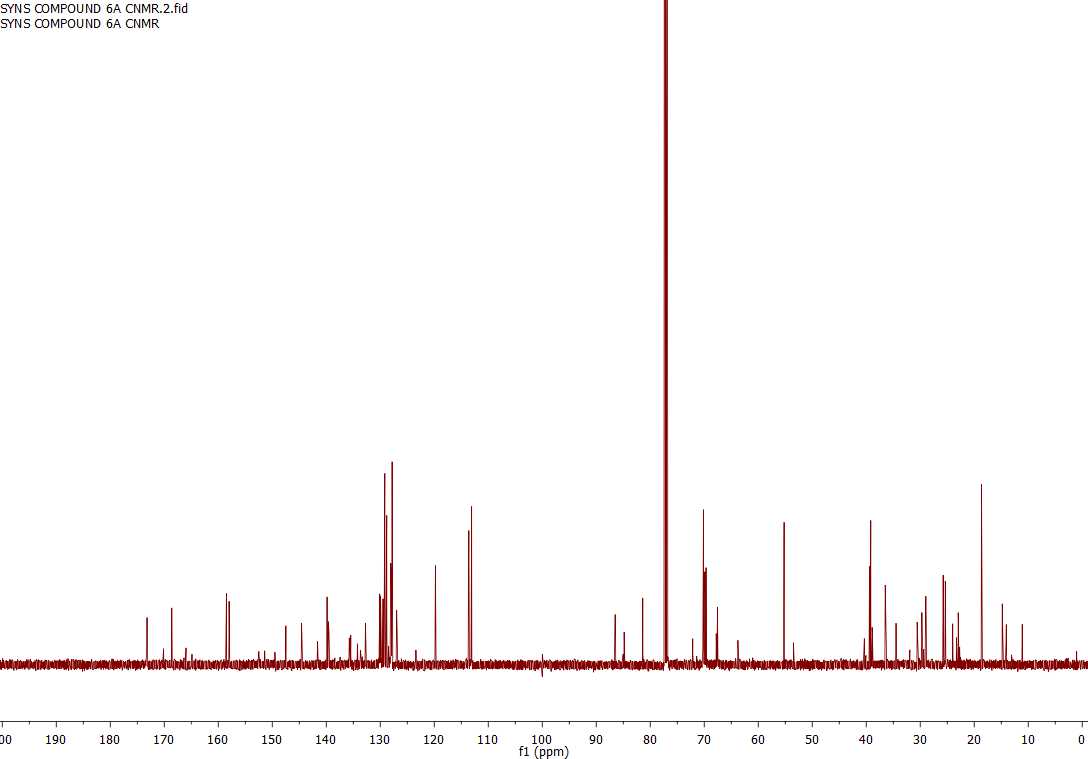
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Image of compound **10c**.



TLC (SiO2, 3:2 acetone/hexanes 5% Et3N) for compound **10c**. Left lane: compound **9**; middle lane: co-spot of samples on left and right lanes; right lane: product after partition and precipitation.





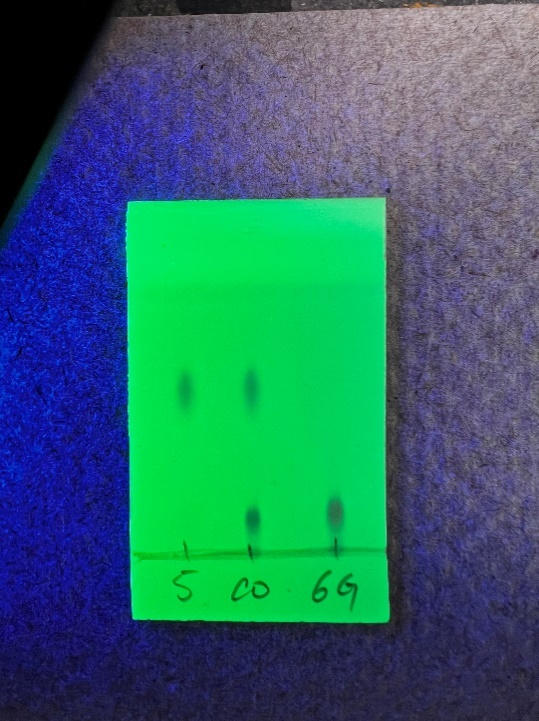




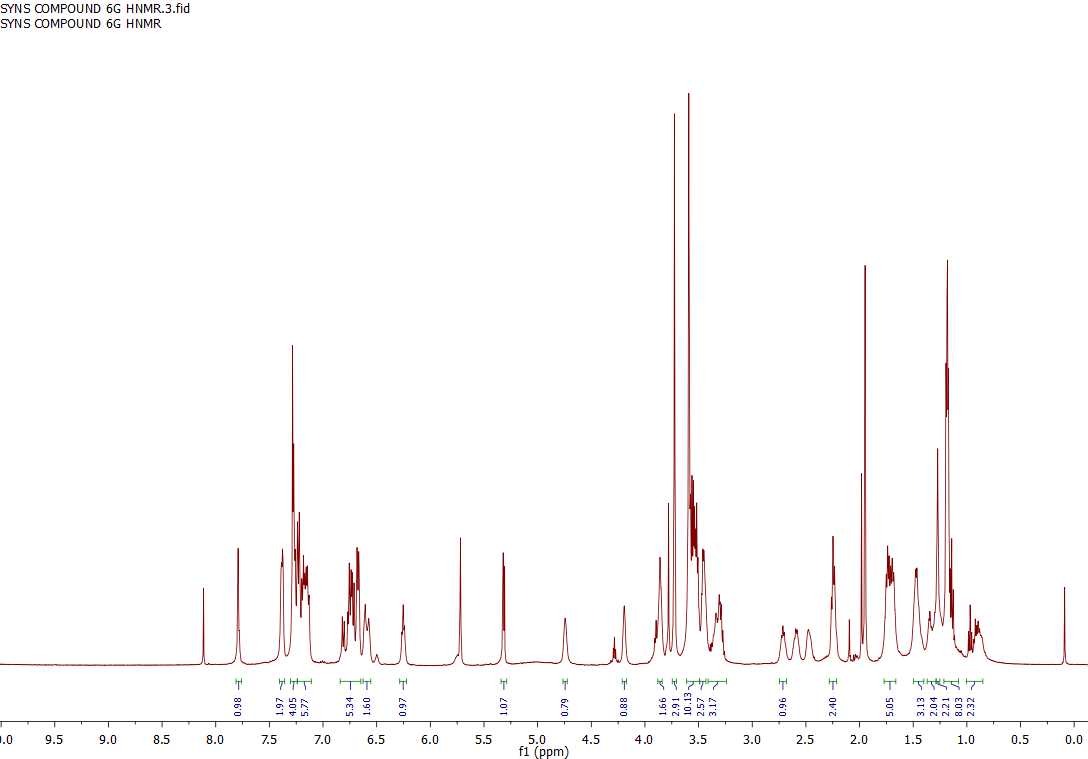
A glass flask with white substance inside

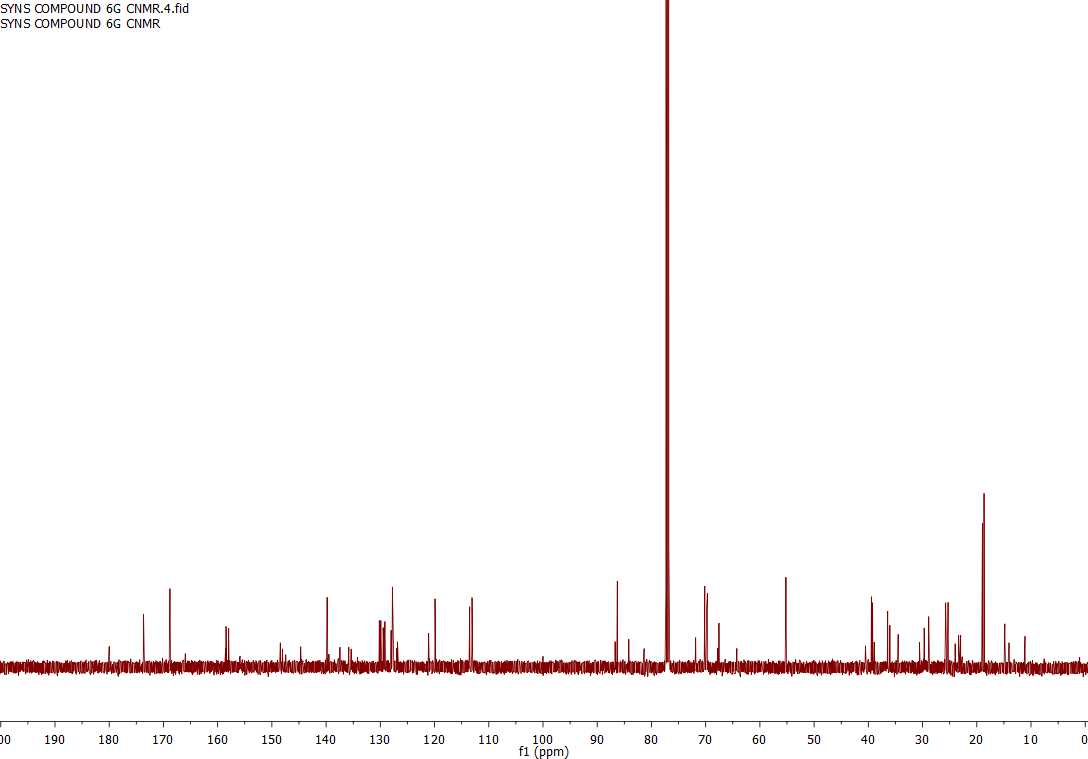
Description automatically generated

Image of compound **10d**.



TLC (SiO2, 3:2 acetone/hexanes 5% Et3N) for compound **10d**. Left lane: compound **9**; middle lane: co-spot of samples on left and right lanes; right lane: product after partition and precipitation.









A green paper with three small black dots

Description automatically generated with medium confidence

TLC (SiO2, acetone/hexane 3:2, 5% Et3N) for compound **1a**. Left lane: starting material compound **10a**; middle lane: co-spot of samples on left and right lanes; right lane: compound **1a** from reaction mixture.

A green paper with writing on it

Description automatically generated

TLC (SiO2, acetone/hexane 3:2, 5% Et3N) for compound **1a**. Left lane: starting material compound **10a**; middle lane: co-spot of samples on left and right lanes; right lane: compound **1a** purified with chromatography.





