Supporting Information

Cobalt-Catalyzed Regioselective Syntheses of Indeno[2,1-*c*]pyridines from Nitriles and Diynes Bearing Propargyl Fragments

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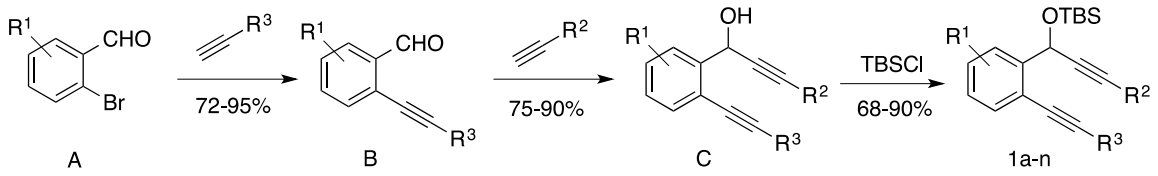
1. Experimental Section

A typical procedure for the synthesis of 1:



Synthesis of the intermediate B: [1]

Under an atmosphere of N_2 the 2-bromo-benzaldehyde (1.0 eq) was dissolved in trimethylamine (50 mL). After stirring for 10 minutes, the terminal alkyne (1.2 eq) were added. 5 mol% of copper(I) iodide and 2.5 mol% of $PdCl_2(PPh_3)_2$ were dissolved in freshly degassed triethylamine under an atmosphere of nitrogen then stirred at 50 ^oC under nitrogen for 24 h. After full conversion of **A** monitored by thin-layer chromatography, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate = 200:1 as the eluent afforded the intermediate **B** with 72-95% yields.

Synthesis of the intermediate C: [2]

To a solution of the corresponding terminal alkyne (1.3 eq.) in THF (40 mL) in Schlenk tube was added *n*-BuLi (2.5 M, 1.2 eq.) at -78 ^oC and then stirred at -78 ^oC under nitrogen for 30 min. Then, a solution of **B** in THF (5 mL) was added dropwise and stirred at rt for 1-2 h. After full conversion of **B** monitored by thin-layer chromatography, the resulting mixture was quenched with saturated solution of ammonium chloride, and extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure.

Purification by flash chromatography on silica gel with petroleum ether/ethyl acetate = 20:1-5:1 as the eluent afforded the intermediate **C** with 71-93% yields.

Synthesis of the intermediate 1a-1p: [3]

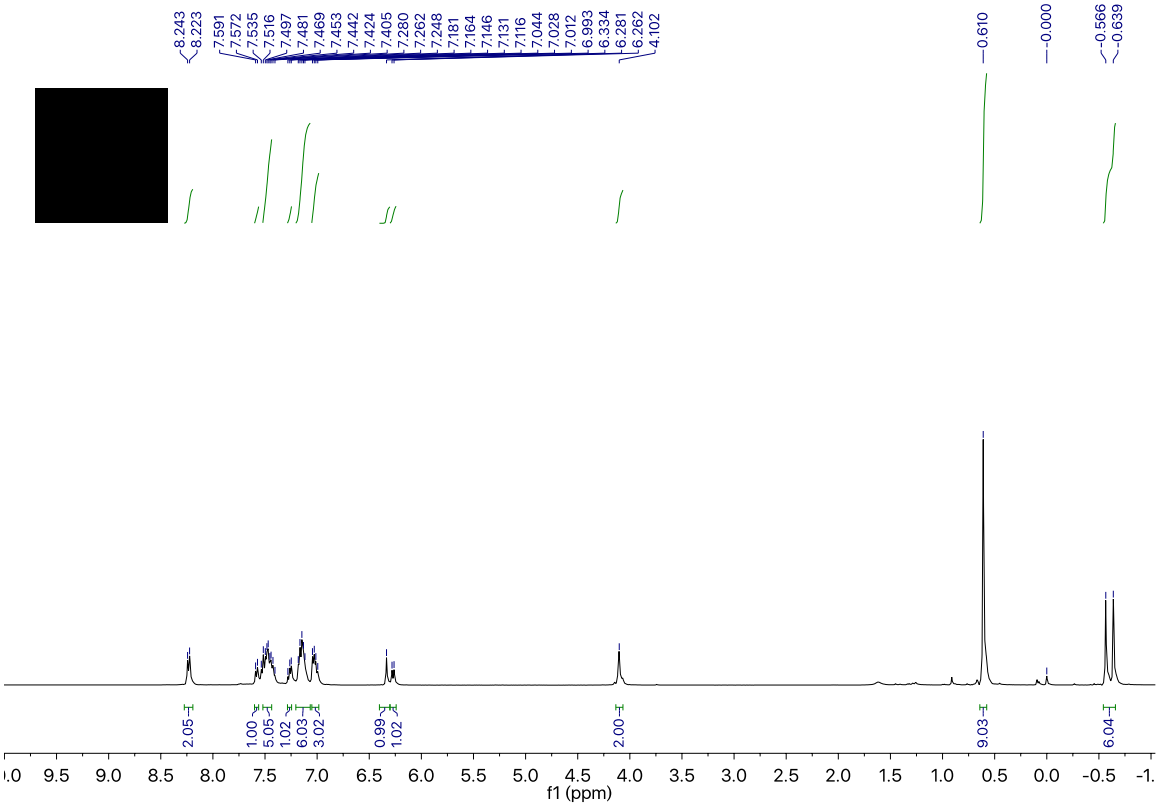
To a solution of the above intermediate **C** in DCM (15.0 mL) were added imidazole (2.0 equiv) and TBSCl (1.2 equiv). The reaction mixture was then stirred at room temperature for 2-5 h, and saturated NH_4Cl (10 mL) solution was added. Then the mixture was extracted with dichloromethane (20 mL × 3), washed with water and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate = 200:1 to afford 1a-1n with 68-99 % yields.

2. References

1 T. Lauterbach, S. Arndt, M. Rudolph, F. Rominger, A. Hashmi, *Adv. Synth. Catal.* 2013, **355**, 1755.
2 Y. L. Zhao, M. R. Xu, Z. Zheng, Y. Yuan, Y. Z. Li, *Chem. Commun*. 2017, **53**, 3721.
3 X. Zhang, X. Xie, Y. H. Liu, *Chem. Sci.* 2016, **7**, 5815.

3. NMR spectra of all new compounds

^{1}H NMR (400 MHz, $CDCl_3$)



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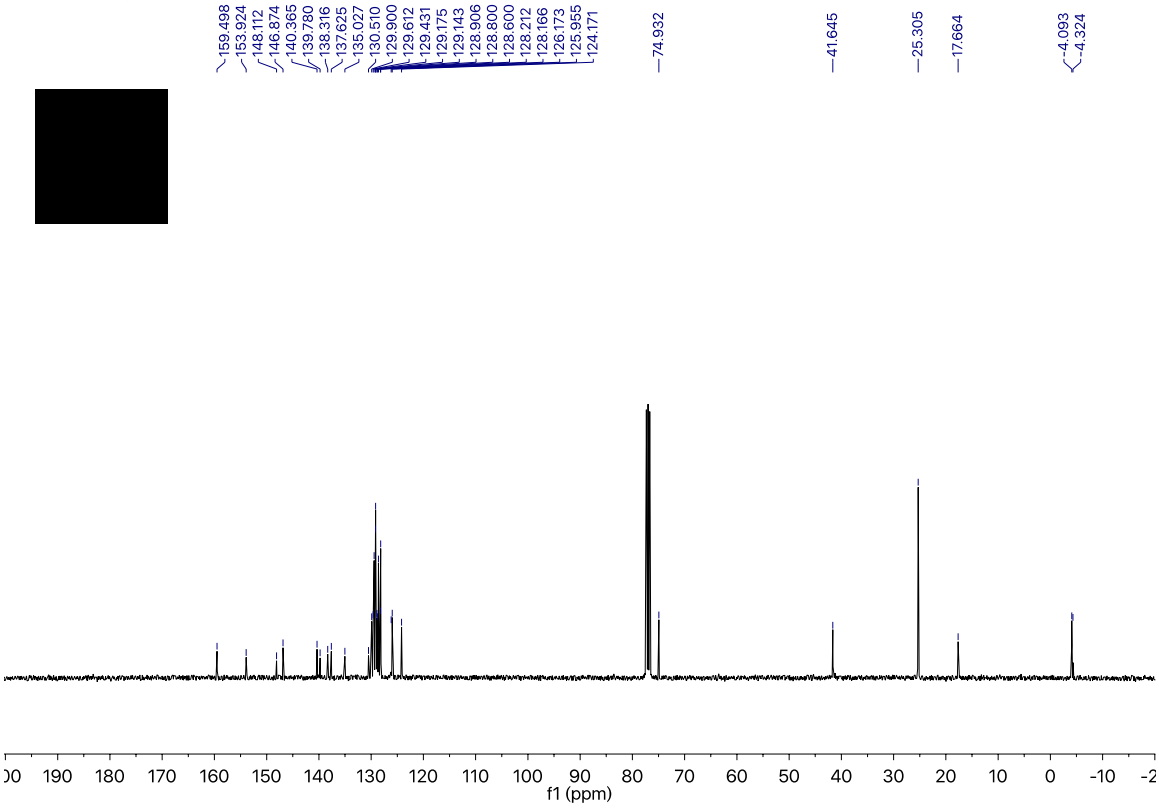

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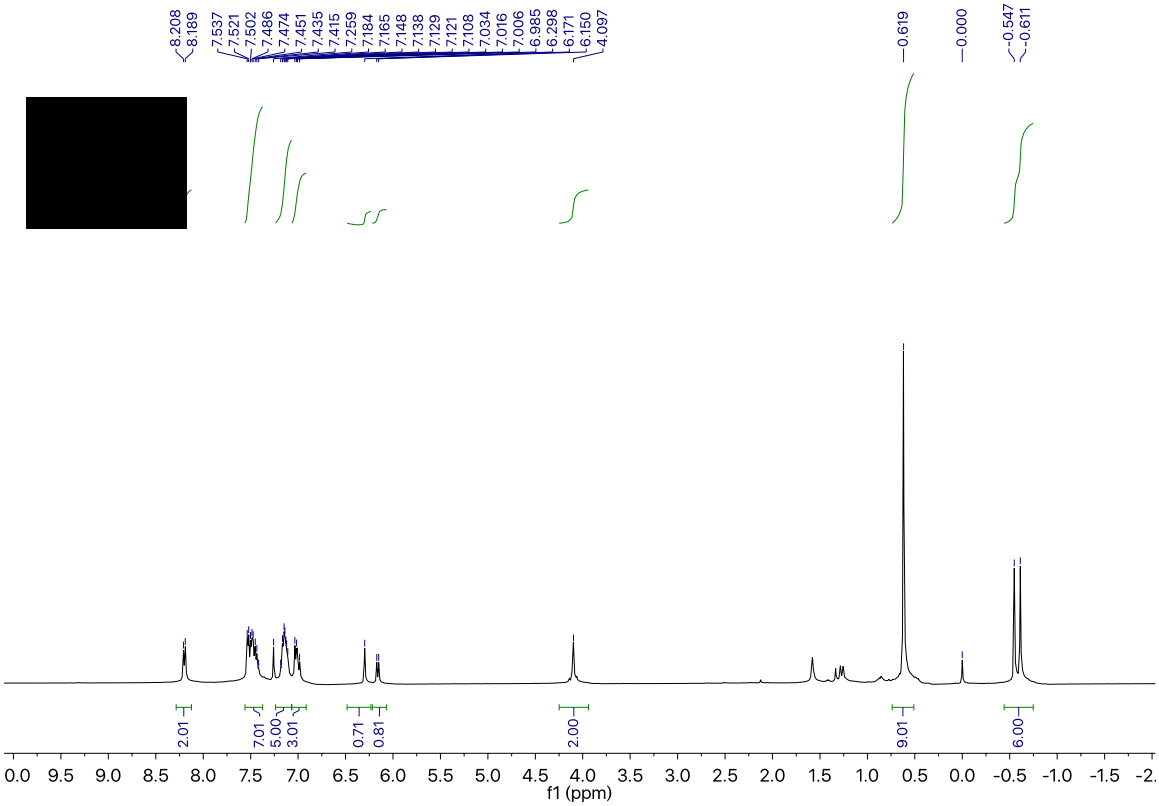

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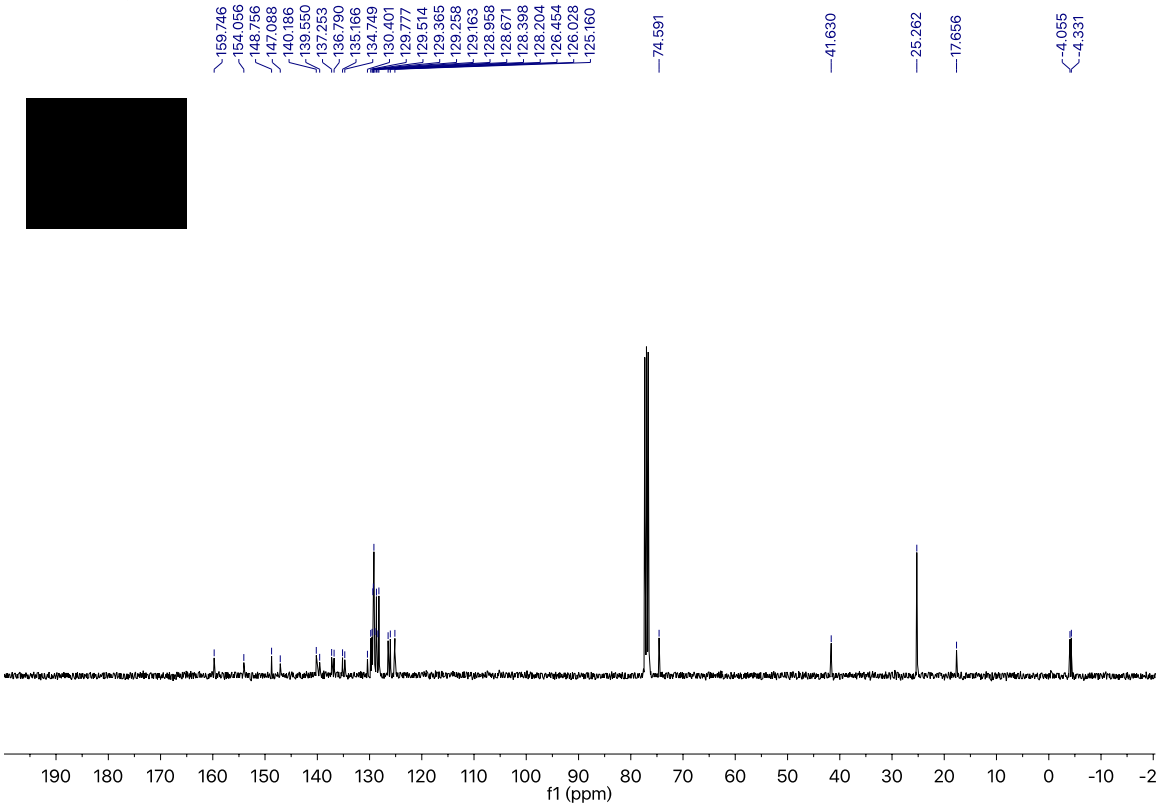

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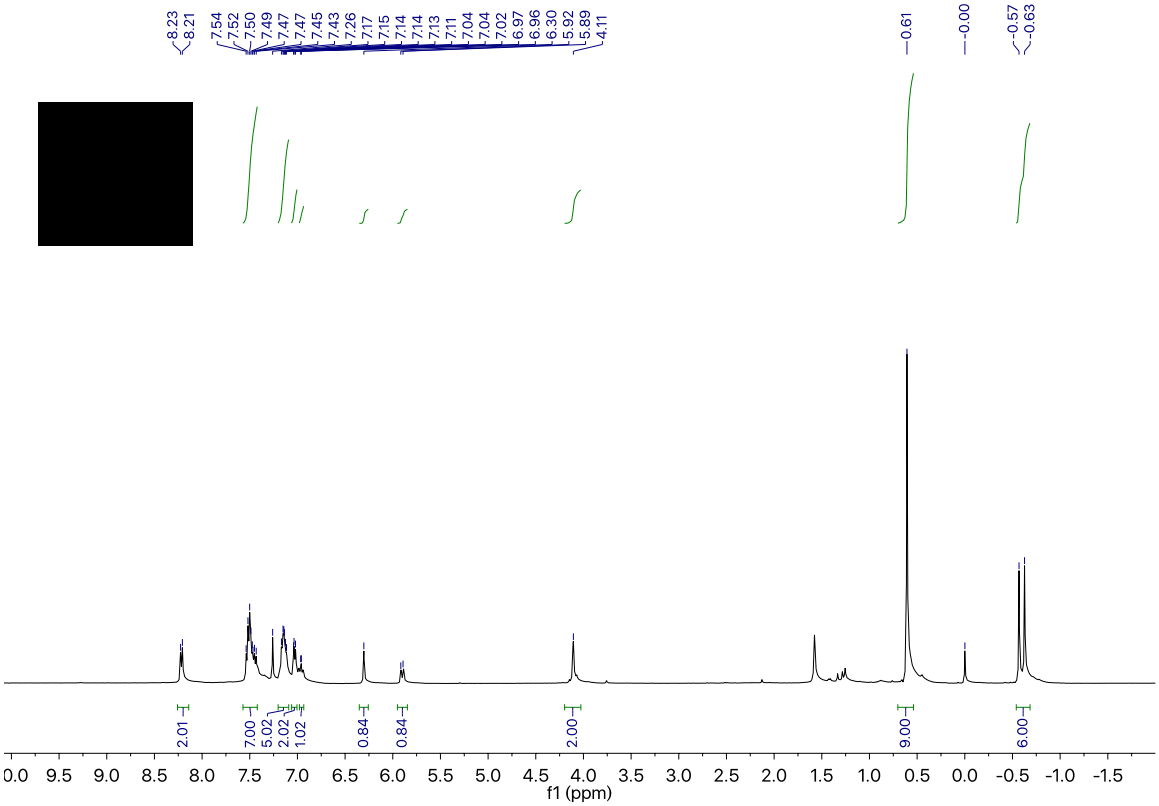

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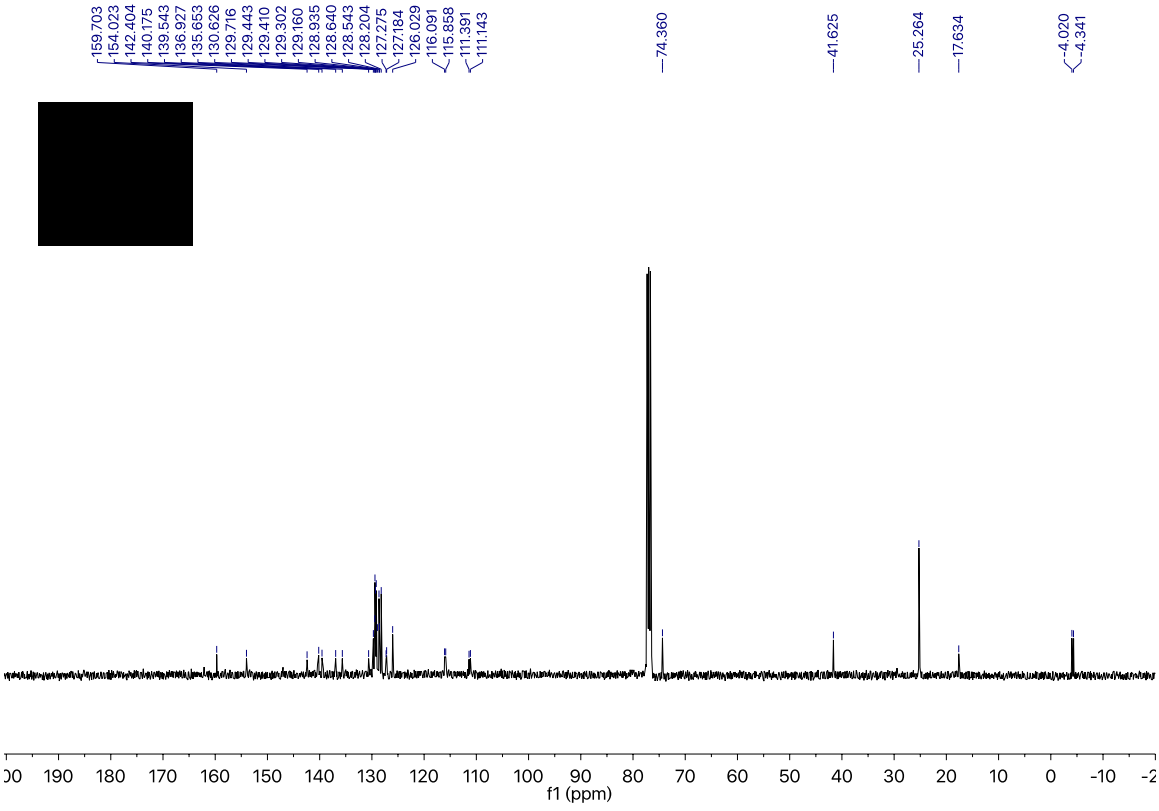

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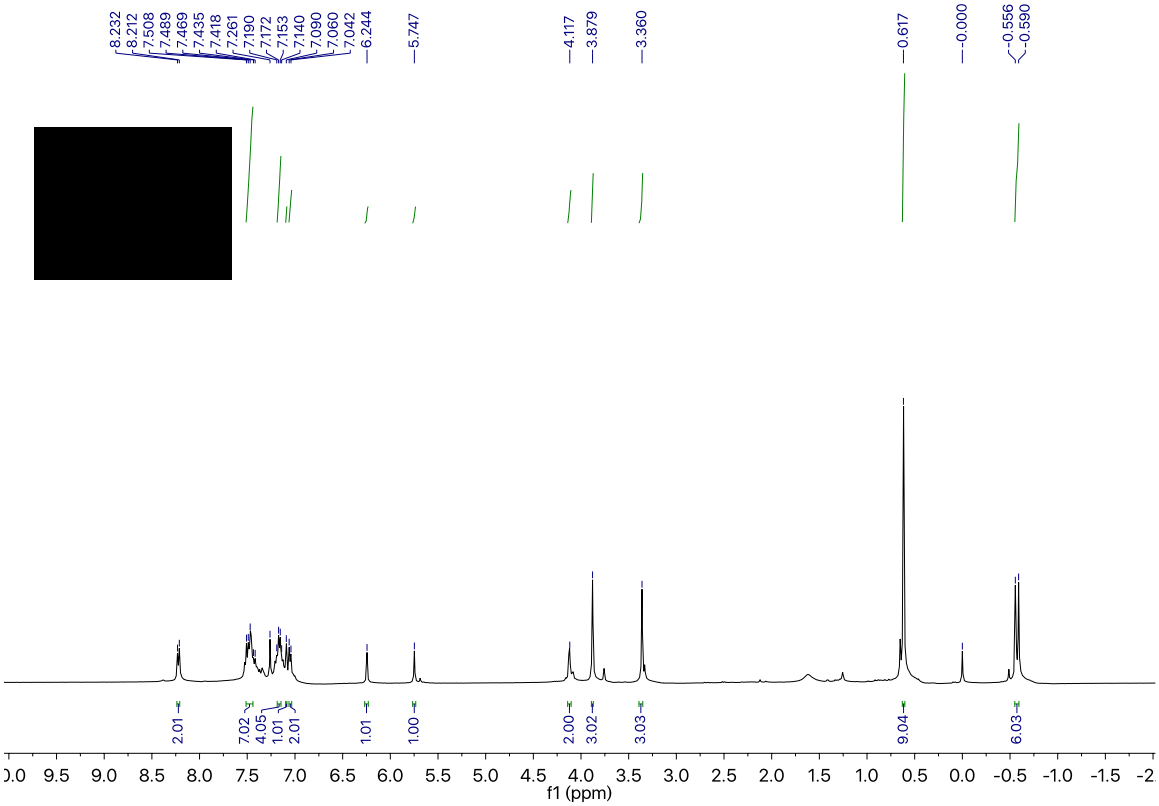

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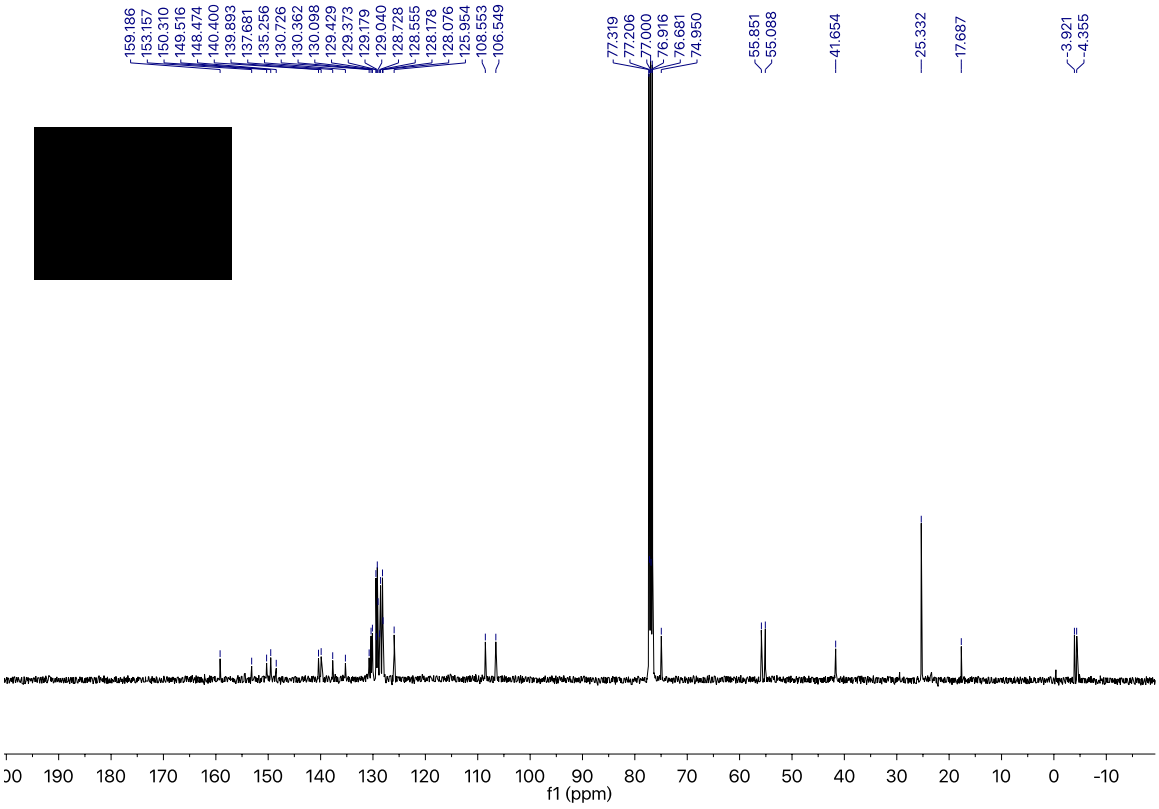

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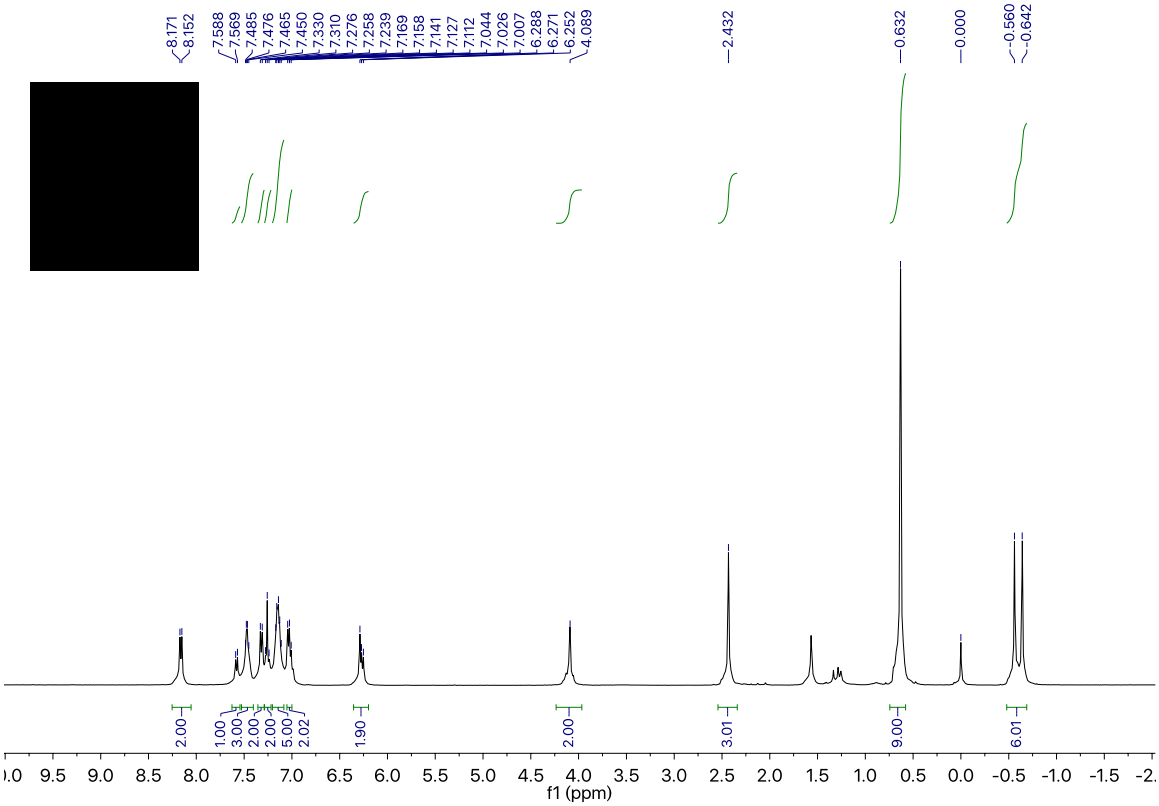

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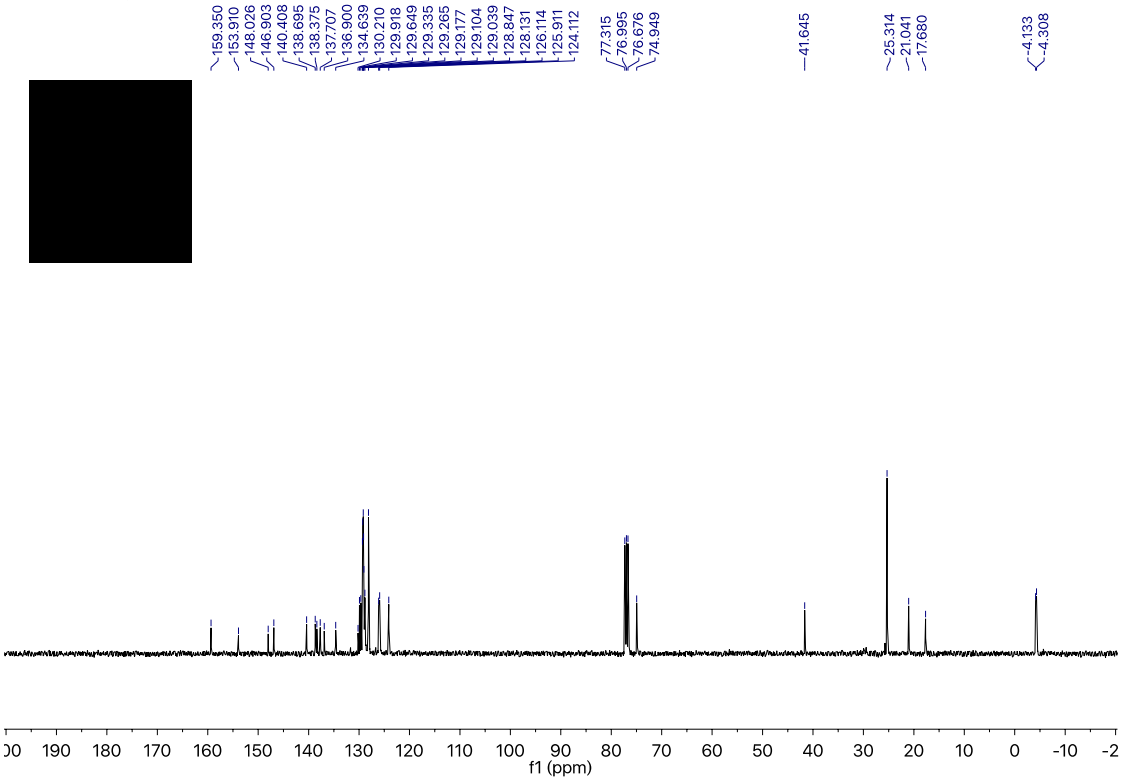

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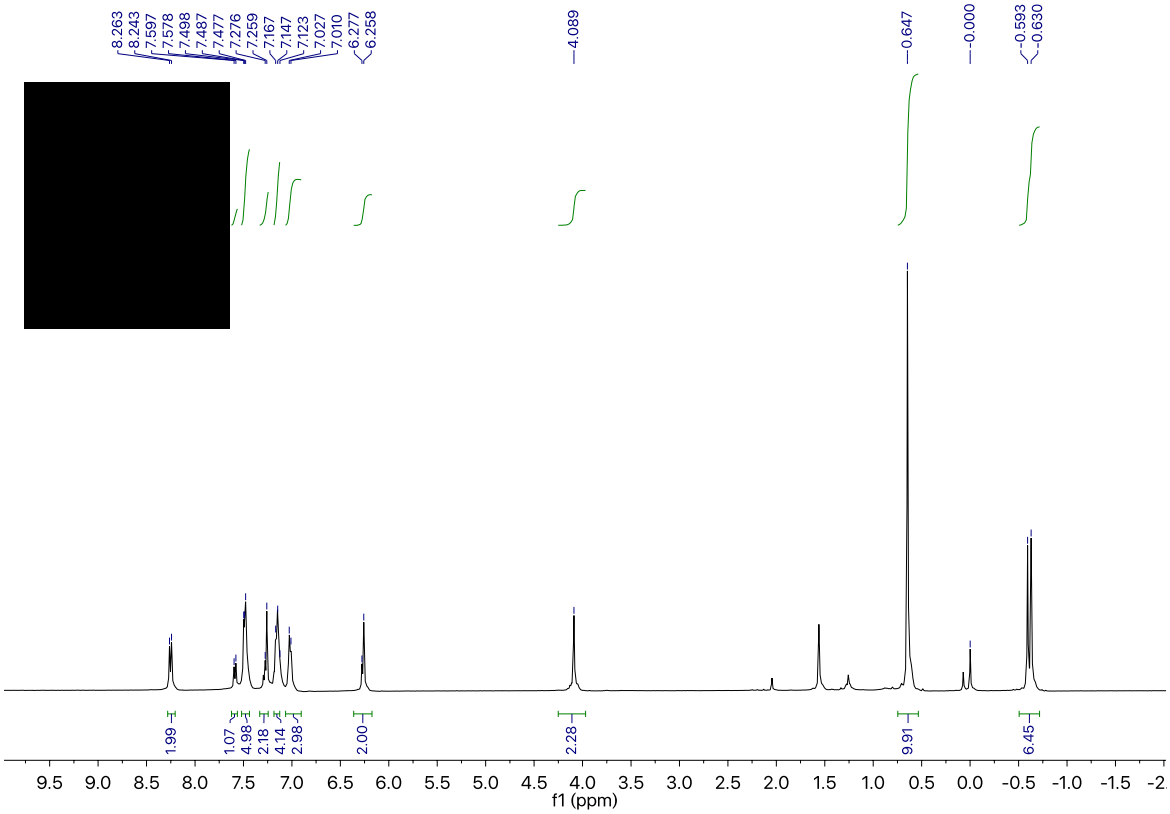

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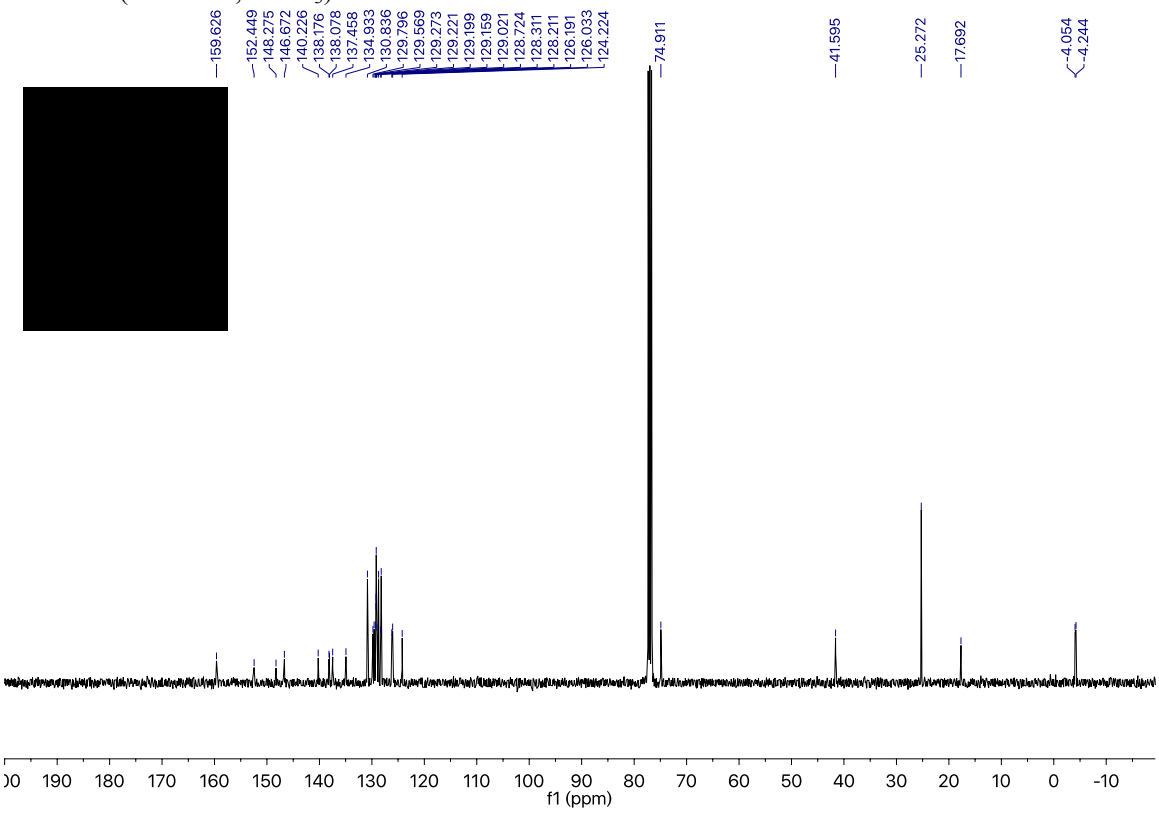

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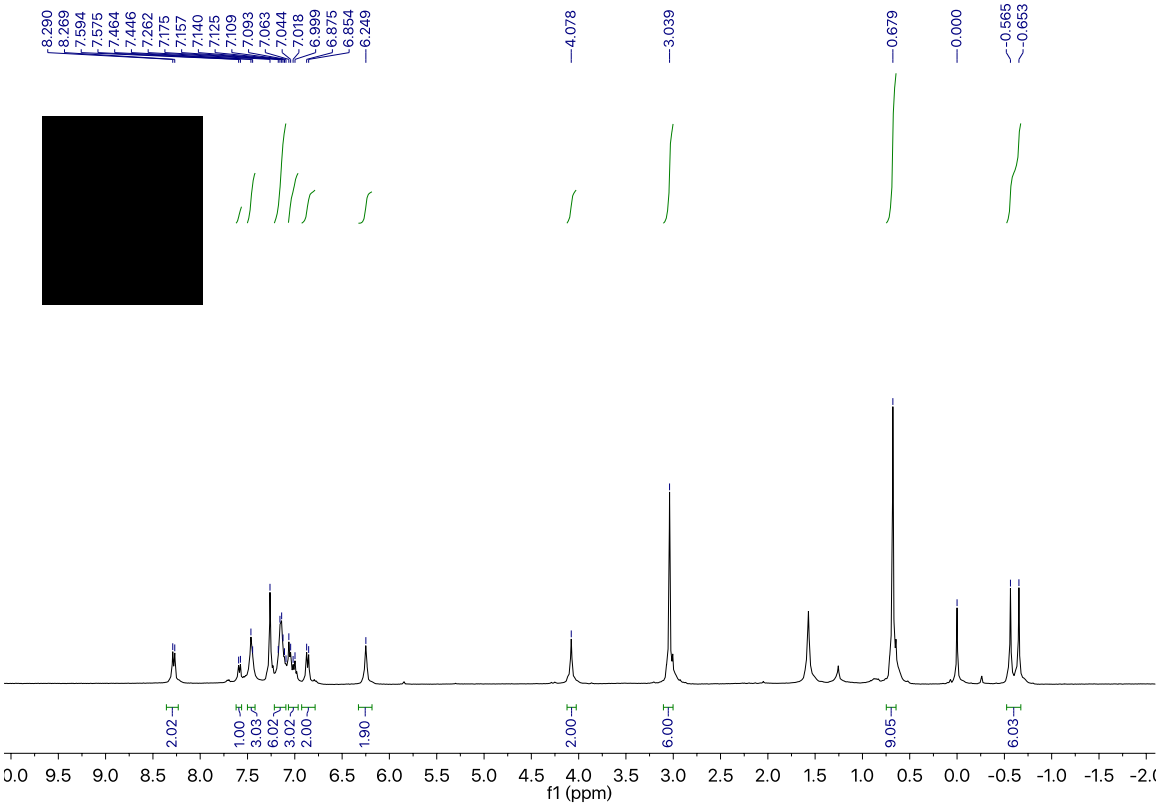

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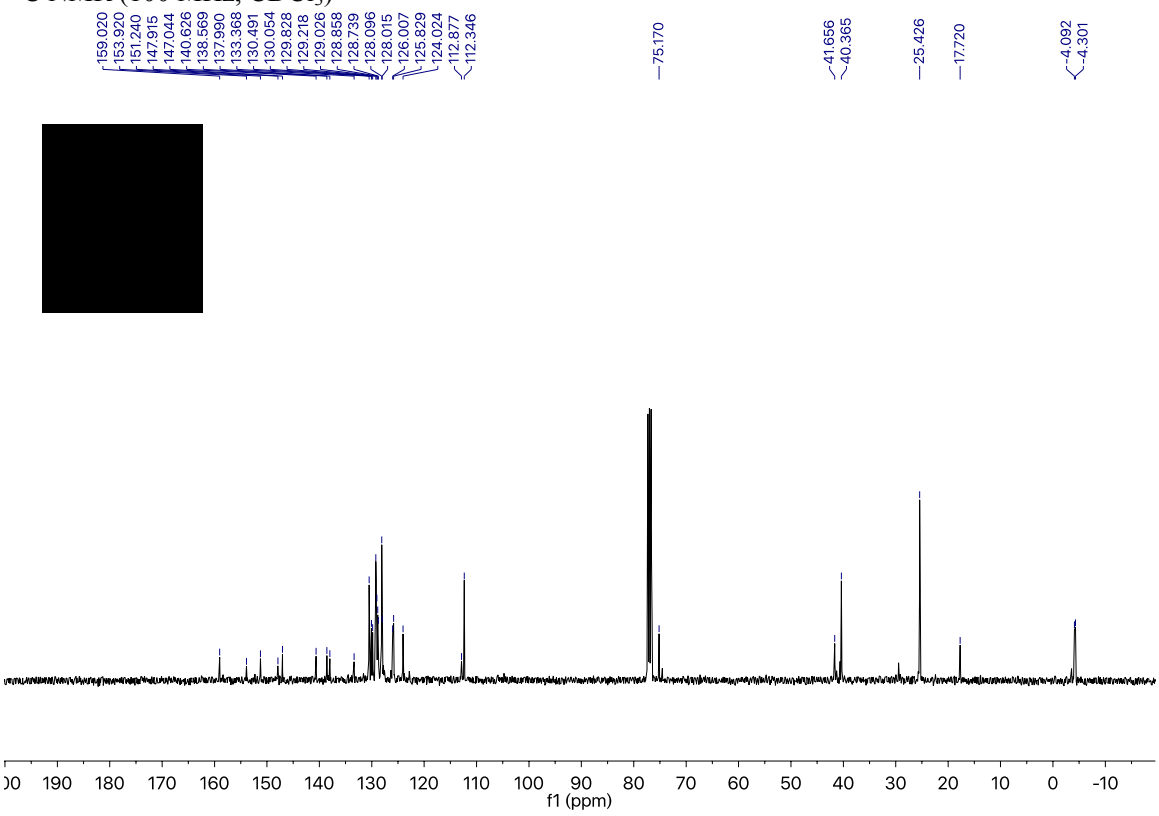

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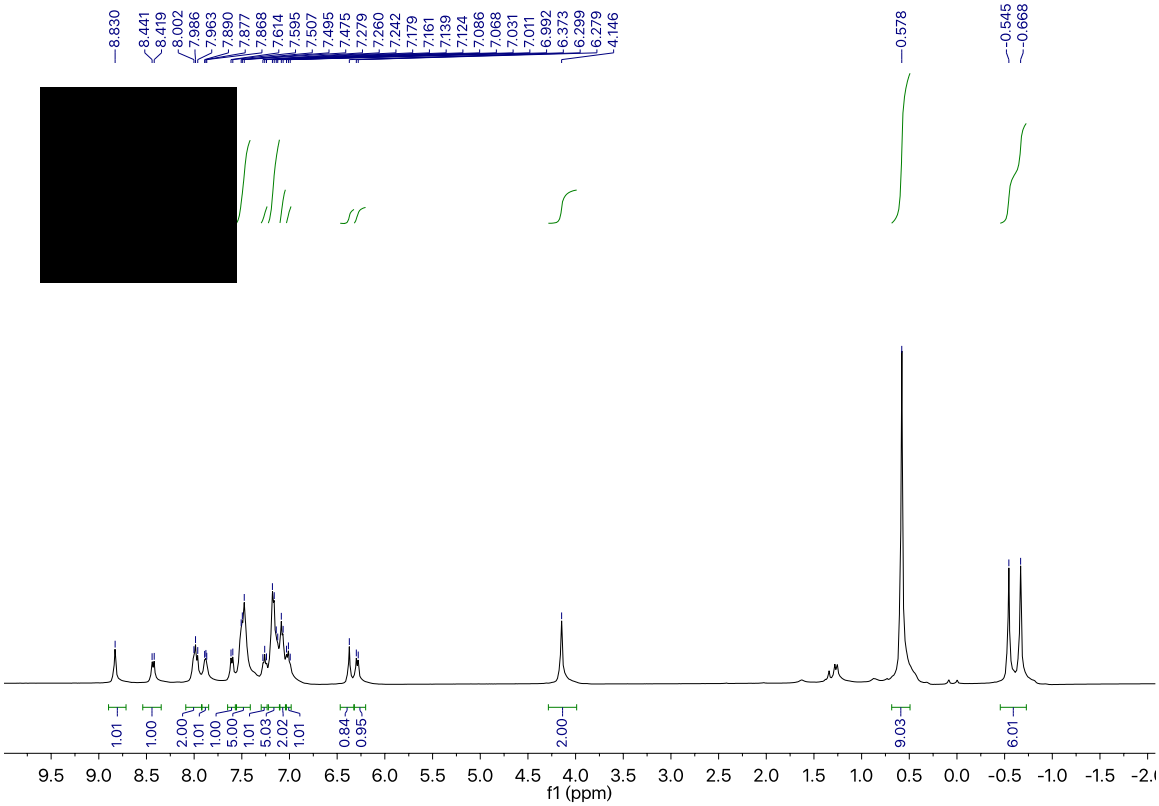

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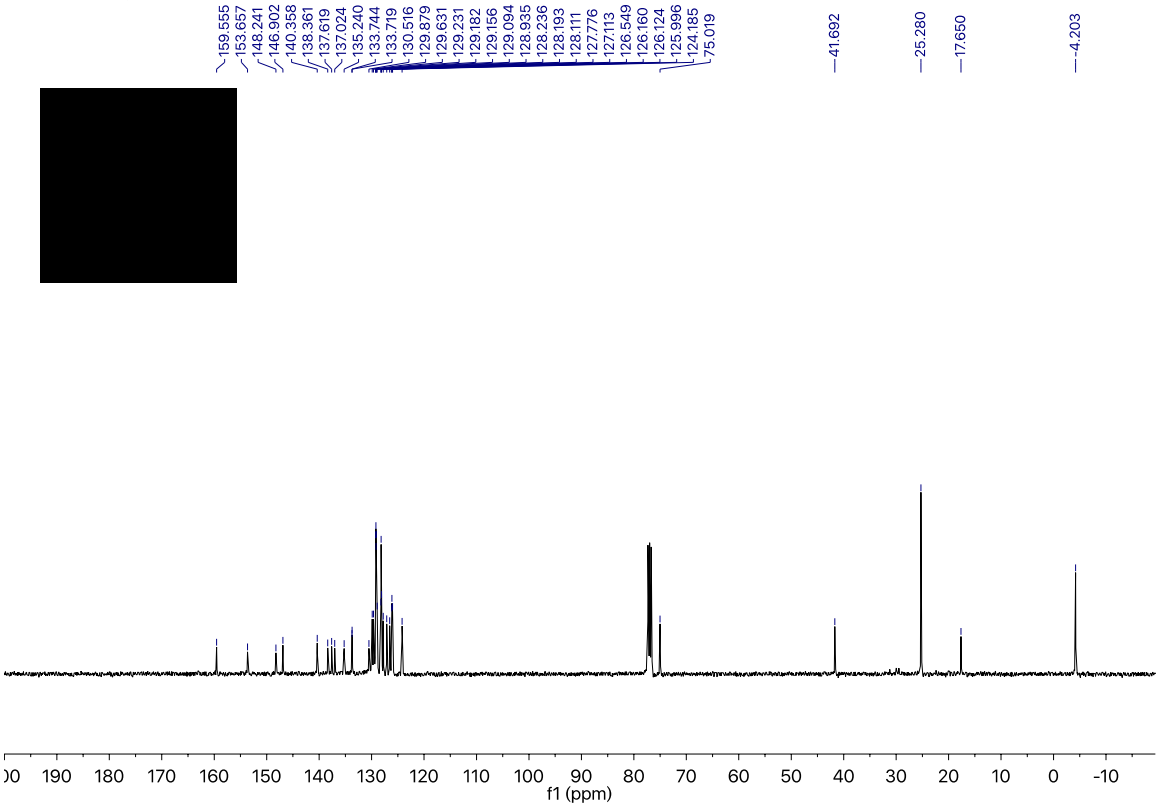

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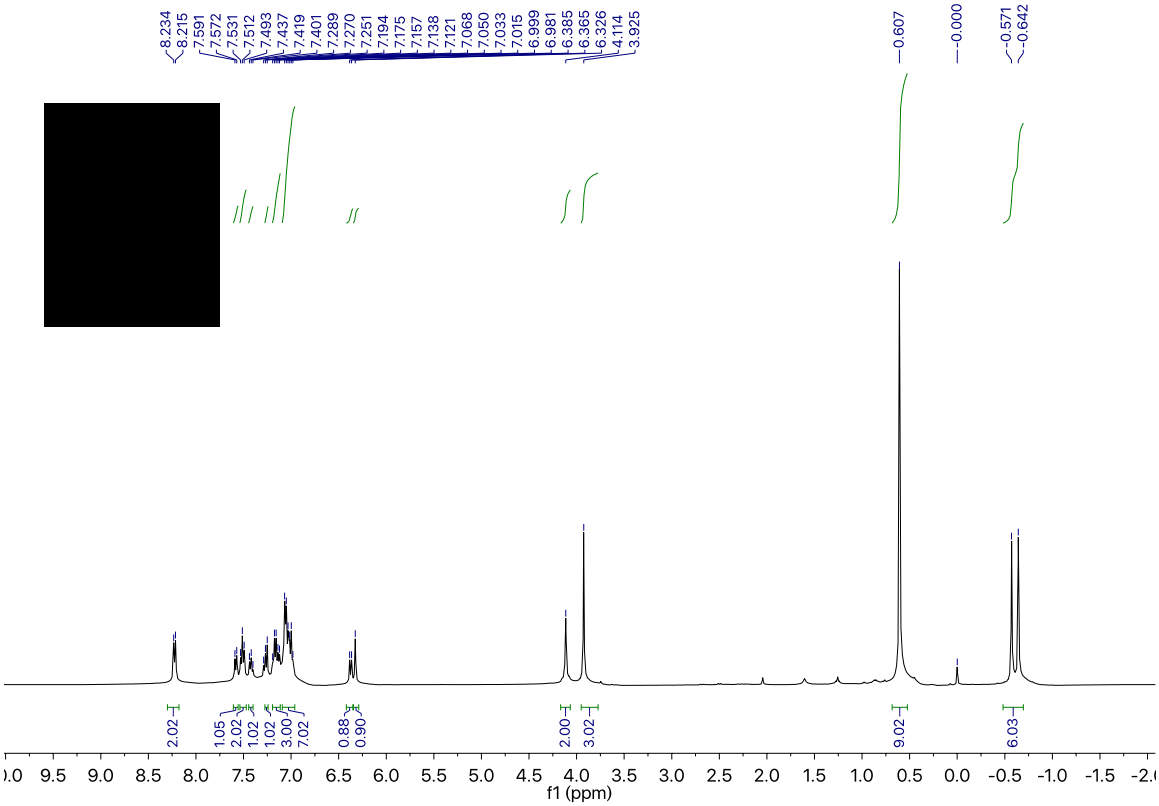

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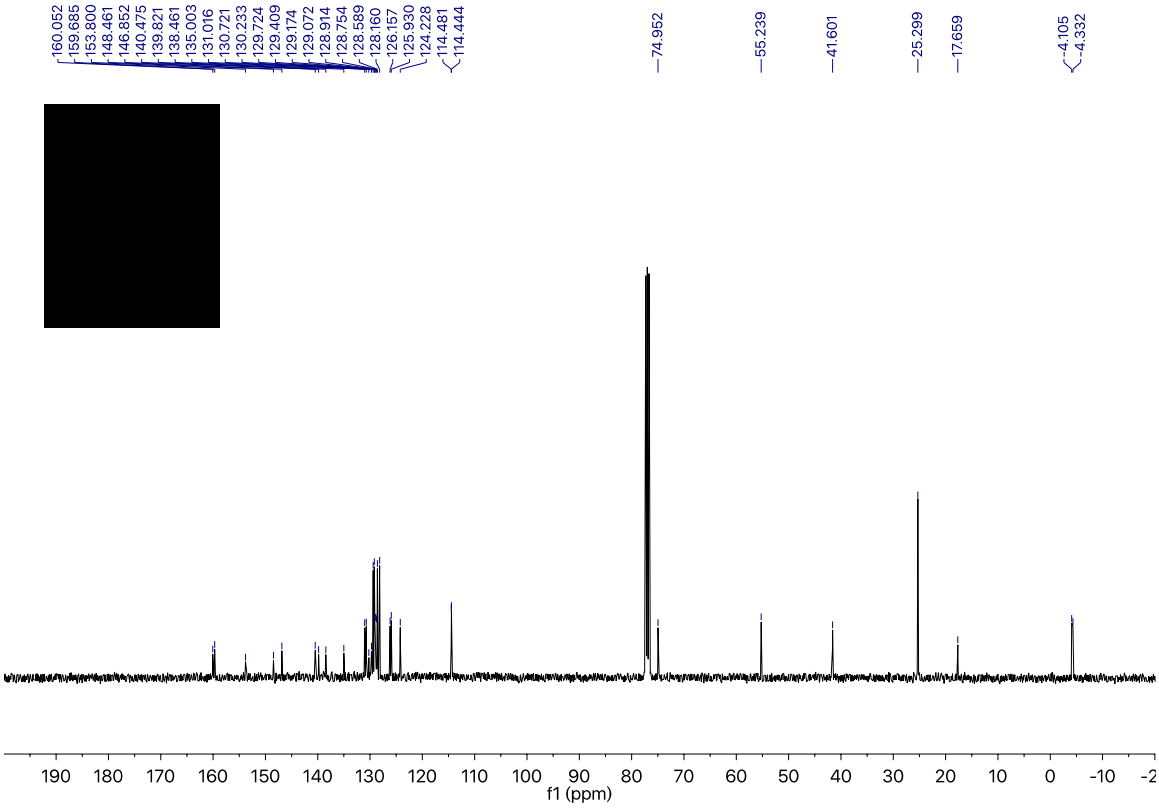

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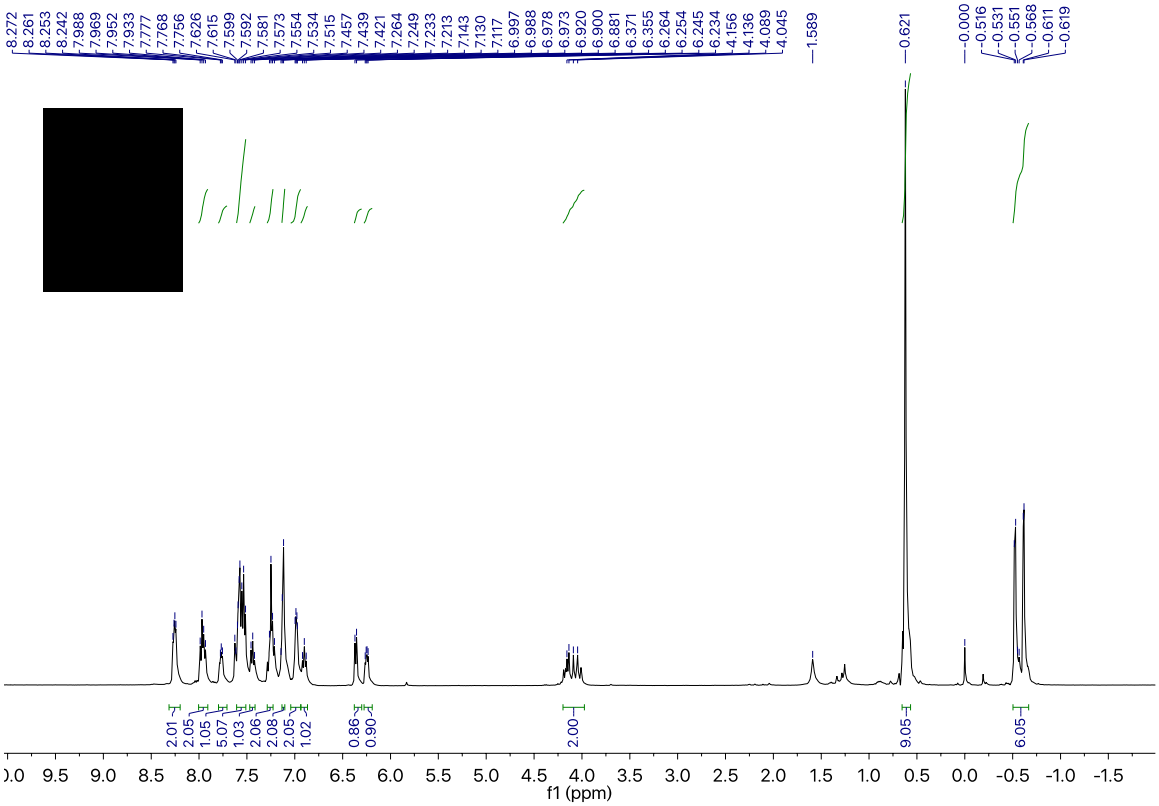

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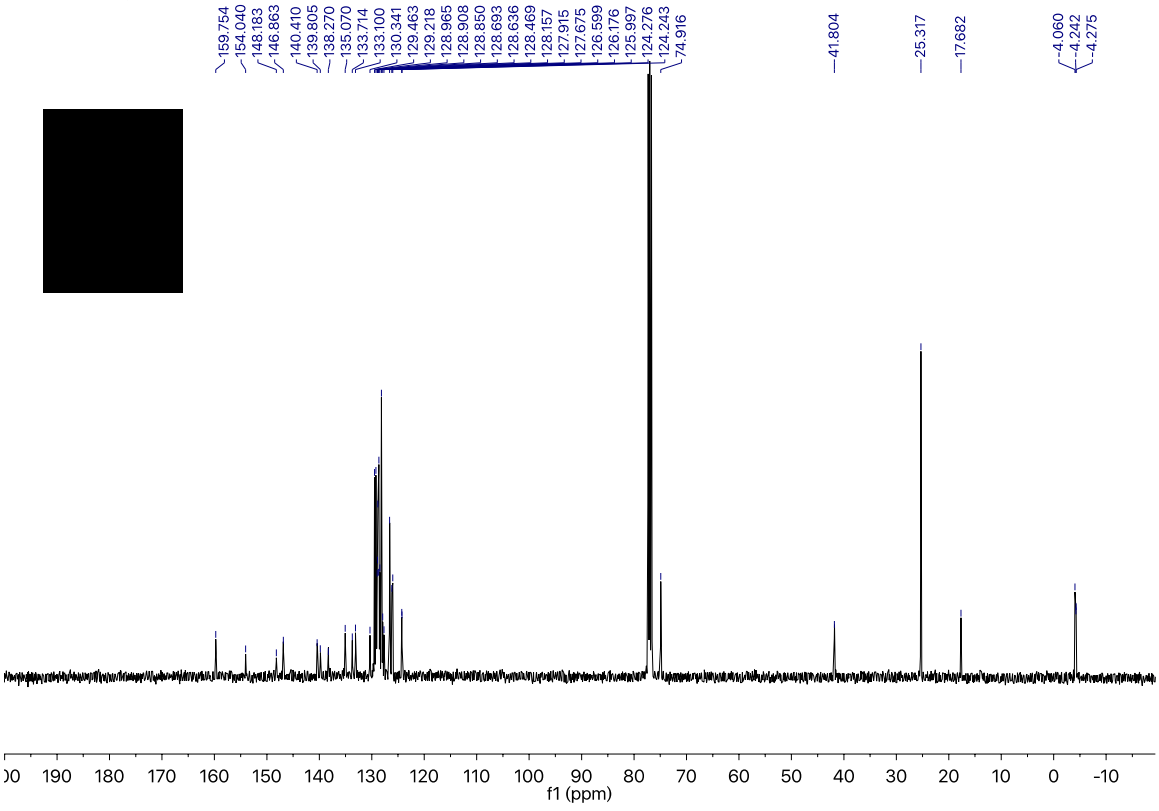

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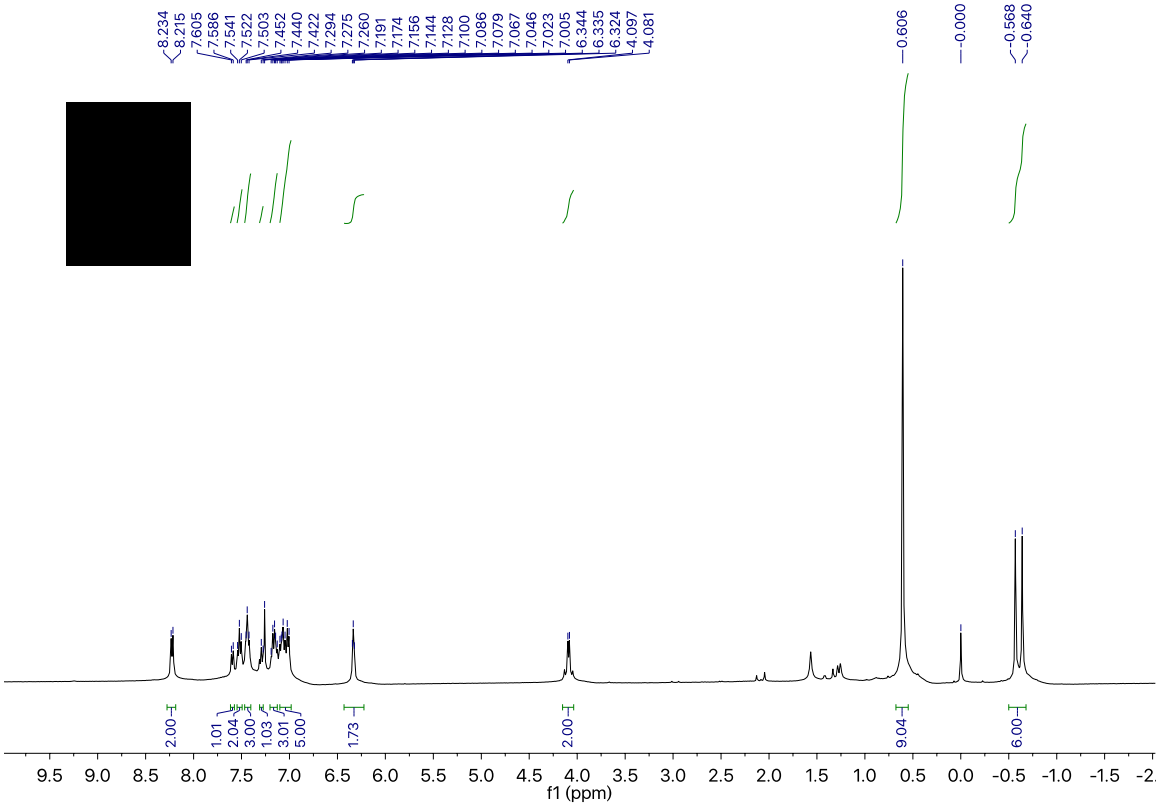

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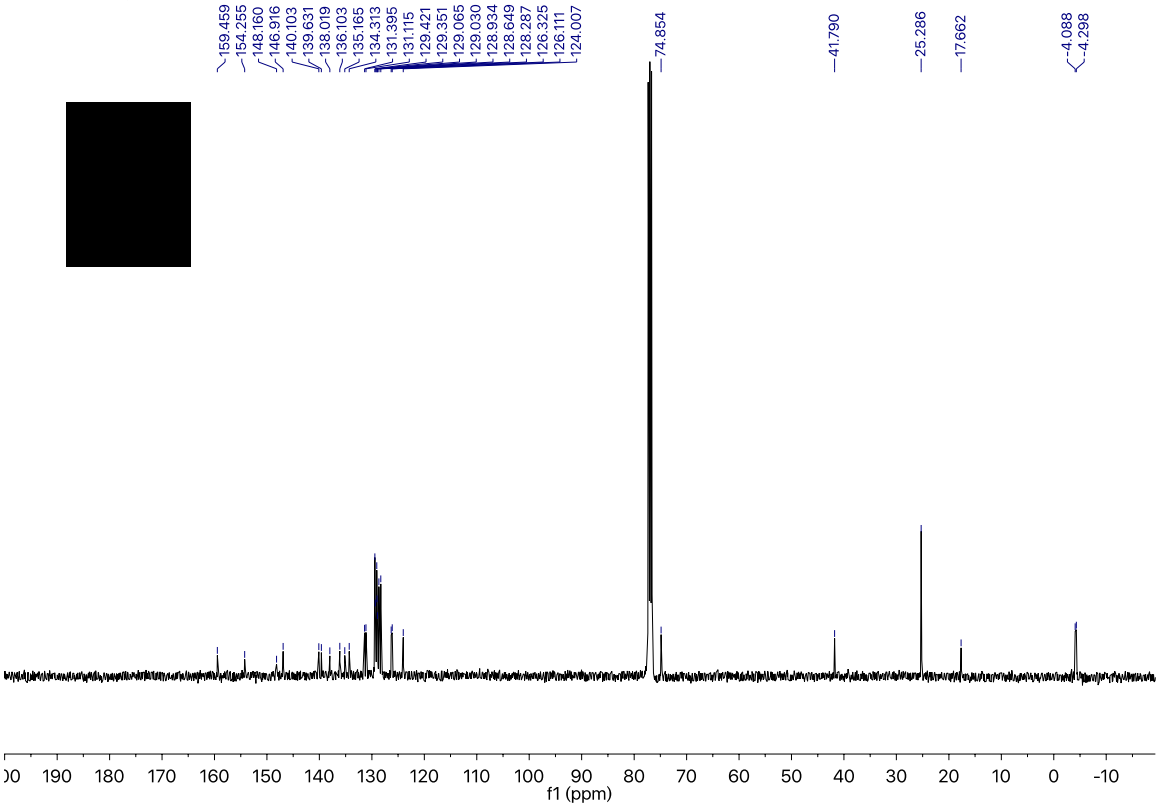

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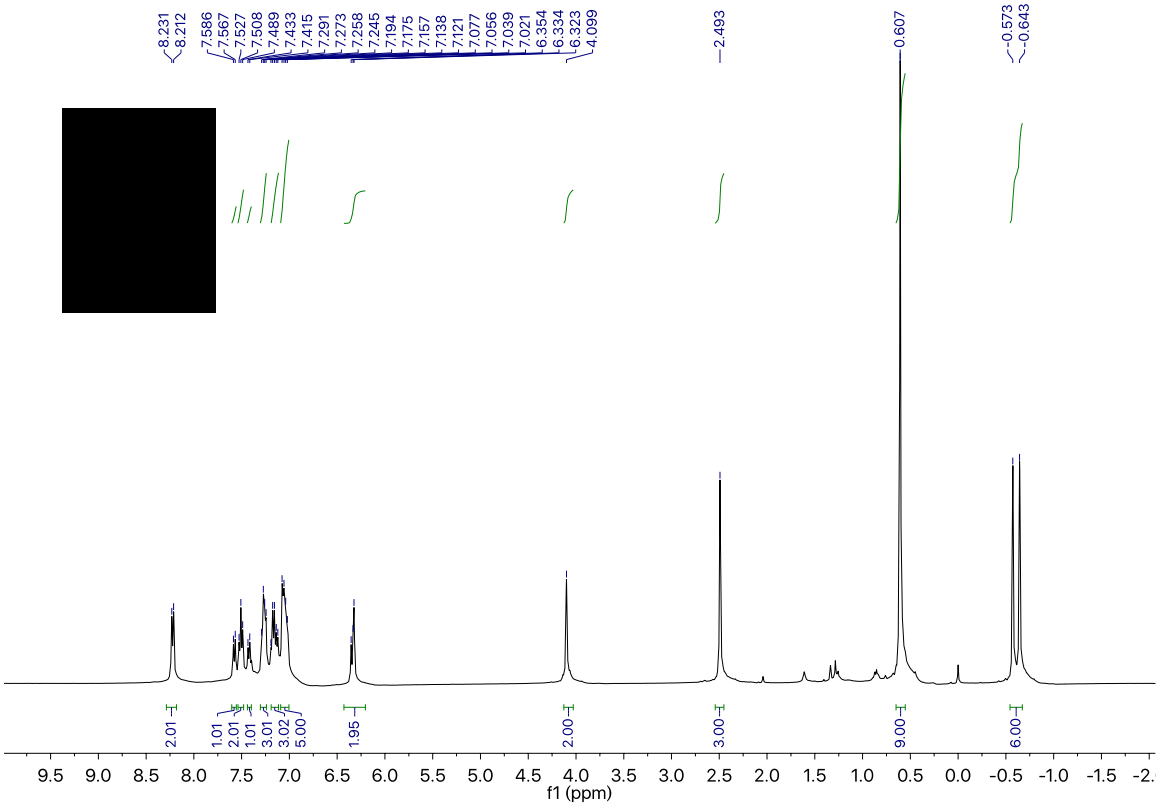

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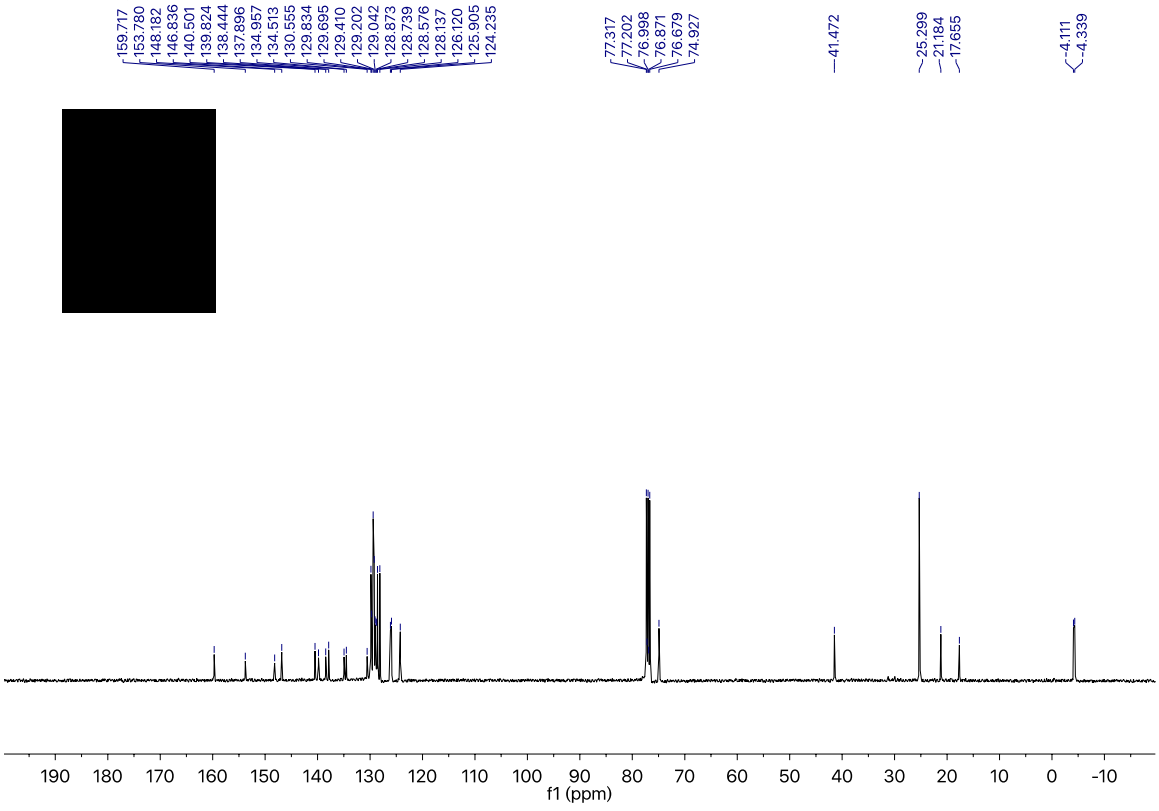

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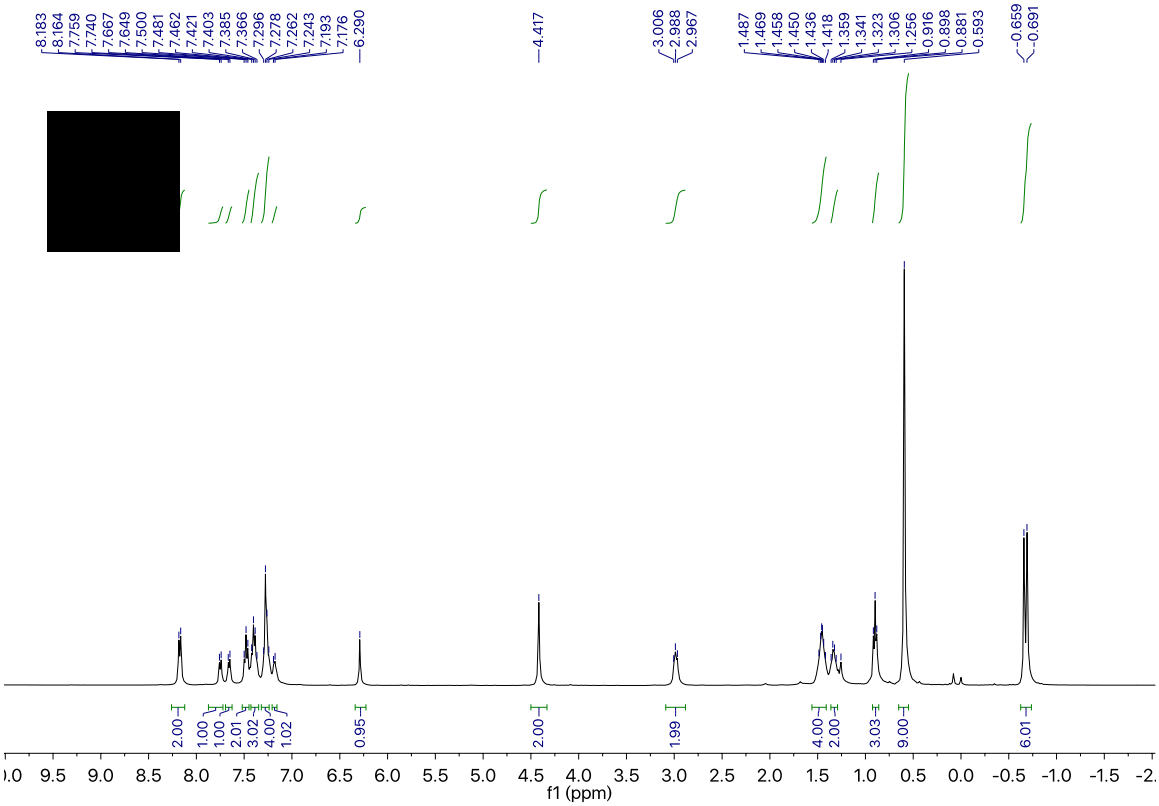

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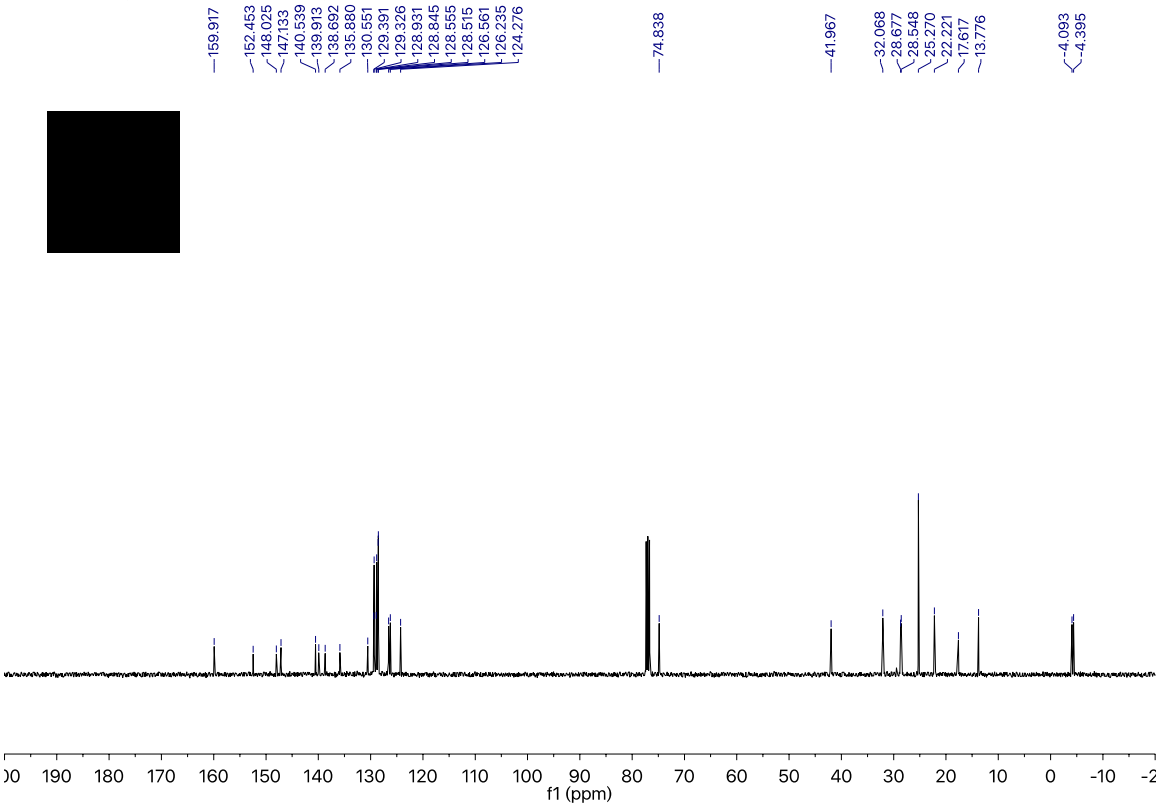

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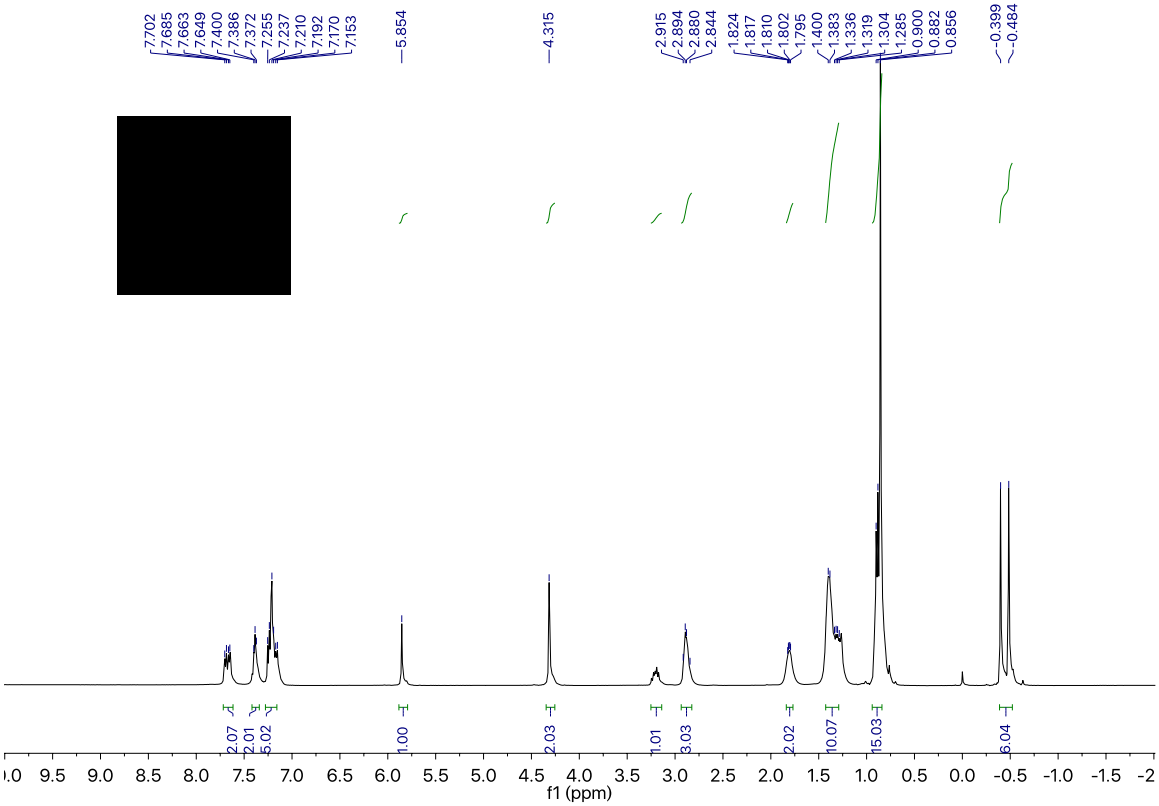

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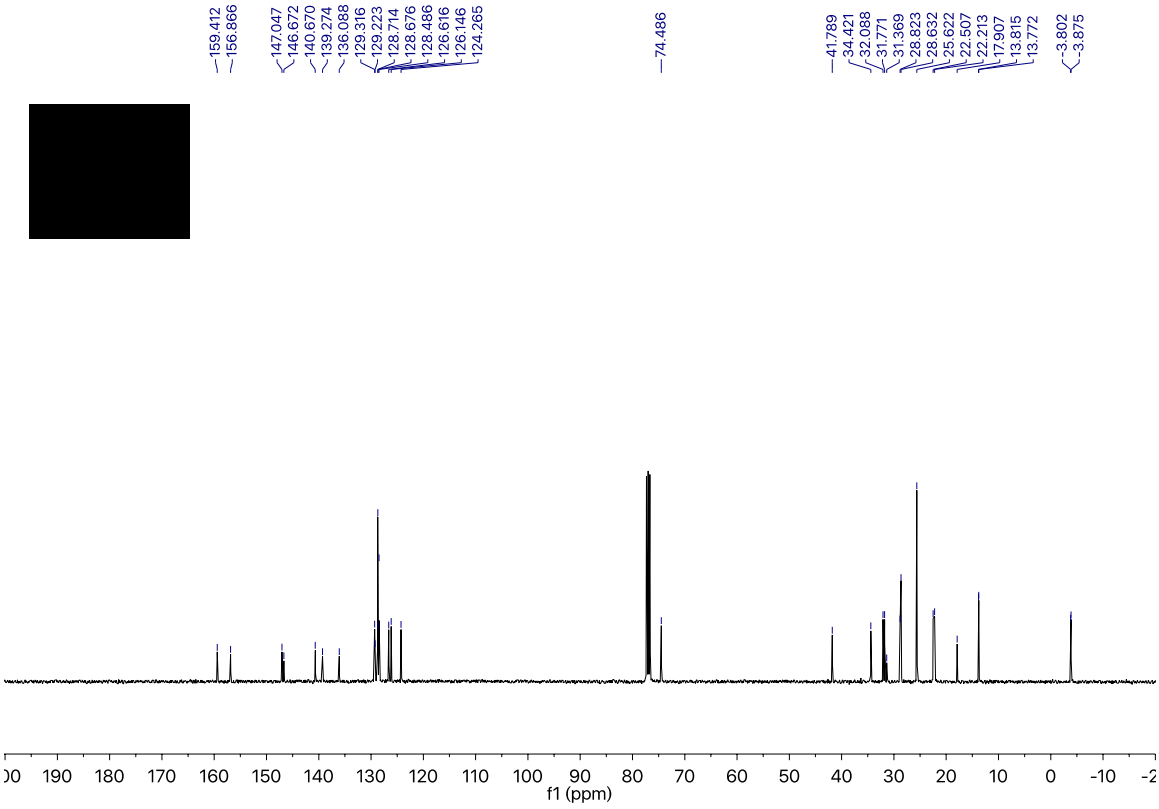

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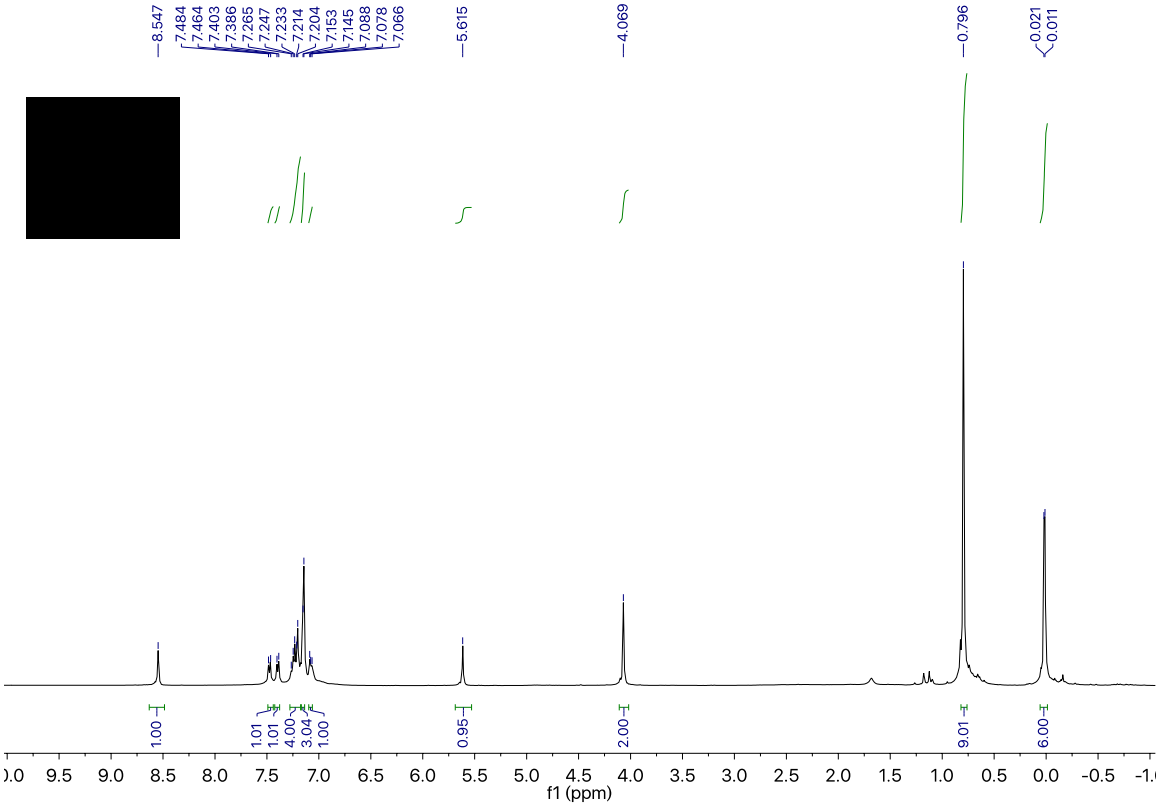

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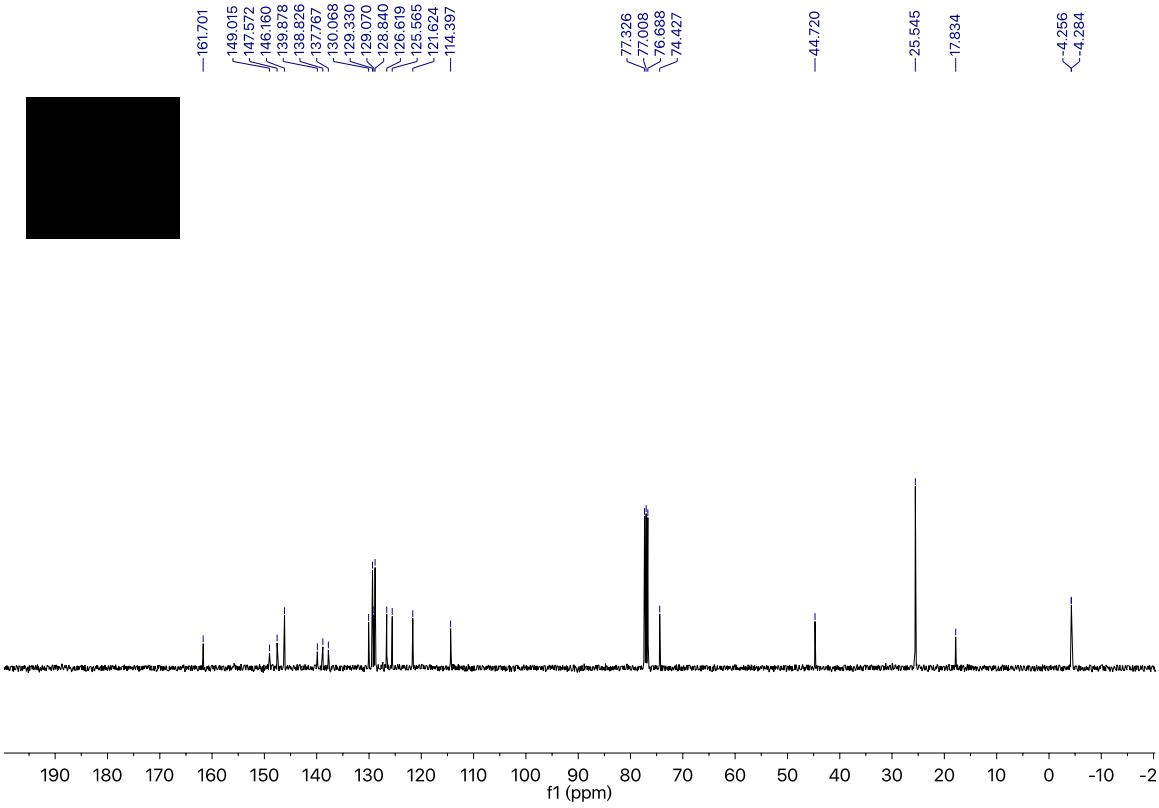

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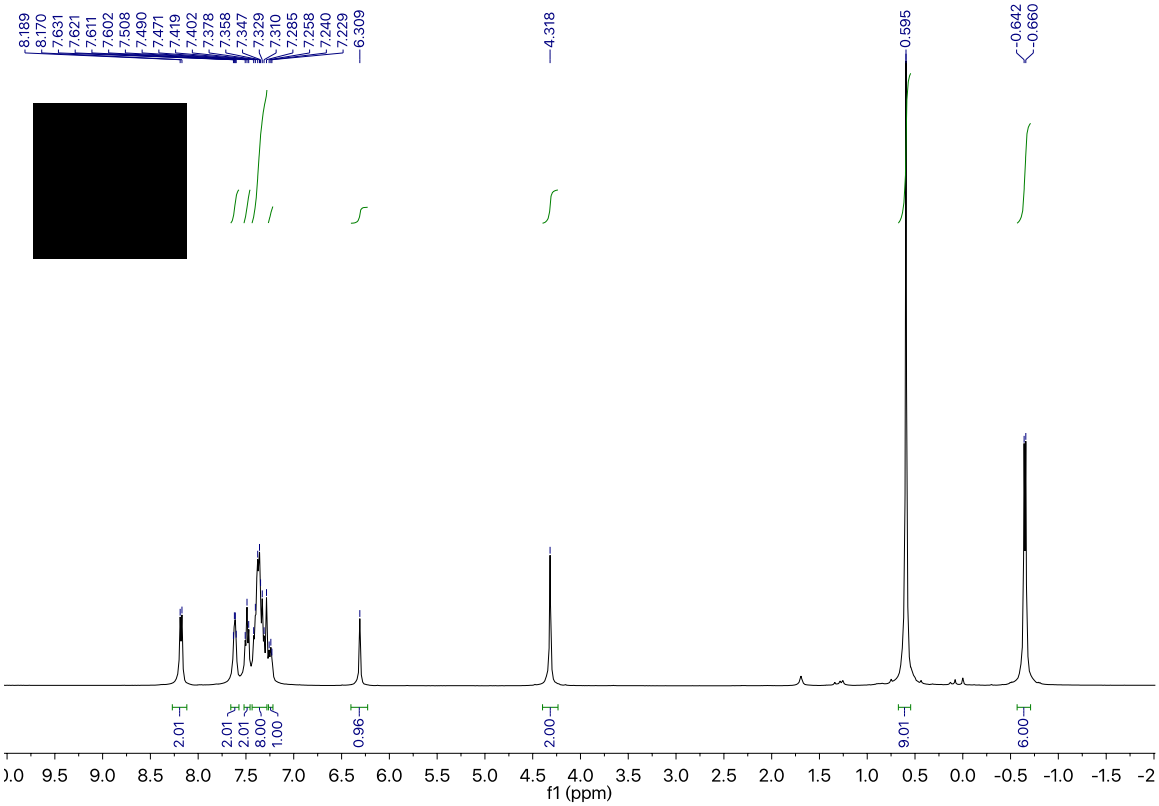

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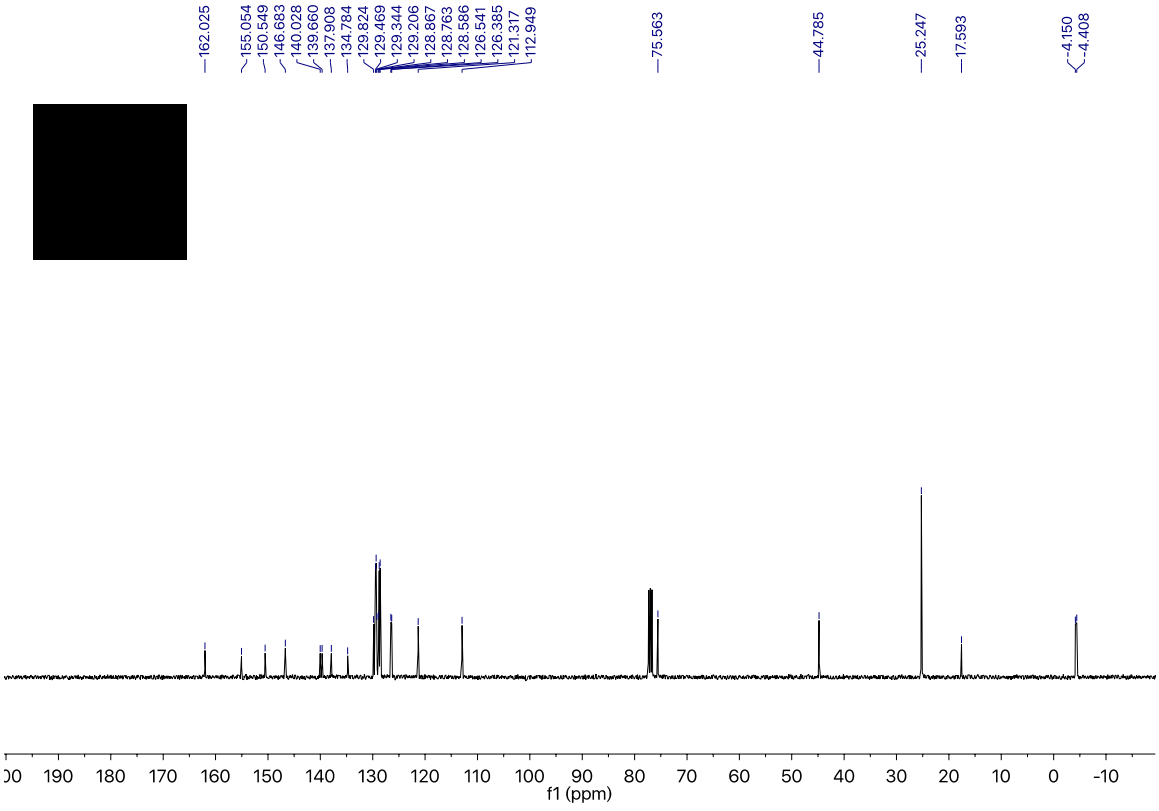

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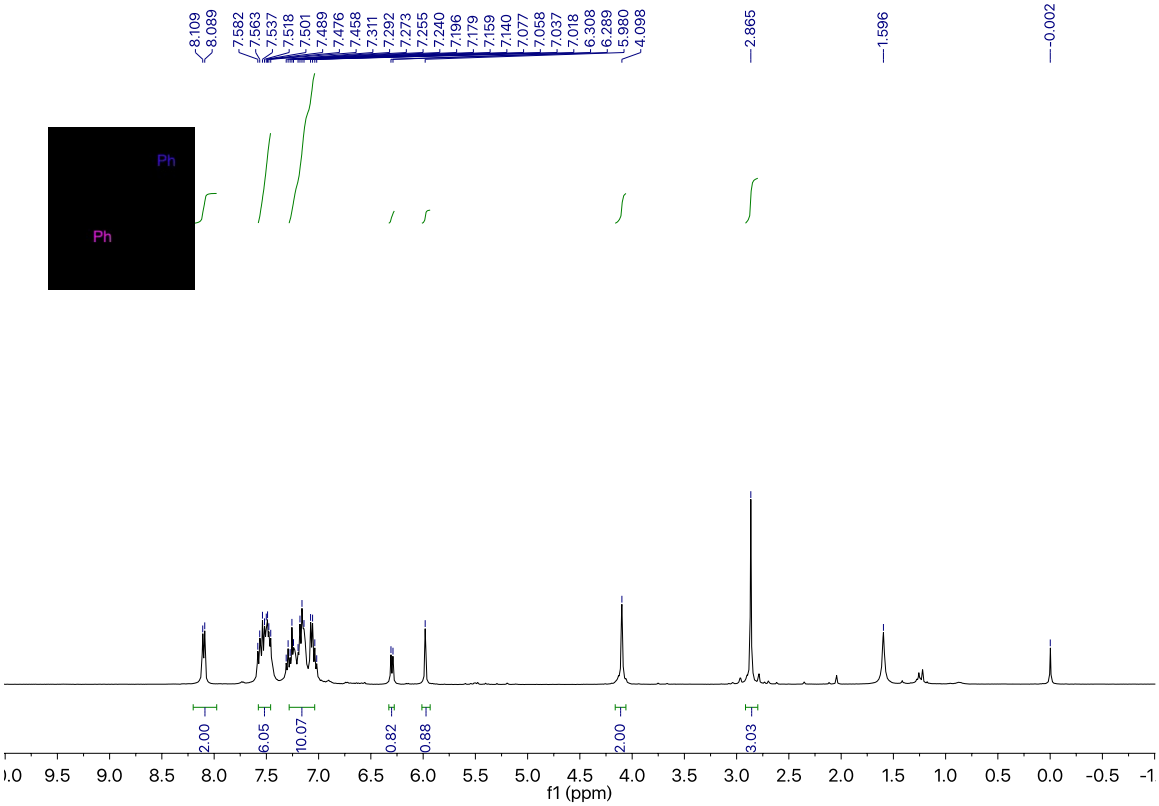

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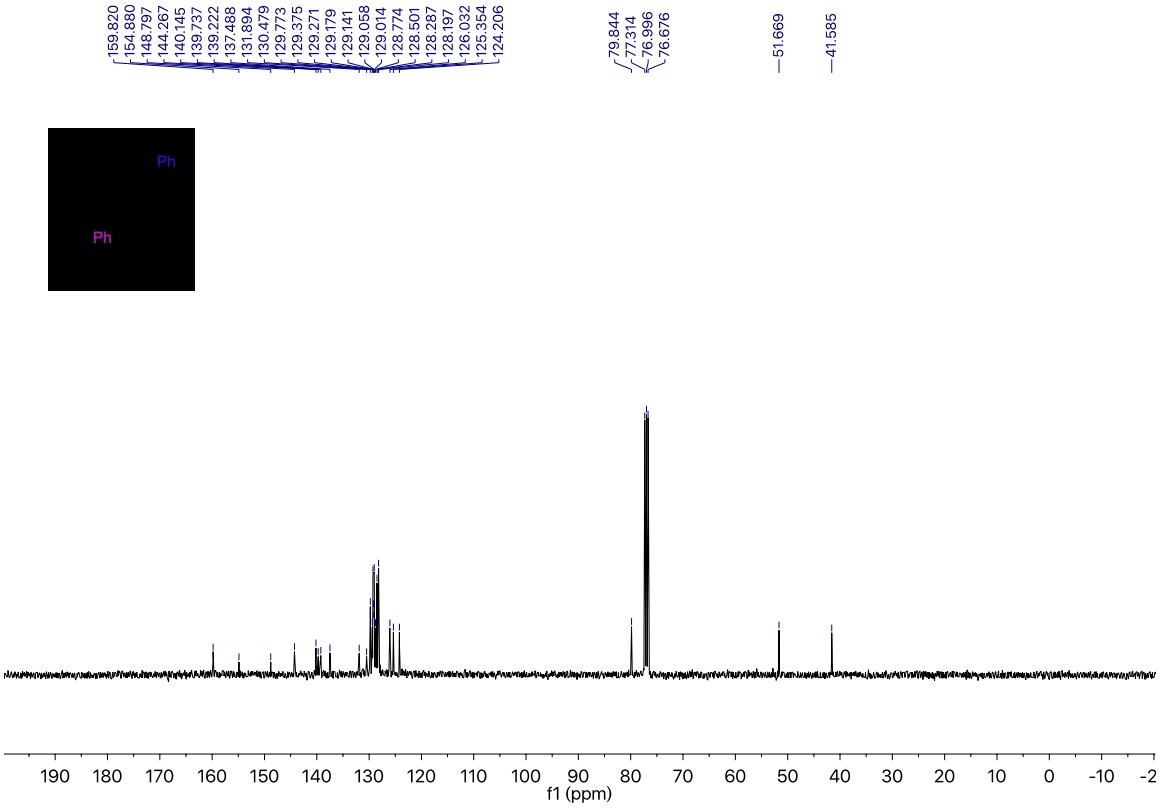

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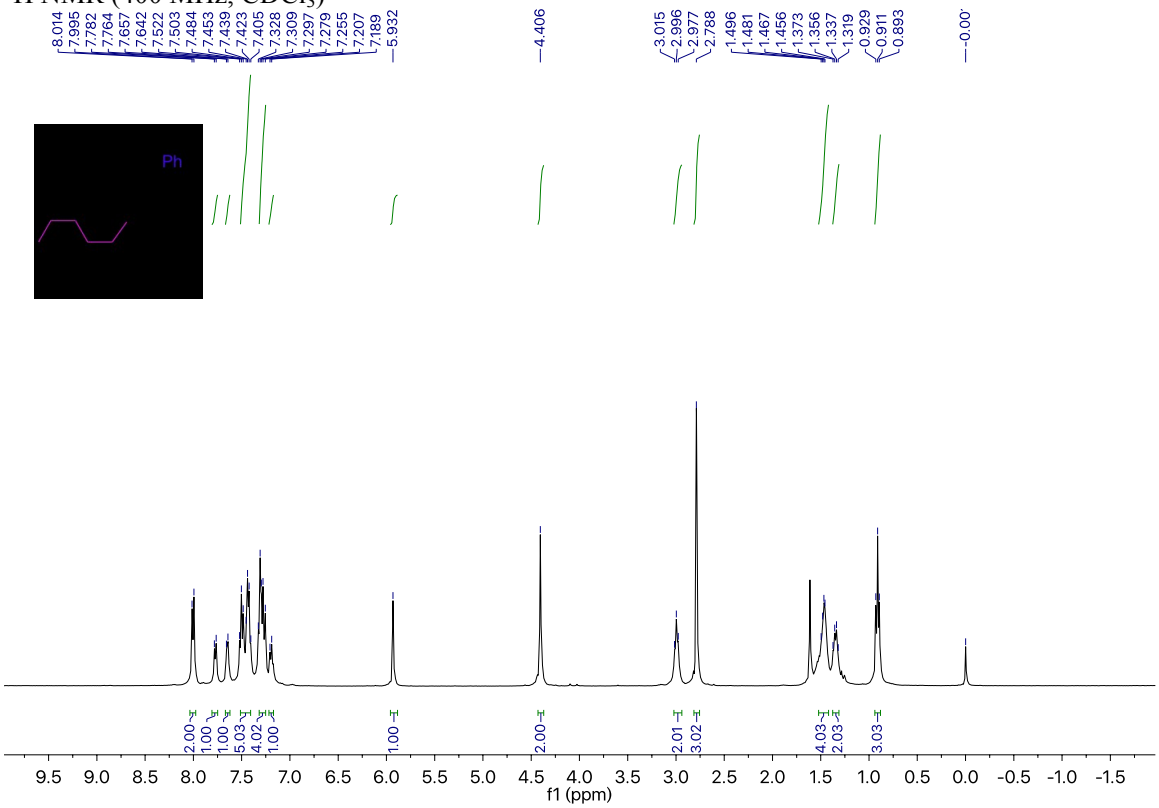

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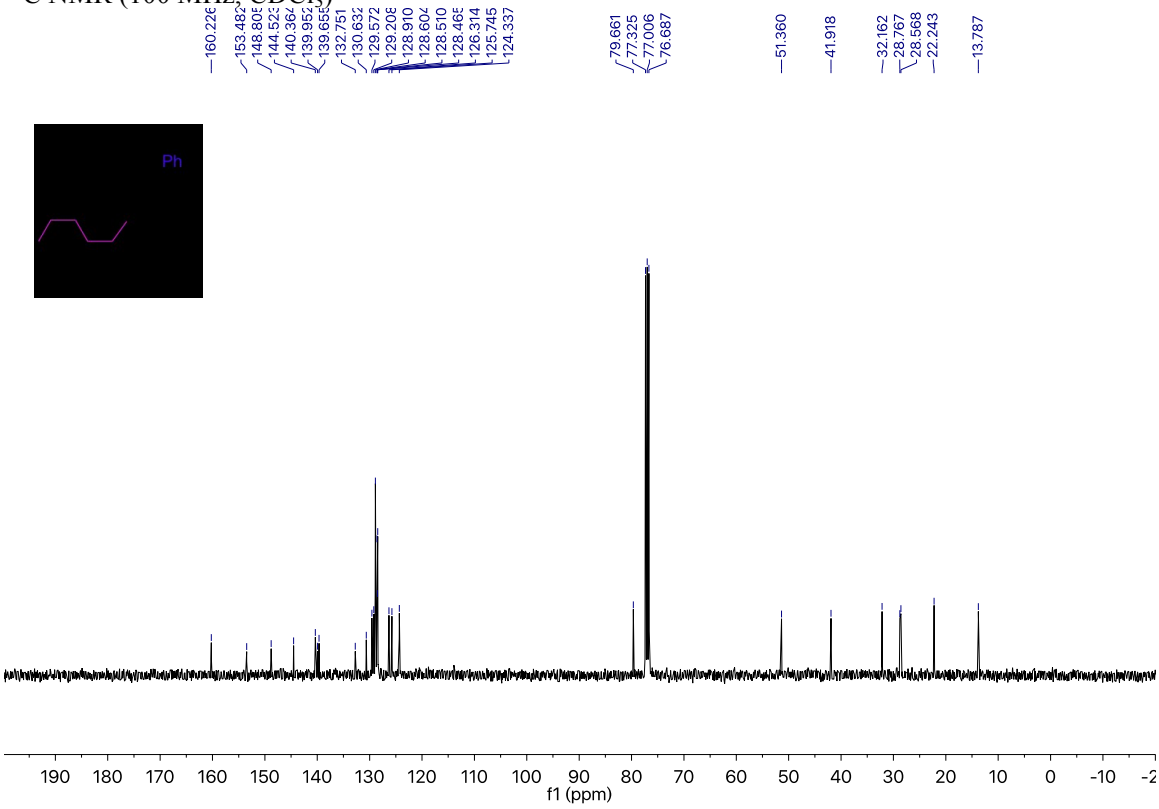

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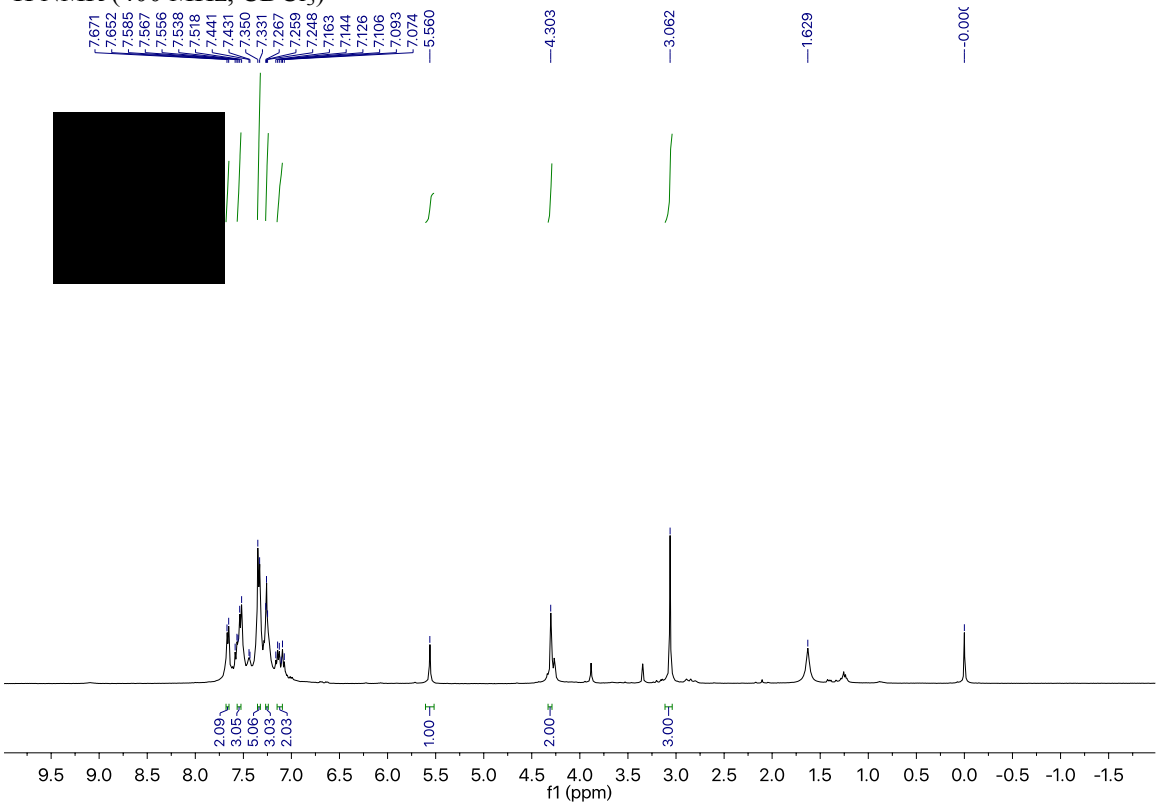

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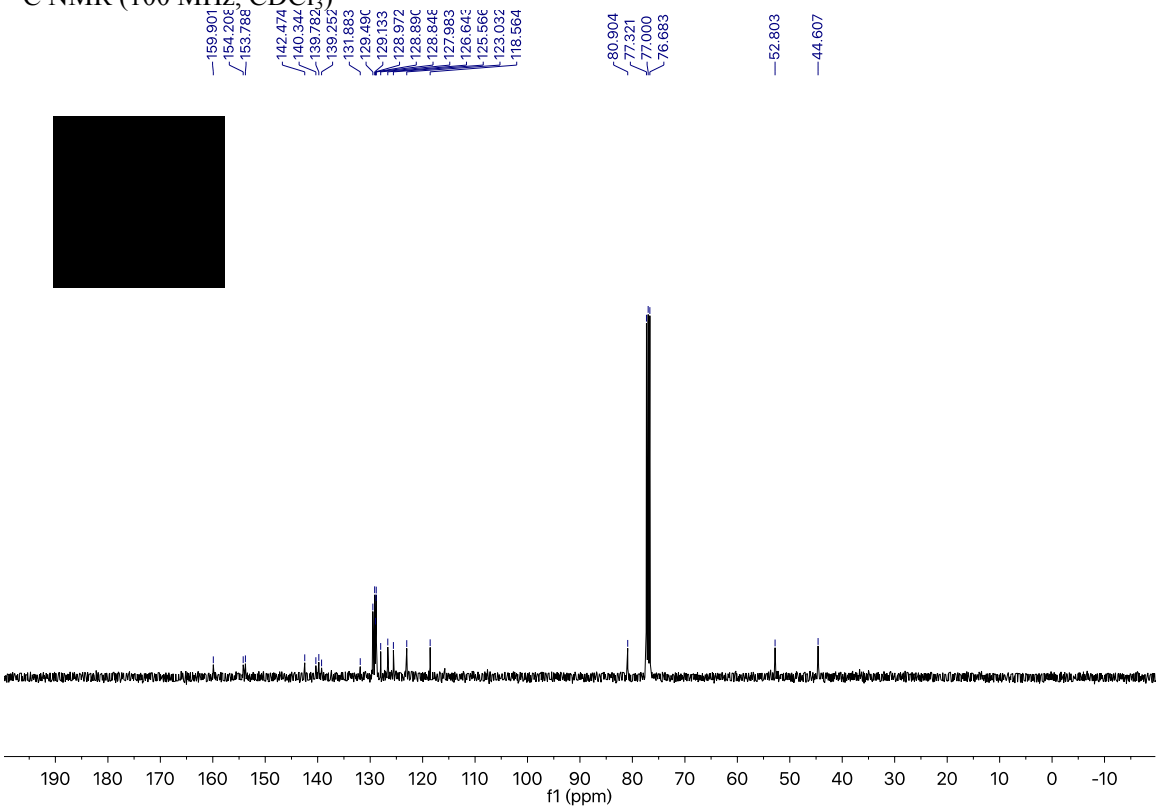

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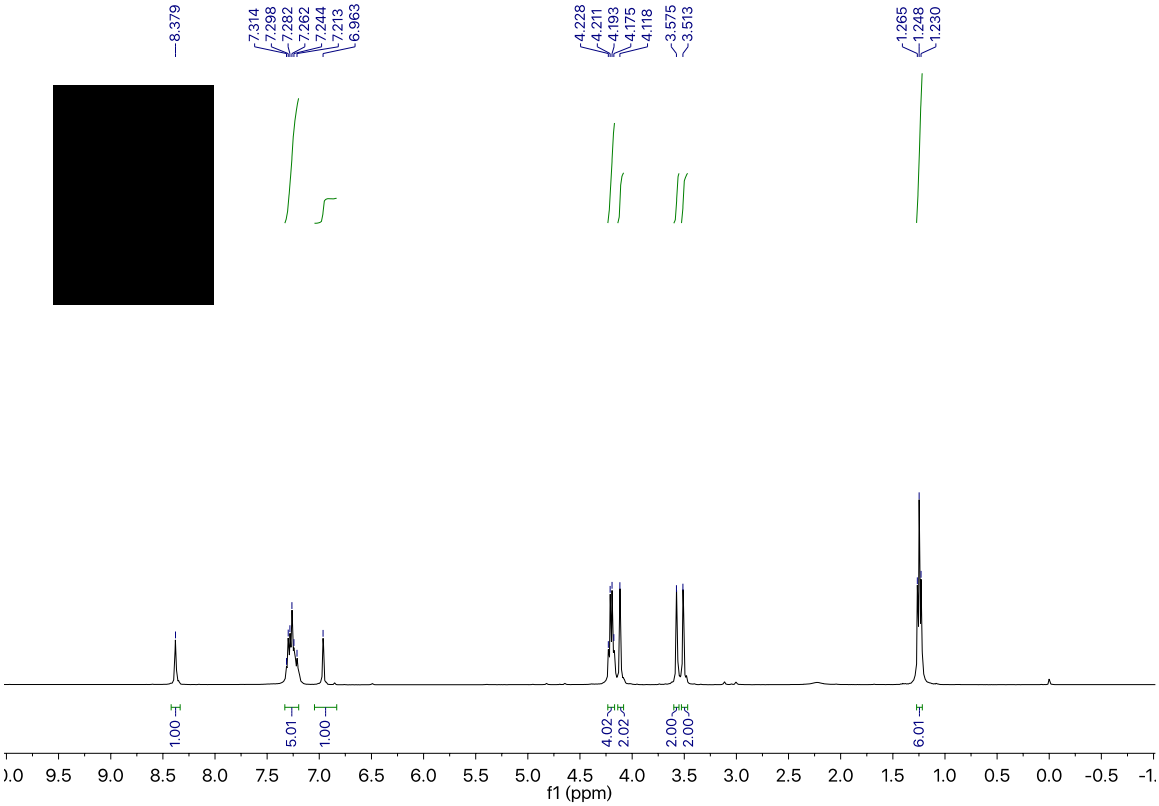

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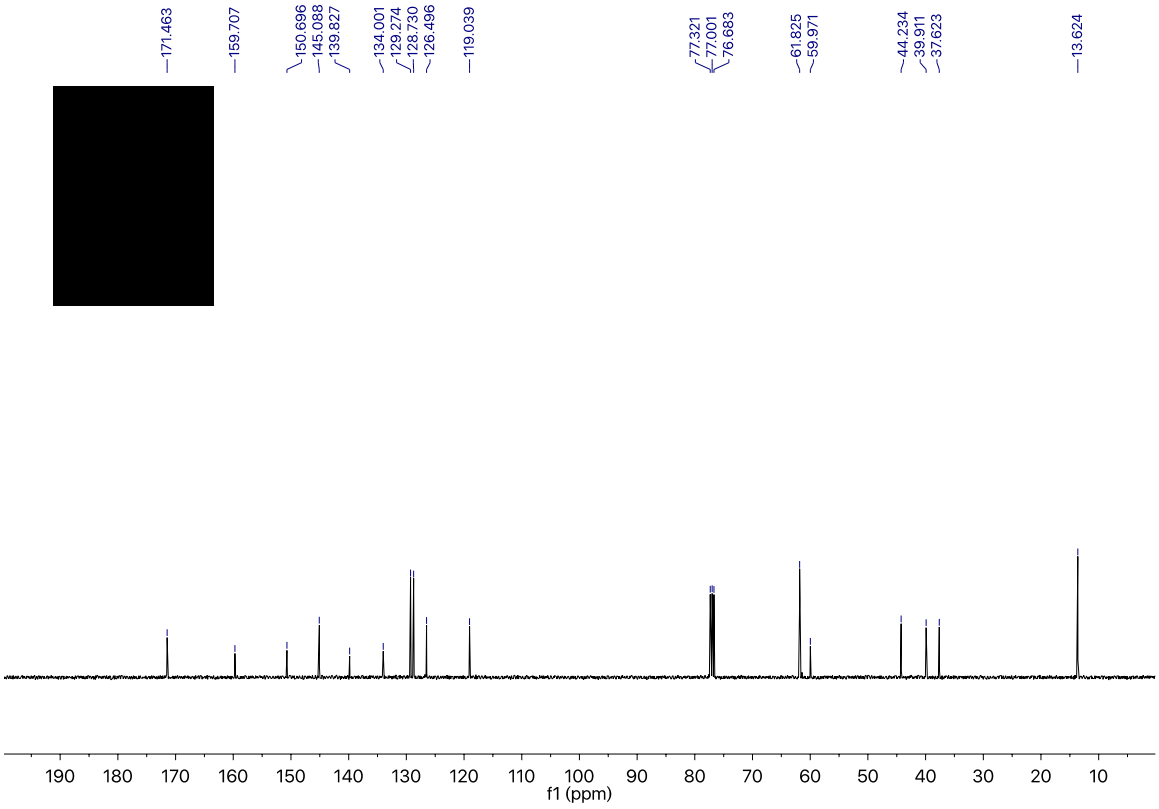

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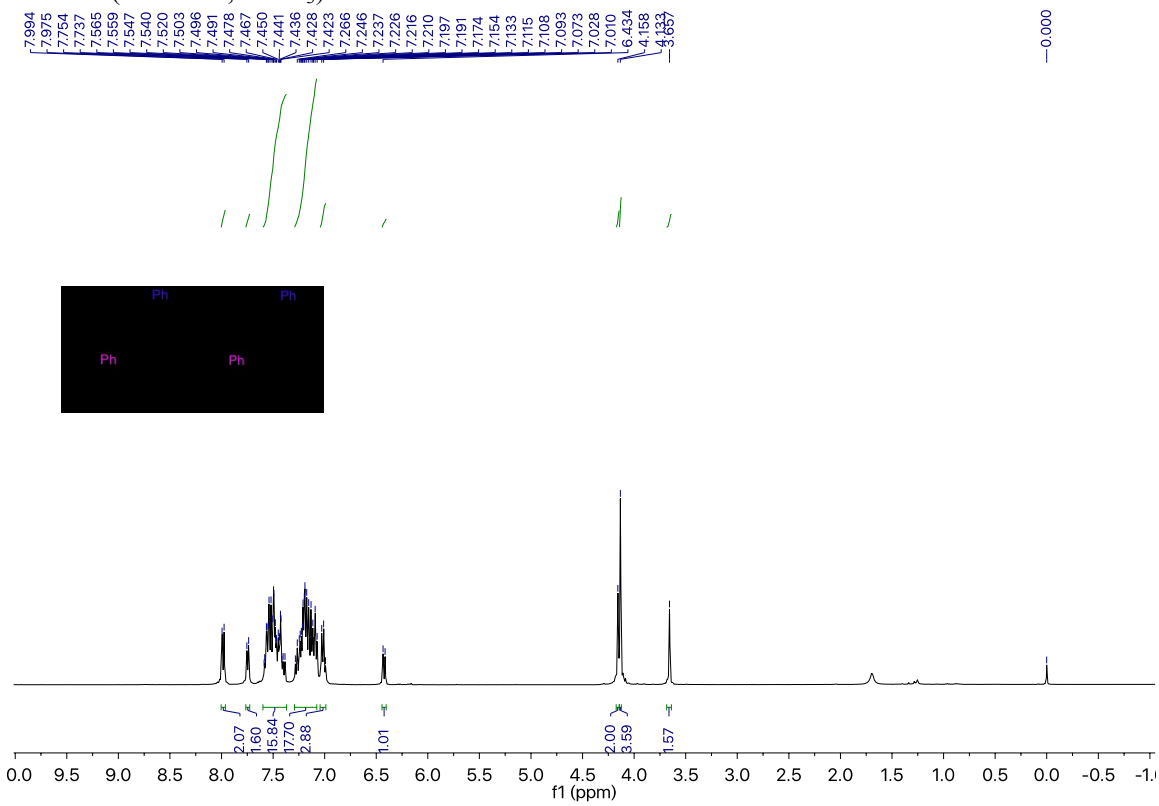

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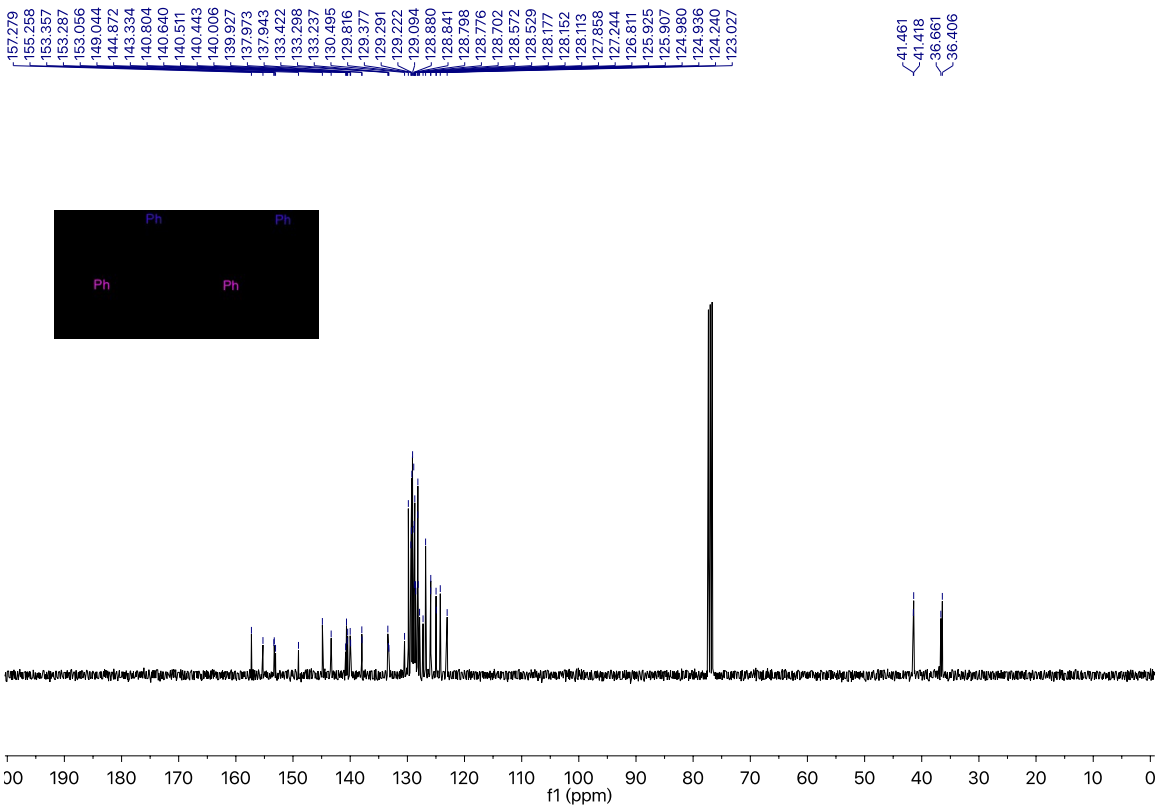

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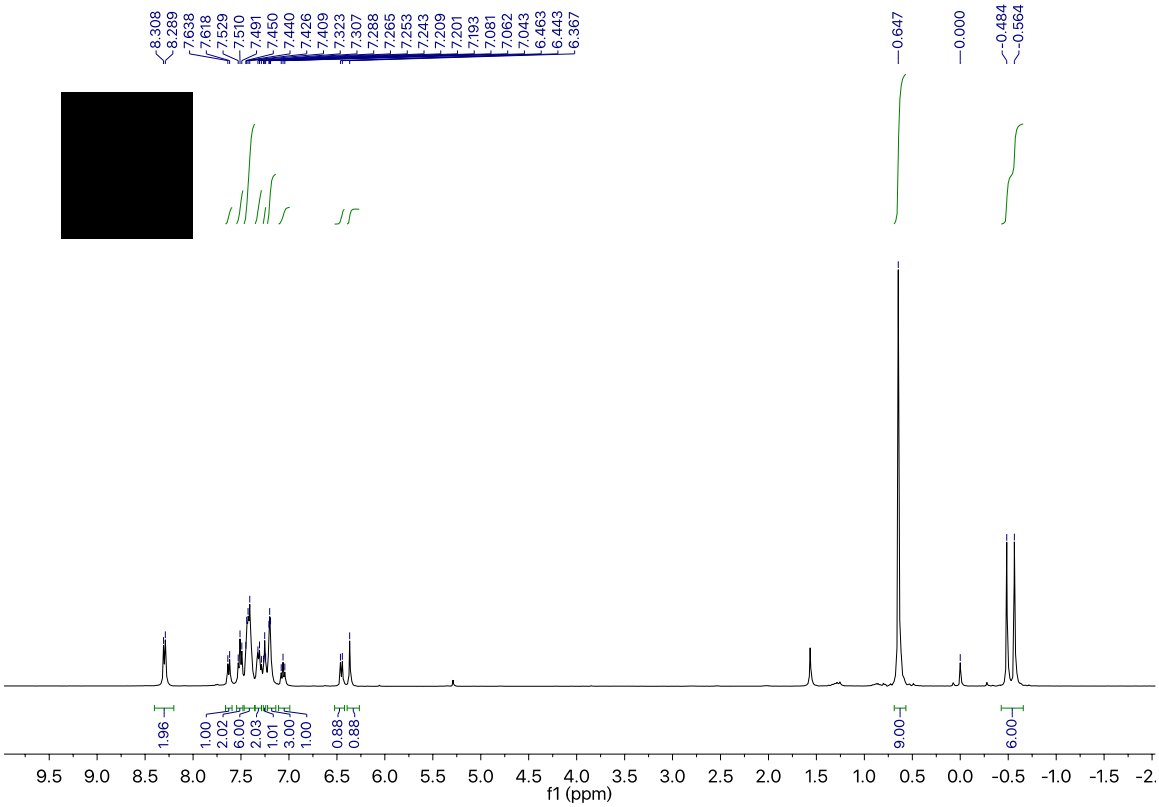

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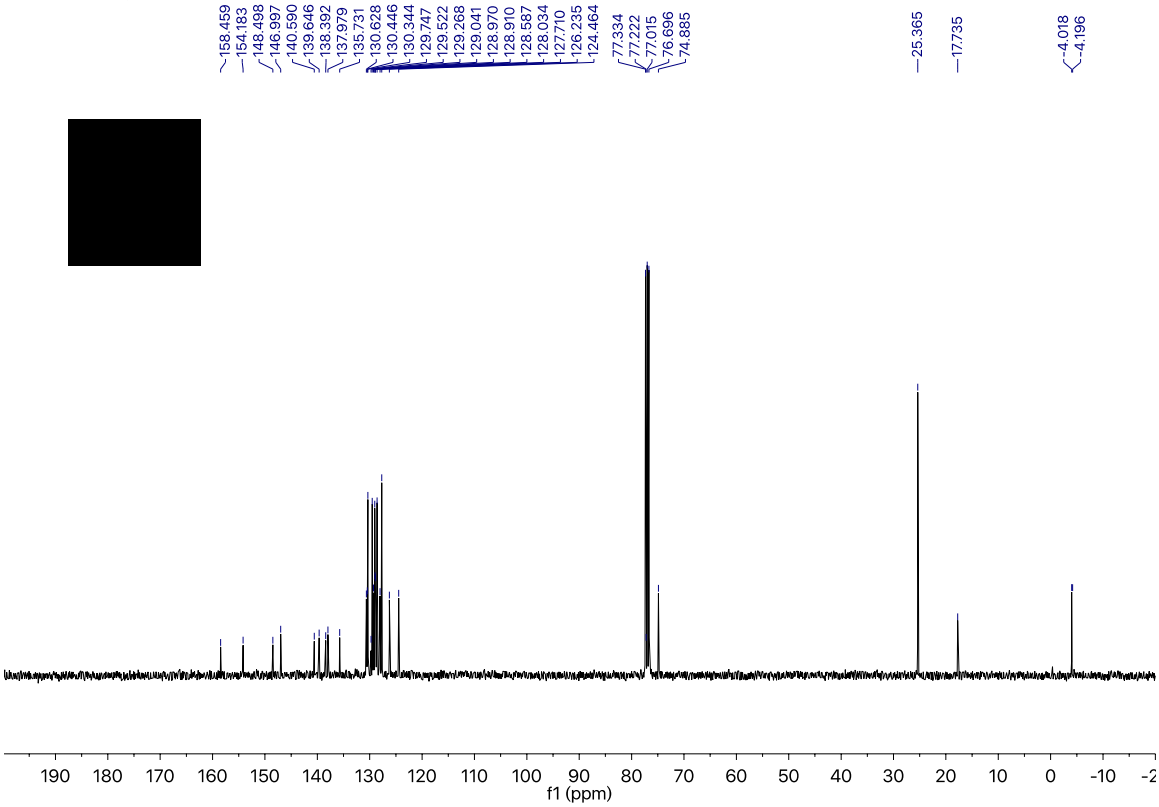

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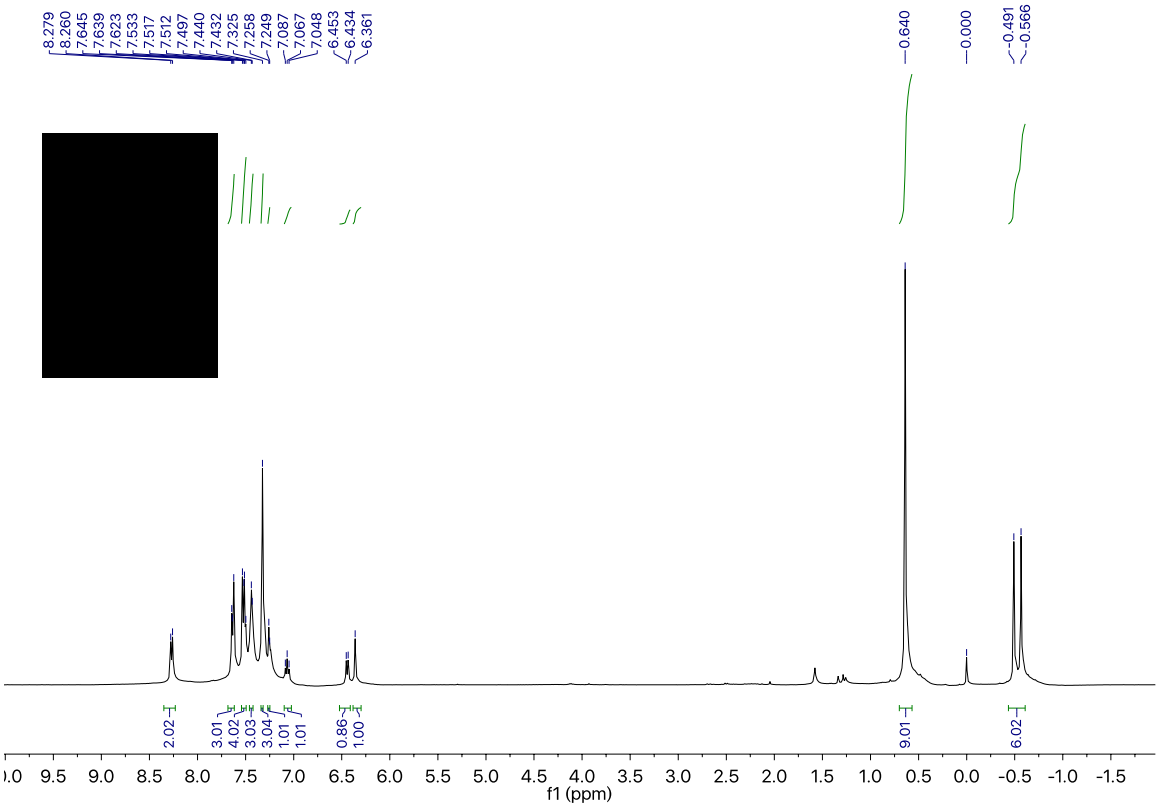

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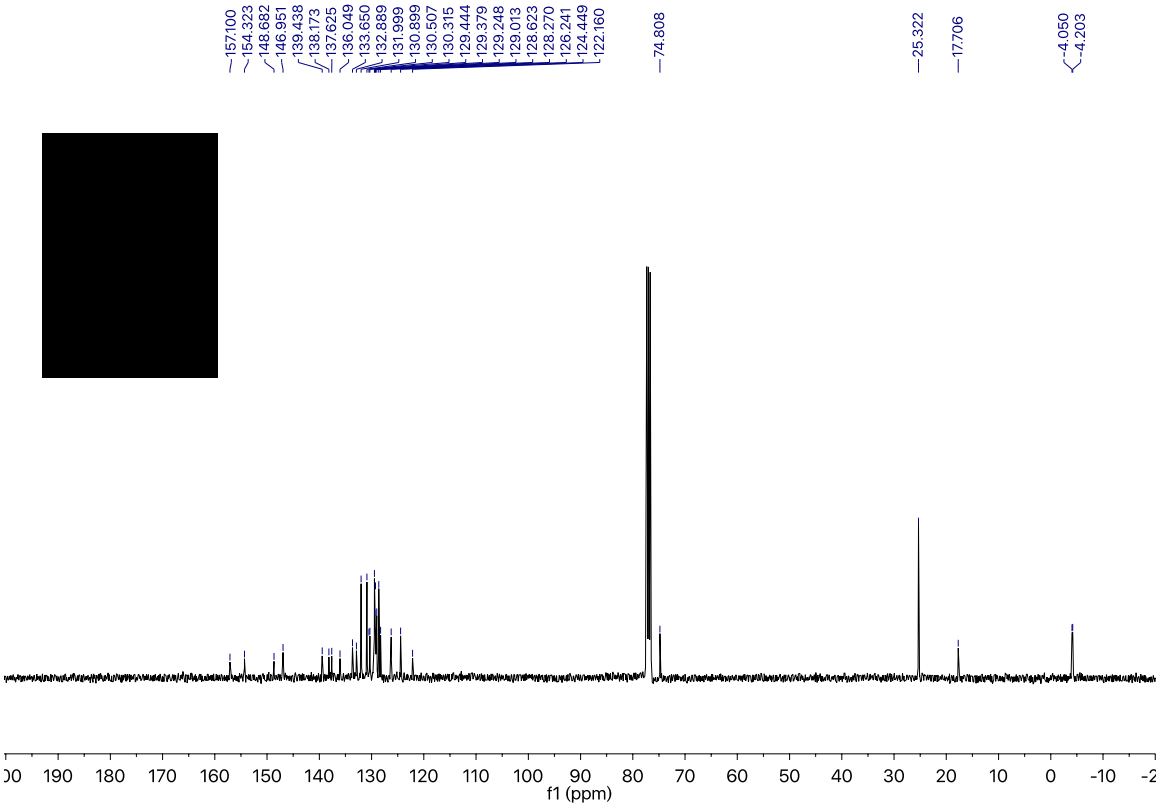

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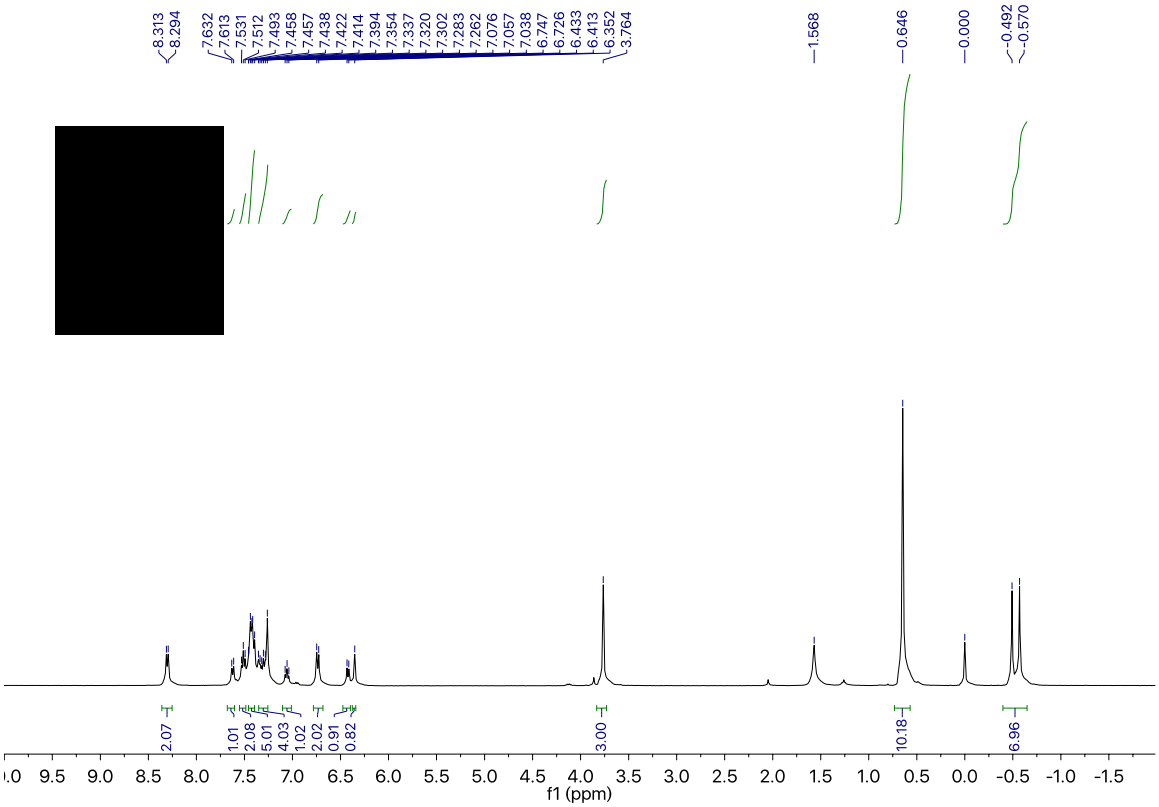

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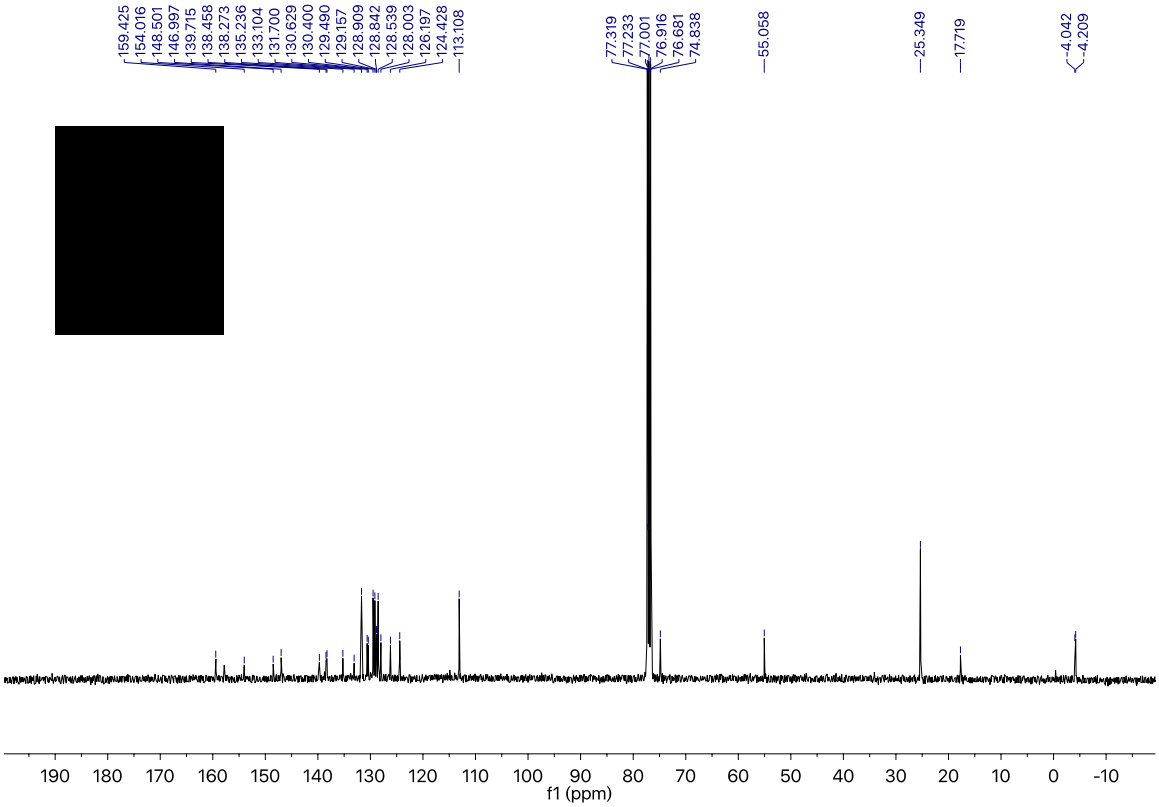
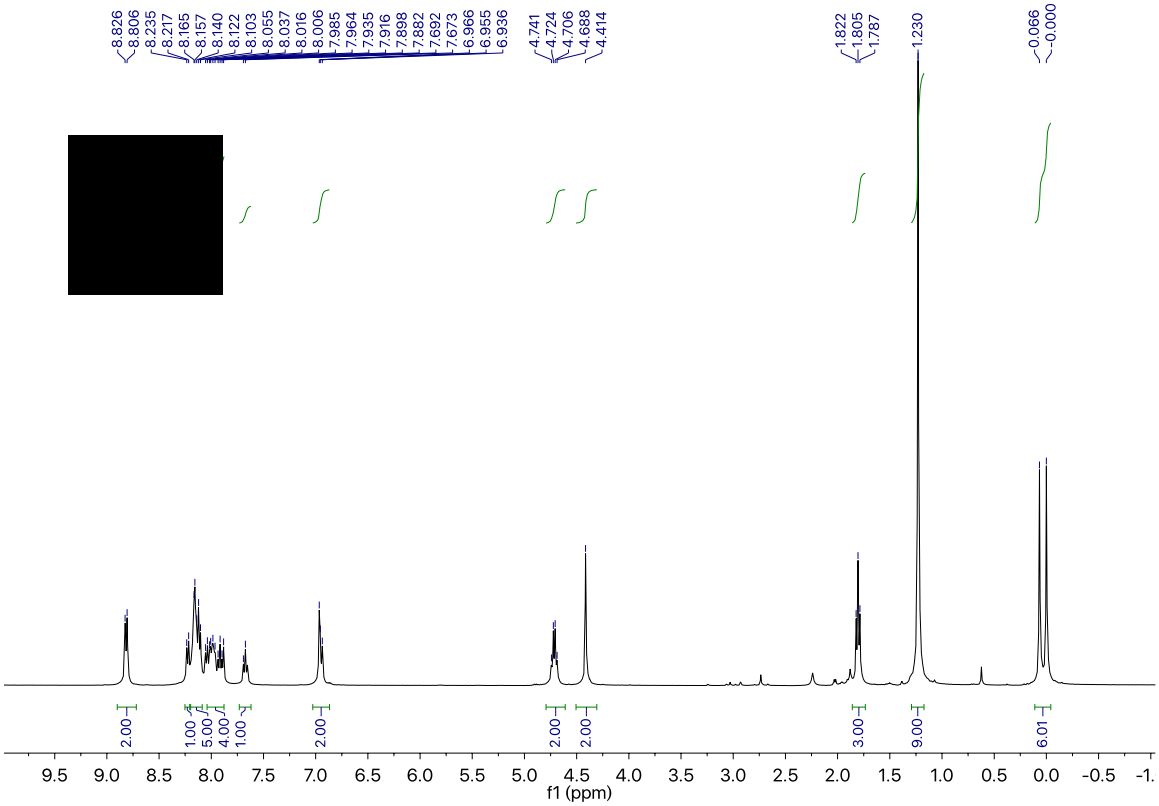
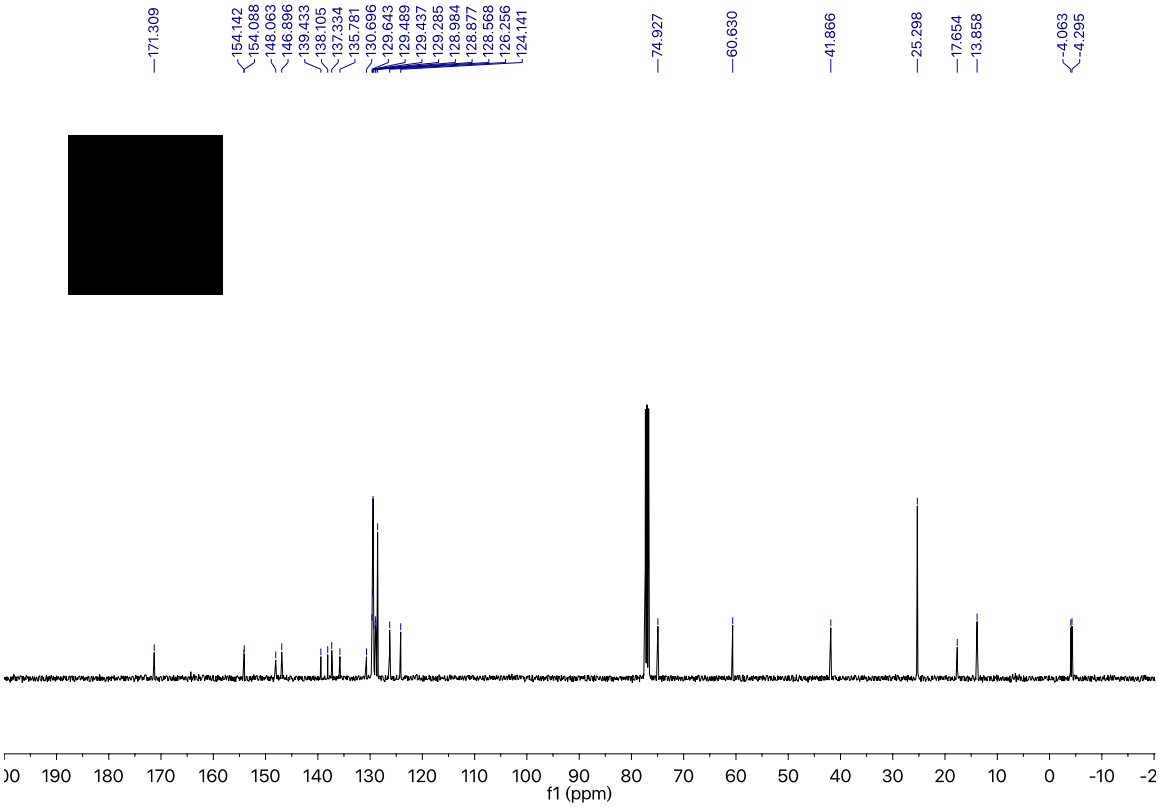


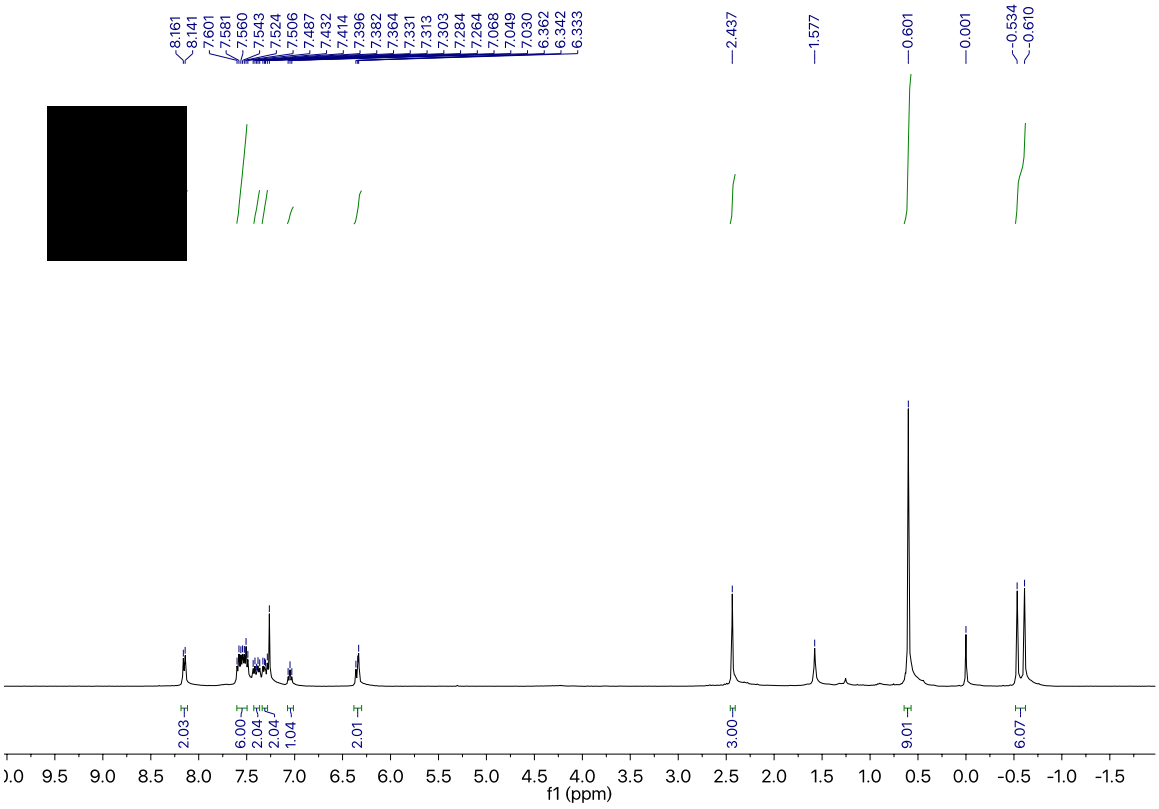
^{1}H NMR (400 MHz, $CDCl_3$)



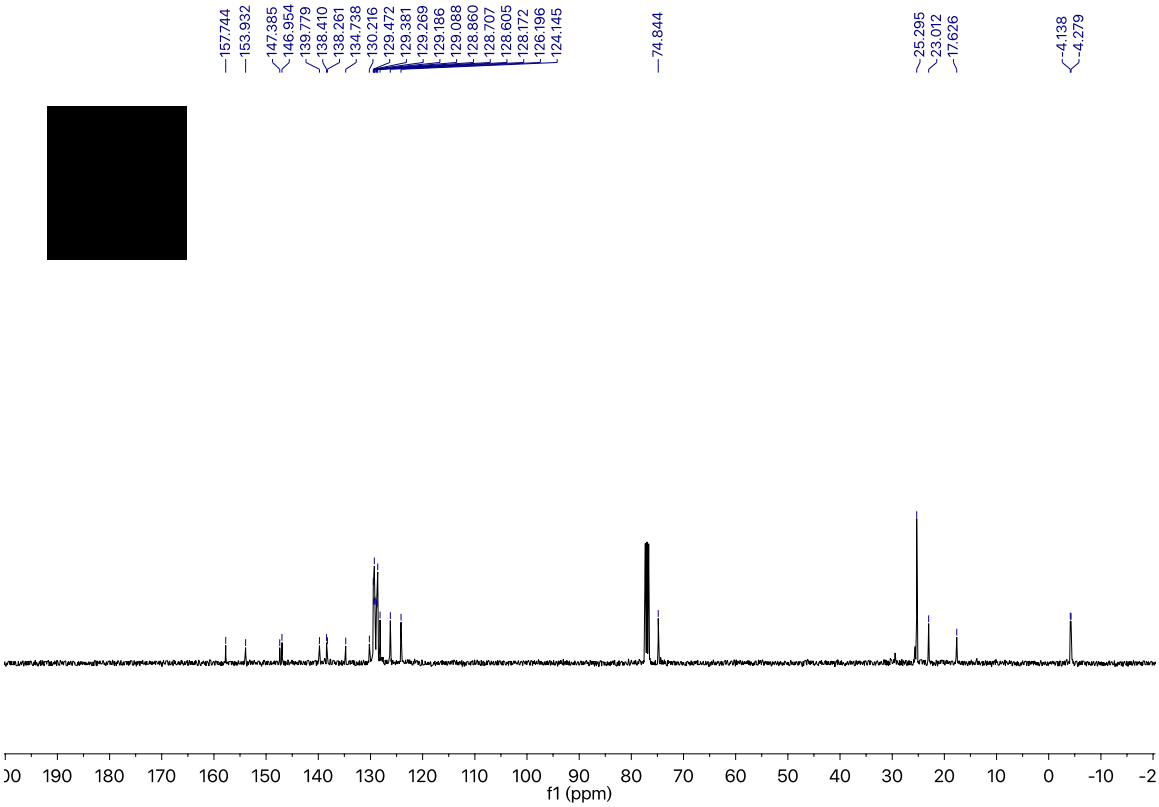
^{13}C NMR (100 MHz, $CDCl_3$)



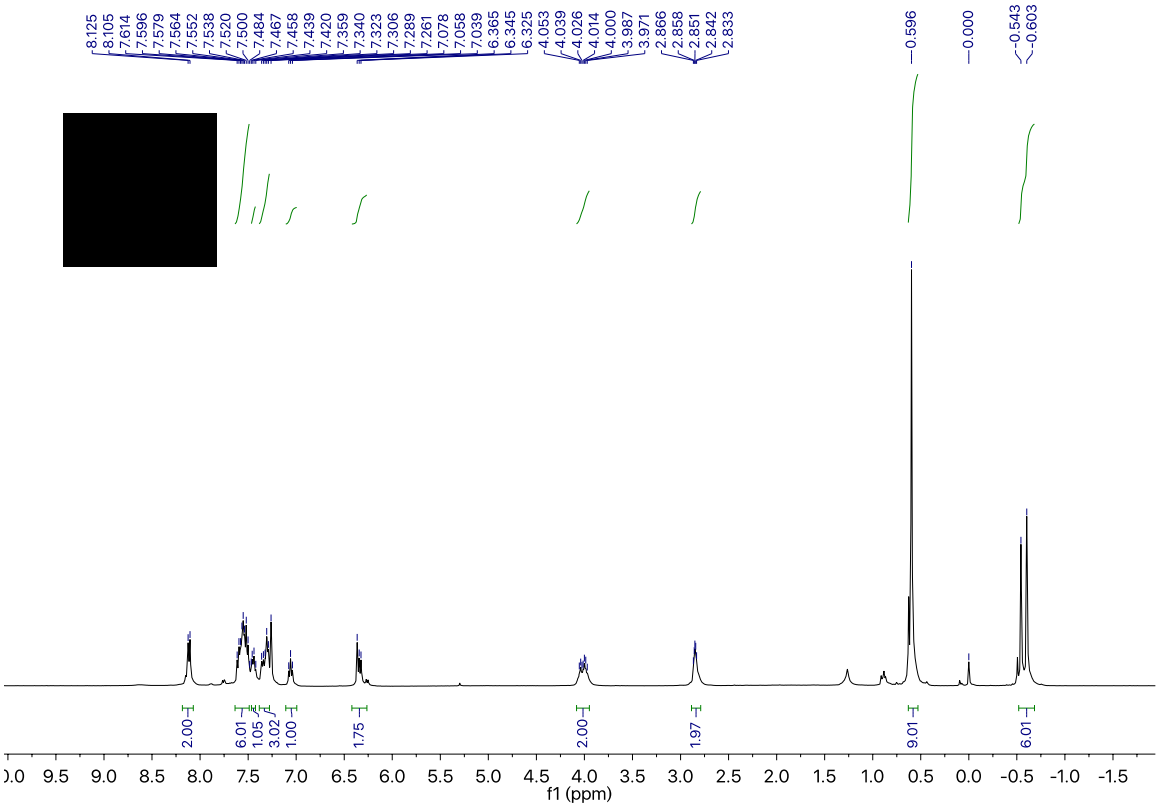
^{1}H NMR (400 MHz, $CDCl_3$)



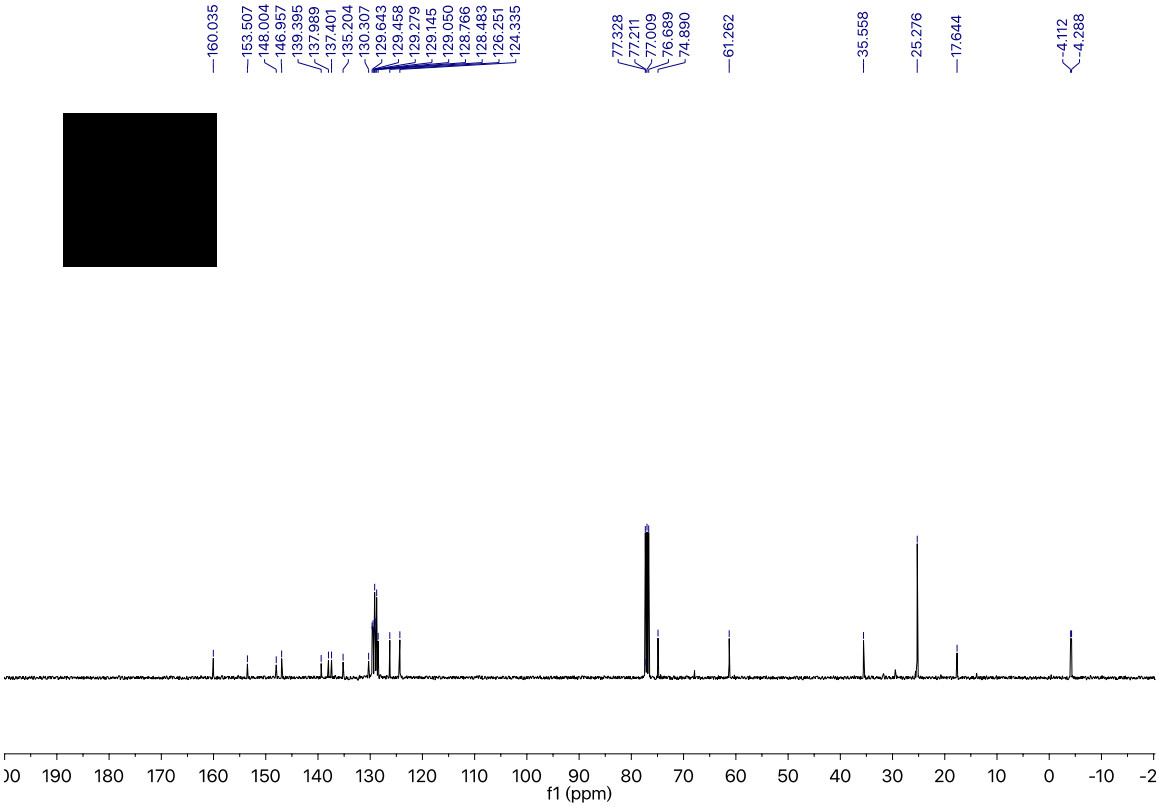
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



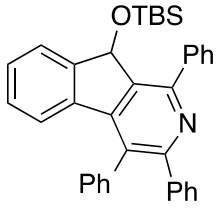
^{13}C NMR (100 MHz, $CDCl_3$)



4. X-ray Crystallography of Compounds 3ab.

9-((*tert*-butyldimethylsilyl)oxy)-1,3,4-triphenyl-9H-indeno[2,1-c]pyridine (3ab, CCDC: 1830393)

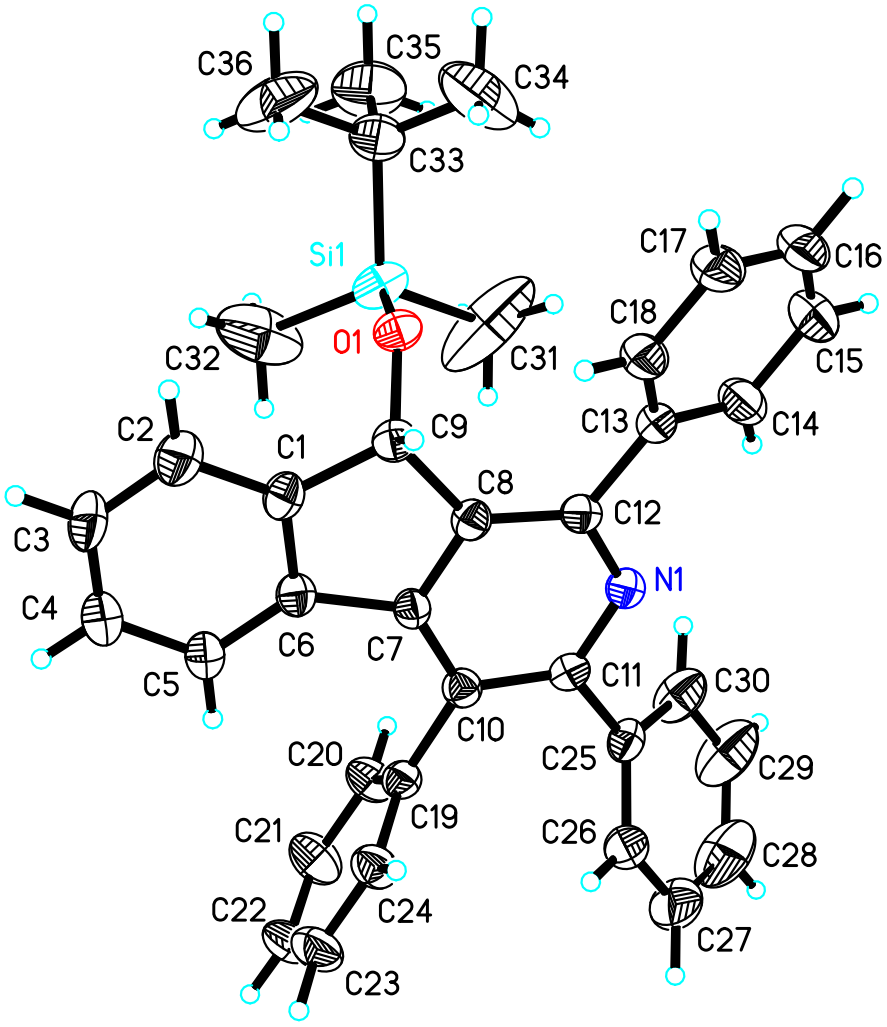
(Ortep ellipsoids are depicted at the 50% level)



3ab

Table 1. Crystal data and structure refinement for **3ab**

Identification code	**3ab**
Empirical formula	$C_{36}H_{35}NOSi$
Formula weight	525.74
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 20.052(4) Å α= 90°. b = 6.3001(12) Å β= 96.918(9)°. c = 48.442(9) Å γ = 90°
Volume	6075(2) $Å^3$
Z	8
Density (calculated)	1.150 Mg/m^3
Absorption coefficient	0.105 mm^{-1}
F(000)	2240
Crystal size	0.200 x 0.170 x 0.110 mm^3
Theta range for data collection	1.694 to 24.995°
Index ranges	-23<=h<=18, -7<=k<=7, -55<=l<=57
Reflections collected	16029
Independent reflections	5375 [R(int) = 0.0787]
Completeness to theta = 26.000°	97.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6034
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5375 / 0 / 356
Goodness-of-fit on F^2	1.117
Final R indices [I>2sigma(I)]	R1 = 0.0890, wR2 = 0.1895
R indices (all data)	R1 = 0.1410, wR2 = 0.2157
Extinction coefficient	n/a
Largest diff. peak and hole	0.258 and -0.216 $e.Å^{-3}$


C36
C35
C34
C33
Si1
C17
C16
C18
C15
O1
C32
C31
C13
C14
C2
C1
C9
C8
C12
C3
N1
C4
C6
C7
C11
C30
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C20
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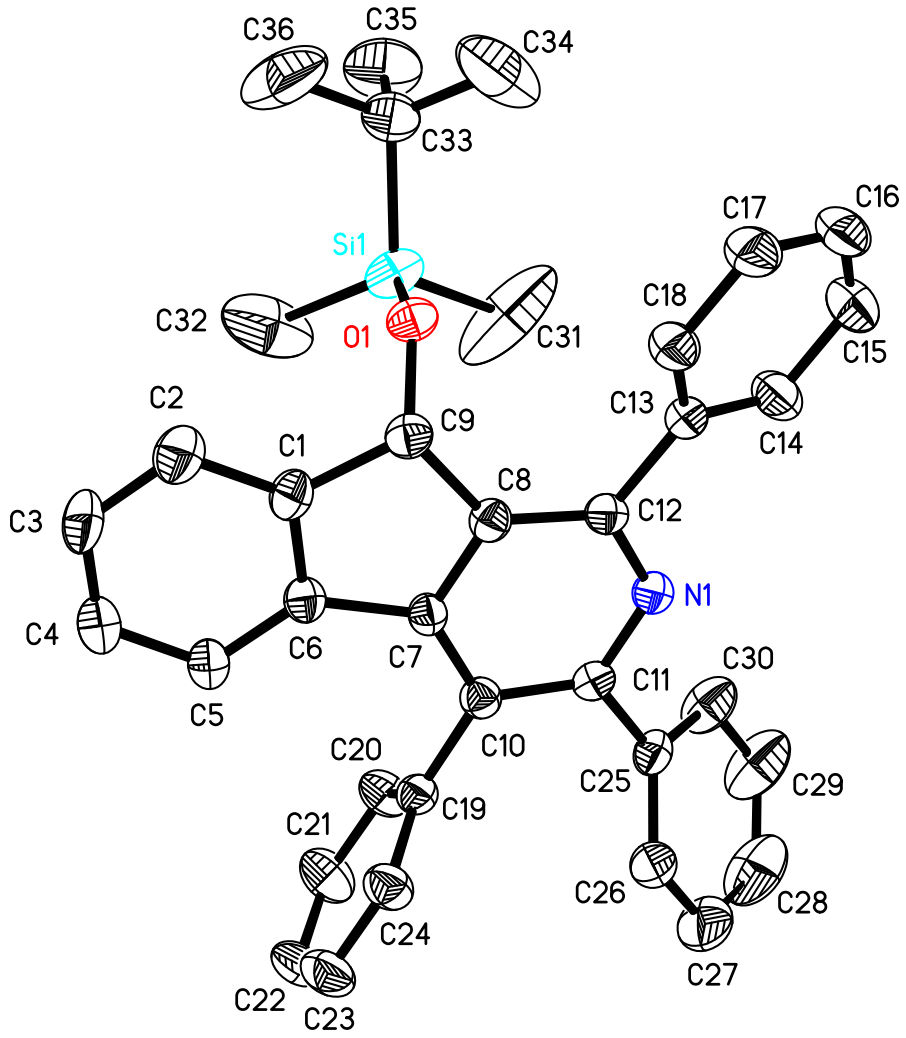
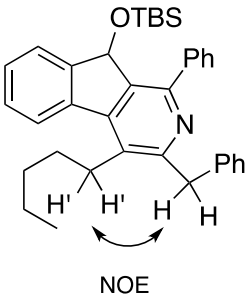
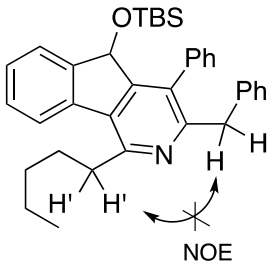
C19
C21
C26
C28
C22
C24
C27
C23



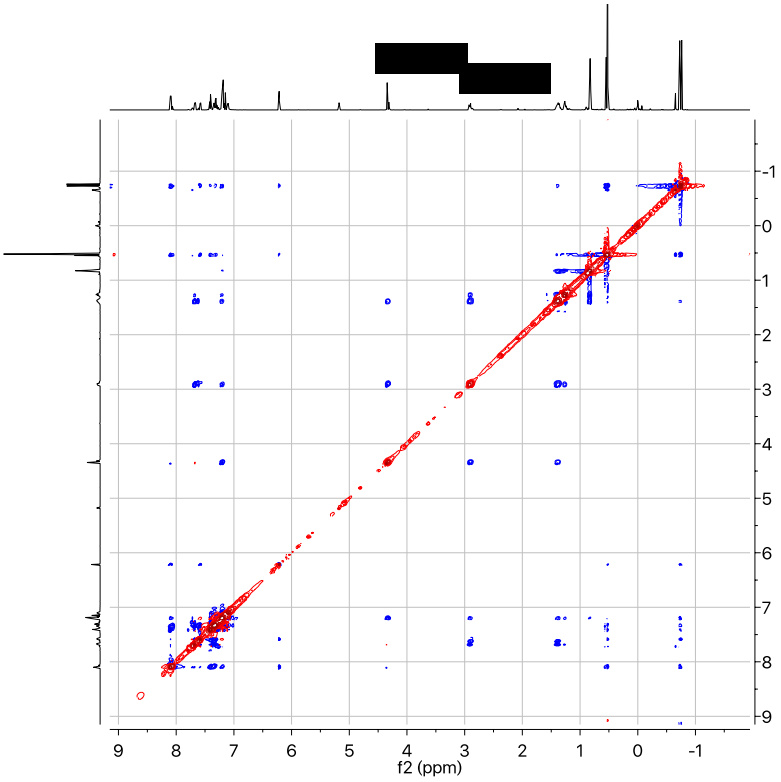
5. NOESY of Compounds 3ma and 3ra.

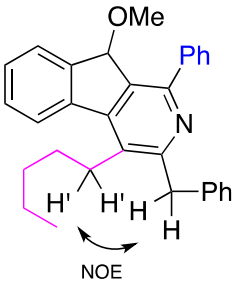


3ma

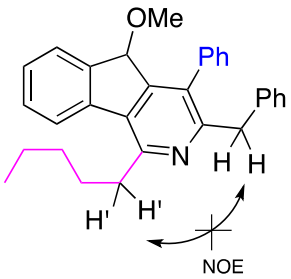


3ma'

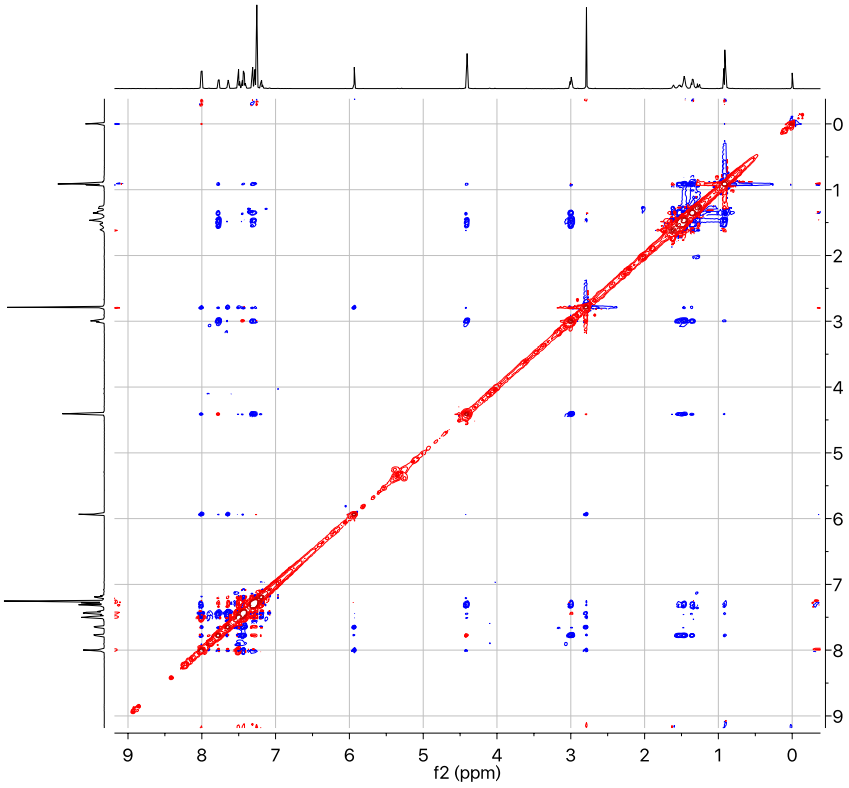




3ra



3ra'


f2 (ppm)
f1 (ppm)