Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.


# Electronically Modified Amine Substituted Alkynols for Regio-selective Synthesis of Dihydrofuran Derivatives

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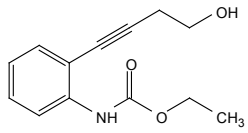
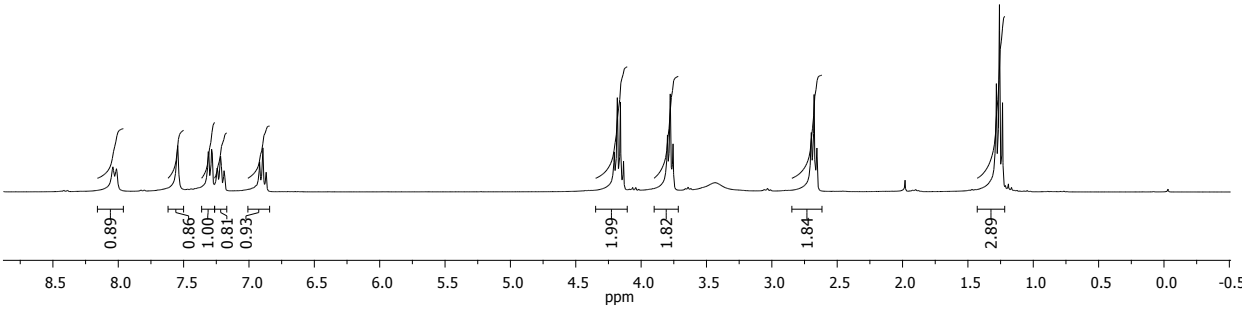
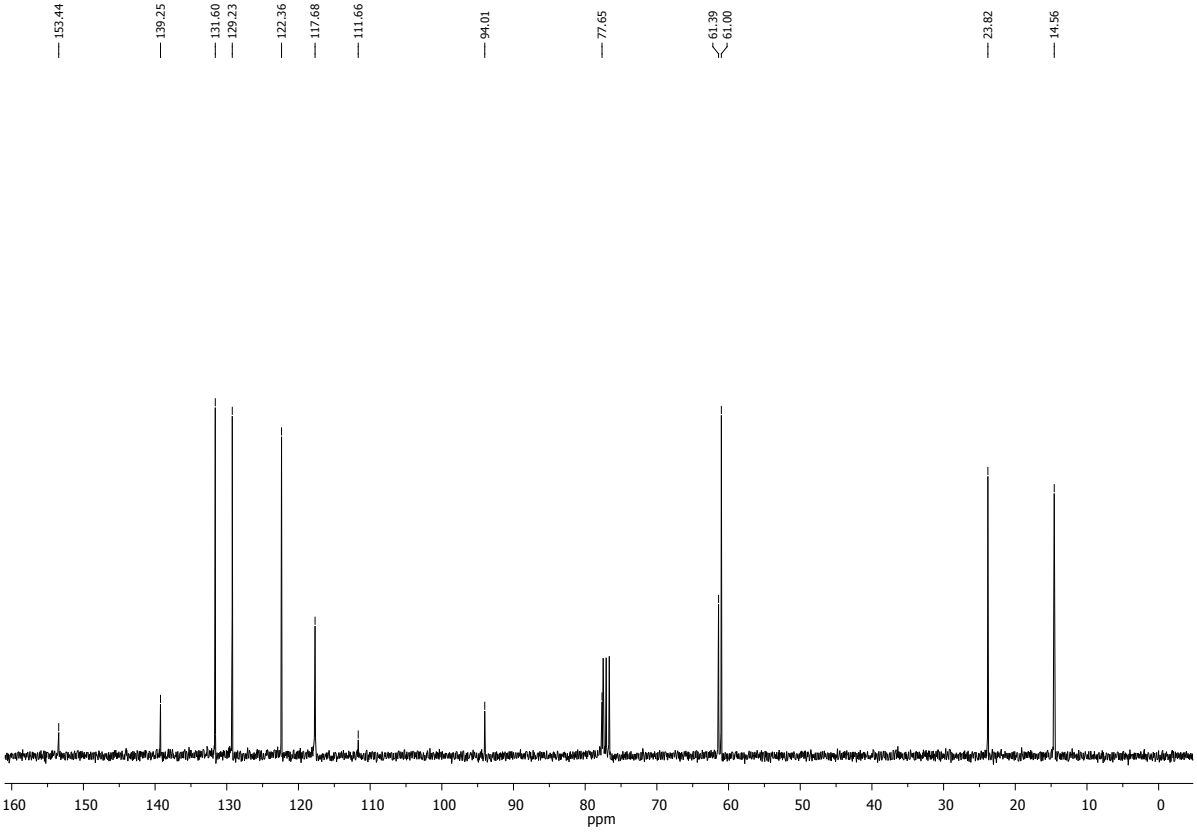
## Contents

## General Techniques:

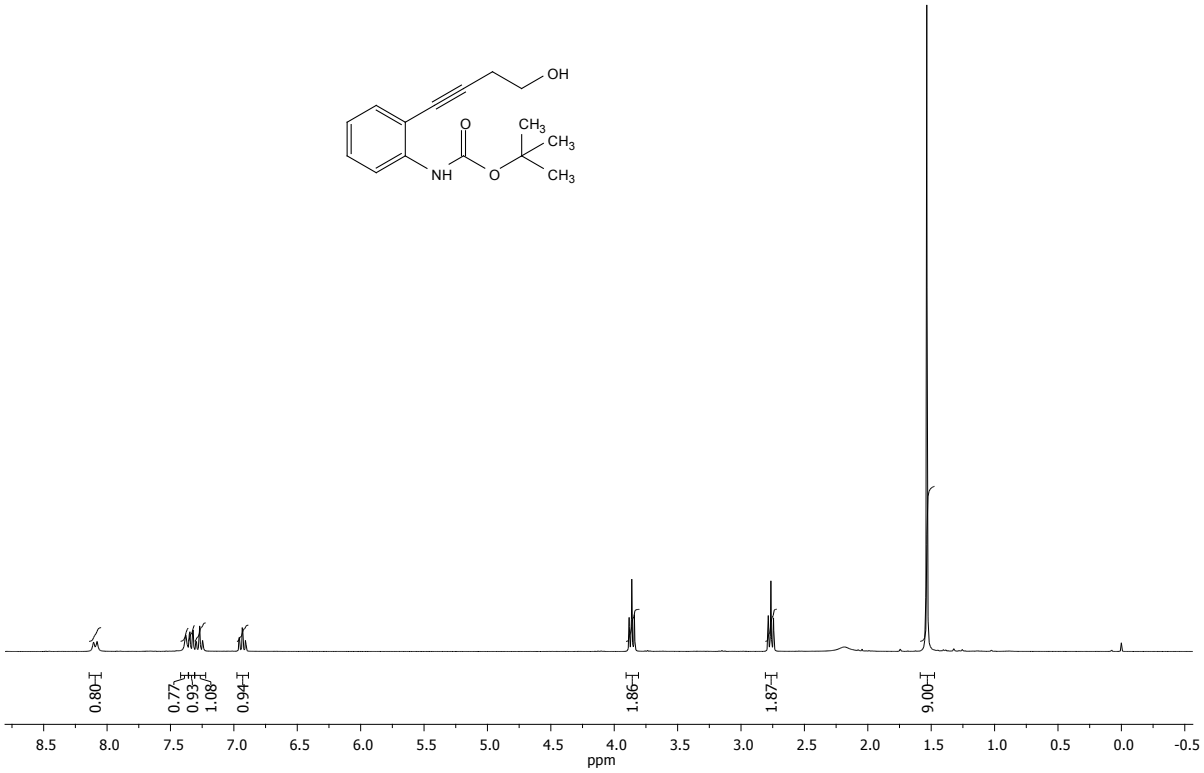
NMR spectra were recorded in Fourier transform mode. The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a 300 MHz, 400 MHz, and 500 MHz spectrophotometer using $CDCl_3$ and TMS as the internal standard. Multiplicities in the $^{1}H$ NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, bs = broad singlet; coupling constants are reported in Hz. Low (MS) and high (HRMS) resolution mass spectra were recorded by ion trap method and mass/charge (m/z) ratios are reported as values in atomic mass units. All the melting point is uncorrected.

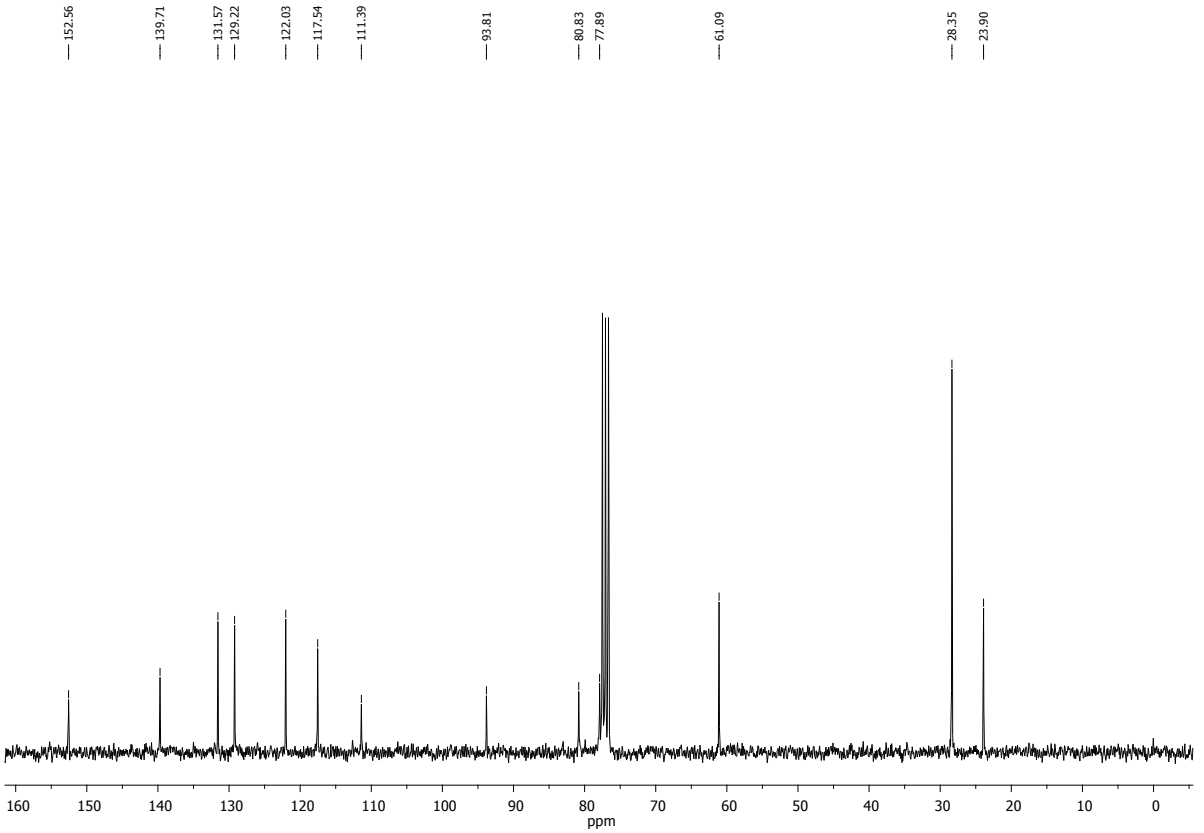



**$^{1}$H NMR** and **$^{13}$C NMR** of **4a**

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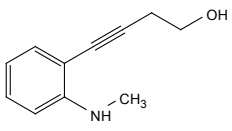


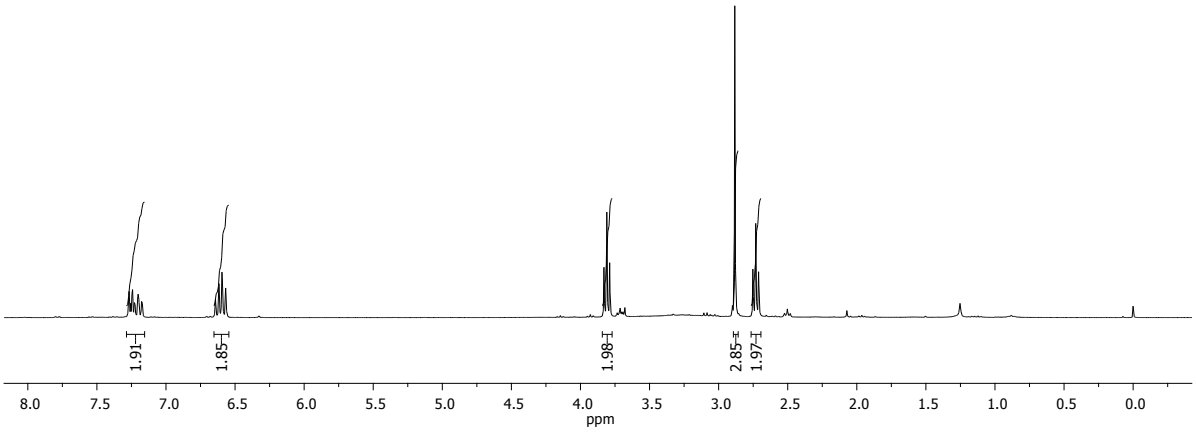


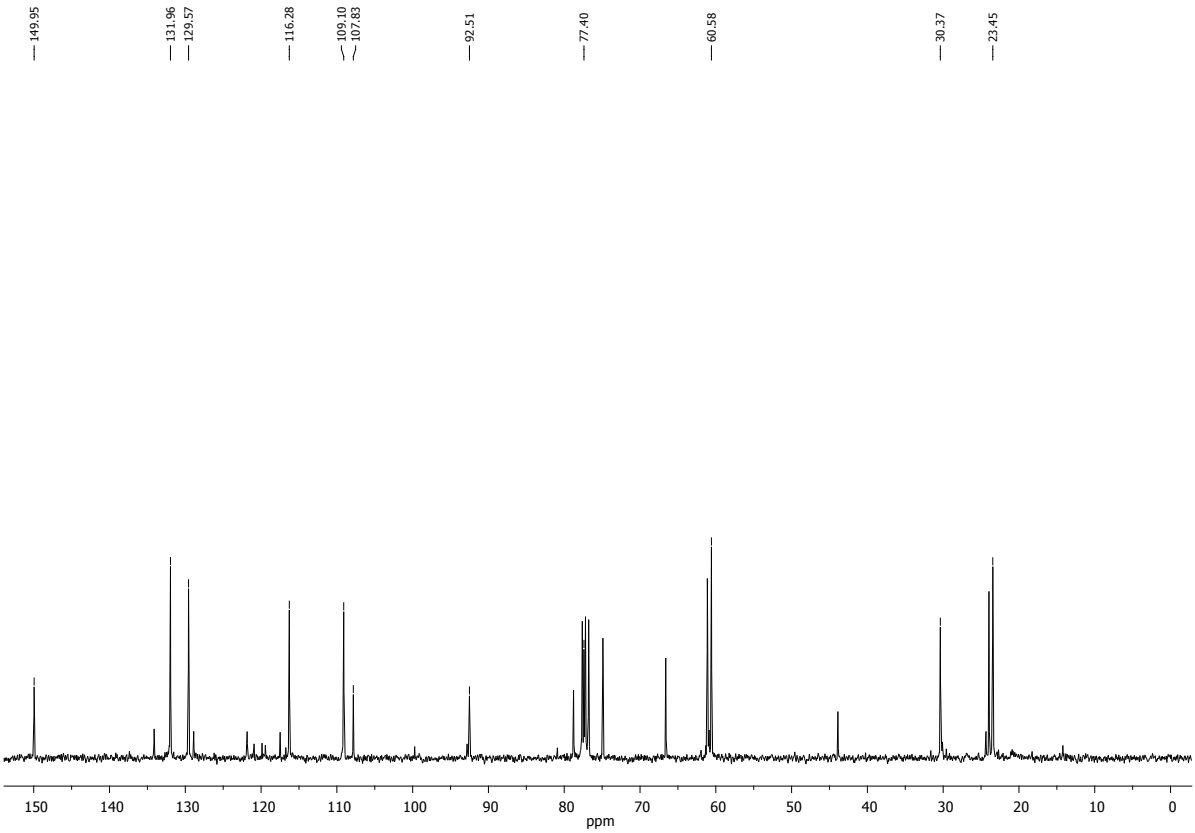


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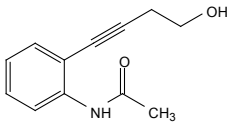


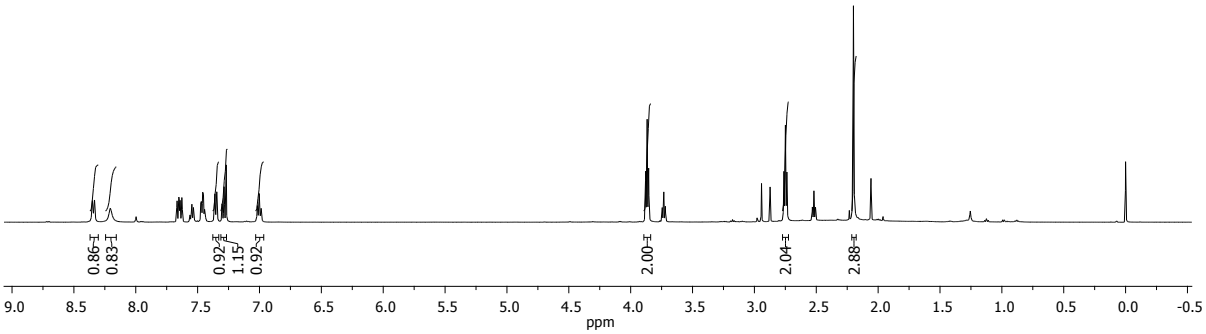


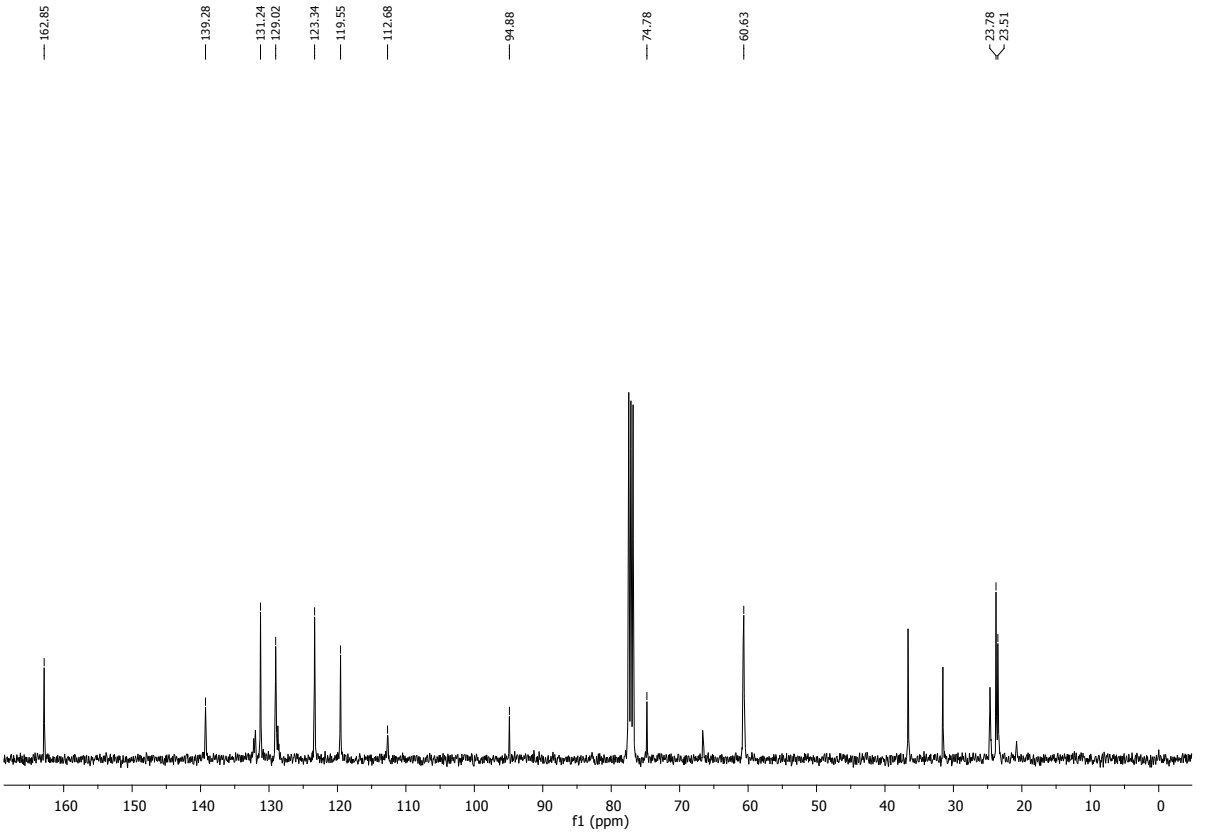


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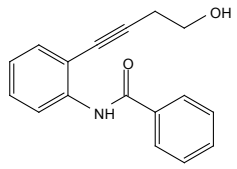
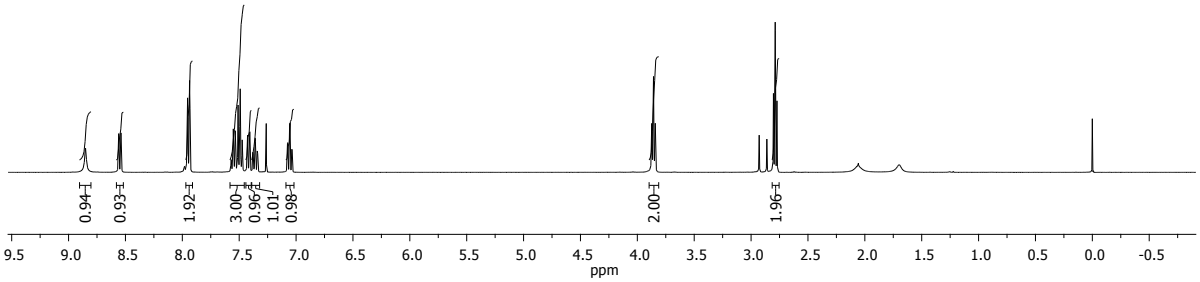
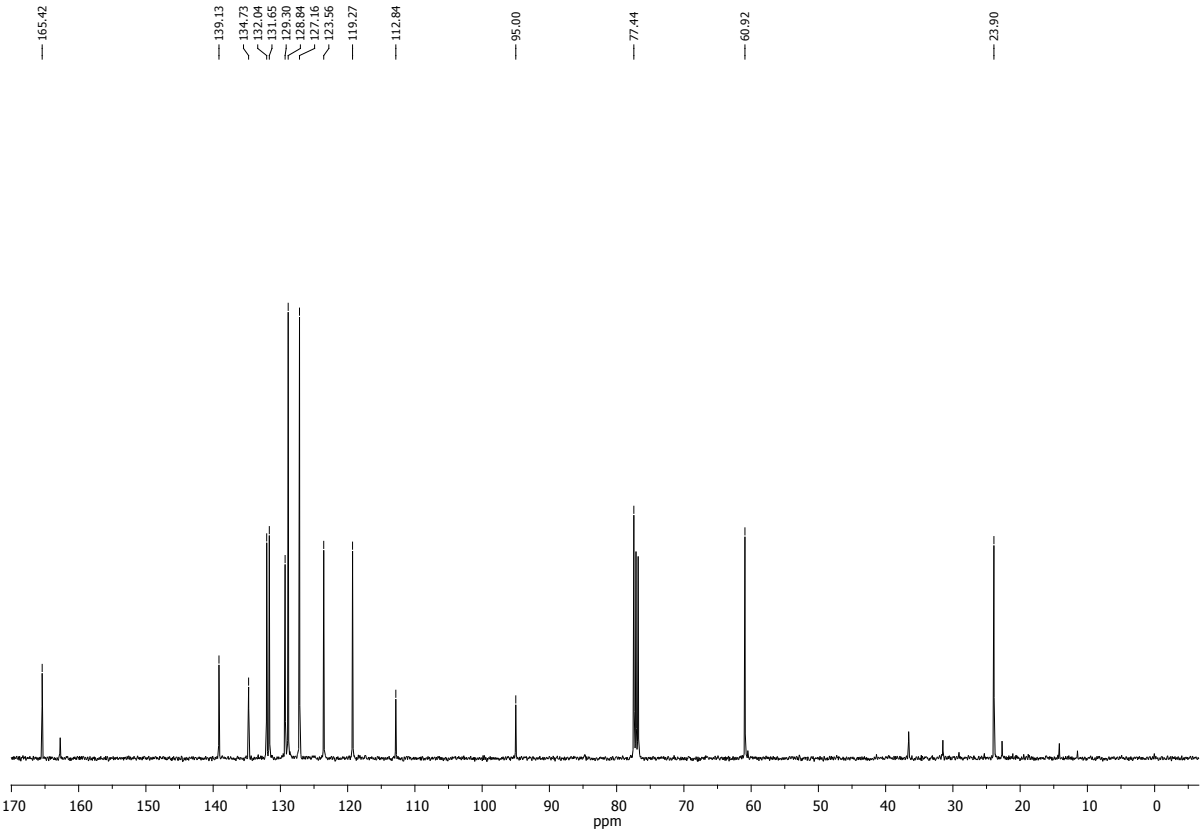
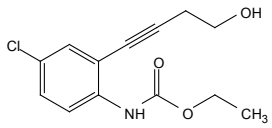
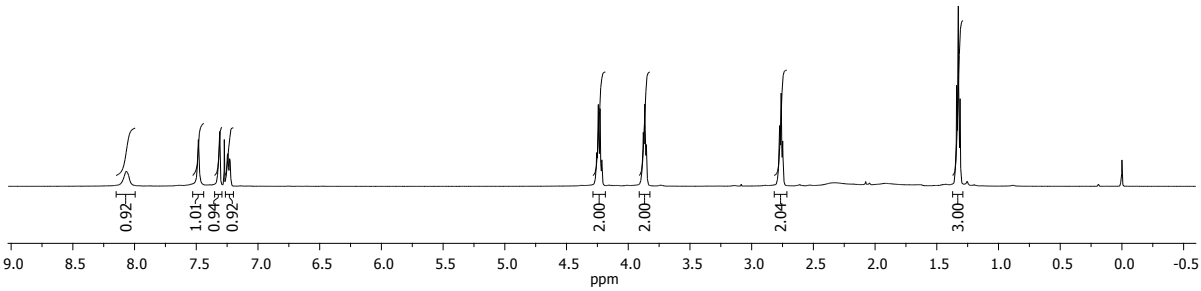


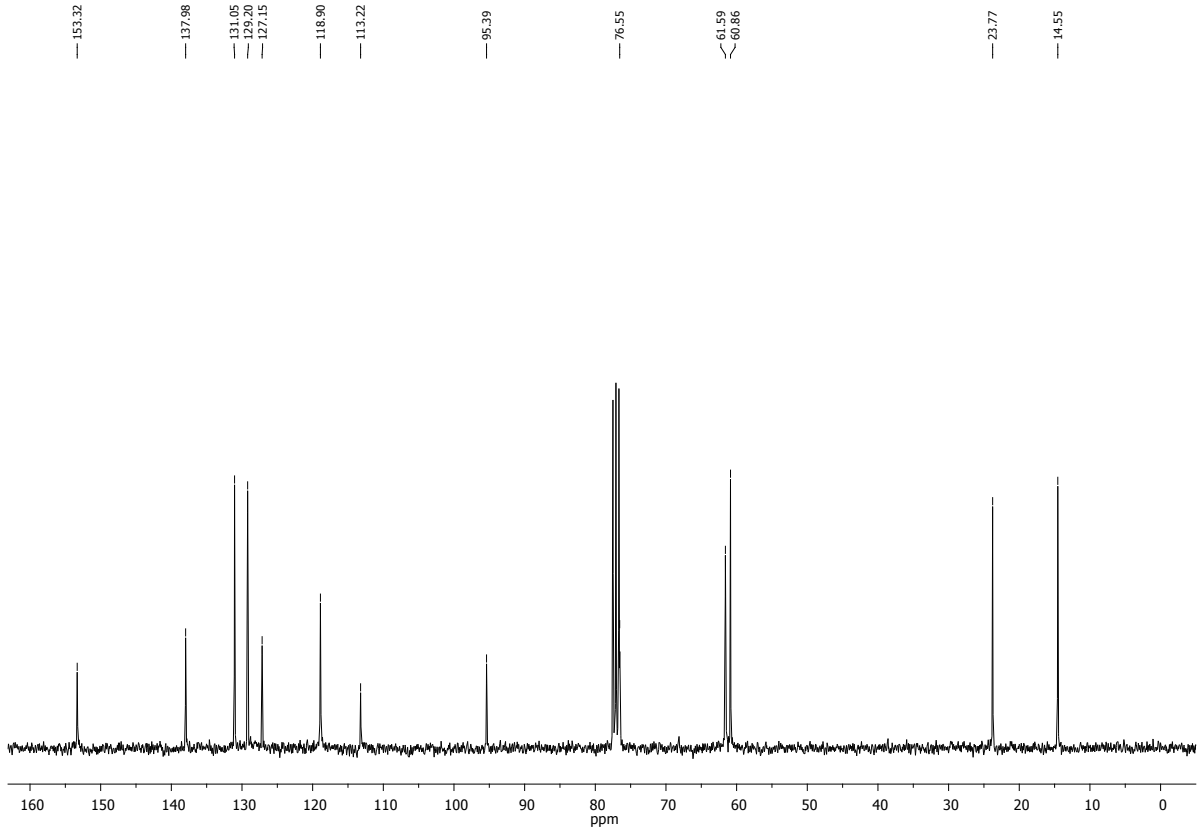



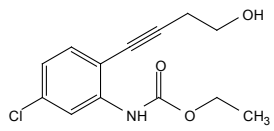

**$^{1}$H NMR** and **$^{13}$C NMR** of **4e**

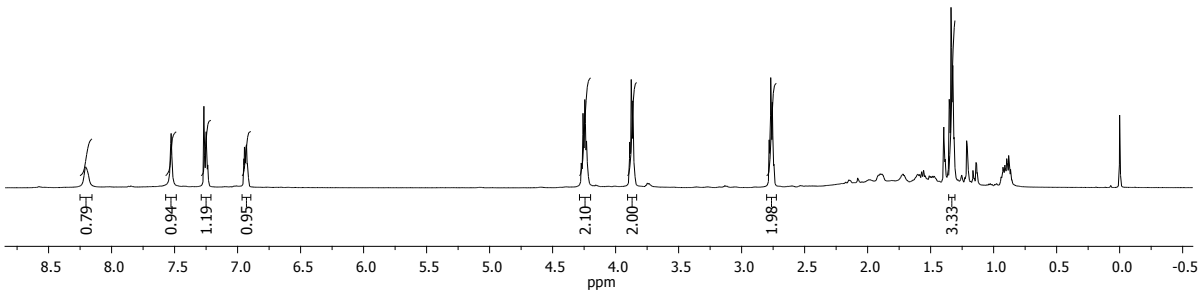


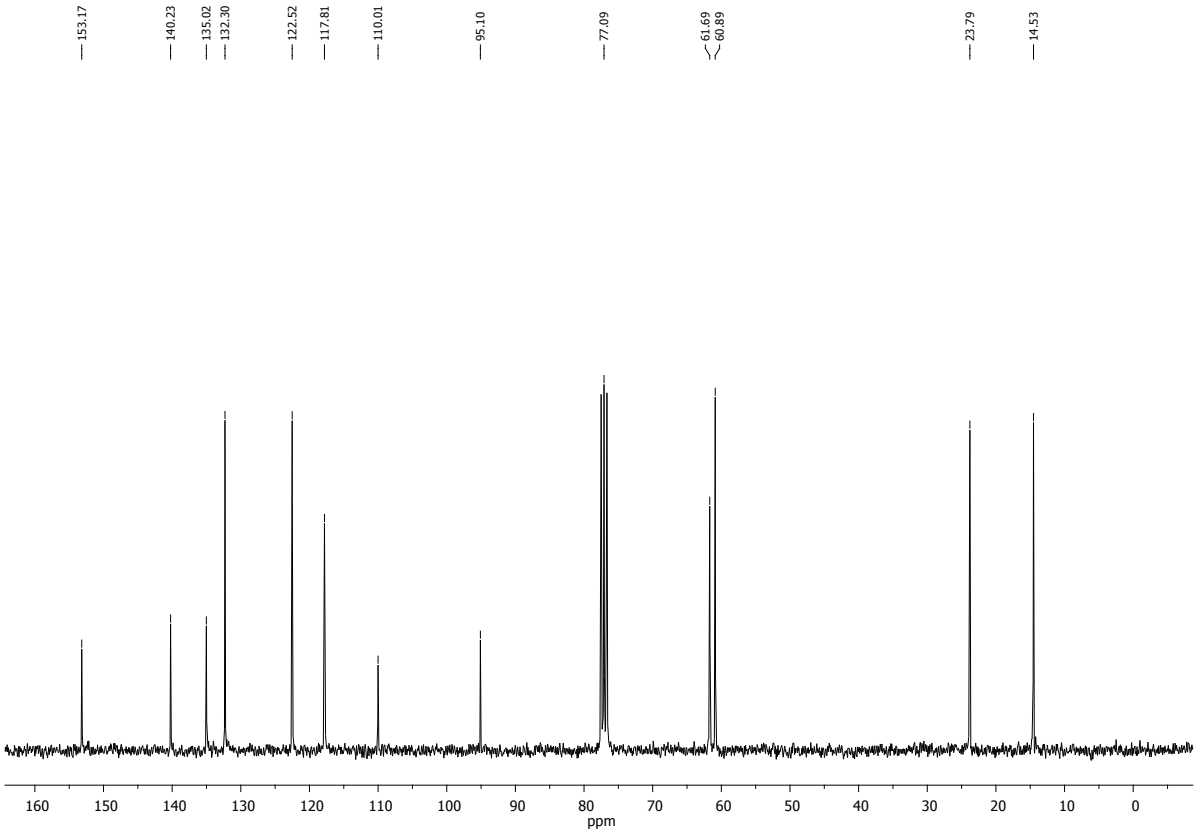



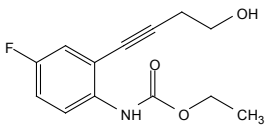

**$^{1}$H NMR** and **$^{13}$C NMR** of **4f**

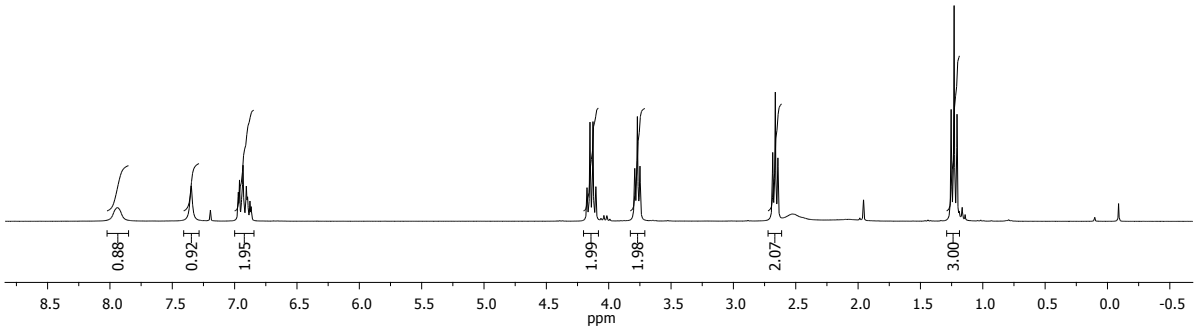


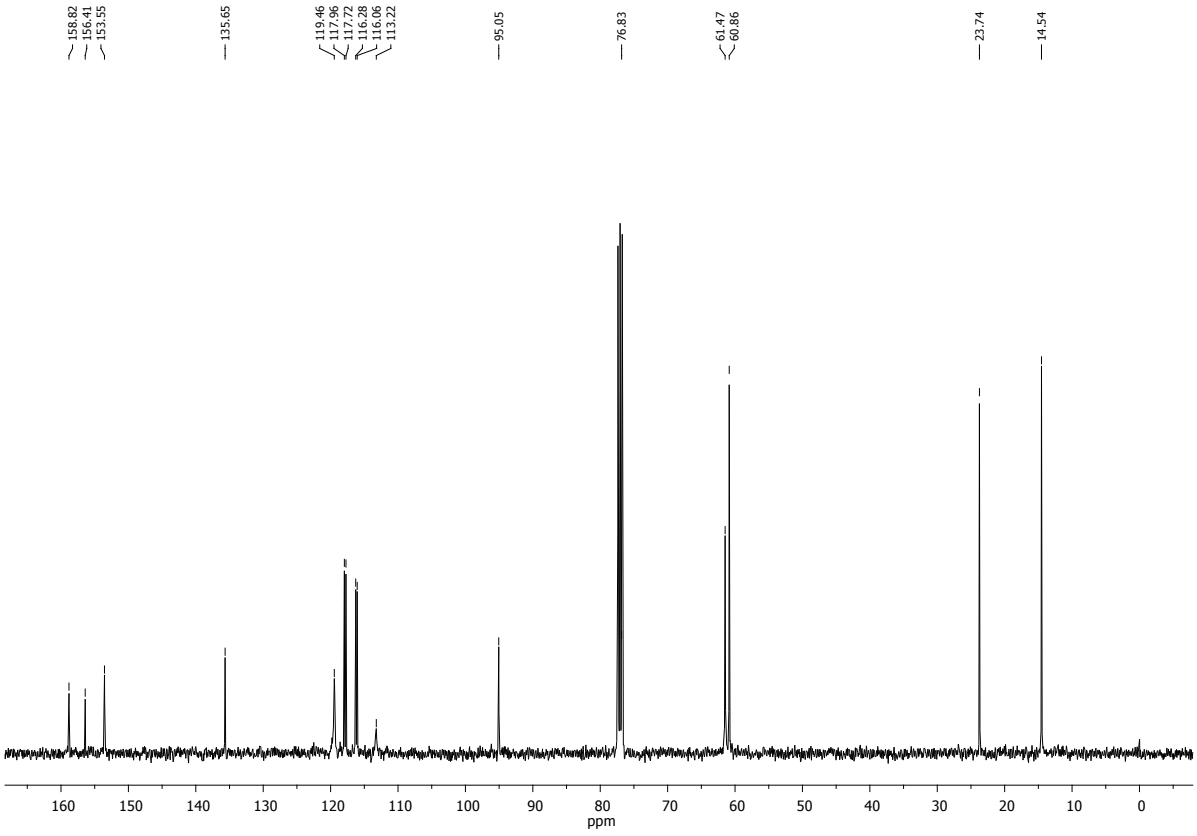




**$^{1}$H NMR** and **$^{13}$C NMR** of **4g**

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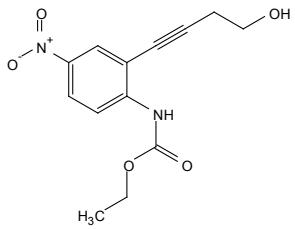
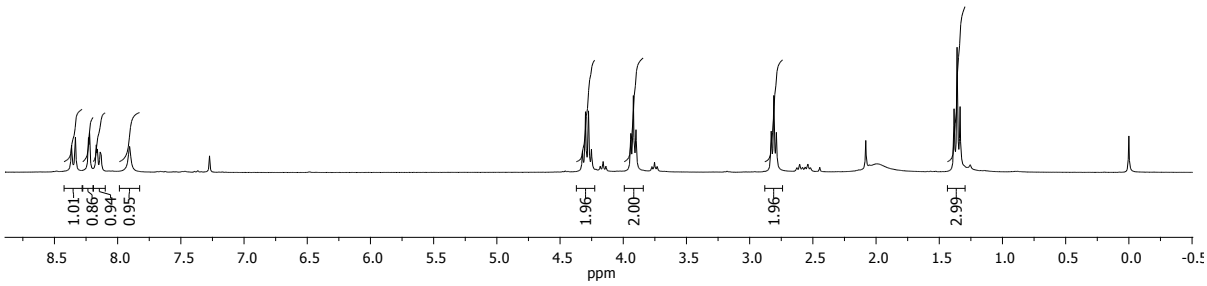
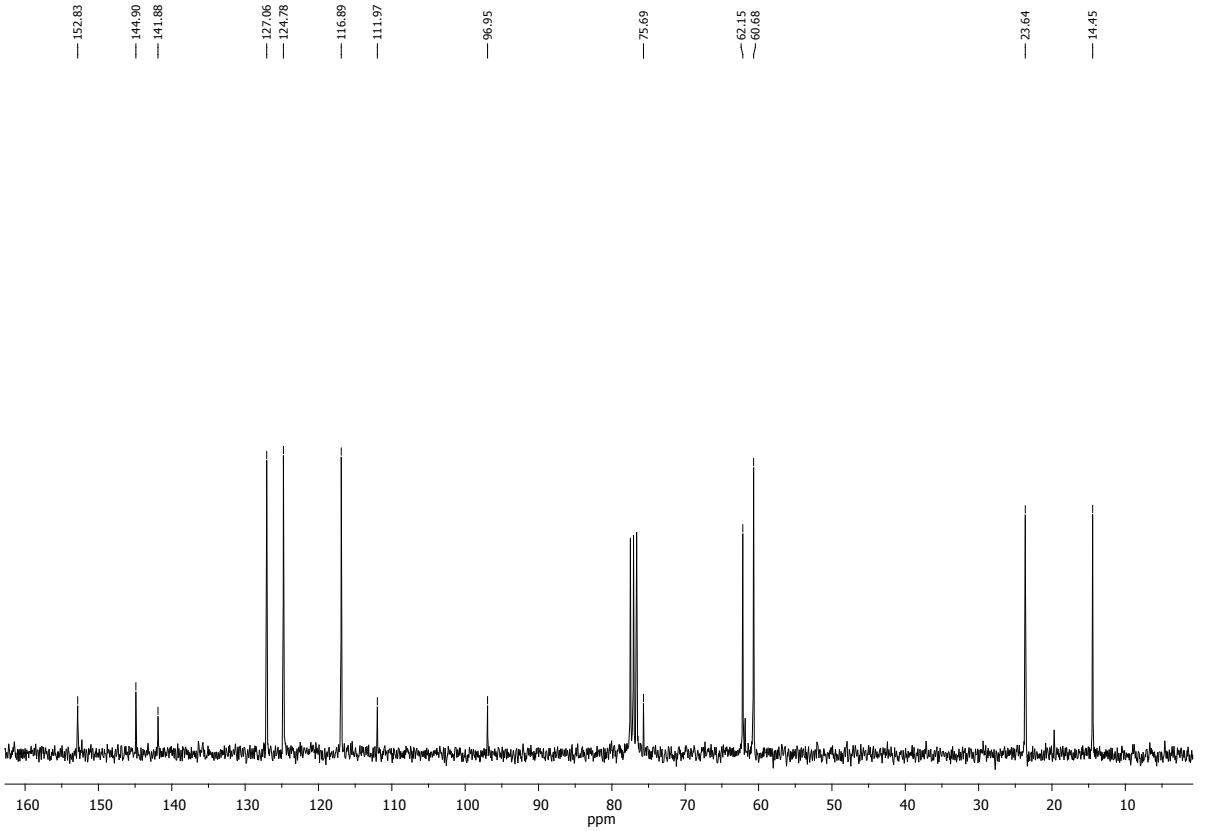
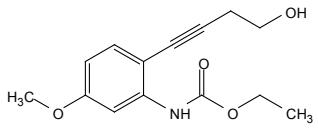
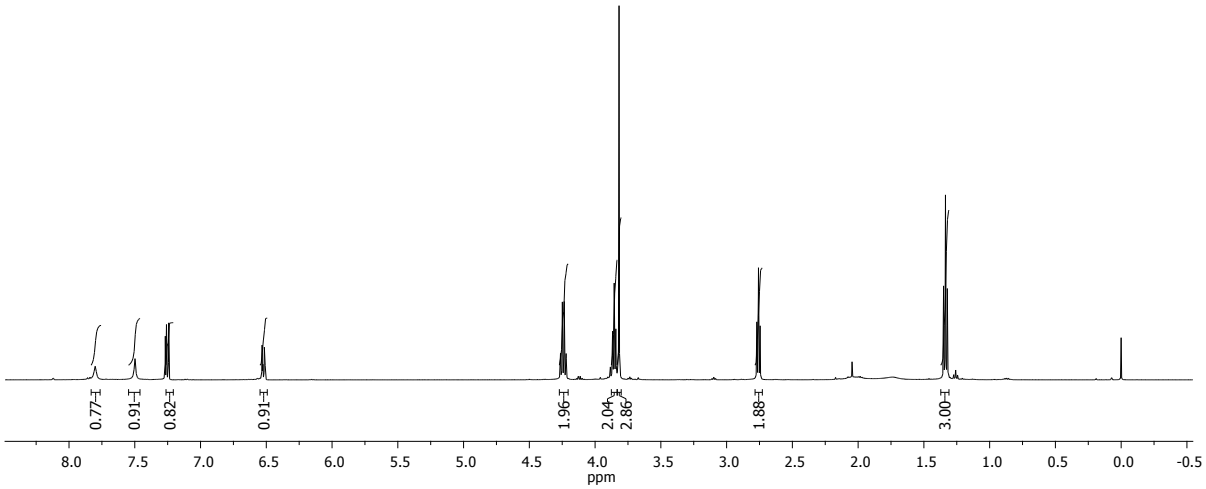


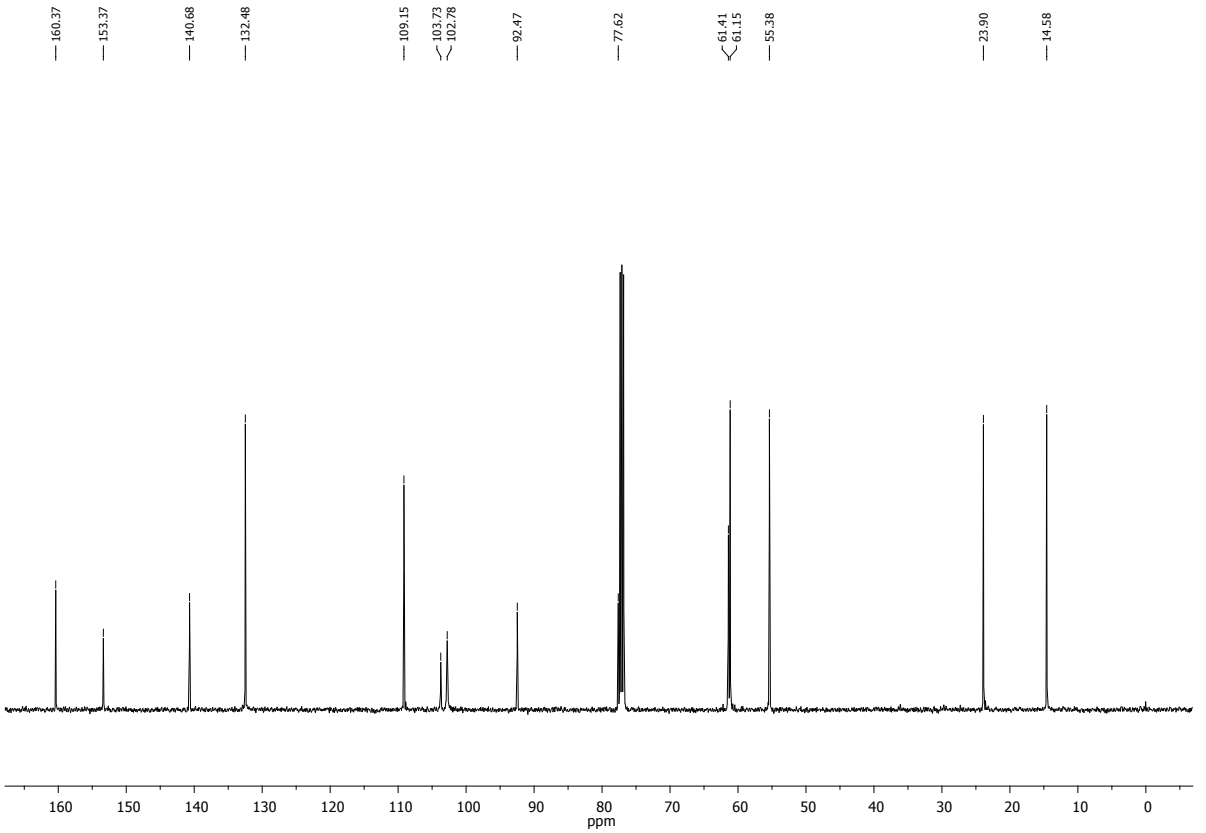




**$^{1}$H NMR** and **$^{13}$C NMR** of **4i**

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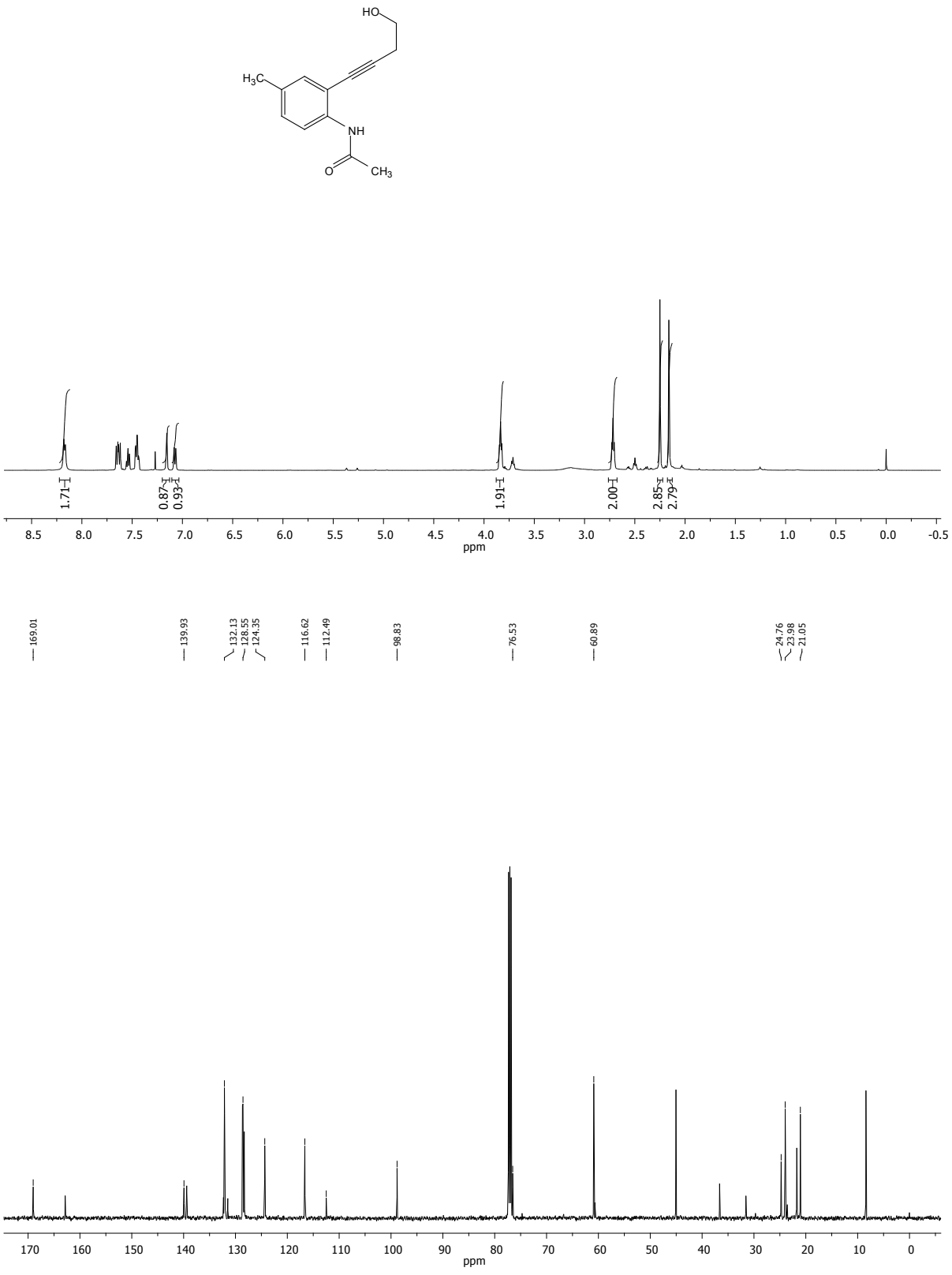


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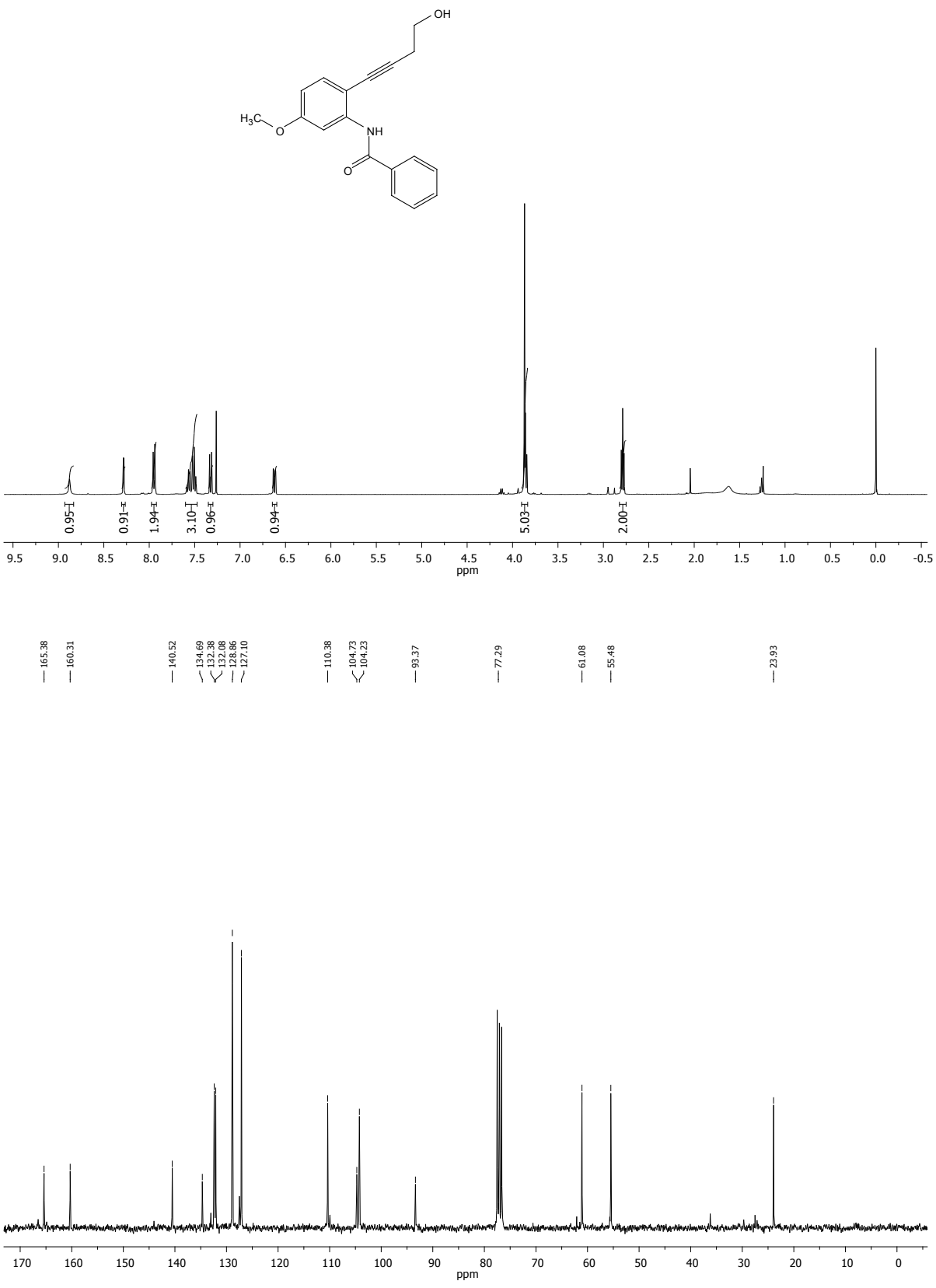


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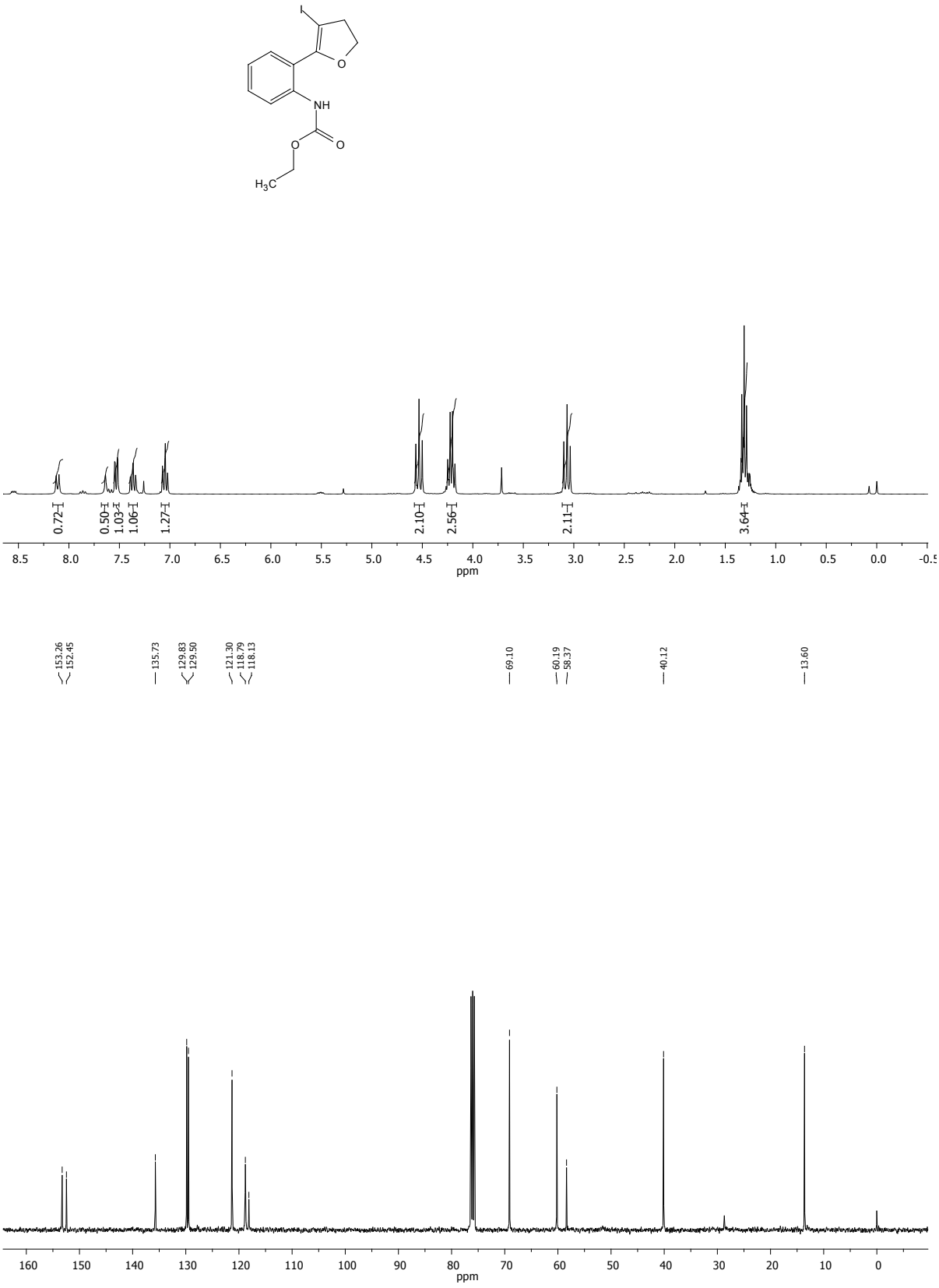
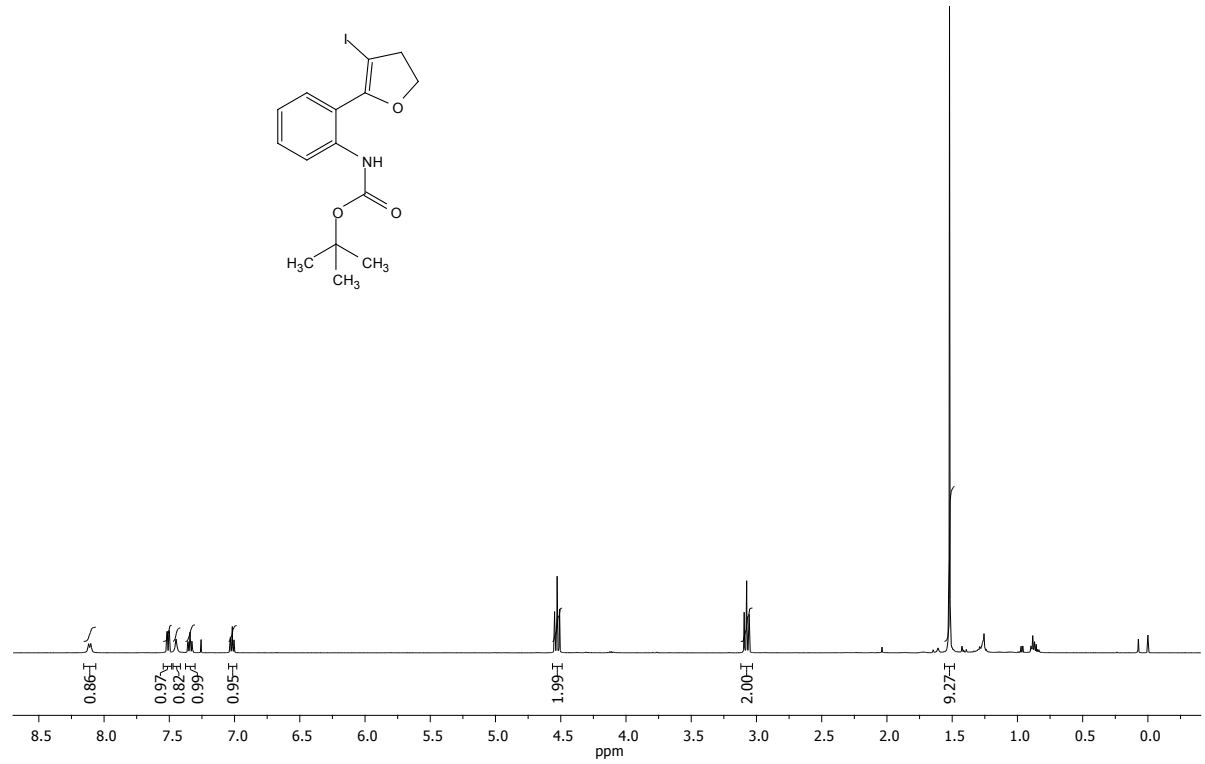
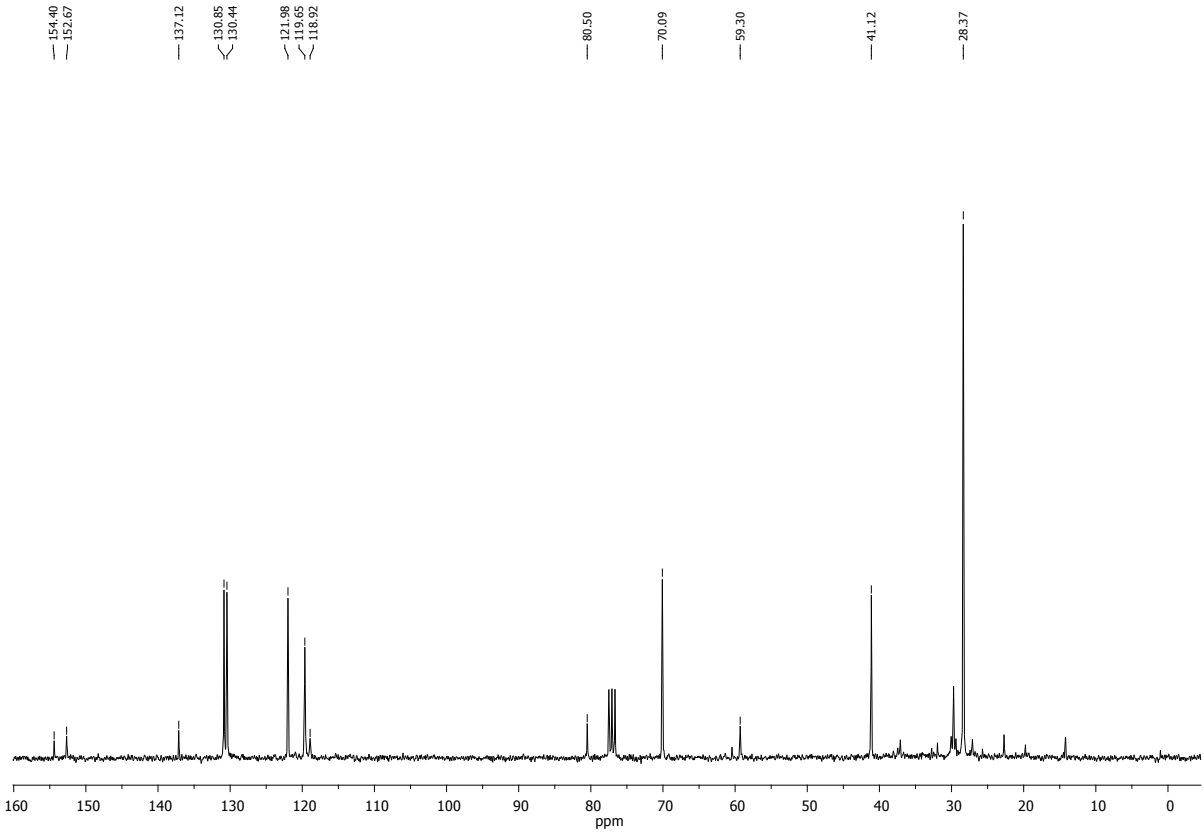
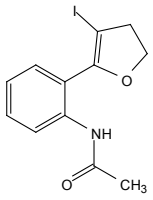


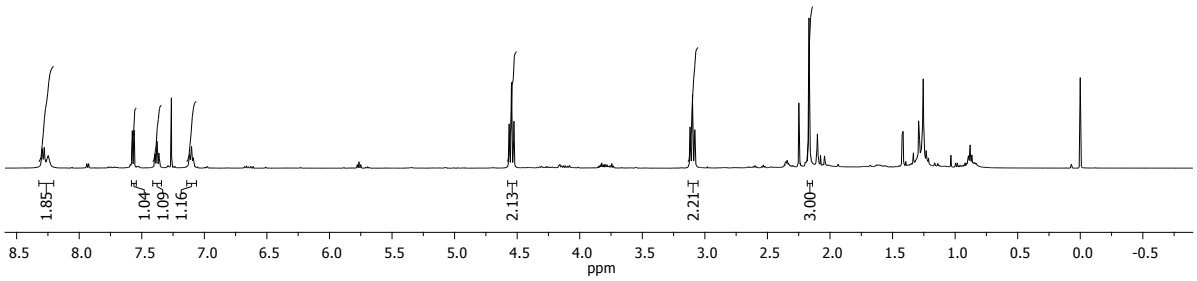

**$^{1}$H NMR** and **$^{13}$C NMR** of **5a**

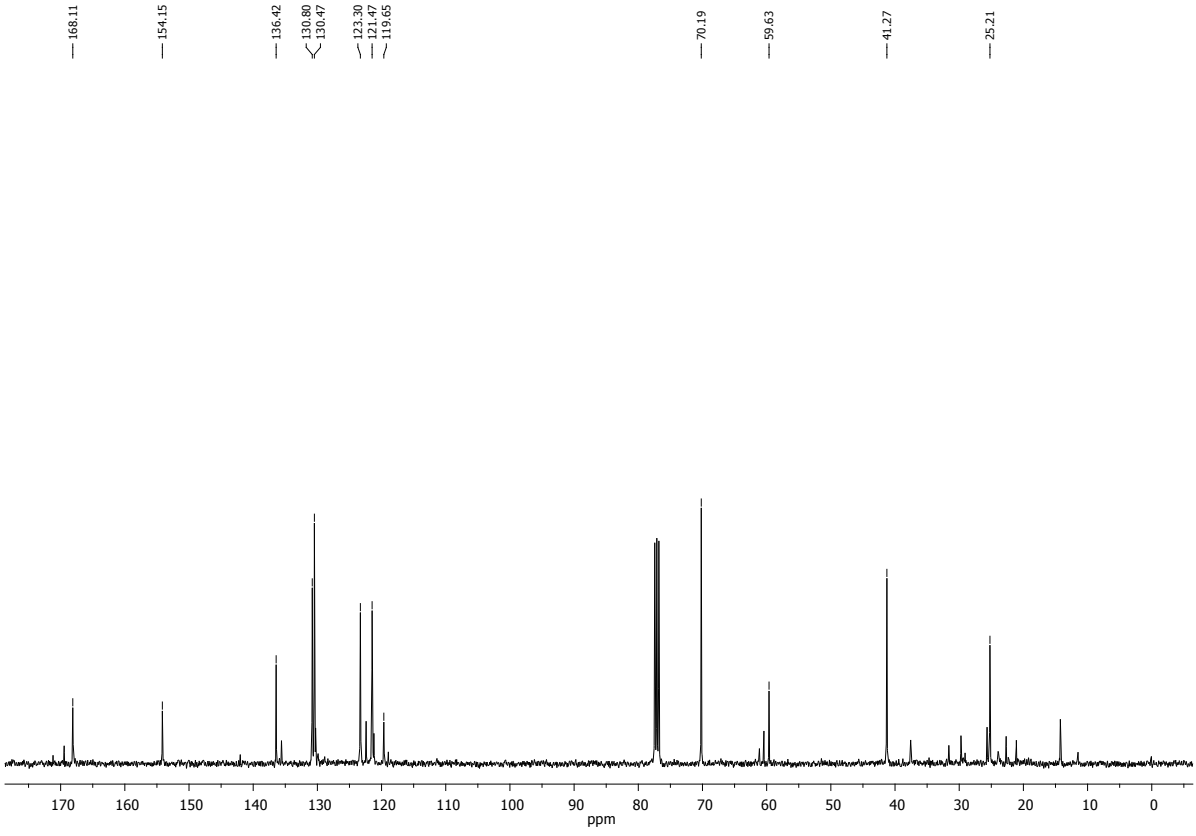



**$^{1}$H NMR** and **$^{13}$C NMR** of **5b**

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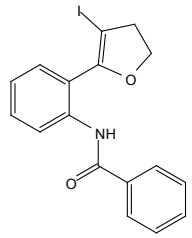


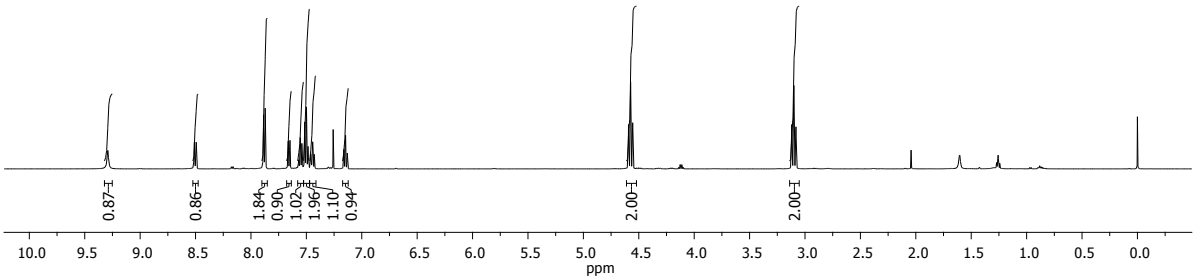


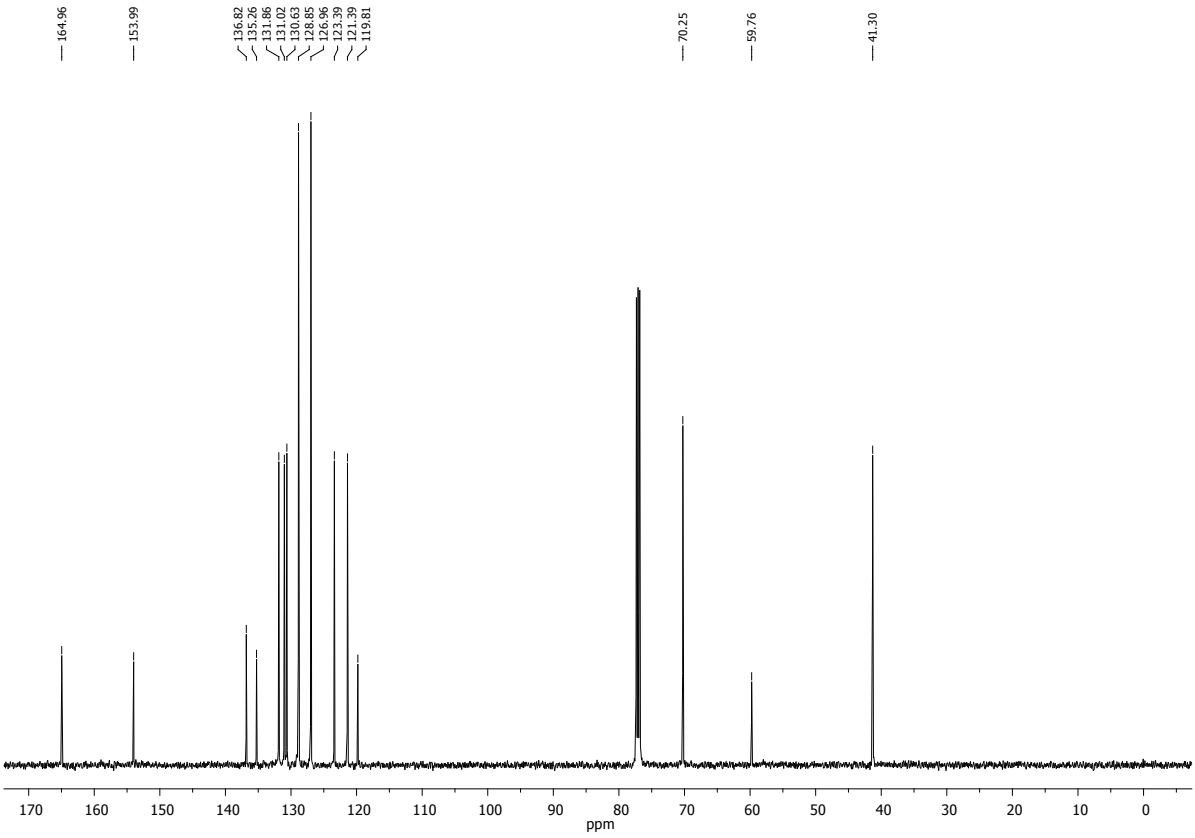


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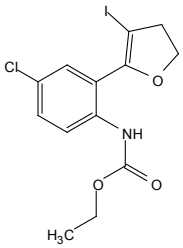


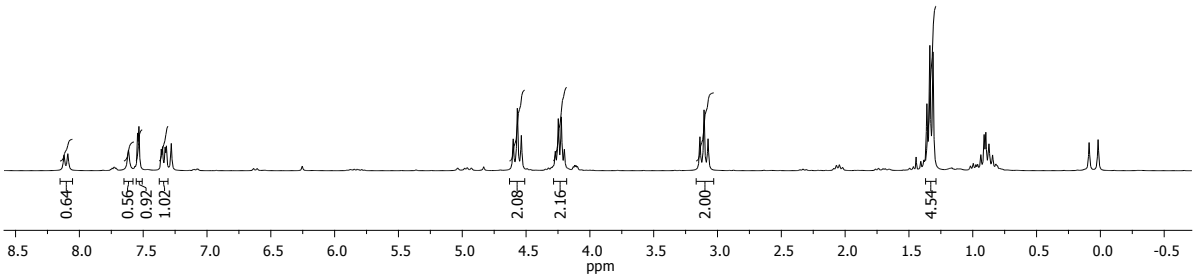


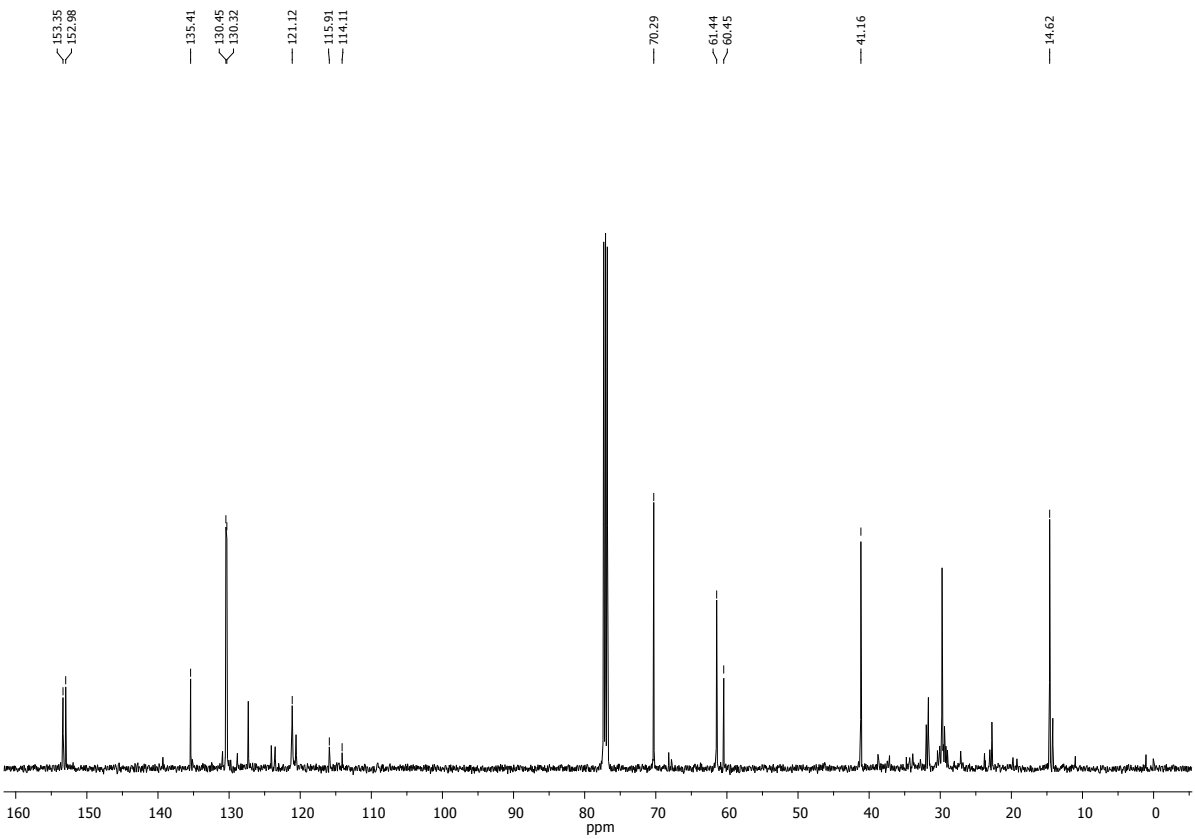


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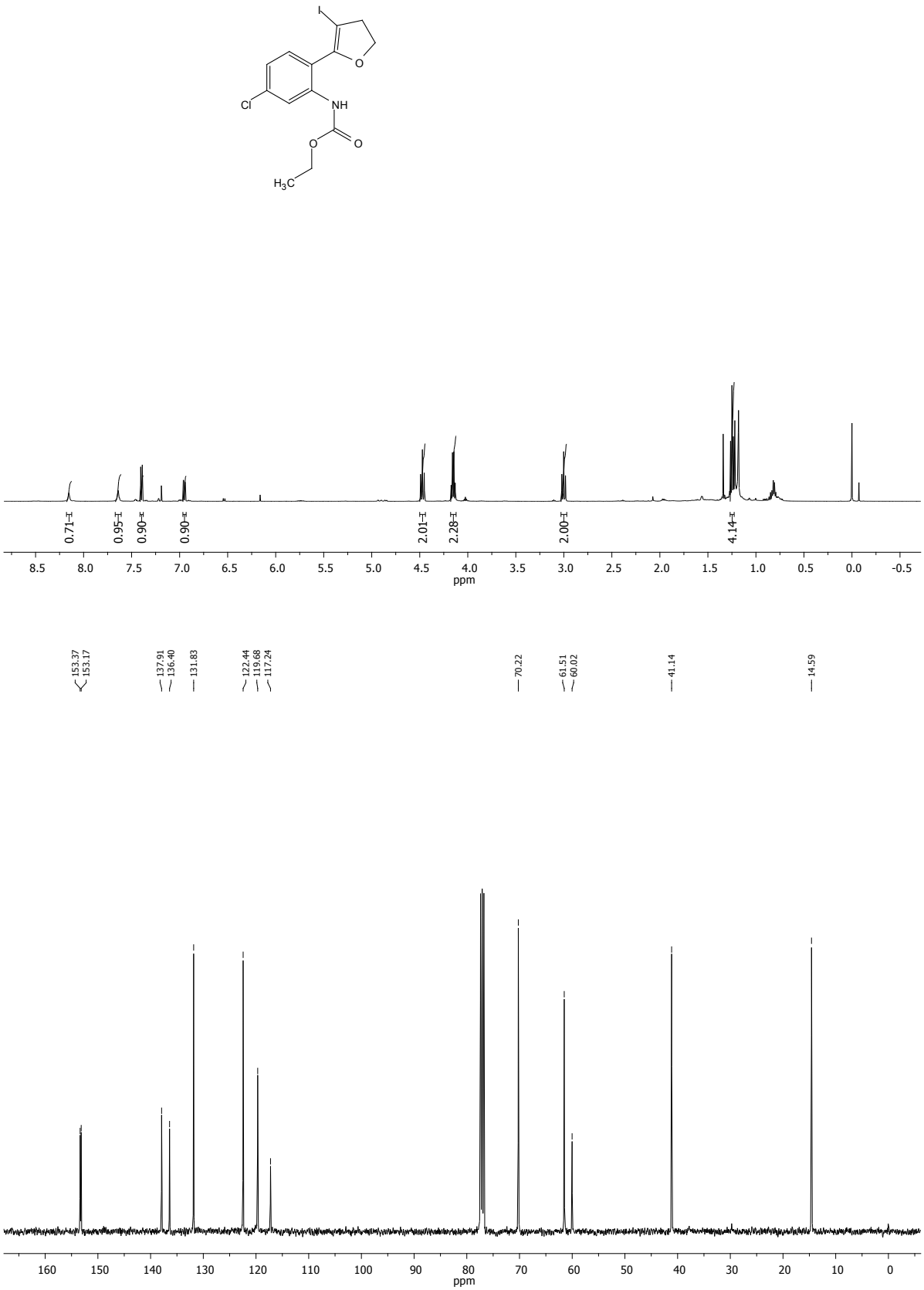


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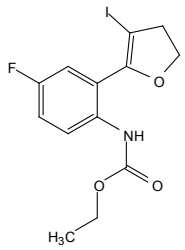


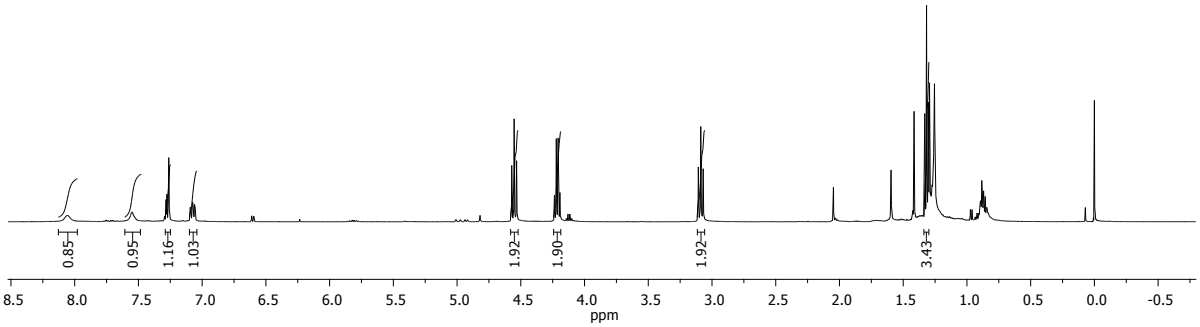


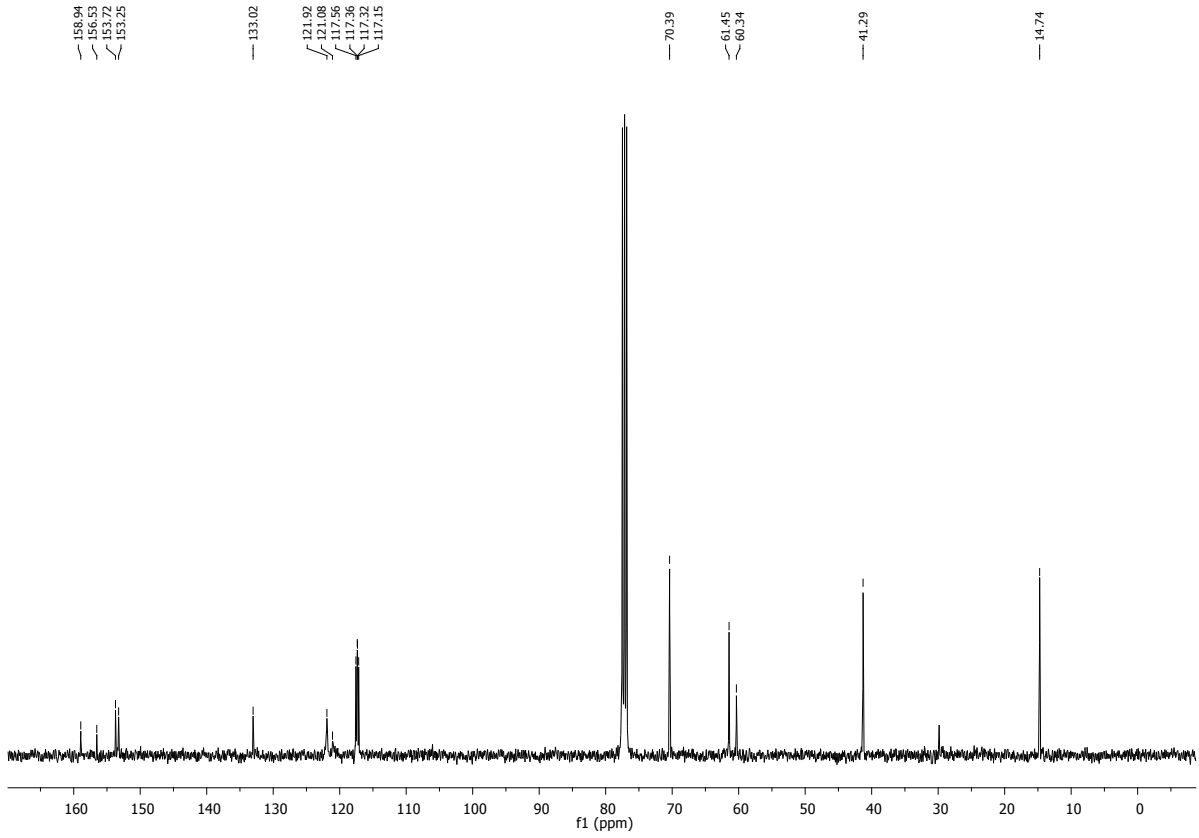


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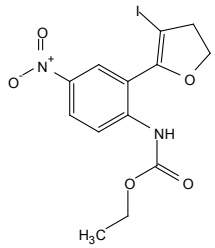
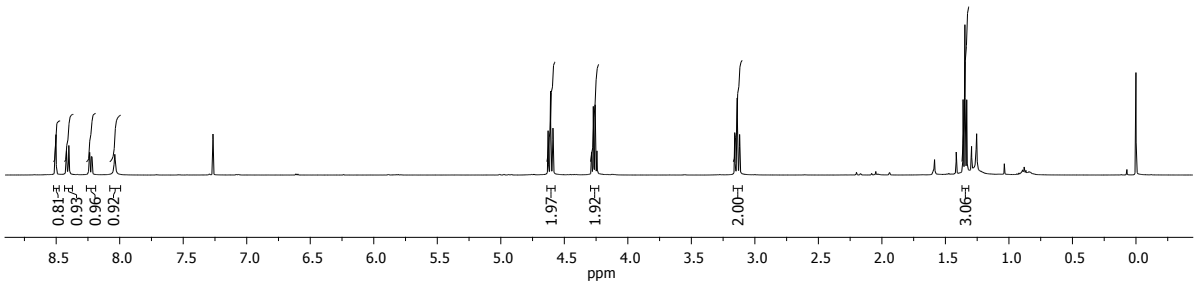
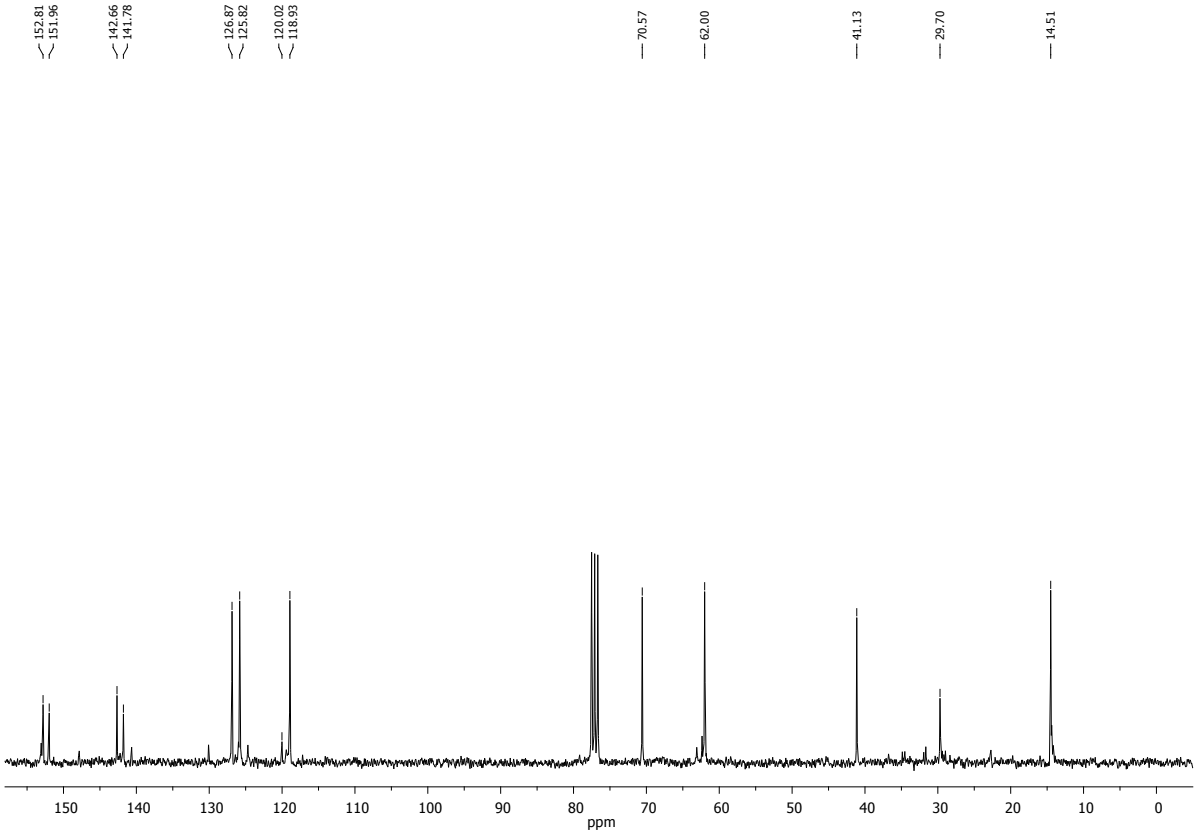
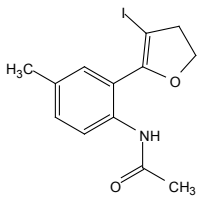
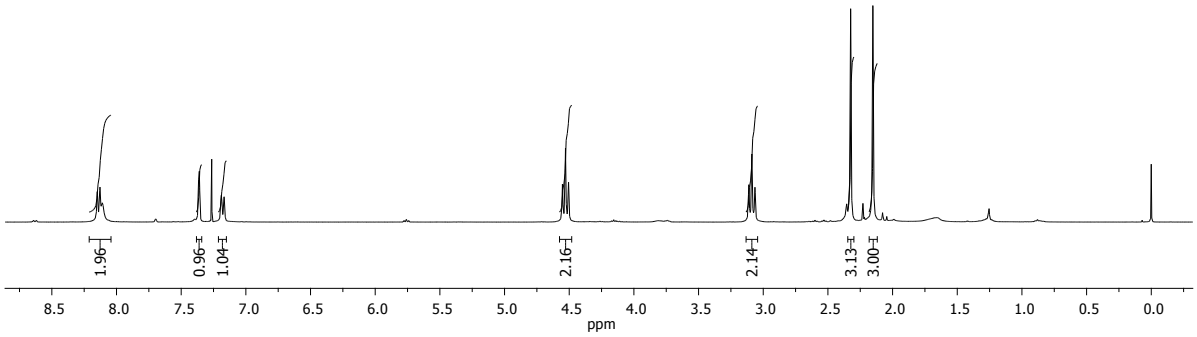


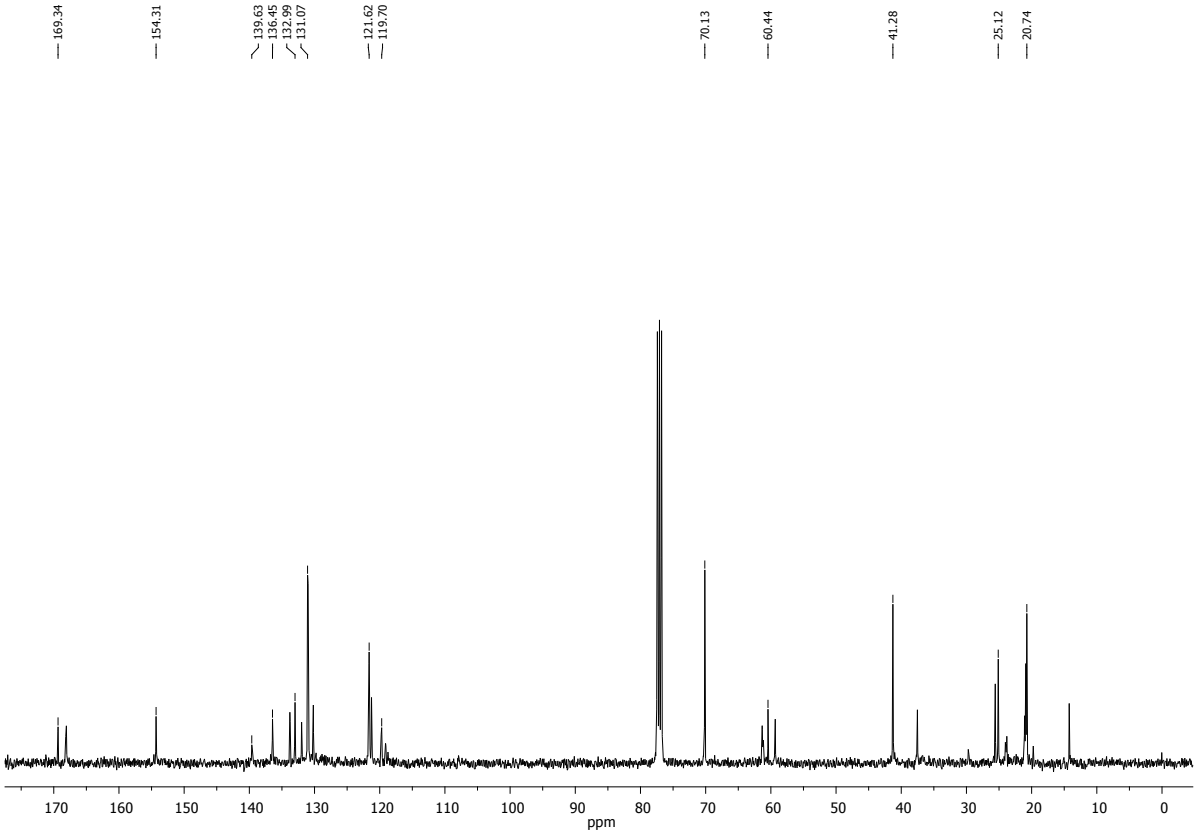



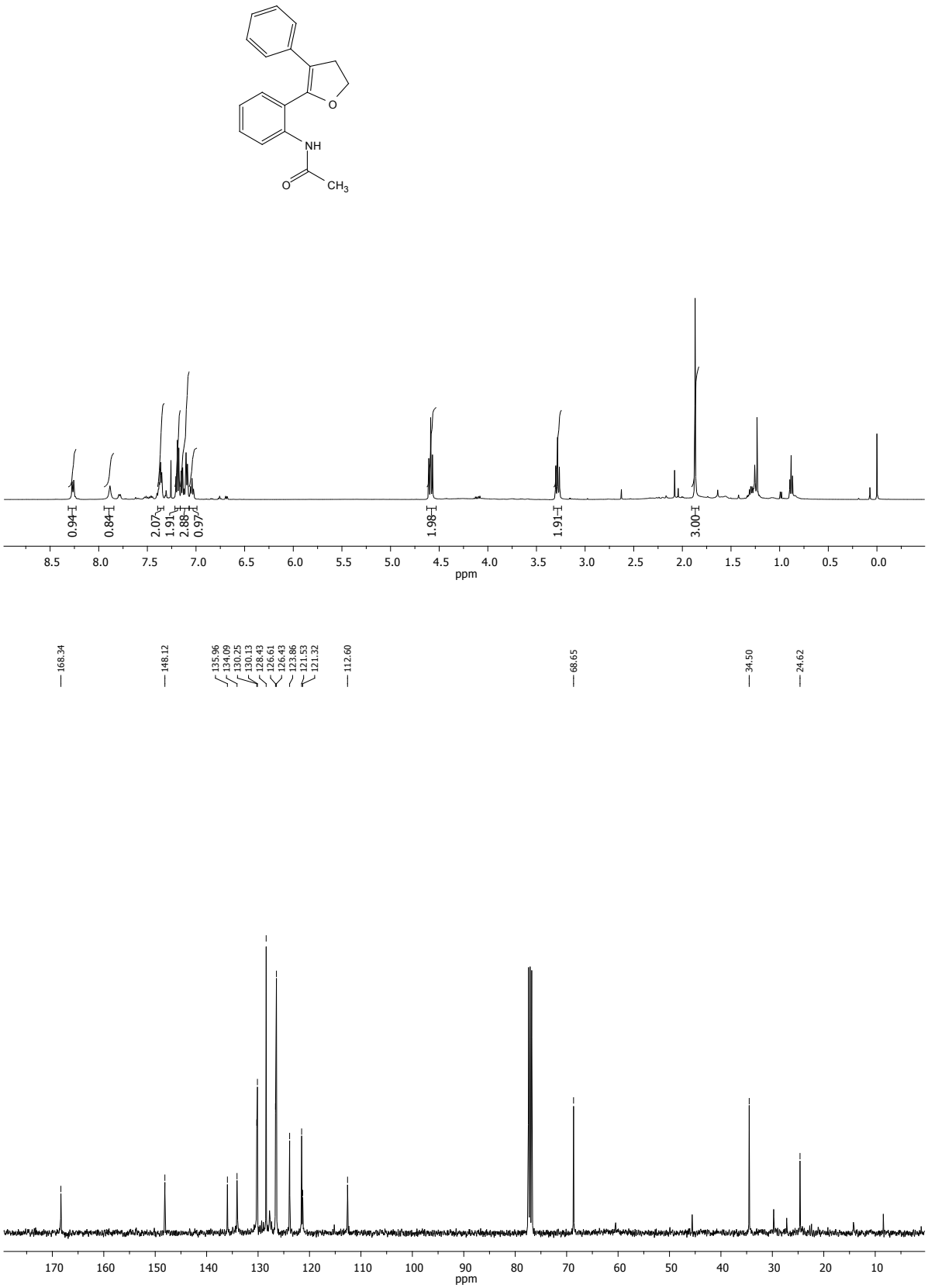

**$^{1}$H NMR** and **$^{13}$C NMR** of **5i**



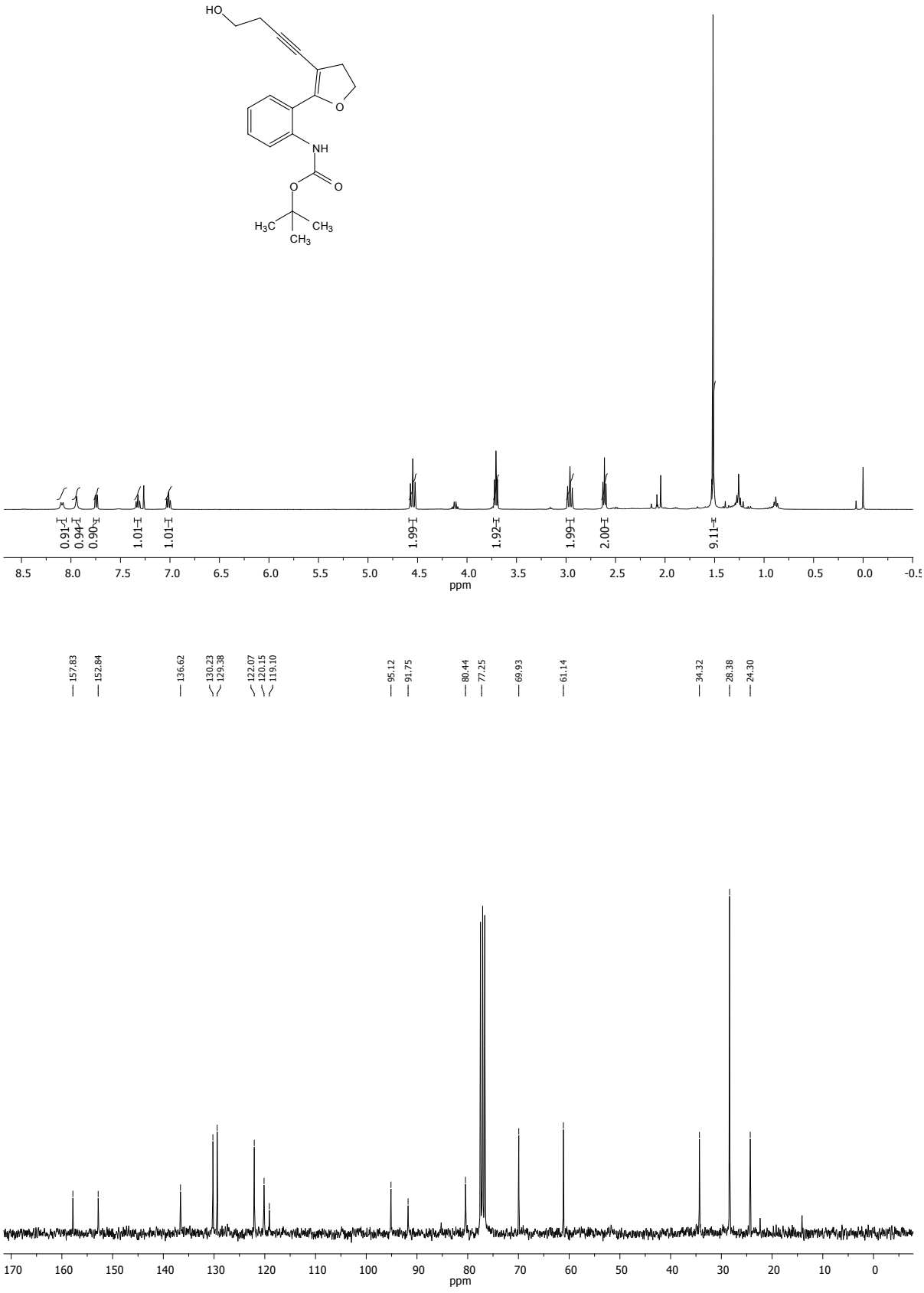



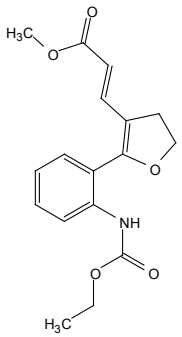

**$^{1}$H NMR** and **$^{13}$C NMR** of **5k**

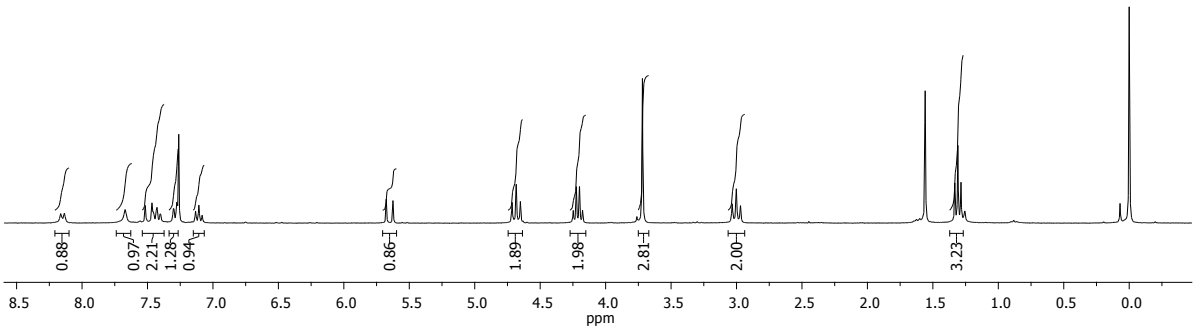


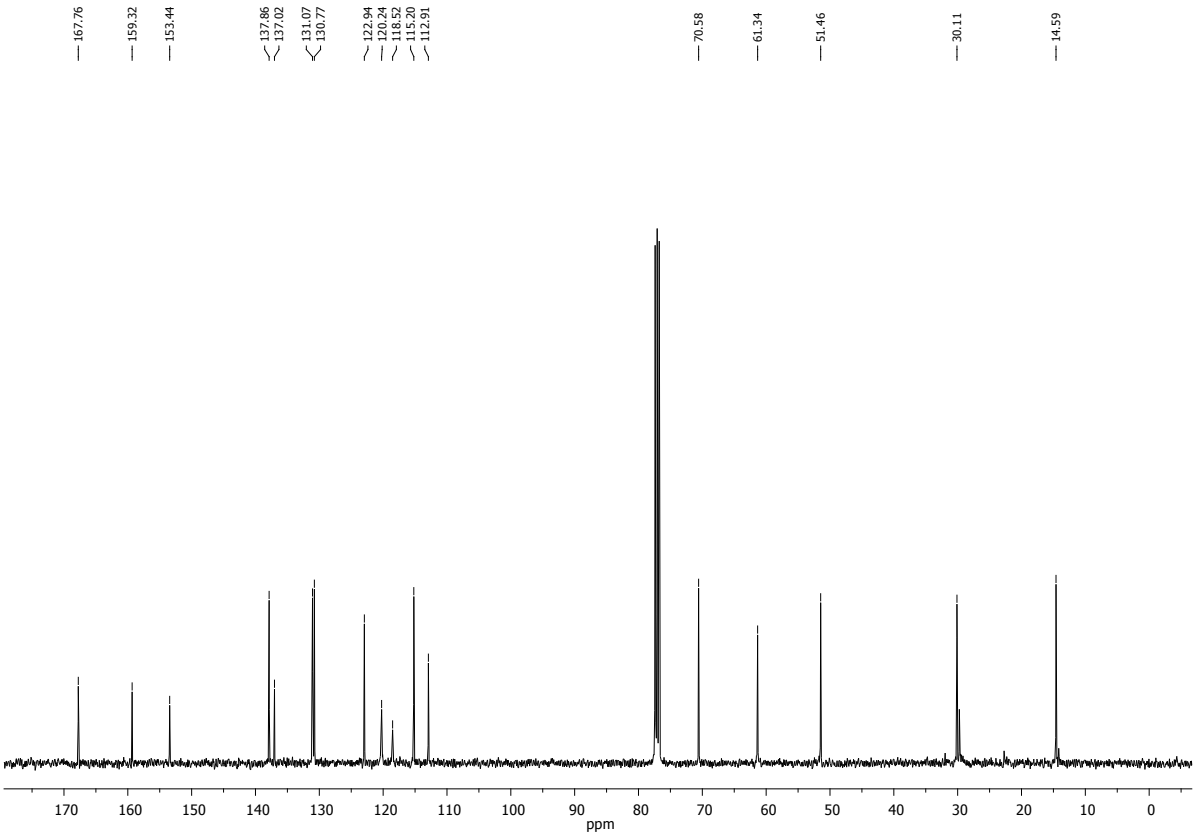

**$^{1}$H NMR** and **$^{13}$C NMR** of **6d**



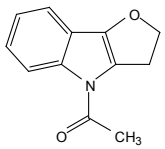

**$^{1}$H NMR** and **$^{13}$C NMR** of **7b**

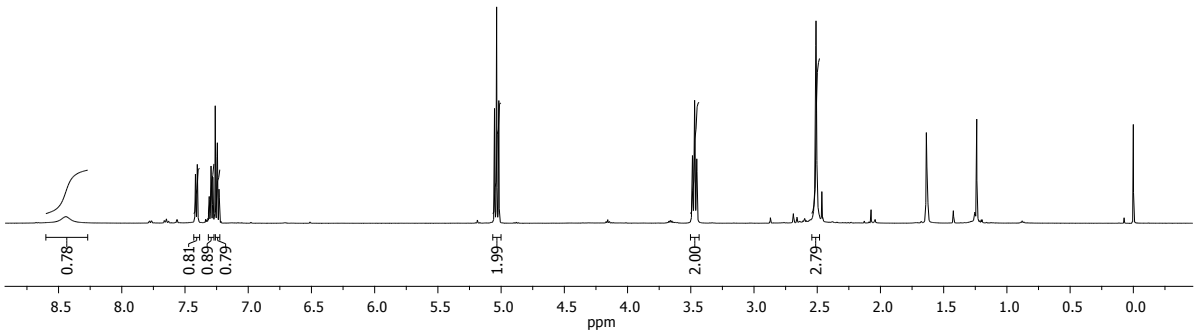


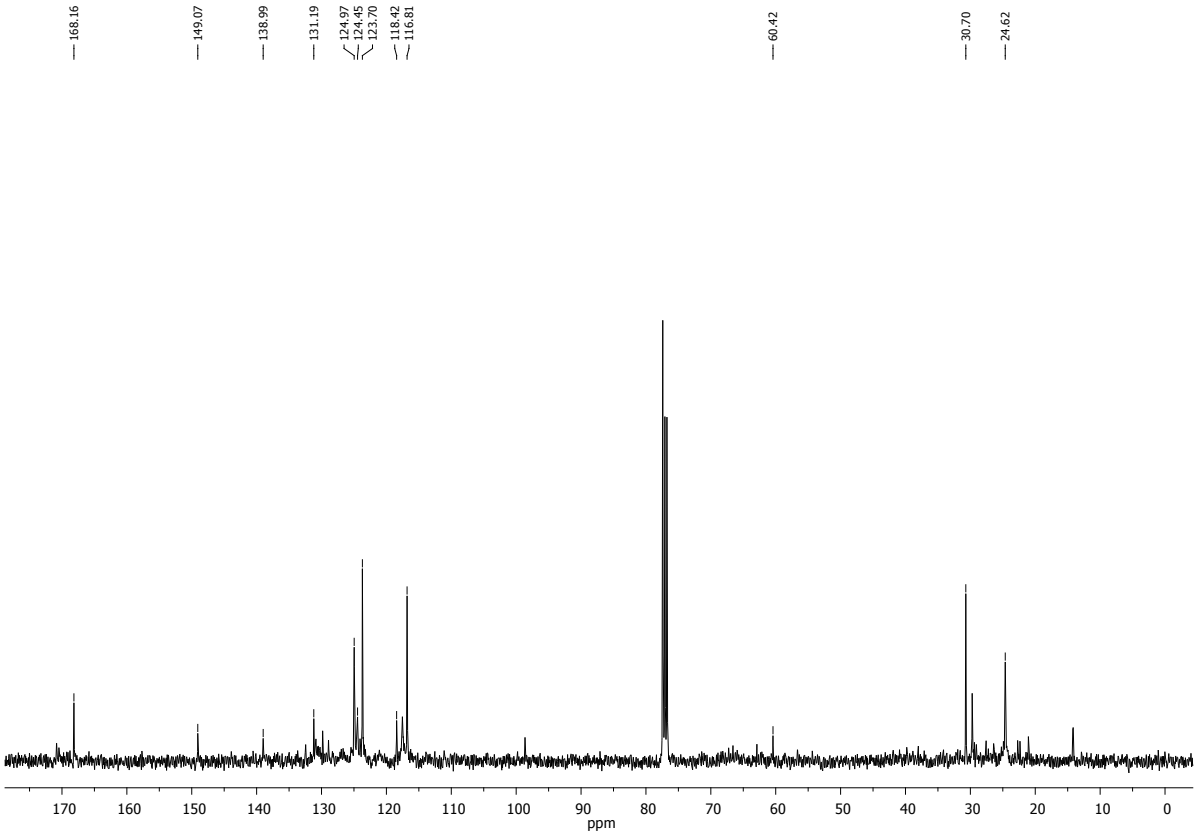




**$^{1}$H NMR** and **$^{13}$C NMR** of **8a**



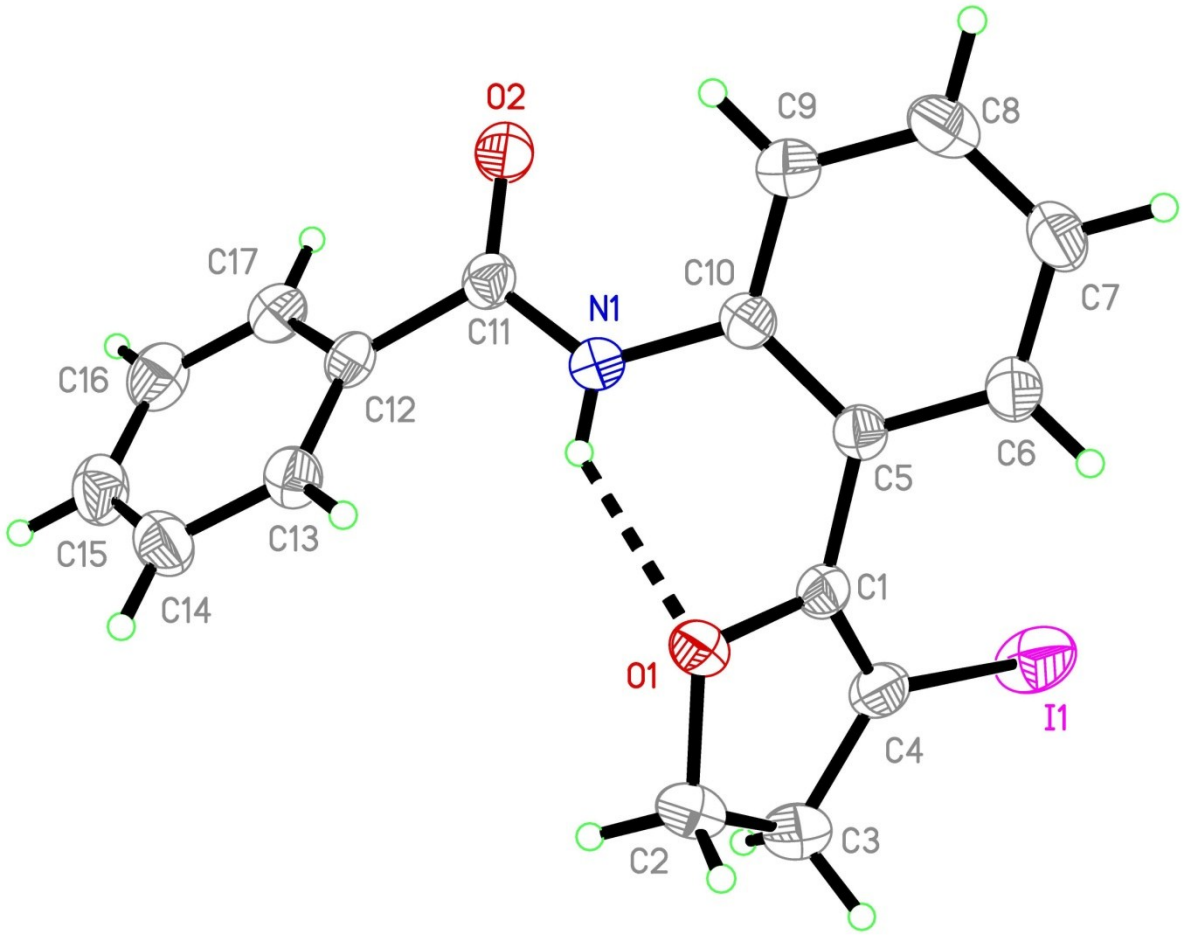




**$^{1}$H NMR** and **$^{13}$C NMR** of **9d**

**X-ray Crystallographic Study:**

**Compound 5e:**




The molecular structure of **5e**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashes line indicate a hydrogen bond.

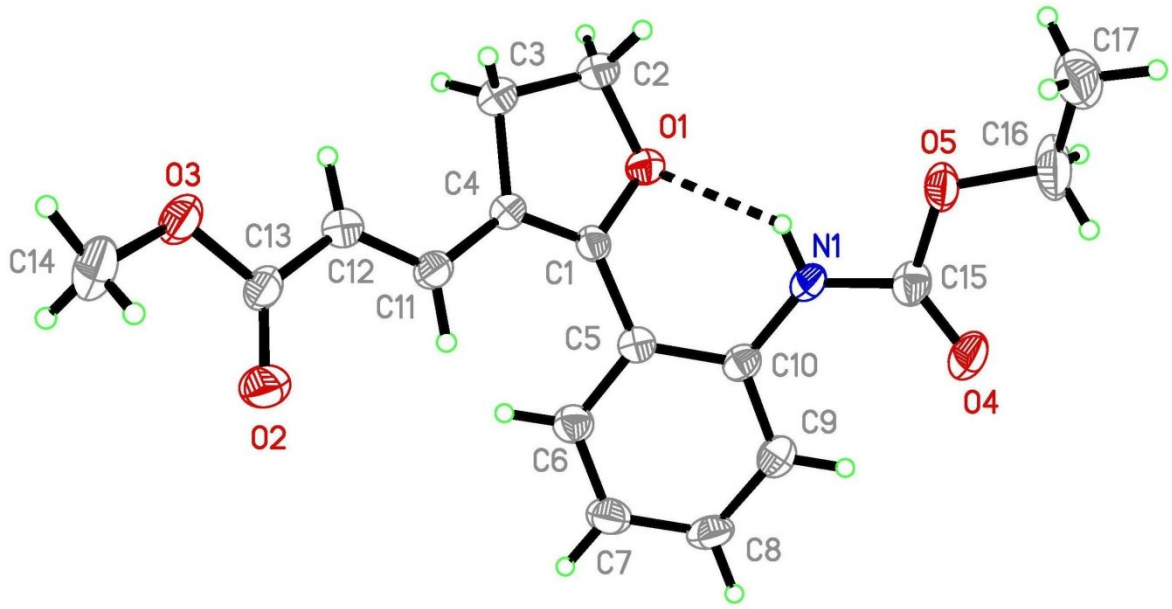
X-ray data of compound **5e** was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS[2] and refinement was carried out by full-matrix least-squares technique using SHELXL.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. The hydrogen atom attached to nitrogen atom was located in a difference density map and refined isotropically. All other H atoms were

positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(c)$ for other H atoms]. The methyl groups were allowed to rotate but not to tip.

**Crystal Data for 5e**: $C_{17}H_{14}INO_2$ ($M$ =391.19): orthorhombic, space group Pbca (no. 61), $a$ = 13.7811(12) Å, $b$ = 13.3475(11) Å, $c$ = 16.9711(15) Å, $V$ = 3121.7(5) Å$^3$, $Z$ = 8, $T$ = 294(2) K, μ(MoKα) = 2.055 mm$^{-1}$, *Dcalc* = 1.665 g/mm$^3$, 33971 reflections measured ($4.8 \leq 2\Theta \leq 56.7$), 3837 unique ($R_{int}$ = 0.0346) which were used in all calculations. The final $R_1$ was 0.0462 (>2σ(I)) and $wR_2$ was 0.1179 (all data). CCDC 1405059 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

**Compound 8a:**




The molecular structure of **8a**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Dashes line indicate a hydrogen bond.

X-ray data of compound **8a** was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-

scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS[2] and refinement was carried out by full-matrix least-squares technique using SHELXL.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. The hydrogen atom attached to nitrogen atom was located in a difference density map and refined isotropically. All other H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(c)$ for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal data for **8a**: $C_{17}H_{19}NO_5$, $M$ = 317.33, 0.18 x 0.16 x 0.09 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 13.6571(12), $b$ = 7.7611(7), $c$ = 14.9680(14) Å, $\beta$ = 91.630(2)°, $V$ = 1585.9(2) Å$^3$, $Z$ = 4, $D_c$ = 1.329 g/cm$^3$, $F_{000}$ = 672, MoKα radiation, λ = 0.71073 Å, $T$ = 294(2)K, $2\theta_{max}$ = 50.0º, 14739 reflections collected, 2794 unique ($R_{int}$ = 0.0706). Final *GooF* = 1.242, *R1* = 0.0975, *wR2* = 0.1684, *R* indices based on 2100 reflections with I >2σ(I) (refinement on $F^2$), 214 parameters, 0 restraints. μ = 0.098 mm$^{-1}$.CCDC 1051824 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

Reference:


1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. (2015). Acta Cryst. C71, 3–8.