

Supplementary Material (ESI) for Chemical Communication

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**Palladium Catalyzed Domino Reaction of 1,4-Disubstituted 1,2,3-Trizoles
via Double C-H Activation: One-pot Synthesis of
Triazolo [1,5-f] Phenanthridines**

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Pravin R. Likhar*^a

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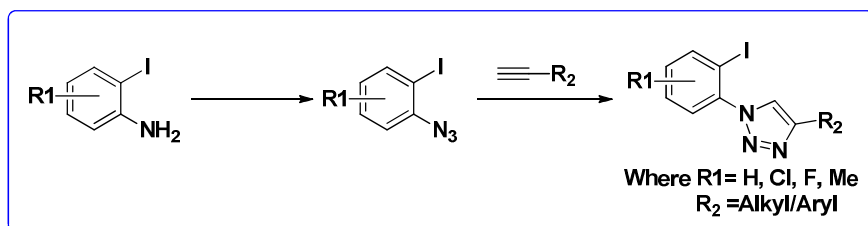
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Experimental Section

General information:

All reagents were purchased from commercial suppliers and used without further purification. All experiments were carried out under nitrogen atmosphere. All the solvents used for the reaction were distilled before use. The product purification by column chromatography was accomplished using silica gel 100-200 mesh. Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker-Avance (300 MHz); Inova (400 MHz) and Avance (500 MHz) spectrophotometer using CDCl_3 and TMS as the internal standard. Chemical shifts (δ) are reported in ppm using TMS as an internal standard, and spin-spin coupling constants (J) are given in Hz. Multiplicities in the ^1H 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 on a Waters 2695 and Thermo Scientific Exactive spectrometer respectively and mass/charge (m/z) ratios are reported as values in atomic mass units. All the melting point is uncorrected.

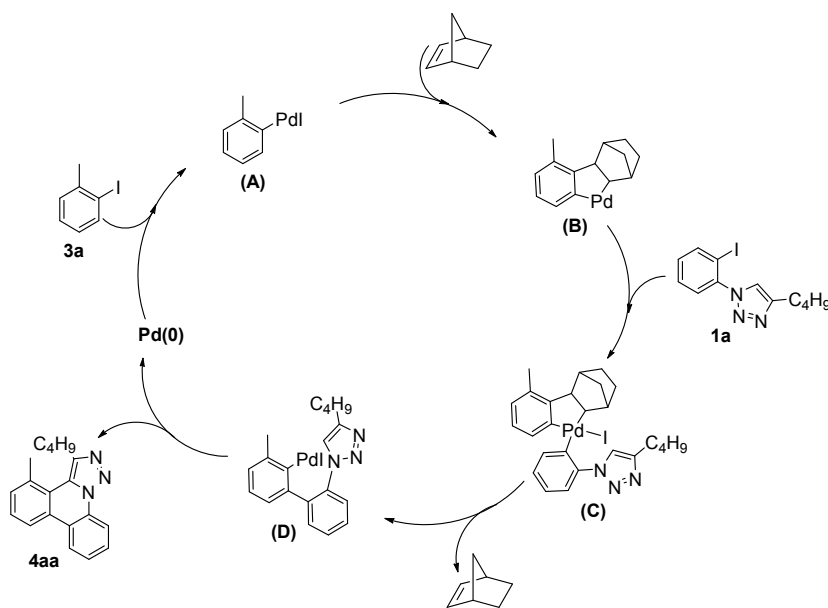
General experimental procedure for the synthesis of 2-iodophenyl 4-alkyl/aryl-1H 1,2,3-triazole (1a-1y)¹:



To a stirred solution of 2-iodoaniline (3.0 mmol) in 4N HCl (10 mL) was added NaNO_2 (0.82 gm, 12 mmol) slowly in portions over a period of 15 mins at 0°C . The reaction mixture was allowed to stir at same temperature for another 30 min. To the above reaction mixture sodium azide (0.59 gm, 9.0 mmol) was slowly added in portions and the mixture allowed to come to the room temperature and stirred for 4-12 hrs (monitored by TLC using hexane: ethyl acetate (8:2) solvent). The reaction mixture was successively diluted with water. The aqueous layer was extracted with ethyl acetate (3 x 60 mL), and combined organic layers were washed with water, followed by brine, dried over Na_2SO_4 and concentrated under reduced pressure to obtain crude azide derivatives which was carried forward for the

click reaction without any further purification. To a solution of crude azide (0.49 gm, 2.0 mmol) and terminal alkyl/aryl acetylene (2.0 mmol) in DMF (10 mL) was added CuI (10 mol%) and the mixture was heated at 100 °C for 8 hrs. The aqueous layer was extracted with ethyl acetate (3 x 40 mL), and combined organic layer was washed with water (3 x 50 mL), followed by brine, dried over Na₂SO₄ and concentrated under reduced pressure to obtain crude triazole derivatives in quantitative yields.

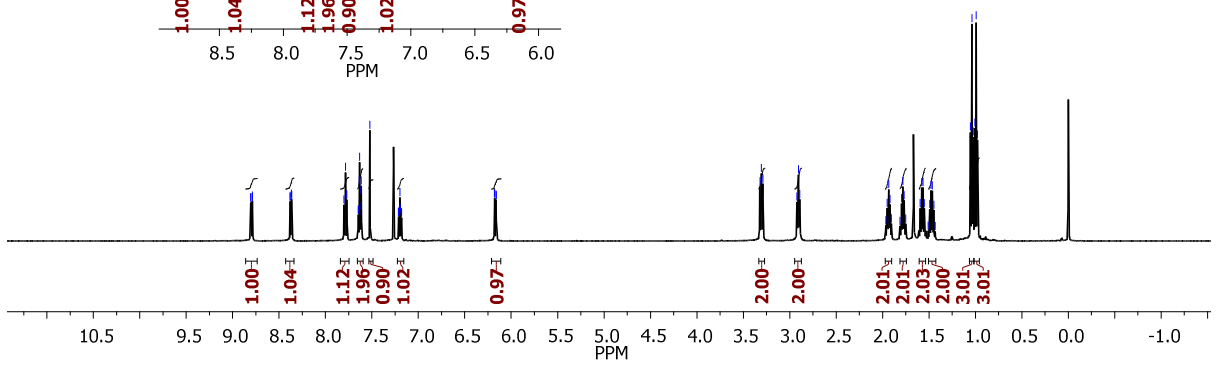
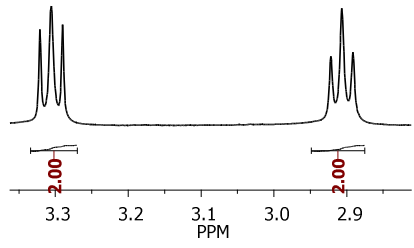
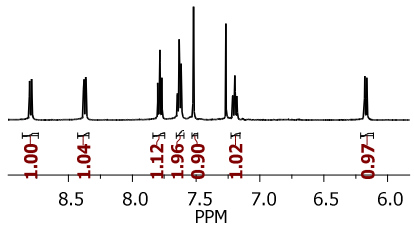
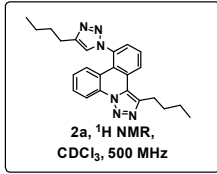
Plausible mechanism for hetero aryl cross coupling: Based on the literature reports² a plausible mechanism for the cross coupling reaction between **1a** and **3a** in the presence norbornene can be rationalized (depicted in ESI-scheme-1). Initially, the aryl iodide (**3a**) oxidatively insert to Pd(0) to give Pd(II) (**A**) species and then norbornene inserts into **A** to give corbopalladacyclic intermediate (**B**) after removal of HI in the presence of base. The oxidative addition of substituted triazole **1a** to corbopalladacyclic intermediate (**B**) to give Pd(IV) intermediate (**C**). Aryl-aryl bond formation takes place *via* reductive elimination and removal of nonbornene to give (**D**) which led to the formation of desired heterocoupled product (**4aa**) *via* intramolecular C-H activation.



ESI-scheme-1: Plausible mechanism for heterocoupling

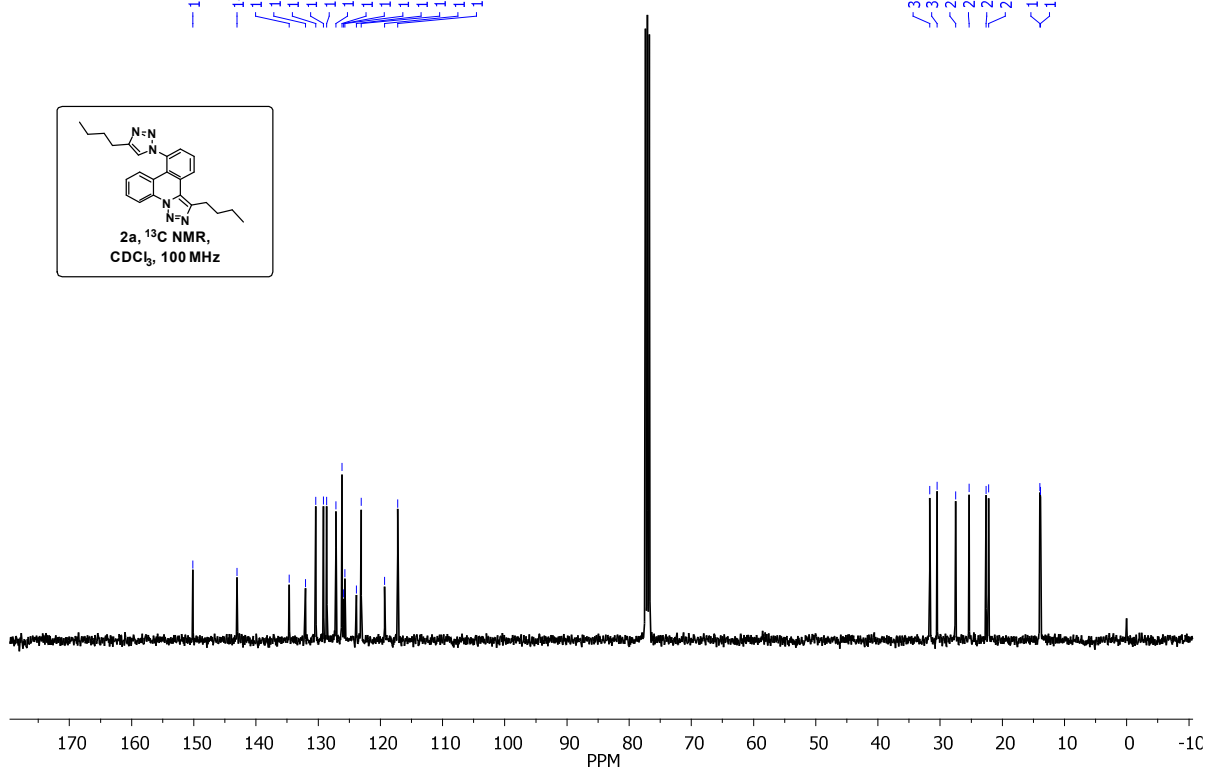
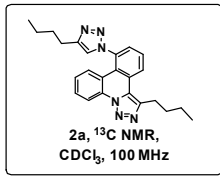
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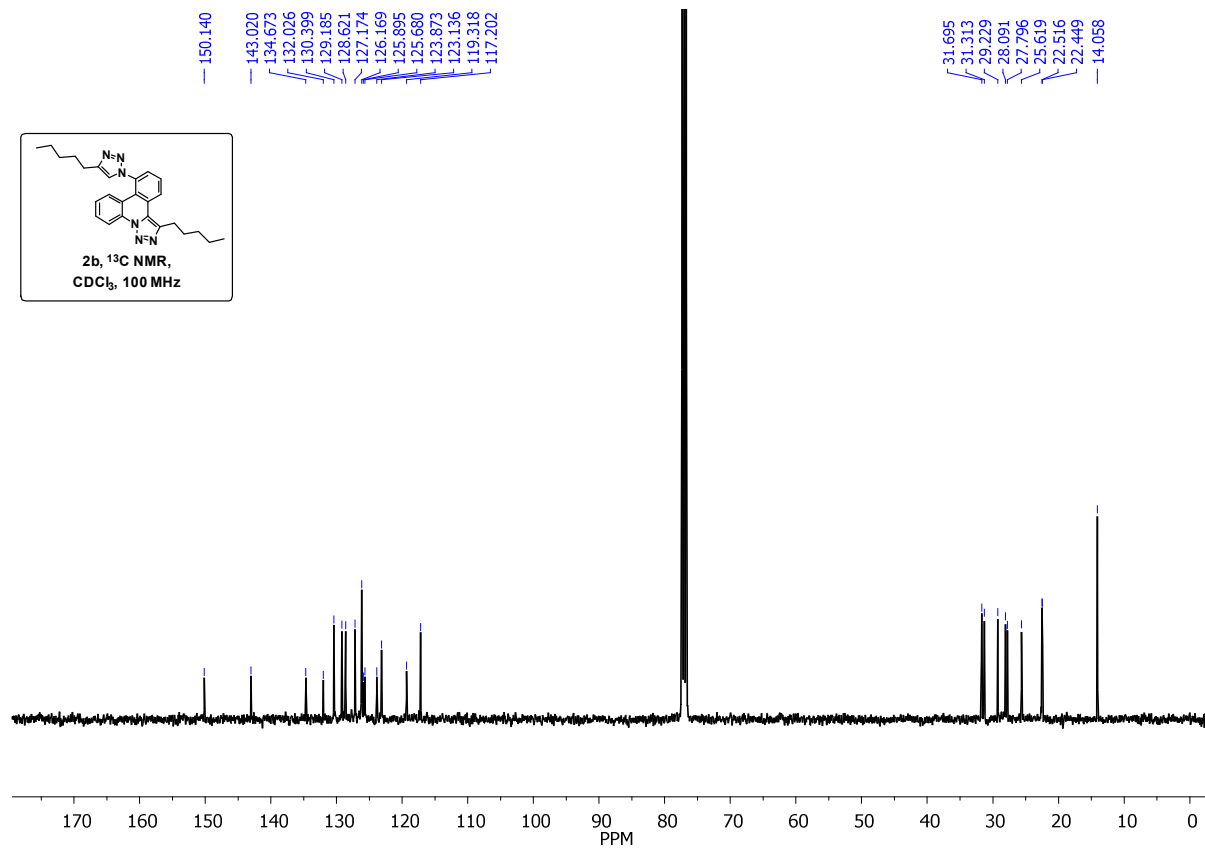
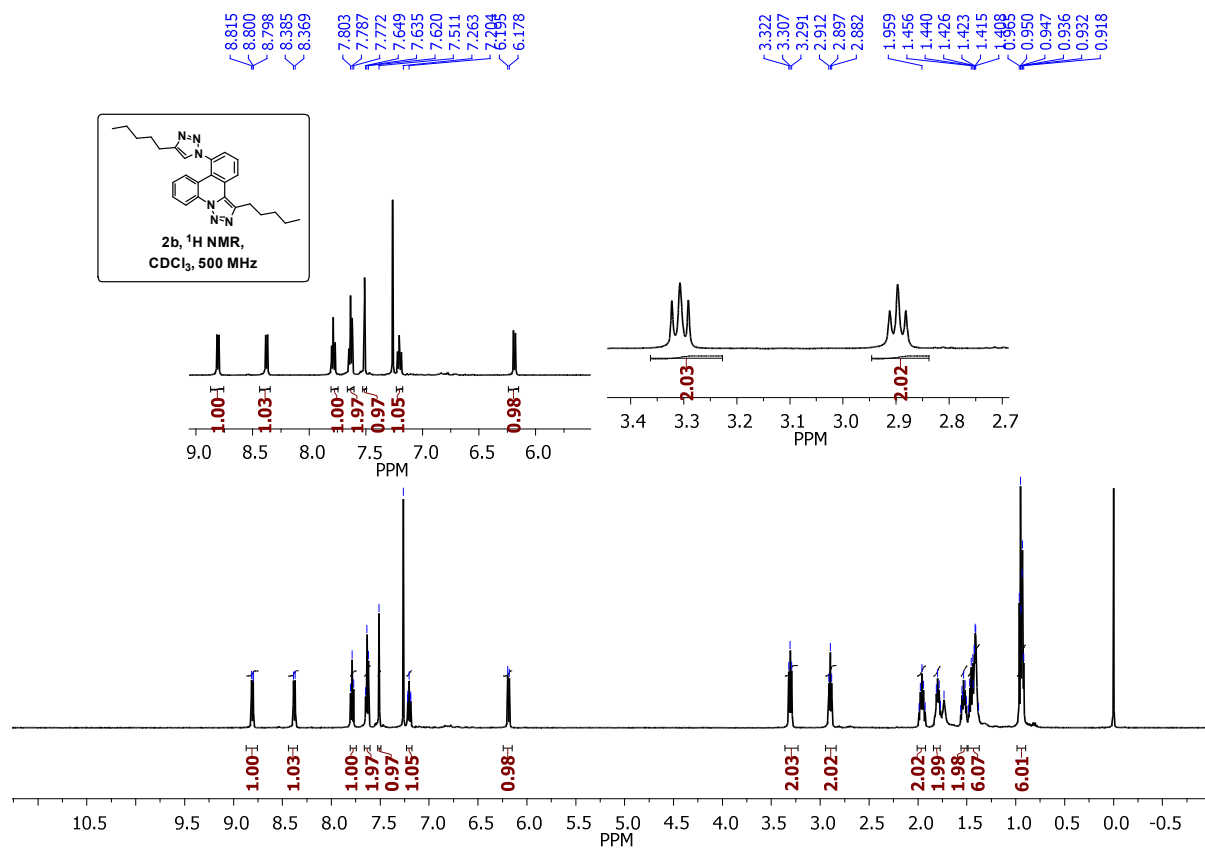
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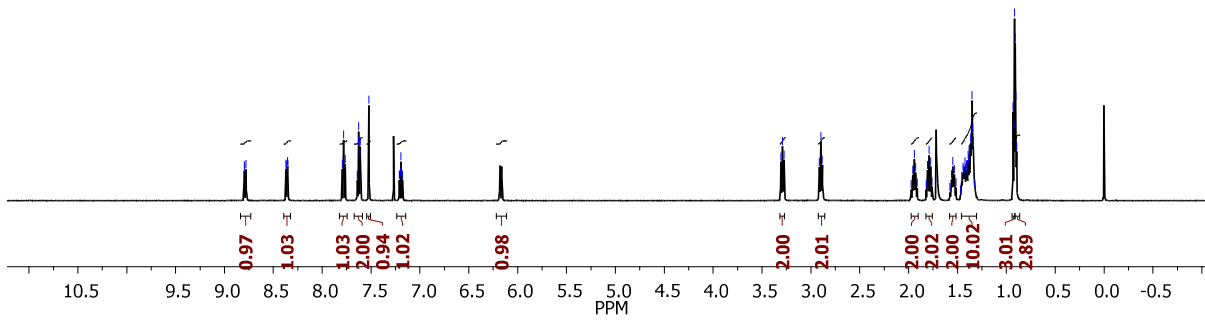
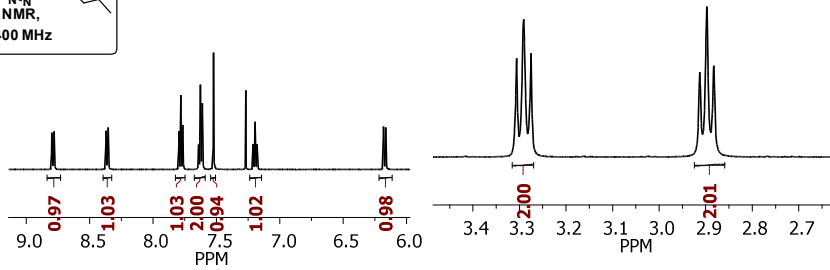
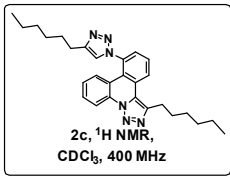
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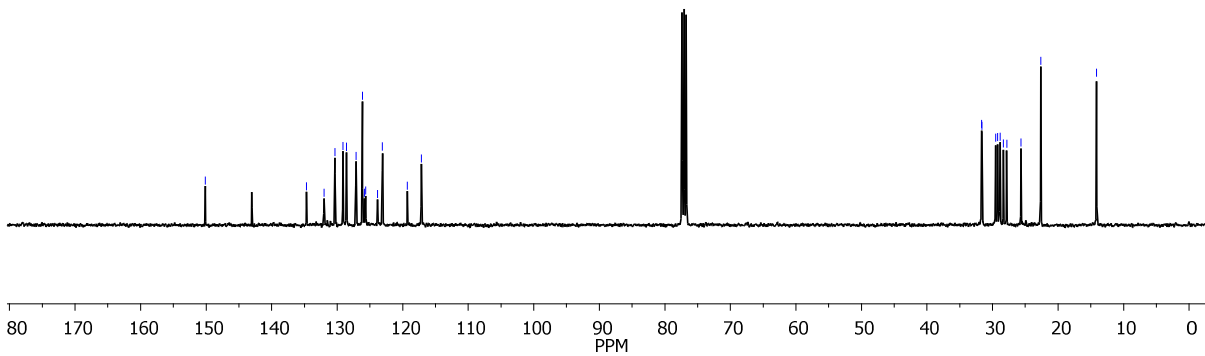
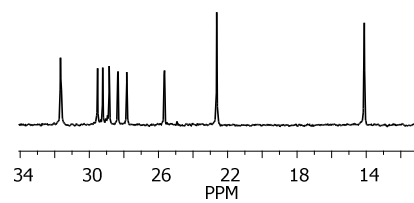
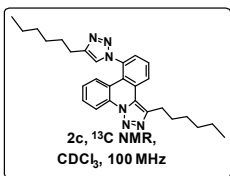


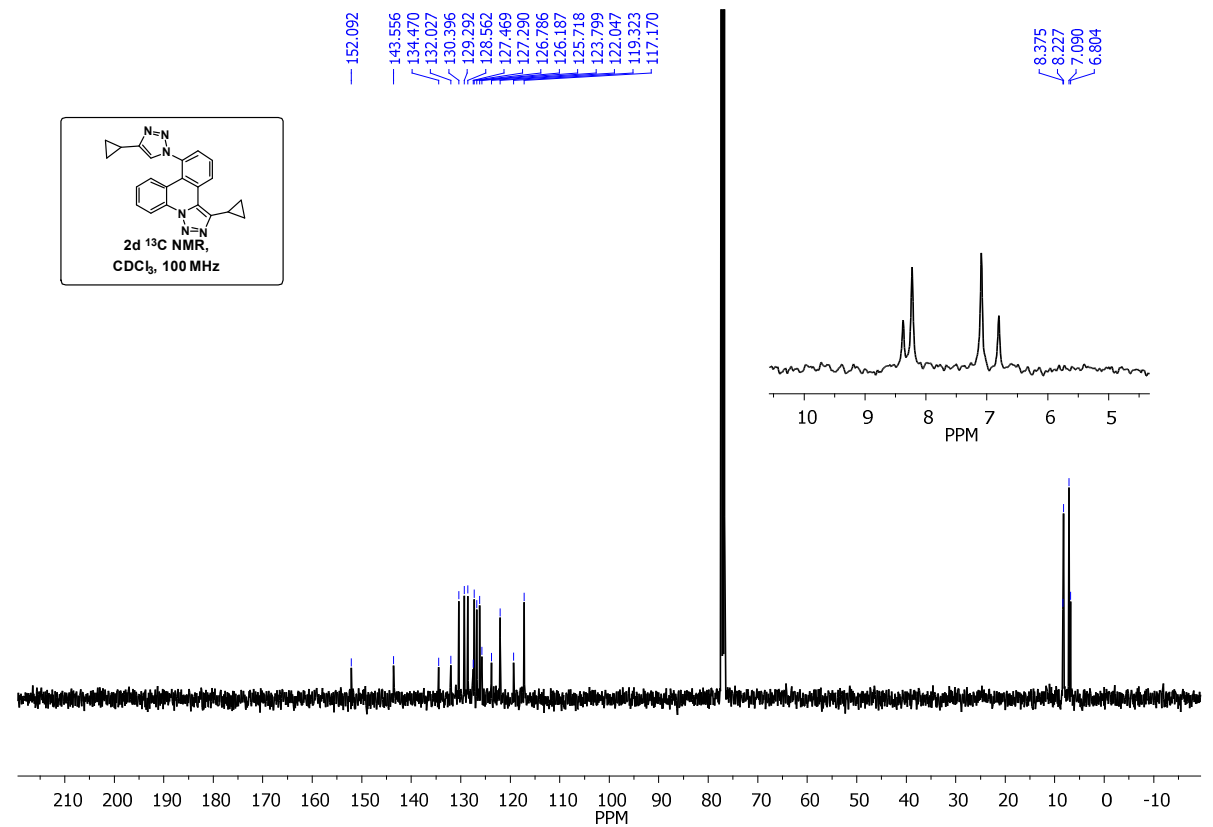
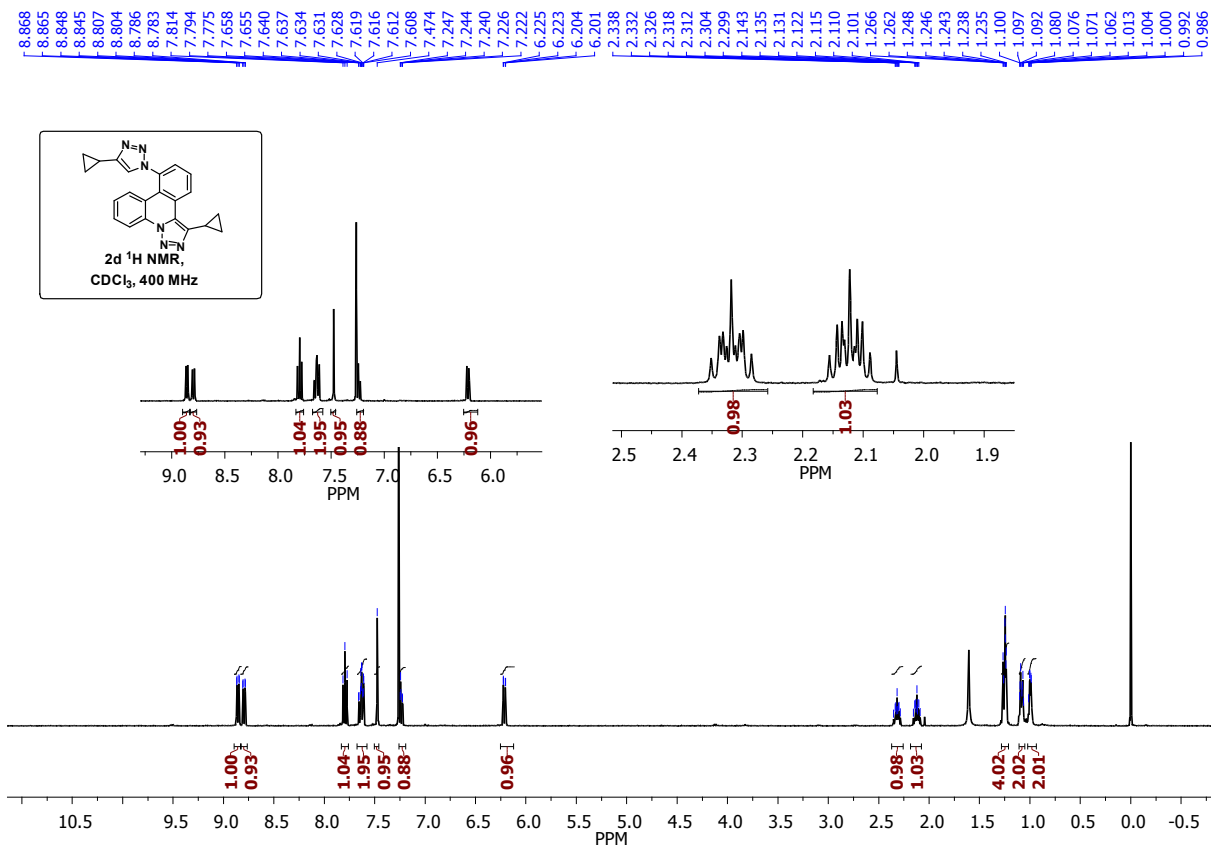
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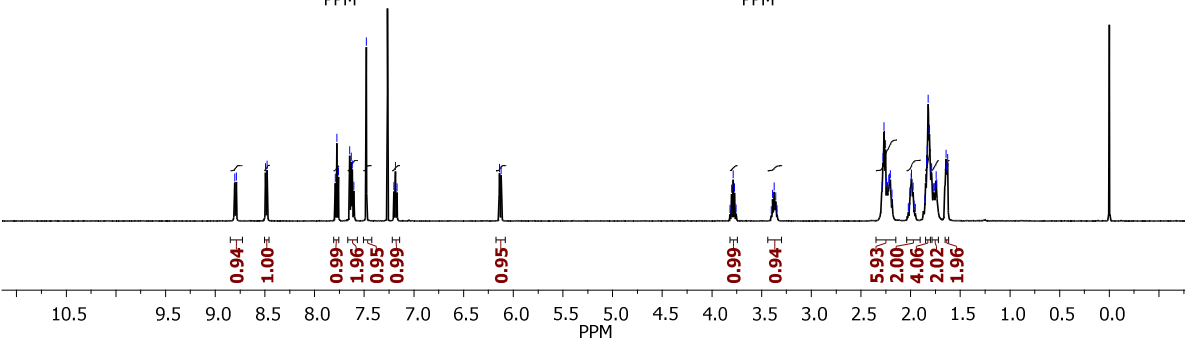
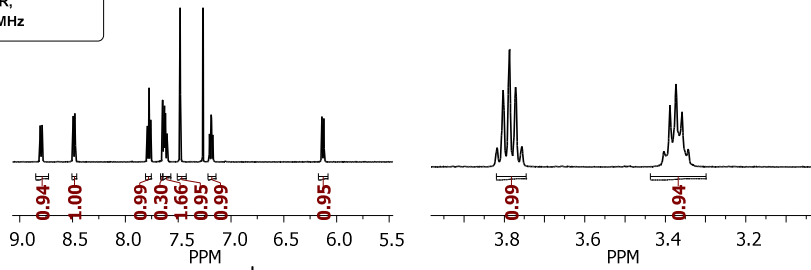
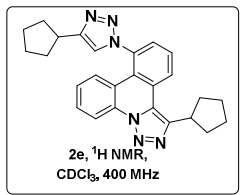
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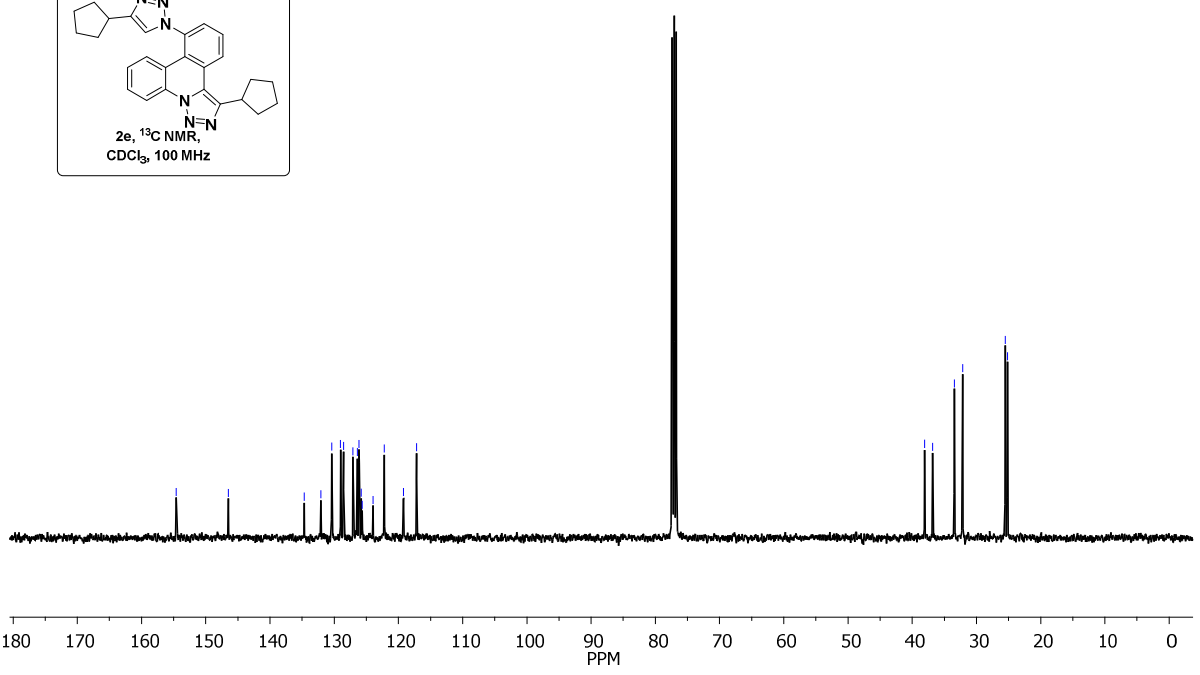
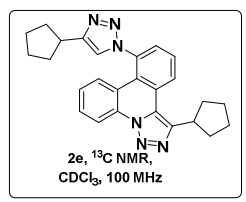


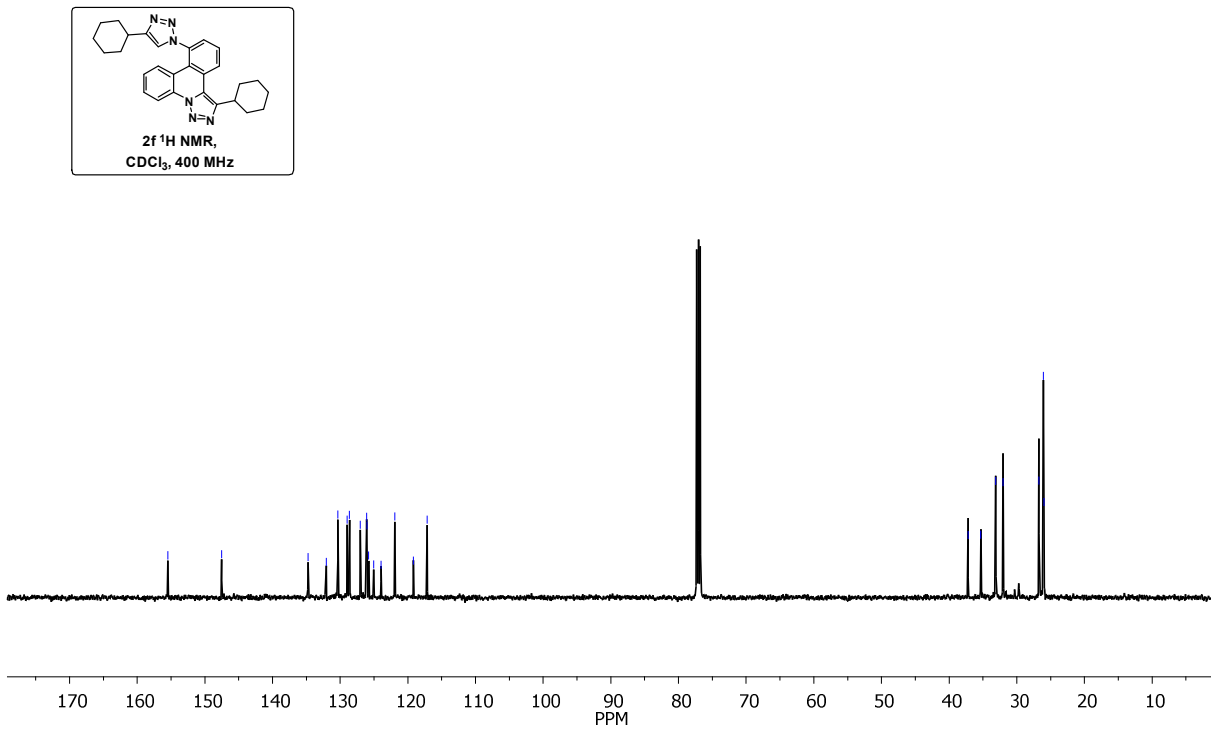
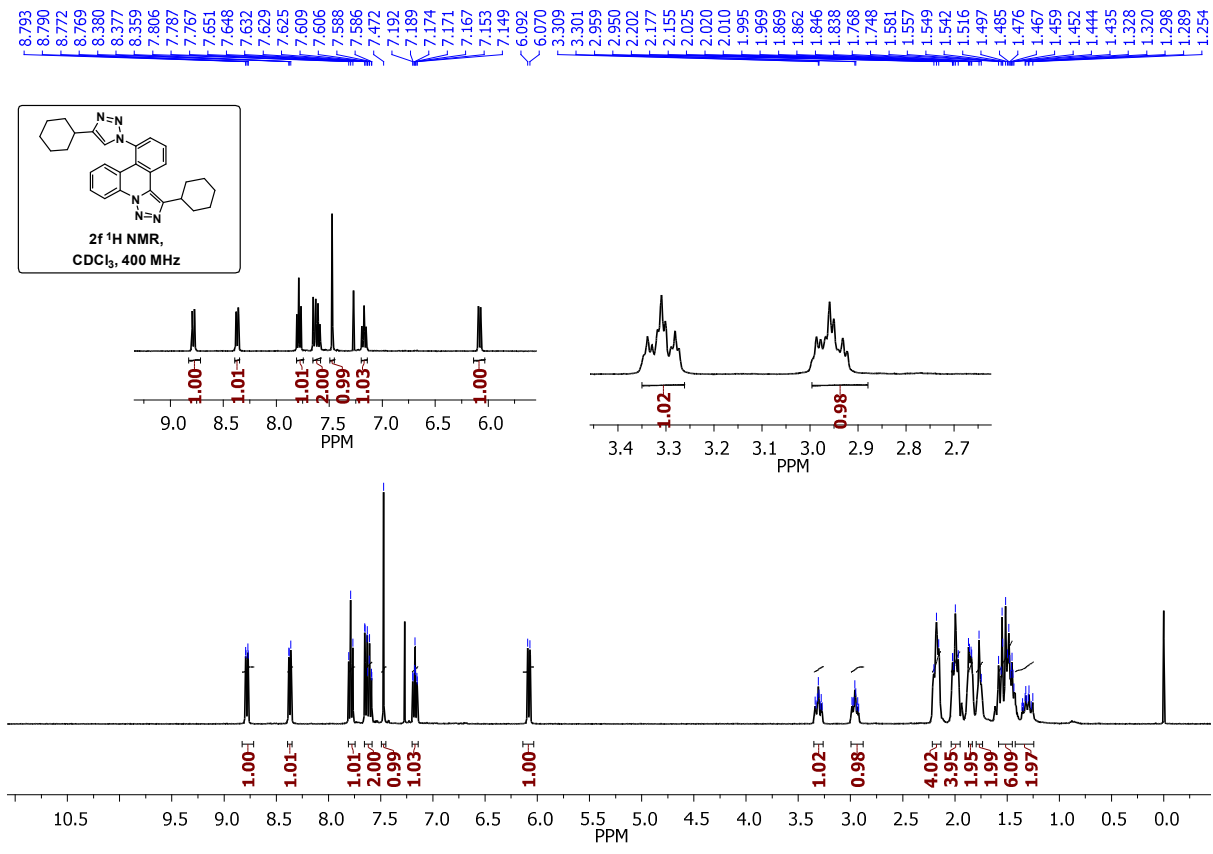


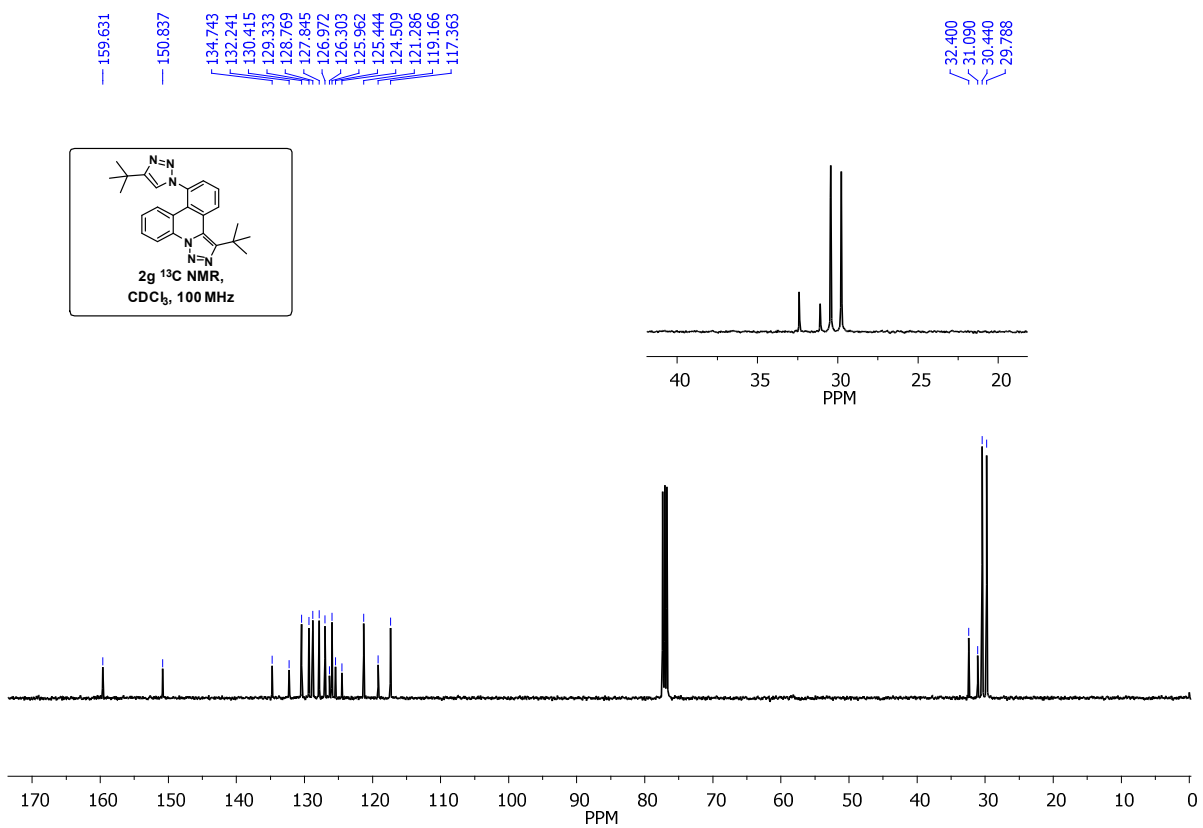
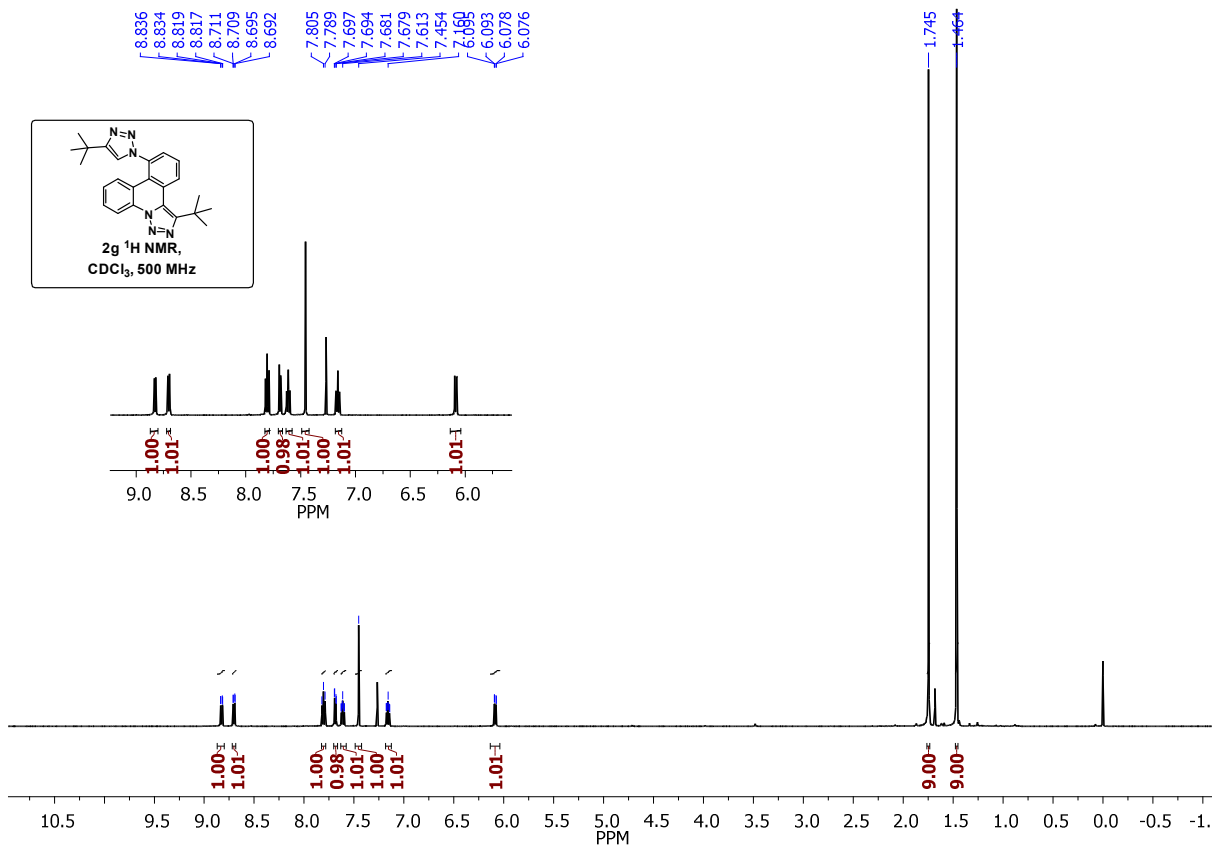
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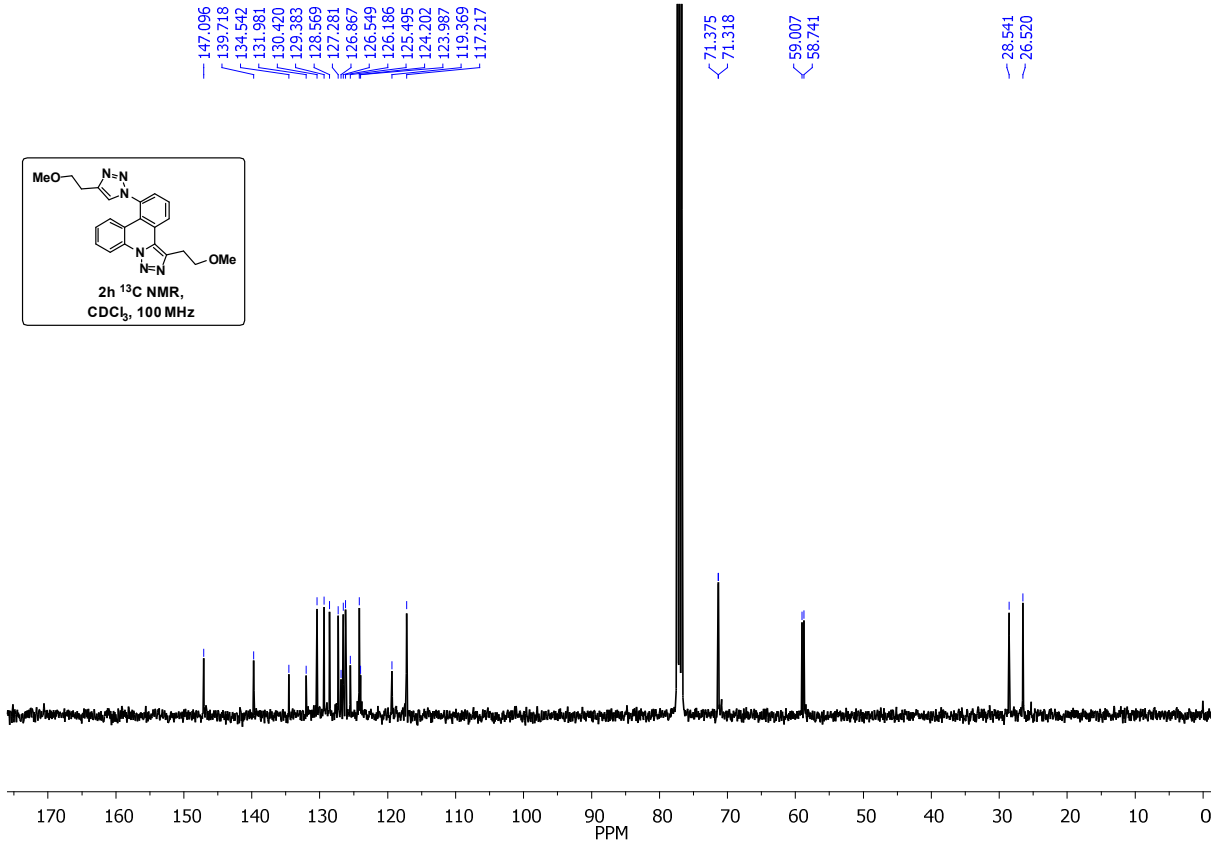
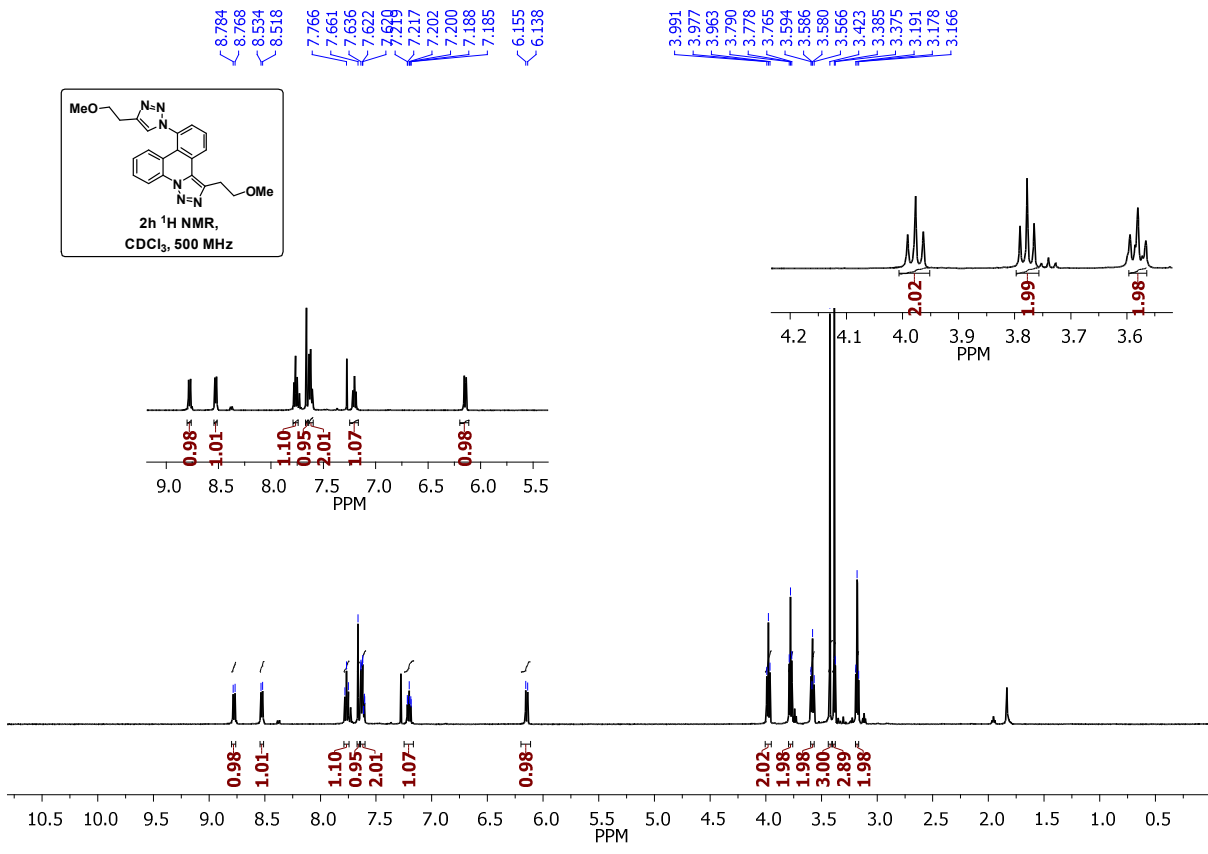


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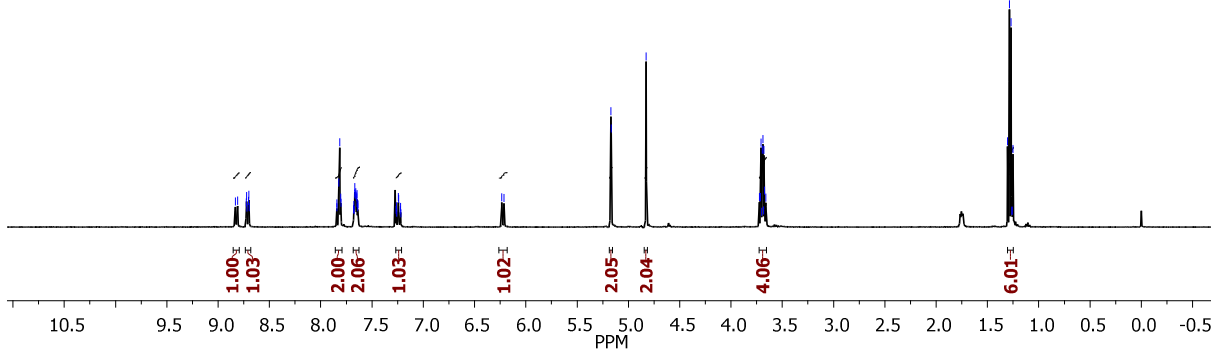
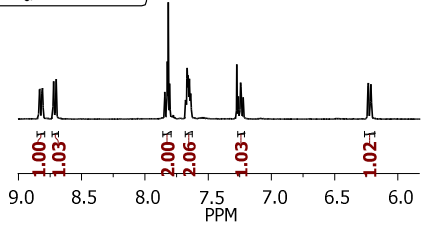
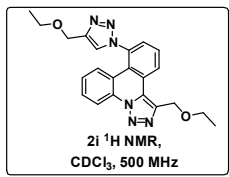




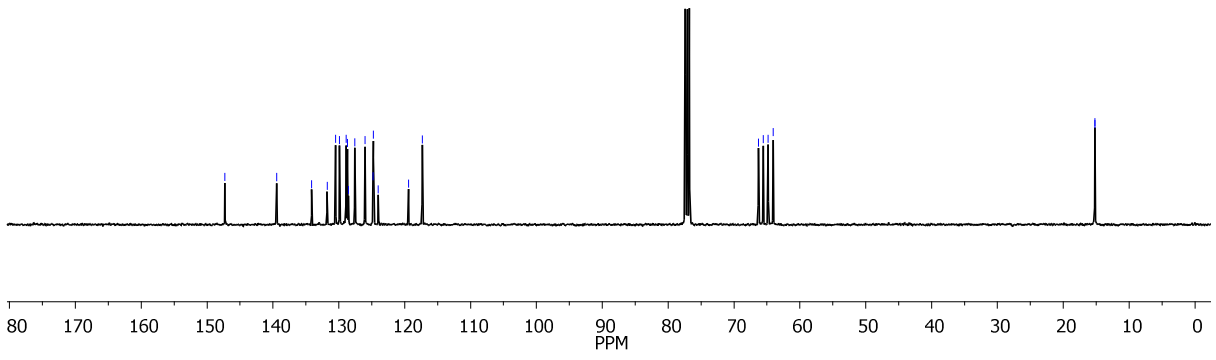
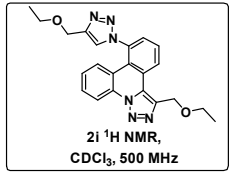


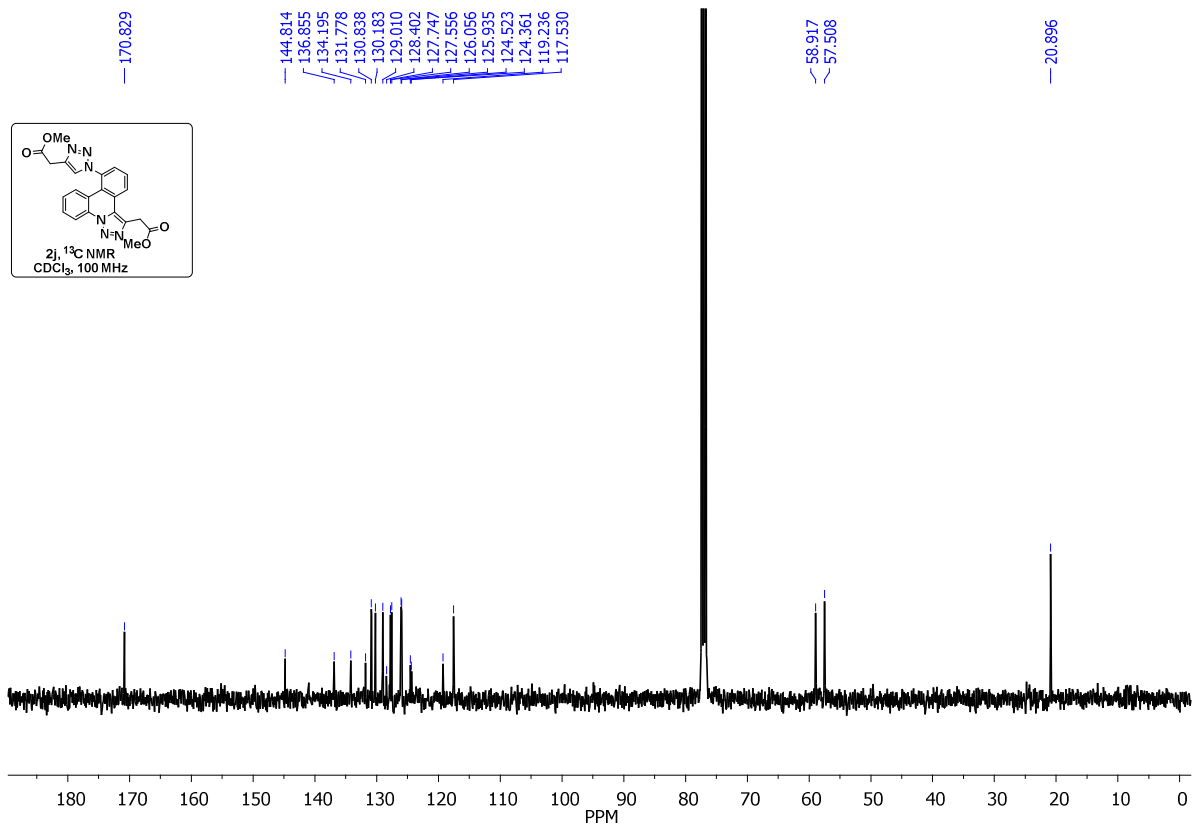
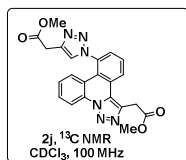
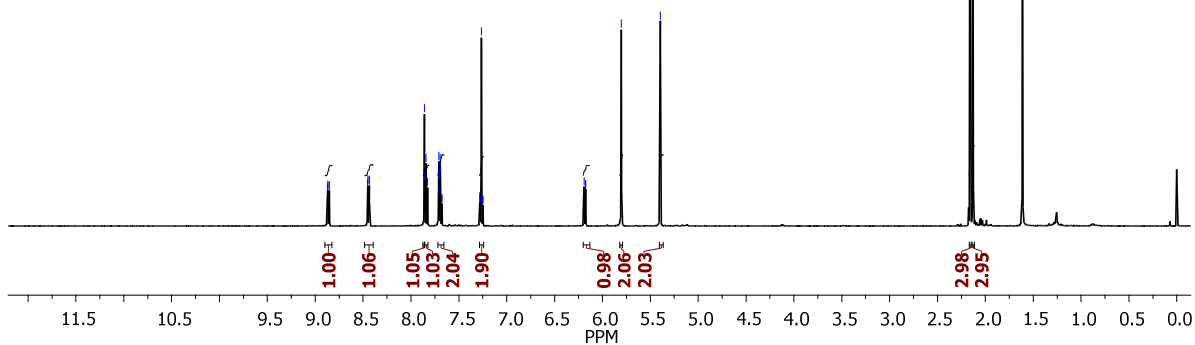
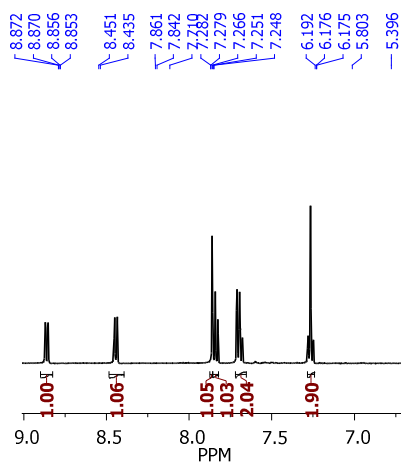
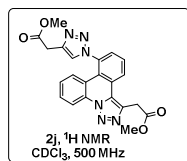


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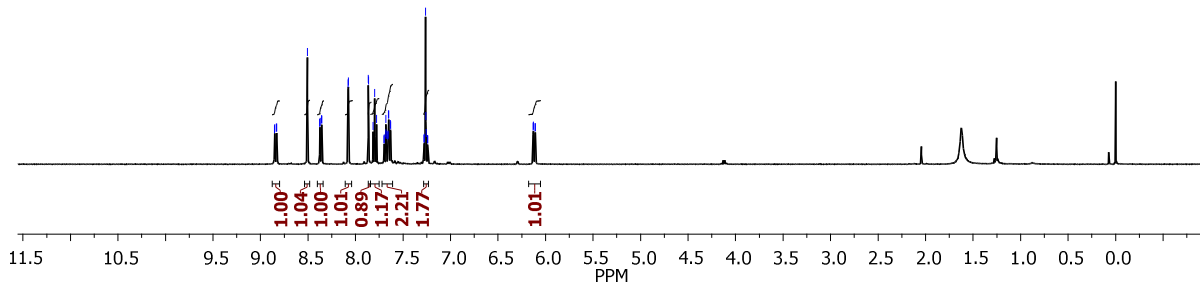
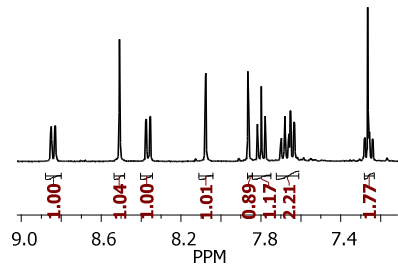
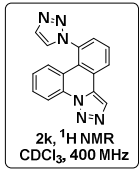


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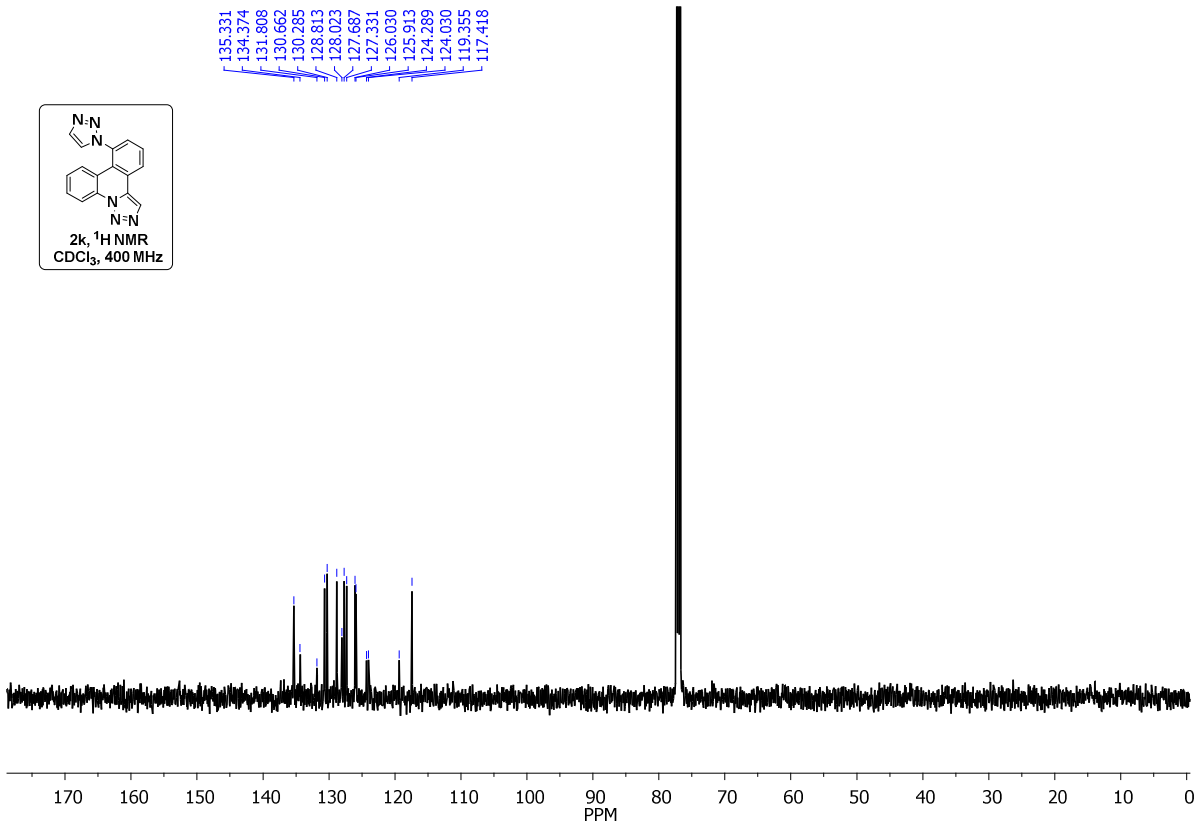
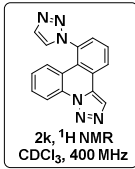


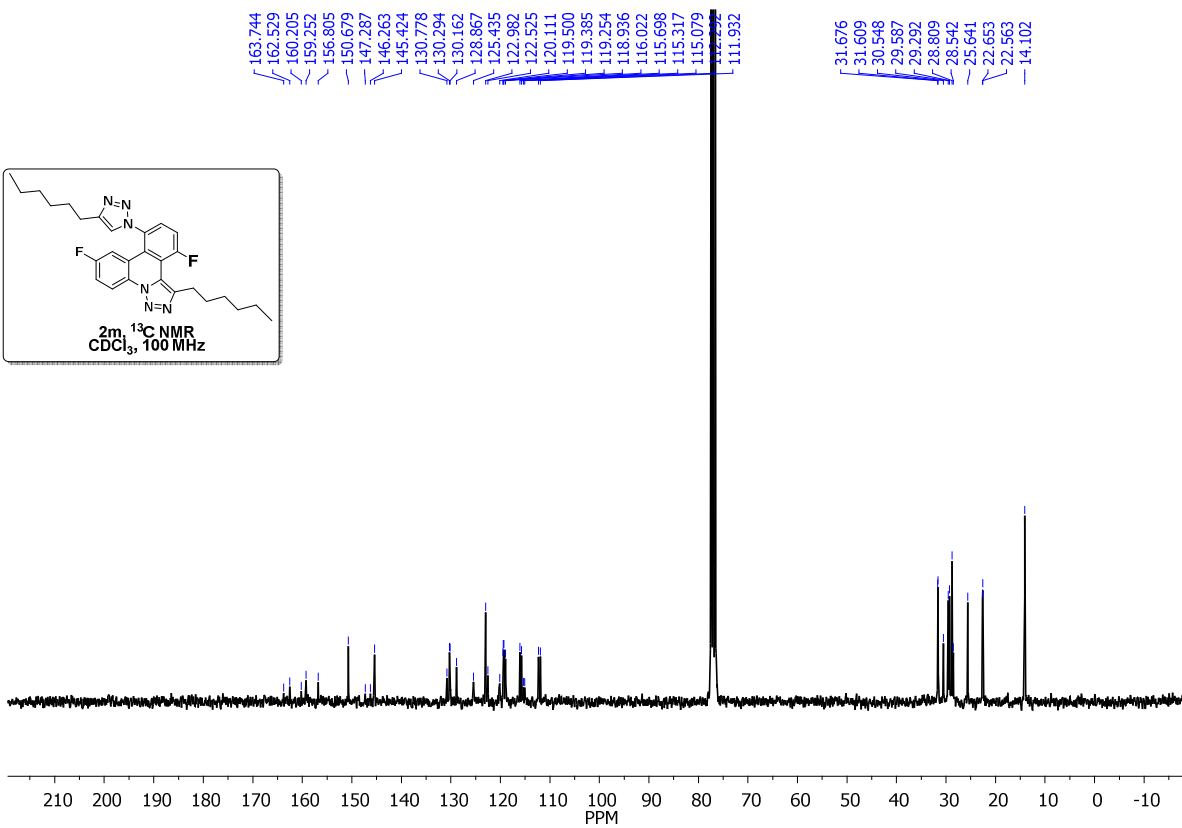
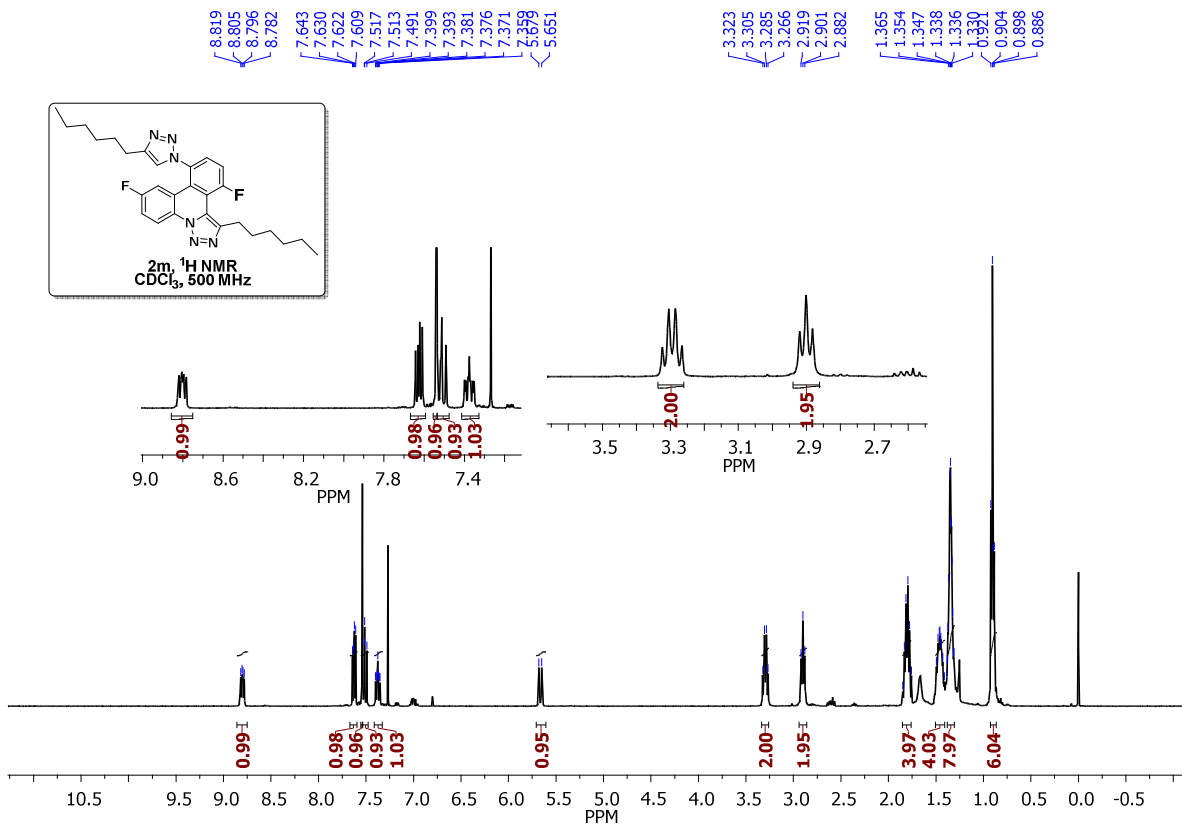


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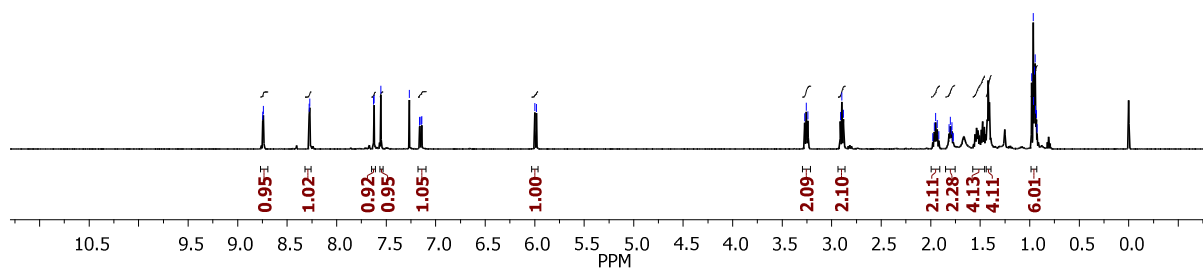
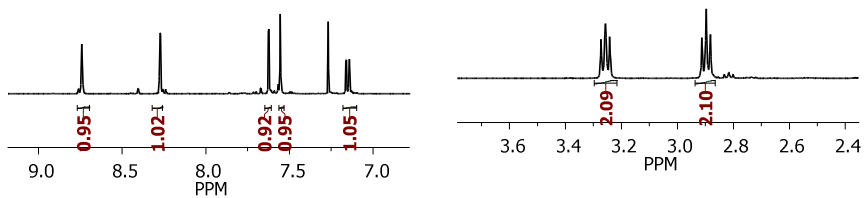
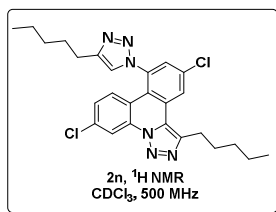
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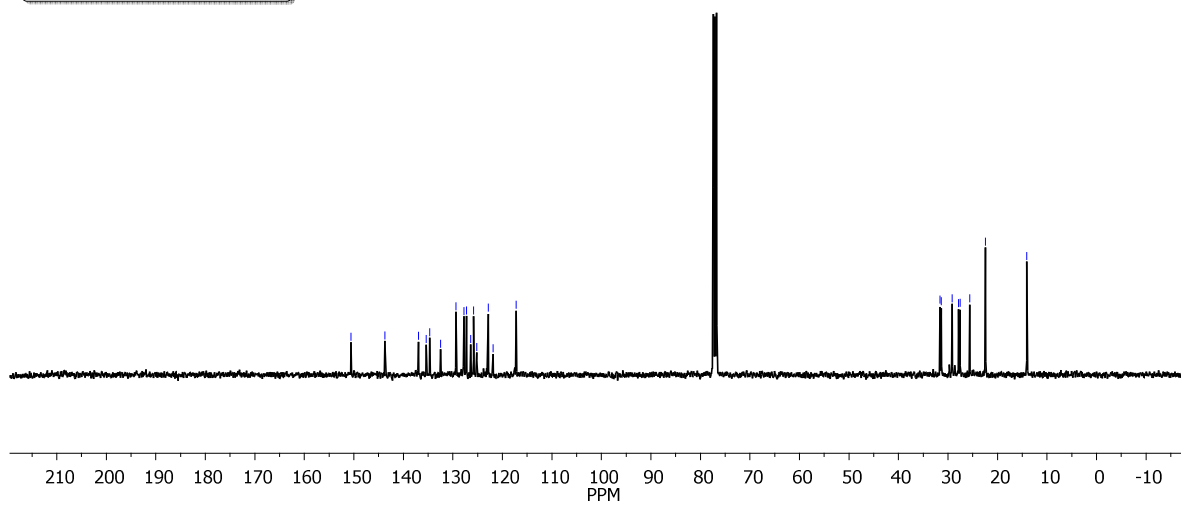
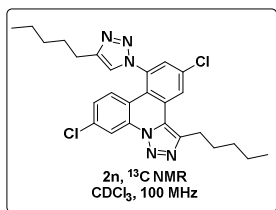
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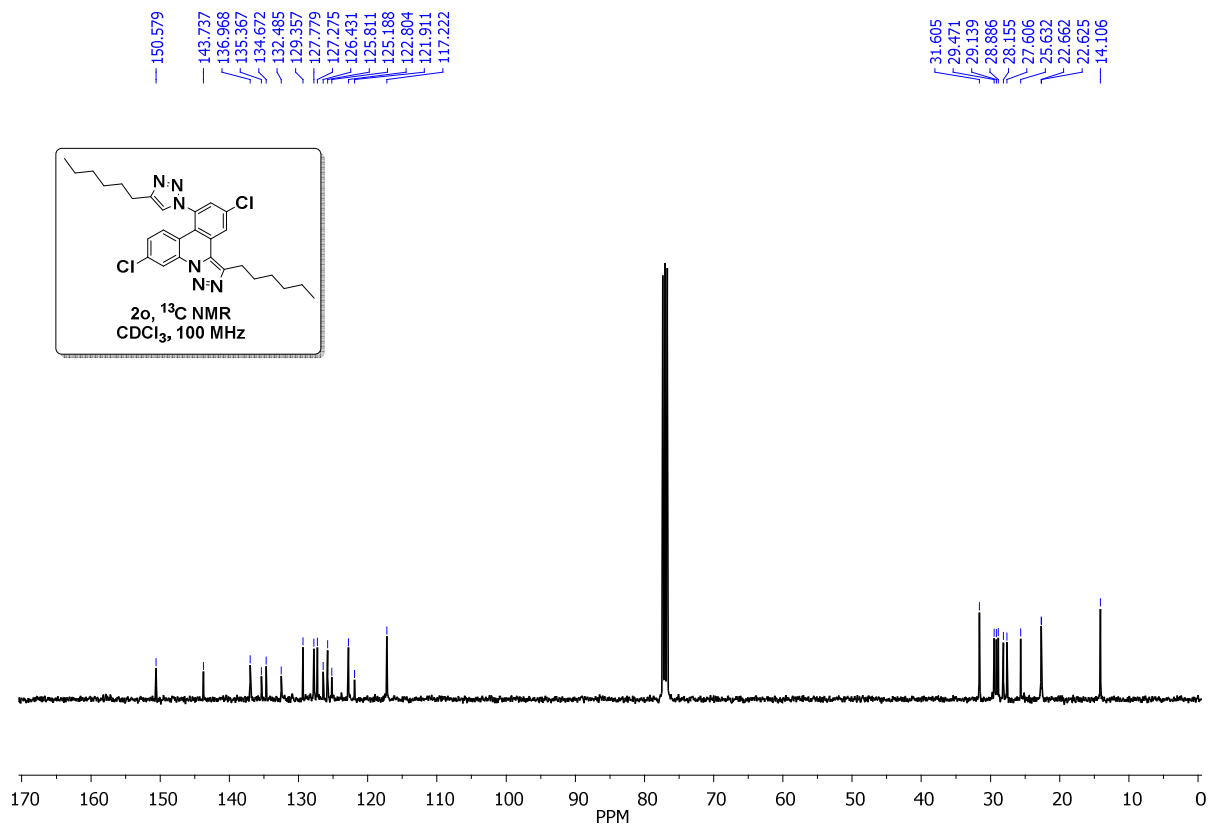
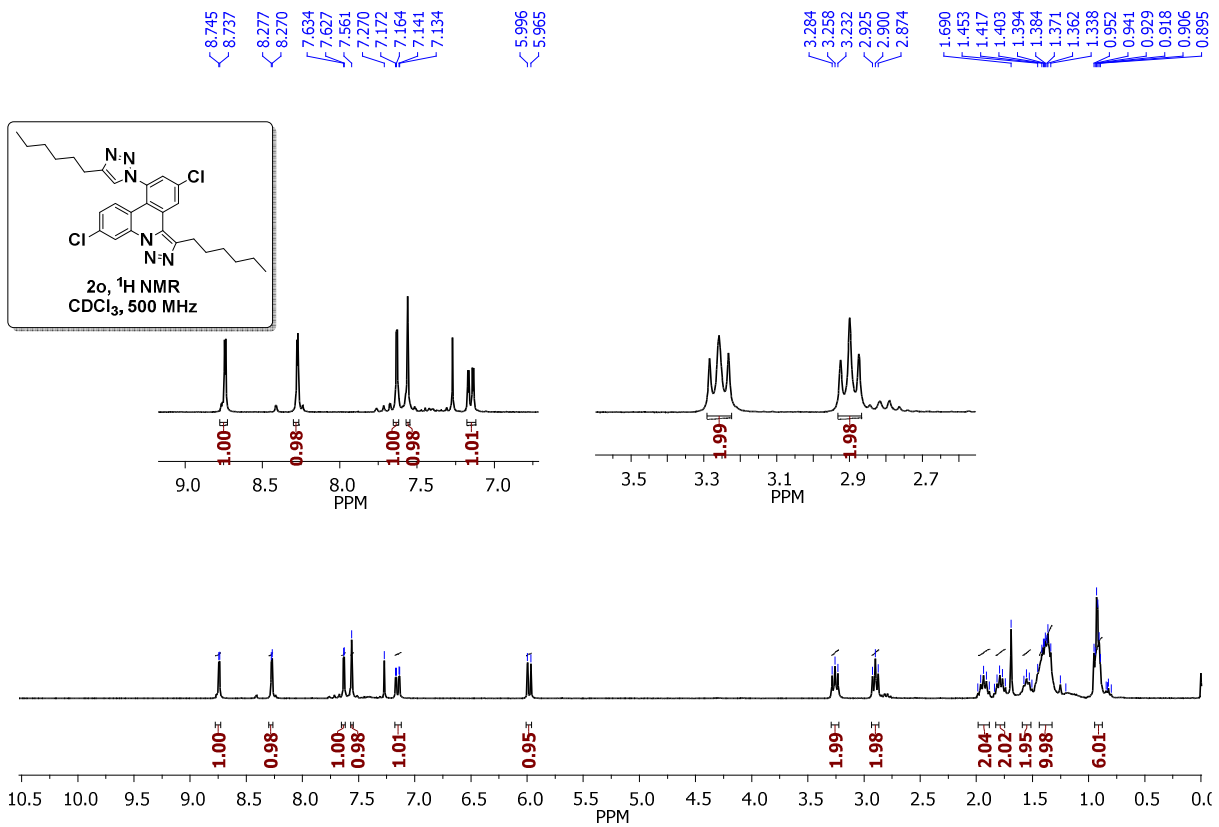
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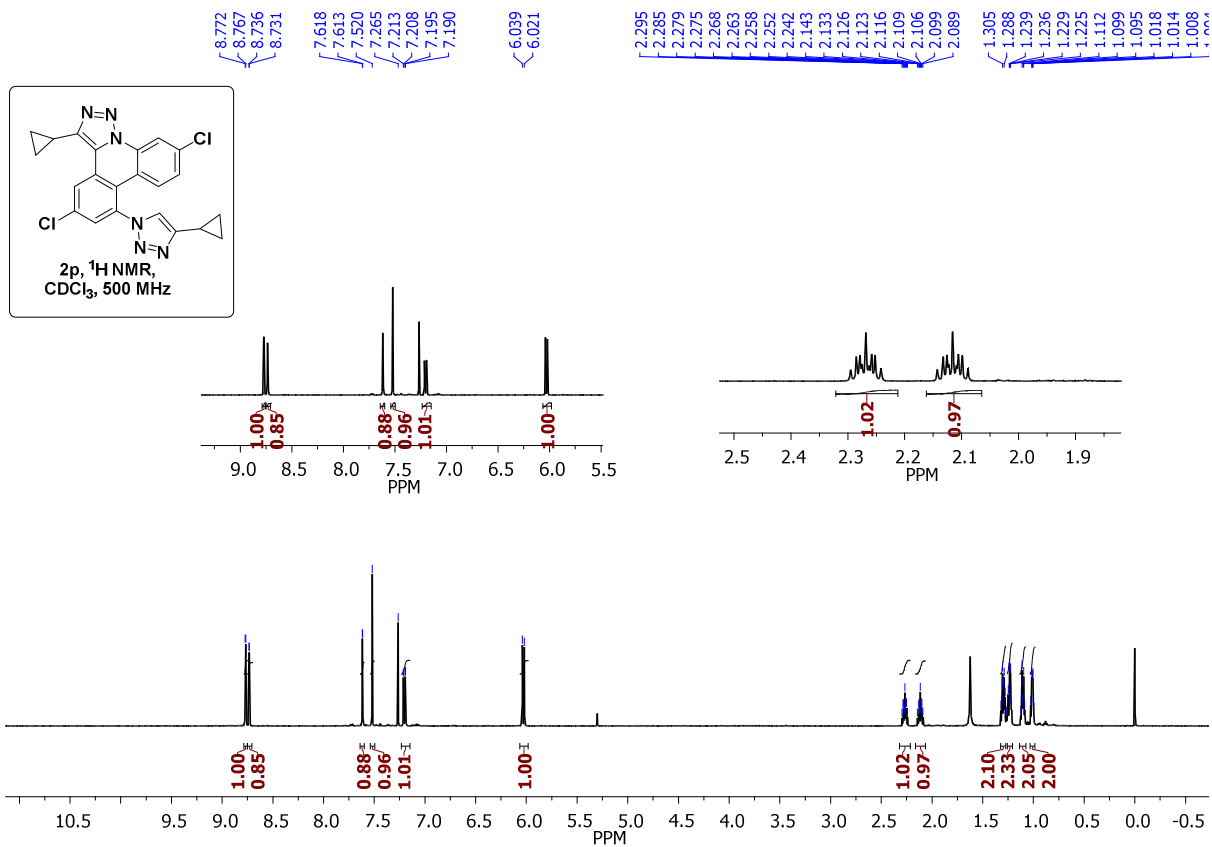


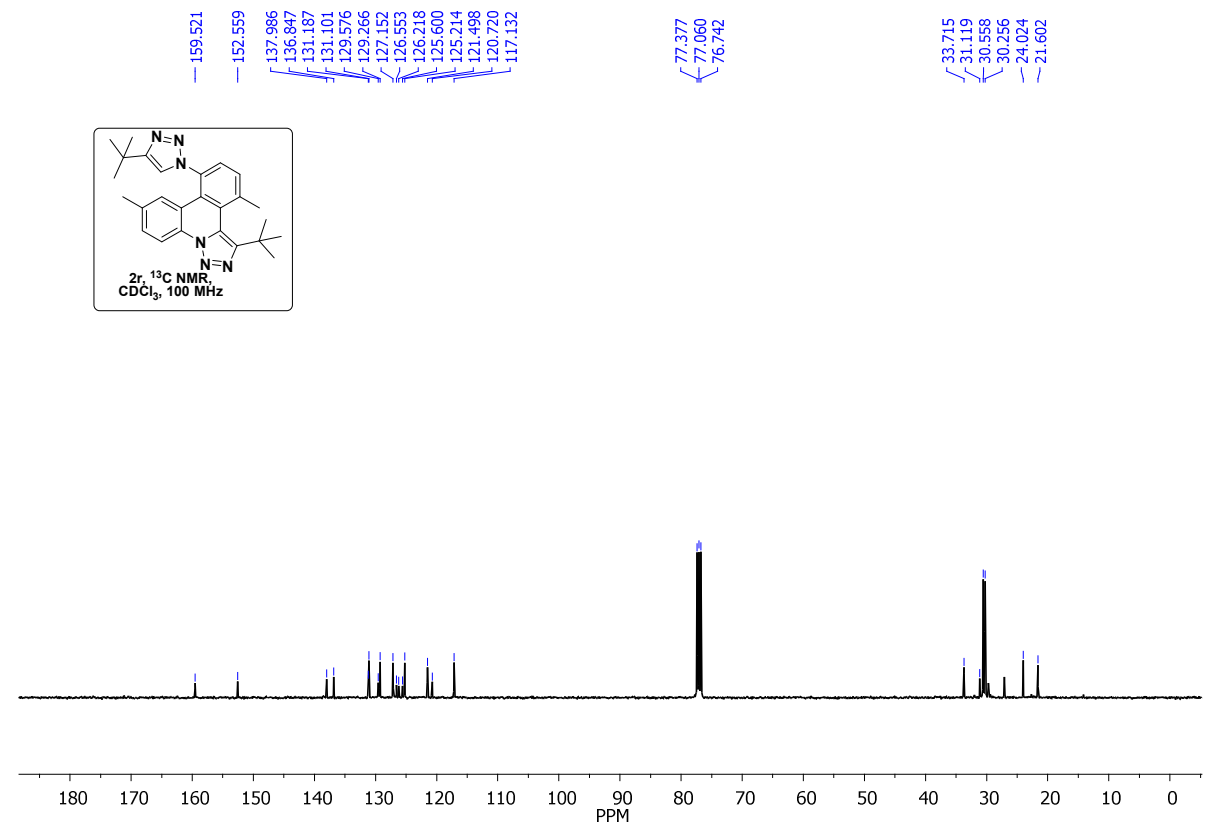
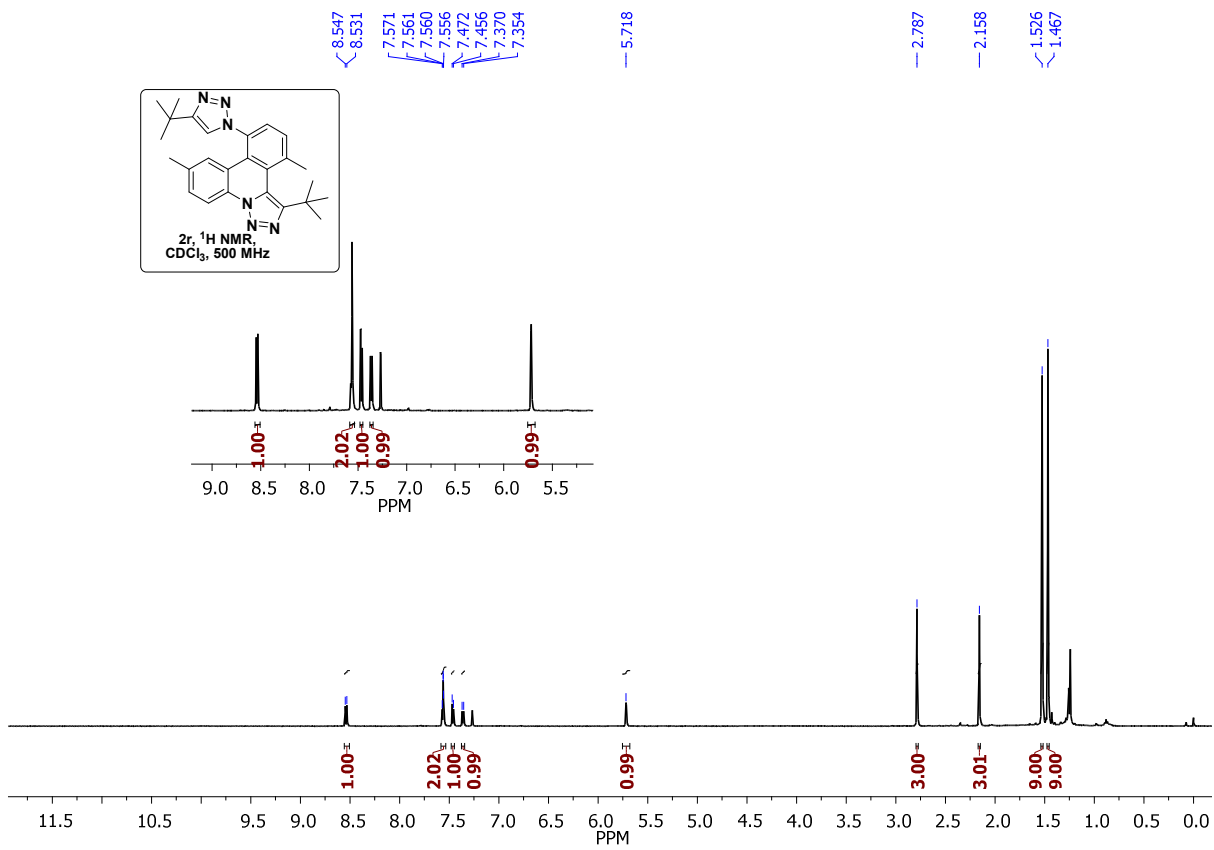
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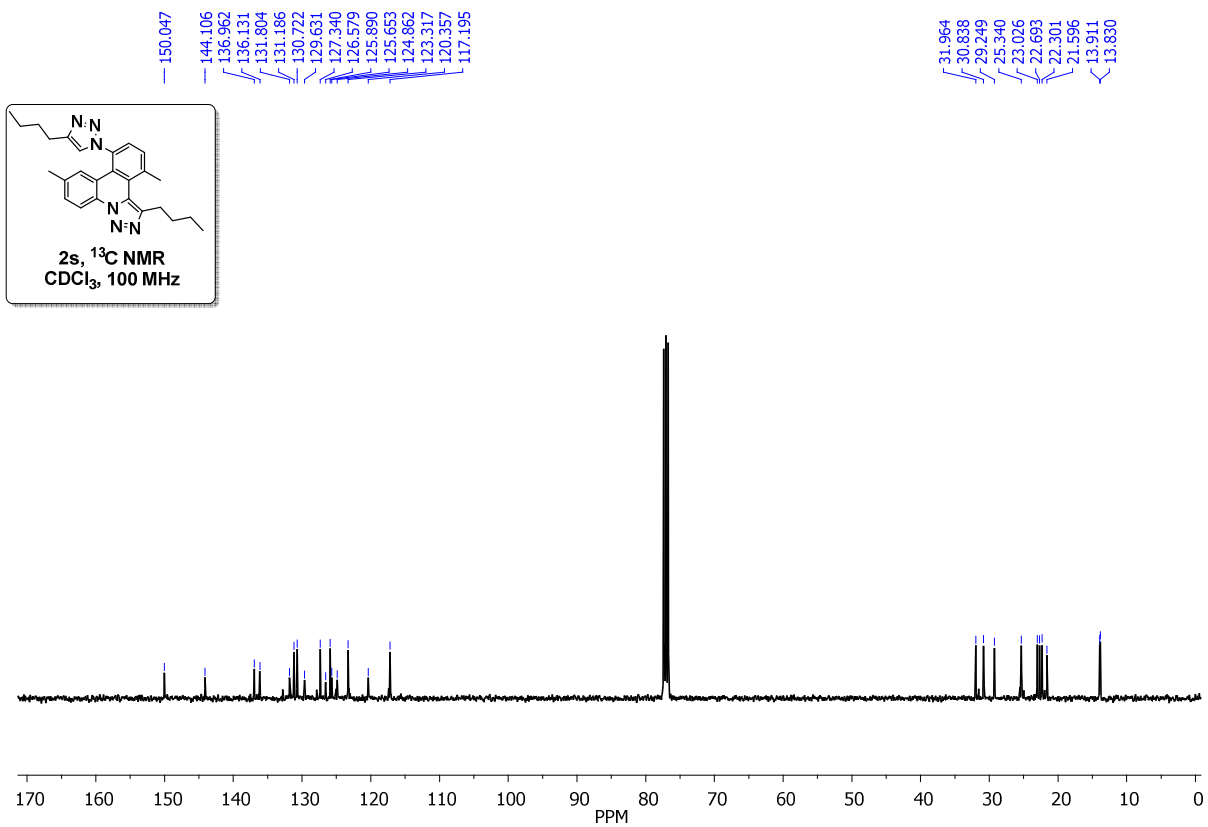
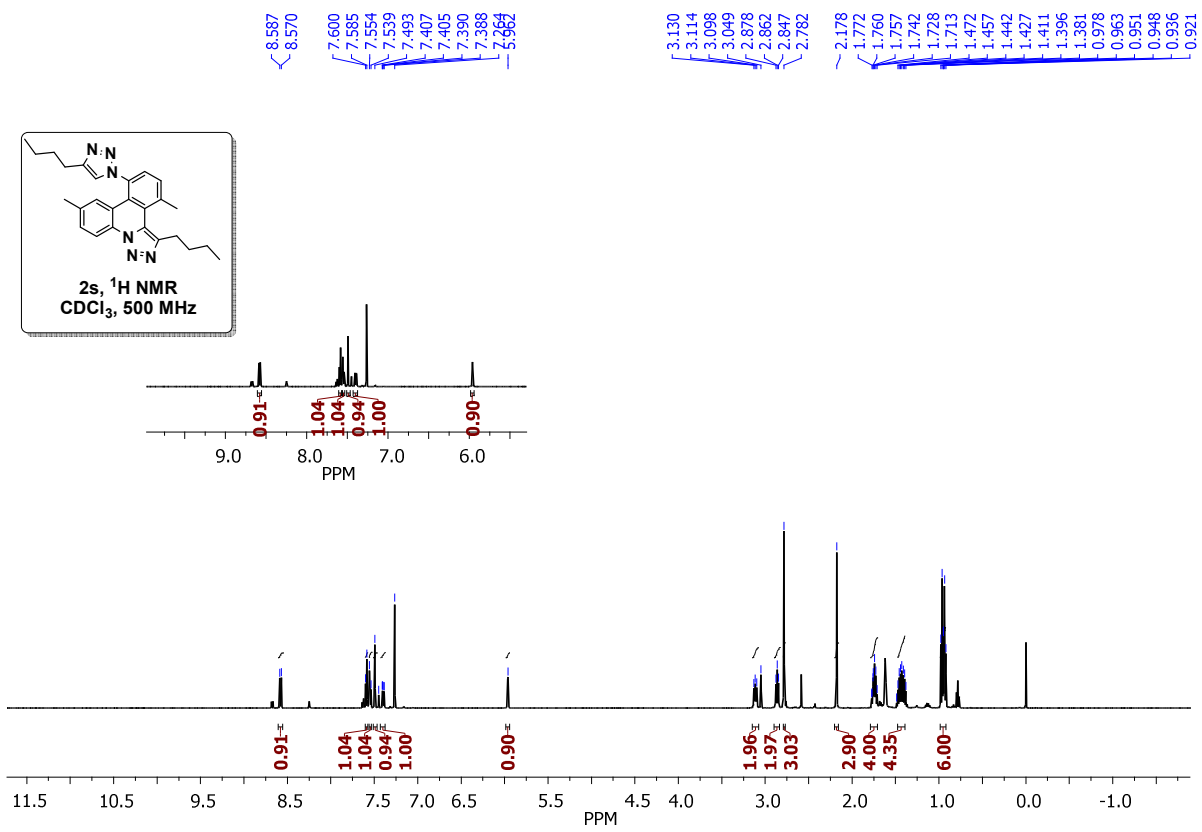
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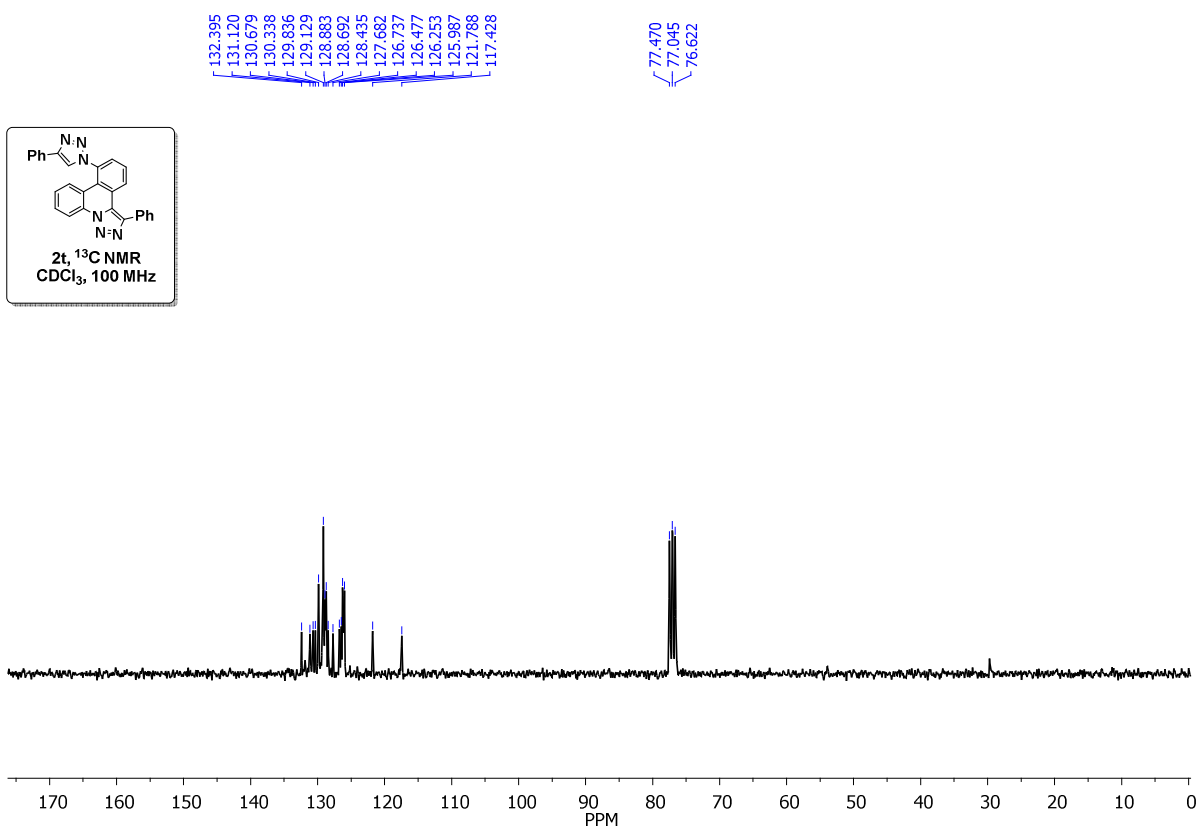
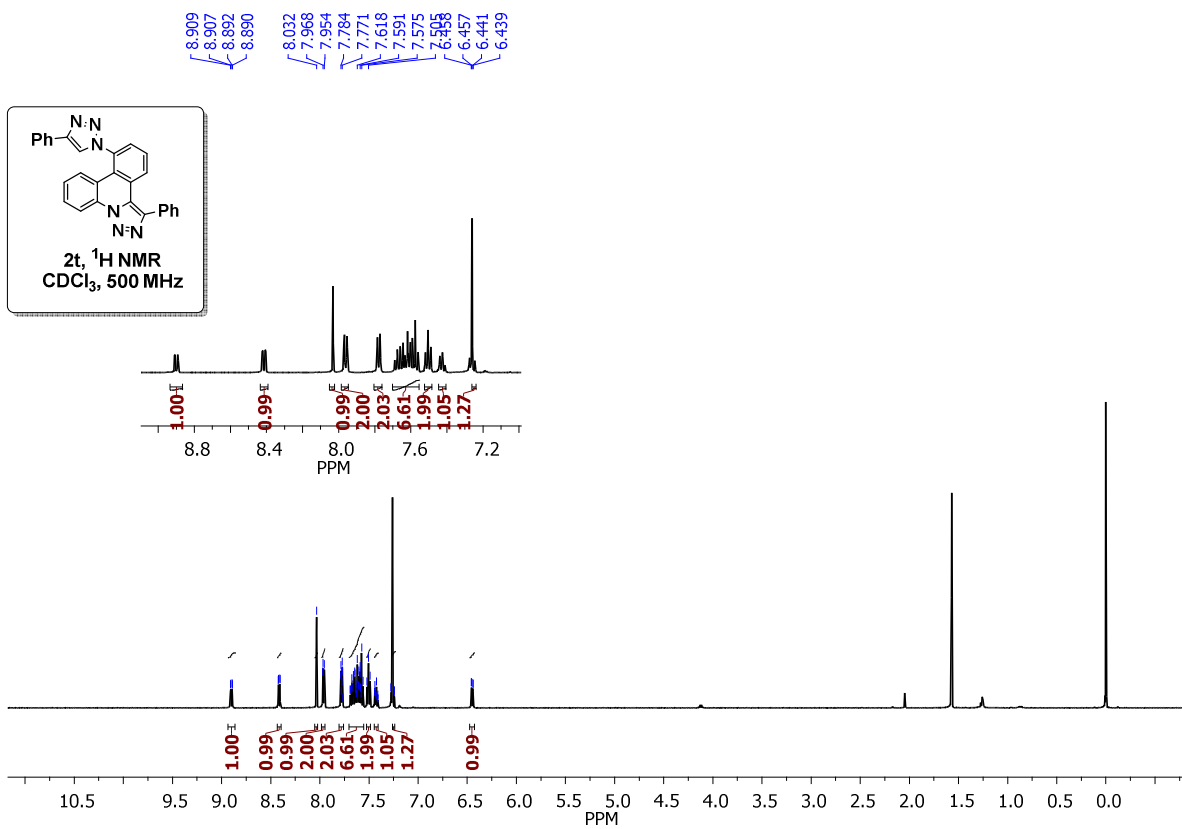


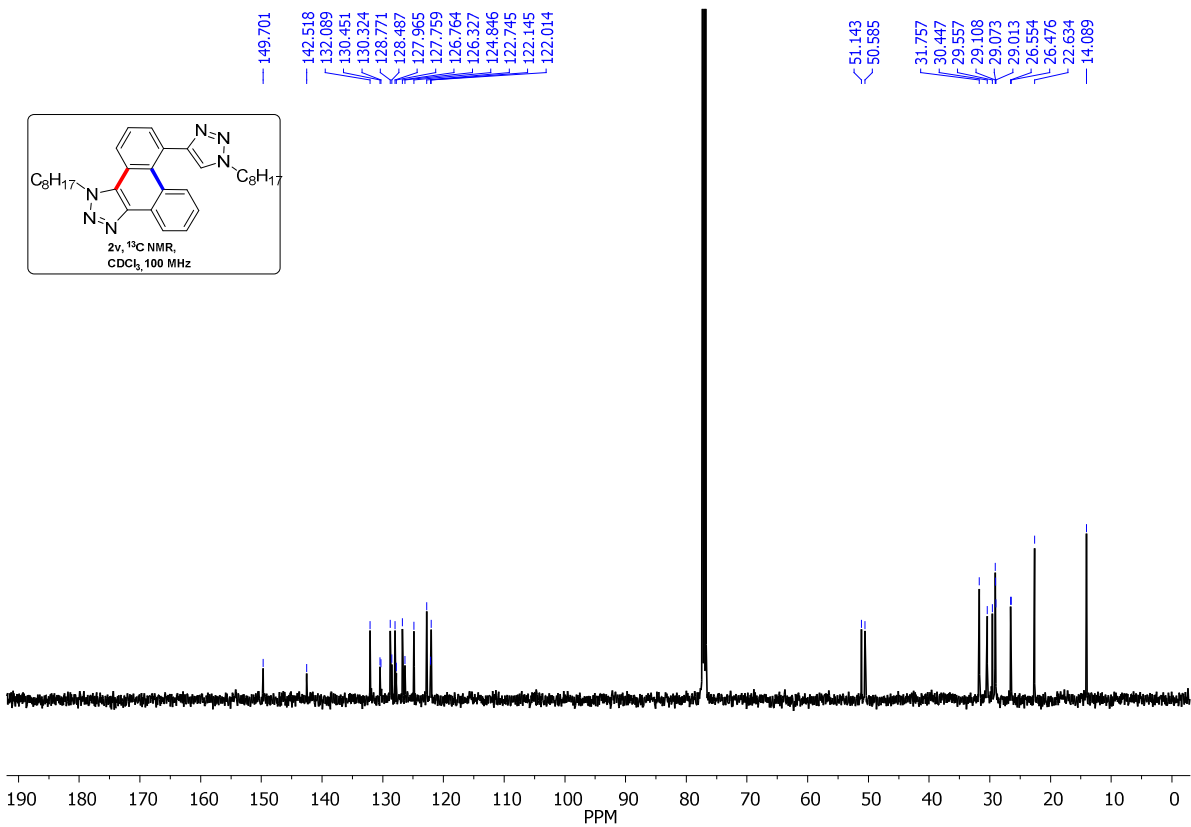
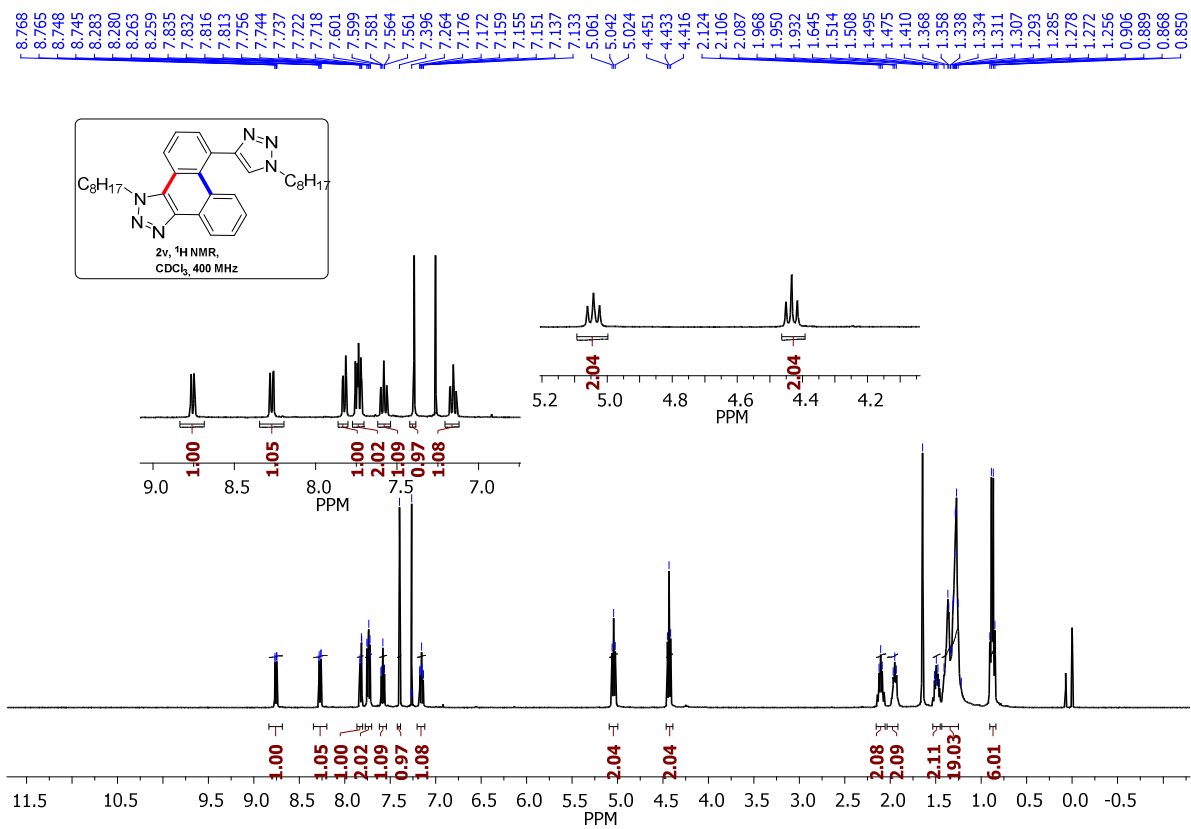


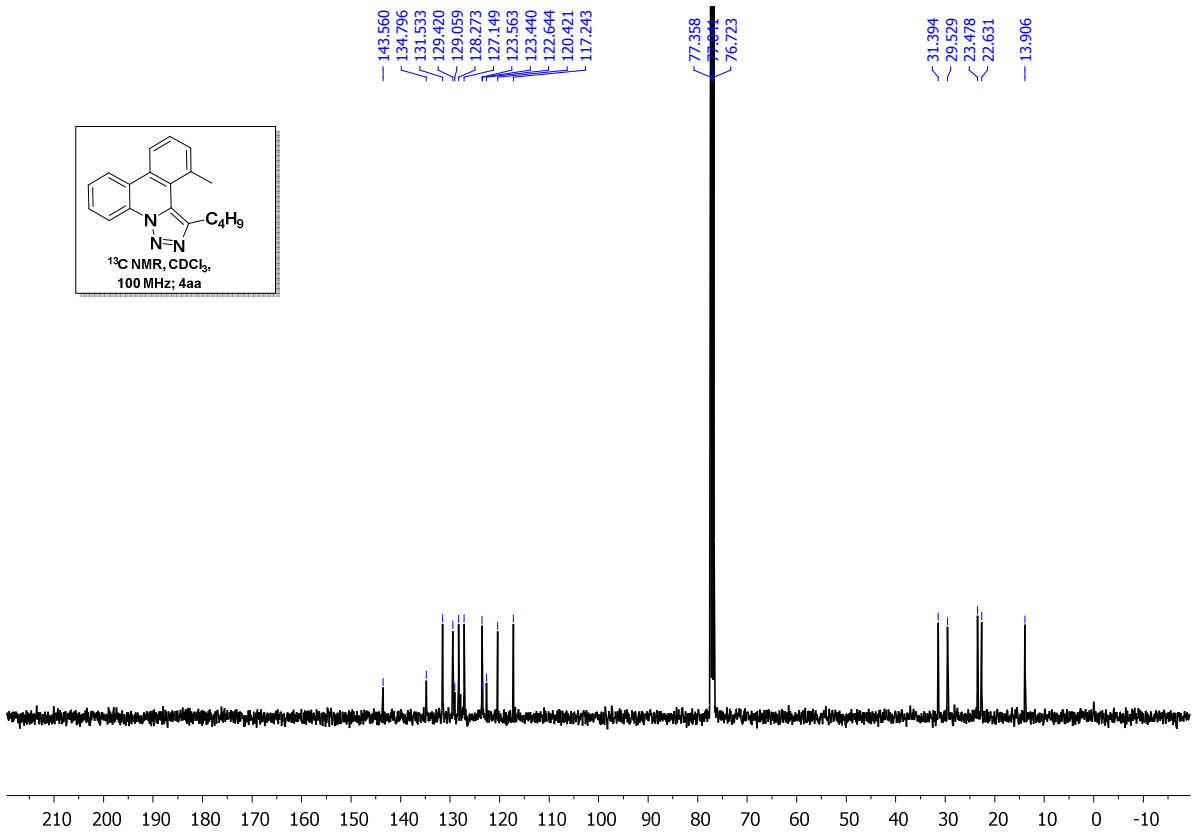
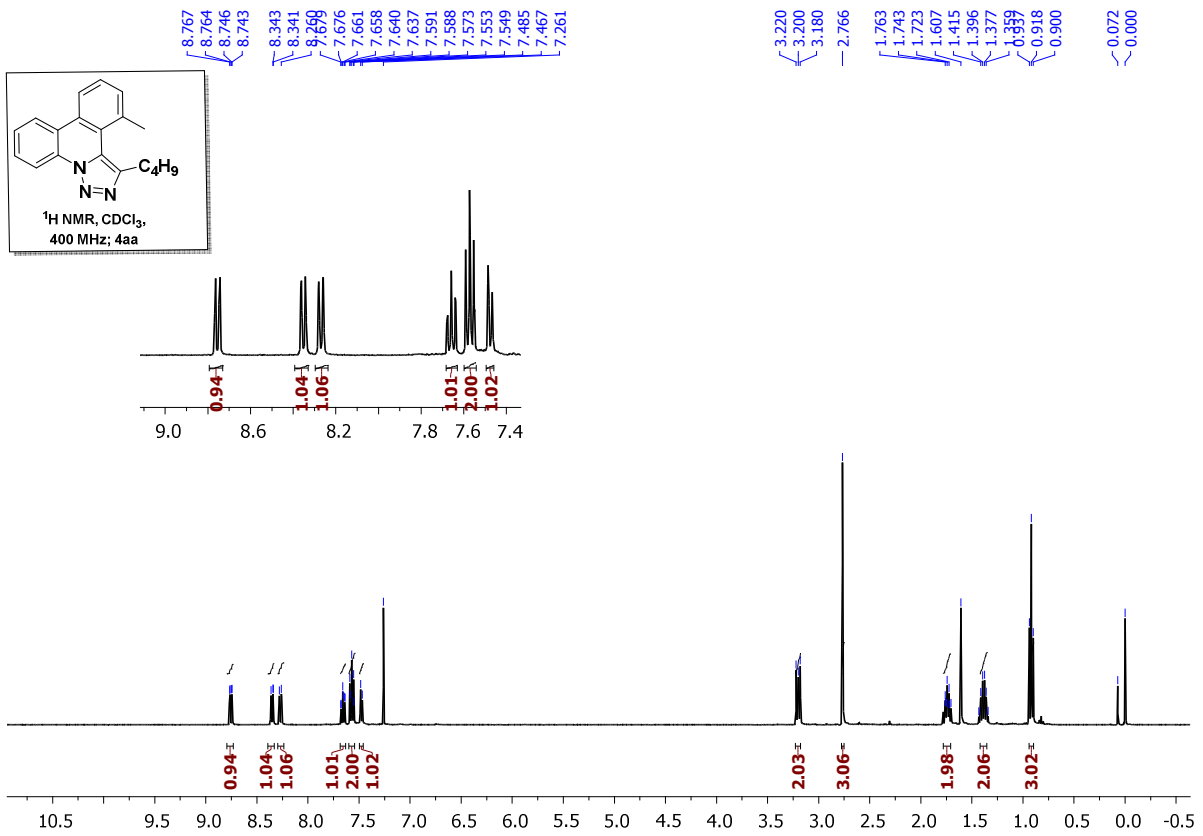


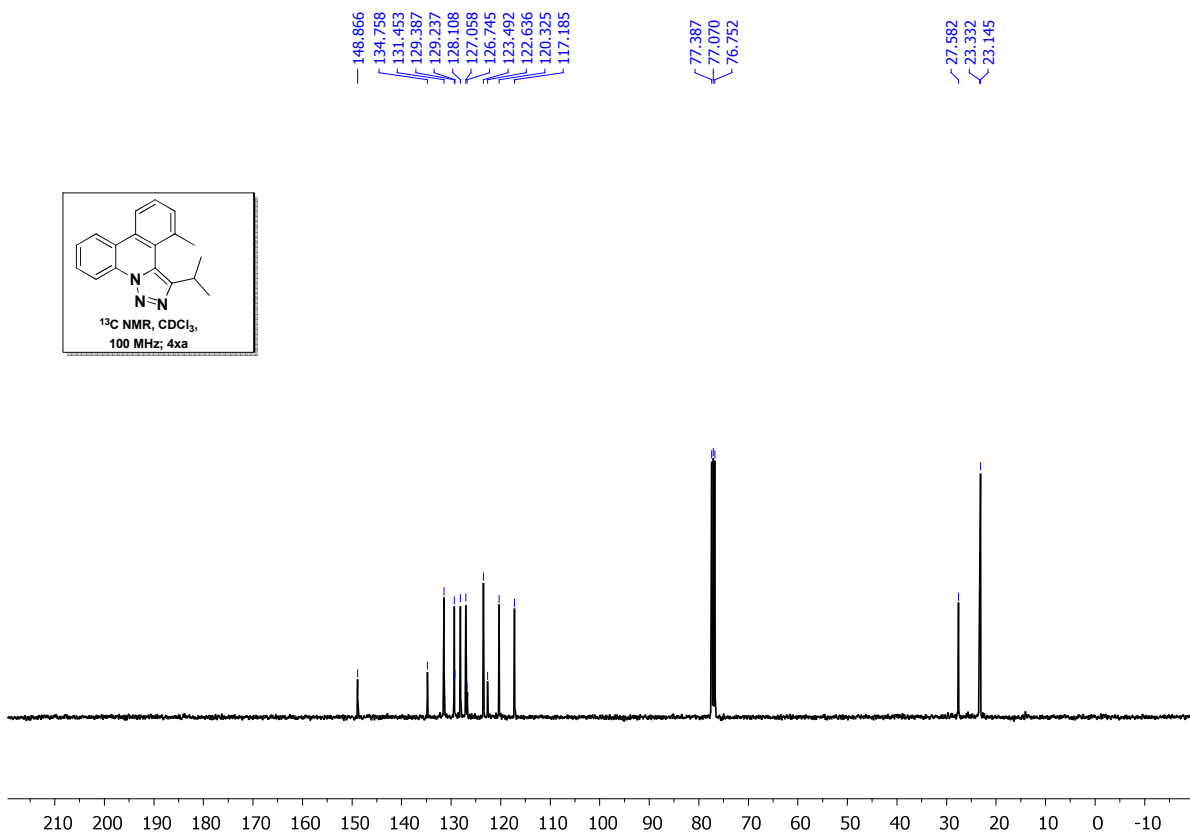
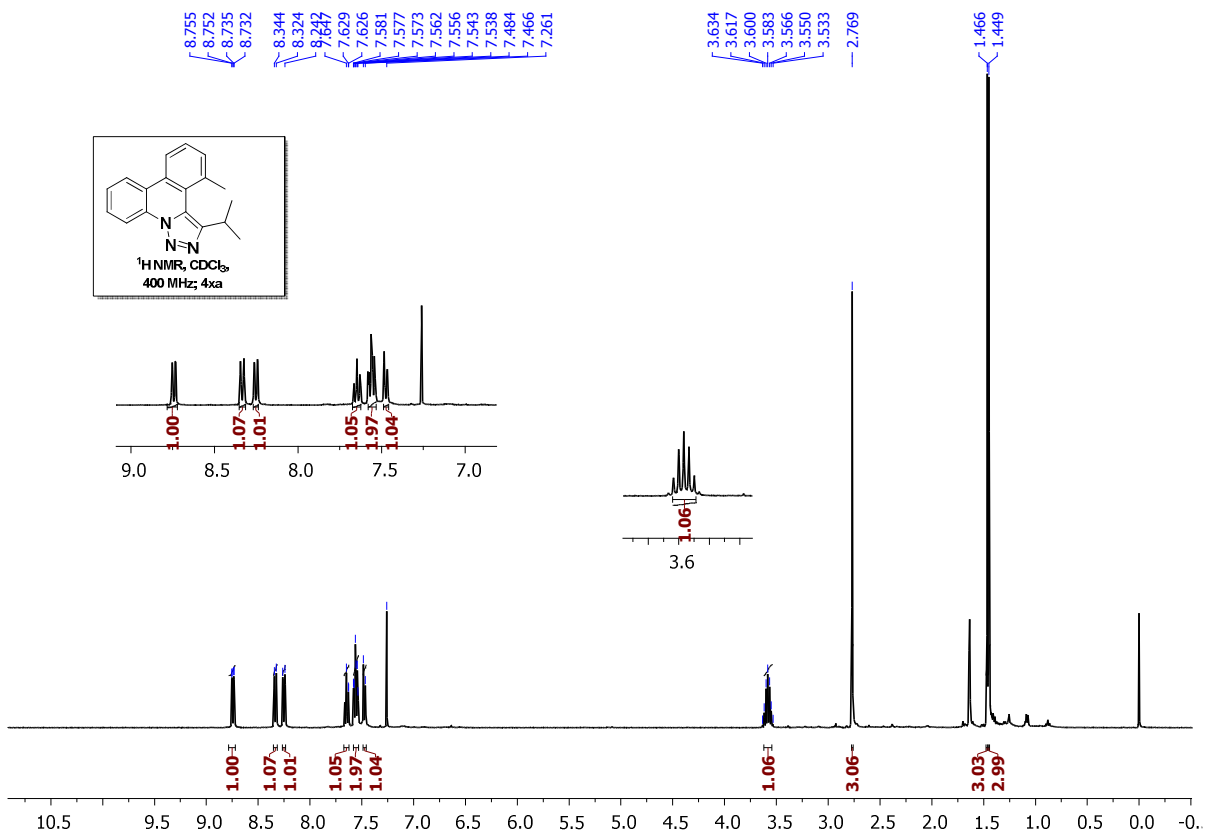


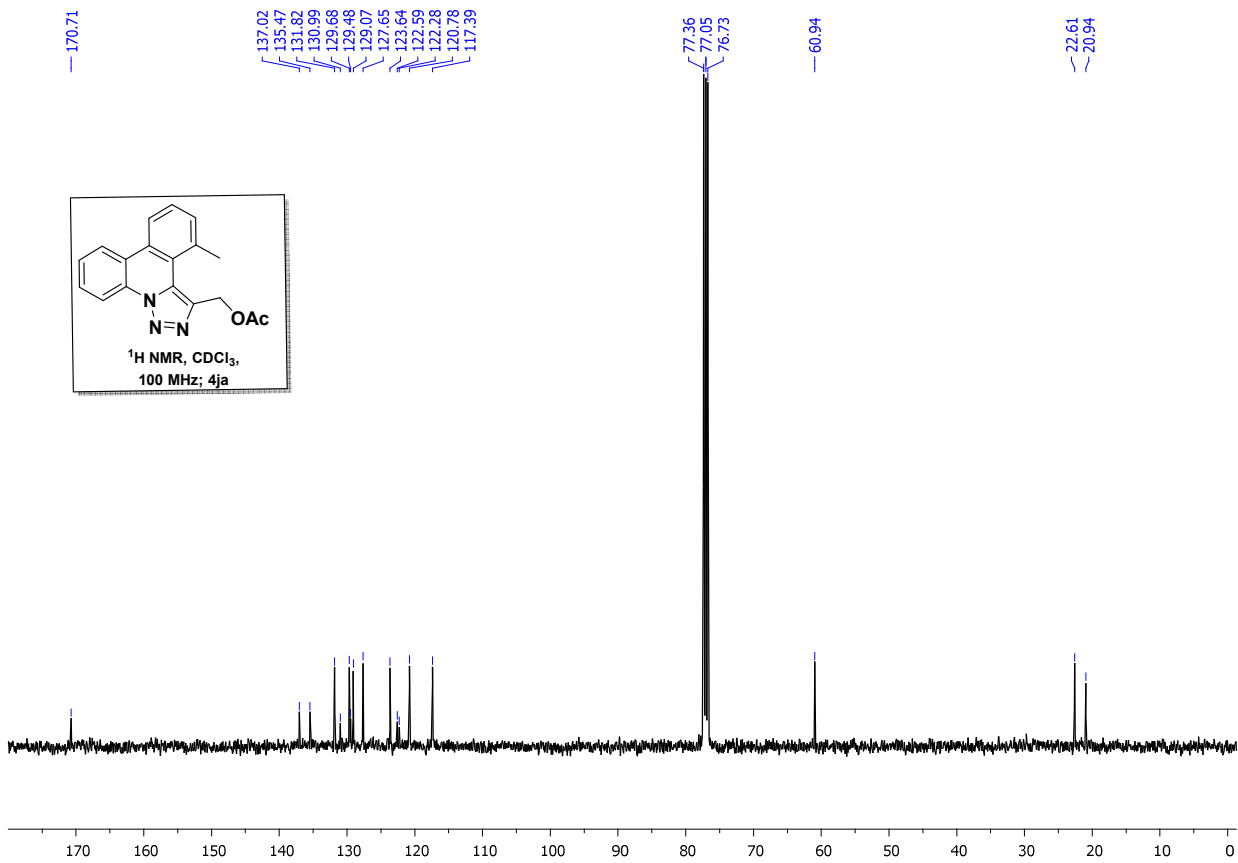
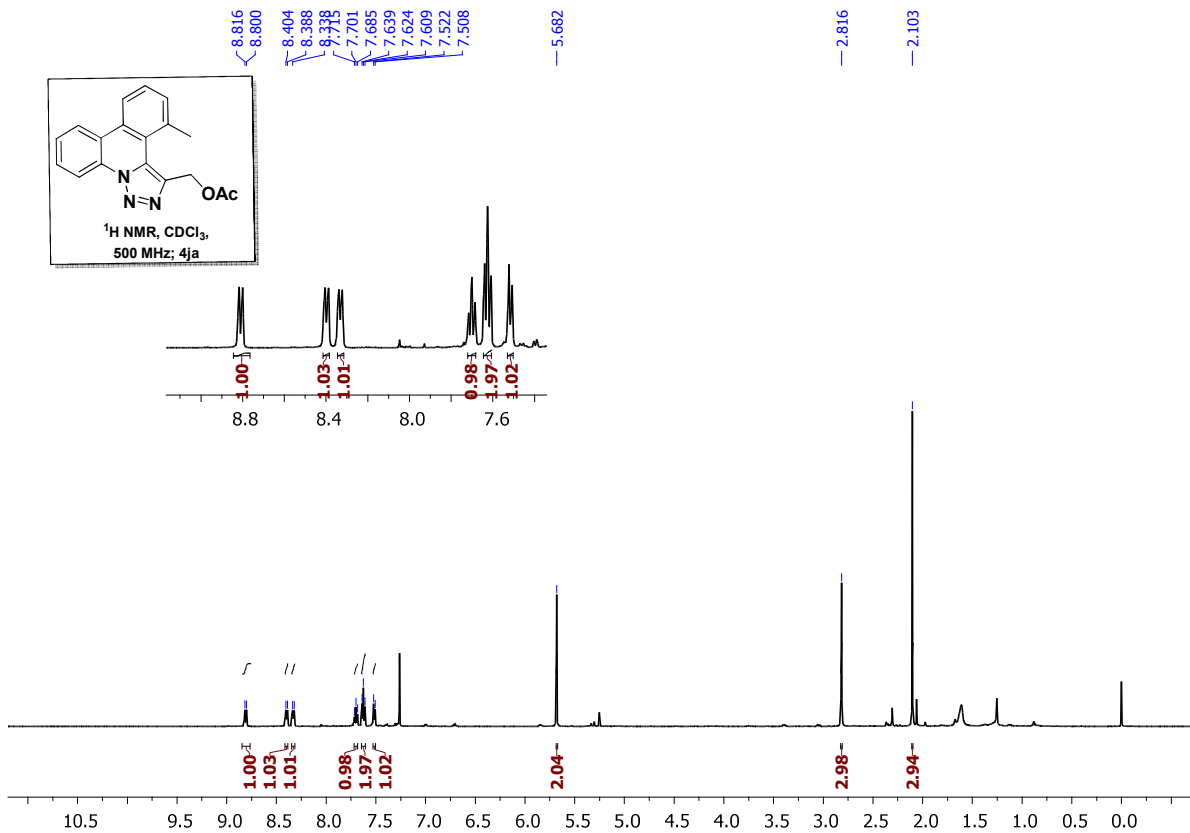


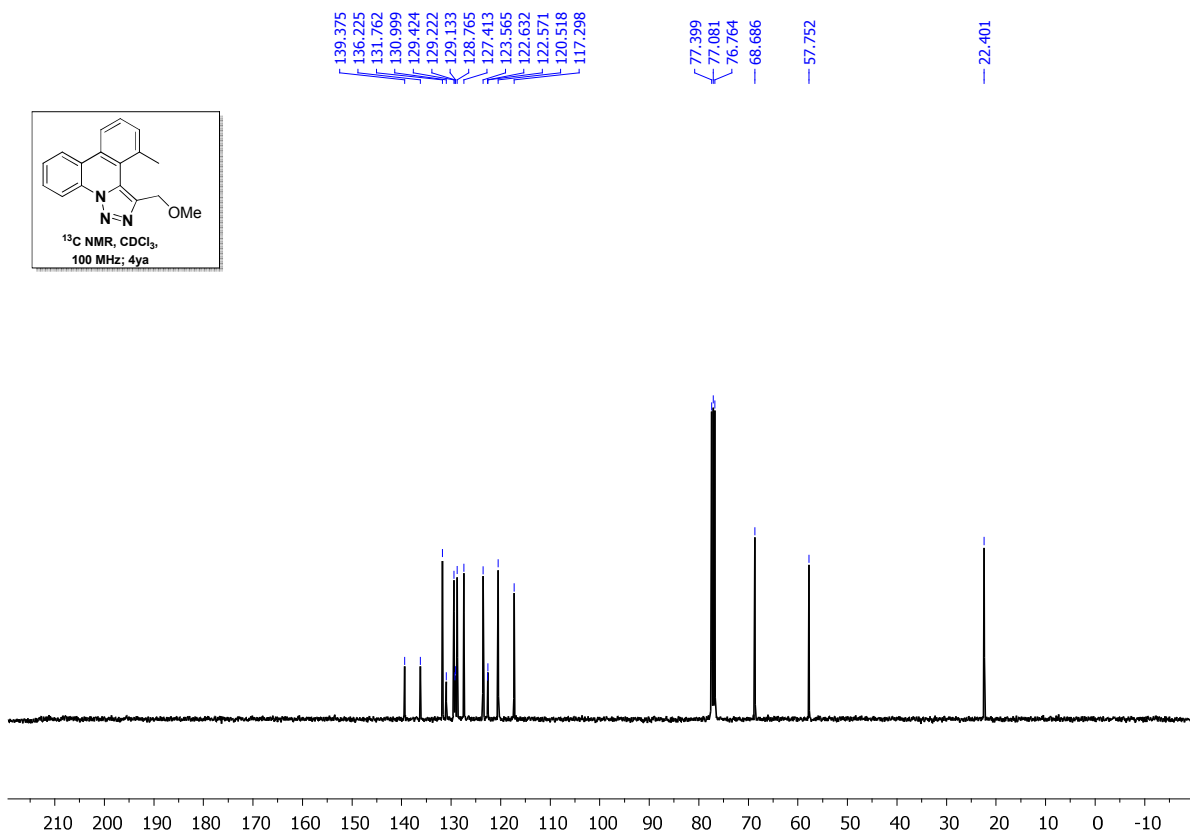
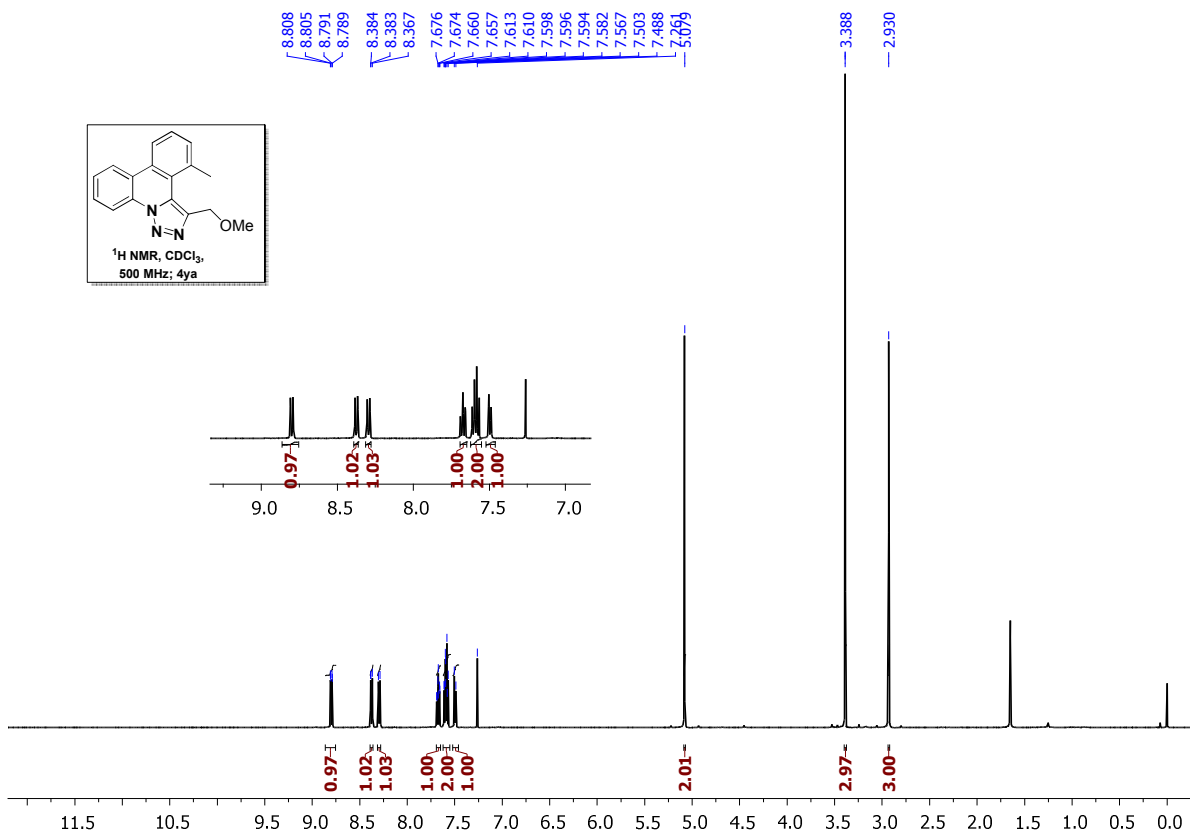


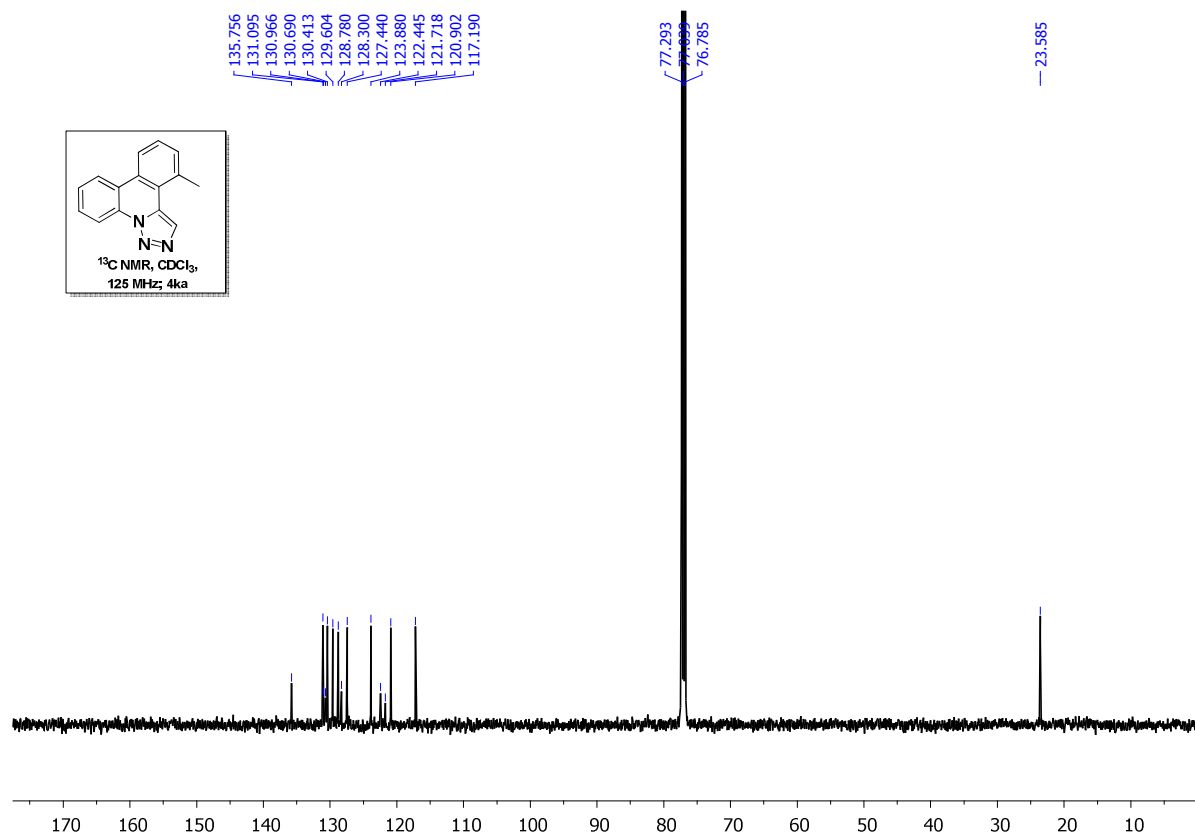
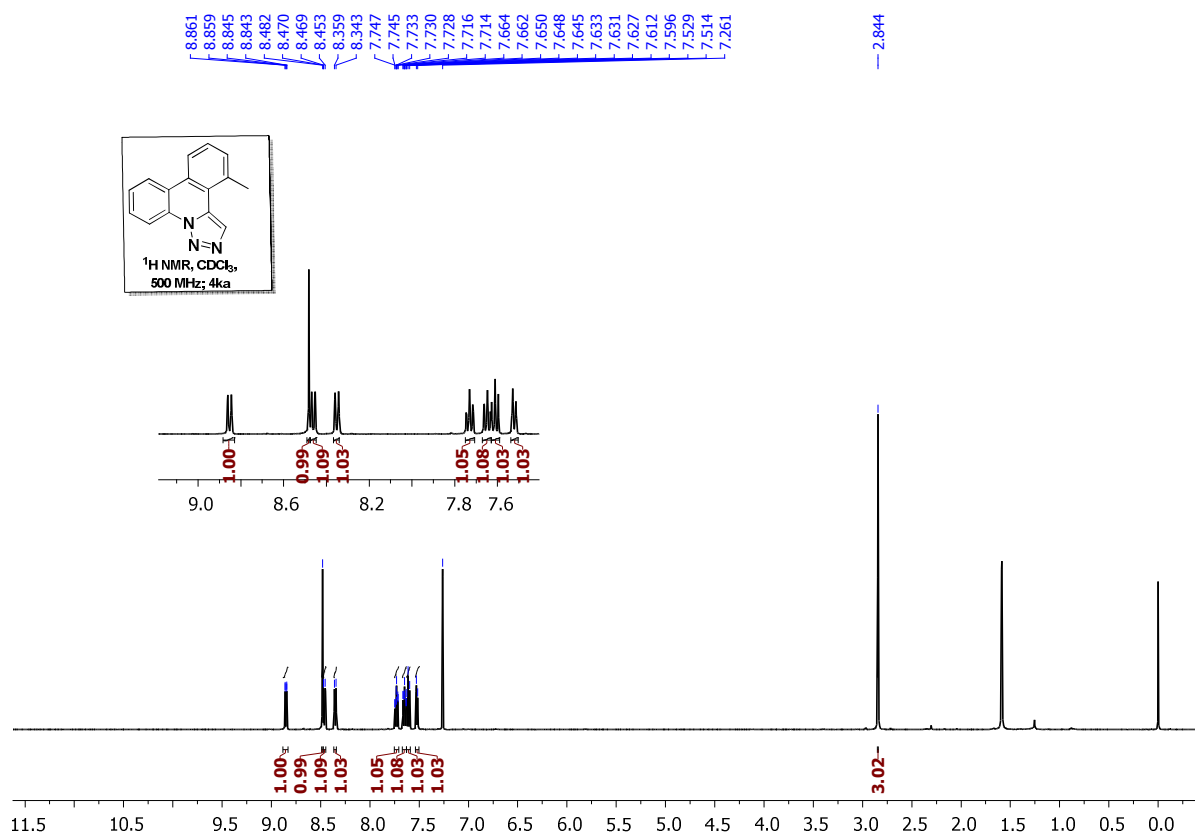


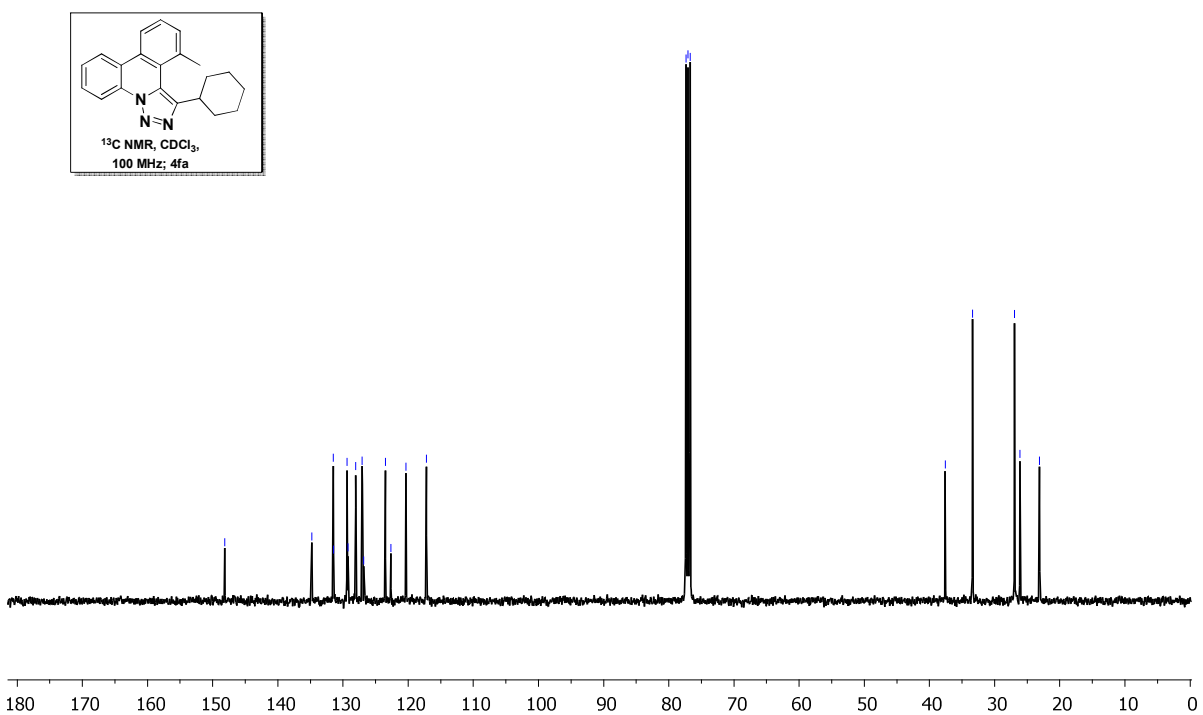
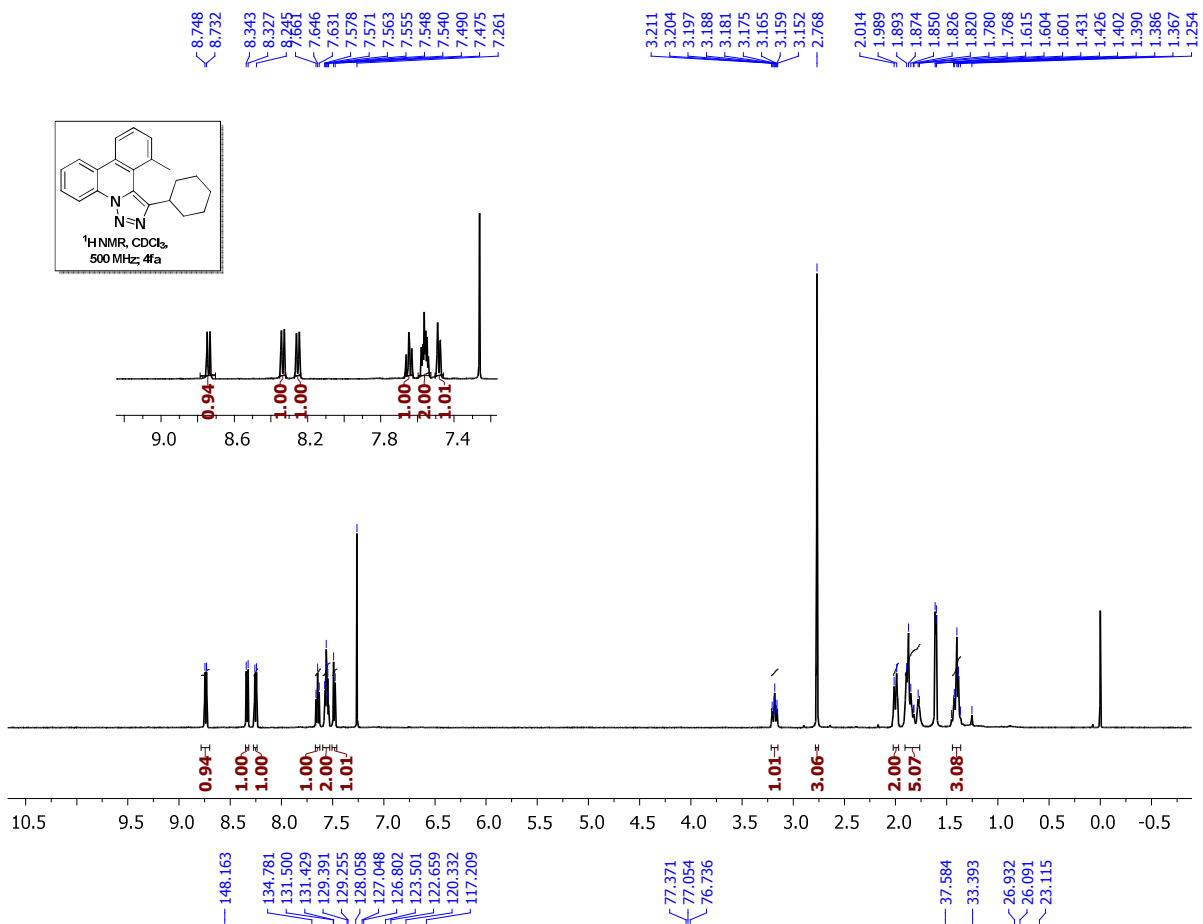


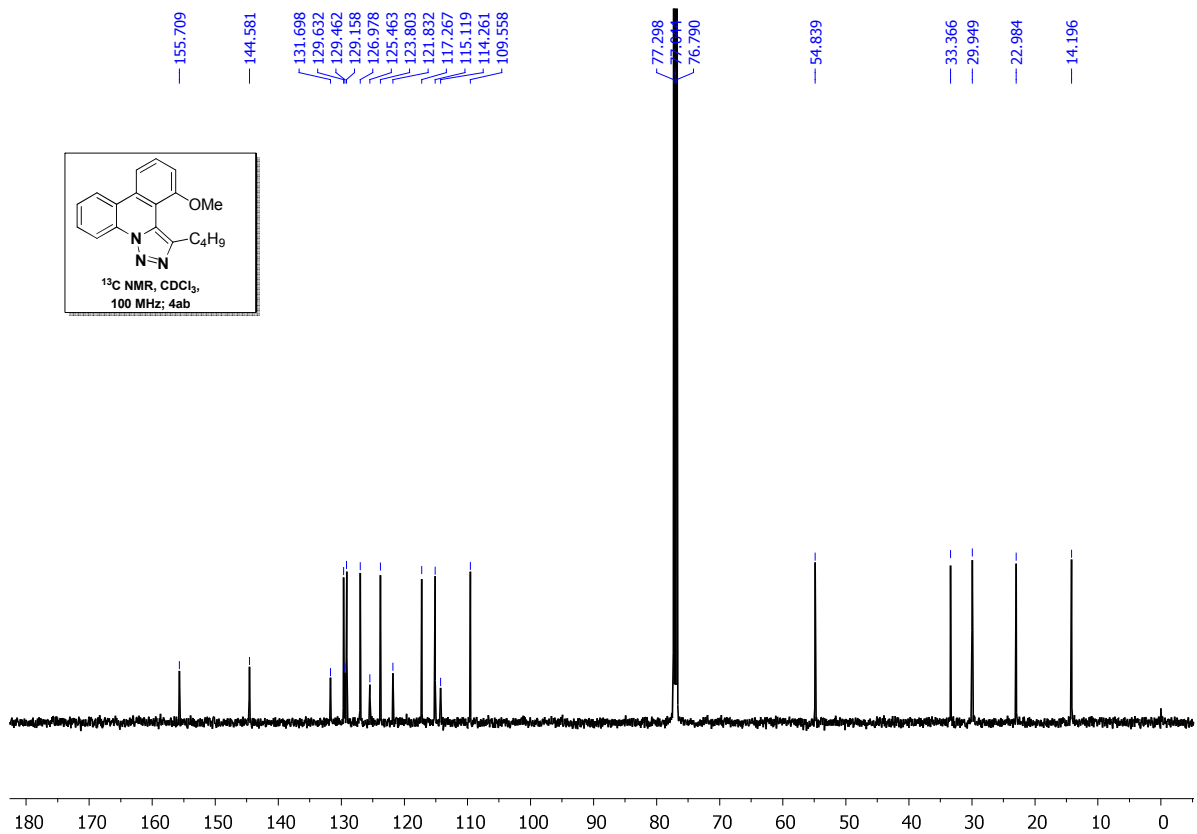
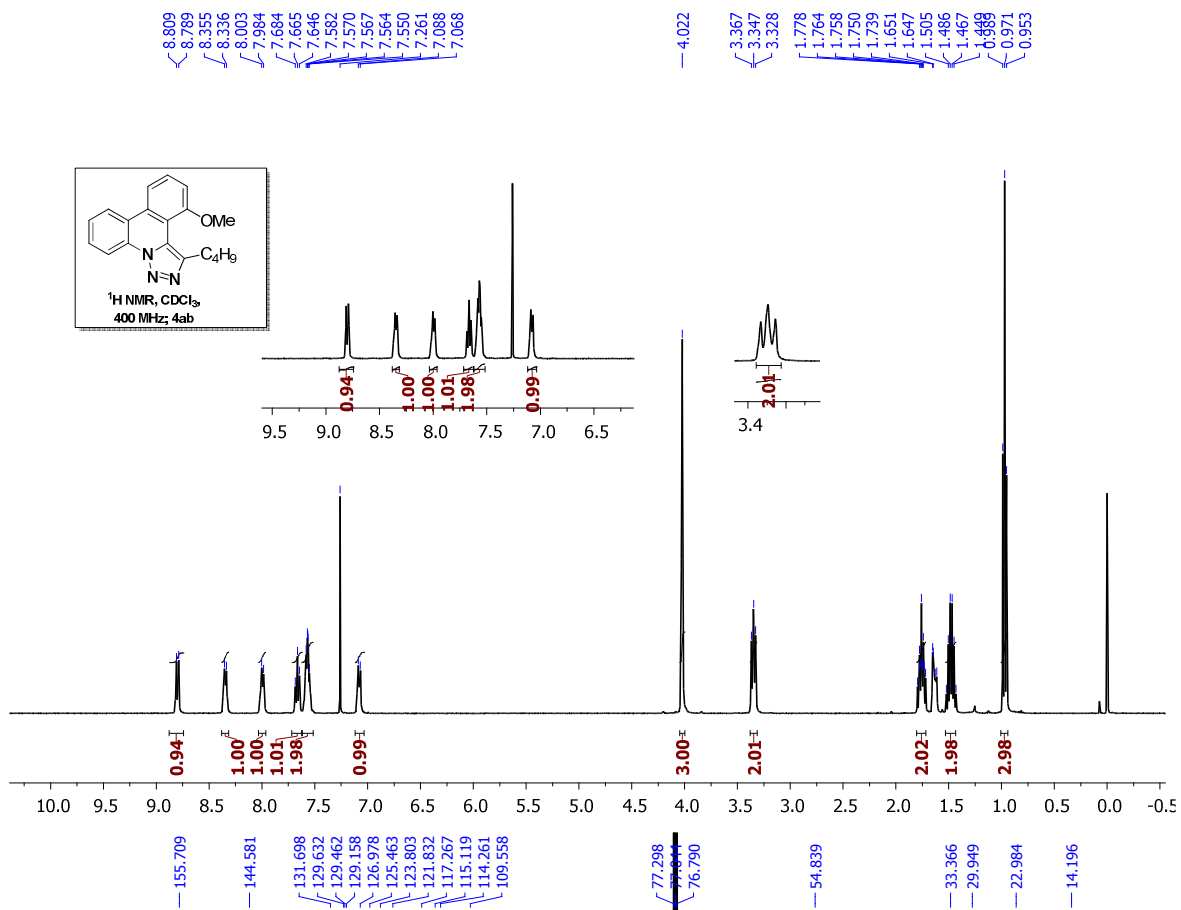


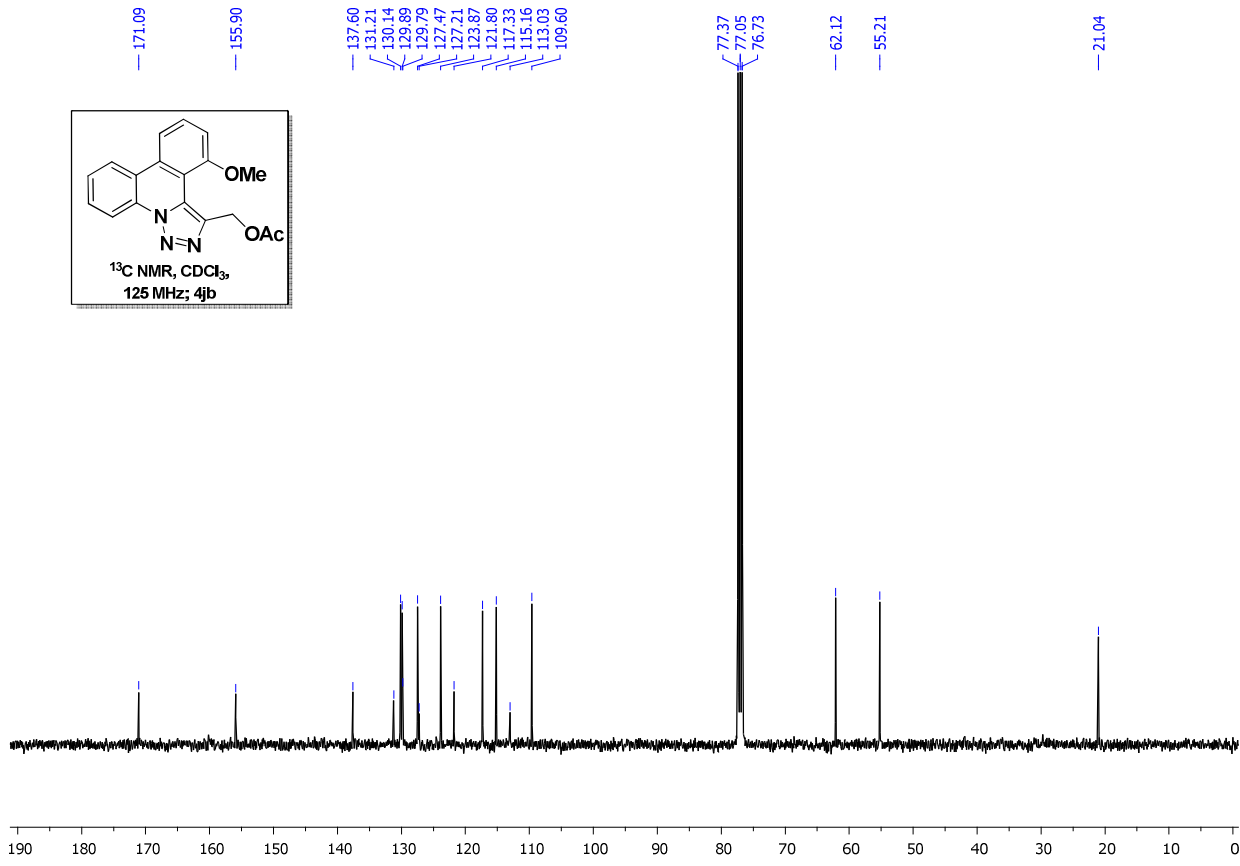
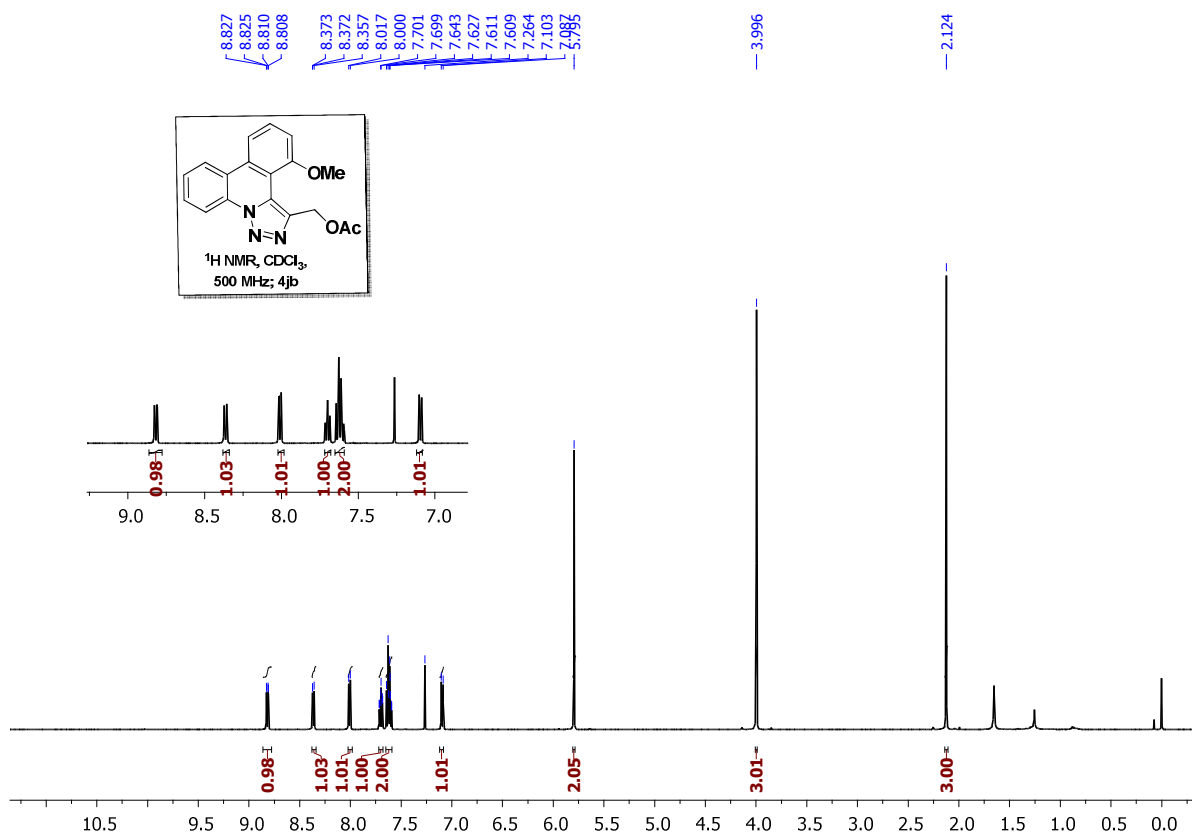


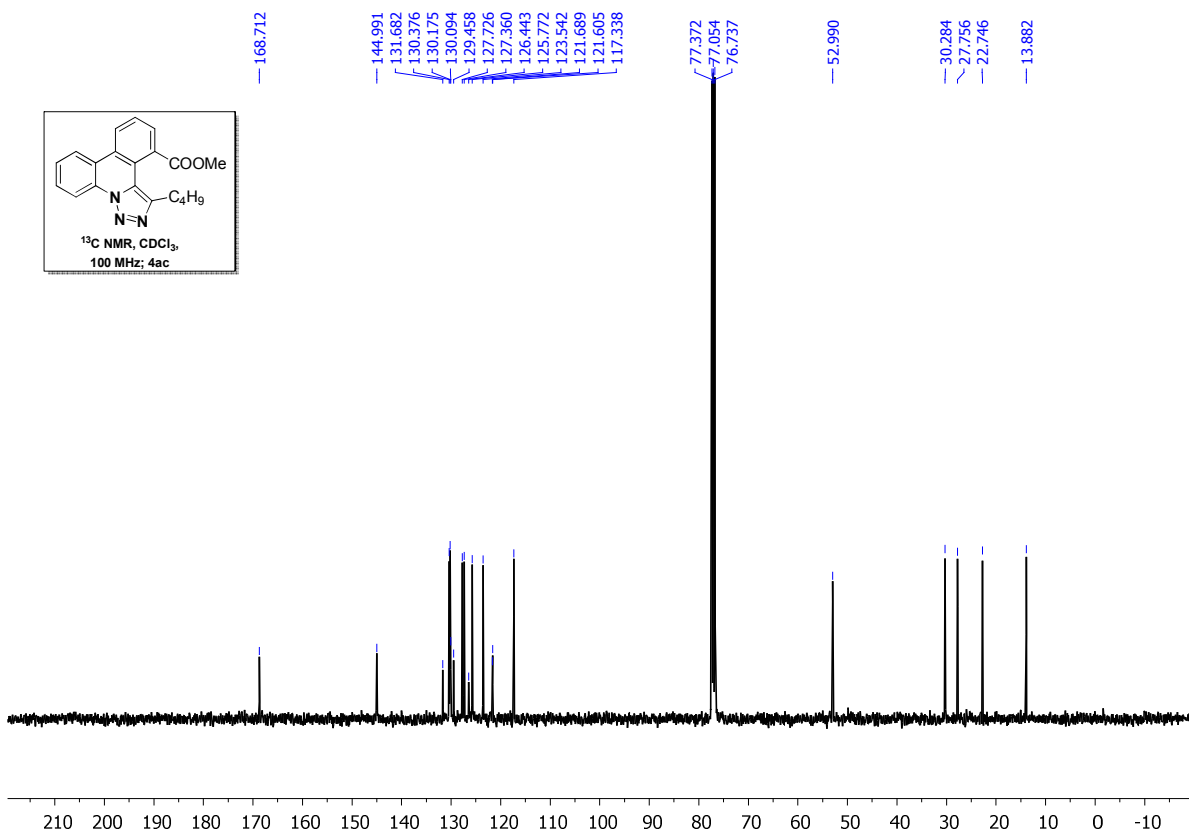
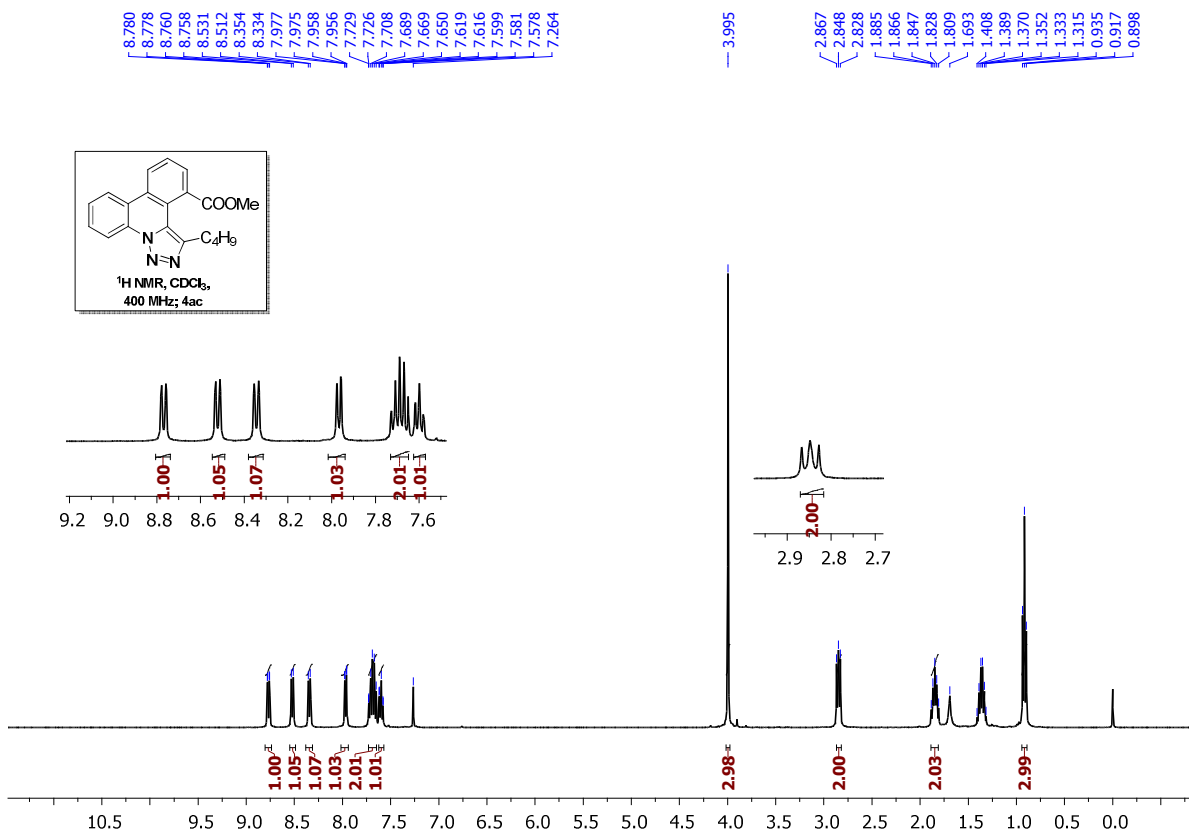


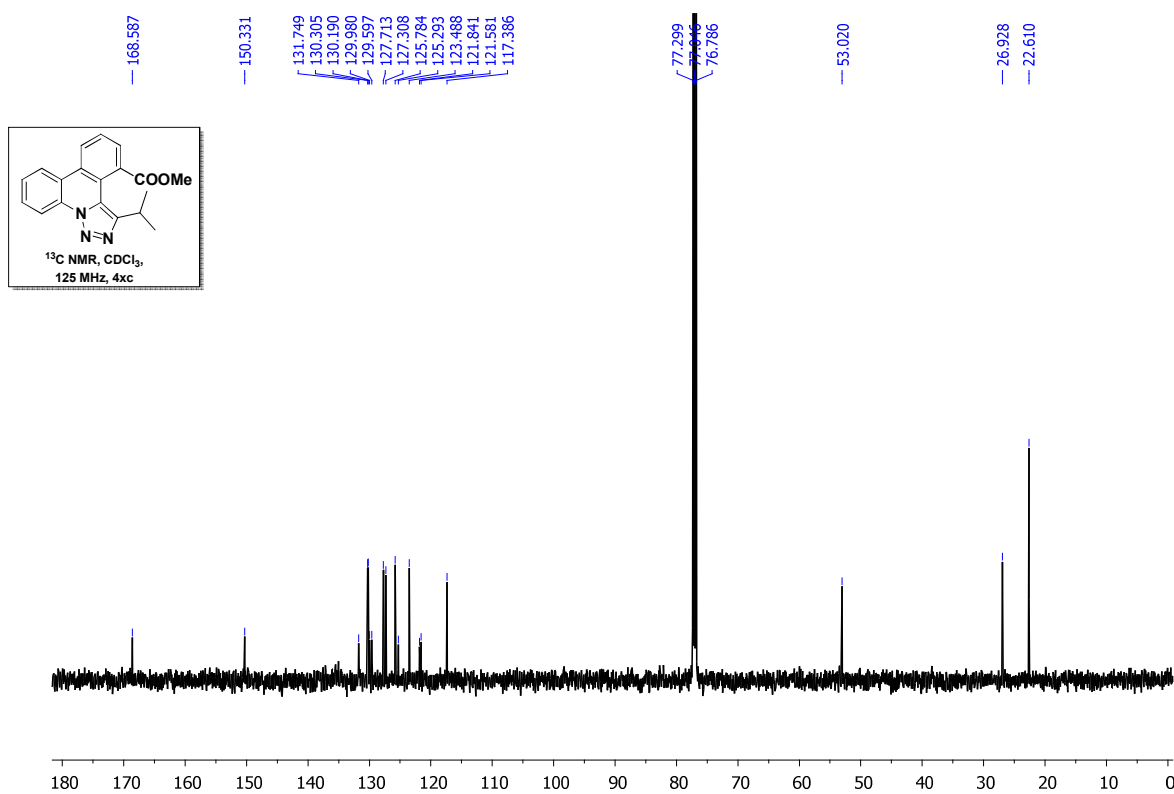
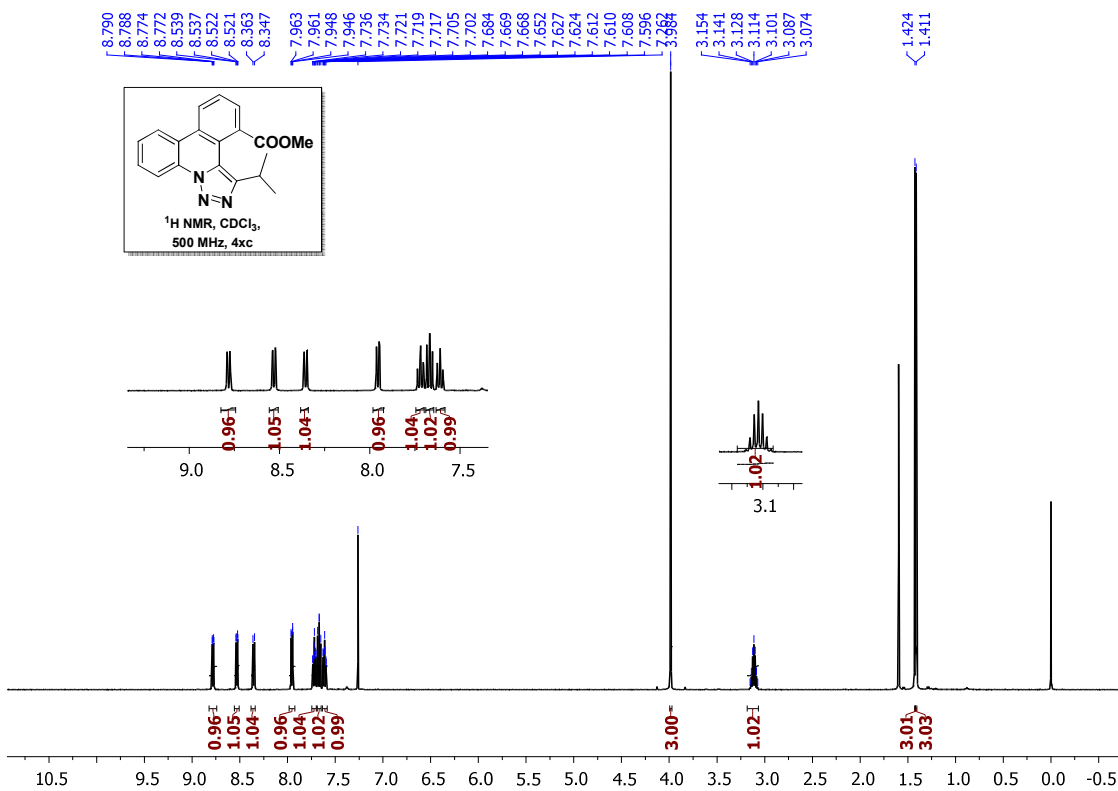


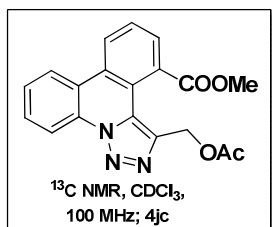
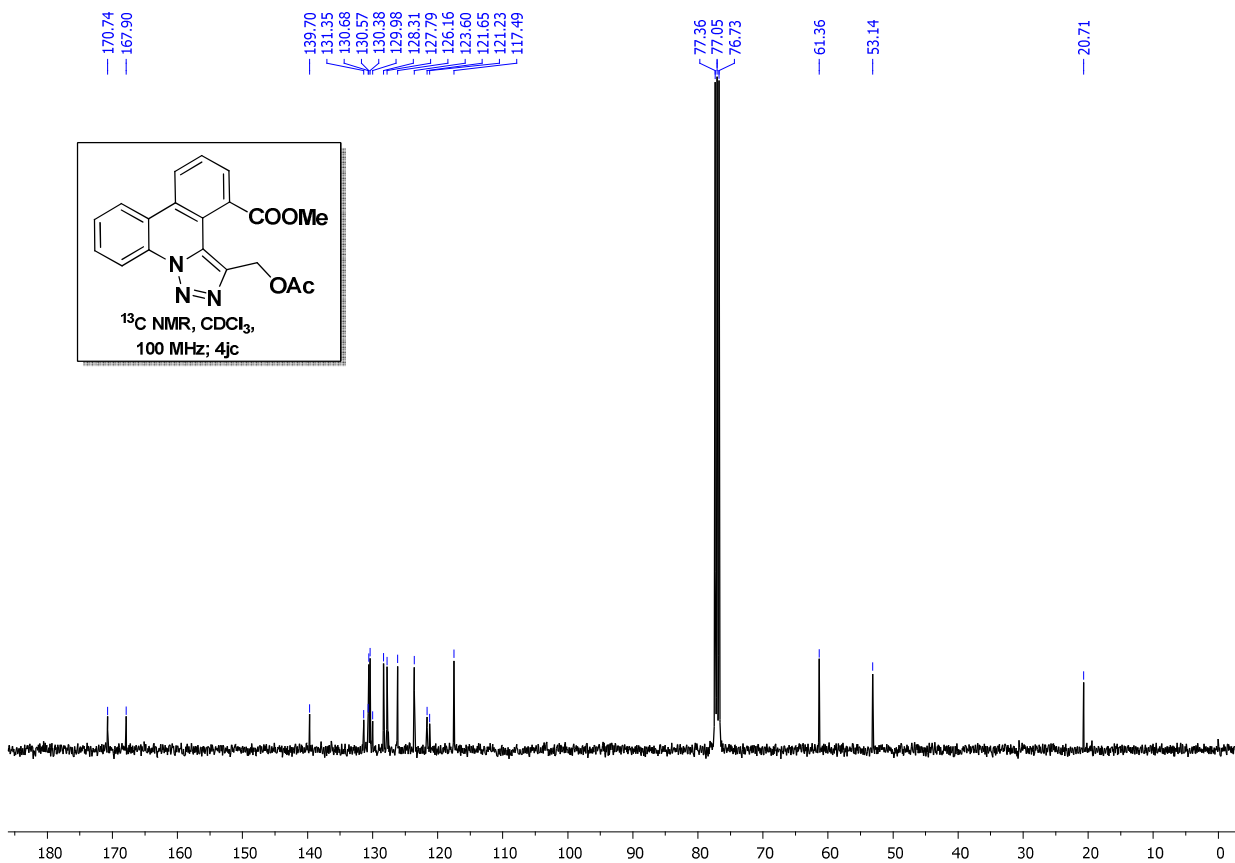
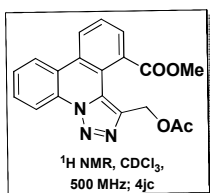
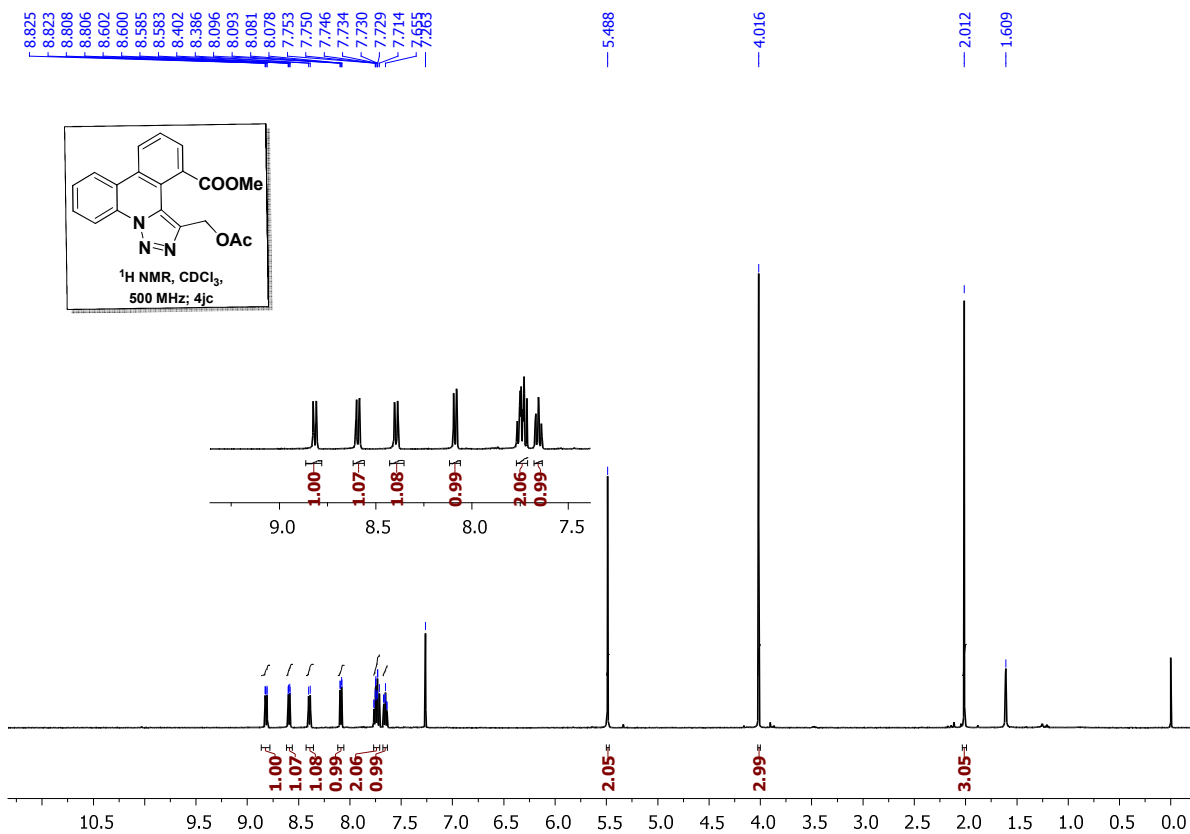


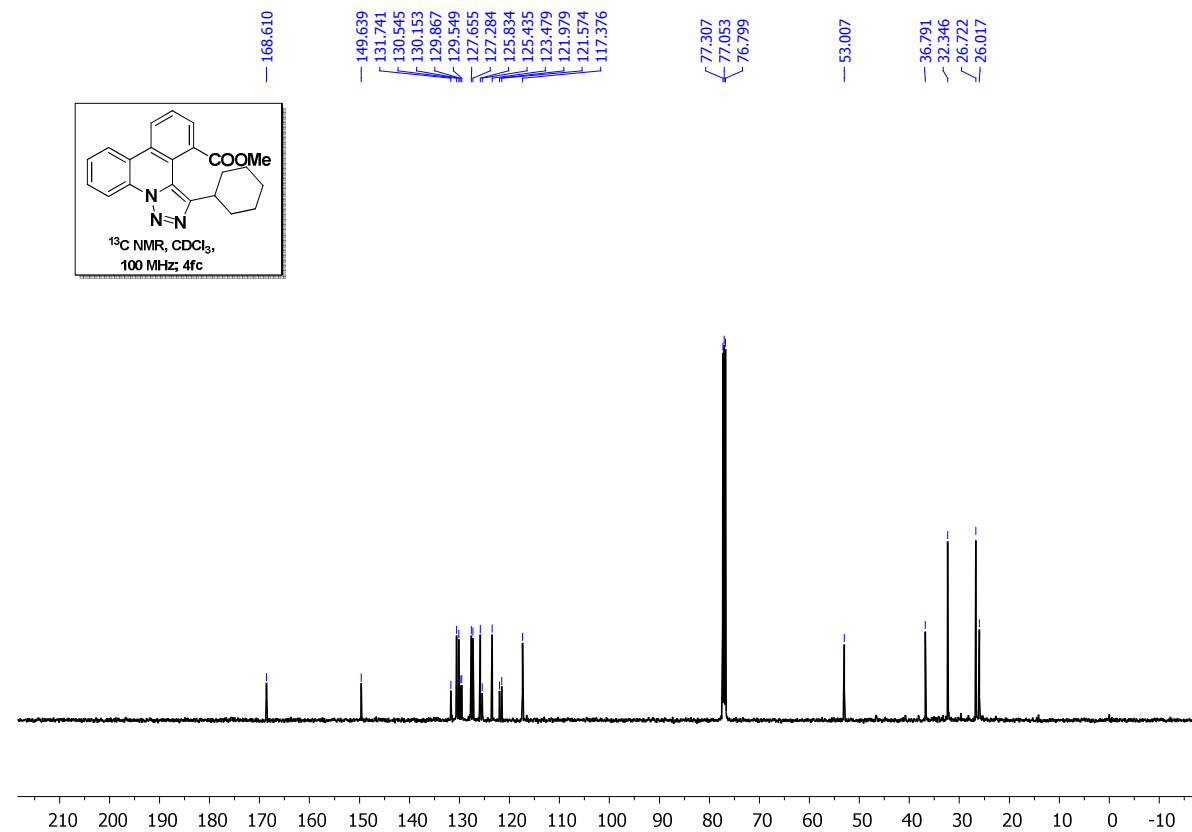
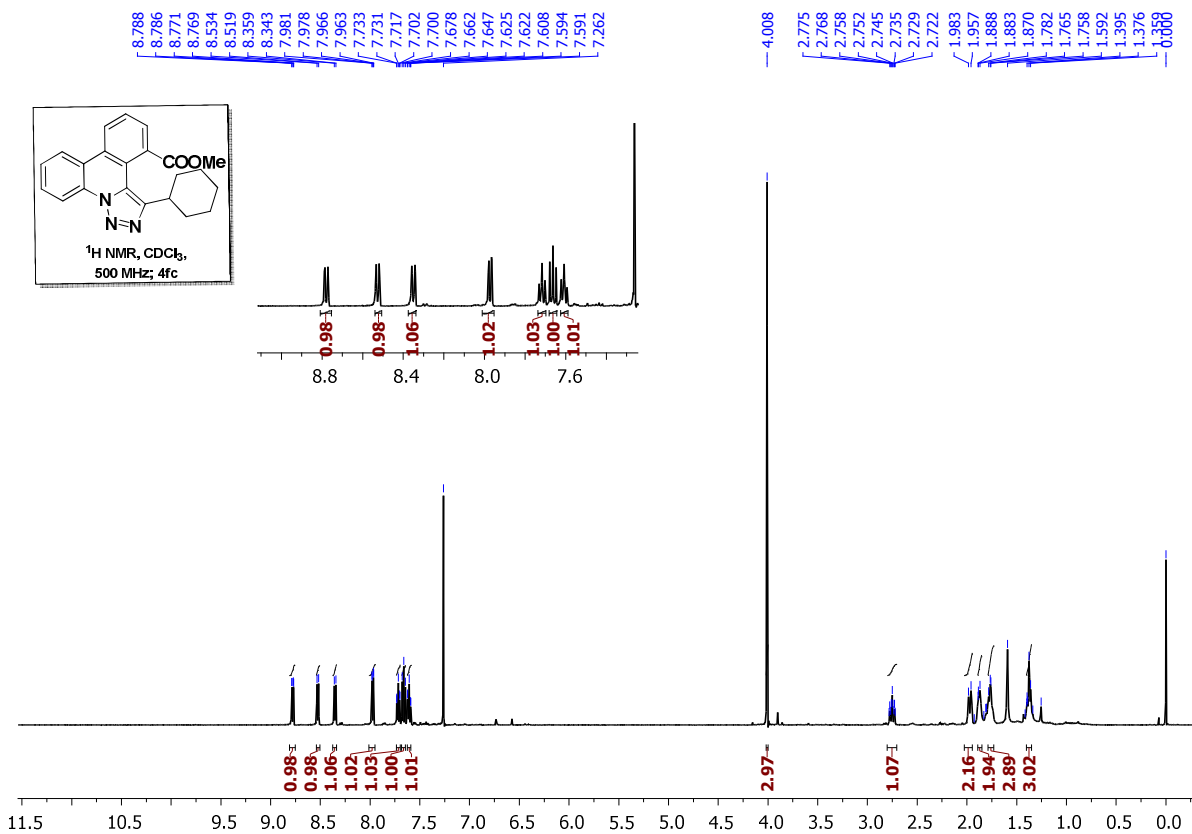


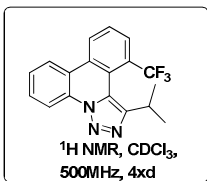








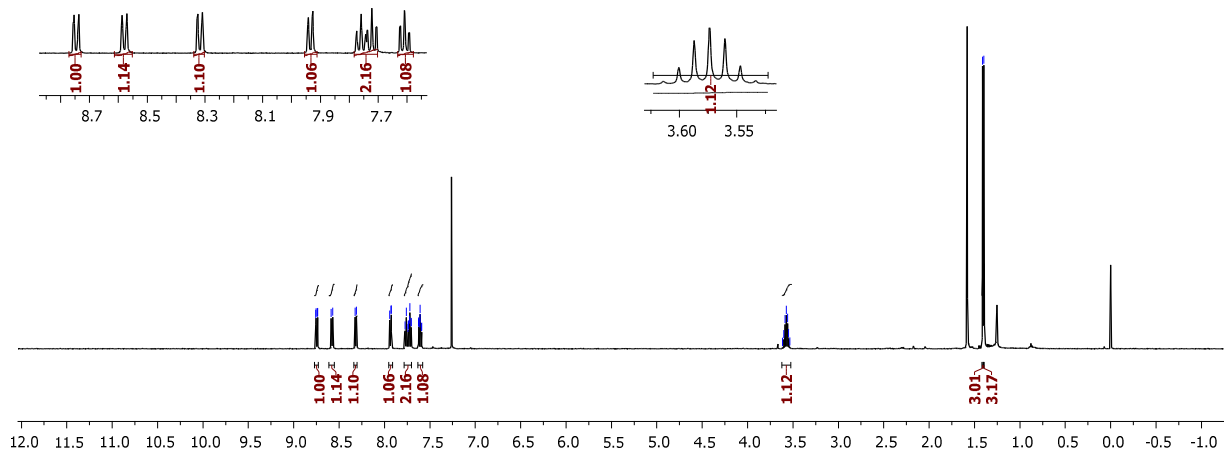




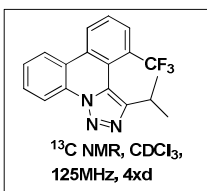
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3.61, 3.60, 3.59, 3.57, 3.56, 3.55, 3.53

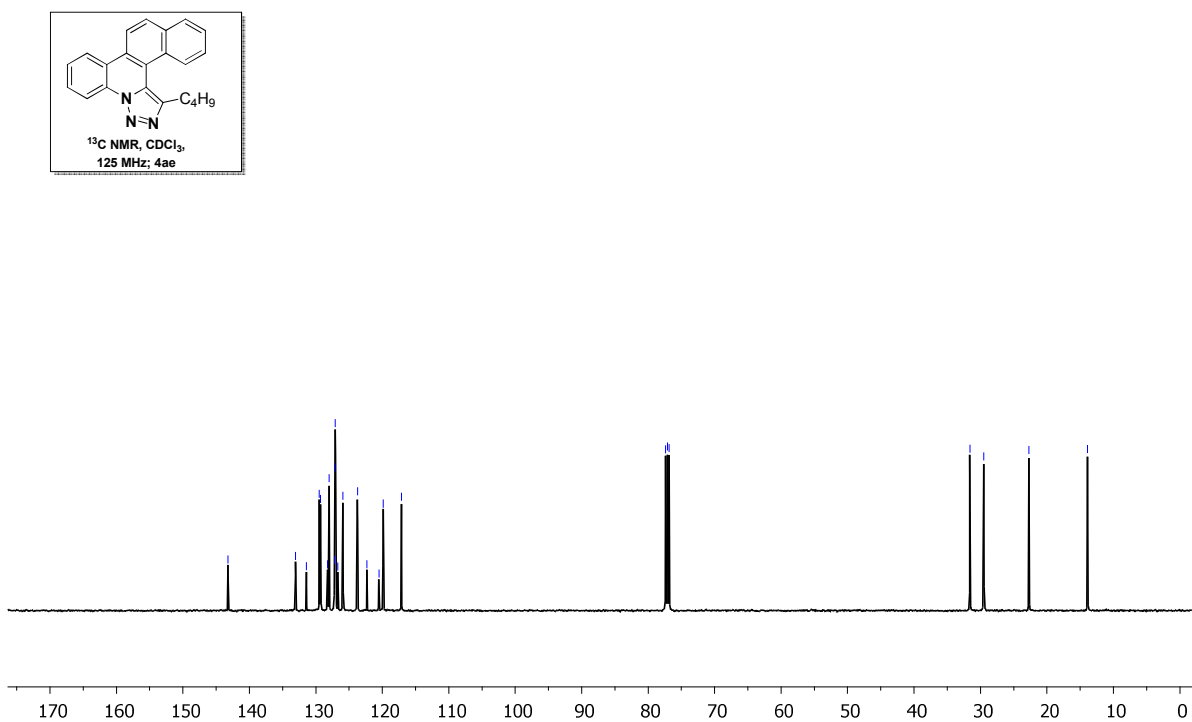
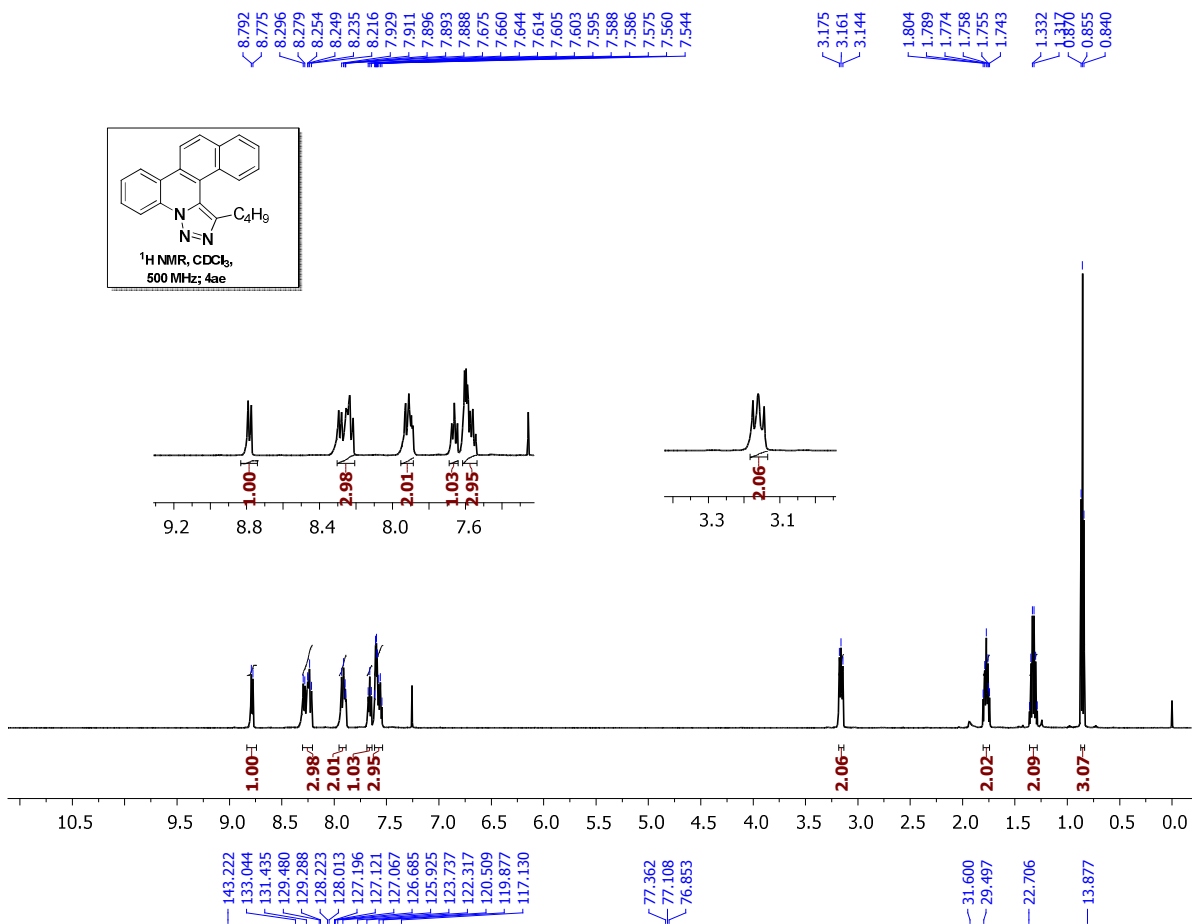
1.41, 1.40



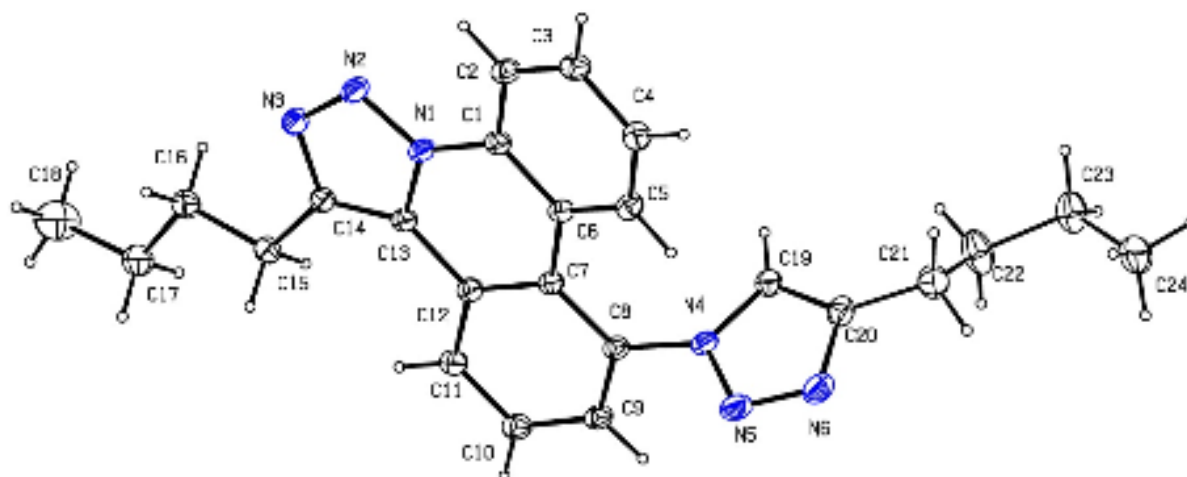
152.74, 131.68, 130.46, 128.96, 127.98, 127.47, 125.97, 123.56, 121.56, 117.50, 77.29, 76.78, 25.74, 23.07



190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0



X-Ray Crystallographic Study:



ORTEP structure of **2a**

X-ray data of **2a** compound was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK α radiation ($\lambda=0.71073\text{\AA}$) with ω -scan method.² Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program.³ The structures were solved by Direct Methods using SHELXS³ and refinement was carried out by full-matrix least-squares technique using SHELXL.⁴ The crystal was twinned, and the structure was refined using a HKLF5 file containing data for two twin domains, with a refined BASF of 0.31. Anisotropic displacement parameters were included for all non-hydrogen atoms. The atoms C21-C24 were disordered over two sites (C21/C22/C23/C24 and C211/C221/C231/C241). The site-occupancy factors of disordered atoms were refined to 0.790(9) and 0.210(9). DELU and DFIX constraints were applied to the disordered atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H or $1.2U_{\text{eq}}(\text{C})$ for other H atoms]. The methyl groups were allowed to rotate but not to tip.

Crystal Data for 2a: C₂₄H₂₆N₆ ($M=398.51$): triclinic, space group P-1 (no. 2), $a = 7.619(2)\text{\AA}$, $b = 9.692(3)\text{\AA}$, $c = 15.884(5)\text{\AA}$, $\alpha = 75.952(5)^\circ$, $\beta = 79.091(5)^\circ$, $\gamma = 71.433(5)^\circ$, $V = 1070.6(6)\text{\AA}^3$, $Z = 2$, $T = 294(2)\text{ K}$, $\mu(\text{MoK}\alpha) = 0.077\text{ mm}^{-1}$, $D_{\text{calc}} = 1.236\text{ g/mm}^3$, 9893 reflections measured ($4.522 \leq 2\theta \leq$

50), 9893 unique which were used in all calculations. The final R_1 was 0.0906 ($I > 2\sigma(I)$) and wR_2 was 0.2933 (all data). [CCDC 1408841](https://www.ccdc.cam.ac.uk/conts/retrieving.html) 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].

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