

Supplementary Material

AuCl₃-catalyzed synthesis of (*E/Z*)-chloroallyl carbazoles via a cascade cyclization process

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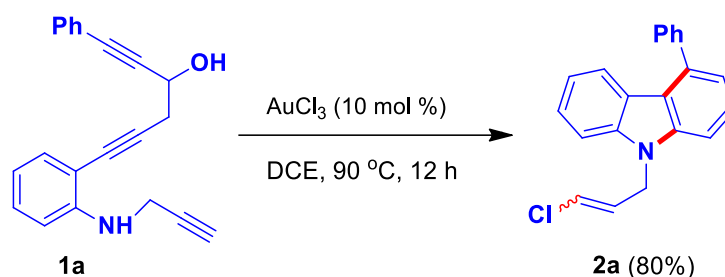
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1.1 General

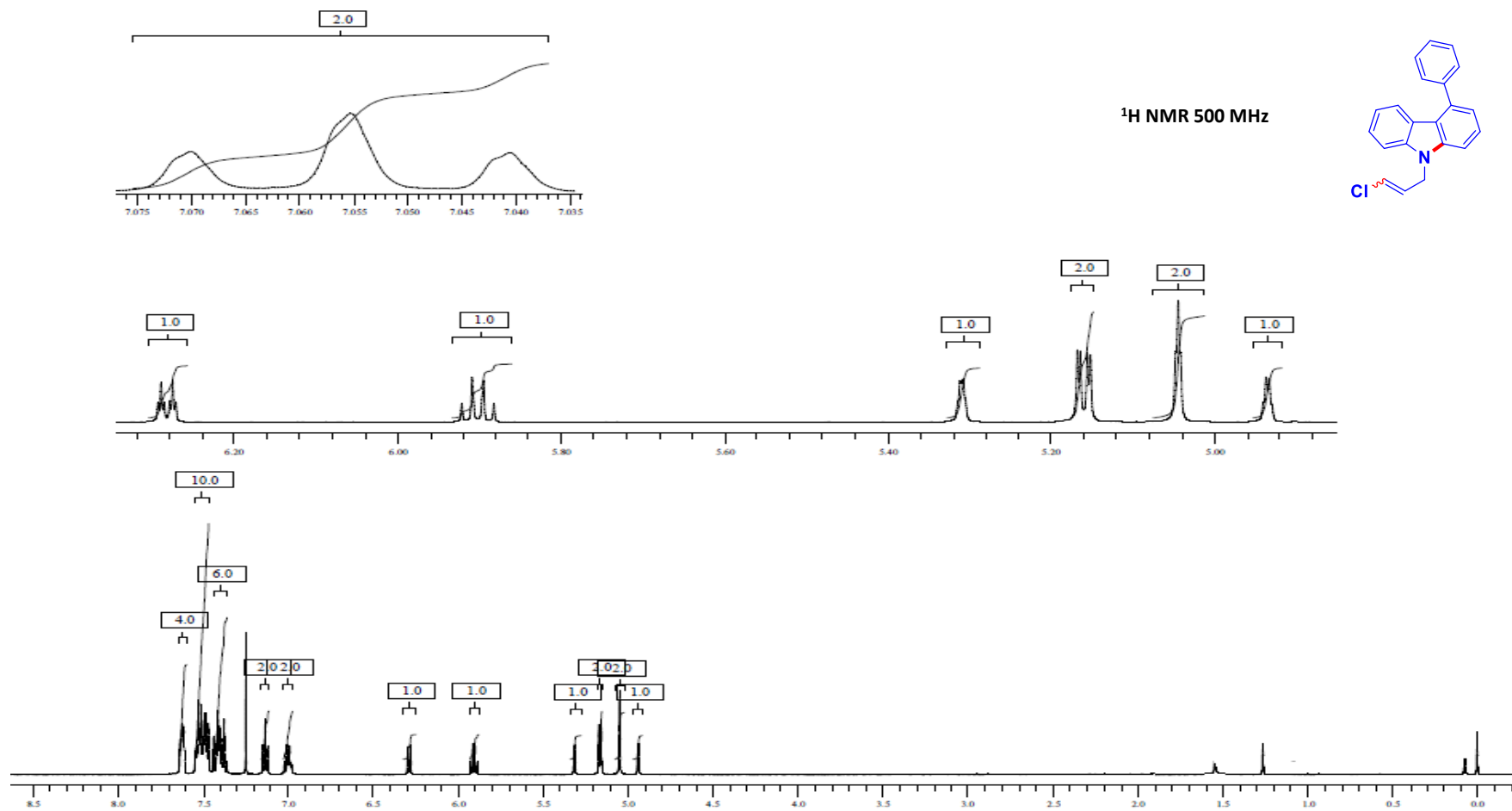
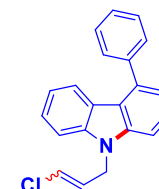
Reactions were carried out in oven dried reaction flasks under nitrogen atmosphere and also solvents and reagents were transferred by oven-dried syringes to ambient temperature. TLC was performed on Merck silica gel aluminium sheets using UV as a visualizing agent. Solvents were removed under reduced pressure. Columns were packed as slurry of silica gel in hexane and ethyl acetate solvent mixture. The elution was assisted by applying pressure with an air pump. ^{13}C NMR spectra were recorded on 75, 100 and 125 MHz spectrometers. ^1H NMR spectra were recorded on 300, 400 and 500 MHz spectrometers in appropriate solvents using TMS as internal standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = double doublet, dt = doublet of triplet, t = triplet, m = multiplet, brs = broad singlet. All reactions were performed under nitrogen atmosphere with freshly distilled and dried solvents. All solvents were distilled using standard procedures. Unless otherwise noted, reagents were obtained from Aldrich, Alfa Aesar, and TCI used without further purification. Synthesis of 2-aminophenyl-1,5-diyn-3-ols **1a-t** were prepared by following reported procedures.¹

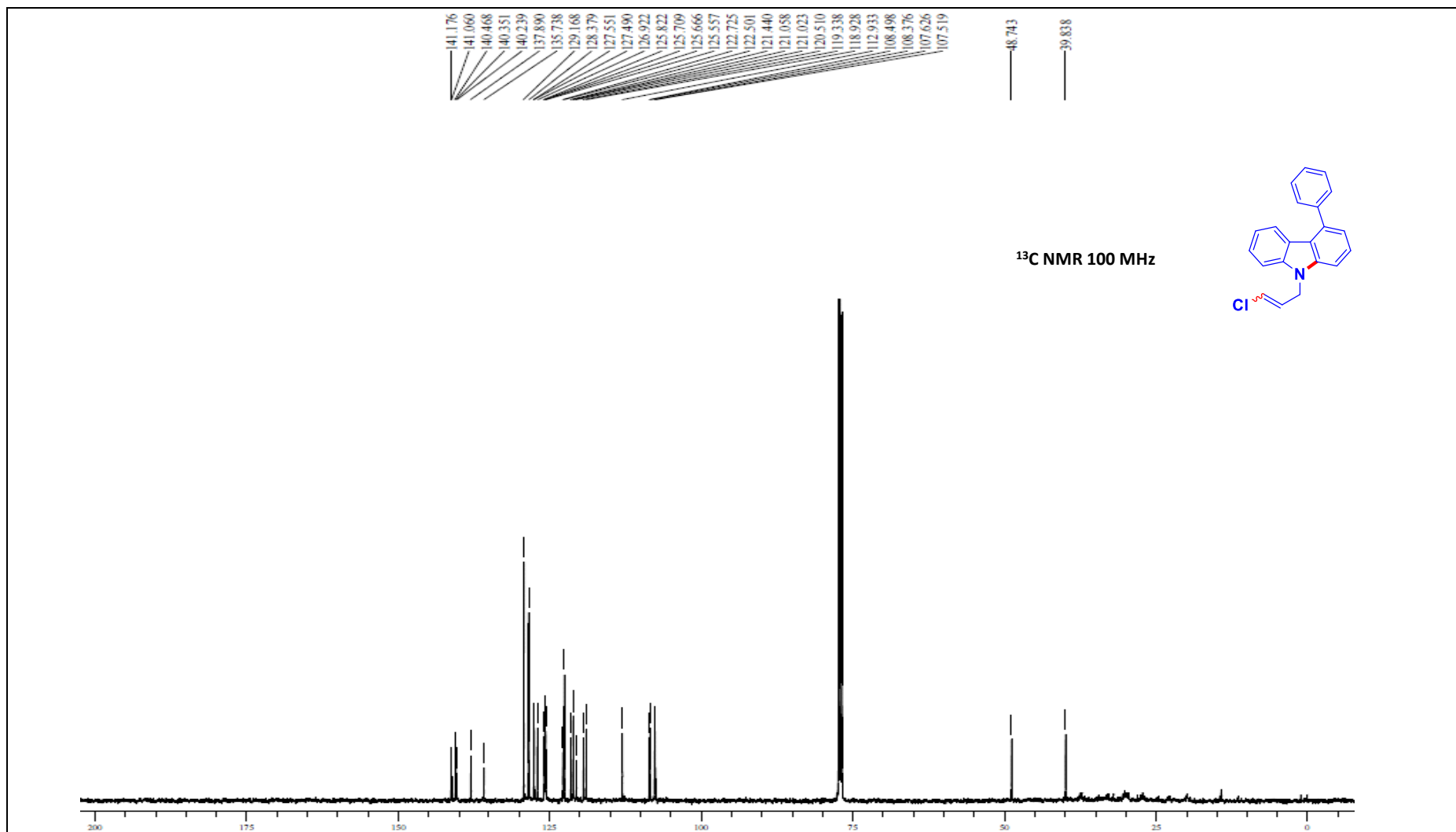
References

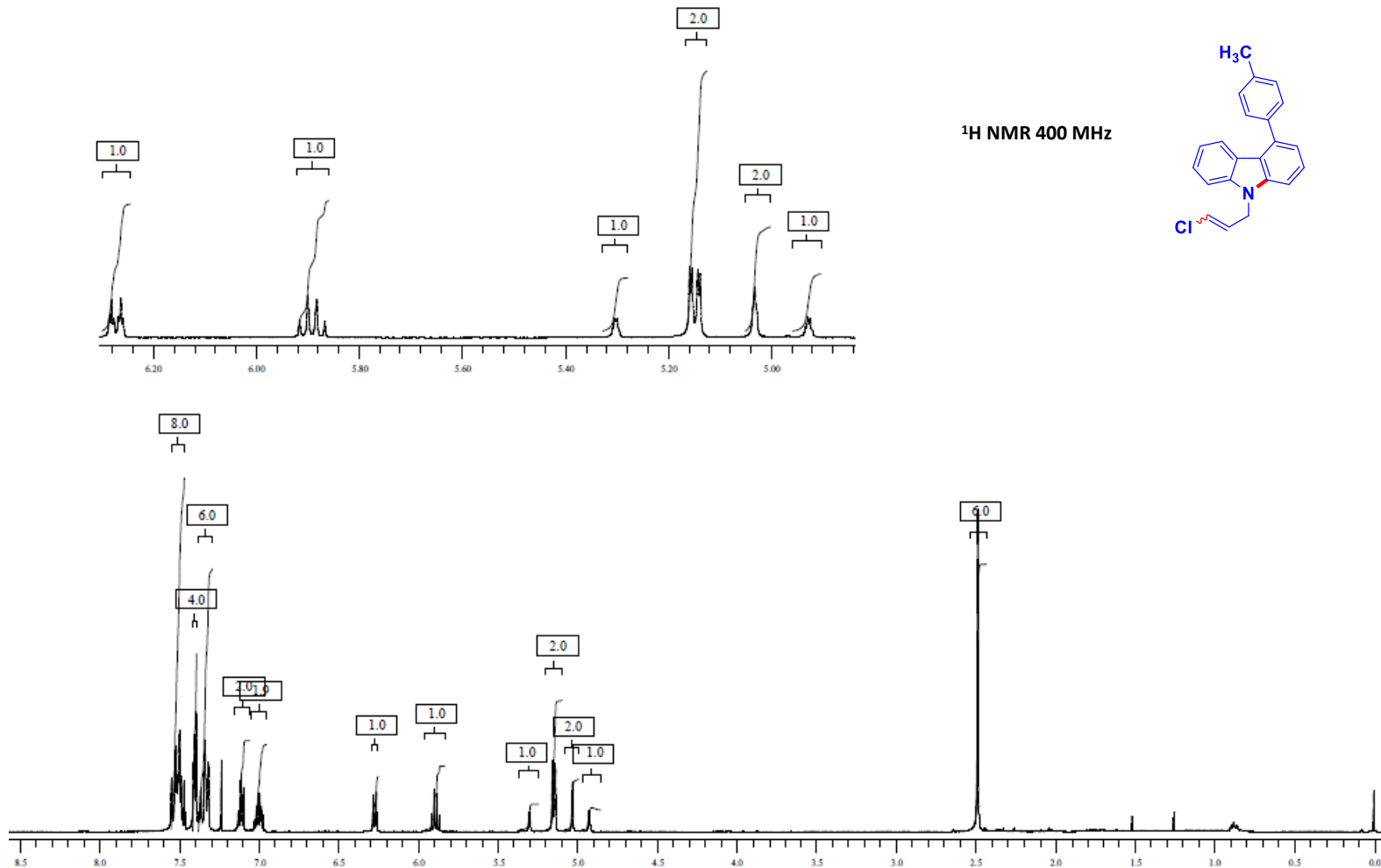
- (a) Hirofumi, K.; Hanaki, E.; Hironori, I.; Michiko, K.; Itahashi, H. *Tetrahedron* **2004**, *60*, 1913. (b) Jogi, A.; Maeorg, U. *Molecules*, **2001**, *6*, 964. (c) Elangovan, A.; Wang, Y. -H.; Ho, T. -I. *Org. Lett.* **2003**, *5*, 1841. (d). Severin, R.; Reimer, J.; Doye, S. *J. Org. Chem.* **2010**, *75*, 3518.

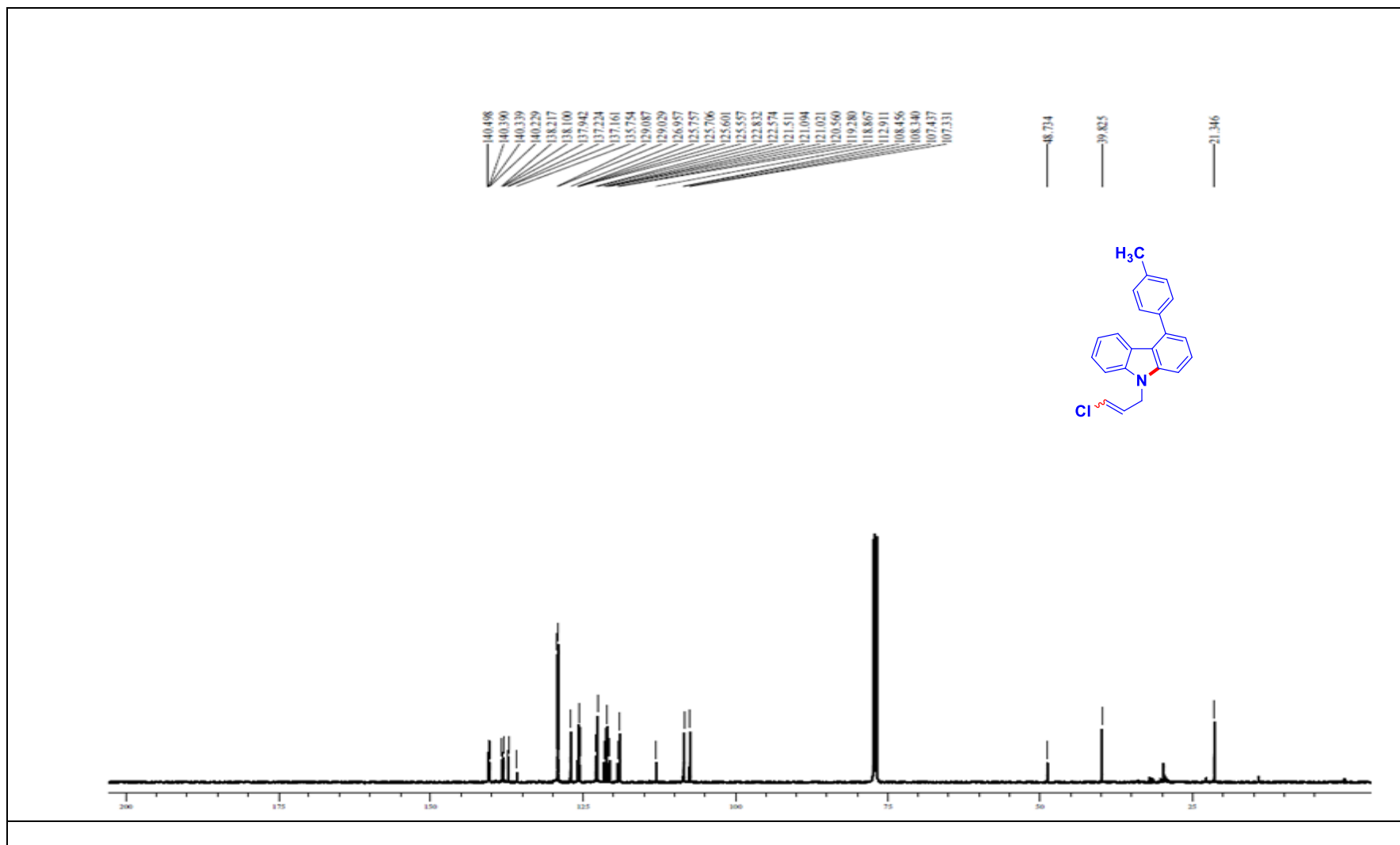
1.2: General procedure for synthesis of substituted (*E/Z*) 9-(3-chloroallyl)-4-phenyl-9*H*-carbazole (2a**).**

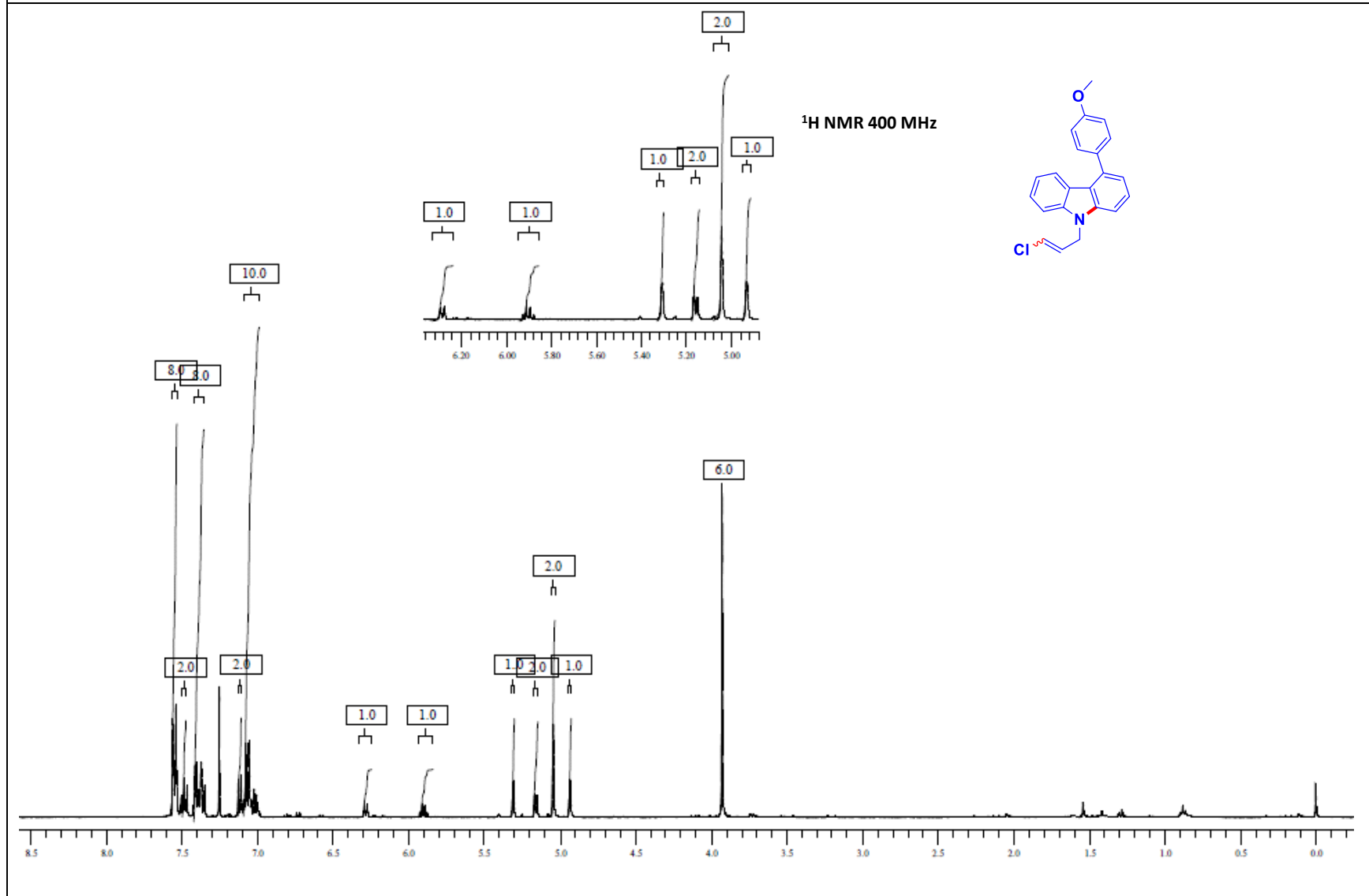
To a 25 mL, round-bottomed, two-neck flask equipped with magnetic stir bar was added 1-phenyl-6-[2-(prop-2-yn-1-ylamino)phenyl]hexa-1,5-dien-3-ol (**1a**) (0.09 g, 0.3 mmol, 1 equiv), the flask was purged with dry nitrogen, then the compound was dissolved in dry DCE (3 mL). To this reaction flask were added AuCl_3 (0.089 g, 0.03 mmol, 10 mol %). The reaction mixture was allowed to stir at 80°C temperature for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was filtered through a Celite pad. The organic layer was removed under reduced pressure and extracted with EtOAc (3×5 mL). The combined organic layers were washed with saturated brine solution, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude residue was purified through a silica gel column chromatography using hexane and EtOAc as eluent (10/0.2) to give mixture of (*E/Z*)-9-(3-chloroallyl)-4-phenyl-9*H*-carbazole (**2a**). A similar experimental procedure was adopted for the synthesis of all compounds **2b-t**.

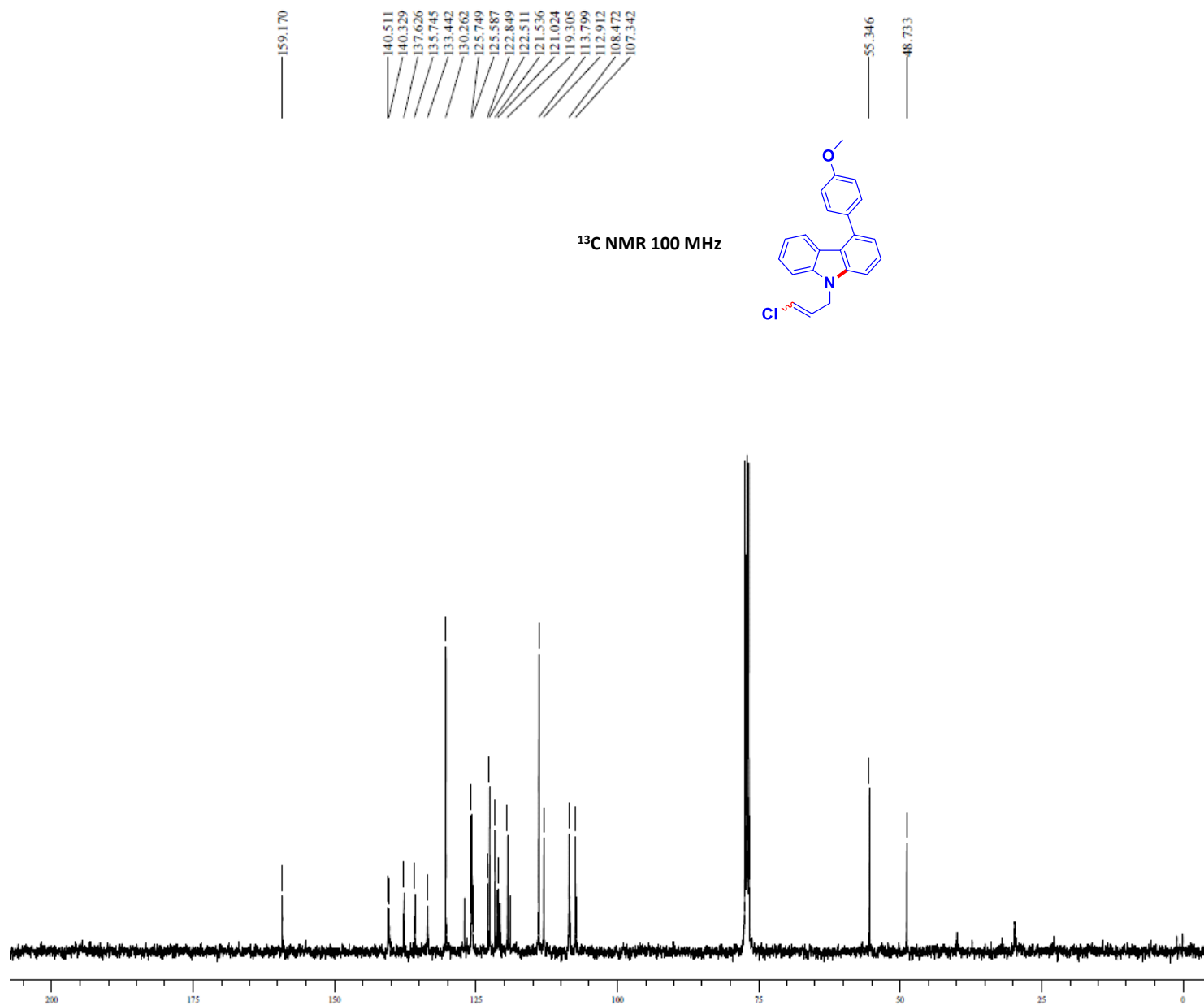
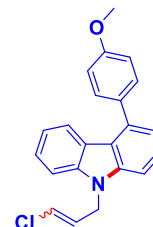
(E/Z) 9-(3-Chloroallyl)-4-phenyl-9H-carbazole 2a¹H NMR 500 MHz

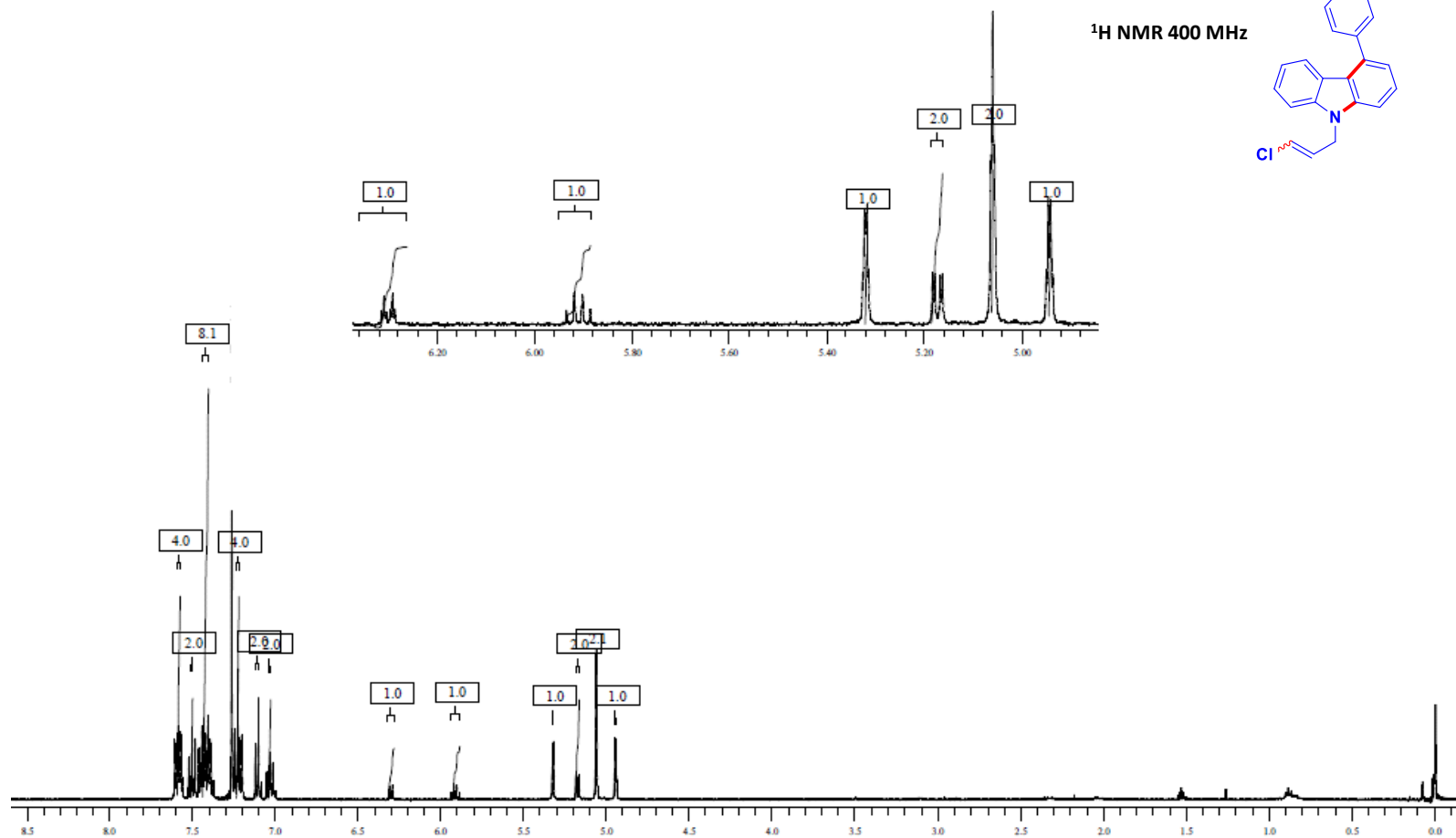
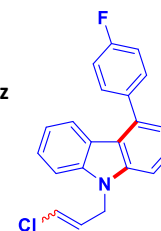


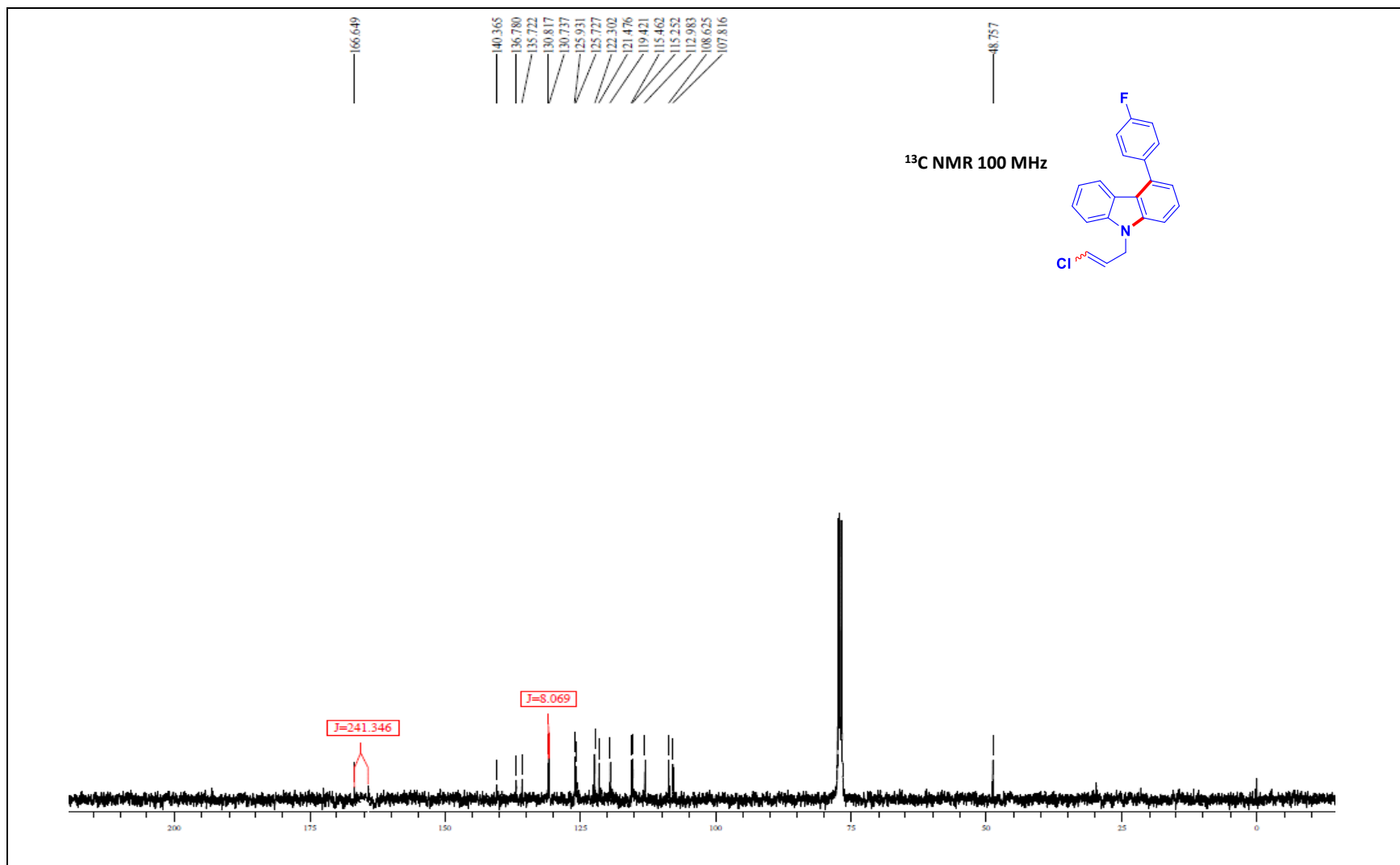
(E/Z) 9-(3-Chloroallyl)-4-(p-tolyl)-9H-carbazole 2b

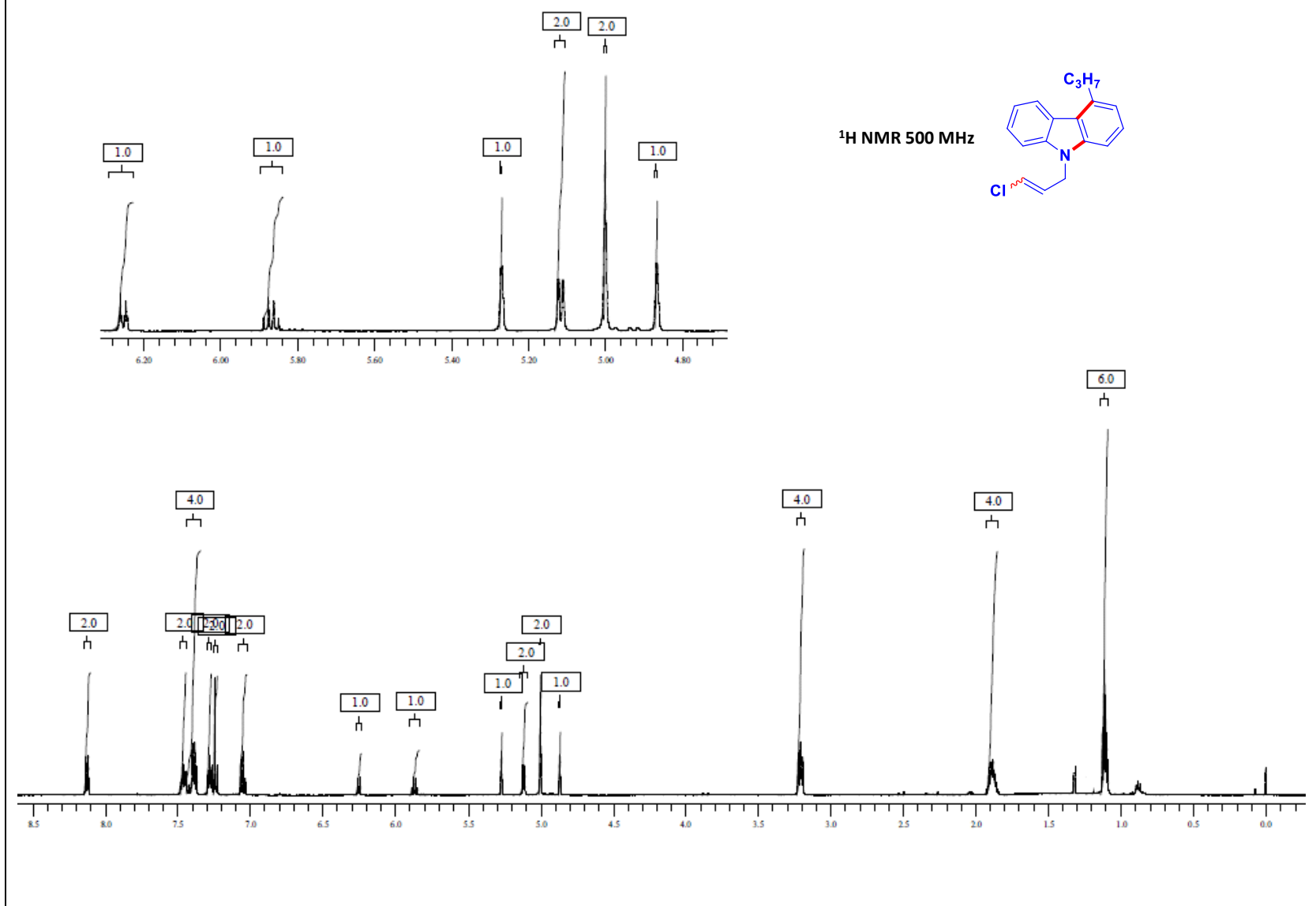


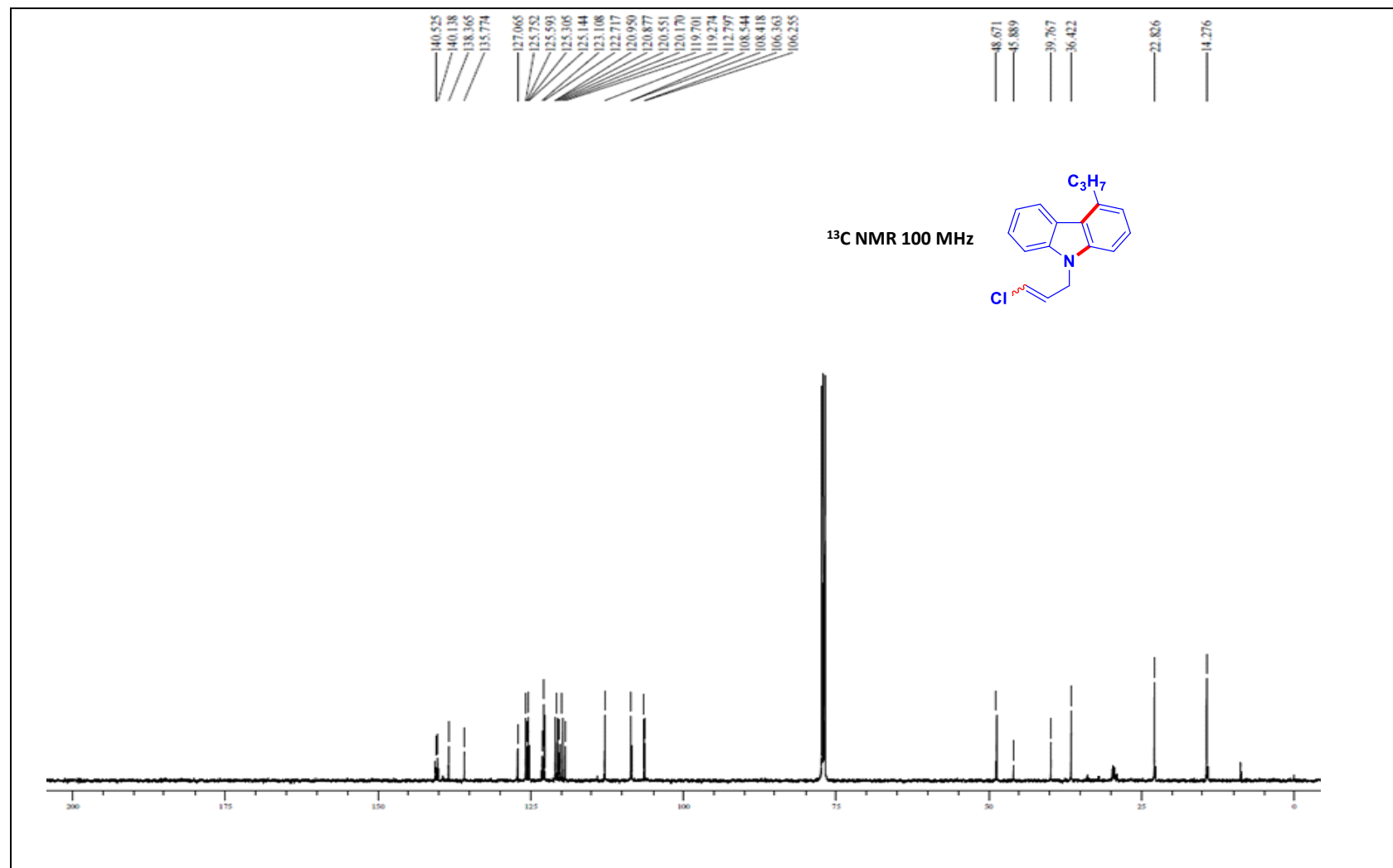
(*E/Z*) 9-(3-Chloroallyl)-4-(4-methoxyphenyl)-9*H*-carbazole 2c

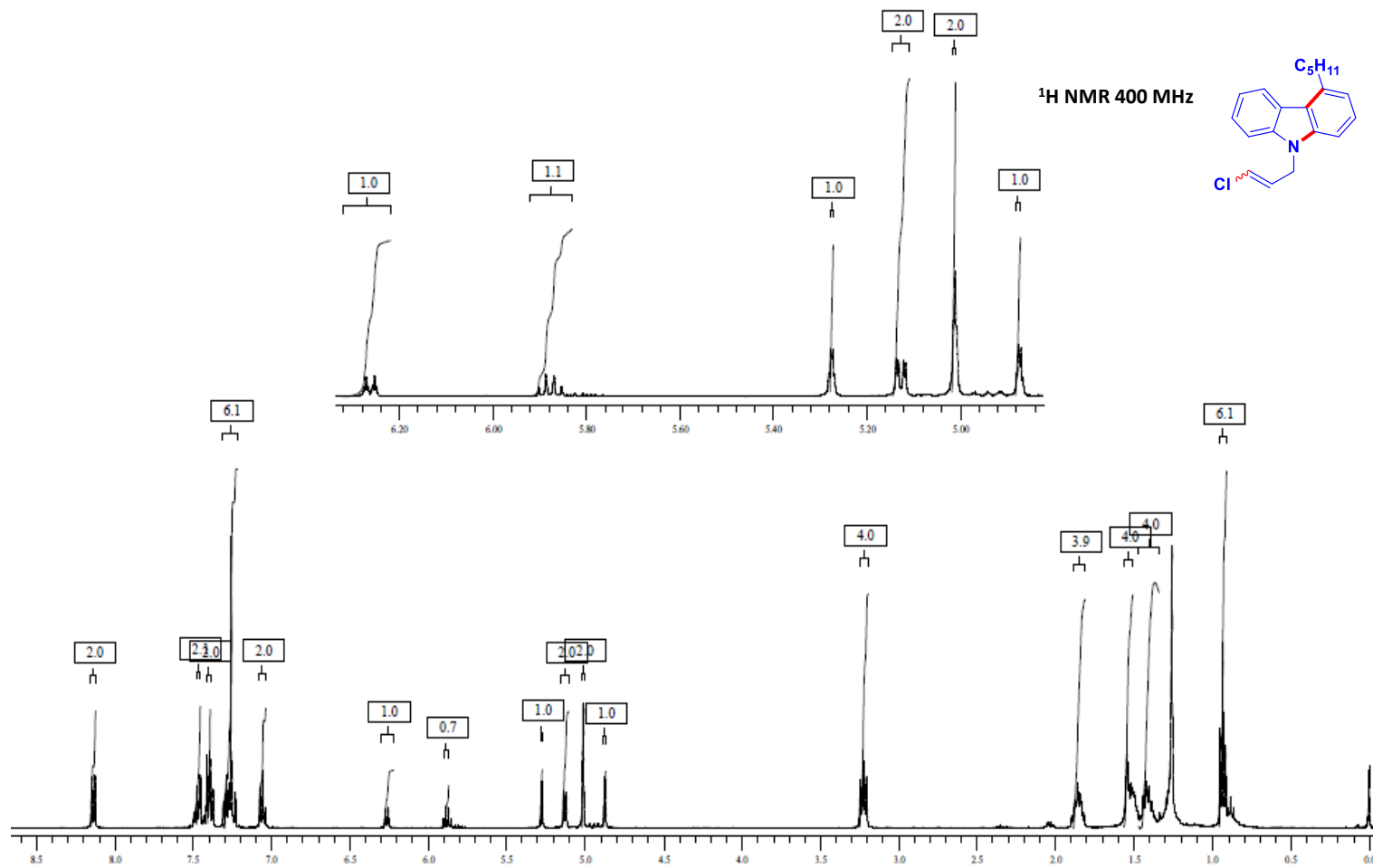
^{13}C NMR 100 MHz

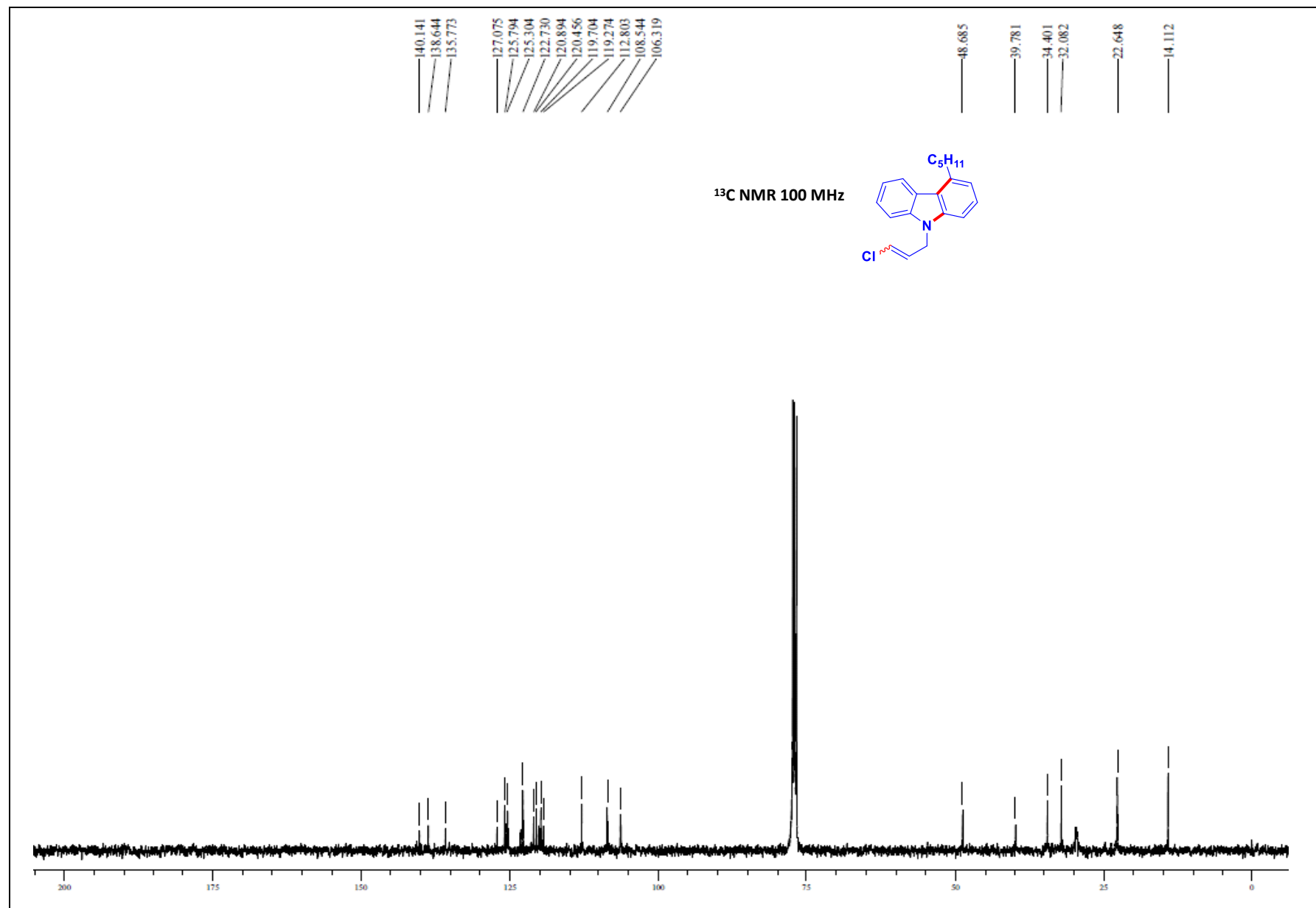
(E/Z) 9-(3-Chloroallyl)-4-(4-fluorophenyl)-9H-carbazole 2d¹H NMR 400 MHz

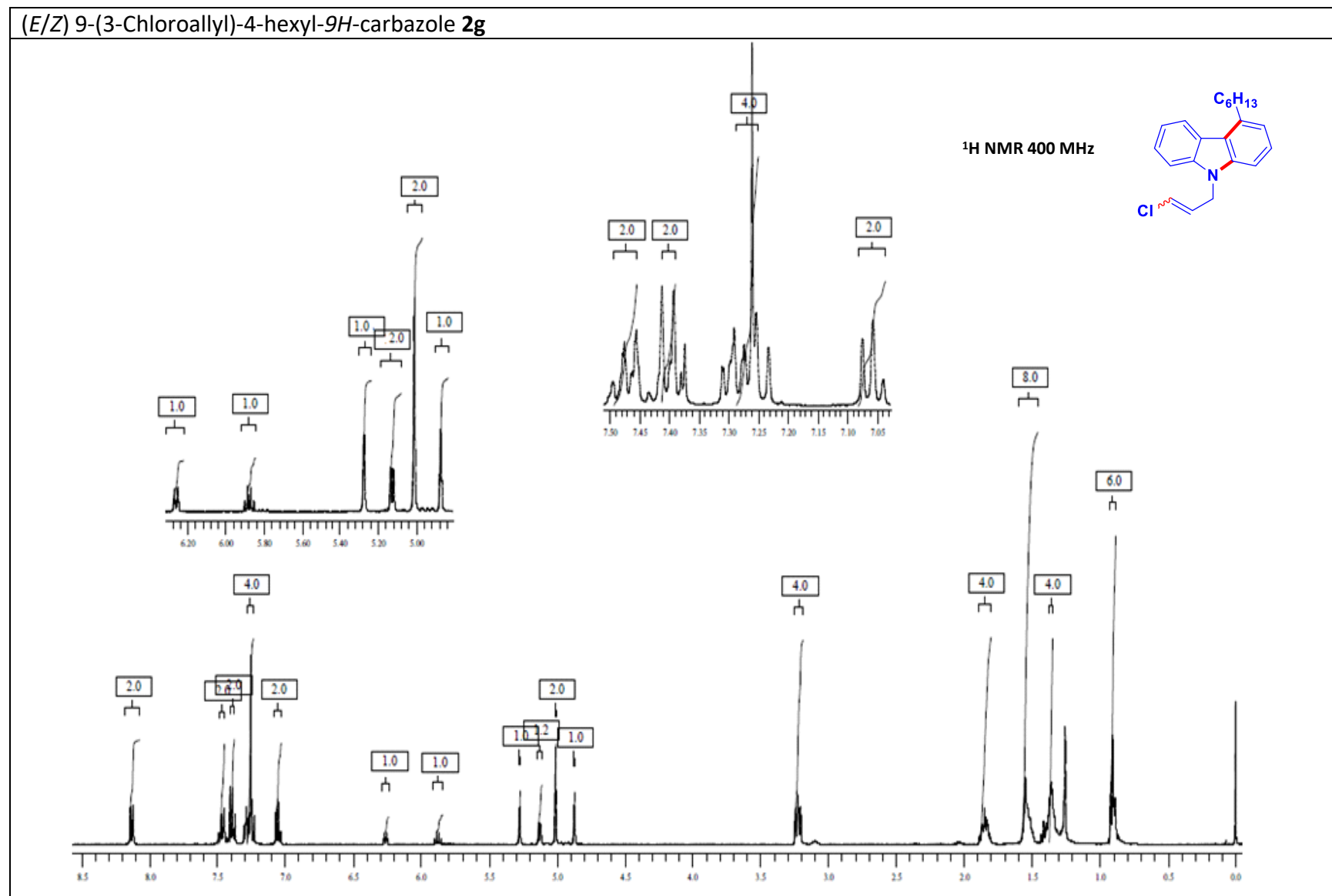


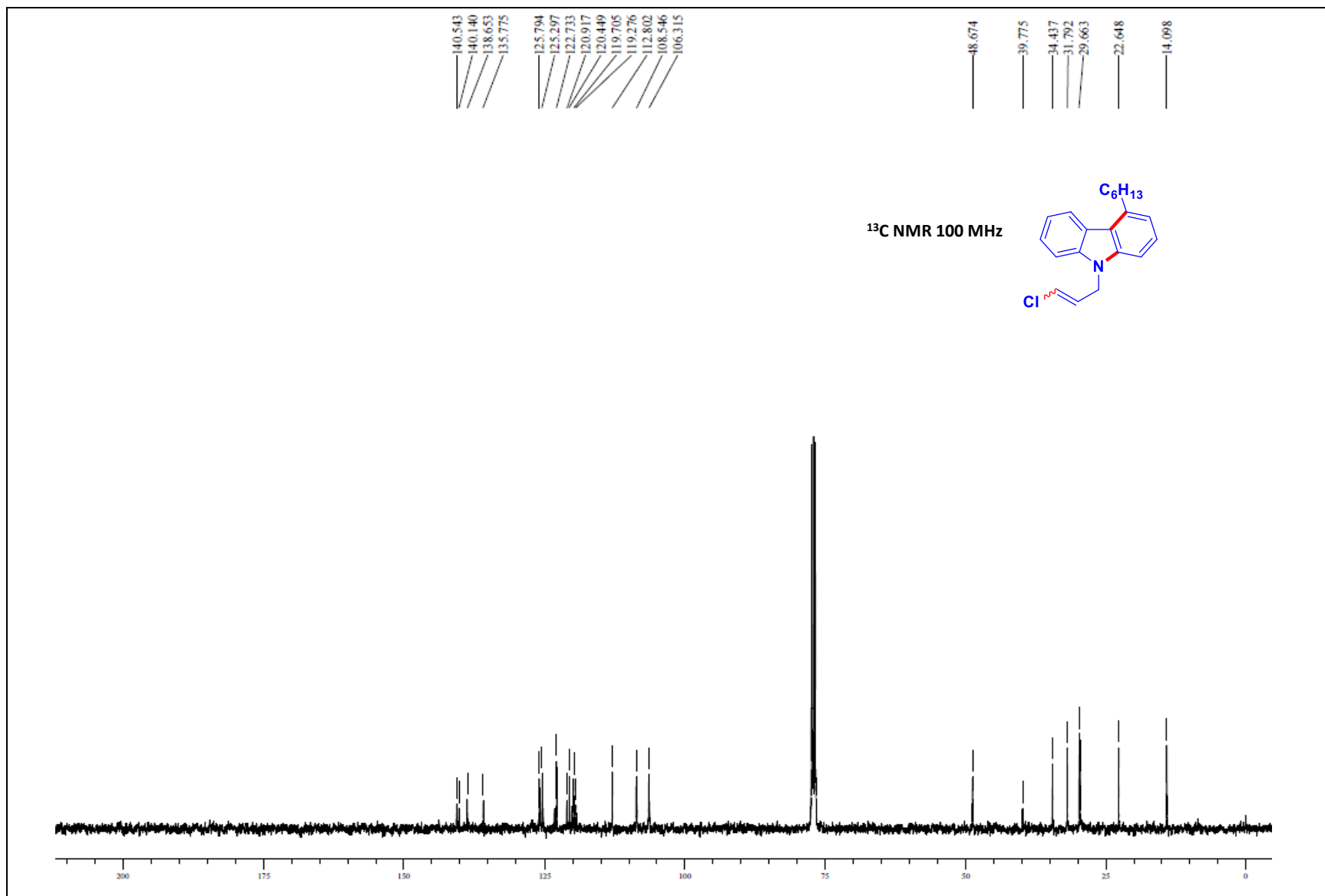
(*E/Z*) 9-(3-Chloroallyl)-4-propyl-9*H*-carbazole **2e**

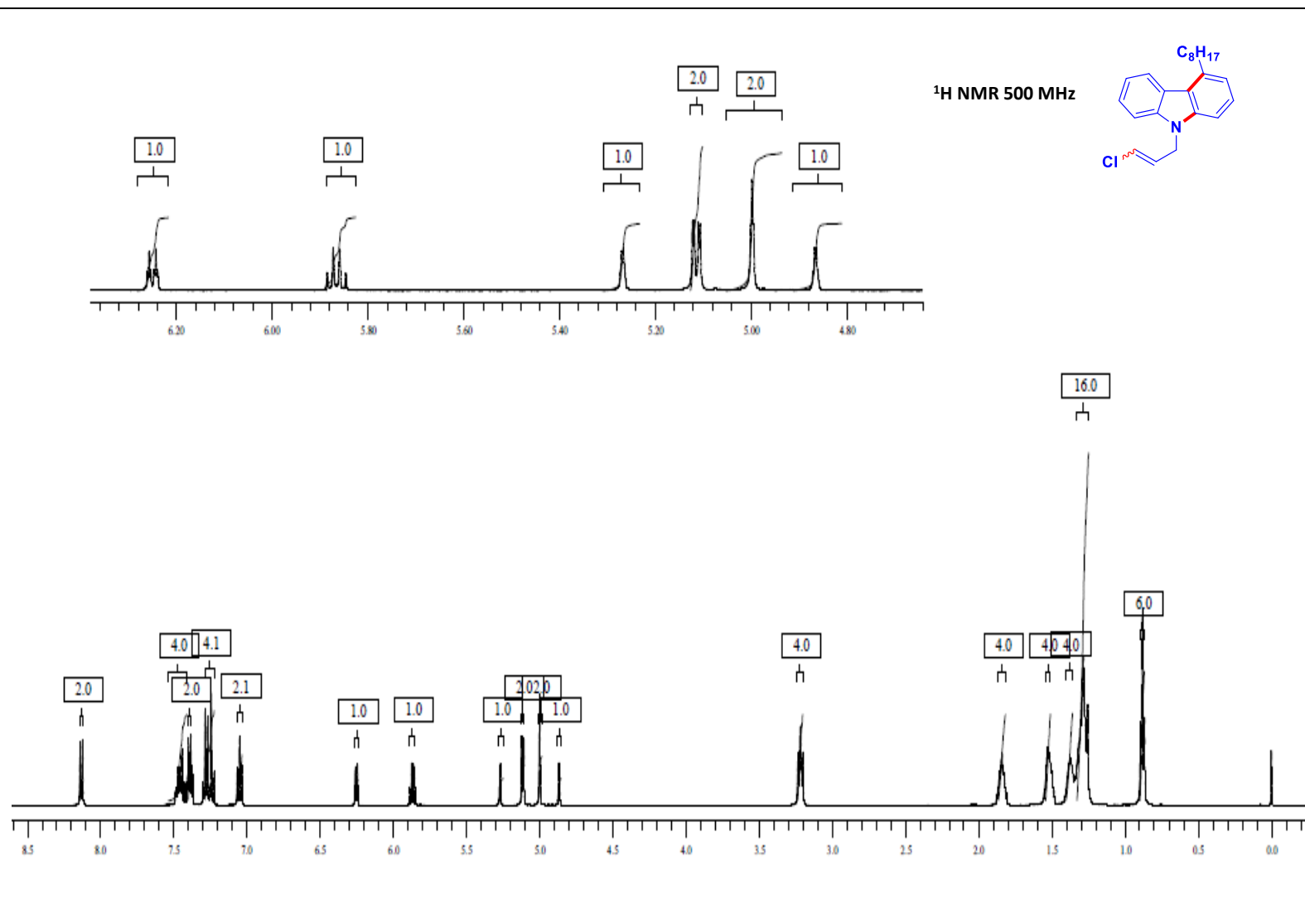


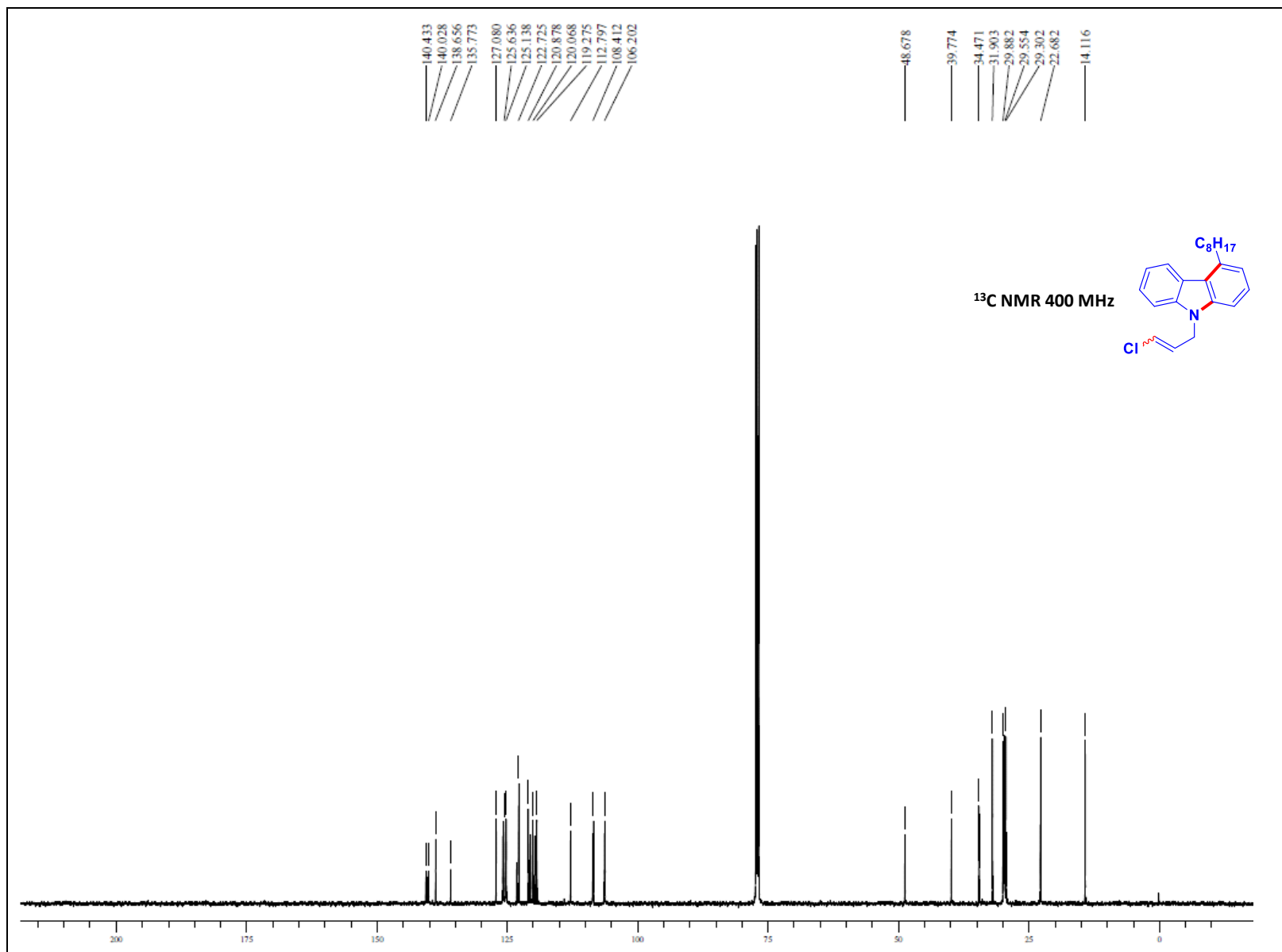
(*E/Z*) 9-(3-Chloroallyl)-4-pentyl-9*H*-carbazole 2f

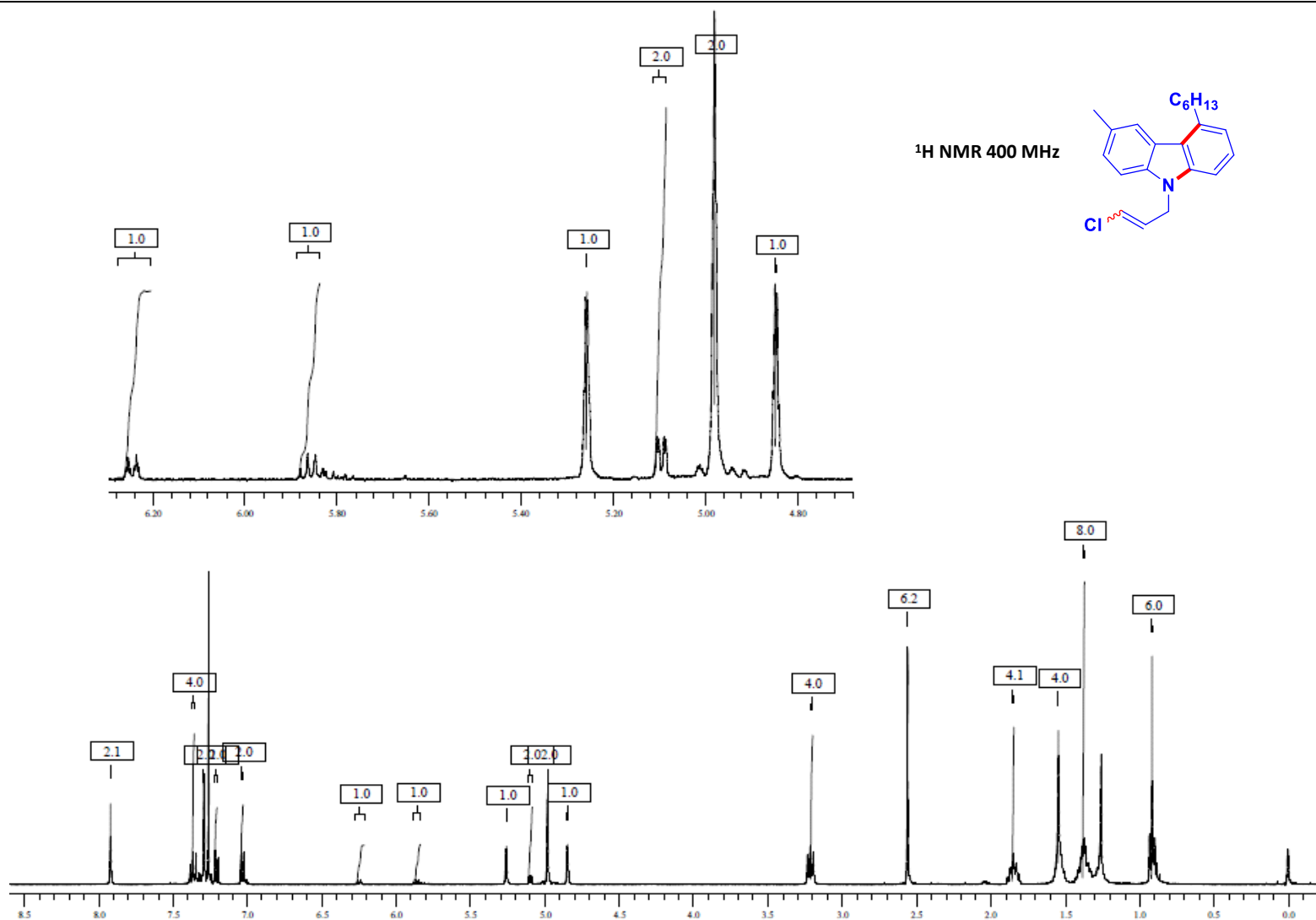


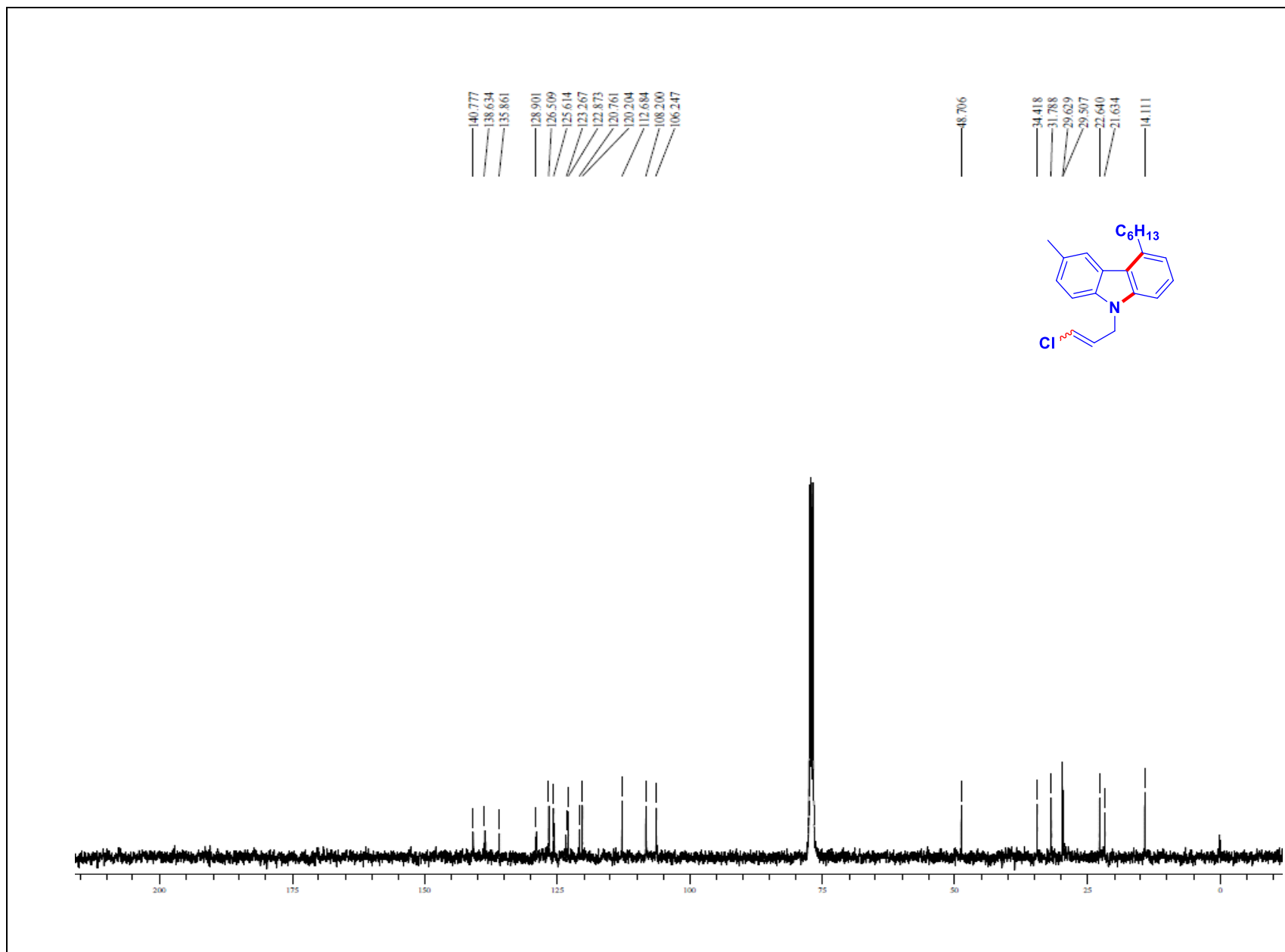
(E/Z) 9-(3-Chloroallyl)-4-hexyl-9H-carbazole 2g

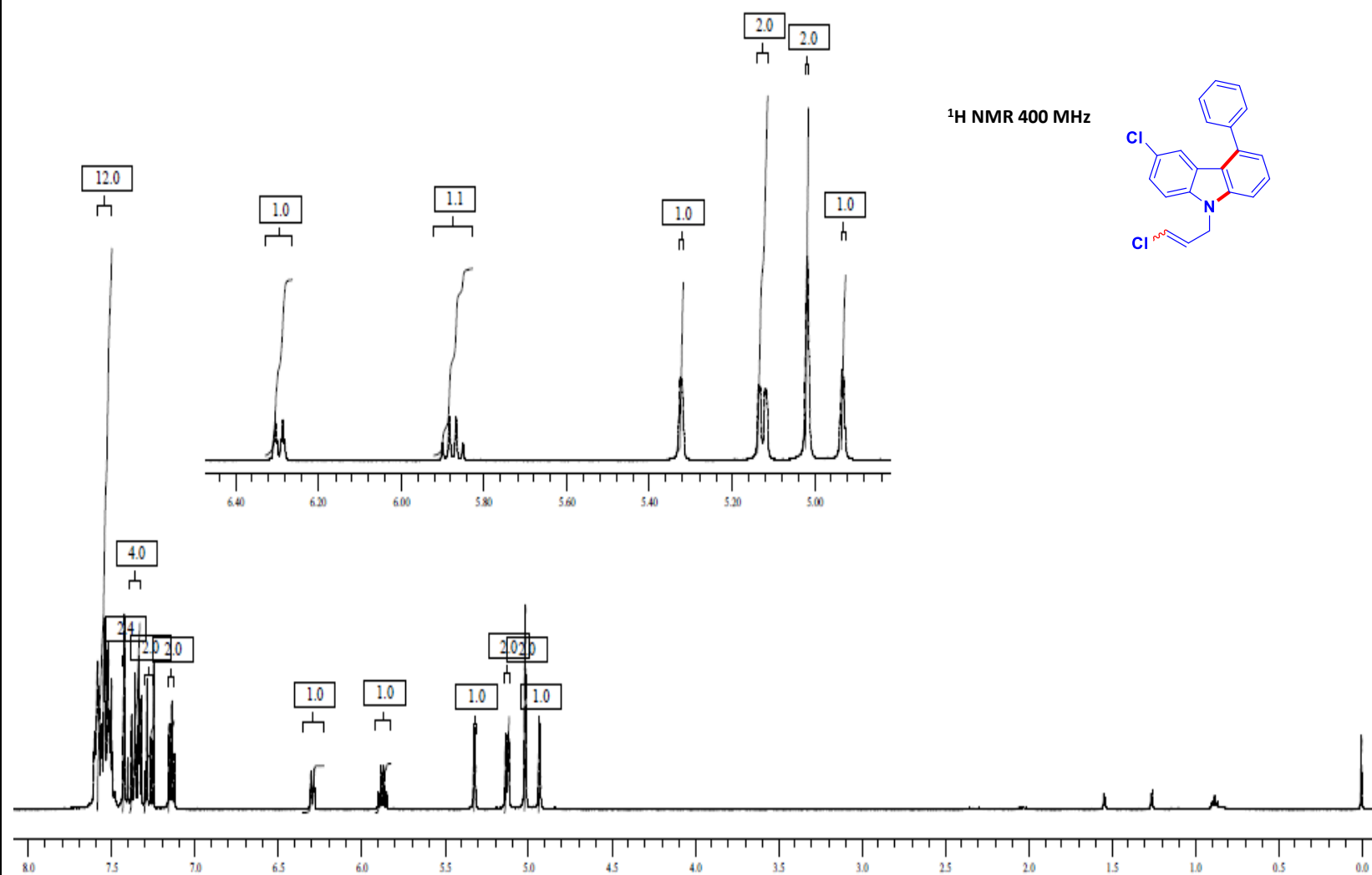


(*E/Z*) 9-(3-Chloroallyl)-4-octyl-9*H*-carbazole 2h

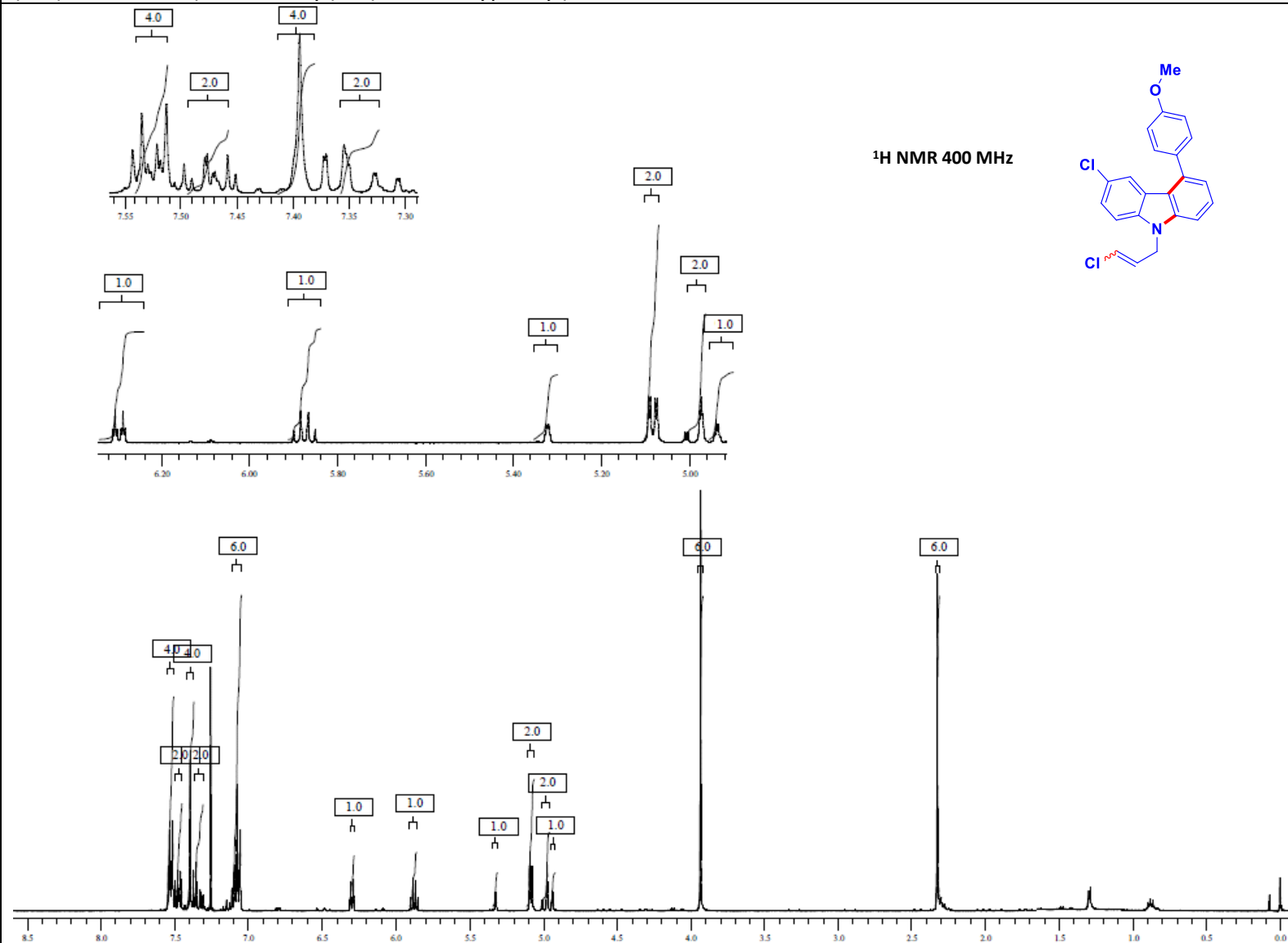


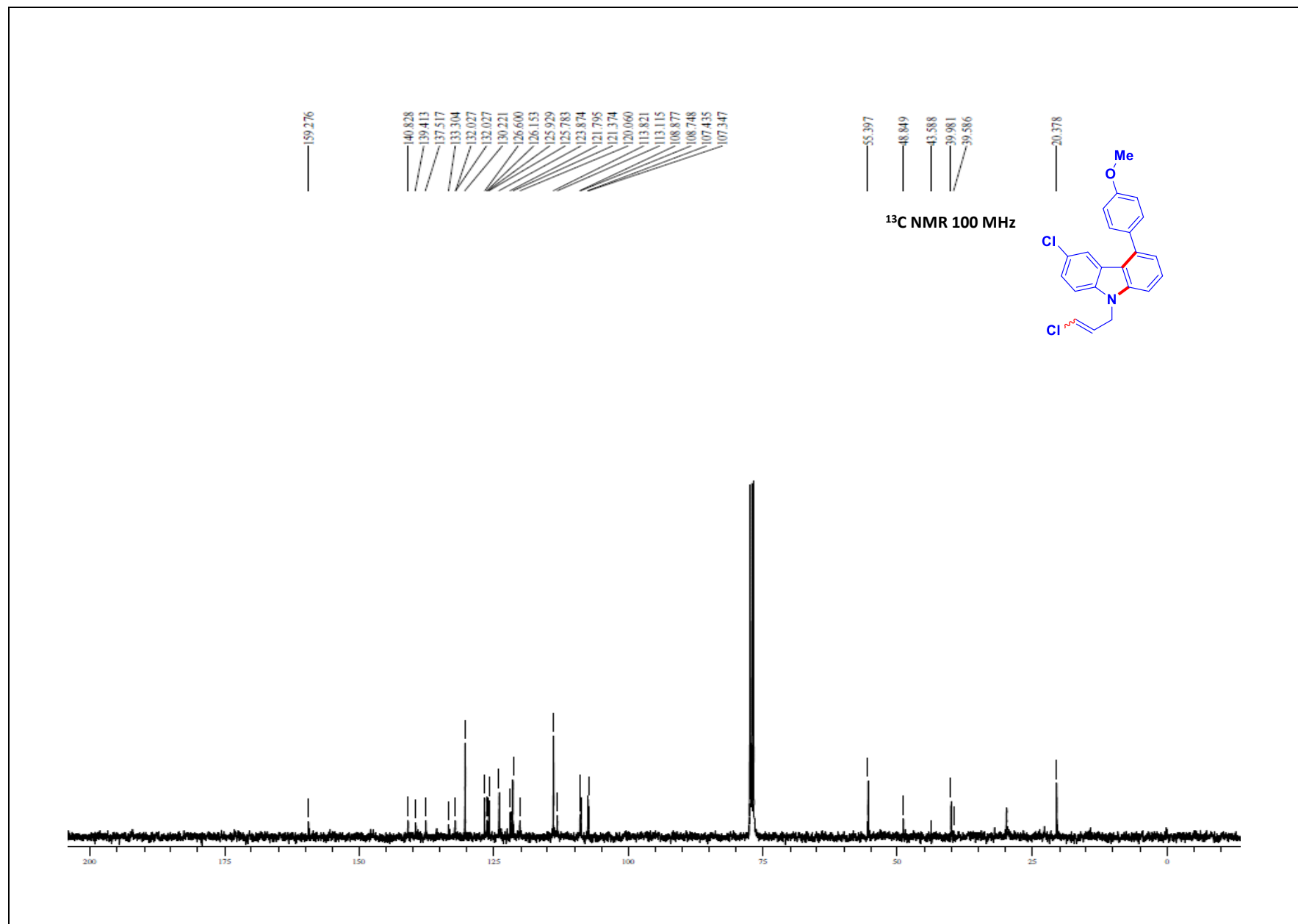
(E/Z) 9-(3-Chloroallyl)-5-hexyl-3-methyl-9H-carbazole **2i**

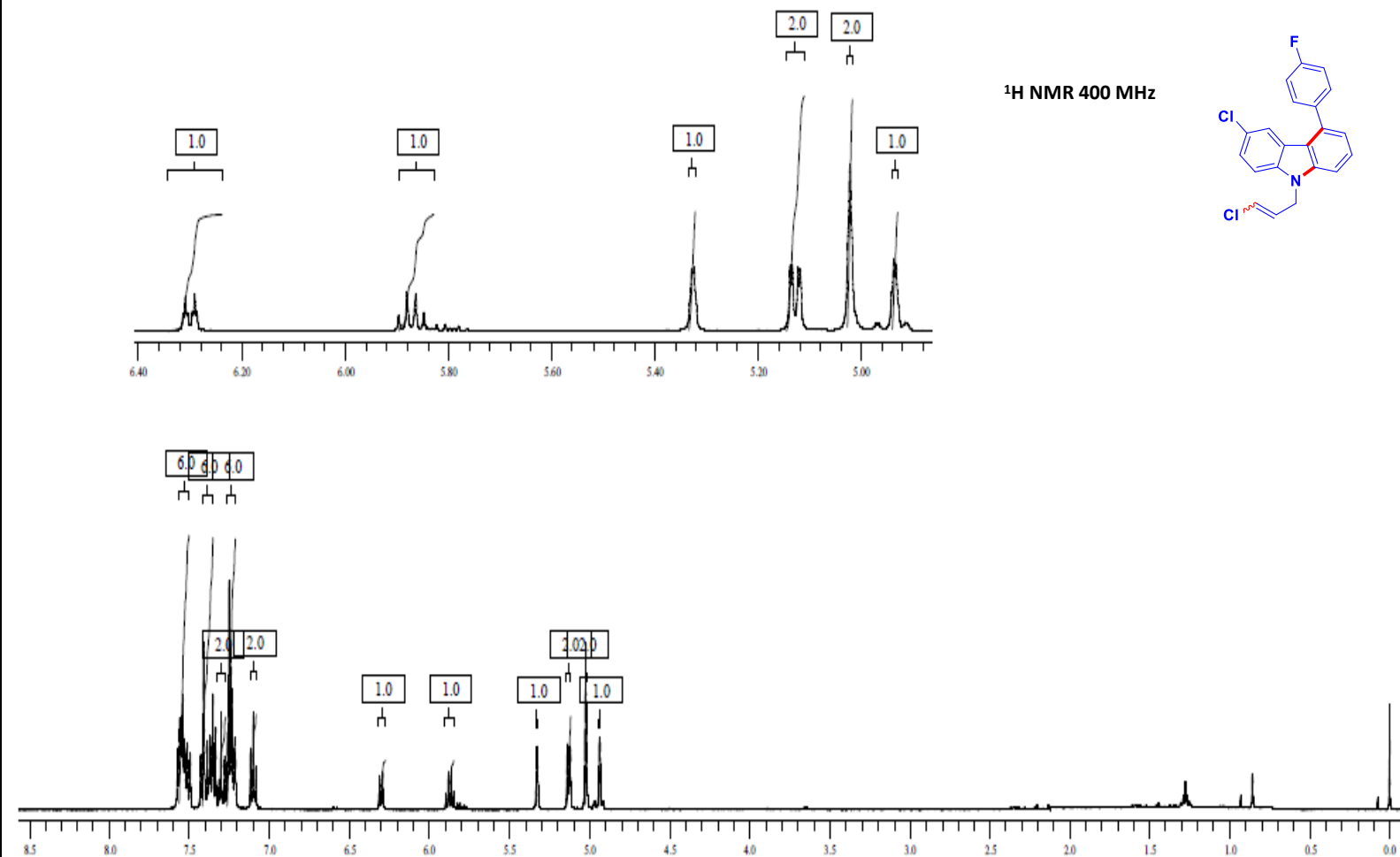


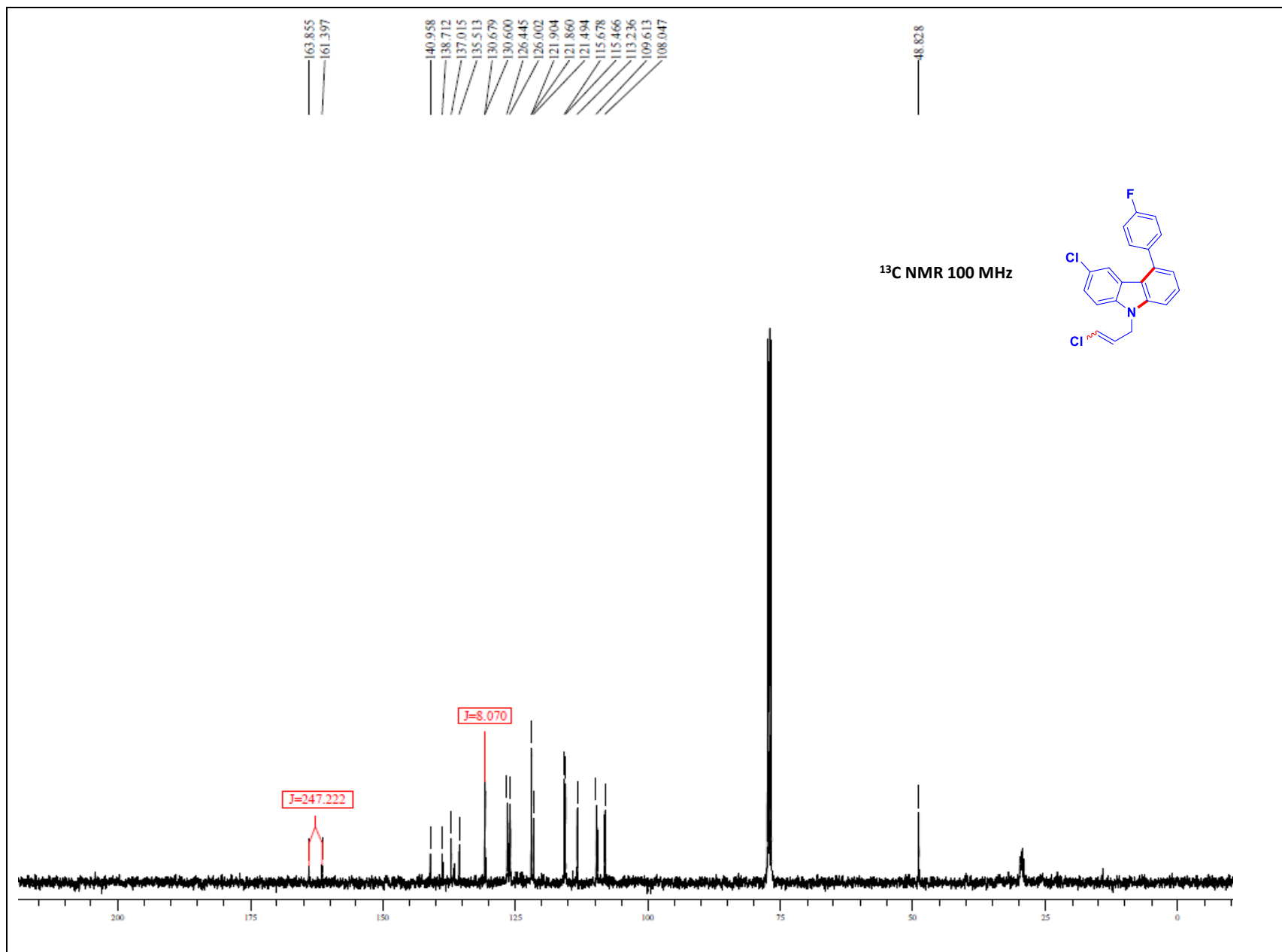
(E/Z) 3-Chloro-9-(3-chloroallyl)-5-phenyl-9H-carbazole 2j

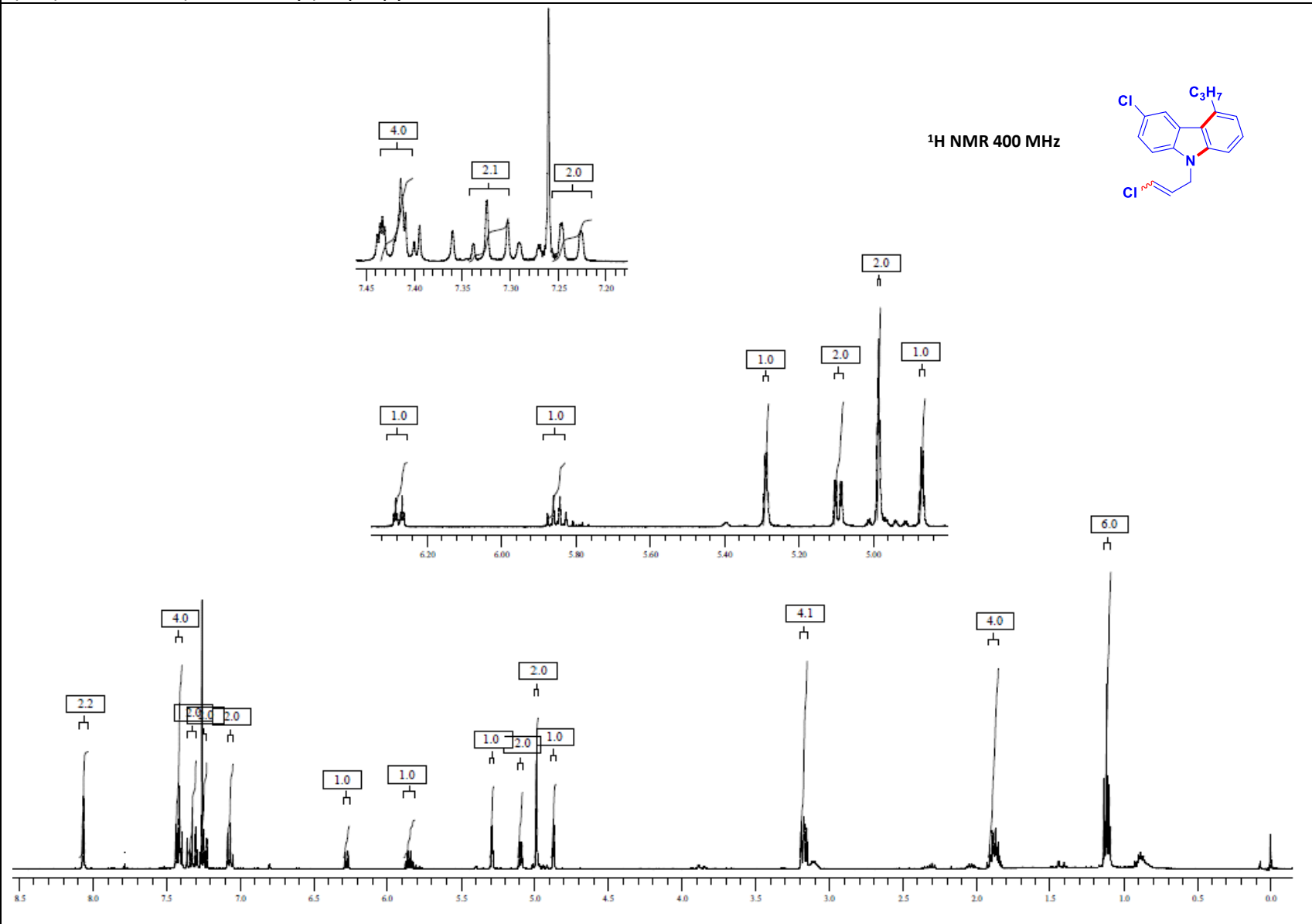


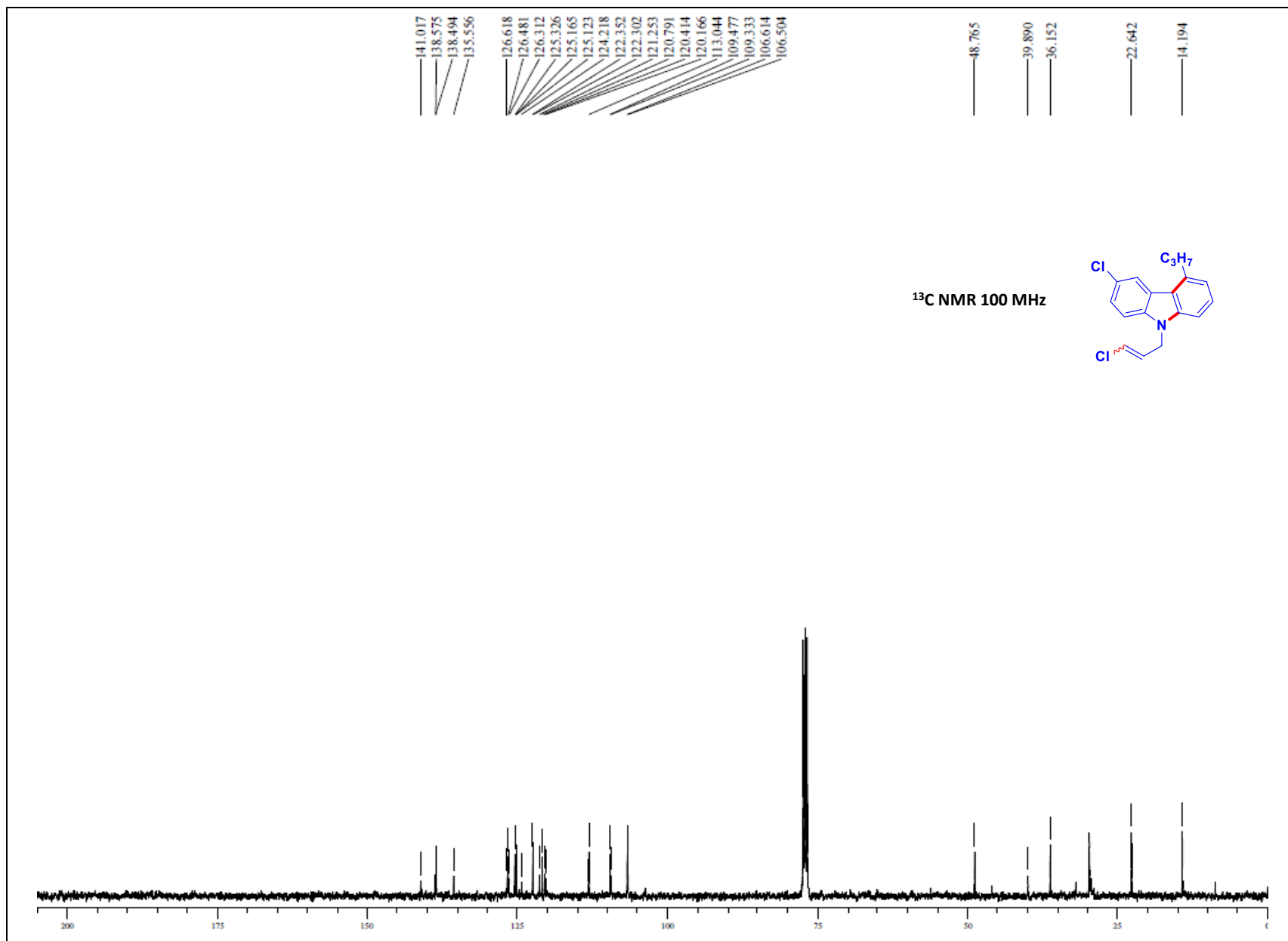
(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-(4-methoxyphenyl)-9*H*-carbazole 2k

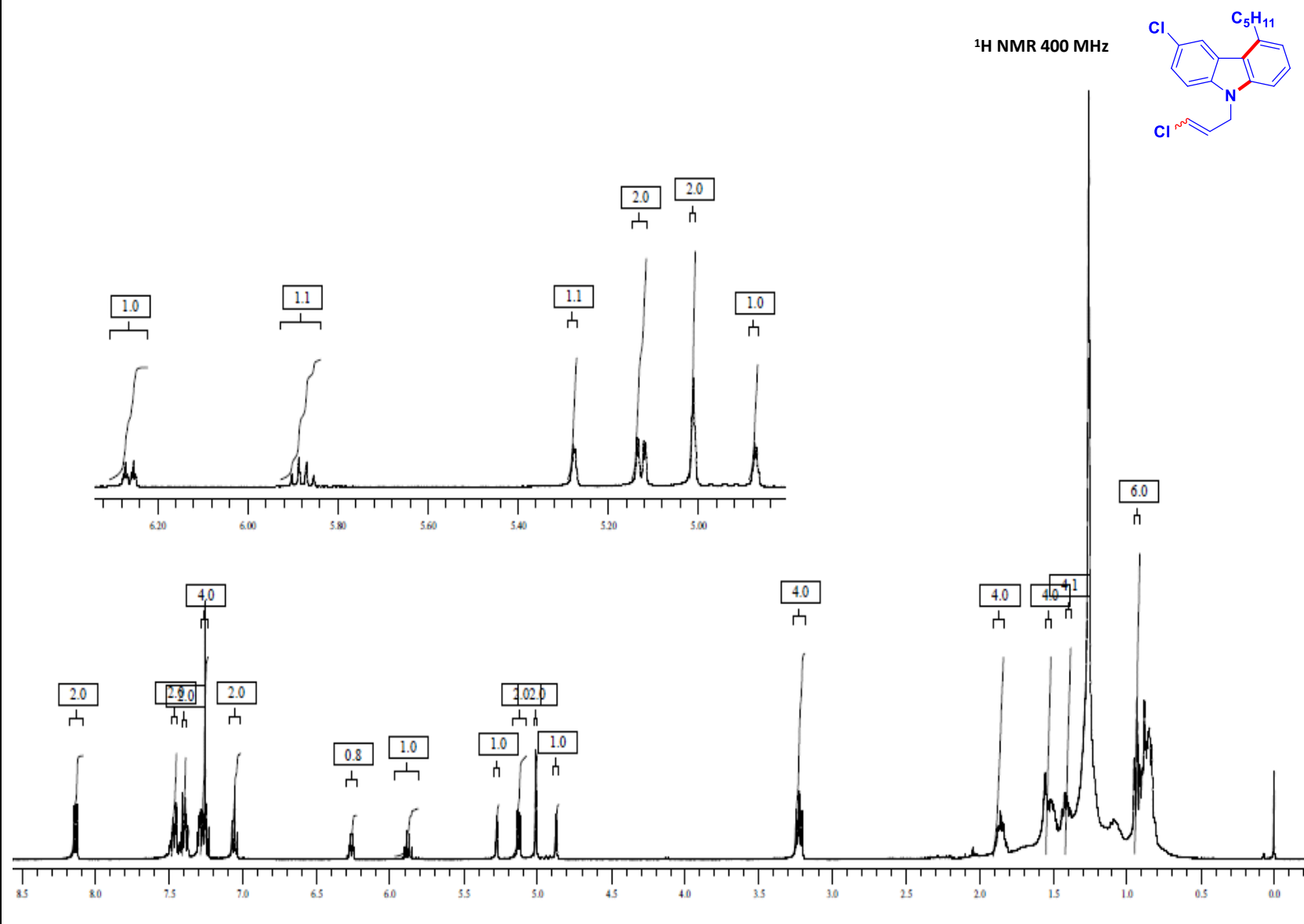


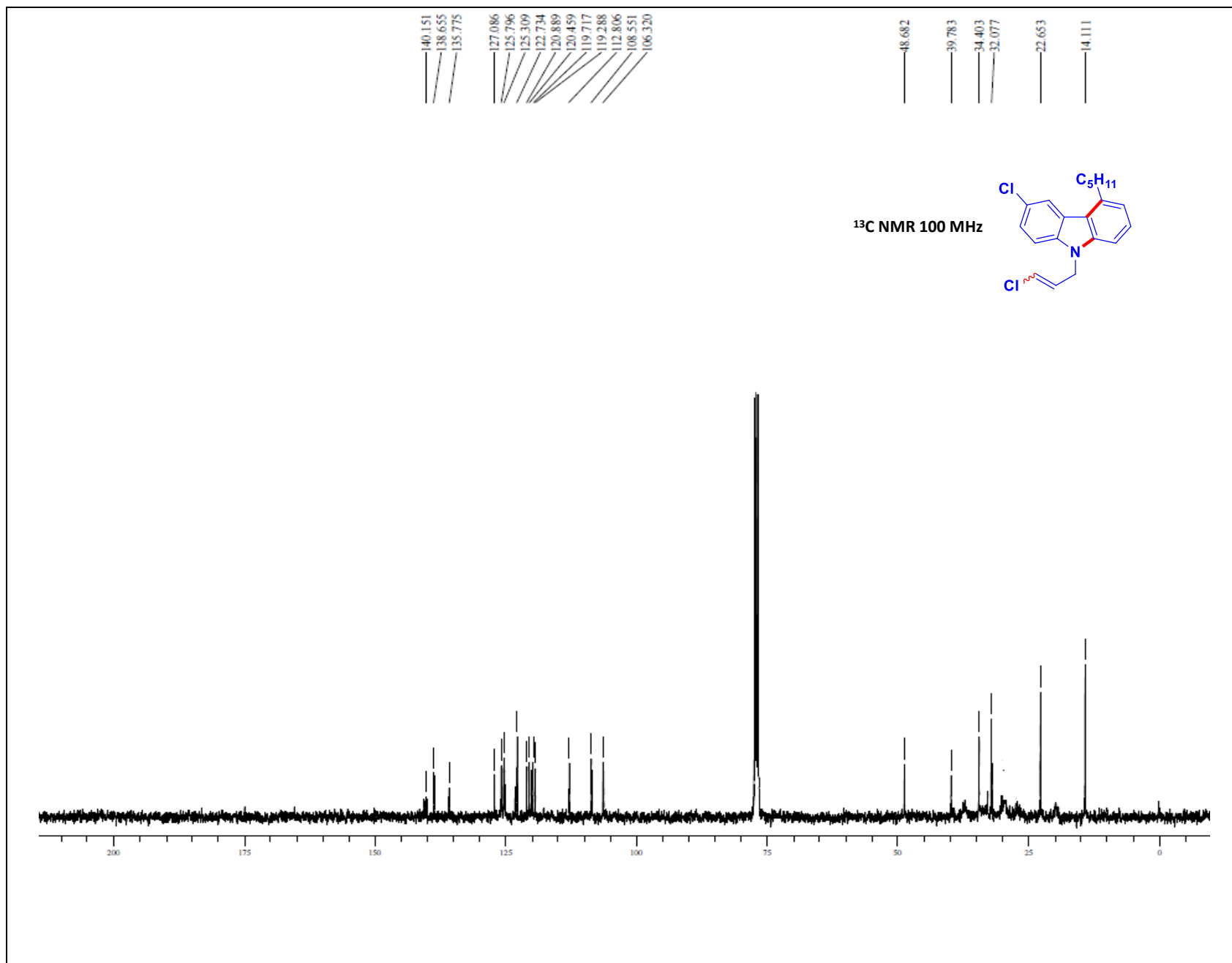
(E/Z) 3-Chloro-9-(3-chloroallyl)-5-(4-fluorophenyl)-9H-carbazole 2I

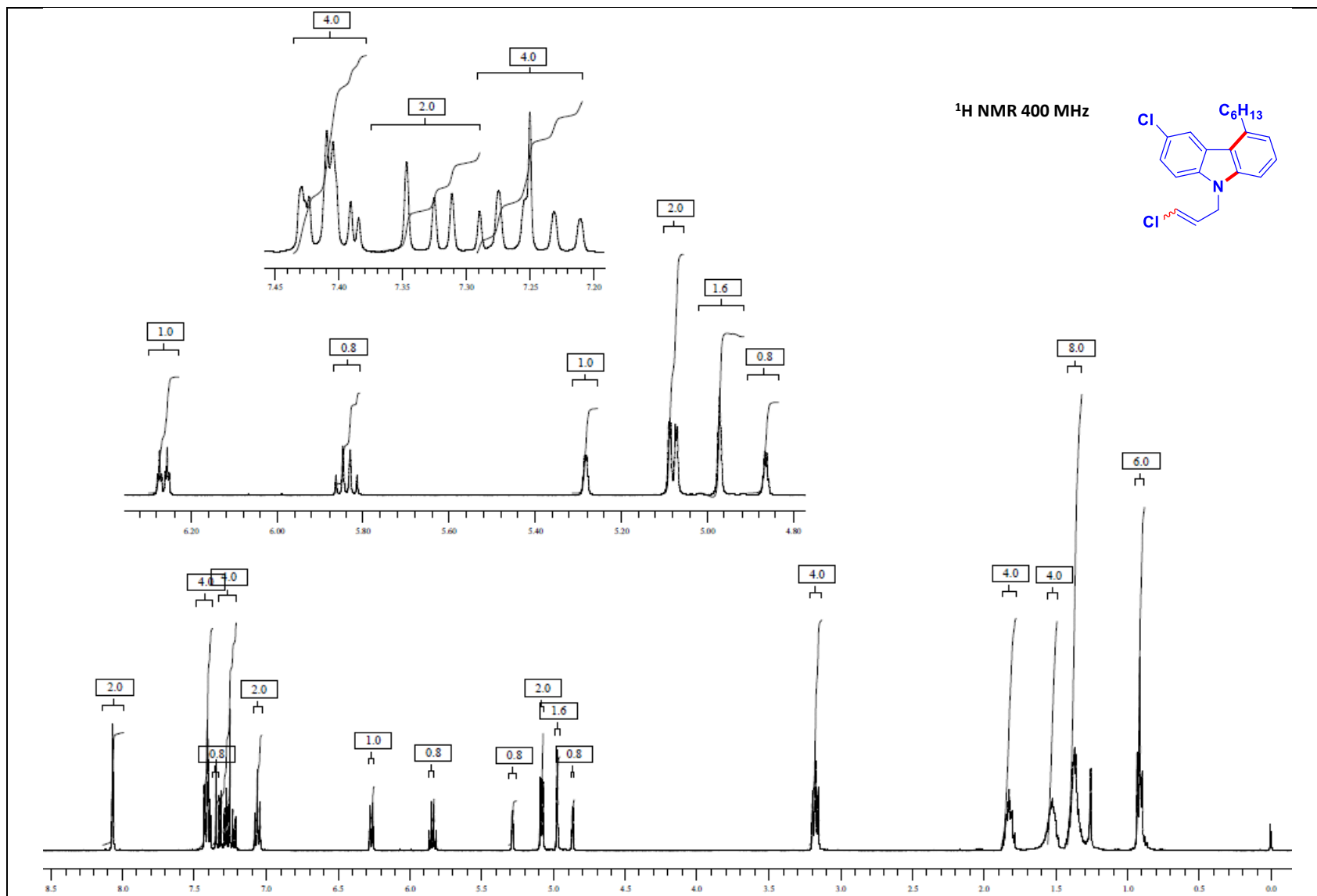


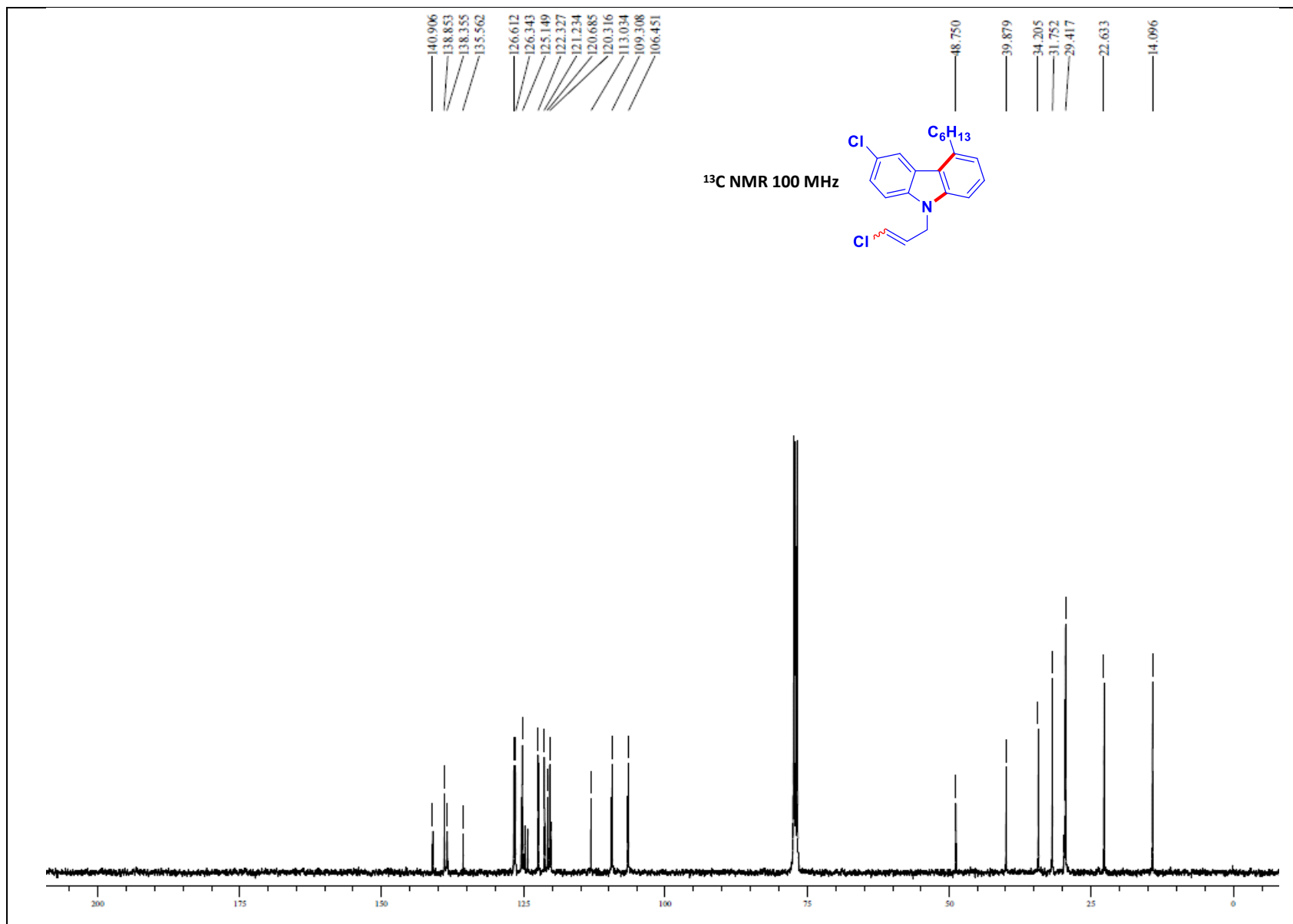
(E/Z) 3-Chloro-9-(3-chloroallyl)-5-propyl-9H-carbazole 2m

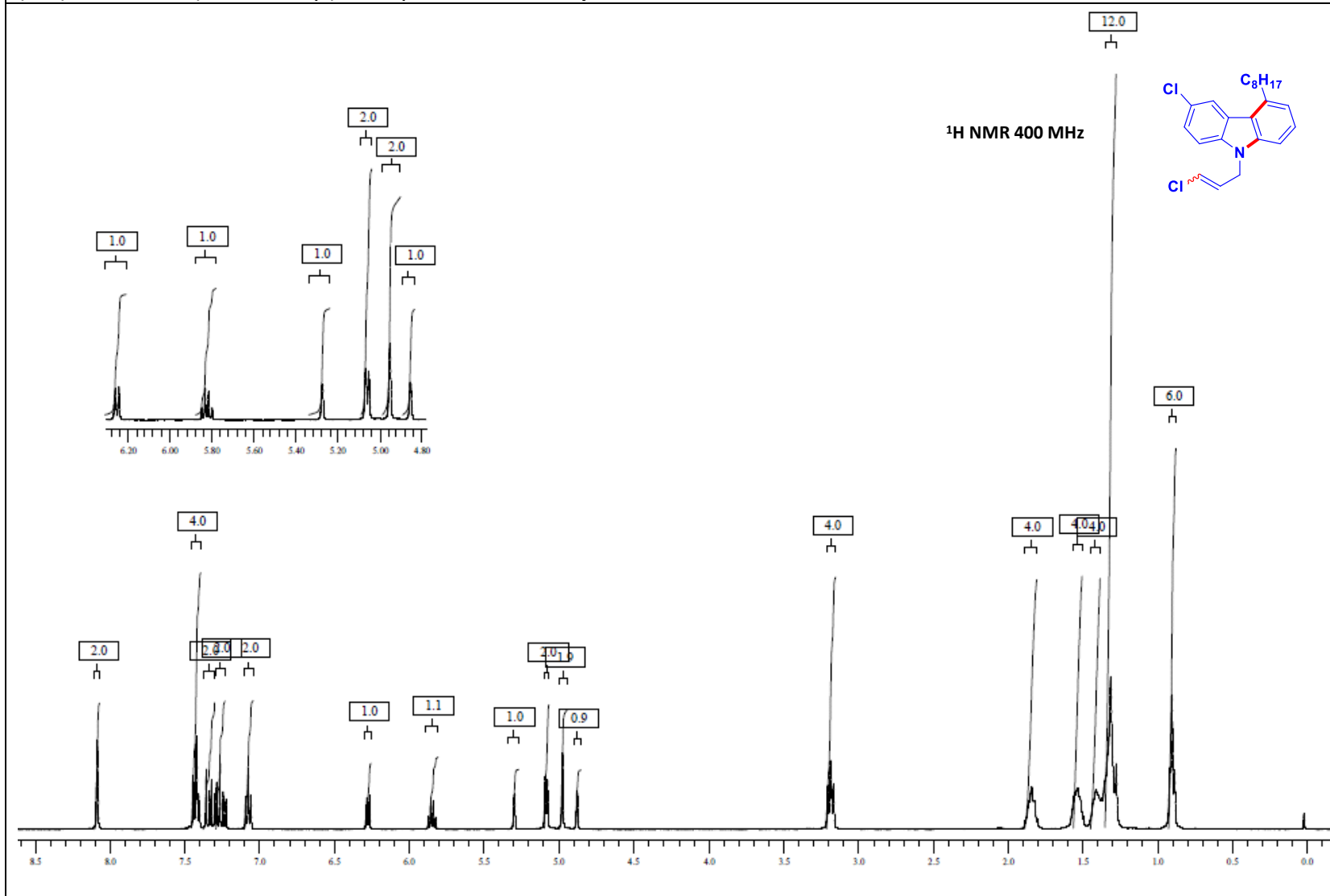


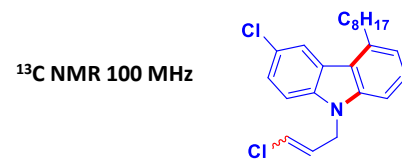
(E/Z) 3-Chloro-9-(3-chloroallyl)-5-pentyl-9H-carbazole 2n

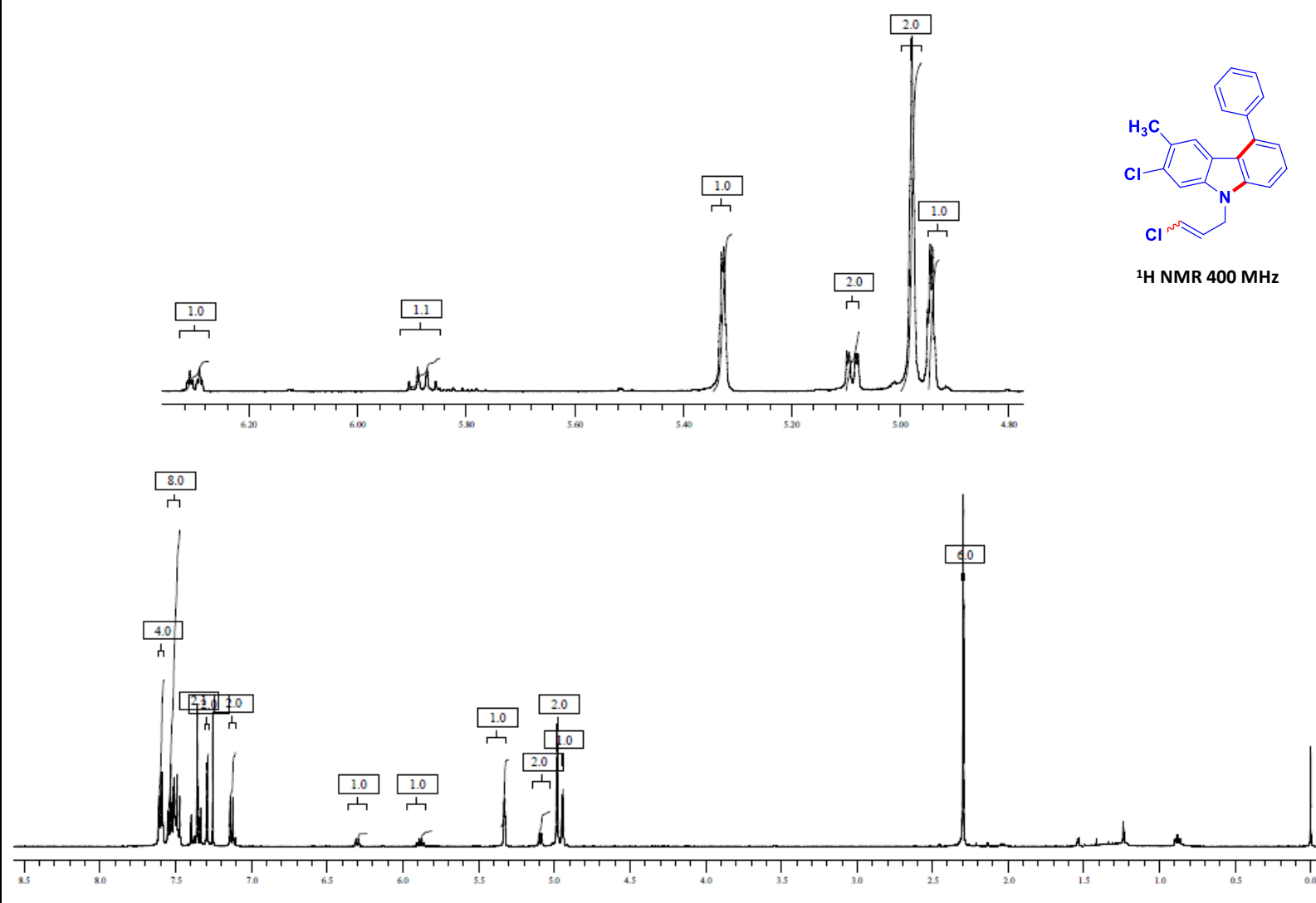


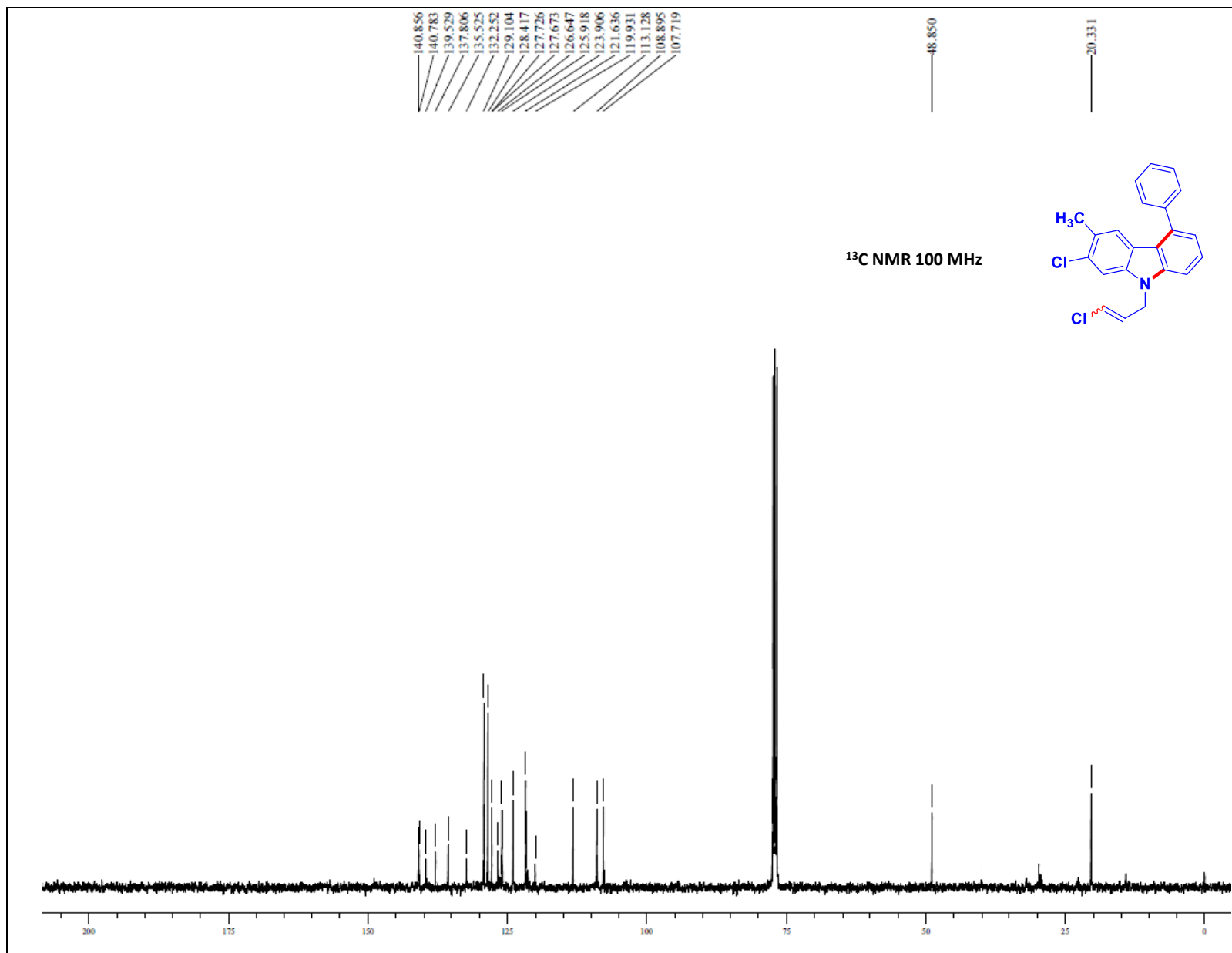




(*E/Z*) 3-Chloro-9-(3-chloroallyl)-5-octyl-9*H*-carbazole **2p**



(E/Z) 2-Chloro-9-(3-chloroallyl)-3-methyl-5-phenyl-9H-carbazole 2q

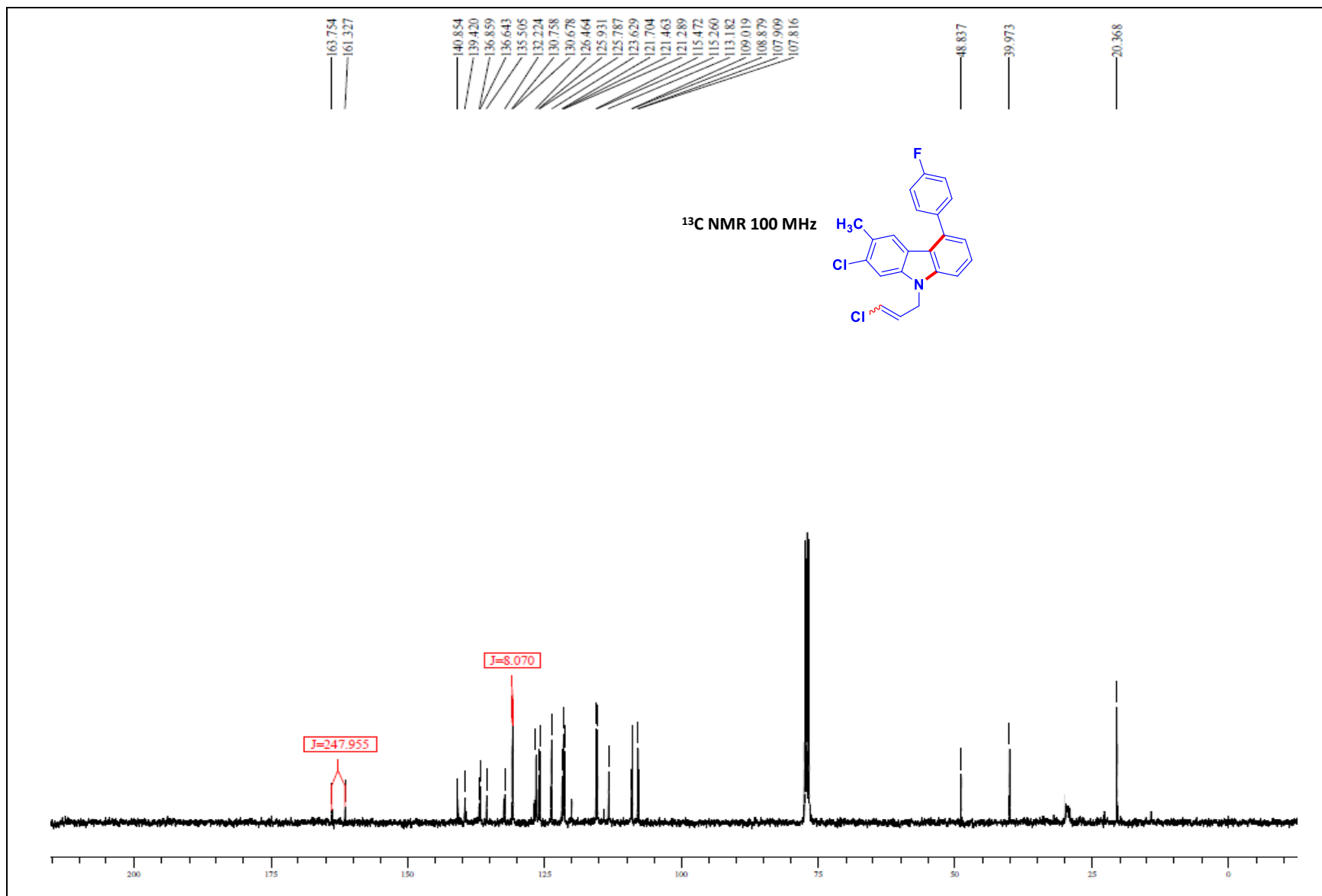


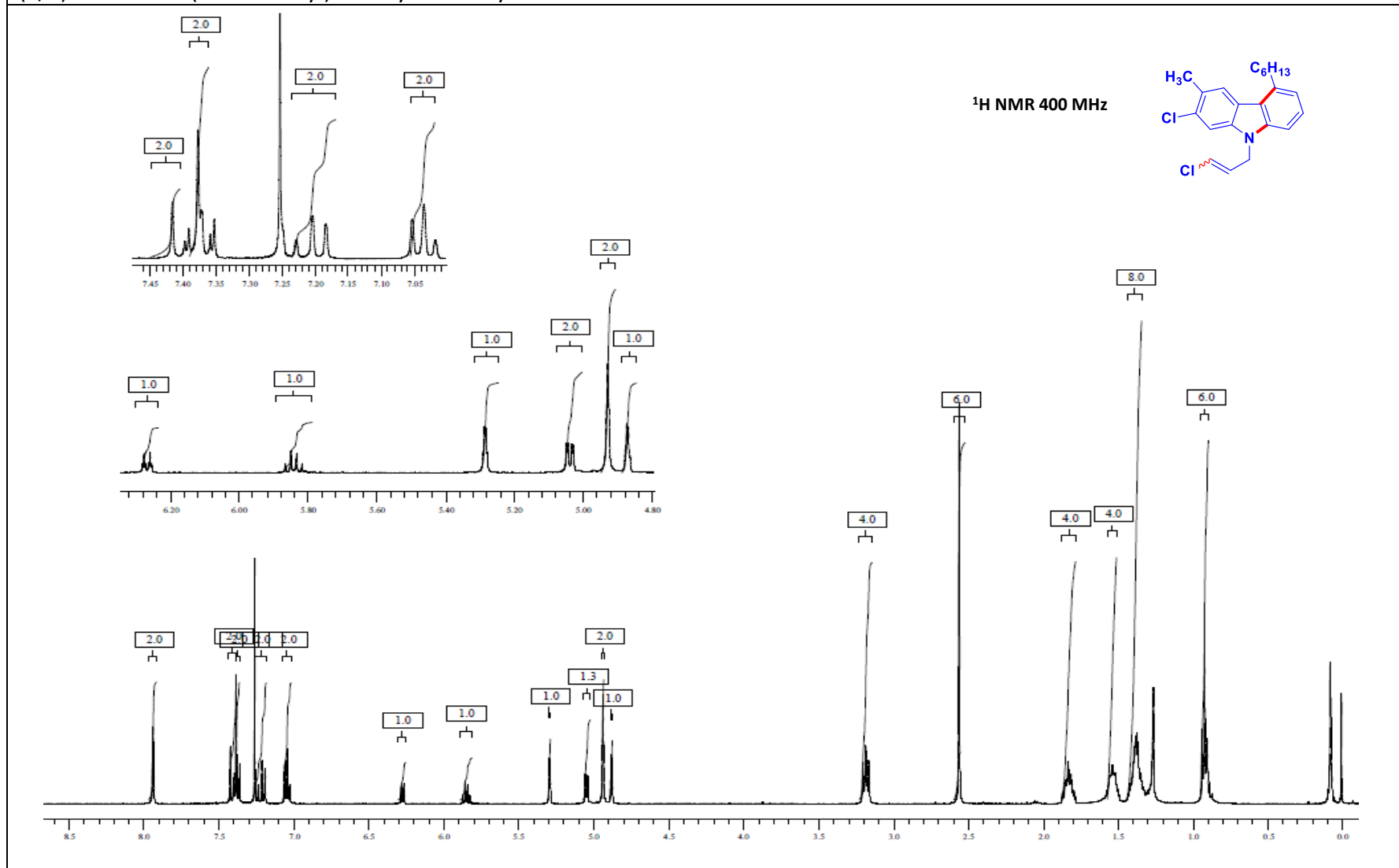
¹H NMR 400 MHz

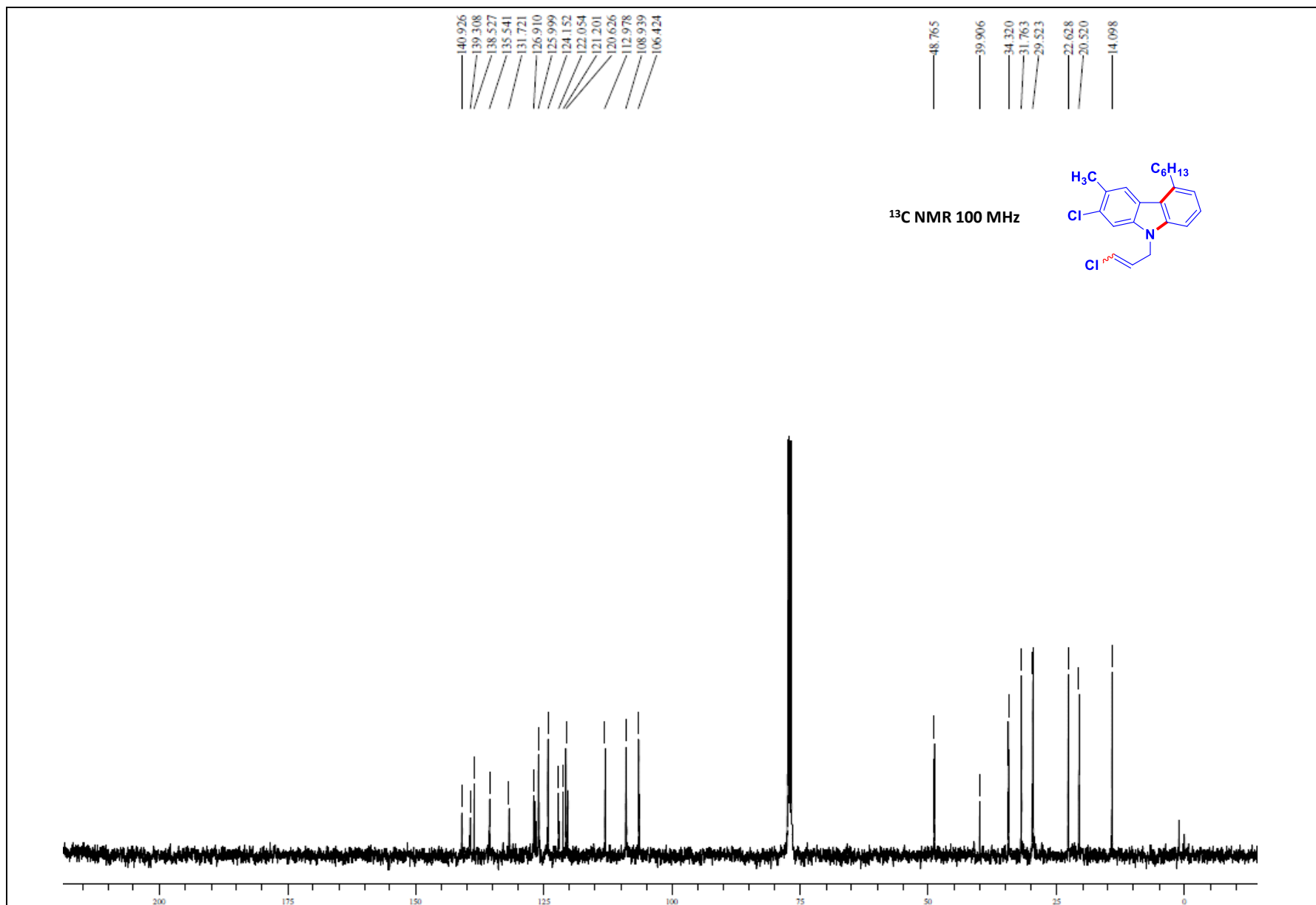
Chemical structure of compound 10 is shown in the inset. The structure is a 4-fluorophenyl-substituted indole derivative. The indole ring is substituted at the 2-position with a 2-chloro-3-methyl-5-(chloromethyl)phenyl group. The structure is labeled with H_3C , Cl , and F .

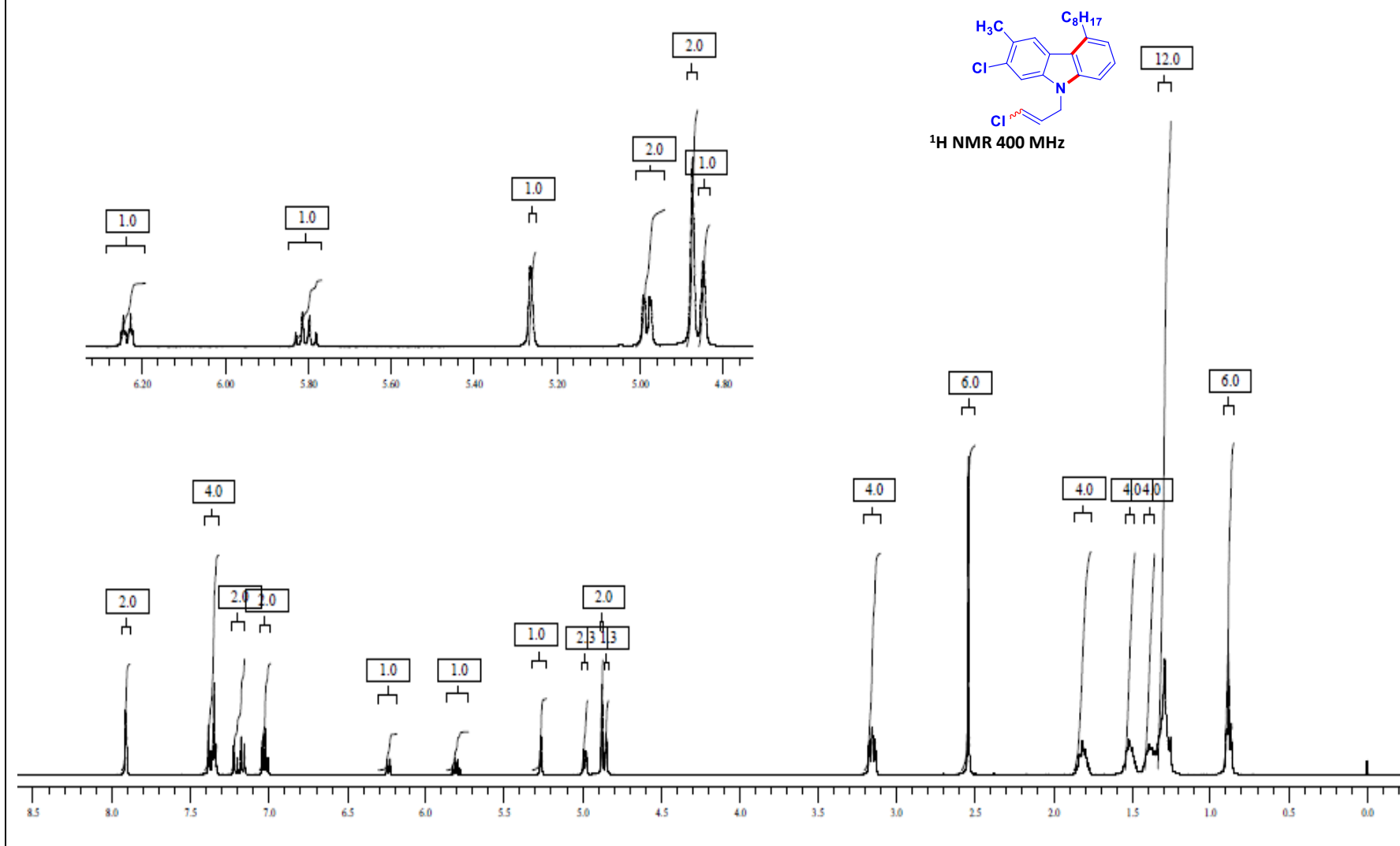
The ¹H NMR spectrum (400 MHz) shows the following peaks and integrations:

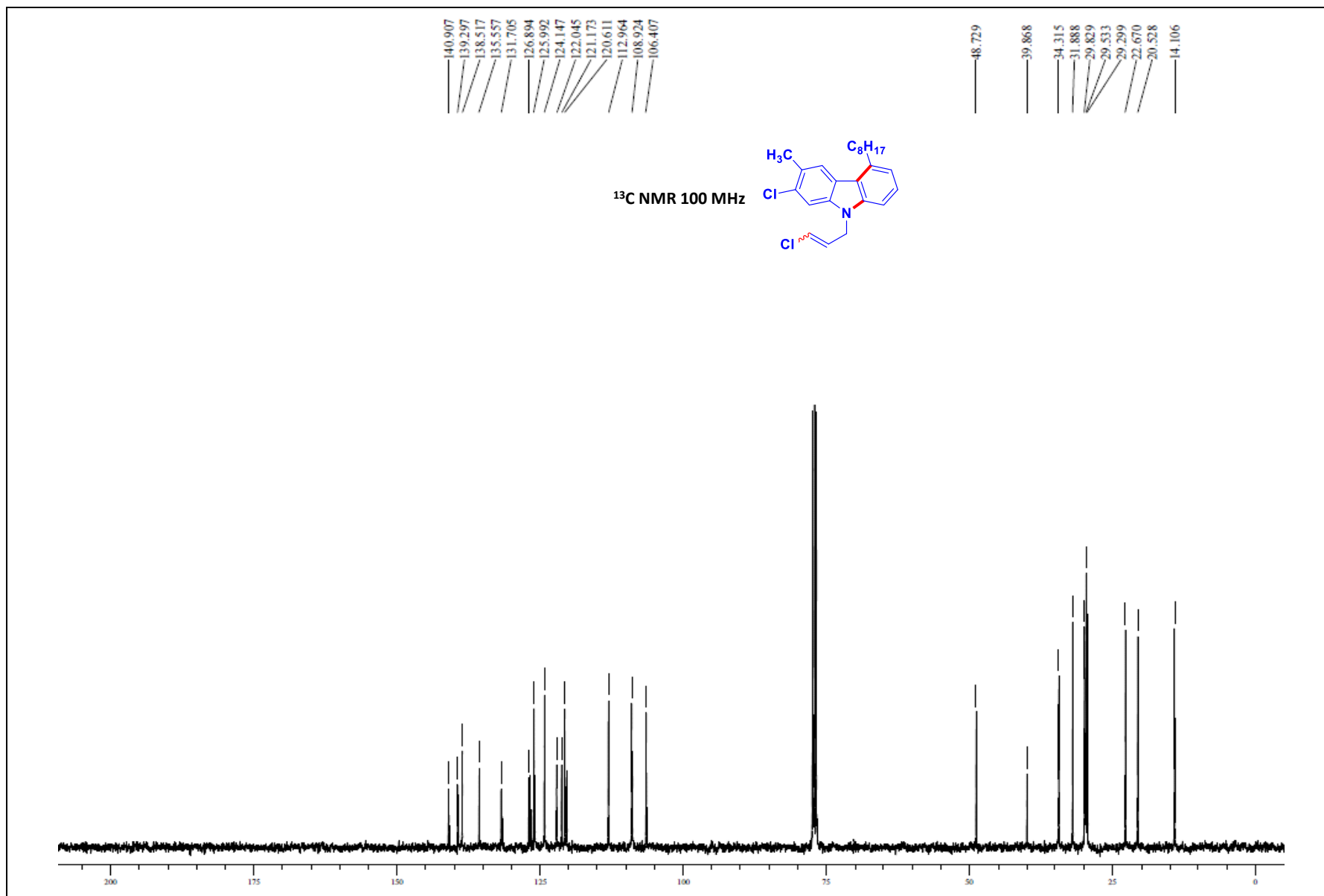
- 7.55 (d, 4H, integration 4.0)
- 7.45 (m, 2H, integration 2.0)
- 7.40 (d, 2H, integration 2.0)
- 7.35 (m, 2H, integration 2.0)
- 7.25 (m, 2H, integration 2.0)
- 7.15 (m, 2H, integration 2.0)
- 6.35 (d, 1H, integration 1.0)
- 5.85 (d, 1H, integration 1.0)
- 5.35 (s, 1H, integration 0.9)
- 3.45 (d, 2H, integration 2.0)
- 3.35 (d, 2H, integration 2.0)
- 3.25 (m, 1H, integration 1.0)
- 2.35 (s, 3H, integration 3.0)
- 2.25 (s, 3H, integration 3.0)
- 0.0 (TMS, 3H, integration 3.0)



(*E/Z*) 2-Chloro-9-(3-chloroallyl)-5-hexyl-3-methyl-9*H*-carbazole 2s



(E/Z) 2-Chloro-9-(3-chloroallyl)-3-methyl-5-octyl-9H-carbazole 2t



X-ray crystallography data of compound 2a.

X-ray data for the compound KA243 was collected on a Bruker D8 QUEST instrument with an I μ S Mo microsource ($\lambda = 0.7107$ Å) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs.^[1] The structure was solved using intrinsic phasing method ^[2] and further refined with the SHELXL ^[2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound 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].

Crystal Data (2a) for KA243: C₂₁H₁₆NCl ($M = 317.80$ g/mol): monoclinic, space group P2₁/n (no. 14), $a = 8.62390(10)$ Å, $b = 18.6051(2)$ Å, $c = 10.17690(10)$ Å, $\beta = 96.7420(5)^\circ$, $V = 1621.58(3)$ Å³, $Z = 4$, $T = 294.15$ K, $\mu(\text{MoK}\alpha) = 0.234$ mm⁻¹, $D_{calc} = 1.302$ g/cm³, 19135 reflections measured ($4.378^\circ \leq 2\theta \leq 52.498^\circ$), 3277 unique ($R_{int} = 0.0309$, $R_{sigma} = 0.0231$) which were used in all calculations. The final R_1 was 0.0415 ($I > 2\sigma(I)$) and wR_2 was 0.1267 (all data). CCDC1877690 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]

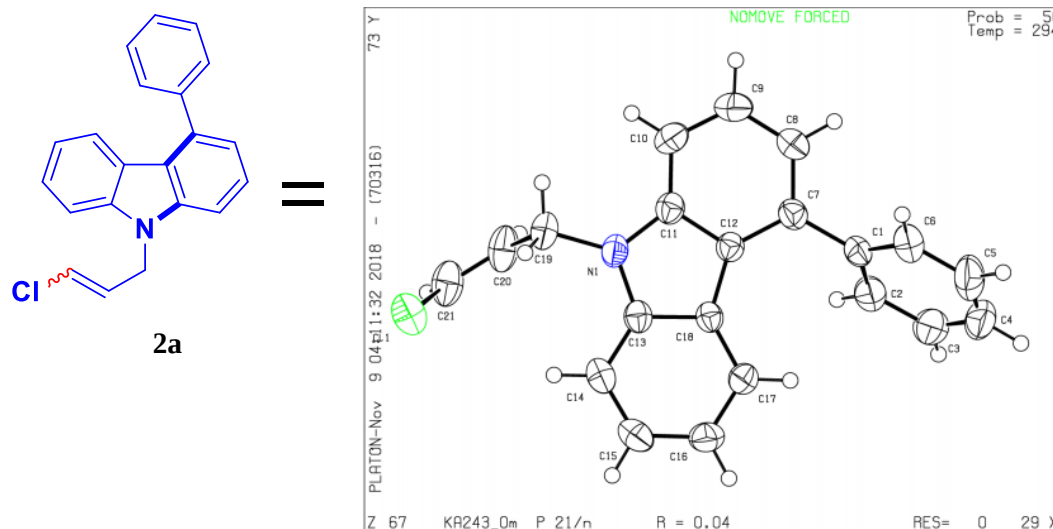


Fig. 1. A view of **2a**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) Acta Crystallogr C71:3-8.