Supporting Information

Copper-catalyzed cascade click/nucleophilic substitution reaction to access fully substituted triazolyl-organosulfurs

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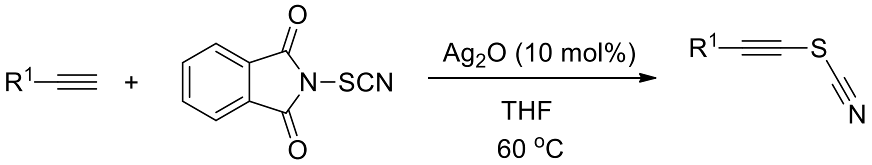
1. General Remarks

Unless otherwise noted, all commercially available reagents and solvents were used without further additional purification. Thin layer chromatography was performed using precoated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40-60 μm). ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on a Bruker Avance II 400 MHz or Bruker Avance III 500 MHz recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$ unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet(t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (*J*) in hertz (Hz). High resolution mass spectra (HRMS) were performed by an Agilent apparatus (TOF mass analyzer type) on an Electron Spray Injection (ESI) mass spectrometer. Melting points were determined by an XP-4 melting point apparatus.

2. General procedure for the preparation of substrates:

2.1 Preparation of internal thiocyanatoalkynes

Following a slight modification of the literature procedure.[S1]

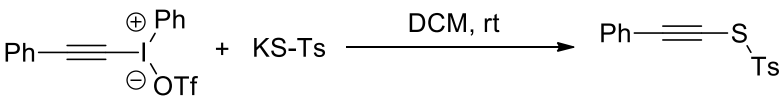


To a stirred solution of terminal alkyne (1 equiv, 1 mmol) and Ag_2O (10 mol%) in anhydrous THF (1.5 mL) was added *N*-thiocyanophthalimide (1.2 equiv, 1.2 mmol). The reaction mixture was stirred at 60 °C overnight. When the reaction was completed as determined by TLC, the mixture was quenched with water (2 mL) and then extracted with Et_2O (3×2 mL). The organic phase was washed by brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification of the residue by column chromatography gave the corresponding internal thiocyanatoalkyne.

All substrates **1a-1q** were prepared by the similar procedure.

2.2 Preparation of internal 1-alkynyl thiotosylate

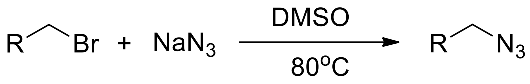
Following a slight modification of the literature procedure.[S2]



To a stirred solution of alkynyl(phenyl)iodonium triflate (1 equiv, 1 mmol) in anhydrous DCM (5 mL) was added potassium *p*-toluenethiosulfonate (1 equiv, 1 mmol). The reaction mixture was stirred at rt overnight. When the reaction was completed as determined by TLC, the mixture was quenched with water (5 mL) and then extracted with Et_2O (3×5 mL). The organic phase was washed by brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification of the residue by column chromatography gave the corresponding internal 1-alkynyl thiotosylate **1'** in 50% yield.

2.3 Preparation of azides[S3]

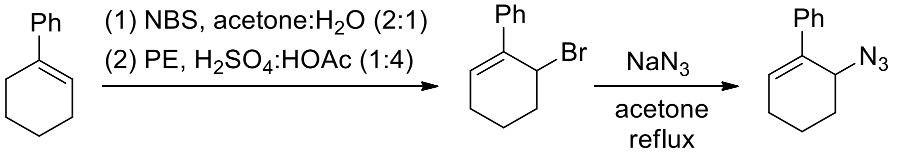
For the preparation of azides **2j**, **2k**, **2l, 2p, 2q** and **2r**
Following a slight modification of the literature procedure.[S3]



To a stirred solution of NaN_3 (71.5 mg, 1.1 mmol) in DMSO (2 mL) was added bromoalkane (1 mmol). The reaction mixture was stirred at 80 °C overnight. Then the reaction mixture was cooled to room temperature and diluted with water (5 mL). The mixture was extracted with ether (3×5 mL) and washed by brine, dried over Na_2SO_4 and concentrated under vacuum to give the products in quantitative yields. It was used directly without further purification.

2s was prepared following the Pericàs's and Smith's procedure.[S4]

For the preparation of azide **2m**
Following a slight modification of the literature procedure.[S5]



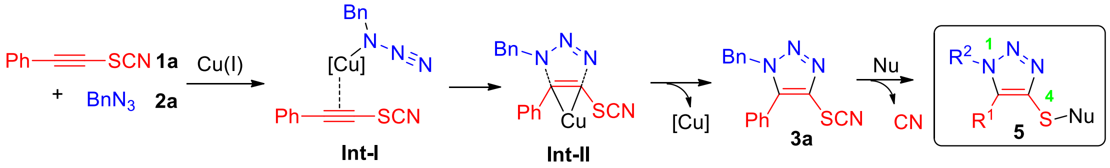
To a stirred solution of 1-phenylcyclohexene (132 mg, 0.7 mmol) in acetone (4 mL) and water (2 mL) was added NBS (125 mg, 0.7 mmol) portionwise in 0 °C. The reaction mixture was stirred for 2 h. Then the reaction mixture was extracted with PE (3×5 mL) and washed by brine, dried over Na_2SO_4 and concentrated under vacuum to give the product used directly in the next step without further purification.

To a stirred solution of above crude bromohydrin in PE (1 mL) was added sulfuric acid solution (1.8 mL, 20% v/v in HOAc) in 0 °C. The reaction mixture was stirred for 10 min. Then the reaction mixture was quenched by ice water and extracted with PE (3×3 mL) and washed by brine, dried over Na_2SO_4 and concentrated under vacuum to give the product used directly in the next step without further purification.

To a stirred solution of above crude allylic bromide in acetone (6 mL) was added sodium azide solution (228 mg in 2 mL water). The reaction mixture was reflux for 1h. Then the reaction mixture was extracted with PE (3×6 mL) and washed by brine, dried over Na_2SO_4 and concentrated under vacuum to give the product **2m** in 61% isolated yield over 3 steps as a colorless oil.

All substrates are known compounds.
Products **5b** and **5h** are known coumpounds.[S6]

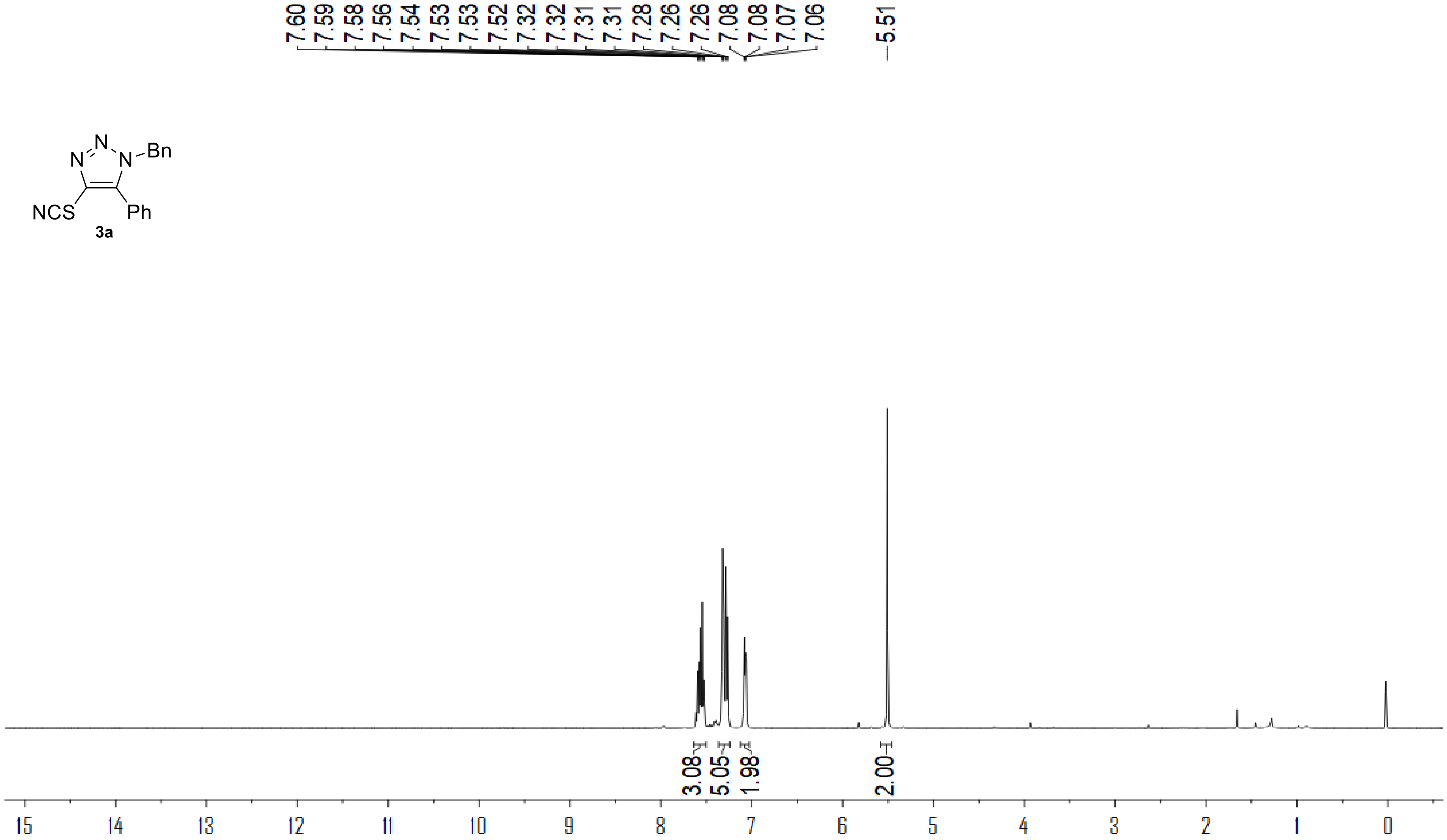
3. Proposed mechanism for the nucleophilic interrupted click reaction



4. Reference:

(S1) See, J. Y.; Zhao, Y. *Org. Lett.* **2018**, *20*, 7433.
(S2) Williamson, B. L.; Murch, P.; Fischer, D. R.; Stang, P. J. *Synlett*, **1993**, 858.
(S3) Xu, J.; Song, Q. *Org. Chem. Front.* **2017**, *4*, 938.
(S4) (a) Neyyappadath, R. M.; Chisholm, R.; Greenhalgh, M. D.; Rodríguez-Escrich, C.; Pericàs, M. A.; Hähner, G.; Smith, A. D. *ACS Catal.* **2018**, *8*, 1067. (b) Izquierdo, J.; Pericàs, M. A. *ACS Catal.* **2016**, *6*, 348–356. (c) Bastero, A.; Font, D.; Pericàs, M. A. *J. Org. Chem.* **2007**, *72*, 2460–2468.
(S5) Liu, E.-C.; Topczewski, J. J. *J. Am. Chem. Soc.* **2019**, *141*, 5135.
(S6) Huang, P.; Su, Q.; Dong, W.; Zhang, Y.; An. D.; *Tetrahedron*, **2017**, *73*, 4275.

5. NMR Spectra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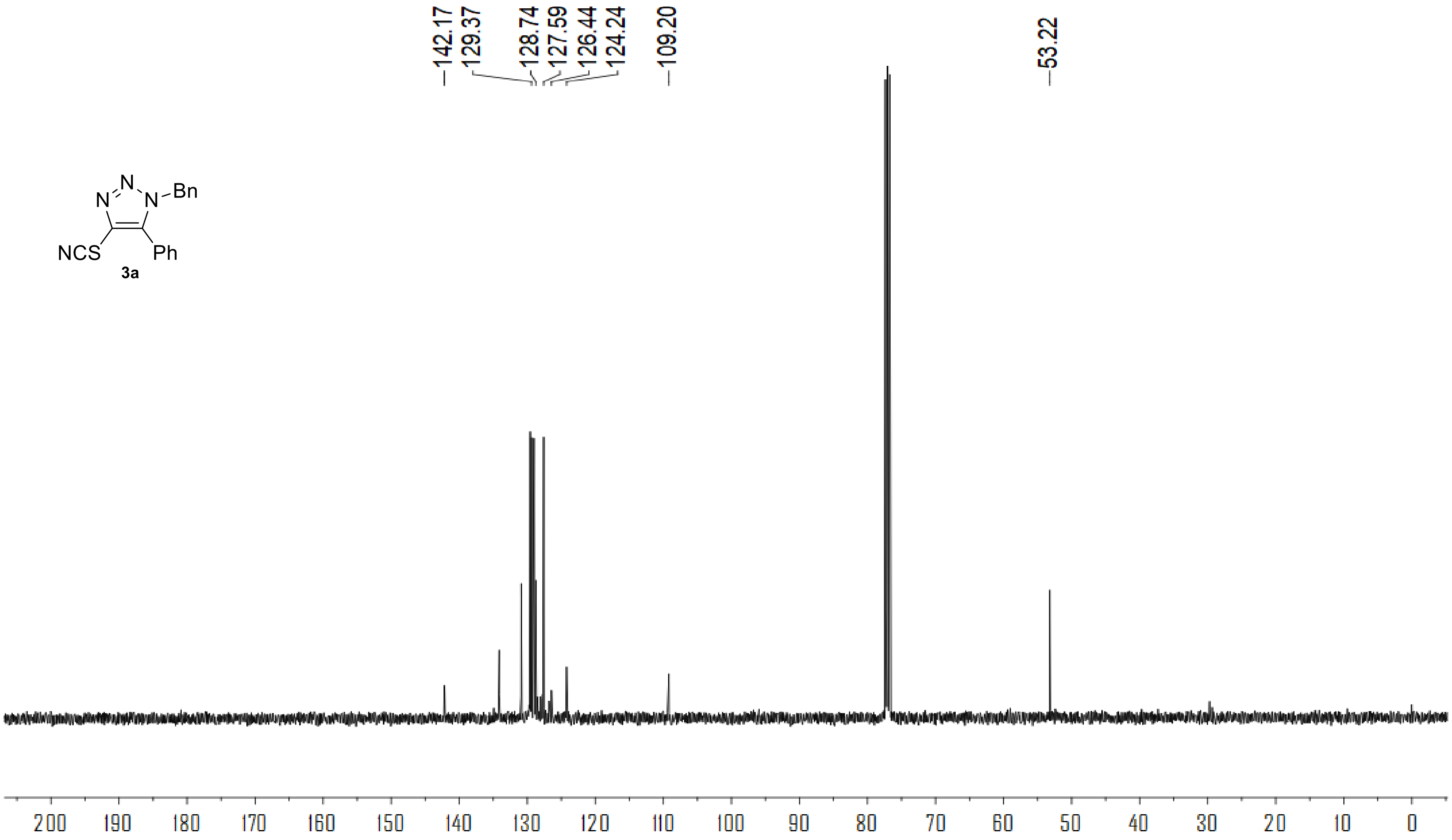

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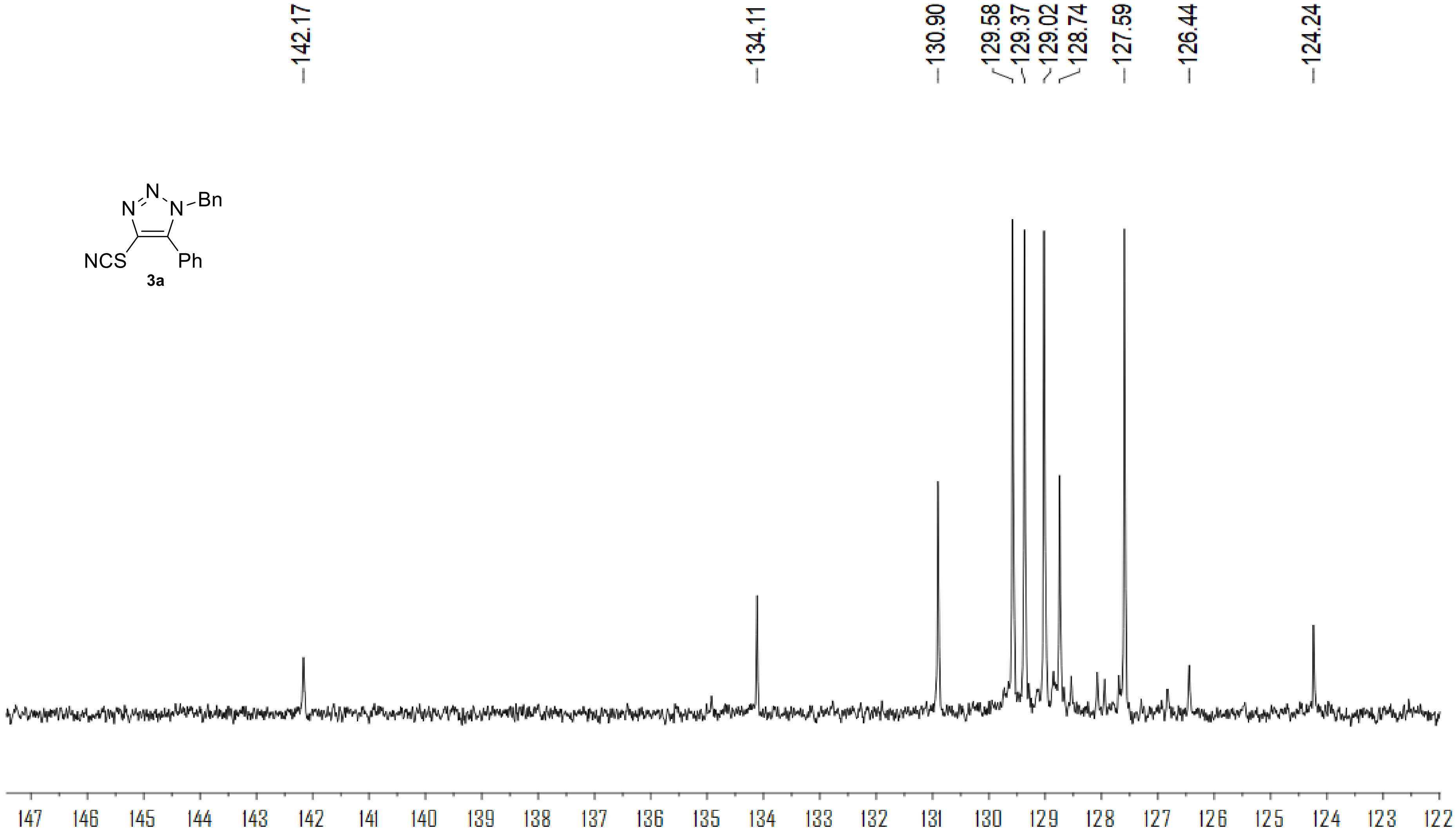
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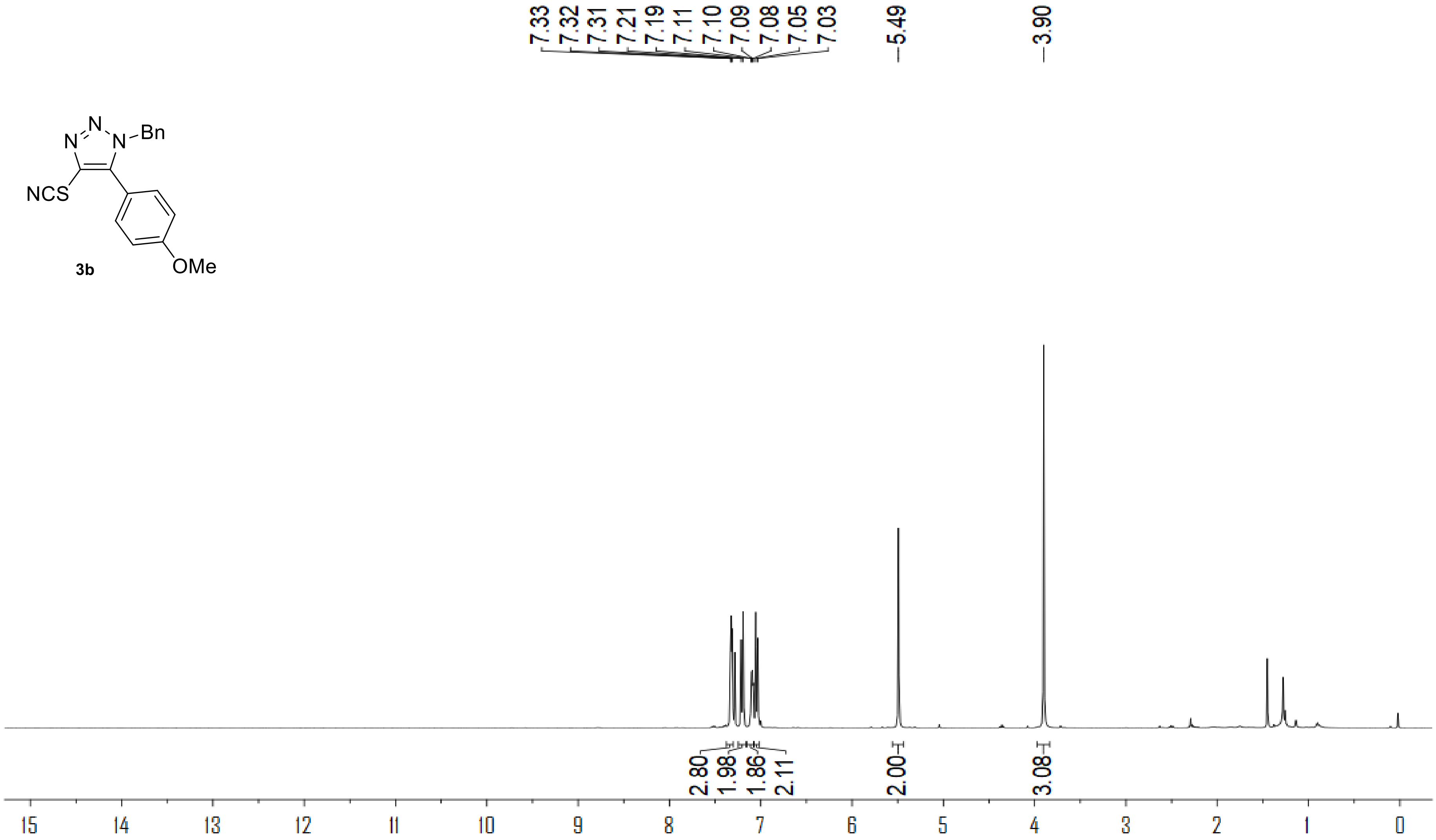
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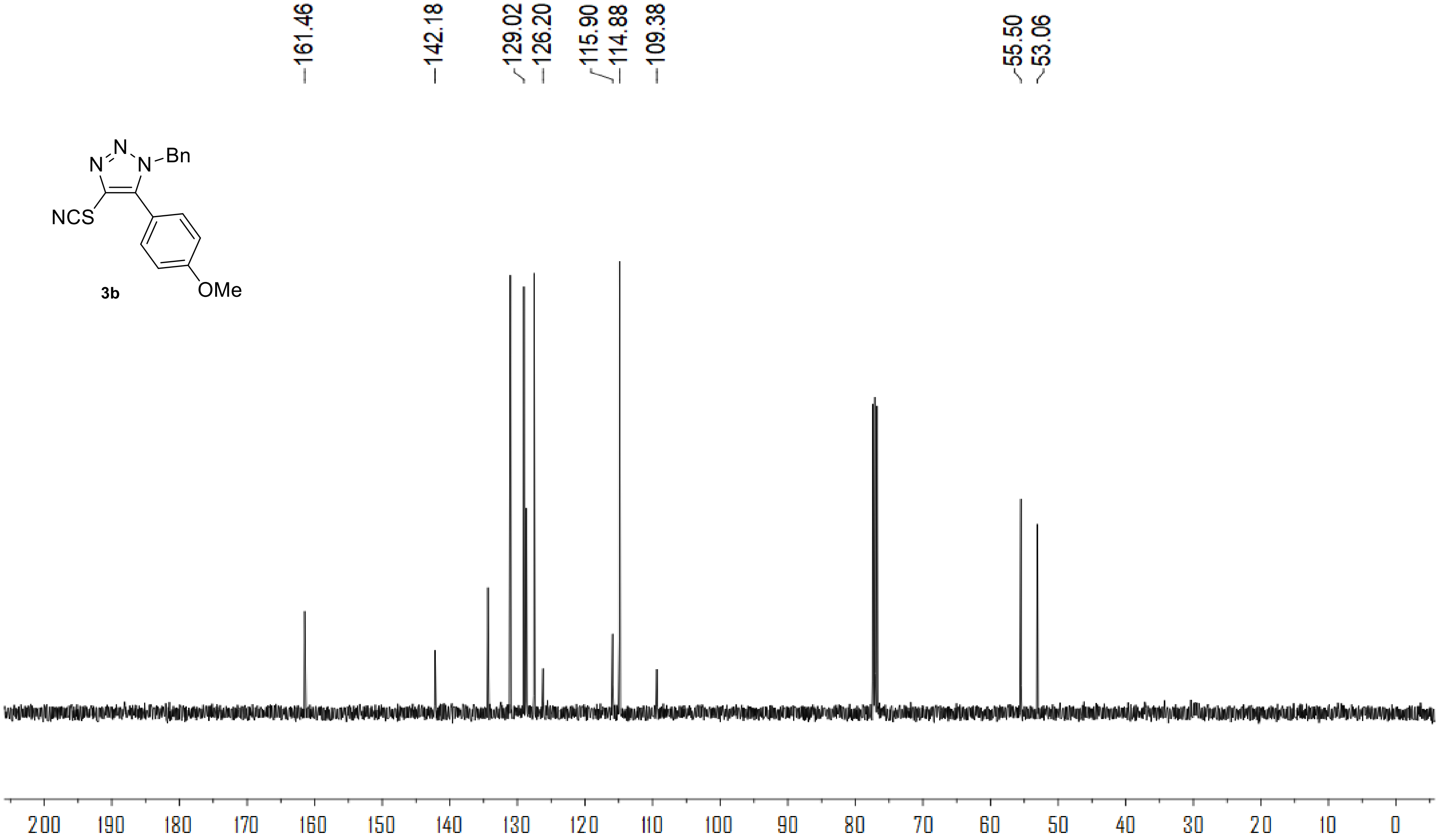
3b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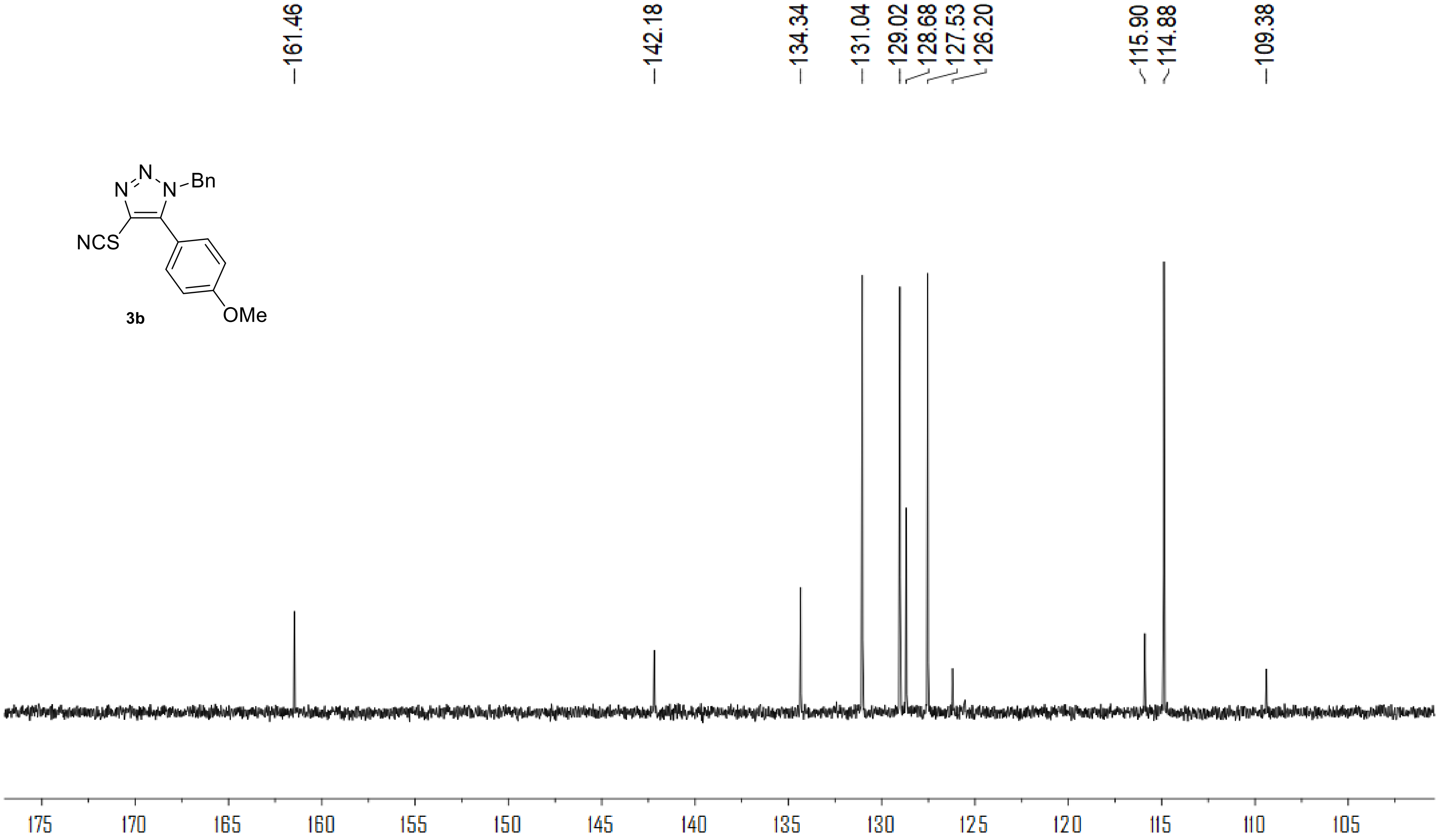
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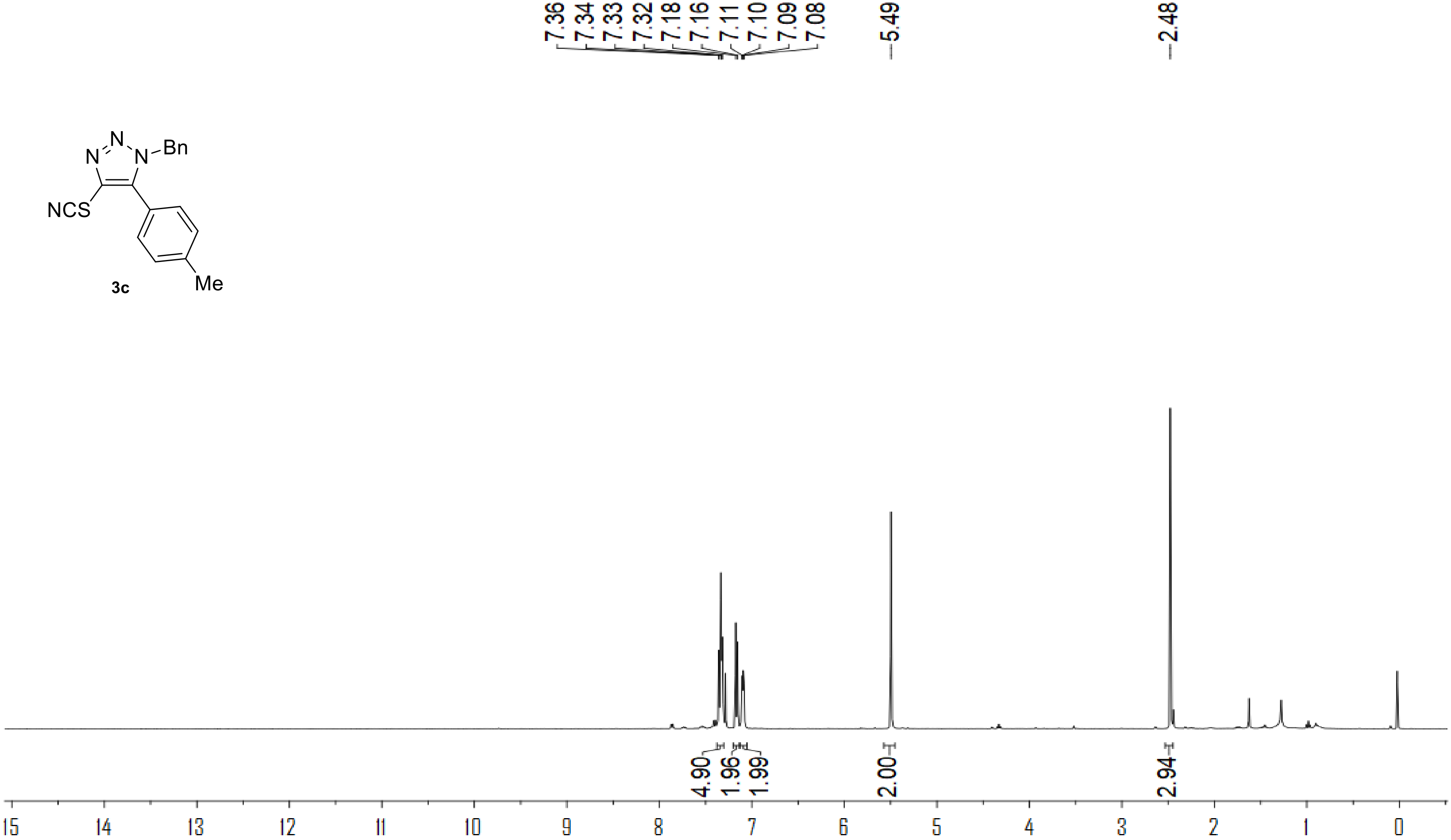
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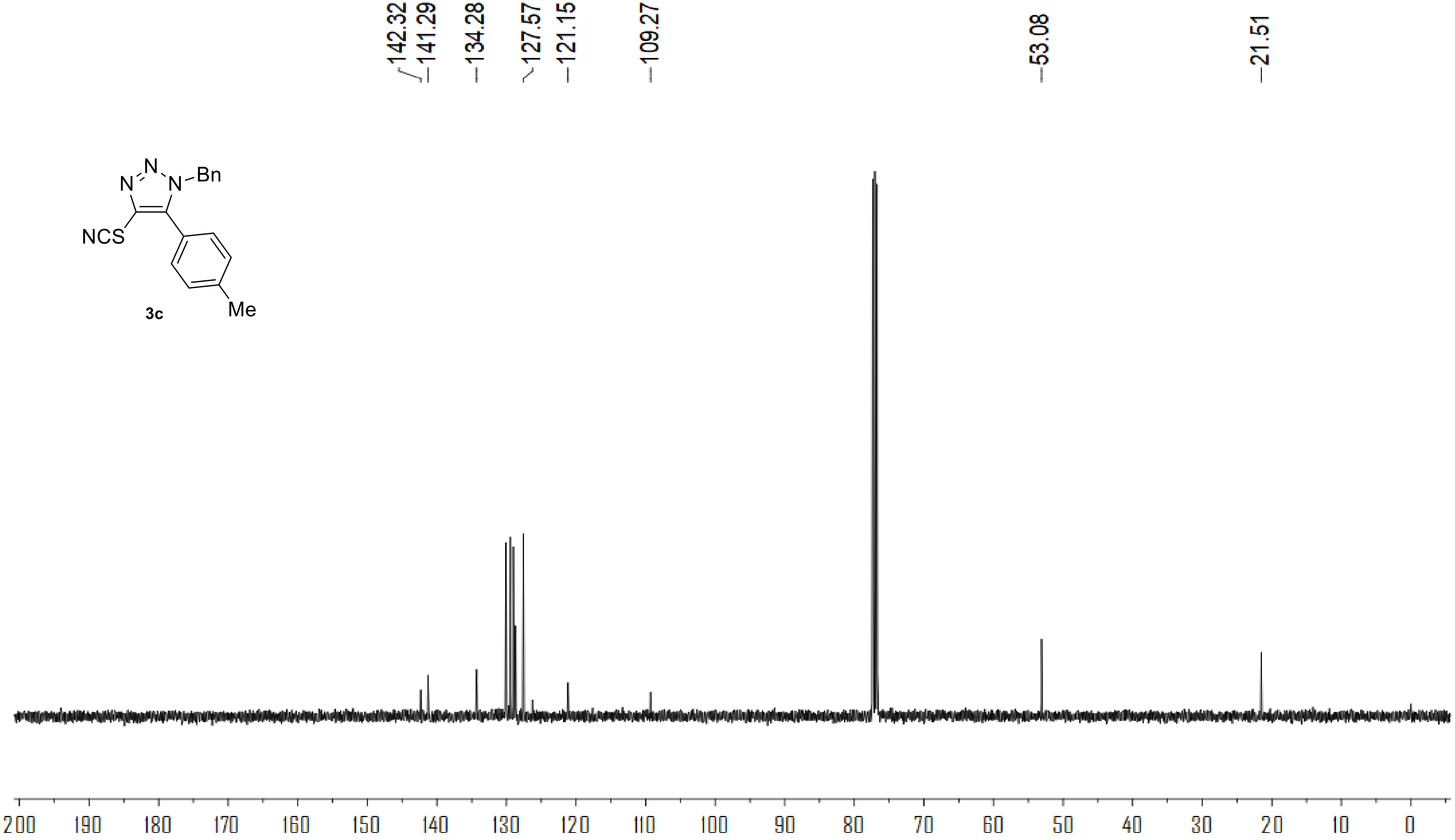
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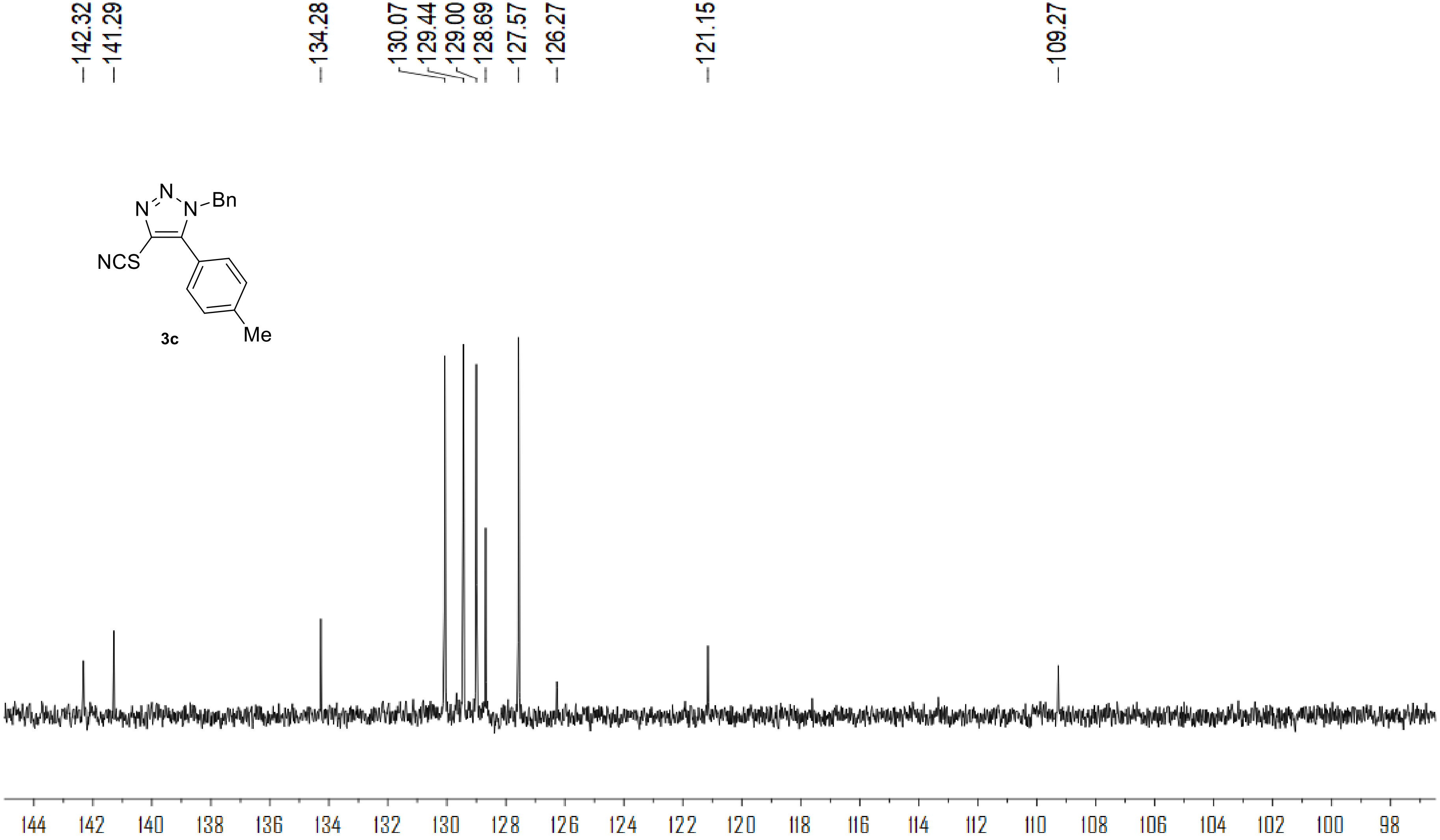
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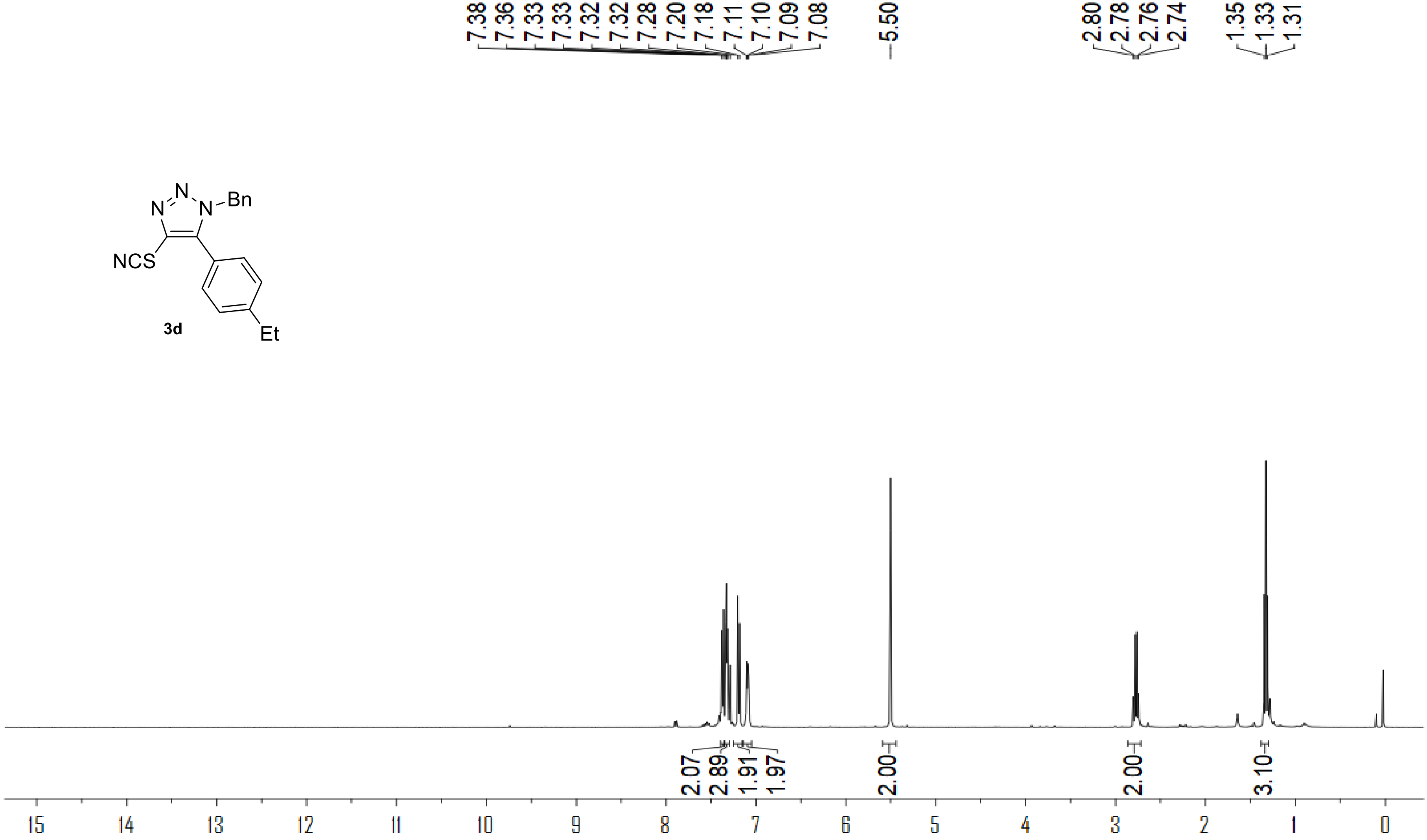

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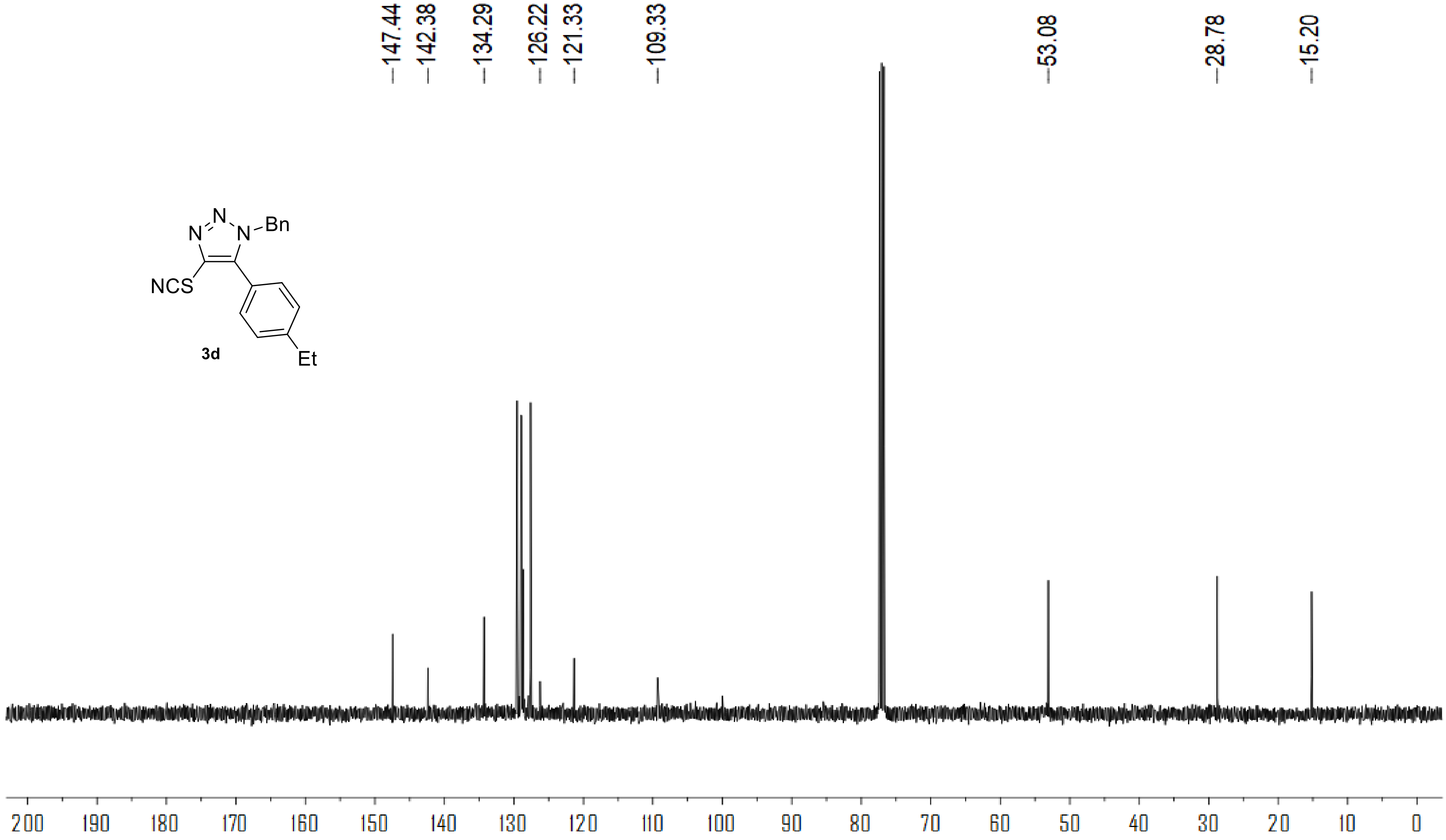
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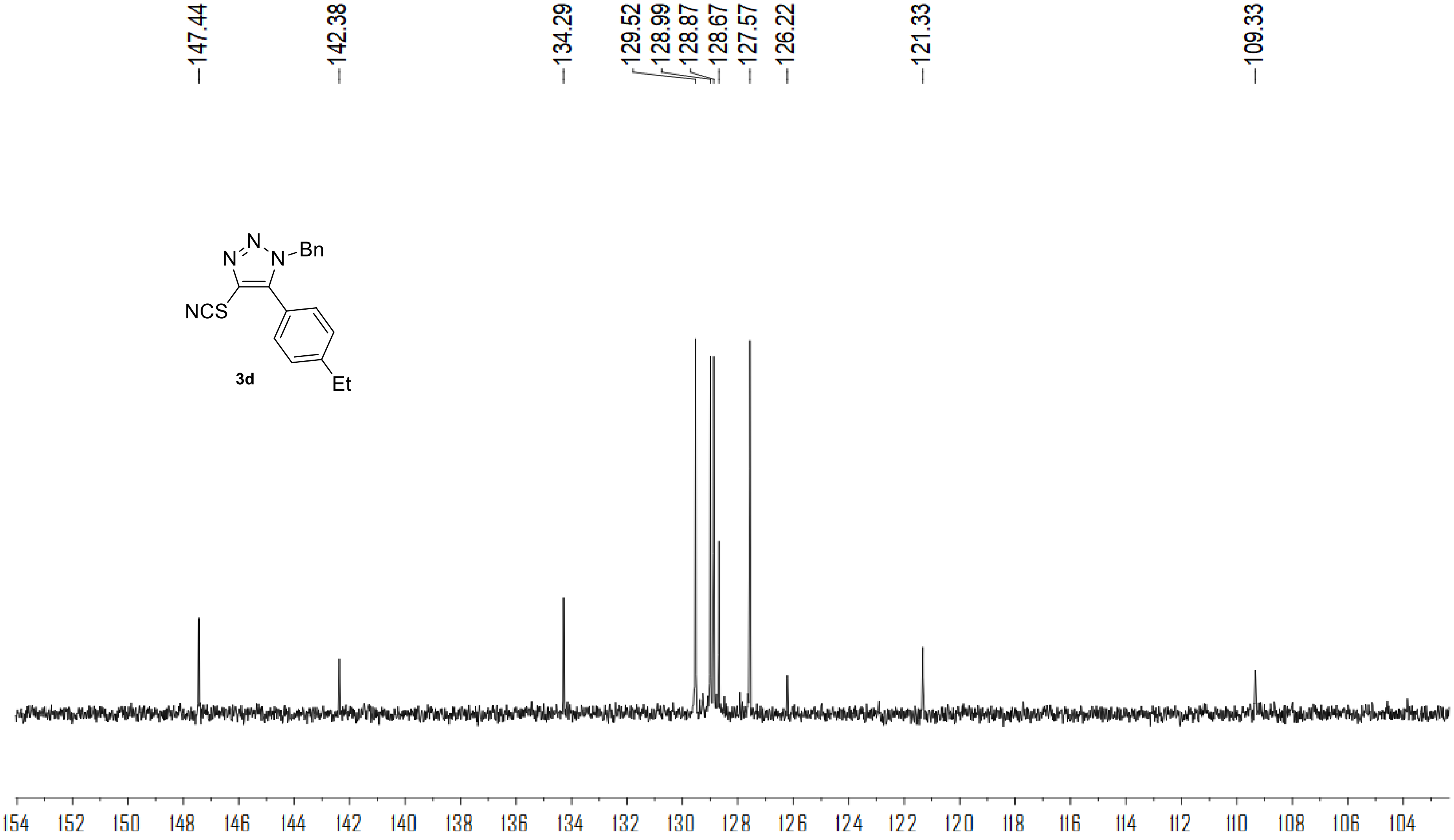
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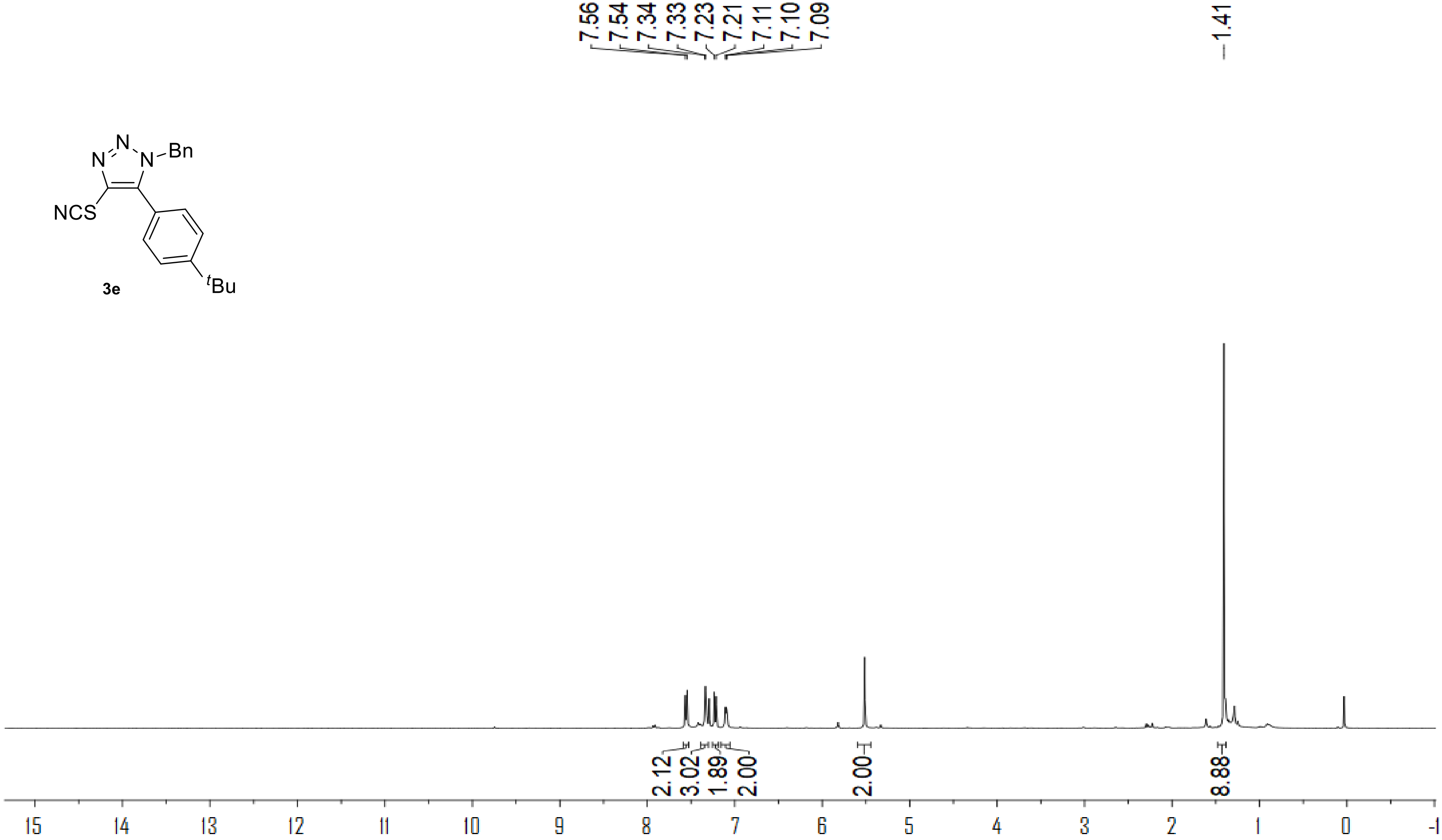

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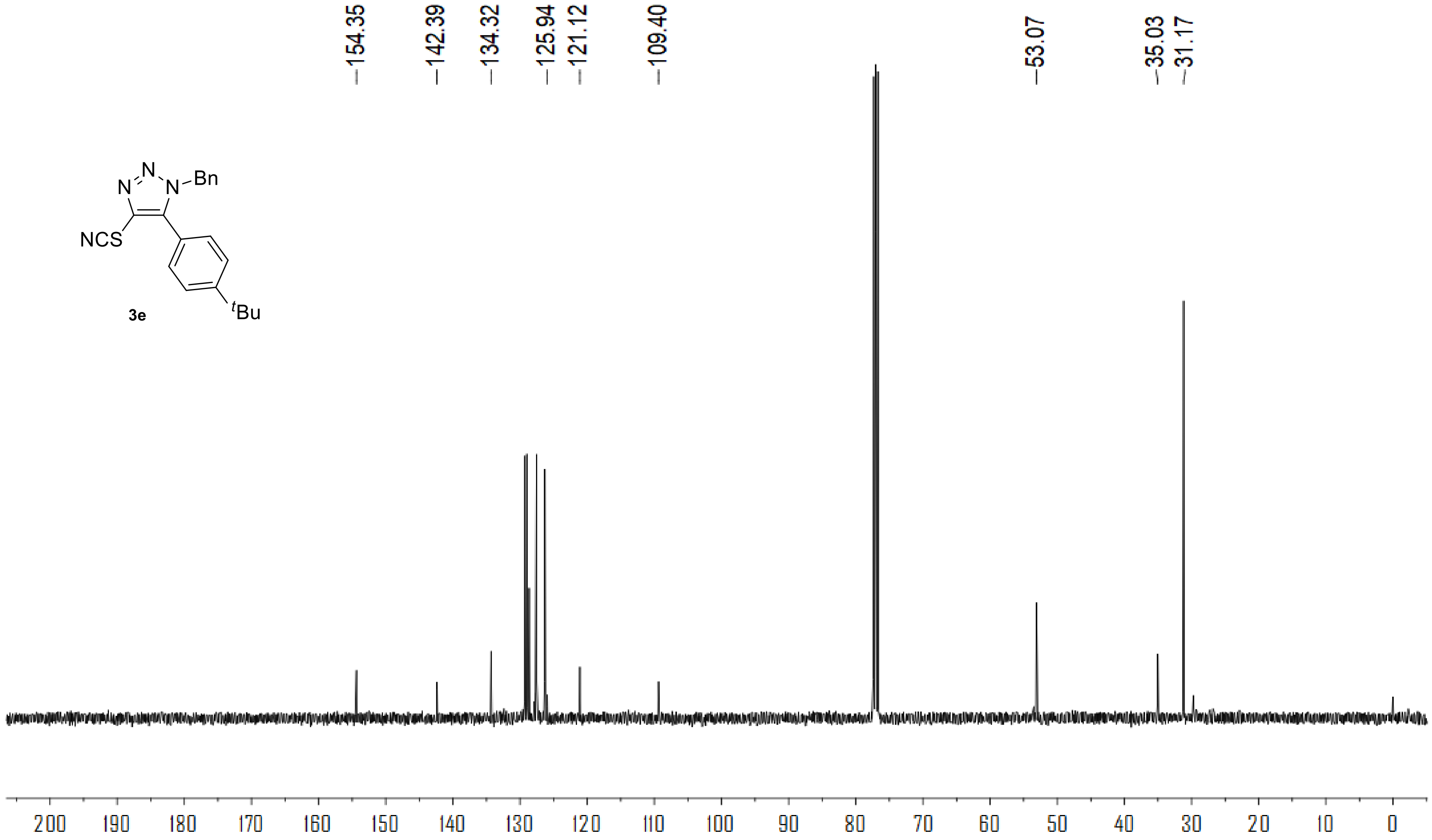
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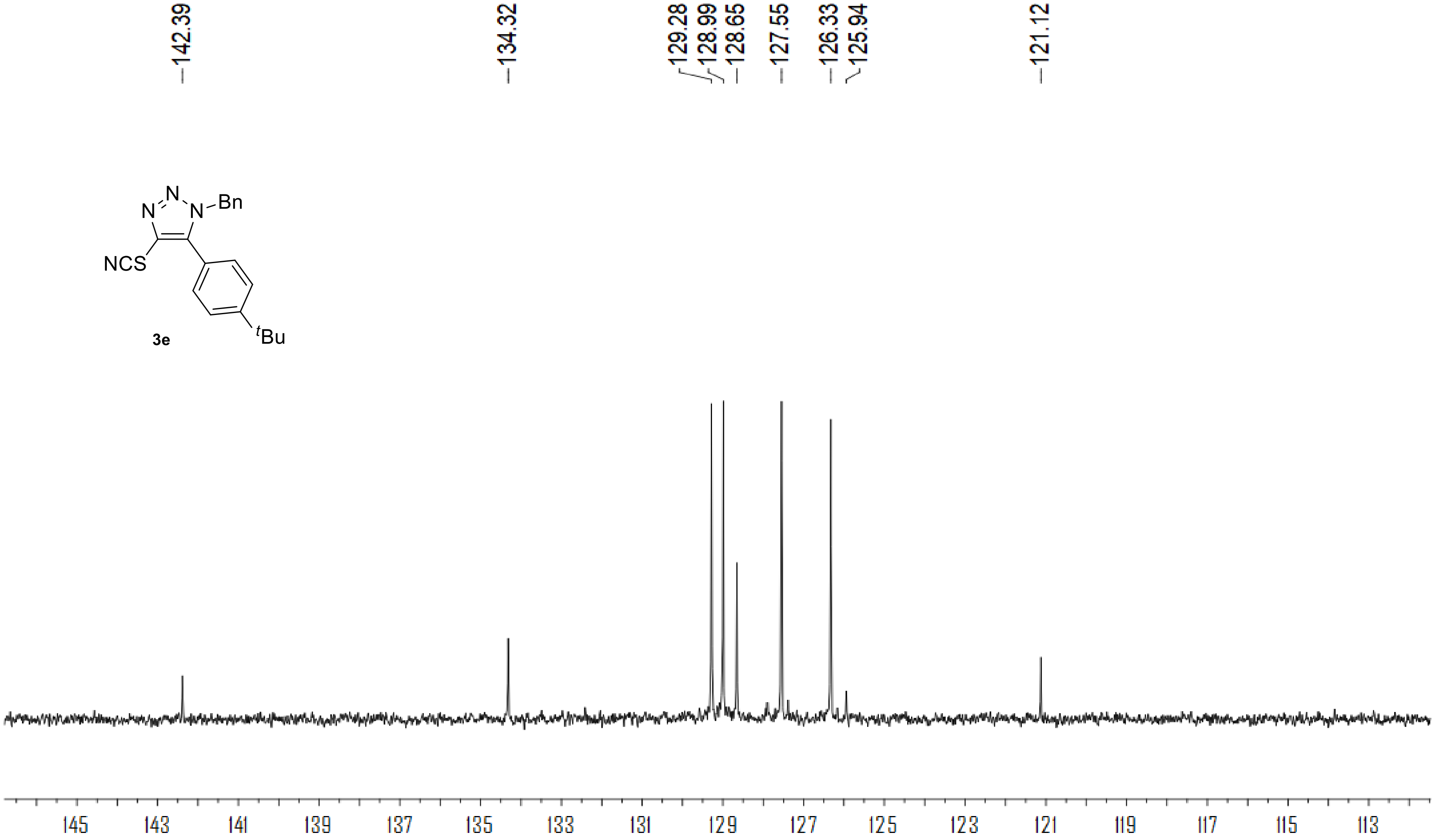
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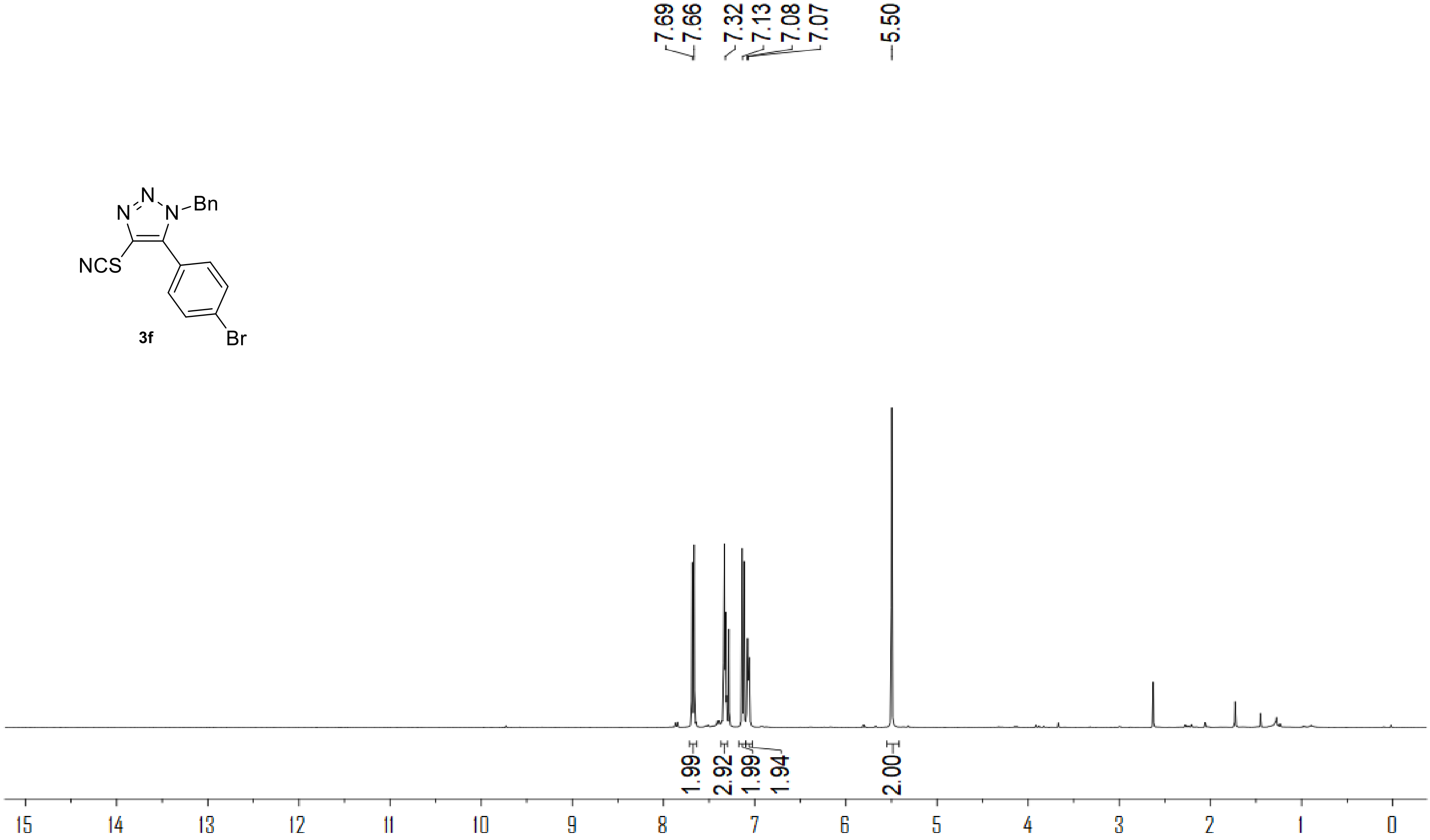
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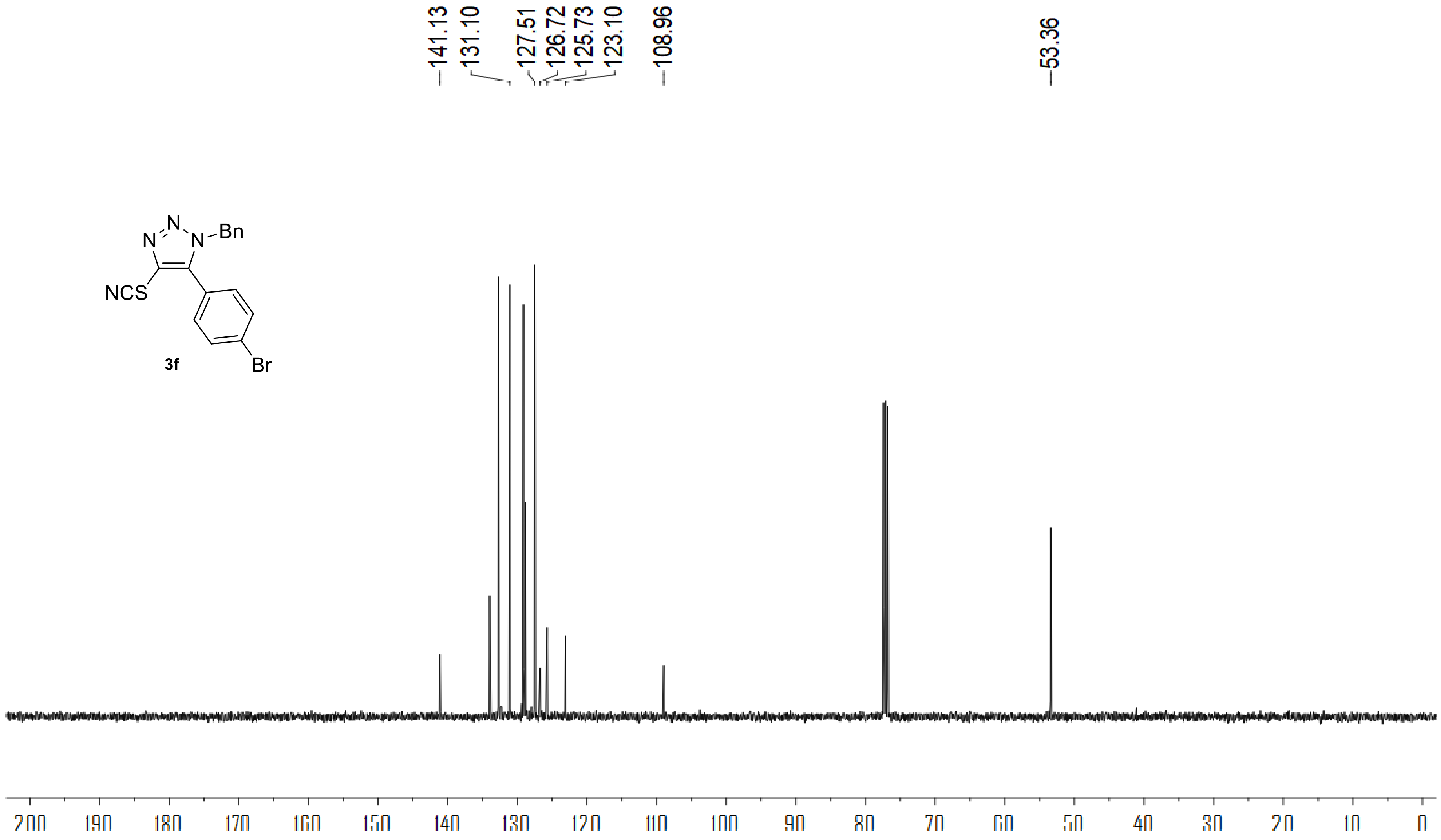
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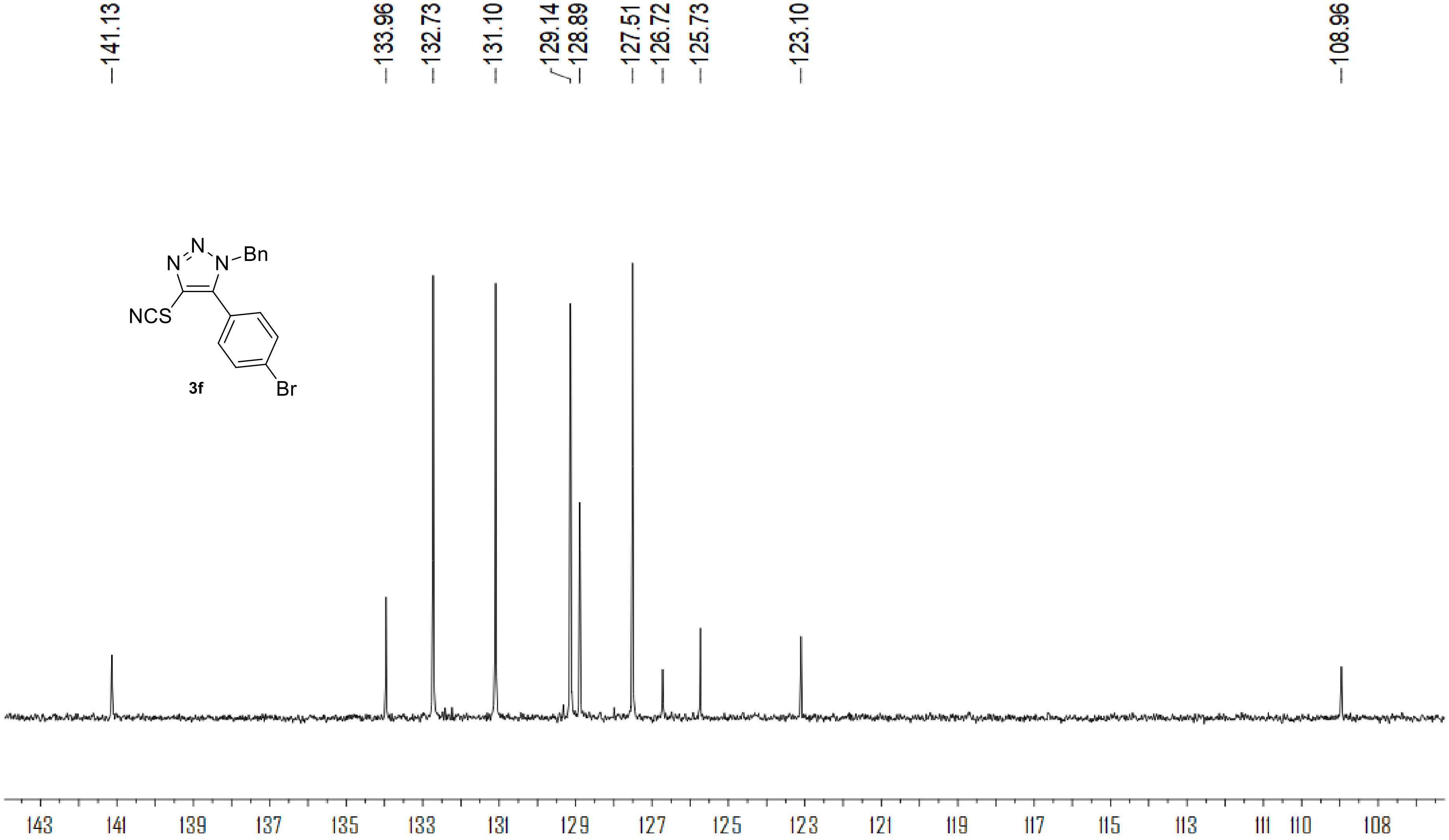
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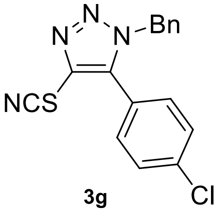
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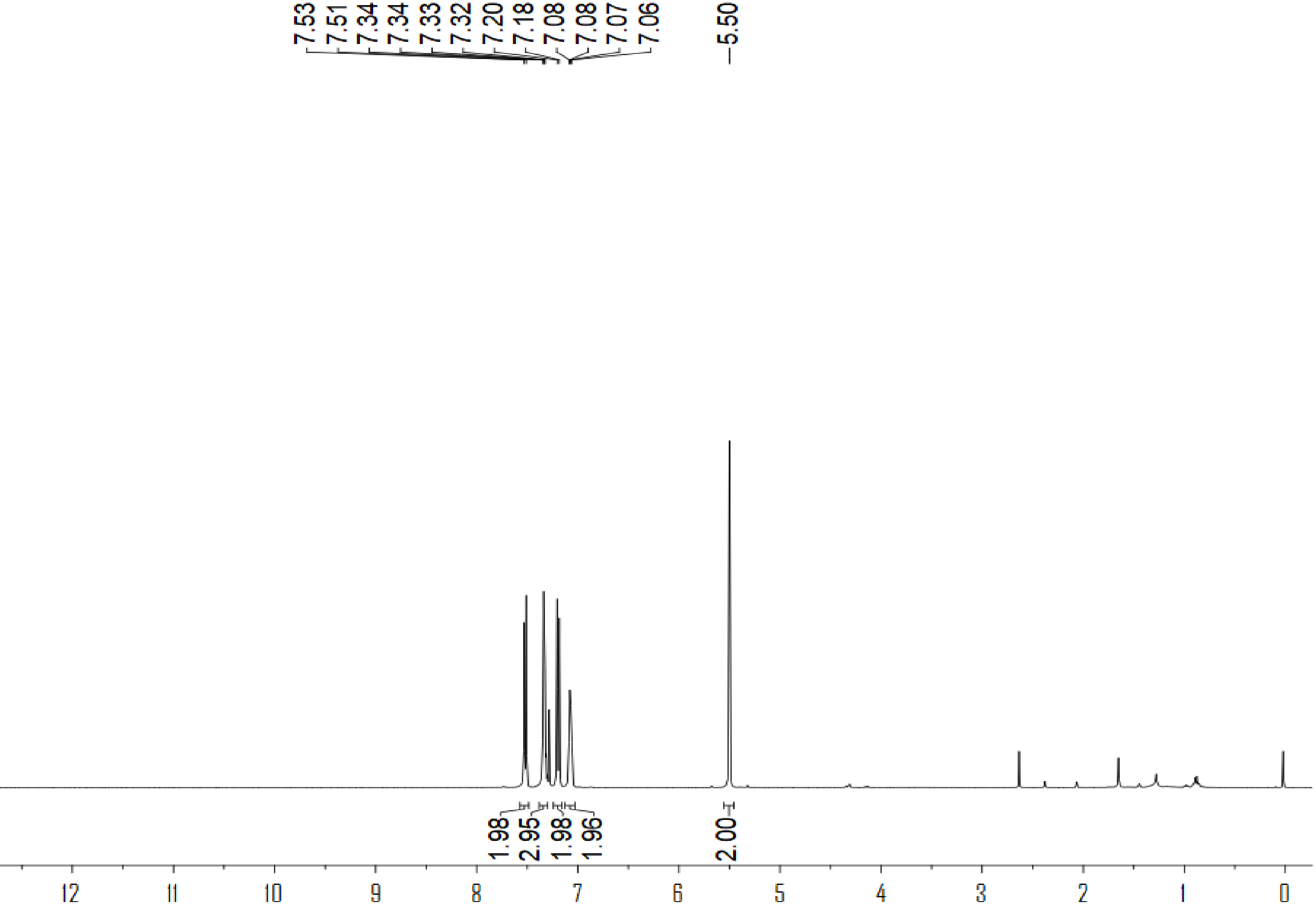
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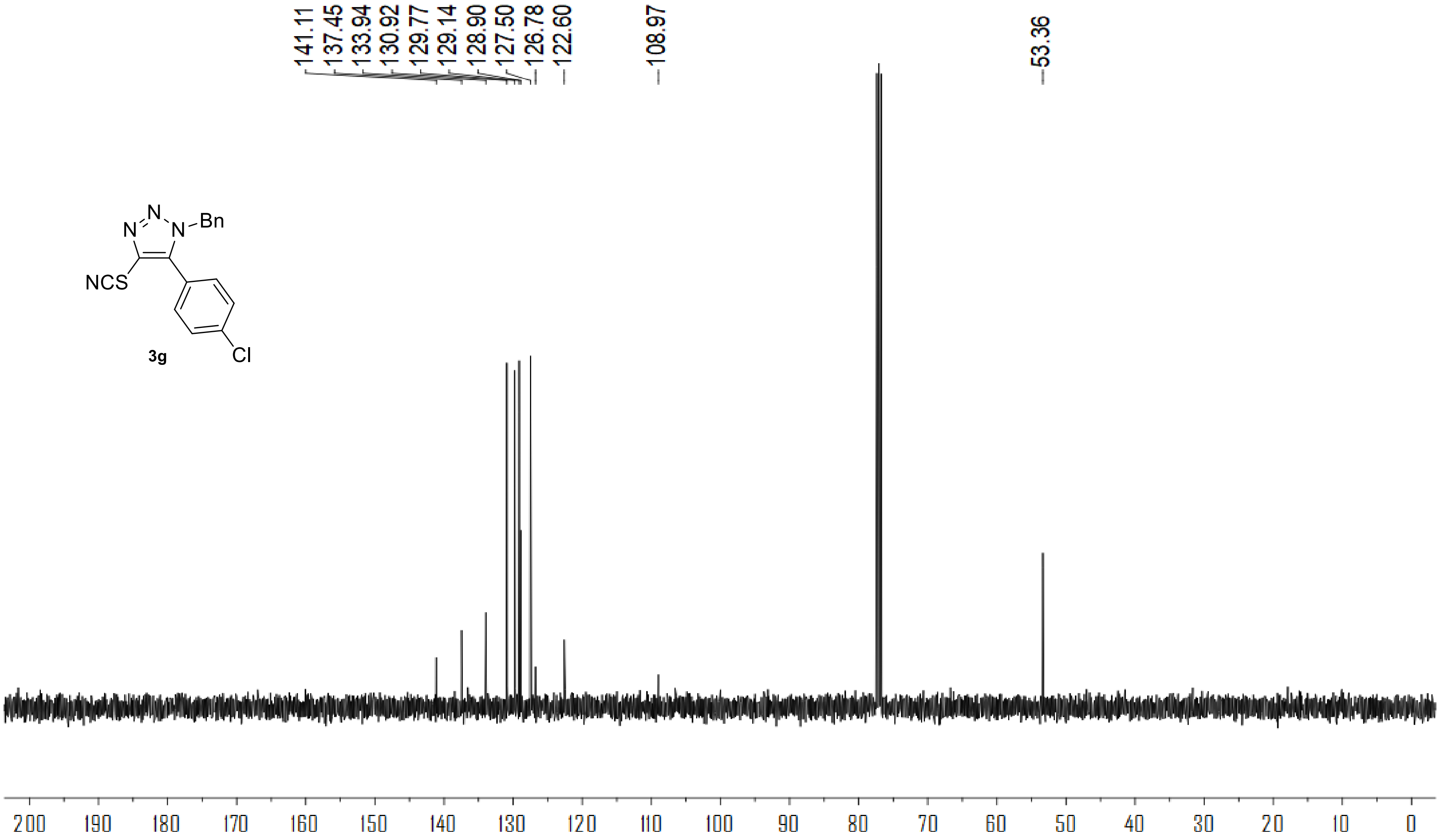
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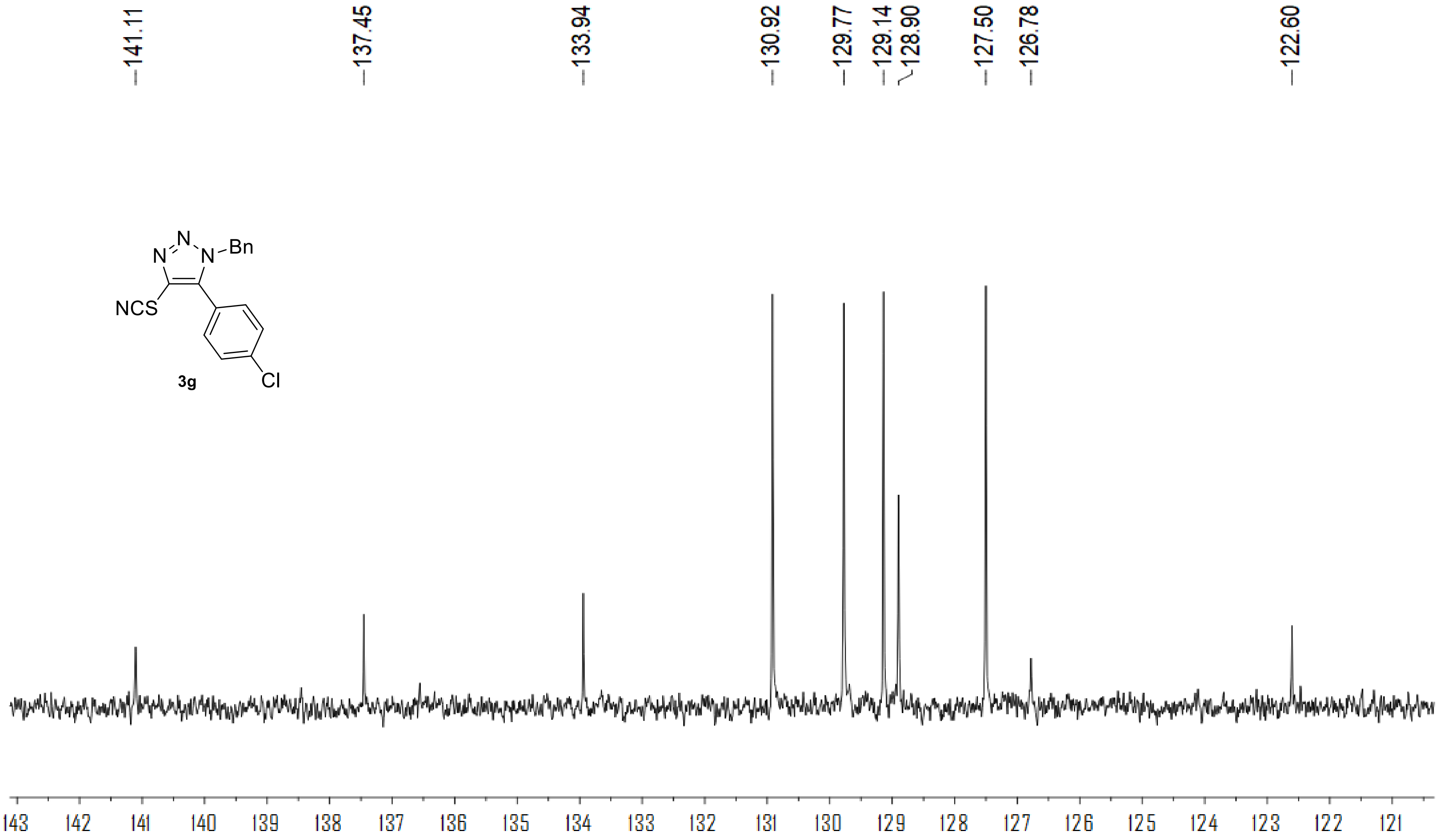
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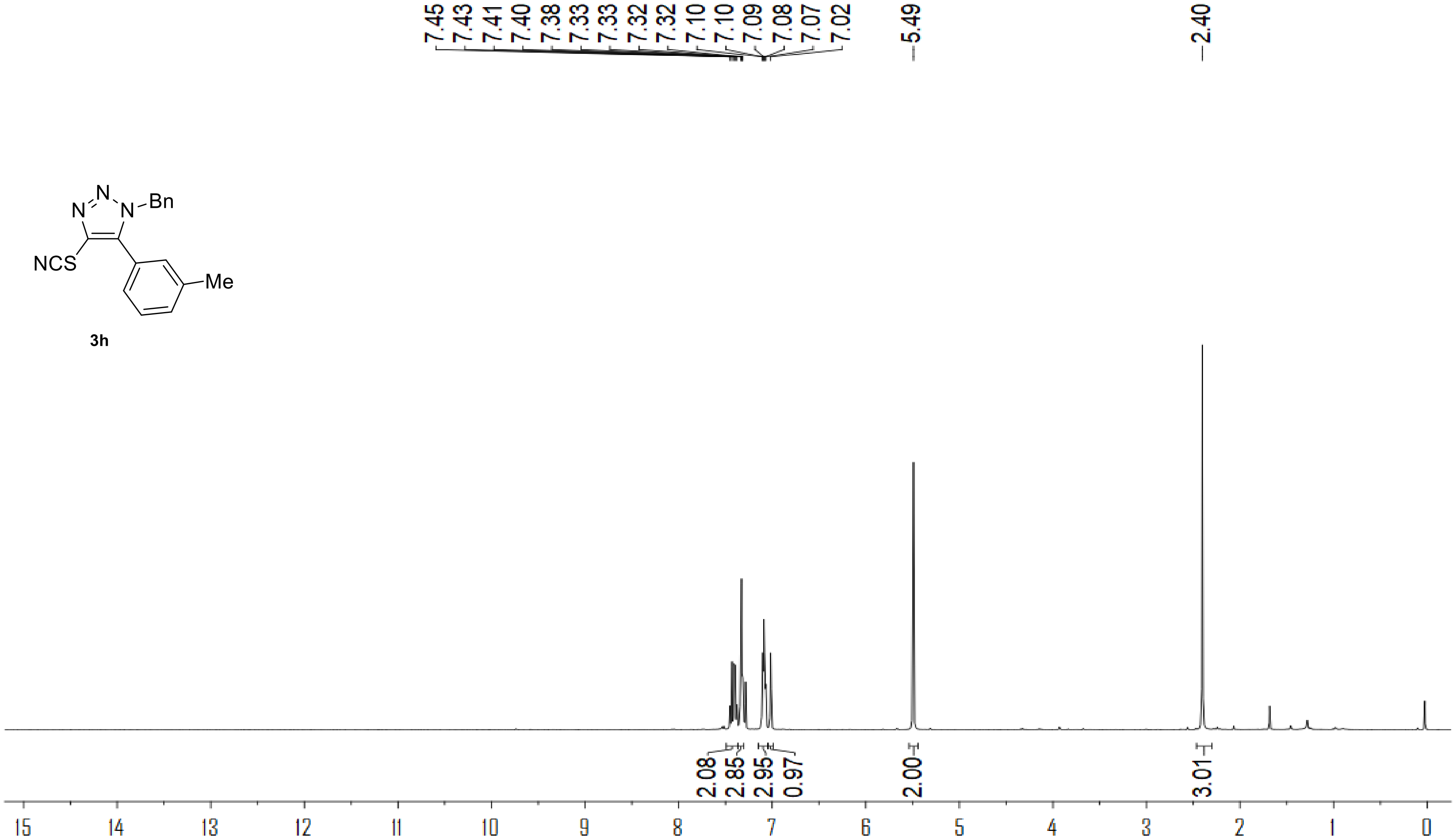
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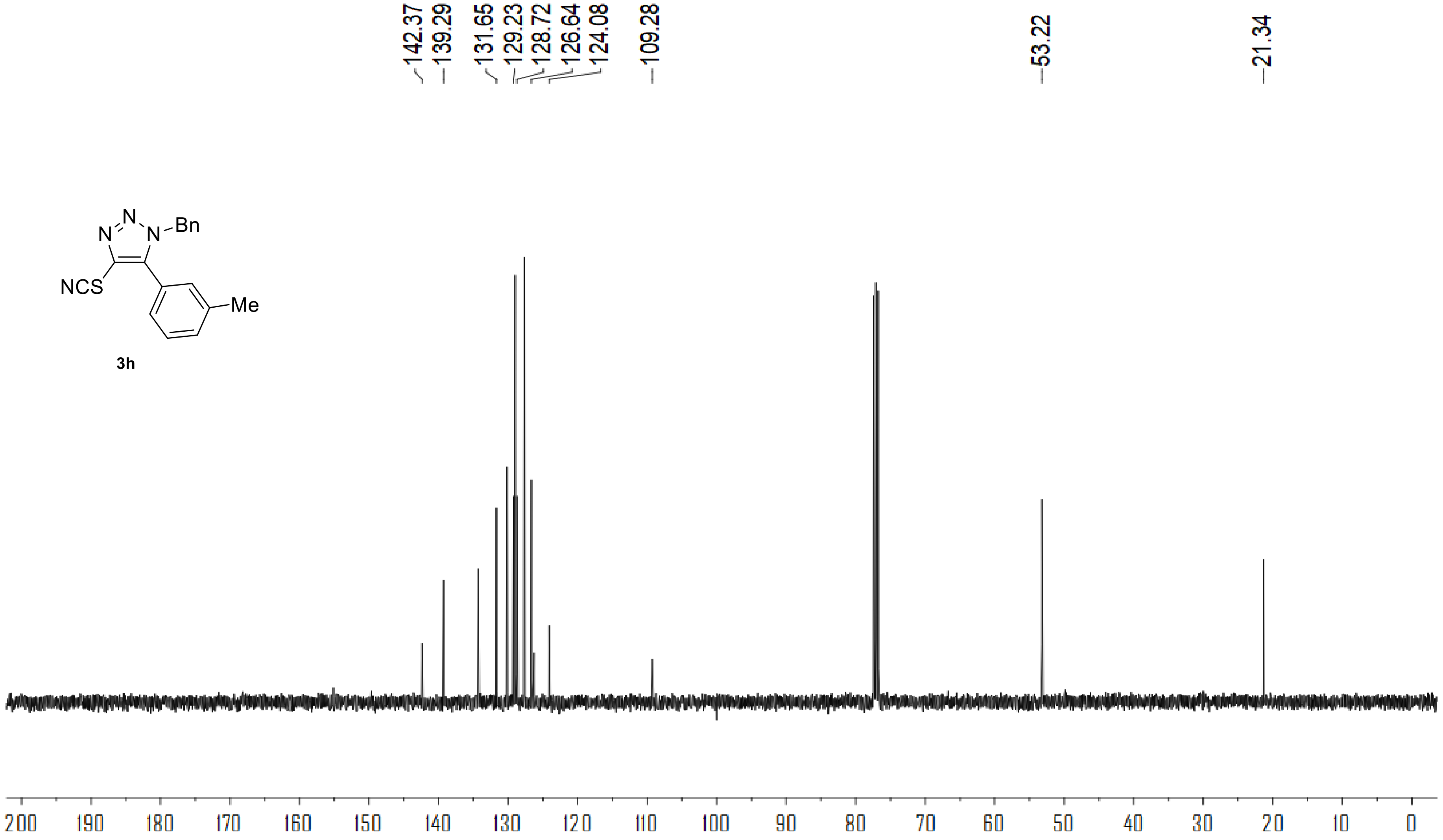
3h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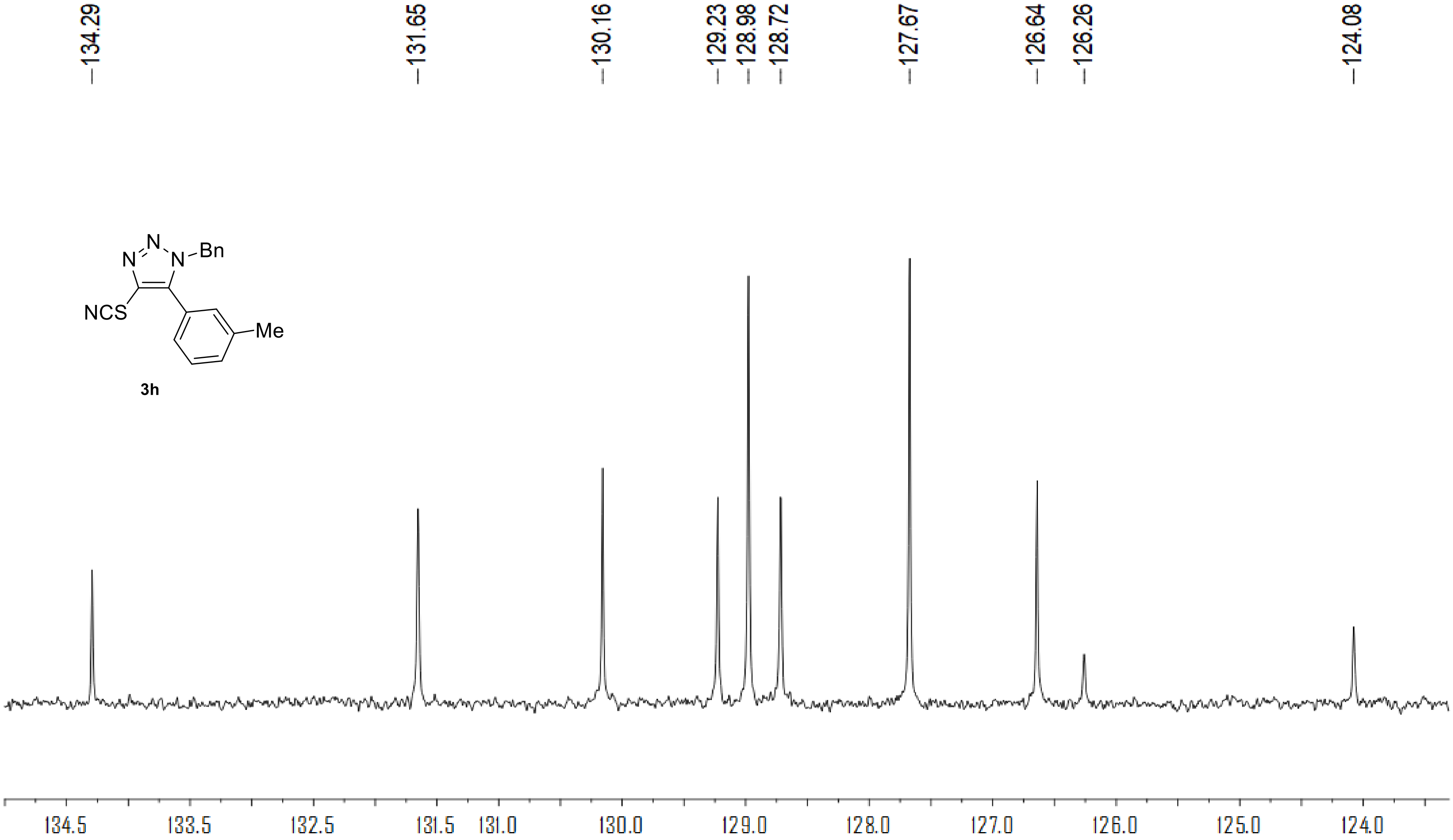
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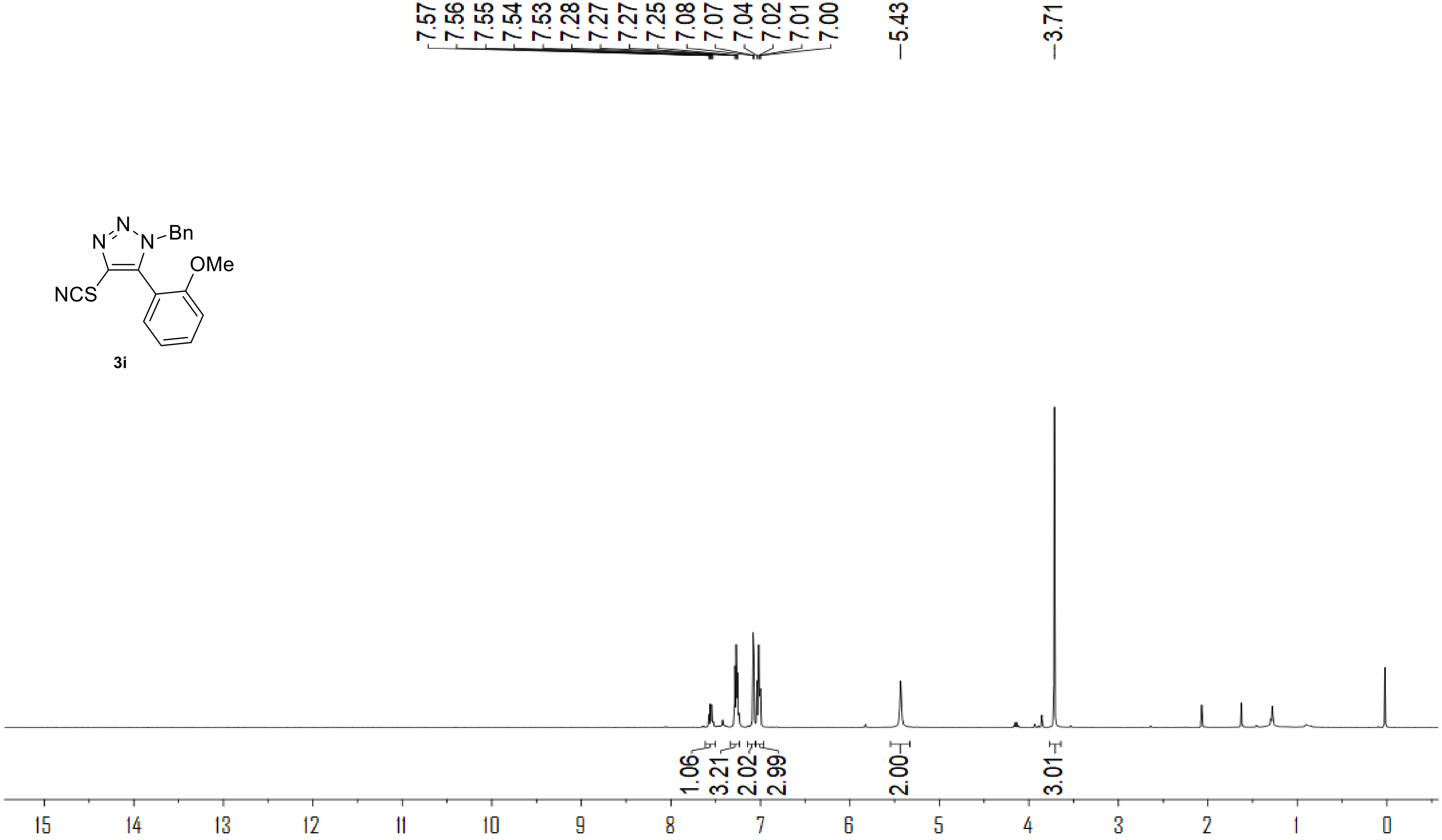
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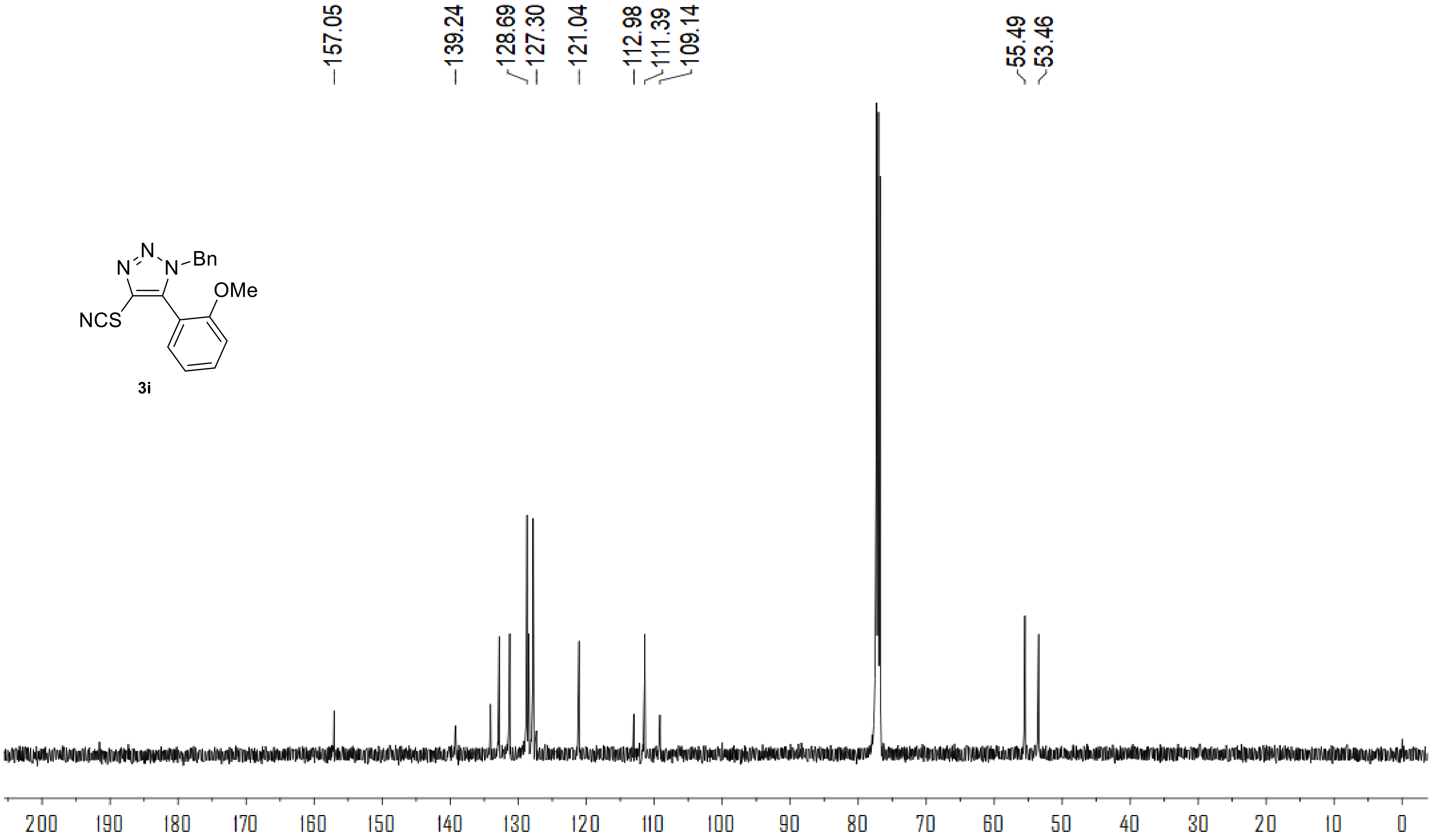

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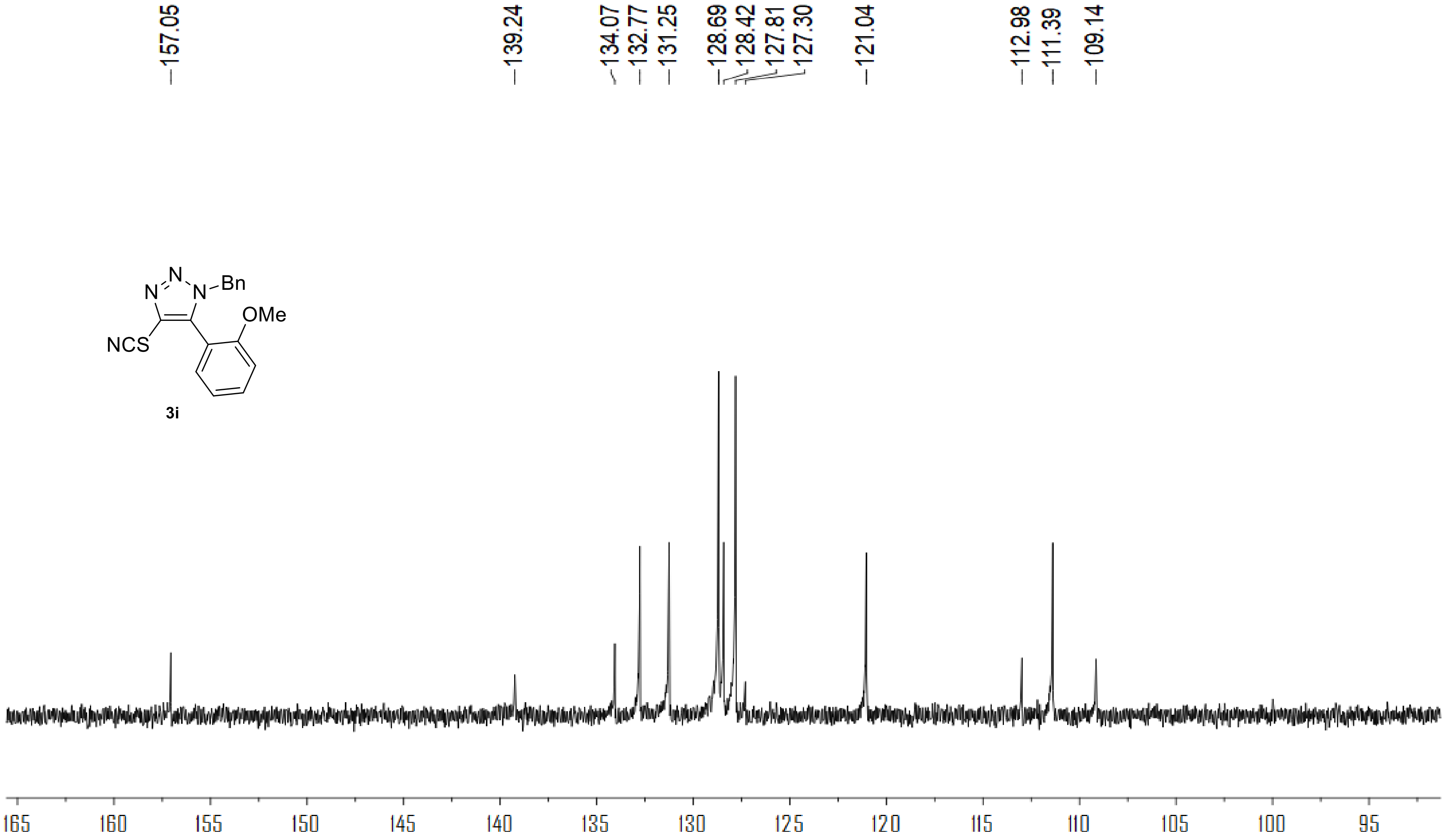
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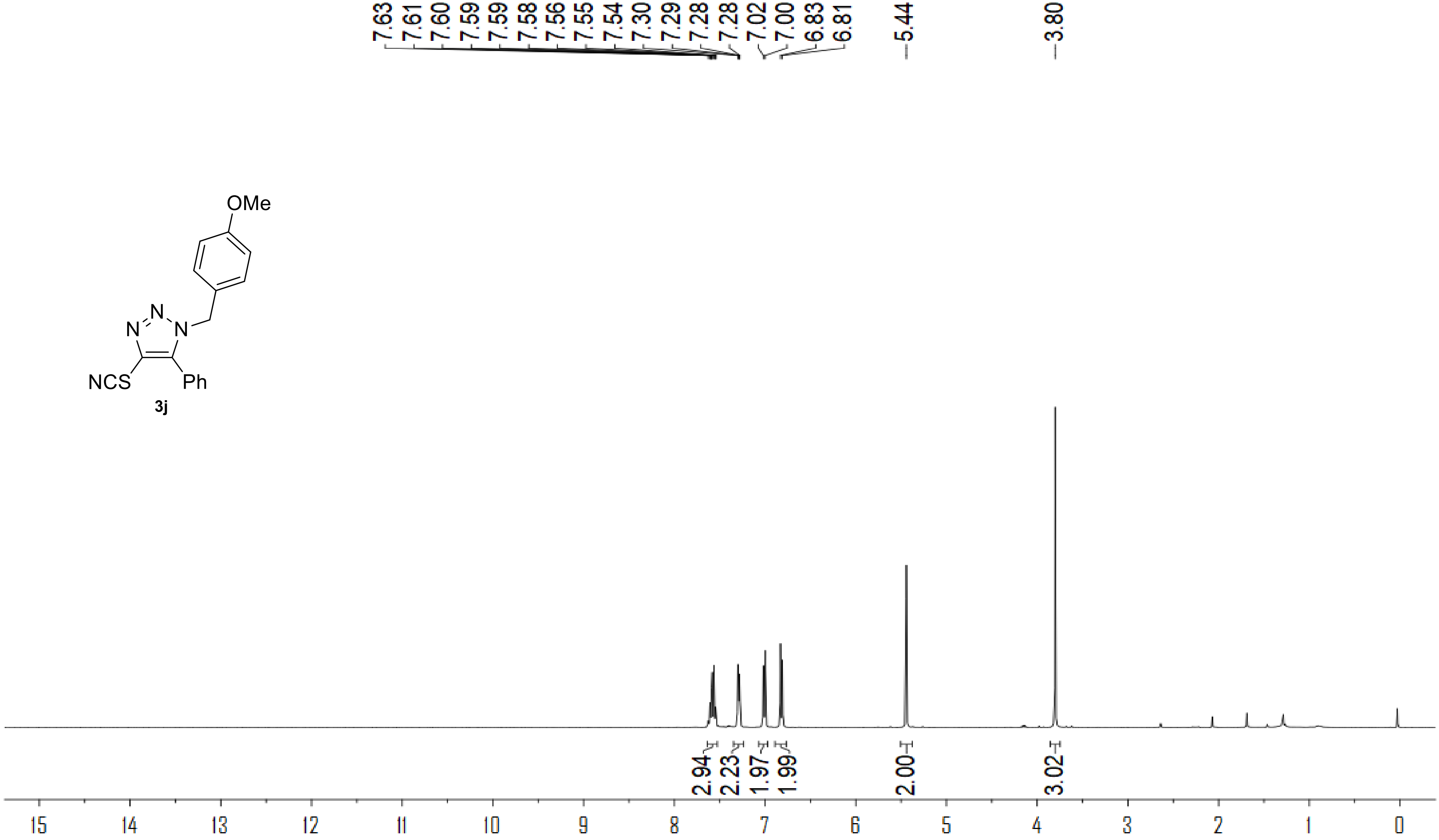
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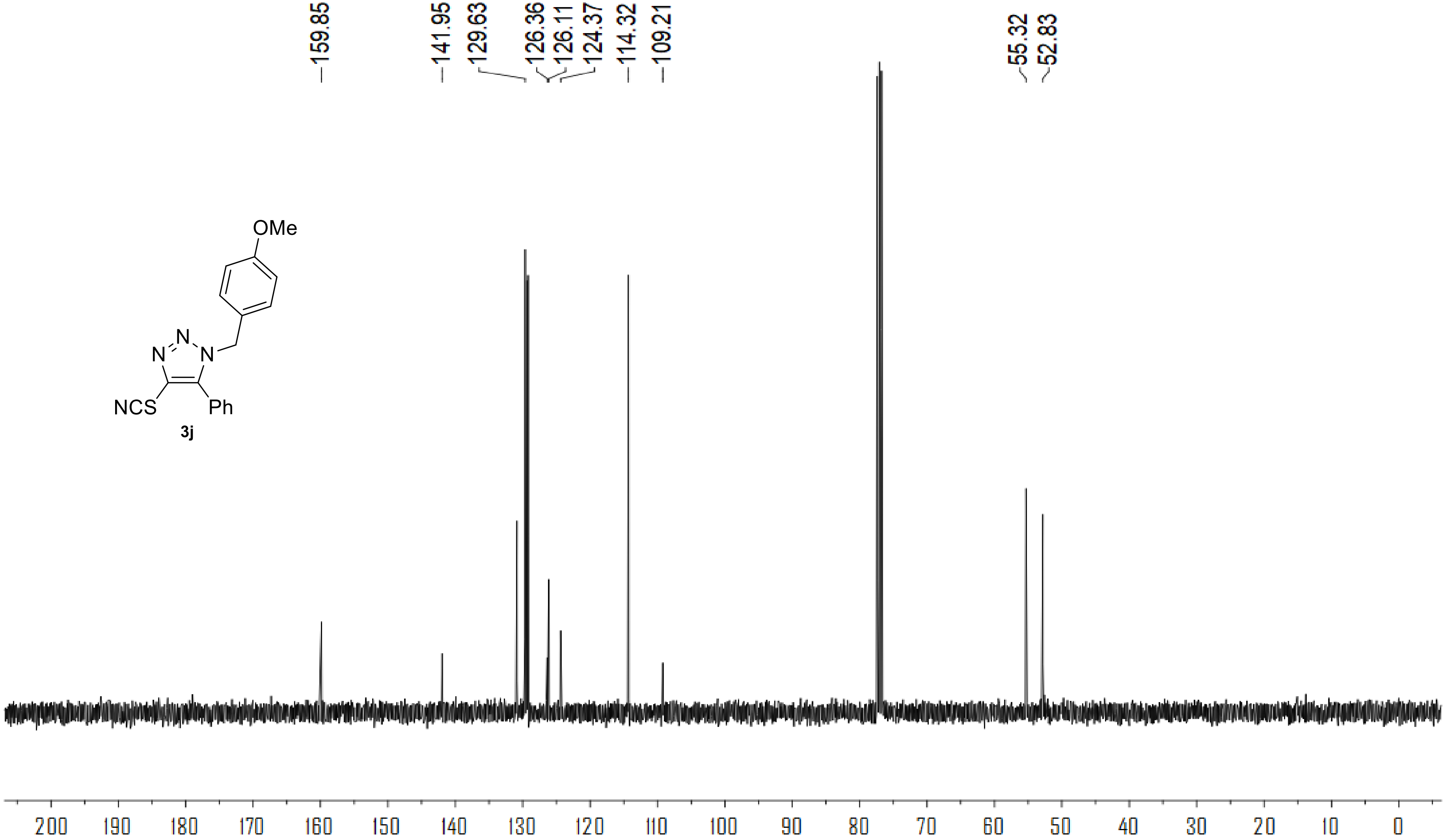
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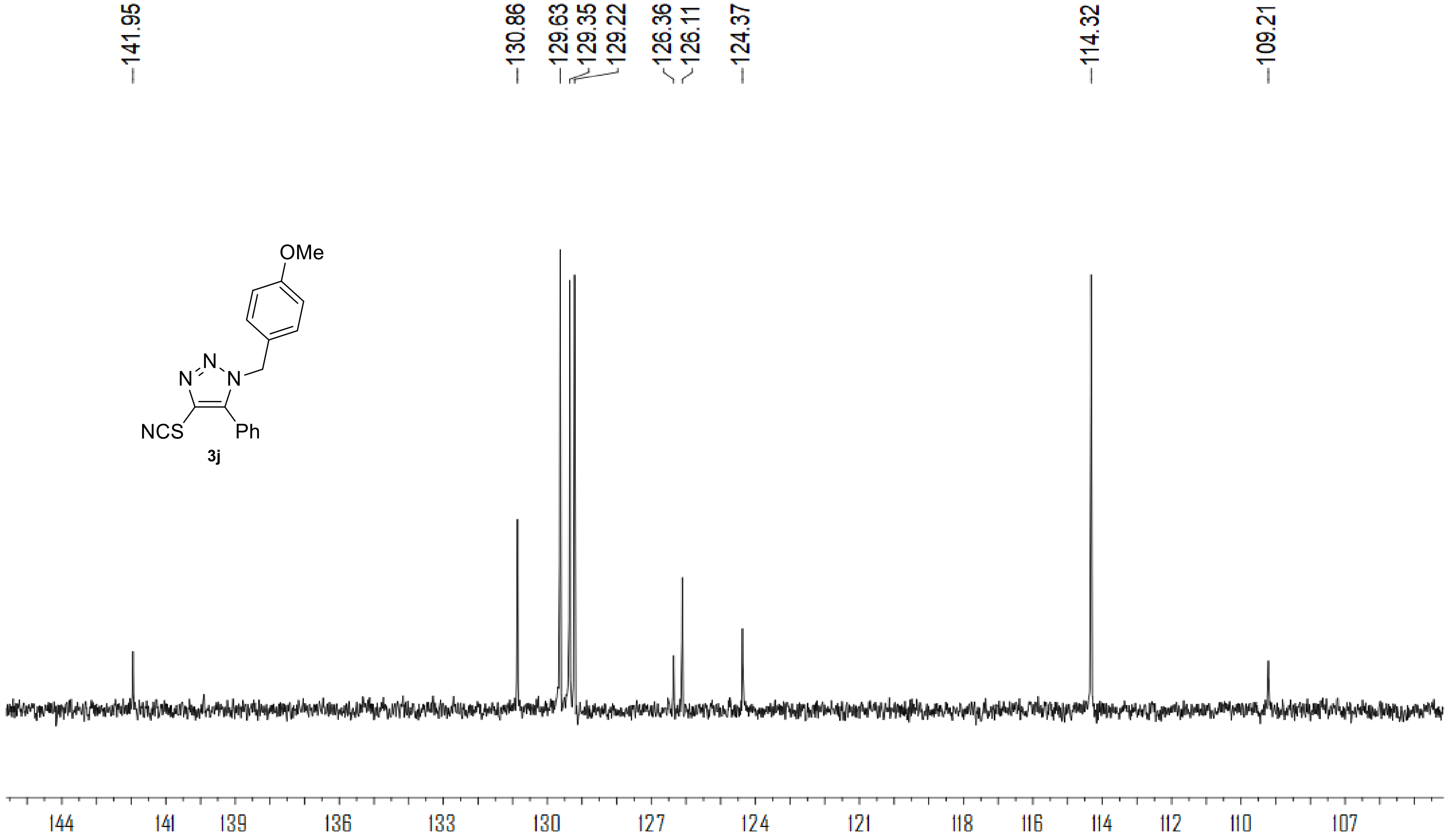
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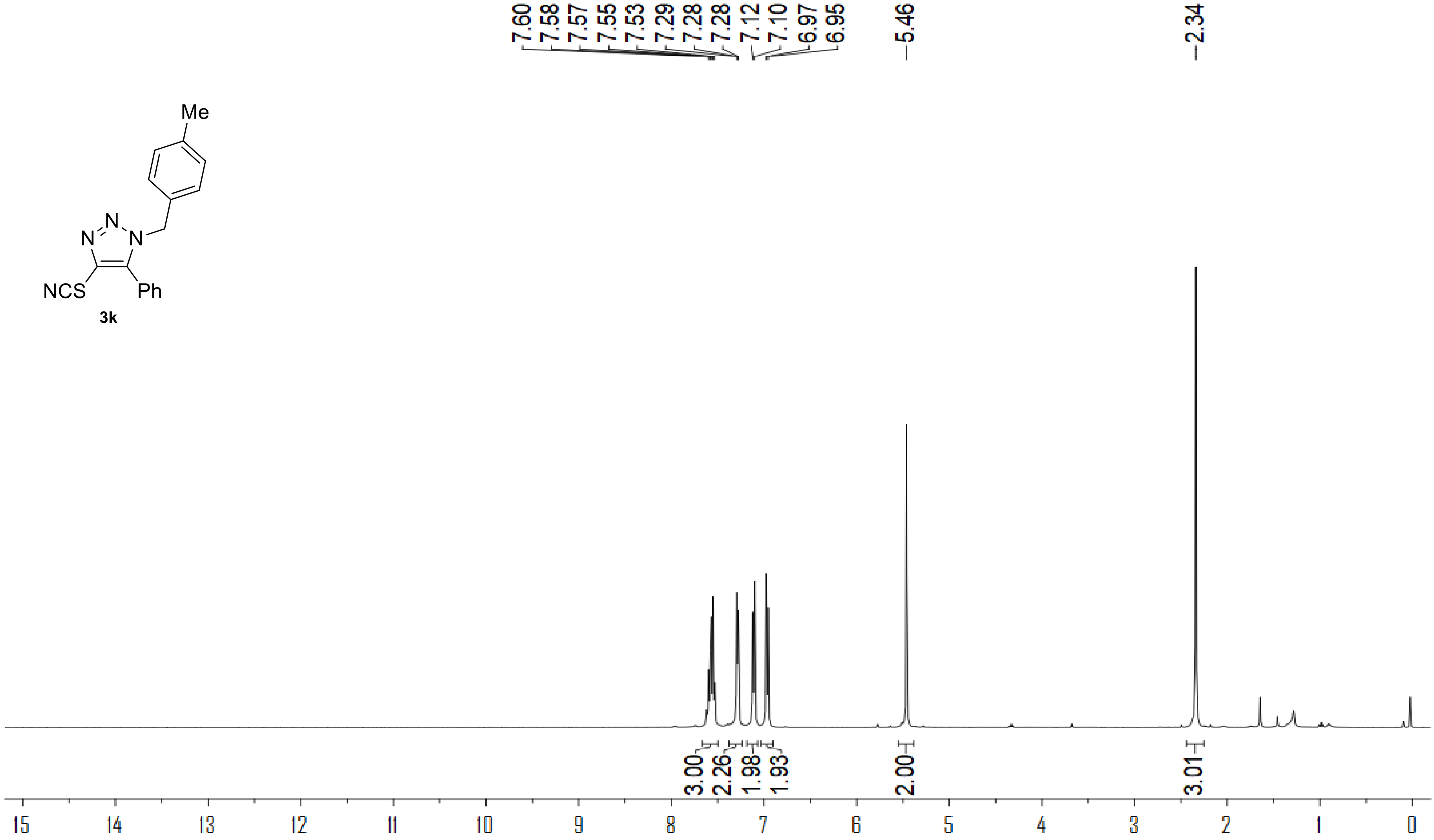
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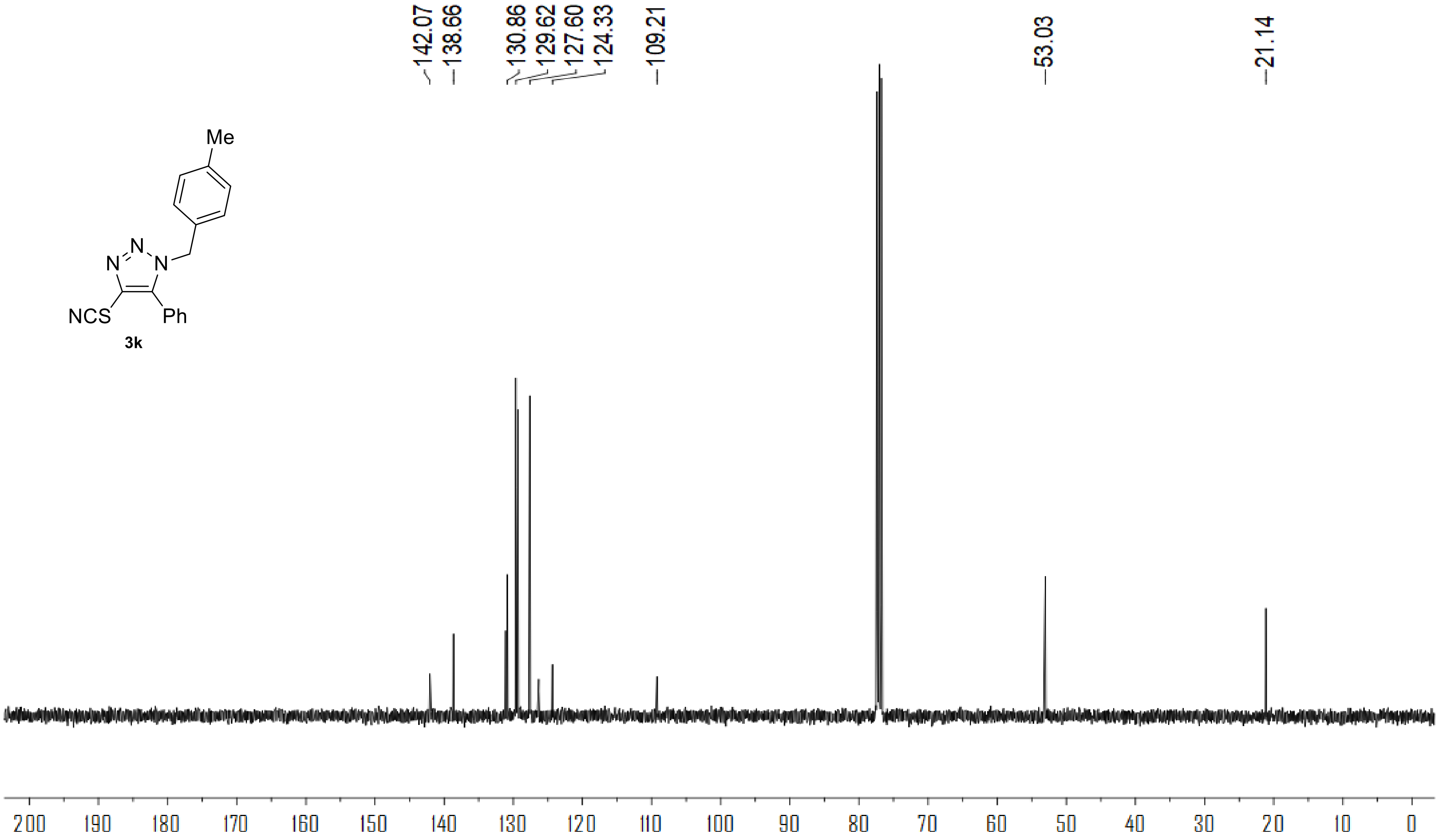
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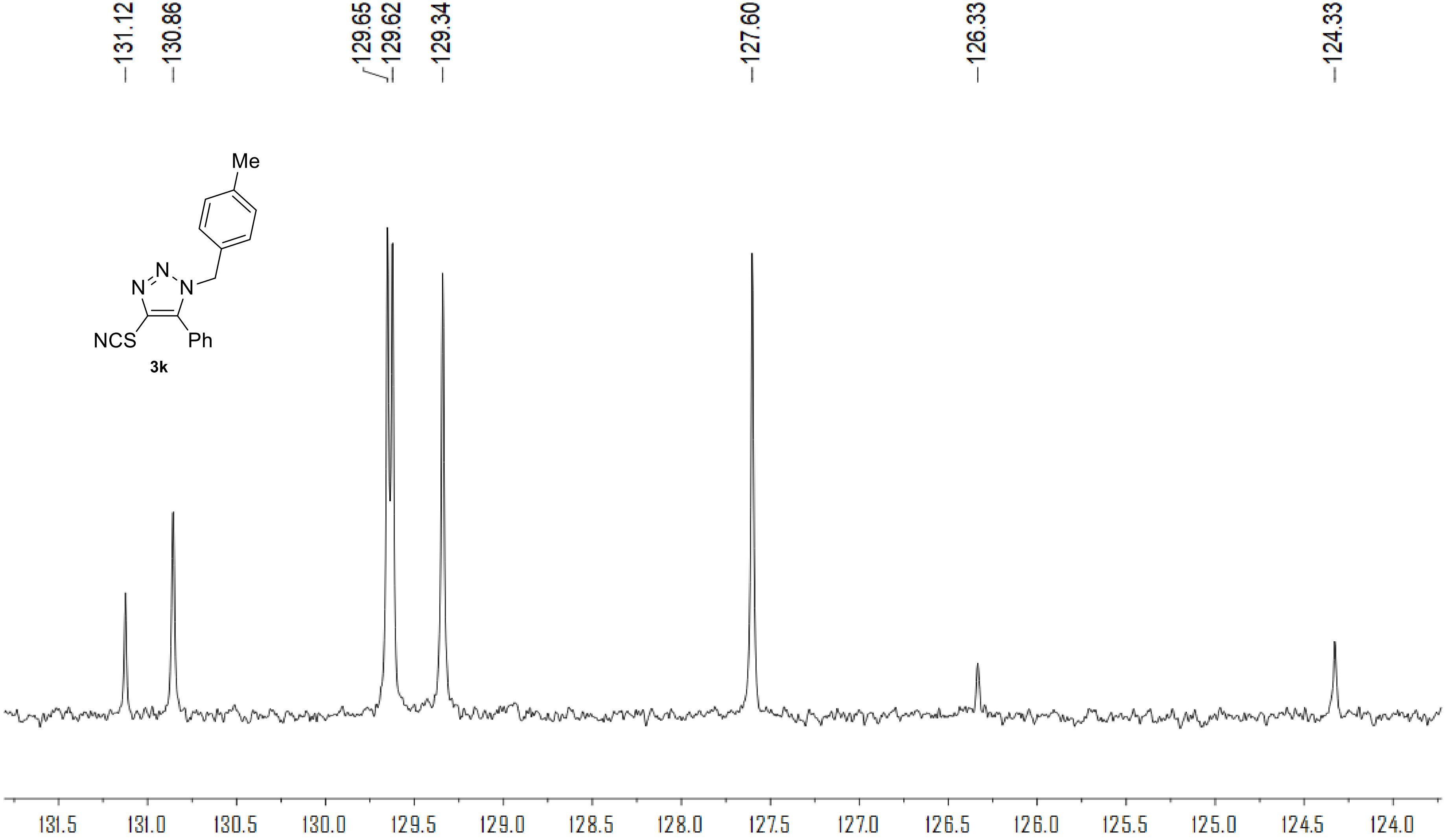
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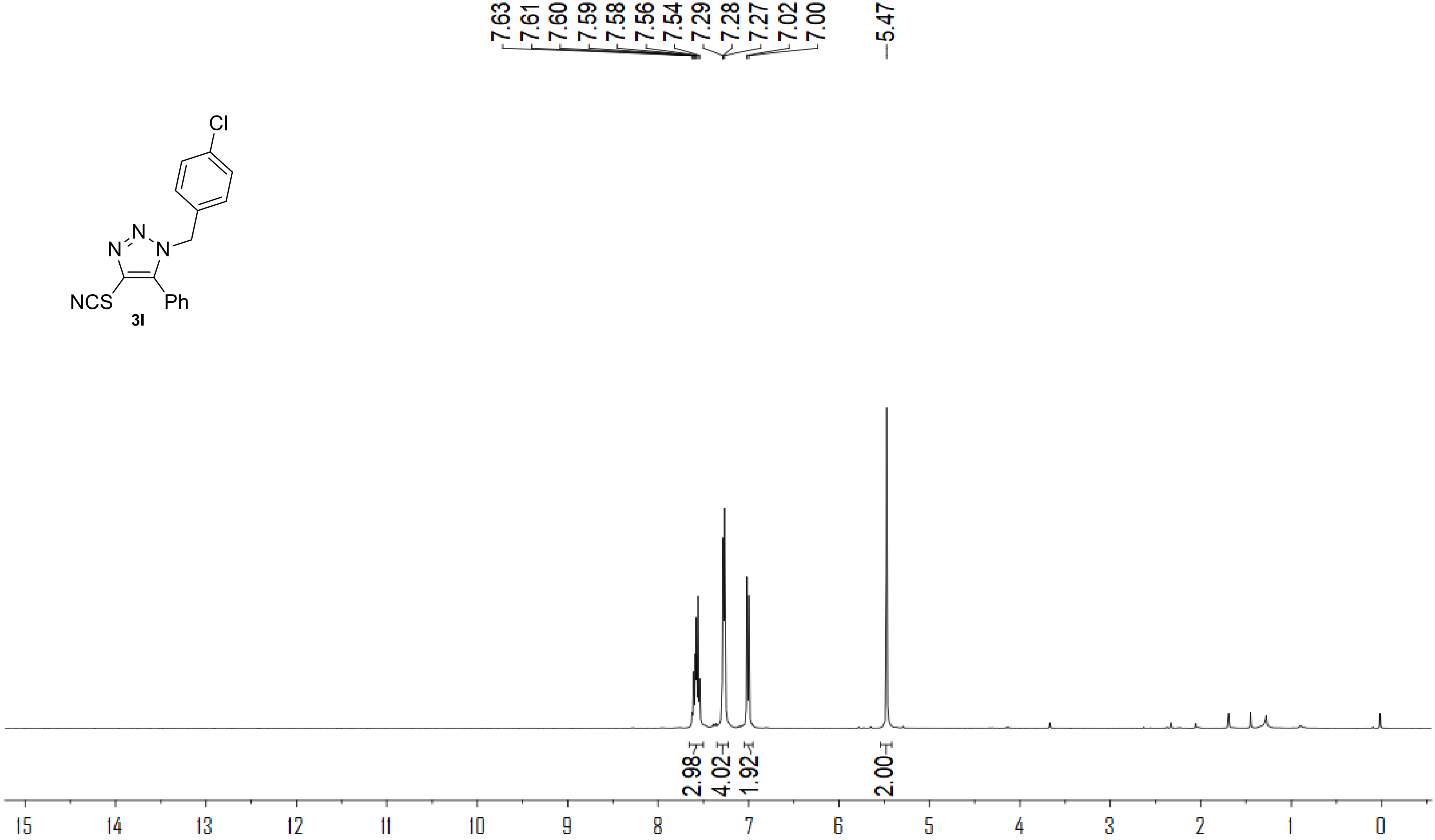
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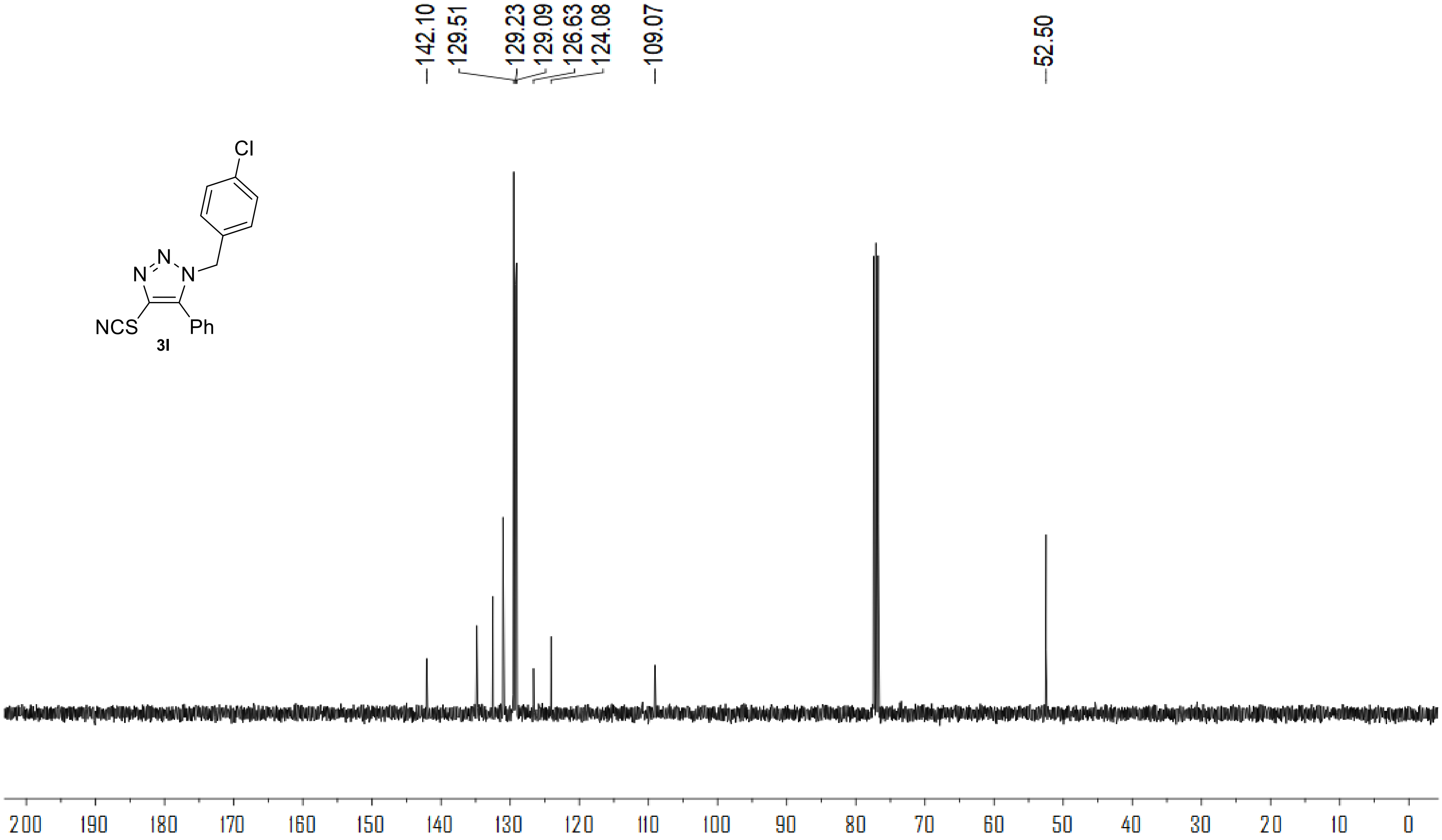
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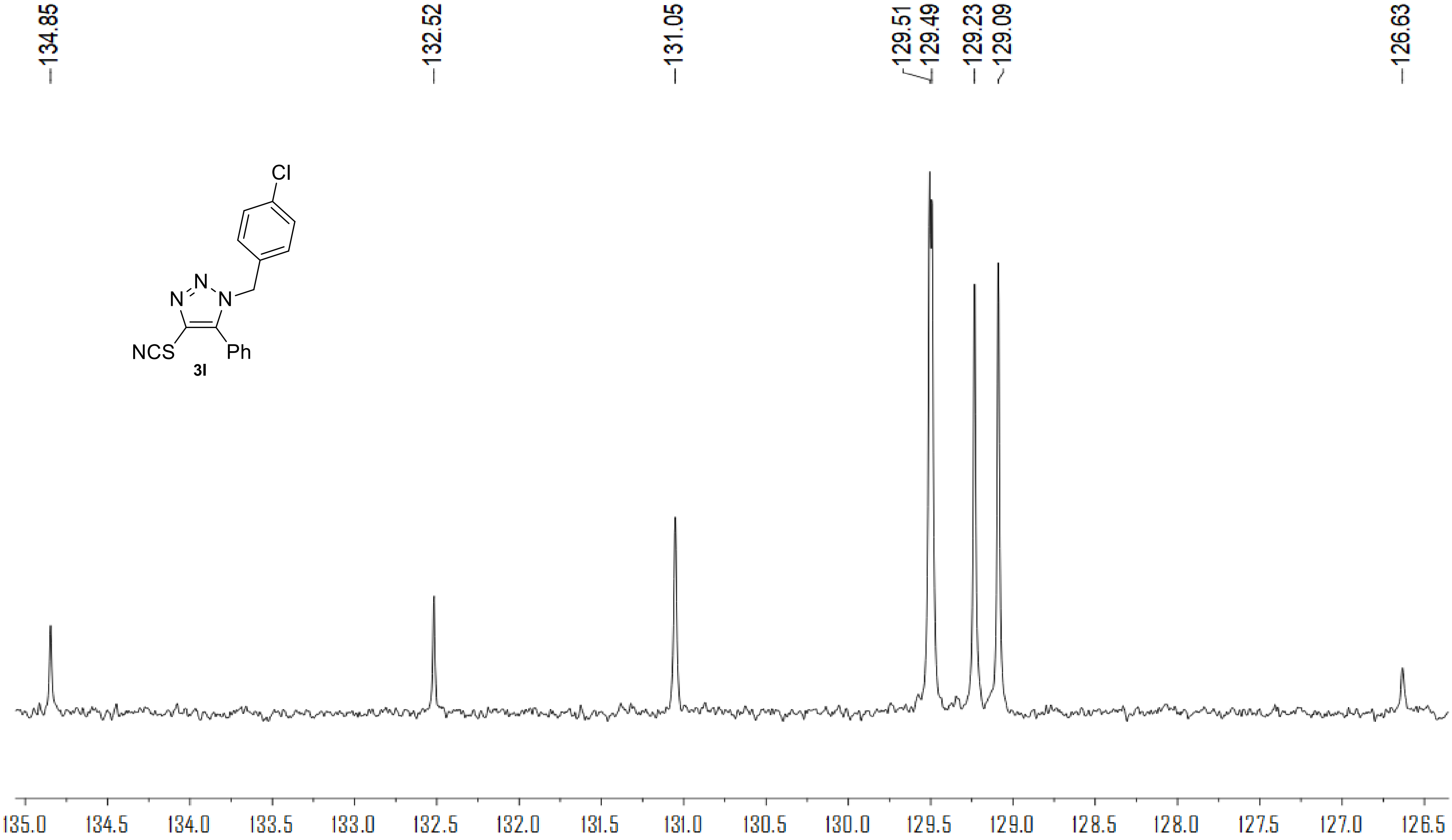
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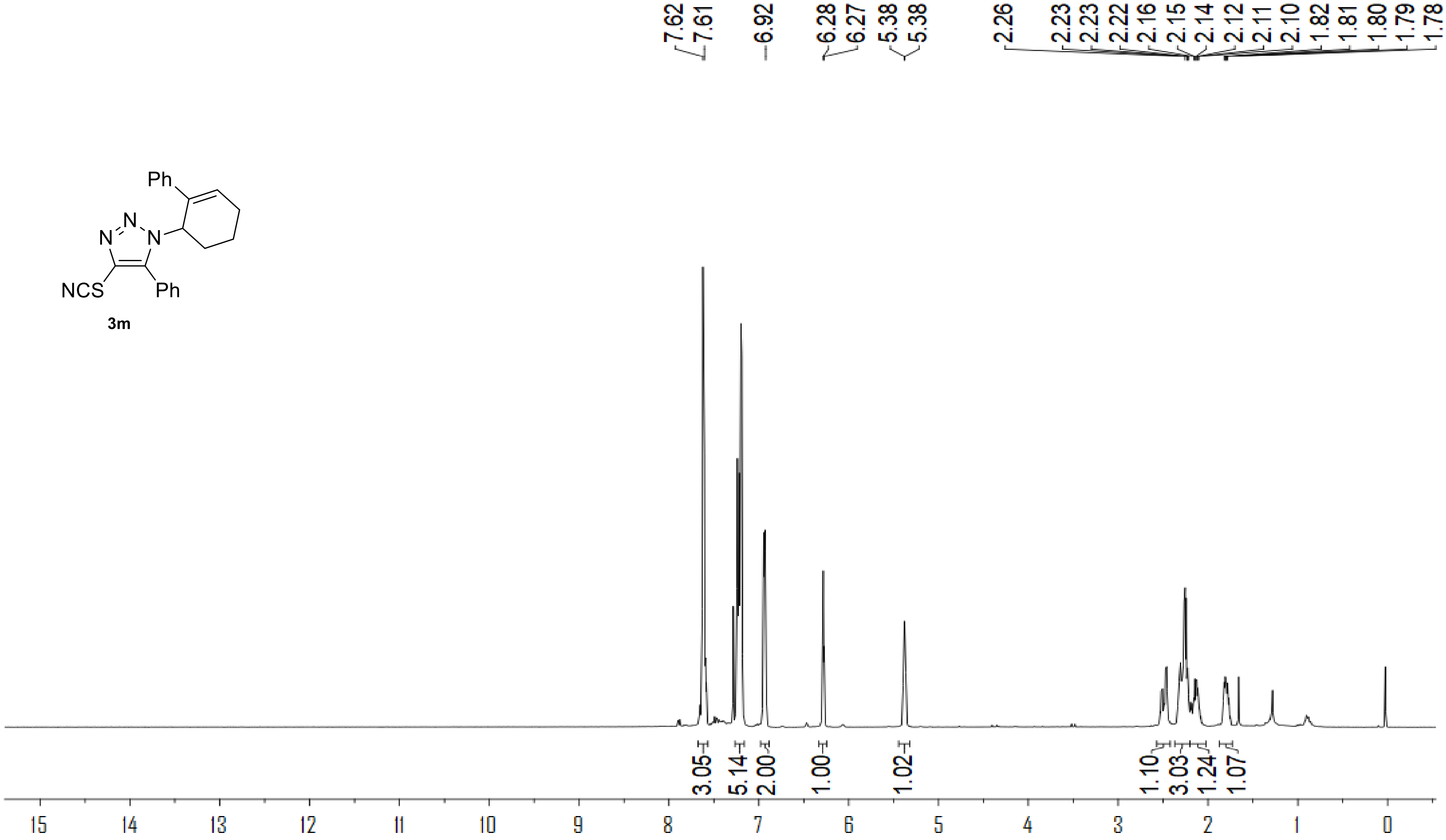
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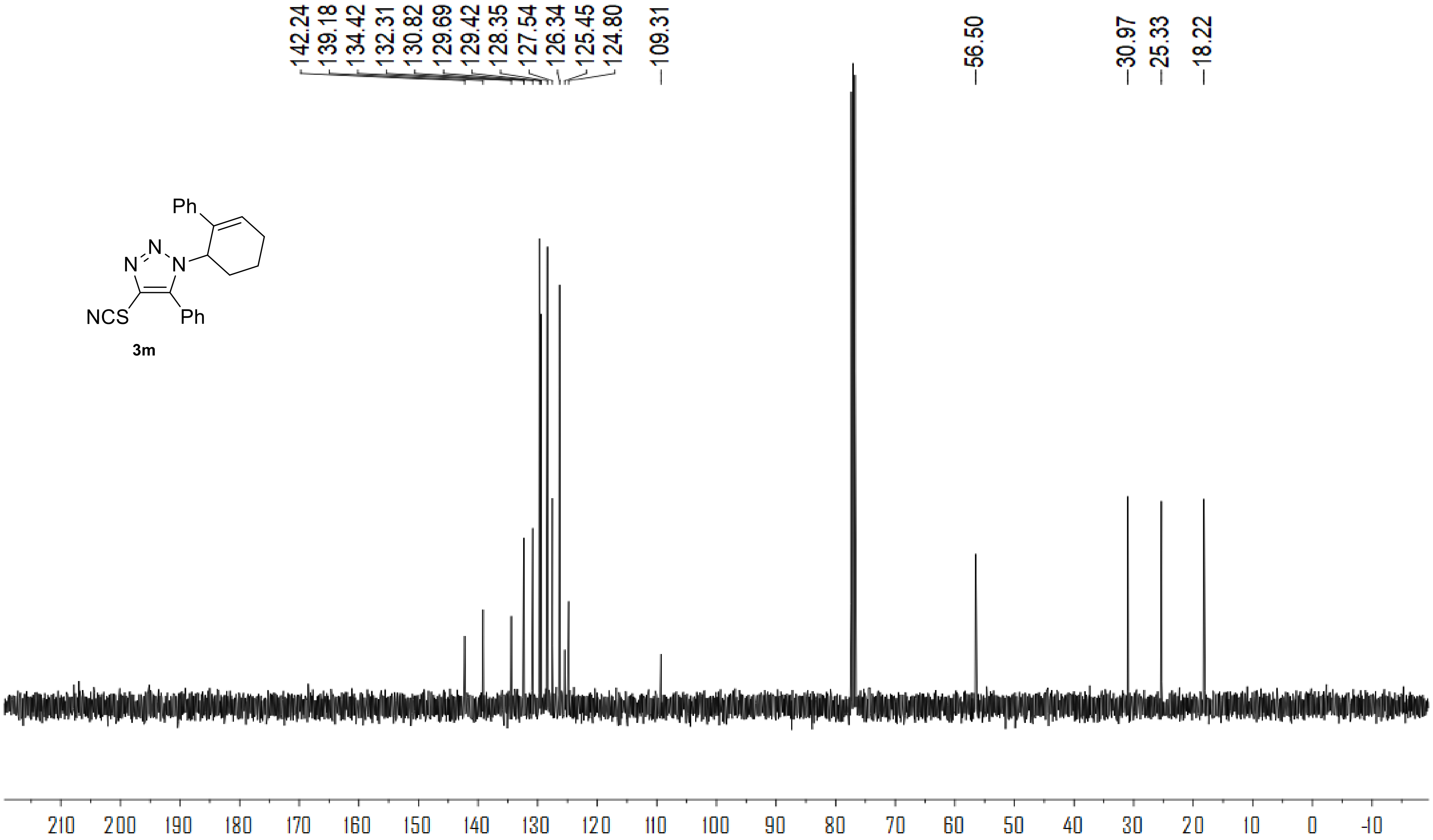
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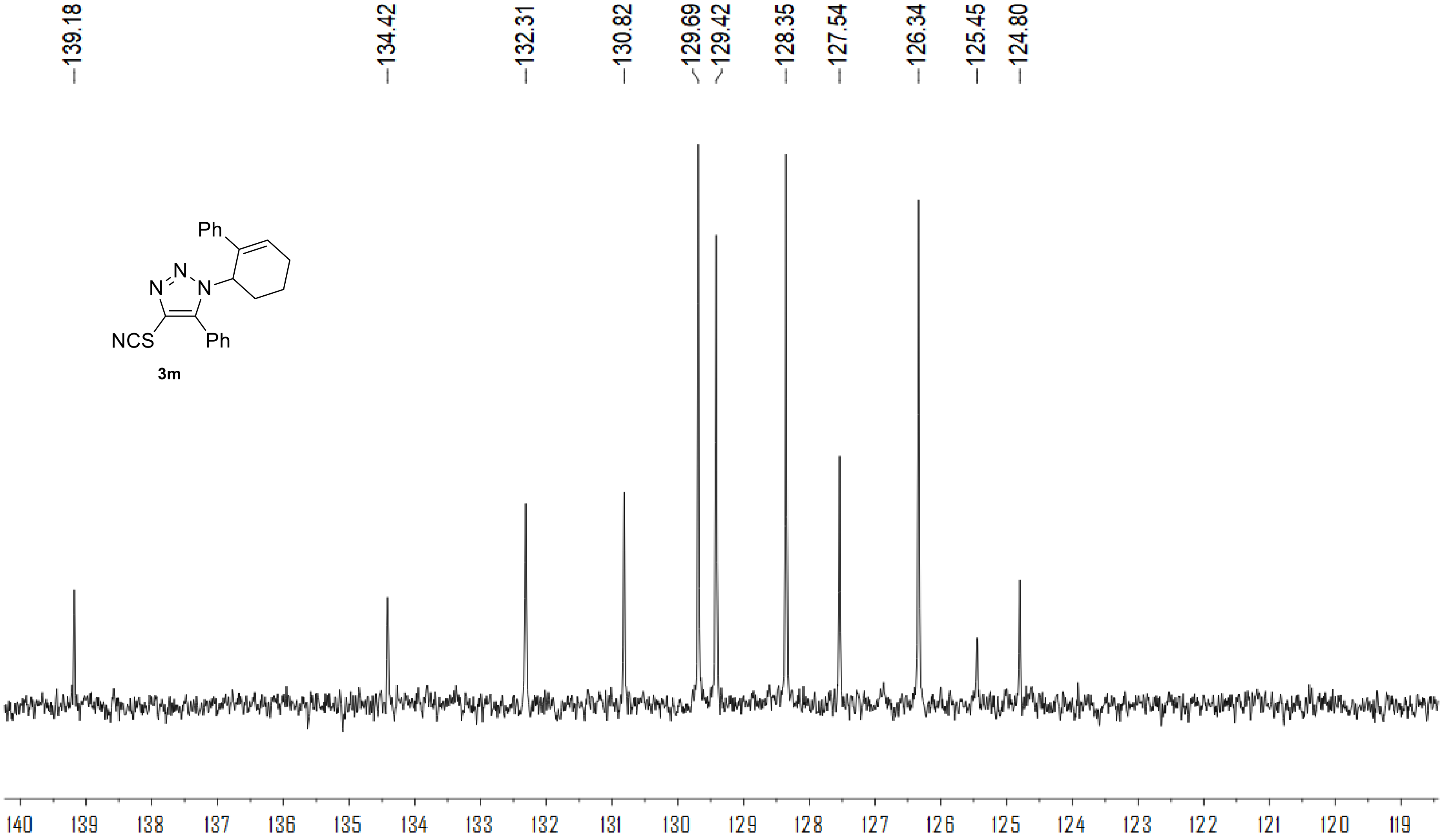
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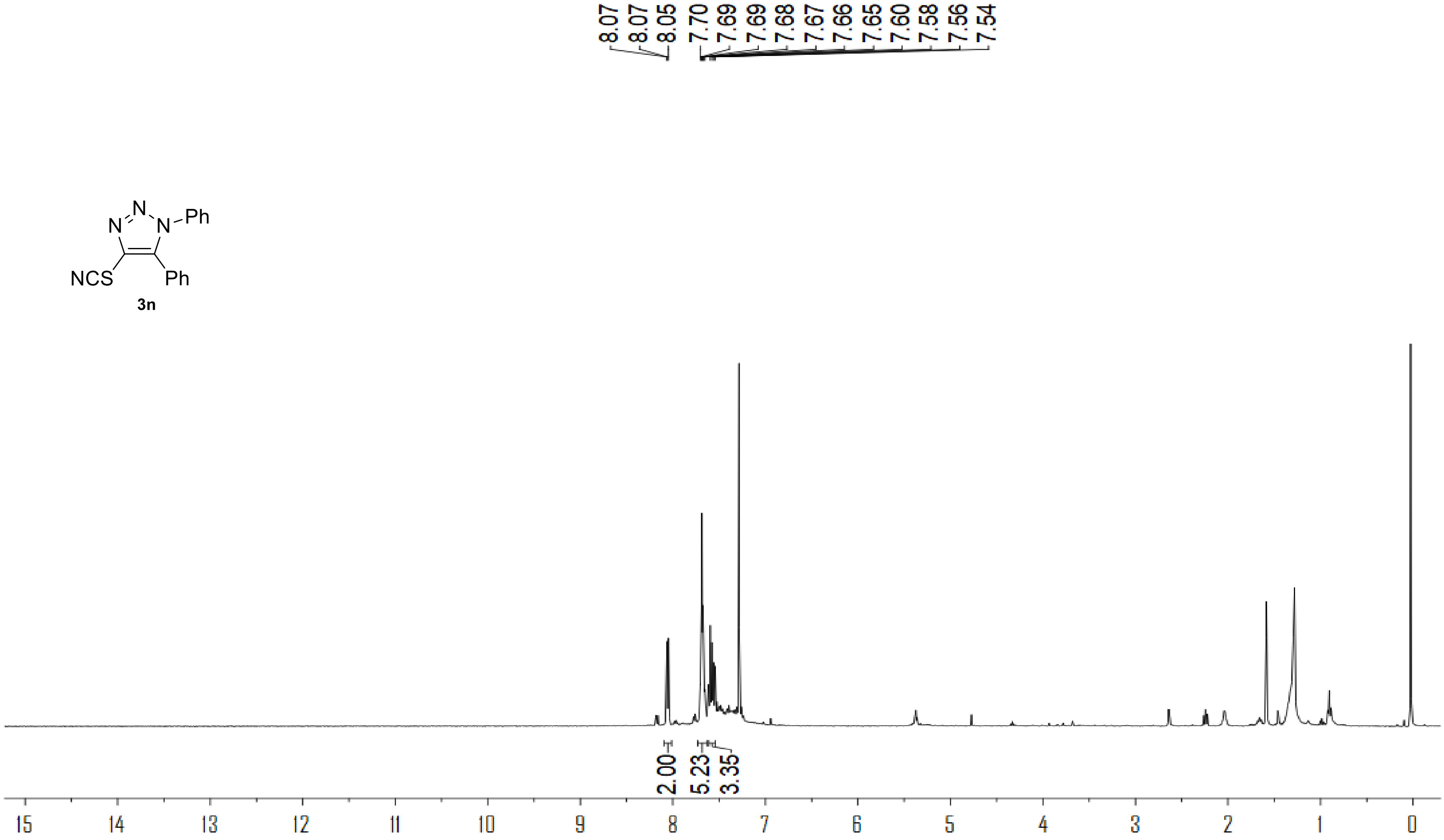
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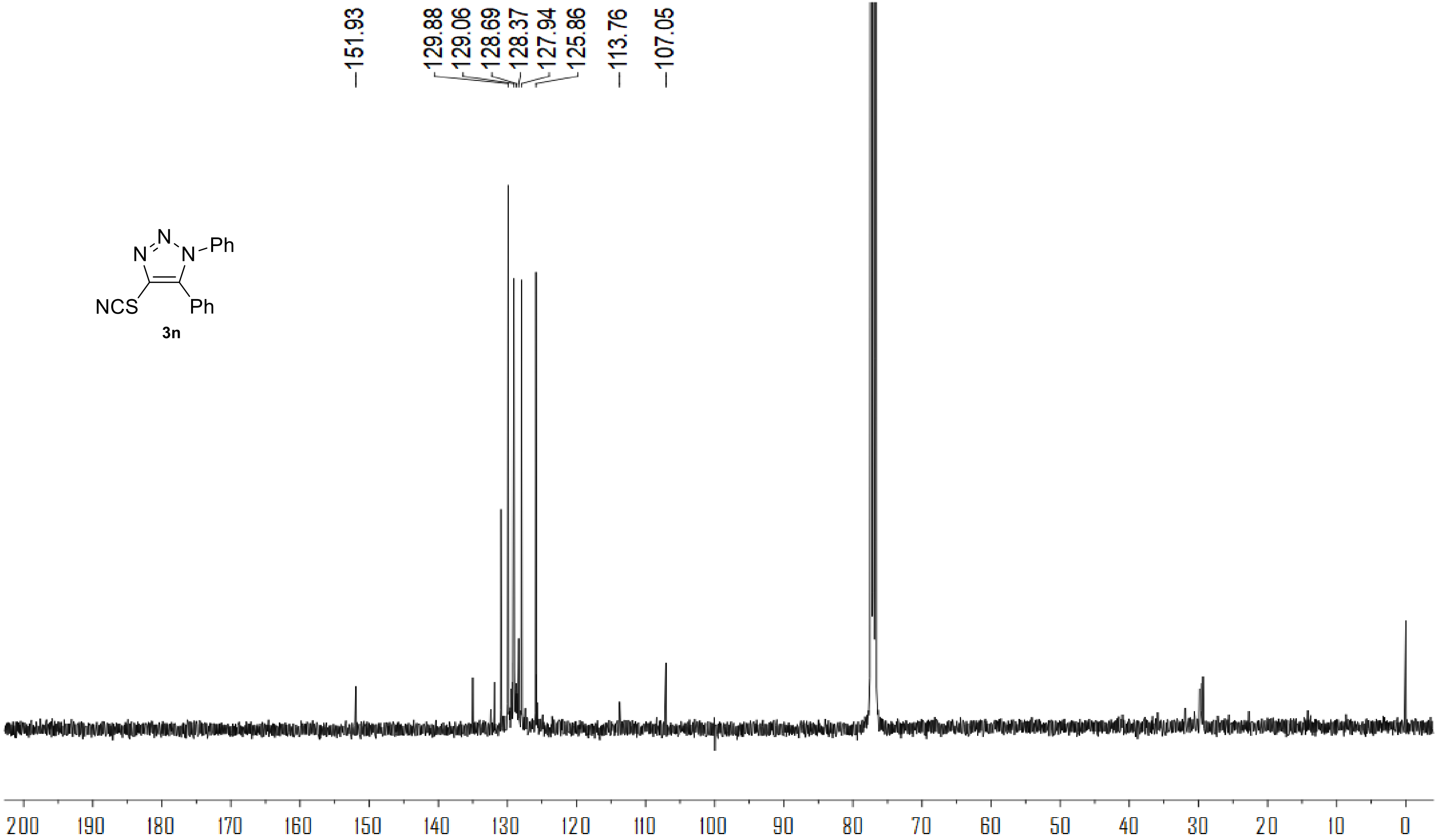
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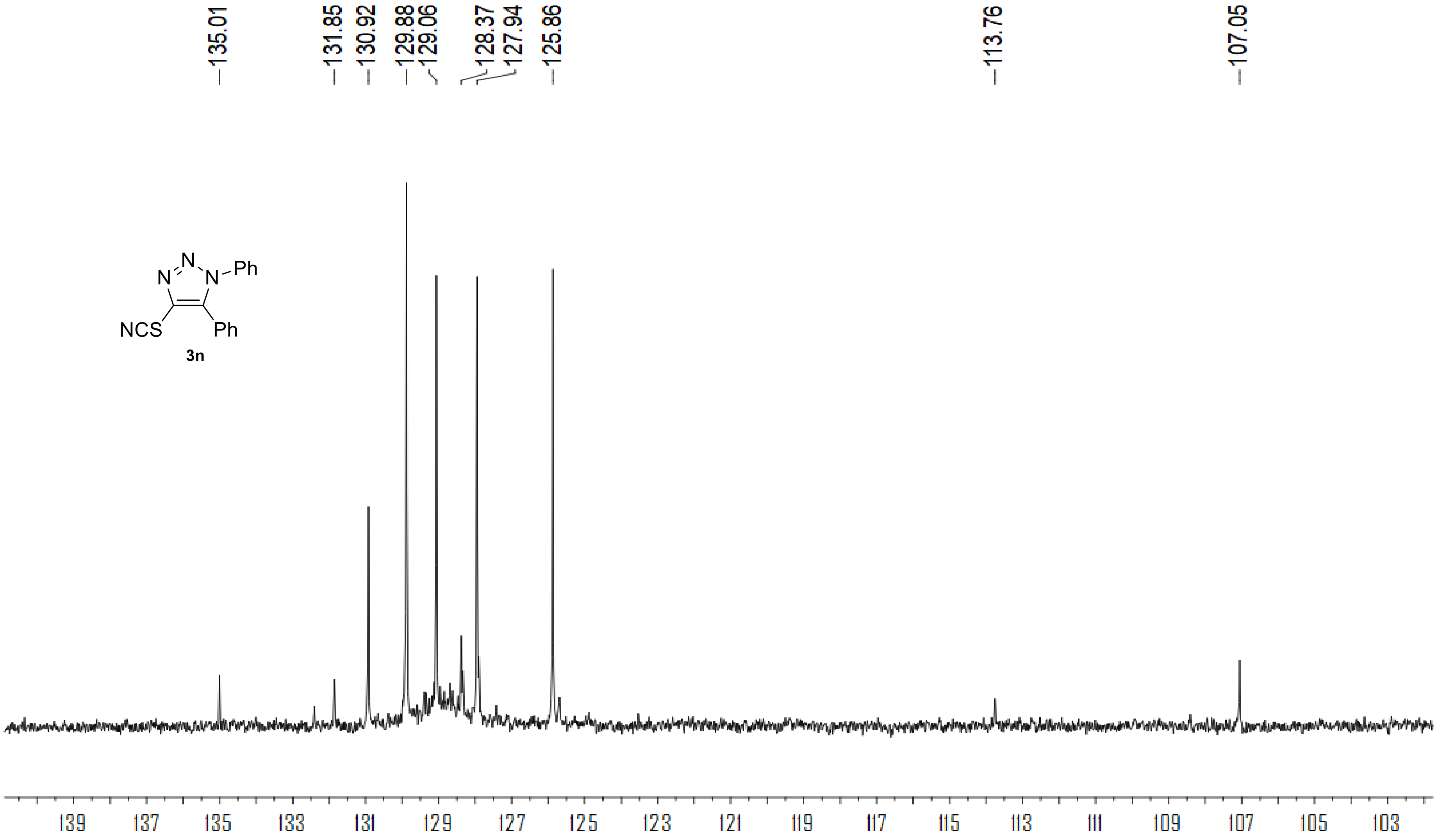
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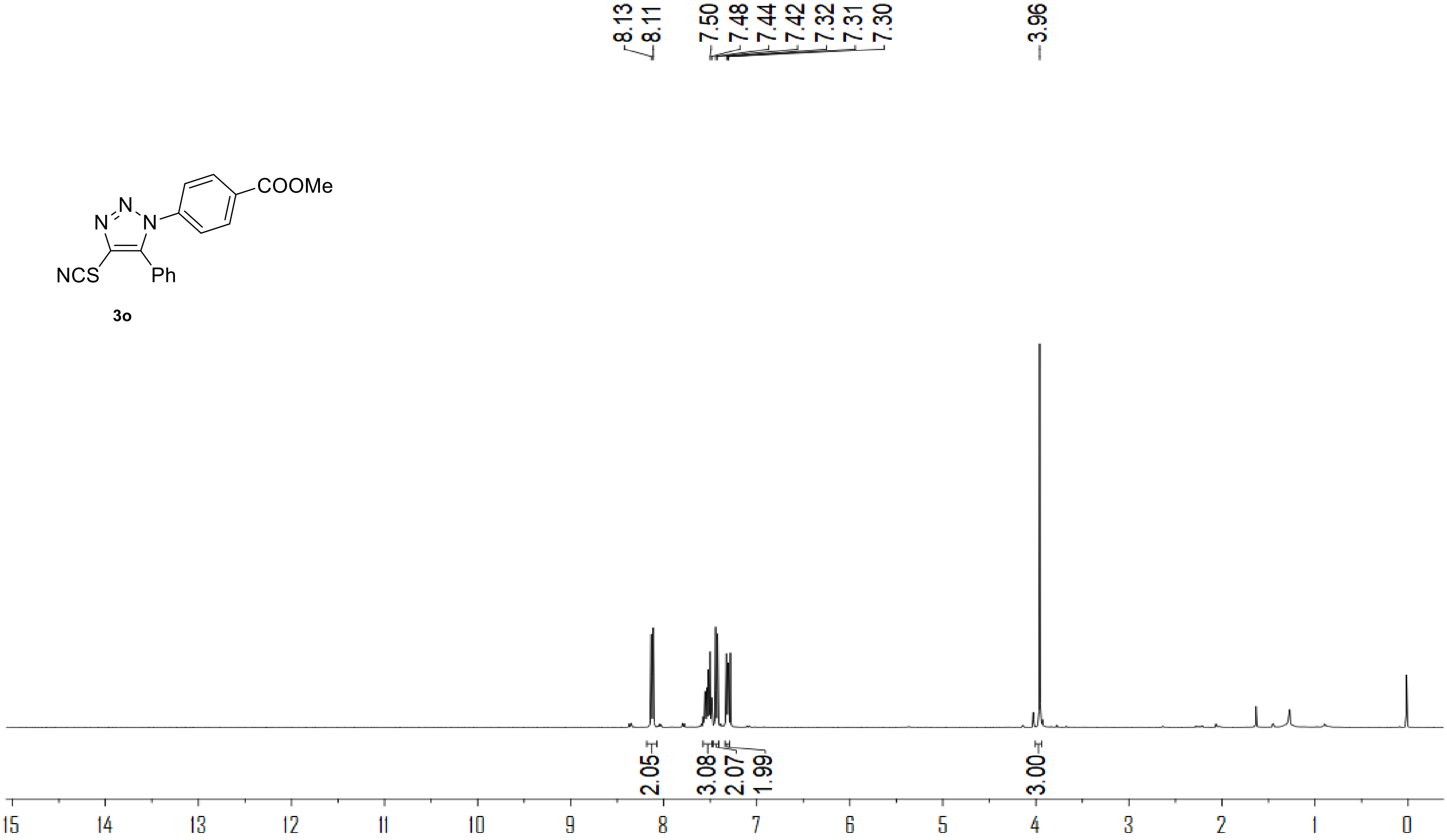
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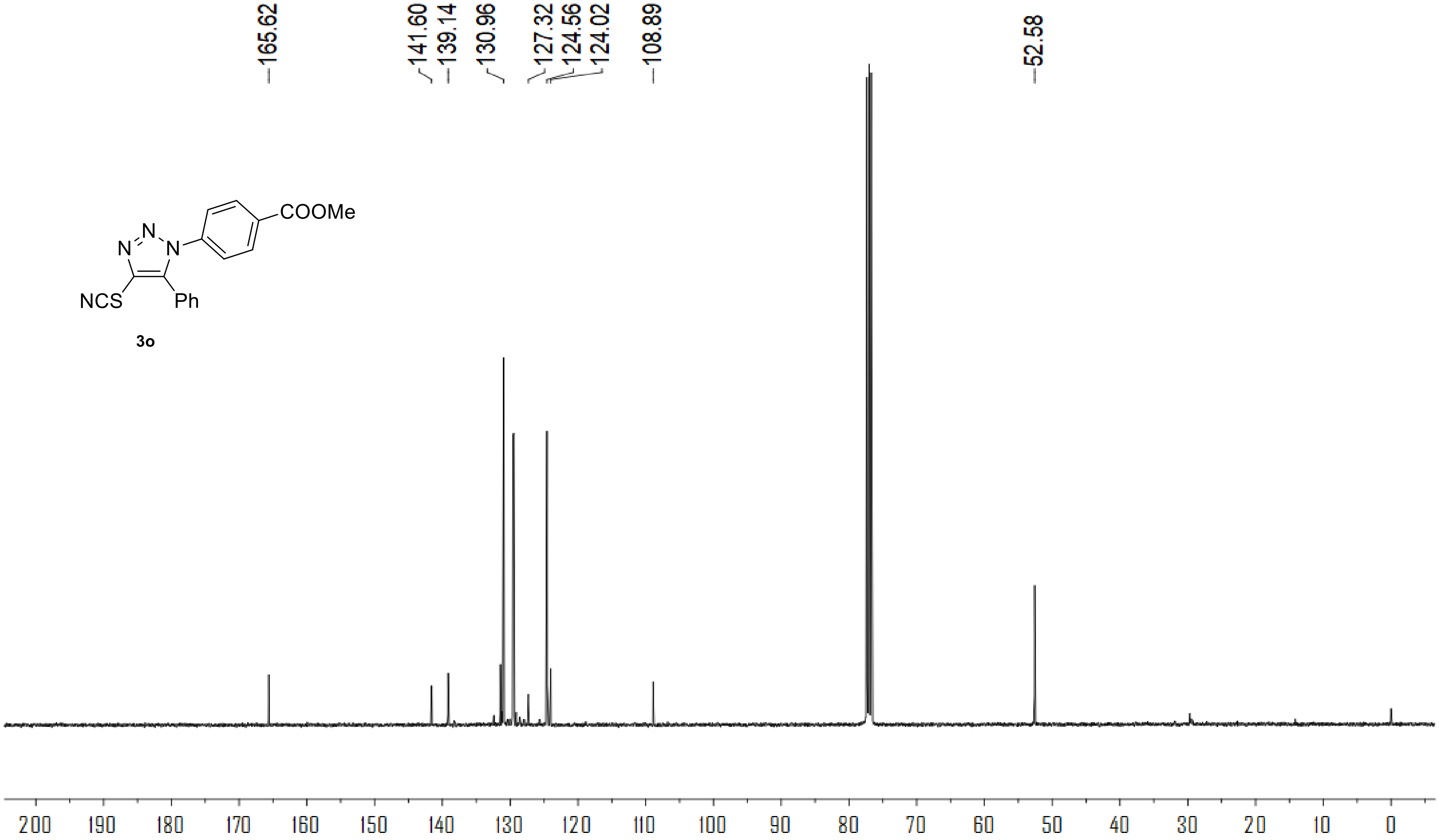
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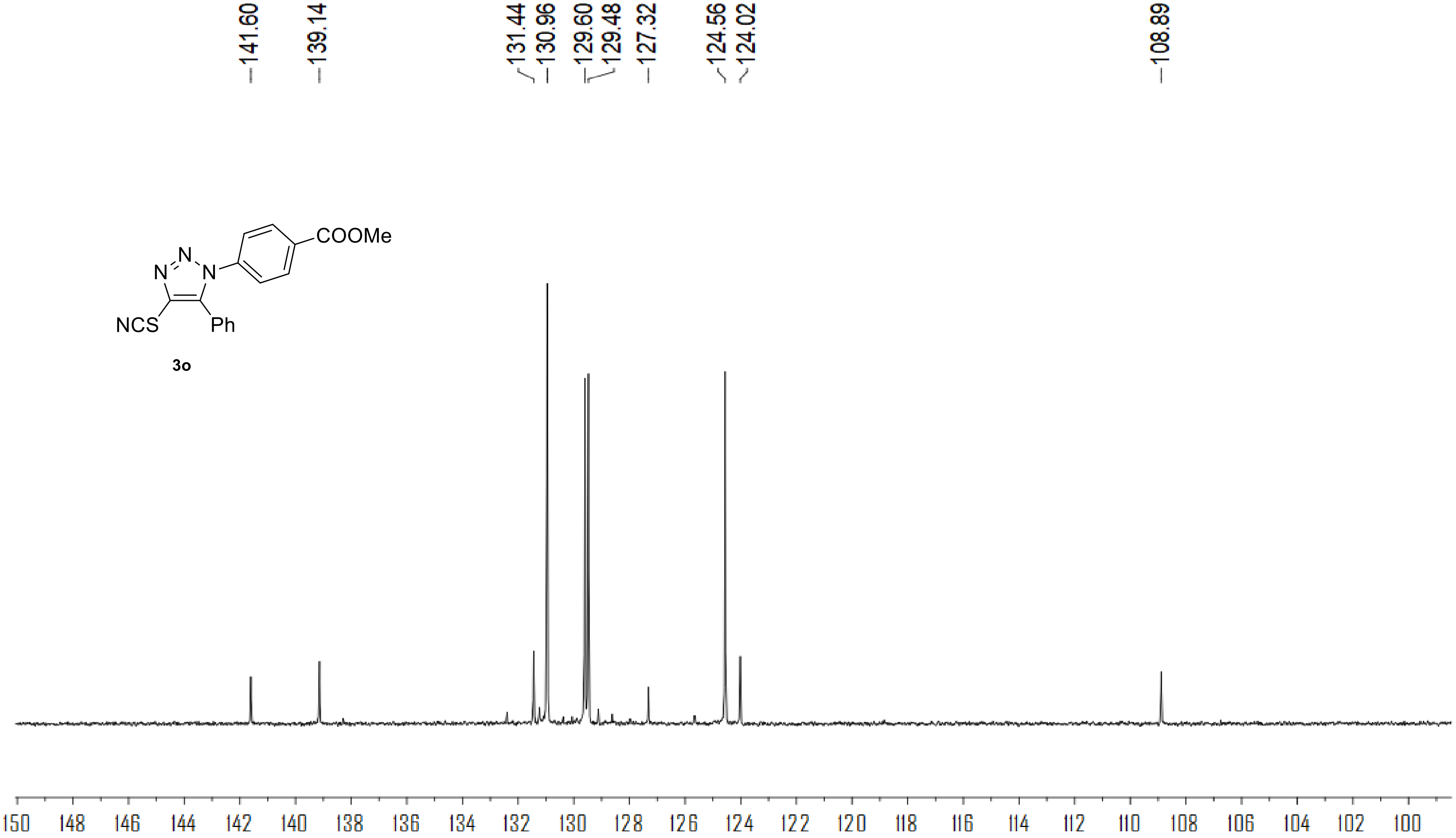
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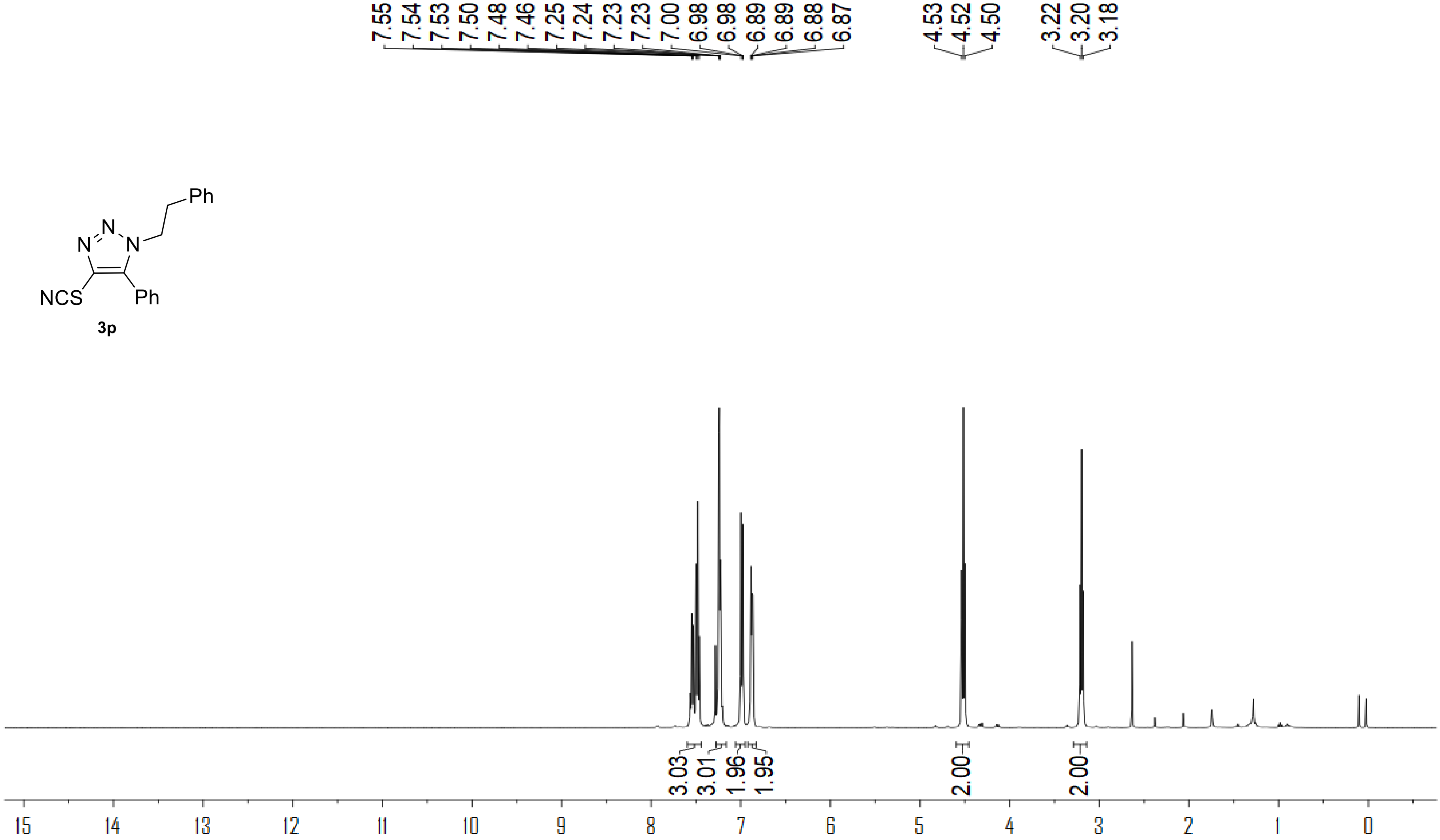
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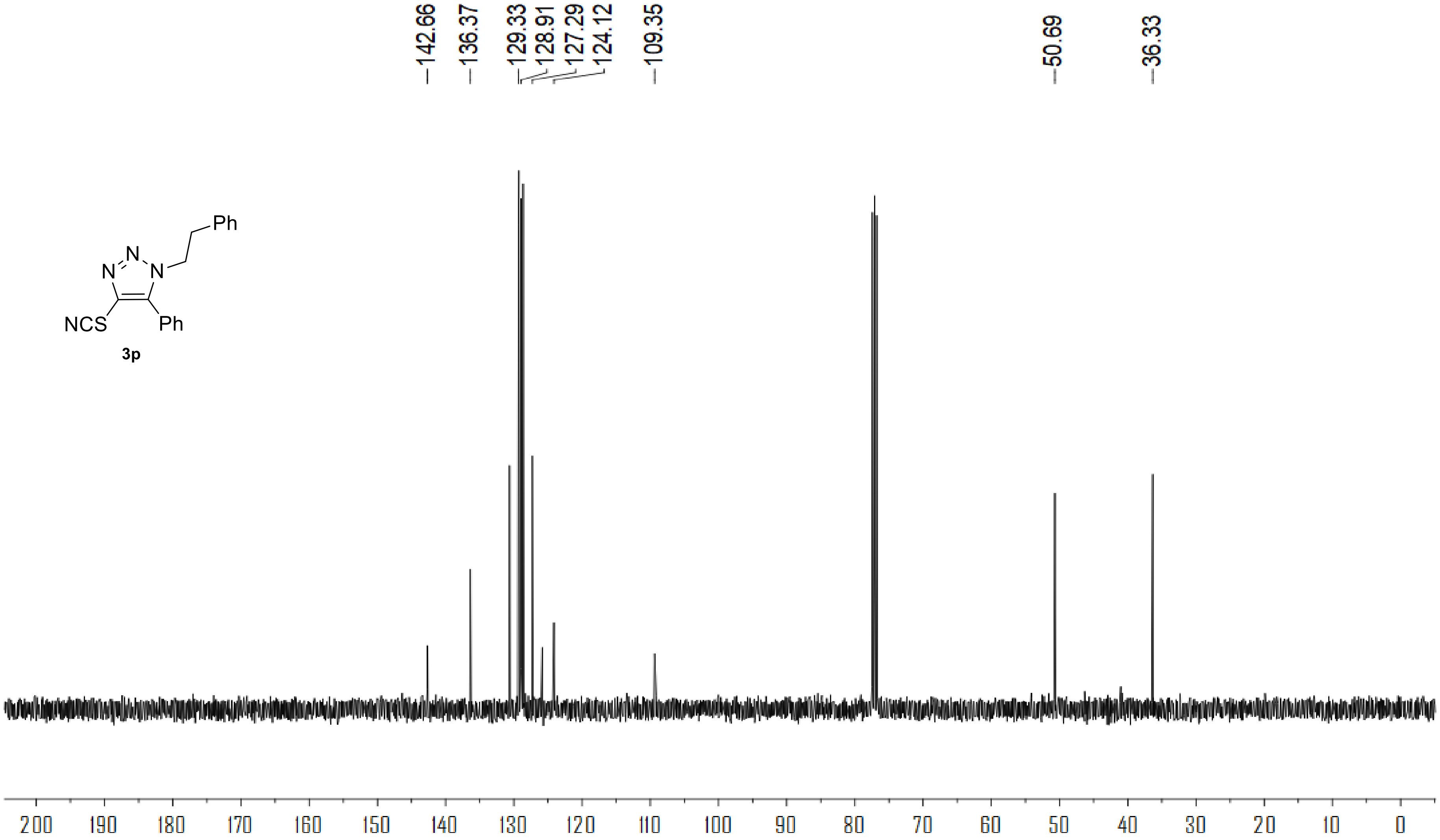
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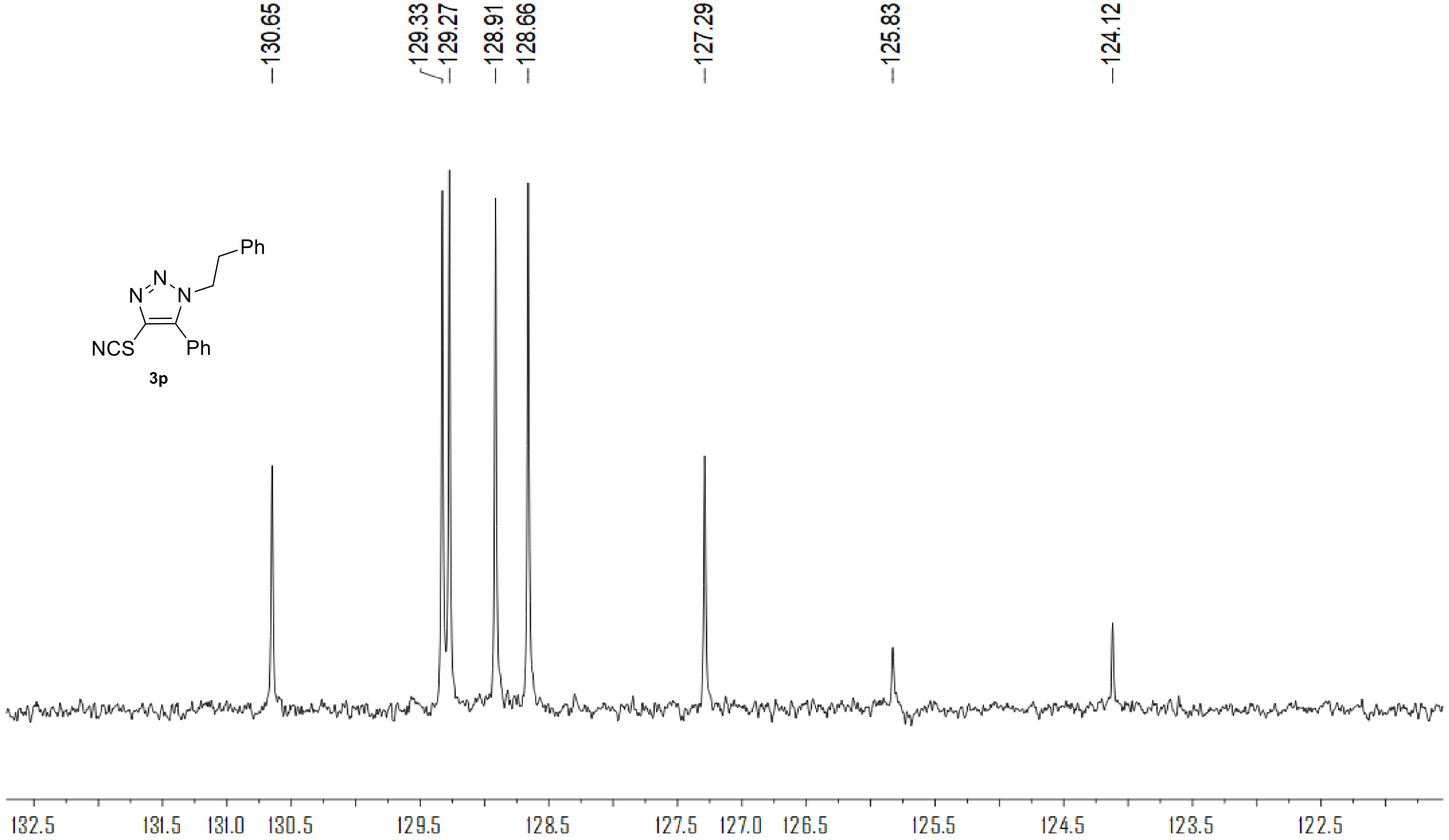
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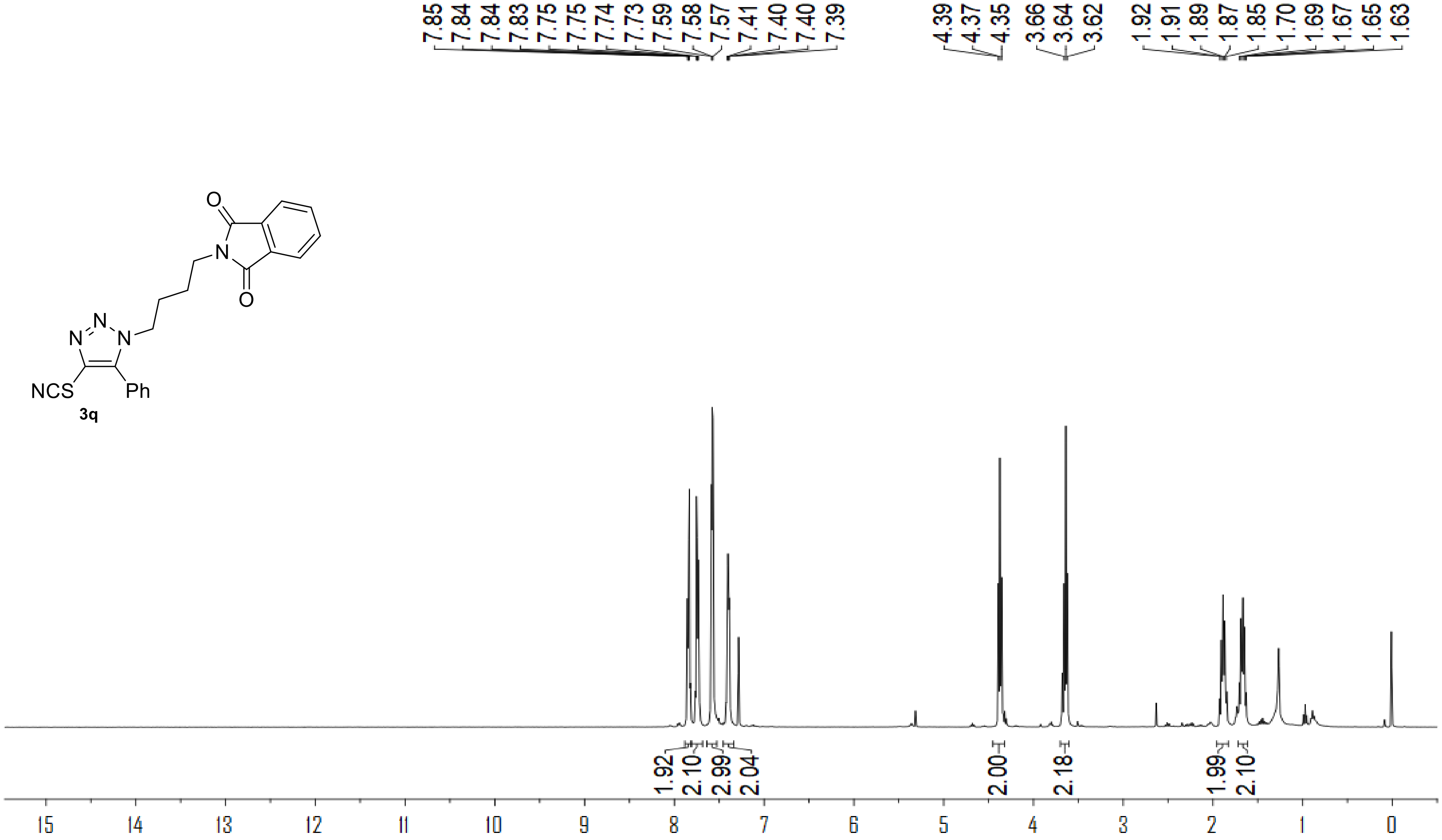
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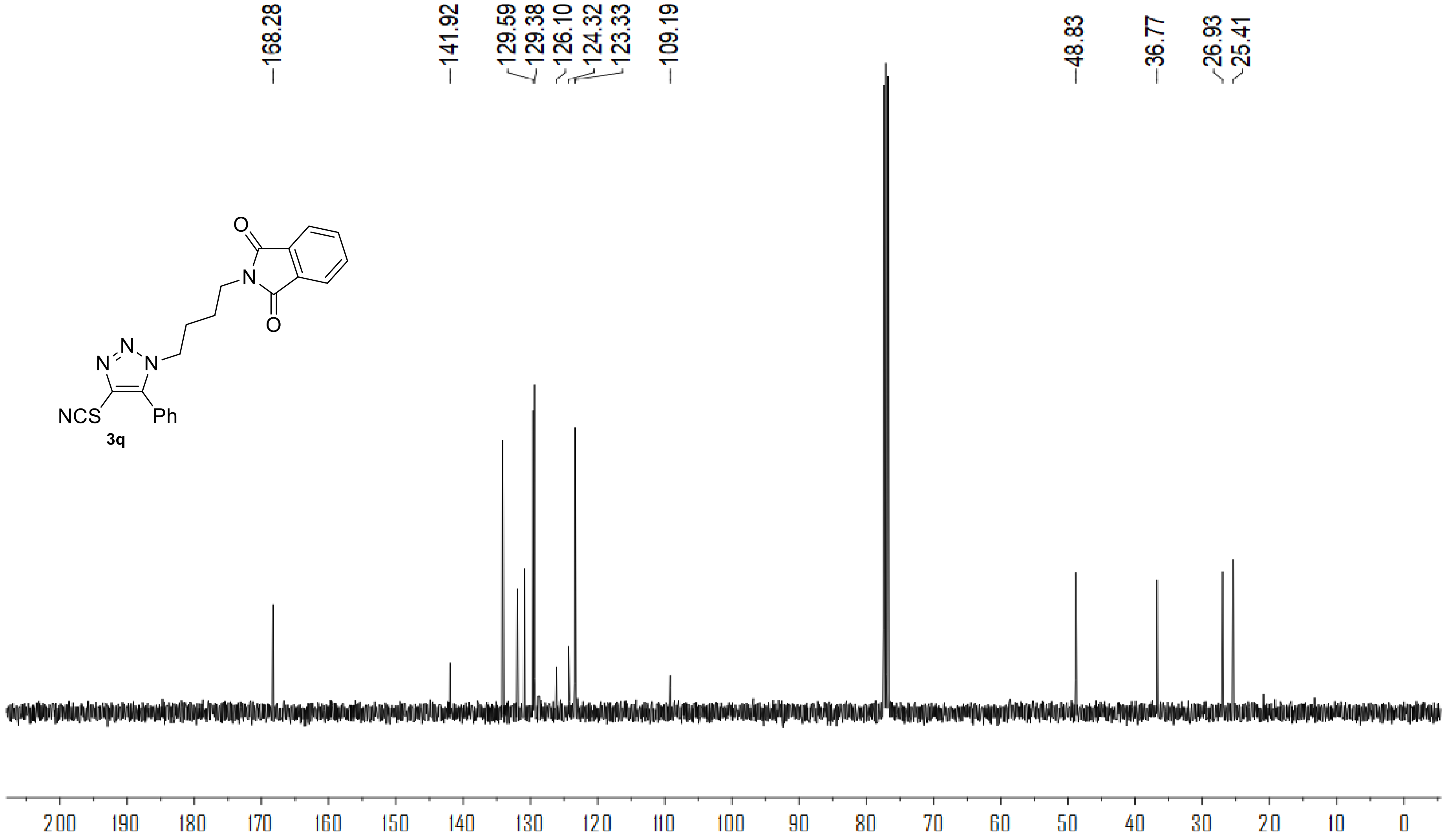
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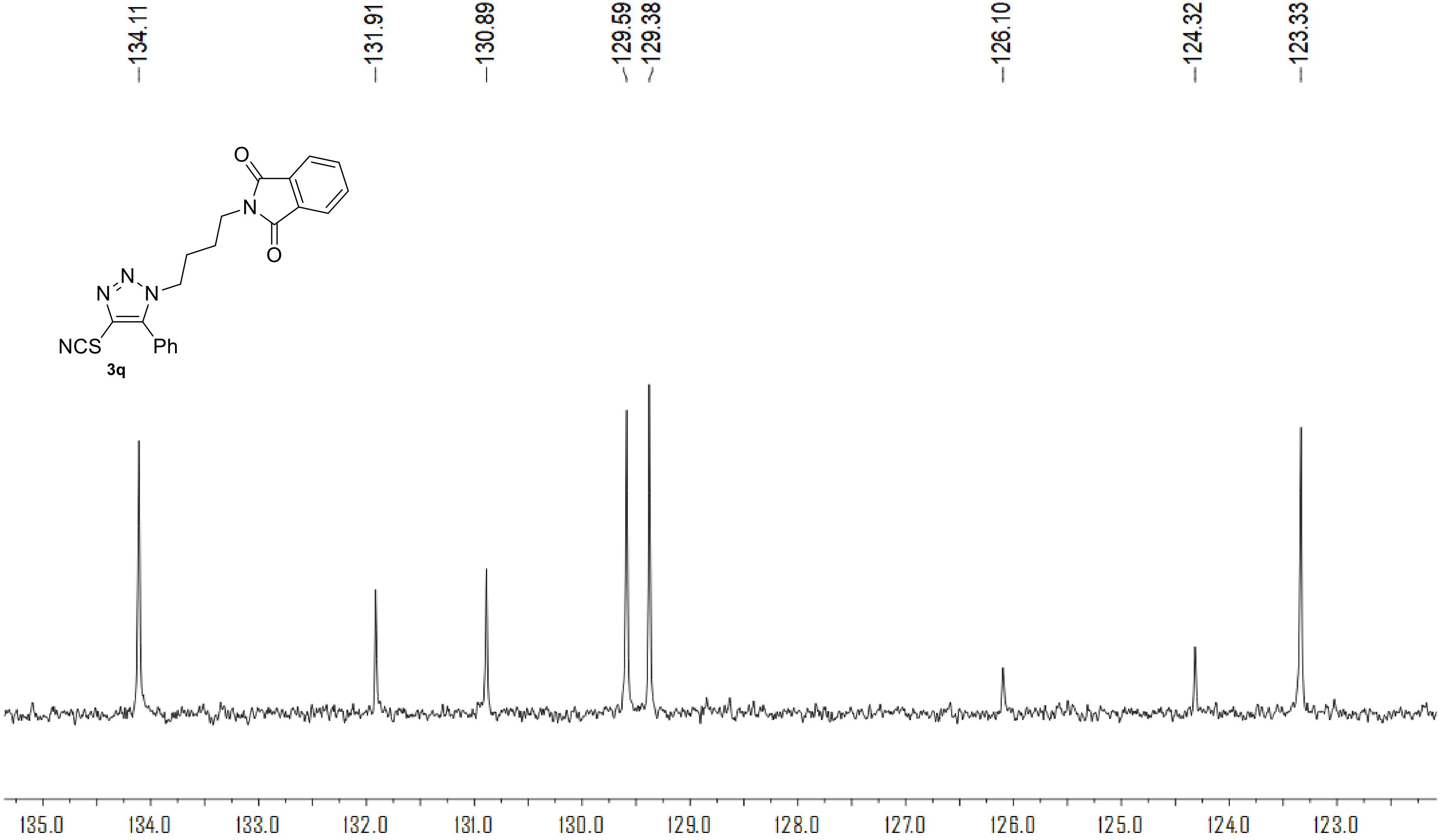
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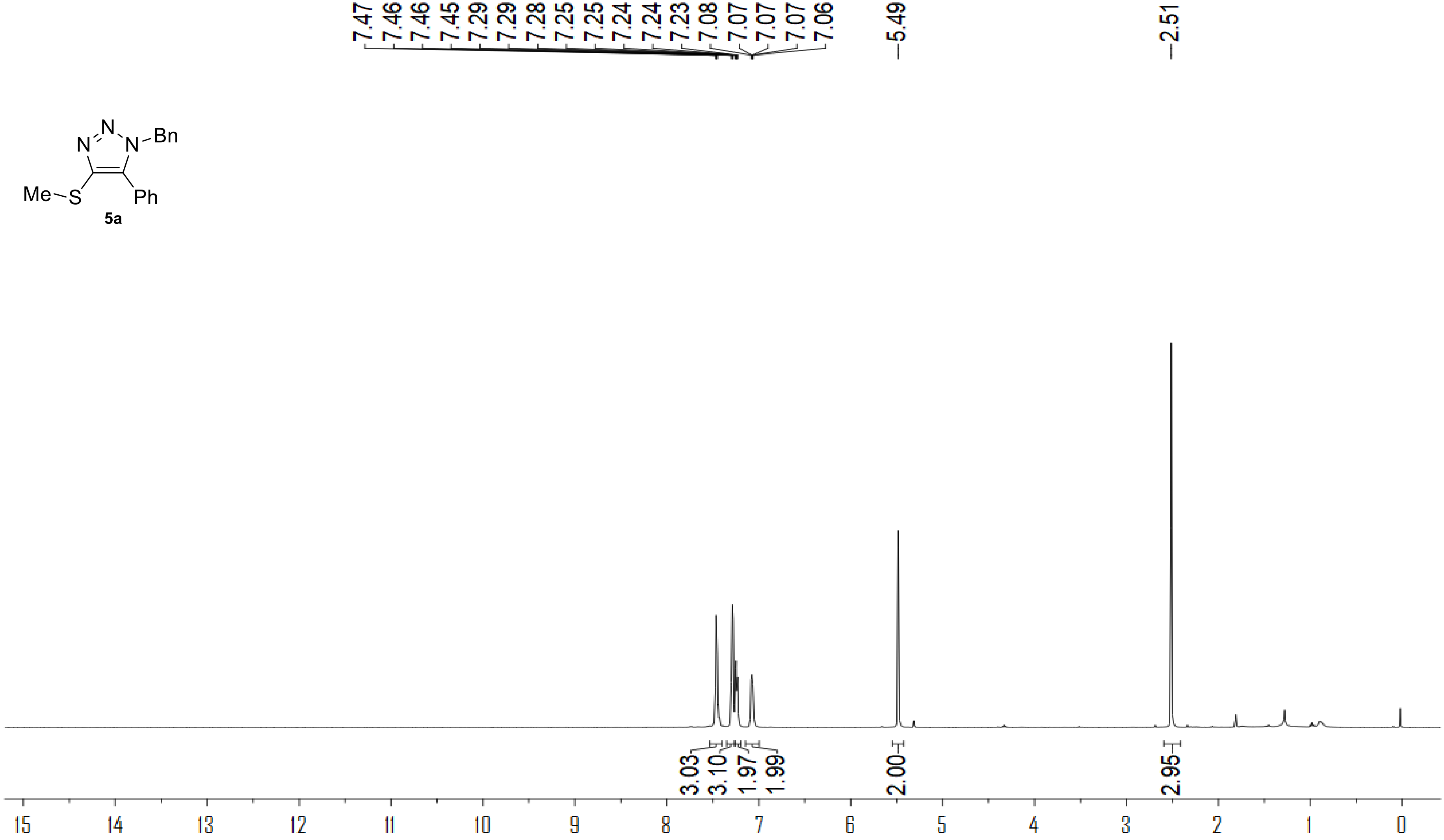
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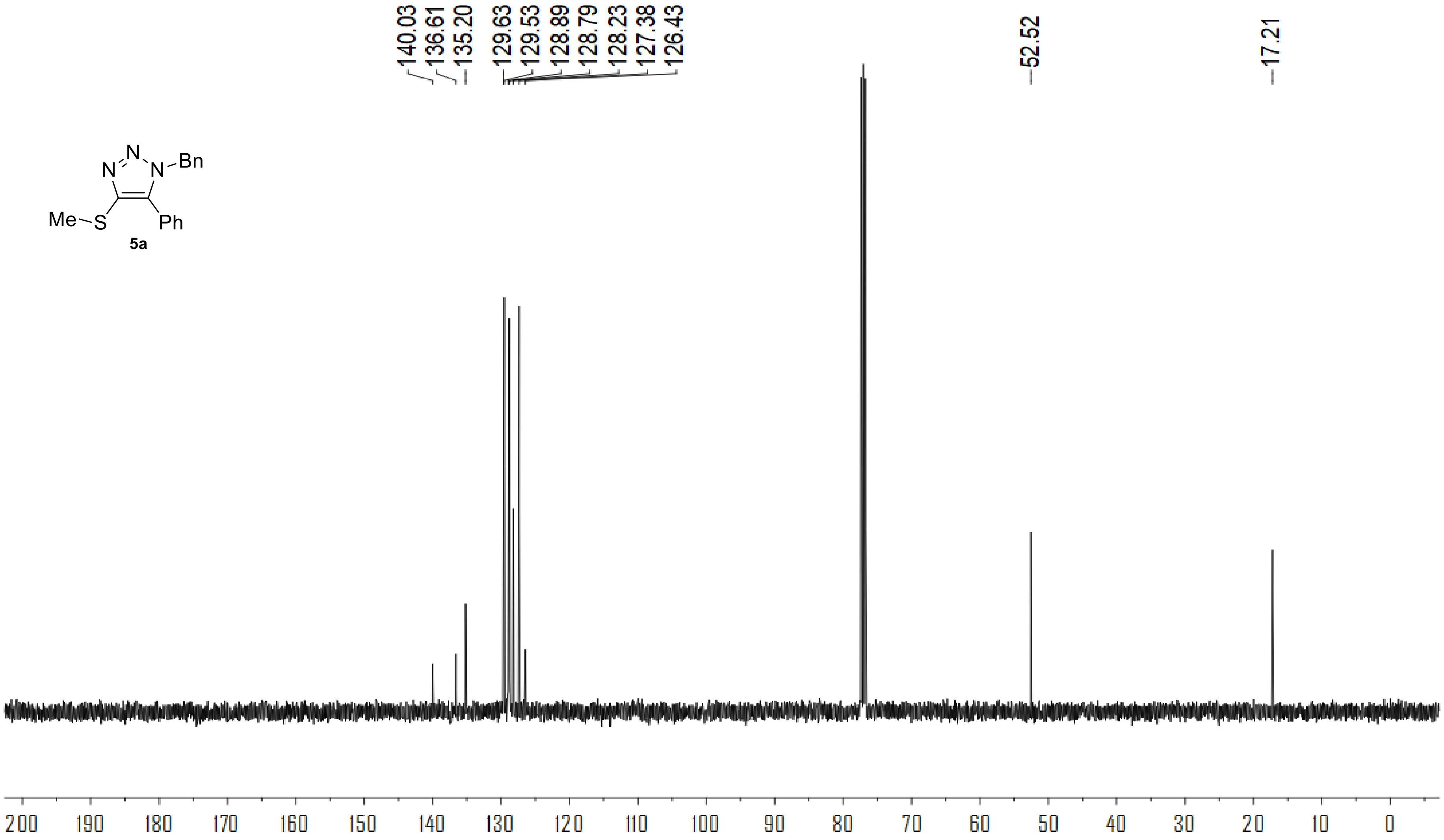
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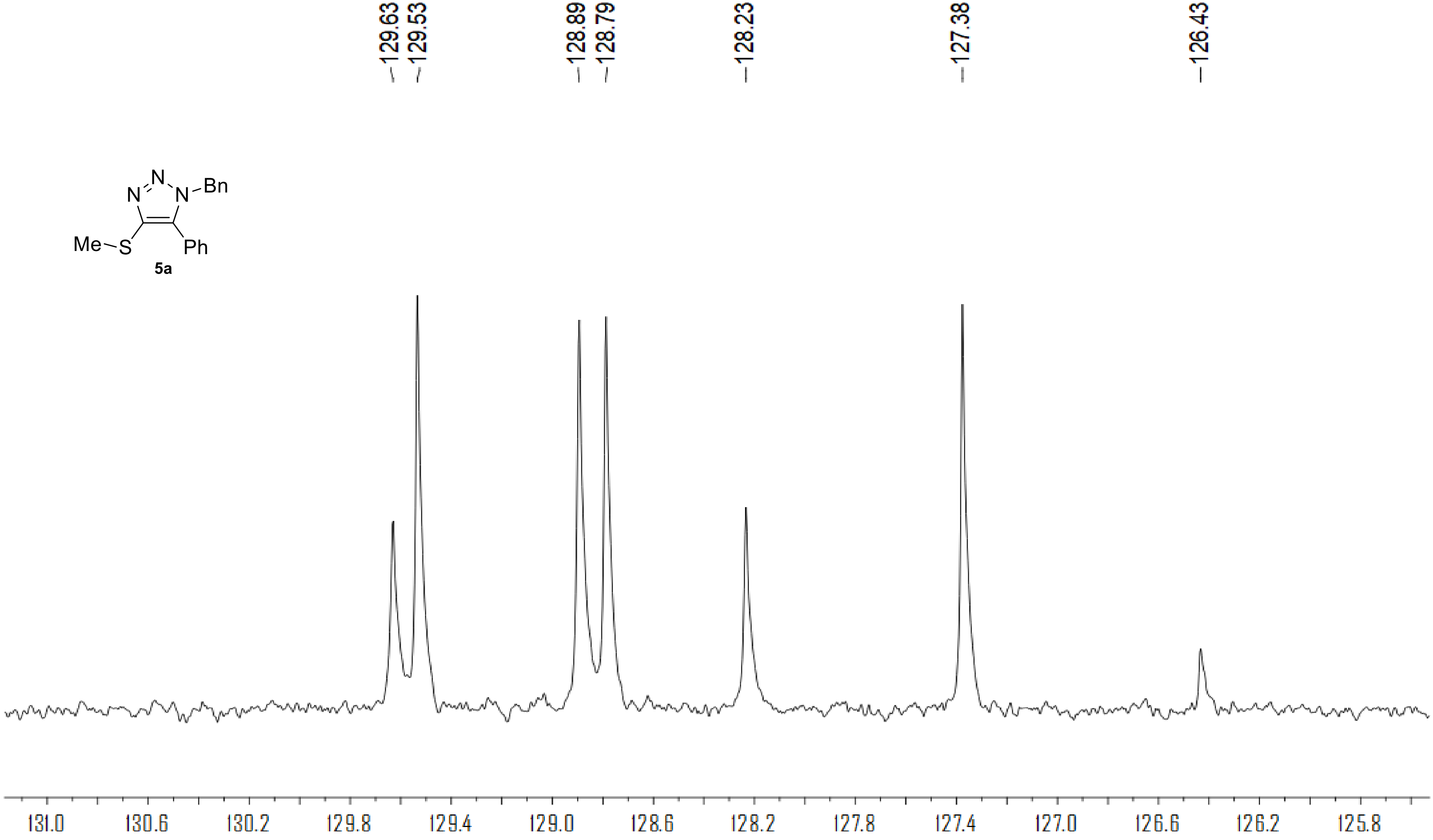

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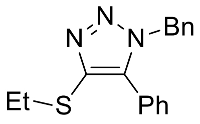
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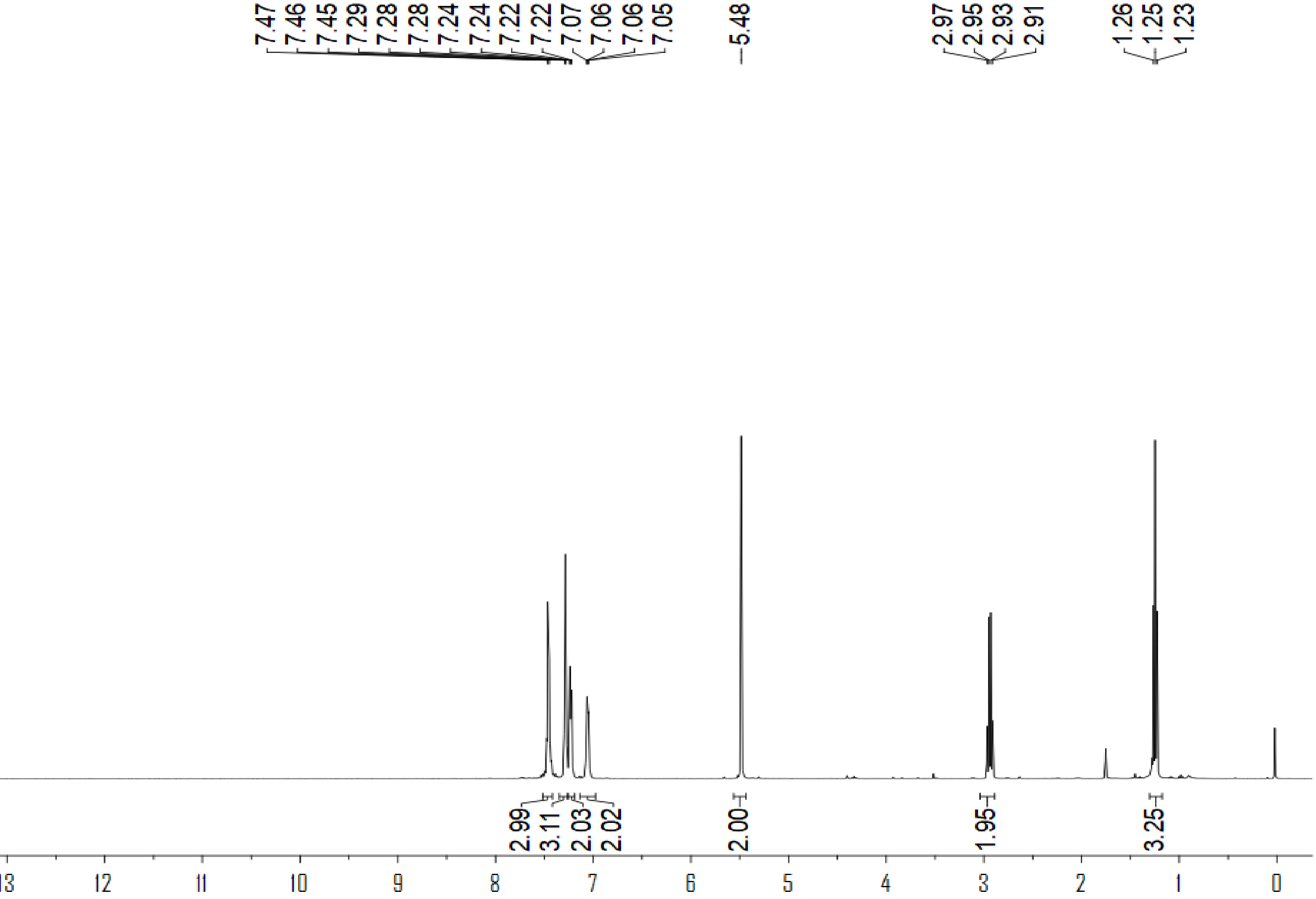
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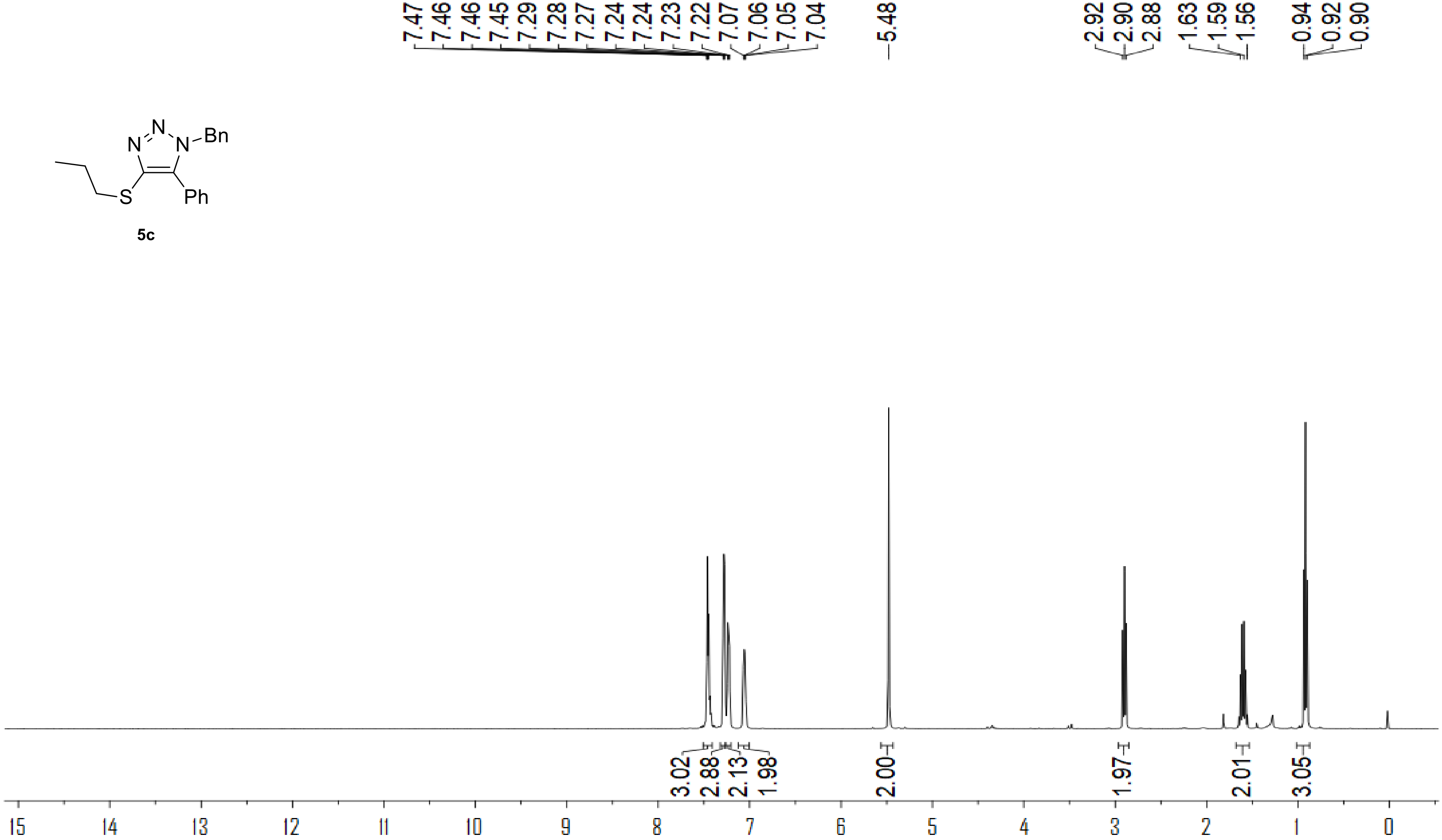
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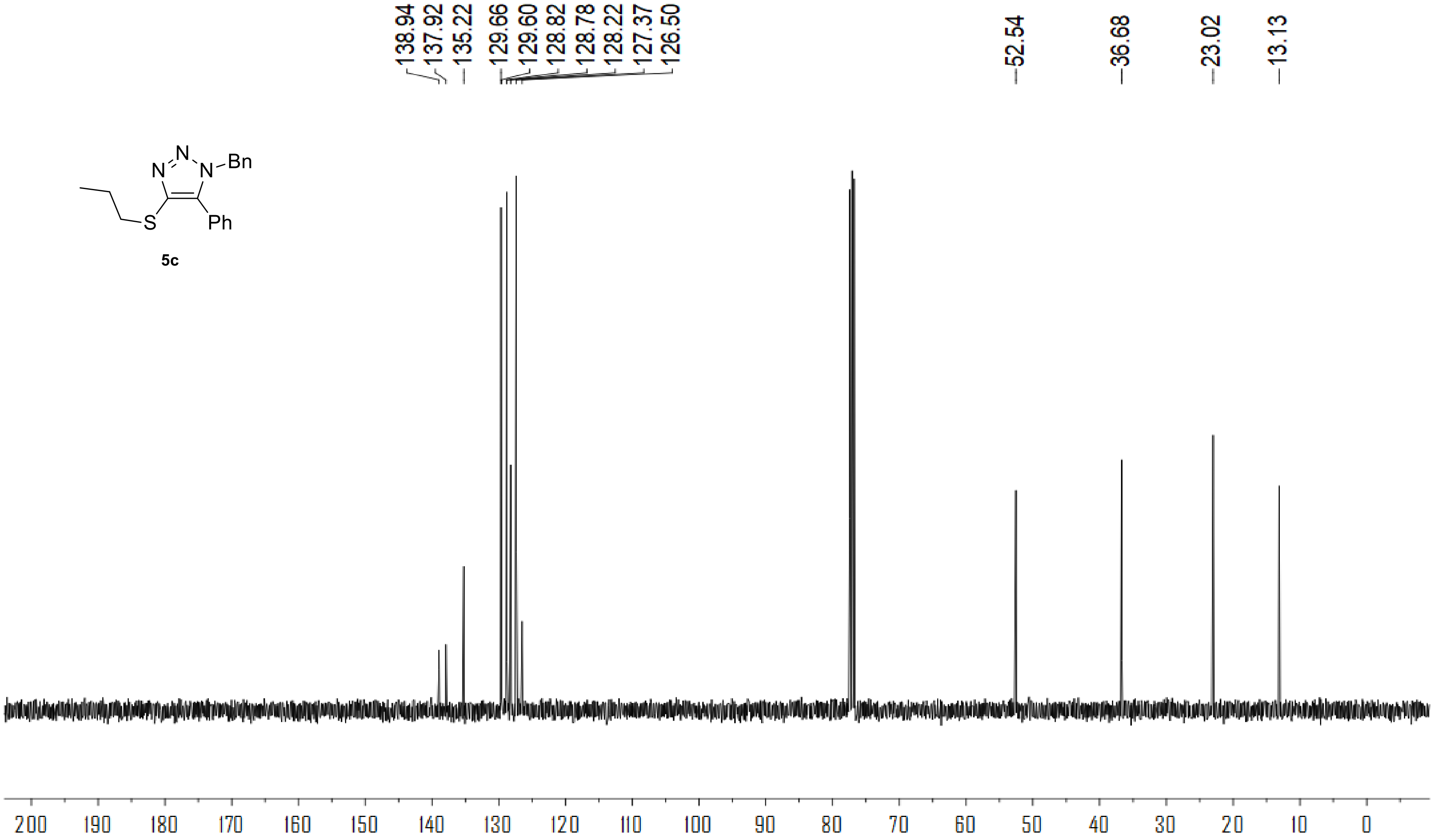
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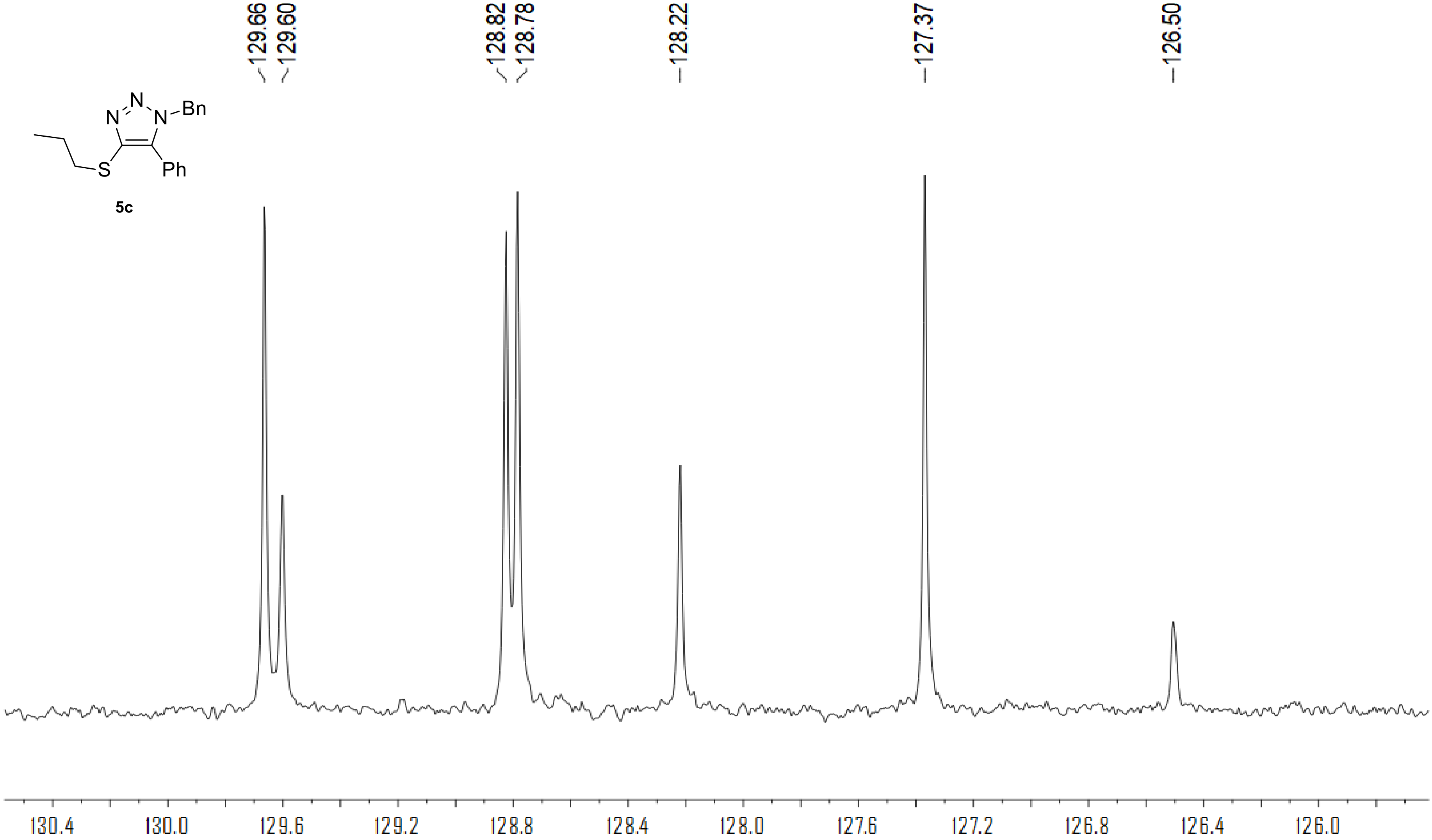

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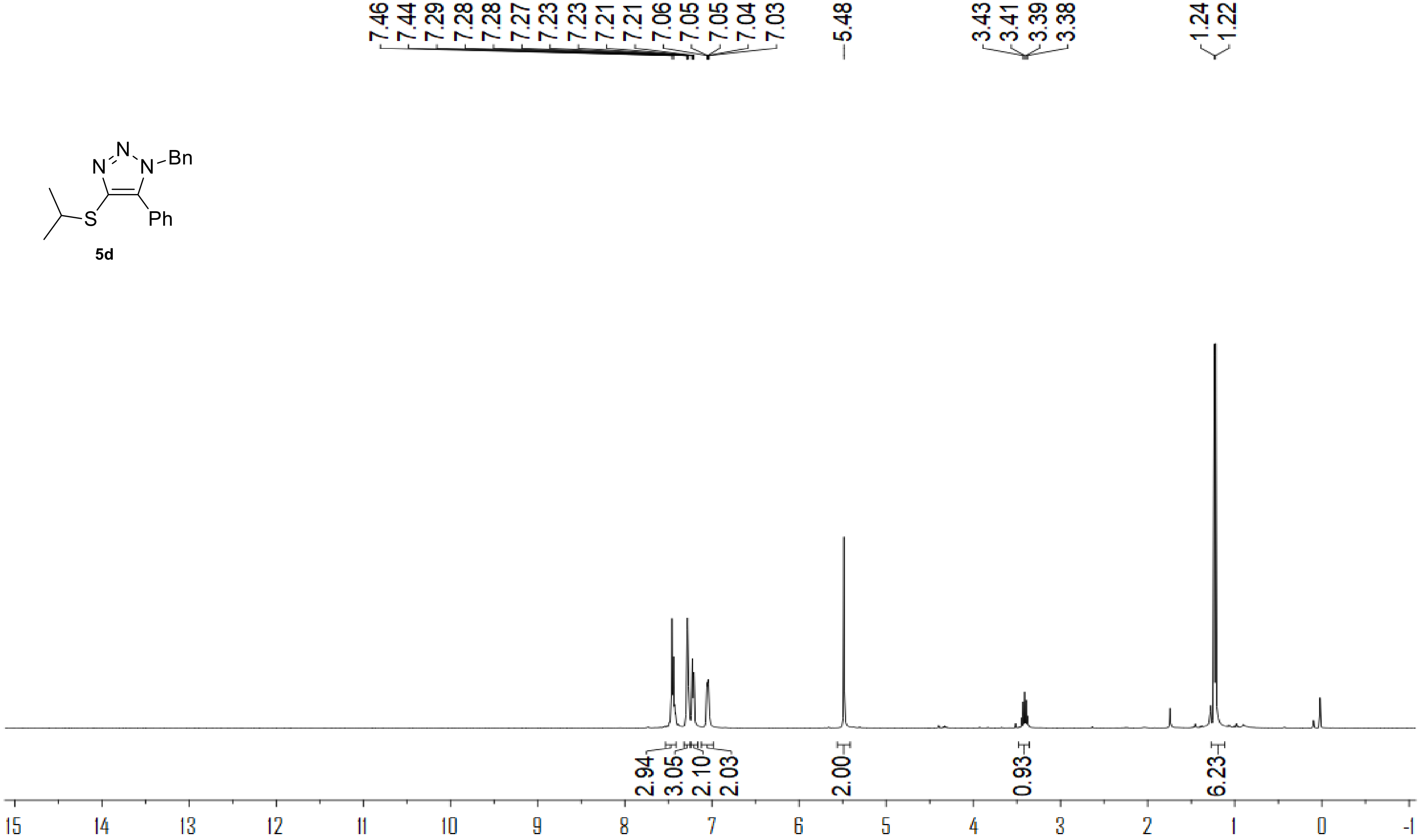
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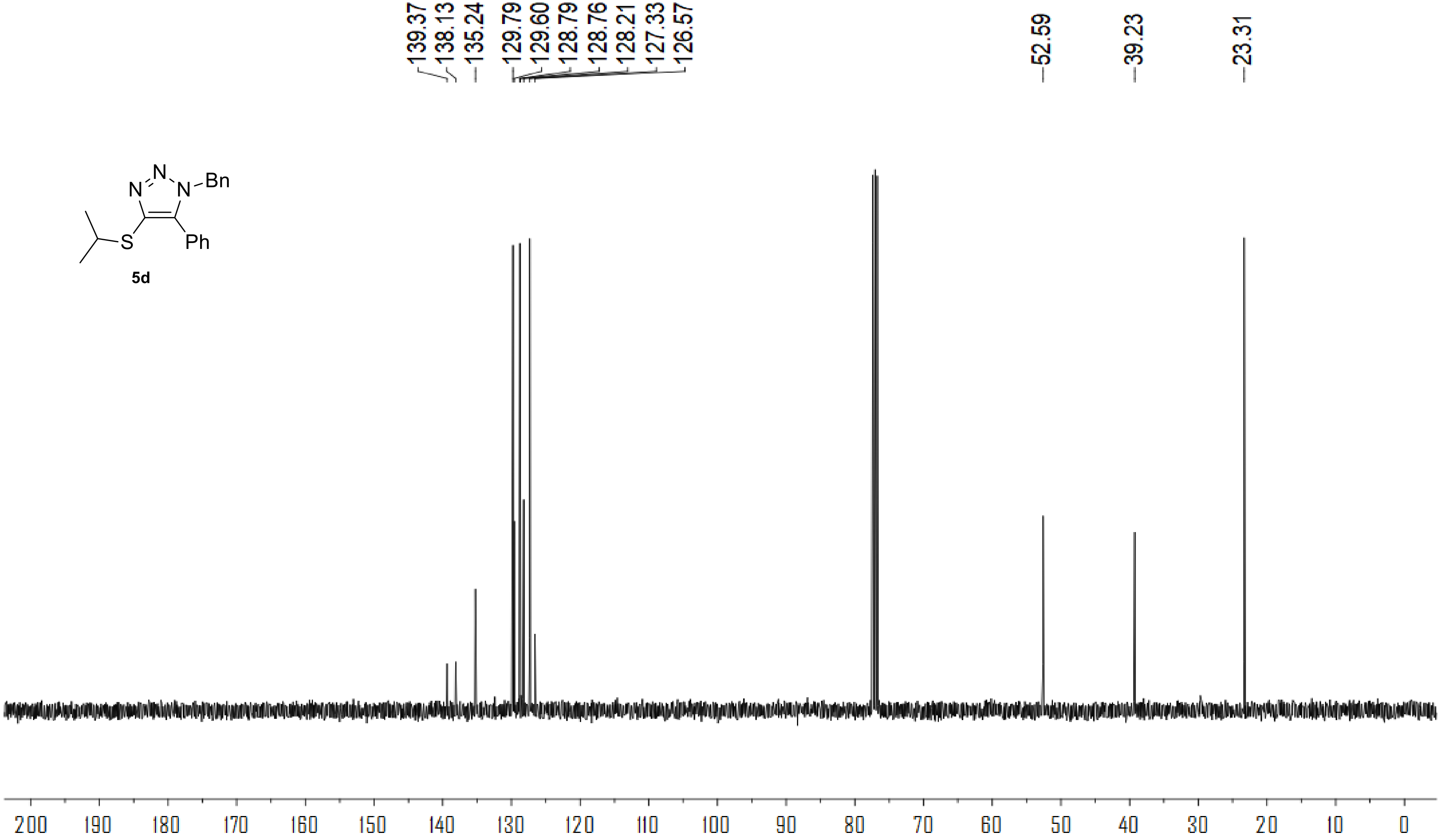
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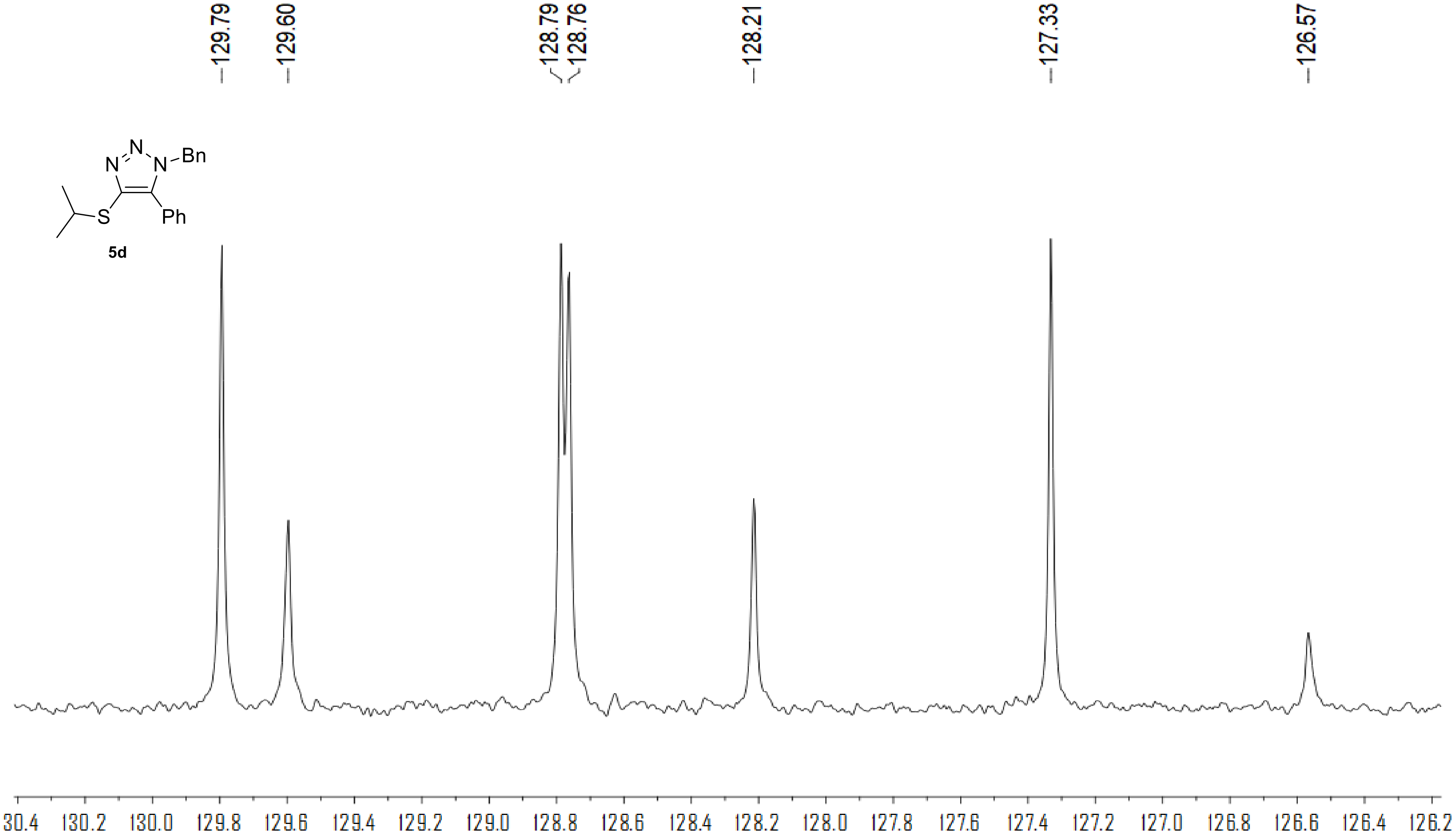
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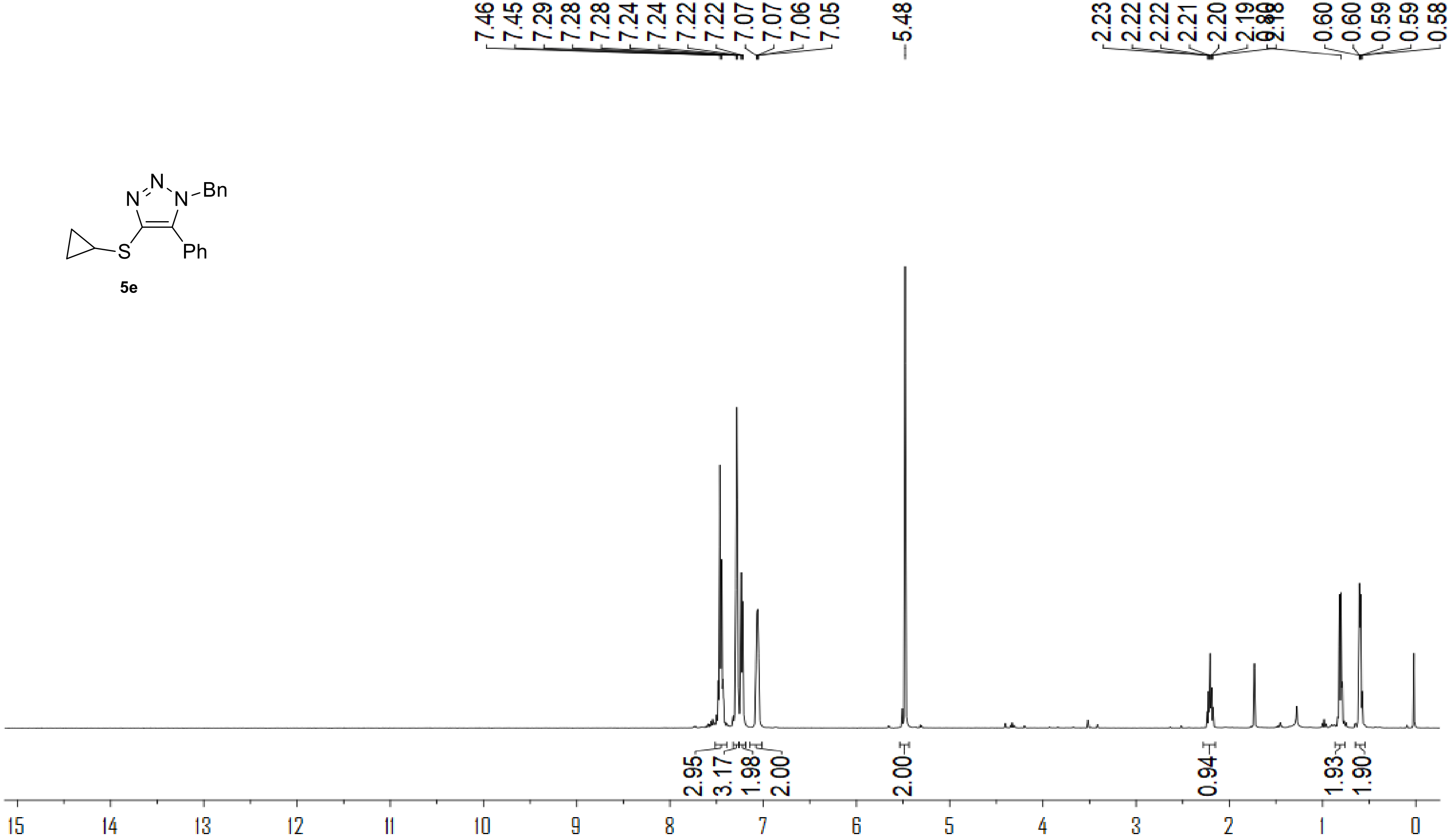

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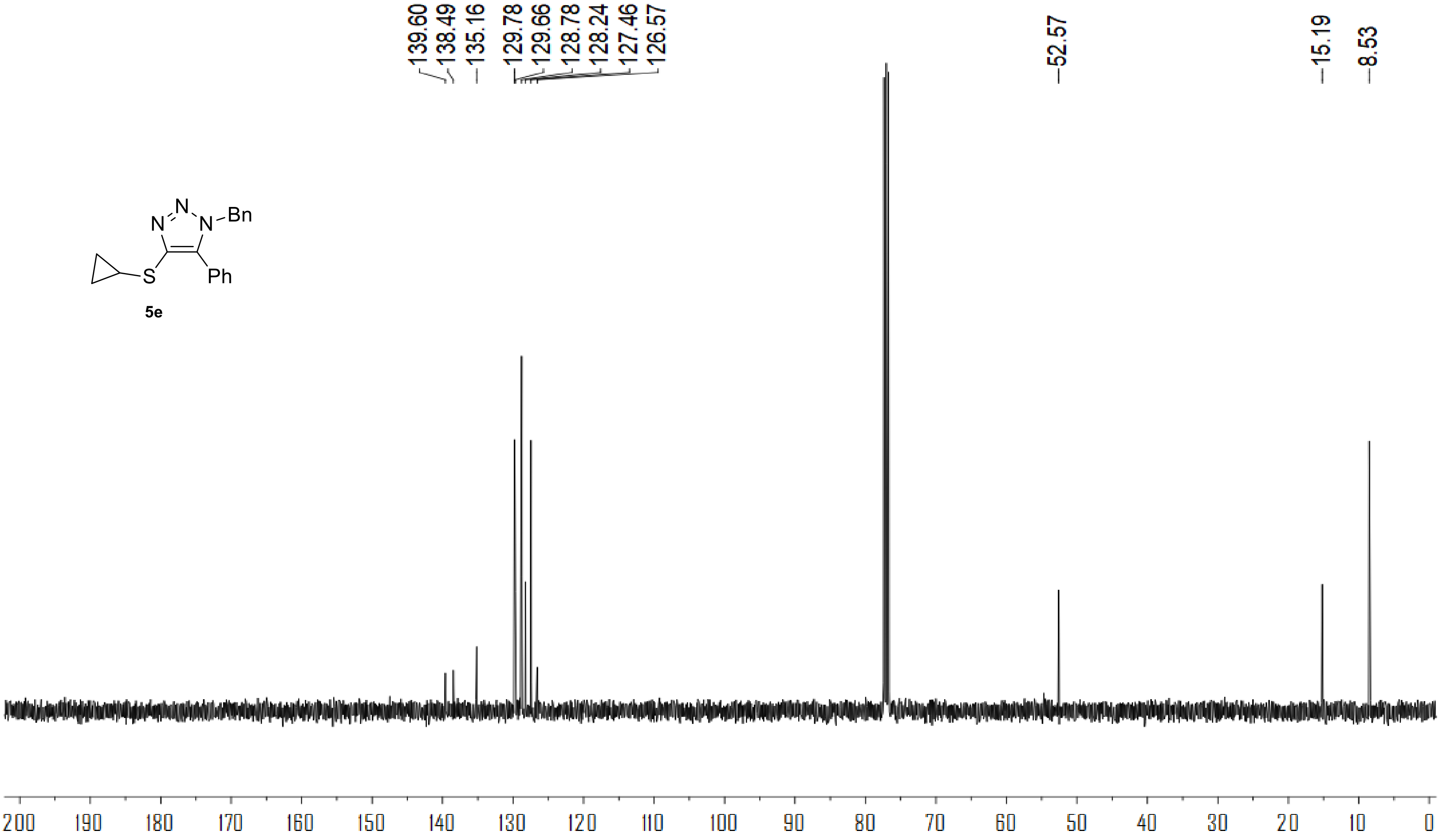
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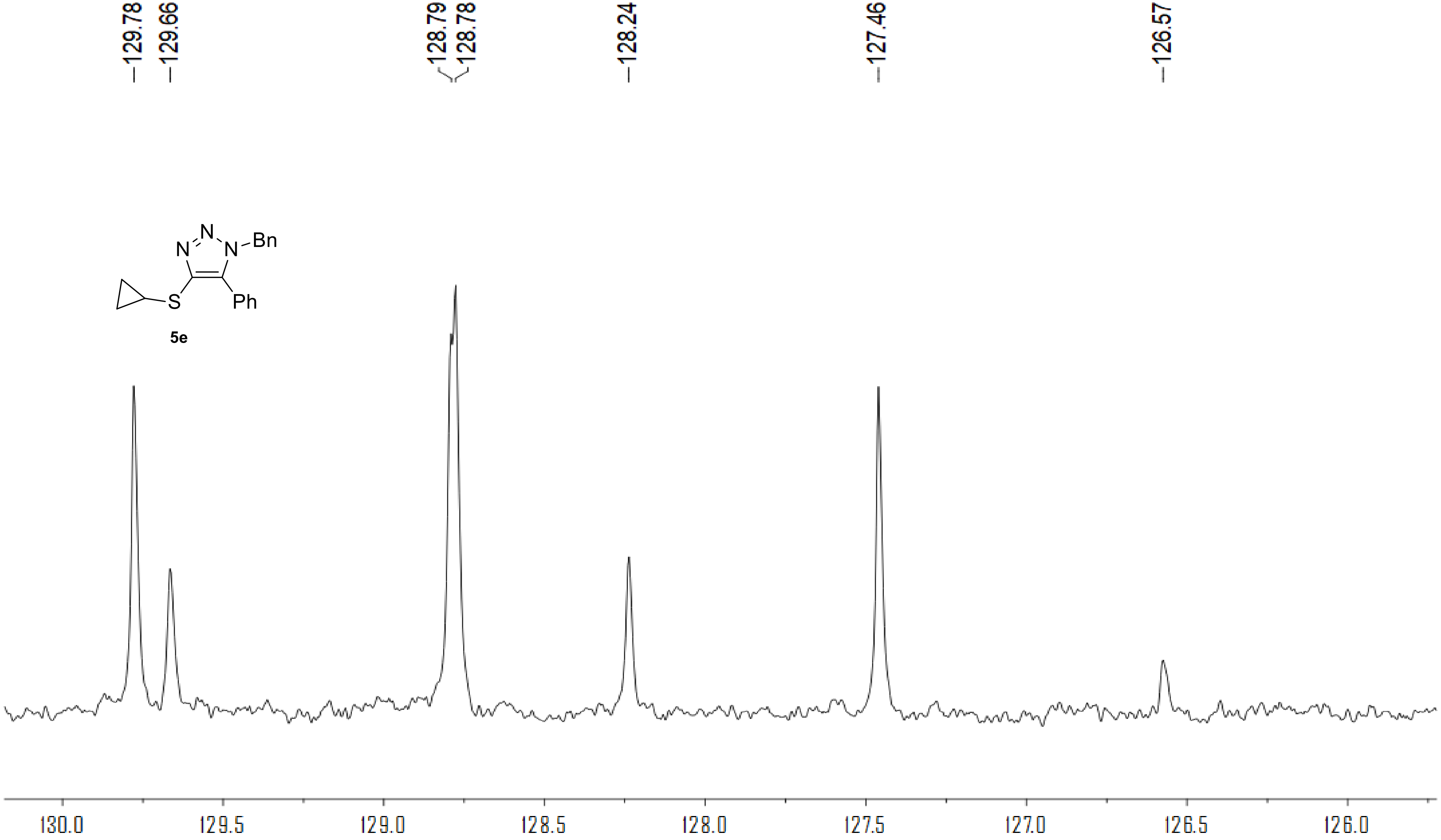
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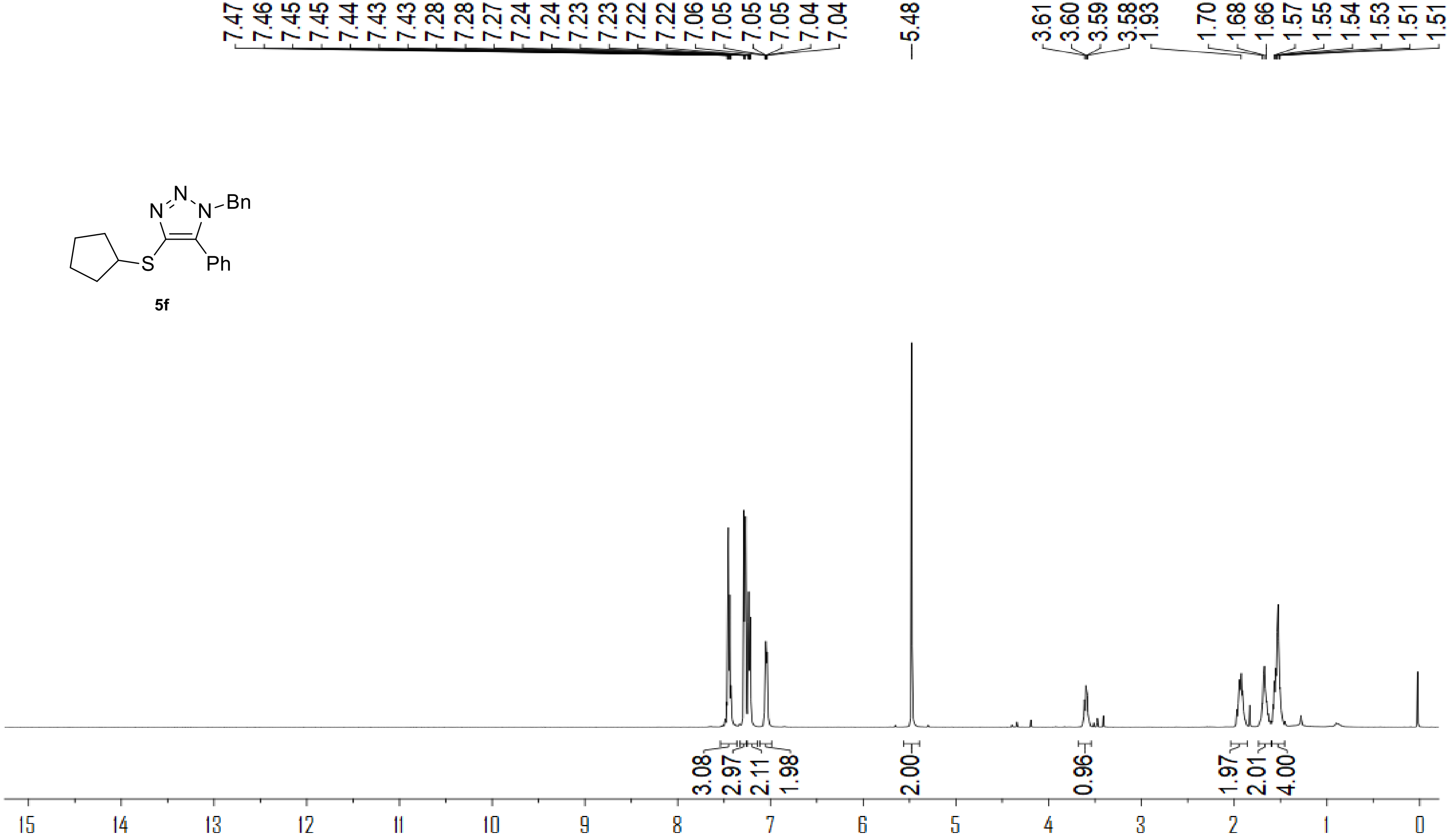
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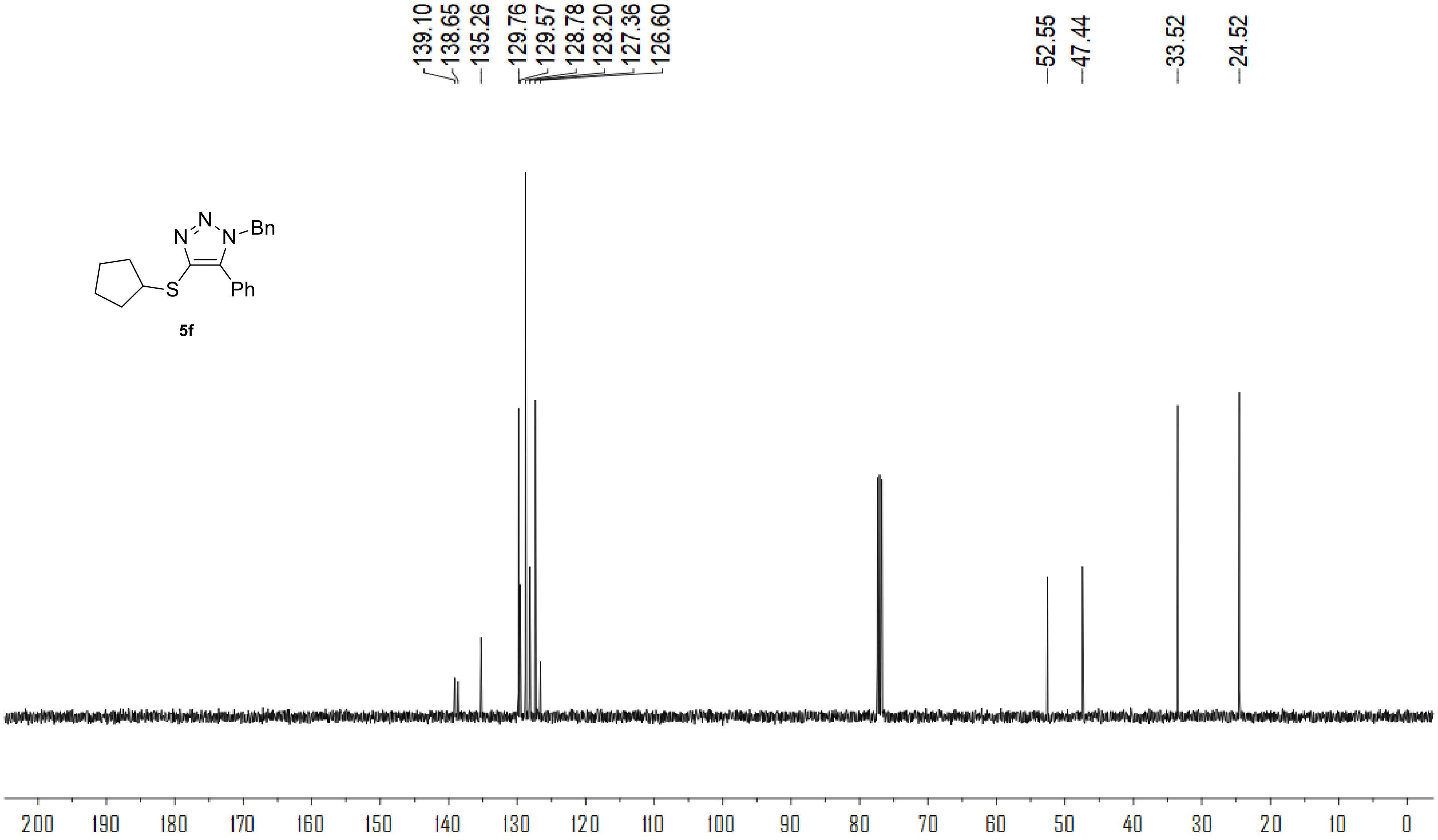
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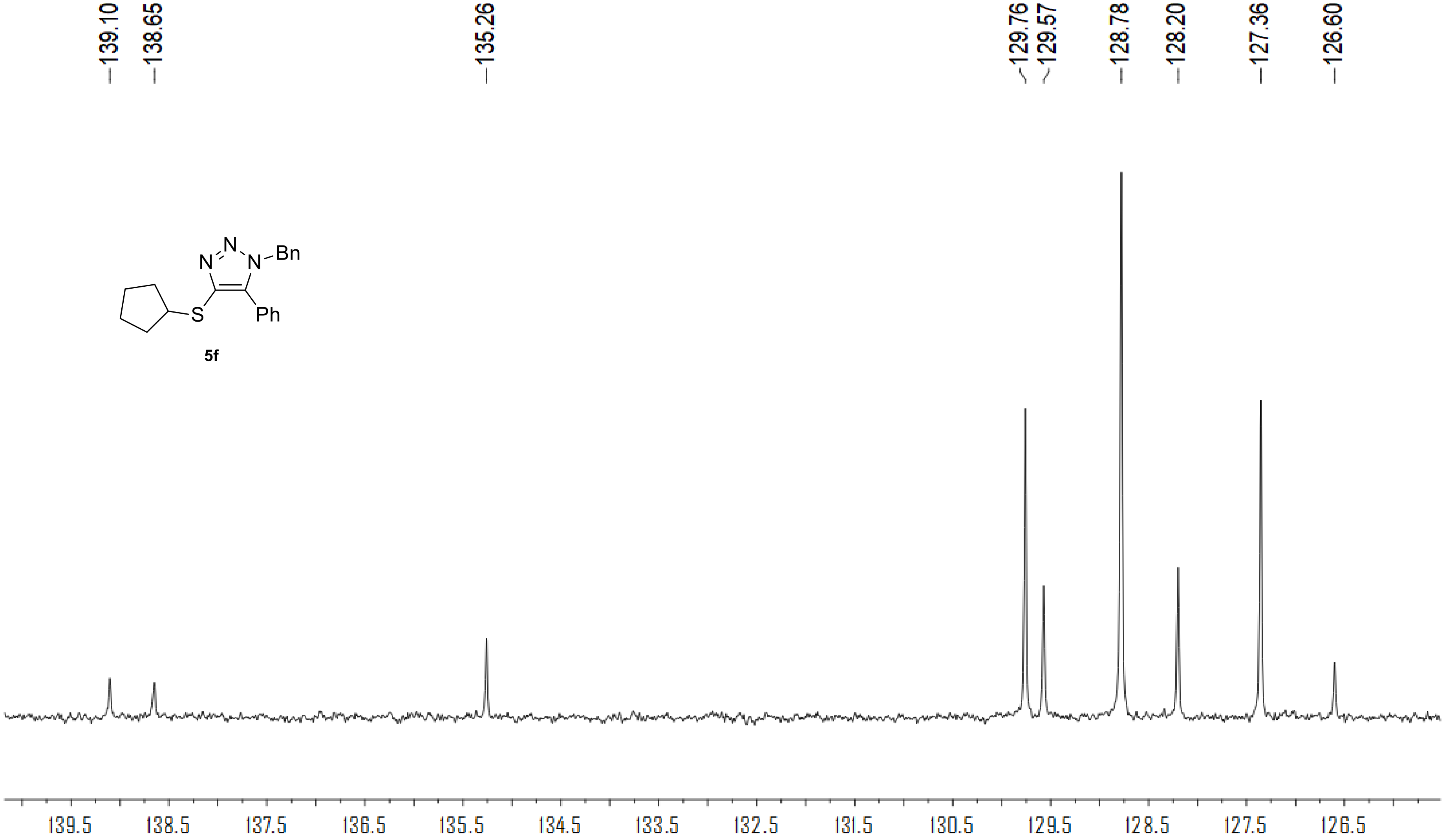
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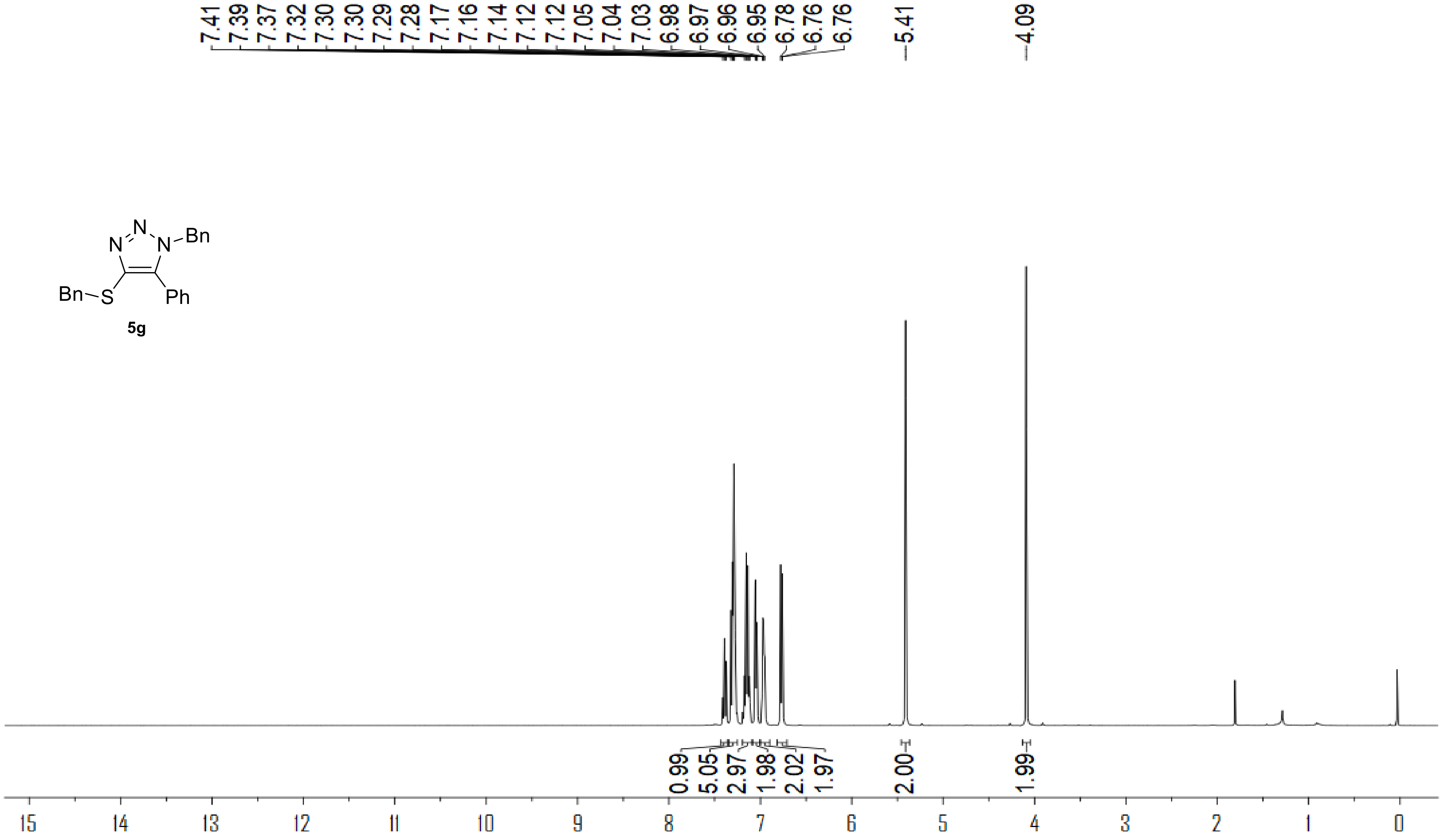
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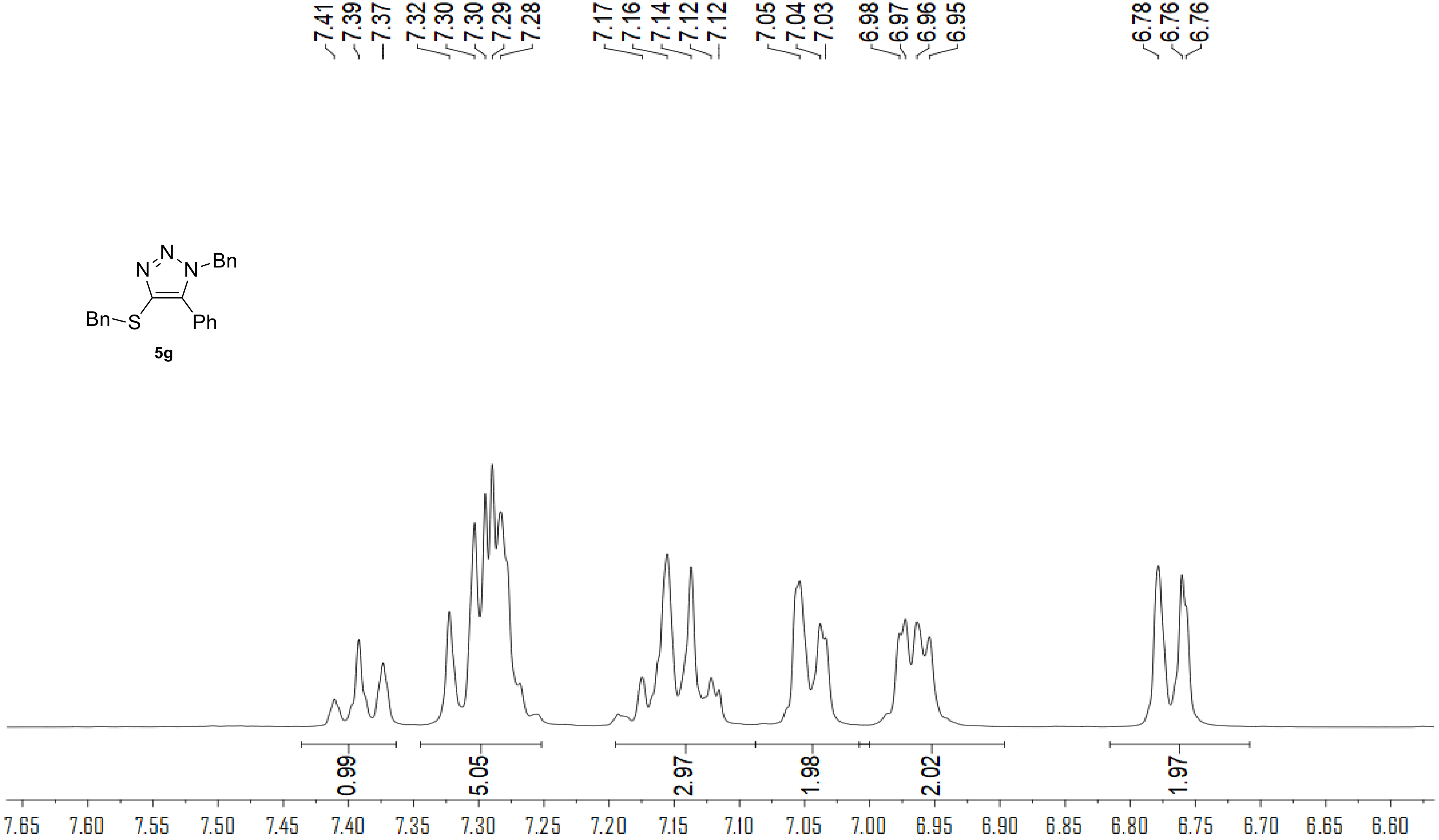
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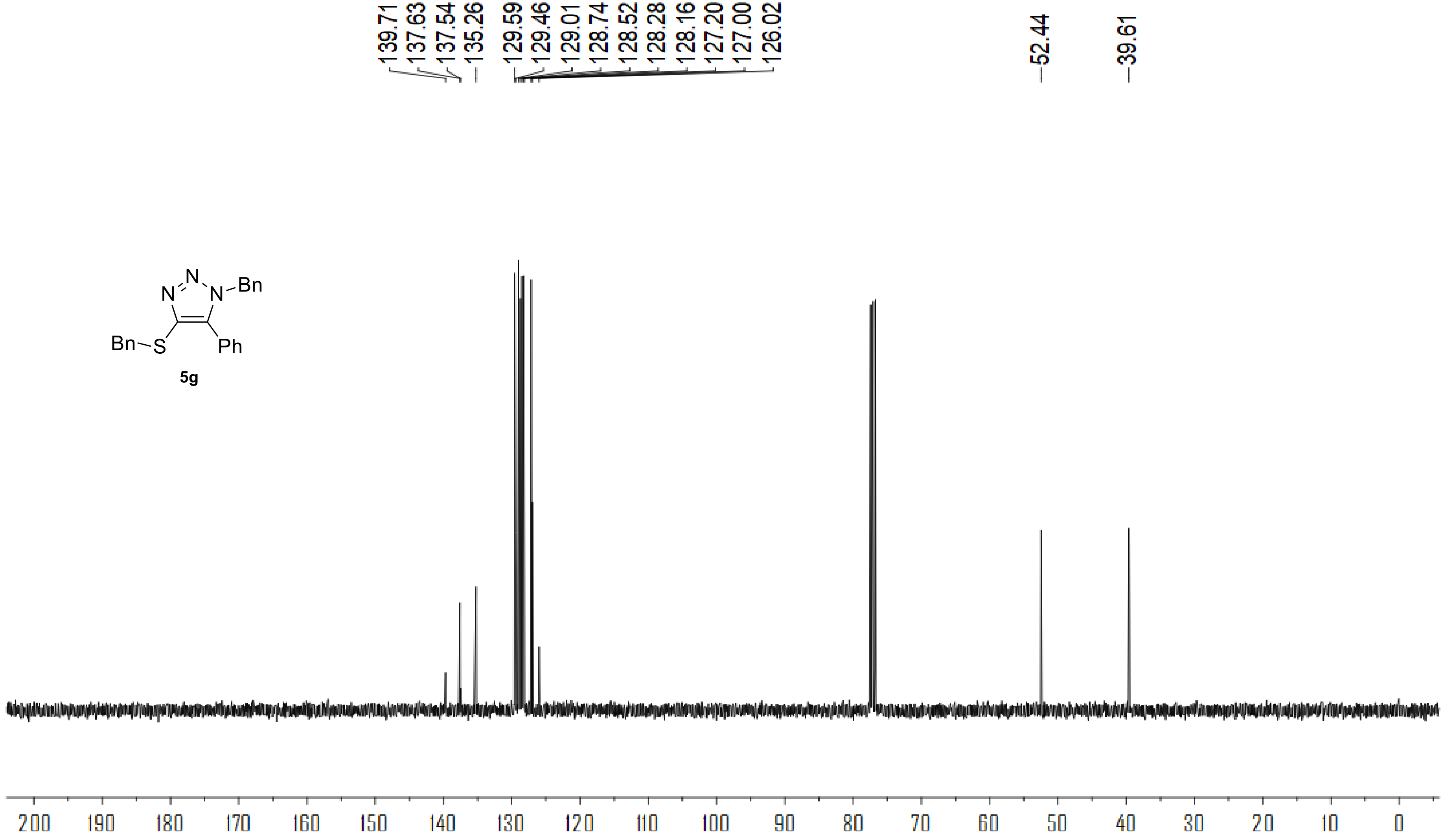
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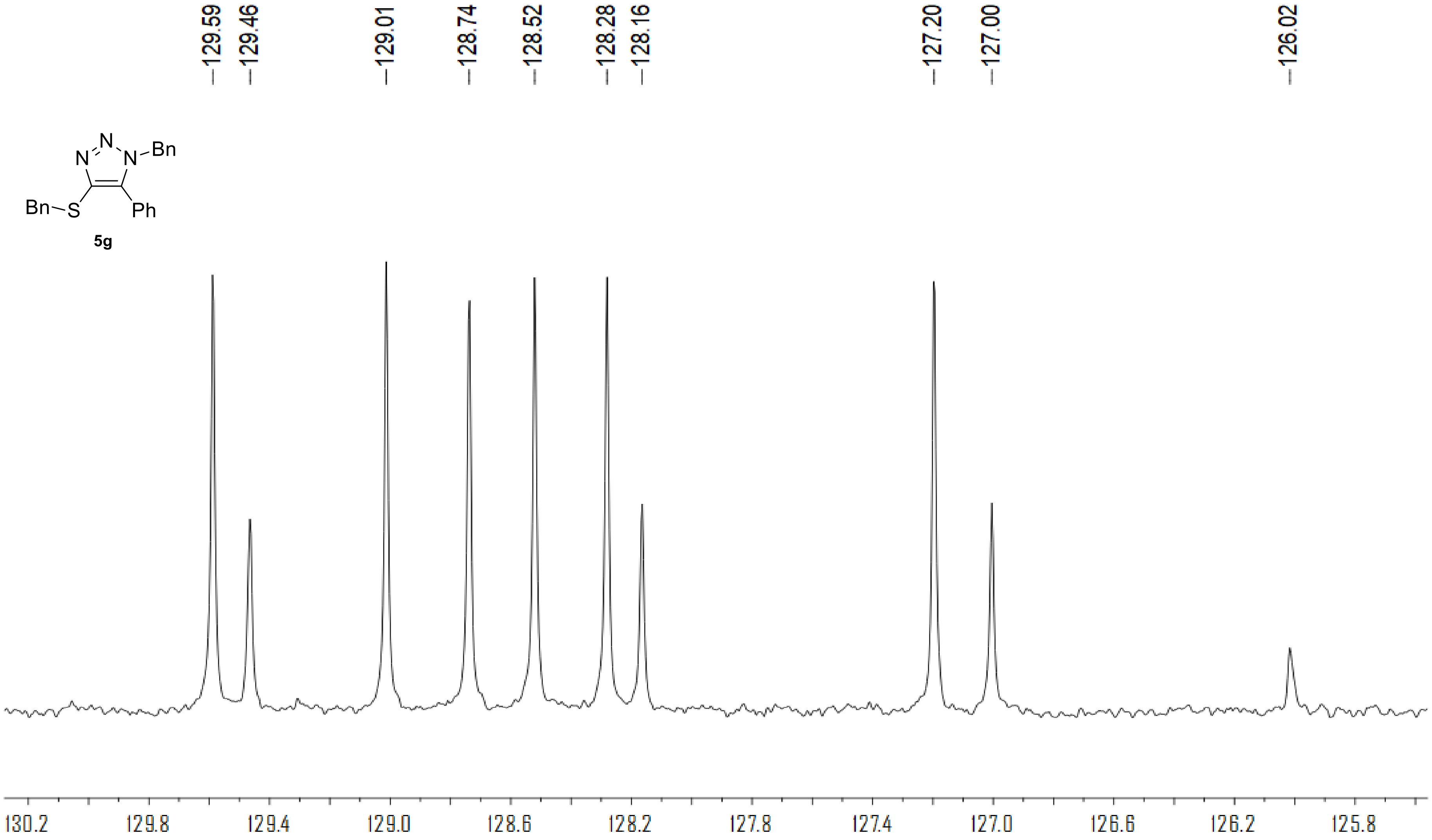
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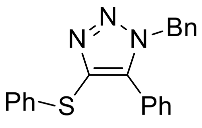

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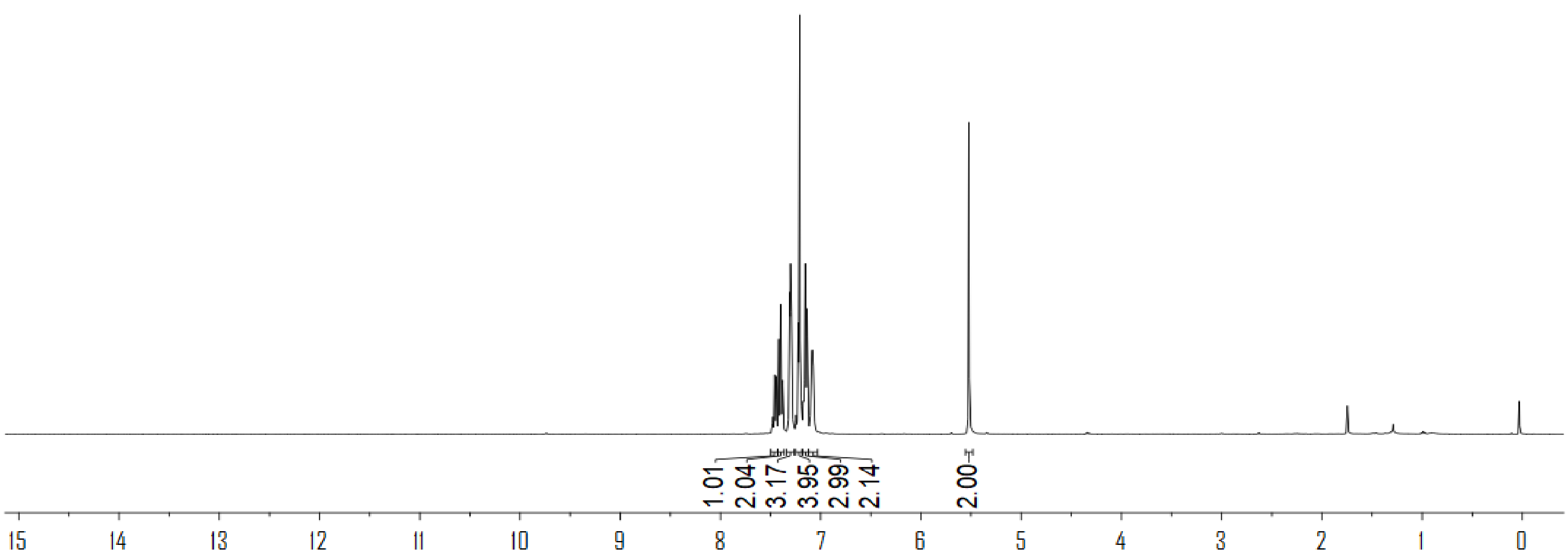
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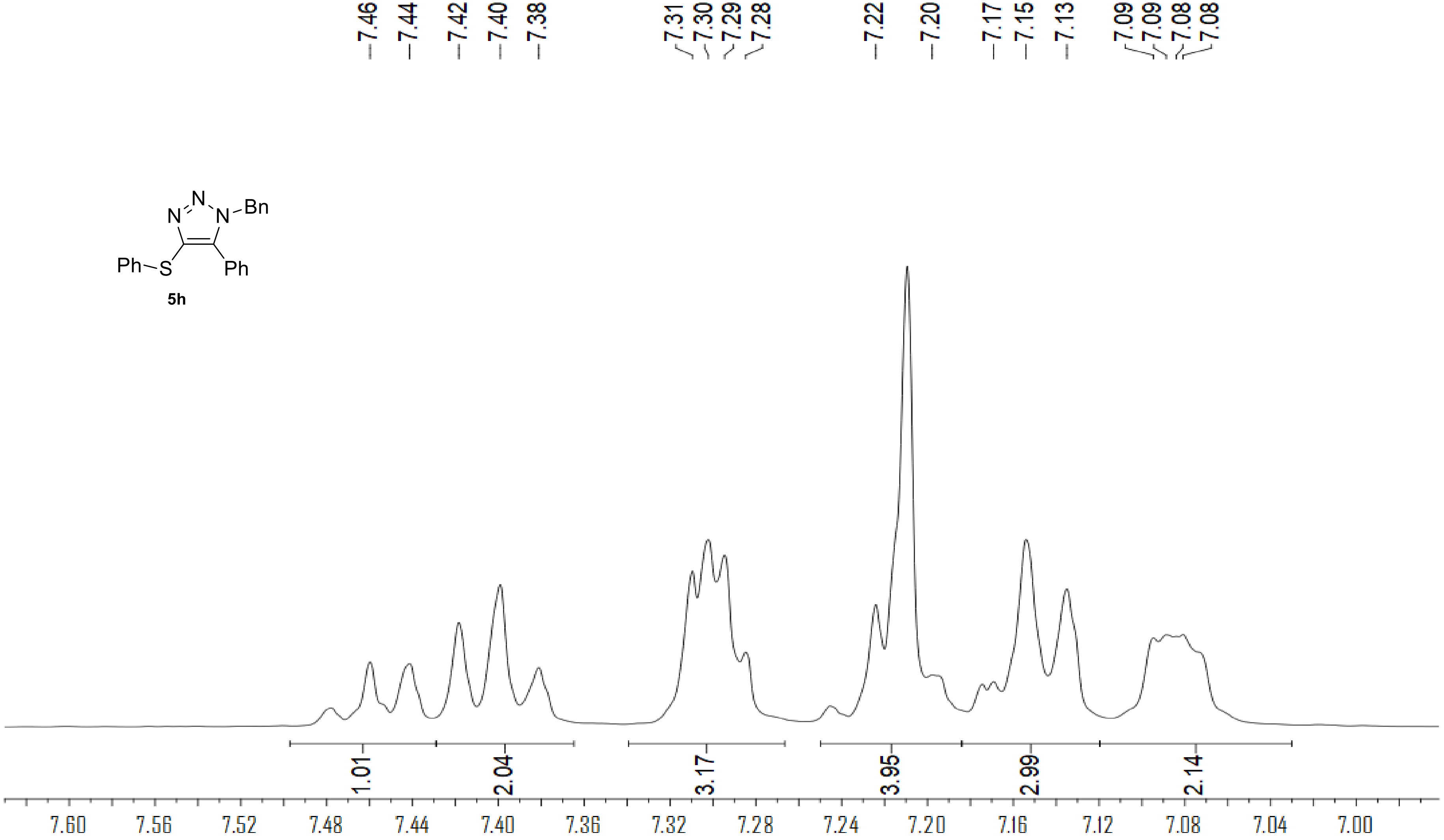
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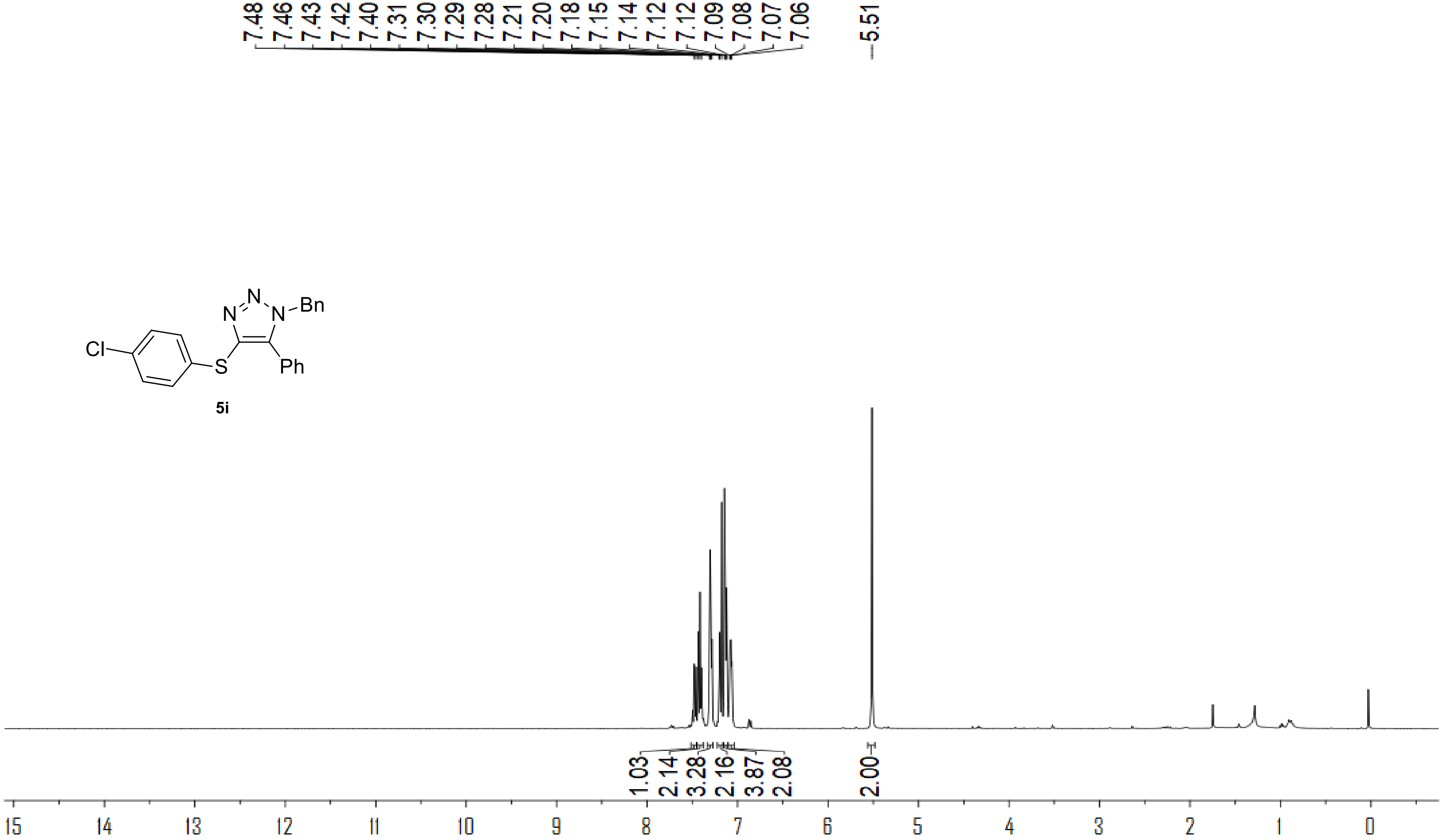

5i

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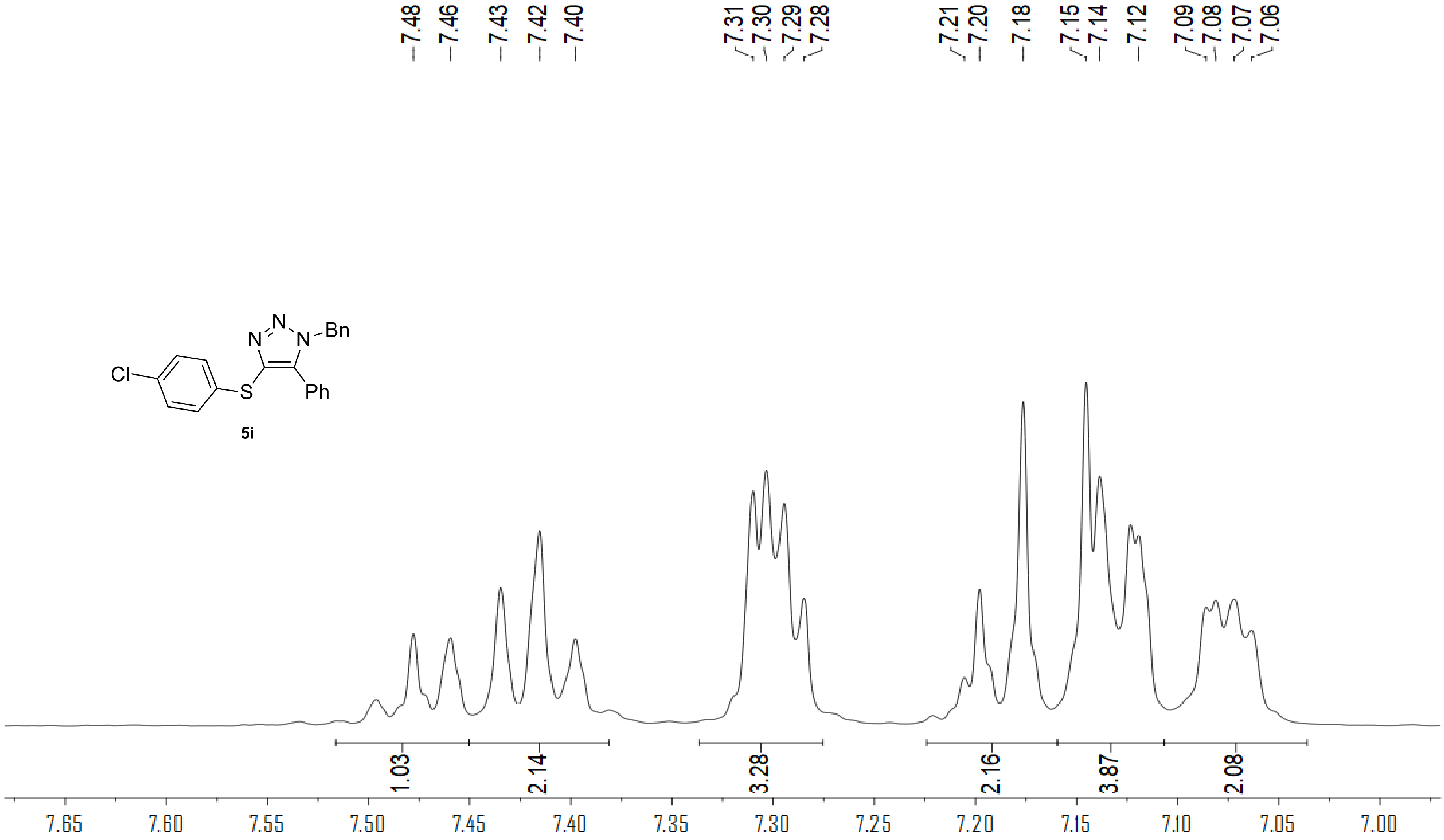
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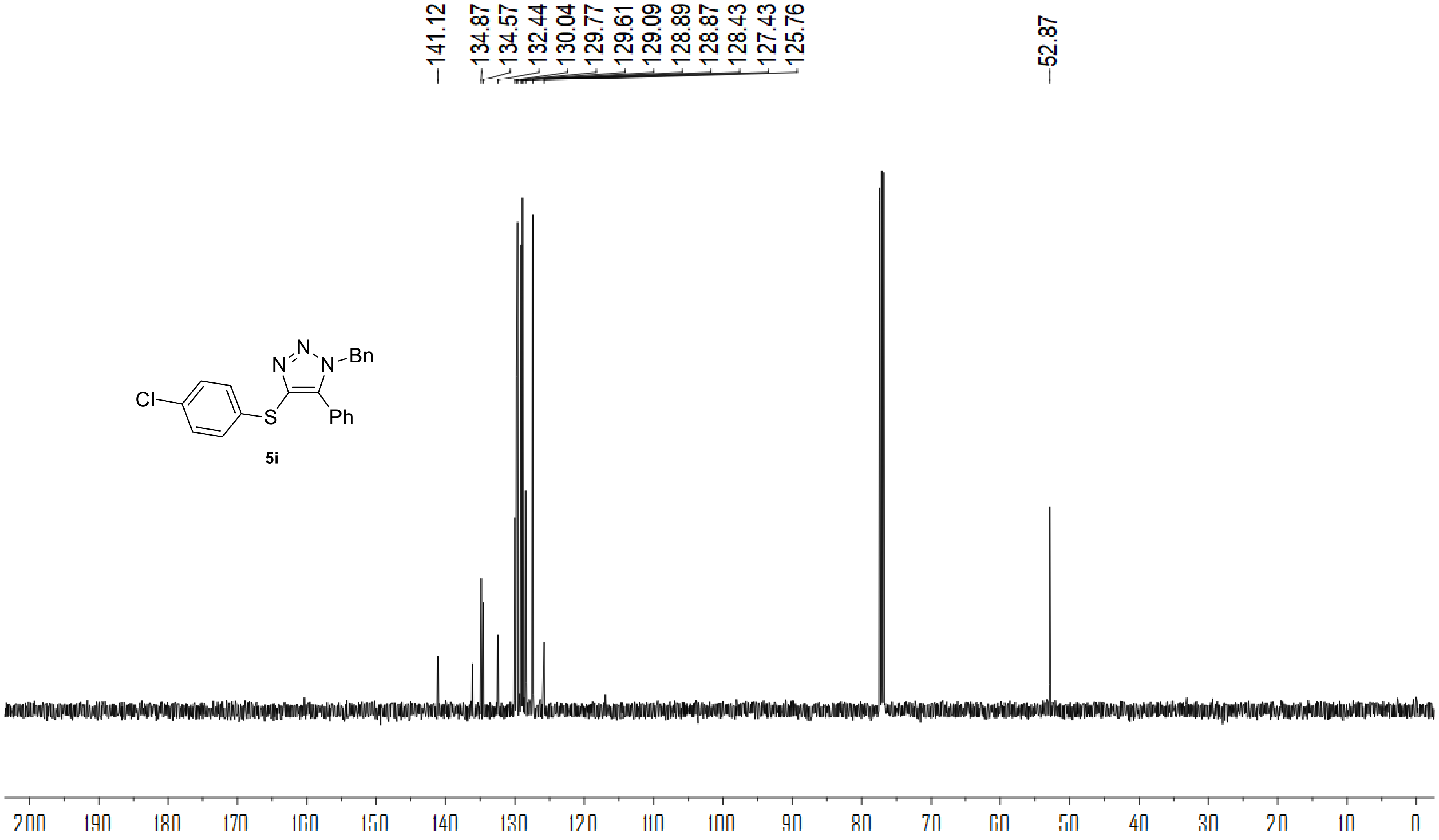
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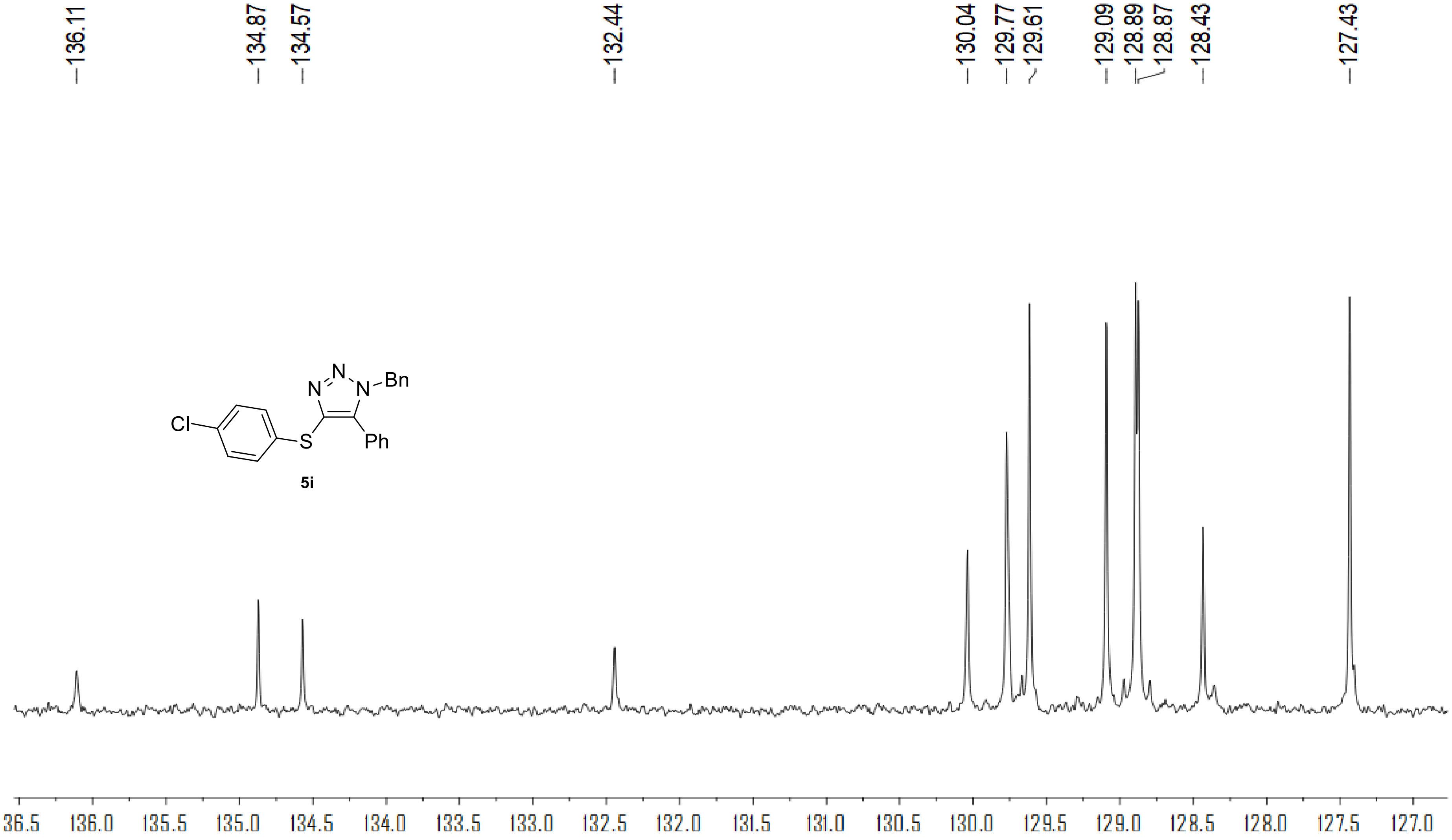
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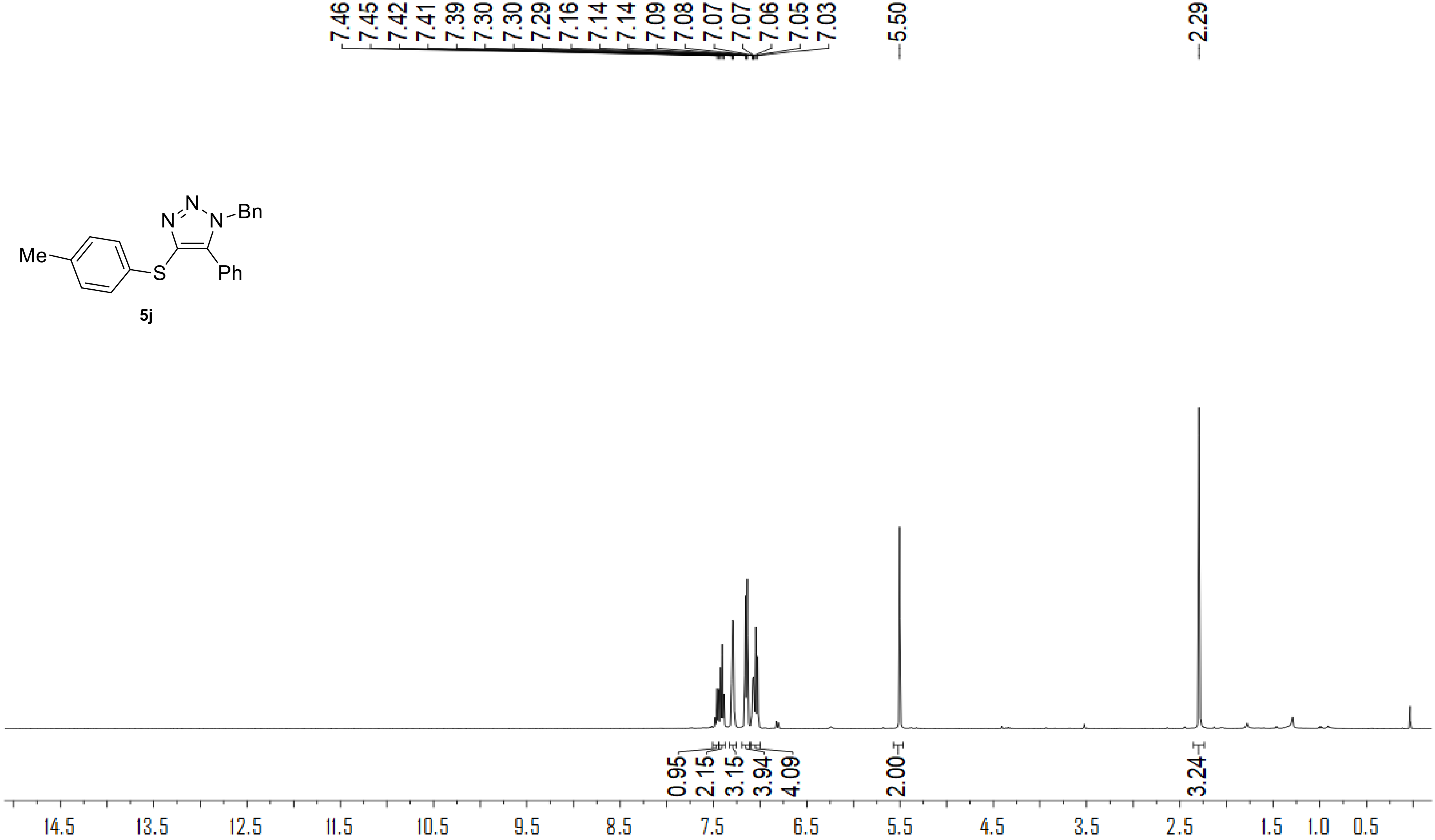
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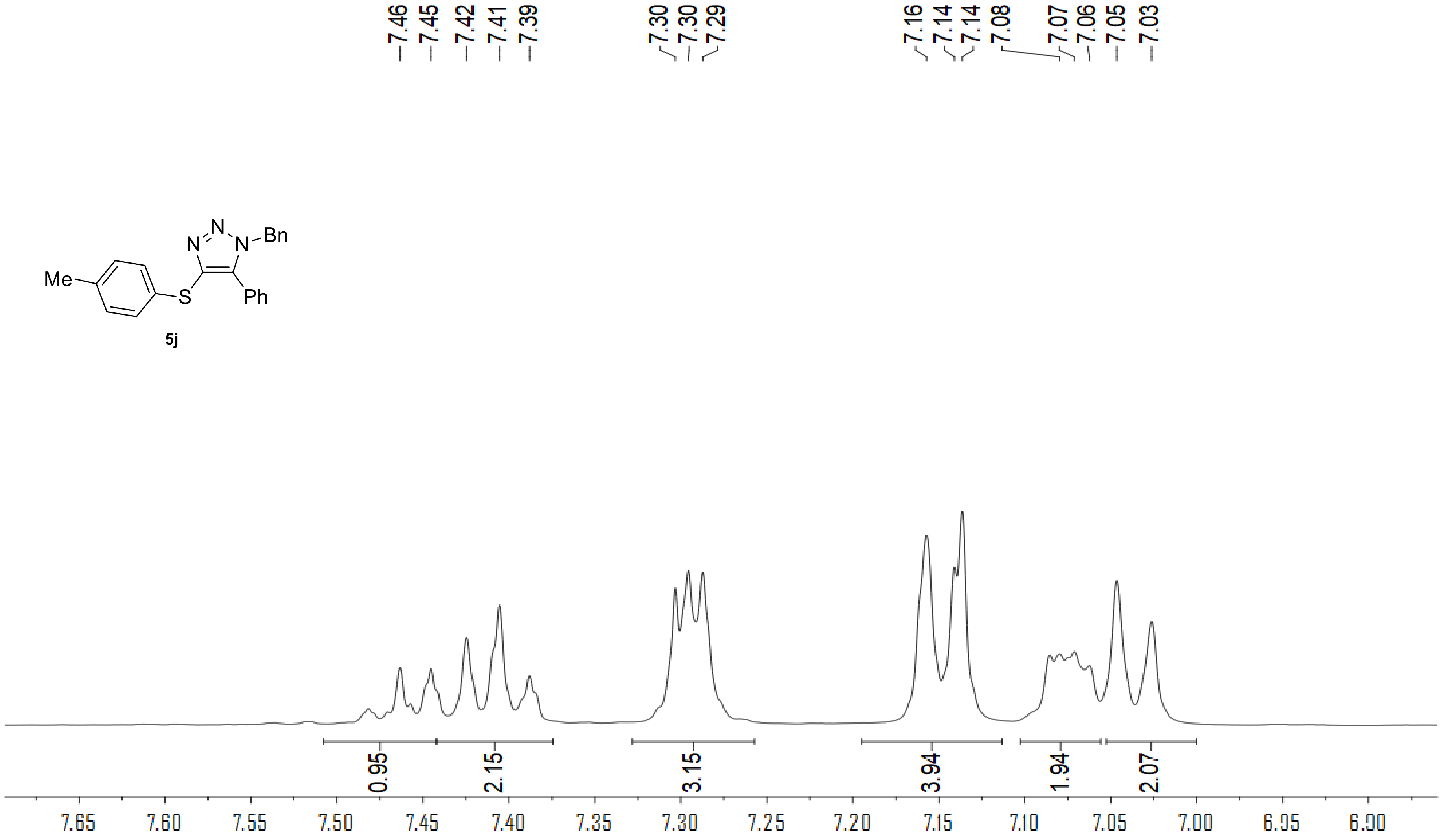

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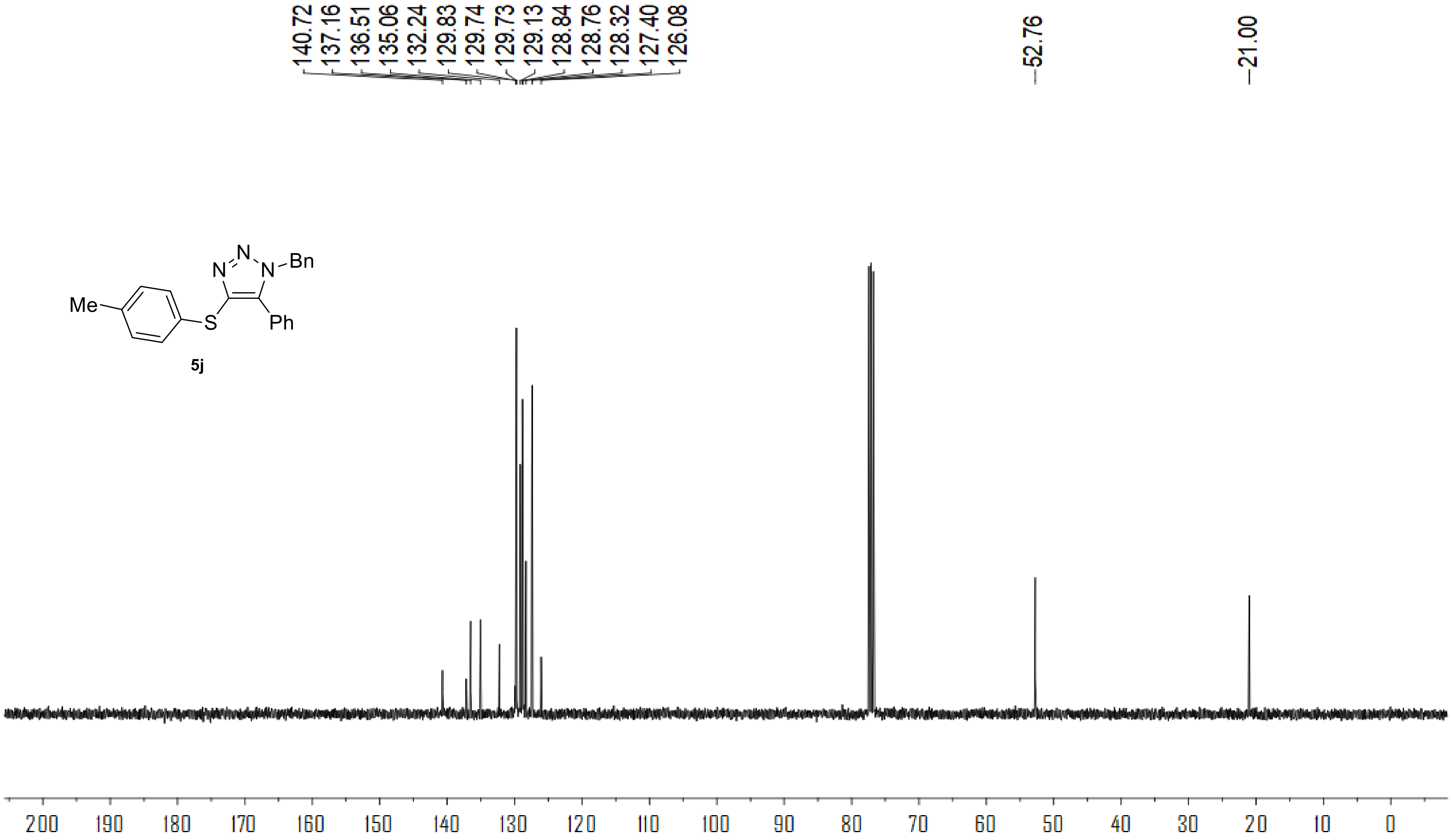
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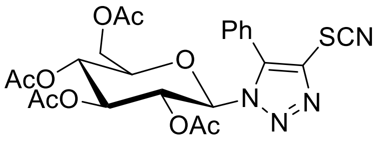

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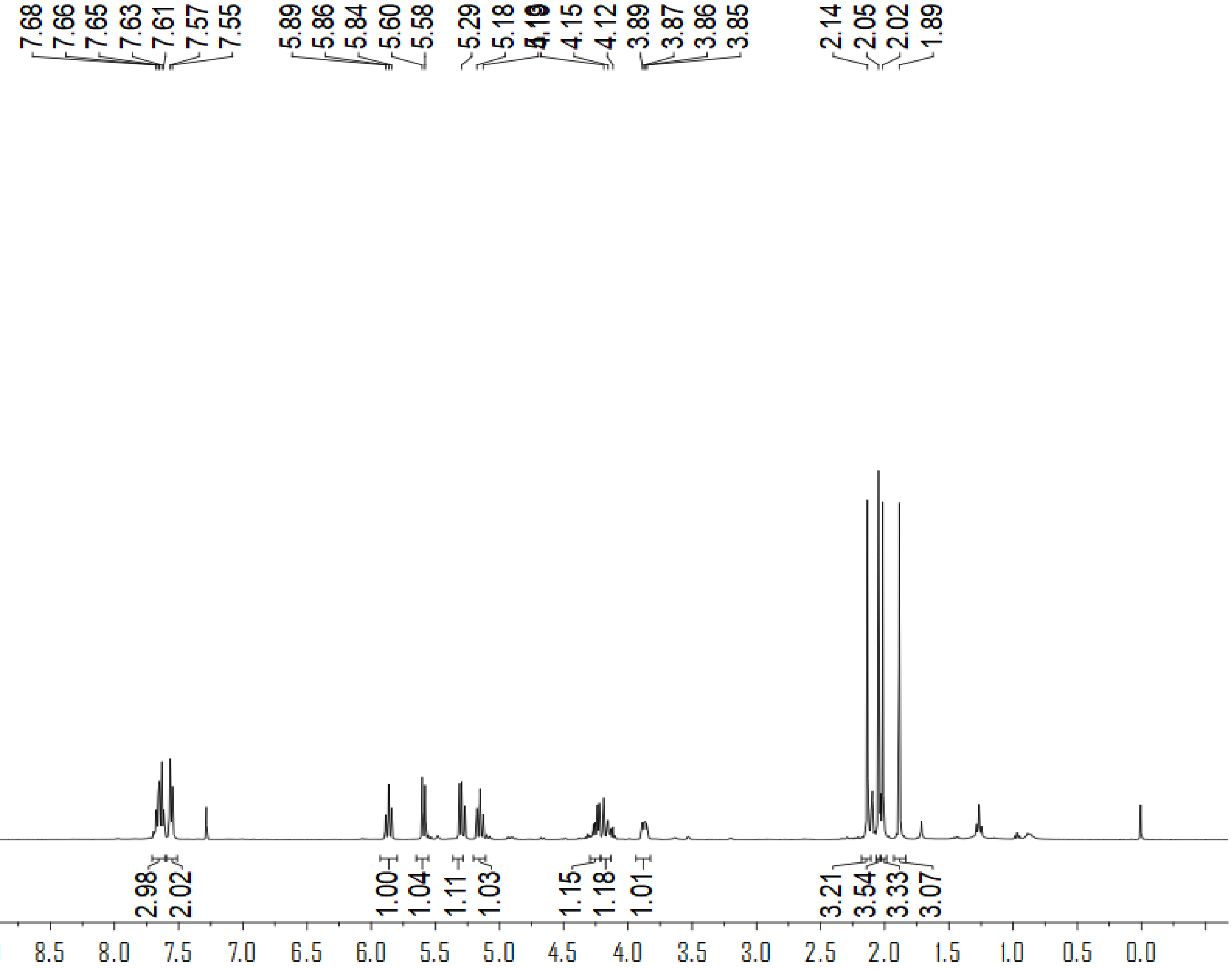
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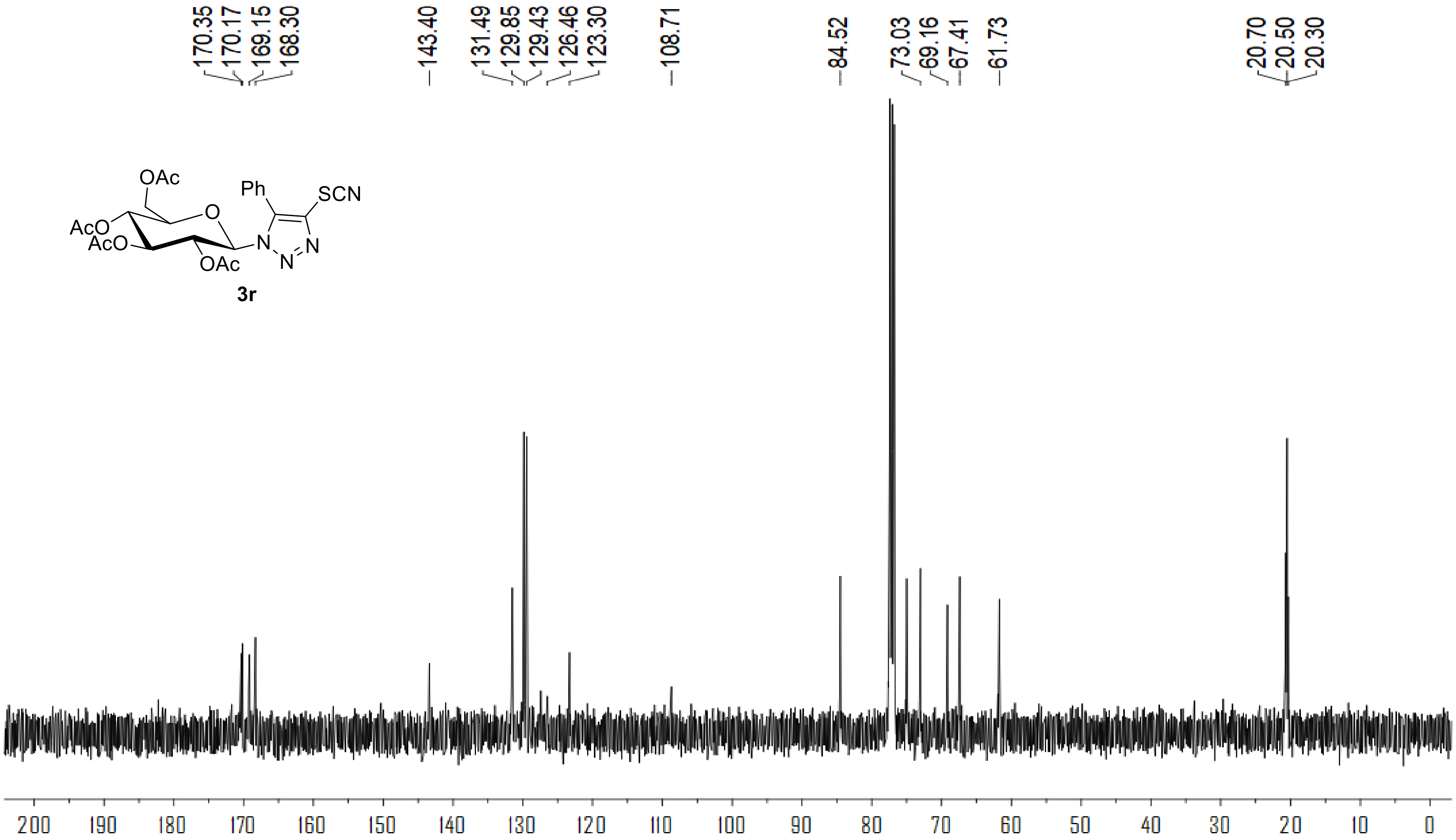
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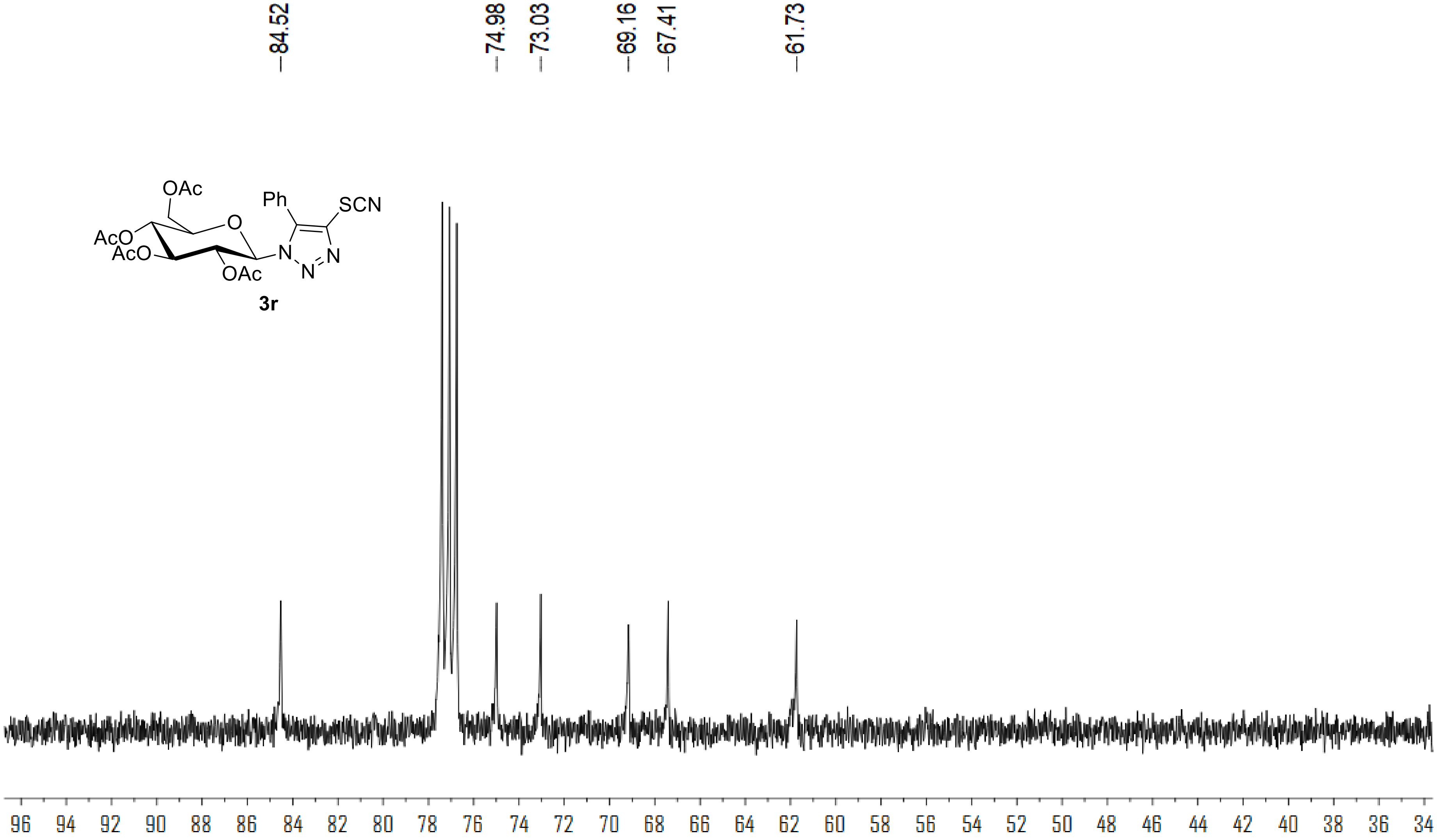
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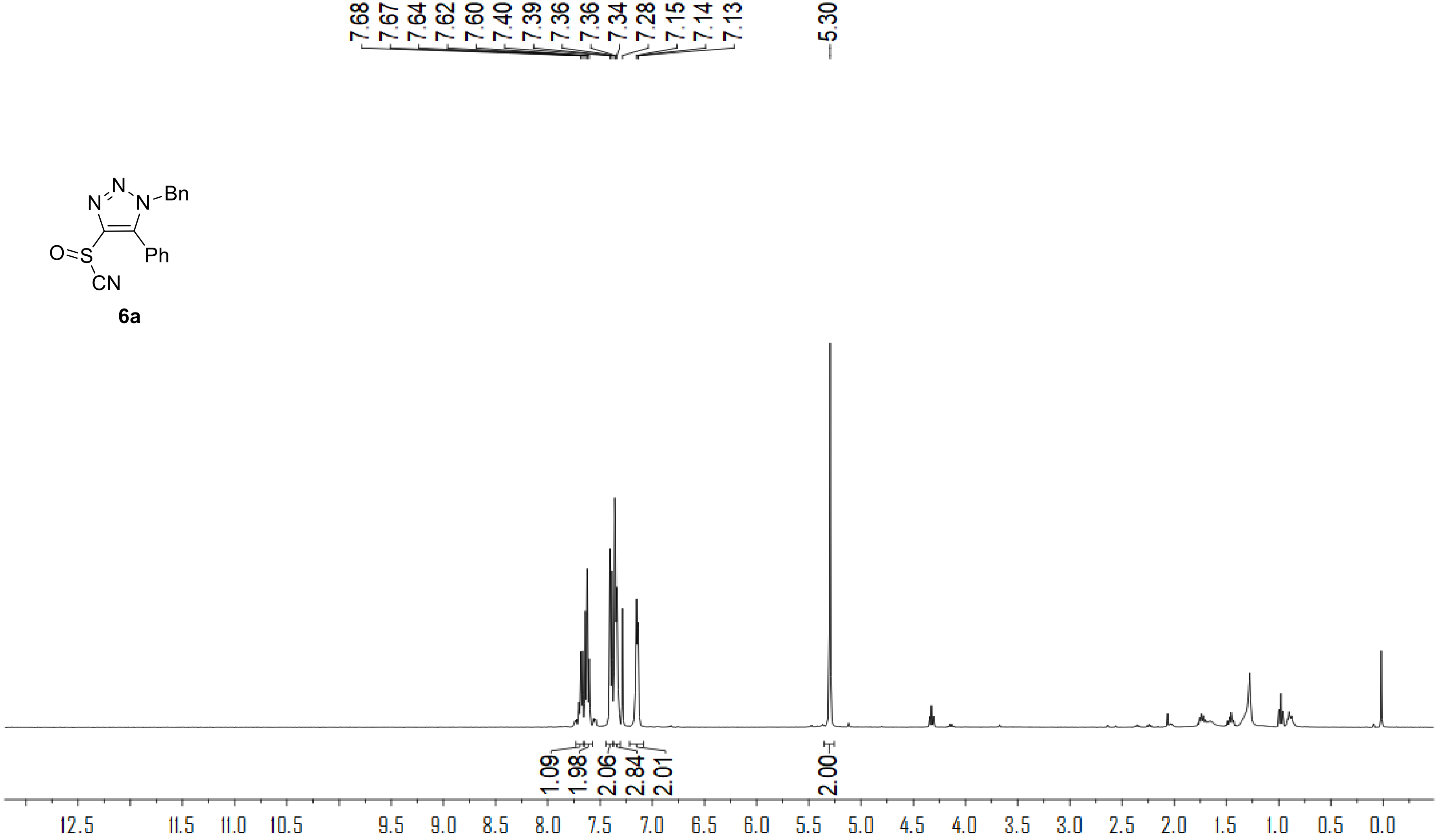
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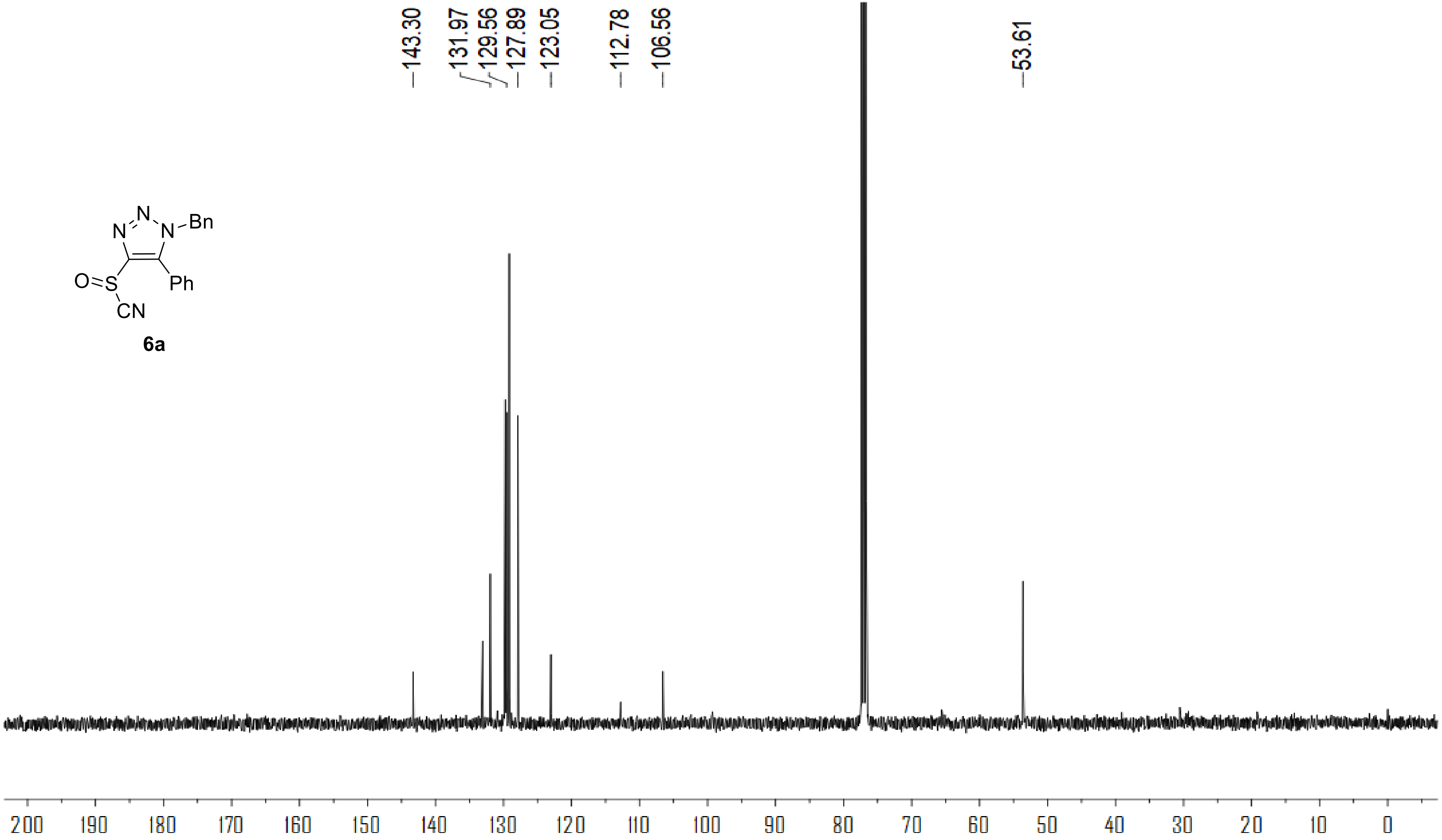
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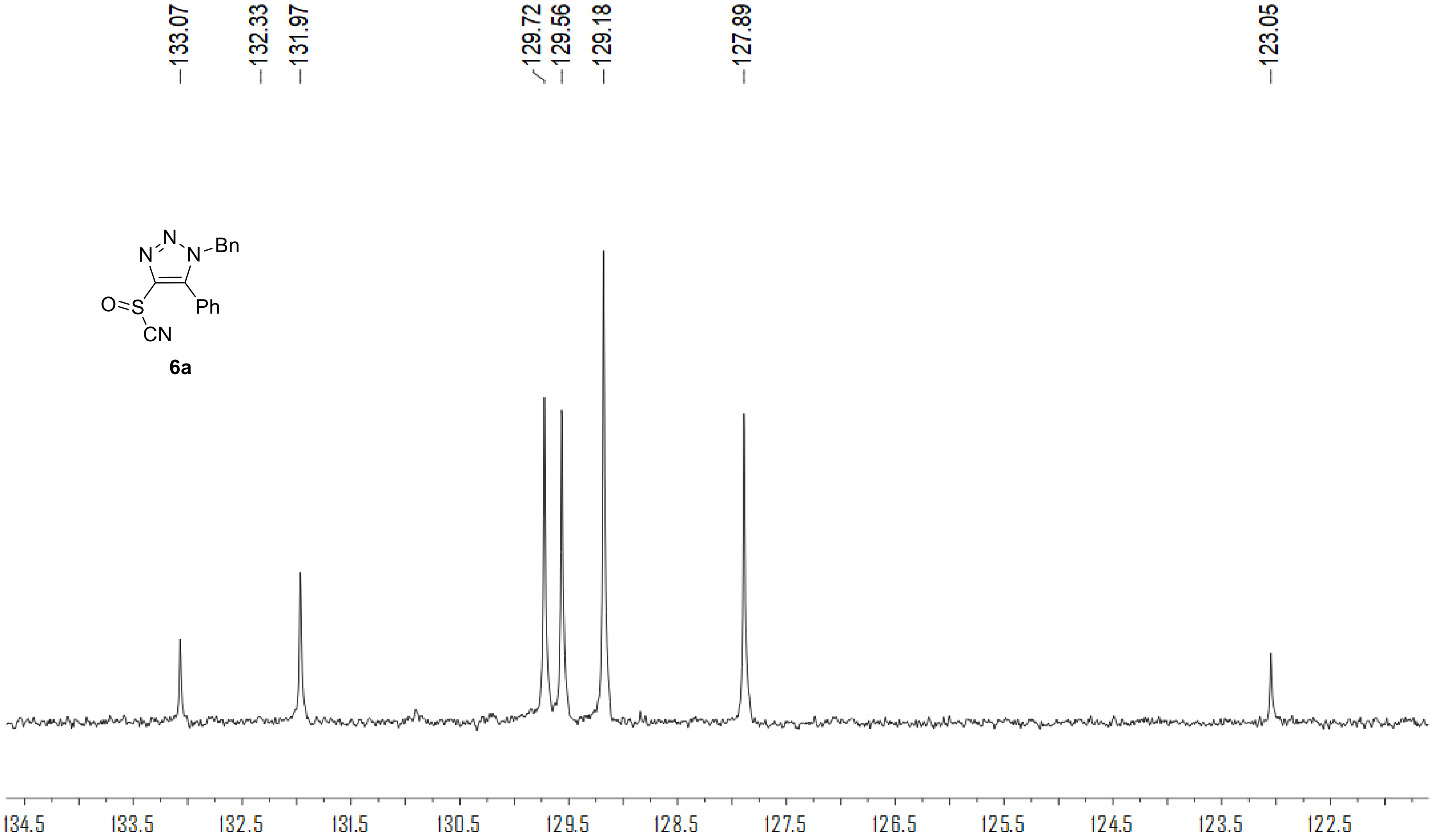
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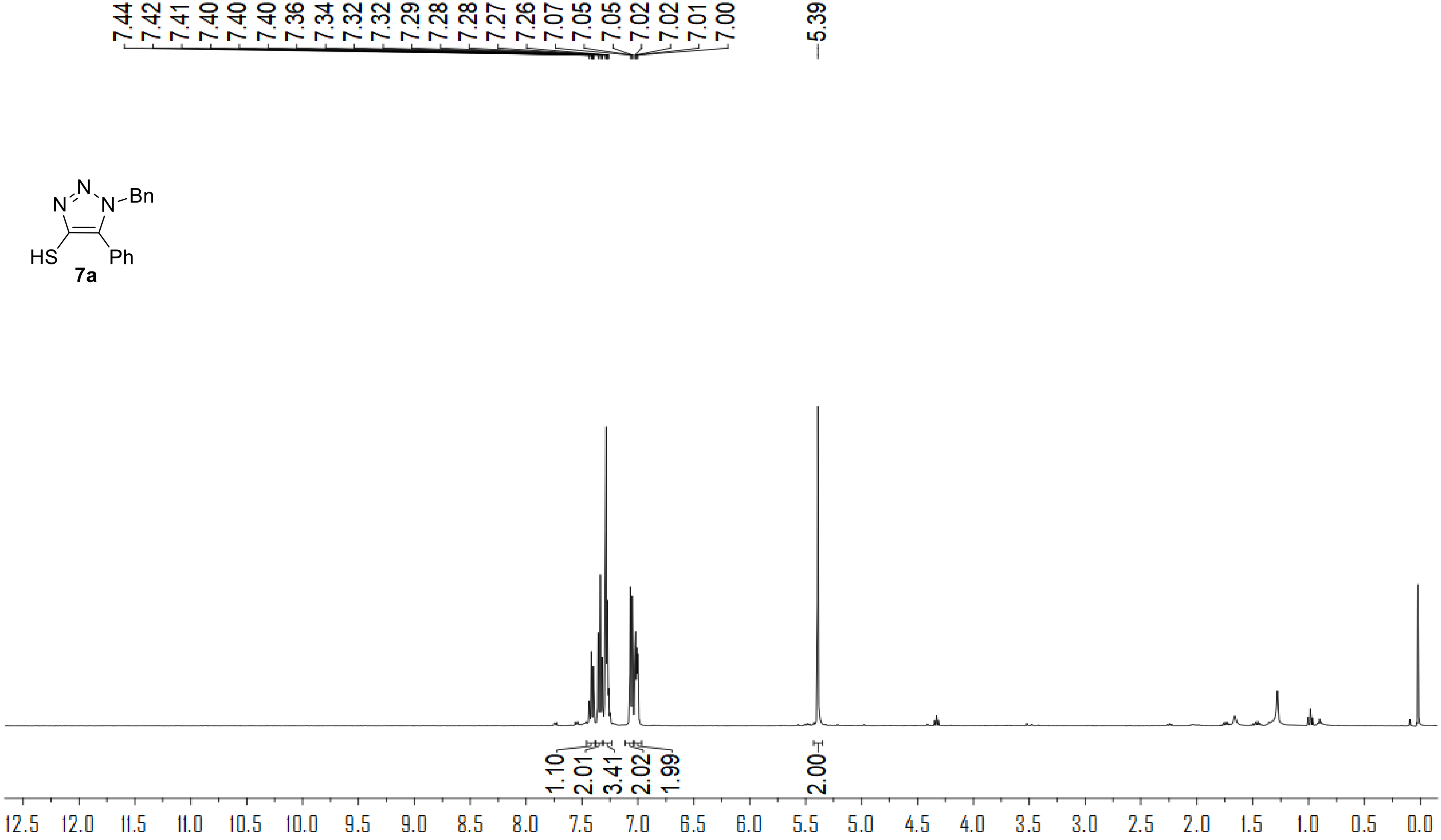
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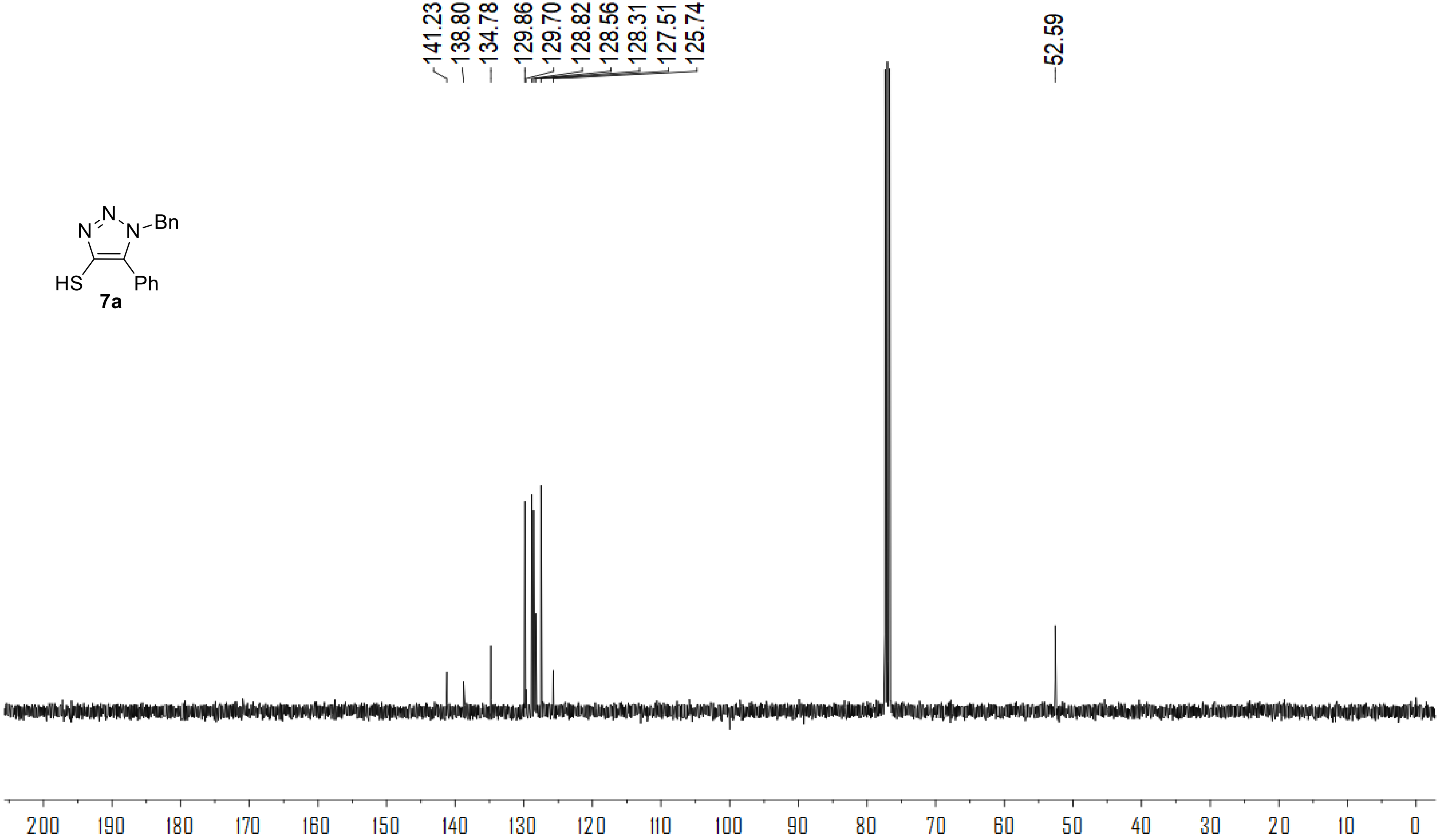
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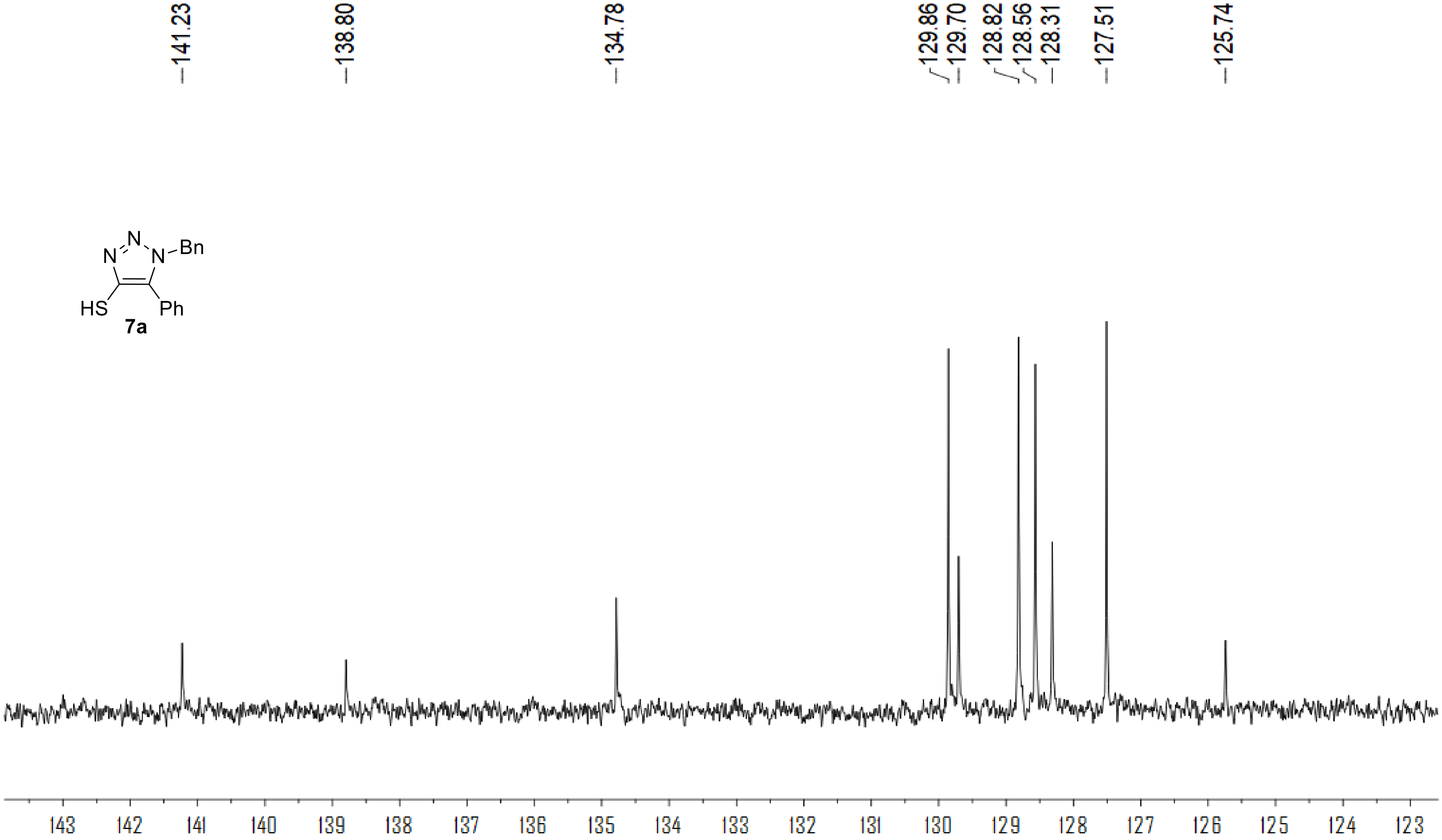
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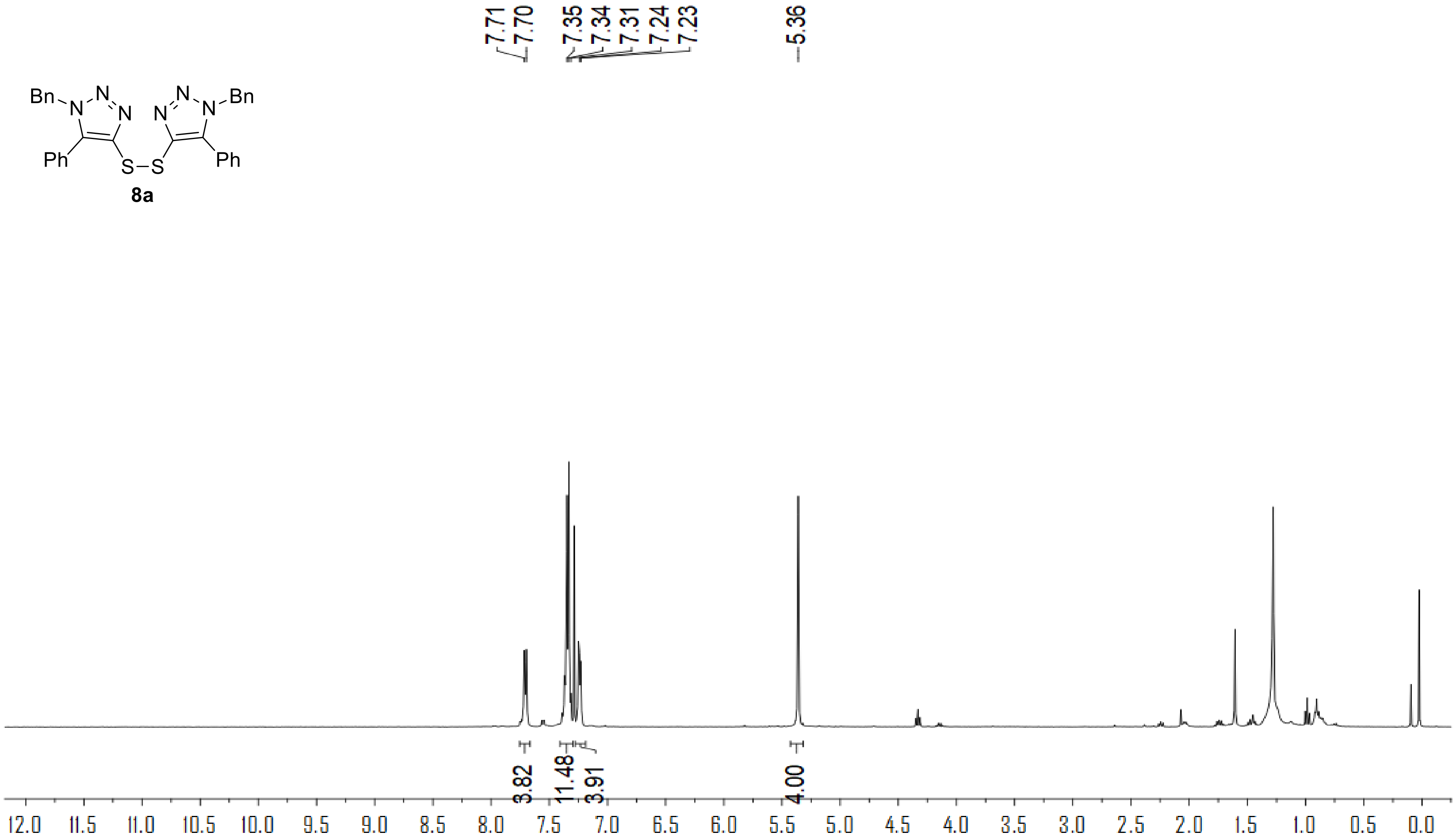
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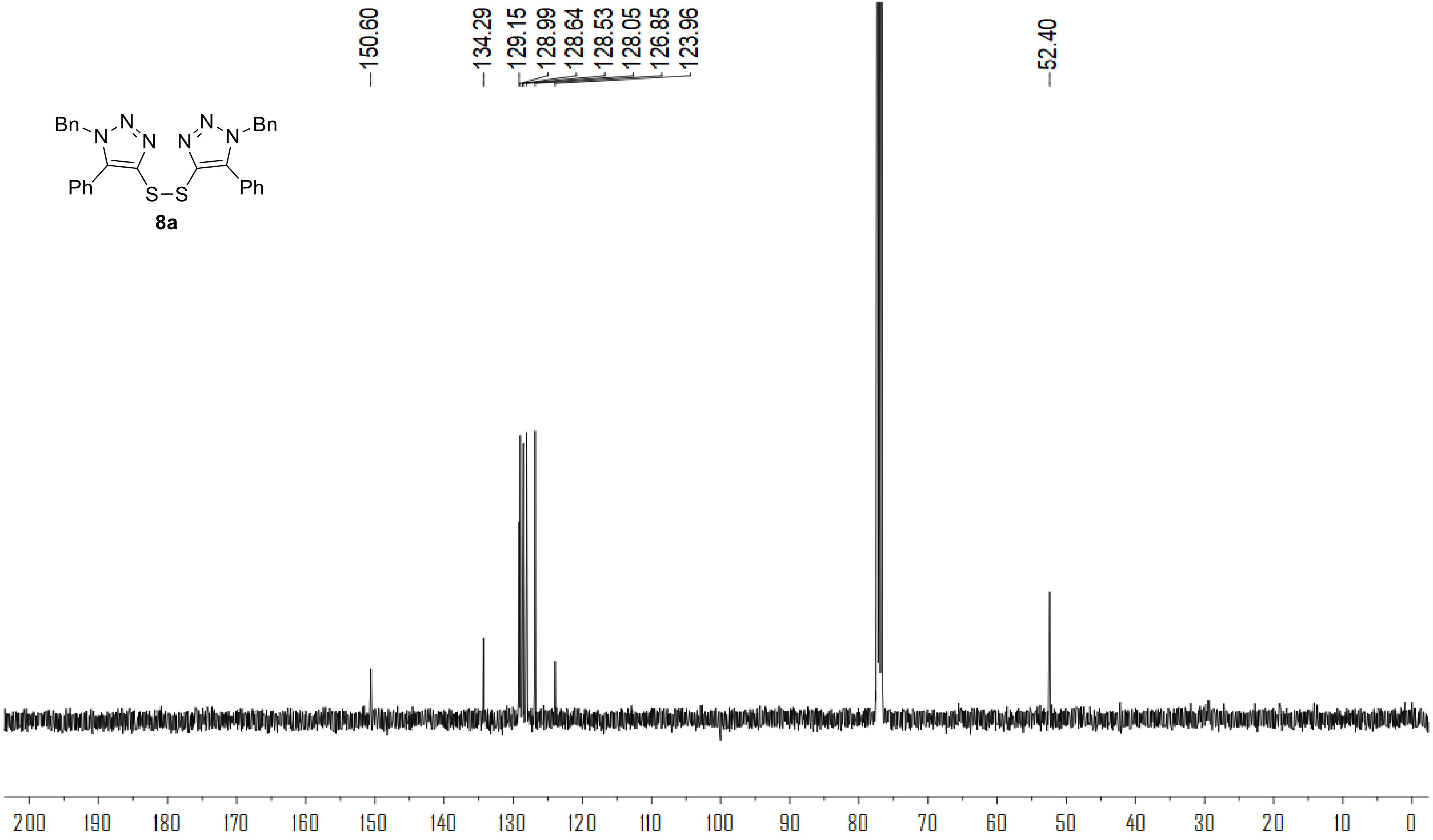
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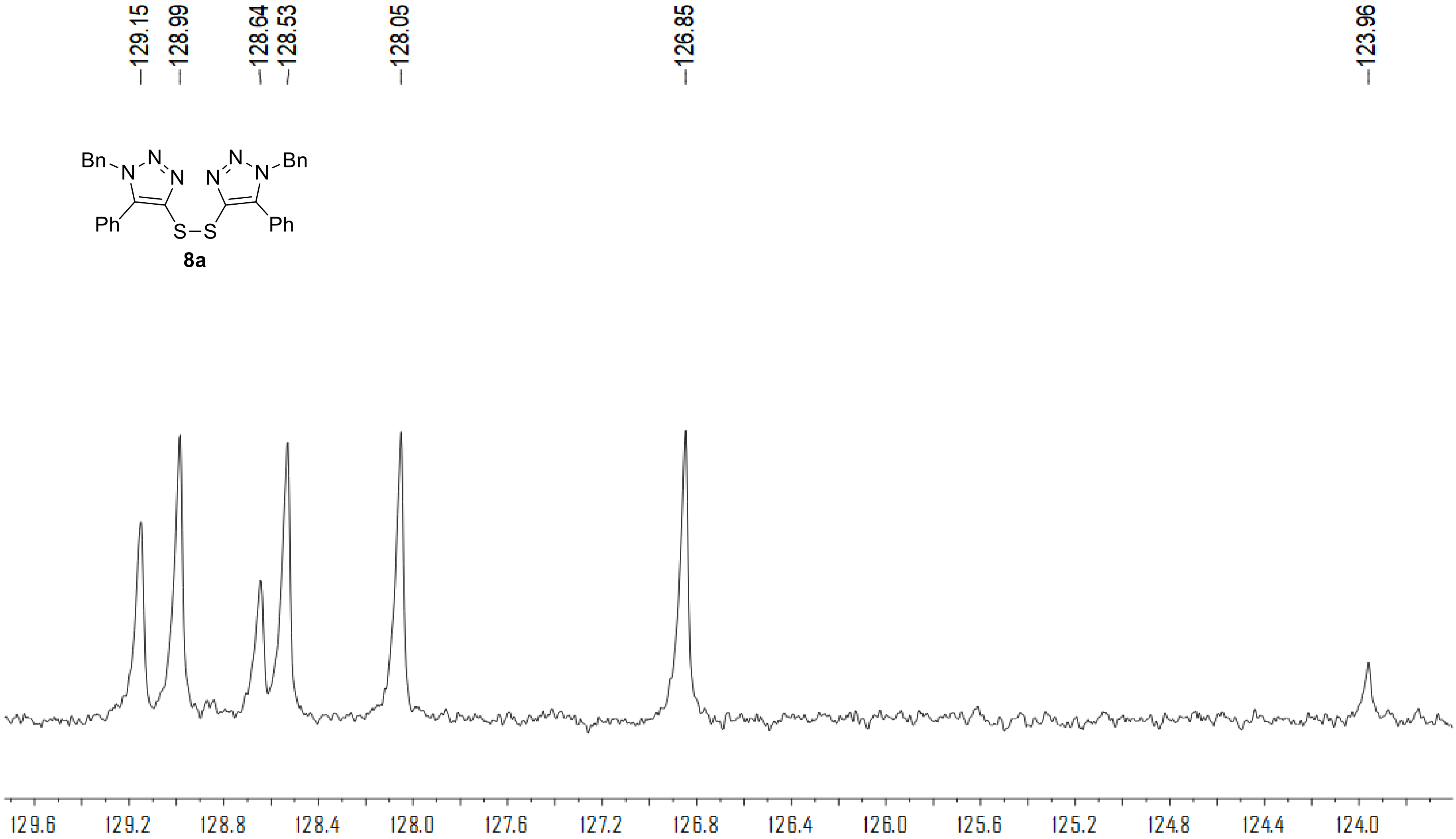
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