

# FACILE SYNTHESIS OF FULLY CONJUGATED AMINOPYRAZINE BASED DIAZOBENZENES AND DIAZOAMINOENZENES WITH ARYLDIAZONIUM SALTS

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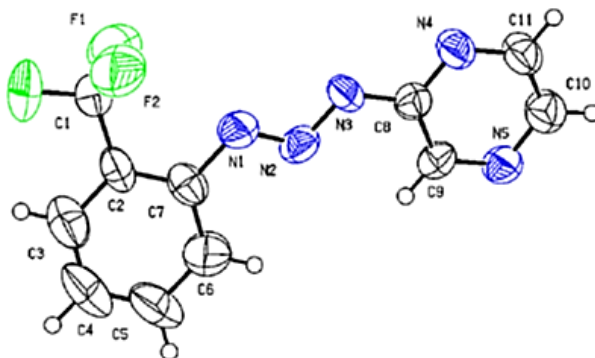
## Supporting Information

### General considerations

All reagents were purchased commercially and used as received. NMR spectra were recorded on a 500 MHz Bruker spectrometer. High-resolution mass spectra were recorded on Agilent QTOF (Quadrupole time-of-flight) spectrometry device. IR spectra were recorded on a PerkinElmer Spectrum 100 FT-IR spectrometer. UV-Vis spectrum of the compounds was recorded with Shimadzu UV-1800 spectrophotometer Thin-layer chromatography (TLC) was applied using Merck silicagel 60 F254 precoated aluminum-backed plates (0.25 mm). The chromatogram was analyzed by UV lamp (254 nm). Flash chromatography was performed on silicagel (230–400 mesh).

### X-ray crystallographic data and structure refinement

Data for the single crystal compound were acquired with Bruker APEX II QUAZAR three-circle diffractometer. Crystal structure validations and geometrical calculations were applied using the Platon software. [1] Mercury software [2] was used for visualization of the .cif files. The structure has been solved by the Bruker SHELXTL Software Package and refined using OLEX2.refine. [3, 4] The software used for molecular graphics: OLEX2 1.3 [5]; to prepare material for publication: OLEX2 1.3. [5] Data integration and reduction were realized with SAINT. [5] The crystallographic refinement data is summarized in Table 1.



**Figure 1:** X-ray structure of compound **5m**

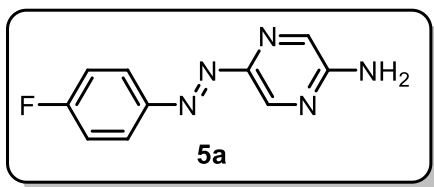
<b>Table 1: Crystal data and structure refinement for 5m.</b>	
Identification code	CCDC 2168505
Empirical formula	C <sub>11</sub> H <sub>7</sub> F <sub>3</sub> N <sub>5</sub>
Formula weight	266.22
Temperature/K	296.15
Crystal system	orthorhombic
Space group	Pbcm
a/Å	16.919(12)
b/Å	10.803(7)
c/Å	19.598(14)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	3582(4)
Z	12
ρ <sub>calc</sub> /cm <sup>3</sup>	1.481
μ/mm <sup>-1</sup>	0.128
F(000)	1620.0
Crystal size/mm <sup>3</sup>	0.444 × 0.105 × 0.082
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.408 to 54.992
Index ranges	-21 ≤ h ≤ 21, -14 ≤ k ≤ 14, -25 ≤ l ≤ 25
Reflections collected	35914
Independent reflections	4228 [R <sub>int</sub> = 0.4487, R <sub>sigma</sub> = 0.2063]
Data/restraints/parameters	4228/0/283
Goodness-of-fit on F <sup>2</sup>	0.966
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.1050, wR <sub>2</sub> = 0.2166
Final R indexes [all data]	R <sub>1</sub> = 0.3597, wR <sub>2</sub> = 0.3234
Largest diff. peak/hole / e Å <sup>-3</sup>	0.29/-0.21

## References

- [1] A. L. Spek, Structure validation in chemical crystallography, *Acta Crystallogr. D* 65 (2009) 148–155.
- [2] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van De Streek, Mercury: visualization and analysis of crystal structures, *J. Appl. Crystallogr.* 39 (2006) 453–457.
- [3] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment-Olex2 dissected, *Acta Crystallographica a-Foundat. Adv.* 71 (2015) 59–75.
- [4] G. M. Sheldrick, SHELXT - integrated space-group and crystal-structure determination, *Acta Crystallographica a-Foundat. Adv.* 71 (2015) 3–8.
- [4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.* 42 (2009) 339–341.
- [5] SAINT, Version 8.34A, Bruker (2013).

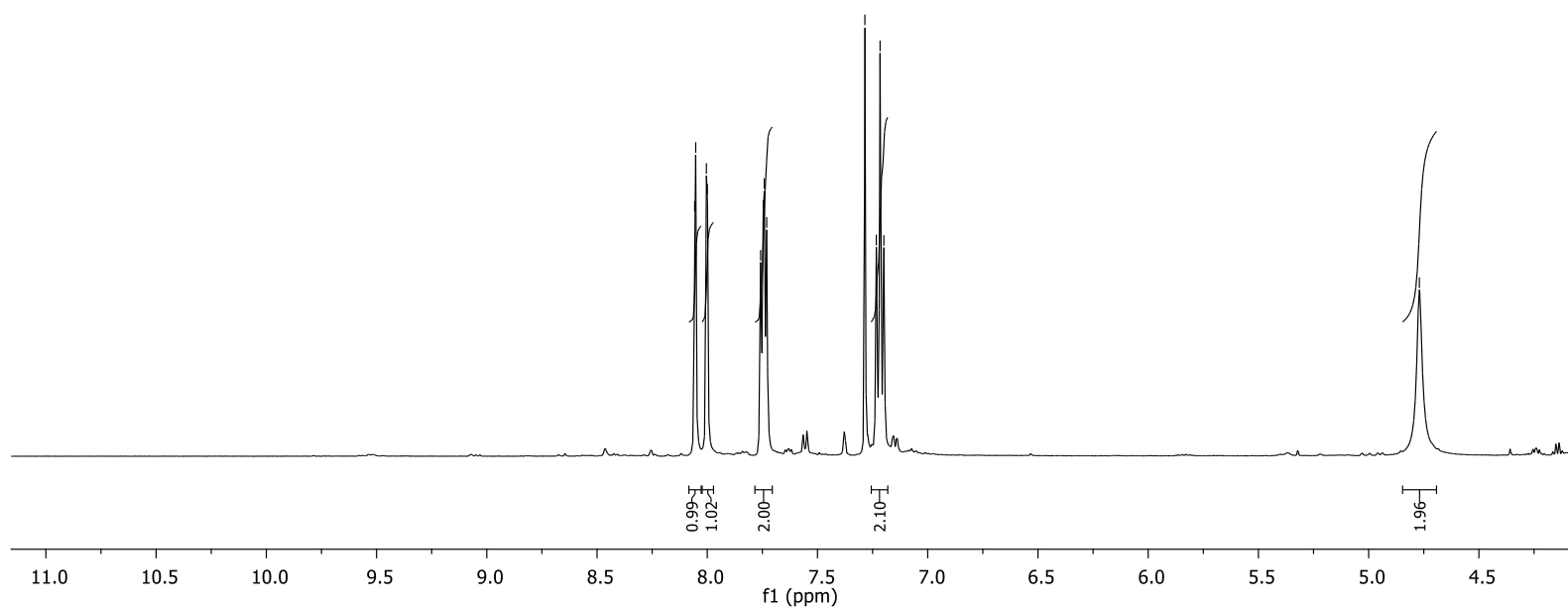
### Spectral Data

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((4-fluorophenyl)diazenyl)pyrazin-2-amine (**5a**)

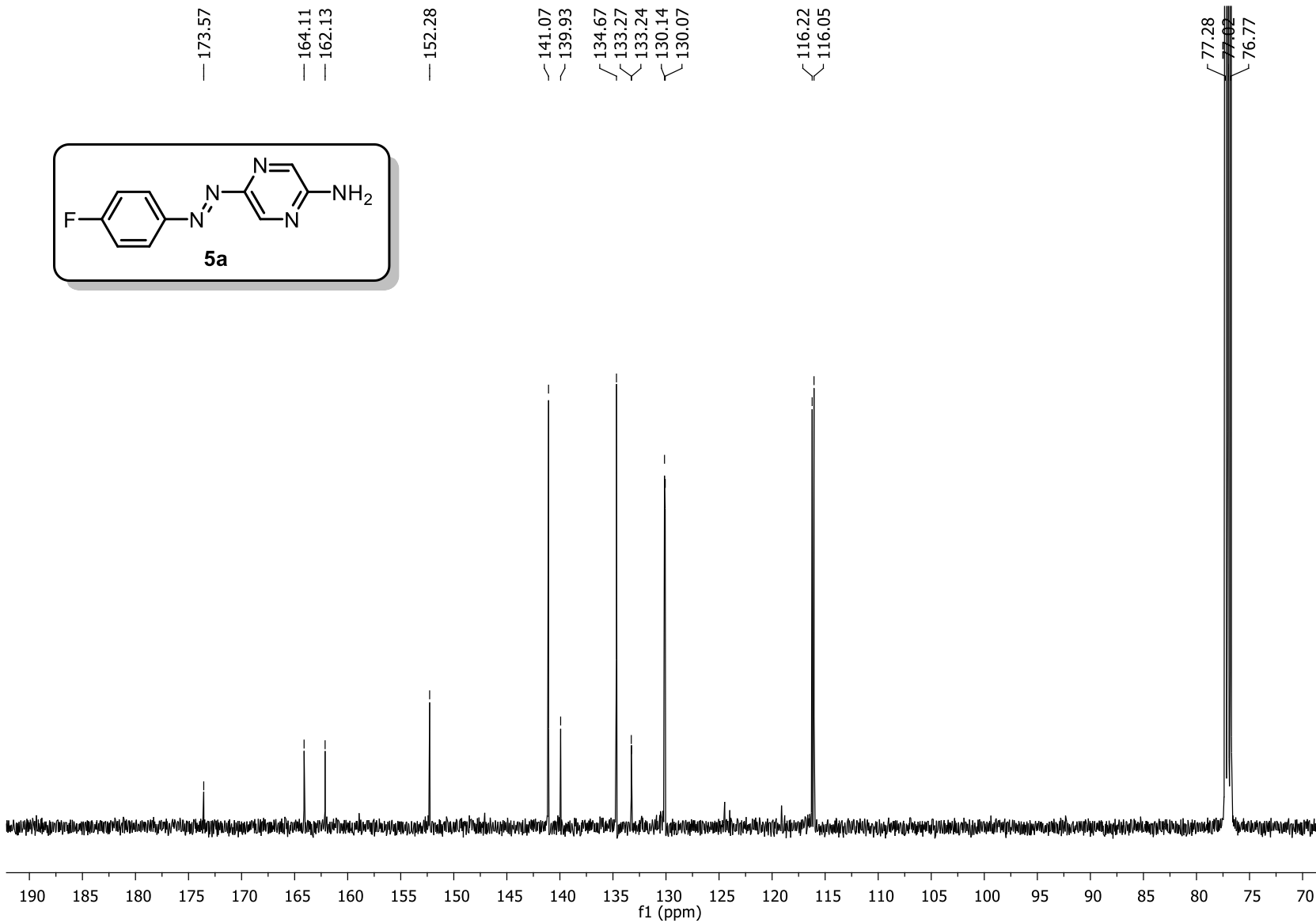


8.06  
8.05  
8.00  
8.00  
7.75  
7.74  
7.73  
7.28  
7.23  
7.22  
7.20

— 4.77



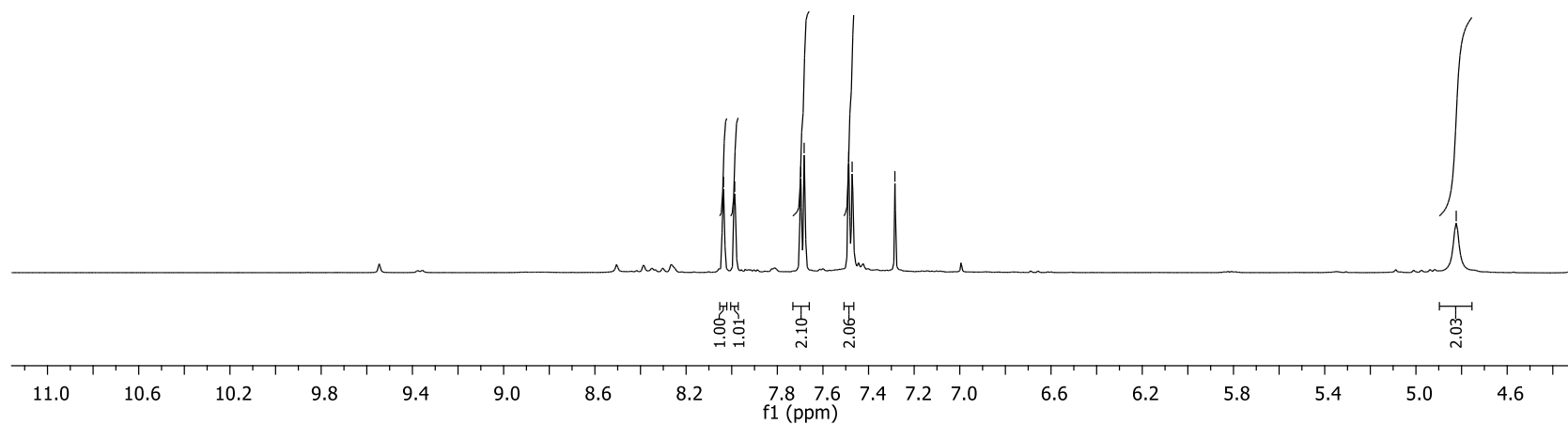
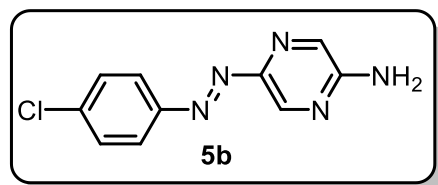
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((4-fluorophenyl)diazenyl)pyrazin-2-amine (**5a**)



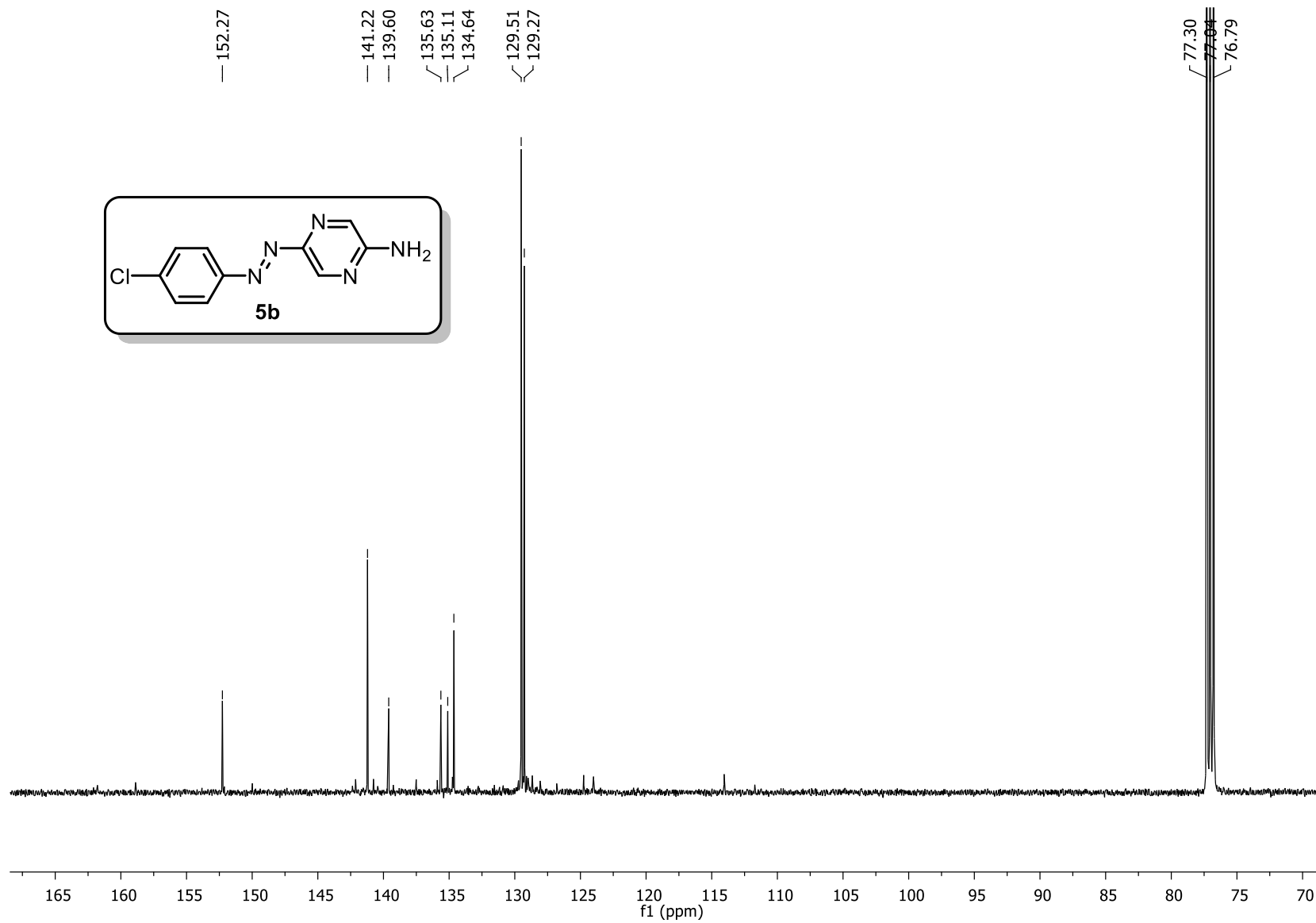
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((4-chlorophenyl)diazenyl)pyrazin-2-amine (**5b**)

8.04  
7.99  
7.70  
7.68  
7.49  
7.47  
7.28

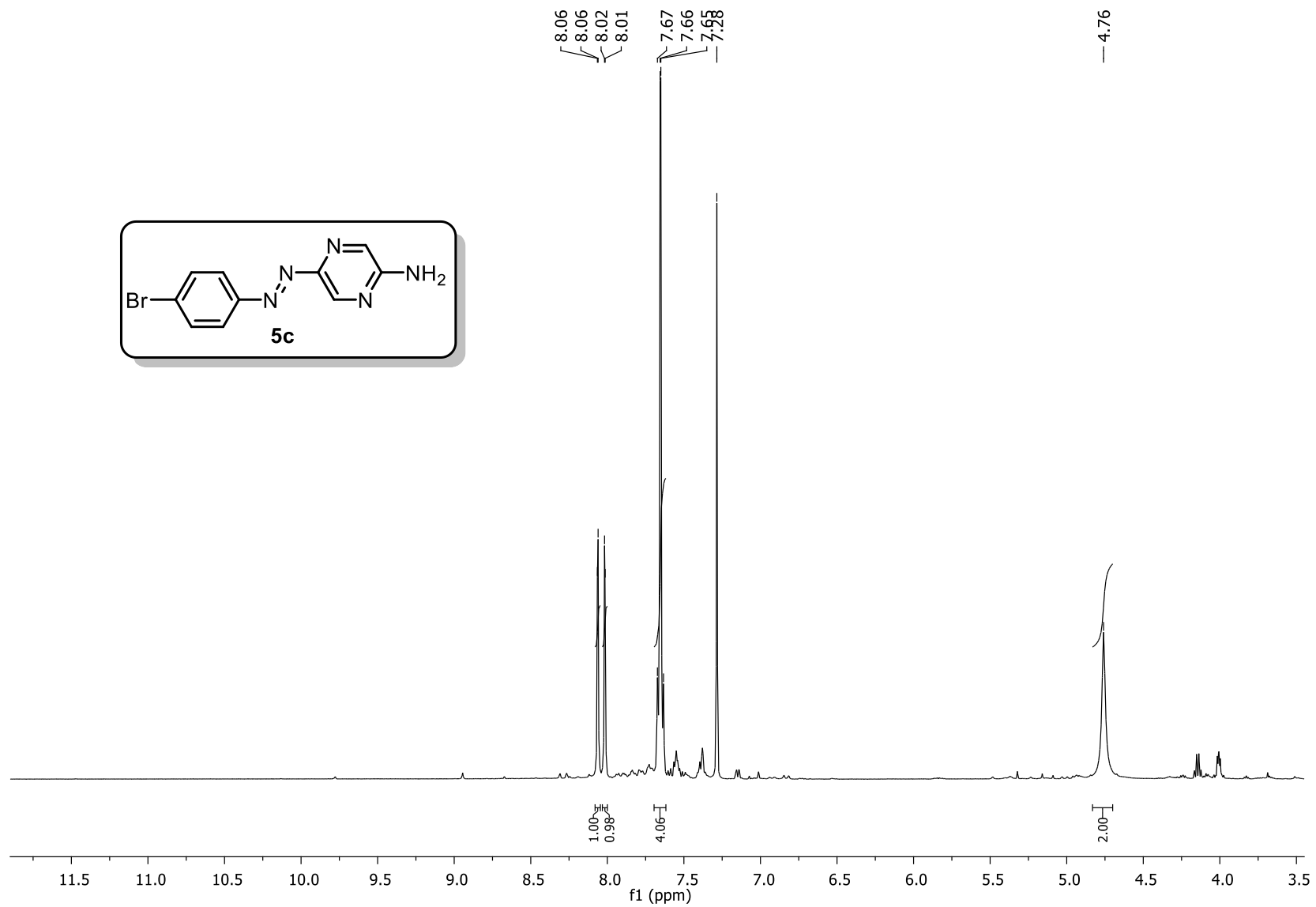
4.82



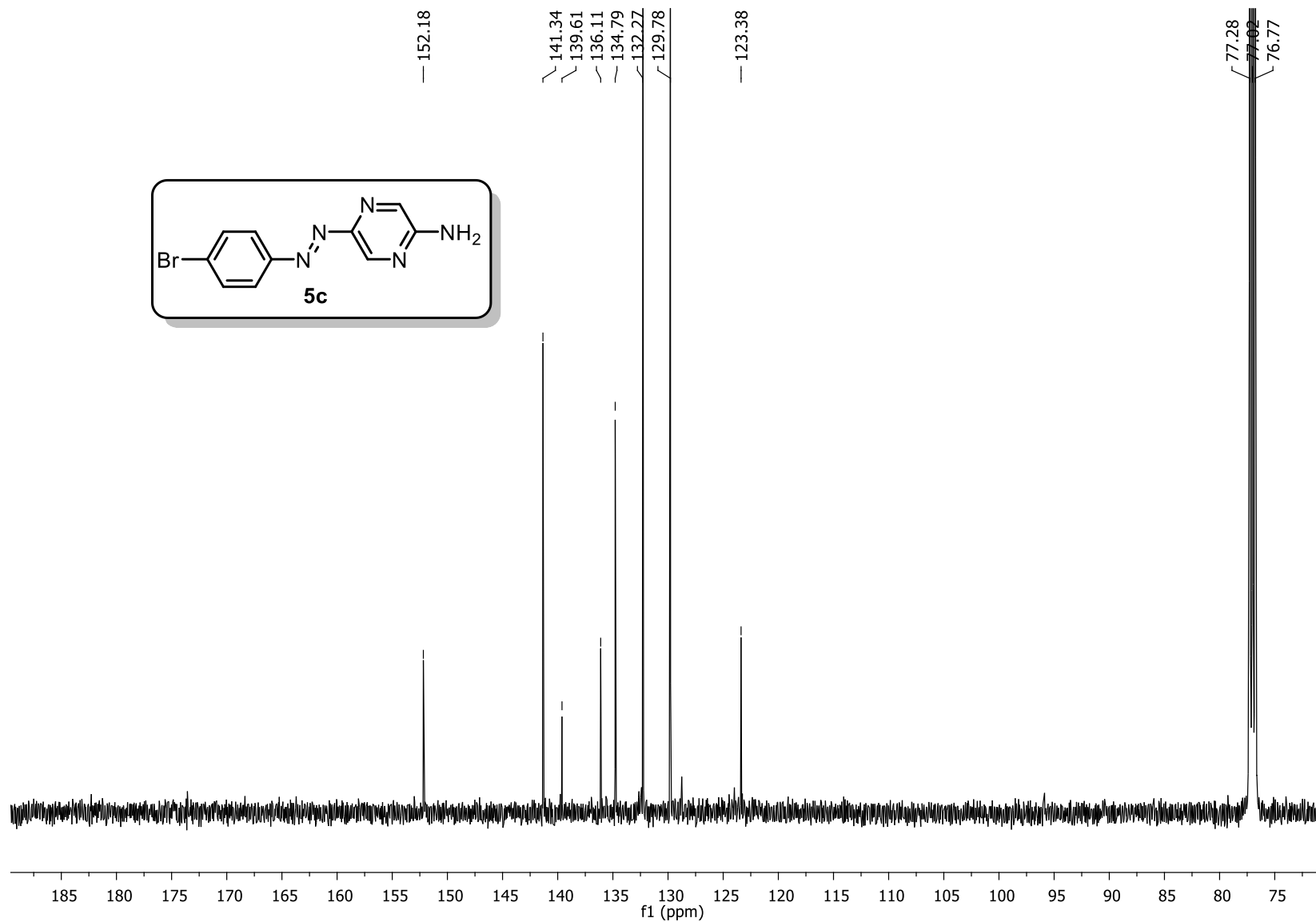
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((4-chlorophenyl)diazenyl)pyrazin-2-amine (**5b**)



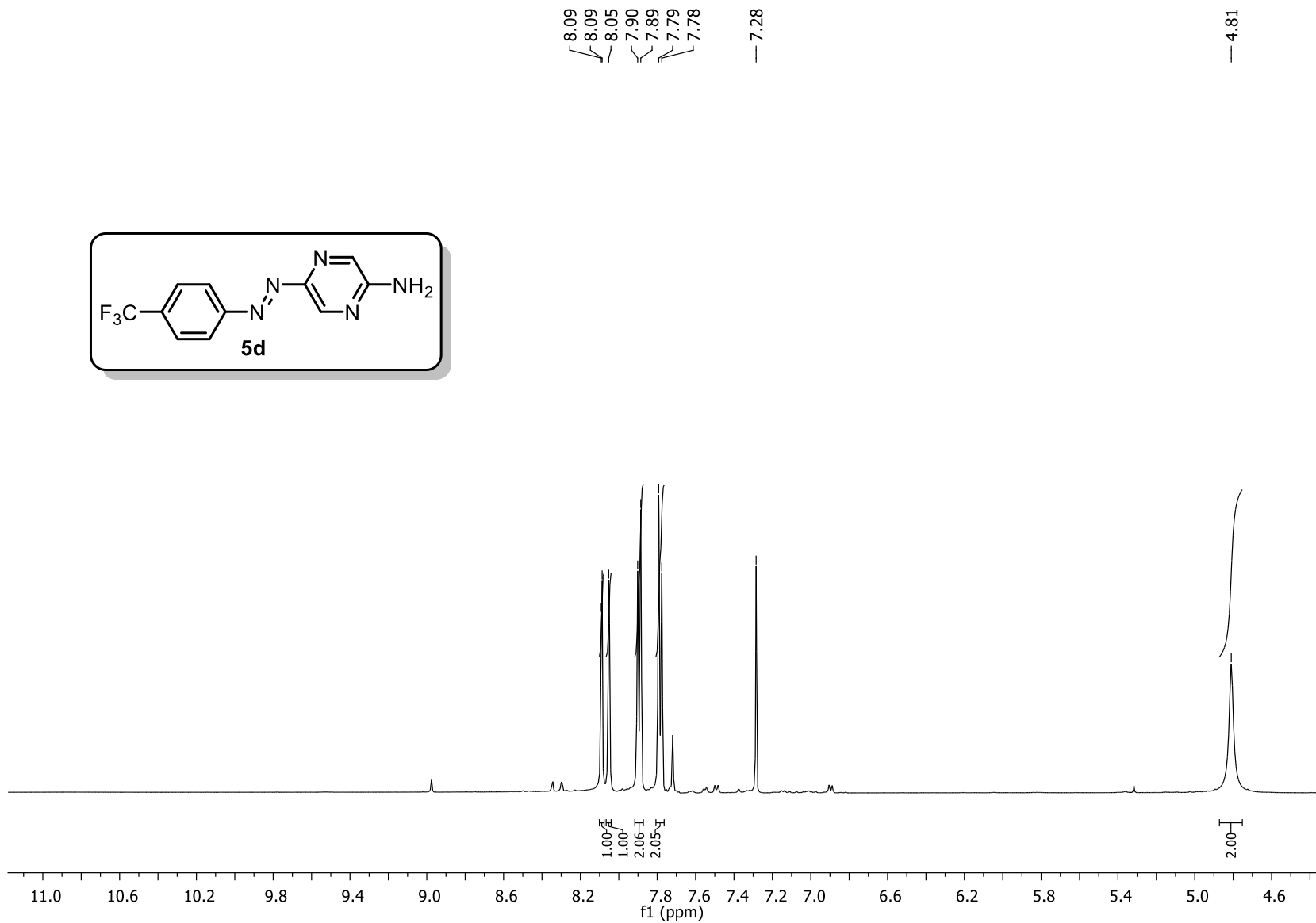
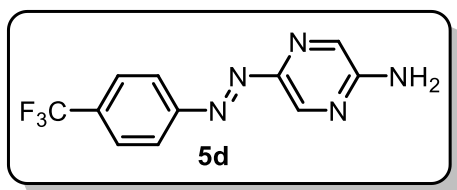
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((4-bromophenyl)diazenyl)pyrazin-2-amine (**5c**)



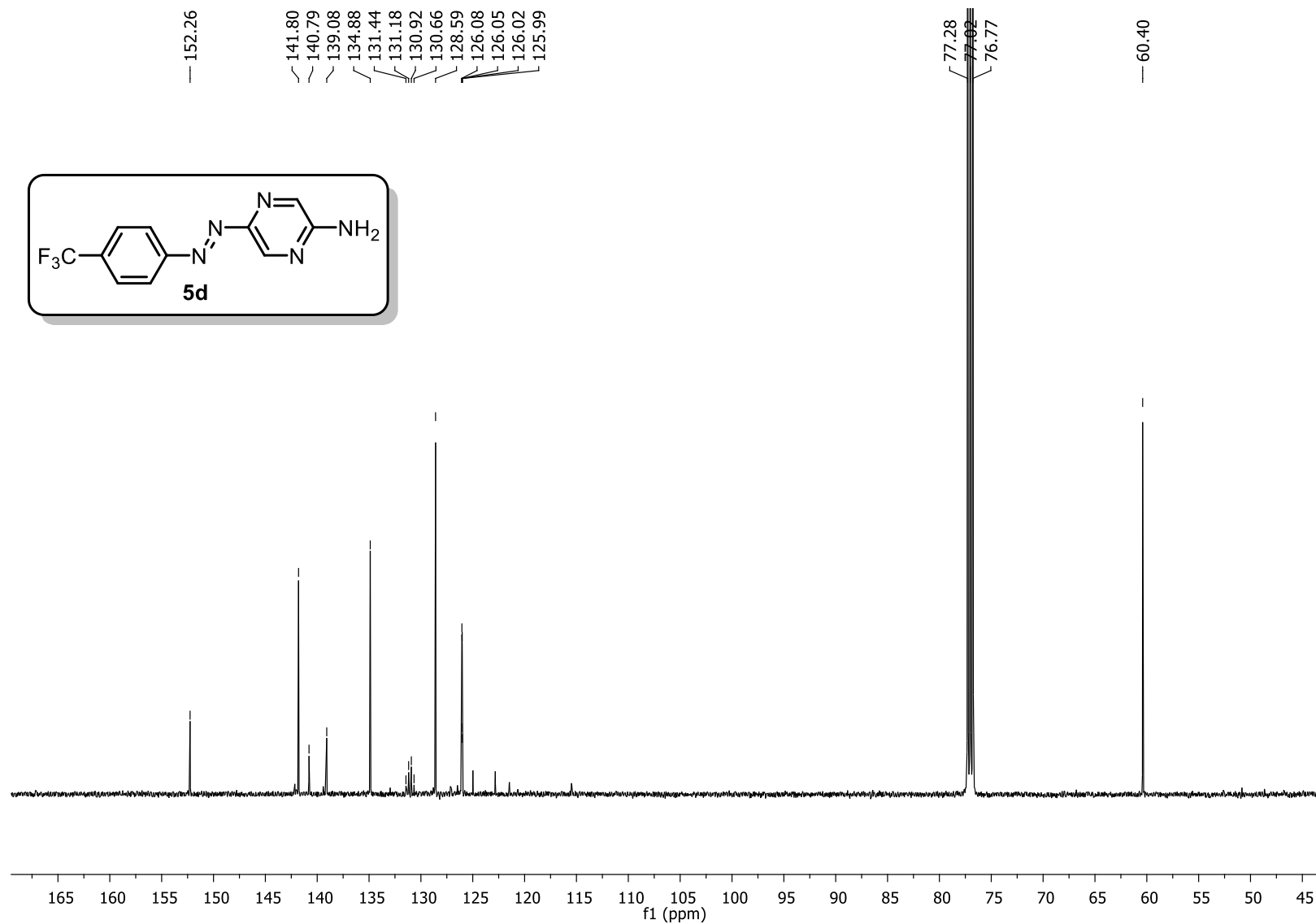
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((4-bromophenyl)diazenyl)pyrazin-2-amine (**5c**)



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((4-(trifluoromethyl)phenyl)diazenyl)pyrazin-2-amine (**5d**)

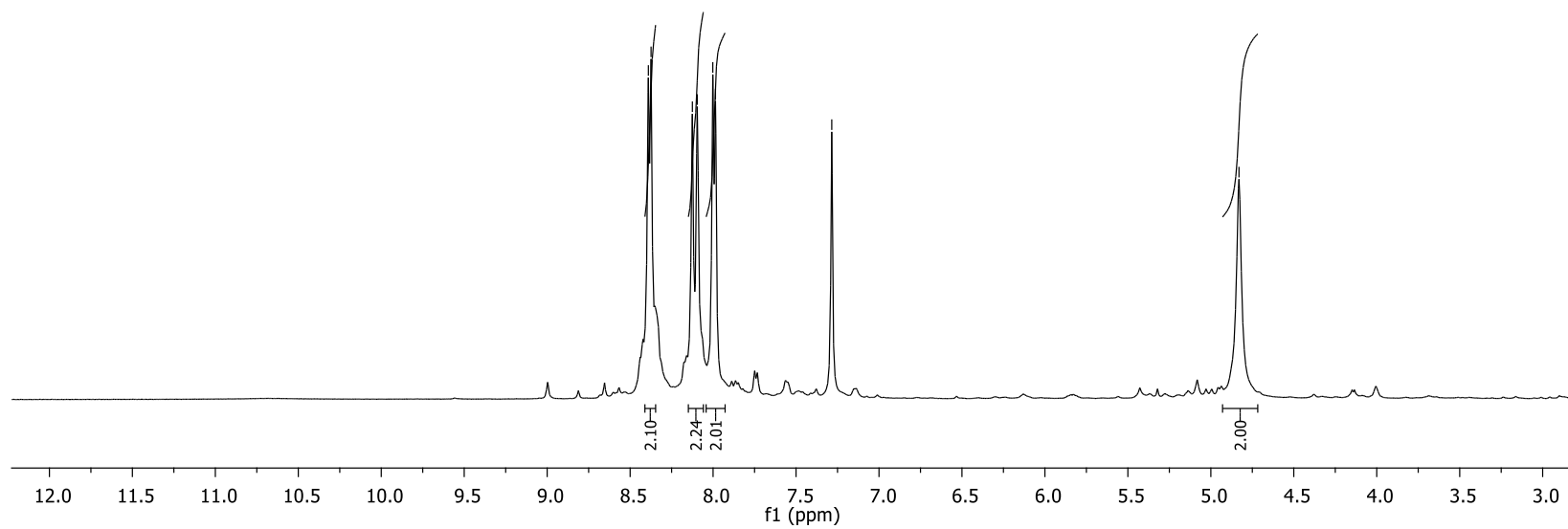
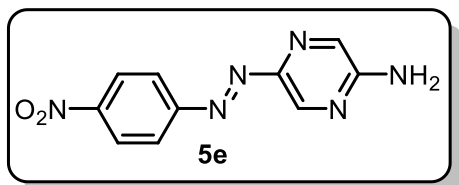


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((4-(trifluoromethyl)phenyl)diazenyl)pyrazin-2-amine (**5d**)

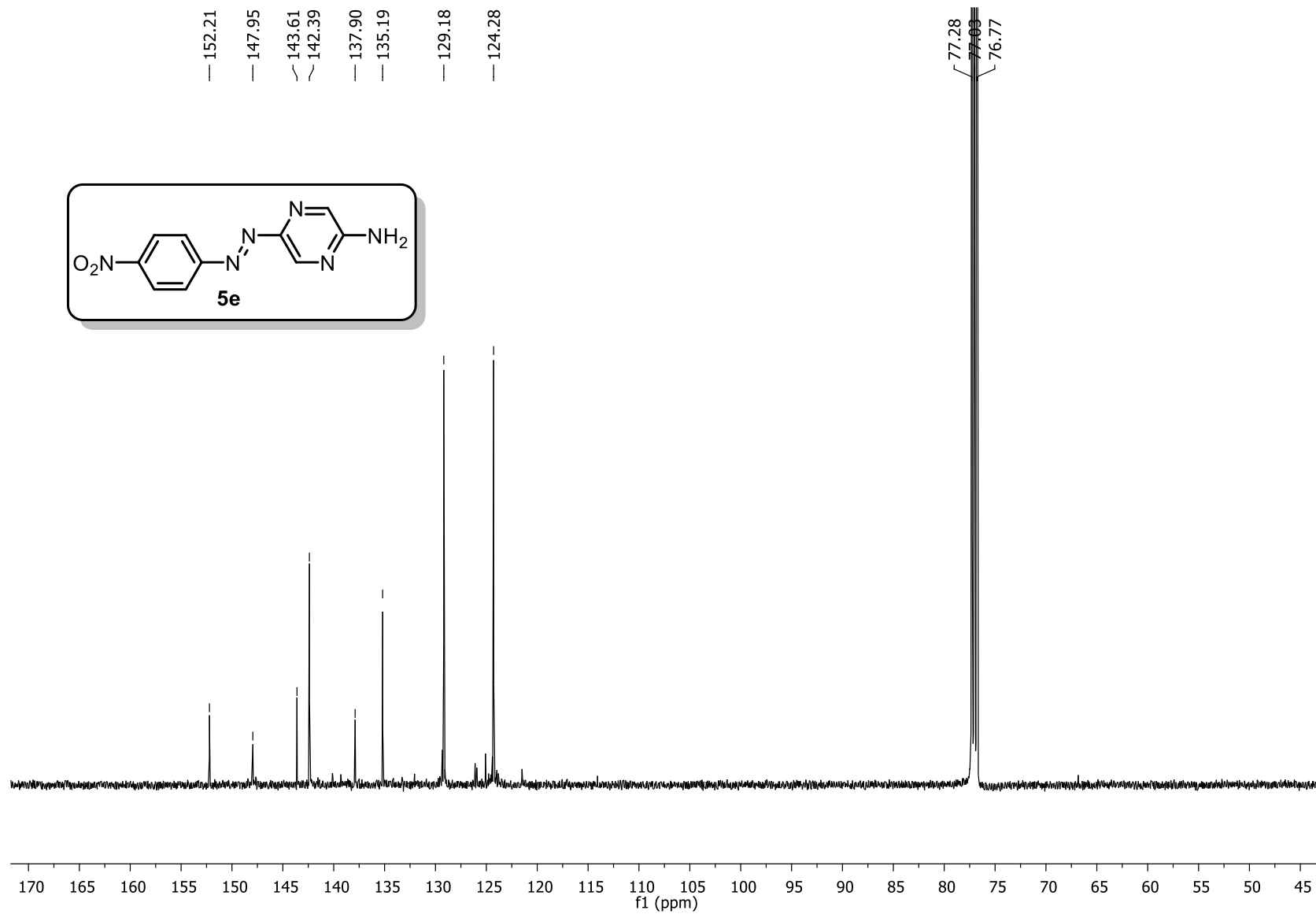


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((4-nitrophenyl)diazenyl)pyrazin-2-amine (**5e**)

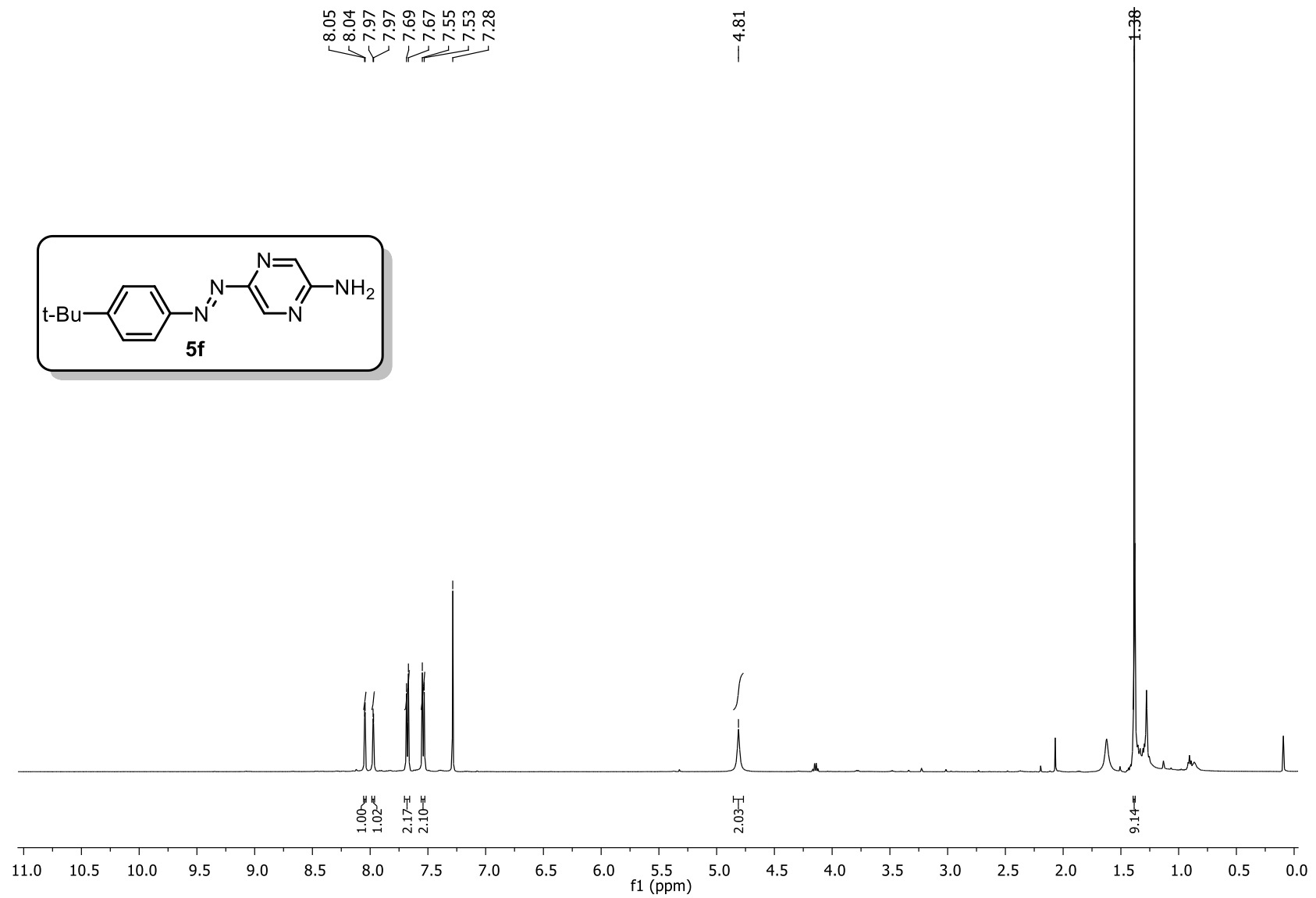
8.39  
8.37  
8.12  
8.10  
8.00  
7.99  
— 7.28  
— 4.83



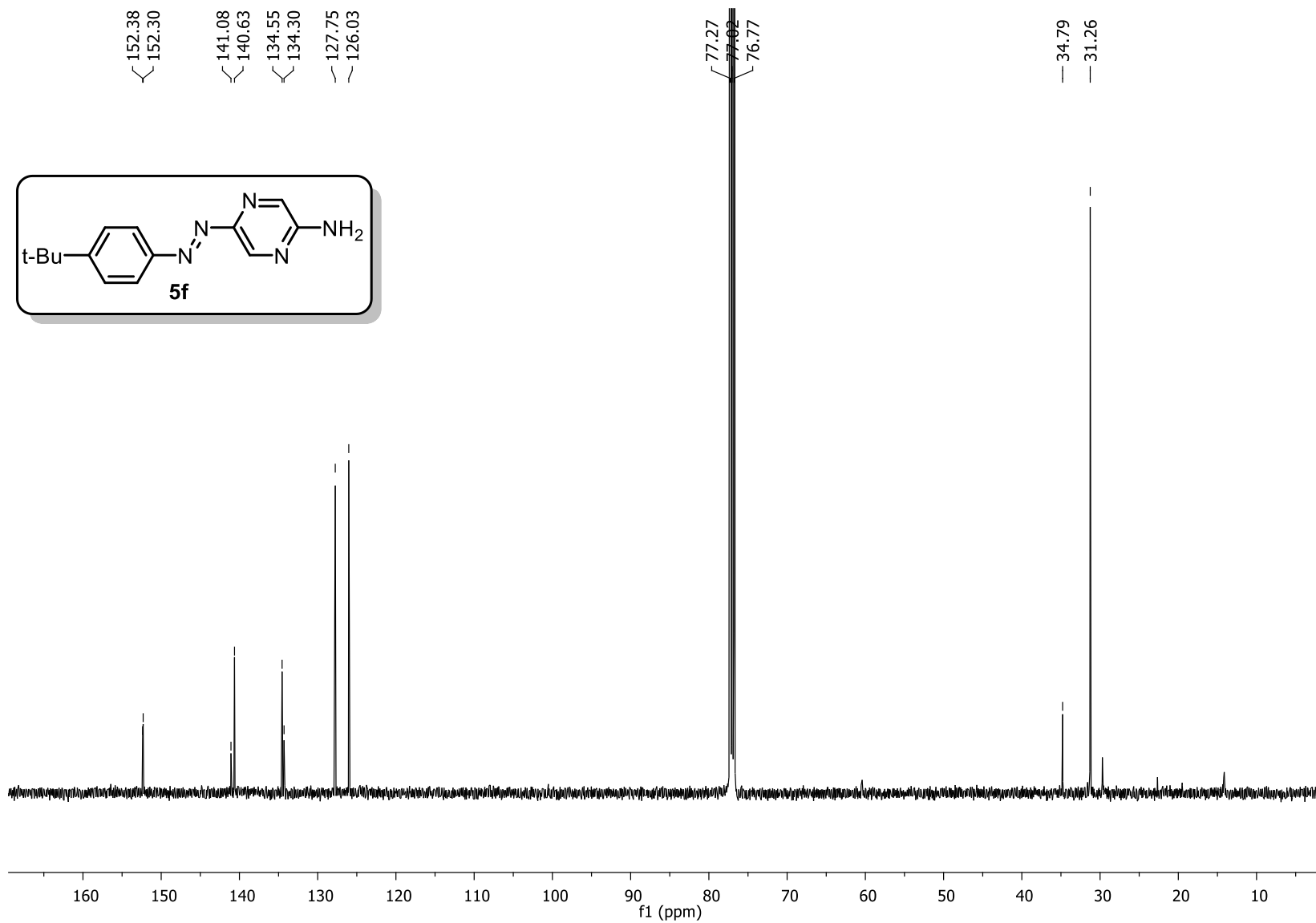
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz) spectrum of (*E*)-5-((4-nitrophenyl)diazenyl)pyrazin-2-amine (**5e**)



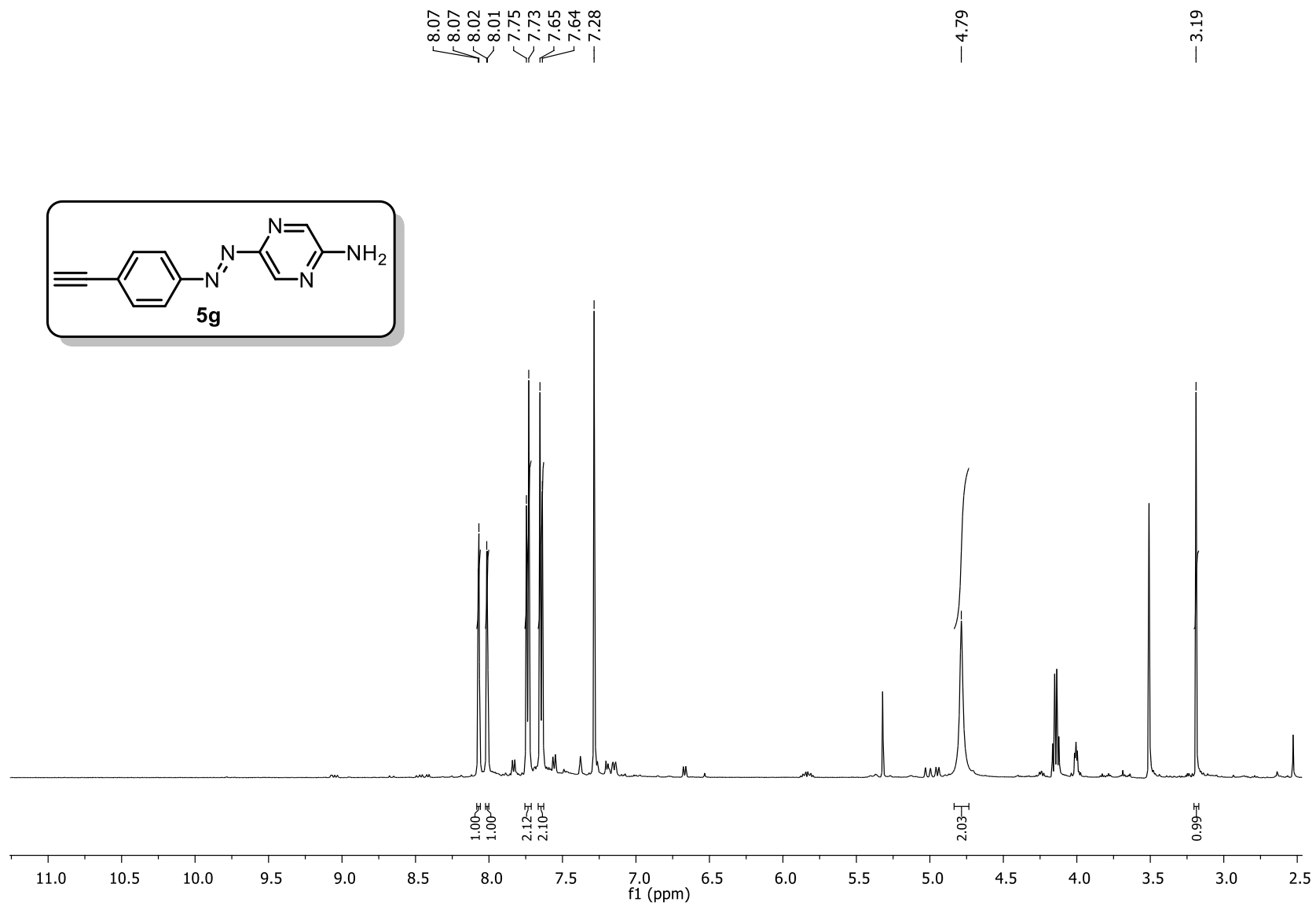
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((4-(tert-butyl)phenyl)diazenyl)pyrazin-2-amine (**5f**)



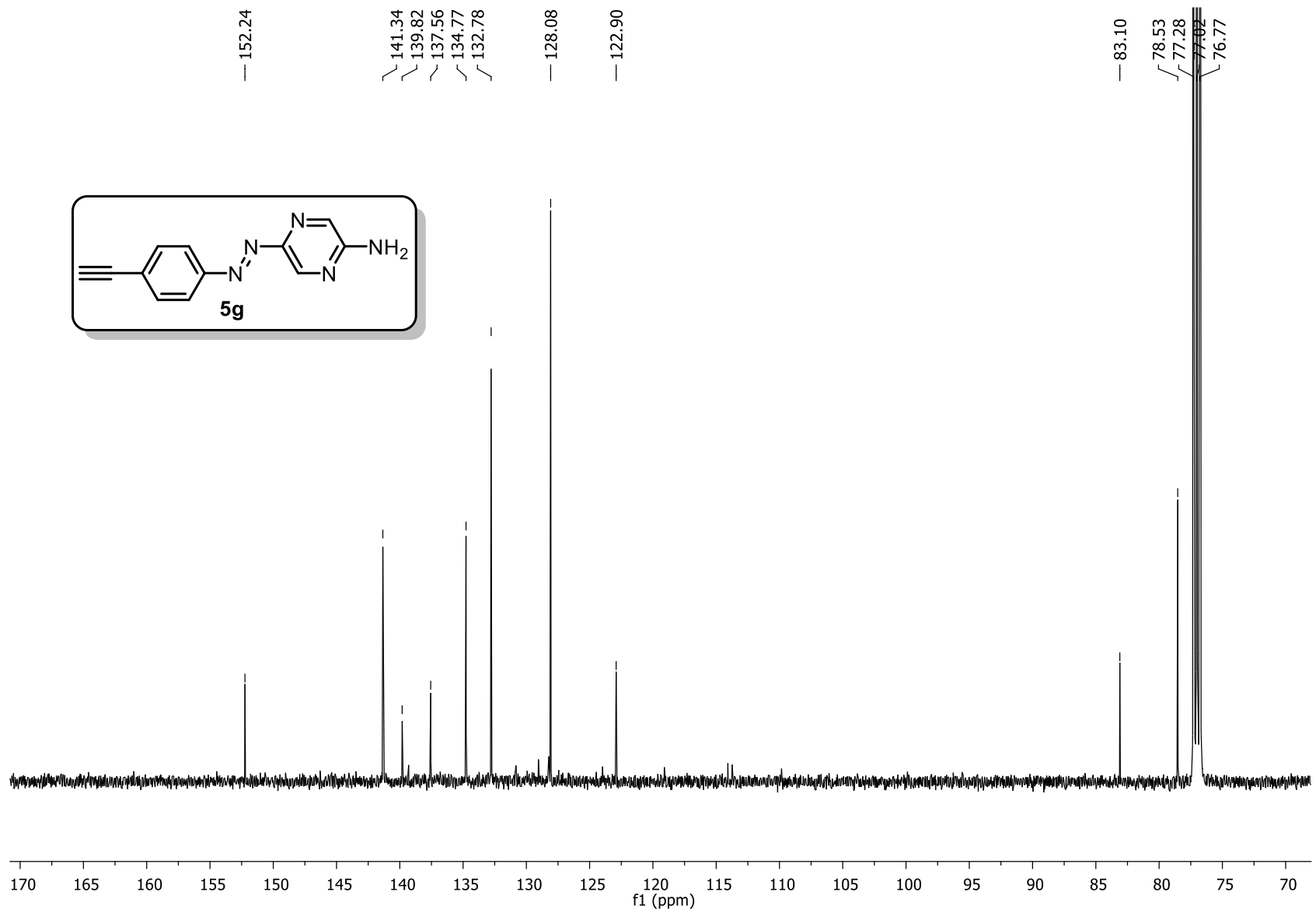
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((4-(tert-butyl)phenyl)diazenyl)pyrazin-2-amine (**5f**)



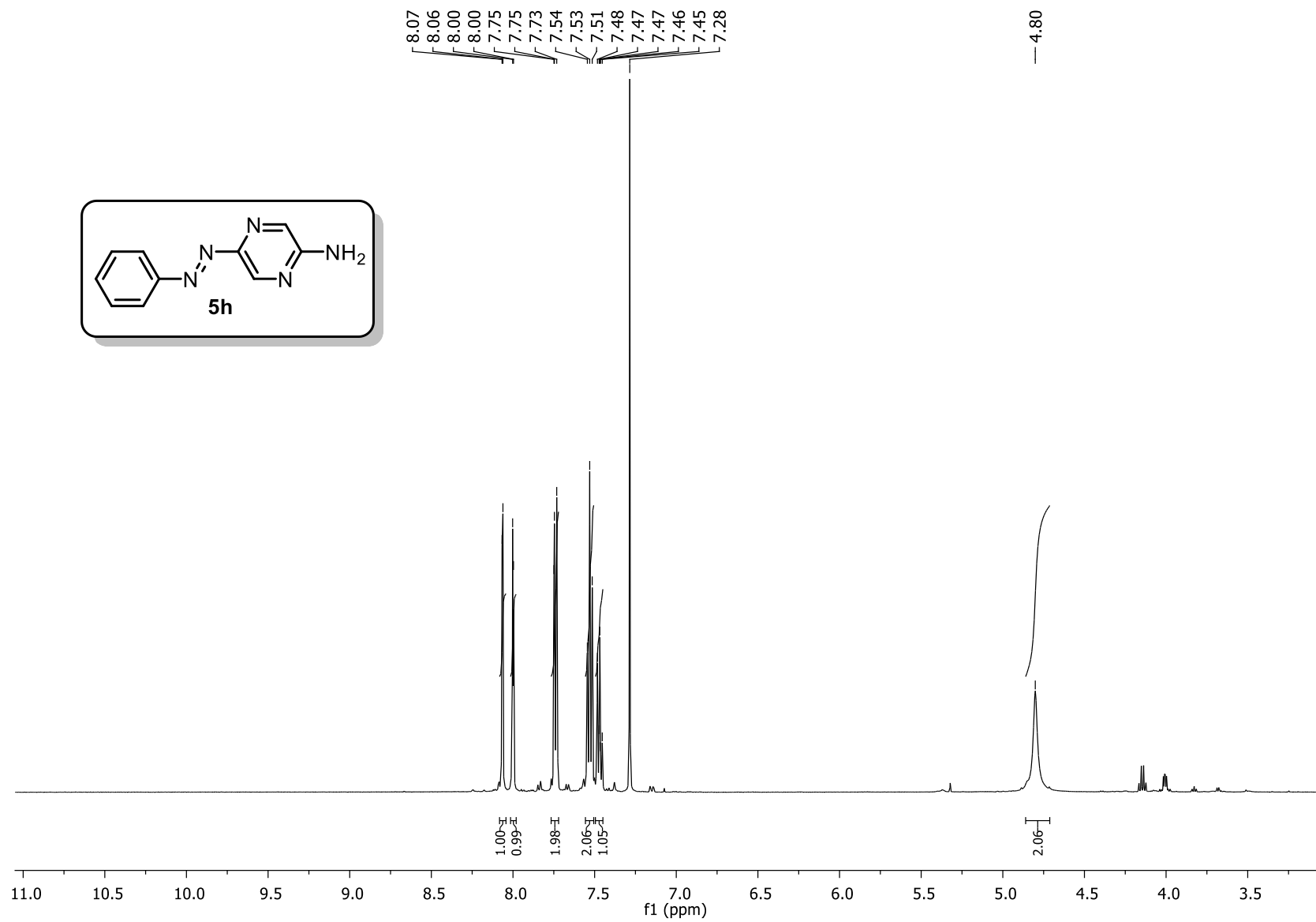
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((4-ethynylphenyl)diazenyl)pyrazin-2-amine (**5g**)



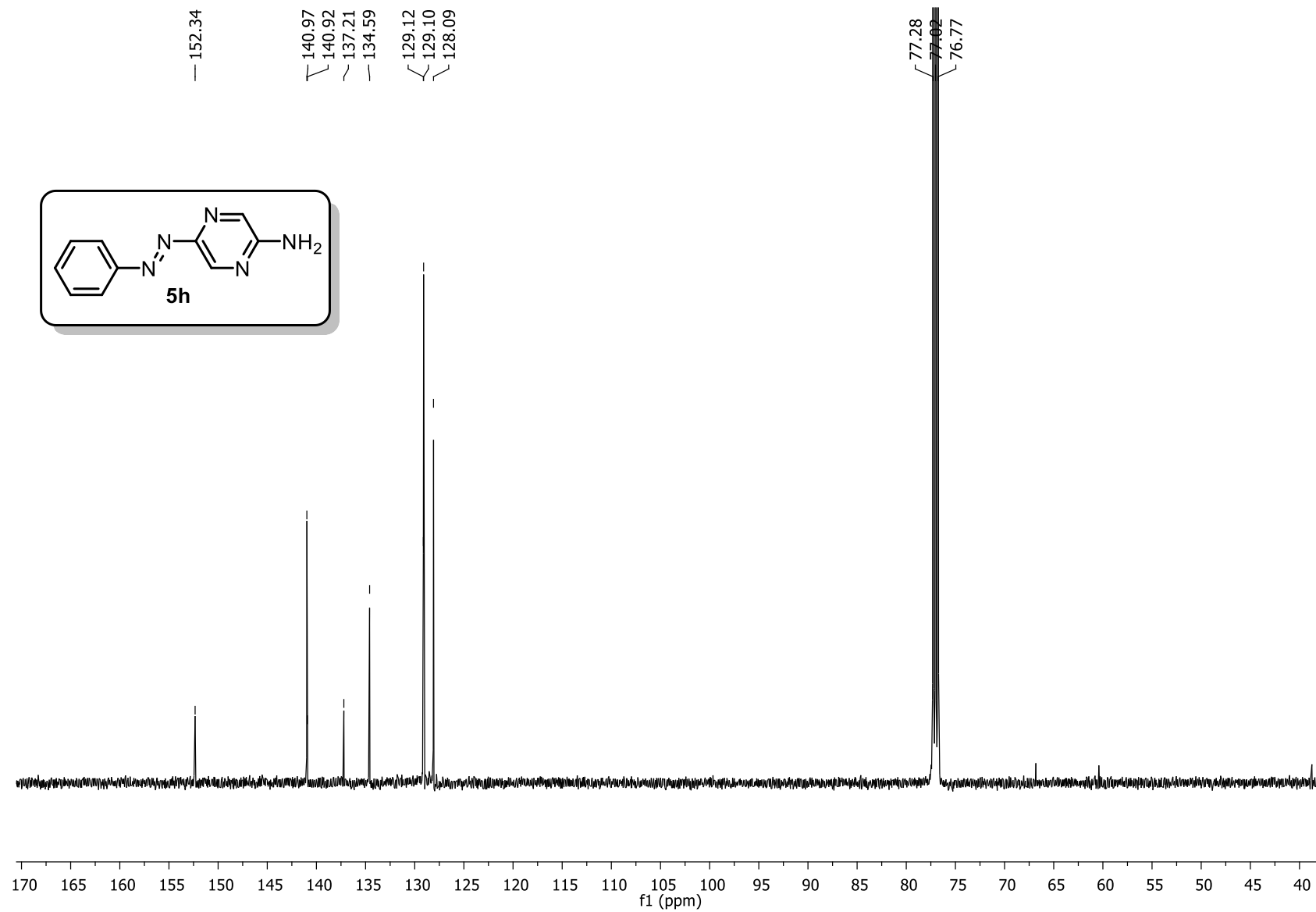
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((4-ethynylphenyl)diazenyl)pyrazin-2-amine (**5g**)



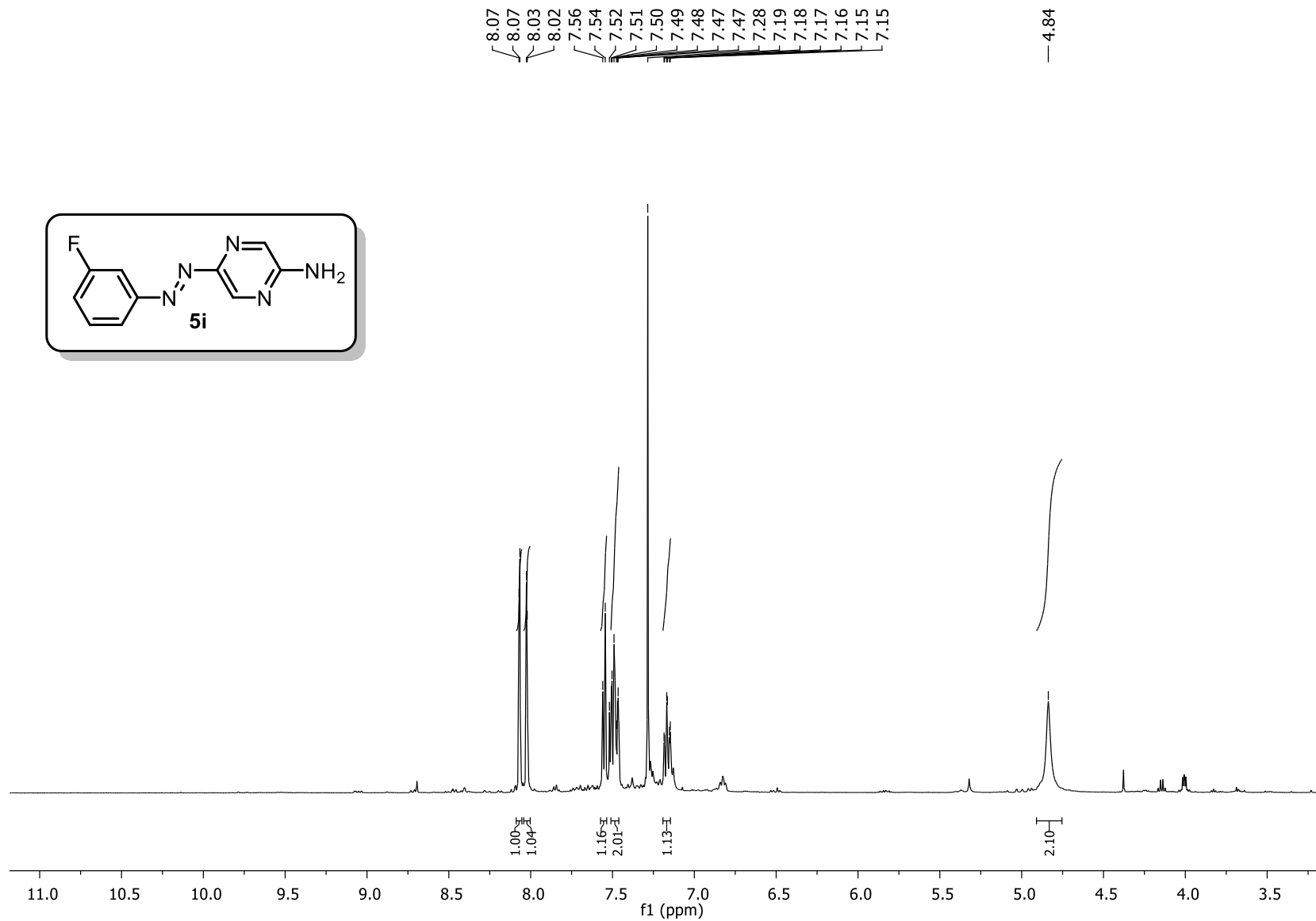
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-(phenyldiazenyl)pyrazin-2-amine (**5h**)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-(phenyldiazenyl)pyrazin-2-amine (**5h**)

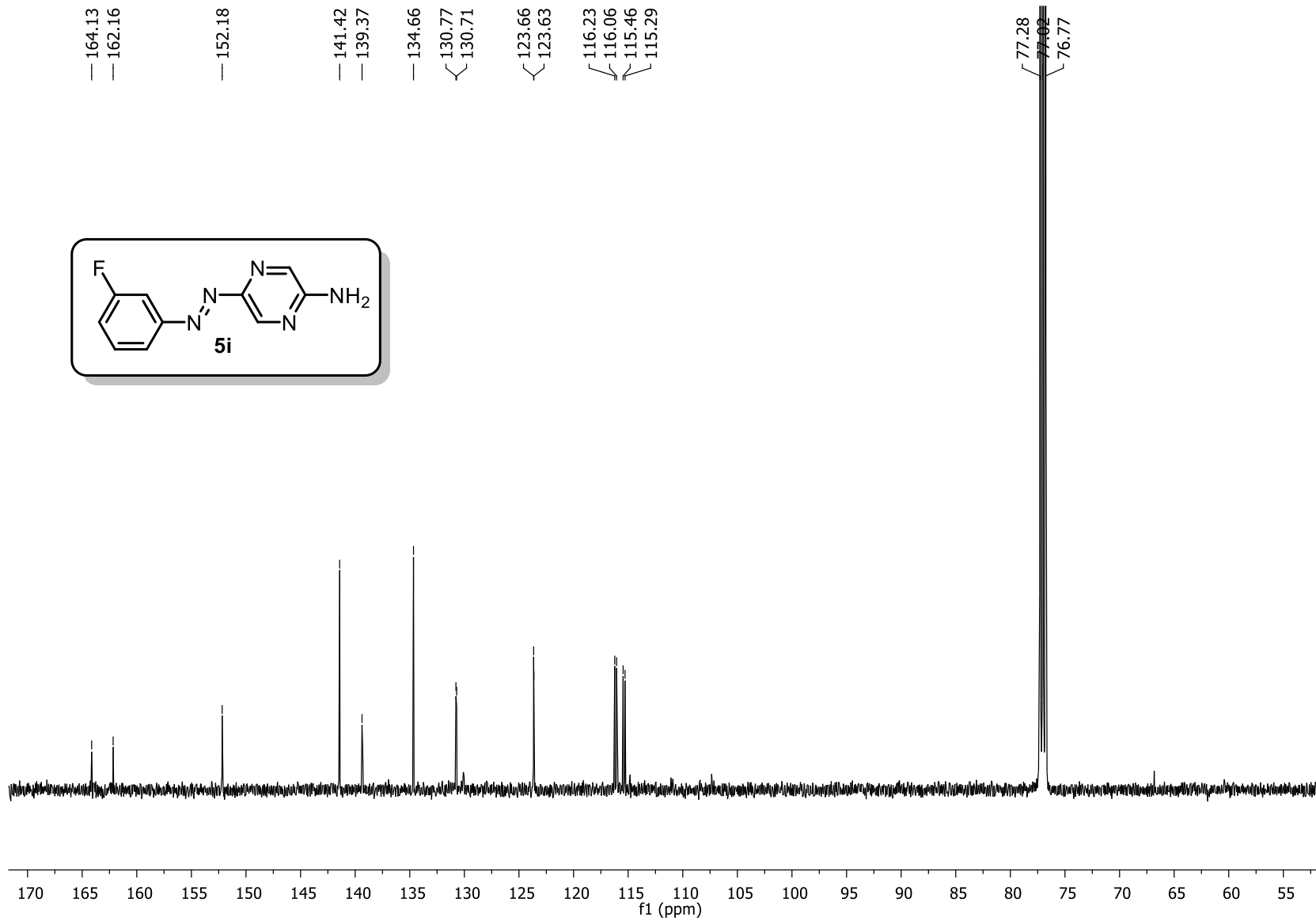
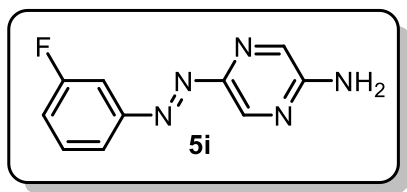


$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) spectrum of (*E*)-5-((3-fluorophenyl)diazenyl)pyrazin-2-amine (**5i**)

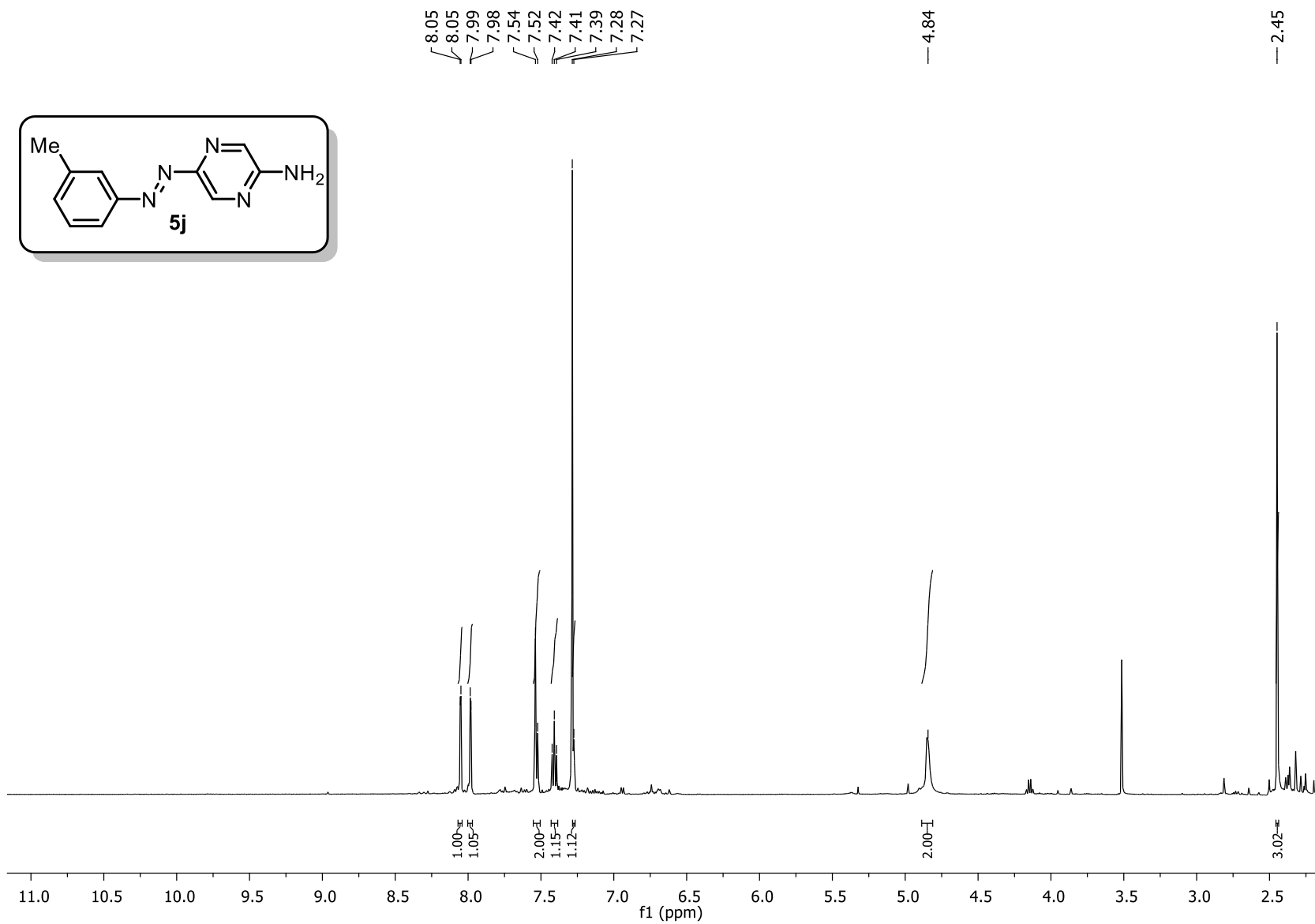


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((3-fluorophenyl)diazenyl)pyrazin-2-amine (**5i**)

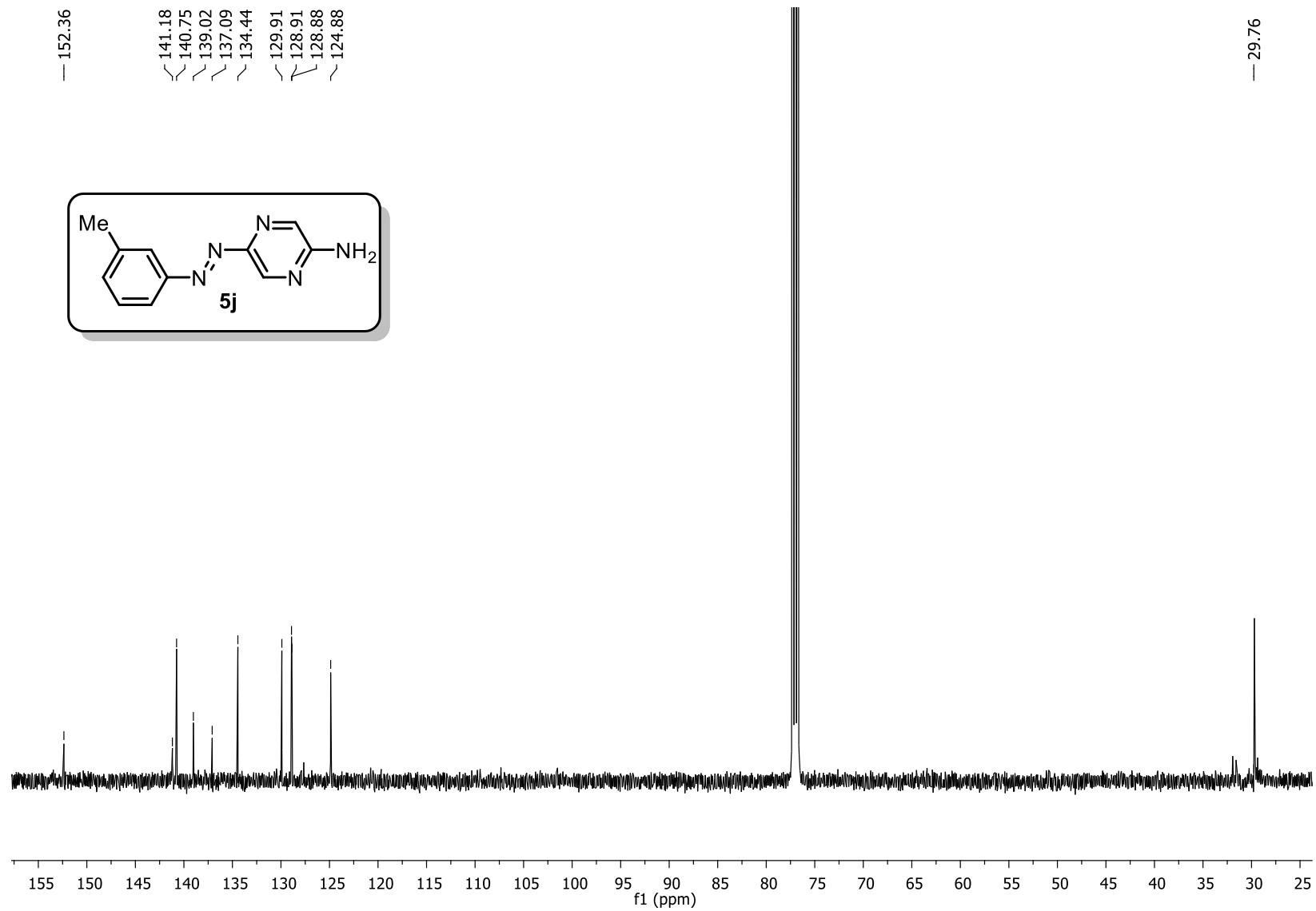
— 164.13  
— 162.16  
  
— 152.18  
  
— 141.42  
— 139.37  
  
— 134.66  
— 130.77  
— 130.71  
  
— 123.66  
— 123.63  
  
— 116.23  
— 116.06  
— 115.46  
— 115.29  
  
— 77.28  
— 77.02  
— 76.77



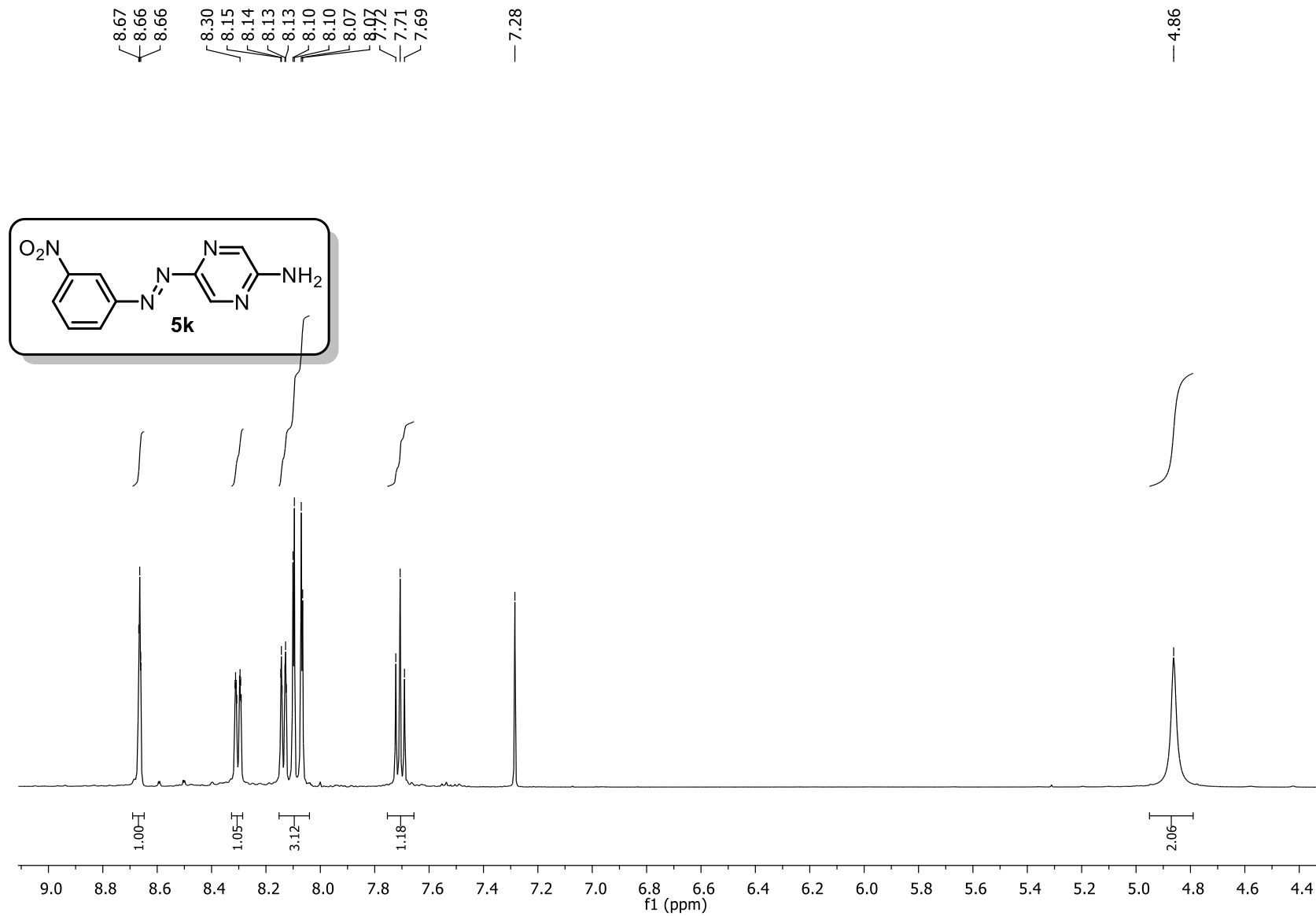
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-(*m*-tolyl diazenyl)pyrazin-2-amine (**5j**)



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz) spectrum of (*E*)-5-(*m*-tolyl diazenyl)pyrazin-2-amine (**5j**)

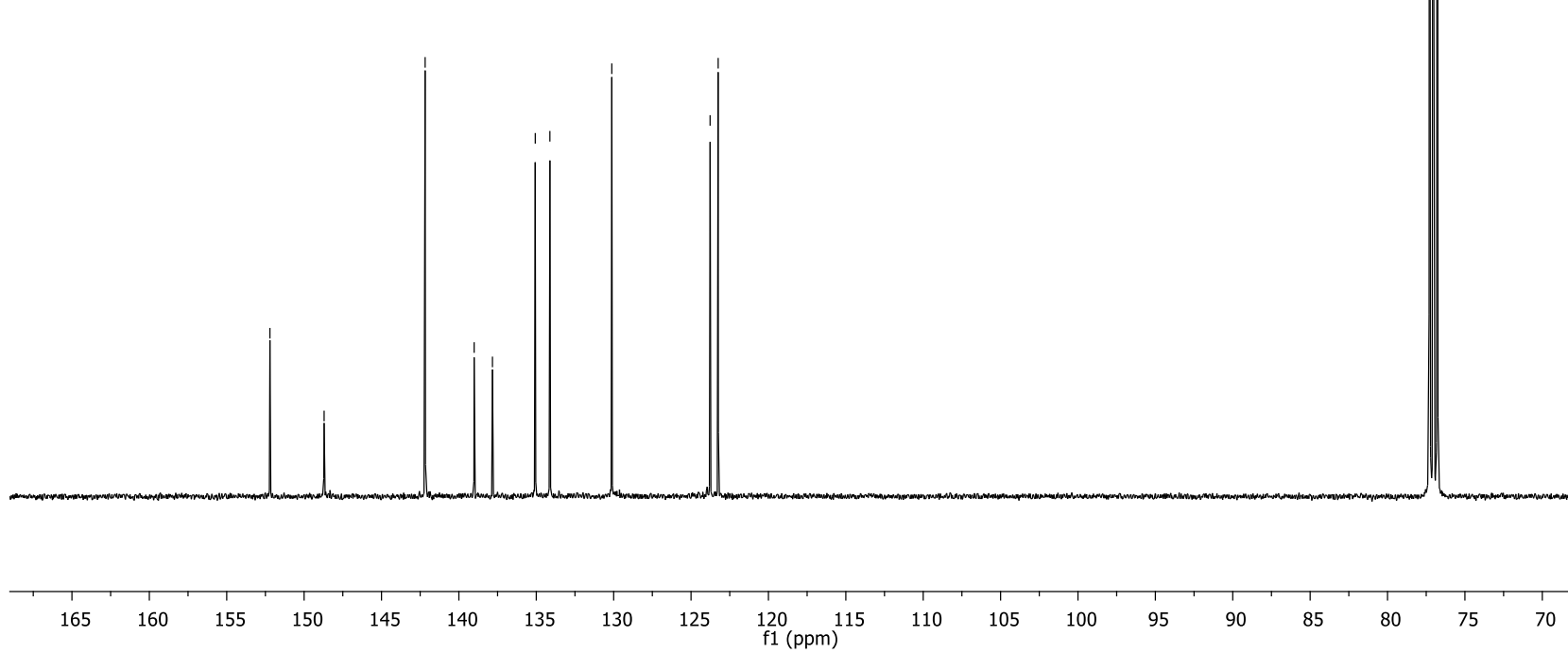
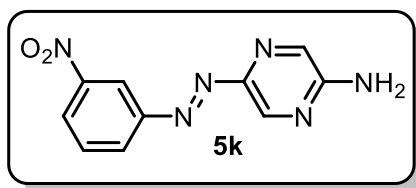


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((3-nitrophenyl)diazenyl)pyrazin-2-amine (**5k**)

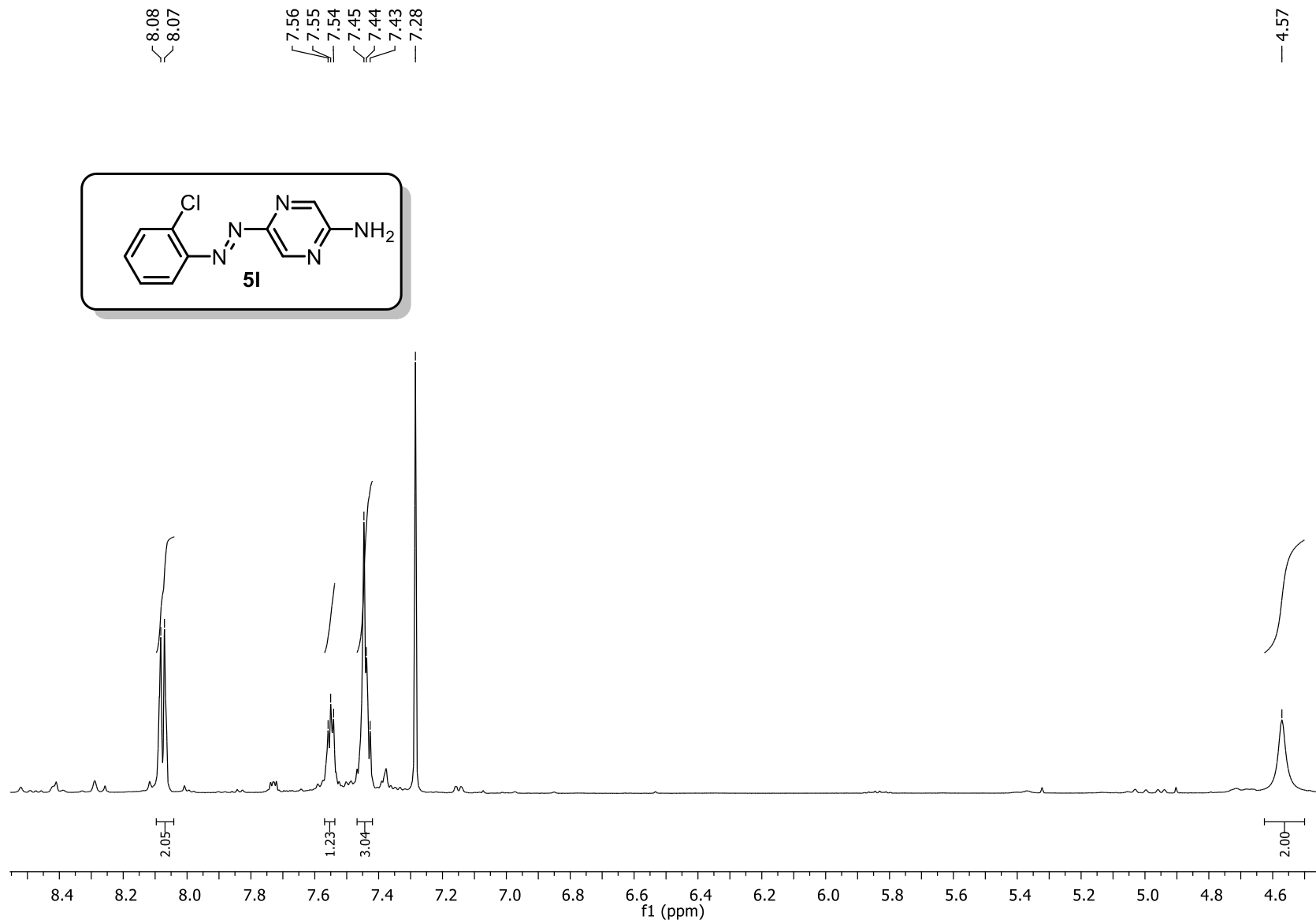


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((3-nitrophenyl)diazenyl)pyrazin-2-amine (**5k**)

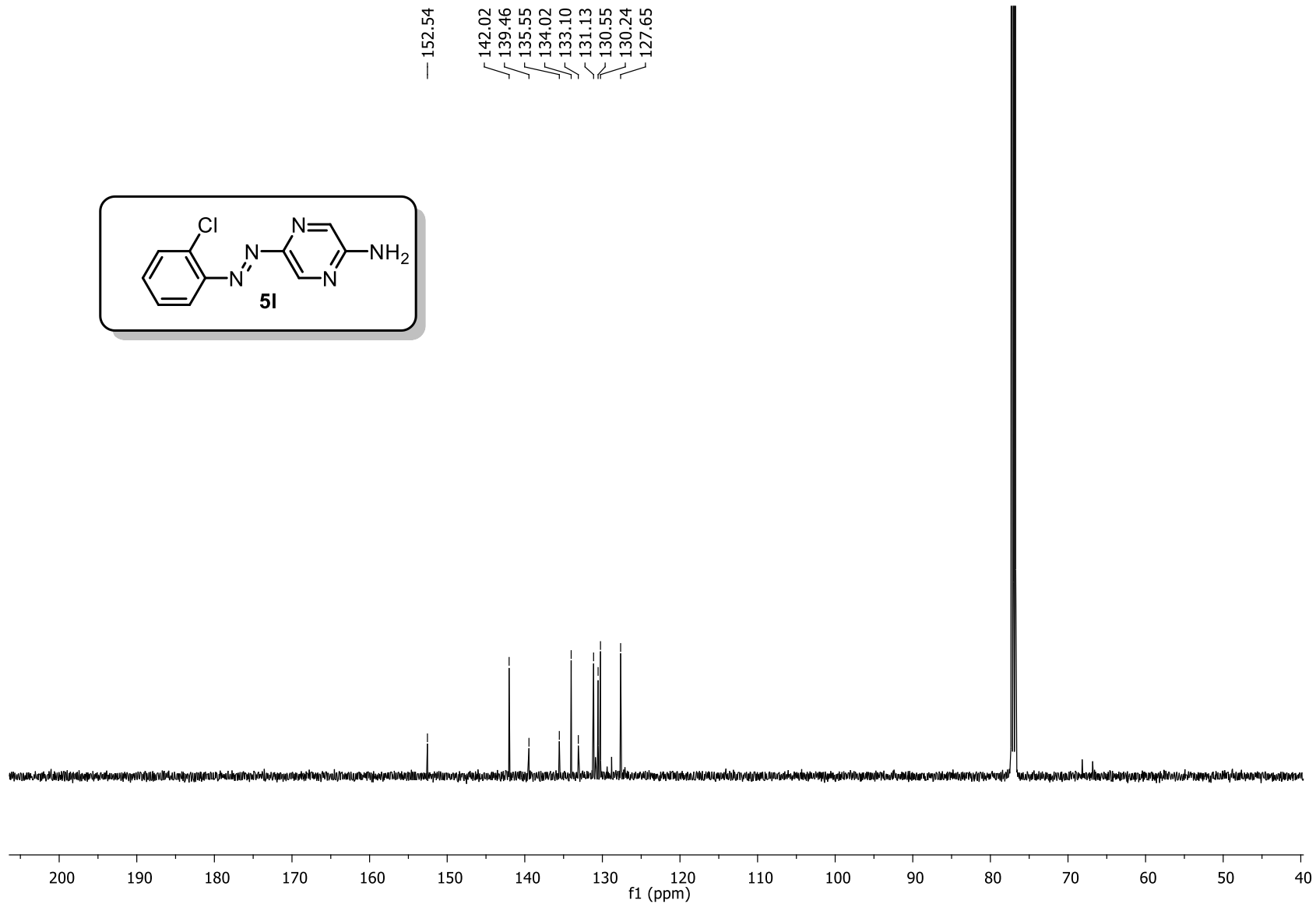
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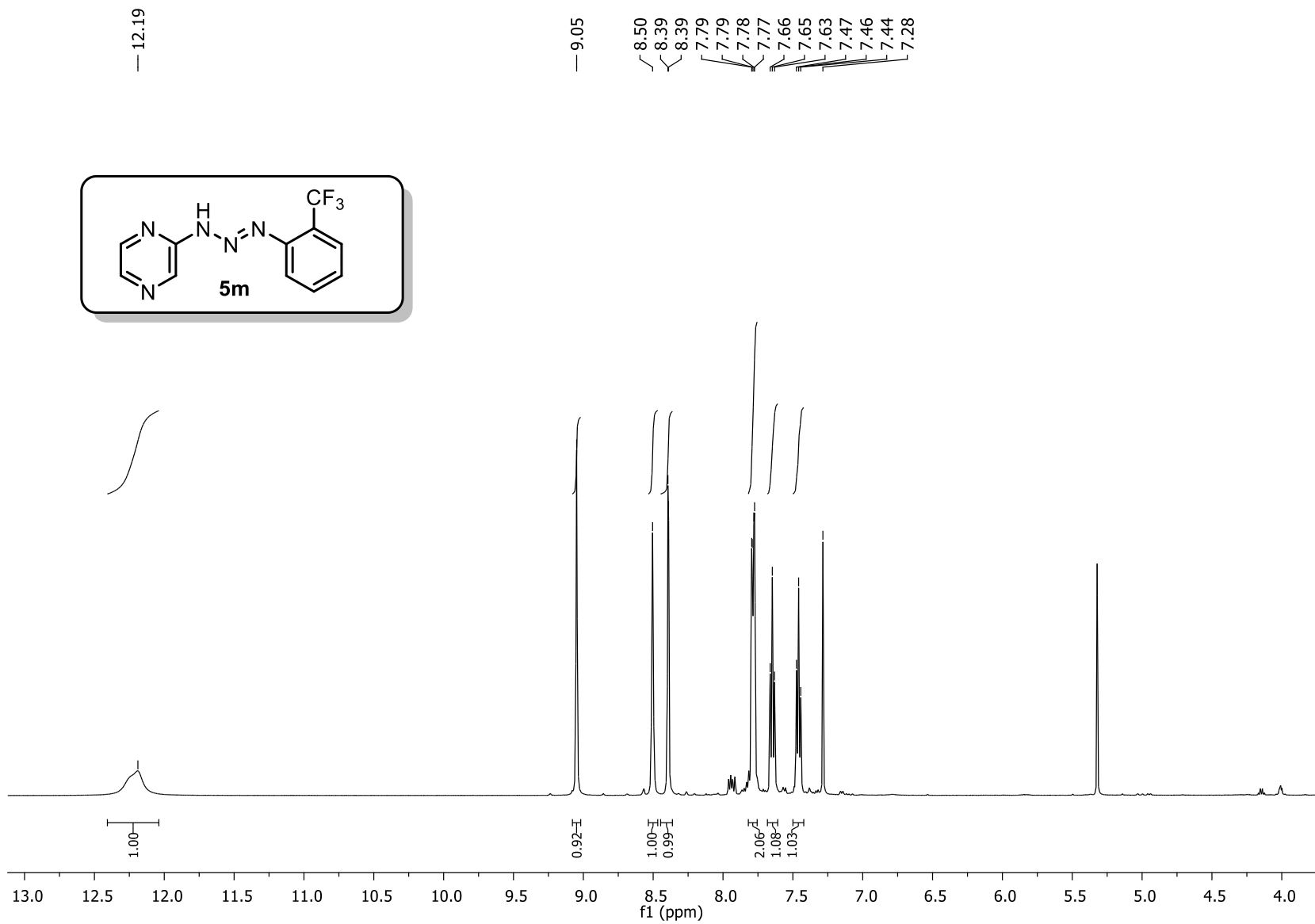
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-5-((2-chlorophenyl)diazenyl)pyrazin-2-amine (**5I**)



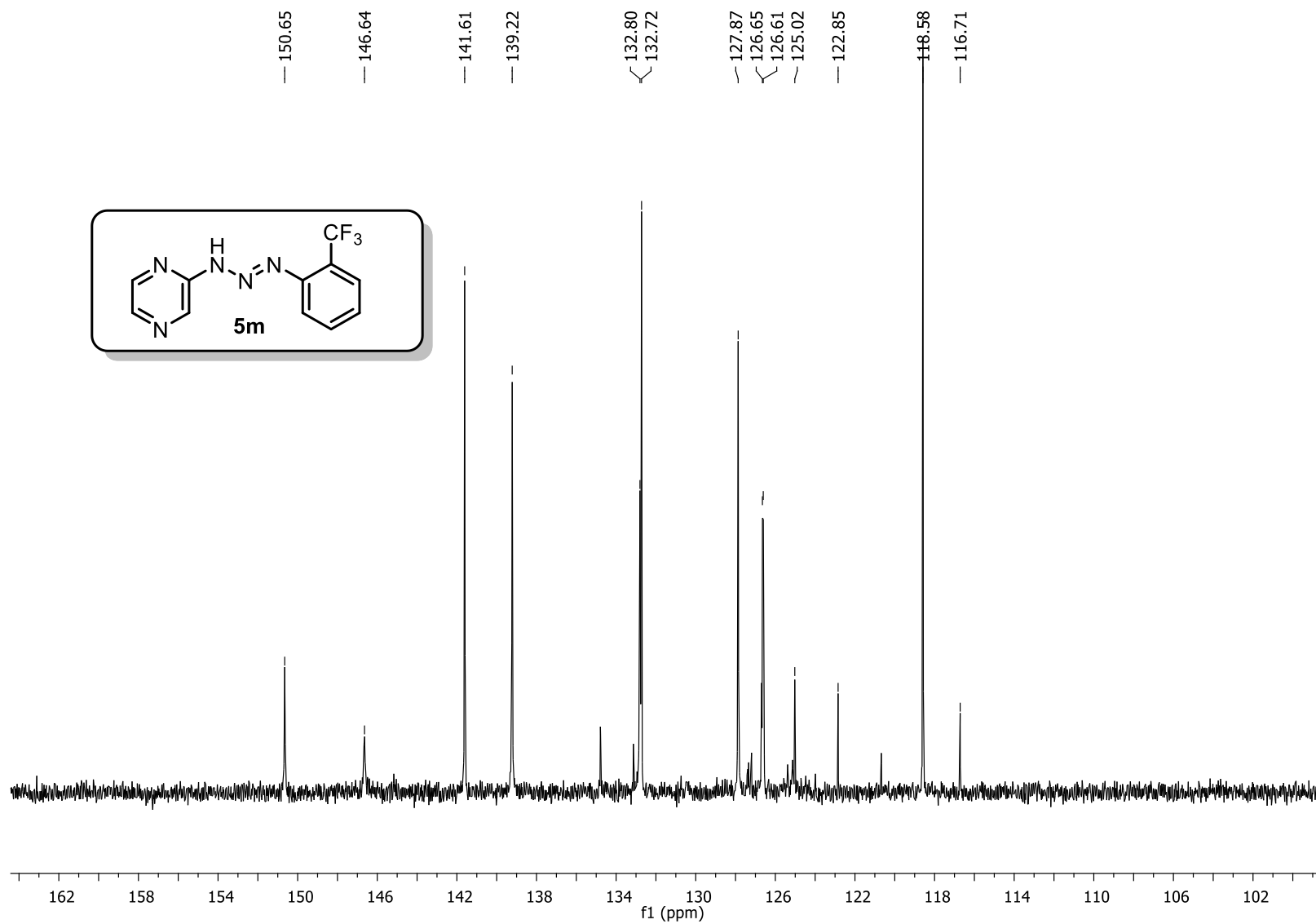
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-5-((2-chlorophenyl)diazenyl)pyrazin-2-amine (**5I**)



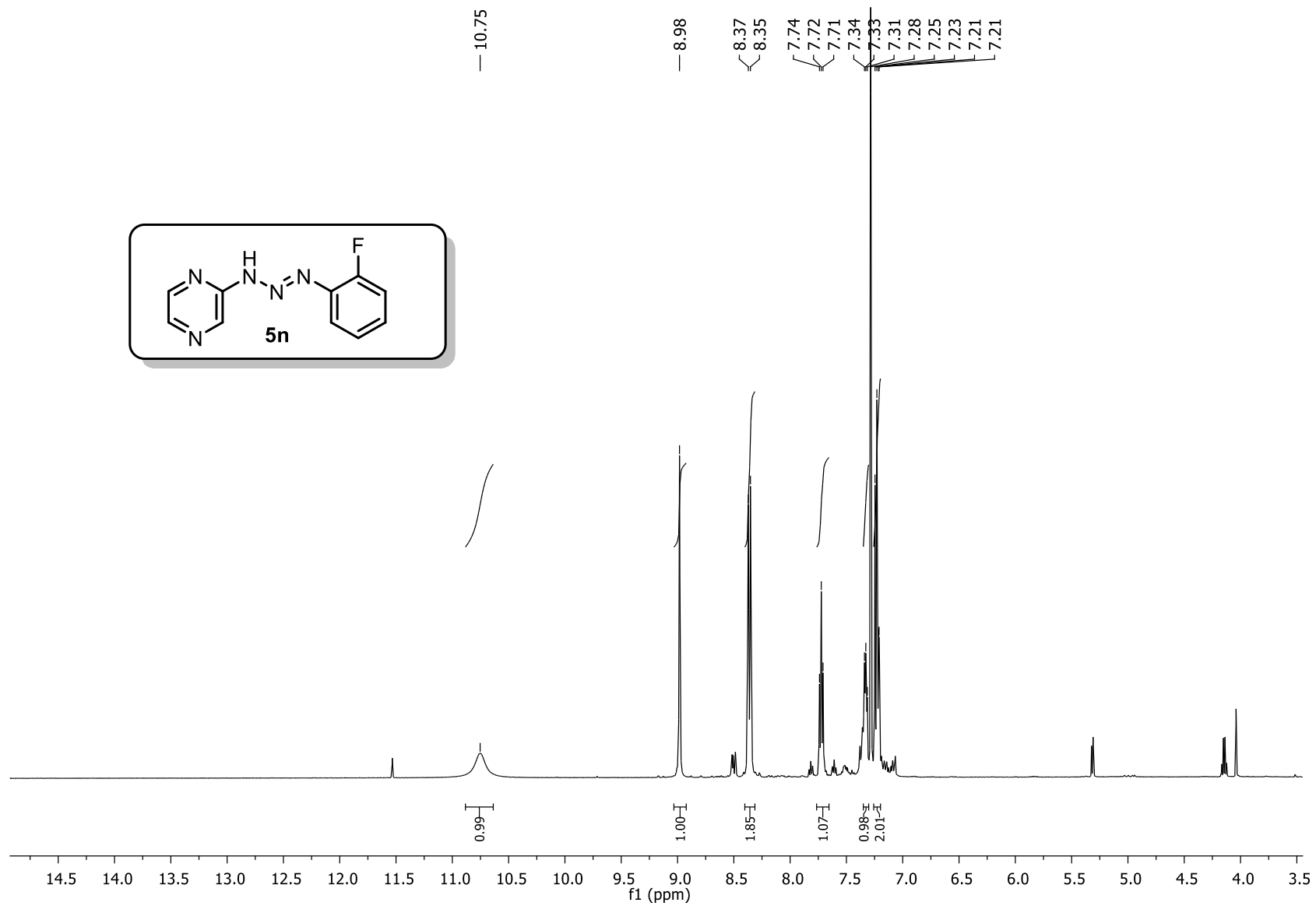
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-2-(3-(2-(trifluoromethyl)phenyl)triaz-2-en-1-yl)pyrazine (**5m**)



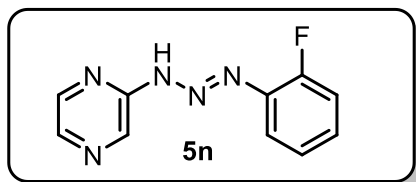
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-2-(3-(2-(trifluoromethyl)phenyl)triaz-2-en-1-yl)pyrazine (**5m**)



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) spectrum of (*E*)-2-(3-(2-fluorophenyl)triaz-2-en-1-yl)pyrazine (**5n**)



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz) spectrum of (*E*)-2-(3-(2-fluorophenyl)triaz-2-en-1-yl)pyrazine (**5n**)



— 150.81  
— 142.05  
— 139.28  
/ 132.96  
/ 129.46  
/ 129.39  
/ 124.89  
/ 124.59  
/ 124.56  
/ 119.37  
/ 116.91  
/ 116.75

