Supplementary Information

1-Iodobuta-1,3-diynes in Copper-Catalyzed Azide-Alkyne Cycloaddition: a One-Step Route to 4-Ethynyl-5-iodo-1,2,3-triazoles.

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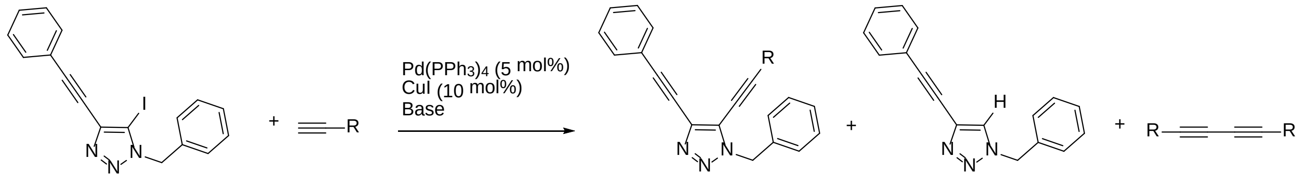
Table S1. Conditions optimization for the Sonogashira reaction of 5-ethynyl-1,2,3-triazoles with alkynes.



9b **12a,b** **13a,b** **A** **Ba,b**

12a, 13a, Ba: 4-MeOC_6H_4
12b, 13b, Bb: C(Me)$_2$OH

entry	Base (equiv) / Solvent / t, °C	H-C≡C-R (equiv)	Yield of **13, A** (%)[a]	
			8a,b	**A**
1	DIPA (6) / DMF / 50 °C	**12a**, 4-MeOC_6H_4 (2.5)	18	76
		12b, C(Me)$_2$OH (4)	11.5	30
2	KF (6) / DMF / 50 °C	**12a**, 4-MeOC_6H_4 (2.5)	[b]	
3	K_2CO_3 (1.5) / THF / 65 °C	**12a**, 4-MeOC_6H_4 (1.1)		
4	Et_3N (6) / $PhCH_3$ / 80 °C	**12b**, C(Me)$_2$OH (4)	17	30
5	K_3PO_4 (1.1) / THF / 65 °C	**12a**, 4-MeOC_6H_4 (2)	77	–
		12b, C(Me)$_2$OH (2)	90	–

[a] The formation of diynes **B** was observed in all cases, these compounds were not isolated. [b] Ratio of **9b**:**13a**:**A** – 6:10:1 for entry 2 and ratio of **9b**:**13a**:**A** – 7:10:0.3 for entry 3 (detected by ^{1}H NMR).

X-Ray data for compounds 13d, 15a,b

Single crystals of compounds **13d, 15a,b** were grown from the chloroform solutions by the vapor exchange with hexane. The single-crystal X-ray diffraction studies were carried out on a diffractometer at 100 K using Cu Kα radiation (λ = 1.54180 Å). Using Olex 2[1] the structure was solved with the Super flip structure solution program[2] using Charge Flipping and refined with the ShelXL refinement package[3] using Least Squares minimization. Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (for CCDC numbers of compounds **13d, 15a,b** see the Table below).

Compound	**13d**	**15a**	**15b**
Empirical formula	$C_{28}H_{24}N_4$	$C_{25}H_{18}F_3N_3O$	$C_{26}H_{21}N_5$
Formula weight	416.51	433.42	403.48
Temperature/K	100(2)	100(2)	100(2)
Crystal system	triclinic	orthorhombic	triclinic
Space group	P-1	$Pna2_1$	P-1
a/Å	11.3428(6)	7.6472(2)	8.0850(2)
b/Å	11.4979(5)	13.1667(4)	9.7409(3)
c/Å	17.2272(7)	20.5771(7)	13.8853(3)
α/°	90.152(3)	90	88.792(2)
β/°	93.927(4)	90	80.674(2)
γ/°	97.454(4)	90	78.623(3)
Volume/$Å^3$	2222.38(18)	2071.88(11)	1057.81(5)
Z	4	4	2
$\rho_{calc}g/cm^3$	1.245	1.389	1.267
μ/mm^{-1}	0.580	0.884	0.608
F(000)	880.0	896.0	424.0
Crystal size/mm^3	0.29 × 0.22 × 0.15	0.1 × 0.1 × 0.1	0.2 × 0.15 × 0.15
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.142 to 139.996	7.972 to 139.898	6.452 to 143.012
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-20 \le l \le 20$	$-9 \le h \le 9$, $-10 \le k \le 16$, $-25 \le l \le 24$	$-9 \le h \le 9$, $-11 \le k \le 10$, $-17 \le l \le 16$
Reflections collected	48068	10895	19963
Independent reflections	8376 [R_{int} = 0.0831, R_{sigma} = 0.0537]	3727 [R_{int} = 0.0510, R_{sigma} = 0.0564]	4080 [R_{int} = 0.0522, R_{sigma} = 0.0351]
Data/restraints/parameters	8376/0/583	3727/1/290	4080/0/282
Goodness-of-fit on F^2	1.060	1.053	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0721, wR_2 = 0.2015	R_1 = 0.0396, wR_2 = 0.1014	R_1 = 0.0399, wR_2 = 0.1046
Final R indexes [all data]	R_1 = 0.0971, wR_2 = 0.2213	R_1 = 0.0451, wR_2 = 0.1042	R_1 = 0.0472, wR_2 = 0.1098
Largest diff. peak/hole / e $Å^{-3}$	1.07/-0.42	0.17/-0.19	0.17/-0.24
CCDC number	1869739	1869738	1869737

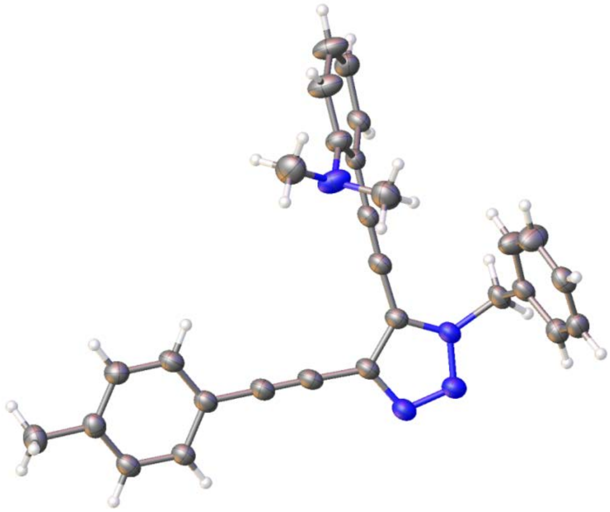


Figure S1. Single crystal X-ray structure of compound **13d.** The ellipsoid contours have 50% probability level.

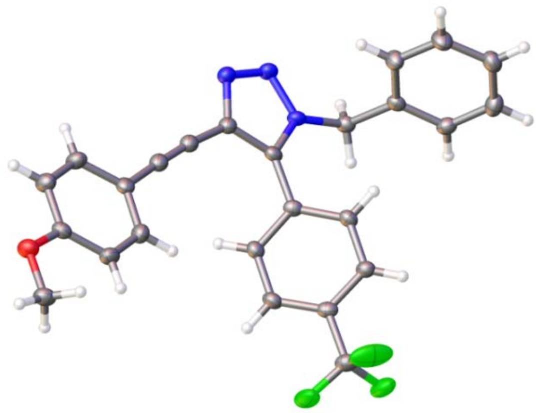


Figure S2. Single crystal X-ray structure of compound **15a.** The ellipsoid contours have 50% probability level.

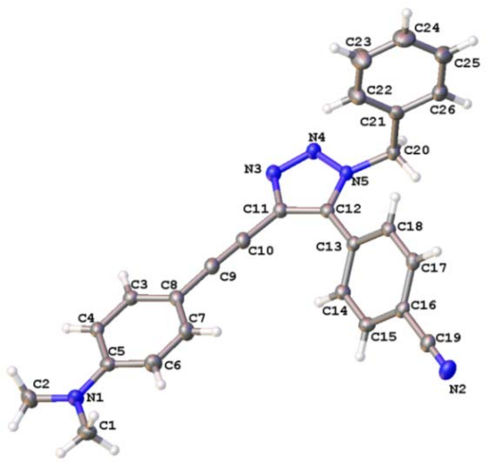


Figure S3. Single crystal X-ray structure of compound **15b.** The ellipsoid contours have 50% probability level.

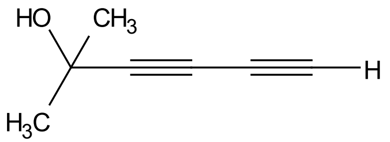
References

(1) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(2) Palatinus, L.; Chapuis, G. SUPERFLIP – a Computer Program for the Solution of Crystal Structures by Charge Flipping in Arbitrary Dimensions. *J. Appl. Crystallogr.* **2007**, *40*, 786–790.

(3) Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122.

^{1}H NMR ($CDCl_3$, 400.13 MHz)



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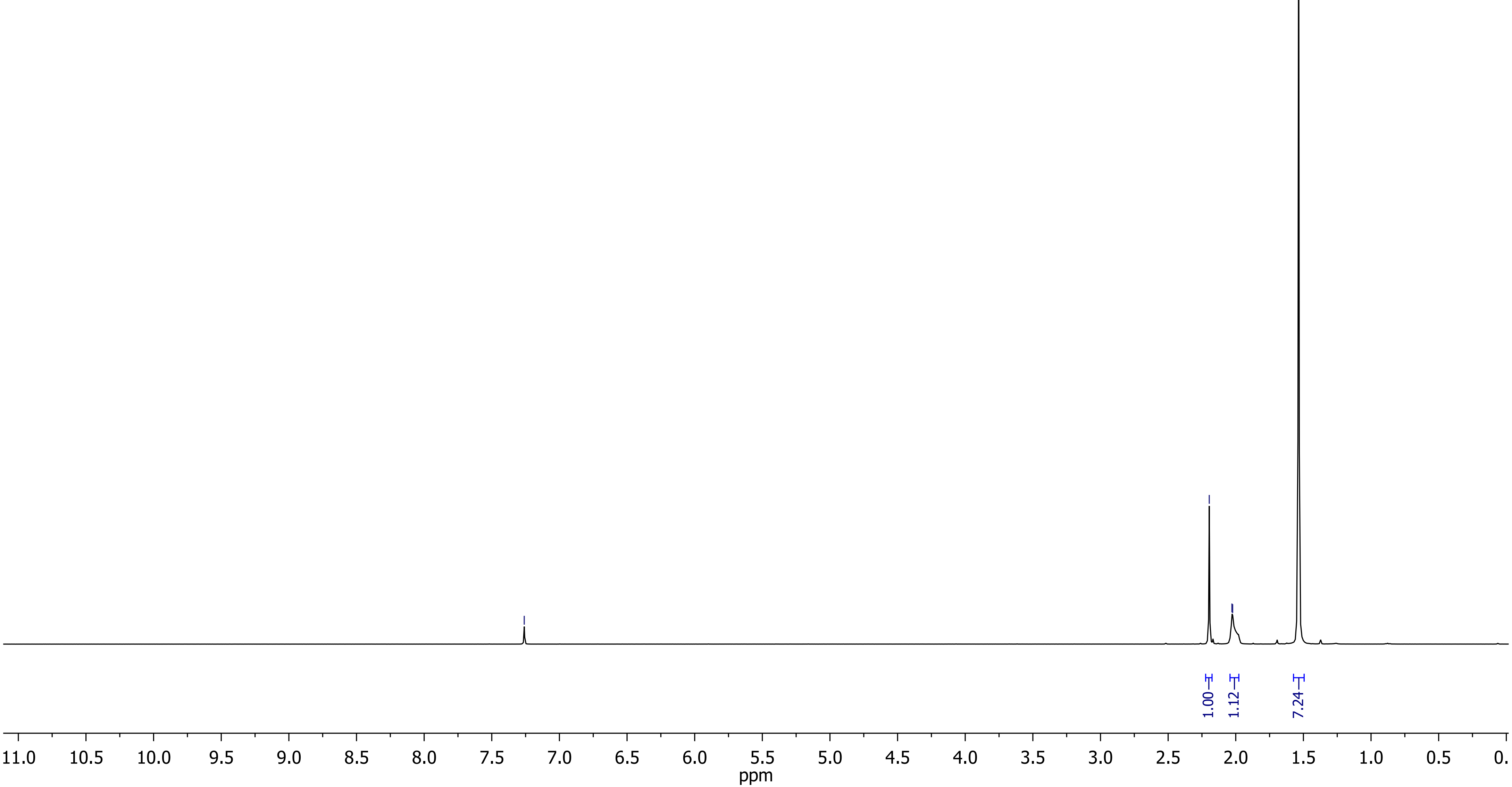

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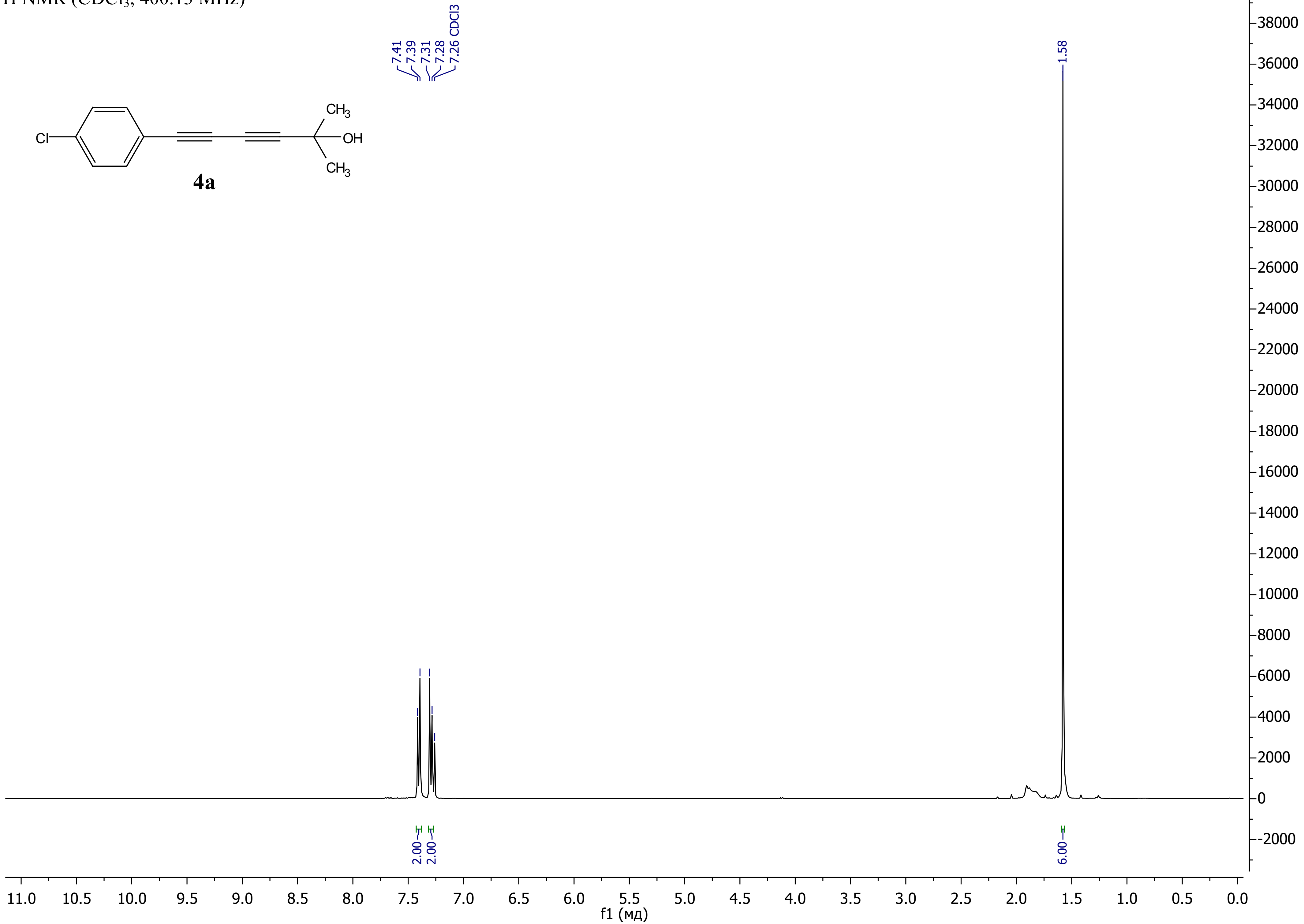

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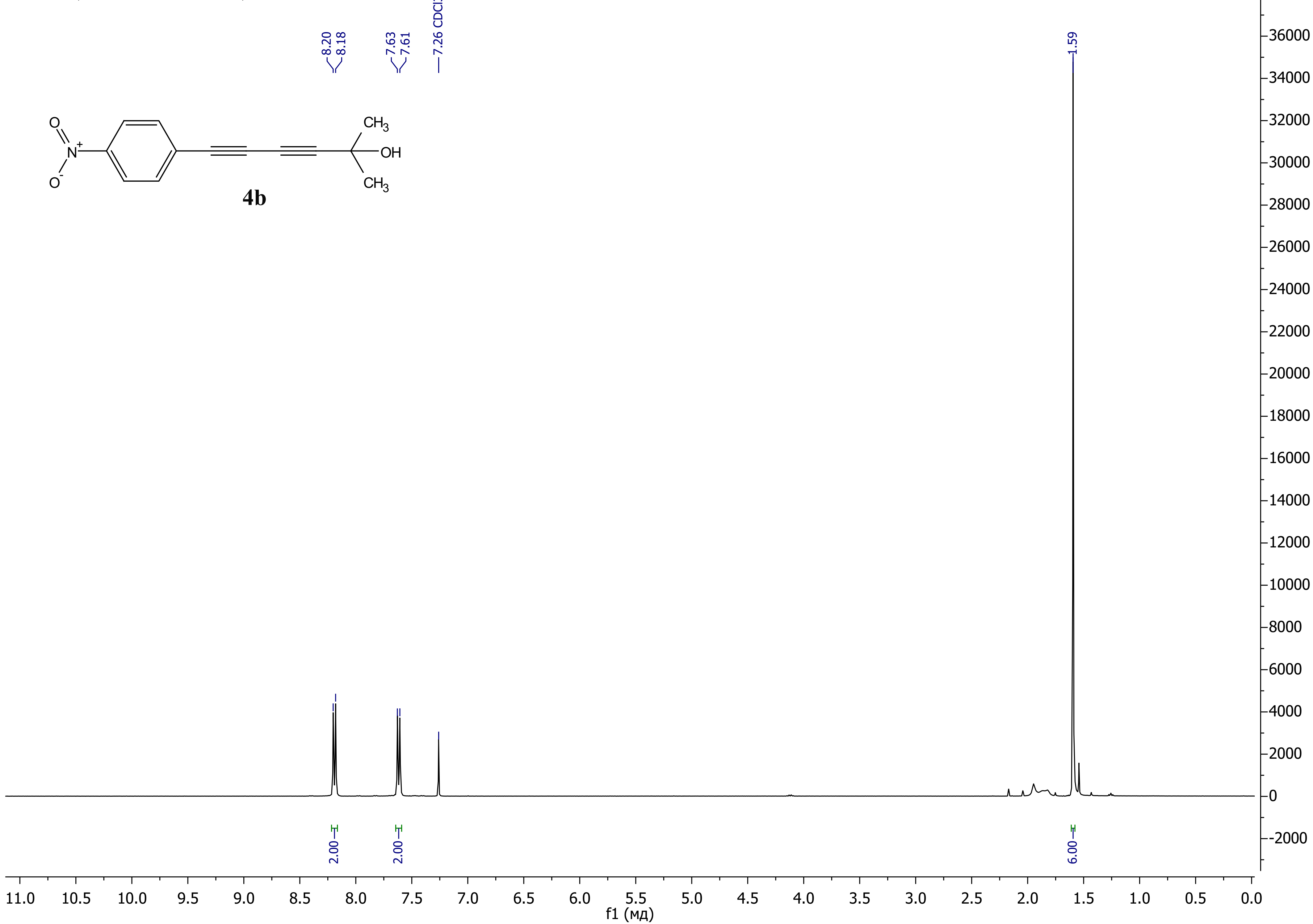

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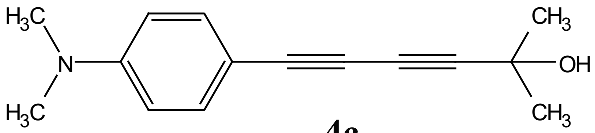

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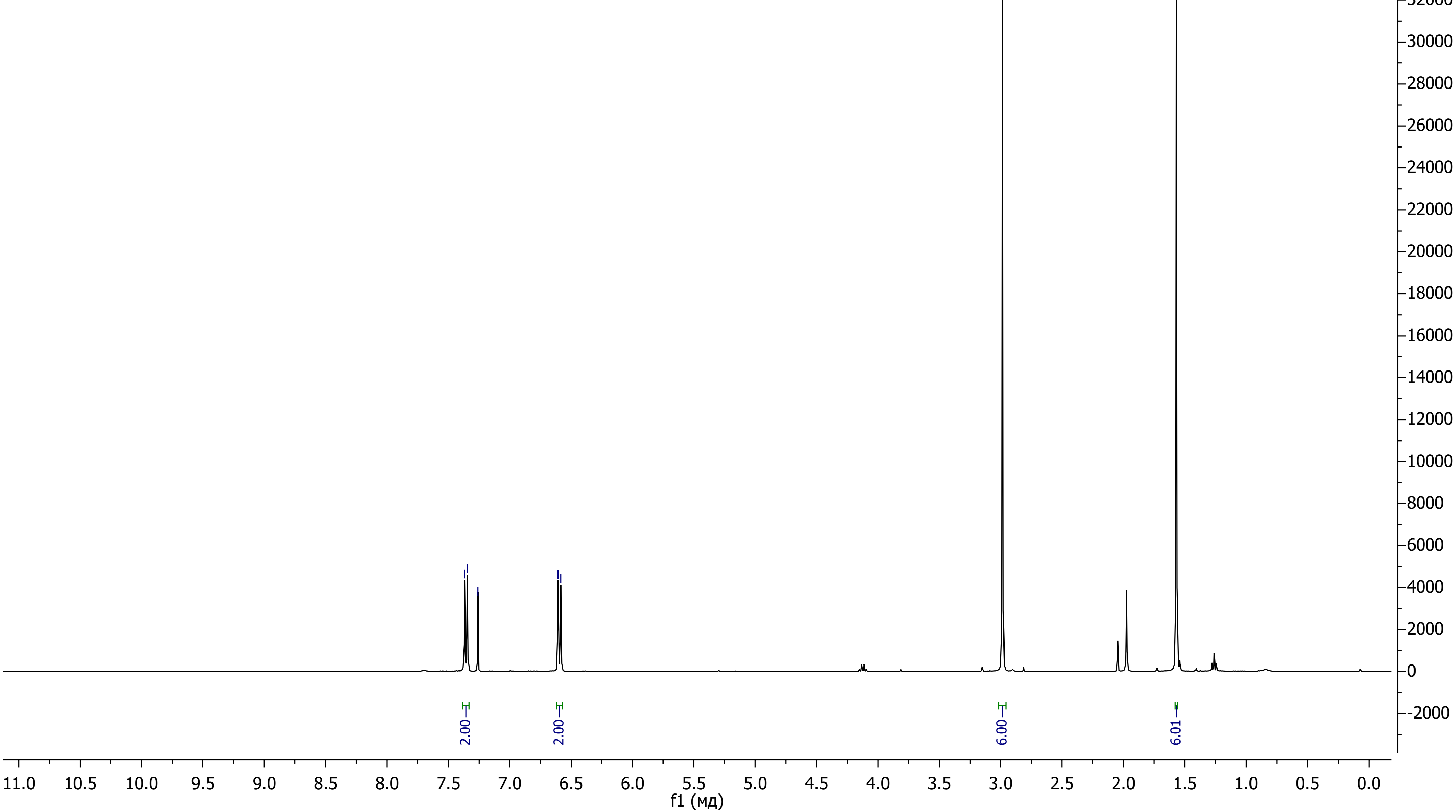

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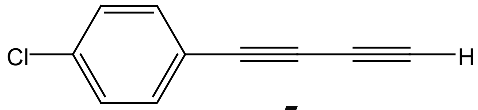

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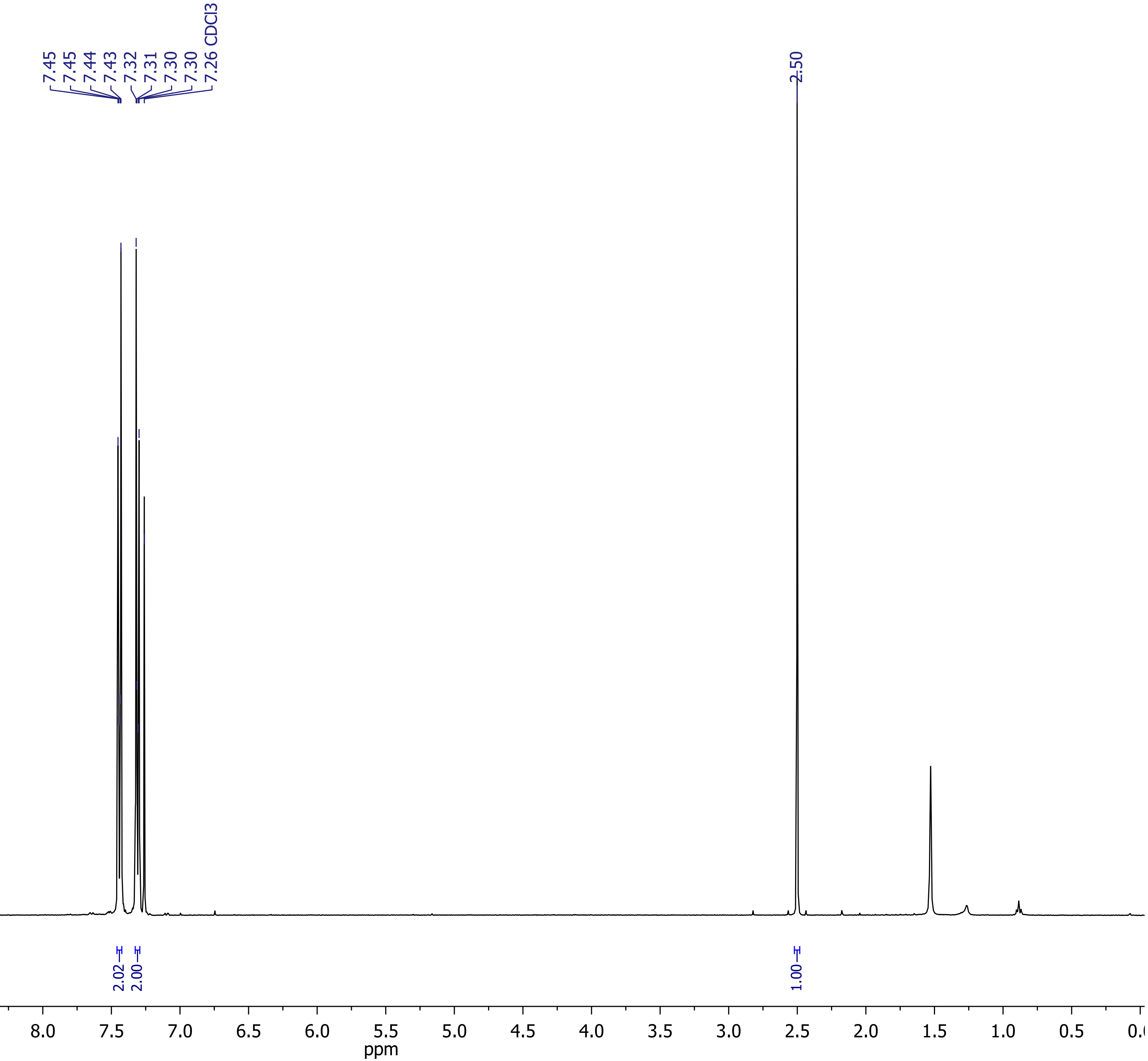

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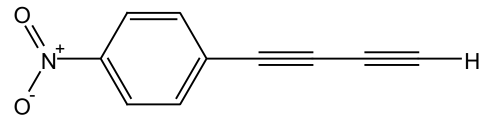

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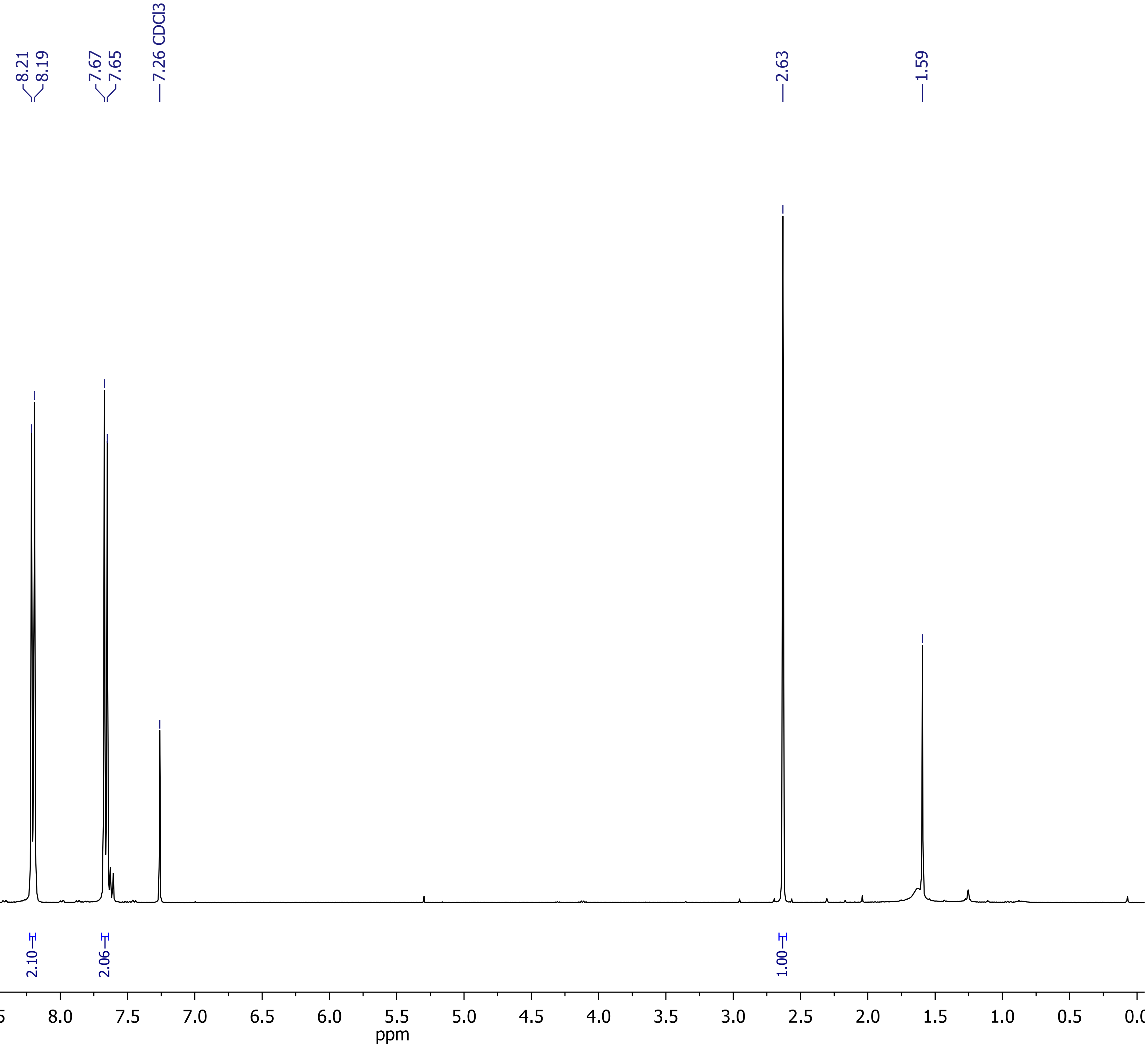

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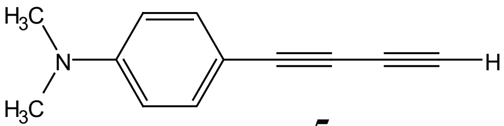

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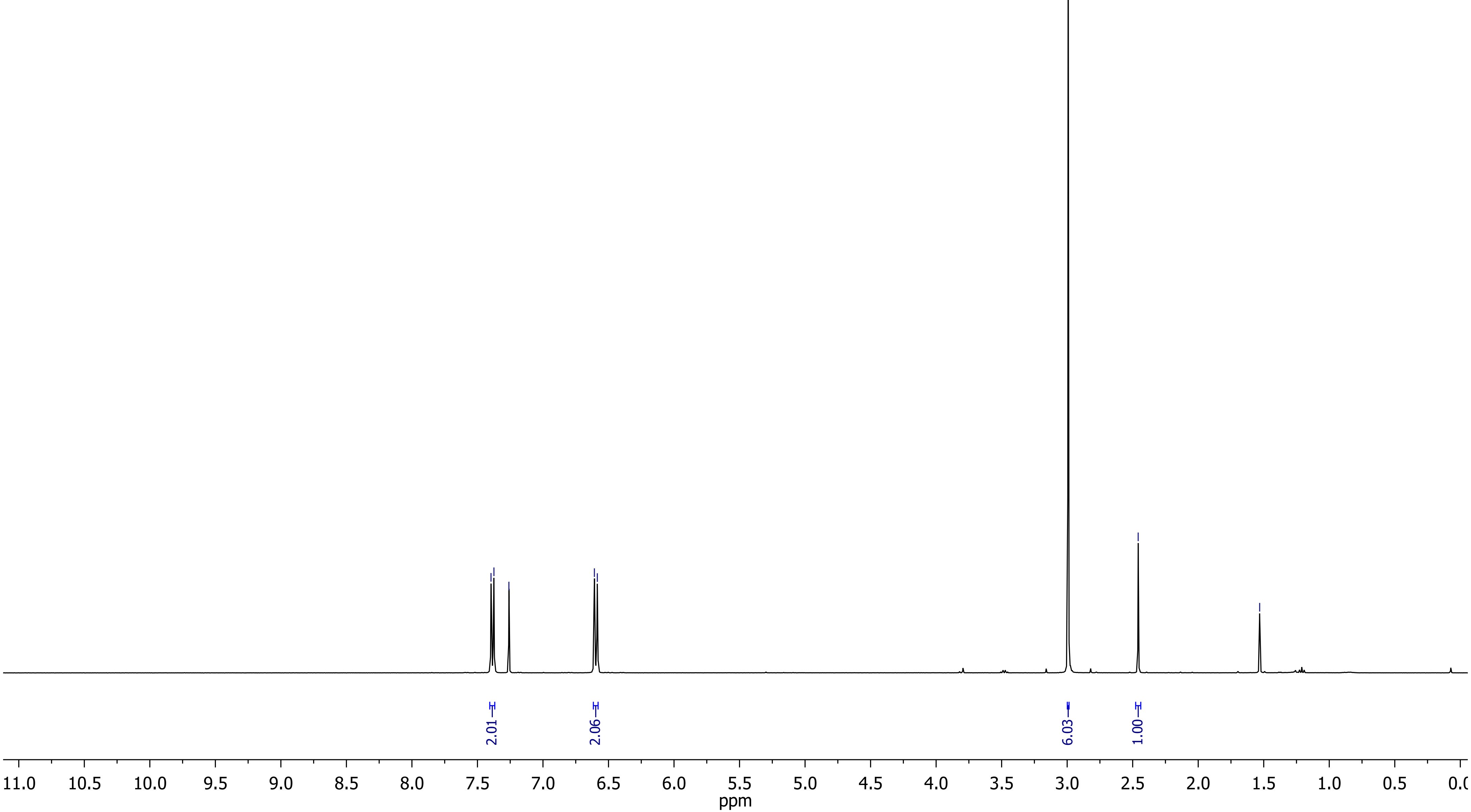

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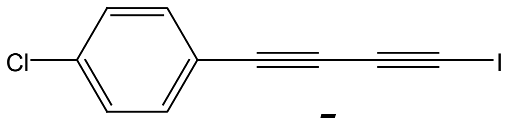

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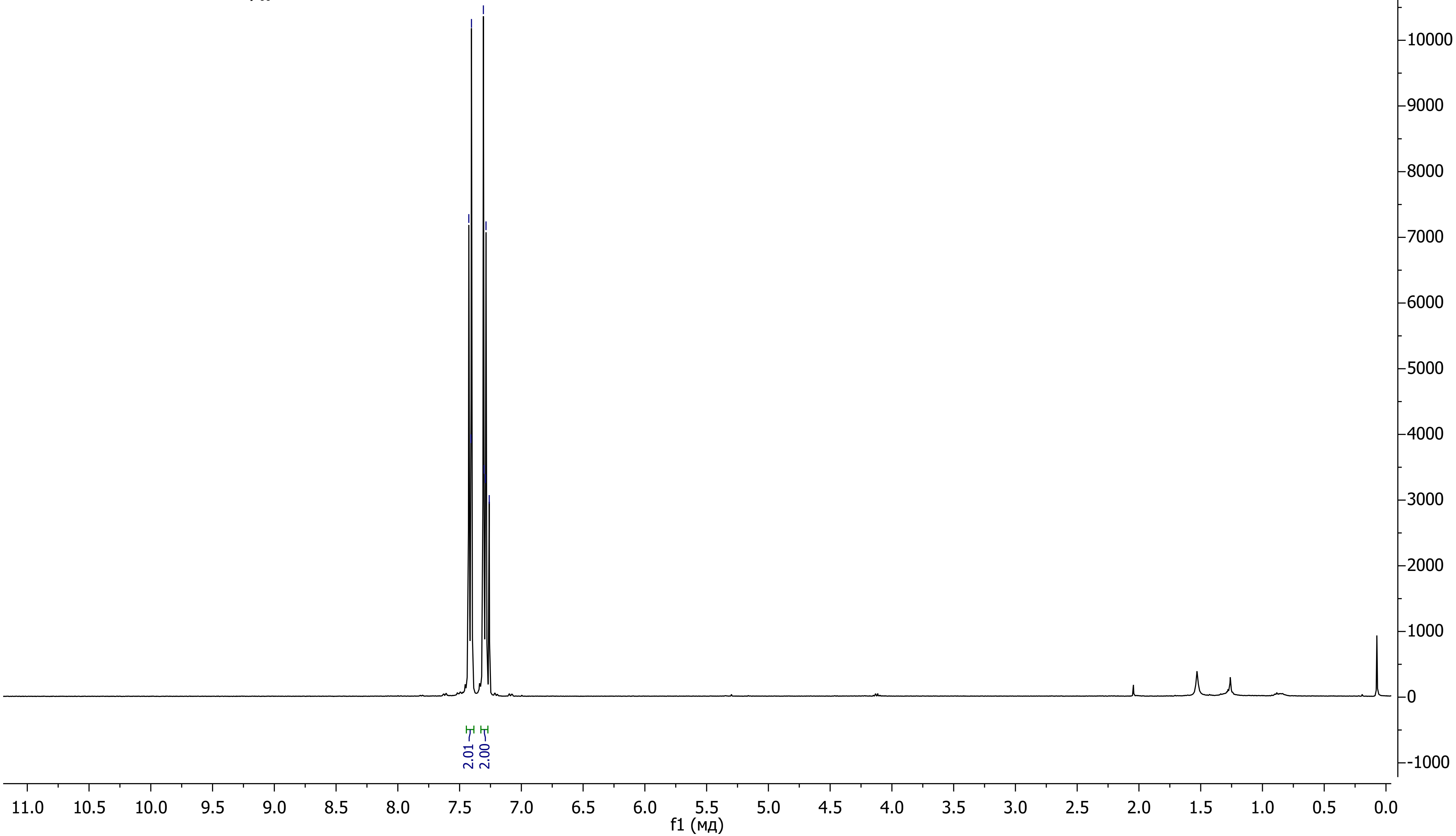

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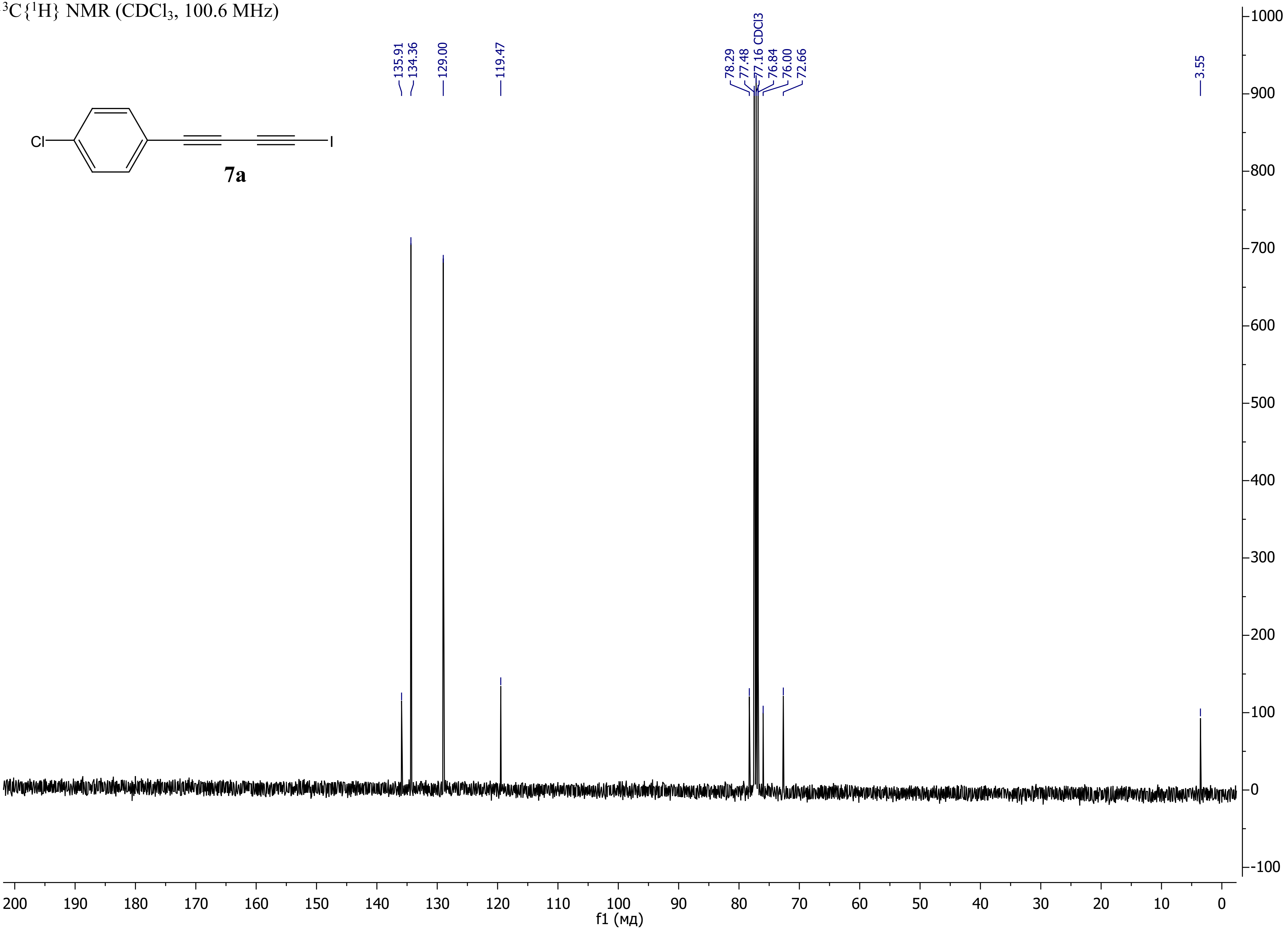

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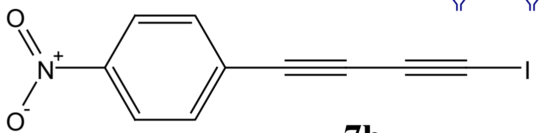

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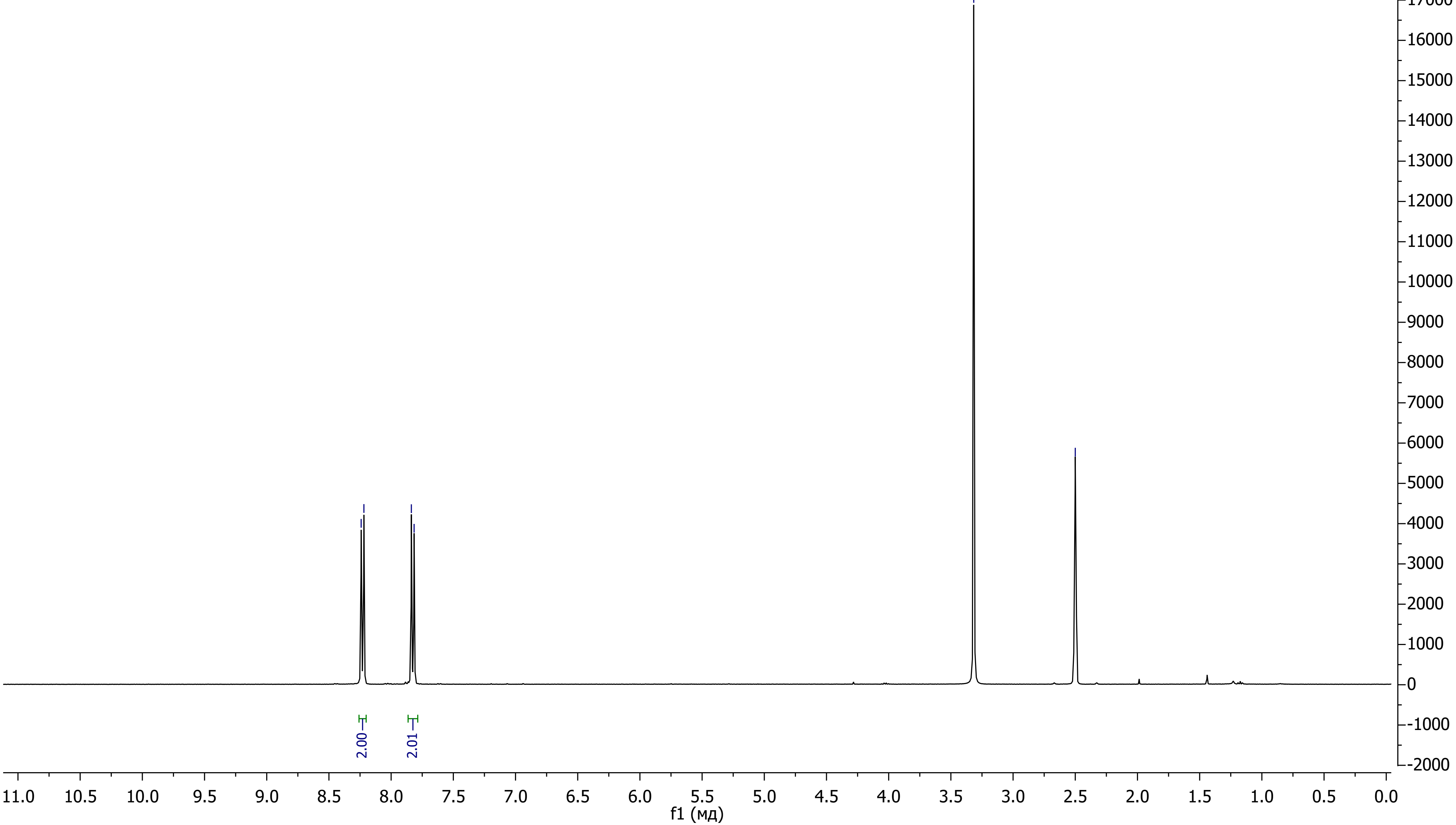

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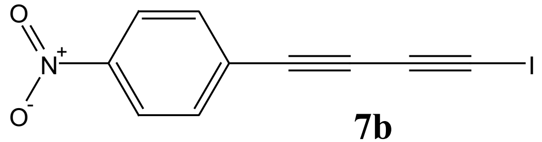

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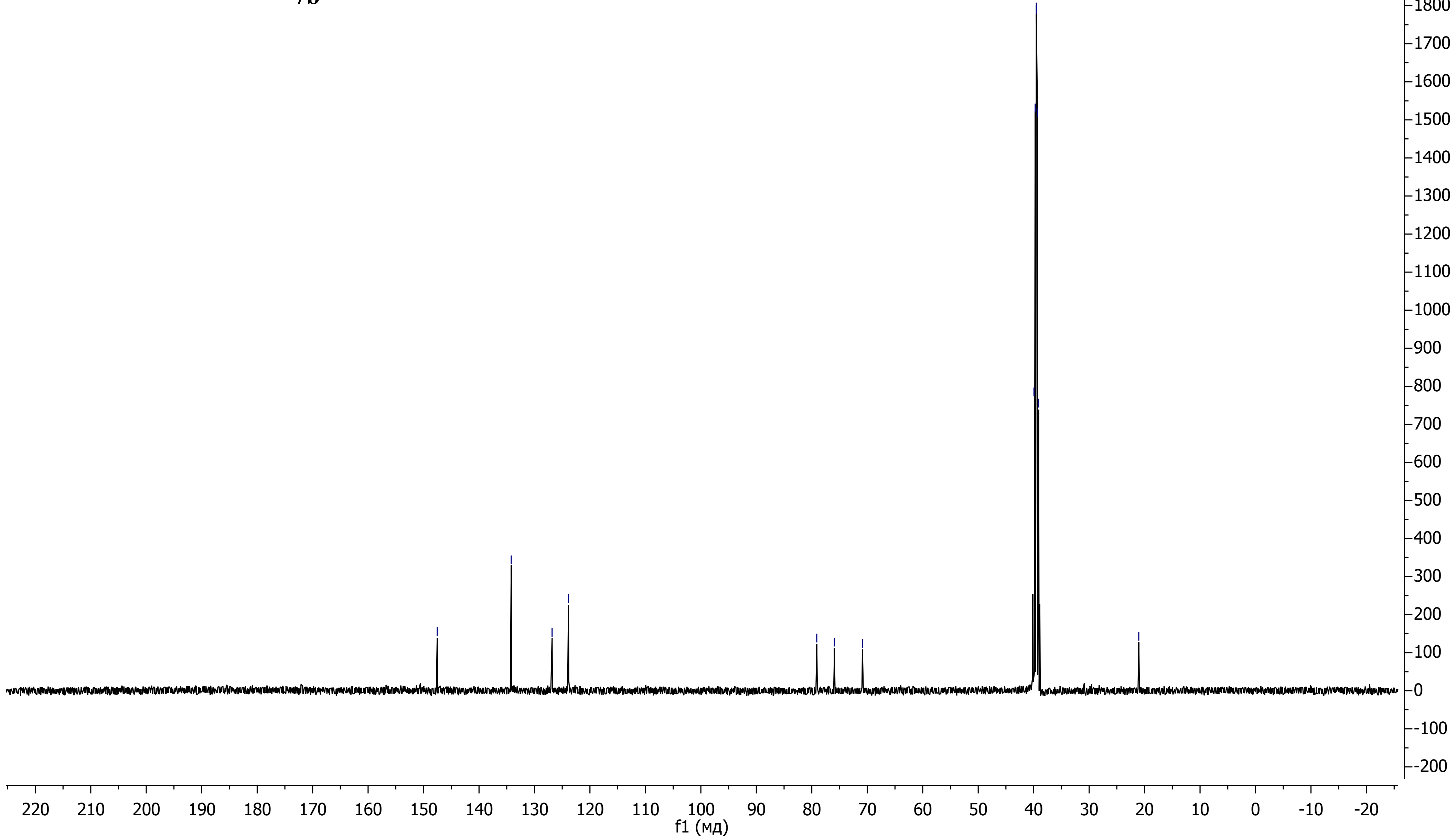

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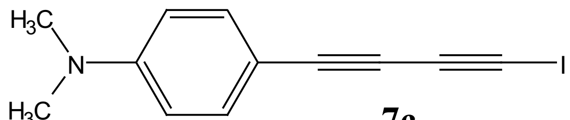

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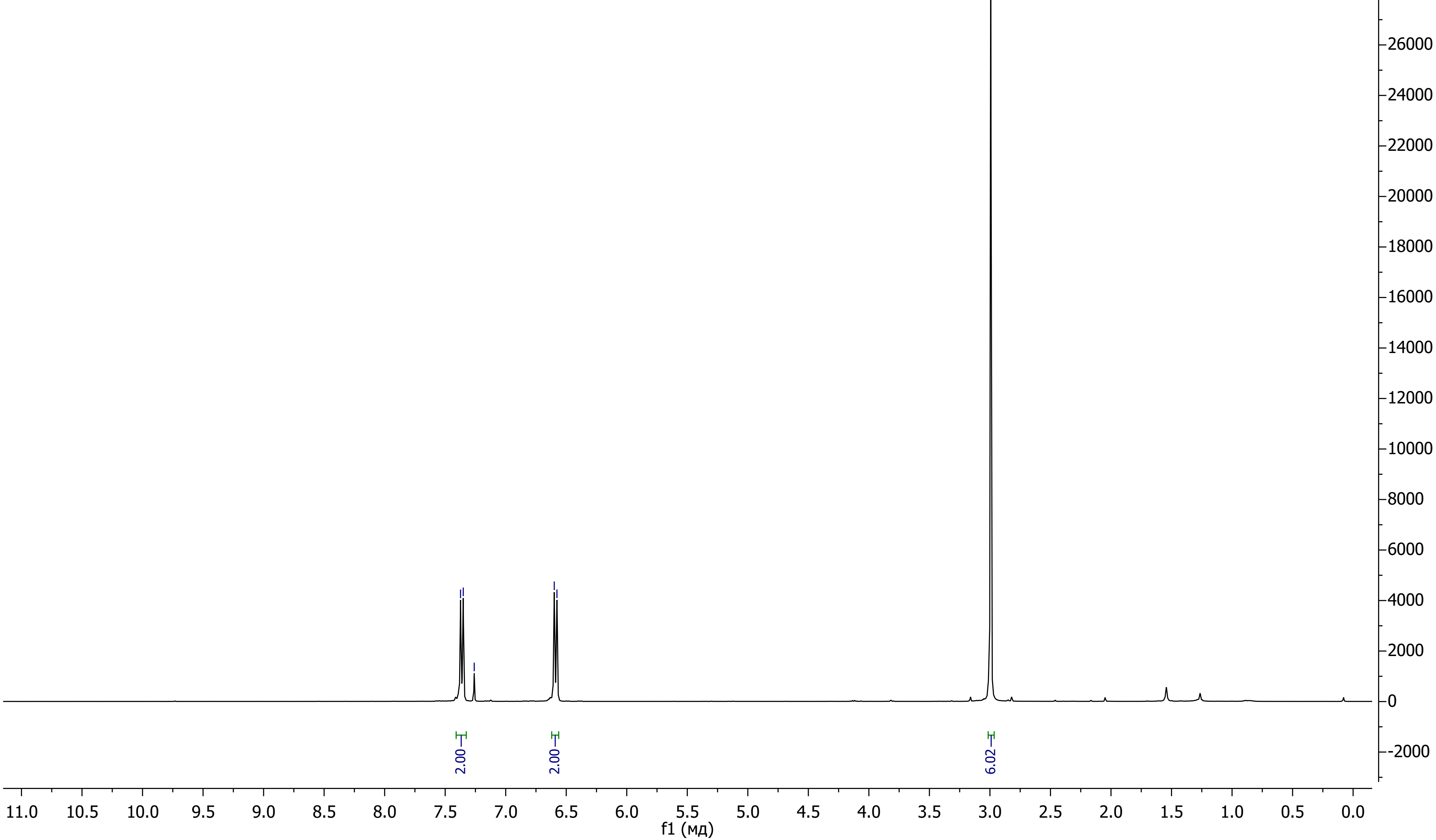

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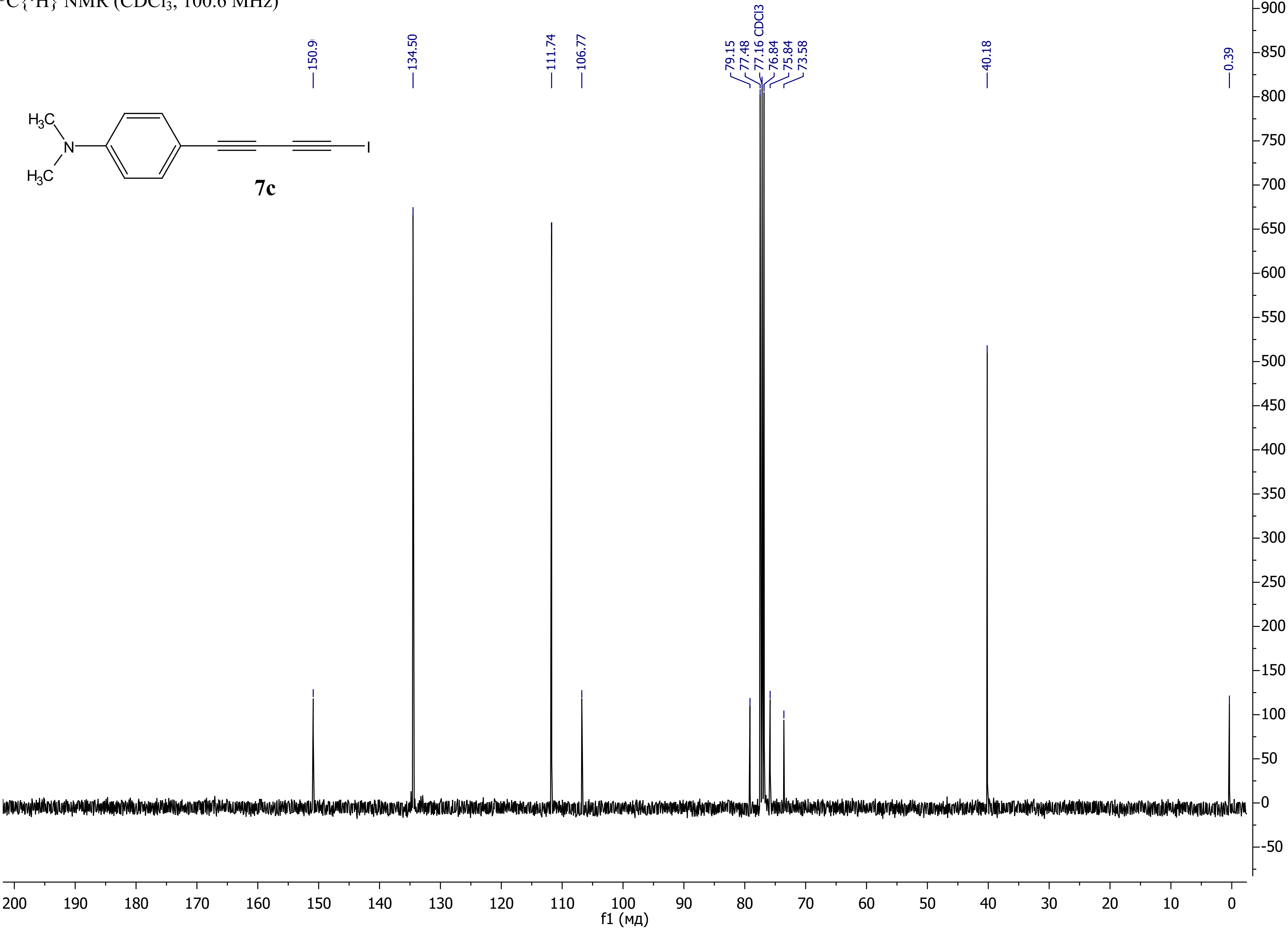

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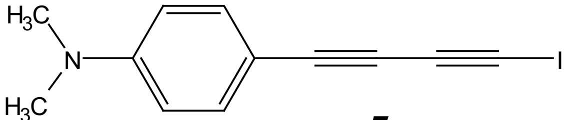

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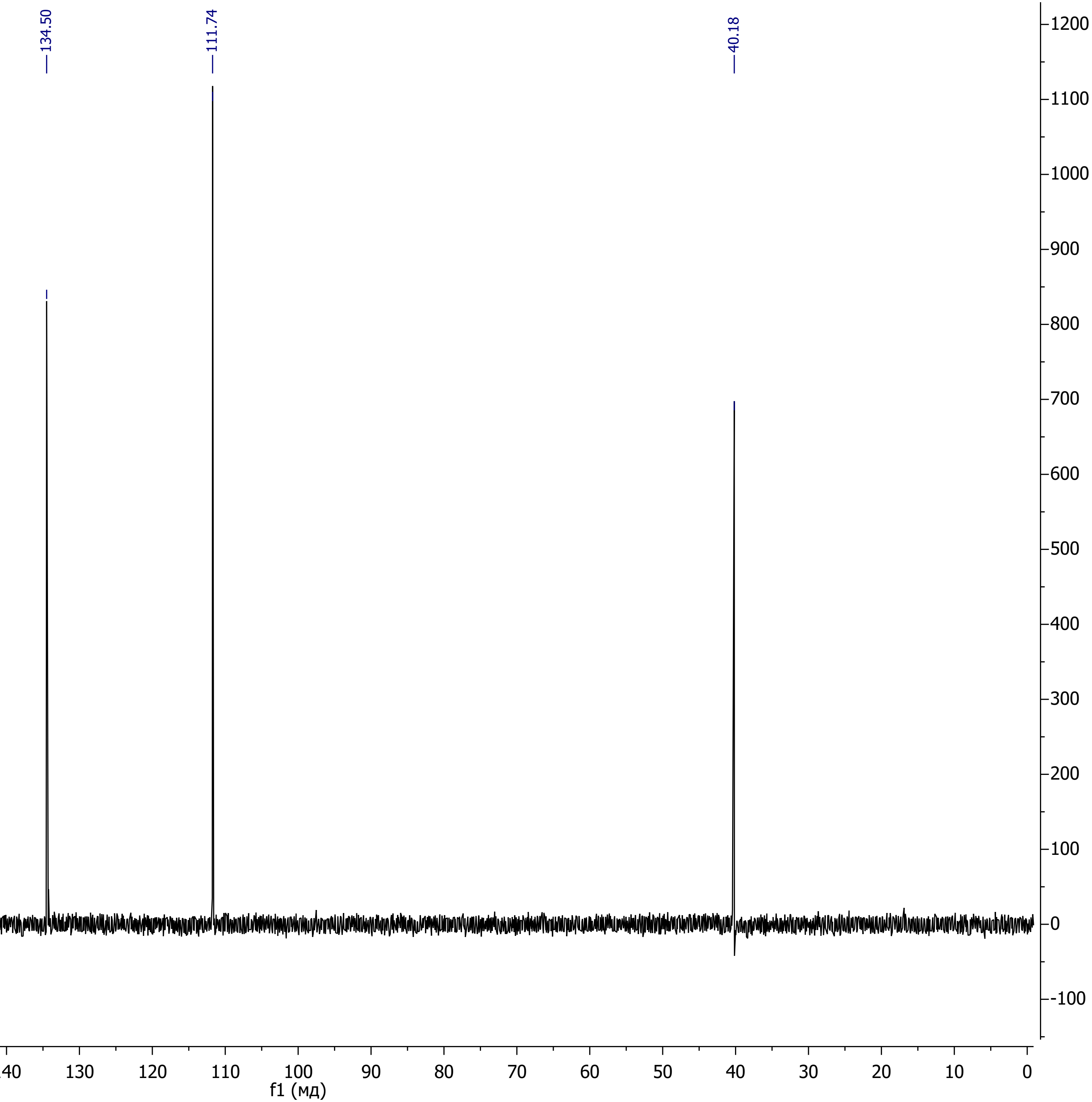

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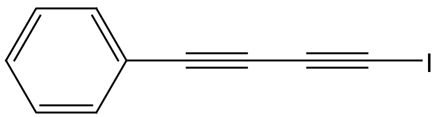

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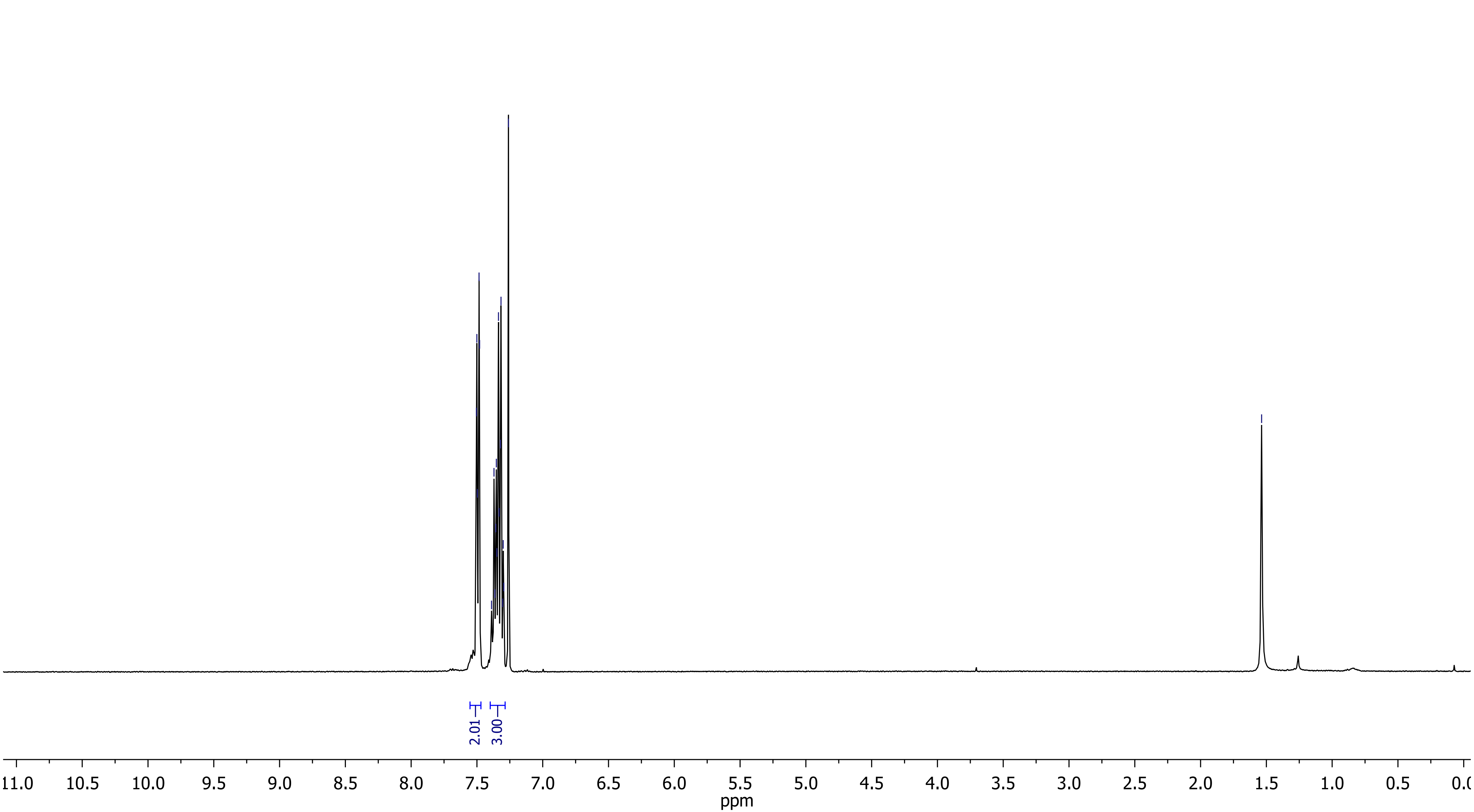

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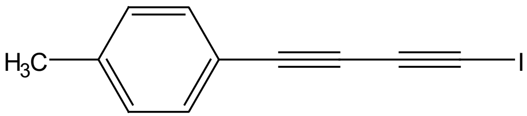

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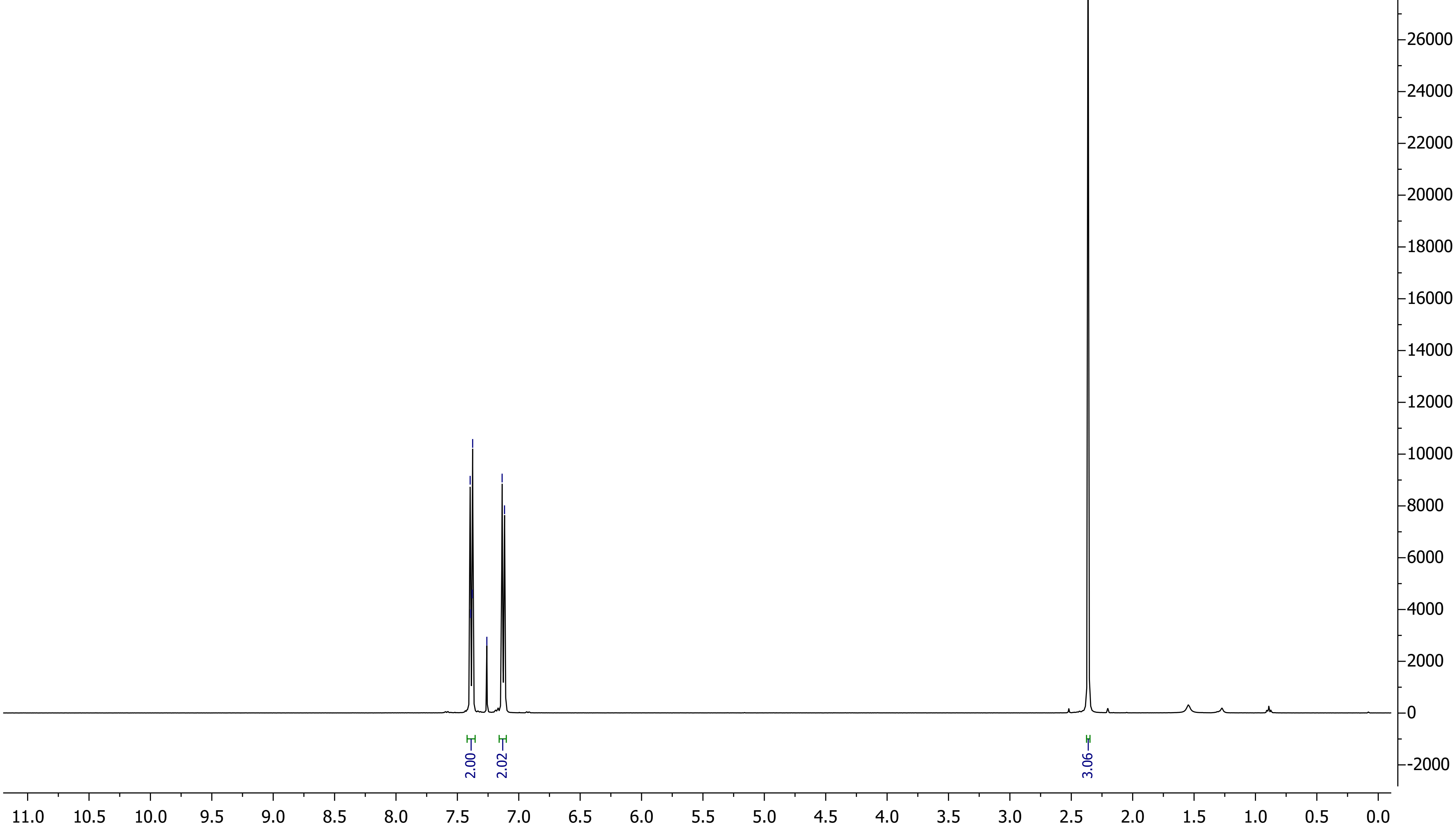

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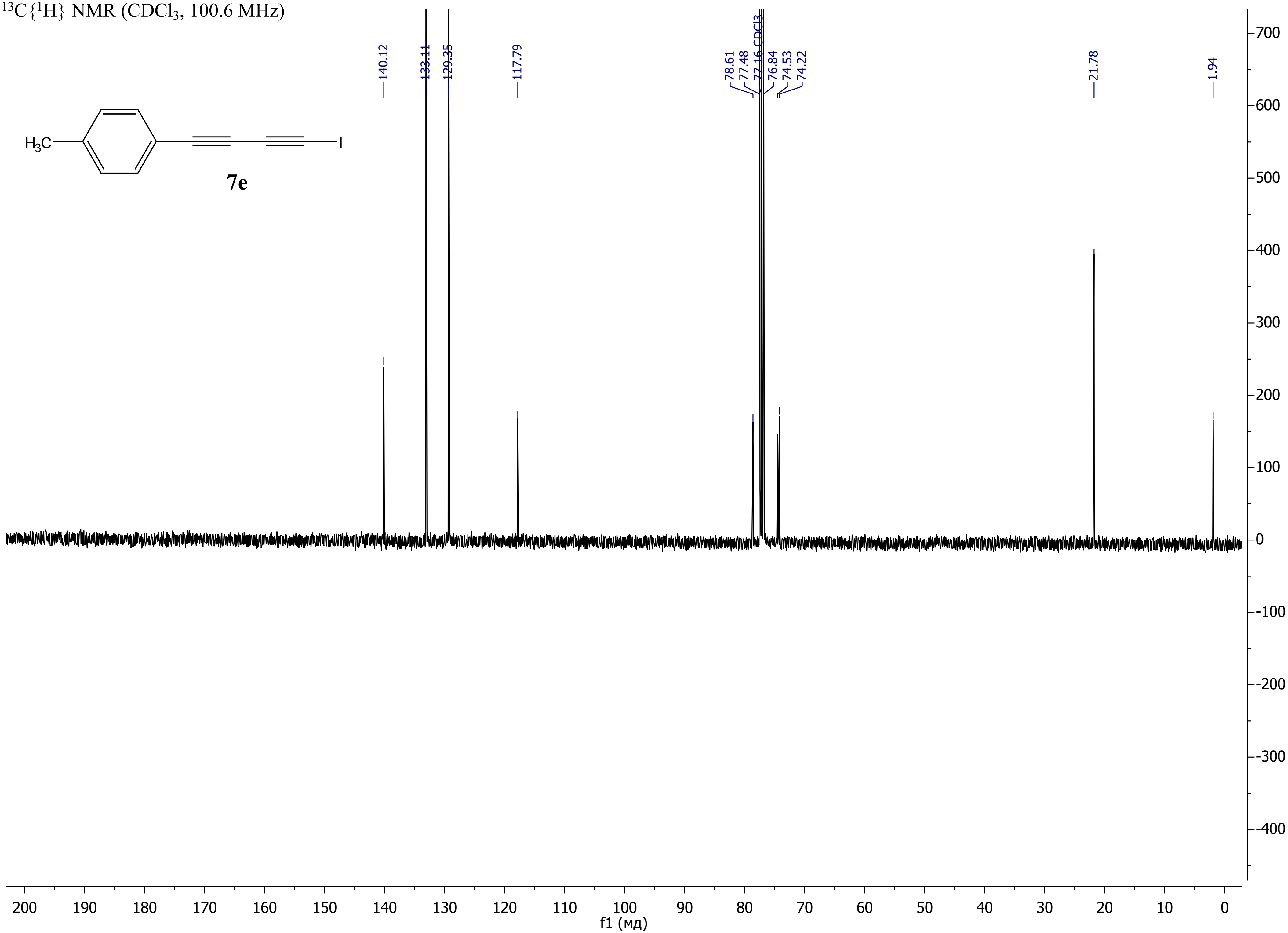

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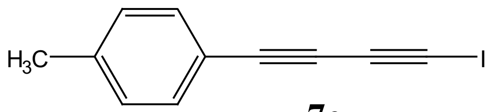

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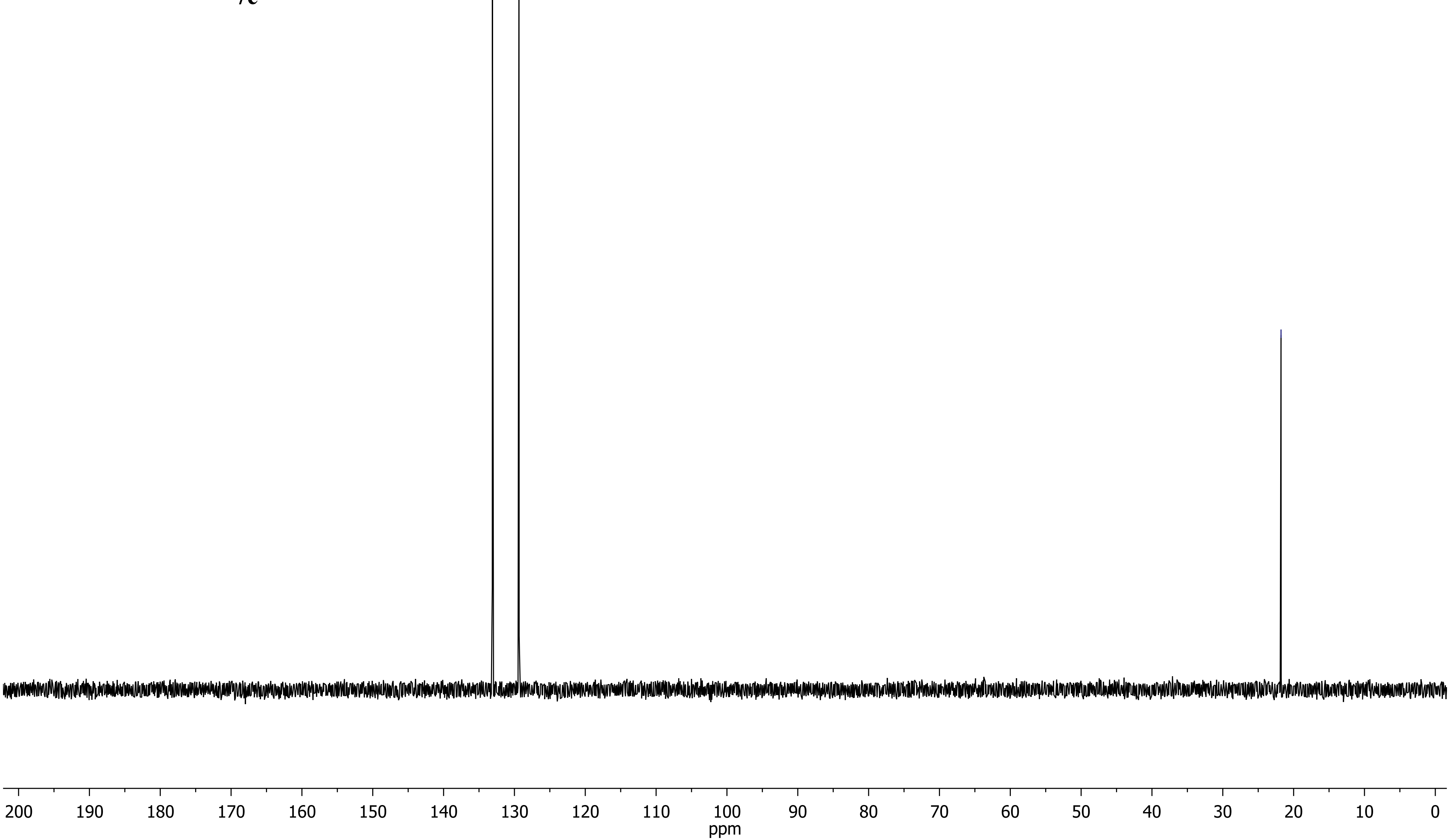

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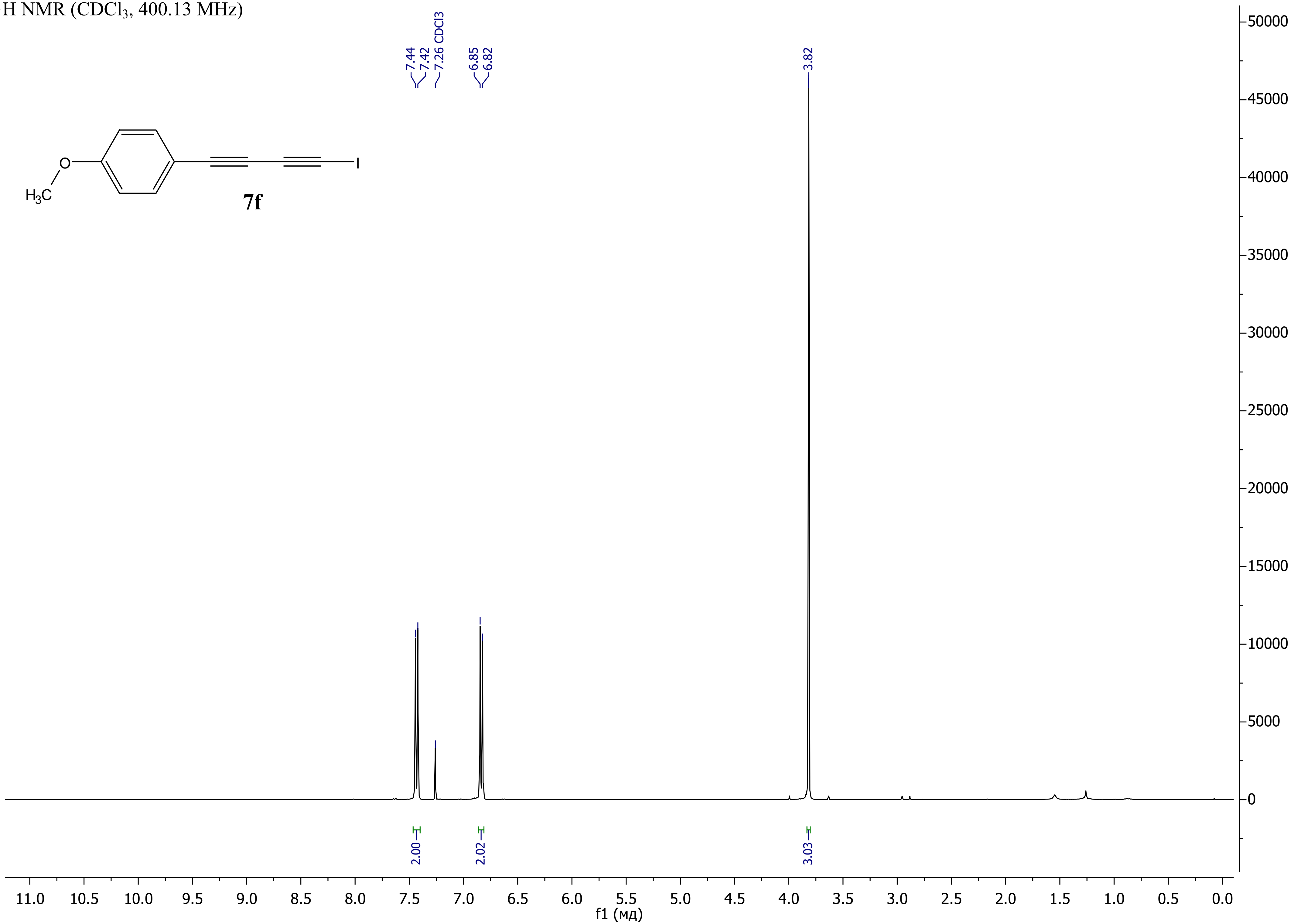

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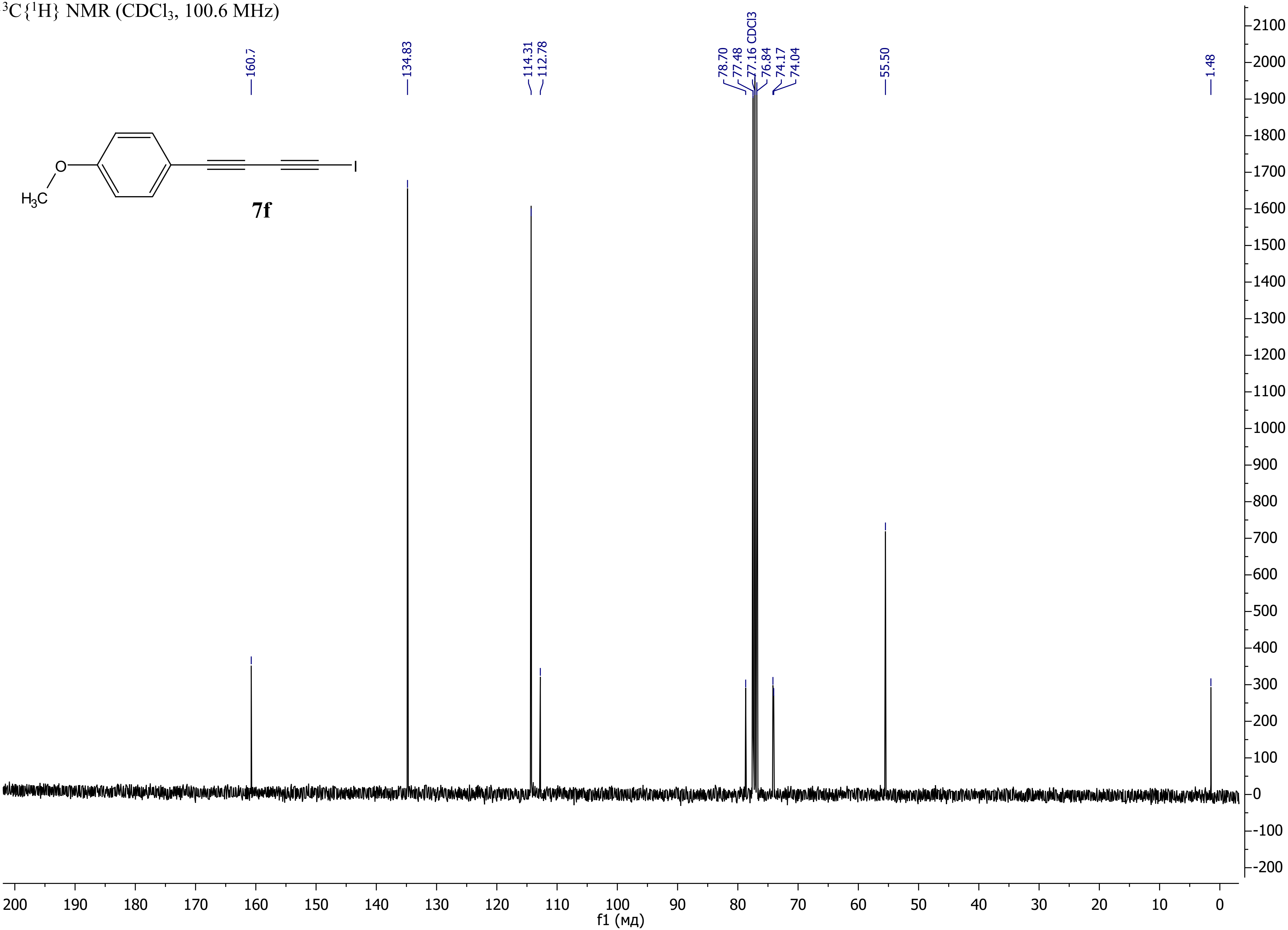

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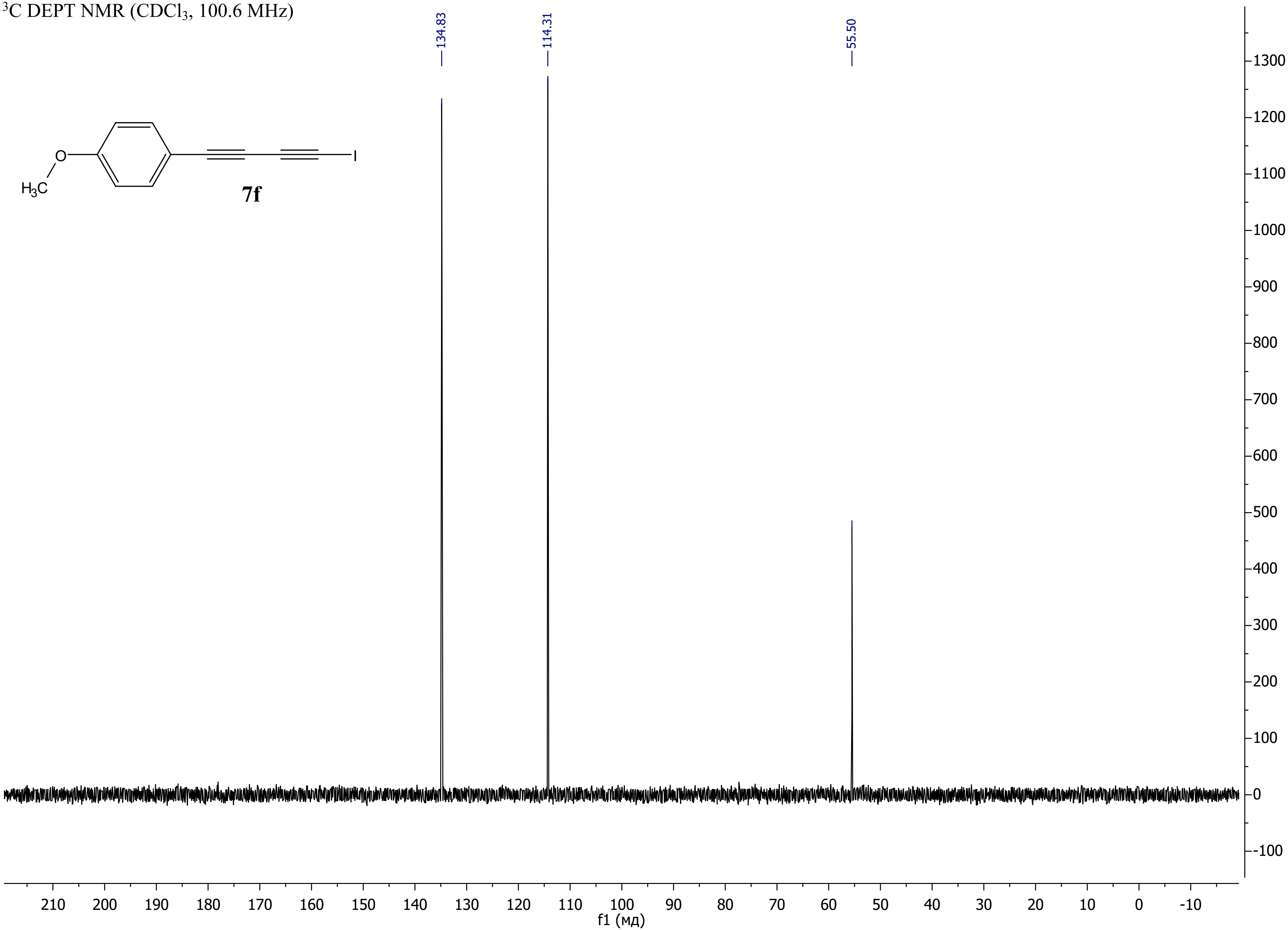

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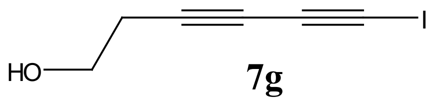

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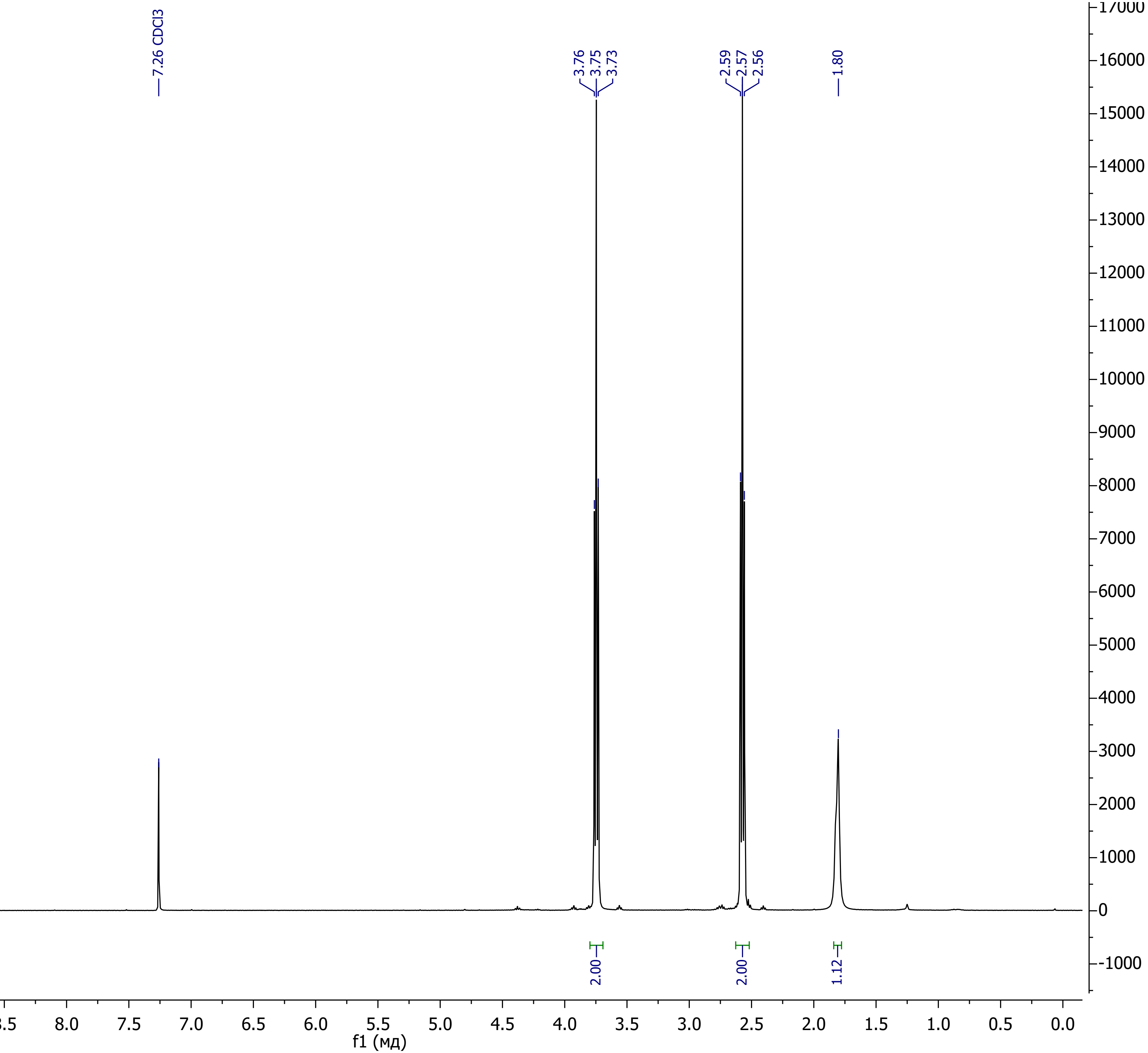

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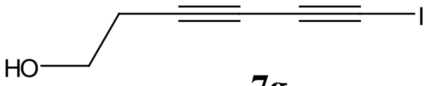

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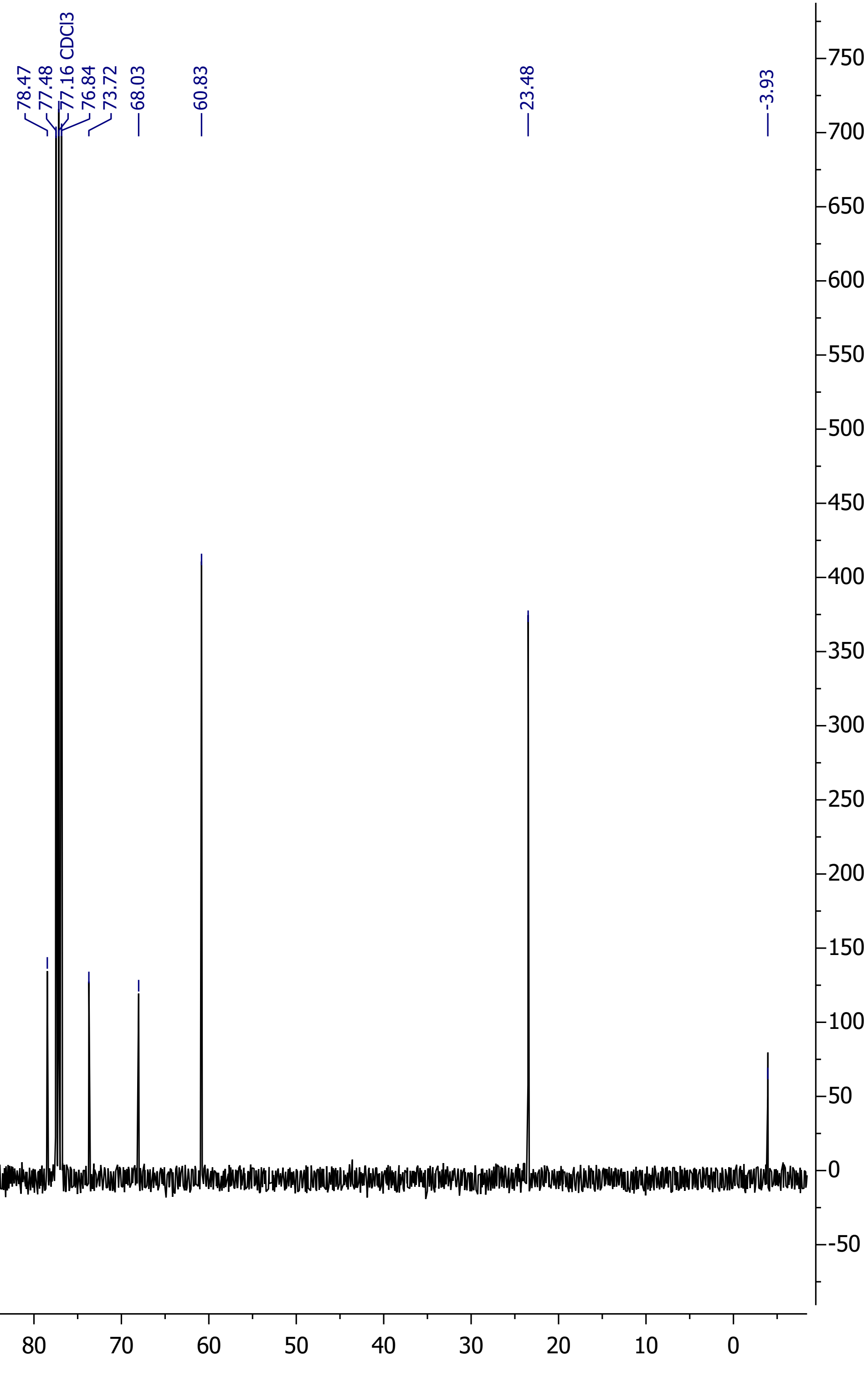

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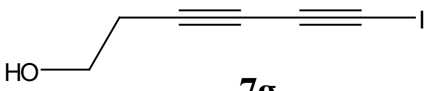

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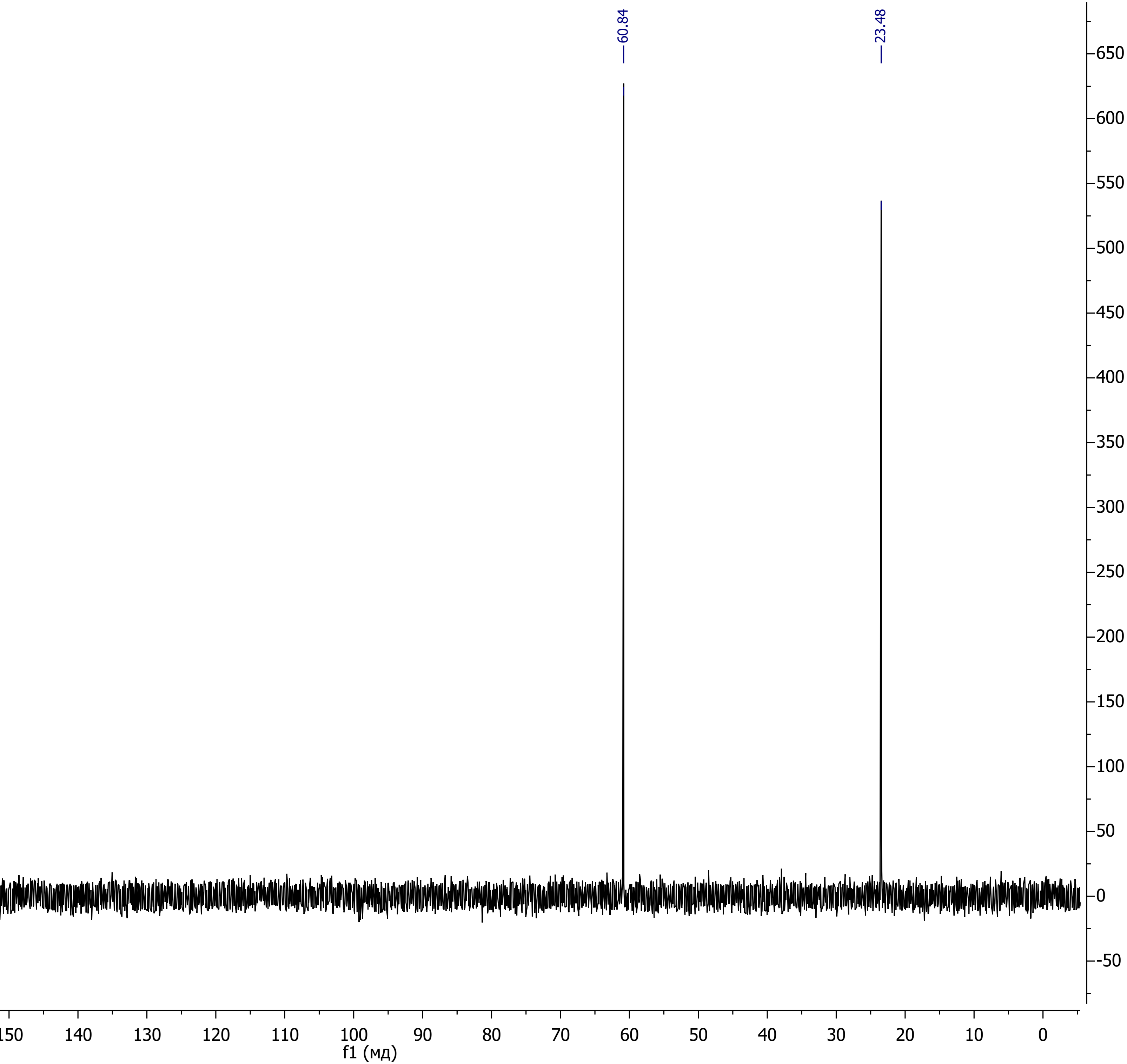

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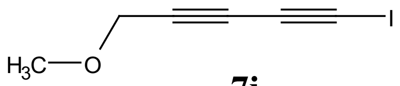

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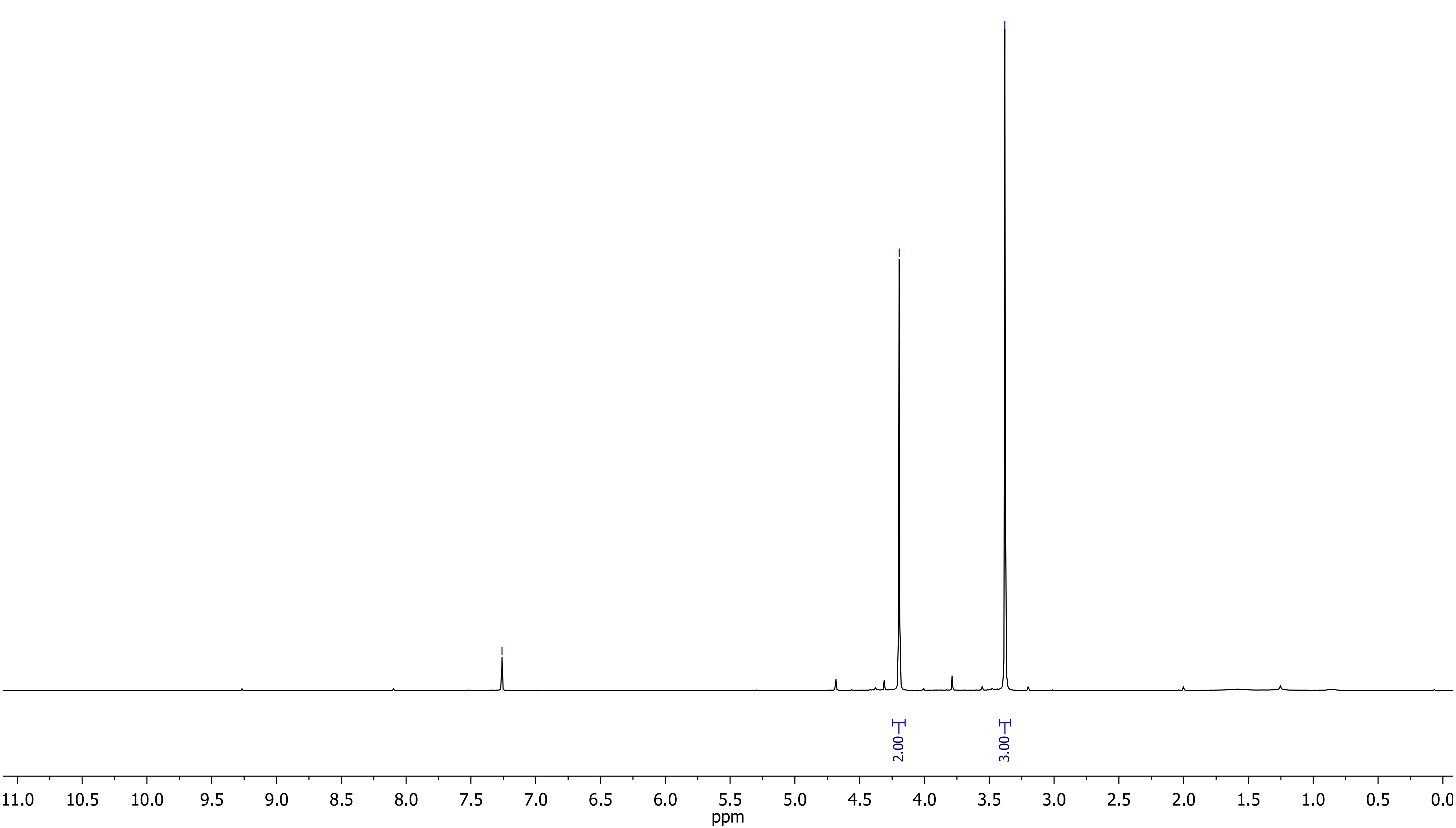

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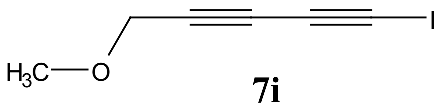

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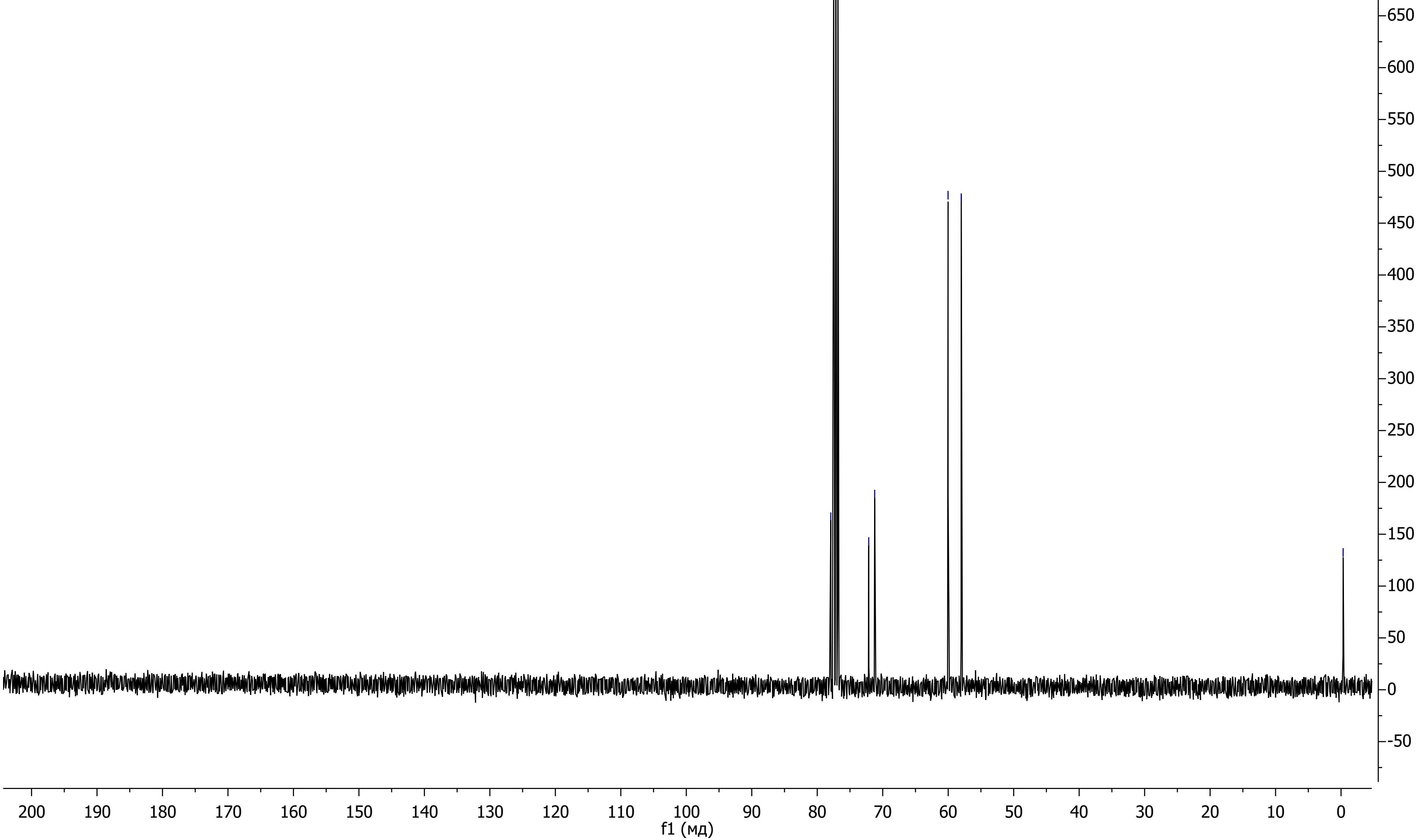

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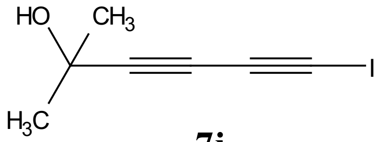

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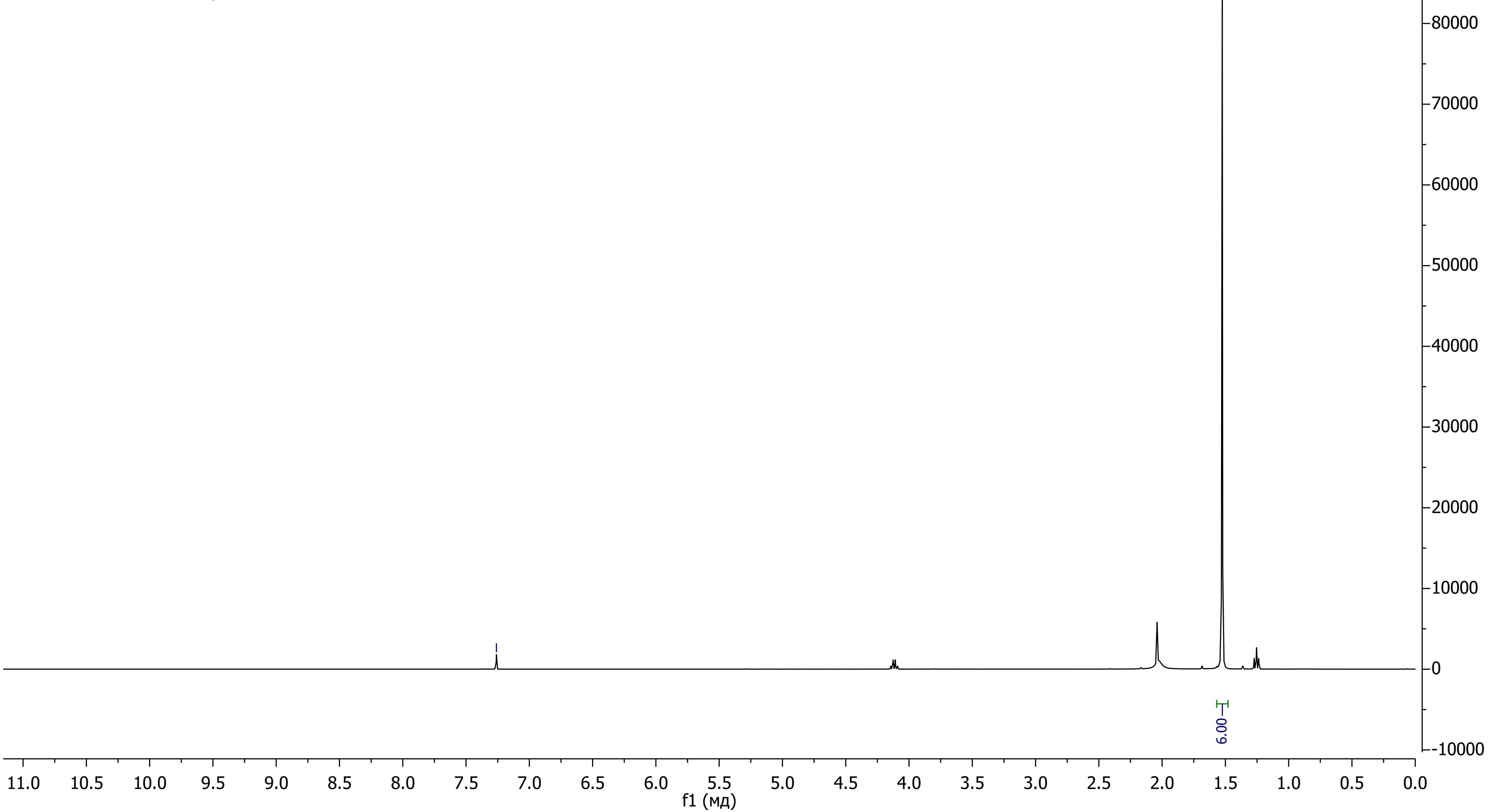

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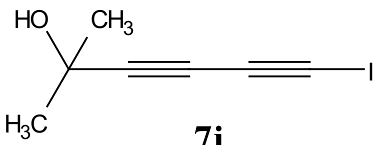

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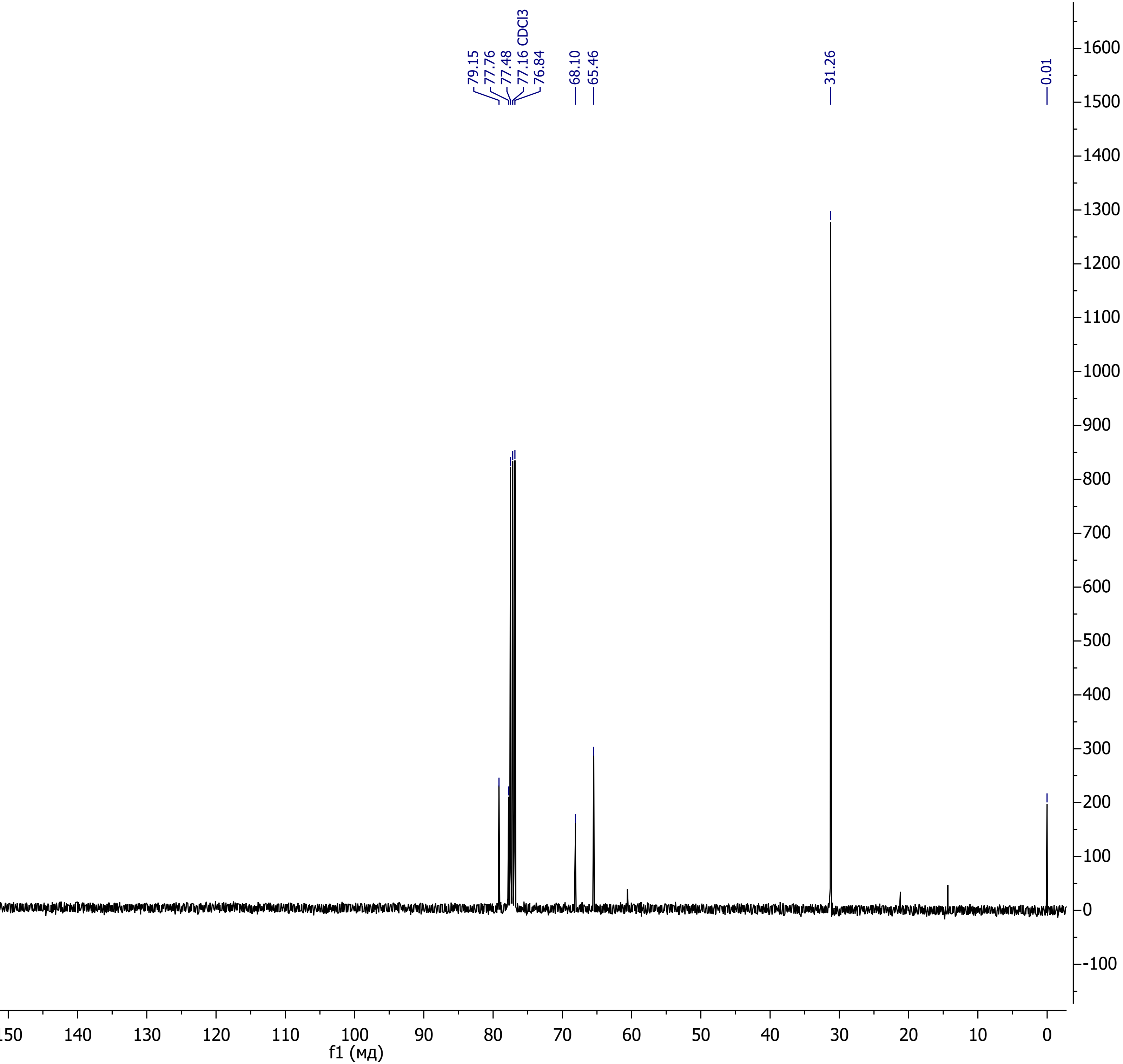

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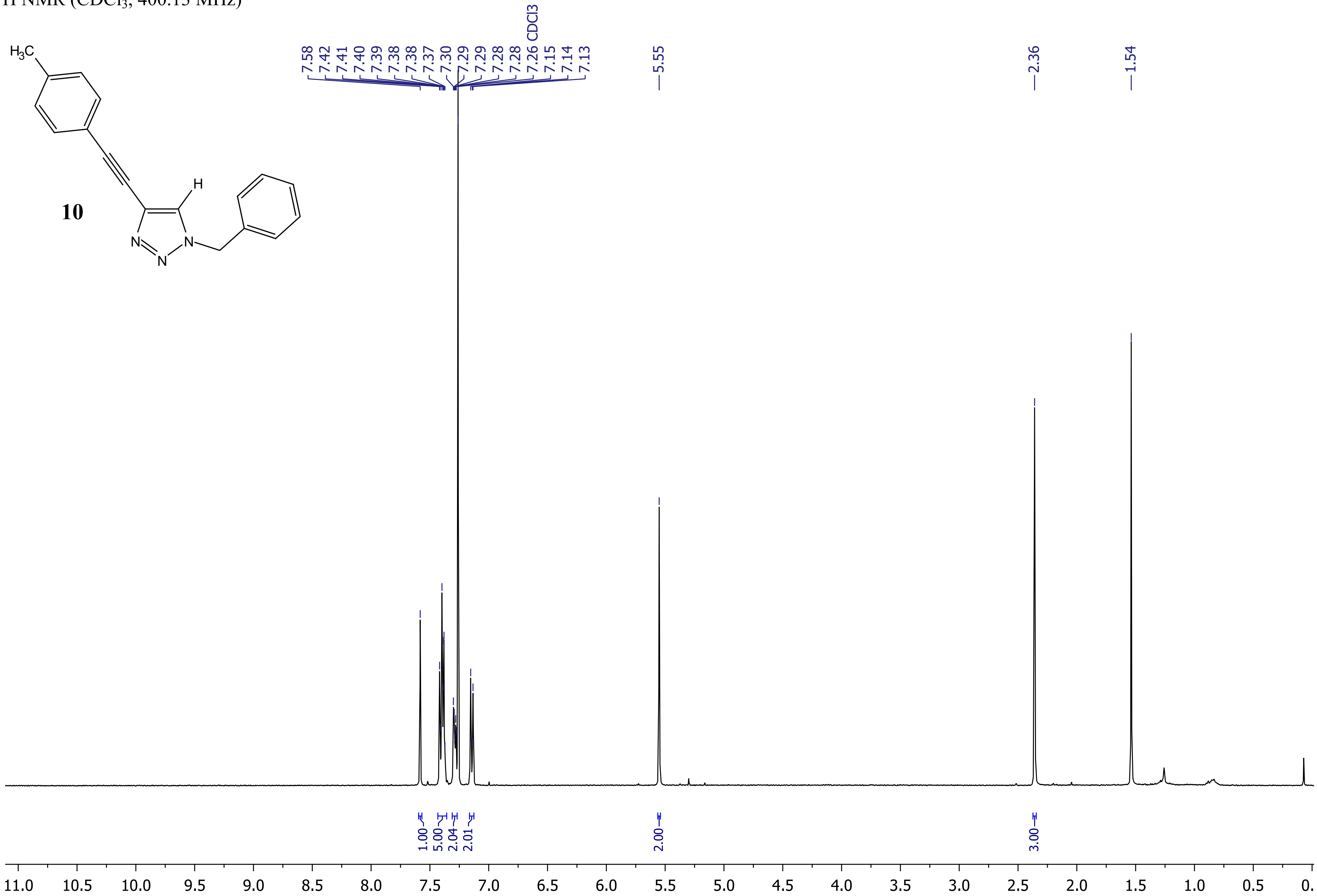
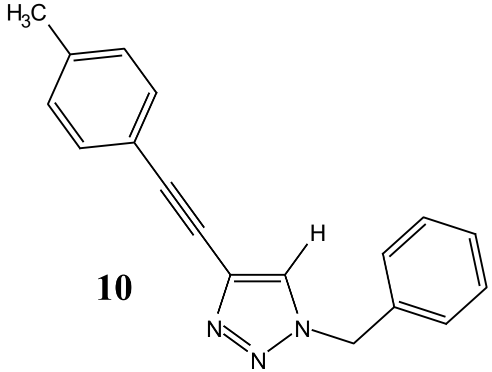


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



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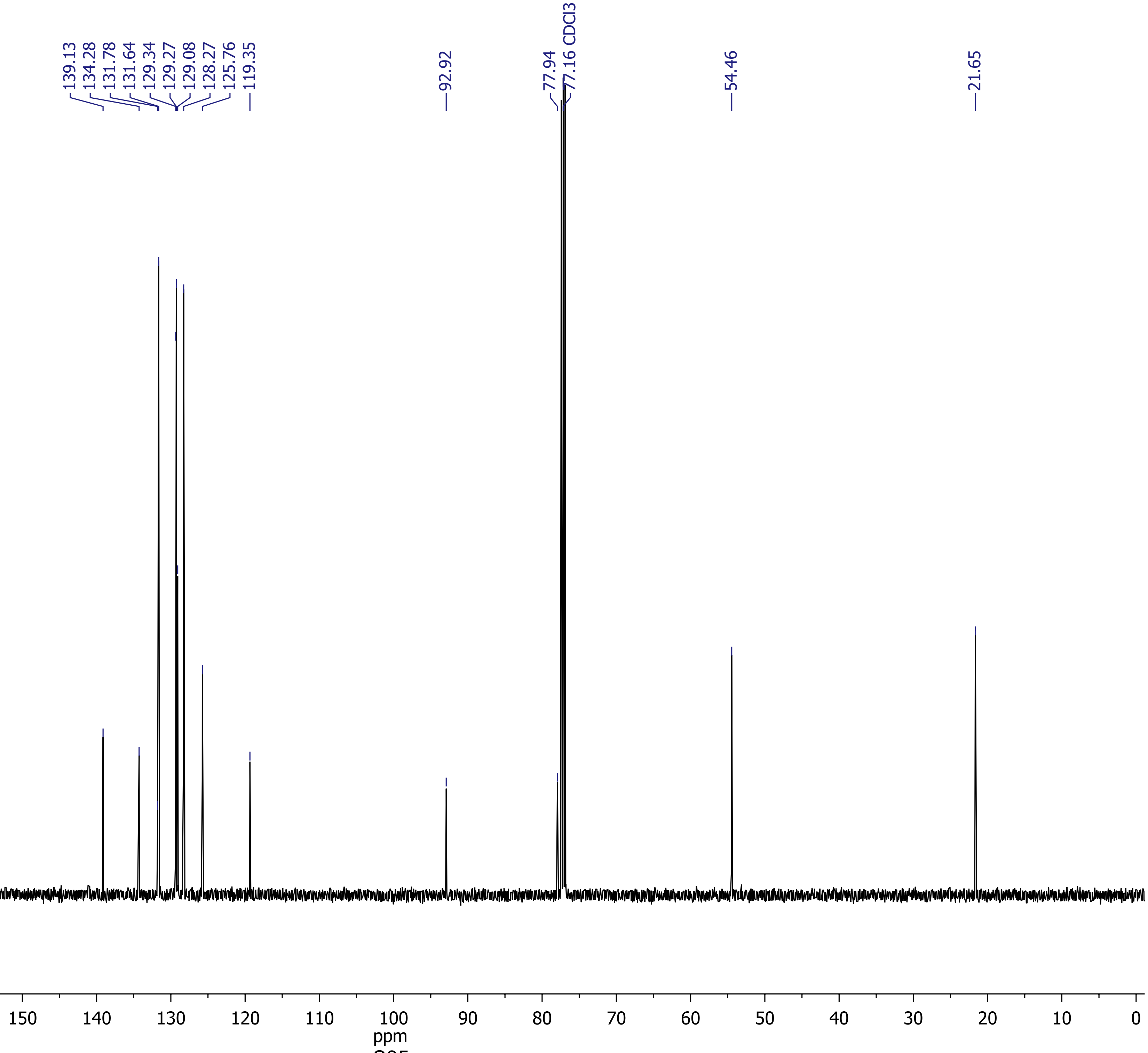
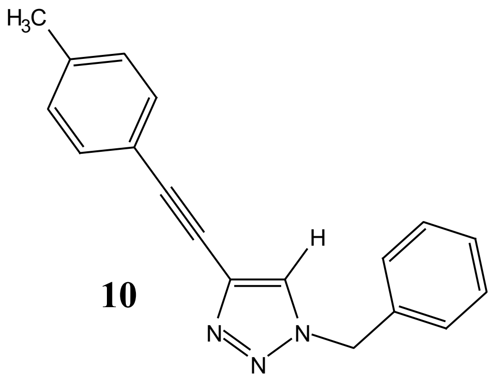


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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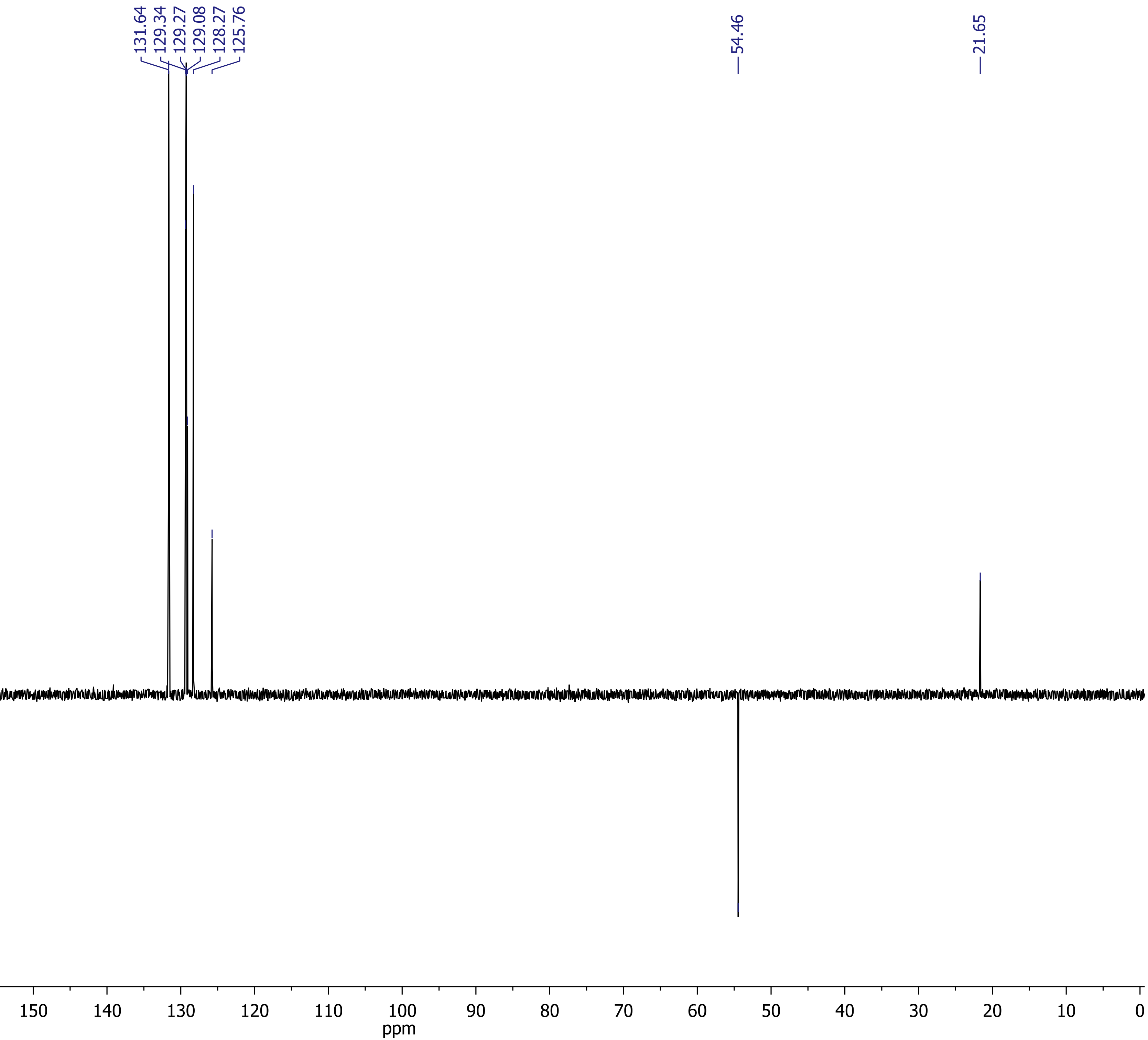
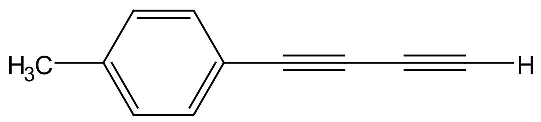


^{1}H NMR ($CDCl_3$, 400.13 MHz)



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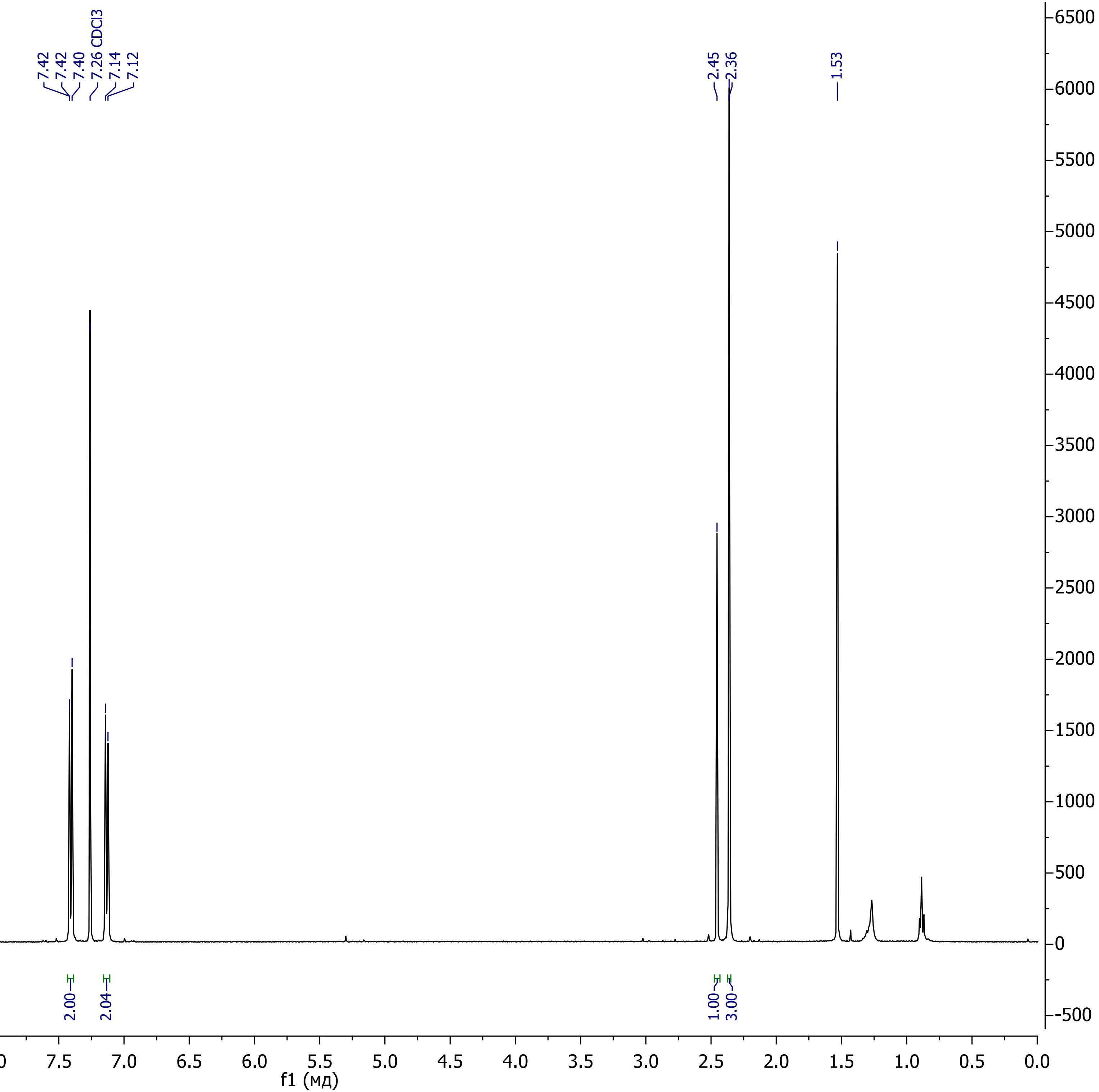
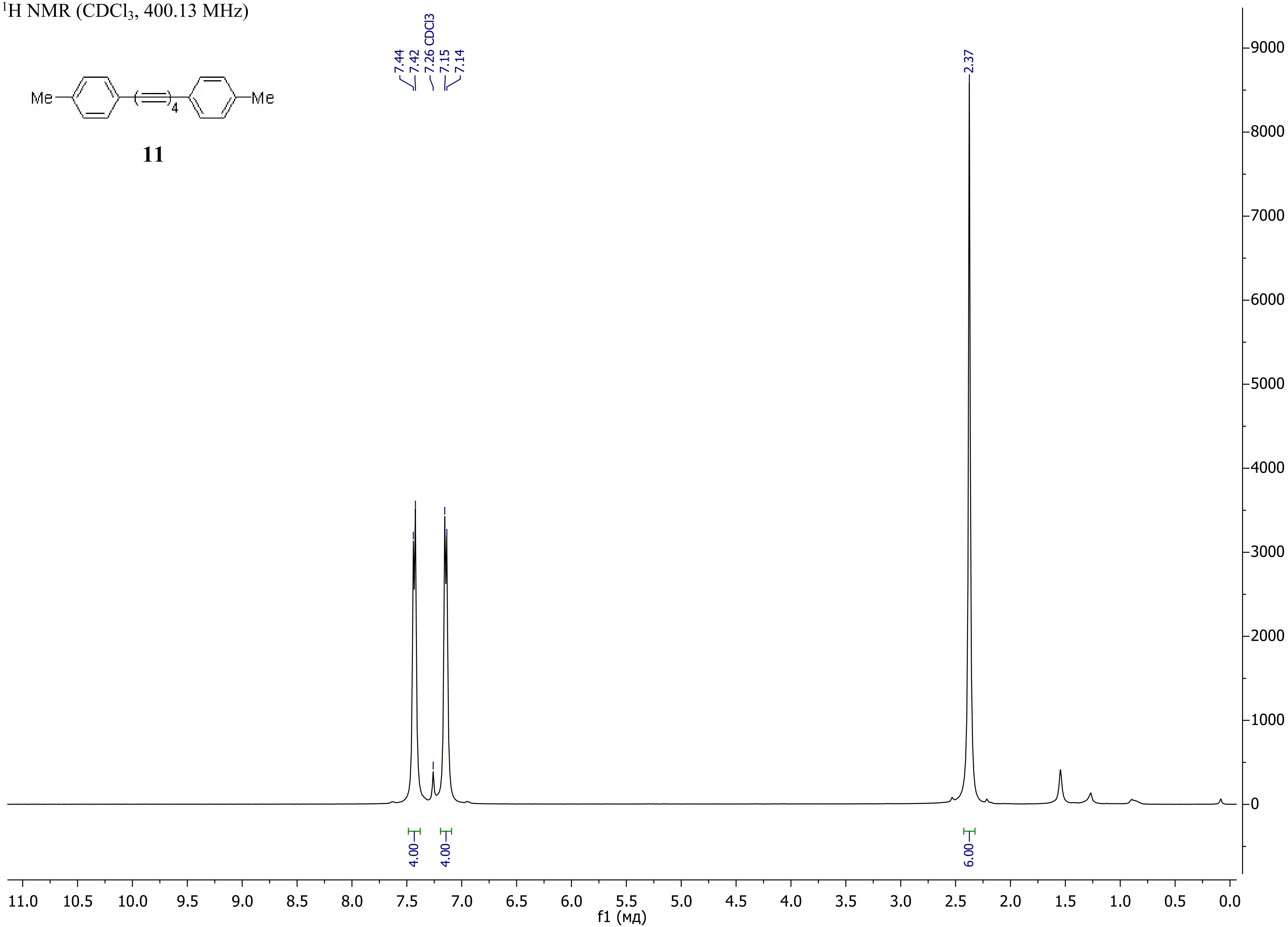


^{1}H NMR ($CDCl_3$, 400.13 MHz)



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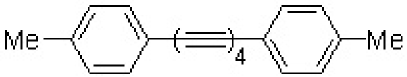
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz)



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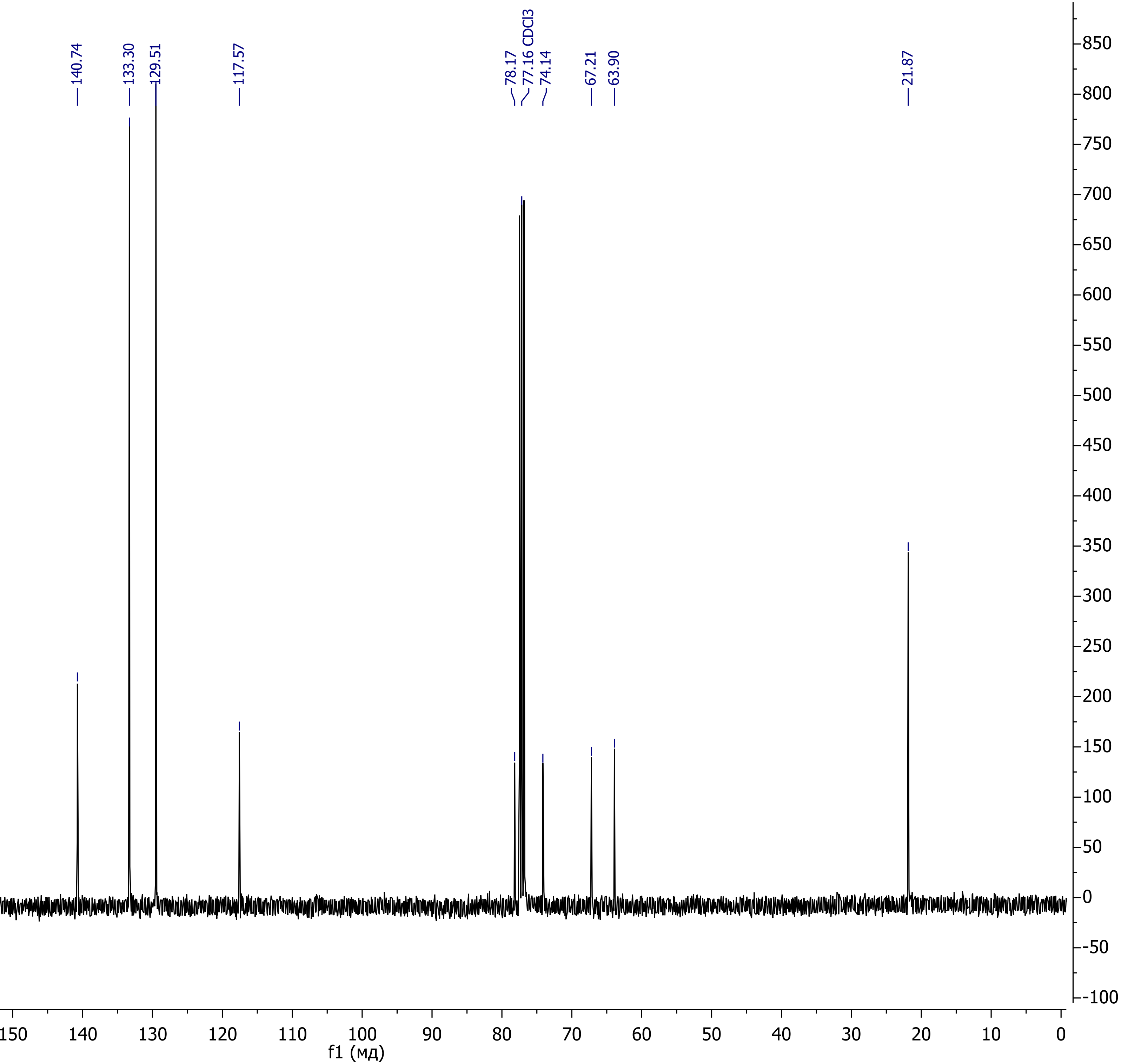
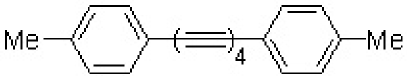


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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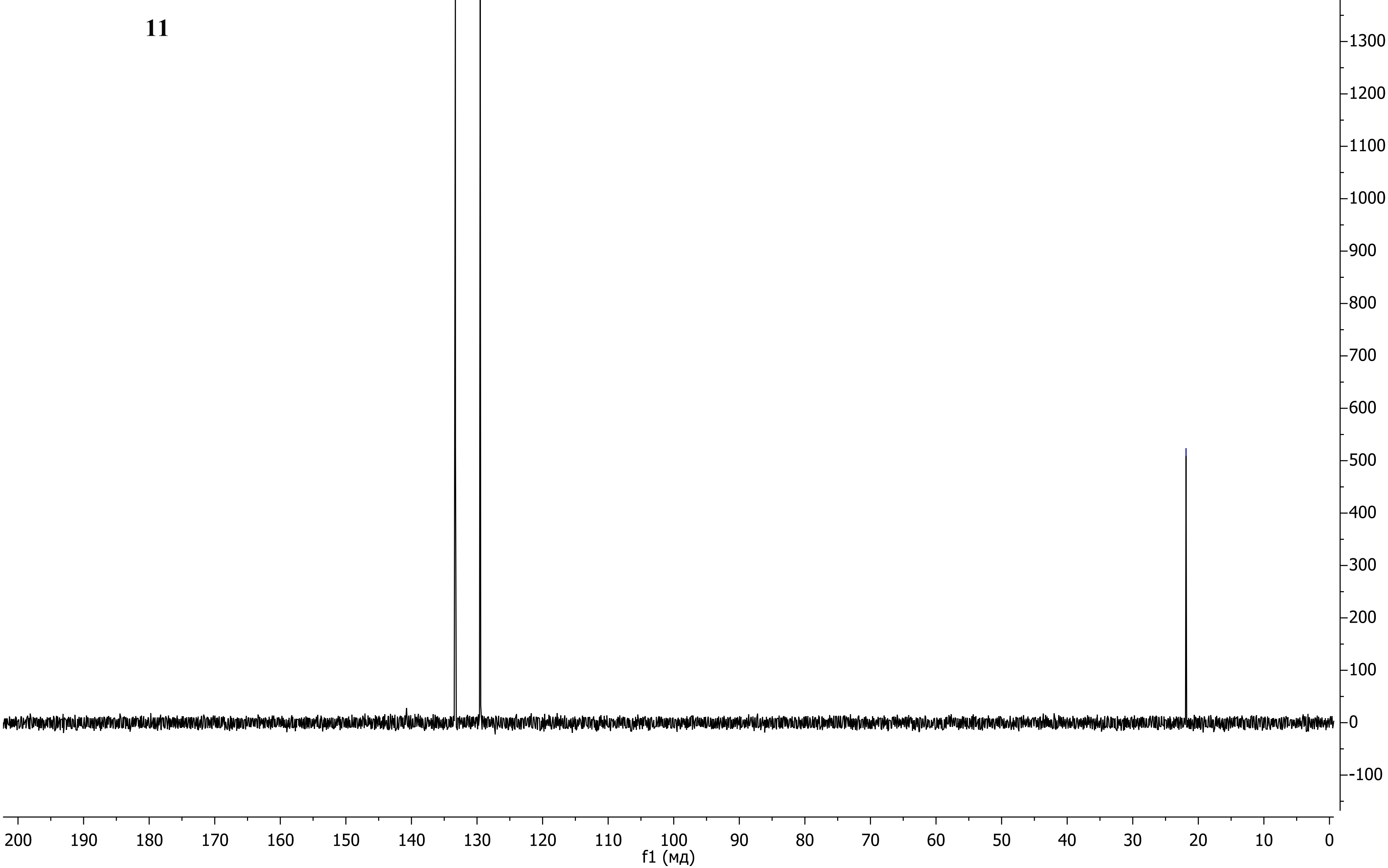
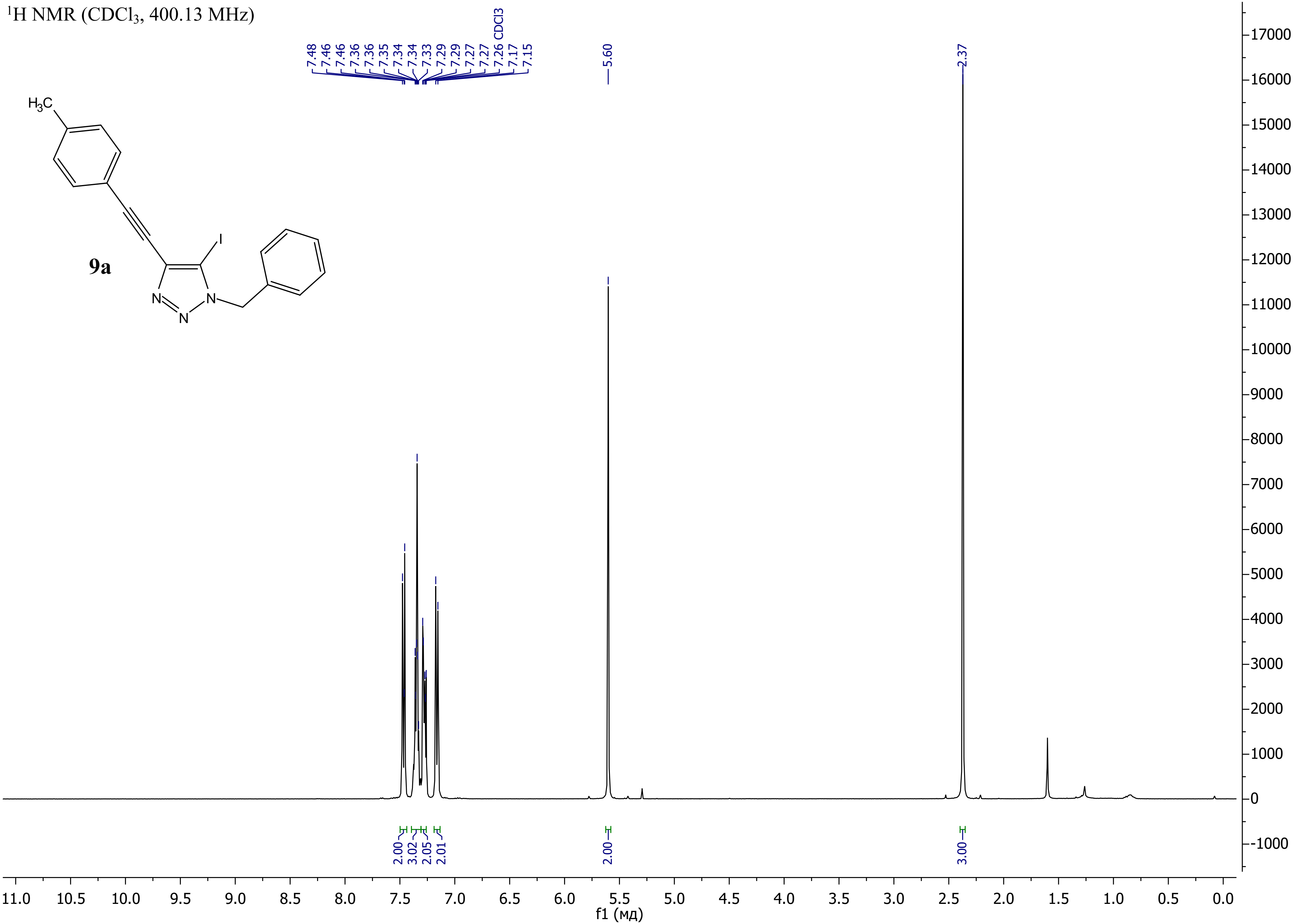
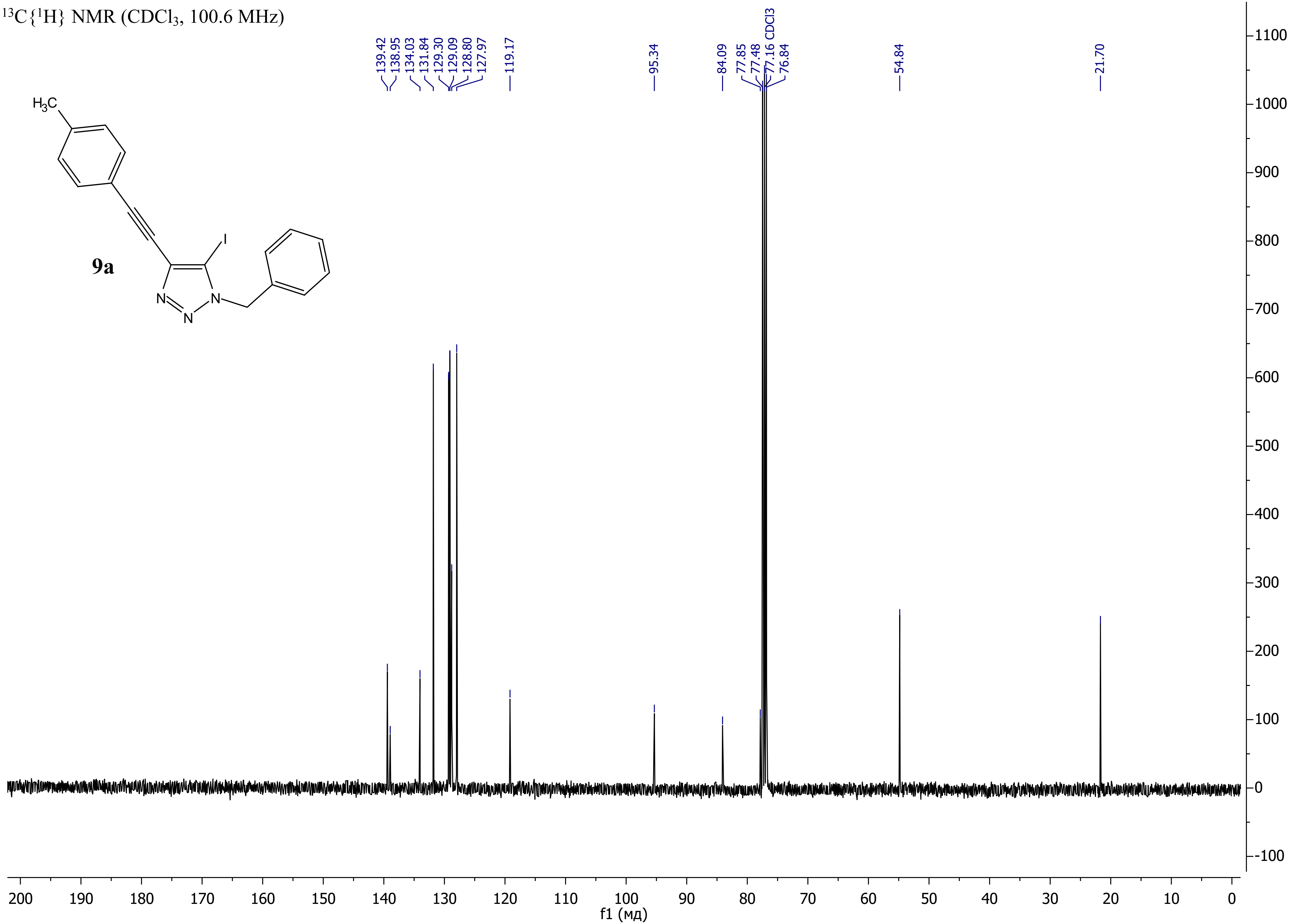


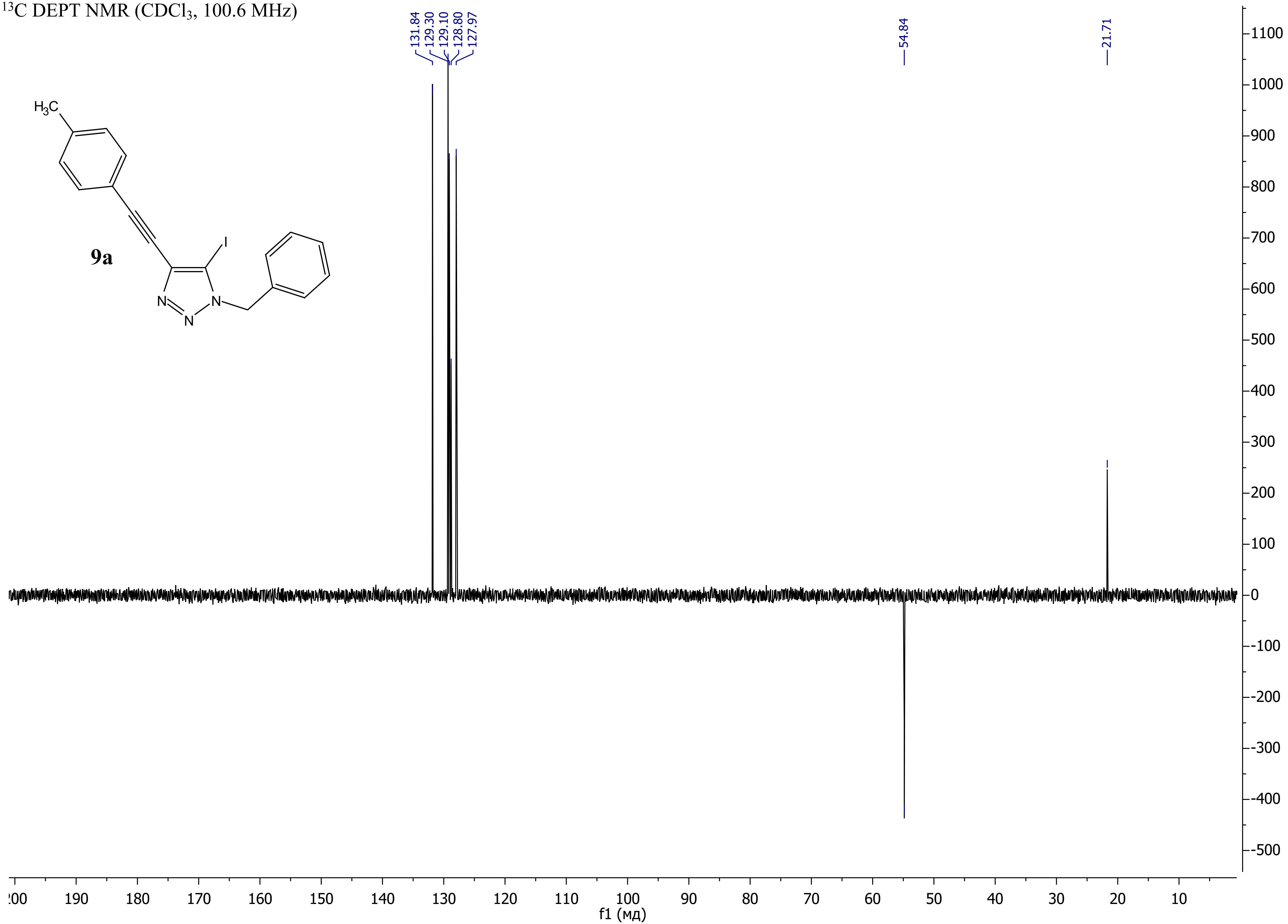
^{1}H NMR ($CDCl_3$, 400.13 MHz)



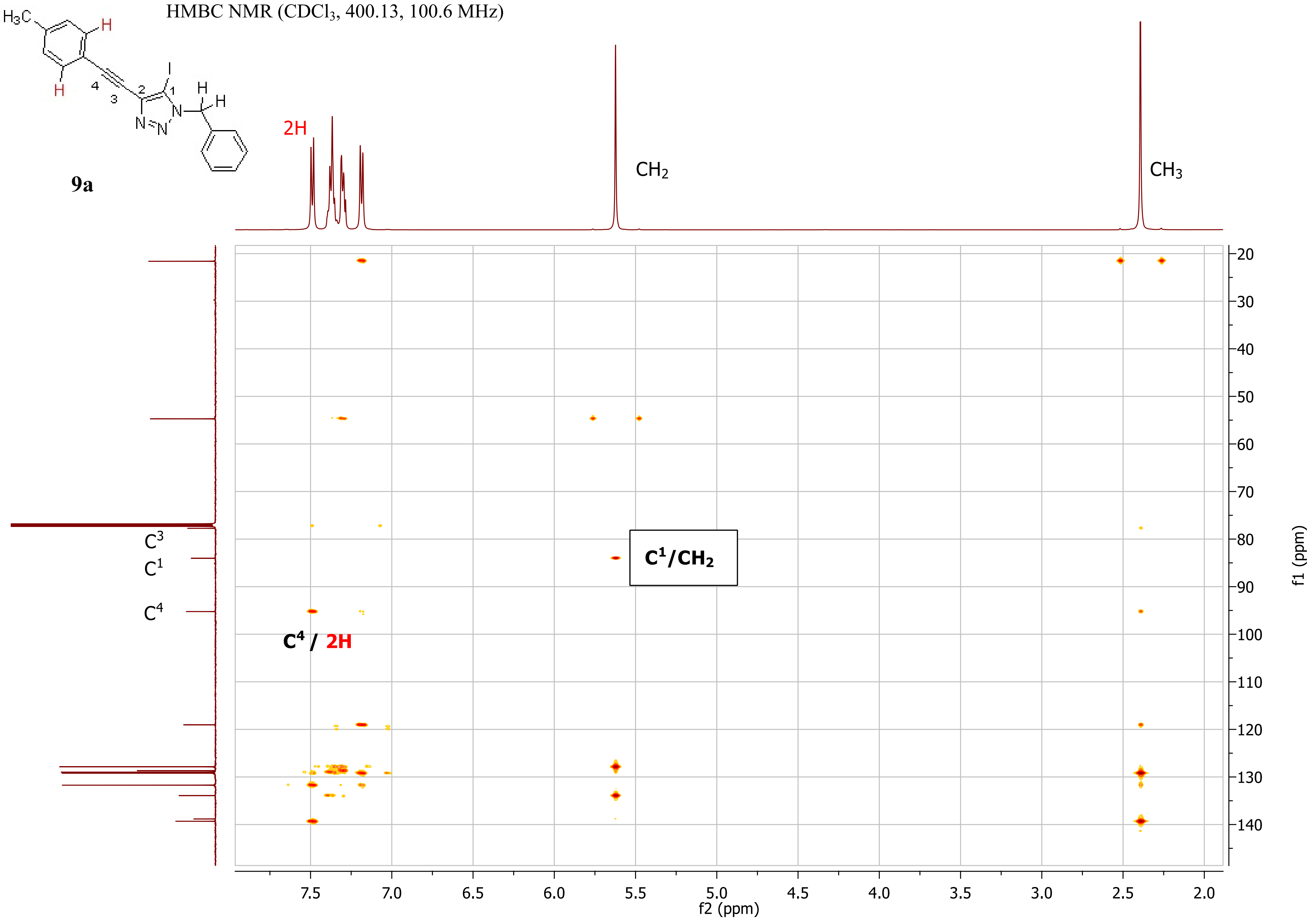
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



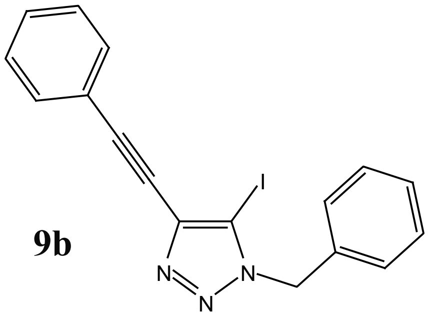
^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



HMBC NMR ($CDCl_3$, 400.13, 100.6 MHz)



^{1}H NMR ($CDCl_3$, 400.13 MHz)



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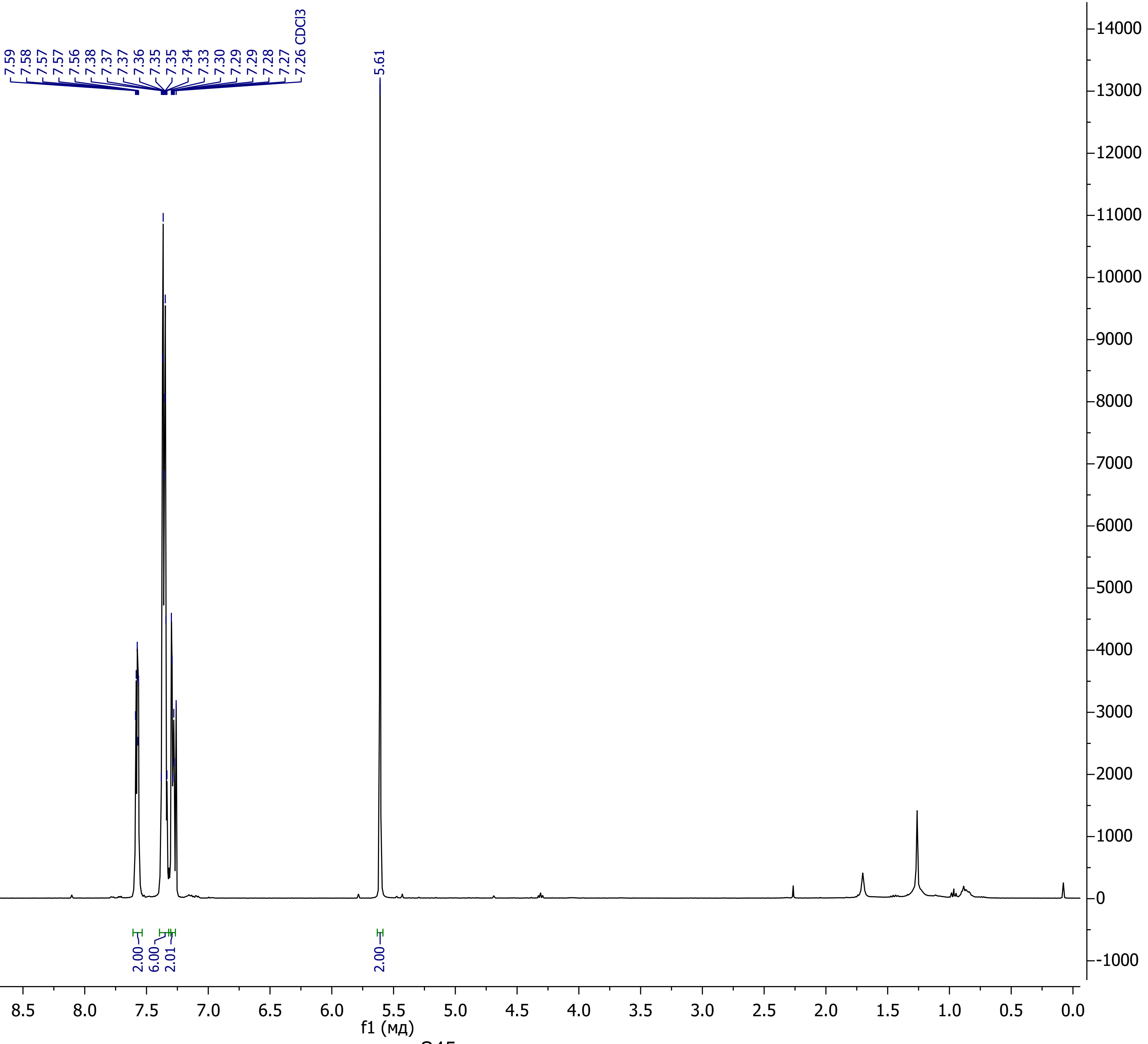
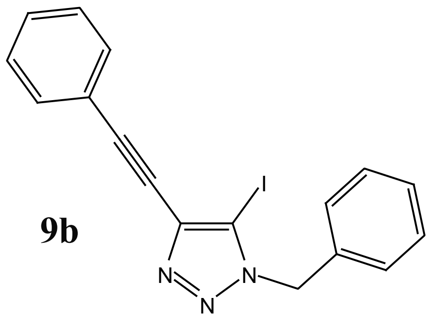


$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz)



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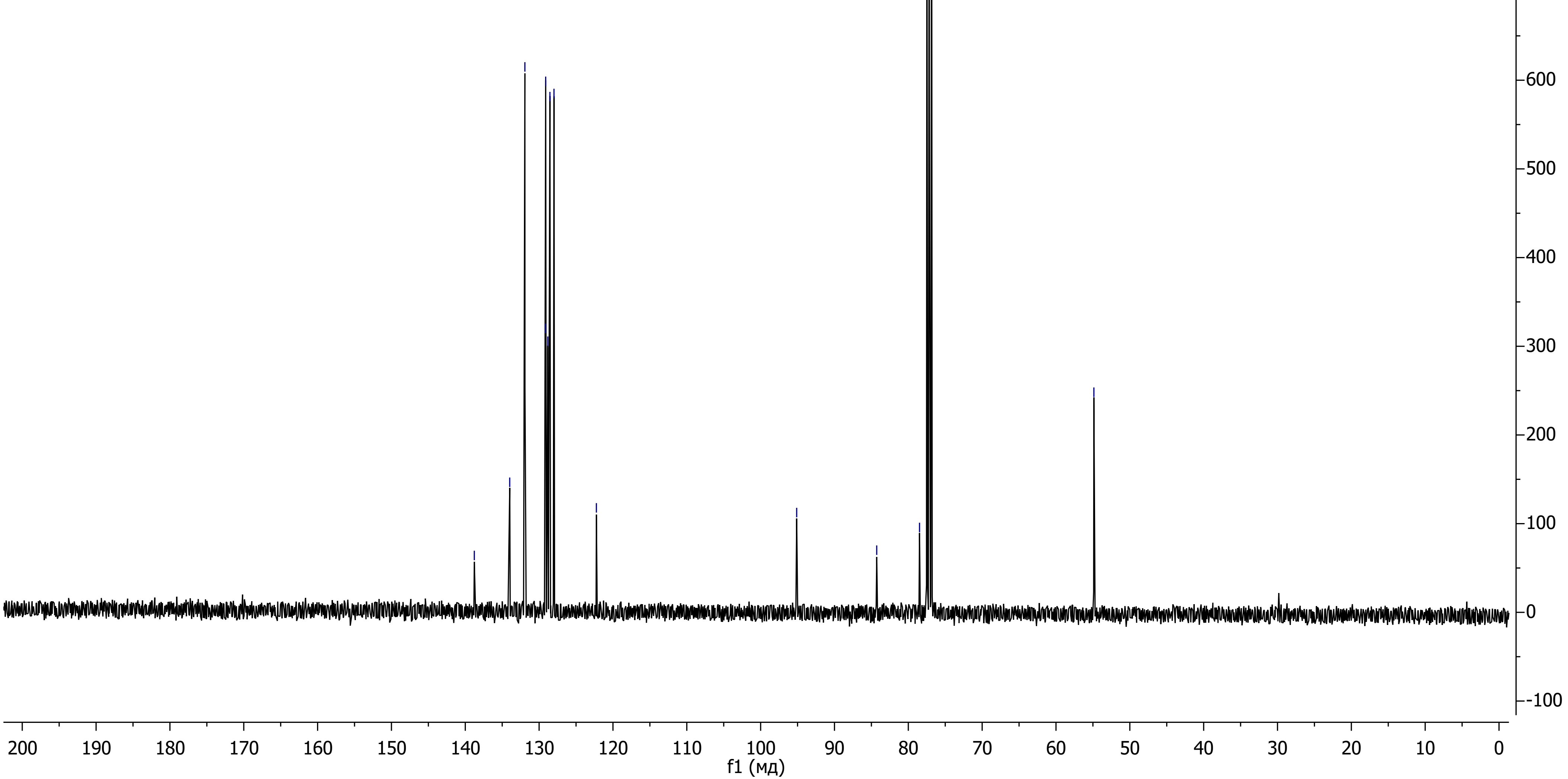
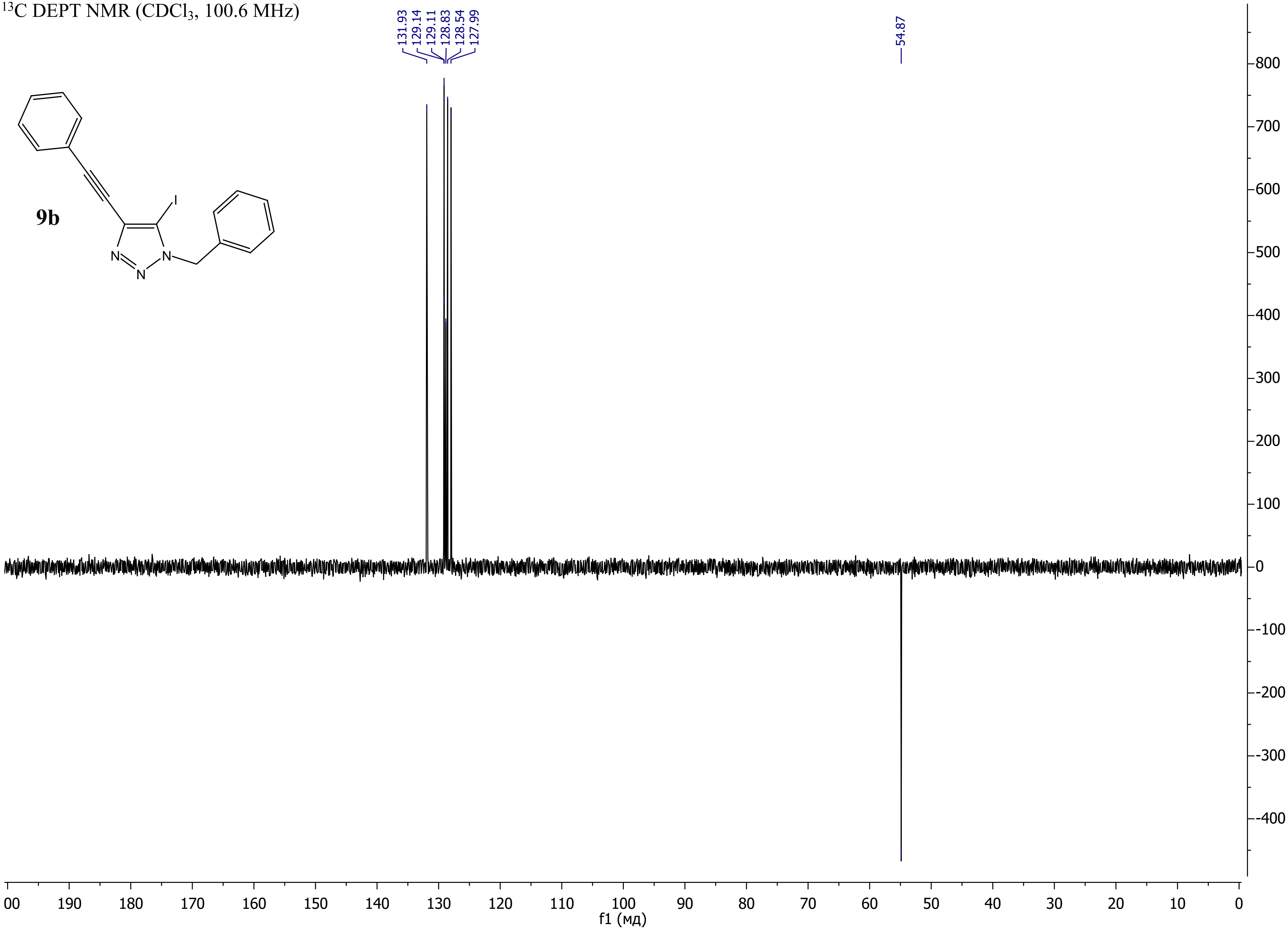
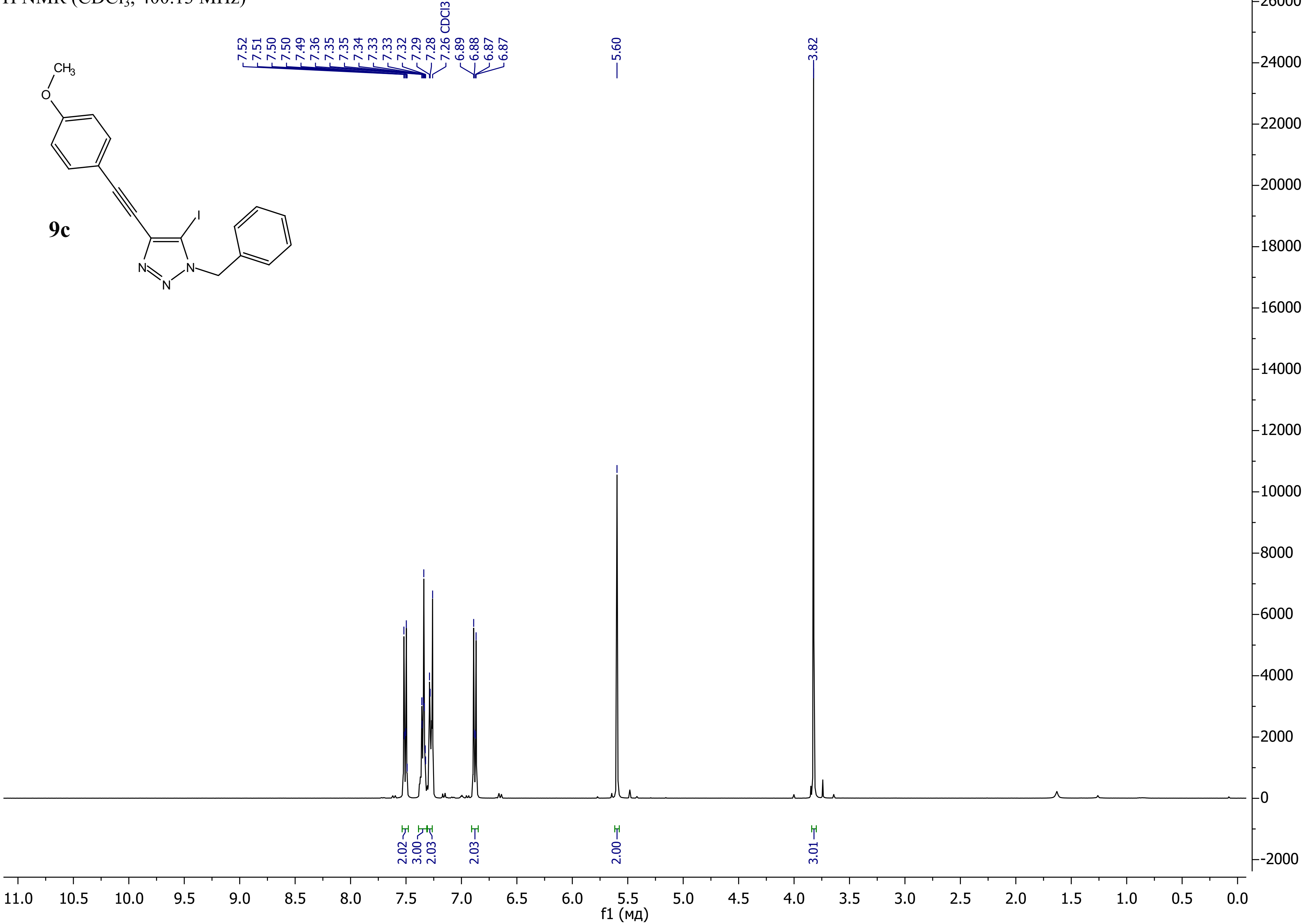


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)

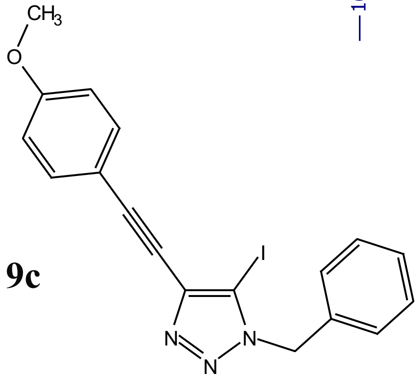
9b



[1]H NMR ($CDCl_3$, 400.13 MHz)



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



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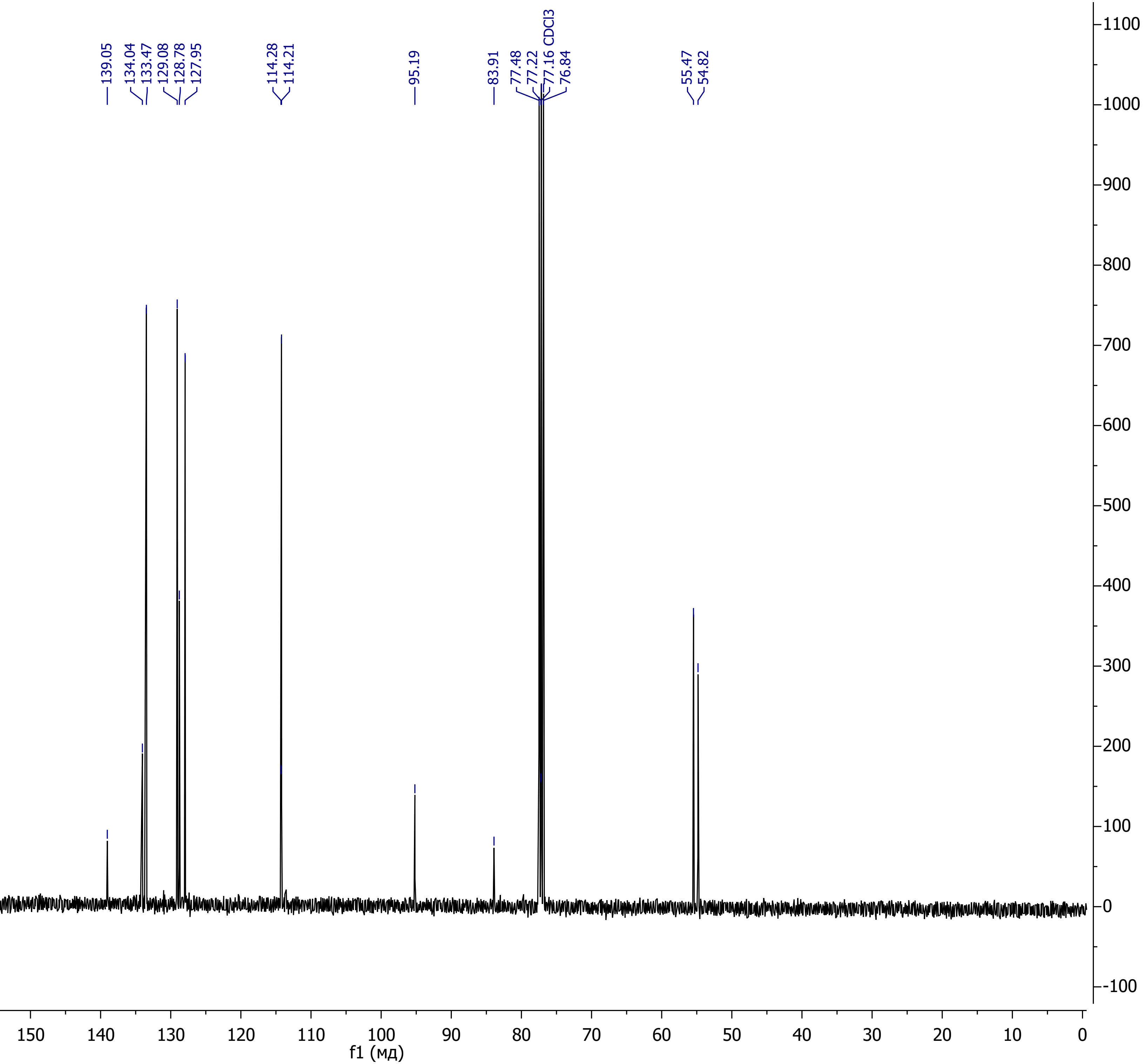
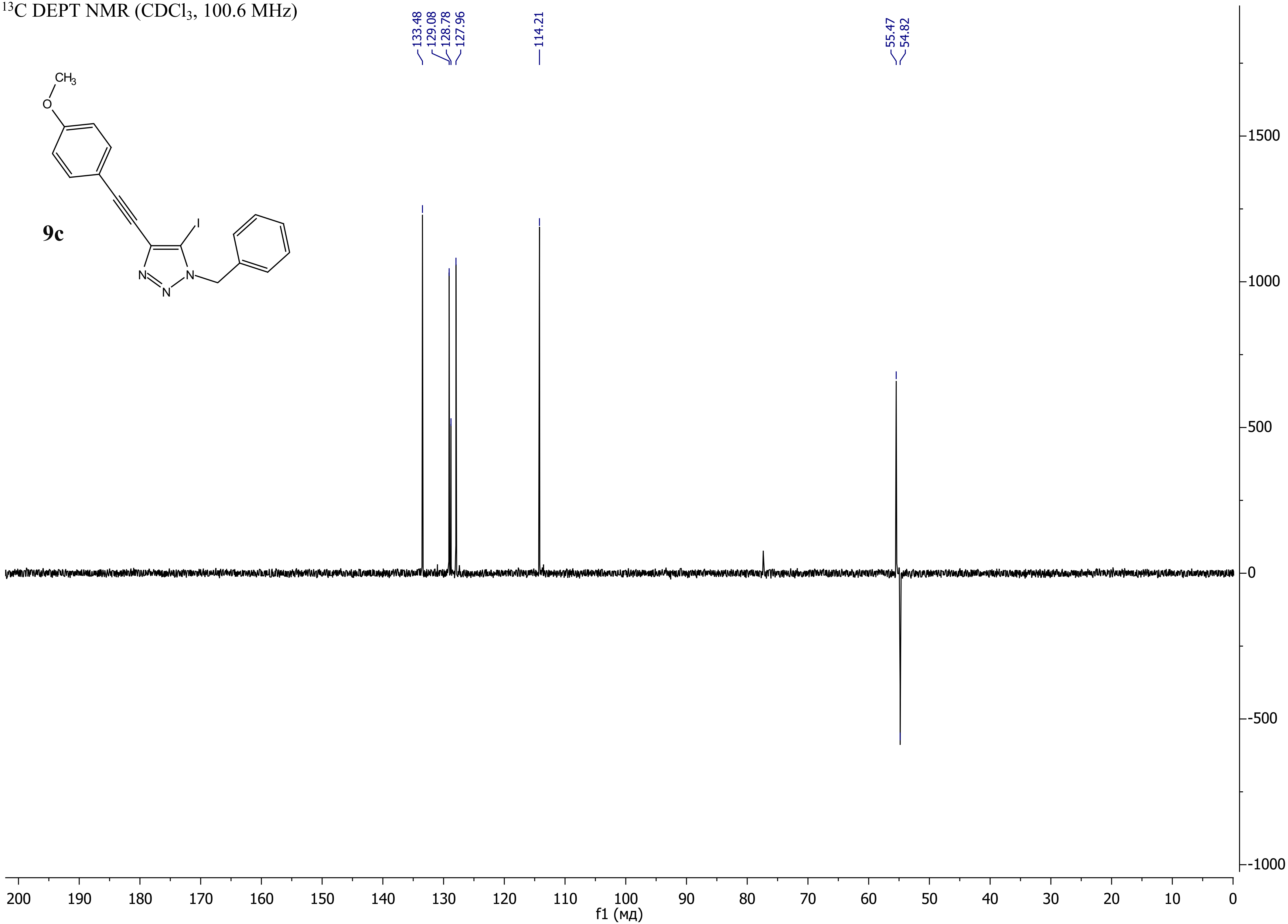
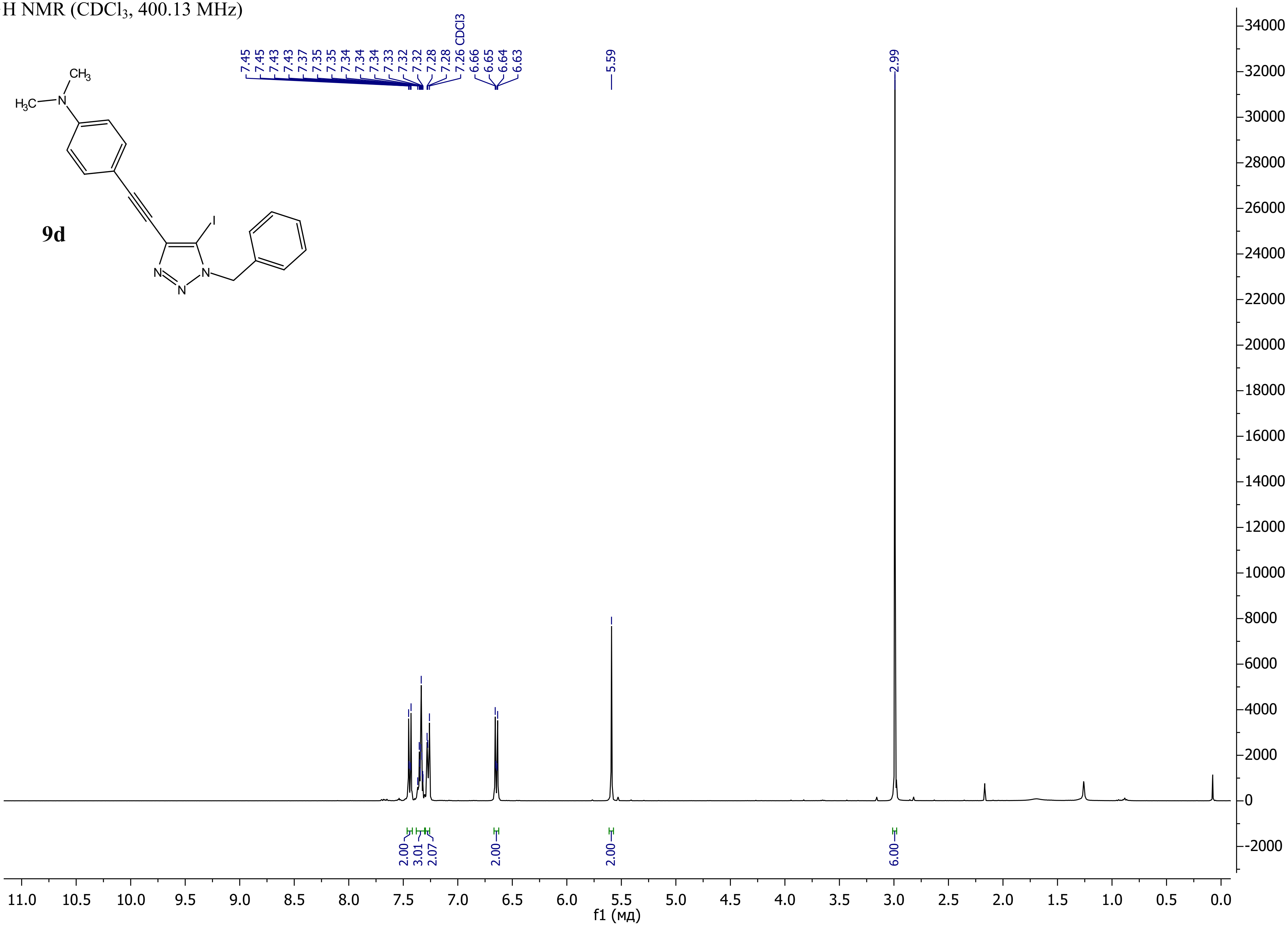


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)

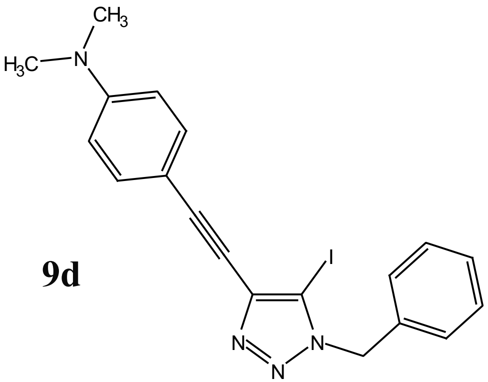


^{1}H NMR ($CDCl_3$, 400.13 MHz)

9d



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



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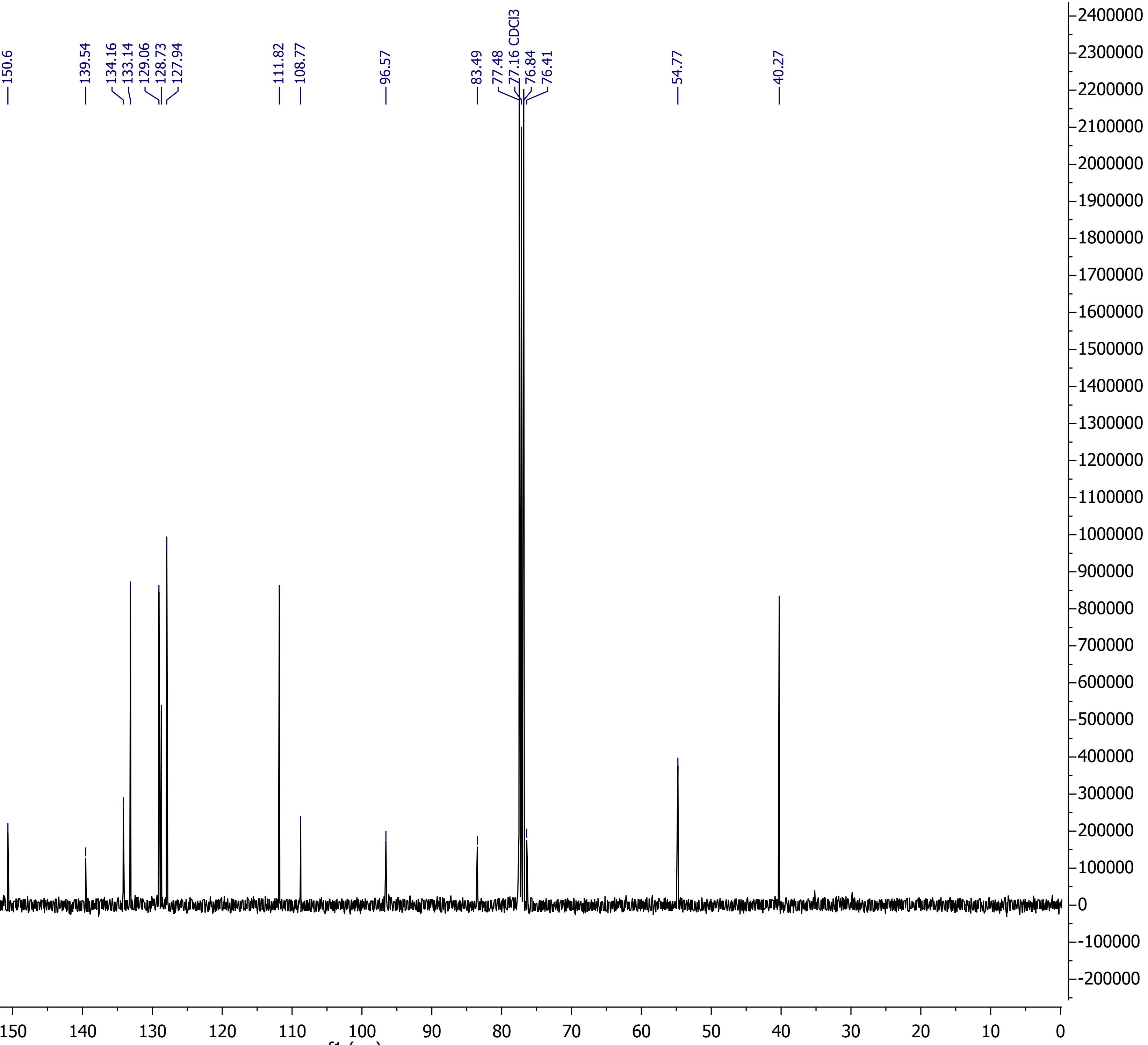
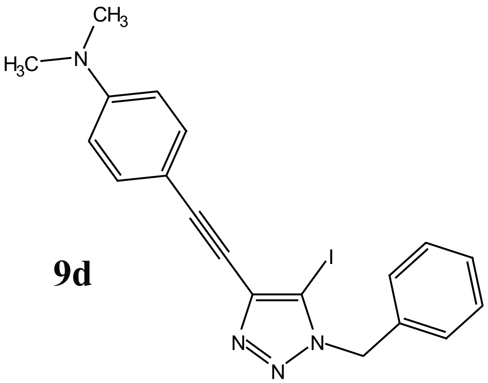


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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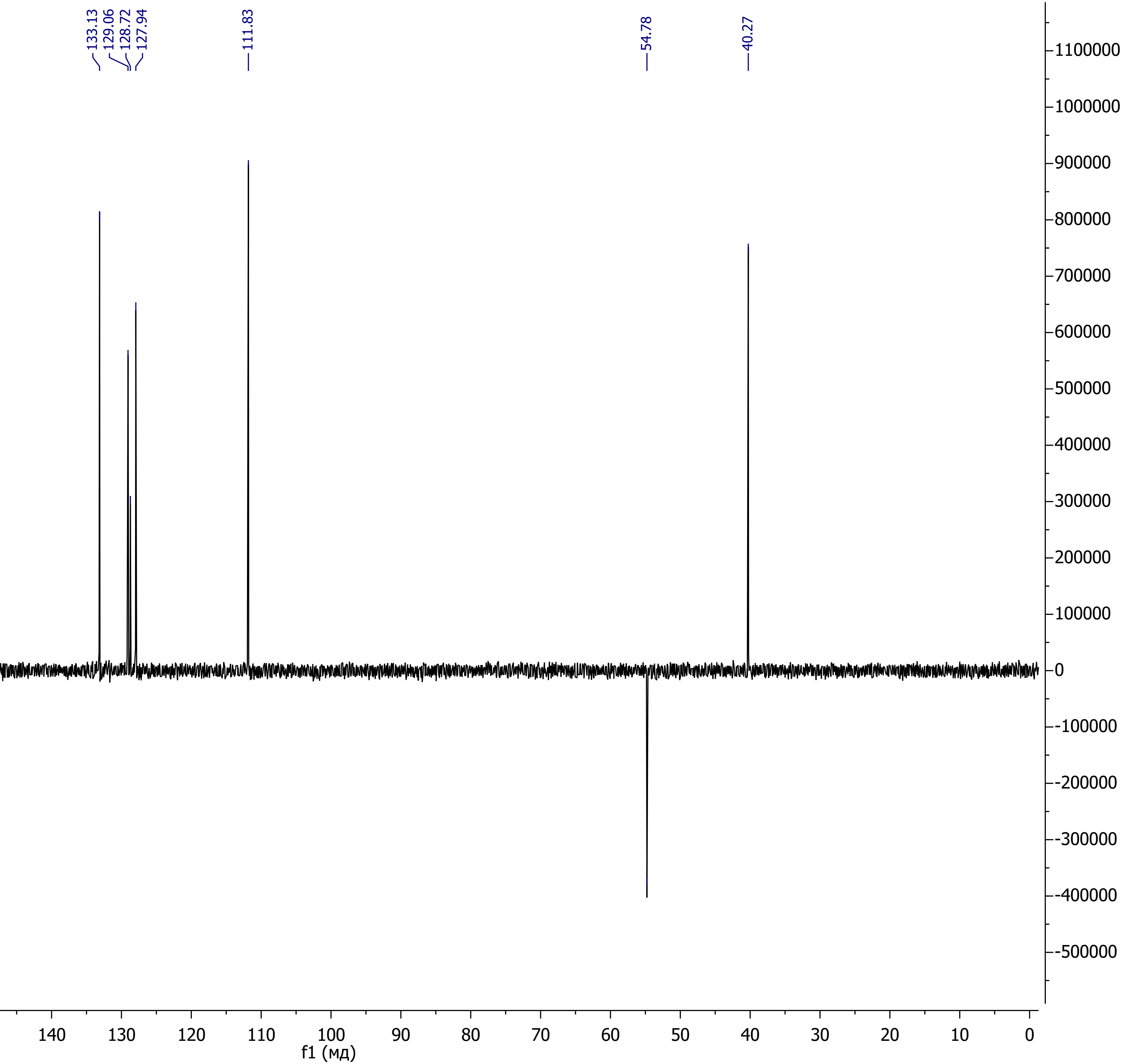

^{1}H NMR ($CDCl_3$, 400.13 MHz)

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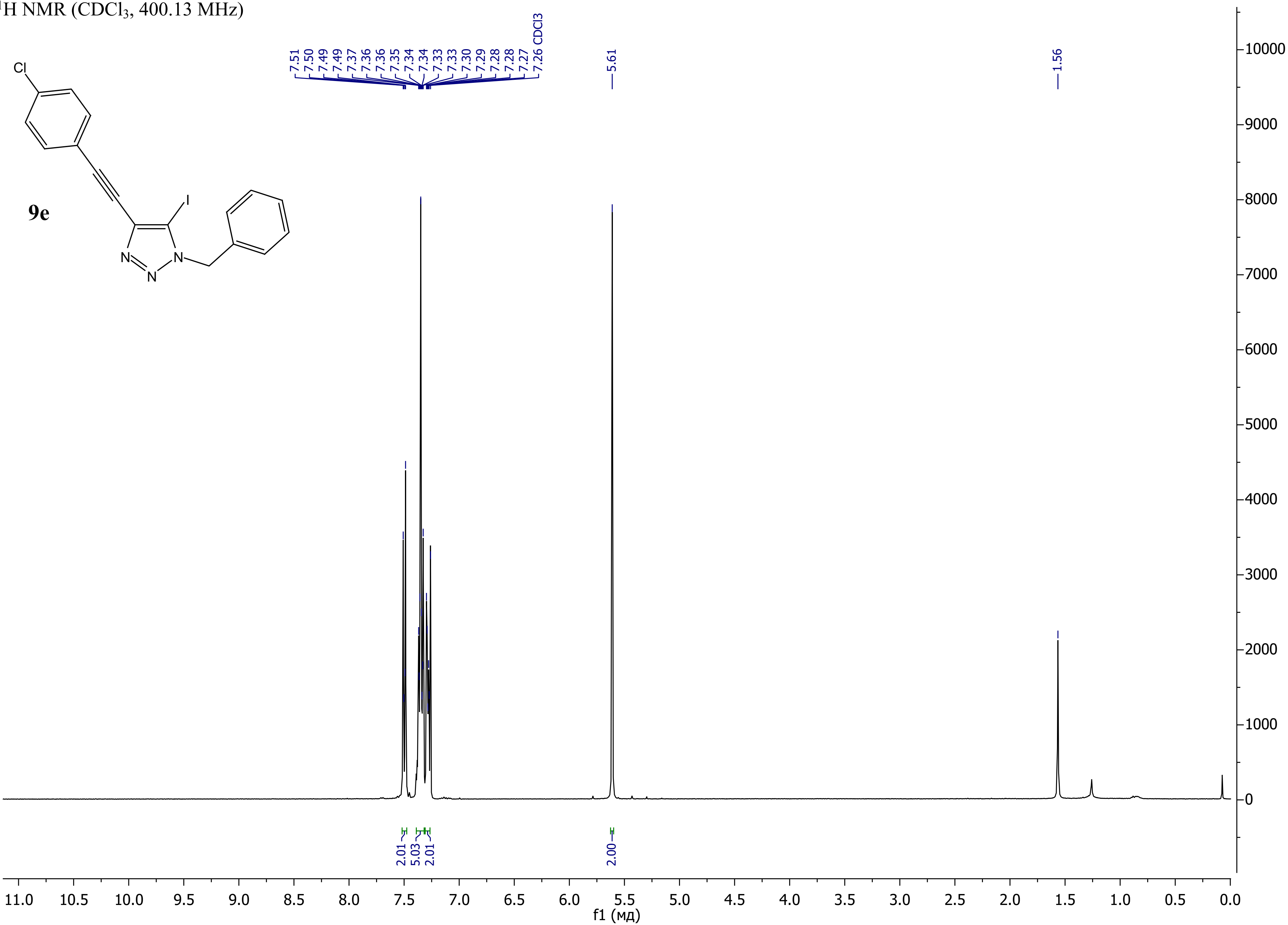
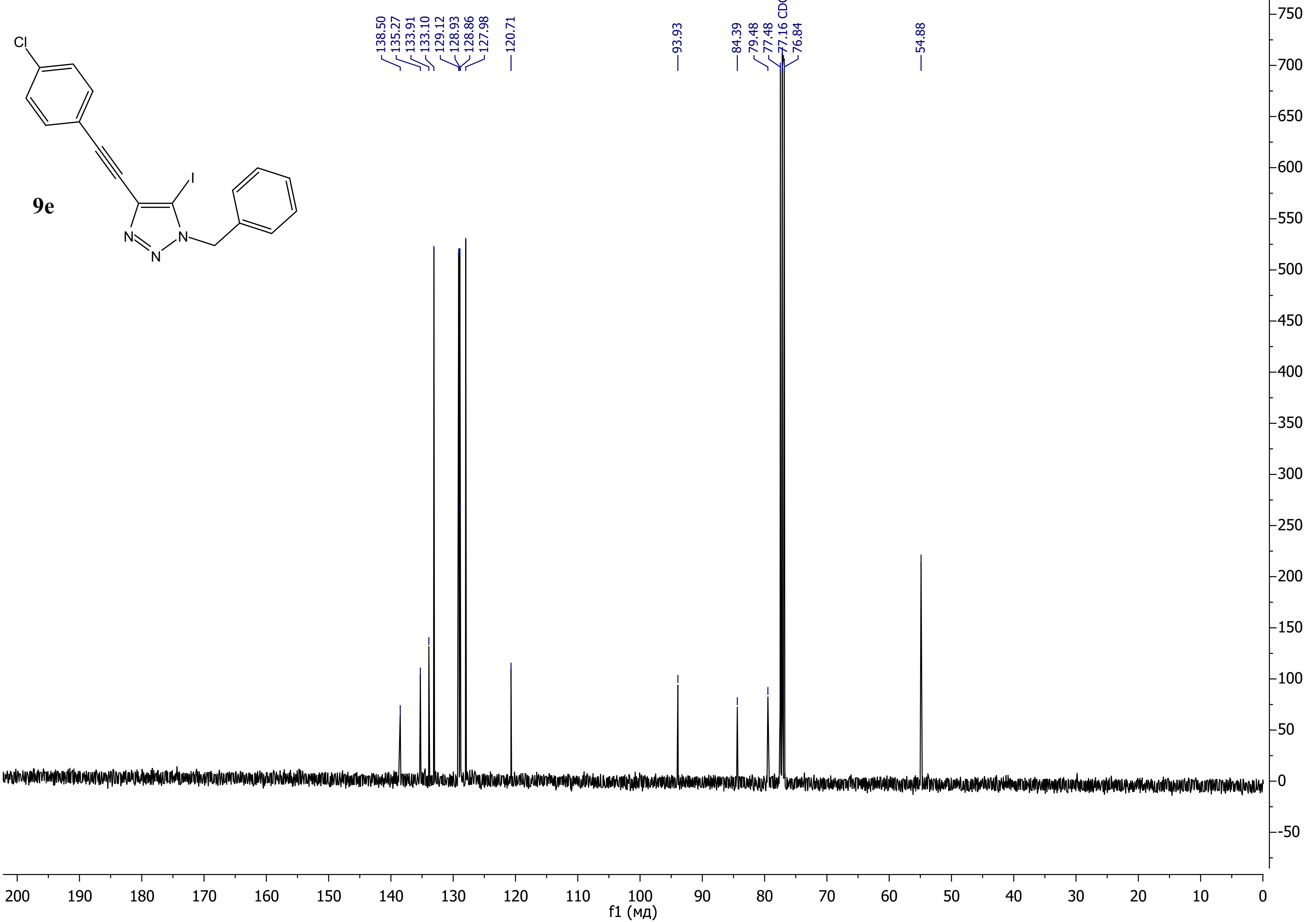
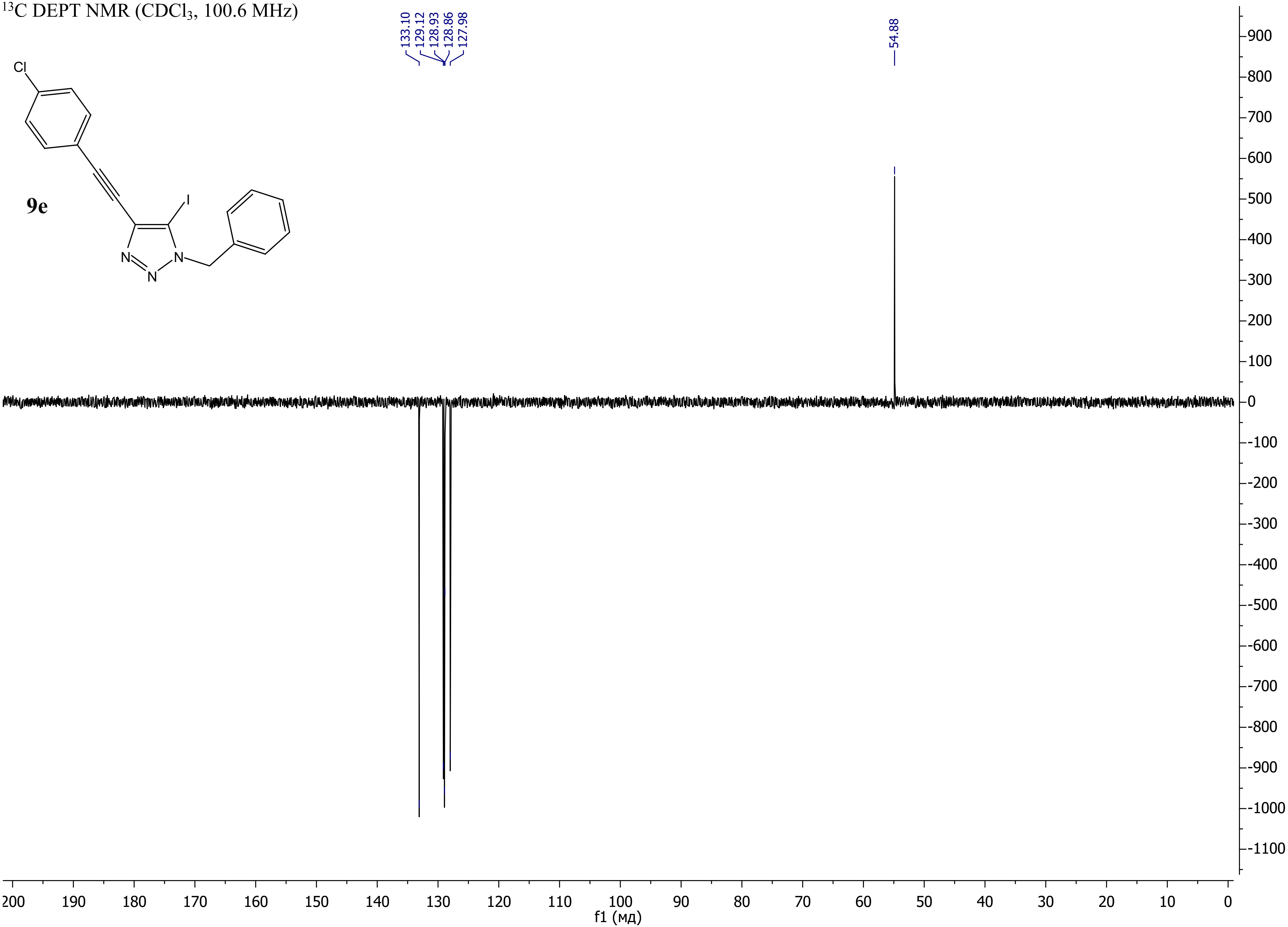


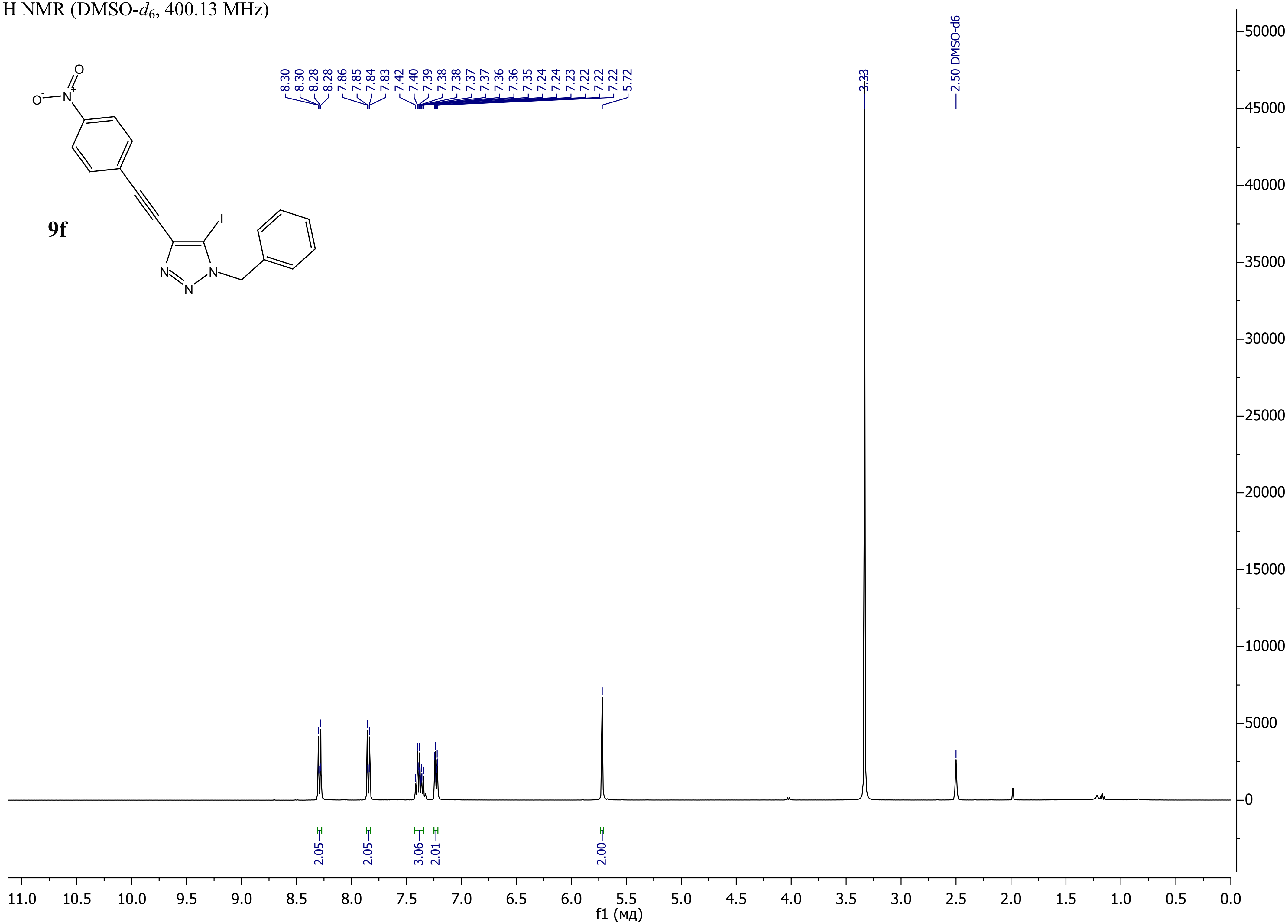
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz)



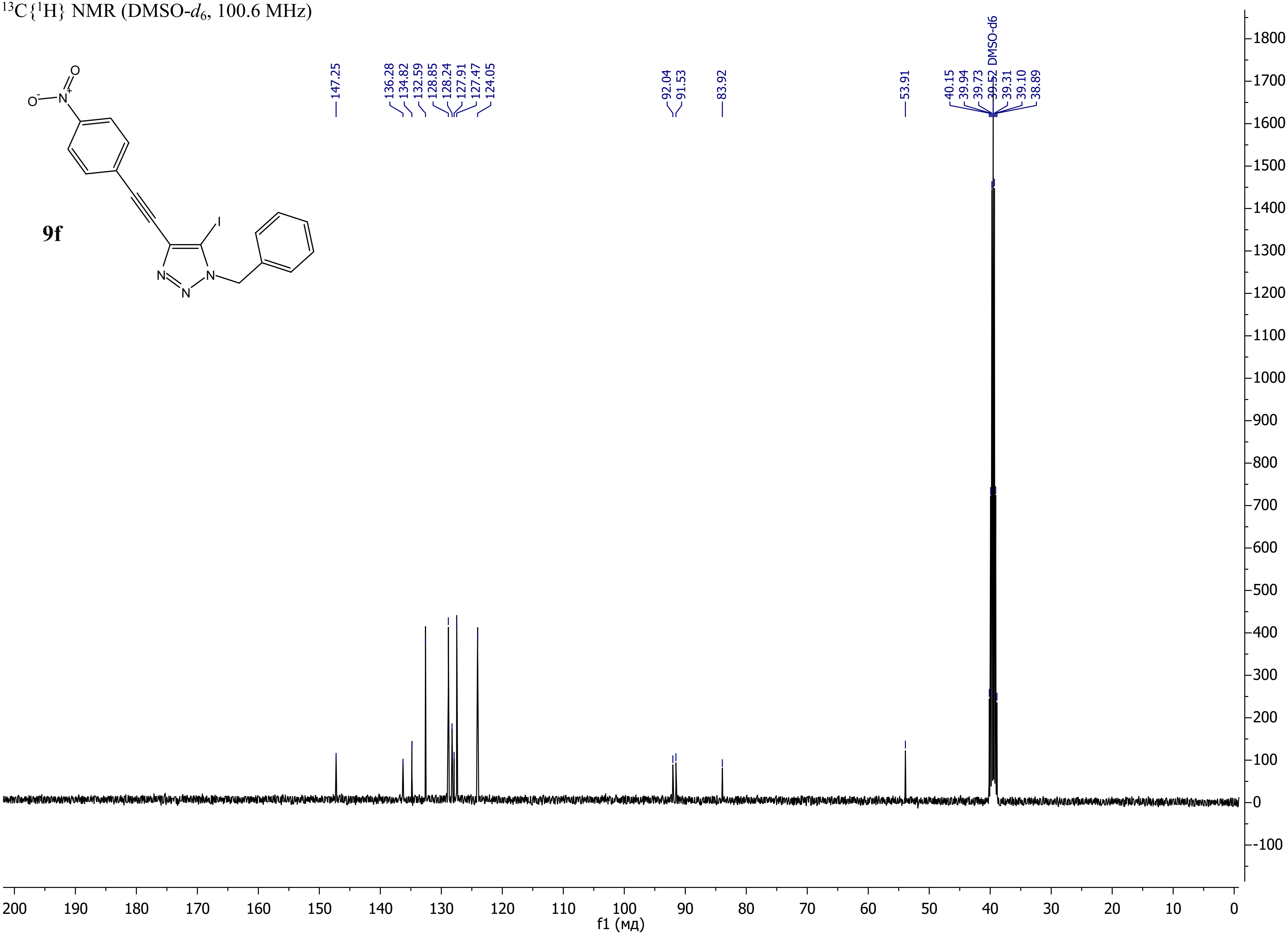
^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



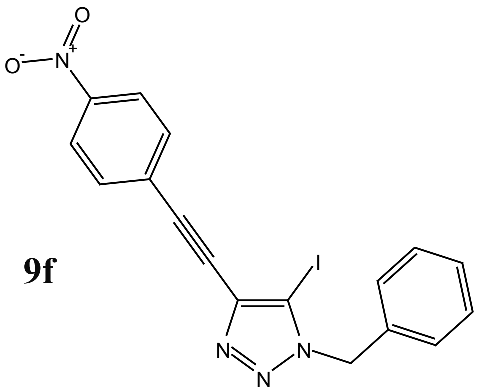
[1]H NMR (DMSO-d_6, 400.13 MHz)



$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100.6 MHz)



^{13}C DEPT NMR (DMSO-d_6, 100.6 MHz)



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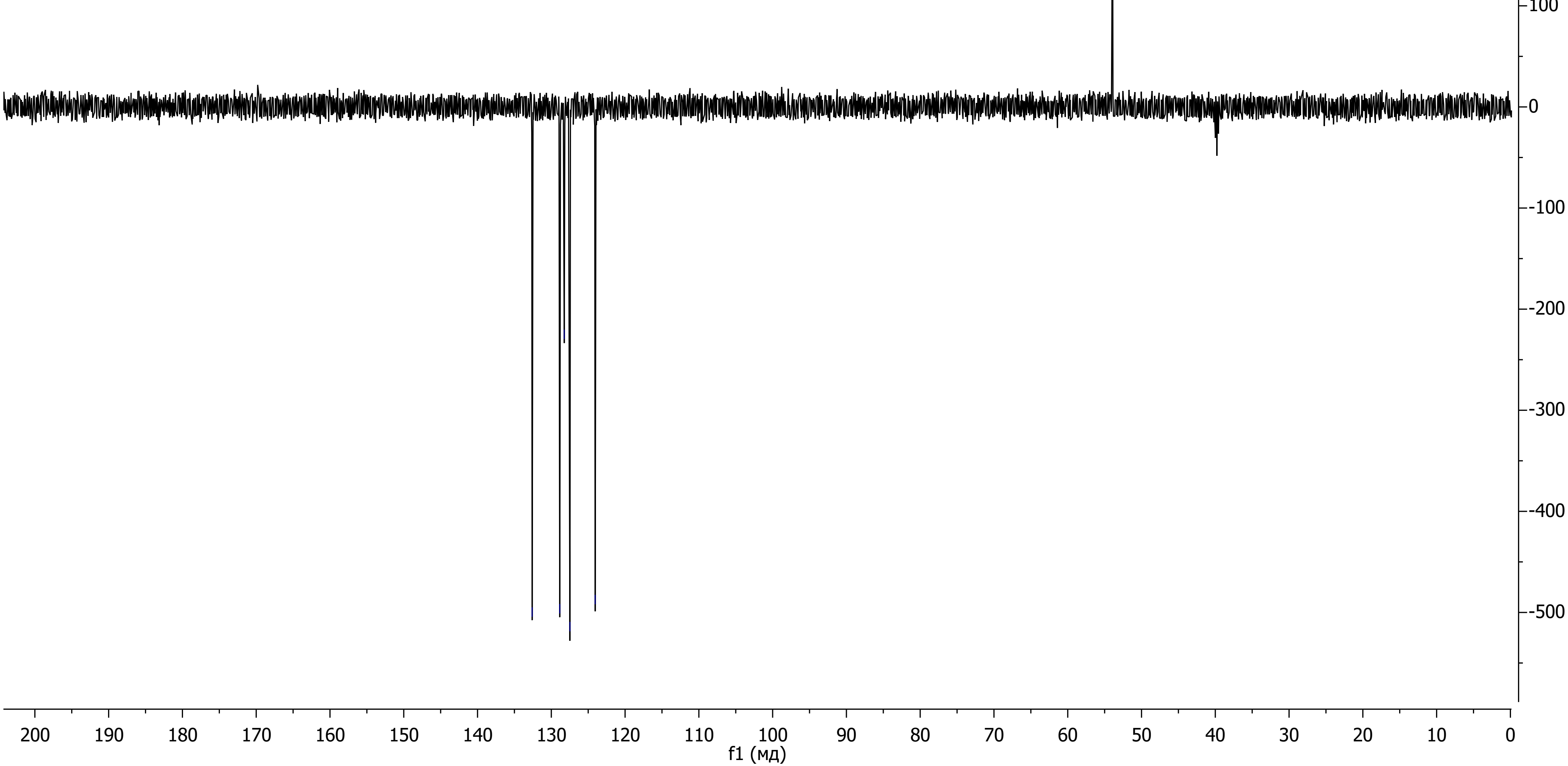
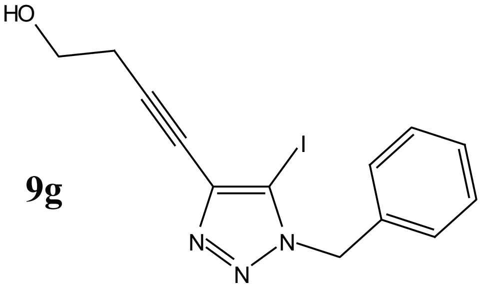


^{1}H NMR ($CDCl_3$, 400.13 MHz)



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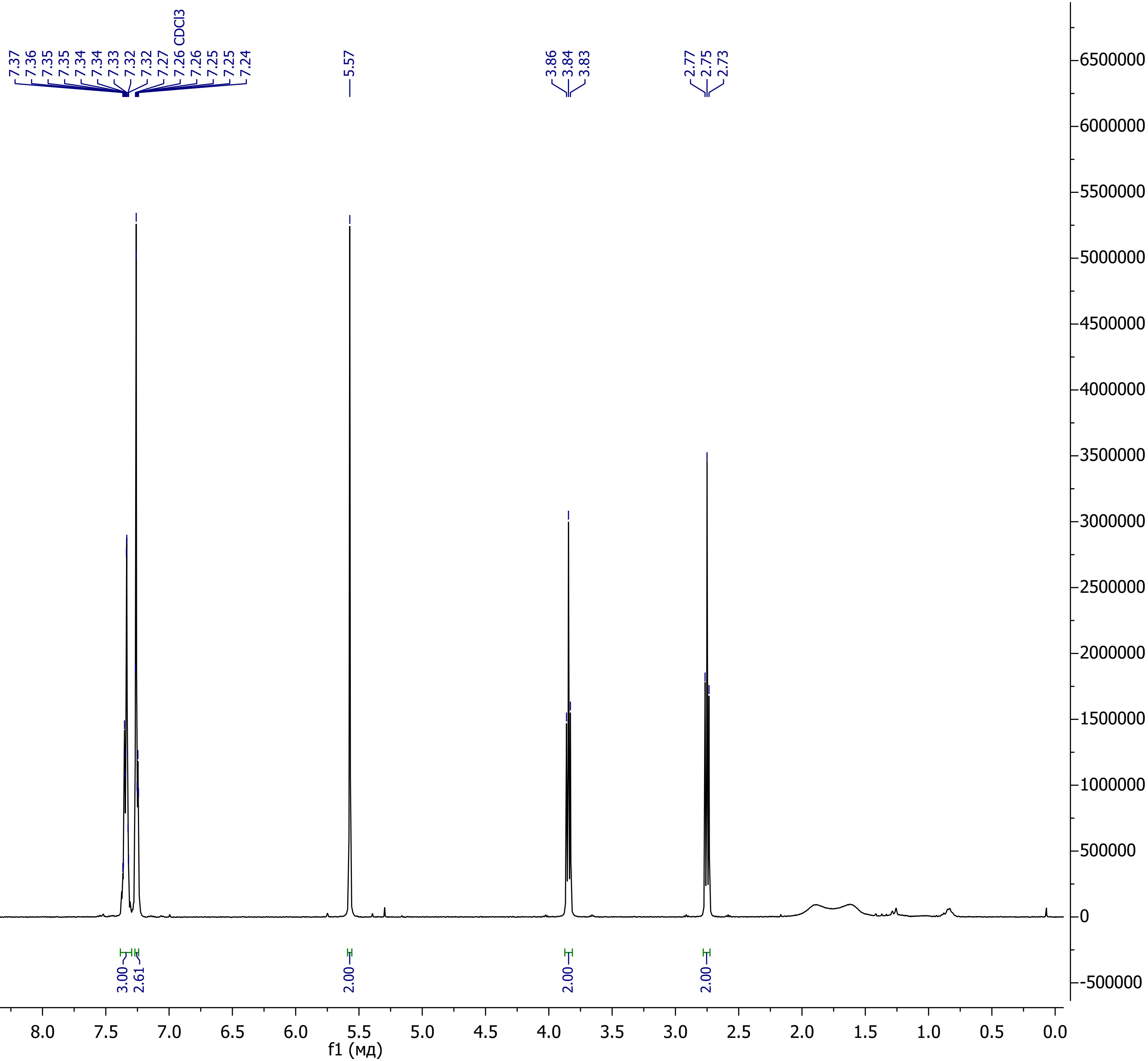
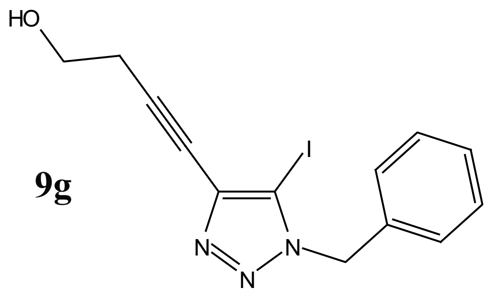
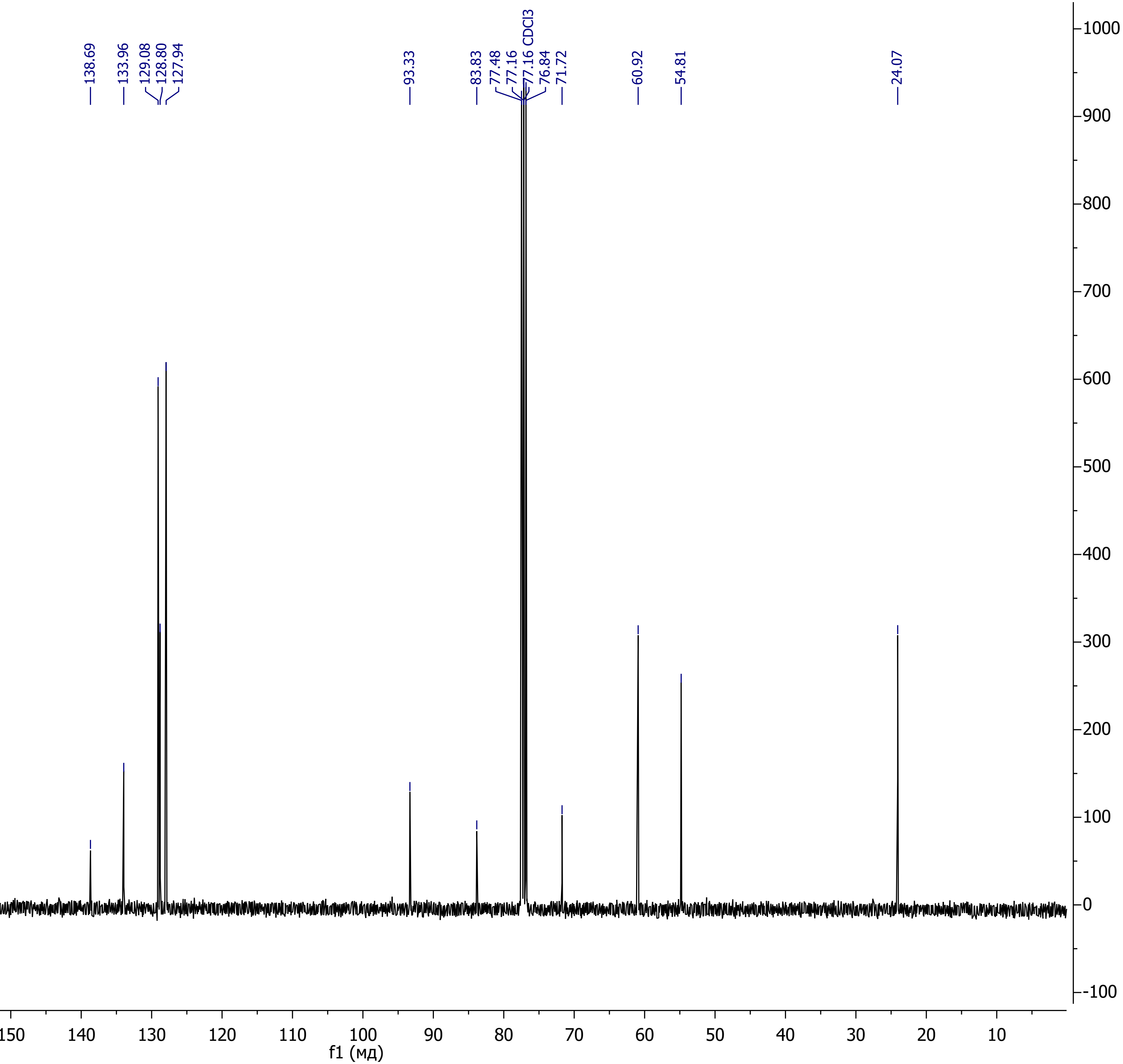


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)

9g





^{13}C DEPT NMR (CDCl$_3$, 100.6 MHz)

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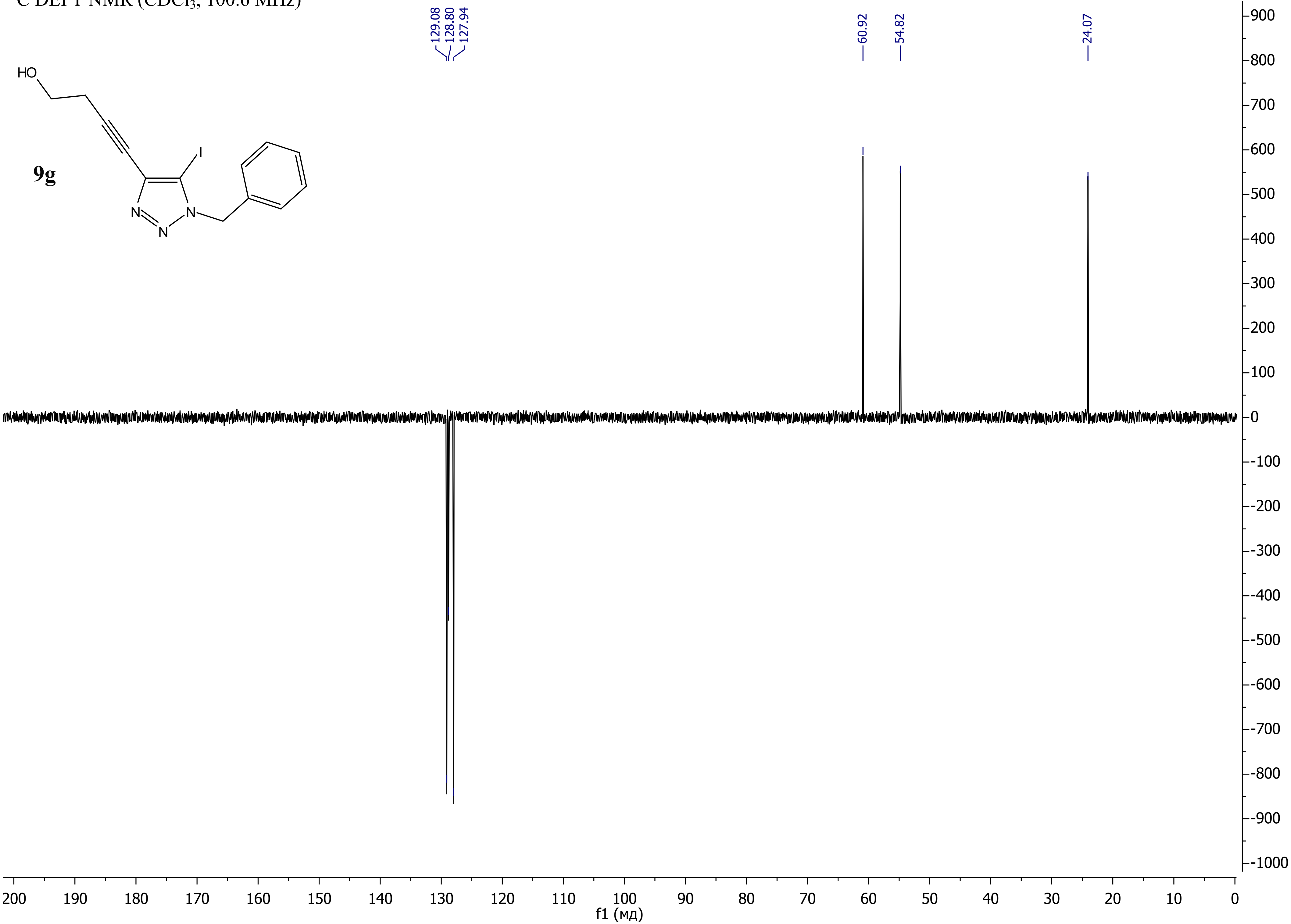
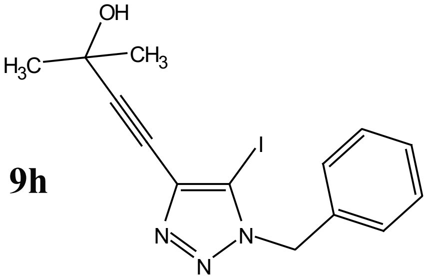
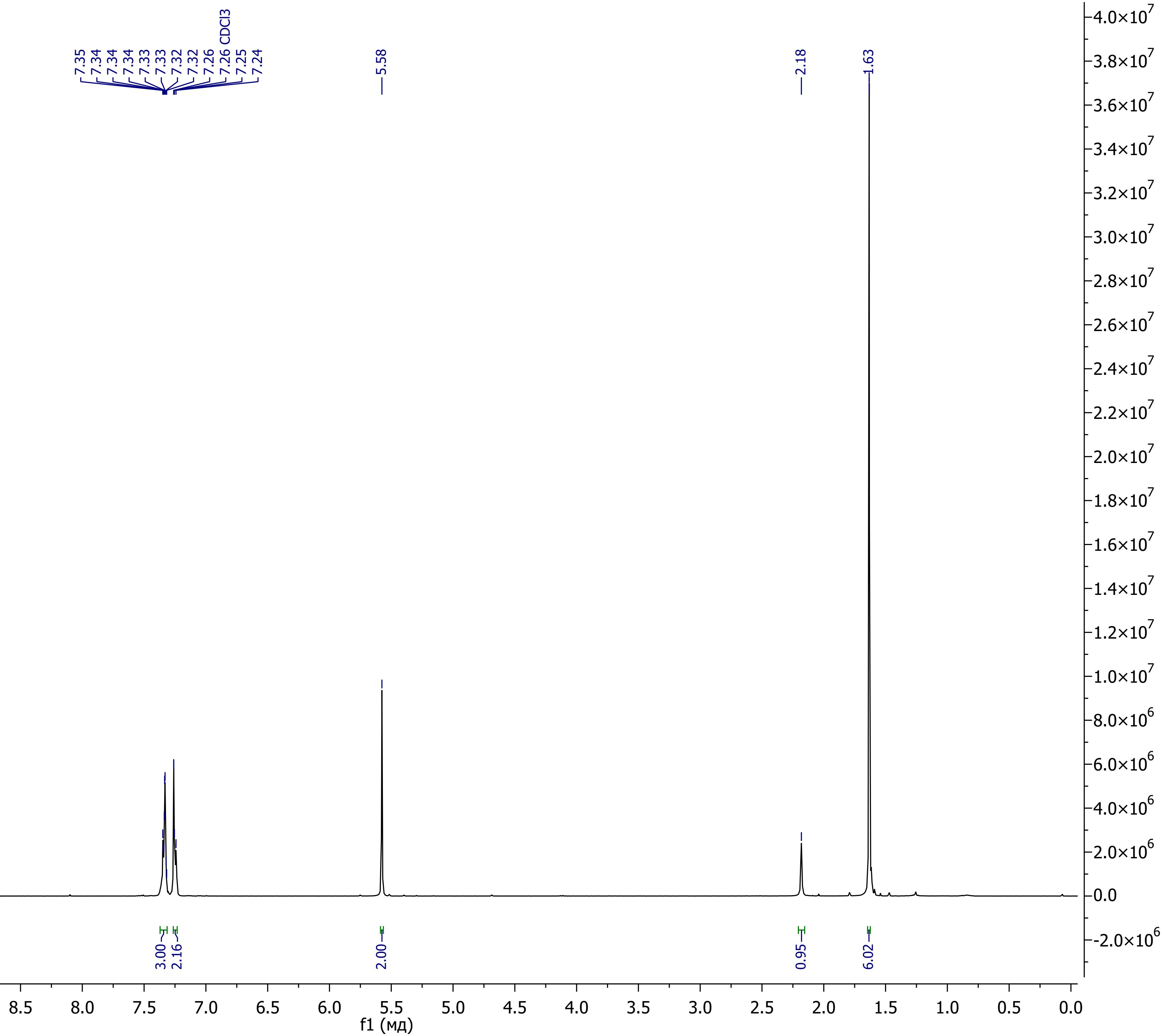


^{1}H NMR ($CDCl_3$, 400.13 MHz)

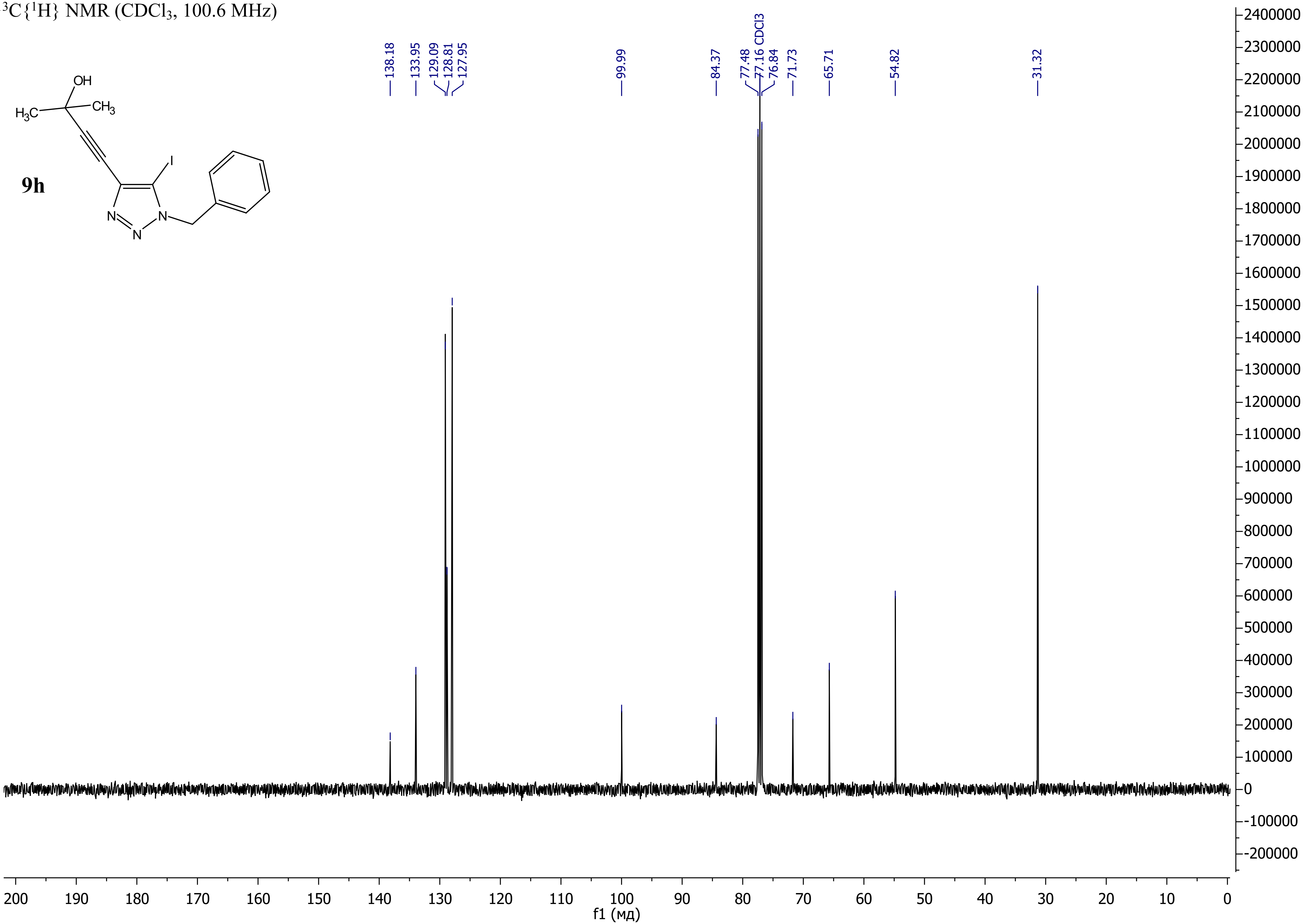
9h





$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)

9h



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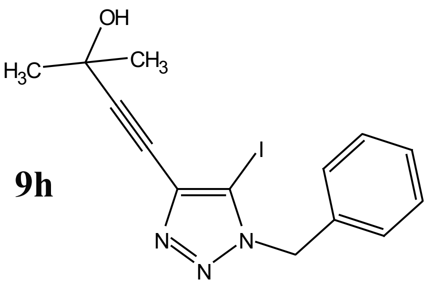

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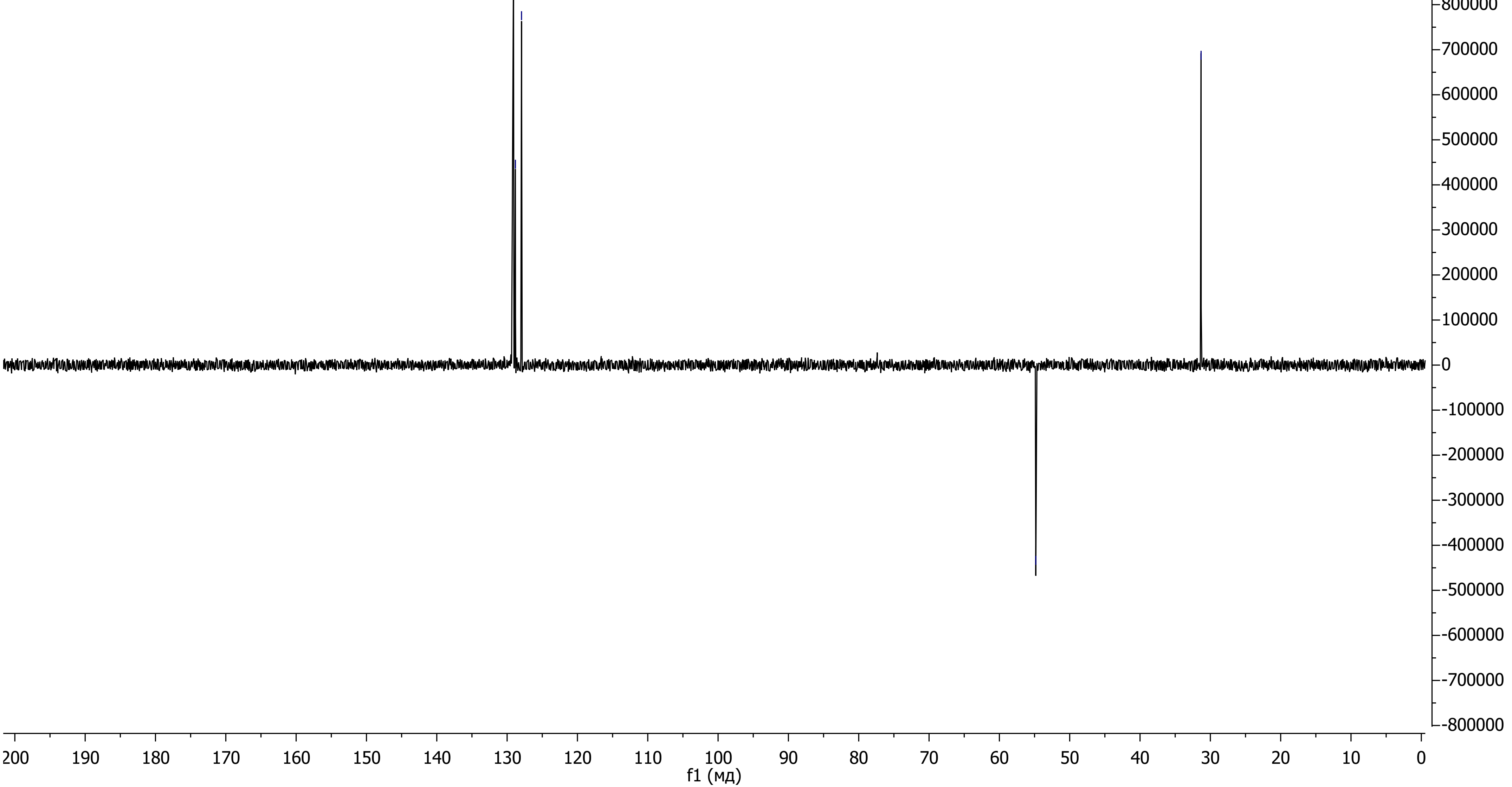

^1H NMR ($CDCl_3$, 400.13 MHz)

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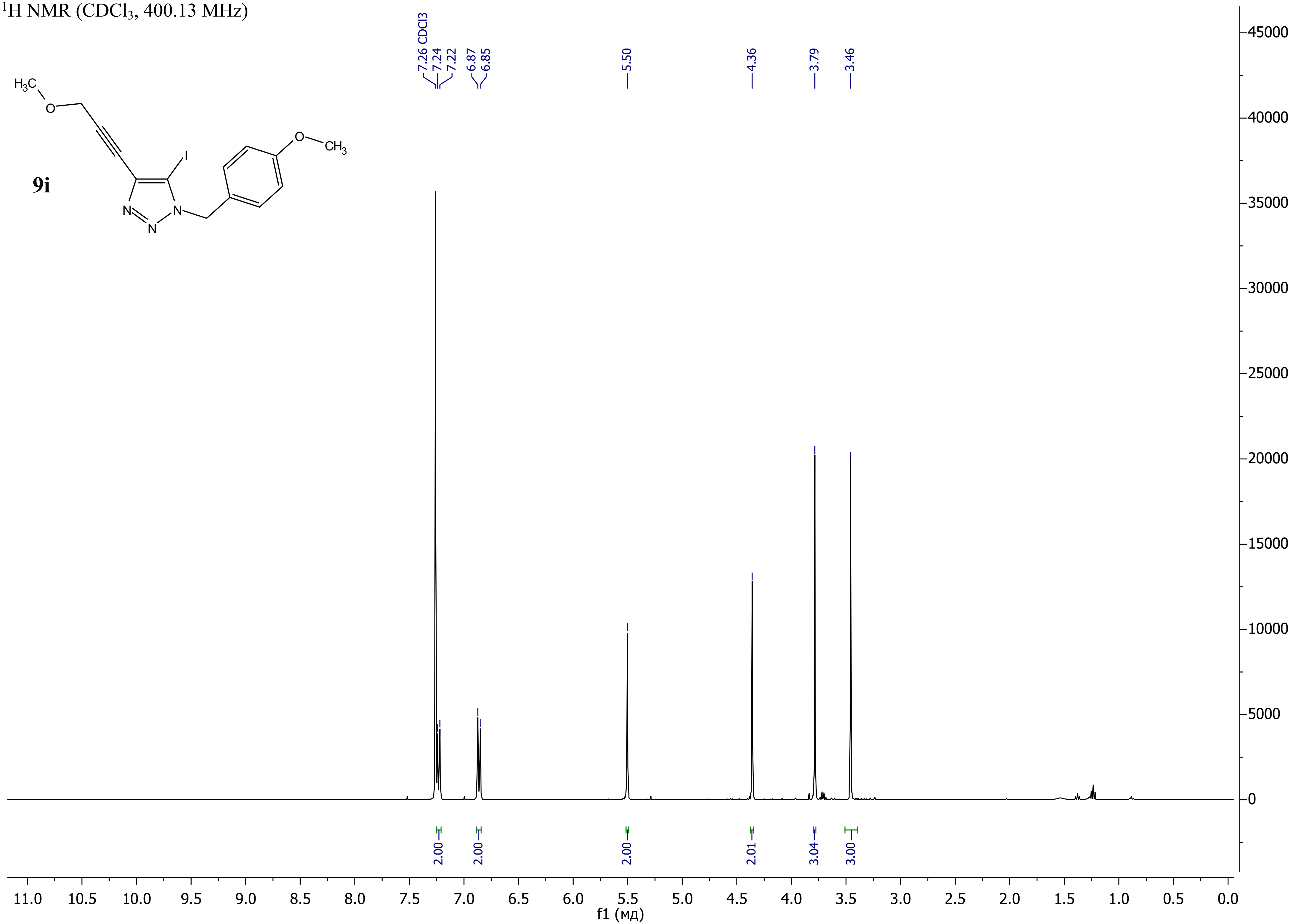

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)

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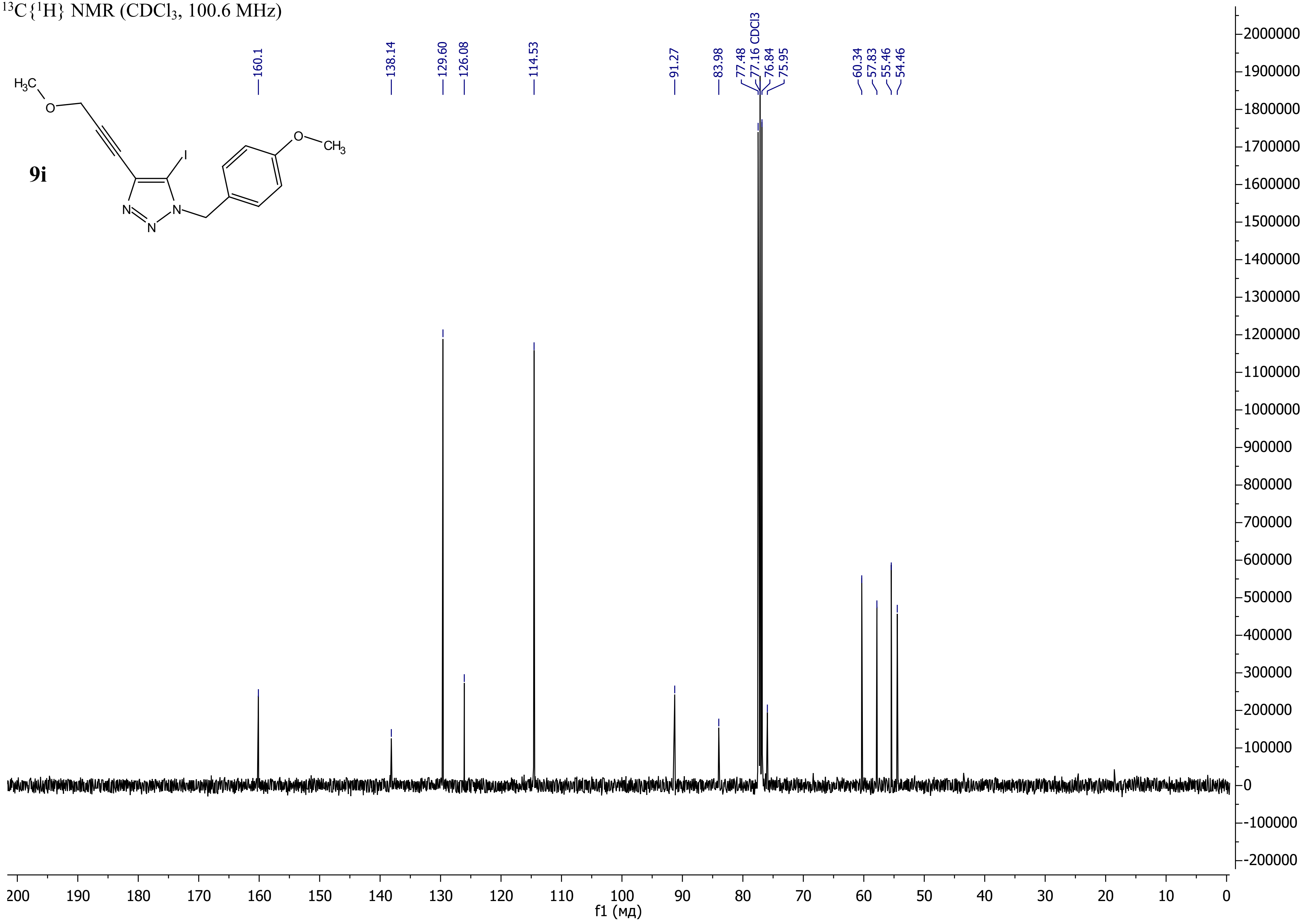
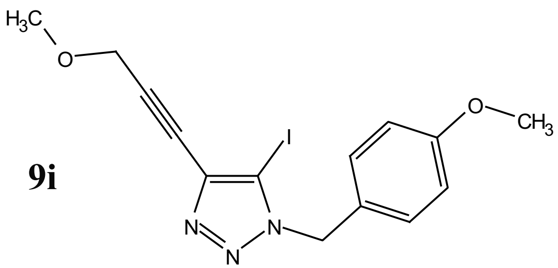


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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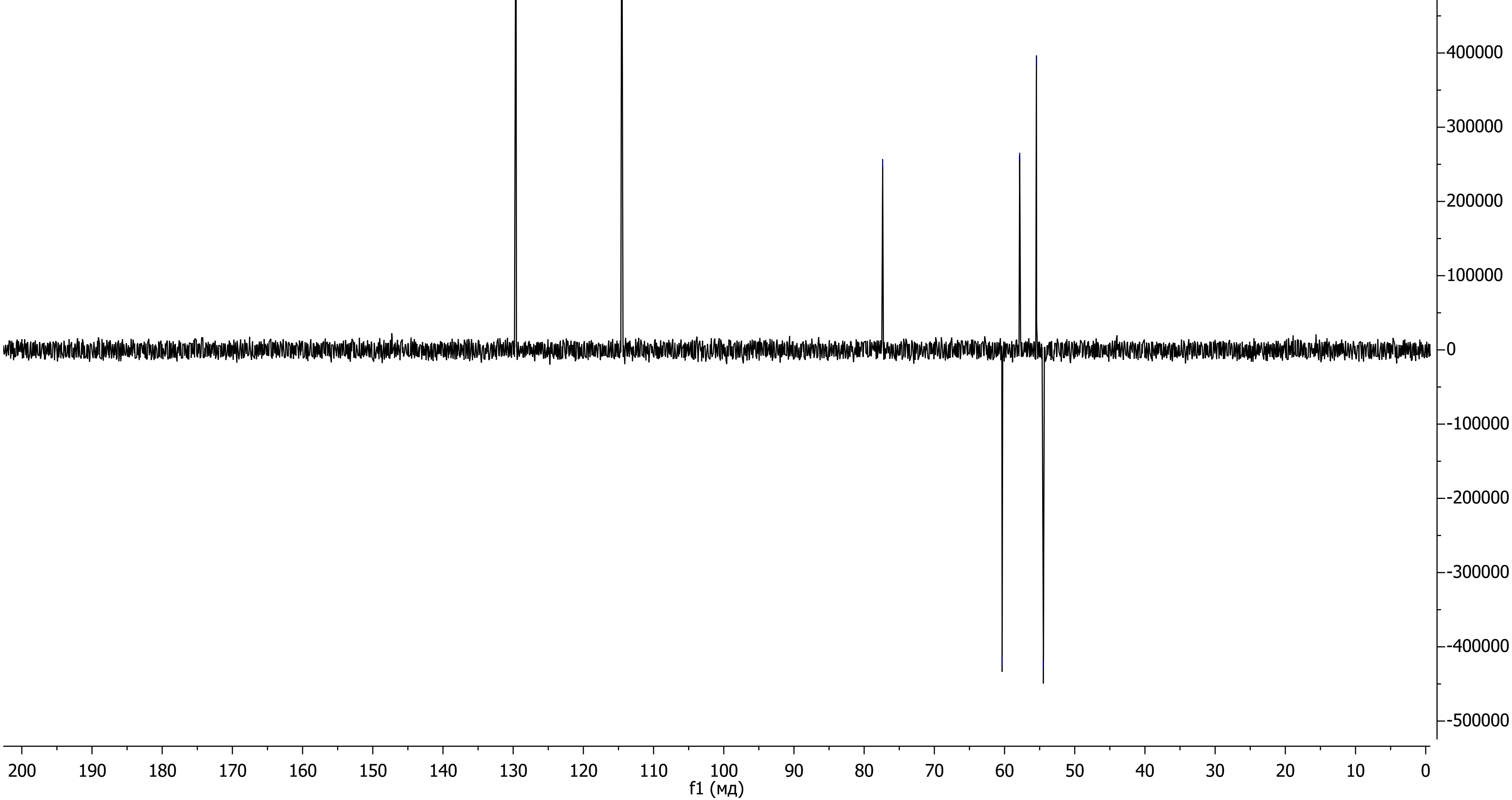
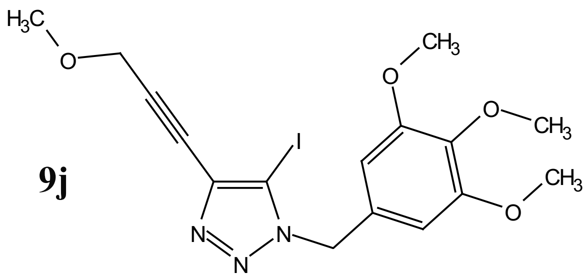


^{1}H NMR ($CDCl_3$, 400.13 MHz)



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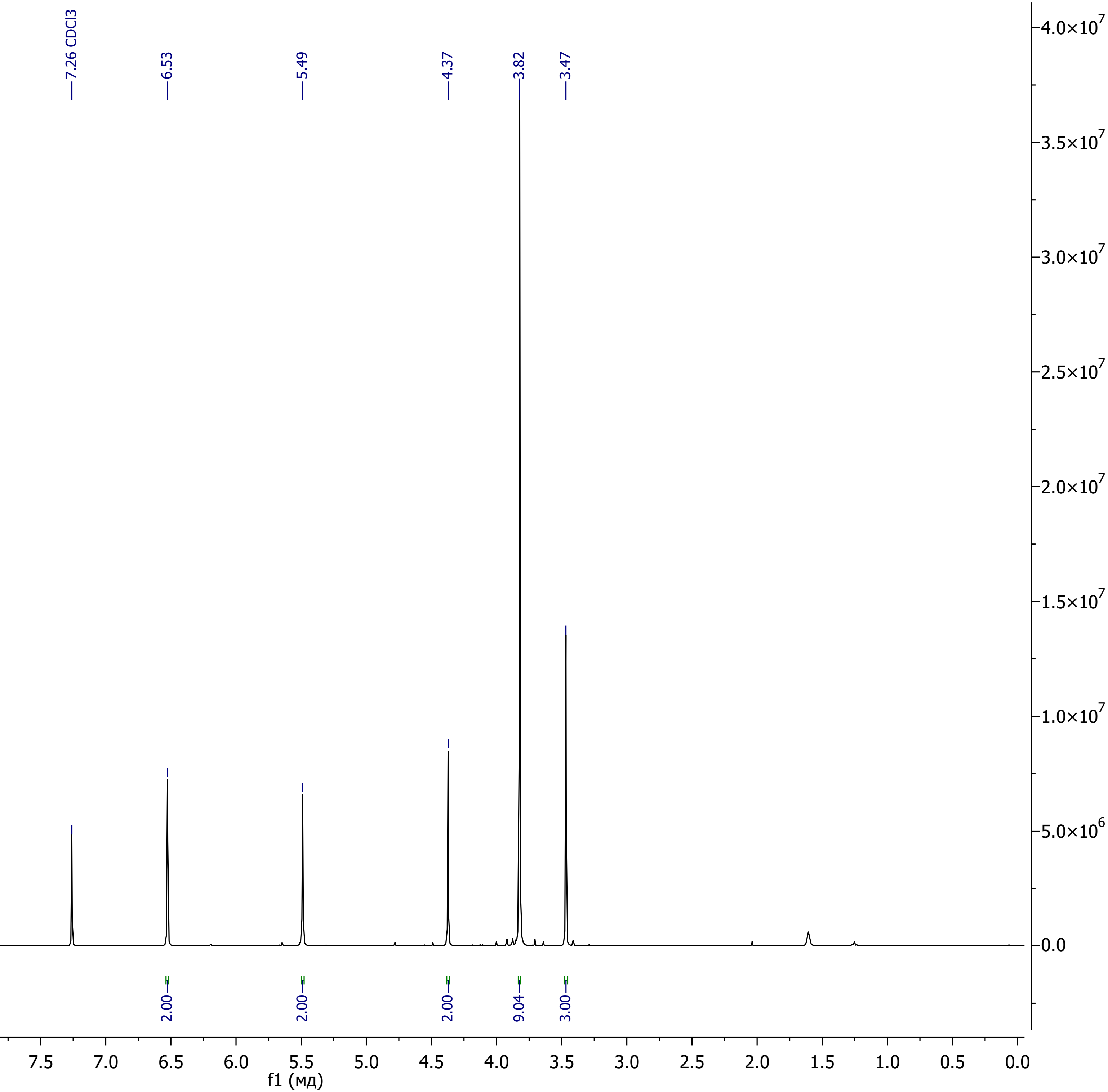

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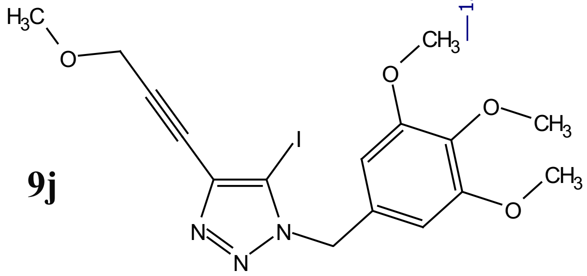

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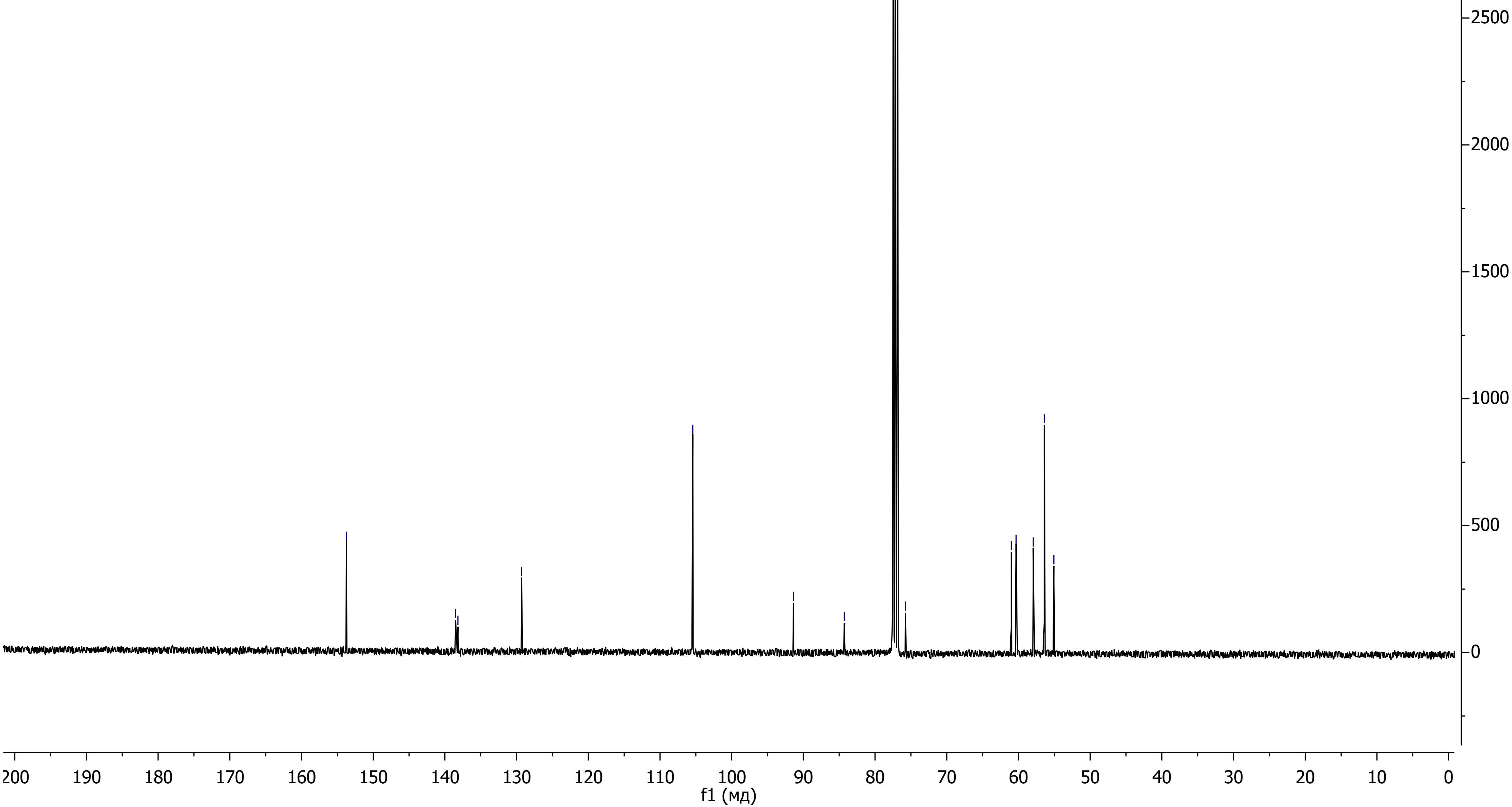

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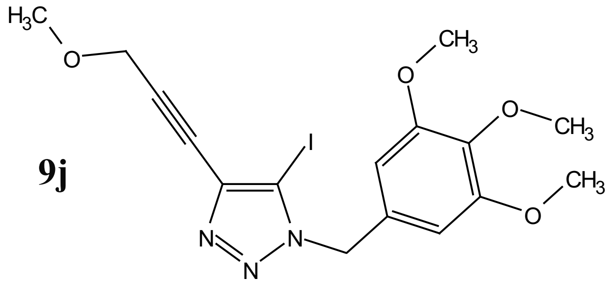

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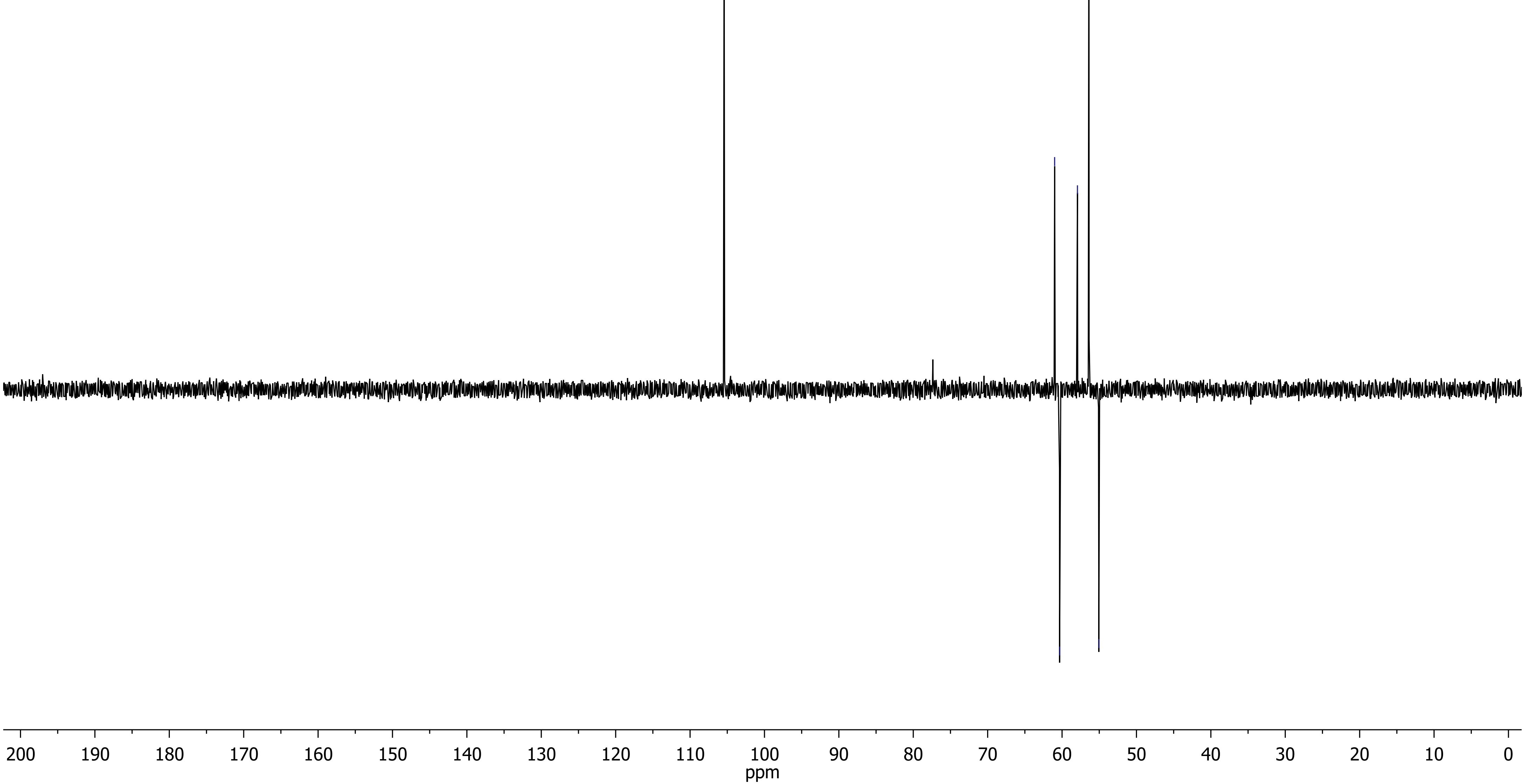
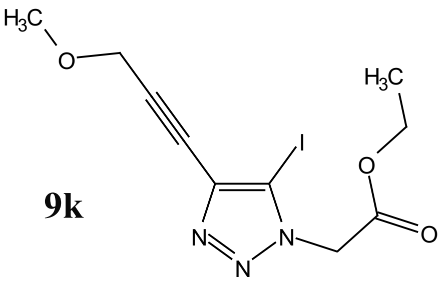


^{1}H NMR ($CDCl_3$, 400.13 MHz)



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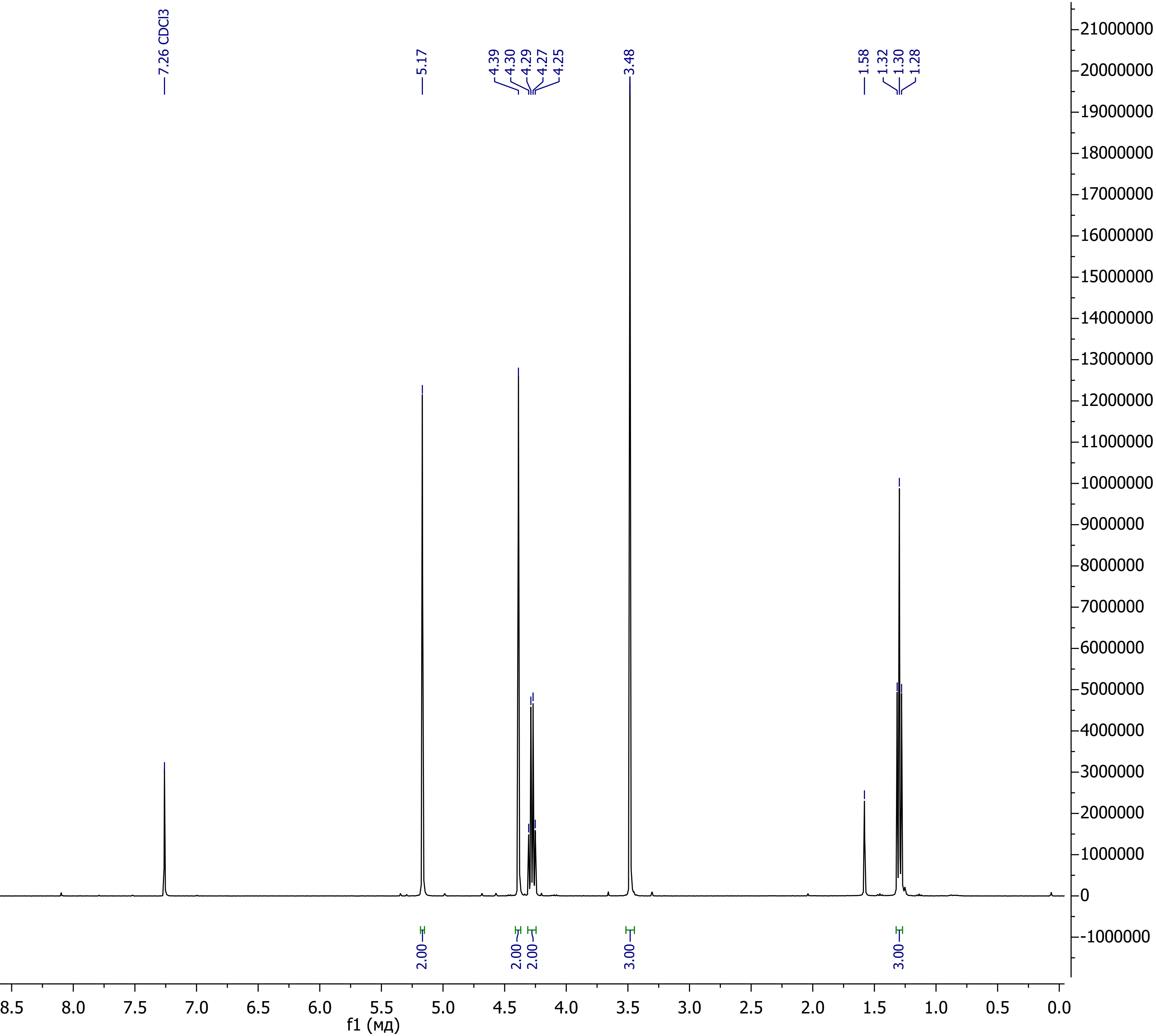
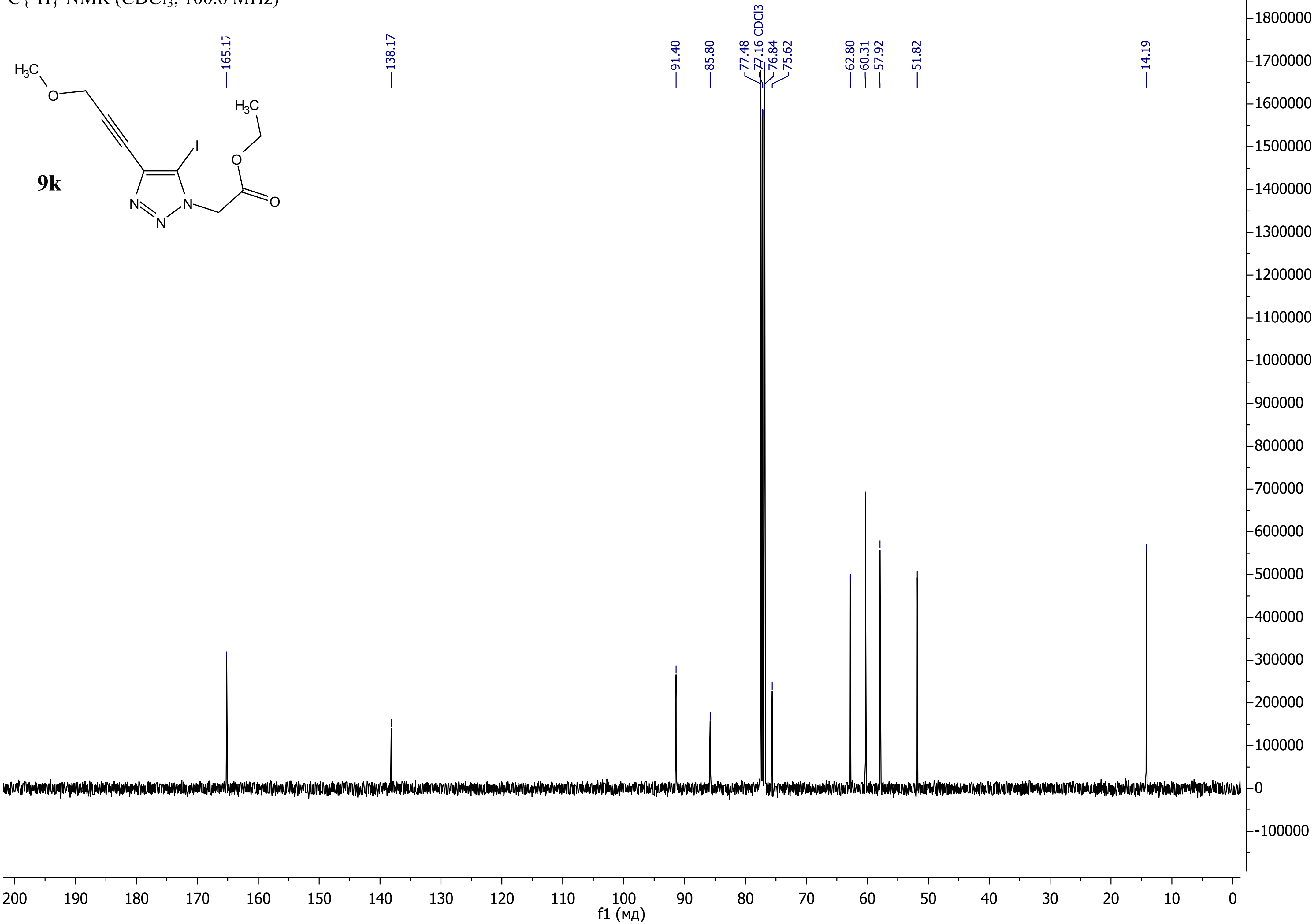


$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz)

9k



^{13}C DEPT NMR (CDCl$_3$, 100.6 MHz)

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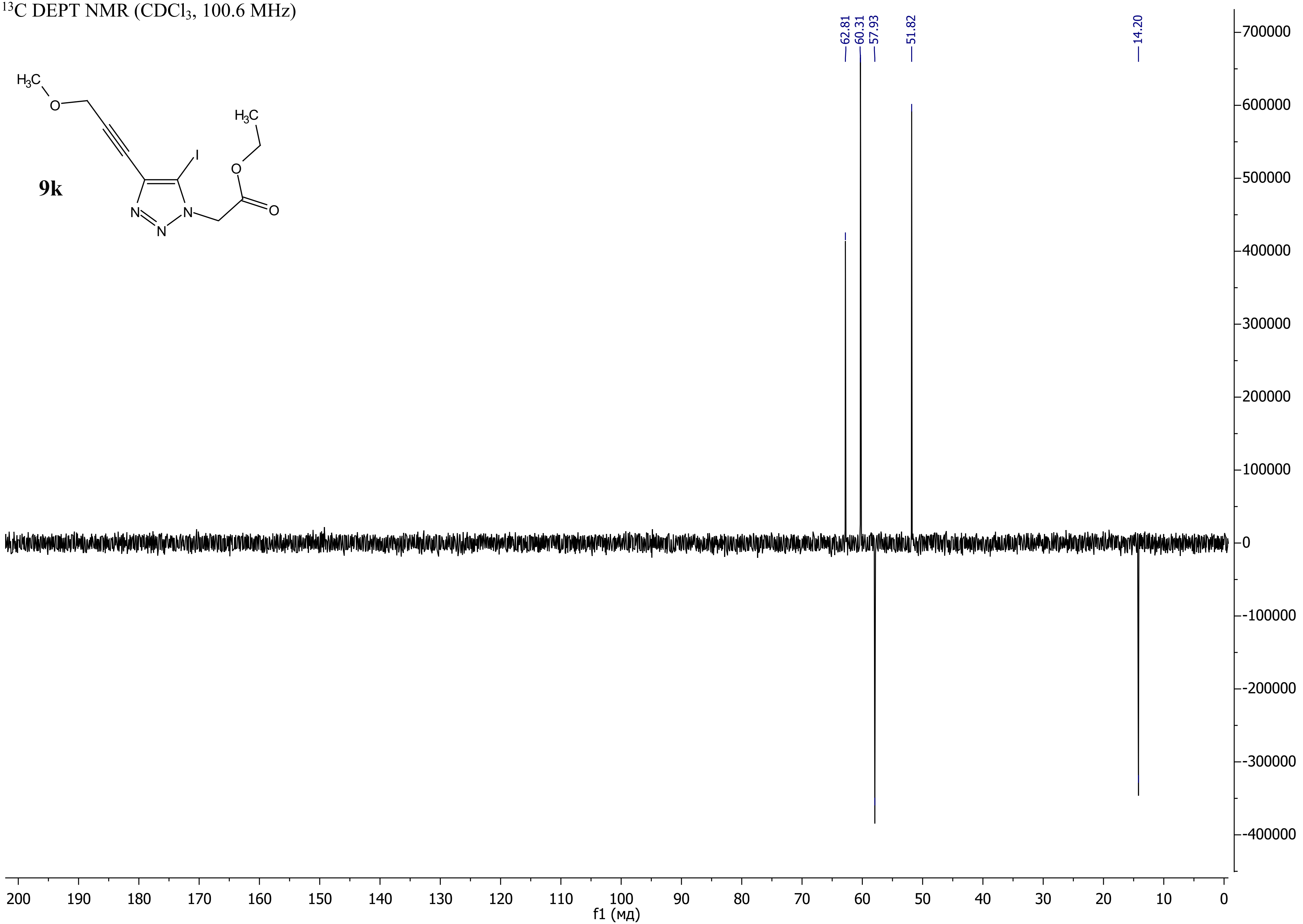
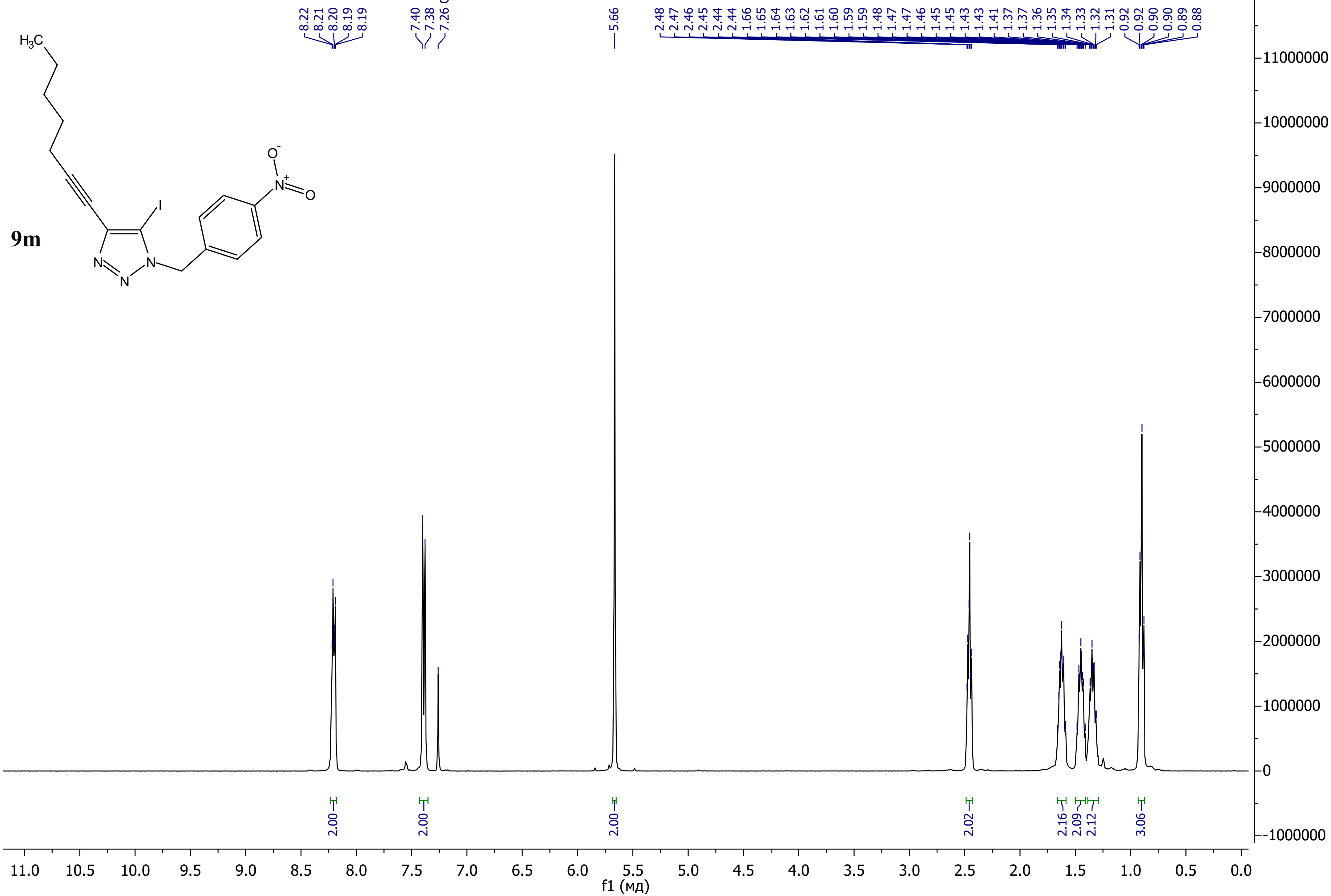
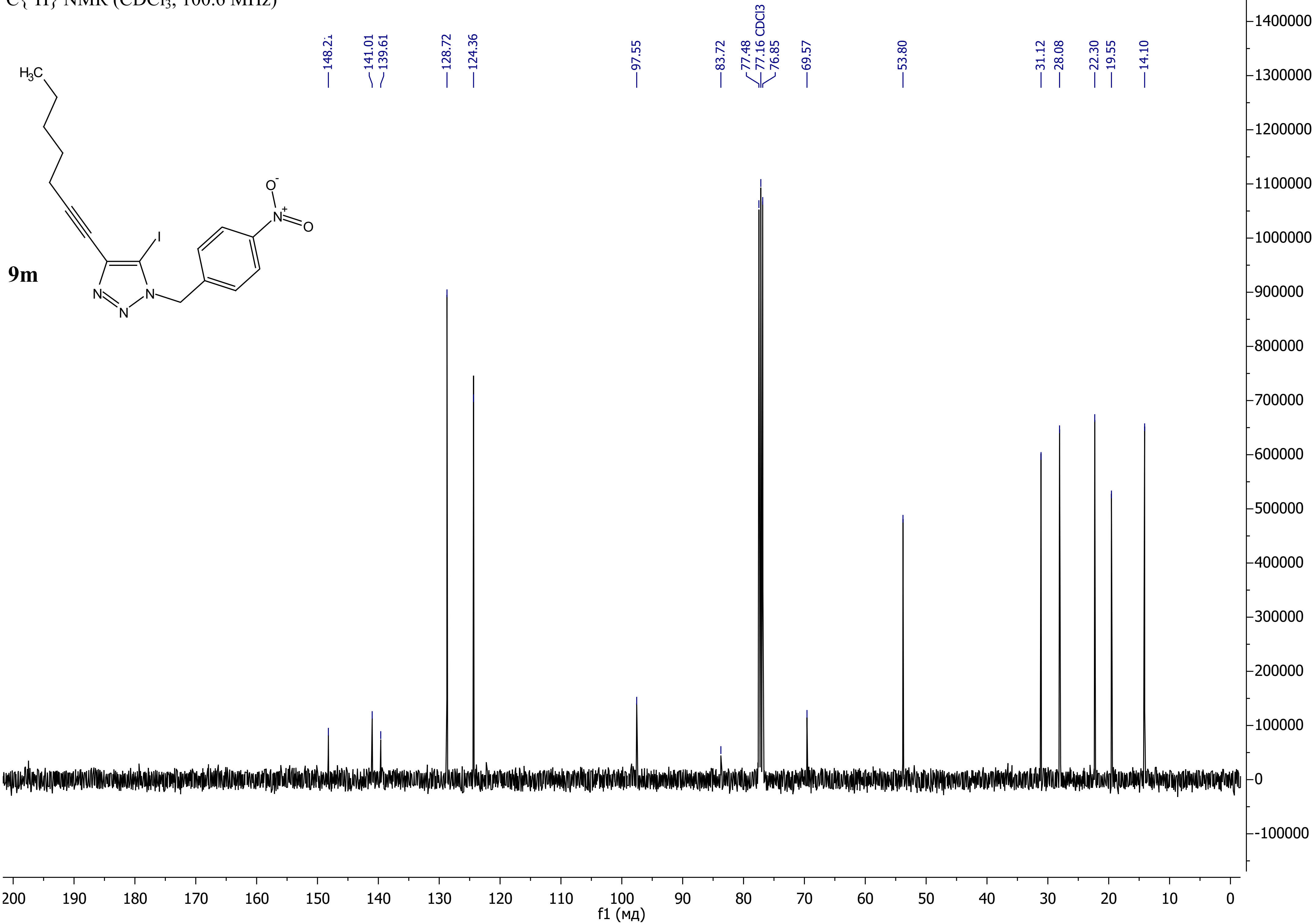


^{1}H NMR ($CDCl_3$, 400.13 MHz)



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)

9m



^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)

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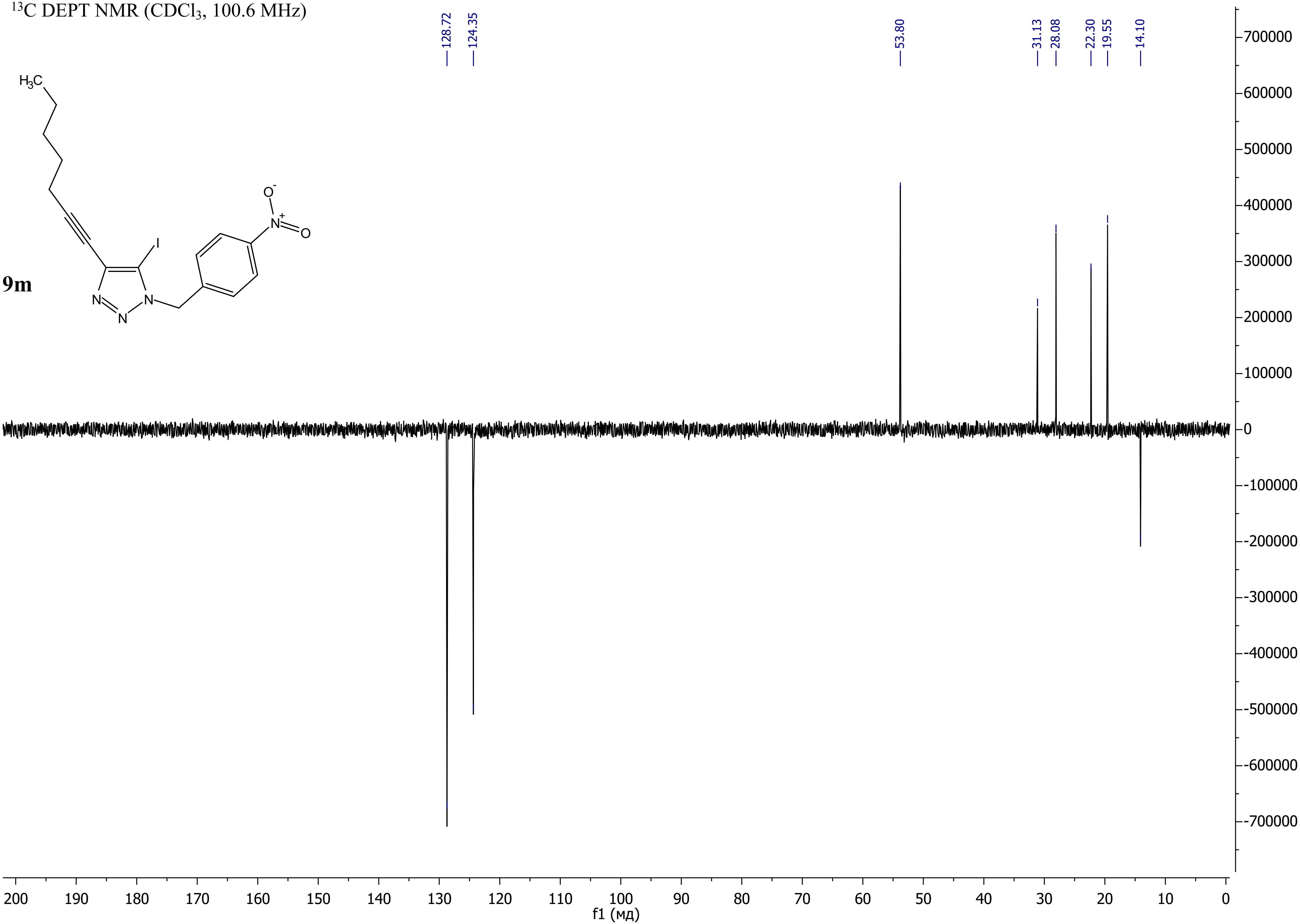
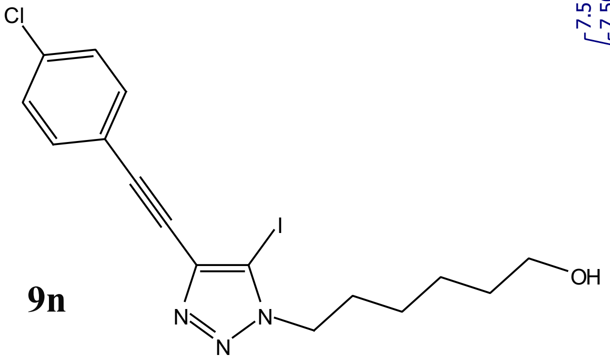


^{1}H NMR ($CDCl_3$, 400.13 MHz)



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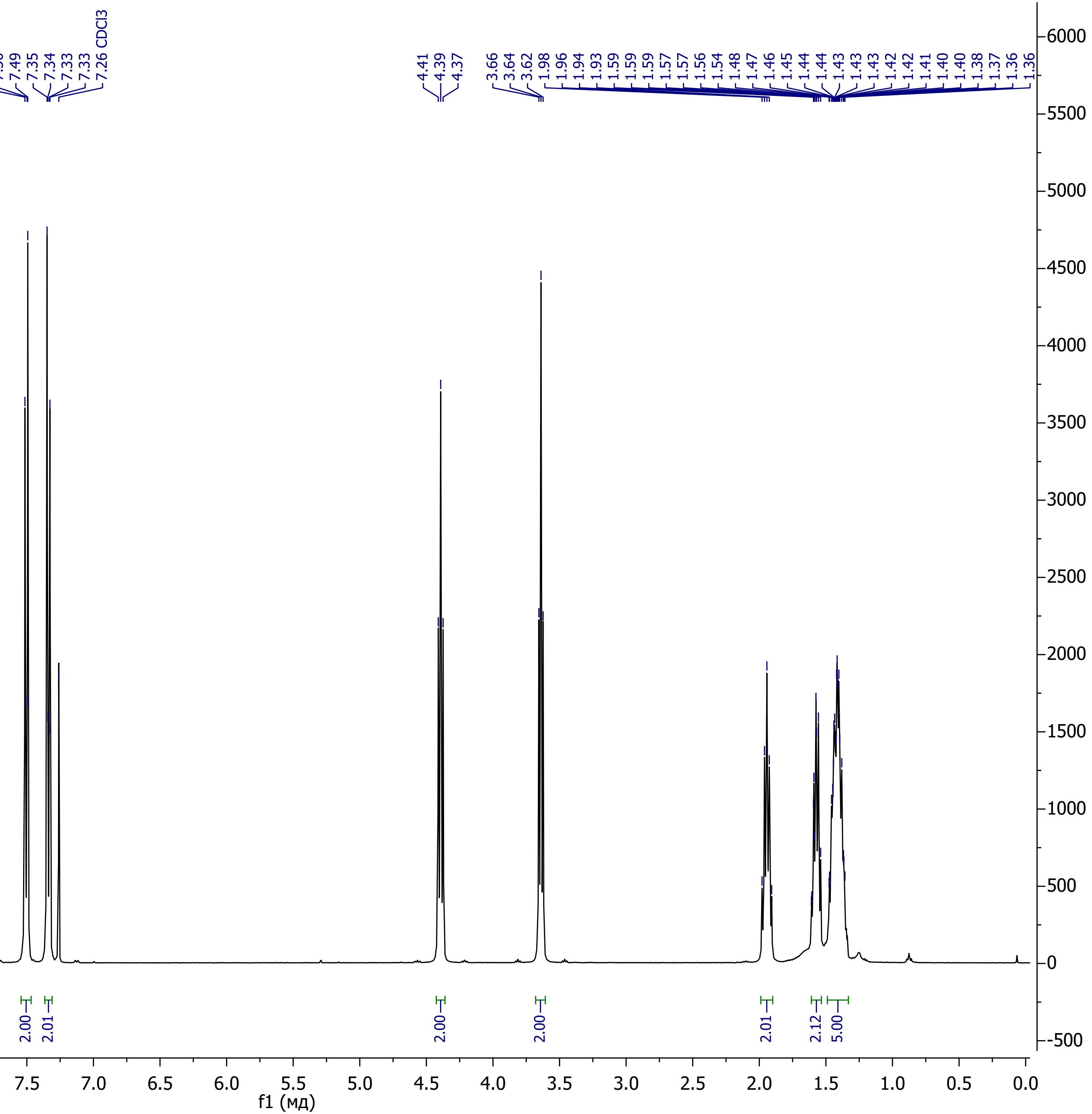

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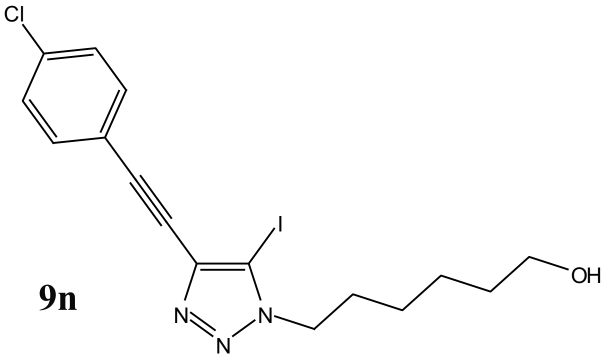

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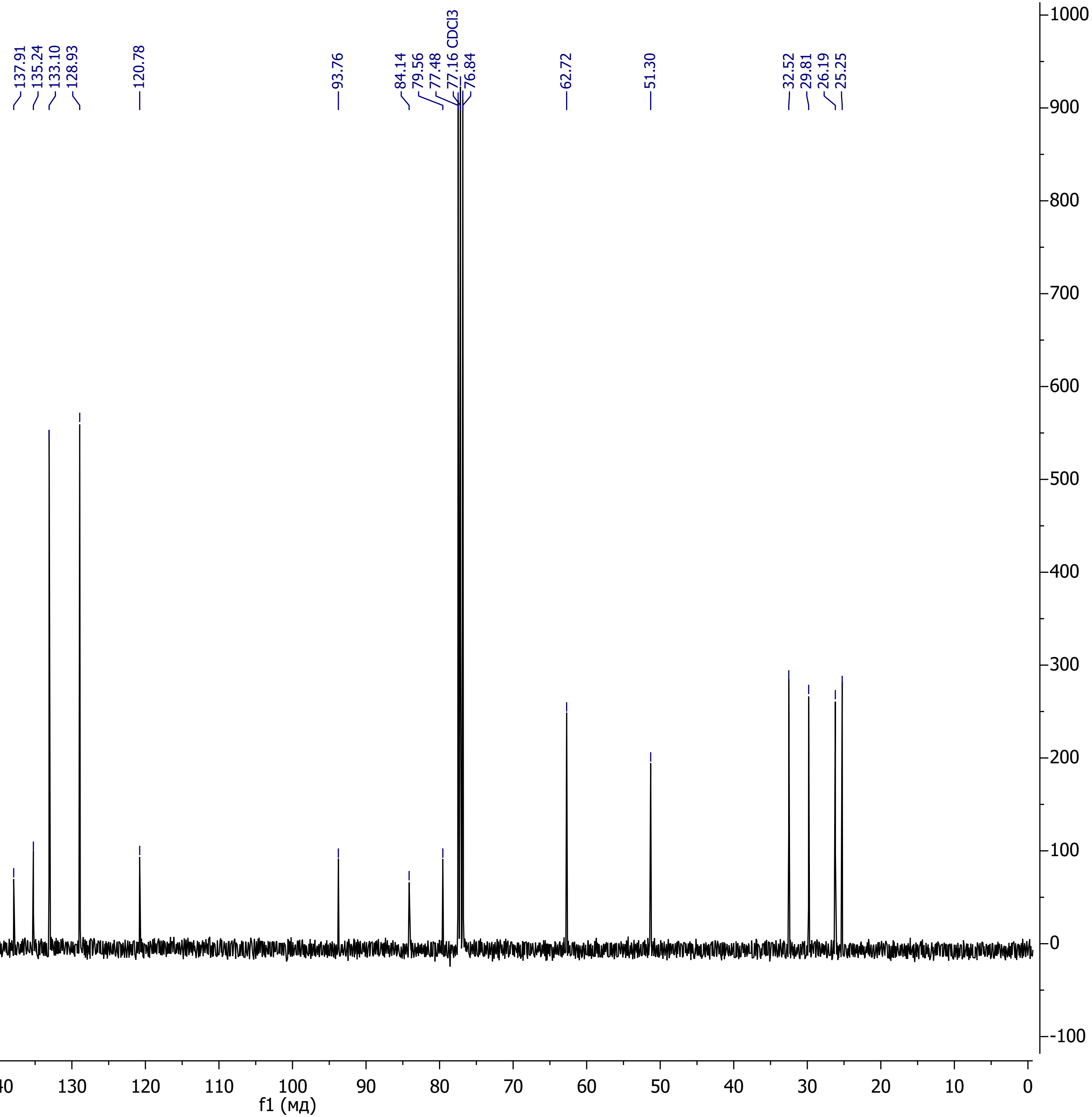
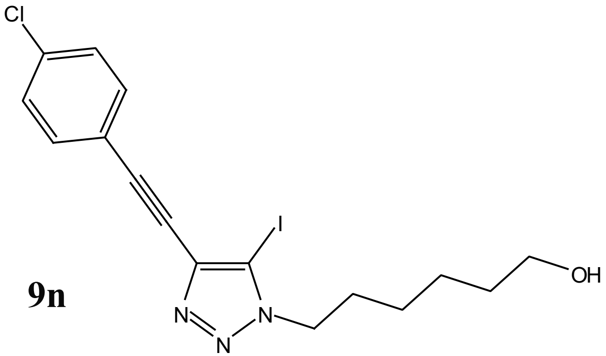


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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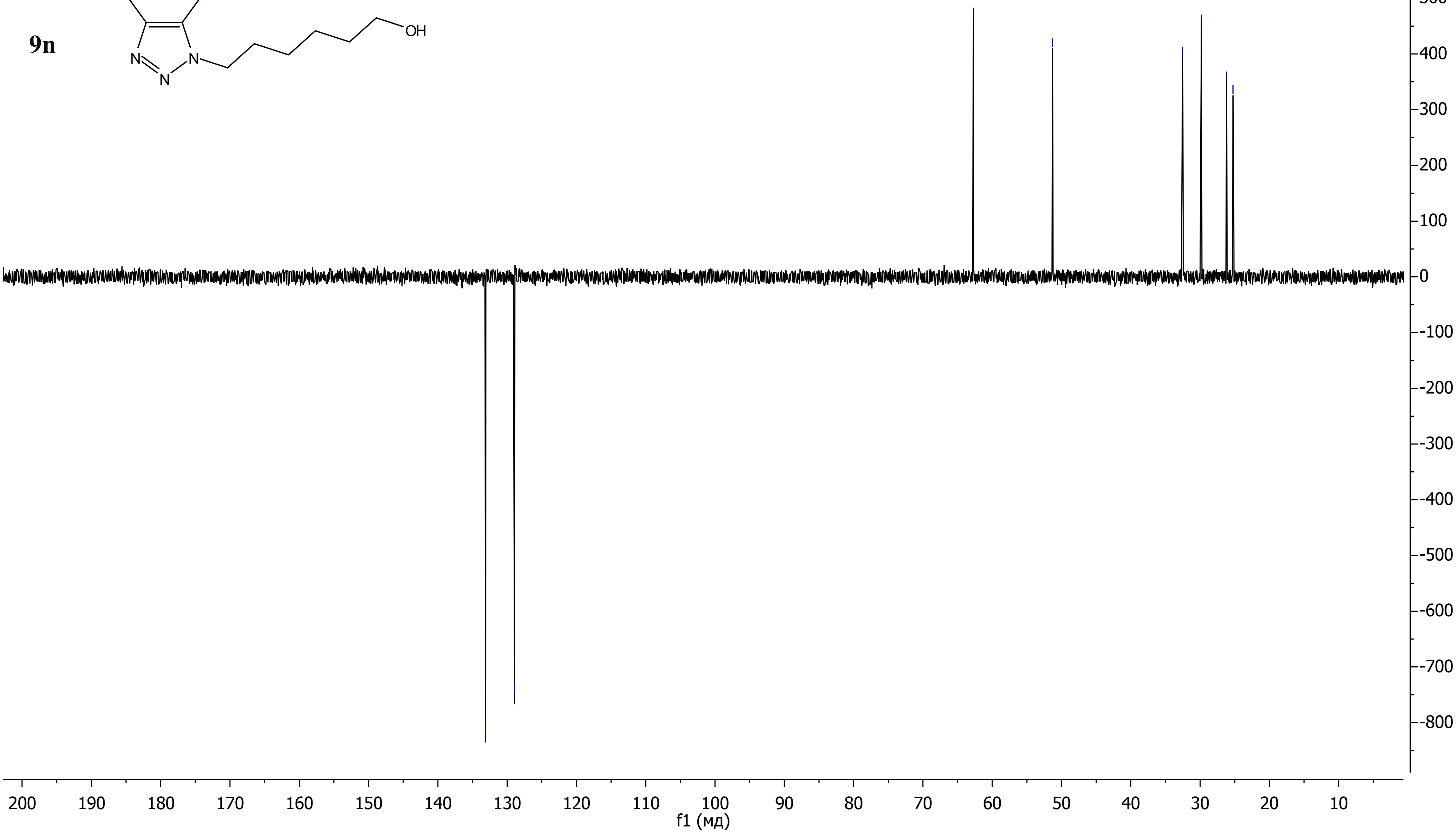
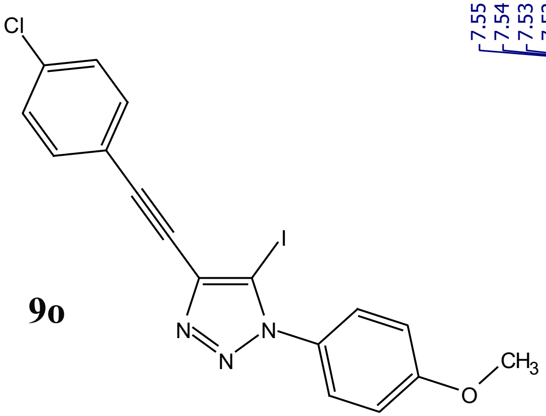


^{1}H NMR ($CDCl_3$, 400.13 MHz)



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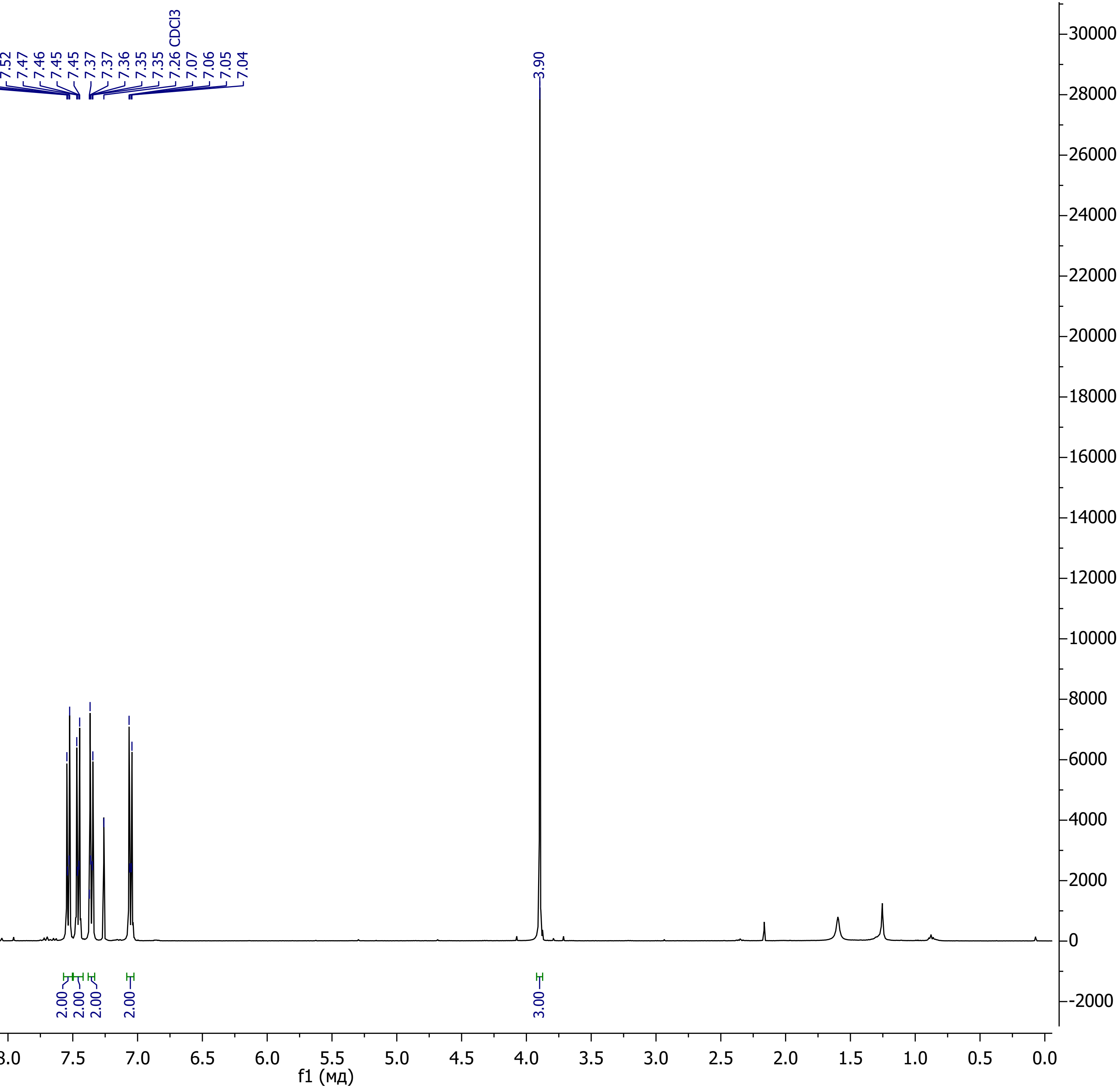
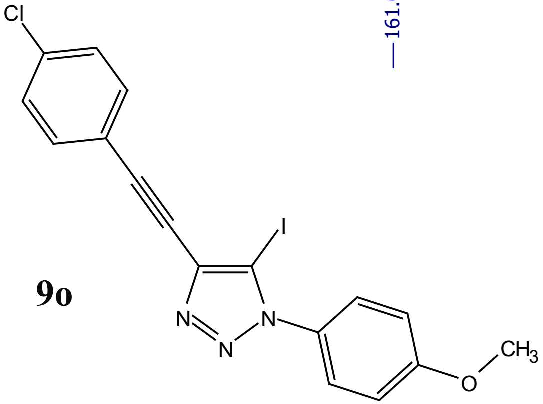


$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz)



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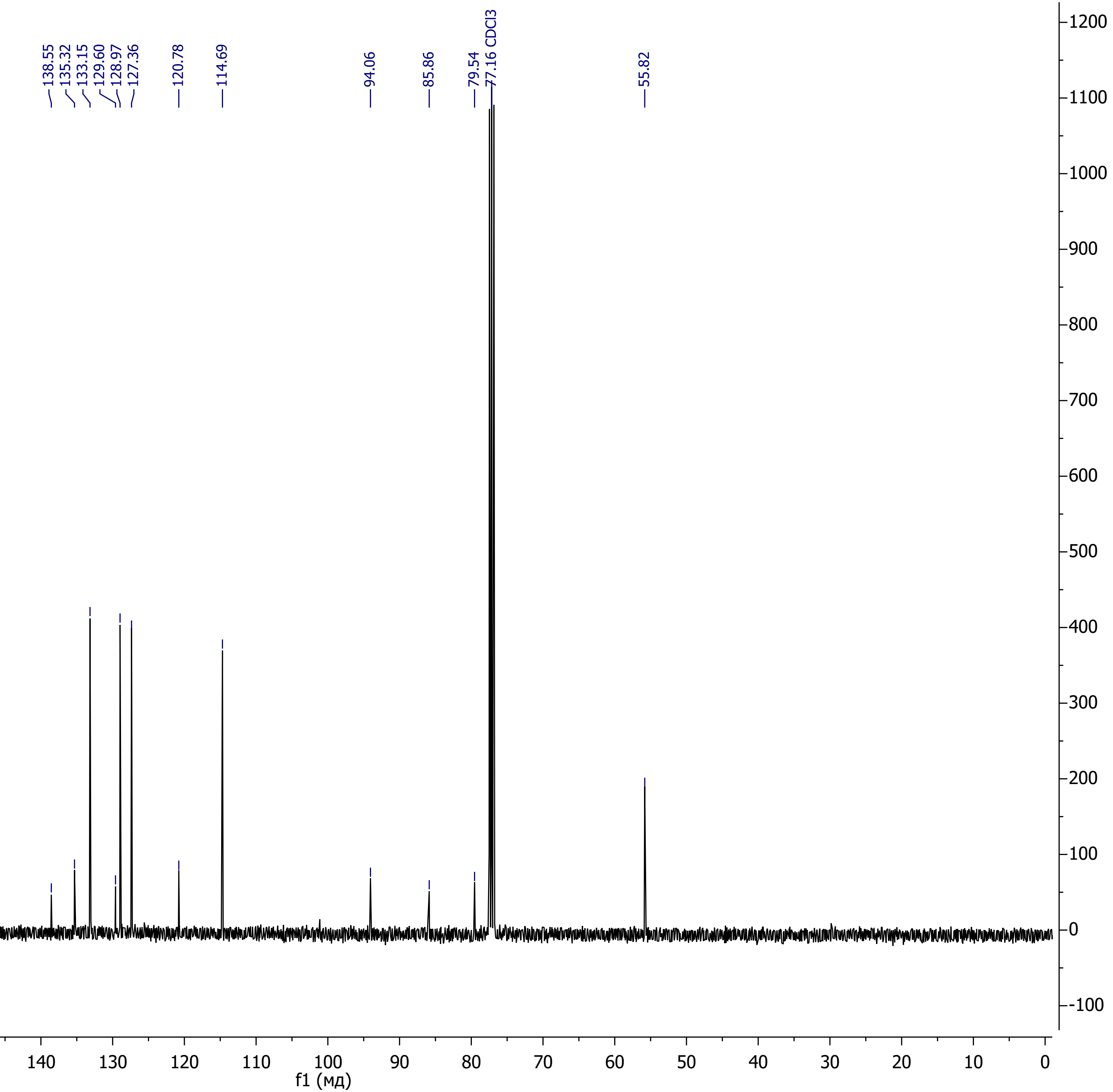
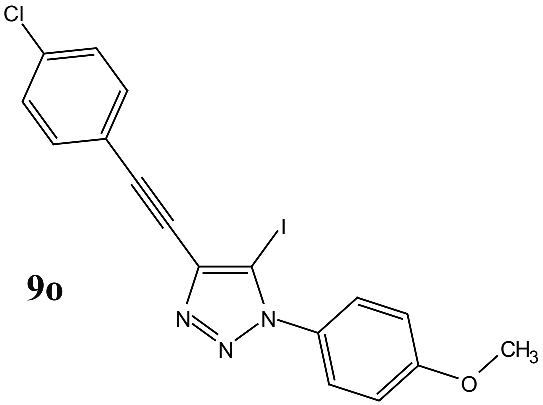


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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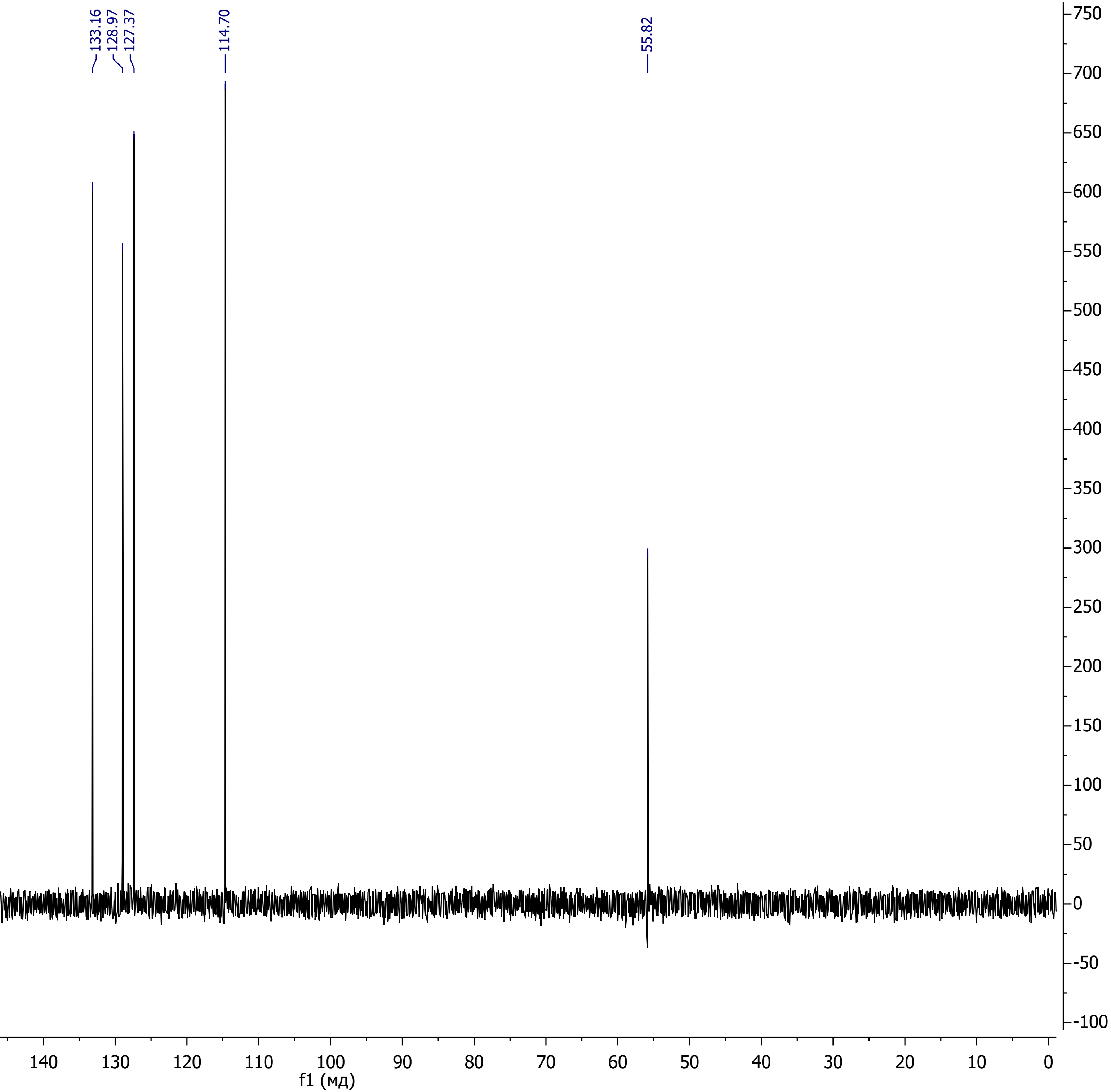
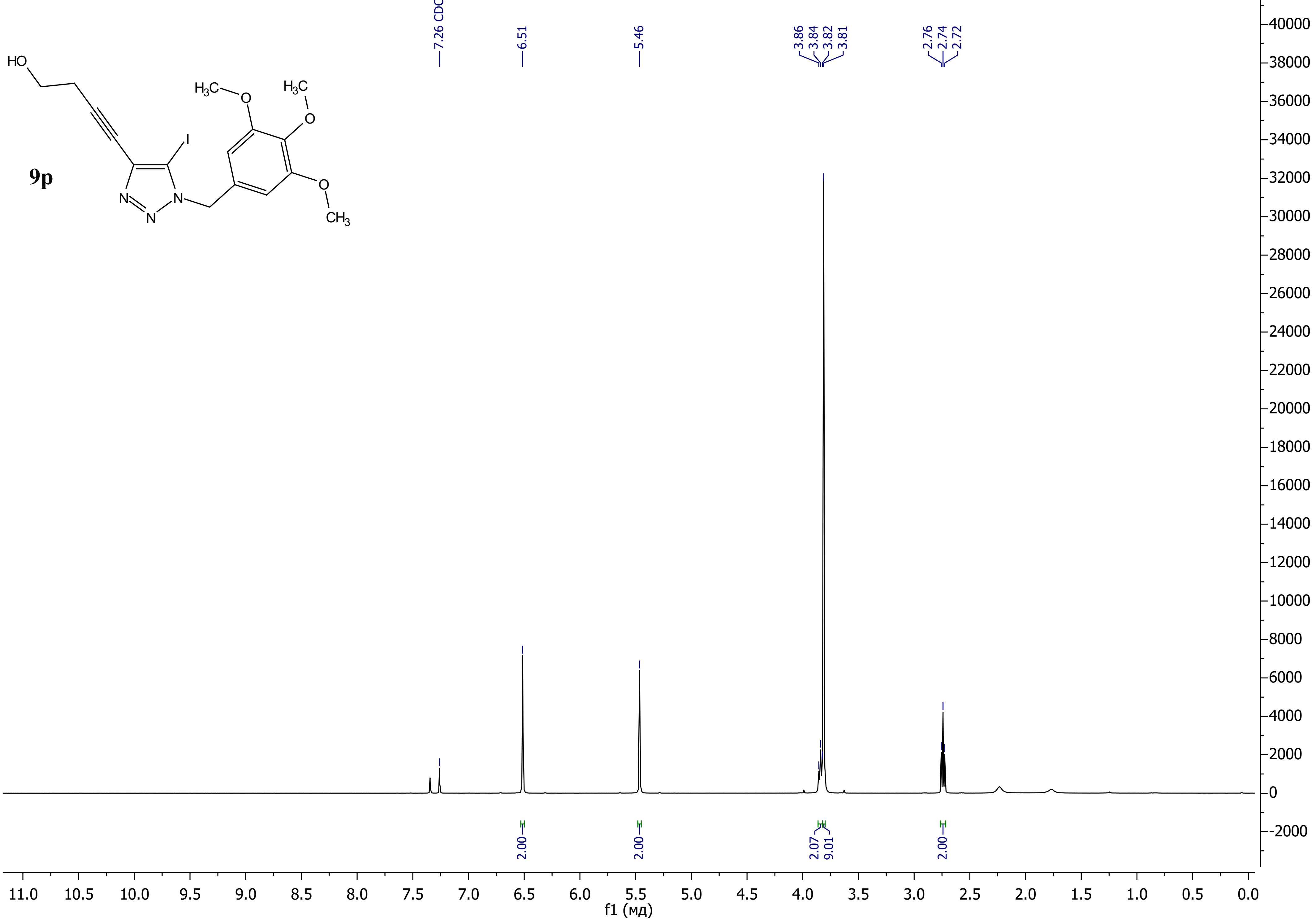
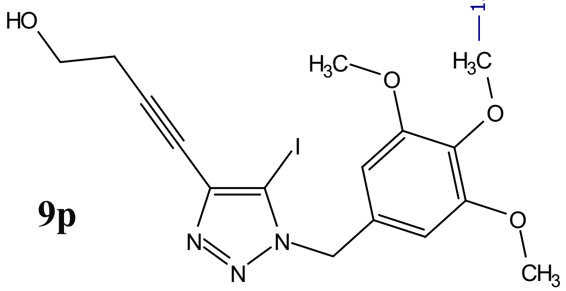


^{1}H NMR ($CDCl_3$, 400.13 MHz)



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



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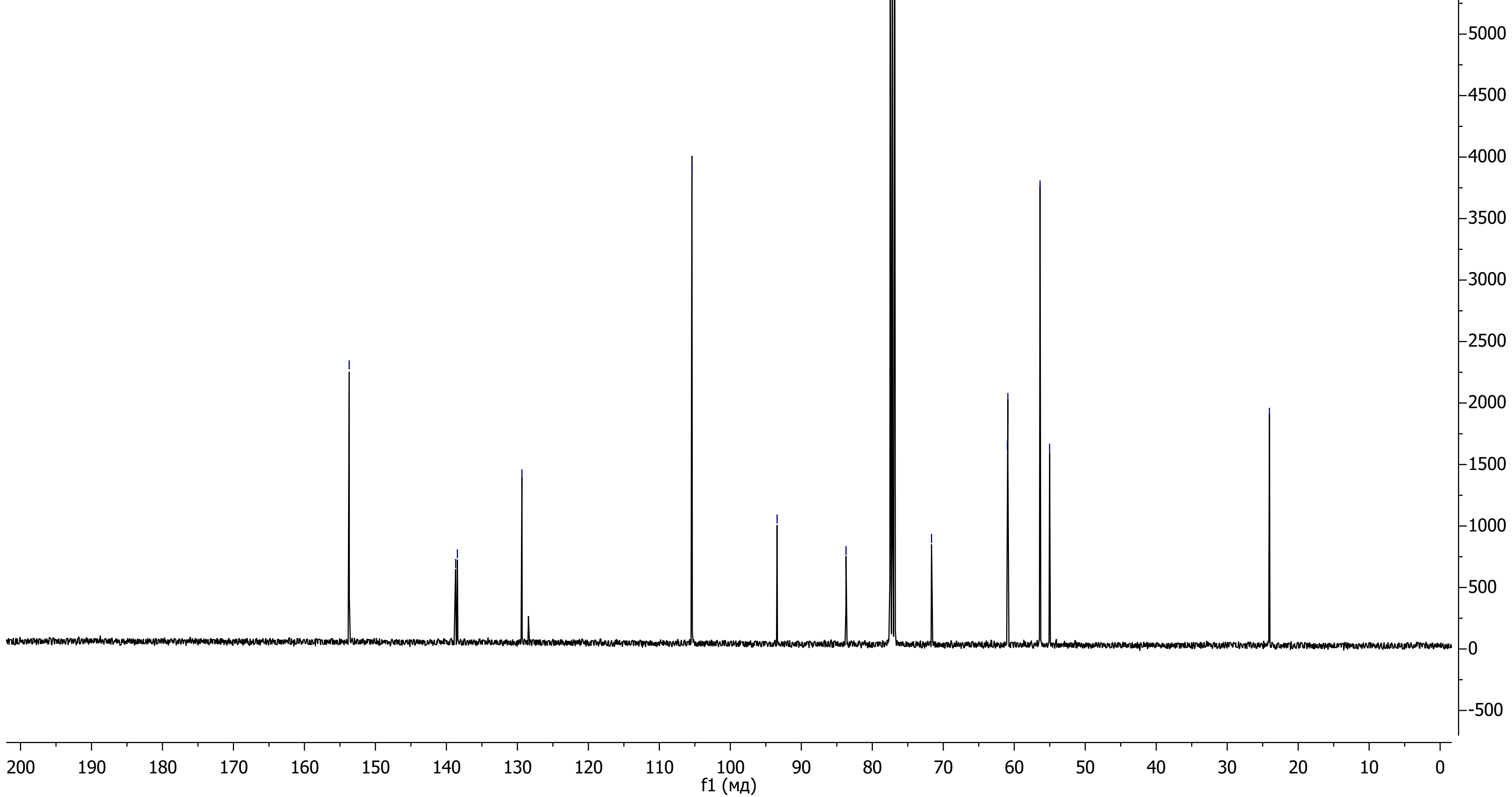
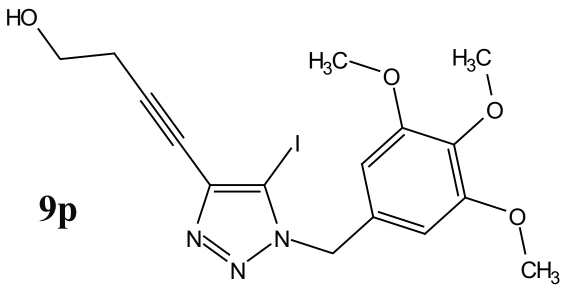


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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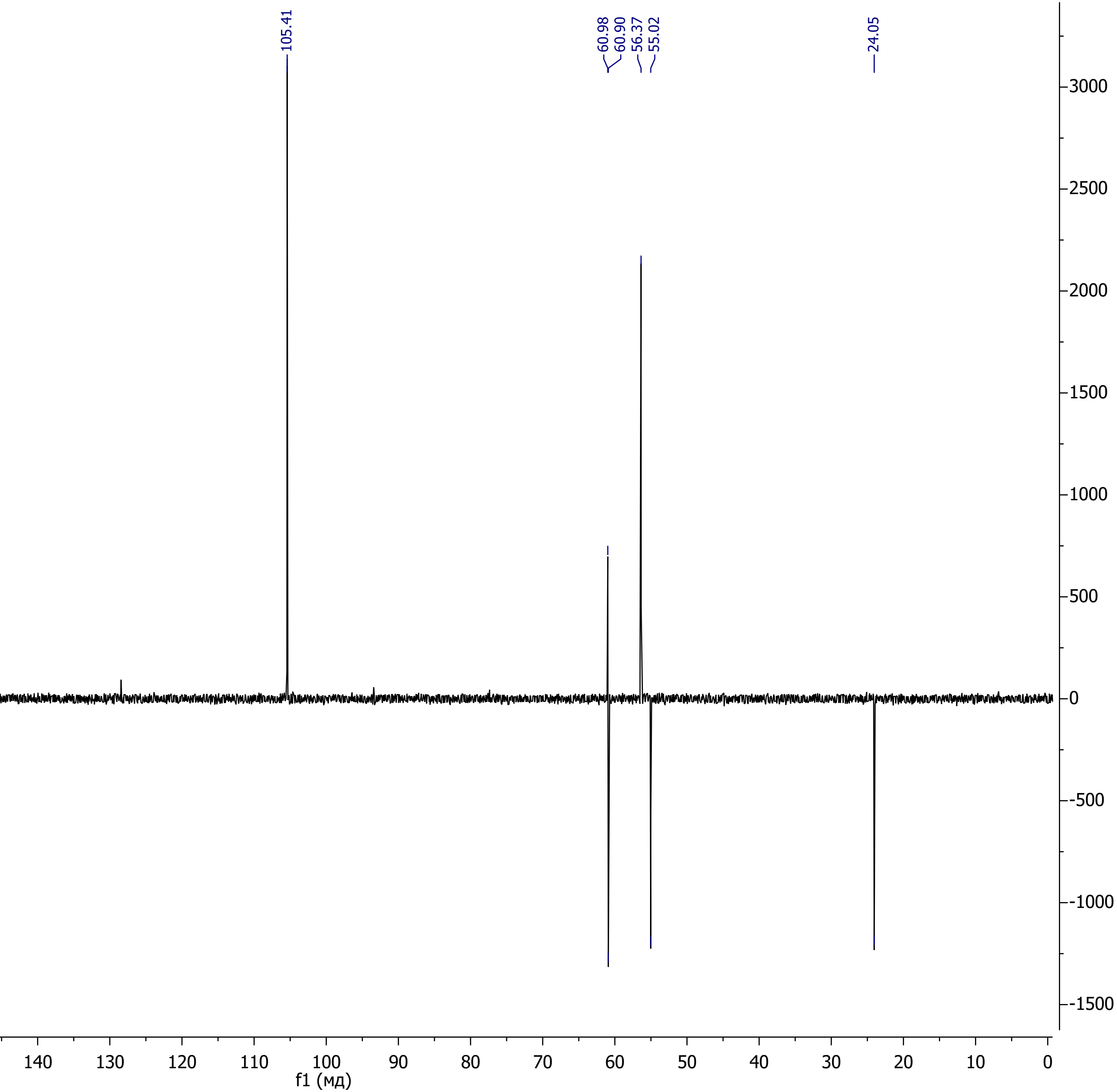
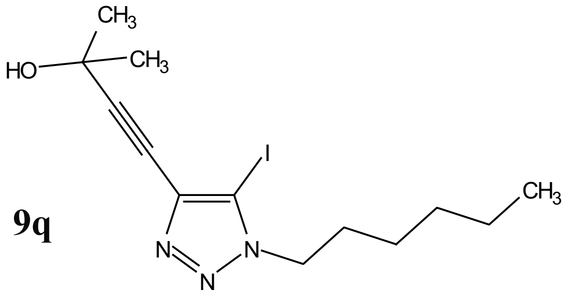


[1]H NMR ($CDCl_3$, 400.13 MHz)



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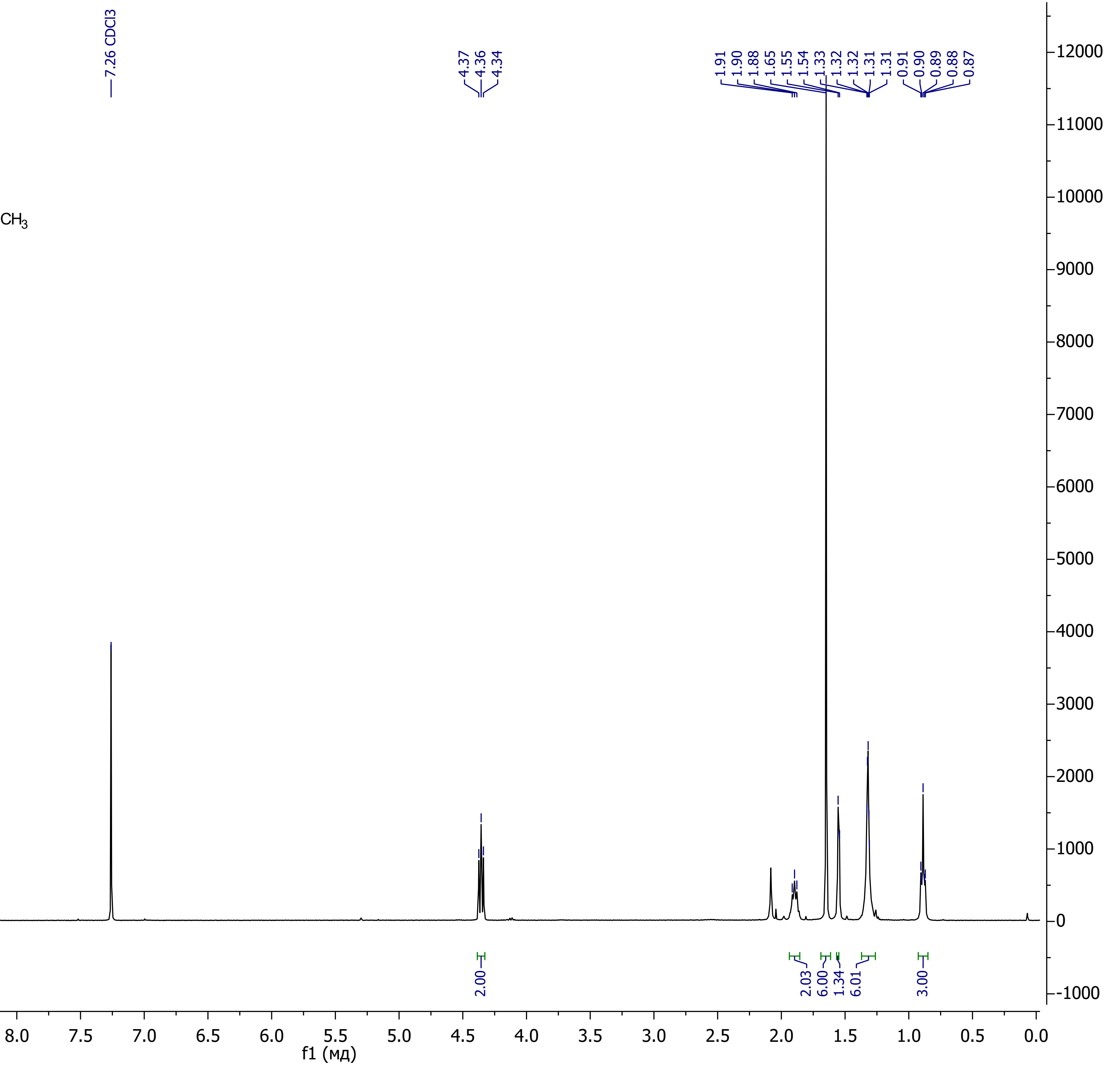
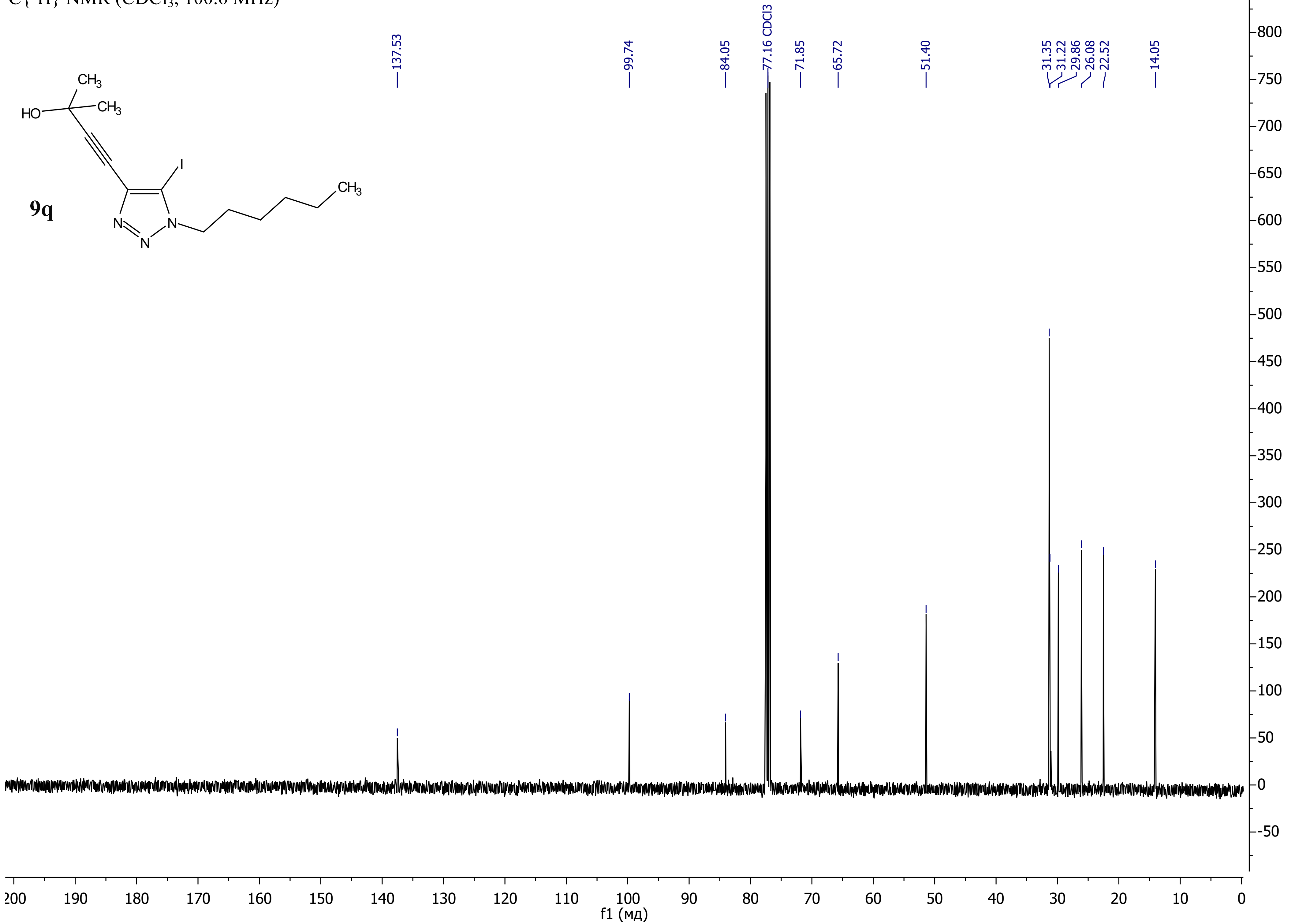
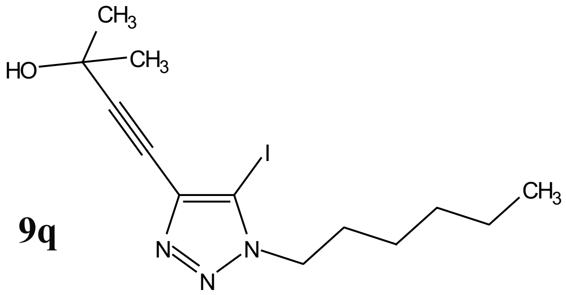


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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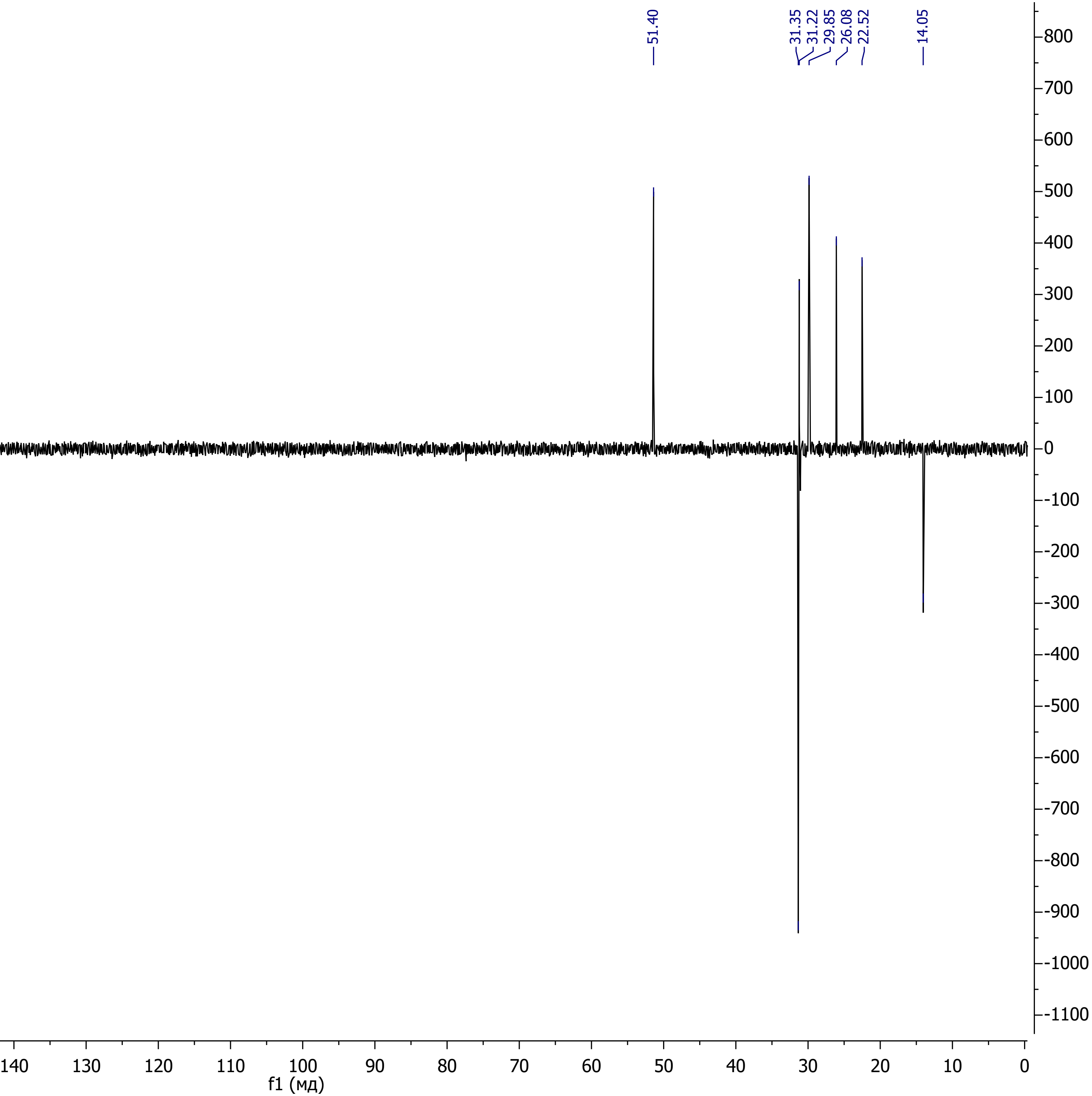
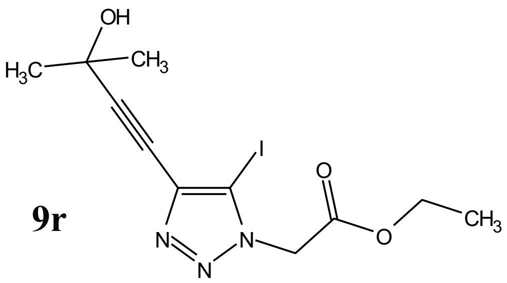


[1]H NMR ($CDCl_3$, 400.13 MHz)



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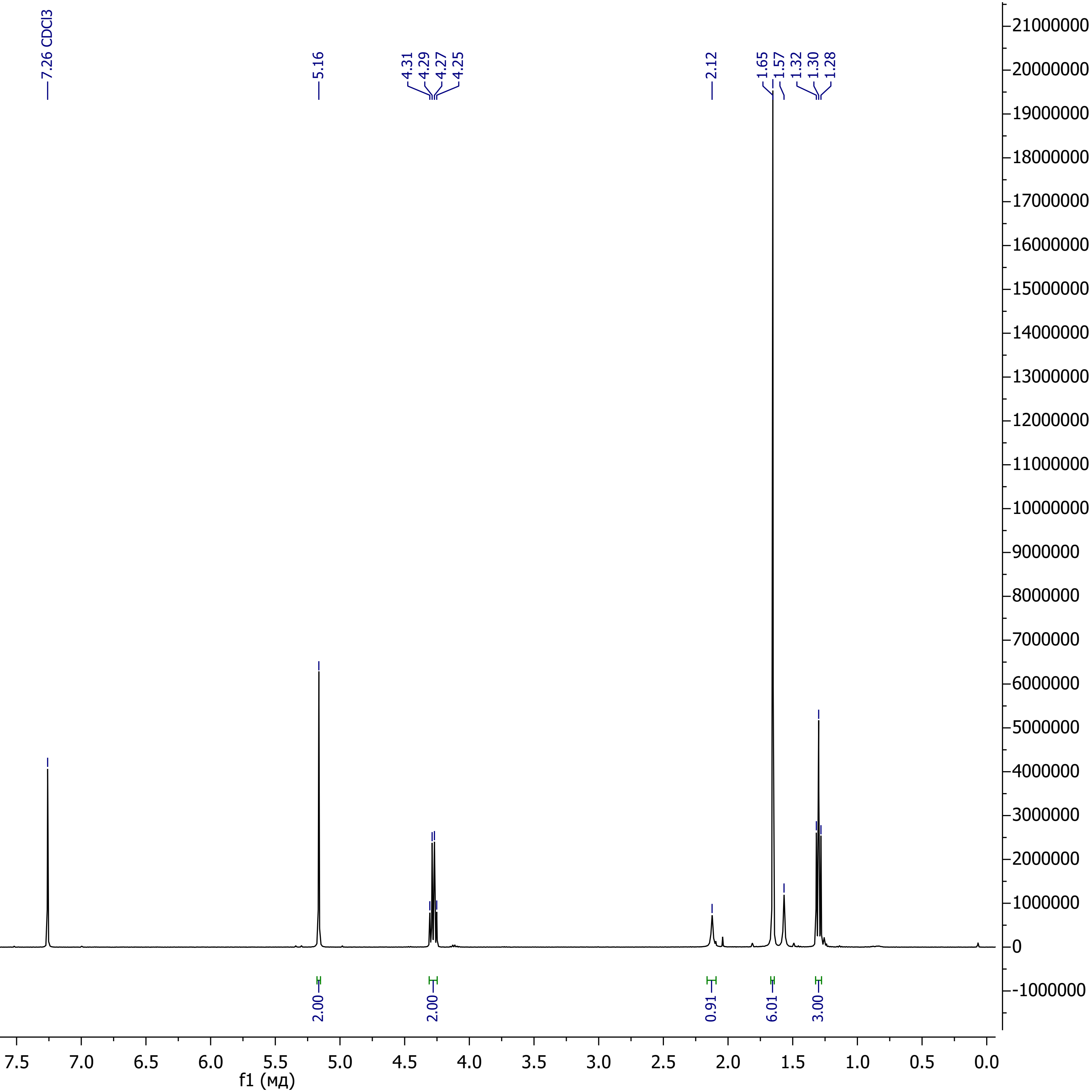
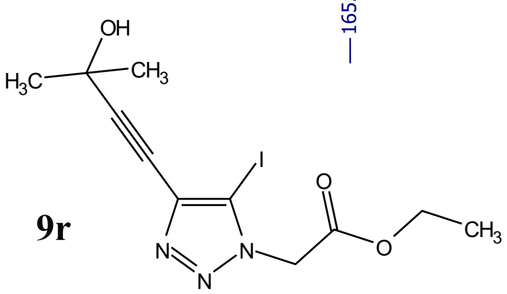


$^{13}C\ \{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



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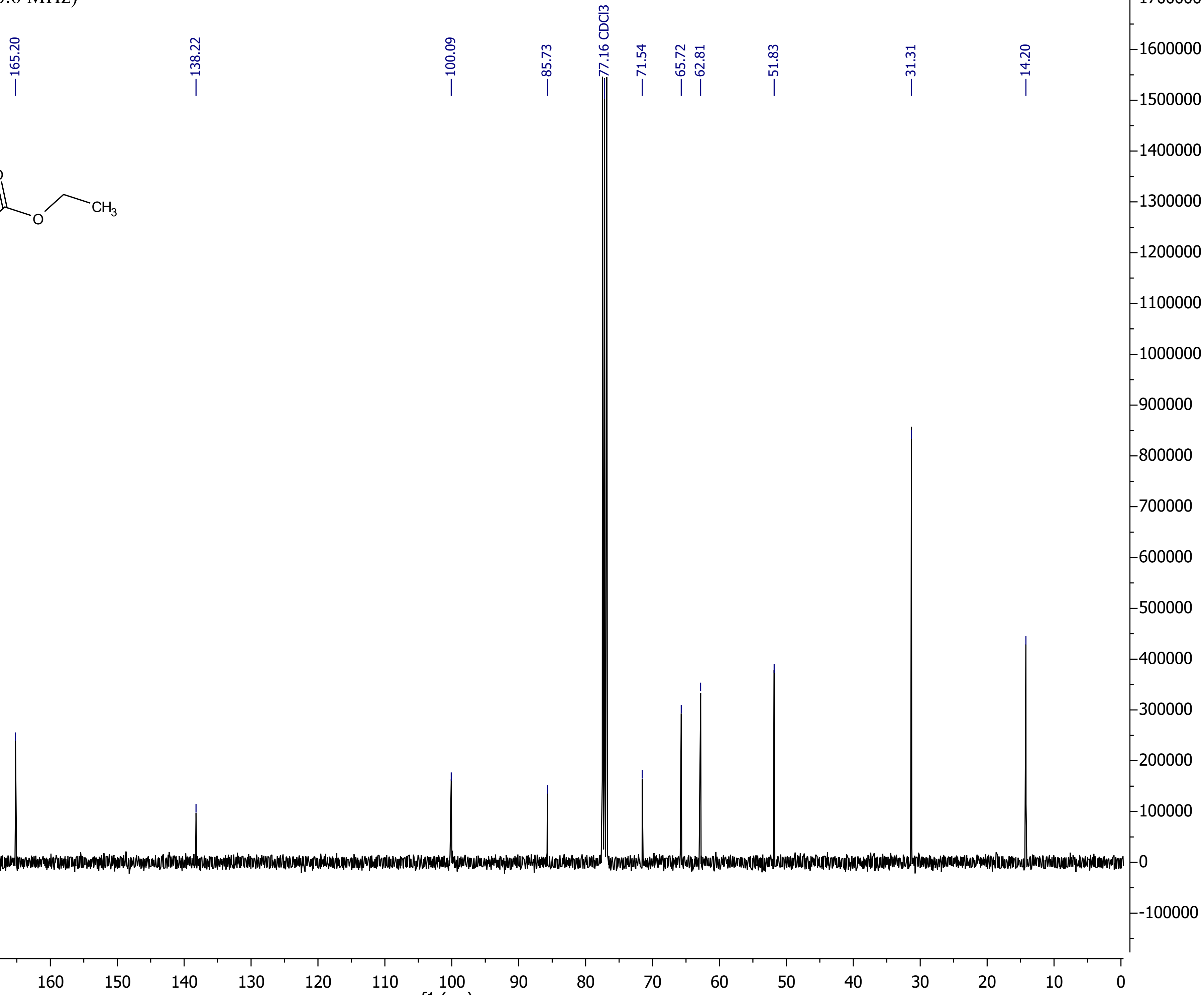
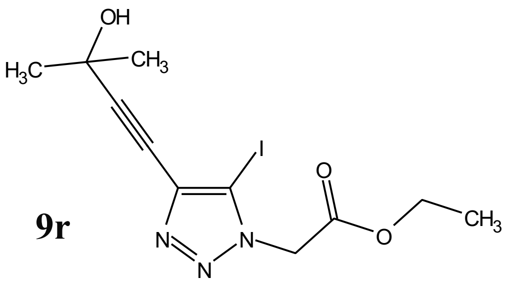


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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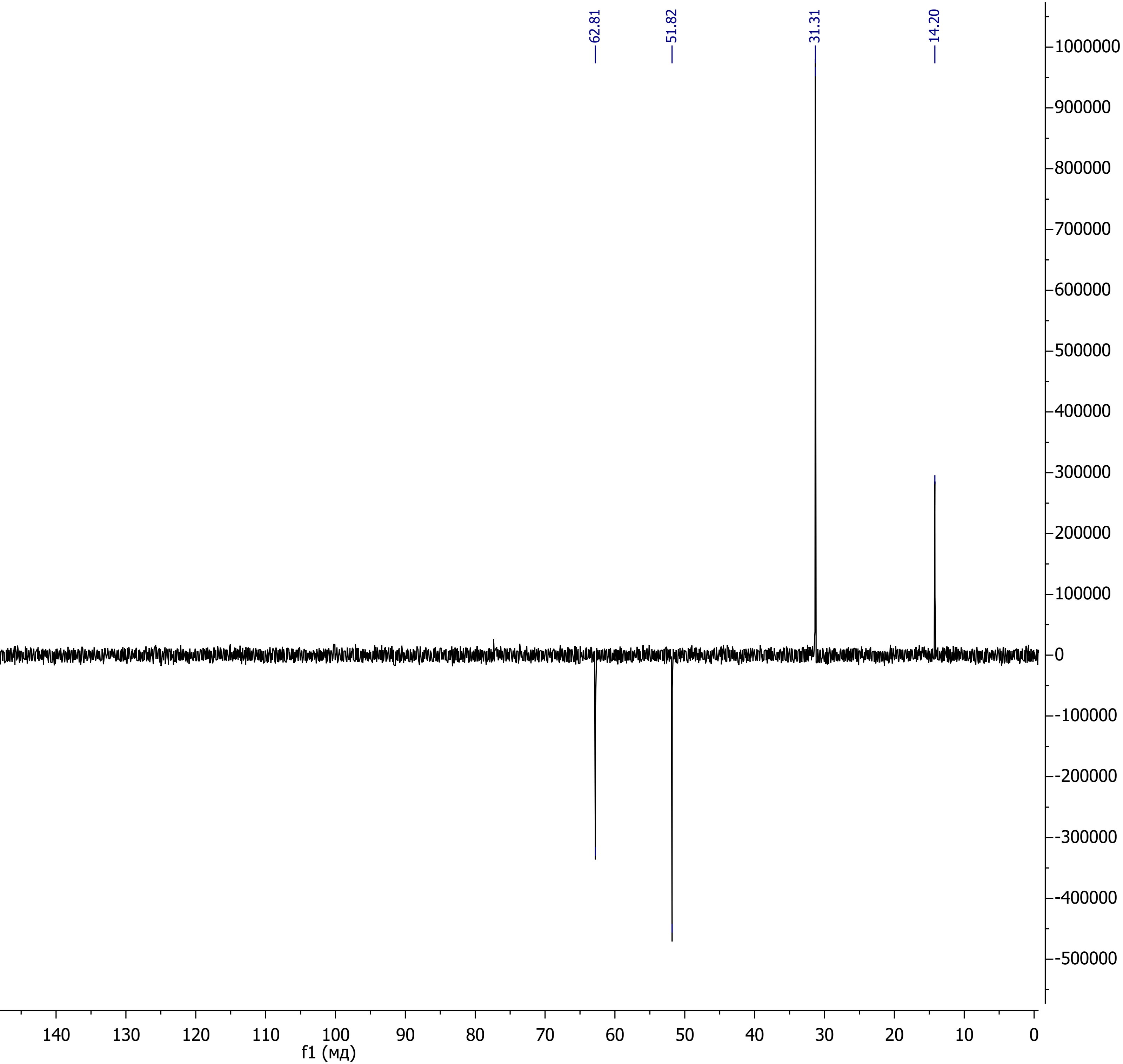
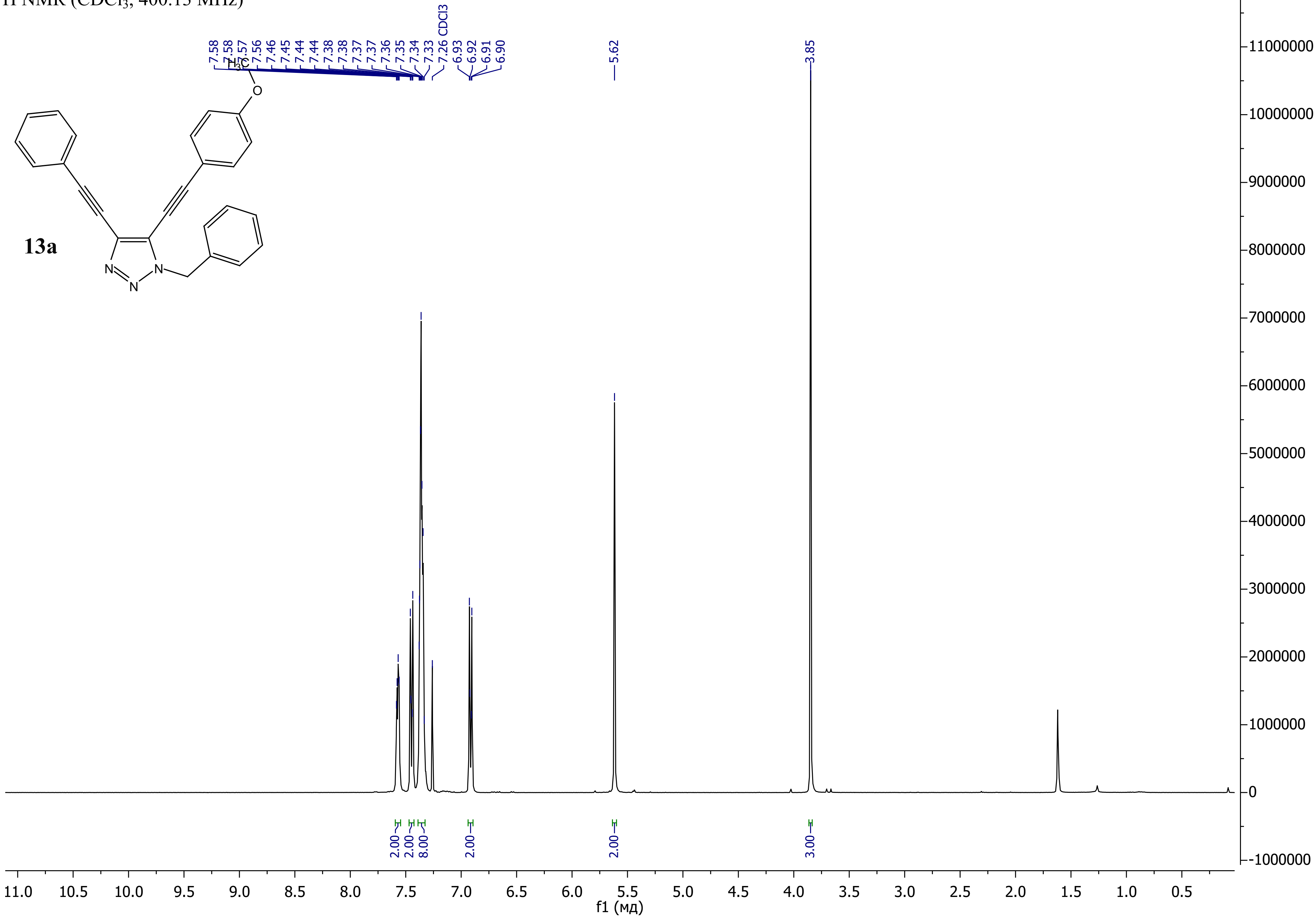
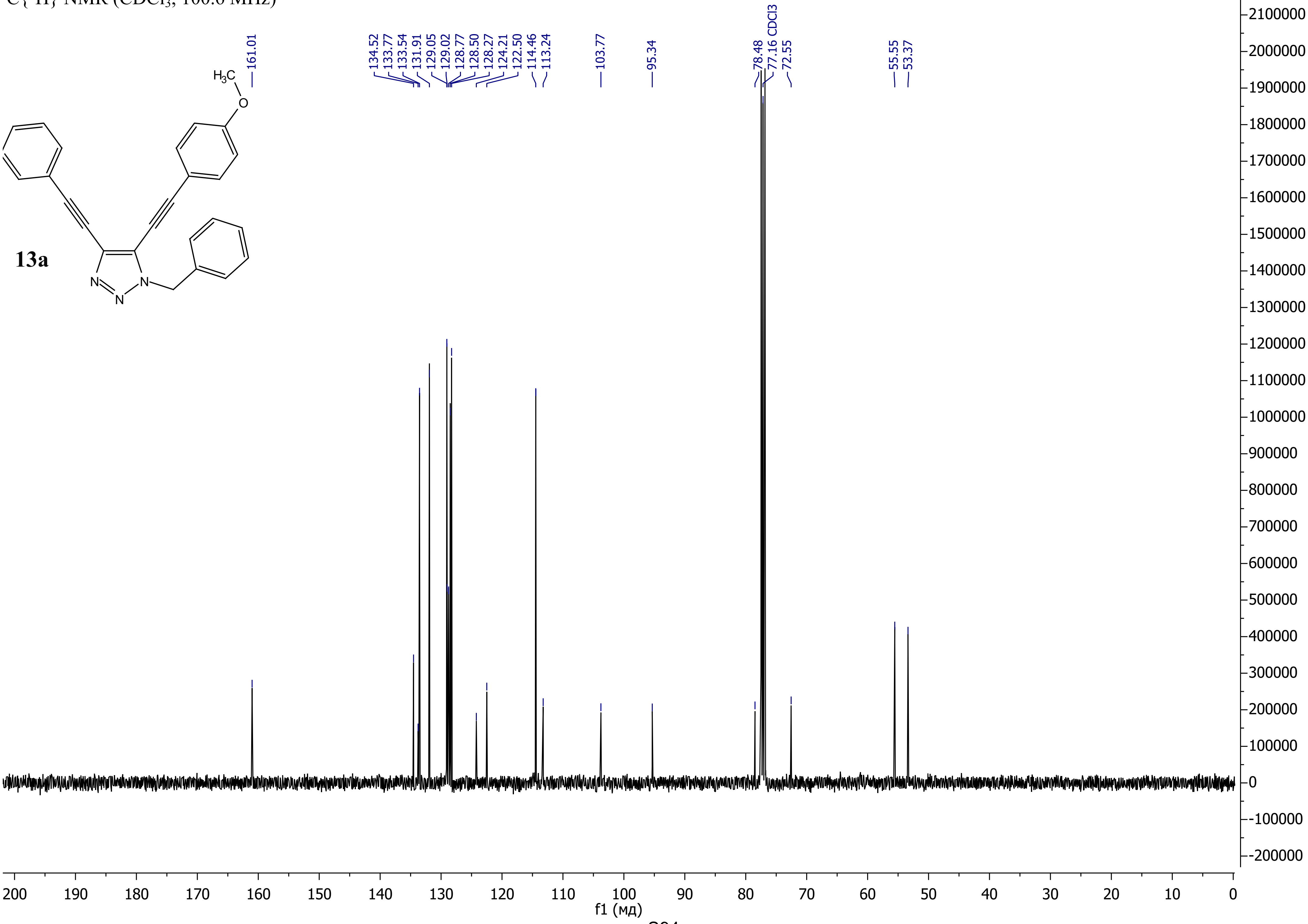


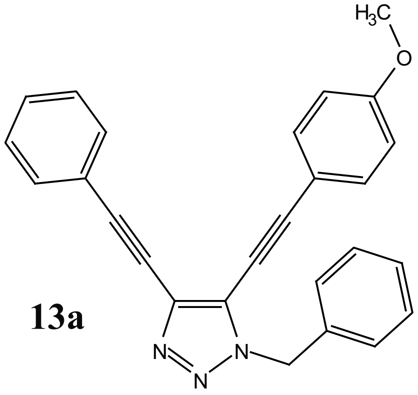
[1]H NMR ($CDCl_3$, 400.13 MHz)



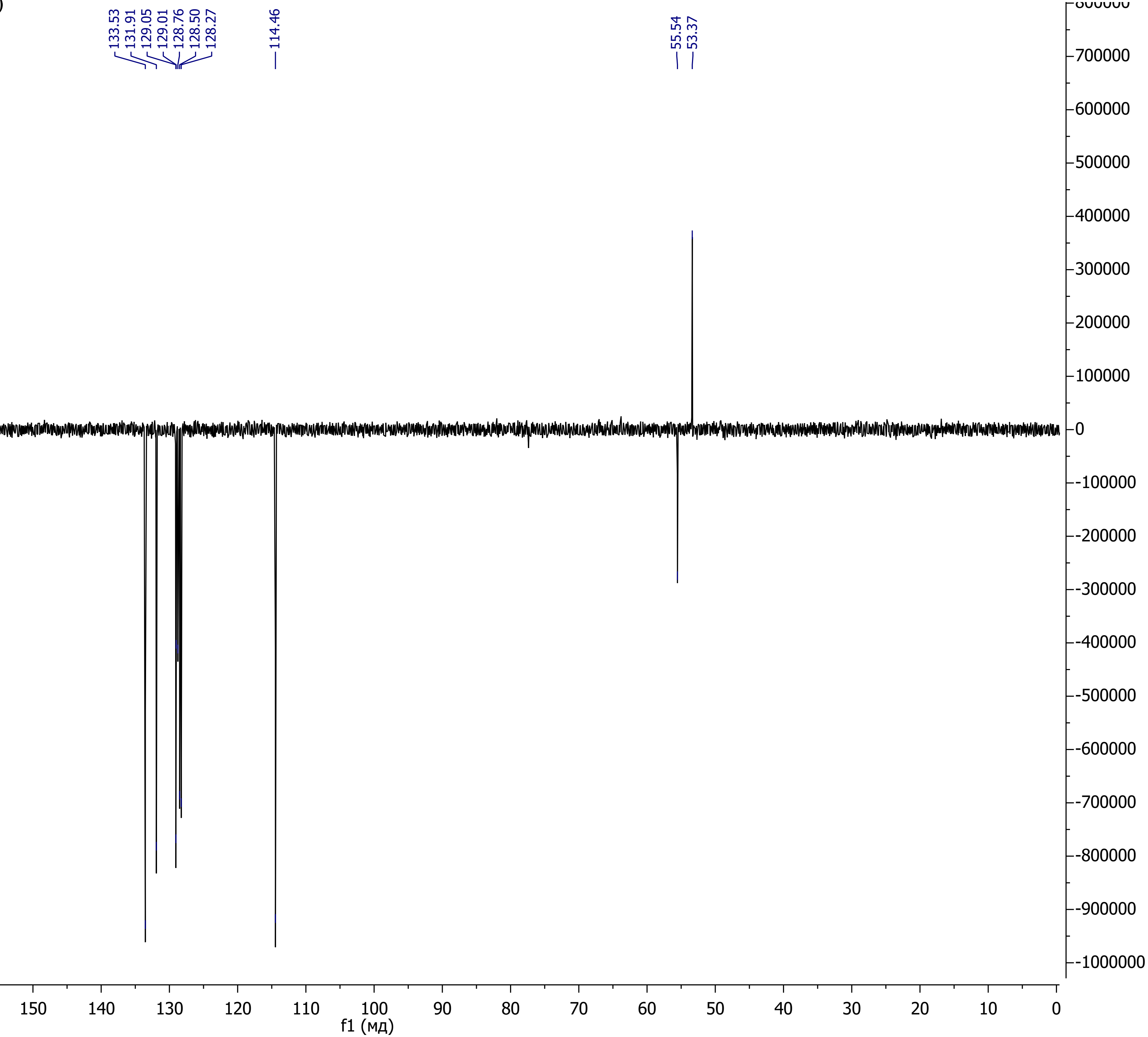
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)

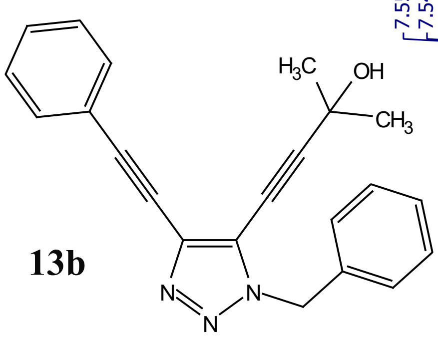


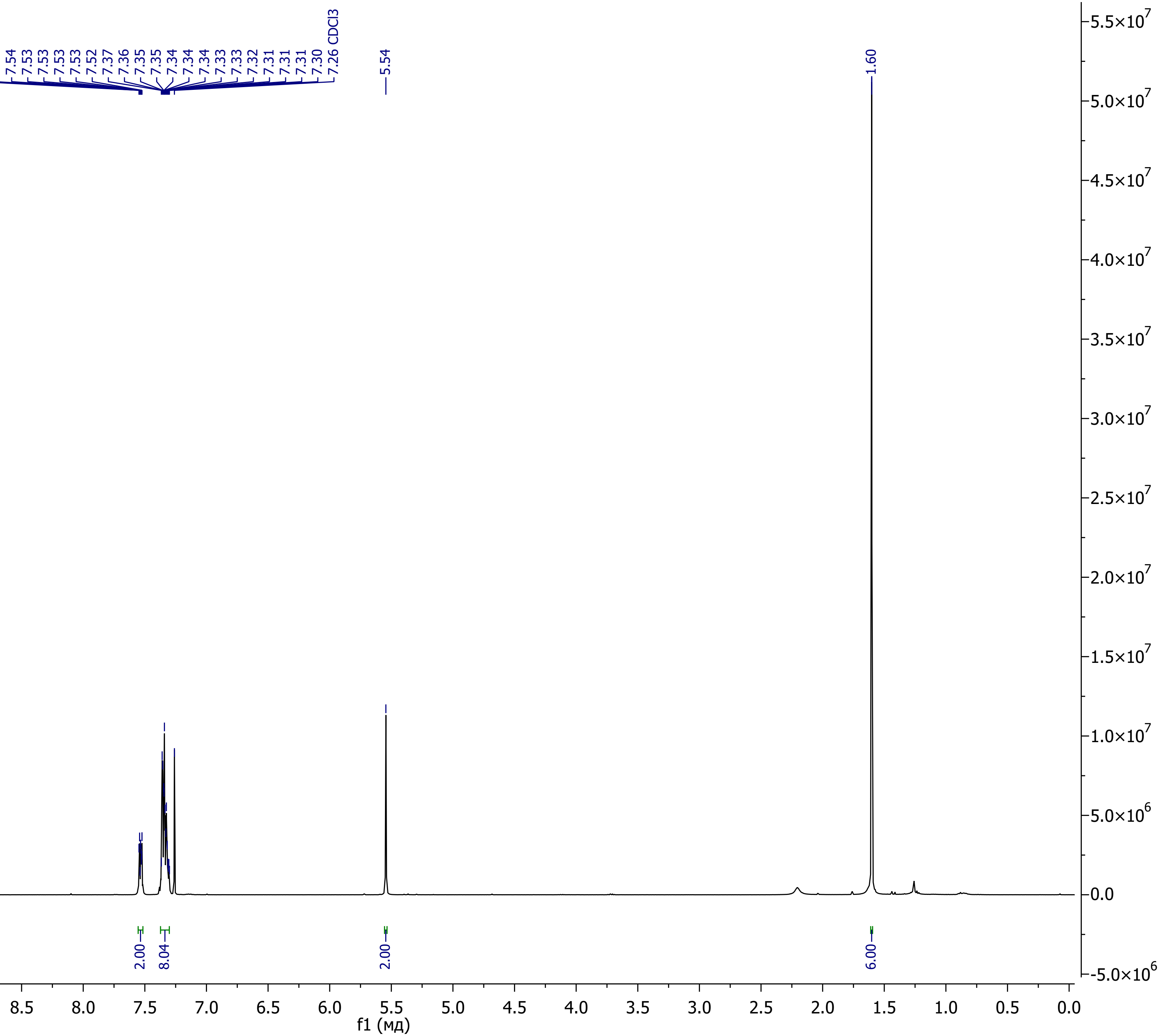
13a



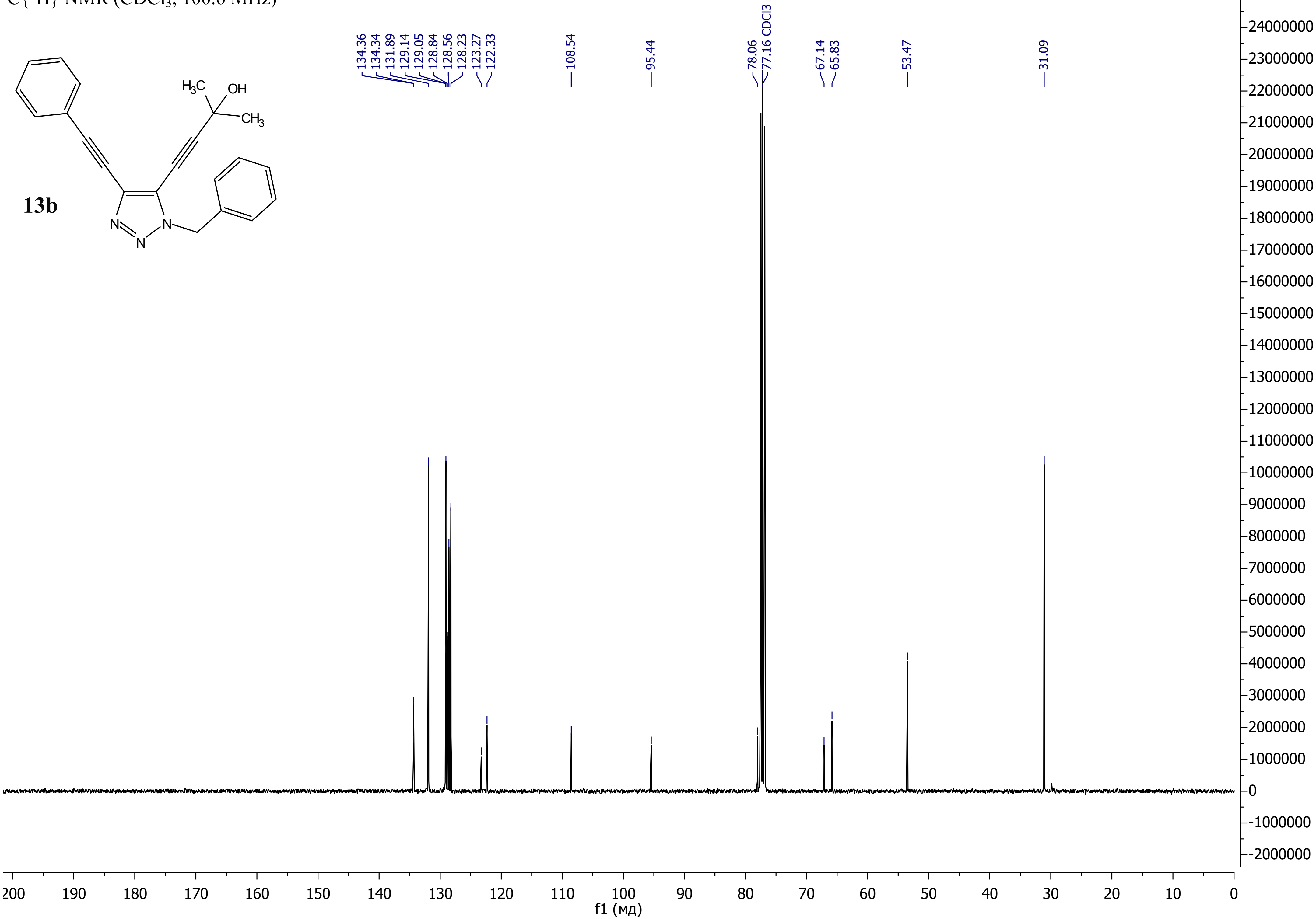
^{1}H NMR ($CDCl_3$, 400.13 MHz)

13b

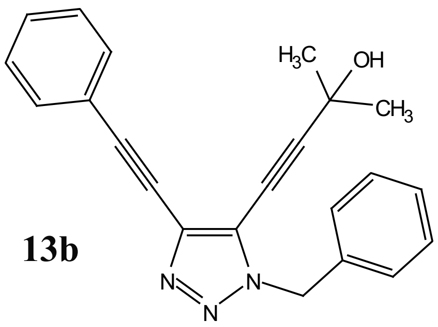




$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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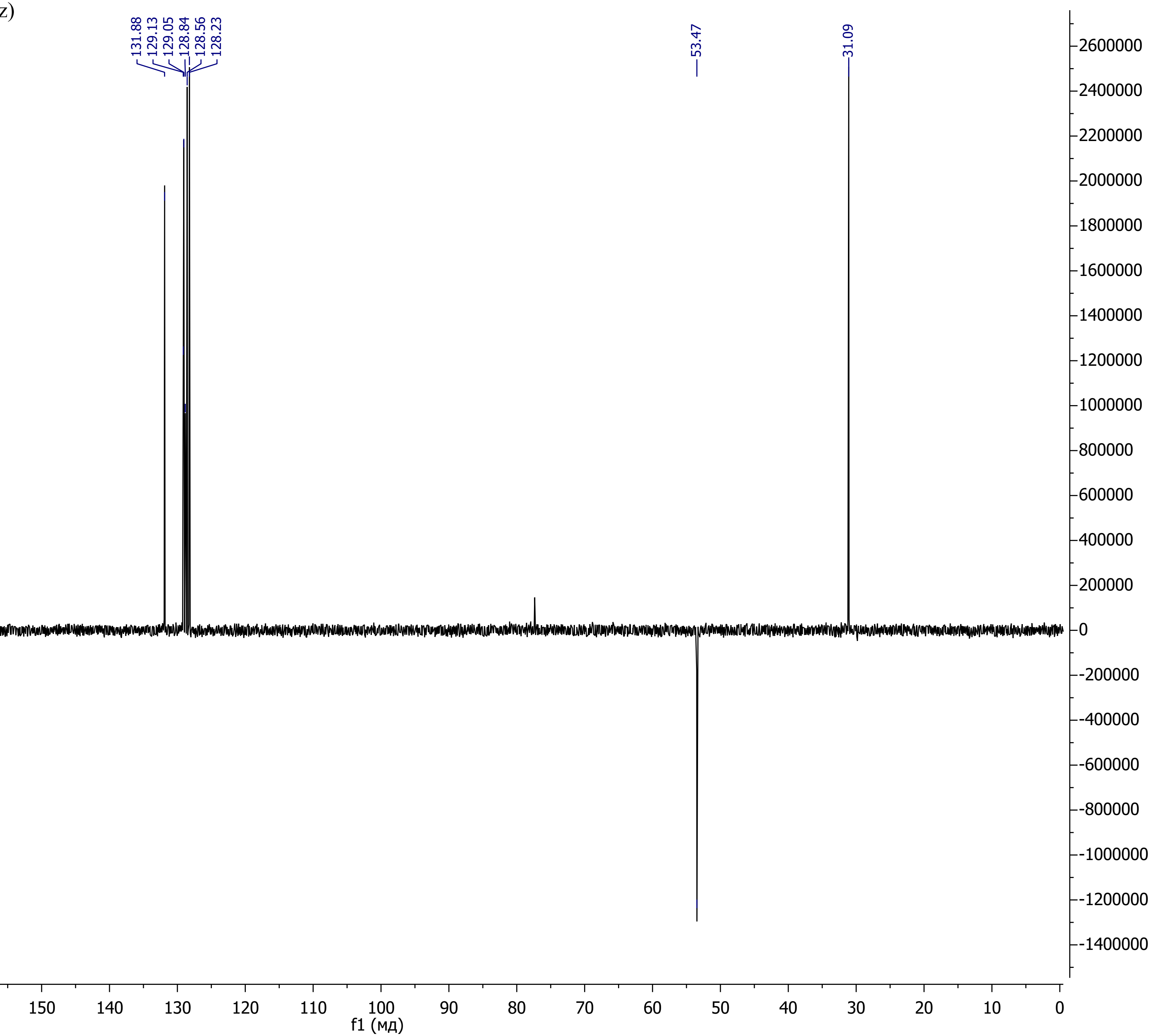
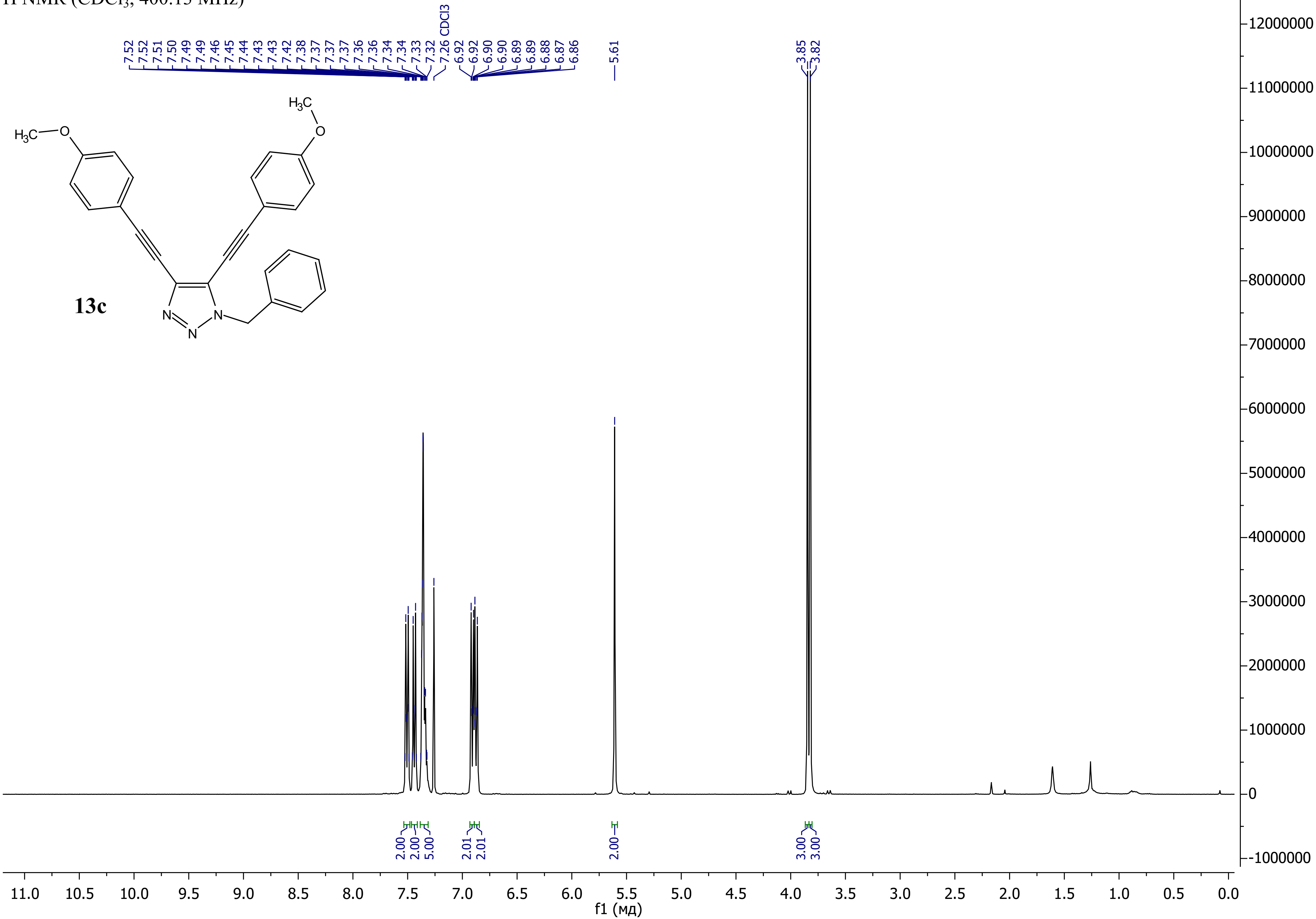
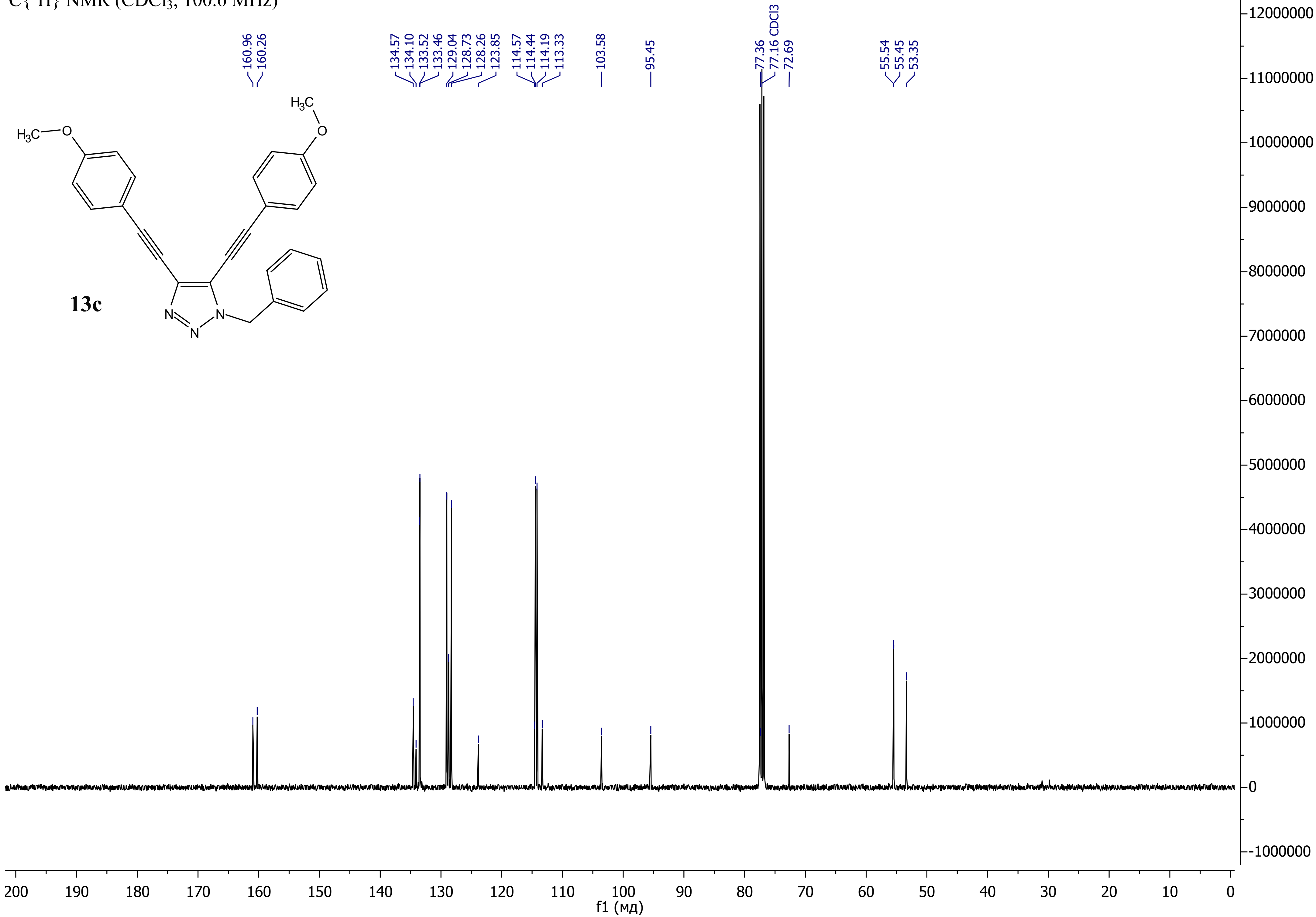


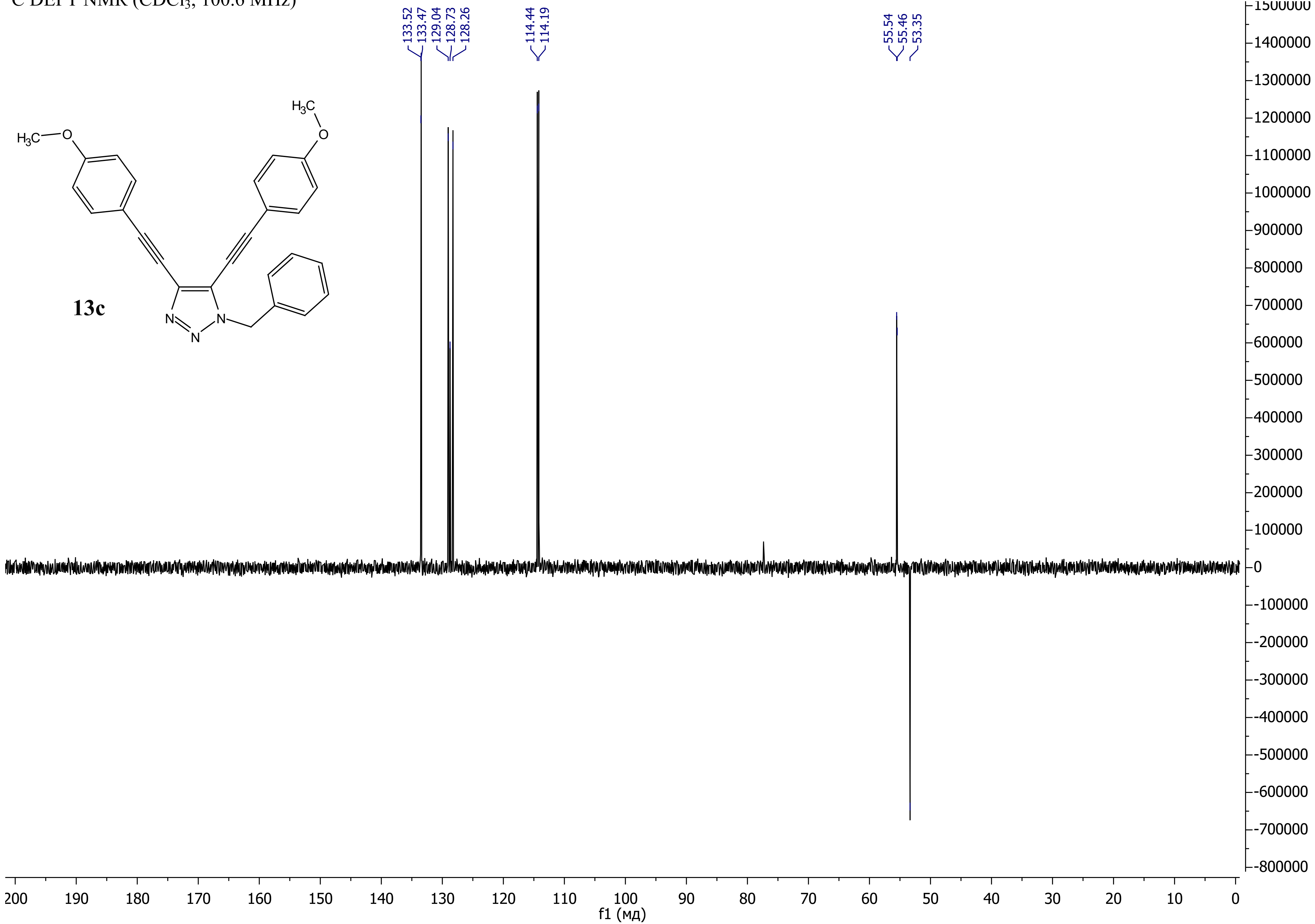
[1]H NMR ($CDCl_3$, 400.13 MHz)



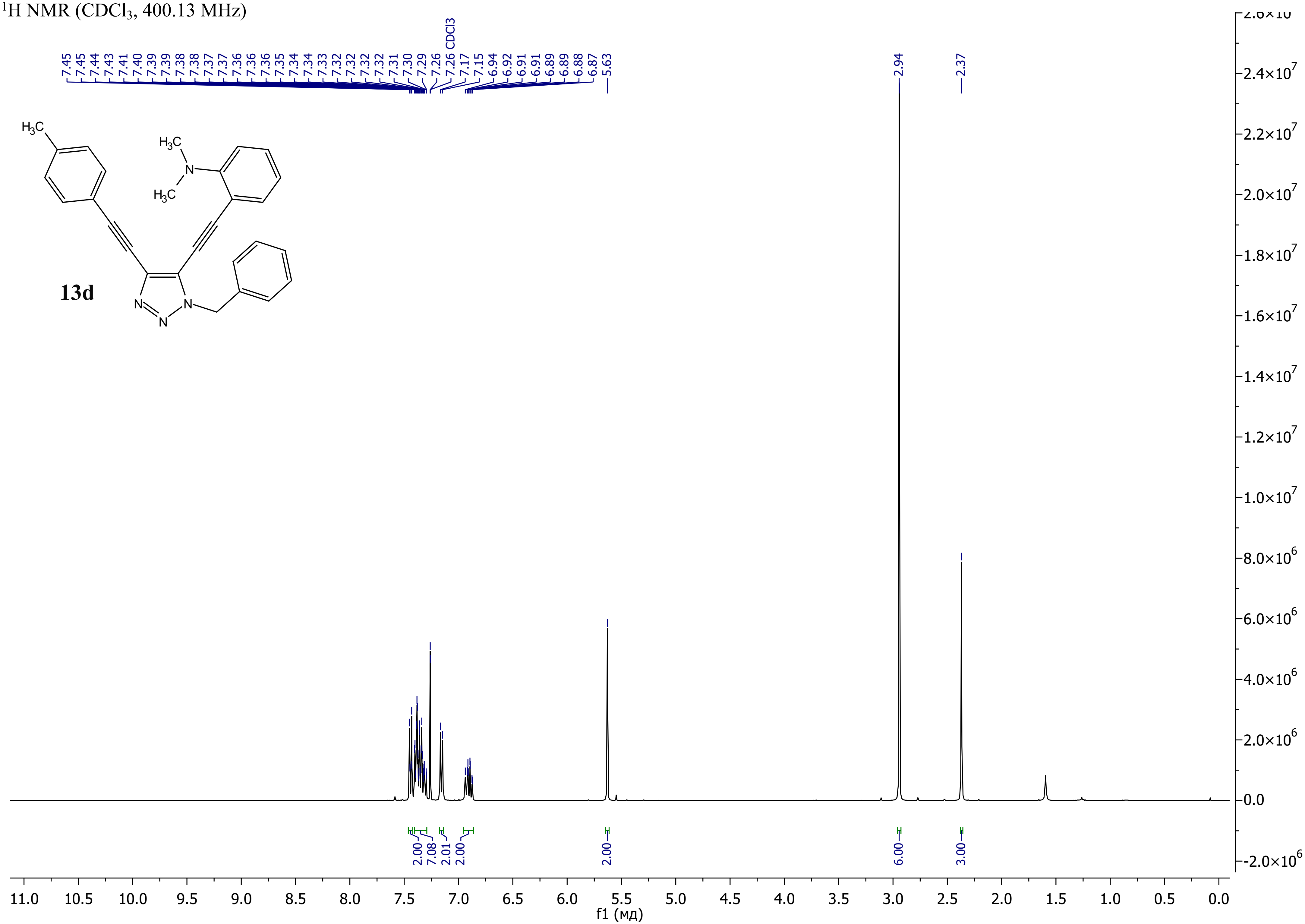
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



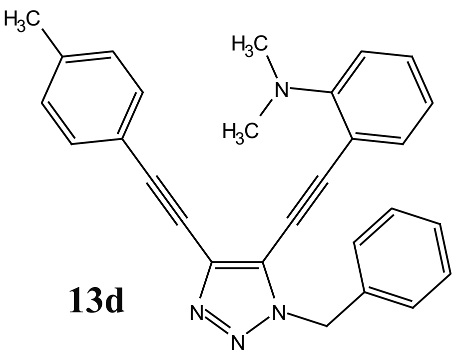
^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



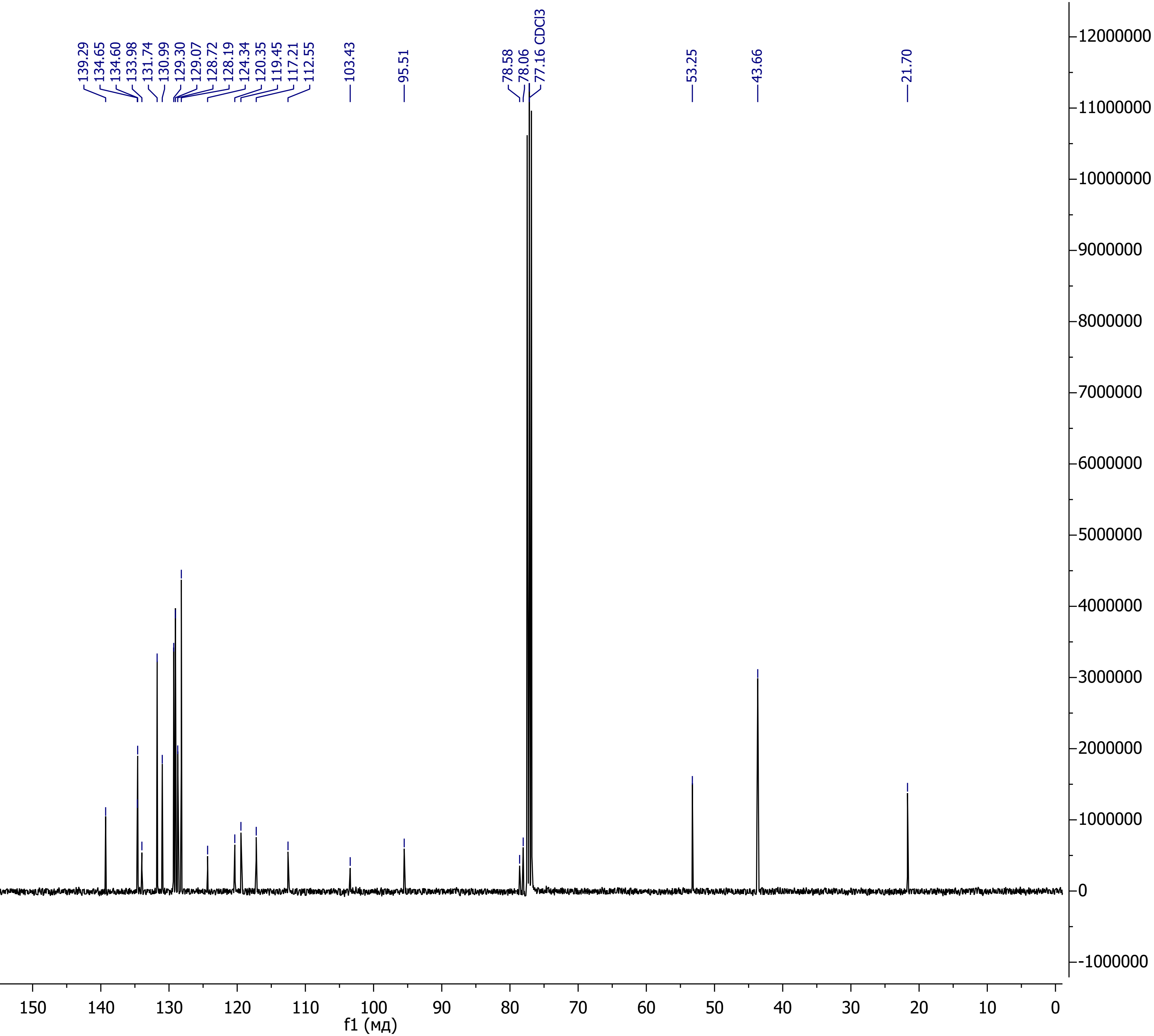
^{1}H NMR ($CDCl_3$, 400.13 MHz)



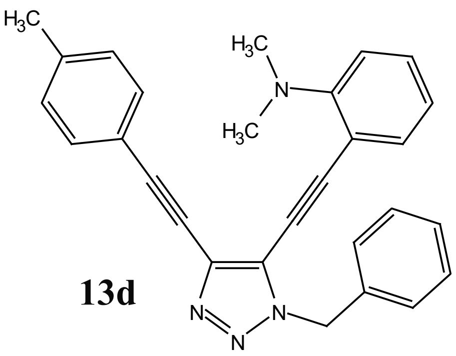
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



13d



^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



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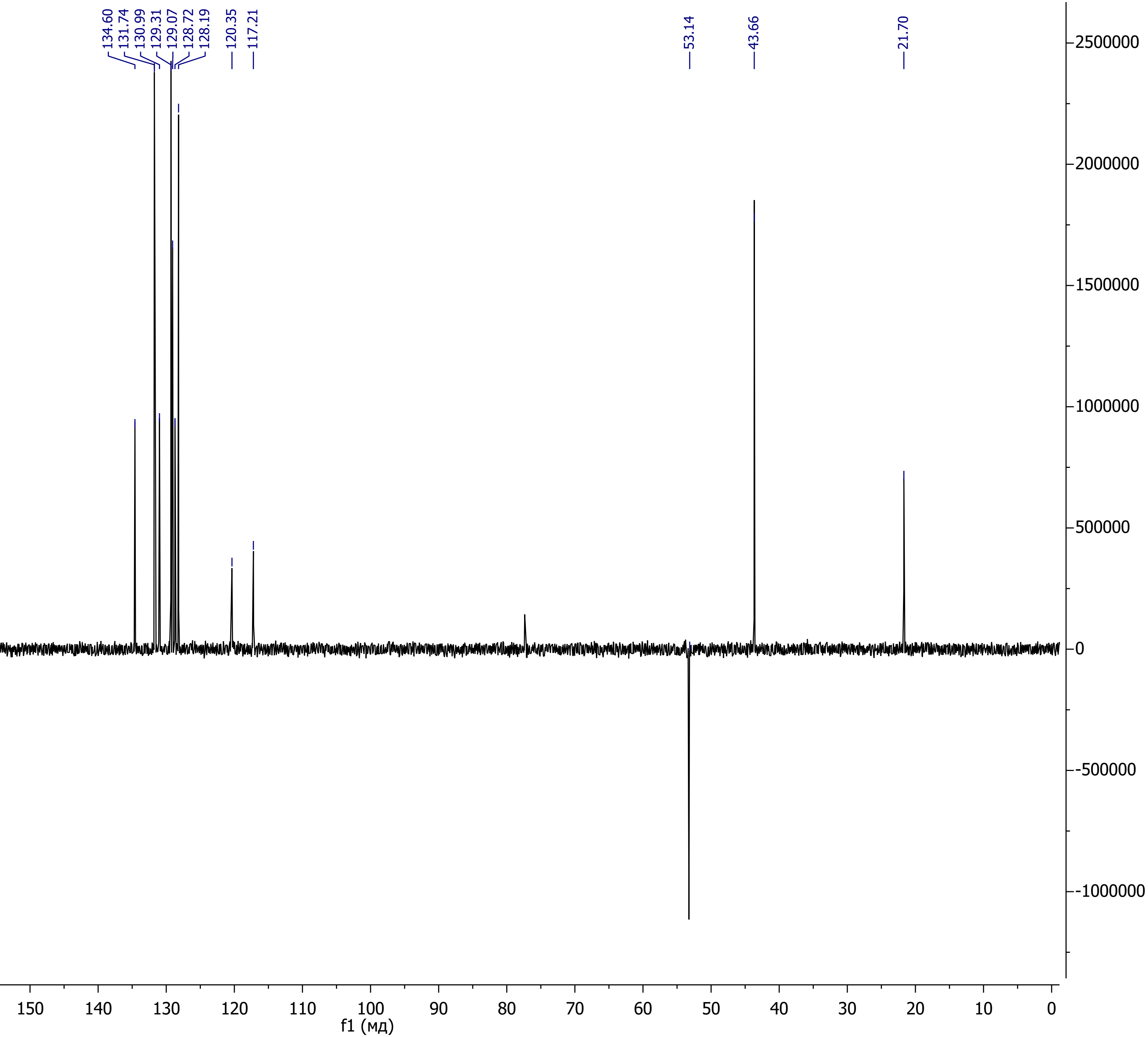
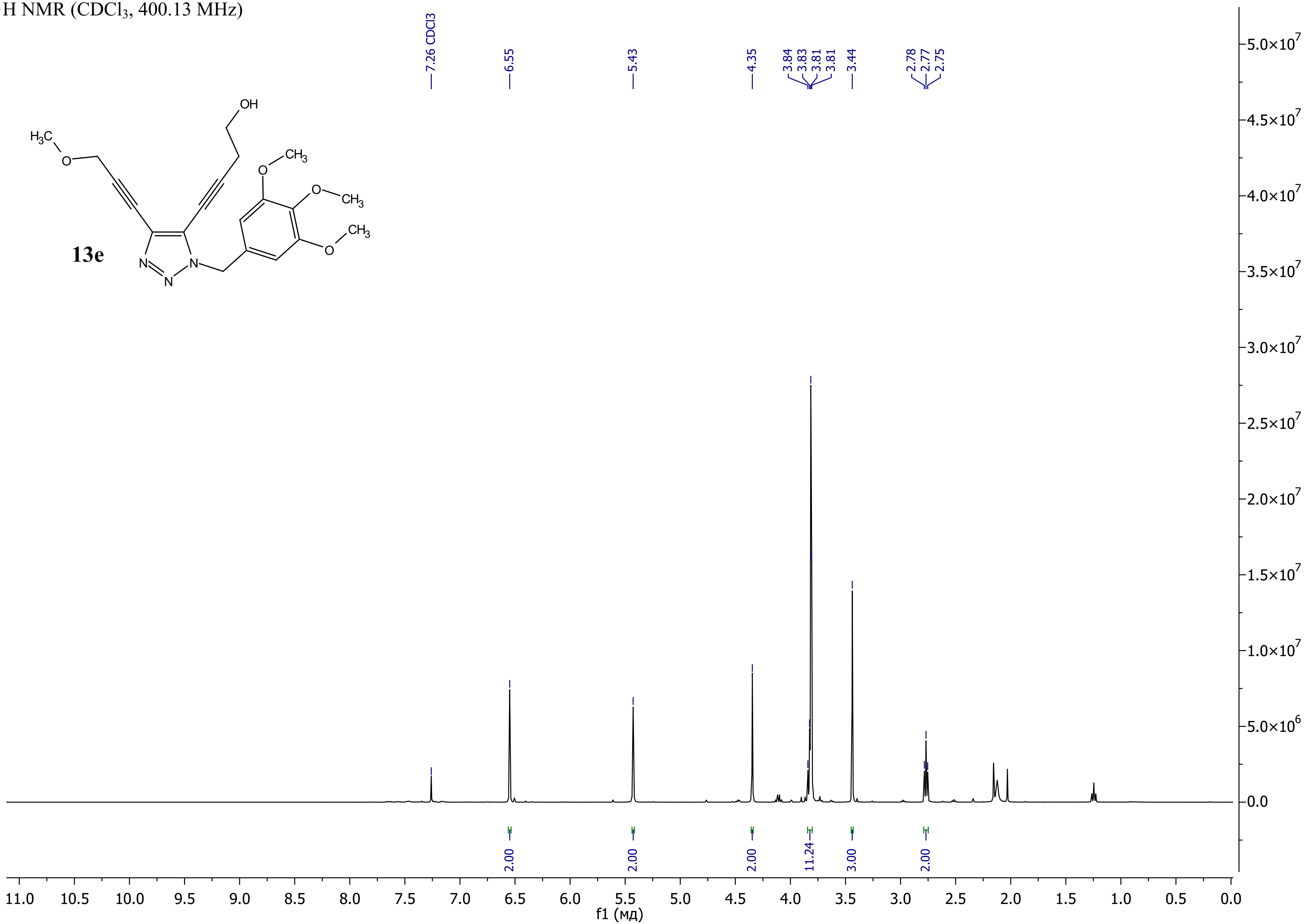
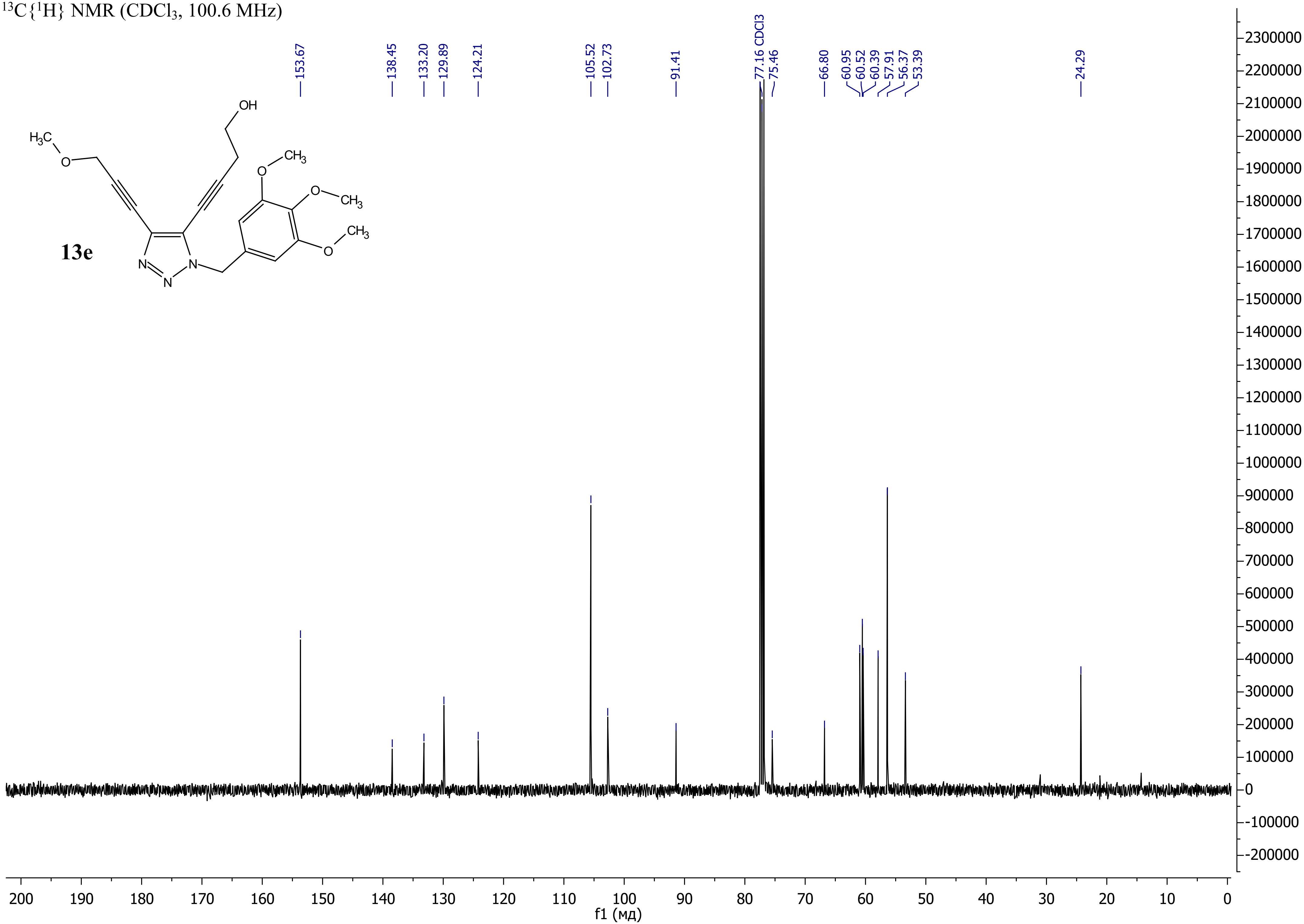


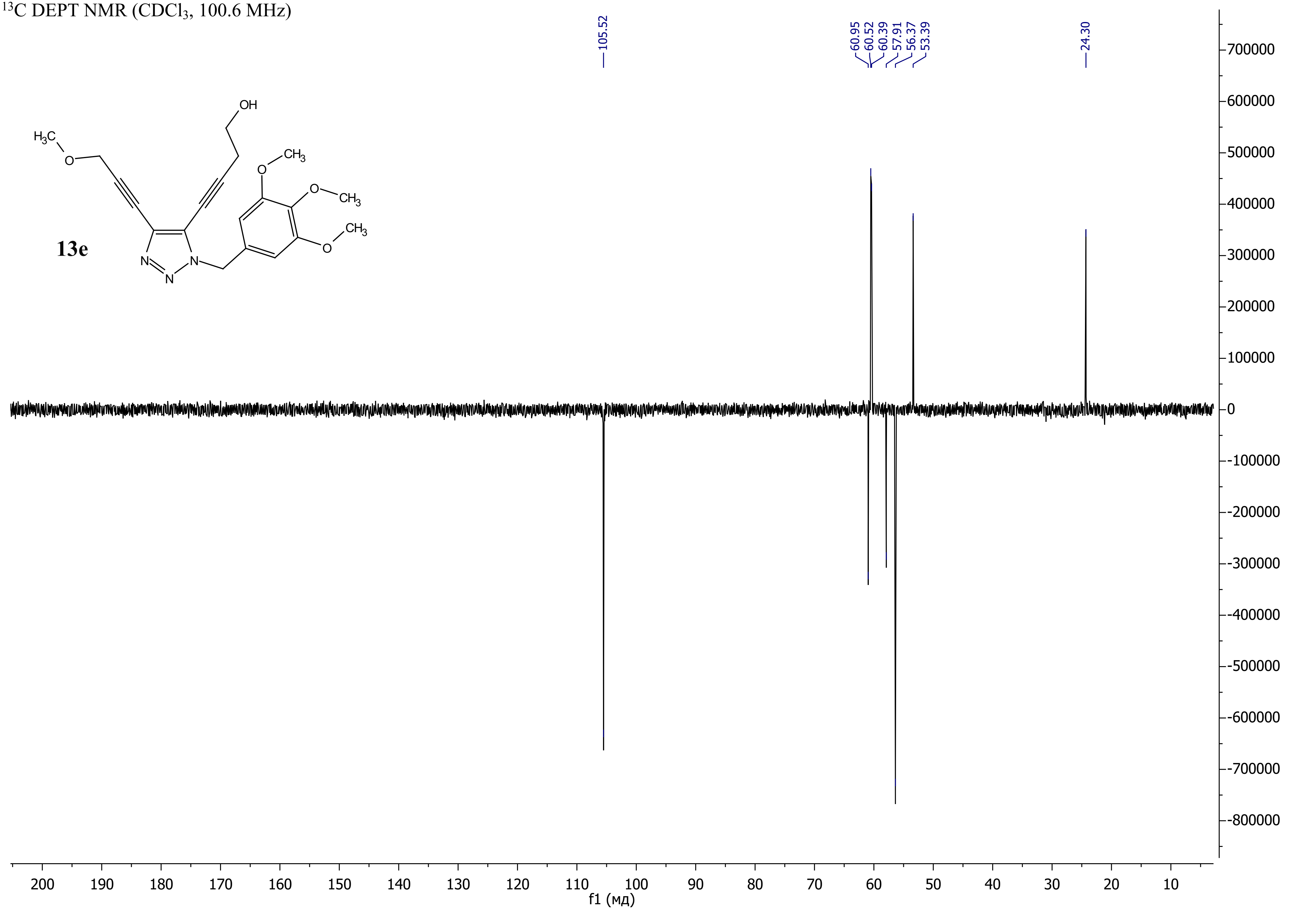
^{1}H NMR ($CDCl_3$, 400.13 MHz)



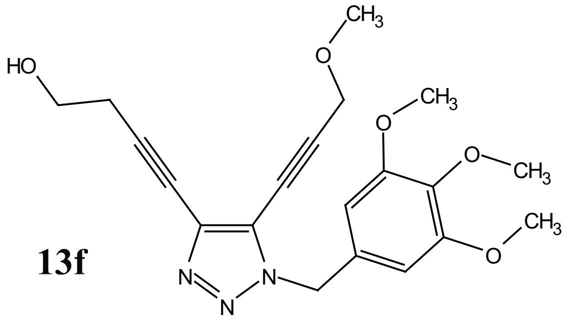
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz)



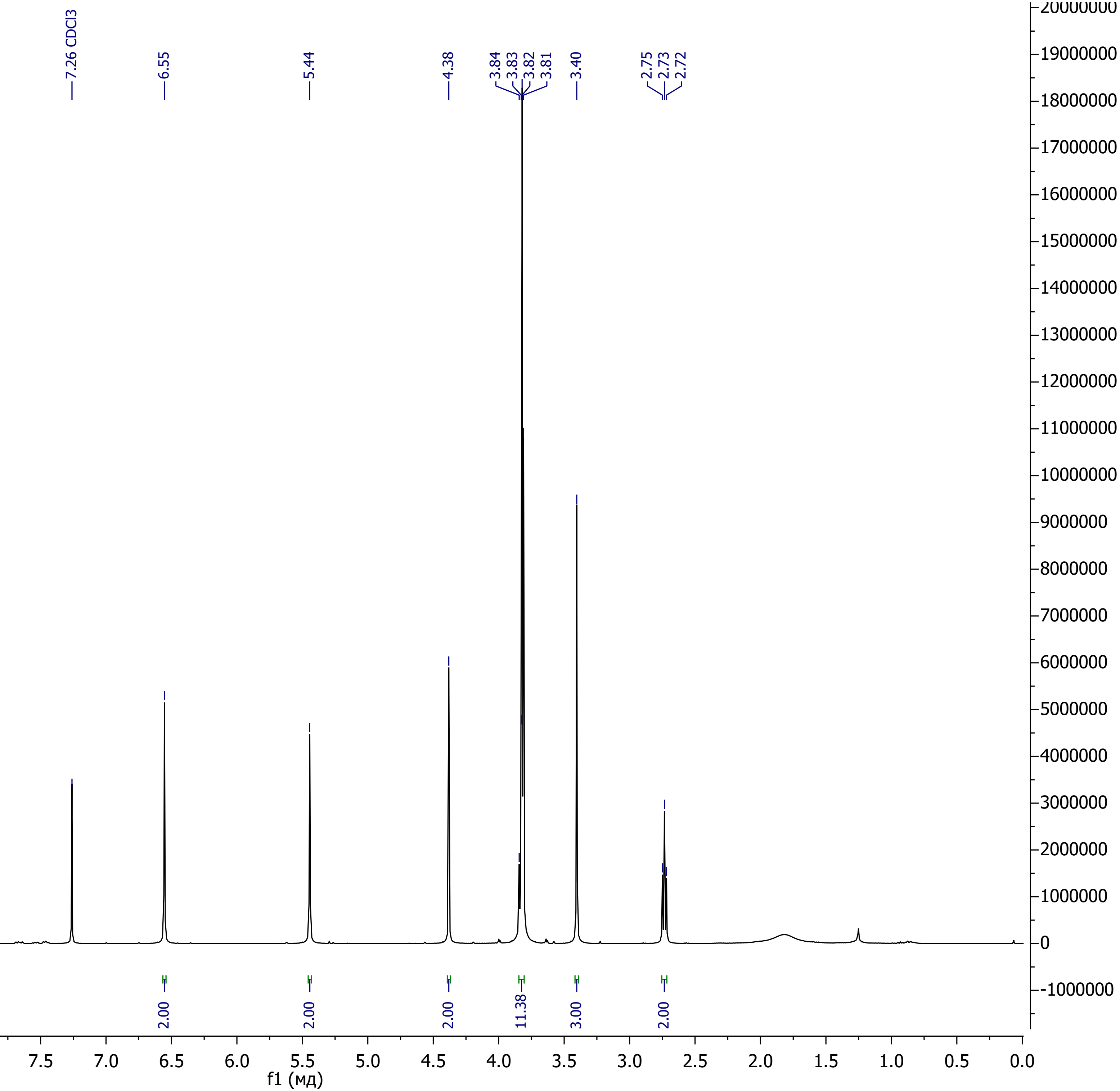
^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



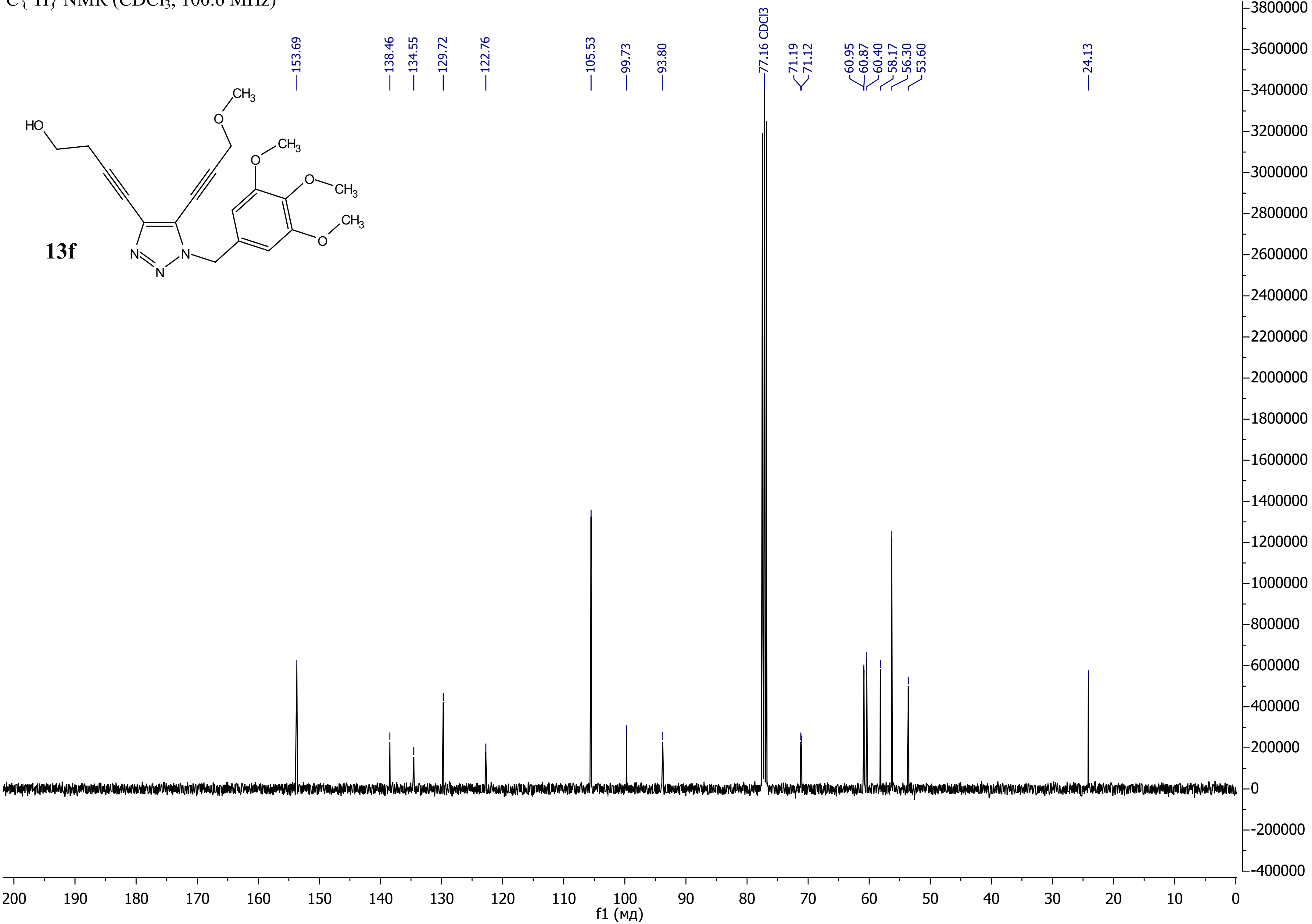
[1]H NMR ($CDCl_3$, 400.13 MHz)



13f

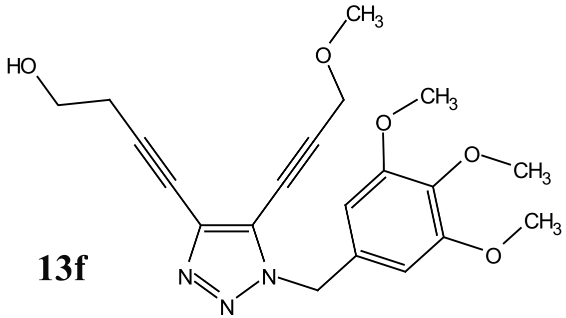


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)

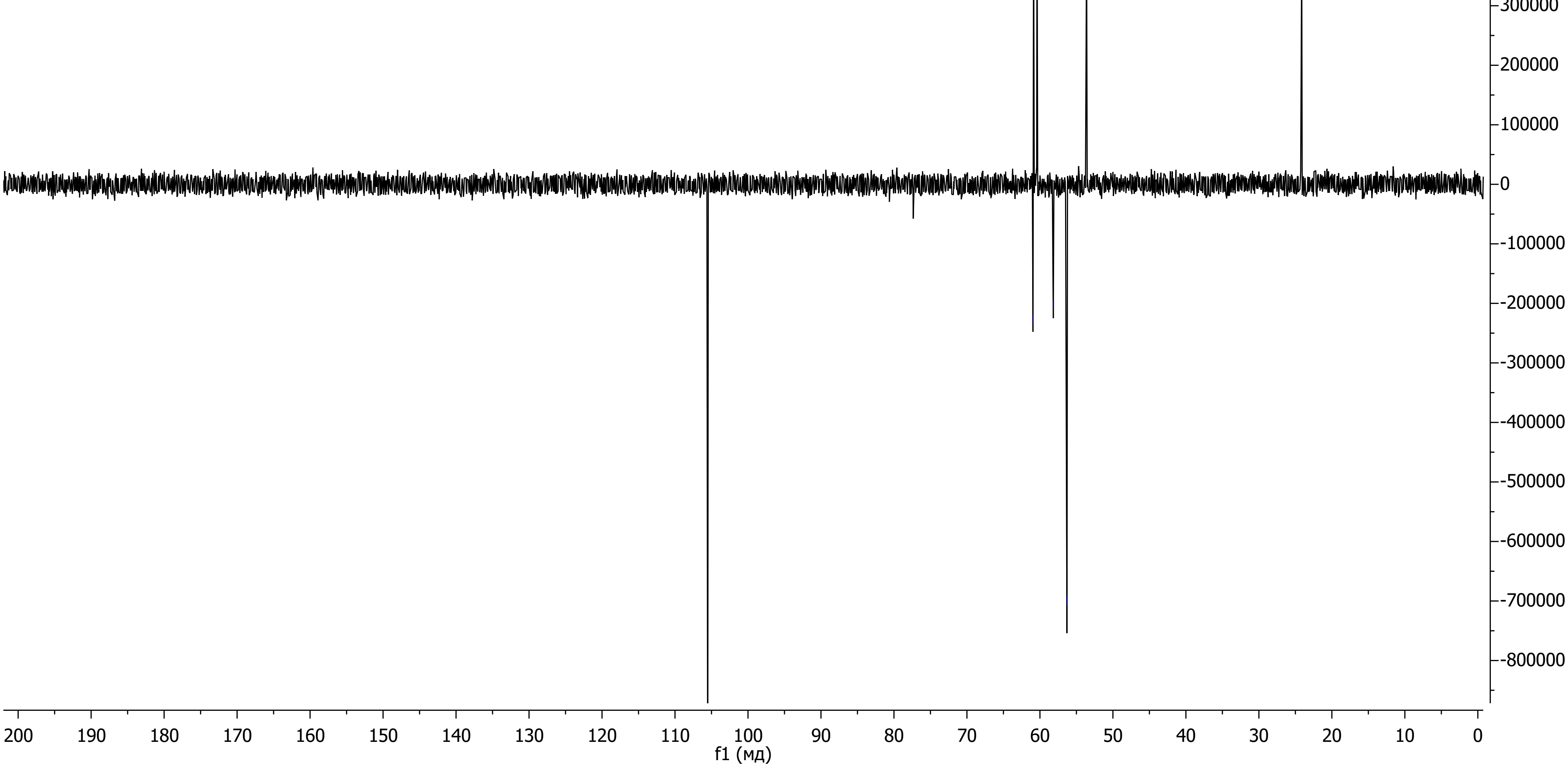


13f

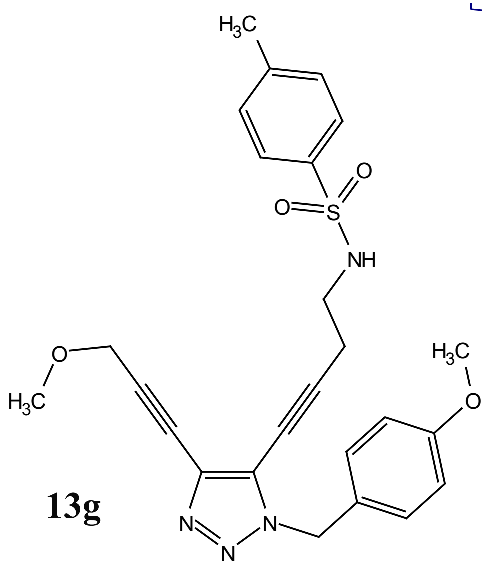
^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



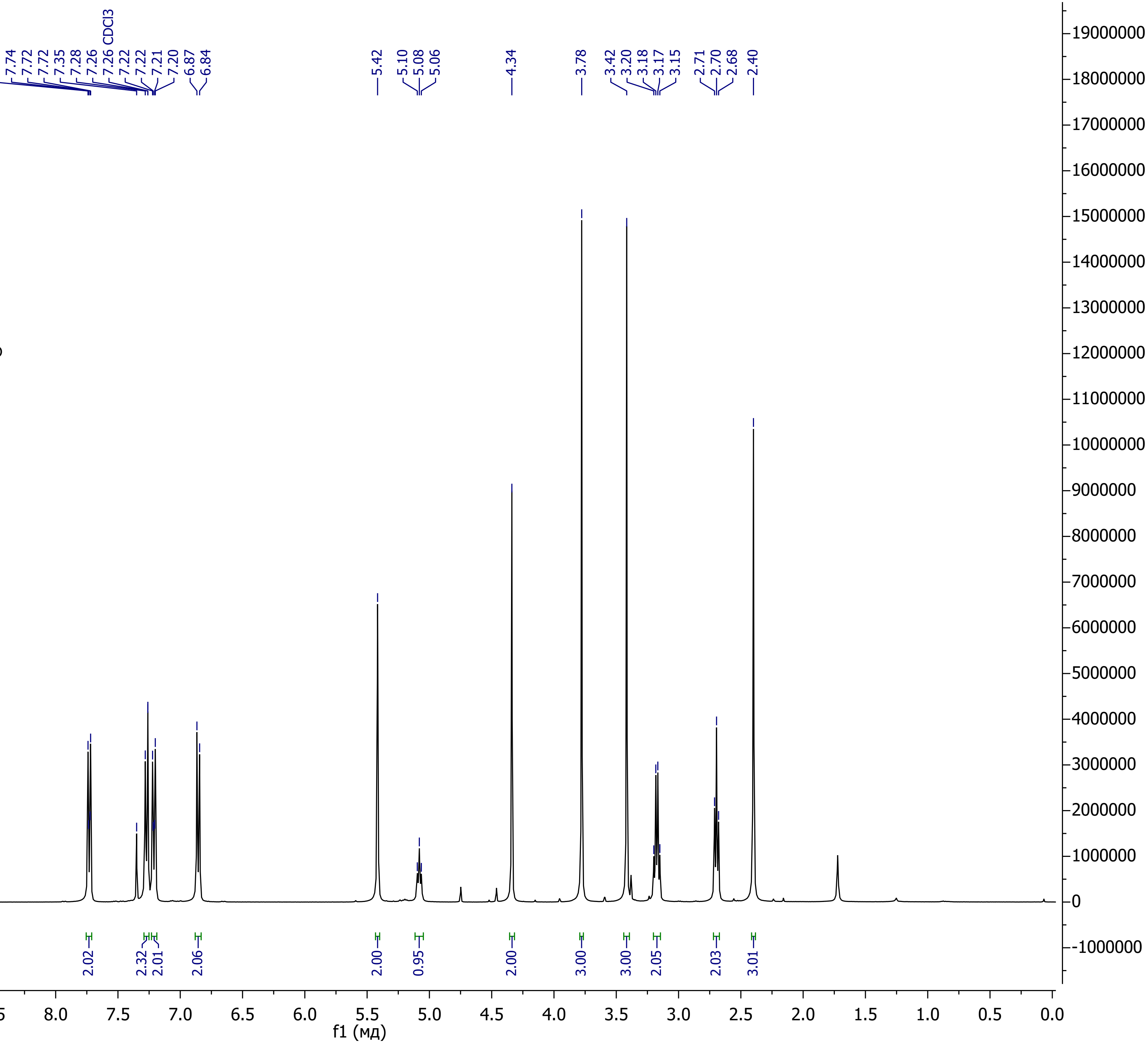
13f



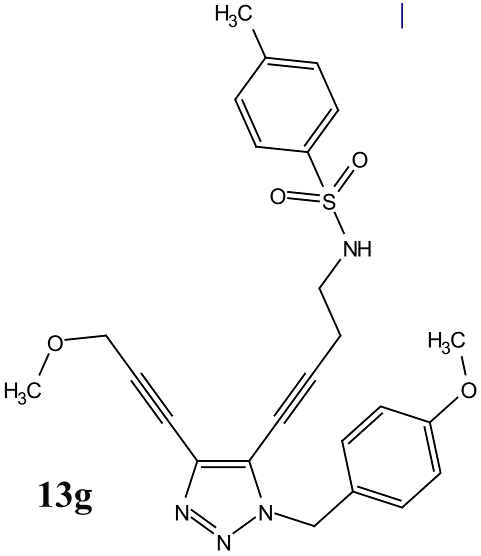
[1]H NMR ($CDCl_3$, 400.13 MHz)



13g



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



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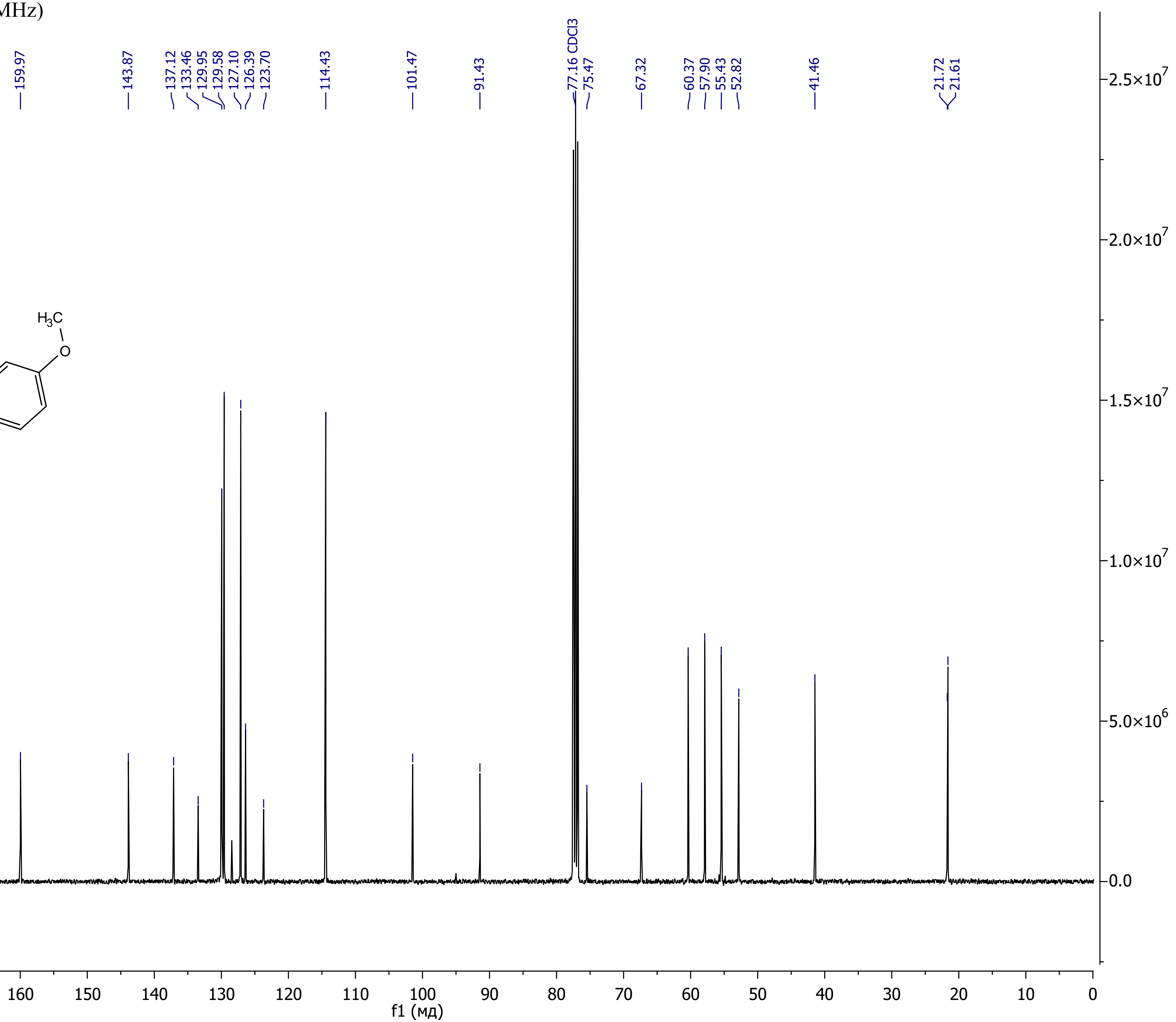
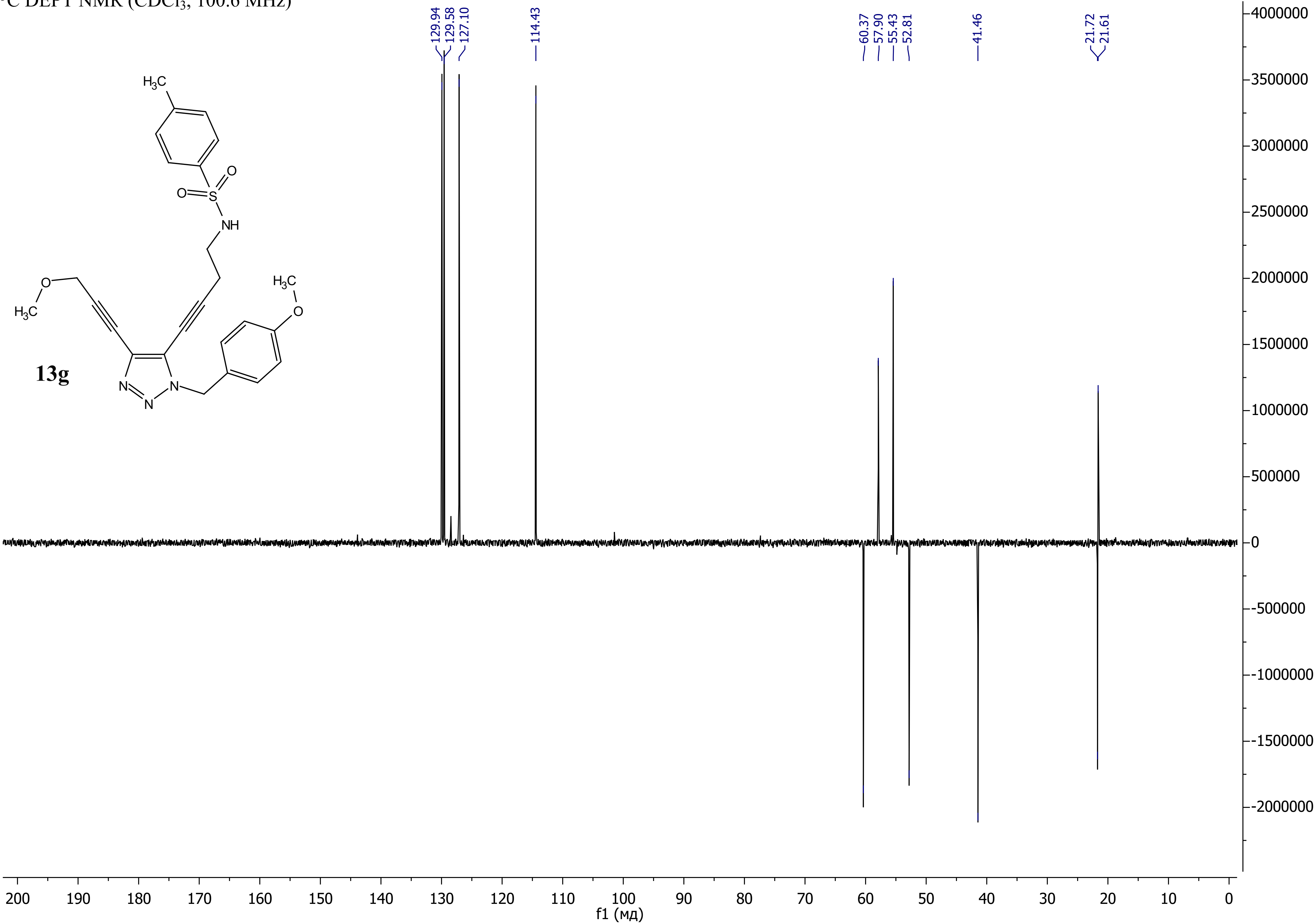


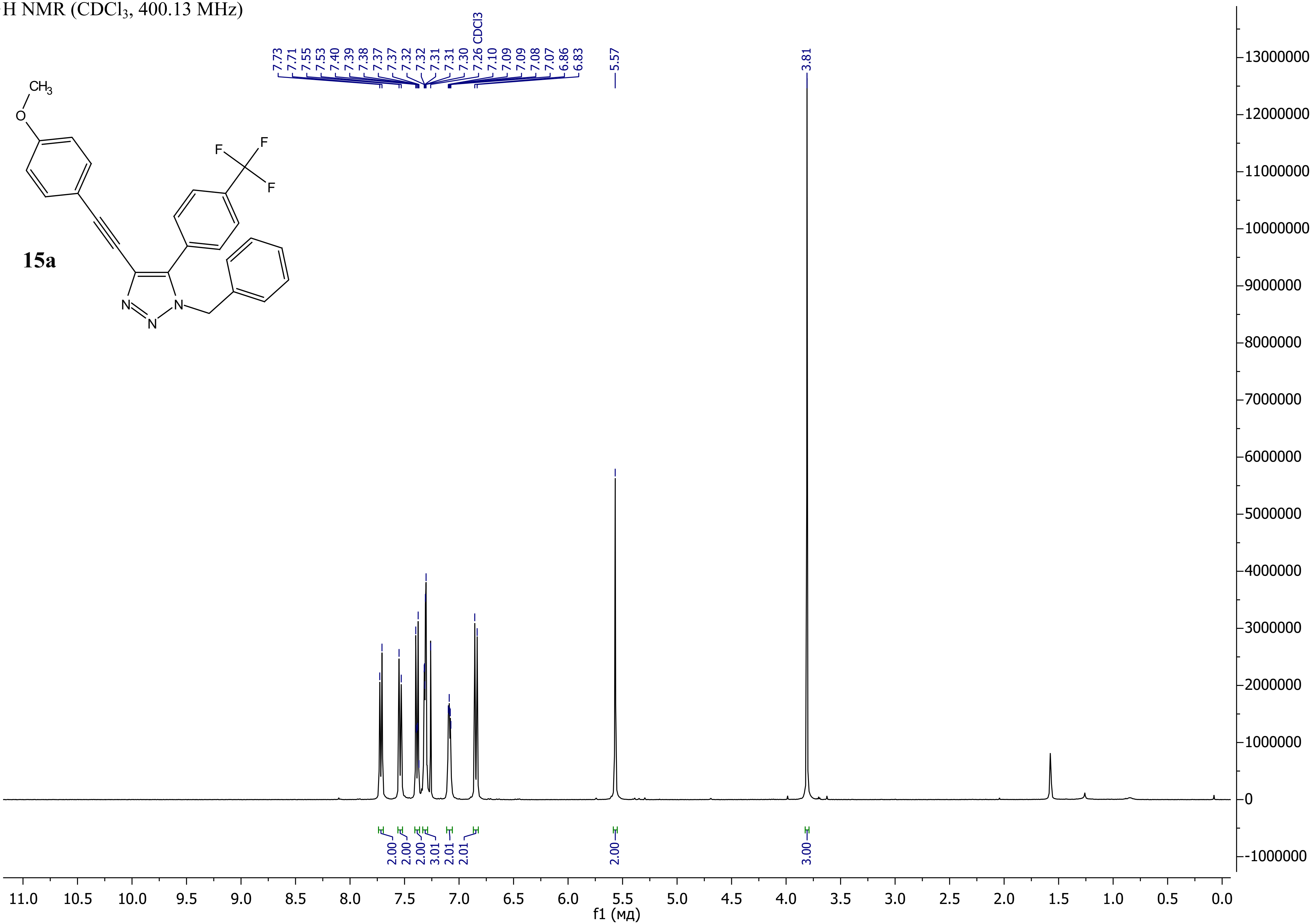
^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



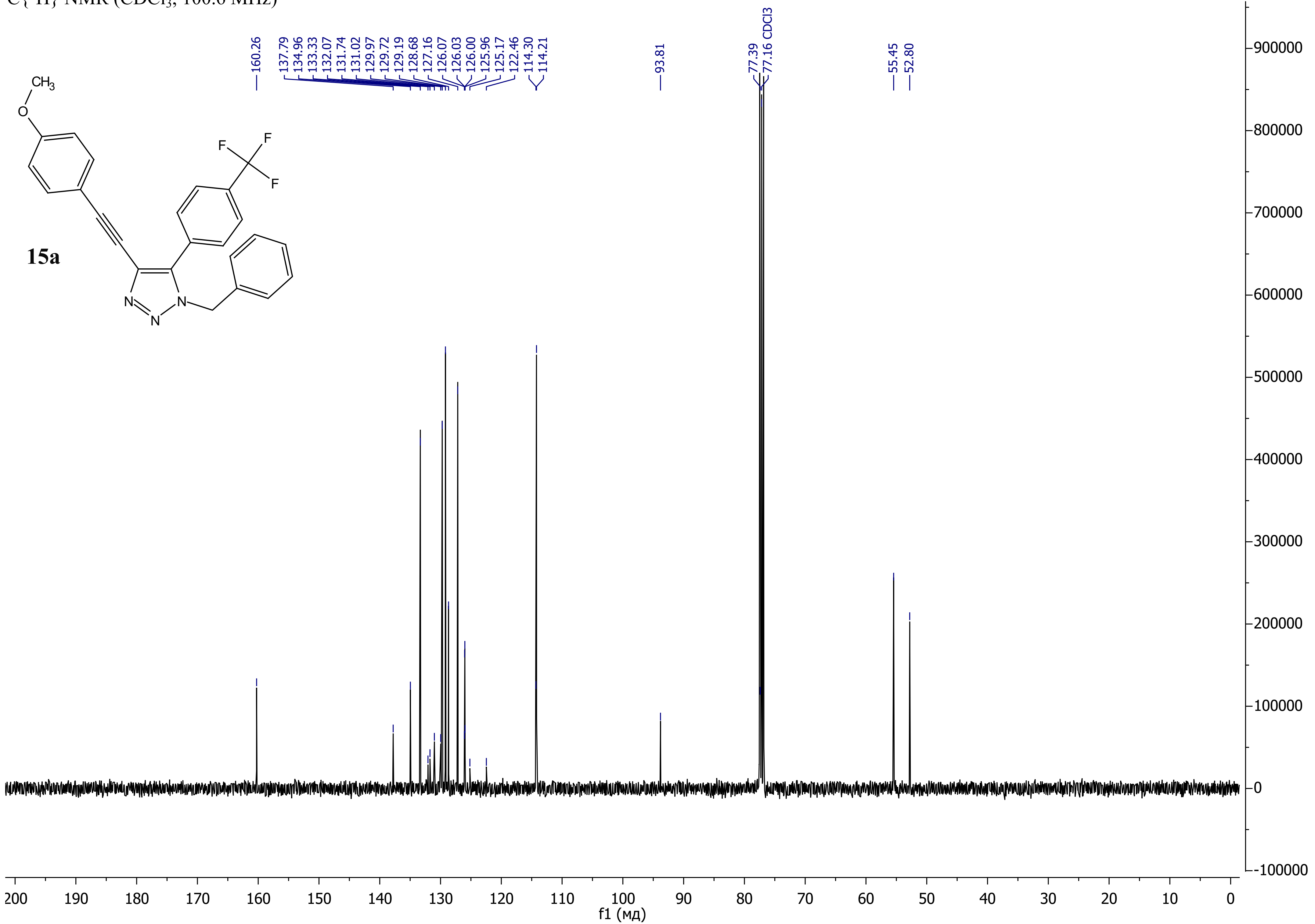
13g

^{1}H NMR ($CDCl_3$, 400.13 MHz)

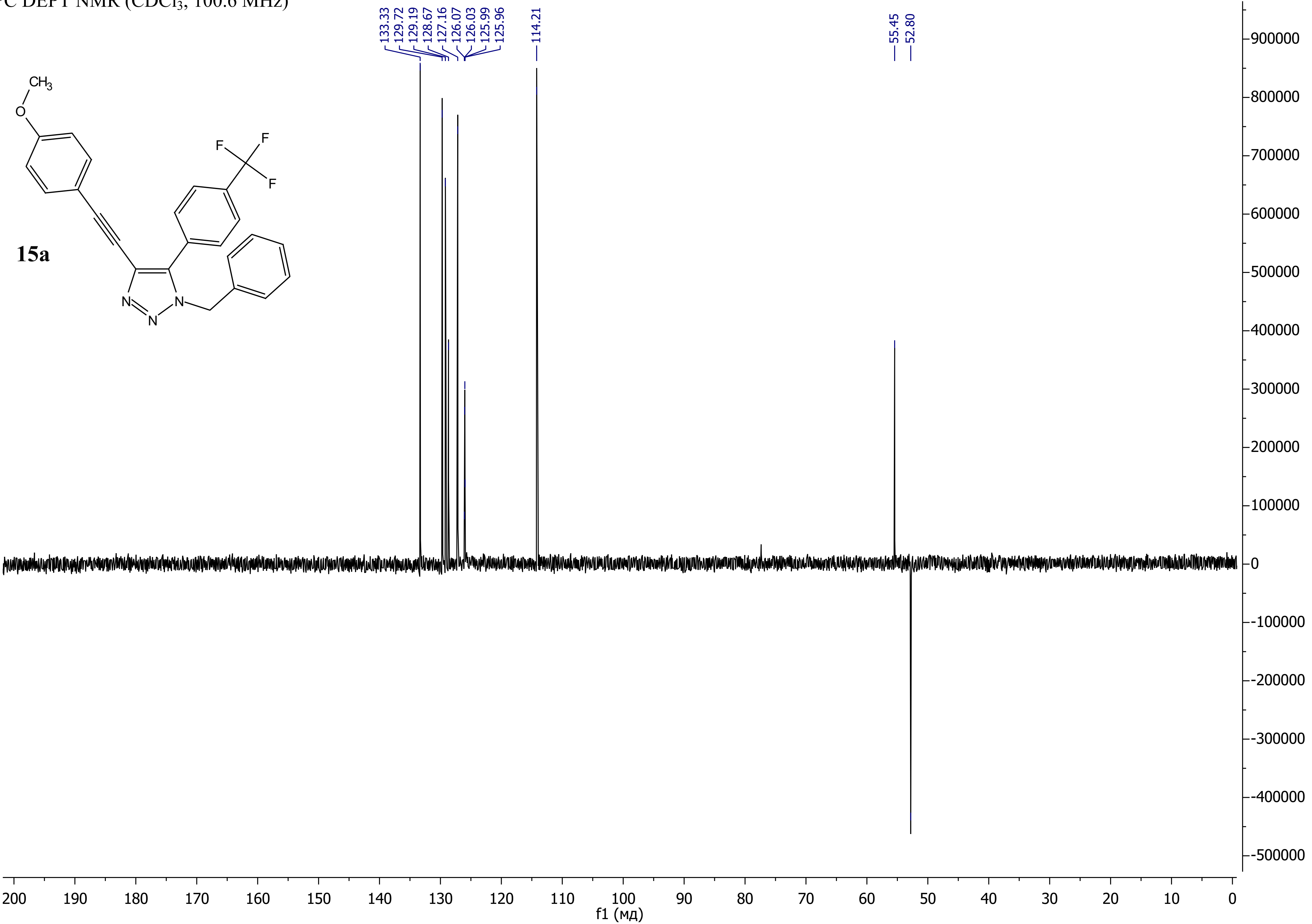
15a



$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz)

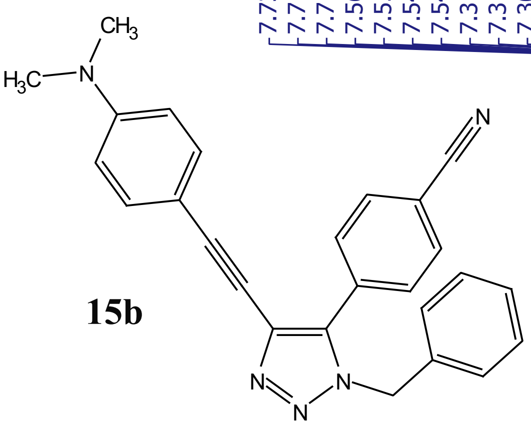


^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)

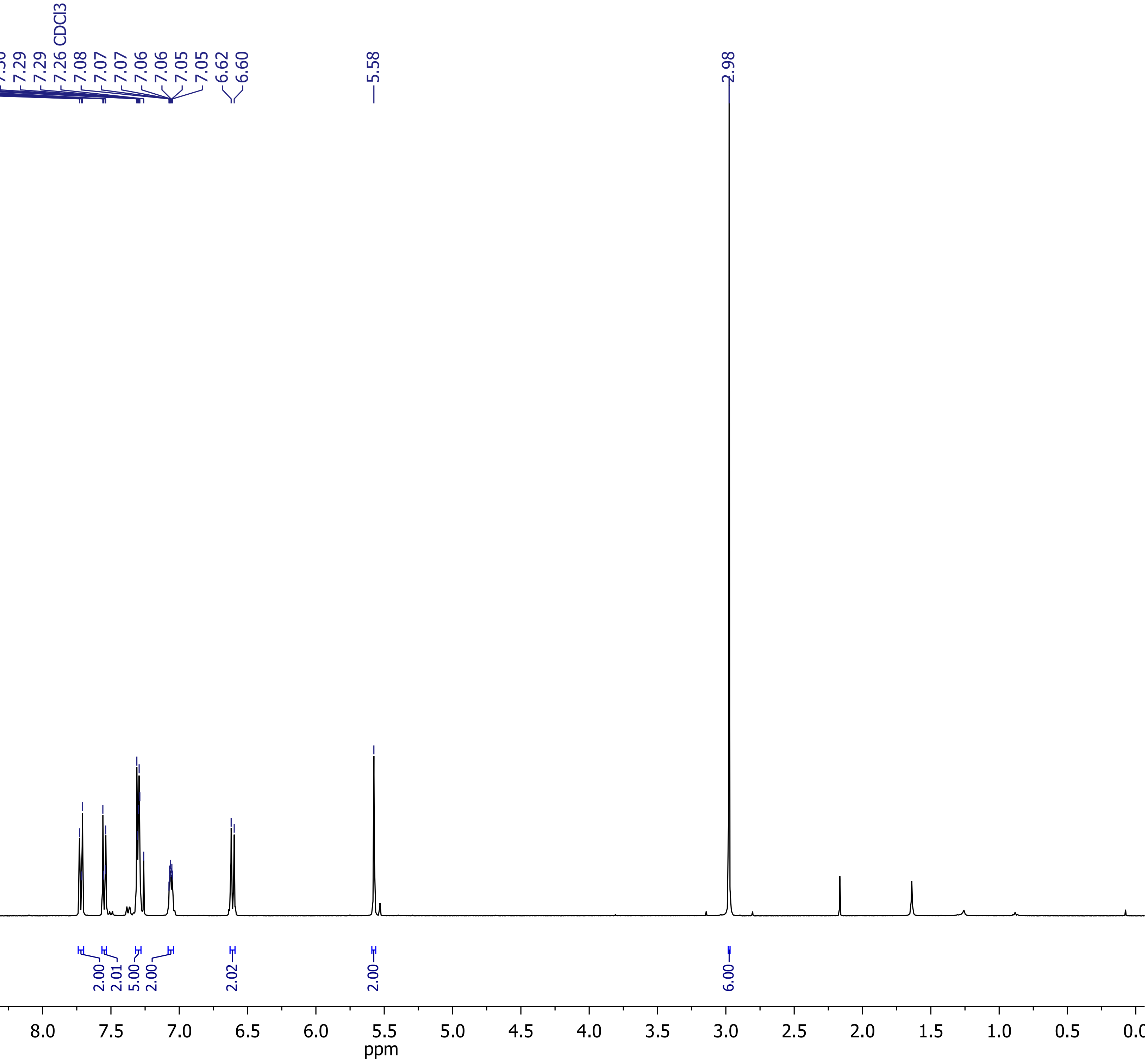


15a

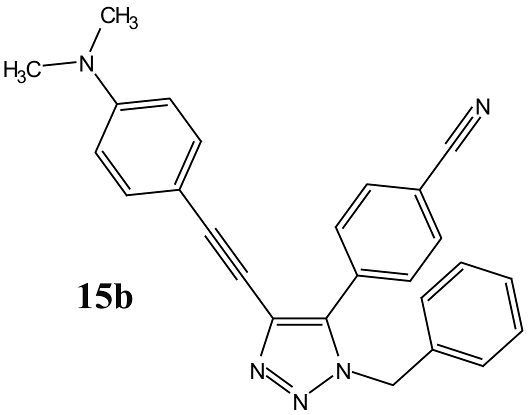
^{1}H NMR ($CDCl_3$, 400.13 MHz)



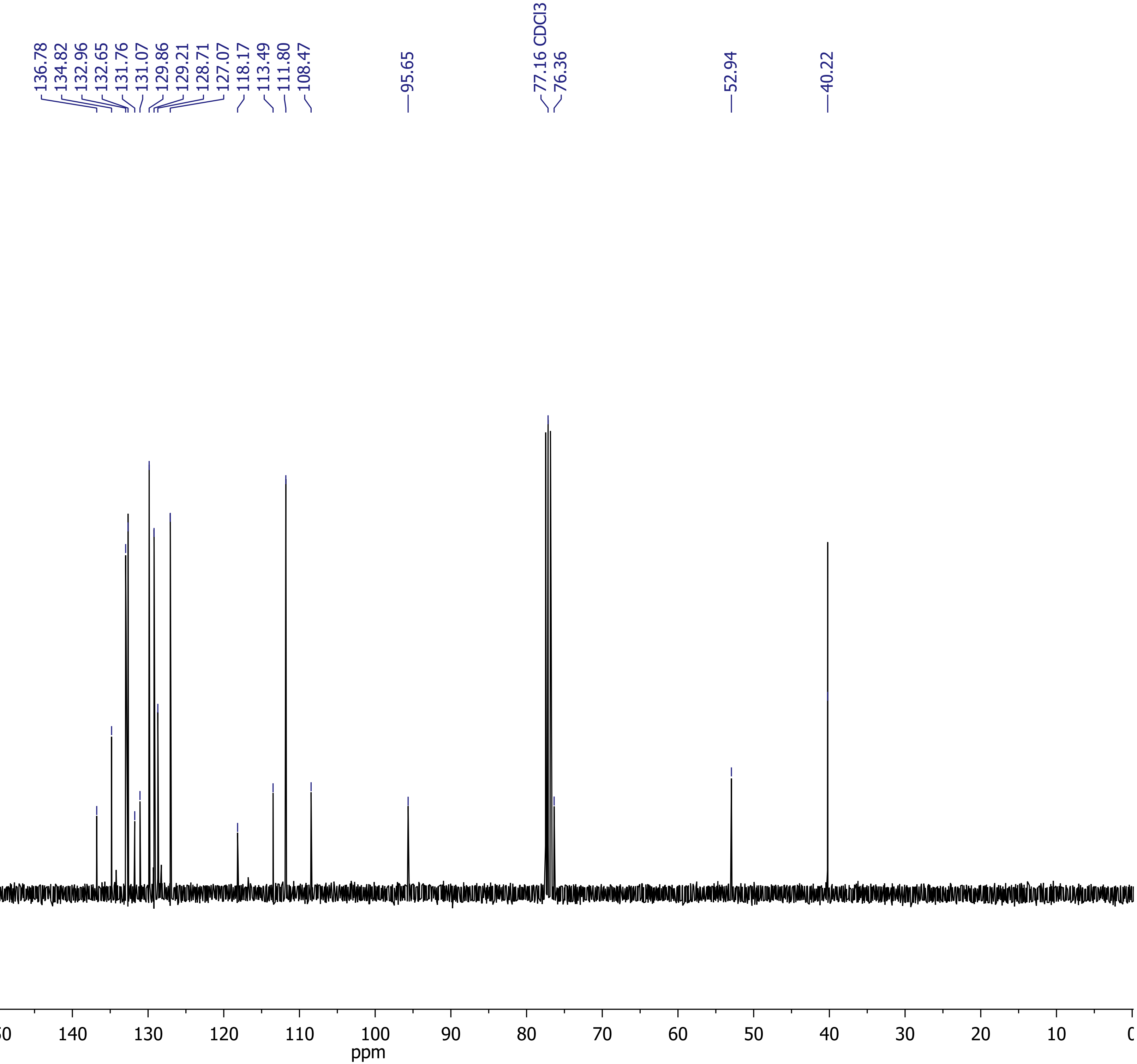
15b



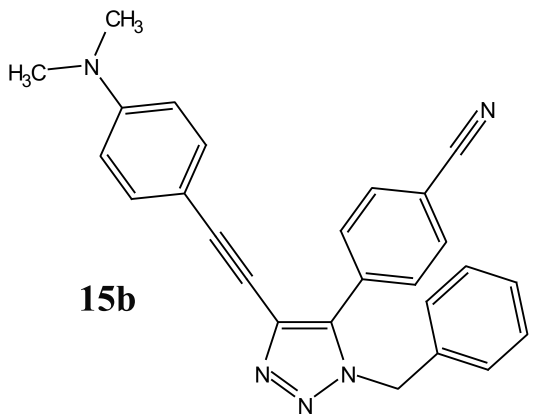
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



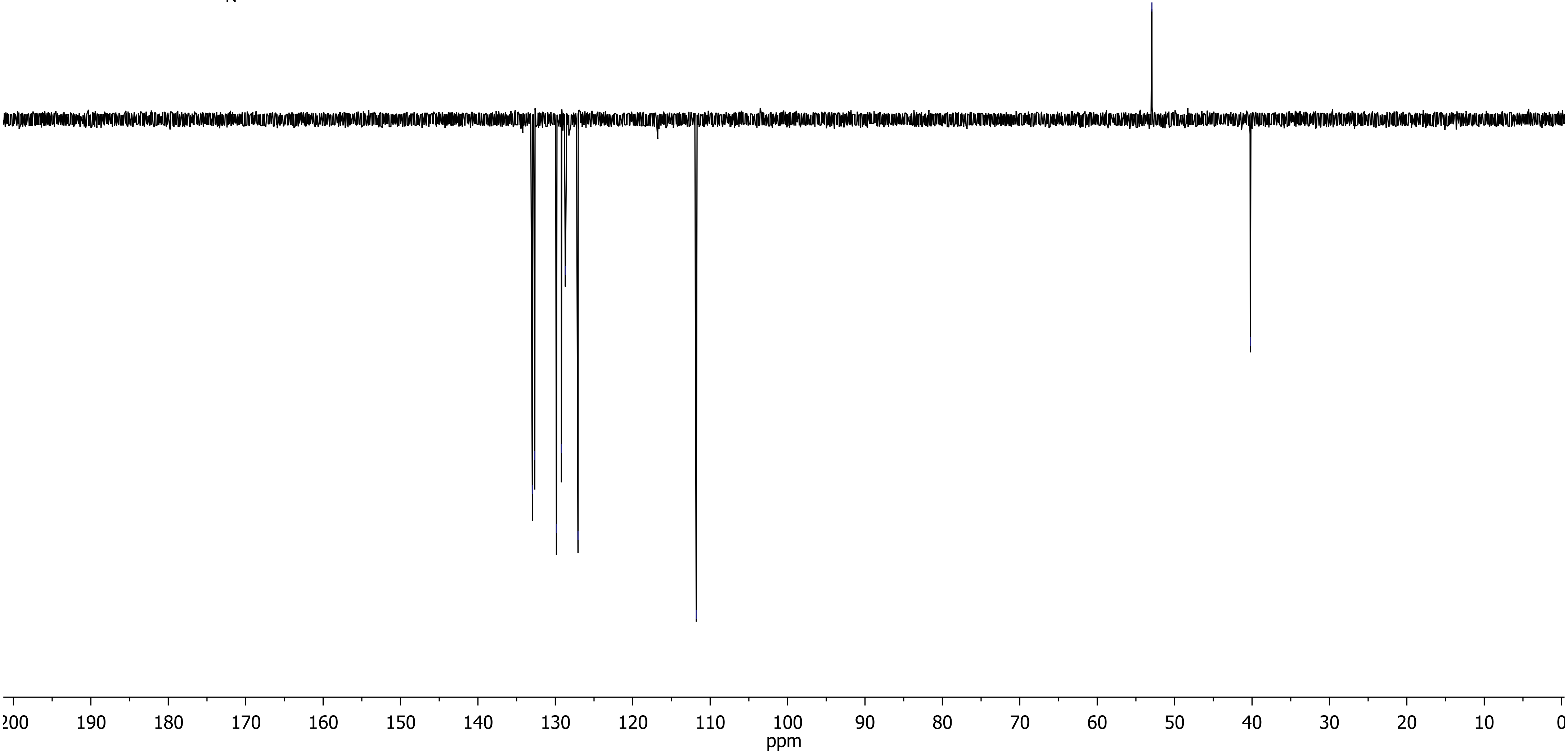
15b



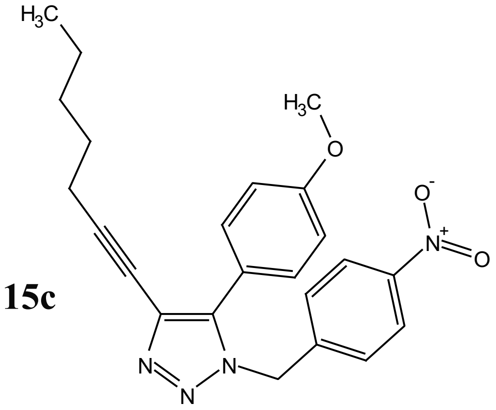
^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



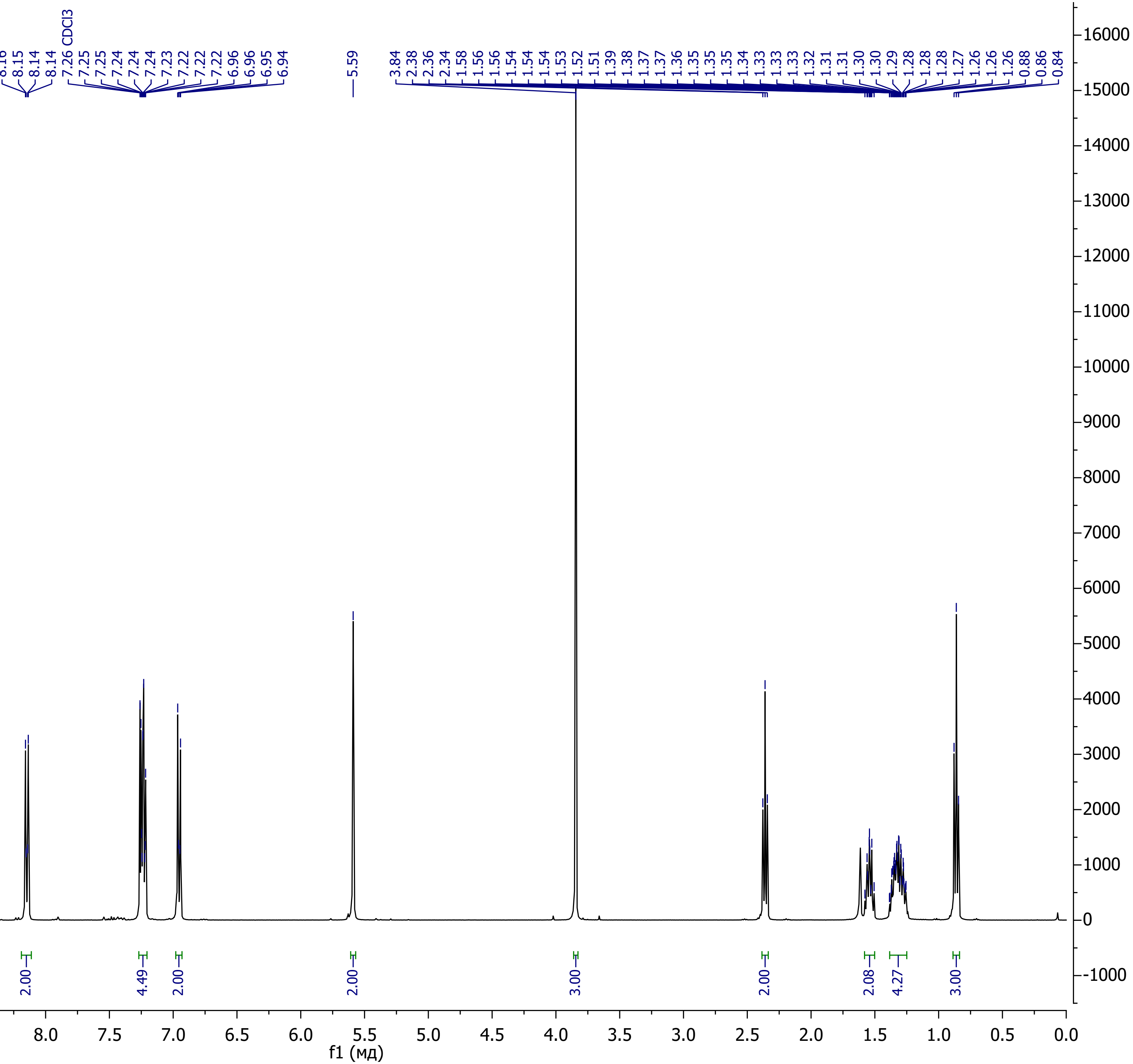
15b



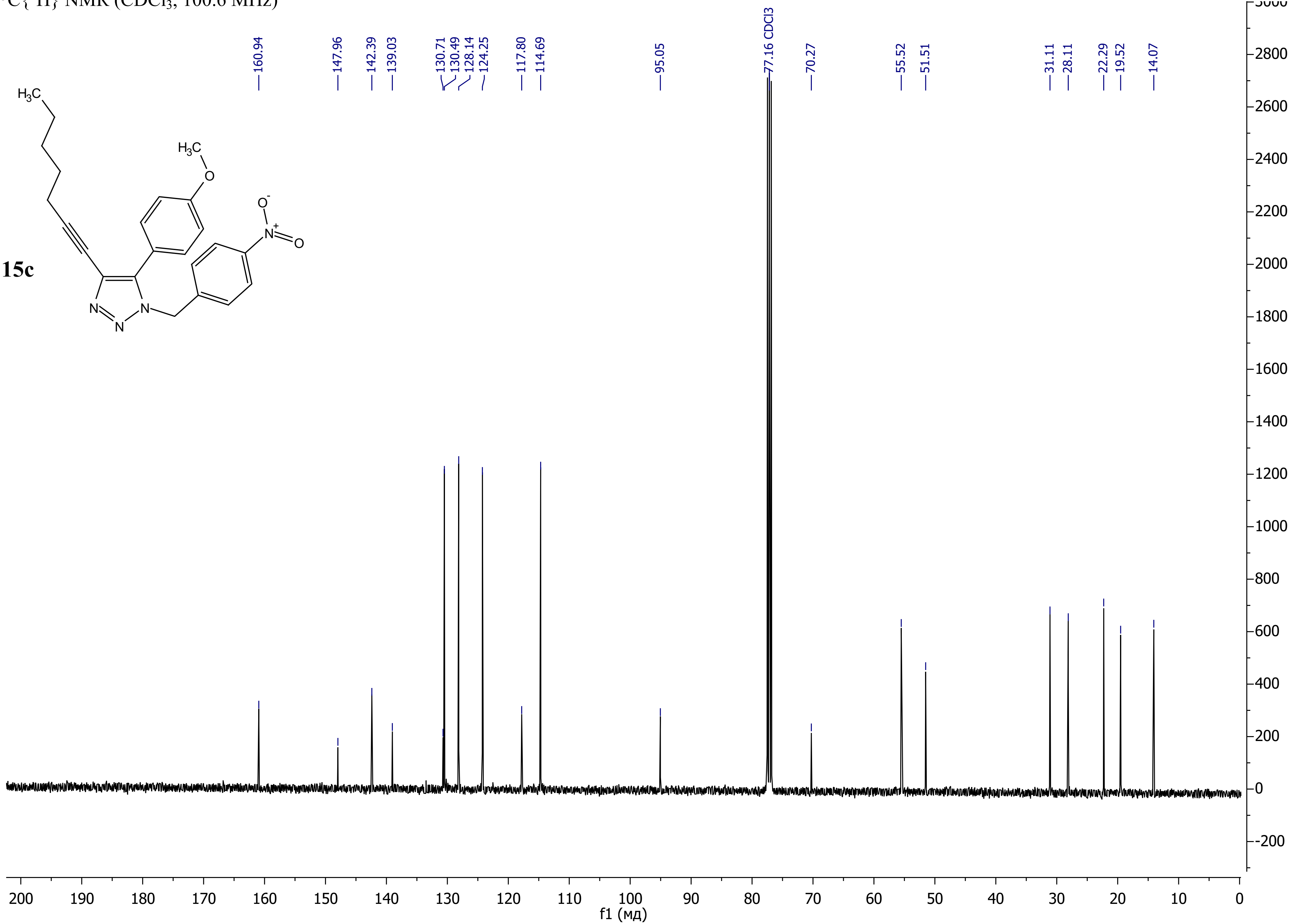
[1]H NMR ($CDCl_3$, 400.13 MHz)



15c

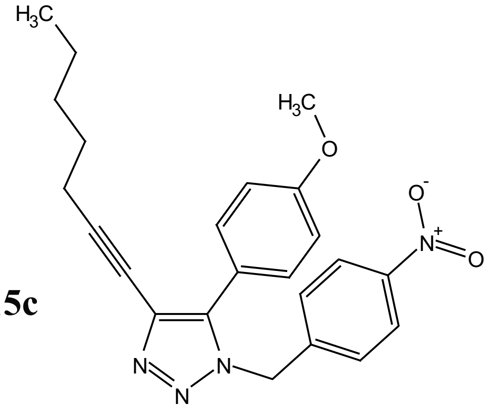


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)

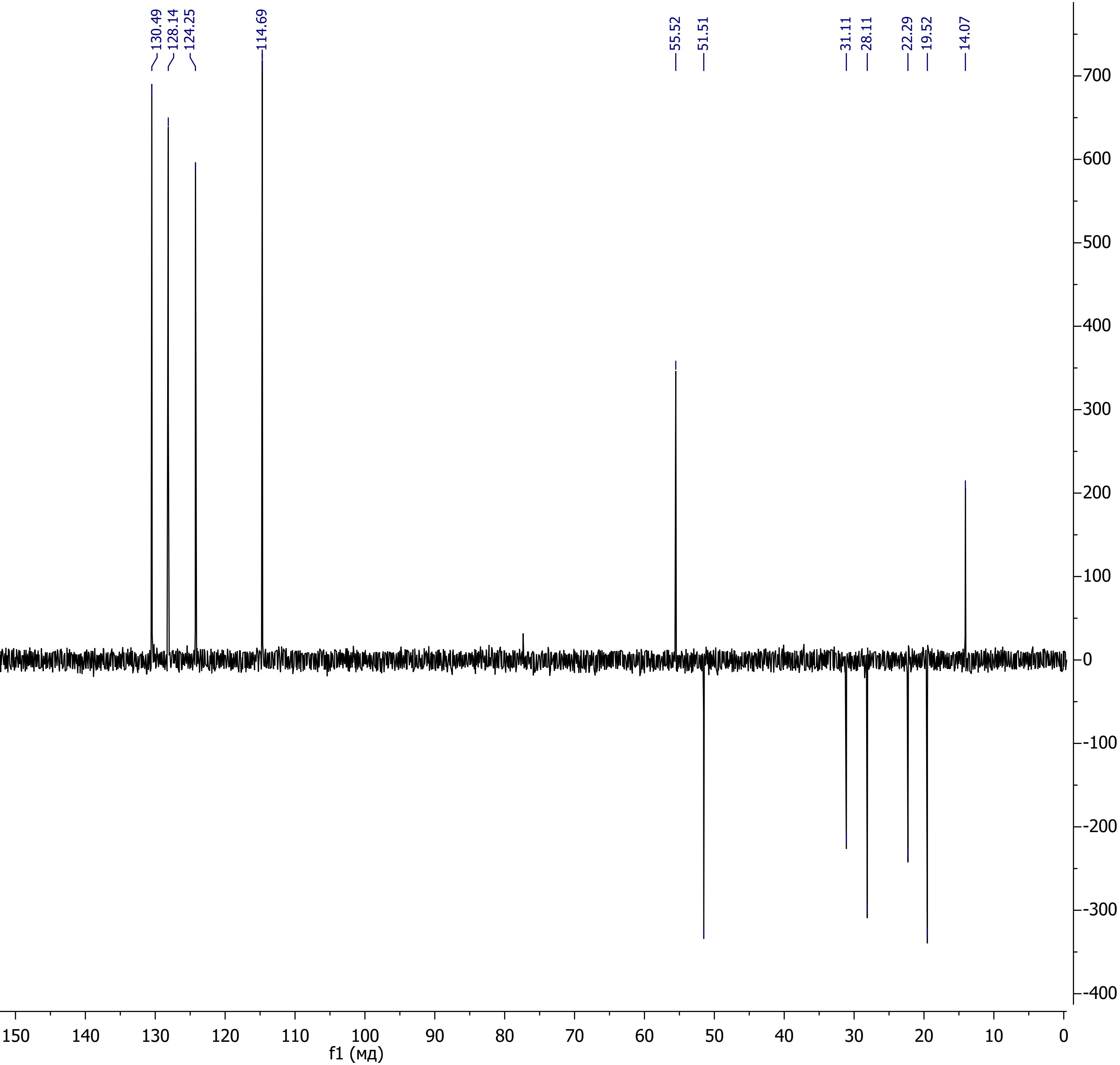


15c

^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)

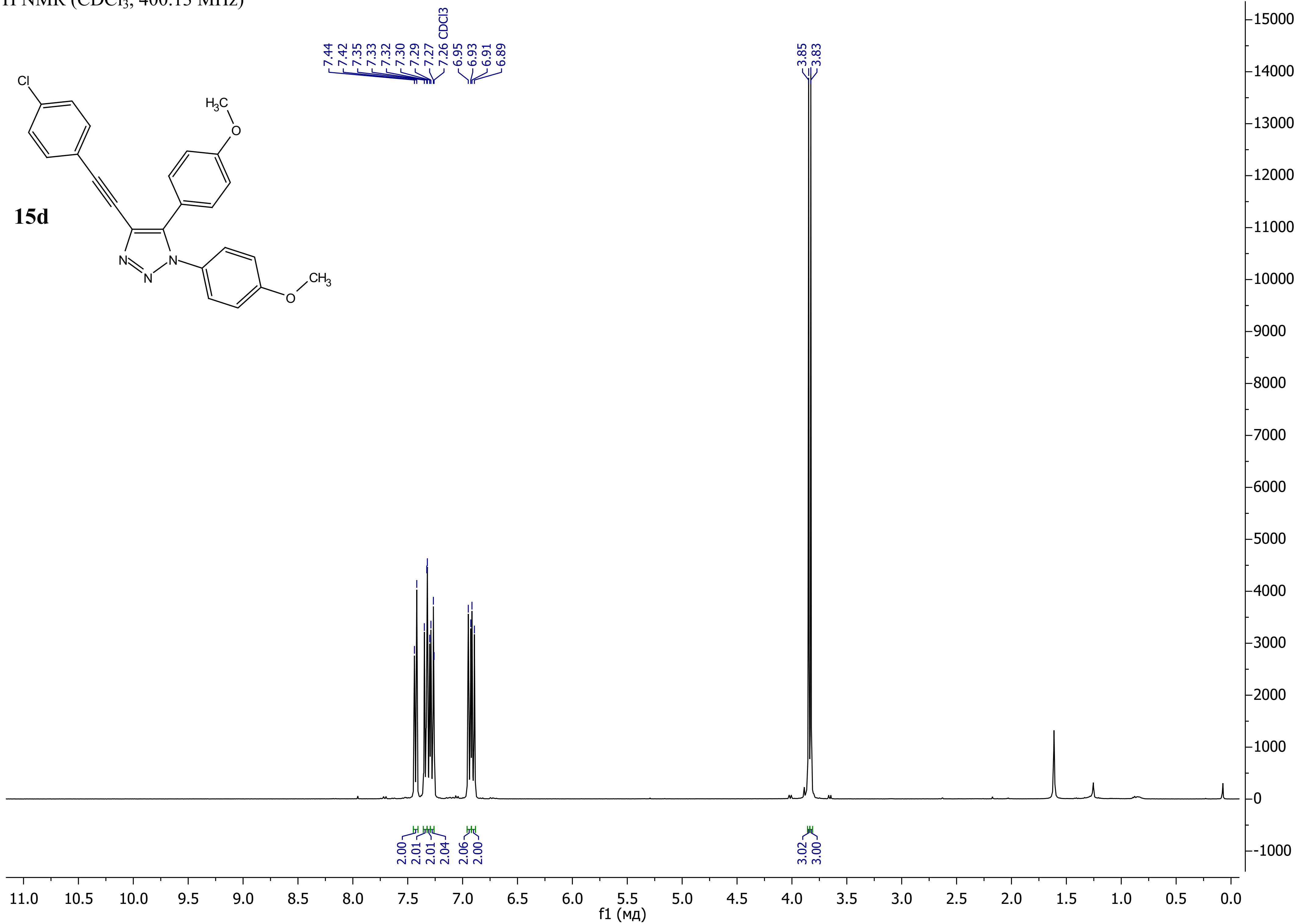


15c



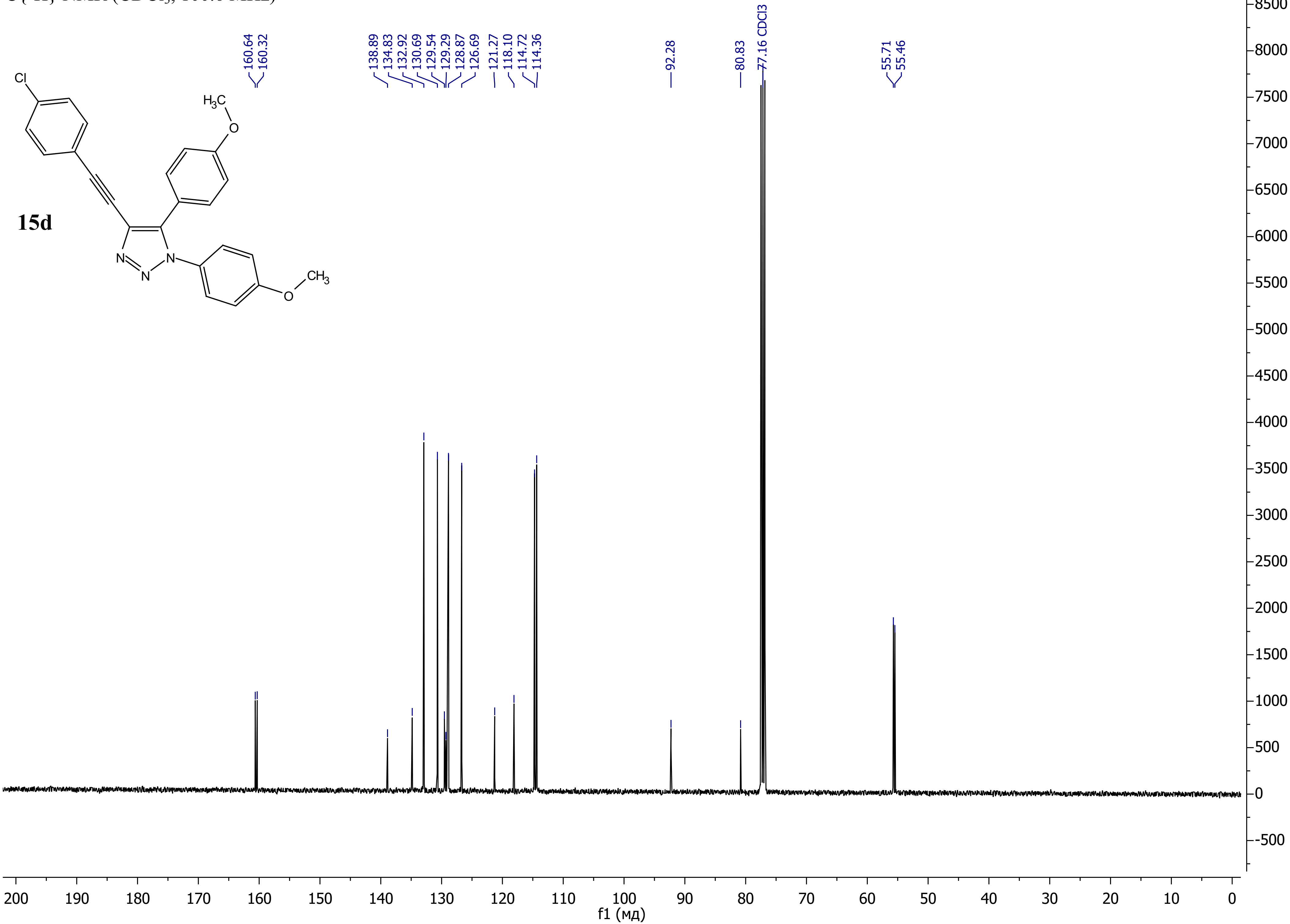
[1]H NMR ($CDCl_3$, 400.13 MHz)

15d

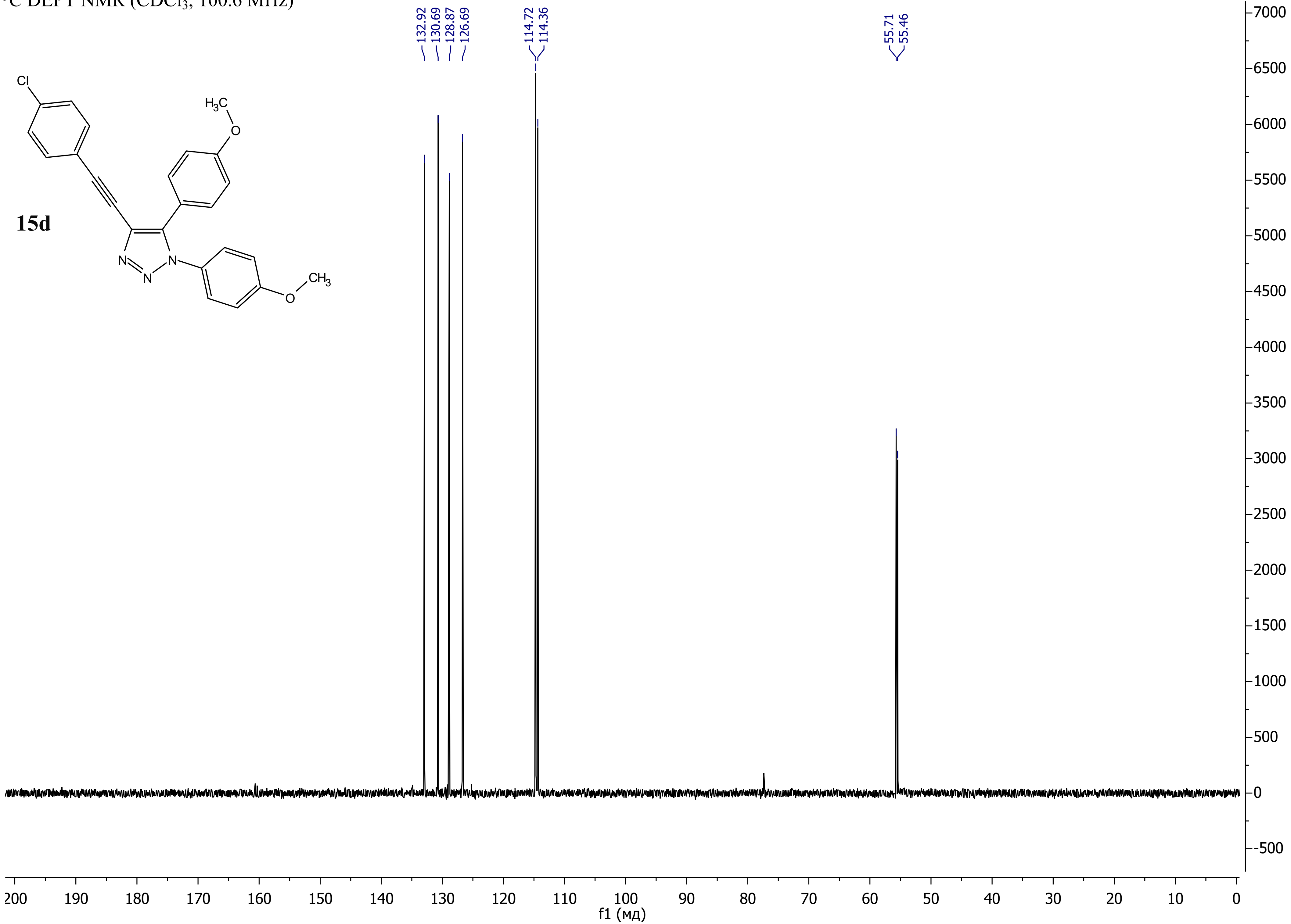


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)

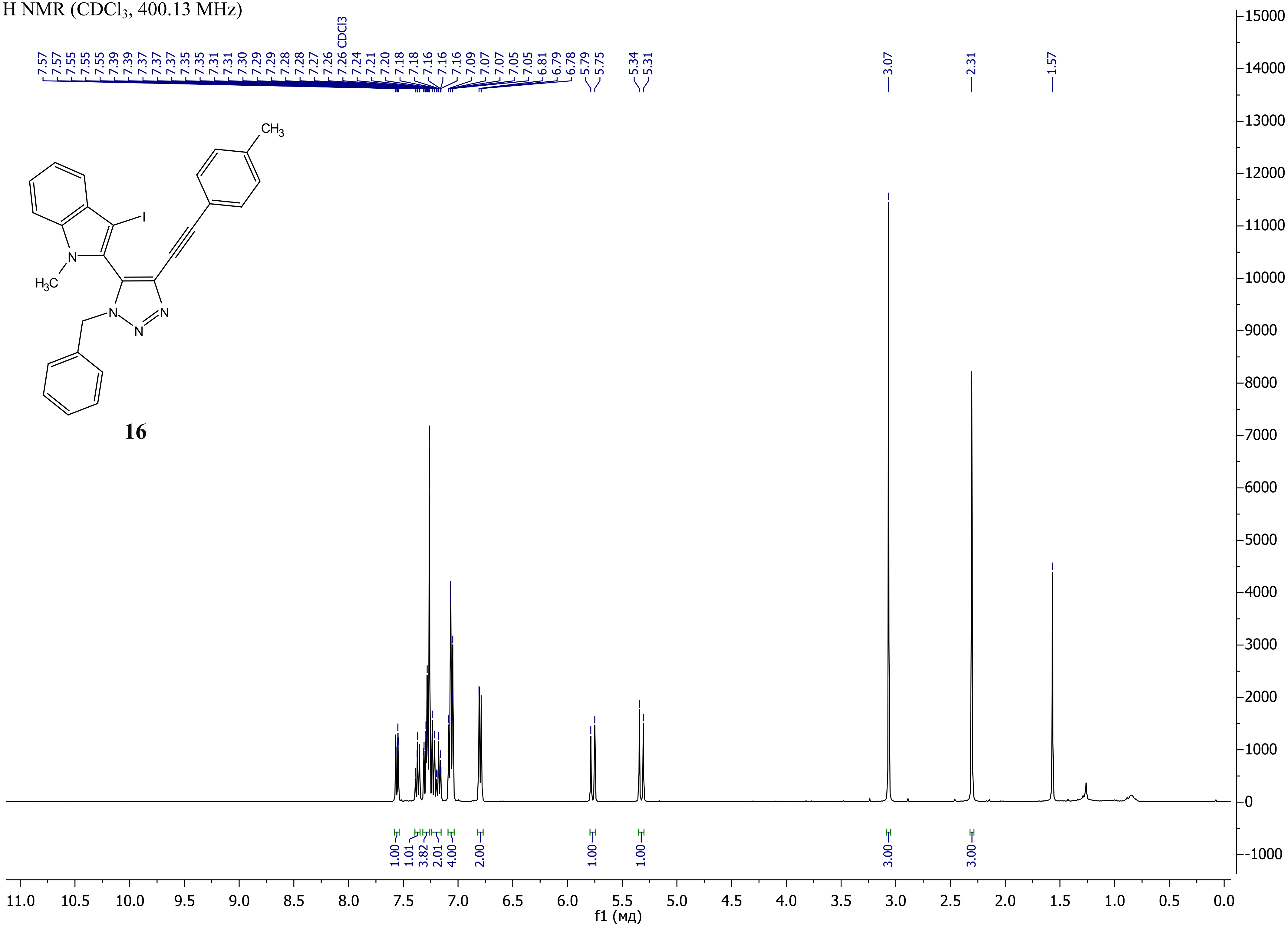
15d



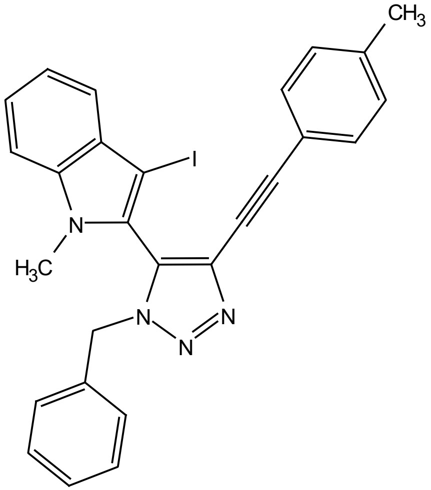
^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)



^{1}H NMR ($CDCl_3$, 400.13 MHz)



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)



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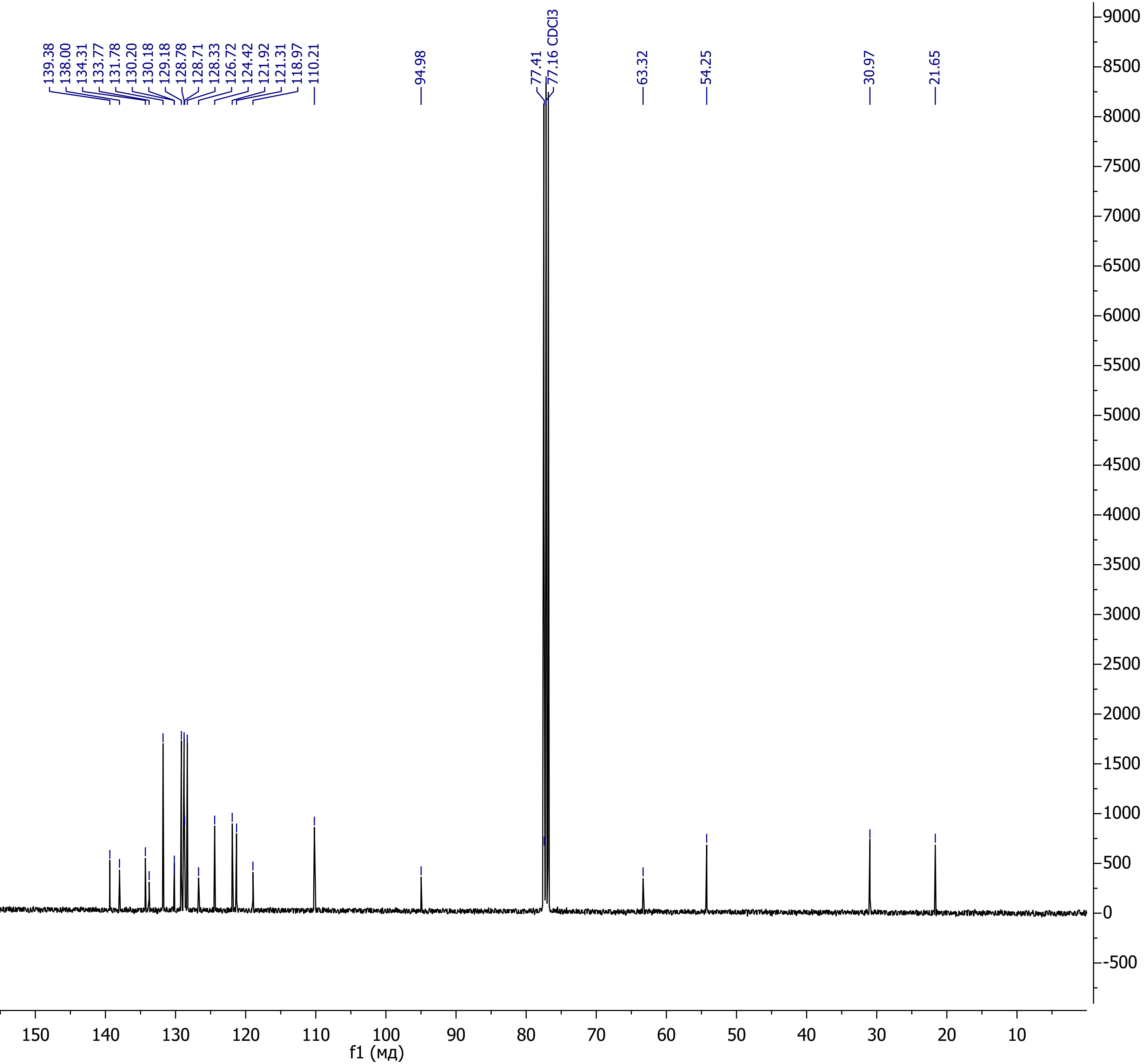

^{13}C DEPT NMR ($CDCl_3$, 100.6 MHz)