SUPPORTING INFORMATION

Heterocyclic and Open-chain Carboranes via Transition Metal-free C–H Functionalization of Mono- and Diazine-N-oxides

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^{1}H, ^{11}B, and ^{13}C NMR Spectra

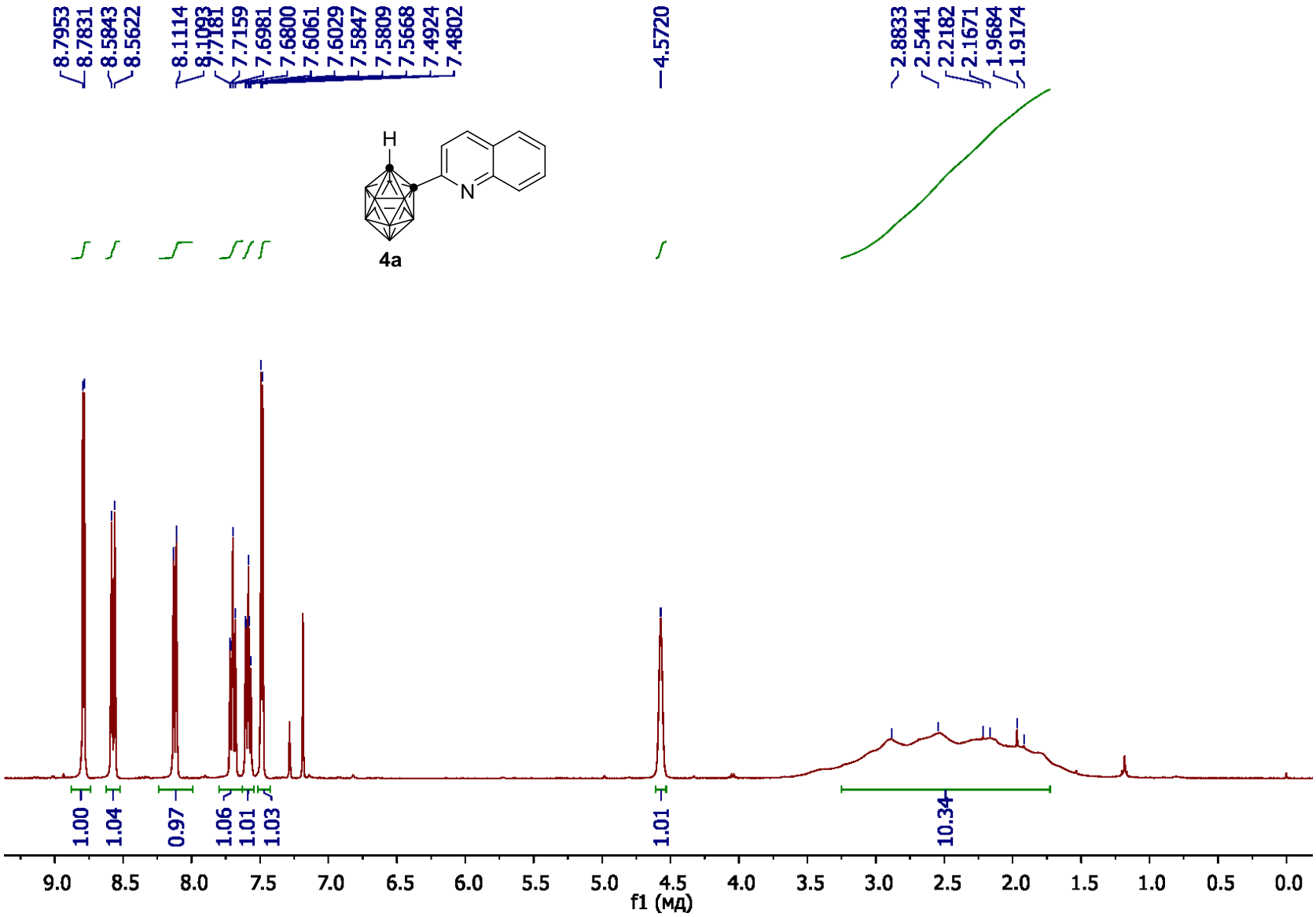

Figure S1. ^{1}H NMR Spectrum of 1-(quinolin-2-yl)-1,2-*closo*-dodecaborane **4a**

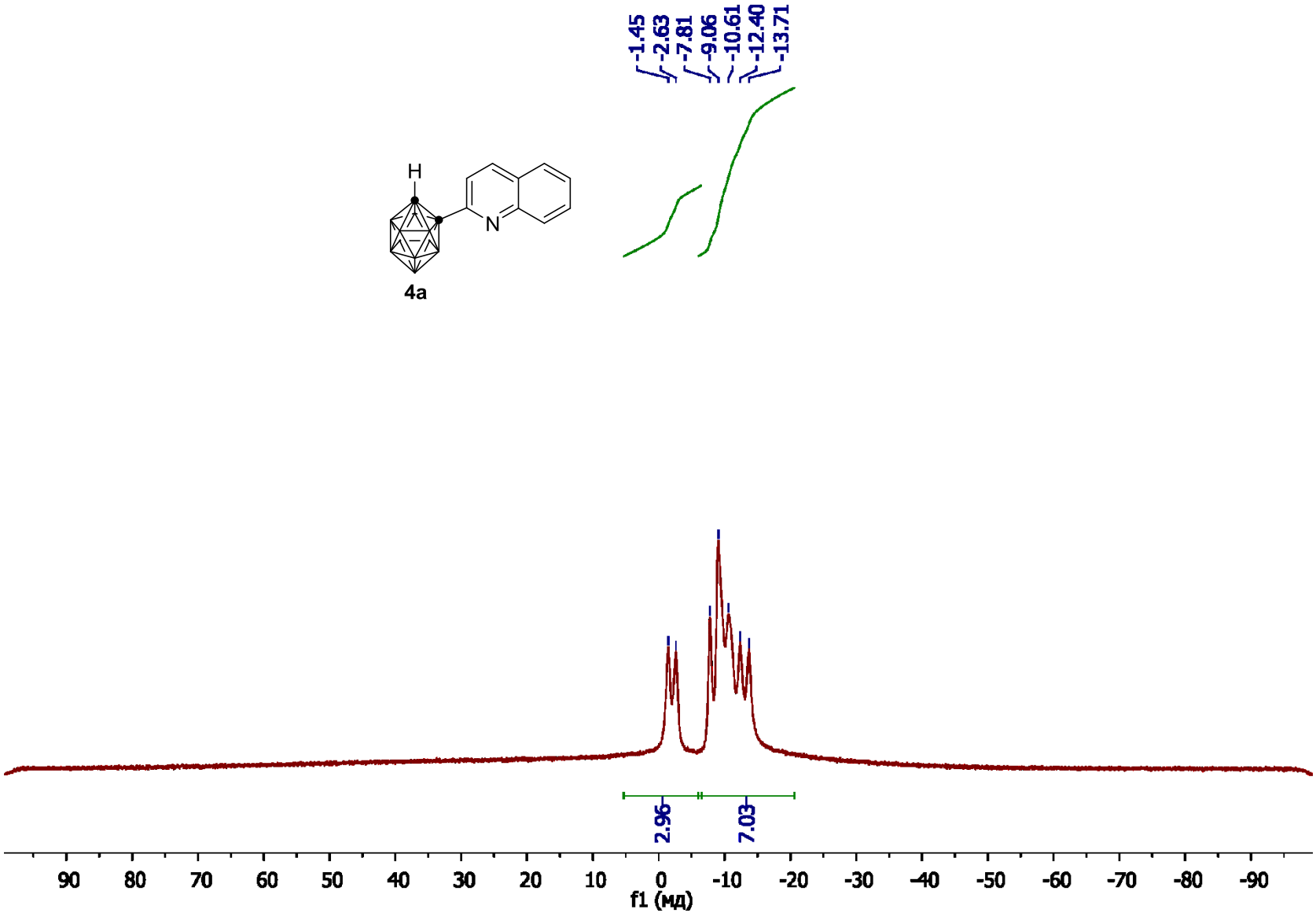

Figure S2. ^{11}B NMR Spectrum of 1-(quinolin-2-yl)-1,2-*closo*-dodecaborane **4a**

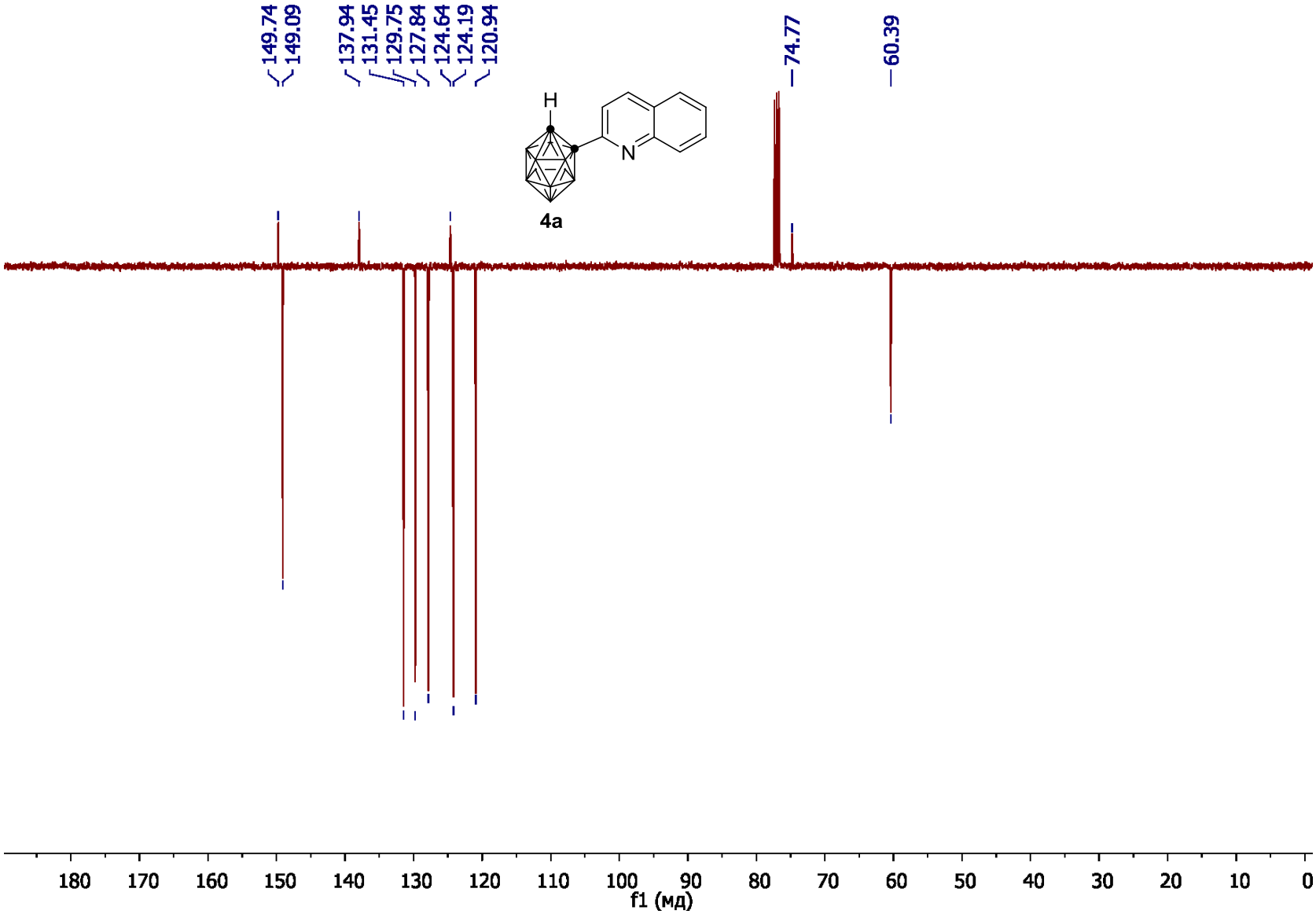

Figure S3. ^{13}C NMR Spectrum (APT) of 1-(quinolin-2-yl)-1,2-*closo*-dodecaborane **4a**

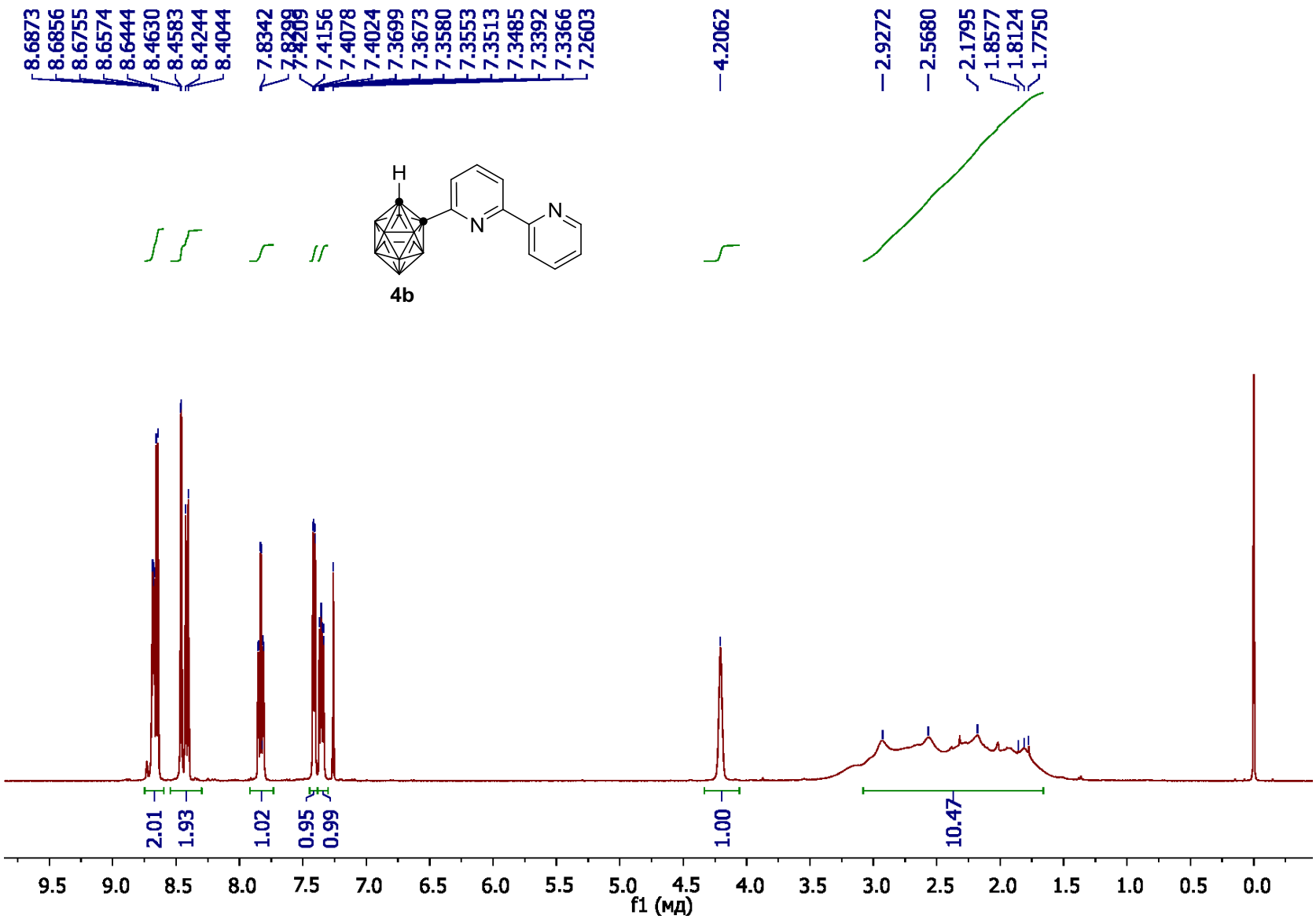

Figure S4. ^{1}H NMR Spectrum of 1-(2,2'-bipyridin-6-yl)-1,2-*closo*-dodecaborane **4b**

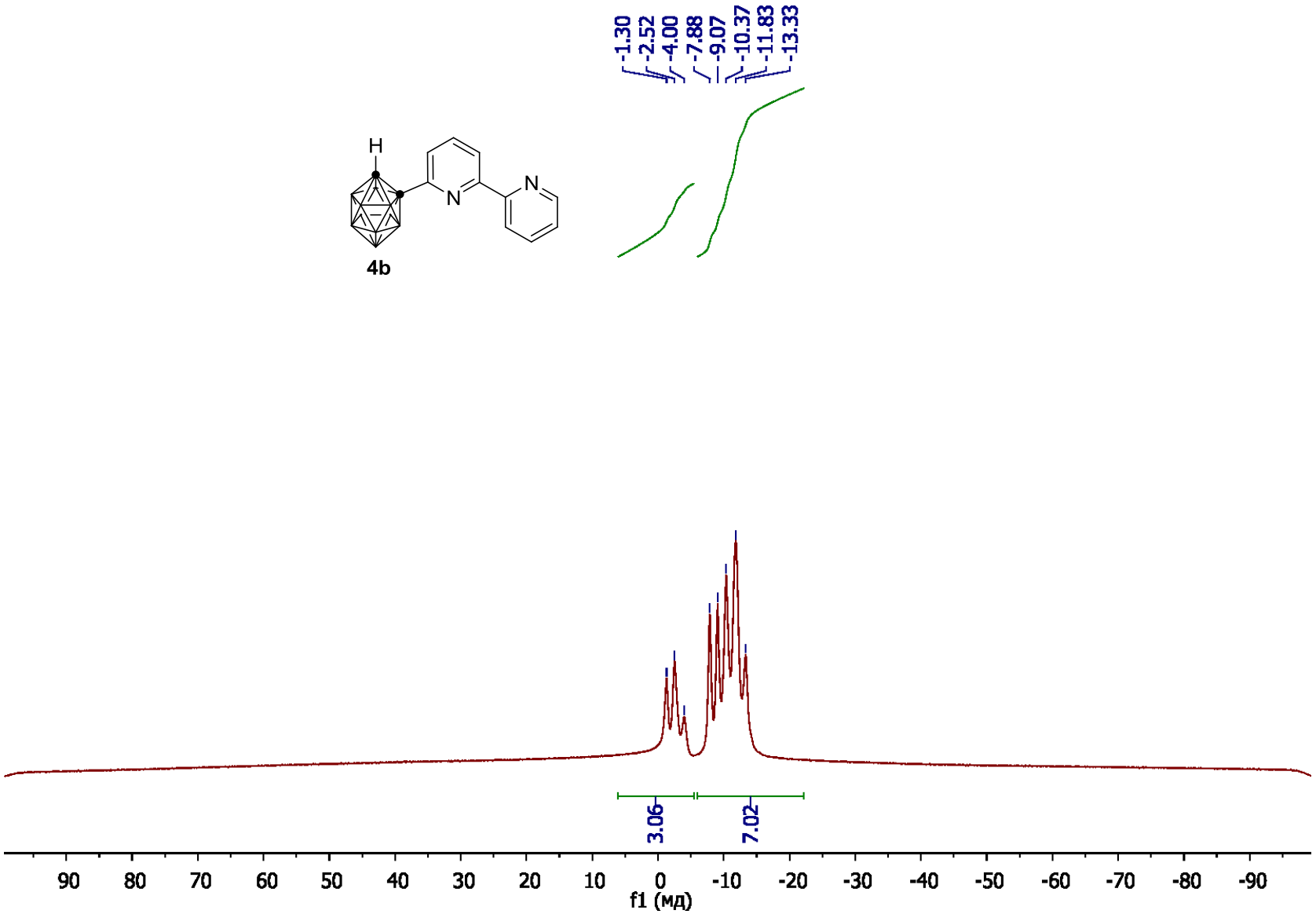

Figure S5. ^{11}B NMR Spectrum of 1-(2,2'-bipyridin-6-yl)-1,2-*closo*-dodecaborane (**4b**)

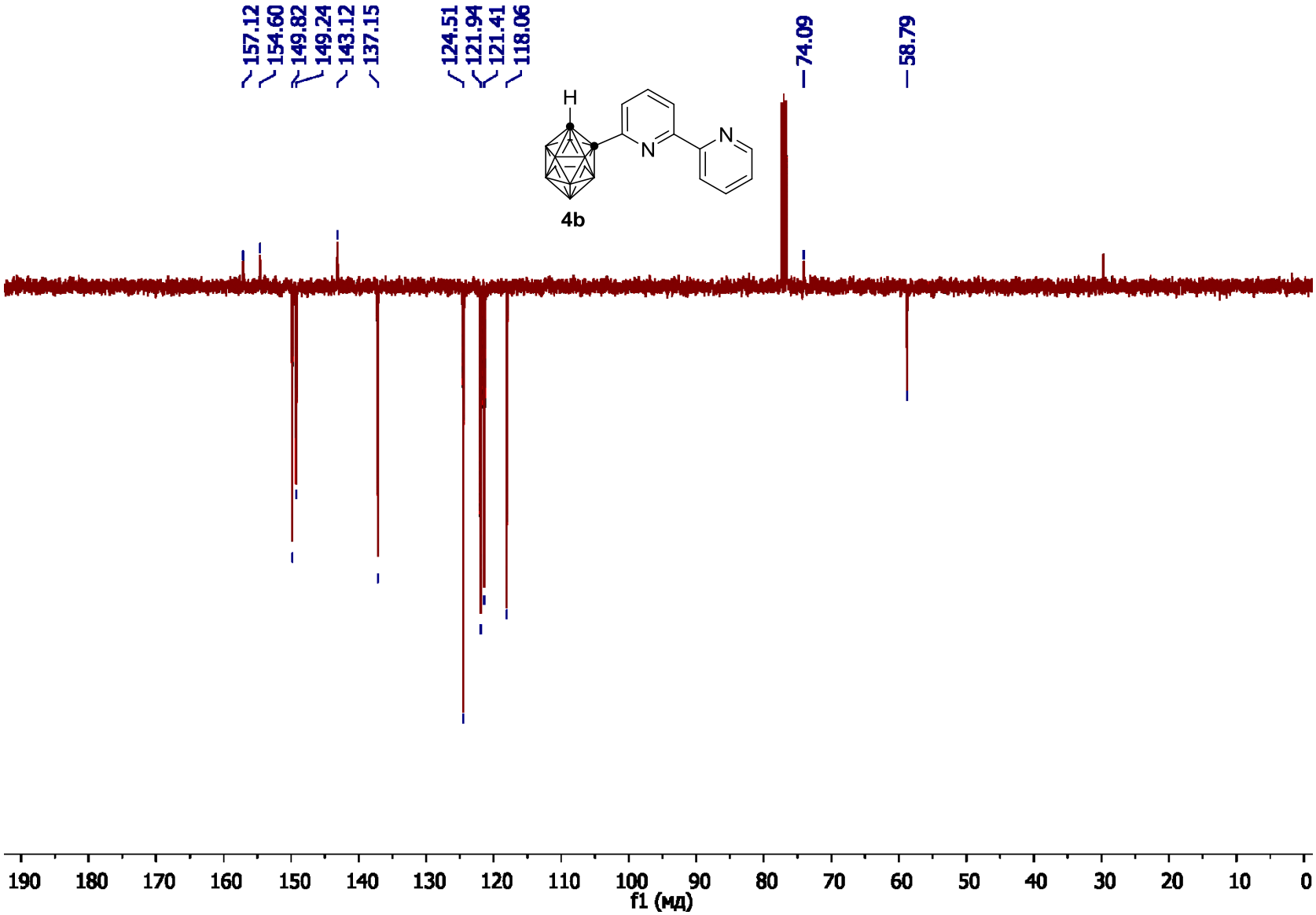

Figure S6. ^{13}C NMR Spectrum (APT) of 1-(2,2'-bipyridin-6-yl)-1,2-*closo*-dodecaborane (**4b**)

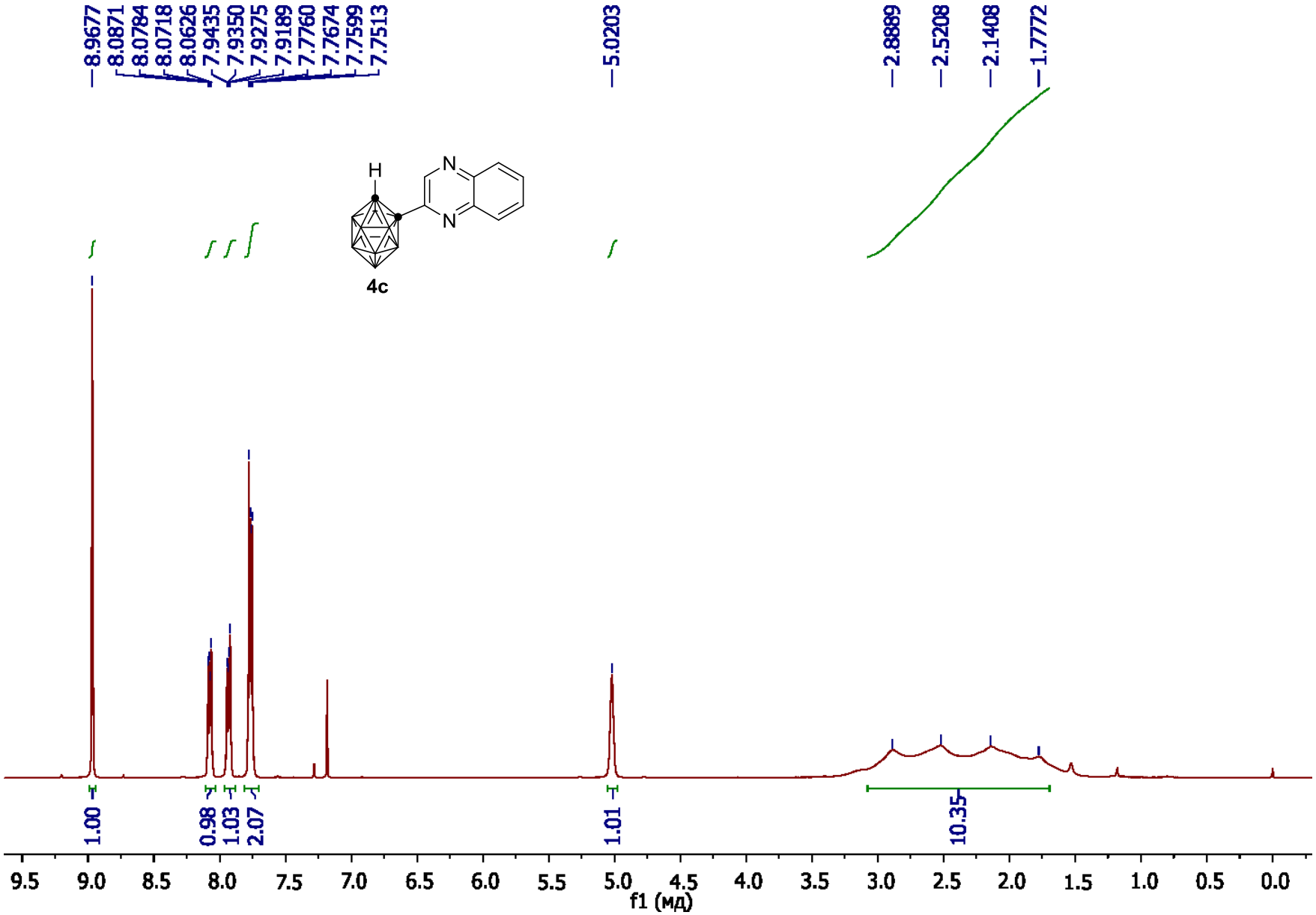

Figure S7. ^{1}H NMR Spectrum of 1-(quinoxalin-2-yl)-1,2-*closo*-dodecaborane (**4c**)

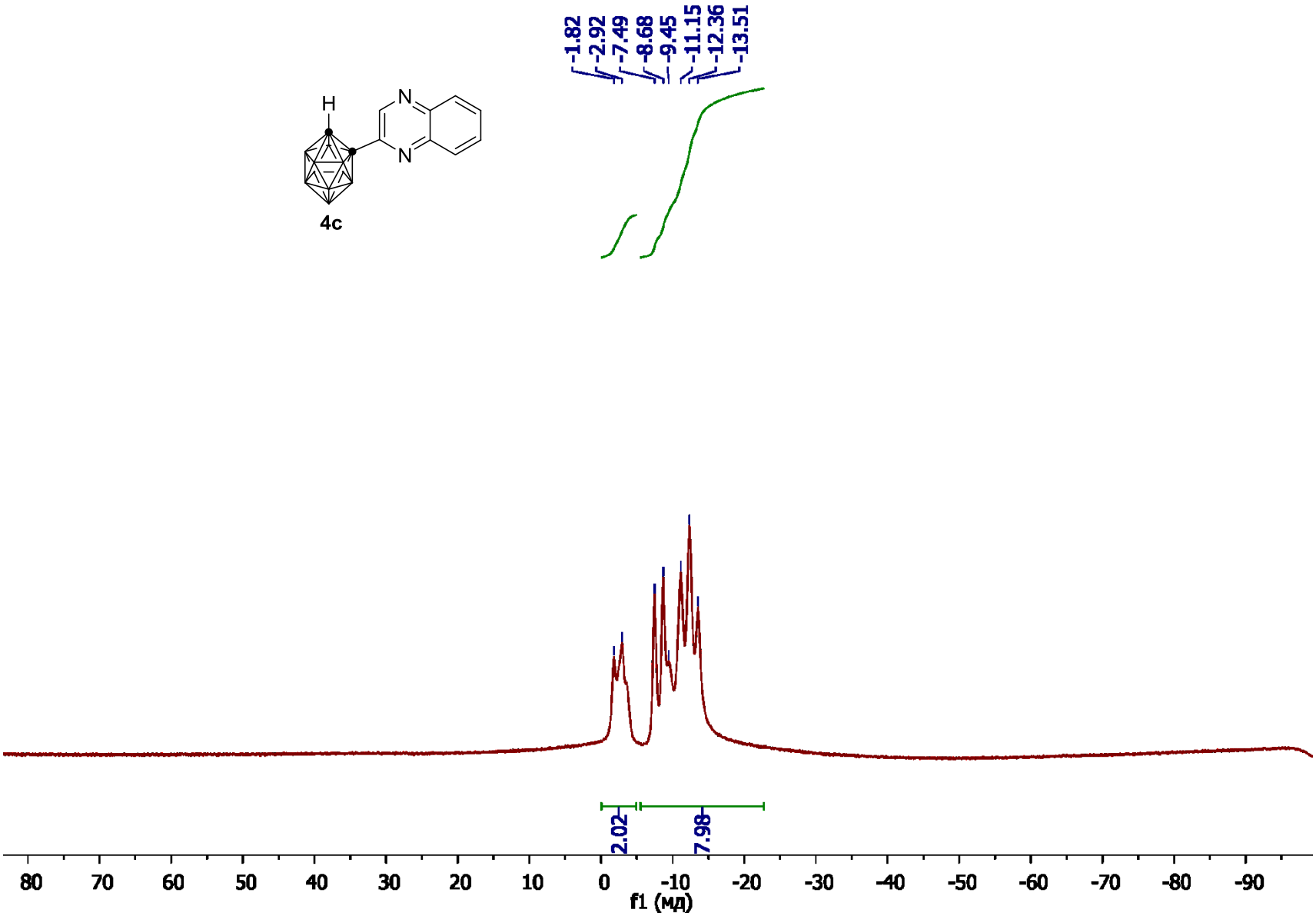

Figure S8. ^{11}B NMR Spectrum of 1-(quinoxalin-2-yl)-1,2-*closo*-dodecaborane (**4c**)

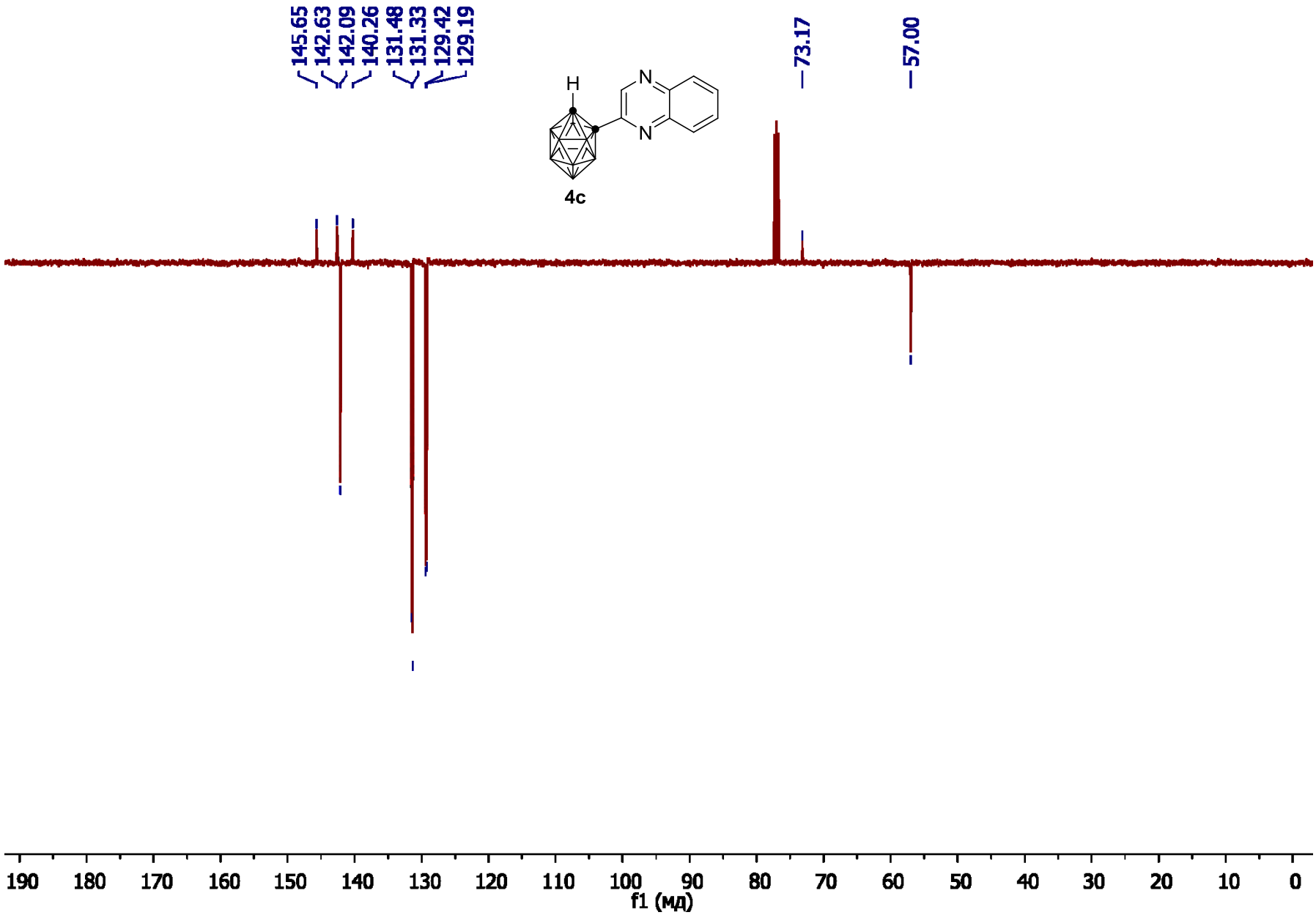

Figure S9. ^{13}C NMR Spectrum (APT) of 1-(quinoxalin-2-yl)-1,2-*closo*-dodecaborane (**4c**)

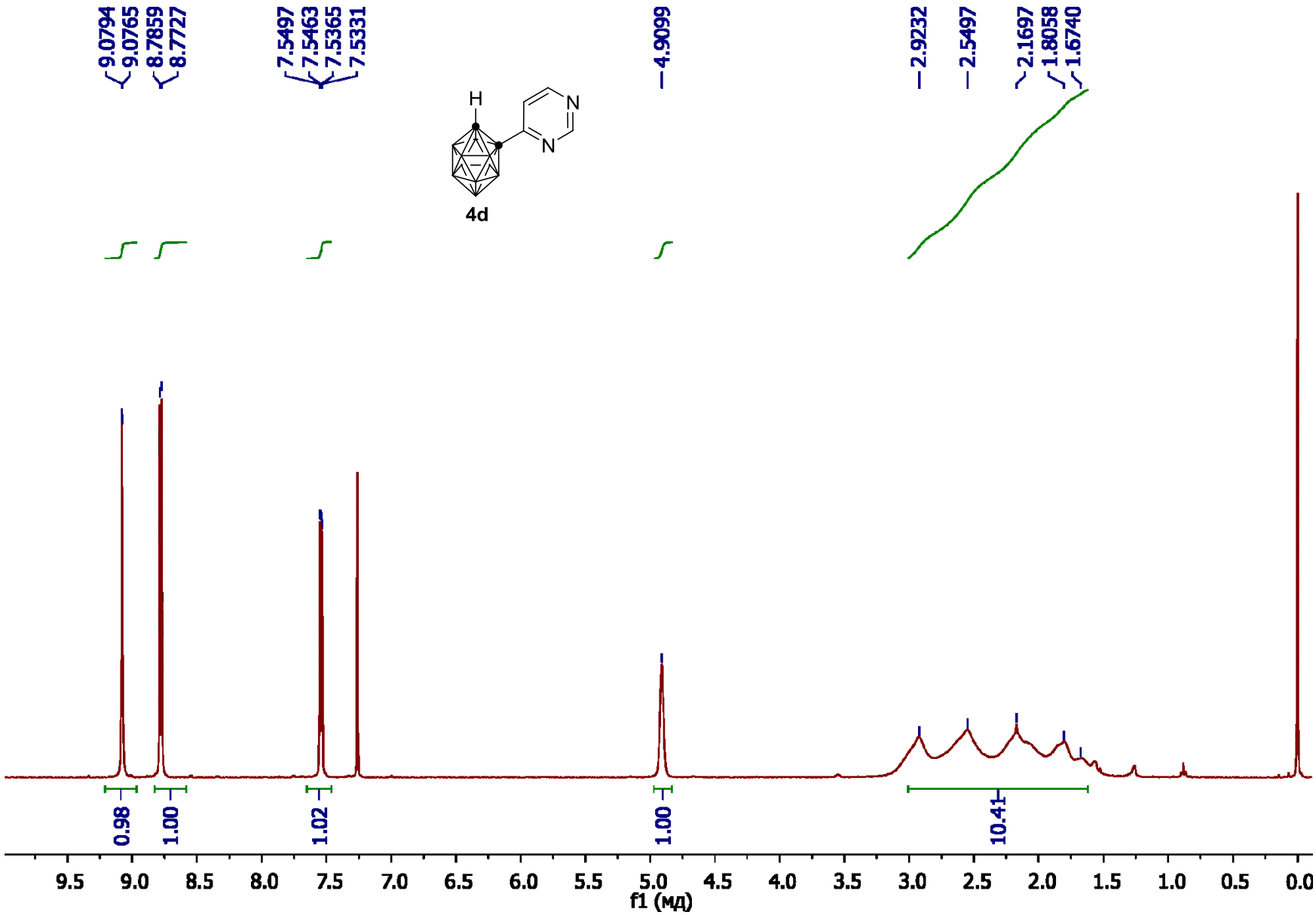

Figure S10. ^{1}H NMR Spectrum of 1-(pyrimidin-4-yl)-1,2-*closo*-dodecaborane (**4d**)

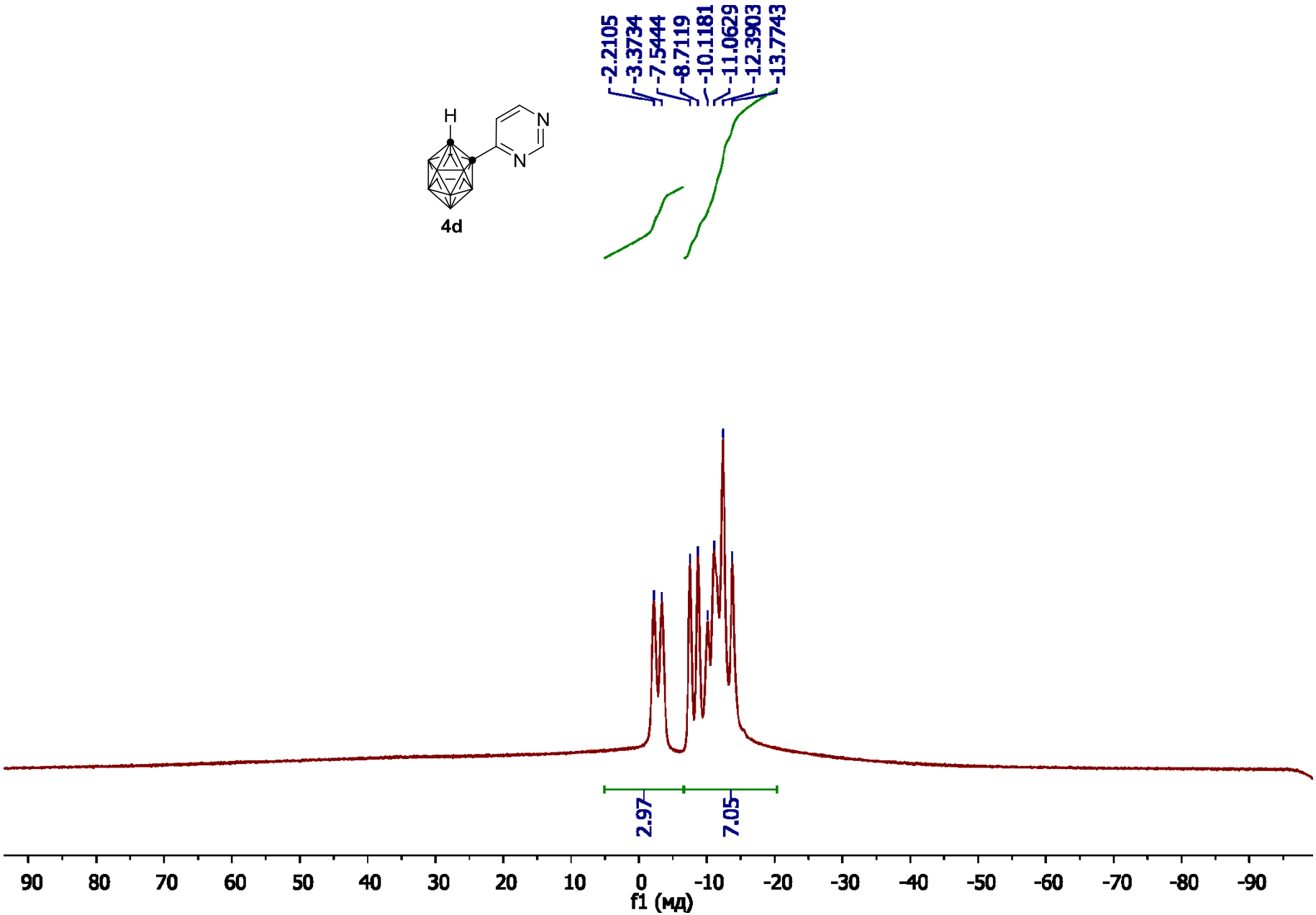

Figure S11. ^{11}B NMR Spectrum of 1-(pyrimidin-4-yl)-1,2-*closo*-dodecaborane (**4d**)

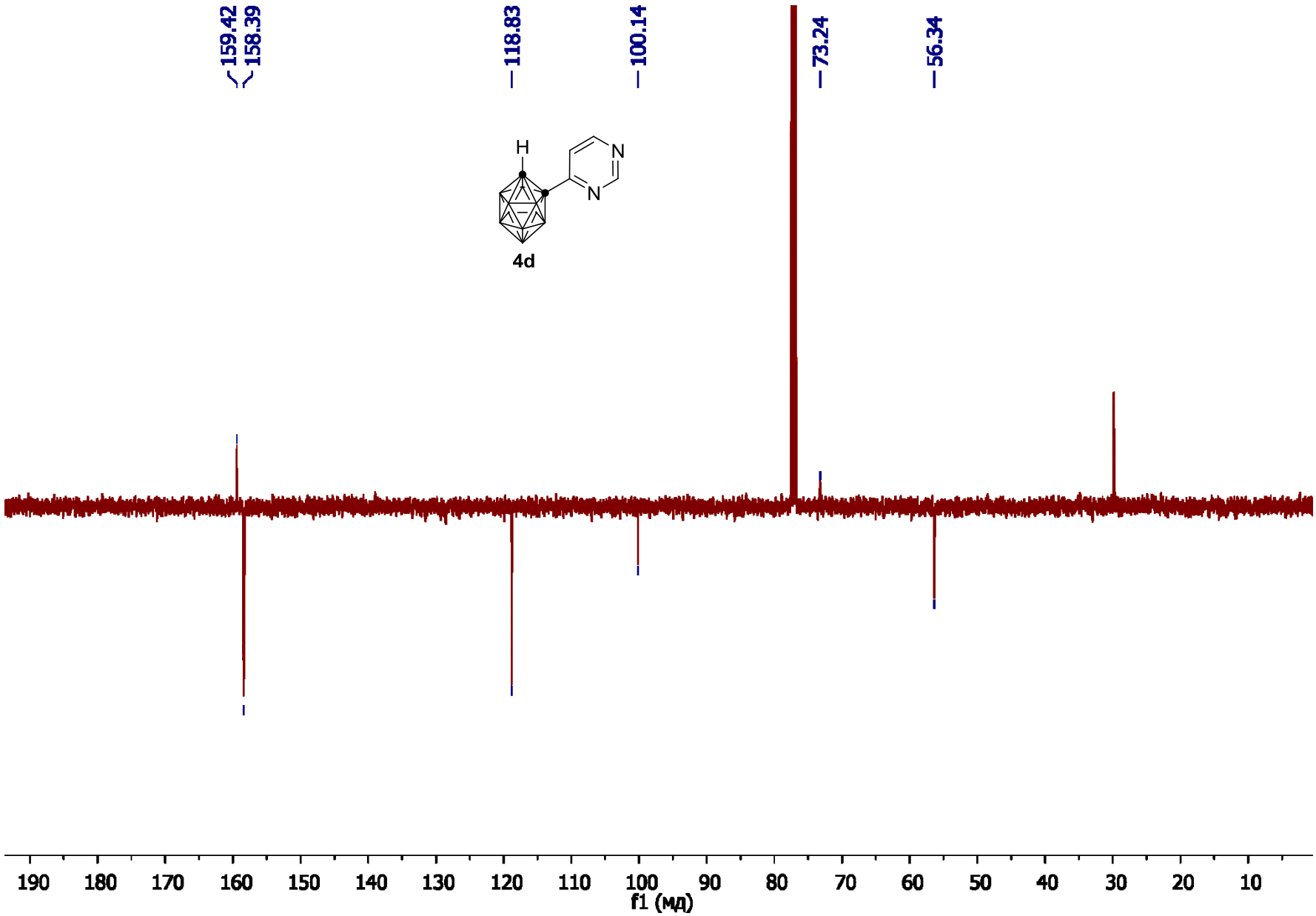

Figure S12. ^{13}C NMR Spectrum (APT) of 1-(pyrimidin-4-yl)-1,2-*closo*-dodecaborane (**4d**)

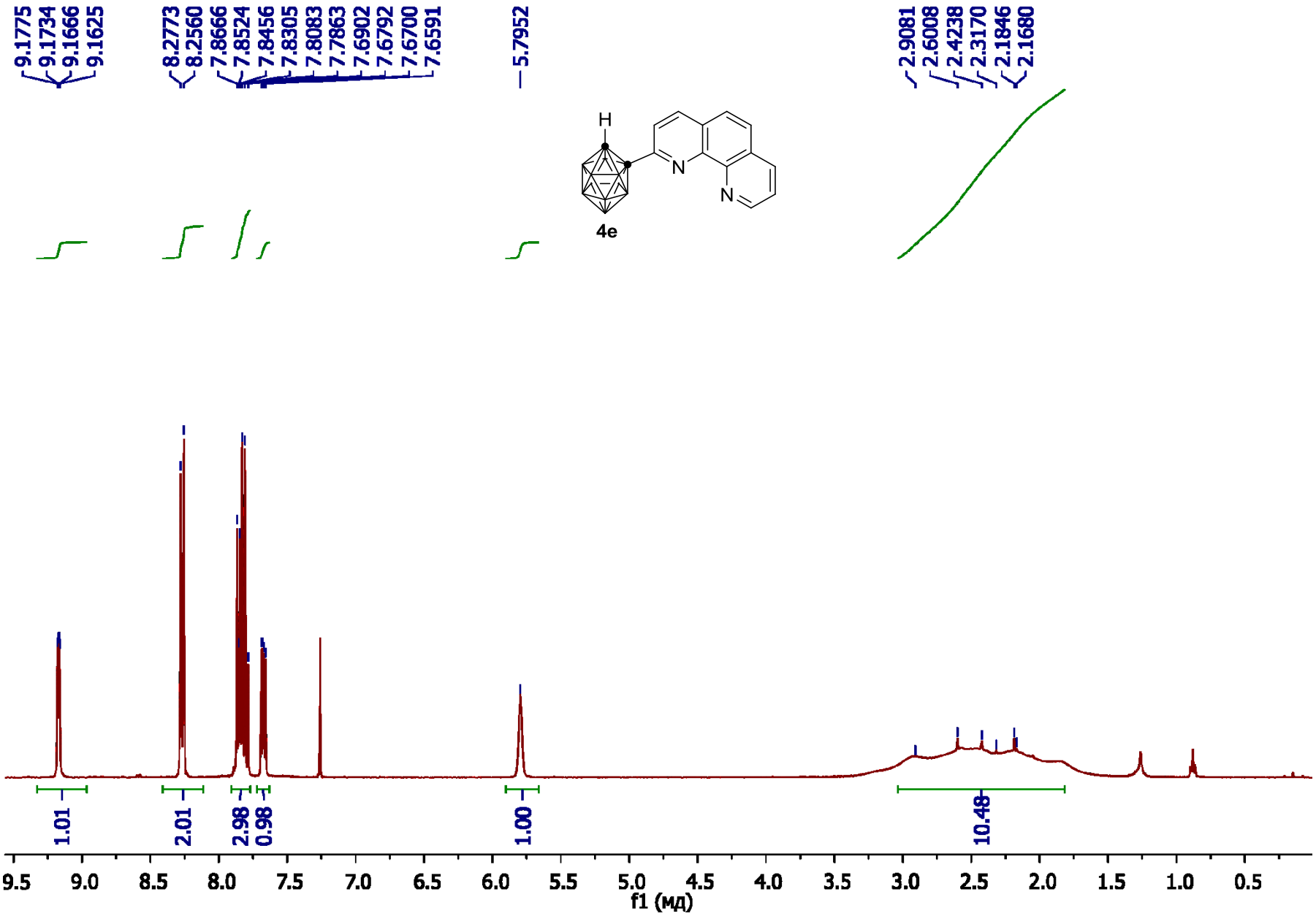

Figure S13. ^{1}H NMR Spectrum of 1-(1,10-phenanthrolin-2-yl)-1,2-*closo*-dodecaborane (**4e**)

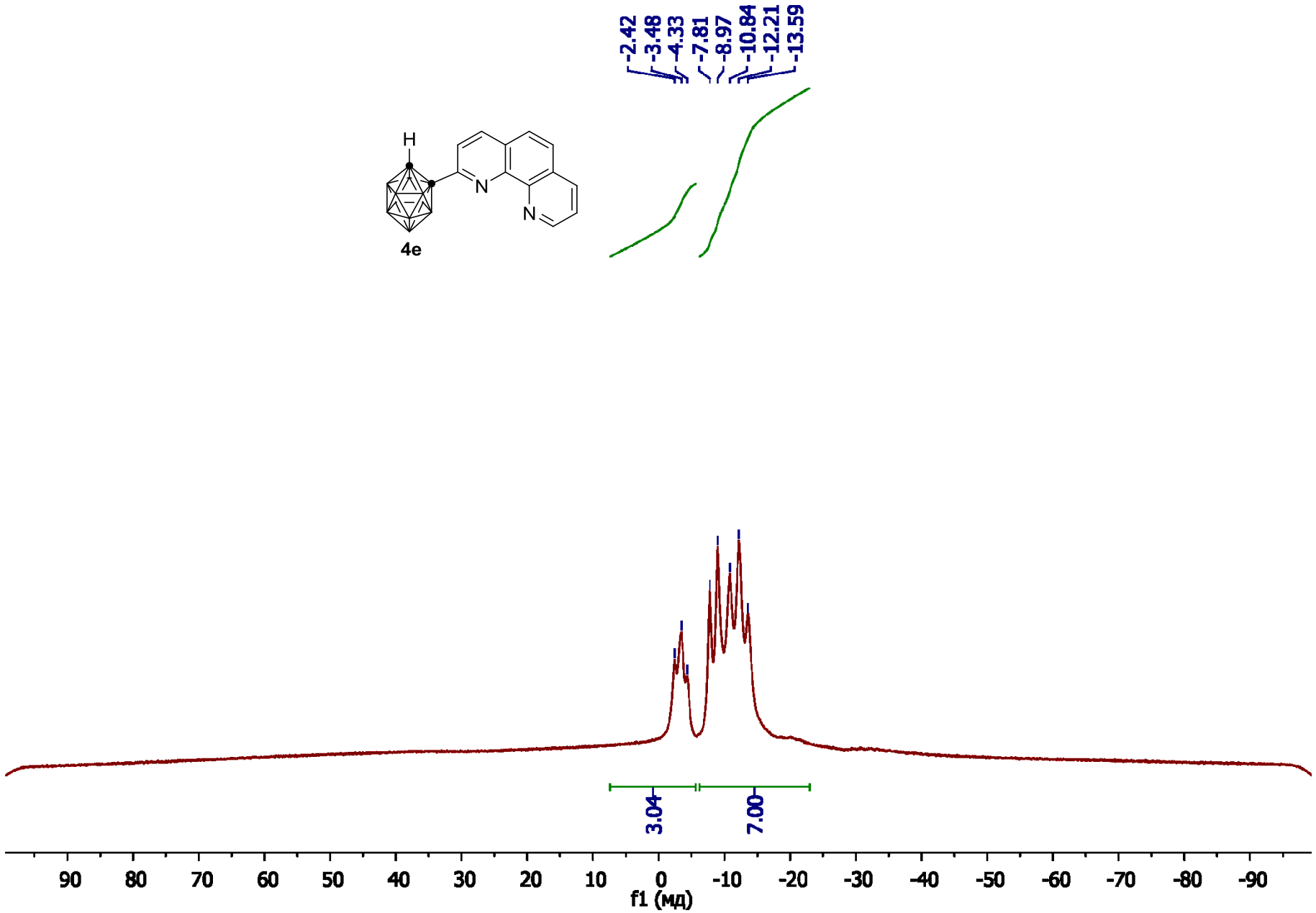

Figure S14. ^{11}B NMR Spectrum of 1-(1,10-phenanthrolin-2-yl)-1,2-*closo*-dodecaborane (**4e**)

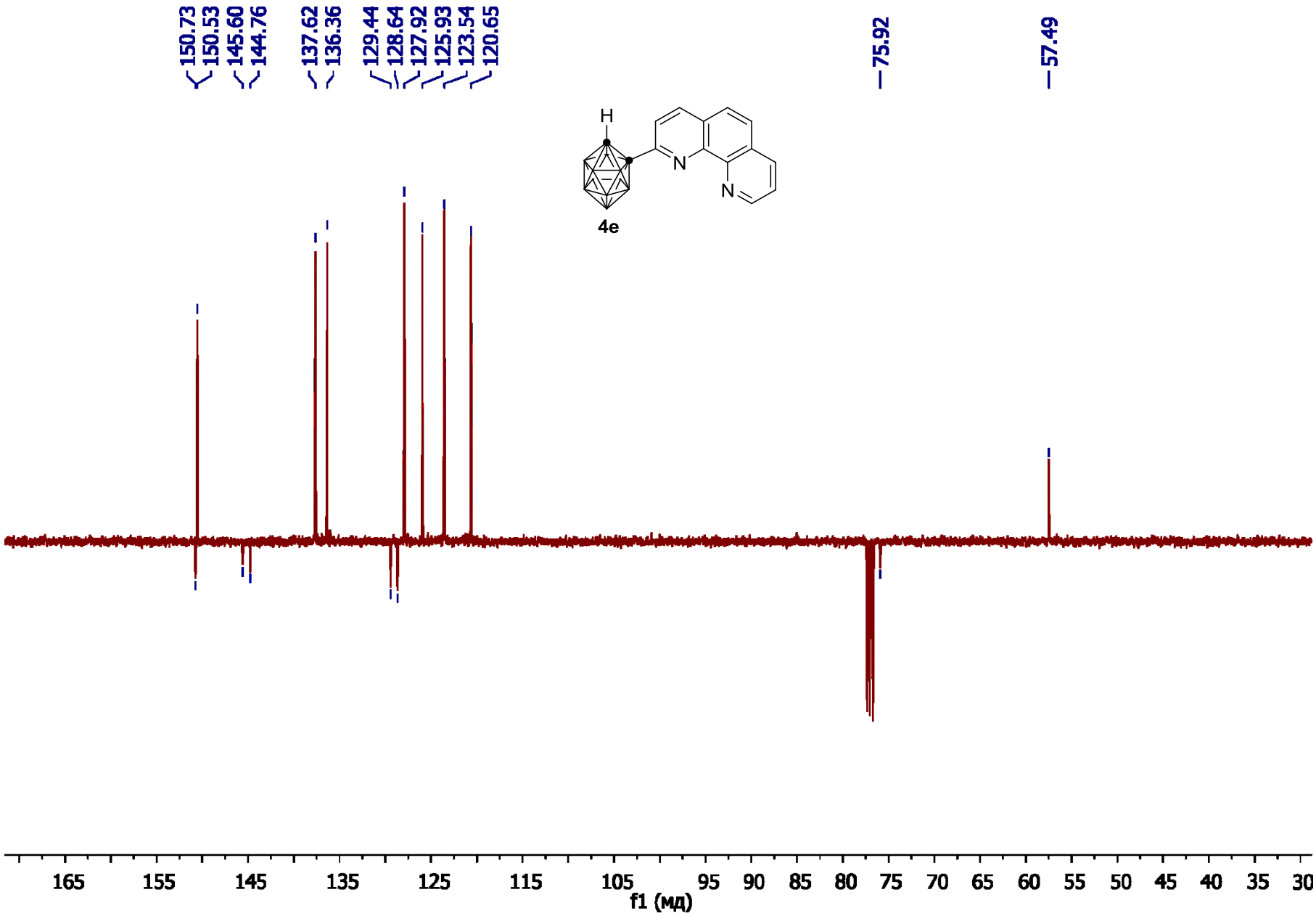

Figure S15. ^{13}C NMR Spectrum (APT) of 1-(1,10-phenanthrolin-2-yl)-1,2-*closo*-dodecaborane (**4e**)

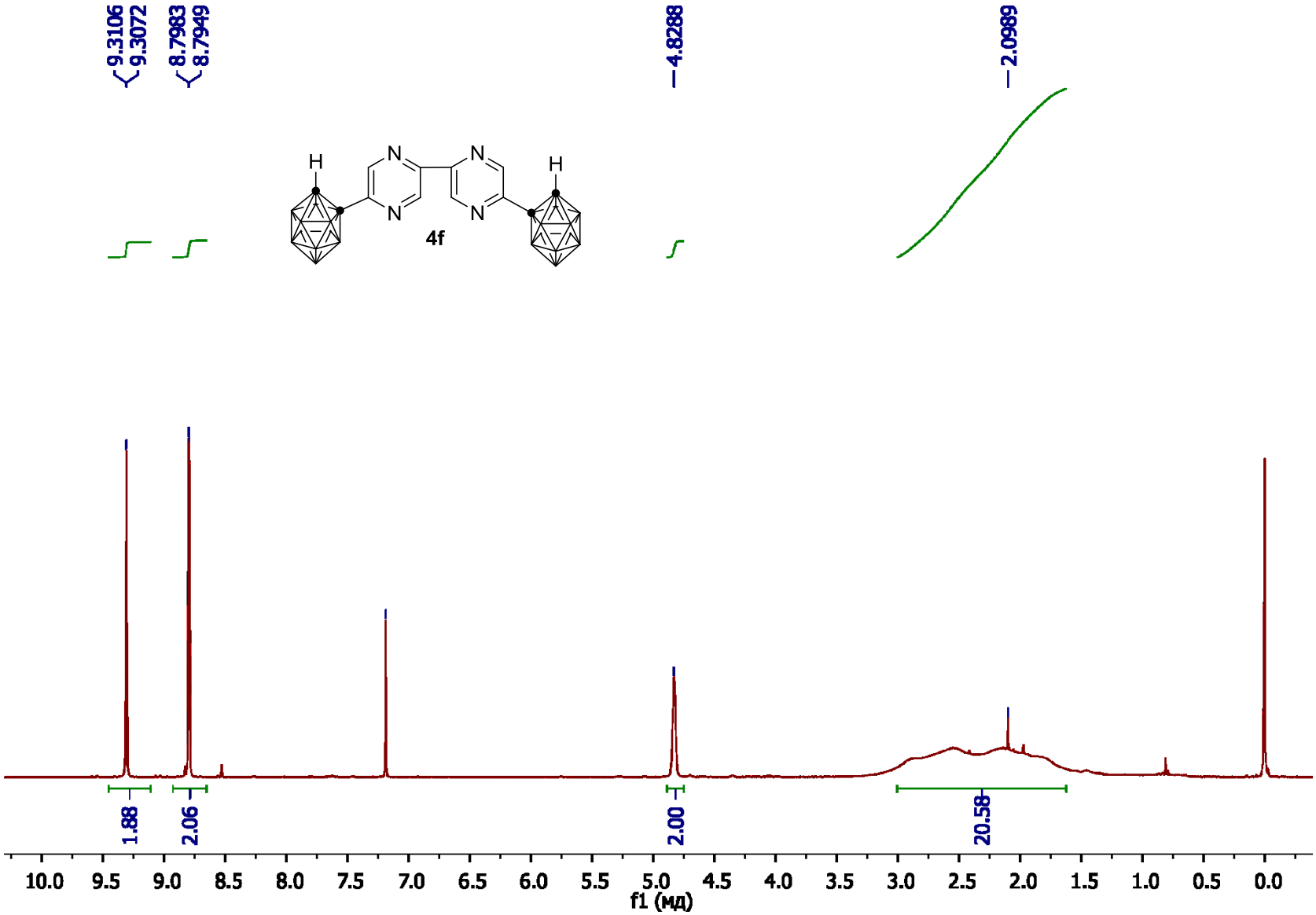

Figure S16. ^{1}H NMR Spectrum 5,5'-bis(1,2-dicarba-*closo*-dodecaborane-1-yl)-2,2'-bipyrazine (**4f**)

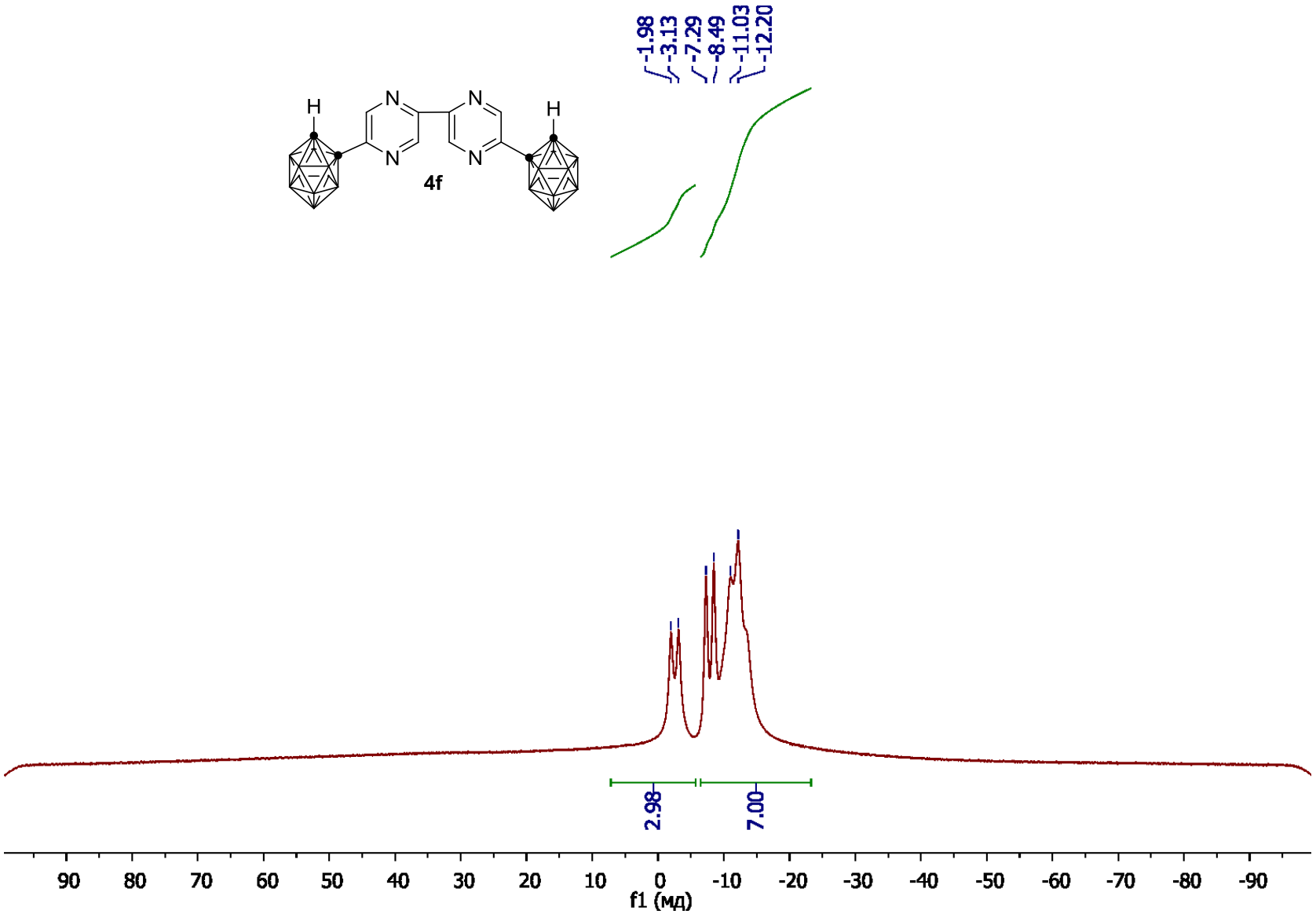

Figure S17. ^{11}B NMR Spectrum 5,5'-bis(1,2-dicarba-*closo*-dodecaborane-1-yl)-2,2'-bipyrazine (**4f**)

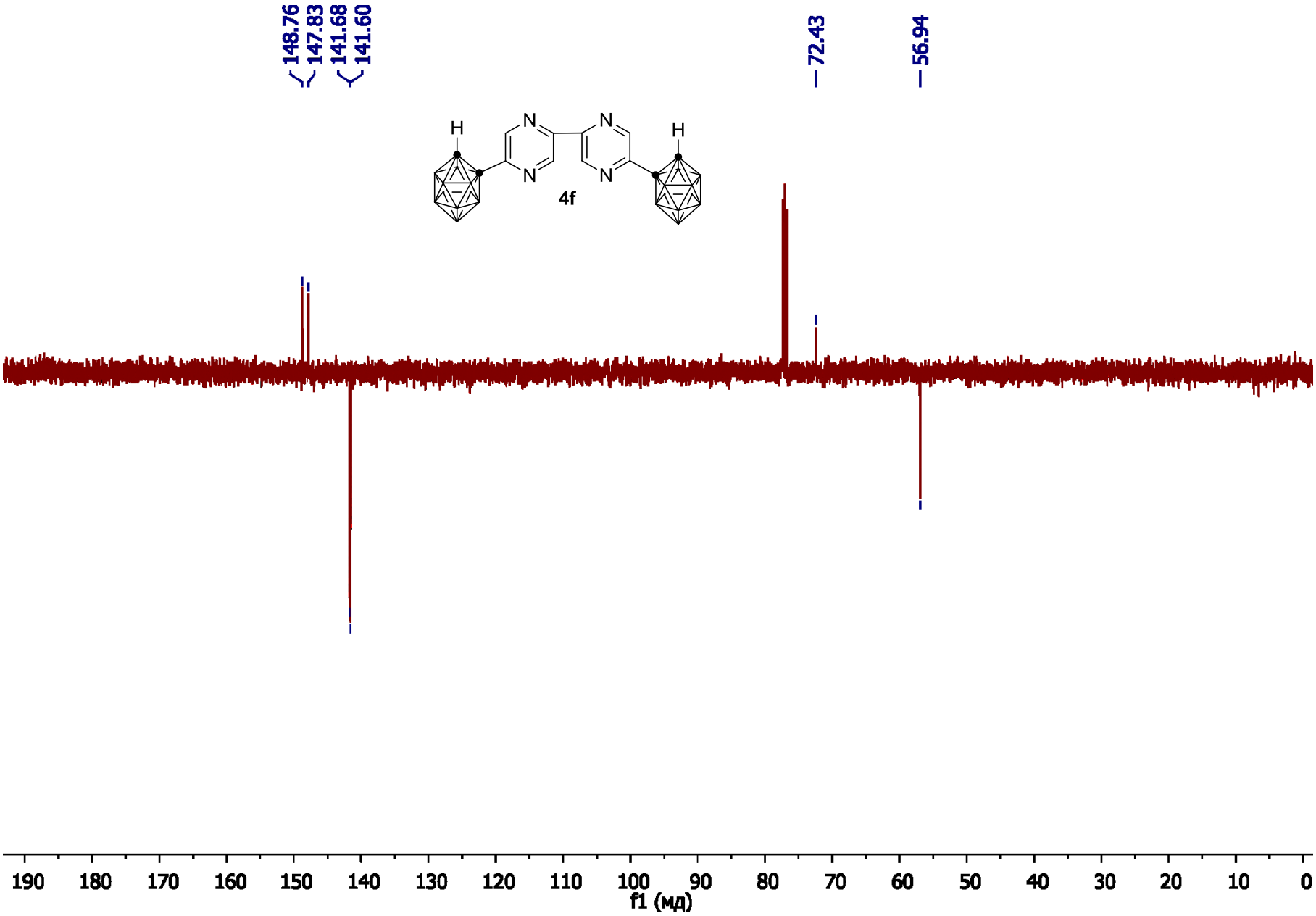

Figure S18. ^{13}C NMR Spectrum (APT) of 5,5'-bis(1,2-dicarba-*closo*-dodecaborane-1-yl)-2,2'-bipyrazine (**4f**)

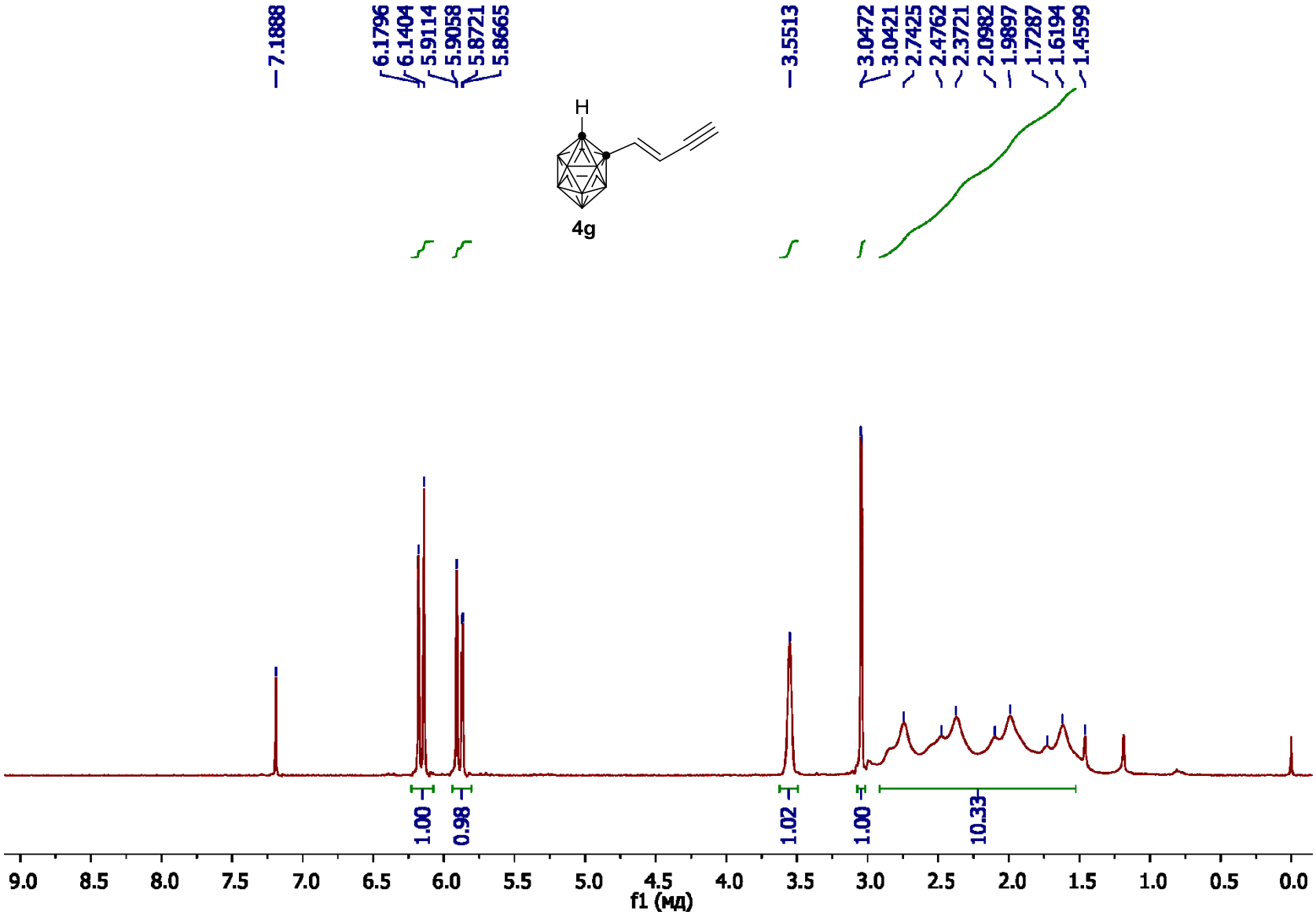

Figure S19. ^{1}H NMR Spectrum of 1-(but-1-en-3-ynyl)-1,2-*closo*-dodecaborane (**4g**)

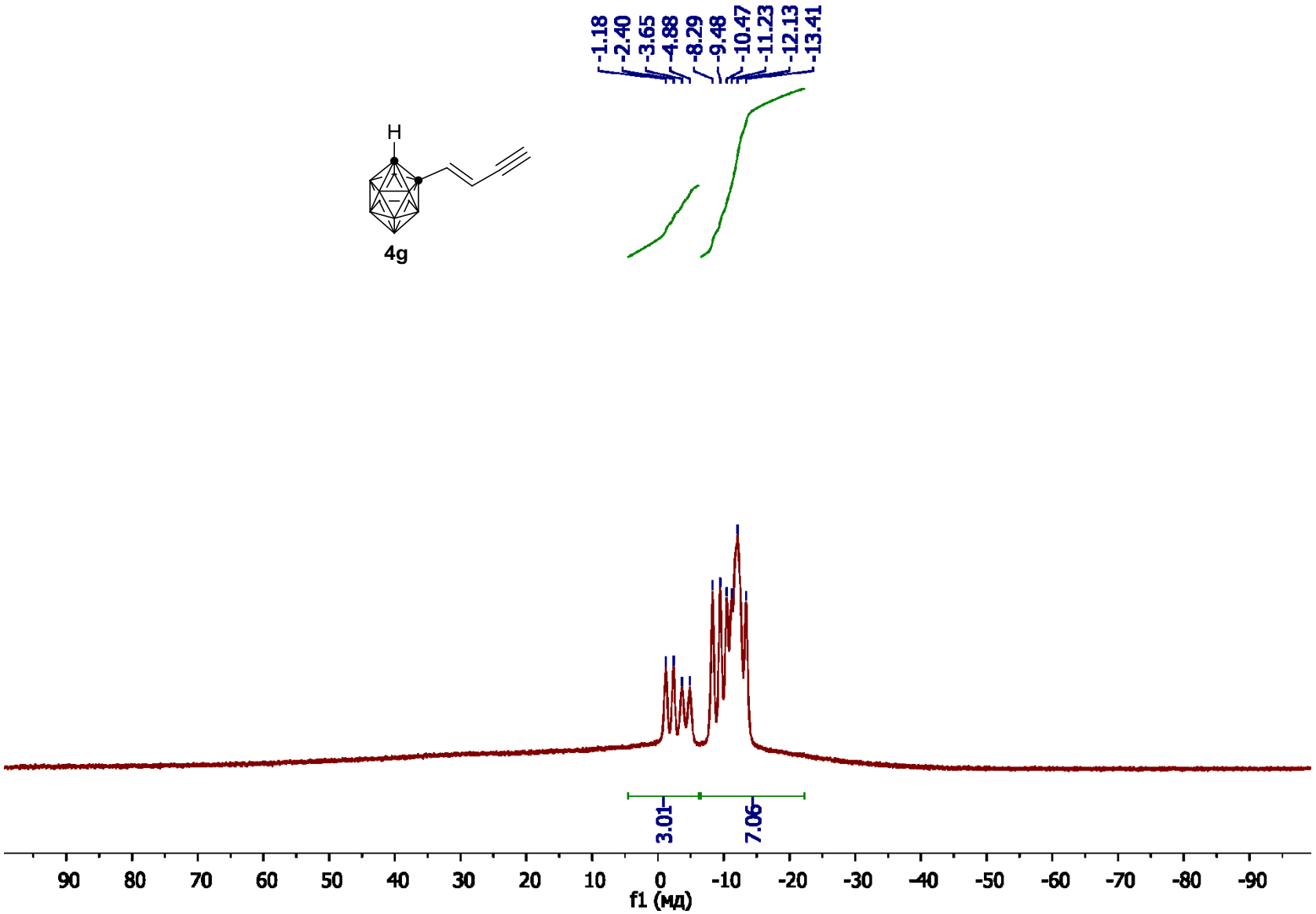

Figure S20. ^{11}B NMR Spectrum of 1-(but-1-en-3-ynyl)-1,2-*closo*-dodecaborane (**4g**)

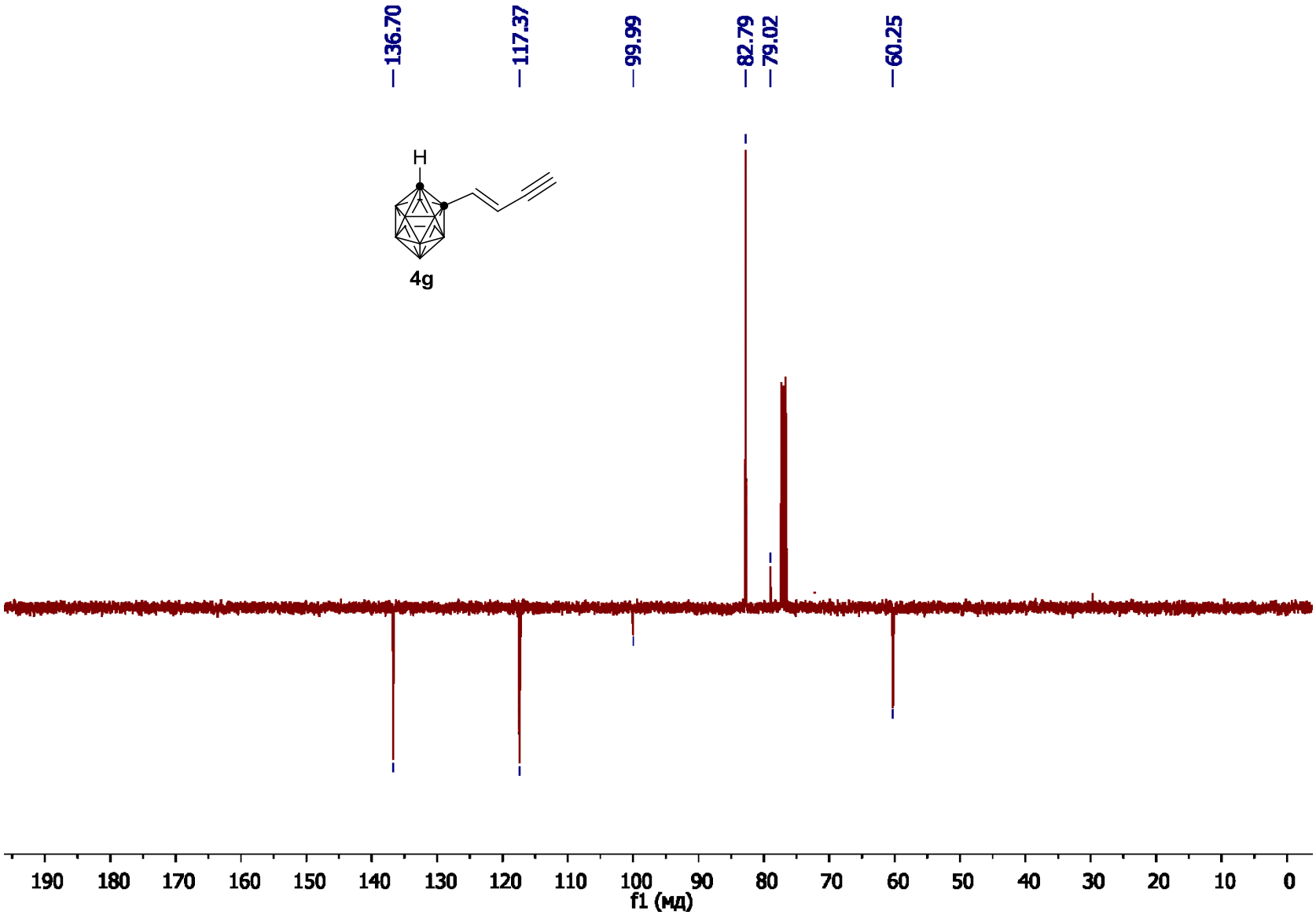

Figure S21. ^{13}C NMR Spectrum (APT) of 1-(but-1-en-3-ynyl)-1,2-*closo*-dodecaborane (**4g**)

X-Ray Diffraction Studies

The crystallographic data and basic refinement parameters for **4f**, **[4e·Cu(hfac)$_2$],** and **[4e·Cu(hfac)$_2$·TFA]$_2$** are shown in Table S1.

Table S1. X-ray analysis data and basic refinement parameters for **4f**, **[4e·Cu(hfac)$_2$]**, and **[4e·Cu(hfac)$_2$·TFA]$_2$**

Parameter	**4f**	**[4e·Cu(hfac)$_2$]**	**[4e·Cu(hfac)$_2$·TFA]$_2$**
Molecular formula	$2(C_6H_{13}B_{10}N_2)$	$4(C_{24}H_{20}B_{10}CuF_{12}N_2O_4)$	$C_{21}H_{19}B_{10}CuF_9N_2O_4$
Molecular weight	442.57	3200.24	706.02
T/K	150.01(10)	150.00(10)	150.00(10)
λ/Å	0.7107	0.7107	0.7107
Syngony	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$
a/Å	10.9462(3)	12.3972(3)	11.9262(4)
b/Å	15.2541(4)	13.6503(3)	19.0285(4)
c/Å	15.0688(4)	19.9916(6)	12.8975(3)
α/deg	90.00	93.587(2)	90.00
β/deg	90.803(2)	92.779(2)	90.309(3)
γ/deg	90.00	94.252(2)	90.00
V, Å^3	2515.85(12)	3362.37(15)	2926.88(13)
Z	4	1	4
d_{calc}/g·cm^{-3}	1.168	1.580	1.602
μ/mm^{-1}	0.058	0.752	0.838
F(000)	904	1588	1404
Crystal size/mm	0.25x0.20x0.15	0.25x0.20x0.15	0.23x0.17x0.06
2θ-Scan range/deg	1.86-30.76	1.89-30.83	2.246-30.88
Completeness based on $2\theta_{max}$	0.8709	0.8690	0.8598
Completeness based on 2θ= 52°	0.9960	0.9997	0.9852
hkl ranges	-14 < h < 15 -20 < k < 11 -21 < l < 8	-16 < h < 14 -19 < k < 15 -28 < l < 27	-16 < h < 15 -27 < k < 26 -9 < l < 18
Total number of reflections	12408	33657	17535
Number of independent reflections	6815	18353	7951
Number of reflections with $I > 2\sigma(I)$	4912	9717	4722
Number of refined parameters	429	1036	451
Absorption correction	multi-scan	multi-scan	multi-scan
GOOF (based on F^2)	1.002	1.011	1.029
R factors (based on reflections with $I > 2\sigma(I)$)			
R_1	0.0533	0.0520	0.0474
wR_2	0.1313	0.1471	0.1239
R factors (based on all reflections)			
R_1	0.0809	0.0754	0.0770
wR_2	0.1491	0.1654	0.1408
$\Delta\rho_{max}$/ $\Delta\rho_{min}$, eÅ^{-3}	0.305/-0.283	1.117/-0.706	0.558/-0.521

Crystallographic data (excluding structure factors) for the structures **4f**, **[4e·Cu(hfac)$_2$]**, and **[4e·Cu(hfac)$_2$·TFA]$_2$** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1417667, CCDC 1417668, and CCDC 1417669. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44(0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).