Supplementary Materials

to the article

Half-Sandwich Nickelacarboranes Derived from [7-(MeO(CH$_2$)$_2$S)-7,8-C$_2$B$_9$H$_{11}$]$^-$

Dmitriy K. Semyonov [1,2], Marina Yu. Stogniy [1,2]*, Kyrill Yu. Suponitsky [3] and Igor B. Sivaev [1,4]

[1] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119334, Moscow, Russia; dksemyonov@mail.ru (D.K.S.); stogniy@ineos.ac.ru (M.Y.S.); sivaev@ineos.ac.ru (I.B.S.);
[2] M. V. Lomonosov Institute of Fine Chemical Technology, MIREA - Russian Technological University, 86 Vernadsky Av., 119571, Moscow, Russia;
[3] N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninskii Av., 119991, Moscow, Russia; kirshik@yahoo.com (K.Y.S.);
[4] Basic Department of Chemistry of Innovative Materials and Technologies, G.V. Plekhanov Russian University of Economics, 36 Stremyannyi Line, 117997 Moscow, Russia
* Correspondence: stogniy@ineos.ac.ru

Single crystal X-ray diffraction experiment was carried out using SMART APEX2 CCD diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans) at 120 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [1]. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program [2].

References

1. APEX2 and SAINT; Bruker AXS Inc.: Madison, WI, USA, **2014**.

2. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst.* C **2015**, *71*, 3-8. DOI: 10.1107/S2053229614024218

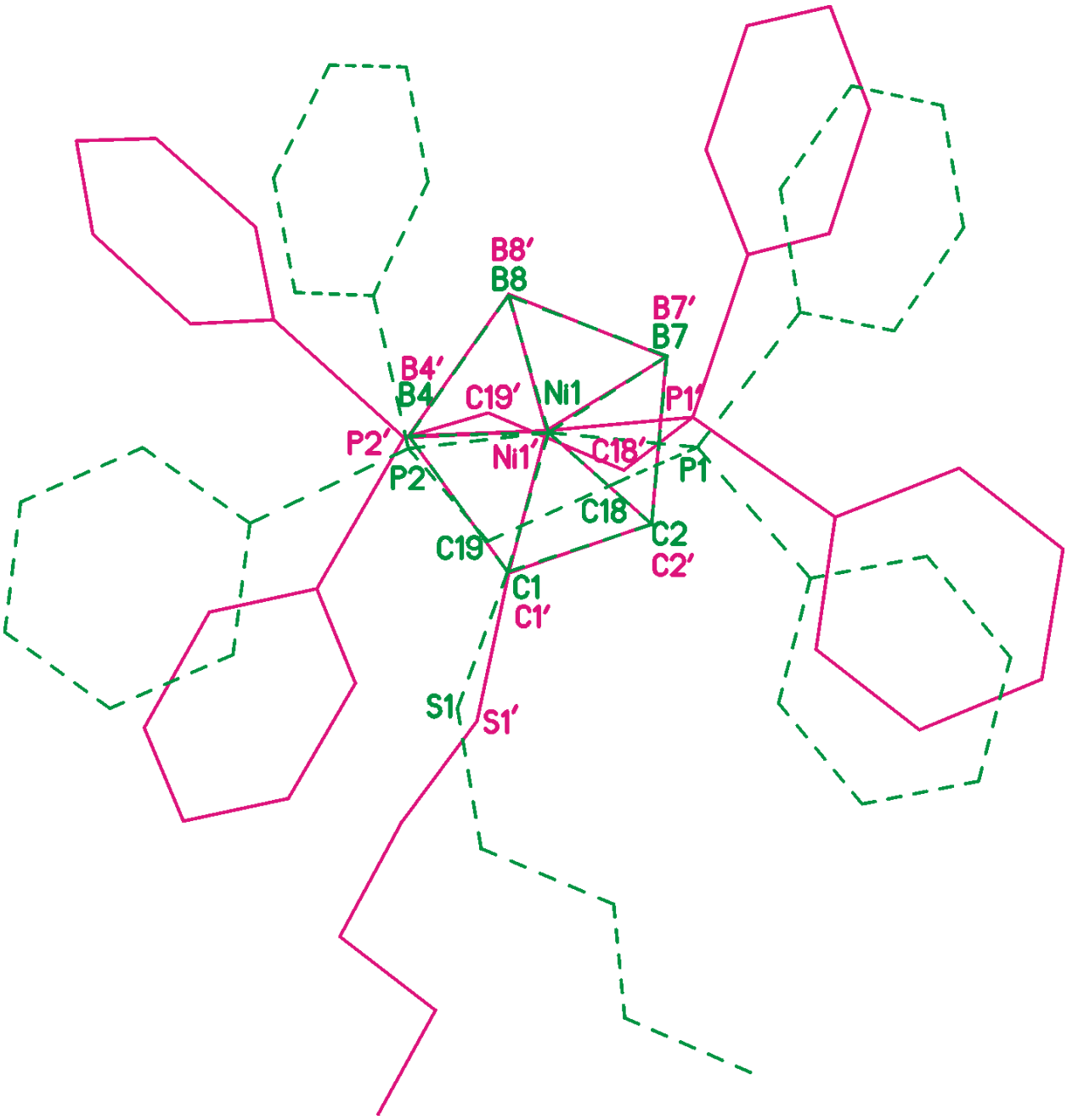

Fig. S1. Superimposition of the coordination environment of the nickel atom in two independent molecules in complexes **5**, showing the difference in the relative orientation of the ligands.

Table 1S. Crystallographic data for compound **5**.

	Compound **5**
formula	$C_{31}H_{41}B_9NiOSP_2$ 0.5(C_3H_6O)
fw	708.76
crystal system	Triclinic
space group	*P*-1
a, Å	12.3355(7)
b, Å	12.7617(7)
c, Å	23.3086(12)
α, deg.	94.623(2)
β, deg.	95.020(2)
γ, deg.	94.286(2)
V, Å^3	3630.9(3)
Z	4
ρ_{calc}, g·cm^{-3}	1.296
F(000)	1480
μ, mm^{-1}	0.709
θ range, deg.	0.88 – 26.07
independent reflections	14295
Completeness to theta θ, %	99.4
refined parameters	931
GOF (F^2)	1.051
reflections with $I>2\sigma(I)$	11059
$R_1(F)$ ($I>2\sigma(I)$)[a]	0.0377
$wR_2(F^2)$ (all data)[b]	0.0876
Largest diff. peak/hole, *e*·Å^{-3}	0.398/-0.383

[a] $R_1 = \sum||F_o| - |F_c||/\sum(F_o)$; [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{½}$

The NMR spectra at 400.1 MHz (^{1}H), 128.4 MHz (^{11}B), 100.0 MHz (^{13}C) and 162 MHz (^{31}P) were recorded with a Varian Inova 400 spectrometer. The residual signal of the NMR solvent relative to tetramethylsilane was taken as an internal reference for ^{1}H and ^{13}C NMR spectra. ^{11}B NMR spectra were referenced using $BF_3 \cdot Et_2O$ as an external standard. ^{31}P NMR spectra are cited relative 85% H_3PO_4 as an external standard. Infrared spectra were recorded on a FSM-2201 (INFRASPEC) instrument. UV/Vis spectra were recorded with SF-2000 spectrophotometer (OKB SPECTR LLC) using 1 cm cuvettes. High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI).

Spectral data for 1-(MeO(CH$_2$)$_2$S)-1,2-C$_2$B$_{10}$H$_{11}$ (1)

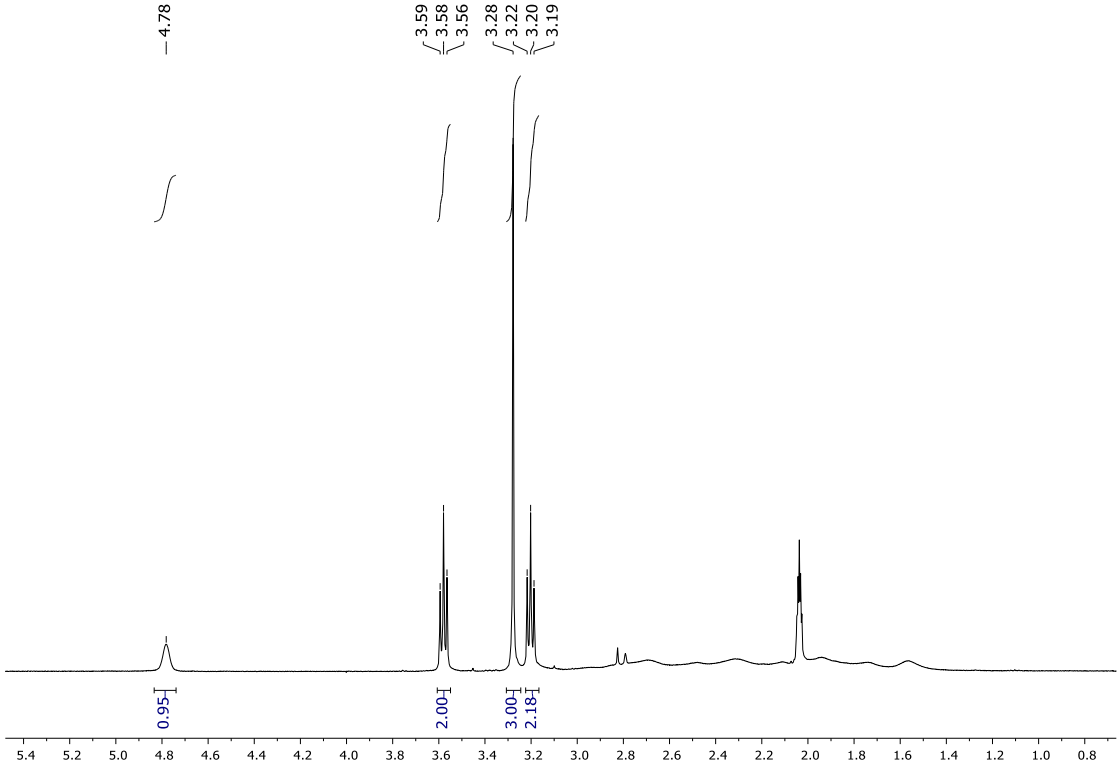

Fig. S2. ^{1}H NMR spectrum of compound **1** in acetone-d$_6$

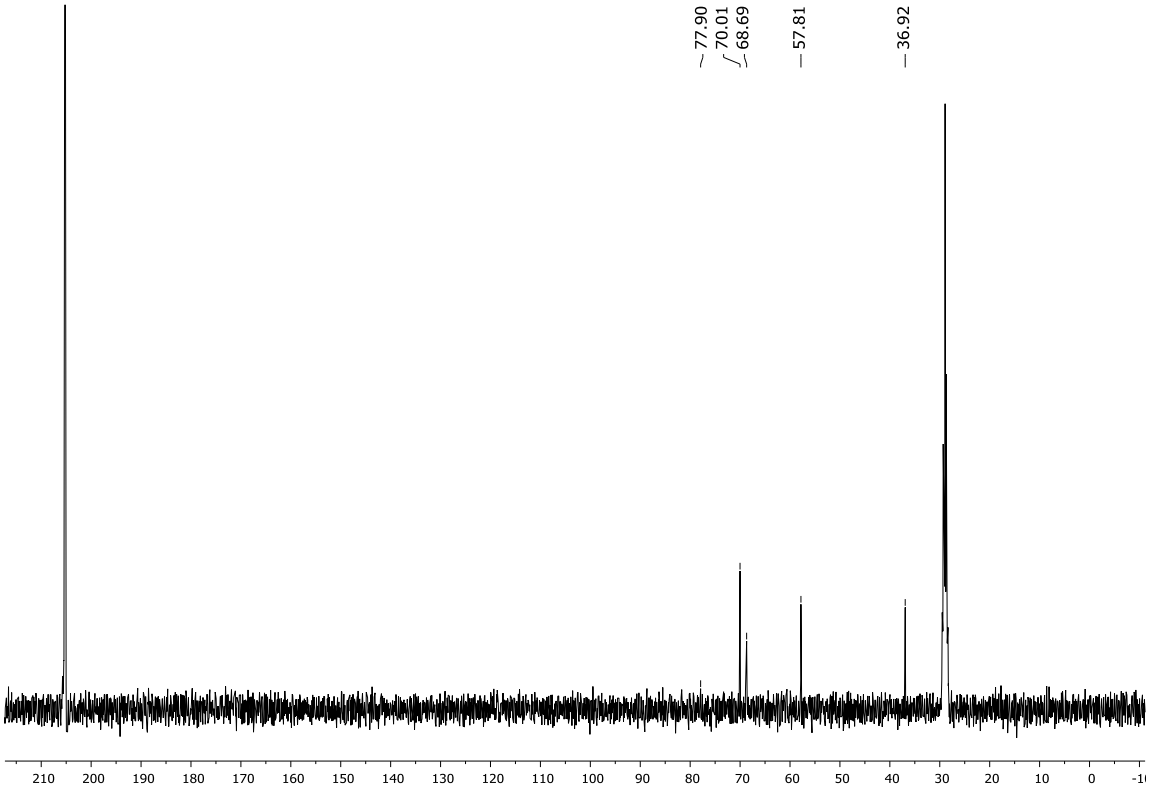

Fig. S3. ^{13}C NMR of compound **1** in acetone-d$_6$

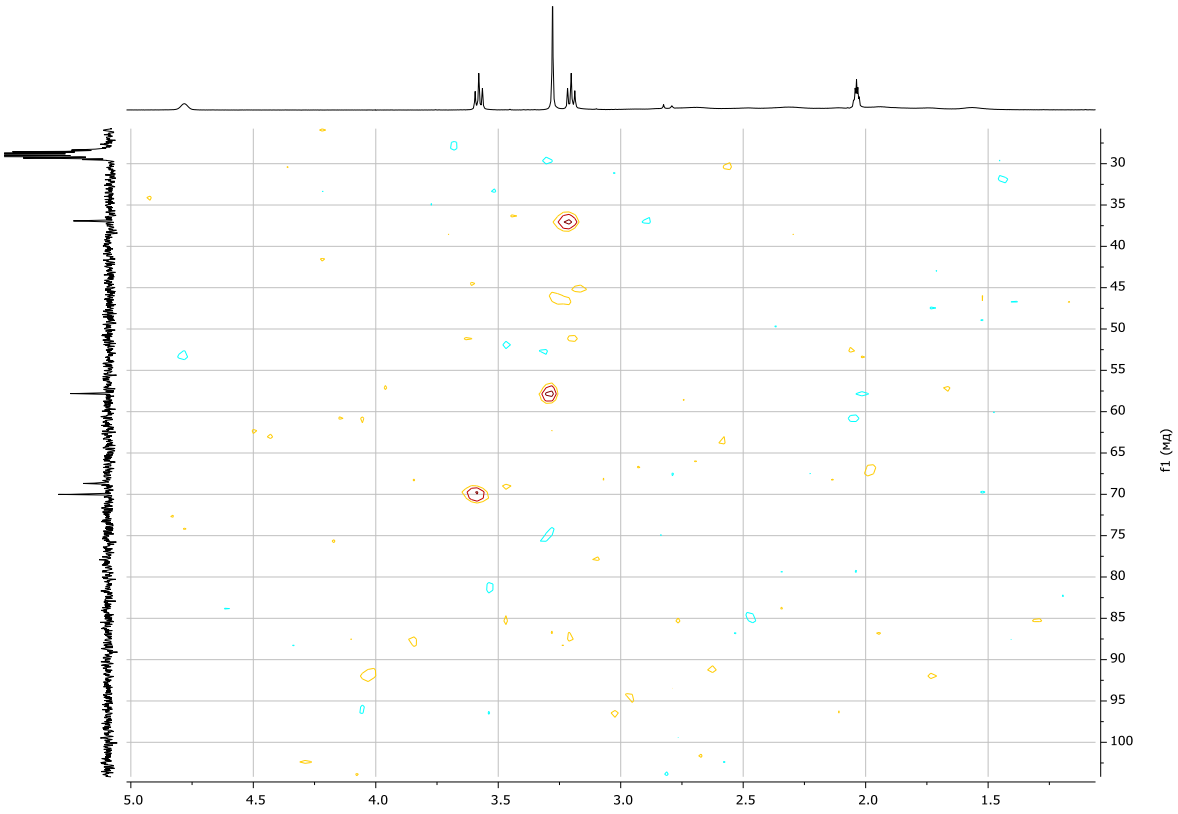

Fig. S4. (HC)HSQC NMR spectrum of compound **1** in acetone-d_6

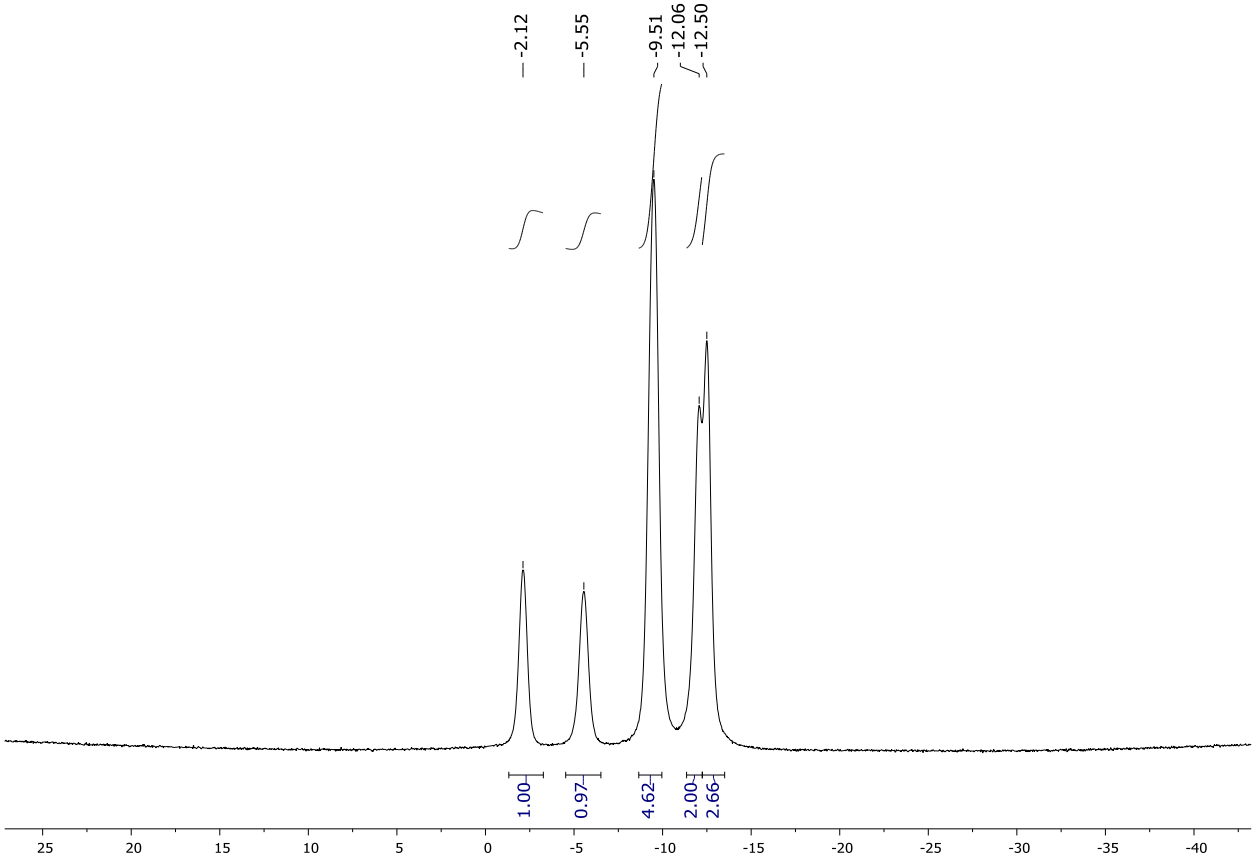

Fig. S5. $^{11}B\{^1H\}$ NMR spectrum of compound **1** in acetone-d_6

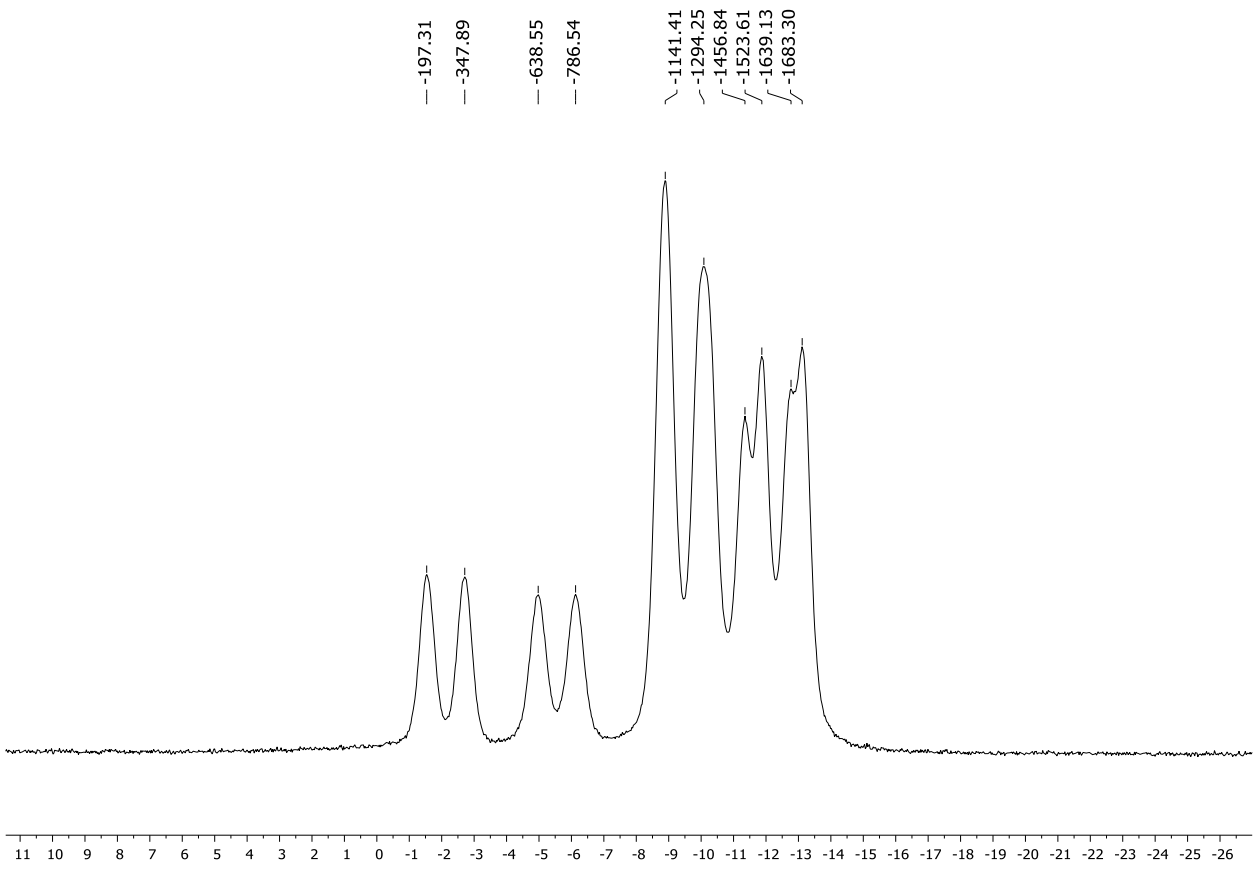

Fig. S6. ^{11}B NMR spectrum of compound **1** in acetone-d_6

Spectral data for 1-(MeO(CH$_2$)$_3$S)-1,2-C$_2$B$_{10}$H$_{11}$ (2)

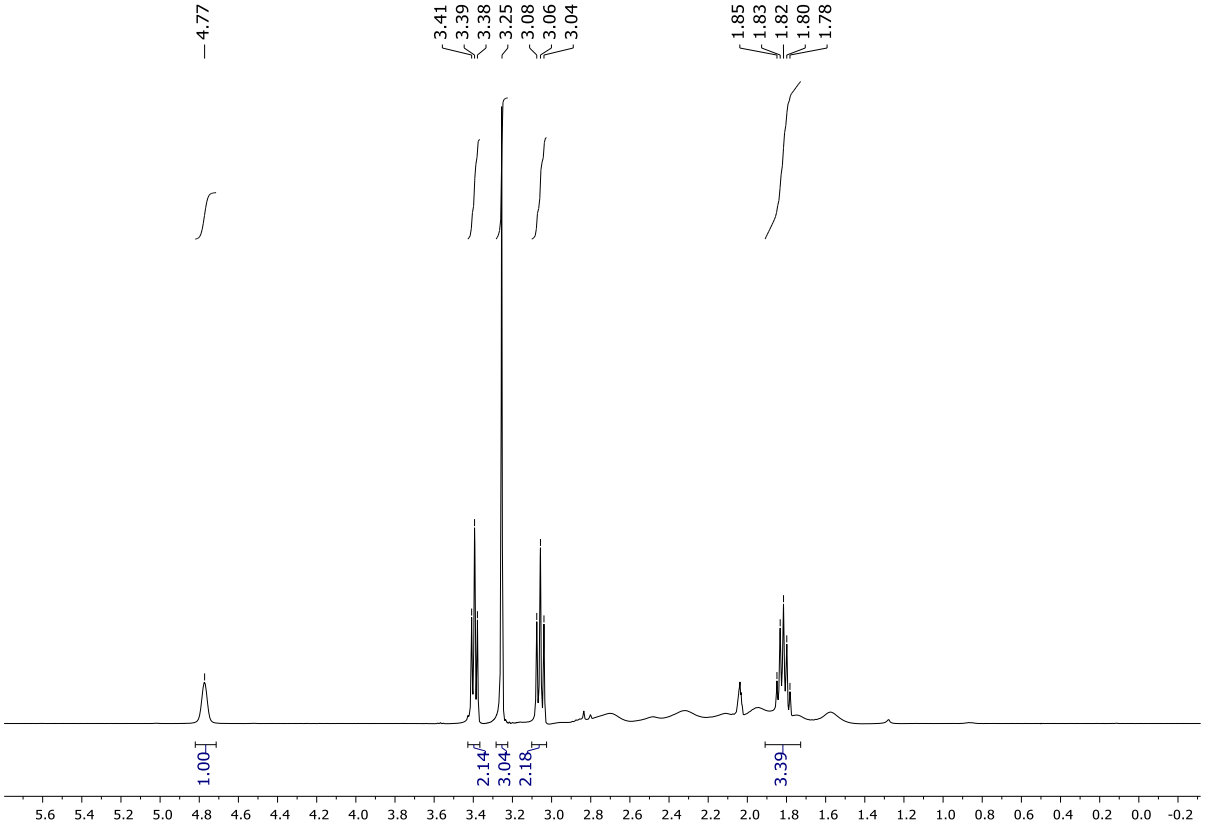

Fig. S7. ^{1}H NMR spectrum of compound **2** in acetone-d$_6$

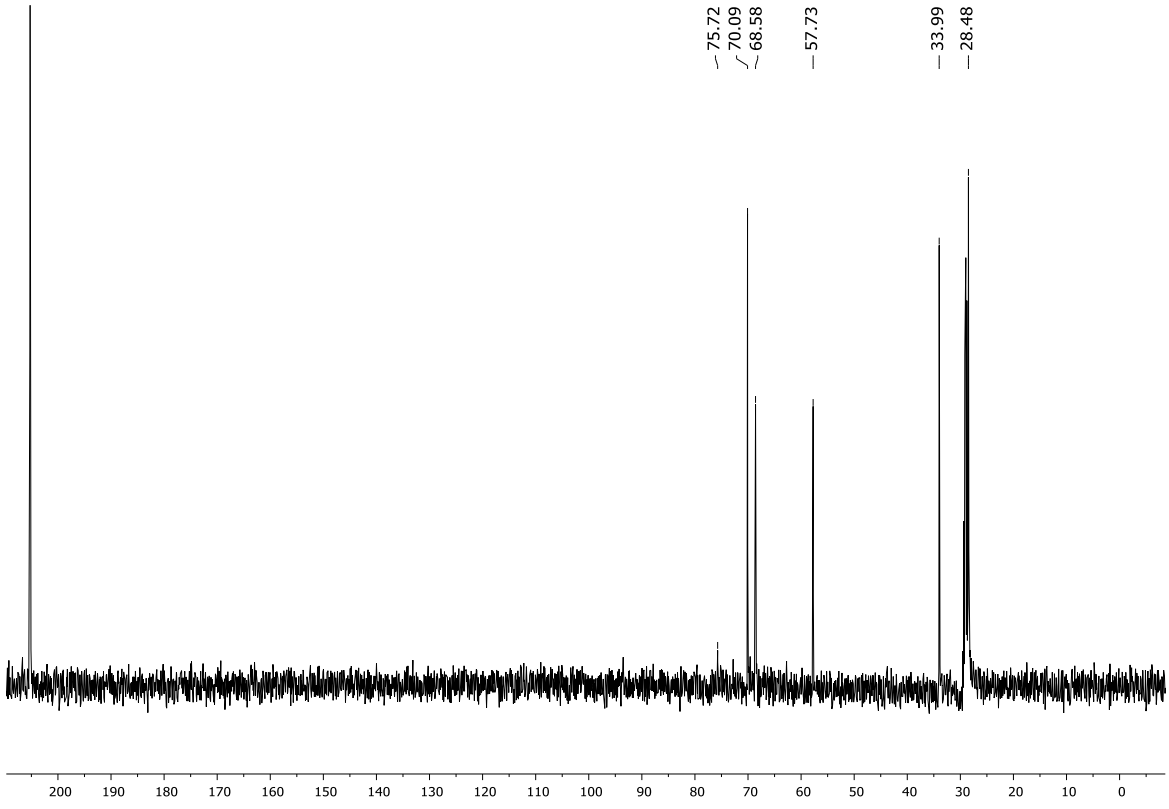

Fig. S8. ^{13}C NMR spectrum of compound **2** in acetone-d$_6$

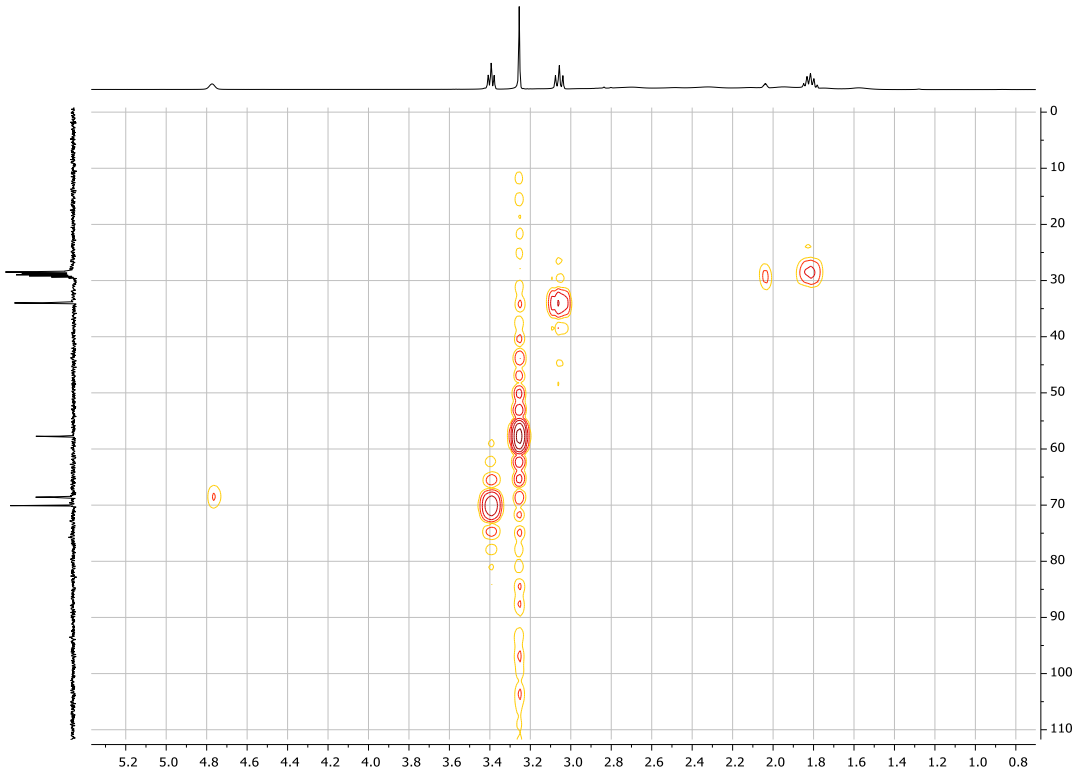

Fig. S9. (HC)HSQC NMR spectrum of compound **2** in acetone-d_6

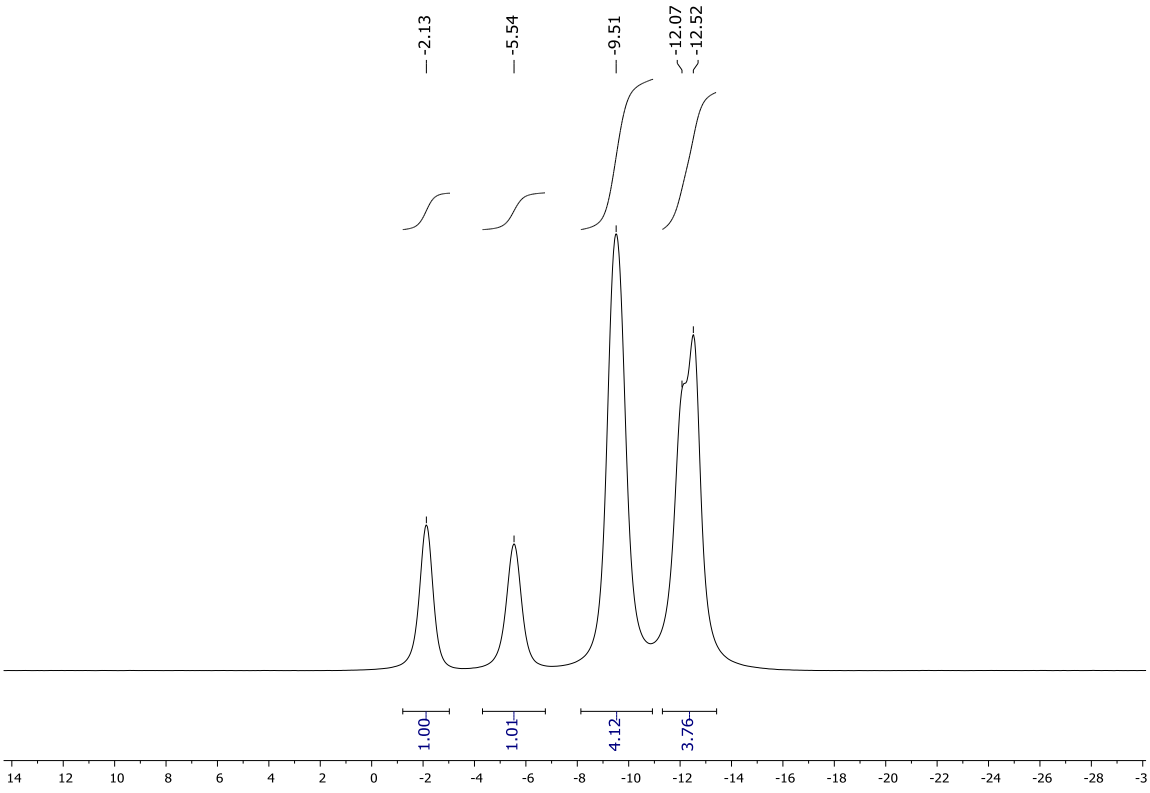

Fig. S10. $^{11}B\{^1H\}$ NMR spectrum of compound **2** in acetone-d_6

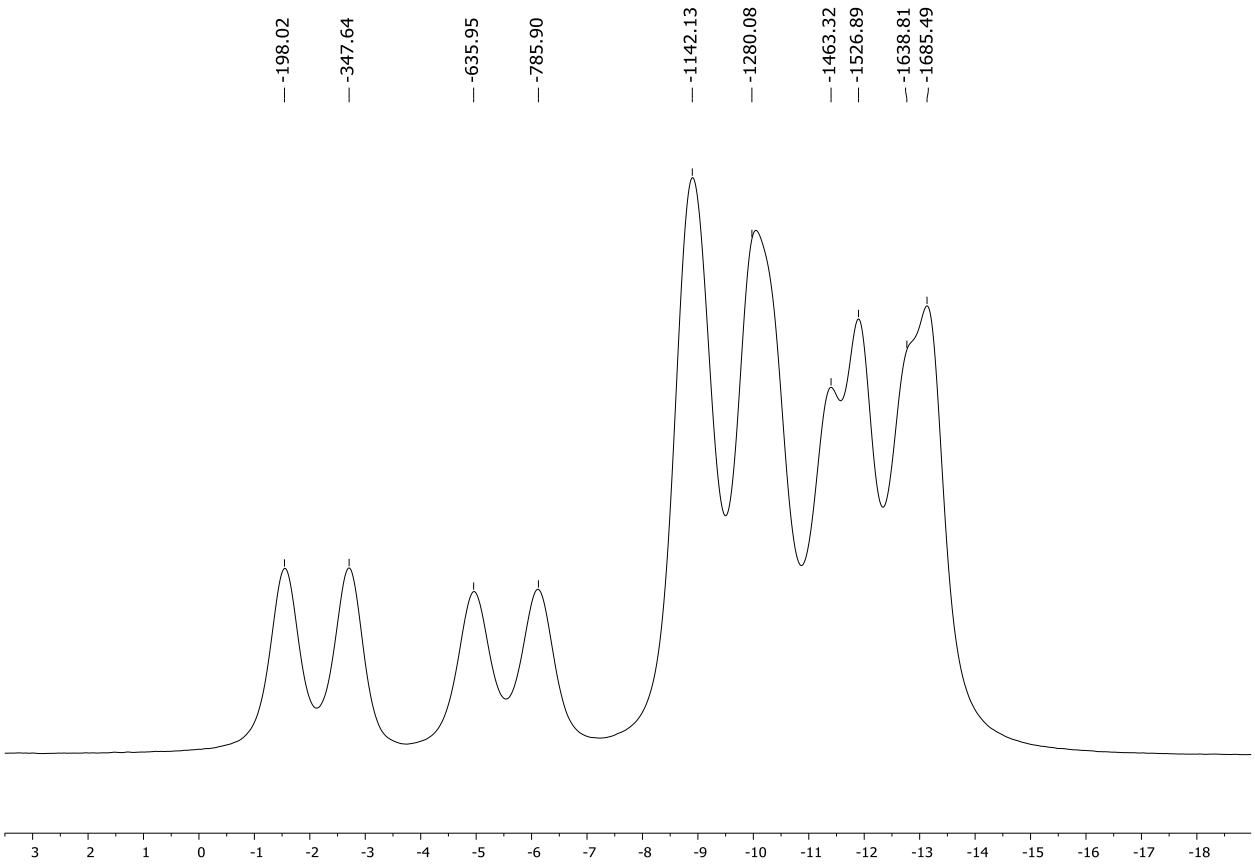

Fig. S11. ^{11}B NMR spectrum of compound **2** in acetone-d_6

Spectral data for Cs[7-(MeO(CH$_2$)$_2$S)-7,8-C$_2$B$_9$H$_{11}$] (3)

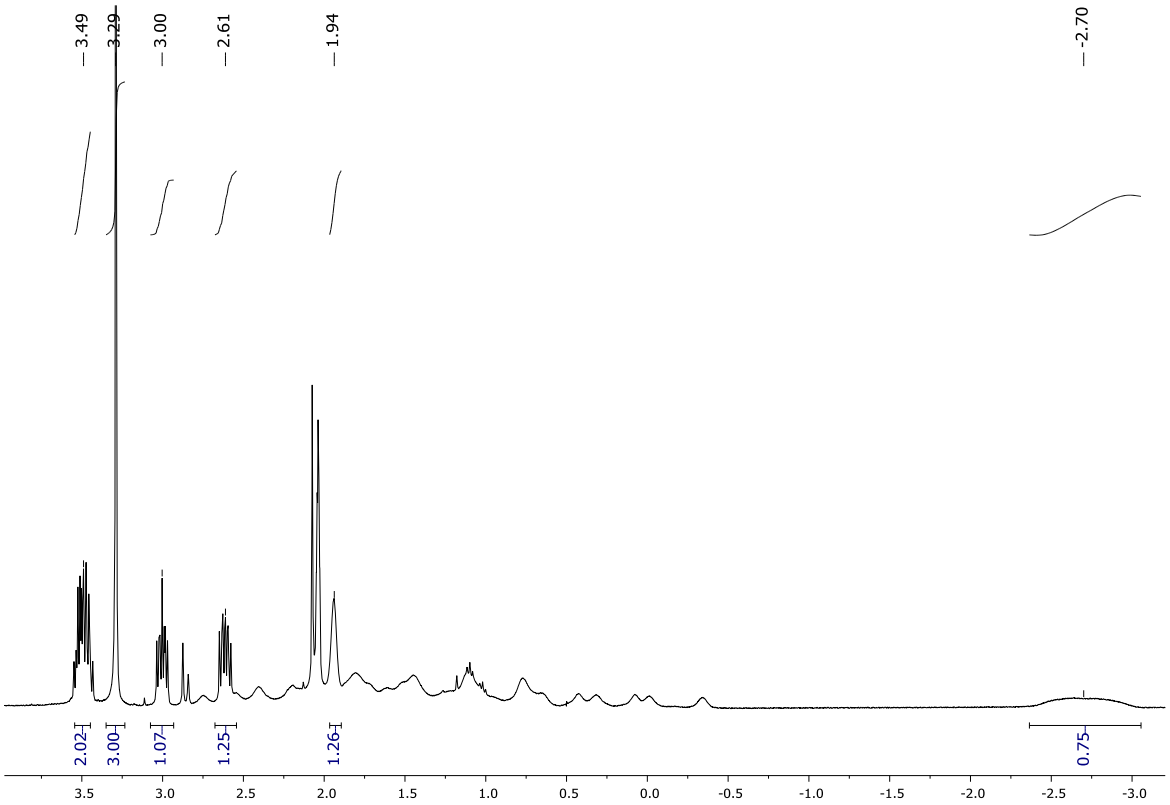

Fig. S12. ^{1}H NMR spectrum of compound **3** in acetone-d$_6$

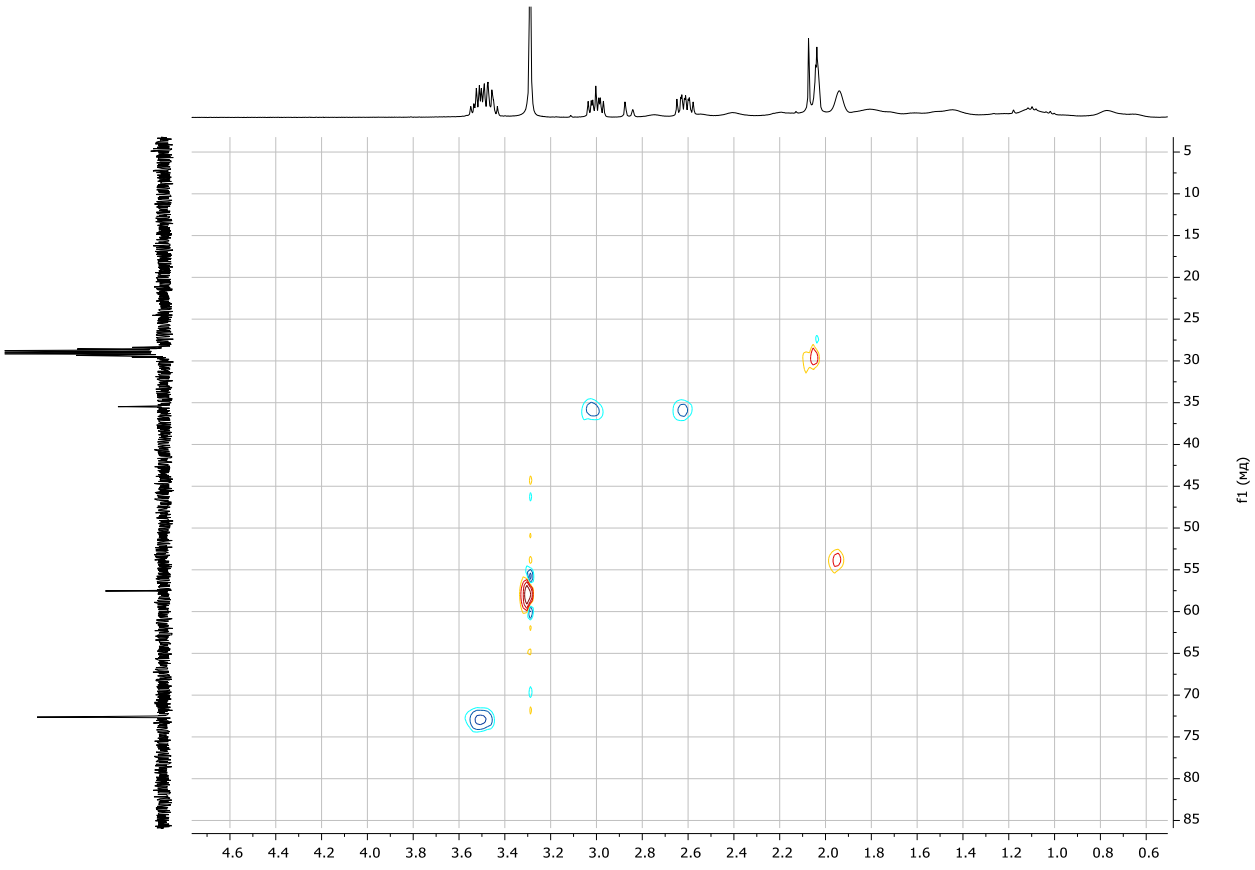

Fig. S13. (HC) HSQC NMR spectrum of compound **3** in acetone-d$_6$

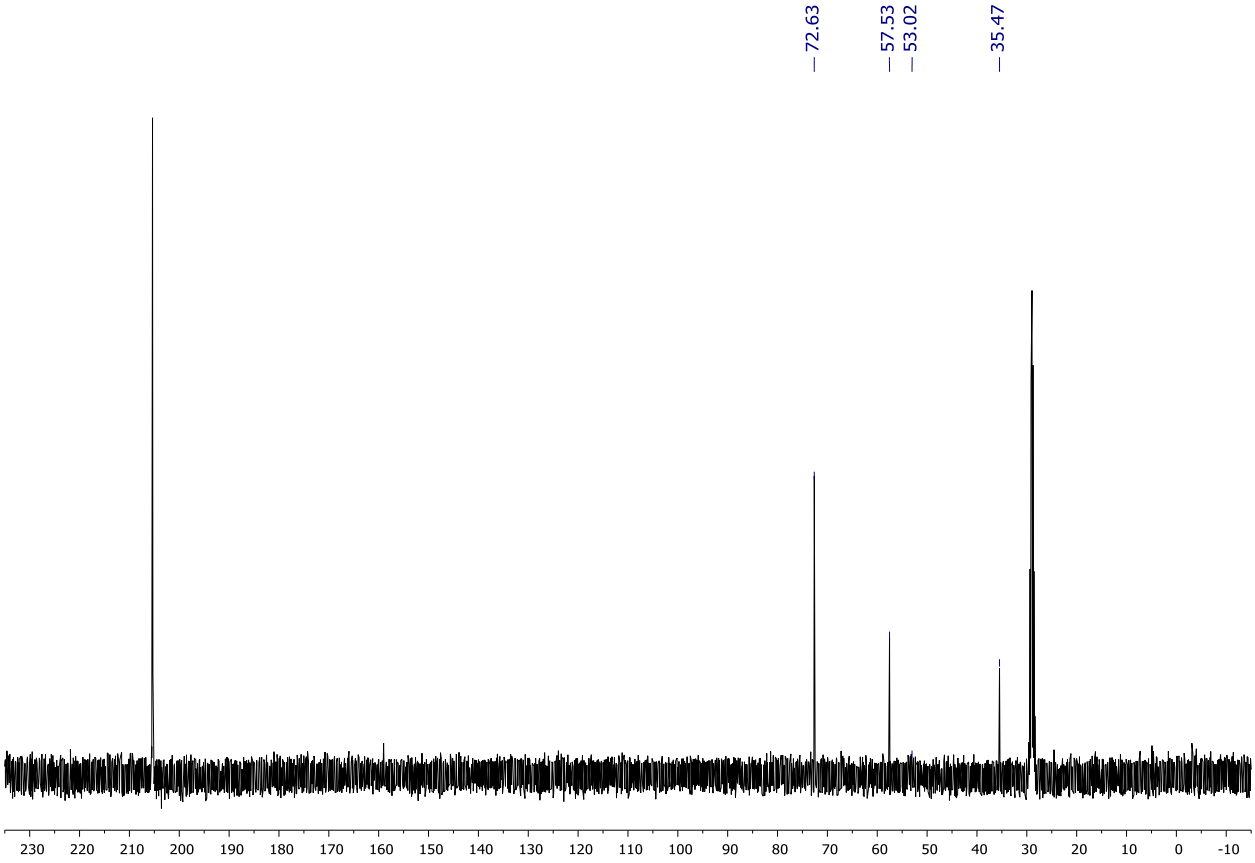

Fig. S14. ^{13}C NMR spectrum of compound **3** in acetone-d_6

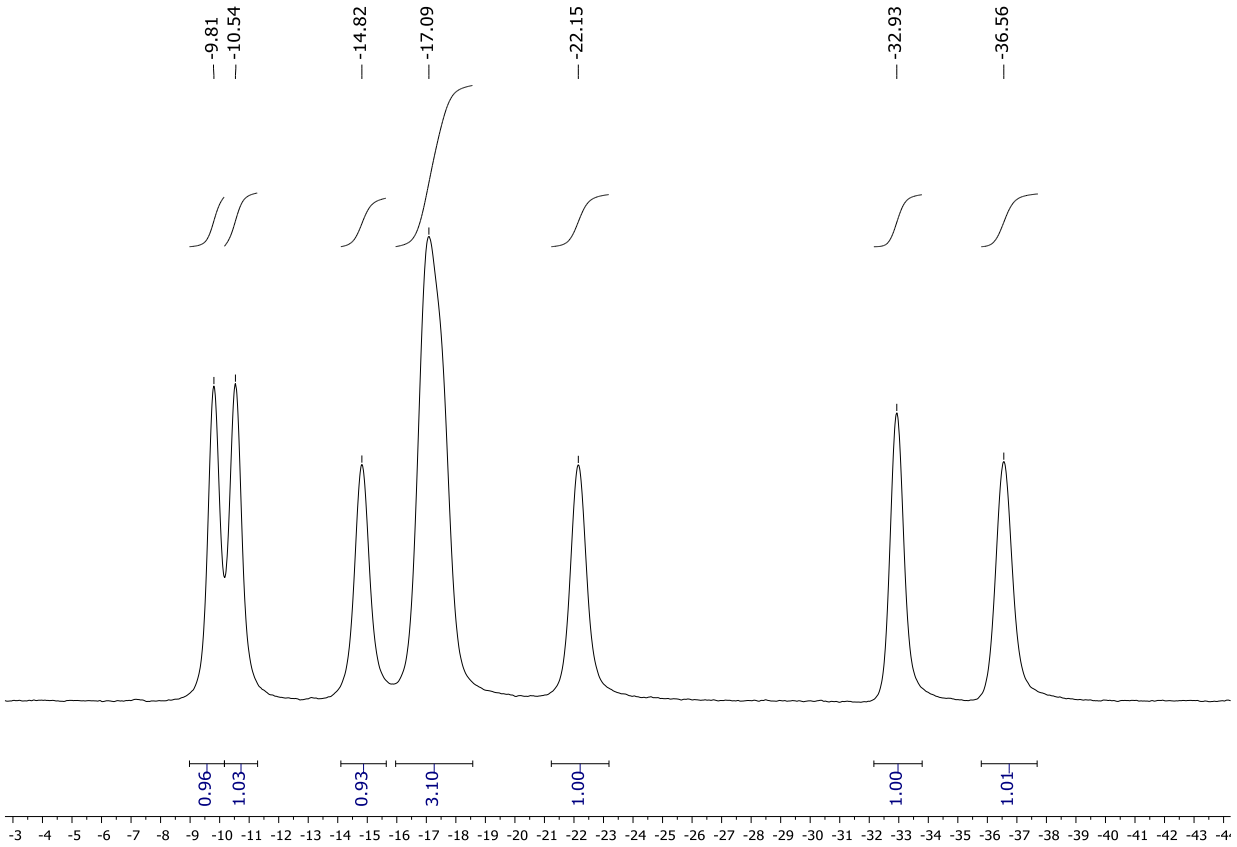

Fig. S15. $^{11}B\{^1H\}$ NMR spectrum of compound **3** in acetone-d_6

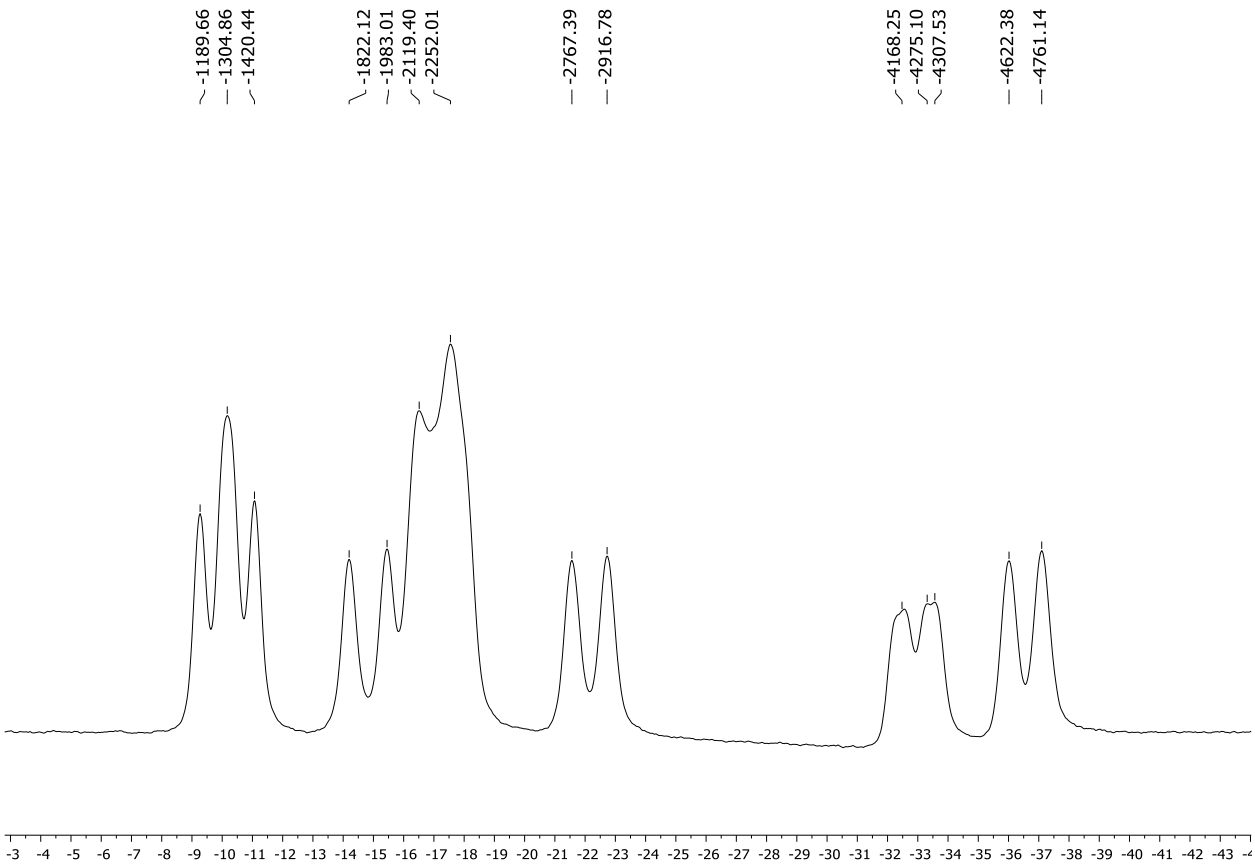

Fig. S16. $^{11}B\{^{1}H\}$ NMR spectrum of compound **3** in acetone-d_6

Spectral data for Cs[7-(MeO(CH$_2$)$_3$S)-7,8-C$_2$B$_9$H$_{11}$] (4)

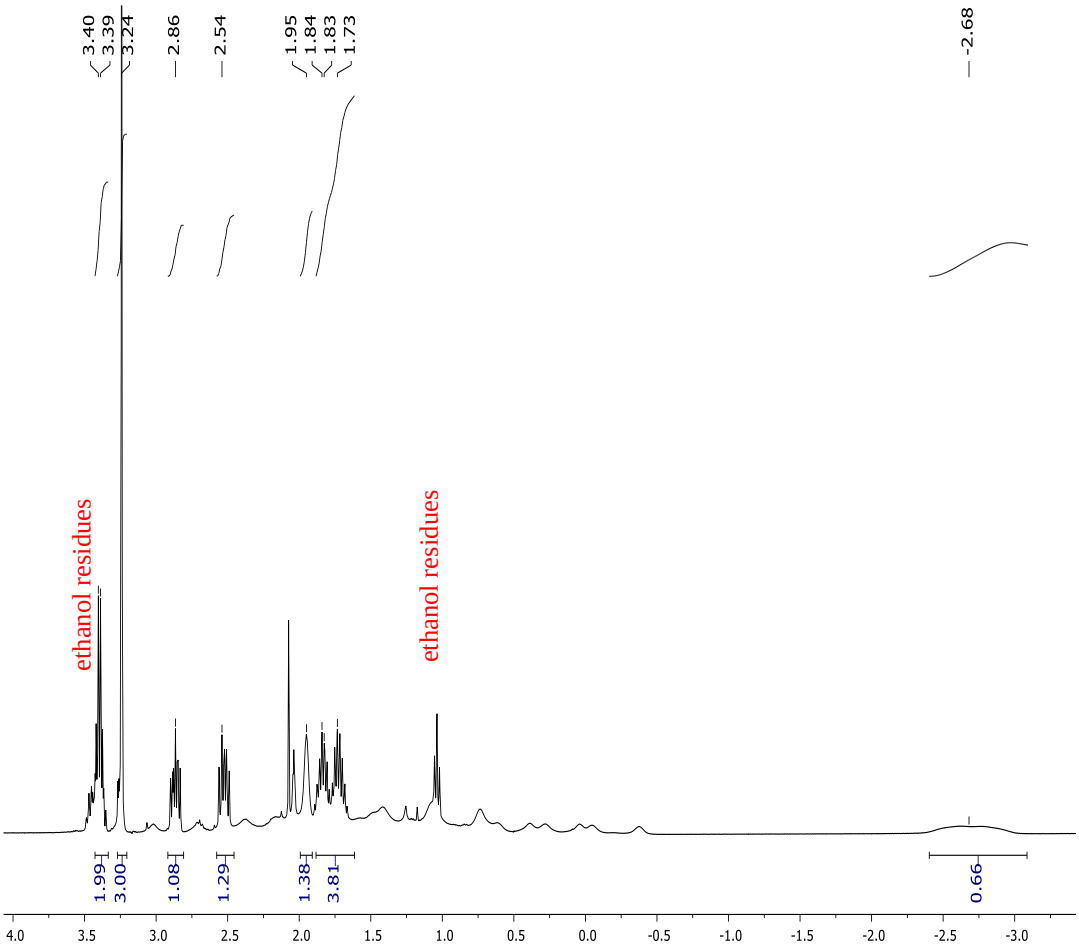

Fig. S17. ^{1}H NMR spectrum of compound **4** in acetone-d$_6$

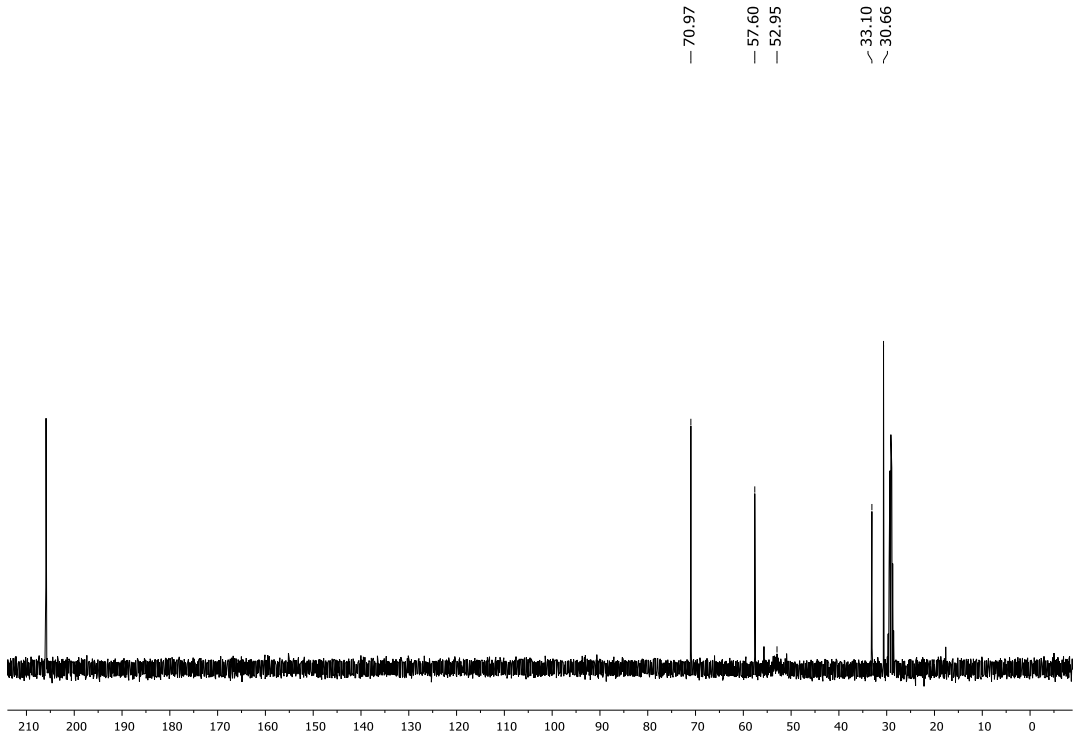

Fig. S18. ^{13}C NMR spectrum of compound **4** in acetone-d$_6$

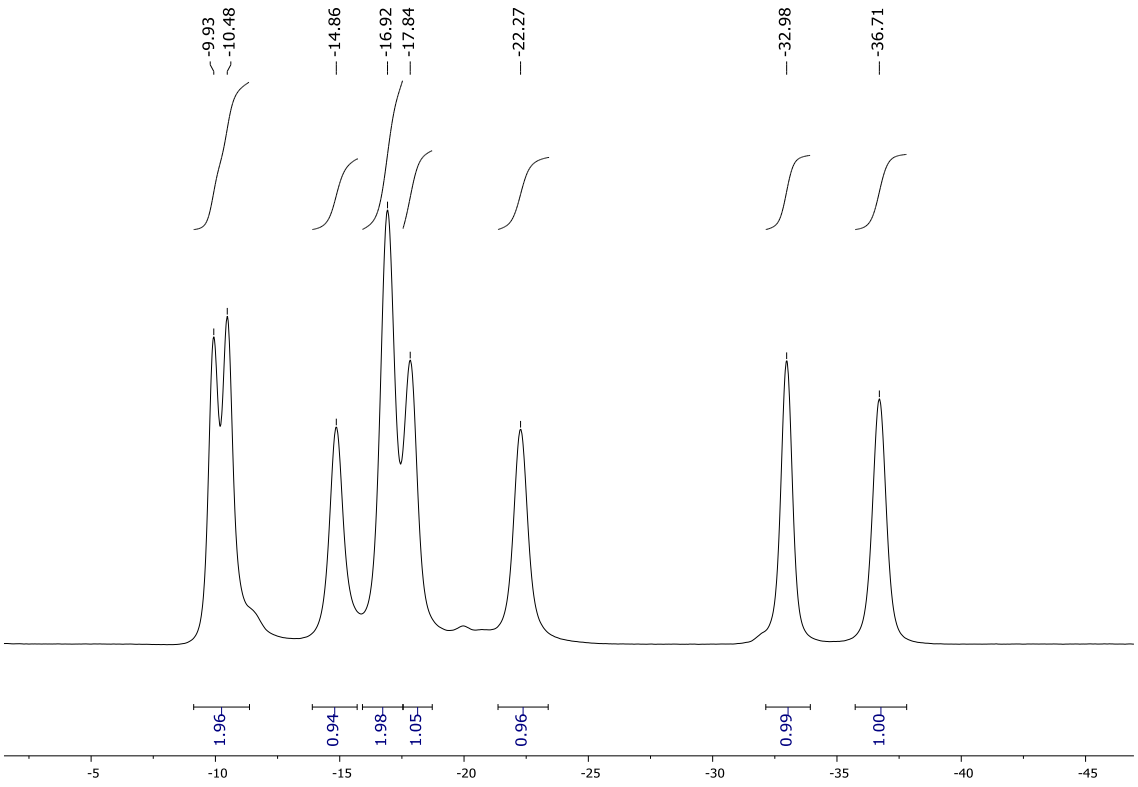

Fig. S19. $^{11}B\{^{1}H\}$ NMR spectrum of compound **4** in acetone-d_6

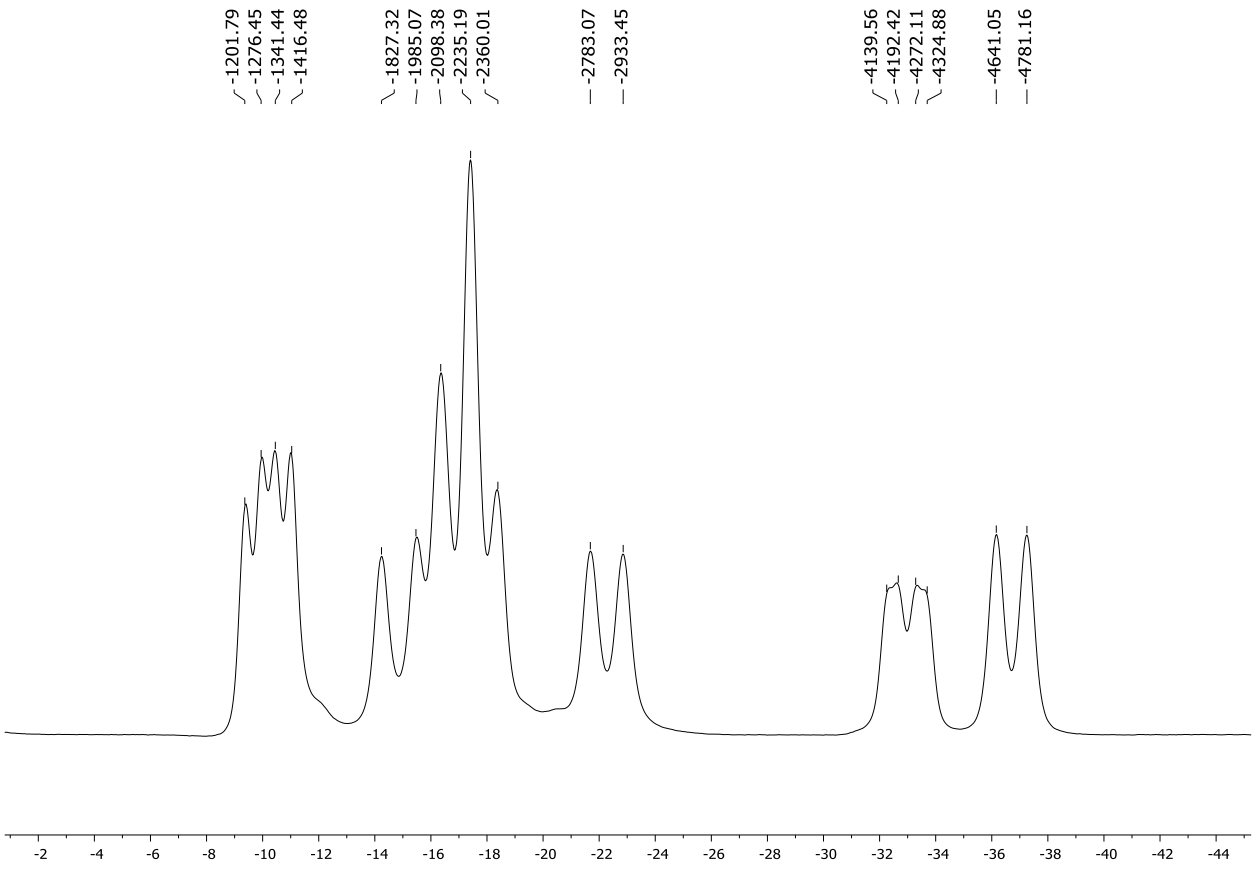

Fig. S20. $^{11}B\{^{1}H\}$ NMR spectrum of compound **4** in acetone-d_6

Spectral data for 3,3-(dppe)-1-(MeO(CH$_2$)$_2$S)-closo-3,1,2-NiC$_2$B$_9$H$_{10}$ (5)

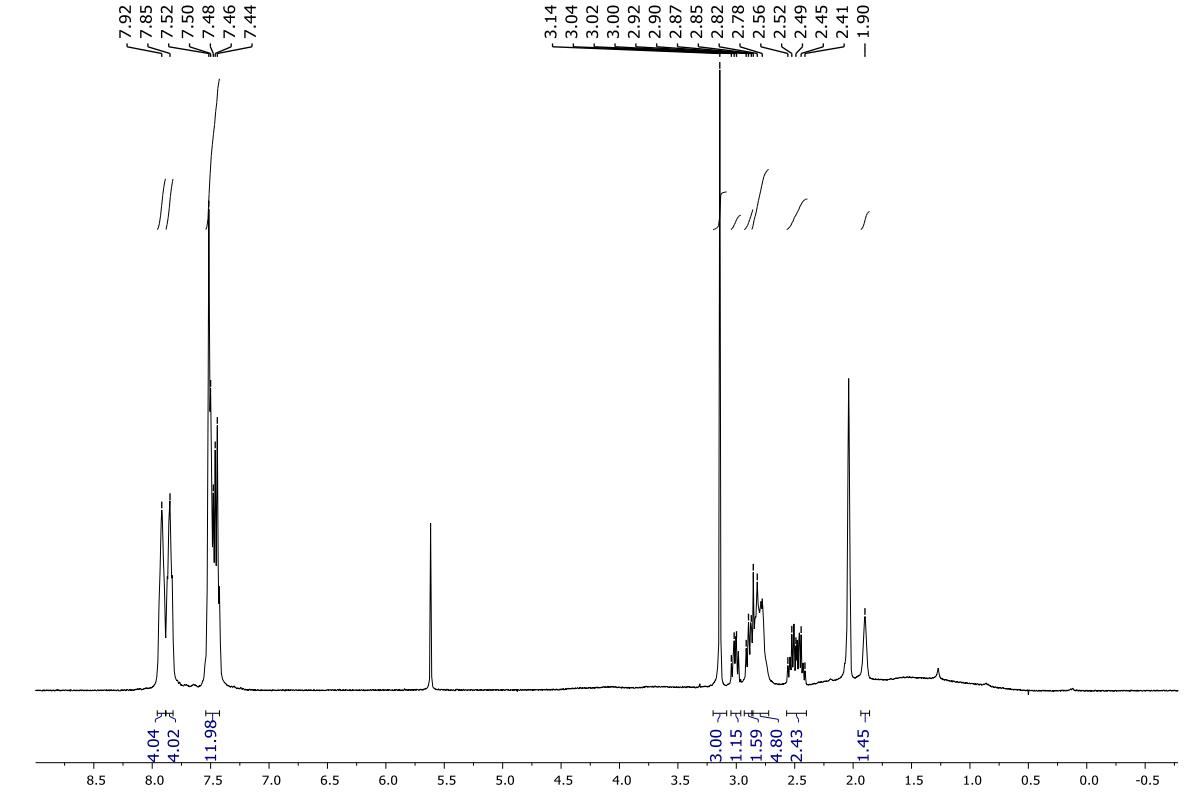

Fig. S21. ^{1}H NMR spectrum of compound **5** in acetone-d$_6$

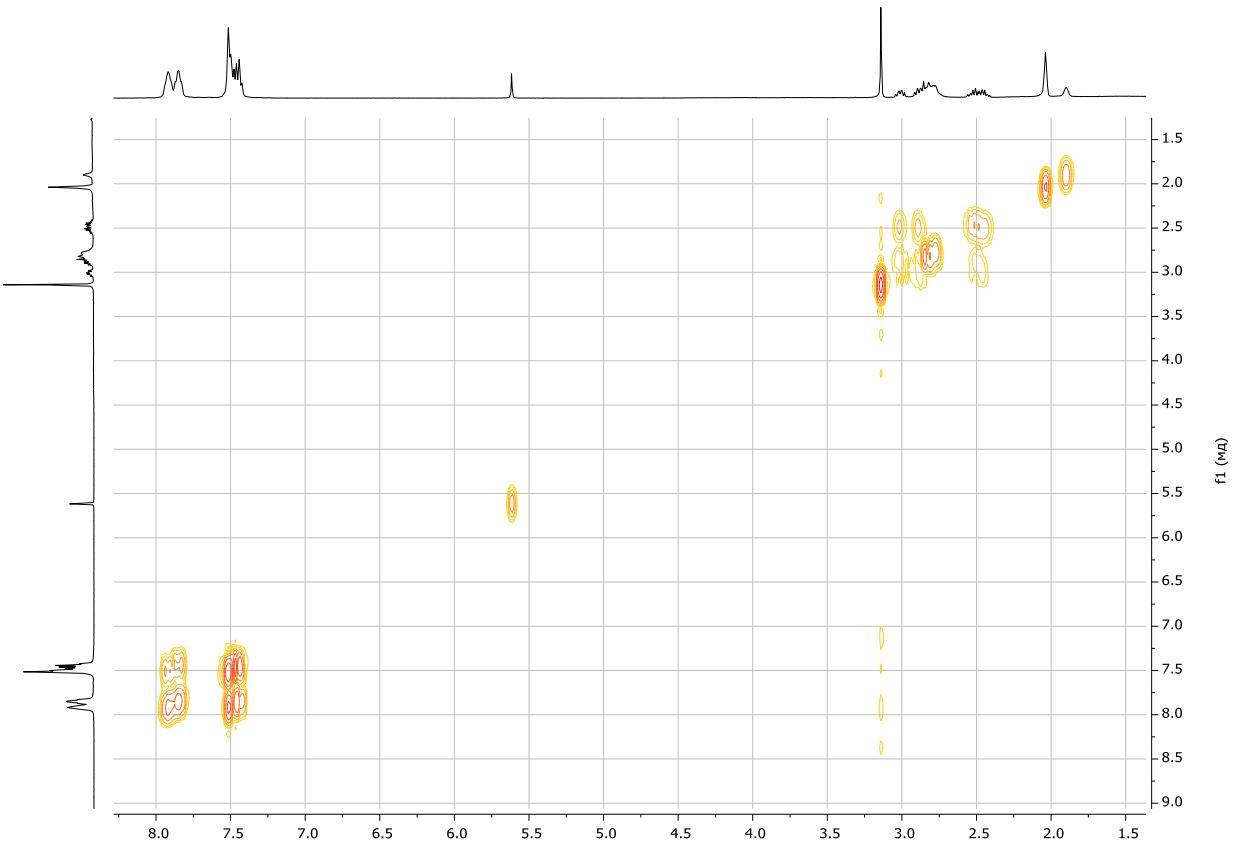

Fig. S22. (HH)COSY NMR spectrum of compound **5** in acetone-d$_6$

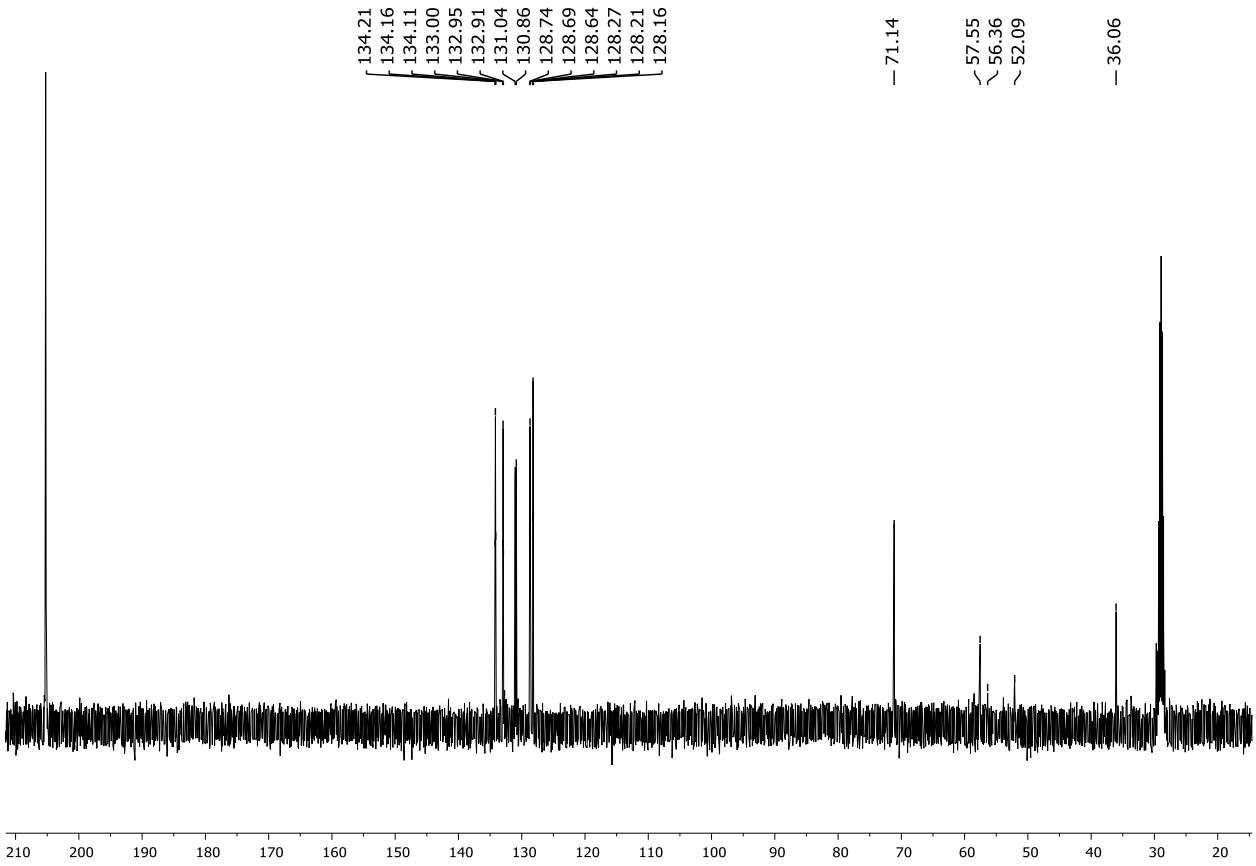

Fig. S23. ^{13}C NMR spectrum of compound **5** in acetone-d_6

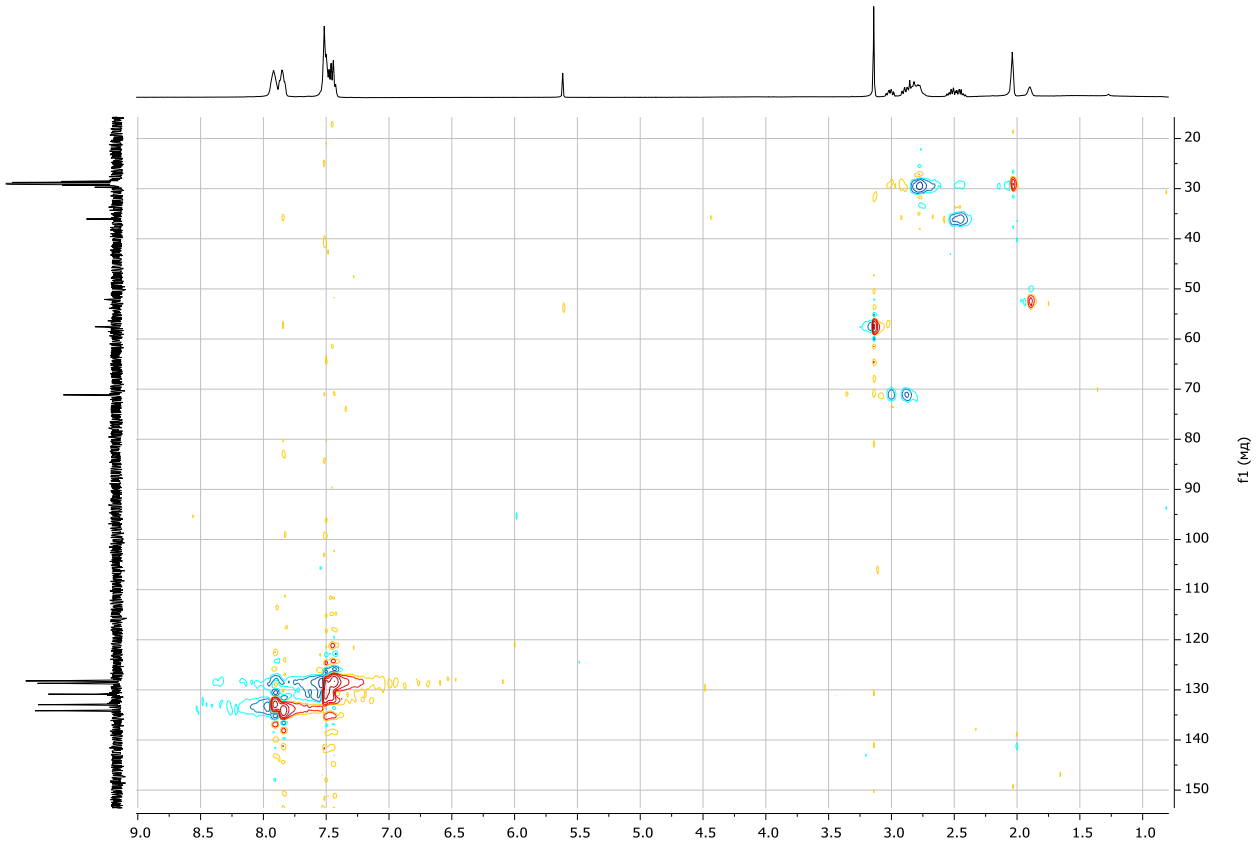

Fig. S24. (HC) HSQC NMR spectrum of compound **5** in acetone-d_6

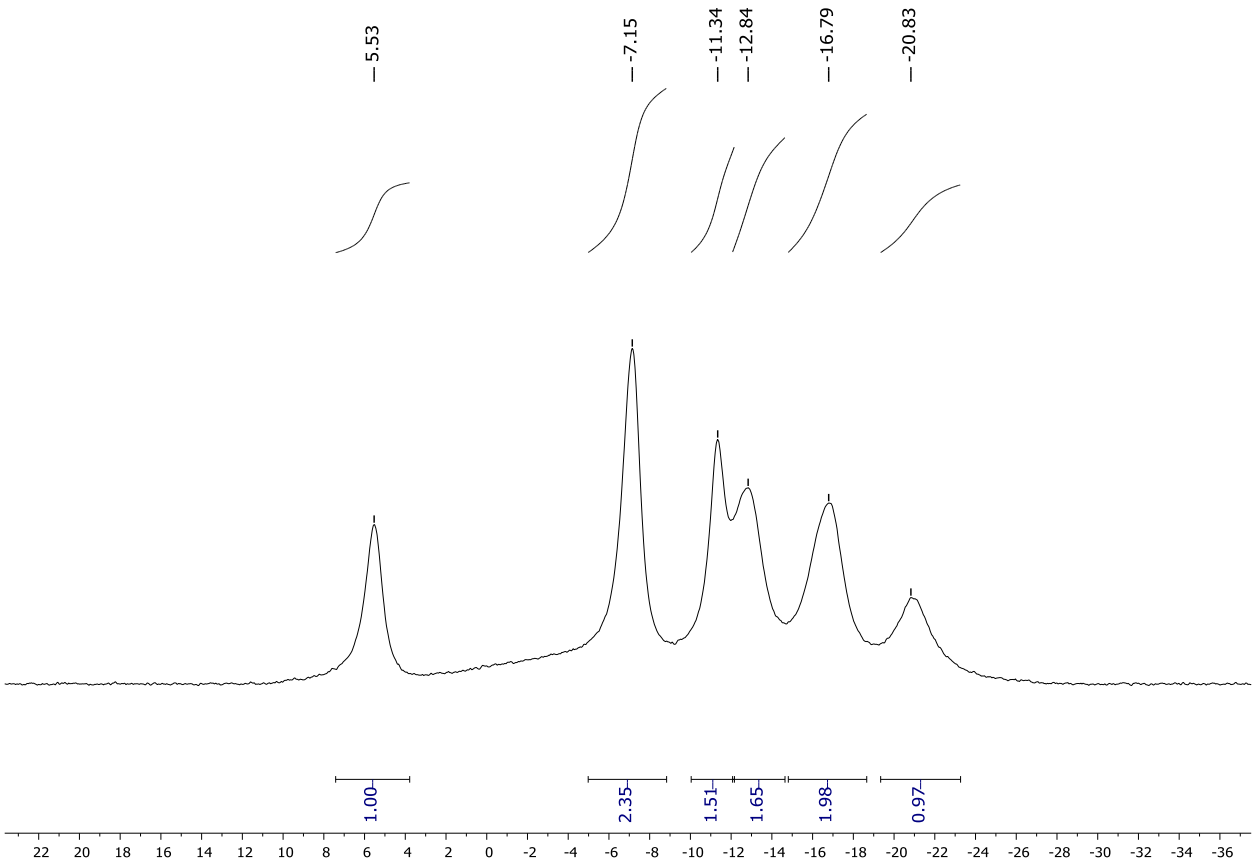

Fig. S25. $^{11}B\{^{1}H\}$ NMR spectrum of compound **5** in acetone-d_6

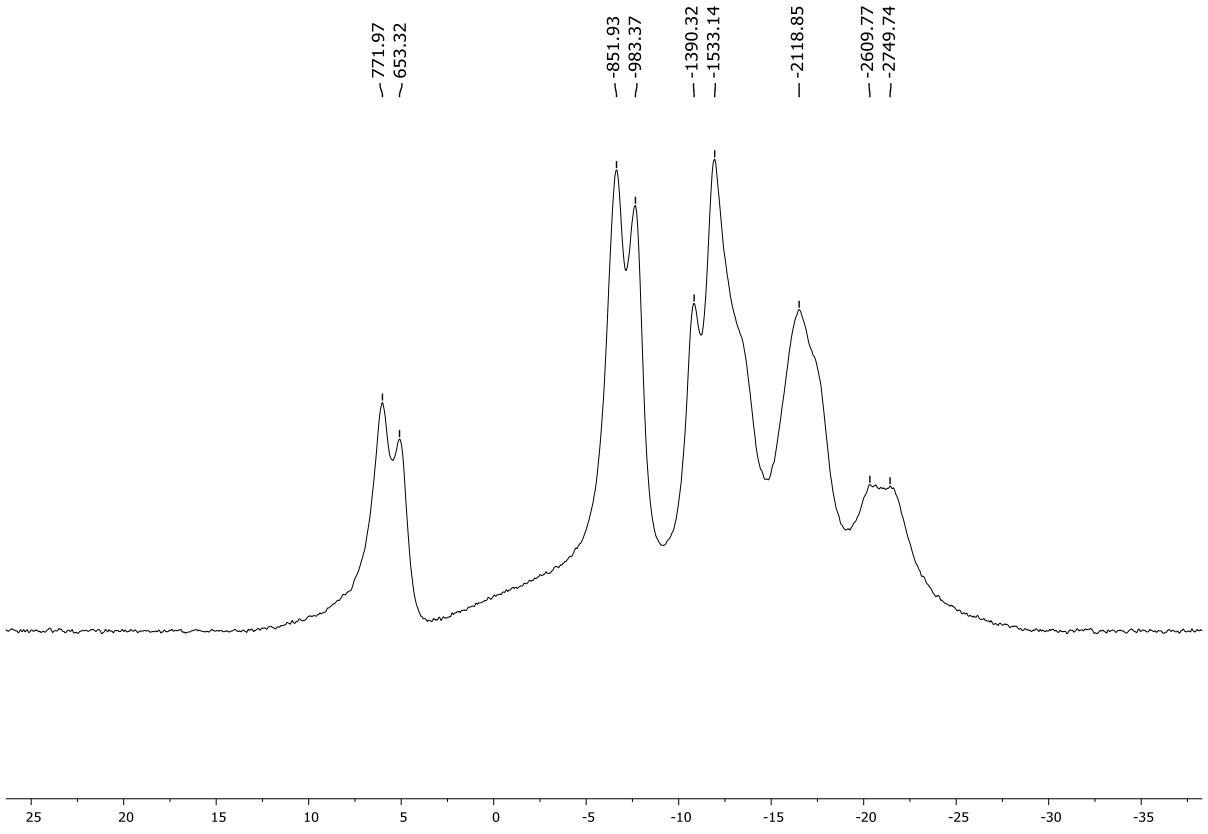

Fig. S26. ^{11}B NMR spectrum of compound **5** in acetone-d_6

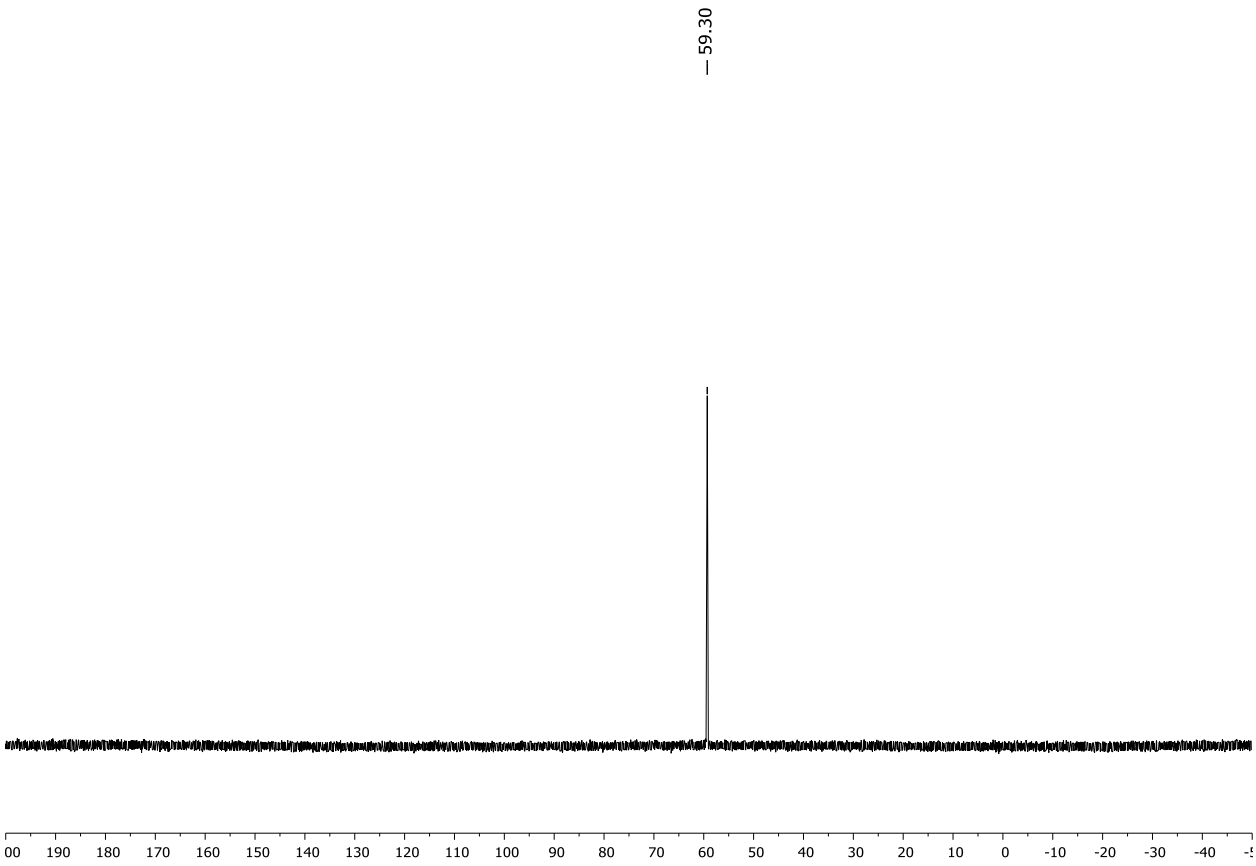

Fig. S27. $^{31}P\{^{1}H\}$ NMR spectrum of compound **5** in acetone-d_6

Spectral data for 3,3-(Me_2PhP)$_2$-1-($MeO(CH_2)_2S$)-*closo*-3,1,2-$NiC_2B_9H_{10}$ (6)

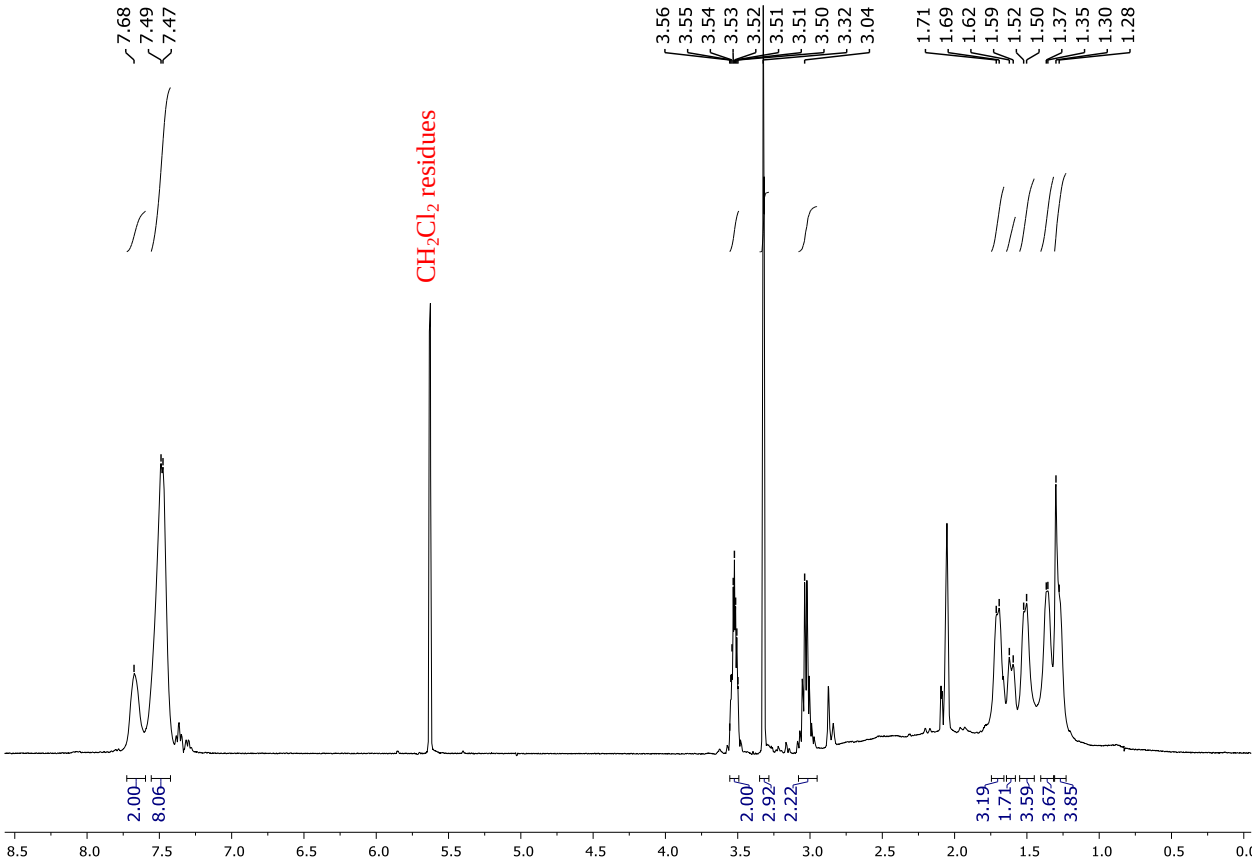

Fig. S28. ^{1}H NMR spectrum of compound **6** in acetone-d_6

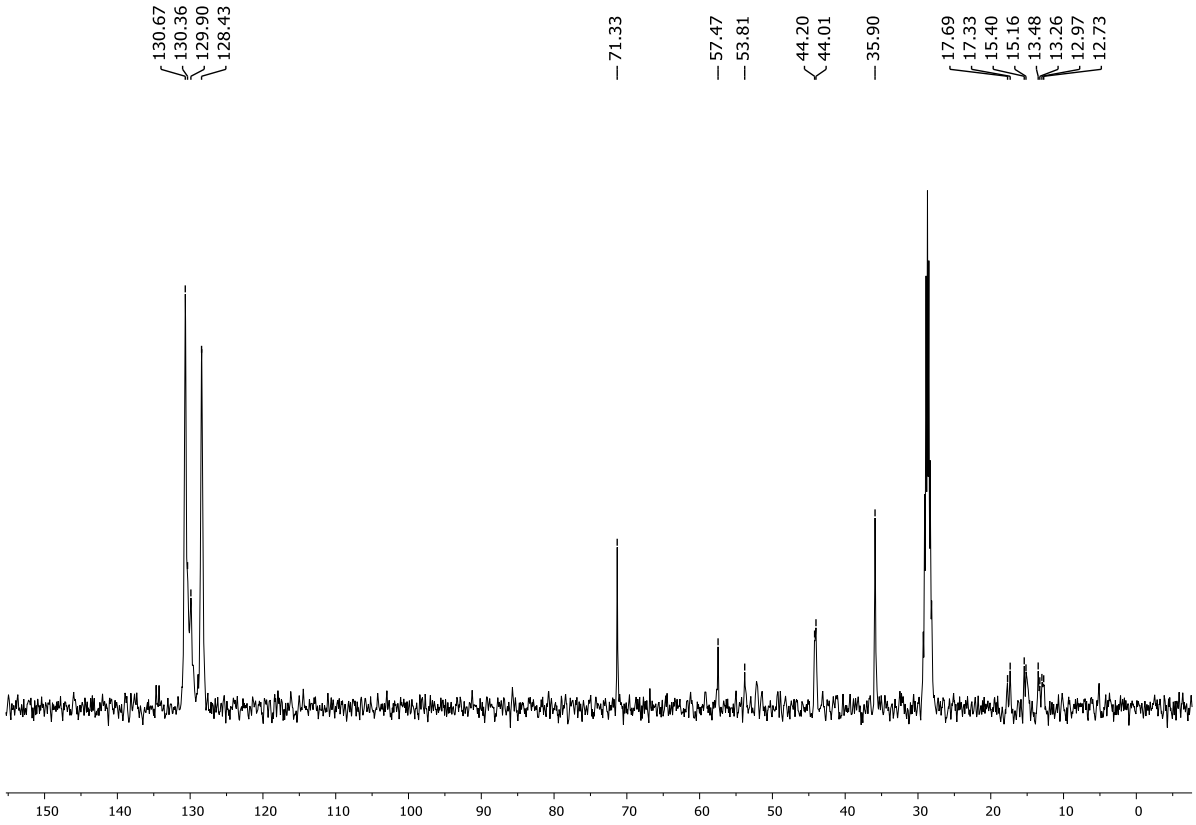

Fig. S29. ^{13}C NMR spectrum of compound **6** in acetone-d_6

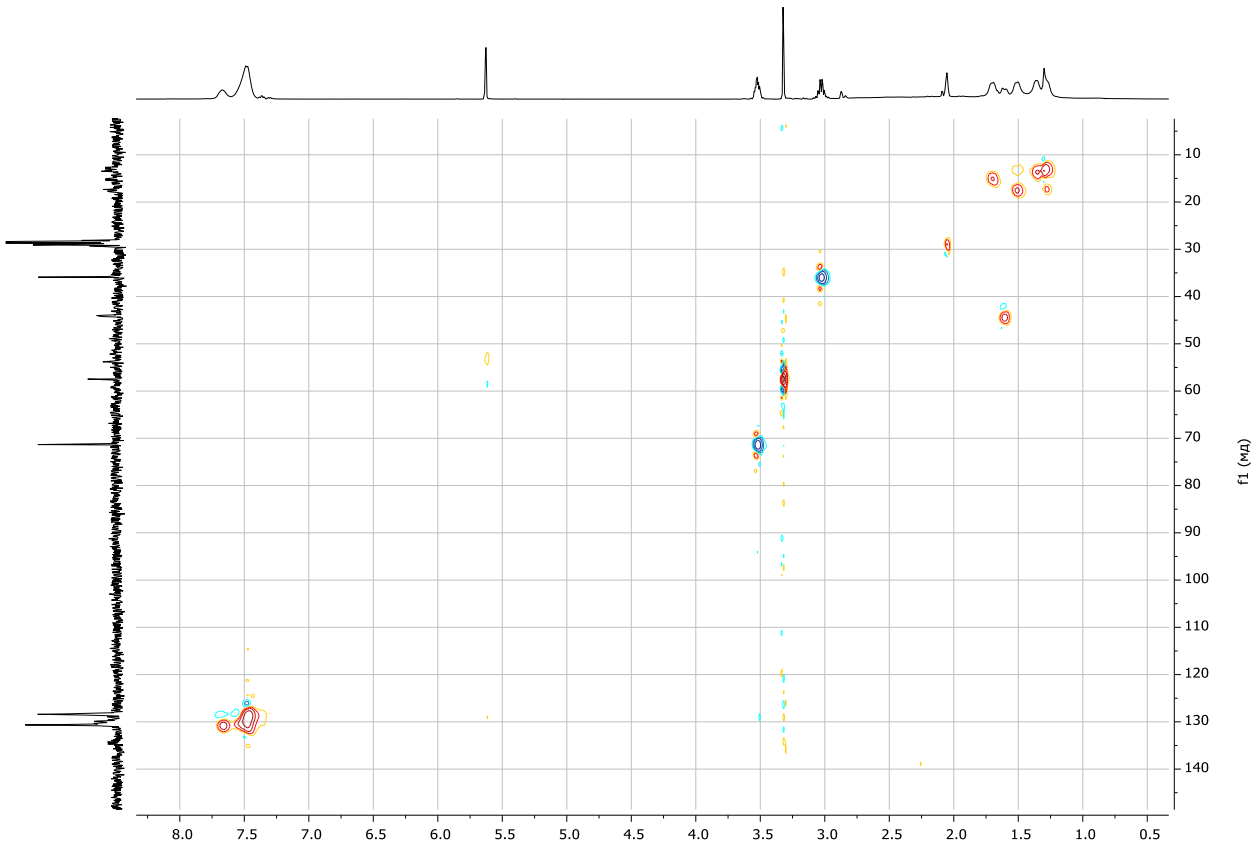

Fig. S30. (HC) HSQC NMR spectrum of compound **6** in acetone-d_6

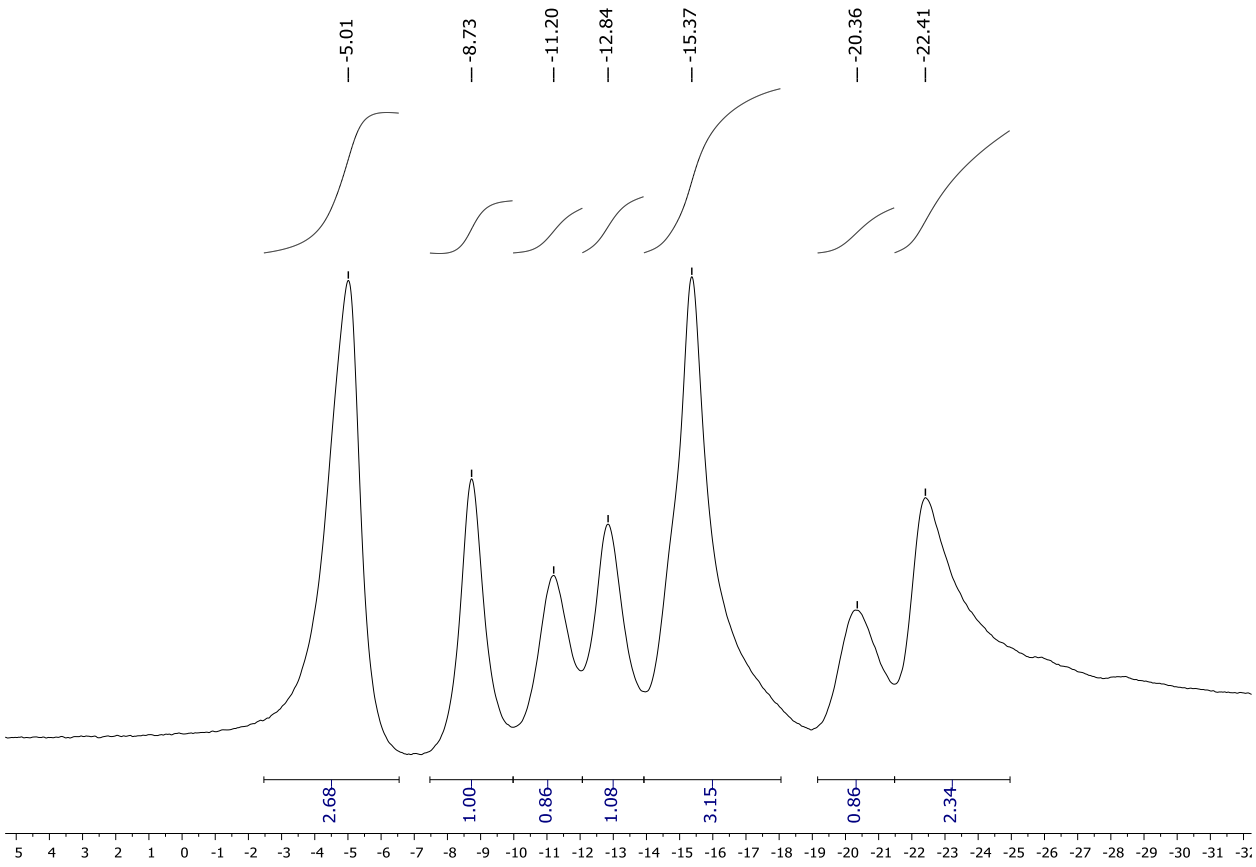

Fig. S31. $^{11}B\{^1H\}$NMR spectrum of compound **6** in acetone-d_6

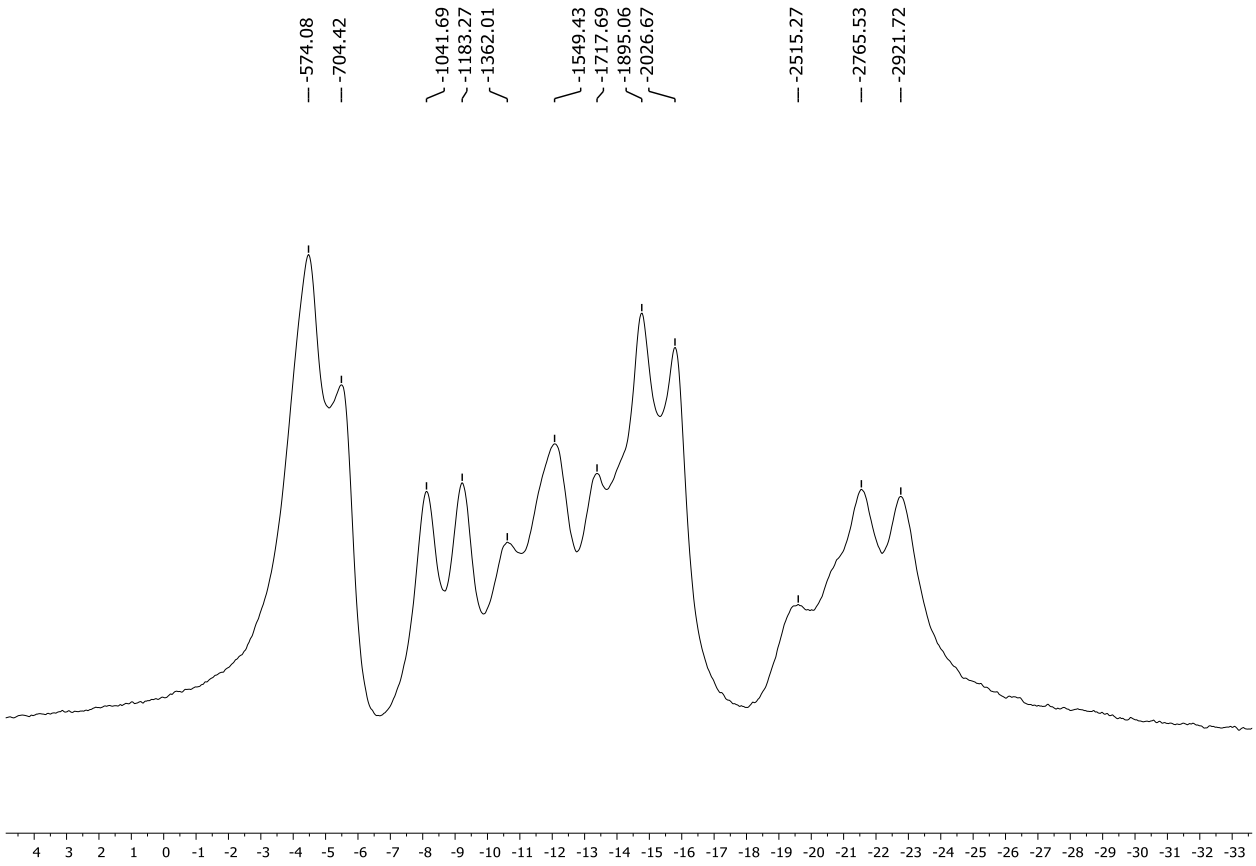

Fig. S32. ^{11}B NMR spectrum of compound **6** in acetone-d_6

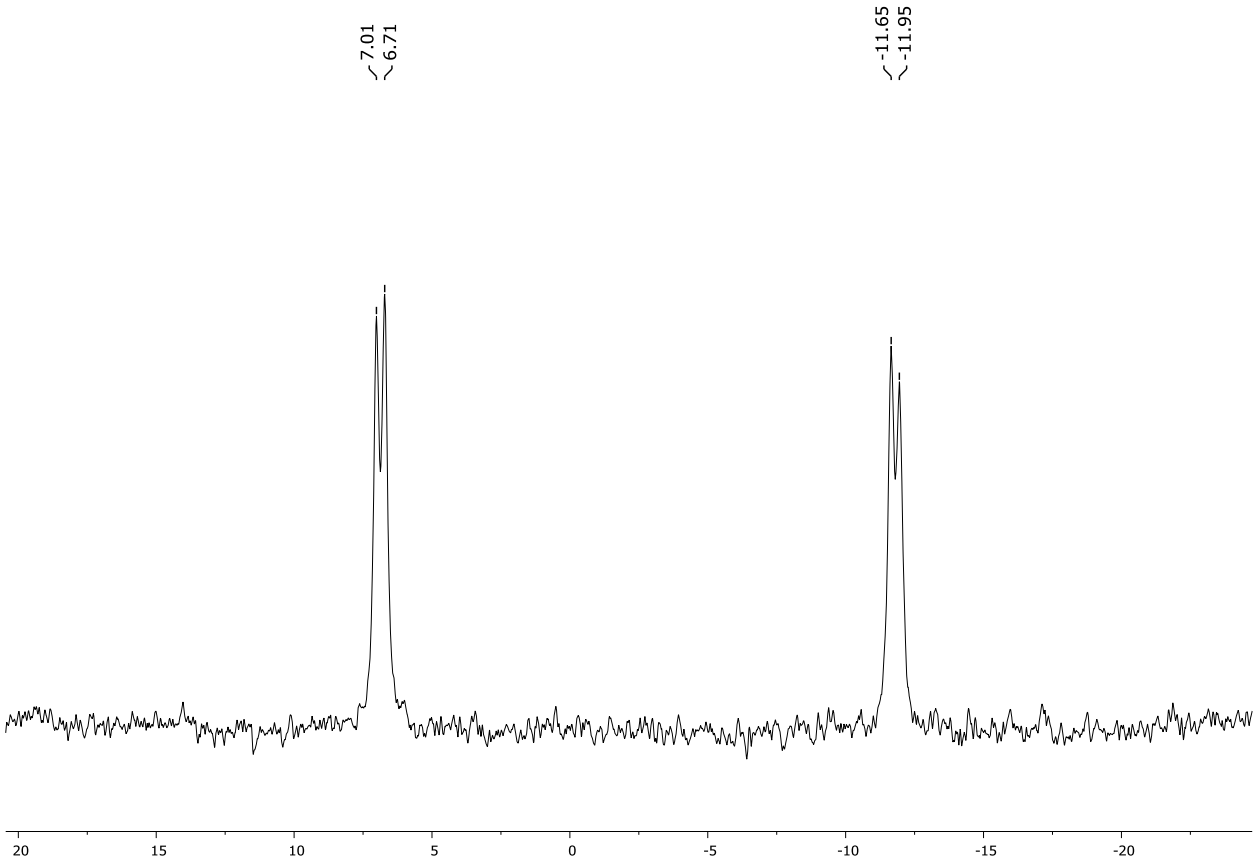

Fig. S33. $^{31}P\{^1H\}$ NMR spectrum of compound **6** in acetone-d_6

Spectral data for 3,3-($MePh_2P$)$_2$-1-($MeO(CH_2)_2S$)-*closo*-3,1,2-$NiC_2B_9H_{10}$ (7)

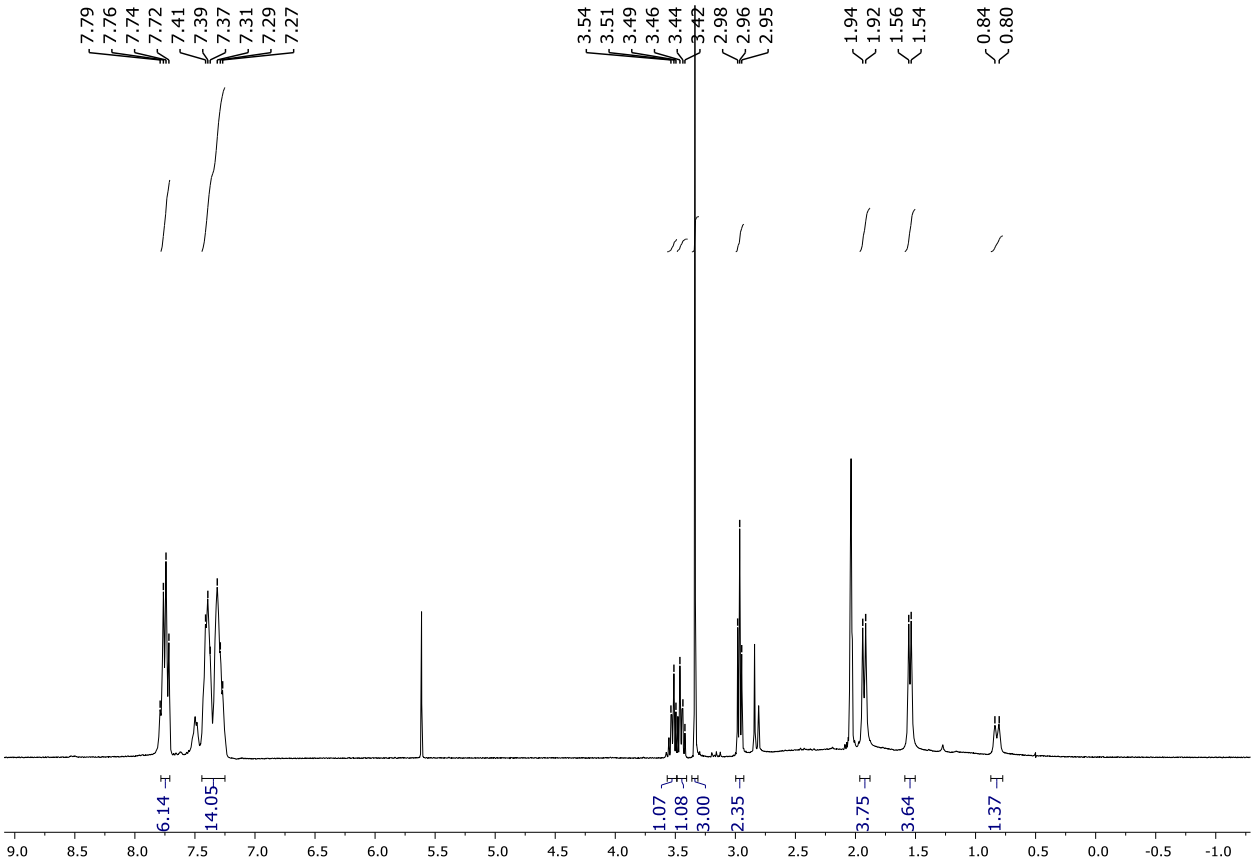

Fig. S34. ^{1}H NMR spectrum of compound **7** in acetone-d_6

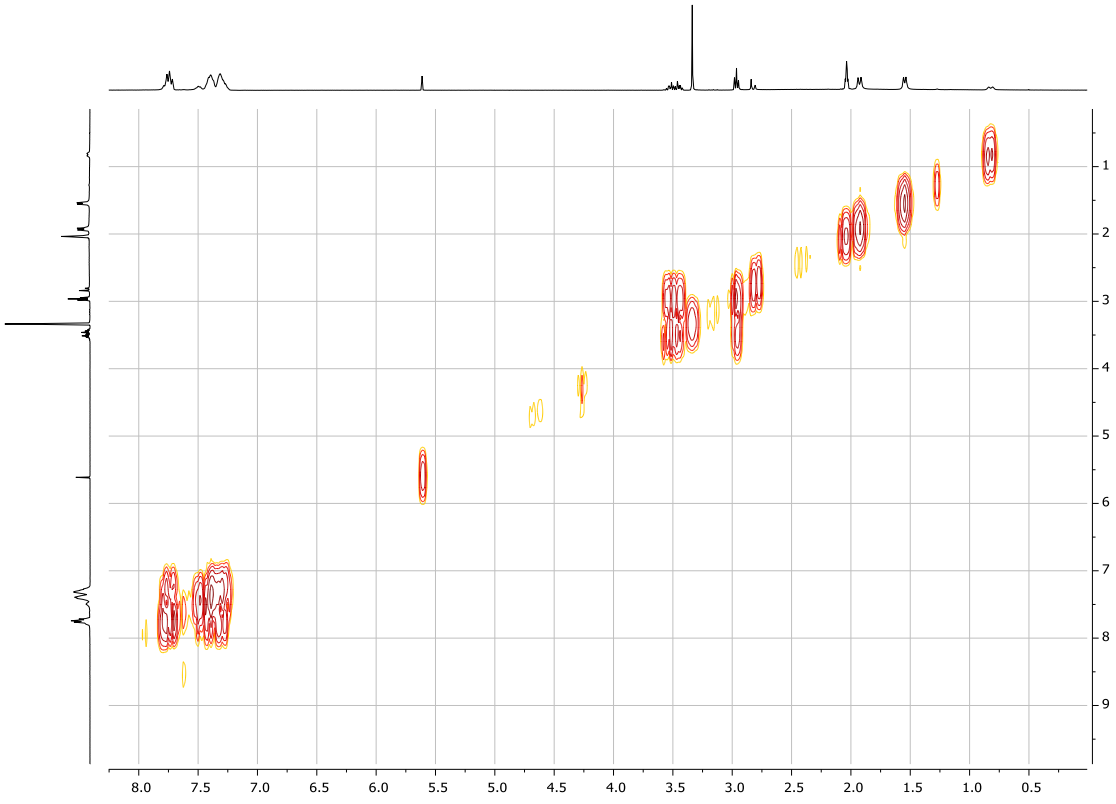

Fig. S35. (HH) COSY NMR spectrum of compound **7** in acetone-d_6

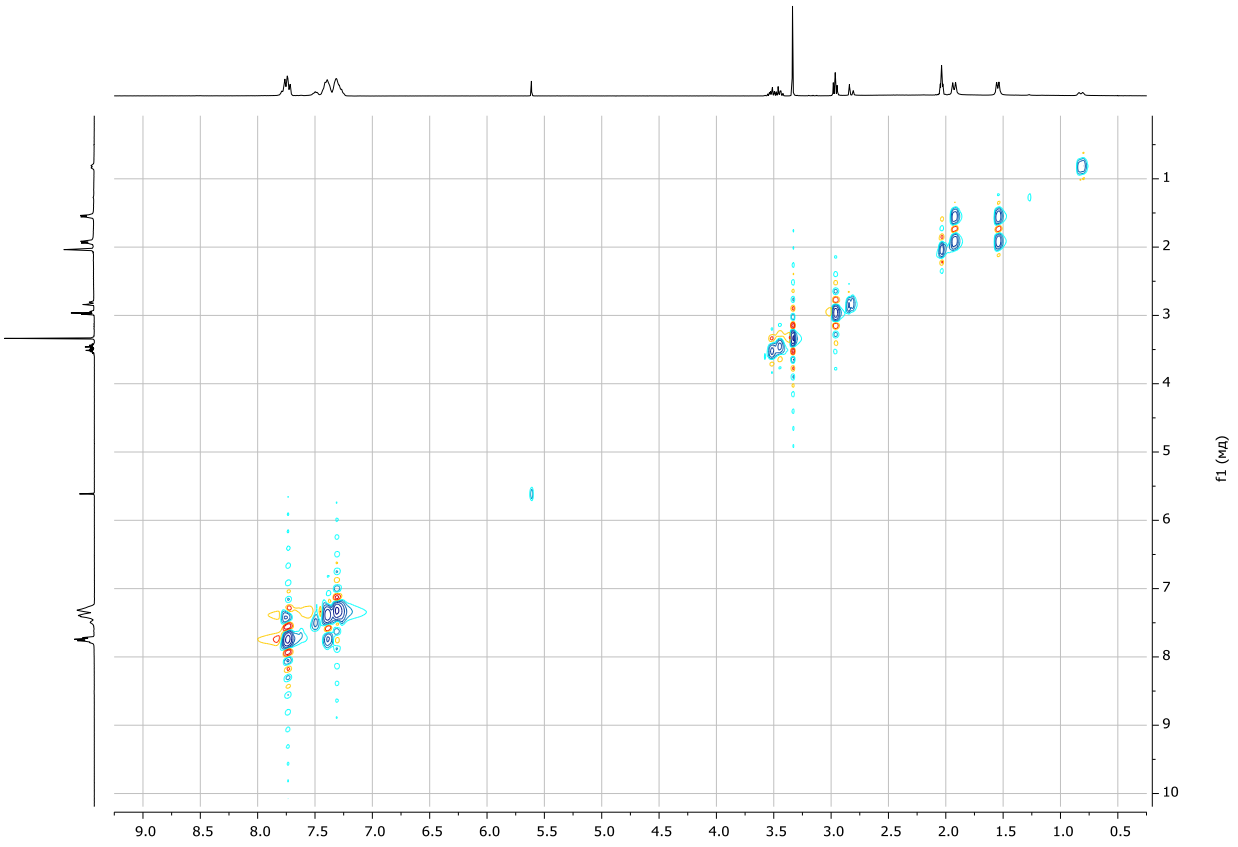

Fig. S36. NOESY NMR spectrum of compound **7** in acetone-d_6

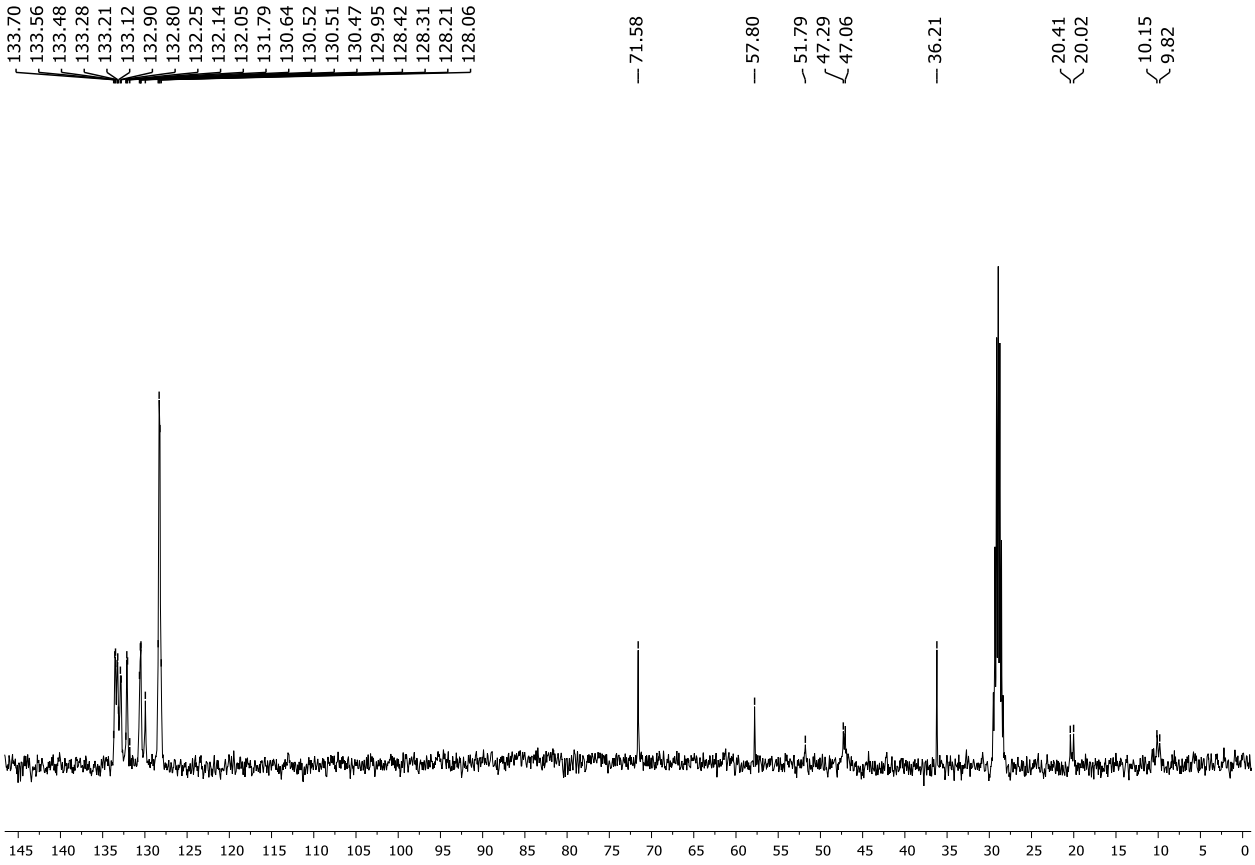

Fig. S37. ^{13}C NMR spectrum of compound **7** in acetone-d_6

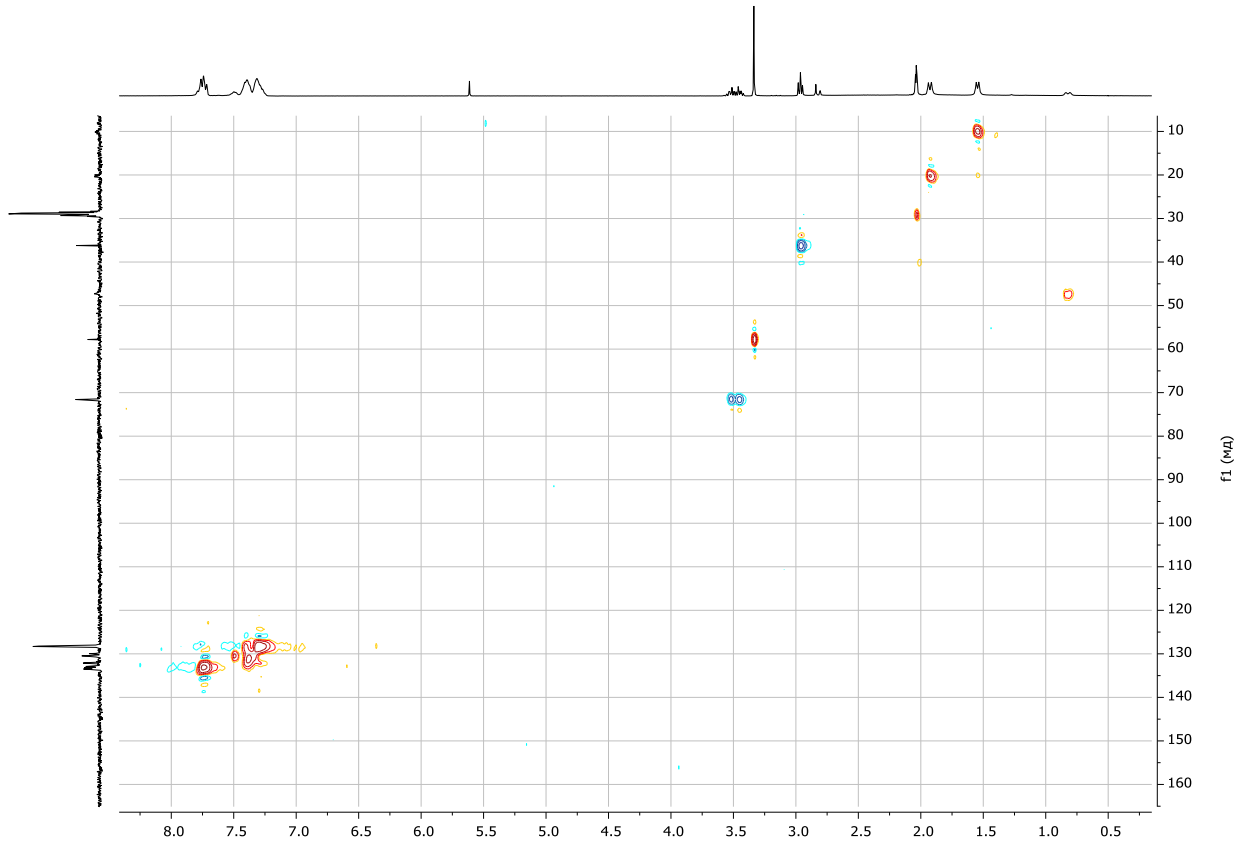

Fig. S38. (HC) HSQC NMR spectrum of compound **7** in acetone-d_6

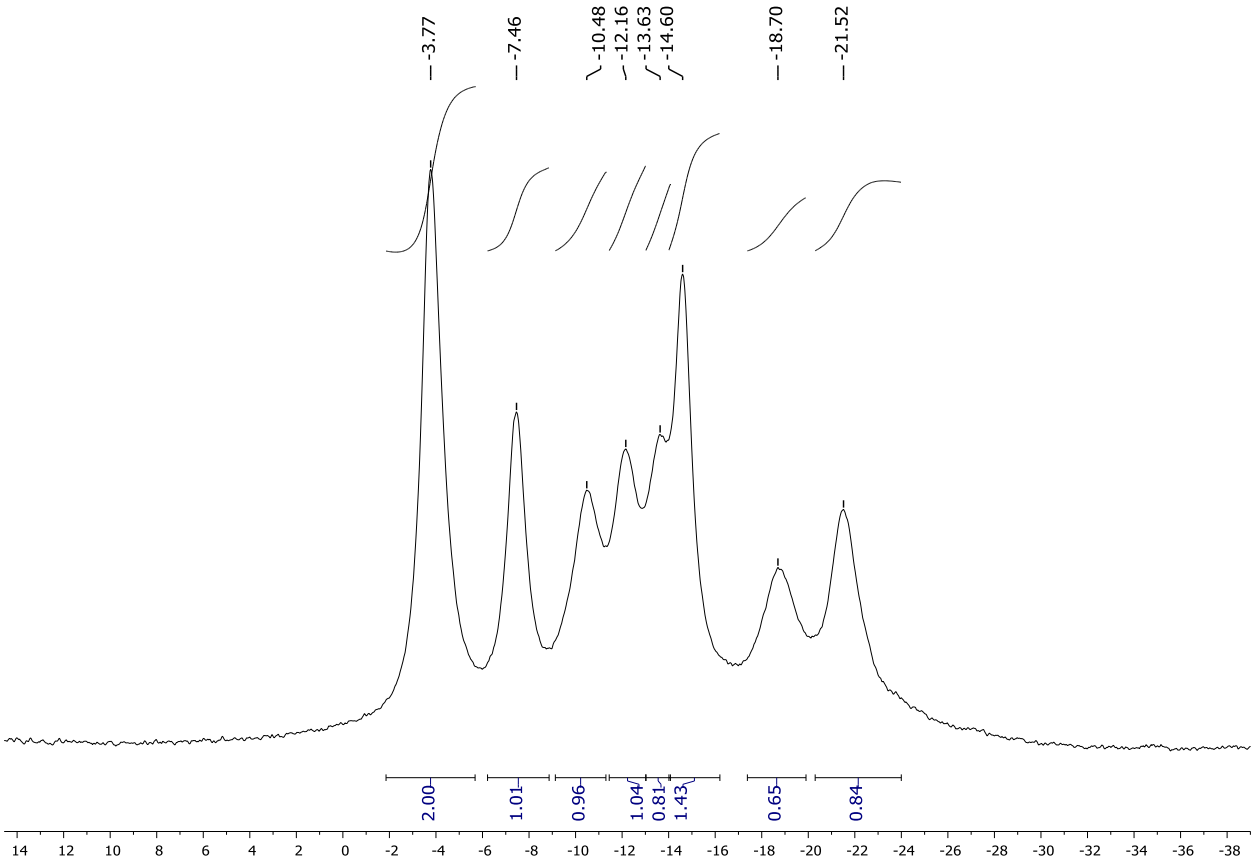

Fig. S39. $^{11}B\{^{1}H\}$NMR spectrum of compound **7** in acetone-d_6

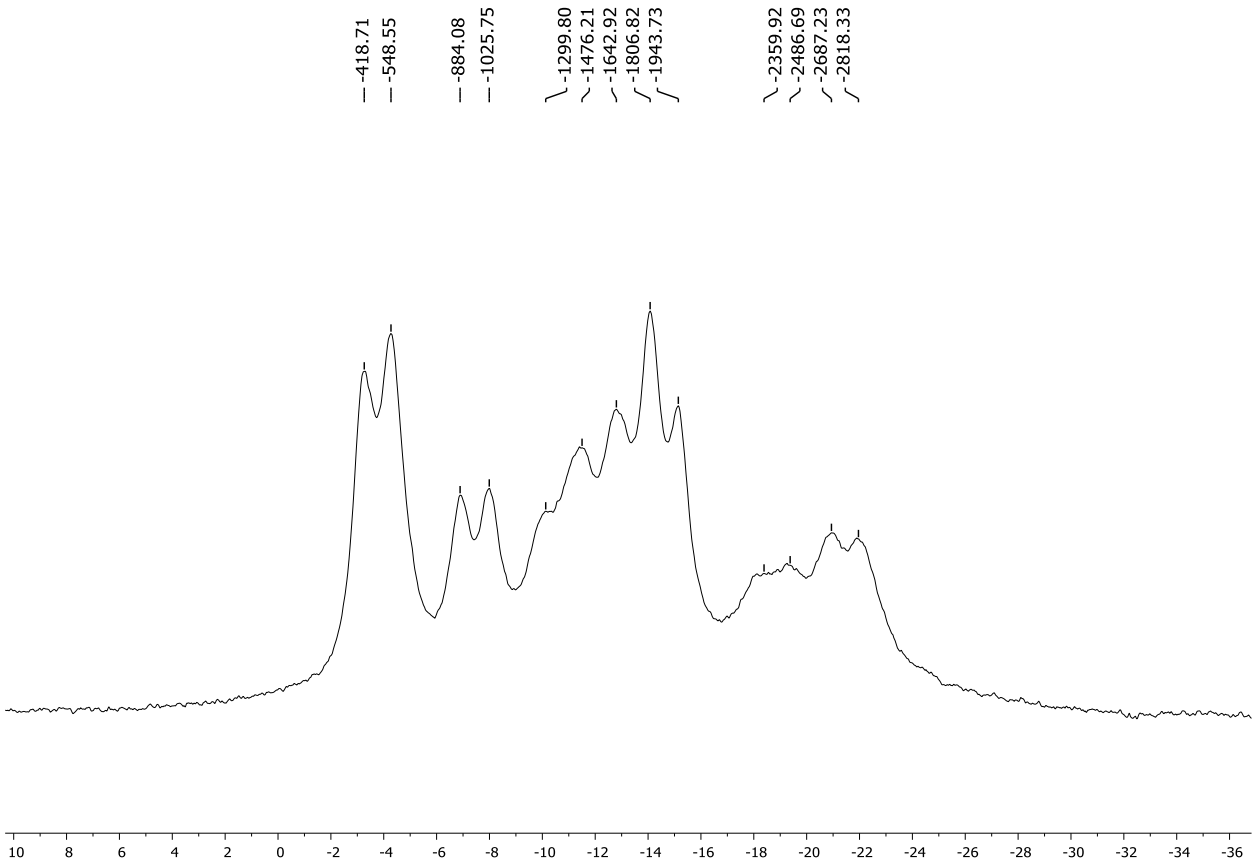

Fig. S40. ^{11}B NMR spectrum of compound **7** in acetone-d_6

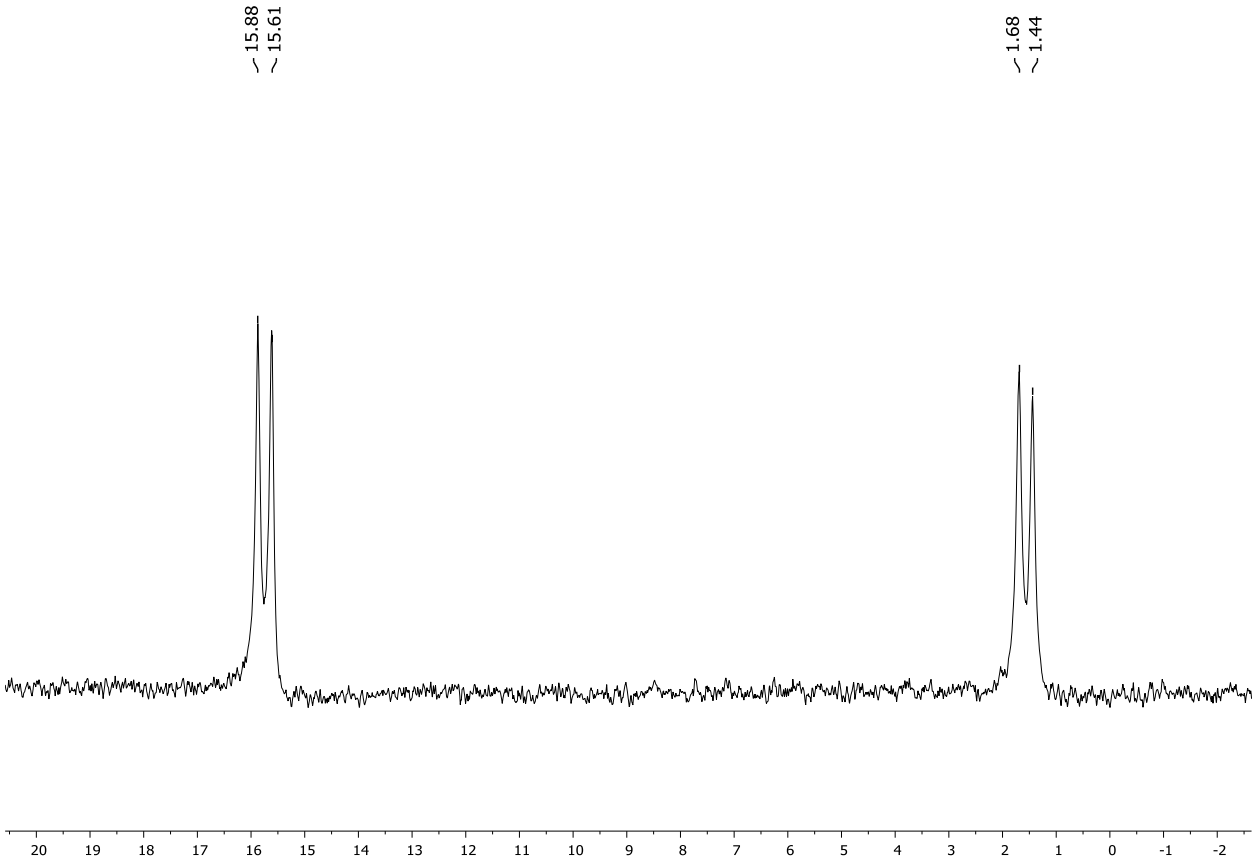

Fig. S41. $^{31}P\{^1H\}$ NMR spectrum of compound **7** in acetone-d_6

Spectral data for 3,3-(EtPh$_2$P)$_2$-1-(MeO(CH$_2$)$_2$S)-*closo*-3,1,2-NiC$_2$B$_9$H$_{10}$ (8)

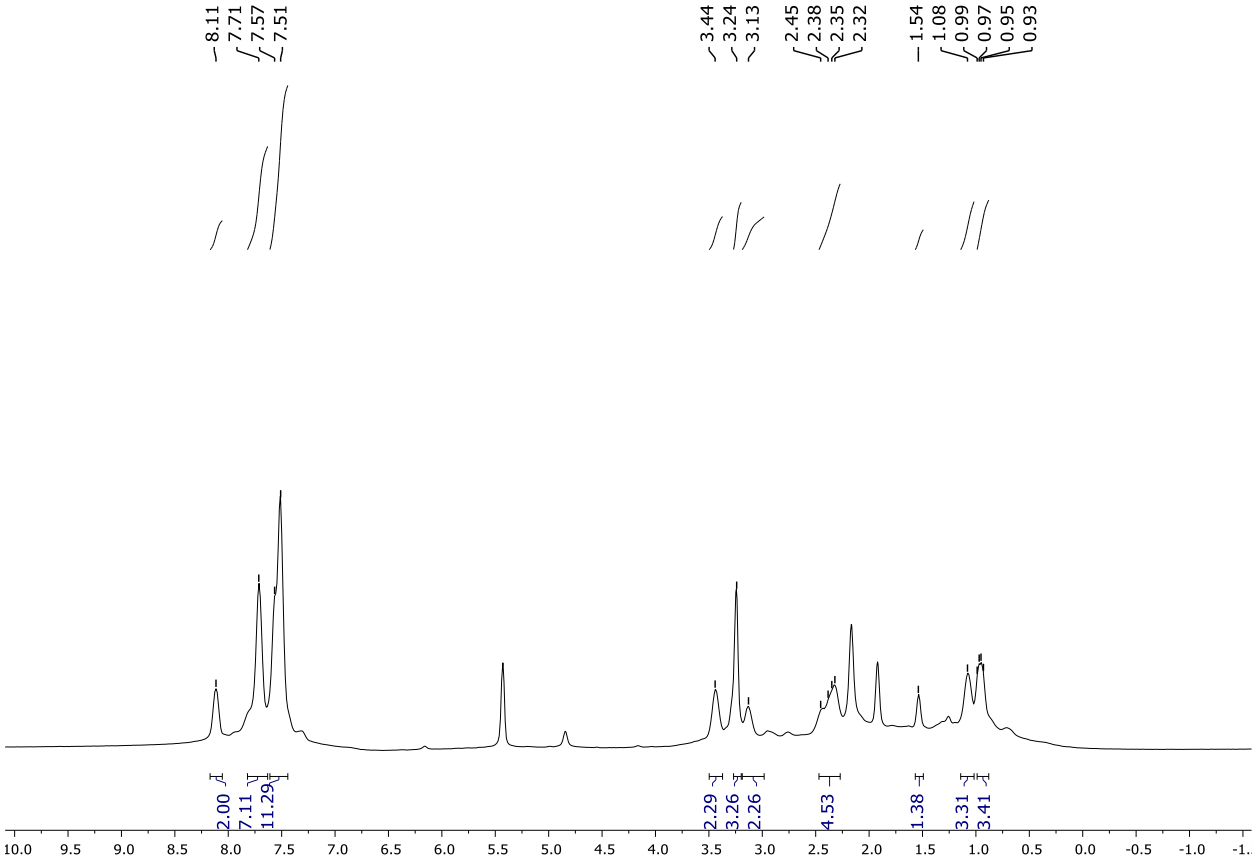

Fig. S42. ^{1}H NMR spectrum of compound **8** in CD$_3$CN

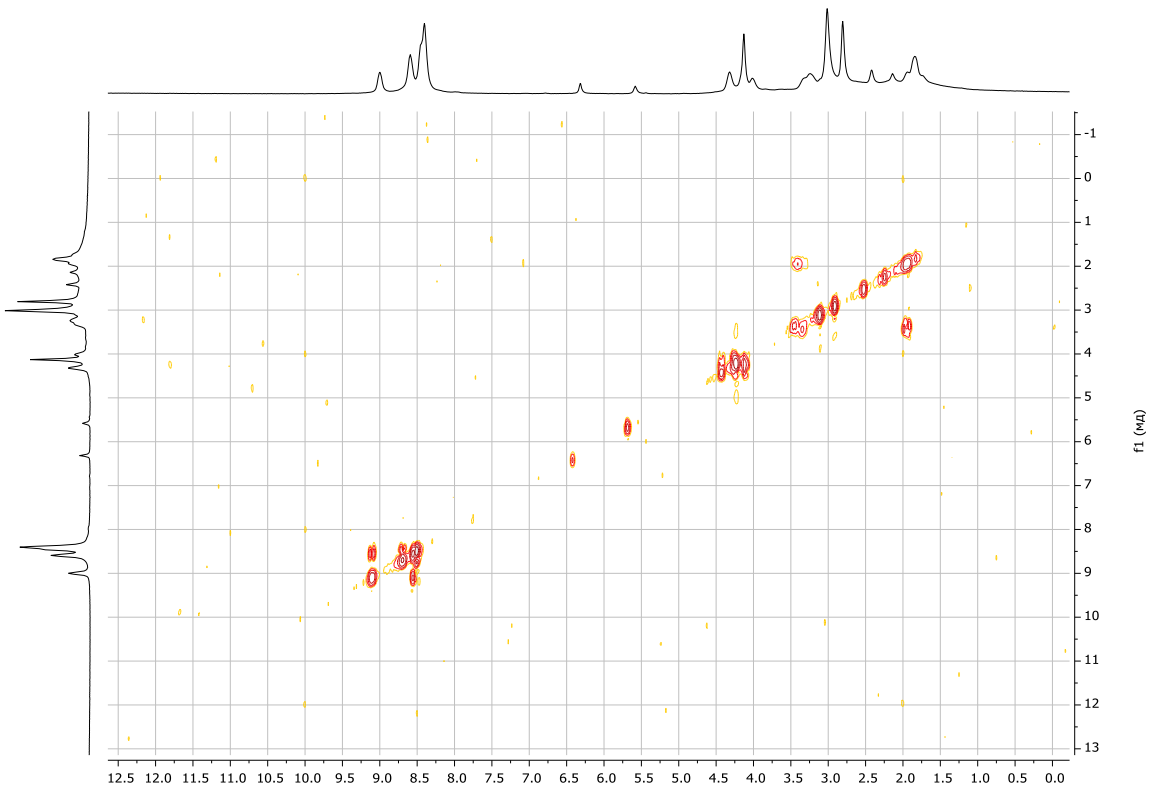

Fig. S43. A fragment of (HH) COSY NMR spectrum of compound **8** in CD$_3$CN

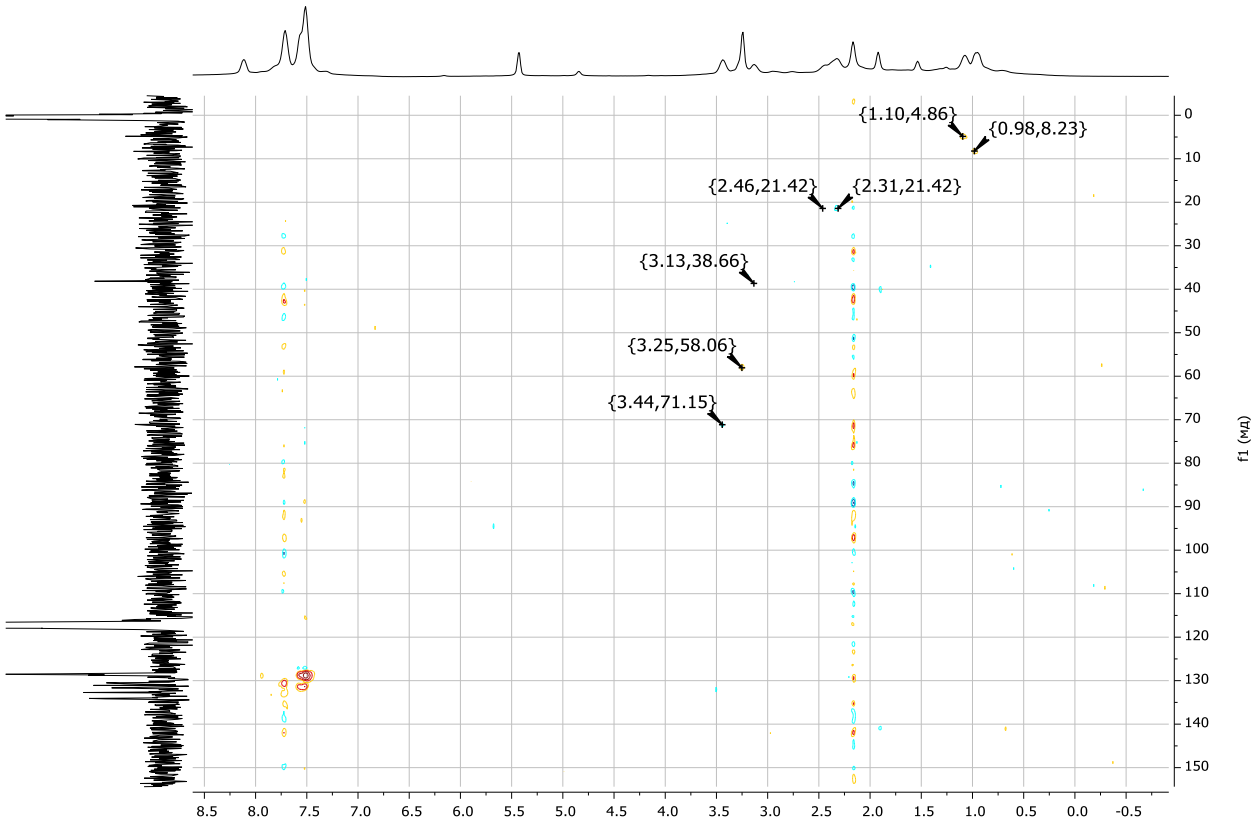

Fig. S44. (HC) HSQC NMR spectrum of compound **8** in CD_3CN

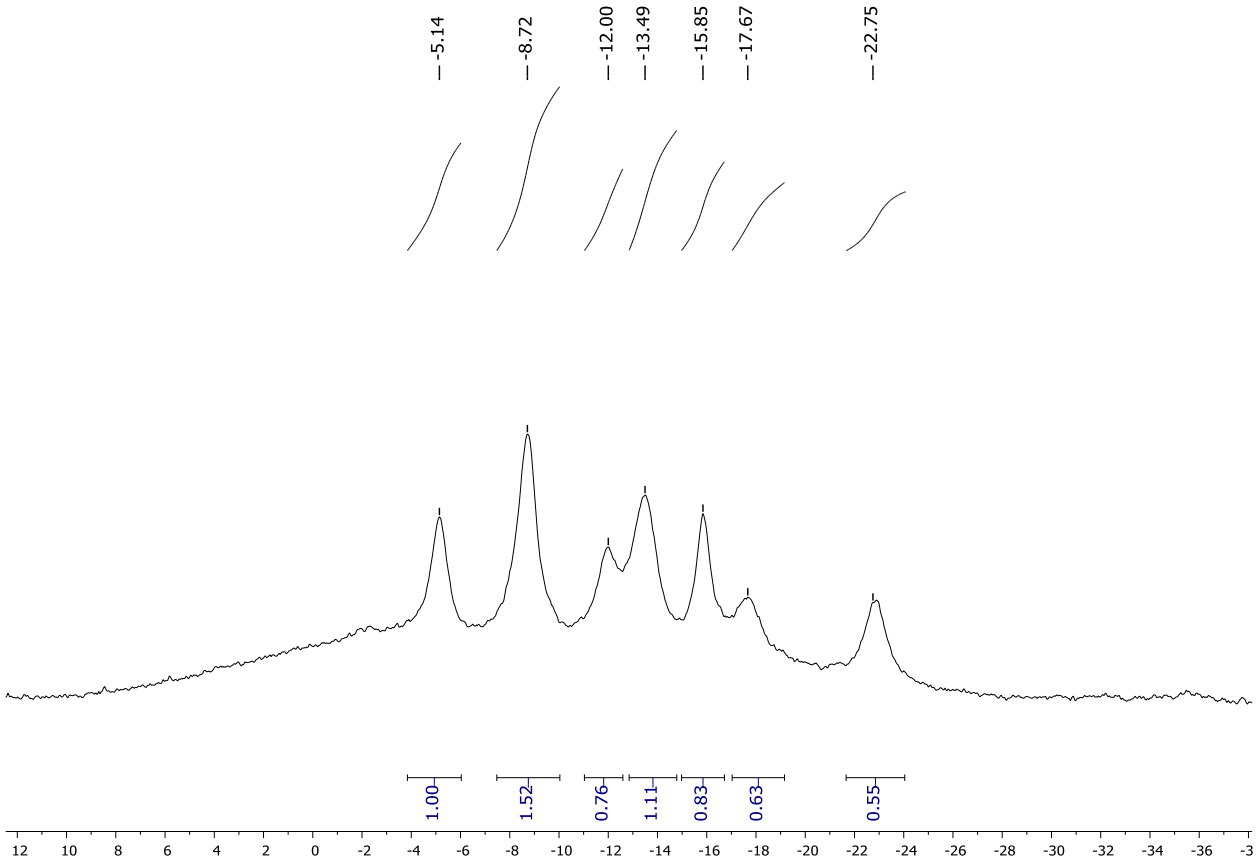

Fig. S45. $^{11}B\{^1H\}$ NMR spectrum of compound **8** in CD_3CN

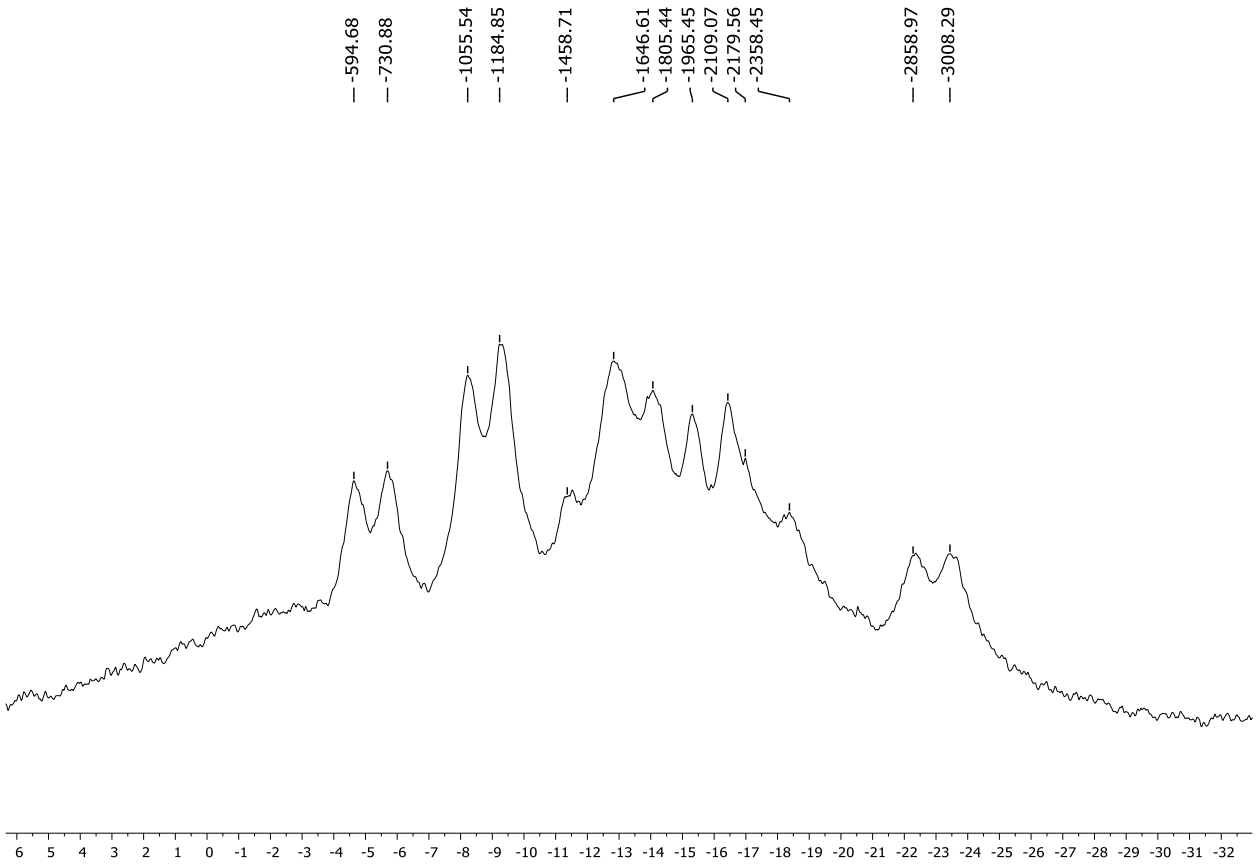

Fig. S46. ^{11}B NMR spectrum of compound **8** in CD_3CN

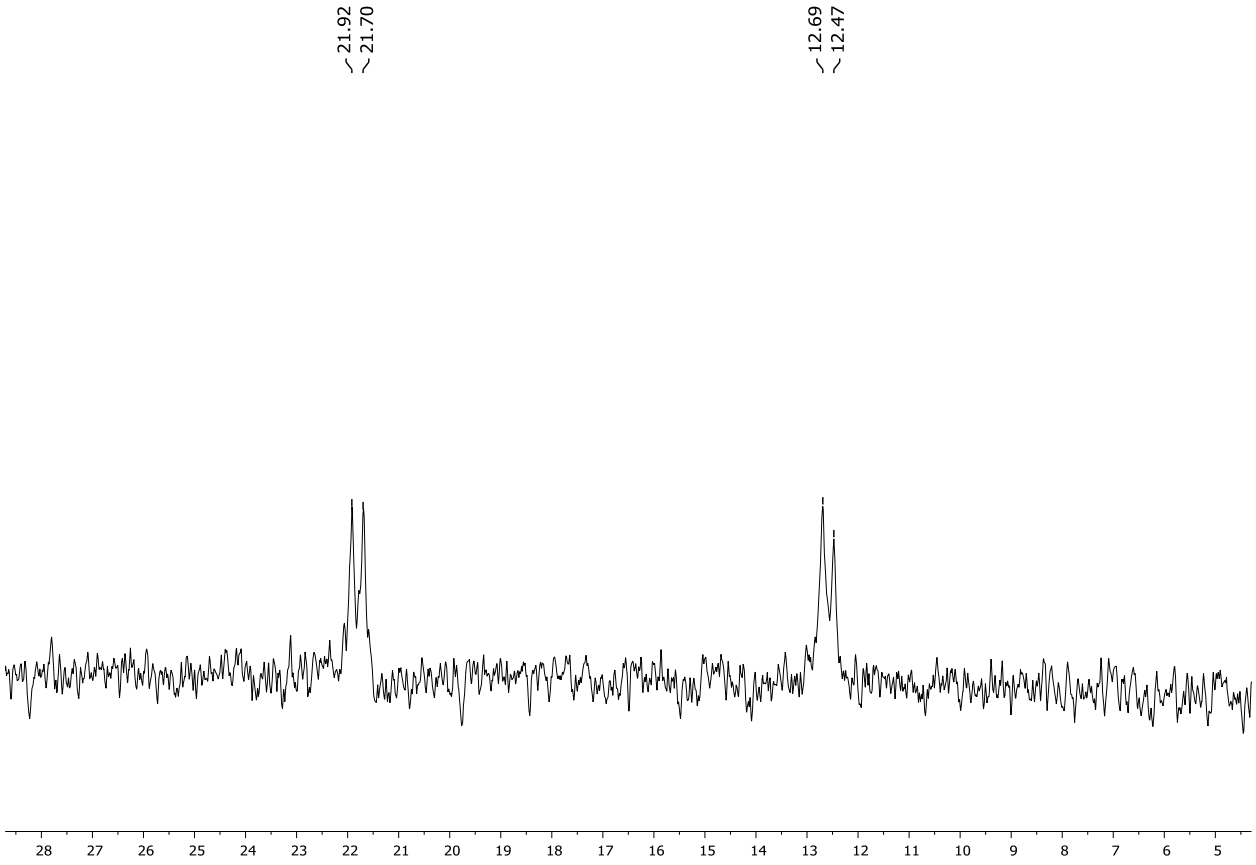

Fig. S47. $^{31}P\{^1H\}$ NMR spectrum of compound **8** in acetone-d_6

Spectral data for 3,3-(Bu_3P)$_2$-1-($MeO(CH_2)_2S$)-*closo*-3,1,2-$NiC_2B_9H_{10}$ (9)

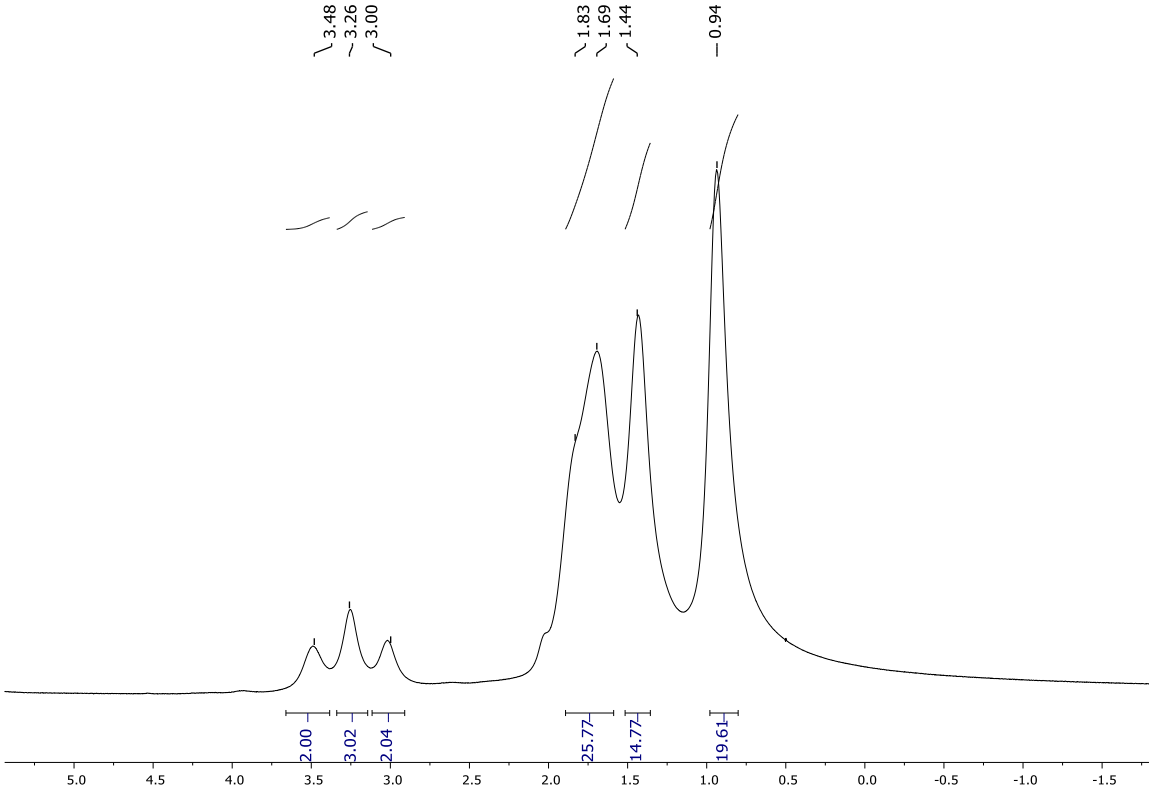

Fig. S48. ^{1}H NMR spectrum of compound **9** in acetone-d_6

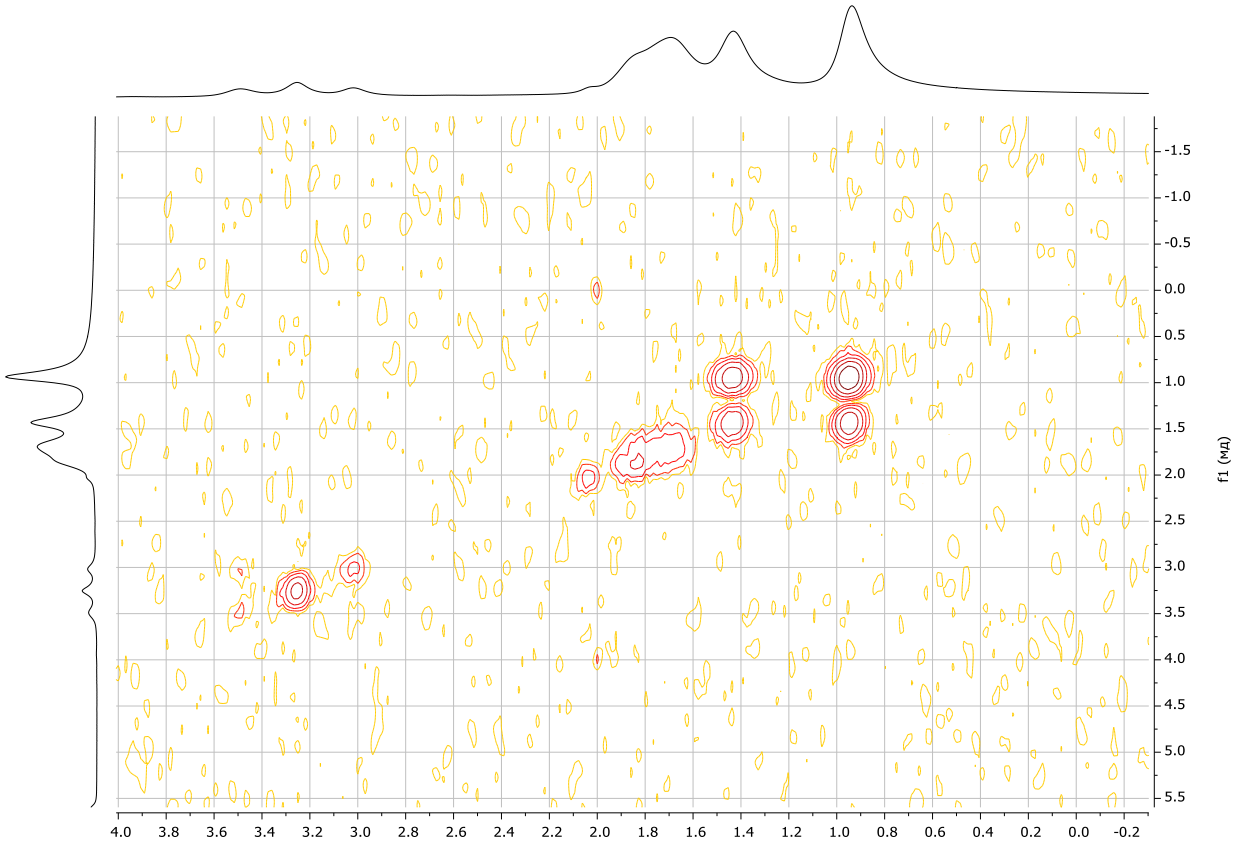

Fig. S49. (HH) COSY NMR spectrum of compound **9** in acetone-d_6

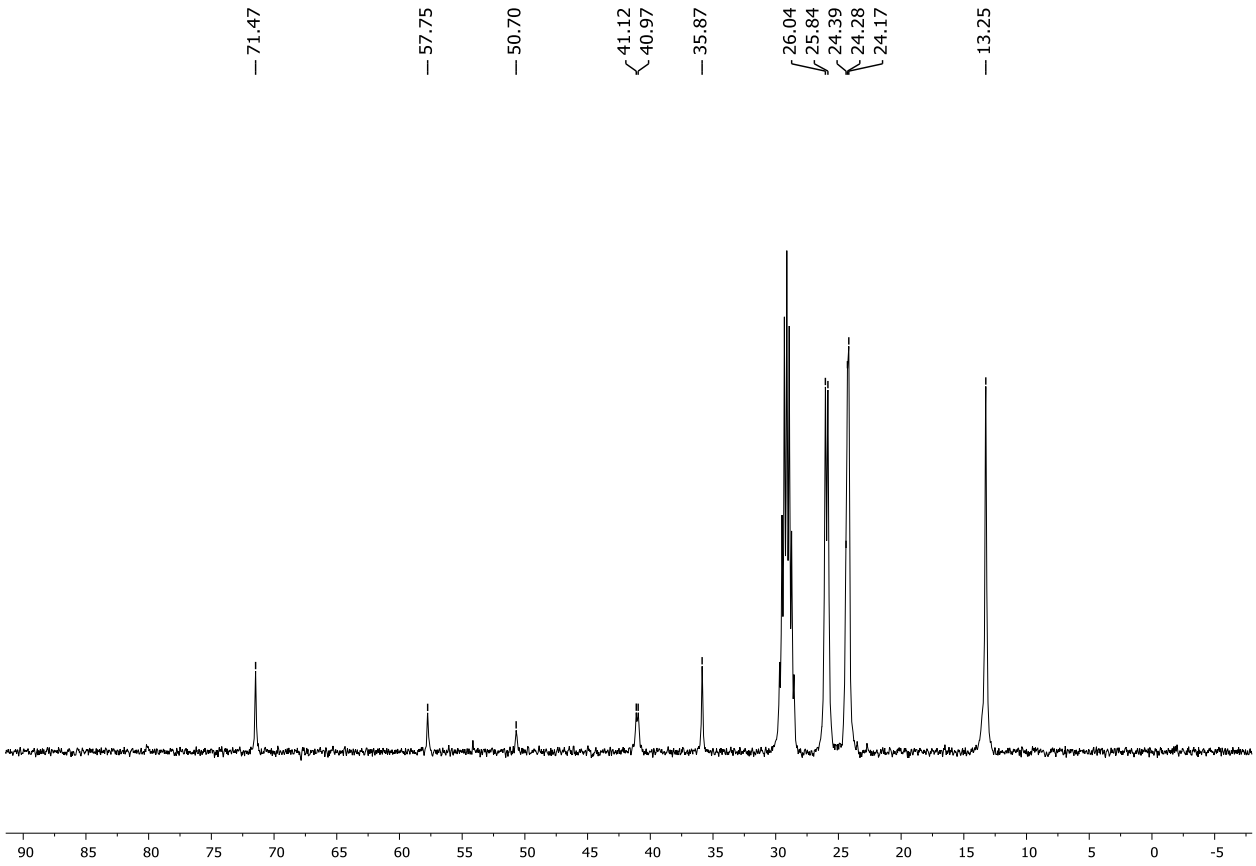

Fig. S50. ^{13}C NMR spectrum of compound **9** in acetone-d_6

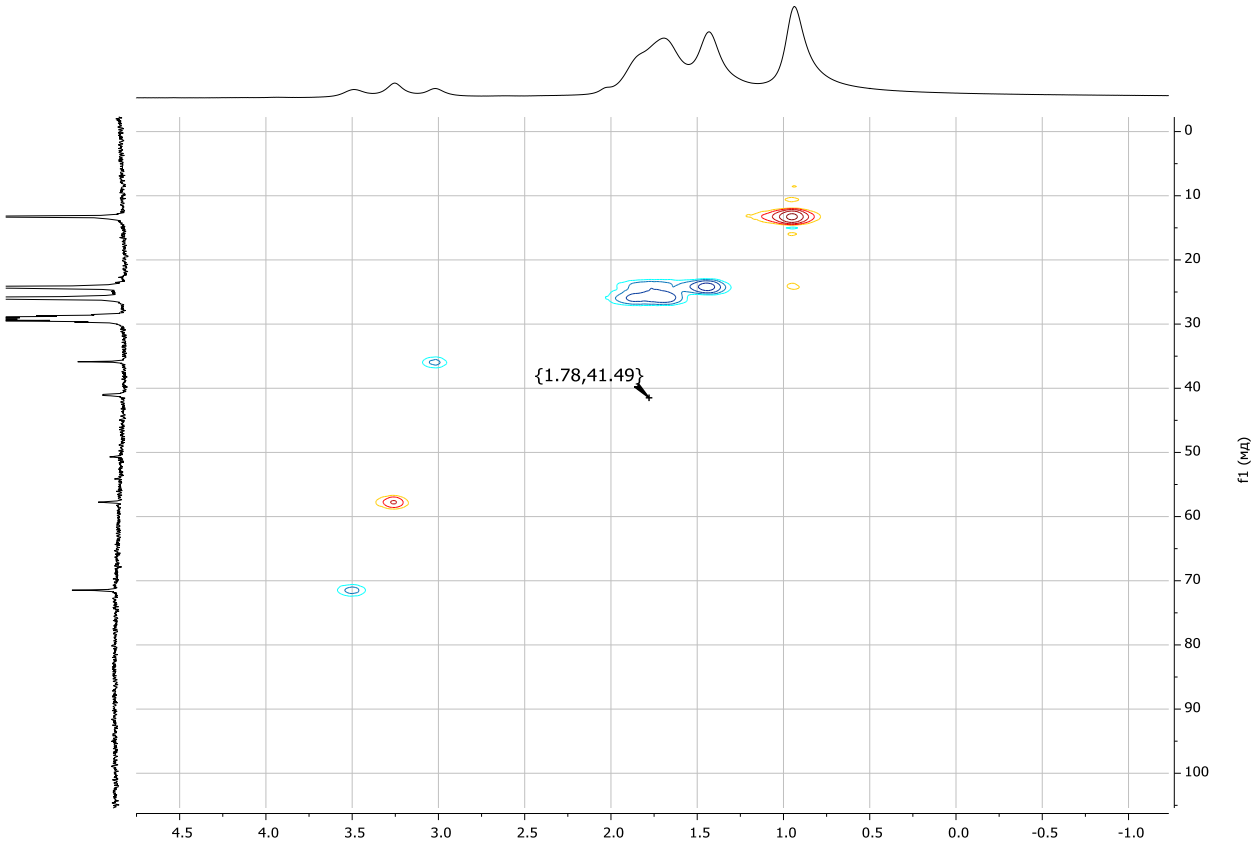

Fig. S51. (HC) HSQC NMR spectrum of compound **9** in acetone-d_6

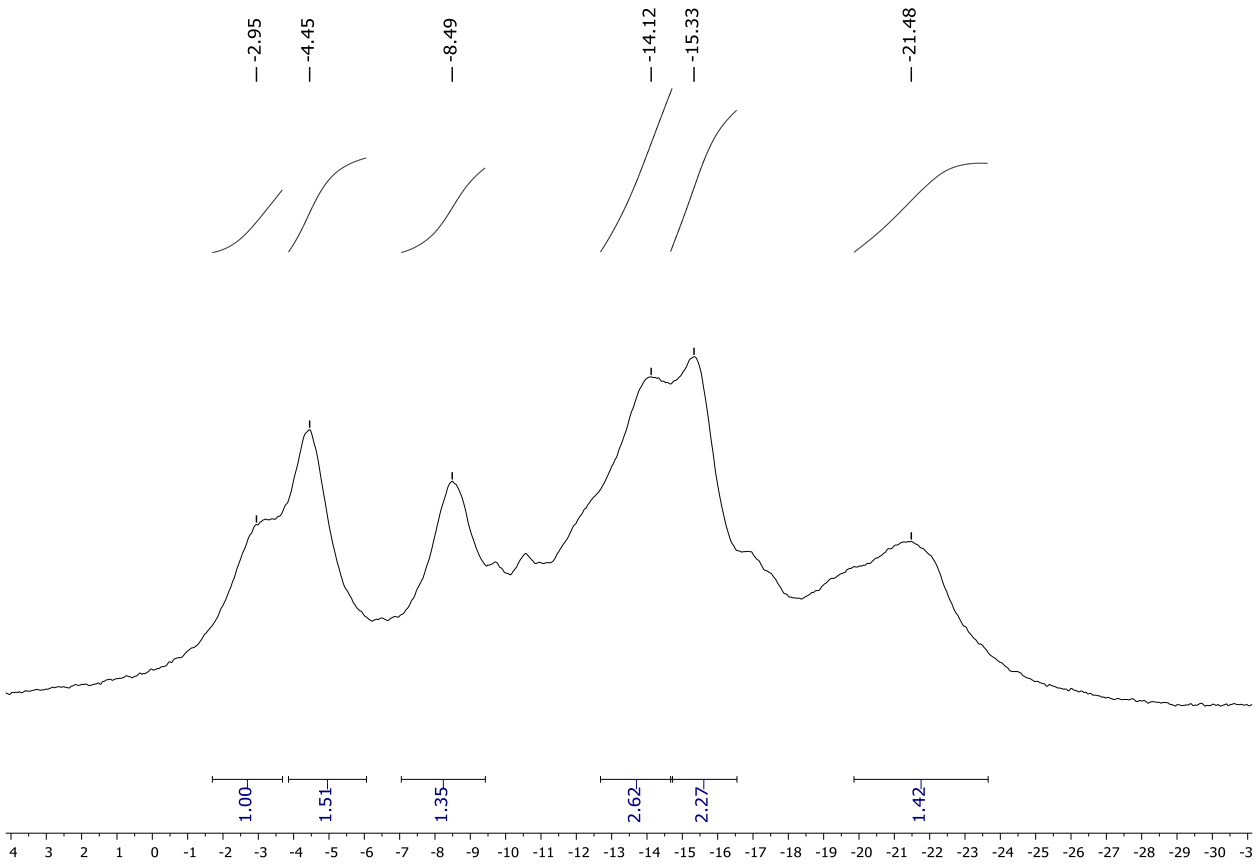

Fig. S52. $^{11}B\{^{1}H\}$ NMR spectrum of compound **9** in acetone-d_6

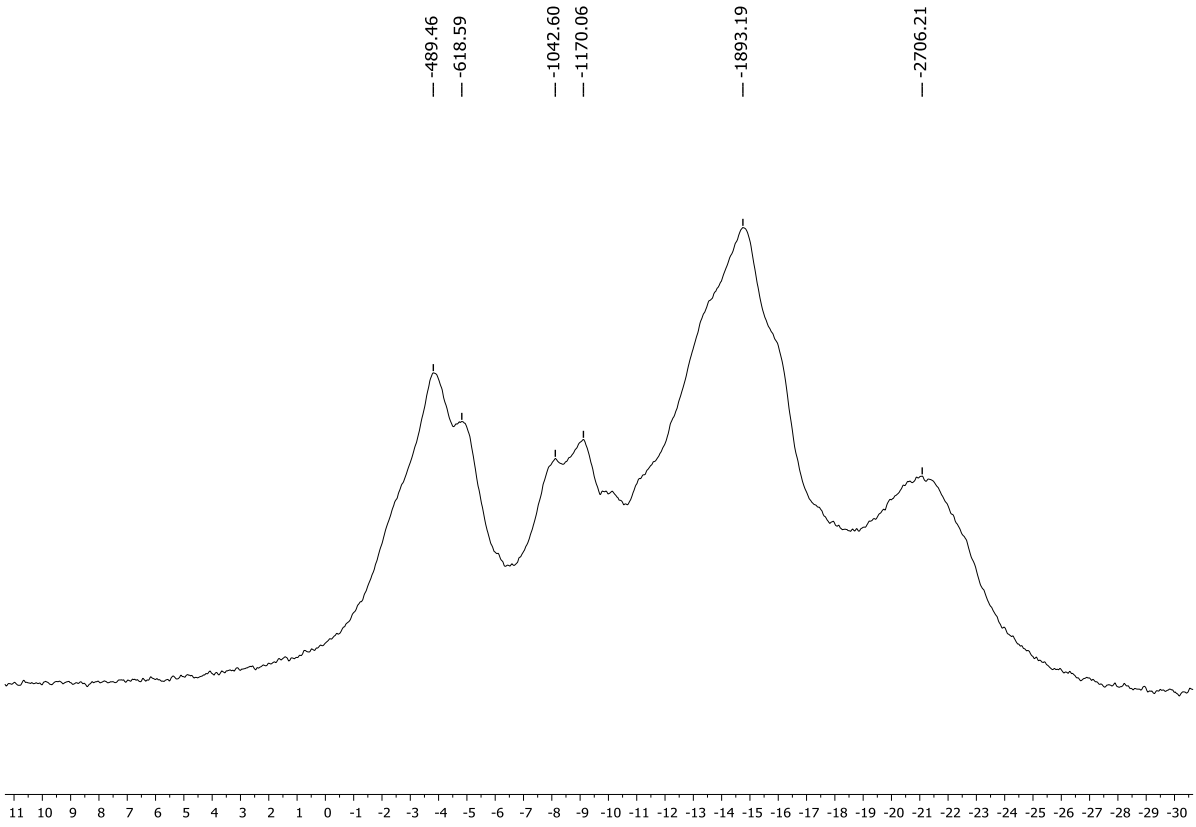

Fig. S53. ^{11}B NMR spectrum of compound **9** in acetone-d_6

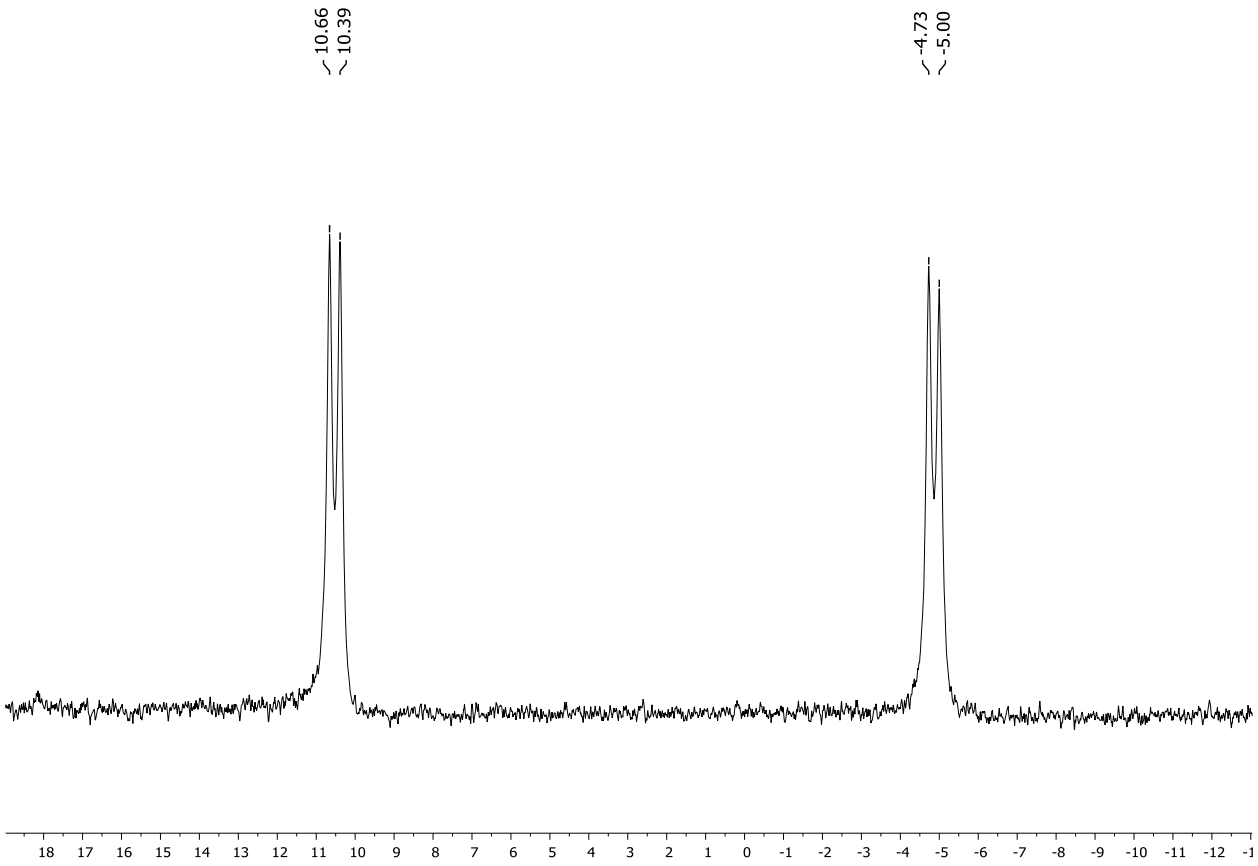

Fig. S54. ^{31}P NMR spectrum of compound **9** in acetone-d_6