

Synthesis and Catalytic Properties of Novel Ruthenacarboranes Based on *nido*-[5-Me-7,8-C₂B₉H₁₀]²⁻ and *nido*-[5,6-Me₂-7,8-C₂B₉H₉]²⁻ Dicarbollide Ligands

Ivan D. Grishin ^{1,*}, Anastasya M. Zimina ¹, Sergey A. Anufriev ², Nadezhda A. Knyaseva ¹, Alexander V. Piskunov ³, Fedor M. Dolgushin ^{2,4} and Igor B. Sivaev ^{2,5*}

¹ Lobachevsky State University of Nizhny Novgorod, 23 Gagarin Prosp., Nizhny Novgorod, 603950, Russia; grishin_i@ichem.unn.ru (I.D.G.); (A.M.Z.); (N.A.K.)

² A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991 Moscow, Russia; trueman476@mail.ru (S.A.A.); fedya@ineos.ac.ru (F.M.D.); sivaev@ineos.ac.ru (I.B.S.)

³ G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 Tropinin Str., Nizhny Novgorod, 603950, Russia; (A.A.P.)

⁴ N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninskii Prosp., 119991 Moscow, Russia

⁵ Basic Department of Chemistry of Innovative Materials and Technologies, G.V. Plekhanov Russian University of Economics, 36 Stremyanniy Line, 117997, Moscow, Russia

* Correspondence: grishin_i@ichem.unn.ru (I.D.G.); sivaev@ineos.ac.ru (I.B.S.)

Supplementary Materials: **Figure S1** ¹H NMR spectrum of 9-methyl-ortho-carborane, **Figure S2** ¹¹B NMR spectrum of 9-methyl-ortho-carborane, **Figure S3** ¹¹B{¹H} NMR spectrum of 9-methyl-ortho-carborane, **Figure S4** ¹H NMR spectrum of 9,12-dimethyl-ortho-carborane, **Figure S5** ¹¹B NMR spectrum of 9,12-dimethyl-ortho-carborane, **Figure S6** ¹¹B{¹H} NMR spectrum of 9,12-dimethyl-ortho-carborane, **Figure S7** ¹H NMR spectrum of cesium 5-methyl-7,8-dicarba-nido-undecaborate (1), **Figure S8** ¹¹B NMR spectrum of cesium 5-methyl-7,8-dicarba-nido-undecaborate (1), **Figure S9** ¹¹B{¹H} NMR spectrum of cesium 5-methyl-7,8-dicarba-nido-undecaborate (1), **Figure S10** ¹H NMR spectrum of cesium 5,6-dimethyl-7,8-dicarba-nido-undecaborate (2), **Figure S11** ¹¹B NMR spectrum of cesium 5,6-dimethyl-7,8-dicarba-nido-undecaborate (2), **Figure S12** ¹¹B{¹H} NMR spectrum of cesium 5,6-dimethyl-7,8-dicarba-nido-undecaborate (2), **Figure S13** ¹H NMR spectrum of complex 3, **Figure S14** ¹¹B{¹H} NMR spectrum of complex 3, **Figure S15** ¹H-¹H 2D COSY NMR spectrum of complex 3, **Figure S16** ¹H-¹³C 2D HSQC NMR spectrum of complex 3, **Figure S17** ¹H NMR spectrum of complex 4, **Figure S18** ¹¹B{¹H} NMR spectrum of complex 4, **Figure S19** ¹H-¹H 2D COSY NMR spectrum of complex 3, **Figure S20** ¹H-¹³C 2D HSQC NMR spectrum of complex 4, **Figure S21** Anisotropic EPR spectrum of complex 7 in toluene matrix at 77 K, **Figure S22** Anisotropic EPR spectrum of complex 9 in toluene matrix at 77 K, **Figure S23** MALDI mass spectrum of complex 3 recorded in negative mode using DCTB as a matrix, **Figure S24** MALDI mass spectrum of complex 4 recorded in negative mode using DCTB as a matrix, **Figure S25** MALDI mass spectrum of complex 6 recorded in negative mode using DCTB as a matrix, **Figure S26** MALDI mass spectrum of complex 7 recorded in negative mode using DCTB as a matrix, **Figure S27** MALDI mass spectrum of complex 8 recorded in negative mode using DCTB as a matrix, **Figure S28** MALDI mass spectrum of complex 9 recorded in negative mode using DCTB as a matrix.

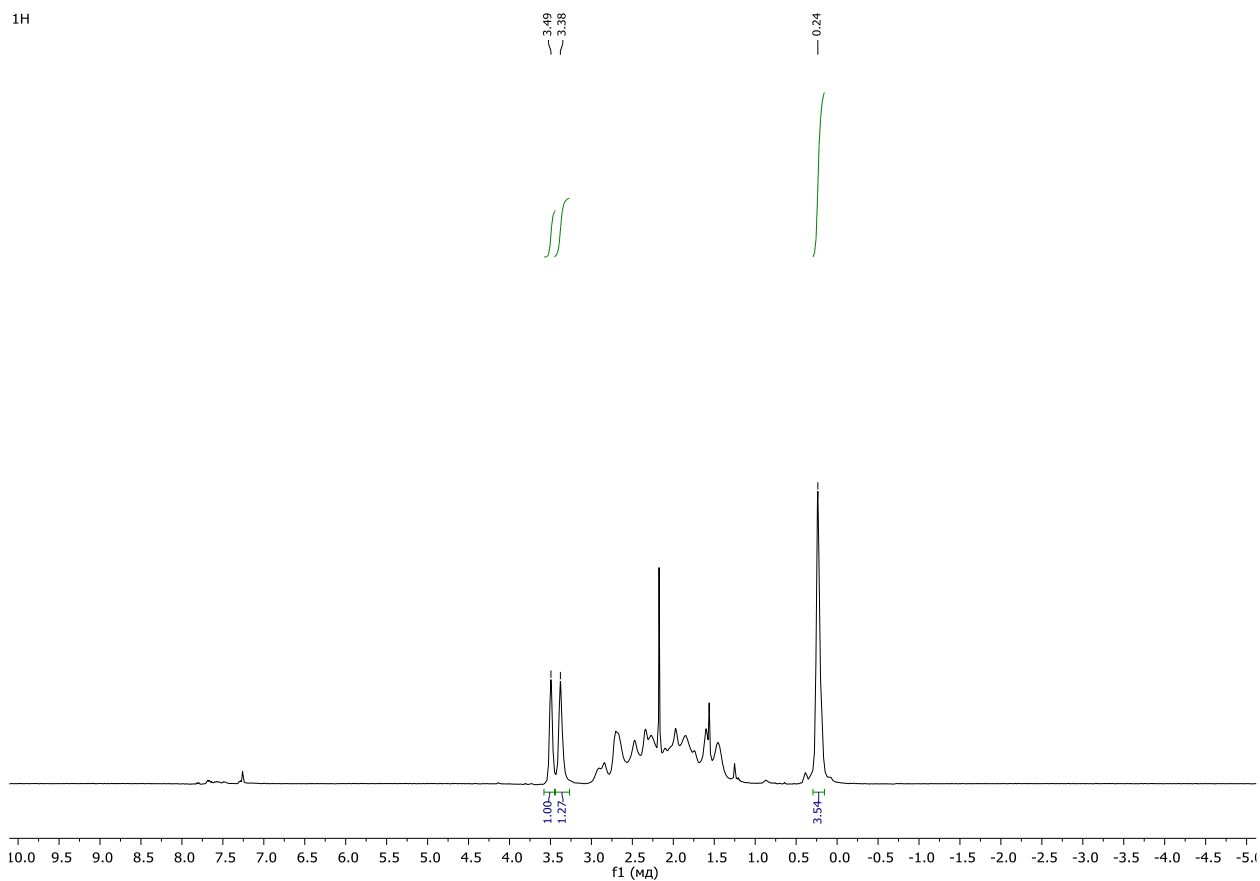


Figure S1. ¹H NMR spectrum of 9-methyl-*ortho*-carborane

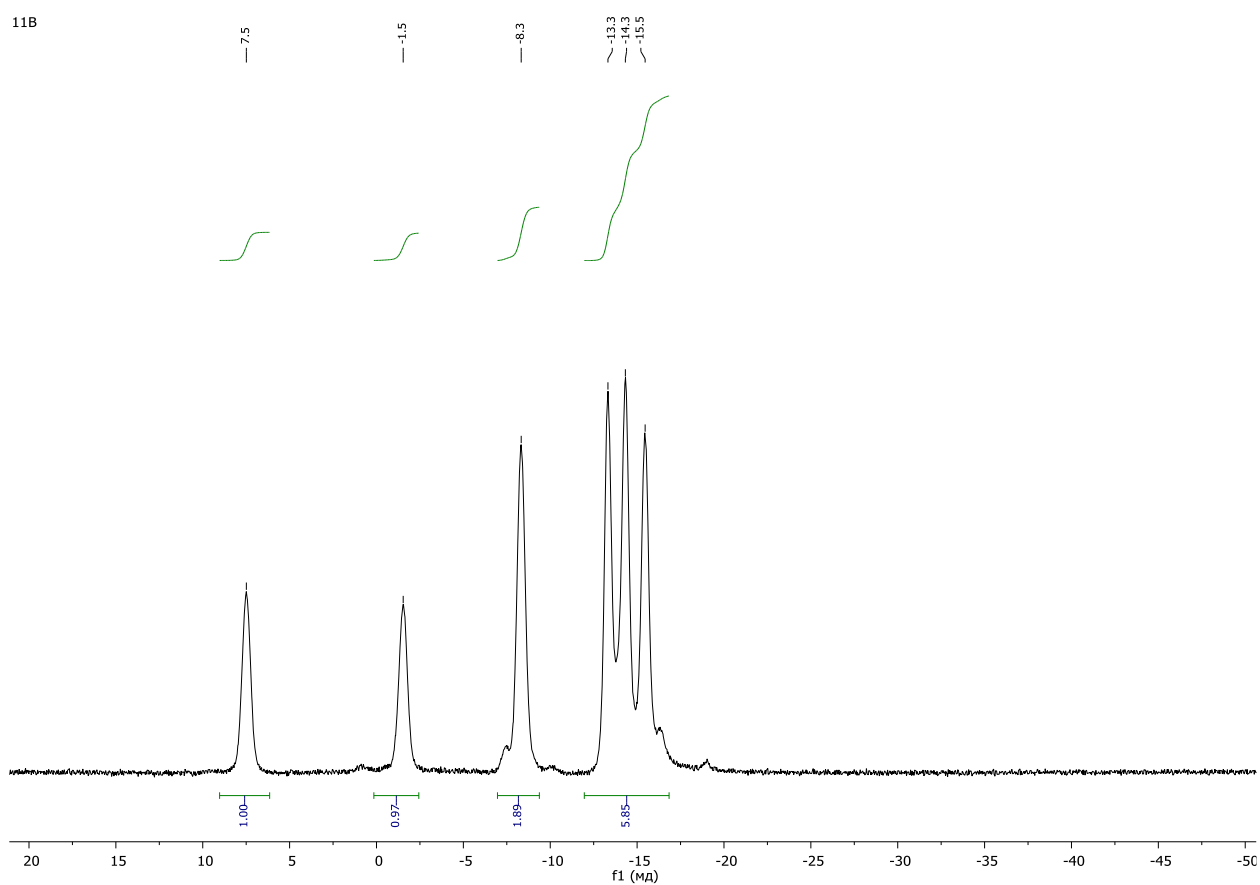


Figure S2. ¹¹B NMR spectrum of 9-methyl-*ortho*-carborane

111B

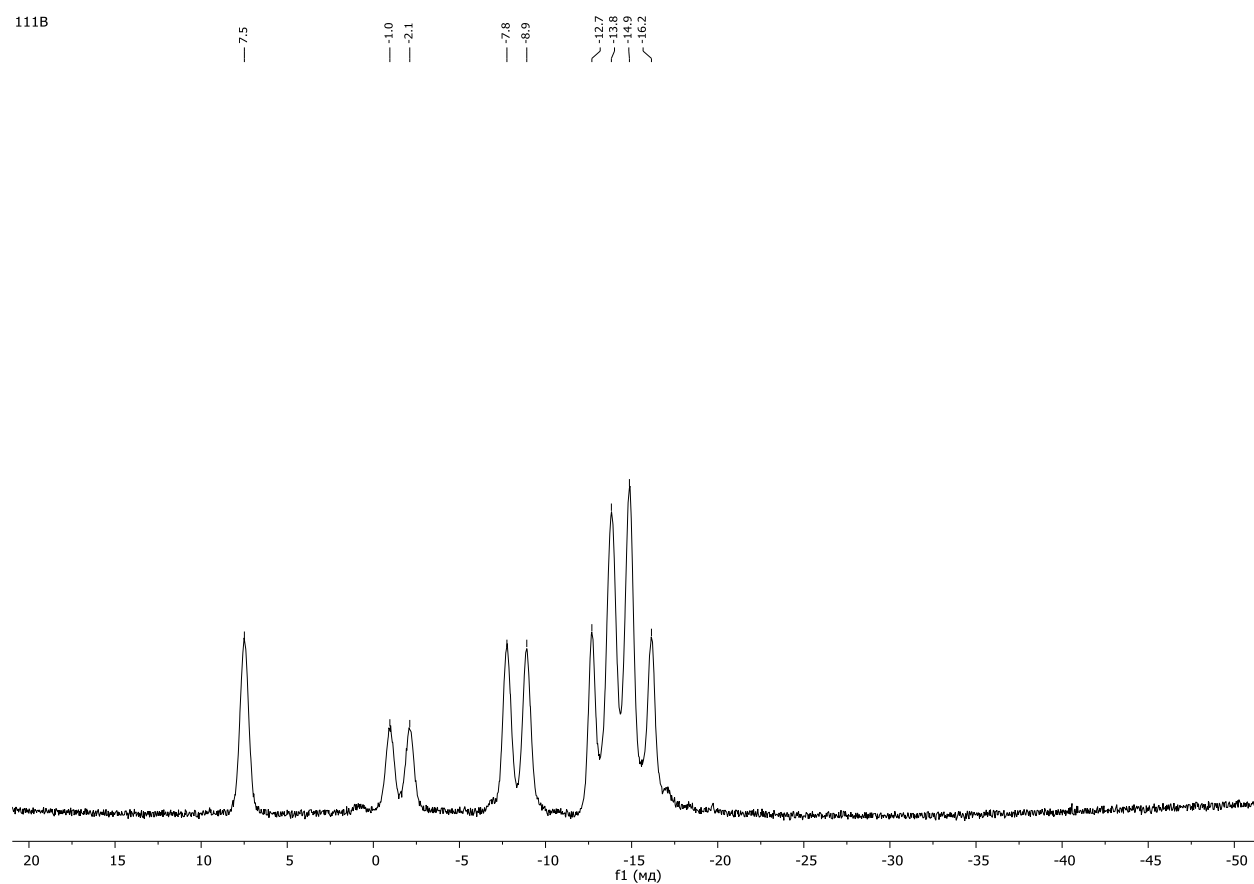


Figure S3. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 9-methyl-*ortho*-carborane

^1H

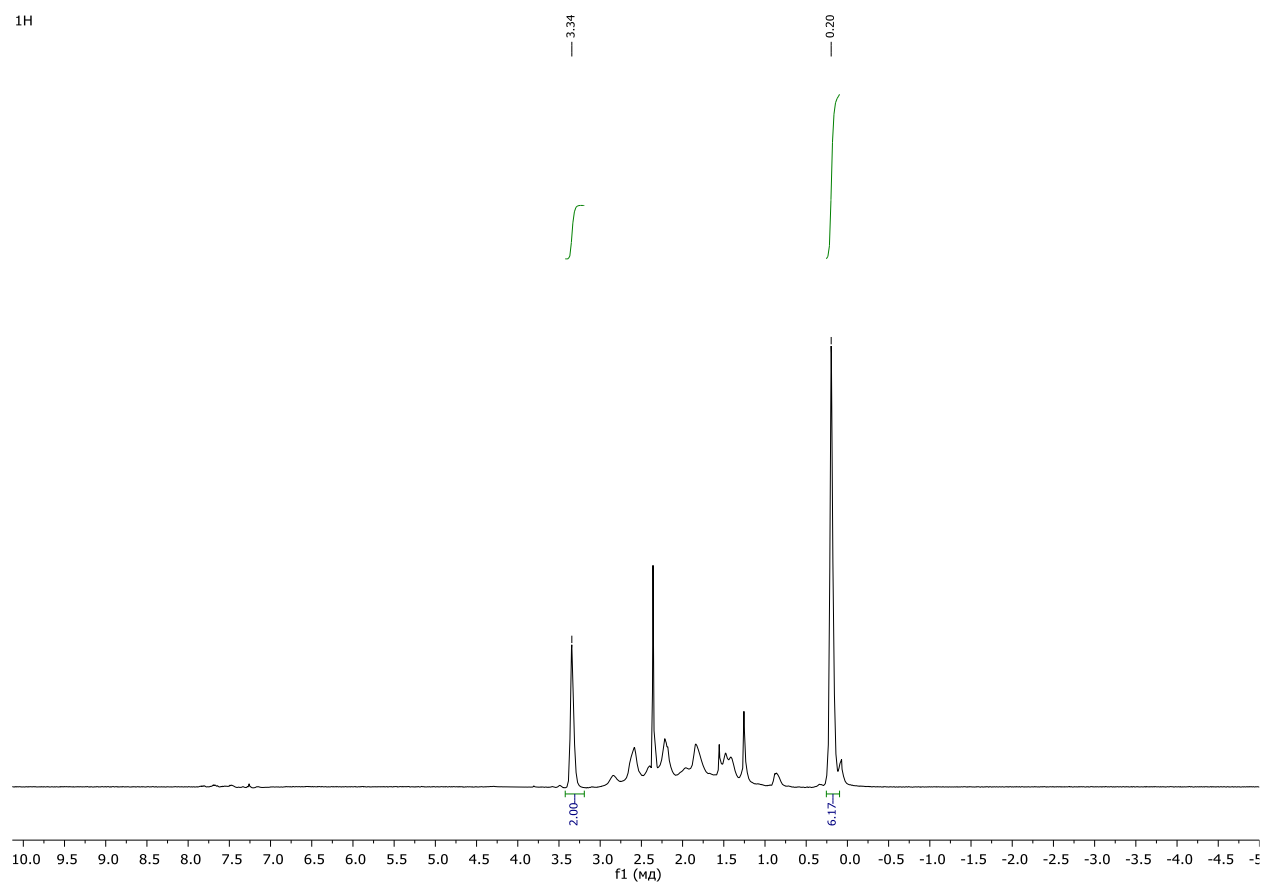


Figure S4. ^1H NMR spectrum of 9,12-dimethyl-*ortho*-carborane

11B

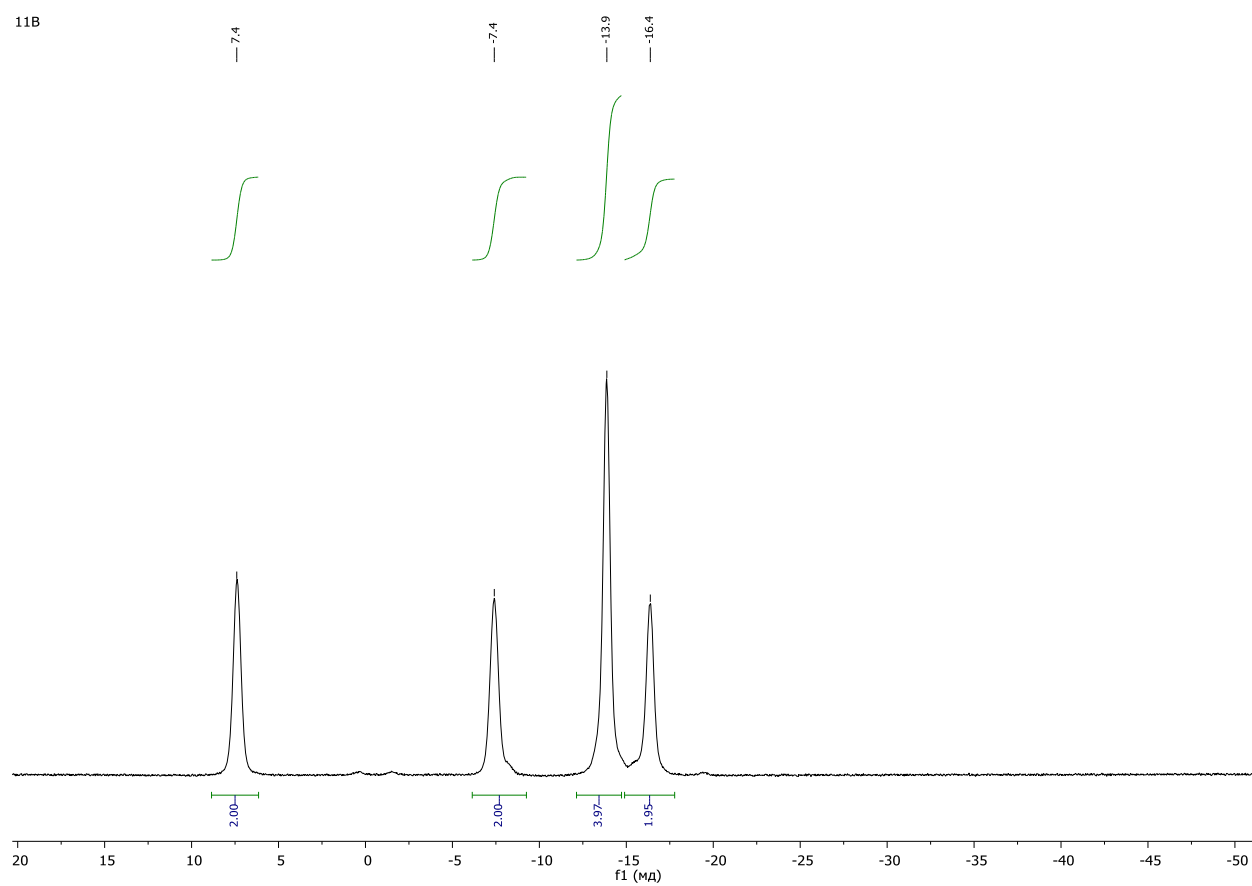


Figure S5. ^{11}B NMR spectrum of 9,12-dimethyl-ortho-carborane

111B

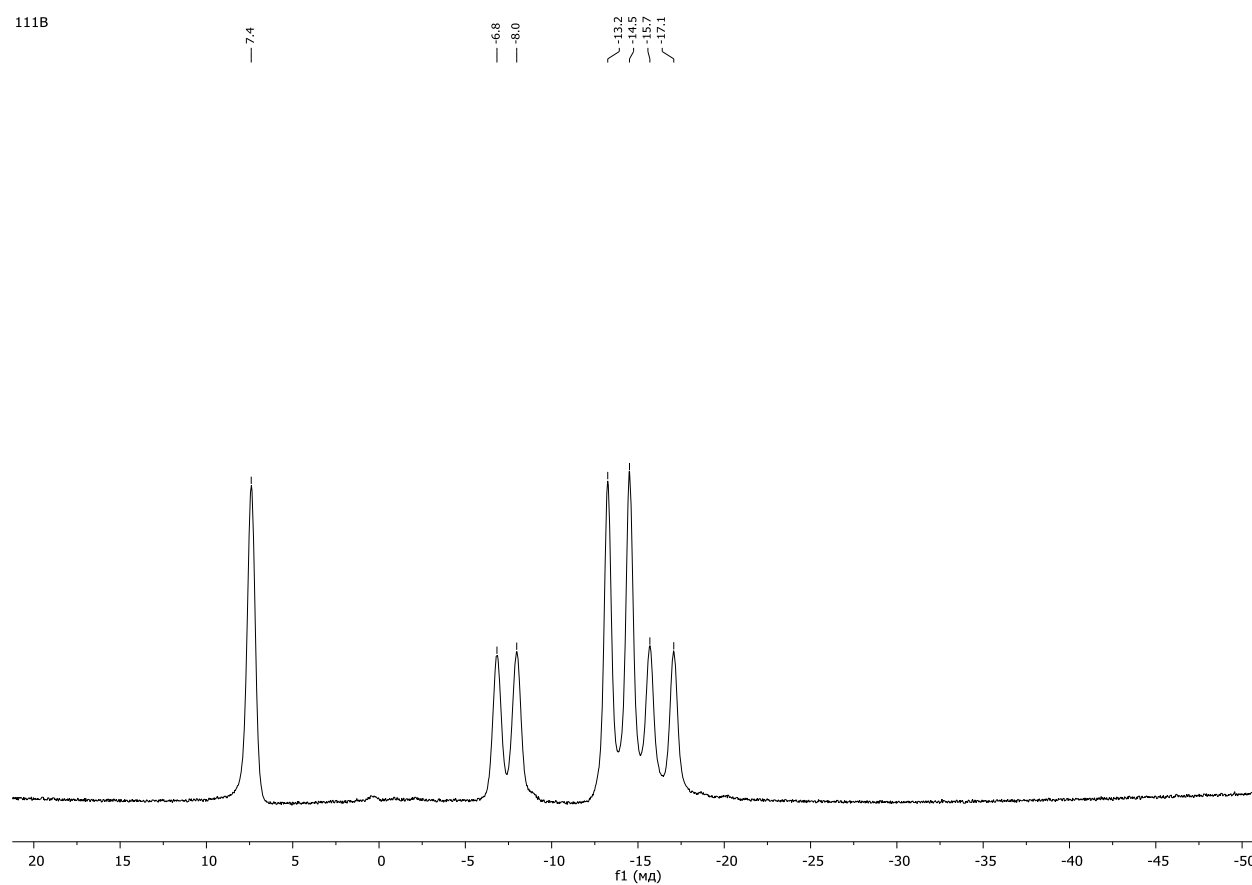


Figure S6. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 9,12-dimethyl-ortho-carborane

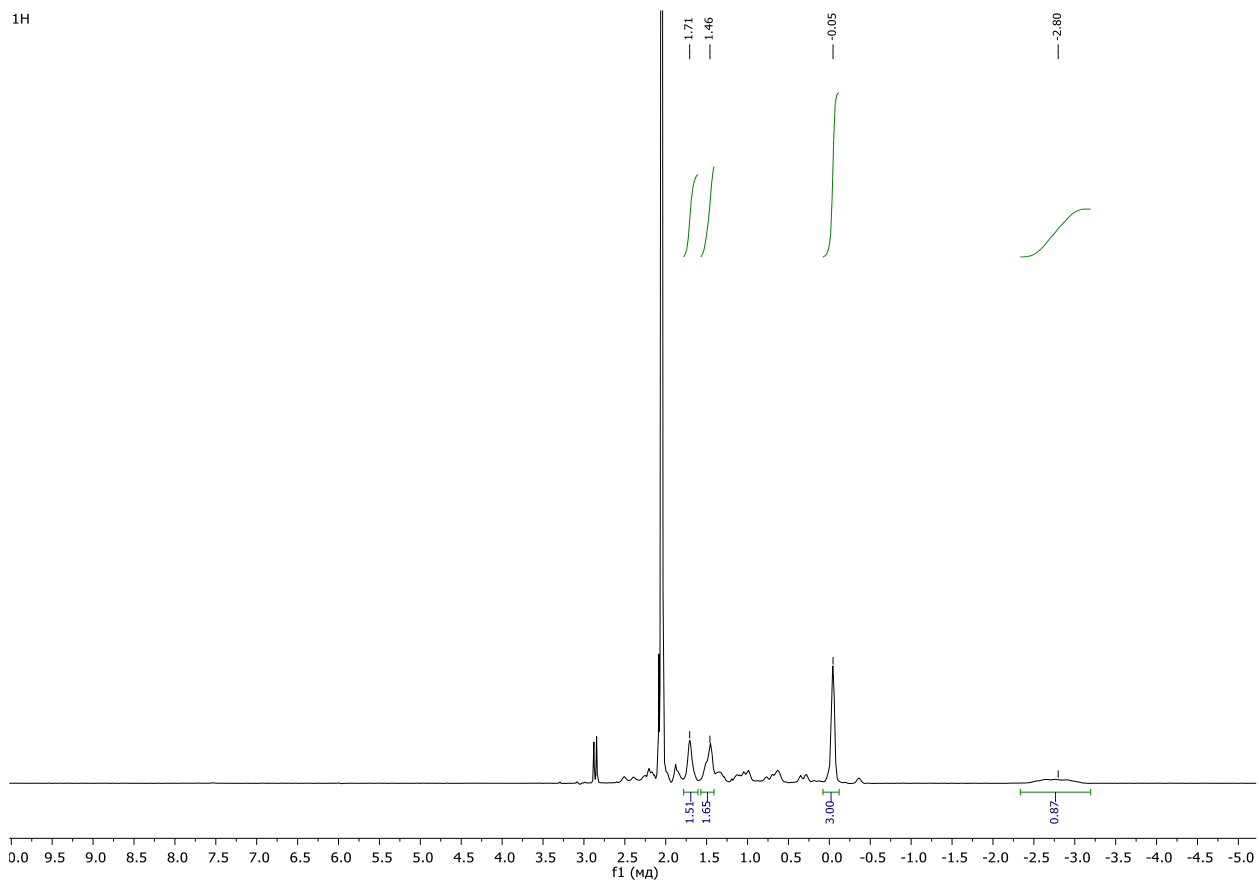


Figure S7. ¹H NMR spectrum of cesium 5-methyl-7,8-dicarba-*nido*-undecaborate (**1**).

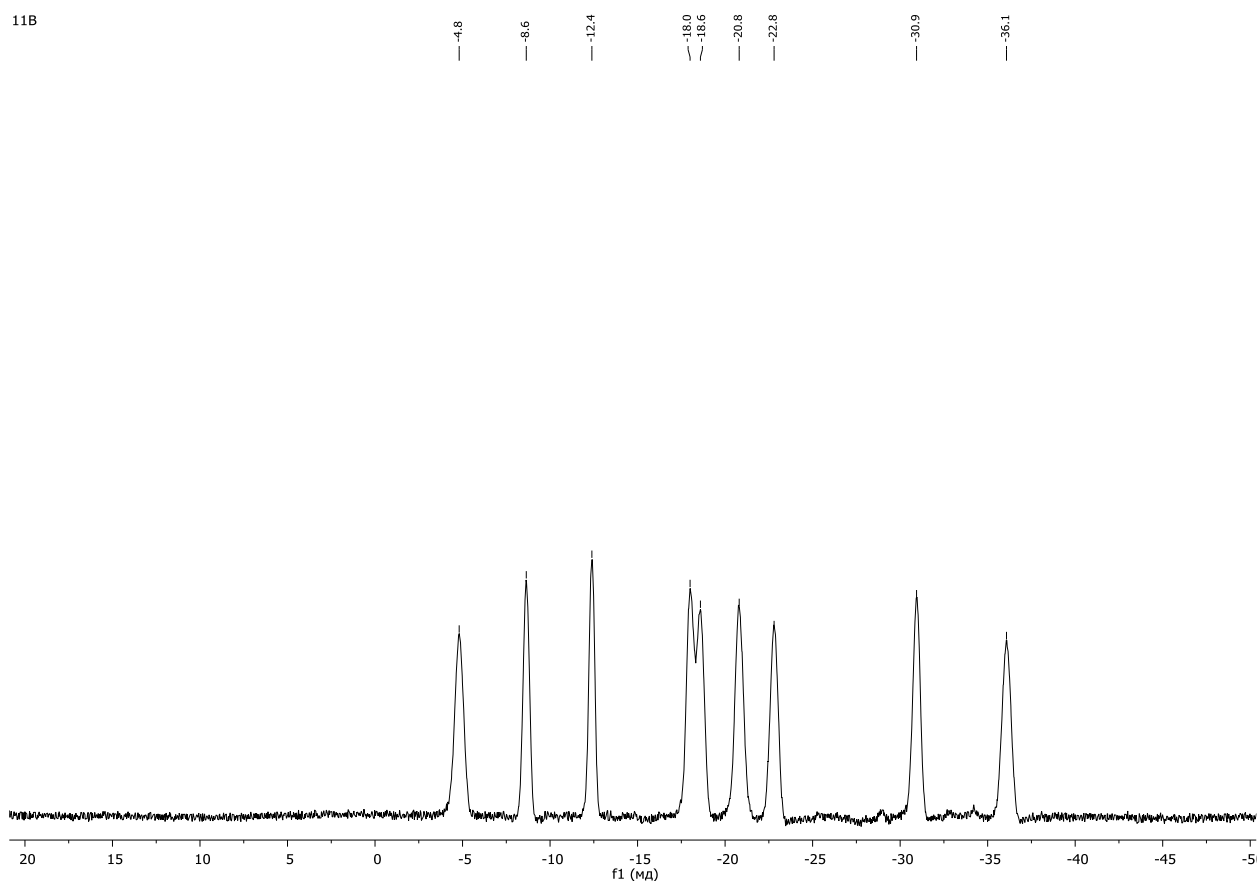


Figure S8. ¹¹B NMR spectrum of cesium 5-methyl-7,8-dicarba-*nido*-undecaborate (**1**).

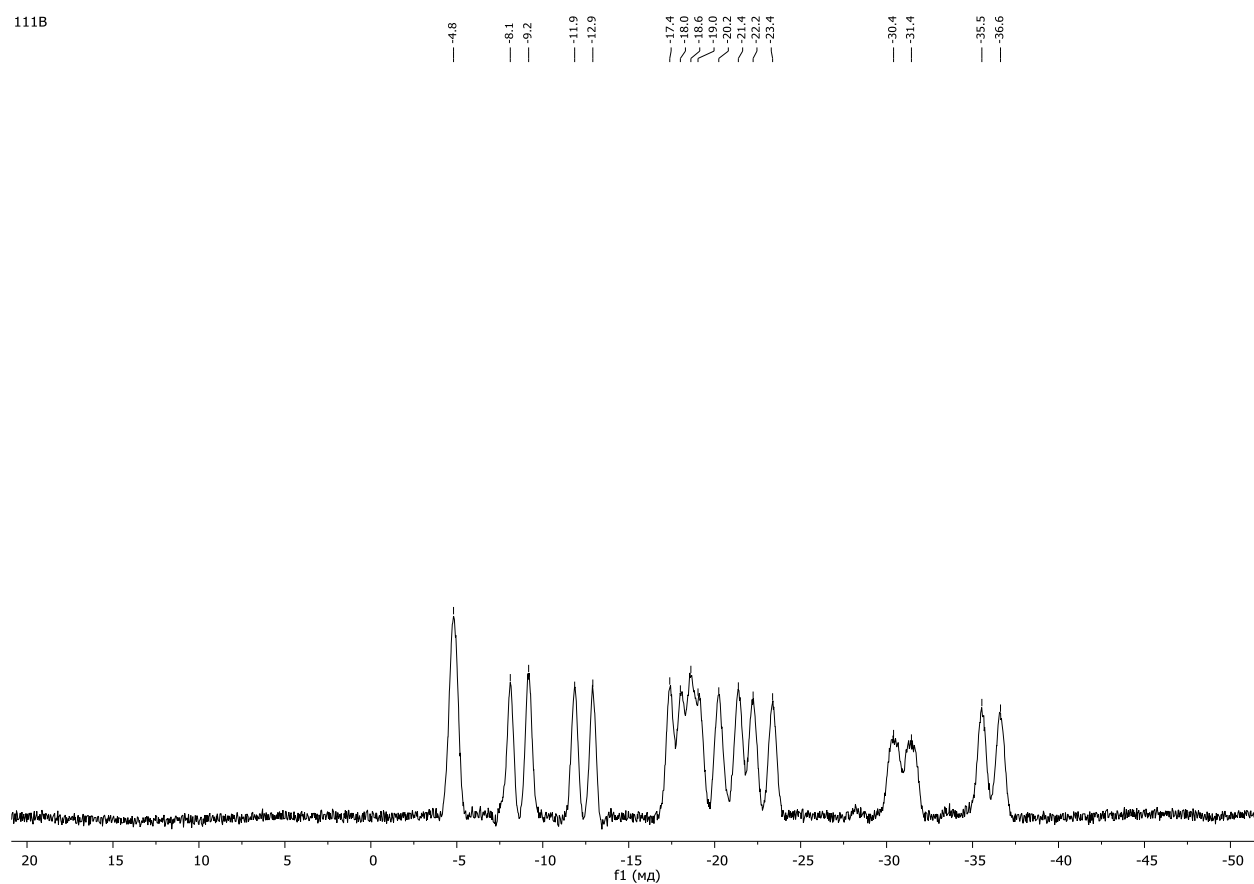


Figure S9. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of cesium 5-methyl-7,8-dicarba-*nido*-undecaborate (**1**).

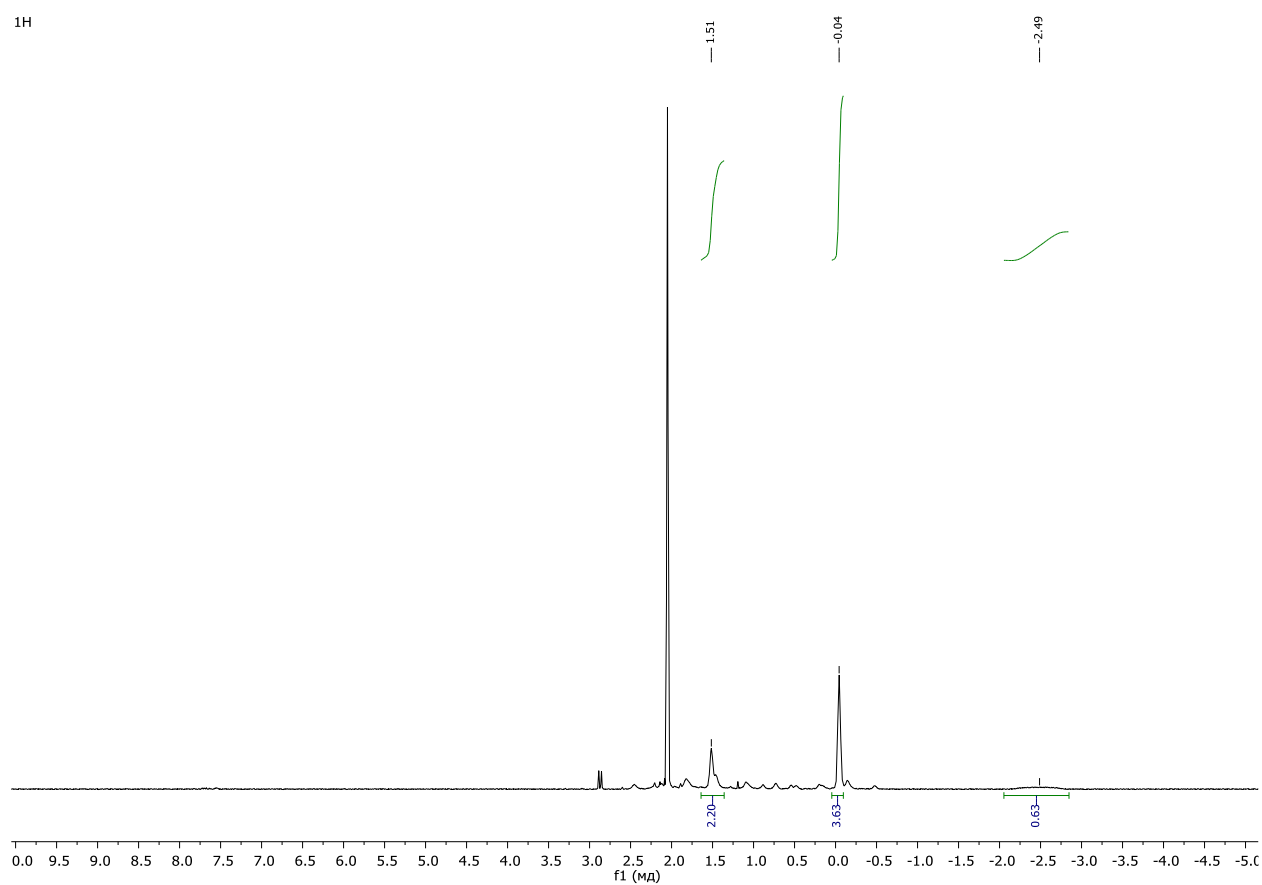


Figure S10. ^1H NMR spectrum of cesium 5,6-dimethyl-7,8-dicarba-*nido*-undecaborate (**2**).

11B

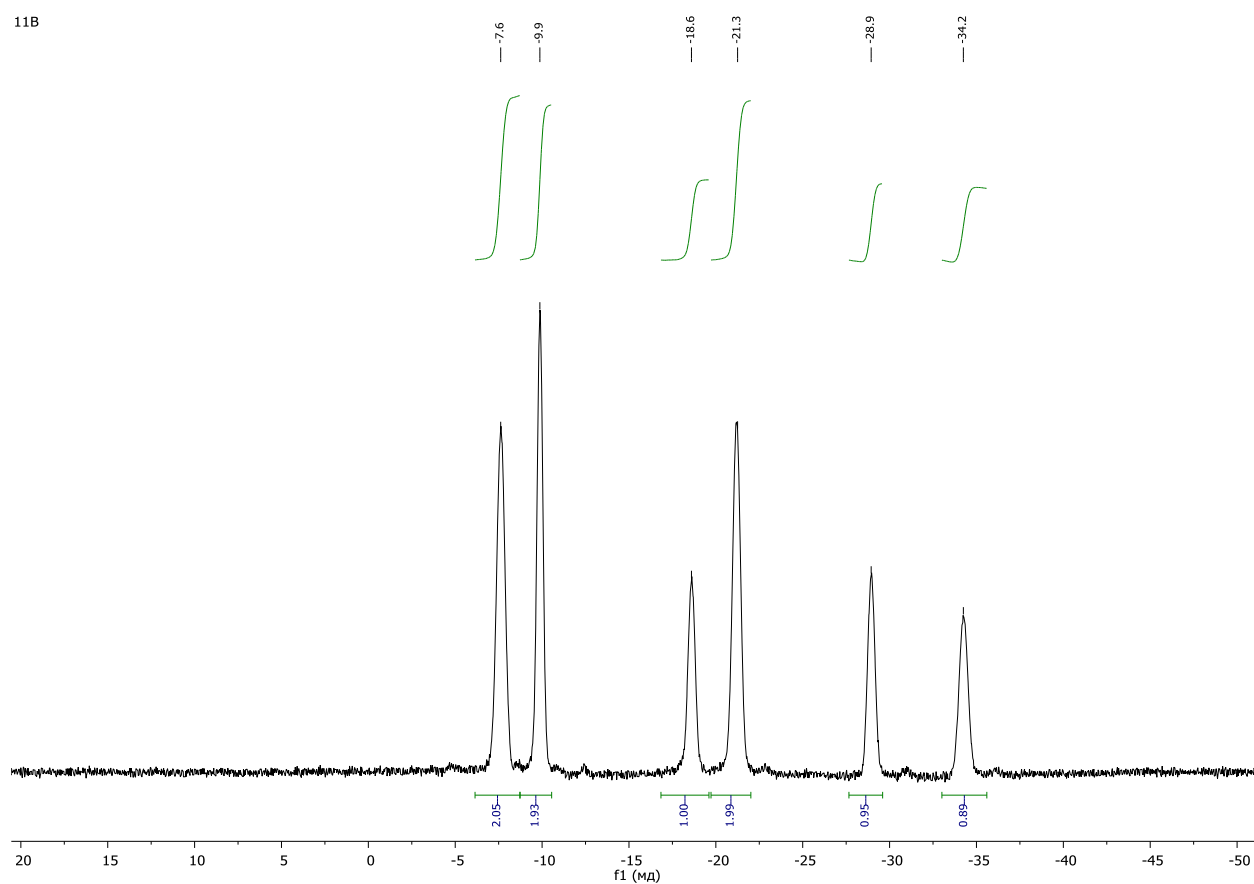


Figure S11. ^{11}B NMR spectrum of cesium 5,6-dimethyl-7,8-dicarba-*nido*-undecaborate (**2**).

11B

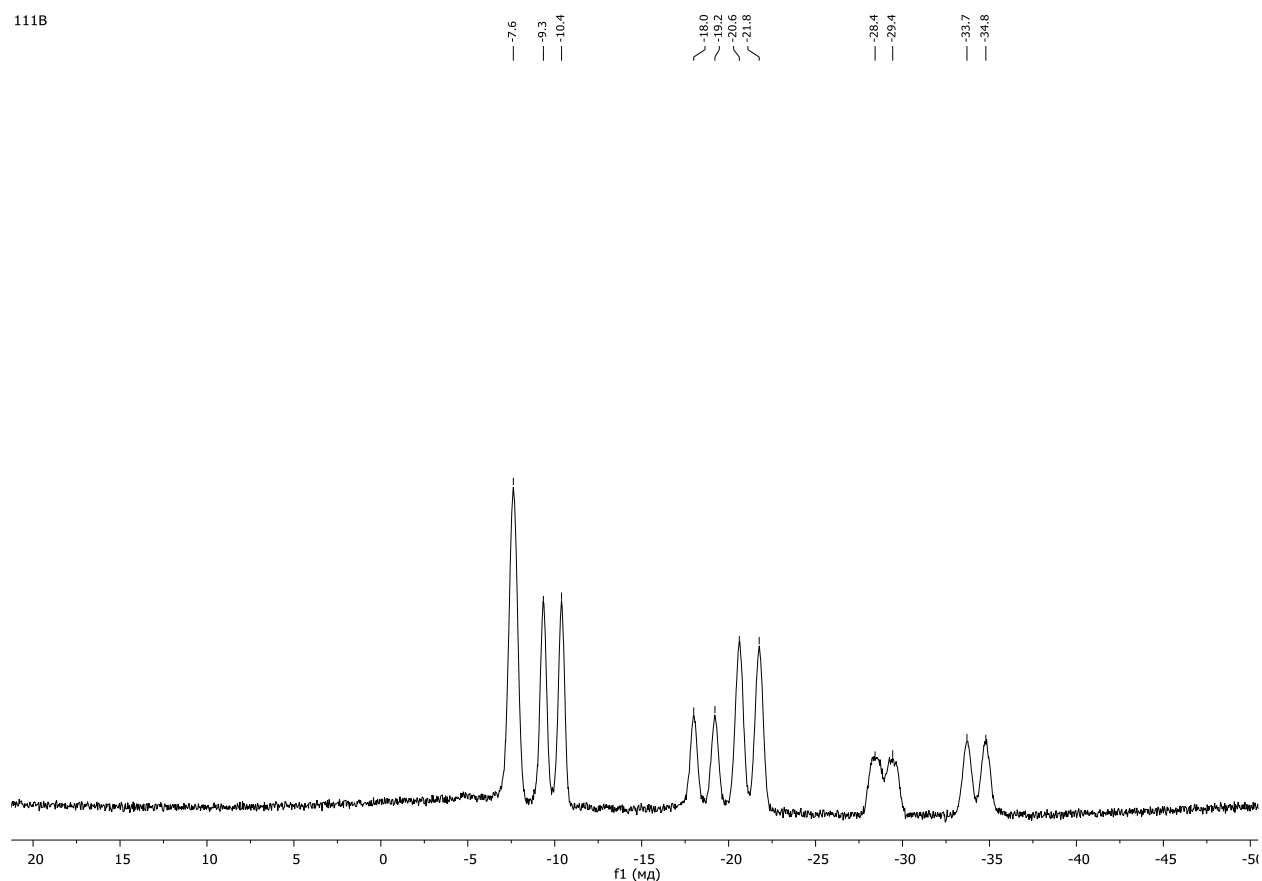


Figure S12. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of cesium 5,6-dimethyl-7,8-dicarba-*nido*-undecaborate (**2**).

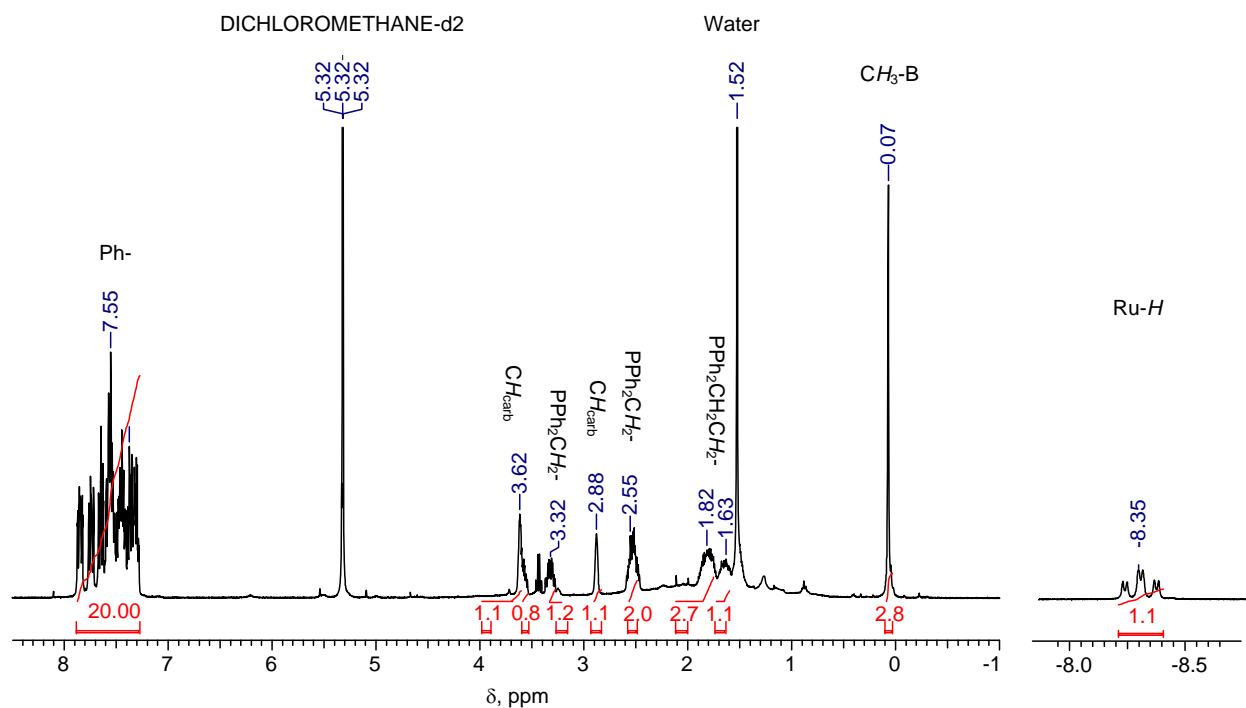


Figure S13. ^1H NMR spectrum of complex 3

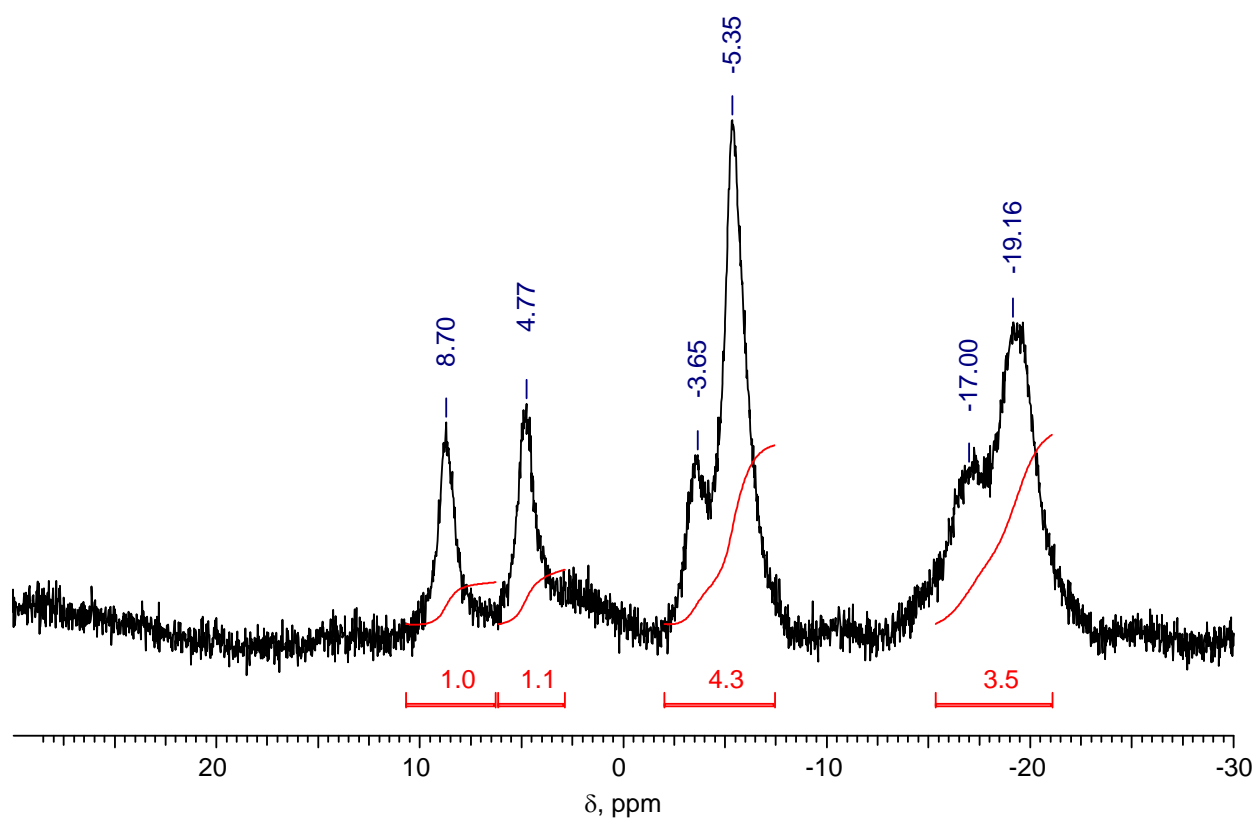


Figure S14. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of complex 3

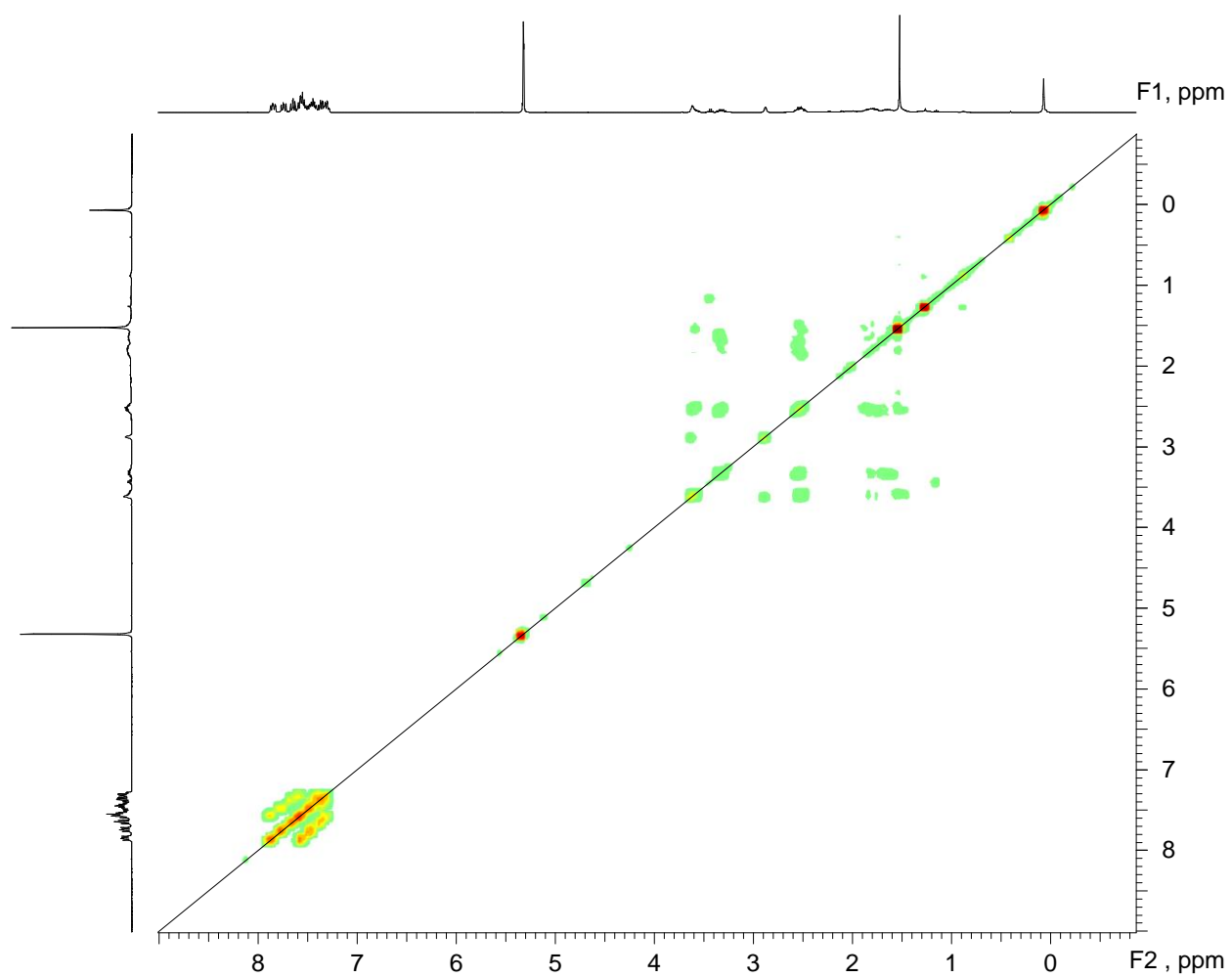


Figure S15. ¹H-¹H 2D COSY NMR spectrum of complex 3

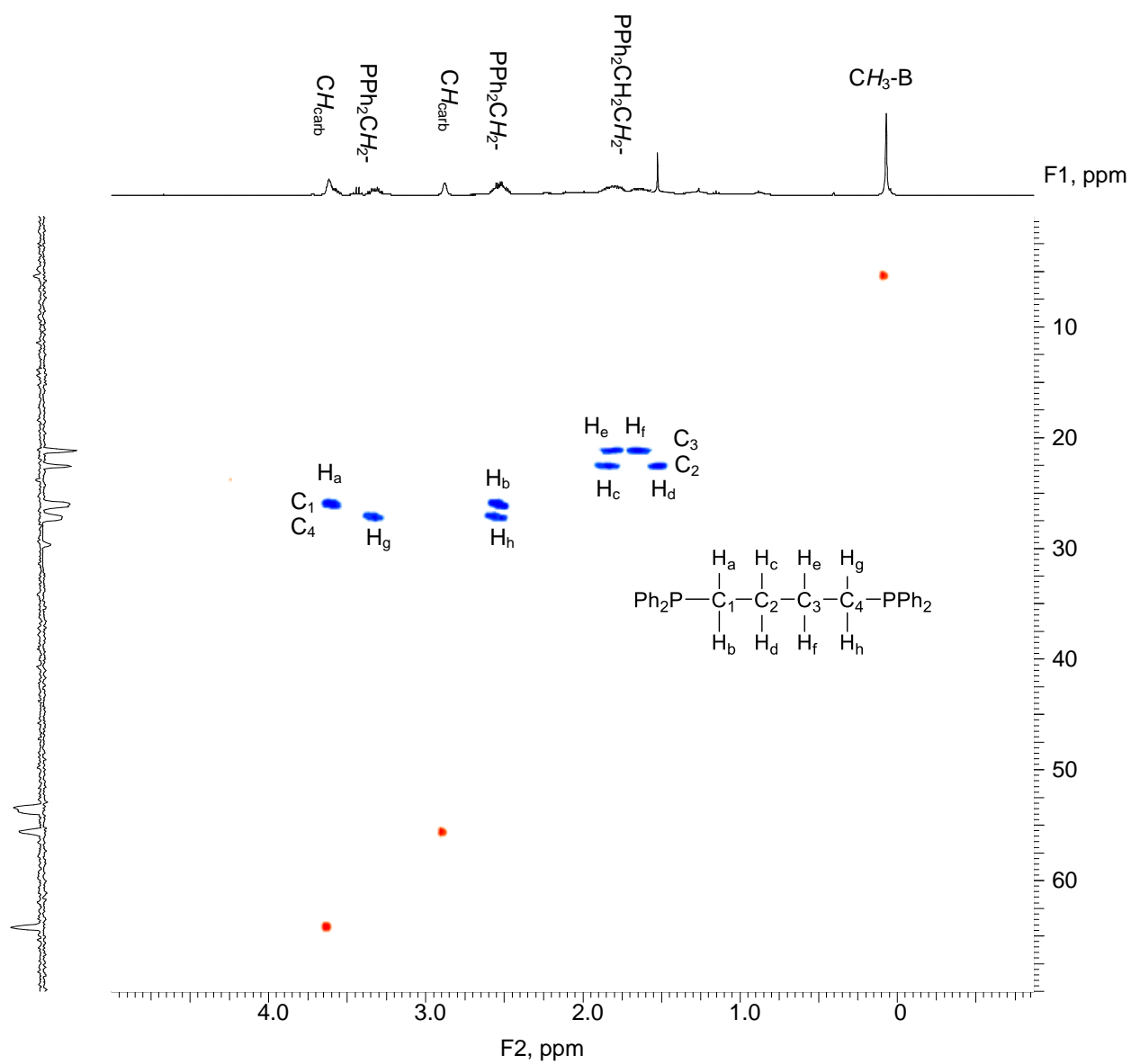


Figure S16. ^1H - ^{13}C 2D HSQC NMR spectrum of complex 3

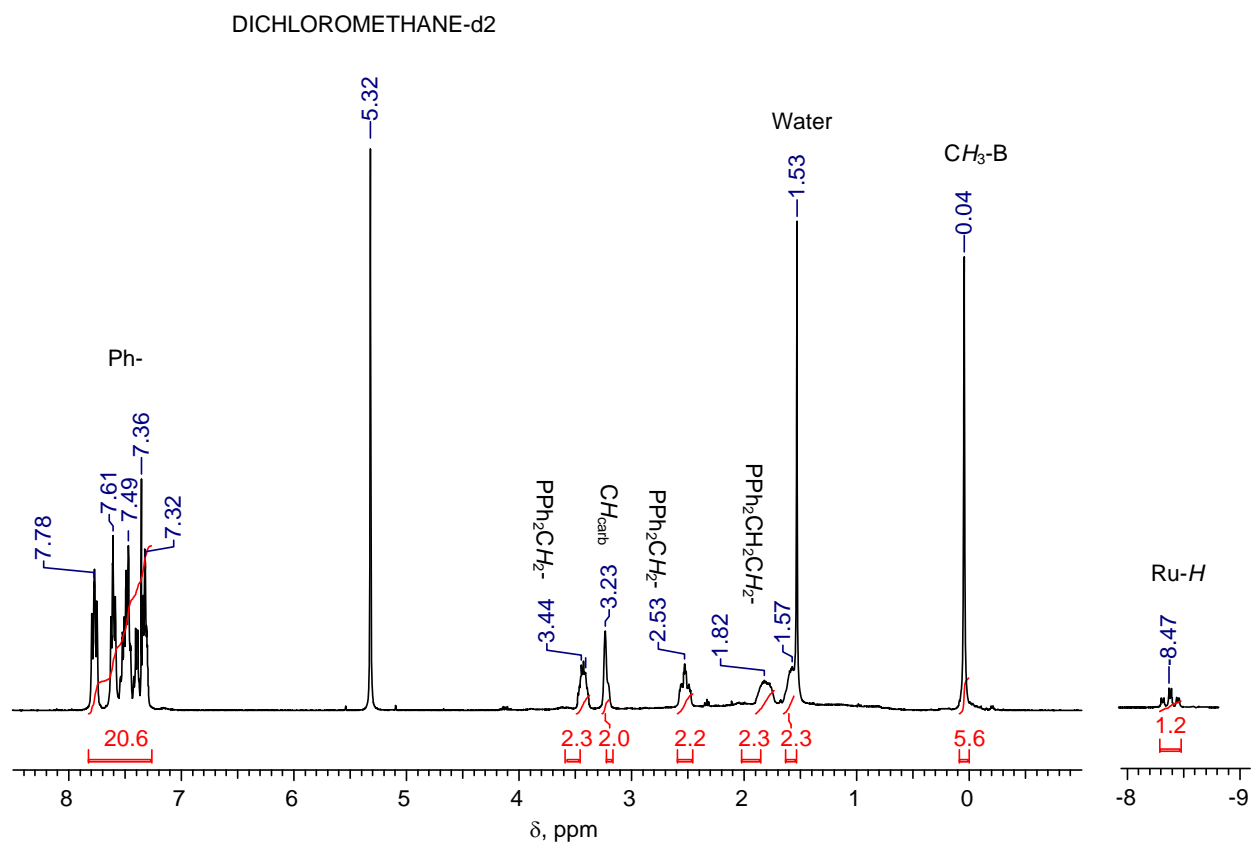


Figure S17. ¹H NMR spectrum of complex 4

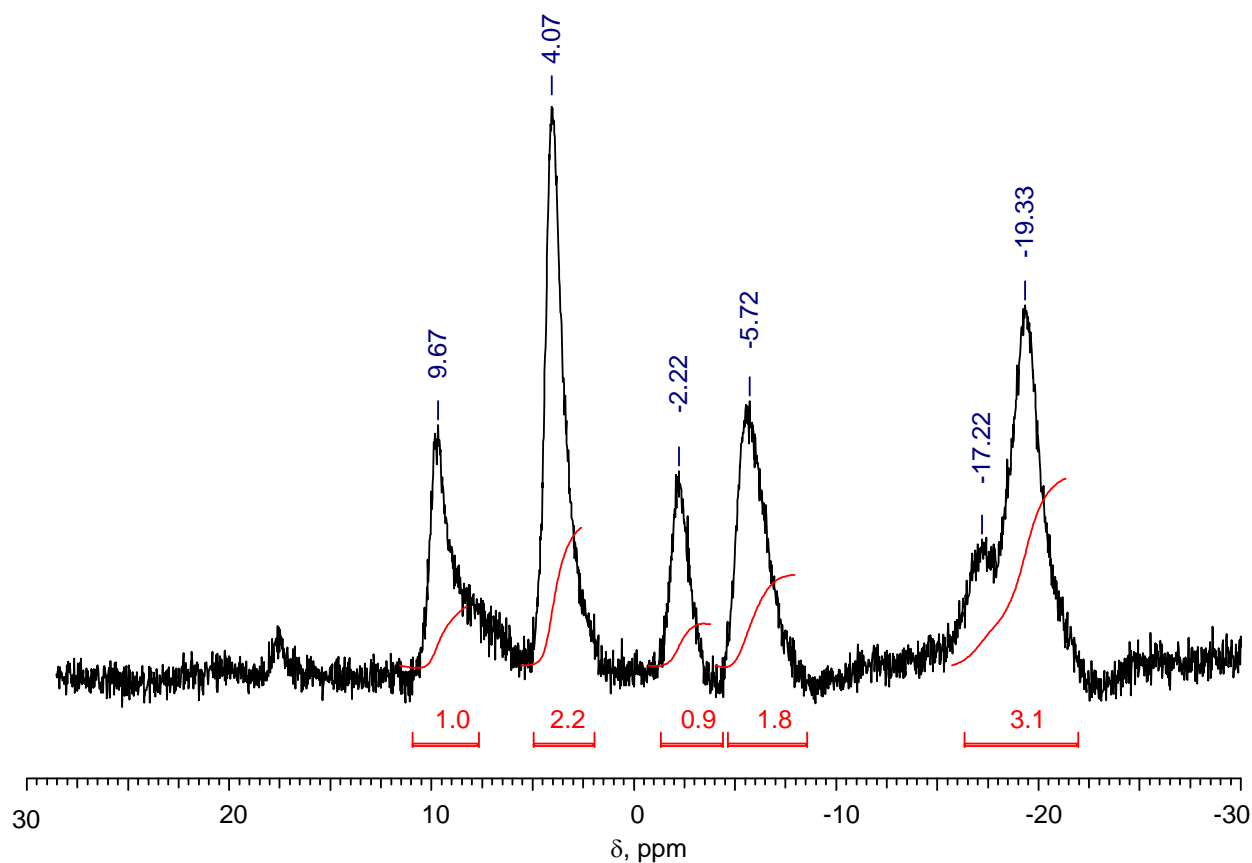


Figure S18. ¹¹B{¹H} NMR spectrum of complex 4

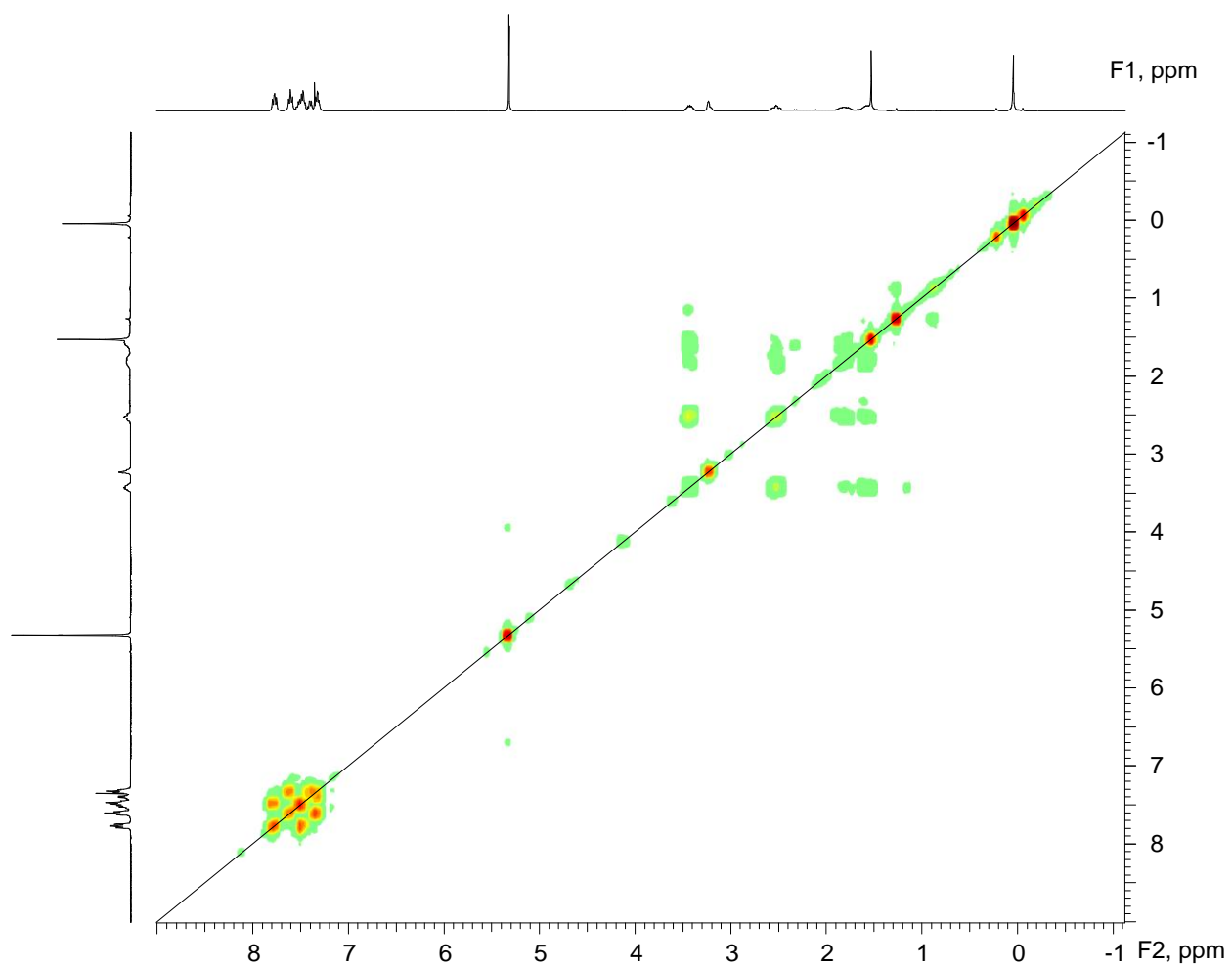


Figure S19. ^1H - ^1H 2D COSY NMR spectrum of complex 3

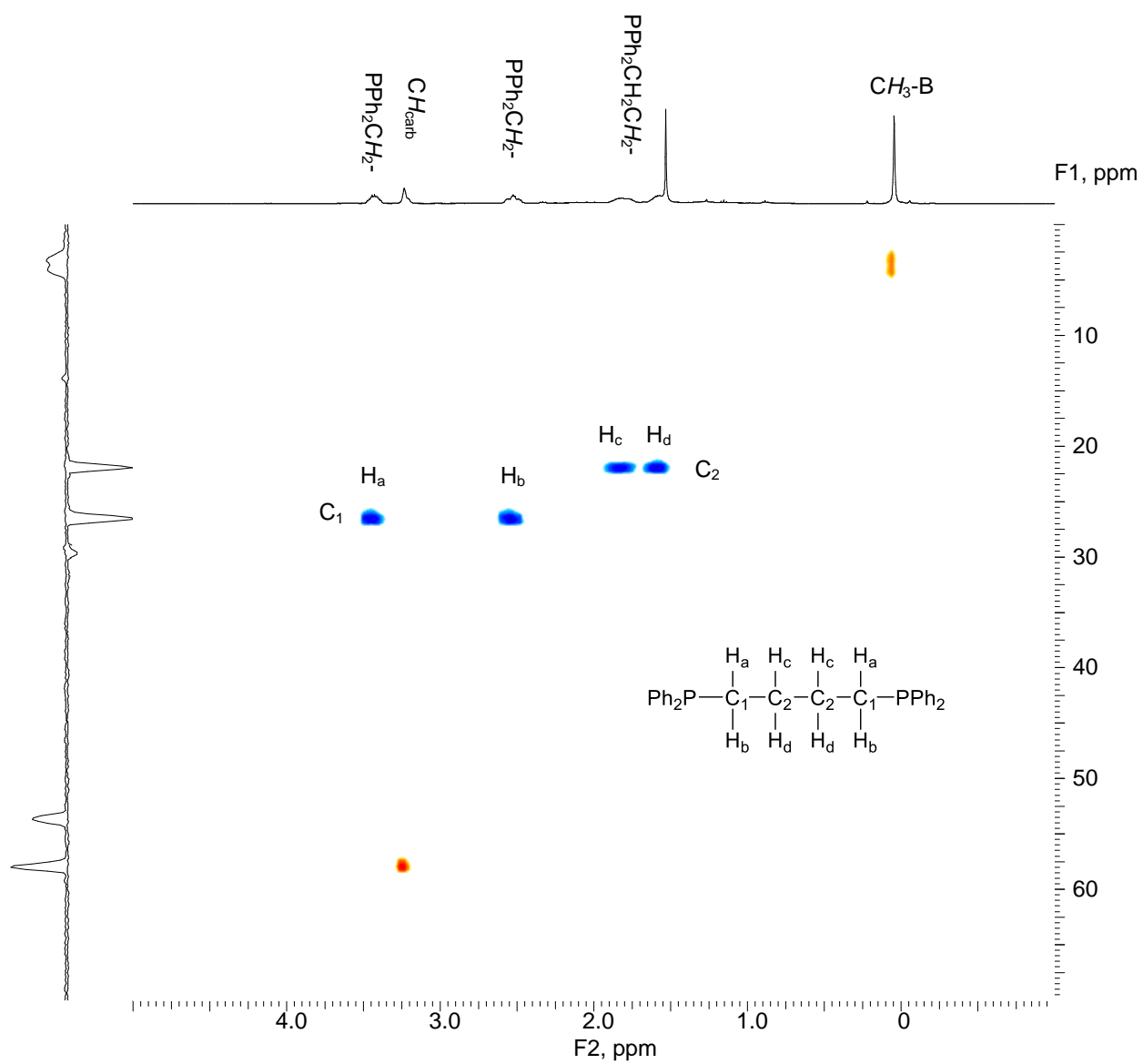


Figure S20 ^1H - ^{13}C 2D HSQC NMR spectrum of complex 4

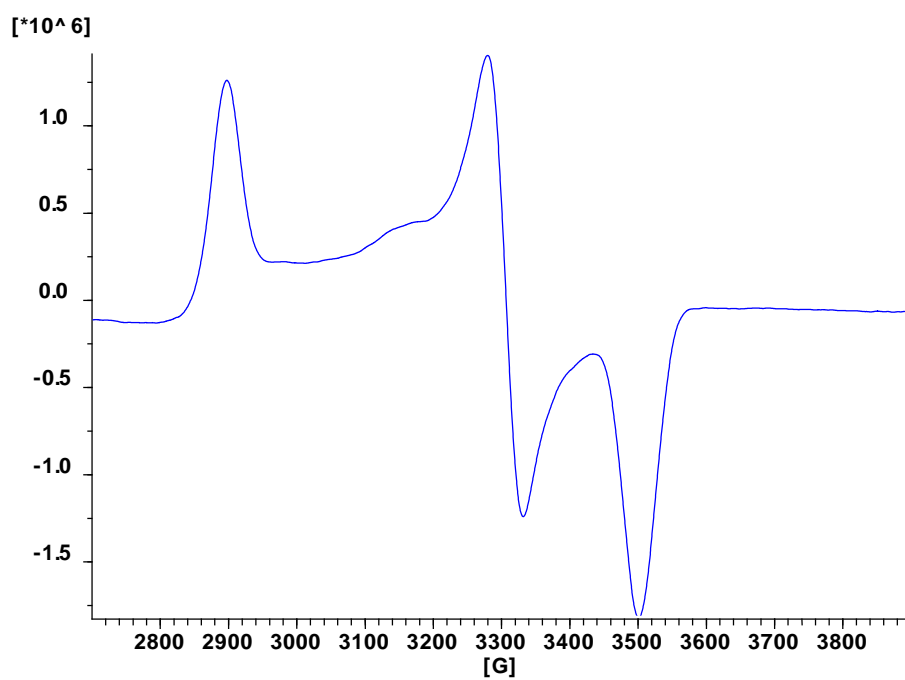


Figure S21. Anisotropic EPR spectrum of complex **7** in toluene matrix at 77 K

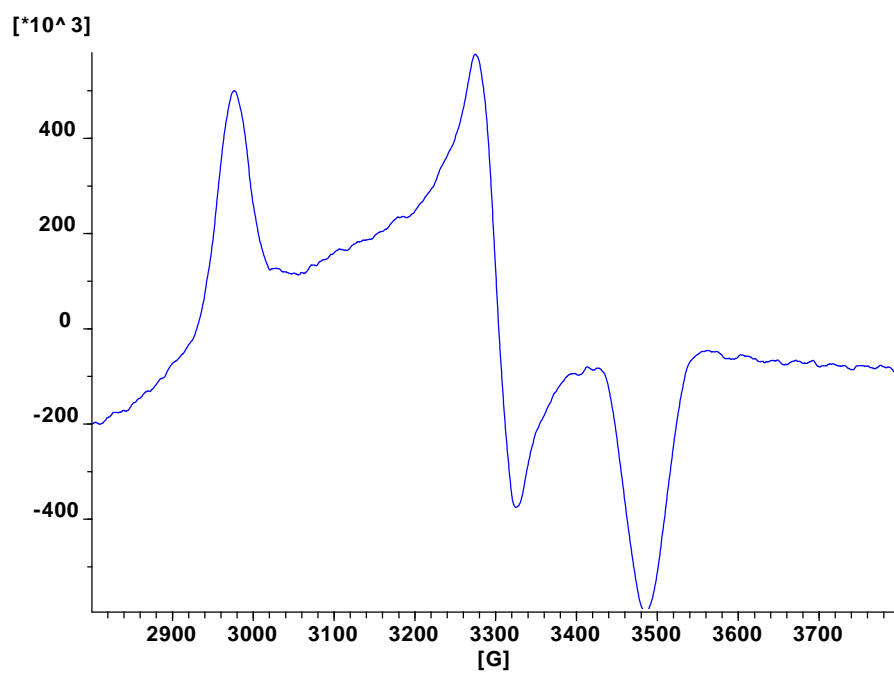


Figure S22. Anisotropic EPR spectrum of complex **9** in toluene matrix at 77 K

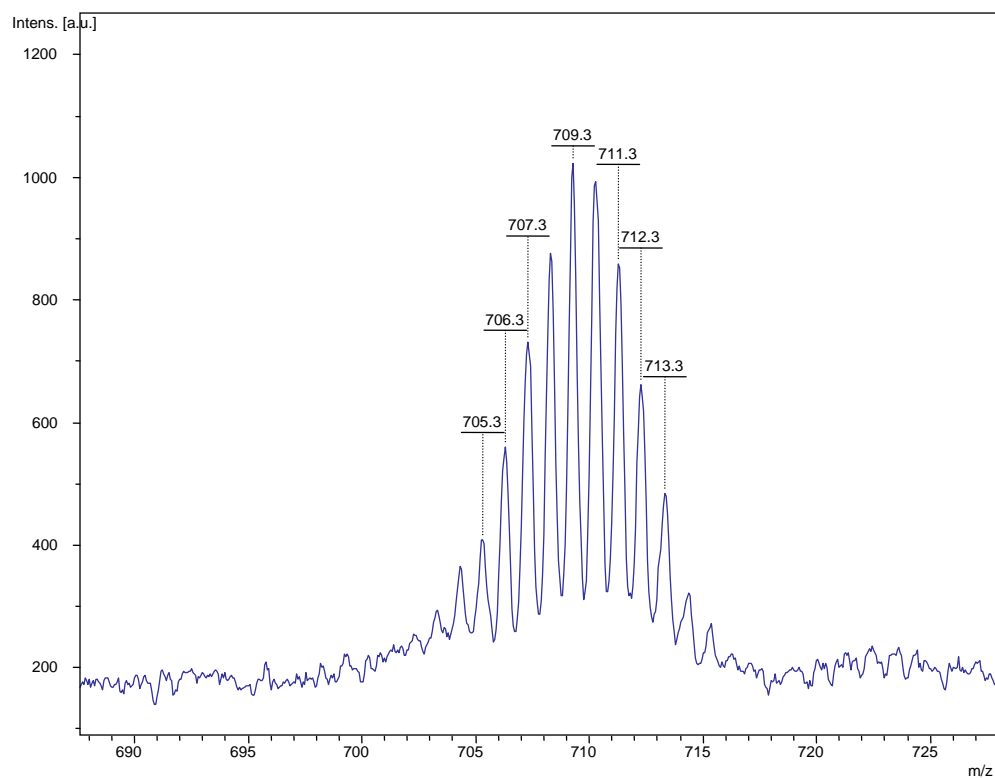


Figure S23. MALDI mass spectrum of complex **3** recorded in negative mode using DCTB as a matrix

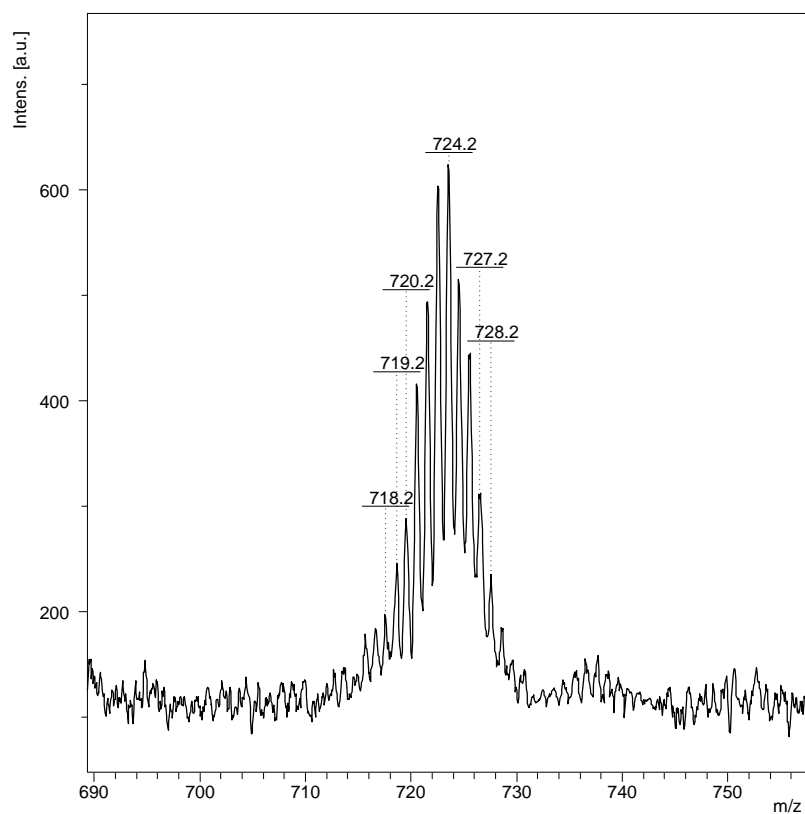


Figure S24. MALDI mass spectrum of complex **4** recorded in negative mode using DCTB as a matrix

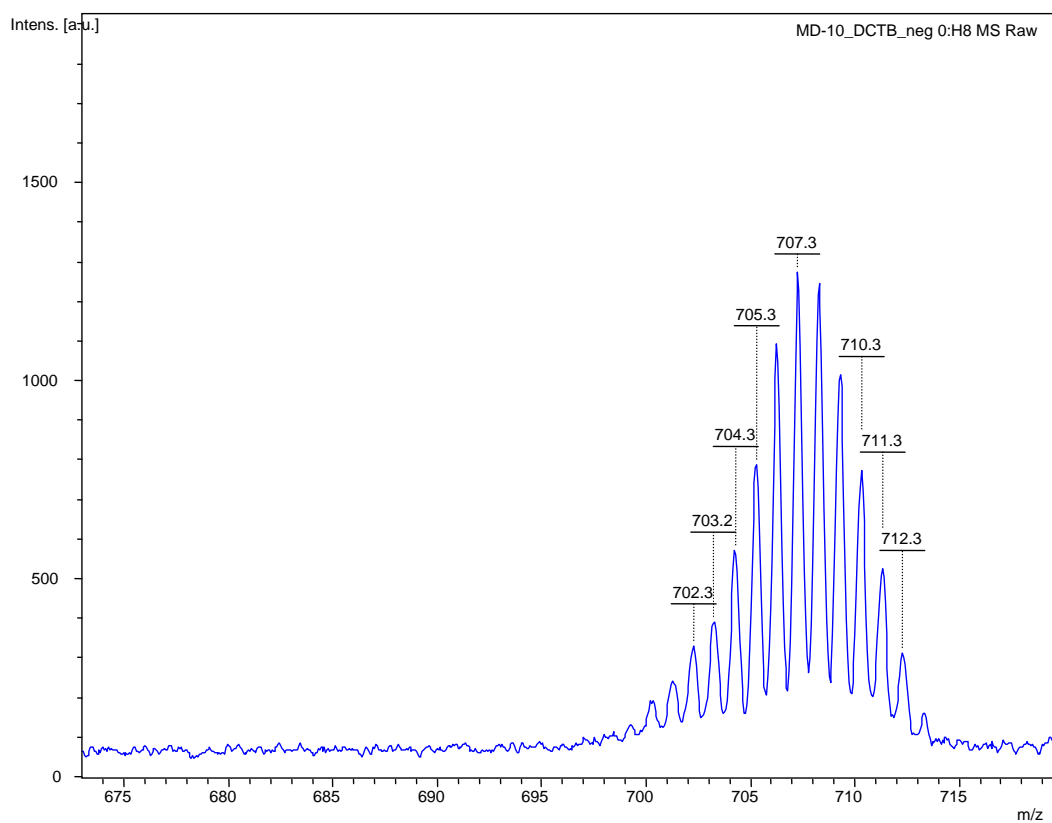


Figure S25. MALDI mass spectrum of complex **6** recorded in negative mode using DCTB as a matrix

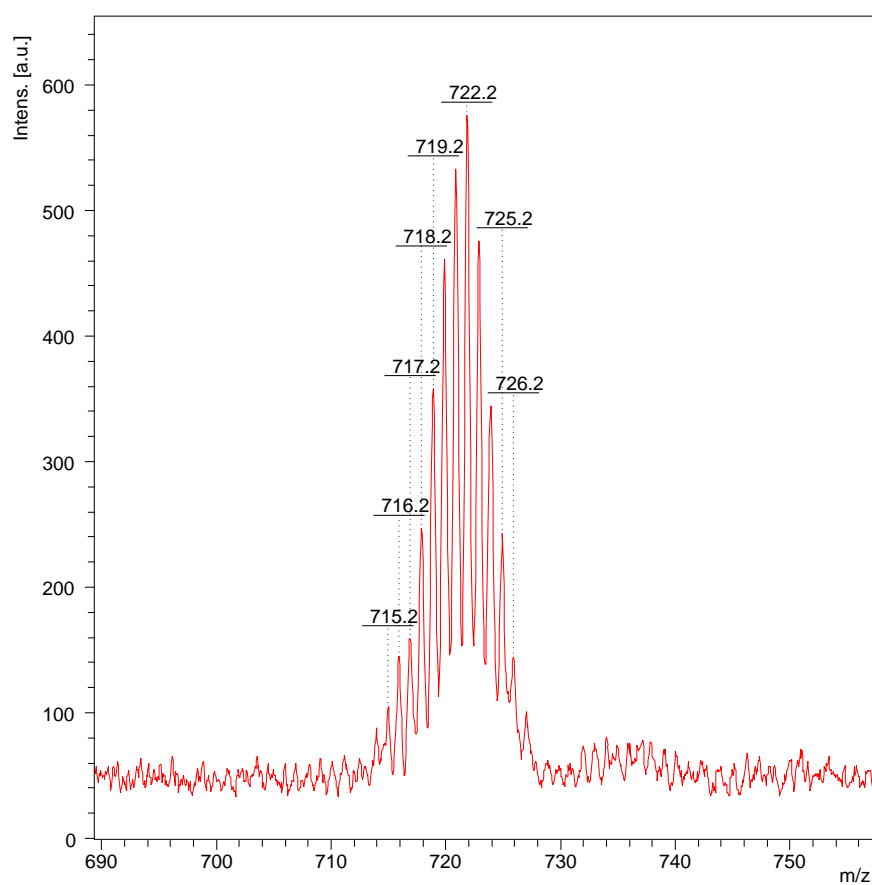


Figure S26. MALDI mass spectrum of complex **7** recorded in negative mode using DCTB as a matrix

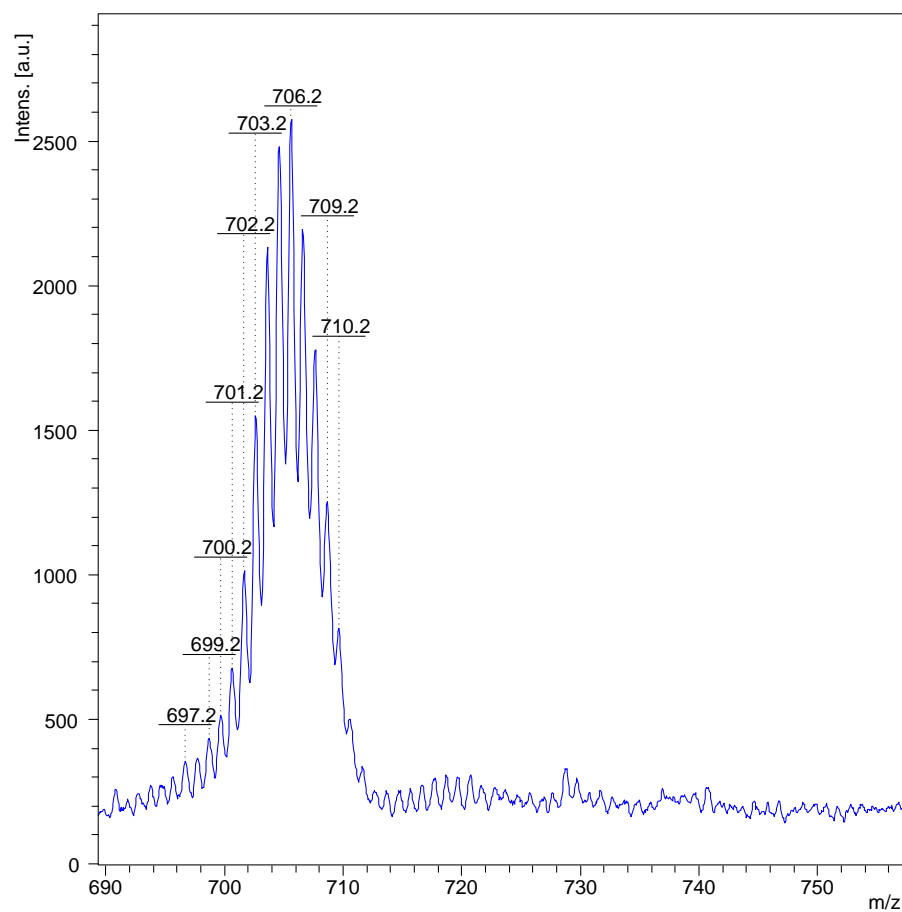


Figure S27. MALDI mass spectrum of complex **8** recorded in negative mode using DCTB as a matrix

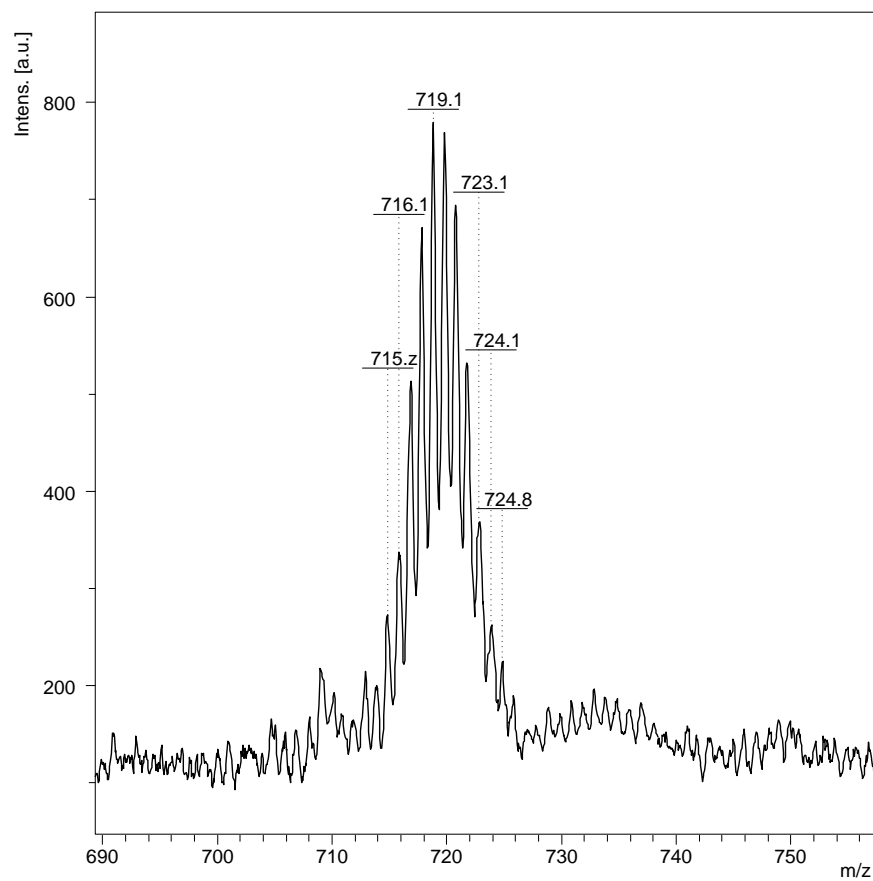


Figure S28. MALDI mass spectrum of complex **9** recorded in negative mode using DCTB as a matrix