

Supplementary Materials

Nickel(II) and Palladium(II) Complexes with $\eta^5:\kappa^1(N)$ -Coordinated Dicarbolide Ligands Containing Pendant Pyridine Group

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Spectral data for Cs[9-(NC₅H₄-2'-S)-7,8-C₂B₉H₁₁] (**1**)

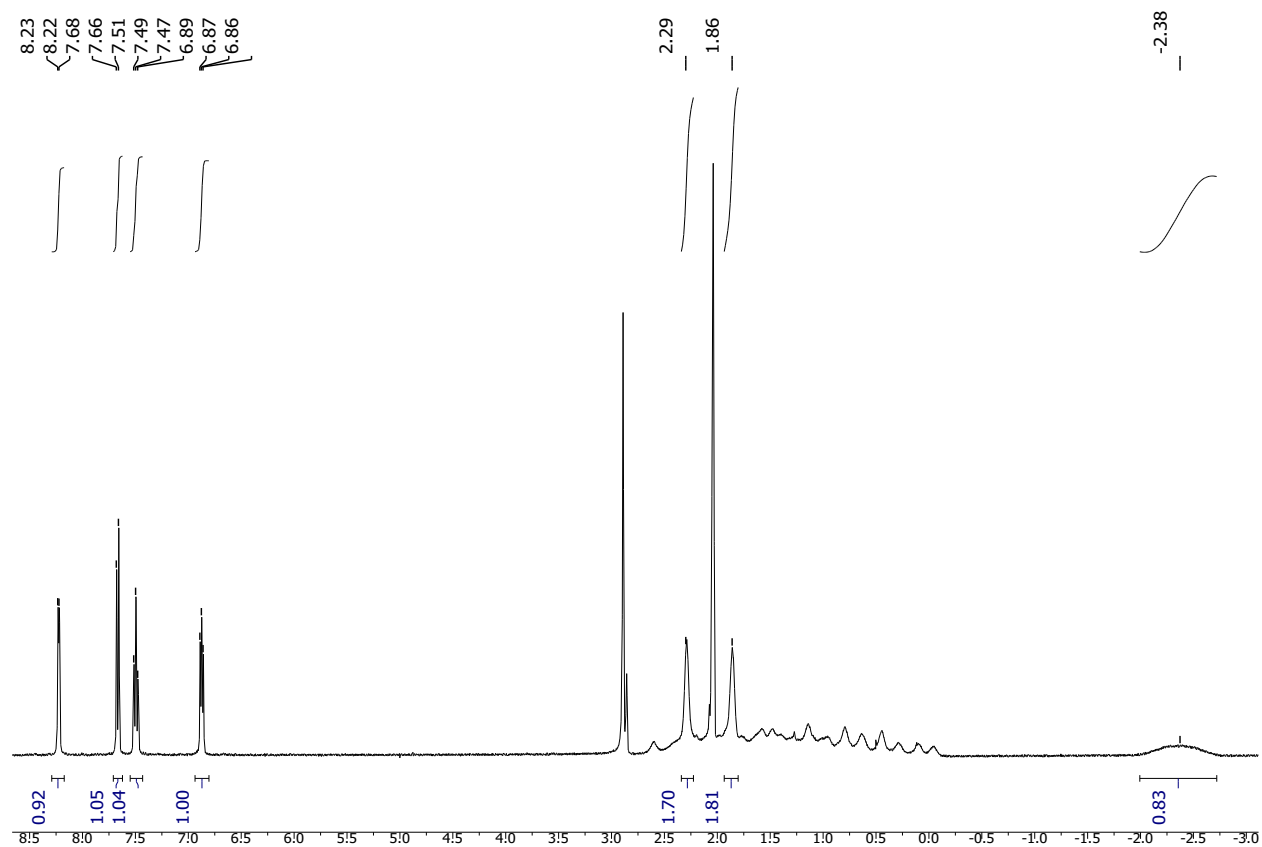


Figure S1. ¹H NMR spectrum of **1** in acetone-d₆

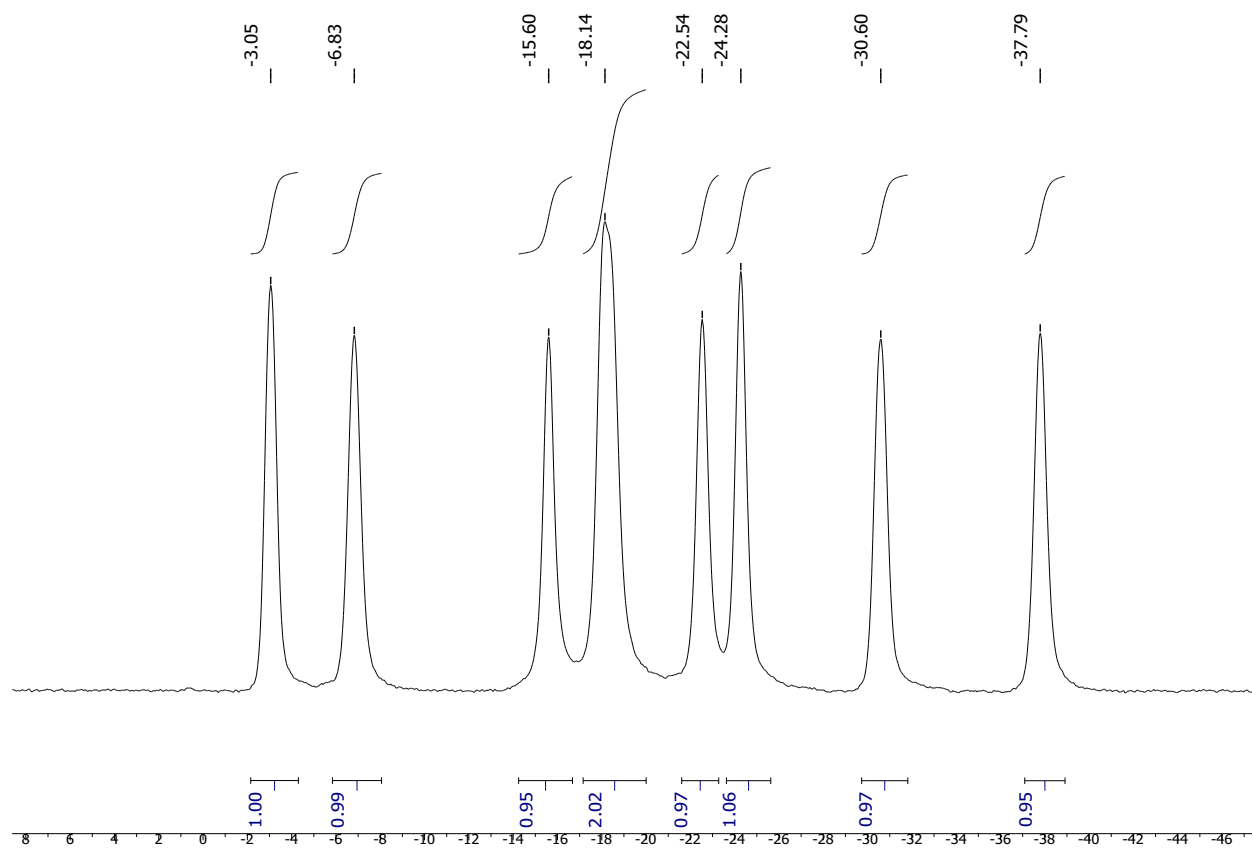


Figure S2. ¹¹B{¹H} NMR spectrum of **1** in acetone-d₆

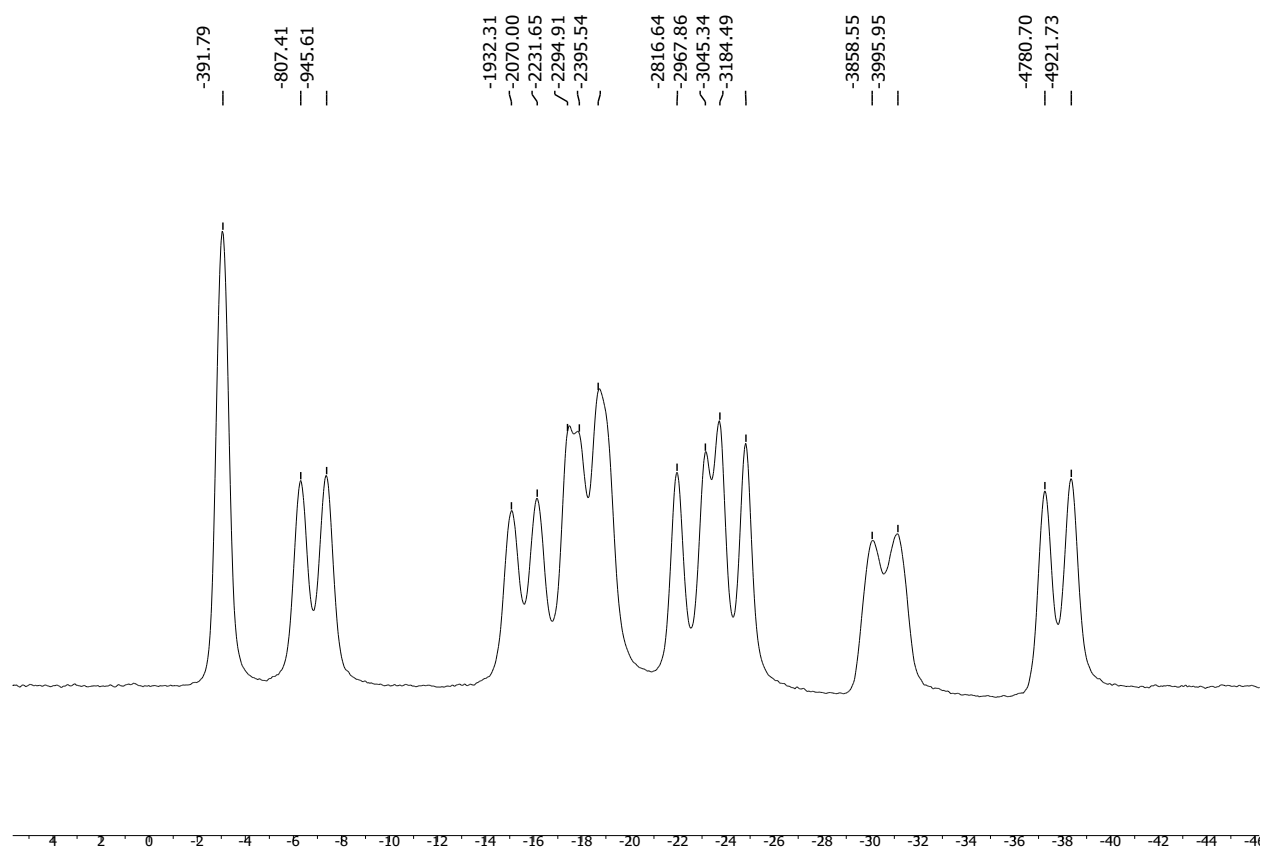


Figure S3. ^{11}B NMR spectrum of **1** in acetone- d_6

Spectral data for 1-(NC₅H₄-2'-S)-1,2-C₂B₁₀H₁₁ (**2**)

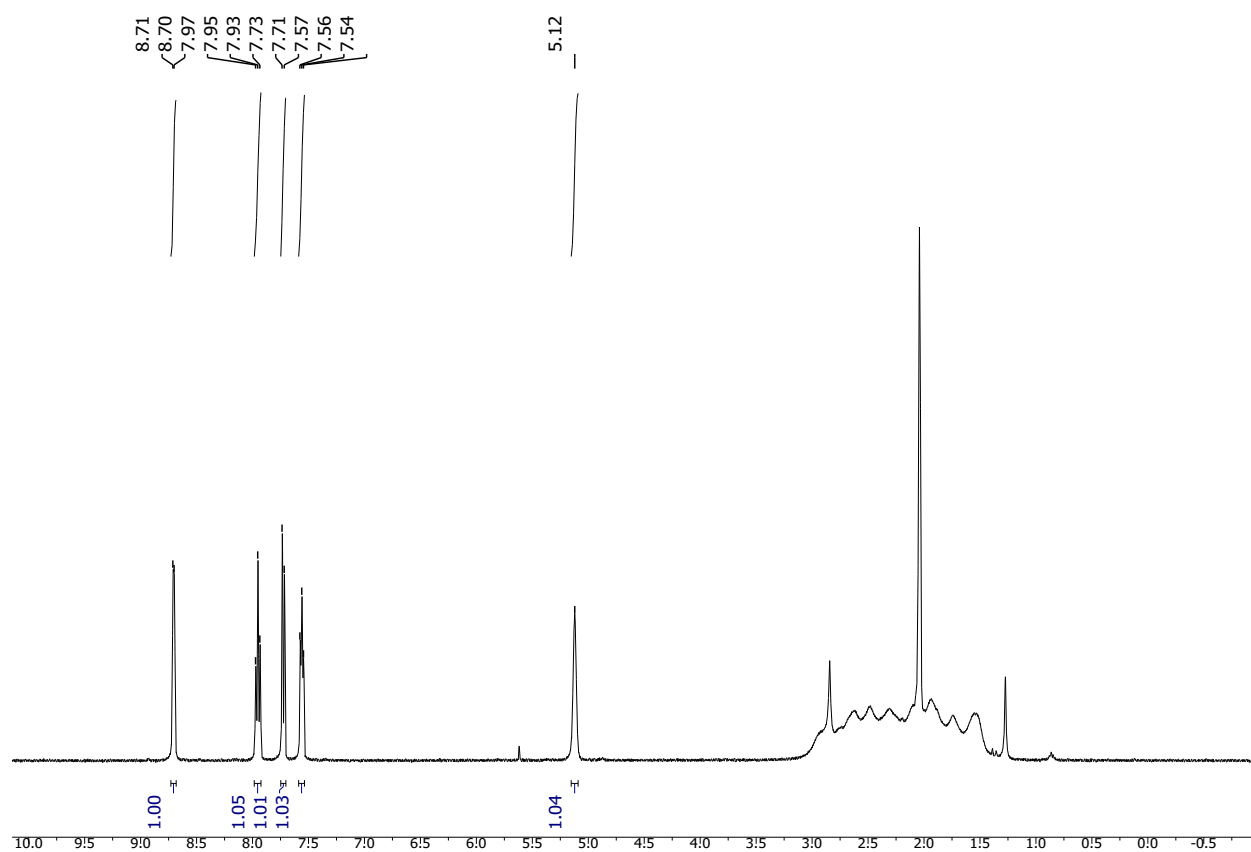


Figure S4. ¹H NMR spectrum of **2** in acetone-d₆

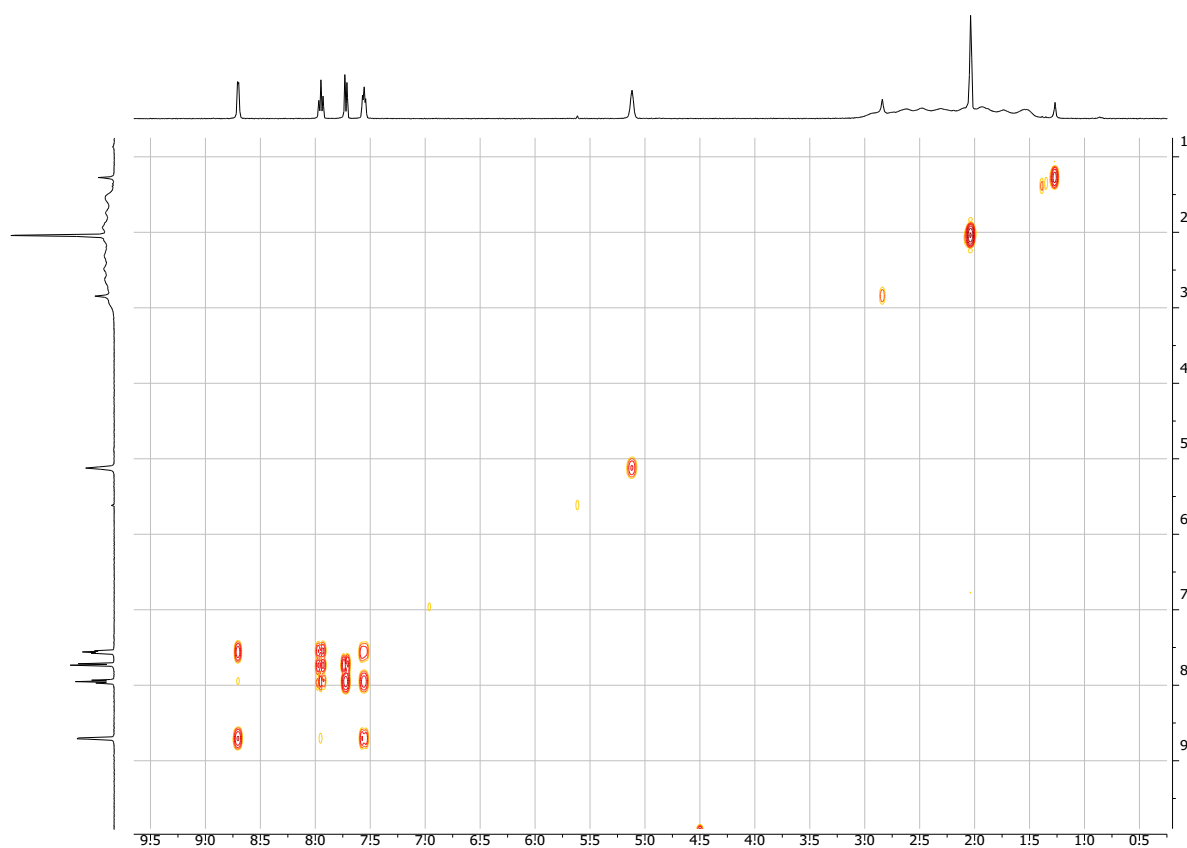


Figure S5. (HH) COSY NMR spectrum of **2** in acetone-d₆

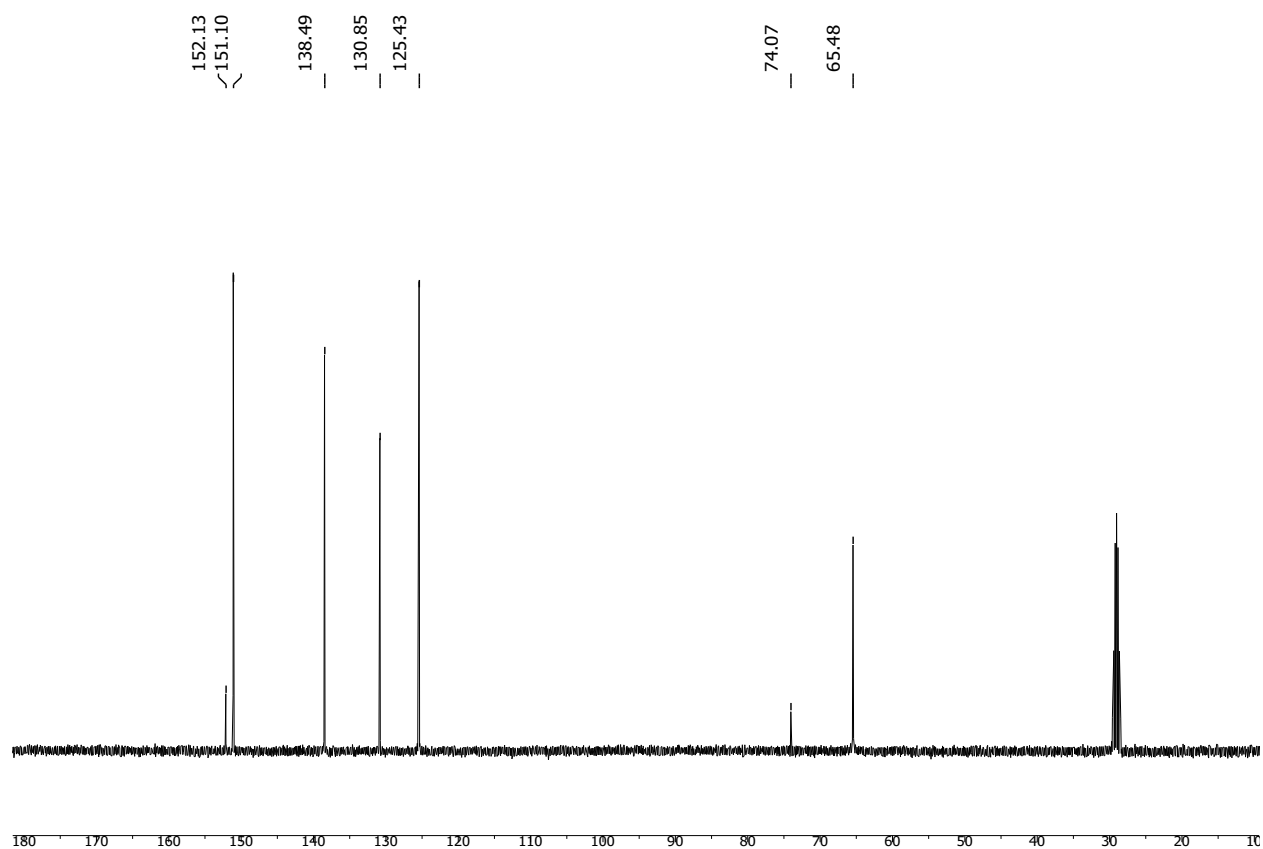


Figure S6. ^{13}C NMR spectrum of **2** in acetone- d_6

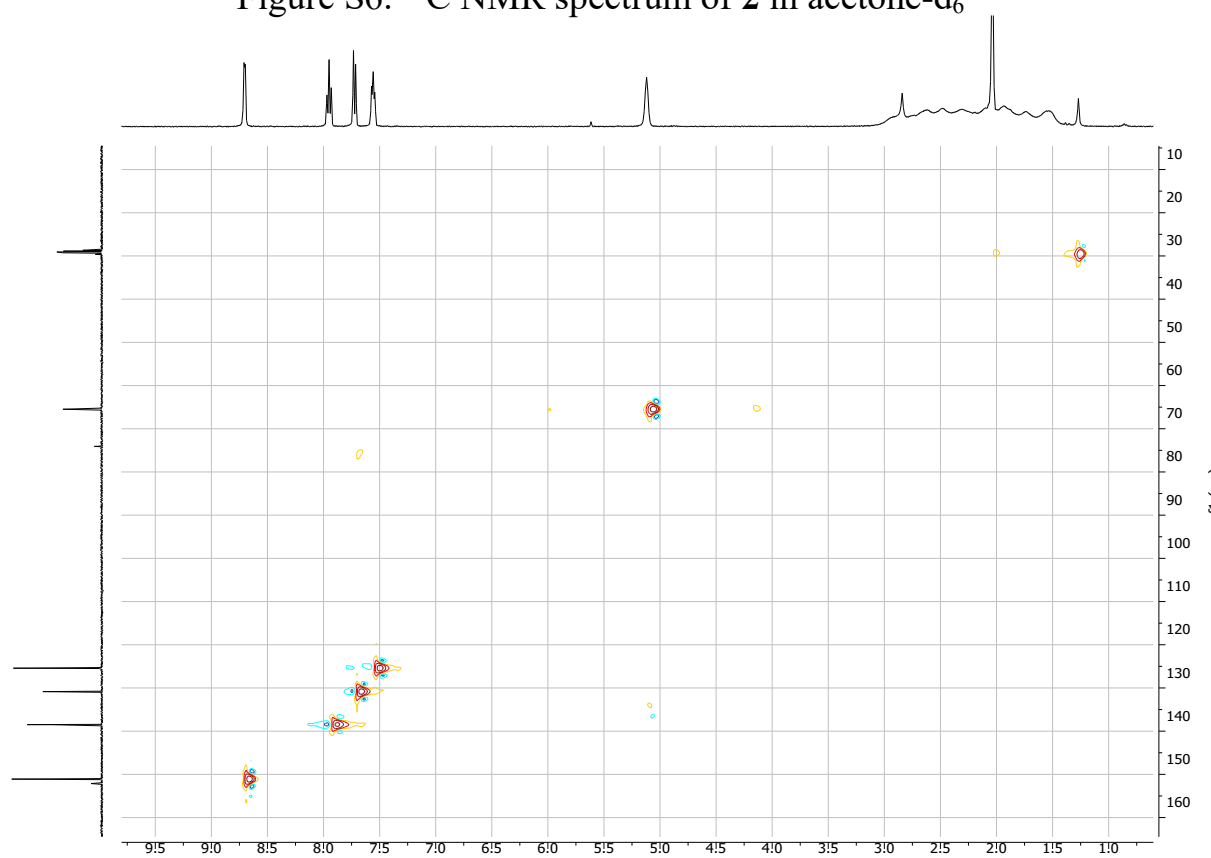


Figure S7. (H,C) HSQC NMR spectrum of **2** in acetone- d_6

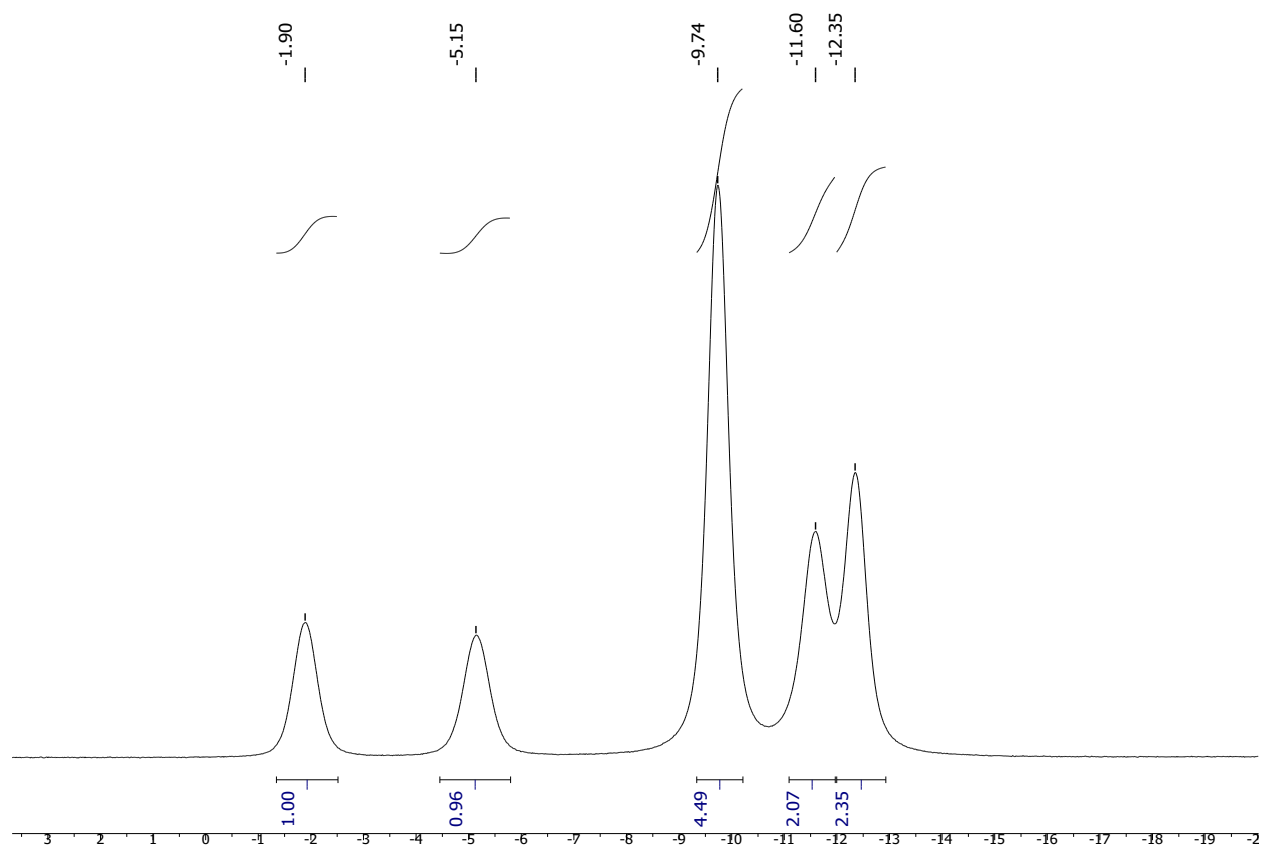


Figure S8. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2** in acetone- d_6

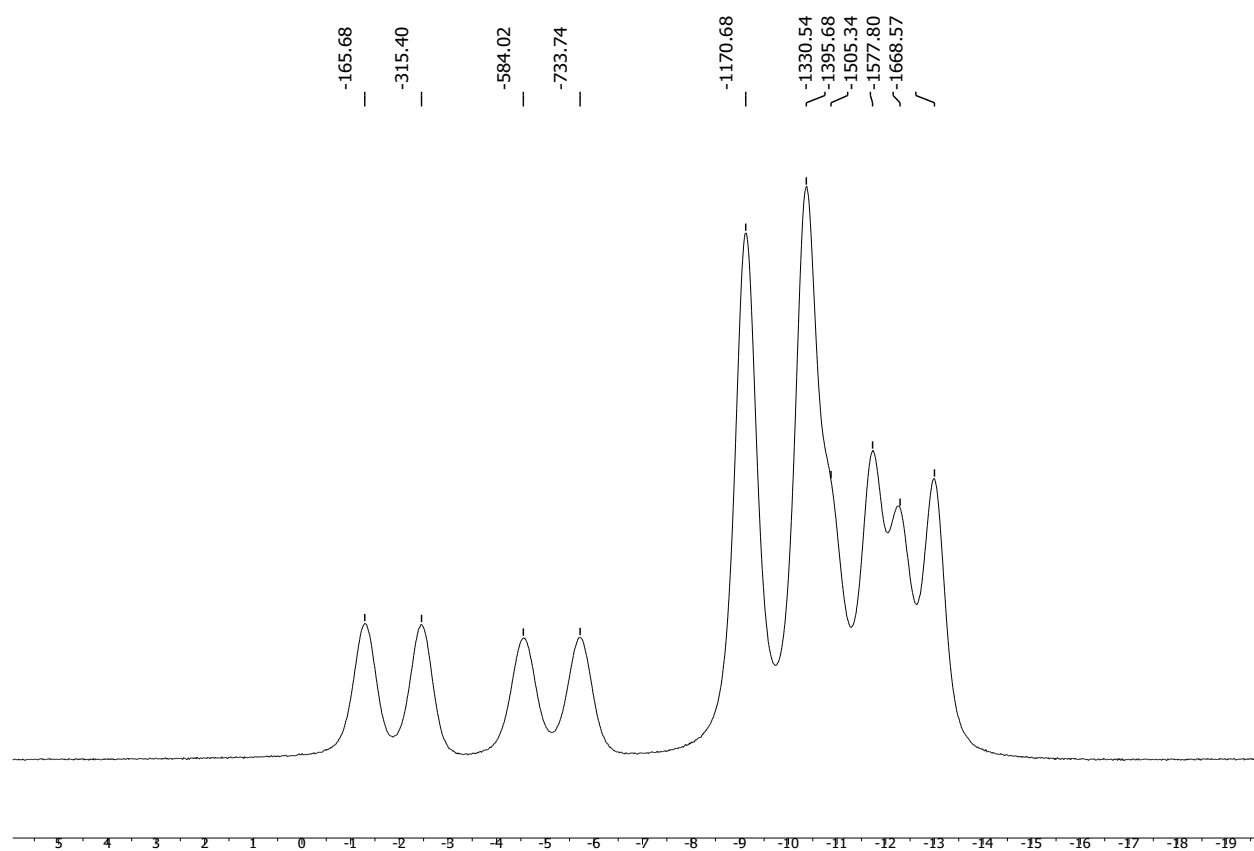


Figure S9. ^{11}B NMR spectrum of **2** in acetone- d_6

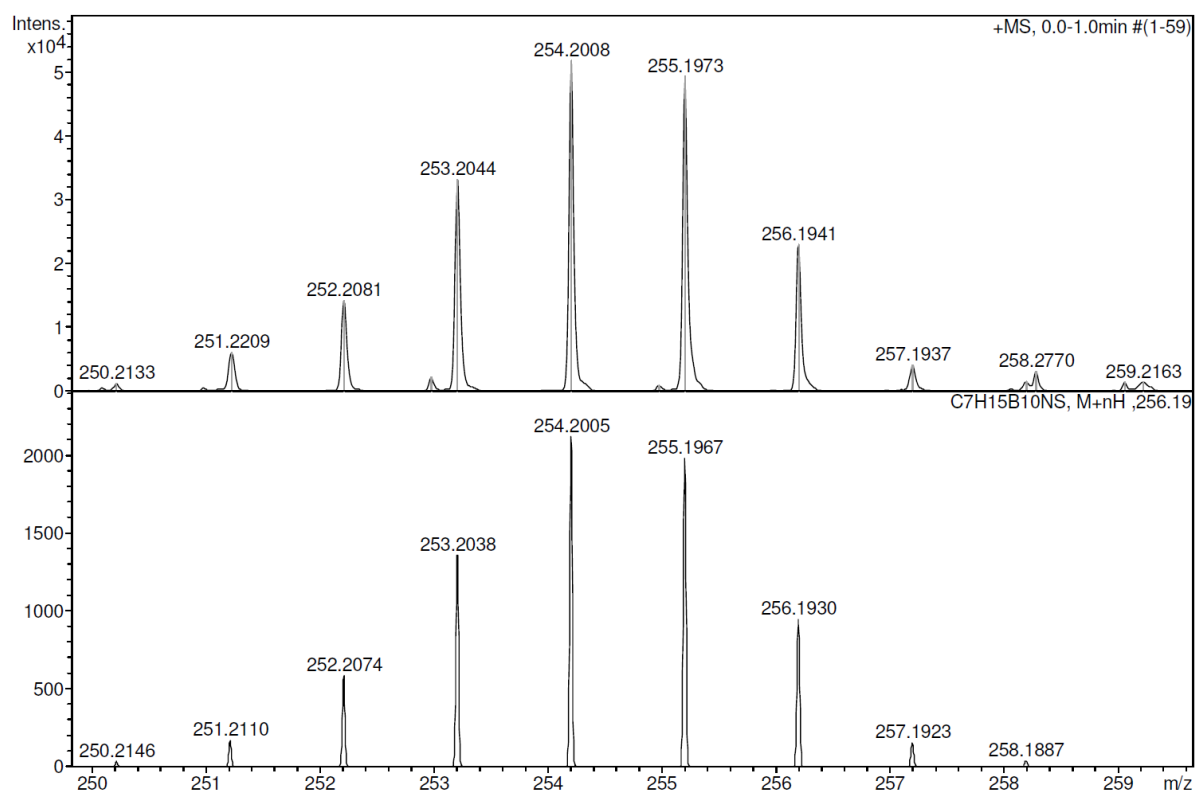


Figure S10. HRMS spectrum of **2**

Spectral data for [7-(HNC₅H₄-2'-S)-7,8-C₂B₉H₁₁] (**H[3]**)

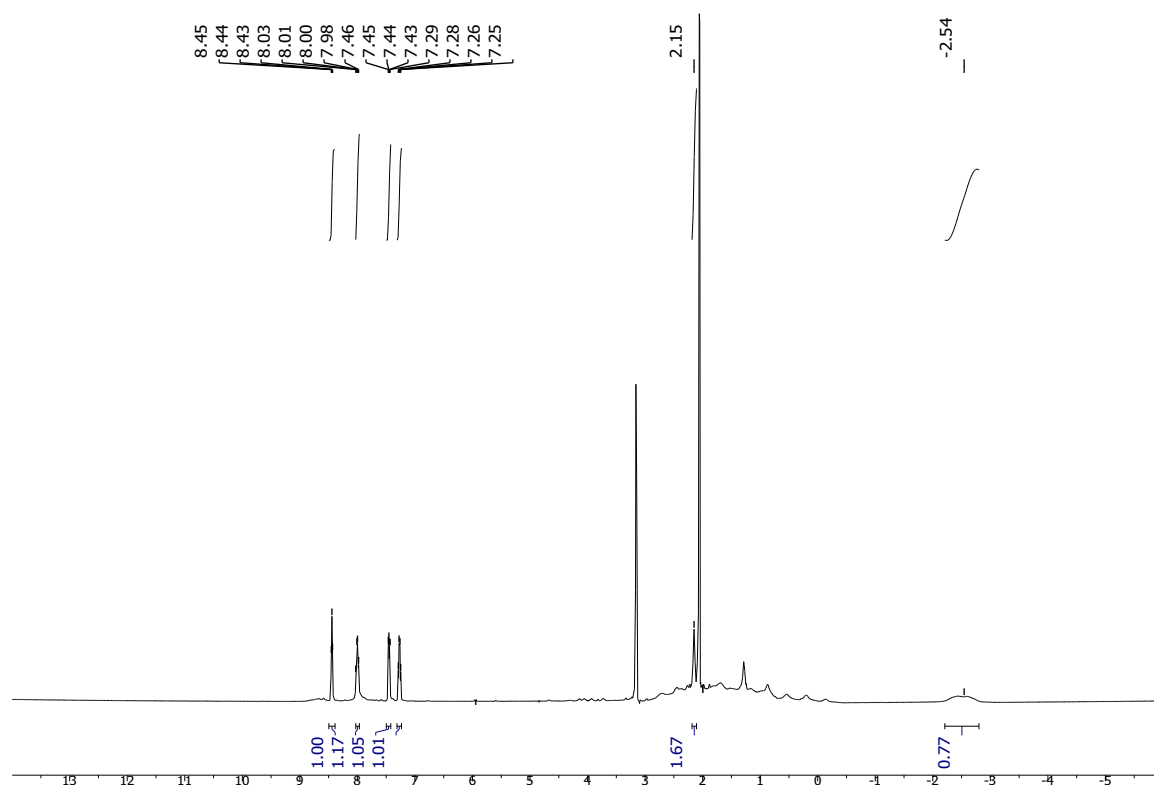


Figure S11. ¹H NMR spectrum of **H[3]** in acetone-d₆

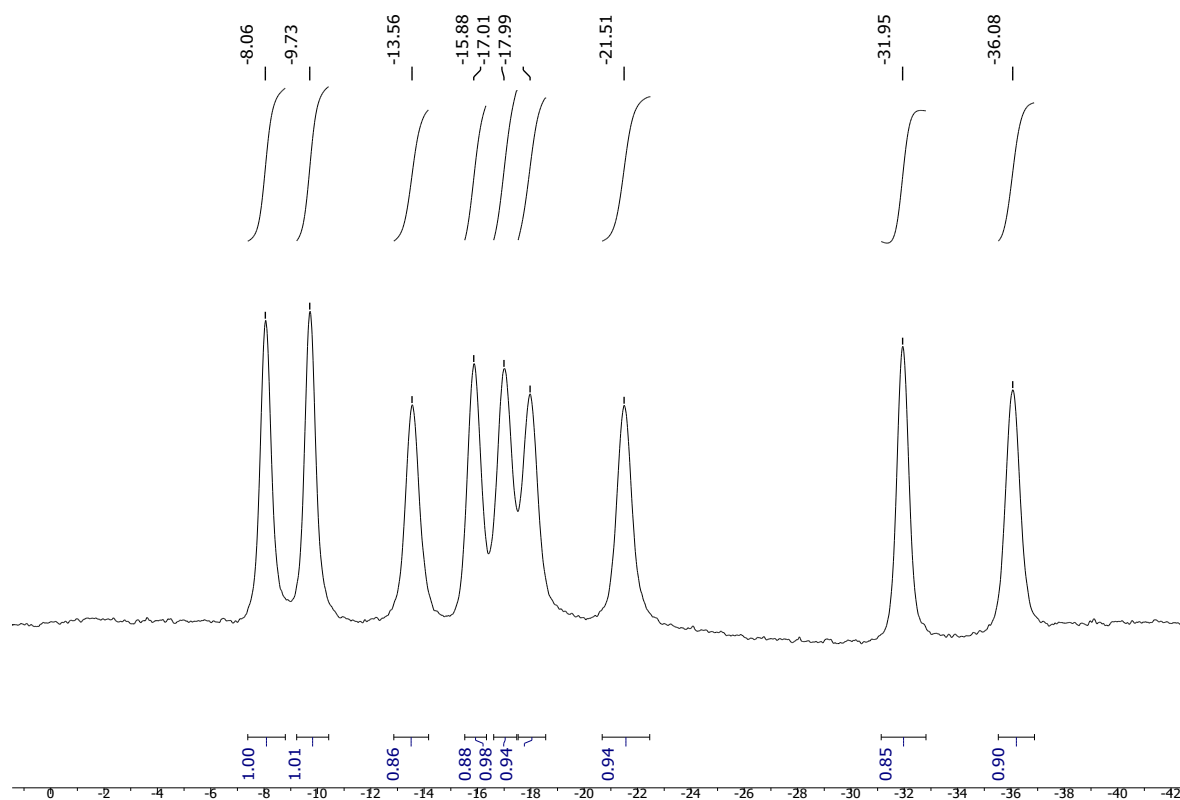


Figure S12. ¹¹B{¹H} NMR spectrum of **H[3]** in acetone-d₆

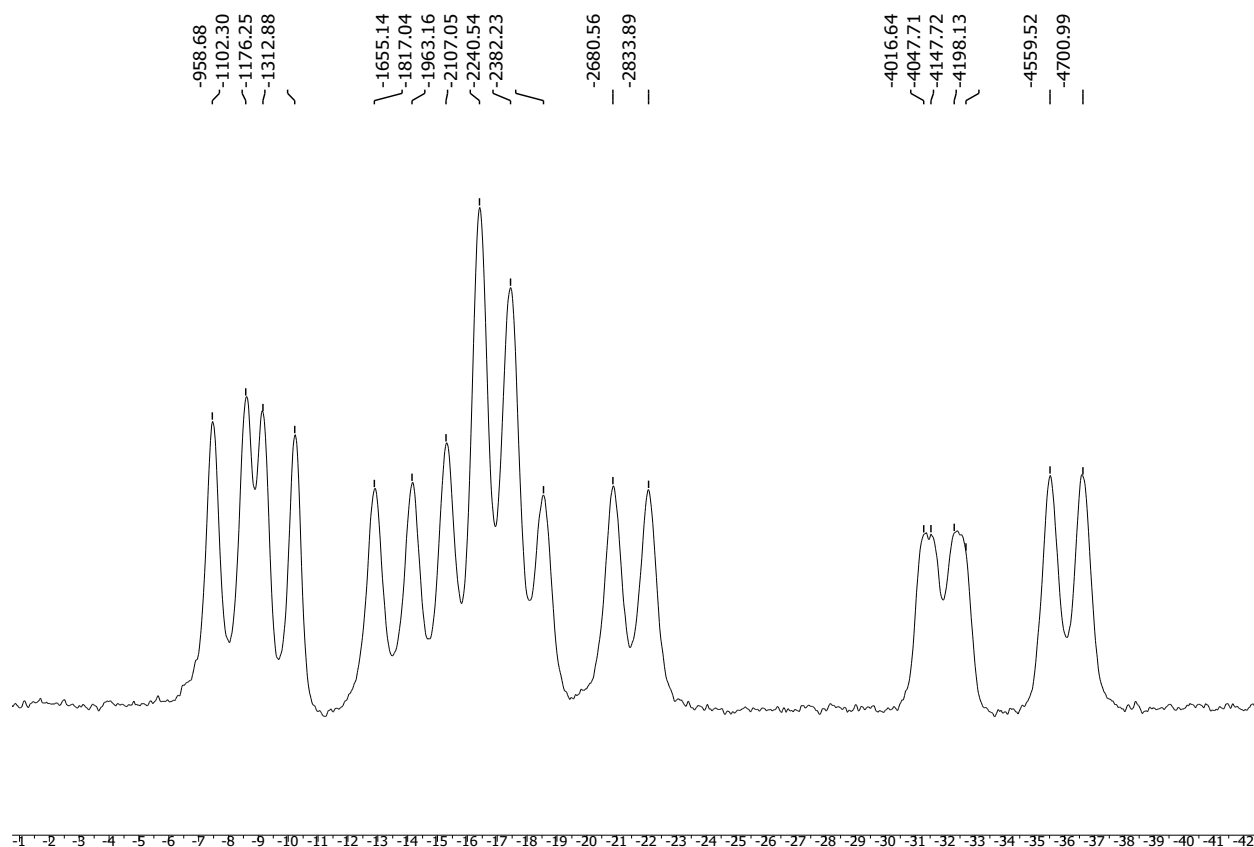


Figure S13. ¹¹B NMR spectrum of **H[3]** in acetone-d₆

Spectral data for Cs[7-(NC₅H₄-2'-S)-7,8-C₂B₉H₁₁] (**Cs[3]**)

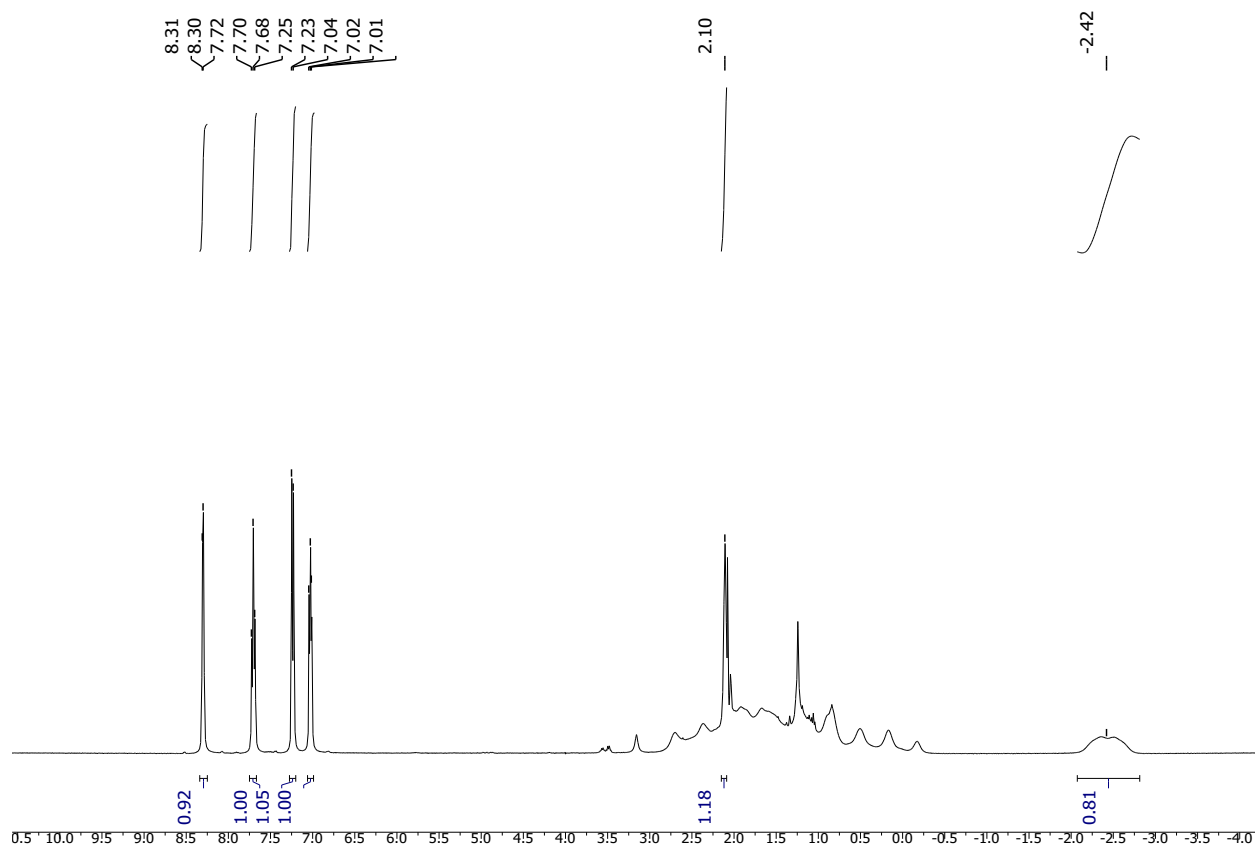


Figure S14. ¹H NMR spectrum of **Cs[3]** in acetone-d₆

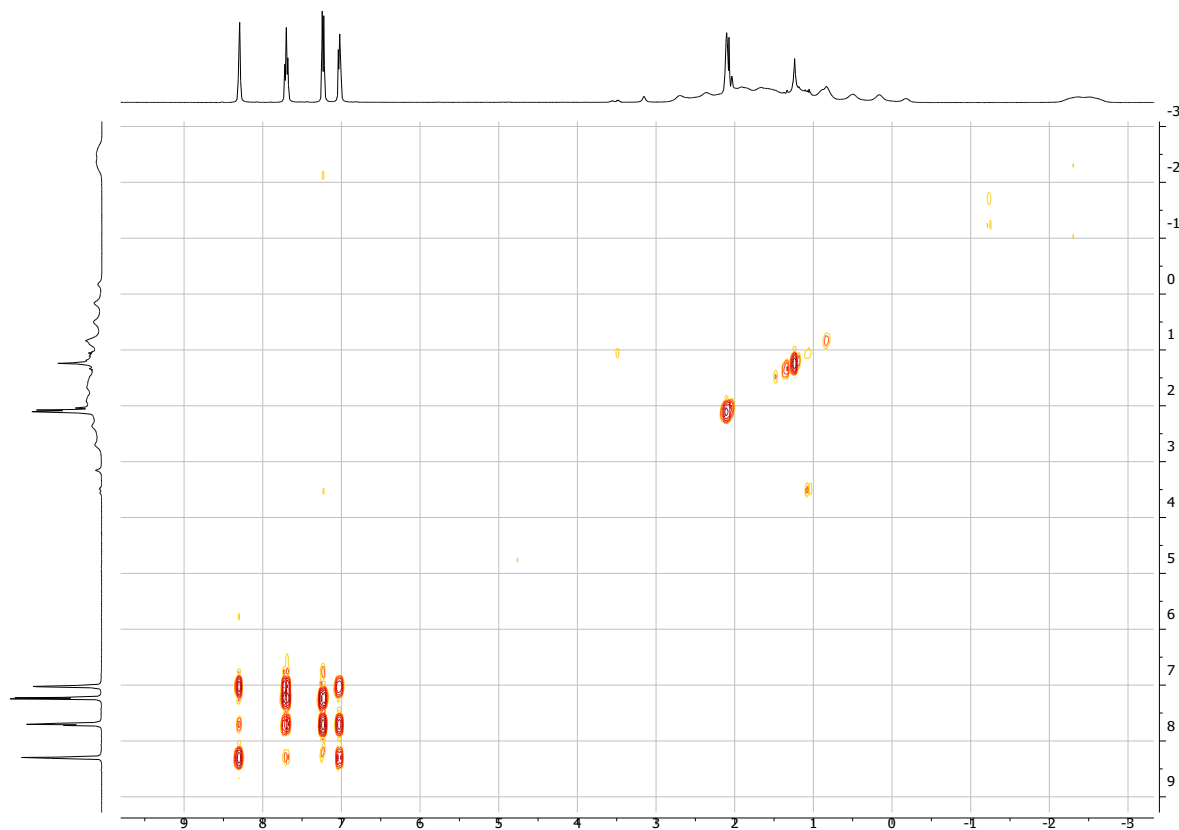


Figure S15. (HH) COSY NMR spectrum of **Cs[3]** in acetone-d₆

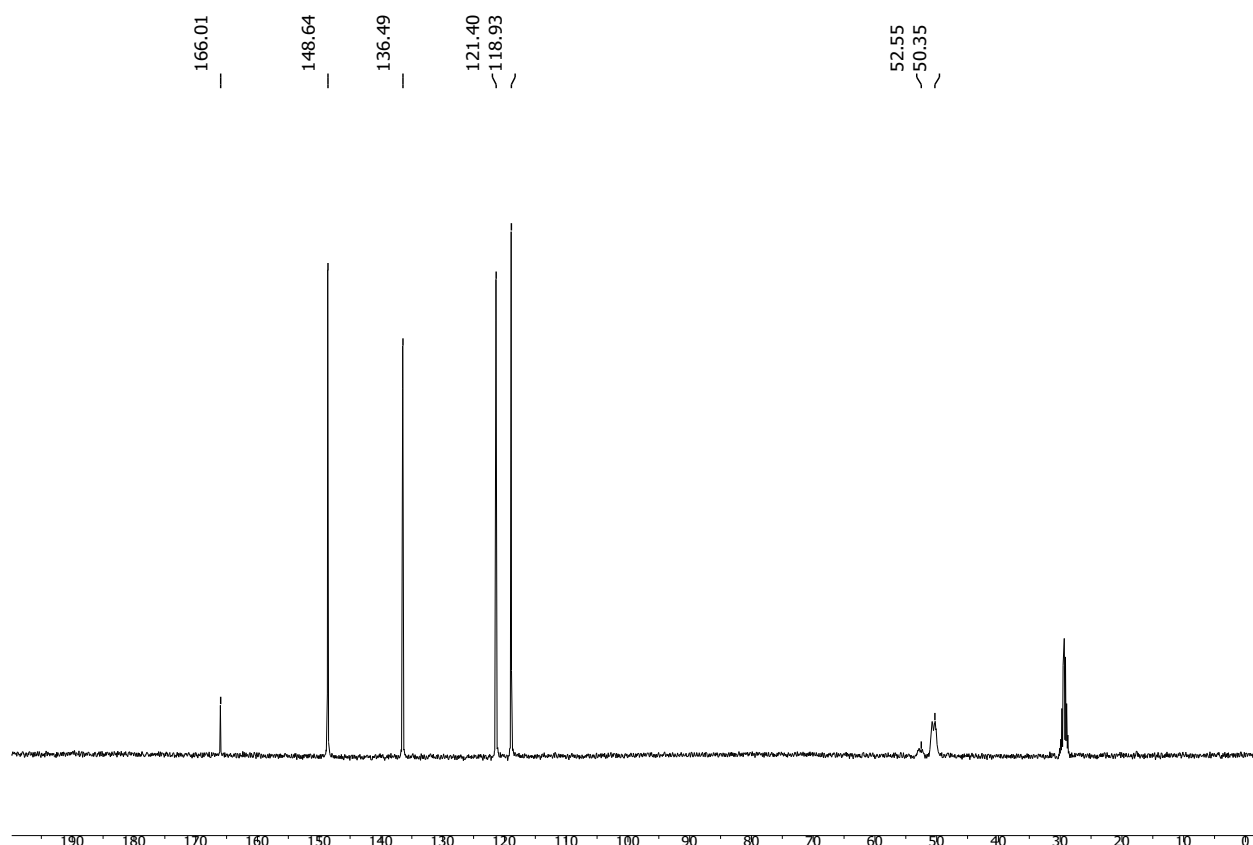


Figure S16. ^{13}C NMR spectrum of **Cs[3]** in acetone- d_6

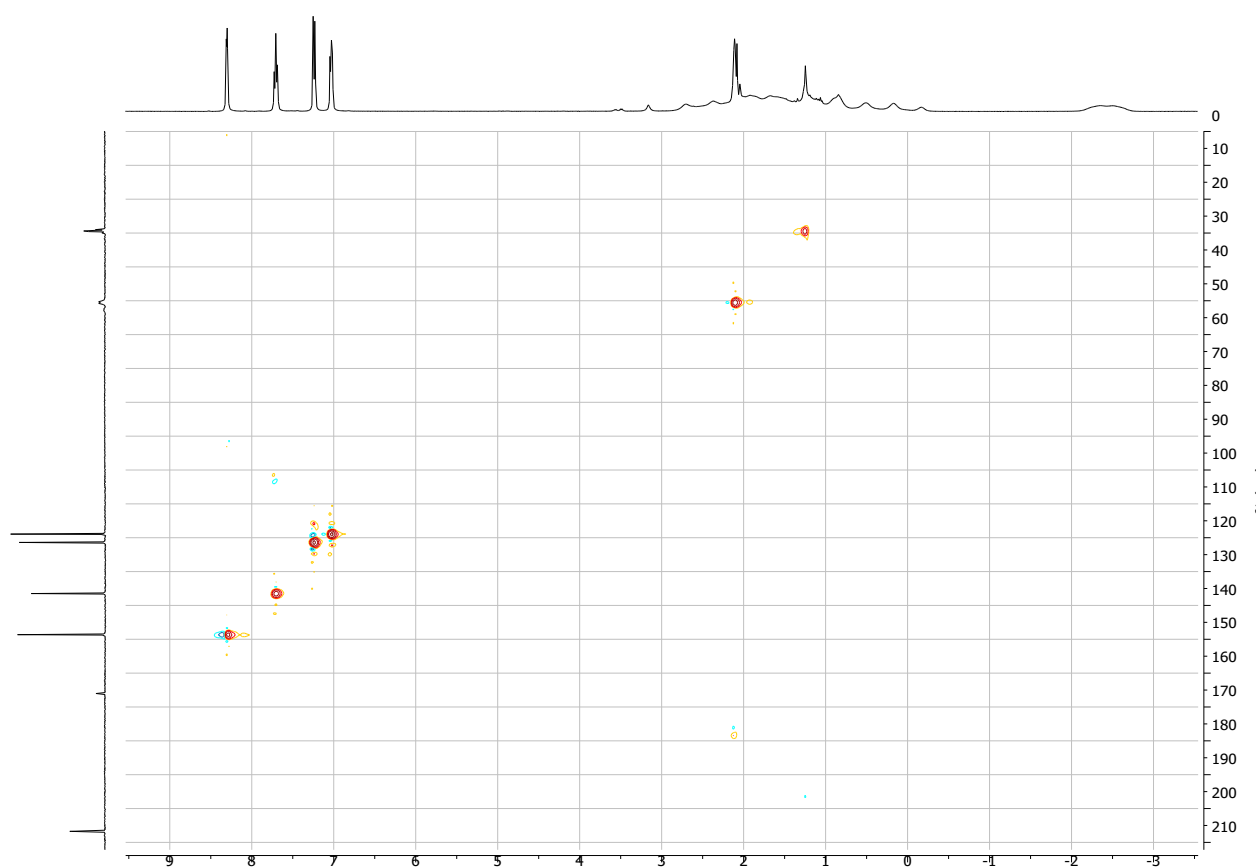


Figure S17. (H)C HSQC NMR spectrum of **Cs[3]** in acetone- d_6

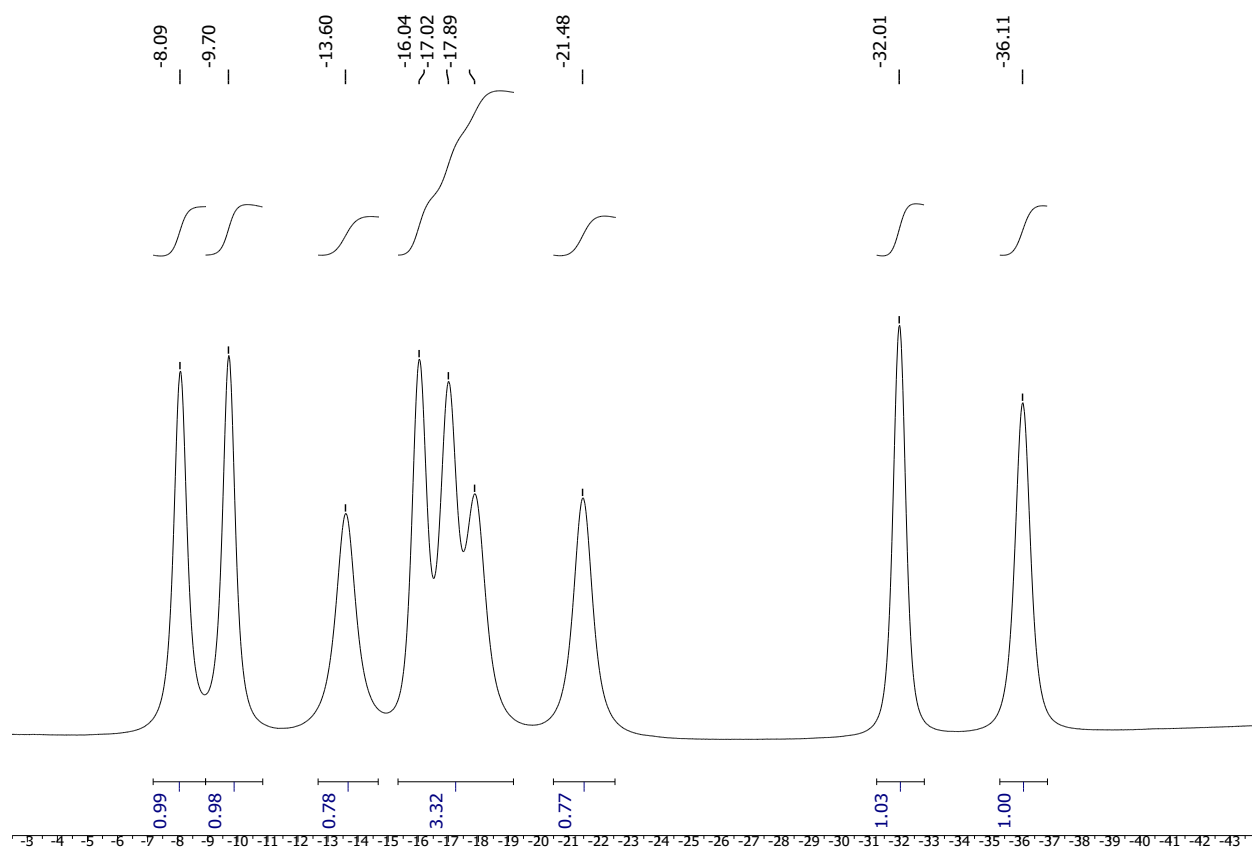


Figure S18. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **Cs[3]** in acetone- d_6

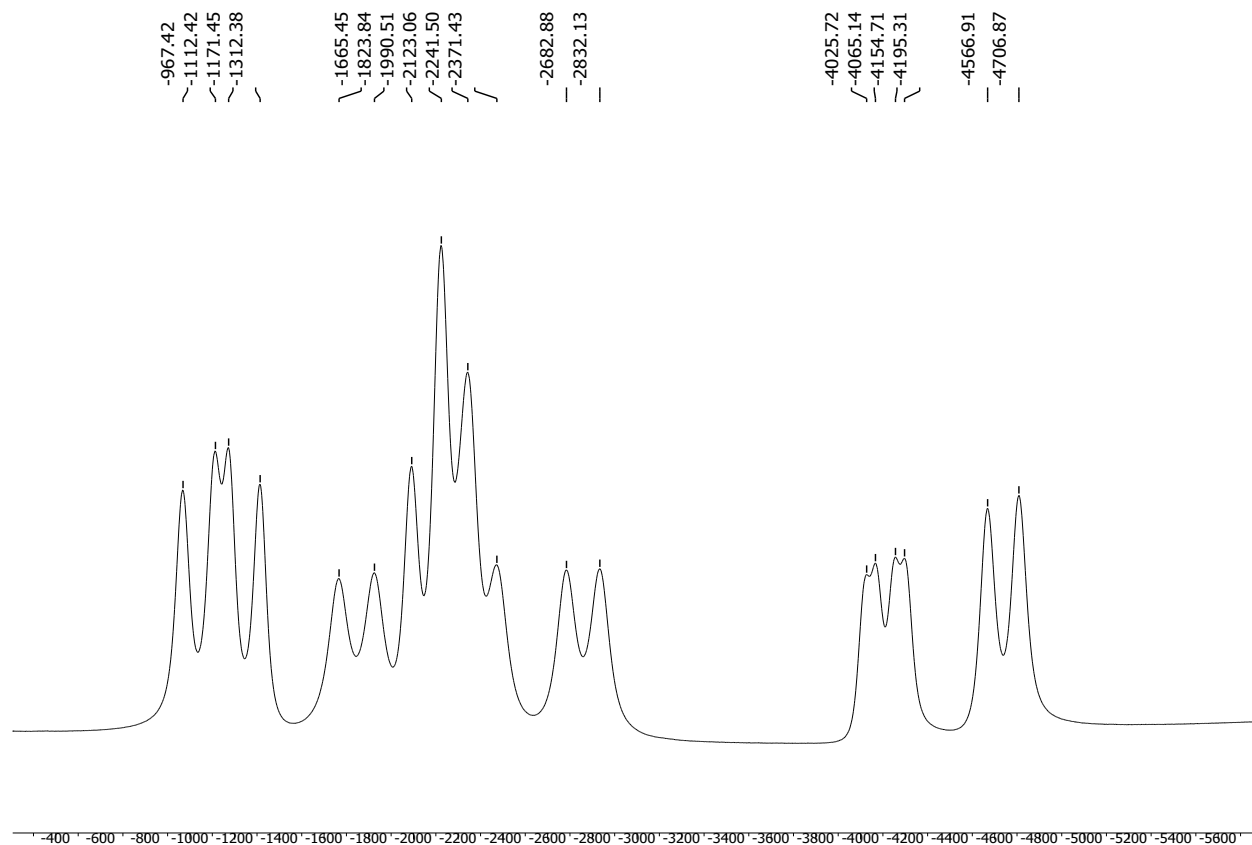


Figure S19. ^{11}B NMR spectrum of **Cs[3]** in acetone- d_6

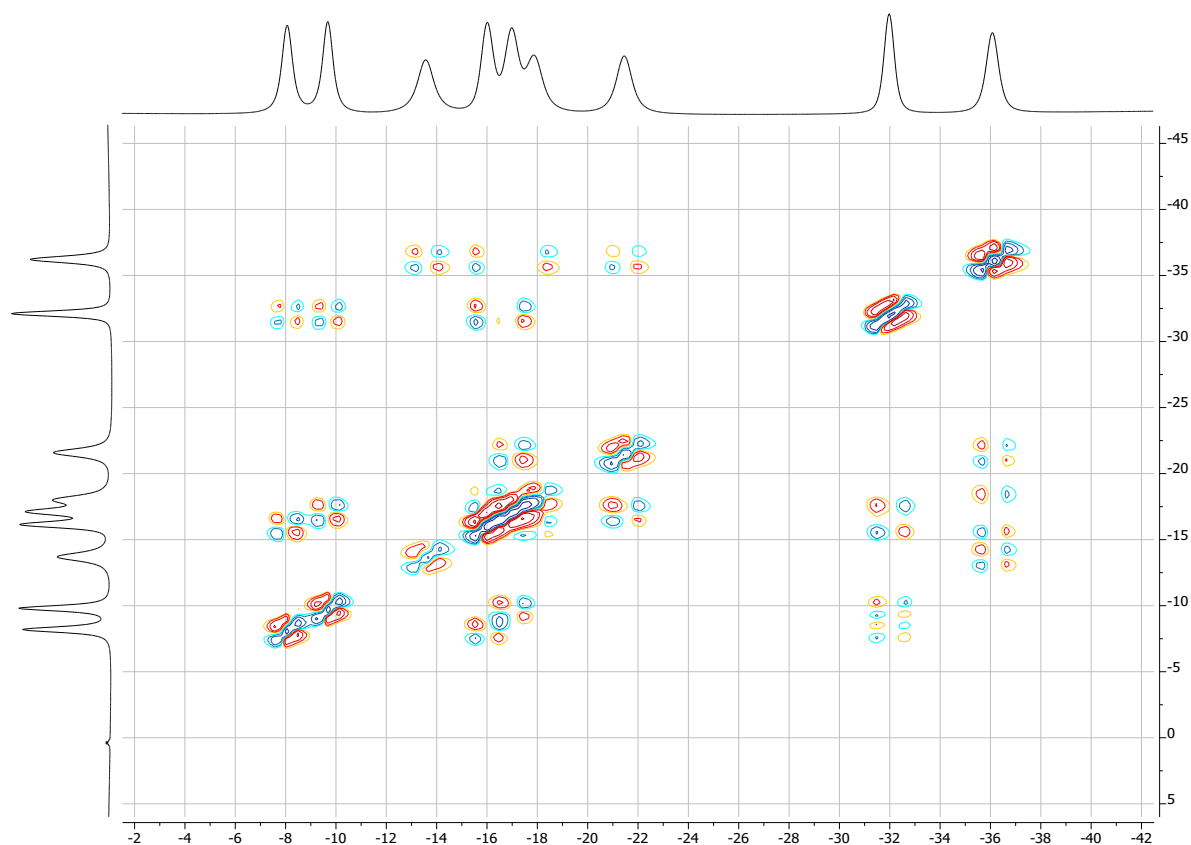


Figure S20. (BB) DQCOSY NMR spectrum of Cs[3] in acetone-d₆

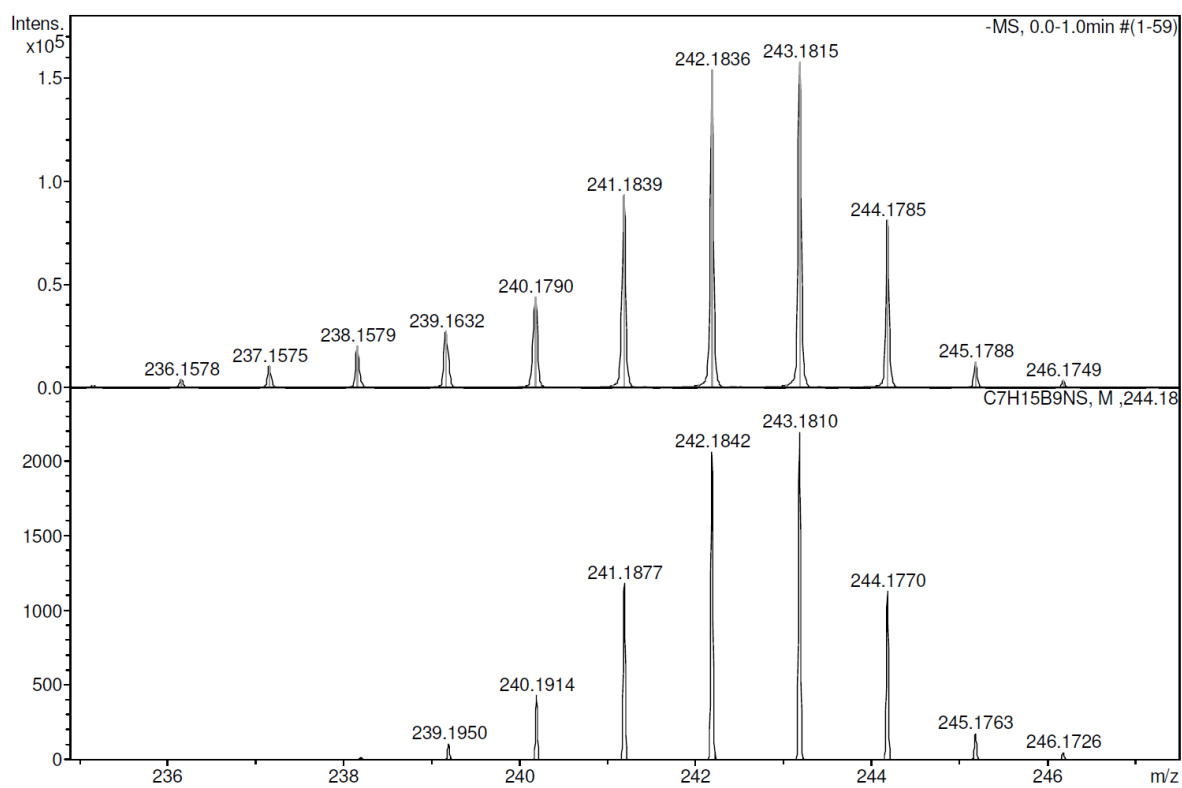


Figure S21. HRMS spectrum of Cs[3]

Spectral data for 1-(NC₅H₄-2'-CH₂S)-1,2-C₂B₁₀H₁₁ (**4**)

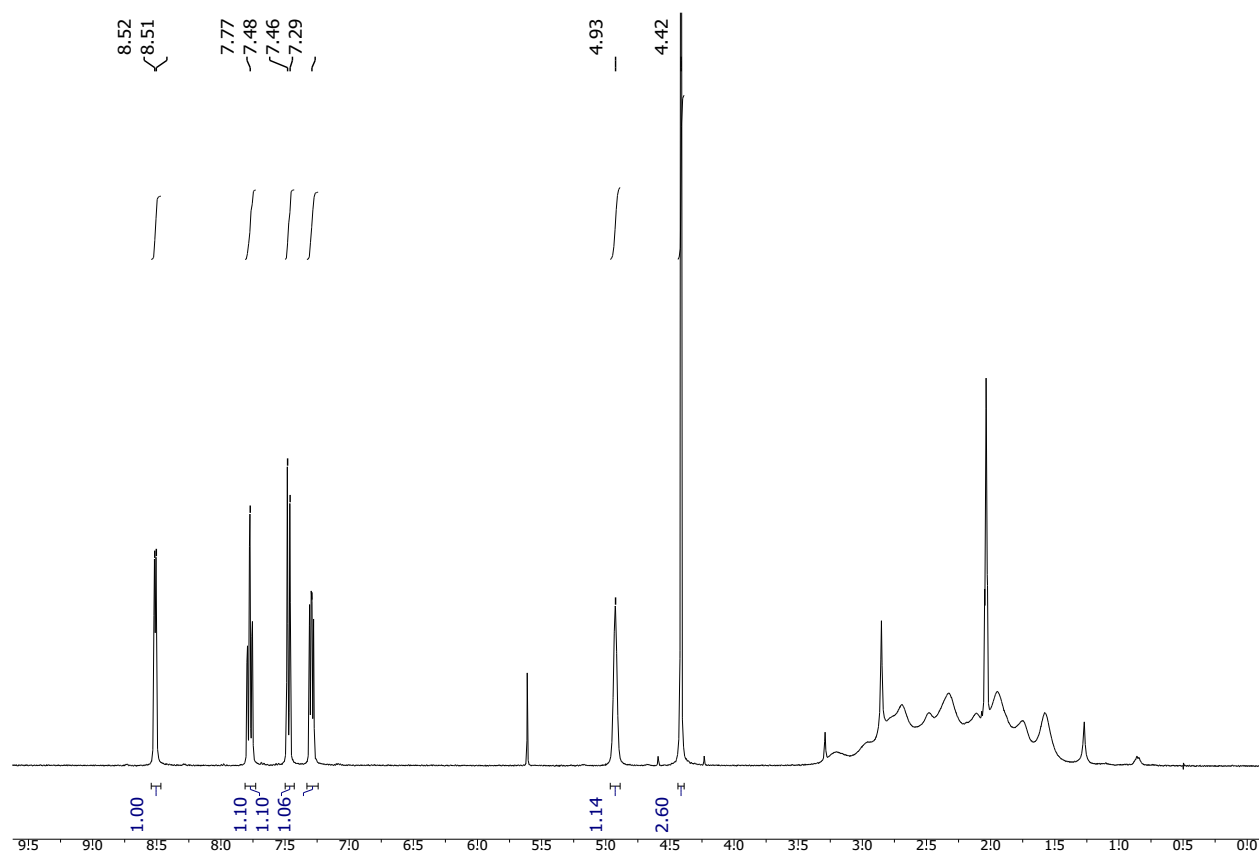


Figure S22. ¹H NMR spectrum of **4** in acetone-d₆

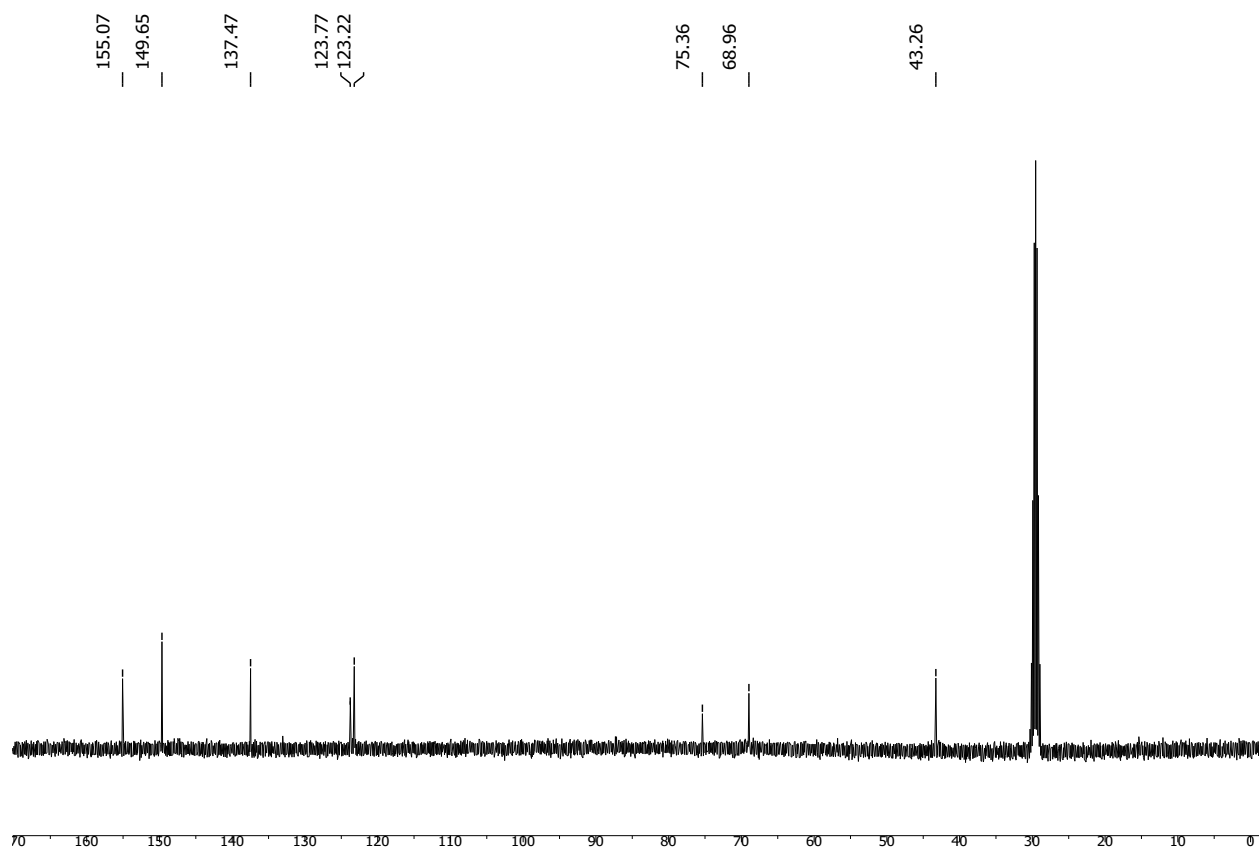


Figure S23. ¹³C NMR spectrum of **4** in acetone-d₆

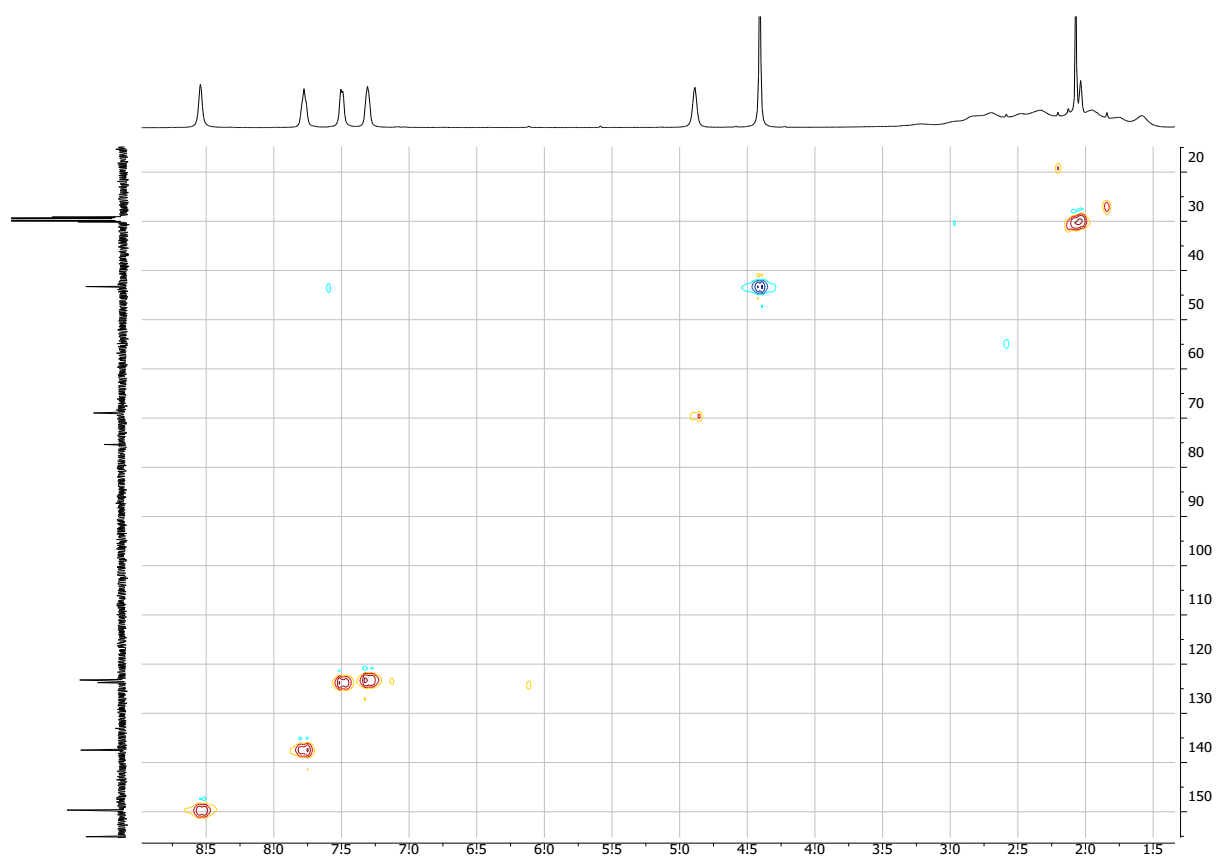


Figure S24. (HC) HSQC NMR spectrum of **4** in acetone- d_6

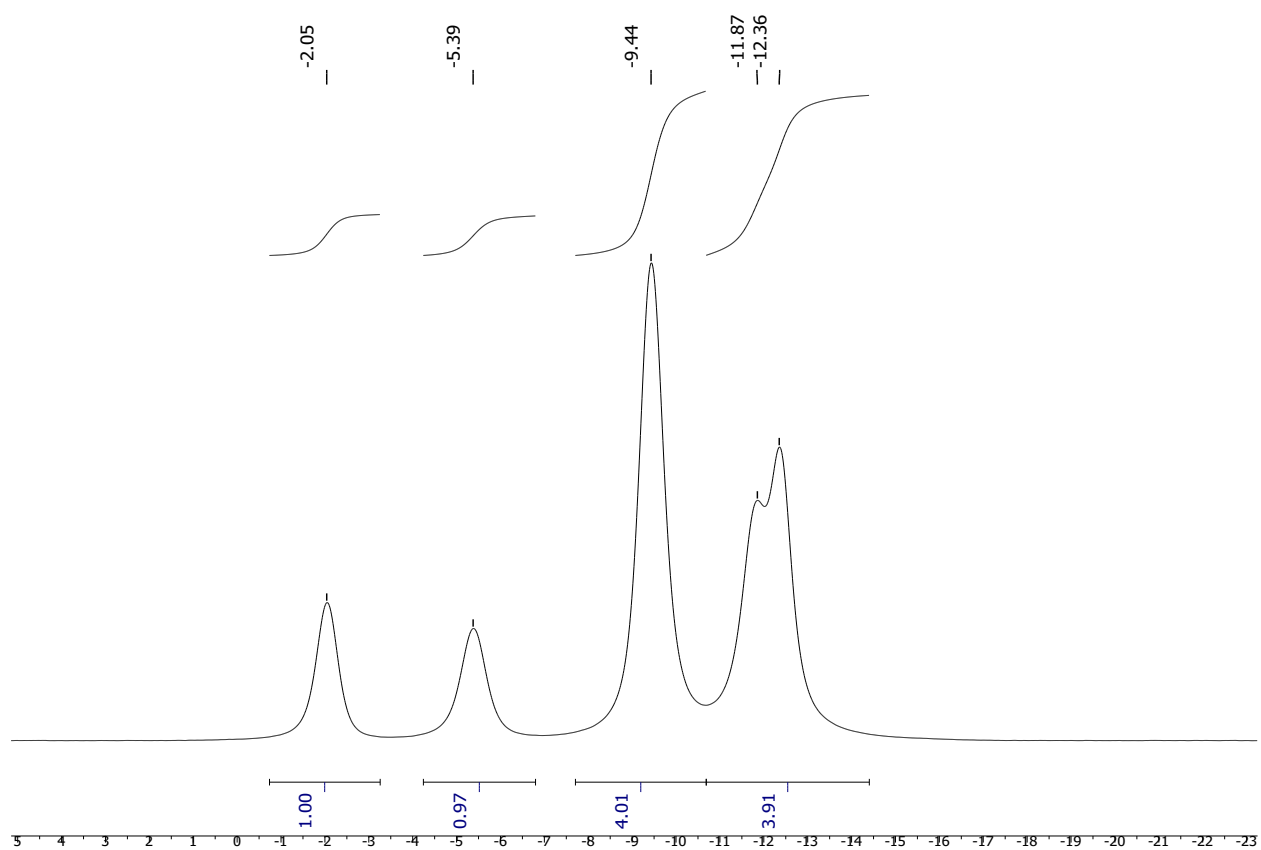


Figure S25. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4** in acetone- d_6

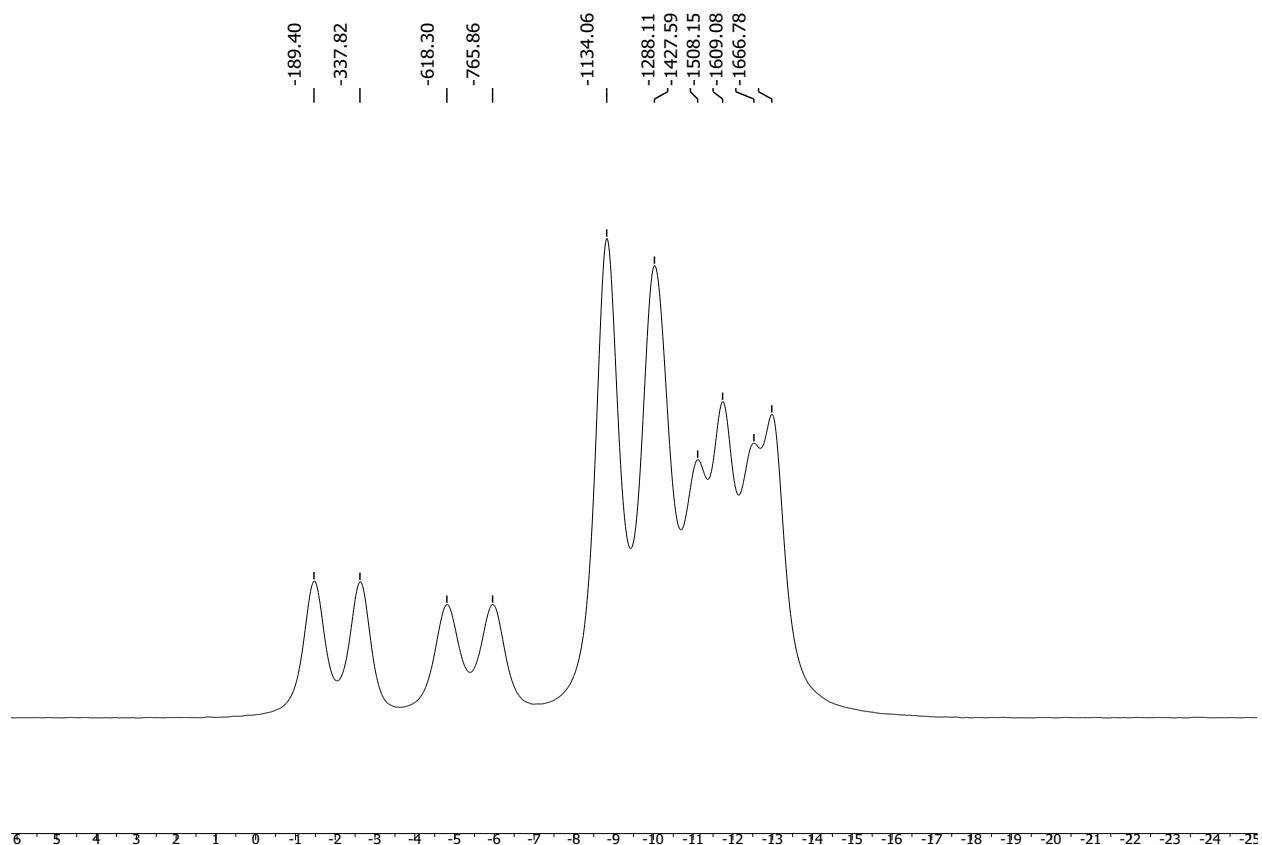


Figure S26. ^{11}B NMR spectrum of **4** in acetone- d_6

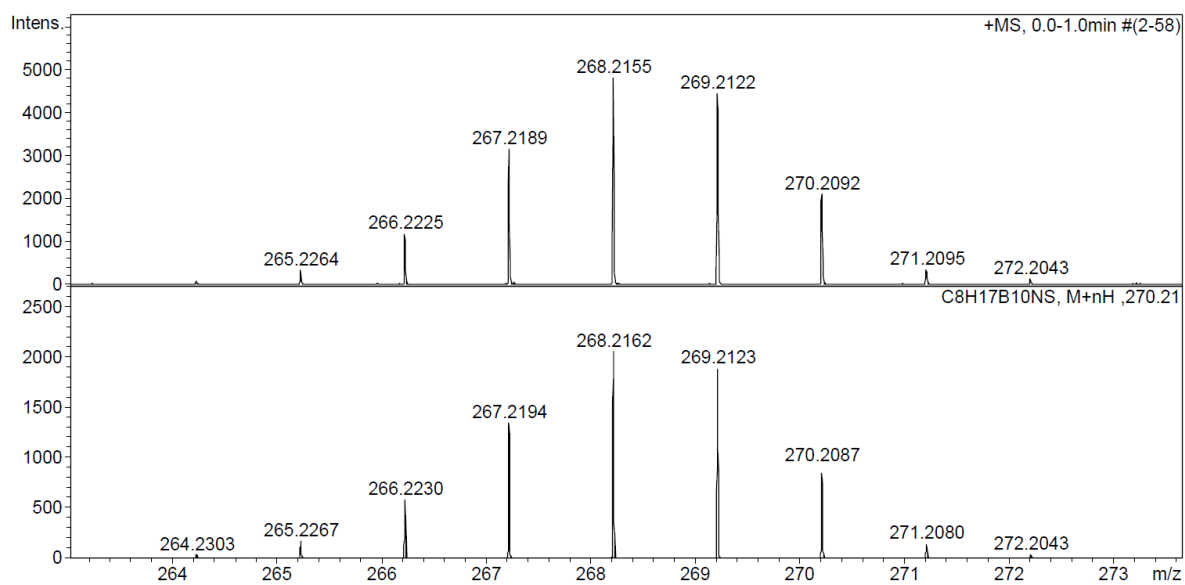


Figure S27. HRMS spectrum of **4**

Spectral data for Cs[7-(NC₅H₄-2'-CH₂S)-7,8-C₂B₉H₁₁] (**5**)

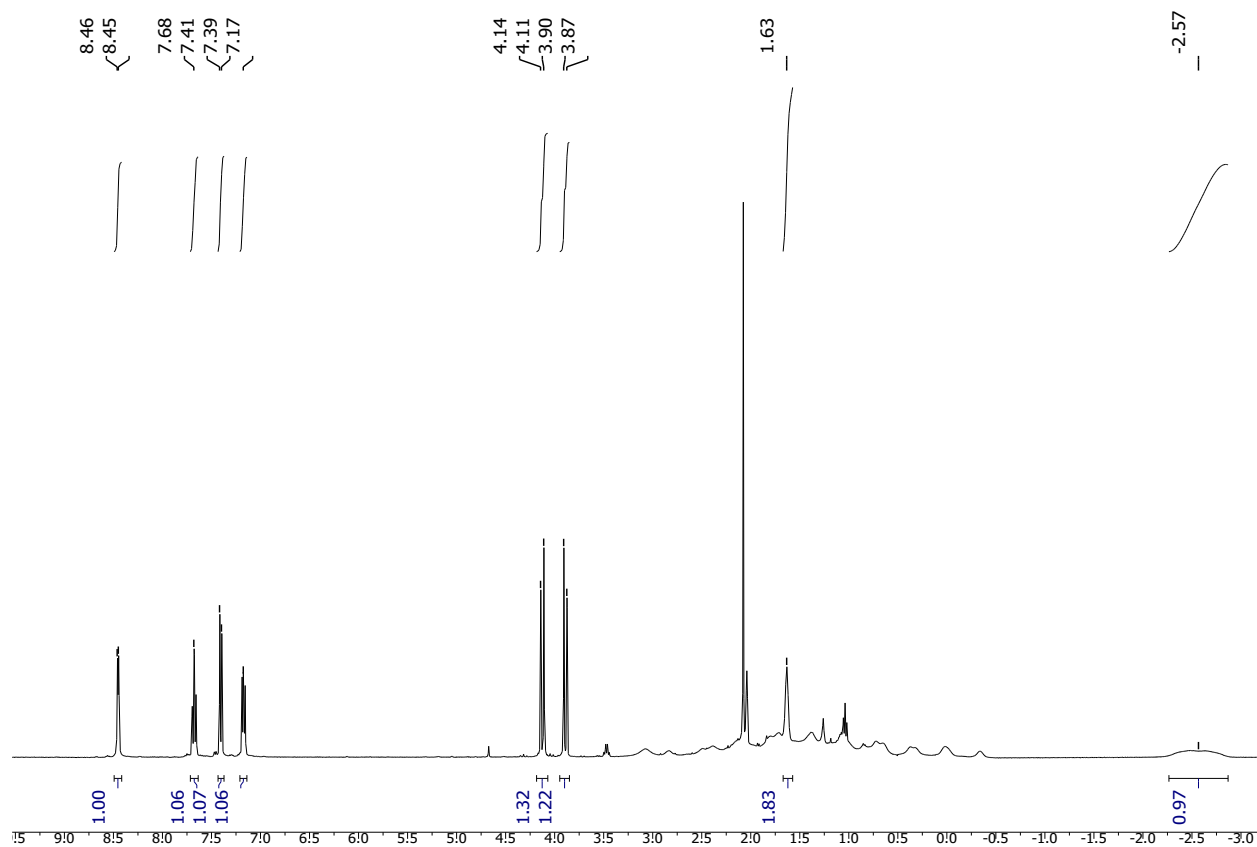


Figure S28. ¹H NMR spectrum of **5** in acetone-d₆

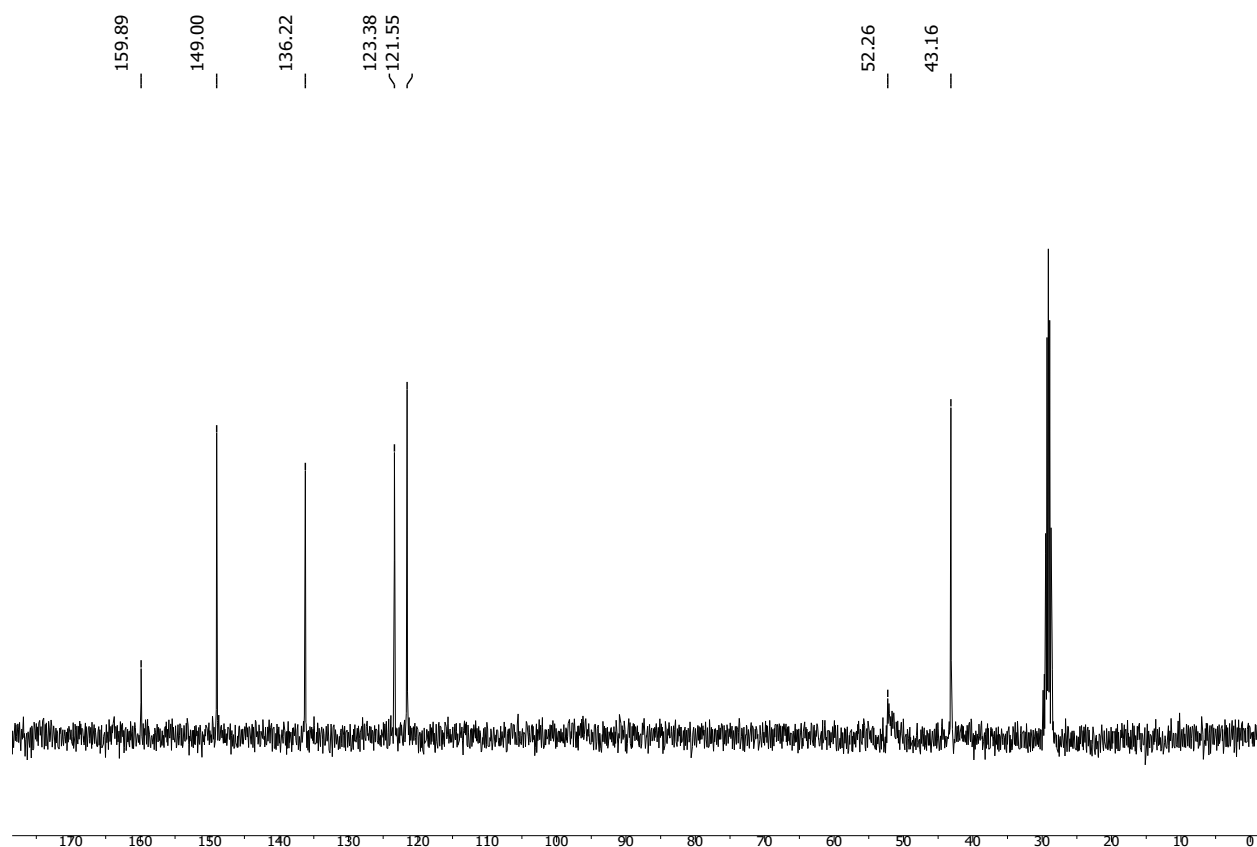


Figure S29. ¹³C NMR spectrum of **5** in acetone-d₆

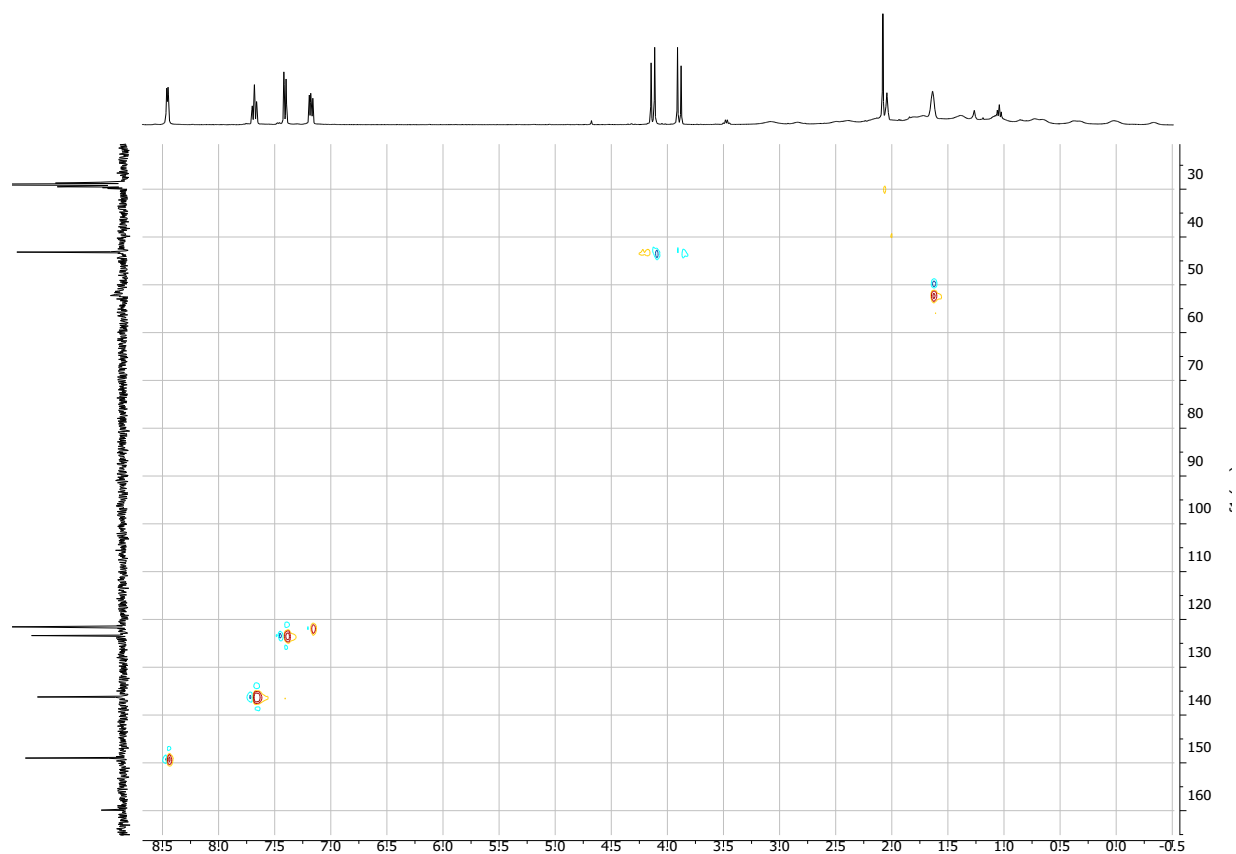


Figure S30. (HC) HSQC NMR spectrum of **5** in acetone- d_6

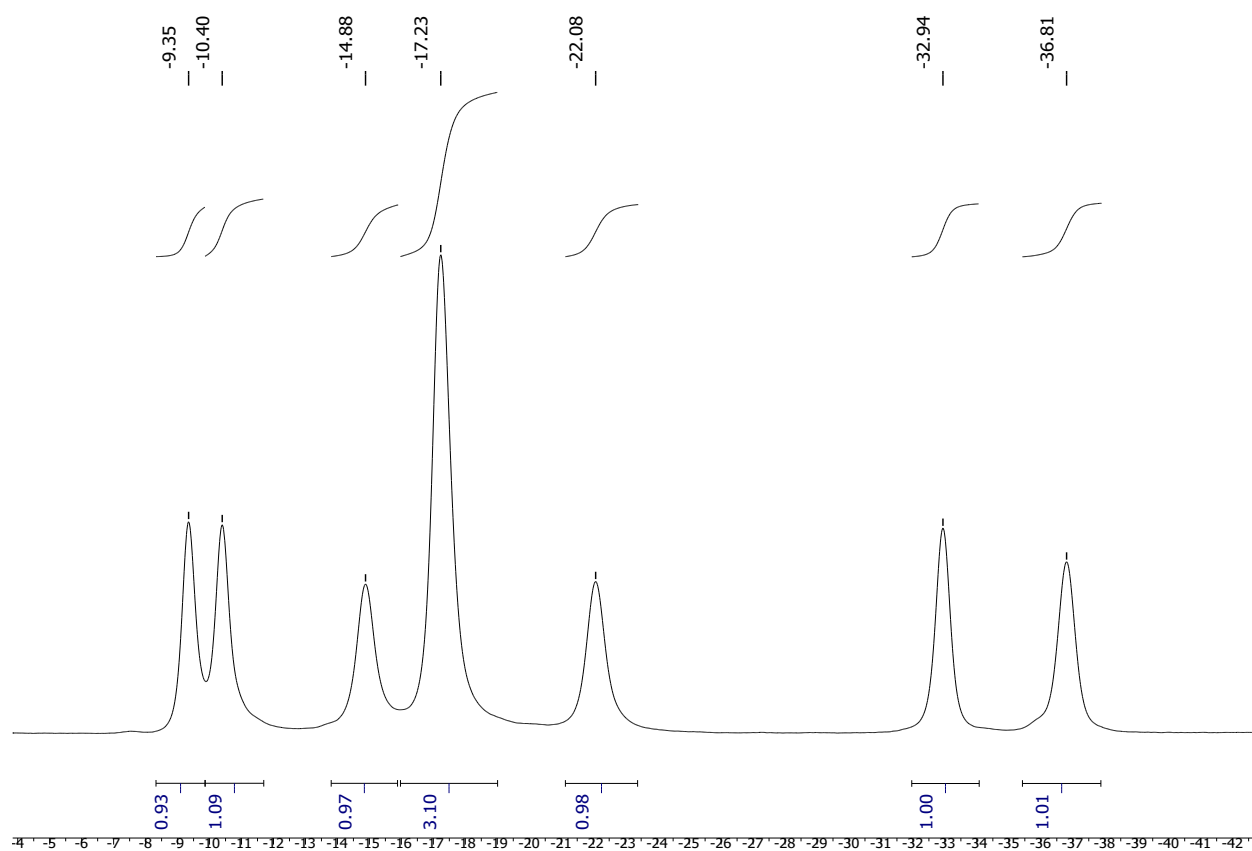


Figure S31. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **5** in acetone- d_6

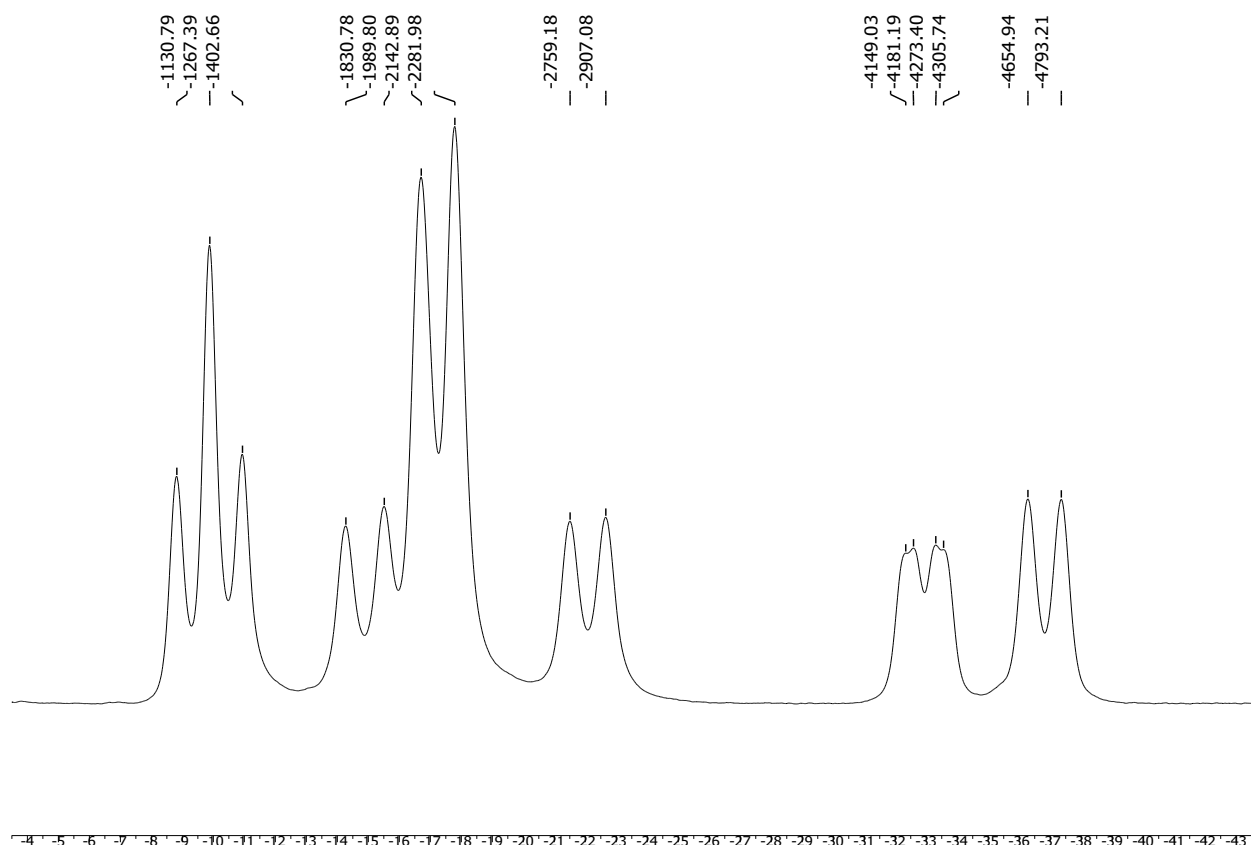


Figure S32. ^{11}B NMR spectrum of **5** in acetone- d_6

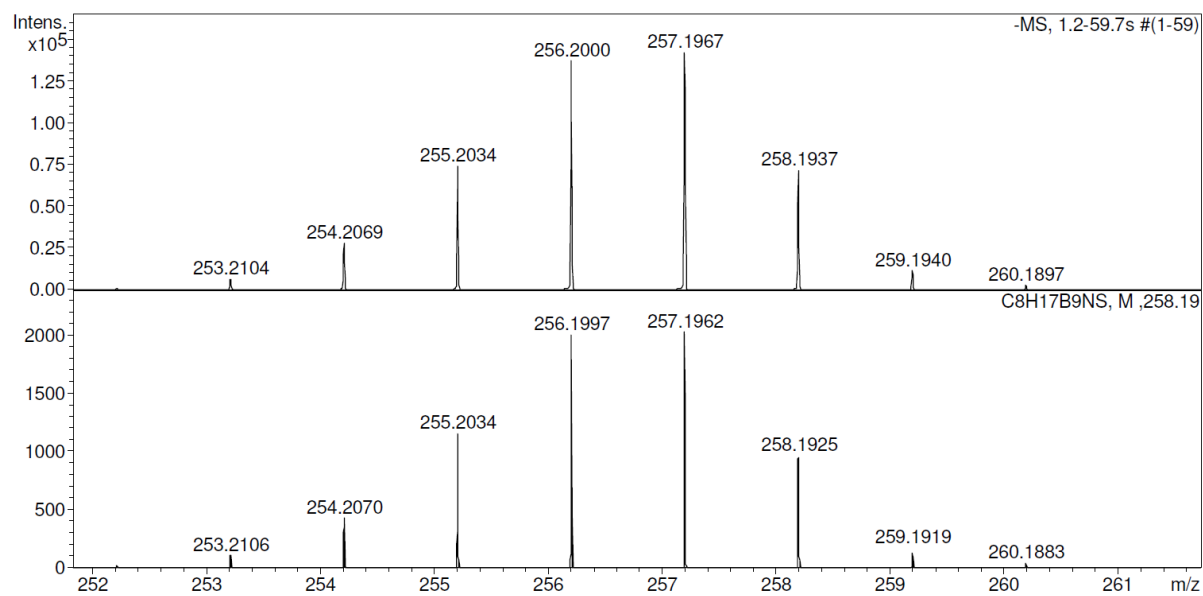


Figure S33. HRMS spectrum of **5**

Spectral data for 3-Ph₃P-3-(4(7)-NC₅H₄-2'-S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**6**)

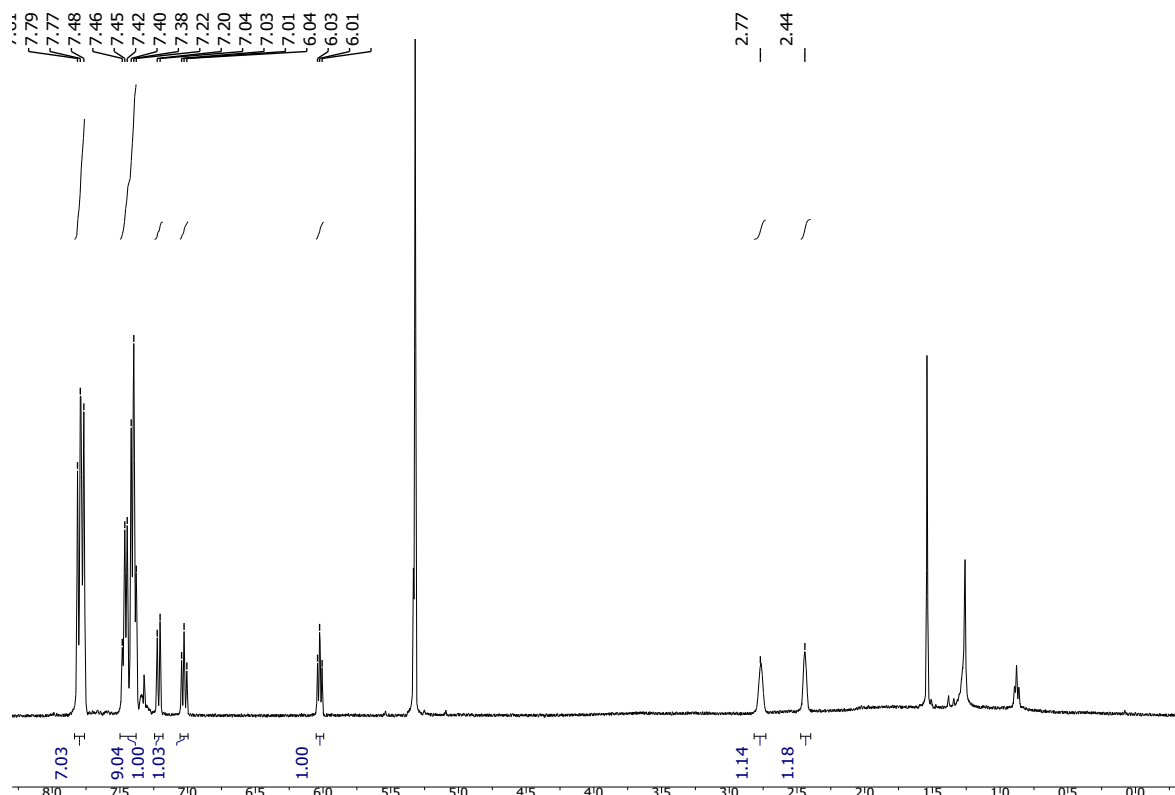


Figure S34. ¹H NMR spectrum of **6** in CD₂Cl₂

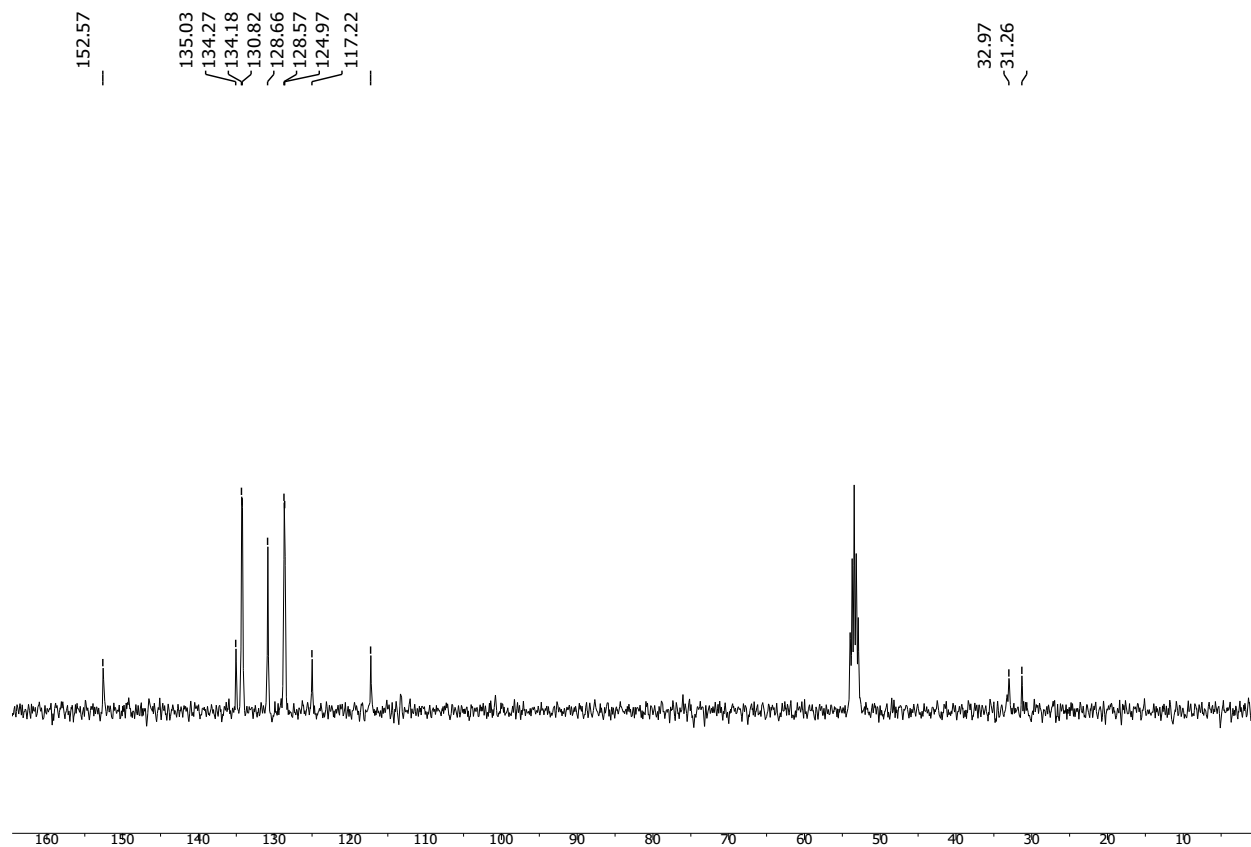


Figure S35. ¹³C NMR spectrum of **6** in CD₂Cl₂

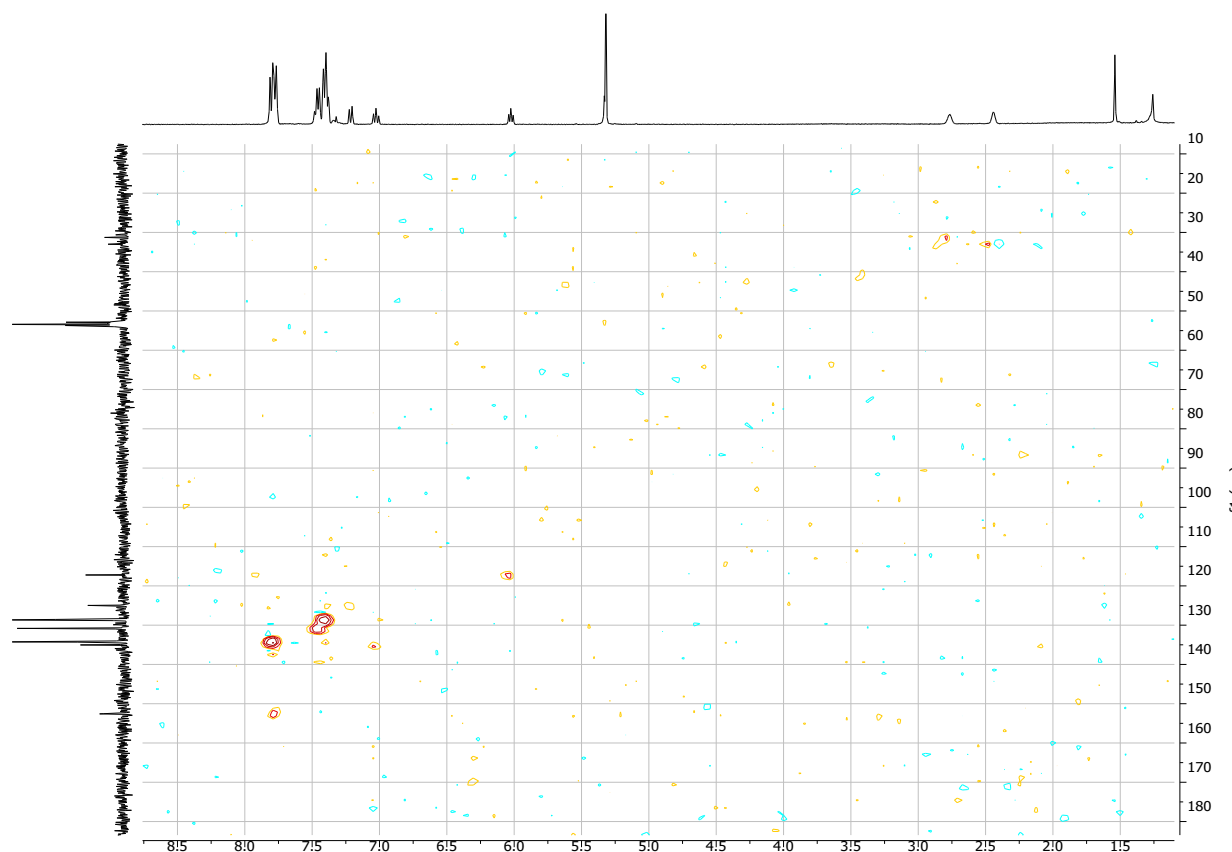


Figure S36. (HC) HSQC NMR spectrum of **6** in CD_2Cl_2

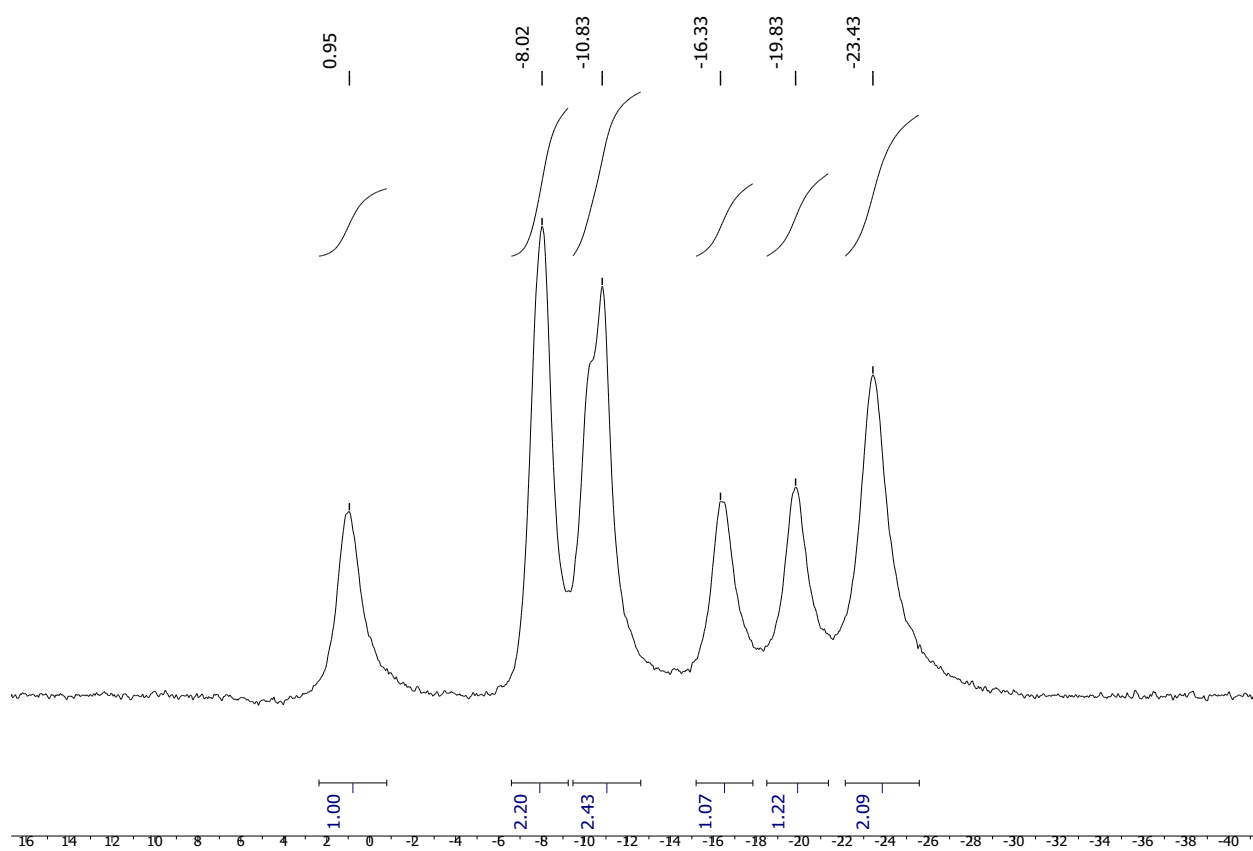


Figure S37. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **6** in CD_2Cl_2

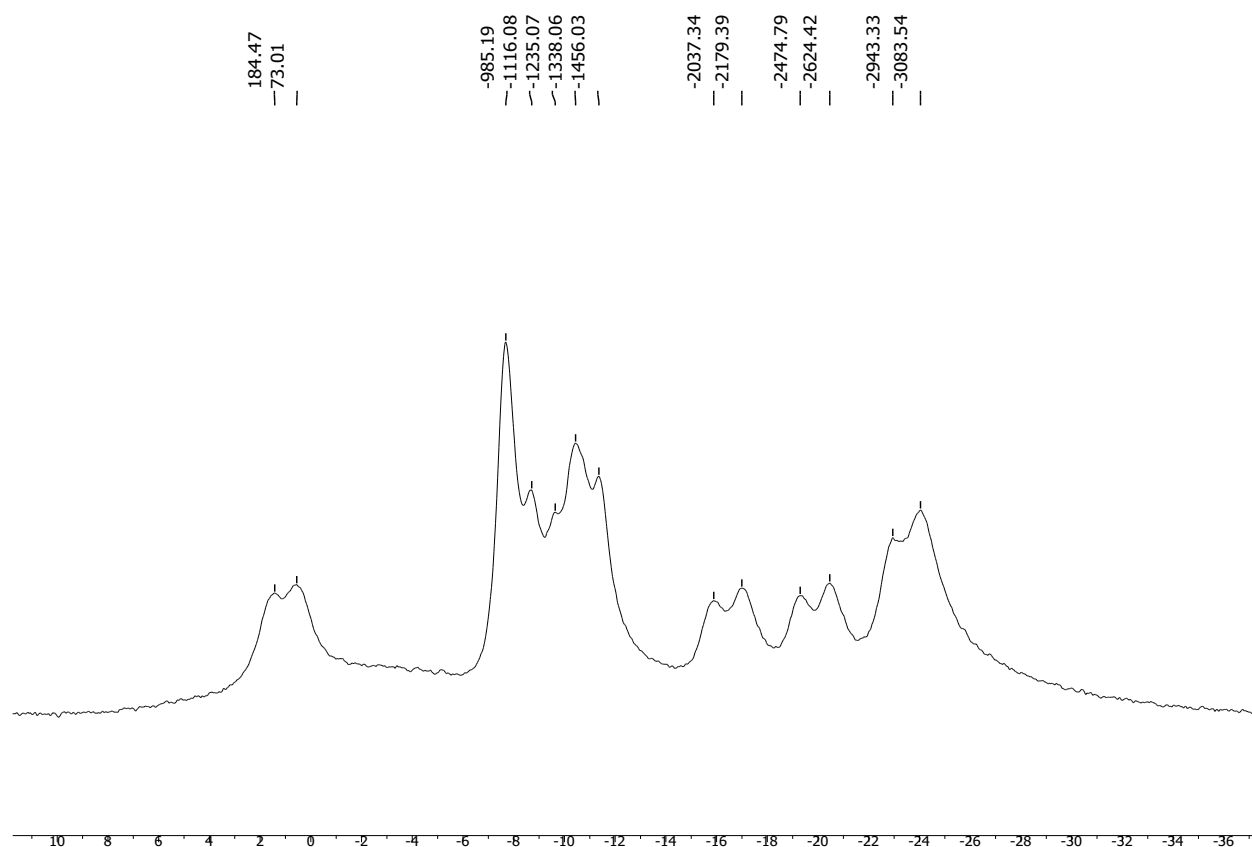


Figure S38. ^{11}B NMR spectrum of **6** in CD_2Cl_2

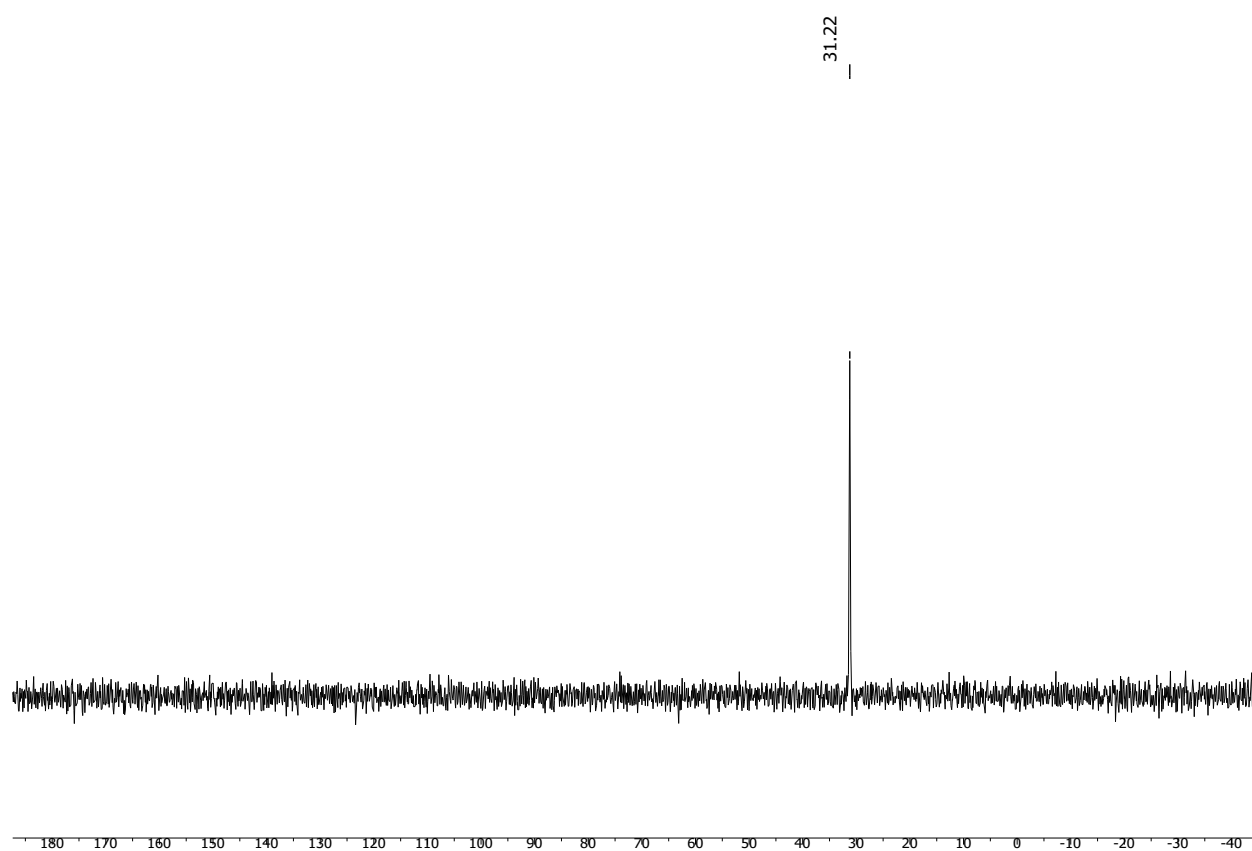


Figure S39. ^{31}P NMR spectrum of **6** in CD_2Cl_2

Spectral data for 3-Ph₃P-3-(4(7)-NC₅H₄-2'-S)-*closo*-3,1,2-PdC₂B₉H₁₀ (**7**)

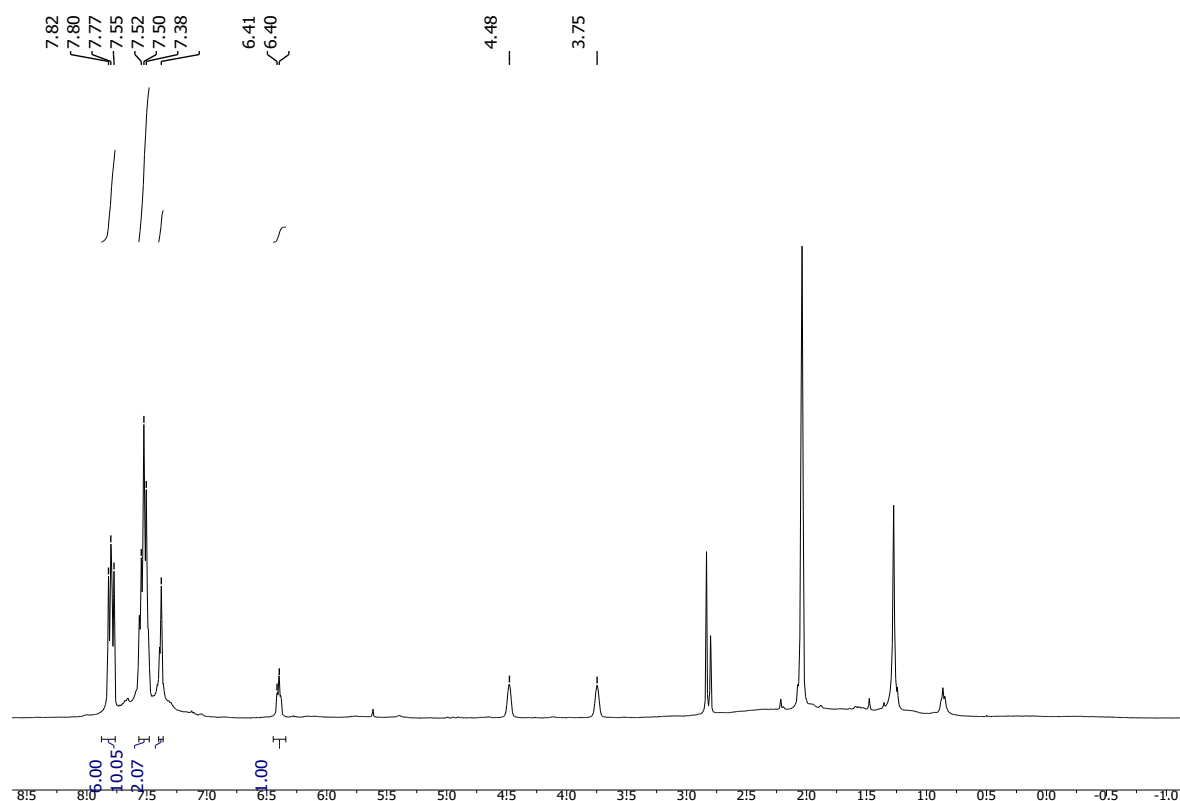


Figure S40. ¹H NMR spectrum of **7** in acetone-d₆

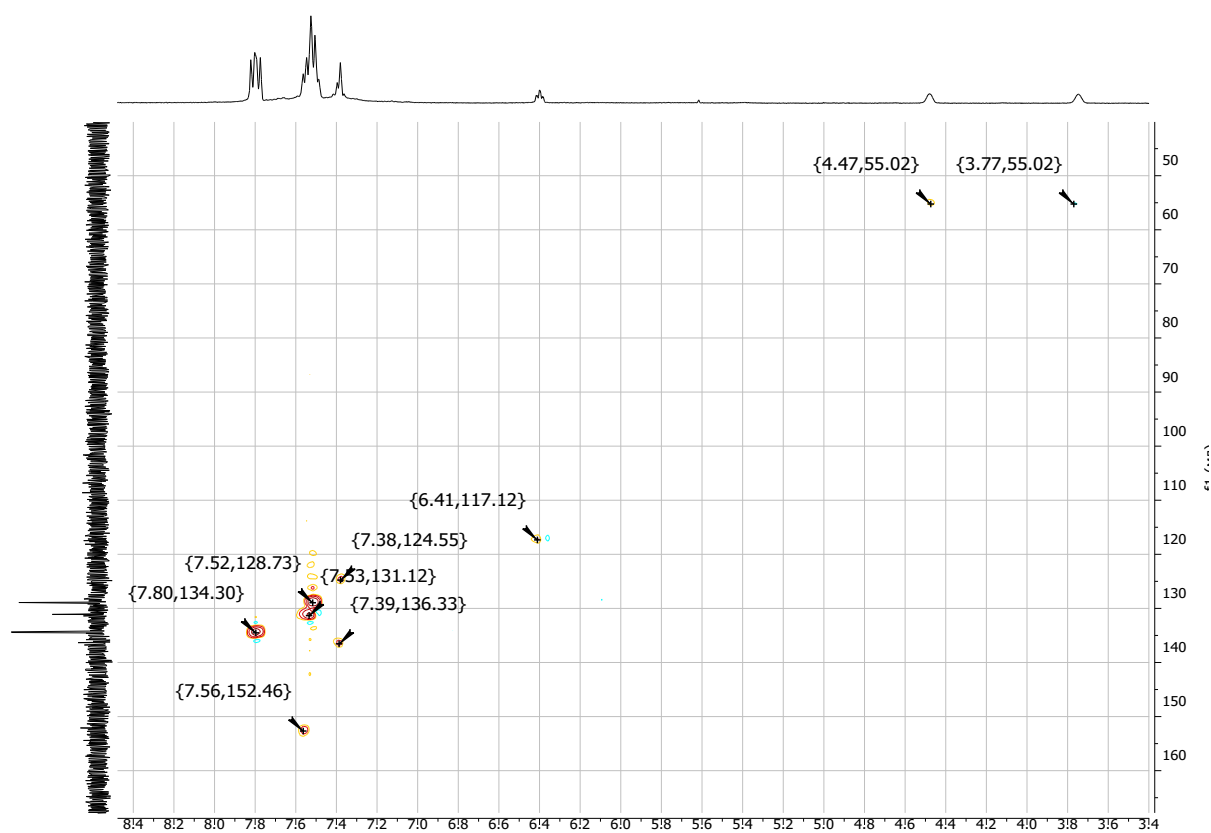


Figure S41. (H)C HSQC NMR spectrum of **7** in acetone-d₆

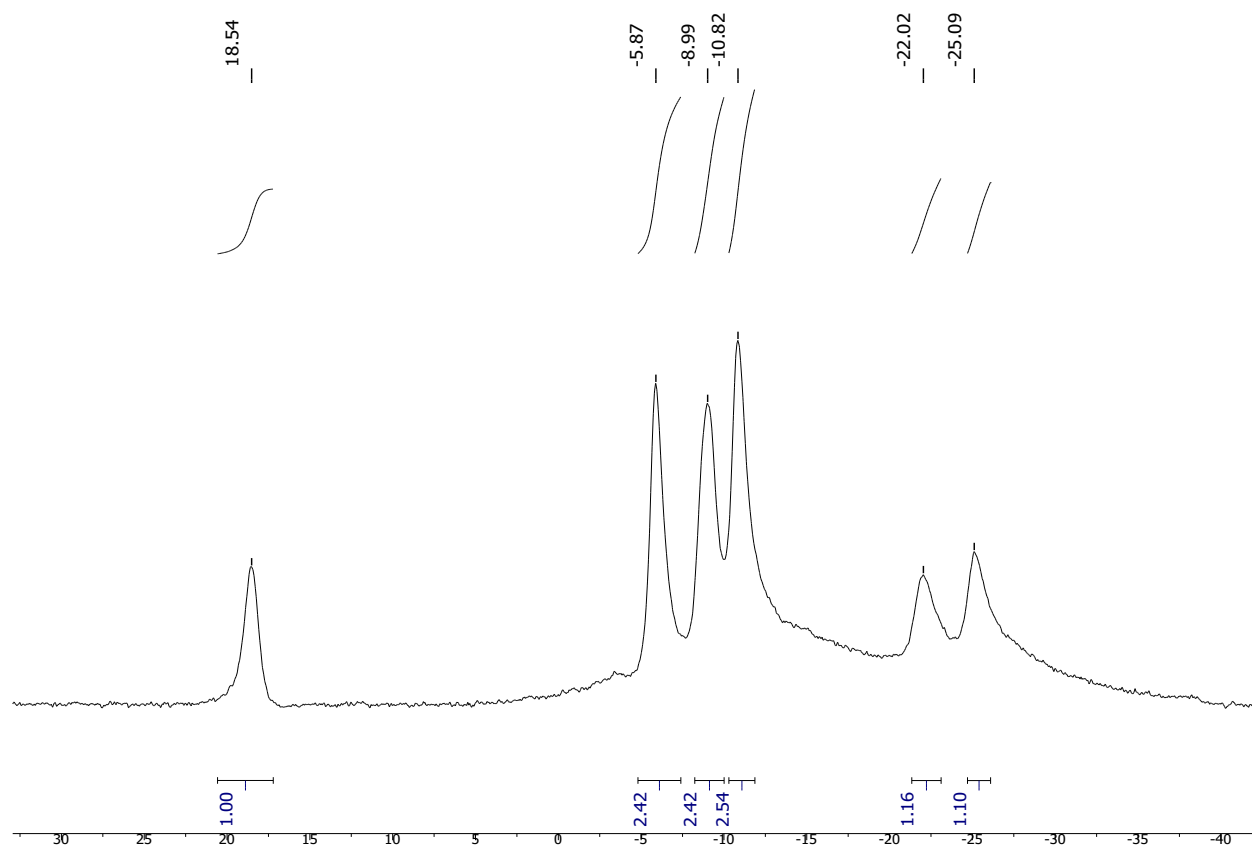


Figure S42. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **7** in acetone- d_6

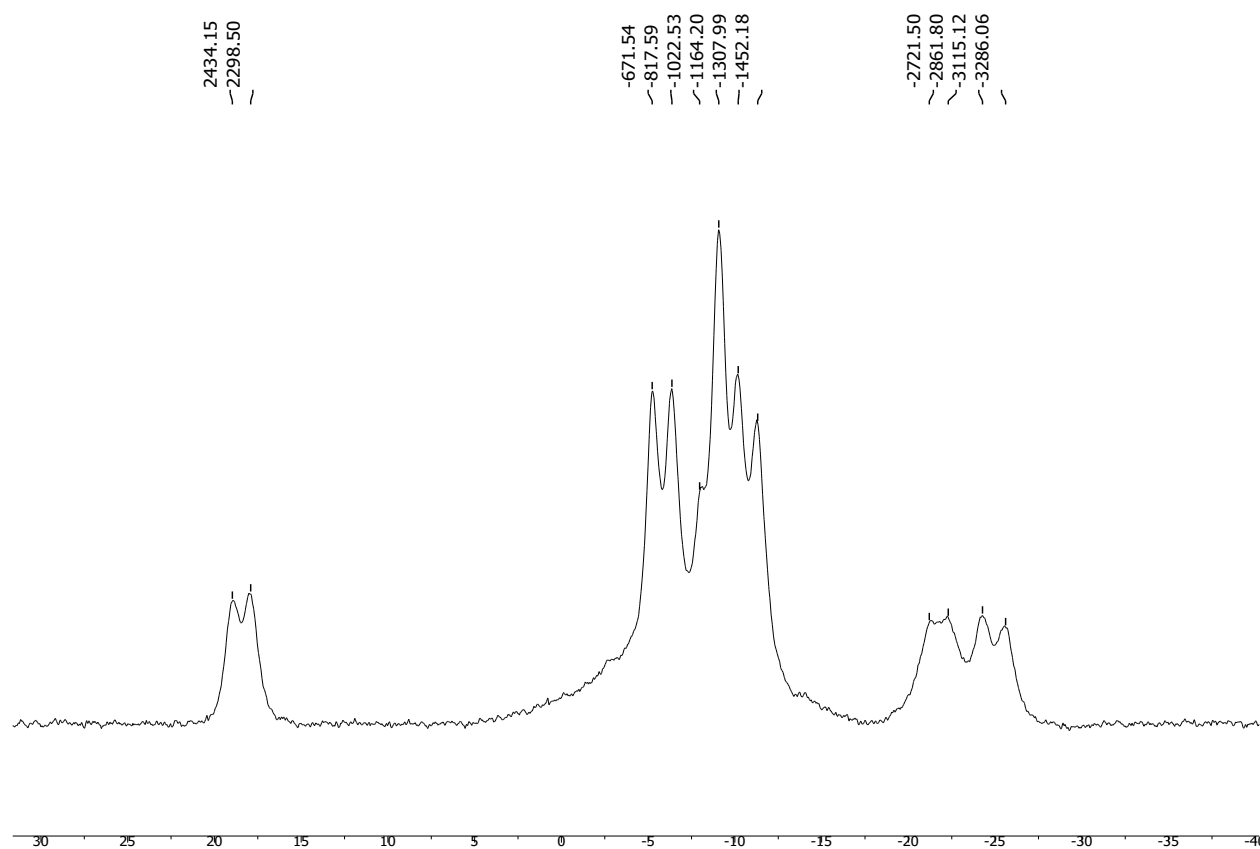


Figure S43. ^{11}B NMR spectrum of **7** in acetone- d_6

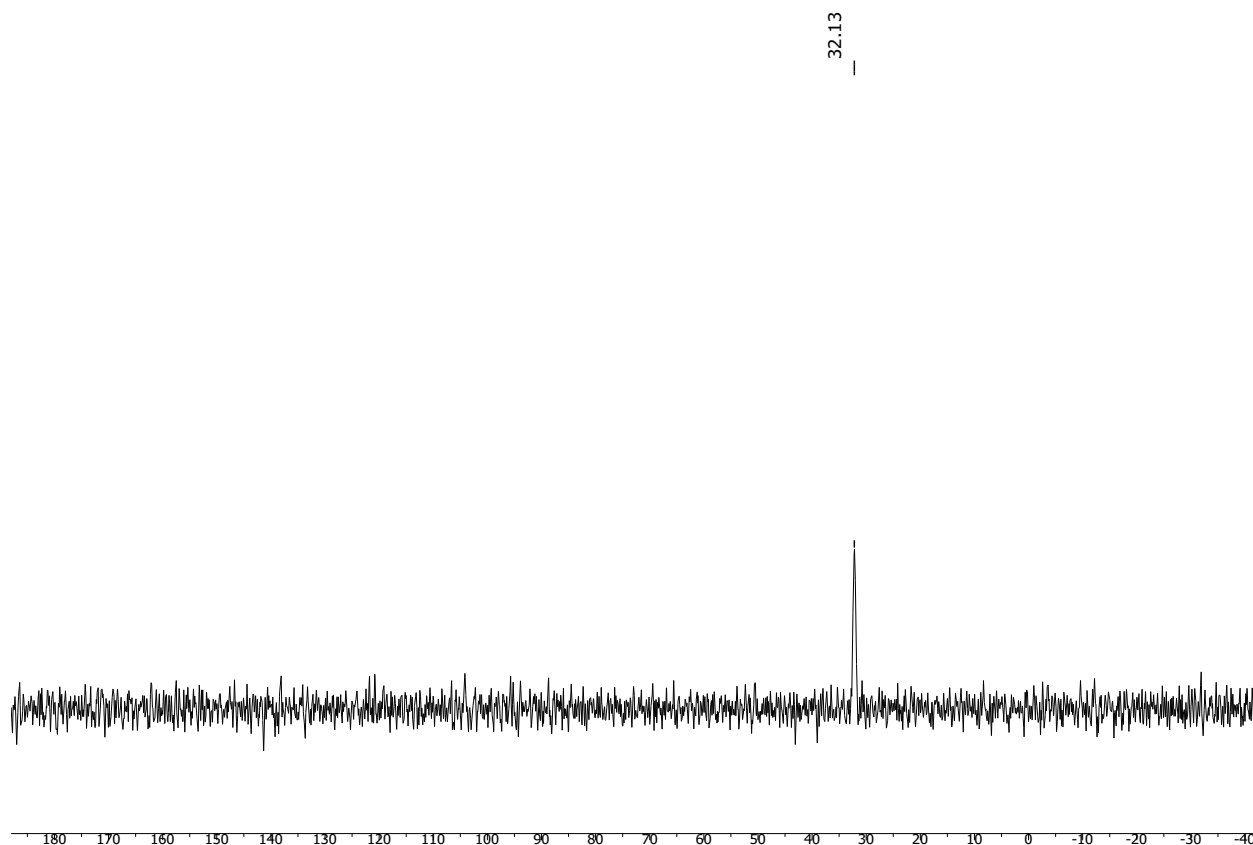


Figure S44. ^{31}P NMR spectrum of **7** in acetone- d_6

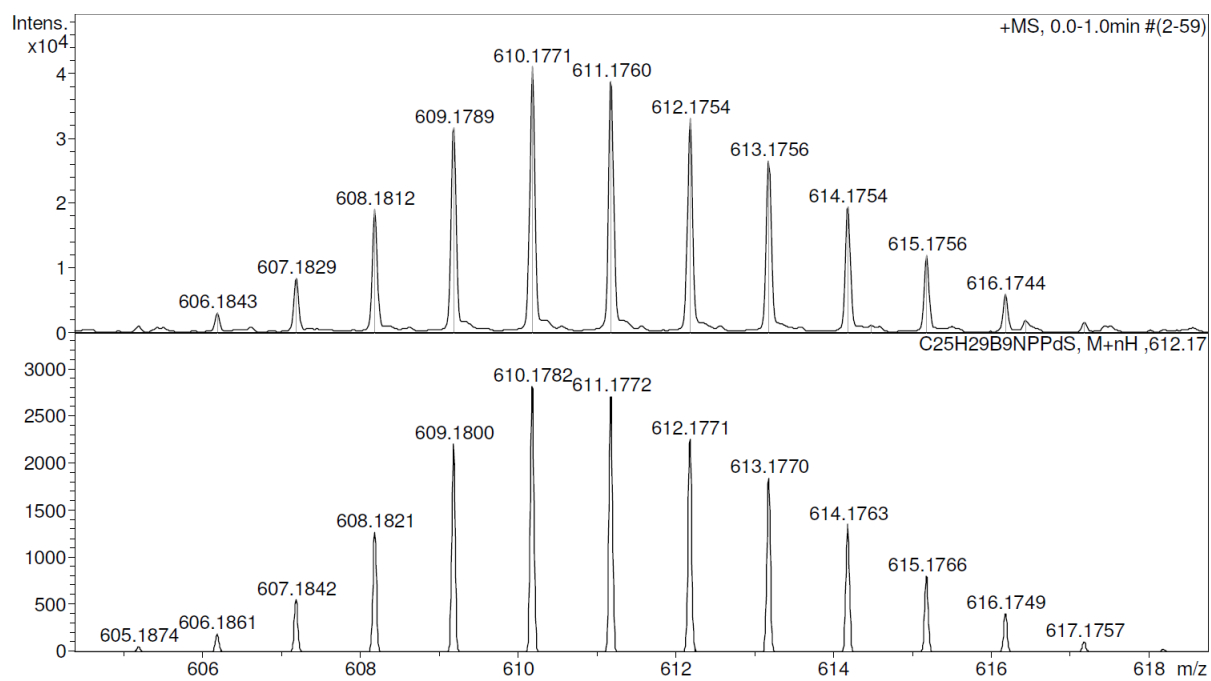


Figure S45. HRMS spectrum of **7**

Spectral data for 3-Ph₃P-3-(1(2)-NC₅H₄-2'-S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**8**)

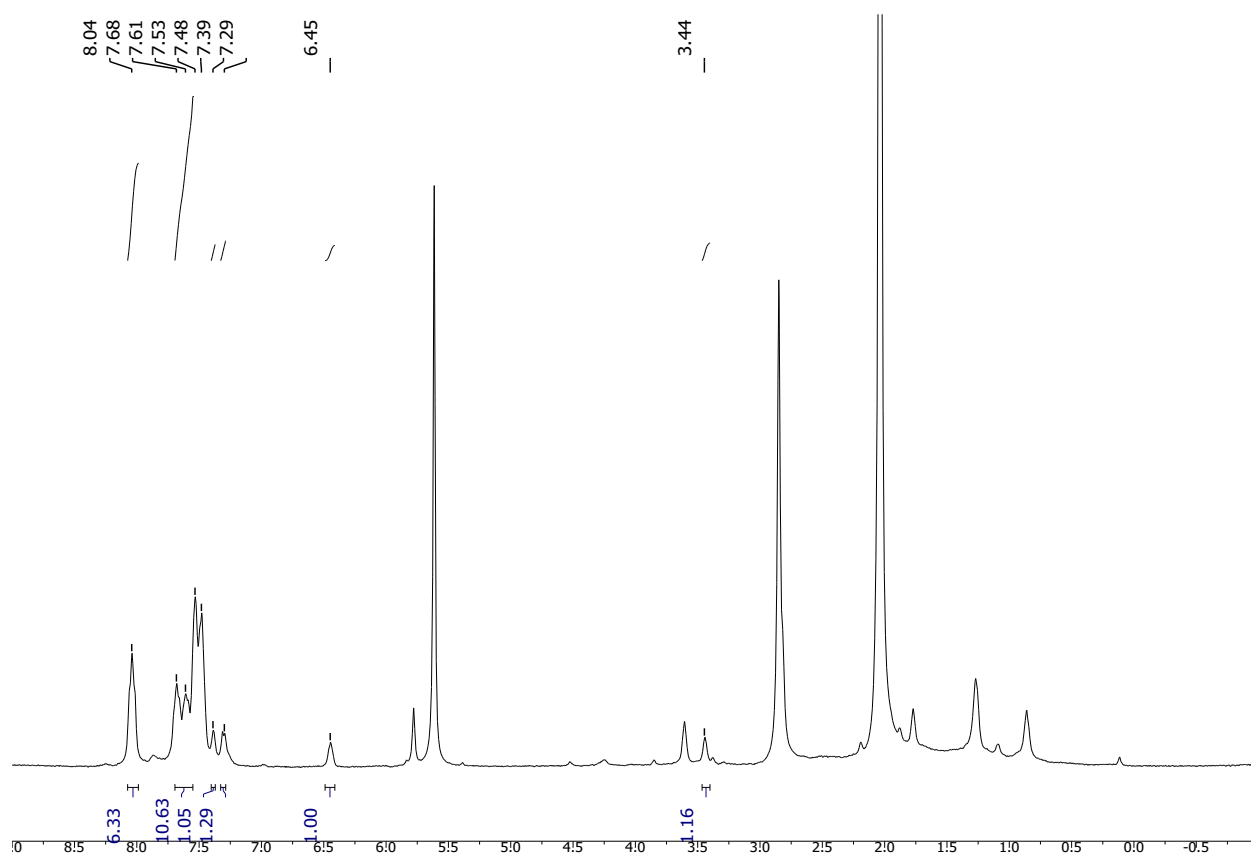


Figure S46. ¹H NMR spectrum of **8** in acetone-d₆

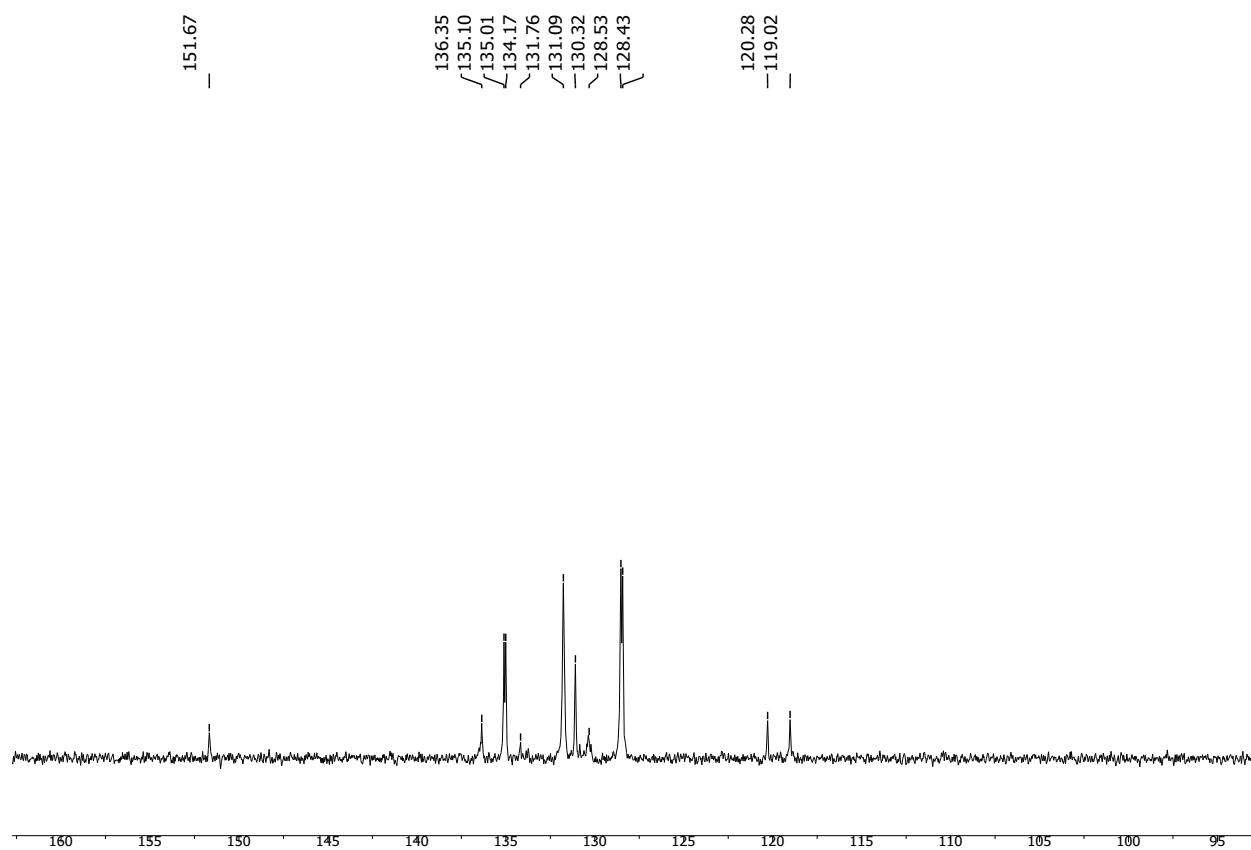


Figure S47. ¹³C NMR spectrum of **8** in acetone-d₆

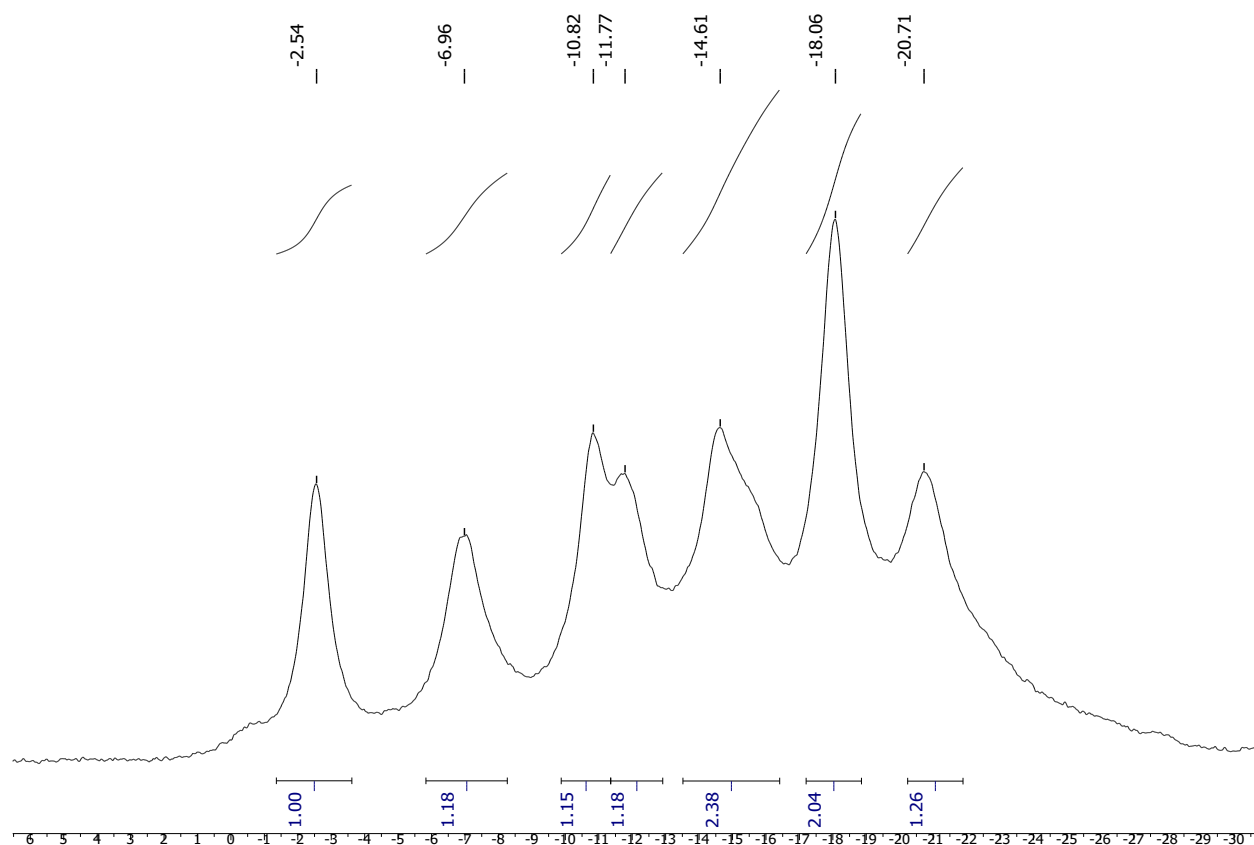


Figure S48. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **8** in acetone- d_6

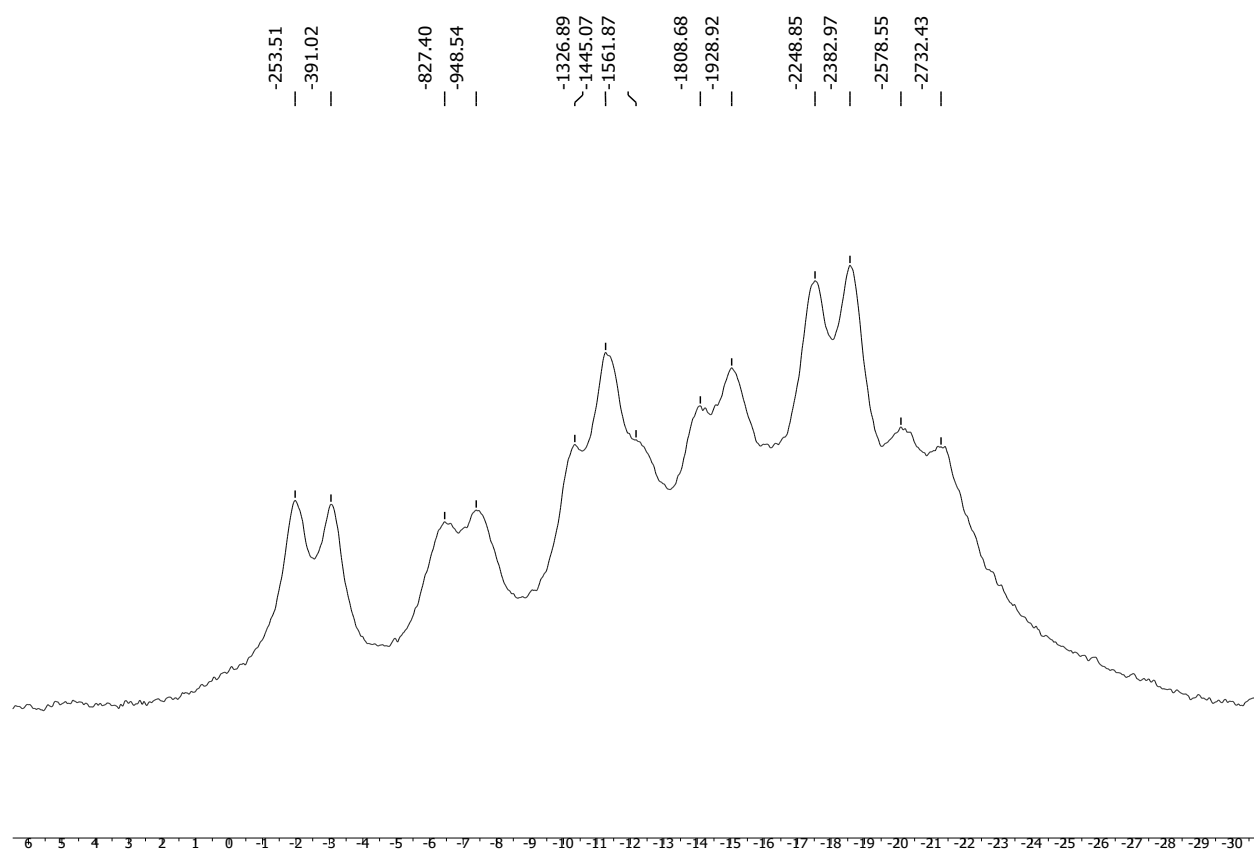


Figure S49. ^{11}B NMR spectrum of **8** in acetone- d_6

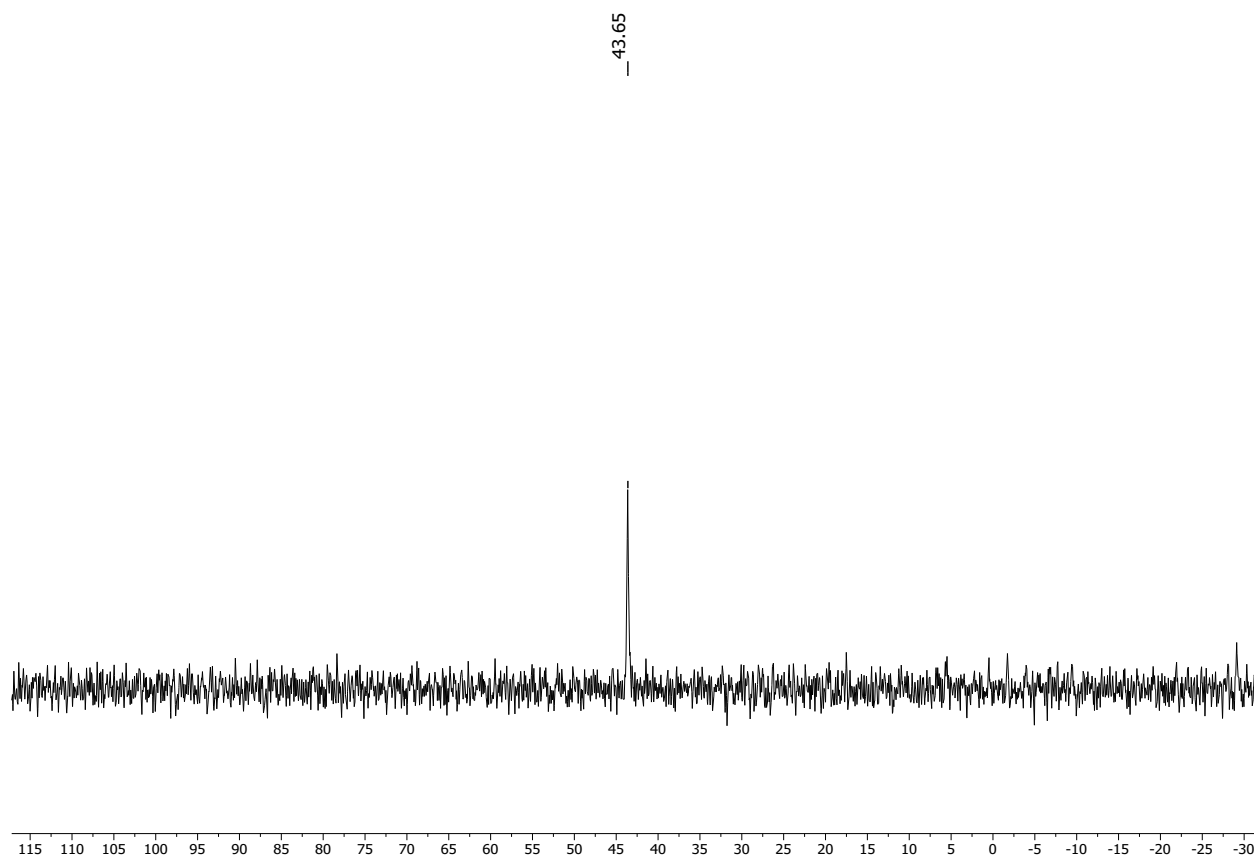


Figure S50. ^{31}P NMR spectrum of **8** in acetone- d_6

Spectral data for 3-Ph₃P-3-(1(2)-NC₅H₄-2'-S)-*closo*-3,1,2-PdC₂B₉H₁₀ (**9**)

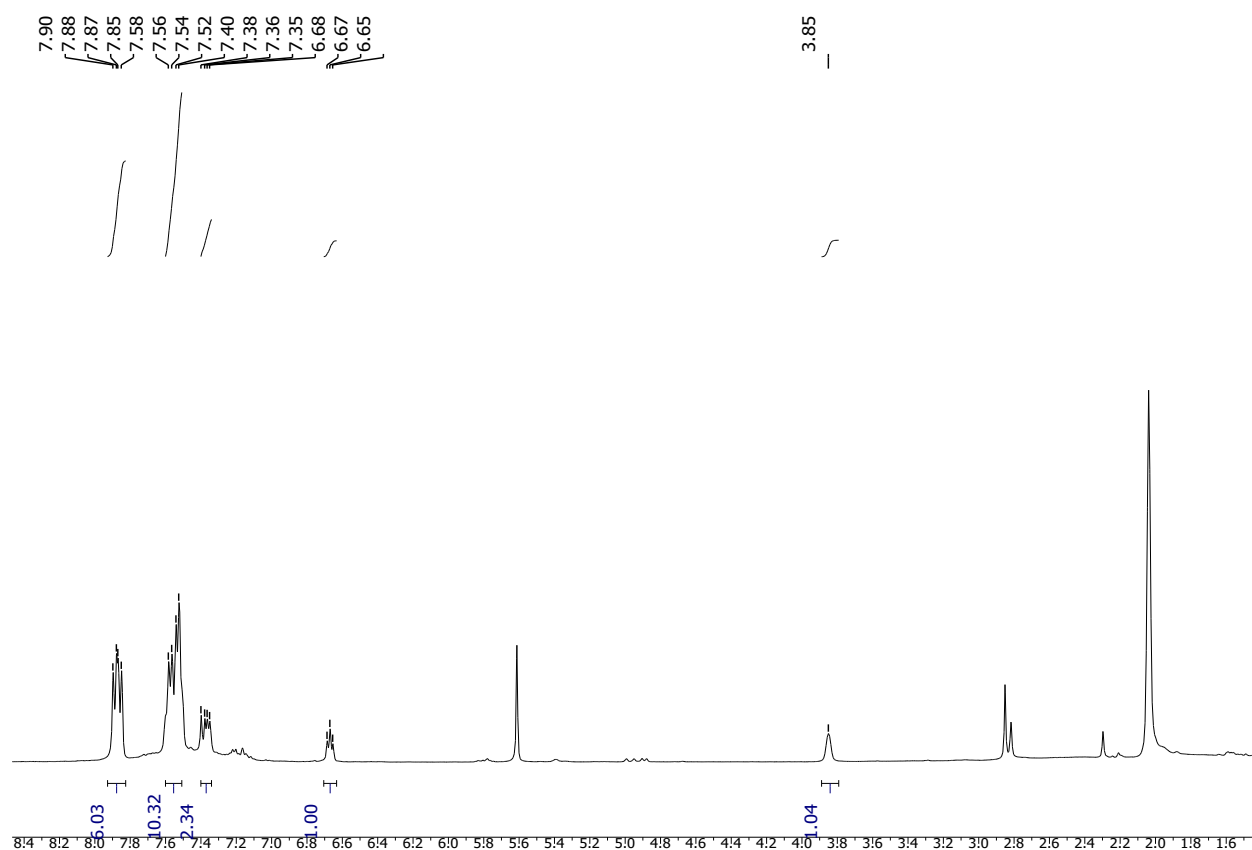


Figure S51. ¹H NMR spectrum of **9** in acetone-d₆

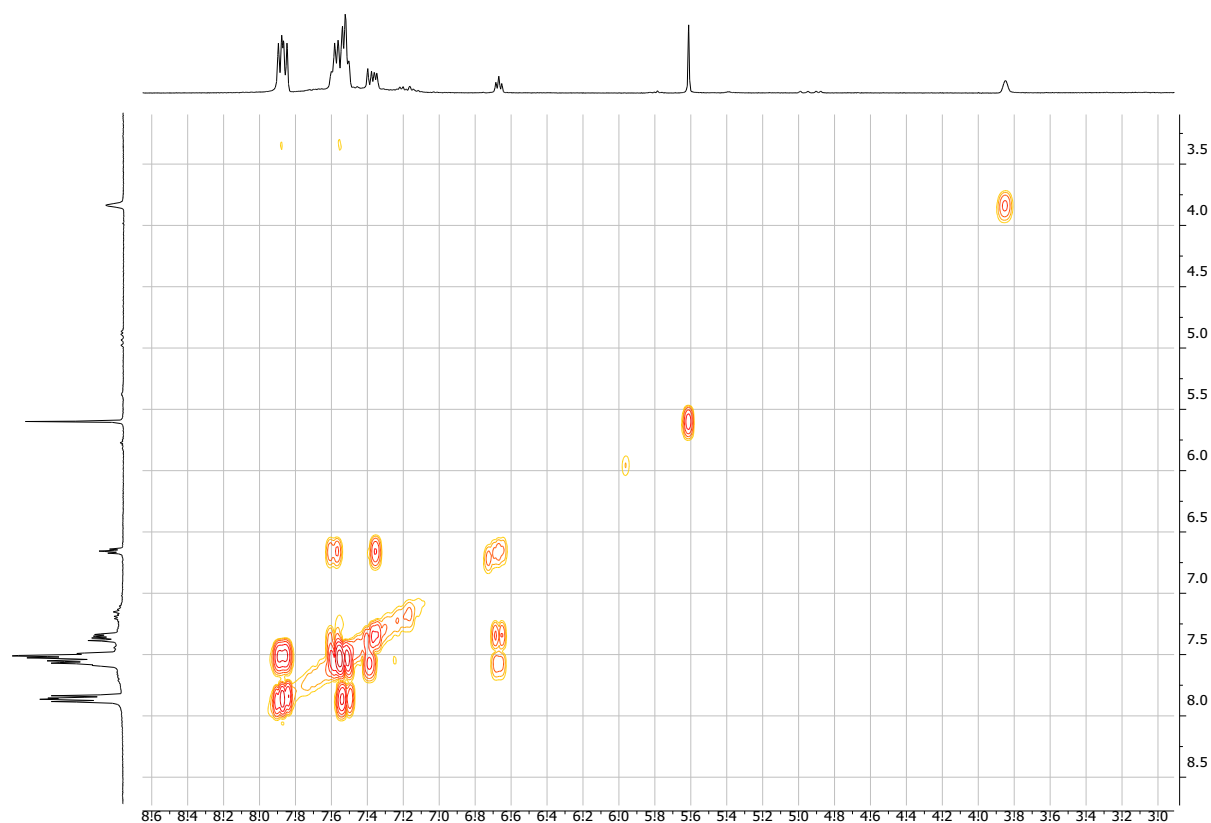


Figure S52. (H,H) COSY NMR spectrum of **9** in acetone-d₆

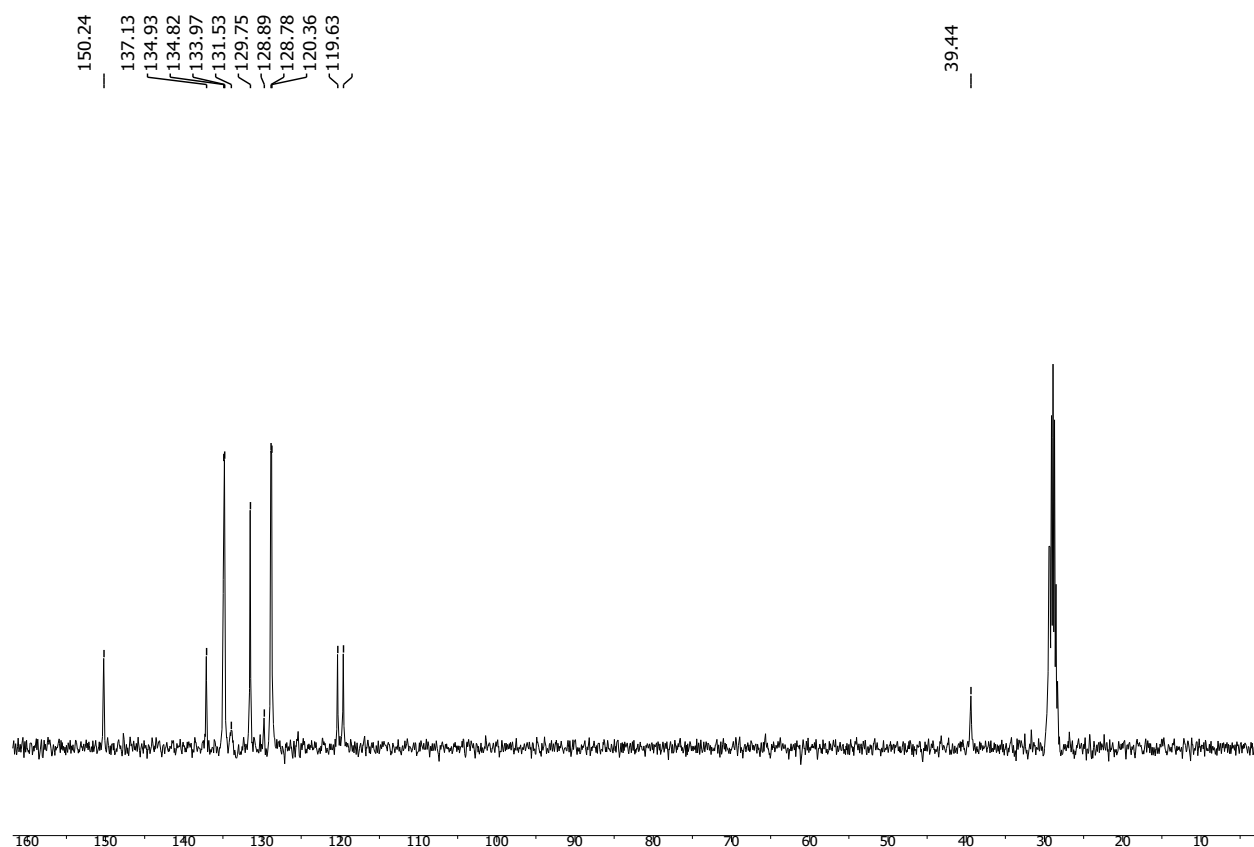


Figure S53. ^{13}C NMR spectrum of **9** in acetone- d_6

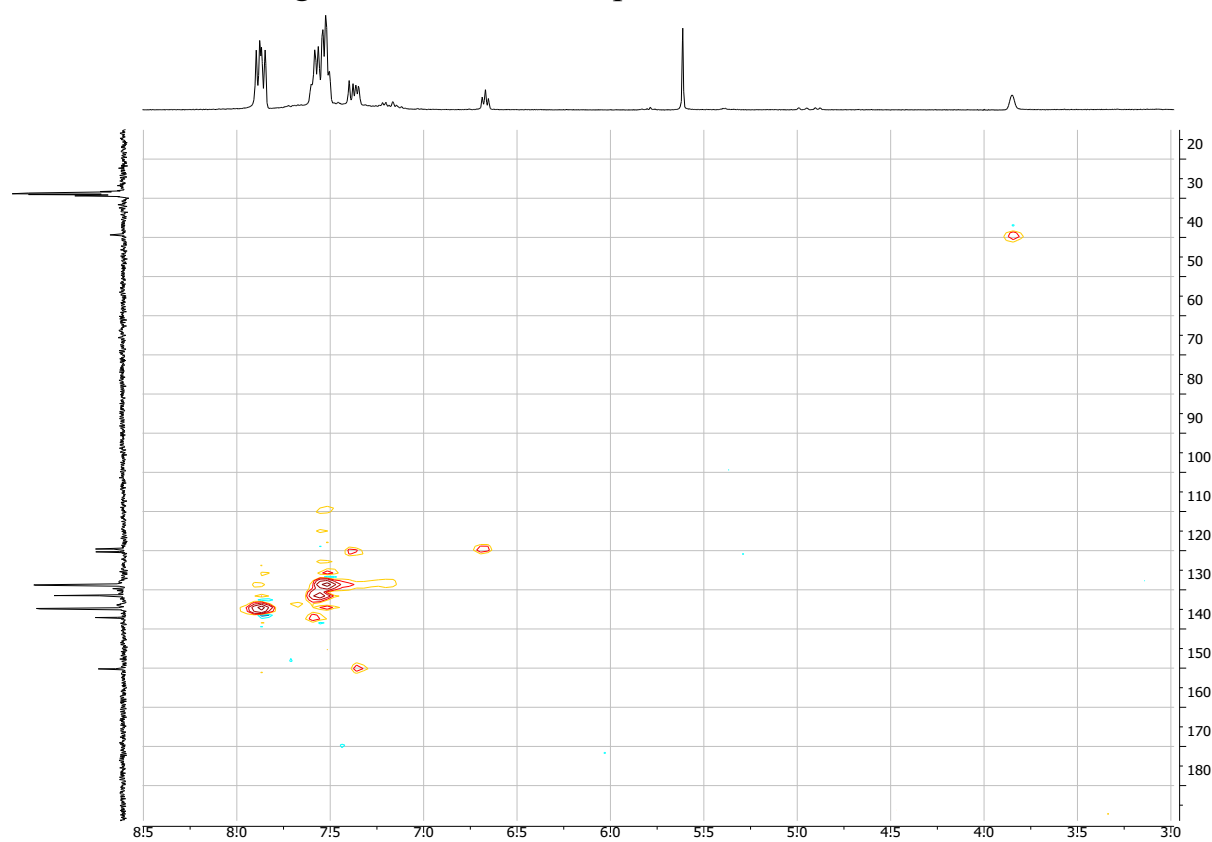


Figure S54. (H)C HSQC NMR spectrum of **9** in acetone- d_6

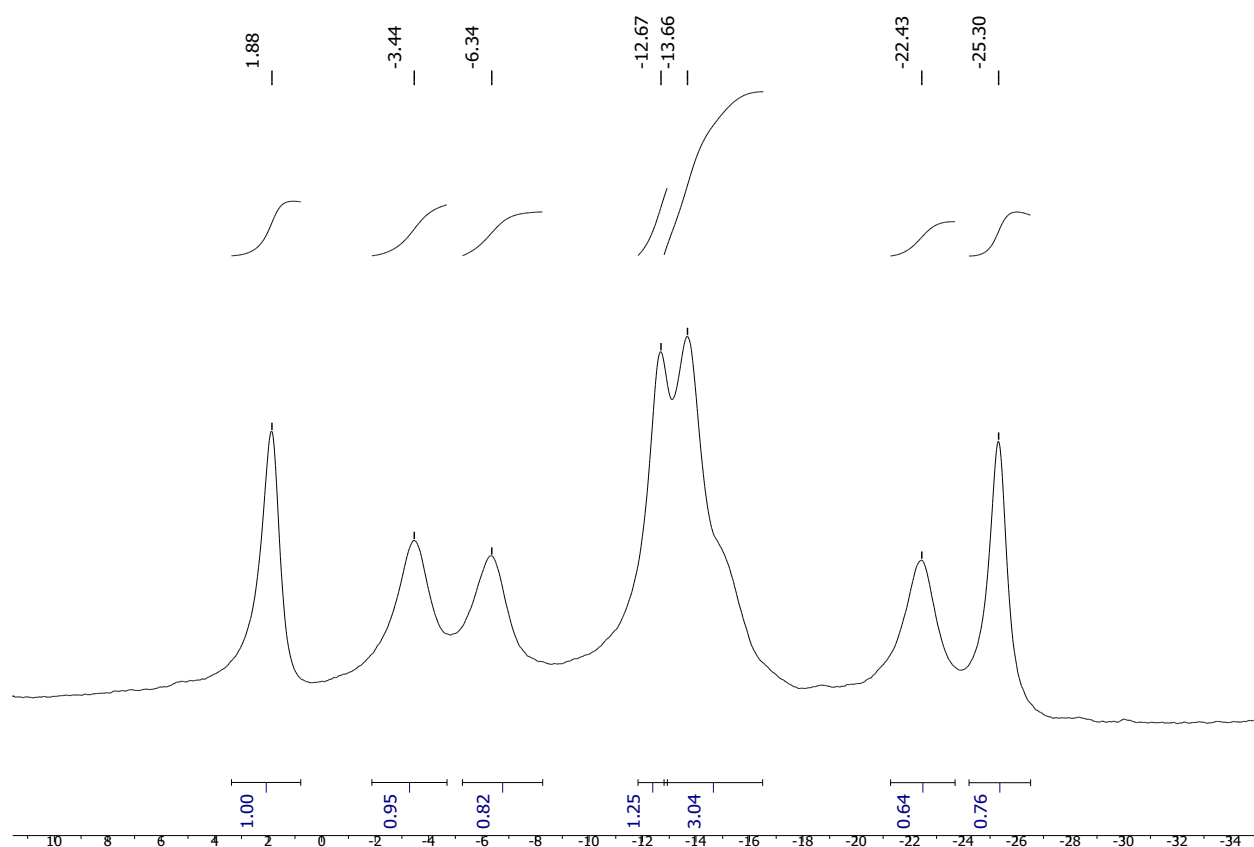


Figure S55. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **9** in acetone- d_6

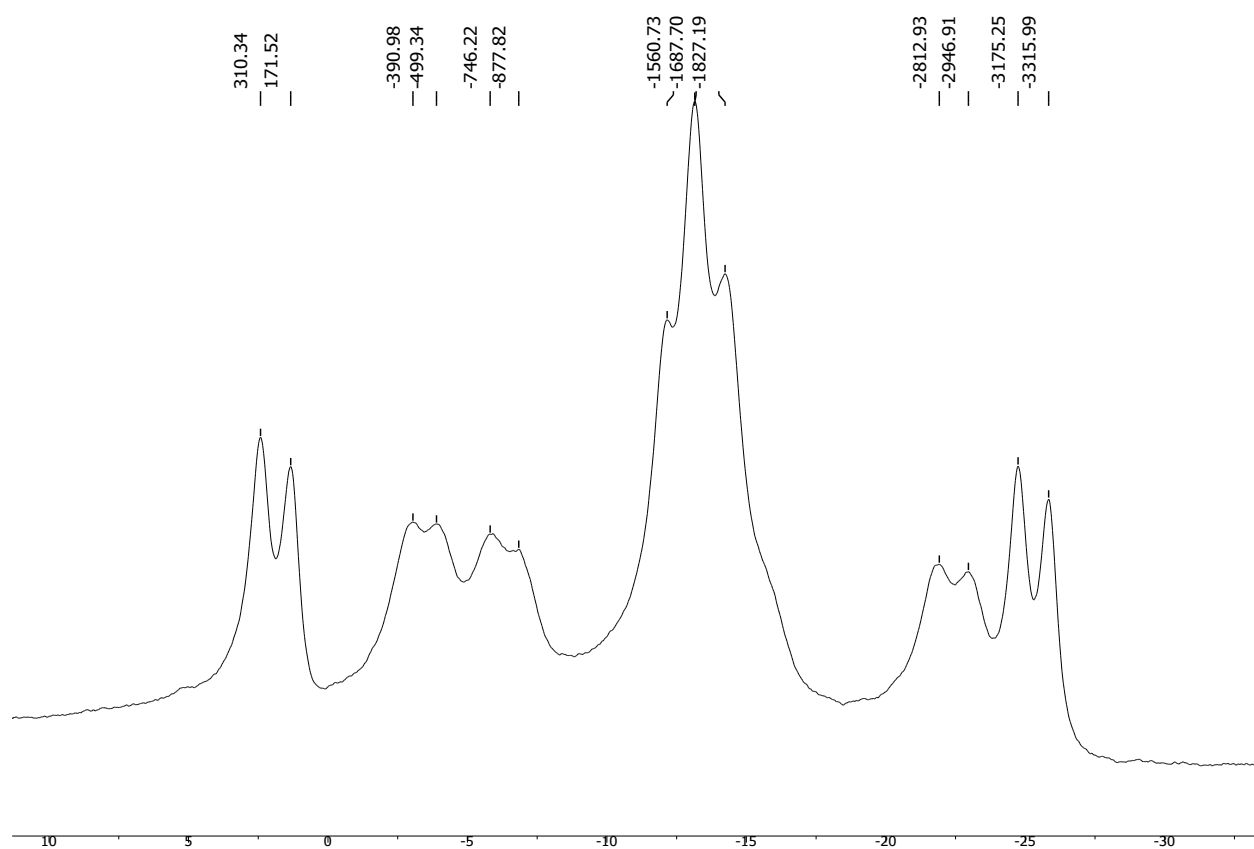


Figure S56. ^{11}B NMR spectrum of **9** in acetone- d_6

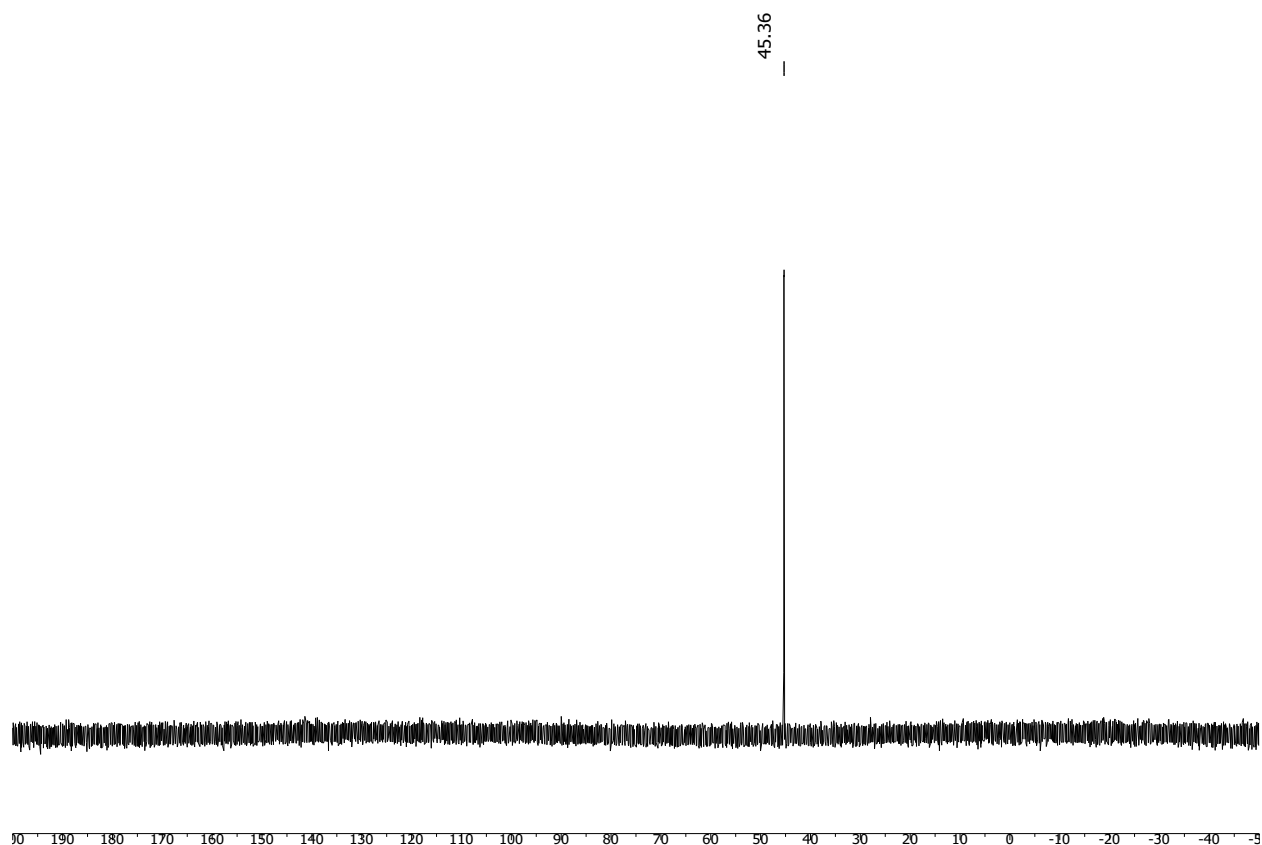


Figure S57. ³¹P NMR spectrum of **9** in acetone-d₆

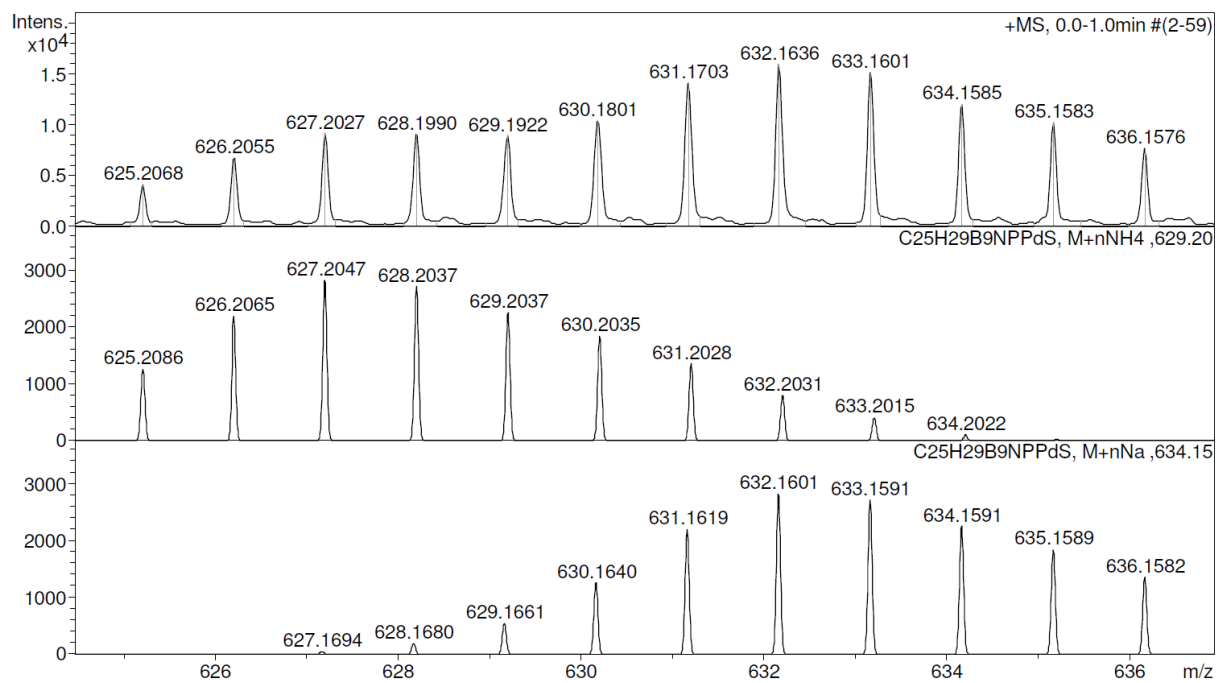


Figure S58. HRMS spectrum of **9**

Spectral data for 3-Ph₃P-3-(1(2)-NC₅H₄-2'-CH₂S)-*closo*-3,1,2-NiC₂B₉H₁₀ (**10**)

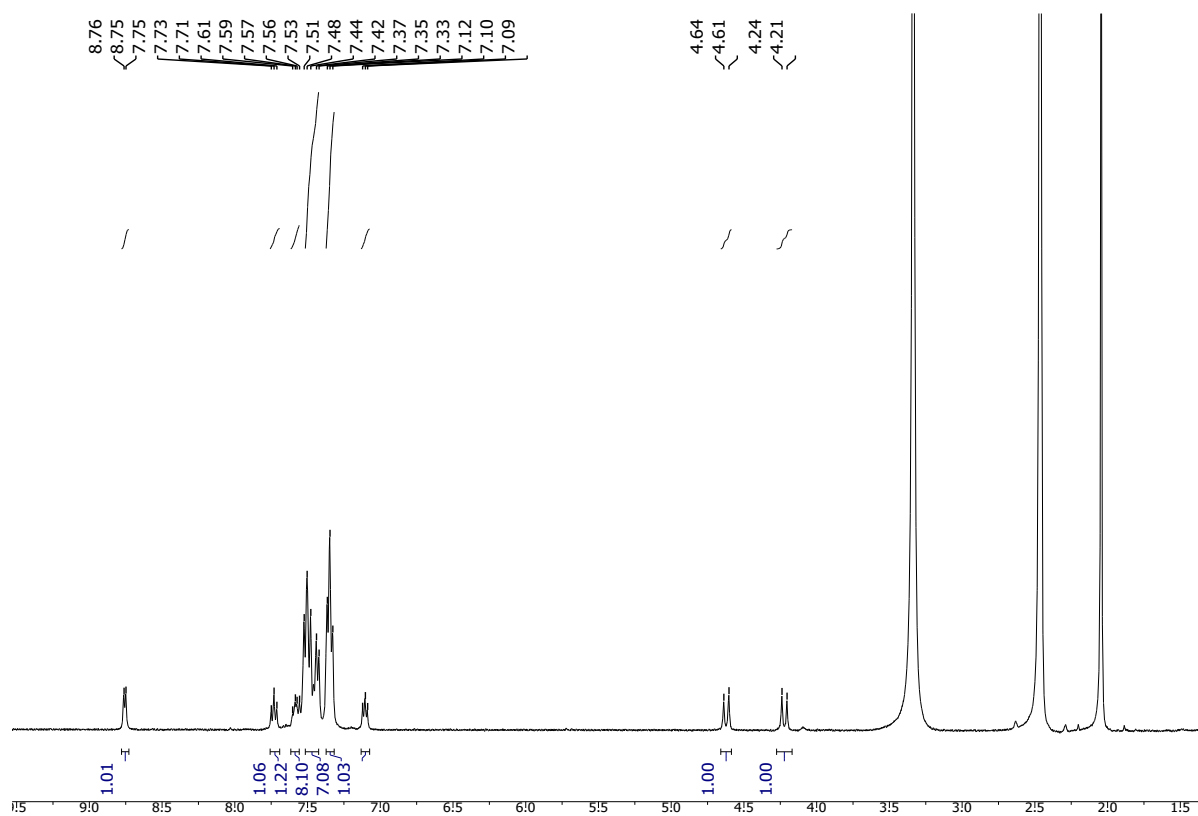


Figure S59. ¹H NMR spectrum of **10** in DMSO-d₆

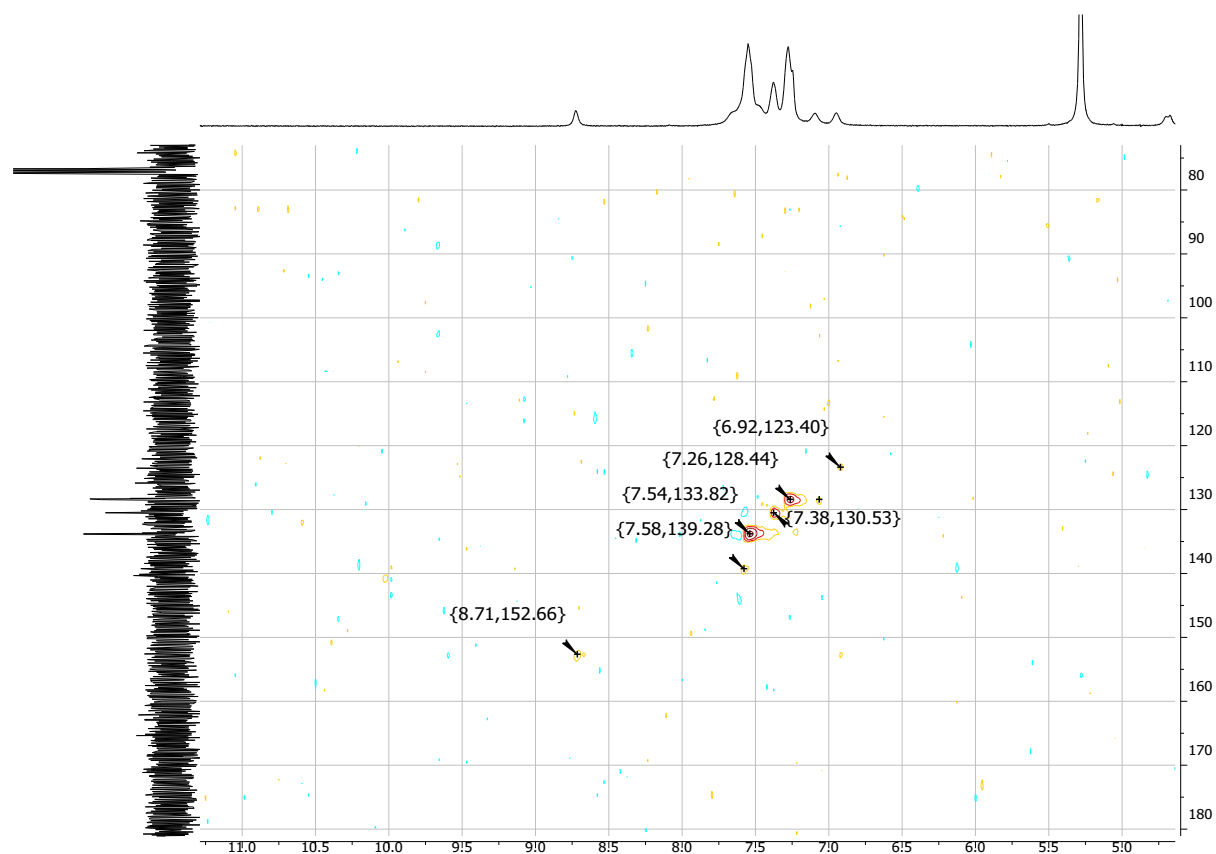


Figure S60. (H)C HSQC NMR spectrum of **10** in CDCl₃

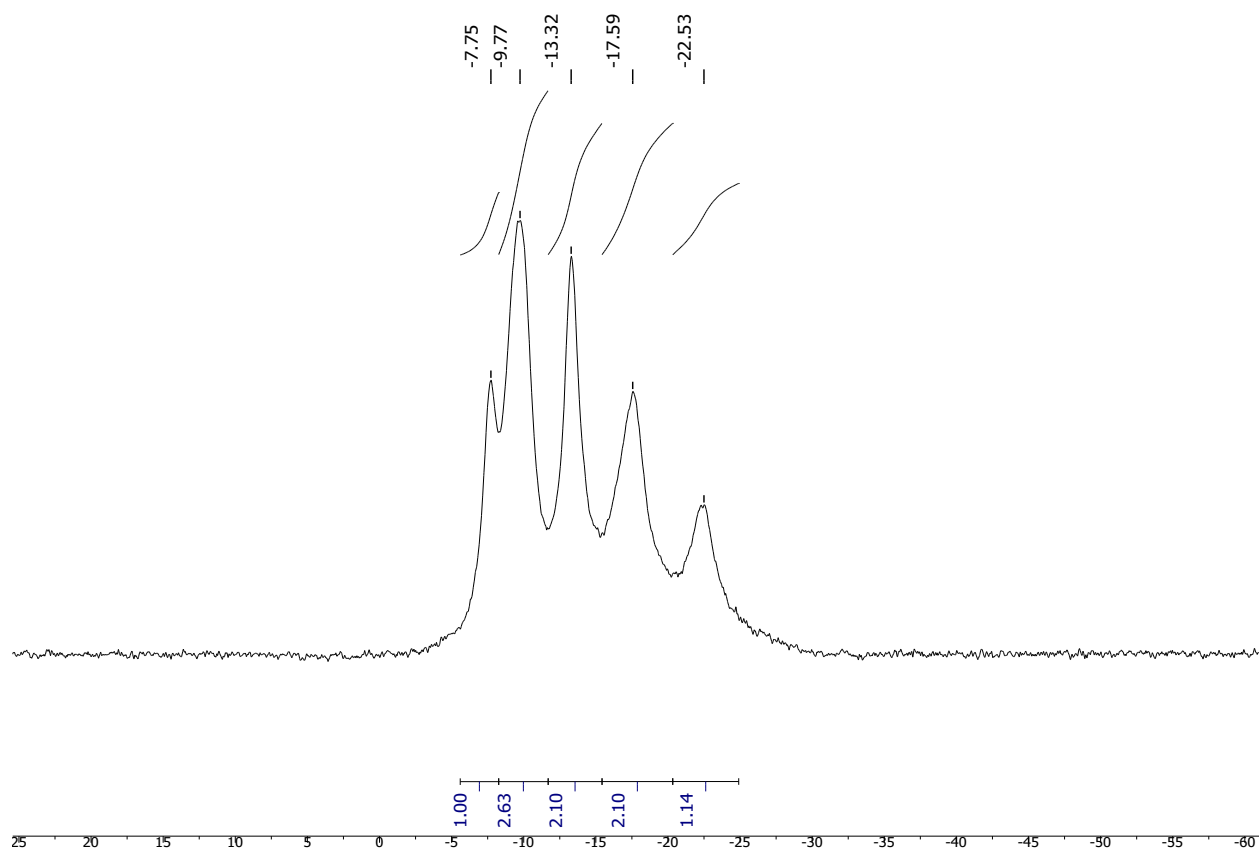


Figure S61. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **10** in CDCl_3

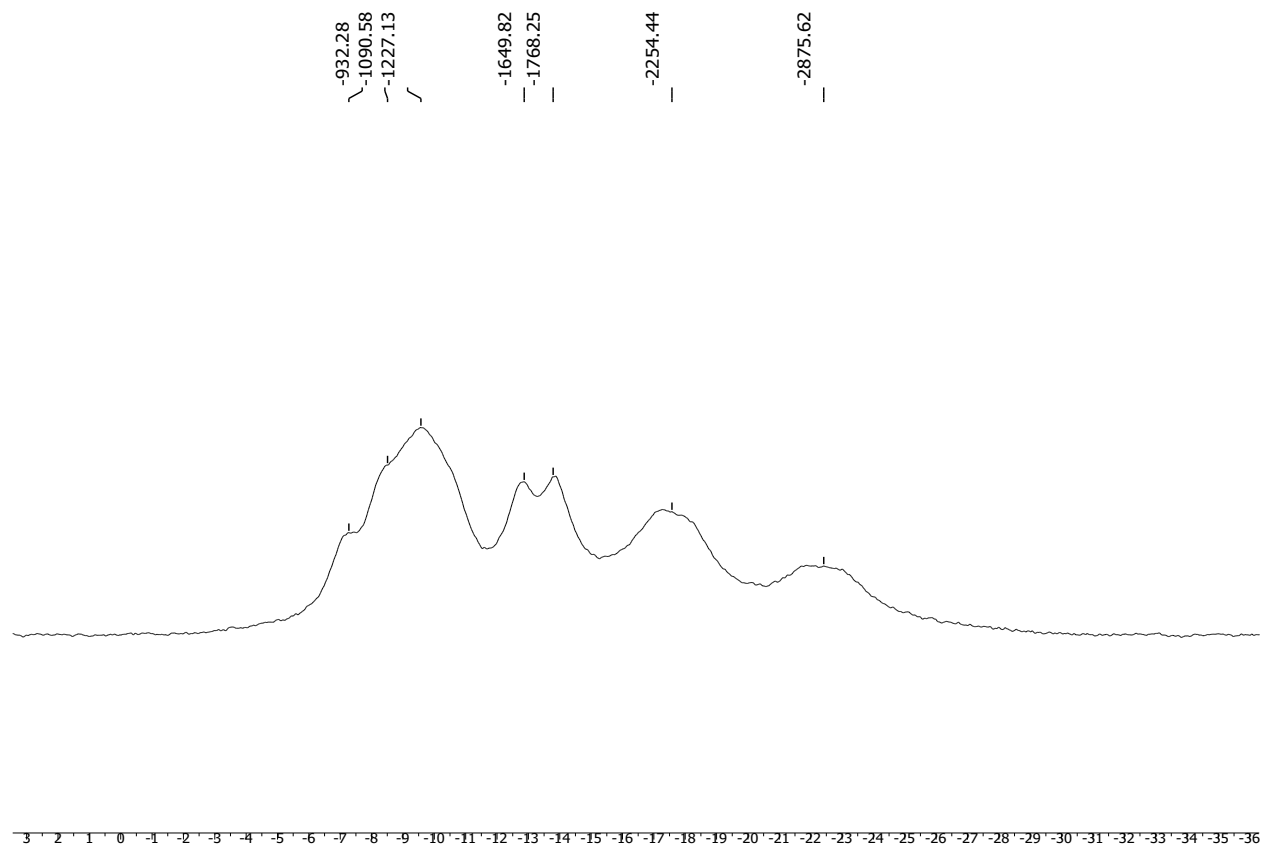


Figure S62. ^{11}B NMR spectrum of **10** in CDCl_3

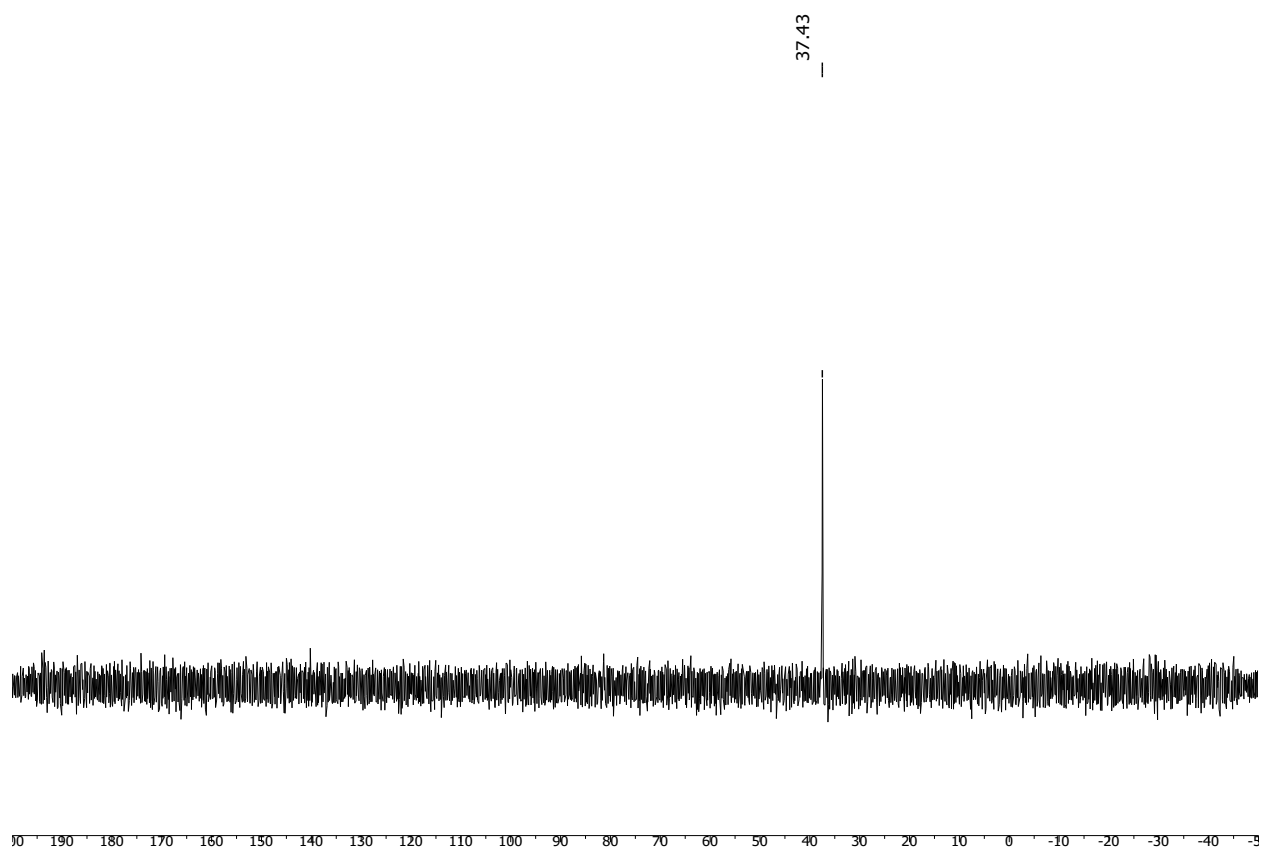


Figure S63. ^{31}P NMR spectrum of **10** in CDCl_3

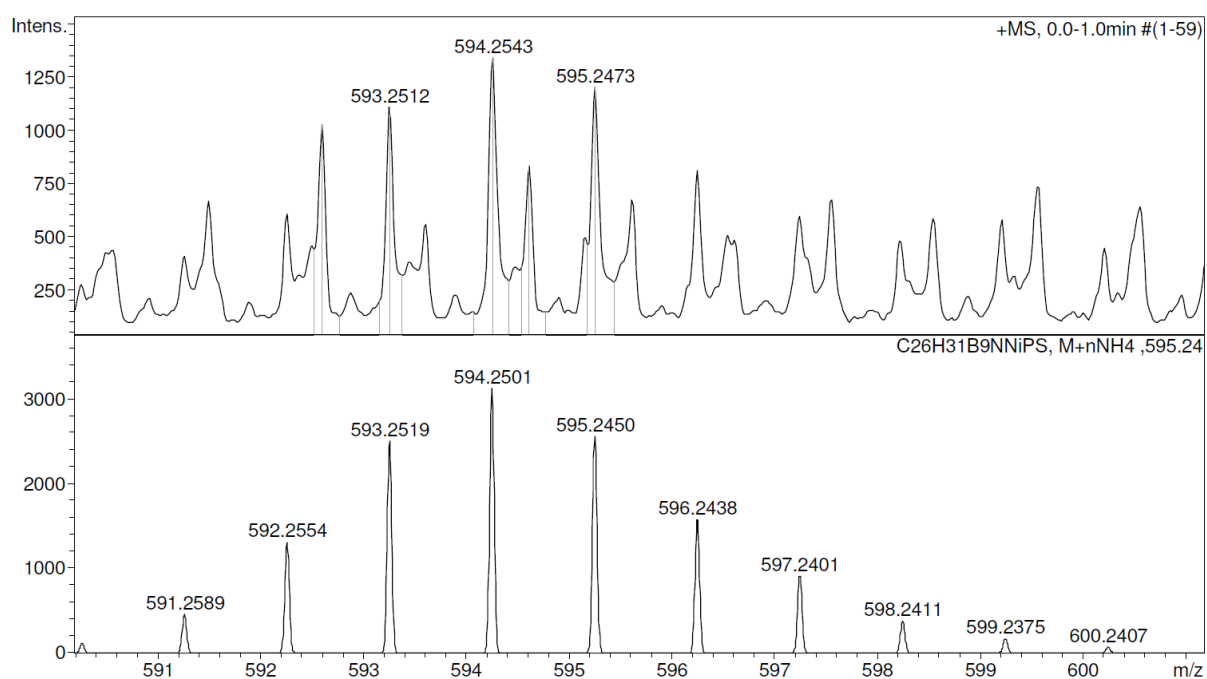


Figure S64. HRMS spectrum of **10**

Spectral data for 3-Ph₃P-3-(1(2)-NC₅H₄-2'-CH₂S)-*closo*-3,1,2-PdC₂B₉H₁₀ (**11**)

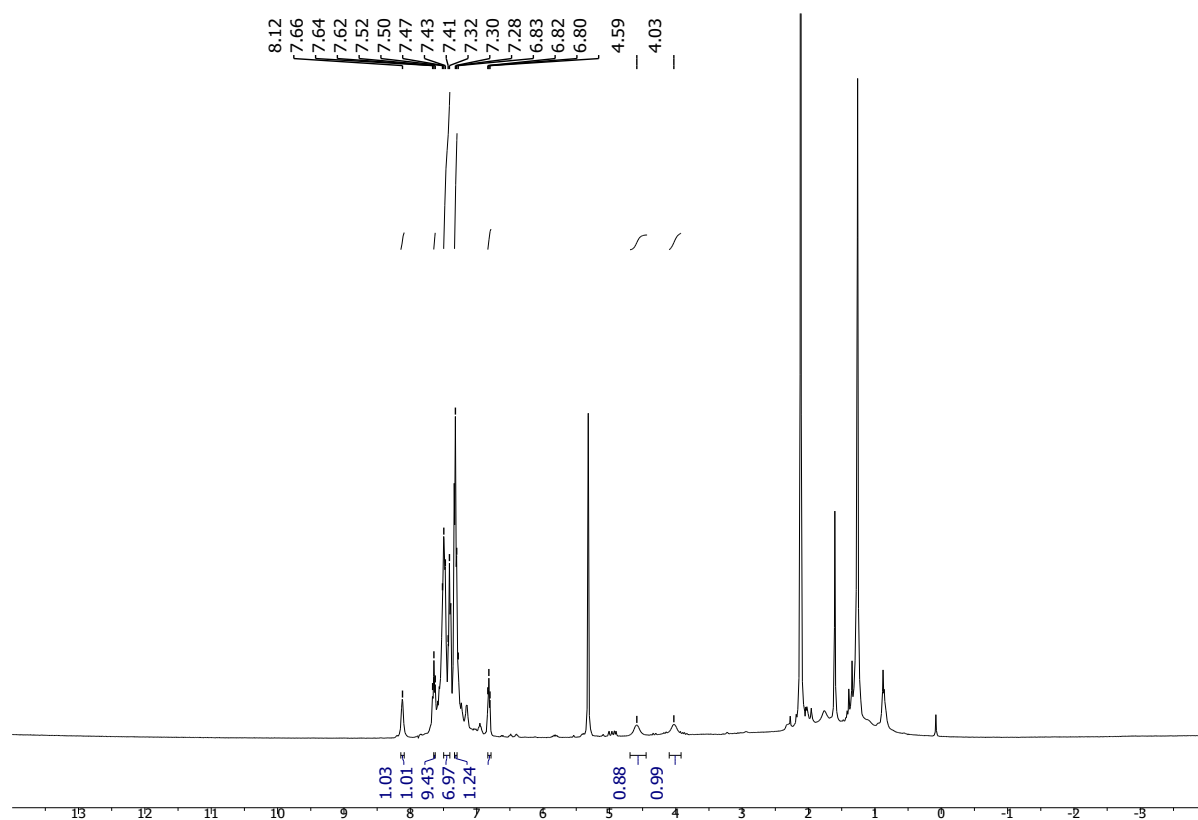


Figure S65. ¹H NMR spectrum of **11** in CD₂Cl₂

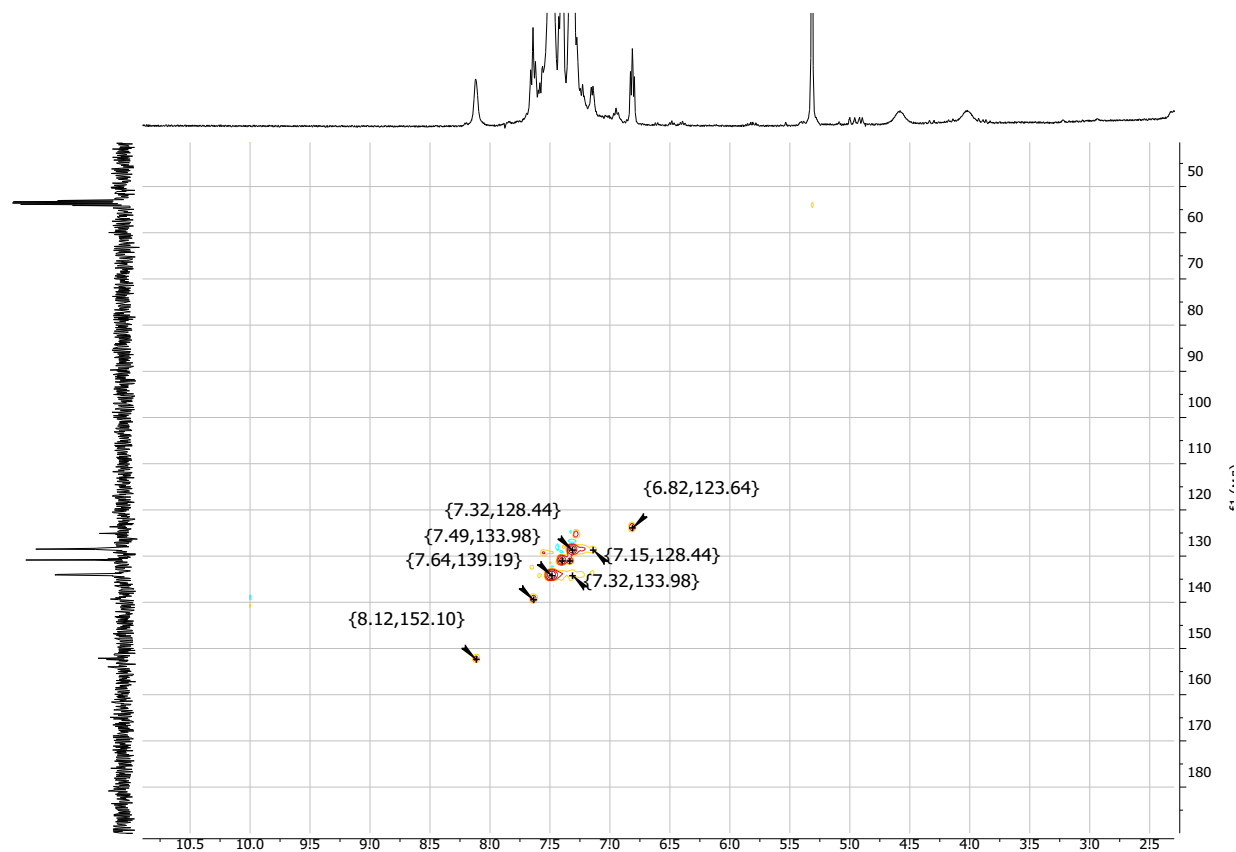


Figure S66. (H)C HSQC NMR spectrum of **11** in CD₂Cl₂

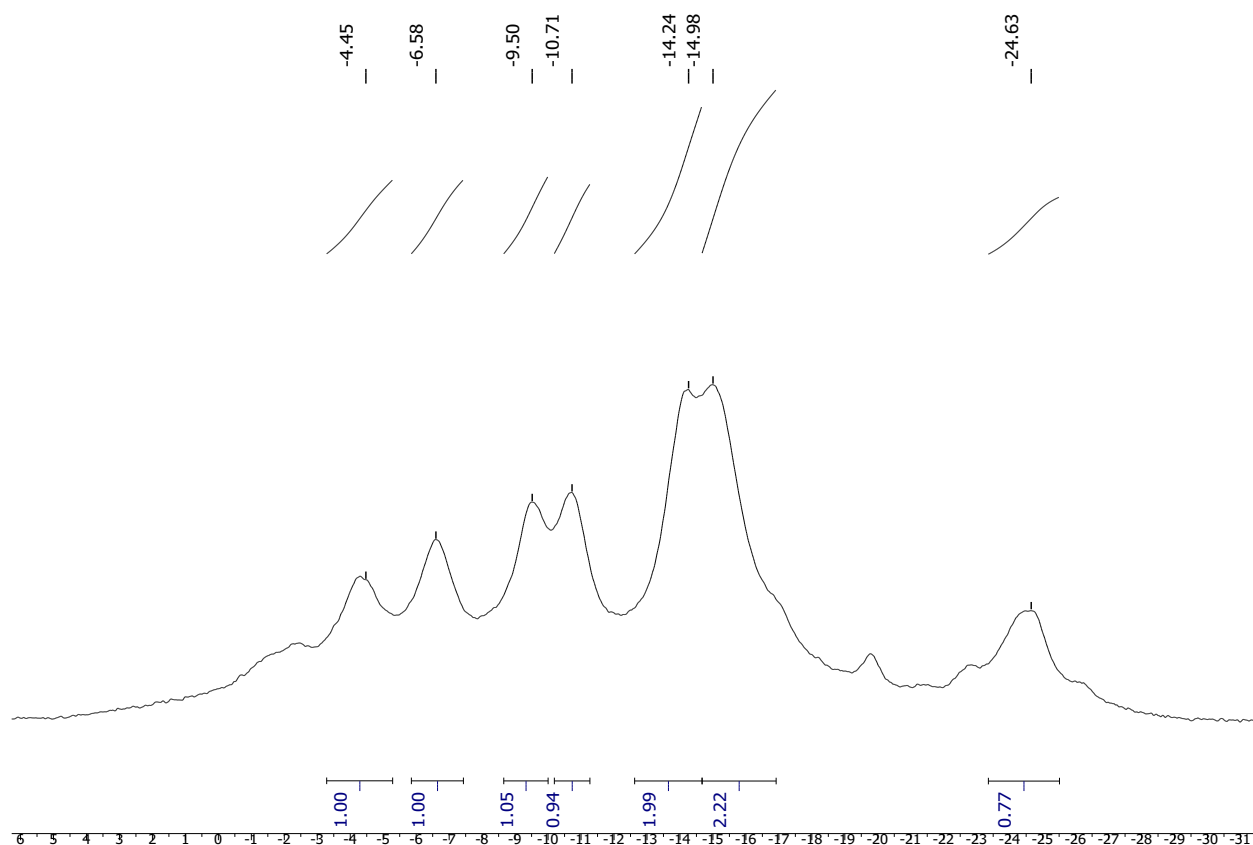


Figure S67. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **11** in CD_2Cl_2

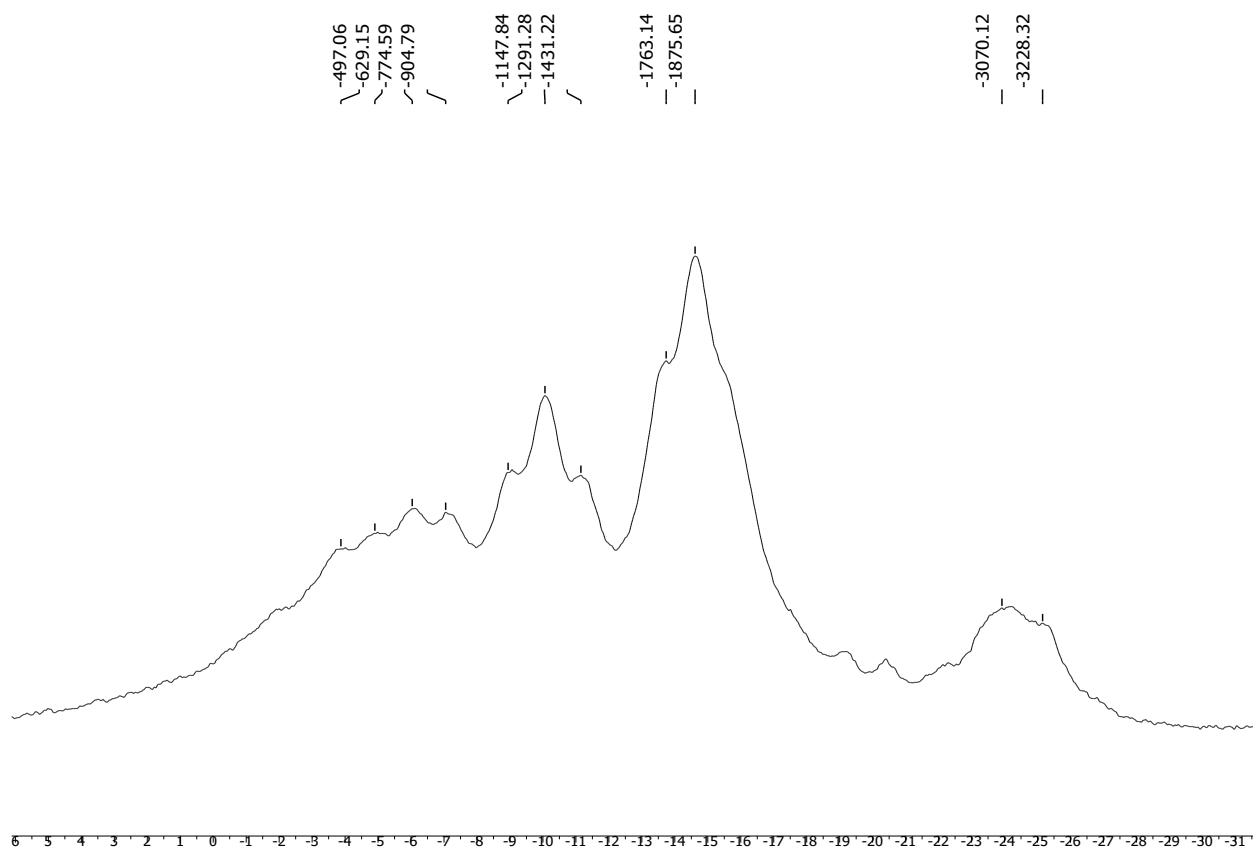


Figure S68. ^{11}B NMR spectrum of **11** in CD_2Cl_2

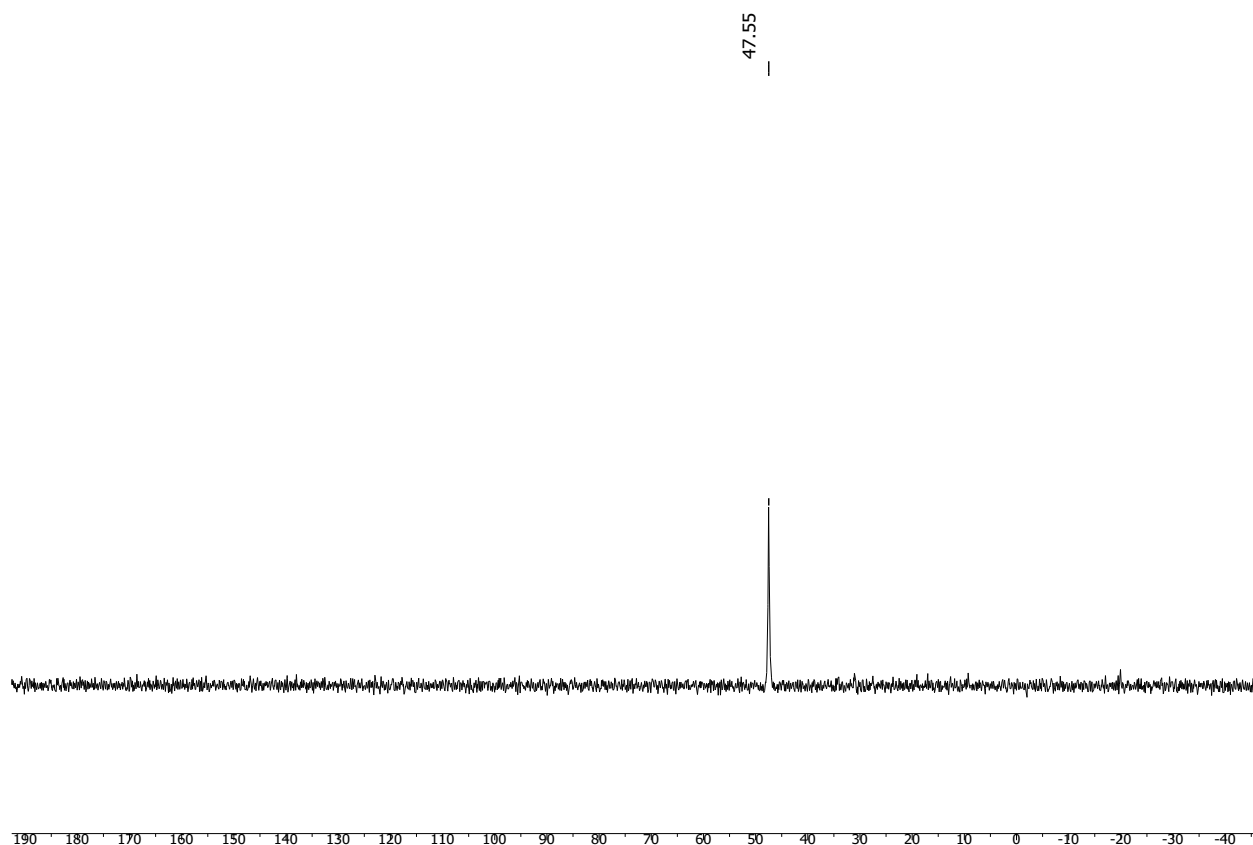


Figure S69. ³¹P NMR spectrum of **11** in CD₂Cl₂

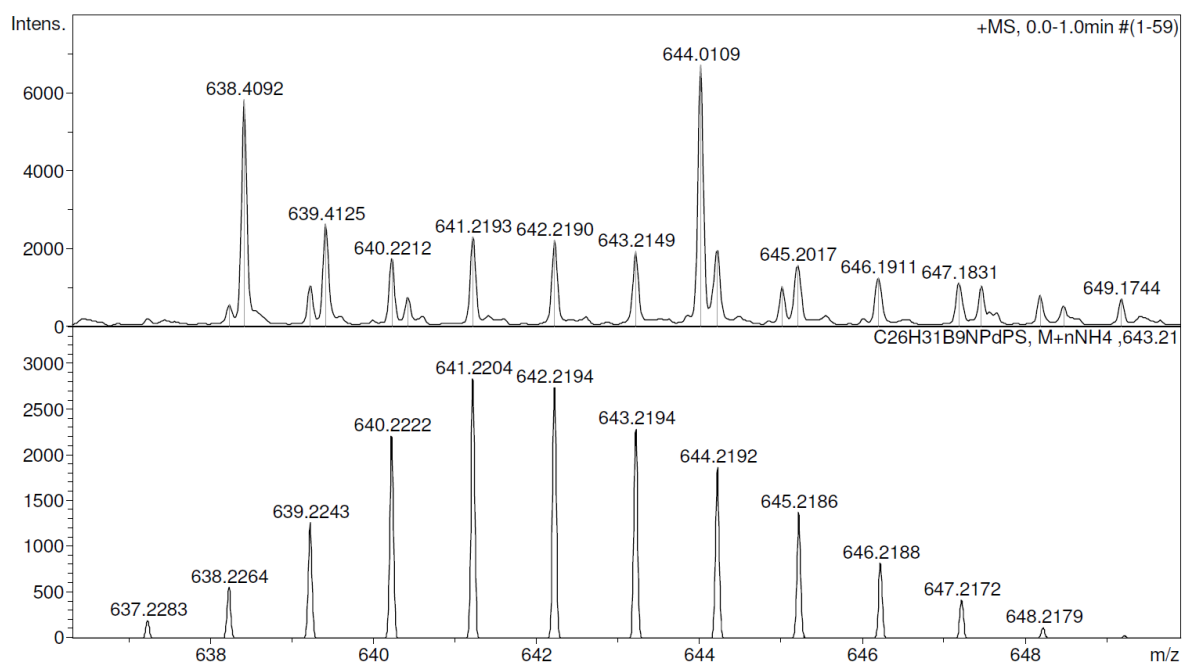


Figure S70. HRMS spectrum of **11**

Table S1. Crystallographic data for compounds **2*HBr**, **4**, **Cs[5]***0.5Me₂CO, **8**, and **10**.

| | 4 | Cs[5] | 2*HBr | 8 | 10 |
|---|---|--|---|--|---|
| formula | C ₈ H ₁₇ B ₁₀ NS | C ₈ H ₁₇ B ₉ NS ⁻ Cs ⁺ ·½(C ₃ H ₆ O) | C ₈ H ₁₇ B ₉ NS ⁺ Br ⁻ | C ₂₅ H ₂₉ B ₉ NNiPS | C ₂₆ H ₃₁ B ₉ NNiPS |
| fw | 267.38 | 418.52 | 418.52 | 562.52 | 576.55 |
| crystal system | Monoclinic | Triclinic | Orthorhombic | Monoclinic | Orthorhombic |
| space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> -1 | <i>Pna</i> 2 ₁ | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ 2 ₁ 2 ₁ |
| <i>a</i> , Å | 11.8345(13) | 7.9686(5) | 24.234(3) | 10.6347(3) | 8.489(3) |
| <i>b</i> , Å | 6.8603(7) | 8.8768(6) | 8.7044(9) | 19.0306(4) | 18.066(5) |
| <i>c</i> , Å | 17.5569(19) | 13.7553(9) | 7.4298(8) | 14.0144(3) | 18.928(7) |
| α , deg. | 90 | 99.784(2) | 90 | 90 | 90 |
| β , deg. | 90.078(3) | 102.455(2) | 90 | 104.6870(10) | 90 |
| γ , deg. | 90 | 107.360(2) | 90 | 90 | 90 |
| <i>V</i> , Å ³ | 1425.4(3) | 877.69(10) | 1567.3(3) | 2743.62(11) | 2902.7(18) |
| <i>Z</i> | 4 | 2 | 4 | 4 | 4 |
| <i>d</i> _{cryst} , g·cm ⁻³ | 1.246 | 1.584 | 1.417 | 1.362 | 1.319 |
| <i>F</i> (000) | 552 | 408 | 664 | 1160 | 1192 |
| μ , mm ⁻¹ | 0.202 | 2.217 | 2.733 | 0.860 | 0.814 |
| θ range, deg. | 1.16 – 27.20 | 2.48 – 28.15 | 2.49 – 28.03 | 2.25 – 26.97 | 2.15 – 26.05 |
| independent rflns | 3171 | 4276 | 3775 | 5968 | 5521 |
| <i>R</i> _{int} | 0.0447 | 0.0239 | 0.0474 | 0.0539 | 0.1380 |
| Completeness to θ , % | 99.8 | 99.7 | 99.8 | 99.9 | 96.9 |
| refined parameters | 226 | 213 | 187 | 383 | 351 |
| <i>GOF</i> (<i>F</i> ²) | 1.040 | 1.111 | 1.078 | 1.038 | 0.952 |
| rflns with <i>I</i> > 2 σ (<i>I</i>) | 2904 | 3980 | 3379 | 4610 | 2702 |
| <i>R</i> ₁ (<i>F</i>) (<i>I</i> > 2 σ (<i>I</i>)) ^a | 0.0275 | 0.0230 | 0.0297 | 0.0298 | 0.0822 |
| <i>wR</i> ₂ (<i>F</i> ²) (all data) ^b | 0.0688 | 0.0603 | 0.0692 | 0.0683 | 0.1986 |
| Largest diff. peak/hole, <i>e</i> ·Å ⁻³ | 0.163/-0.218 | 0.814/-0.888 | 0.400/-0.315 | 0.319/-0.275 | 0.722/-1.139 |

^a $R_1 = \sum |F_o - |F_c|| / \sum (F_o)$; ^b $wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$