

Supporting Information for

“A ^{115}In Solid-State NMR Study of Low-Oxidation State Indium Complexes”

by Hiyam Hamaed,¹ Karen E. Johnston,¹ Benjamin F. T. Cooper,¹ Victor V. Terskikh,² Eric Ye,³ Charles L. B. Macdonald,¹ Donna C. Arnold,⁴ and Robert W. Schurko^{1,*}

¹Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada, N9B 3P4; ²Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, Canada, K1A 0R6; ³Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5, ⁴School of Physical Sciences, University of Kent, Canterbury, Kent, United Kingdom, CT2 7NH

*Author to whom correspondence should be addressed

Phone: (519) 253-3000 x3548. Fax: (519) 973-7098. Email: rschurko@uwindsor.ca

Table of Contents:

| | |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Table S1. ^{115}In NMR experimental parameters at 9.4 T | S2 |
| Table S2. ^{115}In NMR experimental parameters at 21.1 T | S2 |
| Table S3. ^{115}In MAS NMR experimental parameters at 21.1 T | S2 |
| Figure S1. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}][\text{GaCl}_4]$ | S3 |
| Figure S2. The contribution of ^{115}In CSA on the NMR pattern of InI | S4 |
| Figure S3. The contribution of ^{115}In CSA on the NMR pattern of InBr | S5 |
| Figure S4. Simulation of ^{115}In NMR pattern of $[\text{In}][\text{OTf}]$ at 9.4 T with parameters of two indium sites | S6 |
| Figure S5. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}][\text{OTf}]$ | S7 |
| Figure S6. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}([\text{15}]\text{crown-5})_2][\text{OTf}]$ | S8 |
| Figure S7. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}([\text{15}]\text{crown-6})][\text{OTf}]$ | S9 |
| Figure S8. pXRD patterns for $[\text{In}([\text{18}]\text{crown-6})][\text{GaCl}_4]$ and $[\text{In}([\text{18}]\text{crown-6})][\text{AlCl}_4]$ | S10 |
| Figure S9. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}([\text{18}]\text{crown-6})][\text{GaCl}_4]$ | S11 |
| Figure S10. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}([\text{18}]\text{crown-6})][\text{AlCl}_4]$ | S12 |
| Figure S11. Static ^{71}Ga SSNMR spectrum of $[\text{In}([\text{18}]\text{crown-6})][\text{GaCl}_4]$ and ^{27}Al SSNMR spectra of AlCl_4 and $[\text{In}([\text{18}]\text{crown-6})][\text{AlCl}_4]$ at 9.4 T | S13 |
| Figure S12. ^{13}C MAS NMR spectra of $[\text{In}([\text{15}]\text{crown-5})_2][\text{OTf}]$ at 21 °C and at 45 °C | S14 |
| Figure S13. ^1H MAS NMR spectra of $[\text{In}([\text{15}]\text{crown-5})_2][\text{OTf}]$ at 21 °C and at 45 °C | S15 |
| Figure S14. ^{115}In NS tensor orientations | S16 |

Table S1. ^{115}In Static NMR Experimental Parameters at 9.4 T

| | rf power (kHz) | Recycle Delay (s) | Spectral Width (kHz) | Number of Subspectra | Offset Frequency (kHz) | Number of Scans per Subspectrum |
|---------------------------------------|-------------------|----------------------|-------------------------|-------------------------|------------------------------|---------------------------------------|
| [In][GaCl ₄] | 67 | 0.1 | 1000 | 1 | - | 8544 |
| [In([15]crown-5) ₂][OTf] | 77 | 0.1 | 1000 | 1 | - | 579152 |
| [In([18]crown-6)][GaCl ₄] | 111 | 0.1 | 1000 | 3 | 150 | 18848 |
| [In([18]crown-6)][AlCl ₄] | 111 | 0.1 | 1000 | 3 | 150 | 66288 |
| InI | 67 | 0.1 | 2000 | 6 | 100 | 17824 |
| InBr | 67 | 0.1 | 2000 | 8 | 125 | 8544 |
| WURST-Echo | | | | | | |
| [In][OTf] | 17 | 0.1 | 2000 | 5 | 250 | 15736 |

Table S2. ^{115}In Static NMR Experimental Parameters at 21.1 T

| | rf power (kHz) | Recycle Delay (s) | Spectral Width (kHz) | Number of Subspectra | Offset Frequency (kHz) | Number of Scans per Subspectrum |
|---------------------------------------|-------------------|----------------------|-------------------------|-------------------------|------------------------------|---------------------------------------|
| [In][GaCl ₄] | 50 | 1 | 200 | 1 | - | 1024 |
| [In([15]crown-5) ₂][OTf] | 50 | 1 | 200 | 1 | - | 2976 |
| [In([18]crown-6)][GaCl ₄] | 50 | 1 | 500 | 1 | 60 | 2048 |
| [In([18]crown-6)][AlCl ₄] | 50 | 1 | 500 | 1 | 60 | 16384 |
| [In([18]crown-6)][OTf] | 100 | 1 | 2000 | 1 | - | 6144 |
| [In][OTf] | 50 | 1 | 1000 | 3 | 120 | 2048 |
| InI | 50 | 1 | 500 | 1 | - | 1782 |
| InBr | 50 | 1 | 1000 | 1 | - | 5557 |

Table S3. ^{115}In MAS NMR Experimental Parameters at 21.1 T

| | ν_{rot} (kHz) | rf power (kHz) | Recycle Delay (s) | Spectral Width (kHz) | Number of Scans |
|---------------------------------------|--------------------------|-------------------|----------------------|-------------------------|--------------------|
| [In][GaCl ₄] | 18 | 50 | 1 | 200 | 2200 |
| [In([15]crown-5) ₂][OTf] | 12.5 | 50 | 0.5 | 200 | 4096 |
| [In([18]crown-6)][GaCl ₄] | 50 | 100 | 0.5 | 1000 | 20480 |
| [In([18]crown-6)][AlCl ₄] | 50 | 100 | 0.5 | 1000 | 136000 |
| [In][OTf] | 62.5 | 100 | 0.5 | 1000 | 16000 |
| InI | 62.5 | 100 | 0.5 | 1000 | 10240 |
| InBr | 62.5 | 100 | 0.5 | 1000 | 16400 |

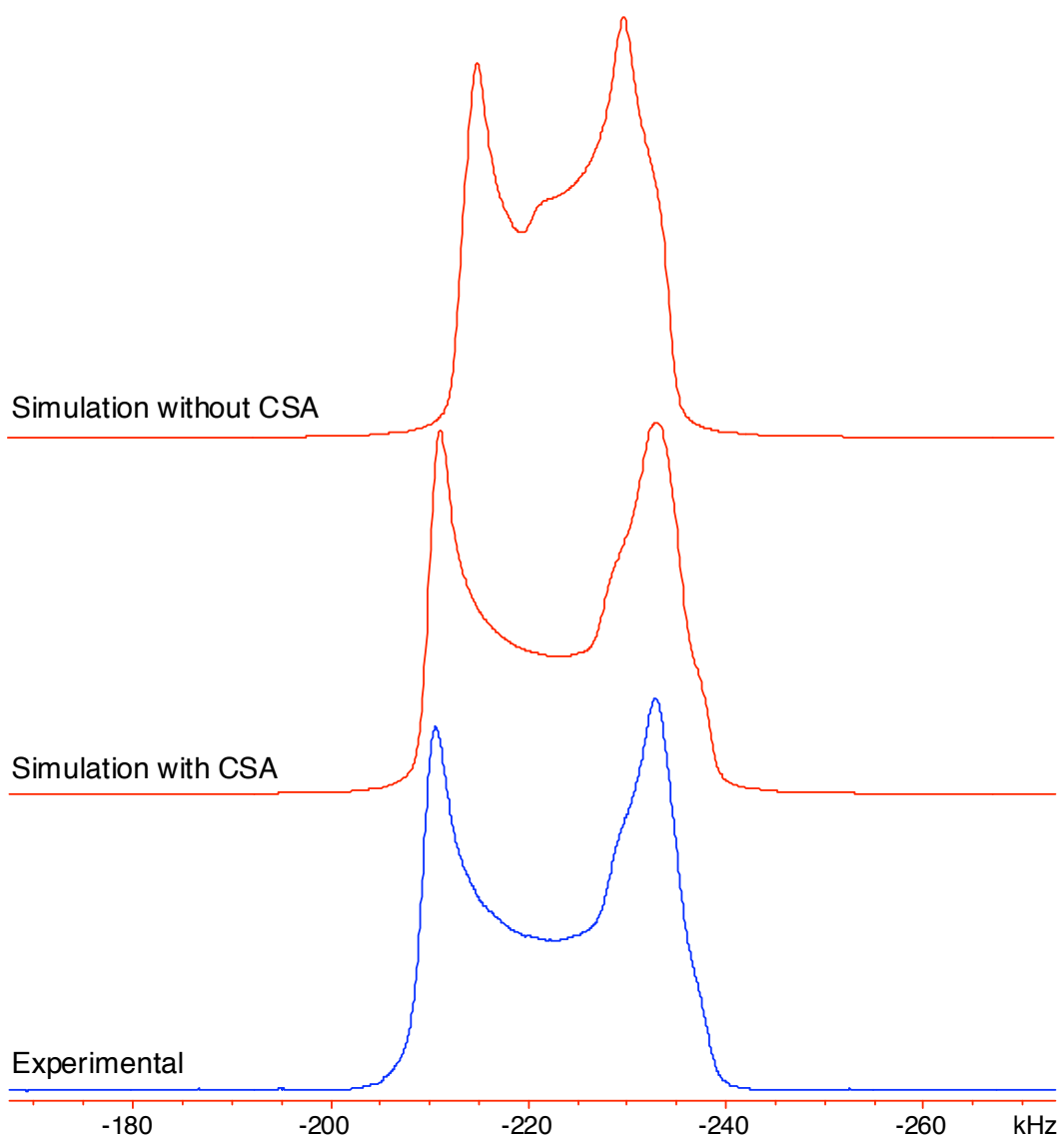


Figure S1. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}][\text{GaCl}_4]$ acquired at 21.1 T.

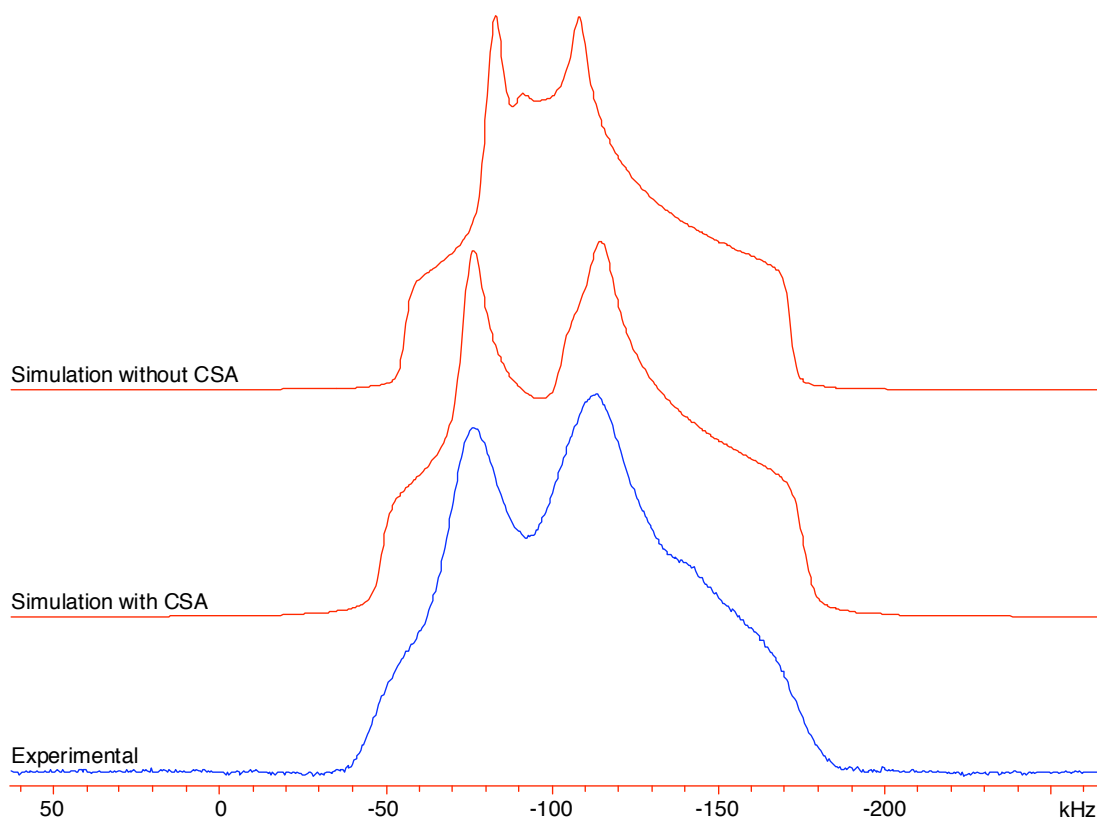


Figure S2. The contribution of ^{115}In CSA on the NMR pattern of InI acquired at 21.1 T.

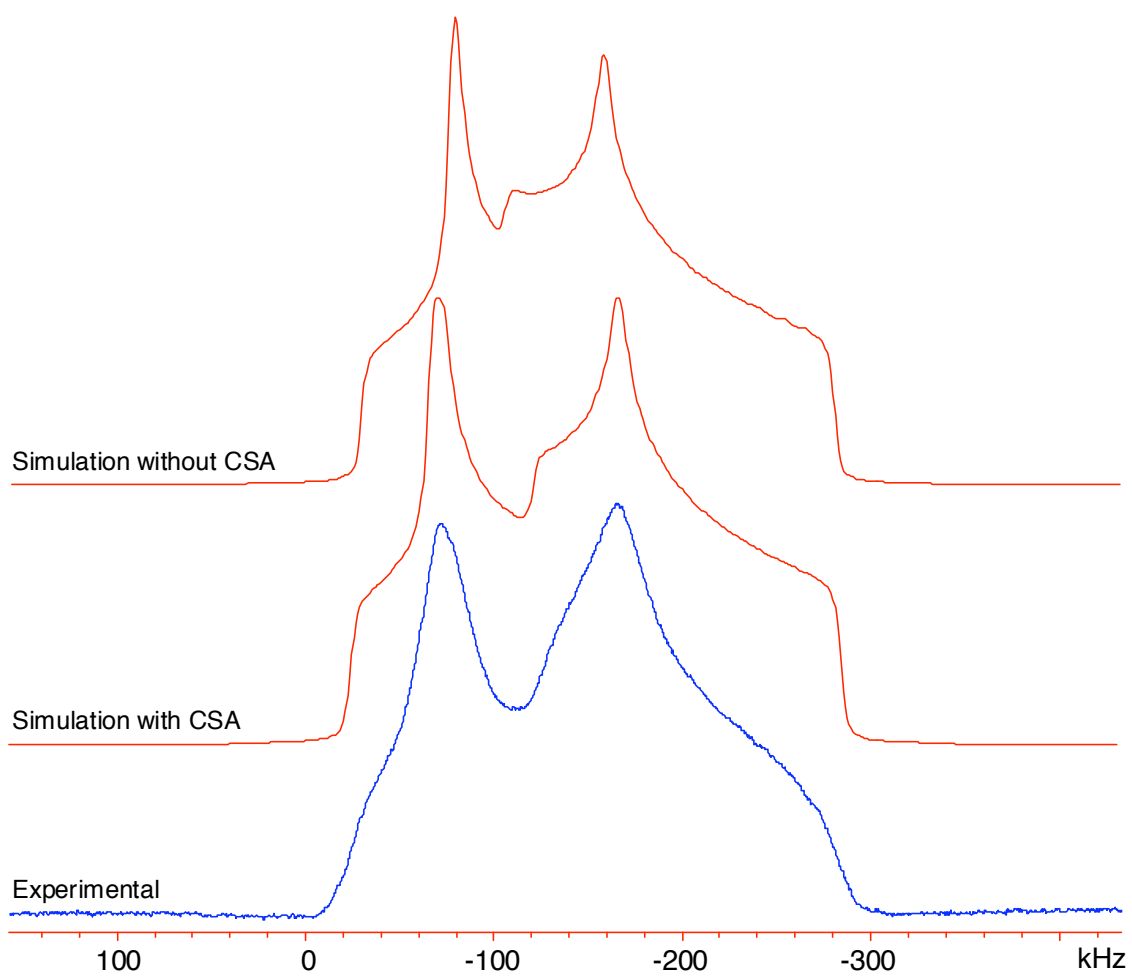


Figure S3. The contribution of ^{115}In CSA on the NMR pattern of InBr acquired at 21.1 T.

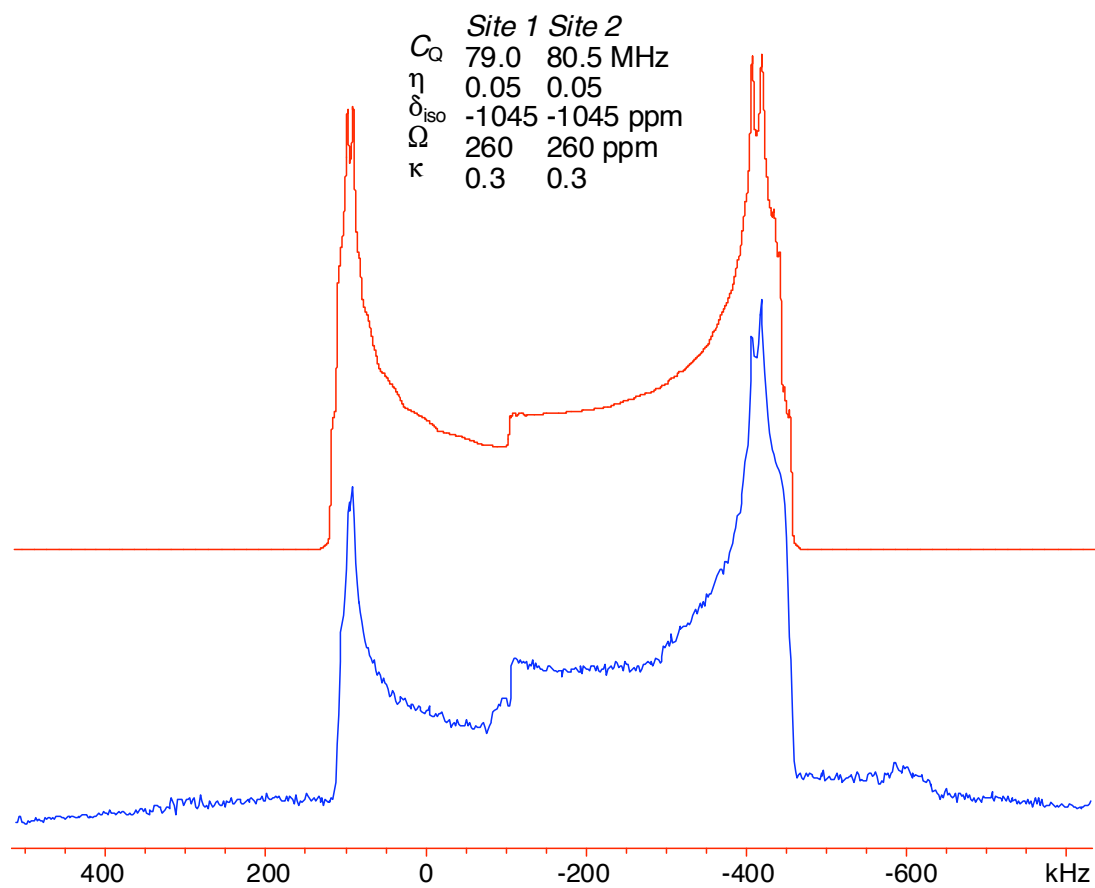


Figure S4. Simulation (top) of ^{115}In NMR pattern (bottom) of $[\text{In}][\text{OTf}]$ at 9.4 T with parameters of two indium sites.

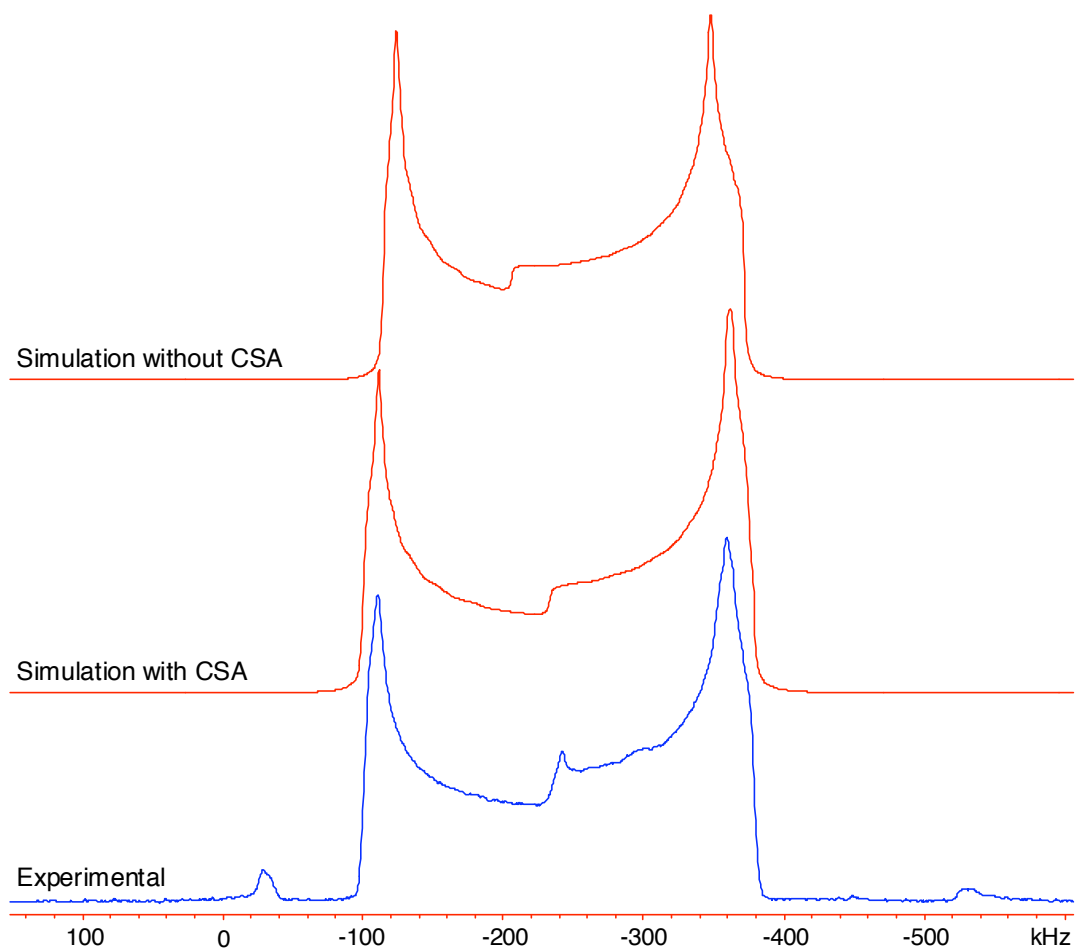


Figure S5. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}][\text{OTf}]$ acquired at 21.1 T.

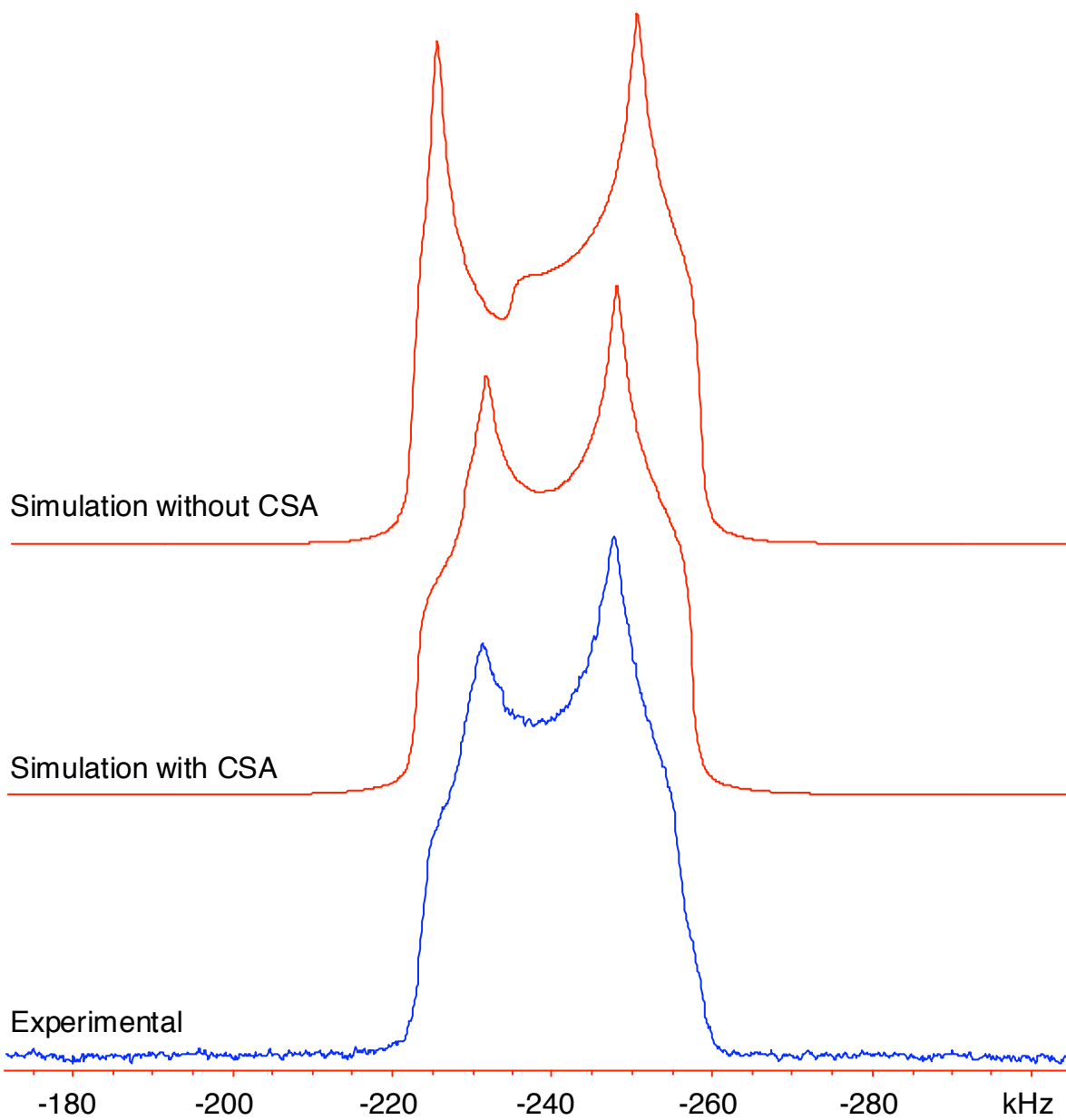


Figure S6. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}([\text{15}]\text{crown-5})_2][\text{OTf}]$ acquired at 21.1 T.

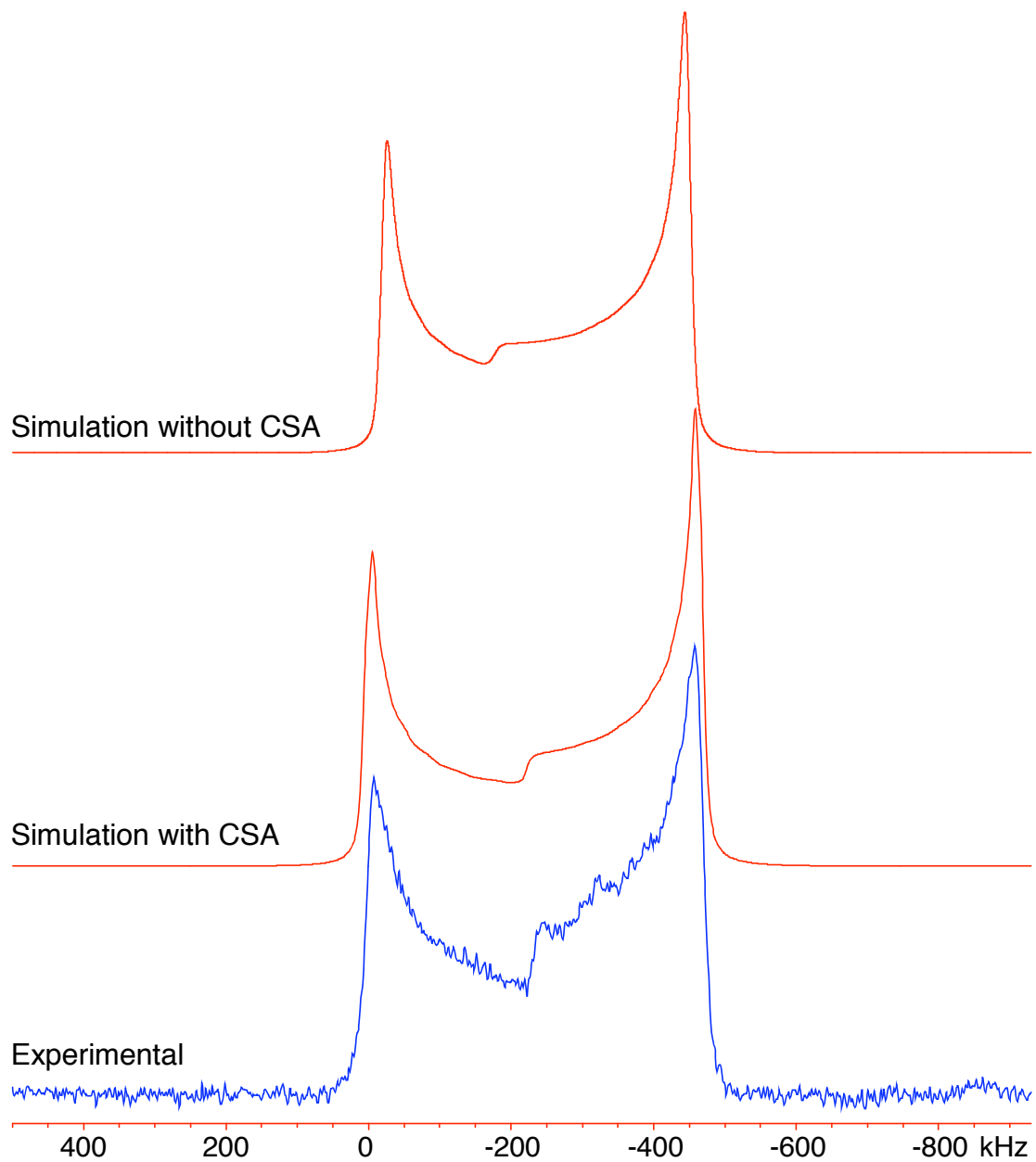


Figure S7. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}([\text{18}]\text{crown-6})][\text{OTF}]$.

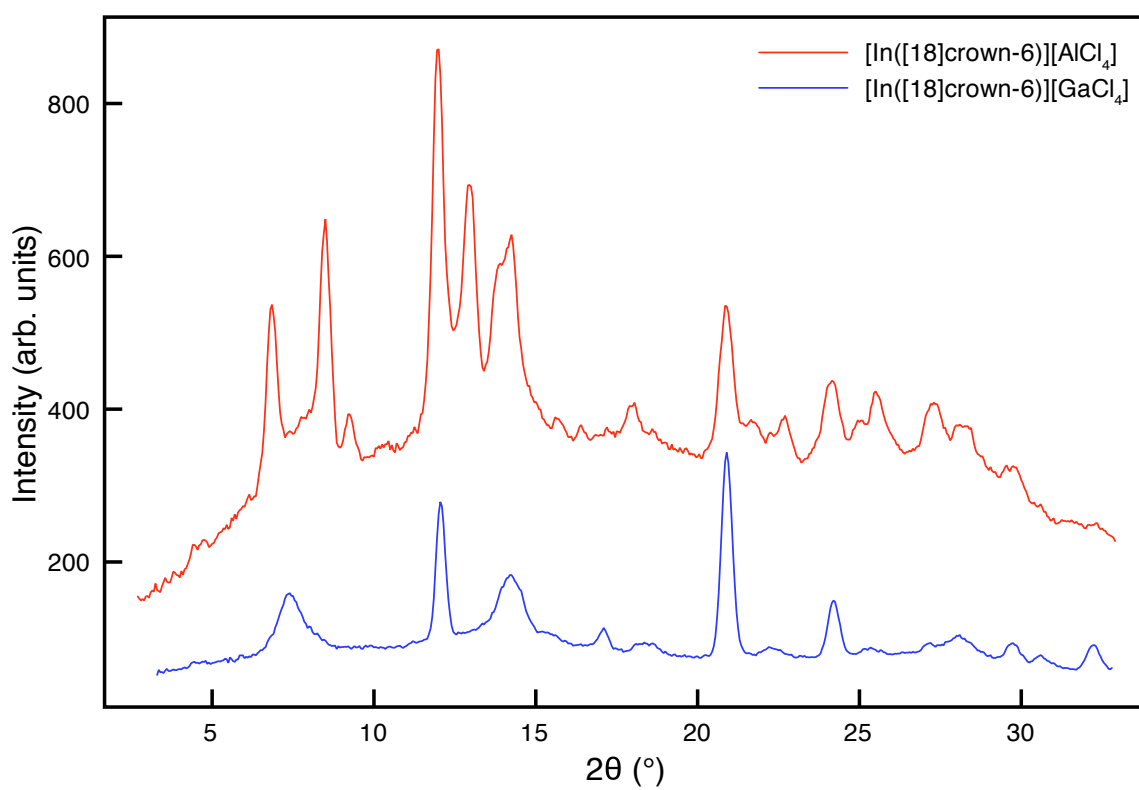


Figure S8. Powder X-ray diffraction patterns of $[\text{In}([18]\text{crown-6})][\text{GaCl}_4]$ and $[\text{In}([18]\text{crown-6})][\text{AlCl}_4]$ acquired at room temperature.

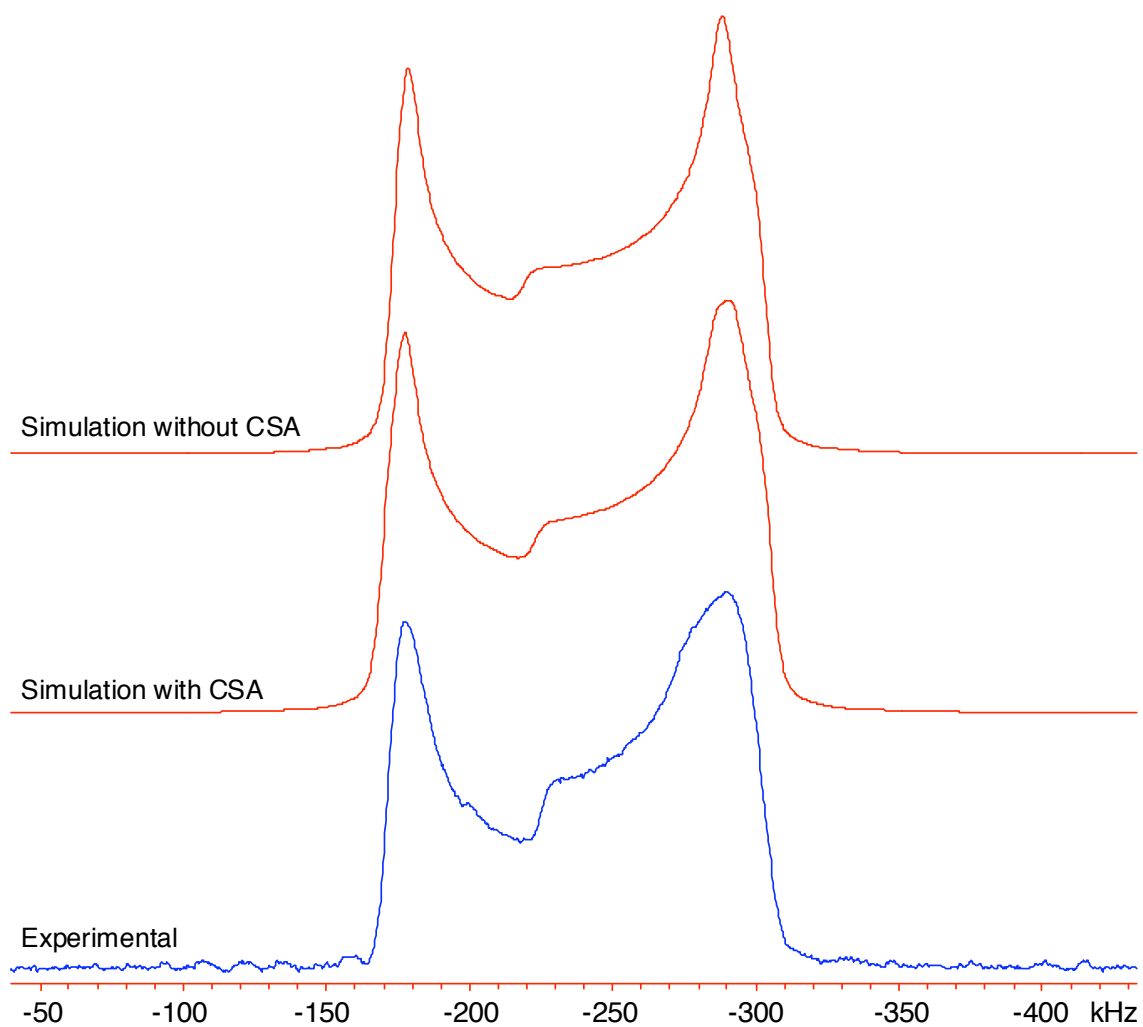


Figure S9. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}([\text{18}]\text{crown-6})][\text{GaCl}_4]$ acquired at 21.1 T.

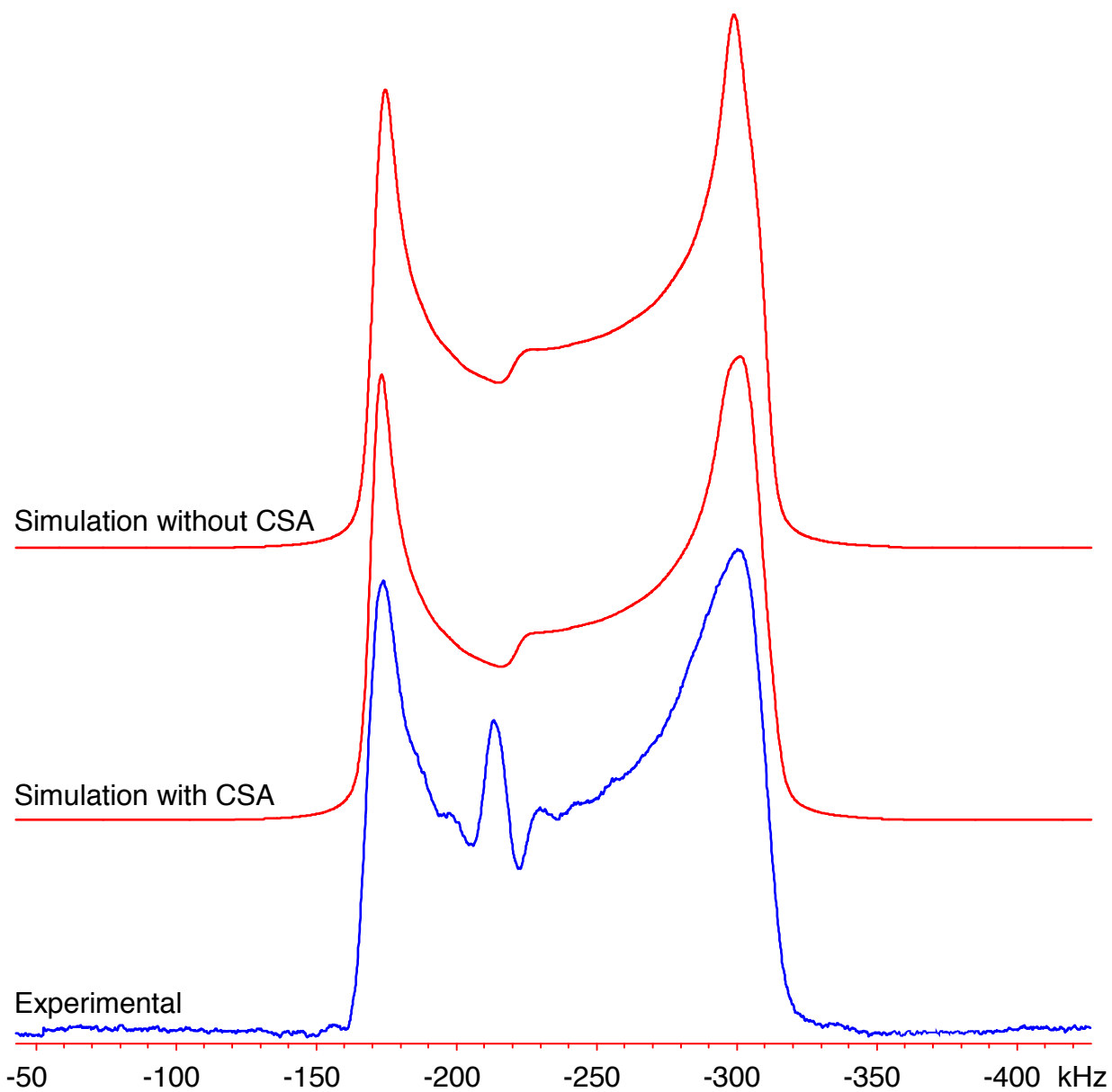


Figure S10. The contribution of ^{115}In CSA on the NMR pattern of $[\text{In}([18]\text{crown-6})][\text{AlCl}_4]$.

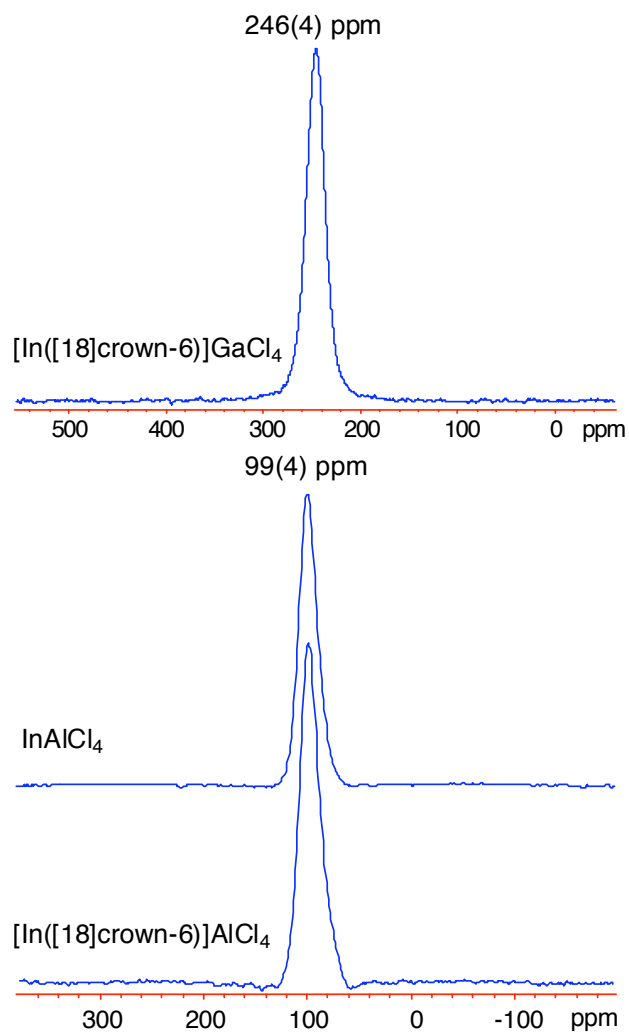


Figure S11. Static ^{71}Ga SSNMR spectrum of $[\text{In}([\text{18}]\text{crown-6})][\text{GaCl}_4]$ and ^{27}Al SSNMR spectra of AlCl_4 and $[\text{In}([\text{18}]\text{crown-6})][\text{AlCl}_4]$ at 9.4 T.

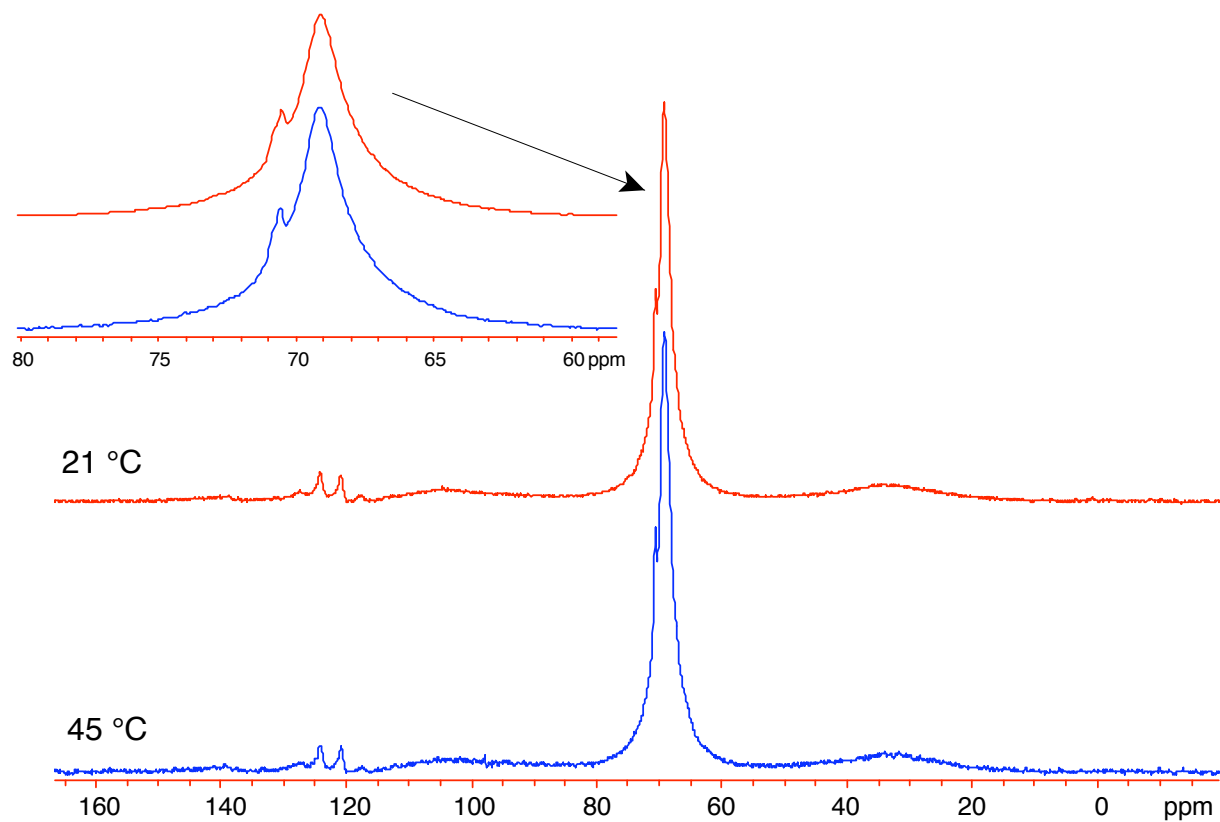


Figure S12. ^{13}C MAS NMR spectra of $[\text{In}([\text{15}]\text{crown-5})_2][\text{OTf}]$ at 21 °C and at 45 °C.

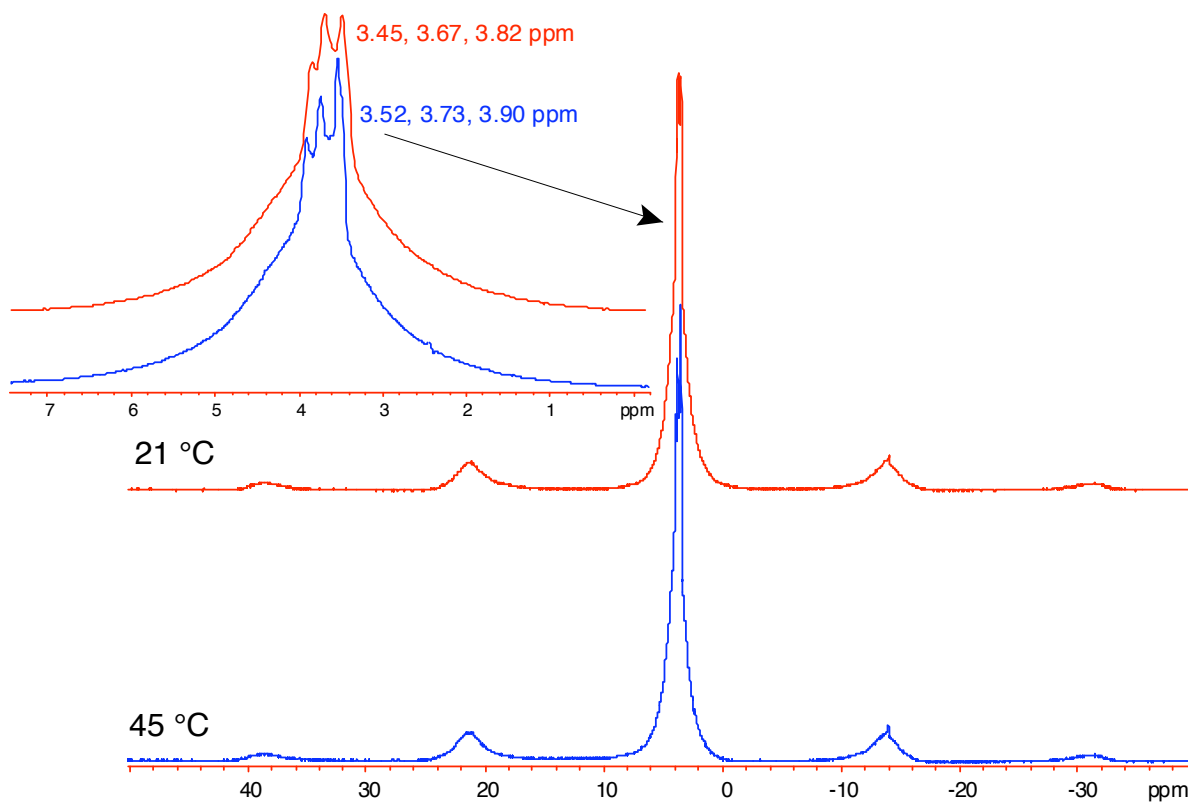


Figure S13. ¹H MAS NMR spectra of [In([15]crown-5)₂][OTf] at 21 °C and at 45 °C.

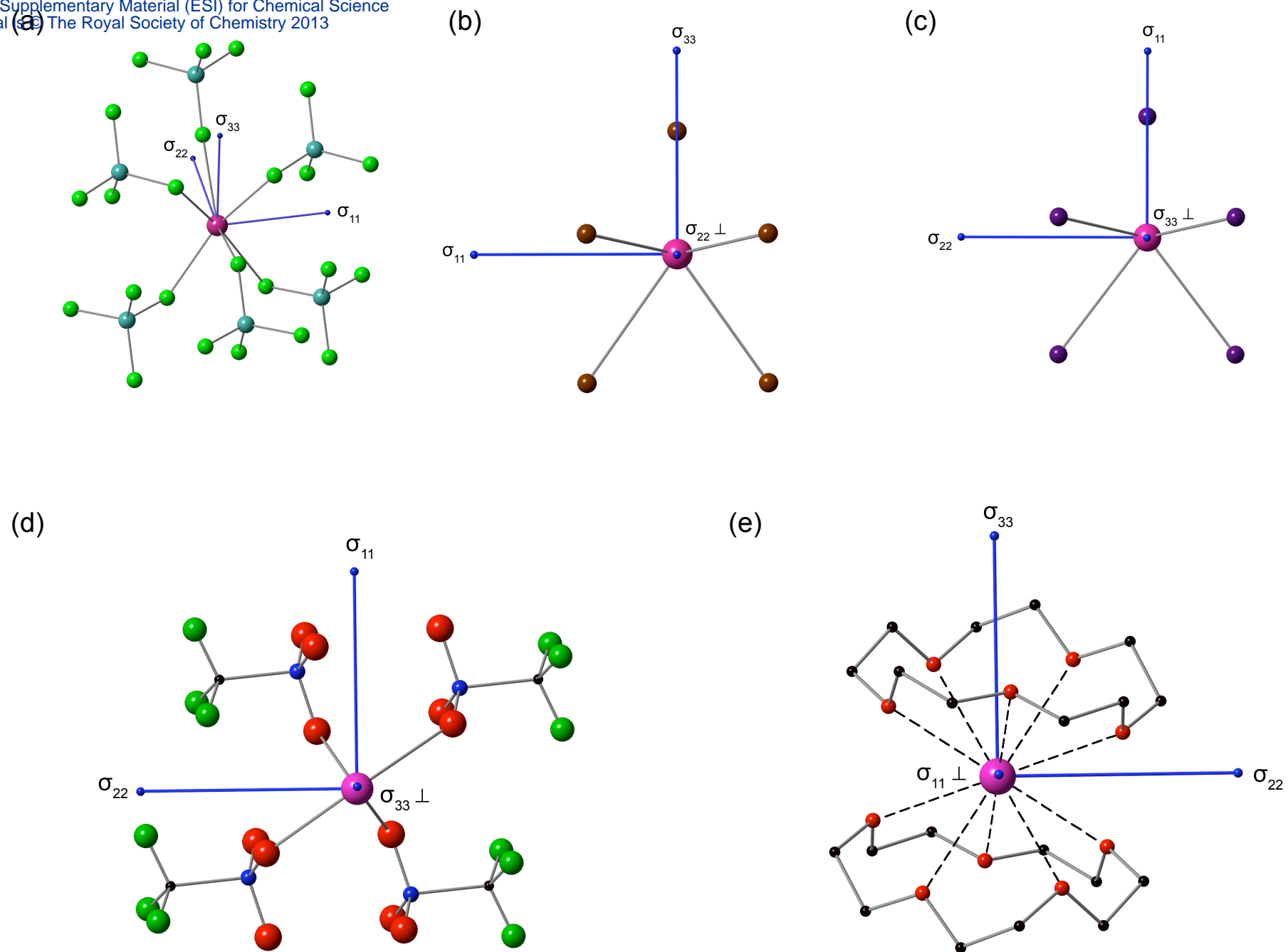


Figure S14. The ^{115}In NS tensor orientations in (a) $[In][GaCl_4]$, (b) $InBr$, (c) InI , (d) $[In][OTf]$ (In site 2) and (e) $[In([15]crown-5)]_2[OTf]$.