

Supporting Information

Silver Halide Complexes of a Borane/Bis(Phosphine) Ligand

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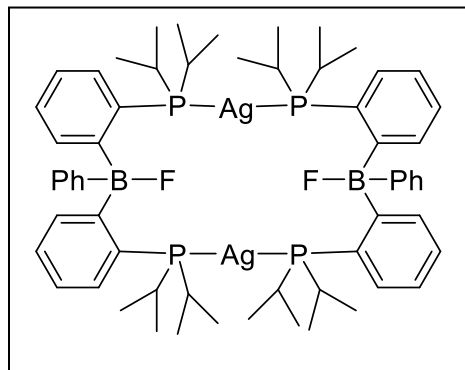
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I. General Considerations.

General Considerations. Unless specified otherwise, all manipulations were performed under an Ar atmosphere using standard Schlenk line or glovebox techniques. Toluene, diethyl ether, pentane, and isooctane were dried and deoxygenated (by purging) using a solvent purification system (Innovative Technology Pure Solv MD-5 Solvent Purification System) and stored over molecular sieves in an Ar-filled glove box. C_6D_6 was dried over NaK/Ph₂CO/18-crown-6, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glovebox. CH_2Cl_2 , $CDCl_3$, cyclohexane, and C_6D_{12} were dried over CaH_2 , distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glove box. All other chemicals were used as received from commercial vendors.

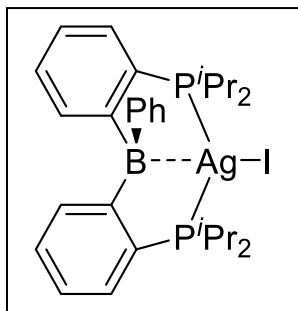
Physical Methods. NMR spectra were recorded on a Varian Inova 400 (1H NMR, 399.535 MHz; ^{11}B NMR, 128.185 MHz; ^{31}P NMR, 161.734 MHz) and Varian Inova 500 (1H NMR, 499.703 MHz; ^{13}C NMR, 125.697 MHz; ^{31}P NMR, 202.265 MHz; ^{19}F NMR, 470.106 Hz) spectrometer. Chemical shifts are reported in δ (ppm). For 1H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference (1H NMR: δ 7.16 for C_6D_6 , 7.24 for $CDCl_3$; ^{13}C NMR: δ 128.62 for C_6D_6 , 77.16 for $CDCl_3$). ^{11}B NMR spectra were referenced externally with BF_3 etherate at δ 0. ^{31}P NMR spectra were referenced externally with 85% phosphoric acid at δ 0. ^{19}F NMR spectra were referenced with pure trifluoro acetic acid to δ -78.5 ppm. Elemental analyses were performed by CALI Labs, Inc. (Highland Park, NJ).

II. Synthesis and Characterization of Silver Complexes.



1-F. To a solution of $\text{PB}^{\text{Ph}}\text{P}$ (71 mg, 0.15 mmol) in toluene (1 mL) was added silver fluoride (19 mg, 0.15 mmol), and the resulting suspension was stirred at room temperature overnight. The solution was filtered through Celite, and the volatiles were removed under vacuum. The resulting solid

was recrystallized in toluene layer pentane (1:3), yielding a white solid (80 mg, 89%). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): δ 25.2 (ddd, $J_{\text{P-P}} = 134$ Hz, $J_{\text{P-F}} = 81$ Hz, $J^{107}_{\text{Ag-P}} = 459$ Hz, $J^{109}_{\text{Ag-P}} = 530$ Hz), 36.6 (ddd, $J_{\text{P-P}} = 134$ Hz, $J_{\text{P-F}} = 103$ Hz, $J^{107}_{\text{Ag-P}} = 502$ Hz, $J^{109}_{\text{Ag-P}} = 579$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ 7.7 (br). ^{19}F NMR (470 MHz, C_6D_6) δ -181.7 (br). ^1H NMR (500 MHz, C_6D_6) δ 8.78 (d, $J_{\text{H-H}} = 5.2$ Hz, 1H), 7.49 (m, 1H), 7.36 (m, 2H), 7.12 (m, 5H), 7.03 (t, $J_{\text{H-H}} = 7.1$ Hz, 1H), 6.97 (d, $J_{\text{H-H}} = 7.4$ Hz, 1H), 6.83 (t, $J_{\text{H-H}} = 7.3$ Hz, 1H), 6.07 (t, $J_{\text{H-H}} = 7.1$ Hz, 1H), 2.80 (m, 1H, CHMe_2), 2.27 (m, 1H, CHMe_2), 2.14 (m, 1H, CHMe_2), 2.08 (m, 1H, CHMe_2), 1.28 (m, 6H, CHMe_2), 1.17 (dd, $J_{\text{H-H}} = 18.1$ Hz, $J_{\text{H-P}} = 7.6$ Hz, 3H, CHMe_2), 1.01 (m, 6H, CHMe_2), 0.94 (dd, $J_{\text{H-H}} = 16.8$ Hz, $J_{\text{H-P}} = 6.7$ Hz, 3H, CHMe_2), 0.78 (dd, $J_{\text{H-H}} = 8.9$ Hz, $J_{\text{H-P}} = 7.5$ Hz, 3H, CHMe_2), 0.74 (dd, $J_{\text{H-H}} = 15.2$ Hz, $J_{\text{H-P}} = 7.0$ Hz, 3H, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6) δ 167.5 (s), 162.9 (s), 158.9 (s), 139.1 (dd, $J_{\text{P-C}} = 12.4$ Hz, $J_{\text{P-C}} = 7.7$ Hz), 137.0 (d, $J_{\text{P-C}} = 14.4$ Hz), 135.4 (s), 133.9 (m), 132.1 (s), 129.9 (d, $J_{\text{P-C}} = 3.5$ Hz), 129.4 (s), 129.0 (s), 128.4 (s), 128.2 (d, $J_{\text{P-C}} = 1.9$ Hz), 127.7 (s), 127.1 (s), 125.5 (s), 124.9 (d, $J_{\text{P-C}} = 4.6$ Hz), 124.4 (d, $J_{\text{P-C}} = 5.8$ Hz), 27.8 (dd, $J_{\text{P-C}} = 12.4$ Hz, $J_{\text{P-C}} = 3.8$ Hz), 25.9 (dd, $J_{\text{P-C}} = 13.1$ Hz, $J_{\text{P-C}} = 5.0$ Hz), 24.6 (dd, $J_{\text{P-C}} = 11.7$ Hz, $J_{\text{P-C}} = 5.5$ Hz), 23.5 (d, $J_{\text{P-C}} = 12.6$ Hz), 23.2 (d, $J_{\text{P-C}} = 13.1$ Hz), 22.1 (d, $J_{\text{P-C}} = 6.7$ Hz), 22.0 (d, $J_{\text{P-C}} = 6.1$ Hz), 21.2 (t, $J_{\text{P-C}} = 10.9$ Hz), 21.0 (t, $J_{\text{P-C}} = 9.4$ Hz), 16.3 (dd, $J_{\text{P-C}} = 7.8$, 4.7 Hz). Elem. Anal. Calcd. for $\text{C}_{60}\text{H}_{82}\text{Ag}_2\text{B}_2\text{F}_2\text{P}_4$: C, 59.93; H, 6.87. Found: C, 60.04; H, 6.89



1-I. To a solution of **1-F** (60 mg, 0.050 mmol) in toluene (4 mL) was added iodotrimethylsilane (20 μ L, 0.10 mmol), and the resulting mixture was stirred at 55 $^{\circ}$ C overnight. Large amounts of solid crashed out gradually during the heating. The volatiles were removed under vacuum,

and the resulting solid was recrystallized in THF layer pentane (1:2), yielding a fluorescent green solid (48 mg, 68 %). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6): δ 32.7 (d, $J_{^{109}\text{Ag-P}} = 410$ Hz), 36.8 (d, $J_{^{107}\text{Ag-P}} = 354$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6): δ 63.5 (br). ^1H NMR (500 MHz, C_6D_6) δ 7.38 (dd, $J_{\text{H-H}} = 7.0, 2.4$ Hz, 2H), 7.21 (d, $J_{\text{H-H}} = 7.5$ Hz, 2H), 7.16 (m, 3H), 7.09 (m, 4H), 7.02 (td, $J_{\text{H-H}} = 7.5, 0.7$ Hz, 2H), 2.39 (m, 2H, CHMe_2), 2.13 (m, 2H, CHMe_2), 1.31 (m, 12H, CHMe_2), 1.09 (dvt, 6H, CHMe_2), 0.78 (dvt, 6H, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 155.8 (m), 144.4 (s), 135.6 (s), 135.4 (td, $J_{\text{P-C}} = 13.3$ Hz, $J_{\text{C-Ag}} = 3.9$ Hz), 132.2 (s), 131.7 (m), 131.5 (t, $J_{\text{P-C}} = 10.3$ Hz), 129.6 (s), 128.3 (s), 127.9 (s), 26.5 (t, $J_{\text{P-C}} = 8.3$ Hz), 24.8 (m), 20.6 (t, $J_{\text{P-C}} = 4.0$ Hz), 20.2 (t, $J_{\text{P-C}} = 4.4$ Hz), 19.5 (s), 17.9 (s). Elem. Anal. Calcd. for $\text{C}_{30}\text{H}_{41}\text{AgBIP}_2$: C, 50.81; H, 5.83. Found: C, 50.57; H, 5.63.

NMR tube reaction to generate 1-Cl. To a solution of **1-F** (12 mg, 0.010 mmol) in C_6D_6 (400 μ L) was added chlorotrimethylsilane (5.0 μ L, 0.040 mmol), and the resulting mixture was heated at 55 $^{\circ}$ C overnight. The *in situ* ^1H NMR (500 MHz, C_6D_6) spectrum indicated the generation of TMSF (0.020 ppm, singlet). The volatiles were removed under vacuum, and the resulting solid was redissolved in C_6D_6 for spectroscopic analysis, showing 97% **1-Cl** in solution according to $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, and the spectroscopic details are similar to **1-I**. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6): δ 36.8 (d, $J_{^{109}\text{Ag-P}} = 430$ Hz), 36.8 (d, $J_{^{107}\text{Ag-P}} = 372$ Hz). ^{11}B NMR (128 MHz, C_6D_6): δ 61.4 (br). ^1H NMR (500 MHz, C_6D_6) δ 7.39 (m, 2H), 7.26 (d, $J_{\text{H-H}} = 7.5$ Hz, 2H), 7.16 (m, 3H), 7.08 (m, 4H), 7.03 (t, $J_{\text{H-H}}$

= 7.1 Hz, 2H), 2.30 (m, 2H, CHMe₂), 2.12 (m, 2H, CHMe₂), 1.34 (dvt, 6H, CHMe₂), 1.28 (dvt, 6H, CHMe₂), 1.08 (dvt, 6H, CHMe₂), 0.81 (dvt, 6H, CHMe₂).

NMR tube reaction to generate 1-Br. To a solution of **1-F** (12 mg, 0.010 mmol) in C₆D₆ (400 μL) was added bromotrimethylsilane (5.0 μL, 0.040 mmol), and the resulting mixture was heated at 55 °C overnight. The *in situ* ¹H NMR (500 MHz, C₆D₆) spectrum indicated the generation of TMSF (0.020 ppm, singlet). The volatiles were removed under vacuum, and the resulting solid was redissolved in C₆D₆ for spectroscopic analysis, showing at least 98% **1-Br** in solution (¹H NMR evidence), which has similar spectroscopic details to **1-I**. ³¹P{¹H} NMR (202 MHz, C₆D₆): δ 35.8 (d, *J*¹⁰⁹_{Ag-P} = 424 Hz), 35.8 (d, *J*¹⁰⁷_{Ag-P} = 367 Hz). ¹¹B NMR (128 MHz, C₆D₆): δ 61.8 (br). ¹H NMR (500 MHz, C₆D₆) δ 7.39 (m, 2H), 7.24 (d, *J*_{H-H} = 7.5 Hz, 2H), 7.16 (m, 3H), 7.05 (m, 4H), 7.03 (t, *J*_{H-H} = 7.4 Hz, 2H). 2.33 (m, 2H, CHMe₂), 2.11 (m, 2H, CHMe₂), 1.31 (m, 12H, CHMe₂), 1.08 (dvt, 6H, CHMe₂), 0.80 (dvt, 6H, CHMe₂).

Table S1. ¹¹B{¹H} NMR, ³¹P{¹H} NMR chemical shifts and J Values (in Hz) of Ag Complexes

	¹¹ B{ ¹ H} NMR	³¹ P{ ¹ H} NMR	<i>J</i> ¹⁰⁷ _{Ag-P}	<i>J</i> ¹⁰⁹ _{Ag-P}
1-F	7.7	25.2; 36.6	459; 502	530; 579
1-Cl	61.5	36.8	372	430
1-Br	61.8	35.8	367	424
1-I	63.6	32.7	354	410

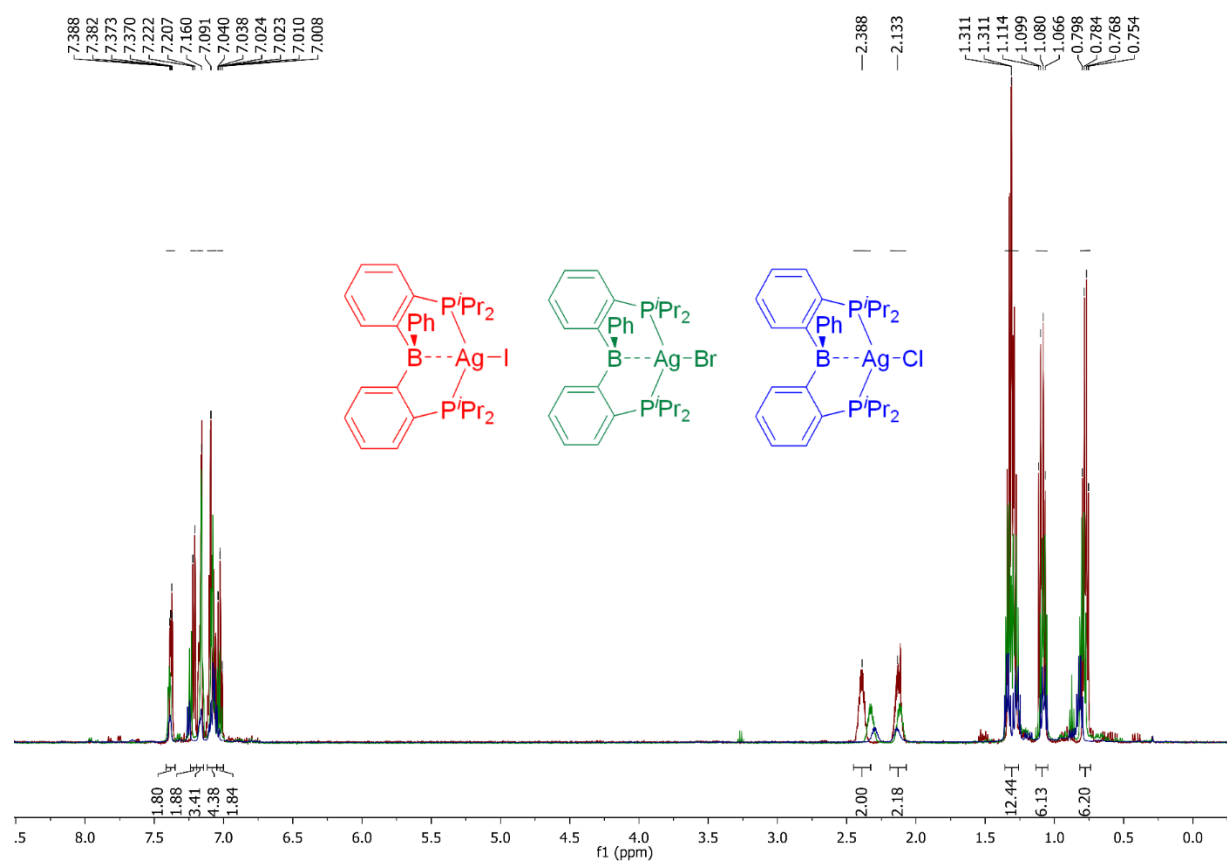


Figure S1. ^1H NMR stacked spectrum (500 MHz, C_6D_6) of **1-I/Br/Cl** in C_6D_6 . Red, **1-I**; Green, **1-Br**; Blue, **1-Cl**.

III. X-Ray Structural Determination Details.

X-Ray data collection, solution, and refinement for $[(\text{PB}^{\text{Ph,F}}\text{P})\text{Ag}]_2$ (1-F, CCDC 1874148). A colorless, multi-faceted block of suitable size (0.52 x 0.29 x 0.28 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, $K_{\alpha} = 0.71073 \text{ \AA}$). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.¹ An absorption correction was applied using SADABS.² The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2 . The structure was solved in the monoclinic $P2_1/n$ space group using XS³ (incorporated in SHELXL). All non-hydrogen atoms were refined with anisotropic thermal parameters. Elongated thermal ellipsoids and the residual electron densities close to toluene and two of the isopropyl groups suggested disorder which were modeled between two positions each. Appropriate restraints and/or constraints were added to keep the bond distances, thermal ellipsoids of the disordered groups meaningful. All hydrogen atoms were placed in idealized positions and refined using riding model. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged. No additional symmetry was found using ADDSYM incorporated in PLATON program.⁴

X-Ray data collection, solution, and refinement for $(\text{PB}^{\text{Ph}}\text{P})\text{AgI}$ (1-I, CCDC 1874150). A Leica MZ 75 microscope was used to identify a suitable colorless block with well-defined faces with dimensions 0.467 x 0.372 x 0.304 mm³ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford)

maintained at 110 K. A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0.¹ The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube ($K_{\alpha} = 0.71073\text{\AA}$ with a potential of 40 kV and a current of 40 mA). 45 data frames were taken at widths of 1.0° . These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the $h\ k\ l$ overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (15 sets) was initiated using omega scans. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.¹ The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS² was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/n$. A solution was obtained readily using XT/XS in APEX2.^{1,3,5} Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Absence of additional symmetry and voids were confirmed

using PLATON (ADDSYM). The structure was refined (weighted least squares refinement on F^2) to convergence.^{3,5-6} Olex2 was employed for the final data presentation.⁶

IV. NMR Spectra

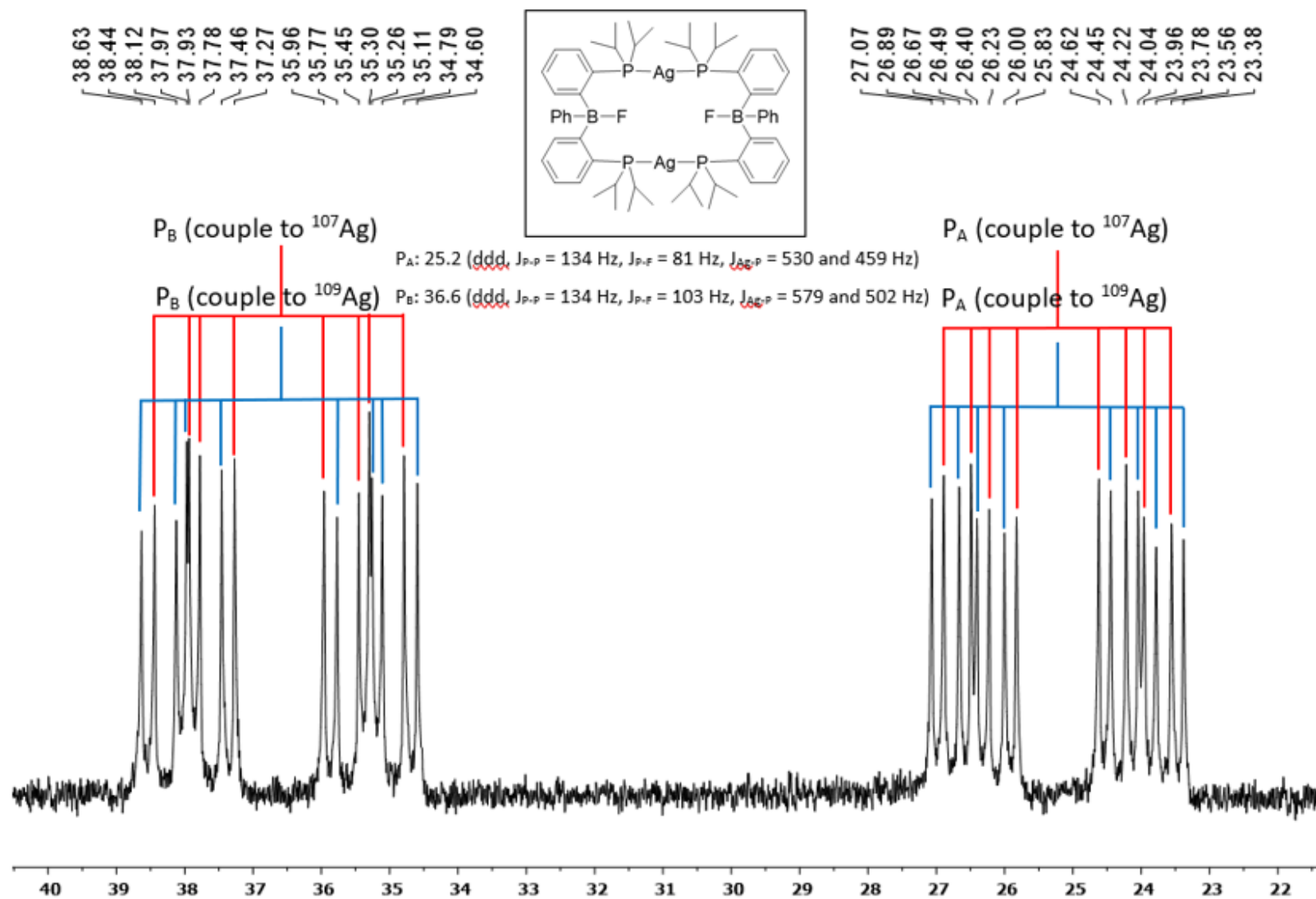


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1-F** in C_6D_6 at RT measured on a 500 MHz Varian NMR.

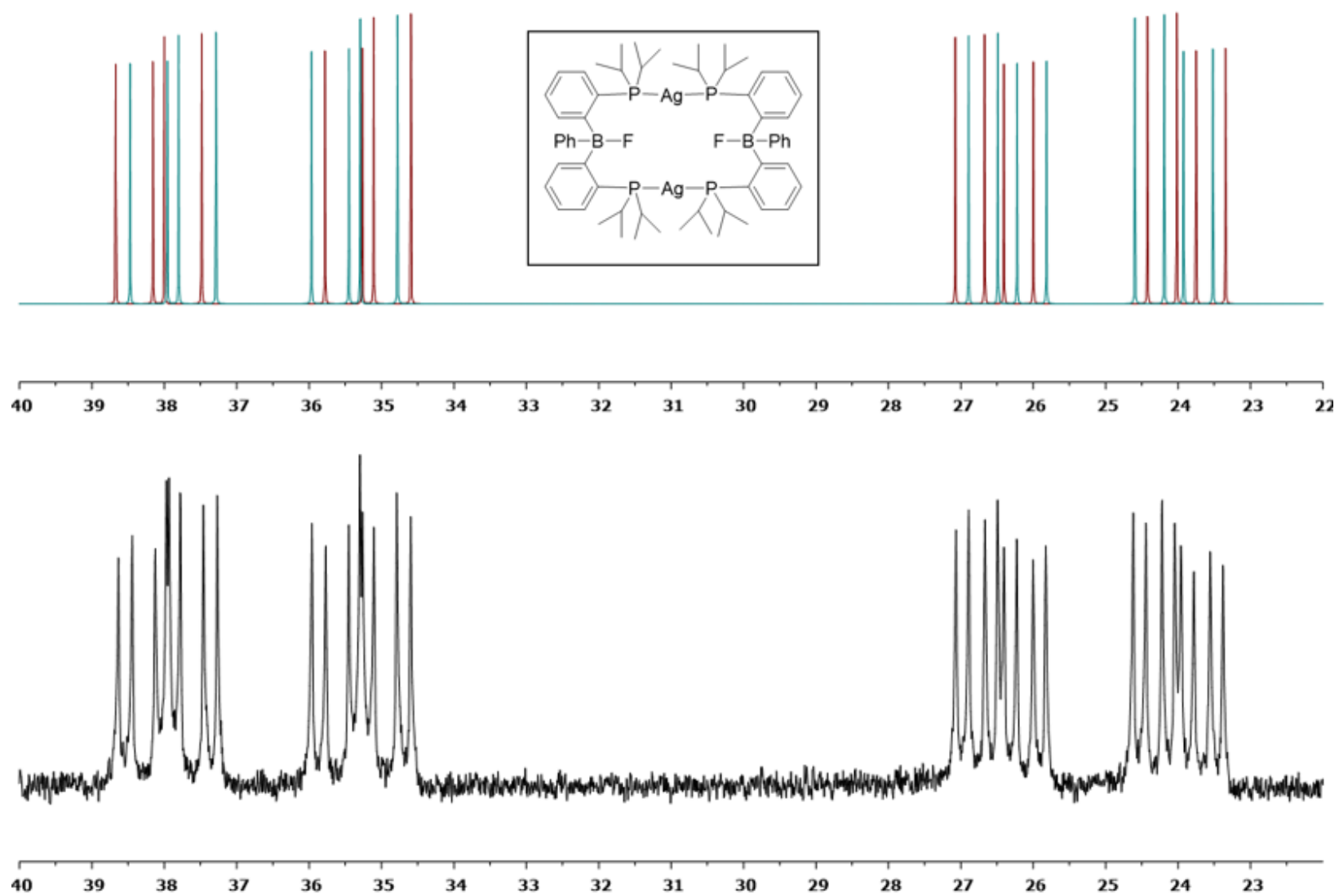


Figure S3. Simulation (using Mestrnova software and the parameters shown in Figure S2) of $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1-F** (top) and comparison with experimental spectrum (bottom).

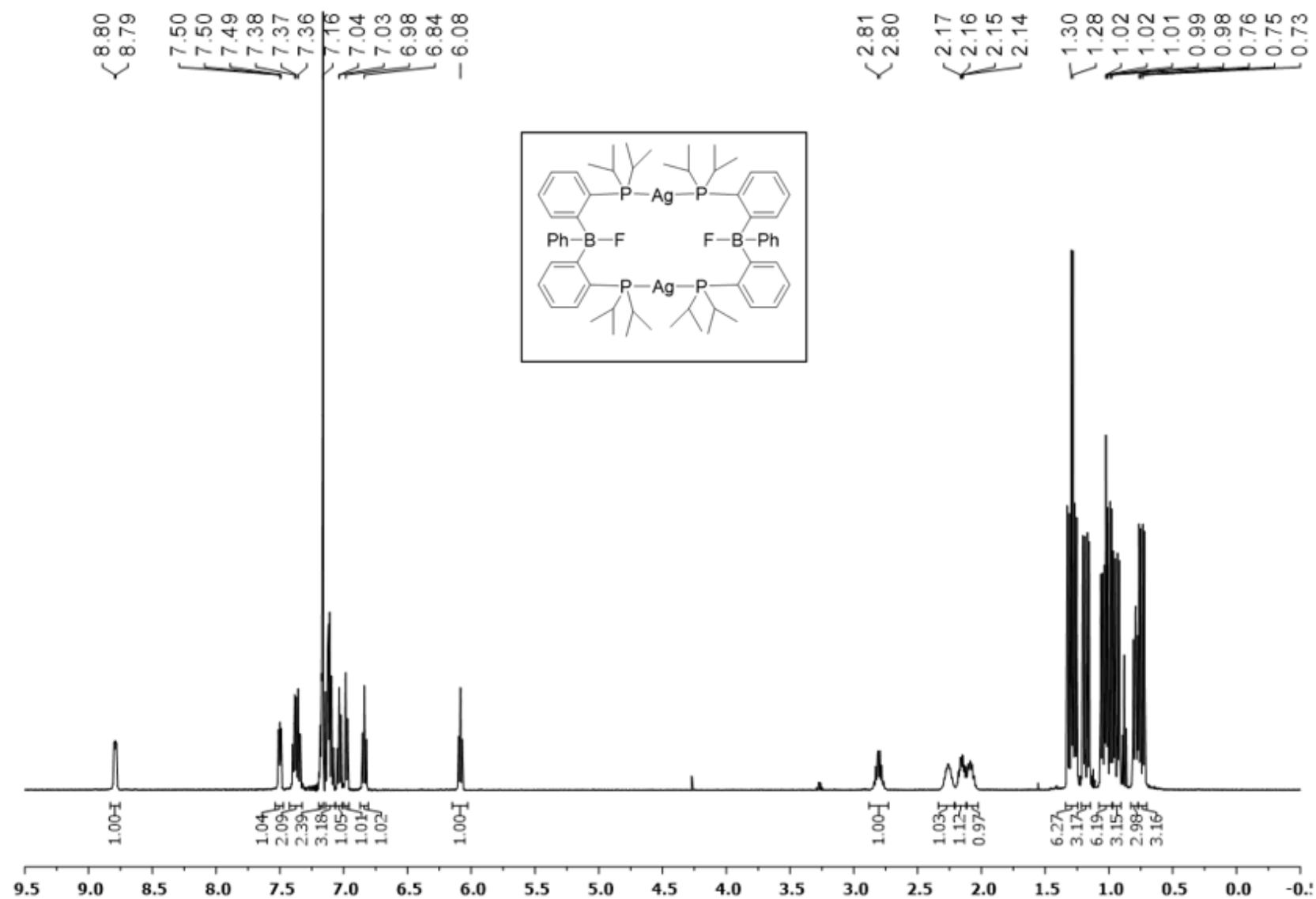


Figure S4. ^1H NMR spectrum of **1-F** in C_6D_6 at RT measured on a 500 MHz Varian NMR.

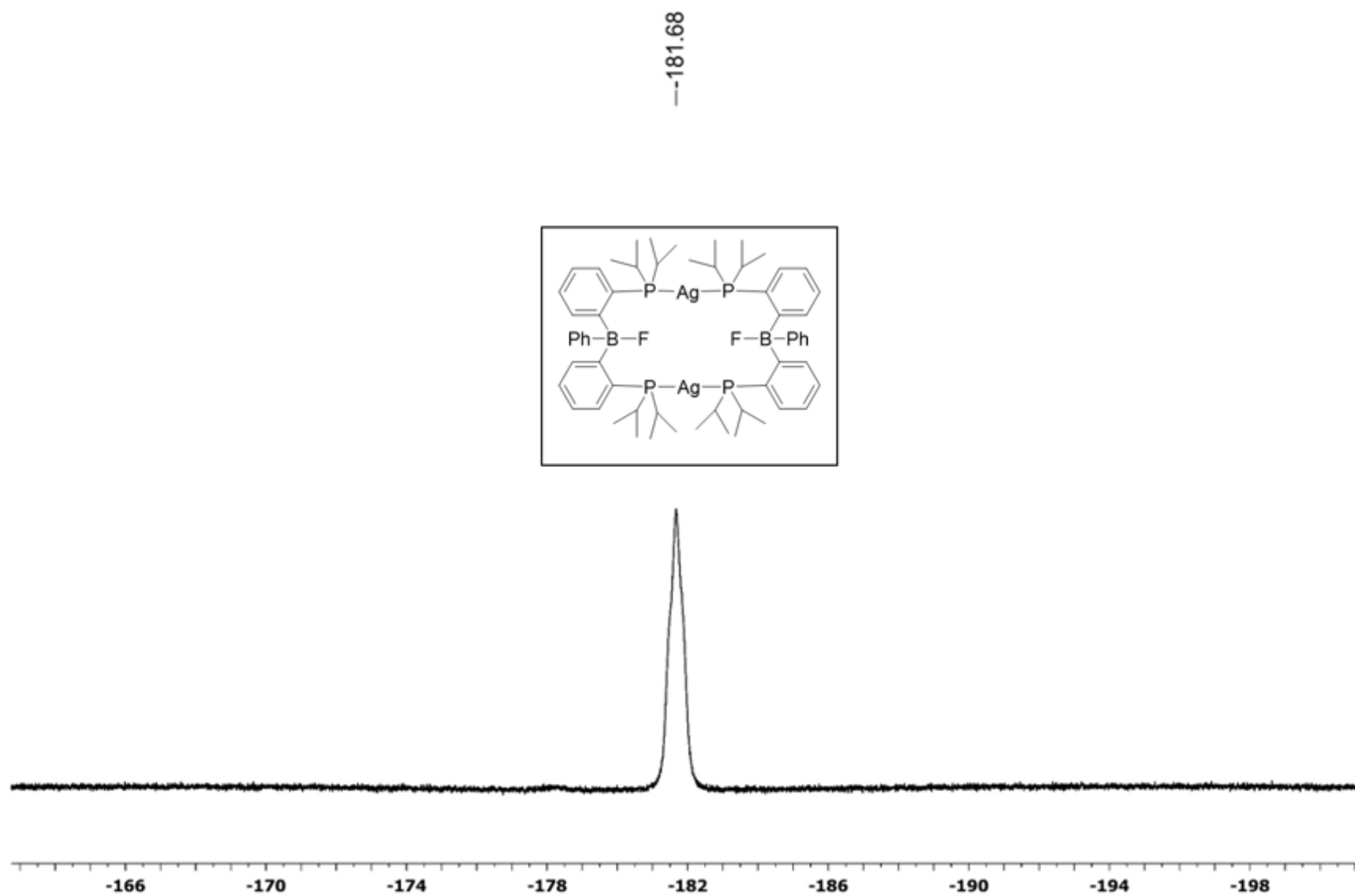


Figure S5. ^{19}F NMR spectrum of **1-F** in C_6D_6 at RT measured on a 500 MHz Varian NMR.

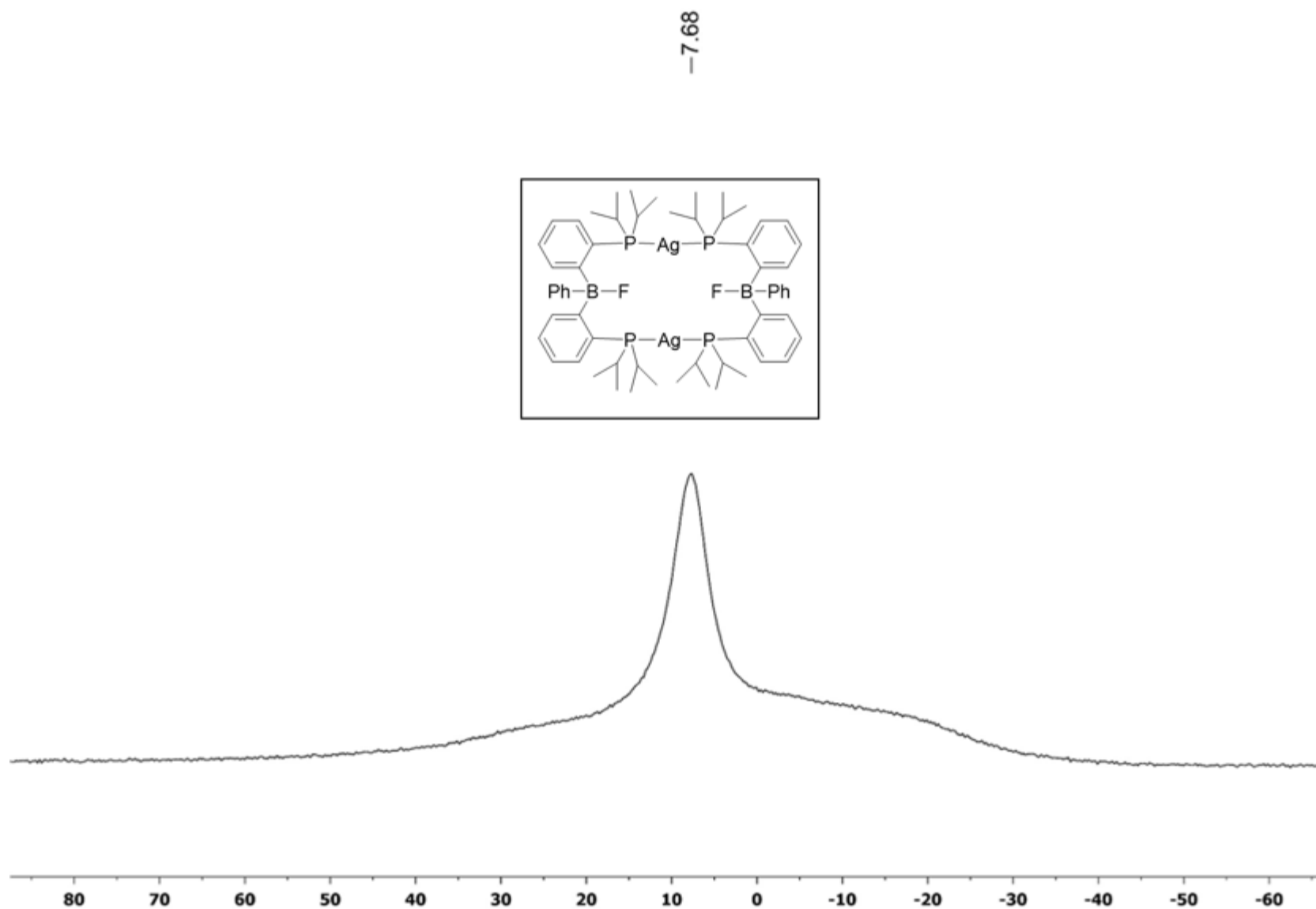


Figure S6. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **1-F** in C_6D_6 at RT measured on a 400 MHz Varian NMR.

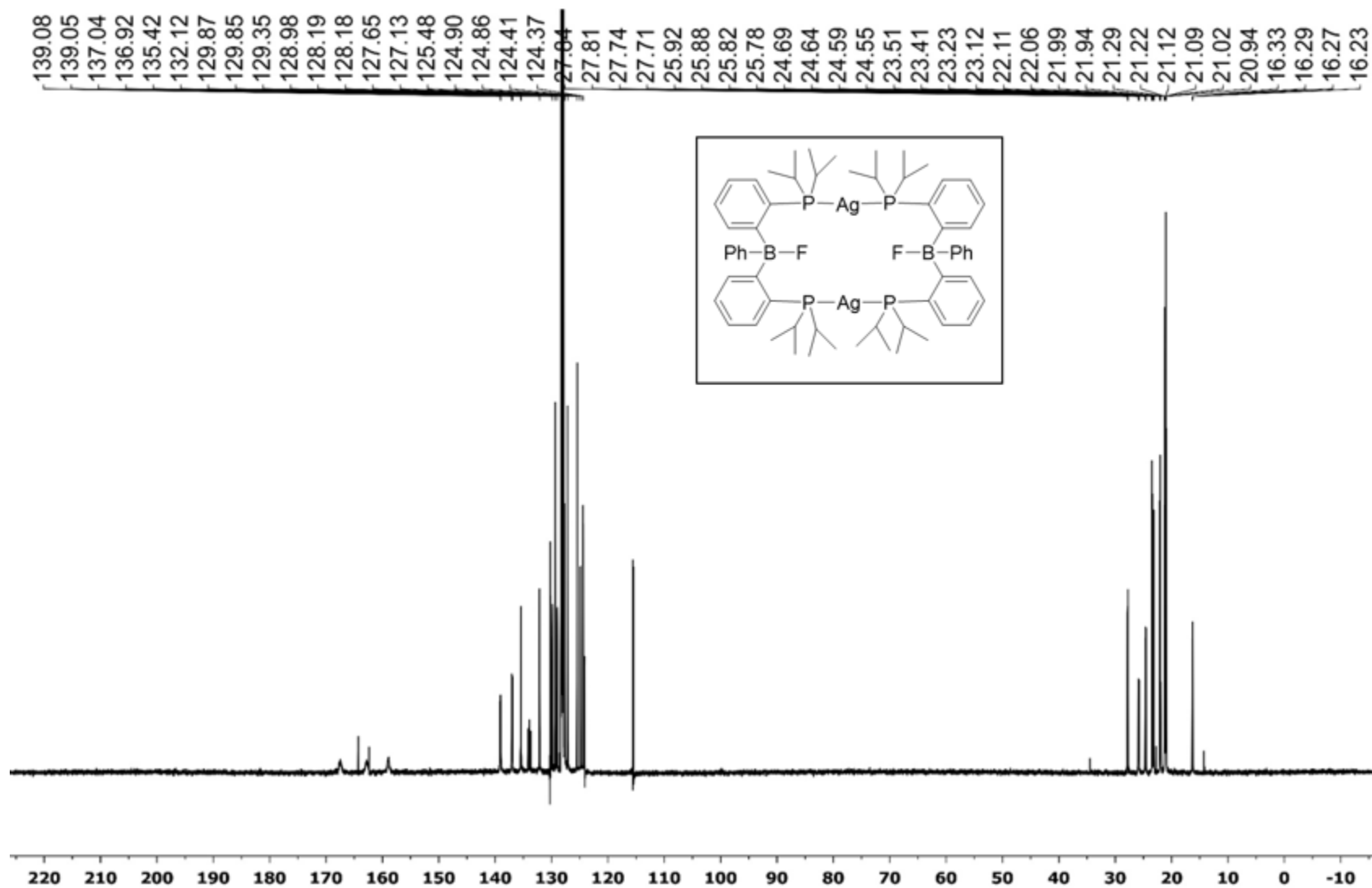


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1-F** in CDCl_3 at RT measured on a 500 MHz Varian NMR.

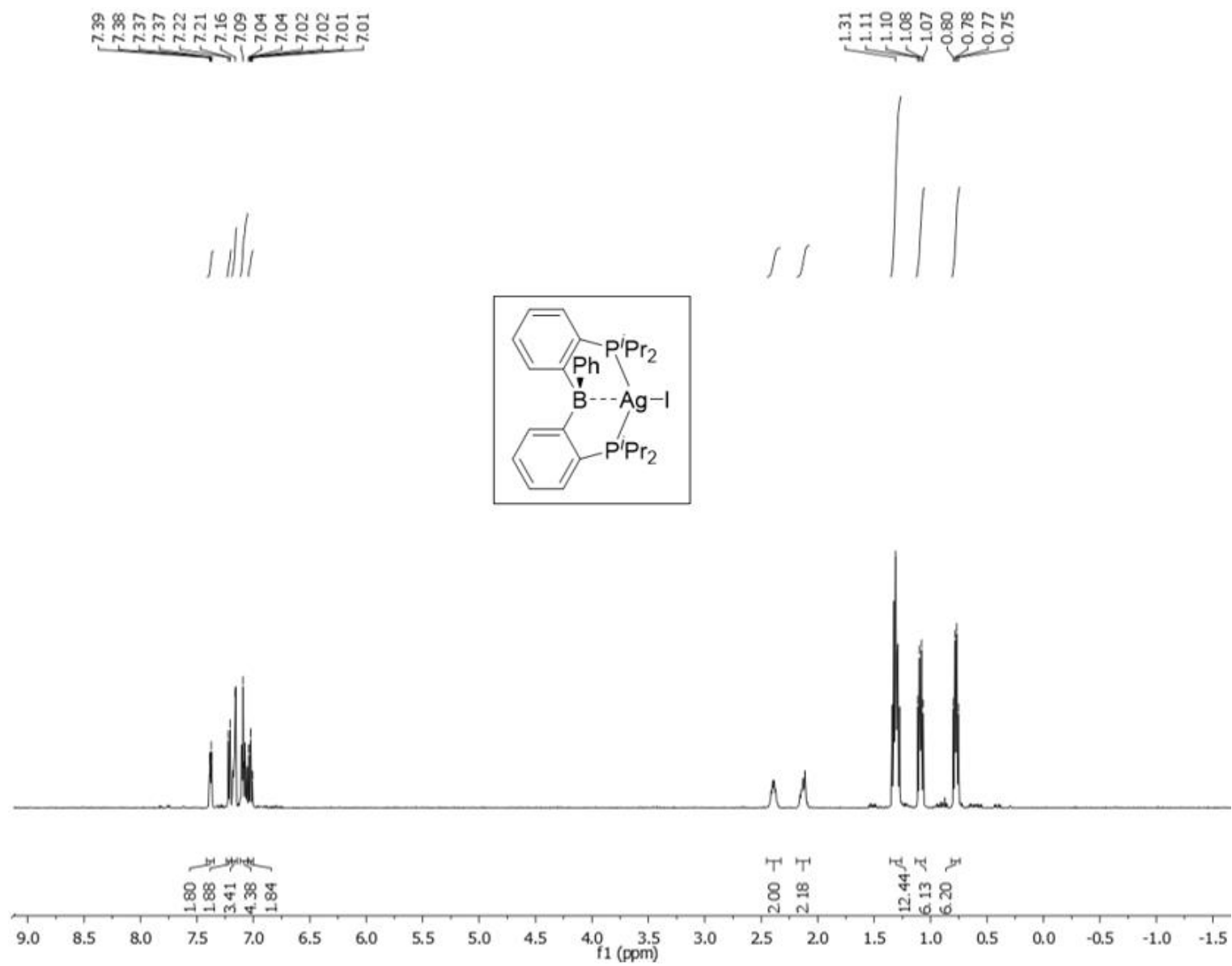


Figure S8. ^1H NMR spectrum of **1-I** in C_6D_6 at RT measured on a 500 MHz Varian NMR.

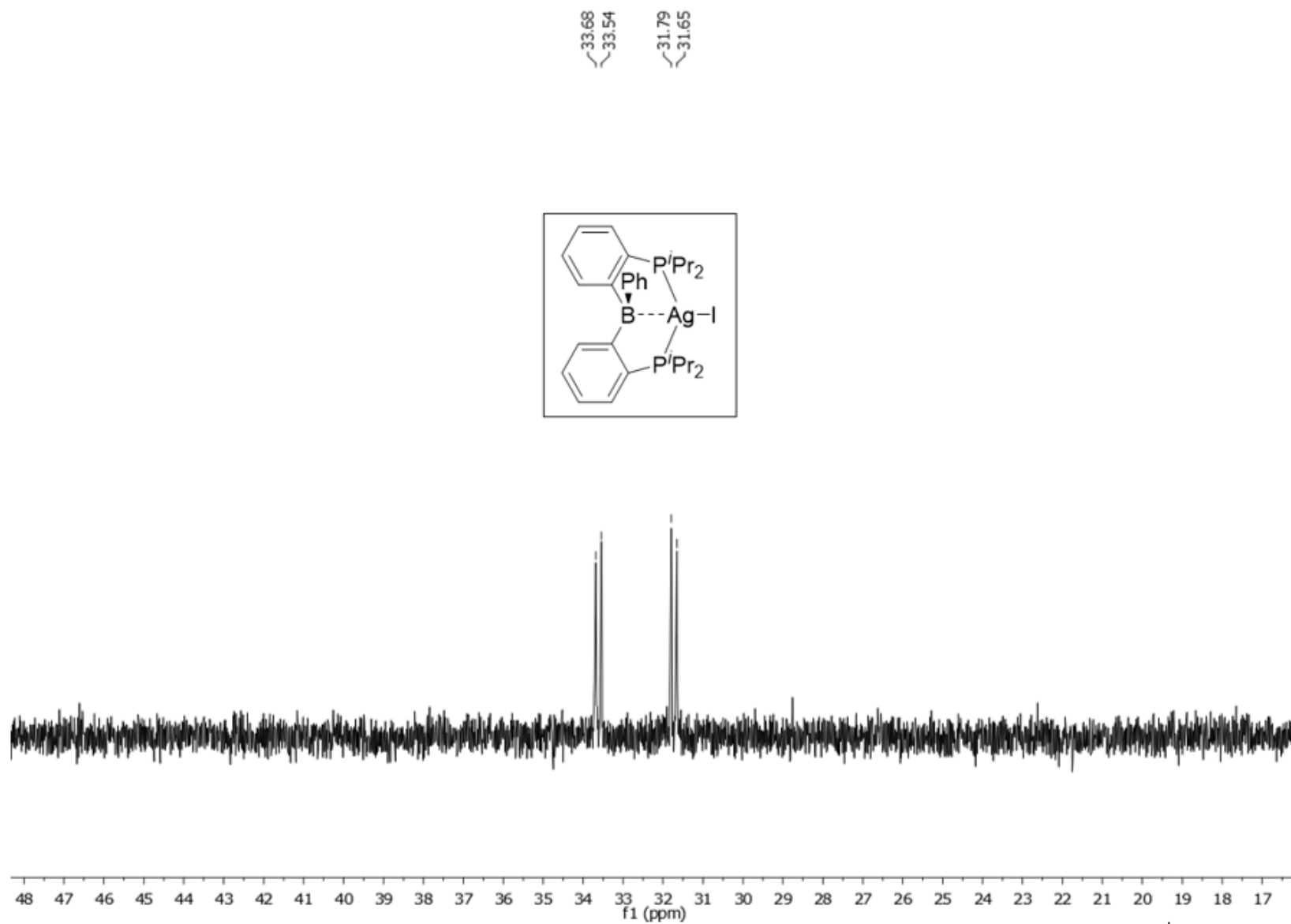


Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1-I** in C_6D_6 at RT measured on a 500 MHz Varian NMR.

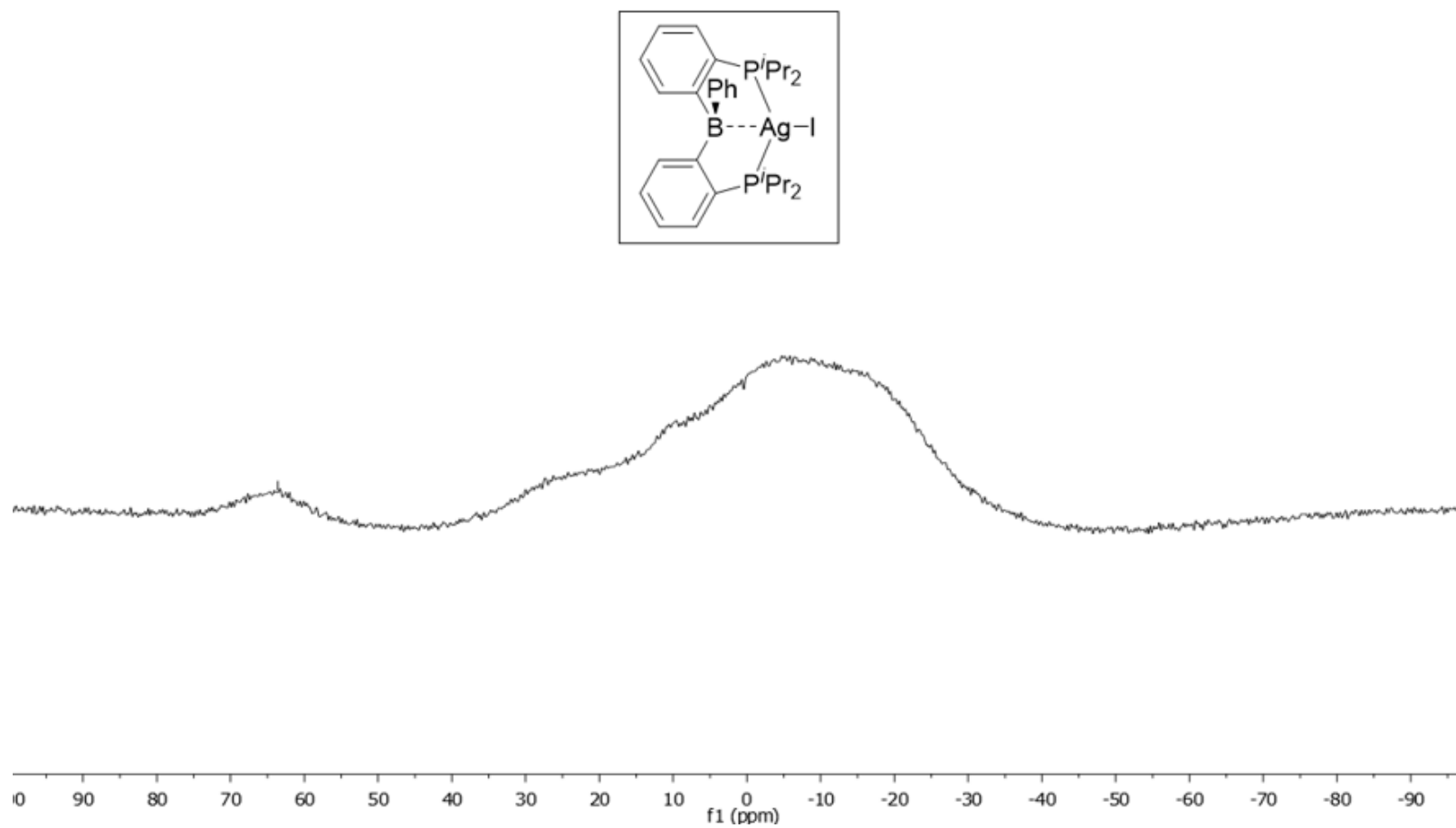


Figure S10. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **1-I** in C_6D_6 at RT measured on a 400 MHz Varian NMR.

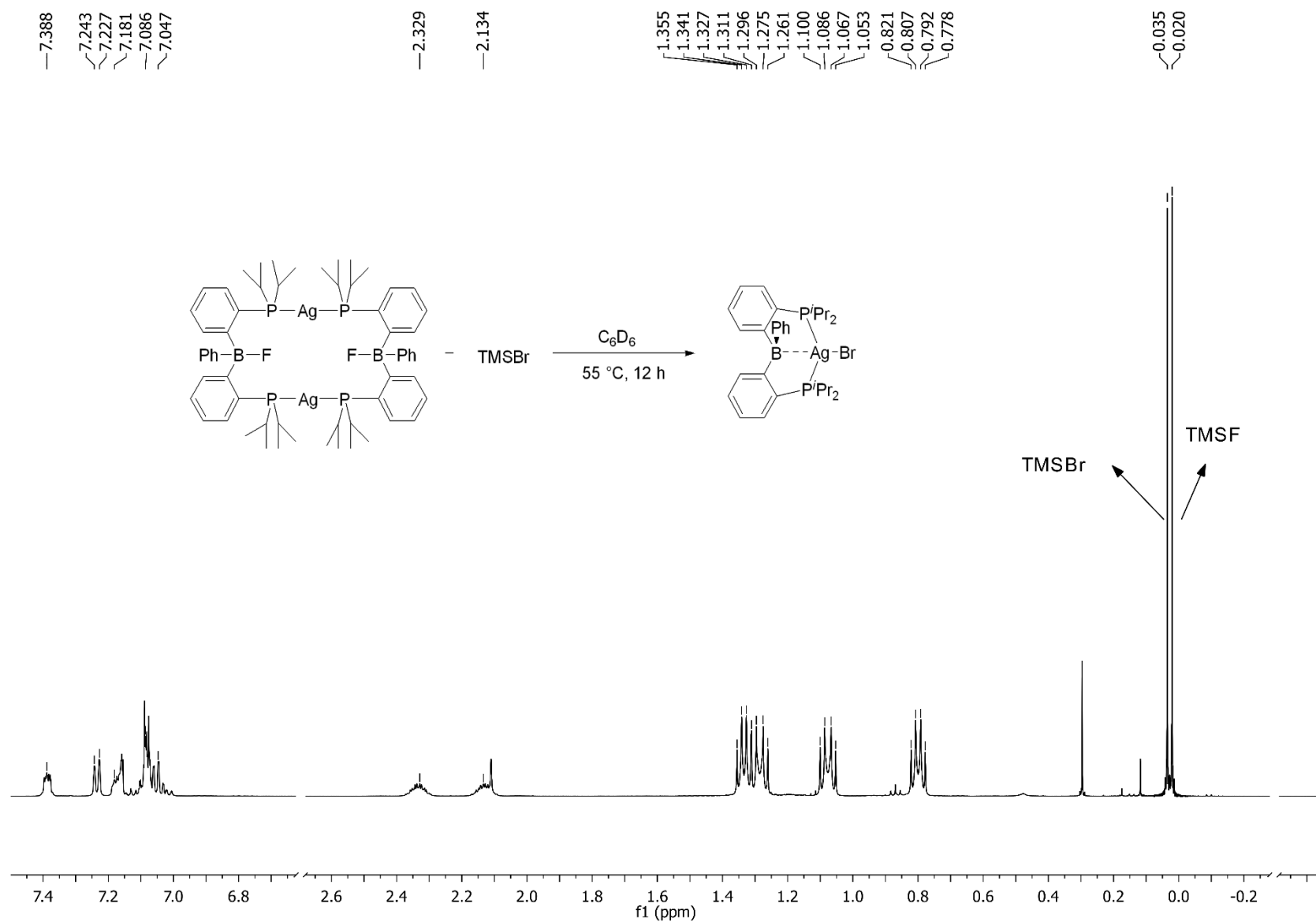


Figure S12. ^1H NMR (500 MHz, C_6D_6) recorded after addition of TMSBr to **1-F**, and heating at $55\text{ }^\circ\text{C}$ for 12 h.

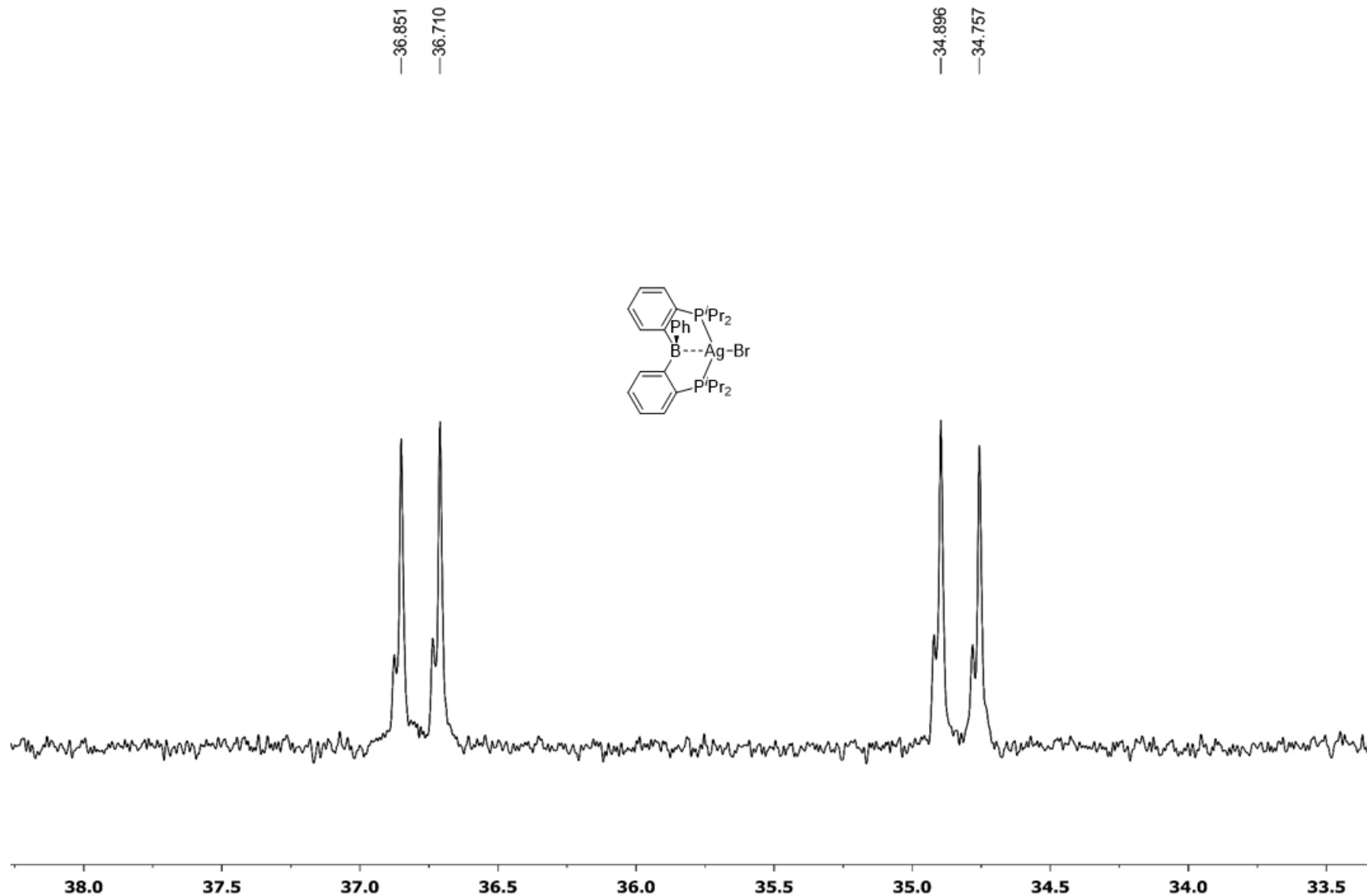


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6) spectrum recorded after addition of TMSBr to **1-F**, and heating at 55 °C for 12 h.

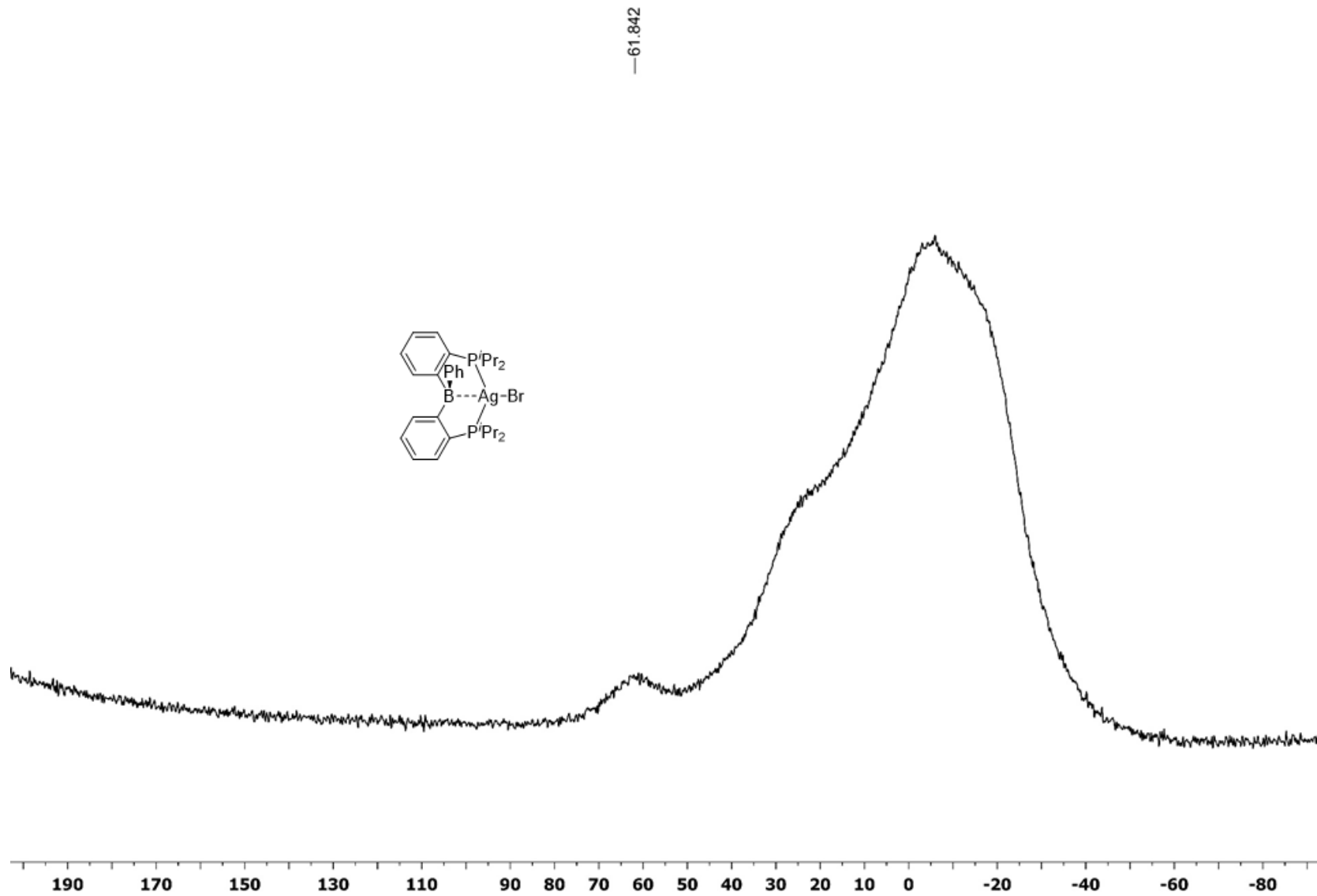


Figure S14. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6) spectrum recorded after addition of TMSBr to **1-F**, and heating at 55 °C for 12 h.

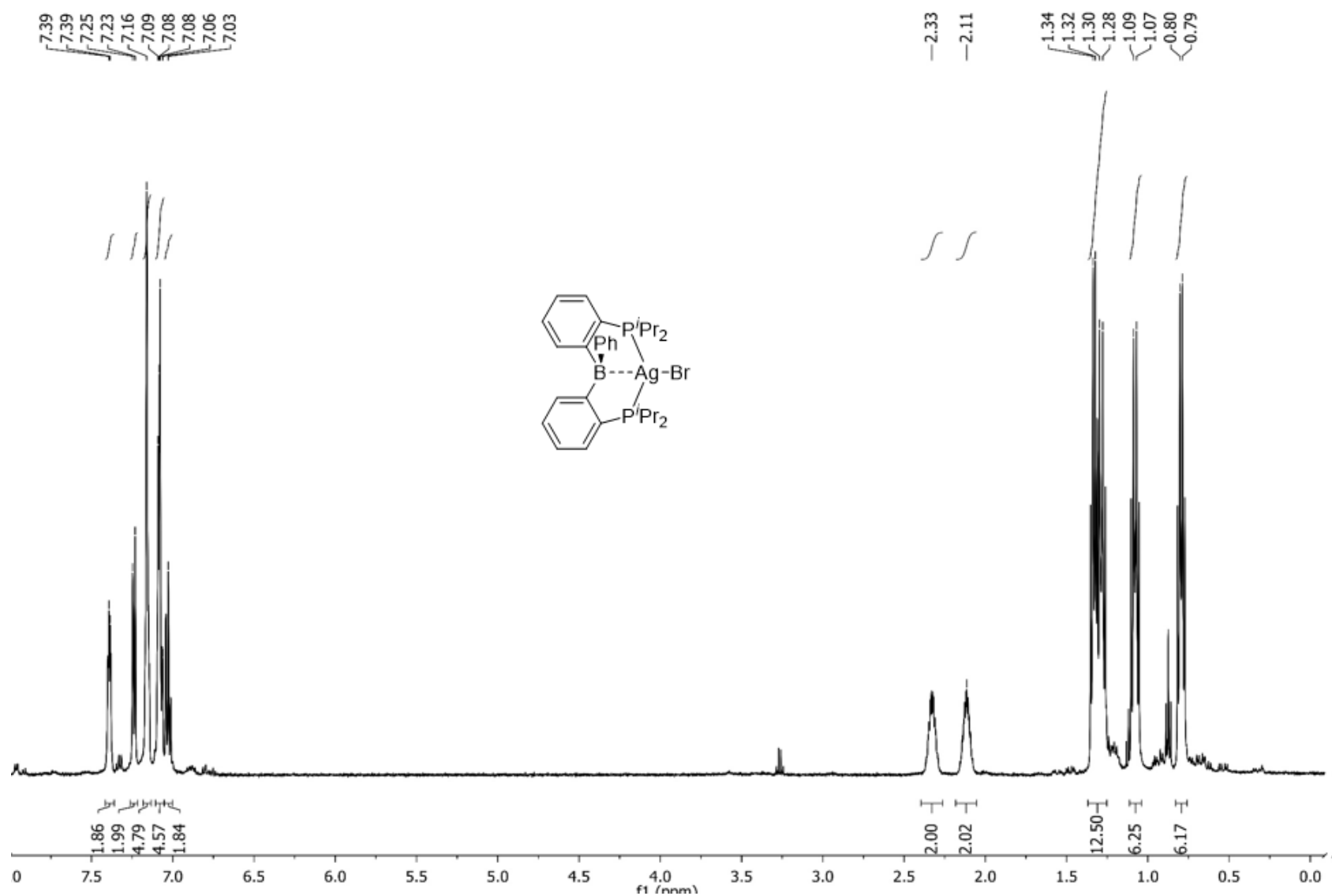


Figure S15. ¹H NMR spectrum (500 MHz, C₆D₆) recorded after addition of TMSBr to **1-F** and heating at 55 °C for 12 h, followed by removing volatiles and redissolving in C₆D₆. Sample contains about 98% **1-Br**.

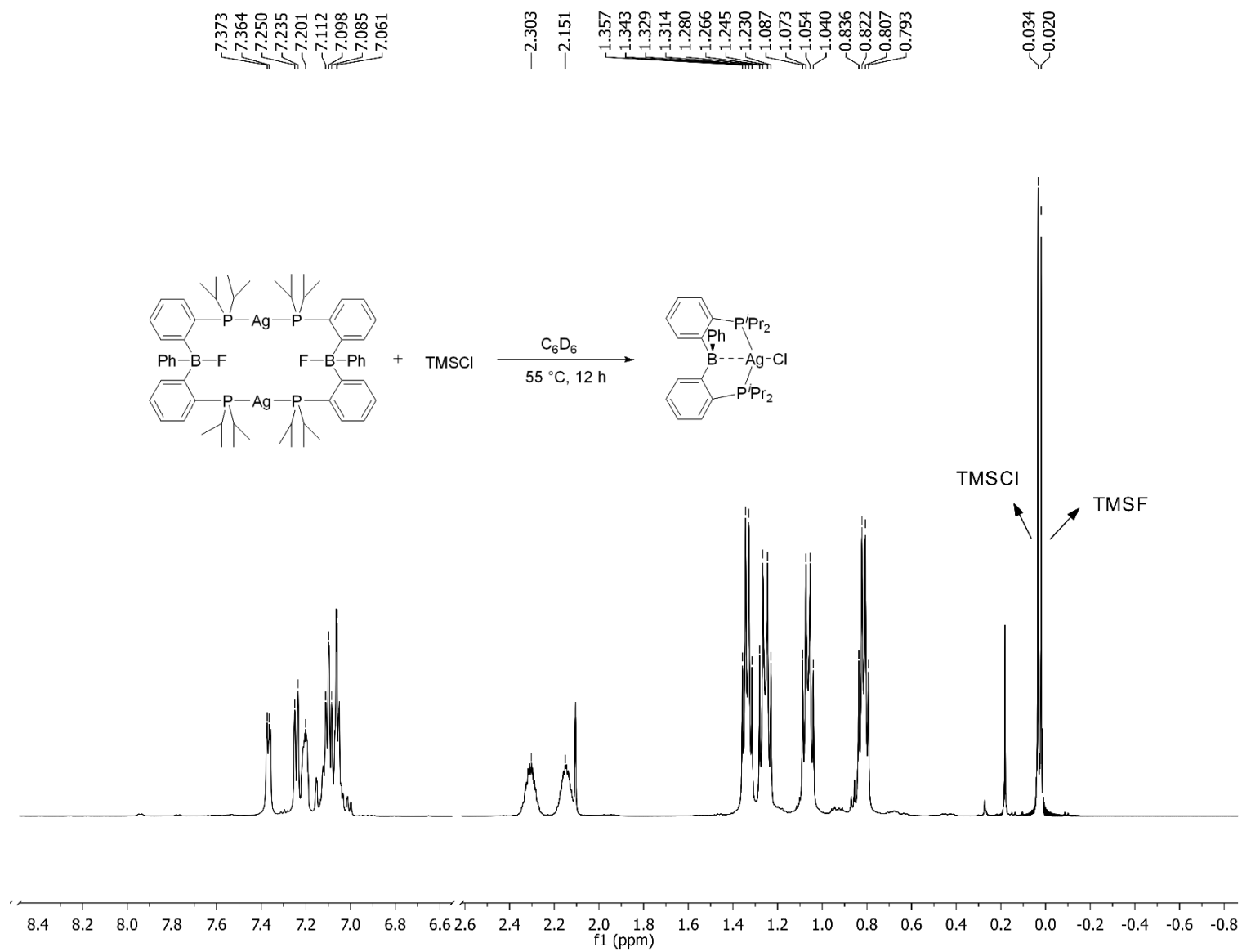


Figure S16. ^1H NMR (500 MHz, C_6D_6) after addition of TMSCl to **1-F**, and heating at 55 °C for 12 h.

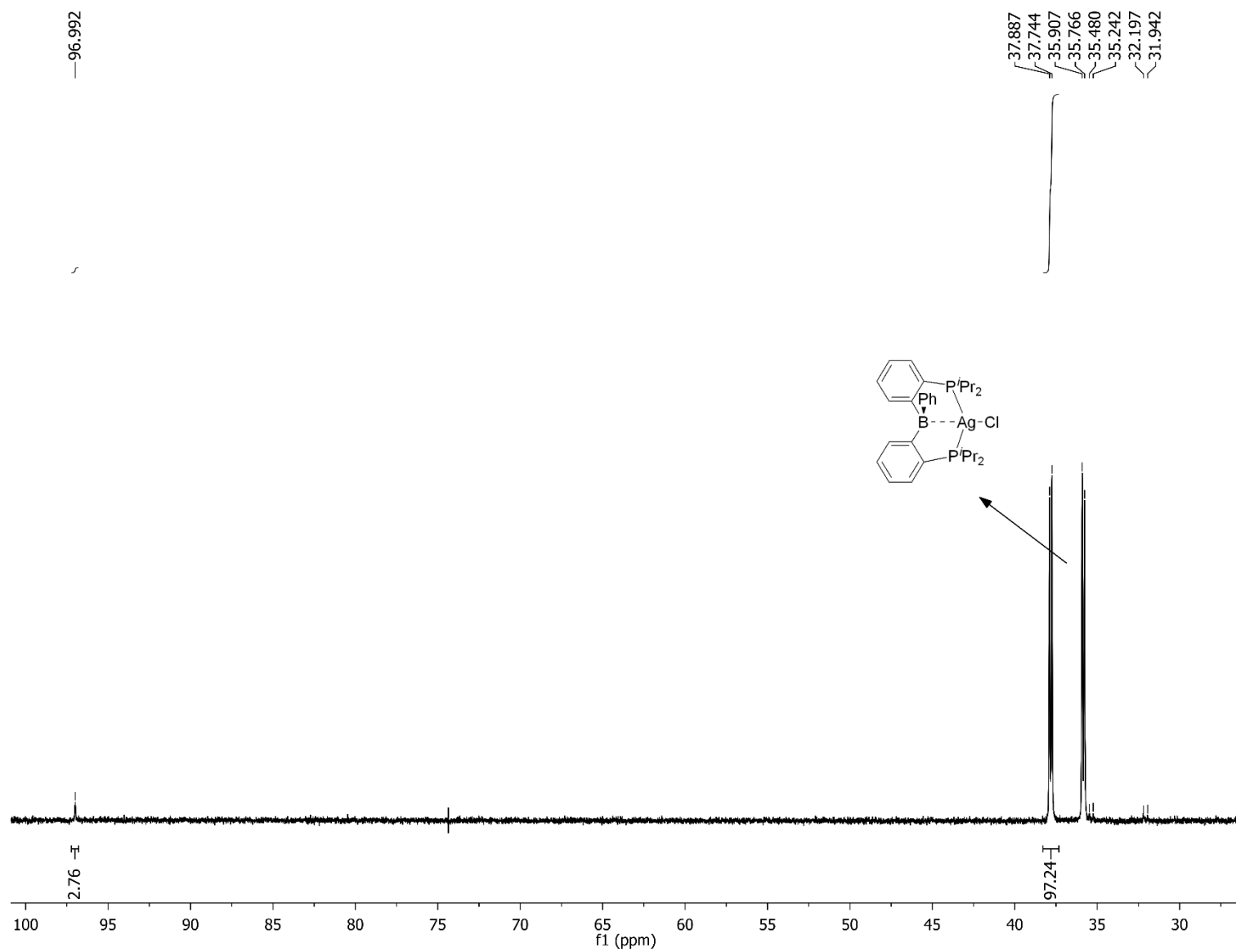


Figure S17. $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6) spectrum recorded after addition of TMSCl to **1-F**, and heating at 55 °C for 12 h.

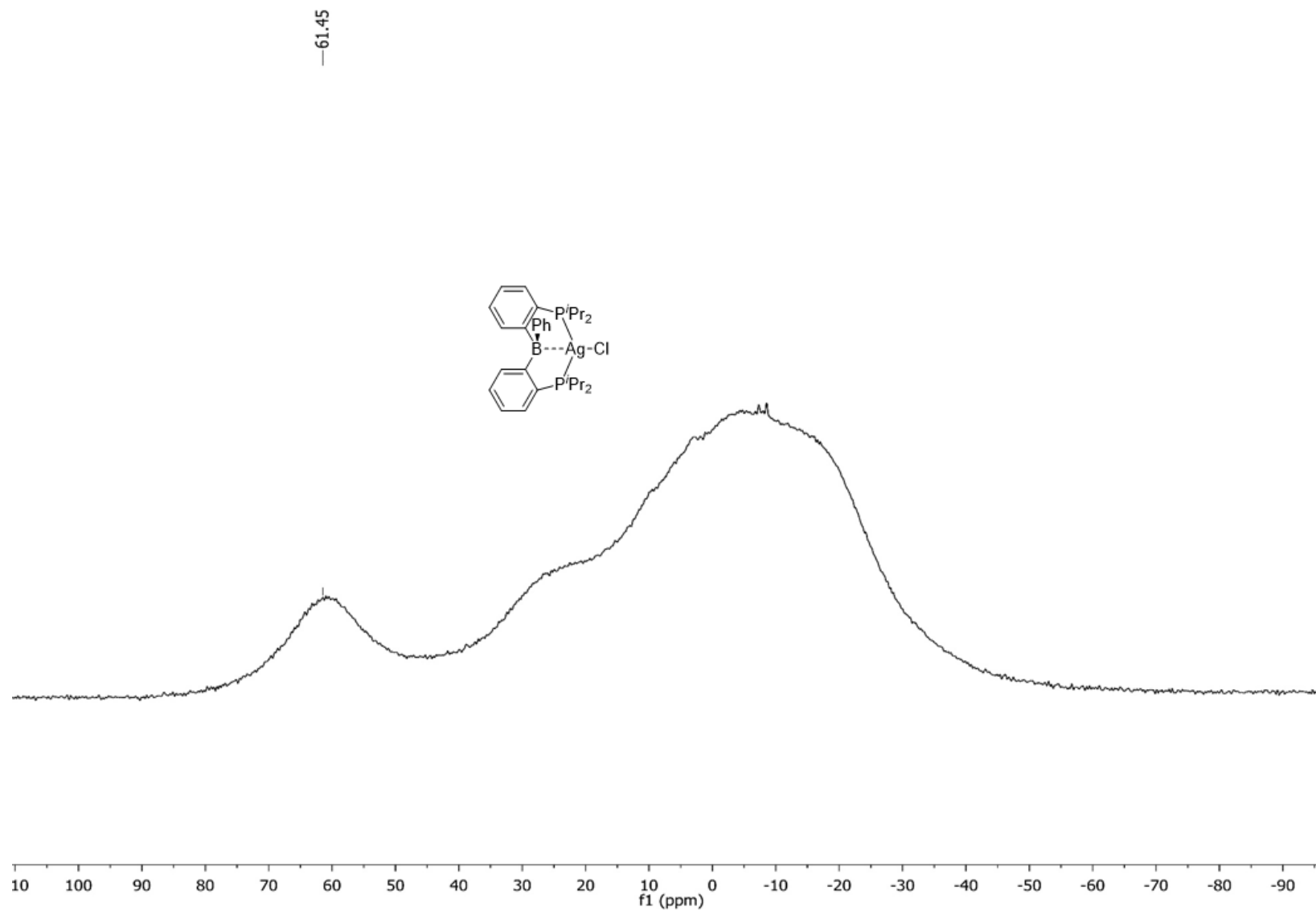


Figure S18. $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6) spectrum recorded after addition of TMSiCl to **1-F**, and heating at 55 °C for 12 h.

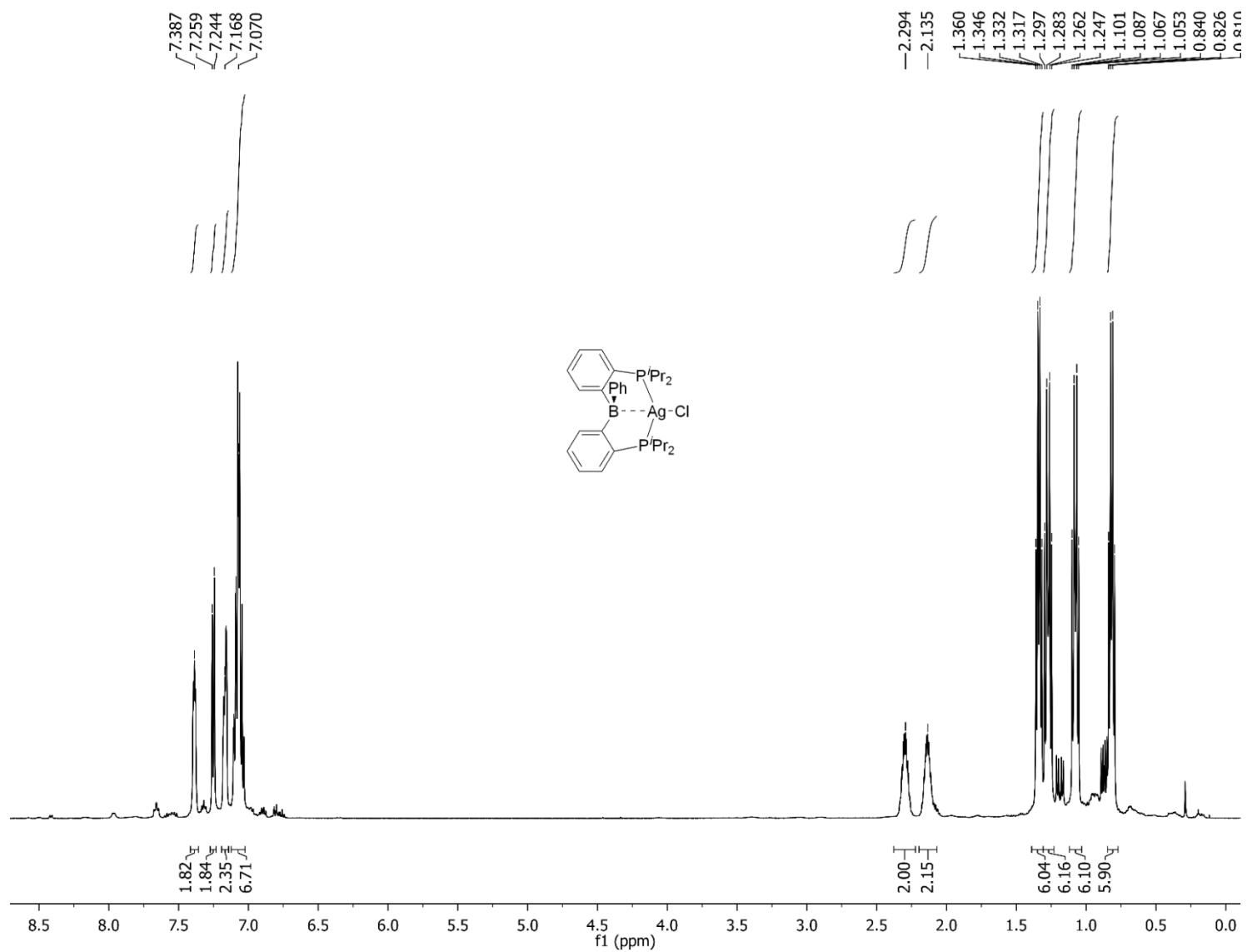


Figure S17. ¹H NMR spectrum (500 MHz, C₆D₆) recorded after addition of TMSCl to **1-F** and heating at 55 °C for 12 h, followed by removing volatiles and redissolving in C₆D₆. Sample contains 97% **1-Cl**.

V. ESI References

¹ *APEX, Version 2 User Manual, M86-E01078*, Bruker Analytical X-ray Systems, Madison, WI, June 2006.

² G. M. Sheldrick, *SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames.*, University of Göttingen, 2008.

³ G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

⁴ A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool.*, Utrecht University: Utrecht, The Netherlands, 1998.

⁵ (a) G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8. (b) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8. (c) XT, XS, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

⁶ O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.