Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information for:

Cationic Tetra- and Pentacoordinate Complexes of Nickel Based on POCN- and POCOP -Type Pincer Ligands: Synthesis, Characterization, and Ligand Exchange Studies

*Naser Rahimi and Davit Zargarian**

Département de chimie, Université de Montréal, Montréal (Québec), Canada H3C 3J7

zargarian.davit@umontreal.ca

TABLE OF CONTENTS:

1. General experimental considerations

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques and an inert-atmosphere box. The transfer/addition of all liquid reagents/reactants was performed with BRAND Transferpette® micropipettes (20-200 µL and 100-1000µL). Reported volumes should be considered to be within ±7 µL (for > 200 µL transfers) and ±3 µL (for < 200 µL transfers) of the measurements, with a >99% confidence level.[1] Solvents were dried by passage over a column of activated alumina, collected under nitrogen, and stored over 3 Å molecular sieves inside transfer/storage flasks equipped with high vacuum valves (Straus flasks). Et_3N was dried over CaH_2. The Ni^{II} precursor $[(i\text{-PrCN})NiBr_2]_n$ used throughout this study was prepared as reported previously.[2] Other reagents were purchased from Sigma-Aldrich or FisherSci and used without further purification.

The NMR spectra were recorded at 500 MHz (^1H), 125.72 MHz (^{13}C), and 202.4 MHz (^{31}P). Chemical shift values are reported in ppm (δ) and referenced internally to the residual solvent signals (^1H and ^{13}C: 1.94 and 118.26 ppm for CD_3CN; 7.26 and 77.16 for $CDCl_3$; 7.16 and 128.06 for C_6D_6) or externally (^{31}P: H_3PO_4 in D_2O, δ = 0). The minimal precision of the NMR spectra was found to be 0.3 Hz for ^1H, 0.7 Hz for ^{13}C and 2 Hz for ^{31}P. The NMR analyses for studying the substitution equilibria were carried out at 298.3 °K.

2. Procedures for the synthesis of precursors

Synthesis of [(POCN)Ni(MeCN)][SbF$_6$], 1a. A 100 mL Schlenk tube was charged with 1.112 g (2.4878 mmol) of (POCN)NiBr, **1**, approximately 25 mL of MeCN, and a stirrer bar. Ag SbF_6 (0.8549 g, 2.4878 mmol) was added in dark, and the reaction mixture was stirred for 2 h. Suspended solid was removed by passing the solution through celite, and the solvent was removed in vacuo. The solid residue was washed with 10 mL hexanes to give 1.4232 g (89%) of yellow solid as the product.

^1H NMR (acetonitrile-d_3): δ 1.29-1.45 (12H, m, $CH(CH_3)_2$), 1.98 (3H, s, CH_3CN), 2.36-2.46 (2H, m, $CH(CH_3)_2$), 3.11 (2H, d, $N(CH_2\text{-}CH_2)_2O$), 3.58-3.65 (4H, m, $N(CH_2\text{-}CH_2)_2O$), 3.96 (2H, dd,

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[1] *Post-facto* calibration of the 100-1000 µL micropipette with 20 × 500 µL aliquots of deionized H_2O revealed that we must allow an accuracy (systematic error) of +4 µL and a precision of ±3 µL for our measurements, with > 99% confidence. The 20-200 µL micropipette was calibrated by the same procedure, with 150 µL aliquots, and revealed an accuracy of +0.3 µL and a precision of ±3 µL for our measurements, with > 99% confidence.

[2] (a) Vabre, B.; Spasyuk, D. M.; Zargarian, D., Impact of Backbone Substituents on POCOP-Ni Pincer complexes: A Structural, Spectroscopic and Electrochemical Study, *Organometallics* **2012**, *31* (24), 8561-8570. (b) Vabre, B.; Lindeperg, F.; Zargarian, D., Direct, one-pot synthesis of POCOP-type pincer complexes from metallic nickel, *Green Chemistry* **2013**, *15* (11), 3188-3194.

N(C*H*$_2$-C*H*$_2$)$_2$O), 4.41 (2H, s, NC*H*$_2$-Ar), 6.52 (1H, d, Ar), 6.69 (1H, d, Ar), 7.05 (1H, t, Ar). ^{13}C{^{1}H} NMR (acetonitrile-*d*$_3$): δ 16.9, 17.9, 28.9, 29.1, 55.4, 61.8, 63.3, 109.6, 117.9, 129.9, 137.7, 137.9, 153.0, 166.6. ^{31}P{^{1}H} NMR (acetonitrile-*d*$_3$): 202.4

Synthesis of [(POCN)Ni(py)][SbF$_6$], 1b. 0.1181 g (0.1834 mmol) of [(POCN)Ni(MeCN)][SbF$_6$], **1a**, was dissolved in 3 mL of pyridine. The ^{31}PNMR spectrum of the resulting yellow-orange solution showed that the starting complex had completely reacted. The solvent was removed in vacuo and the solid residue was dissolved in about 2 mL CH$_2$Cl$_2$. It was then layered with 1 mL of hexane and left at -35 °C to give 0.0781 g (62%) of light-yellow solid.

^{1}H NMR (acetone-*d*$_6$): δ 1.10 and 1.14 (3H each, d, *J* 7.3, CH(C*H*$_3$)$_2$), 1.32 and 1.36 (3H each, d, *J* 6.9, CH(C*H*$_3$)$_2$), 2.19-2.32 (2H, m, C*H*(CH$_3$)$_2$), 2.96 (2H, td, N(C*H*$_2$-C*H*$_2$)$_2$O), 3.17 (2H, d, *J* 13.1, N(C*H*$_2$-C*H*$_2$)$_2$O), 3.41 (2H, dd, N(C*H*$_2$-C*H*$_2$)$_2$O), 3.98 (2H, td, N(C*H*$_2$-C*H*$_2$)$_2$O), 4.59 (2H, s, NC*H*$_2$-Ar), 6.62 (1H, d, *J* 8.0, Ar), 6.82 (1H, d, *J* 7.5, Ar), 7.12 (1H, t, *J* 8.0, Ar), 7.78 (2H, t, *J* 7.0, *m*-pyr), 8.10 (1H, d, *J* 7.7, *p*-pyr), 9.22 (2H, d, *J* 5.0, *o*-pyr) . ^{13}C{^{1}H} NMR (acetone-*d*$_6$): δ 16.6 (d, *J* 2), 17.1 (d, *J* 4.6), 28.0, 28.3, 54.4 (d, *J* 1.5), 60.8, 62.8 (d, *J* 2), 109.2 (d, *J* 13.1), 117.5 (d, *J* 2), 127.9, 129.4, 140.7, 151.4, 151.9, 166.3 (d, *J* 9), 210.1. ^{31}P{^{1}H} NMR (acetone-*d*$_6$): 195.8

Synthesis of [(POCN)Ni(bipy)][SbF$_6$], 1c. A 50 mL Schlenk tube was charged with 0.2025 g (0.3145 mmol) of [(POCN)Ni(MeCN)][SbF$_6$], approximately 15 mL of CH$_2$Cl$_2$, and a stir bar. Bipy (0.0491 g, 0.3145 mmol) was added and the yellowish solution quickly turned dark red. The reaction was stopped after 1 h and the solvent was reduced to 3 mL. The solution was layered with 1 mL of hexane and kept motionless at -35 °C to give 0.1983 g (82%) of dark red crystals suitable for X-ray crystallography.

^{1}H NMR (acetone-*d*$_6$): δ 0.95-1.02 (12H, m, CH(C*H*$_3$)$_2$), 2.35-2.40 (2H, m, C*H*(CH$_3$)$_2$), 2.63 (2H, d, N(C*H*$_2$-C*H*$_2$)$_2$O), 2.88 (2H, t, N(C*H*$_2$-C*H*$_2$)$_2$O), 3.26 (2H, d, N(C*H*$_2$-C*H*$_2$)$_2$O), 3.83 (2H, t, N(C*H*$_2$-C*H*$_2$)$_2$O), 4.25 (2H, s, NC*H*$_2$-Ar), 6.59 (1H, d, Ar), 6.88 (1H, d, Ar), 7.09 (1H, t, Ar), 7.79 (2H, t, bipy), 8.26 (2H, t, bipy), 8.61 (2H, d, bipy), 8.88 (2H, d, bipy). ^{13}C{^{1}H} NMR (acetone-*d*$_6$): δ 15.7, 17.1, 28.9, 29.0, 55.0, 61.3, 109.1, 109.2, 118.4, 124.4, 127.7, 128.3, 140.4, 148.9, 151.0, 154.6, 165.6, 165.7, 210.1. ^{31}P{^{1}H} NMR (acetone-*d*$_6$): 189.8

Synthesis of [(POCN)Ni(phen)][SbF$_6$], 1d. A 50 mL Schlenk tube was charged with 0.0964 g (0.1497 mmol) of [(POCN)Ni(MeCN)][SbF$_6$], approximately 15 mL of CH$_2$Cl$_2$, and a stir bar.

1,10-Phenanthroline monohydrate (0.0297 g, 0.1497 mmol) was added and the yellowish solution quickly turned dark red. The reaction was stopped after 1 h and the solvent was reduced to 3 mL. The solution was layered with 1 mL of hexane and kept motionless at -35 °C to give 0.1063 g (91%) of dark red crystals suitable for X-ray crystallography.

^{1}H NMR (acetone-d_6): δ 0.82-0.87 (12H, m, CH(CH_3)$_2$), 2.25-2.37 (2H, m, CH(CH$_3$)$_2$), 2.54 (2H, d, N(CH_2-CH_2)$_2$O), 2.91 (2H, t, N(CH_2-CH_2)$_2$O), 3.17 (2H, d, N(CH_2-CH_2)$_2$O), 3.76 (2H, t, N(CH_2-CH_2)$_2$O), 4.29 (2H, s, NCH_2-Ar), 6.63 (1H, d, Ar), 6.90 (1H, d, Ar), 7.13 (1H, t, Ar), 8.11 (2H, dd, phen), 8.26 (2H, s, phen), 8.83 (2H, dd, phen), 9.25 (2H, dd, phen). ^{13}C{^{1}H} NMR (acetone-d_6): δ 15.6, 16.8, 61.1, 61.4, 69.2, 109.0, 109.1, 118.2, 127.0, 127.6, 131.1, 139.1, 145.5, 151.4, 154.1, 165.6, 165.7, 197.9, 210.0. ^{31}P{^{1}H} NMR (acetone-d_6): 188.5

Synthesis of [(POCN)$_2$Ni$_2$(μ-bipy*)][SbF$_6$]$_2$, 1e. A 20 mL reaction vessel was charged with 0.0626 g (0.0076 mmol) of [(POCN)Ni(MeCN)][SbF$_6$] and approximately 1 mL of CH$_2$Cl$_2$. The solution was slowly added 4,4'bipyridine (0.0076 g, 0.0466 mmol) in 3 mL of CH$_2$Cl$_2$ and the reaction mixture was stirred for 6 h. The solvent was removed in vacuo. The solid residue was washed with 5 mL of THF and dried in vacuo to give 0.040 g (63%) of yellow solid. Suitable single crystals for X-ray studies were obtained by careful layering (1:0.5) of THF solutions of [(POCN)Ni(MeCN)][SbF$_6$] and 4,4'-BiPy. We were unable to study this compound by NMR spectroscopy as it was insoluble in usual organic solvents. The complex was insoluble in MeCN in which a partial decomposition occurred. The ^{31}PNMR spectrum of the top layer of the solution showed the presence of the starting complex **1a**.

Synthesis of [(POCOP)Ni(py)][SbF$_6$], 2b. 0.1348 g (0.1991 mmol) of [(POCOP)Ni(MeCN)]-[SbF$_6$] was dissolved in 3 mL of pyridine. The ^{31}PNMR spectrum of the resulting yellow-orange solution showed that the starting complex had completely reacted. The solvent was removed in vacuo and the solid residue was dissolved in about 2 mL CH$_2$Cl$_2$. It was then layered with 1 mL of hexane and left at -35 °C to give 0.1047 g (74%) of X-ray quality crystals.

^{1}H NMR (acetone-d_6): δ 1.07 and 1.12 (6H each, d, *J* 7.5, CH(CH_3)$_2$), 1.35 and 1.39 (6H each, d, *J* 7.0, CH(CH_3)$_2$), 2.44 (4H, septet, *J* 7.0, CH(CH$_3$)$_2$), 6.62 (2H, d, *J* 8.0, *m*-Ar), 7.18 (1H, t, *J* 8, *p*-Ar), 7.82 (2H, t, *J* 8.0, *m*-pyr), 8.10 (1H, t, *J* 7.8, *p*-pyr), 9.05 (2H, d, *J* 5.0, *o*-pyr). ^{13}C{^{1}H} NMR (acetone-d_6): δ 16.7, 17.0 (d, *J* 2.6), 106.7 (d, *J* 6.3), 128.4, 132.1, 140.8, 151.4, 152.0, 169.6 (d, *J* 8.7), 210.1. ^{31}P{^{1}H} NMR (acetone-d_6): 185.5

Synthesis of [(POCOP)Ni(bipy)][SbF$_6$], 2c. A 50 mL Schlenk tube was charged with 0.2589 g (0.3825 mmol) of [(POCOP)Ni(MeCN)][SbF$_6$], approximately 15 mL of CH_2Cl_2, and a stir bar. bipy (0.0619 g, 0.3966 mmol) was added and the yellowish solution quickly turned dark red. The reaction was stopped after 1 h and the solvent was reduced to 3 mL. The solution was layered with 1 mL of hexane and kept motionless at -35 °C to give 0.2068 g (82%) of dark red crystals suitable for X-ray crystallography.

^{1}H NMR (acetone-d_6): δ 0.82-1.02 (24H, m, CH(C*H*$_3$)$_2$), 2.31-2.39 (4H, m, C*H*(CH$_3$)$_2$), 6.55 (2H, d, Ar), 7.12 (1H, t, Ar), 7.71 (2H, t, bipy), 8.26 (2H, t, bipy), 8.71 (2H, d, bipy), 8.79 (2H, d, bipy). ^{13}C{^{1}H} NMR (acetone-d_6): δ 16.6, 17.2, 30.0, 106.7, 124.6, 127.8, 129.8, 140.3, 152.1, 154.4, 166.9, 210.1. ^{31}P{^{1}H} NMR (acetone-d_6): 176.2

Synthesis of [(POCOP)Ni(phen)][SbF$_6$], 2d. A 50 mL Schlenk tube was charged with 0.250 g (0.3693 mmol) of [(POCOP)Ni(MeCN)][SbF$_6$], approximately 15 mL of CH_2Cl_2, and a stir bar. 1,10-Phenanthroline (0.0665 g, 0.3693 mmol) was added and the yellowish solution quickly turned dark red. The reaction was stopped after 1 h and the solvent was reduced to 3 mL. The solution was layered with 1 mL of hexane and kept motionless at -35 °C to give 0.2327 g (90%) of dark red crystals suitable for X-ray crystallography.

^{1}H NMR (acetone-d_6): δ 0.61-0.81 (24H, m, CH(C*H*$_3$)$_2$), 2.13-2.27 (4H, m, C*H*(CH$_3$)$_2$), 6.49 (2H, d, Ar), 7.08 (1H, t, Ar), 7.93 (2H, t, phen), 8.19 (2H, s, phen), 8.75 (2H, t, phen), 9.06 (2H, d, phen). ^{13}C{^{1}H} NMR (acetone-d_6): δ 16.5, 17.1, 30.0, 106.8, 126.8, 129.8, 131.4, 139.0, 145.7, 152.8, 167.0, 210.2. ^{31}P{^{1}H} NMR (acetone-d_6): 176.8

Synthesis of [(POCOP)$_2$Ni$_2$(μ-bipy*)][SbF$_6$]$_2$, 2e. A 20 mL reaction vessel was charged with 0.0669 g (0.0988 mmol) of [(POCOP)Ni(MeCN)][SbF$_6$] and approximately 3 mL of THF. 4,4'-bipyridine (0.0077 g, 0.0494 mmol) was added. No color change occurred, and the reaction mixture was stirred for 1 h. The solvent was removed under a reduced pressure. The solid residue was dissolved in 2 mL of CH_2Cl_2. The solution was layered with 1 mL of hexane and kept motionless at -35 °C to give 0.0472 g (67%) of yellow solid as product. Suitable single crystals for

X-ray studies were obtained by layering of a concentrated CH_2Cl_2 solution of [(POCOP)Ni(4,4’-BiPy)Ni(POCOP)][SbF_6]$_2$ with double amount of hexane.

^{1}H NMR (acetone-d_6): δ 1.14 and 1.19 (12H each, d, *J* 7.8, CH(C*H*$_3$)$_2$), 1.37 and 1.41 (12H each, d, *J* 7.2, CH(C*H*$_3$)$_2$), 2.49 (8H, septet, *J* 7.2, C*H*(CH$_3$)$_2$), 6.64 (4H, d, *J* 8.0, *m*-Ar), 7.20 (2H, t, *J* 8.0, *p*-Ar), 8.32 (4H, d, *J* 6.4, *m*-pyr), 9.29 (4H, d, *J* 6.0, *o*-pyr). ^{13}C{^{1}H} NMR (acetone-d_6): δ 16.8, 17.2, 28.3 (t, *J* 11.6), 106.8 (d, *J* 6.2), 125.7, 132.3, 146.4, 153.1, 169.7 (t, *J* 8.6), 210.1. ^{31}P{^{1}H} NMR (acetone-d_6): 185.5

3. NMR spectra for characterization of the new compounds

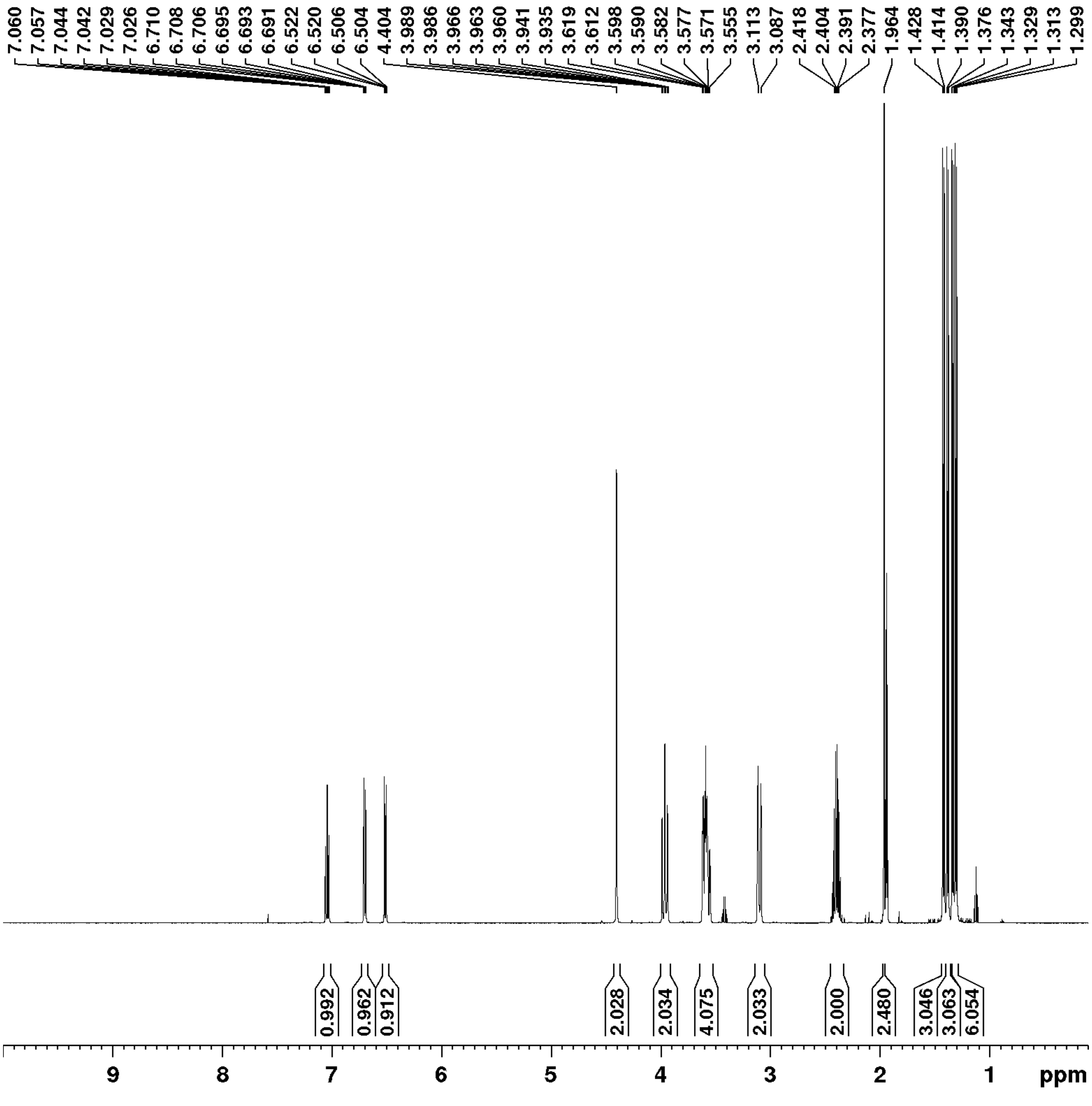


Figure S1. ^{1}HNMR spectrum of [(POCN)Ni(MeCN)][SbF$_6$] (**1a**) in CD$_3$CN.

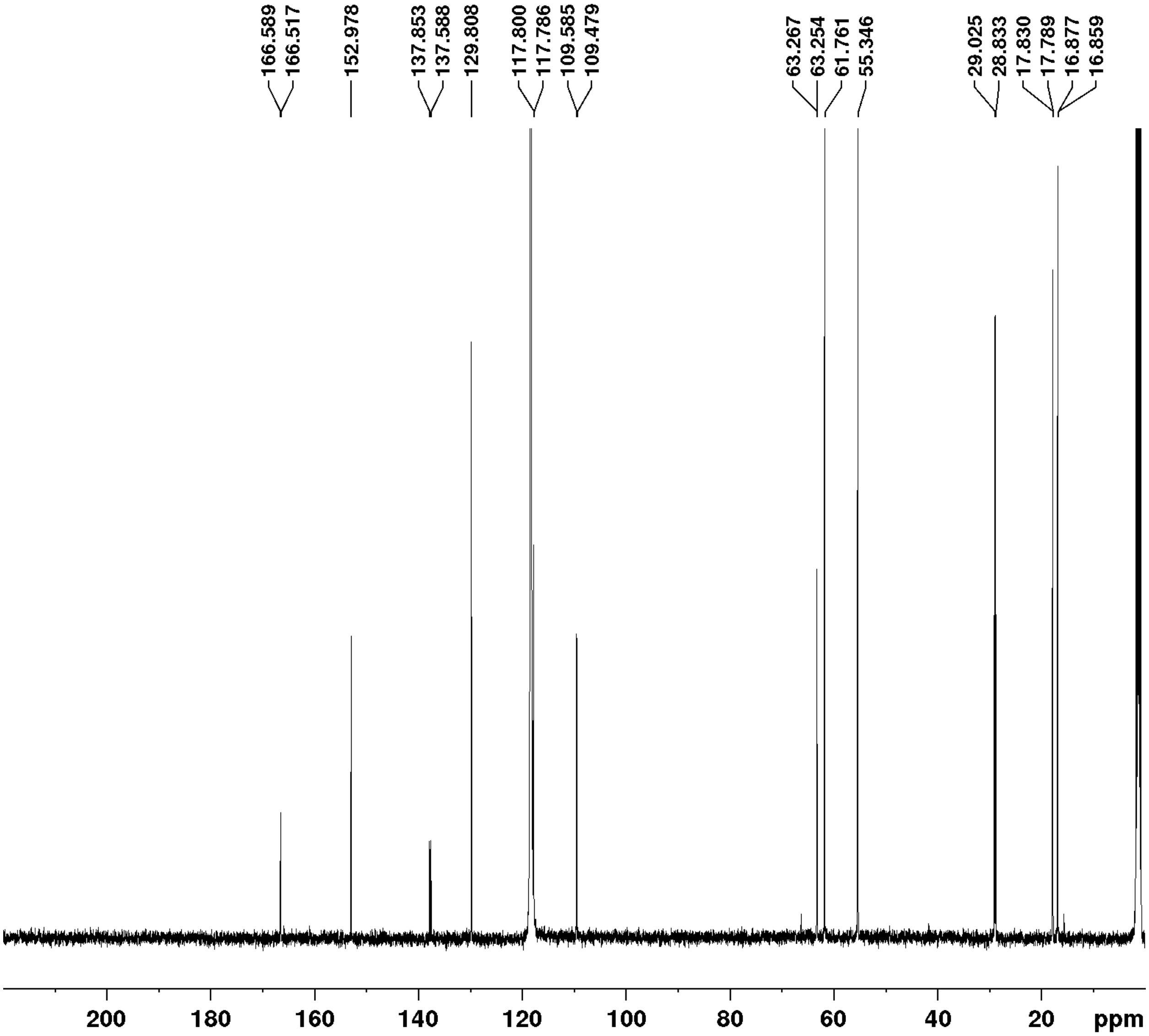


Figure S2. ^{13}CNMR spectrum of [(POCN)Ni(MeCN)][SbF$_6$] (**1a**) in CD$_3$CN.

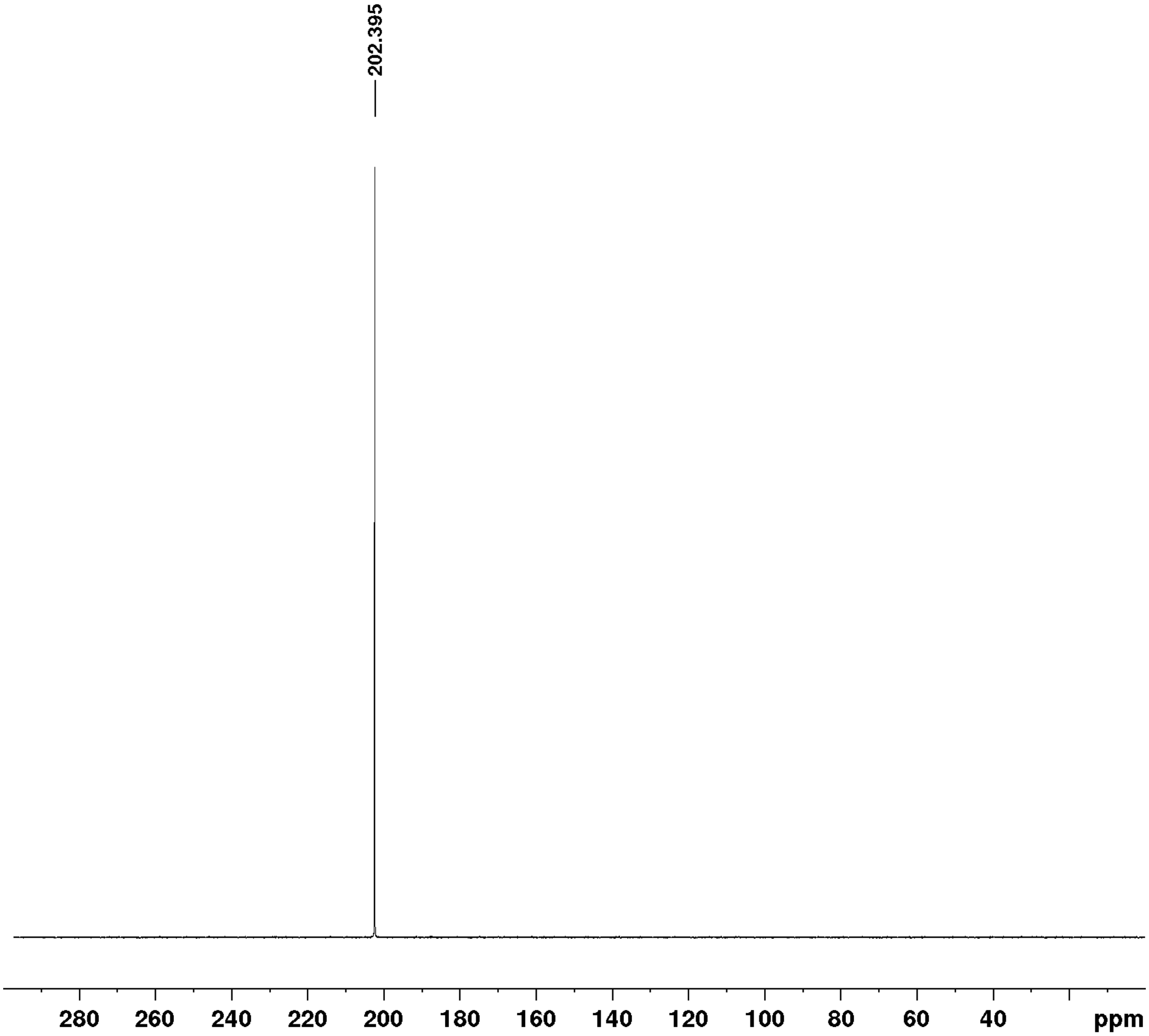


Figure S3. ^{31}PNMR spectrum of [(POCN)Ni(MeCN)][SbF6] (1a) in CD3CN.

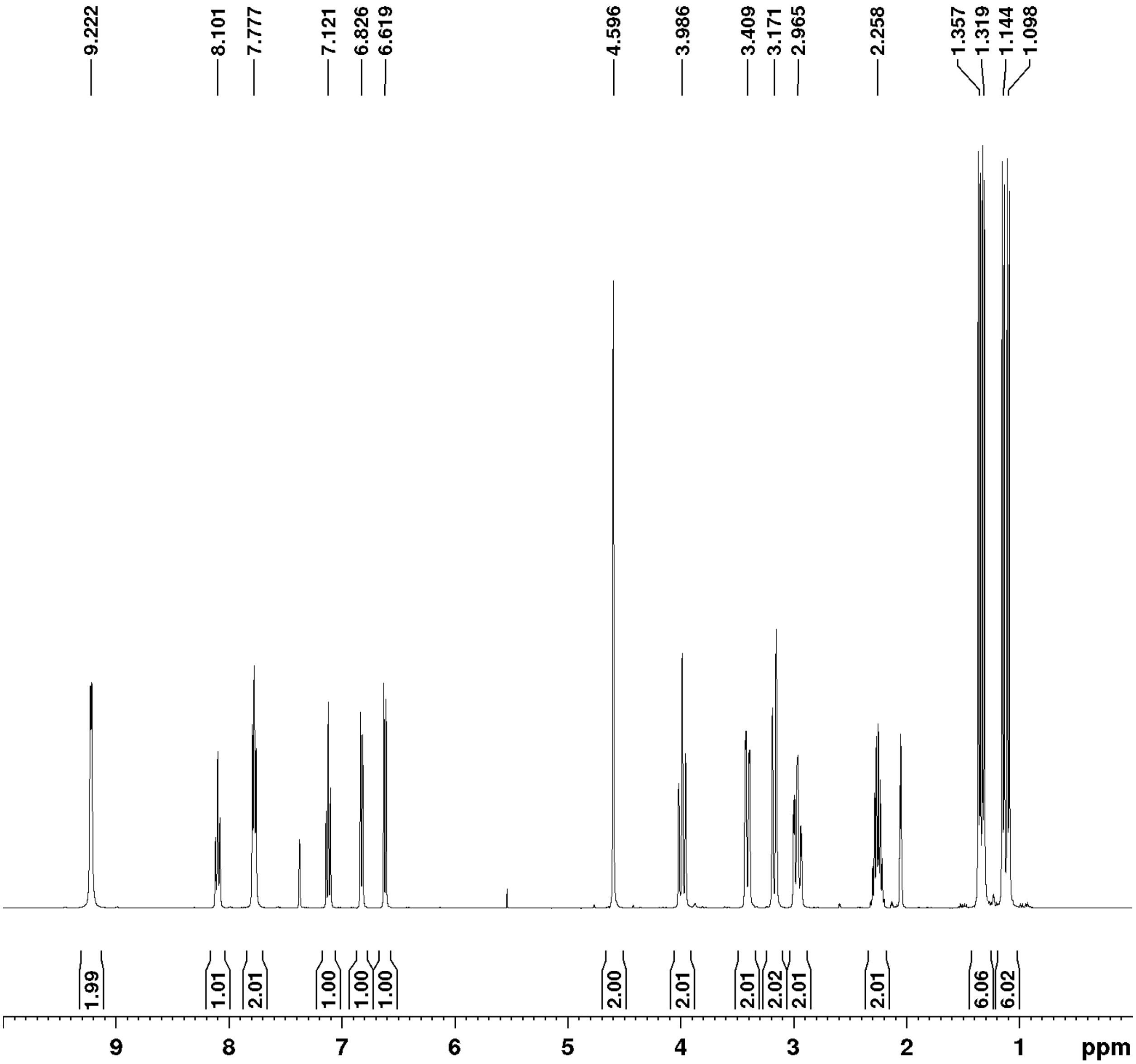


Figure S4. ^{1}HNMR spectrum of [(POCN)Ni(py)][SbF$_6$] (**1b**) in $(CD_3)_2CO$.

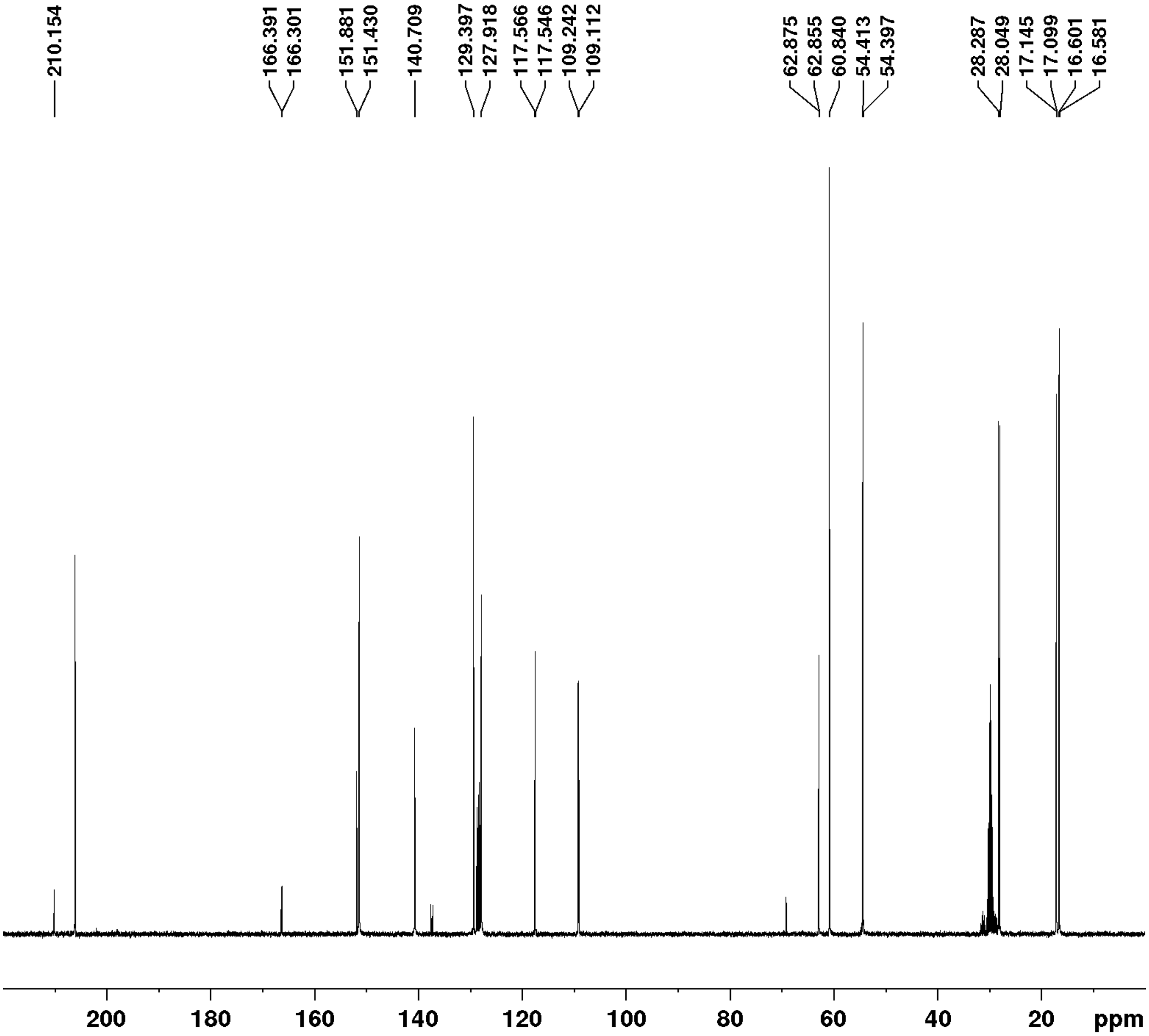


Figure S5. ^{13}CNMR spectrum of [(POCN)Ni(py)][SbF$_6$] (**1b**) in $(CD_3)_2CO$.

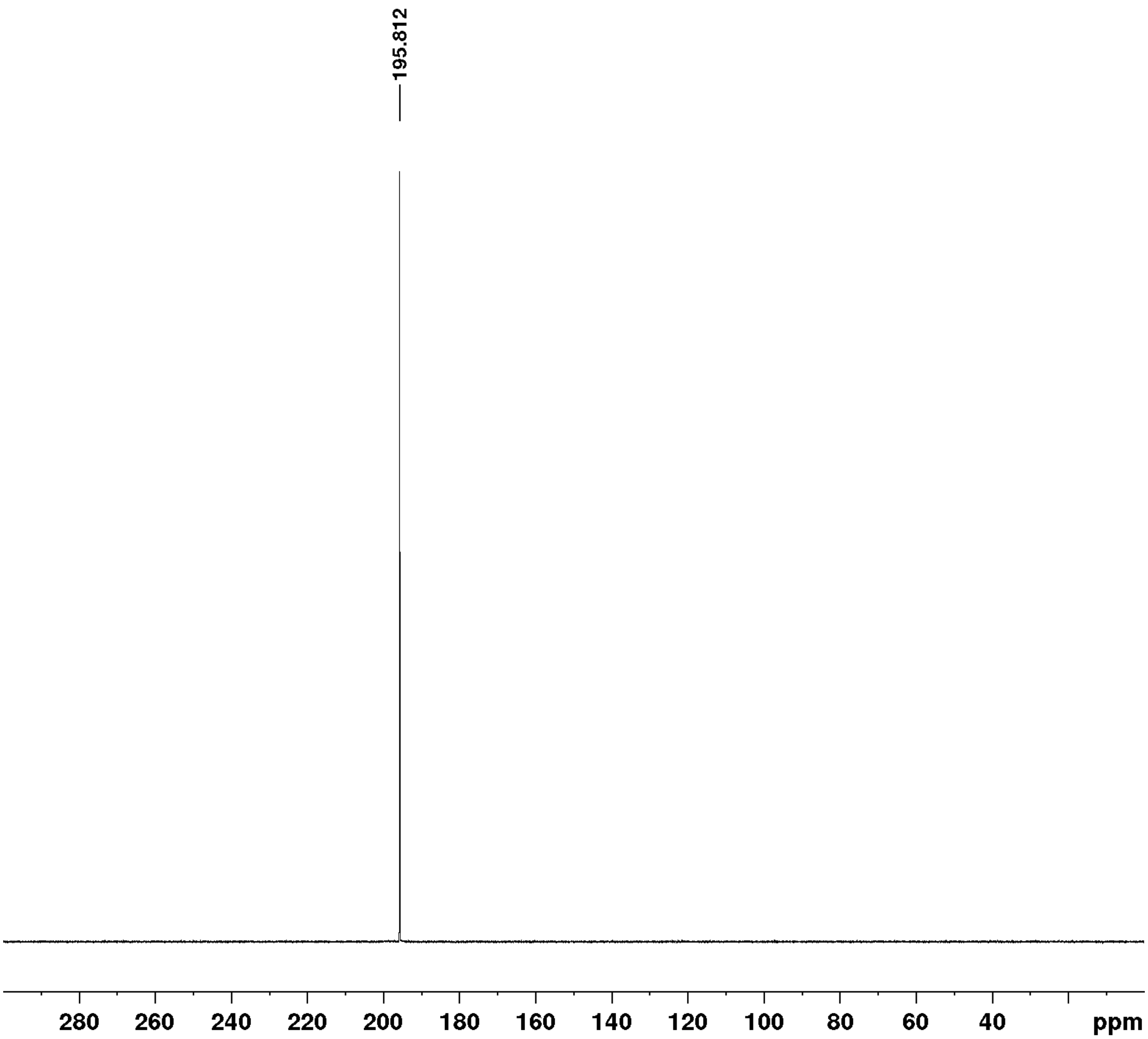


Figure S6. ^{31}PNMR spectrum of [(POCN)Ni(py)][SbF$_6$] (**1b**) in (CD$_3$)$_2$CO.

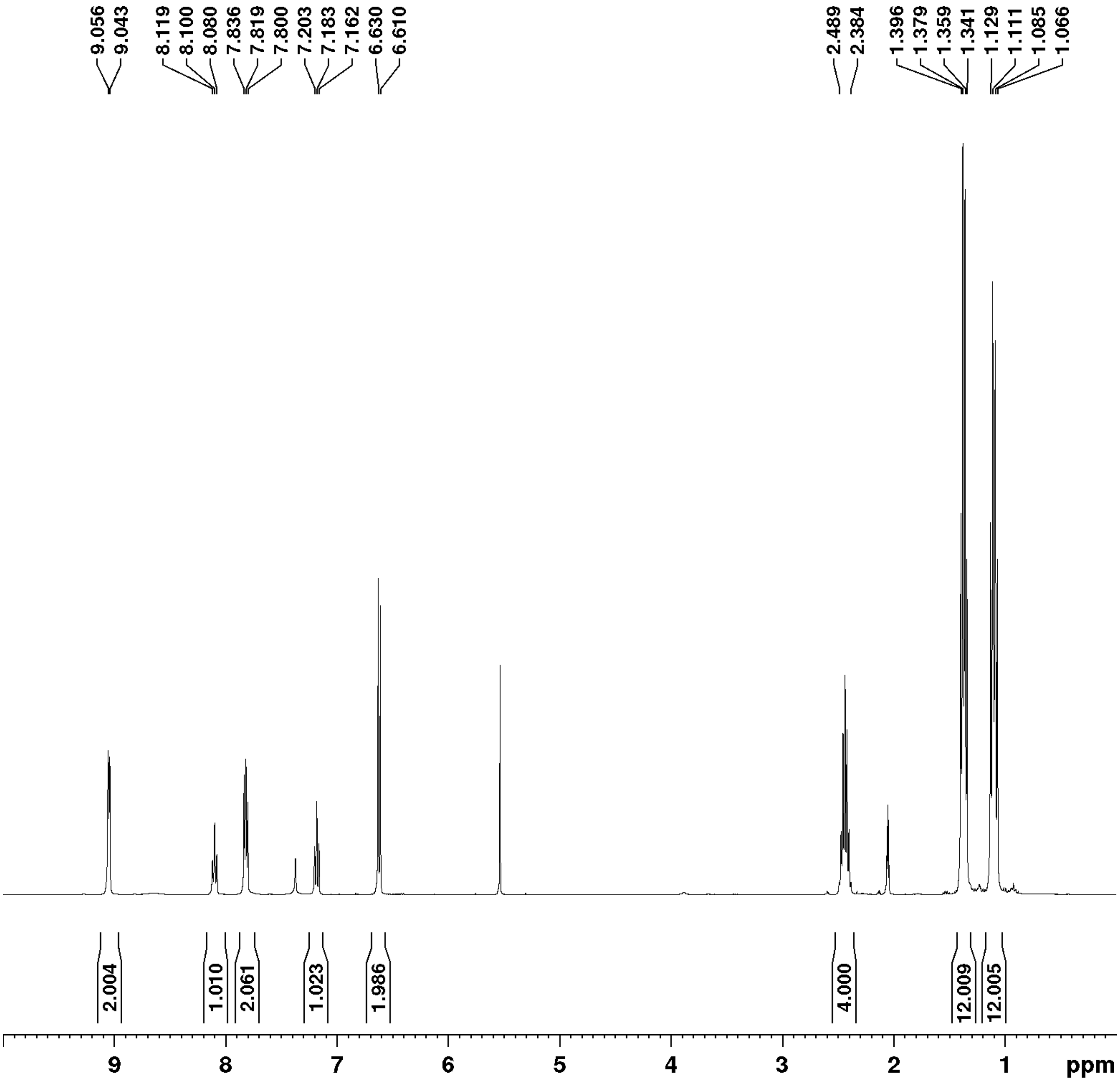


Figure S7. ^{1}HNMR spectrum of [(POCOP)Ni(py)][SbF$_6$] (**2b**) in (CD$_3$)$_2$CO.

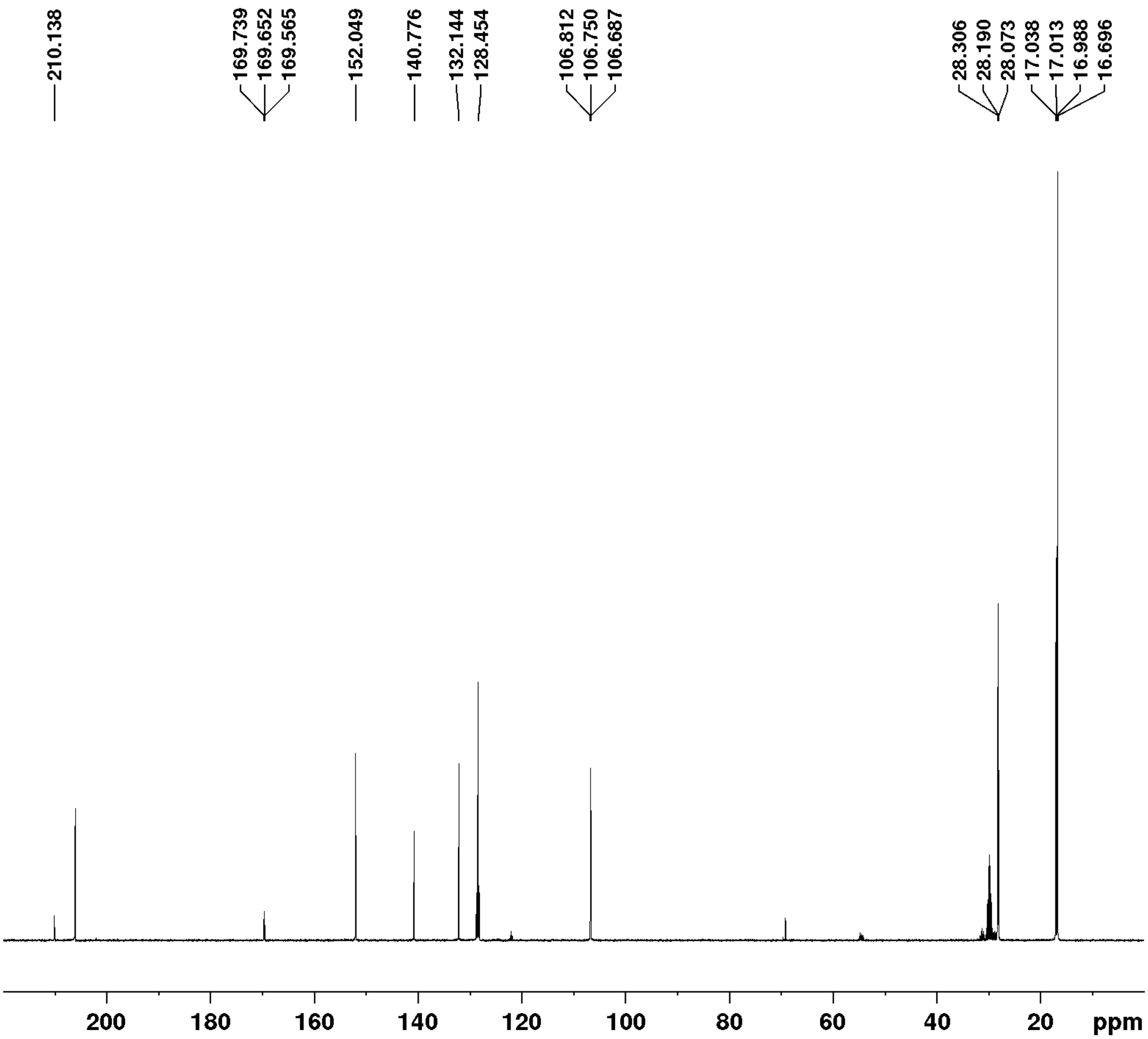


Figure S8. ^{13}CNMR spectrum of [(POCOP)Ni(py)][SbF$_6$] (**2b**) in (CD$_3$)$_2$CO.

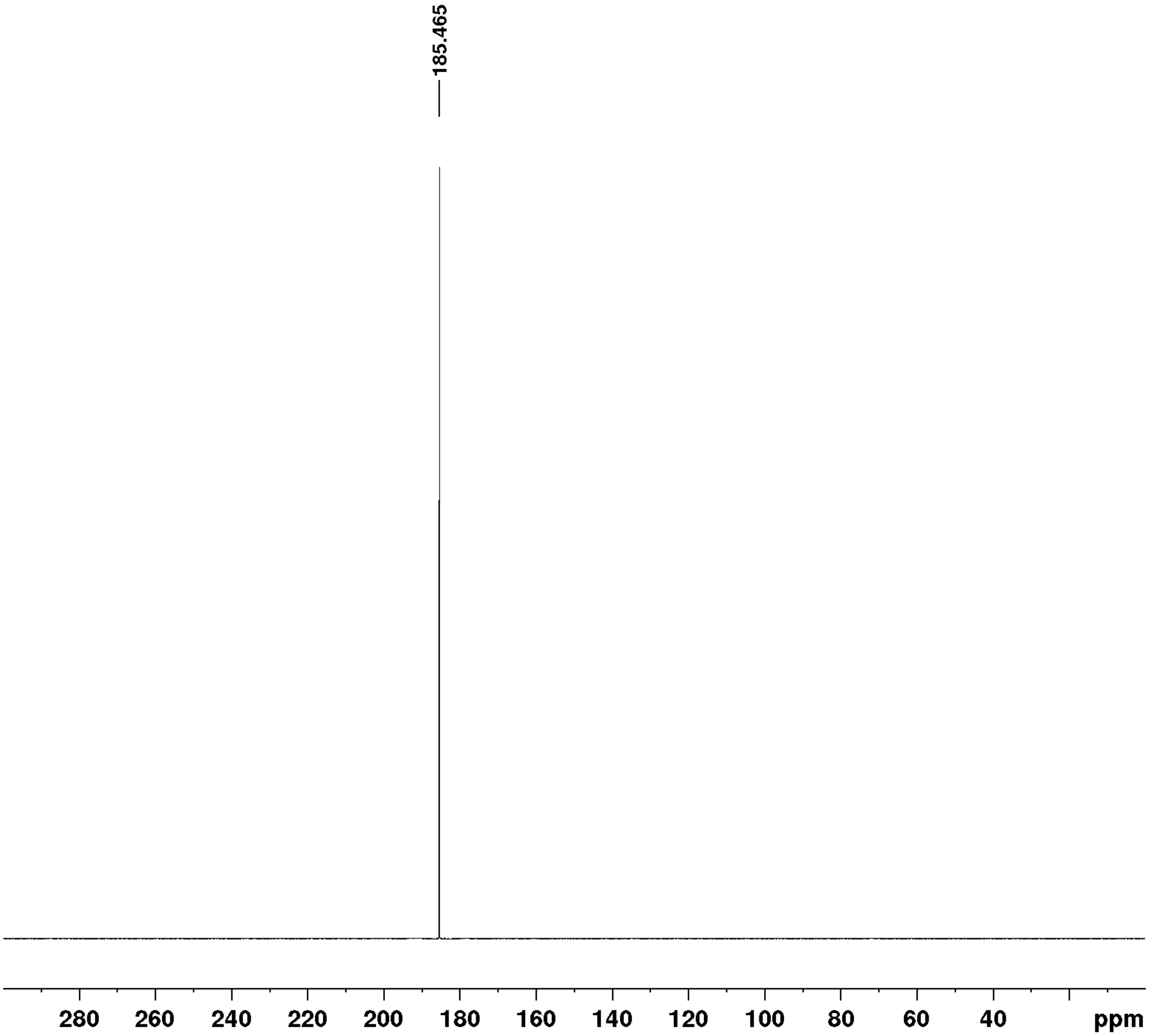


Figure S9. ^{31}PNMR spectrum of [(POCOP)Ni(py)][SbF$_6$] (**3**) in $(CD_3)_2CO$.

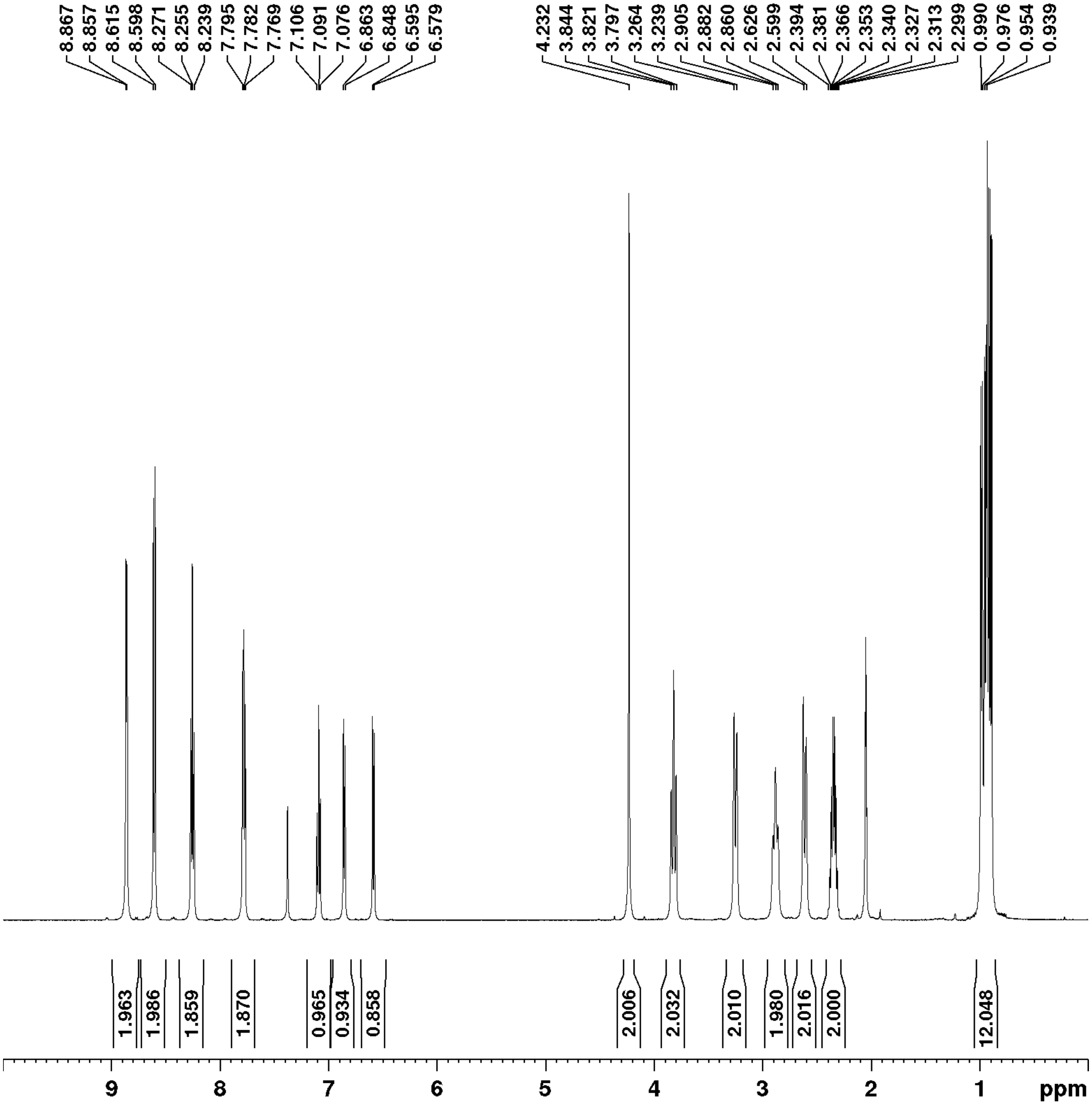


Figure S10. ^{1}HNMR spectrum of [(POCN)Ni(bipy)][SbF$_6$] (**1c**) in $(CD_3)_2CO$.

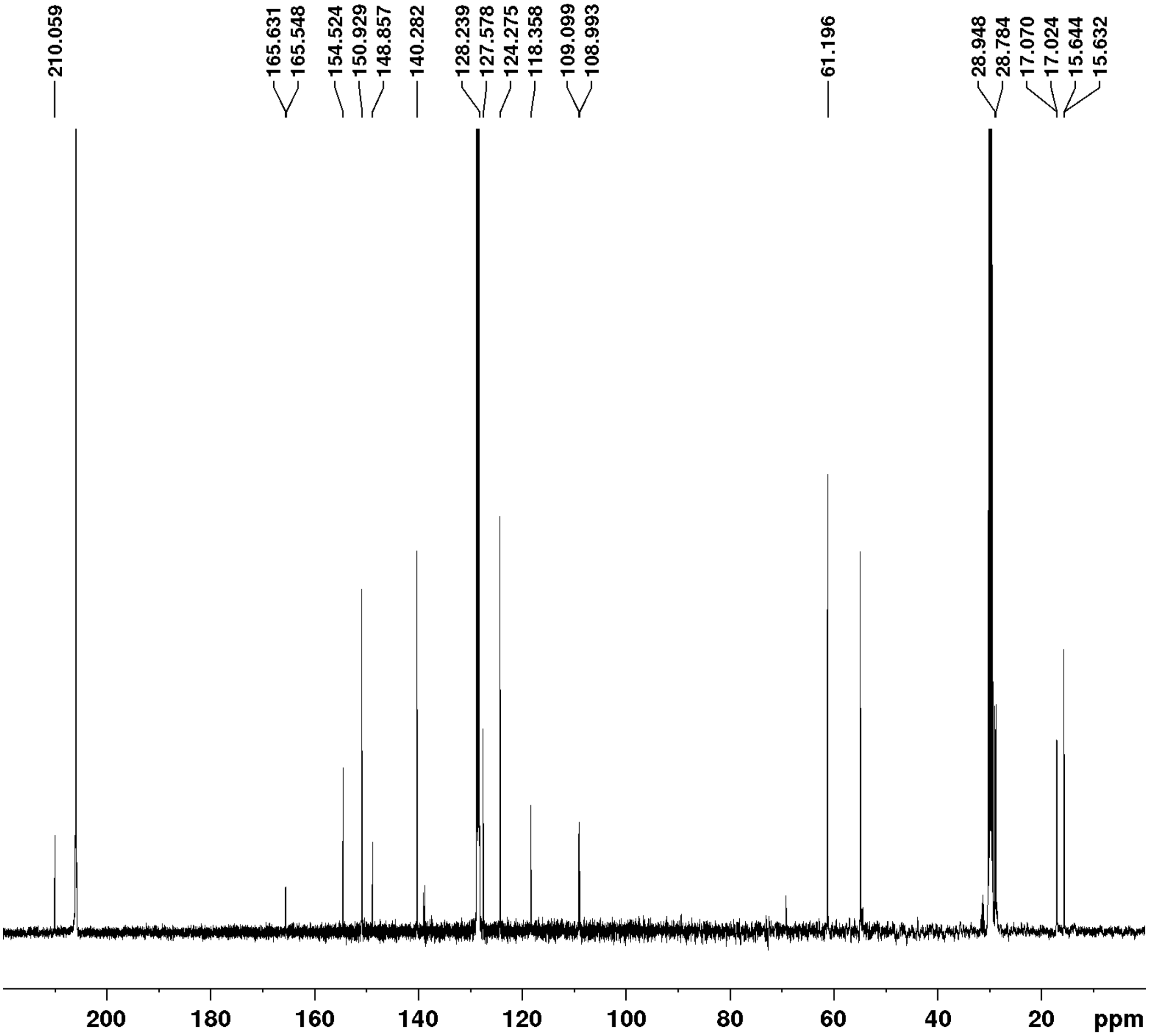


Figure S11. ^{13}CNMR spectrum of [(POCN)Ni(bipy)][SbF$_6$] (**1c**) in (CD$_3$)$_2$CO.

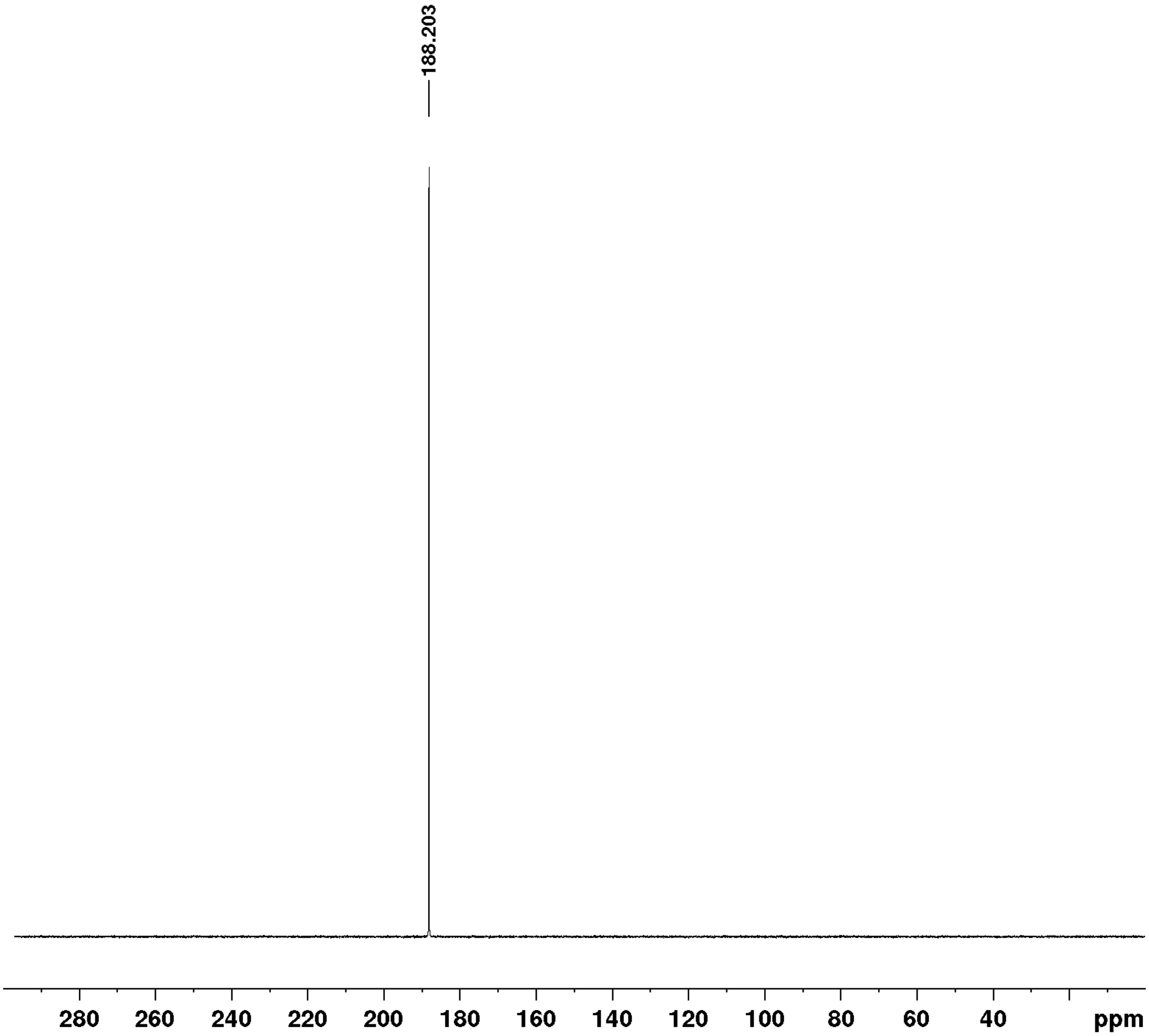


Figure S12. ^{31}PNMR spectrum of [(POCN)Ni(bipy)][SbF$_6$] (**1c**) in $(CD_3)_2CO$.

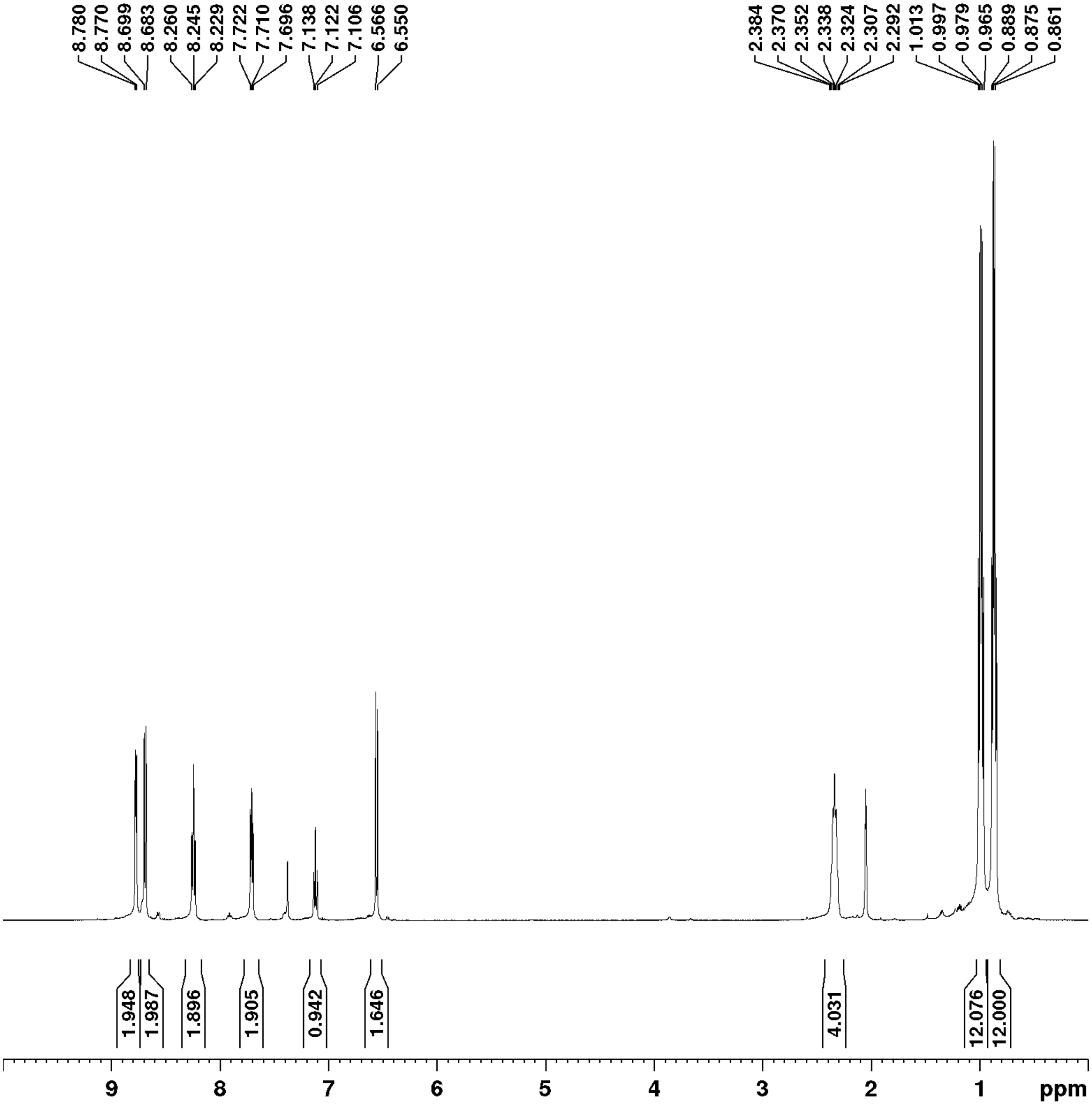


Figure S13. ^{1}HNMR spectrum of [(POCOP)Ni(bipy)][SbF$_6$] (**2c**) in $(CD_3)_2CO$.

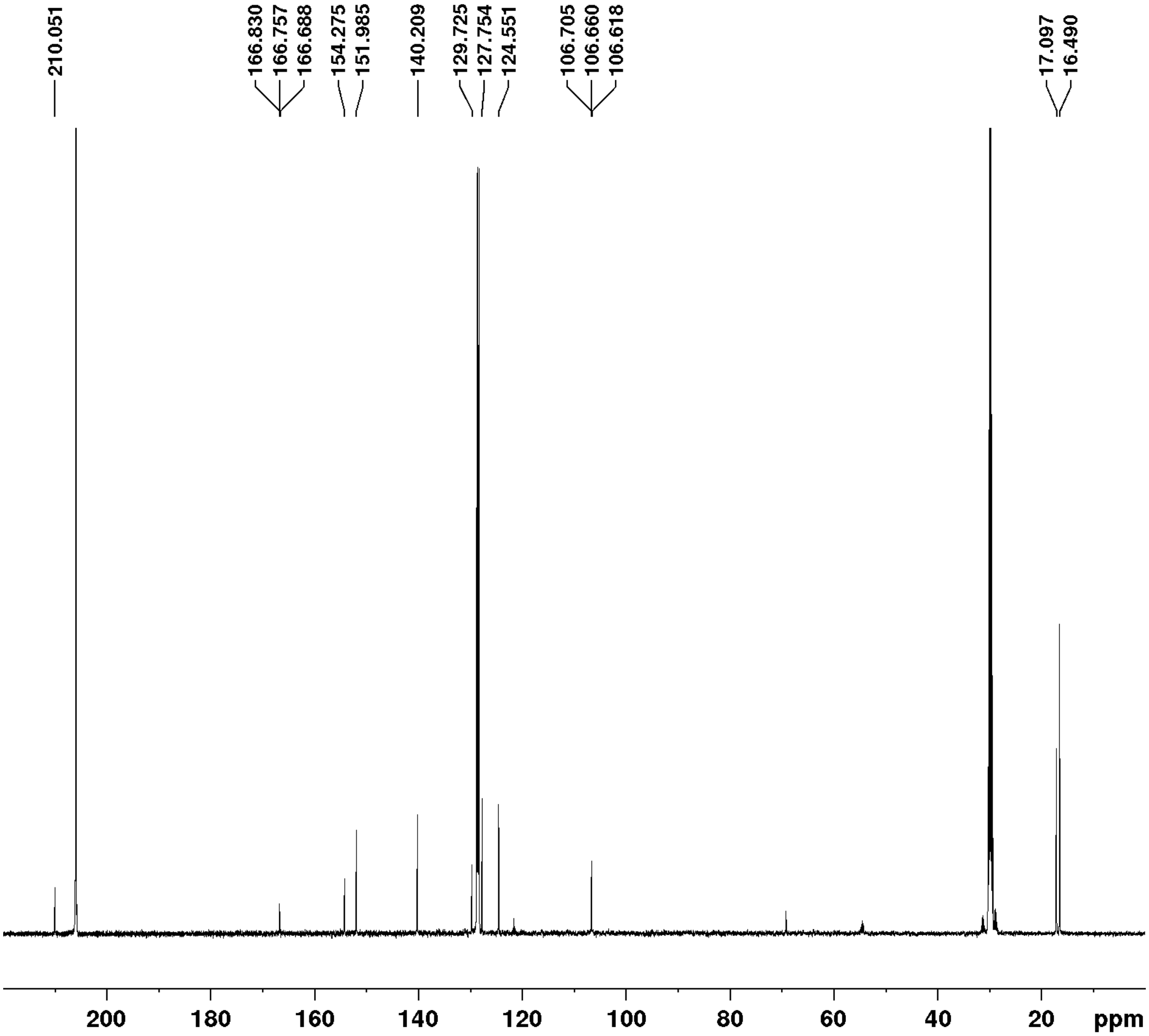


Figure S14. ^{13}CNMR spectrum of [(POCOP)Ni(bipy)][SbF$_6$] (**2c**) in $(CD_3)_2CO$.

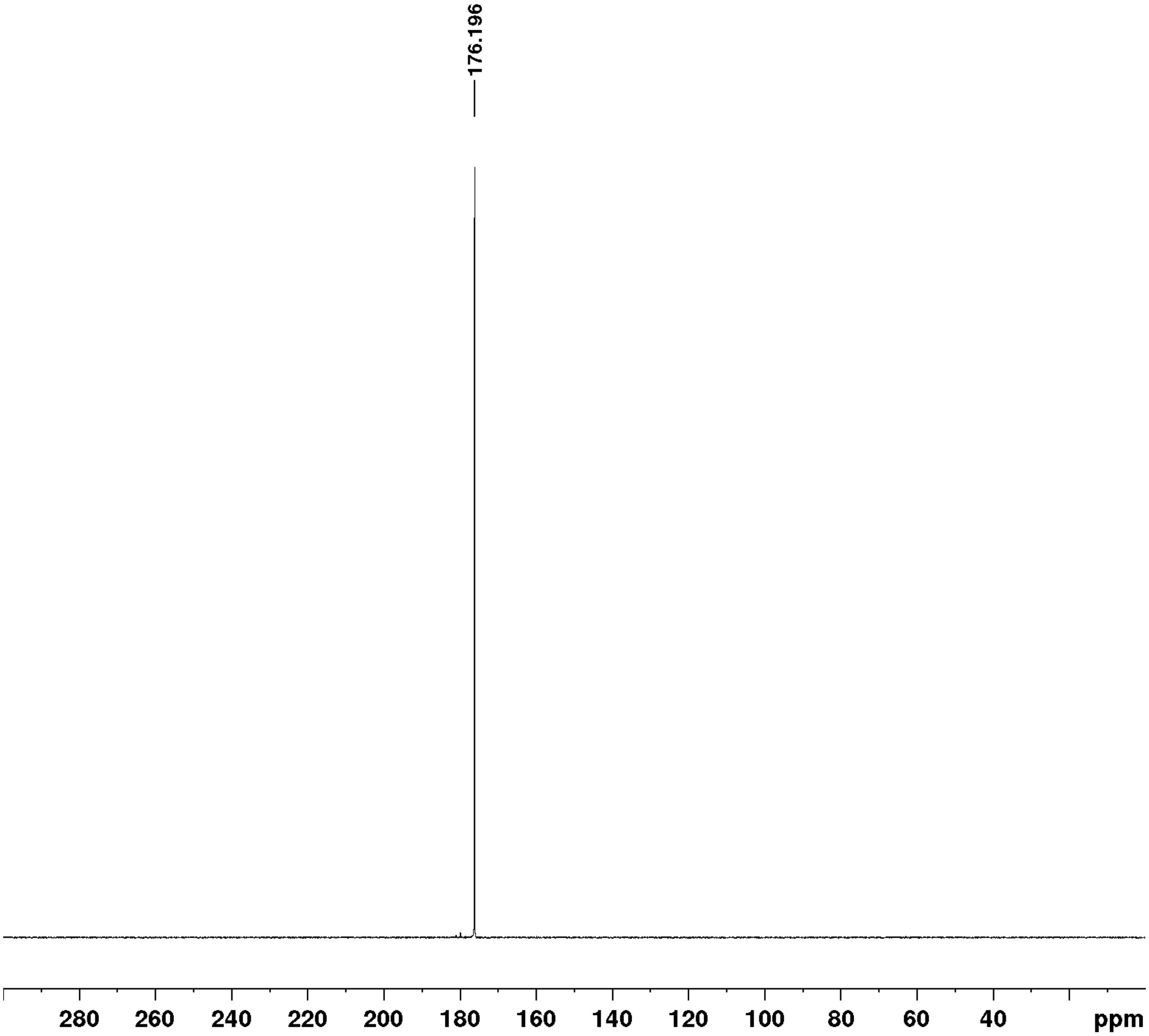


Figure S15. ^{31}PNMR spectrum of [(POCOP)Ni(bipy)][SbF$_6$] (**2c**) in $(CD_3)_2CO$.

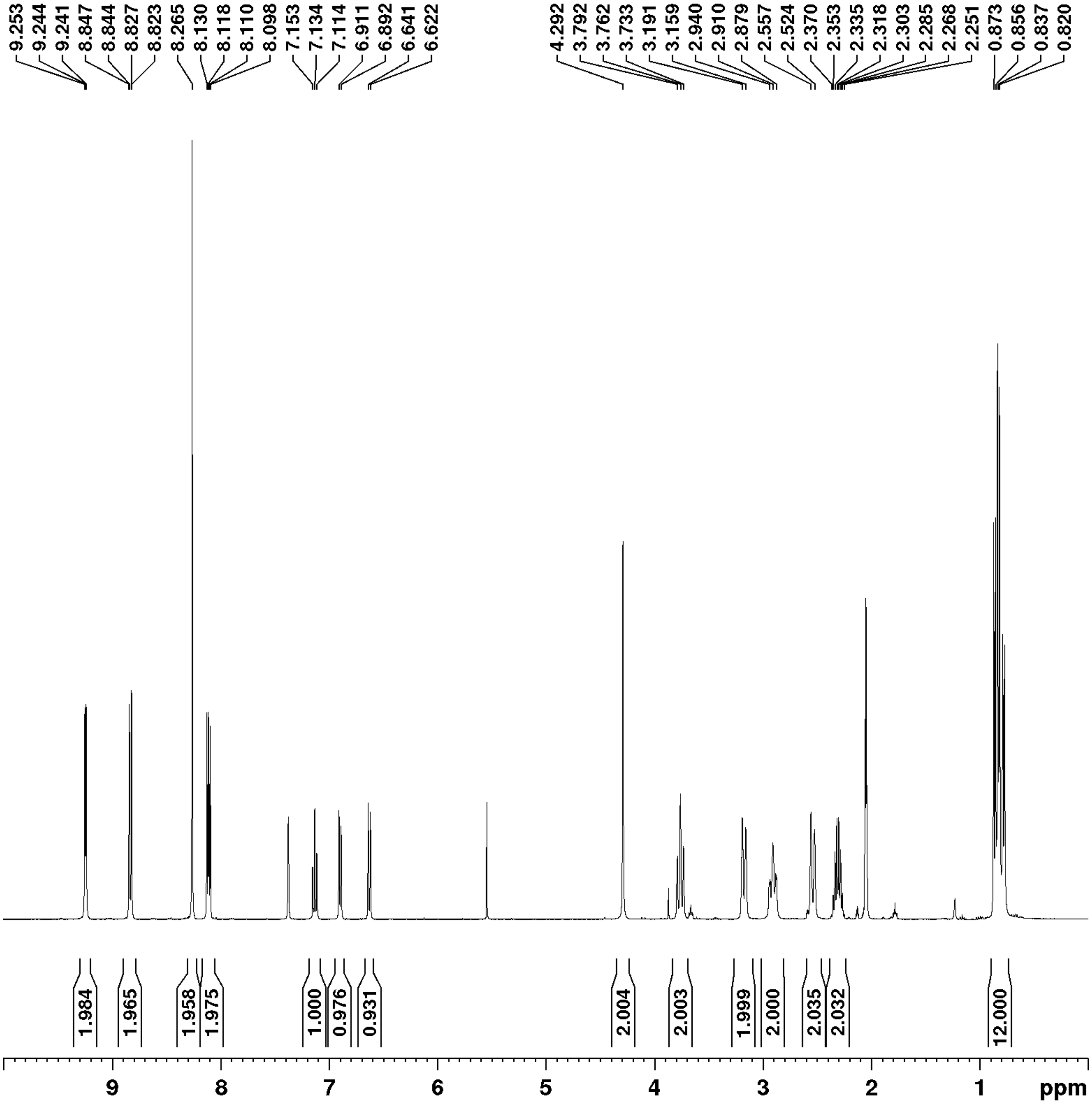


Figure S16. ^{1}HNMR spectrum of [(POCN)Ni(phen)][SbF$_6$] (**1d**) in $(CD_3)_2CO$.

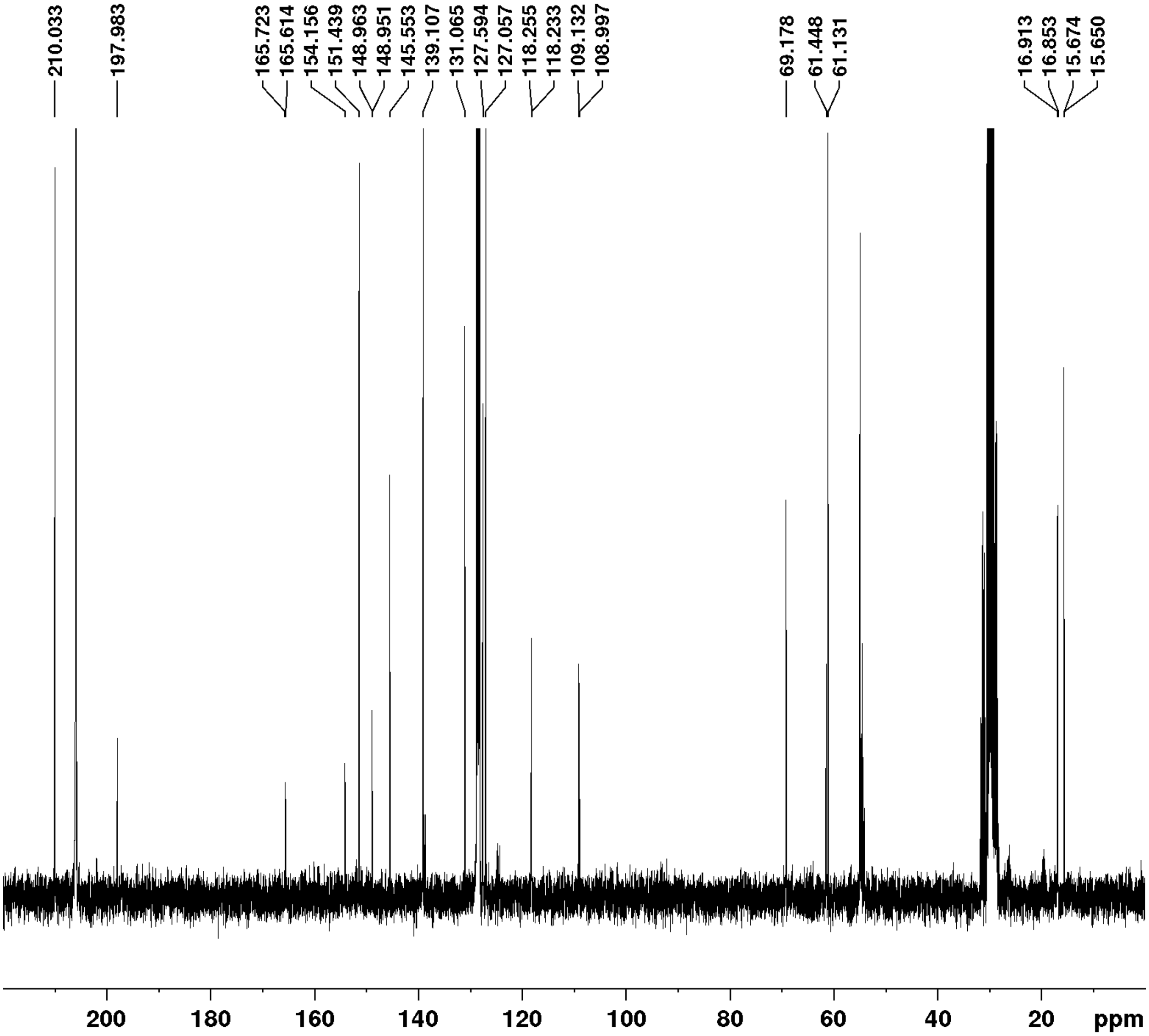


Figure S17. ^{13}CNMR spectrum of [(POCN)Ni(phen)][SbF$_6$] (**1d**) in (CD$_3$)$_2$CO.

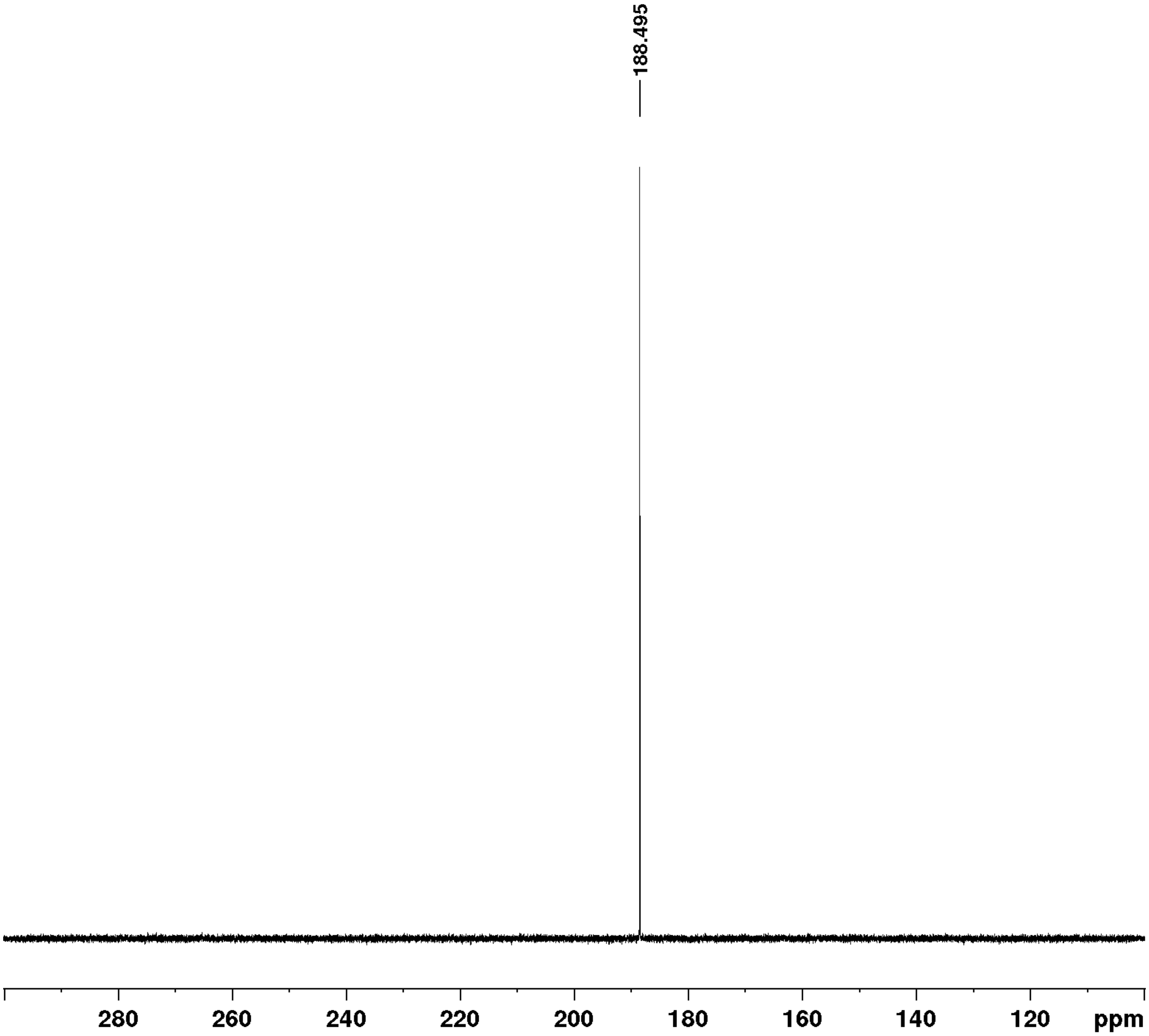


Figure S18. ^{31}PNMR spectrum of [(POCN)Ni(phen)][SbF$_6$] (**1d**) in (CD$_3$)$_2$CO.

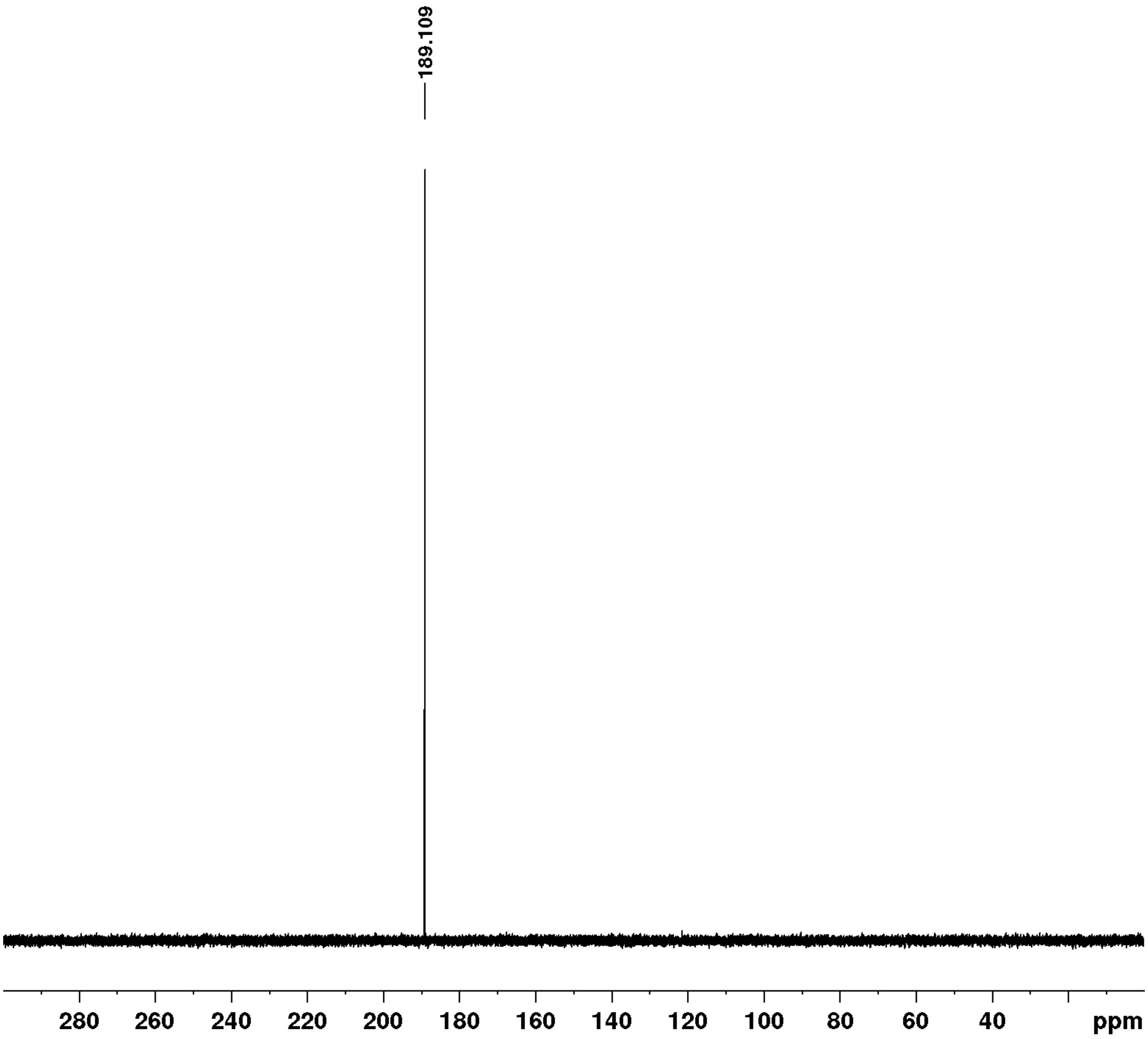


Figure S19. ^{31}PNMR spectrum of [(POCN)Ni(phen)][SbF$_6$] (**1d**) in CH$_3$CN

(This sample was prepared in the one-pot reaction of (POCN)NiBr with phenanthroline and AgSbF$_6$ in CH$_3$CN.)

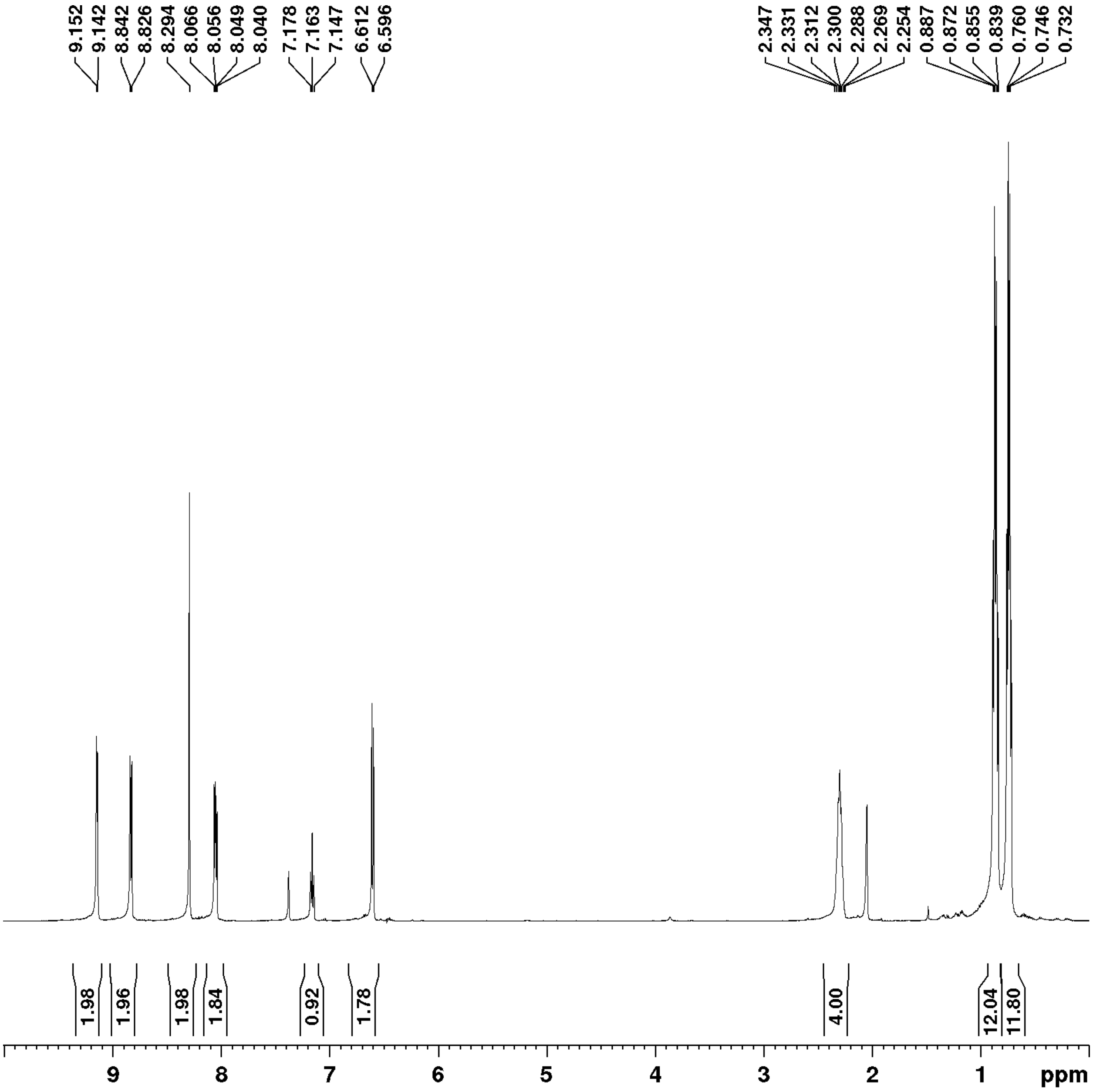


Figure S20. ^{1}HNMR spectrum of [(POCOP)Ni(phen)][SbF$_6$] (**2d**) in $(CD_3)_2CO$.

h

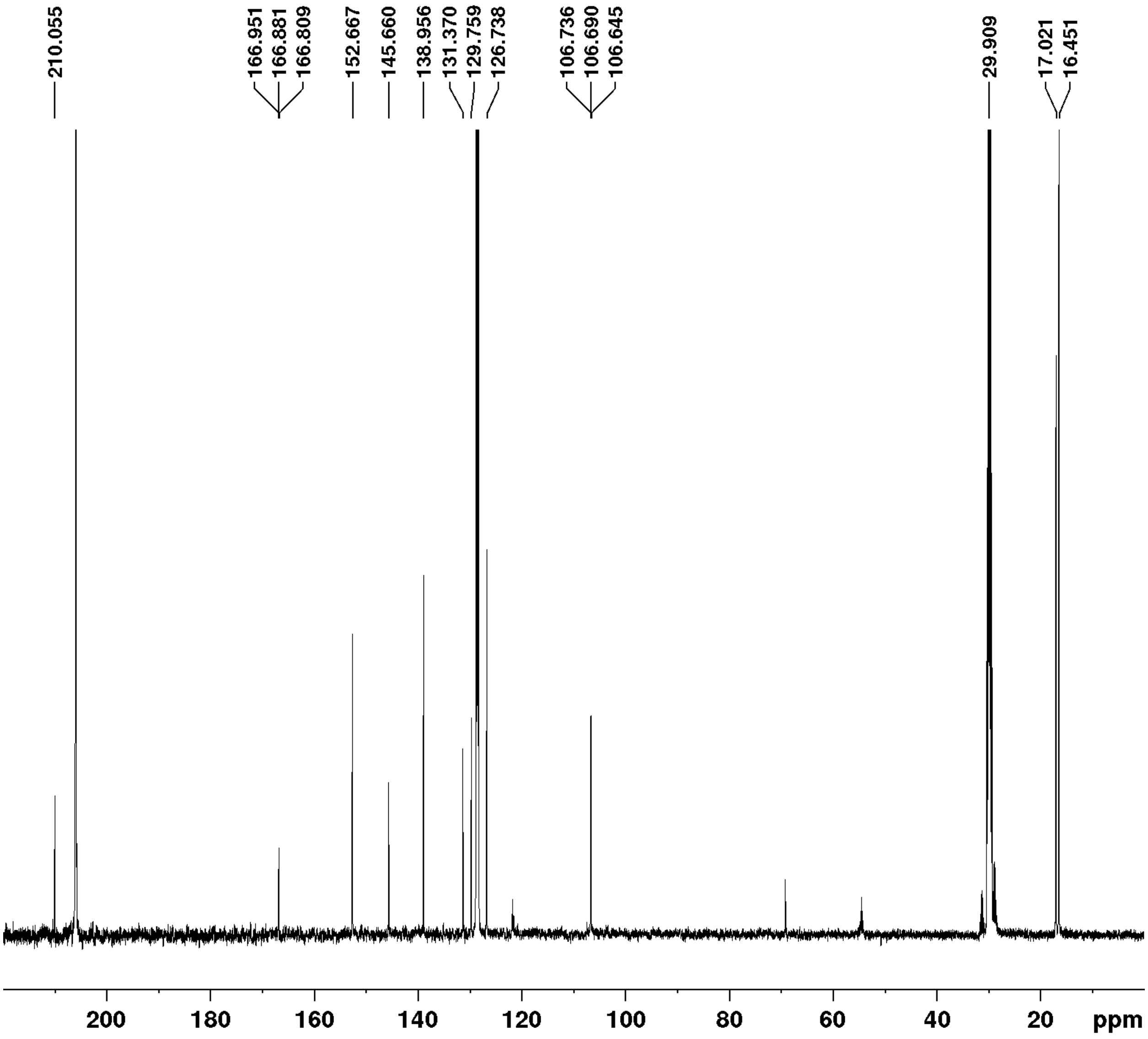


Figure S21. ^{13}CNMR spectrum of [(POCOP)Ni(phen)][SbF$_6$] (**2d**) in $(CD_3)_2CO$.

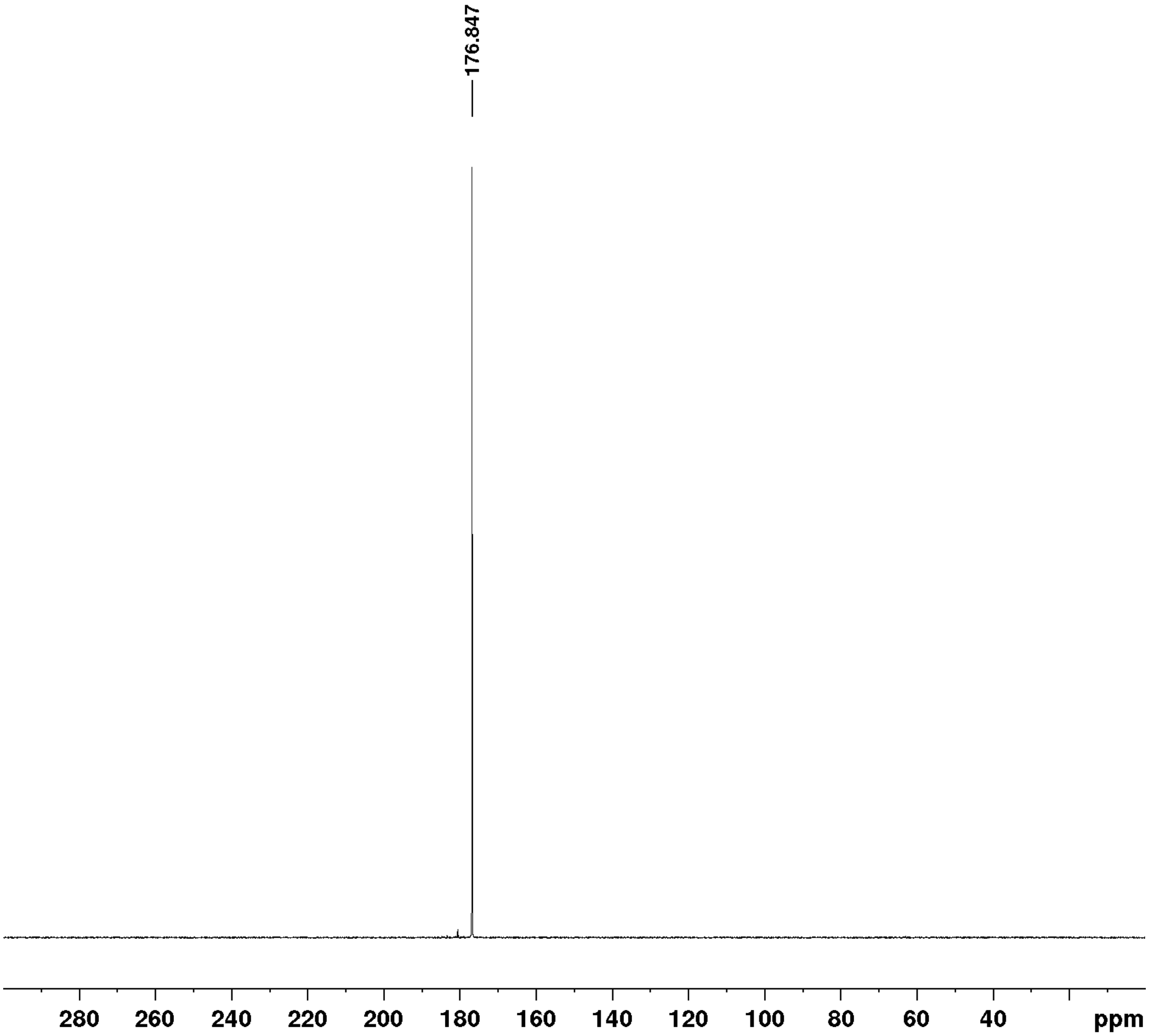


Figure S22. ^{31}PNMR spectrum of [(POCOP)Ni(phen)][SbF$_6$] (**2d**) in $(CD_3)_2CO$.

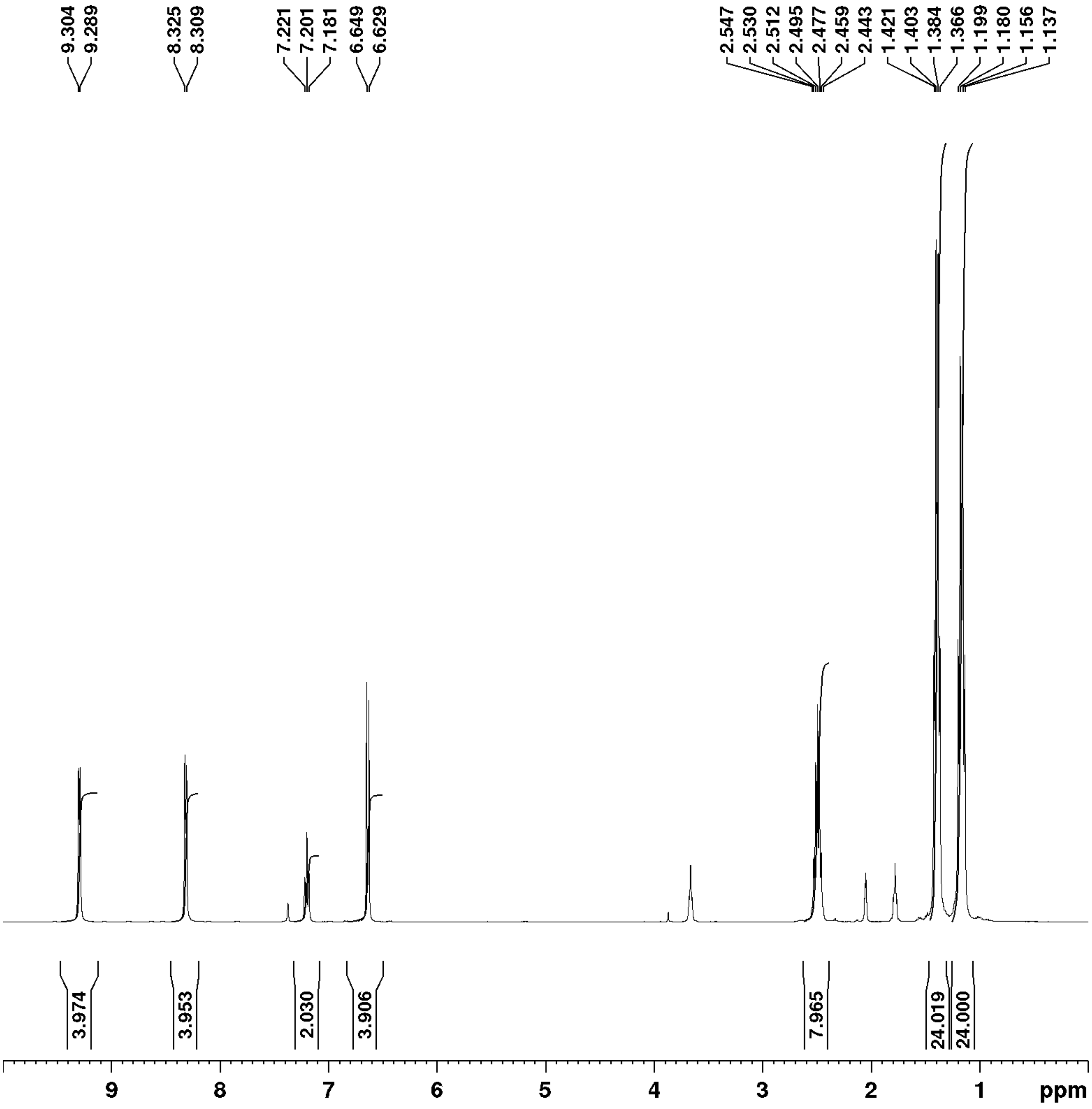


Figure S23. ^{1}HNMR spectrum of [((POCOP)$_2$Ni$_2$(μ-4,4'-bipy)][SbF$_6$]$_2$ (**2e**) in (CD$_3$)$_2$CO.

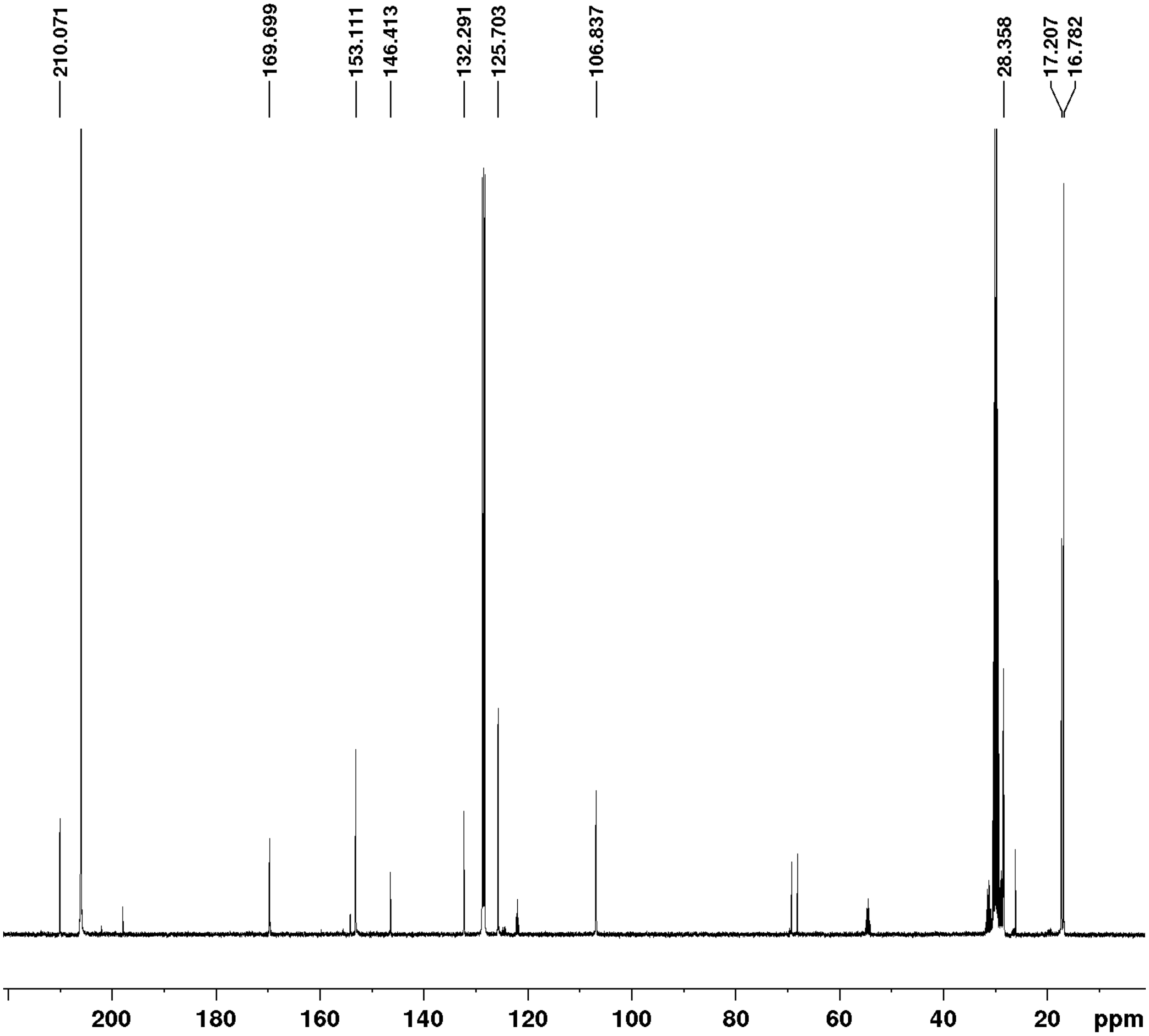


Figure S24. ^{13}CNMR spectrum of [((POCOP)$_2$Ni$_2$((μ-4,4'-bipy)][SbF$_6$]$_2$ (**2e**) in (CD$_3$)$_2$CO.

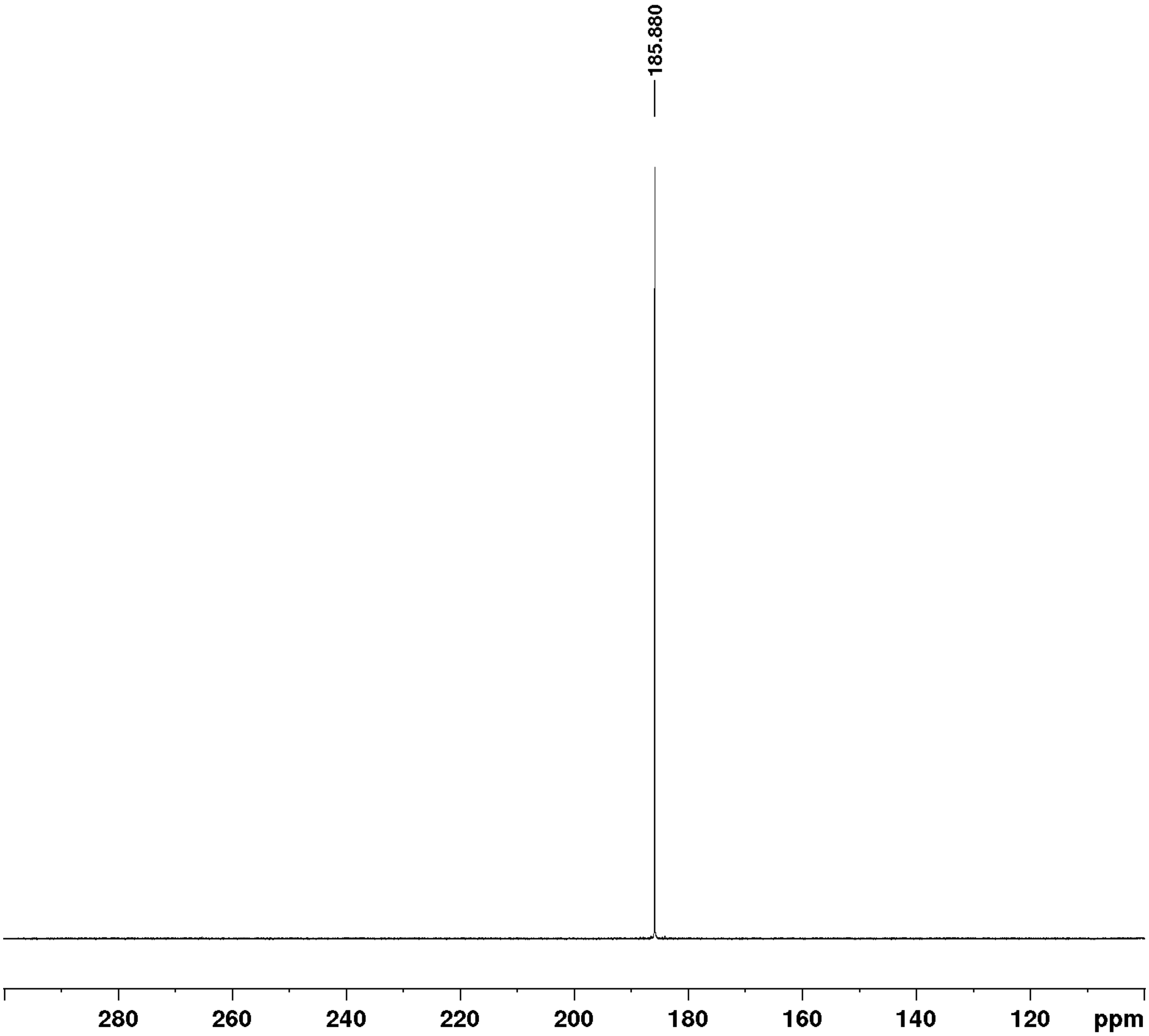


Figure S25. ^{31}PNMR spectrum of [((POCOP)$_2$Ni$_2$((μ-4,4’-bipy)][SbF$_6$]$_2$ (**2e**) in (CD$_3$)$_2$CO.

4. Procedures for the ligand exchange experiments

Reaction of (POCN)NiBr with phenanthroline. A 20 mL reaction vessel was charged with 0.0202 g (0.0452 mmol) of (POCN)NiBr and approximately 3 mL of MeCN. Phenanthroline monohydrate (0.0081 g, 0.0452 mmol) was added to the yellow-orange solution which quickly turned into dark red. The ^{31}PNMR spectrum of the reaction mixture showed two signals at 200.91 and 189.19 ppm for (POCN)NiBr and the ionic product with the ratio of 21.81:78.19, respectively. Dissolution of the isolated [(POCN)Ni(Phen)][SbF$_6$] in MeCN did not result in the replacement of phenanthroline with the solvent. The ^{31}PNMR spectrum of the solution showed only one signal at 189.10 ppm for [(POCN)Ni(Phen)][SbF$_6$].

Reaction of (POCN)NiBr with Bipyridine. A 20 mL reaction vessel was charged with 0.0675 g (0.151 mmol) of (POCN)NiBr and approximately 3 mL of MeCN. Bipyridine (0.0231 g, 0.151 mmol) was added to the yellow-orange solution which quickly turned into dark red. The ^{31}PNMR spectrum of the reaction mixture showed two signals at 200.93 and 188.80 ppm for (POCN)NiBr and the ionic product with the ratio of 81:19, respectively. Addition of 2, 4, 6 and 8 equivalents of bipyridine resulted in the formation of higher amounts of the corresponding ionic product judged by the ^{31}PNMR spectra (2 (73:27); 4 (61.7:38.3); 6 (54.5:45.5); 8 (45.6:54.4). Upon addition of AgSbF$_6$ (0.0519 g, 0.151 mmol), the ^{31}PNMR spectrum of the reaction mixture showed two peaks at 202.17 and 188.79 ppm for [(POCN)Ni(MeCN)][SbF$_6$] and [(POCN)Ni(Bipy)][SbF$_6$] with the ratio of 22.45:77.54, respectively.

Reaction of (POCN)NiCl with 1,10-Phenanthroline monohydrate. A 20 mL reaction vessel was charged with 0.0155 g (0.0385 mmol) of (POCN)NiCl and approximately 3 mL of MeCN. Phenanthroline (0.0069 g, 0.0385 mmol) was added to the yellow-orange solution which turned orange red. The ^{31}PNMR spectrum of the reaction mixture showed two signals at 198.28 and 189.15 ppm for (POCN)NiCl and the ionic product with the ratio of 74.72:25.28, respectively.

Reaction of (POCN)NiCl with bipyridine. A 20 mL reaction vessel was charged with 0.0163 g (0.0405 mmol) of (POCN)NiCl and approximately 3 mL of MeCN. Phenanthroline (0.0063 g, 0.0405 mmol) was added to the yellow-orange solution which did not result in any observable colour change. The ^{31}PNMR spectrum of the reaction mixture showed two signals at 198.28 and 188.78 ppm for (POCN)NiCl and the ionic product with the ratio of 99.19:0.81, respectively.

Reaction of (POCOP)NiBr with 1,10-Phenanthroline monohydrate. A 20 mL reaction vessel was charged with 0.0695 g (0.1448 mmol) of (POCOP)NiBr and approximately 3 mL of MeCN. 1,10-Phenanthroline monohydrate (0.0287 g, 0.1448 mmol) was added to the yellow-orange solution which gradually turned dark red. The ^{31}PNMR spectrum of the reaction mixture showed two signals at 188.54 and 177.17 ppm for (POCOP)NiBr and the ionic product with the ratio of 82.89:17.11 2, respectively. (The ^{31}PNMR spectrum of (POCOP)NiBr in MeCN displays a peak at 188.54 ppm.)

Reaction of (POCOP)NiBr with Bipyridine. A 20 mL reaction vessel was charged with 0.055 g (0.1146 mmol) of (POCOP)NiBr and approximately 3 mL of MeCN. Bipyridine (0.0179 g, 0.1146 mmol) was added to the yellow-orange solution which did not result in any color change. The ^{31}PNMR spectrum of the reaction mixture showed two signals at 188.54 and 176.52 ppm for (POCOP)NiBr and the ionic product with the ratio of 99.2:0.8, respectively.

Reaction of (POCOP)NiBr with Pyridine. 0.0394 g (0.082 mmol) of [(POCN)Ni(MeCN)][SbF$_6$] was dissolved in 3 mL of pyridine. The ^{31}PNMR spectrum of the resulting yellow-orange solution showed only one signal at 188.6 ppm for (POCOP)NiBr.

Reaction of (POCOP)NiCl with 1,10-Phenanthroline monohydrate. A 20 mL reaction vessel was charged with 0.2172 g (0.4987 mmol) of (POCOP)NiCl and approximately 3 mL of MeCN. 1,10-Phenanthroline monohydrate (0.0988 g, 0.4987 mmol) was added to the yellow-orange solution which quickly turned dark red. The ^{31}PNMR spectrum of the reaction mixture showed two signals at 185.42 and 177.16 ppm for (POCOP)NiCl and the ionic product with the ratio of h89.98:10.02, respectively. Upon addition of AgSbF$_6$ (0.1714 g, 0.4987 mmol), the ^{31}PNMR spectrum of the reaction mixture showed two peaks at 193.19 and 177.20 ppm for [(POCOP)Ni(MeCN)][SbF$_6$] and [(POCOP)Ni(Phen)][SbF$_6$] with the ratio of 12.85:87.15, respectively.

Reaction of (POCOP)NiCl with Bipyridine. A 20 mL reaction vessel was charged with 0.1997 g (0.4585 mmol) of (POCOP)NiCl and approximately 3 mL of MeCN. Bipyridine (0.0716 g, 0.4585 mmol) was added to the yellow-orange solution which did not result in a colour change. The ^{31}PNMR spectrum of the reaction mixture showed two signals at 185.42 and 176.52 ppm for (POCOP)NiCl and the ionic product with the ratio of 99.37:0.63, respectively. Upon addition of

$AgSbF_6$ (0.1575 g, 0.4585 mmol), the ^{31}PNMR spectrum of the reaction mixture showed two peaks at 193.18 and 176.56 ppm for [(POCOP)Ni(MeCN)][SbF_6] and [(POCOP)Ni(Bipy)][SbF_6] with the ratio of 29.41:70.59, respectively.

Halide exchange reaction of (POCN)NiCl with (POCOP)NiBr. A 20 mL reaction vessel was charged with 0.0219 g (0.0544 mmol) of (POCN)NiCl and approximately 3 mL of MeCN. (POCOP)NiBr (0.0261 g, 0.0544 mmol) was added to the yellow-orange solution which did not result in a colour change. The ^{31}PNMR spectrum of the reaction mixture showed four signals at 200.93, 198.27, 188.55 and 185.42 ppm for (POCN)NiBr, (POCN)NiCl, (POCOP)NiBr and (POCOP)NiCl with the ratio of 8.77:18.90:50.99:21.34, respectively.

Bromide/phenanthroline exchange reaction of (POCN)NiBr with [(POCOP)Ni(Phen)][SbF_6]. A 20 mL reaction vessel was charged with 0.0073 g (0.0162 mmol) of (POCN)NiBr and approximately 3 mL of MeCN. Complex [(POCOP)Ni(Phen)][SbF_6] (0.014 g, 0.0171 mmol), as a dark red solution in MeCN, was added to the yellow-orange solution. The ^{31}PNMR spectrum of the reaction mixture after 1 hour at room temperature showed two signals at 189.16 and 188.59 ppm for [(POCN)Ni(Phen)][SbF_6] and (POCOP)NiBr, respectively, indicating the reaction completion. (As the complex [(POCOP)Ni(Phen)][SbF_6] was in a bit excess, the remnant of this complex appeared as a peak at 177.19 ppm.)

Solvolysis equilibria with pyridine, bipyridine, and phenanthroline adducts. Solvolysis of the cationic POCN- and POCOP-adducts under study was probed by dissolving in 3 mL of acetonitrile sufficient masses of the solids to give ca. 0.207-0.0326 M solutions, as follows: (a) 0.0204 g (0.0299 mmol) of [(POCN)Ni(py)][SbF_6]; (b) 0.0191 g (0.0252 mmol) of [(POCN)Ni(Bipy)][SbF_6]; (c) 0.0185 g (0.0236 mmol) of [(POCN)Ni(Phen)][SbF_6]; 0.0233 g (0.0326 mmol) of [(POCOP)Ni(py)][SbF_6]; 0.0164 g (0.0207 mmol) of [(POCOP)Ni(Bipy)][SbF_6]; and 0.0189 g (0.0232 mmol) of [(POCOP)Ni(Phen)][SbF_6]. All solutions were allowed to stand at room temperature about 30 min before transferring a 1 mL aliquot to NMR tubes and recording their ^{31}PNMR spectra. The results showed complete solvolysis of the two pyridine adducts, partial displacement of bipyridine in both of its adducts, partial displacement of phenanthroline in [(POCOP)Ni(Phen)][SbF_6], and no solvolysis with [(POCN)Ni(Phen)][SbF_6]. See below for the NMR spectra.

Calculation of K_{eq} values for the halide displacement and solvolysis equilibria. The halide displacement reactions of (pincer)NiX and the solvolysis reactions of $[(\text{pincer})\text{Ni}(\text{ligand})]^+$ in acetonitrile are represented by the equations shown below. The K_{eq} values for these substitution reactions were determined from the ^{31}P NMR spectra of the reaction mixtures (vide infra), using the K_{eq} expressions shown under each equation wherein the equilibrium concentrations for the P-bearing species are derived from their integration values x and 1-x or n-x (n= no. of equiv of Ligand used).

$$\begin{array}{ccccccc} (\text{pincer})\text{NiX} & + & \text{Ligand} & \leftrightarrows & [(\text{pincer})\text{Ni}(\text{Ligand})]^+ & + & \text{Br}^- \\ 1-x & & n-x & & x & & x \end{array}$$

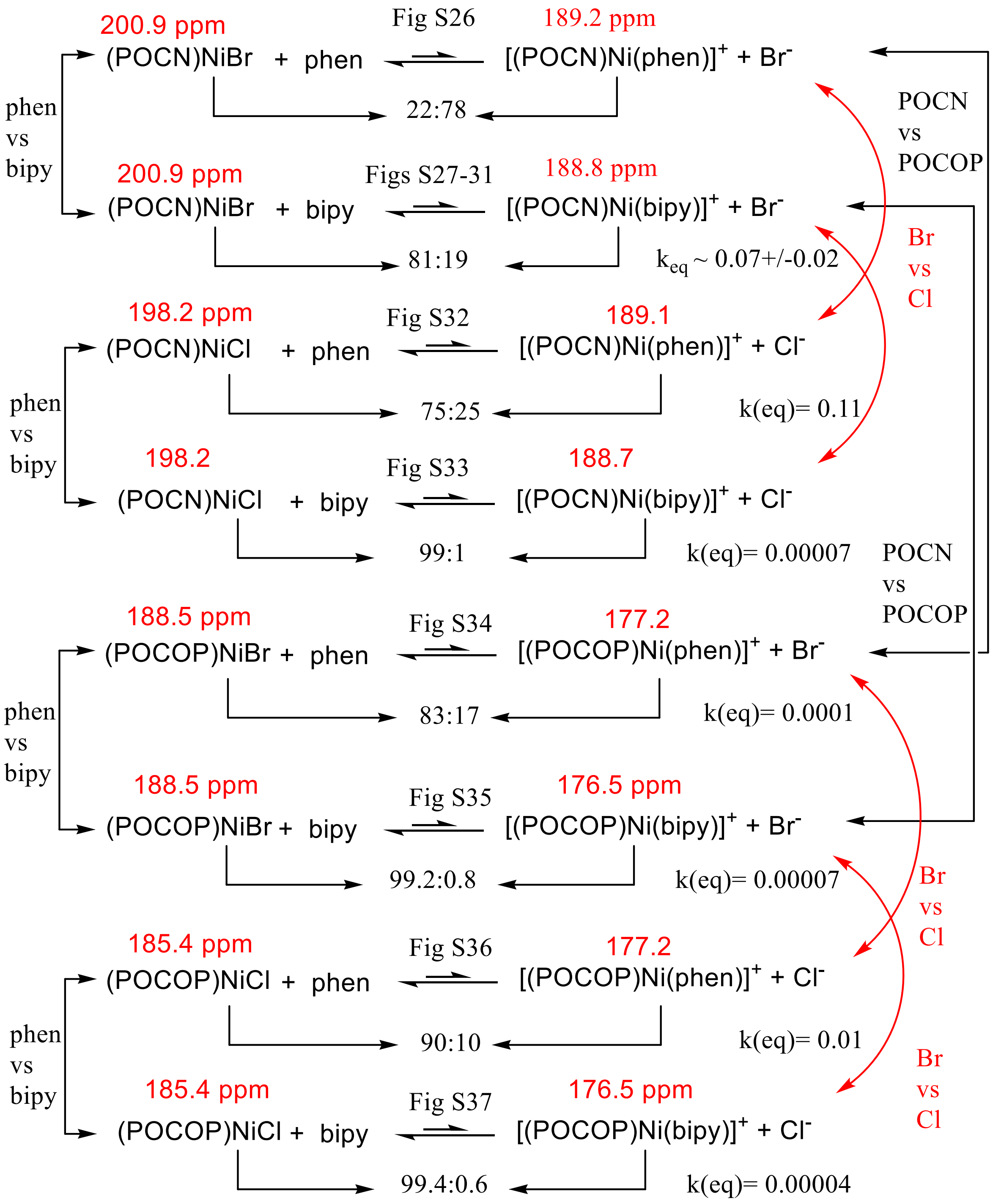
$$K_{eq} = x^2 /(1-x)(n-x)$$

$$\begin{array}{ccccccc} [(\text{pincer})\text{Ni}(\text{Ligand})]^+ & + & \text{MeCN} & \leftrightarrows & [(\text{pincer})\text{Ni}(\text{NCMe})]^+ & + & \text{Ligand} \\ 1-x & & n-x & & x & & x \end{array}$$

$$K_{eq} = x^2 /(1-x)(n-x) \sim x^2 /(1-x)n$$

Acetonitrile is present in very large excess in all but one of the solvolysis reactions (3 mL, n varying from 1748 to 2753). For the sample containing $[(\text{POCN})\text{Ni}(\text{py})]^+$ in a 0.99:0.01 mixture of THF:acetonitrile the value of n is 12.6.

Summary of substitution reactions between halide precursors and phen/bipy



5. Other relevant NMR spectra

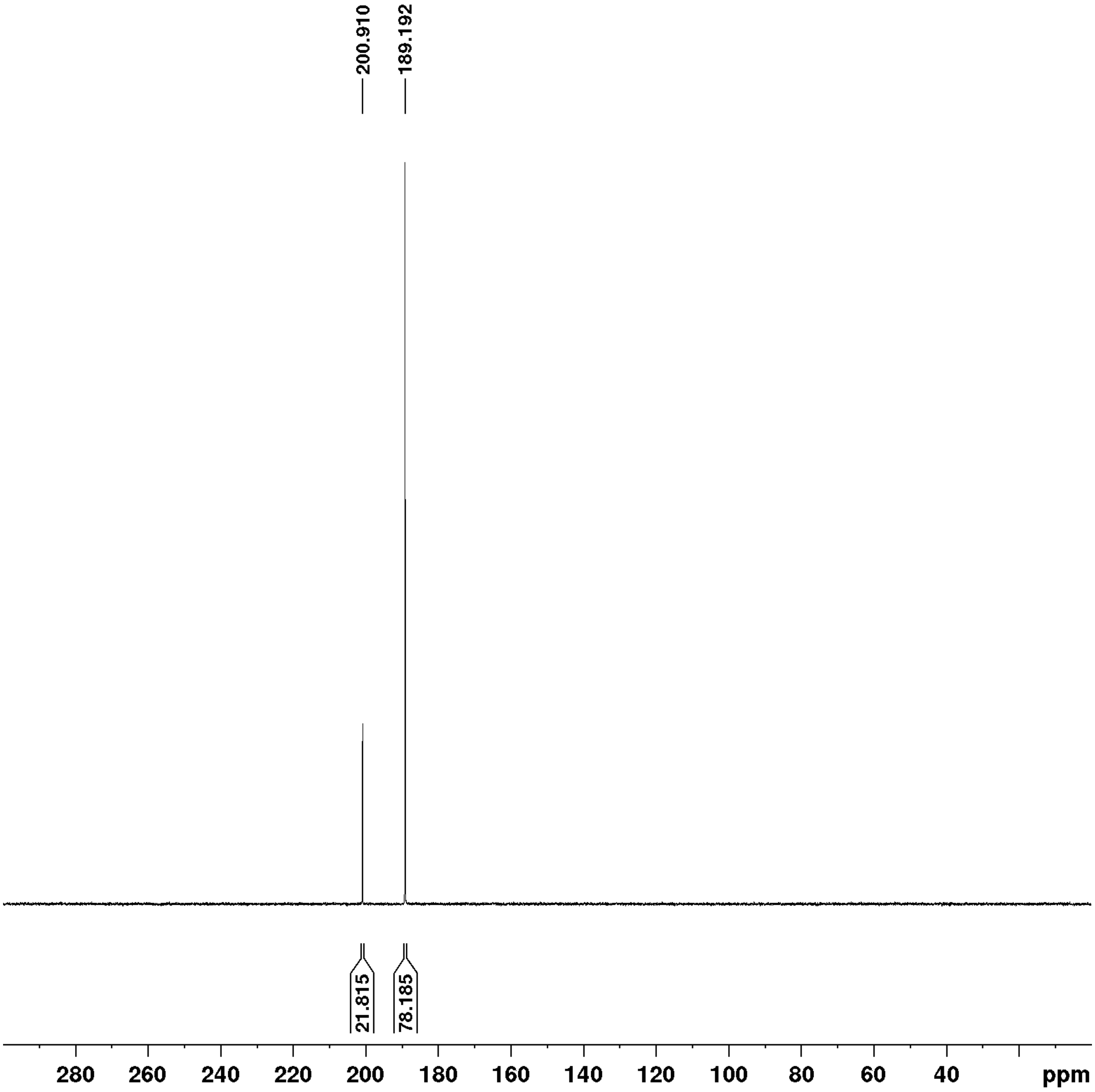


Figure S26. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCN)NiBr + phen (1 equiv) ⇆ $[(POCN)Ni(phen)]^+ + Br^-$

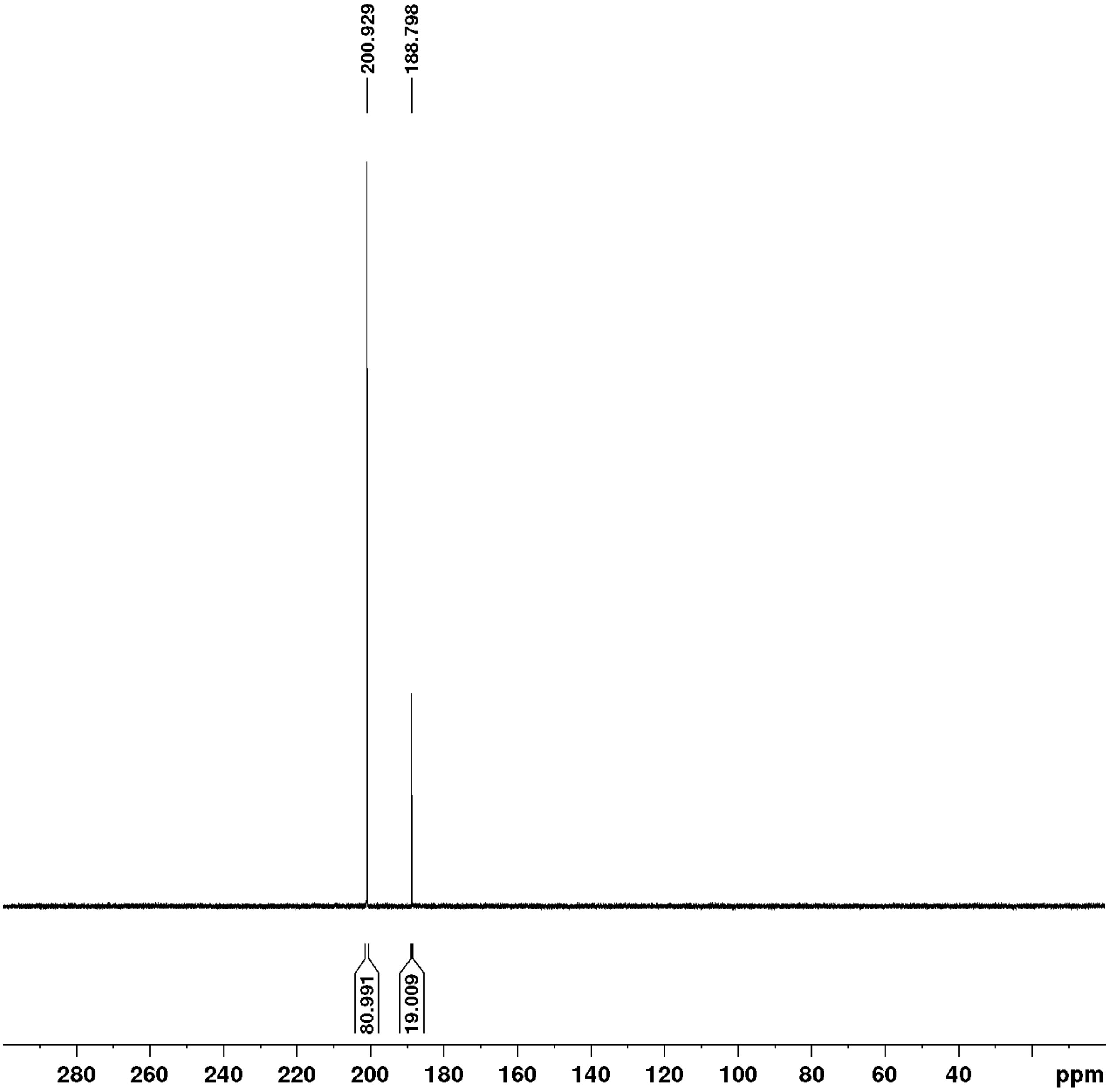


Figure S27. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCN)NiBr + bipy (1 equiv) ⇆ [(POCOP)Ni(bipy)]$^+$ + Br$^-$

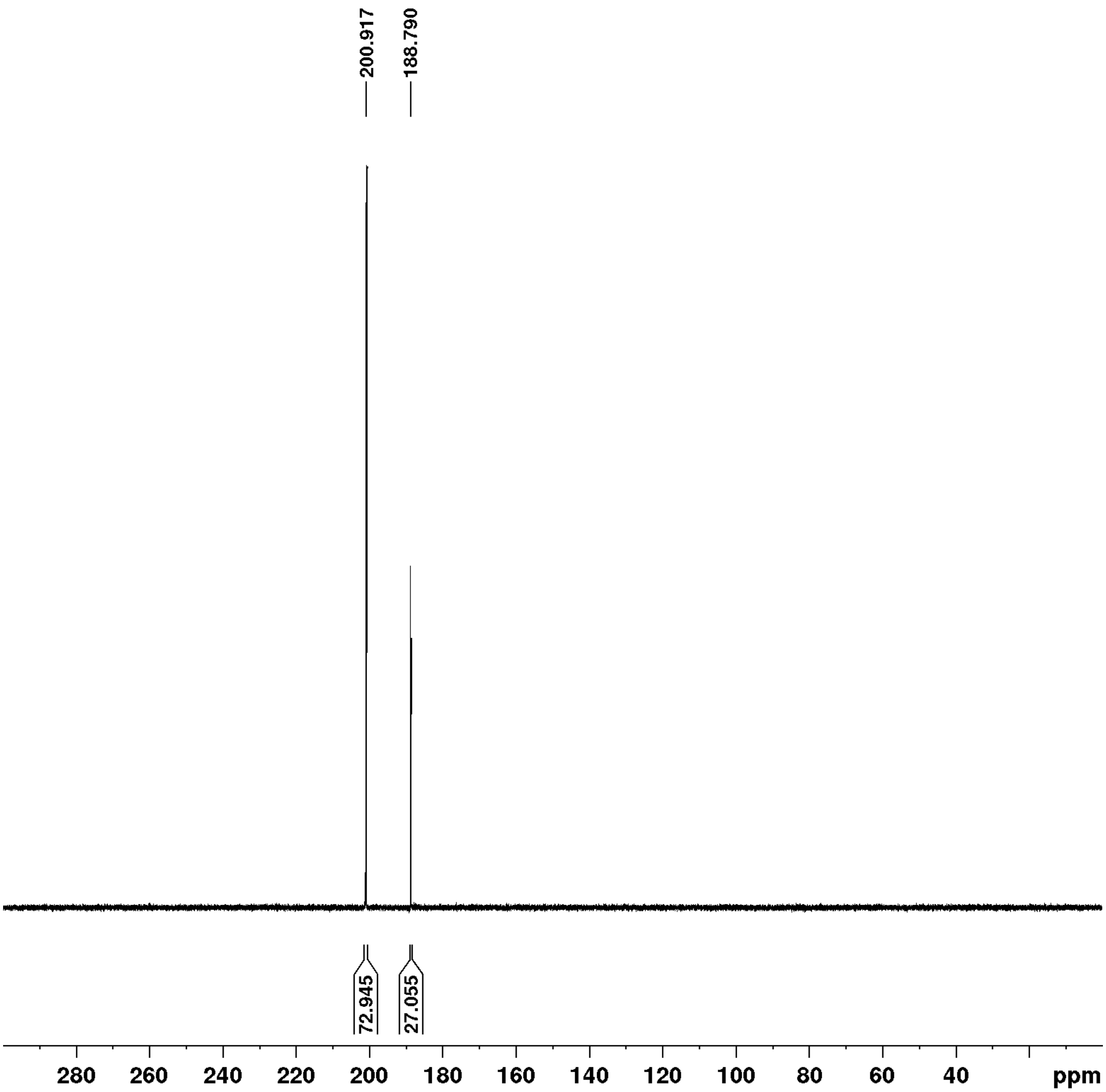


Figure S28. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction h

(POCN)NiBr + bipy (2 equiv) ⇆ $[(POCN)Ni(bipy)]^+ + Br^-$

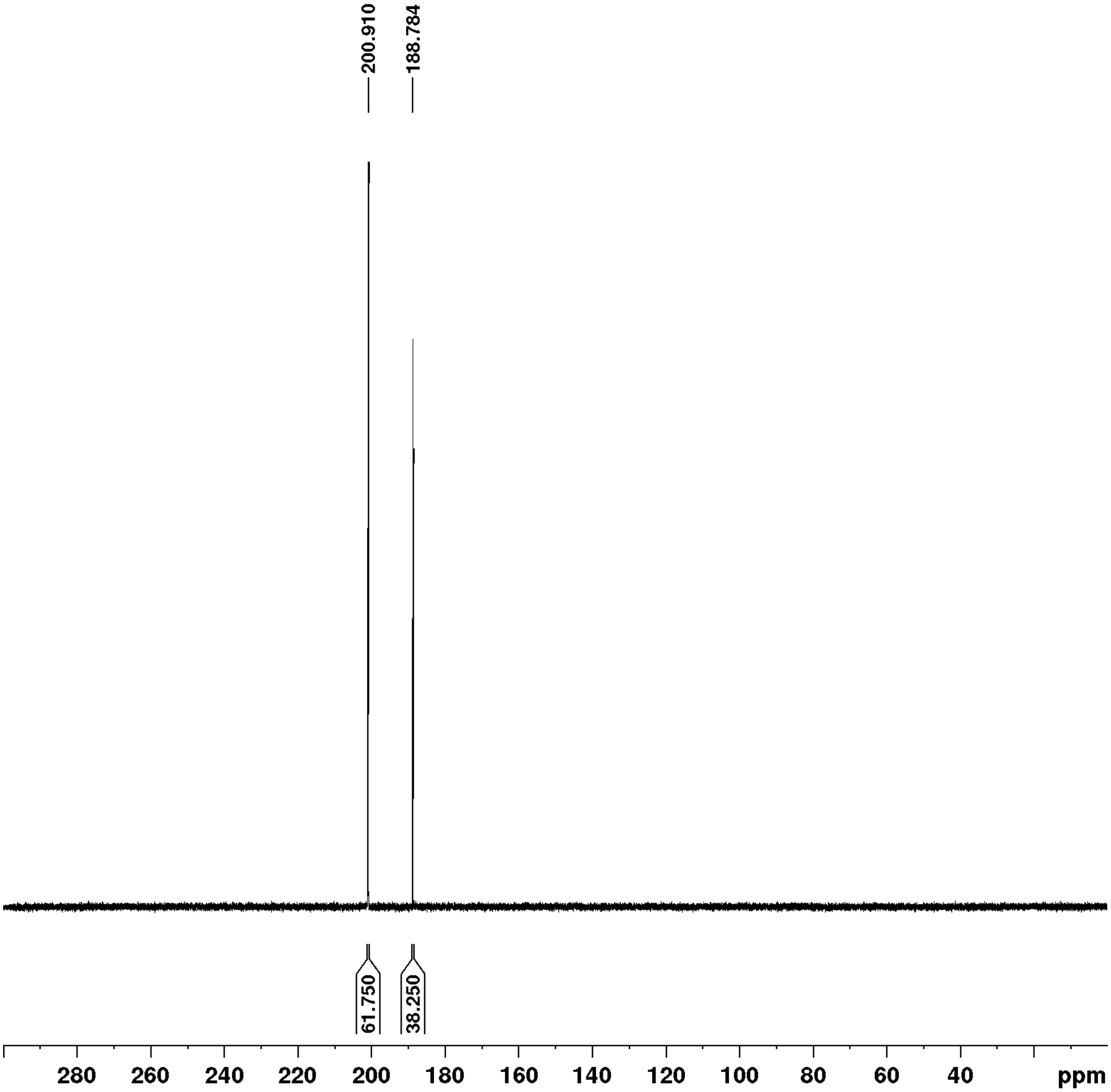


Figure S29. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCN)NiBr + bipy (4 equiv) $\leftrightarrows$ $[(POCN)Ni(bipy)]^+$ + Br^-

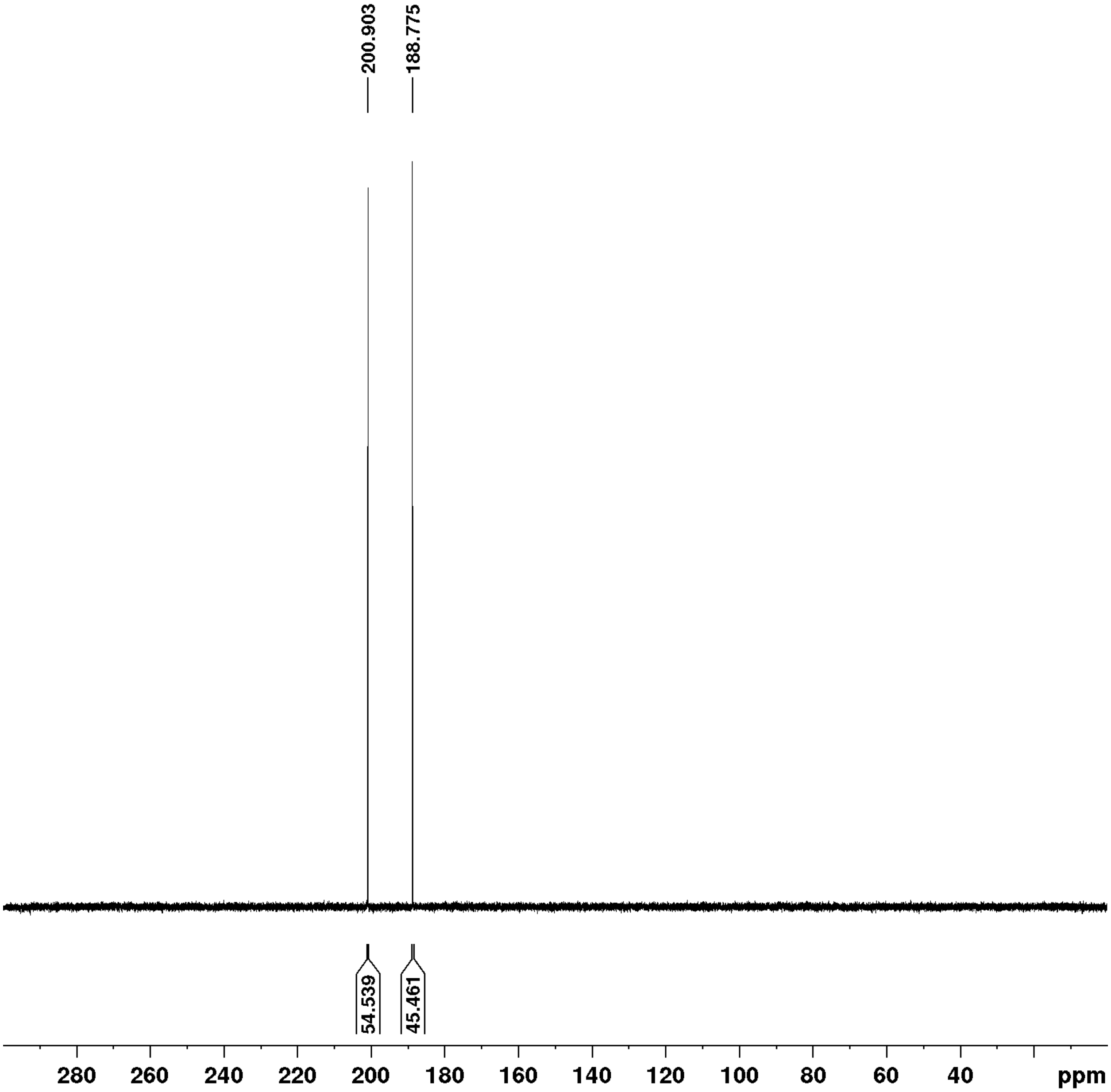
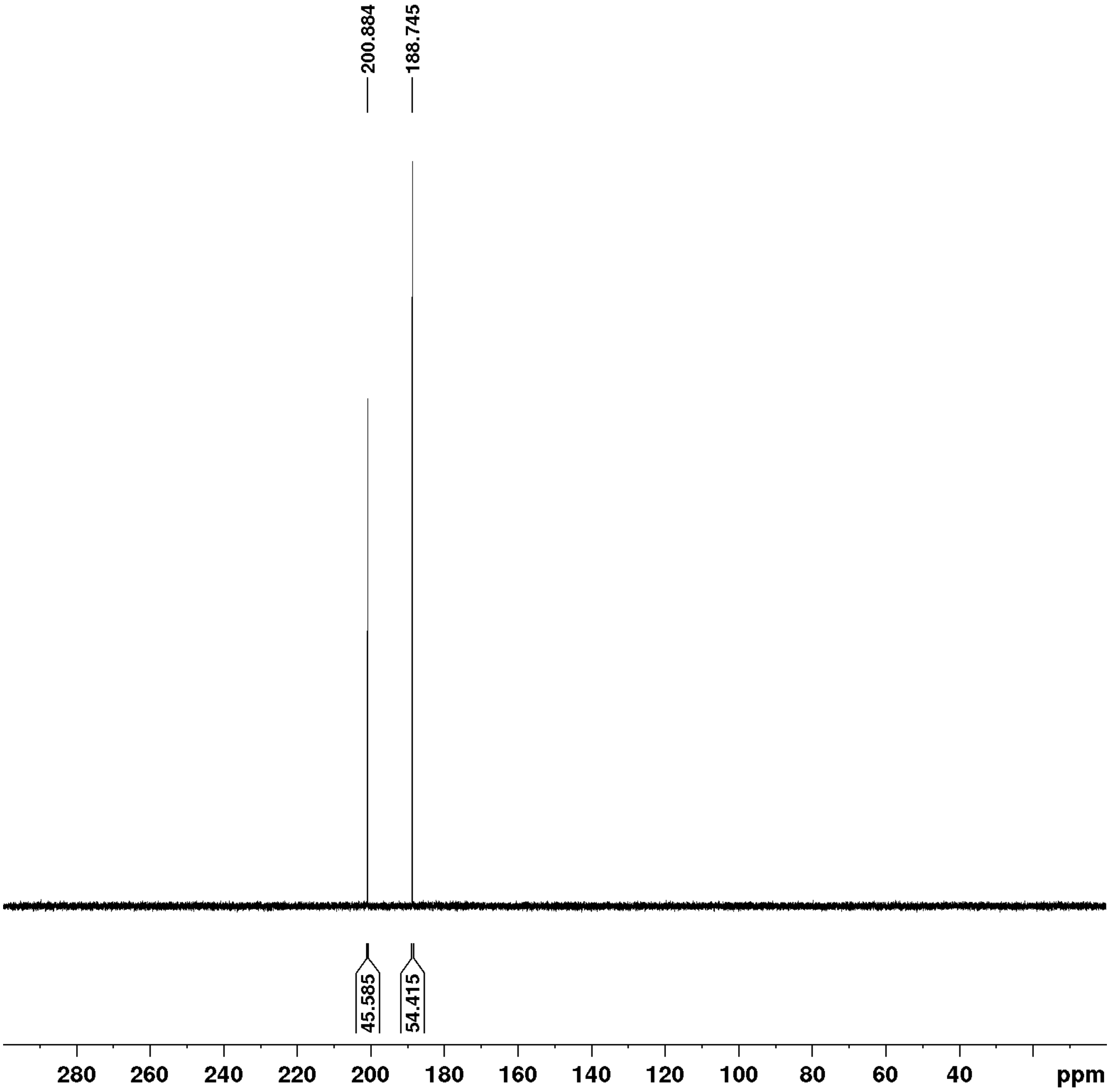


Figure S30. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCN)NiBr + bipy (6 equiv) ⇆ $[(POCOP)Ni(bipy)]^{+} + Br^{-}$



h

Figure S31. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCN)NiBr + bipy (8 equiv) ⇆ [(POCOP)Ni(bipy)]$^{+}$ + Br^{-}

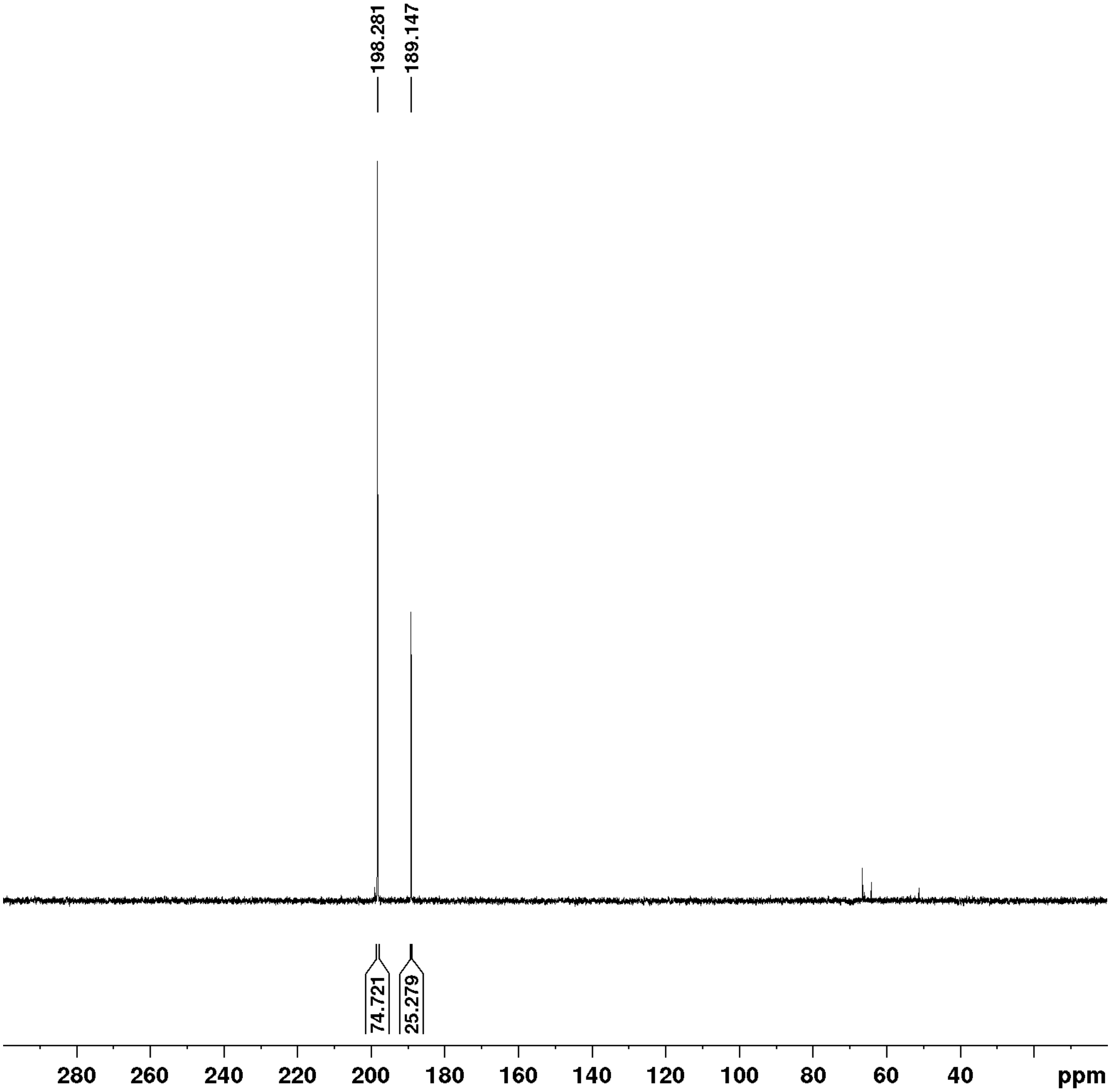


Figure S32. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCN)NiCl + phen (1 equiv) $\leftrightarrows$ [(POCN)Ni(phen)]$^{+}$ + Cl^{-}

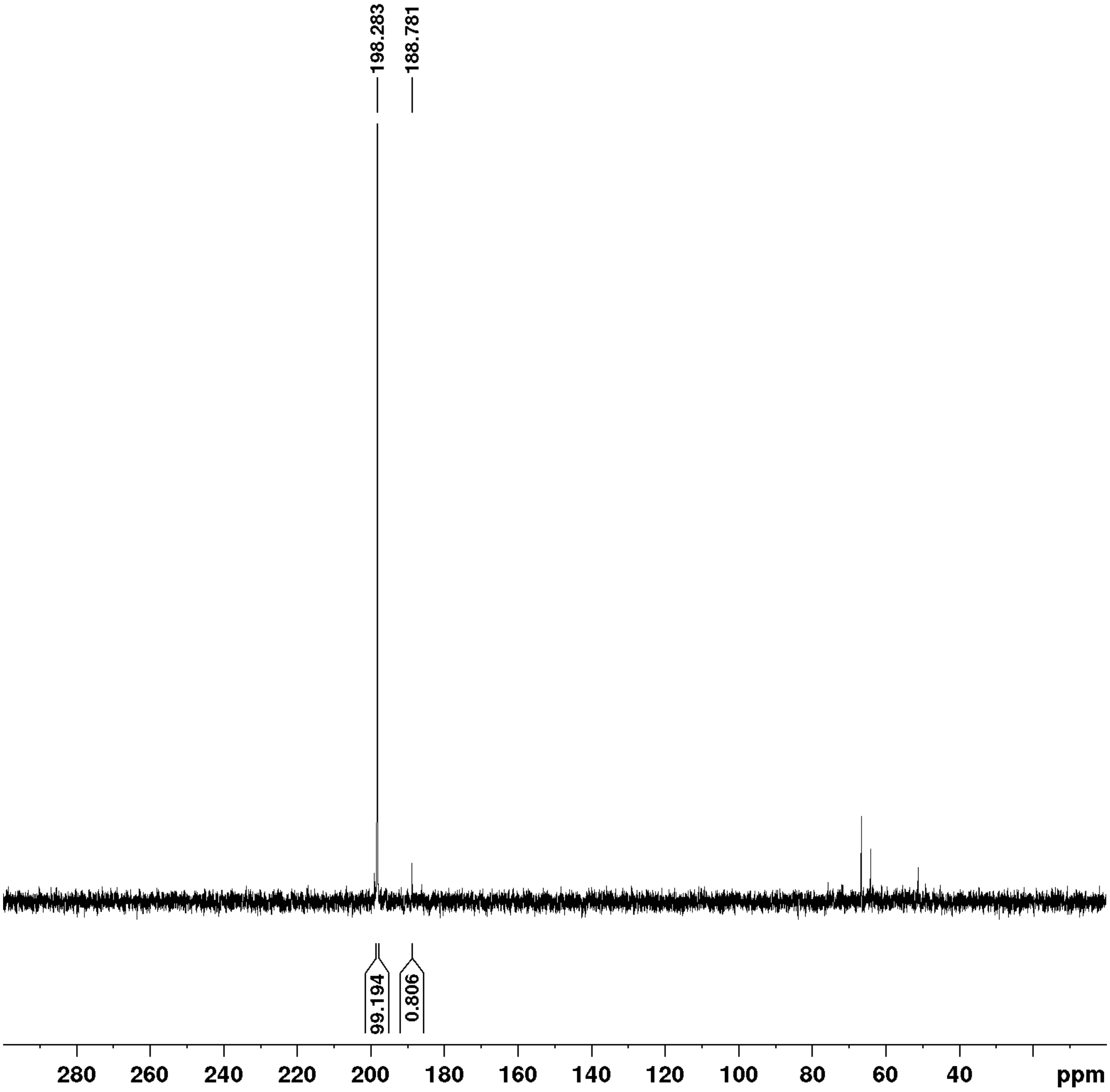


Figure S33. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCN)NiCl + bipy (1 equiv) $\leftrightarrows$ [(POCN)Ni(bipy)]$^+$ + Cl$^-$

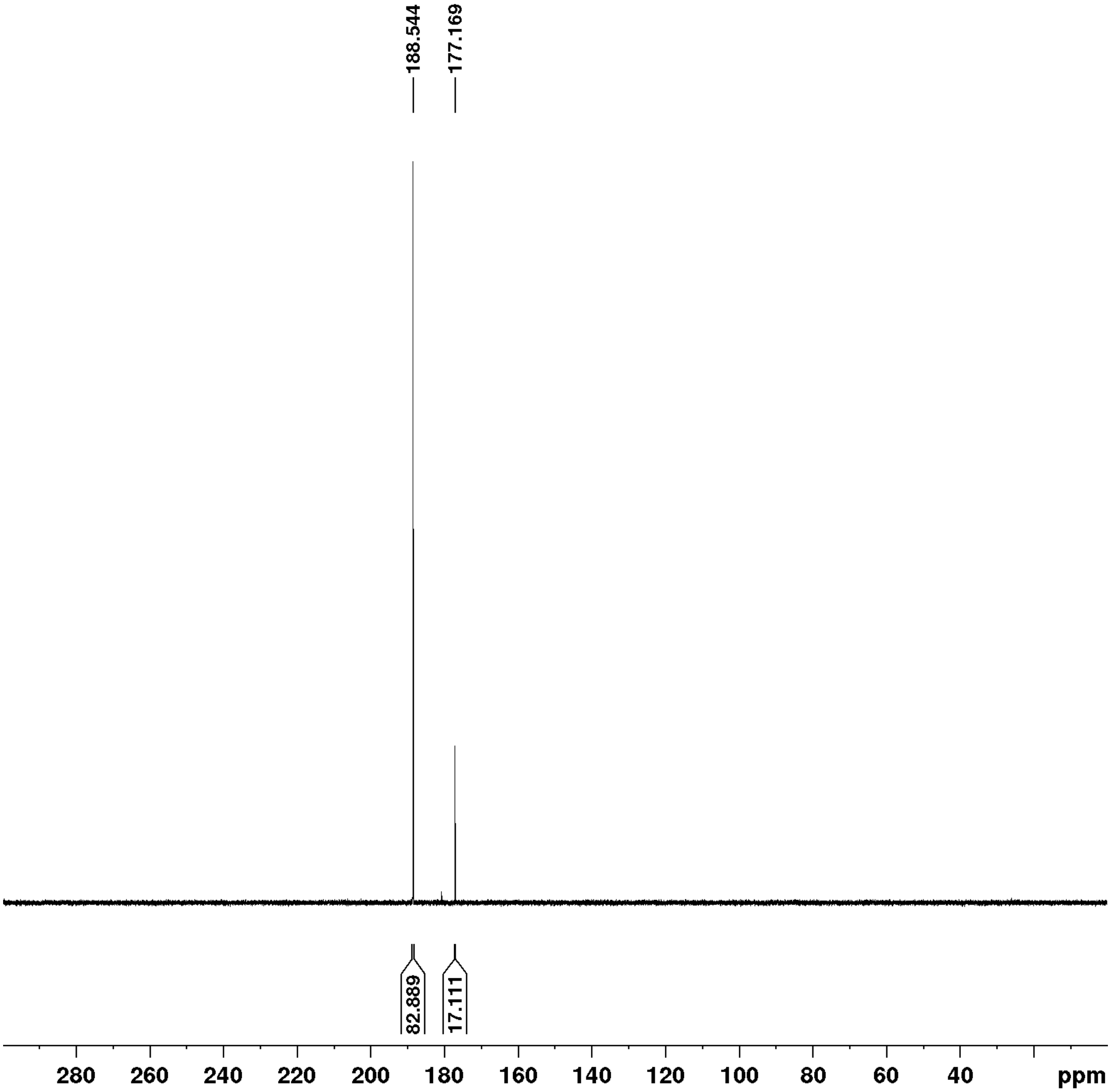


Figure S34. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCOP)NiBr + phen (1 equiv) ⇆ [(POCOP)Ni(phen)]$^+$ + Br$^−$

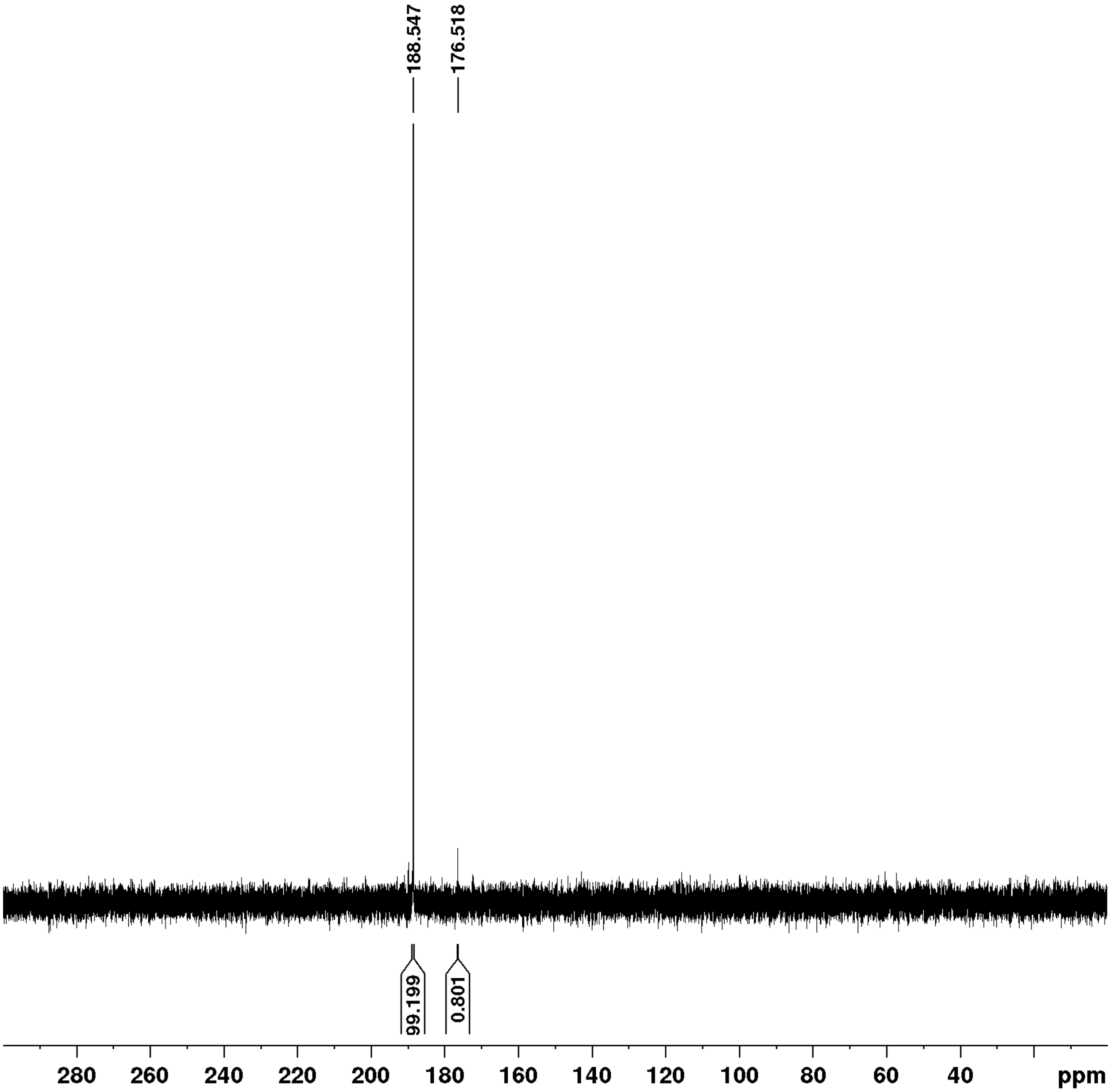


Figure S35. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCOP)NiBr + bipy (1 equiv) $\leftrightarrows$ [(POCOP)Ni(bipy)]$^+$ + Br$^-$

δ : 188.5 176.5

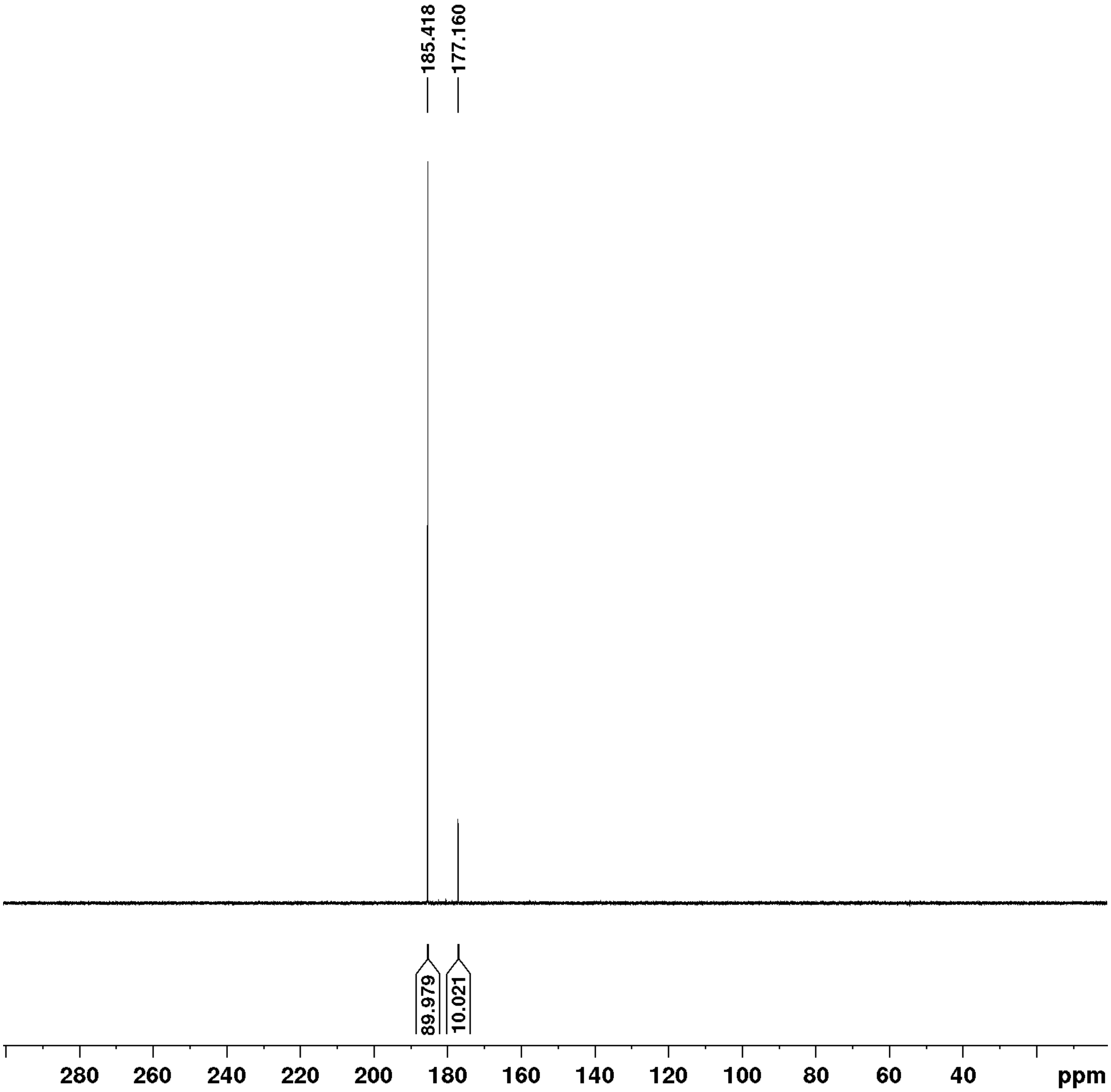


Figure S36. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCOP)NiCl + phen (1 equiv) $\leftrightarrows$ [(POCOP)Ni(phen)]$^+$ + Cl$^-$

δ : 185.4 177.2

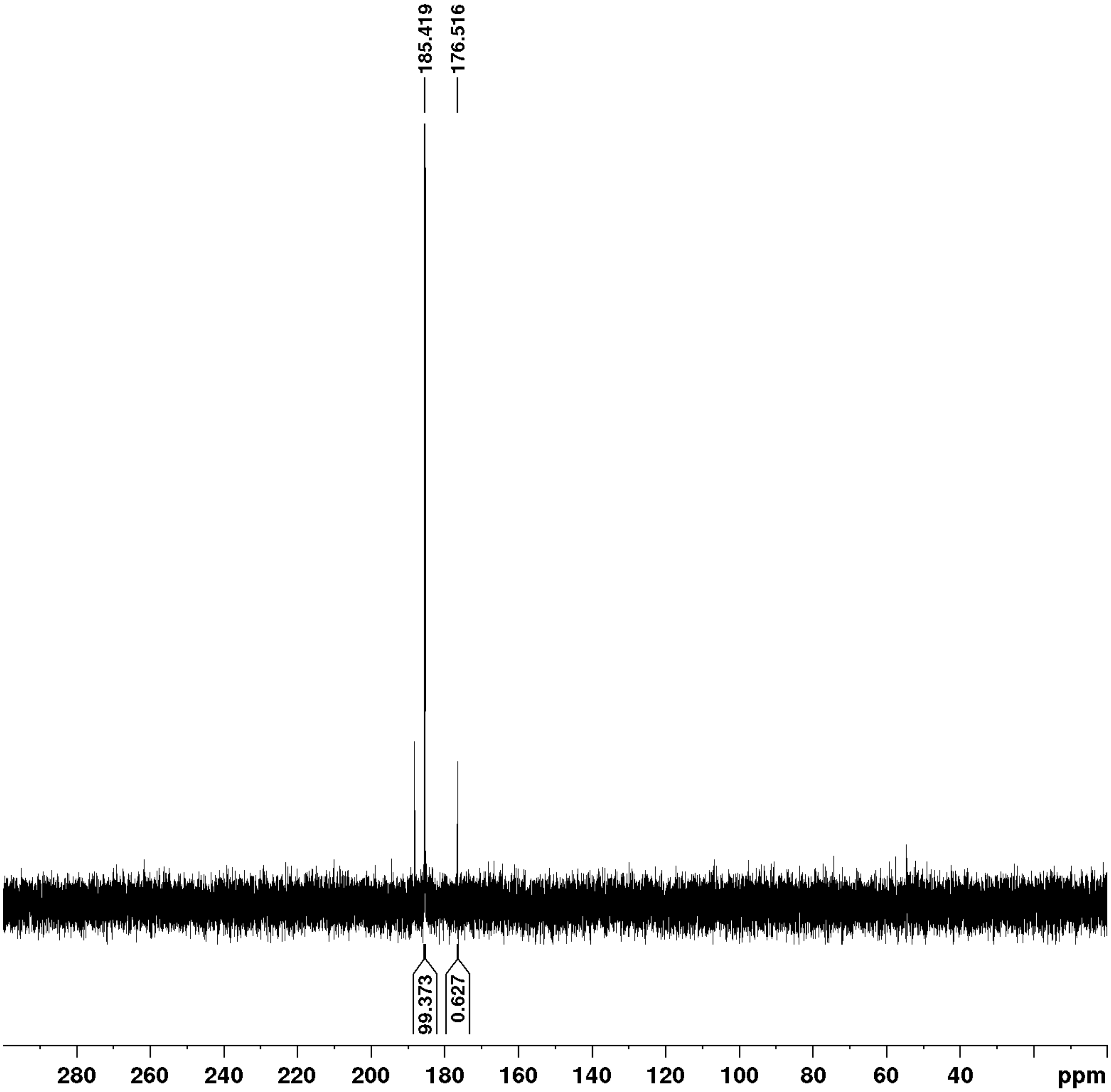
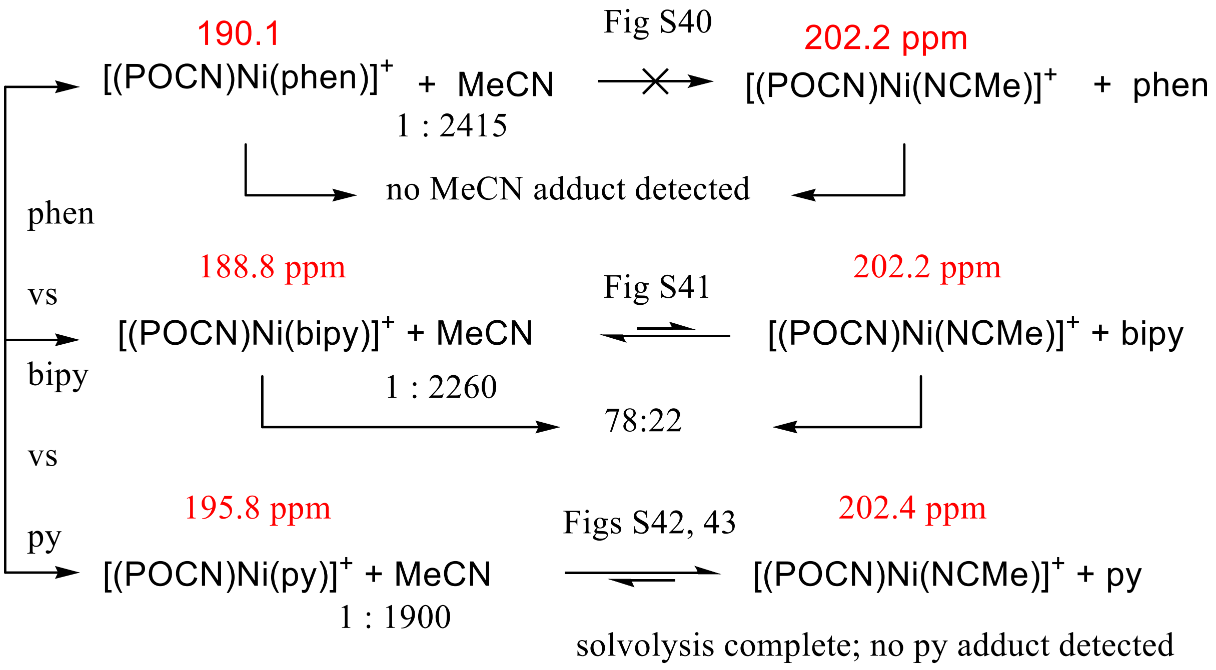


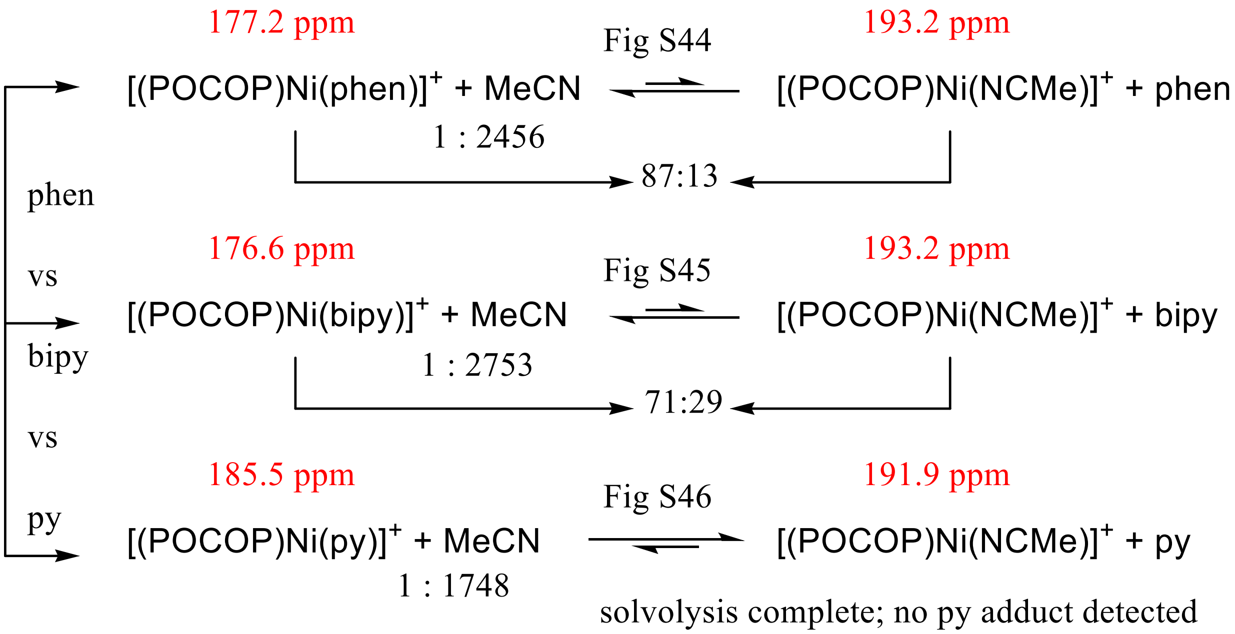
Figure S37. ^{31}PNMR spectrum (acetonitrile) of the substitution reaction

(POCOP)NiCl + bipy (1 equiv) ⇆ [(POCOP)Ni(bipy)]$^{+}$ + Cl^{-}

δ : 185.4 176.5

Summary of substitution reactions between various cationic adducts and MeCN





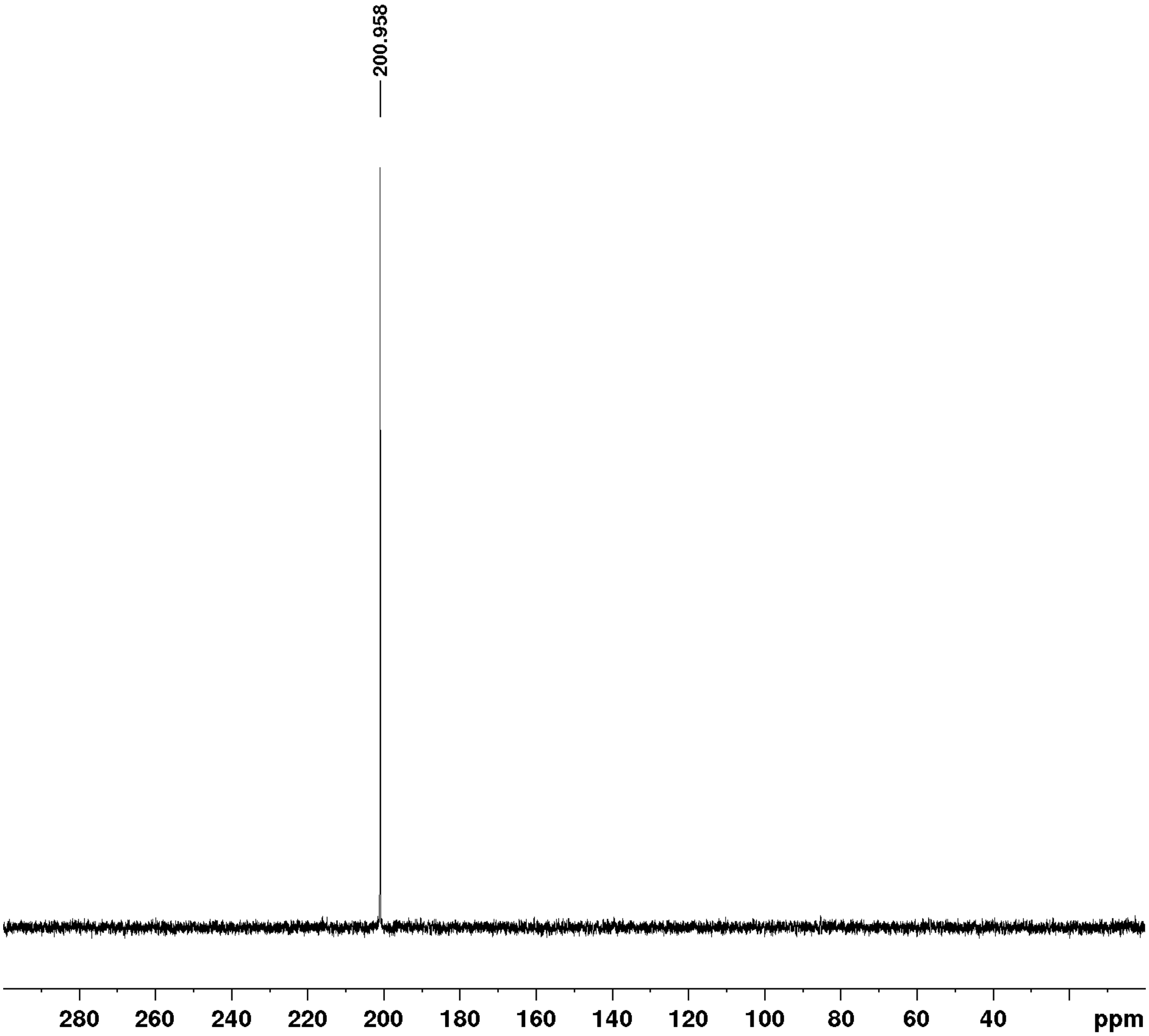


Figure S38. ^{31}PNMR spectrum of (POCN)NiBr in CH_3CN

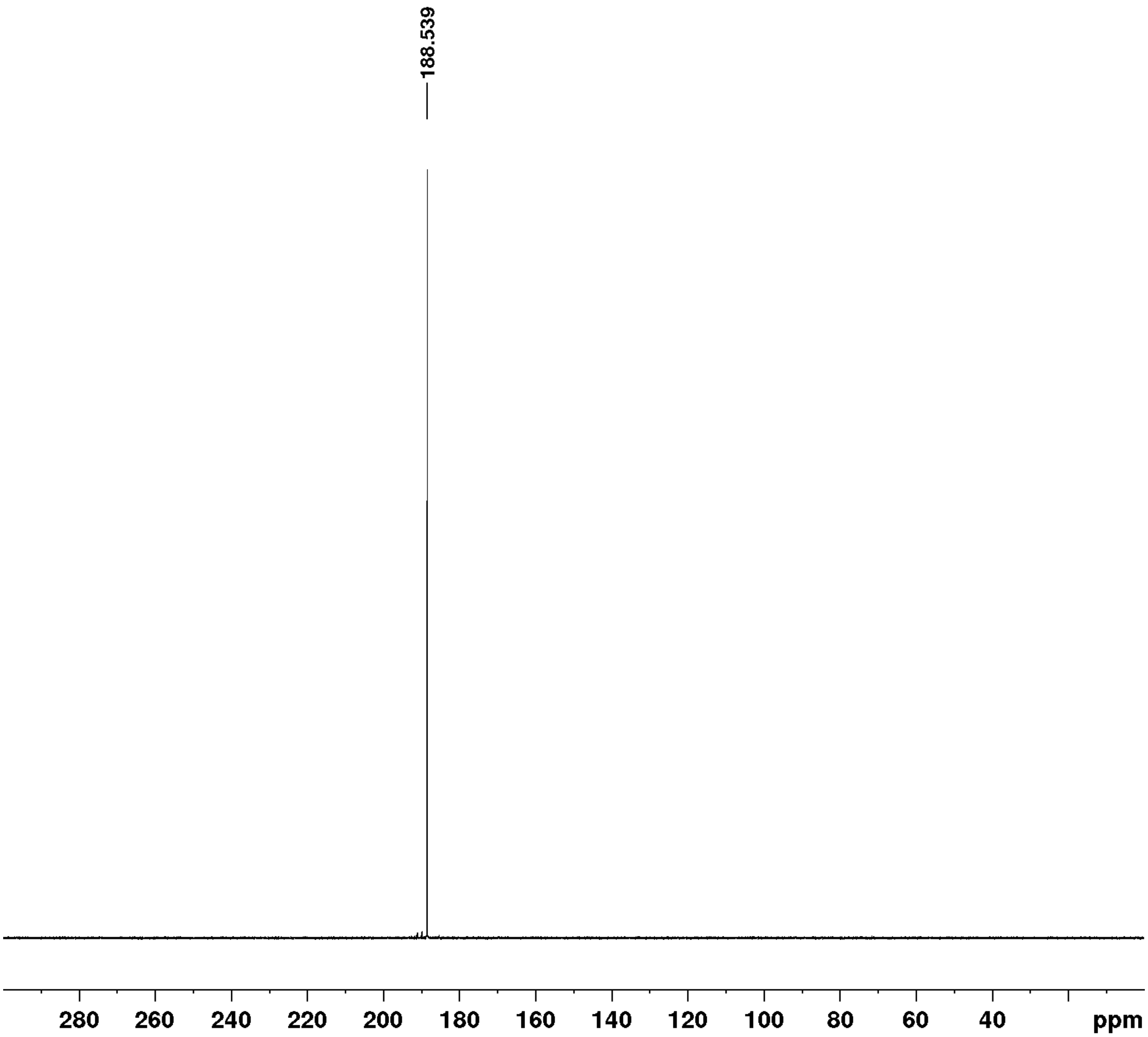


Figure S39. ^{31}PNMR spectrum of (POCOP)NiBr in CH_3CN

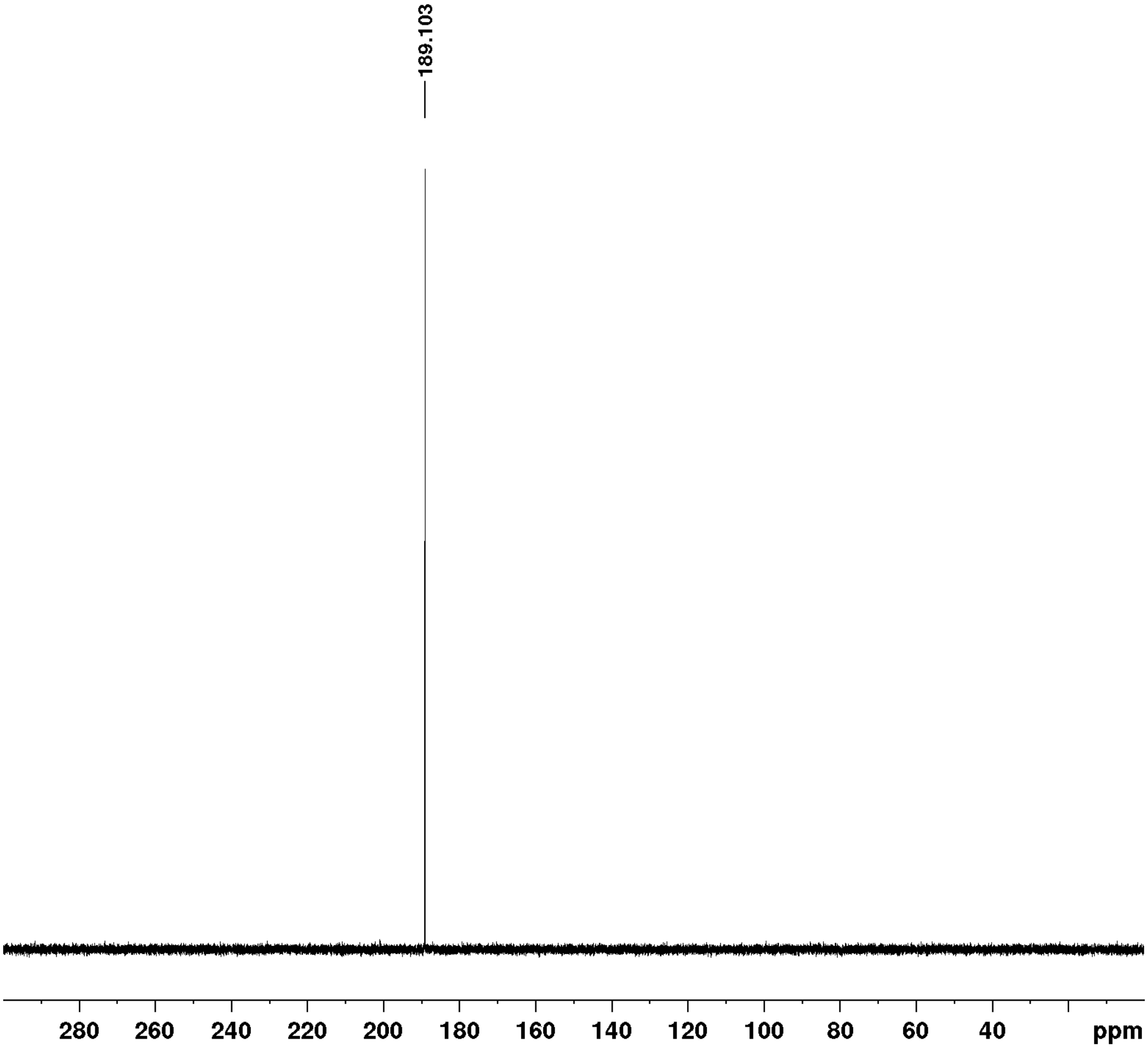


Figure S40. ^{31}PNMR spectrum of [(POCN)Ni(phen)][SbF$_6$] (**1d**) in CH$_3$CN

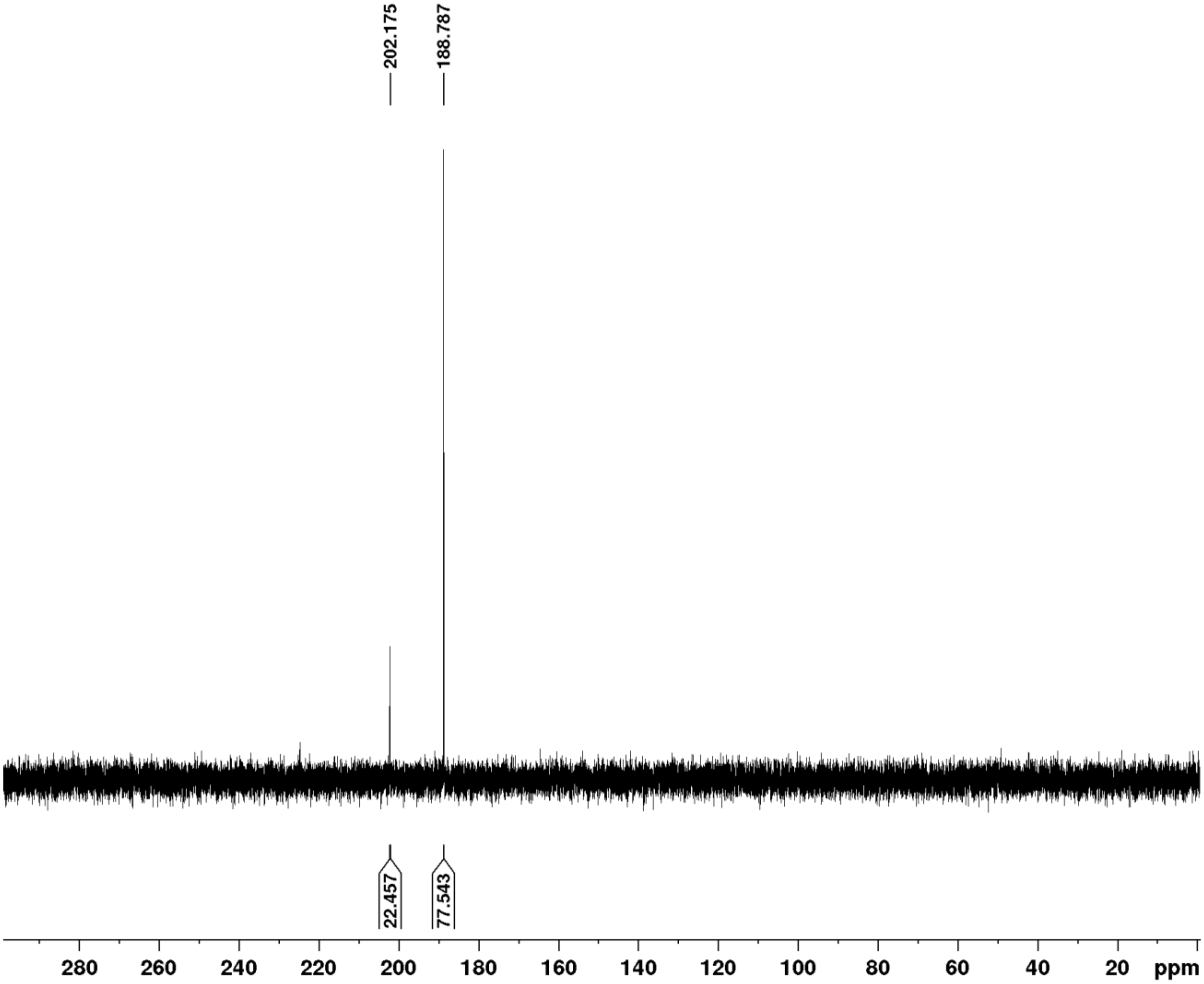


Figure S41. ^{31}PNMR spectrum (CH_3CN) of the substitution reaction

[(POCN)Ni(bipy)][SbF_6] + CH_3CN (large excess) ⇆ [(POCN)Ni(MeCN)][SbF_6] + bipy

δ : 188.8 202.2

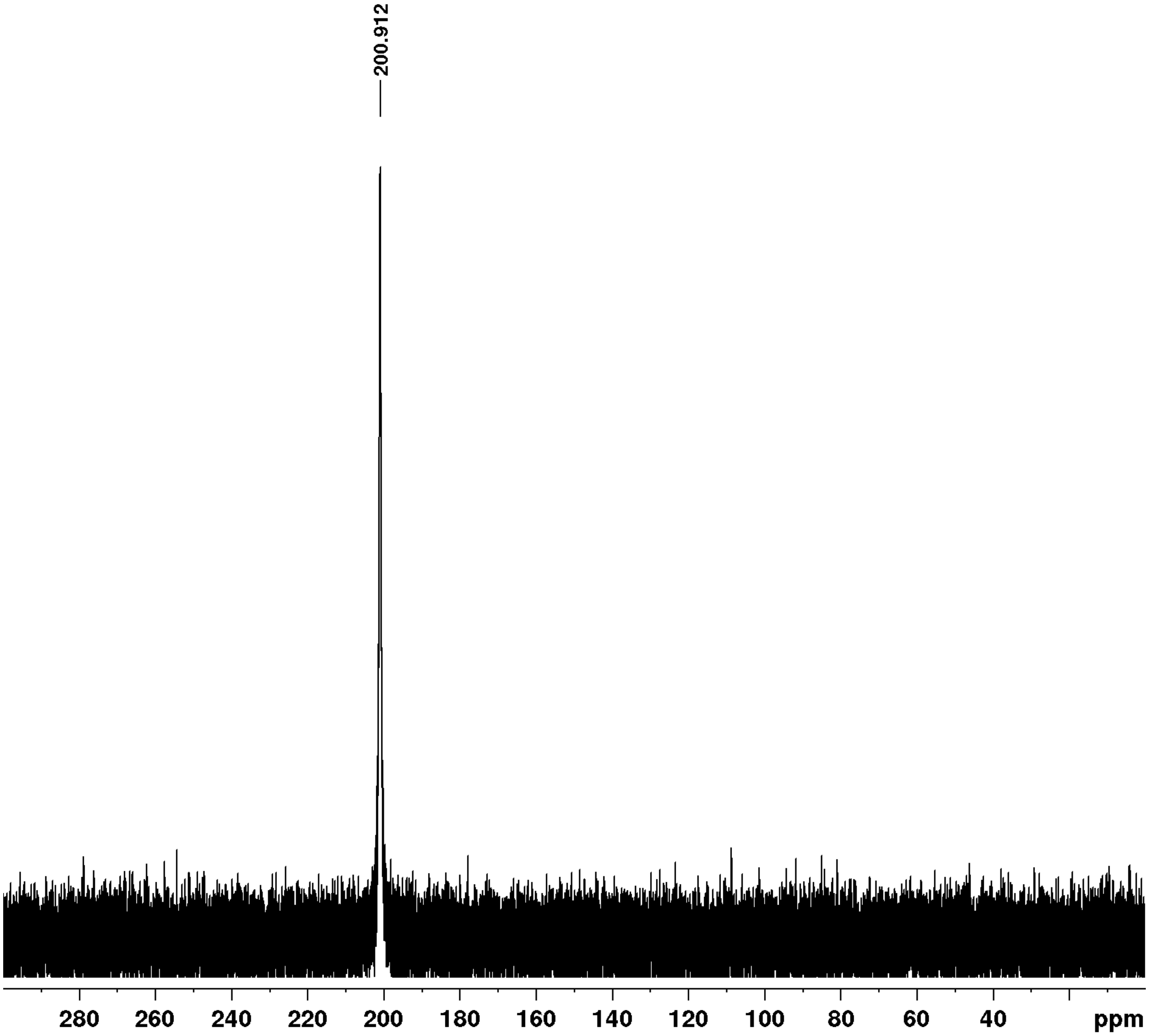


Figure S42. ^{31}PNMR spectrum of the substitution reaction

[(POCN)Ni(py)][SbF$_6$] (**1b**) + CH$_3$CN (large excess) ⇆ [(POCN)Ni(MeCN)][SbF$_6$] (**1a**) + py

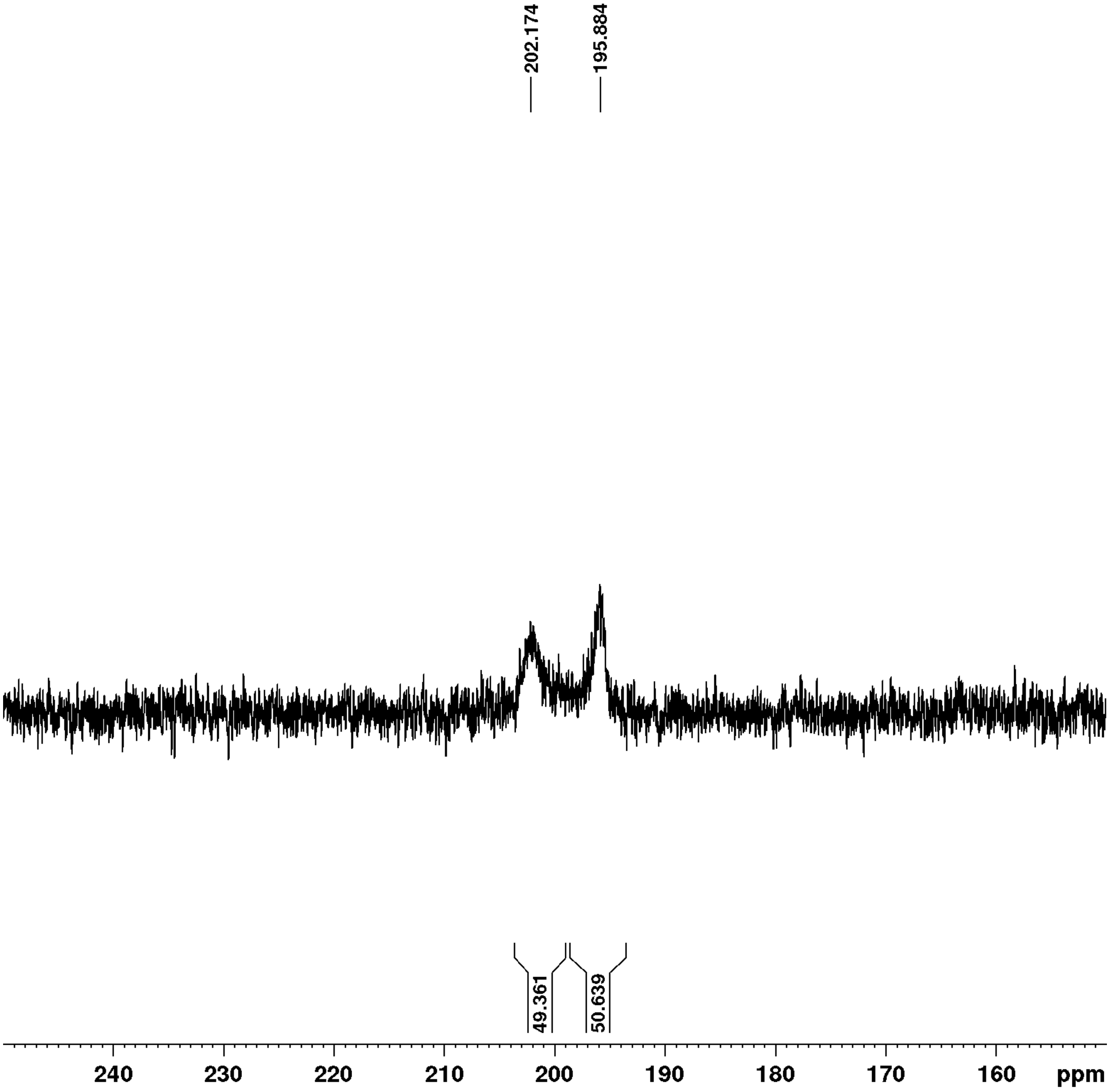


Fig. S43. ^{31}PNMR spectrum of 10 mg of [(POCN)Ni(py)][SbF$_6$] in 0.99 mL of THF and 0.01 mL of MeCN.

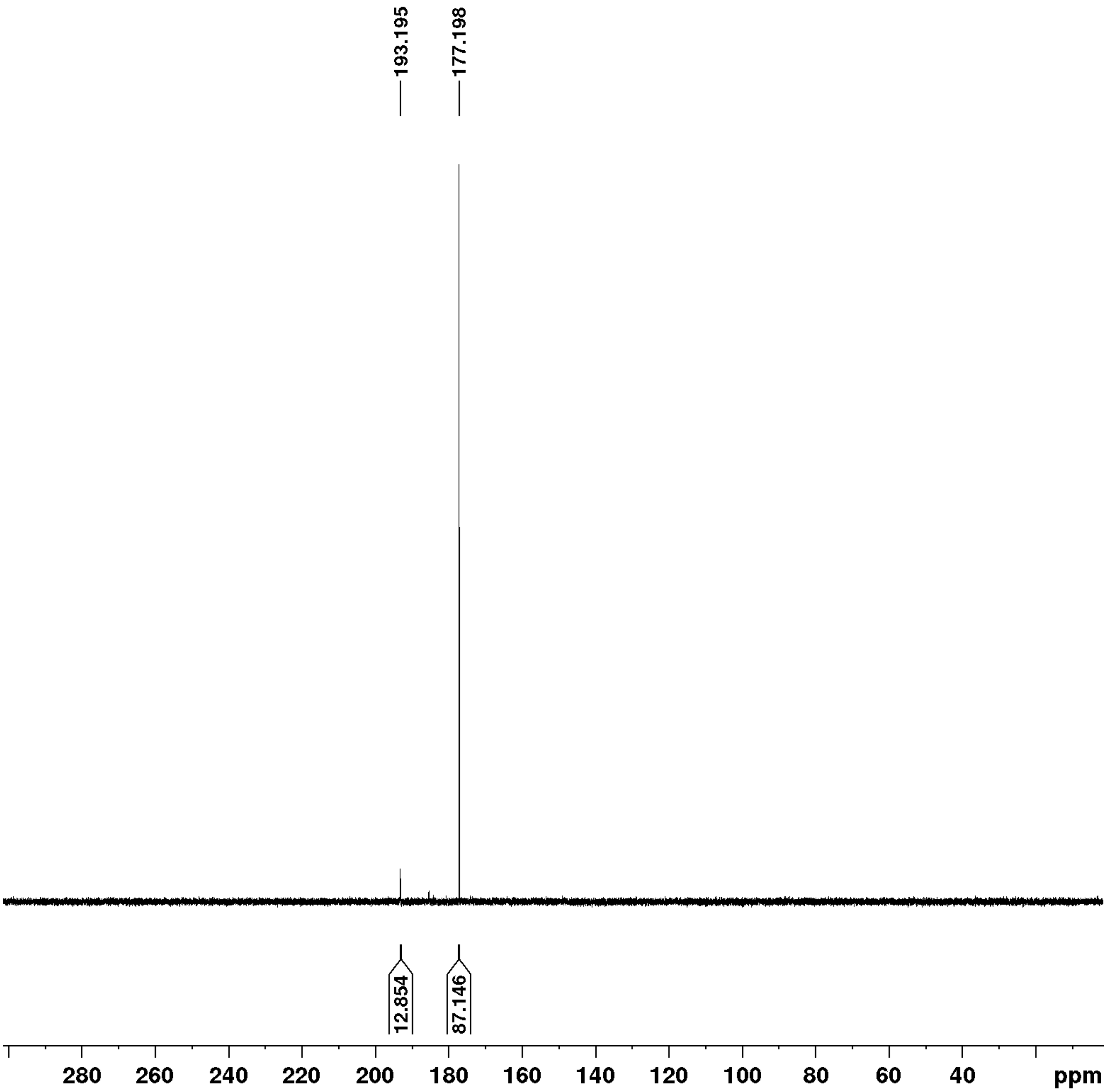


Figure S44. ^{31}PNMR spectrum (CH_3CN) of the substitution reaction

[(POCOP)Ni(phen)][SbF_6] + CH_3CN (large excess) ⇆ [(POCOP)Ni(MeCN)][SbF_6] + phen

δ : 177.2 193.2

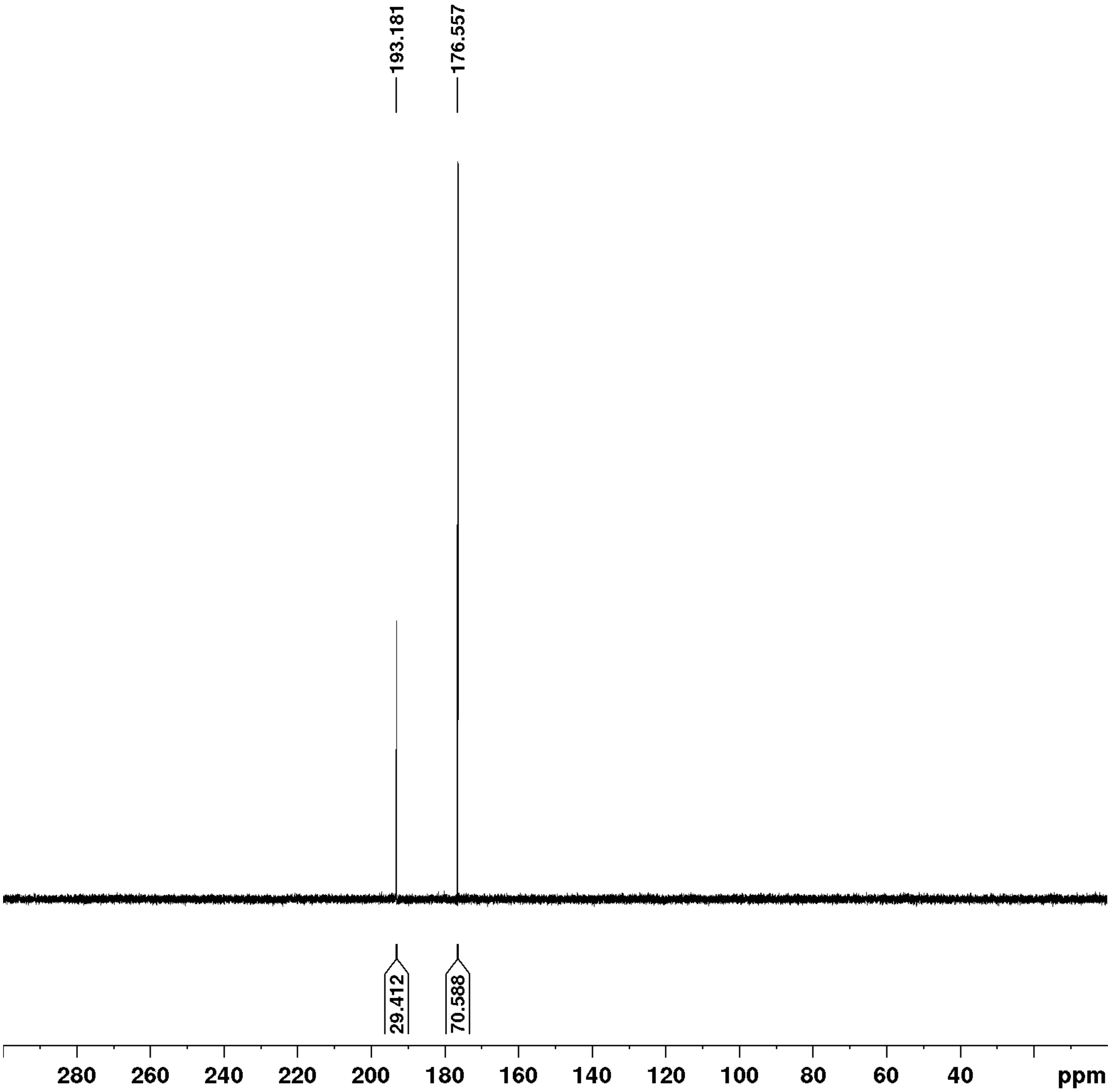


Figure S45. ^{31}PNMR spectrum (CH_3CN) of the substitution reaction

$[(POCOP)Ni(bipy)]^+ + CH_3CN$ (large excess) ⇆ $[(POCOP)Ni(MeCN)]^+$ + bipy

δ : 176.6 193.2

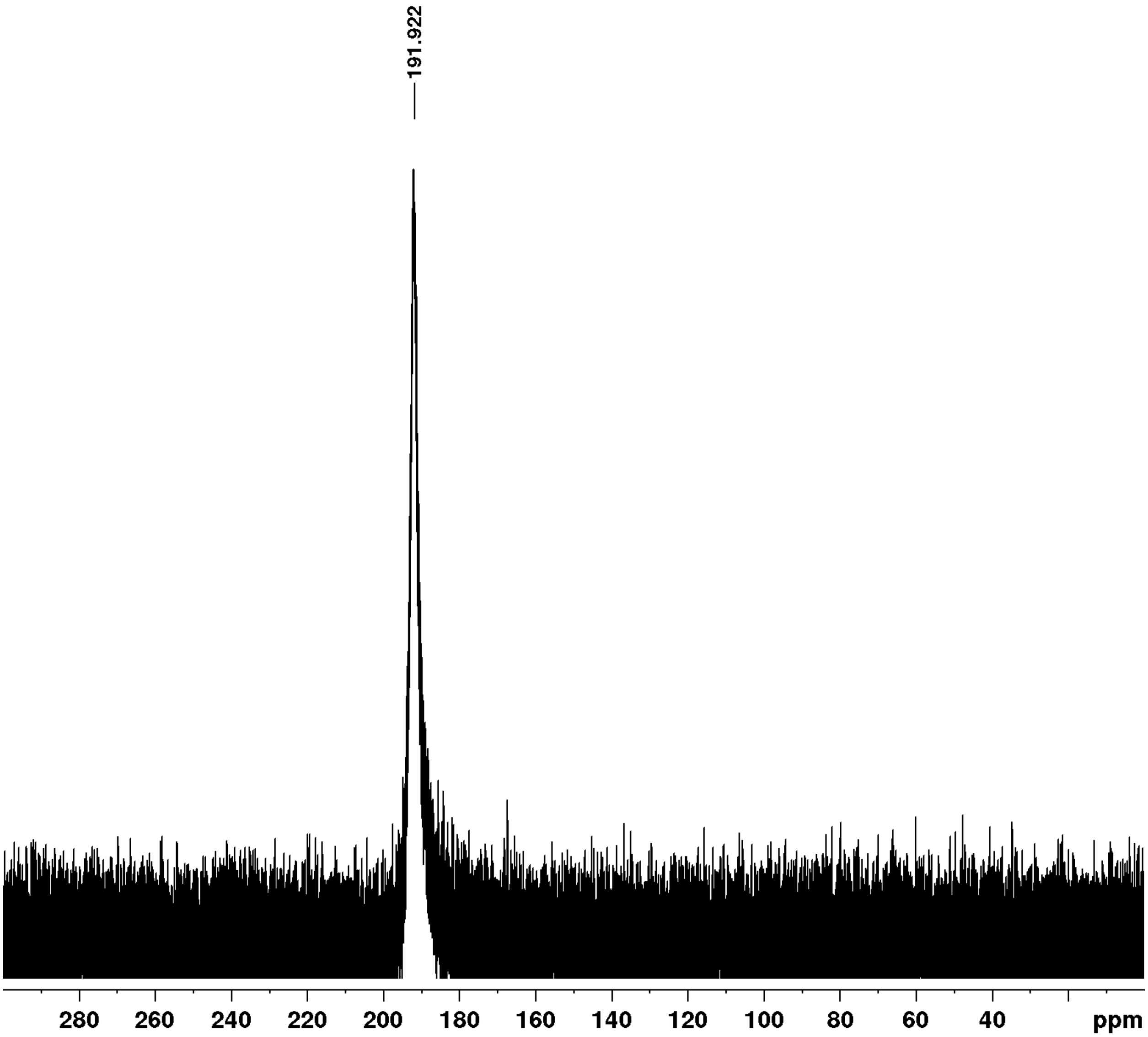


Figure S46. ^{31}PNMR spectrum of the substitution reaction

[(POCOP)Ni(py)]$^+$ (**2b**) + CH_3CN (large excess) ⇆ [(POCOP)Ni(MeCN)] (**2a**) + py

Exchange reactions between bromo precursors and a cationic adduct

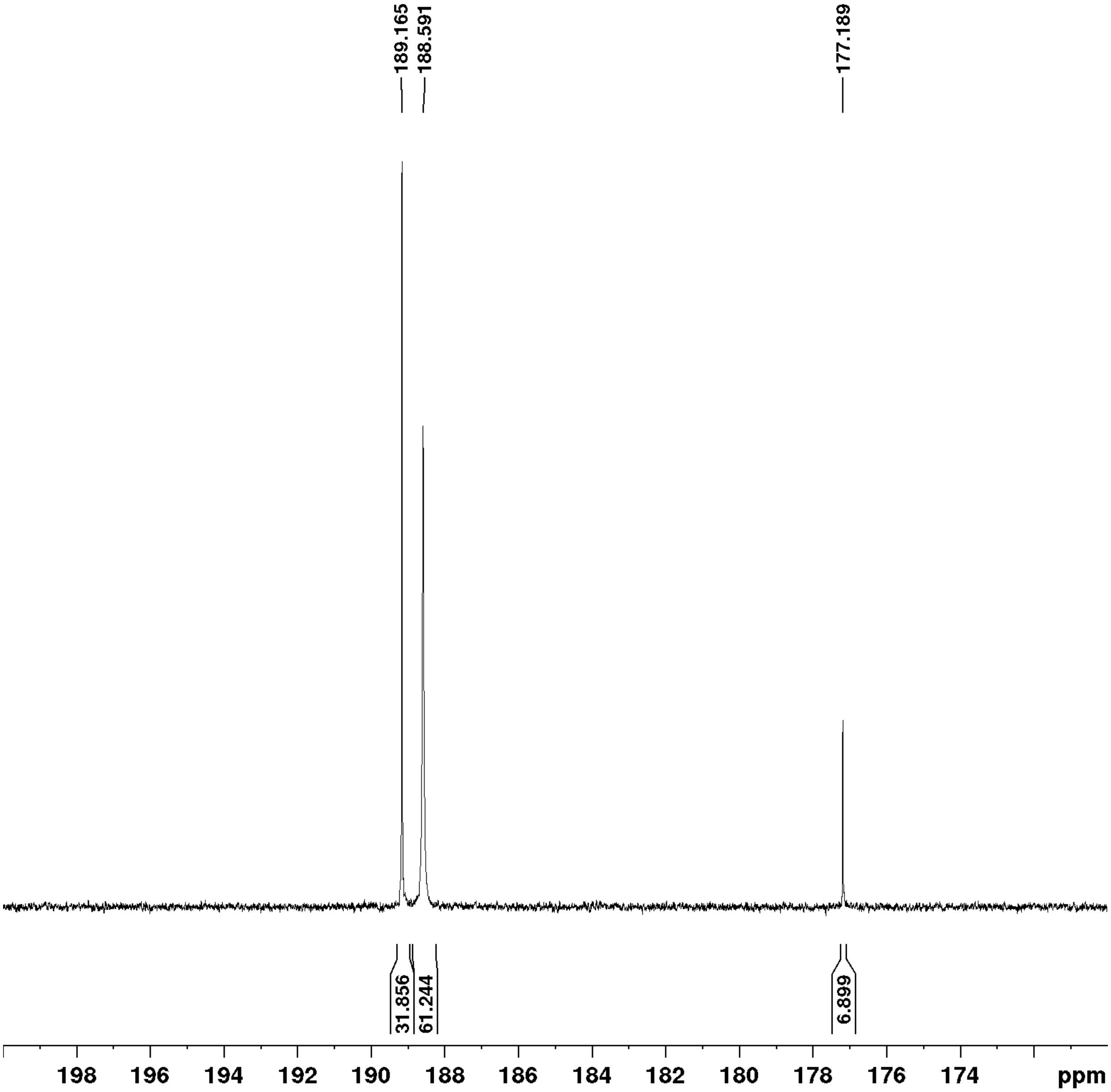


Figure S47. ^{31}PNMR spectrum (CH_3CN) of the substitution reaction

(POCN)NiBr + [(POCOP)Ni(phen)][SbF_6] ⇆ [(POCN)Ni(phen)][SbF_6] + (POCOP)NiBr

189.1 ppm 188.6 ppm

(The peak at 177.19 ppm represents the excess amount of complex **2d** used in the reaction.)

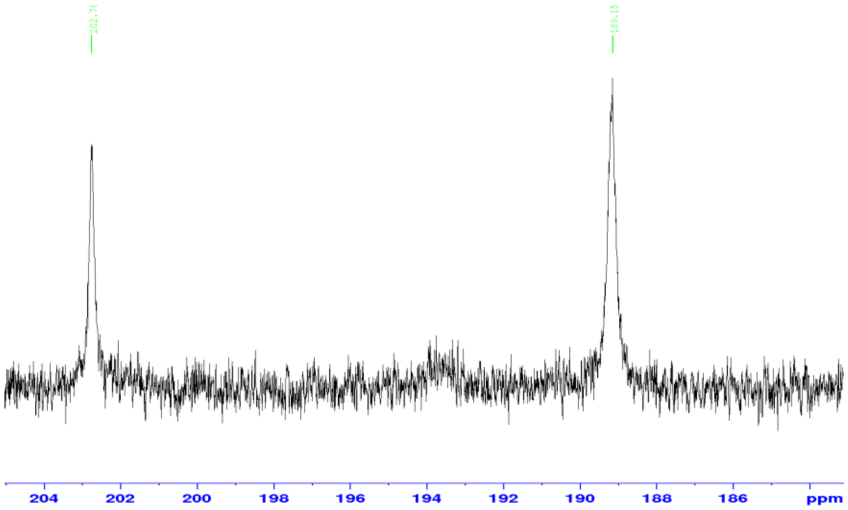


Figure S48. ^{31}PNMR spectrum (CH_3CN) of the substitution reaction

(POCN)NiBr + [(POCOP)Ni(NCMe)][SbF_6] $\leftrightarrows$ [(POCN)Ni(NCMe)][SbF_6] + (POCOP)NiBr

189.1 ppm 188.6 ppm

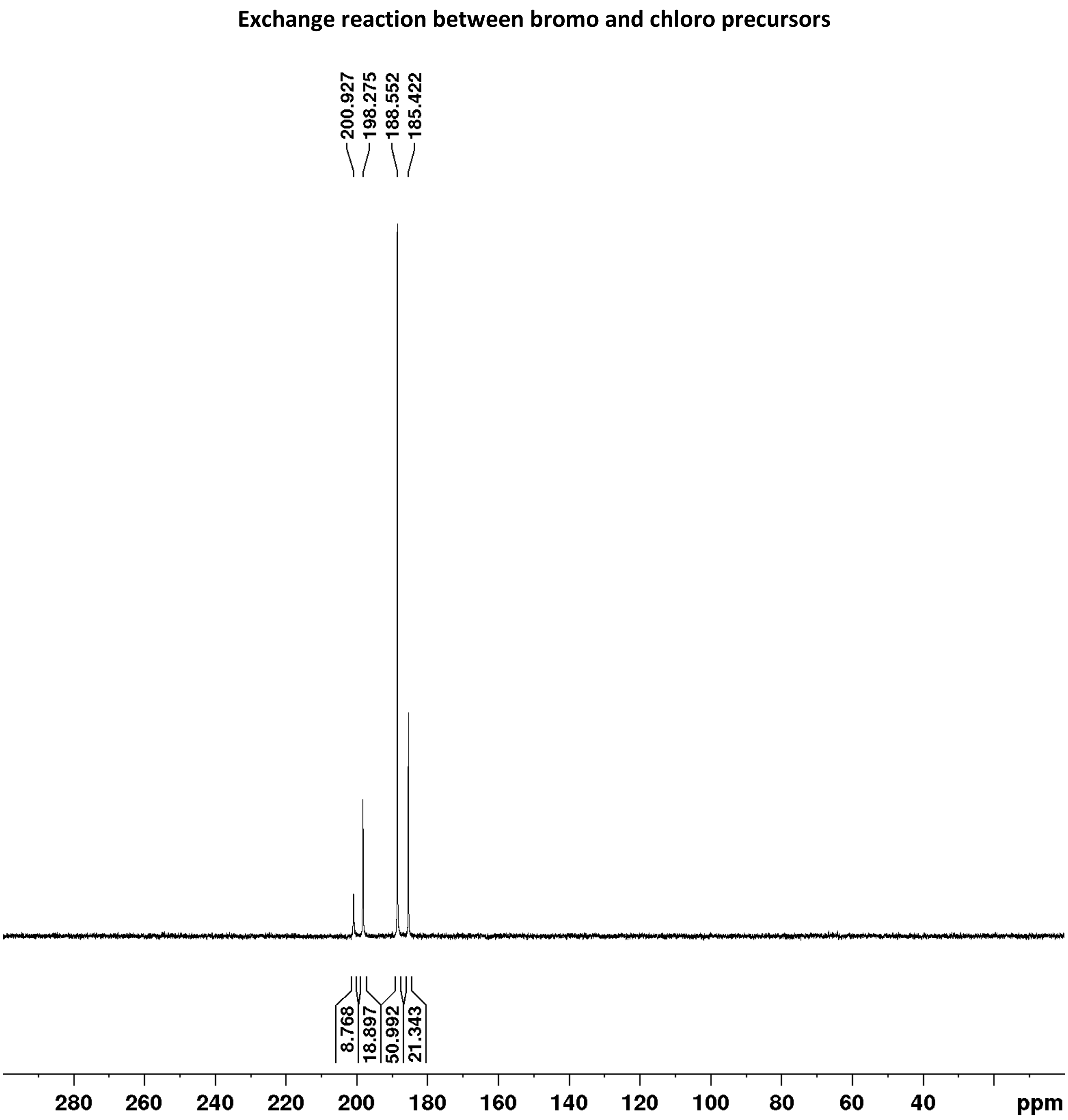


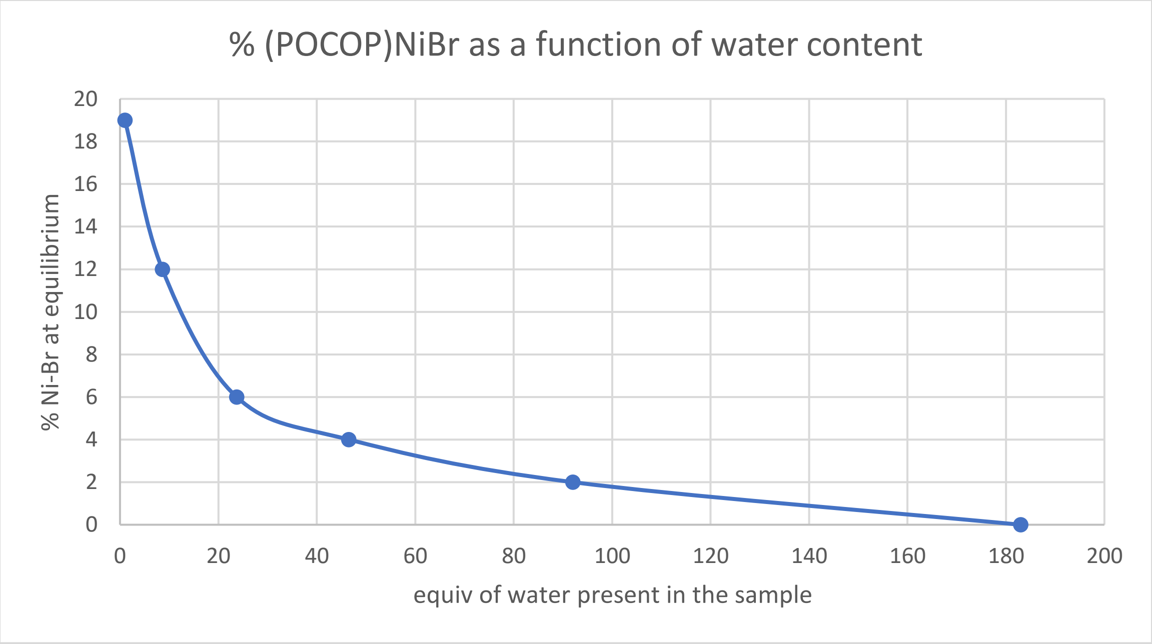
Figure S49. ^{31}PNMR spectrum (CH_3CN) of the substitution reaction

(POCN)NiBr + (POCOP)NiCl ⇆ (POCN)NiCl + (POCOP)NiBr

δ : 200.9 185.4 198.3 188.6

Probing the impact of residual water on displacement of Br by phen

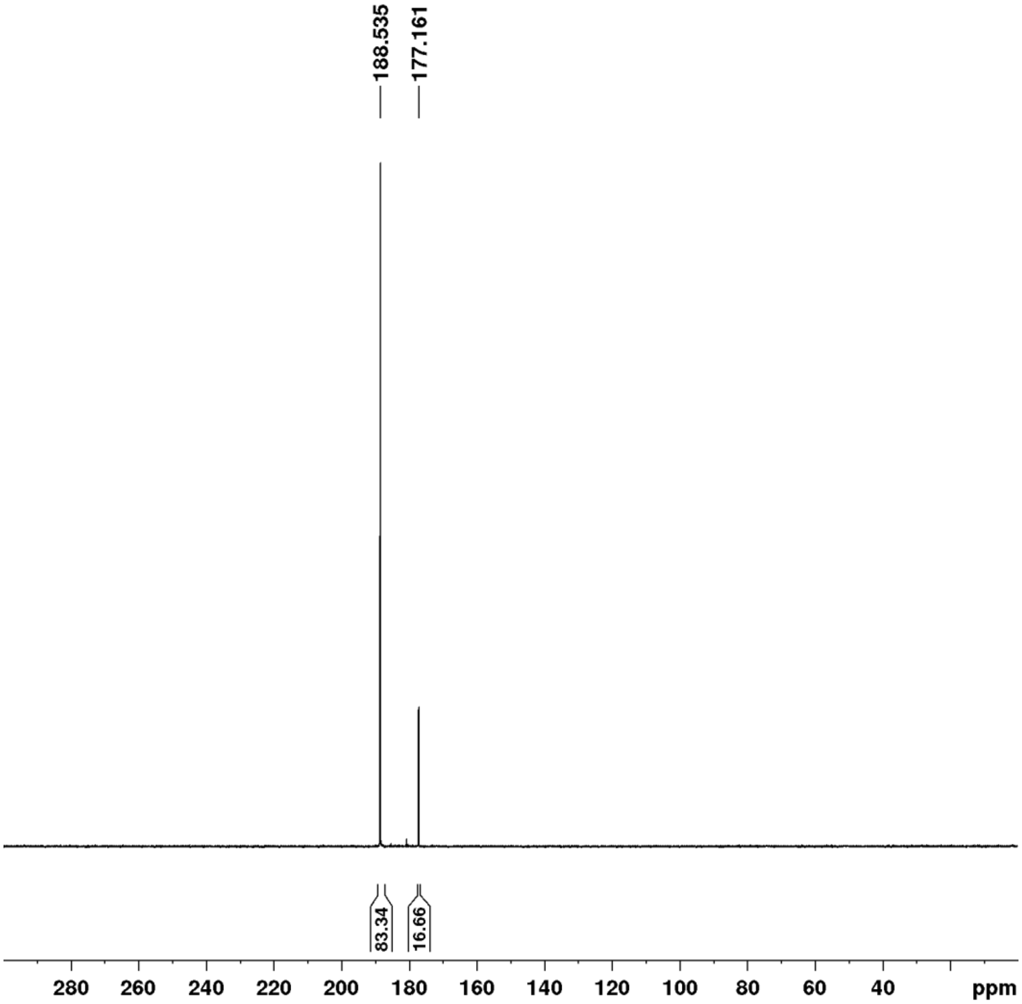
In response to a reviewer's comment regarding the impact of using 1,10-Phenanthroline monohydrate (phen.H_2O) instead of dry phen, we repeated the equilibrium displacement of bromide from (POCN)NiBr with phen.H_2O in the presence of excess water added to NMR samples. The initial sample was assumed to have one equiv of water coming from phen.H_2O, i.e., we neglect the residual moisture that might be present in the solvent (which might well be non-negligible given that acetonitrile is not that easy to dry). Analysis of this sample as usual by ^{31}P NMR allowed us to establish the equilibrium ratio of the bromide vs the phen adduct [(POCN)Ni(phen)]Br. Afterwards, additional quantities of water were added successively to this reference sample and the equilibrium ratios of (POCN)NiBr : [(POCN)Ni(phen)]Br were measured as before to gain some insight on the impact of water content on the displacement reaction. One last experiment was conducted at the end by stirring the final sample over a large excess of MgSO4, followed by filtration and NMR analysis as before, to estimate the impact of drying on the equilibrium position. The results of these tests, shown below in the form of a plot, confirm the reviewer's correct prediction that increasing quantities of water favor the displacement of bromide, while drying the sample over $MgSO_4$ favors the starting material.



We conclude from the above plot that, the limitations of these tests notwithstanding (i.e., the presence of residual moisture in the solvent, the error in volume measurements while adding water, and partial drying of the sample over $MgSO_4$), the error in the integration ratios obtained from the NMR spectra of samples containing phen.H_2O would be smaller or on the same order as the inherent error in our measurements, i.e., about 1-2%. This can be deduced from the Ni-Br: Ni-phen ratio of 19:81 in the presence of one equiv of water, vs the 20:80 ratio after drying over $MgSO_4$. Therefore, the data presented indicate that the original data is still largely valid and the degree of error arising from the use of phen.H_2O is small and tolerable for the purposes of our study.

Testing the impact of using dry phen on the displacement of Br by phen

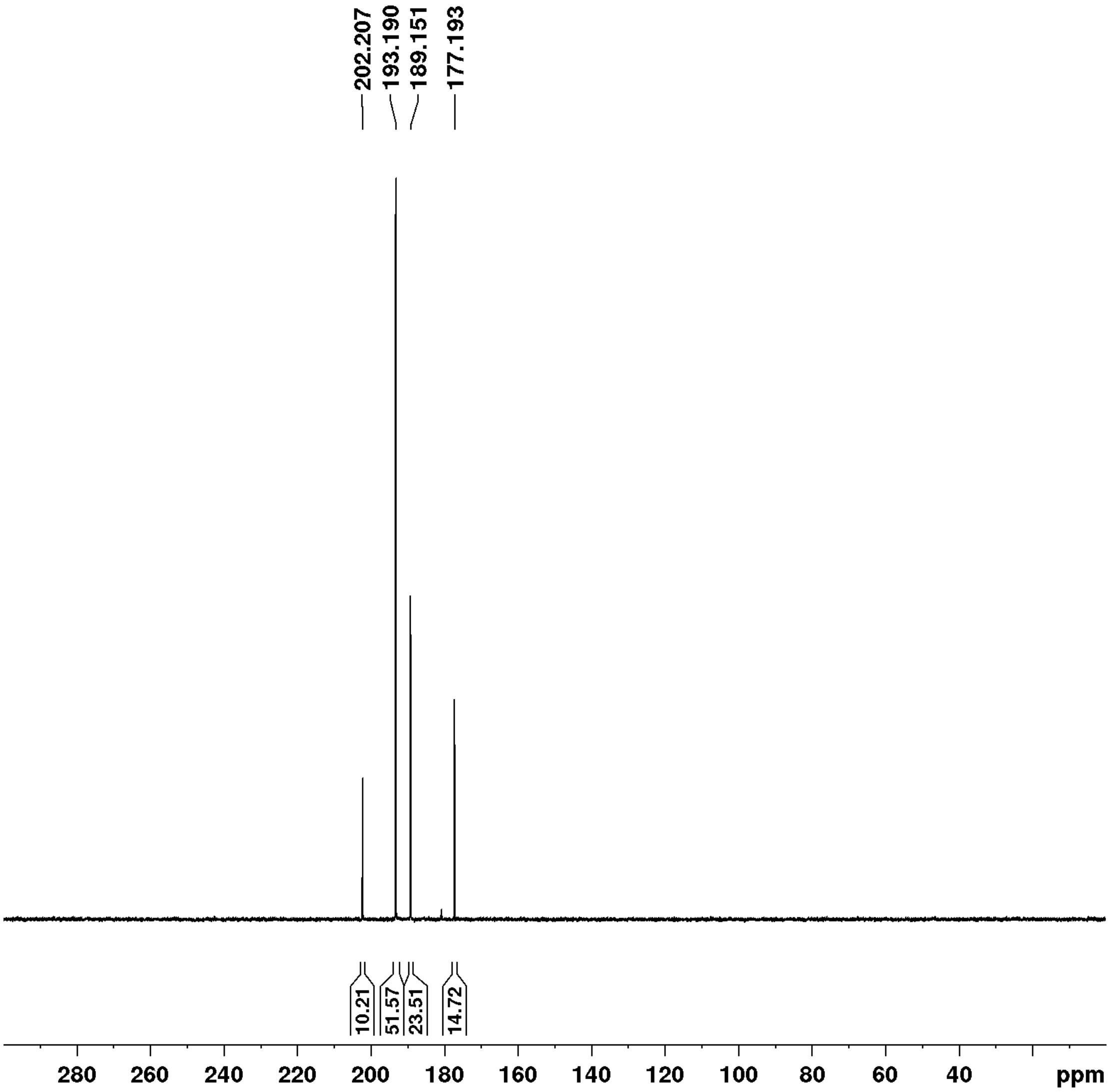
On the basis of the plot on page S61, we expected to find ca. 80% substitution of bromide in (POCN)NiBr by dry phen (non-hydrated purchased from commercial sources and kept in the dry box). The spectrum below shows ca. 83% substitution, the small difference presumably reflecting the true moisture content of the commercial sample of “dry” phen.



S50. The ^{31}PNMR spectrum of the reaction of (POCOP)NiBr with dry phen in MeCN

Compound	Chemical shift (ppm)	Area under the peak
(POCOP)NiBr	188.535	83
(POCOP)Ni(phen)	177.161	17

Testing the relative stabilities of acetonitrile and phen adducts



S51. The 31PNMR spectrum of the mixture of [(POCN)Ni(MeCN)][SbF_6] and [(POCOP)Ni(MeCN)][SbF_6] (in MeCN) with one equiv of dry phen

Compound	Chemical shift (ppm)	Area under the peak
(POCN)Ni(MeCN)	202.207	10
(POCN)Ni(phen)	189.151	23
(POCOP)Ni(MeCN)	193.190	52
(POCOP)Ni(phen)	177.193	15

6. Procedure for cyclic voltammetry measurements

The electrochemical cell was prepared in the glovebox. 25 µmol of the complex under study (1 mM) and 2.5 mmol of [*n*-Bu_4N]PF_6 (969 mg, 100 mM) were dissolved in 25.0 mL dried and deoxygenated MeCN. The resulting solution was transferred to the cell, the Teflon electrode holder was placed on top and the cell was sealed with parafilm. At the last minute, the parafilm was punctured to allow insertion of the glassy-carbon working electrode, the Ag/AgCl reference electrode and the platinum wire counter electrode. Measurements were recorded outside the glovebox with a Bio-Logic SAS SP-50 potentiostat. After all the measurements were recorded, ca. 25 µmol ferrocene (4.6 mg) was introduced into the electrochemical cell and its cyclic voltammogram recorded in order to extract its $E_{1/2}$ in our conditions to serve as the reference.

7. Procedure for X-ray diffraction studies and structure resolution protocols

The crystallographic data for all structures were collected on either a Bruker Microsource (Cu radiation) or a Bruker Venture Metaljet (Ga radiation) via the Bruker APEX II or APEX III[3] software packages. Cell refinement and data reduction were performed using SAINT.[4] An empirical absorption correction, based on multiple measurements of equivalent reflections, was applied using the program SADABS or TWINABS.[5] The space group was confirmed by the XPREP[6] routine in APEX. The structures were solved in OLEX[7] using the SHELX[8] suite and refined by full-matrix least squares with SHEXL.[9] All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were set in calculated positions and refined via the riding model, with thermal parameters being 1.5 times that of the carbon bearing the H in question. All Thermal ellipsoid plots were drawn using OLEX.

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[3] Bruker (2012). APEX2 / Bruker (2016) APEX3, Bruker AXS Inc., Madison, WI, USA.

[4] Bruker (2012). “SAINT Integration Software for Single Crystal Data”, Bruker AXS Inc., Madison, WI, USA.

[5] (a) Sheldrick, G. M. (1996). *SADABS/TWINABS.* University of Göttingen, Germany. (b) Bruker (2001). *SADABS/TWINABS.* Bruker AXS Inc., Madison, Wisconsin, USA.

[6] Bruker (2012). Data Preparation and Reciprocal Space Exploration Program, Bruker AXS Inc., Madison, WI, USA.

[7] A: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. “OLEX2: a complete structure solution, refinement and analysis program”. *J. Appl. Cryst.* 2009, *42*, 339-341.

[8] Sheldrick, G. M., “SHELXT - Integrated space-group and crystal structure determination”, *Acta Cryst.*, 2015, A71, 3-8.

[9] Sheldrick, G. M., Crystal structure refinement with SHELXL, *Acta Cryst.*, 2015, C71, 3-8.

8. Crystallographic data tables

Table S1: Crystal description and refinement indicators for compounds 1a-1c

	1a	**1b**	**1c**
Empirical formula	$C_{19}H_{30}F_6N_2NiO_2PSb$	$C_{22}H_{32}F_6N_2NiO_2PSb$	$C_{27.69}H_{36.38}Cl_{1.38}F_6N_3NiO_2PSb$
Formula weight	643.88	681.92	817.61
Temperature/K	100	120	100
Crystal system	monoclinic	triclinic	monoclinic
Space group	P21/n	P-1	P21/n
a/Å	17.1313(9)	12.2664(3)	14.5548(7)
b/Å	8.0007(4)	13.2418(3)	15.2342(7)
c/Å	17.8969(9)	17.5270(5)	14.8051(8)
α/°	90	68.3830(10)	90
β/°	94.072(2)	85.9400(10)	95.070(3)
γ/°	90	87.0200(10)	90
Volume/Å^3	2446.8(2)	2639.00(12)	3269.9(3)
Z	4	4	4
ρcalcg/cm^3	1.748	1.716	1.661
μ/mm^{-1}	10.922	10.221	9.343
F(000)	1288.0	1368.0	1644.0
Crystal size/mm^3	0.18 . 0.14 . 0.07	0.204 . 0.062 . 0.06	0.154 . 0.142 . 0.098
Radiation	CuKα (λ = 1.54178)	GaKα (λ = 1.34139)	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.902 to 144.298	6.248 to 121.602	8.166 to 145.236
Index ranges	$-17 \leq h \leq 20$ $-9 \leq k \leq 9$ $-22 \leq l \leq 22$	$-15 \leq h \leq 15$ $-17 \leq k \leq 17$ $-22 \leq l \leq 22$	$-17 \leq h \leq 17$ $-18 \leq k \leq 18$ $-18 \leq l \leq 18$
Reflections collected	87803	92015	406371
Independent reflections	4717 [R_{int} = 0.0280, R_{sigma} = 0.0096]	12104 [R_{int} = 0.0600, R_{sigma} = 0.0471]	6314 [R_{int} = 0.0495, R_{sigma} = 0.0329
Data/restraints/parameters	4717/0/294	12104/0/639	6314/10/413
Goodness-of-fit on F^2	1.122	1.070	1.211
Final R indexes [I>=2σ (I)]	R_1 = 0.0229, wR_2 = 0.0599	R_1 = 0.0400, wR_2 = 0.1056	R1 = 0.1023 wR_2 = 0.1873
Final R indexes [all data]	R_1 = 0.0229, wR_2 = 0.0620	R_1 = 0.0410, wR_2 = 0.1071	R_1 = 0.0856 wR_2 = 0.2739
Largest diff. peak/hole / e Å^{-3}	0.45/-1.47	1.18/-1.38	2.05/-1.70

Table S2: Crystal description and refinement indicators for compounds 1d and 1e

	1d	**1e**
Empirical formula	$C_{30}H_{37}Cl_2F_6N_3NiO_2PSb$	$C_{48}H_{70}F_{12}N_4Ni_2O_5P_2Sb_2$
Formula weight	867.95	1433.94
Temperature/K	130	100
Crystal system	monoclinic	monoclinic
Space group	P21/n	P21/c
a/Å	17.2593(15)	18.3475(5)
b/Å	13.5102(12)	12.6233(4)
c/Å	29.393(3)	24.3404(6)
α/°	90	90
β/°	93.580(5)	98.0150(10)
γ/°	90	90
Volume/Å^3	6840.3(11)	5582.3(3)
Z	8	4
ρcalcg/cm^3	1.686	1.706
μ/mm^{-1}	8.917	9.661
F(000)	3488.0	2888.0
Crystal size/mm^3	0.3 . 0.1 . 0.02	0.13 . 0.03 . 0.03
Radiation	GaKα (λ = 1.34139)	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.032 to 110.152	4.864 to 140.178
Index ranges	$-21 \leq h \leq 21$ $0 \leq k \leq 16$ $0 \leq l \leq 35$	$-22 \leq h \leq 22$ $-15 \leq k \leq 15$ $-29 \leq l \leq 29$
Reflections collected	13036	52101
Independent reflections	13036 [R_{int} = 0.1164, R_{sigma} = 0.0356]	10576 [R_{int} = 0.0426, R_{sigma} = 0.0311]
Data/restraints/parameters	13036/42/865	10576/0/684
Goodness-of-fit on F2	1.066	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0575, wR_2 = 0.1513	R_1 = 0.0368 wR_2 = 0.0939
Final R indexes [all data]	R_1 = 0.0654, wR_2 = 0.1575	R1 = 0.0432 wR_2 = 0.0982
Largest diff. peak/hole / e Å^{-3}	1.11/-1.11	0.97/-0.81

Table S3: Crystal description and refinement indicators for compounds 2b-2d

	2b	**2c**	**2d**
Empirical formula	$C_{23}H_{36}F_6NNiO_2P_2Sb$	$C_{32}H_{47}F_6N_2NiO_3P_2Sb$	$C_{30}H_{39}F_6N_2NiO_2P_2Sb$
Formula weight	714.93	864.11	816.03
Temperature/K	120	130	100
Crystal system	monoclinic	monoclinic	triclinic
Space group	P21/c	P21/c	P1
a/Å	8.6586(3)	16.9127(6)	12.6698(6)
b/Å	26.4721(7)	9.2788(3)	13.6736(6)
c/Å	14.4377(4)	23.5436(8)	20.1046(9)
α/°	90	90	104.063(2)
β/°	107.032(2)	91.766(2)	100.134(2)
γ/°	90	90	90.206(2)
Volume/Å^3	3164.14(17)	3692.9(2)	3321.9(3)
Z	4	4	4
ρcalcg/cm^3	1.501	1.554	1.632
μ/mm^{-1}	8.838	7.662	8.632
F(000)	1440.0	1760.0	1648.0
Crystal size/mm^3	0.177 . 0.086 . 0.074	0.13 . 0.065 . 0.05	0.22 . 0.1 . 0.09
Radiation	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.81 to 121.81	4.548 to 109.974	4.608 to 144.65
Index ranges	$-11 \leq h \leq 11$ $-31 \leq k \leq 34$ $-18 \leq l \leq 18$	$-20 \leq h \leq 20$ $-10 \leq k \leq 11$ $-28 \leq l \leq 28$	$-15 \leq h \leq 14$ $-16 \leq k \leq 16$ $-24 \leq l \leq 24$
Reflections collected	57823	51194	22257
Independent reflections	7287 [R_{int} = 0.0534, R_{sigma} =0.0316]	7057 [R_{int} = 0.0844, R_{sigma} = 0.0603]	22257 [R_{int} = 0.077, R_{sigma} = 0.0173]
Data/restraints/parameters	7287/0/333	7057/254/567	22257/3/1618
Goodness-of-fit on F2	1.133	1.055	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0410 wR_2 = 0.0999	R_1 = 0.0439, wR_2 = 0.1069	R1 = 0.0321, wR_2 = 0.0893
Final R indexes [all data]	R_1 = 0.0427 wR_2 = 0.1009	R_1 = 0.0559, wR_2 = 0.1133	R_1 = 0.0323, wR_2 = 0.0896
Largest diff. peak/hole / e Å^{-3}	1.19/-0.70	0.74/-1.80	1.07/-0.50
Flack parameter			0.0024(14)

9. **Figure S52.** Molecular structure for [(POCN)Ni(bipy)][SbF$_6$], **1c**. The anions, all the hydrogen atoms, and the isopropyl CH$_3$ groups have been omitted for clarity.