Ligand-Switching and Counteranion-Induced Hierarchical Self-Assembly of Silver-NHC Complexes

Siping Wei, Xiyu Li, Zhuang Yang, Jingbo Lan, Ge Gao, Ying Xue, and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Biotherapy, West China Hospital, West China Medical School, Sichuan University, 29 Wangjiang Road, Chengdu 610064 (PR China)

Fax: 86-28-85412203; *E-mail*: jsyou@scu.edu.cn

Supporting Information

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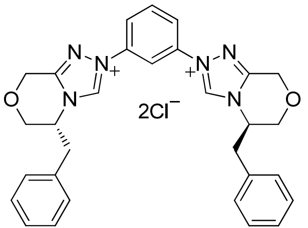
I. General Remarks

^{1}H NMR spectra were obtained with a Bruker AV II-400 (400 MHz), a Varian Inova-400 (400 MHz) or a Bruker AV II-600 (600 MHz) spectrometer, while ^{13}C NMR spectra were recorded with a Bruker AV II-400 (100 MHz) or a Bruker AV II-600 (150 MHz) spectrometer. ^{19}F NMR spectra were recorded with a Bruker AV II-400 (376 MHz) spectrometer. ROESY and HMQC NMR spectra were obtained with a Bruker AV II-400 (400 MHz) spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were recorded with TMS, $CDCl_3$, DMSO-d_6, or CD_3COCD_3 as the internal standard. Elemental analyses were performed with a Euro EA 3000 instrument. Mass spectra were obtained on a Waters Quattro Premier XE Mass spectrometer or a Finnigan-LCQDECA instrument. The ESI-TOF mass spectra were recorded with a Waters Q-Tof premier instrument. Transmission electron microscopy (TEM) studies were carried out on a Tecnai G2 F20 S-TWIN, operating at 200 kV, or a HITACHI H-600, operating at 75 kV. Scanning transmission electron microscope (STEM) studies were carried out on a Tecnai G2 F20 S-TWIN, operating at 200 kV. Circular Dichroism (CD) spectra were recorded on an Aviv Model 215 Circular Dichroism Sepctrometer at 25 °C.

X-Ray single-crystal diffraction data were collected on an Oxford Diffraction Xcalibur Eos Gemini Diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) with ω scan mode. Empirical absorption correction using spherical harmonics was implemented in SCALE3 ABSPACK scaling algorithm. All the structures were solved by direct methods using the SHELXS SHELXS-97 program and refined by full-matrix least-squares methods with SHELXL-97.[1] All non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Hydrogen atoms were included in calculated positions and refined with constrained thermal parameters riding on their parent atoms. Drawings were produced with Ortep, Diamod, and OLEX2.[2]

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Unless otherwise indicated, all syntheses and manipulations were carried out under dry inert atmosphere. (*R*)-**1**·2HCl, (*S*)-**2**·2HCl, (*R*)-**2**·2HCl, and (*S*)-**3**·2HCl were prepared according to our previous report.[3]

II. Data of (*R*)-2·2HCl

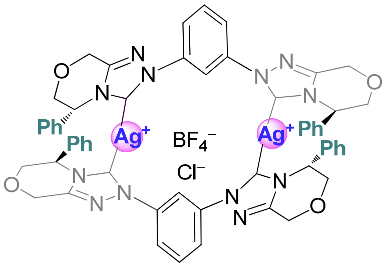


(*R*)-**2**·2HCl

1,3-Bis{(*R*)-5-benzyl-6,8-dihydro-5*H*-[1,4]oxazino[2,1-*c*]-[1,2,4]triazol-2-ium-2-yl}benzene dichloride (*R*)-**2**·2HCl. The compound (*R*)-**2**·2HCl was prepared according to our previous report.[3] m.p > 300 ºC. $[\alpha]_D^{20}$: -0.48 cm^3 g^{-1} dm^{-1} (c = 0.50 in CH_3OH). ^1H NMR (400 MHz, DMSO-d_6): δ 3.18 (dd, *J* = 10.4 Hz, 10.4 Hz, 2H), 3.56 (dd, *J* = 4.4 Hz, 4.4 Hz, 2H), 3.95-4.04 (m, 4H), 4.92-4.95 (m, 2H), 5.20 (dd, *J* = 16.4 Hz, 16.4 Hz, 4H), 7.39-7.45 (m, 10H), 8.10 (t, *J* = 8.0 Hz, 1H), 8.21-8.23 (m, 2H), 8.56 (s, 1H), 11.34 (s, 2H) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): 37.9, 57.0, 61.9, 65.5, 113.3, 122.5, 128.0, 129.5, 129.9, 133.0, 135.4, 136.5, 136.6, 142.3, 150.6 ppm. HR-MS (ESI) calcd for $[M - Cl]^+$: 541.2117, found. 541.2119. Anal. Calcd for $C_{30}H_{30}Cl_2N_6O_2$: C, 62.39; H, 5.24; N, 14.55; Found: C, 62.61; H, 5.51; N, 14.39.

III. Preparation and characterization of silver- and gold-NHC complexes

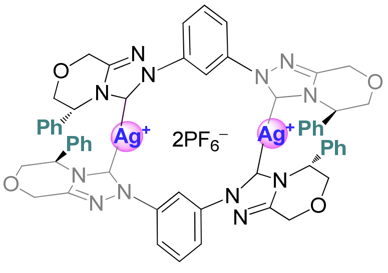
1. Preparation and characterization of [(*R*)-1·Ag]$_2$(BF$_4$)(Cl)



[(*R*)-**1**•Ag]$_2$(BF$_4$)(Cl)

Bis-triazolium salt (*R*)-**1**·2HCl (110 mg, 0.2 mmol), silver oxide (46 mg, 0.2 mmol), and $NaBF_4$ (24 mg, 0.22 mmol) were added to CH_2Cl_2 (5 mL) under argon. The mixture became gray after being stirred for 10 h at room temperature, and the solvent was then removed in vacuo at room temperature to give a gray solid, followed by extraction with hot DMSO (2~3 mL). The colorless crystalline product was prepared by slow diffusion of ethyl ether into the solution of crude product in DMSO at room temperature in *ca.* 80 % yield. Colorless block crystals [(*R*)-**1**·Ag]$_2$(BF$_4$)(Cl) suitable for X-ray analysis were obtained by slow diffusion of ethyl ether into the DMSO solution at ambient temperature through several days. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 3.97 (dd, *J* = 6.0 Hz, 6.0 Hz, 4H), 4.32 (dd, *J* = 4.4 Hz, 4.4 Hz, 4H), 5.23 (d, *J* = 15.6 Hz, 4H), 5.40 (d, *J* = 16.0 Hz, 4H), 5.94 (s, 4H), 6.47 (t, *J* = 7.2 Hz, 4H), 6.56 (t, *J* = 7.2 Hz, 8H), 6.96 (d, *J* = 7.2 Hz, 8H), 7.44 (s, 2H), 7.88 (t, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 59.0, 62.3, 69.7, 110.5, 121.8, 127.6, 128.1, 128.6, 131.9, 137.9, 139.2, 150.6, 178.7 (dd, ^1J ^{107}Ag = 189.4 Hz, ^1J ^{109}Ag = 214.2 Hz, carbene N-C-N) ppm. ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ -148.2 (s, BF$_4^-$) ppm. Anal. Calcd for $C_{56}H_{48}Ag_2BClF_4N_{12}O_4$: C, 52.10; H, 3.75; N, 13.02; Found: C, 51.87; H, 4.03; N, 12.71. ESI-TOF found: *m/z* = 583.10 (calcd for [(*R*)-**1**·Ag]$^+$ 583.10); *m/z* = 1203.17 (calcd for [[(*R*)-**1**·Ag]$_2$Cl]$^+$ 1203.17); *m/z* = 1255.20 (calcd for [[(*R*)-**1**·Ag]$_2$(BF$_4$)]$^+$ 1255.19).

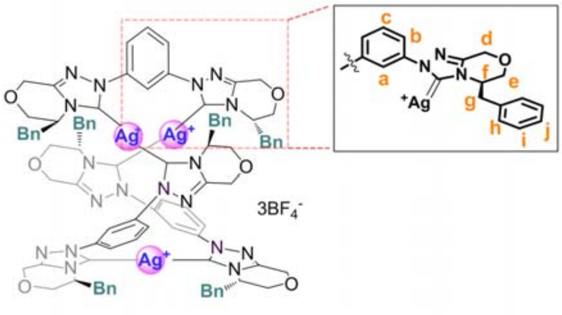
2. Preparation and characterization of [(*R*)-1·Ag]$_2$(PF$_6$)$_2$



[(*R*)-**1**•Ag]$_2$(PF$_6$)$_2$

Bis-triazolium salt (*R*)-**1**·2HCl (110 mg, 0.2 mmol), silver oxide (46 mg, 0.2 mmol), and KPF$_6$ (40.5 mg, 0.22 mmol) were added to CH$_2$Cl$_2$ (5 mL) under argon. The mixture became gray after being stirred for 10 h at room temperature, and the solvent was then removed in vacuo at room temperature to give a gray solid, followed by extraction with hot DMSO (2~3 mL). The crystalline product was prepared by slow diffusion of ethyl ether into the solution of crude product in DMSO at ambient temperature in *ca.* 85 % yield. Colorless block crystals [(*R*)-**1**·Ag]$_2$(PF$_6$)$_2$ suitable for X-ray analysis were obtained by slow diffusion of ethyl ether into the corresponding DMSO solution at room temperature through several days. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 3.97 (dd, *J* = 6.8 Hz, 6.8 Hz, 4H), 4.32 (dd, *J* = 4.8 Hz, 4.8 Hz, 4H), 5.25 (d, *J* = 15.6 Hz, 4H), 5.41 (d, *J* = 16.0 Hz, 4H), 5.77 (t, *J* = 5.6 Hz, 4H), 6.47 (t, *J* = 7.2 Hz, 4H), 6.56 (t, *J* = 7.6 Hz, 8H), 6.94 (d, *J* = 7.6 Hz, 8H), 7.38 (s, 2H), 7.90 (t, *J* = 8.4 Hz, 2H), 8.02-8.05 (m, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 59.3, 62.3, 69.7, 110.3, 121.9, 127.6, 128.2, 128.6, 132.1, 137.8, 139.0, 150.8, 178.0 (dd, ^1J ^{107}Ag = 188.86 Hz, ^1J ^{109}Ag = 214.7 Hz, carbene N-C-N) ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ -69.2 (d, J = 756 Hz, PF_6^-) ppm. Anal. Calcd for $C_{56}H_{48}Ag_2F_{12}N_{12}O_4P$: C, 46.11; H, 3.32; N, 11.52; Found: C, 45.79; H, 3.63; N, 11.75. ESI-TOF found: m/z = 583.10 (calcd for [(*R*)-**1**·Ag]$^+$ 583.10); m/z = 1313.17 (calcd for [[(*R*)-**1**·Ag]$_2$(PF_6)]$^+$ 1313.17).

3. Preparation and characterization of [(*S*)-2·Ag]$_3$(BF_4)$_3$



[(*S*)-**2**·Ag]$_3$(BF_4)$_3$

Bis-triazolium salt (*S*)-**2**·2HCl (116 mg, 0.2 mmol), silver oxide (46 mg, 0.2 mmol), and $NaBF_4$ (24 mg, 0.22 mmol) were added to CH_2Cl_2 (5 mL) under argon. The mixture was stirred for 10 h at room temperature, and filtered through Celite. The solvent was removed in vacuo at room temperature to give a white solid, which was recrystallized from $CHCl_3$/EtOAc to afford a colorless crystalline product in 95% yield. Colorless block crystals [(*S*)-**2**·Ag]$_3$(BF_4)$_3$ suitable for X-ray analysis were obtained by slow evaporation of the corresponding $CHCl_3$/EtOAc solution at ambient temperature through several days.

In addition, [(*S*)-**2**·Ag]$_3$(BF_4)$_3$ could also be prepared by anion-exchange reaction of [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or $AgCl_2$) with $NaBF_4$ (~ 3.3 equiv) in CH_2Cl_2 for 24 h at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84-2.97 (m, 12H_g), 3.70 (dd, J = 11.2 Hz, 12.0 Hz, 12H_e), 3.98 (t, J = 7.6 Hz, 6H_f), 4.62 (d, J = 15.6 Hz, 6H_d), 5.02 (d, J = 16.0 Hz, 6H_d), 6.45 (d, J = 7.2 Hz, 12H_h), 7.03 (t, J = 7.2 Hz, 12H_i), 7.08 (t, J = 7.2 Hz, 6H_j), 7.87 (d, J = 7.6 Hz, 6H_b), 8.00 (t, J = 8.0 Hz, 3H_c) 8.50 (s, 3H_a) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.5, 57.0, 62.1, 65.4, 120.1, 125.6, 127.2, 129.0, 130.7, 136.0, 141.4, 148.6, 148.7 ppm (Note: the carbene resonance of [(*S*)-**2**·Ag]$_3$(BF_4)$_3$ was inconspicuous). ^{18}F NMR (376 MHz, $CDCl_3$): δ -154.2 (s, 8F), -150.7 (s, 4F) ppm. Anal. Calcd for $C_{90}H_{84}Ag_3N_{18}O_6B_3F_{12}$: C, 51.53; H, 4.04; N, 12.02; Found: C, 51.72; H, 4.21; N, 12.43. ESI-TOF found: m/z = 611.11 (calcd for [(*S*)-**2**·Ag]$^+$ 611.13); m/z = 2012.41 (calcd for [[(*S*)-**2**·Ag]$_3$(BF_4)$_2$]$^+$ 2012.41).

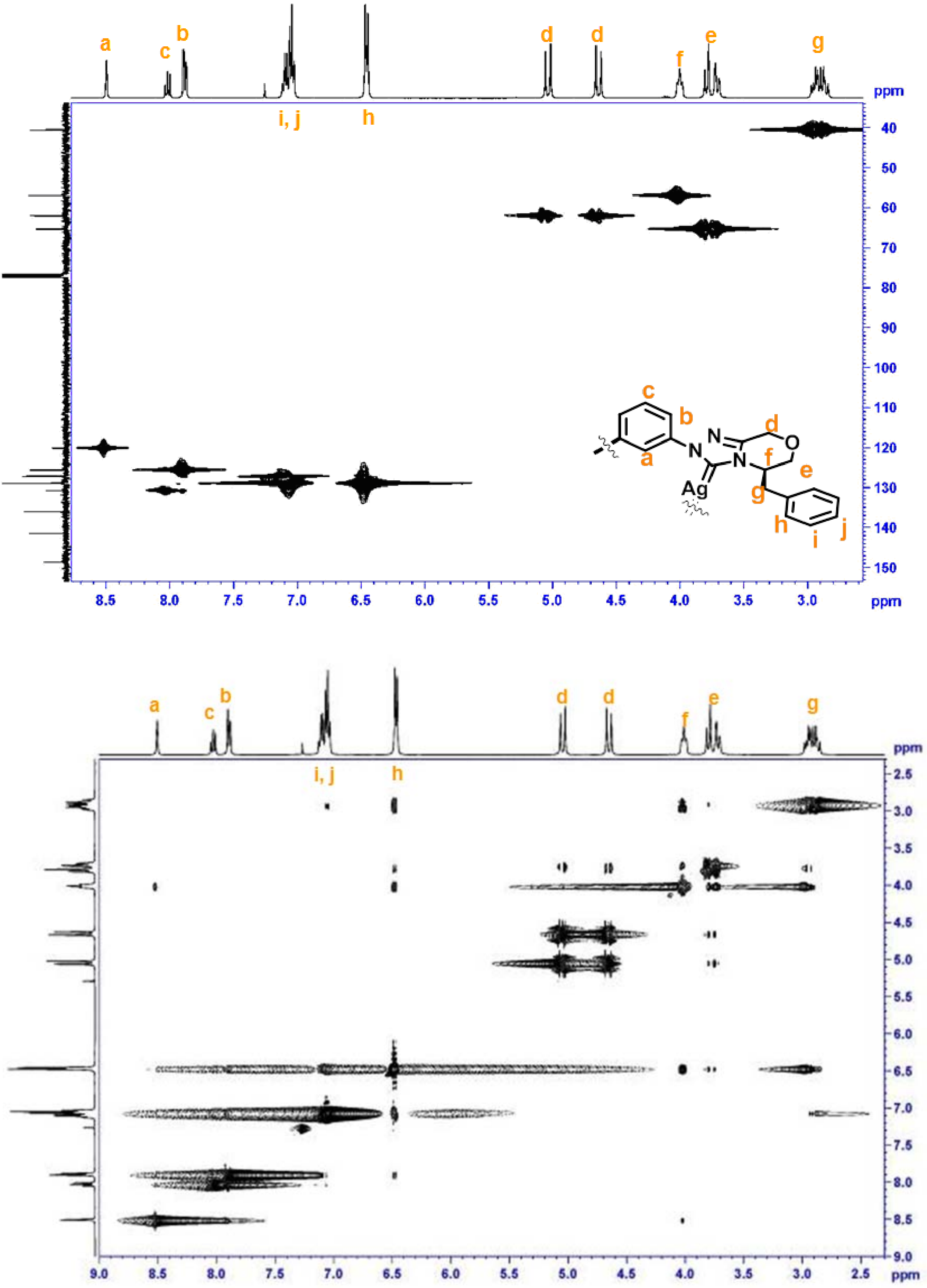
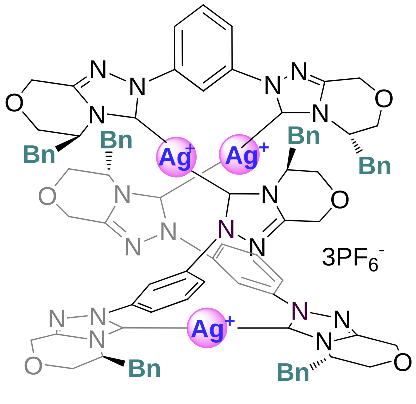


Figure S1. The HMQC and ROESY NMR of $[(S)\text{-}\mathbf{2}\cdot\mathrm{Ag}]_3(\mathrm{BF}_4)_3$ in CDCl_3.

4. Preparation and characterization of [(*S*)-2·Ag]$_3$(PF$_6$)$_3$



[(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$

Bis-triazolium salt (*S*)-**2**·2HCl (58 mg, 0.1 mmol), silver oxide (23 mg, 0.1 mmol), and KPF$_6$ (20 mg, 0.11 mmol) were added to CH$_2$Cl$_2$ (4 mL) under argon. The mixture was stirred for 10 h at room temperature, and filtered through Celite. The solvent was removed in vacuo at room temperature to afford a white solid, which was recrystallized from CHCl$_3$/EtOAc to afford a colorless crystalline product in 75% yield.

In addition, [(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$ could also be prepared by anion-exchange reaction of [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$) with KPF$_6$ (~3.3 equiv) in CH$_2$Cl$_2$ for 24 h at room temperature. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.85-2.98 (m, 12H), 3.70 (dd, *J* = 12.0 Hz, 11.2 Hz, 12H), 3.98 (t, *J* = 7.6 Hz, 6H), 4.63 (d, *J* = 16.0 Hz, 6H), 5.02 (d, *J* = 16.0 Hz, 6H), 6.45 (d, *J* = 7.2 Hz, 12H), 7.03-7.13 (m, 18 H), 7.88 (d, *J* = 8.0 Hz, 6H), 8.00 (t, *J* = 8.0 Hz, 3H) 8.51 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 40.0, 57.0, 62.2, 65.2, 117.5, 122.2, 122.6, 126.5, 128.4, 129.8, 130.2, 130.3, 136.1, 140.5, 147.7 ppm (Note: the carbene resonance of [(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$ was inconspicuous). ^{19}F NMR (376 MHz, CDCl$_3$): δ -72.4 (d, *J* = 840 Hz, 6F), -71.5 (d, *J* = 840 Hz, 12F). Anal. Calcd for $C_{90}H_{84}Ag_3N_{18}O_6P_3F_{18}$: C, 47.57; H, 3.73; N, 11.10; Found: C, 48.22; H, 4.19; N, 11.37. ESI-TOF found: *m/z* = 611.12 (calcd for [(*S*)-**2**·Ag]$^+$ 611.13); *m/z* = 2125.24 (calcd for [[(*S*)-**2**·Ag]$_3$(PF$_6$)$_2$]$^+$ 2125.33).

Colorless block crystals [(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$ suitable for X-ray analysis were obtained by slow evaporation of the corresponding dichloromethane/ethyl acetate solution at ambient temperature through several days. Because the counteranions and solvent molecules could not be precisely located from the difference maps due to their high thermal disorder, these counteranions and solvent molecules were omitted by Squeeze program, and the Squeeze results were appended to the CIF file.

The crystal structure of [(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$ was shown in Figure S2. The dihedral angle between the two NHC rings connected by a 1,3-phenylene unit was 82.73º, which was close to that in [(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$ (82.81º).

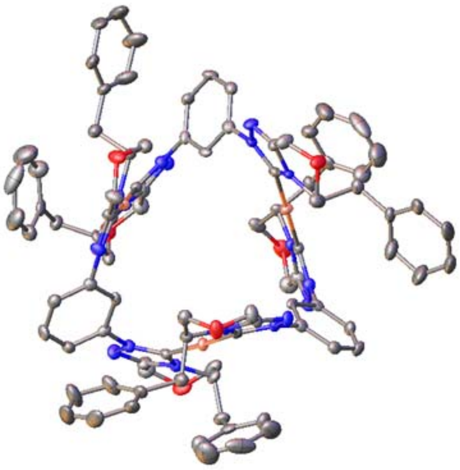
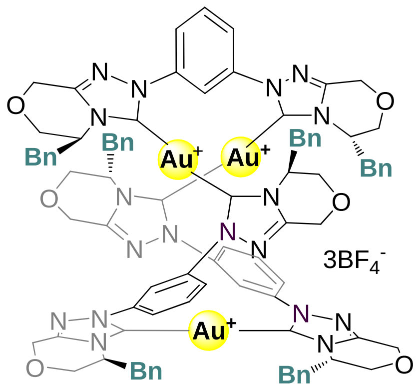


Figure S2. The crystal structure of [(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$ viewed along the c axis. The counteranions and solvent molecules were omitted by Squeeze program. Hydrogen atoms have been omitted for clarity. Atom color code: C (gray), N (blue), O (red), and Ag (orange).

5. Preparation and characterization of [(*S*)-2·Au]$_3$(BF$_4$)$_3$

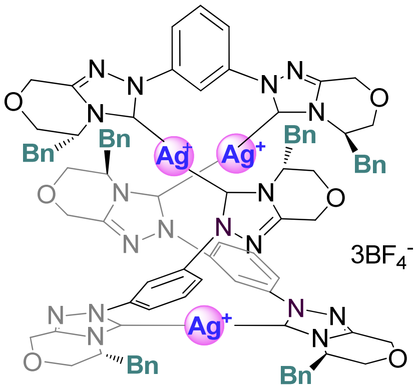


[(*S*)-**2**·Au]$_3$(BF$_4$)$_3$

[(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$ (63 mg, 0.03 mmol) and (dimethylsulfide)gold(I) chloride [AuCl(Me$_2$S)] (29.5 mg, 0.1 mmol, 3.3 equiv) were added to CHCl$_3$ (10 mL) under argon. The mixture was stirred for 10 h at room temperature, and filtered through Celite. The filtrate was washed with water (5 mL), and the solvent was then removed in vacuo at room temperature to give a white solid, which was recrystallized from CHCl$_3$/EtOAc to afford colorless crystals (43 mg, ~ 60% yield). Colorless block crystals [(*S*)-**2**·Au]$_3$(BF$_4$)$_3$ suitable for X-ray analysis were obtained by slow evaporation of the corresponding chloroform/ethyl acetate solution at ambient temperature through several days. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.84-2.98 (m, 12H), 3.70 (dd, *J* = 12.0 Hz, 11.2 Hz, 12H), 3.98 (t, *J* =

7.6 Hz, 6H), 4.63 (d, *J* = 15.6 Hz, 6H), 5.02 (d, *J* = 15.6 Hz, 6H), 6.45 (d, *J* = 7.6 Hz, 12H), 7.03-7.12 (m, 18 H), 7.88 (d, *J* = 7.6 Hz, 6H), 8.00 (t, *J* = 8.0 Hz, 3H) 8.51 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.5, 57.0, 62.1, 65.3, 120.1, 125.5, 127.2, 129.0, 130.7, 136.0, 141.4, 148.8, 148.7, 181.2 (dd, *J* = 60 Hz, 60 Hz, carbene N-C-N) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): 150.7 (s, 8F), 154.1 (s, 4F). Anal. Calcd for $C_{90}H_{84}Au_3N_{18}O_6B_3F_{12}$: C, 45.71; H, 3.58; N, 10.66; Found: C, 45.36; H, 3.93; N, 10.29. ESI-TOF found: *m/z* = 701.19 (calcd for $[(S)\text{-}\mathbf{2}\cdot Au]^+$ 701.19); *m/z* = 2277.57 (calcd for $[[(S)\text{-}\mathbf{2}\cdot Au]_3(BF_4)_2]^+$ 2277.59).

6. Preparation and characterization of $[(R)\text{-}\mathbf{2}\cdot Ag]_3(BF_4)_3$



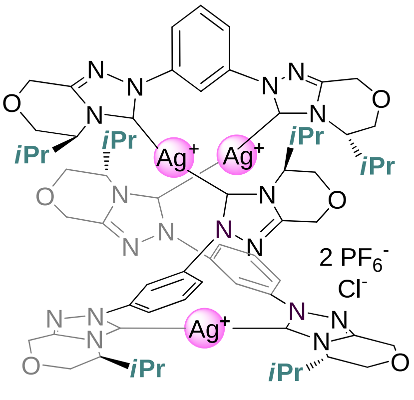
$[(R)\text{-}\mathbf{2}\cdot Ag]_3(BF_4)_3$

Bis-triazolium salt (*R*)-**2**·2HCl (58 mg, 0.1 mmol), $NaBF_4$ (12 mg, 0.11 mmol), and silver oxide (23 mg, 0.1 mmol) were added to CH_2Cl_2 (4 mL) under argon. The mixture was stirred for 10 h at room temperature, and filtered through Celite. The solvent was removed in vacuo at room temperature to give a white solid, which was recrystallized from $CHCl_3$/EtOAc to afford a colorless crystalline product in 90% yield. Colorless block crystals $[(R)\text{-}\mathbf{2}\cdot Ag]_3(BF_4)_3$ suitable for X-ray analysis were obtained by slow evaporation of the corresponding dichloromethane/ethyl acetate solution at ambient temperature through several days. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85-2.98 (m, 12H), 3.71 (dd, *J* = 11.2 Hz, 12.0 Hz, 12H), 3.98 (t, *J* = 7.6 Hz, 6H), 4.63 (d, *J* = 15.6 Hz, 6H), 5.02 (d, *J* = 15.6 Hz, 6H), 6.45 (d, *J* = 7.6 Hz, 12H), 7.03-7.13 (m, 18 H), 7.88 (d, *J* = 7.6 Hz, 6H), 8.00 (t, *J* = 8.0 Hz, 3H) 8.54 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.5, 57.0, 62.1, 65.3, 125.5, 127.2, 129.0, 129.0, 130.7, 136.0, 141.4, 148.8 ppm (Note: the carbene resonance of $[(R)\text{-}\mathbf{2}\cdot Ag]_3(BF_4)_3$ was inconspicuous). Anal. Calcd for $C_{90}H_{84}Ag_3N_{18}O_6B_3F_{12}$: C, 51.53; H, 4.04; N, 12.02; Found: C, 51.63; H, 4.27; N, 12.08. ESI-TOF found: *m/z* = 611.12 (calcd for $[(R)\text{-}\mathbf{2}\cdot Ag]^+$ 611.13); *m/z* = 2012.40 (calcd for $[[(R)\text{-}\mathbf{2}\cdot Ag]_3(BF_4)_2]^+$ 2012.41).

7. Preparation and characterization of silver-NHC complexes through the reaction of Ag_2O and the mixture of (*S*)-2·2HCl and (*R*)-2·2HCl at a 1:1 ratio

A mixture of bis-triazolium salts (*S*)-**2**·2HCl and (*R*)-**2**·2HCl (at a 1:1 ratio) (116 mg, 0.2 mmol), $NaBF_4$ (24 mg, 0.22 mmol), and silver oxide (46 mg, 0.2 mmol) were added to CH_2Cl_2 (4 mL) under argon. The suspension became clear after being stirred for 10 h at room temperature, and then filtered through Celite. The solvent was removed in vacuo at room temperature to give a white solid (135 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85-2.98 (m, 12H), 3.70 (dd, *J* = 11.2 Hz, 12.0 Hz, 12H), 3.98 (t, *J* = 7.6 Hz, 6H), 4.63 (d, *J* = 15.6 Hz, 6H), 5.02 (d, *J* = 15.6 Hz, 6H), 6.45 (d, *J* = 7.6 Hz, 12H), 7.03-7.13 (m, 18 H), 7.88 (d, *J* = 8.0 Hz, 6H), 8.00 (t, *J* = 7.6 Hz, 3H), 8.53 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.0, 57.0, 62.2, 65.2, 117.5, 122.7, 126.5, 128.4, 129.9, 130.1, 136.0, 140.5, 147.7 ppm (Note: the carbene resonances of the mixture were inconspicuous). Anal. Calcd for $C_{90}H_{84}Ag_3N_{18}O_6B_3F_{12}$: C, 51.53; H, 4.04; N, 12.02; Found: C, 51.07; H, 3.64; N, 11.75. ESI-TOF found: *m/z* = 611.13 (calcd for [**2**·Ag]$^+$ 611.13); *m/z* = 2012.44 (calcd for [(**2**·Ag)$_3$(BF$_4$)$_2$]$^+$ 2012.41).

8. Preparation and characterisation of [(*S*)-3·Ag]$_3$(PF$_6$)$_2$(Cl)



[(*S*)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl)

Bis-triazolium salt (*S*)-**3**·2HCl (48.5 mg, 0.1 mmol), KPF_6 (20 mg, 0.11 mmol), and silver oxide (23 mg, 0.1 mmol) were added to CH_2Cl_2 (4 mL) under argon. The mixture was stirred for 10 h at room temperature, and then filtered through Celite. The solvent was removed in vacuo at room temperature to give a white solid, which was recrystallized from $CHCl_3$/EtOAc to afford a colorless crystalline product (41 mg, ~ 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.56 (d, *J* = 6.8 Hz, 12H), 0.74 (d, *J* = 7.2 Hz, 12H), 0.84 (s, 6H), 0.95 (s, 6H), 2.22 (d, *J* = 4.8 Hz, 4H), 2.38 (s, 2H), 3.76 (d, *J* = 9.2 Hz, 6H), 4.02 (t, *J* = 11.6 Hz, 6H), 4.22 (d, *J* = 12.8 Hz, 3H), 4.51 (s, 2H), 4.68 (d, *J* = 15.6

Hz, 4H), 4.84 (d, *J* = 16.0 Hz, 3H), 4.99 (dd, *J* = 2.8 Hz, 2.8 Hz, 6H), 7.59 (t, *J* = 8.0 Hz, 1 H), 7.73-7.78 (m, 6H), 7.85 (d, *J* = 7.6 Hz, 2H), 8.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.3, 17.7, 19.3, 19.8, 29.7, 33.1, 59.7, 59.8, 61.7, 61.9, 63.5, 64.4, 119.0, 125.2, 130.6, 131.3, 134.0, 141.3, 149.7, 149.9 ppm (Note: the carbene resonances in [(*S*)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl) were inconspicuous). ^{19}F NMR (376 MHz, $CDCl_3$): δ -71.43 (d, 1012 Hz, PF$_6$) ppm. Anal. Calcd for $C_{66}H_{84}Ag_3N_{18}O_6P_2F_{12}Cl$: C, 42.29; H, 4.52; N, 13.45; Found: C, 42.01; H, 4.25; N, 13.17. ESI-TOF found: *m/z* = 515.11 (calcd for [(*S*)-**3**·Ag]$^+$ 515.13); *m/z* = 1582.37 (calcd for [[(*S*)-**3**·Ag]$_3$Cl]$^{2+}$ 1582.37).

Colorless block crystals [(*S*)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl)·(CHCl$_3$)·(EtOAc) suitable for X-ray analysis were obtained by slow evaporation of the corresponding chloroform/ethyl acetate solution at ambient temperature through several days. The crystal structure of [(*S*)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl)·(CHCl$_3$)·(EtOAc) viewed from different angles are shown in Figure S3.

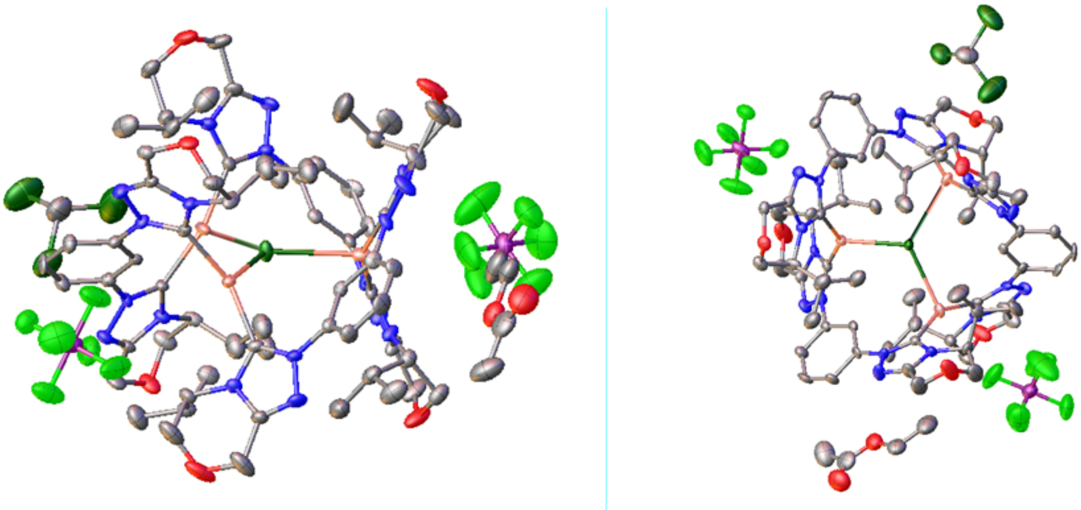
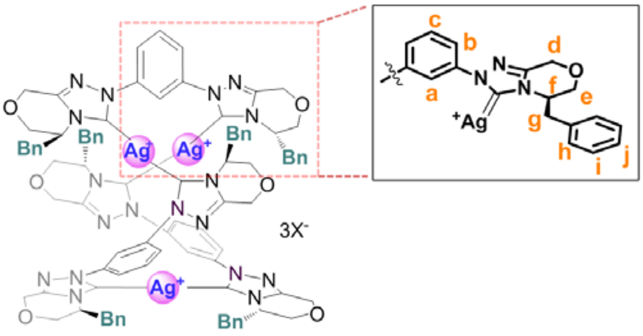


Figure S3. The crystal structure of [(*S*)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl)·(CHCl$_3$)·(EtOAc) viewed from different angles. Hydrogen atoms and solvents have been omitted for clarity. Atom color code: C (gray), N (blue), O (red), Ag (dark gray), Cl (bottle green), P (cyan), and F (green).

9. Preparation and characterization of [(*S*)-2·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$)



$[(S)\text{-}\mathbf{2}\cdot Ag]_3(X)_3$ (X = Cl and/or $AgCl_2$)

Bis-triazolium salt (*S*)-**2**·2HCl (58 mg, 0.1 mmol), and silver oxide (23 mg, 0.1 mmol) were added to CH_2Cl_2 (4 mL) under argon. The mixture was stirred for 10 h at room temperature, and then filtered through Celite. The solvent was removed in vacuo at room temperature to give a grey solid. The solid was then dissolved in $CHCl_3$, followed by addition of activated carbon. The mixture was refluxed under argon for 15 min, and then filtered through Celite. The filtrate was concentrated to *ca.* 5 mL, and then added to ethyl ester (50 mL) under stirring at room temperature to afford a white solid in 95% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 2.54 (t, *J* = 12.0 Hz, $6H_g$), 3.52 (d, *J* = 12.4 Hz, $6H_e$), 3.68 (dd, *J* = 4.4 Hz, 4.0 Hz, $6H_g$), 3.78 (d, *J* = 12.4 Hz, $6H_e$), 4.70 (s, br, $6H_f$), 4.70 (d, *J* = 15.4 Hz, $6H_d$), 5.01 (d, *J* = 16.0 Hz, $6H_d$), 7.11 (s, $12H_i$ and $6H_j$), 7.29 (s, $12H_h$), 7.58 (s, $3H_c$), 7.80 (d, *J* = 7.6 Hz, $6H_b$), 9.49 (s, $3H_a$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.9, 57.0, 62.2, 65.1, 117.5, 122.6, 126.5, 128.4, 128.9, 129.9, 130.1, 136.1, 140.5, 147.7 ppm (Note: the carbene resonances in $[(S)\text{-}2\cdot Ag]_3(X)_3$ (X = Cl and/or $AgCl_2$) were inconspicuous). ESI-TOF found: *m/z* = 611.13 (calcd for $[(S)\text{-}\mathbf{2}\cdot Ag]^+$ 611.13); *m/z* = 1905.97 (calcd for $[(S)\text{-}\mathbf{2}\cdot Ag]_3Cl_2]^+$ 1905.33); *m/z* = 2049.08 (calcd for $[(S)\text{-}\mathbf{2}\cdot Ag]_3Cl(AgCl_2)]^+$ 2049.20). Anal. calcd found: C, 51.01; H, 4.51; N, 12.39. It is difficult to calculate the relative amounts of anions (Cl^- and $AgCl_2^-$) from the elemental analysis data of $[(S)\text{-}2\cdot Ag]_3(X)_3$ (X = Cl and/or $AgCl_2$).

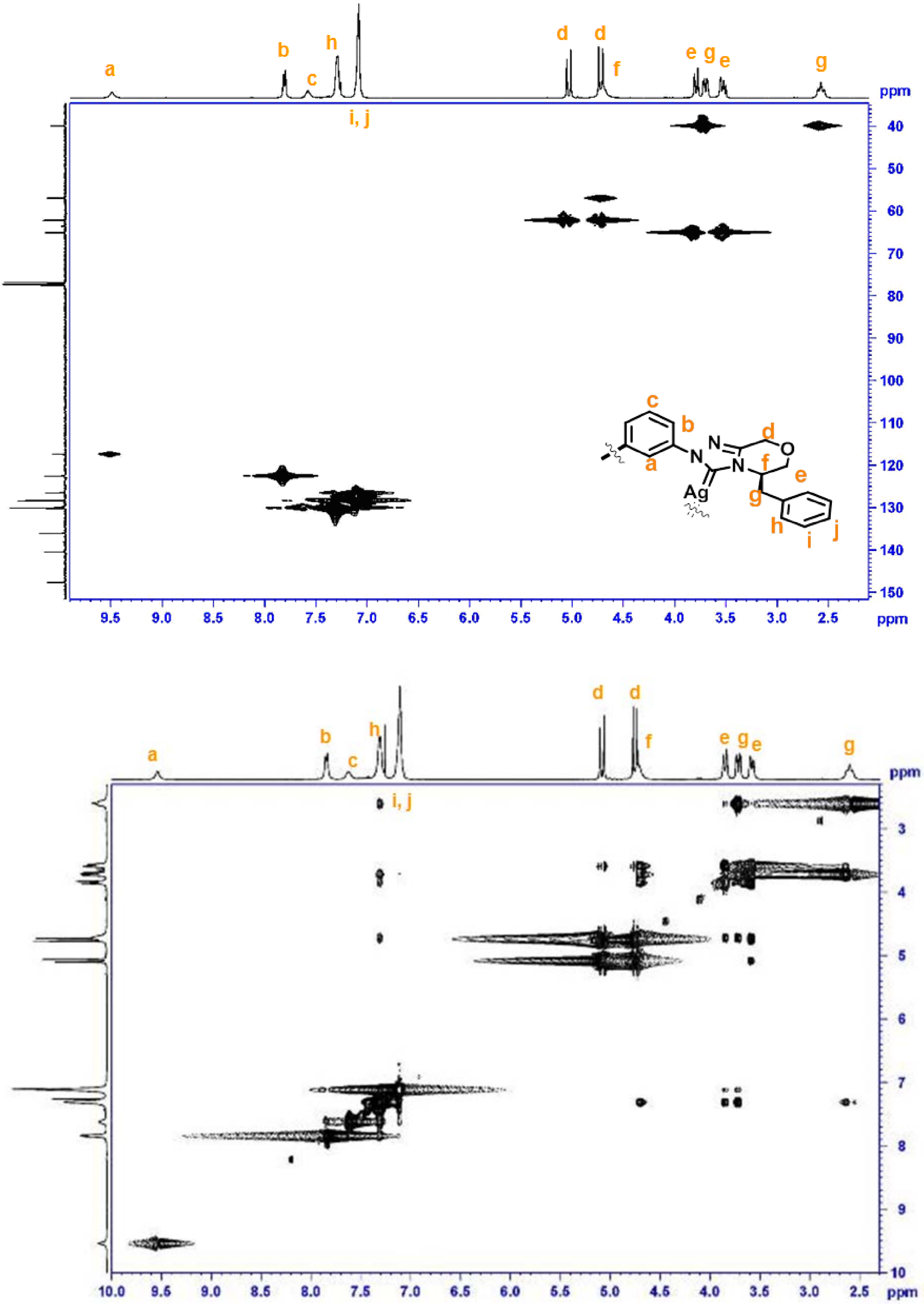
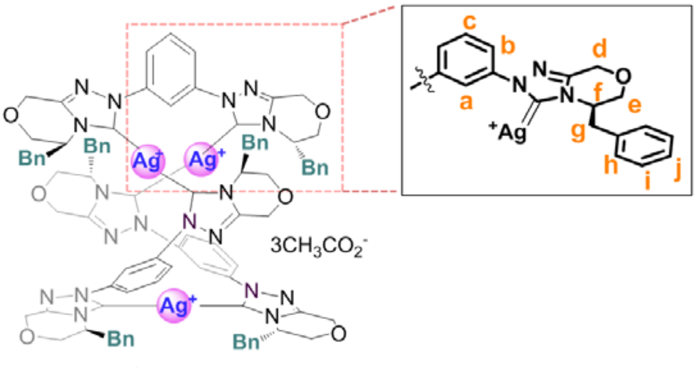


Figure S4. The HMQC and ROESY NMR of [(*S*)-**2**·Ag$]_3$(X)$_3$ (X = Cl and/or AgCl$_2$) in CDCl$_3$.

10. Preparation and characterization of [(*S*)-2·Ag]$_3$(CH_3CO_2)$_3$



[(*S*)-**2**·Ag]$_3$(CH_3CO_2)$_3$

[(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or $AgCl_2$) (62 mg, ~ 0.03 mmol) and silver acetate (17 mg, 0.1 mmol, 3.3 equiv) were added to $CHCl_3$ (10 mL) under argon. The mixture was stirred for 10 h at room temperature, followed addition of activated carbon. The resulting mixture was stirred at 30 ºC for 15 min, and then filtered through a Celite. The filtrate was washed with water (5 mL), concentrated to *ca.* 4 mL, and then added to ethyl ester (50 mL) under stirring to afford a white solid (56 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 9H, CH_3CO_2), 3.17 (t, *J* = 12.4 Hz, 6H_g), 3.58 (dd, *J* = 4.4 Hz, 4.4 Hz, 6H_g), 3.79 (d, *J* = 10.8 Hz, 6H_e), 4.11 (d, *J* = 12.4 Hz, 6H_e), 4.70 (s, br, 6H_f), 4.83 (d, *J* = 16.4 Hz, 6H_d), 5.13 (dd, *J* = 16.0 Hz, 6H_d), 7.28 (t, *J* = 4.0 Hz, 6H_j), 7.34-7.35 (m, 12H_i and 12H_h), 7.58 (t, *J* = 7.6 Hz, 3H_c), 8.01 (d, *J* = 8.0 Hz, 6H_b) 8.68 (s, 3H_a) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.8, 40.0, 57.7, 62.2, 65.6, 116.3, 122.5, 127.5, 129.1, 129.8, 130.1, 135.5, 140.0, 148.6, 178.9 ppm (Note: the carbene resonance of [(*S*)-2·Ag]$_3$(CH_3CO_2)$_3$ was inconspicuous). Anal. Calcd for $C_{96}H_{93}Ag_3N_{18}O_{12}$: C, 57.24; H, 4.65; N, 12.52; Found: C, 57.65; H, 4.88; N, 12.28; ESI-TOF found: *m/z* = 611.10 (calcd for [(*S*)-**2**·Ag]$^+$ 611.13); *m/z* = 1954.41 (calcd for [[(*S*)-**2**·Ag]$_3$(CH_3CO_2)$_2$]$^+$ 1954.43); *m/z* = 2014.40 (calcd for [[(*S*)-**2**·Ag]$_3$(CH_3CO_2)$_3$ + H]$^+$ 2014.45).

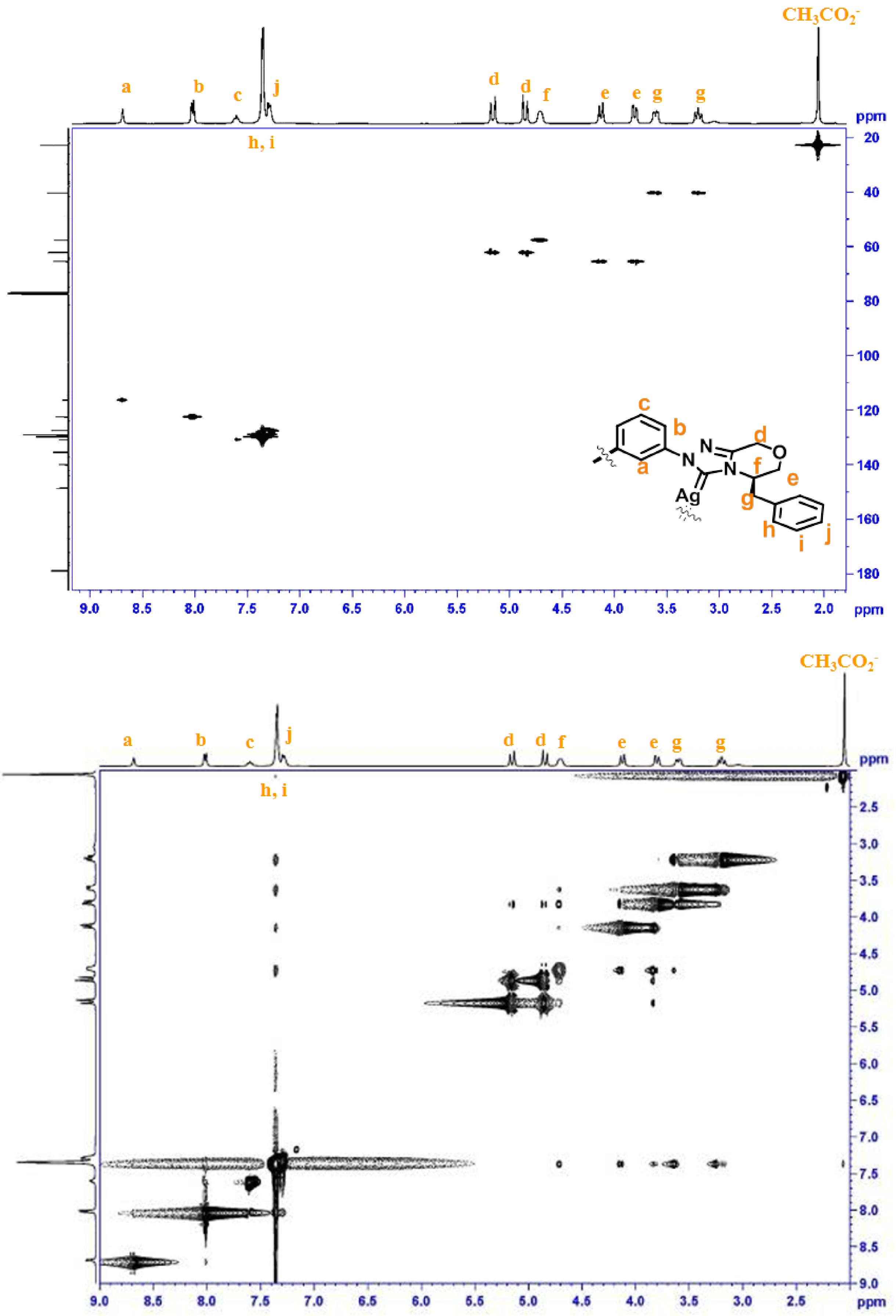
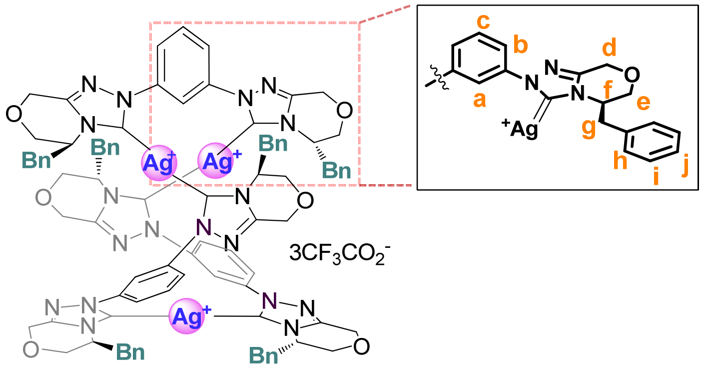


Figure S5. The HMQC and ROESY NMR of [(*S*)-**2**·Ag]$_3$(CH$_3$CO$_2$)$_3$ in CDCl$_3$.

11. Preparation and characterization of [(*S*)-2·Ag]$_3$(CF$_3$CO$_2$)$_3$



[(*S*)-**2**·Ag]$_3$(CF$_3$CO$_2$)$_3$

[(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$) (62 mg, ~ 0.03 mmol), and silver trifluoroacetate (22.1 mg, 0.1 mmol, 3.3 equiv) were added to CHCl$_3$ (10 mL) under argon. The mixture was stirred for 10 h at room temperature, and activated carbon was added. The mixture was stirred for 15 min at 30 ºC, and then filtered through a Celite. The filtrate was washed with water (5 mL), concentrated to *ca.* 4 mL, and then added to ethyl ester (50 mL) under stirring to afford a white solid (55 mg, 85% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.08 (d, *J* = 11.2 Hz, 6H$_g$), 3.31 (s, 6H$_g$), 3.82 (d, *J* = 11.2 Hz, 6H$_e$), 4.02 (d, *J* = 11.2 Hz, 6H$_e$), 4.76 (s, br, 3H$_f$), 4.80 (d, *J* = 16.0 Hz, 6H$_{d)}$, 4.80 (d, *J* = 16.0 Hz, 6H$_{d)}$, 7.06-7.16 (m, 12H$_h$, 12H$_i$ and 6H$_j$), 7.38 (s, 3H$_c$), 7.92 (d, *J* = 6.8 Hz, 6H$_b$), 8.64 (s, 3H$_a$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 40.4, 57.2, 62.1, 65.8, 112.9, 115.9, 117.1, 118.8, 121.7, 123.0, 127.3, 129.0, 129.5, 130.6, 135.7, 140.4, 148.9, 161.2, 161.5, 181.6 ppm. ^{19}F NMR (376 MHz, CDCl$_3$): δ 74.0 (s, CF$_3$) ppm. Anal. Calcd for C$_{96}$H$_{84}$Ag$_3$N$_{18}$O$_{12}$F$_9$: C, 52.98; H, 3.89; N, 11.58; Found: C, 53.25; H, 4.22; N, 11.24. ESI-TOF found: *m/z* = 611.13 (calcd for [(*S*)-**2**·Ag]$^+$ 611.13); *m/z* = 2062.36 (calcd for [(*S*)-**2**·Ag]$_3$(CF$_3$CO$_2$)]$^{2+}$ 2062.37).

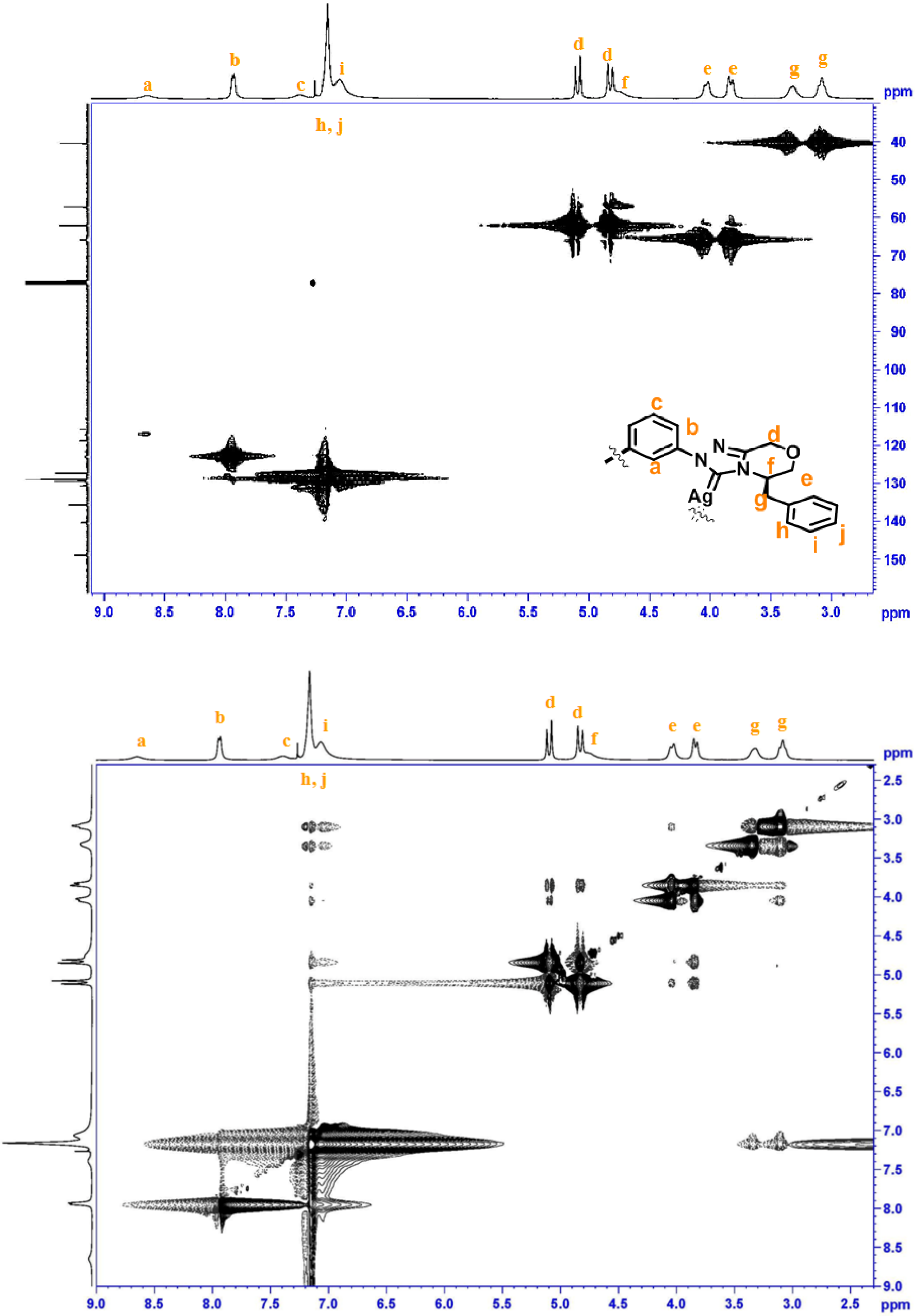


Figure S6. The HMQC and ROESY NMR of [(*S*)-**2**·Ag]$_3$(CF$_3$CO$_2$)$_3$ in CDCl$_3$.

IV. Crystal parameters and refinement results of [(*R*)-1·Ag]$_2$(PF$_6$)$_2$, [(*R*)-1·Ag]$_2$(BF$_4$)(Cl), [(*S*)-2·Ag]$_3$(PF$_6$)$_3$, [(*S*)-2·Ag]$_3$(BF$_4$)$_3$, [(*S*)-2·Au]$_3$(BF$_4$)$_3$, [(*R*)-2·Ag]$_3$(BF$_4$)$_3$, and [(*S*)-3·Ag]$_3$(PF$_6$)$_2$(Cl)·(CHCl$_3$)·(EtOAc)

Table S1. Crystal Parameters and Refinement Results of [(*R*)-**1**·Ag]$_2$(PF$_6$)$_2$, [(*R*)-**1**·Ag]$_2$(BF$_4$)(Cl), [(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$, [(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$, [(*S*)-**2**·Au]$_3$(BF$_4$)$_3$, [(*R*)-**2**·Ag]$_3$(BF$_4$)$_3$, and [(*S*)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl)·(CHCl$_3$)·(EtOAc)

	[(*R*)-**1**·Ag]$_2$(BF$_4$)(Cl)	[(*R*)-**1**·Ag]$_2$(PF$_6$)$_2$	[(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$^{a}
Chemical formula	$C_{56}H_{48}Ag_2BClF_4N_{12}O_4$	$C_{56}H_{48}Ag_2F_{12}N_{12}O_4P$	$C_{90}H_{84}Ag_3N_{18}O_6$
Formula weight (M)	1291.06	1458.74	1837.36
Temperature (K)	150.0	293(2)	150.0
Wavelength (Å)	0.7107	0.71073	0.7107
Crystal system	hexagonal	monoclinic	hexagonal
Space group (H-M)	*P* 622	*P* 1 2/c 1	*P* 63
Crystal size (mm^3)	0.25×0.20×0.20	0.28×0.20×0.04	0.32×0.23×0.22
a (Å)	22.2009(5)	14.883(9)	17.2761(2)
b (Å)	22.2009(5)	11.843(10)	17.2761(2)
c (Å)	12.58554(19)	19.893(10)	18.7097(2)
α (deg)	90	90	90
β (deg)	90	118.38(4)	90
γ (deg)	120	90	120
Volume (Å^3)	5372.11(18)	3085(4)	4836.01(10)
Z	3	4	2
Calculated density (g cm^{-3})	1.197	1.276	1.262
μ (mm^{-1})	0.639	0.778	0.658
Reflections collected	6655	6044	13550
Independent reflections	3134	5535	5251
R_{int}	0.0303	0.0574	0.0228
F(000)	1956	1464	1878
GOF	1.097	1.059	1.078
R_1, wR_2 [I >2σ(I)]	0.0688, 0.1874	0.0982, 0.2019	0.0409, 0.1165
R_1, wR_2 (all data)	0.0769, 0.1963	0.2709, 0.2388	0.0462, 0.1202

	[(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$	[(*S*)-**2**·Au]$_3$(BF$_4$)$_3$	[(*R*)-**2**·Ag]$_3$(BF$_4$)$_3$	[(*S*)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl) ·(CHCl$_3$)·(EtOAc)
Chemical formula	$C_{90}H_{84}Ag_3B_3F_{12}N_{18}O_6$	$C_{90}H_{84}Au_3B_3F_{12}N_{18}O_9$	$C_{90}H_{84}Ag_3B_3F_{12}N_{18}O_6$	$C_{71}H_{93}Ag_3Cl_4F_{12}N_{18}O_8P_2$
Formula weight (M)	2097.79	2413.08	2097.79	2082.99
Temperature (K)	294.15	294.15	294.15	150.1
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107
Crystal system	hexagonal	hexagonal	hexagonal	triclinic
Space group	*P* 63	*P* 63	*P* 63	*P* 1
Crystal size (mm^3)	0.42×0.36×0.30	0.38×0.30×0.28	0.32×0.28×0.24	0.25×0.20×0.20
a (Å)	17.3366(4)	17.4146(4)	17.3399(3)	12.6553(3)
b (Å)	17.3366(4)	17.4146(4)	17.3399(3)	13.0092(5)
c (Å)	18.9739(3)	18.8187(4)	18.9738(3)	15.1663(4)

α (deg)	90	90	90	104.239(3)
β (deg)	90	90	90	112.900(3)
γ (deg)	120	120	120	99.765(3)
Volume (Å^3)	4938.72(18)	4943.51(18)	4862.46(14)	2128.74(12)
Z	2	2	2	1
Calculated density (g cm^{-3})	1.443	1.621	1.433	1.625
μ (mm^{-1})	0.674	4.526	0.681	0.936
Reflections collected	15602	13406	13681	13449
Independent reflections	6563	6306	6407	12951
R_{int}	0.0207	0.0245	0.0162	0.0168
F(000)	2172	2364	2124	1057
GOF	1.043	0.959	1.027	1.032
R_1, wR_2 [I >2σ(I)]	0.0350, 0.1043	0.0363, 0.0963	0.0363, 0.1120	0.0391, 0.1015
R_1, wR_2 (all data)	0.0522, 0.1095	0.0556, 0.1002	0.0476, 0.1156	0.0413, 0.1045

[a] The counteranions (PF_6^-) in [(*S*)-**2**·Ag]$_3$(PF_6)$_3$ were omitted by Squeeze program.

V. Circular dichroism (CD) spectrum investigation of the silver NHC complexes

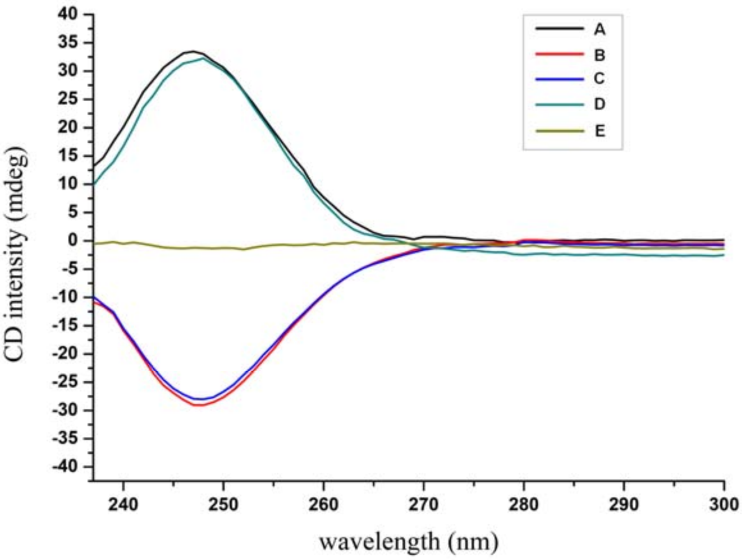


Figure S7. CD spectra of the silver NHC complexes at a concentration of 0.1 mg mL^{-1} in $CHCl_3$. **A** (black line): [(*S*)-**2**·Ag]$_3$(BF_4)$_3$; **B** (red line): [(*R*)-**2**·Ag]$_3$(BF_4)$_3$; **C** and **D** (blue and cyan line): two typical CD spectra of the randomly picked bulk single crystals obtained from recrystallization of the rude mixture of the reaction of Ag_2O and the mixture of (*S*)-**2**·2HCl and (*R*)-**2**·2HCl at a 1:1 ratio; **E** (tan line): CD spectrum of the rude mixture of the reaction of Ag_2O and the mixture of (*S*)-**2**·2HCl and (*R*)-**2**·2HCl at a 1:1 ratio (before recrystallization).

VI. ^{1}H NMR spectral changes of [(*S*)-2·Ag]$_3$(BF$_4$)$_3$ upon addition of 10 equiv TBACl in CDCl$_3$

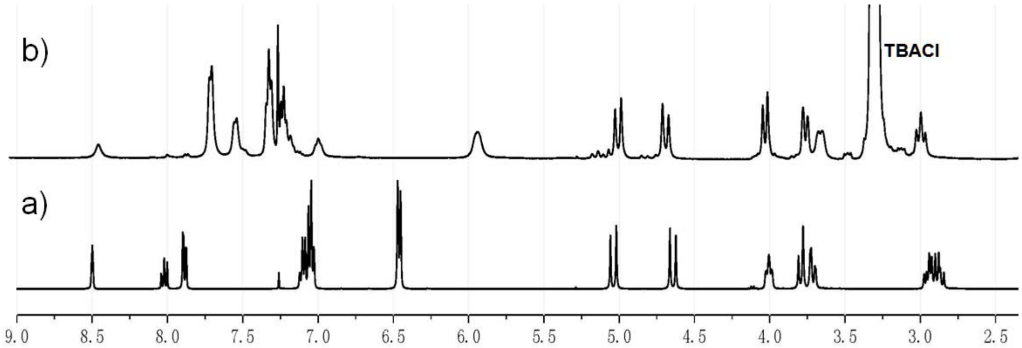


Figure S8. ^{1}H NMR spectra (400 MHz, CDCl$_3$) of a) [(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$; and b) upon addition of 10 equivalents of tetrabutylammonium chloride (TBACl) to a CDCl$_3$ solution of [(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$ at 20 °C.

VII. Influence of the counteranions of [(*S*)-2·Ag]$_3$(X)$_3$ on the hierarchical self-assemblies

The compound [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$, CH$_3$CO$_2$, or CF$_3$CO$_2$) was dispersed in 1 mL of solvent in a test tube. The resulting suspension was transferred to translucent gel after heating. The gel was simply confirmed by the “stable to inversion of a test tube” method. The results of gelation test in different solvents were summarized in Table S2.

Table S2. Gelation Test of Silver NHC Complexes (2 wt%) in Different Solvents

Solvent	Result		
	[(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$)	[(*S*)-**2**·Ag]$_3$(CH$_3$CO$_2$)$_3$	[(*S*)-**2**·Ag]$_3$(CF$_3$CO$_2$)$_3$
CH$_2$Cl$_2$	S	S	S
CH$_2$Cl$_2$/EtOAc (~ 1/10 v/v)	G	G	G
CHCl$_3$/EtOAc (~ 1/10 v/v)	G	G	G
CHCl$_3$/MeOH (~ 1/10 v/v)	G	G	G
CHCl$_3$/CH$_3$CN (~ 1/10 v/v)	G	G	Gp
MeOH	P	P	P
^{i}PrOH	G	P	P
acetone	S	G	G
CH$_3$CN	Gp	G	G
THF	S	G	Gp
EtOAc	P	Gp	Gp
dioxane	S	G	G
toluene	S	Gp	Gp
CHCl$_3$^{a}	G	G	G

[a] Higher concentrations (~ 50 %) of [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$, CH$_3$CO$_2$, CF$_3$CO$_2$) at 0 ºC. S: solution; G: steady gel; G$_p$: partial gel; P: precipitate.

VIII. Morphology analysis of [(*S*)-2·Ag]$_3$(X)$_3$ (X = BF$_4$, Cl and/or AgCl$_2$, CH$_3$CO$_2$, CF$_3$CO$_2$)

The morphologies of [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = BF$_4$, Cl and/or AgCl$_2$, CH$_3$CO$_2$, CF$_3$CO$_2$) were investigated using transmission electron microscope (TEM) and scanning transmission electron microscope (STEM). The TEM and STEM specimens were prepared by gently placing a carbon-coated copper grid on a surface of the sample. The grid was removed, stained with phosphotungstic acid aqueous solution (1 wt%) for [(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$ and [(*S*)-**2**·Ag]$_3$(CF$_3$CO$_2$)$_3$, BaCl$_2$ aqueous solution (1 wt%) for [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$), and uranyl acetate aqueous solution (1%) for [(*S*)-**2**·Ag]$_3$(CH$_3$CO$_2$)$_3$ (or unstained), dried for 10 min at room temperature, and then subjected to observation.

IX. ^{1}H NMR spectrum studies of [(*S*)-2·Ag]$_3$(X)$_3$ (X = BF$_4$, Cl and/or AgCl$_2$, CH$_3$CO$_2$, CF$_3$CO$_2$)

The proton assignment of [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = BF$_4$, Cl and/or AgCl$_2$, CH$_3$CO$_2$, and CF$_3$CO$_2$) was confirmed by HMQC and ROESY NMR experiments in CDCl$_3$ (Figure S1, S4-S6). Compared with the ^{1}H NMR spectrum of [(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$, the chemical shifts of H$_a$, H$_h$, and H$_f$ of [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$, CH$_3$CO$_2$, and CF$_3$CO$_2$) downfielded significantly, and the signals of H$_c$ were distinctly upfield shifted (Figure S9). These observations suggested significant differences in cation-anion interactions and noncovalent interactions of neighboring cation frameworks.

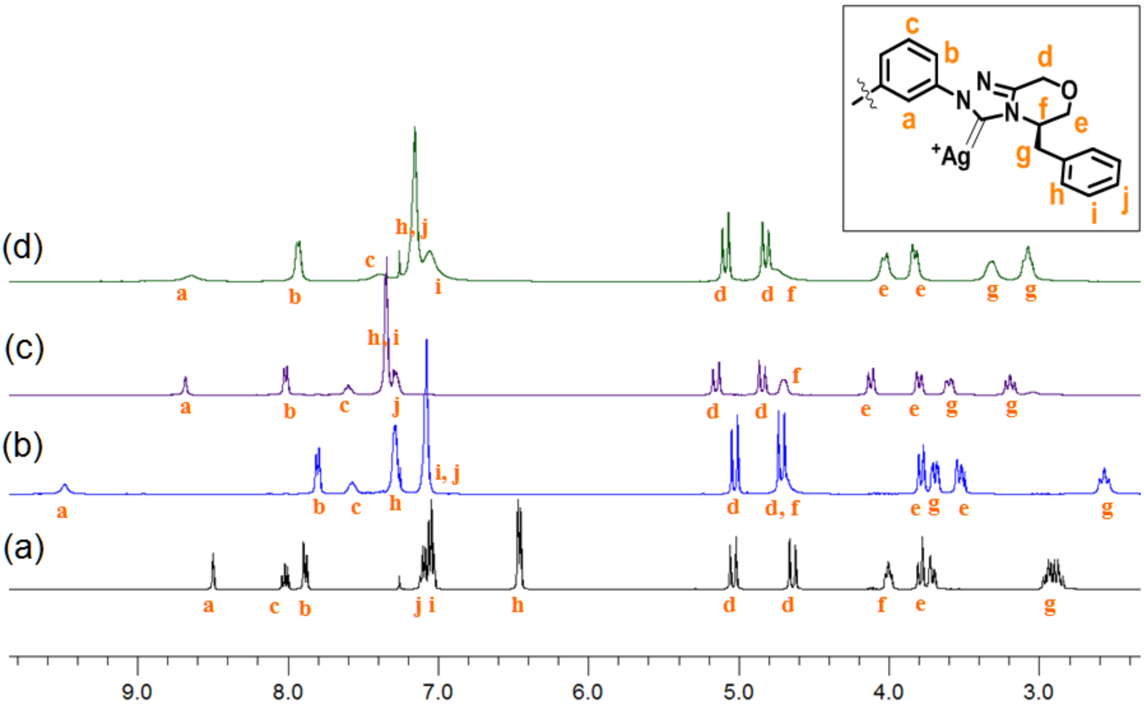


Figure S9. ^{1}H NMR spectra (400 MHz, CDCl$_3$) of (a) [(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$; (b) [(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$); (c) [(*S*)-**2**·Ag]$_3$(CH$_3$CO$_2$)$_3$; and (d) [(*S*)-**2**·Ag]$_3$(CF$_3$CO$_2$)$_3$.

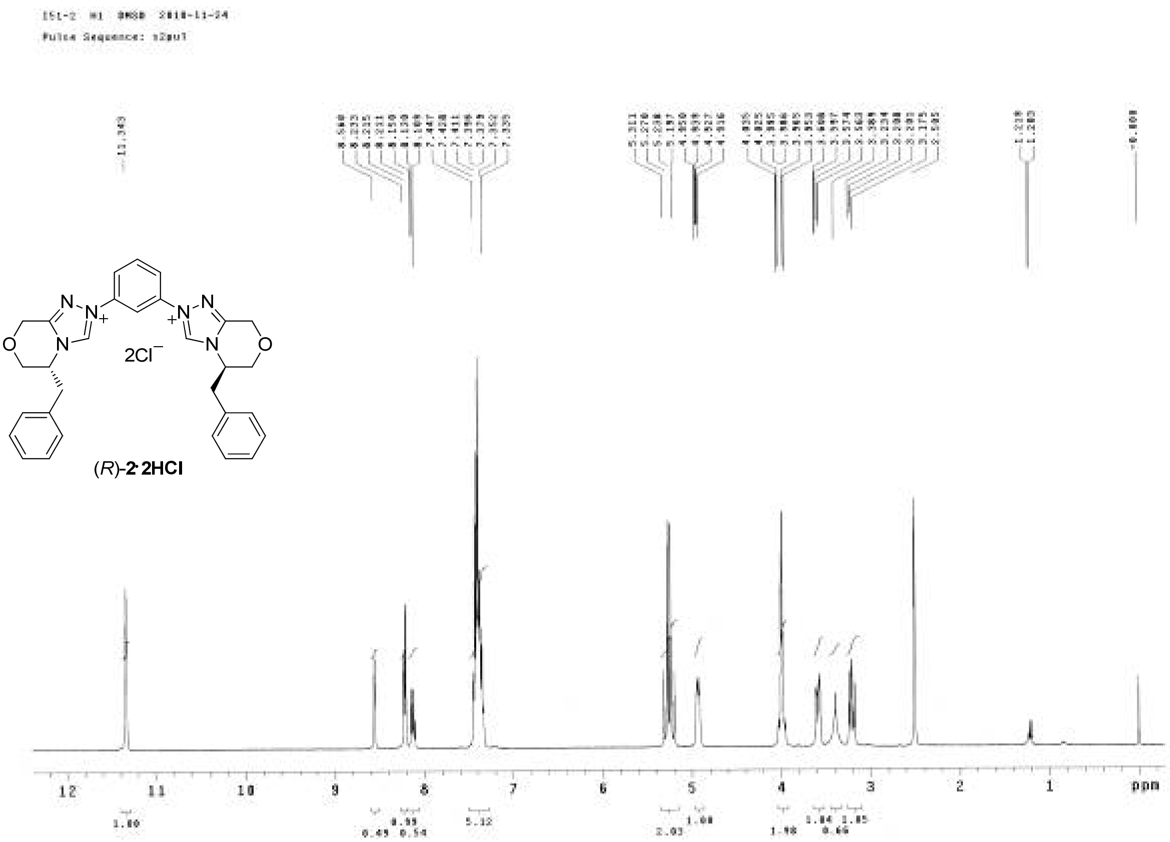
X. References

1 G. M. Scheldrick, *SHELX-97 and SHELXL-97, Program for Solution and Refinement of Crystal Structures* University of Göttingen: Germany, **1997**.

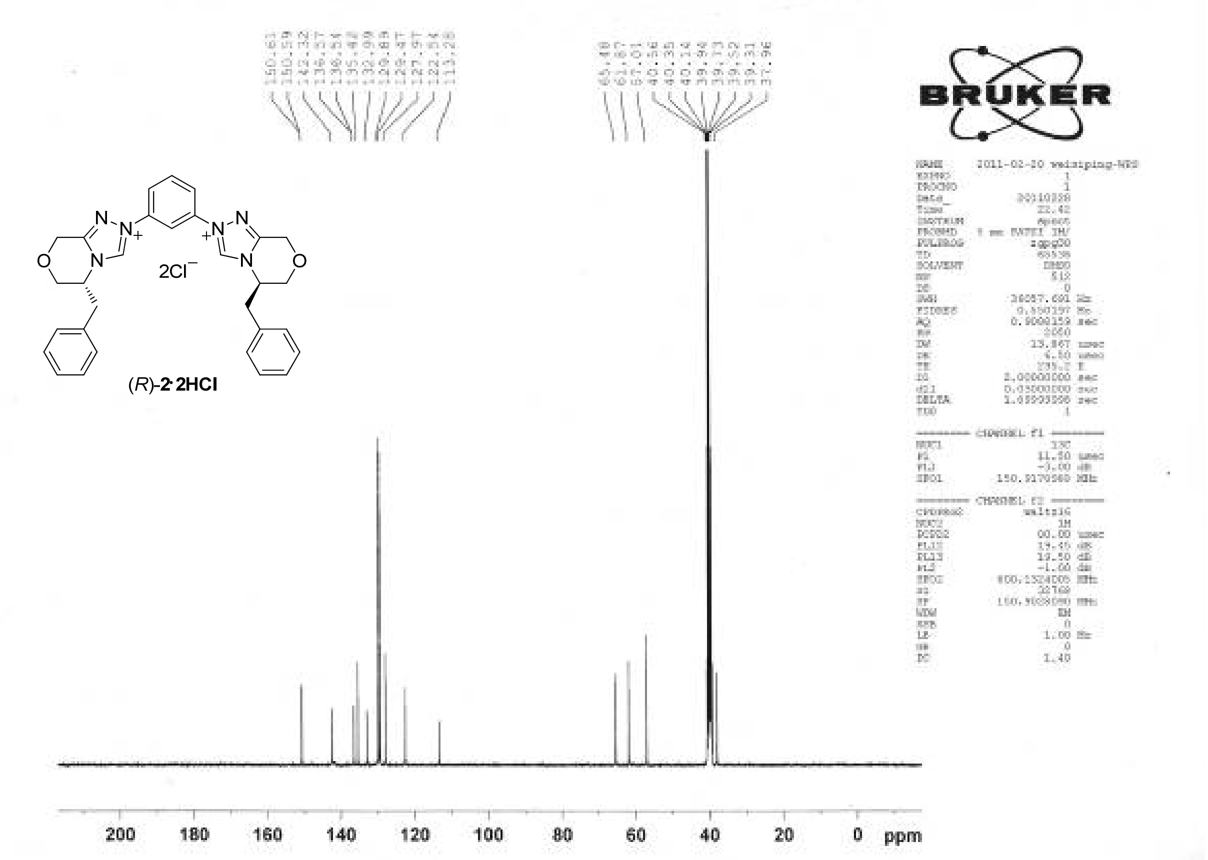
2 (a) L. J. Farrugia, *J. Appl. Cryst.* **1997**, *30*, 565; (b) A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7; (c) O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.

3 Y. Ma, S. Wei, J. Wu, F. Yang, B. Liu, J. Lan, S. Yang and J. You, *Adv. Synth. Catal.* **2008**, *350*, 2645.

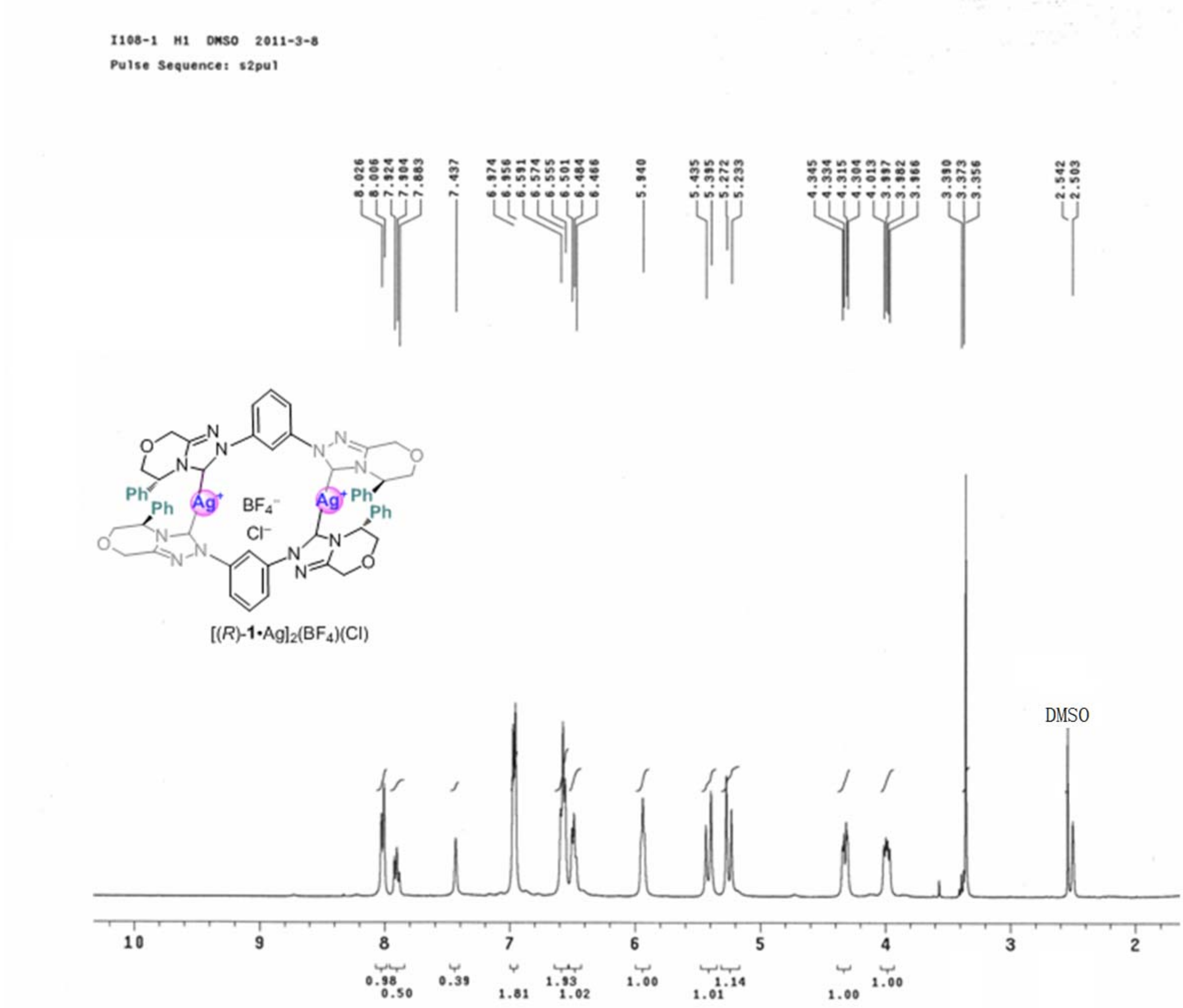
XI. Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra

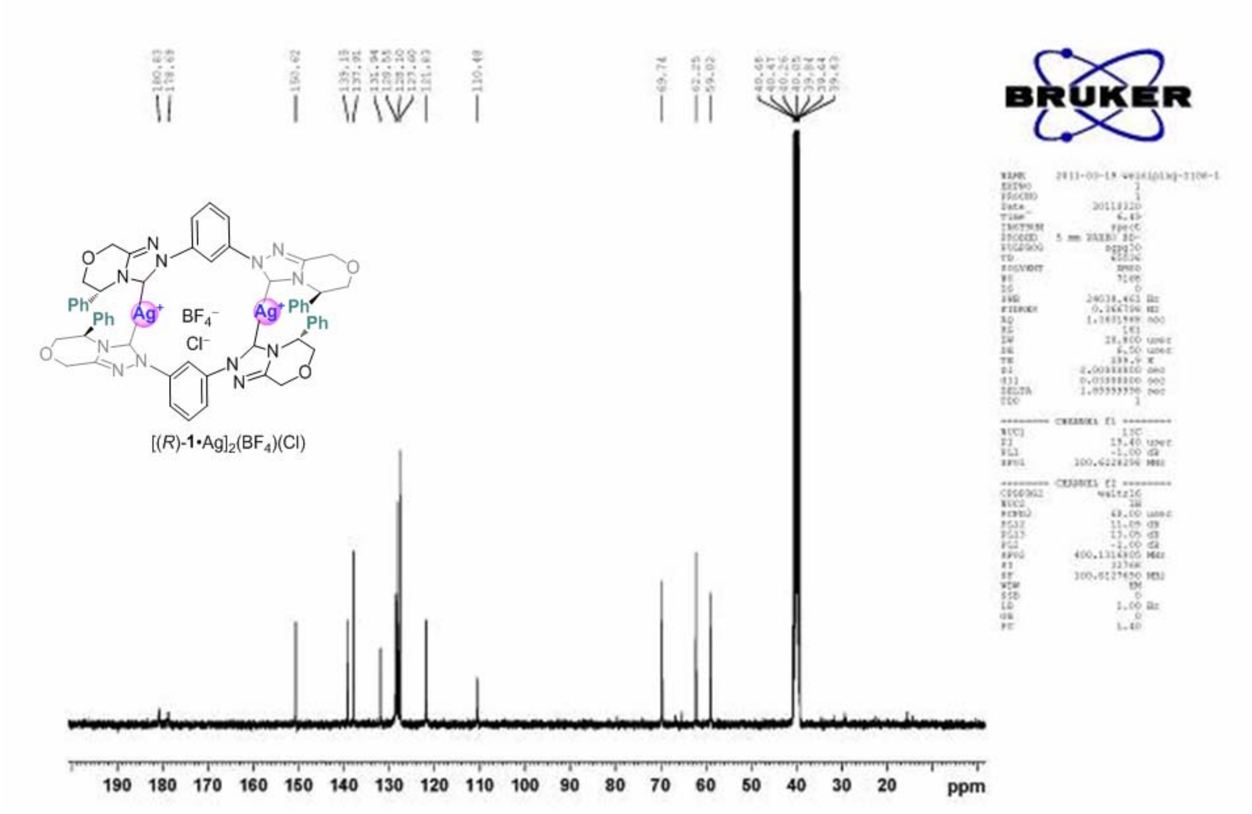


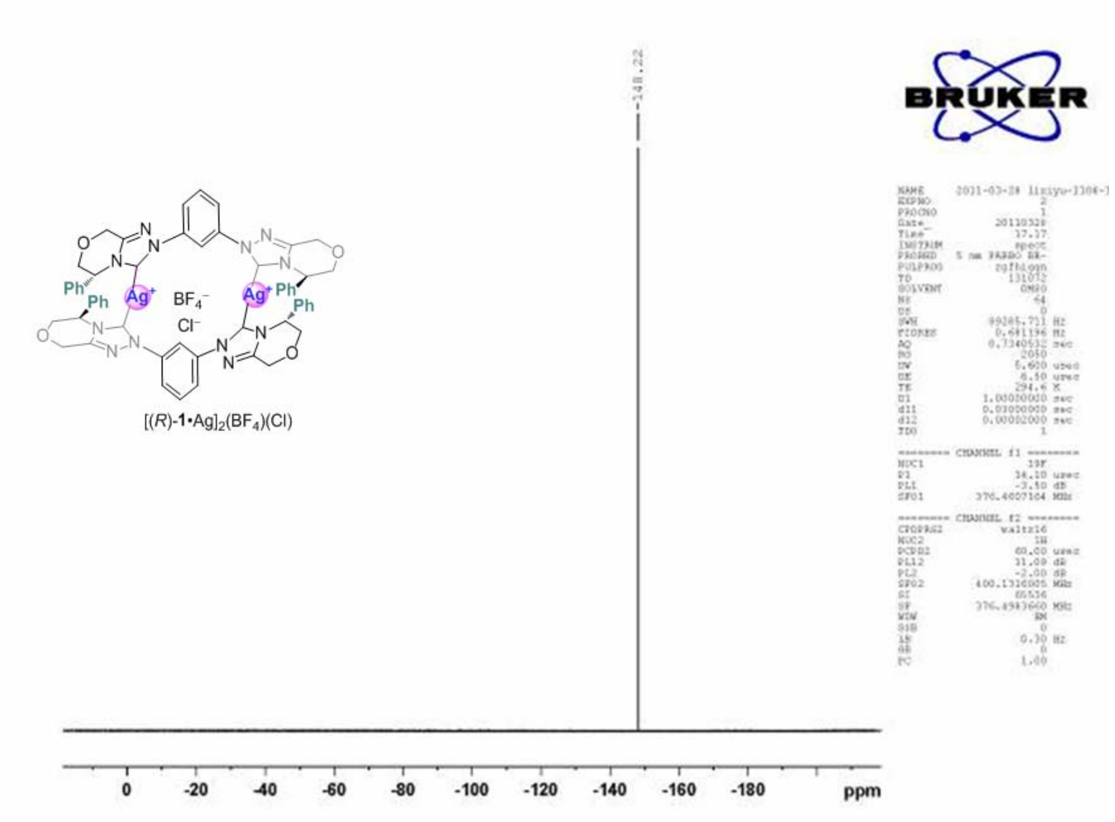
(*R*)-**2**·**2HCl**

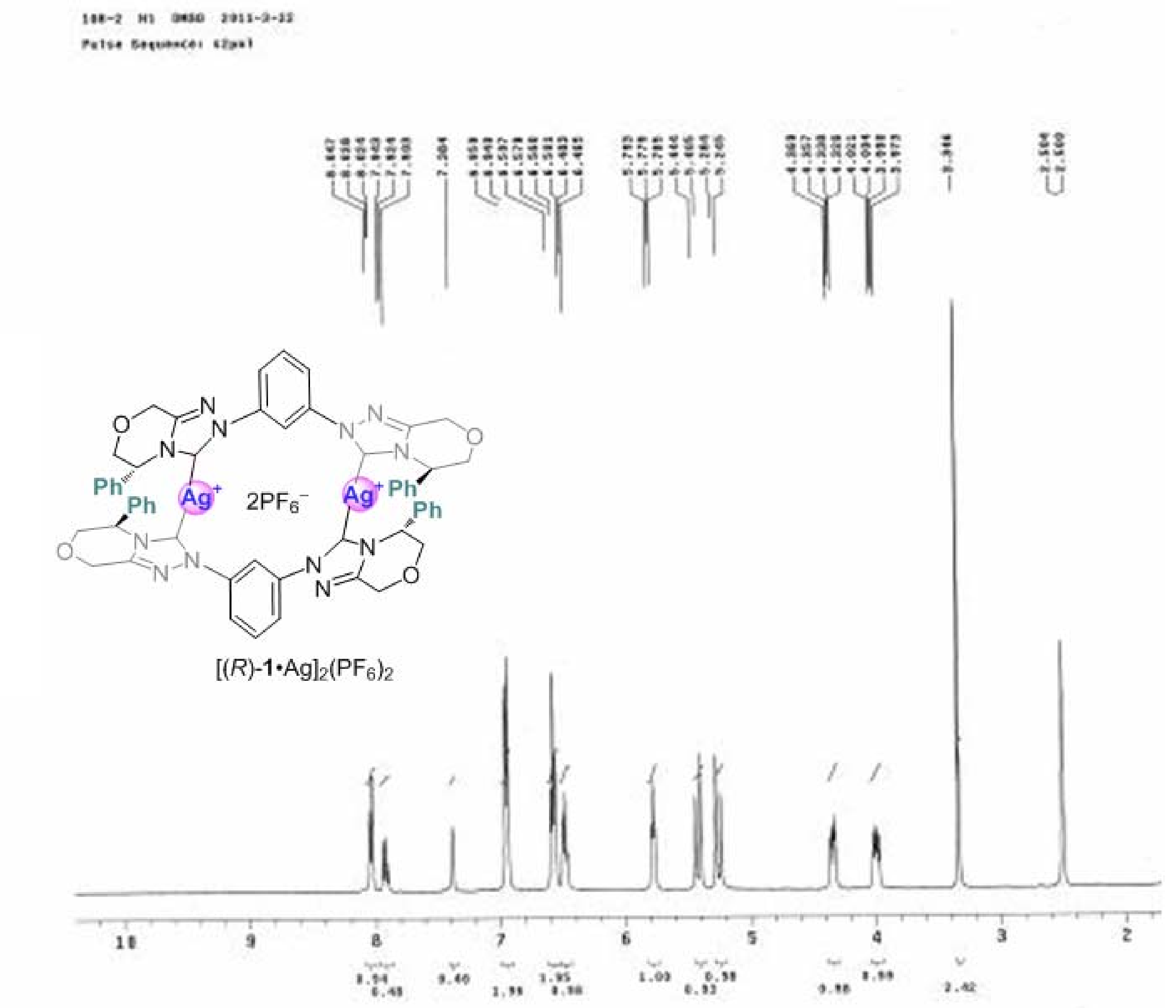


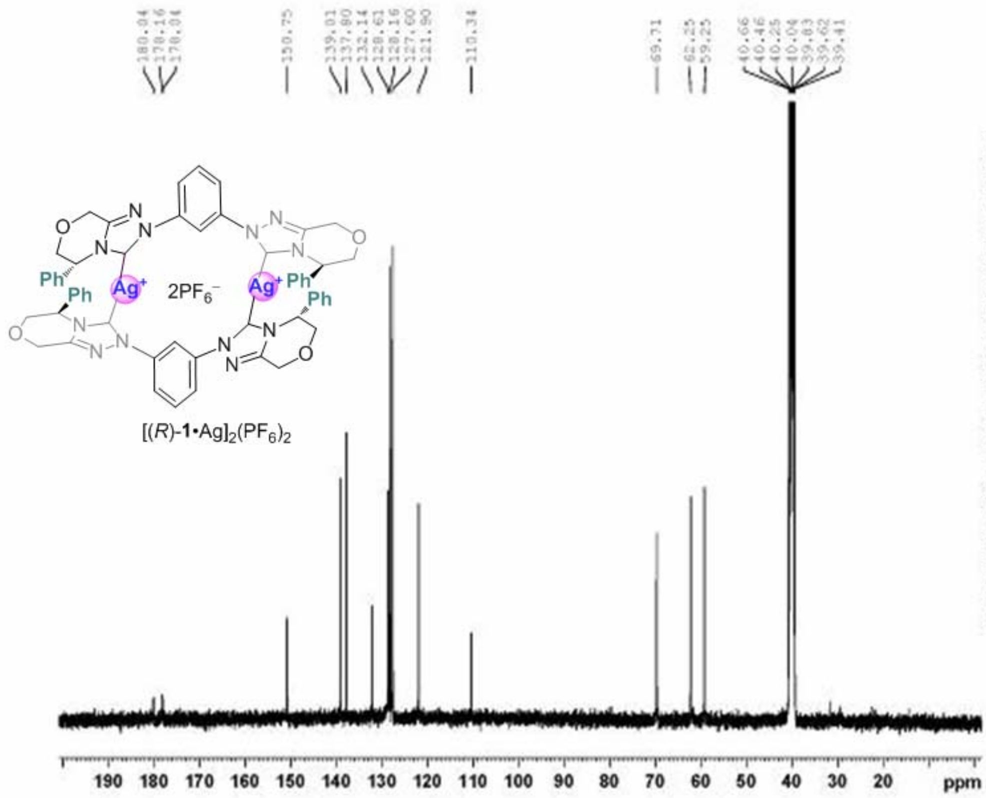
(*R*)-**2**·**2HCl**


I108-1 H1 DMSO 2011-3-8
Pulse Sequence: s2pul
8.026
8.006
7.924
7.904
7.883
7.437
6.974
6.956
6.591
6.574
6.555
6.501
6.484
6.466
5.940
5.435
5.395
5.272
5.233
4.345
4.334
4.315
4.304
4.013
3.997
3.982
3.966
3.390
3.373
3.356
2.542
2.503
Ph
Ph
Ag+
BF4−
Cl−
Ag+
Ph
Ph
O
N
N
N
O
DMSO
10
9
8
7
6
5
4
3
2
0.98
0.50
0.39
1.81
1.93
1.02
1.00
1.01
1.14
1.00
1.00
[(R)-1•Ag]2(BF4)(Cl)


180.83
178.69
150.62
139.15
137.91
131.94
128.55
128.10
127.60
121.83
110.48
69.74
62.25
59.02
40.68
40.47
40.26
40.05
39.84
39.64
39.43
BRUKER
Ph
Ph
Ag+
BF4−
Cl−
Ag+
Ph
Ph
[(R)-1•Ag]2(BF4)(Cl)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

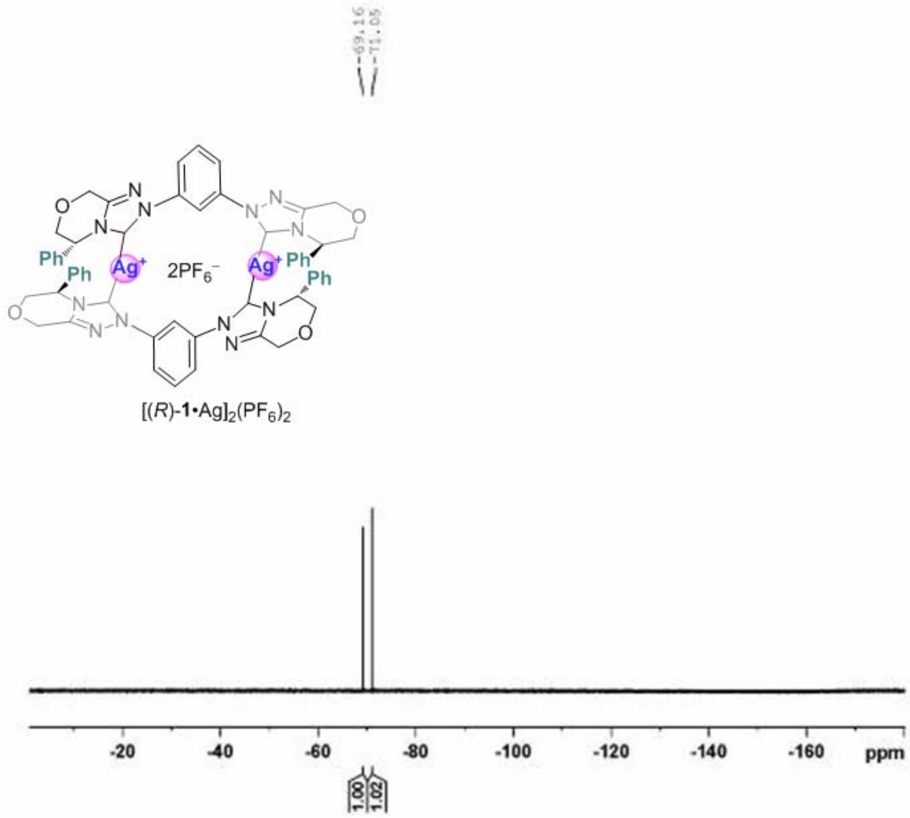

-148.22
Ph
Ph
Ag+
BF4−
Cl−
Ag+
Ph
Ph
[(R)-1•Ag]2(BF4)(Cl)
NAME 2011-03-28 lixiyu-1104-1
EXPNO 2
PROCNO 1
Date_ 20110328
Time 17.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgfhigqn
TD 131072
SOLVENT DMSO
NS 64
DS 0
SWH 89285.711 Hz
FIDRES 0.681196 Hz
AQ 0.7340532 sec
RG 2050
DW 5.600 usec
DE 6.50 usec
TE 294.6 K
D1 1.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 14.10 usec
PL1 -3.50 dB
SFO1 376.4607164 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL12 11.00 dB
PL2 -2.00 dB
SFO2 400.1316005 MHz
SI 65536
SF 376.4983660 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


108-2 H1 DMSO 2011-3-22
Pulse Sequence: s2pul
Ph
Ph
Ag+
2PF6−
Ag+
Ph
Ph
[(R)-1•Ag]2(PF6)2
10
9
8
7
6
5
4
3
2



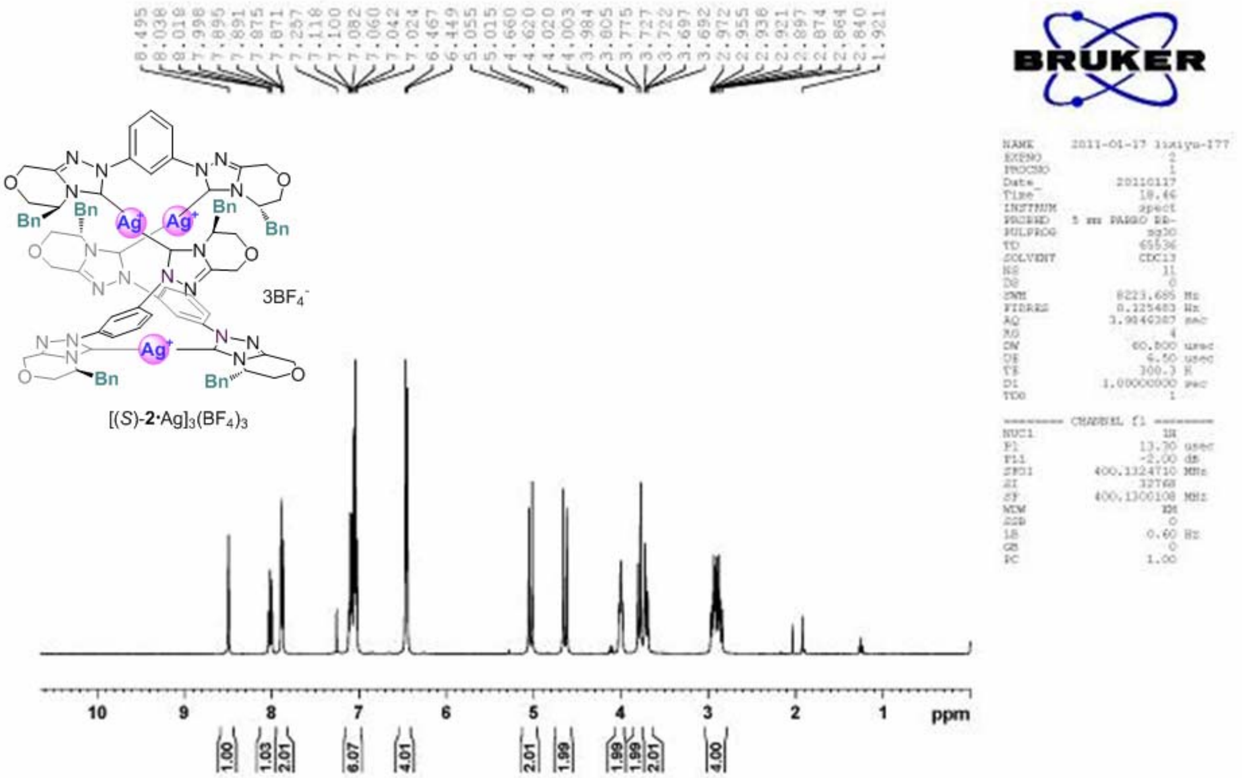
[(R)-**1**•Ag]$_2$(PF$_6$)$_2$

```
NAME       2011-03-28 lixiyu-I108-2
EXPNO                     3
PROCNO                    1
Date_              20110329
Time                  14.41
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                     8000
DS                        0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                     6.50 usec
TE                    298.5 K
D1               5.00000000 sec
d11              0.03000000 sec
DELTA            4.90000010 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    19.50 usec
PL1                   -1.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL12                  11.09 dB
PL13                  13.05 dB
PL2                   -2.00 dB
SFO2            400.1316005 MHz
SI                    32768
SF              100.6127690 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

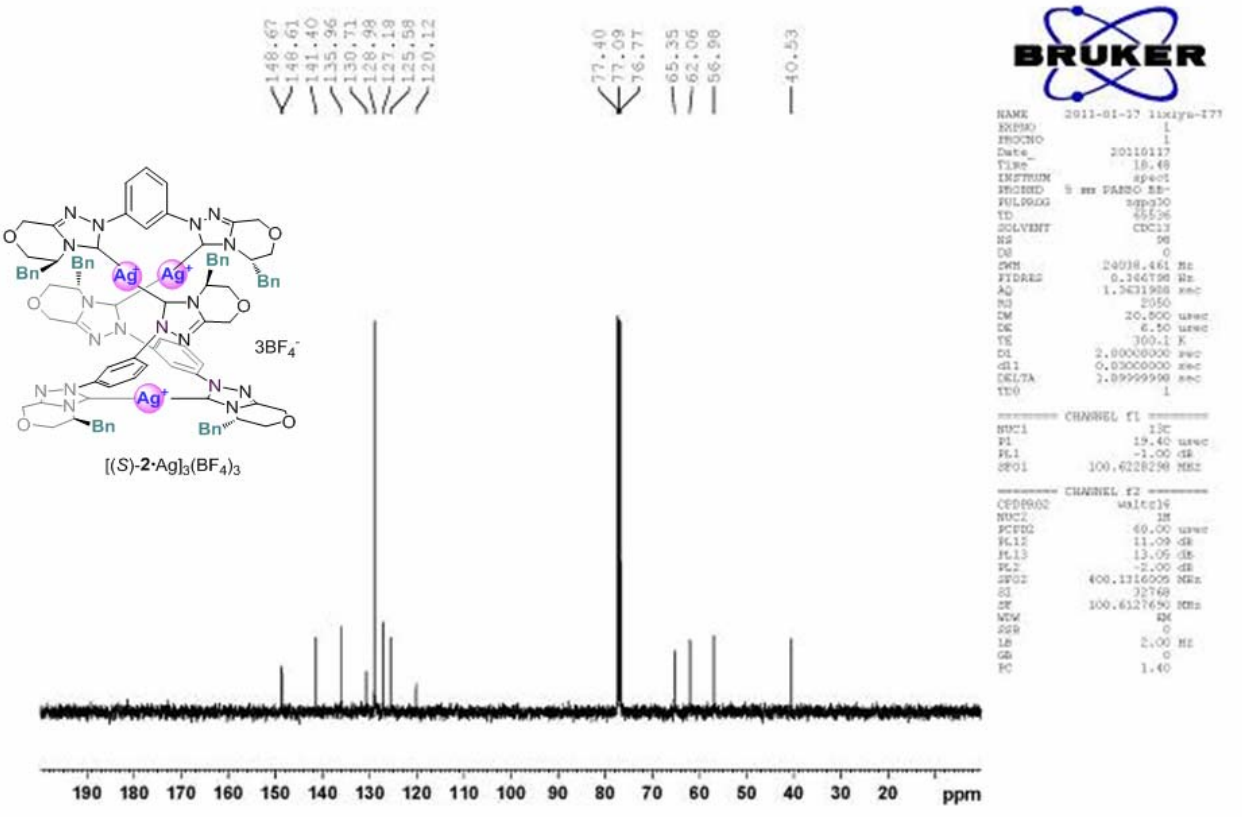


[(R)-**1**•Ag]$_2$(PF$_6$)$_2$

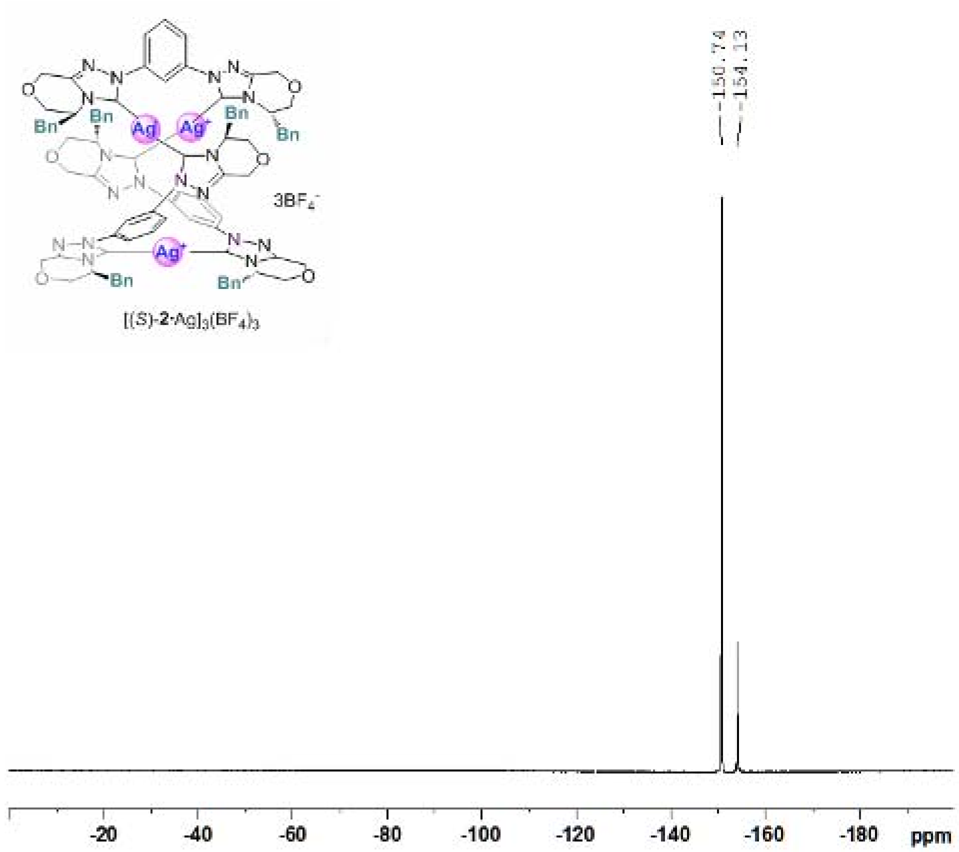
```
NAME       2011-03-28 lixiyu-1108-2
EXPNO                     2
PROCNO                    1
Date_              20110328
Time                  17.11
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG            zgfhigqn
TD                   131072
SOLVENT                DMSO
NS                       64
DS                        0
SWH              89285.711 Hz
FIDRES            0.681196 Hz
AQ               0.7340532 sec
RG                     2050
DW                    5.600 usec
DE                     6.50 usec
TE                    294.6 K
D1               1.00000000 sec
d11              0.03000000 sec
d12              0.00002000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    19F
P1                    14.10 usec
PL1                   -3.50 dB
SFO1            376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL12                  11.09 dB
PL2                   -2.00 dB
SFO2            400.1316005 MHz
SI                    65536
SF              376.4983660 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



[(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$



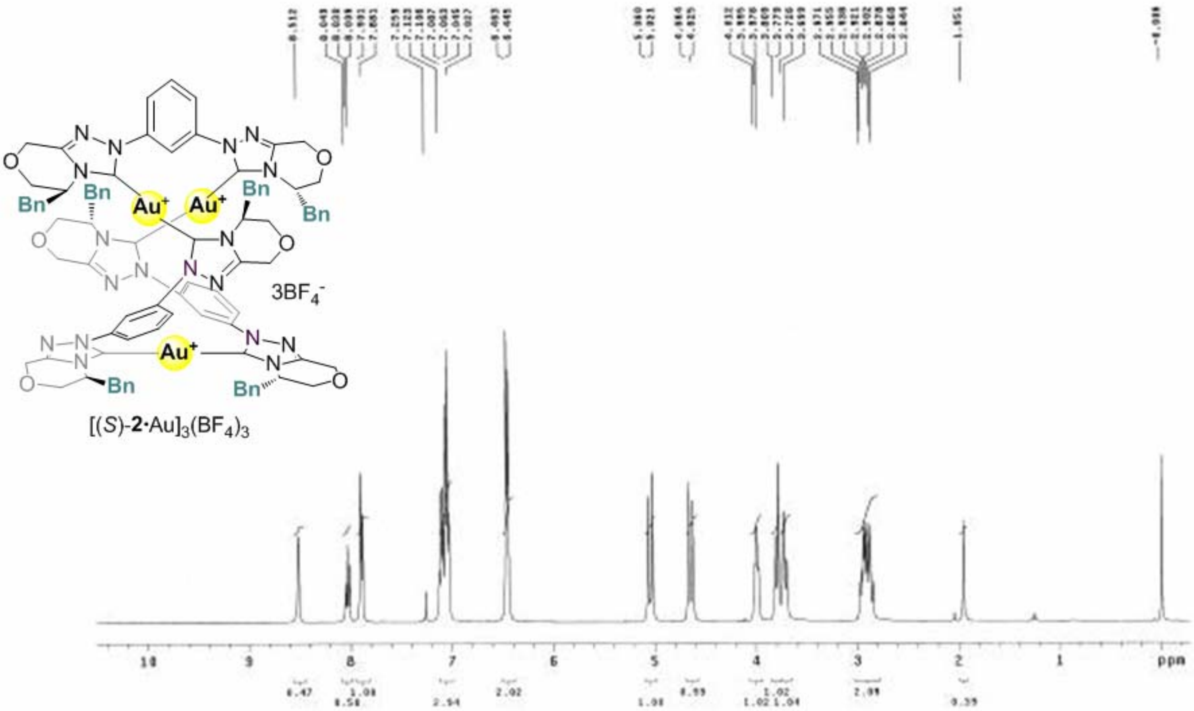
[(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$



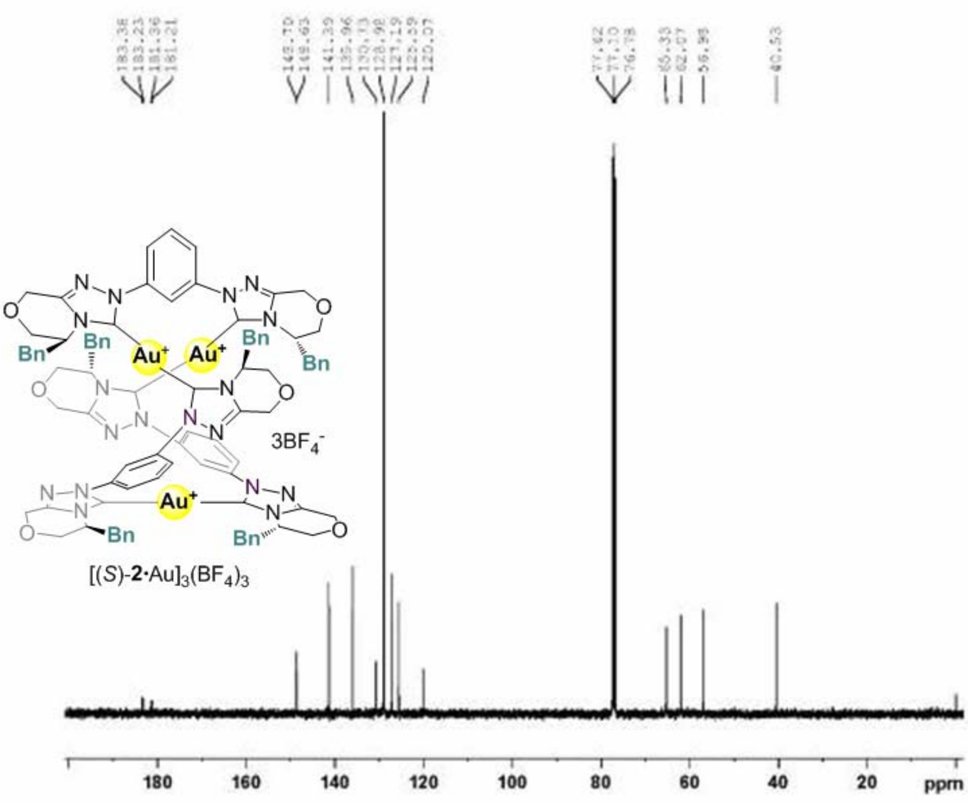
[(*S*)-**2**·Ag]$_3$(BF$_4$)$_3$

```
NAME          2010-12-01 I8-F
EXPNO                       1
PROCNO                      1
Date_                20101201
Time                    18.07
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG              zgfhigqn
TD                     131072
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH             150000.000 Hz
FIDRES            1.144409 Hz
AQ               0.4369567 sec
RG                       90.5
DW                  3.333 usec
DE                   6.50 usec
TE                    300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      19F
P1                  19.50 usec
PL1                  -4.00 dB
SFO1          376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2              100.00 usec
PL12                 18.00 dB
PL2                  -4.00 dB
SFO2          400.1316005 MHz
SI                      65536
SF            376.4983660 MHz
WDW                        EM
SSB                         0
LB                    0.60 Hz
GB                          0
PC                       1.00
```

ISa-CDCL3-H1-2011-3-21
Pulse Sequence: s2pul



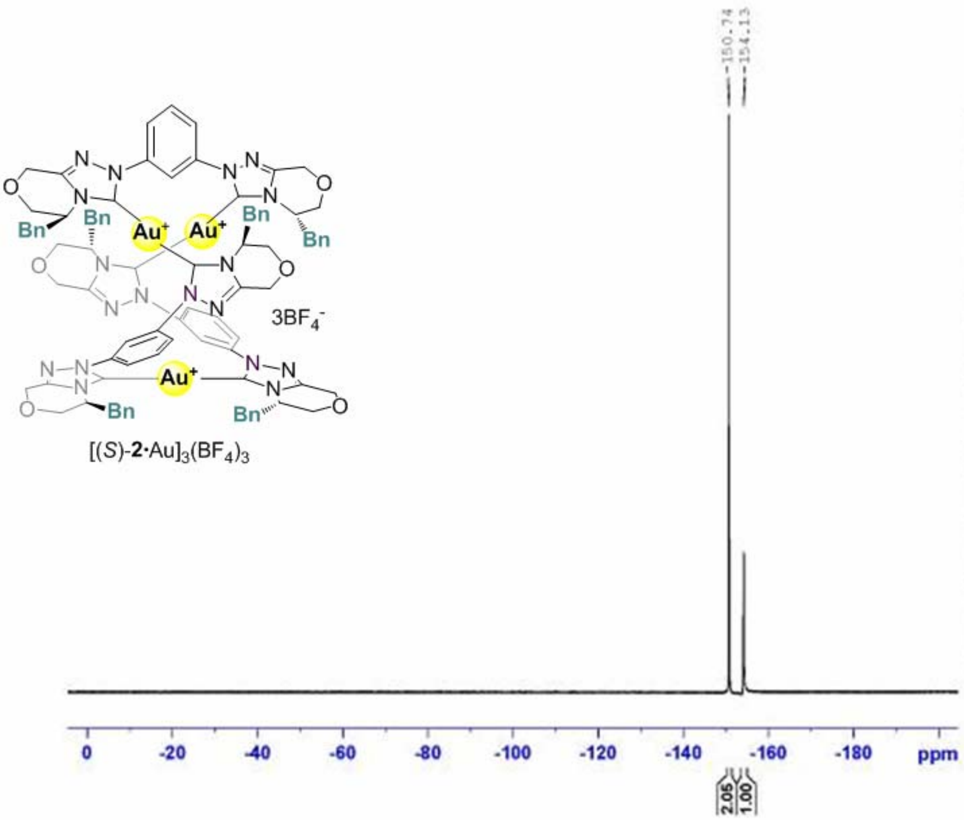
[(*S*)-**2**·Au]$_3$(BF$_4$)$_3$



$[(S)\text{-}\mathbf{2}\cdot\mathrm{Au}]_3(\mathrm{BF_4})_3$

BRUKER

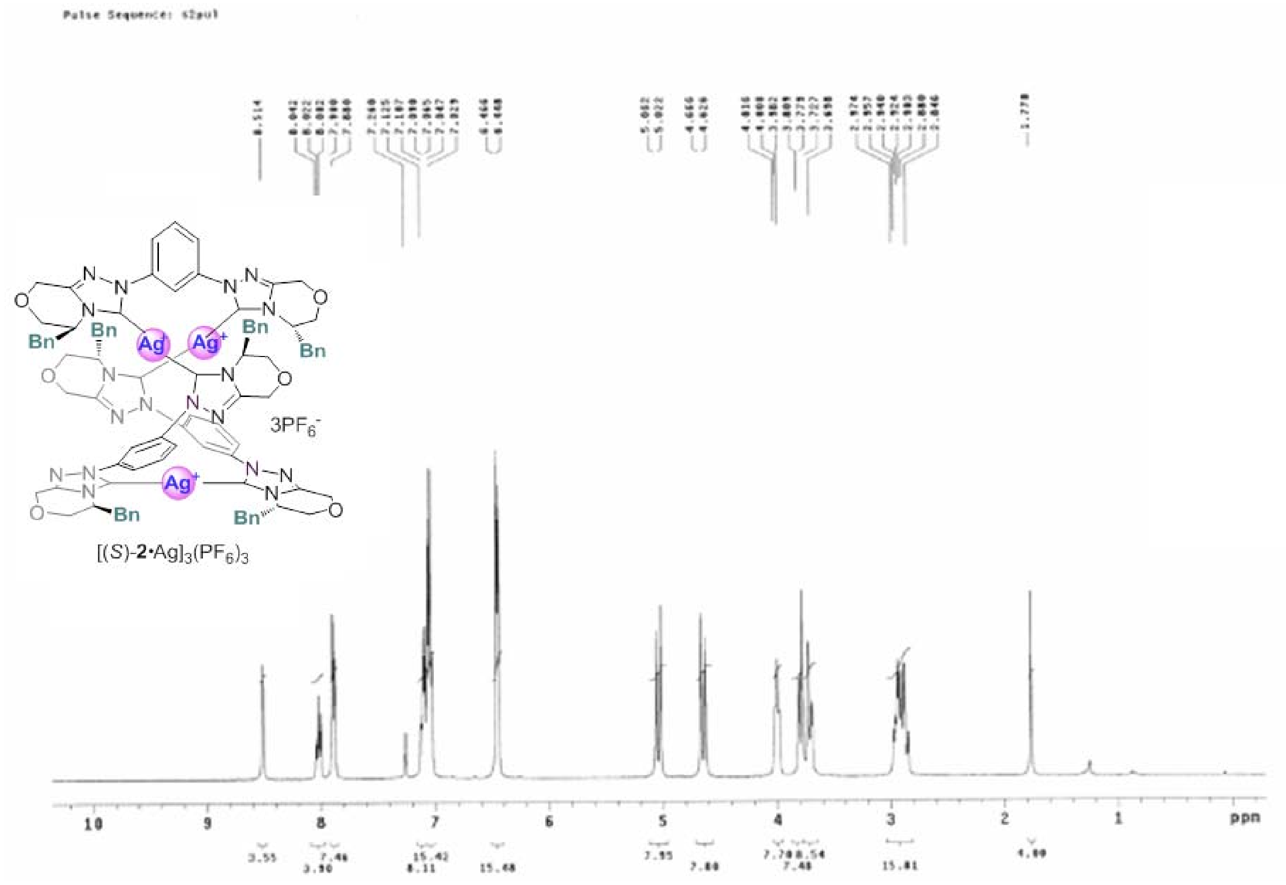
```
NAME      2011-03-28 lixiyu-1sa
EXPNO                     1
PROCNO                    1
Date_              20110328
Time                  16.42
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                    6.50 usec
TE                   295.9 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   19.40 usec
PL1                  -1.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                60.00 usec
PL12                 11.09 dB
PL13                 13.05 dB
PL2                  -2.00 dB
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

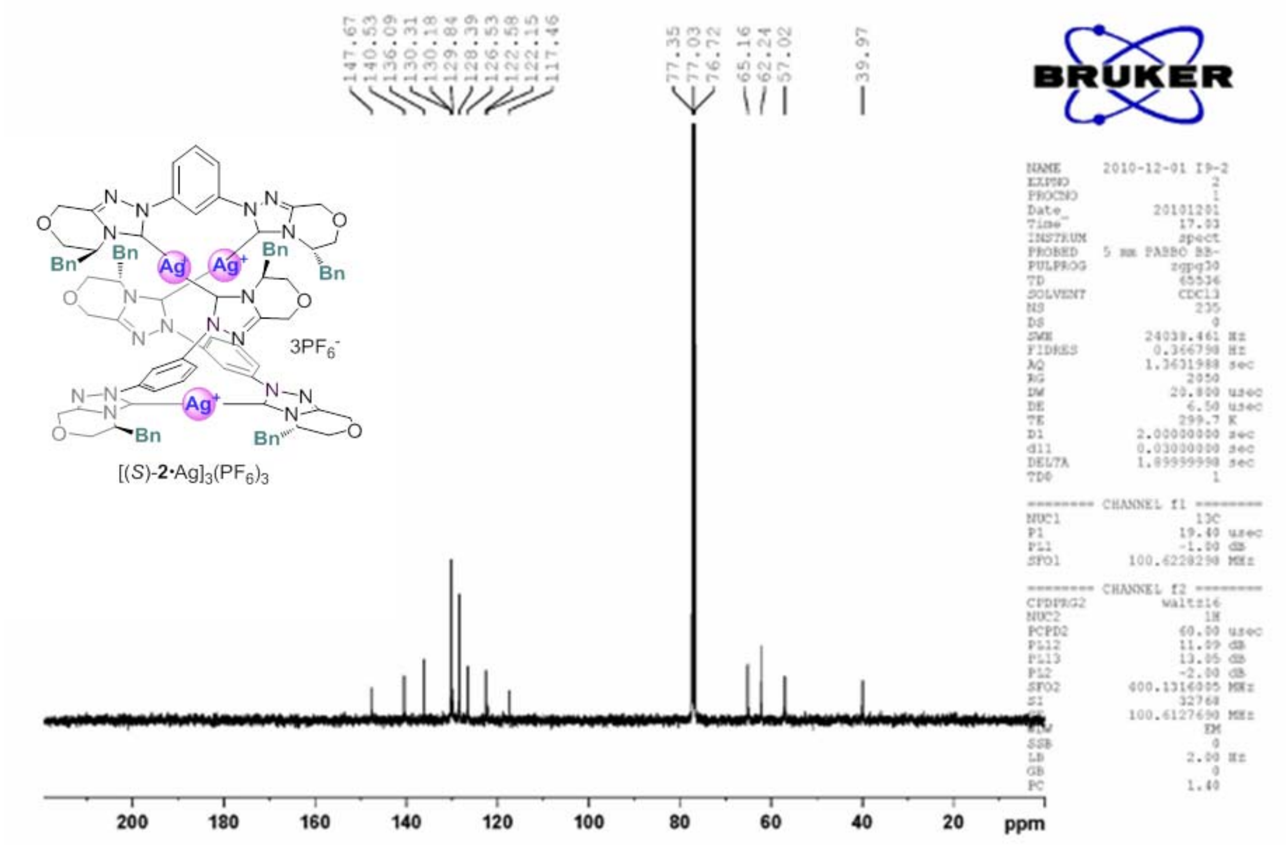


$[(S)\text{-}\mathbf{2}\cdot\mathrm{Au}]_3(\mathrm{BF_4})_3$

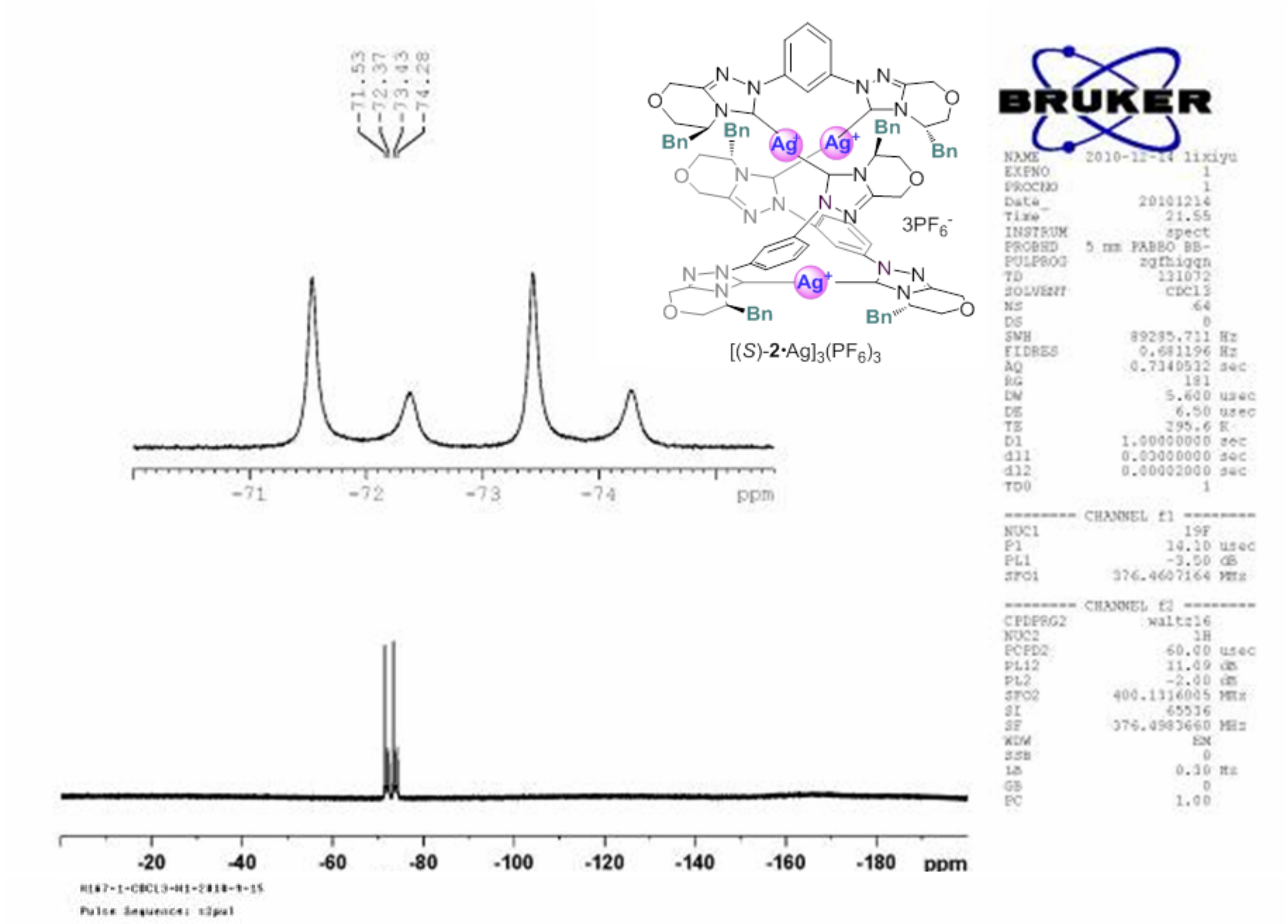
BRUKER

```
NAME      2011-03-28 lixiyu-1sa
EXPNO                     2
PROCNO                    1
Date_              20110328
Time                  16.45
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG            zgfhigqn
TD                  131072
SOLVENT              CDCl3
NS                      64
DS                       0
SWH              89285.711 Hz
FIDRES            0.681196 Hz
AQ               0.7340532 sec
RG                    2050
DW                   5.600 usec
DE                    6.50 usec
TE                   295.4 K
D1              1.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   19F
P1                   14.10 usec
PL1                  -3.50 dB
SFO1           376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                60.00 usec
PL12                 11.09 dB
PL2                  -2.00 dB
SFO2           400.1316005 MHz
SI                   65536
SF             376.4983660 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



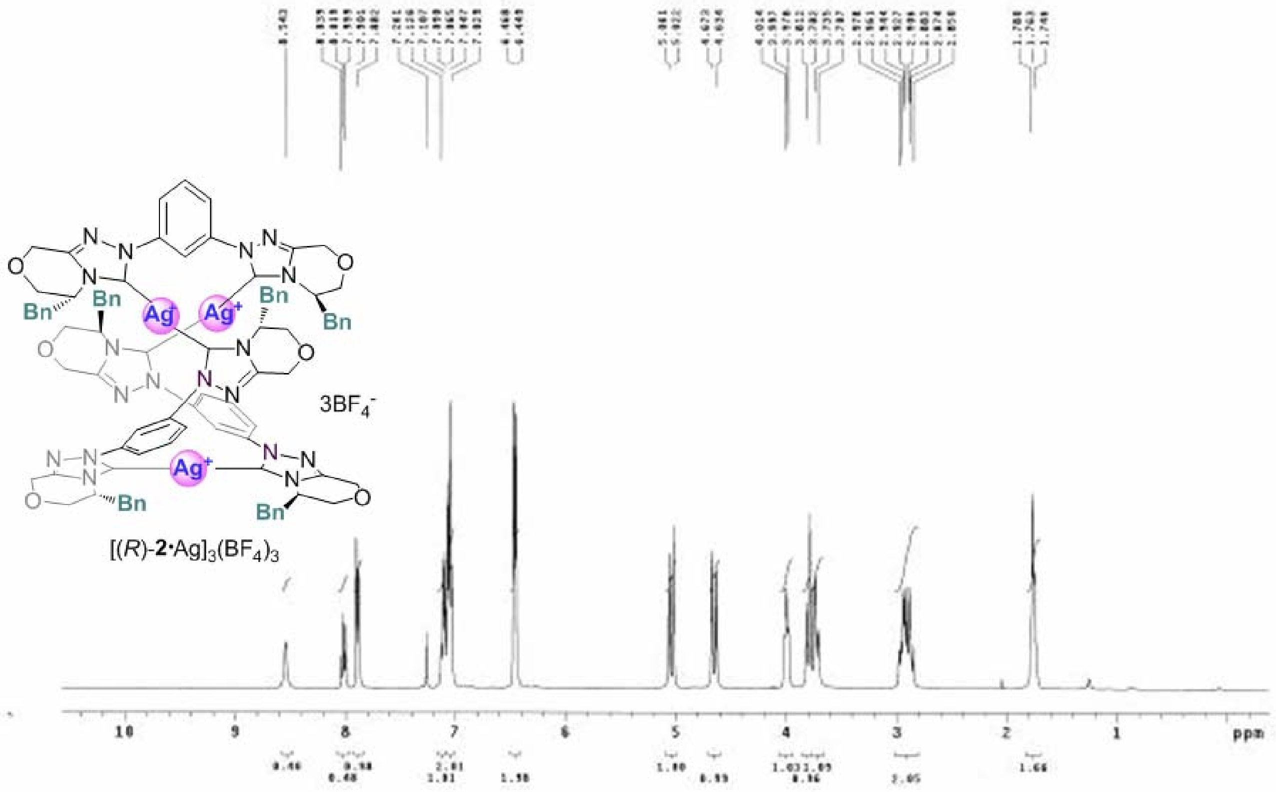


```
NAME       2010-12-01 I9-2
EXPNO                    2
PROCNO                   1
Date_             20101201
Time                 17.03
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     235
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                    6.50 usec
TE                   299.7 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   19.40 usec
PL1                  -1.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                60.00 usec
PL12                 11.09 dB
PL13                 13.05 dB
PL2                  -2.00 dB
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

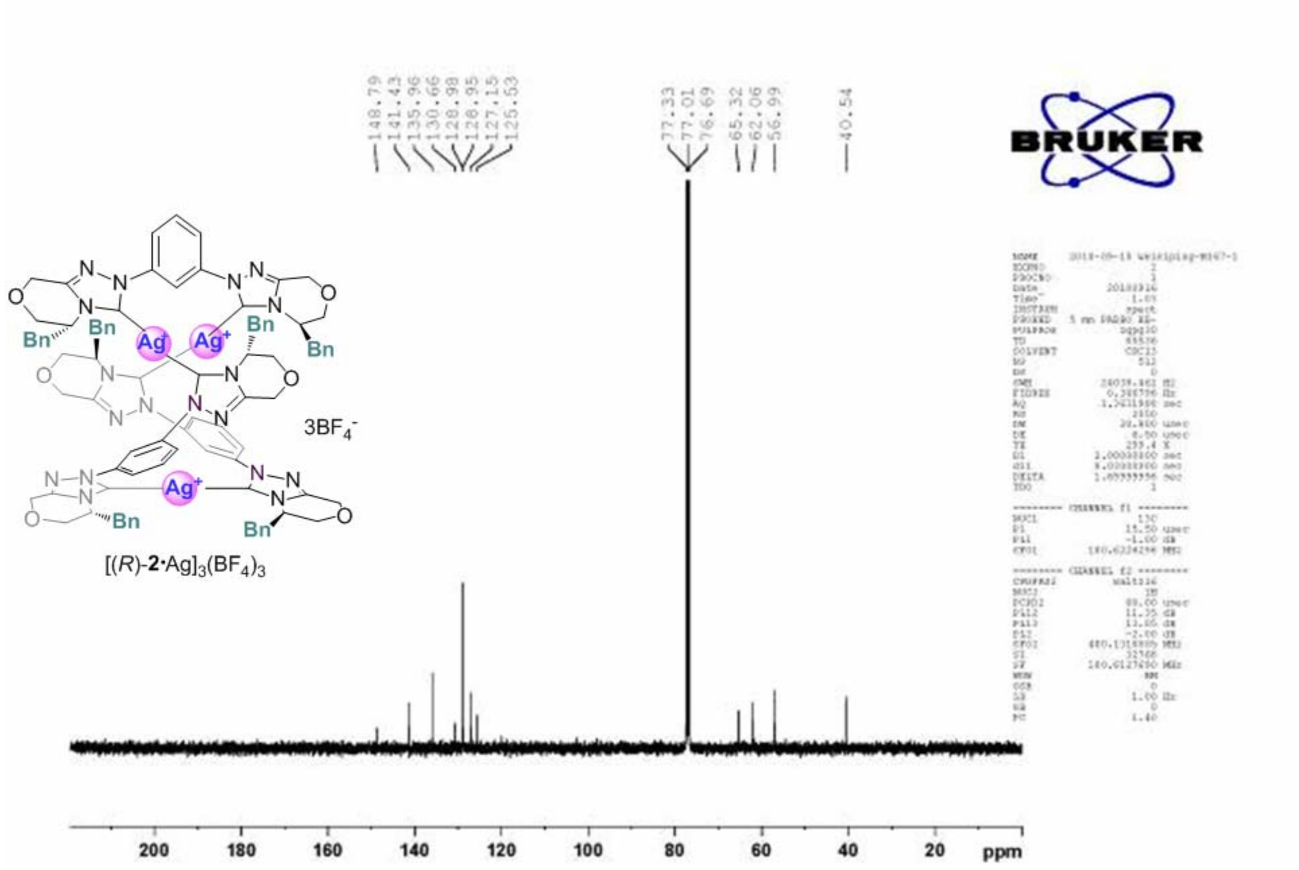


[(*S*)-**2**·Ag]$_3$(PF$_6$)$_3$

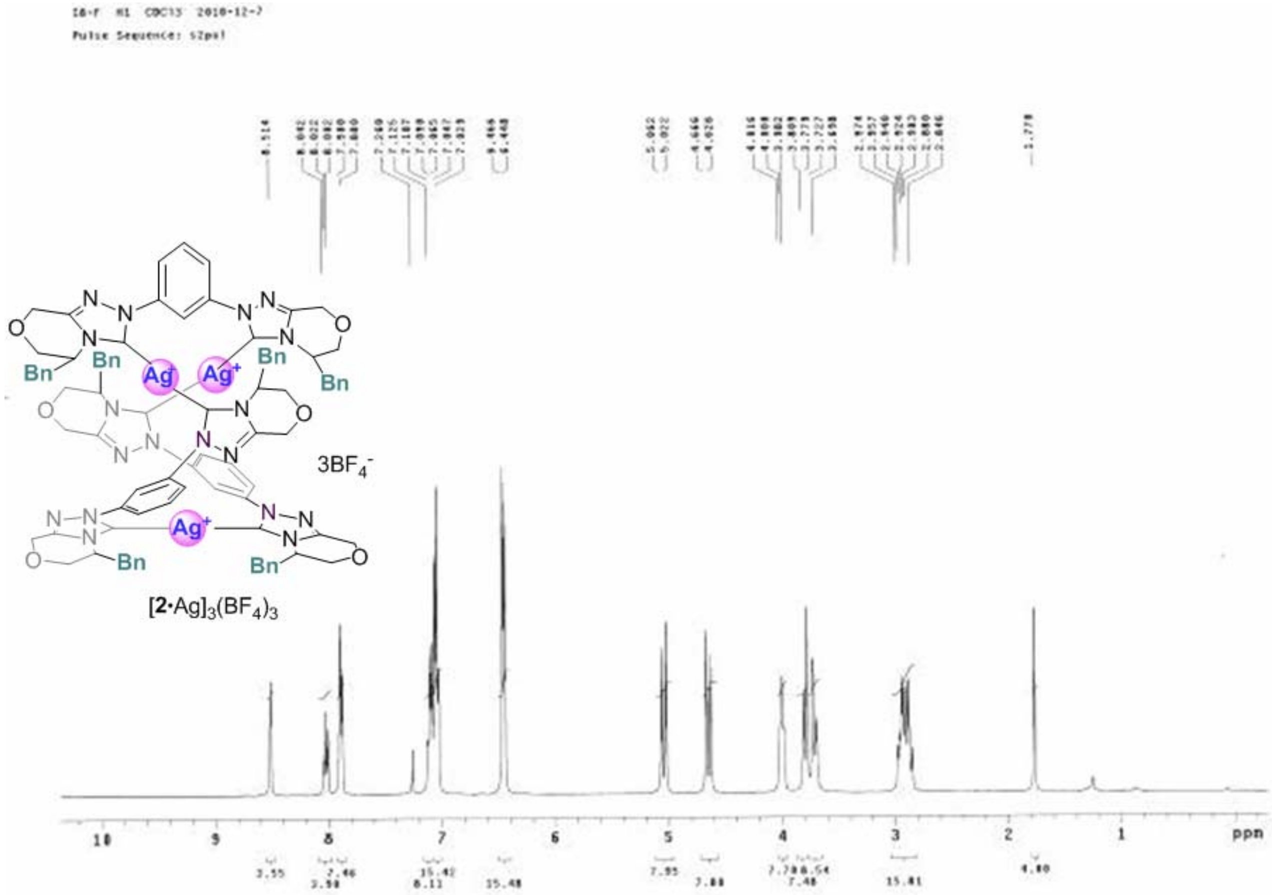
```
NAME        2010-12-14 lixiyu
EXPNO                   1
PROCNO                  1
Date_            20101214
Time                21.55
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgfhigqn
TD                 131072
SOLVENT             CDCl3
NS                     64
DS                      0
SWH            89285.711 Hz
FIDRES          0.681196 Hz
AQ             0.7340532 sec
RG                    181
DW                  5.600 usec
DE                   6.50 usec
TE                  295.6 K
D1             1.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  19F
P1                  14.10 usec
PL1                 -3.50 dB
SFO1          376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               60.00 usec
PL12                11.09 dB
PL2                 -2.00 dB
SFO2          400.1316005 MHz
SI                  65536
SF            376.4983660 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



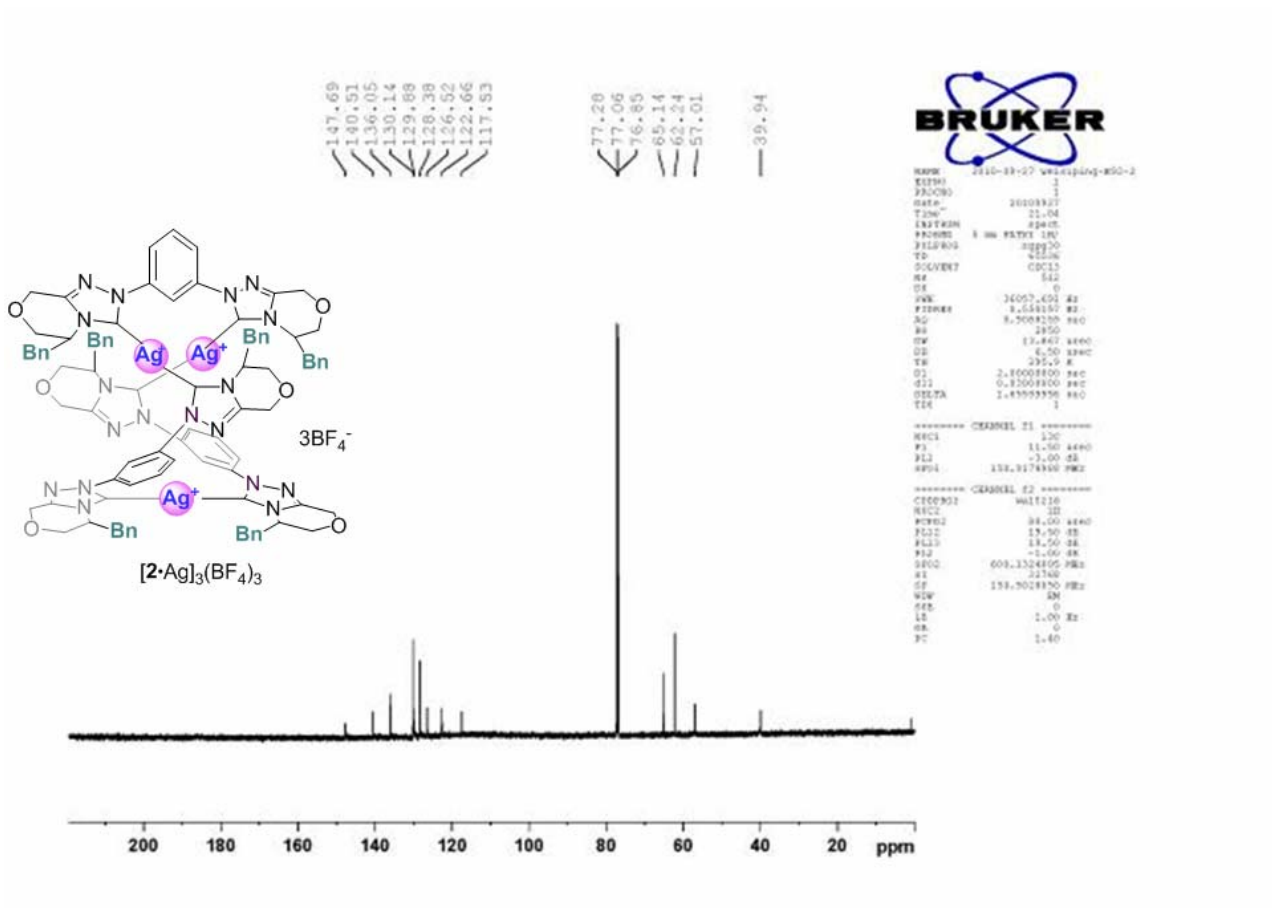
[(*R*)-**2**·Ag]$_3$(BF$_4$)$_3$

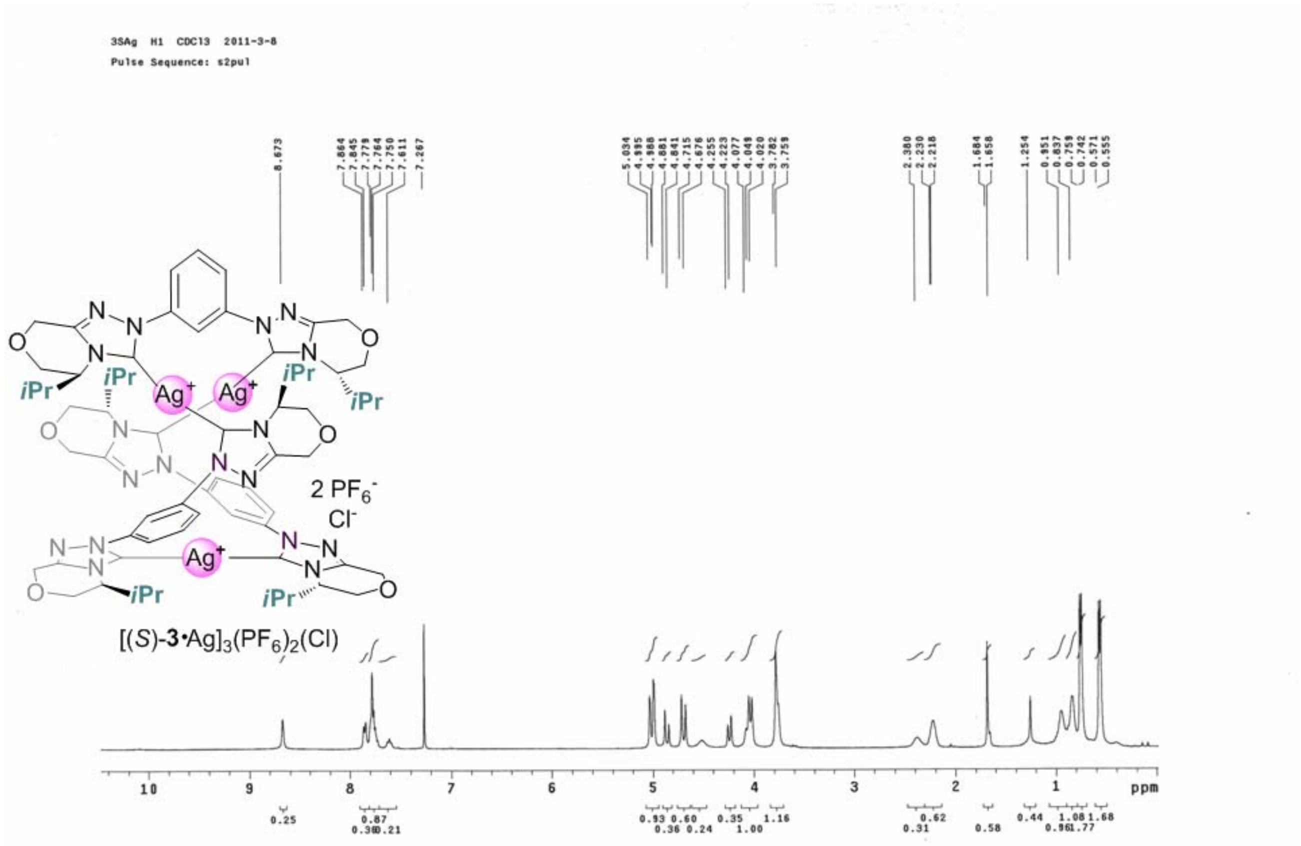


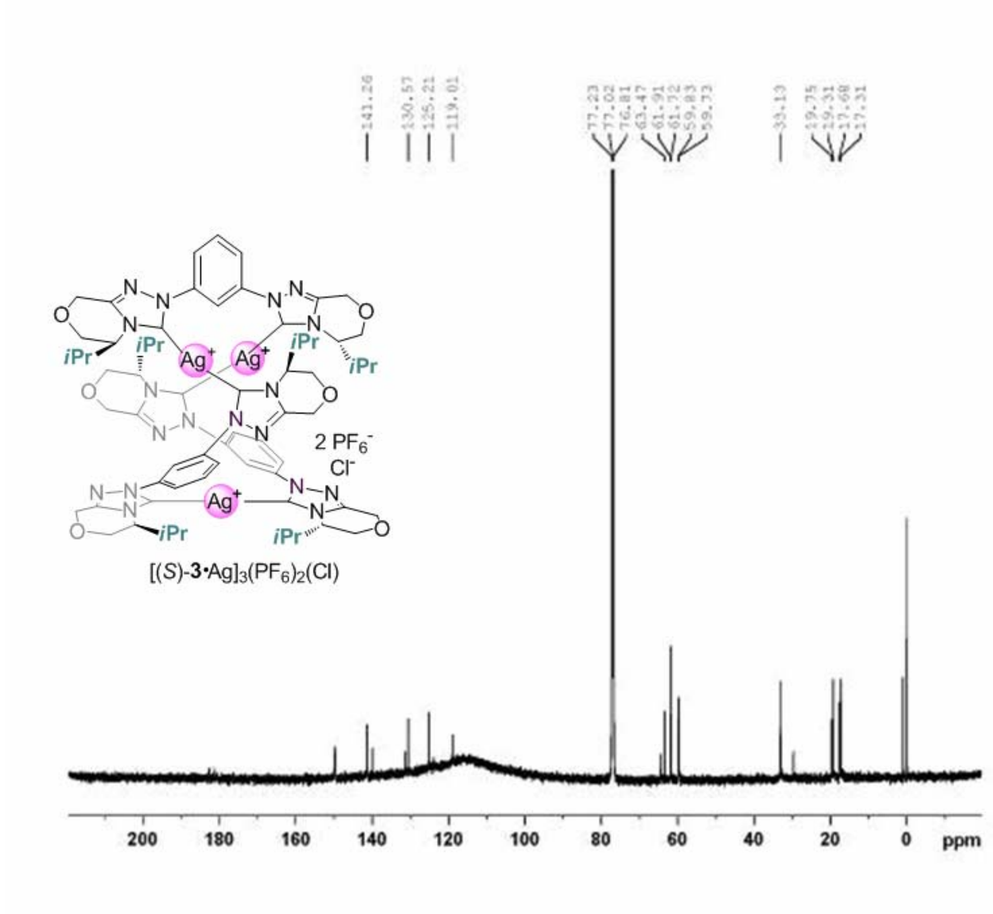
[(*R*)-**2**·Ag]$_3$(BF$_4$)$_3$



[**2**·Ag]$_3$(BF$_4$)$_3$

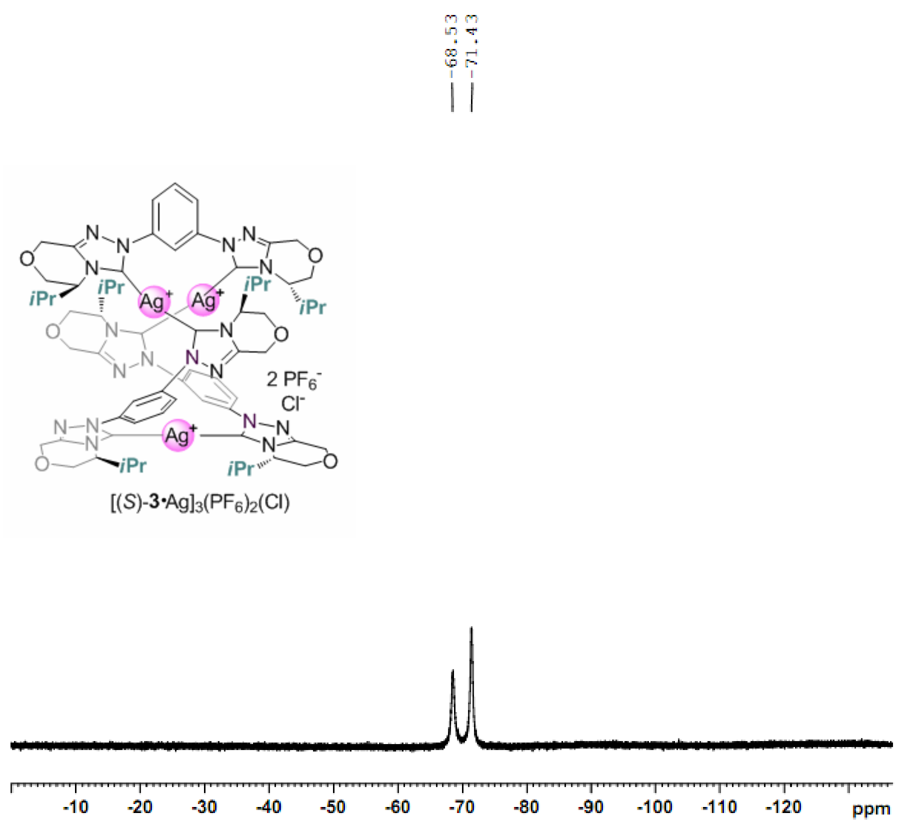

147.69
140.51
136.05
130.14
129.88
128.38
126.52
122.66
117.53
77.28
77.06
76.85
65.14
62.24
57.01
39.94
BRUKER
3BF$_4^-$
Bn
Ag$^+$
[2•Ag]$_3$(BF$_4$)$_3$
200
180
160
140
120
100
80
60
40
20
ppm


3SAg H1 CDCl3 2011-3-8
Pulse Sequence: s2pul
8.673
7.864
7.845
7.779
7.764
7.750
7.611
7.267
5.034
4.995
4.986
4.881
4.861
4.841
4.715
4.676
4.255
4.223
4.077
4.049
4.020
3.782
3.759
2.380
2.230
2.218
1.684
1.658
1.254
0.951
0.837
0.759
0.742
0.571
0.555
iPr
Ag$^+$
2 PF$_6^-$
Cl$^-$
[(S)-3•Ag]$_3$(PF$_6$)$_2$(Cl)
10
9
8
7
6
5
4
3
2
1
ppm
0.25
0.87
0.38
0.21
0.93
0.60
0.36
0.24
0.35
1.00
1.16
0.62
0.31
0.58
0.44
1.08
0.96
1.68
1.77



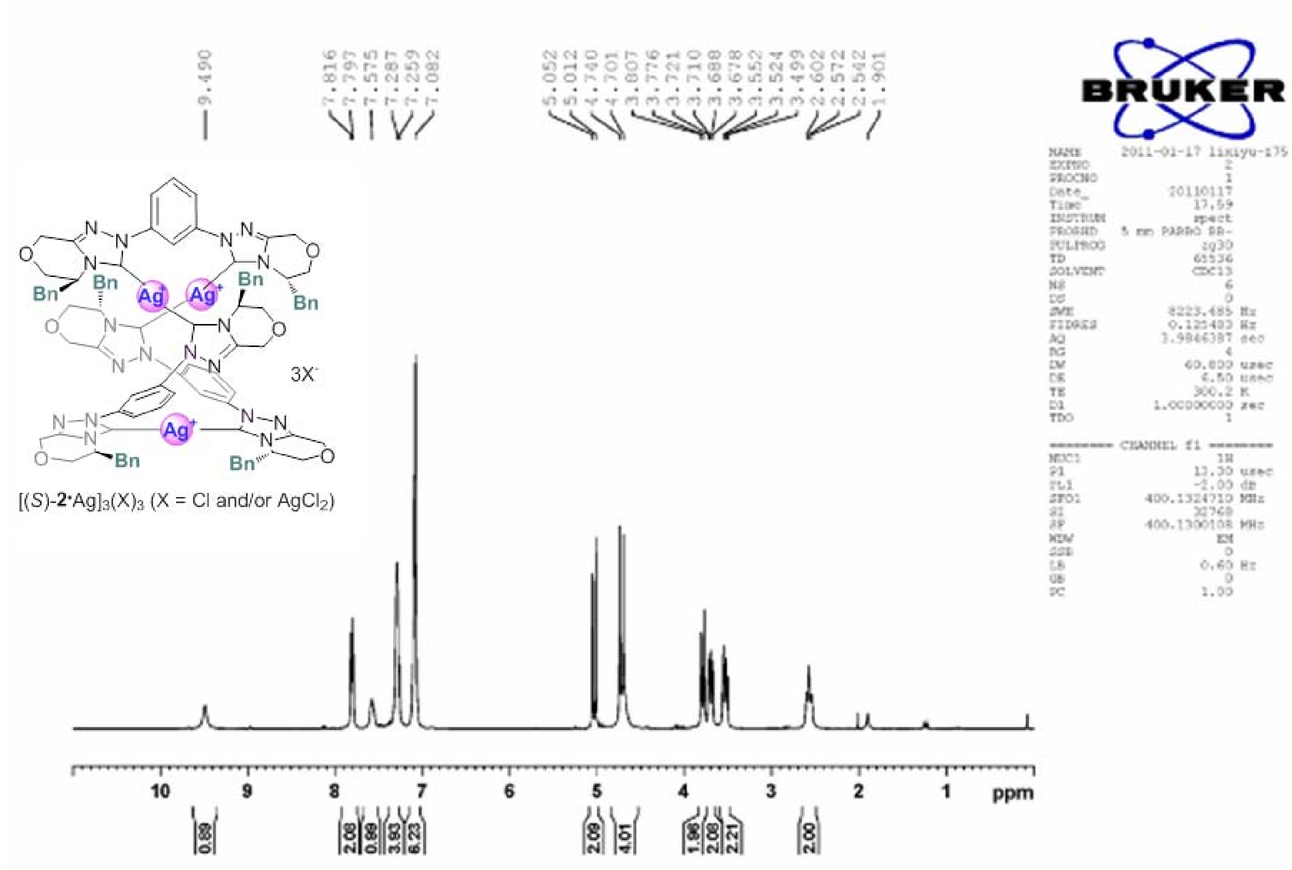
[(S)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl)

```
NAME      2011-03-21 weibiping-3SAg
EXPNO                    2
PROCNO                   1
Date_             20110322
Time                 13.27
INSTRUM              spect
PROBHD    5 mm PATXI 1H/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   4020
DS                      0
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                   2050
DW                 13.867 usec
DE                   6.50 usec
TE                  295.5 K
D1             5.00000000 sec
d11            0.03000000 sec
DELTA          4.90000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.60 usec
PL1                 -3.00 dB
SFO1          100.6176988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL12                19.45 dB
PL13                19.50 dB
PL2                 -3.00 dB
SFO2          400.1324005 MHz
SI                  32768
SF            100.6028068 MHz
WDW                    EM
SSB                     0
LB                   1.70 Hz
GB                      0
PC                   1.40
```



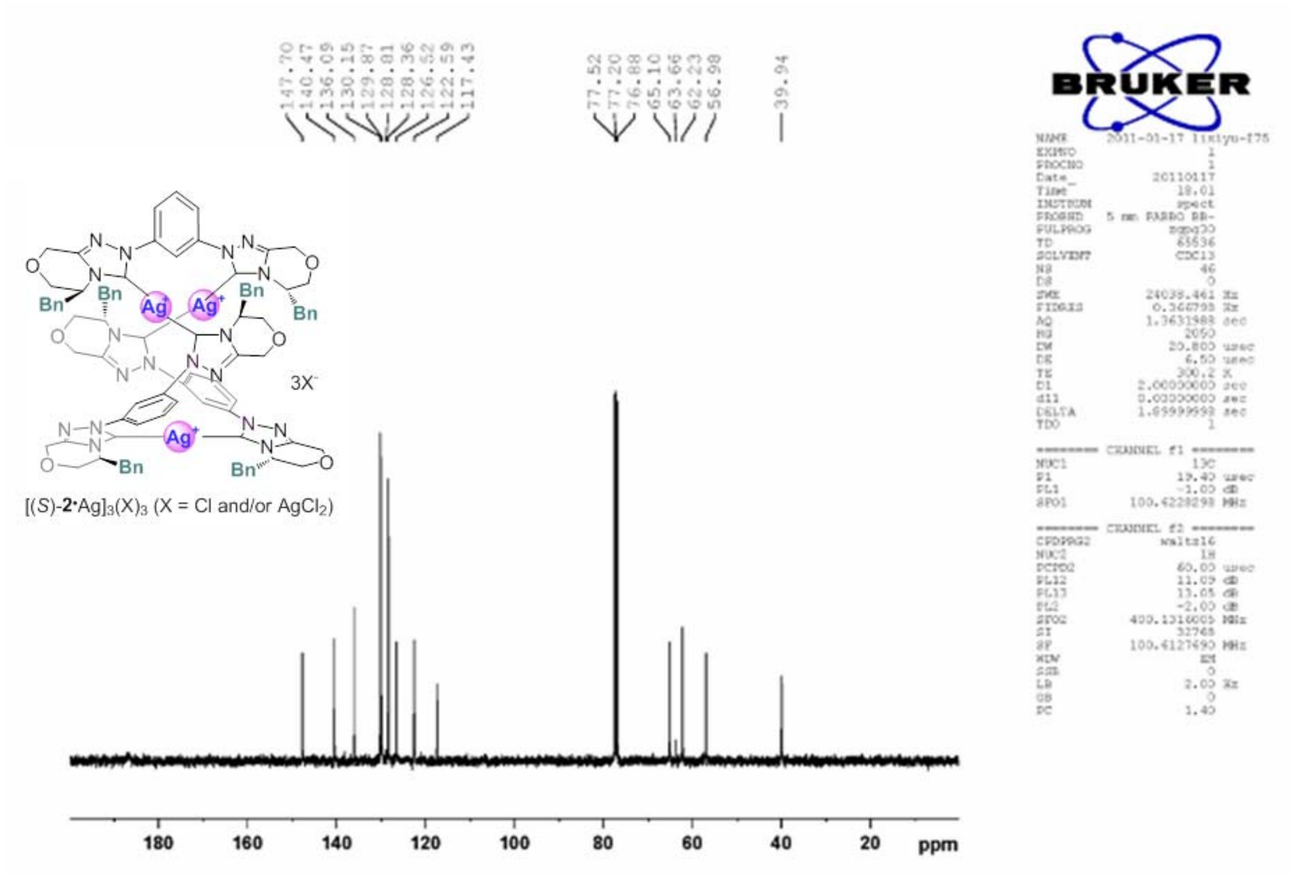
[(S)-**3**·Ag]$_3$(PF$_6$)$_2$(Cl)

```
NAME      2011-03-28 lixiyu-3sAg
EXPNO                    2
PROCNO                   1
Date_             20110328
Time                 16.59
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgfhigqn
TD                 131072
SOLVENT             CDCl3
NS                    128
DS                      0
SWH             89285.711 Hz
FIDRES           0.681196 Hz
AQ              0.7340532 sec
RG                   2050
DW                  5.600 usec
DE                   6.50 usec
TE                  294.8 K
D1             1.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  19F
P1                  14.10 usec
PL1                 -3.50 dB
SFO1          376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               60.00 usec
PL12                11.09 dB
PL2                 -2.00 dB
SFO2          400.1316005 MHz
SI                  65536
SF            376.4675667 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



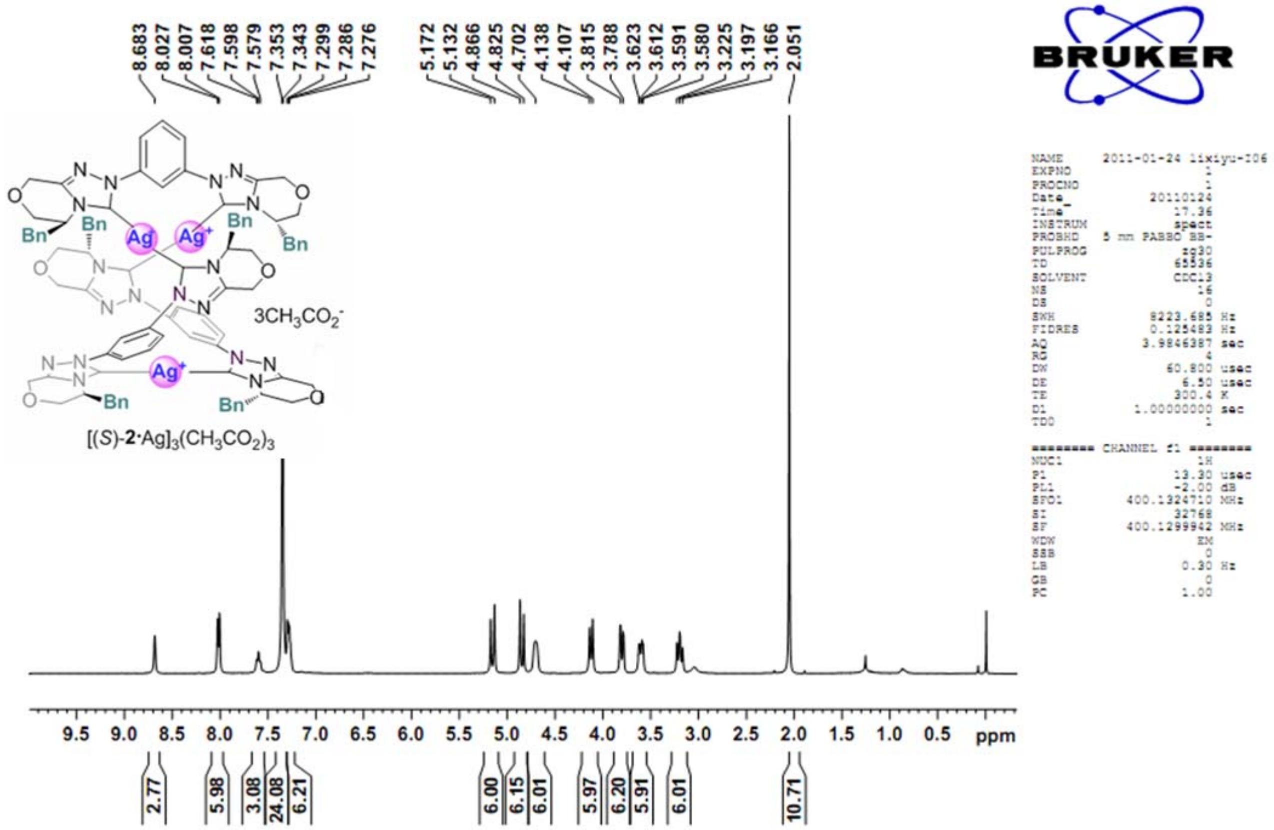
[(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$)

```
NAME     2011-01-17 lixiyu-I75
EXPNO                  2
PROCNO                 1
Date_           20110117
Time               17.59
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     6
DS                     0
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ          3.9846387 sec
RG                     4
DW            60.800 usec
DE              6.50 usec
TE               300.2 K
D1        1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1             13.30 usec
PL1             -2.00 dB
SFO1     400.1324710 MHz
SI                 32768
SF       400.1300108 MHz
WDW                   EM
SSB                    0
LB               0.60 Hz
GB                     0
PC                  1.00
```

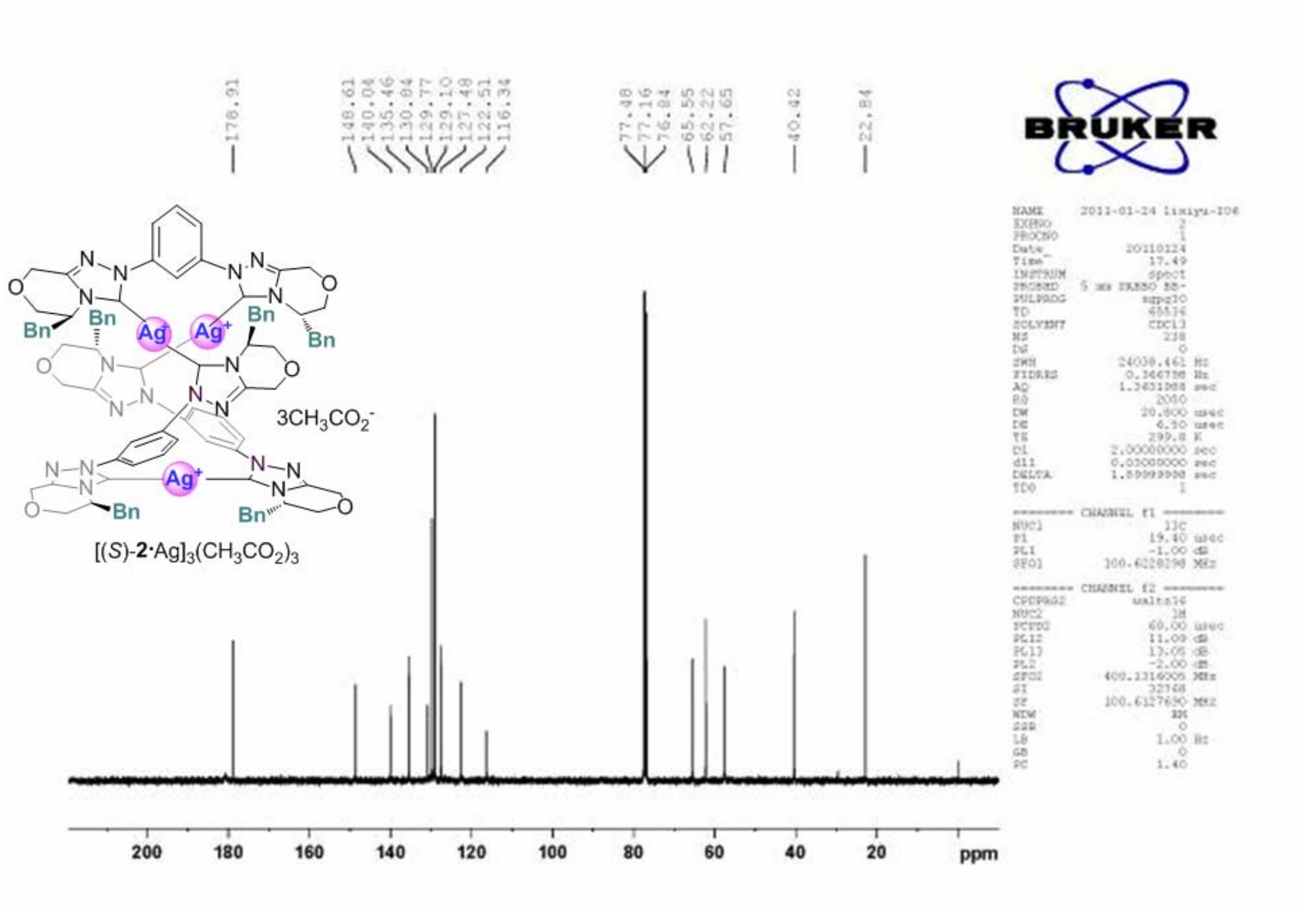


[(*S*)-**2**·Ag]$_3$(X)$_3$ (X = Cl and/or AgCl$_2$)

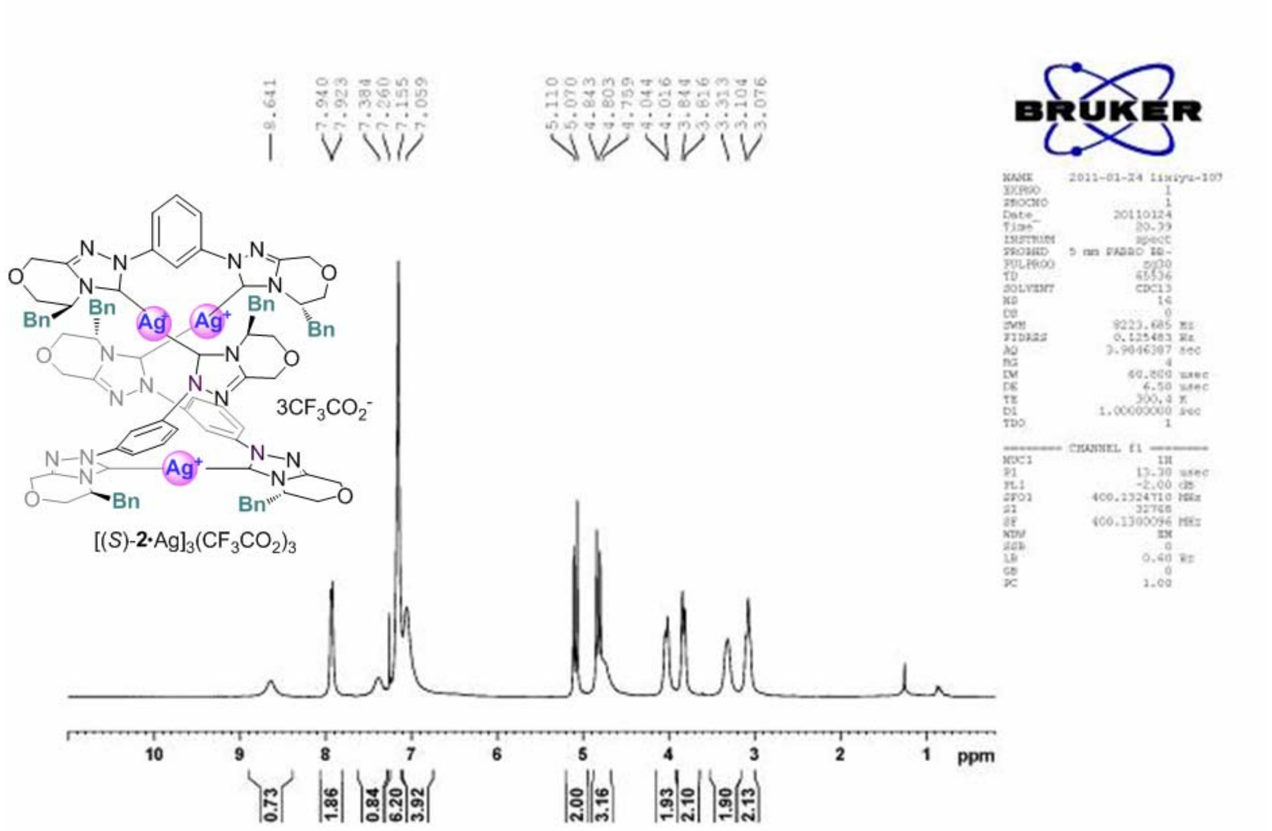
```
NAME     2011-01-17 lixiyu-I75
EXPNO                  1
PROCNO                 1
Date_           20110117
Time               18.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    46
DS                     0
SWH         24038.461 Hz
FIDRES       0.366798 Hz
AQ          1.3631988 sec
RG                  2050
DW            20.800 usec
DE              6.50 usec
TE               300.2 K
D1        2.00000000 sec
d11       0.03000000 sec
DELTA     1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1             19.40 usec
PL1             -1.00 dB
SFO1     100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2          60.00 usec
PL12             11.09 dB
PL13             13.05 dB
PL2             -2.00 dB
SFO2     400.1316005 MHz
SI                 32768
SF       100.6127690 MHz
WDW                   EM
SSB                    0
LB               2.00 Hz
GB                     0
PC                  1.40
```



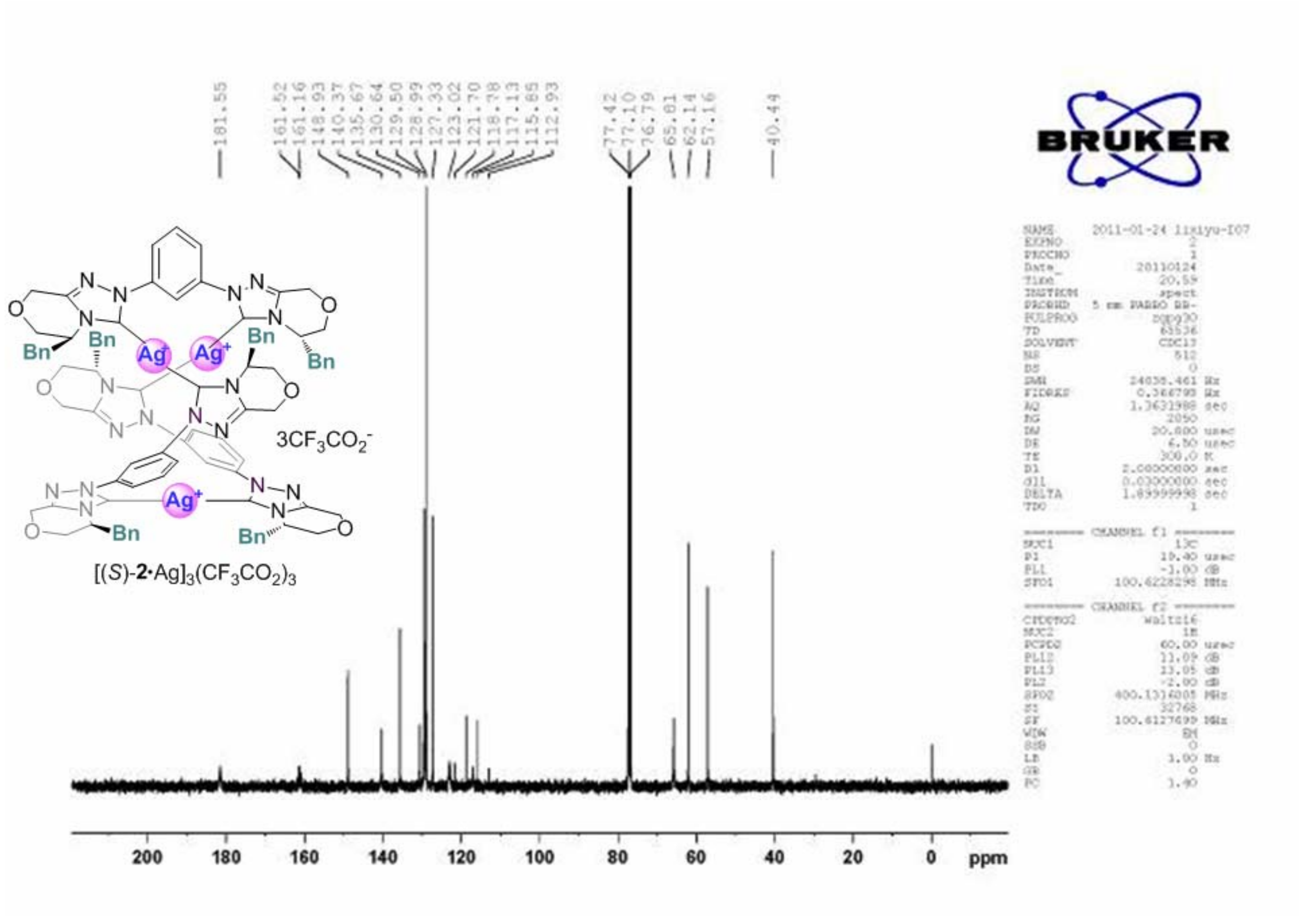
```
NAME     2011-01-24 lixiyu-I06
EXPNO                    1
PROCNO                   1
Date_             20110124
Time                 17.36
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9846387 sec
RG                       4
DW                  60.800 usec
DE                    6.50 usec
TE                   300.4 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.30 usec
PL1                  -2.00 dB
SFO1           400.1324710 MHz
SI                   32768
SF             400.1299942 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



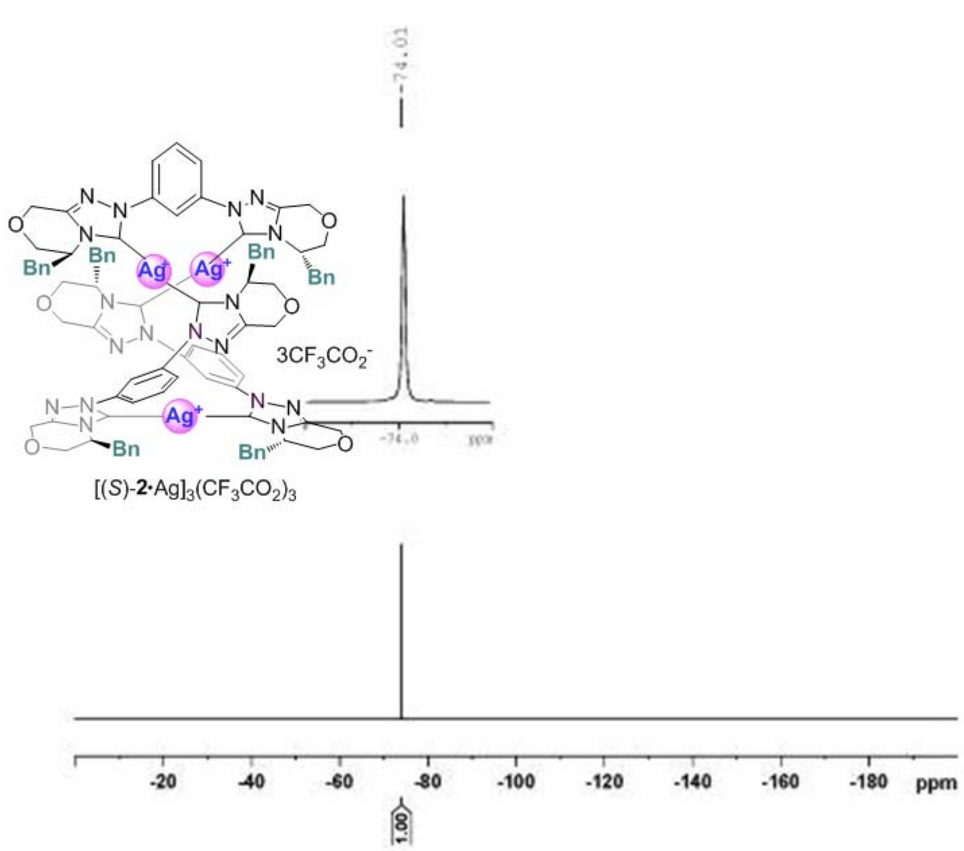
```
NAME     2011-01-24 lixiyu-I06
EXPNO                    2
PROCNO                   1
Date_             20110124
Time                 17.49
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     238
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                    6.50 usec
TE                   299.8 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   19.40 usec
PL1                  -1.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                60.00 usec
PL12                 11.00 dB
PL13                 13.06 dB
PL2                  -2.00 dB
SFO2           400.1316005 MHz
SI                   32768
SF             100.6127690 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



```
NAME       2011-01-24 lixiyu-I07
EXPNO                   1
PROCNO                  1
Date_            20110124
Time                20.39
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      0
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9846387 sec
RG                      4
DW                 60.800 usec
DE                   6.50 usec
TE                  300.4 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.30 usec
PL1                 -2.00 dB
SFO1          400.1324710 MHz
SI                  32768
SF            400.1300096 MHz
WDW                    EM
SSB                     0
LB                   0.40 Hz
GB                      0
PC                   1.00
```



```
NAME       2011-01-24 lixiyu-I07
EXPNO                   2
PROCNO                  1
Date_            20110124
Time                20.59
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      0
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                   2050
DW                 20.800 usec
DE                   6.50 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.40 usec
PL1                 -1.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               60.00 usec
PL12                11.09 dB
PL13                13.05 dB
PL2                 -2.00 dB
SFO2          400.1316005 MHz
SI                  32768
SF            100.6127699 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



[(*S*)-**2**·Ag]$_3$(CF$_3$CO$_2$)$_3$

```
NAME       2011-01-24 lixiyu-107
EXPNO                      6
PROCNO                     1
Date_               20110124
Time                   23.15
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgfhigqn
TD                    131072
SOLVENT                CDCl3
NS                       128
DS                         0
SWH              89285.711 Hz
FIDRES            0.681196 Hz
AQ               0.7340532 sec
RG                      2050
DW                     5.600 usec
DE                      6.50 usec
TE                     299.8 K
D1                1.00000000 sec
d11               0.03000000 sec
d12               0.00002000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     19F
P1                     14.10 usec
PL1                    -3.50 dB
SFO1             376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL12                   11.09 dB
PL2                    -2.00 dB
SFO2             400.1316005 MHz
SI                     65536
SF               376.4983660 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```