

Supplementary Information

Phenylsilver

An unexpected one-dimensional coordination polymer of silver(I) tetrads

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General Procedures

Reactions of air-sensitive compounds were performed in an inert atmosphere (argon) utilising Schlenk techniques. THF was dried over sodium/benzophenone and benzene over lithium aluminium hydride. All solvents were freshly distilled before use. Deuterated THF was dried over molecular sieves (3/4 Å). All laboratory glassware was dried at 120 °C and cooled under vacuum before use. All commercially available chemical reagents were used without further purification. NMR experiments were recorded on Bruker Avance (III) 400, Avance Neo 400 or Avance Neo 500 spectrometers at 300 K. ¹H and ¹³C NMR shifts were given in ppm relative to solvent residual signal of the deuterated solvents. ¹¹B NMR shifts were given in ppm relative to a solution of BF₃·OEt₂ (15%) in CDCl₃. The following abbreviations were used for the multiplicities: s (singlet), d (doublet), m (multiplet), t (triplet), bs (broad singlet). Mass spectra were recorded on an Impact II mass spectrometer (Bruker) with electrospray ionisation. X-ray single crystal measurements were performed on a D8 Venture + APEX II Quazar diffractometer (Bruker). NMR data were analysed with the Software MestReNova 14.2.0 and the single crystal X-ray data with the Software APEX 3/4.

Syntheses

Synthesis of boronate **1**

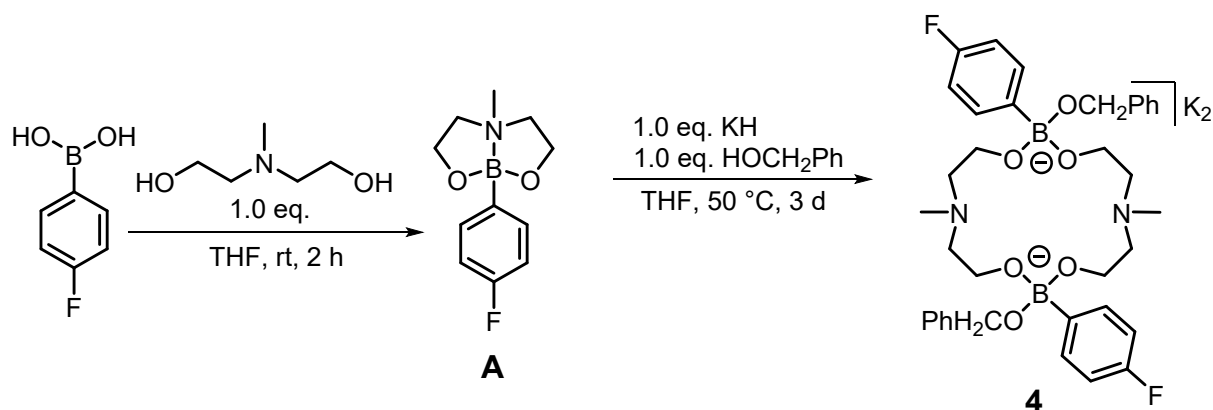
Boronate **1** was synthesised according to the literature.¹

Co-crystallisation of phenylsilver with THF (**2**)

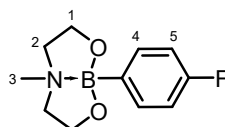
Boronate **1** (300 mg, 0.43 mmol, 0.5 eq.) and silver benzoate (195 mg, 0.85 mmol, 1.0 eq.) were suspended in THF (7 mL) under light exclusion and stirred for 10 min. After filtration, the yellow-coloured solution was concentrated to half the volume under reduced pressure. Phenylsilver (**2**) was obtained as colourless single crystals suitable for X-ray diffraction from a solution in THF at -26 °C.

Crystallisation of neat phenylsilver (**3**)

Boronate **1** (94 mg, 0.12 mmol, 0.5 eq.) and silver benzoate (62 mg, 0.27 mmol, 1.0 eq.) were suspended in MTBE (5 mL) under light exclusion and stirred for 10 min. After filtration, the yellow-coloured solution was concentrated to half the volume under reduced pressure. Phenylsilver (**3**) was obtained as colourless single crystals suitable for X-ray diffraction from a solution in MTBE at 4 °C.



Synthesis of Dioxazaborocane A



N-Methyldiethanolamine (1.23 mL, 10.7 mmol) was added to a solution of 4-fluorophenylboronic acid (1.50 g, 10.7 mmol) in THF (25 mL) at room temperature. After stirring the reaction mixture at room temperature for two hours, the solvent was removed under reduced pressure. After crystallisation, the white solid was dried *in vacuo*. Dioxazaborocane **A** was obtained as a white solid (2.09 g, 9.36 mmol, 87%). Single crystals suitable for X-ray diffraction crystallised from a solution of Dioxazaborocane **A** in MTBE at room temperature.

$^1\text{H NMR}$ (400 MHz, CD_2Cl_2 , 300 K) δ (ppm) = 7.58 – 7.52 (m, H-4, 2H), 7.00 – 6.94 (m, H-5, 2H), 4.15 – 4.07 (m, H-1, 2H), 4.07 – 4.00 (m, H-1, 2H), 3.20 – 3.12 (m, H-2, 2H), 2.99 – 2.91 (m, H-2, 2H) 2.25 (s, H-3, 3H).

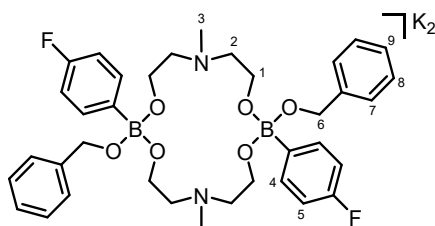
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CD_2Cl_2 , 300 K) δ (ppm) = 12.2 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2 , 300 K) δ (ppm) = 163.4 (d, $^1J_{\text{C-F}} = 243.3$ Hz, Cq^F), 138.9 (bs, Cq), 135.3 (d, $^3J_{\text{C-F}} = 7.5$ Hz, C-4), 114.2 (d, $^2J_{\text{C-F}} = 19.1$ Hz, C-5), 62.7 (C-1), 61.0 (C-2), 48.0 (C-3).

$^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CD_2Cl_2 , 300 K) δ (ppm) = –116.6 (s).

ESI-MS(+): $m/z = 224.126$ ($[\text{M}+\text{H}]^+$, calc.: 224.126).

Synthesis of boronate 4



Benzyl alcohol (0.93 mL, 8.97 mmol) and dioxazaborocane **A** (2.00 g, 8.97 mmol) in THF (40 mL) were added to a suspension of potassium hydride (360 mg, 8.97 mmol) in THF (30 mL) successively. The reaction mixture was stirred at 50 °C for 3 d. The solvent was removed under reduced pressure. The solid residue was washed with benzene (3 x 10 mL) and dried *in vacuo*. A second product fraction was crystallised from the benzene filtrate and dried *in vacuo* after filtration. Both fractions were combined and boronate **4** was obtained as a white solid (1.74 g, 2.35 mmol, 52%). Single crystals suitable for X-ray diffraction crystallised from a solution of **4** in MTBE at room temperature.

$^1\text{H NMR}$ (500 MHz, THF- d_8 , 300 K) δ (ppm) = 7.47 – 7.40 (m, H-4/H-7, 8H), 7.29 (*pseudo-t*, $^3J_{\text{H-H}} = 7.7$ Hz, H-8, 4H), 7.16 (*pseudo-t*, $^3J_{\text{H-H}} = 7.4$ Hz, H-9, 2H), 6.83 (dd, $^3J_{\text{H-H}} = 9.7$ Hz, $^3J_{\text{H-F}} = 8.5$ Hz, H-5, 4H), 4.70 (s, H-6, 4H), 3.90 (td, $^{2/3}J_{\text{H-H}} = 9.9$ Hz, $^3J_{\text{H-H}} = 2.2$ Hz, H-1, 4H), 3.33 (d, $^2J_{\text{H-H}} = 10.6$ Hz, H-1, 4H), 2.84 (td, $^{2/3}J_{\text{H-H}} = 11.8$ Hz, $^3J_{\text{H-H}} = 3.8$ Hz, H-2, 4H), 2.34 (s, H-3, 6H), 2.07 (d, $^2J_{\text{H-H}} = 12.9$ Hz, H-2, 4H).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, THF- d_8 , 300 K) δ (ppm) = 4.9 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, THF- d_8 , 300 K) δ (ppm) = 162.6 (d, $^1J_{\text{C-F}} = 239.7$ Hz, Cq^F), 146.4 (Cq^{Bz}), 135.3 (d, $^3J_{\text{C-F}} = 6.2$ Hz, C-4), 128.6 (C-8), 126.5 (C-7), 126.5 (C-9), 113.6 (d, $^2J_{\text{C-F}} = 18.3$ Hz, C-5), 66.2 (C-6), 59.2 (C-1), 59.1 (C-2), 44.1 (C-3), (Cq^{PhF} not visible due to quadrupole relaxation).

^{15}N NMR (41 MHz, THF- d_8 , 300 K) δ (ppm) = 25.

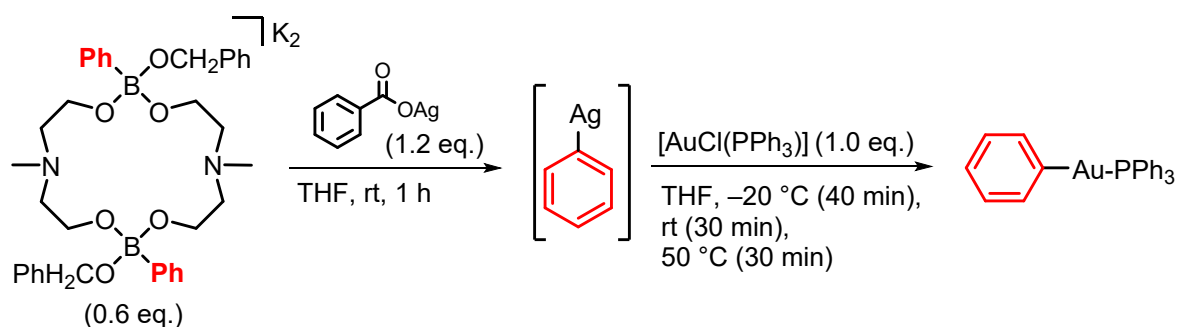
$^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, THF- d_8 , 300 K) δ (ppm) = -120.8 (s).

ESI-MS(-): $m/z = 683.3249$ ([M-2K+Na]⁻, calc.: 683.3257).

Co-crystallisation of fluorinated phenylsilver 5 with MTBE

Boronate **4** (150 mg, 0.20 mmol, 0.5 eq.) and silver benzoate (92 mg, 0.4 mmol, 1.0 eq.) were suspended in MTBE (5 mL) and stirred for 10 min. After filtration, the slightly yellow-coloured solution was concentrated to half the volume under reduced pressure. 4-Fluorophenylsilver (**5**) was obtained as colourless single crystals suitable for X-ray diffraction from a solution in MTBE at 4 °C.

Transmetalation reaction with phenylsilver



Boronate **1** (150 mg, 0.21 mmol, 0.6 eq.) and silver benzoate (96 mg, 0.42 mmol, 1.2 eq.) were suspended in THF (5 mL) under light exclusion and stirred for 1 h at room temperature. After filtration, the pale yellow-coloured solution was added to a solution of chloro(triphenylphosphine)gold(I) (173 mg, 0.35 mmol, 1.0 eq.) in THF (5 mL) at $-20\text{ }^{\circ}\text{C}$. The reaction temperature was increased stepwise: $-20\text{ }^{\circ}\text{C}$ (40 min), room temperature (30 min) and $50\text{ }^{\circ}\text{C}$ (30 min). The solvent was removed under reduced pressure and the residue was extracted with benzene (10 mL). The suspension was filtered through celite[®] and the solvent was removed under reduced pressure. After washing the solid residue with *n*-pentane (2 x 5 mL), the white solid was dried *in vacuo*. Phenyl(triphenylphosphine)gold(I) was obtained as white solid. ^1H NMR (400 MHz, C_6D_6 , 300 K) δ (ppm) = 8.09 (dd, $^3J_{\text{H,H}} = 7.2\text{ Hz}$, $^4J_{\text{H,H}} = 3.7\text{ Hz}$, 2H), 7.49 (t, $^3J_{\text{H,H}} = 7.6\text{ Hz}$, 2H), 7.42 (dd, $^3J_{\text{H,P}} = 11.5\text{ Hz}$, $^3J_{\text{H,H}} = 8.0\text{ Hz}$, 6H), 7.23 (tt, $^3J_{\text{H,H}} = 7.4\text{ Hz}$, $^4J_{\text{H,H}} = 1.5\text{ Hz}$, 1H), 6.98 (dd, $^3J_{\text{H,P}} = 13.5\text{ Hz}$, $^3J_{\text{H,H}} = 6.5\text{ Hz}$, 9H). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 300 K) δ (ppm) = 43.5 (s).

The NMR data are consistent with the data in the literature.³

To compare the reactivity of phenylsilver with that of boraza-crown ether, the experiment was repeated on the same scale. However, in this iteration, to the solution of chloro(triphenylphosphine)gold(I) in tetrahydrofuran only boronate **1** in THF was added, excluding silver benzoate. All subsequent steps were carried out in an analogous manner. In this instance as well, phenyl(triphenylphosphine)gold(I) was obtained as a white solid, and its NMR spectroscopic data were found to be consistent with the data in the literature.¹

The yield determination (Figure S12) for both reactions was conducted using quantitative NMR spectroscopy with 1,4-dinitrobenzene (8 mg, 0.05 mmol) as an internal standard (^1H NMR (C_6D_6 , 300 K) δ (ppm) = 7.36 (400 MHz) or 7.34 (500 MHz) (s, 4H)). The reaction involving silver benzoate resulted in a yield of 34% (0.12 mmol), while the comparative reaction without silver benzoate resulted in a yield of 5% (0.018 mmol).

NMR spectra

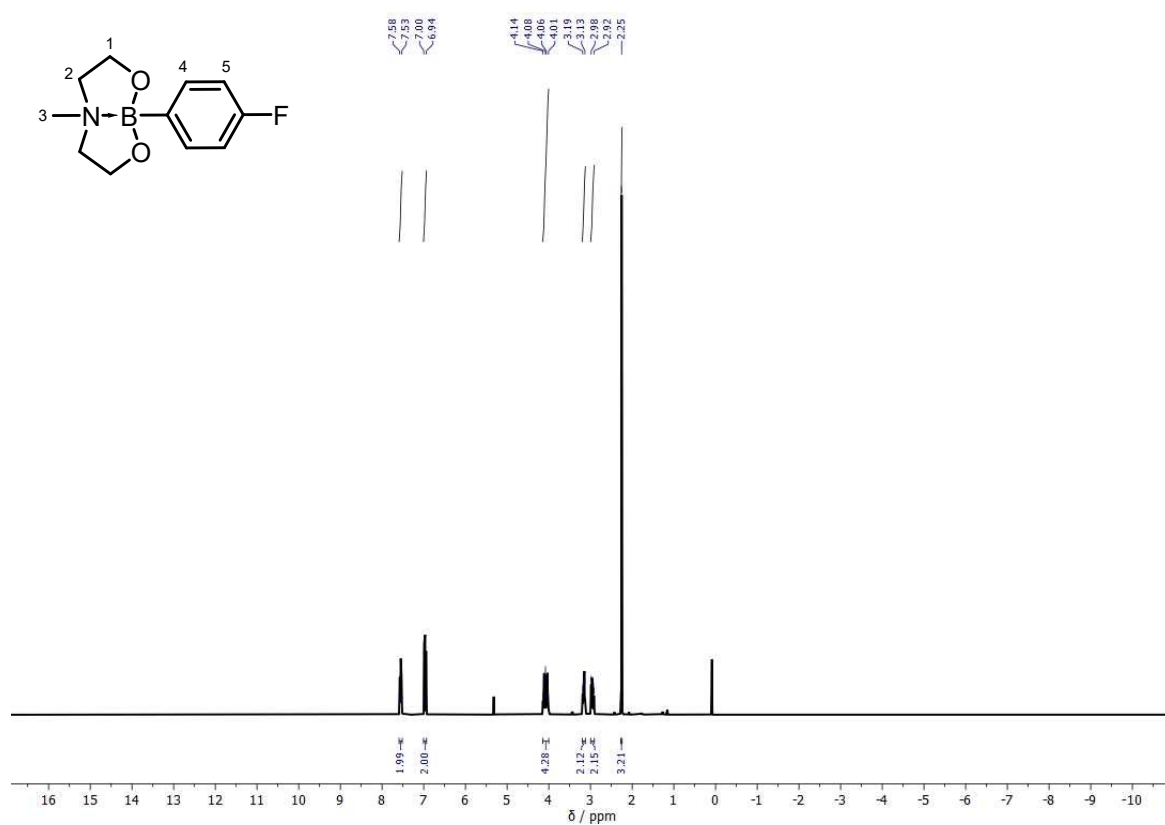


Figure S1: ¹H NMR spectrum (400 MHz, DCM-d₂) of dioxazaborocane A.

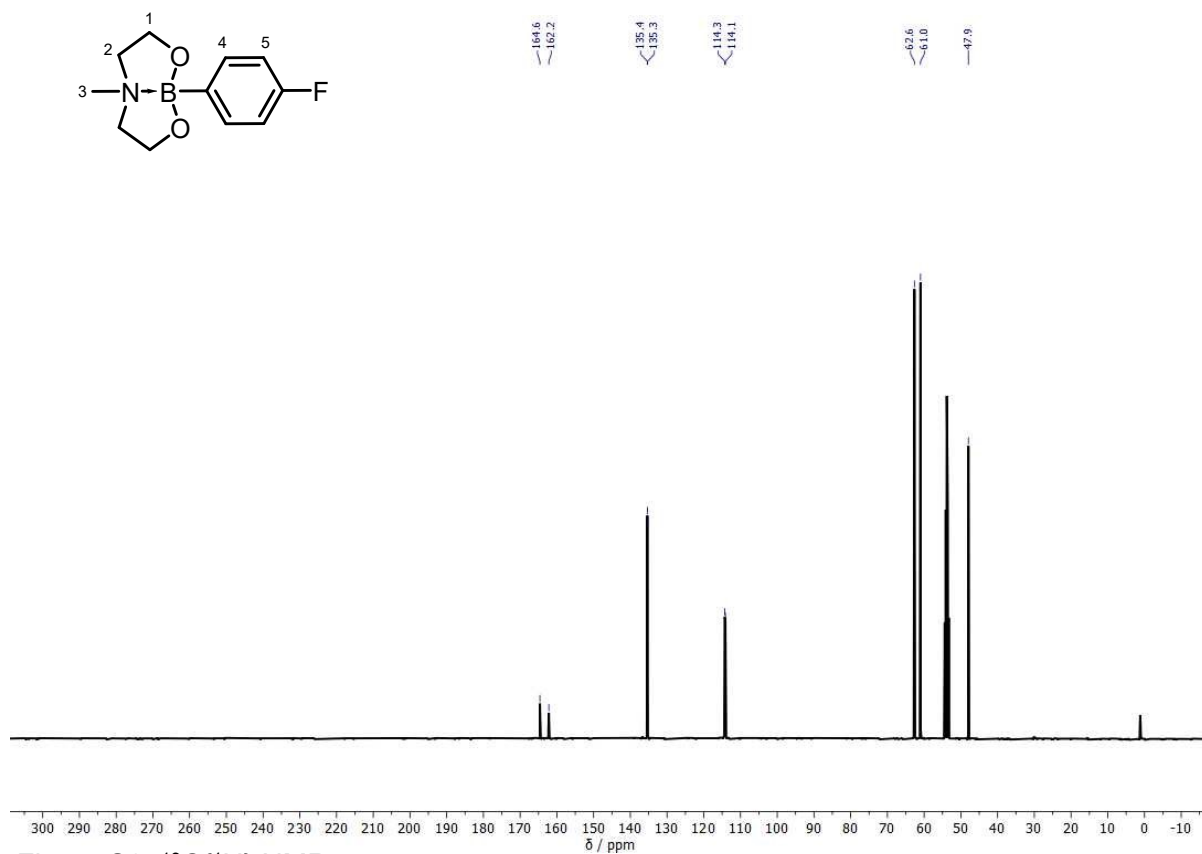


Figure S2: ¹³C{¹H} NMR spectrum (100 MHz, DCM-d₂) of dioxazaborocane A.

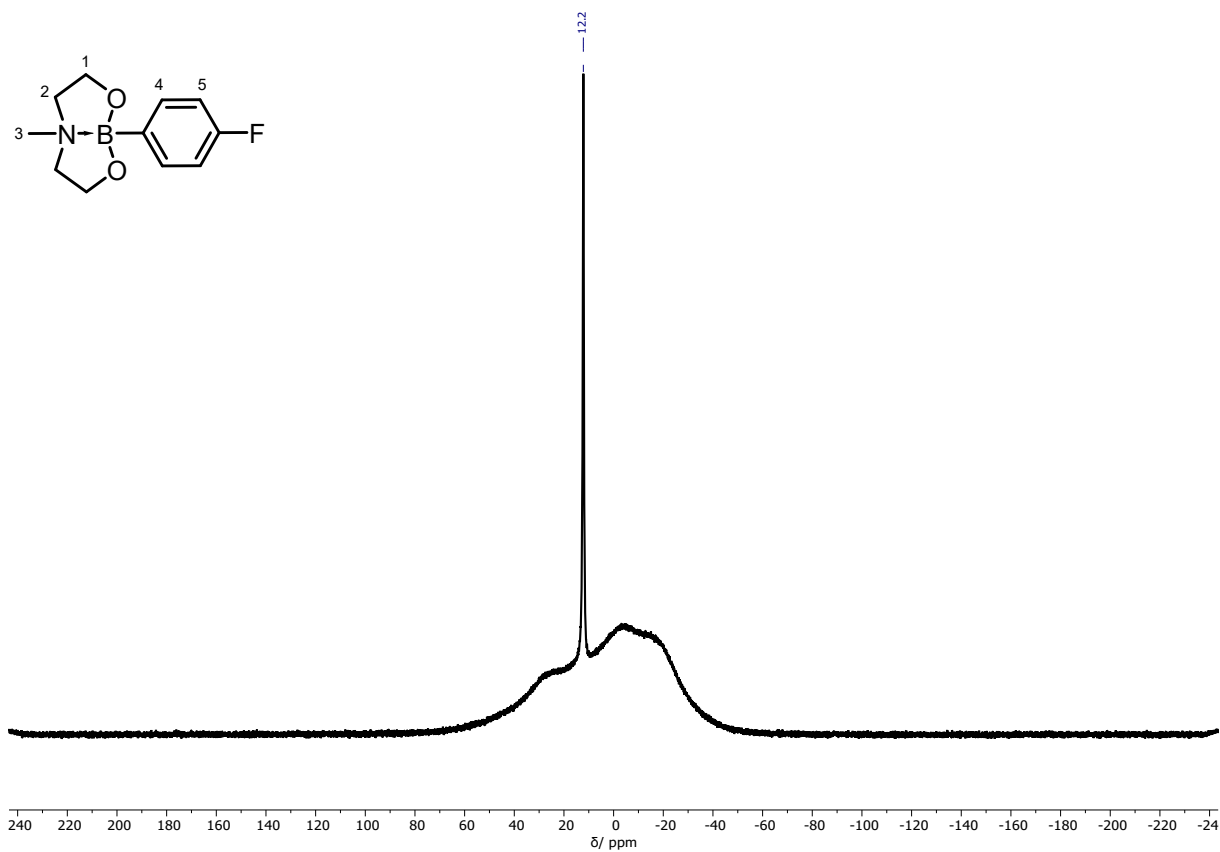


Figure S3: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (128 MHz, DCM-d_2) of dioxazaborocane A.

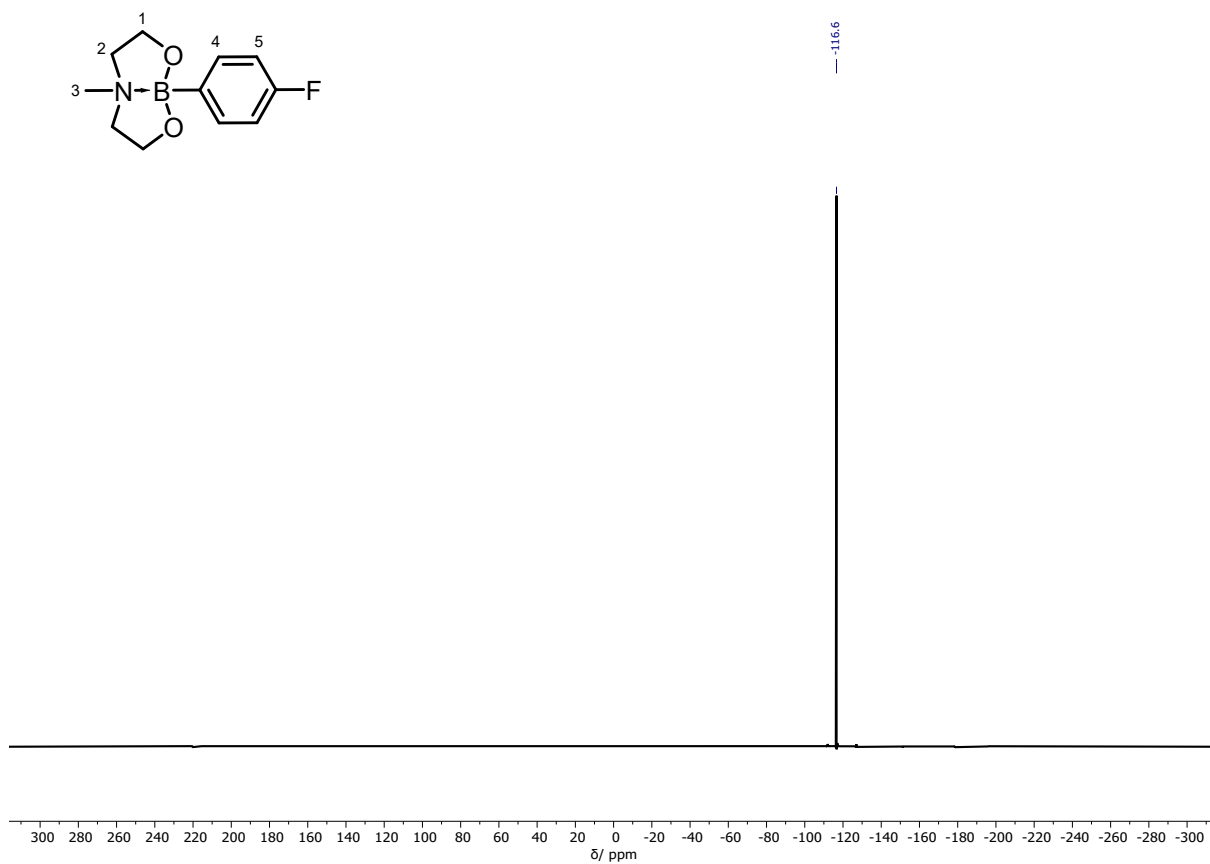


Figure S4: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (376 MHz, DCM-d_2) of dioxazaborocane A.

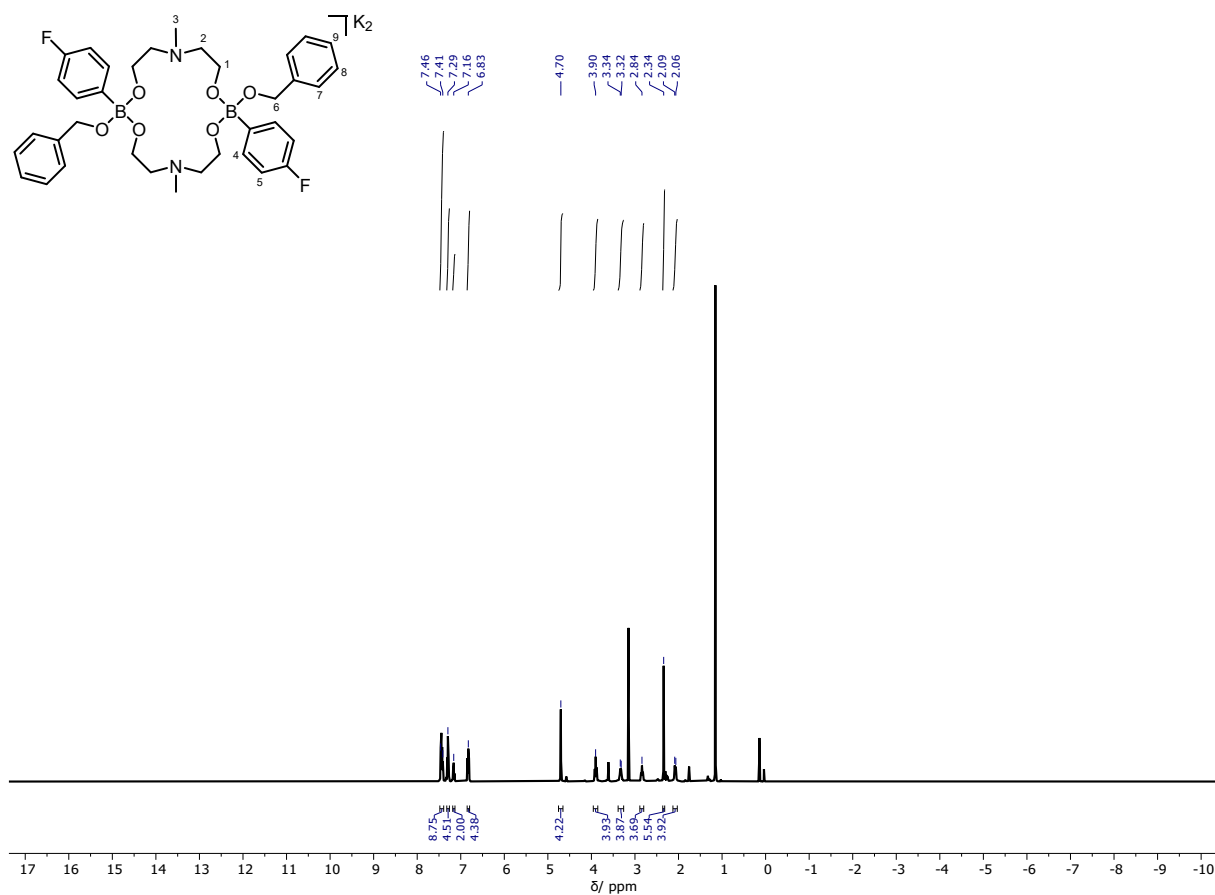


Figure S5: ^1H NMR spectrum (500 MHz, THF-d_8) of boronate 4.

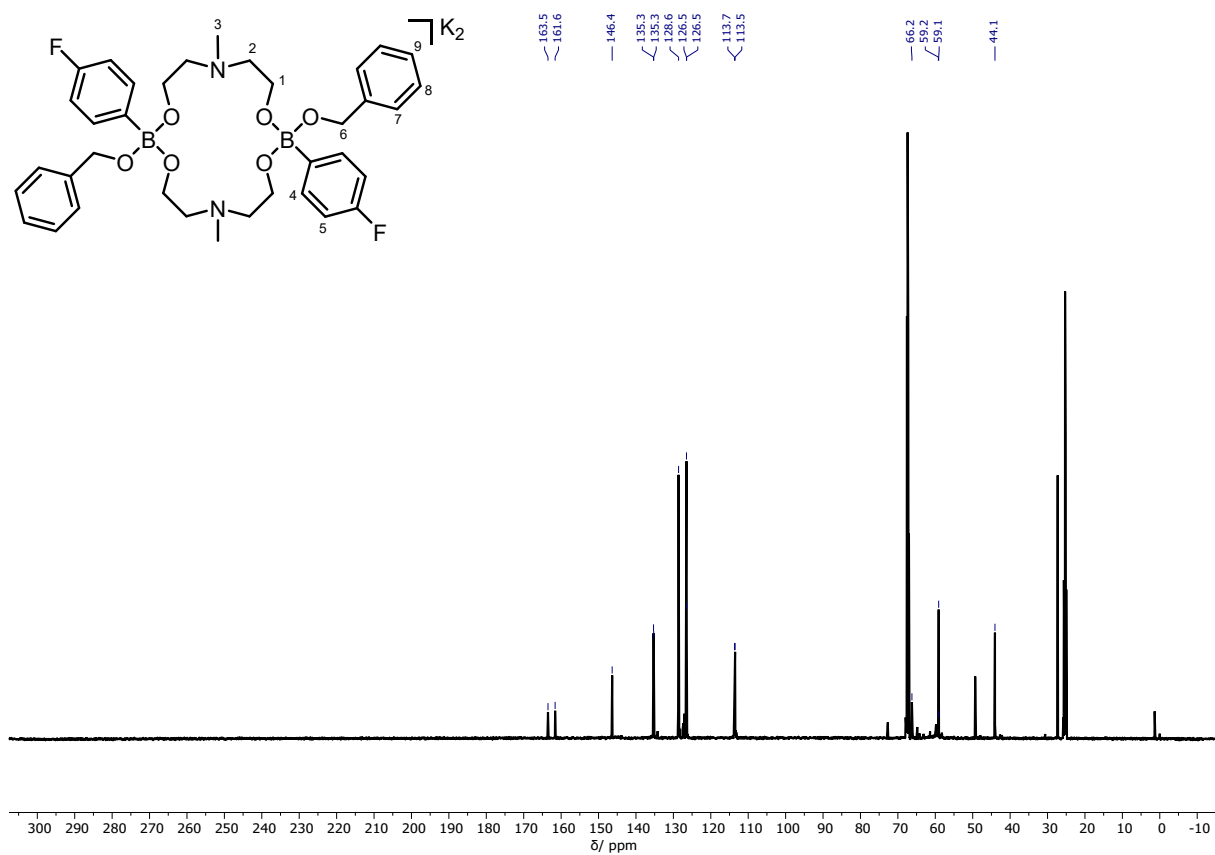


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, THF-d_8) of boronate 4.

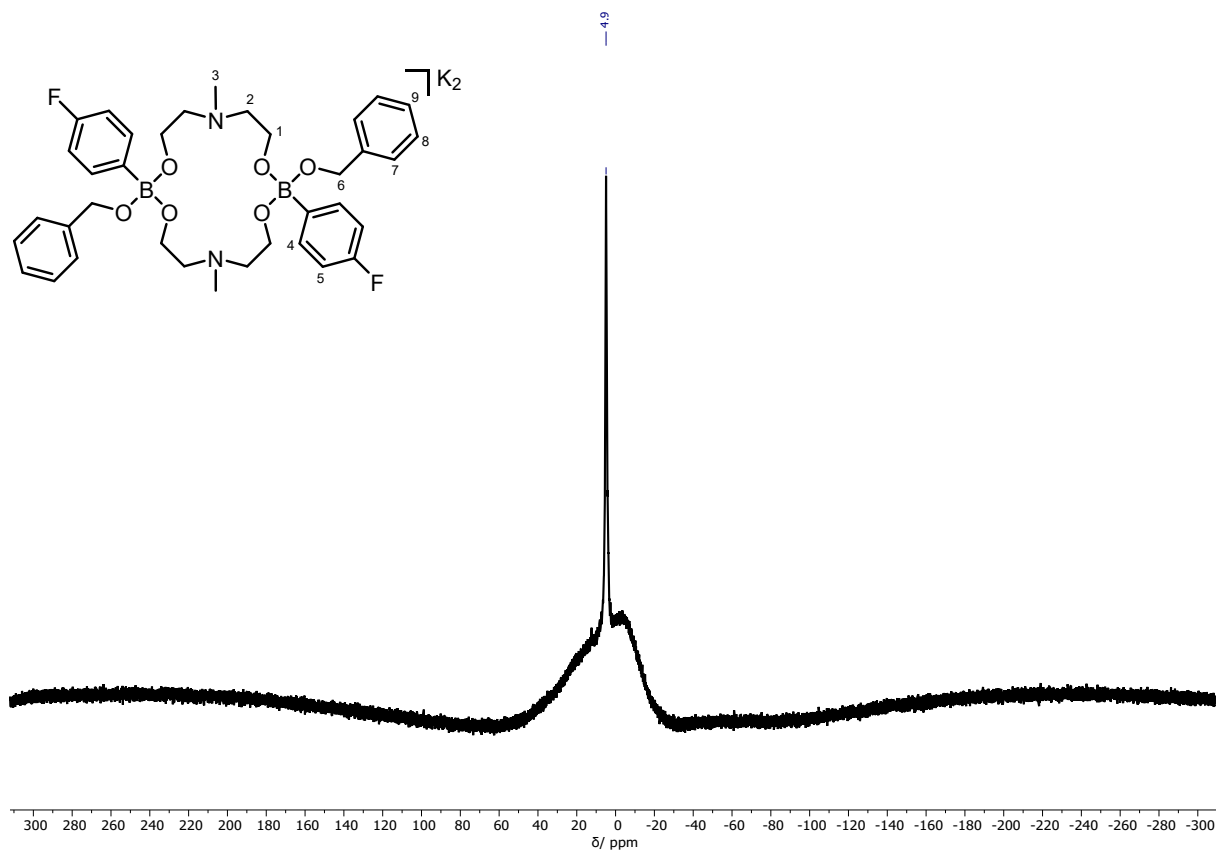


Figure S7: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (160 MHz, THF-d_8) of boronate 4.

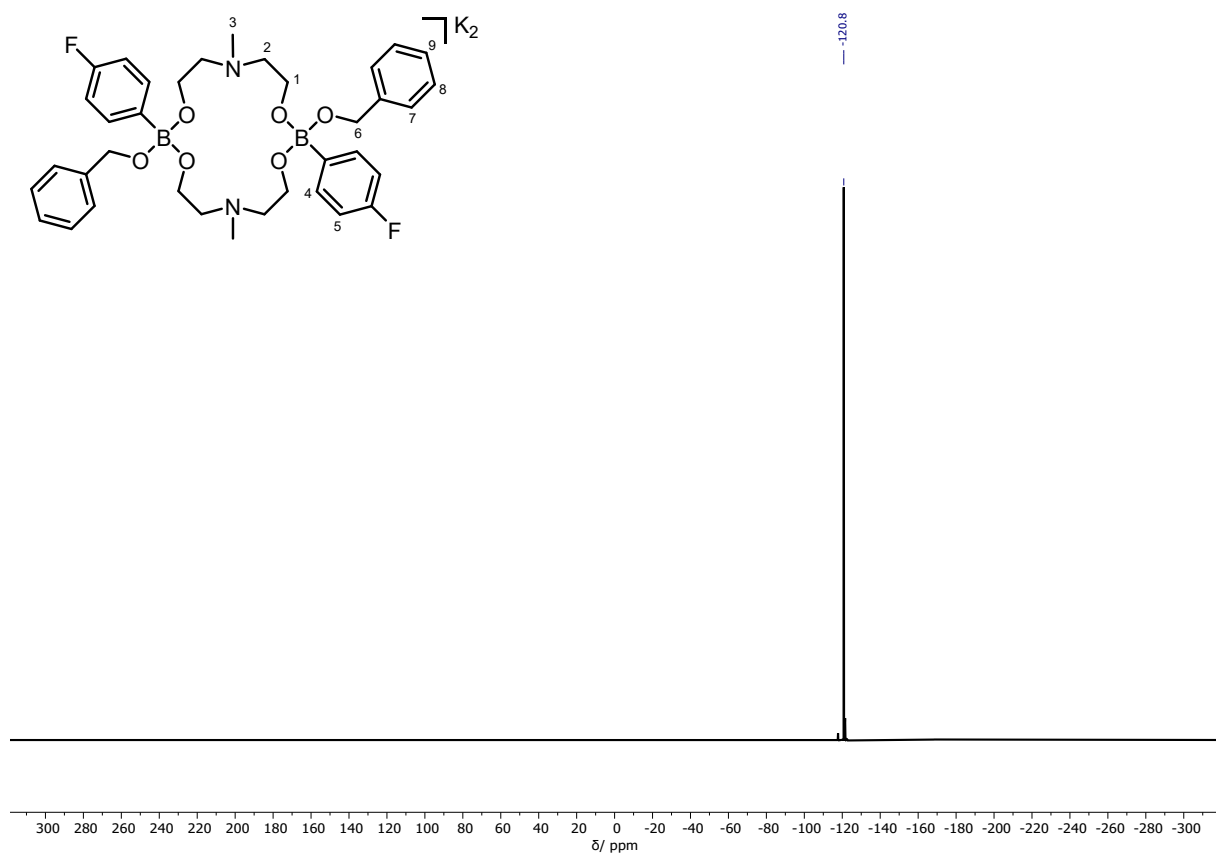


Figure S8: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (471 MHz, THF-d_8) of boronate 4.

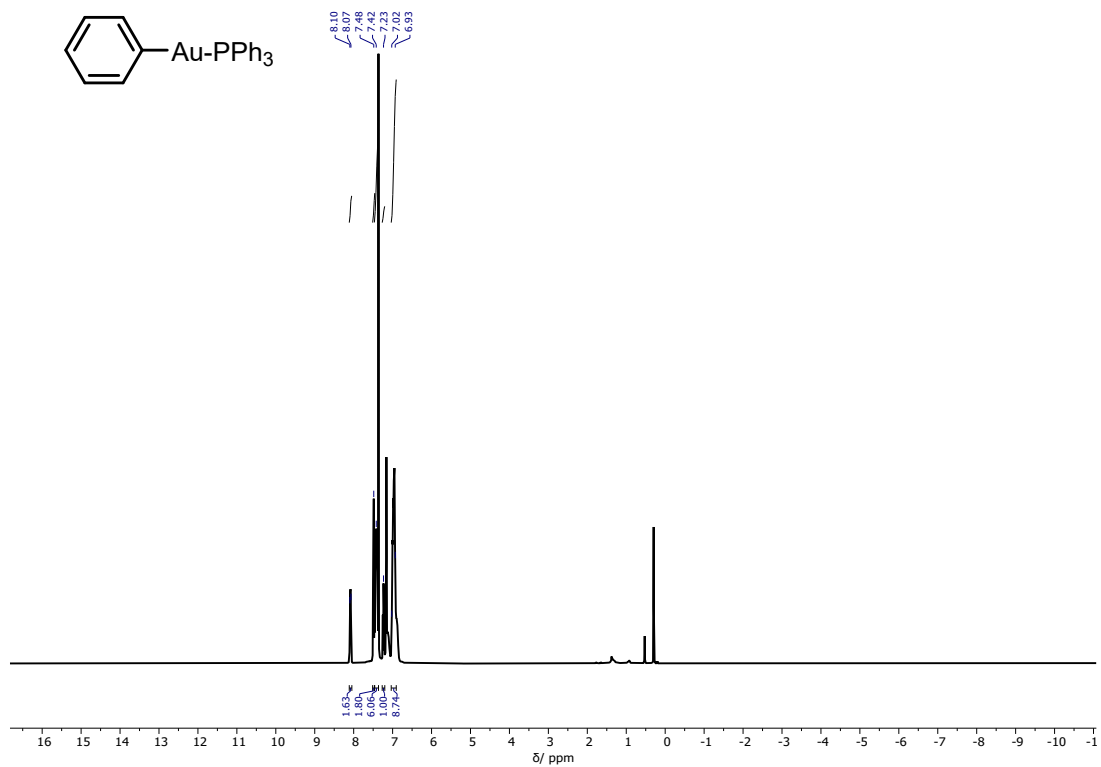


Figure S9: ^1H NMR spectrum (400 MHz, C_6D_6) of the product fraction resulting from the reaction of boronate **1** with chloro(triphenylphosphine)gold(I), in the presence of silver benzoate.

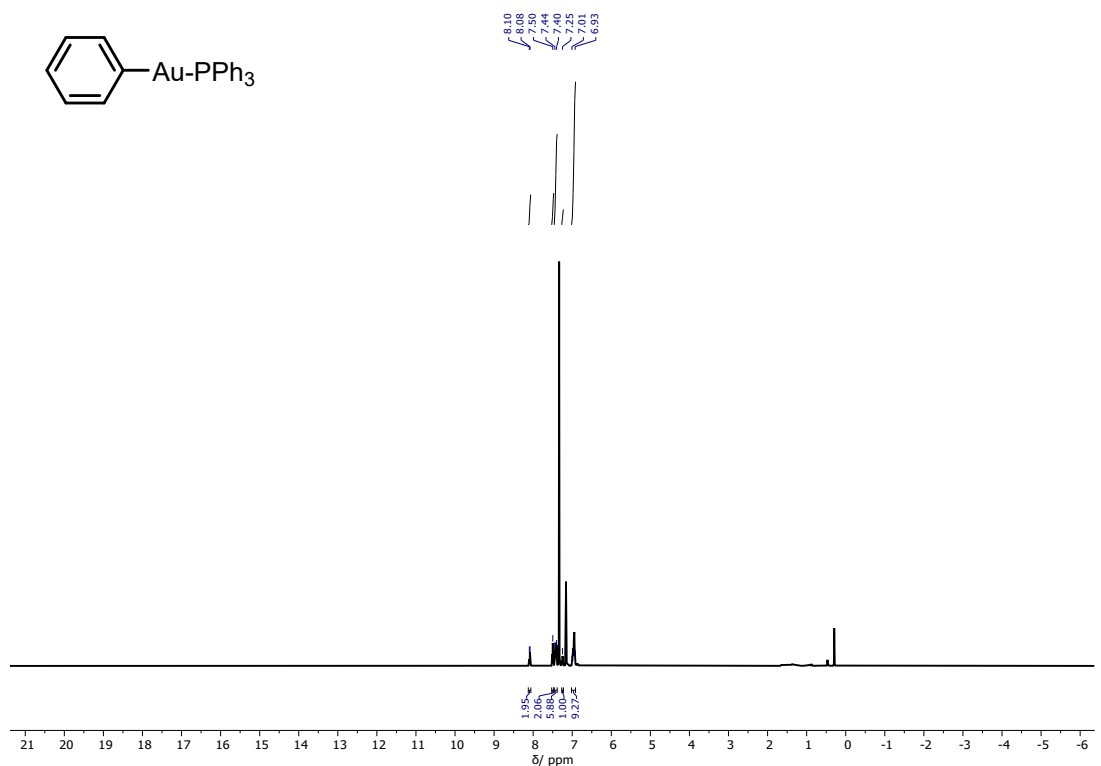


Figure S10: ^1H NMR spectrum (500 MHz, C_6D_6) of the product fraction resulting from the reaction of boronate **1** with chloro(triphenylphosphine)gold(I), in the absence of silver benzoate.

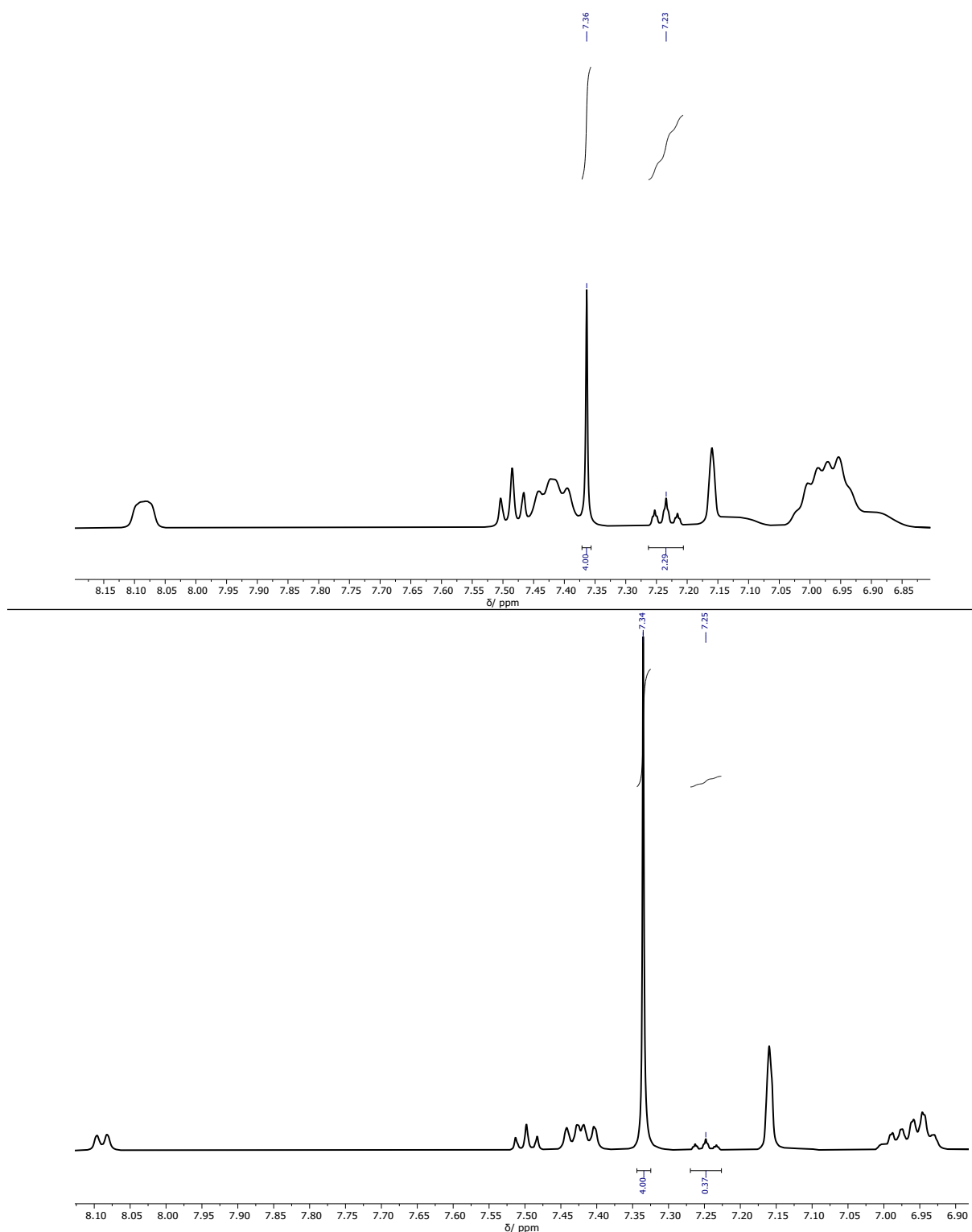
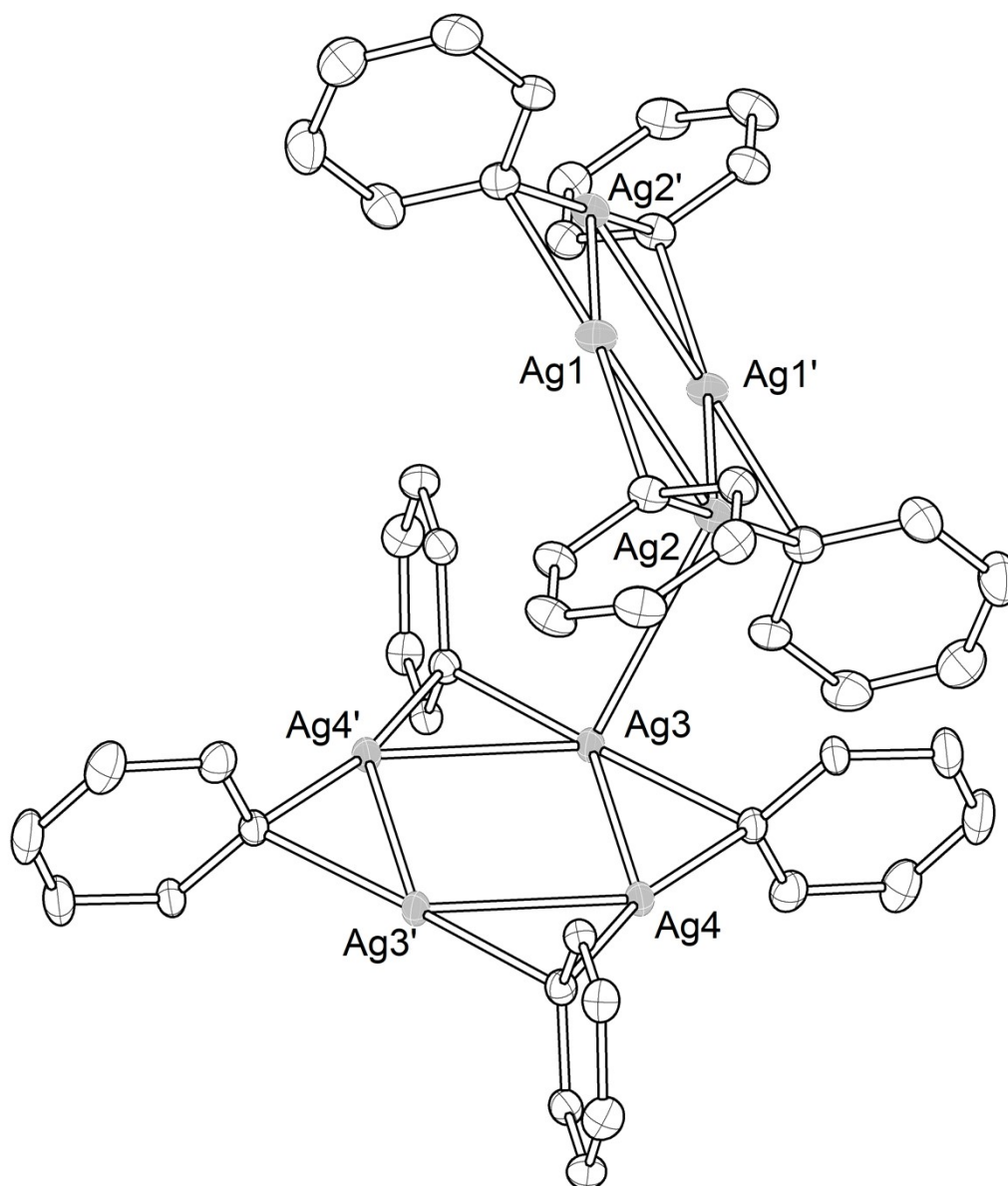


Figure S12: Detail of the quantitative ¹H-NMR spectrum (400 MHz (A) or 500 MHz (B), C₆D₆) of the product fraction obtained from the transmetalation reaction of boronate **1** with chloro(triphenylphosphine)gold(I), with the addition of silver benzoate (A), and without the addition of silver benzoate (B)

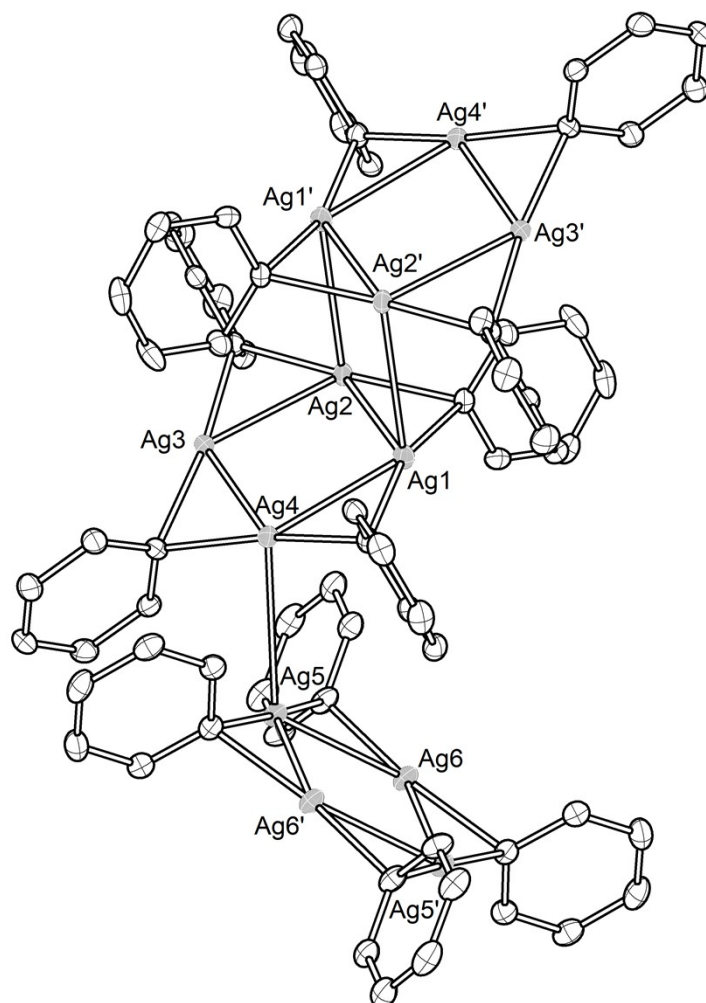
Crystal Data

Compound 2



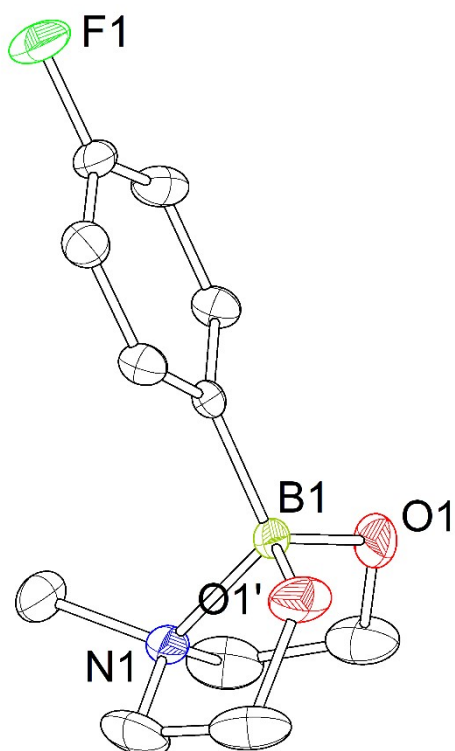
Crystal Data for 2: $C_{24}H_{20}Ag_4$, $M_r = 739.88$, colourless fragment, $0.100 \times 0.100 \times 0.050 \text{ mm}^3$, monoclinic space group $C 2/c$, $a = 21.9136(6) \text{ \AA}$, $b = 10.3277(3) \text{ \AA}$, $c = 20.6655(5) \text{ \AA}$, $\beta = 95.496(1)^\circ$, $V = 4655.5(2) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 2.111 \text{ g/cm}^3$, $\mu = 3.321 \text{ mm}^{-1}$, $F(000) = 2816$, $T = 100(2) \text{ K}$, $R1 = 0.0179$, $wR2 = 0.0481$, 5779 independent reflections, $S = 1.100$, 308 parameters. Symmetry equivalent atoms: $-x, y, -z+1/2$. The unit cell contains 1 tetrahydrofuran molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON³. The structure contains a positionally disordered phenyl group with an occupancy ratio of 0.69:0.31 (only the major compound shown). CCDC number: 2291152.

Compound 3



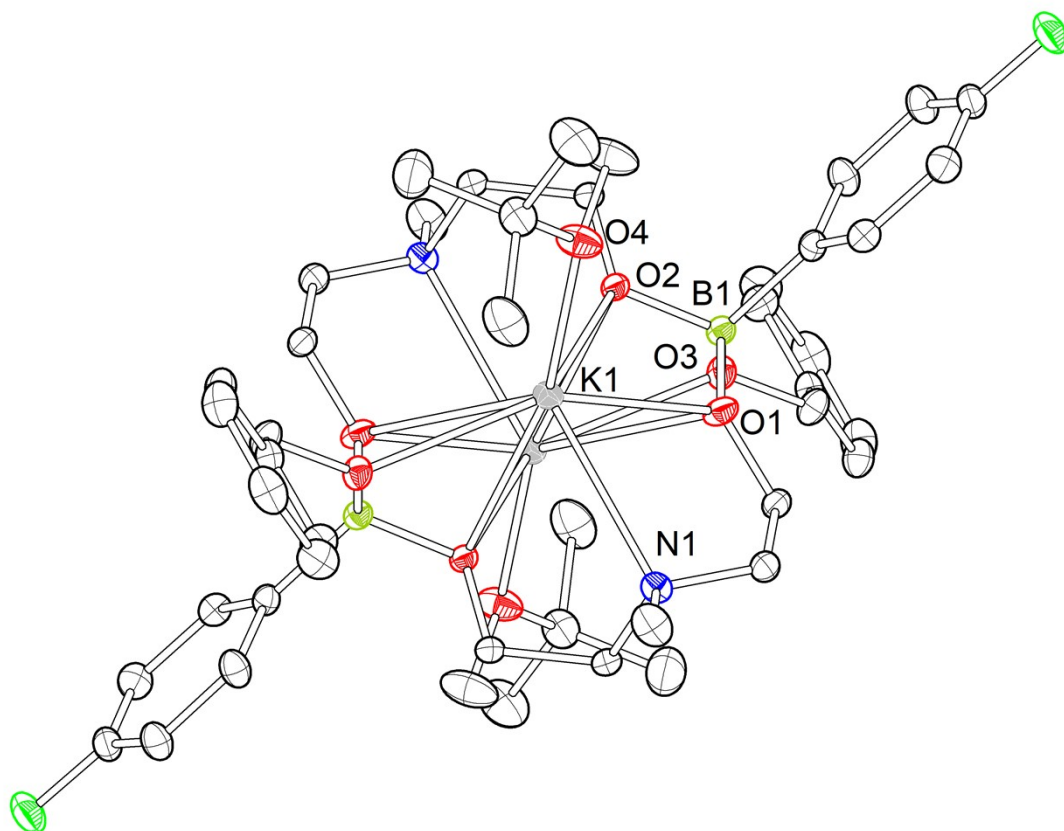
Crystal Data for 3: $C_{72}H_{60}Ag_{12}$, $M_r = 2219.64$, colourless fragment, $0.150 \times 0.050 \times 0.020 \text{ mm}^3$, triclinic space group $P\bar{1}$, $a = 9.9863(4) \text{ \AA}$, $b = 10.8351(4) \text{ \AA}$, $c = 15.2489(6) \text{ \AA}$, $\alpha = 107.410(1)^\circ$, $\beta = 93.102(1)^\circ$, $\gamma = 90.732(1)^\circ$, $V = 1571.35(11) \text{ \AA}^3$, $Z = 1$, $\rho_{\text{calcd}} = 2.346 \text{ g/cm}^3$, $\mu = 3.690 \text{ mm}^{-1}$, $F(000) = 1056$, $T = 100(2) \text{ K}$, $R1 = 0.0173$, $wR2 = 0.0440$, 7113 independent reflections, $S = 1.117$, 379 parameters. CCDC number: 2291151.

Compound Dioxazaborocane A



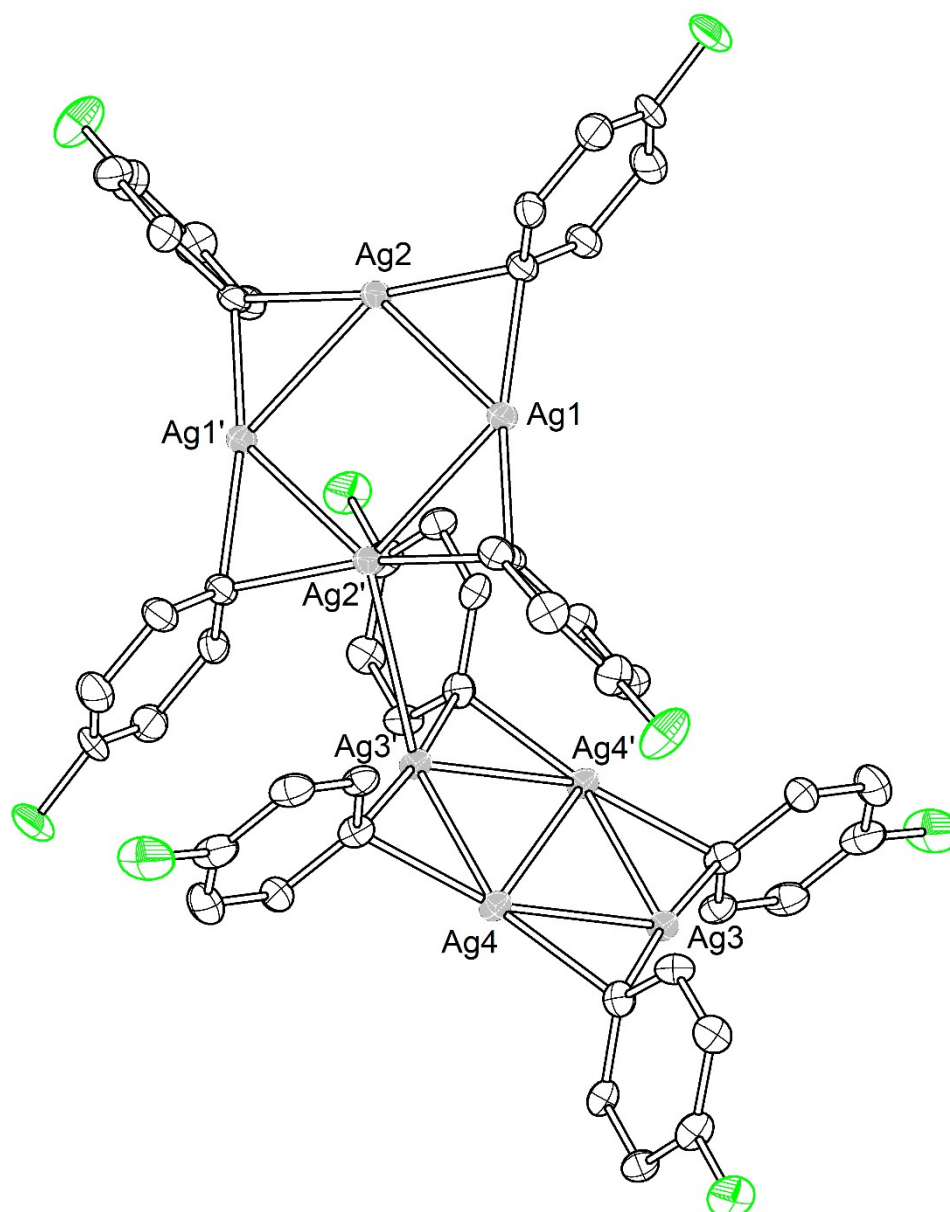
Crystal Data for A: $C_{11}H_{15}BFNO_2$, $M_r = 914.8$ 223.05, colourless fragment, 0.360 x 0.300 x 0.170 mm³, orthorhombic space group $Pnma$, $a = 6.7095(3)$ Å, $b = 10.7458(5)$ Å, $c = 15.4294(6)$ Å, $V = 1112.44(8)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.332$ g/cm³, $\mu = 0.100$ mm⁻¹, $F(000) = 472$, $T = 102(2)$ K, $R1 = 0.0453$, $wR2 = 0.1109$, 1338 independent reflections, $S = 1.052$, 102 parameters. The structure contains a positionally disordered diethanolamine backbone with an occupancy ratio of 0.52:0.48 (only the major compound shown). CCDC number: 2291149.

Compound 4



Crystal Data for 4: $C_{46}H_{68}B_2F_2K_2N_2O_8$, $M_r = 914.84$, colourless fragment, $0.380 \times 0.230 \times 0.150 \text{ mm}^3$, triclinic space group $P-1$, $a = 9.5750(3) \text{ \AA}$, $b = 11.8169(4) \text{ \AA}$, $c = 11.8374(4) \text{ \AA}$, $\alpha = 81.688(1)^\circ$, $\beta = 67.140(1)^\circ$, $\gamma = 81.851(1)^\circ$, $V = 1215.81(7) \text{ \AA}^3$, $Z = 1$, $\rho_{\text{calcd}} = 1.250 \text{ g/cm}^3$, $\mu = 0.254 \text{ mm}^{-1}$, $F(000) = 488$, $T = 102(2) \text{ K}$, $R1 = 0.0347$, $wR2 = 0.0969$, 7033 independent reflections, $S = 1.044$, 285 parameters. CCDC number: 2291153.

Compound 5



Crystal Data for 5: $C_{24}H_{16}Ag_4F_4$, $M_r = 2219.64$, colourless fragment, $0.270 \times 0.040 \times 0.040$ mm³, triclinic space group $P\bar{1}$, $a = 11.578(2)$ Å, $b = 12.302(2)$ Å, $c = 12.477(3)$ Å, $\alpha = 113.157(5)^\circ$, $\beta = 108.215(5)^\circ$, $\gamma = 100.881(4)^\circ$, $V = 1449.9(5)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.860$ g/cm³, $\mu = 2.694$ mm⁻¹, $F(000) = 768$, $T = 102(2)$ K, $R1 = 0.0303$, $wR2 = 0.0954$, 5779 independent reflections, $S = 1.092$, 290 parameters. The unit cell contains 2 MTBE molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON³. CCDC number: 2291150.

Compound 2 and 3 - Details

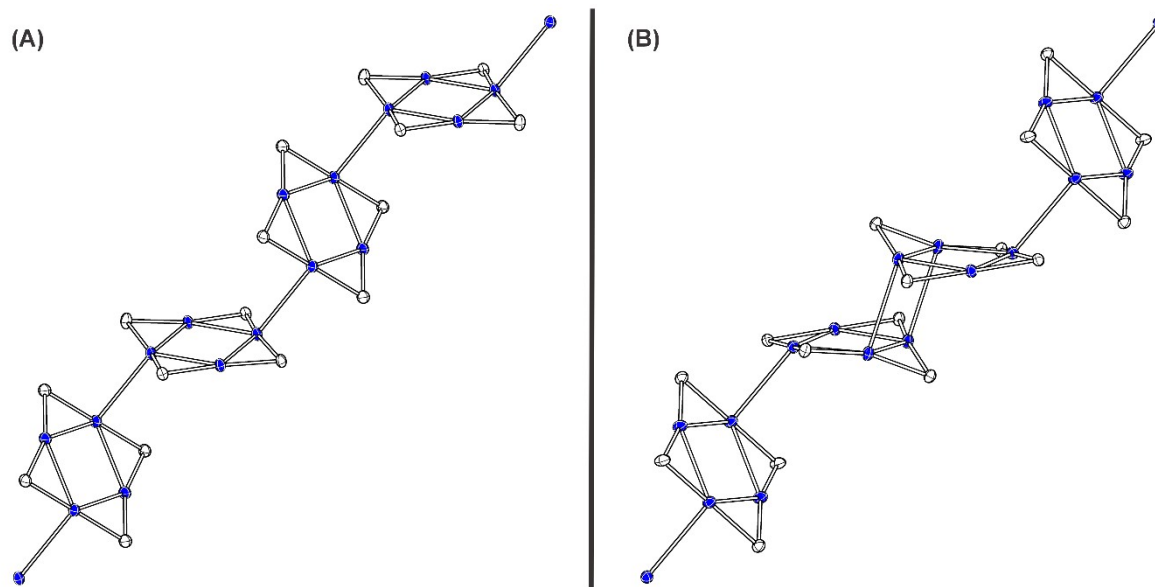


Figure S13: Details of the polymeric chain of coordination polymer **2** (A) and coordination polymer **3** (B).

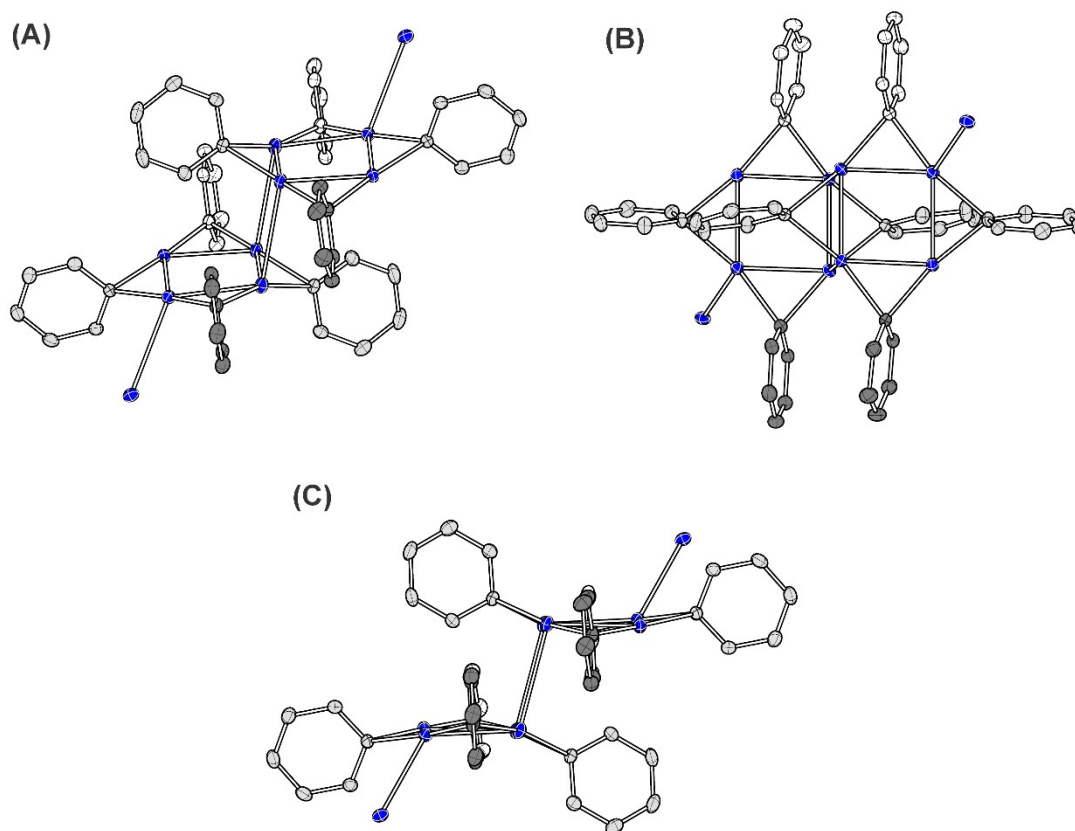


Figure S14: Details of two connected Type II tetrads of coordination polymer **3** in different orientations (A), (B) and (C). For clarity the carbon atoms of the phenyl ligands are coloured in different shades of grey.

Table S1: Summary of average bond lengths [Å] and angles [°] of documented monomeric Ag₄Aryl₄ tetrads.

Database Identifier	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	b_1	b_2	b_3	b_4	c/d_1	c/d_2	α_1	α_2	α_3	α_4	β_1	β_2	β_3	β_4	T [K]
BUKNUT	2,186	2,206	2,221	2,2	2,186	2,206	2,221	2,2	2,779	2,731	2,731	2,779	4,275	3,477	88,524	83,991	88,524	83,991	11,419	2,272	11,419	2,272	125
CAGBIV	2,216	2,216	2,211	2,162	2,216	2,216	2,211	2,162	2,733	2,755	2,755	2,733	3,788	3,971	88,723	89,325	88,723	89,325	0,155	0,397	0,155	0,397	295
CAGBIV10	2,216	2,216	2,162	2,211	2,216	2,216	2,162	2,211	2,733	2,755	2,755	2,733	3,971	3,788	88,723	89,325	88,723	89,325	0,155	0,397	0,155	0,397	295
CEGZEU	2,229	2,186	2,228	2,194	2,229	2,186	2,228	2,194	2,736	2,746	2,746	2,736	3,9	3,852	89,205	88,586	89,205	88,586	0,611	0,79	0,611	0,79	148
LEWLUU	2,191	2,261	2,199	2,274	2,191	2,261	2,199	2,274	2,754	2,726	2,726	2,754	3,843	3,885	83,156	79,018	83,156	79,018	13,818	14,811	13,818	14,811	153
NOWMER	2,162	2,402	2,41	2,135	2,168	2,359	2,351	2,159	2,733	2,748	2,731	2,744	3,613	4,117	86,544	84,941	89,819	86,461	27,083	32,714	31,303	31,875	170
PENNEE	2,196	2,196	2,191	2,191	2,196	2,196	2,191	2,191	2,718	2,739	2,739	2,718	3,859	3,859	90	79,085	90	79,085	0,357	0	0,357	0	104
PUNQOG	2,174	2,229	2,201	2,192	2,152	2,259	2,207	2,214	2,797	2,764	2,771	2,753	3,445	4,341	81,935	86,409	83,977	88,719	11,394	16,563	0,885	11,526	173
PUNQUM	2,194	2,216	2,178	2,232	2,192	2,213	2,189	2,231	2,761	2,776	2,764	2,768	3,469	4,302	78,008	86,475	80,363	81,539	29,463	29,108	15,602	19,414	173
PUNRAT	2,353	2,173	2,189	2,271	2,353	2,173	2,189	2,271	2,744	2,793	2,793	2,744	4,095	3,194	56,856	68,159	56,856	68,159	43,487	32,134	43,487	32,134	173
PUNREX	2,203	2,224	2,216	2,215	2,196	2,219	2,215	2,229	2,762	2,77	2,774	2,779	3,152	4,557	88,703	85,239	89,801	83,559	13,56	21,987	13,182	24,355	173
PUNRIB	2,183	2,224	2,185	2,23	2,186	2,228	2,187	2,213	2,761	2,782	2,772	2,753	3,349	4,398	81,852	86,293	75,727	85,426	17,537	17,439	23,486	27,832	173
PUNROH	2,368	2,166	2,219	2,249	2,358	2,172	2,221	2,253	2,766	2,786	2,78	2,774	3,812	3,466	51,758	63,771	54,608	62,165	43,185	32,795	46,186	35,445	173
PUNRUN	2,186	2,245	2,234	2,253	2,186	2,245	2,234	2,253	2,815	2,782	2,782	2,815	4,5	3,327	84,956	83,07	84,956	83,07	10,972	3,252	10,972	3,252	173
PUNSAU	2,206	2,289	2,206	2,289	2,206	2,289	2,206	2,289	2,775	2,775	2,775	2,775	3,742	3,742	62,543	62,543	62,543	62,543	39,406	39,406	39,406	39,406	173
PUNSEY	2,198	2,224	2,204	2,232	2,2	2,233	2,208	2,227	2,768	2,789	2,796	2,756	3,192	4,537	88,984	81,047	87,814	81,347	11,658	26,222	12,005	23,397	173
PUNSIC	2,183	2,243	2,231	2,2	2,183	2,243	2,231	2,2	2,782	2,796	2,796	2,782	2,994	4,706	87,95	87,227	87,95	87,227	6,238	6,255	6,238	6,255	173
PUNSOI	2,25	2,223	2,186	2,334	2,25	2,223	2,186	2,334	2,745	2,778	2,778	2,745	3,103	4,437	73,15	69,592	73,15	69,592	37,113	54,425	37,113	54,425	173
QIVHUB	2,146	2,29	2,296	2,148	2,146	2,29	2,296	2,148	2,781	2,762	2,762	2,781	3,778	4,057	84,975	82,287	84,975	82,287	16,644	18,797	16,644	18,797	123
QIVHUB01	2,139	2,268	2,298	2,144	2,139	2,268	2,298	2,144	2,786	2,772	2,772	2,786	3,848	4,012	84,398	83,794	84,398	83,794	16,481	18,338	16,481	18,338	298

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