Electronic Supplementary Material (ESI) for ChemComm.

Janus-type homo-, hetero- and mixed valence-bimetallic complexes with one metal encapsulated in a cyclodextrin

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Supporting information

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1. General information

Reactions in organic solvents were performed in oven-dried screw-cap tube flushed with argon. Reagents were purchased from commercial sources and used as received unless stated otherwise. Acetone 99.5% and DMSO 99.5% for synthesis were used as received as dry solvents. Dichloromethane (DCM) and acetonitrile were distilled from CaH_2. DCM was degassed by running 4-5 vacuum/argon cycles. The bis-mesylate **2** was prepared according to a reported procedure.[1] Purifications by column chromatography were performed on silica gel (Kieselgel 60 Merck, granulometry 40–60 or 15–40 μm). High Resolution Mass Spectroscopy (HRMS) were recorded on a Bruker micrOTOF spectrometer, using Agilent ESI-L Low Concentration Tuning-Mix as reference. NMR spectra were recorded on a Bruker AM-400 MHz or Brucker Avance II 600 MHz using the signal of the residual solvent as an internal reference. Assignments were aided by COSY, HSQC, NOESY, TOCSY and HMBC experiments. The following numbering was used for ^{1}H and ^{13}C NMR signal attributions in the glycosyl units (Figure S1-A). The six different glycosyl units of the α-CD core are named with capital letters according to the order shown in Figure S1-B.

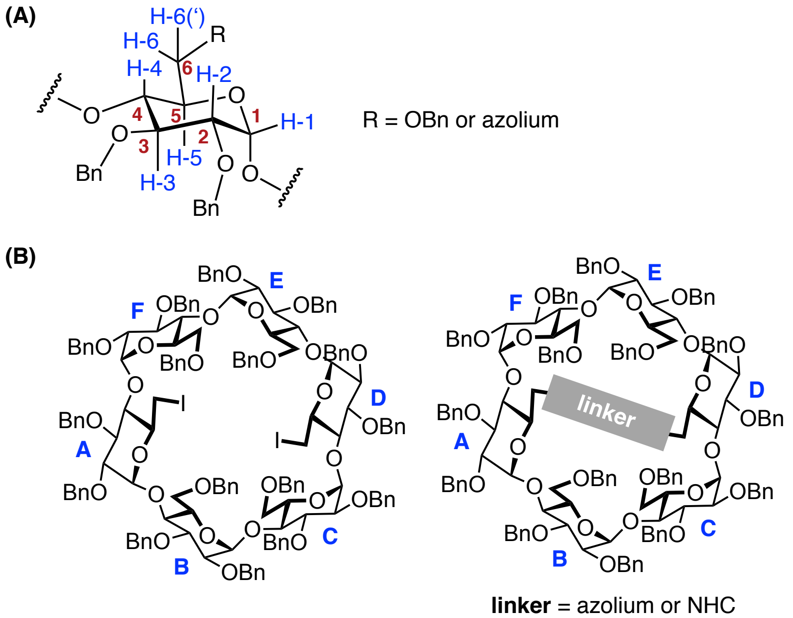
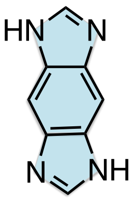


Figure S1. Identification of protons, carbons and glycosyl units for of NMR signal attributions.

[1] a) M. Guitet, P. Zhang, F. Marcelo, C. Tugny, J. Jiménez-Barbero, O. Buriez, C. Amatore, V. Mouriès-Mansuy, JP. Goddard , L. Fensterbank, Y. Zhang, S. Roland, M. Ménand, M. Sollogoub, *Angew. Chem. Int. Ed.* **2013**, *52*, 7213–7218; b) B. Bertino-Ghera, F. Perret, B. Fenet, H. Parrot-Lopez *J. Org. Chem.*, **2008**, *73*, 7317–7326.

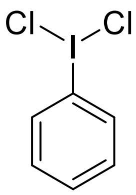
2. Synthesis and characterisation of metal complexes

Benzobis(imidazole) (**BBI**)[2]



A mixture of 1,2,4,5-benzenetetraamine tetrahydrochloride (716 mg, 2.52 mmol) in formic acid (21 mL) was heated at 100 °C for 48 h. After cooling, the reaction mixture was poured into ice-cold water (21 mL) and neutralized by addition of aqueous NaOH 10%. The product was precipitated by cooling, collected via vacuum filtration, rinsed with cold water, and dried in a freeze dryer to give Benzobis(imidazole) as a brown powder in 87% yield (347 mg, 2.19 mmol). **^{1}H NMR** (400 MHz, DMSO-d_6): δ 12.24 (s, 2H), 8.17 (s, 2H), 7.69 (s, 2H) ppm. The NMR data are in agreement with the literature.[2]

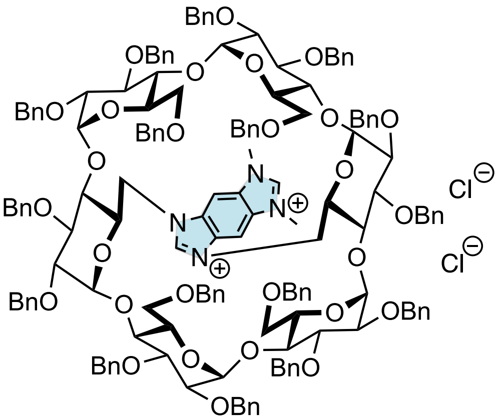
Iodobenzene dichloride ($PhICl_2$)



The title compound was freshly prepared according to a reported procedure:[3] To a vigorously stirred emulsion of iodobenzene (1.12 mL, 10 mmol) in diluted HCl (20 mL conc. HCl in 50 mL H_2O), $NaClO_2$ (5.66 g, 50 mmol) was added portionwise over a period of 0.5 h. The flask was protected from light by an aluminium foil and the mixture was stirred for 4.5 h. The yellow precipitate was collected by filtration, washed with water (500 mL), ice-cooled *n*-hexane (300 mL), and dried overnight in a freeze dryer with exclusion of light, to give Iodobenzene dichloride as a fluffy yellow powder in 87% yield (2.4 g, 8.7 mmol). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.19 (d, J = 8.1 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H) ppm. The NMR data are in agreement with the literature.

[2] A. J. Boydston, K. A. Williams, C. W. Bielawski, *J. Am. Chem. Soc.* **2005**, *127*, 12496–12497.
[3] D. Canestrar, S. Lancianesi, E. Badiola, C. Strinna, H. Ibrahim, M. F. A. Adamo, *Org. Lett.* **2017**, *19*, 918–921.

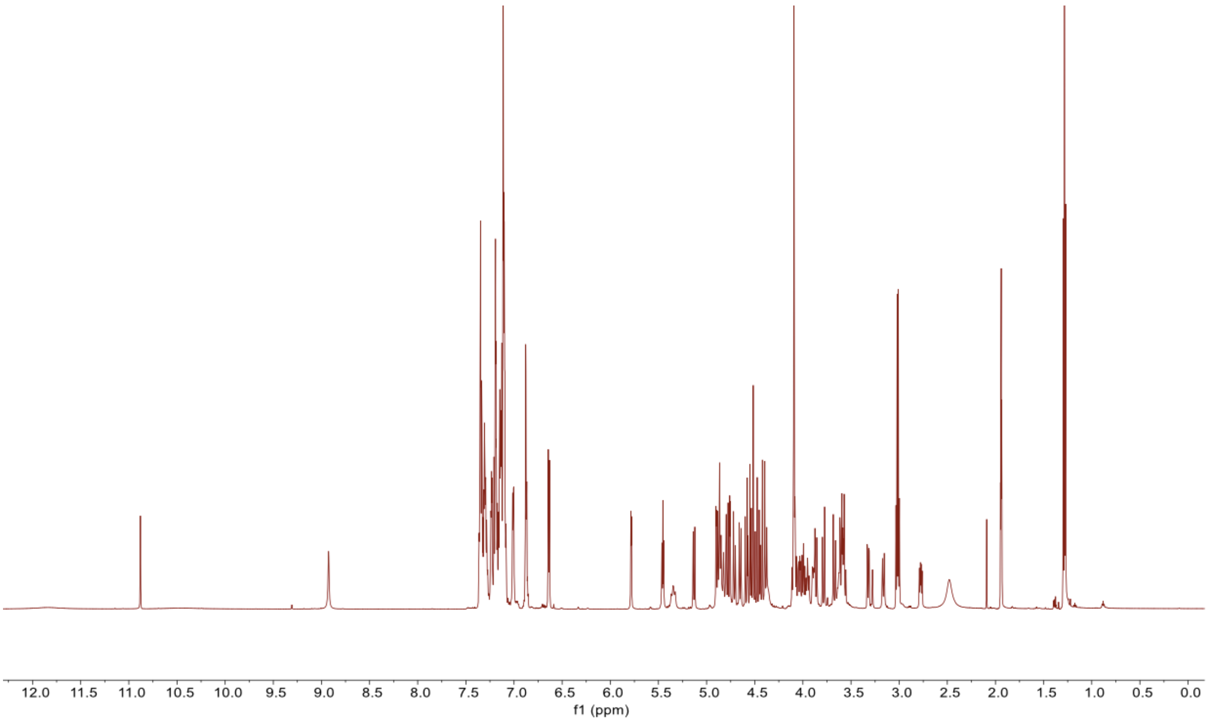
α-CD^{Bn}(BBI) bis-azolium bis-chloride (1)



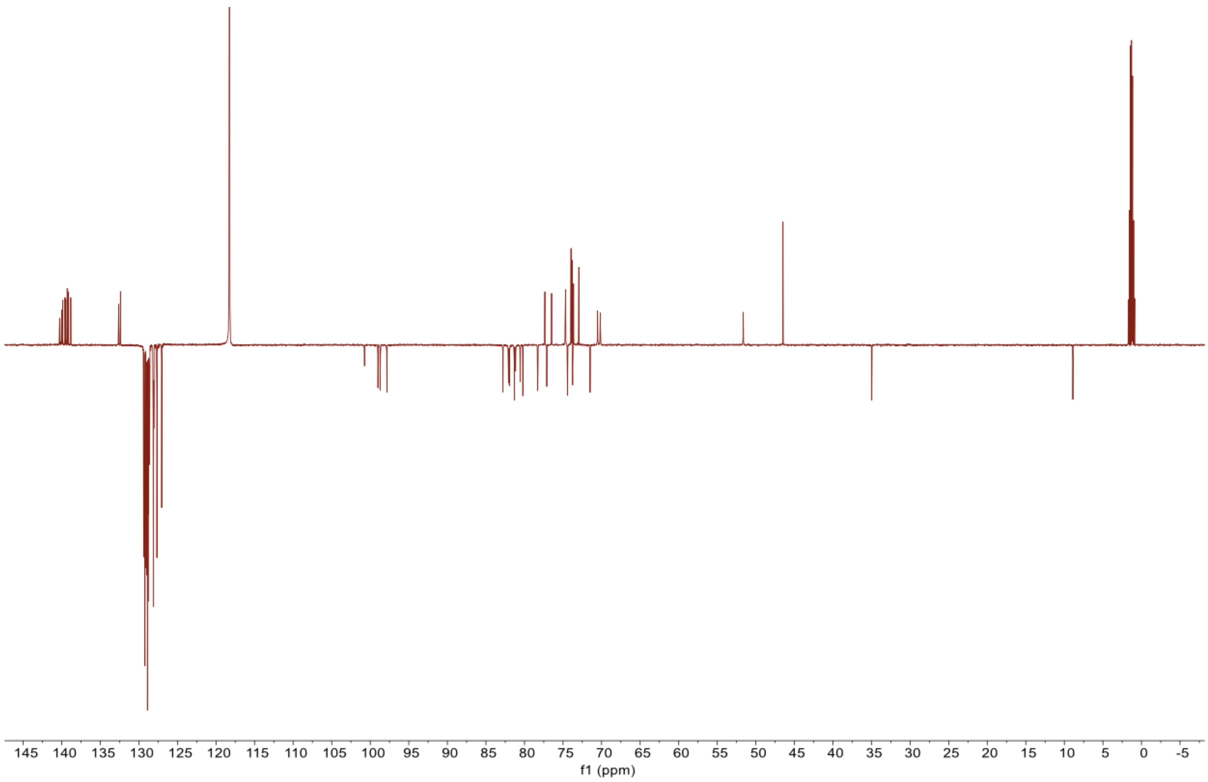
1

Chemical Formula: $C_{158}H_{164}Cl_2N_4O_{28}$
Molecular Weight: 2637,9500

A mixture of mono-azolium iodide **4** (1 g, 0.389 mmol) and K_2CO_3 (59.1 mg, 0.428 mmol) in dry acetonitrile (30 mL) was stirred at 20 °C for 0.5 h. Iodomethane (0.048 mL, 0.778 mmol) was added and the resulting mixture was stirred at 20 °C for 27 h. The mixture was poured into DCM (50 mL) and washed with water (3 × 30 mL). The organic phase was dried over $MgSO_4$ and concentrated under vacuum. The as-obtained residue was dissolved in dry acetonitrile (10 mL) and a second portion of iodomethane (0.25 mL, 4.02 mmol) was added. The resulting solution was stirred at 80 °C for 22 h. After cooling, the reaction mixture was poured into DCM (50 mL), washed with water (3 × 30 mL), and dried over $MgSO_4$. After filtration, the solution was concentrated to ca. 10–15 mL, Amberlite® IRA-410 chloride form (3 g) was added, and the suspension was stirred for 2 h. The chloride resin was filtered off, rinsed with DCM (20 mL), and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel (DCM/MeOH, 25:1) to give compound **1** as a pale yellow powder in 55% yields over three steps (562 mg, 0.213 mmol). **Rf** 0.4 (DCM/MeOH, 7:1). **^{1}H NMR** (CD_3CN, 600 MHz, 300K): δ 10.88 (s, 1H, external N-C*H*=N+), 10.45 (s, 1H, internal N-C*H*=N+), 8.93 (s, 2H, 2 × CH_{arom} BBI), 7.38–7.07 (m, 66H, 66 × H_{arom}), 7.02–6.99 (m, 4H, 4 × H_{arom}), 6.90–6.83 (m, 6H, 6 × H_{arom}), 6.64 (d, J = 7.3 Hz, 4H, 4 × H_{arom}), 5.78 (d, J = 3.6 Hz, 2H, 2 × H-1^{C,F}), 5.46 (d, J = 10.6 Hz, 2H, 2 × H-C*H*Ph), 5.35 (t, $^2J_{6a,6b}$ = 12.5 Hz, 2H, 2 × H-6^{A,D}), 5.13 (d, J = 10.5 Hz, 2H, 2 × H-C*H*Ph), 4.90 (d, J= 3.1 Hz, 2H, 2 × H-1^{A,D}), 4.89 – 4.77 (m, 10H, 2 × H-5^{A,D}, 2 × H-6'^{A,D}, 6 × H-C*H*Ph), 4.76 (d,J= 3.3 Hz, 2H, 2 × H-1^{B,E}), 4.71 (d, J = 11.2 Hz, 2H, 2 × H-C*H*Ph), 4.65 (d, J = 10.5 Hz, 2H, 2 × H-C*H*Ph), 4.61 –4.34 (m, 16H, 2 × H-3^{C,F}, 14 × H-C*H*Ph), 4.12–3.92 (m, 16H, 2 × H-4^{C,F}, 2 × H-6^{C,F}, 2 × H-3^{A,D}, 2 × H-4^{A,D}, 2 × H-3^{B,E}, 2 × N-CH_3), 3.91 – 3.84 (m, 4H, 2 × H-5^{C,F}, 2 × H-6'^{C,F}), 3.79 (d, J = 13.3 Hz, 2H, 2 × H-C*H*Ph), 3.67 (d, J = 13.4 Hz, 2H, 2 × H-C*H*Ph), 3.65–3.55 (m, 8H, 2 × H-2^{C,F}, 2 × H-2^{A,D}, 2 × H-4^{B,E}, 2 × H-5^{B,E}), 3.32 (dd, J = 9.9 and 3.3 Hz, 2H, 2 × H-2^{B,E}), 3.16 (d, J = 11.0 Hz, 2H, 2 × H-6^{B,E}), 2.78 (dd, J = 11.2 and 6.4 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** (CD_3CN, 150 MHz, 300K): δ 148.62 (external N-*C*H=N+), 140.28, 140.01, 139.88, 139.58, 139.47, 139.29, 139.18, 138.83 (16 × Cq Ar), 132.63 (2 × external N-*C*=*C*-N), 132.39 (2 × internal N-*C*=*C*-N), 129.38, 129.25, 129.21, 129.05, 128.97, 128.95, 128.91, 128.89, 128.81, 128.79, 128.74, 128.67, 128.64, 128.61, 128.15, 128.12, 128.10, 128.07, 127.67, 127.04 (80 × *C*H Ar), 100.75 (2 × central *C*H BBI), 99.00 (2 × C-1^{C,F}), 98.69 (2 × C-1^{A,D}), 97.84 (2 × C-1^{B,E}), 82.79 (2 × C-4^{B,E}), 82.07 (2 × C-4^{C,F}), 81.96 (2 × C-3^{A,D}), 81.33 (2 × C-3^{B,E}), 81.16 (2 × C-3^{C,F}), 80.56 (2 × C-2^{A,D}), 80.21 (2 × C-2^{B,E}), 78.29 (2 × C-2^{C,F}), 77.36 (2 × *C*H_2Ph), 77.11 (2 × C-4 ^{A,D}), 76.49, 74.69, 74.67 (6 × *C*H_2Ph), 74.43 (2 × C-5^{C,F}), 73.96, 73.84 (4 × *C*H_2Ph), 73.75 (2 × C-5^{B,E}), 73.64, 72.95 (4 × *C*H_2Ph), 71.50 (2 × C-5^{A,D}), 70.52 (2 × C-6^{C,F}), 70.17 (2 × C-6^{B,E}), 51.63 (2 × C-6^{A,D}), 34.97 (2 × N-CH_3) ppm. The ^{13}C signal of internal N-*C*H=N+ was not detected. **HRMS** (ESI, micrOTOF) *m/z* calcd. for $C_{158}H_{164}N_4O_{28}$ [M-2Cl]$^{2+}$ 1282.5761, found 1282.5774 (err. -1.1 ppm).

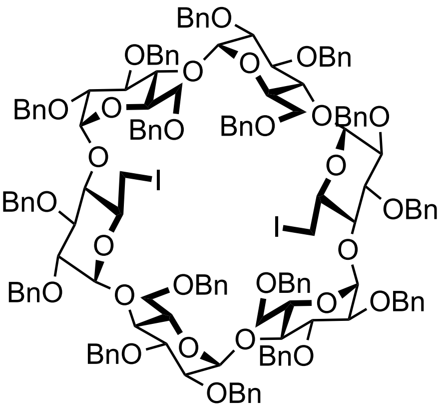


^1H NMR spectrum in CD_3CN (300 K, 600 MHz)



^{13}C NMR spectrum in CD_3CN (300 K, 151 MHz)

Di-iodo-α-CD^{Bn} (3)[4]

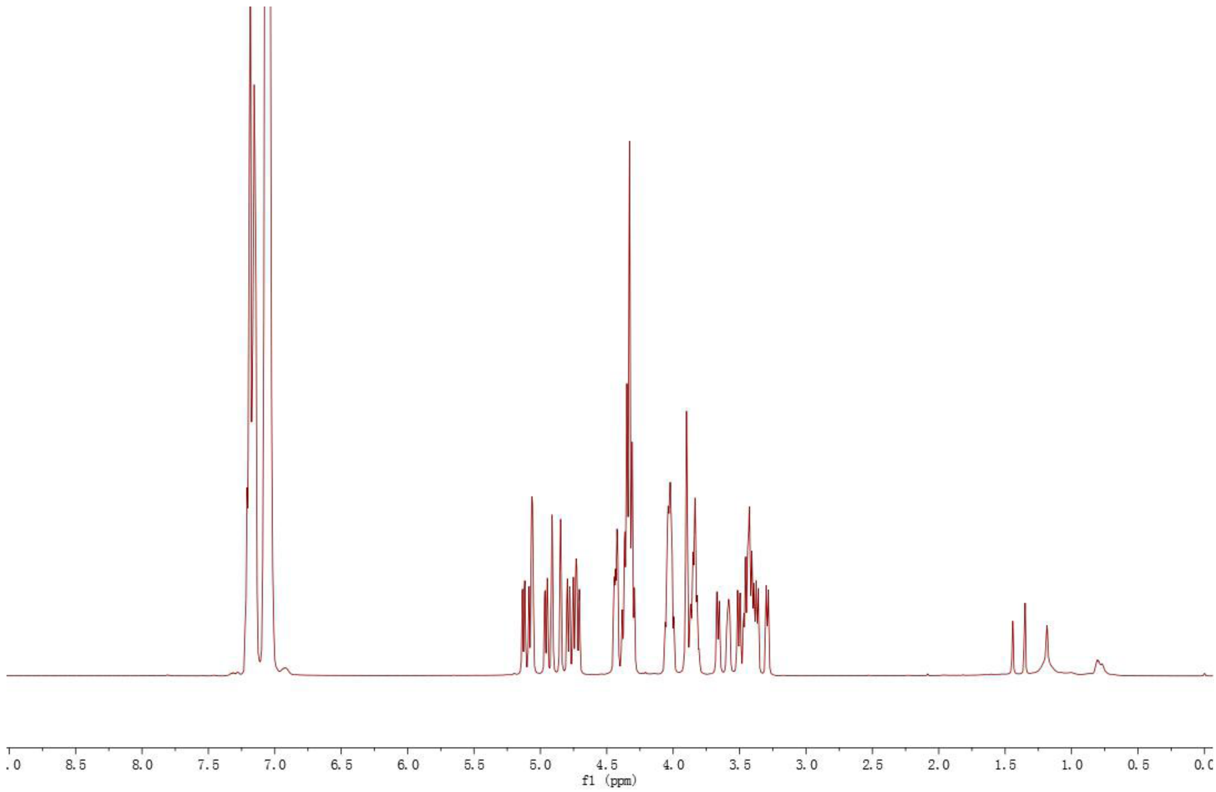


3

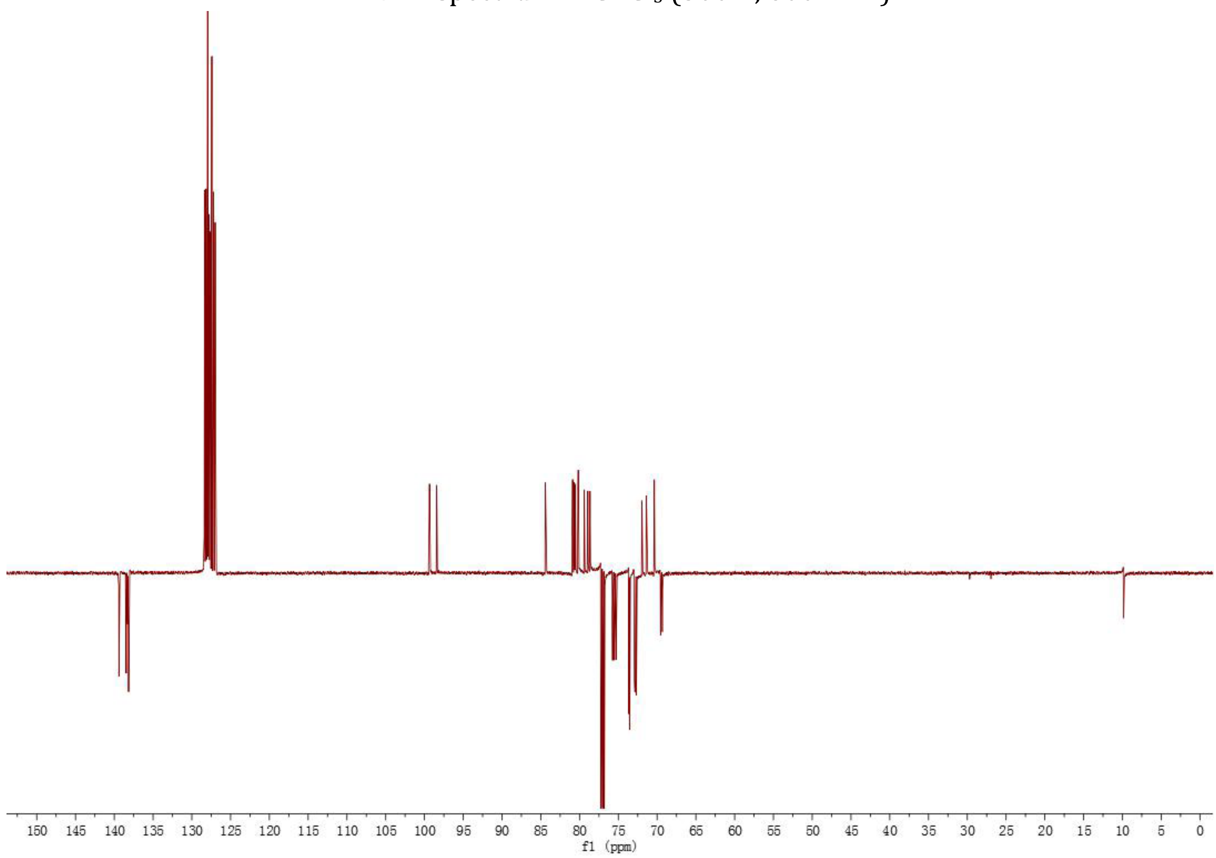
Chemical Formula: $C_{148}H_{154}I_2O_{28}$
Molecular Weight: 2634,6409

A mixture of **di-OMs-α-CD^{Bn} (2)**[1] (5.0 g, 1.94 mmol) and NaI (2.92 g, 19.45 mmol) in dry acetone (100 mL) was refluxed at 65 °C for 18 h. After cooling, DCM (100 mL) and water (100 mL) were added. The organic phase was separated and the aqueous layer was extracted with DCM (50 mL × 2). The combined organic phases were washed with brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The as-obtained residue was purified by column chromatography on silica gel (*c*Hex/EtOAc, 7:1) to give compound **3** as a white powder in 92% yield (4.7 g, 1.78 mmol). **Rf** 0.5 (*c*Hex/EtOAc, 3:1). (**^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.26–6.97 (m, 80H, 80 × H_{arom}), 5.13 (dd, J = 11.0 and 2.7 Hz, 2H, 2 × H-C*H*Ph), 5.10–5.02 (m, 4H, 2 × H-C*H*Ph, 2 × H-1^{CF}), 4.96 (dd, J = 11.0 and 2.8 Hz, 2H, 2 × H-C*H*Ph), 4.91 (d, J = 4.0 Hz, 2H, 2 × H-1^{BE}), 4.85 (d, J = 3.8 Hz, 2H, 2 × H-1^{AD}), 4.79 (dd, J = 11.0 and 2.8 Hz, 2H, 2 × H-C*H*Ph), 4.77–4.68 (m, 4H, 4 × H-C*H*Ph), 4.47–4.26 (m, 20H, 20 × H-C*H*Ph), 4.10–3.96 (m, 8H, 2 × H-3^{BE}, 2 × H-3^{AD}, 2 × H-3^{CF}, 2 × H-6^{BE}), 3.92–3.87 (d, J = 4.4 Hz, 4H, 2 × H-4^{BE}, 2 × H-5^{BE}), 3.89–3.78 (m, 6H, 2 × H-6^{CF}, 2 × H-5^{CF}, 2 × H-4^{CF}), 3.66 (d, J = 10.5 Hz, 2H, 2 × H-6^{CF}), 3.59 (dd, J = 8.8 and 4.1 Hz, 2H, 2 × H-5^{AD}), 3.50 (d, J = 11.2 Hz, 2H, 2 × H-6^{BE}), 3.48–3.33 (m, 10H, 2 × H-2^{CF}, 2 × H-2^{BE}, 4 × H-6^{AD}, 2 × H-4^{AD}), 3.29 (d, J = 9.8 Hz, 2H, 2 × H-2^{AD}) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.40, 139.38, 139.31, 138.46, 138.27, 138.17, 138.16, 138.09 (16 × Cq_{arom}), 128.38, 128.34, 128.20, 128.17, 128.16, 128.12, 127.98, 127.97, 127.86, 127.81, 127.79, 127.69, 127.63, 127.62, 127.49, 127.42, 127.20, 126.99, 126.94, 126.91, 126.89 (80 × CH_{arom}), 99.39 (2 × C-1^{BE}), 99.35 (2 × C-1^{AD}), 98.42 (2 × C-1^{CF}), 84.41 (2 × C-4^{AD}), 80.89 (2 × C-3^{BE}), 80.73 (2 × C-3^{CF}), 80.57 (2 × C-4^{CF}), 80.21 (2 × C-4^{BE}), 80.17 (2 × C-3^{AD}), 79.40 (2 × C-2^{AD}), 78.93 (2 × C-2^{BE}), 78.65 (2 × C-2^{CF}), 75.74, 75.52, 75.30 (6 × O*C*H_2Ph), 73.64, 73.53, 72.94, 72.85, 72.67 (10 × O*C*H_2Ph), 71.97 (2 × C-5^{CF}), 71.39 (2 × C-5^{BE}), 70.36 (2 × C-5^{AD}), 69.55 (2 × C-6^{CF}), 69.33 (2 × C-6^{BE}), 9.84 (2 × C-6^{AD}) ppm. **HRMS** (ESI, micrOTOF) m/z calcd. for $C_{148}H_{154}I_2O_{28}$ $[M+Na]^+$ 2655.8608, found 2655.8703 (err. -3.6 ppm).

[4] The protocol was adapted from Guangcan Xu PhD Thesis, Sorbonne-Université, 08/07/2021, Paris.

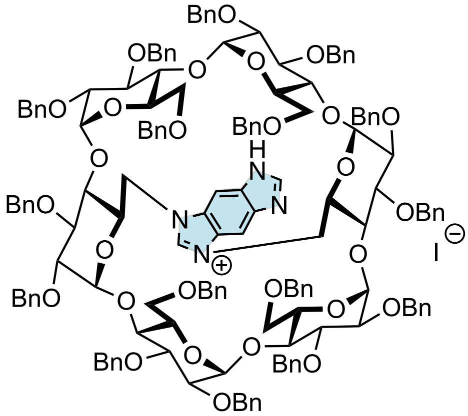


^{1}H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)



^{13}C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

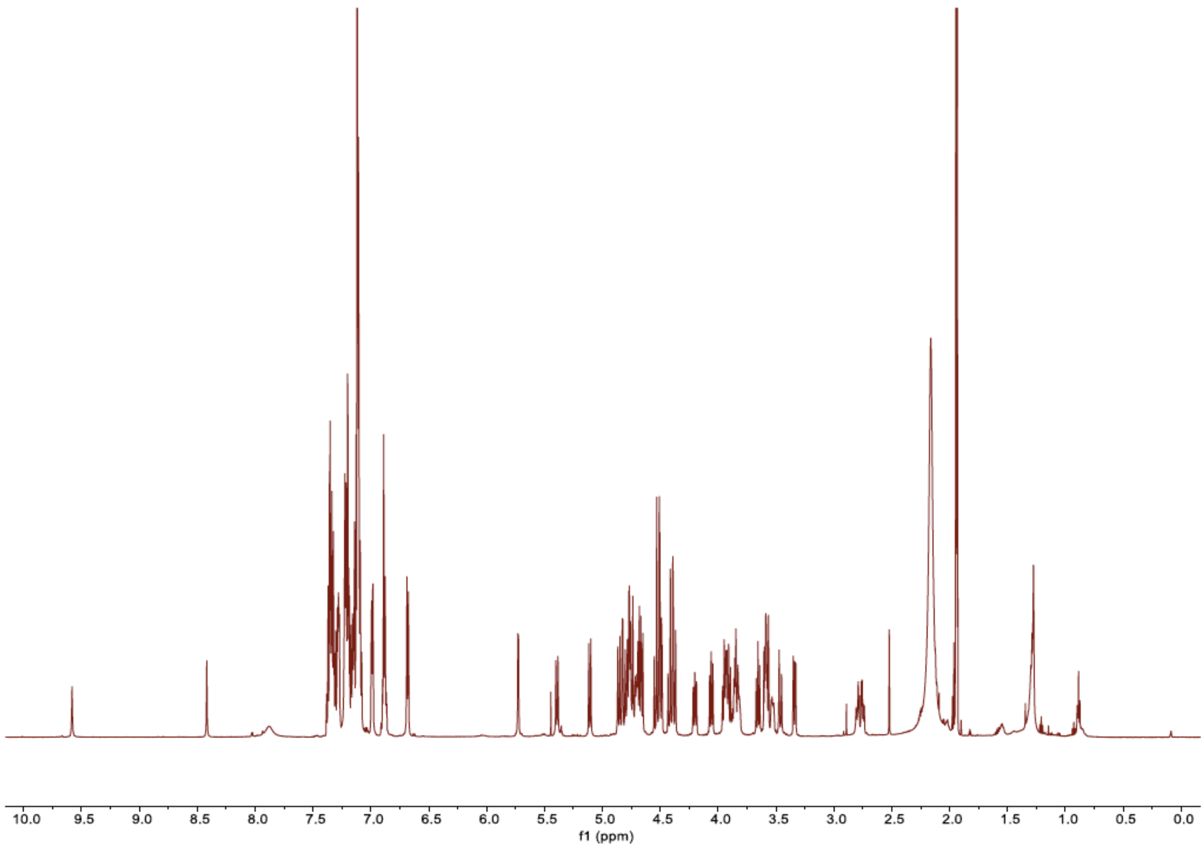
α-CD^Bn^(BBI) mono-azolium iodide (**4**)



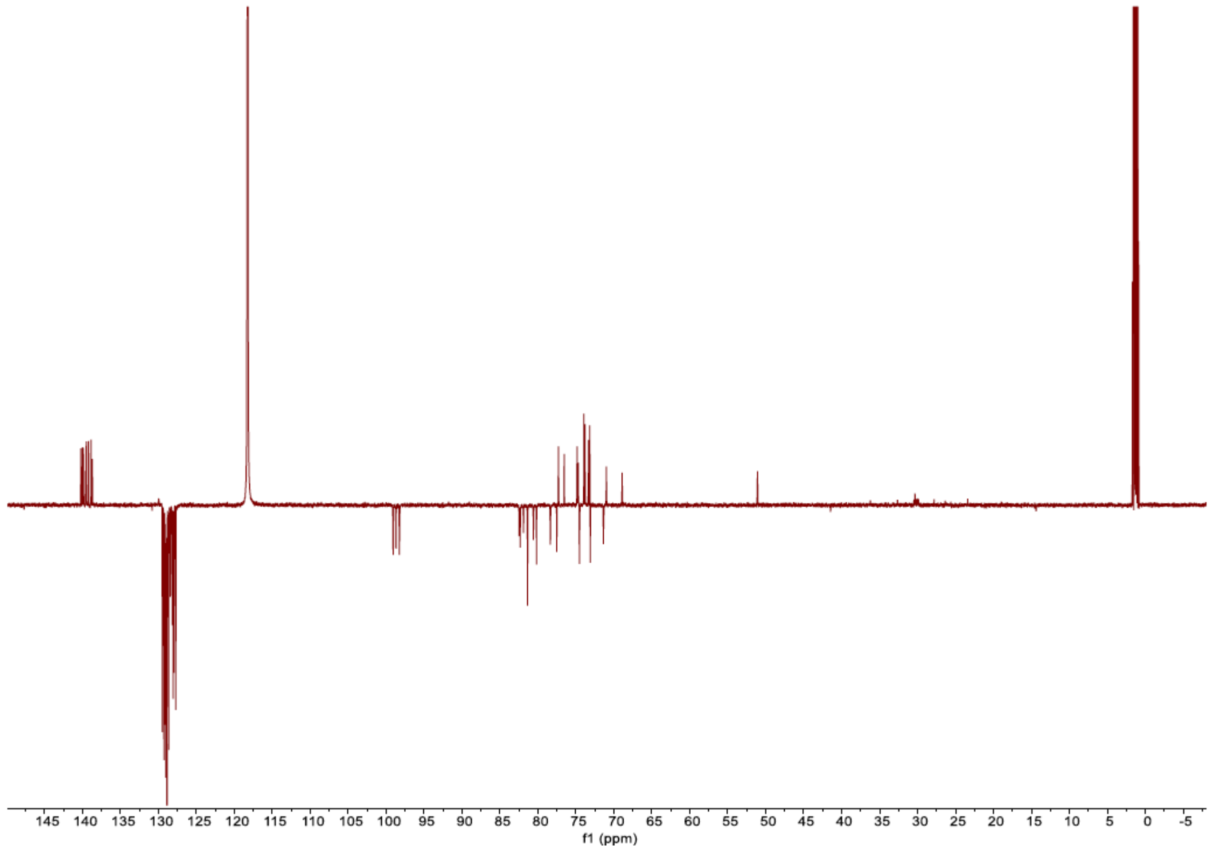
4

Chemical Formula: $C_{156}H_{159}IN_4O_{28}$
Molecular Weight: 2664,8919

A solution of **di-iodo-α-CD^{Bn} 3** (2.0 g, 0.76 mmol) and benzobis(imidazole) (BBI) (1.2 g, 7.6 mmol) in dry DMSO (20 mL) was heated at 120 °C for 32 h. After cooling, DMSO was eliminated under vacuum. DCM was added. After stirring, the solid residue which is obtained was filtered off and rinsed with several portions of DCM. The filtrate (DCM solution) was washed with water, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (DCM/MeOH, 80:1) to give compound **4** as a pale yellow powder in 51% yield (1.04 g, 0.39 mmol). **Rf** 0.4 (DCM/MeOH, 7:1). **^{1}H NMR** (CD_3CN, 600 MHz, 300K): δ 9.58 (s, 1H, internal N-C*H*=N+), 8.42 (s, 1H, external N-C*H*=N), 7.88 (s, 2H, 2 × CH_{arom} BBI), 7.40–7.26 (m, 20H, 20 × H_{arom}), 7.25–7.06 (m, 46H, 46 × H_{arom}), 6.99 (dd, *J* = 7.6 and 1.9 Hz, 4H, 4 × H_{arom}), 6.93–6.83 (m, 6H, 6 × H_{arom}), 6.68 (d, *J* = 7.4 Hz, 4H, 4 × H_{arom}), 5.73 (d, $^3J_{1,2}$ = 3.7 Hz, 2H, 2 × H-1^{C,F}), 5.39 (d, *J* = 10.7 Hz, 2H, 2 × H-C*H*Ph), 5.11 (d, *J* = 10.4 Hz, 2H, 2 × H-C*H*Ph), 4.86 (d, *J* = 11.5 Hz, 2H, 2 × H-C*H*Ph), 4.83 (d, *J* = 3.1 Hz, 2H, 2 × H-1^{A,D}), 4.79 (d, *J* = 10.7 Hz, 2H, 2 × H-C*H*Ph), 4.77 (d, *J* = 3.3 Hz, 2H, 2 × H-1^{B,E}), 4.75 (d, *J* = 11.2 Hz, 2H, 2 × H-6^{A,D}), 4.73–4.64 (m, 8H, 2 × H-5^{A,D}, 2 × H-6'^{A,D}, 4 × H-C*H*Ph), 4.58–4.34 (m, 16H, 16 × H-C*H*Ph), 4.20 (dd, *J* = 10.1 and 7.9 Hz, 2H, 2 × H-3^{C,F}), 4.06 (dd, *J* = 9.7 and 7.7 Hz, 2H, 2 × H-3^{A,D}), 3.98–3.79 (m, 12H, 2 × H-6^{C,F}, 2 × H-6'^{C,F}, 2 × H-4^{C,F}, 2 × H-5^{C,F}, 2 × H-4^{A,D}, 2 × H-3^{B,E}), 3.66 (dd, *J* = 9.7 and 8.5 Hz, 2H, 2 × H-4^{B,E}), 3.62–3.51 (m, 8H, 2 × H-2^{C,F}, 2 × H-2^{A,D}, 2 × H-5^{B,E}, 2 × H-C*H*Ph), 3.46 (d, *J* = 12.4 Hz, 2H, 2 × H-C*H*Ph), 3.34 (dd, *J* = 9.9 and 3.3 Hz, 2H, 2 × H-2^{B,E}), 2.83–2.71 (m, 4H, 2 × H-6^{B,E}, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** (CD_3CN, 150 MHz, 300K): δ 147.70 (external N-*C*H=N), 140.20, 140.01, 139.90, 139.59, 139.50, 139.21 (12 × Cq Ar), 138.87 (internal N-*C*H=N), 138.71 (2 × Cq Ar), 135.08 (2 × external N-*C*=*C*-N), 129.99 (2 × internal N-*C*=*C*-N), 129.48, 129.29, 129.27, 129.25, 129.14, 129.09, 129.03, 129.00, 128.98, 128.94, 128.89, 128.74, 128.70, 128.66, 128.44, 128.22, 128.17, 128.06, 127.95, 127.71 (82 × *C*H Ar), 99.08 (2 × C-1^{C,F}), 98.70 (2 × C-1^{A,D}), 98.25 (2 × C-1^{B,E}), 82.49 (2 × C-4^{C,F}), 82.36 (2 × C-4^{B,E}), 81.92 (2 × C-3^{A,D}), 81.39 (2 × C-3^{C,F}, 2 × C-3^{B,E}), 80.66 (2 × C-2^{A,D}), 80.21 (2 × C-2^{B,E}), 78.39 (2 × C-2^{C,F}), 77.53 (2 × C-4^{A,D}), 77.30, 76.54, 74.85, 74.70 (8 × *C*H_2Ph), 74.54 (2 × C-5^{C,F}), 73.96, 73.80 (4 × *C*H_2Ph), 73.33 (2 × *C*H_2Ph), 73.18(2 × *C*H_2Ph), 73.11 (2 × C-5^{B,E}), 71.37 (2 × C-5^{A,D}), 70.99 (2 × C-6^{C,F}), 68.92 (2 × C-6^{B,E}), 51.08 (2 × C-6^{A,D}) ppm. The ^{13}C signal of BBI *C*H_{arom} was not detected. **HRMS** (ESI, micrOTOF) *m*/*z* calcd. for $C_{156}H_{159}N_4O_{28}$ [M-I]$^+$ 2536.1135, found 2536.1130 (err. 0.2 ppm).

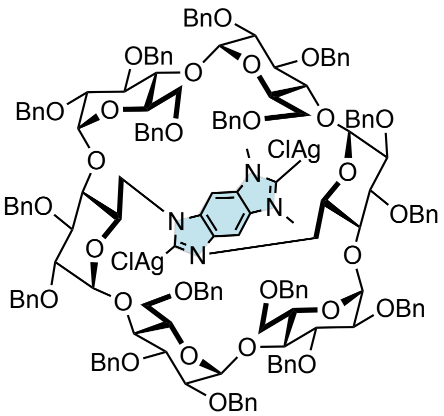


[1]H NMR spectrum in CD_3CN (300 K, 600 MHz)



[13]C NMR spectrum in CD_3CN (300 K, 151 MHz)

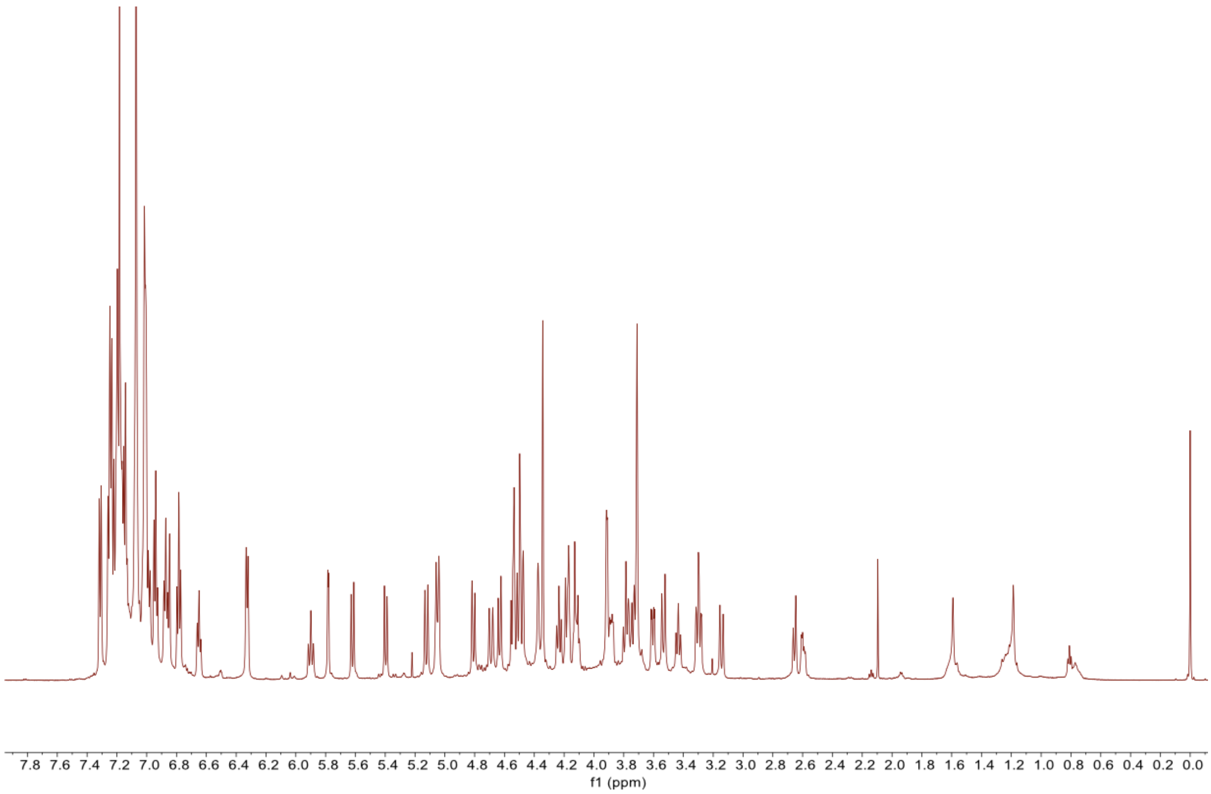
α-CD^{Bn}(BBI) bis-silver complex (**5**)



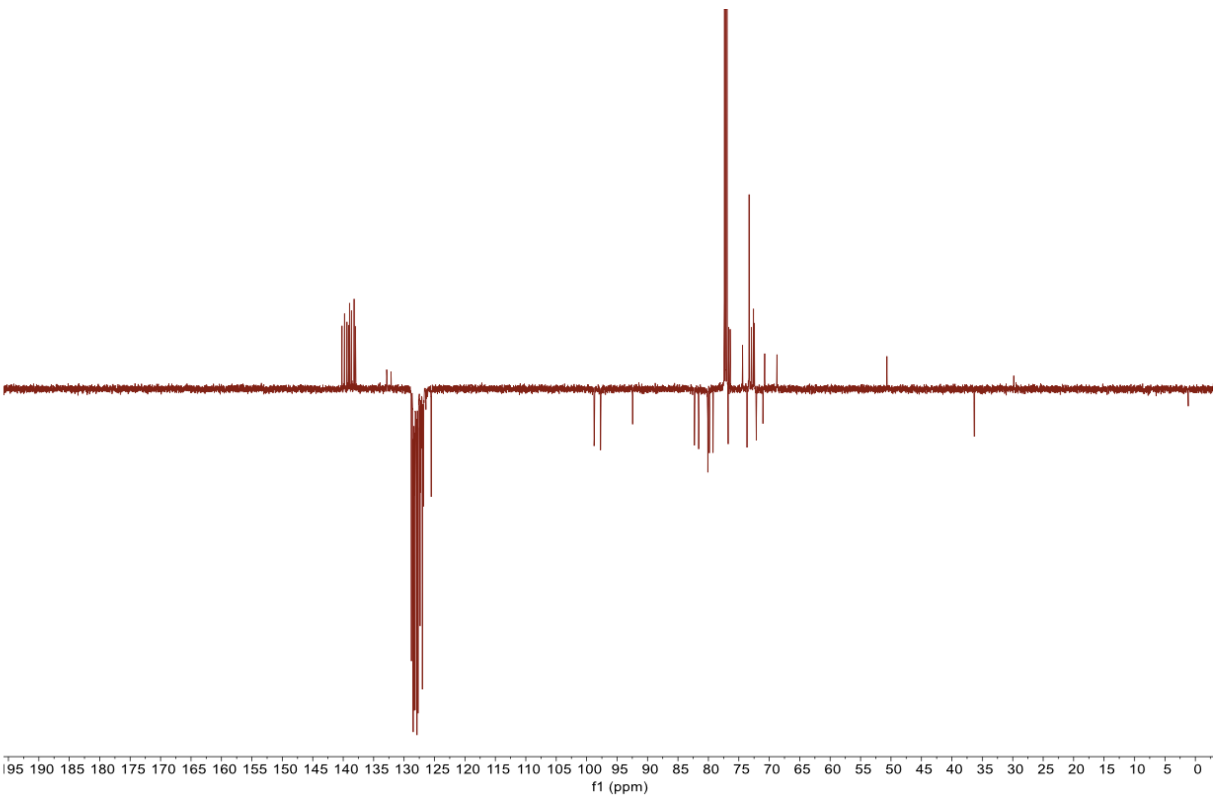
5

Chemical Formula: $C_{158}H_{162}Ag_2Cl_2N_4O_{28}$
Molecular Weight: 2851,6704

A mixture of bis-azolium **1** (500 mg, 0.19 mmol) and Ag_2O (148 mg, 0.64 mmol) in dry and degassed DCM (1.5 mL) was stirred at 45 °C for 44 h with exclusion of light (protection using an aluminum foil). The brown suspension was filtered over Celite and the filtrate was concentrated and dried under vacuum to give compound **5** as a brown powder in 98% yield (531 mg, 0.186 mmol). **Rf** 0.5 (DCM/MeOH, 7:1). **^{1}H NMR** ($CDCl_3$, 600 MHz, 300K): δ 7.31 (d, J = 7.7 Hz, 4H, 4 × H_{arom}), 7.28–7.11 (m, 26H, 26 × H_{arom}), 7.10–6.97 (m, 32H, 32 × H_{arom}), 6.94 (t, J = 7.4 Hz, 4H, 4 × H_{arom}), 6.87 (t, J = 7.5 Hz, 4H, 4 × H_{arom}), 6.85 (s, 2H, 2 × CH_{arom} BBI), 6.78 (t, J = 7.5 Hz, 4H, 4 × H_{arom}), 6.65 (t, J = 7.4 Hz, 2H, 2 × H_{arom}), 6.33 (d, J = 7.5 Hz, 4H, 4 × H_{arom}), 5.90 (t, J = 10.1 Hz, 2H, 2 × H-5^{A,D}), 5.78 (d, J = 3.8 Hz, 2H, 2 × H-1^{C,F}), 5.62 (d, J = 10.5 Hz, 2H, 2 × H-C*H*Ph), 5.40 (d, J = 10.5 Hz, 2H, 2 × H-C*H*Ph), 5.12 (d, J = 12.0 Hz, 2H, 2 × H-C*H*Ph), 5.08 – 5.02 (m, 4H, 2 × H-3^{C,F}, 2 × H-C*H*Ph), 4.81 (d, J = 11.3 Hz, 2H, 2 × H-C*H*Ph), 4.69 (d, J = 14.1 Hz, 2H, 2 × H-6^{A,D}), 4.63 (d, J = 11.1 Hz, 2H, 2 × H-C*H*Ph), 4.56– 4.45 (m, 10 H, 2 × H-1^{B,E}, 8 × H-C*H*Ph), 4.39–4.32 (m, 6H, 2 × H-1^{A,D}, 4 × H-C*H*Ph), 4.24 (t, J = 9.3 Hz, 2H, 2 × H-3^{B,E}), 4.20–4.15 (m, 4H, 2 × H-3^{A,D}, 2 × H-C*H*Ph), 4.15–4.08 (m, 4H, 2 × H-6'^{A,D}, 2 × H-C*H*Ph), 3.93–3.86 (m, 6H, 2 × H-4^{C,F}, 2 × H-5^{C,F}, 2 × H-5^{B,E}), 3.81–3.66 (m, 12H, 2 × H-6^{C,F}, 2 × H-6'^{C,F}, 2 × H-4^{A,D}, 2 × N-CH_3), 3.61 (dd, J = 10.1 Hz, J = 3.7 Hz, 2H, 2 × H-2^{C,F}), 3.53 (d, J = 12.9 Hz, 2H, 2 × H-C*H*Ph), 3.44 (t, J = 9.2 Hz, 2H, 2 × H-4^{B,E}), 3.32–3.26 (m, 4H, 2 × H-2^{A,D}, 2 × H-2^{B,E}), 3.14 (d, J = 13.1 Hz, 2H, 2 × H-C*H*Ph), 2.65 (d, J = 10.4 Hz, 2H, 2 × H-6^{B,E}), 2.59 (dd, J = 10.9 Hz, J = 5.0 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz, 300K): δ 193.38 (external $C_{carbene}$–Ag), 140.19, 139.79, 139.38, 139.09, 138.94, 138.66, 138.21, 137.98 (16 × Cq Ar), 132.84 (d, J = 6.5 Hz, 2 × internal N-*C*=*C*-N), 132.13 (2 × external N-*C*=*C*-N), 128.80, 128.51, 128.50, 128.47, 128.42, 128.40, 128.35, 128.31, 128.24, 128.04, 128.00, 127.98, 127.95, 127.89, 127.87, 127.84, 127.77, 127.74, 127.70, 127.37, 127.28, 127.17, 127.00, 126.95, 126.87, 126.80, 125.54 (80 × *C*H Ar), 98.75 (2 × C-1^{C,F}), 98.72 (2 × C-1^{A,D}), 97.71 (2 × C-1^{B,E}), 92.46 (2 × central *C*H BBI), 82.29 (2 × C-4 ^{C,F}), 82.24 (2 × C-4^{B,E}), 81.60 (2 × C-3^{A,D}), 80.10 (2 × C-2^{A,D}, 2 × C-3^{B,E}), 79.84 (2 × C-3^{C,F}), 79.23 (2 × C-2^{B,E}), 77.02 (2 × C-2^{C,F}), 76.75 (2 × C-4^{A,D}), 76.67, 76.42, 74.38 (6 × *C*H_2Ph), 73.66 (2 × C-5^{C,F}), 73.32, 72.92, 72.58, 72.45 (8 × *C*H_2Ph), 72.13 (2 × C-5^{B,E}), 71.05 (2 × C-5^{A,D}), 70.75 (2 × C-6^{C,F}, 2 × *C*H_2Ph), 68.75 (2 × C-6^{B,E}), 50.66 (2 × C-6^{A,D}), 36.32 (2 × N-*C*H_3) ppm. The ^{13}C signal of the internal $C_{carbene}$–Ag could not be detected. **HRMS ESI-TOF**: *m/z* calcd. for $C_{158}H_{162}Ag_2Cl_2N_4O_{28}Na$ $[M+Na]^+$ 2869.8747, found 2869.8736 (err. 0.4 ppm).

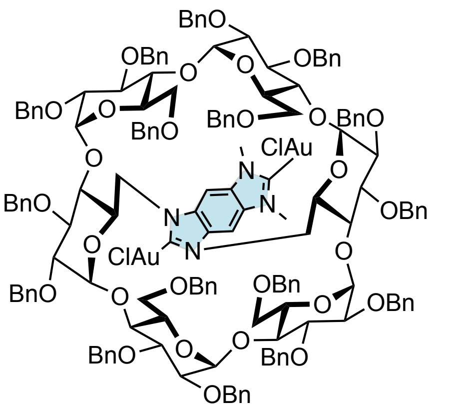


[1]H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)



[13]C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

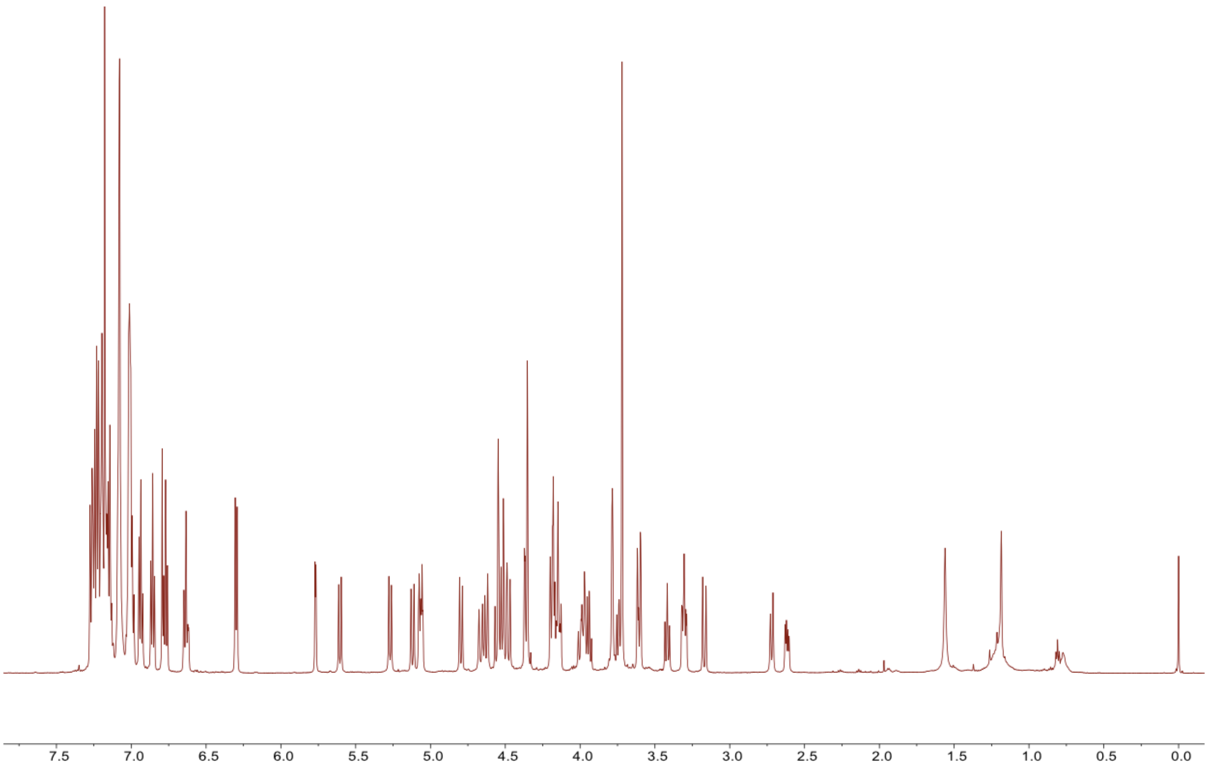
α-CD^{Bn}(BBI) bis-gold(I) complex (6)



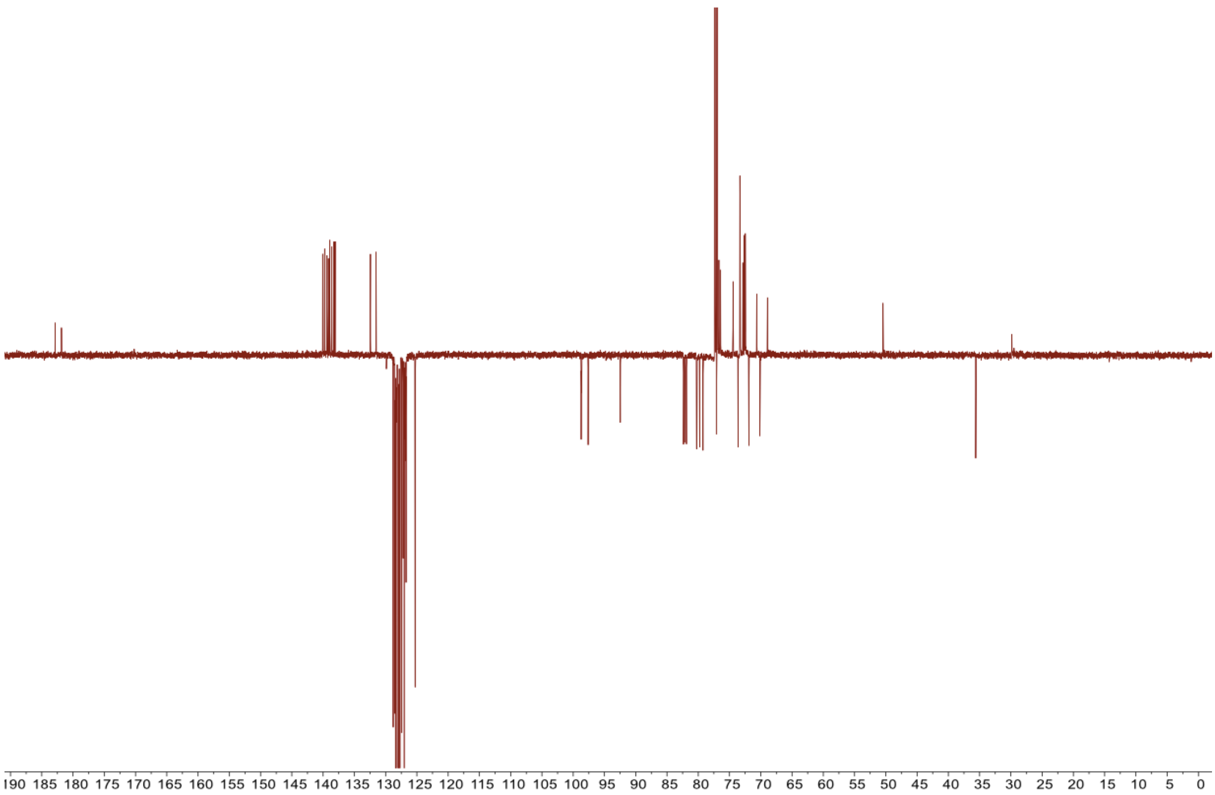
6

Chemical Formula: $C_{158}H_{162}Au_2Cl_2N_4O_{28}$
Molecular Weight: 3029,8671

Complex **6** was initially obtained in low yield (8%) from the bis-azolium salt **1**, K_2CO_3 and an excess of $AuCl.SMe_2$ (see Figure 3 in the main text). The alternative optimized procedure from Pd(allyl)Cl complex **10** is presented here: A mixture of **10** (38.8 mg, 0.014 mmol), $AuCl.SMe_2$ (16.4 mg, 0.06 mmol) and K_2CO_3 (26.9 mg, 0.2 mmol) in dry and degassed DCM (1 mL) was stirred at 60 °C for 43 h with exclusion of light (using an aluminum foil). After cooling, the reaction mixture was filtered off over a 0.2 μm PET filter, the precipitate was rinsed with DCM, and the filtrate was concentrated under vacuum. The as-obtained residue was purified by chromatography on a silica gel preparative glass plate (*c*Hex/EtOAc, 2:1) to give compound **6** as a white powder in 31% yield (13.1 mg, 0.004 mmol). **Rf** 0.4 (*c*Hex/EtOAc, 2:1). **^{1}H NMR** ($CDCl_3$, 600 MHz, 300K): δ 7.29–7.11 (m, 30H, 30 × H_{arom}), 7.11–6.98 (m, 32H, 32 × H_{arom}), 6.94 (t, *J* = 7.4 Hz, 4H, 4 × H_{arom}), 6.86 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.79 (s, 2H, 2 × CH_{arom} BBI), 6.77 (t, *J* = 7.6 Hz, 4H, 4 × H_{arom}), 6.66–6.61 (m, 4H, 2 × H-5^{A,D}, 2 × H_{arom}), 6.30 (d, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 5.77 (d, *J* = 3.7 Hz, 2H, 2 × H-1^{C,F}), 5.60 (d, *J* = 10.4 Hz, 2H, 2 × H-C*H*Ph), 5.27 (d, *J* = 10.4 Hz, 2H, 2 × H-C*H*Ph), 5.12 (d, *J* = 12.0 Hz, 2H, 2 × H-C*H*Ph), 5.09–5.03 (m, 4H, 2 × H-3^{C,F}, 2 × H-C*H*Ph), 4.80 (d, *J* = 11.2 Hz, 2H, 2 × H-C*H*Ph), 4.69–4.60 (m, 4H, 2 × H-6^{A,D}, 2 × H-C*H*Ph), 4.58–4.46 (m, 12H, 2 × H-1^{B,E}, 10 × H-C*H*Ph), 4.38–4.34 (m, 6H, 2 × H-1^{A,D}, 4 × H-C*H*Ph), 4.21–4.11 (m, 10H, 2 × H-3^{A,D}, 2 × H-3^{B,E}, 2 × H-5^{B,E}, 4 × H-C*H*Ph), 4.02–3.92 (m, 6H, 2 × H-6'^{A,D}, 2 × H-4^{C,F}, 2 × H-5^{C,F}), 3.81–3.73 (m, 6H, 2 × H-4^{A,D}, 2 × H-6^{C,F}, 2 × H-6'^{C,F}), 3.72 (s, 6H, 2 × N-CH_3), 3.63–3.58 (m, 4H, 2 × H-2^{C,F}, 2 × H-C*H*Ph), 3.42 (t, *J* = 9.2 Hz, 2H, 2 × H-4^{B,E}), 3.33–3.28 (m, 4H, 2 × H-2^{A,D}, 2 × H-2^{B,E}), 3.17 (d, *J* = 13.3 Hz, 2H, 2 × H-C*H*Ph), 2.72 (d, *J* = 10.5 Hz, 2H, 2 × H-6^{B,E}), 2.62 (dd, *J* = 10.7 and 5.1 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz, 300K): δ 182.85 (external $C_{carbene}$–Au), 181.85 (internal $C_{carbene}$–Au), 140.07, 139.75, 139.37, 139.14, 138.94, 138.63, 138.26, 138.07 (16 × Cq Ar), 132.42 (2 × internal N-*C*=*C*-N), 131.54 (2 × external N-*C*=*C*-N), 128.79, 128.52, 128.48, 128.42, 128.32, 128.25, 128.02, 128.00, 127.96, 127.88, 127.77, 127.70, 127.69, 127.42, 127.19, 127.03, 126.95, 126.84, 126.80, 126.73, 125.28 (80 × *C*H Ar), 98.72 (2 × C-1^{A,D}), 98.67 (2 × C-1^{C,F}), 97.61 (2 × C-1^{B,E}), 92.46 (2 × central *C*H BBI), 82.36 (2 × C-4^{B,E}), 82.20 (2 × C-4 ^{C,F}), 81.89 (2 × C-3^{A,D}), 80.27 (2 × C-2^{A,D}), 80.21 (2 × C-3^{B,E}), 79.78 (2 × C-3^{C,F}), 79.24 (2 × C-2^{B,E}), 77.10 (2 × C-2^{C,F}), 76.99 (2 × C-4^{A,D}), 76.69, 76.44, 74.43 (6 × *C*H_2Ph), 73.63 (2 × C-5^{C,F}), 73.34, 73.29, 72.87, 72.62, 72.47 (10 × *C*H_2Ph), 71.90 (2 × C-5^{B,E}), 70.64 (2 × C-6^{C,F}), 70.14 (2 × C-5^{A,D}), 68.92 (2 × C-6^{B,E}), 50.45 (2 × C-6^{A,D}), 35.62 (2 × N-*C*H_3) ppm. **HRMS ESI-TOF**: *m/z* calcd. for $C_{158}H_{162}Au_2Cl_2N_4O_{28}Na$ $[M+Na]^+$ 3049.9976, found 3049.9972 (err. 0.2 ppm).

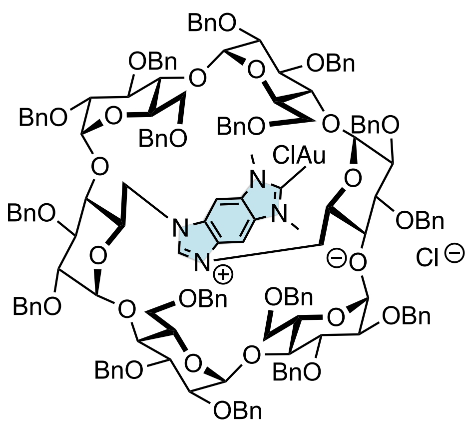


^{1}H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)



^{13}C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

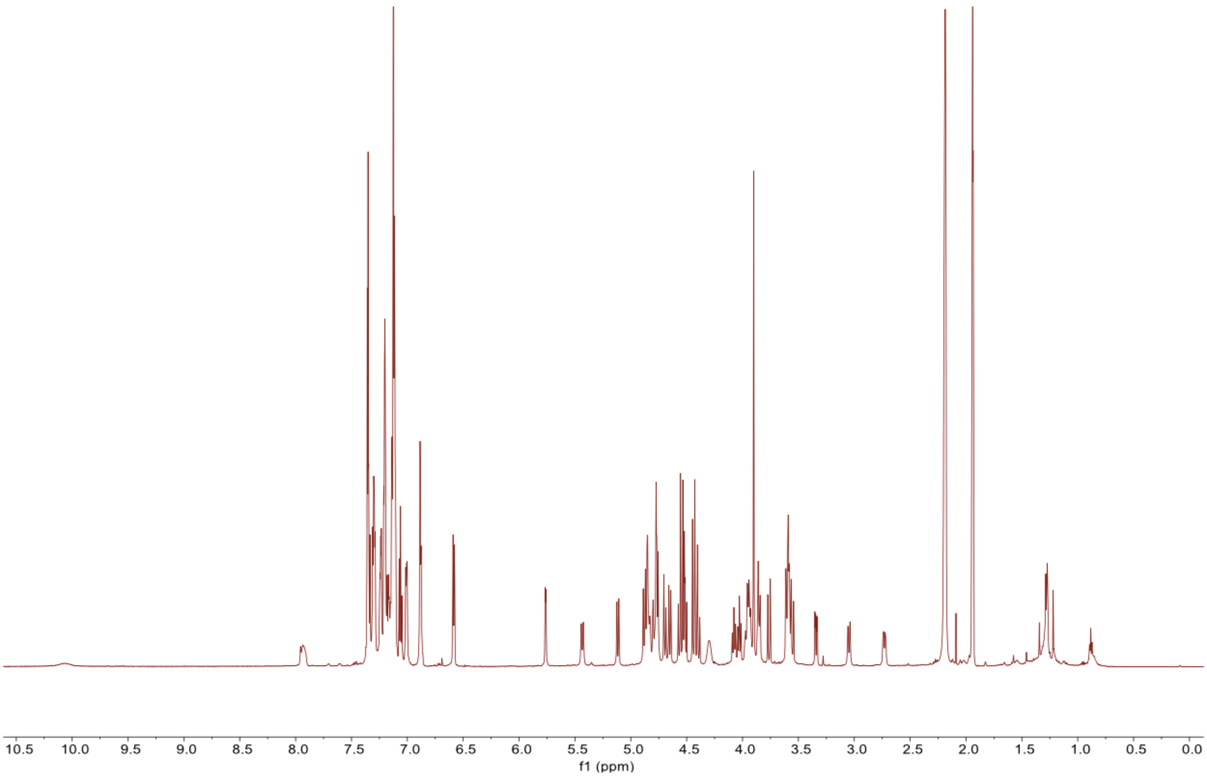
α-CD^{Bn}(BBI) mono-gold(I) complex (**7**)



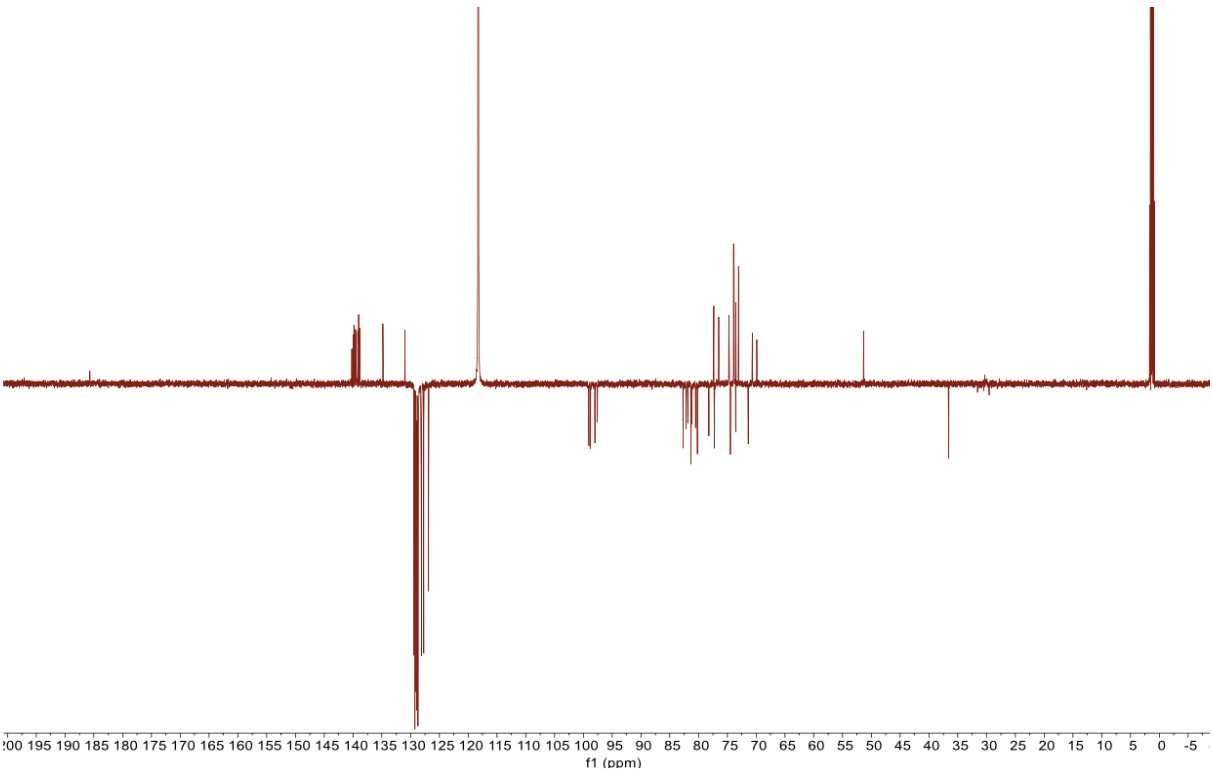
7

Chemical Formula: $C_{158}H_{163}AuClN_4O_{28}$
Molecular Weight: 2798,4586

A mixture of bis-azolium **1** (40 mg, 0.015 mmol), AuCl.SMe$_2$ (4.5 mg, 0.015 mmol, 1 equiv.) and K_2CO_3 (4.2 mg, 0.03 mmol) in dry and degassed DCM (1 mL) was stirred at 40 °C for 39 h with exclusion of light (using an aluminum foil). After cooling, the reaction mixture was filtered off over a 0.2 μm PET filter, the filter was rinsed with DCM, and the filtrate was concentrated under vacuum. The as-obtained residue was purified by column chromatography on silica gel (DCM/MeOH, 30:1) to give **7** in 32% yield (13.7 mg, 0.005 mmol). **Rf** 0.5 (DCM/MeOH, 7:1). **^{1}H NMR** (CD_3CN, 600 MHz, 300K): δ 10.07 (s, 1H, internal N-C*H*=N+), 7.98–7.88 (m, 2H, 2 × CH_{arom} BBI), 7.38–6.98 (m, 70H, 70 × H_{arom}), 6.91–6.85 (m, 6H, 6 × H_{arom}), 6.58 (d, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 5.76 (d, *J* = 3.6 Hz, 2H, 2 × H-1^{C,F}), 5.43 (d, *J* = 10.5 Hz, 2H, 2 × H-C*H*Ph), 5.12 (d, *J* = 10.5 Hz, 2H, 2 × H-C*H*Ph), 4.90–4.73 (m, 16H, 2 × H-1^{A,D}, 2 × H-5^{A,D}, 2 × H-6^{A,D}, 2 × H-6'^{A,D}, 2 × H-1^{B,E}, 6 × H-C*H*Ph), 4.69 (d, *J* = 11.1 Hz, 2H, 2 × H-C*H*Ph), 4.65 (d, *J* = 10.5 Hz, 2H, 2 × H-C*H*Ph), 4.59–4.48 (m, 8H, 8 × H-C*H*Ph), 4.46–4.38 (m, 6H, 6 × H-C*H*Ph), 4.35–4.26 (m, 2H, 2 × H-3^{C,F}), 4.08 (t, *J* = 8.8 Hz, 2H, 2 × H-3^{A,D}), 4.03 (t, *J* = 8.3 Hz, 2H, 2 × H-4^{C,F}), 3.99–3.92 (m, 6H, 2 × H-6^{C,F}, 2 × H-4^{A,D}, 2 × H-3^{B,E}), 3.90 (s, 6H, 2 × N-CH_3), 3.88–3.83 (m, 4H, 2 × H-5^{C,F}, 2 × H-6'^{C,F}), 3.76 (d, *J* = 13.2 Hz, 2H, 2 × H-C*H*Ph), 3.63–3.53 (m, 10H, 2 × H-2^{C,F}, 2 × H-2^{A,D}, 2 × H-4^{B,E}, 2 × H-5^{B,E}, 2 × H-C*H*Ph), 3.35 (dd, *J* = 10.0 Hz, *J* = 3.3 Hz, 2H, 2 × H-2^{B,E}), 3.05 (d, *J* = 11.0 Hz, 2H, 2 × H-6^{B,E}), 2.73 (dd, *J* = 11.6 Hz, *J* = 4.3 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** (CD_3CN, 150 MHz, 300K): δ 185.69 ($C_{carbene}$–Au), 140.21, 139.99, 139.84, 139.55, 139.47, 139.18, 139.03, 138.83 (16 × Cq Ar), 134.82 (2 × external N-*C*=*C*-N), 131.00 (2 × internal N-*C*=*C*-N), 129.43, 129.27, 129.24, 129.05, 129.03, 129.00, 128.95, 128.93, 128.91, 128.80, 128.72, 128.70, 128.67, 128.64, 128.21, 128.16, 128.15, 128.13, 128.10, 127.72, 126.89 (80 × *C*H Ar), 99.05 (2 × C-1^{C,F}), 98.78 (2 × C-1^{A,D}), 98.00 (2 × C-1^{B,E}), 97.59 (2 × central *C*H BBI), 82.69 (2 × C-4^{B,E}), 82.18 (2 × C-4^{C,F}), 81.88 (2 × C-3^{A,D}), 81.31 (2 × C-3^{B,E}), 81.18 (2 × C-3^{C,F}), 80.53 (2 × C-2^{C,F}), 80.20 (2 × C-2^{B,E}), 78.21 (2 × C-2^{A,D}), 77.36 (2 × *C*H_2Ph), 77.26 (2 × C-4^{A,D}), 76.51, 74.74, 74.69 (6 × *C*H_2Ph), 74.49 (2 × C-5^{C,F}), 73.92, 73.84 (4 × *C*H_2Ph), 73.56 (2 × C-5^{B,E}), 73.54 (2 × *C*H_2Ph), 73.06 (2 × *C*H_2Ph), 71.38 (2 × C-5^{A,D}), 70.67 (2 × C-6^{C,F}), 69.89 (2 × C-6^{B,E}), 51.35 (2 × C-6^{A,D}), 36.57 (2 × N-*C*H_3) ppm. The ^{13}C signal of internal N-*C*H=N+ could not be detected. **HRMS ESI-TOF**: *m/z* calcd. for $C_{158}H_{163}AuClN_4O_{28}$ $[M-Cl]^+$ 2796.0802, found 2796.0914 (err. -4.0 ppm).

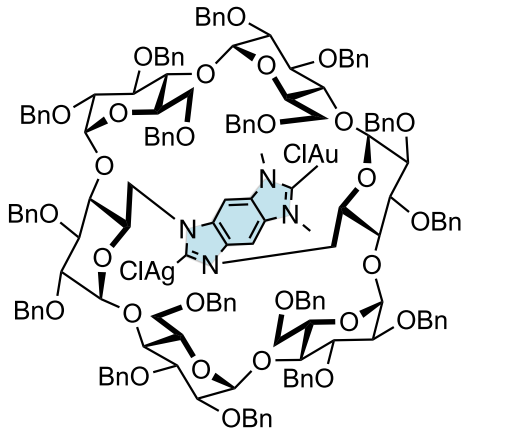


^{1}H NMR spectrum in CD_3CN (300 K, 600 MHz)



^{13}C NMR spectrum in CD_3CN (300 K, 151 MHz)

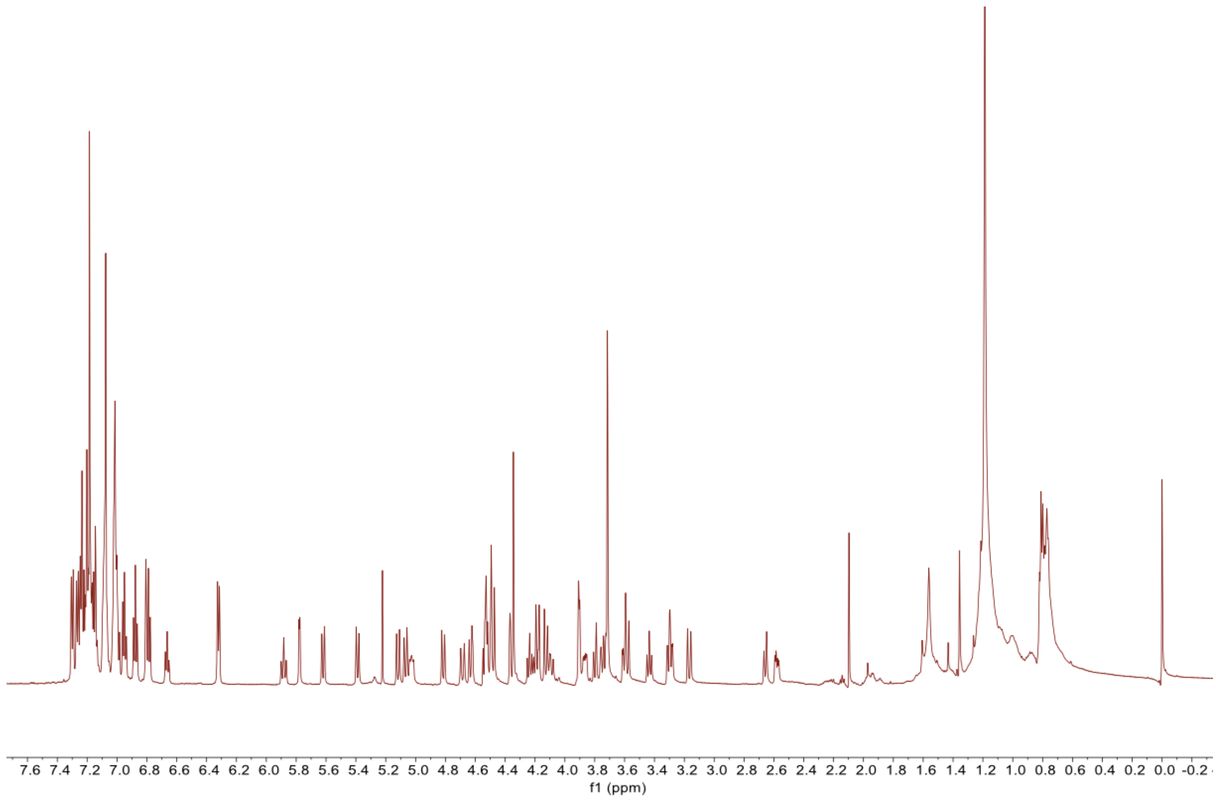
α-CD^{Bn}(BBI) gold(I)/silver(I) complex (8)



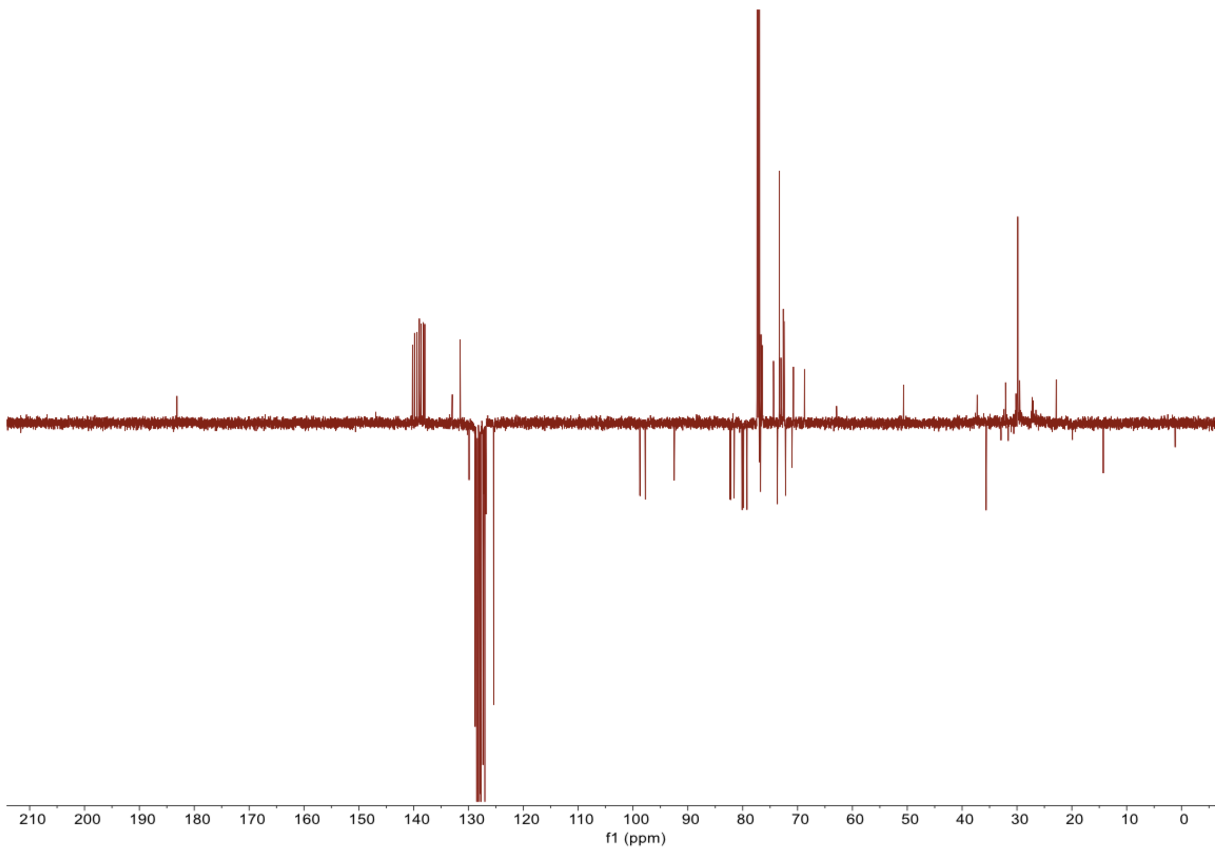
8

Chemical Formula: $C_{158}H_{162}AgAuCl_2N_4O_{28}$
Molecular Weight: 2940,7688

A solution of bis-silver complex **5** (500 mg, 0.175 mmol) and AuCl.SMe_2 (76.2 mg, 0.259 mmol, 1.5 equiv.) in dry and degassed DCM (10 mL) was stirred at 20 °C for 21 h with exclusion of light. A black purple suspension formed which was filtered off over a 0.2 μm PET filter. The black precipitate in the filter was rinsed with DCM, and the combined filtrates were concentrated under vacuum. The as-obtained residue was purified by column chromatography on silica gel (*c*Hex/EtOAc, 3:1) to give **8** as a white powder in 59% yield (304 mg, 0.103 mmol). **Rf** 0.5 (*c*Hex/EtOAc, 3:2). **^{1}H NMR** ($CDCl_3$, 600 MHz, 300K): δ 7.30 (d, *J* = 7.7 Hz, 4H, 4 × H_{arom}), 7.28–6.97 (m, 58H, 58 × H_{arom}), 6.95 (t, *J* = 7.4 Hz, 4H, 4 × H_{arom}), 6.88 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.82–6.77 (m, 6H, 2 × CH_{arom} BBI, 4 × H_{arom}), 6.66 (t, *J* = 7.4 Hz, 2H, 2 × H_{arom}), 6.32 (d, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 5.88 (t, *J* = 10.1 Hz, 2H, 2 × H-5^{A,D}), 5.78 (d, *J* = 3.7 Hz, 2H, 2 × H-1^{C,F}), 5.62 (d, *J* = 10.6 Hz, 2H, 2 × H-C*H*Ph), 5.39 (d, *J* = 10.6 Hz, 2H, 2 × H-C*H*Ph), 5.12 (d, *J* = 11.9 Hz, 2H, 2 × H-C*H*Ph), 5.07 (d, *J* = 11.4 Hz, 2H, 2 × H-C*H*Ph), 5.05–5.00 (m, 2H, 2 × H-3^{C,F}), 4.81 (d, *J* = 11.3 Hz, 2H, 2 × H-C*H*Ph), 4.69 (d, *J* = 14.1 Hz, 2H, 2 × H-C*H*Ph), 4.65–4.59 (m, 2H, 2 × H-6^{A,D}), 4.57–4.46 (m, 10H, 2 × H-1^{B,E}, 8 × H-C*H*Ph), 4.38–4.32 (m, 6H, 2 × H-1^{A,D}, 4 × H-C*H*Ph), 4.26–4.16 (m, 6H, 2 × H-3^{A,D}, 2 × H-3^{B,E}, 2 × H-C*H*Ph), 4.15–4.05 (m, 4H, 2 × H-6'^{A,D}, 2 × H-C*H*Ph), 3.94–3.83 (m, 6H, 2 × H-4^{C,F}, 2 × H-5^{C,F}, 2 × H-5^{B,E}), 3.81–3.72 (m, 6H, 2 × H-6^{C,F}, 2 × H-6'^{C,F}, 2 × H-4^{A,D}), 3.71 (s, 6H, 2 × N-CH_3), 3.63–3.55 (m, 4H, 2 × H-2^{C,F}, 2 × H-C*H*Ph), 3.44 (t, *J* = 9.2 Hz, 2H, 2 × H-4^{B,E}), 3.33–3.25 (m, 4H, 2 × H-2^{A,D}, 2 × H-2^{B,E}), 3.17 (d, *J* = 13.1 Hz, 2H, 2 × H-C*H*Ph), 2.66 (d, *J* = 10.6 Hz, 2H, 2 × H-6^{B,E}), 2.58 (dd, *J* = 10.8 Hz, *J* = 5.0 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz, 300K): *δ* 189.93 ($C_{carbene}$–Ag), 183.15 ($C_{carbene}$–Au), 140.20, 139.83, 139.38, 139.02, 138.95, 138.65, 138.22, 137.97 (16 × Cq Ar), 132.97 (d, *J* = 6.8 Hz, 2 × internal N-*C*=*C*-N), 131.52 (2 × external N-*C*=*C*-N), 129.89, 128.78, 128.51, 128.43, 128.31, 128.25, 128.03, 128.01, 127.99, 127.90, 127.88, 127.77, 127.71, 127.37, 127.27, 127.18, 127.03, 127.01, 126.87, 126.84, 126.81, 125.41 (80 × *C*H Ar), 98.78 (2 × C-1^{C,F}), 98.72 (2 × C-1^{A,D}), 97.76 (2 × C-1^{B,E}), 92.49 (2 × central *C*H BBI), 82.31 (2 × C-4^{C,F}), 82.22 (2 × C-4^{B,E}), 81.56 (2 × C-3^{A,D}), 80.13 (2 × C-2^{A,D}), 80.09 (2 × C-3^{B,E}), 79.86 (2 × C-3^{C,F}), 79.22 (2 × C-2^{B,E}), 76.98 (2 × C-2^{C,F}), 76.76 (2 × C-4^{A,D}), 76.67 , 76.43, 74.39 (6 × *C*H_2Ph), 73.68 (2 × C-5^{C,F}), 73.33, 73.03, 72.61, 72.48 (8 × *C*H_2Ph), 72.18 (2 × C-5^{B,E}), 71.02 (2 × C-5^{A,D}), 70.75 (2 × C-6^{C,F}, 2 × *C*H_2Ph), 68.73 (2 × C-6^{B,E}), 50.68 (2 × C-6^{A,D}), 35.62 (2 × N-*C*H_3) ppm. **HRMS ESI-TOF**: *m/z* calcd. for $C_{158}H_{162}AgAuClN_4O_{28}Na$ $[M-Cl]^+$ 2901.9775, found 2901.9724 (err. 1.8 ppm).

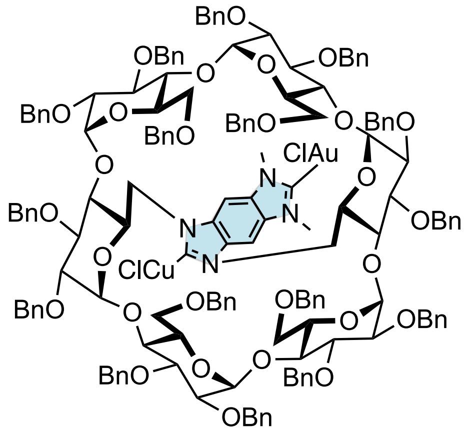


^{1}H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)



^{13}C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

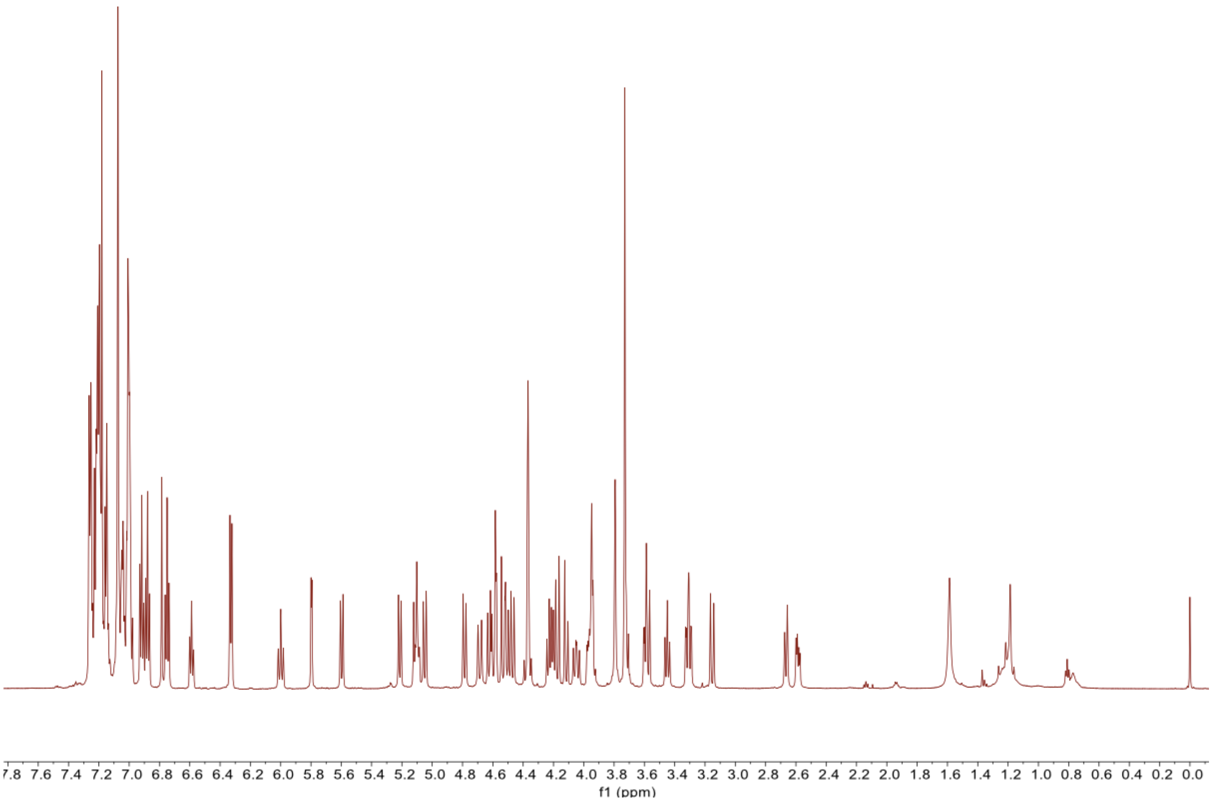
α-CD^{Bn}(BBI) gold(I)/copper(I) complex (**9**)



9

Chemical Formula: $C_{158}H_{162}AuCl_2CuN_4O_{28}$
Molecular Weight: 2896,4466

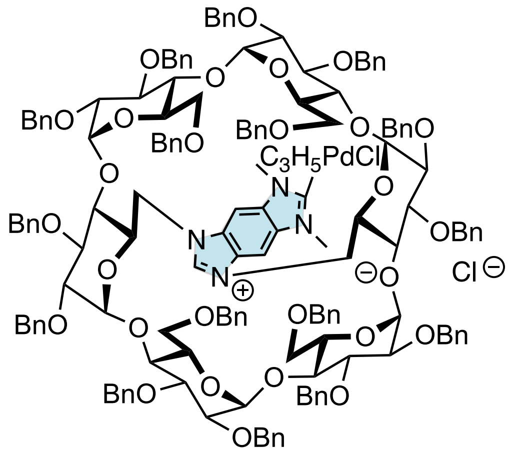
A mixture of gold(I)/silver(I) complex **8** (83.2 mg, 0.028 mmol) and CuCl (28 mg, 0.28 mmol) in dry and degassed DCM (2 mL) was stirred at 40 °C for 44 h with exclusion of light. A white suspension formed which was filtered off over a 0.2 μm PET filter and rinsed with DCM. The filtrate was concentrated under vacuum. The as-obtained residue was purified by column chromatography on silica gel (*c*Hex/EtOAc, 3:1) to give the title compound as a white powder in 78% yield (63.7 mg, 0.022 mmol). **Rf** 0.5 (*c*Hex/EtOAc, 3:2). **^{1}H NMR** ($CDCl_3$, 600 MHz, 300K): δ 7.30–7.11 (m, 30H, 30 × H_{arom}), 7.10–6.96 (m, 32H, 32 × H_{arom}), 6.92 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.88 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.79 (s, 2H, 2 × CH_{arom} BBI), 6.75 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.59 (t, *J* = 7.4 Hz, 2H, 2 × H_{arom}), 6.33 (d, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.00 (t, *J* = 10.1 Hz, 2H, 2 × H-5^{A,D}), 5.80 (d, *J* = 3.6 Hz, 2H, 2 × H-1^{C,F}), 5.60 (d, *J* = 10.2 Hz, 2H, 2 × H-C*H*Ph), 5.21 (d, *J* = 10.2 Hz, 2H, 2 × H-C*H*Ph), 5.14–5.07 (m, 4H, 2 × H-3^{C,F}, 2 × H-C*H*Ph), 5.05 (d, *J* = 11.3 Hz, 2H, 2 × H-C*H*Ph), 4.79 (d, *J* = 11.3 Hz, 2H, 2 × H-C*H*Ph), 4.69 (d, *J* = 13.9 Hz, 2H, 2 × H-6^{A,D}), 4.64–4.44 (m, 12H, 2 × H-1^{B,E}, 10 × H-C*H*Ph), 4.41–4.33 (m, 6H, 2 × H-1^{A,D}, 4 × H-C*H*Ph), 4.27–4.10 (m, 8H, 2 × H-3^{A,D}, 2 × H-3^{B,E}, 4 × H-C*H*Ph), 4.05 (dd, *J* = 14.0 and 10.2 Hz, 2H, 2 × H-6'^{A,D}), 4.00–3.91 (m, 6H, 2 × H-4^{C,F}, 2 × H-5^{C,F}, 2 × H-5^{B,E}), 3.79 (s, 4H, 2 × H-6^{C,F}, 2 × H-6'^{C,F}), 3.75 –3.70 (m, 8H, 2 × H-4^{A,D}, 2 × N-CH_3), 3.62–3.54 (m, 4H, 2 × H-2^{C,F}, 2 × H-C*H*Ph), 3.45 (t, *J* = 9.2 Hz, 2H, 2 × H-4^{B,E}), 3.37–3.26 (m, 4H, 2 × H-2^{A,D}, 2 × H-2^{B,E}), 3.15 (d, *J* = 13.2 Hz, 2H, 2 × H-C*H*Ph), 2.67 (d, *J* = 10.5 Hz, 2H, 2 × H-6^{B,E}), 2.59 (dd, *J* = 10.7 and 4.9 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz, 300K): δ 185.66 ($C_{carbene}$–Cu), 182.74 ($C_{carbene}$–Au), 139.89, 139.82, 139.37, 139.15, 138.92, 138.65, 138.25, 138.00 (16 × Cq Ar), 132.83 (2 × internal N-*C*=*C*-N), 131.40 (2 × external N-*C*=*C*-N), 128.97, 128.53, 128.50, 128.42, 128.41, 128.32, 128.22, 128.05, 128.03, 128.02, 127.88, 127.85, 127.78, 127.69, 127.54, 127.40, 127.22, 127.18, 127.01, 126.78, 126.76, 126.65, 125.40 (80 × *C*H Ar), 98.72 (2 × C-1^{A,D}), 98.55 (2 × C-1^{C,F}), 97.40 (2 × C-1^{B,E}), 92.30 (2 × central *C*H BBI), 82.24 (2 × C-4^{B,E}), 81.92 (2 × C-4^{C,F}), 81.56 (2 × C-3^{A,D}), 80.14 (2 × C-2^{A,D}), 80.09 (2 × C-3^{B,E}), 79.89 (2 × C-3^{C,F}), 79.34 (2 × C-2^{B,E}), 77.01 (2 × C-2^{C,F}), 76.69 (2 × C-4^{A,D}), 76.58, 76.55, 74.33 (6 × *C*H_2Ph), 73.59 (2 × C-5^{C,F}), 73.32, 72.81, 72.58, 72.45 (8 × *C*H_2Ph), 72.07 (2 × C-5^{B,E}), 71.66 (2 × C-5^{A,D}), 70.69 (2 × C-6^{C,F}, 2 × *C*H_2Ph), 68.77 (2 × C-6^{B,E}), 50.42 (2 × C-6^{A,D}), 35.61 (2 × N-CH_3) ppm. **HRMS ESI-TOF**: *m/z* calcd. for $C_{158}H_{162}AuCuCl_2N_4O_{28}Na$ $[M+Na]^+$ 2915.9606, found 2915. 9692 (err. -2.9 ppm)



^{1}H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)

^{13}C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

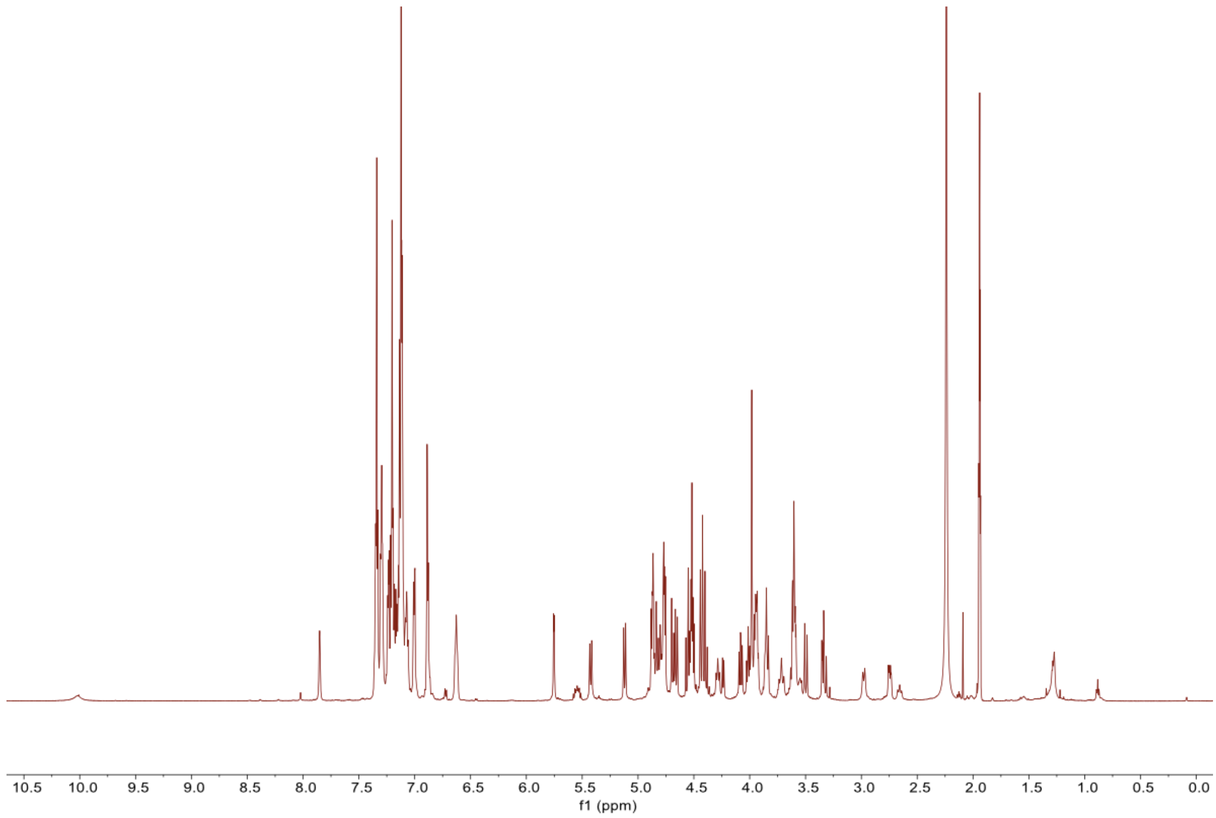
α-CD^{Bn}(BBI) palladium(II)(allyl)Cl complex (10)



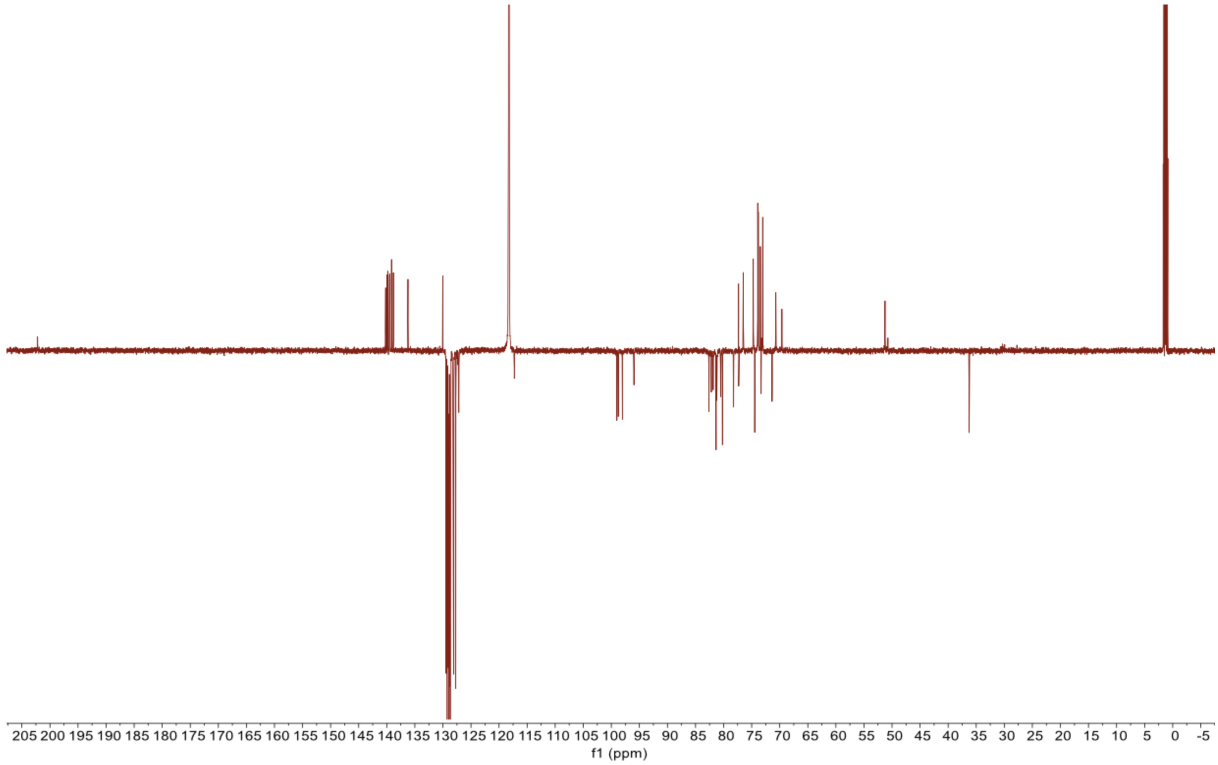
10

Chemical Formula: $C_{161}H_{168}Cl_2N_4O_{28}Pd^-$
Molecular Weight: 2784,4355

A mixture of bis-azolium **1** (200 mg, 0.075 mmol), $[Pd(allyl)Cl]_2$ dimer (16.5 mg, 0.045 mmol, 0.6 equiv.) and K_2CO_3 (146.7 mg, 1.05 mmol) in dry and degassed DCM (5 mL) was stirred at 20 °C for 19 h with exclusion of light. The reaction mixture was filtered off over a 0.2 μm PET filter (rinsing with DCM), and the filtrate was concentrated under vacuum. The as-obtained residue was purified by column chromatography on silica gel (DCM/MeOH, 30:1) to give the title compound as a pale yellow powder in 72% yield (153 mg, 0.054 mmol). **Rf** 0.5 (DCM/MeOH, 7:1). **^{1}H NMR** (CD_3CN, 600 MHz, 300K): δ 10.01 (s, 1H, internal N-C*H*=N+), 7.85 (s, 2H, 2 × CH_{arom} BBI), 7.39–6.97 (m, 70H, 70 × H_{arom}), 6.91–6.86 (m, 6H, 6 × H_{arom}), 6.66–6.60 (m, 4H, 4 × H_{arom}), 5.75 (d, *J* = 3.7 Hz, 2H, 2 × H-1^{C,F}), 5.59 – 5.49 (m, 1H, H-2$_{allyl}$), 5.42 (d, *J* = 10.6 Hz, 2H, 2 × H-C*H*Ph), 5.12 (d, *J* = 10.5 Hz, 2H, 2 × H-C*H*Ph), 4.92–4.74 (m, 16H, 2 × H-1^{A,D}, 2 × H-5^{A,D}, 2 × H-6^{A,D}, 2 × H-6'^{A,D}, 2 × H-1^{B,E}, 6 × H-C*H*Ph), 4.69 (d, *J* = 11.2 Hz, 2H, 2 × H-C*H*Ph), 4.66 (d, *J* = 10.5 Hz, 2H, 2 × H-C*H*Ph), 4.58–4.49 (m, 8H, 8 × H-C*H*Ph), 4.45–4.37 (m, 6H, 6 × H-C*H*Ph), 4.29 (t, *J* = 9.0 Hz, 2H, 2 × H-3^{C,F}), 4.24 (d, *J* = 7.8 Hz, 1H, H-1$_{allyl}$ *syn*), 4.11–4.06 (m, 2H, 2 × H-3^{A,D}), 4.01 (t, *J* = 8.4 Hz, 2H, 2 × H-4^{C,F}), 3.98 (s, 6H, 2 × N-CH_3), 3.97–3.92 (m, 6H, 2 × H-6^{C,F}, 2 × H-4^{A,D}, 2 × H-3^{B,E}), 3.87–3.82 (m, 4H, 2 × H-5^{C,F}, 2 × H-6'^{C,F}), 3.72 (t, *J* = 13.2 Hz, 2H, 2 × H-C*H*Ph), 3.64–3.57 (m, 8H, 2 × H-2^{C,F}, 2 × H-2^{A,D}, 2 × H-4^{B,E}, 2 × H-5^{B,E}), 3.57–3.52 (m, 1H, H-3$_{allyl}$ *syn*), 3.50 (d, *J* = 12.9 Hz, 2H, 2 × H-C*H*Ph), 3.34 (dd, *J* = 10.0 Hz and 3.1 Hz, 2H, 2 × H-2^{B,E}), 3.33 (d, *J* = 14.2 Hz, 1H, H-1$_{allyl}$ *anti*), 2.98 (d, *J* = 10.9 Hz, 2H, 2 × H-6^{B,E}), 2.75 (dd, *J* = 11.0 and 5.0 Hz, 2H, 2 × H-6'^{B,E}), 2.66 (t, *J* = 10.6 Hz, 1H, H-3$_{allyl}$ *anti*) ppm. **^{13}C NMR** (CD_3CN, 150 MHz, 300K): δ 202.20 ($C_{carbene}$–Pd), 140.20, 139.99, 139.83, 139.53, 139.47, 139.15, 138.85, 138.82 (16 × Cq Ar), 136.22 (2 × external N-*C*=*C*-N), 130.02 (2 × internal N-*C*=*C*-N), 129.42, 129.26, 129.23, 129.08, 129.03, 128.99, 128.94, 128.92, 128.90, 128.88, 128.80, 128.74, 128.70, 128.66, 128.64, 128.24, 128.20, 128.16, 128.13, 128.10, 128.08, 127.71, 127.17 (80 × *C*H Ar), 117.28 (C-2$_{allyl}$), 99.01 (2 × C-1^{C,F}), 98.75 (2 × C-1^{A,D}), 98.02 (2 × C-1^{B,E}), 95.97 (2 × central *C*H BBI), 82.61 (2 × C-4^{B,E}), 82.18 (2 × C-4^{C,F}), 81.86 (2 × C-3^{A,D}), 81.33 (2 × C-3^{B,E}), 81.20 (2 × C-3^{C,F}), 80.50 (2 × C-2^{A,D}), 80.20 (2 × C-2^{B,E}), 78.23 (2 × C-2^{C,F}), 77.33 (2 × *C*H_2Ph), 77.31 (2 × C-4^{A,D}), 76.50, 74.74, 74.71 (6 × *C*H_2Ph), 74.46 (2 × C-5^{C,F}), 73.92, 73.82, 73.45 (6 × *C*H_2Ph), 73.31 (2 × C-5^{B,E}), 73.23 (C-1$_{allyl}$), 73.04 (2 × *C*H_2Ph), 71.36 (2 × C-5^{A,D}), 70.69 (2 × C-6^{C,F}), 69.61 (2 × C-6^{B,E}), 51.24 (2 × C-6^{A,D}), 50.73 (C-3$_{allyl}$), 36.25 (2 × N-*C*H_3) ppm. The ^{13}C chemical shift of internal N-*C*H=N could not be detected. **HRMS ESI-TOF**: *m/z* calcd. for $C_{161}H_{168}PdClN_4O_{28}$ $[M-Cl]^+$ 2746.0611, found 2746.0680 (err. -2.5 ppm).

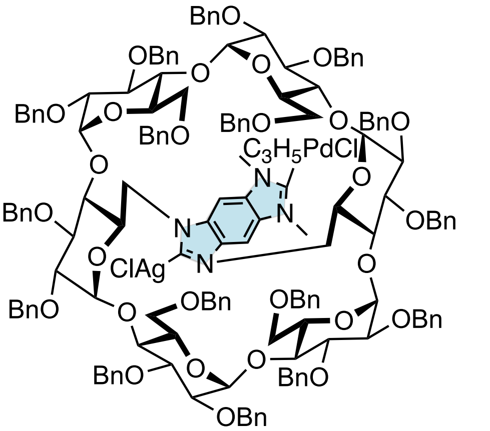


^{1}H NMR spectrum in CD_3CN (300 K, 600 MHz)



^{13}C NMR spectrum in CD_3CN (300 K, 151 MHz)

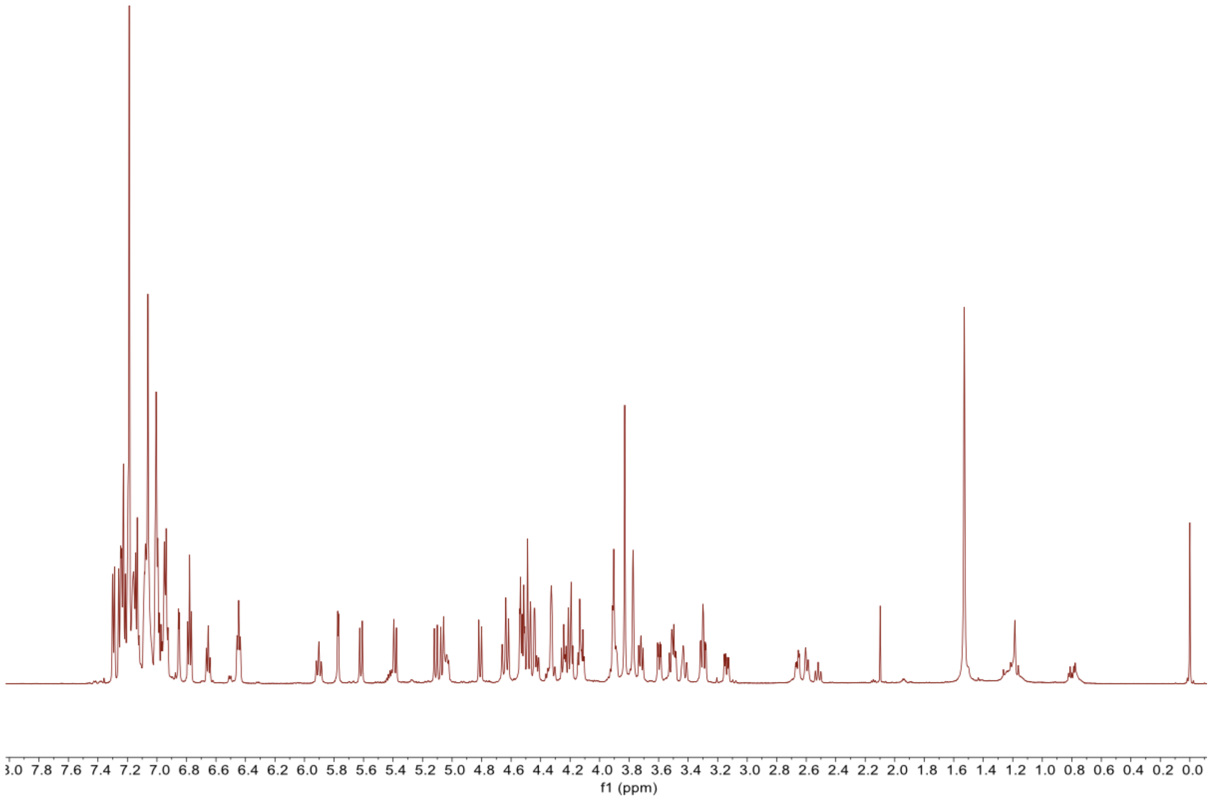
α-CD^{Bn}(BBI) palladium(II)/silver(I) complex (**11**)



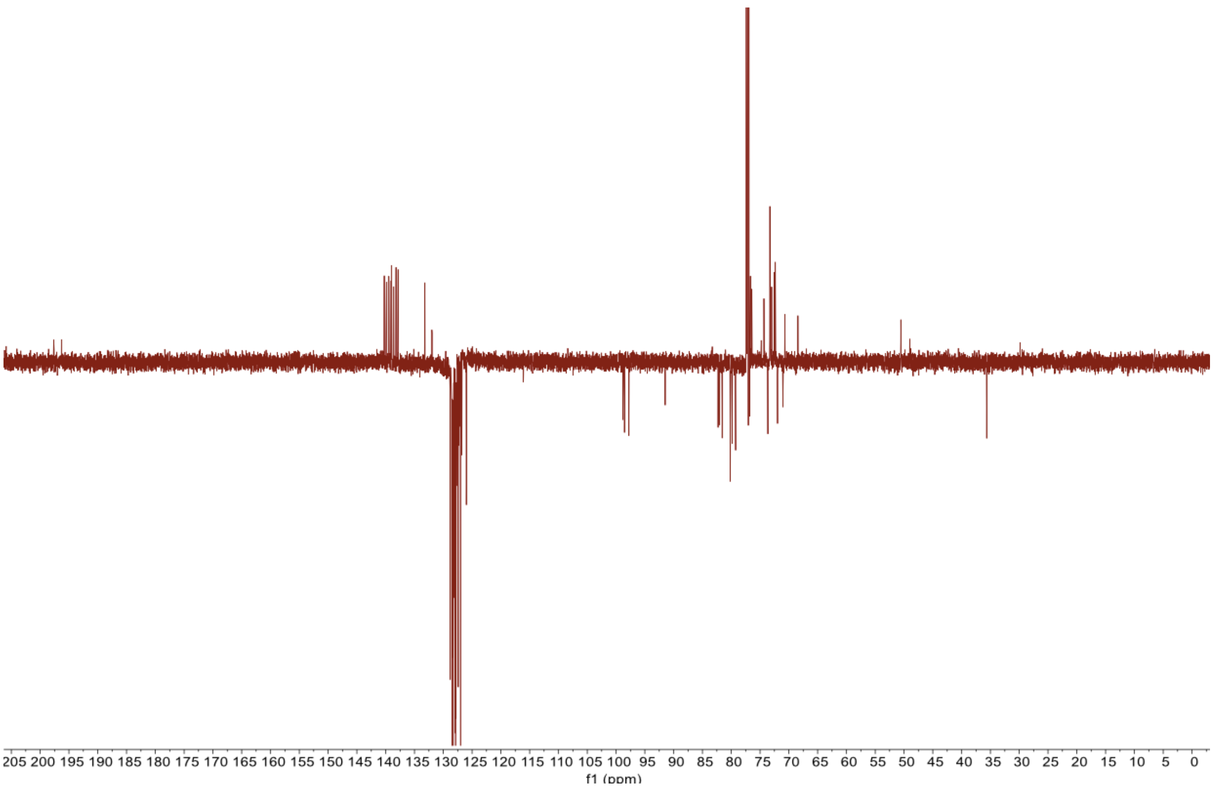
11

Chemical Formula: $C_{161}H_{167}AgCl_2N_4O_{28}Pd$
Molecular Weight: 2891,2952

A solution of complex **10** (50 mg, 0.018 mmol) and Ag_2O (41.6 mg, 0.18 mmol, 10 equiv.) in dry and degassed DCM (2 mL) was stirred at 20 °C for 20 h with exclusion of light. A black suspension formed which was filtered off over a 0.2 µm PET filter (rinsing with DCM). The filtrate was concentrated under vacuum. The as-obtained residue was purified by column chromatography on silica gel (*c*Hex/EtOAc, 1.2:1) to give the title compound as pale brown solid in 45% yield (23.3 mg, 0.008 mmol). **Rf** 0.7 (*c*Hex/EtOAc, 1:2). **^{1}H NMR** ($CDCl_3$, 600 MHz, 300K): δ 7.29 (d, J = 7.7 Hz, 4H, 4 × H_{arom}), 7.27–6.91 (m, 64H, 64 × H_{arom}), 6.85 (d, J = 3.6 Hz, 2H, 2 × H_{arom}), 6.78 (t, J = 7.5 Hz, 4H, 4 × H_{arom}), 6.65 (t, J = 7.4 Hz, 2H, 2 × H_{arom}), 6.44 (t, J = 6.9 Hz, 4H, 4 × H_{arom}), 5.90 (t, J = 10.2 Hz, 2H, 2 × H-5^{A,D}), 5.77 (d, $^3J_{1,2}$ = 3.8 Hz, 2H, 2 × H-1^{C,F}), 5.62 (d, J = 10.6 Hz, 2H, 2 × H-C*H*Ph), 5.46–5.35 (m, 3H, 1 × H-2_{allyl}, 2 × H-C*H*Ph), 5.11 (d, J = 12.0 Hz, 2H, 2 × H-C*H*Ph), 5.09–5.01 (m, 4H, 2 × H-3^{C,F}, 2 × H-C*H*Ph), 4.81 (d, J = 11.3 Hz, 2H, 2 × H-C*H*Ph), 4.67–4.61 (m, 4H, 2 × H-6^{A,D}, 2 × H-C*H*Ph), 4.56– 4.43 (m, 12H, 2 × H-1^{A,D}, 2 × H-1^{B,E}, 8 × H-C*H*Ph), 4.42 (d, J = 7.8 Hz, 1H, H-1_{allyl} *syn*) 4.37–4.28 (m, 4H, 4 × H-C*H*Ph), 4.27–4.17 (m, 6H, 2 × H-3^{A,D}, 2 × H-3^{B,E}, 2 × H-C*H*Ph), 4.16–4.09 (m, 4H, 2 × H-6'^{A,D}, 2 × H-C*H*Ph), 3.93–3.86 (m, 6H, 2 × H-4^{C,F}, 2 × H-5^{C,F}, 2 × H-5^{B,E}), 3.83 (s, 6H, 2 × N-CH_3), 3.80–3.69 (m, 6H, 2 × H-6^{C,F}, 2 × H-6'^{C,F}, 2 × H-4^{A,D}), 3.60 (dd, J= 10.1 and 3.8 Hz, 2H, 2 × H-2C,F), 3.54–3.47 (m, 4H, 2 × H-4^{B,E}, 2 × H-C*H*Ph), 3.46–3.39 (m, 2H, H-3_{allyl} *syn*, H-1_{allyl} *anti*), 3.33–3.26 (m, 4H, 2 × H-2^{A,D}, 2 × H-2^{B,E}), 3.14 (d,J = 12.8 Hz, 2H, 2 × H-C*H*Ph), 2.66 (dd, J = 10.7 Hz and 4.6 Hz, 2H, 2 × H-6^{B,E}), 2.59 (d, J = 10.6 Hz, 2H, 2 × H-6'^{B,E}), 2.52 (t, J = 11.1 Hz, 1H, H-3_{allyl} *anti*) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz, 300K): δ 197.62 ($C_{carbene}$–Pd), 188.78 ($C_{carbene}$–Ag), 140.23, 139.87, 139.45, 139.00, 138.99, 138.59, 138.19, 137.83 (16 × Cq Ar), 133.19 (2 × external N-*C*=*C*-N), 131.95 (d, J = 7.0 Hz, 2 × internal N-*C*=*C*-N), 128.76, 128.52, 128.48, 128.40, 128.34, 128.26, 128.23, 128.20, 128.14, 128.12, 127.98, 127.95, 127.85, 127.83, 127.80, 127.78, 127.71, 127.68, 127.39, 127.28, 127.10, 127.02, 126.97, 126.81, 126.80, 126.76, 125.99, 125.97 (80 × CH Ar), 116.06 (d, J = 4.7 Hz, C-2 allyl), 98.78 (2 × C-1^{C,F}), 98.51 (2 × C-1^{A,D}), 97.78 (2 × C-1^{B,E}), 91.46 (2 × central *C*H BBI), 82.28 (2 × C-4^{C,F}), 82.04 (2 × C-4^{B,E}), 81.53 (2 × C-3^{A,D}), 80.15 (2 × C-2^{A,D}, 2 × C-3^{B,E}), 79.83 (2 × C-3^{C,F}), 79.22 (2 × C-2^{B,E}), 77.03 (2 × C-2^{C,F}), 76.84 (2 × C-4^{A,D}), 76.66, 76.42 (4 × *C*H_2Ph), 74.79 (d, J = 1.9 Hz, C-1 allyl), 74.30, 73.64 (2 × C-5^{C,F}), 73.28, 73.26, 73.03, 72.51, 72.40, 72.34 (12 × *C*H_2Ph), 71.95 (2 × C-5^{B,E}), 71.01 (2 × C-5^{A,D}), 70.65(2 × C-6^{C,F}), 70.40 (2 × *C*H_2Ph), 68.41 (2 × C-6^{B,E}), 50.54 (2 × C-6^{A,D}), 48.99 (d, J = 7.3 Hz, C-3 allyl), 35.63 (2 × N-*C*H_3) ppm. **HRMS ESI-TOF**: *m/z* calcd. for $C_{161}H_{167}AgPdClN_4O_{28}$ $[M-Cl]^+$ 2851.9569, found 2851.9660 (err. -3.2 ppm).

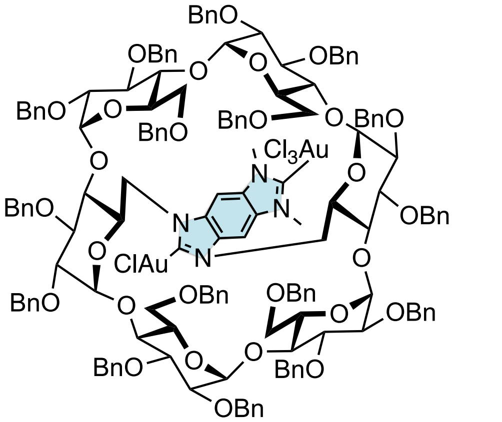


[1]H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)



[13]C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

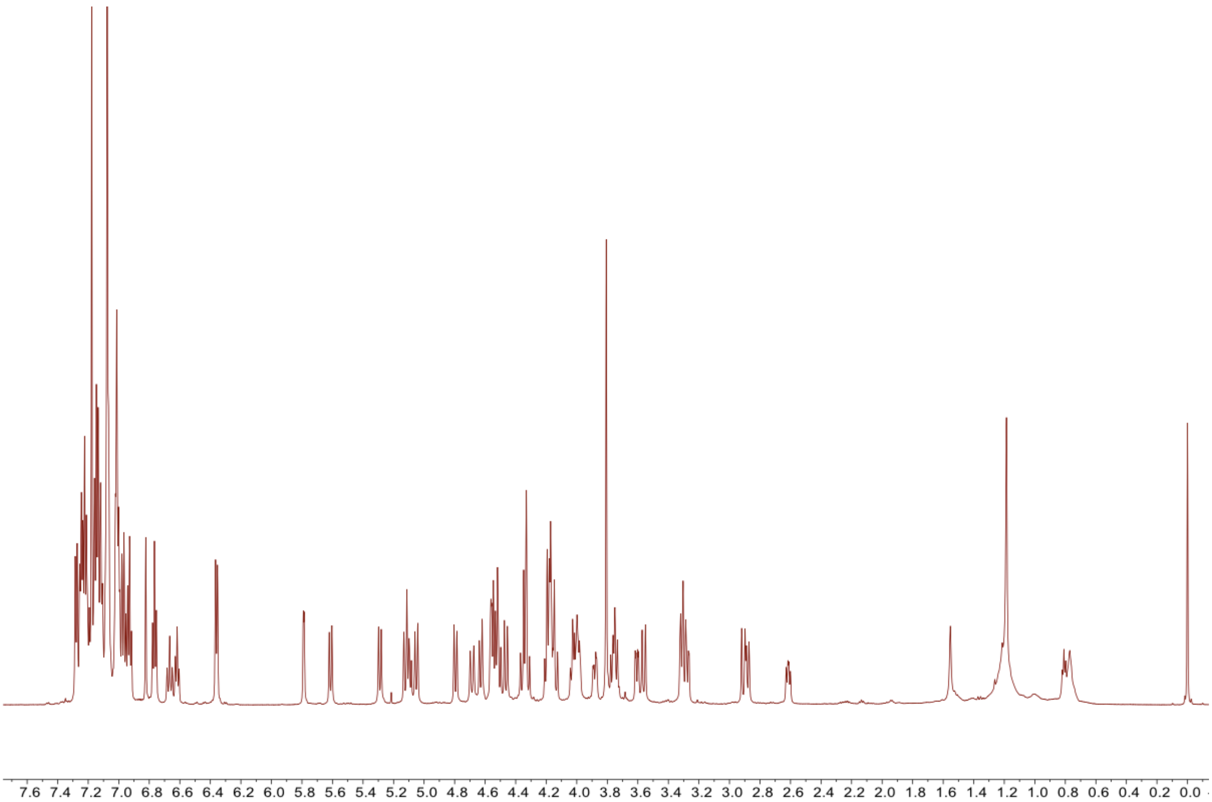
α-CD^{Bn}(BBI) gold(III)/gold(I) complex (**12**)



12

Chemical Formula: $C_{158}H_{162}Au_2Cl_4N_4O_{28}$
Molecular Weight: 3100,7671

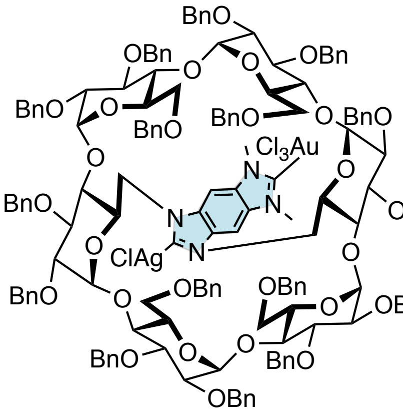
To a solution of **6** (35.1 mg, 0.012 mmol) in dry and degassed DCM (1 mL) was injected at 0 °C with exclusion of light a solution of (dichloroiodo)benzene (25.5 mg, 0.092 mmol) in DCM (1 mL). After stirring for 96 h, the reaction mixture was directly transferred onto a LH-20 column, and the column was eluted with a 1:1 solution of DCM/MeOH. after concentration of the fractions, the title compound was isolated in 90% yield as a pale yellow powder (32.3 mg, 0.01 mmol). **Rf** 0.4 (*c*Hex/EtOAc, 2:1). **^{1}H NMR** ($CDCl_3$, 600 MHz, 300K): δ 7.31–7.05 (m, 46H, 46 × H_{arom}), 7.04–6.90 (m, 24H, 24 × H_{arom}), 6.82 (s, 2H, 2 × CH_{arom} BBI), 6.77 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.67 (t, *J* = 10.2 Hz, 2H, 2 × H-5^{A,D}), 6.62 (t, *J* = 7.4 Hz, 2H, 2 × H_{arom}), 6.36 (d, *J* = 7.6 Hz, 4H, 4 × H_{arom}), 5.79 (d, *J* = 3.7 Hz, 2H, 2 × H-1^{C,F}), 5.61 (d, *J* = 10.3 Hz, 2H, 2 × H-C*H*Ph), 5.29 (d, *J* = 10.4 Hz, 2H, 2 × H-C*H*Ph), 5.15–5.02 (m, 6H, 2 × H-3^{C,F}, 4 × H-C*H*Ph), 4.79 (d, *J* = 11.1 Hz, 2H, 2 × H-C*H*Ph), 4.69 (d, *J* = 14.0 Hz, 2H, 2 × H-6^{A,D}), 4.63 (d, *J* = 11.1 Hz, 2H, 2 × H-C*H*Ph), 4.58–4.49 (m, 8H, 2 × H-1^{B,E}, 6 × H-C*H*Ph), 4.46 (d, *J* = 12.0 Hz, 2H, 2 × H-C*H*Ph), 4.38–4.30 (m, 6H, 2 × H-1^{A,D}, 4 × H-C*H*Ph), 4.22–4.11 (m, 10H, 2 × H-3^{A,D}, 2 × H-3^{B,E}, 2 × H-5^{B,E}, 4 × H-C*H*Ph), 4.05–3.95 (m, 6H, 2 × H-6'^{A,D}, 2 × H-4^{C,F}, 2 × H-5^{C,F}), 3.88 (dd, *J* = 11.1 Hz, *J* = 4.2 Hz, 2H, 2 × H-6^{C,F}), 3.81 (s, 6H), 3.79–3.72 (m, 4H, 2 × H-4^{A,D}, 2 × H-6'^{C,F}), 3.61 (dd, *J* = 10.1 Hz, *J* = 3.7 Hz, 2H, 2 × H-2^{C,F}), 3.56 (d, *J* = 13.1 Hz, 2H, 2 × H-C*H*Ph), 3.34–3.25 (m, 6H, 2 × H-2^{A,D}, 2 × H-2^{B,E}, 2 × H-4^{B,E}), 2.91 (d, *J* = 13.2 Hz, 2H, 2 × H-C*H*Ph), 2.88 (d, *J* = 10.0 Hz, 2H, 2 × H-6^{B,E}), 2.61 (dd, *J* = 10.4 and 6.4 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz, 300K): δ 183.86 (internal $C_{carbene}$–Au^{I}), 155.62 (external $C_{carbene}$–Au^{III}), 140.07, 139.70, 139.38, 139.18, 138.88, 138.44, 138.17 (16 × Cq Ar), 133.01 (2 × internal N-*C*=*C*-N), 131.36 (2 × external N-*C*=*C*-N), 128.80, 128.52, 128.47, 128.43, 128.32, 128.24, 128.22, 128.01, 127.92, 127.88, 127.78, 127.72, 127.70, 127.60, 127.29, 127.18, 126.95, 126.86, 126.80, 126.68, 125.14 (80 × CH Ar), 98.82 (2 × C-1^{A,D}), 98.69 (2 × C-1^{C,F}), 97.47(2 × C-1^{B,E}), 93.41 (2 × central *C*H BBI), 82.96 (2 × C-4^{B,E}), 81.98 (2 × C-4^{C,F}), 81.87 (2 × C-3^{A,D}), 80.24 (2 × C-2^{A,D}), 80.10 (2 × C-3^{B,E}), 79.79 (2 × C-3^{C,F}), 79.22 (2 × C-2^{B,E}), 77.12 (2 × C-2^{C,F}), 76.84 (2 × C-4^{A,D}), 76.72, 76.42, 74.38 (6 × *C*H_2Ph), 73.62 (2 × C-5^{C,F}), 73.43, 73.25, 72.91, 72.52, 72.47 (10 × *C*H_2Ph), 71.79 (2 × C-5^{B,E}), 70.55 (2 × C-6^{C,F}), 70.11 (2 × C-5^{A,D}), 69.62 (2 × C-6^{B,E}), 50.68 (2 × C-6^{A,D}), 35.37 (2 × N-*C*H_3) ppm. **HRMS ESI-TOF**: *m/z* calcd. for $C_{158}H_{162}Au_2Cl_4N_4O_{28}K$ [M+K]$^+$ 3135.9092, found 3135.9150 (err. -1.8 ppm)



^{1}H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)

^{13}C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

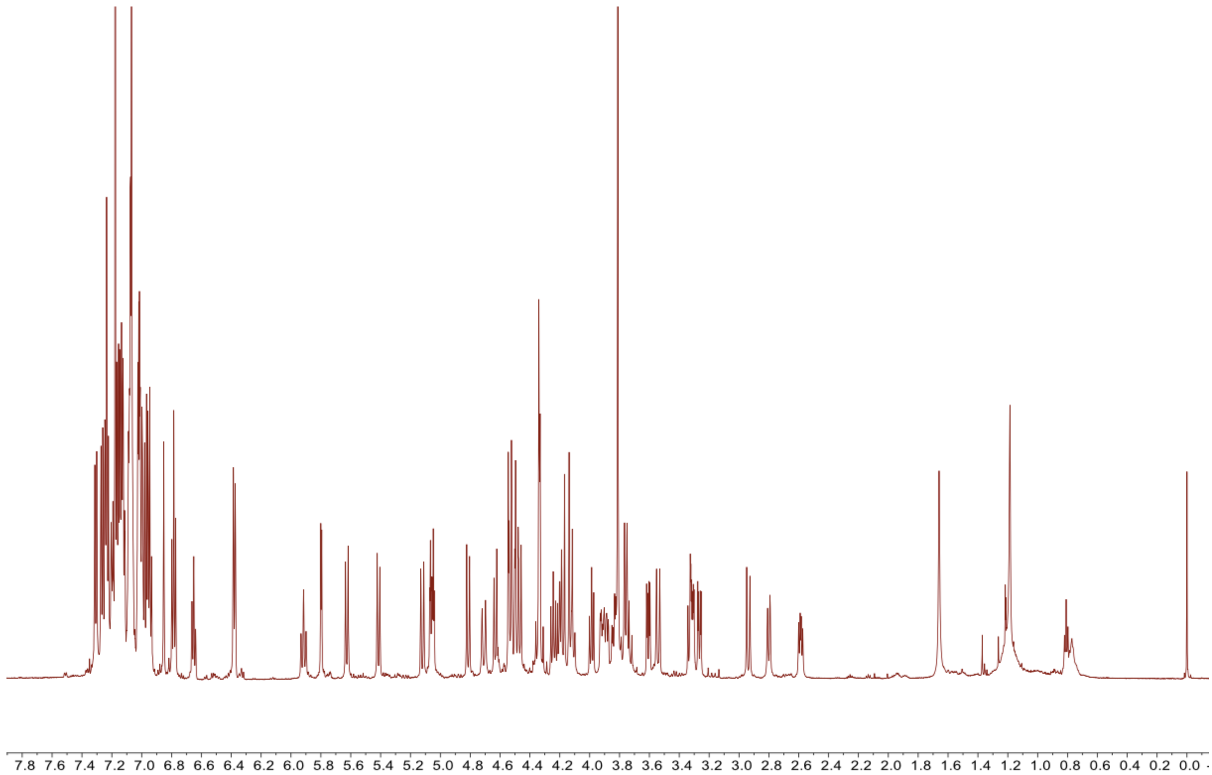
α-CD^{Bn}(BBI) gold(III)/silver(I) complex (13)



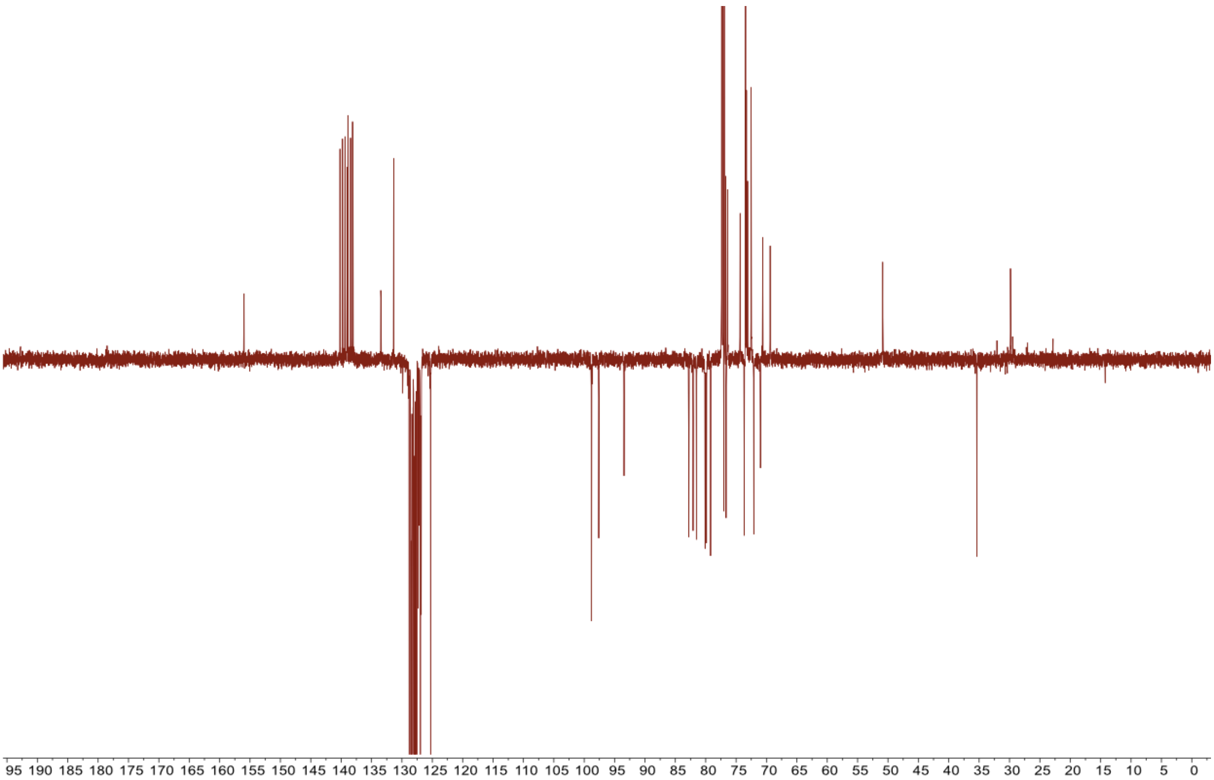
13

Chemical Formula: $C_{158}H_{162}AgAuCl_4N_4O_{28}$
Molecular Weight: 3011,6688

To a solution of **8** (40 mg, 0.014 mmol) in dry and degassed DCM (1 mL) was injected at –10 °C with exclusion of light a solution of (dichloroiodo)benzene (22.4 mg, 0.084 mmol) in DCM (1 mL). After stirring for 72 h, the reaction mixture was directly transferred onto a LH-20 column and the column was eluted with a 1:1 solution of DCM/MeOH. Concentration of the fractions gave the title compound in 94% yield as a pale yellow powder (38.4 mg, 0.013 mmol). **Rf** 0.5 (*c*Hex/EtOAc, 3:2). **^{1}H NMR** ($CDCl_3$, 600 MHz, 300K): δ 7.33–6.90 (m, 70H), 6.86 (s, 2H, 2 × CH_{arom} BBI), 6.78 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.65 (t, *J* = 7.3 Hz, 2H, 2 × H_{arom}), 6.38 (d, *J* = 7.6 Hz, 4H, 4 × H_{arom}), 5.92 (t, *J* = 10.1 Hz, 2H, 2 × H-5^{A,D}), 5.80 (d, *J* = 3.7 Hz, 2H, 2 × H-1^{C,F}), 5.63 (d, *J* = 10.5 Hz, 2H, 2 × H-C*H*Ph), 5.41 (d, *J* = 10.6 Hz, 2H, 2 × H-C*H*Ph), 5.12 (d, *J* = 11.9 Hz, 2H, 2 × H-C*H*Ph), 5.08– 5.03 (m, 4H, 2 × H-3^{C,F}, 2 × H-C*H*Ph), 4.81 (d, *J* = 11.2 Hz, 2H, 2 × H-C*H*Ph), 4.71 (d, *J* = 14.1 Hz, 2H, 2 × H-6^{A,D}), 4.63 (d, *J* = 11.1 Hz, 2H, 2 × H-C*H*Ph), 4.55–4.45 (m, 10H, 2 × H-1^{B,E}, 8 × H-C*H*Ph), 4.38–4.30 (m, 4H, 2 × H-1^{A,D}, 2 × H-C*H*Ph), 4.24 (t, *J* = 9.3 Hz, 2H, 2 × H-3^{B,E}), 4.22–4.09 (m, 10H, 2 × H-3^{A,D}, 2 × H-6'^{A,D}, 6 × H-C*H*Ph), 3.99 (t, *J* = 8.5 Hz, 2H, 2 × H-4^{C,F}), 3.94–3.87 (m, 4H, 2 × H-5^{C,F}, 2 × H-5^{B,E}), 3.84 (dd, *J* = 10.9 and 4.3 Hz, 2H, 2 × H-6^{C,F}), 3.81 (s, 6H, 2 × N-CH_3), 3.80–3.70 (m, 4H, 2 × H-4^{A,D}, 2 × H-6'^{C,F}), 3.61 (dd, *J* = 10.2 and 3.7 Hz, 2H, 2 × H-2^{C,F}), 3.54 (d, *J* = 13.1 Hz, 2H, 2 × H-C*H*Ph), 3.35–3.20 (m, 6H, 2 × H-2^{A,D}, 2 × H-2^{B,E}, 2 × H-4^{B,E}), 2.94 (d, *J* = 13.1 Hz, 2H, 2 × H-C*H*Ph), 2.80 (d, *J* = 10.2 Hz, 2H 2 × H-6^{B,E}), 2.59 (dd, *J* = 10.4 and 6.1 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz, 300K): δ 192.05 ($C_{carbene}$–Ag), 155.86 ($C_{carbene}$–Au^{III}), 140.19, 139.77, 139.37, 138.99, 138.88, 138.45, 138.12, 138.05 (16 × Cq Ar), 133.45 (d, *J* = 7.0 Hz, 2 × internal N-*C*=*C*-N), 131.34 (2 × external N-*C*=*C*-N), 128.77, 128.51, 128.45, 128.43, 128.29, 128.25, 128.21, 128.00, 127.98, 127.92, 127.87, 127.76, 127.74, 127.71, 127.55, 127.32, 127.16, 127.01, 126.94, 126.87, 126.84, 126.81, 125.27 (80 × CH Ar), 98.79 (2 × C-1^{A,D}, 2 × C-1^{C,F}), 97.61 (2 × C-1^{B,E}), 93.46 (2 × central *C*H BBI), 82.76 (2 × C-4^{B,E}), 82.07 (2 × C-4^{C,F}), 81.50 (2 × C-3^{A,D}), 80.11(2 × C-2^{A,D}), 79.98 (2 × C-3^{B,E}), 79.86 (2 × C-3^{C,F}), 79.19 (2 × C-2^{B,E}), 77.01 (2 × C-2^{C,F}), 76.68 (2 × *C*H_2Ph), 76.64 (2 × C-4^{A,D}), 76.40, 74.32 (4 × *C*H_2Ph), 73.66 (2 × C-5^{C,F}), 73.42, 73.28, 73.11, 72.52, 72.48 (10 × *C*H_2Ph), 72.08 (2 × C-5^{B,E}), 70.98 (2 × C-5^{A,D}), 70.61 (2 × C-6^{C,F}), 69.38 (2 × C-6^{B,E}), 50.86 (2 × C-6^{A,D}), 35.37 (2 × N-*C*H_3) ppm. **HRMS ESI-TOF**: *m/z* calcd. for $C_{158}H_{162}AgAuCl_4N_4O_{28}Na$ $[M+Na]^+$ 3029.8738, found 3029.8766 (err. -0.9 ppm).

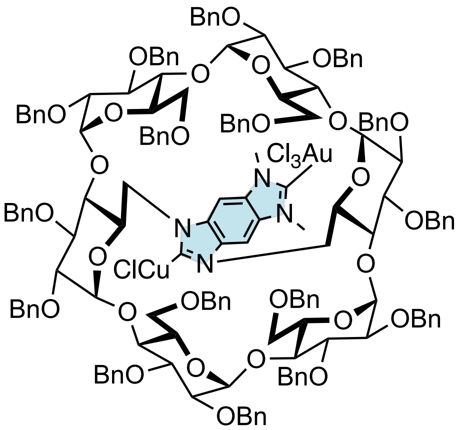


^{1}H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)



^{13}C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

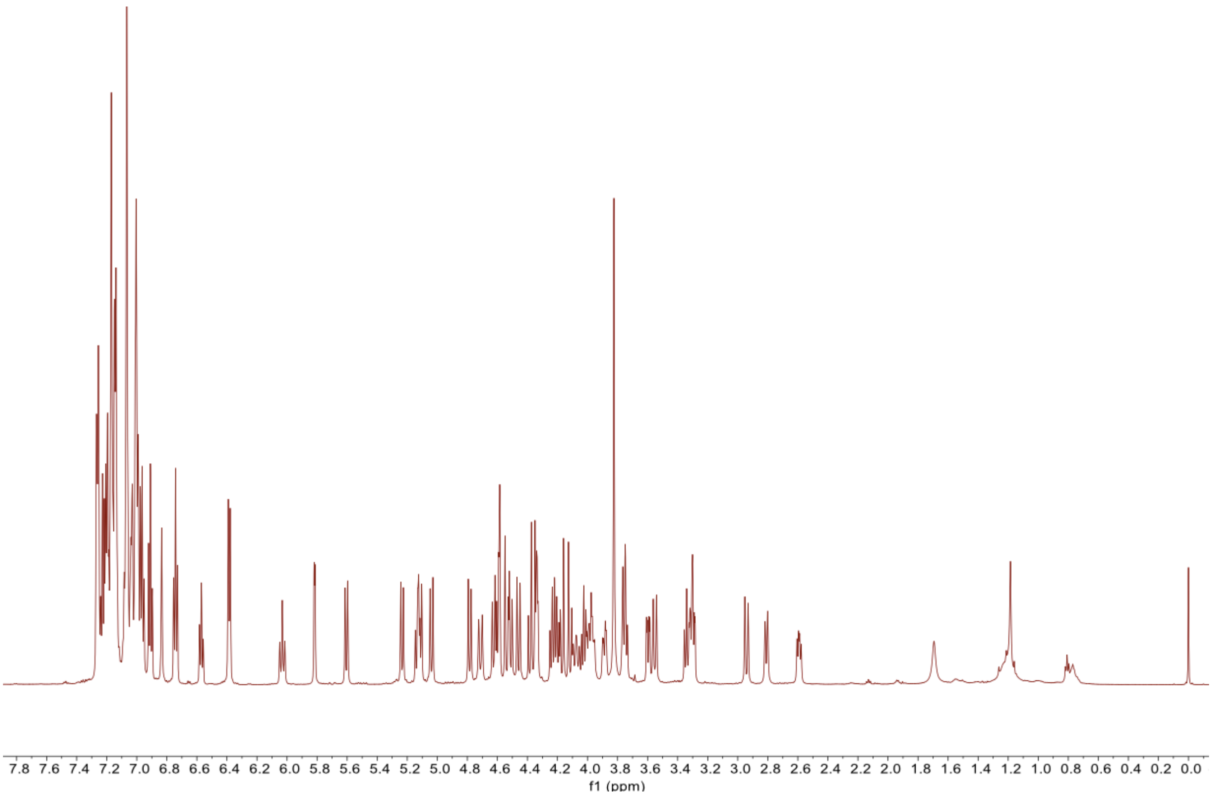
α-CD^{Bn}(BBI) gold(III)/copper(I) complex (14)



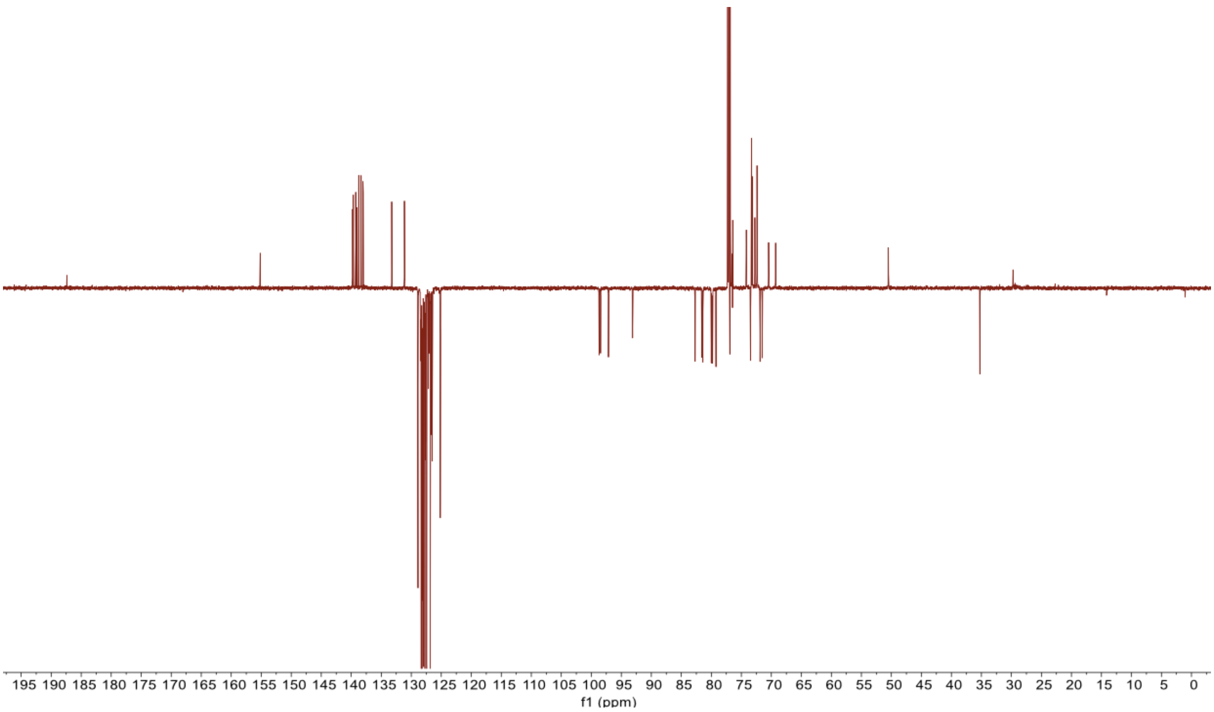
14

Chemical Formula: $C_{158}H_{162}AuCl_4CuN_4O_{28}$
Molecular Weight: 2967,3466

To a solution of **9** (40 mg, 0.014 mmol) in dry and degassed DCM (1 mL) was injected at –5 °C with exclusion of light a solution of (dichloro-iodo)benzene (22.8 mg, 0.084 mmol) in DCM (1 mL). After stirring for 70 h, the reaction mixture was di transferredrectly onto a LH-20 column and the column was eluted with a 1:1 solution of DCM/MeOH. Concentration of the fractions gave the title compound in 93% yield as a pale yellow powder (37.9 mg, 0.013 mmol). **Rf** 0.5 (*c*Hex/EtOAc, 3:2). **^{1}H NMR** ($CDCl_3$, 600 MHz, 300K): *δ* 7.31–6.94 (m, 66H), 6.91 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.83 (s, 2H, 2 × CH_{arom} BBI), 6.74 (t, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.57 (t, *J* = 7.4 Hz, 2H, 2 × H_{arom}), 6.38 (d, *J* = 7.5 Hz, 4H, 4 × H_{arom}), 6.03 (t, *J* = 10.1 Hz, 2H, 2 × H-5^{A,D}), 5.82 (d, *J* = 3.6 Hz, 2H, 2 × H-1^{C,F}), 5.61 (d, *J* = 10.1 Hz, 2H, 2 × H-C*H*Ph), 5.23 (d, *J* = 10.2 Hz, 2H, 2 × H-C*H*Ph), 5.16–5.09 (m, 4H, 2 × H-3^{C,F}, 2 × H-C*H*Ph), 5.04 (d, *J* = 11.2 Hz, 2H, 2 × H-C*H*Ph), 4.78 (d, *J* = 11.3 Hz, 2H, 2 × H-C*H*Ph), 4.71 (d, *J* = 13.9 Hz, 2H, 2 × H-6^{A,D}), 4.66–4.57 (m, 6H, 2 × H-1^{B,E}, 4 × H-C*H*Ph), 4.57–4.49 (m, 4H, 4 × H-C*H*Ph), 4.46 (d, *J* = 12.1 Hz, 2H, 2 × H-C*H*Ph), 4.41–4.31 (m, 6H, 2 × H-1^{A,D}, 4 × H-C*H*Ph), 4.26–3.93 (m, 16H, 2 × H-3^{A,D}, 2 × H-6'^{A,D}, 2 × H-4^{C,F}, 2 × H-5^{C,F}, 2 × H-3^{B,E}, 2 × H-5^{B,E}, 4 × H-C*H*Ph), 3.89 (dd, *J* = 11.0 Hz, *J* = 4.2 Hz, 2H, 2 × H-6^{C,F}), 3.82 (s, 6H, 2 × N-C*H*$_3$), 3.78–3.72 (m, 4H, 2 × H-4^{A,D}, 2 × H-6'^{C,F}), 3.60 (dd, *J* = 10.2 and 3.6 Hz, 2H, 2 × H-2^{C,F}), 3.55 (d, *J* = 13.1 Hz, 2H, 2 × H-C*H*Ph), 3.36–3.27 (m, 6H, 2 × H-2^{A,D}, 2 × H-2^{B,E}, 2 × H-4^{B,E}), 2.94 (d, *J* = 13.1 Hz, 2H, 2 × H-C*H*Ph), 2.81 (d, *J* = 10.1 Hz, 2H, 2 × H-6^{B,E}), 2.59 (dd, *J* = 10.4 Hz, *J* = 6.1 Hz, 2H, 2 × H-6'^{B,E}) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz, 300K): δ 187.48 ($C_{carbene}$–Cu), 155.28 ($C_{carbene}$–Au^{III}), 139.88, 139.76, 139.36, 139.16, 138.86, 138.46, 138.15, 138.10 (16 × Cq Ar), 133.36 (2 × internal N-*C*=*C*-N), 131.25 (2 × external N-*C*=*C*-N), 128.98, 128.53, 128.45, 128.42, 128.31, 128.24, 128.19, 128.04, 128.03, 127.90, 127.84, 127.78, 127.72, 127.57, 127.52, 127.28, 127.16, 127.02, 126.94, 126.77, 126.60, 125.26 (80 × CH Ar), 98.81(2 × C-1^{A,D}), 98.56 (2 × C-1^{C,F}), 97.24 (2 × C-1^{B,E}), 93.22 (2 × central *C*H BBI), 82.81 (2 × C-4^{B,E}), 81.69 (2 × C-4^{C,F}), 81.51 (2 × C-3^{A,D}), 80.11 (2 × C-2^{B,E}), 80.00 (2 × C-3^{B,E}), 79.90 (2 × C-3^{C,F}), 79.33 (2 × C-2^{A,D}), 77.02 (2 × C-2^{C,F}), 76.60 (2 × *C*H$_2$Ph), 76.58 (2 × C-4^{A,D}), 76.54 (2 × *C*H$_2$Ph), 74.28 (2 × *C*H$_2$Ph), 73.58 (2 × C-5^{C,F}), 73.42, 73.27, 72.85, 72.49, 72.48 (10 × *C*H$_2$Ph), 71.98 (2 × C-5^{B,E}), 71.62 (2 × C-5^{A,D}), 70.56 (2 × C-6^{C,F}), 69.40 (2 × C-6^{B,E}), 50.61 (2 × C-6^{A,D}), 35.36 (2 × N-*C*H$_3$) ppm. **HRMS ESI-TOF**: *m/z* calcd. for $C_{158}H_{162}AuCuCl_4N_4O_{28}K$ $[M+K]^+$ 3001.8723, found 3001.8779 (err. -1.9 ppm).

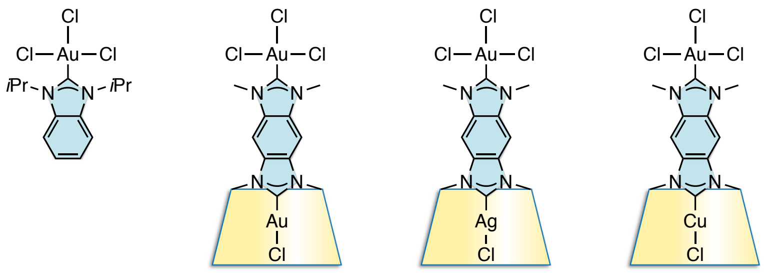


^{1}H NMR spectrum in $CDCl_3$ (300 K, 600 MHz)



^{13}C NMR spectrum in $CDCl_3$ (300 K, 151 MHz)

3. Cyclic Voltametry



(*i*Pr$_2$-bimy)AuCl$_3$ **12** **13** **14**

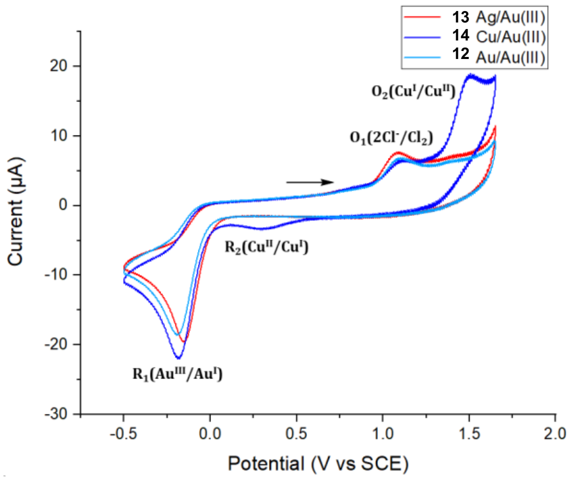


Figure S2. Second anodic scan, scan rate 100 mV/s

Complex	R$_1$ (Au^{III}/Au^I)	O$_1$ (2 Cl$^-$/Cl$_2$)
12[a]	-0.19	1.10
13[a]	-0.15	1.08
14[a]	-0.19	1.10
(*i*Pr$_2$-bimy)AuCl$_3$[b,5]	-0.26	1.12

Redox potentials of bimetallic complexes. [a]From cyclic voltammetry in CH_3CN/0.1 M NBu_4PF_6; Concentration of compounds: 1 mM; Potentials in V vs. SCE; Anodic scan rate 100 mV/s. [b] In DCM/0.1 M NBu_4PF_6 at a scan rate of 100 mV/s.

[5] H. Vinh Huynh, S. Guo, W. Wu, *Organometallics*, 2013, **32**, 4591–4600