# European Journal of Organic Chemistry 

Supporting Information

## Helically Chiral NHC-Gold(I) Complexes: Synthesis, Chiroptical Properties and Electronic Features of the [5]Helicene-Imidazolylidene Ligand

Etienne S. Gauthier, Marie Cordier, Vincent Dorcet, Nicolas Vanthuyne, Ludovic Favereau, J. A. Gareth Williams, and Jeanne Crassous*

## Supporting Information

## Outline

1. General methods ..... S2
2. Synthetic procedures. ..... S2
3. NMR Spectra. ..... S12
4. X-ray crystallographic data ..... S28
5. Chiral HPLC separations ..... S33
6. Photophysical studies ..... S37
7. Optical rotations. ..... S38
8. References ..... S38

## 1. General methods

Experiments were performed using standard Schlenk techniques. Column chromatography purifications were performed in air over silica gel (Macherey Nagel $60 \mathrm{M}, 0.04-0.063 \mathrm{~mm}$ ). Irradiation reactions were conducted using a Heraeus TQ 150 mercury vapor lamp. All reactions were monitored by TLC analysis and visualizations were accomplished by irradiation with a UV light at 254 nm and 356 nm . THF was dried using $\mathrm{Na} /$ Benzophenone method. Dry toluene was obtained from an MB-SPS-800 distillation machine and was degassed by an argon bubbling at least 30 minutes before use. Potassium carbonate and grounded 4Å molecular sieves were dried in a $110^{\circ} \mathrm{C}$ oven for several days and stored at the same temperature. Sodium tert-butoxide was bought from common providers and bulk powder was stored in a Schlenk tube under Ar sealed with a Teflon cap. Other reagents or solvents were purchased from usual providers and were used as received unless otherwise noted.
${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR spectra were recorded at room temperature either on a Bruker Avance I 300 MHz , Bruker Avance III 300 MHz or 400 MHz spectrometer equipped with a tunable BBFO probe. Chemical shifts $\delta$ are given in ppm and coupling constants $J$ in $\mathrm{Hz} .{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR chemical shifts were determined using residual signals of the deuterated solvents: deuterated dichloromethane ( ${ }^{1} \mathrm{H} \delta=5.32$ $\mathrm{ppm},{ }^{13} \mathrm{C} \delta=54.0 \mathrm{ppm}$ ) and deuterated chloroform ( ${ }^{1} \mathrm{H} \delta=7.26 \mathrm{ppm},{ }^{13} \mathrm{C} \delta=77.16 \mathrm{ppm}$ ). The terms s, $\mathrm{d}, \mathrm{t}, \mathrm{q}$, hept, m indicate respectively singlet, doublet, triplet, quartet, heptuplet, multiplet; $b$ is for broad; dd is doublet of doublets, dt - doublet of triplets, td - triplet of doublets. Assignment of proton and carbon signals is based on COSY, NOESY, edited-HSQC, and HMBC experiments. ${ }^{1} \mathrm{H}$ dipolar couplings were studied using NOESY sequence, with a 500 or 800 ms mixing time. High-resolution mass spectrometry (HR-MS) measurements were performed by the CRMPO, University of Rennes 1. IR spectra were recorded on a Perkin-Elmer Spectrum Two (ATR measurements) and on a Jasco FT/IR$4600\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ measurements using a cell with $\mathrm{BaF}_{2}$ windows) spectrometers.

UV-visible (UV-vis, in $\mathrm{M}^{-1} \mathrm{~cm}^{-1}$ ) and electronic circular dichroism ( $E C D$, in $\mathrm{M}^{-1} \mathrm{~cm}^{-1}$ ) were measured on a Jasco J-815 Circular Dichroism Spectrometer IFR140 facility. Part of this work has been performed using the PRISM core facility (Biogenouest©, UMS Biosit, Université de Rennes 1 - Campus de Villejean35043 Rennes Cedex, France).

## 2. Synthetic procedures

[5]Helicene-imidazole $\mathbf{4}^{[1]}$ and benzimidazole $7^{[2]}$ were prepared as reported in the literature. Unless otherwise specified, NHC-gold(I) complexes were prepared under air with technical grade solvents following Nolan et al. ${ }^{[3]}$

## $N$-(3,5-Dimethylphenyl)-[5]helicene-imidazole 5



In a round-bottom flask were placed 4Å molecular sieves, [5]helicene-imidazole 4 ( $59.3 \mathrm{mg}, 0.22 \mathrm{mmol}$ ), 3,5 -dimethylphenylboronic acid ( $69.2 \mathrm{mg}, 0.46 \mathrm{mmol}$ ), and anhydrous copper(II) acetate ( $61.3 \mathrm{mg}, 0.33$ mmol ) followed by dichloromethane (analytical grade, 3 mL ) and triethylamine ( $0.1 \mathrm{ml}, 0.71 \mathrm{mmol}$ ). The reaction mixture was then stirred at room temperature for 63 hours. The crude mixture was then filtered over a Celite© pad washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and further purified by column chromatography ( $\mathrm{SiO}_{2}$, $n$-Heptane/EtOAc $=1: 0$ to $8: 2$ ) to afford the desired product 5 as a white powder ( $68 \mathrm{mg}, 83 \%$ yield)
${ }^{1}{ }^{1} \mathrm{~N}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=9.23-9.15(\mathrm{~m}, 1 \mathrm{H}, 26), 8.13(\mathrm{~s}, 1 \mathrm{H}, 5), 8.00-7.95(\mathrm{~m}, 3 \mathrm{H}, 19$, 20, 29), 7.92 ( $\mathrm{d}, \mathrm{J}=8.6,1 \mathrm{H}, 23$ ), 7.86 ( $\mathrm{d}, J=8.6,1 \mathrm{H}, 22$ ), 7.82 ( $\mathrm{d}, J=4.4,1 \mathrm{H}, 12$ ), 7.80 ( $\mathrm{d}, J=4.6,1 \mathrm{H}$, 13), 7.62 (ddd, $J=8.0,6.9,1.3,1 \mathrm{H}, 28$ ), 7.54 (ddd, $J=8.4,6.9,1.5,1 \mathrm{H}, 27$ ), 7.23 (s, 2H, 7, 11), 7.16 (s, $1 \mathrm{H}, 9$ ), $2.47(\mathrm{~s}, 6 \mathrm{H}, 24,25)$; ${ }^{13} \mathrm{C}$ NMR ( $\mathbf{1 0 1} \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=140.7,140.2,138.8,136.3,133.1,132.3$, $132.0,131.0,130.8,130.5,130.1,128.3,127.8,127.2,126.8,126.5,126.3,125.5,125.3,124.1,123.6$, 122.5, 111.2, 21.5; HR-MS (ESI, $\left.\mathrm{CH}_{3} \mathrm{OH} / \mathrm{CH}_{2} \mathrm{Cl}_{2}=90 / 10\right)[\mathrm{M}+\mathrm{Na}]^{+}\left(\mathrm{C}_{27} \mathrm{H}_{20} \mathrm{~N} \mathrm{Na}\right)$ : calculated for $395.15187 \mathrm{~m} / \mathrm{z}$, found 395.1523 ( $\Delta=1 \mathrm{ppm}$ ).

## $N$-(3,5-Dimethylphenyl)-1-methyl-[5]helicene-imidazol-1-ium iodide [(rac)-6].HI



In a dried Schlenk tube was placed acetonitrile ( 7 mL ). After 3 vacuum/argon cycles, $\mathbf{5}$ ( $85 \mathrm{mg}, 0.22$ mmol ) was introduced. Then, an excess of methyl iodide was added. The reaction mixture was then sealed with a Teflon Cap and heated at $110^{\circ} \mathrm{C}$ overnight. The resulting heterogenous mixture was cooled down to room temperature and the solvent was stripped off. The solid was then washed with $\mathrm{Et}_{2} \mathrm{O}$ and EtOAc to afford pure iodide salt [(rac)-6]. HI as a light-brown solid ( $105 \mathrm{mg}, 89 \%$ yield).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=10.77(\mathrm{~s}, 1 \mathrm{H}, 5), 8.38-8.30(\mathrm{~m}, 1 \mathrm{H}, 27), 8.19(\mathrm{~d}, \mathrm{~J}=8.9,1 \mathrm{H}, 23)$, $8.14-8.05(\mathrm{~m}, 4 \mathrm{H}, 13,19,20,30), 8.00(\mathrm{~d}, \mathrm{~J}=8.6,1 \mathrm{H}, 12), 7.90(\mathrm{~d}, \mathrm{~J}=8.9,1 \mathrm{H}, 22), 7.73-7.60(\mathrm{~m}, 4 \mathrm{H}$, $7,11,28,29), 7.32(\mathrm{~s}, 1 \mathrm{H}, 9), 3.60(\mathrm{~s}, 3 \mathrm{H}, 24), 2.50(\mathrm{~s}, 6 \mathrm{H}, 25,26) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta=141.5$, $141.3,133.5,133.2,133.2,133.1,132.8,131.5,131.2,131.1,129.9,129.5,129.2,129.0,128.0,127.8$, $\left(\mathrm{C}_{28} \mathrm{H}_{23} \mathrm{~N}_{2}\right)$ : calculated for $387.18557 \mathrm{~m} / \mathrm{z}$, found 387.1858 ( $\Delta=1 \mathrm{ppm}$ ).

## $N$-(3,5-Dimethylphenyl)-1-methyl-[5]helicene-imidazol-1-ium chloride [(rac)-6].HCl



A glass column was charged with about 9 g of ion exchange DOWEX© resin, activated with 15 mL of $\mathrm{HCl} 37 \%$ then washed with MilliQ water until $\mathrm{pH}=7$. Salt [(rac)-6]. HI ( $105 \mathrm{mg}, 0.204 \mathrm{mmol}$ ) was then loaded as a liquid deposit (acetone/methanol, 1:1) and slowly eluted through the column with the same eluent. Solvents were then removed under vacuum and the obtained solid was triturated in acetone and $\mathrm{Et}_{2} \mathrm{O}$ and finally dried under air. The desired chloride salt [(rac)-6]. HCl was obtained as a white solid ( $85 \mathrm{mg}, 98 \%$ yield).
${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=11.86(\mathrm{~s}, 1 \mathrm{H}, 5), 8.30(\mathrm{~d}, \mathrm{~J}=8.3,1.2,1 \mathrm{H}, 27), 8.18(\mathrm{~d}, \mathrm{~J}=8.8,1 \mathrm{H}$, 23), $8.15-8.05$ (m, 4H, 13, 19, 20, 30), 8.01 (d, J = 8.6, 1H, 12), 7.91 (d, J = 8.8, 1H, 22), $7.74-7.66$ (m, $1 \mathrm{H}, 29), 7.66-7.61(\mathrm{~m}, 1 \mathrm{H}, 28), 7.59(\mathrm{~d}, \mathrm{~J}=1.6,2 \mathrm{H}, 7,11), 7.34(\mathrm{~s}, 1 \mathrm{H}, 9), 3.65(\mathrm{~s}, 3 \mathrm{H}, 24), 2.52(\mathrm{~s}, 6 \mathrm{H}$, 25, 26); ${ }^{13}$ C NMR ( $75 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=143.6,141.6,133.6,133.5,133.2,133.0,132.9,131.6,131.3$, 131.3, 129.9, 129.3, 129.3, 128.9, 128.0, 127.9, 127.7, 126.4, 125.5, 124.6, 123.3, 117.1, 112.9, 39.2, 21.7; HR-MS (ESI, $\left.\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{CH}_{3} \mathrm{OH}=90 / 10\right)[\mathrm{M}]^{+}\left(\mathrm{C}_{28} \mathrm{H}_{23} \mathrm{~N}_{2}\right)$ : calculated for $387.18557 \mathrm{~m} / \mathrm{z}$, found $387.1860(\Delta=1 \mathrm{ppm})$, the cluster $[2 \mathrm{M}+\mathrm{Cl}]^{+}\left(\mathrm{C}_{56} \mathrm{H}_{46} \mathrm{~N}_{4}{ }^{35} \mathrm{Cl}\right)$ was also detected: calculated for 809.34055 $\mathrm{m} / \mathrm{z}$, found 809.3401 ( $\Delta=1 \mathrm{ppm}$ ).

## 1-(3,5-Dimethylphenyl)-3-methyl-1H-benzimidazol-3-ium iodide [8]. HI




In a dried Schlenk tube was placed acetonitrile ( 6 mL ). After 3 vacuum/argon cycles, 7 ( $106 \mathrm{mg}, 0.47$ mmol ) was added. Under argon, was added an excess of methyl iodide. The reaction mixture was then sealed with a Teflon Cap and was heated at $110^{\circ} \mathrm{C}$ overnight. The resulting heterogenous mixture was finally allowed to cool to room temperature and the solvent was stripped off. The resulting residue was transferred into a round-bottom flask by dissolution and evaporation of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The solid was then washed with acetone, $\mathrm{Et}_{2} \mathrm{O}$ and EtOAc to afford pure iodide salt [8]. HI as a light-brown solid ( 164 mg , 94\% yield).
${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=10.86(\mathrm{~s}, 1 \mathrm{H}, 5), 7.85(\mathrm{~d}, \mathrm{~J}=8.2,1 \mathrm{H}, 15), 7.78-7.67(\mathrm{~m}, 3 \mathrm{H}, 12$, 13, 14), 7.45 ( $s, 2 \mathrm{H}, 7,11$ ), $7.28(\mathrm{~s}, 1 \mathrm{H}, 9), 4.41(\mathrm{~s}, 3 \mathrm{H}, 16), 2.45(\mathrm{~s}, 6 \mathrm{H}, 17,18) ;{ }^{13} \mathrm{C}$ NMR ( 126 MHz , $\left.\mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta=142.0,141.5,133.2,132.9,132.7,131.7,128.3,128.1,122.8,114.3,113.6,34.9,21.5$; HRMS (ESI, $\left.\mathrm{CH}_{3} \mathrm{OH} / \mathrm{CH}_{2} \mathrm{Cl}_{2}=\mathbf{9 0} / \mathbf{1 0}\right)[\mathrm{M}]^{+}\left(\mathrm{C}_{16} \mathrm{H}_{17} \mathrm{~N}_{2}\right)$ : calculated for $237.13862 \mathrm{~m} / \mathrm{z}$, found 237.1387 ( $\Delta=$ 0 ppm ).
[5]Helicenic NHC iridium(I) 1,5-cyclooctadiene chloride complex (rac)-9/(rac)-9'


In a dried Schlenk tube protected from light with an aluminum foil, was added $\mathrm{Ag}_{2} \mathrm{O}(4.9 \mathrm{mg}, 0.021$ $\mathrm{mmol})$ and salt [(rac)-6]. HI ( $22.8 \mathrm{mg}, 0.044 \mathrm{mmol})$. The solids were degassed by 3 vacuum/argon cycles and further dissolved in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$. The mixture was stirred at r.t. for 2 hours and $[\operatorname{lr}(\mathrm{COD}) \mathrm{Cl}]_{2}$ $(14.8 \mathrm{mg}, 0.022 \mathrm{mmol})$ was added. The reaction was then stirred overnight at r.t. and the crude was filtered over a Celite© pad and washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The yellow filtrate was evaporated under reduced pressure and the obtained residue was purified by column chromatography ( $\mathrm{SiO}_{2}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) affording the desired complex as a yellow powder ( $13.5 \mathrm{mg}, 43 \%$ yield) and as a mixture of conformers ((rac)-9 : (rac)-9' $=79 \% / 21 \%$, determined by ${ }^{1} \mathrm{H}$ NMR).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=8.39(\mathrm{~d}, J=8.0,0.2 \mathrm{H}, 13$ ), $8.29(\mathrm{~d}, \mathrm{~J}=8.5,1 \mathrm{H}, 13), 8.13-8.00$ $(\mathrm{m}, 3 \mathrm{H}), 8.03-7.89(\mathrm{~m}, 2 \mathrm{H}), 7.89-7.78(\mathrm{~m}, 4 \mathrm{H}), 7.80-7.73(\mathrm{~m}, 1 \mathrm{H}), 7.71-7.59(\mathrm{~m}, 2 \mathrm{H}), 7.58-7.47$ $(\mathrm{m}, 1 \mathrm{H}), 7.27-7.20(\mathrm{~m}, 1 \mathrm{H}), 4.76\left(\mathrm{td}, J=3.9,0.1 \mathrm{H}, \mathrm{C}\left(\mathrm{sp}^{2}\right)(\mathrm{rac})-9^{\prime}\right), 4.62\left(\mathrm{td}, J=7.7,3.3,1 \mathrm{H}, \mathrm{C}\left(\mathrm{sp}^{2}\right)(\mathrm{rac})-\right.$ 9), $4.49-4.39\left(\mathrm{~m}, 0.2 \mathrm{H}, \mathrm{C}\left(\mathrm{sp}^{2}\right)(\mathrm{rac})-9^{\prime}\right), 4.40-4.29\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C}\left(\mathrm{sp}^{2}\right)(\mathrm{rac})-9\right), 3.51\left(\mathrm{~s}, 0.7 \mathrm{H}, \mathrm{N}-\mathrm{CH}_{3}(\mathrm{rac})-\right.$ $9^{\prime}$ ), $3.47-3.40(\mathrm{~m}, 0.8 \mathrm{H}), 3.41\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{N}-\mathrm{CH}_{3}(\mathrm{rac})-9\right), 2.79-2.70\left(\mathrm{~m}, 0.2 \mathrm{H}, \mathrm{C}\left(\mathrm{sp}^{3}\right)(\mathrm{rac})-9^{\prime}\right), 2.60$ (td, $\left.\mathrm{J}=7.4,3.5,1 \mathrm{H}, \mathrm{C}\left(\mathrm{sp}^{3}\right)(\mathrm{rac})-9\right), 2.52\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{3}(\mathrm{rac})-9^{\prime}\right), 2.50\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{CH}_{3}(\mathrm{rac})-9\right), 2.43-2.29(\mathrm{~m}, 1 \mathrm{H})$, $2.19-2.05(\mathrm{~m}, 1 \mathrm{H}), 2.06-1.77(\mathrm{~m}, 2 \mathrm{H}), 1.76-1.65(\mathrm{~m}, 1 \mathrm{H}), 1.65-1.56(\mathrm{~m}, 0.7 \mathrm{H}), 1.52-1.41(\mathrm{~m}$, 0.4 H ), $1.38-1.26(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=192.3$ ( $\mathrm{C}^{\text {carbene ( }}$ (rac)-9), 192.0 ( $\mathrm{C}^{\text {carbene ( } \mathrm{rac} \text { )- }}$ $9^{\prime}$ ), 139.3, 139.2, 138.3, 138.1, 134.9, 134.7, 134.1, 133.6, 132.6, 132.5, 132.3, 131.7, 131.7, 131.5, $130.9,130.4,130.3,128.9,128.9,128.7,128.4,128.1,127.8,127.6,127.1,127.1,127.0,126.6,126.5$, $126.4,126.3,126.2,126.2,125.9,125.7,124.9,124.7,124.5,124.1,116.0,111.9,111.1,86.4,85.5$, 84.7, 84.4, 54.2, 53.0, 52.0, 51.6, 40.6, 39.6, 35.2, 34.3, 32.9, 32.5, 30.5, 29.9, 29.4, 29.2, 21.7, 21.6; HR-MS (ESI, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) [M] ${ }^{+\bullet}\left(\mathrm{C}_{36} \mathrm{H}_{34} \mathrm{~N}_{2}{ }^{35} \mathrm{Cl}{ }^{193} \mathrm{Ir}\right)$ : calculated for $722.20344 \mathrm{~m} / \mathrm{z}$, found 722.2027 ( $\Delta=1$ ppm).

## Model NHC iridium(I) 1,5-cyclooctadiene chloride 10





In a dried Schlenk tube protected from light with an aluminum foil, was added $\mathrm{Ag}_{2} \mathrm{O}$ (11.3 mg, 0.049 mmol ) and salt [8]. HI ( $35.5 \mathrm{mg}, 0.097 \mathrm{mmol}$ ). The solids were degassed by 3 vacuum/argon cycles, further dissolved in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$. The mixture was stirred at r.t. for 1 h 30 and $[\mathrm{Ir}(\mathrm{COD}) \mathrm{Cl}]_{2}(33 \mathrm{mg}$, 0.049 mmol ) was added. The reaction was then stirred overnight at $r . t$. and the crude was filtered over a Celite $\bigcirc$ pad and washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The yellow filtrate was evaporated under reduced pressure and the obtained residue was purified by column chromatography ( $\mathrm{SiO}_{2}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) affording the desired complex 10 as a yellow powder ( $40 \mathrm{mg}, 72 \%$ yield)
${ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl ${ }_{3}$ ) $\delta=7.65(\mathrm{~s}, 2 \mathrm{H}, 9,13), 7.41-7.34(\mathrm{~m}, 2 \mathrm{H}, 14,17), 7.35-7.26(\mathrm{~m}$, $1 \mathrm{H}, 16), 7.28-7.21(\mathrm{~m}, 1 \mathrm{H}, 15), 7.18-7.13(\mathrm{~m}, 1 \mathrm{H}, 11), 4.77$ (td, J=7.7, 3.6, 1H, 114), $4.62-4.51(\mathrm{~m}$, $1 \mathrm{H}, 115), 4.27(\mathrm{~s}, 3 \mathrm{H}, 18), 3.09-2.98(\mathrm{~m}, 1 \mathrm{H}, 108), 2.47(\mathrm{~s}, 6 \mathrm{H}, 19,20), 2.38$ (td, J=7.3, 3.6, 1H, 109), $2.33-2.11(\mathrm{~m}, 2 \mathrm{H}, 116,118), 1.92-1.76(\mathrm{~m}, 1 \mathrm{H}, 113), 1.73-1.55(\mathrm{~m}, 3 \mathrm{H}, 110,112,117,119), 1.42-$ 1.19 ( $\mathrm{m}, 1 \mathrm{H}, 111$ ); ${ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ) $\delta=191.6$ ( $5, \mathrm{C}^{\text {Carbene }}$ ), 138.6, 137.7, 135.6, 135.2, 129.7, 125.0, 123.1, 122.9, 110.9, 109.7, 86.1, 84.9, 52.3, 52.1, 34.6, 34.5, 32.3, 29.7, 28.9, 21.4; HR-MS (ESI, $\left.\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)[\mathrm{M}]^{+\bullet}\left(\mathrm{C}_{24} \mathrm{H}_{28} \mathrm{~N}_{2}{ }^{35} \mathrm{Cl}{ }^{193} \mathrm{Ir}\right)$ : calculated for $572.15649 \mathrm{~m} / \mathrm{z}$, found 572.1558 ( $\Delta=1 \mathrm{ppm}$ ).
[5]Helicenic NHC iridium(I) dicarbonyl chloride complex (rac)-11


In a round-bottom flask, was placed complex (rac)-9 ( $5 \mathrm{mg}, 0.01 \mathrm{mmol}$, as a mixture of conformers) and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \mathrm{~mL})$. Gaseous carbon monoxide was bubbled inside the solution for 15 min then volatiles were removed under reduced pressure. The obtained crude was precipitated and triturated with $n$ -
pentane then dried under vacuum to afford complex (rac)-11 as a yellow powder ( 7 mg , quantitative yield).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=8.43-8.37(\mathrm{~m}, 1 \mathrm{H}, 27), 8.09-8.01(\mathrm{~m}, 3 \mathrm{H}, 9,10,30), 7.99-$ 7.93 (m, 3H, 12, 13, 15), $7.69-7.62(\mathrm{~m}, 2 \mathrm{H}, 28,29), 7.57(\mathrm{~d}, \mathrm{~J}=8.6,1 \mathrm{H}, 16), 7.41(\mathrm{~s}, 2 \mathrm{H}, 19,23), 7.30$ $(\mathrm{s}, 1 \mathrm{H}, 21), 3.45(\mathrm{~s}, 3 \mathrm{H}, 26), 2.50(\mathrm{~s}, 6 \mathrm{H}, 31,32) ;{ }^{13} \mathrm{C}$ NMR resolution was not enough to record proper spectra; IR (ATR, cm ${ }^{-1}$ ) 2062 (CO), 1979 (CO); IR (solution in CH $_{2} \mathrm{Cl}_{2}$, cm $^{-1}$ ) 2067 (CO), 1984 (CO); HRMS (ESI, $\left.\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{CH}_{3} \mathrm{OH}=95 / 5\right)[\mathrm{M}+\mathrm{H}]^{+}\left(\mathrm{C}_{30} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{2}{ }^{35} \mathrm{Cl}{ }^{193} \mathrm{Ir}\right)$ : calculated for $671.1072 \mathrm{~m} / \mathrm{z}$, found $671.1072(\Delta=0 \mathrm{ppm}),[\mathrm{M}-\mathrm{Cl}]^{+}\left(\mathrm{C}_{30} \mathrm{H}_{22} \mathrm{~N}_{2} \mathrm{O}_{2}{ }^{193} \mathrm{r}\right)$ ) calculated for $635.13052 \mathrm{~m} / \mathrm{z}$, found $635.1305(\Delta=$ $0 \mathrm{ppm})$.



Figure S1. FT-IR spectra of (rac)-11 measured in powder (ATR) (left) and in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ (liquid cell with BaF windows (right).

## Model NHC iridium(I) dicarbonyl chloride 12



In a round-bottom flask, was placed complex $\mathbf{1 0}(7 \mathrm{mg}, 0.014 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \mathrm{~mL})$. Gaseous carbon monoxide was bubbled inside the solution for 15 min then volatiles were removed under reduced pressure. The obtained crude was precipitated and triturated with $n$-pentane and dried under vacuum to afford complex $\mathbf{1 2}$ as a brown powder ( 8 mg , quantitative yield).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=7.55(\mathrm{dt}, J=8.2,1.0,1 \mathrm{H}, 9), 7.46$ ( $\mathrm{ddd}, J=8.2,7.0,1.2,1 \mathrm{H}, 8$ ), 7.38 (ddd, $J=8.3,7.1,1.1,1 \mathrm{H}, 7$ ), 7.31 (dt, J = 8.2, 1.0, 1H, 6), 7.26 (s, 2H, 11, 15), 7.23 (s, 1H), 4.20 (s, $3 \mathrm{H}, 18$ ), $2.43(\mathrm{~s}, 6 \mathrm{H}, 19,20) ;{ }^{13} \mathrm{C}$ NMR ( $\mathbf{1 0 1} \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=183.2\left(2, \mathrm{C}^{\text {carbene }}\right), 182.2,168.6,140.0,137.3$, ( $\mathrm{C}_{18} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{O}_{2}{ }^{35} \mathrm{Cl}{ }^{193} \mathrm{Ir}$ ): calculated for $521.06025 \mathrm{~m} / \mathrm{z}$, found 521.0601 ( $\Delta=0 \mathrm{ppm}$ ).


Figure S2. FT-IR spectra of 12 measured in powder (ATR) (left) and in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ (liquid cell with $\mathrm{BaF}_{2}$ windows (right).

## 3-(3,5-Dimethylphenyl)-1-methyl-[5]helicene-imidazole-2-selenone (rac)-13




Method A: ${ }^{[4]}$ In a dried Schlenk tube, was placed salt [(rac)-6].HI ( $13.5 \mathrm{mg}, 0.026 \mathrm{mmol}$ ) and elemental selenium powder ( $7.4 \mathrm{mg}, 0.093 \mathrm{mmol}$ ). After 3 vacuum/argon cycles, dried THF ( 1 mL ) was added and the suspension was cooled down to $-78^{\circ} \mathrm{C}$. A NaHMDS solution ( $0.03 \mathrm{~mL}, 1.0 \mathrm{M}$ in THF) was added dropwise and the obtained mixture was allowed to heat up to r.t. then stirred overnight. The solvent was stripped off and the obtained residue was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and filtered over a Celite pad and evaporated. The filtrate was purified by column chromatography ( $\mathrm{SiO}_{2}, n$-Heptane/EtOAc = 1:0 to 9:1) to afford the desired product (rac)-13 as a grey powder ( $3.8 \mathrm{mg}, 32 \%$ yield). Method B: ${ }^{[5]}$ In a screwcapped vial, was placed salt [(rac)-6]. HI ( $9.2 \mathrm{mg}, 0.018 \mathrm{mmol}$ ), elemental selenium powder ( 3.5 mg , 0.044 mmol ) and acetone (technical grade, 1 mL ). The mixture was stirred at $40^{\circ} \mathrm{C}$ for 15 min . $\mathrm{NEt}_{3}$ (8 $\mu \mathrm{L}, 0.057 \mathrm{mmol}$ ) was then added and the obtained mixture was heated to $60^{\circ} \mathrm{C}$ and stirred overnight. Then, the heterogenous mixture was filtered through a plug of silica gel, washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ then EtOAc. The solvents were removed under reduced pressure and the obtained wax was dried under vacuum to afford the desired product ( $\mathbf{r a c}$ )-13 as a fine yellow powder ( $5.3 \mathrm{mg}, 63 \%$ yield).
${ }^{1} \mathrm{H}$ NMR ( 400 MHz , Acetone $-d_{6}$ ) $\delta=8.39(\mathrm{~d}, \mathrm{~J}=8.5,1 \mathrm{H}, 28), 8.19-8.11(\mathrm{~m}, 2 \mathrm{H}, 20,31), 8.11-$ $8.02(\mathrm{~m}, 2 \mathrm{H}, 21,23), 7.99-7.92(\mathrm{~m}, 2 \mathrm{H}, 14,24), 7.72-7.65(\mathrm{~m}, 1 \mathrm{H}, 30), 7.61-7.53(\mathrm{~m}, 1 \mathrm{H}, 29), 7.39$ (d, J = 8.6, 1H, 13), $7.30(\mathrm{~s}, 2 \mathrm{H}, 8,12), 7.27(\mathrm{~s}, 1 \mathrm{H}, 10), 3.17(\mathrm{~s}, 3 \mathrm{H}, 25), 2.46(\mathrm{~s}, 6 \mathrm{H}, 26,27) ;{ }^{13} \mathrm{C}$ NMR $\left(101 \mathrm{MHz}\right.$, Acetone $\left.-d_{6}\right) \delta=169.8$ (5, C=Se), 149.3, 140.3, 138.1, 135.1, 133.3, 133.0, 132.4, 132.1, 132.0, $131.7,129.4,129.4,128.9,127.4,127.2,127.1,127.1,126.7,125.5,124.9,115.8,111.8,40.3,21.3$; ${ }^{77}$ Se NMR ( $76 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=106.2$; ${ }^{77}$ Se NMR ( 76 MHz , Acetone- $\boldsymbol{d}_{6}$ ) $\delta=133.0$; HR-MS (ASAP, 230${ }^{\circ} \mathrm{C}$ ) $[\mathrm{M}+\mathrm{H}]^{+}\left(\mathrm{C}_{28} \mathrm{H}_{23} \mathrm{~N}_{2}{ }^{80} \mathrm{Se}\right)$ : calculated for $467.10209 \mathrm{~m} / \mathrm{z}$, found 467.1021 ( $\Delta=0 \mathrm{ppm}$ ).

## 1-(3,5-Dimethylphenyl)-3-methyl-benzimidazole-2-selenone 14




In a dried Schlenk tube, was placed salt [8]. $\mathbf{H I}$ ( $38.9 \mathrm{mg}, 0.106 \mathrm{mmol}$ ) and elemental selenium powder ( $31.8 \mathrm{mg}, 0.4 \mathrm{mmol}$ ). After 3 vacuum/argon cycles, dried THF ( 2 mL ) was added and the suspension was cooled down to $-78^{\circ} \mathrm{C}$. A NaHMDS solution ( $0.12 \mathrm{~mL}, 1.0 \mathrm{M}$ in THF) was added dropwise and the obtained solution was allowed to heat up to r.t. then stirred overnight. The solvent was then stripped off and the obtained residue was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, filtered over a Celite® pad and evaporated. The residue was dissolved several times in $\mathrm{Et}_{2} \mathrm{O}$ to precipitate the remaining inorganic impurities while the supernatant was removed with a pipette. The combined liquid layers were finally evaporated to afford the desired product 14 as a white crystalline solid ( $27 \mathrm{mg}, 81 \%$ yield).
${ }^{1} \mathrm{H}$ NMR ( 400 MHz, Acetone $-d_{6}$ ) $\delta=7.54(\mathrm{~d}, \mathrm{~J}=8.0,0.8,1 \mathrm{H}, 16), 7.33(\mathrm{t}, \mathrm{J}=8.2,7.5,1.1,1 \mathrm{H}$, 15), 7.23 (t, $J=8.4,7.4,1.1,1 \mathrm{H}, 14$ ), $7.19(\mathrm{~s}, 1 \mathrm{H}, 10), 7.13(\mathrm{~s}, 2 \mathrm{H}, 8,12), 7.02$ (d, J=8.0, $0.9,1 \mathrm{H}, 13$ ), 3.94 ( $\mathrm{s}, 3 \mathrm{H}, 17$ ), 2.39 ( $\mathrm{s}, 6 \mathrm{H}, 18,19$ ); ${ }^{13} \mathrm{C}$ NMR ( 101 MHz , Acetone- $\boldsymbol{d}_{6}$ ) $\delta=169.1$ ( $5, \mathrm{C}=\mathrm{Se}$ ), 140.0, 137.7, $135.2,134.6,131.3,126.7,124.4,124.3,110.9,110.7,33.5,21.2$; ${ }^{77} \mathrm{Se}$ NMR ( $76 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=91.5$; ${ }^{77}$ Se NMR ( 76 MHz , Acetone- $\boldsymbol{d}_{6}$ ) $\delta=112.7$; HR-MS (ESI, $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{CH}_{3} \mathrm{OH}=\mathbf{9 0} / \mathbf{1 0}$ ) $[\mathrm{M}+\mathrm{Na}]^{+}\left(\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{~N}_{2}\right.$ $\mathrm{Na}{ }^{80} \mathrm{Se}$ ): calculated for $339.03709 \mathrm{~m} / \mathrm{z}$, found 339.0368 ( $\Delta=1 \mathrm{ppm}$ ).
[5]Helicenic NHC gold(I) chloride complex (rac)-1


In a screw-capped vial protected from light with an aluminum foil, were placed salt (rac)-7 ( 21.7 mg , $0.051 \mathrm{mmol}),\left[\mathrm{AuCl}\left(\mathrm{Me}_{2} \mathrm{~S}\right)\right](15.4 \mathrm{mg}, 0.052 \mathrm{mmol})$ and dried $\mathrm{K}_{2} \mathrm{CO}_{3}(22.6 \mathrm{mg}, 0.163 \mathrm{mmol})$. The solids were dissolved in acetone (technical grade, 1 mL ) and the mixture was stirred at $60^{\circ} \mathrm{C}$ for 1 hour under
air. After completion of the reaction, the solvent was stripped off and the heterogenous violet/brown mixture was directly filtered on a silica gel plug and washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. After evaporation under reduced pressure, the desired gold chloride complex (rac)-1 was obtained as a white powder by precipitation with $\mathrm{Et}_{2} \mathrm{O}$ and drying under vacuum ( $30 \mathrm{mg}, 94 \%$ yield).
${ }^{1} \mathbf{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=8.32(\mathrm{~d}, \mathrm{~J}=8.3,1 \mathrm{H}, 29), 8.12-8.05(\mathrm{~m}, 2 \mathrm{H}, 24,32), 8.05-8.01$ (m, 1H, 25), $7.99-7.92(\mathrm{~m}, 3 \mathrm{H}, 15,21,22), 7.69-7.63(\mathrm{~m}, 1 \mathrm{H}, 31), 7.63-7.57(\mathrm{~m}, 1 \mathrm{H}, 30), 7.58(\mathrm{~d}, \mathrm{~J}=$ $8.6,1 \mathrm{H}, 14$ ), 7.39 ( $\mathrm{s}, 2 \mathrm{H}, 9,13$ ), 7.31 ( $\mathrm{s}, 1 \mathrm{H}, 11$ ), 3.38 ( $\mathrm{s}, 3 \mathrm{H}, 26$ ), $2.50\left(\mathrm{~s}, 6 \mathrm{H}, 27,28\right.$ ); ${ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CD}_{2} \mathrm{Cl}_{2}\right) \delta=140.7,137.4,134.1,132.8,132.6,132.3,132.1,131.6,129.2,129.1,128.1,127.4,127.3$, $127.2,126.6,126.4,126.0,125.4,124.8,116.7,112.6,40.8,21.7$. One quaternary carbon and the carbenic carbon cannot be seen. The $\mathrm{C}^{\text {carbene }}$ was identified at 178.3 ppm with ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ heteronuclear coupling with 26; HR-MS (ESI, $\left.\mathrm{CH}_{3} \mathrm{OH} / \mathrm{CH}_{2} \mathrm{Cl}_{\mathbf{2}}=\mathbf{9 0} / 10\right)[\mathrm{M}+\mathrm{Na}]^{+}\left(\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{~N}_{2}{ }^{35} \mathrm{Cl} \mathrm{Na} \mathrm{Au}\right)$ : calculated for $641.10293 \mathrm{~m} / \mathrm{z}$, found 641.1029 ( $\Delta=0 \mathrm{ppm}$ ).
[5]Helicenic NHC phenyacetylide gold(I) complex (rac)-2



In a round-bottom flask, were placed ( rac ) $-1(47 \mathrm{mg}, 0.075 \mathrm{mmol})$ and dried $\mathrm{K}_{2} \mathrm{CO}_{3}(36.4 \mathrm{mg}, 0.26$ mmol ) and the solids were dissolved in methanol ( 2 mL ). Phenylacetylene ( $25 \mu \mathrm{l}, 0.22 \mathrm{mmol}$ ) was added dropwise and the reaction mixture was stirred at $70^{\circ} \mathrm{C}$ for 2 hours. After completion of the reaction, the solvent was stripped off and the obtained mixture was directly filtered over a basic alumina plug and washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. After evaporation under reduced pressure, the desired gold acetylide complex ( rac )-2 was obtained as a white powder by precipitation with $\mathrm{Et}_{2} \mathrm{O}$ and drying under vacuum ( $42 \mathrm{mg}, 81 \%$ yield).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=8.40-8.32(\mathrm{~m}, 1 \mathrm{H}, 36), 8.08(\mathrm{t}, \mathrm{J}=8.4,2 \mathrm{H}, 31,39), 8.05-7.99$ (m, 1H, 32), $7.98-7.90(\mathrm{~m}, 3 \mathrm{H}, 22,28,29), 7.69-7.63(\mathrm{~m}, 1 \mathrm{H}, 38), 7.63-7.59(\mathrm{~m}, 1 \mathrm{H}, 37), 7.59-7.51$ (m, 1H, 21), 7.42 ( $\mathrm{s}, 2 \mathrm{H}, 16,20$ ), 7.32 ( $\mathrm{s}, 1 \mathrm{H}, 18$ ), $7.31-7.25$ (m, 2H, 10, 14), $7.21-7.09(\mathrm{~m}, 3 \mathrm{H}, 11,12$, 13), $3.42(\mathrm{~s}, 3 \mathrm{H}, 33), 2.52(\mathrm{~s}, 6 \mathrm{H}, 34,35) ;{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=194.5$ ( $5, \mathrm{C}^{\text {carbene }}$ ), 140.6, 137.6, $137.6,134.4,132.7,132.6,132.5,132.3,132.2,131.9,131.7,130.4,130.3,129.1,129.0,128.4,128.1$, $127.3,127.2,127.2,126.8,126.5,126.4,126.3,126.1,126.1,125.5,125.5,124.9,116.7,112.5,104.8$, 40.4, 21.7; HR-MS (ESI, $\left.\mathrm{CH}_{3} \mathrm{OH} / \mathrm{CH}_{2} \mathrm{Cl}_{2}=\mathbf{9 0} / 10\right)[\mathrm{M}+\mathrm{Na}]^{+}\left(\mathrm{C}_{36} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{Na} \mathrm{Au}\right)$ : calculated for 707.1732 $\mathrm{m} / \mathrm{z}$, found 707.1725 ( $\Delta=1 \mathrm{ppm}$ ).

## [5]Helicenic NHC carbazolide gold(I) complex (rac)-3



In a dried Schlenk tube, were placed (rac)-1 ( $17.6 \mathrm{mg}, 0.028 \mathrm{mmol}$ ), 9 H -Carbazole ( $14.2 \mathrm{mg}, 0.084$ $\mathrm{mmol})$ and $\mathrm{NaOtBu}(8.4 \mathrm{mg}, 0.087 \mathrm{mmol})$. After 3 vacuum/argon cycles, the solids were dissolved in freshly distilled THF ( 2 mL ) and the reaction mixture was stirred under argon at $70^{\circ} \mathrm{C}$ overnight. The solvent was stripped off and the obtained mixture was directly filtered over a basic alumina plug and washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. After evaporation under reduced pressure, the desired gold carbazolide complex ( rac ) $-\mathbf{3}$ was obtained as a white powder by precipitation with $\mathrm{Et}_{2} \mathrm{O}$, washing with acetone and $\mathrm{Et}_{2} \mathrm{O}$ and drying under vacuum ( $14.7 \mathrm{mg}, 69 \%$ yield).
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=8.43(\mathrm{~d}, 1 \mathrm{H}, 41), 8.15-8.05(\mathrm{~m}, 3 \mathrm{H}, 32,33,44), 8.04-7.95(\mathrm{~m}$, $5 \mathrm{H}, 15,23,29,30,38), 7.71(\mathrm{~d}, \mathrm{~J}=8.5,1 \mathrm{H}, 22), 7.71-7.61(\mathrm{~m}, 2 \mathrm{H}, 42,43), 7.59(\mathrm{~s}, 2 \mathrm{H}, 17,21), 7.45(\mathrm{~d}$, $J=8.1,0.9,2 \mathrm{H}, 12,35), 7.41(\mathrm{~s}, 1 \mathrm{H}, 19), 7.23(\mathrm{t}, \mathrm{J}=8.2,6.9,1.3,2 \mathrm{H}, 13,36), 6.98(\mathrm{t}, \mathrm{J}=7.8,7.0,1.0,2 \mathrm{H}$, 14,37 ), 3.58 ( $\mathrm{s}, 3 \mathrm{H}, 34$ ), $2.58(\mathrm{~s}, 6 \mathrm{H}, 39,40)$; ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}$ ) $\delta=182.5$ ( $5, \mathrm{C}^{\text {carbene }}$ ), 150.1, $140.8,137.8,134.3,132.9,132.7,132.6,132.3,132.0,131.7,129.2,129.0,128.2,127.4,127.3,127.3$, $126.5,126.5,126.4,126.1,125.5,124.9,124.4,124.2,120.7,119.9,119.9,116.8,116.6,114.1,112.5$, 111.2, $40.6,21.8$; HR-MS (ESI, $\left.\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)[\mathrm{M}+\mathrm{H}]^{+}\left(\mathrm{C}_{40} \mathrm{H}_{31} \mathrm{~N}_{3} \mathrm{Au}\right)$ : calculated for $750.21781 \mathrm{~m} / \mathrm{z}$, found 750.2171 ( $\Delta=1 \mathrm{ppm})$.

## 3. NMR Spectra



Figure S3. ${ }^{1} \mathrm{H}$ NMR spectrum of $5 \mathrm{in} \mathrm{CDCl}_{3}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S4. ${ }^{13} \mathrm{C}$ NMR spectrum of 5 in $\mathrm{CDCl}_{3}$ at $298 \mathrm{~K}(101 \mathrm{MHz})$.


Figure S5. ${ }^{1} \mathrm{H}$ NMR spectrum of [(rac)-6]. HI in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S6. ${ }^{1} \mathrm{H}_{-}{ }^{13} \mathrm{C}$ satellites of the imidazolium proton in ${ }^{1} \mathrm{H} N M R$ and determination of the ${ }^{1} \mathrm{~J}(\mathrm{C}, \mathrm{H})$ coupling constant [(rac)6]. $\mathrm{HI}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 400 \mathrm{MHz}, 298 \mathrm{~K}\right)$.


Figure S7. ${ }^{13} \mathrm{C}$ NMR spectrum of $[(\mathrm{rac})-6] . \mathrm{HI}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(101 \mathrm{MHz})$.


Figure S8. ${ }^{1} \mathrm{H}$ NMR spectrum of [(rac)-6]. HCl in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(300 \mathrm{MHz})$.


Figure S9. ${ }^{13} \mathrm{C}$ NMR spectrum of $[(\mathrm{rac})-6] . \mathrm{HCl}$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(75 \mathrm{MHz})$.


Figure S10. ${ }^{1} \mathrm{H}$ NMR spectrum of [8]. HI in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(500 \mathrm{MHz})$.

|  | $\text { lium) }=222 \mathrm{~Hz}$ |
| :---: | :---: |
| 1.6011 .5511 .5011 .4511 .4011 .3511 .3011 .2511 .2011 .1511 .1011 .0511 .0010 .95 | 10.8510 .8010 .7510 .7010 .6510 .6010 .5510 .5010 .4510 .4010 .3510 .3010 .25 |

Figure S11. ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ satellites of the imidazolium proton in ${ }^{1} \mathrm{H} N M R$ and determination of the ${ }^{1} \mathrm{~J}(\mathrm{C}, \mathrm{H})$ coupling constant [8]. HI ( $\mathrm{CD}_{2} \mathrm{Cl}_{2}, 400 \mathrm{MHz}, 298 \mathrm{~K}$ ).


Figure S12. ${ }^{13} \mathrm{C}$ NMR spectrum of [8]. HI in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(125 \mathrm{MHz})$.

## 



Figure S13. ${ }^{1} \mathrm{H}$ NMR spectrum of (rac)-9/(rac)-9' in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S14. ${ }^{13} \mathrm{C}$ NMR spectrum of (rac)-9/(rac)-9'in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$.


Figure S15. ${ }^{1} \mathrm{H}$ NMR spectrum of $10 \mathrm{in} \mathrm{CDCl}_{3}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S16. ${ }^{13} \mathrm{C}$ NMR spectrum of 10 in $\mathrm{CDCl}_{3}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$.


Figure S17. ${ }^{1} \mathrm{H}$ NMR spectrum of (rac)-11 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(500 \mathrm{MHz})$.


Figure S18. ${ }^{1} \mathrm{H}$ NMR spectrum of 12 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S19. ${ }^{13} \mathrm{C}$ NMR spectrum of 12 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$.


Figure S20. ${ }^{1} \mathrm{H}$ NMR spectrum of $(\mathrm{rac})-13$ in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{CO}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S21. ${ }^{13} \mathrm{C}$ NMR spectrum of $(\mathrm{rac})-13$ in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{CO}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$.


Figure S22. ${ }^{77}$ Se NMR spectrum of (rac)-13 in $\mathrm{CDCl}_{3}$ at $298 \mathrm{~K}(76 \mathrm{MHz})$.


Figure S23. ${ }^{77}$ Se NMR spectrum of $(\mathrm{rac})-13$ in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{CO}$ at $298 \mathrm{~K}(76 \mathrm{MHz})$.


Figure S24. ${ }^{1} \mathrm{H}$ NMR spectrum of $14 \mathrm{in}\left(\mathrm{CD}_{3}\right)_{2} \mathrm{CO}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S25. ${ }^{13} \mathrm{C}$ NMR spectrum of $14 \mathrm{in}\left(C D_{3}\right)_{2} \mathrm{CO}$ at $298 \mathrm{~K}(100 \mathrm{MHz})$.


Figure S26. ${ }^{77}$ Se NMR spectrum of 14 in $\mathrm{CDCl}_{3}$ at $298 \mathrm{~K}(76 \mathrm{MHz})$.


Figure S27. ${ }^{77} \mathrm{Se}$ NMR spectrum of (rac)-13 in $\left(\mathrm{CD}_{3}\right)_{2} \mathrm{CO}$ at $298 \mathrm{~K}(76 \mathrm{MHz})$.


Figure S28. ${ }^{1} \mathrm{H}$ NMR spectrum of (rac)-1 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S29. ${ }^{13} \mathrm{C}$ NMR spectrum of (rac)-1 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(101 \mathrm{MHz})$ (inset: ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ hetereonuclear correlation between the unresolved carbene signal in ${ }^{13} \mathrm{CNMR}$ and the $\mathrm{N}-\mathrm{CH}_{3}$ group in ${ }^{1} \mathrm{H}$ NMR).


Figure S30. ${ }^{1} \mathrm{H}$ NMR spectrum of (rac)-2 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure S31. ${ }^{13} \mathrm{C}$ NMR spectrum of (rac)-2 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(101 \mathrm{MHz})$.


Figure S32. ${ }^{1} \mathrm{H}$ NMR spectrum of (rac)-3 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(400 \mathrm{MHz})$.


Figure $\mathrm{S} 33 .{ }^{13} \mathrm{C}$ NMR spectrum of (rac)-3 in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ at $298 \mathrm{~K}(101 \mathrm{MHz})$.

## 4. X-ray crystallographic data

X-ray crystallographic data were measured on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K $\alpha$ radiation ( $\lambda=0.71073 \AA$, multilayer monochromator). The structures were solved by dual-space algorithm using the SHELXT program [1a], and then refined with full-matrix least-squares methods based on $F^{2}$ (SHELXL) [2a]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters.

Compound 8: Crystal under study has revealed to be twinned, composed by two different domains founded with the CELL_now program [3a]. Twin law of this non-meroedral twinning is the following : 1.0000 .0000 .328 0.000-1.000 0.000 0.000 0.000-1.000

The diffraction frames of the data collection were then integrated with SAINT [4a] and TWINABS [5a] program was used for scaling, empirical absorption corrections and generation of HKLF5 type data set. Final structural refinement has been refined using these total integrated intensities, leading to a twinning of 0.43 .
[1a] G. M. Sheldrick, Acta Cryst. A71 (2015) 3-8
[2a] G.M. Sheldrick Acta Cryst. C71 (2015) 3-8
[3a] G. M. Sheldrick (2008). CELL_NOW. Georg-August-Universität, Göttingen, Germany
[4a] Bruker (2017). SAINT v.8.38A. Bruker, Madison, Wisconsin, USA
[5a] G. M. Sheldrick (2012). TWINABS 2012/1. Bruker, Madison, Wisconsin, USA »









Figure S34. ORTEP figures for [(rac)-6].HI, [8].HI, (rac)-9, 10, (rac)-11, 12, 14 (50\% probability).


Figure S35. Heterochiral supramolecular arrangement of (rac)-6. Hydrogens and solvent molecules have been omitted for clarity.

Table S1. Selected metrics (bond length and angles) for the gold complexes.

| Complexe | Helicity ( ${ }^{\circ}$ ) | Au-C Carbene <br> bond length <br> $(\AA \AA)$ | Au-Y <br> bond <br> length (Å) | $C_{\text {carbene-Au-Y }}$ <br> dihedral angle ( ${ }^{\circ}$ ) | Shortest Au-Au <br> distance (Å) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (rac)-1 | 47.87 | 1.962 | 2.280 | 178.30 | 3.893 |
| (rac)-2 | 48.12 | 2.014 | 2.021 | 175.98 | 3.567 |
| (rac)-3 | 54.66 | 1.991 | 2.020 | 173.24 | 4.026 |

Table S2. X-ray crystallographic data

|  | [(rac)-6].HI | [8].HI | (rac)-9 | 10 | 12 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Empirical Formula | $\begin{gathered} \mathrm{C}_{28} \mathrm{H}_{23} \mathrm{IN}_{2} \bullet \\ \mathrm{CH}_{2} \mathrm{Cl}_{2} \end{gathered}$ | $\mathrm{C}_{16} \mathrm{H}_{17} \mathrm{IN}$ | $\mathrm{C}_{36} \mathrm{H}_{34} \mathrm{ClIrN}_{2}$ | $\mathrm{C}_{24} \mathrm{H}_{28} \mathrm{ClIrN}_{2}$ | $\mathrm{C}_{18} \mathrm{H}_{26} \mathrm{ClIrN} \mathrm{N}_{2} \mathrm{O}_{2}$ |
| CCDC number | 2085972 | 2085973 | 2086202 | 2086203 | 2086204 |
| Formula Weight | 599.31 | 364.21 | 722.30 | 572.13 | 519.98 |
| Temperature (K) | 150 | 150 | 150 | 150 | 150 |
| Wavelenght (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | monoclinic | monoclinic | triclinic | orthorhombic | triclinic |
| Space Group | C2/c | $P 2_{1} / \mathrm{C}$ | P-1 | Pbca | P-1 |
| a ( $\AA$ ) | 29.179(4) | 10.8827(14) | 7.5502(11) | 14.1044(16) | 8.5209(6) |
| b ( $\AA$ ) | 8.1815(12) | 11.2420(15) | 11.232(3) | 16.0957(15) | 14.7543(9) |
| c ( $\AA$ ) | 21.986(3) | 12.6771(15) | 18.367(4) | 18.991(2) | 15.9605(10) |
| $\alpha\left({ }^{\circ}\right)$ | 90 | 90 | 77.346(8) | 90 | 111.063(2) |
| $\beta\left({ }^{\circ}\right)$ | 99.880(5) | 101.022(5) | 79.074(8) | 90 | 92.649(2) |
| $\gamma\left({ }^{\circ}\right)$ | 90 | 90 | 71.436(8) | 90 | 106.753(4) |
| Volume ( $\AA^{\mathbf{3}}$ ) | 5170.8(13) | 1522.3(3) | 1428.5(5) | 4311.3(8) | 1767.6(2) |
| Z | 8 | 4 | 2 | 8 | 4 |
| Color | colourless | colourless | yellow | yellow | green |
| $\rho_{\text {calculated }}\left(\mathrm{g} . \mathrm{cm}^{-3}\right)$ | 1.540 | 1.589 | 1.679 | 1.763 | 1.954 |
| Absorption coefficient ( $\mathrm{mm}^{-1}$ ) | 1.466 | 2.093 | 4.795 | 6.329 | 7.716 |
| Tmin | 0.708 | 0.580 | 0.292 | 0.088 | 0.255 |
| Tmax | 0.916 | 0.882 | 0.487 | 0.181 | 0.462 |
| F (000) | 2400 | 720 | 716 | 2240 | 992 |
| Crystal size (mm) | $\begin{gathered} 0.350 \times 0.220 \mathrm{x} \\ 0.060 \end{gathered}$ | $\begin{gathered} 0.260 \times 0.210 \mathrm{x} \\ 0.060 \end{gathered}$ | $\begin{gathered} 0.430 \times 0.370 \mathrm{x} \\ 0.150 \end{gathered}$ | $\begin{gathered} 0.530 \times 0.400 \mathrm{x} \\ 0.270 \end{gathered}$ | $\begin{gathered} 0.290 \times 0.250 \mathrm{x} \\ 0.100 \end{gathered}$ |
| $\theta$ range for data collection ( ${ }^{\circ}$ ) | 2.542 to 27.535 | 2.442 to 27.508 | 2.292 to 27.668 | 2.199 to 27.507 | 2.463 to 27.597 |
| Limiting indices | $\begin{gathered} -37 \leq h \leq 37 \\ -8 \leq k \leq 10 \\ -28 \leq 1 \leq 28 \end{gathered}$ | $\begin{gathered} -14 \leq h \leq 13 \\ 0 \leq k \leq 14 \\ 0 \leq \mathrm{l} \leq 16 \end{gathered}$ | $\begin{aligned} -9 & \leq h \leq 8 \\ -14 & \leq k \leq 14 \\ -23 & \leq 1 \leq 23 \end{aligned}$ | $\begin{aligned} & -18 \leq h \leq 18 \\ & -20 \leq k \leq 19 \\ & -24 \leq 1 \leq 23 \end{aligned}$ | $\begin{aligned} & -11 \leq h \leq 11 \\ & -19 \leq k \leq 19 \\ & -19 \leq \mathrm{l} \leq 20 \end{aligned}$ |
| Data completeness | 97.5\% | 98.7\% | 99.6\% | 99.4\% | 97.9\% |
| Reflection collected | 33516 | 3457 | 33483 | 23588 | 50754 |
| Reflections uniques | $\begin{gathered} 5825[R(\text { int })= \\ 0.0572] \end{gathered}$ | 3457 | $\begin{gathered} 6643[R(\text { int })= \\ 0.0545] \end{gathered}$ | $\begin{gathered} 4925[R(\text { int })= \\ 0.0921] \end{gathered}$ | $\begin{gathered} 8018[R(\text { int })= \\ 0.0405] \end{gathered}$ |
| Data / restraints / parameters | 5825 / 0 / 310 | 3457 / 0 / 176 | 6643 / 0 / 361 | 4925 / 0 / 256 | 8018 / 0 / 439 |
| Goodness-on-fit on $\boldsymbol{F}^{\mathbf{2}}$ | 1.094 | 1.089 | 1.026 | 1.054 | 1.168 |
| Final $R$ indices $[1>2 \sigma]$ | $\begin{gathered} R 1=0.0443 \\ w R 2=0.1088 \end{gathered}$ | $\begin{gathered} R 1=0.0311 \\ w R 2=0.0748 \end{gathered}$ | $\begin{gathered} R 1=0.0247 \\ w R 2=0.0603 \end{gathered}$ | $\begin{gathered} R 1=0.0467, \\ w R 2=0.1073 \end{gathered}$ | $\begin{gathered} R 1=0.0275, \\ w R 2=0.0586 \end{gathered}$ |
| R indices (all data) | $\begin{aligned} & \hline R 1=0.0609 \\ & w R 2=0.1187 \end{aligned}$ | $\begin{gathered} \hline R 1=0.0376 \\ w R 2=0.0776 \end{gathered}$ | $\begin{gathered} \hline R 1=0.0288, \\ w R 2=0.0622 \end{gathered}$ | $\begin{gathered} \hline R 1=0.0744, \\ w R 2=0.1271 \end{gathered}$ | $\begin{aligned} & \hline R 1=0.0334, \\ & w R 2=0.0621 \end{aligned}$ |
| Largest diff peak and hole ( $\mathrm{e} \AA^{-3}$ ) | $\begin{gathered} 2.157 \text { and - } \\ 1.145 \end{gathered}$ | $\begin{gathered} 0.468 \text { and - } \\ 1.091 \end{gathered}$ | $\begin{gathered} 1.313 \text { and - } \\ 1.819 \end{gathered}$ | $\begin{gathered} 2.292 \\ \text { and }-1.866 \end{gathered}$ | $\begin{gathered} 1.627 \\ \text { and }-1.523 \end{gathered}$ |


|  | (rac)-1 | (rac)-2 | (rac)-3 |
| :---: | :---: | :---: | :---: |
| Empirical Formula | $\begin{gathered} \mathrm{C}_{28} \mathrm{H}_{22} \mathrm{AuClN}_{2} \\ \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2} \end{gathered}$ | $\mathrm{C}_{36} \mathrm{H}_{27} \mathrm{AuN}_{2}$ | $\mathrm{C}_{40} \mathrm{H}_{30} \mathrm{AuN}_{3}$ |
| CCDC number | 2085969 | 2085970 | 2085971 |
| Formula Weight | 703.82 | 684.56 | 749.63 |
| Temperature (K) | 150 | 150 | 150 |
| Wavelenght (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | monoclinic | triclinic | monoclinic |
| Space Group | C2/c | P-1 | $P 2_{1} / \mathrm{c}$ |
| a ( $\AA$ ) | 22.953(2) | 10.7486(11) | 14.6402(9) |
| b ( $\AA$ ) | 15.8832(17) | 12.3503(12) | 13.5945(9) |
| c ( $\AA$ ) | 15.4461(18) | 12.5806(12) | 16.2108(9) |
| $\alpha\left({ }^{\circ}\right)$ | 90 | 87.492(3) | 90 |
| $\beta\left({ }^{\circ}\right)$ | 111.559(4) | 66.568(3) | 112.724(2) |
| $\gamma\left({ }^{\circ}\right)$ | 90 | 66.219(3) | 90 |
| Volume ( $\AA^{3}$ ) | 5237.3(10) | 1388.6(2) | 2975.9(3) |
| Z | 8 | 2 | 4 |
| Color | colourless | colourless | green |
| $\rho_{\text {calculated }}\left(\mathrm{g} . \mathrm{cm}^{-3}\right)$ | 1.785 | 1.637 | 1.673 |
| Absorption coefficient ( $\mathrm{mm}^{-1}$ ) | 5.945 | 5.325 | 4.978 |
| Tmin | 0.068 | 0.568 | 0.117 |
| Tmax | 0.172 | 0.766 | 0.370 |
| F (000) | 2736 | 672 | 1480 |
| Crystal size (mm) | $0.440 \times 0.340 \times 0.240$ | $0.240 \times 0.180 \times 0.050$ | $0.600 \times 0.450 \times 0.200$ |
| $\theta$ range for data collection ( ${ }^{\circ}$ ) | 2.931 to 27.484 | 3.265 to 27.484 | 2.961 to 27.484 |
| Limiting indices | $\begin{aligned} & -29 \leq h \leq 29 \\ & -20 \leq k \leq 20 \\ & -20 \leq 1 \leq 20 \end{aligned}$ | $\begin{aligned} & -13 \leq h \leq 13 \\ & -16 \leq k \leq 16 \\ & -16 \leq l \leq 16 \end{aligned}$ | $\begin{aligned} & -18 \leq h \leq 19 \\ & -17 \leq k \leq 17 \\ & -18 \leq \mathrm{l} \leq 21 \end{aligned}$ |
| Data completeness | 99.9\% | 99.8\% | 99.8\% |
| Reflection collected | 32205 | 31422 | 31299 |
| Reflections uniques | 6001 [R(int) = 0.0424] | 6371 [R(int) = 0.0392] | 6809 [R(int) $=0.0489$ ] |
| Data / restraints / parameters | 6001 / 3 / 326 | 6371 / 0 / 355 | 6809 / 0 / 400 |
| Goodness-on-fit on $F^{\mathbf{2}}$ | 1.034 | 1.098 | 1.038 |
| Final $R$ indices $[1>2 \sigma]$ | $\begin{gathered} R 1=0.0258 \\ w R 2=0.0592 \end{gathered}$ | $\begin{gathered} R 1=0.0202 \\ w R 2=0.0414 \end{gathered}$ | $\begin{gathered} R 1=0.0267, \\ w R 2=0.0629 \end{gathered}$ |
| R indices (all data) | $\begin{aligned} & R 1=0.0318 \\ & w R 2=0.0623 \end{aligned}$ | $\begin{gathered} R 1=0.0245, \\ w R 2=0.0428 \end{gathered}$ | $\begin{aligned} & R 1=0.0362 \\ & w R 2=0.0678 \end{aligned}$ |
| Largest diff peak and hole (e $\AA^{-3}$ ) | 0.934 and -1.500 | 0.788 and -1.001 | 1.563 and -1.873 |

## 5. Chiral HPLC separations

## Analytical chiral HPLC separation for 1

- The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm . The flow-rate is $1 \mathrm{~mL} / \mathrm{min}$.


| Column | Mobile Phase | $\mathbf{t 1}$ | k1 | t2 | k2 | $\boldsymbol{\alpha}$ | Rs |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Chiralpak IH | Heptane / isopropanol / <br> dichloromethane (80/10/10) | $9.45(-)$ | 2.20 | $12.37(+)$ | 3.19 | 1.45 | 5.64 |




| RT [min] | Area | Area\% | Capacity Factor | Enantioselectivity | Resolution (USP) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 9.45 | 4189 | 49.89 | 2.20 |  |  |
| 12.37 | 4207 | 50.11 | 3.19 | 1.45 | 5.64 |
| Sum | 8396 | 100.00 |  |  |  |

## Preparative separation for 1:

- Sample preparation: About 26 mg of $\mathbf{1}$ are dissolved in 4.5 mL of a mixture of dichloromethane and hexane
(1/1).
- Chromatographic conditions: Chiralpak IH ( $250 \times 10 \mathrm{~mm}$ ), Hexane / isopropanol / dichloromethane (80/10/10) as mobile phase, flow-rate $=5 \mathrm{~mL} / \mathrm{min}$, UV detection at 254 nm .
- Injections (stacked): 15 times $300 \mu \mathrm{~L}$, every 6 minutes.
- First fraction: 10 mg of the $(P)$ enantiomer with ee $>98 \%$

DAD1 C, $\mathrm{Sig}=254,4$ Ref=off


| RT [min] | Area | Area\% |
| :---: | :---: | :---: |
| 9.54 | 3655 | 99.10 |
| 12.40 | 33 | 0.90 |
| Sum | 3689 | 100.00 |

- Second fraction: 10 mg of the $(M)$ enantiomer with ee > $98 \%$



## Analytical chiral HPLC separation for 2

- The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm . The flow-rate is 1 $\mathrm{mL} / \mathrm{min}$.


| Column | Mobile Phase | t1 | k1 | t2 | k2 | $\boldsymbol{\alpha}$ | Rs |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Chiralpak IB | Heptane / isopropanol / <br> dichloromethane (80/10/10) | $5.52(-)$ | 0.87 | $7.32(+)$ | 1.48 | 1.70 | 5.18 |

DAD1 C, Sig=254,4 Ref=off



| RT [min] | Area | Area\% | Capacity Factor | Enantioselectivity | Resolution (USP) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 5.52 | 2816 | 45.34 | 0.87 |  |  |
| 7.32 | 3395 | 54.66 | 1.48 | 1.70 | 5.18 |
| Sum | 6211 | 100.00 |  |  |  |

## Preparative separation for 2:

- Sample preparation: About 35 mg of $\mathbf{2}$ are dissolved in 4 mL of a mixture of dichloromethane and hexane (1/1).
- Chromatographic conditions: Chiralpak IB ( $250 \times 10 \mathrm{~mm}$ ), Hexane / isopropanol / dichloromethane (80/10/10) as mobile phase, flow-rate $=5 \mathrm{~mL} / \mathrm{min}$, UV detection at 254 nm .
- Injections (stacked): 20 times $200 \mu \mathrm{~L}$, every 7 minutes.
- First fraction: 16 mg of the $(P)$ enantiomer with ee > 97.5 \%

- Second fraction: 16 mg of the $(M)$ enantiomer with ee > 98.5 \%


DAD1 E, Sig=254,4 Ref=off



| RT [min] | Area | Area\% | Capacity Factor | Enantioselectivity | Resolution (USP) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 4.93 | 2531 | 52.62 | 0.67 |  |  |
| 7.09 | 2279 | 47.38 | 1.40 | 2.09 | 7.45 |
| Sum | 4810 | 100.00 |  |  |  |

The compound seems unstable and forms the peak at 4.4 min , which is found in all other fractions after preparative separation.

## Preparative separation for 3:

- Sample preparation: About 12 mg of compound 3 are dissolved in 2.5 mL of a mixture hexane / dichloromethane (1/1).
- Chromatographic conditions: Chiralpak IA ( $250 \times 10 \mathrm{~mm}$ ), Hexane / ethanol / dichloromethane (70/20/10) as mobile phase, flow-rate $=5 \mathrm{~mL} / \mathrm{min}$, UV detection at 254 nm .
- Injections (stacked): 100 times $250 \mu \mathrm{~L}$, every 5.5 minutes.
- First fraction: 3.2 mg of the first eluted enantiomer with ee $>92 \%$

DAD1 E, $\operatorname{Sig}=254,4$ Ref=off


- Second fraction: 4.7 mg of the second eluted enantiomer with ee $>84 \%$

DAD1 E, $\mathrm{Sig}=254,4$ Ref=off


## 6. Photophysical studies

Absorption spectra in solution were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm path length. Samples for emission measurements were contained within quartz cuvettes of 1 cm pathlength modified to allow connection to a high-vacuum line. Degassing was achieved via a minimum of three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77 K was $<5 \times 10^{-2} \mathrm{mbar}$, as monitored using a Pirani gauge. Luminescence quantum yields were determined using aqueous $\left[\mathrm{Ru}(\mathrm{bpy})_{3}\right] \mathrm{Cl}_{2}$ as the standard ( $\left.\Phi_{\text {lum }}=0.040\right) .{ }^{[6]}$ The luminescence lifetimes of the complexes were measured by multichannel scaling (MCS) following excitation into the lowest-energy absorption band with a microsecond pulsed xenon lamp. The emitted light was detected at $90^{\circ}$ using a Hamamatsu R928 photomultiplier tube, Peltier-cooled to - $20^{\circ} \mathrm{C}$, after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is $\pm 10 \%$ or better. Under air-equilibrated conditions, the intensity of phosphorescence is negligible and certainly too weak to determine a lifetime. We were not able to determine the lifetime of the fluorescence around 400 nm . Using a 374 nm laser diode in conjunction with a time-correlated single photon counting set-up, the detected light was too weak and/or the decay too short to reliably deconvolute the lifetime from the instrument response function. The spectra and lifetimes at 77 K were recorded using the same equipment in a glass of EPA (= diethyl ether / isopentane / ethanol, 2:2:1 v/v) contained within 4 mm diameter quartz tubes in a Dewar.

Table S3. UV-Vis and emission data for the helicenic gold complexes 1 and 2.

| Complex | $\begin{gathered} \text { Absorption } \\ \lambda_{\text {max }} / \mathrm{nm} \\ \left(\varepsilon / \mathbf{M}^{-1} \mathbf{c m}^{-1}\right)^{a} \end{gathered}$ | $\lambda_{\max }^{\text {Emission } / n m^{b}}$ | $\begin{aligned} & \Phi \\ & \times 10^{2 c} \end{aligned}$ | $\tau_{\text {phos }}$ | Emission at $77 \mathrm{~K}^{e}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $\lambda_{\text {max }} / \mathrm{nm}$ | $\tau / \mu s$ |
| 1 | $\begin{gathered} 268(36239), 293 \\ (41594), 302(41847), \\ 314(34455), 370 \\ (2497), 390(1963) \end{gathered}$ | $\begin{gathered} \text { 393, 415, } 439 \\ \text { (Fluo) } \\ 514,551,602 \text { sh } \\ \text { (Phos) } \end{gathered}$ | 0.46 | $\begin{aligned} & 800 \\ & \text { (Phos) } \end{aligned}$ | $\begin{gathered} 511,546,592 \\ 642,700 \end{gathered}$ | 52000 |


|  | $280(42795), 291$ <br> $(47380), 318(37200)$, <br> $371(2828), 391$ <br> $(2166)$ | $393,415,439$ <br> (Fluo) <br> $516,551,598 s h$ <br> (Phos) | 1.6 | 1500 <br> (Phos) | $511,546,592$, <br> 644,704 | 19000 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |

${ }^{\text {a }}$ In $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $295 \pm 1 \mathrm{~K} .{ }^{\mathrm{b}}$ In deoxygenated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $295 \pm 1 \mathrm{~K} . \lambda_{\text {max }}=\lambda_{(0,0)}{ }^{c}$ Quantum yield in deoxygenated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $295 \pm 1 \mathrm{~K}$ were measured using $\left[\mathrm{Ru}(\mathrm{bpy})_{3}\right] \mathrm{Cl}_{2(\mathrm{aq})}$ as the standard, for which $\Phi=0.04$. ${ }^{[6] \mathrm{d}}$ Lifetime of the phosphorescence band in deoxygenated $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $295 \pm 1 \mathrm{~K}$, recorded at $\lambda_{\mathrm{em}}=550 \mathrm{~nm}$ estimated uncertainty in the values is around $\pm 10 \%{ }^{\mathrm{e}} \mathrm{In}$ diethyl ether / isopentane / ethanol, 2:2:1, $\mathrm{v} / \mathrm{v} / \mathrm{v}$; the lifetimes indicated again refer to the phosphorescence, $\lambda_{\mathrm{em}}=550 \mathrm{~nm}$.

## 7. Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp ( 589 nm ) in a 1 or 10 cm cell, thermostated with a Peltier controlled cell holder. Specific rotations are given in $10^{-1}$ deg $\cdot \mathrm{cm}^{2} \cdot \mathrm{~g}^{-1}$, and molar rotations are given in $10^{-3} \mathrm{deg} \cdot \mathrm{cm}^{2} \cdot \mathrm{~mol}^{-1}$. Specific and molar rotations of the stereoisomers of $\mathbf{1}$ and $\mathbf{2}$ were measured in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $25^{\circ} \mathrm{C}$ with an uncertainty of $\pm 6 \%$.

Table S4. Specific and molar rotations values for $\mathbf{1}$ and $\mathbf{2}$ enantiomers.

|  | Conc. <br> $\left(\mathrm{mol} . \mathrm{L}^{-1}\right)$ | $[\alpha]_{D}^{25}$ <br> $\left(10^{-1} \mathrm{deg} \cdot \mathrm{cm}^{2} \cdot \mathrm{~g}^{-1}\right)$ | $[\phi]_{D}^{25}$ <br> $\left(10^{-3} \mathrm{deg} \cdot \mathrm{cm}^{2} \cdot \mathrm{~mol}^{-1}\right)$ |
| :---: | :---: | :---: | :---: |
| $(P) \mathbf{- \mathbf { 1 }}$ | $3.4 \times 10^{-4}$ | +880 | +5420 |
| $(M)-\mathbf{1}$ | $4.7 \times 10^{-4}$ | -895 | -5550 |
| $(P)-\mathbf{2}$ | $4.2 \times 10^{-4}$ | +940 | +6420 |
| $(M)-\mathbf{2}$ | $4.1 \times 10^{-4}$ | -830 | -5700 |

## 8. References

[1] N. Hellou, M. Srebro-Hooper, L. Favereau, F. Zinna, E. Caytan, L. Toupet, V. Dorcet, M. Jean, N. Vanthuyne, J. A. G. Williams, L. Di Bari, J. Autschbach, J. Crassous, Angew. Chem. Int. Ed. 2017, 56, 8236-8239.
[2] A. Klapars, J. C. Antilla, X. Huang, S. L. Buchwald, J. Am. Chem. Soc. 2001, 123, 7727-7729.
[3] A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Z. Slawin, S. P. Nolan, Chem. Commun. 2013, 49, 5541.
[4] A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, Organometallics 2013, 32, 5269-5272.
[5] N. V. Tzouras, F. Nahra, L. Falivene, L. Cavallo, M. Saab, K. Van Hecke, A. Collado, C. J. Collett, A. D. Smith, C. S. J. Cazin, S. P. Nolan, Chem. Eur. J. 2020, 26, 4515-4519.
[6] K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, Y. Shiina, S. Oischi, S. Tobita, PhysChemChemPhys 2009, 11, 9850.

