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# Electronic Supplementary Information

## [7]-Helicene: A Chiral Molecular Tweezer for Silver(I) Salts.

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## Characterisation of [7]-helicene

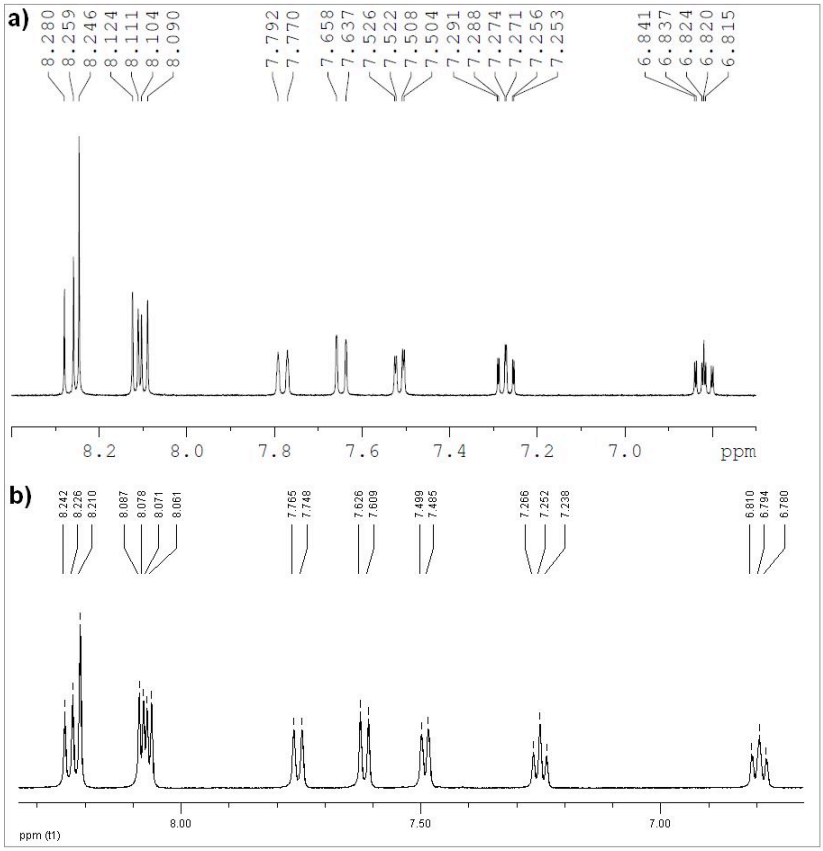


**Figure S1**. $^1$H-NMR comparison: a) [7]-helicene:Ag complex in $CDCl_3$; b) [7]-helicene + 3.0 equiv. $Ag^+$ in $CH_2Cl_2$.

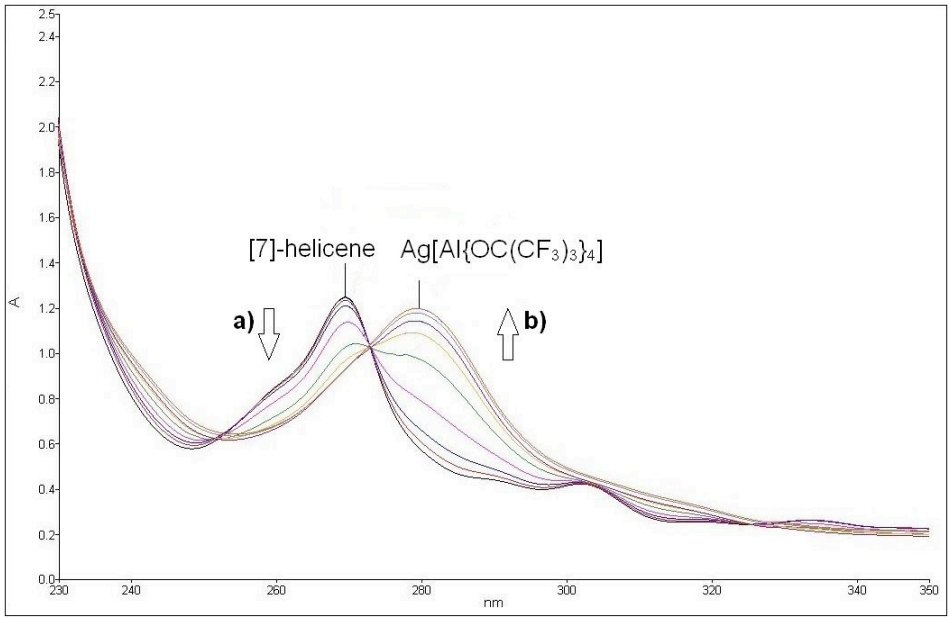


**Figure S2**. UV-vis spectrum monitoring the addition of aliquots of $Ag^+$ to a solution of [7]-helicene: a) Increase of $Ag^+$ from 0.0 equiv. to 6.0 equiv.; b) Increase of $Ag^+$ from 6.0 equiv. to 12.3 equiv.

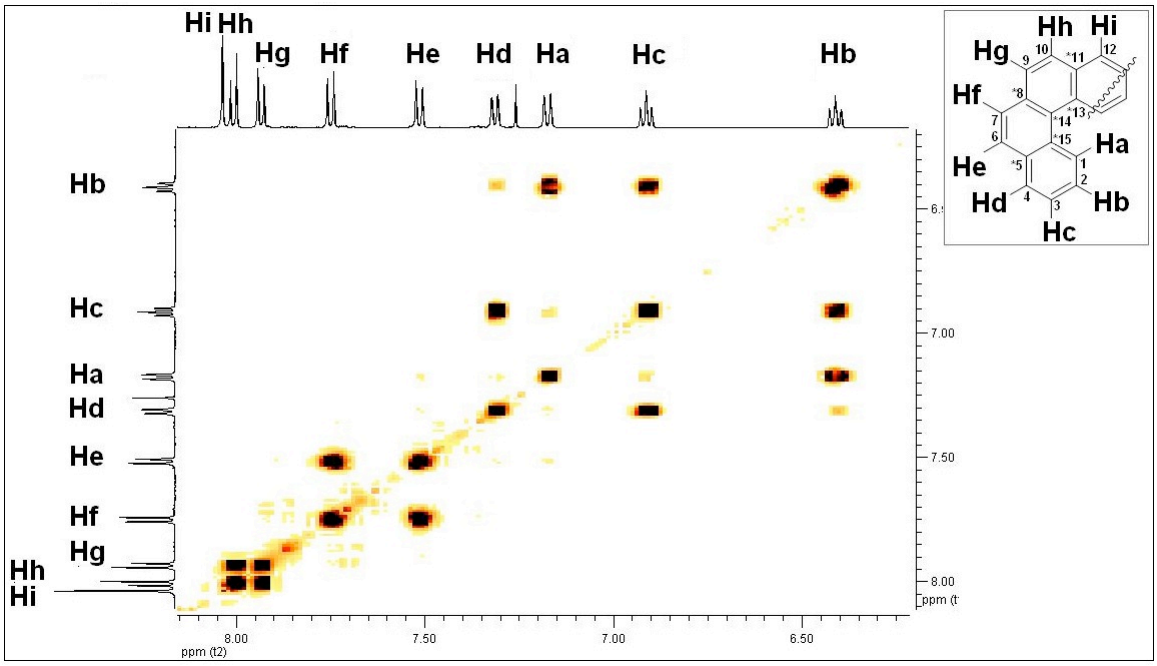


**Figure S3**. COSY of [7]-helicene in $CDCl_3$

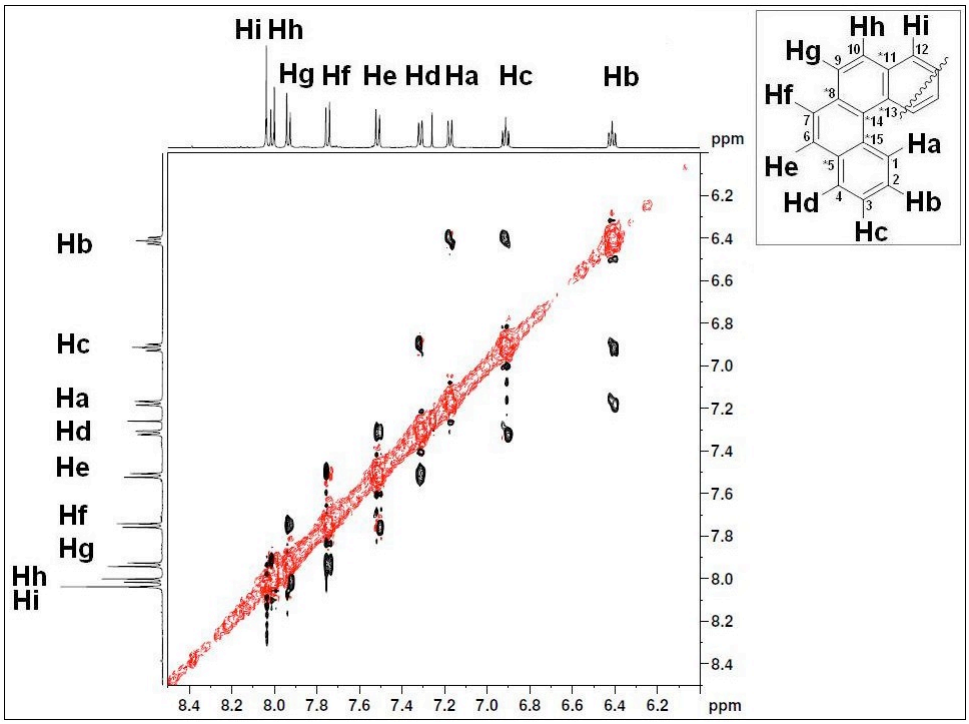


**Figure S4**. NOESY of [7]-helicene in $CDCl_3$

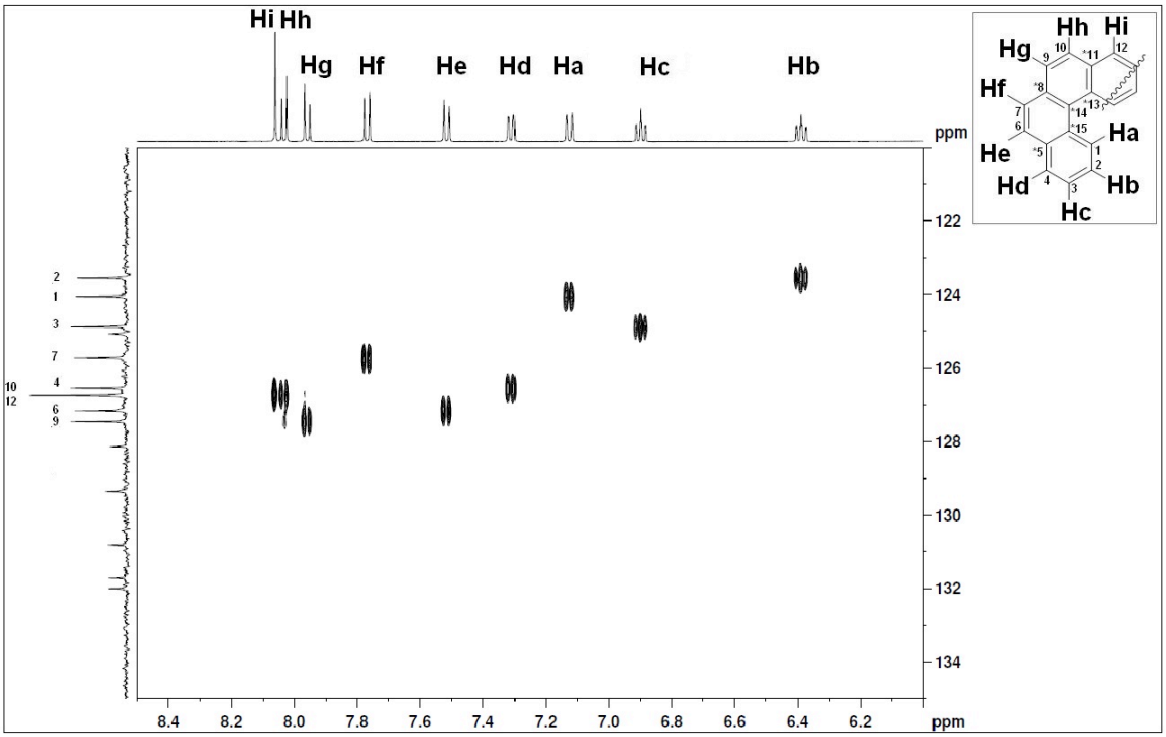


**Figure S5**. HSQC of [7]-helicene in $CH_2Cl_2$

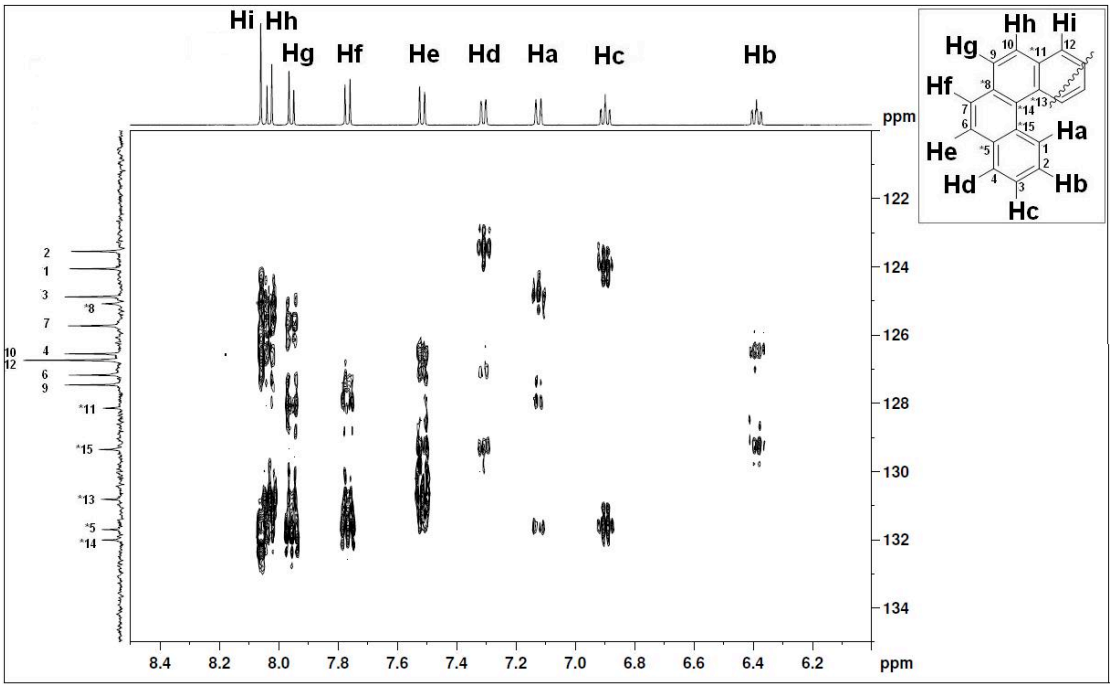


**Figure S6**. HMBC of [7]-helicene in $CH_2Cl_2$

## Characterisation of Ag(I)-[7]-helicene complex

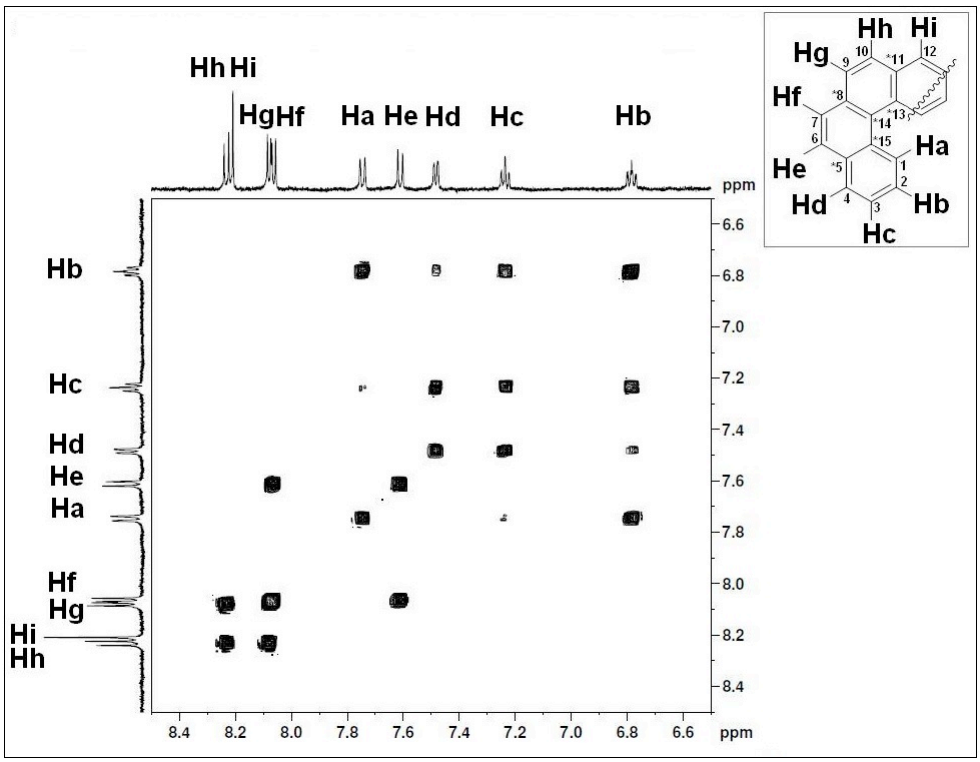


**Figure S7**. COSY of [7]-helicene + 2.0 equiv. $Ag^+$ in $CH_2Cl_2$.

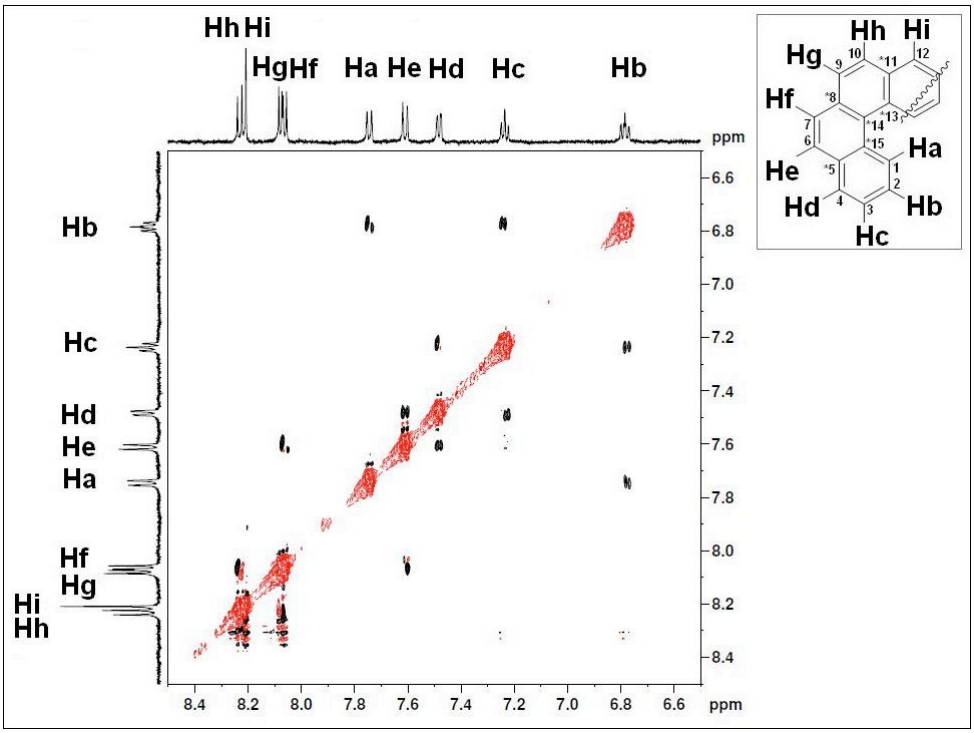


**Figure S8**. NOESY of [7]-helicene + 2.0 equiv. $Ag^+$ in $CH_2Cl_2$

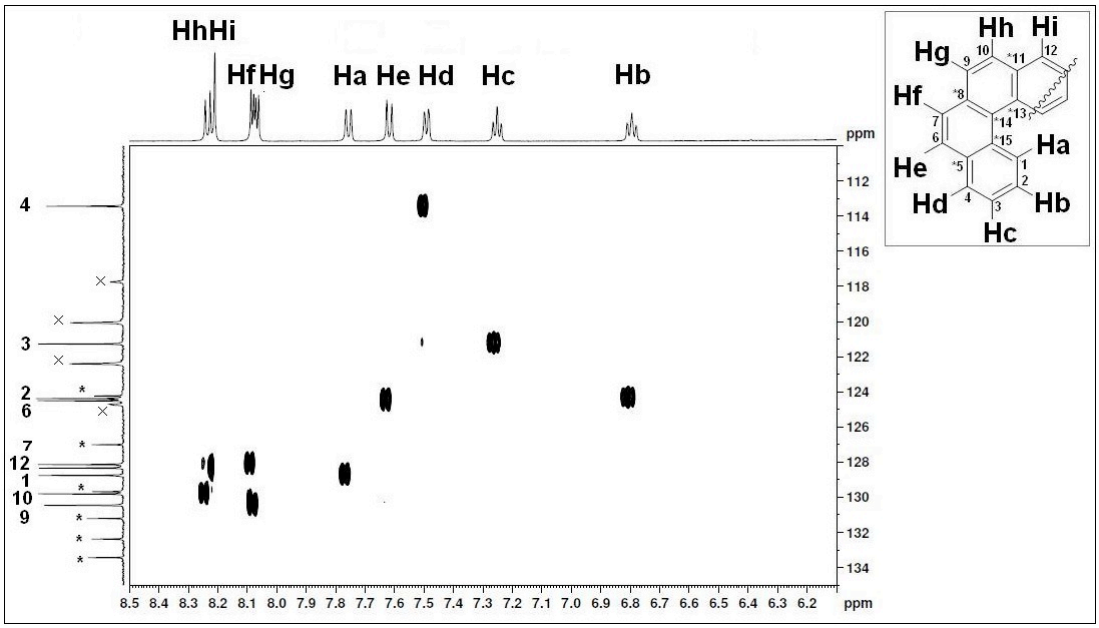


**Figure S9**. HSQC of [7]-helicene + 3.0 equiv. $Ag^+$ in $CH_2Cl_2$ (NB * represents the quaternary carbons and $^X$ represents the peaks corresponding to the WCA)

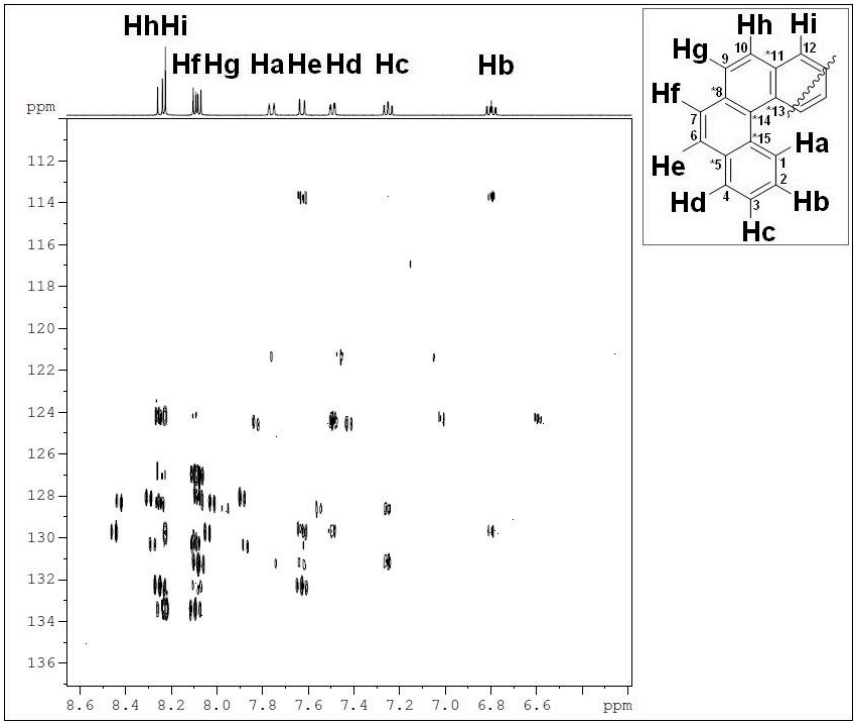


**Figure S10**. HMBC of Ag(I) - [7]-helicene complex in $CD_2Cl_2$

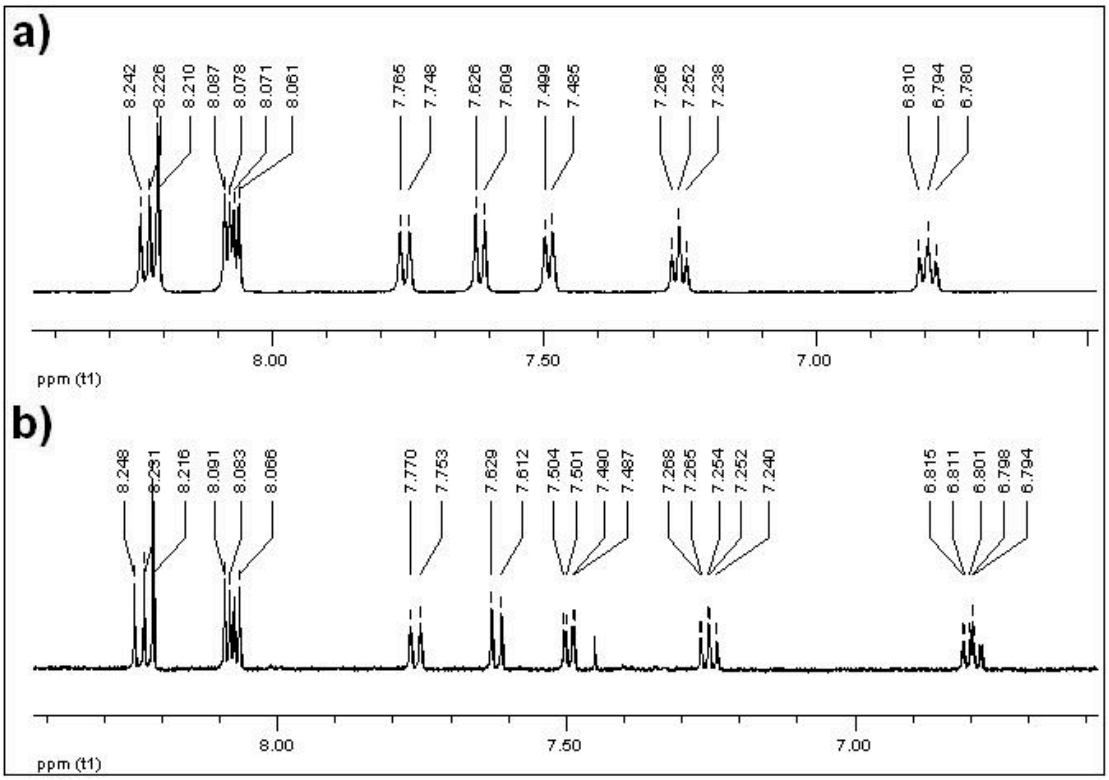


**Figure S11**. $^{1}$H-NMR comparison: a) *P* [7]-helicene + 3.0 equiv. $Ag^{+}$ in $CH_2Cl_2$; b) racemic [7]-helicene + 3.0 equiv. $Ag^{+}$ in $CH_2Cl_2$.

## Evaluation of the formation constant of the silver(I) complex with [7]-helicene

By using a nonlinear least-squares regression analysis with variable weighting of the data points,[1,2] the formation constant of $Ag[AlOC(CF_3)_3)_4]$ with [7]-helicene was determined to be 167 ± 10 $M^{-1}$. The following assumptions have been made: (i) The binding mode between silver(I) complex and [7]-helicene is 1:1 and (ii) as the silver(I) complex is added, it is consumed by binding to the [7]-helience. The calculated chemical shifts (for proton Ha) are within the experimental error associated with the measurement of a chemical shift.

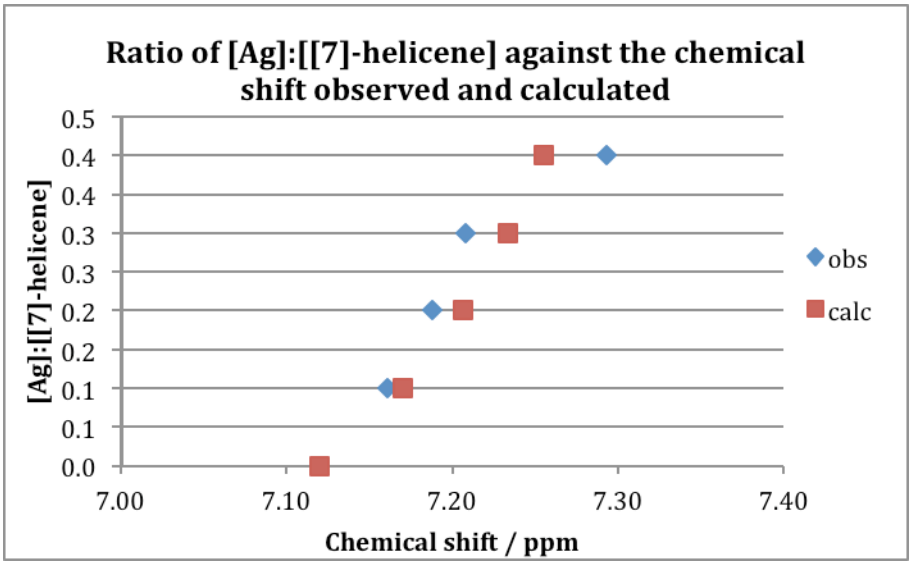


**Figure S12**. A plot to show the ratio of silver(I):[7]-helicene against the observed and calculated chemical shift of proton Ha of [7]-helicene

## Evaluation of the formation constant of the silver(I) complex with ligand 1

Using the same method as above, the formation constant of $Ag[AlOC(CF_3)_3)_4]$ with ligand **1** was determined to be 269 ± 10 $M^{-1}$.

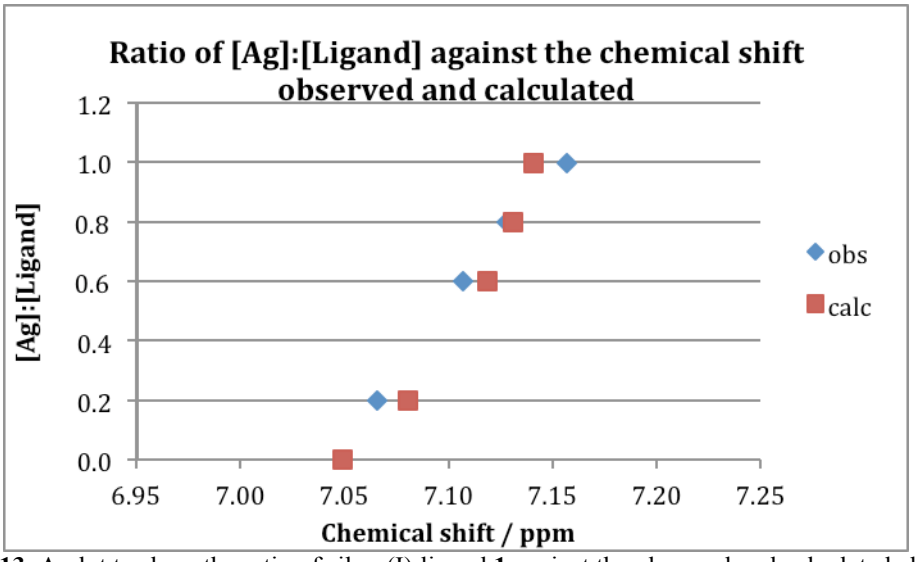


**Figure S13**. A plot to show the ratio of silver(I):ligand **1** against the observed and calculated chemical shift of proton Ha of ligand **1**

## A competition experiment between [7]-helicene and ligand 1 for Ag(I) using $^1$H NMR spectroscopy

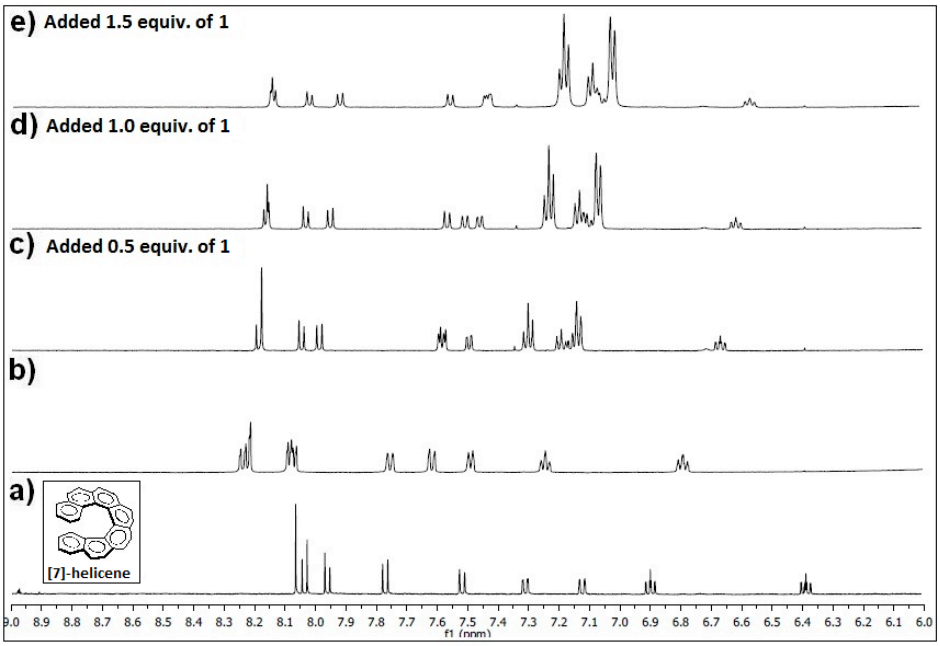


**Figure S14**. $^1$H-NMR in $CH_2Cl_2$: a) [7]-helicene; b) [7]-helicene + 2.0 equiv. $Ag^+$; c) – e) The $^1$H-NMR spectra recorded after each incremental addition (as indicated in the spectra) of ligand **1**.

## A inverse competition experiment between [7]-helicene and ligand 1 for Ag(I) using $^1$H NMR spectroscopy

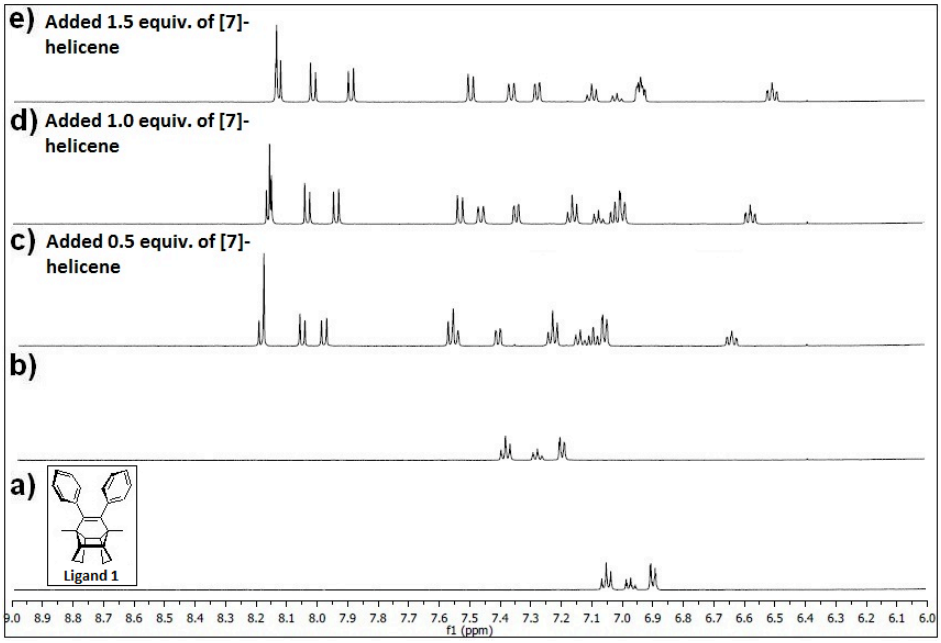


**Figure S15**. $^1$H-NMR in $CH_2Cl_2$: a) Phenyl region of ligand **1**; b) Ligand **1** + 2.0 equiv. $Ag^+$; c) – e) The $^1$H- NMR spectra recorded after each incremental addition (as indicated in the spectra) of [7]-helicene.

## Synthesis and Characterisation of $[Ag(C_{30}H_{18})*CH_2Cl_2)]^+[Al(OC(CF_3)_3)_4]^-$

$Ag[AlOC(CF_3)_3)_4]$ (45.5 mg, 42.3 x $10^{-3}$ mmol) and [7]Helicene (16.0 mg, 42.3 x $10^{-3}$ mmol) were weighed in the glove box into a special two-flask fritplate vessel with J. Young valves. $CH_2Cl_2$ was condensed to the reaction mixture at 233 K. The mixture was stirred for 48 h at room temperature and the colour turned from colourless to green. Crystallization of the filtrate at 253 K led to green crystals. The entire product was used for analytical methods, therefore the yield could not be determined.

$^1$H NMR (400.17 MHz, $CD_2Cl_2$): δ = 8.25 (d, Ha), 8.22 (s, Hi), 8.09 (d, Hg), 8.08 (d, Hf), 7.76 (m, Ha), 7.63 (d,He), 7.49 (m, Hd), 7.25 (m,Hc), 6.80 (m, Hb). $^{19}$F NMR (104.27 MHz, $CD_2Cl_2$): δ = –75.8 (s, CC*F*$_3$). $^{27}$Al (376.49 MHz, $CD_2Cl_2$): 34.6 (s, *Al*$(OC(CF_3)_3)_4$).

IR: υ (intensity) = 1612 (w), 1352 (m), 1297 (ms), 1274 (s), 1241 (s), 1211 (vs), 970 (s), 880 (vw), 851 (w), 827 (w), 783 (w), 758 (w), 726 (m), 611 (vw), 561 (w), 536 (w), 443 (w).

X-ray data for **1**

Single crystals were mounted under $N_2$ atmosphere in perfluoroetheroil at 253 K. Data were collected on a Bruker SMART APEX II CCD area detector diffractometer with Mo-$K_\alpha$ radiation (0.71073 Å). The structure was solved by direct methodes in SHELXTL[1] and refined by least squares on weighted $F^2$ values for all reflections. Multiple disorders of the anion were handled according to the shelx-97 manual:

[1] G. Sheldrick, University of Göttingen, Germany

Special details of the refinement:As both anions are highly disorderd, many restraints and constraints were necessary to treat the disorder. This has the unfortunate consequence of a low parameter to data ratio (8.8). All necessary measures to save parameters were taken (SIMU and DELU instructions, see the list of instructions from the SHELX-ins-file below). A larger crystal might have corrected this problem, but was not possible for us to obtain. However, one of the standard problems with this anion is precisely the data-parameter ratio, especially in structures with low (istropically refined) hydrogen atom content like here: All of the fluorine atoms have to be treated anisotropically,but the inherent propensity of the twelve CF3-groups per anion to disorder often leads to multiply disordered structures, which then end up with a low paramater data ratio. The current case was to optimum we could achieve.

A complete list of all constraints and restrains used for the refinement of [Ag(C30H18)*CH2Cl2)]+ [Al(OC(CF3)3)4]- is given below:

```
EADP F72 F71
EADP F39 F37A
EADP F59 F60A
EADP F65A F65
EADP C6 C6A
SIMU $F $O
SIMU C1 C2 C3 C4 C5 C5A C6 C6A C7 C7A C8 C8A C9 C9A C10 C10A C11
C11A C12 C12A C13 C13A C14 C14A C15 C15A C16 C16A C17 C17A C18 C18A
```

C19 C19A C20 C20A C21 C21A C22 C22A C23 C23A C24 C24A C25 C25A C26 C26A C27 C27A C28 C28A C29 C29A C30 C30A C31 C31A C32 C32A
DELU $F $O
DELU C1 C2 C3 C4 C5 C5A C6 C6A C7 C7A C8 C8A C9 C9A C10 C10A C11 C11A C12 C12A C13 C13A C14 C14A C15 C15A C16 C16A C17 C17A C18 C18A C19 C19A C20 C20A C21 C21A C22 C22A C23 C23A C24 C24A C25 C25A C26 C26A C27 C27A C28 C28A C29 C29A C30 C30A C31 C31A C32 C32A

All disordered $OC(CF_3)_3$ were handled with the SAME O1 > F9.
The main domain for the disordered $OC(CF_3)_3$-groups in both anions is assigned to part 1 the second orientation is assigned to part 2. The occupancy factor FVAR for Part1(anion1) is 0.65, FVAR for Part1(anion2) is 0.52. The disorder in the molecule $CH_2Cl_2$ is decribed with an occupancy factor of 0.60 (for part1). The disorder of the coordinated $CH_2Cl_2$ in one of the silver helicene complexes does not impact upon the binding between the silver and the helicene, which is the interesting part of the structure. The H-atoms of the [7]-helicenes are fixed with the AFIX 43 constraint, the H-atoms of the disordered solvent molecule with the AFIX 23 constraint.

| | | |
|---|---|---|
| CCDC | 846098 | |
| Identification code | p21c | |
| Empirical formula | C48 H22 Ag Al Cl4 F36 O4 | |
| Formula weight | 1623.31 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 35.2189(8) Å | α= 90°. |
| | b = 11.0863(2) Å | β= 115.412(1)°. |
| | c = 31.1869(7) Å | γ = 90°. |
| Volume | 10998.7(4) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.961 $Mg/m^3$ | |
| Absorption coefficient | 0.746 $mm^{-1}$ | |
| F(000) | 6352 | |
| Crystal size | 0.2 x 0.05 x 0.03 $mm^3$ | |
| Theta range for data collection | 1.82 to 25.35°. | |
| Index ranges | -42<=h<=37, -13<=k<=13, -34<=l<=37 | |
| Reflections collected | 62362 | |
| Independent reflections | 20091 [R(int) = 0.0649] | |
| Completeness to theta = 25.35° | 99.8 % | |
| Max. and min. transmission | 0.7454 and 0.6856 | |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 20091 / 4245 / 2544 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final R indices [I>2sigma(I)] | R1 = 0.0689, wR2 = 0.1655 |
| R indices (all data) | R1 = 0.1152, wR2 = 0.1884 |
| Largest diff. peak and hole | 0.882 and -0.690 e.$Å^{-3}$ |

## References

[1] H. C. Hang, A. W. Hanson, B. Eaton and V. Boekelheide, *J. Am. Chem. Soc.*, **1985**, *107*, 1979.

[2] J. E. Gano, G. Subramaniam and R. Birnbaum, *J. Org. Chem.*, **1990**, *55*, 4760.