Supplementary Material (ESI) for Analyst


# SUPLEMENTARY INFORMATION

# High throughput screening arrays of rhodium and iridium complexes as catalysts for intramolecular hydroamination using parallel factor analysis

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**Table S1.** Chemical composition of 80 wells of a 96-well plate in THF. SM: starting material, PR: product, Metal Precursors: Ircod: $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene), IrCO: $[Ir(CO)_2Cl]_n$, IrCOE: $[Ir(COE)_2Cl]_2$, IrCp*: $[IrCp^*Cl_2]_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadiene), Rhcod: $[Rh(COD)Cl]_2$, RhCO: $[Rh(CO)_2Cl]_2$, RhCOE: $[Rh(COE)_2Cl]_2$, RhCp*: $[RhCp^*Cl_2]_2$ and RhCp: $[RhCpCl_2]_2$) (Cp = cyclopentadiene). Ligands: bim: *bis*(*N*-methyl2-imidazolyl)methane, bpm: *bis*(1-pyrazolyl)methane, phen: 1,10-phenanthroline, ptolDAD: *N*,*N*'-*bis*(p-tolyl)diazabutadiene, dmptolDAD: *N*,*N*'-*bis*(p-tolyl)1,2-dimethyldiazabutadiene, dmmestDAD: *N*,*N*'-*bis*(mesityl)1,2-dimethyldiazabutadiene, mestBIAN: *bis*(2,4,6-trimethylphenylimino)acenapthene.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| **A (no ligand)** | Ircod $NaBF_4$ SM | IrCO $NaBF_4$ SM | IrCOE $NaBF_4$ SM | IrCp* $NaBF_4$ SM | Rhcod $NaBF_4$ SM | RhCO $NaBF_4$ SM | RhCOE $NaBF_4$ SM | RhCp* $NaBF_4$ SM | RhCp $NaBF_4$ SM | Rhbim SM |
| **B** | Ircod bim $NaBF_4$ SM | IrCO bim $NaBF_4$ SM | IrCOE bim $NaBF_4$ SM | IrCp* bim $NaBF_4$ SM | Rhcod bim $NaBF_4$ SM | RhCO bim $NaBF_4$ SM | RhCOE bim $NaBF_4$ SM | RhCp* bim $NaBF_4$ SM | RhCp bim $NaBF_4$ SM | Irbpm SM |
| **C** | Ircod bpm $NaBF_4$ SM | IrCO bpm $NaBF_4$ SM | IrCOE bpm $NaBF_4$ SM | IrCp* bpm $NaBF_4$ SM | Rhcod bpm $NaBF_4$ SM | RhCO bpm $NaBF_4$ SM | RhCOE bpm $NaBF_4$ SM | RhCp* bpm $NaBF_4$ SM | RhCp bpm $NaBF_4$ SM | Rhbim SM |
| **D** | Ircod phen $NaBF_4$ SM | IrCO phen $NaBF_4$ SM | IrCOE phen $NaBF_4$ SM | IrCp* phen $NaBF_4$ SM | Rhcod phen $NaBF_4$ SM | RhCO phen $NaBF_4$ SM | RhCOE phen $NaBF_4$ SM | RhCp* phen $NaBF_4$ SM | RhCp phen $NaBF_4$ SM | Irbpm SM |
| **E** | Ircod ptolDAD $NaBF_4$ SM | IrCO ptolDAD $NaBF_4$ SM | IrCOE ptolDAD $NaBF_4$ SM | IrCp* ptolDAD $NaBF_4$ SM | Rhcod ptolDAD $NaBF_4$ SM | RhCO ptolDAD $NaBF_4$ SM | RhCOE ptolDAD $NaBF_4$ SM | RhCp* ptolDAD $NaBF_4$ SM | RhCp ptolDAD $NaBF_4$ SM | SM |
| **F** | Ircod dmptolDAD $NaBF_4$ SM | IrCO dmptolDAD $NaBF_4$ SM | IrCOE dmptolDAD $NaBF_4$ SM | IrCp* dmptolDAD $NaBF_4$ SM | Rhcod dmptolDAD $NaBF_4$ SM | RhCO dmptolDAD $NaBF_4$ SM | RhCOE dmptolDAD $NaBF_4$ SM | RhCp* dmptolDAD $NaBF_4$ SM | RhCp dmptolDAD $NaBF_4$ SM | SM |
| **G** | Ircod dmmestDAD $NaBF_4$ SM | IrCO dmmestDAD $NaBF_4$ SM | IrCOE dmmestDAD $NaBF_4$ SM | IrCp* dmmestDAD $NaBF_4$ SM | Rhcod dmmestDAD $NaBF_4$ SM | RhCO dmmestDAD $NaBF_4$ SM | RhCOE dmmestDAD $NaBF_4$ SM | RhCp* dmmestDAD $NaBF_4$ SM | RhCp dmmestDAD $NaBF_4$ SM | PR |
| **H** | Ircod mestBIAN $NaBF_4$ SM | IrCO mestBIAN $NaBF_4$ SM | IrCOE mestBIAN $NaBF_4$ SM | IrCp* mestBIAN $NaBF_4$ SM | Rhcod mestBIAN $NaBF_4$ SM | RhCO mestBIAN $NaBF_4$ SM | RhCOE mestBIAN $NaBF_4$ SM | RhCp* mestBIAN $NaBF_4$ SM | RhCp mestBIAN $NaBF_4$ SM | PR |

**Table S2.** Chemical composition of 80 wells of a 96-well plate in acetone. SM: starting material, PR: product, Metal Precursors: Ircod: $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene), IrCO: $[Ir(CO)_2Cl]_n$, IrCOE: $[Ir(COE)_2Cl]_2$, IrCp*: $[IrCp^*Cl_2]_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadiene), Rhcod: $[Rh(COD)Cl]_2$, RhCO: $[Rh(CO)_2Cl]_2$, RhCOE: $[Rh(COE)_2Cl]_2$, RhCp*: $[RhCp^*Cl_2]_2$ and RhCp: $[RhCpCl_2]_2$) (Cp = cyclopentadiene). Ligands: bim: *bis*(*N*-methyl2-imidazolyl)methane, bpm: *bis*(1-pyrazolyl)methane, phen: 1,10-phenanthroline, ptolDAD: *N*,*N*'-*bis*(p-tolyl)diazabutadiene, dmptolDAD: *N*,*N*'-*bis*(p-tolyl)1,2-dimethyldiazabutadiene, dmmestDAD: *N*,*N*'-*bis*(mesityl)1,2-dimethyldiazabutadiene, mestBIAN: *bis*(2,4,6-trimethylphenylimino)acenapthene.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| **A (no ligand)** | Ircod $NaBF_4$ SM | IrCO $NaBF_4$ SM | IrCOE $NaBF_4$ SM | IrCp* $NaBF_4$ SM | Rhcod $NaBF_4$ SM | RhCO $NaBF_4$ SM | RhCOE $NaBF_4$ SM | RhCp* $NaBF_4$ SM | RhCp $NaBF_4$ SM | Rhbim |
| **B** | Ircod bim $NaBF_4$ SM | IrCO bim $NaBF_4$ SM | IrCOE bim $NaBF_4$ SM | IrCp* bim $NaBF_4$ SM | Rhcod bim $NaBF_4$ SM | RhCO bim $NaBF_4$ SM | RhCOE bim $NaBF_4$ SM | RhCp* bim $NaBF_4$ SM | RhCp bim $NaBF_4$ SM | Irbpm |
| **C** | Ircod bpm $NaBF_4$ SM | IrCO bpm $NaBF_4$ SM | IrCOE bpm $NaBF_4$ SM | IrCp* bpm $NaBF_4$ SM | Rhcod bpm $NaBF_4$ SM | RhCO bpm $NaBF_4$ SM | RhCOE bpm $NaBF_4$ SM | RhCp* bpm $NaBF_4$ SM | RhCp bpm $NaBF_4$ SM | 100% SM 0% PR |
| **D** | Ircod phen $NaBF_4$ SM | IrCO phen $NaBF_4$ SM | IrCOE phen $NaBF_4$ SM | IrCp* phen $NaBF_4$ SM | Rhcod phen $NaBF_4$ SM | RhCO phen $NaBF_4$ SM | RhCOE phen $NaBF_4$ SM | RhCp* phen $NaBF_4$ SM | RhCp phen $NaBF_4$ SM | 76% SM 24% PR |
| **E** | Ircod ptolDAD $NaBF_4$ SM | IrCO ptolDAD $NaBF_4$ SM | IrCOE ptolDAD $NaBF_4$ SM | IrCp* ptolDAD $NaBF_4$ SM | Rhcod ptolDAD $NaBF_4$ SM | RhCO ptolDAD $NaBF_4$ SM | RhCOE ptolDAD $NaBF_4$ SM | RhCp* ptolDAD $NaBF_4$ SM | RhCp ptolDAD $NaBF_4$ SM | 50% SM 50% PR |
| **F** | Ircod dmptolDAD $NaBF_4$ SM | IrCO dmptolDAD $NaBF_4$ SM | IrCOE dmptolDAD $NaBF_4$ SM | IrCp* dmptolDAD $NaBF_4$ SM | Rhcod dmptolDAD $NaBF_4$ SM | RhCO dmptolDAD $NaBF_4$ SM | RhCOE dmptolDAD $NaBF_4$ SM | RhCp* dmptolDAD $NaBF_4$ SM | RhCp dmptolDAD $NaBF_4$ SM | 24% SM 760% PR |
| **G** | Ircod dmmestDAD $NaBF_4$ SM | IrCO dmmestDAD $NaBF_4$ SM | IrCOE dmmestDAD $NaBF_4$ SM | IrCp* dmmestDAD $NaBF_4$ SM | Rhcod dmmestDAD $NaBF_4$ SM | RhCO dmmestDAD $NaBF_4$ SM | RhCOE dmmestDAD $NaBF_4$ SM | RhCp* dmmestDAD $NaBF_4$ SM | RhCp dmmestDAD $NaBF_4$ SM | 0% SM 100% PR |
| **H** | Ircod mestBIAN $NaBF_4$ SM | IrCO mestBIAN $NaBF_4$ SM | IrCOE mestBIAN $NaBF_4$ SM | IrCp* mestBIAN $NaBF_4$ SM | Rhcod mestBIAN $NaBF_4$ SM | RhCO mestBIAN $NaBF_4$ SM | RhCOE mestBIAN $NaBF_4$ SM | RhCp* mestBIAN $NaBF_4$ SM | RhCp mestBIAN $NaBF_4$ SM | Acetone only |

## General Procedure for the Preparation of the High Throughput Catalyst Screening Reaction plate

The 96 well reaction plates in this project were all prepared using the same method under inert conditions in an Argon filled glove bag. All of the components were added as standard solutions and the plate was sealed in a Calypso reaction blockand heated at 50 ºC. After the desired reaction time the reaction block was cooled to room temperature and opened in an Ar filled glove bag. An aliquot was removed from each well using a multi-channel pipettor and the reaction block was resealed and heated further. For UV analysis the aliquot extracted was diluted with 95 % EtOH to a concentration suitable for UV spectroscopy and transferred to a Helma quartz microtitre plate. The UV spectrum was acquired for each well between 200 and 400 nm using a UV plate reader.

## Procedure for the screening of hydroamination in THF

Standard solutions of all metal complexes, ligands and substrate (2-(2-phenylethynyl)aniline) were prepared in THF. A standard solution of $NaBF_4$ was prepared in MeOH. All standard solutions were transferred to the appropriate wells using Eppendorf pipettors. The $NaBF_4$ standard solution was pipetted into each well (columns 1–9, 125 μL, 4.8 mM, final conc, ~1.0 μmol), 125 μL of blanks (THF) were pipetted into the column 10. Metal complex standard solutions were pipetted into the appropriate wells (columns 1–9, 125 μL, ~ 8.6 mM, final conc, ~1.1 μmol), along with the ligand standard solutions (rows A–H, 250 μL, ~ 8 mM, final conc, ~1.8 μmol). Row A contained blank thf (250 μL) as well as column 10 (125 μL).Standard solutions of $[Rh(bim)(CO)_2]BPh_4$

(wells A10 and C10, 500 μL, 4.9 mM, final conc ~2.4 μmol) and [Ir(bpm)$(CO)_2$]$BPh_4$ (wells B10 and D10, 500 μL, 2.6 mM, final conc ~1.3 μmol) were pipetted followed by the substrate solution (all the wells except for G10 and H10, 125 μL, 21 mM, final conc 2.6 μmol). The standard solution of the product 2-phenylindole was added to the plate in wells G10/H10, respectively.As an initial analysis at 0 time 30 μL aliquots were taken from each well, the plate was then sealed, removed from the glove bag and placed in a 50 ºC oven. After 18 hours the plate was removed from the oven, cooled and opened in a glove bag filled with argon, 30 μL aliquots were removed. For the reaction aliquots obtained at each time point, the aliquots from each well were diluted using 95% ethanol to give solutions which were 0.4 mM in substrate and 100 μL transferred to a Helma quartz 96 well plate. UV data was acquired between 250–400 nm for each well.

## Procedure for the screening of hydroamination in acetone

Standard solutions of all metal complexes, ligands and substrate were prepared in acetone. A standard solution of $NaBF_4$ was prepared in MeOH. All standard solutions were transferred to the appropriate wells using Eppendorf pipettors. The $NaBF_4$ standard solution was pipetted into each well (columns 1–9, 250 μL, 25.6 mM, final conc. 6.4 μmol), 250 μL of blanks (acetone) were pipetted into the column 10. Metal complex standard solutions were pipetted into the appropriate wells (columns 1–9, 125 μL, ~ 0.6 mM, final conc. 1.0 μmol), along with the ligand standard solutions (rows A–H, 125 μL, ~ 4.1 mM, final conc. 1.0 μmol). THF blanks were pipetted into row A (250 μL) and column 10 (125 μL). Standard solutions of [Rh(bim)$(CO)_2$]$BPh_4$ (well A10, 500 μL, 1.3

mM, final conc. 0.6 μmol) and $[Ir(bpm)(CO)_2]BPh_4$ (well B10, 500 μL, 1.4 mM, final conc. 0.7 μmol) were pipetted followed by the substrate solution (columns 1–11, 125 μL, 25.2 mM, final conc. 3.3 μmol and 12 A and B). In the wells C10 to G10 mixtures of standard solutions of substrate (25.2 mM) and product (24.7 mM) were pipetted (well C10, 0.125 μL, 25.2 mM substrate, well D10, 95 μL, 25.2 mM substrate and 30 μL, 24.7 mM product, well E10, 63 μL, 25.2 mM substrate and 63 μL, 24.7 mM product, well F10, 30 μL, 25.2 mM substrate and 95 μL, 24.7 mM product, well G10, 125 μL, 24.7 mM product). Finally 30 μL aliquots were taken from each well for measurements at time zero. The plate was then sealed, removed from the glove bag and placed in a 50 ºC oven. Aliquots taken from each well after 24 hours were diluted using 95% ethanol to give solutions which were 0.4 mM in substrate and 100 μL of this solution was transferred to a Helma quartz 96 well plate. UV data was acquired between 250–400 nm for each well. The same procedure used on a separate set of samples at time zero, that is, without heating the plate in the oven.

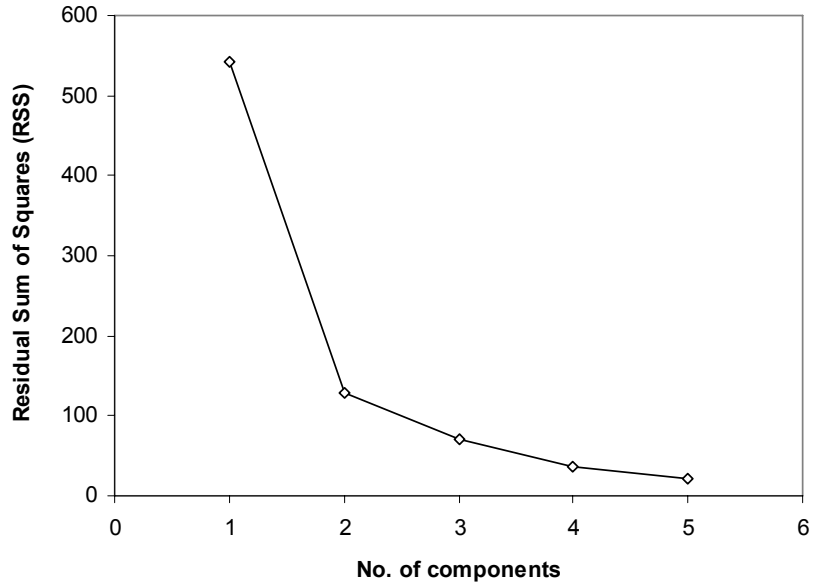


**Fig. S1** Residual sum of squares (RSS) of PARAFAC models with one to five components applied to the UV-Vis data of cyclization reaction of 2-(2-phenylethynyl) aniline in THF catalyzed by organometallic complexes.

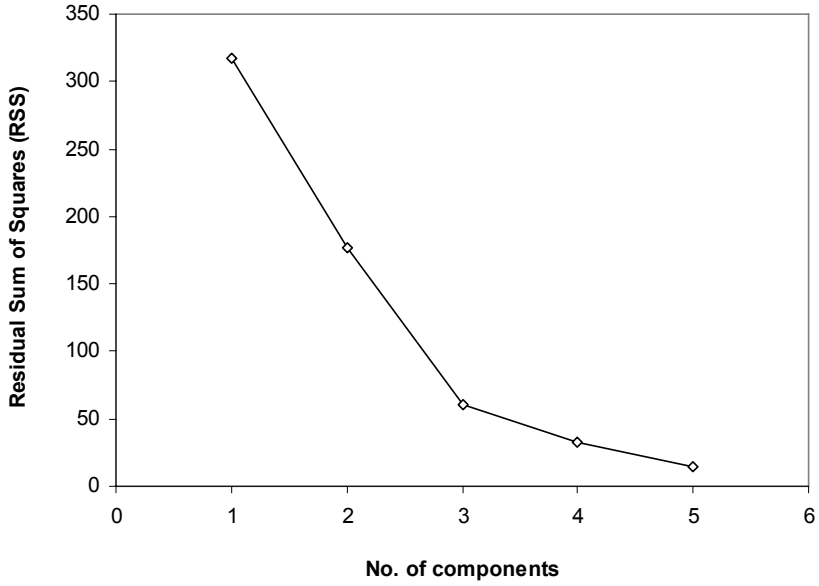


**Fig. S2** Residual sum of squares (RSS) of PARAFAC models with one to five components applied to the UV-Vis data of cyclization reaction of 2-(2-phenylethynyl) aniline in acetone catalyzed by organometallic complexes.

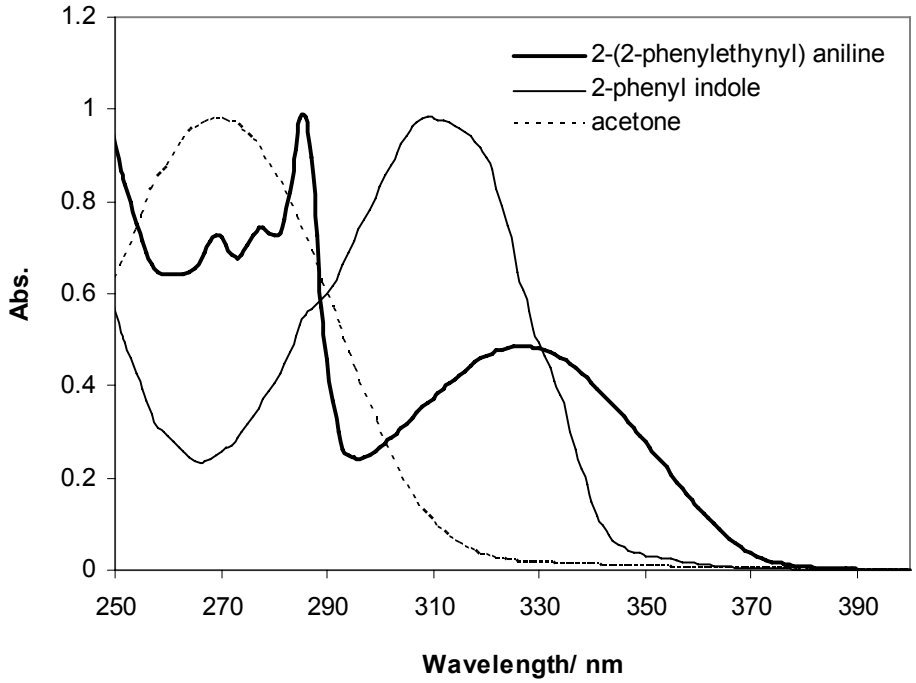


**Fig. S3** Overlaid UV-Vis spectra of authentic samples of 2-(2-phenylethynyl)aniline, 2-phenyl indole, and acetone.