Electronic supplementary information

Synthesis of Chiral-at-Metal Rhodium Complexes from Achiral Tripodal Tetradentate Ligands: Resolution and Application to Enantioselective Diels-Alder and 1,3-Dipolar Cycloadditions

Alvaro G. Tejero,[a] María Carmona,[a] Ricardo Rodríguez,[a,*] Fernando Viguri,[a,*] Fernando J. Lahoz,[a] Pilar García-Orduña,[a] and Daniel Carmona[a,*]

a Departamento de Catálisis y Procesos Catalíticos. Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC - Universidad de Zaragoza. Pedro Cerbuna 12, 50009 Zaragoza, Spain

E-mail: dcarmona@unizar.es; riromar@unizar.es; fviguri@unizar.es

Table of Contents

1. ^{1}H, $^{31}P\{^{1}H\}$, $^{19}F\{^{1}H\}$ and $^{13}C\{^{1}H\}$ spectra for the complexes 2, 3 and (C_{Rh},R_N,S_C)/(A_{Rh},S_N,S_C)-4

Figure S1. ^{1}H NMR (CD_2Cl_2/acetone-d_6, RT) spectrum of 2

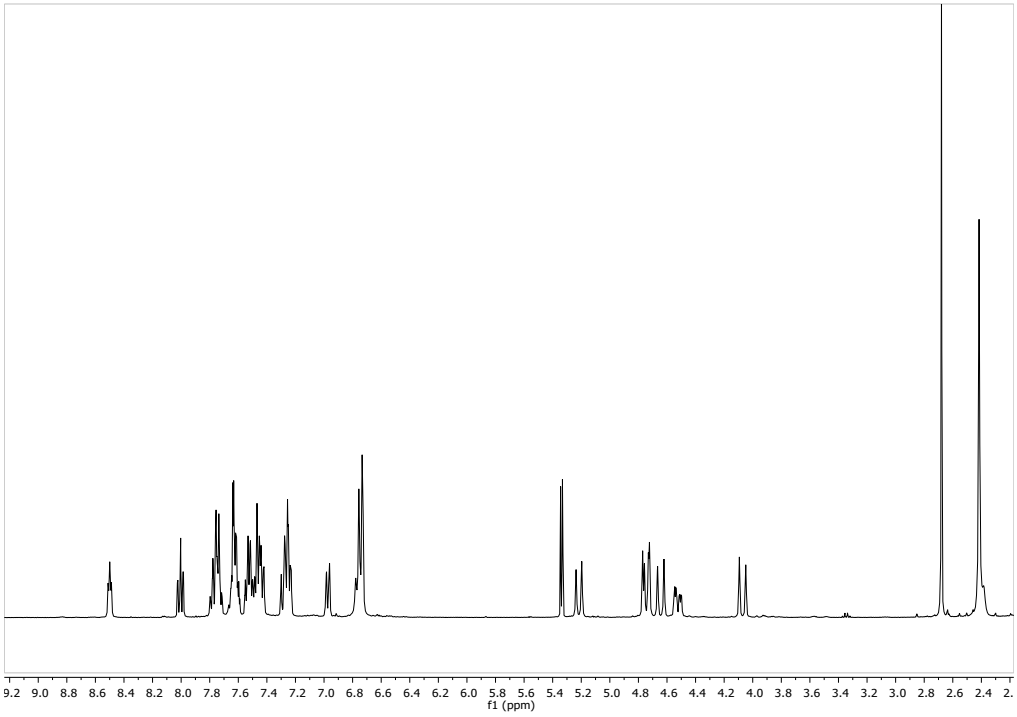


Figure S2. $^{31}P\{^{1}H\}$ (CD_2Cl_2/acetone-d_6, RT) spectrum of 2

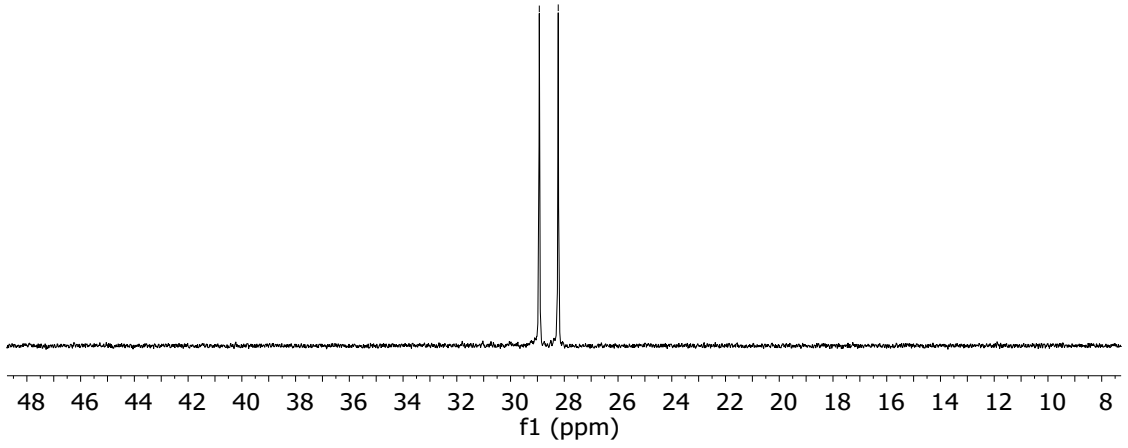


Figure S3. $^{19}F\{^{1}H\}$ (CD_2Cl_2/acetone-d_6, RT) spectrum of 2

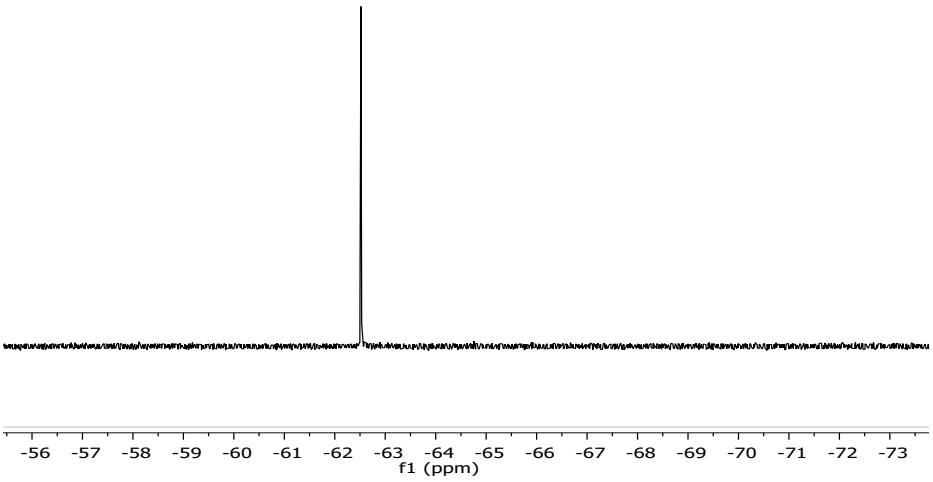


Figure S4. $^{13}C\{^{1}H\}$ (CD_2Cl_2/acetone-d_6, RT) spectrum of 2

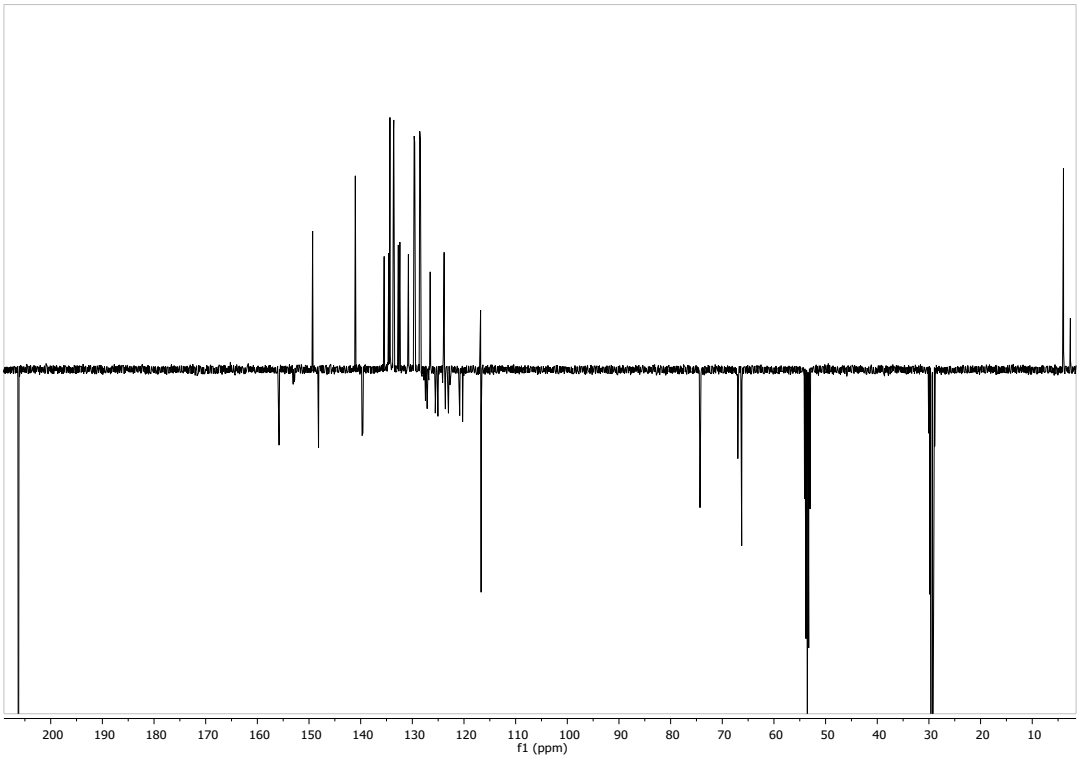


Figure S5. ^{1}H NMR (CD_2Cl_2, RT) spectrum of 3

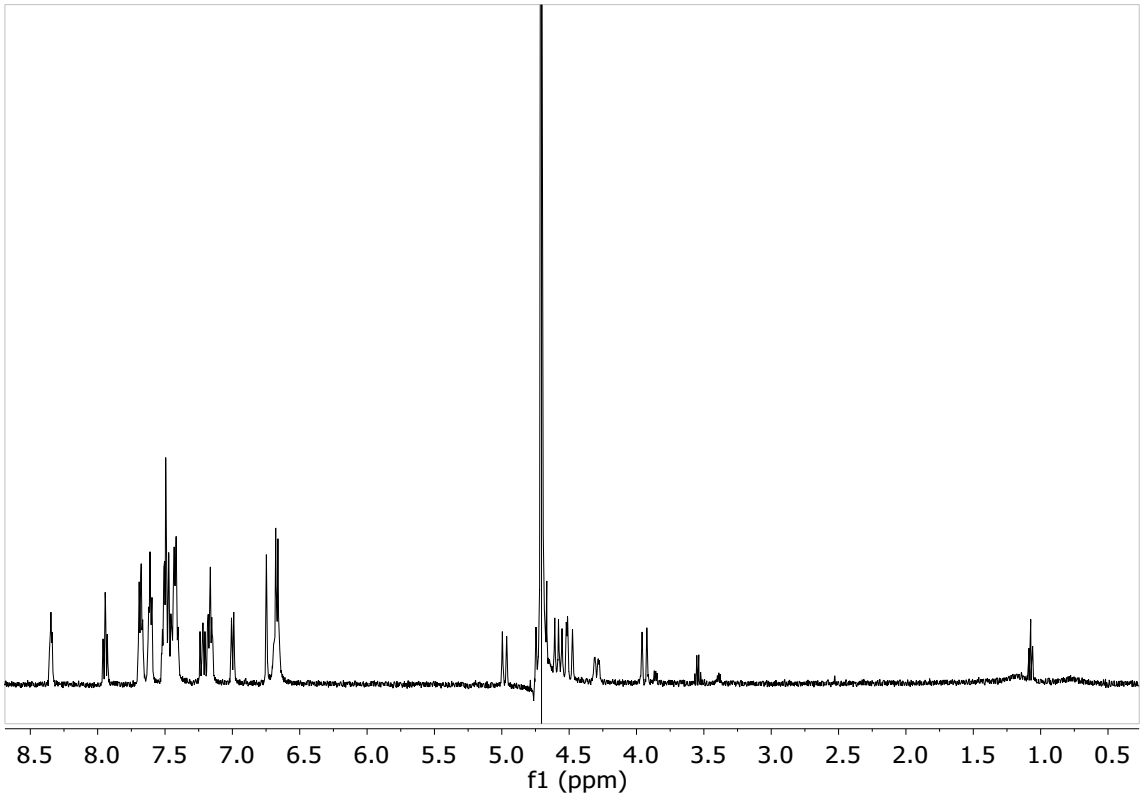


Figure S6. $^{31}P\{^{1}H\}$ (CD_2Cl_2, RT) spectrum of 3

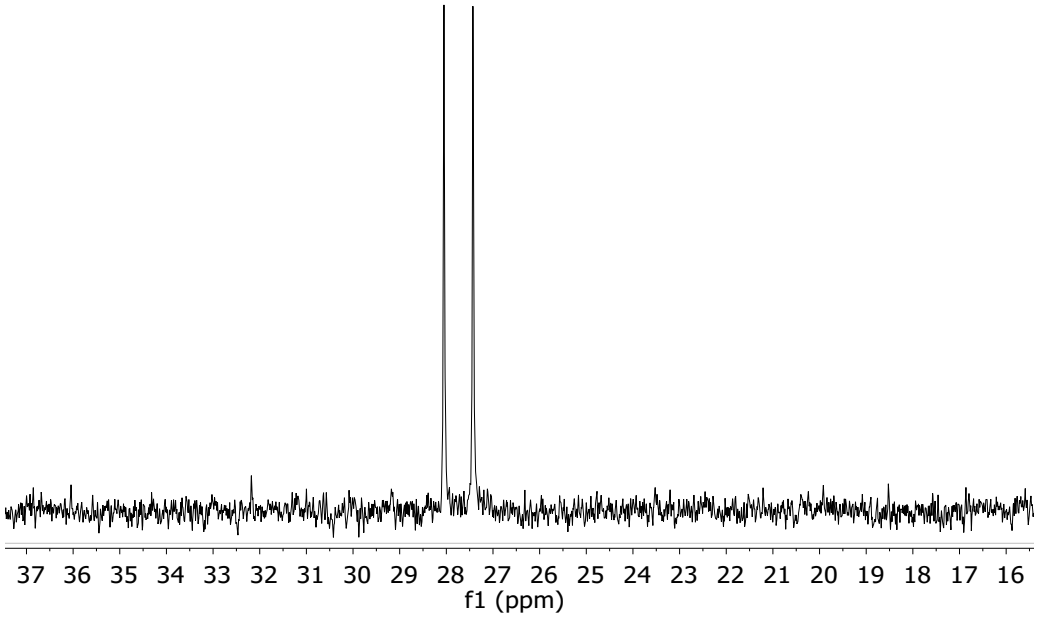


Figure S7. $^{19}F\{^{1}H\}$ (CD_2Cl_2, RT) spectrum of 3

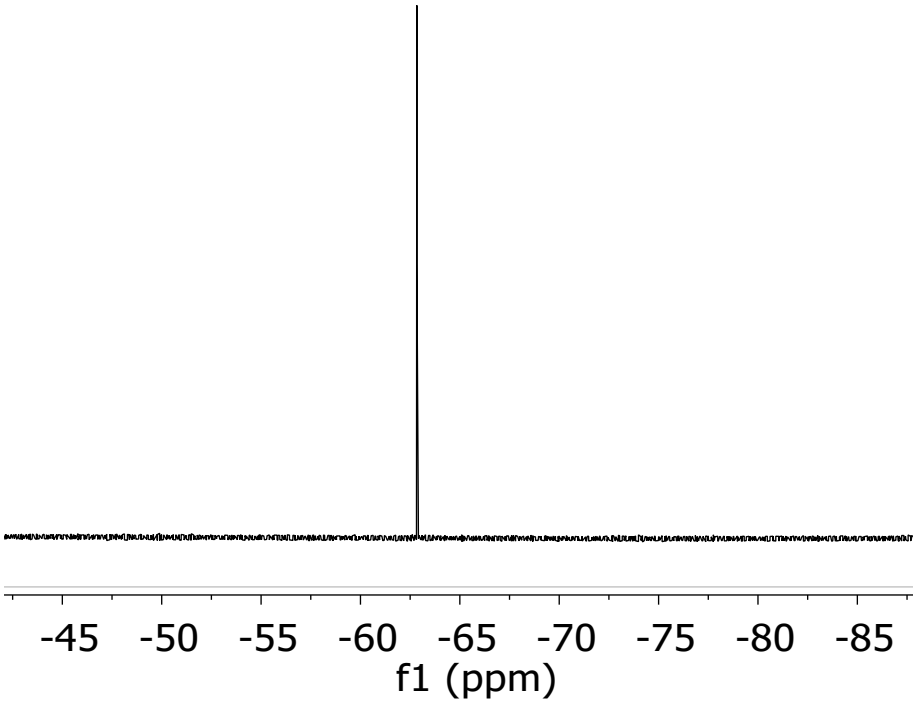


Figure S8. $^{13}C\{^{1}H\}$ (CD_2Cl_2, RT) spectrum of 3

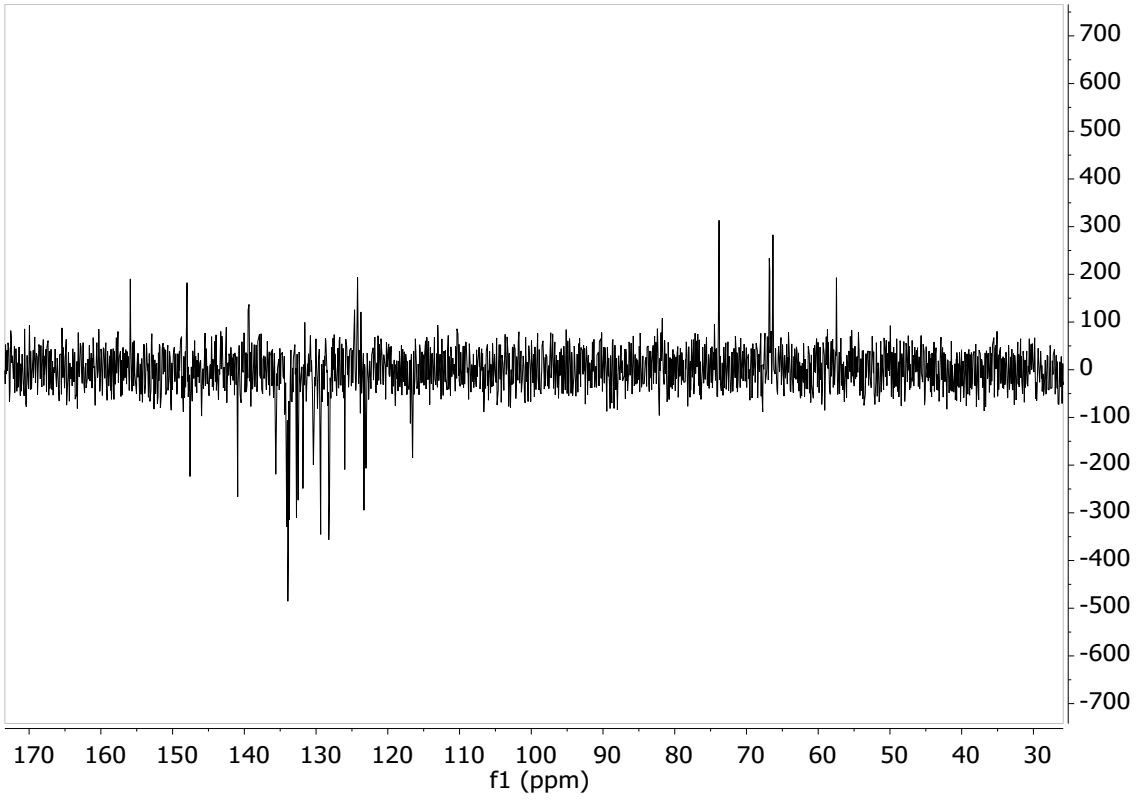


Figure S9. ^{1}H NMR (CD_2Cl_2, RT) spectrum of (C_{Rh},R_N,S_C)/(A_{Rh},S_N,S_C)-4

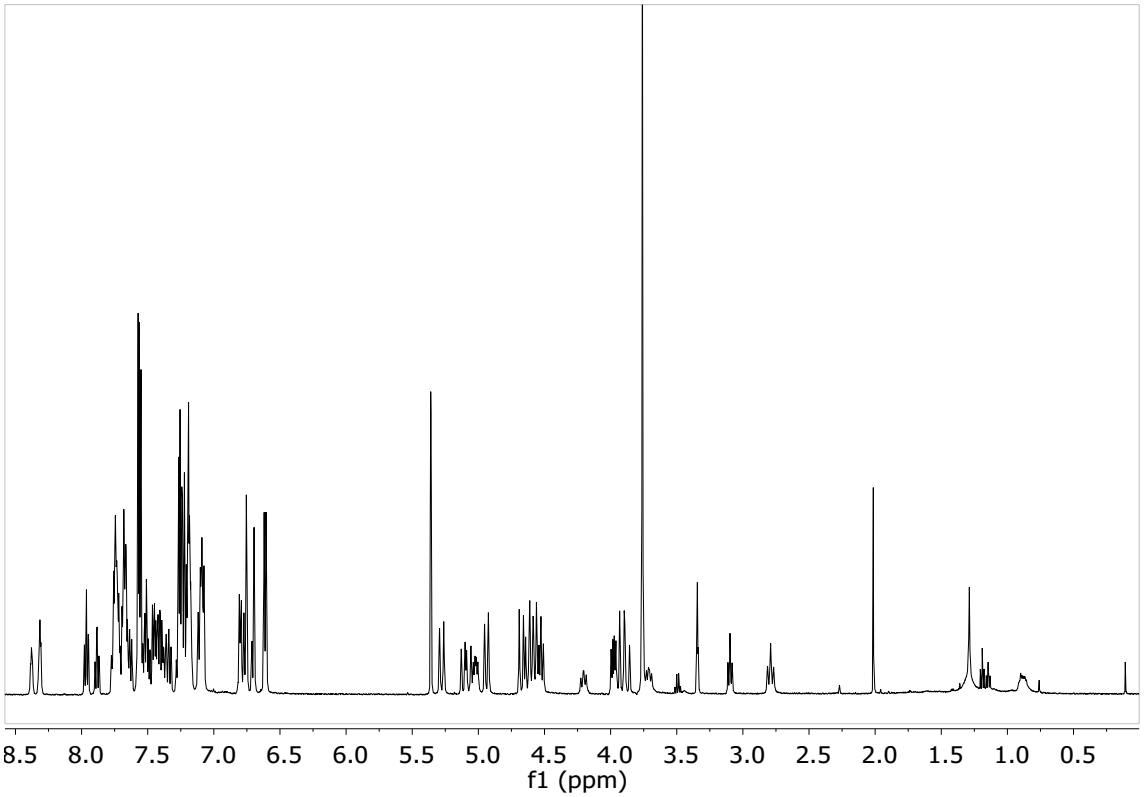


Figure S10. ^{31}P{^{1}H} (CD_2Cl_2, RT) spectrum of (C_{Rh},R_N,S_C)/(A_{Rh},S_N,S_C)-4

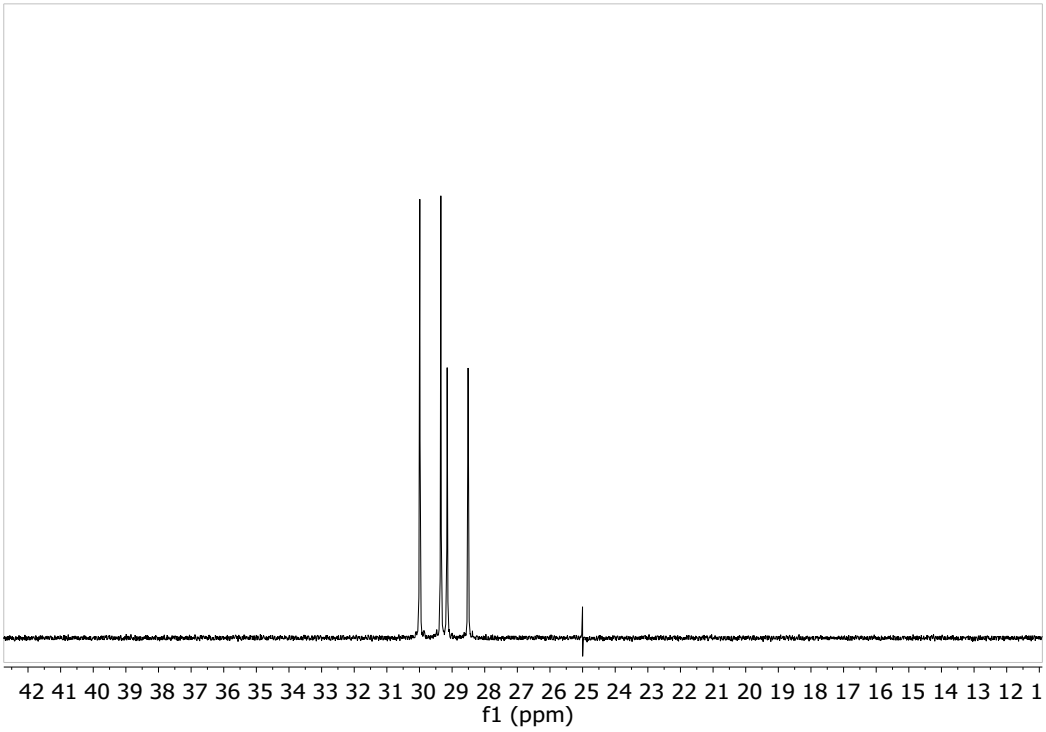


Figure S11. $^{19}F\{^1H\}$ (CD_2Cl_2, RT) spectrum of (C_{Rh},R_N,S_C)/(A_{Rh},S_N,S_C)-4

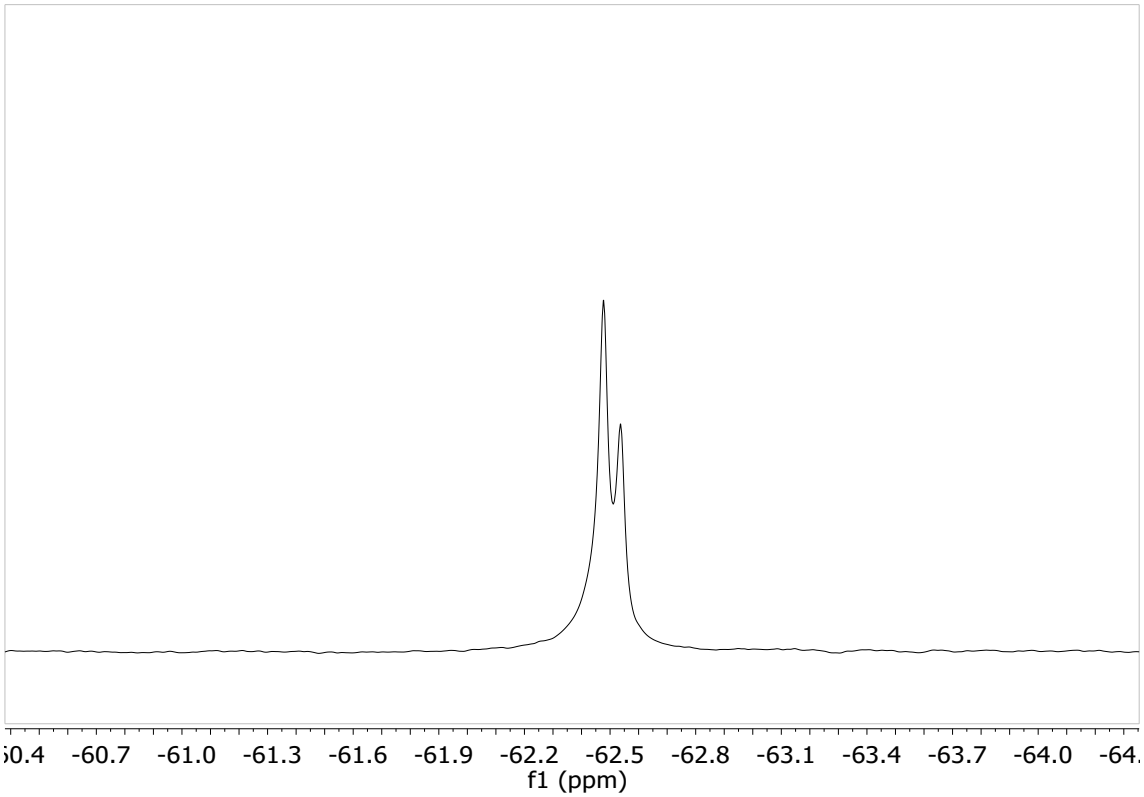


Figure S12. $^{13}C\{^1H\}$ (CD_2Cl_2, RT) spectrum of (C_{Rh},R_N,S_C)/(A_{Rh},S_N,S_C)-4

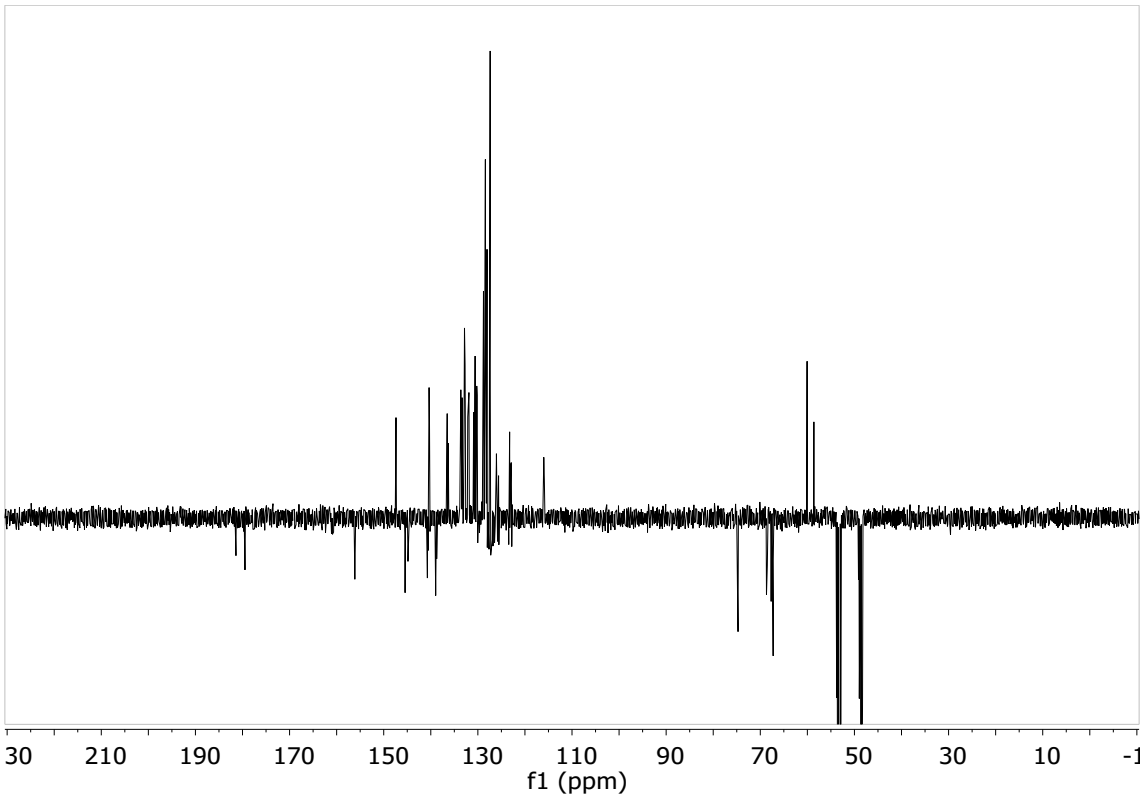
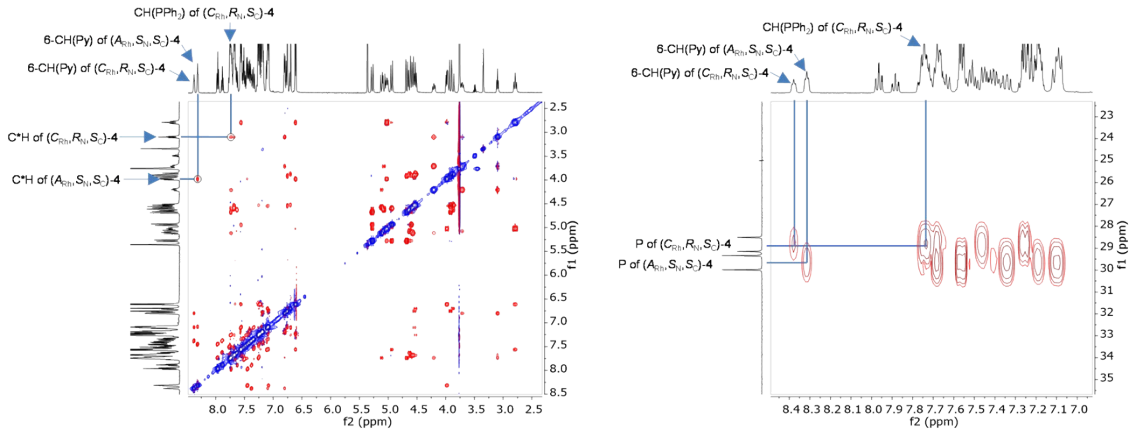


Figure S13. NOESY ^{1}H-^{1}H (CD_2Cl_2, RT) and HMBC ^{31}P-^{1}H (CD_2Cl_2, RT) experiments of (C_{Rh},R_N,S_C)/(A_{Rh},S_N,S_C)-4



2. HPLC chromatograms

Figure S14. HPLC chromatogram for *rac*-2

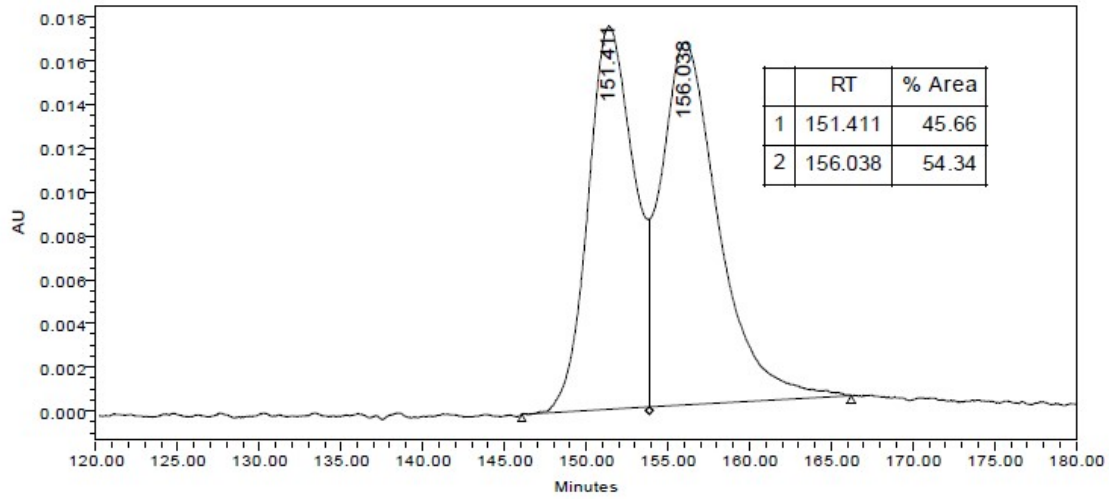


Figure S15. HPLC chromatogram for (A_{Rh},R_N)-2

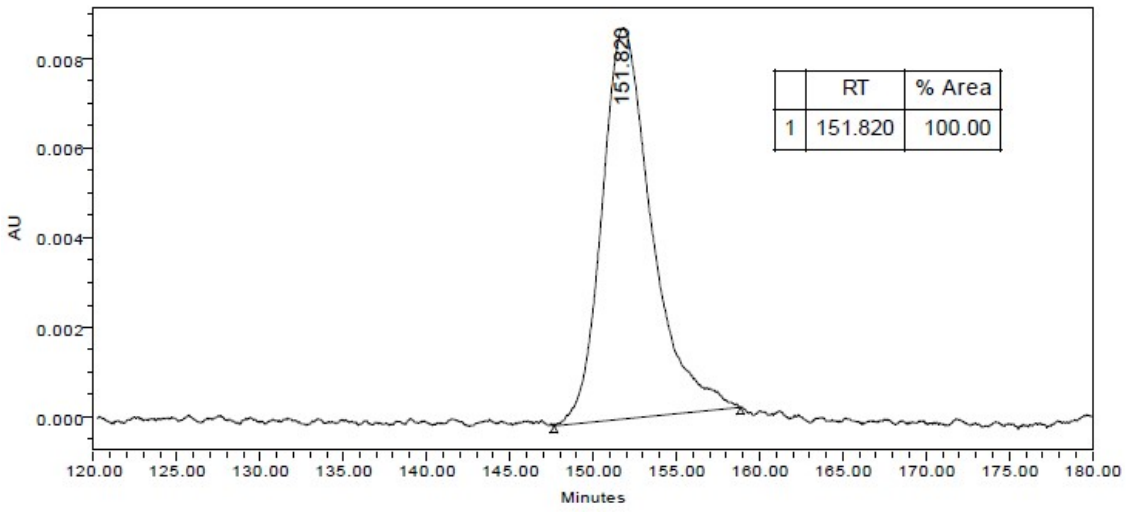


Figure S16. HPLC chromatogram for (A_{Rh},R_N)-2 after heating 48 h at 80 ºC in MeOH

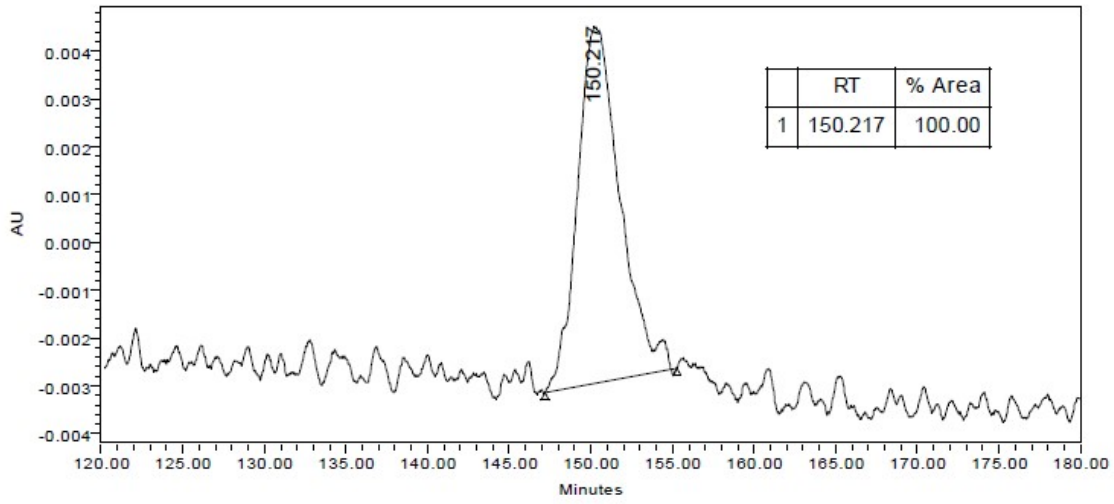
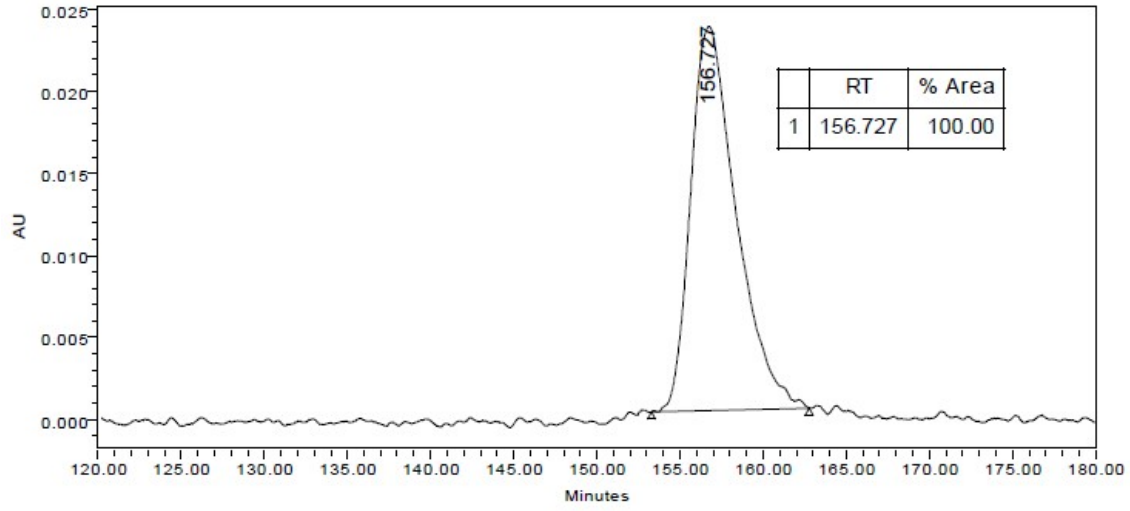


Figure S17. HPLC chromatogram for (C_{Rh},S_N)-2



3. Structural characterization of the complex 2 (X-ray crystallography)

X-ray diffraction data were collected on APEX DUO Bruker diffractometer, using graphite-monochromated Mo κα radiation (λ = 0.71073 Å). Selected crystal was mounted on a fiber, coated with a protecting perfluoropolyether oil and cooled to 100(2) K with an open-flow nitrogen gas. Data were collected using ω-scans with narrow oscillation frame strategy (Δω = 0.3°). Data were integrated and corrected from absorption effects with SAINT[S1] and SADABS[S2] programs, included in APEX2 package. Crystal structures were solved by direct methods with SHELXS-2013[S3] and refined by full-matrix least squares on F^2 with SHELXL program[S4] included in Wingx program system.[S5] Hydrogen atoms have been included in the model in calculated positions and refined with a riding model.

Crystal data for complex 2: $C_{37}H_{33}F_{15}N_4PRhSb_2 \cdot 2(CH_2Cl_2)$; M_r = 1365.90; colourless prism, 0.070 × 0.115 × 0.200 mm^3; triclinic $P\bar{1}$; a = 12.2805(9) Å, b = 13.6365(9) Å, c = 14.6021(10) Å, α = 96.0690(10) °, β = 102.032(2) °, γ = 92.269(2) °; V = 2373.4(3) Å^3, Z = 2, D_c = 1.911 g/cm^3; μ = 1.826 cm^{-1}; min. and max. absorption correction factors: 0.7569 and 0.8373; $2\theta_{max}$ = 58.374°; 32424 reflections measured, 12574 unique; R_{int} = 0.0436; number of data/restraint/parameters 12574/0/597; R_1 = 0.0485 [9063 reflections, $I > 2\sigma(I)$], w$R(F^2)$ = 0.1180 (all data); largest difference peak 2.977 e·Å^{-3}.

4. References

S1 SAINT+, version 6.01: Area-Detector Integration Software, Bruker AXS, Madison, WI, 2001.

S2 SADABS, Area Detector Absorption Program. Bruker AXS, Madison, WI, 1996; L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst*. 2015, **48**, 3-10.

S3 G. M. Sheldrick. A short history of SHELX. *Acta Crystallogr*. 2008, **A64**, 112-122.

S4 G. M. Sheldrick. Crystal structure refinement with SHELXL. *Acta Crystallogr*. 2015, **C71**, 3-8.

S5 L. J. Farrugia. WinGX and ORTEP for Windows: an update. *J. Appl. Cryst*. 2012, **45**, 849-854.