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Title: Bulky and Modular 3,3′-Bipyrazoles as Ligands: Synthesis, Characterization, and Catalytic Activity of Pd Complexes
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**General.** All reagents and solvents were obtained from Acros, ABCR, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. Dichloromethane was freshly distilled from calcium hydride under argon atmosphere; THF was freshly distilled from sodium under argon atmosphere. Deuterated solvents were purchased from Euriso-Top. Acetonitrile was dried by a MB SPS-800 with the aid of drying columns. Handling of air- and moisture-sensitive materials was carried out in flame dried flasks under an atmosphere of argon using Schlenk-techniques. Thin layer chromatography (TLC) was performed using Polygram® precoated plastic sheets SIL G/UV254 (SiO₂, 0.20 mm thickness) from Macherey-Nagel. NMR spectra were recorded on Bruker Avance 500, Bruker Avance 300 and Bruker ARX-250 spectrometers at RT. Chemical shifts (in ppm) were referenced to residual solvent protons. Signal multiplicity was determined as s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). ¹³C assignment was achieved via DEPT135 spectra and HSQC experiments. GC-and GC-MS measurements were performed on a Thermo PolarisQ Trace GC-MS, equipped with split injector (250°C), FID (250°C) and a quadrupole ion-trap MS (Thermo, San Jose, CA). MS spectra were recorded on a Finnigan MAT TSQ 700 or a JEOL JMS-700 spectrometer. IR spectra were recorded on a Bruker Vector 22 FT-IR. CD-and UV-Vis spectra were recorded on a JASCO J-810 spectropolarimeter. Crystal structure analysis was accomplished on Bruker Smart CCD and Bruker APEX diffractometers. Melting points were determined on a Büchi melting point apparatus and temperatures were uncorrected. Elemental analysis was performed on an Elementar Vario EL.
$^1$H and $^{13}$C NMR spectra of ligands 1 – 3(a–k)
$^1\text{H}$ and $^{13}\text{C}$ NMR spectra of palladium complexes 4a–k
CD spectra of ligand $3h$ and palladium complex $4h$ in various solvents
All solution spectra were recorded in distilled solvents.

SI Figure 1: CD spectra of palladium complex $4h$ and the free ligand $3h$ in tetrahydrofuran.

CD spectra of palladium complexes $4h$, $4j$, $4d$ and $4k$
The solution spectra were recorded in distilled tetrahydrofuran.

SI Figure 2: CD spectra of palladium complexes $4h$, $4j$, $4d$ and $4k$ in tetrahydrofuran.
UV-Vis spectra of palladium complexes 4h, 4j, 4d and 4k:
The solution spectra (c = 0.03 mM) of the palladium complexes were recorded in distilled tetrahydrofurane.

SI Figure 3: UV-Vis spectra of palladium complexes 4h, 4j, 4d and 4k in tetrahydrofurane.