Surface Immobilized Cu-1,10-Phenanthroline Complexes with α-Aminophosphonate Groups in the 5-Position as Heterogenous Catalysts for Efficient Atom-Transfer Radical Cyclizations

Sarah E. Maier\textsuperscript{a}, Osman Bunjaku\textsuperscript{a}, Elif Kaya\textsuperscript{a}, Michael Dyballa\textsuperscript{a}, Wolfgang Frey\textsuperscript{b}, Deven P. Estes\textsuperscript{a*}

\textsuperscript{a} Institute of Technical Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany.
\textsuperscript{b} Institute of Organic Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany.
\textsuperscript{*} deven.estes@itc.uni-stuttgart.de

Supporting Information

Original raw datasets can be obtained free of charge through the Data Repository of the University of Stuttgart (DARUS) via the DOI: 10.18419/darus-3467.

Figure S1. X-ray structure of L1, water of crystallization omitted for clarity (Cambridge Crystallographic Database deposition number 2253908)
NMR-Spectra of new ligands

Figure S2. $^1$H-NMR of L1 in CDCl$_3$ at 25°C.

Figure S3. $^{31}$P($^1$H)-NMR of L1 in CDCl$_3$ at 25°C.
Figure S4. $^{13}$C($^1$H)-NMR of L1 in CDCl$_3$ at 25°C.
Figure S5. $^1$H-NMR of L2 in CDCl$_3$ at 25°C (top) Close up of CHP and amino-region of the $^1$H NMR of L2 with (middle) and without (bottom) addition of D$_2$O.
$^{19}$F-$^1$H-NMR

Figure S6. $^{19}$F-$^1$H-NMR of L2 in CDCl$_3$ at 25°C.

$^{31}$P-$^1$H-NMR

Figure S7. $^{31}$P-$^1$H-NMR of L2 in CDCl$_3$ at 25°C.
Figure S8. $^{13}\text{C}^{1}\text{H}$-NMR of L2 in CDCl$_3$ at 25°C.

Figure S9. $^1\text{H}$-NMR of L3 in CDCl$_3$ at 25°C.
Figure S10. $^{31}{\text{P}}\{^{1}\text{H}\}$-NMR of L3 in CDCl$_3$ at 25°C.

Figure S11. $^{13}{\text{C}}\{^{1}\text{H}\}$-NMR of L3 in CDCl$_3$ at 25°C.
Figure S12. $^1$H-NMR of L4 in CDCl$_3$ at 25°C.

Figure S13. $^{31}$P($^1$H)-NMR of L4 in CDCl$_3$ at 25°C.
Figure S14. $^{13}$C($^1$H)-NMR of L4 in CDCl$_3$ at 25°C.

Figure S15. $^1$H-NMR of L5 in CDCl$_3$ at 25°C.
Figure S16. $^{31}\text{P}^{(1\text{H})}$-NMR of L5 in CDCl$_3$ at 25°C.

Figure S17. $^{13}\text{C}^{(1\text{H})}$-NMR of L1 in CDCl$_3$ at 25°C.
Figure S18. $^{31}$P-CPMAS NMR of Cu(L3)$_2$BF$_4$@SiO$_2$.

Figure S19. $^{31}$P CPMAS NMR of L1@Al$_2$O$_3$. 
**Figure S20.** $^{31}$P CPMAS NMR of Cu(L1)BF$_4$@Al$_2$O$_3$.

**Figure S21.** UV/Vis measurements of L3 (orange), Cu(L3)$_2$BF$_4$ (blue) and Cu(L3)$_2$@SiO$_2$ (grey)
Figure S22. UV/Vis measurements of L1 (black) and L1@alumina (red).

Figure S23. Exemplary NMR-spectrum after the cyclization reaction of 1.
Figure S24. Exemplary NMR-spectrum after the cyclization reaction of 2.

Figure S25. Exemplary NMR-spectrum after the cyclization reaction of 3.