SUPPLEMENTARY INFORMATION 2

On the Mechanism of the Copper-Catalyzed Enantioselective 1,4-Addition of Grignard Reagents to \( \alpha, \beta \)-Unsaturated Carbonyl Compounds

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**Figure S1.** \(^1\)H (left) and \(^{31}\)P (right) NMR spectra of the complex 1a in CD$_2$Cl$_2$ at -60 \(^\circ\)C.
Figure S2. APT NMR (100.57 MHz) spectra of the complex 1a in CD$_2$Cl$_2$ at RT.

Figure S3. $^1$H (left) and $^{31}$P (right) NMR spectra of the complex 1b in CD$_2$Cl$_2$ at -60 °C.

Figure S4. $^{13}$C NMR (125.7 MHz) spectra of the complex 1b in CD$_2$Cl$_2$ at RT.
Figure S5. $^1$H (left) and $^{31}$P (right) NMR spectra of the complex 1c in CD$_2$Cl$_2$ at -60 °C.

Figure S6. $^{13}$C NMR (76.43 MHz) spectra of the complex 1c in CD$_2$Cl$_2$ at RT.

Figure S7. $^1$H (left) and $^{31}$P (right) NMR spectra of the complex 2a in CD$_2$Cl$_2$ at -60 °C.
Figure S8. $^{13}$C NMR (76.43 MHz) spectra of the complex 2a in CD$_2$Cl$_2$ at RT.

Figure S9. $^1$H (left) and $^{31}$P (right) NMR spectra of the complex 3 in CD$_2$Cl$_2$ at RT.

Figure S10. $^{13}$C NMR (76.43 MHz) spectra of the complex 3 in CD$_2$Cl$_2$ at RT.
Figure S11. $^1$H (left) and $^{31}$P (right) NMR spectra of the complex 1a and MeMgBr in CD$_2$Cl$_2$ at -60 °C.

Figure S12. $^1$H (left) and $^{31}$P (right) NMR spectra of the complex 1a and MeLi (3equiv.) in CD$_2$Cl$_2$ at -60 °C.

Figure S13. $^1$H (left) and $^{31}$P (right) NMR spectra of the complex 1a, 3 equiv. of MeMgBr and 3 equiv. dioxane in CD$_2$Cl$_2$ at -60 °C.
Figure S14. $^1$H (left) and $^{31}$P (right) NMR spectra of the complex 1a in toluene-$d_8$ at -60.

Figure S15. $^1$H (left) and $^{31}$P NMR spectra of the complex 1a and MeMgBr in toluene-$d_8$ at -60 $^0$C.

Figure S16. $^1$H (left) and $^{31}$P NMR spectra of the complex 1a in THF-$d_8$ at -60.
Figure S17. $^1$H (left) and $^{31}$P NMR spectra of the complex 1a and MeMgBr in THF-$d_8$ at -60.

Figure S18. $^1$H (left) and $^{31}$P NMR spectra of the complex 1b and MeMgCl in CD$_2$Cl$_2$ at -60.

Figure S19. $^1$H (left) and $^{31}$P NMR spectra of the complex 1c and MeMgI in CD$_2$Cl$_2$ at -60.
Figure S20. $^1$H (left) and $^{31}$P NMR spectra of the species B formed from A in CD$_2$Cl$_2$ at -60.