Supporting information

Nickel-Catalyzed Transfer Hydrogenation of Ketones Using Ethanol as Solvent and Hydrogen Donor

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Figure S1. ¹H spectrum of reaction between 2 equiv of Ni(COD)₂ (a) and 3 equiv of (dippe) (b) at RT in THF- d_8 .



Figure S2. ¹H spectrum of [(dippe)Ni(COD)] (c) in THF- d_8 .



Figure S3. ³¹P{¹H} spectrum of [(dippe)Ni(COD)] (c) in THF- d_8 .



Figure S4. ¹H spectrum of $[(dippe)_2Ni]$ (d) in THF- d_8 .



Figure S5. ³¹P{¹H} spectrum of $[(dippe)_2Ni]$ (d) in THF-*d*₈.



Figure S6. ¹H spectrum of [(dippe)Ni(η^2 -C,O-acetophenone)] (3) in THF-*d*₈.



Figure S7. ³¹P{¹H} spectrum of [(dippe)Ni(η^2 -C,O-acetophenone)] (3) in THF-*d*₈.



Figure S8. IR spectrum of [(dippe)Ni(η^2 -C,O-acetophenone)] (3).



Figure S9. ¹H spectrum of [(dippe)Ni(η^2 -C,O-4-fluoroacetophenone)] (4) in THF- d_8 .



Figure S10. ³¹P{¹H} spectrum of [(dippe)Ni(η^2 -C,O-4-fluoroacetophenone)] (4) in THF- d_8 .



Figure S11. IR spectrum of $[(dippe)Ni(\eta^2-C,O-4-fluoroacetophenone)]$ (4).



Figure S12. ¹H spectrum of [(dippe)Ni(η^2 -C,O-2-furylmethylketone)] (5).



Figure S13. ³¹P{¹H} spectrum of [(dippe)Ni(η^2 -C,O-2-furylmethylketone)] (5).



Figure S14. IR spectrum of [(dippe)Ni(η^2 -C,O-2-furylmethylketone)] (5).



Figure S15. ³¹P{¹H} spectrum of [(dcype)Ni(COD)] (c) in THF- d_8 .



Figure S16. ³¹P{¹H} spectrum of $[(dcype)_2Ni]$ (c) in THF- d_8 .



Figure S17. Chromatogram of α -Methylbenzyl alcohol C₈H₁₀O 1a, Table 3, entry 1.



Figure S18. Mass spectrum of α -Methylbenzyl alcohol C₈H₁₀O 1a, Table 3, entry 1.



Figure S19. ¹H spectrum of α -Methylbenzyl alcohol C₈H₁₀O 1a in CDCl₃ (300 MHz).



Figure S20. ¹³C{¹H} spectrum of α -Methylbenzyl alcohol C₈H₁₀O 1a in CDCl₃ (300 MHz).





Figure S21. Chromatogram of 1-(4-fluorophenyl)ethanol C₈H₉FO, Table 3, entry 3.



Figure S22. Mass spectrum of 1-(4-fluorophenyl)ethanol C₈H₉FO, Table 3, entry 3.



Figure S23. Chromatogram of 1-(perfluorophenyl)ethanol C₈H₅F₅O, Table 3, entry 4.



Figure S24. Mass spectrum of 1-(perfluorophenyl)ethanol C₈H₅F₅O, Table 3, entry 4.



Figure S25. Chromatogram of diphenylmethanol $C_{13}H_{12}O$, Table 3, entry 5.



Figure S26. Mass spectrum of diphenylmethanol C₁₃H₁₂O, Table 3, entry 5.



Figure S27. Chromatogram of phenyl(*p*-tolyl)methanol C₁₄H₁₄O, **Table 3**, entry 6.



Figure S28. Mass spectrum of phenyl(*p*-tolyl)methanol C₁₄H₁₄O, **Table 3**, entry 6.



Figure S29. Chromatogram of 1-(furan-2-yl)ethanol C₆H₈O₂, Table 3, entry 7.



Figure S30. Mass spectrum of 1-(furan-2-yl)ethanol C₆H₈O₂, Table 3, entry 7.



Figure S31. Chromatogram of cyclohexanol C₆H₁₂O, Table 3, entry 9.



Figure S32. Mass spectrum of cyclohexanol C₆H₁₂O, Table 3, entry 9.



Figure S33. Chromatogram of 1-adamantanol C₁₀H₁₆O, Table 3, entry 10.



Figure S34. Mass spectrum of 1-adamantanol C₁₀H₁₆O, Table 3, entry 10.





Figure S35. Chromatogram of 1,2-diphenylethane-1,2-diol C₁₄H₁₄O₂, Table 3, entry 11.



Figure S36. Mass spectrum of 1,2-diphenylethane-1,2-diol C₁₄H₁₄O₂, Table 3, entry 11.



Figure S37. Mass spectrum of 1,2-diphenylethanol, C₁₄H₁₄O, Table 3, entry 11.



Figure S38. Mass spectrum of 1,2-diphenylethane, C₁₄H₁₄, Table 3, entry 11.





Figure S39. Mass spectrum of ethyl acetate, C₄H₈O₂.



Figure S40. Mass spectrum of acetaldehyde, C₂H₄O.



Figure S41. ³¹P{¹H} NMR spectra of reaction between 1 equiv of [(dippe)Ni(η^2 -*C*,*O*-acetophenone)] (3) and 5 equiv of Ethanol (THF-*d*₈, 121.32 MHz).

Table S1	. Mercury	Drop	Experiments.	
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	O └ CH ₃ + ⊦	[(dcype (I ₃ С ^{^^} ОН 130	e)Ni(COD)] (e) mol %) [•] °C, t (h) [Hg]	OH CH ₃	+ н₃с [⊥] н
Entry	1a (e)	Hg (drops) b	T (°C)	2a t (h)	2a (%)
1	(mol %)	0	130	48	72
2	1	1	130	48	70
3	2	0	130	36	99
4	2	1	130	36	96

^{*a*} **1a** (1.1 mmol, 130.8 mg), **ethanol** (119.88 mmol, 7 mL); Conversion and yields were determined by GC-MS.

^b Hg drop test (0.30 mmol).

The reaction between alkyl diphosphines (dcype, dippe, or dtbpe) with $[Ni(COD)_2]$ generates the catalytic precursor **A**, which upon reaction with ketone can be converted to catalyst **B** by heating via the sequence shown in **Scheme 2** (main text), followed by the oxidative addition of ethanol and hydride transfer to the nickel complex **B** to give an intermediate **C**. Then, a hydride addition to the β -position produces the intermediate **D**. The nickel complex **D** undergoes β -hydride elimination to produce acetaldehyde. It is known that acetaldehyde reacts with other equivalents of ethanol obtaining ethyl acetate with the liberation of hydrogen.^{4h, 3f} The resulting nickel hydride complex **D** reacts with a ketone releasing the secondary alcohol, thereby re-generating the catalytically active nickel complex **B**.

