

SUPPORTING INFORMATION

Etheric C—O Bond Hydrogenolysis Using a Tandem Lanthanide Triflate/Supported Palladium Nanoparticle Catalyst System

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1. Experimental Section

1.1. Materials and Methods. All manipulations of reagents were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk-line, or interfaced to a high-vacuum line (10^{-6} Torr), or in a nitrogen-filled vacuum atmospheres glovebox with a high capacity recirculator (<1 ppm O_2). Argon (Matheson, prepurified) was purified by passage through a MnO oxygen-removal column and a Davison 4A molecular sieve column. $CDCl_3$ was obtained from commercial sources and stored over molecular sieves. Substrate **1** was obtained from Aldrich Chemical Co.. Substrates **3**, **5**, **7**, **9**, **11**, **13**, **15**, **16** and 2-*t*-butyltetrahydrofuran were prepared as reported in the literature.^[S1] All substrates were dried twice over freshly activated Davison 4A molecular sieves and were degassed by freeze-pump-thaw methods. They were then stored in vacuum-tight storage flasks. The lanthanide complexes $Ln(OTf)_3$, ($Ln = La$ and Yb)^[S2] and Pd nanoparticles on alumina

(Pd@ALD)^[S3] containing 2% Pd by weight were synthesized according to previously published procedures. The ¹H NMR integration internal standard, 1,1,2,2-tetrachloroethane, was purchased from Aldrich Chemical Co., distilled under reduced pressure, and stored under N₂ in a vacuum-tight storage flask before use. The room temperature ionic liquids, [EMIM][OTf] was prepared according to a published procedure,^[S4] dried and stored in the glove box before use.

1.2. Physical and Analytical Measurements. NMR spectra were recorded on a Varian Inova-500 (FT, 500 MHz, ¹H, 100 MHz, ¹³C), Varian Inova-400 (FT, 400 MHz, ¹H, 100 MHz, ¹³C, 376 MHz, ¹⁹F) or Mercury-400 (FT, 400MHz, ¹H; 100 MHz, ¹³C, 76.7 MHz, ²H) spectrometers. Chemical shifts (δ) for ¹H, and ¹³C are referenced to internal solvent. Mass spectral data were obtained on a Varian 1200 Quadrupole mass spectrometer. The C-O cleavage reactions were performed in a 100 mL Parr reactor (model 4590, Parr Company, Moline, IL), capable of reaching a maximum temperature of 300 °C, a maximum pressure of 1000 psi, and a maximum stirring rate of 3000 rpm.

2. General Reaction Information.

2.1 Ln(OTf)₃ mediated reactions. The C-O bond scission/hydrogenation reactions of each substrate were run in the presence of Ln³⁺ metal Ln(OTf)₃ complexes in [EMIM][OTf] as the solvent. In the glove box, Ln(OTf)₃, (Ln = La, Yb, 10 mol%, 6.5 x 10⁻⁵ mol), Pd@ALD (1.3 x 10⁻⁵ mol Pd), [EMIM][OTf] (2.6 x 10⁻² mol) and substrate (6.5 x 10⁻⁴ mol, 10 equiv with respect to Ln(OTf)₃) were added to a 100 mL Teflon sleeve. The Teflon sleeve was then put into the Parr reactor in the glovebox and sealed. The reaction vessel was purged 10x with 100 psi hydrogen, after which the reactor was heated to the reaction temperature, incrementally pressurized to the reaction pressure, and stirred at 1000 rpm for 18 h. Aliquots during the reaction were taken when needed through a needle valve on the Parr reactor after cooling the

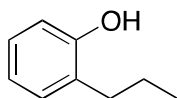
reaction mixture to 80 °C, and decreasing the pressure to 30 psi. Upon reaction completion, the reactor was cooled down to the room temperature and depressurized. The final product was extracted with small portions of diethyl ether and passed through a plug of silica to remove any ionic liquid that might have mixed with the ether. Alternatively, products were vacuum distilled from the reaction mixture.

2.2 Reactions in the presence of excess alcohol. The reactor was prepared in an analogous fashion as above, with the exception that 5 equiv. (3.0×10^{-3} mol) of product alcohol was injected into the reactor prior to purging with H₂.

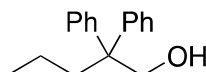
2.3 Reactions in the presence of proton-rapping reagent -phenyltrimethylsilane. The reactor was prepared in an analogous fashion as above, with the exception that phenyltrimethylsilane (1.0 equiv. with respect to [Yb(OTf)₃]) was injected into the reactor prior to purging with H₂.

2.4 HOTf mediated reactions. In the glove box, [EMIM][OTf] (2.6×10^{-2} mol) and substrate (6.5×10^{-4} mol) were added to a 100 mL Teflon sleeve. The Teflon sleeve was then put into the Parr reactor in the glovebox and sealed. After removing the reactor from the glovebox, HOTf (1.9×10^{-4} mol) was injected into the reactor. The reaction vessel was purged 10x with 100 psi hydrogen, after which the reactor was heated to the reaction temperature, incrementally pressurized to the reaction pressure, and stirred at 1000 rpm. Aliquots during the reaction were taken when needed through a needle valve on the Parr reactor after cooling the reaction mixture to 80 °C, and decreasing the pressure to 30 psi. Upon reaction completion, the reactor was cooled down to the room temperature and depressurized. The final product was extracted with small portions of diethyl ether and passed through a plug of silica to remove any ionic liquid that might have mixed with the ether.

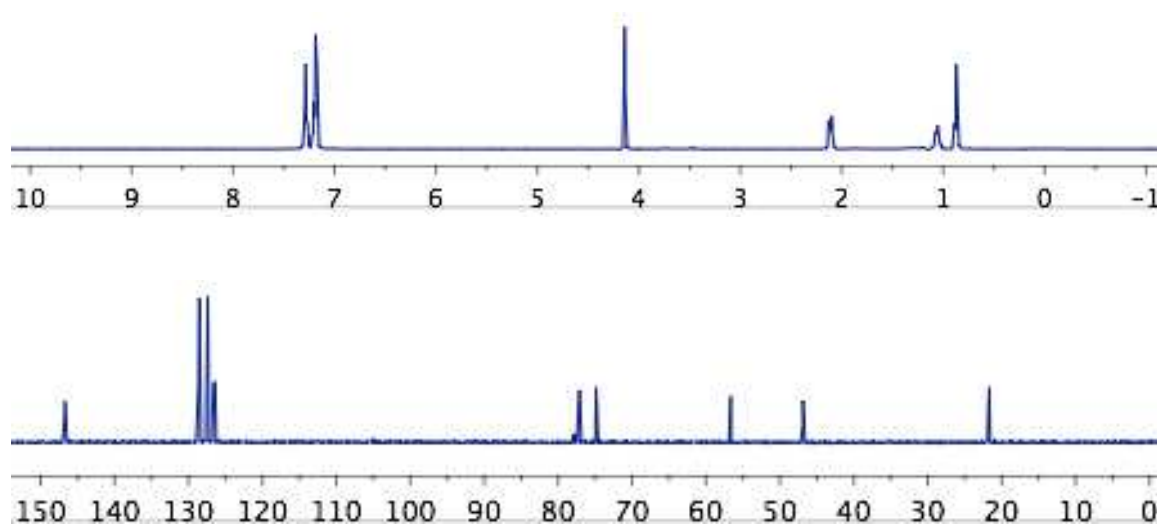
3. Final Product Characterization

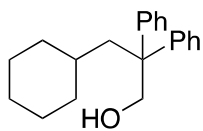


2-propylphenol (2). The title compound was obtained from substrate **1** as a colorless liquid (89%). Spectral data matched literature reference.^[S5]

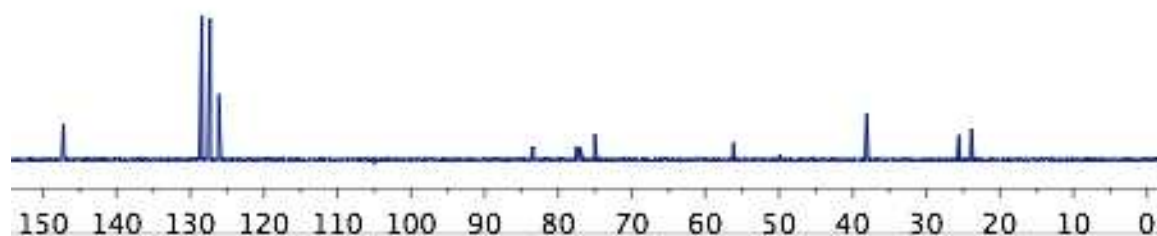
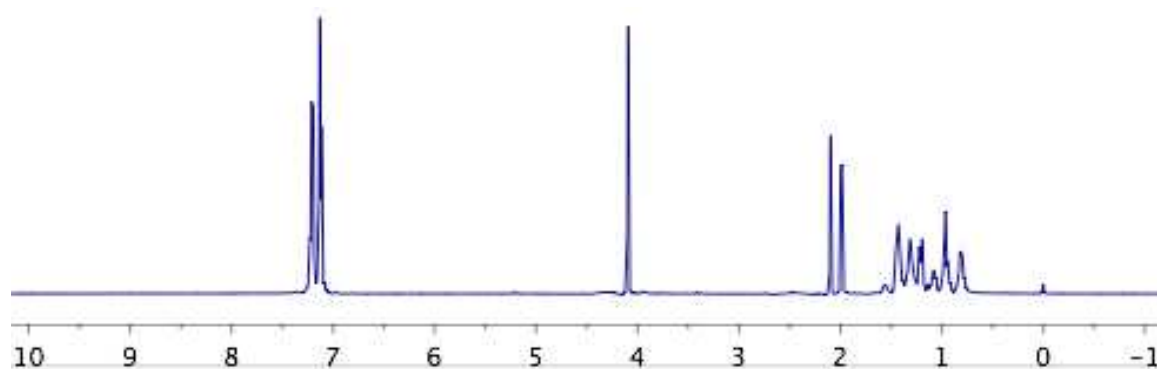


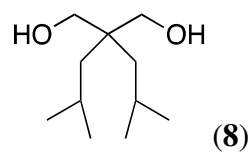
2,2-diphenylpenten-1-ol (4). The title compound was obtained from substrate **3** as a viscous colorless liquid (92%). ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.10 (m, 10H), 4.14 (s, 2H), 2.11 (m, 2H), 1.06 (m, 2 H), 0.87 (t, *J*=8.0 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 146.5, 128.6, 127.4, 126.4, 77.1, 74.9, 56.6, 146.9, 21.7. HRMS-ESI(*m/z*): [(*M*+)⁺] calcd for C₁₇H₂₀O, 240.1508; found 240.1514.



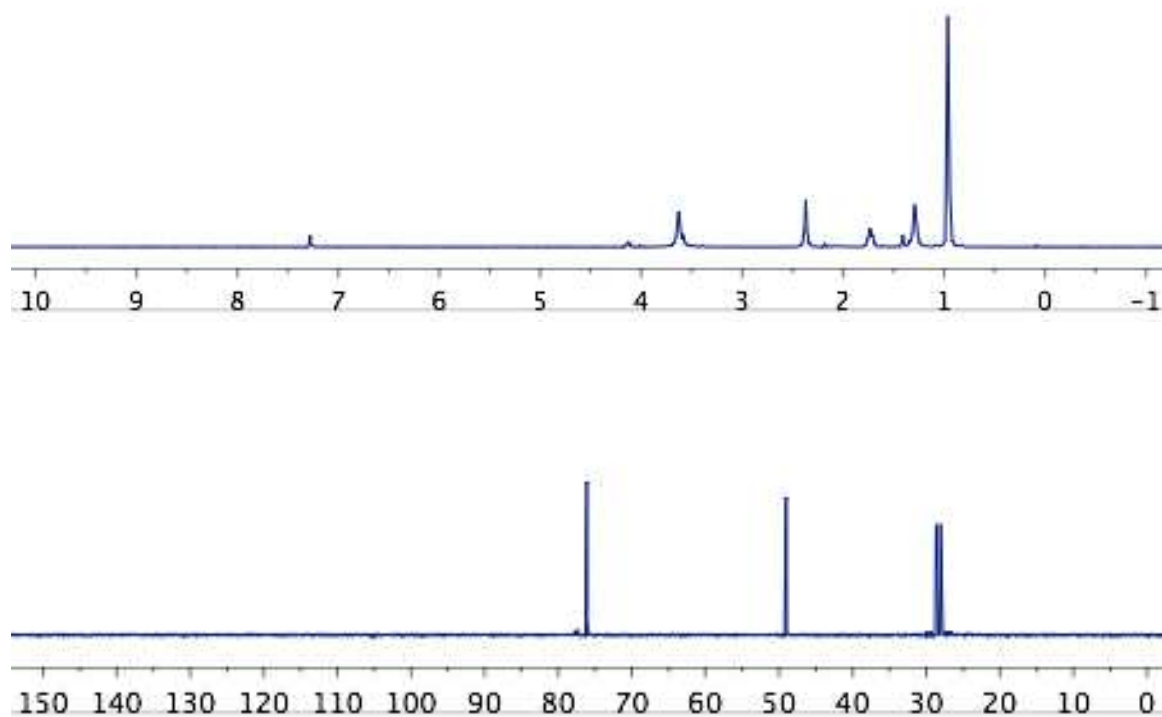


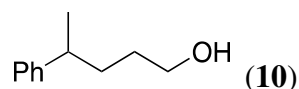
3-cyclohexyl-2,2-diphenylpropan-1-ol (6). The title compound was obtained from substrate **5** as a viscous pale yellow liquid (88%). ^1H NMR (CDCl_3 , 400 MHz): δ 7.30-7.05 (m, 10 H), 4.09 (s, 2 H), 2.10 (s, 1 H), 1.99 (d, $J = 4$ Hz, 2 H), 1.65-0.70 (m, 11 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 147.2, 128.4, 127.3, 126.1, 83.5, 75.0, 56.2, 49.9, 38.1, 25.6, 23.9. HRMS-ESI(m/z): $[(\text{M})^+]$ calcd for $\text{C}_{21}\text{H}_{26}\text{O}$, 294.1980; found 294.1975.



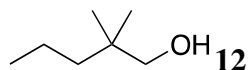


2,2-bis(2-methylpropyl)-1,3-propanediol (8). The title compound was obtained from substrate **7** as a colorless liquid (82%). ^1H NMR (CDCl_3 , 400 MHz): δ 3.63 (br s, 4 H), 2.37 (br s, 2 H), 1.72 (m, 2 H), 1.30 (br s, 4 H), 0.95 (d, $J = 4$ Hz, 12 H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 76.1, 49.0, 28.6, 28.1; HRMS-ESI(m/z): $[(\text{M})^+]^+$ calcd for $\text{C}_{11}\text{H}_{24}\text{O}_2$, 188.1769; found 188.1778.

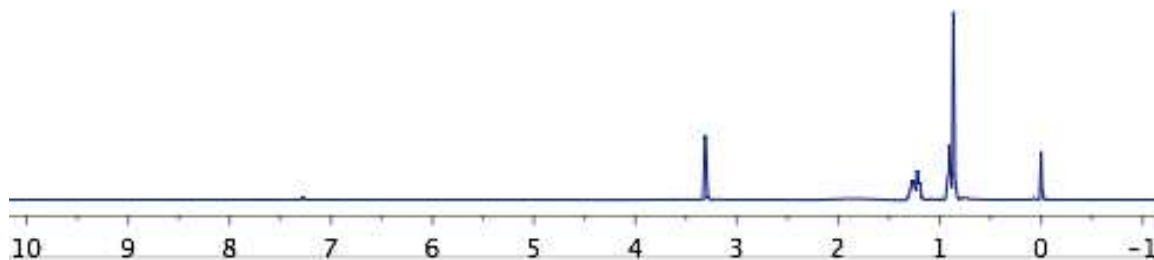




4-phenyl-penten-1-ol (10). The title compound was obtained from substrate **9** as a viscous colorless liquid (83%). Spectral data matched literature reference.^[S6]



2,2-dimethyl-penten-1-ol (12). Compound **12** was obtained from substrate **11** as a pale yellow liquid (77%). ¹H NMR (CDCl₃, 400 MHz): δ 3.31 (s, 2H), 1.35-1.15 (m, 4 H), 0.89 (t, *J* = 4 Hz, 3H), 0.86 (s, 6 H); ¹³C NMR (CDCl₃, 100 MHz): δ 72.3, 42.1, 35.0, 24.7, 17.5, 15.0. HRMS-ESI(*m/z*): [(*M*+)⁺] calcd for C₇H₁₆O, 116.1197; found 116.1194.



Substrates **13** gave 1-hexanol in 90% yield. Spectral data matched those of commercially available 1-hexanol.

Substrate **14** gave phenol and octane in 92% yield. Spectral data matched those of commercially available phenol and octane.

Substrate **15** gave 1-octanol and octane in 85% yield. Spectral data matched those of commercially available 1-octanol and octane.

References

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