# SUPPORTING INFORMATION

## Intramolecular Hydroalkoxylation/Cyclization of Alkynyl Alcohols Mediated by Lanthanide Catalysts. Scope and Reaction Mechanism

SungYong Seo, Xianghua Yu, and Tobin J. Marks*

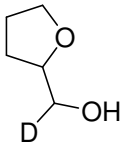
Department of Chemistry, Northwestern University, Evanston, Illinois 60208

## *Experimental Section*

**Materials and Methods.** All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk line, interfaced to a high-vacuum line ($10^{-6}$ Torr), or in a nitrogen-filled vacuum atmospheres glovebox with a high capacity recirculator (<1 ppm of $O_2$). Argon (Airgas, prepurified) was purified by passage through a MnO oxygen-removal column and a Davison 4 A molecular sieve column. Pentane was dried using activated alumina columns according to the method described by Grubbs.[S1] Ether and THF were distilled from sodium benzophenone ketyl. Benzene was dried through vacuum-transfer from Na/K alloy immediately prior to use if employed for catalyst synthesis or catalytic reactions. $D_2O$ (Cambridge Isotope Laboratories; all 99+ atom % D) was used directly as received. Benzene-$d_6$ (Cambridge Isotope Laboratories; all 99+ atom % D) used for NMR reactions and kinetic measurements was stored *in vacuo* over Na/K alloy in resealable bulbs and were vacuum-transferred immediately prior to use. All liquid substrates were dried twice as solutions in benzene-$d_6$ over freshly activated Davison 4 A molecular sieves and were degassed by freeze-pump-thaw methods. They were then stored in vacuum-tight storage flasks. Solid substrates were sublimed under high-vacuum and stored in the glove box before use. The lanthanide complexes $Ln[N(SiMe_3)_2]_3$, (Ln = La, Nd, Sm, Y, and Lu), were prepared according to published procedures.[S2] The $^1H$ NMR integration internal standard $Ph_3SiMe$ was purchased from Strem Inc., sublimed under high-vacuum, and stored in the glove box before use.

**Physical and Analytical Measurements.** NMR spectra were recorded on a Varian Gemini 300 (300 MHz, $^{1}$H; 75 MHz, $^{13}$C), Mercury-400 (FT, 400 MHz, $^{1}$H; 100 MHz, $^{13}$C), or Inova-500 (500 MHz, $^{1}$H; 125 MHz, $^{13}$C, 76.7 MHz, $^{2}$H) instrument. Chemical shifts (δ) for $^{1}$H, $^{2}$H, and $^{13}$C are referenced to internal solvent resonances and reported relative to $SiMe_4$. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed J. Young tubes.

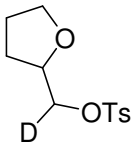
## Authentic Samples of the Hydroalkoxylation Products of Compound 3



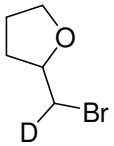

**Deutero(tetrahydrofuran-2-yl)methanol (S1).** Dimethyl sulfoxide (DMSO) (6.5 mL, 90.8 mmol) was added over a period of 20 min at –78 °C to a stirring 2.0 M solution of oxalyl chloride (22.7 mL, 45.4 mmol) dissolved in THF (80 mL). After the solution was stirred at –78 °C for an additional 10 min, tetrahydrofurfuryl alcohol (4.0 mL, 41.3 mmol) dissolved in THF (30 mL) was next added dropwise. The reaction mixture was stirred at –78 °C for 30 min, and triethylamine (28.8 mL, 206.5 mmol) was then added dropwise at –78 °C. The reaction mixture was stirred for an additional 30 min and then allowed to warm to room temperature. The mixture was filtered, the filtercake was washed with THF, and the filtrate stored under nitrogen at 0 °C.

A solution of $NaBD_4$ (1.73 g, 41.3 mmol) in water (3 mL) was added to the filtrate described above. The solution was stirred for 1 h, combined with ethyl ether (150 mL), and washed with water. The organic layer was next dried over $Na_2SO_4$. After filtration, the solvent was removed *in vacuo*. Column chromatography on silica gel

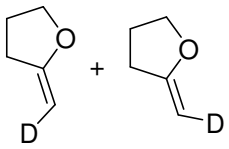
(pentane : $Et_2O$ = 1 : 1) afforded pure alcohol (1.82 g; 43% yield); $^1$H NMR (500 MHz, $CDCl_3$): δ 3.98-3.95(m, 1H), 3.86-3.73(m, 2H), 3.62(s, 1H), 3.48-3.44(m, 1H), 1.92-1.83(m, 3H), 1.63-1.59(m, 1H); $^2$H NMR (77 MHz, $CDCl_3$): 3.63, 3.50.; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 79.57, 68.47, 65.12, 64.99, 64.56, 27.31, 26.25.




**Deutero(tetrahydrofuran-2-yl)methyl-4-methylbenzenesulfonate (S2).** A solution of the deuterated alcohol (1.82 g, 17.7 mmol) prepared above in $CH_2Cl_2$ (50 mL) was added to the solution of TsCl (5.06 g, 26.6 mmol) and pyridine (4.3 mL, 53.1 mmol) in $CH_2Cl_2$ (50 mL) at room temperature, and this solution was stirred for 16 h. Water (100 mL) and $CH_2Cl_2$ (100 mL) were next added and the resulting two layers were separated. The organic layer was washed with 10% aqueous HCl, then washed with brine. The organic layer was next dried over $Na_2SO_4$. After filtration, the solvent was removed *in vacuo*. Column chromatography on silica gel (hexane : EtOAc = 5 : 1) afforded pure tosylate (3.3 g; 74% yield); $^1$H NMR (500 MHz, $CDCl_3$): δ 7.76(d, 8.1 Hz, 2H), 7.31(d, 8.1 Hz, 2H), 4.05(q, 6.6 Hz, 5.9 HZ, 1H), 3.96(m, 1H), 3.76-3.68(m, 2H), 2.41(s, 3H), 1.93(m, 1H), 1.85-1.81(m, 2H), 1.65-1.61(m, 1H); $^2$H NMR (77 MHz, $CDCl_3$): 3.99.; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 145.03, 133.11, 130.03, 128.16, 76.04, 71.61, 71.38, 71.14, 68.82, 28.01, 25.78, 21.87.

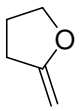


**2-(bromodeuteromethyl)-tetrahydrofuran (S3).** The tosylate (3.3 g, 12.8 mmol) prepared above and lithium bromide (2.23 g, 25.6 mmol) were dissolved in acetone (50 mL), refluxed for 16 h, and filtered. Water was added and the mixture extracted with Ether. The organic layer was next dried over $Na_2SO_4$. After filtration, the solvent was removed *in vacuo* to yield analytically pure compound (1.12 g; 53% yield); $^1$H NMR (500 MHz, $CDCl_3$): δ 4.13-4.08(q, 6.6 Hz, 1H), 3.93-3.87(m, 1H), 3.81-3.75(m, 1H), 3.38-3.31(m, 1H), 2.09-2.01(m, 1H), 1.97-1.85(m, 2H), 1.75-1.66(m, 1H); $^2$H NMR (77 MHz, $CDCl_3$): 3.41, 3.36.; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 78.34, 69.09, 35.95, 35.71, 35.49, 30.56, 26.12.



4b 4a

**2-Deuteromethylene-tetrahydrofuran (4a** and **4b).** In a simple distillation apparatus, a suspension of powdered KOH (505 mg, 9 mmol) and the bromide (747.1 mg, 4.5 mmol) prepared above was heated up to 150 $^o$C for 50 min and afford colorless liquid (254 mg; 68% yield). This liquid is mixture of isomer; $^1$H NMR (500 MHz, $CDCl_3$): δ 4.49(s, 1H), 3.87(s, 1H), 3.63(t, 6.6 Hz, 4H), 2.09(t, 7.3 Hz, 4H), 1.33(m, 4H); $^2$H NMR (77 MHz, $CDCl_3$): 4.50, 3.88.; $^{13}$C NMR (125 MHz, $CDCl_3$): δ 163.11, 79.02, 70.27, 29.05, 25.07.




**2-Methylene-tetrahydrofuran (2).** Follow same process as preparing **4a** and **4b**. This liquid is mixture of isomer; $^1$H NMR (500 MHz, $CDCl_3$): δ 4.51(s, 1H), 3.89(s, 1H),

3.63(t, 6.6 Hz, 2H), 2.09(t, 7.3 Hz, 2H), 1.33(m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 163.16, 79.03, 70.27, 29.10, 25.07.

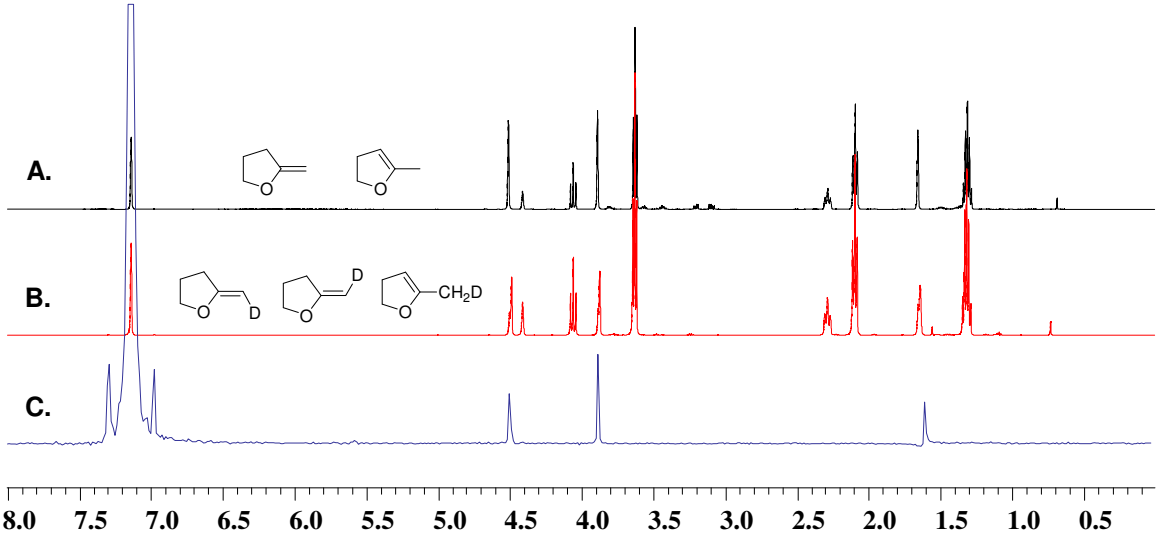



Figure S1. (A) $^1$H NMR spectrum of 2-methylene-tetrahydrofuran (**2**) in $C_6D_6$, (B) $^1$H NMR spectrum of an authentic sample of 2-deuteromethylene-tetrahydrofuran (**4a** and **4b**) in $C_6D_6$, (C) $^2$H NMR spectrum of an authentic sample of 2-deuteromethylene-tetrahydrofuran (**4a** and **4b**) in $C_6D_6$.

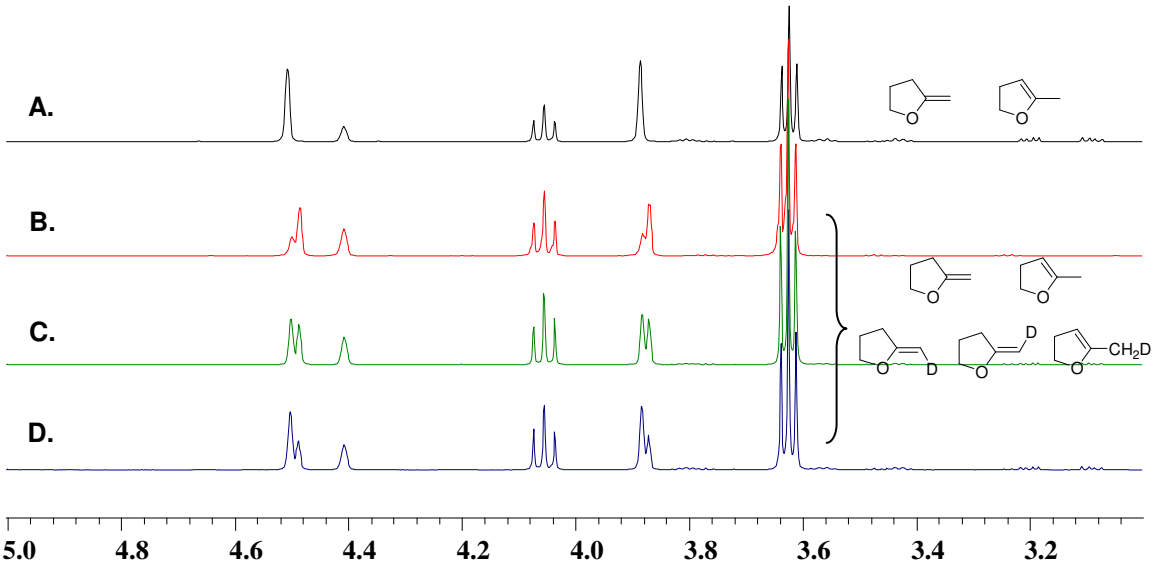
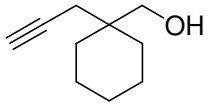


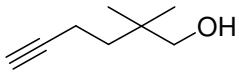

Figure S2. (A) $^1$H NMR spectrum of an authentic sample of 2-methylene-tetrahydrofuran (**2**) in $C_6D_6$, (B), (C), (D) $^1$H NMR spectrum of a mixture of compounds **4a**, **4b** and **2** in $C_6D_6$ as a function of **2** concentration.

## Substrate Syntheses

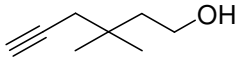

**2,2-Dimethylpent-4-yn-1-ol (5).** 2,2-dimethylpent-4-yn-1-ol was synthesized employing a published procedure.[S3] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 3.45(s, 2H), 2.18(s, 2H), 2.02(s, 1H), 0.99(s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 82.34, 71.07, 35.67, 28.53, 23.96, 23.92.




**(1-(Prop-2-ynyl)cyclohexyl)methanol (7).** (1-(prop-2-ynyl) cyclohexyl)methanol was synthesized employing a published procedure.[S4] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 3.55(d, 3.9 Hz, 1H), 2.27(d, 2.0 Hz, 2H), 2.01(t, 2.4 Hz, 1H), 1.69(t, 5.3 Hz, 1H), 1.48-1.39(m, 10H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 82.26, 70.67, 68.81, 37.85, 32.09, 26.38, 25.33, 21.74.

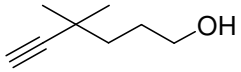



**2,2-Dimethylhex-5-yn-1-ol (11).** 2,2-dimethylhex-5-yn-1-ol was synthesized employing a published procedure.[S5] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 3.35(d, 6.0 Hz, 2H), 2.19(td, 7.9, 2.6 Hz, 2H), 1.96(t, 2.6 Hz, 1H), 1.56(m, 3H), 0.89(s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 85.59, 71.33, 68.23, 37.56, 35.36, 23.99, 13.71.

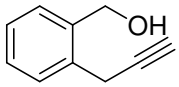



**3,3-Dimethylhex-5-yn-1-ol (13).** 3,3-dimethylhex-5-yn-1-ol was synthesized employing a published procedure.[S5] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 3.74(t, 7.3 Hz, 2H), 2.13(d, 2.9

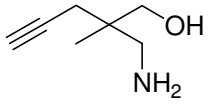
Hz, 2H), 2.02(t, 2.4 Hz, 1H), 1.66(t, 7.3 Hz, 2H), 1.02(s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 82.58, 70.44, 59.98, 43.79, 32.88, 32.30, 27.36.




**4,4-Dimethylhex-5-yn-1-ol (15).** 4,4-dimethylhex-5-yn-1-ol was synthesized employing a published procedure. [S5,S6] $^1$H NMR (500 MHz, $CDCl_3$): δ 3.68(t, 6.4 Hz, 2H), 2.09(d, 2.0 Hz, 1H), 1.76-1.71(m, 2H), 1.49-1.46.(m, 3H), 1.22(s, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 91.86, 68.20, 63.42, 39.44, 30.99, 29.35, 28.91.



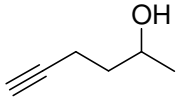

**(2-(Prop-2-ynyl)phenyl)methanol (19).** (2-prop-2-ynyl)phenyl)methanol was synthesized employing a published procedure.[S7] $^1$H NMR (500 MHz, $CDCl_3$): δ 7.49(d, 6.8 Hz, 1H), 7.37(d, 6.8 Hz, 1H), 7.36-7.29(m, 2H), 4.72(s, 2H), 3.67(d, 1.9 Hz, 2H), 2.22(t, 2.9 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 138.39, 134.70, 129.24, 128.72, 128.56, 127.58, 82.21, 71.18, 63.34, 22.29.



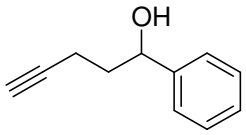

**2-(aminomethyl)-2-methylpent-4-yn-1-ol (23).** A solution of ethyl-2-cyanopropanoate(3 g, 23.6 mmol) and $K_2CO_3$ (3.6 g, 26 mmol) in THF (100 mL) was stirred for 30 min at room temperature. Propargyl bromide (2.9 mL, 26 mmol) was added in this solution. The reaction mixture was stirred under reflux for 24 h. Water (100 mL) and $Et_2O$ (100 mL) were next added and the resulting two layers were separated. The organic layer was washed with brine and water. The organic layer was next dried over $Na_2SO_4$. After filtration, the solvent was evaporated and the crude material was purified

by column chromatography on silica gel (hexane : EtOAc = 15 : 1) to afford the ethyl 2-cyano-2-methylpent-4-ynoate as a colorless liquid (3.76 g, 96.4%). $^{1}$H NMR (500 MHz, $CDCl_3$): δ 4.34-4.29(q, 6.8 Hz, 2H), 2.87(dd, 2.9 Hz, 16.6 Hz, 1H), 2.74(dd, 2.9 Hz, 16.6 Hz, 1H), 2.23(t, 2.9 Hz, 1H), 1.70(s, 3H), 1.35(t, 6.8 Hz, 3H), 1.91(br, 1H), 1.53(d, 5.9 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 168.12, 119.13, 73.38, 63.51, 43.35, 28.22, 22.69, 22.67, 14.22.

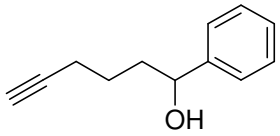
To a stirred suspension of $LiAlH_4$ (574 mg, 15.1 mmol) in $Et_2O$ at 0 °C under $N_2$ was slowly added a solution of the above propargyl ester (1.00 g, 6.1 mmol) in $Et_2O$. The reaction mixture was allowed to warm to room temperature and stirred under reflux for 2 h. Next, the mixture was diluted with $Et_2O$ and then carefully quenched by sequential additions of water, 15% aqueous NaOH, and water. Stirring at room temperature for a further 30 min yielded a colorless solution with a white precipitate, which was then removed by filtration through a Celite pad. The filtrate was then dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by recrystallization from $Et_2O$ to yield the 2-(aminomethyl)-2-methylpent-4-yn-1-ol **23** as a grey solid (620 mg; 80.6% yield); $^{1}$H NMR (500 MHz, $CDCl_3$): δ 3.66(d, 10.7 Hz, 1H), 3.57(d, 10.7 Hz, 1H), 3.00(d, 12.7 Hz, 1H), 2.76(d, 12.7 Hz, 1H), 2.61(br, 3H), 2.45(d, 17.6 Hz, 1H), 2.18(d, 17.6 Hz,, 1H), 2.01(s, 1H), 0.93 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 81.52, 72.18, 70.65, 50.48, 38.03, 24.75, 20.42. HRMS-ESI(m/z): [$(M+H)^+$] calcd for $C_7H_{14}NO$, 128.1075; found, 128.1071.



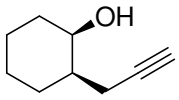
**Hex-5-yn-2-ol (25).** Hex-5-yn-2-ol was synthesized employing a published procedure.[S8] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 3.98-3.94(m, 1H), 2.35-2.30(m, 2H), 2.28(br, 1H), 1.97(t, 2.93 Hz, 1H), 1.68-1.65(m, 2H), 1.23(d, 6.8 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 84.36, 69.00, 67.20, 37.57, 23.65, 15.27.




**1-Phenylpent-4-yn-1-ol (27).** 1-phenylpent-4-yn-1-ol was synthesized employing a published procedure.[S9] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.38-7.28(m, 5H), 4.88(m, 1H), 2.36(m, 1H), 2.28(m, 1H), 2.09(s, 1H), 2.03-2.00(m, 1H), 1.94-1.91(m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 144.25, 128.82, 128.01, 126.07, 84.13, 73.41, 69.24, 37.65, 15.39.

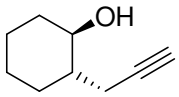



**1-Phenylhex-5-yn-1-ol (29).** 1-phenylhex-5-yn-1-ol was synthesized employing a published procedure.[S10] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.41-7.28(m, 5H), 4.72(dd, 5.9 Hz, 1.9 Hz, 1H), 2.26-2.23(m, 2H), 1.97-1.82(m, 4H), 1.721.68(m, 1H), 1.59-1.53(m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 144.80, 128.77, 127.90, 126.10, 84.44, 74.39, 68.87, 38.19, 24.94, 18.52.

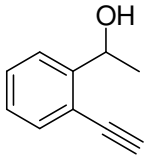



**(1R,2R)-2-(Prop-2-ynyl)cyclohexanol (31).** (1R,2R)-2-(prop-2-ynyl) cyclohexanol was synthesized employing a published procedure.[S11] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 4.06(m, 1H), 2.32-2.26(m, 1H), 2.20-2.14(m, 1H), 1.99(s, 1H), 1.81-1.78(m, 1H), 1.67-1.64(m,

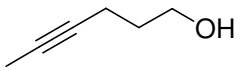
3H), 1.58-1.43(m, 5H), 1.28-1.25(m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 83.73, 69.51, 68.56, 41.06, 33.18, 26.49, 25.28, 21.76, 20.30.



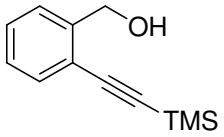

**(1R,2S)-2-(Prop-2-ynyl)cyclohexanol (33).** (1R,2S)-2-(prop-2-ynyl)cyclohexanol was synthesized employing a published procedure.[S12] $^1$H NMR (500 MHz, $CDCl_3$): δ 3.37(m, 1H), 2.47-2.44(m, 1H), 2.33-2.28(m, 1H), 2.08-2.03(m, 1H), 1.99-1.95(m, 2H), 1.87-1.84(m, 1H), 1.75-1.65(m, 2H), 1.43-1.41(m, 1H), 1.29-1.14(m, 4H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 83.23, 73.67, 69.94, 44.14, 35.77, 30.49, 25.64, 25.12, 22.00.



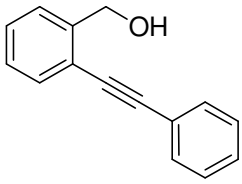

**1-(2-Ethynylphenyl)ethanol (35).** 1-(2-ethynylphenyl)ethanol was synthesized employing a published procedure.[S13] $^1$H NMR (500 MHz, $CDCl_3$): δ 7.54(d, 7.8 Hz, 1H), 7.48(d, 7.8 Hz, 1H), 7.38(t, 7.8Hz, 1H), 7.24(t, 7.8Hz, 1H), 5.34(q, 6.8 Hz, 1H), 3.34(s, 1H), 2.52(br, 1H), 1.50(d, 6.8 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.54, 133.16, 129.64, 127.25, 125.01, 119.41, 82.43, 81.68, 66.42, 24.27.



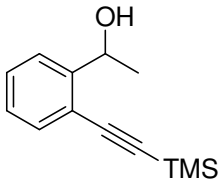

**Hex-4-yn-1-ol (44).** hex-4-yn-1-ol was synthesized employing a published procedure.[S8,14] $^1$H NMR (500 MHz, $CDCl_3$): δ 3.73(t, 5.9 Hz, 2H), 2.26-2.23(m, 2H), 1.97(s, 1H), 1.77(s, 3H), 1.71(t, 6.8 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 78.70, 76.42, 62.13, 31.75, 15.56, 3.64.




**(2-((Trimethylsilyl)ethynyl)phenyl)methanol (48).** (2-((trimethylsilyl)ethynyl)phenyl)methanol was synthesized employing a published procedure.[S15,S16c] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.48(d, 8.8 Hz, 1H), 7.41(d, 7.8 Hz, 1H), 7.34(t, 6.8 Hz, 1H), 7.25(t, 6.8 Hz, 1H), 4.82(d, 6.8 Hz, 2H), 2.53(t, 6.3 Hz, 1H), 0.28(s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 143.41, 132.63, 129.20, 127.54, 127.31, 121.29, 102.84, 99.81, 64.15, 0.20.

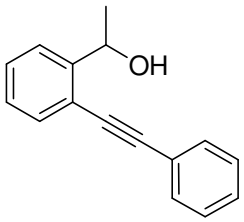



**(2-(Phenylethynyl)phenyl)methanol (51).** (2-(phenylethynyl) phenyl)methanol was synthesized employing a published procedure.[S16] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.58(d, 5.9 Hz, 3H), 7.52(d, 8.8 Hz, 1H), 7.40(m, 4H), 7.30(t, 7.3 Hz, 1H), 4.95(s, 2H), 2.62(br, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 142.88, 132.41, 131.85, 129.04, 128.84, 128.75, 127.69, 127.42, 123.23, 121.46, 94.51, 87.08, 64.11.




**1-(2-((Trimethylsilyl)ethynyl)phenyl)ethanol (55).** 1-(2-((trimethylsilyl)ethynyl)phenyl)ethanol was synthesized employing a published procedure.[S13] $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.50(d, 7.8 Hz, 1H), 7.44(d, 7.8 Hz, 1H), 7.34(t, 7.8 Hz, 1H), 7.21(t, 7.8 Hz, 1H), 5.30(m, 1H), 2.52(m, 1H), 1.52(d, 5.9 Hz, 3H),

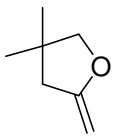
0.28(s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 148.41, 132.72, 129.33, 127.12, 124.89, 120.35, 103.13, 99.98, 68.73, 23.97, 0.15.



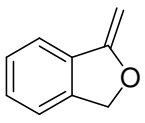

**1-(2-(Phenylethynyl)phenyl)ethanol (58).** 1-(2-(phenylethynyl) phenyl)ethanol was synthesized employing a published procedure.[S12a] $^1$H NMR (500 MHz, $CDCl_3$): δ 7.60-7.53(m, 4H), 7.41-7.37(m, 4H), 7.27(t, 7.3 Hz, 1H), 5.44(q, 3.9 Hz, 1H), 2.21(br, 1H), 1.60(t, 5.9 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 147.81, 132.50, 131.71, 129.17, 128.75, 128.70, 127.35, 124.97, 123.31, 120.57, 94.59, 87.23, 68.77, 24.27.

**Typical NMR-Scale Catalytic Reactions.** In a glovebox, the homoleptic lanthanide amide $Ln[N(SiMe_3)_2]_3$ (7.1 μmol) and methyltriphenylsilane (53.2 μmol, internal integration standard) were weighed into a vial, and 500 μL of benzene-$d_6$ was added by syringe. The reagents were mixed to yield a homogeneous, clear solution and then transferred to a J. Young NMR tube equipped with a Teflon valve. The tube was then closed, removed from the glovebox, and attached to the high-vacuum line. The substrate (*ca.* 1.0 M in benzene-$d_6$, 0.15 mL, 20-fold molar excess) was added by syringe to the catalyst solution under an argon stream. The NMR tube was next sealed and frozen at −78 °C until the time for NMR analysis, and then brought to the desired temperature, and the ensuing hydroalkoxylation/cyclization reaction was monitored by $^1$H NMR spectroscopy.

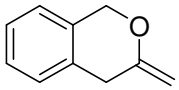
**Typical Preparative-Scale Catalytic Reactions.** Scale-up catalytic reactions were carried out using the following procedure. In a glovebox, the homoleptic lanthanide amide $La[N(SiMe_3)_2]_3$ (31 mg, 50 μmol) was weighed into a vial, and 500 μL of benzene-$d_6$ was added by syringe. The ingredients were mixed to yield a homogeneous, clear solution and then transferred to a storage tube equipped with a Teflon valve and a magnetic stir bar. The tube was then closed, removed from the glovebox, and attached to the high-vacuum line. The substrate (*ca.* 1.0 M in benzene-$d_6$, 1 mL, 20-fold molar excess) was added by syringe to the catalyst solution under an argon stream. The mixture was then freeze-pump-thaw degassed and warmed to room temperature. The resulting solution was stirred with heating at 60 °C for 5 h. At completion of the reaction, this reaction mixture was filtered through a small plug of silica gel to remove the catalyst. This crude product was then purified by flash column chromatography or Kugelrohr distillation.



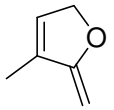
**4,4-Dimethyl-2-methylene-tetrahydrofuran (6).** Spectral data matched literature references.[S17] $^1$H NMR (500 MHz, $C_6D_6$): δ 4.55(s, 1H), 3.92(s, 1H), 3.42(s, 2H), 1.97(s, 2H), 0.72(s, 6H); $^{13}$C NMR (100 MHz, $C_6D_6$): δ 163.07, 81.33, 80.21, 43.95, 37.96, 24.52.



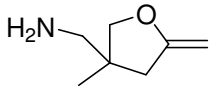
**1-Methylene-1, 3-dihydroisobenzofuran (18).** Spectral data matched literature references.[S18,S19] $^1$H NMR (500 MHz, $C_6D_6$): δ 7.19(m, 1H), 6.93(m, 2H), 6.64(m, 1H), 4.78(s, 2H), 4.71(s, 1H), 4.54(s, 1H); $^{13}$C NMR (125 MHz, $C_6D_6$): δ 162.38, 140.47, 134.11, 128.72, 128.20, 121.21, 120.67, 78.06, 73.38.



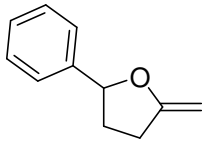
**3-Methyleneisochroman (20).** Spectral data matched literature references.[S19] $^1$H NMR (500 MHz, $C_6D_6$): δ 7.03(m, 1H), 6.93(m, 1H), 6.78(m, 1H), 6.67(m, 1H), 4.79(s, 1H), 4.51(s, 1H), 3.12(s, 2H), 1.70(s, 2H).



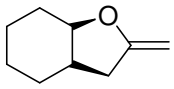
**3-Methyl-2-methylene-2, 5-dihydrofuran (22).** Spectral data matched literature references.[S12b] $^1$H NMR (500 MHz, $C_6D_6$): δ 5.29(s, 1H), 4.52(s, 1H), 4.35(m, 2H), 3.94(s, 1H), 1.49(s, 3H).



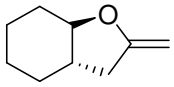
**(3-methyl-5-methylene-tetrahydrofuran-3-yl)methanamine (24)**. $^1$H NMR (500 MHz, $C_6D_6$): δ 4.50(s, 1H), 3.87(s, 1H), 3.65(d, 8.6 Hz, 1H), 3.37(d, 8.6 Hz, 1H), 2.14-2.10(m, 3H), 1.86(dt, 1.6 Hz, 14.9 Hz, 1H), 0.81(s, 3H). $^{13}$C NMR (125 MHz, $C_6D_6$): δ 163.28, 80.05, 78.19, 48.36, 43.28, 40.18, 20.39.



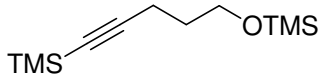
**2-Methylene-5-phenyl-tetrahydrofuran (28).** Spectral data matched literature references.[S20] $^1$H NMR (500 MHz, $C_6D_6$): δ 7.22-7.02(m, 5H), 4.90(t, 7.8 Hz, 1H), 4.63(s, 1H), 3.95(s, 1H), 2.24-2.17(m, 2H), 1.78-1.72(m, 2H).



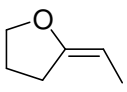
**(3a*S*, 7a*S*)-2-Methylene-octahydrobenzofuran (32).** Spectral data matched literature references.[S12b] $^1$H NMR (500 MHz, $CDCl_3$): δ 4.59(s, 1H), 3.95(s, 1H), 3.91(dd, 10.7 Hz, 3.9 Hz, 1H), 2.32-2.28(m, 1H), 1.97-1.89(m, 2H), 1.54(m, 1H), 1.40-1.31(m, 2H), 1.25-1.10(m, 5H).



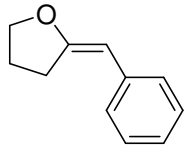
**(3a*S*, 7a*S*)-2-Methylene-octahydrobenzofuran (34).** Spectral data matched literature references.[S12b] $^1$H NMR (500 MHz, $CDCl_3$): δ 4.48(s, 1H), 3.90(s, 1H), 3.10(m, 1H), 2.25-2.20(m, 1H), 1.95-1.85(m, 2H), 1.48-1.41(m, 2H), 1.33-1.18(m, 4H), 0.87-0.84(m, 2H).



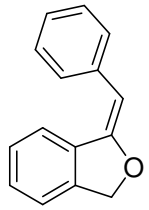
**Trimethyl(5-(trimethylsilyl)pent-4-ynyloxy)silane (43).** Spectral data matched literature references.[S21] $^1$H NMR (500 MHz, $C_6D_6$): δ 3.51(t, 6.3 Hz, 2H), 2.21(t, 7.3 Hz, 2H), 1.58(p, 6.8 Hz, 2H), 0.18(s, 9H), 0.05(s, 9H). $^{13}$C NMR (125 MHz, $C_6D_6$): δ 107.39, 84.61, 60.70, 31.66, 16.42, 0.18, -0.58.



**(*E*)-2-Ethylidene-tetrahydrofuran (45).** Spectral data matched literature references.[S22] $^{1}$H NMR (500 MHz, $C_6D_6$): δ 5.01-4.97(m, 1H), 3.63(t, 6.8 Hz, 2H), 2.05(t, 6.8 Hz, 2H), 1.52(d, 6.8 Hz, 3H), 1.35(p, 6.8 Hz, 2H). $^{13}$C NMR (125 MHz, $C_6D_6$): δ 156.68, 89.55, 69.22, 25.58, 24.79, 2.97.



**(*E*)-2-Benzylidene-tetrahydrofuran (47).** Spectral data matched literature references.[S23] $^{1}$H NMR (500 MHz, $C_6D_6$): δ 7.20-7.12(m, 3H), 7.00(t, 6.8 Hz, 2H), 6.21(s, 1H), 3.59(t, 6.8 Hz, 2H), 2.25(t, 7.8 Hz, 2H), 1.29(p, 7.8 Hz, 2H). $^{13}$C NMR (125 MHz, $C_6D_6$): δ 159.58, 138.48, 128.51, 127.27, 124.59, 99.43, 69.01, 28.29, 25.06.



***(E)*-1-Benzylidene-1,3-dihydroisobenzofuran (52).** Spectral data matched literature references.[S24] $^{1}$H NMR (500 MHz, $C_6D_6$): δ 7.47(d, 8.2 Hz, 1H), 7.36(d, 7.0 Hz, 2H), 7.12(m, 2H), 7.03(t, 7.0 Hz, 1H), 6.82(t, 7.0 Hz, 1H), 6.70(t, 7.0 Hz, 1H), 6.61(d, 7.0 Hz, 1H), 6.49(s, 1H), 4.80(s, 2H); $^{13}$C NMR (125 MHz, $C_6D_6$): δ 157.13, 142.24, 136.47, 132.90, 129.81, 128.84, 128.59, 127.41, 126.50, 123.17, 121.18, 100.74, 72.56.

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