Supporting Information

Directed Hydrozirconation of Propargylic Alcohols

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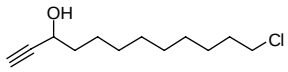
Method and Materials

General. Unless otherwise stated, reactions were performed under a nitrogen atmosphere using freshly purified solvents. Solvents were purified using solvent purification columns purchased from Glass Contour, Laguna Beach, CA. All reactions were monitored by thin-layer chromatography with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Gas chromatography (GC) was performed on an HP 6890N autosampling GC with an HP-5 capillary column and equipped with a FID detector. Flash chromatography was performed with indicated solvents using silica gel (particle size 0.032-0.063 □m) purchased from Sorbent Technologies. ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova-400 or Mercury-300 spectrometer. Chemical shift are reported relative to internal chloroform or methanol ($CDCl_3$: ^{1}H, δ = 7.27, ^{13}C, δ = 77.23). Coupling constants are in Hz and are reported as d (doublet), t (triplet), q (quartet), quin (quintet). For signals having multiple coupling patterns, the coupling constant are listed in the same order as the pattern (e.g. dt, J = 2.0, 4.0; 2.0 is the coupling constant for the doublet and 4.0 is for the coupling constant for the triplet). Mass spectra were acquired on a Shimadzu QP5000 GC/MS using the indicated ionization method. Optical rotations were measured on a Rudolph Research Analytical Autopol® IV Polarimeter

Materials

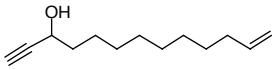
$Cp_2Zr(H)Cl$ was purchased from Strem Chemicals Inc. and used within three months. All propargylic alcohols were prepared by addition of appropriate aldehyde (1.0 equiv.) to ethynyl magnesiumbromide (1.2 equiv.) in THF at 0 °C unless otherwise noted. Known compounds exhibited spectral data consistent with literature reports: dodec-1-yn-3-ol[1] (table 1), 1-(benzyloxy)but-3-yn-2-ol[2] (entry 1), 5-phenylpent-1-yn-3-ol[3] (entry 2), 5-(tert-butyldimethylsilyloxy)pent-1-yn-3-ol[4] (entry 4) , 1-cyclohexylprop-2-yn-1-ol[5] (entry 5), octa-1,7-diyn-3-ol[6](entry7). The following are the characterization data for synthetic new starting materials:

12-chlorododec-1-yn-3-ol (Table 2, entry 3):



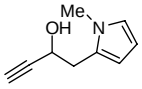
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.28 (br. S, 8H), 1.38-1.45 (m, 4H), 1.65-1.78 (m, 4H), 2.38 (d, J = 4.8, 1H), 2.44 (d, J = 2.0, 1H), 3.51 (t, J = 6.8, 2H), 4.34 (q, J = 4.8, 1H). ^{13}C NMR ($CDCl_3$) = 25.1, 27.0, 29.0, 29.3, 29.4, 29.5, 32.7, 37.7, 45.3, 62.3, 72.9, 85.2.

tridec-12-en-1-yn-3-ol (Table 2, entry 6):



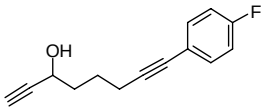
Colorless oil, ^{1}H NMR ($CDCl_3$) δ= 1.29-1.47 (m, 2H), 1.66-1.76 (m, 2H), 2.01-2.06 (m, 2H), 2.46 (d, J = 2.0, 1H), 4.37 (q, J = 4.4, 1H), 4.93 (d, J = 10.4, 1H), 5.01 (d, J = 17.2, 1H), 5.81 (ddt, J = 16.8, 10.0, 6.8, 1H). ^{13}C NMR ($CDCl_3$) = 25.2, 29.0, 29.3, 29.4, 29.5, 29.6, 34.0, 37.8, 62.4, 73.0, 85.2, 114.3, 139.4. EI-MS (m/z): 193 $[M-1]^+$.

1-(1-methyl-1H-pyrrol-2-yl)but-3-yn-2-ol (Table 2, entry 8):



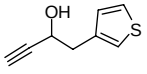
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 2.27 (br. s, 1H), 2.49 (d, J = 2.0, 1H), 3.01 (dd, J = 13.6, 6.8, 1H), 3.06 (dd, J = 15.2, 5.6, 1H), 3.63 (s, 3H), 4.54 (m, 1H), 6.08-6.12 (m, 2H), 6.61 (q, J = 2.4, 1H). ^{13}C NMR ($CDCl_3$) = 34.2, 34.5, 61.8, 73.6, 84.4, 107.2, 108.6, 122.7, 127.4. EI-MS (m/z): 149 $[M]^+$.

8-(4-fluorophenyl)octa-1,7-diyn-3-ol (Table 2, entry 9):



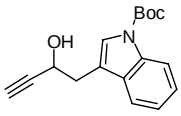
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.75-1.93 (m, 4H), 2.24 (br. s, 1H), 2.46 (t, J = 6.8, 2H), 2.50 (s, 1H), 4.46 (m, 1H), 6.97 (t, J = 8.4, 2H), 7.36 (dd, J = 6.0, 8.0, 2H). ^{13}C NMR ($CDCl_3$) = 19.2, 24.4, 36.8, 62.0, 73.4, 80.3, 84.8, 89.3 (d, J = 4.8), 115.6 (d, J = 87.3), 120.0 (d, J = 14.7), 133.5 (d, J = 33.9), 162.2 (d, J = 988). EI-MS (m/z): 215 $[M-1]^+$.

1-(thiophen-3-yl)but-3-yn-2-ol (Table 2, entry 10):



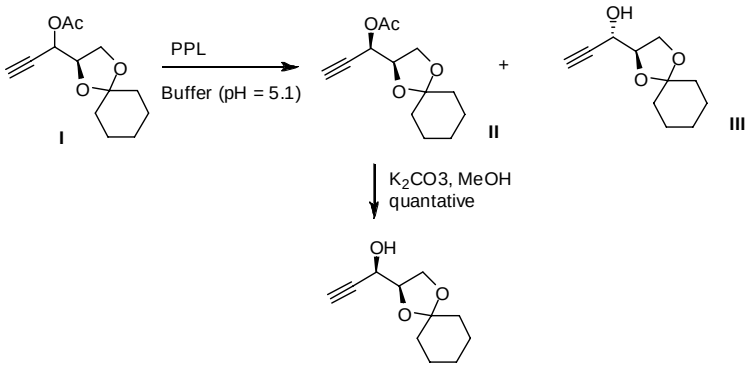
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 2.49 (d, J = 1.6, 1H), 2.51 (s, 1H), 3.03 (dd, J = 14.0, 6.4, 1H), 3.08 (dd, J = 14.0, 6.0, 1H), 4.56 (br. s, 1H), 7.06 (d, J = 4.8, 1H), 7.15 (s, 1H), 7.28 (dd, J = 4.4, 3.2, 1H). ^{13}C NMR ($CDCl_3$) = 38.3, 62.4, 73.8, 84.4, 123.2, 125.7, 129.1, 136.6. EI-MS (m/z): 151 $[M-1]^+$.

1-(1-Boc-1H-indol-3-yl)but-3-yn-2-ol (Table 2, entry 11):



Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.69 (s, 9H), 2.33 (br. s, 1H), 2.49 (br. s, 1H), 3.12 (dd, J = 14.4, 6.8, 1H), 3.17 (dd, J = 14.8, 6.0, 1H), 4.70 (br. s, 1H), 7.24-7.28 (m, 1H), 7.34 (t, J = 8.0, 1H), 7.59-7.61 (m, 2H), 8.15 (br. d, J = 6.0, 1H). ^{13}C NMR ($CDCl_3$) = 28.4, 33.6, 61.9, 73.7, 83.9, 84.5, 115.5, 119.3, 122.7, 124.6, 124.7, 130.7, 135.6, 149.9. EI-MS (m/z): 185 $[M - Boc + 1]^+$.

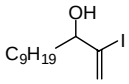
(R)-1-((R)-1,4-dioxaspiro[4.5]decan-2-yl)prop-2-yn-1-ol (Table 2, entry 12):



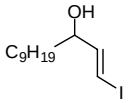
This compound was prepared according to a revised procedure[7]: racemic acetate **I** (4.3g, 18.1 mmol) was added to KH_2PO_4 buffer solution (0.2 M, pH = 5.1, 330 mL) at 23 °C. PPL (2.6 g, porcine pancreatic lipase, EC 3.1.1.3, Type II, from Sigma) was added. The reaction mixture was stirred vigorously at 23 °C and monitored by NMR. After about 6h, ether was added to quench the reaction the reaction mixture filtered through a fritted funnel. The filtration was extracted with ether. The acetate **II** and alcohol **III** were separated by chromatography column to yield 1.7 g of acetate **II** (40%, d. r. = 56:1). Methanolysis of acetate **II** by K_2CO_3 in MeOH gave (R)-1-((R)-1,4-dioxaspiro [4.5]decan-2-yl)prop-2-yn-1-ol in quantitative yield.

Acetate 2[8]:
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.35-1.70 (m, 10H), 2.11 (s, 3H), 2.47 (d, *J* = 2.0, 1H), 3.96 (dd, *J* = 8.8, 6.0, 1H), 4.10 (dd, *J* = 8.4, 6.4, 1H), 4.31 (dt, *J* = 4.8, 6.0, 1H), 5.47 (dd, *J* = 4.4, 2.4, 1H).
(R)-1-((R)-1,4-dioxaspiro[4.5]decan-2-yl)prop-2-yn-1-ol:
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.38-1.71 (m, 10H), 2.25 (d, *J* = 5.0, 1H), 2.48 (d, *J* = 2.5, 1H), 4.06 (dd, *J* = 8.5, 6.5, 1H), 4.10 (dd, *J* = 8.5, 6.0, 1H), 4.26 (dt, *J* = 3.5, 6.5, 1H), 4.49 (dt, *J* = 2.5, 4.5, 1H). ^{13}C NMR ($CDCl_3$) = 23.9, 24.1, 25.2, 34.7, 36.1, 62.6, 65.0, 74.6, 77.5, 81.3, 111.0. EI-MS (m/z): 196 $[M]^+$. $[\alpha]_D$ = +21.1° (*c* = 1.07, $CHCl_3$).

Characterization data for compounds in Table 1.

2-iodododec-1-en-3-ol (Table 1, **3a**):


Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 0.88 (t, *J* = 6.4, 3H), 1.26 (br. s, 14H), 1.56 (br. s, 2H), 1.98 (d, *J* = 5.2, 1H), 3.58 (q, *J* = 6.0, 1H), 5.87 (s, 1H), 6.35 (s, 1H).. ^{13}C NMR ($CDCl_3$) = 14.3, 22.9, 25.3, 29.5(x2), 29.7, 32.1, 36.6, 78.2, 119.3, 125.6. EI-MS (m/z): 197 $[M - C_8H_{17}]^+$.

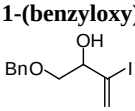
(E)-1-iodododec-1-en-3-ol (Table 1, **2a**):


Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 0.89 (t, *J* = 7.2, 3H), 1.27 (br. s, 14H), 1.56 (br. s, 2H), 1.66 (d, *J* = 4.0, 1H), 4.10 (quin, *J* = 5.2, 1H), 6.35 (d, *J* = 14.0, 1H), 6.58 (dd, *J* = 14.4, 6.0, 1H).

General procedure for hydrozirconation/I_2 trapping of propargylic alcohols (Table 2).
Methyl lithium (0.32 mL, 1.6M, 0.50mmol) was added to a solution of propargylic alcohol (0.50 mmol) in THF (1.5 mL) at -78 °C. After 20 min, the solution was warmed up to 23 °C and ready for use.
During this time, $ZnCl_2$ (408 mg, 3.0 mmol) was weighed to another flask and fused under vacuum. After the flask cooled to 23 °C, $Cp_2Zr(H)Cl$ (258 mg, 1.0 mmol) and THF (1.0 mL) were added sequentially. The resulting mixture was stirred until all $Cp_2Zr(H)Cl$ dissolved (about 3 min; solid $ZnCl_2$ remained suspended). The prepared solution of alkoxide was then transferred via cannula into the mixture of $ZnCl_2$ and $Cp_2Zr(H)Cl$ in THF, followed by rinsing with THF (0.5 mL). The result clear solution was stirred for 2h and gave a mixture with some gray precipitate. Anhydrous CH_3CN (0.26 mL, 5.0 mmol) was then added. After 10 min, the reaction was cooled to -78 °C and a solution of I_2 (254 mg, 1.0 mmol) in 1.5 mL of THF was added dropwise. After 1h at this temperature, an aqueous solution of $Na_2S_2O_3$ in saturated aqueous $NaHCO_3$ solution was added to quench the excess I_2. After dilution with ether, the reaction mixture was separated and the aqueous layer was extracted with ether. The combined organic phases were dried over $MgSO_4$, concentrated and purified by flash chromatography on silica gel.

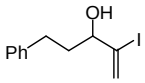
Note: It is important to keep the concentration of substrate at least 0.2M. Otherwise, the reaction is much slower, which will give a significant amount of allene.

Characterization data for synthetic new compounds and reaction details (Table 2).

1-(benzyloxy)-3-iodobut-3-en-2-ol (Table 2, entry 1):


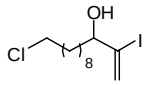
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 2.87 (d, *J* = 4.5, 1H), 3.55 (dd, *J* = 9.6, 6.9, 1H), 3.67 (dd, *J* = 9.9, 6.9, 1H), 4.10 (m, 1H), 4.60 (s, 2H), 5.98 (s, 1H), 6.52 (s, 1H), 7.32-7.39 (m, 5H). ^{13}C NMR ($CDCl_3$) δ = 73.0, 73.7, 76.4, 110.9, 127.2, 128.0, 128.1, 128.7, 137.7. EI-MS (m/z): 304 $[M]^+$.

2-iodo-5-phenylpent-1-en-3-ol (Table 2, entry 2):



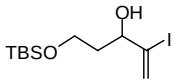
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.90-1.96 (m, 2H), 2.09 (d, *J* = 5.6, 1H), 2.68 (t, *J* = 8.0, 2H), 3.64 (q, *J* = 5.6, 1H), 5.92 (d, *J* = 1.2, 1H), 6.38 (s, 1H), 7.20-7.33 (m, 5H). ^{13}C NMR ($CDCl_3$) = 31.4, 38.0, 77.3, 118.6, 126.1, 126.2, 128.7, 141.4. EI-MS (m/z): 270 $[M\text{-}H_2O]^+$.

12-chloro-2-iodododec-1-en-3-ol (Table 2, entry 3):



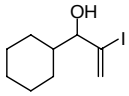
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.29 (br. s, 10H), 1.41 (t, *J* = 7.2, 2H), 1.55 (t, *J* = 7.2, 2H), 1.76 (dt, *J* = 8.5, 4.2, 2H), 2.00 (t, *J* = 5.2, 1H), 3.52 (t, *J* = 6.8, 2H), 3.58 (q, *J* = 6.0, 1H), 5.86 (d, *J* = 1.6, 1H), 6.35 (t, *J* = 0.8, 1H). ^{13}C NMR ($CDCl_3$) δ = 25.2, 27.0, 29.0, 29.4, 29.5 (x2), 32.8, 36.5, 45.4, 78.2, 119.2, 125.6. EI-MS (m/z): 217 $[M\text{-}I]^+$.

5-(tert-butyldimethylsilyloxy)-2-iodopent-1-en-3-ol (Table 2, entry 4):



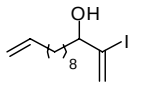
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 0.08 (s, 6H), 0.09 (s, 9H), 1.88-1.92 (m, 2H), 3.79 (dt, *J* = 10.8, 5.2, 1H), 3.85-3.90 (m, 2H), 4.13, (q, *J* = 4.8, 1H), 5.90 (s, 1H), 6.48 (s, 1H). ^{13}C NMR ($CDCl_3$) δ = -5.4, -5.3, 18.3, 26.0, 37.1, 61.2, 77.9, 116.0, 125.3. EI-MS (m/z): 285 $[M\text{-}^t\text{Bu}]^+$.

1-cyclohexyl-2-iodoprop-2-en-1-ol (Table 2, entry 5):



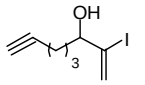
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 0.78-0.92 (m, 1H), 0.97-1.31 (m, 4H), 1.41-1.57 (m, 2H), 1.74-1.80 (m, 3H), 1.92 (d, *J* = 5.7, 1H), 1.96-2.03 (m, 1H), 3.14 (dd, *J* = 7.2, 5.7, 1H), 5.90 (d, *J* = 1.5, 1H), 6.32 (q, *J* = 1.5, 1H). ^{13}C NMR ($CDCl_3$) δ = 25.9, 26.0, 26.5, 28.1, 29.4, 42.3, 82.5, 118.5, 126.5. EI-MS (m/z): 266 $[M]^+$.

2-iodotrideca-1, 12-dien-3-ol (Table 2, entry 6):



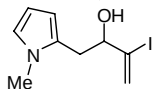
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.28-1.39 (m, 12H), 1.54-1.59 (m, 2H), 2.01-2.06 (m, 3H), 3.58 (q, *J* = 6.0, 1H), 4.93 (ddt, *J* = 10.4, 2.4, 1.2, 1H), 4.99 (dq, *J* = 17.2, 1.6, 1H), 5.81 (ddt, *J* = 17.2, 10.4, 6.8, 1H), 5.86 (d, *J* = 1.6, 1H), 6.35 (d, *J* = 1.2, 1H). ^{13}C NMR ($CDCl_3$) δ = 25.2, 29.1, 29.3, 29.5 (x2), 29.6, 34.0, 36.6, 78.2, 114.3, 119.3, 125.6, 139.4. EI-MS (m/z): 177 $[M\text{-}I\text{-}H_2O]^+$.

2-iodooct-1-en-7-yn-3-ol (Table 2, entry 7):



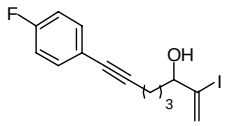
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.53-1.77 (m, 4H), 1.98 (t, *J* = 2.7, 1H), 2.05 (d, *J* = 4.8, 1H), 2.23 (dt, *J* = 2.4, 6.9, 2H), 3.66 (q, *J* = 6.0, 1H), 5.88 (d, *J* = 1.8, 1H), 6.38 (d, *J* = 1.8, 1H). ^{13}C NMR ($CDCl_3$) δ = 18.4, 24.2, 35.5, 69.0, 77.7, 84.1, 118.5, 125.9. EI-MS (m/z): 123 $[M\text{-}I]^+$.

3-iodo-1-(1-methyl-1H-pyrrol-2-yl)but-3-en-2-ol (Table 2, entry 8):



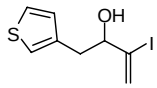
Red oil, ^{1}H NMR ($CDCl_3$) δ = 2.34 (d, *J* = 4.5, 1H), 2.82 (dd, *J* = 15.5, 8.0, 1H), 3.00 (dd, *J* = 15.0, 4.5, 1H), 3.62 (s, 3H), 3.94 (dt, *J* = 9.0, 4.5, 1H), 5.91 (d, *J* = 2.0, 1H), 6.05 (t, *J* = 1.5, 1H), 6.10 (t, *J* = 3.0, 1H), 6.40 (t, *J* = 1.3, 1H), 6.60 (t, *J* = 4.0, 1H). ^{13}C NMR ($CDCl_3$) δ = 33.9. 34.3, 77.1, 107.2, 108.3, 116.0, 122.6, 126.0, 127.7. EI-MS (m/z): 277 $[M]^+$.

8-(4-fluorophenyl)-2-iodooct-1-en-7-yn-3-ol (Table 2, entry 9):



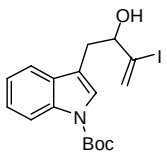
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.61-1.67 (m, 2H), 1.72-1.78 (m, 2H), 2.08 (d, *J* = 5.1, 1H), 2.44 (t, *J* = 6.9, 2H), 3.69 (q, *J* = 6.0, 1H), 5.90 (d, *J* = 1.5, 1H), 6.39 (m, 1H), 6.94-7.02 (m, 2H), 7.34-7.41 (m, 2H). ^{13}C NMR ($CDCl_3$) δ = 19.3, 24.4, 35.6, 77.6, 80.3, 89.3 (d, *J* = 5.1), 115.6 (d, *J* = 87.3), 118.6, 120.0 (d, *J* = 14.4), 125.9, 133.5 (d, *J* = 31.5), 162.2 (d, *J* = 988). EI-MS (m/z): 315 $[M\text{-}1]^+$.

3-iodo-1-(thiophen-3-yl)but-3-en-2-ol (Table 2, entry 10):



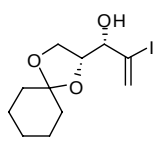
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 2.22 (d, *J* = 5.2, 1H), 2.92 (dd, J = 6.8, 14.0, 1H), 2.99 (dd, J = 5.6, 14.0, 1H), 3.92 (bq, *J* = 5.6, 1H), 5.86 (d, *J* = 2.0, 1H), 6.28 (s, 1H), 7.01 (dd, *J* = 4.8, 0.8, 1H), 7.10 (d, *J* = 2.0, 1H), 7.28 (dd, *J* = 4.8, 2.8, 1H). ^{13}C NMR ($CDCl_3$) δ = 37.5, 78.2, 116.7, 122.9, 125.9, 126.3, 128.8, 136.9. EI-MS (m/z): 2780 $[M]^+$.

3-iodo-1-(1-Boc-1H-indol-3-yl)but-3-en-2-ol (Table 2, entry 11):

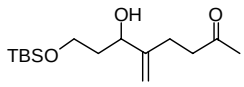


Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 1.69 (s, 9H), 2.35 (d, *J* = 4.4, 1H), 2.93 (dd, *J* = 14.4, 7.6, 1H), 3.11 (dd, *J* = 14.4, 4.8, 1H), 4.05-4.09 (m, 1H), 5.88 (d, *J* = 2.0, 1H), 6.35 (s, 1H), 7.27 (t, *J* = 7.2, 1H), 7.34 (dt, *J* = 0.8, 8.0, 1H), 7.54 (br. s, 1H), 7.61 (d, *J* = 7.6, 1H), 8.14 (dr. d, *J* = 6.8, 1H). ^{13}C NMR ($CDCl_3$) δ = 28.4, 32.9, 77.3, 83.8, 115.5, 115.8, 116.8, 119.2, 122.7, 124.5, 124.7, 126.2, 130.6, 135.6, 149.8. EI-MS (m/z): 286 $[M\text{-}I]^+$.

(S)-2-iodo-1-((R)-1,4-dioxaspiro[4.5]decan-2-yl)prop-2-en-1-ol (Table 2, entry 12):



White solid, ^{1}H NMR ($CDCl_3$) δ = 1.36-1.40 (m, 2H), 1.50-1.63 (m, 8H), 2.64 (d, *J* = 3.6, 1H), 3.92 (t, *J* = 4.8, 1H), 3.95- 4.00 (m, 2H), 4.27 (q, *J* = 6.0, 1H), 5.98 (s, 1H), 6.53 (s, 1H). ^{13}C NMR ($CDCl_3$) δ = 22.8, 23.1, 24.2, 33.7, 35.5, 63.6, 75.3, 76.0, 109.5, 109.6, 126.5. EI-MS (m/z): 324 $[M]^+$. $[\alpha]_D^{20}$ = -11.1° (*c* = 1.08, $CHCl_3$).

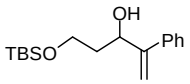


8-(tert-butyldimethylsilyloxy)-6-hydroxy-5-methyleneoctan-2-one (Table 2, entry 13):

The procedure for hydrozirconation is the same as described in general procedure. After hydrozirconation was

completed, the reaction was cooled to -78 °C and a solution of CuCN·2LiCl (0.50 mmol) in 1.0 mL THF was added to give a yellow-green mixture. After 20 min, HMPA (0.43 mL, 2.50 mmol) and a THF (2.0 mL) solution containing methylvinylketone (0.10 mL, 1.25 mmol) and trimethylsilyl chloride (0.32 mL, 2.5 mmol) were added sequentially. The reaction was stirred at -30 °C for 2.5h and then quenched with aqueous NH_4Cl. The resulting mixture was diluted with ether and separated. The aqueous layer was extracted with ether. The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was dissolved in MeOH and K_2CO_3 was added to remove TMS group selectively. After the reaction was complete (monitored by TLC), water was added and the mixture was extracted with ether. The combined organic phases were dried over $MgSO_4$, concentrated and purified by flash chromatography on silica gel to give 98 mg of product as colorless oil (68% yield). ^{1}H NMR ($CDCl_3$) δ = 0.06 (s, 3H), 0.07 (s, 3H), 0.89 (s, 9H), 1.73-1.81 (m, 2H), 2.15 (s, 3H), 2.22 (dt, *J* = 15.6, 7.6, 1H), 2.35 (dt, *J* = 15.6, 7.2, 1H), 2.58-2.72 (m, 2H), 3.63 (br. s, 1H), 3.75-3.81 (m, 1H), 3.86 (dt, *J* =10.4, 5.2, 1H), 4.27 (m, 1H), 4.79 (d, *J* = 0.8, 1H), 5.10 (s, 1H). ^{13}C NMR ($CDCl_3$) = -5.4, 18.3, 25.6, 26.1, 30.2, 37.3, 42.4, 62.5, 75.1, 109.7, 150.2, 208.7. EI-MS (m/z): 253 $[M\text{-}Me\text{-}H_2O]^+$.

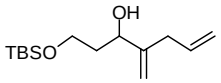
5-(tert-butyldimethylsilyloxy)-2-phenylpent-1-en-3-ol (Table 2, entry 14):



The procedure for hydrozirconation is the same as described in the general procedure. After hydrozirconation CH_3CN (0.1mL, 2.0 mmol) and phenyl iodide (0.17 mL, 1.5 mmol) were added. After 10 min, $Pd(PPh_3)_4$ (58 mg, 0.050 mmol) in THF (1 mL) was added and the reaction was stirred overnight. The reaction was quenched with aqueous NH_4Cl and extracted with ether. The combined organic phases were dried over $MgSO_4$, concentrated and purified by flash chromatography on silica gel to give 105 mg of product as colorless oil (72% yield)

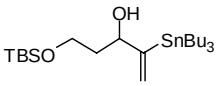
Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 0.09 (s, 6H), 0.93 (s, 9H), 1.57 (d, *J* = 2.0, 1H), 1.65 (dtd, *J* = 14.8, 7.6, 3.6, 1H), 1.85 (dddd, *J* = 14.4, 6.8, 3.8, 2.8, 1H), 3.76 (dq, *J* = 10.0, 3.6, 1H), 3.85 (d, *J* = 3.6, 1H), 3.86 (dq, *J* = 10.4, 3.6, 1H), 4.89-4.93 (m, 1H), 5.36 (s, 1H), 5.49 (s, 1H), 7.28-7.39 (m, 5H). ^{13}C NMR ($CDCl_3$) δ = -5.4, -5.3, 18.3, 26.0, 37.1, 62.3, 73.4, 122.7, 126.9, 127.7, 128.5, 140.4, 151.2. EI-MS (m/z): 235 $[M\text{-}^t\text{Bu}]^+$.

1-(tert-butyldimethylsilyloxy)-4-methylenehept-6-en-3-ol (Table 2, entry 15):



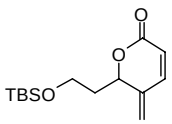
The procedure for hydrozirconation is the same as described in general procedure. After hydrozirconation was completed, the reaction was cooled to -78°C and a solution of CuCN·2LiCl (0.50 mmol) in 1.0 mL THF was added to give a yellow-green mixture. After 20 min, allyl bromide (0.13 mL, 1.50 mmol) was added. The reaction was warmed up to -25°C for 3h and then quenched with aqueous NH_4Cl. The resulting mixture was diluted with ether and separated. The aqueous layer was extracted with ether. The combined organic phases were dried over $MgSO_4$, concentrated and purified by flash chromatography on silica gel to give 90 mg of product as colorless oil (70% yield). Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 0.08 (s, 6H), 0.90 (s, 9H), 1.71-1.84 (m, 2H), 2.74 (dd, *J* = 16.0, 7.2, 1H), 2.85 (dd, *J* = 16.0, 6.8, 1H), 3.46 (s, 1H), 3.76-3.82 (m, 1H), 3.85-3.90 (m, 1H), 4.30 (d, *J* = 7.6, 1H), 4.89 (s, 1H), 5.05 (s, 1H), 5.08 (d, *J* = 9.6, 1H), 5.14 (s, 1H), 5.83 (ddt, *J* = 10.0, 16.8, 6.8, 1H). ^{13}C NMR ($CDCl_3$) δ = -5.4(x2), 18.3, 26.0, 36.8, 37.1, 62.3, 74.5, 110.7, 116.5, 136.5, 149.8. EI-MS (m/z): 215 $[M\text{-}C_3H_5]^+$.

5-(tert-butyldimethylsilyloxy)-2-(tributylstannyl) pent-1-en-3-ol (Table 2, entry 16):



The procedure for hydrozirconation is the same as described in general procedure. After hydrozirconation was completed, Bu_3SnCl (0.49 mL, 1.50 mmol) was added to give a red solution. The reaction was stirred overnight and quenched with aqueous NH_4Cl. The resulting mixture was extracted with ether. The combined organic phases were dried over $MgSO_4$ and concentrated. The crude product was dissolved in 20 mL ether and triethylamine (5.0 mL) was added. After stirring for 30 min, the mixture was loaded on a short column and flashed with ether. The solvent was evaporated and the Bu_3SnCl-free crude product was purified by flash chromatography on silica gel to give 167 mg of product as colorless oil (66% yield). Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 0.08 (s, 6H), 0.88-0.95 (m, 25H), 1.27-1.37 (m, 6H), 1.46-1.54 (m, 6H), 1.55-1.78 (m, 2H), 3.40 (d, *J* = 2.4, 1H), 3.81-3.88 (m, 2H) 4.44 (m, $^3J_{Sn\text{-}H}$ = 42, 1H), 5.21 (t, *J* = 1.6, $^3J_{Sn\text{-}H}$ = 64, 1H), 5.82 (t, *J* = 1.6, $^3J_{Sn\text{-}H}$ = 132). ^{13}C NMR ($CDCl_3$) = -5.31, 10.4, 13.9, 18.3, 26.1, 26.4, 29.3, 29.5, 62.5, 78.5, 123.1, 159.7. EI-MS (m/z): 449 $[M\text{-}Bu]^+$.

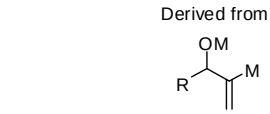
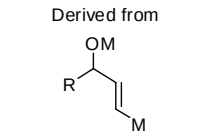
6-(2-(tert-butyldimethylsilyloxy)ethyl)-5-methylene-5,6-dihydro-2H-pyran-2-one (Table 2, entry 17):



The procedure for hydrozirconation is the same as described in general procedure. When starting material disappeared, (Z)-ethyl 3-iodoacrylate (0.19 mL, 1.5 mmol) was added. After 10 min, $Pd(PPh_3)_4$ (58 mg, 0.050 mmol) in THF (1 mL) was added and the reaction was stirred overnight. The reaction was quenched with aqueous NH_4Cl and extracted with ether. The combined organic phases were dried over $MgSO_4$, concentrated and purified by flash chromatography on silica gel to give 85 mg of product as colorless oil (63% yield).Colorless oil, ^{1}H NMR ($CDCl_3$) δ = 0.07 (s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.93 (ddt, *J* = 13.2, 8.0, 5.6, 1H), 2.11 (ddt, *J* = 14.0, 8.8, 4.8, 1H), 3.73 (dt, *J* = 10.4, 5.2, 1H), 3.85 (ddd, *J* = 10.4, 8.0, 4.8, 1H), 5.26 (dd, *J* = 8.8, 4.8, 1H), 5.36 (s, 1H), 5.41 (s, 1H), 5.94 (dd, *J* = 9.6, 0.8, 1H), 7.00 (d, *J* = 9.6, 1H). ^{13}C NMR ($CDCl_3$) δ = -5.2(x2), 18.4, 26.1, 39.0, 58.3, 119.2, 119.4, 138.8, 143.1, 163.4. EI-MS (m/z): 253 $[M\text{-}Me]^+$.

Kinetic and Thermodynamic effects of $ZnCl_2$ (Table 3).

Hydrozirconations were performed as described in the general procedure, except using the amounts of $Cp_2ZrH(Cl)$ and $ZnCl_2$ indicated. For the experiment described in entry 5, a solution of $ZnCl_2$ was added after TLC analysis indicated that hydrozirconation was complete. Product yields were determined by ^1H NMR.

	$Cp_2ZrH(Cl)$ (equiv.)	$ZnCl_2$ (equiv.)	Derived from  **I**	**II**	**III**	**IV**	Derived from  **V**		Origin Uncertain 	regioisomeric ratio (**I**+**II**+**III**+**IV** : **V**)
1	0.5	0	24%	--	--	--	4%	--	--	6:1
2	2.0	0	42%	--	--	--	42%	--	6%	1:1
3	0.5	6	6%	--	--	--	--	--	--	>10:1
4	2.0	6	73%	7%	--	--	--	--	--	>20:1
5	2.0	6 after H-Zr	32%	5%	2%	5%	12%	13%	11%	1-2:1

Product **II** arises from elimination from the branched organometallic. Products **III** and **IV** result from hydrozirconation of **II**.

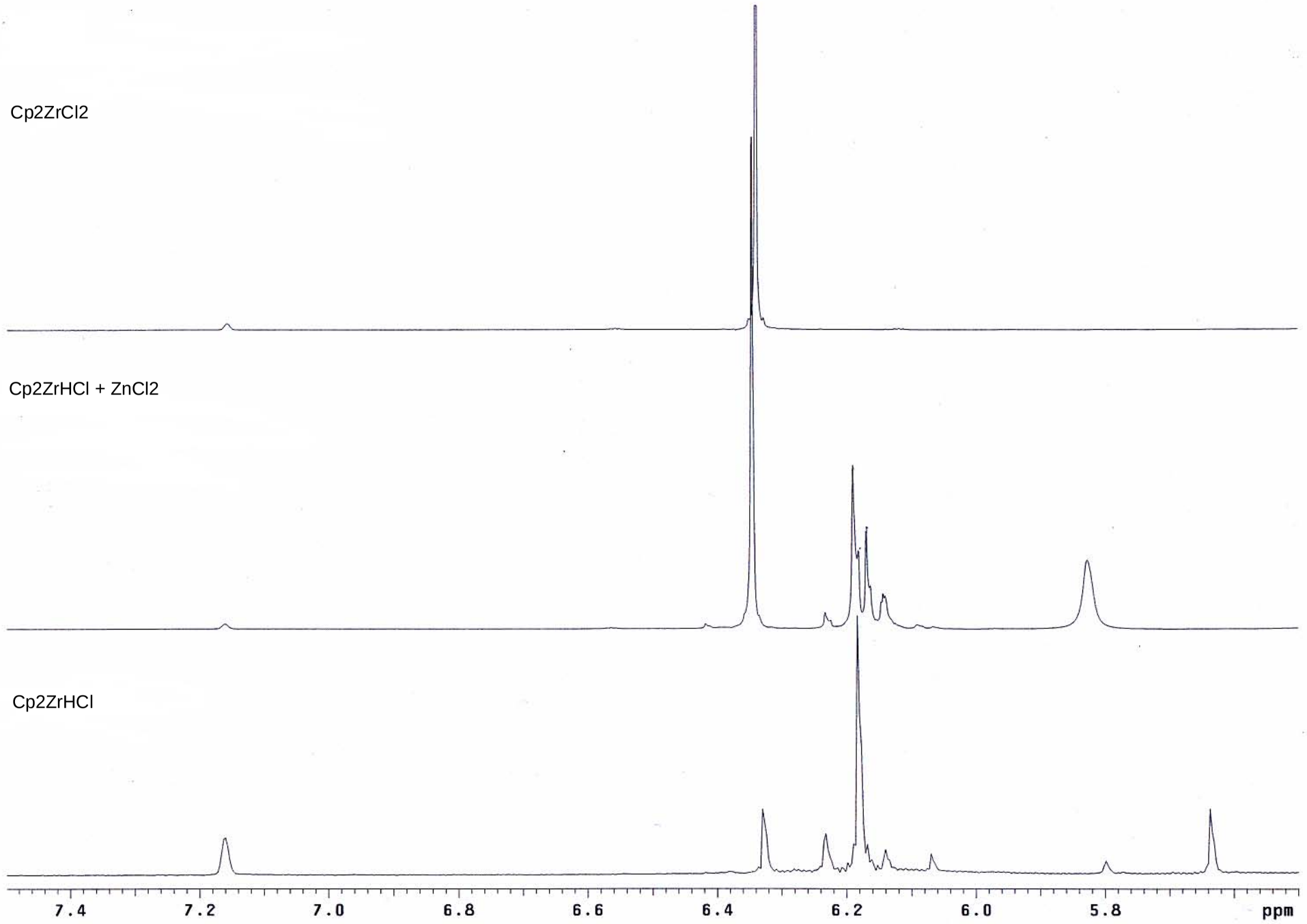


Figure SI1. 1H NMR spectra of zirconium complexes, downfield region. Spectra were recorded unlocked in THF (ref 9). The resonance at 7.16 is benzene, to which all samples were referenced.

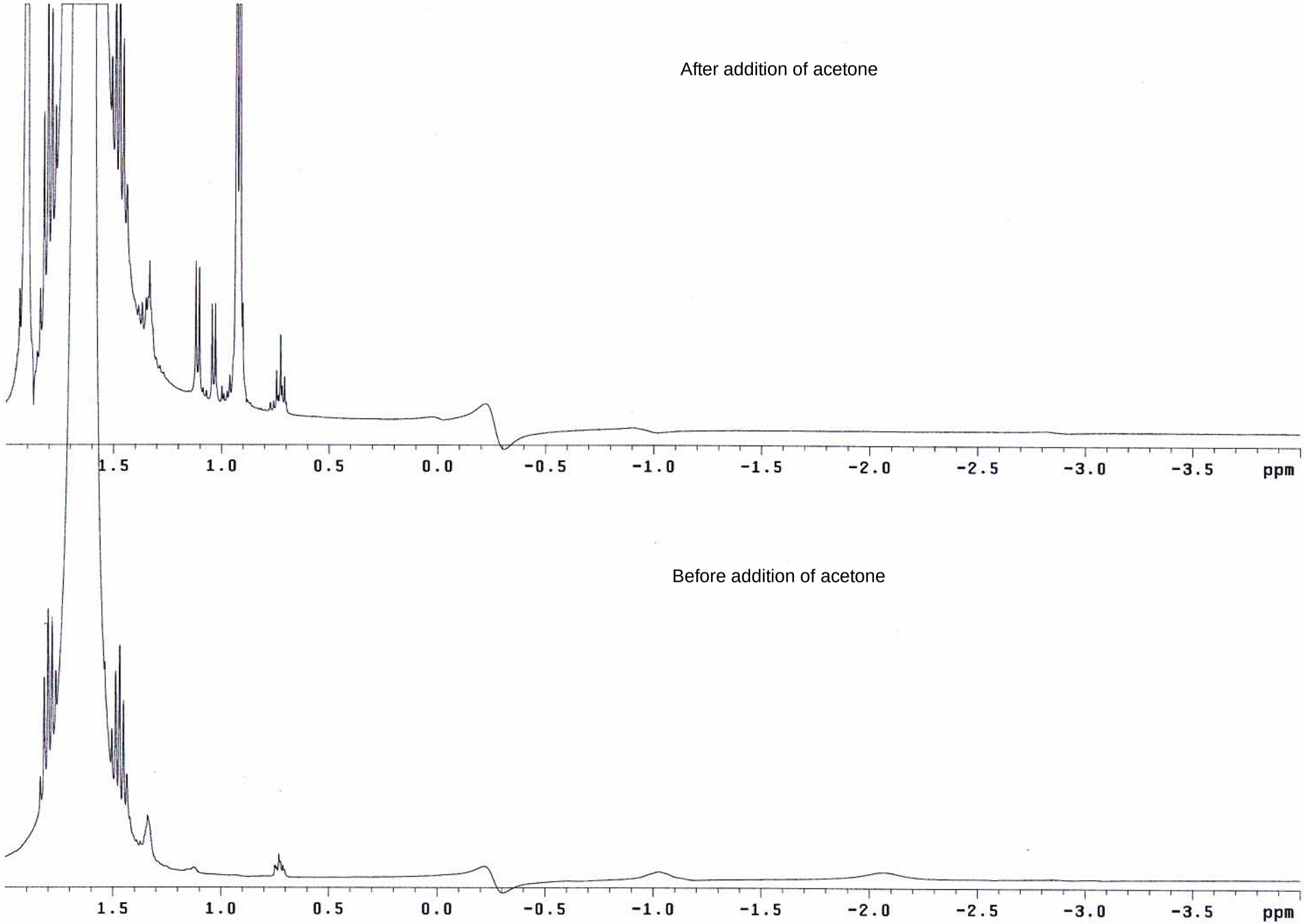
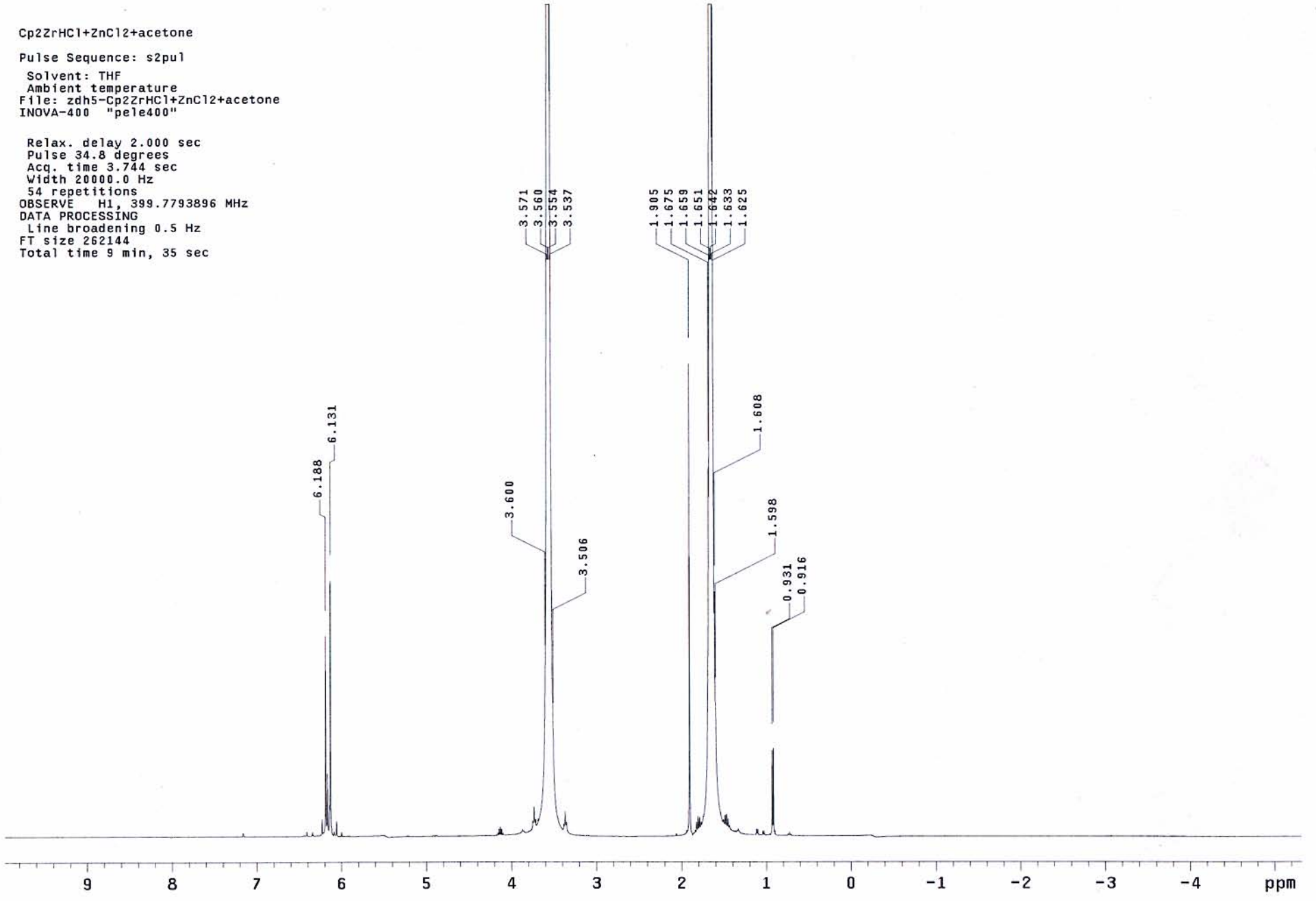


Figure SI2. Hydride region of 1H NMR before and after addition of acetone. Spectra were recorded unlocked in THF. Resonances at -1.05 and -2.1 are assigned as metal hydrides.

Cp2ZrHCl + ZnCl2


Cp2ZrHCl+ZnCl2+acetone
Pulse Sequence: s2pul
Solvent: THF
Ambient temperature
File: zdh5-Cp2ZrHCl+ZnCl2+acetone
INOVA-400 "pele400"
Relax. delay 2.000 sec
Pulse 34.8 degrees
Acq. time 3.744 sec
Width 20000.0 Hz
54 repetitions
OBSERVE H1, 399.7793896 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 9 min, 35 sec
6.188
6.131
3.600
3.571
3.560
3.554
3.537
3.506
1.905
1.675
1.659
1.651
1.642
1.633
1.625
1.608
1.598
0.931
0.916
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
ppm

References:

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