Supporting Information

Cross Silyl Benzoin Additions Catalyzed by Lanthanum Tricyanide

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General Procedure (A) for the preparation of LaCN₃.¹ A flame-dried 25 mL round-bottom flask with a magnetic stir bar was charged with 0.04 mmol of LaCl₃ and 3 mL THF in a dry box. The flask was removed and cooled to -78 °C while maintaining an N₂ environment. After 15 min, *n*-butyllithium (1.6 M in hexanes, 0.12 mmol, 3.0 equiv) was added *via* syringe. This was stirred for 15 min at the same temperature, then warmed to 0 °C. After stirring for 30 min, 0.12 mmol of trimethylsilyl cyanide (3.0 equiv) was added and stirred for 30 min at the same temperature then warmed over 30 min to room temperature.

General Procedure (B) for the reaction of acylsilanes with aldehydes. To a suspension of La(CN)₃ prepared according to General Procedure A was added at 23 °C, a solution of acylsilane (0.40 mmol, 1.0 equiv) and aldehyde (0.44 mmol, 1.1 equiv) in 8 mL of THF *via* cannula. Upon completion of the reaction (TLC analysis), 5 mL of 1 M

HCl was added at 23 °C to quench the reaction and remove the silyl protecting group. After 30 min, 10 mL of Et₂O was added and the organic layer was washed twice with 10 mL of H₂O. The aqueous layer was extracted with three 20 mL portions of Et₂O. The organic extracts were dried (MgSO₄), filtered, and the solvent was removed with a rotary evaporator. The product was purified by flash chromatography, eluting with the indicated solvent system to provide the pure α -hydroxy ketone.

2-(4-Chlorophenyl)-2-hydroxy-1-phenyl-ethanone (6a). The title compound was prepared according to General Procedure **B** using 80 mg (0.34 mmol) of acylsilane,^{2,3} 52 mg (0.37 mmol) of 4-chlorobenzaldehyde, 0.034 mmol of La(CN)₃, and 11 mL THF. After 5 min at 23 °C, the reaction was quenched and the product was purified by flash chromatography with 20% EtOAc/hexanes to afford 62.0 mg (75%) of the product as a white solid. Spectral data corresponds to that previously reported.⁴ Analytical data for the title compound: ¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.25-7.29 (m, 4H), 5.92 (s, 1H), 4.57 (b s, 1H).

2-(4-Chlorophenyl)-2-hydroxy-1-phenyl-ethanone (6a). The title compound was prepared according to General Procedure **B** using 60 mg (0.34 mmol) of acylsilane, 52 mg (0.37 mmol) of 4-chlorobenzaldehyde, 0.034 mmol of La(CN)₃, and 11 mL THF. After 5 min at 23 °C, the reaction was quenched and the product was purified by flash chromatography with 20% EtOAc/hexanes to afford 71.9 mg (87%) of the product as a white solid. Spectral data corresponds to that previously reported.⁴ Analytical data for the title compound: ¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.29-7.25 (m, 4H), 5.92 (s, 1H), 4.57 (br s, 1H).

2-Hydroxy-2-(4-methoxyphenyl)-1-phenyl-ethanone (6b). The title compound was prepared according to General Procedure **B** using 70 mg (0.39 mmol) of acylsilane, 59 mg (0.43 mmol) of 4-methoxybenzaldehyde, 0.039 mmol of $\text{La}(\text{CN})_3$, and 11 mL THF. After 5 min at 23 °C, the reaction was quenched and the product was purified by flash chromatography with 20% EtOAc/hexanes to afford 76.8 mg (81%) of the product as a white solid. Spectral data corresponds to that previously reported.⁴ Analytical data for the title compound: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.90 (d, $J = 7.5$ Hz, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 2H), 7.25 (d, $J = 8.7$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 5.91 (d, $J = 5.7$ Hz, 1 H), 4.51 (d, $J = 6.0$, 1H), 3.74 (s, 3H).

2-(2-Furyl)-1-phenyl-2-triethylsilyloxy-ethanone (5a). The catalyst was generated according to General Procedure **A** in 3 ml THF. A solution of 80 mg (0.36 mmol) of acylsilane and 38 mg (0.40 mmol) of 2-furaldehyde in 8 mL of THF were added *via* cannula. After 5 min at 23 °C, 10 ml of Et_2O was added and the resulting solution was washed twice with 10 mL of H_2O and the aqueous layer was extracted with three 20 mL portions of Et_2O . The organic extracts were dried (MgSO_4), filtered, and the solvent was removed with a rotary evaporator. The product was purified by flash chromatography with 10% EtOAc/hexanes to afford 101 mg (88%) of the product as a clear oil. Spectral data corresponds to that previously reported.⁵ Analytical data for the title compound: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.06 (d, $J = 7.2$ Hz, 2H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.42-7.37 (m, 3H), 6.35-6.30 (m, 2H), 5.89 (s, 1H), 0.91 (t, $J = 7.8$ Hz, 9H), 0.62 (q, $J = 8.7$ Hz, 6H).

2-(2-*N*-methyl-pyrrolyl)-1-phenyl-2-triethylsilyloxy-ethanone (5b). The catalyst was generated according to General Procedure A in 3 mL THF. A solution of 70 mg (0.32 mmol) of acylsilane and 38 mg (0.35 mmol) of *N*-methyl-pyrrole-2-carbaldehyde in 8 mL THF were added *via* cannula. After 5 min at 23 °C, 10 ml Et₂O was added and the resulting solution was washed twice with 10 mL H₂O and the aqueous layer was extracted with three 20 mL portions of Et₂O. The organic extracts were dried (MgSO₄), filtered, and the solvent was removed with a rotary evaporator. The product was purified by flash chromatography with 10% EtOAc/hexanes to afford 94 mg (93%) of the product as a clear oil. Analytical data for the title compound: **IR** (thin film, cm⁻¹) 1699, 2877, 2956, 3054; **¹H NMR** (400 MHz, C₆D₆) δ 8.08-8.06 (m, 2H), 7.02-6.80 (m, 3H), 6.24-6.23 (m, 2H), 6.09 (t, *J* = 3.2 Hz, 1H), 6.06 (s, 1H), 3.29 (s, 3H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.63 (q, *J* = 8.0 Hz, 6H); **¹³C NMR** (100 MHz, C₆D₆) δ 196.6, 136.3, 133.1, 129.9, 128.8, 124.7, 111.1, 108.1, 73.6, 34.7, 7.4, 5.7; TLC (15% EtOAc/hexanes) *R_f* 0.42; **Anal.** Calcd. for C₁₉H₂₇NO₂Si: C, 69.26; H, 8.26; N, 4.25. Found: C, 69.30; H, 8.49; N, 4.34.

1-(4-Methoxyphenyl)-2-phenyl-2-triethylsilyloxy-ethanone (5c). The catalyst was generated according to General Procedure A in 3 mL THF. A solution of 90 mg (0.36 mmol) of acylsilane and 42 mg (0.40 mmol) of benzaldehyde in 8 mL of THF was added *via* cannula. After 5 min at 23 °C, 10 ml Et₂O was added and the organic layer was washed twice with 10 mL H₂O. The aqueous layer was extracted with three 20 mL portions of Et₂O. The organic extracts were dried (MgSO₄), filtered, and the solvent was removed with a rotary evaporator. The product was purified by flash chromatography with 10% EtOAc/hexanes to afford 109.2 mg (84%) of the product as a clear oil. Spectral data corresponds to that previously reported.⁵ Analytical data for the title

compound: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 (d, $J = 8.0$ Hz, 2H), 7.35-7.29 (m, 5H), 6.85 (d, $J = 8.0$ Hz, 2H), 5.81 (s, 1H), 3.79 (s, 3H), 0.93 (t, $J = 8.0$ Hz, 9H), 0.52 (q, $J = 8.0$ Hz, 6H).

1-(4-Chlorophenyl)-2-phenyl-2-triethylsilyloxy-ethanone (5d). The catalyst was generated according to General Procedure A in 3 mL THF. A solution of 90 mg (0.34 mmol) of acylsilane and 45 mg (0.37 mmol) of benzaldehyde in 8 mL of THF were added *via* cannula. After 5 min at 23 °C, 10 mL Et_2O was added and the organic layer was washed twice with 10 mL H_2O and the aqueous layer was extracted with three 20 mL portions of Et_2O . The organic extracts were dried (MgSO_4), filtered, and the solvent was removed with a rotary evaporator. The product was purified by flash chromatography with 10% EtOAc /hexanes to afford 106 mg (83%) of the product as a clear oil. Spectral data corresponds to that previously reported.⁵ Analytical Data for the title compound: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.8$ Hz, 2H), 7.51 (d, $J = 8$ Hz, 2H), 7.35-7.29 (m, 5H), 5.71 (s, 1H), 0.89 (t, $J = 8$ Hz, 9H), 0.65-0.58 (m, 6H).

(E)-1,4-Diphenyl-2-hydroxybut-3-en-1-one (6c). The catalyst was generated according to General Procedure A in 3 mL THF. A solution of 90 mg (0.40 mmol) of acylsilane and 81 mg (0.61 mmol) of cinnamaldehyde in 8 mL THF was added *via* cannula. After 15 min at 23 °C, 10 mL Et_2O was added and the organic layer was washed twice with 10 mL H_2O . The aqueous layer was extracted with three 20 mL portions of Et_2O . The organic extracts were dried (MgSO_4), filtered, and the solvent was removed with a rotary evaporator. The product was dissolved in 10 mL EtOH , 10 mL of 1M HCl was added stirred for 20 minutes. Once deprotection was complete, 10 mL Et_2O was added and the organic layer was washed twice with 10 mL H_2O and the aqueous layer was extracted with three 20 mL portions of Et_2O . The organic extracts were dried

(MgSO₄), filtered, and the solvent was removed with a rotary evaporator. The product was purified by flash chromatography with 20% EtOAc/hexanes to afford 60 mg (50%) of the product as a clear oil. Analytical Data for the title compound: **IR** (thin film, cm⁻¹) 1680, 3026, 3078, 3379, 3423; **¹H NMR** (400 MHz, CDCl₃) δ 8.03-8.01 (m, 2H), 7.61 (dt, *J* = 1.6, 7.2 Hz, 1H) 7.52-7.48 (m, 2H), 7.33-7.20 (m, 5H), 6.87 (dd, *J* = 1.2, 15.6 Hz, 1H), 6.22 (dd, *J* = 6.4, 15.6 Hz, 1H), 5.68 (dt, *J* = 1.6, 6.4 Hz, 1H), 4.17 (d, *J* = 6.0, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 199.0, 136.4, 134.5, 134.0, 133.8, 129.3, 129.2, 128.9, 128.5, 127.0, 126.4, 74.5; TLC (20% EtOAc/hexanes) *R_f* 0.23. Attempts to obtain acceptable combustion analysis were not successful. See Appendix for ¹H NMR spectrum.

1,4-Diphenyl-2-hydroxy-butan-1-one (6d). The title compound was prepared according to General Procedure **B** using 75 mg (0.42 mmol) of acylsilane, 62 mg (0.46 mmol) of hydrocinnamaldehyde, 0.042 mmol of La(CN)₃, and 11 mL of THF. After 15 min at 23 °C, the reaction was quenched and the product was purified by flash chromatography with 15% EtOAc/hexanes to afford 64.5 mg (64%) of the product as a clear oil. Analytical data for the title compound: **IR** (thin film, cm⁻¹) 1682, 2860, 2923, 3483; **¹H NMR** (400 MHz, CDCl₃) δ 7.78-7.75 (m, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.29-7.16 (m, 5H), 5.03 (ddd, *J* = 2.8, 6.4, 8.8 Hz, 1H), 3.79 (d, *J* = 6.4, 1H), 2.75 (m, 2H) 2.16 (dddd, *J* = 2.8, 8.0, 9.2, 12 Hz, 1H), 1.82 (dddd, *J* = 4.8, 8.8, 9.6, 14.4 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 202.2, 141.3, 134.2, 133.8, 129.1, 129.0, 128.8, 128.7, 126.4, 72.5, 38.0, 31.6; TLC (15% EtOAc/hexanes) *R_f* 0.17; **Anal.** Calcd. for C₁₆H₁₆O₂: C, 79.97; H, 6.71. Found: C, 79.68; H, 6.72.

1-(4-Chlorophenyl)-1-hydroxy-propan-2-one (6e). The title compound was prepared according to General Procedure **B** using 90 mg (0.77 mmol) of acylsilane, 163

mg (1.16 mmol) 4-chlorobenzaldehyde, 0.042 mmol of La(CN)₃, and 13 mL THF. After 15 min at 23 °C, the reaction was quenched and the product was purified by flash chromatography with 20% EtOAc/hexanes to afford 100 mg (70%) of the product as a clear oil. Spectral data corresponds to that previously reported.⁶ Analytical data for the title compound: ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 4.8 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 4.99 (s, 1H), 1.99 (s, 3H).

3-Hydroxy-5-phenyl-pentan-2-one (6f). The title compound was prepared according to General Procedure **B** using 90 mg (0.57 mmol) of acylsilane, 114 mg (0.85 mmol) hydrocinnamaldehyde, 0.057 mmol of La(CN)₃, and 13 mL THF. After 15 min at 23 °C, the reaction was quenched and the product was purified by flash chromatography with 20% EtOAc/hexanes to afford 80 mg (48%) of the product as a clear oil. Spectral data corresponds to that previously reported.⁷ Analytical data for the title compound: ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.18 (m, 5H), 4.19-4.14 (m, 1H), 3.57 (d, *J* = 4.8 Hz, 1H), 2.85-2.68 (m, 2H), 2.20-2.09 (m, 1H), 2.16 (s, 3H), 1.83 (dddd, *J* = 4.8, 8.3, 9.1, 13.7 Hz, 1H).

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Appendix. ¹H NMR spectrum of 6c

Current Data Parameters
NAME c6b2_020
PROCNO 1
F2 - Acquisition Parameters
Date_ 2016-05-16
Time 14:59
PROBHD 5 mm TWD 51-01
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 4237.268 Hz
FIDRES 0.119312 Hz
AQ 3.866779 sec
RG 2048
DM 118.000 usec
DE 19.000 usec
TE 293.0 K
HPL 1 dB
NUC1 13C
P1 11.00 usec
SFO1 300.131900 MHz
Nucleus 13C
F2 - Processing parameters
SI 32768
SF 300.130041 MHz
WDW EM
SS 0
LB 0.30 Hz
GB 0
PC 1.00