

Supporting Information

Cobalt-Catalyzed Silylcarbonylation of Unactivated Secondary Alkyl Tosylates at Low Pressure

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Table of Contents

General Methods and Materials	S1
List of Abbreviations	S2
Cobalt Catalyst Synthesis	S3
Substrate Synthesis	S3-S11
Cobalt Catalyzed Silyl Carbonylation Reactions	S12-S16
Post-Reactions of Silyl Enol Ethers	S17-S18
Mechanistic Studies	S19-20
References	S21
¹ H and ¹³ C NMR Spectra	S22-S54

General Methods and Materials

All reactions were carried in pre-dried glassware under argon or nitrogen atmosphere with dry solvents unless otherwise specified. Carbon monoxide, Research Purity 99.999% (part number G2119118), was purchased from Matheson Tri-Gas. Solvents were dried by passage through a column of neutral alumina under nitrogen. $\text{Co}_2(\text{CO})_8$ was purchased from Strem Chemicals, Inc. Other chemicals were obtained from commercial sources and were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker ADVANCE III 600 CryoProbe, (^1H NMR at 600 MHz and ^{13}C NMR at 151 MHz) or a Varian Inova 600 MHz spectrometer (^1H NMR at 600 MHz) with solvent resonance as the internal standard (^1H NMR: CDCl_3 at 7.26 ppm, ^{13}C NMR: CDCl_3 at 77.0 ppm). ^1H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet), coupling constants (Hz), and integration. Mass spectra were obtained using a Thermo LTQ-FT-ICR mass spectrometer or the Thermo GC Exactive with mass spectrometer. The Thermo LTQ-FT-ICR is equipped with electrospray ionization (ESI) or atmospheric pressure photoionization (APPI) and external calibration. The Thermo GC Exactive is equipped with chemical ionization (CI) and external calibration. Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Thin layer chromatography (TLC) was performed on SilicaPlate 250 μm thick silica gel plated provided by Silicycle. Visualization was accomplished with short wave UV light (254 nm), aqueous basic potassium permanganate solution, or ethanolic acidic *p*-anisaldehyde solution followed by heating. Flash chromatography was performed using SilicaFlash P60 silica gel (40-63 μm) purchased from Silicycle. The sealed tubes used were purchased from Ace Glass. Pressure adapters were assembled from Swagelock parts (Figure 1 below).



Figure 1: Swagelock Air-Free System

List of Abbreviations

DCM = dichloromethane

DMF = *N,N*-dimethylformamide

THF = tetrahydrofuran

EtOAc = ethyl acetate

HMDS = hexamethyldisiloxane

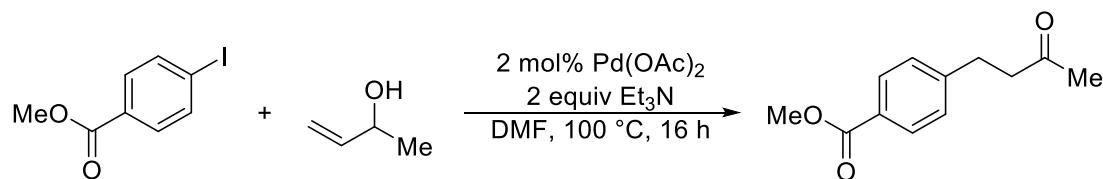
PCC = pyridinium chlorochromate

Cobalt Catalyst Synthesis

Synthesis of Potassium Tetracarbonylcobaltate, $\text{K}[\text{Co}(\text{CO})_4]$

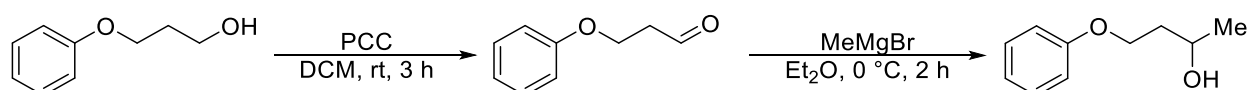
Following the method by Ellis and coworkers.¹ Under inert atmosphere, to a suspension of KOH (220 mmol, 12 g) in THF (75 mL) was added $\text{Co}_2(\text{CO})_8$ (15 mmol, 5 g) portionwise. The resulting solution was stirred overnight. Then, the reaction was filtered and the filtrate was concentrated under vacuum to yield an off white solid (4.7 g, 77% yield).

Substrate Synthesis



Methyl 4-(3-oxobutyl)benzoate

A Heck coupling was employed to synthesize methyl 4-(3-oxobutyl)benzoate, following a method published by Sargent and Alexanian.² To a solution of methyl 4-iodobenzoate (16 mmol, 4.2 g) in DMF [0.15 M] was added 3-buten-2-ol (1.2 equiv., 19 mmol, 1.4 g), Et_3N (1.3 equiv., 21 mmol, 2.9 mL), and $\text{Pd}(\text{OAc})_2$ (2 mol%, 0.3 mmol, 72 mg). The resulting mixture was stirred overnight at 100 °C. Then, the reaction was cooled to room temperature, diluted with EtOAc, washed twice with water and once with brine. The organic layer was then dried over MgSO_4 , filtered, and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography (4:1 hexanes/ethyl acetate) to yield a yellow oil (2.1 g, 63% yield). Spectroscopic and physical data are reported.³



3-Phenoxypropanal (S1)

3-phenoxypropan-1-ol (1 equiv., 13 mmol, 2 g) was added to DCM (40 mL). To this solution, pyridinium chlorochromate (2 equiv., 26 mmol, 5.7 g) in DCM (40 mL), was added. The resulting solution was stirred at room temperature for 3 hours. Then, the solution was diluted with pentane (130 mL) and filtered through celite. The resulting filtrate was concentrated under vacuum and purified by flash chromatography (6:1 hexanes/ethyl acetate) to yield a yellow oil (1.6 g, 79%).

¹H NMR (600 MHz, CDCl_3) δ 9.90 (dt, J = 3.2, 1.6 Hz, 1H), 7.35–7.29 (m, 2H), 7.03–6.97 (m, 1H), 6.98–6.90 (m, 2H), 4.34 (td, J = 6.1, 2.1 Hz, 2H), 2.93 (dt, J = 6.1, 3.3, 1.6 Hz, 2H).

¹³C NMR (151 MHz, CDCl_3) δ 200.25, 158.40, 129.54, 121.20, 114.53, 61.53, 43.26.

HRMS (CI): calculated for $\text{C}_9\text{H}_{10}\text{O}_2$ $[\text{M}]^+$ 150.068, found 150.067.

FTIR (thin film, cm^{-1}): 3041.2, 2832.9, 1723.1, 1599.7, 1496.5, 1386.6, 1292.1, 1042.3.

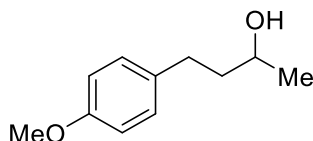
4-Phenoxybutan-2-ol

3-phenoxypropanal (1 equiv., 10 mmol, 1.5 g) was added to diethyl ether (20 mL). The resulting solution was cooled down to 0 °C in an ice/water bath. Then, methyl magnesium bromide (1.2 equiv., 12 mmol, 4 mL of a 3 M solution) was added dropwise. The resulting mixture was stirred

at 0 °C under argon for 2 hours. Then, the solution was quenched with 1 M HCl and diluted with DCM. The aqueous layer was extracted 3 times with DCM and the resulting organic layers were combined up, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting crude mixture was purified by flash chromatography (6:1 hexanes/ethyl acetate) to yield a colorless oil (1.1 g, 66%). Spectroscopic and physical data are reported.⁴

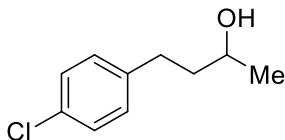
General Method A. Ketone Reduction

Ketones were reduced following a modified method by Sargent and Alexanian.² To a 0 °C ice bath cooled solution of ketone (1 equiv.) in methanol [0.15 M] was added sodium borohydride (1.1 equiv.) portionwise. The solution was then stirred for 0.5 to 1 hour at 0 °C, monitoring by TLC. After completion, the methanol was removed under vacuum and the residue was diluted with DCM, then poured into water. The aqueous layer was then extracted 3 times with DCM. The organic layers were then combined, dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting crude mixture was utilized without further purification, unless otherwise noted.



4-(4-Methoxyphenyl)butan-2-ol

4-(4-Methoxyphenyl)butan-2-one (56 mmol, 10 g) was reduced with sodium borohydride (62 mmol, 2.6 g) following General Method A. The reaction afforded 92% crude product (9.2 g). Spectroscopic and physical data are reported.⁵



4-(4-Chlorophenyl)butan-2-ol (S2)

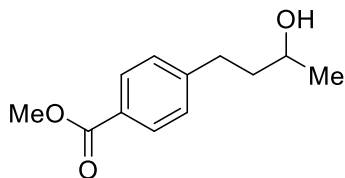
4-(4-Chlorophenyl)butan-2-one (11 mmol, 2 g) was reduced with sodium borohydride (12 mmol, 458 mg) following General Method A. The reaction afforded 93% crude product (4.7 g).

¹H NMR (600 MHz, CDCl₃) δ 7.32–7.22 (m, 2H), 7.19–7.09 (m, 2H), 3.83 (ddt, *J* = 7.4, 6.0, 4.8 Hz, 1H), 2.76 (ddd, *J* = 13.9, 9.5, 6.0 Hz, 1H), 2.67 (ddd, *J* = 13.9, 9.4, 6.9 Hz, 1H), 1.83–1.68 (m, 2H), 1.43 (td, *J* = 2.7, 1.3 Hz, 1H), 1.25 (d, *J* = 6.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 140.51, 131.50, 129.75, 128.47, 77.25, 77.04, 76.83, 67.31, 40.69, 31.46, 23.73.

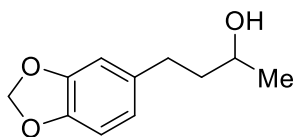
HRMS (CI): calculated for C₁₀H₁₃OCl [M]⁺ 184.065, found 184.065.

FTIR (thin film, cm⁻¹): 3368.1, 3028.7, 2966.5, 1698.0, 1491.6, 1374.0, 1127.2, 1014.4, 660.5.



Methyl 4-(3-hydroxybutyl)benzoate

Methyl 4-(3-oxobutyl)benzoate (10 mmol, 2 g) was reduced with sodium borohydride (11 mmol, 400 mg) following General Method A. The crude reaction mixture was purified by flash chromatography (3:1 hexanes/ethyl acetate) to yield a colorless oil (2.1 g, quantitative). Spectroscopic and physical data are reported.⁶



4-(3,4-Methylenedioxyphenyl)-2-butanol (S3)

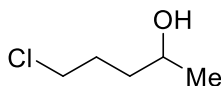
4-(3,4-Methylenedioxyphenyl)-2-butanone (10 mmol, 2 g) was reduced with sodium borohydride (11 mmol, 420 mg) following General Method A. The reaction afforded quantitative crude product.

¹H NMR (600 MHz, CDCl₃) δ 6.75 (d, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 1.6 Hz, 1H), 6.68–6.66 (m, 1H), 5.94 (s, 2H), 3.88–3.78 (m, 1H), 2.70 (ddd, *J* = 13.8, 9.4, 6.1 Hz, 1H), 2.62 (ddd, *J* = 13.8, 9.2, 6.9 Hz, 1H), 1.81–1.69 (m, 2H), 1.42 (q, *J* = 5.6, 4.2 Hz, 1H), 1.24 (d, *J* = 6.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 147.57, 145.58, 135.88, 121.06, 108.88, 108.18, 100.78, 67.40, 41.08, 31.89, 23.70.

HRMS (ESI): calculated for C₁₁H₁₄O₃Na [M+Na]⁺ 217.084, found 217.084.

FTIR (thin film, cm⁻¹): 3365.2, 2966.0, 2926.5, 1504.2, 1489.7, 1441.5, 1373.1, 1244.8, 1187.9, 1127.2, 1039.4.



5-Chloropentan-2-ol (S4)

5-Chloropentan-2-one (17 mmol, 2 g) was reduced with sodium borohydride (2 portions of 18 mmol, 691 mg) following General Method A. The reaction was stirred overnight. Crude product was purified by flash chromatography (6:1 pentane/diethyl ether) to yield a yellow oil (450 mg, 22% yield).

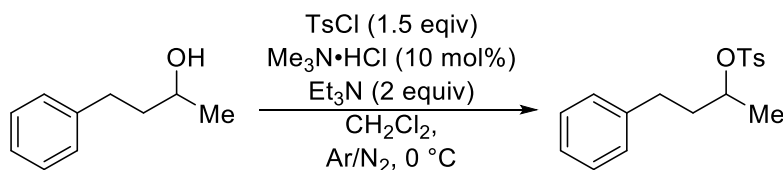
¹H NMR (600 MHz, CDCl₃) δ 3.91–3.81 (m, 1H), 3.60 (tt, *J* = 6.6, 3.7 Hz, 2H), 1.95 (ddt, *J* = 16.4, 12.3, 6.0 Hz, 1H), 1.85 (ddd, *J* = 14.0, 10.0, 6.5 Hz, 1H), 1.69–1.53 (m, 2H), 1.48 (s, 1H), 1.24 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 67.47, 45.16, 36.34, 28.93, 23.75.

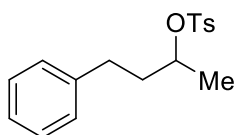
HRMS (CI): calculated for C₅H₁₀OCl [M-H]⁺ 121.041, found 121.041.

FTIR (thin film, cm⁻¹): 3366.1, 2966.0, 2873.4, 1716.3, 1540.9, 1457.0, 1314.3, 1080.9, 649.9.

General Method B. Tosylation of Secondary Alcohols



Substrates were tosylated following a modified method by Tanabe, et al.⁷ To a 0 °C ice bath cooled solution of *p*-toluene sulfonyl chloride (1.5 equiv.) and trimethylamine hydrochloride (0.1 equiv.) in DCM [0.5 M] was added triethylamine (2 equiv.) dropwise. To the resulting mixture was added a solution of alcohol (1 equiv.) in DCM. The solution was then stirred for 0.5 to 2 hours at 0 °C, monitoring by TLC. After completion, the reaction was quenched with 0.5 equiv. of *N,N*-dimethyl-1,3-propanediamine and stirred for 20 minutes, then warmed to room temperature. The reaction was mixed with water and extracted 3 times with DCM. The combined organic layers were then washed with HCl (1 M), saturated NaHCO₃, and brine, then dried over Mg₂SO₄, filtered, and concentrated. The resulting crude mixture was purified by flash chromatography.



4-Phenylbutan-2-yl 4-methylbenzenesulfonate (1)

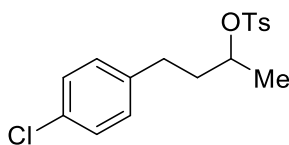
4-Phenylbutan-2-ol (133 mmol, 20 g) was tosylated with *p*-toluene sulfonyl chloride (200 mmol, 38 g) following General Method B. The crude product was isolated (10:1 hexanes/ethyl acetate) as a pure white solid (34 g, 85% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.87–7.77 (m, 2H), 7.38–7.32 (m, 2H), 7.30–7.25 (m, 2H), 7.23–7.16 (m, 1H), 7.13–7.05 (m, 2H), 4.67 (dq, *J* = 7.5, 6.3, 4.9 Hz, 1H), 2.63 (ddd, *J* = 13.9, 10.2, 5.8 Hz, 1H), 2.52 (ddd, *J* = 13.9, 10.2, 5.9 Hz, 1H), 2.48 (s, 3H), 1.96 (dddd, *J* = 14.3, 10.2, 7.4, 5.9 Hz, 1H), 1.83 (dddd, *J* = 14.2, 10.5, 5.9, 4.9 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 144.53, 140.84, 134.43, 129.79, 128.46, 128.28, 127.76, 126.06, 79.91, 38.18, 31.19, 21.68, 20.89.

HRMS (ESI): calculated for C₁₇H₂₀O₄S+Na [M+Na]⁺ 327.103, found 327.103.

FTIR (thin film, cm⁻¹): 3063.4, 2980.5, 1716.3, 1558.2, 1540.9, 1456.0, 1361.5, 1175.4, 1097.3.



4-(4-Chlorophenyl)butan-2-yl 4-methylbenzenesulfonate (3)

4-(4-Chlorophenyl)butan-2-ol (26 mmol, 4.7 g) were tosylated with *p*-toluene sulfonyl chloride (38 mmol, 7.3 g) following General Method B. The crude product was isolated (19:1 hexanes/ethyl acetate) as a yellow oil (6.7 g, 77% yield).

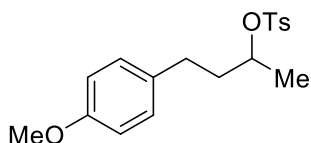
¹H NMR (600 MHz, CDCl₃) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.23 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 4.69–4.59 (m, 1H), 2.66–2.56 (m, 1H), 2.52 (ddd, *J* = 14.3,

9.8, 6.1 Hz, 1H), 2.47 (s, 3H), 1.92 (dddd, $J = 13.5, 9.9, 7.3, 5.9, 1.3$ Hz, 1H), 1.86–1.74 (m, 1H), 1.30 (dd, $J = 6.3, 1.0$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 144.66, 139.29, 134.33, 131.76, 129.83, 129.68, 128.53, 127.73, 79.56, 38.04, 30.51, 21.69, 20.83.

HRMS (ESI): calculated for $\text{C}_{17}\text{H}_{19}\text{O}_3\text{SCl}+\text{Na}$ $[\text{M}+\text{Na}]^+$ 361.064, found 361.064.

FTIR (thin film, cm^{-1}): 3031.6, 2866.7, 1492.6, 1360.5, 1188.9, 1093.4, 1015.3, 918.0, 814.8.



4-(4-Methoxyphenyl)butan-2-yl 4-methylbenzenesulfonate (5)

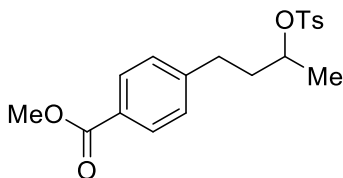
4-(4-Methoxyphenyl)butan-2-ol (51 mmol, 9 g) was tosylated with *p*-toluene sulfonyl chloride (77 mmol, 15 g) following General Method B. The crude product was isolated (6:1 hexanes/ethyl acetate) as a colorless oil (13 g, 76% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.84–7.80 (m, 2H), 7.38–7.34 (m, 2H), 7.02–6.98 (m, 2H), 6.84–6.79 (m, 2H), 4.69–4.61 (m, 1H), 3.80 (s, 3H), 2.57 (ddd, $J = 14.0, 10.1, 5.9$ Hz, 1H), 2.50–2.43 (m, 4H), 1.92 (dddd, $J = 14.2, 10.0, 7.4, 5.9$ Hz, 1H), 1.79 (dddd, $J = 14.1, 10.0, 6.0, 5.0$ Hz, 1H), 1.31 (d, $J = 6.3$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 157.88, 144.54, 134.44, 132.85, 129.80, 129.20, 127.75, 113.83, 79.95, 55.27, 38.43, 30.27, 21.68, 20.88.

HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{22}\text{O}_4\text{S}+\text{Na}$ $[\text{M}+\text{Na}]^+$ 357.113, found 357.112.

FTIR (thin film, cm^{-1}): 3031.6, 2980.5, 1612.2, 1356.7, 1245.8, 1187.9, 1096.3, 916.0, 817.7.



Methyl 4-(3-(tosyloxy)butyl)benzoate (7)

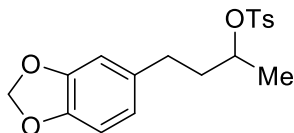
Methyl 4-(3-hydroxybutyl)benzoate (9.7 mmol, 2.0 g) was tosylated with *p*-toluene sulfonyl chloride (15 mmol, 2.8 g) following General Method B. The crude product was isolated (4:1 hexanes/ethyl acetate) as a colorless oil (2.1 g, 40% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.94 (d, $J = 8.3$ Hz, 2H), 7.81 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.3$ Hz, 2H), 4.66 (s, 1H), 3.92 (s, 3H), 2.69 (s, 1H), 2.59 (s, 1H), 2.47 (s, 3H), 1.95 (s, 1H), 1.85 (s, 1H), 1.31 (d, $J = 6.3$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 167.01, 146.33, 144.66, 134.32, 129.83, 129.80, 128.34, 128.07, 127.73, 79.52, 52.07, 37.74, 31.19, 21.68, 20.85.

HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{22}\text{O}_5+\text{Na}$ $[\text{M}+\text{Na}]^+$ 385.108, found 385.109.

FTIR (thin film, cm^{-1}): 2984.3, 2951.5, 1718.3, 1610.3, 1360.5, 1280.5, 1188.9, 1109.8, 1019.2, 896.7, 816.7.



4-(Benzo[d][1,3]dioxol-5-yl)butan-2-yl 4-methylbenzenesulfonate (9)

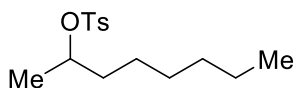
4-(3,4-Methylenedioxyphenyl)-2-butanol (5 mmol, 1 g) was tosylated with *p*-toluene sulfonyl chloride (7.5 mmol, 1.5 g) following General Method B. The crude product was isolated (6:1 hexanes/ethyl acetate) as a white solid (1.7 g, 97% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.53 (d, *J* = 12.1 Hz, 2H), 5.94 (d, *J* = 3.3 Hz, 2H), 4.64 (d, *J* = 11.6 Hz, 1H), 2.54 (s, 1H), 2.48 (s, 3H), 2.44 (s, 1H), 1.90 (s, 1H), 1.78 (s, 1H), 1.31 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 147.60, 145.76, 144.59, 144.58, 134.59, 134.42, 129.81, 127.75, 121.03, 108.72, 108.19, 100.83, 79.76, 77.28, 77.26, 77.18, 77.07, 77.04, 76.86, 76.83, 60.44, 38.41, 30.89, 21.68, 20.89, 14.23.

HRMS (ESI): calculated for C₁₈H₂₀O₅S+Na [M+Na]⁺ 371.093, found 371.092.

FTIR (thin film, cm⁻¹): 2981.4, 1505.2, 1489.7, 1358.6, 1245.8, 1188.9, 1038.5, 896.7, 812.8.



Octan-2-yl 4-methylbenzenesulfonate (11)

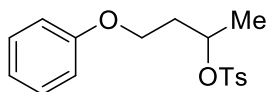
Octan-2-ol (38 mmol, 5 g) was tosylated with *p*-toluene sulfonyl chloride (57 mmol, 11 g) following General Method B. The crude product was isolated (10:1 hexanes/ethyl acetate) as a colorless oil (11 g, 98% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.87–7.75 (m, 2H), 7.40–7.30 (m, 2H), 4.66–4.54 (m, 1H), 2.46 (s, 3H), 1.61 (ddt, *J* = 14.8, 12.3, 5.1 Hz, 1H), 1.48 (ddt, *J* = 13.5, 9.6, 5.1 Hz, 1H), 1.25 (dd, *J* = 22.3, 6.6 Hz, 7H), 1.21–1.09 (m, 5H), 0.86 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 144.40, 134.53, 129.70, 127.72, 80.74, 36.49, 31.60, 28.81, 24.83, 22.50, 21.64, 20.89, 14.07.

HRMS (ESI): calculated for C₁₅H₂₄O₃S+Na [M+Na]⁺ 307.134, found 307.134.

FTIR (thin film, cm⁻¹): 2954.4, 2859.0, 1598.7, 1458.9, 1363.4, 1176.4, 1096.3, 914.1, 815.7.



4-Phenoxybutan-2-yl 4-methylbenzenesulfonate (13)

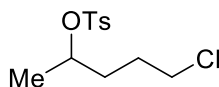
4-Phenoxybutan-2-ol (6.6 mmol, 1.1 g) was tosylated with *p*-toluene sulfonyl chloride (10 mmol, 1.7 g) following General Method B. The crude product was isolated (4:1 hexanes/ethyl acetate) as a white solid (1.6 g, 76 % yield).

¹H NMR (600 MHz, CDCl₃) δ 7.77–7.72 (m, 2H), 7.30–7.22 (m, 3H), 7.18–7.12 (m, 2H), 6.95 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.72–6.65 (m, 2H), 4.89 (dq, *J* = 8.7, 6.3, 3.8 Hz, 1H), 3.82 (dt, *J* = 9.7, 5.0 Hz, 1H), 3.66 (td, *J* = 9.1, 4.5 Hz, 1H), 2.29 (s, 3H), 2.09–1.93 (m, 2H), 1.47 (d, *J* = 6.3 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 158.35, 144.57, 133.73, 129.69, 129.31, 127.57, 120.71, 114.18, 77.27, 77.25, 77.04, 76.83, 62.81, 36.21, 21.68, 21.61.

HRMS (ESI): calculated for C₁₇H₂₀O₄S+Na [M+Na]⁺ 343.097, found 343.099.

FTIR (thin film, cm⁻¹): 2981.4, 1599.7, 1540.9, 1497.5, 1362.5, 1244.8, 1188.9, 1090.6, 1047.2.



5-Chloropentan-2-yl 4-methylbenzenesulfonate (15)

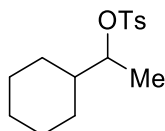
5-Chloropentan-2-ol (5 mmol, 0.62 g) was tosylated with *p*-toluene sulfonyl chloride (1.5 mmol, 1.4 g) following General Method B. The crude product was isolated (9:1 hexanes/ethyl acetate) as a colorless oil (1.4 g, 99% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.85–7.71 (m, 2H), 7.39–7.31 (m, 2H), 4.70–4.59 (m, 1H), 3.59–3.40 (m, 2H), 2.46 (s, 3H), 1.87–1.75 (m, 1H), 1.75–1.62 (m, 3H), 1.27 (dd, *J* = 6.3, 1.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 144.72, 134.23, 129.85, 127.68, 79.46, 44.39, 33.72, 27.87, 21.67, 20.90.

HRMS (ESI): calculated for C₁₂H₁₇O₃SCl+Na [M+Na]⁺ 299.048, found 299.048.

FTIR (thin film, cm⁻¹): 2981.4, 2873.4, 1597.7, 1457.0, 1354.8, 1188.9, 1097.3, 895.8, 815.7.



1-Cyclohexylethyl 4-methylbenzenesulfonate (17)

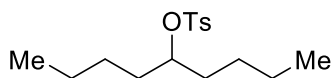
1-Cyclohexylethan-1-ol (40 mmol, 5 g) was tosylated with *p*-toluene sulfonyl chloride (60 mmol, 11 g) following General Method B. The crude product was isolated (10:1 hexanes/ethyl acetate) as a colorless oil (10.4 g, 92% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.46 (p, *J* = 6.3 Hz, 1H), 2.46 (s, 3H), 1.71 (t, *J* = 2.7 Hz, 3H), 1.68–1.58 (m, 2H), 1.47 (tdt, *J* = 12.0, 6.2, 3.1 Hz, 1H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.20–1.05 (m, 3H), 0.98 (qd, *J* = 12.4, 3.6 Hz, 1H), 0.92–0.84 (m, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 144.32, 134.67, 129.67, 127.71, 84.52, 77.26, 77.05, 76.84, 43.06, 28.20, 28.02, 26.16, 25.85, 25.83, 21.67, 17.79.

HRMS (ESI): calculated for C₁₅H₂₂O₃S+Na [M+Na]⁺ 305.118, found 305.118.

FTIR (thin film, cm⁻¹): 2929.3, 1450.2, 1361.5, 1188.9, 1094.4, 1027.9, 945.9, 878.4, 814.8.



Nonan-5-yl 4-methylbenzenesulfonate (19)

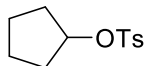
Nonan-5-ol (7 mmol, 1.2 g) was tosylated with *p*-toluene sulfonyl chloride (10 mmol, 2 g) following General Method B. The crude product was isolated (10:1 hexanes/ethyl acetate) as a colorless oil (2.3 g, 90% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.86–7.69 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.55 (p, *J* = 6.0 Hz, 1H), 4.45 (s, 1H), 2.45 (s, 3H), 1.70–1.45 (m, 4H), 1.31–1.07 (m, 9H), 0.82 (t, *J* = 7.0 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 144.37, 134.67, 129.64, 127.70, 84.59, 33.79, 26.81, 22.40, 21.62, 13.88.

HRMS (CI): calculated for C₁₆H₂₆O₃S+Na [M+Na]⁺ 321.15, found 321.15.

FTIR (thin film, cm⁻¹): 2956.3, 2864.7, 1457.0, 1176.4, 900.6, 813.8, 667.3.



Cyclopentyl 4-methylbenzenesulfonate (21)

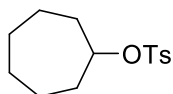
Cyclopentanol (12 mmol, 1 g) was tosylated with *p*-toluene sulfonyl chloride (18 mmol, 3.4 g) following General Method B. The crude product was isolated (20:1 hexanes/ethyl acetate) as a colorless oil (2.7 g, 93% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.83 – 7.76 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.97 (tt, *J* = 5.6, 2.9 Hz, 1H), 2.46 (s, 3H), 1.84–1.75 (m, 3H), 1.74 (dp, *J* = 9.2, 3.6, 2.9 Hz, 4H), 1.59–1.49 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 144.43, 134.47, 129.78, 127.69, 85.59, 77.28, 77.07, 76.86, 33.12, 23.12, 21.67.

HRMS (ESI): calculated for C₁₂H₁₆O₃S+Na [M+Na]⁺ 263.072, found 263.071.

FTIR (thin film, cm⁻¹): 2966.0, 1598.7, 1452.1, 1363.4, 1176.4, 1096.3, 914.1, 895.8, 815.7.



Cycloheptyl 4-methylbenzenesulfonate (23)

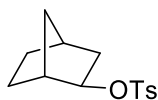
Cycloheptanol (9 mmol, 1 g) was tosylated with *p*-toluene sulfonyl chloride (13.5 mmol, 2.6 g) following General Method B. The crude product was isolated (20:1 hexanes/ethyl acetate) as a colorless oil (1.9 g, 79% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.80 (dt, *J* = 8.3, 1.6 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 4.68 (m, 1H), 2.46 (s, 3H), 1.93–1.81 (m, 2H), 1.82–1.70 (m, 2H), 1.67–1.59 (m, 2H), 1.60–1.45 (m, 4H), 1.36 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 144.33, 134.63, 134.62, 129.73, 127.62, 84.50, 77.28, 77.07, 76.85, 43.92, 34.54, 30.46, 28.13, 24.37, 22.17, 21.67.

HRMS (ESI): calculated for C₁₄H₂₀O₃S+Na [M+Na]⁺ 291.103, found 291.103.

FTIR (thin film, cm⁻¹): 2930.3, 2860.9, 1598.7, 1458.9, 1353.8, 1187.9, 1097.3, 947.8, 814.8.



(1*R*,2*R*,4*S*)-Bicyclo[2.2.1]heptan-2-yl 4-methylbenzenesulfonate (25)

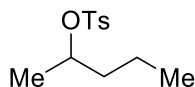
Exo-norborneol (27 mmol, 3 g) was tosylated with *p*-toluene sulfonyl chloride (41 mmol, 7.8 g) following General Method B. The crude product was isolated (10:1 hexanes/ethyl acetate) as a gray-white solid (2.9 g, 41% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.80 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.48–4.39 (m, 1H), 2.47 (d, *J* = 1.6 Hz, 3H), 2.36 (d, *J* = 5.1 Hz, 1H), 2.27 (q, *J* = 3.3 Hz, 1H), 1.66–1.52 (m, 3H), 1.51 (dddt, *J* = 13.5, 9.3, 4.5, 1.8 Hz, 1H), 1.45–1.34 (m, 1H), 1.16 (dq, *J* = 10.1, 1.8 Hz, 1H), 1.08–0.94 (m, 2H).

¹³C NMR (151 MHz, CDCl₃) δ 144.40, 134.59, 129.78, 127.67, 85.46, 77.27, 77.06, 76.84, 42.07, 39.64, 35.33, 35.25, 35.01, 27.89, 23.92, 21.68, 21.67.

HRMS (ESI): calculated for C₁₄H₁₈O₃S+Na [M+Na]⁺ 289.087, found 289.087.

FTIR (thin film, cm⁻¹): 2962.1, 2874.4, 1188.9, 1098.3, 962.3, 915.1, 891.0, 814.8.



Pentan-2-yl 4-methylbenzenesulfonate (32)

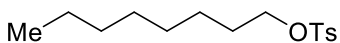
Pentan-2-ol (11 mmol, 1 g) was tosylated with *p*-toluene sulfonyl chloride (17 mmol, 3.2 g) following General Method B. The crude product was isolated (10:1 hexanes/ethyl acetate) as a colorless oil (2.4 g, quantitative).

¹H NMR (600 MHz, CDCl₃) δ 7.85–7.75 (m, 2H), 7.40–7.30 (m, 2H), 4.72–4.55 (m, 1H), 2.46 (s, 3H), 1.61 (dddd, *J* = 14.1, 10.2, 7.3, 5.3 Hz, 1H), 1.51–1.40 (m, 1H), 1.38–1.15 (m, 5H), 0.82 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 144.42, 134.53, 129.72, 127.69, 80.45, 77.29, 77.08, 76.87, 38.60, 21.65, 20.81, 18.19, 13.65.

HRMS (ESI): calculated for C₁₂H₁₈O₃S+Na [M+Na]⁺ 265.087, found 265.087.

FTIR (thin film, cm⁻¹): 2962.1, 2875.3, 1598.7, 1457.0, 1341.5, 1188.9, 1094.4, 900.6, 816.7.

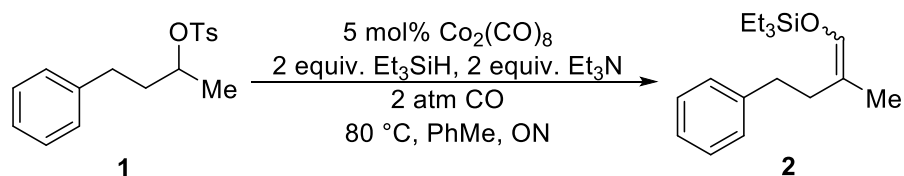


Octyl 4-methylbenzenesulfonate (33)

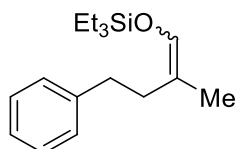
Octanol (38 mmol, 5 g) was tosylated with *p*-toluene sulfonyl chloride (57 mmol, 11 g) following General Method B. The crude product was isolated (10:1 hexanes/ethyl acetate) as a colorless oil (9.5 g, 88% yield). Spectroscopic and physical data are reported.^{8,9}

Cobalt-Catalyzed Silyl Carbonylation

General Silyl Carbonylation Method



In a glovebox, alkyl tosyl (1 mmol, 1.0 equiv.), triethylsilane (2.0 or 5.0 equiv.), triethylamine (2.0 equiv.), toluene [0.5 M], and $\text{Co}_2(\text{CO})_8$ (5 mol%) were combined in an Ace Glass pressure tube. The tube was sealed with a Swagelok gas quick-connect adapter and removed from the glovebox. Then, the tube was purged with CO three times, then pressurized to 2 atm (unless otherwise noted). The reaction was stirred at 80 °C (unless otherwise noted) for 20 h. After this period, the reaction was cooled to room temperature, then depressurized and left stirring under air for 2-4 hours to decompose the cobalt. The resulting solution was diluted with ether and washed with 1 M HCl. The aqueous layer was then extracted with ether twice. The combined organic layers were dried over MgSO_4 and filtered through a silica plug with diethyl ether. The resulting crude mixture was purified by flash chromatography.



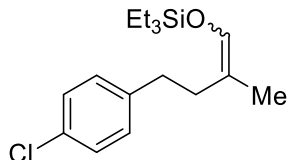
Triethyl((2-methyl-4-phenylbut-1-en-1-yl)oxy)silane (2) was obtained from the General Silyl Carbonylation Method and the crude product purified by flash chromatography (80:1 hexanes/triethylamine) to yield a colorless oil (193 mg, 70% yield). Z/E: 1.9:1

^1H NMR (600 MHz, CDCl_3) δ 7.35–7.27 (m, 2H), 7.27–7.24 (m, 1H), 7.24–7.16 (m, 2H), 6.16–6.09 (m, 0.34H), 6.07 (h, J = 1.3 Hz, 0.66H), 2.76–2.65 (m, 2H), 2.47–2.40 (m, 0.7H), 2.22 (ddd, J = 9.2, 5.6, 1.1 Hz, 1.3H), 1.70 (d, J = 1.5 Hz, 2H), 1.59 (d, J = 1.5 Hz, 1H), 1.00 (dt, J = 15.8, 8.0 Hz, 9H), 0.66 (dq, J = 19.9, 8.0 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 142.83, 142.36, 134.46, 133.93, 128.44, 128.40, 125.65, 125.57, 116.54, 116.23, 35.95, 34.87, 33.83, 30.78, 17.26, 12.68, 6.67, 6.61, 4.51, 4.44.

HRMS (APPI): calculated for $\text{C}_{17}\text{H}_{28}\text{OSi}$ $[\text{M}]^+$ 276.190, found 276.190.

FTIR (thin film, cm^{-1}): 3063.4, 2956.3, 1671.0, 1540.9, 1240, 1178.3, 1006.7, 827.3, 743.4.



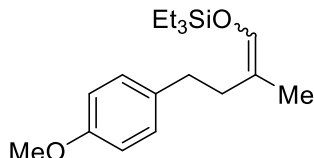
((4-(4-Chlorophenyl)-2-methylbut-1-en-1-yl)oxy)triethylsilane (4) was obtained from General Silyl Carbonylation Method and the crude product purified by flash chromatography (100:1 hexanes/triethylamine) to yield a colorless oil (256 mg, 82% yield). Z/E: 2.8:1

¹H NMR (600 MHz, CDCl₃) δ 7.27–7.22 (m, 2H), 7.18–7.12 (m, 0.6H), 7.10 (d, *J* = 8.3 Hz, 1.5H), 6.12–6.07 (m, 0.3H), 6.01 (q, *J* = 1.4 Hz, 0.7H), 2.67 (td, *J* = 7.6, 4.5 Hz, 2H), 2.39 (dd, *J* = 9.2, 6.7 Hz, 0.6H), 2.21–2.12 (m, 2H), 1.66 (d, *J* = 1.4 Hz, 2.3H), 1.55 (d, *J* = 1.5 Hz, 0.8H), 0.97 (dt, *J* = 12.5, 7.9 Hz, 9H), 0.63 (dq, *J* = 16.0, 8.0 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 141.14, 140.70, 134.72, 134.18, 131.33, 129.76, 128.25, 115.92, 115.51, 35.76, 34.04, 33.01, 30.50, 17.18, 12.58, 6.63, 6.57, 4.48, 4.42.

HRMS (APPI): calculated for C₁₇H₂₈OSiCl [M]⁺ 311.159, found 311.159.

FTIR (thin film, cm⁻¹): 3028.7, 2956.3, 1671.0, 1540.9, 1490.7, 1239.0, 1181.2, 1093.4, 811.9.



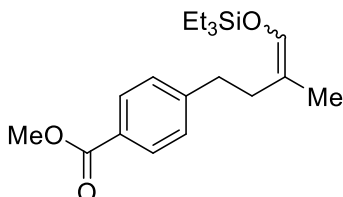
Triethyl((4-(4-methoxyphenyl)-2-methylbut-1-en-1-yl)oxy)silane (6) was obtained from General Silyl Carbonylation Method and the crude product purified by flash chromatography (30:1 hexanes/triethylamine) to yield a colorless oil (278 mg, 90% yield). Z/E: 2.2:1

¹H NMR (600 MHz, CDCl₃) δ 7.16 (d, *J* = 2.1 Hz, 0.6H), 7.12–7.09 (m, 1.2H), 6.87–6.83 (m, 2H), 6.10 (q, *J* = 1.2 Hz, 0.33H), 6.05 (q, *J* = 1.3 Hz, 0.61H), 3.82 (s, 1H), 3.81 (s, 2H), 2.69–2.60 (m, 2H), 2.43–2.34 (m, 0.6H), 2.21–2.13 (m, 1.3H), 1.68 (d, *J* = 1.4 Hz, 2H), 1.57 (d, *J* = 1.4 Hz, 1H), 0.99 (dt, *J* = 14.0, 8.0 Hz, 9H), 0.70–0.59 (m, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 157.58, 134.93, 134.47, 134.41, 133.86, 129.29, 129.24, 116.58, 116.29, 113.59, 55.25, 36.16, 33.90, 30.96, 17.25, 12.67, 6.66, 6.60, 4.50, 4.44.

HRMS (APPI): calculated for C₁₈H₃₀O₂Si [M]⁺ 306.201, found 306.201.

FTIR (thin film, cm⁻¹): 3030.6, 2955.4, 1671.0, 1540.9, 1246.8, 1177.3, 1015.3, 819.6, 744.4.



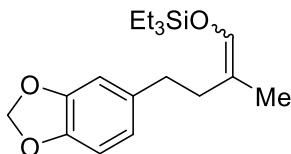
Methyl 4-(3-methyl-4-((triethylsilyl)oxy)but-3-en-1-yl)benzoate (8) was obtained from General Silyl Carbonylation Method and the crude product purified by flash chromatography (100:2:2 hexanes/ethyl acetate/triethylamine) to yield a colorless oil (259 mg, 78% yield). Z/E: 1.2:1

¹H NMR (600 MHz, CDCl₃) δ 7.97 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.33–7.26 (m, 1H), 7.26–7.21 (m, 1H), 6.10 (s, 0.45H), 6.02 (m, 0.56H), 3.92 (d, *J* = 0.8 Hz, 3H), 2.76 (dt, *J* = 8.1, 6.0 Hz, 2H), 2.43 (m, 1H), 2.21 (td, *J* = 7.6, 1.1 Hz, 1H), 1.67 (d, *J* = 1.5 Hz, 1.8H), 1.55 (d, *J* = 1.5 Hz, 1.5H), 0.97 (dt, *J* = 17.3, 8.0 Hz, 9H), 0.62 (dq, *J* = 22.2, 8.0 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 167.24, 167.18, 148.35, 147.89, 134.77, 134.25, 129.58, 128.49, 128.44, 127.55, 115.85, 115.44, 51.95, 51.93, 35.52, 34.81, 33.78, 30.30, 17.17, 12.58, 6.61, 6.55, 4.48, 4.41.

HRMS (APPI): calculated for [C₁₉H₃₁O₃Si]⁺ 335.204, found, 335.204.

FTIR (thin film, cm⁻¹): 3032.5, 2954.4, 1725.0, 1671.0, 1435.7, 1278.6, 1242.9, 1178.3, 1109.8, 1019.2.



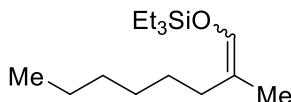
((4-(Benzo[d][1,3]dioxol-5-yl)-2-methylbut-1-en-1-yl)oxy)triethylsilane (10) was obtained from General Silyl Carbonylation Method and the product purified by flash chromatography (100:0.5:1 hexanes/ethyl acetate/triethylamine) to yield a colorless oil (238 mg, 74% yield). Z/E: 1.7:1

¹H NMR (600 MHz, CDCl₃) δ 6.76–6.73 (m, 1.5H), 6.70–6.67 (m, 1H), 6.63 (dd, *J* = 7.9, 1.6 Hz, 0.7H), 6.10 (d, *J* = 1.6 Hz, 0.4H), 6.05 (q, *J* = 1.4 Hz, 0.7H), 5.94 (d, *J* = 2.2 Hz, 2H), 2.65–2.60 (m, 2H), 2.38 (dd, *J* = 9.3, 6.8 Hz, 0.8H), 2.18–2.13 (m, 1.4H), 1.66 (d, *J* = 1.3 Hz, 2H), 1.56 (d, *J* = 1.4 Hz, 1H), 0.99 (dt, *J* = 12.0, 8.0 Hz, 9H), 0.70–0.60 (m, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 147.39, 147.35, 145.43, 145.38, 136.69, 136.22, 134.53, 133.98, 121.12, 121.03, 116.32, 115.95, 108.93, 108.92, 108.02, 107.99, 100.69, 100.66, 36.16, 34.51, 33.48, 30.95, 17.23, 12.63, 6.64, 6.59, 4.49, 4.44.

HRMS (APPI): calculated for C₁₈H₂₈O₃Si [M]⁺ 320.180, found 320.180.

FTIR (thin film, cm⁻¹): 3032.5, 2956.3, 1671.0, 1505.2, 1489.7, 1244.8, 1178.3, 1042.3, 1015.3.



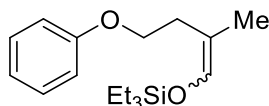
Triethyl((2-methyloct-1-en-1-yl)oxy)silane (12) was obtained from General Silyl Carbonylation Method and the crude product purified by flash chromatography (100:0.5 hexanes/triethylamine) to yield a colorless oil (175 mg, 68% yield). Z/E: 1.3:1

¹H NMR (600 MHz, CDCl₃) δ 6.09 (p, *J* = 1.3 Hz, 0.5H), 6.07 (q, *J* = 1.2 Hz, 0.5H), 2.13–2.05 (m, 1H), 1.87 (td, *J* = 7.4, 1.1 Hz, 1H), 1.60 (d, *J* = 1.4 Hz, 1.5H), 1.52 (d, *J* = 1.5 Hz, 1.5H), 1.39–1.23 (m, 8H), 1.00 (td, *J* = 7.9, 3.0 Hz, 9H), 0.90 (td, *J* = 7.0, 1.9 Hz, 3H), 0.66 (qd, *J* = 7.9, 5.6 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 133.59, 133.26, 117.68, 117.29, 33.71, 31.84, 29.20, 28.84, 28.42, 27.99, 27.26, 22.71, 17.08, 14.17, 12.51, 6.63, 4.49.

HRMS (APPI): calculated for C₁₅H₃₂O₂Si [M]⁺ 256.222, found 256.222.

FTIR (thin film, cm⁻¹): 2957.3, 2926.5, 1675.8, 1458.9, 1239.0, 1164.8, 1006.7, 836.0.



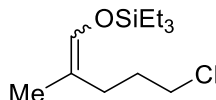
Triethyl((2-methyl-4-phenoxybut-1-en-1-yl)oxy)silane (14) was obtained from General Silyl Carbonylation Method and the crude product purified by flash chromatography (100:0.5:1 hexanes/ethyl acetate/triethylamine) to yield a colorless oil (165 mg, 56% yield). Z/E: 2.1:1

¹H NMR (600 MHz, CDCl₃) δ 7.32 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.97 (tdd, *J* = 6.0, 2.1, 1.1 Hz, 2.4H), 6.95–6.91 (m, 0.6H), 6.25 (q, *J* = 1.3 Hz, 0.3H), 6.23–6.20 (m, 0.6H), 4.06 (t, *J* = 7.4 Hz, 1.4H), 4.02 (t, *J* = 7.0 Hz, 0.6H), 2.63 (t, *J* = 7.4 Hz, 1.4H), 2.40 (t, *J* = 7.0, 1.0 Hz, 0.6), 1.72 (d, *J* = 1.4 Hz, 1H), 1.66 (d, *J* = 1.5 Hz, 2H), 1.03 (td, *J* = 8.0, 4.0 Hz, 9H), 0.71 (qd, *J* = 8.0, 1.7 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.04, 158.94, 135.81, 135.37, 129.41, 120.52, 120.38, 114.51, 113.42, 112.71, 66.76, 65.99, 33.70, 28.94, 17.76, 12.90, 6.64, 6.63, 4.52, 4.49.

HRMS (APPI): calculated for $\text{C}_{17}\text{H}_{28}\text{O}_2\text{Si}$ $[\text{M}]^+$ 292.185, found 292.185.

FTIR (thin film, cm^{-1}): 3063.4, 2956.3, 2877.3, 1671.0, 1540.9, 1240, 1178.29, 1139.7, 1006.7.



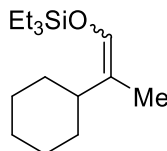
((5-Chloro-2-methylpent-1-en-1-yl)oxy)triethylsilane (16) was obtained from General Silyl Carbonylation Method and the product was purified by flash chromatography (100:0.5 hexanes/triethylamine) to yield a colorless oil (119 mg, 48% yield). Z/E: 1.1:1

^1H NMR (600 MHz, CDCl_3) δ 6.16 (q, J = 1.3 Hz, 0.5H), 6.12 (q, J = 1.3 Hz, 0.5H), 3.53 (dt, J = 8.5, 6.8 Hz, 2H), 2.23 (t, J = 7.4 Hz, 1H), 2.12–1.98 (m, 1H), 1.90–1.78 (m, 2H), 1.61 (d, J = 1.5 Hz, 1.5H), 1.54 (d, J = 1.5 Hz, 1.5H), 1.00 (td, J = 7.9, 4.5 Hz, 9H), 0.67 (qd, J = 7.9, 6.4 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 134.86, 134.46, 115.18, 114.91, 45.00, 44.46, 30.70, 30.66, 30.62, 26.15, 17.10, 12.32, 6.60, 6.59, 4.47.

HRMS (APPI): calculated for $\text{C}_{12}\text{H}_{17}\text{OSiCl}$ $[\text{M}]^+$ 248.136, found 248.136.

FTIR (thin film, cm^{-1}): 2957.3, 2877.3, 1673.0, 1540.9, 1457.0, 1239.0, 1178.3, 1133.9, 1015.3.



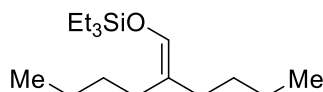
((2-Cyclohexylprop-1-en-1-yl)oxy)triethylsilane (18) was obtained from General Silyl Carbonylation Method (with 5 equiv. triethylsilane) and the crude product was purified by flash chromatography (100:0.5 hexanes/triethylamine) to yield a colorless oil (144.1 mg, 57% yield). Z/E: 1.3:1

^1H NMR (600 MHz, CDCl_3) δ 6.14 (dt, J = 2.3, 1.1 Hz, 0.6H), 6.00 (d, J = 1.0 Hz, 0.4H), 1.81–1.70 (m, 3H), 1.68 (dddt, J = 12.4, 4.5, 3.0, 1.4 Hz, H), 1.61 (dt, J = 10.7, 2.3 Hz, 1H), 1.58 (d, J = 1.5 Hz, 1.7H), 1.52–1.47 (m, 0.8H), 1.45 (d, J = 1.5 Hz, 1.3H), 1.34–1.17 (m, 4H), 1.15 (ddd, J = 12.6, 6.7, 3.4 Hz, 1H), 0.99 (d, J = 7.9 Hz, 9H), 0.66 (qd, J = 8.0, 2.9 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 132.97, 132.23, 123.27, 122.32, 42.39, 36.34, 32.07, 30.59, 26.38, 26.34, 13.74, 10.45, 6.64, 4.52, 4.46.

HRMS (APPI): calculated for $\text{C}_{15}\text{H}_{30}\text{OSi}$ $[\text{M}]^+$ 254.206, found 254.206.

FTIR (thin film, cm^{-1}): 2955.4, 2877.3, 1668.1, 1449.2, 1237.1, 1162.9, 1123.3, 1015.3.



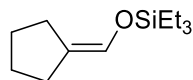
((2-Butylhex-1-en-1-yl)oxy)triethylsilane (20) was obtained from General Silyl Carbonylation Method and the product purified by flash chromatography (100:0.5 hexanes/triethylamine) to yield a colorless oil (104 mg, 38% yield).

^1H NMR (600 MHz, CDCl_3) δ 6.10–6.07 (m, 1H), 2.13–2.05 (m, 2H), 1.91–1.82 (m, 2H), 1.40–1.26 (m, 9H), 1.00 (t, J = 8.0 Hz, 9H), 0.92 (dt, J = 9.4, 7.1 Hz, 6H), 0.67 (q, J = 8.0 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 133.65, 121.60, 31.00, 30.51, 29.85, 25.98, 22.76, 22.42, 14.07, 14.00, 6.62, 4.49.

HRMS (APPI): calculated for $\text{C}_{16}\text{H}_{34}\text{OSi}$ $[\text{M}]^+$ 270.2373, found 270.2373.

FTIR (thin film, cm^{-1}): 2956.3, 2876.3, 1669.1, 1540.9, 1456.0, 1162.9, 1005.7, 831.2, 744.4.



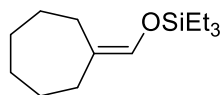
(Cyclopentylidenemethoxy)triethylsilane (22) was obtained from General Silyl Carbonylation Method and the crude product purified by flash chromatography (100:1 hexanes/triethylamine) to yield a colorless oil (68 mg, 32% yield).

^1H NMR (600 MHz, CDCl_3) δ 6.23 (p, J = 2.2 Hz, 1H), 2.31–2.25 (m, 2H), 2.17 (ddt, J = 7.0, 5.3, 1.7 Hz, 2H), 1.69–1.57 (m, 4H), 1.00 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 130.66, 124.90, 77.24, 77.03, 76.82, 28.82, 26.87, 26.04, 6.61, 4.54.

HRMS (APPI): calculated for $\text{C}_{12}\text{H}_{24}\text{OSi}$ $[\text{M}]^+$ 212.159, found 212.159.

FTIR (thin film, cm^{-1}): 2955.4, 2877.3, 1748.2, 1683.6, 1540.9, 1457.0, 1240, 1171.5, 1120.4.



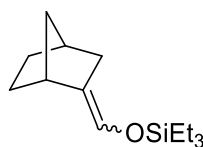
(Cycloheptylidenemethoxy)triethylsilane (24) was obtained from General Silyl Carbonylation Method and the crude product purified by flash chromatography (100:1 hexanes/triethylamine) to yield a colorless oil (146 mg, 60% yield).

^1H NMR (600 MHz, CDCl_3) δ 6.12 (p, J = 1.4 Hz, 1H), 2.36–2.30 (m, 2H), 2.09–2.04 (m, 2H), 1.67–1.48 (m, 8H), 1.01 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 133.49, 123.45, 77.24, 77.03, 76.82, 31.43, 30.28, 30.21, 29.78, 27.43, 26.82, 6.62, 4.53.

HRMS (APPI): calculated for $\text{C}_{14}\text{H}_{28}\text{OSi}$ $[\text{M}]^+$ 240.190, found 240.191.

FTIR (thin film, cm^{-1}): 2956.3, 2877.3, 1716.3, 1652.7, 1540.9, 1457.0, 1240, 1192.8, 1166.7.



(((1R,4S)-Bicyclo[2.2.1]heptan-2-ylidene)methoxy)triethylsilane (26) was obtained from General Silyl Carbonylation Method and the crude was purified by flash chromatography (100:0.5 hexanes/triethylamine) to yield a colorless oil (144 mg, 61% yield). Z/E: 1.7:1

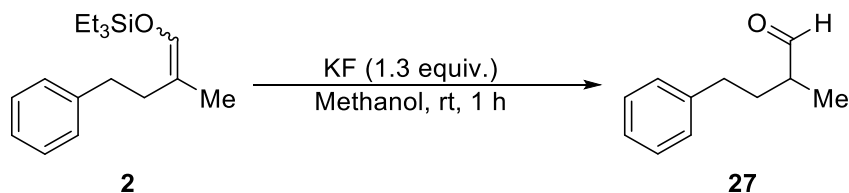
^1H NMR (600 MHz, CDCl_3) δ 6.25–6.18 (m, 0.6H), 5.99 (tt, J = 1.4, 0.7 Hz, 0.4H), 3.14 (dt, J = 2.7, 1.3 Hz, 0.4H), 2.62 (dd, J = 3.7, 1.7 Hz, 0.6H), 2.41–2.31 (m, 0.6H), 2.22–2.15 (m, 0.6H), 2.15–2.09 (m, 0.4H), 1.89 (dt, J = 15.9, 2.5 Hz, 0.6H), 1.80 (dt, J = 14.5, 2.2 Hz, 0.5H), 1.65–1.55 (m, 2H), 1.38–1.17 (m, 5H), 1.00 (td, J = 8.0, 6.0 Hz, 9H), 0.66 (qd, J = 8.0, 5.7 Hz, 6H).

^{13}C NMR (151 MHz, CDCl_3) δ 129.07, 128.64, 128.54, 127.09, 40.65, 39.69, 38.89, 38.24, 36.41, 36.34, 34.31, 34.10, 30.65, 29.26, 28.70, 28.51, 6.64, 4.54, 4.47.

HRMS (APPI): calculated for $\text{C}_{14}\text{H}_{26}\text{OSi}$ $[\text{M}]^+$ 238.175, found 238.175.

FTIR (thin film, cm^{-1}): 2956.3, 2876.3, 1771.3, 1696.1, 1646.9, 1540.9, 1241.9, 1166.7, 1144.6.

Post-Reactions of Silyl Enol Ethers



2-Methyl-4-phenylbutanal (**27**)

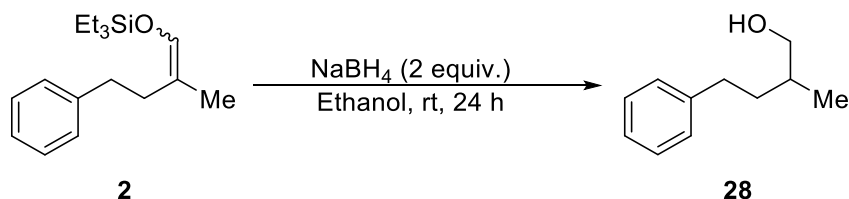
To a solution of KF (1.3 mmol, 76 mg) in methanol (1.0 mL) was added a solution of crude silyl enol ether in methanol (1.5 mL). The resulting mixture was stirred at room temperature for 1 hour. Then, the methanol solvent was removed under vacuum, the resulting mixture was diluted in DCM and to this 1 M HCl was added. The aqueous layer was extracted twice with DCM. The combined organic layers were dried over MgSO₄, filtered, and concentrated. The crude mixture was purified by flash chromatography (40:1 pentane/diethyl ether) to yield a colorless oil (90 mg, 56% yield).

¹H NMR (600 MHz, CDCl₃) δ 9.66 (d, *J* = 1.8 Hz, 1H), 7.33 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.26–7.19 (m, 3H), 2.70 (qdd, *J* = 13.8, 9.4, 6.4 Hz, 2H), 2.41 (qd, *J* = 6.9, 1.8 Hz, 1H), 2.10 (ddt, *J* = 13.5, 9.5, 6.6 Hz, 1H), 1.71 (ddt, *J* = 13.6, 9.5, 6.8 Hz, 1H), 1.19 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 204.89, 141.39, 128.51, 128.43, 126.12, 77.31, 77.10, 76.88, 45.66, 33.08, 32.18, 13.39.

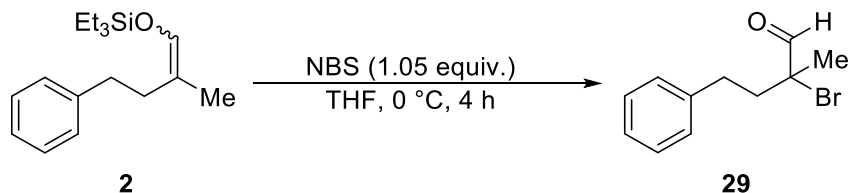
HRMS (CI): calculated for C₁₁H₁₄O [M]⁺ 162.104, found 162.104.

FTIR (thin film, cm⁻¹): 3063.7, 3027.7, 2929.3, 2858.0, 1725.0, 1698.0, 1456.0, 746.3, 699.1.



2-Methyl-4-phenylbutan-1-ol (**28**)

To a solution of crude silyl enol ether in 2.5 mL ethanol was added NaBH₄ (2 mmol, 76 mg). The resulting mixture was stirred at room temperature for 24 hours. Then, the ethanol was removed under vacuum. The resulting mixture was diluted in dichloromethane and 1 M HCl was added. The aqueous layer was extracted twice with DCM. The organic layer was dried over MgSO₄ and concentrated. The resulting crude mixture was purified by flash chromatography (6:1 pentane/diethyl ether) to yield a colorless oil (117 mg, 71% yield). Spectroscopic and physical data are reported.¹⁰



2-Bromo-2-methyl-4-phenylbutanal (29)

To a solution of crude silyl enol ether in THF (2.5 mL) at 0 °C was added *N*-bromosuccinimide (1.05 mmol, 187 mg). The resulting mixture was stirred at 0 °C for 4 hours. Then, the reaction was quenched with Na₂S₂O₃. The aqueous layer was extracted twice with diethyl ether and once with DCM. The organic layers were mixed, dried over MgSO₄, and concentrated. The crude mixture was purified by flash chromatography (40:1 pentane/diethyl ether) to yield a colorless oil (166 mg, 67% yield).

¹H NMR (600 MHz, CDCl₃) δ 9.43 (s, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 (dd, *J* = 13.8, 7.9 Hz, 3H), 2.89 (ddd, *J* = 13.5, 11.8, 4.8 Hz, 1H), 2.74 (ddd, *J* = 13.4, 11.9, 5.1 Hz, 1H), 2.39 (ddd, *J* = 14.3, 11.9, 4.8 Hz, 1H), 2.24 (ddd, *J* = 14.4, 11.8, 5.1 Hz, 1H), 1.88 (s, 3H).

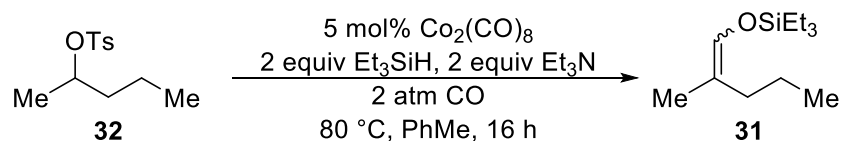
¹³C NMR (151 MHz, CDCl₃) δ 192.96, 140.41, 128.66, 128.41, 126.43, 77.30, 77.08, 76.87, 68.94, 40.78, 31.86, 24.05.

HRMS (CI): calculated for C₁₁H₁₃O [M-Br]⁺ 161.096, found 161.096.

FTIR (thin film, cm⁻¹): 3027.7, 2929.3, 2825.2, 2717.2, 1730.8, 1496.5, 1456.0, 1660.7, 747.3, 699.1.

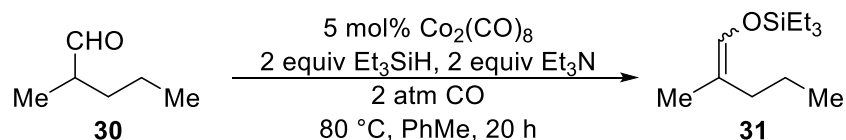
Mechanistic Studies

Cobalt-Catalyzed Silyl Carbonylation of Substrate 32

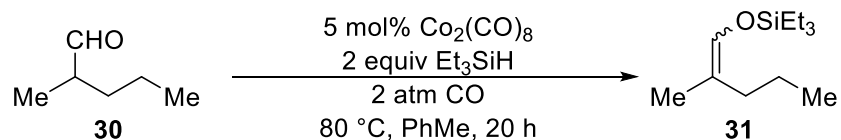


Following General Silyl Carbonylation Method, the crude silyl enol ether was quantified by ^1H NMR against HMDS as the internal standard.

Cobalt-Catalyzed Protection of 2-Methylpentanal

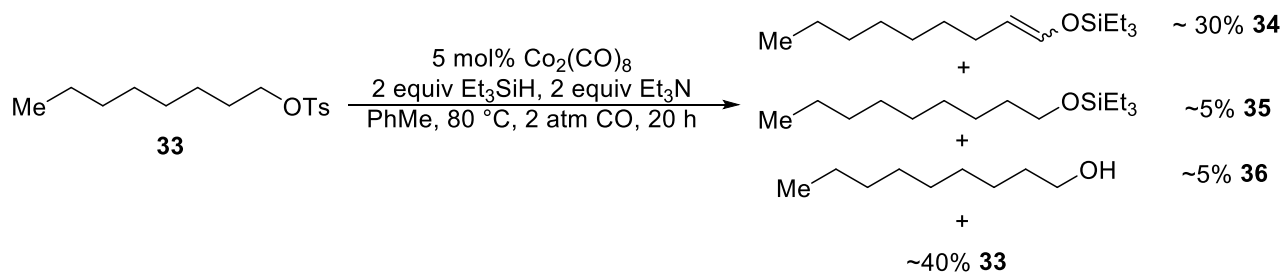


Following General Silyl Carbonylation Method, the crude silyl enol ether was quantified by ^1H NMR against HMDS as the internal standard.



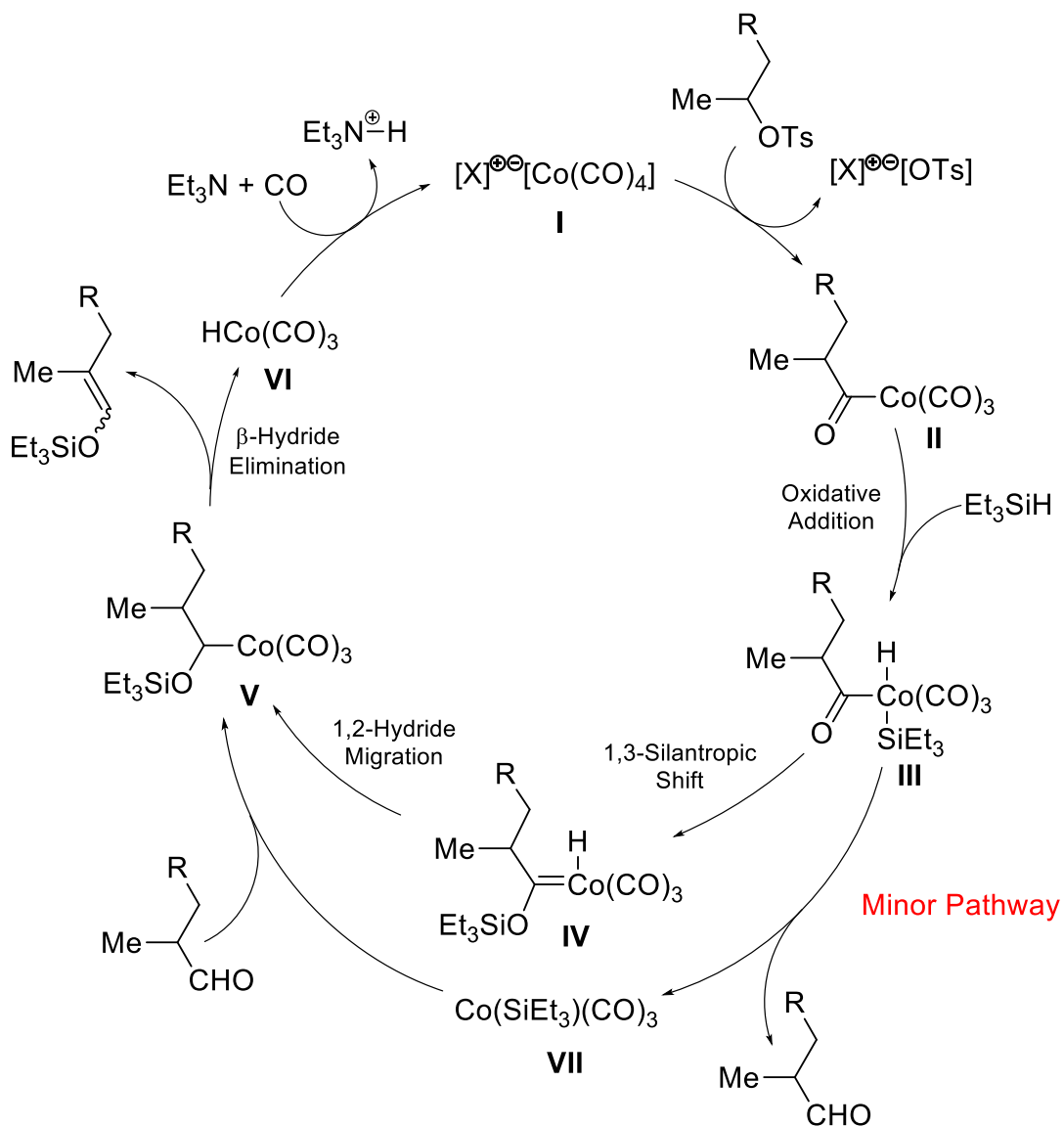
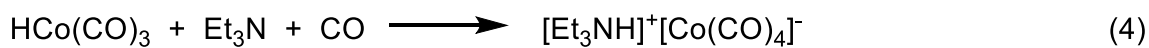
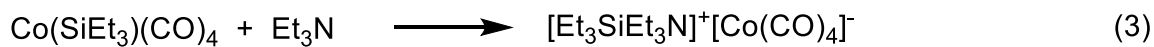
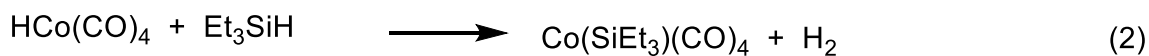
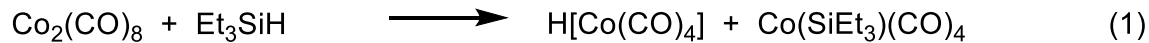
Following General Silyl Carbonylation Method, without triethylamine, the crude silyl enol ether was quantified by ^1H NMR against HMDS as the internal standard.

Cobalt-Catalyzed Silyl Carbonylation of 1-Octyl Tosyl (33)



Following General Silyl Carbonylation Method, the crude reaction mixture was identified and quantified by ^1H NMR against HMDS as the internal standard.

Plausible Catalytic Cycle



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¹H and ¹³C NMR Spectra

