Stereoconvergent Palladium-Catalyzed Carbonylation of Both *E* and *Z* Isomers of a 2-Trifloxy-1,3-Butadiene

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Supporting Information

General Information. All reactions were conducted under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise indicated. High pressure reactions were carried out in a Parr stainless steel pressure vessel equipped with a pressure gauge, gas inlet and pressure release valve. Flash chromatography was performed as described by Still[1] on EM silica gel 60 (230-240 mesh). Tetrahydrofuran (THF) was distilled from sodium or potassium metal/benzophenone ketyl. Dichloromethane, triethylamine, diisopropylethylamine, DMSO and HMPA were distilled from calcium hydride. Methanol was distilled from $Mg(OMe)_2$. Oxalyl chloride was distilled prior to use. Acrolein was distilled from $CaSO_4$. Benzonitrile and $Pd(PPh_3)_4$ were used as received. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker DRX-300WB (300 MHz) spectrometer and a Bruker DMX-500 (500 MHz) spectrometer and are reported in ppm from internal tetramethylsilane. Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; integration; coupling constant(s) in Hz; assignment). Proton decoupled ^{13}C NMR spectra were recorded on a Varian VXR-300 (75 MHz) spectrometer using $CDCl_3$ (77.0 ppm) as internal standard. High resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer in the Columbia University Mass Spectrometry Laboratory.

β-hydroxyketone (6): To a solution of 390 μl (2.76 mmol) diisopropylamine in 4 ml THF at –78 °C was added 2.12 ml of n-butyllithium (1.3 M in hexanes, 2.76 mmol). The solution was warmed to 0ºC for 30 min then cooled to –78 °C. To this solution 1.23 g (2.3 mmol) of ketone **5**

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(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978,** *43*, 2923-2925.

was added by cannula as solution in 4 ml THF. After 30 minutes at –78 ºC the solution was warmed to –10 ºC and stirred for an additional 30 minutes. A deep yellow color developed over this time. The reaction was cooled again to –78 ºC and 215 μl of acrolein (3.2 mmol) was added. After 20 minutes the reaction was removed from the dry ice/acetone bath and quenched while cold by addition of 2 ml saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with 3 x 10 ml Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel eluting with 3 - 10% Et_2O/hexanes to give 1.35 g (2.28 mmol, 99% yield) of aldol **6** as clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 (dd, 1H, *J* = 10.6 and 18.0 Hz, C(13)-**H**), 5.69 (m, 1H, C(28)-**H**), 5.41 (m, 2H, C(23)-**H**, C(24)-**H**), 5.26 (m, 4H, C(29)-$\mathbf{H_2}$, C(13)-$\mathbf{H_2}$), 4.33 (m, 1H, C(14)-**H**), 3.81 (s, 1H, C(14)-O**H**), 3.63 (m, 2H, C(7)-$\mathbf{H_2}$), 2.85 (m, 1H, C(10)-**H**), 2.50 (m, 1H, C(9)-**H**), 2.03 (d, 1H, *J* = 1.5 Hz, C(16)-**H**), 1.97 (broad s, 2H, C(22)-$\mathbf{H_2}$), 1.80 (m, 3H, C(18)-**H**, C(15)-**H**, C(8)-**H**), 1.66 (m, 5H, C(25)-$\mathbf{H_3}$, C(18)-**H**, C(17)-**H**), 1.35 (m, 7H, C(8)-**H**, C(19)-$\mathbf{H_2}$, C(20)-$\mathbf{H_2}$, C(21)-$\mathbf{H_2}$), 0.93 (m, 18H, C(7)OSi($CH_2C\mathbf{H_3}$)$_3$, C(11)OSi($CH_2C\mathbf{H_3}$)$_3$) 0.59 (m, 12H, C(7)OSi($C\mathbf{H_2}CH_3$)$_3$, C(11)OSi($C\mathbf{H_2}CH_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 218.8, 139.6, 137.9, 131.5, 124.6, 119.2, 117.0, 86.2, 74.9, 62.6, 61.5, 60.6, 53.8, 50.2, 38.8, 36.5, 35.1, 32.5, 31.6, 29.5, 29.3, 28.7, 22.6, 17.9, 14.1, 6.9, 6.8, 6.3, 4.4; IR (thin film) 3505, 2953, 2318, 2873, 2358, 2331, 1725, 1458, 1418, 1236, 1112, 1005 cm^{-1}. HRMS (FAB+) calculated for $C_{34}H_{63}O_4Si_2$ 591.4265, found 591.4240.

β-Diketone (7): To a solution of 1.28 g (2.16 mmol) β-hydroxyketone **6** in 20 ml CH_2Cl_2 was added 5.6 ml (32.4 mmol) of diisopropylethylamine followed by 2.3 ml (32.4 mmol) DMSO. To this solution was added 0.675 g (4.3 mmol) of sulfur trioxide pyridine complex as a solid in one portion. After 1 hour an additional 0.337 g (2.15 mmol) portion of solid sulfur trioxide pyridine complex was added. The reaction mixture was stirred for 1 h and then quenched by the addition of 10 ml saturated aqueous $NaHCO_3$. The mixture was diluted with 10 mL Et_2O and the layers were separated. The aqueous layer was extracted with 3 x 15 ml Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel eluting with 30 - 40% benzene/hexanes to give

0.962 g (1.63 mmol, 76% yield) of β-diketone **7**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.26 (broad s, 1H, C(14)O**H**), 6.19 (dd, 1H, *J* = 17.2 and 10.1 Hz, C(28)-**H**), 6.18 (dd, 1H, *J* = 17.1 and 2.2 Hz, *trans*-C(29)-**H**), 5.92 (dd, 1H, *J* = 17.7 and 10.7 Hz, C(12)-**H**), 5.61 (dd, 1H, *J* = 10.1 and 2.2 Hz, *cis*-C(29)-**H**) 5.43 (m, 2H, C(23)-**H**, C(24)-**H**), 5.18 (dd, 2H, *J* = 17.3 and 10.4 Hz, C(13)-$\mathbf{H_2}$), 3.64 (m, 2H, C(7)-$\mathbf{H_2}$), 2.77 (d, 1H, *J* = 4 Hz, C(10)-**H**), 2.72 (s, 1H, C(16)-**H**), 2.52 (m, 1H, C(9)-**H**), 1.98 (broad s, 2H, C(22)-$\mathbf{H_2}$), 1.83 (m, 1H, C(18)-**H**), 1.63 (m, 5H, C(25)-$\mathbf{H_3}$, C(18)-**H**, C(8)-**H**), 1.36 (m, 8H, C(19)-$\mathbf{H_2}$, C(20)-$\mathbf{H_2}$, C(21)-$\mathbf{H_2}$, C(17)-**H**, C(8)-**H**), 0.94 (m, 19H, C(7)OSi($CH_2C\mathbf{H_3}$)$_3$, C(11)OSi($CH_2C\mathbf{H_3}$)$_3$) 0.59 (m, 12H, C(7)OSi($C\mathbf{H_2}CH_3$)$_3$, C(11)OSi($C\mathbf{H_2}CH_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9, 156.3, 138.8, 131.5, 128.1, 124.6, 123.6, 118.2, 117.9, 87.7, 61.4, 60.8, 51.7, 50.2, 39.4, 36.3, 34.2, 32.5, 29.5, 29.3, 28.9, 17.9, 6.9, 6.8, 6.3, 4.4; IR (thin film) 2953, 2918, 2882, 2358, 2331, 1685, 1632, 1583, 1458, 1418, 1352, 1214, 1169, 1112, 1005, 854 cm^{-1}. HRMS (FAB+) calculated for $C_{34}H_{61}O_4Si_2$ 589.4108, found 589.4086.

***Z*-Enoltriflate 8 & *E*-enoltriflate 9**: To a solution of 491 mg (0.834 mmol) β-diketone **7** and 146 μl (0.834 mmol) HMPA in 3 ml THF at –78 °C was added 2.17 ml (1.08 mmol) of KHMDS (0.50 M in toluene). The reaction mixture was warmed to –10 °C for 30 minutes then cooled to –78 °C. To the cooled solution was added 520 mg (1.32 mmol) of 2-[*N*,*N*-bis(trifluoromethylsulfonyl)amino]-5-chloropyridine (Comins' reagent[2]) in 2 ml of THF by cannula (1 ml THF rinse). The reaction was allowed to warm to room temperature over 2 hours. The reaction was quenched by the addition of 6 ml saturated aqueous $NaHCO_3$ and the mixture was diluted with 15 ml Et_2O. The layers were separated and the aqueous layer was extracted with 3 x 20 ml Et_2O and 1 x 20 ml hexanes. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel eluting with 20 - 30% benzene/hexanes to give 262 mg (0.363 mmol, 44% yield) of *E*-enoltriflate **9** and 201 mg (0.279 mmol, 33% yield) of *Z*-enoltriflate **8**. Characterization data for *Z*-

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(2) Comins, D. L.; Dehghani, A. *Tet. Lett.* **1992,** *33,* 6299-6302.

enoltriflate **8**: ^{1}H NMR (300 MHz, C_6D_6) δ 5.97 (dd, 1H, *J* = 17.1 and 11.3 Hz, C(28)-**H**), 5.76 (dd, 1H, *J* = 17.7 and 10.9, C(12)-**H**), 5.69 (d, 1H, *J* = 17.1 Hz, *trans*-C(29)-**H**), 5.46 (m, 2H, C(23)-**H**, C(24)-**H**), 5.11 (m, 2H, *trans*-C(13)-**H**, *cis*-C(29)-**H**), 4.94 (d, 1H, *J* = 10.8 Hz, *cis*-C(13)-**H**), 3.72 (m, 1H, C(7)-**H**), 3.60 (m, 1H, C(7)-**H**), 2.97 (s, 1H, C(10)-**H**), 2.79 (m, 1H, C(9)-**H**), 2.77 (s, 1H, C(16)-**H**), 2.02 (m, 2H, C(22)-$\mathbf{H_2}$), 1.85 (m, 2H, C(18)-$\mathbf{H_2}$), 1.78 (m, 1H, C(8)-**H**), 1.65 (m, 4H, C(25)-$\mathbf{H_3}$, C(8)-**H**), 1.54 (m, 1H, C(17)-**H**), 1.35 (m, 6H, C(19)-$\mathbf{H_2}$, C(20)-$\mathbf{H_2}$, C(21)-$\mathbf{H_2}$), 1.00 (m, 18H, C(7)OSi($CH_2C\mathbf{H_3}$)$_3$, C(11)OSi($CH_2C\mathbf{H_3}$)$_3$) 0.60 (m, 12H, C(7)OSi($C\mathbf{H_2}CH_3$)$_3$, C(11)OSi($C\mathbf{H_2}CH_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 139.4, 137.7, 134.2, 131.4, 126.6, 124.7, 123.8, 119.6, 85.0, 61.9, 60.4, 53.3, 50.5, 39.6, 35.4, 34.6, 32.5, 29.5, 29.3, 28.7, 17.9, 6.9, 6.8, 6.3, 4.4; IR (thin film) 2958, 2926, 2885, 2356, 1872, 1737, 1638, 1602, 1462, 1432, 1306, 1213, 1140, 1000, 969, 938, 901, 839, 741 cm^{-1}. HRMS (FAB+) calculated for $C_{35}H_{60}F_3O_6SSi_2$: 721.3601, found 721.3580. Characterization data for *E*-enoltriflate **9**: ^{1}H NMR (300 MHz, C_6D_6) δ 7.68 (dd, 1H, *J* = 17.3 and 11.5 Hz, C(28)-**H**), 5.96 (dd, 1H, *J* = 17.7 and 10.8 Hz, C(12)-**H**), 5.68 (d, 1H, *J* = 17.3, *trans*-C(29)-**H**), 5.45 (m, 2H, C(23)-**H**, C(24)-**H**), 5.14 (d, 1H, *J* = 17.7 Hz, *trans*-C(13)-**H**), 5.06 (d, 1H, *J* = 11.5 Hz, *cis*-C(29)-**H**), 4.87 (d, 1H, *J* = 10.8 Hz), 3.73 (m, 1H, C(7)-**H**), 3.64 (m, 1H, C(7)-**H**), 3.36 (s, 1H, C(16)-**H**), 3.05 (s, 1H, C(10)-**H**), 2.82 (m, 1H, C(9)-**H**), 2.04 (m, 3H, C(22)-$\mathbf{H_2}$, C(18)-**H**), 1.93 (m, 1H, C(18)-**H**), 1.71 (m, 2H, C(17)-**H**, C(8)-**H**), 1.61 (m, 3H, C(25)-$\mathbf{H_3}$), 1.47 (m, 7H, C(8)-**H**, C(19)-$\mathbf{H_2}$, C(20)-$\mathbf{H_2}$, C(21)-$\mathbf{H_2}$) 1.00 (m, 18H, C(7)OSi($CH_2C\mathbf{H_3}$)$_3$, C(11)OSi($CH_2C\mathbf{H_3}$)$_3$) 0.60 (m, 12H, C(7)OSi($C\mathbf{H_2}CH_3$)$_3$, C(11)OSi($C\mathbf{H_2}CH_3$)$_3$); ^{13}C NMR (75 MHz, C_6D_6) δ 200.1, 145.4, 138.7, 134.8, 131.8, 127.6, 124.8, 121.9, 120.6, 119.1, 117.4, 85.4, 62.8, 60.8, 54.2, 50.1, 40.2, 36.4, 35.5, 32.9, 30.0, 29.8, 28.8, 18.1, 7.1, 7.1, 7.0, 6.7, 6.6, 4.8; IR (thin film) 2958, 2916, 2885, 2366, 1867, 1732, 1643, 1601, 1462, 1420, 1301, 1223, 1135, 1109, 1005, 969, 917, 829, 741 cm^{-1}. HRMS (FAB+) calculated for $C_{35}H_{60}F_3O_6SSi_2$: 721.3601, found 721.3616.

Hydroxy-(*Z*)-Enoltriflate (3): To a solution of 201 mg (0.279 mmol) *Z*-enoltriflate **8** in 5 ml of THF was added 1.5 ml of MeOH. The solution was cooled to –10 °C and 10 mg (0.065

mmol) of (1*S*)-(+)-10-camphorsulfonic acid was added. After 1 h the reaction was quenched by the addition of 1 ml aqueous saturated $NaHCO_3$ and the mixture was diluted with 25 ml Et_2O. The mixture was treated with $NaHCO_3$ and $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2 to give 156 mg (0.257 mmol, 92% yield) of *Z*-enoltriflate **3** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (dd, 1H, *J* = 17.1 and 11.3 Hz, C(28)-**H**), 5.72 (m, 2H, C(12)-**H**, *trans*-C(29)-**H**), 5.46 (m, 2H, C(24)-**H**, C(23)-**H**), 5.11 (d, 1H, *J* = 17.7 Hz, *trans*-C(13)-**H**) 5.09 (d, 1H, *J* = 11.2 Hz, *cis*-C(29)-**H**), 4.65 (d, 1H, *J* = 10.8 Hz, *cis*-C(13)-**H**), 3.46 (m, 2H, C(7)-$\mathbf{H_2}$), 2.99 (d, 1H, *J* = 2.2 Hz, C(10)-**H**), 2.74 (s, 1H, C(16)-**H**), 2.59 (m, 1H, C(9)-**H**), 2.02 (m, 2H, C(22)-$\mathbf{H_2}$), 1.86 (m, 1H, C(18)-**H**), 1.75 (m, 1H, C(18)-**H**), 1.63 (m, 4H, C(25)-$\mathbf{H_3}$, C(8)-**H**), 1.55 (m, 1H, C(8)-**H**), 1.46 (m, 1H, C(17)-**H**), 1.31 (m, 6H, C(19)-$\mathbf{H_2}$, C(20)-$\mathbf{H_2}$, C(21)-$\mathbf{H_2}$), 0.94 (t, 9H, C(11)OSi($CH_2C\mathbf{H_3}$)$_3$) 0.55 (q, 6H, C(11)OSi($C\mathbf{H_2}CH_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 139.6, 137.6, 134.1, 131.4, 126.5, 124.7, 124.1, 119.7, 85.1, 62.2, 61.5, 53.1, 50.7, 40.7, 35.5, 34.6, 32.5, 29.5, 29.3, 28.8, 17.9, 6.8, 6.3; IR (thin film) 3445, 2926, 2885, 2356, 2335, 2251, 1877, 1732, 1638, 1602, 1431, 1306, 1213, 1140, 1000, 938, 907, 844, 735, 652, 611 cm^{-1}. HRMS (FAB+) calculated for $C_{29}H_{46}F_3O_6SSi$: 607.2736, found 607.2747.

Hydroxy-(*E*)-Enoltriflate (4): To a solution of 262 mg (0.363 mmol) *E*-enoltriflate **9** in 5 ml of THF was added 1.5 ml of MeOH. The solution was cooled to –10 °C and 10 mg (0.065 mmol) of (1*S*)-(+)-10-camphorsulfonic acid was added. After 1 h the reaction was quenched by the addition of 1 ml aqueous saturated $NaHCO_3$ and the mixture was diluted with 25 ml Et_2O. The mixture was treated with $NaHCO_3$ and $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica gel eluting with CH_2Cl_2 to give 206 mg (0.339 mmol, 93% yield) of *E*-enoltriflate **4** as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6) δ 7.66 (dd, 1H, *J* = 17.3 and 11.5 Hz, C(28)-**H**), 5.94 (dd, 1H, *J* = 17.7 and 10.8 Hz, C(12)-**H**), 5.68 (d, 1H, *trans*-C(29)-**H**), 5.45 (m, 2H, C(24)-**H**, C(23)-**H**), 5.10 (d, 1H, *J* = 17.7 Hz, *trans*-C(13)-**H**), 5.07 (d, 1H, *J* = 11.5 Hz, *cis*-C(29)-**H**), 4.85 (d, 1H, *J* = 10.8 Hz, *cis*-C(13)-**H**), 3.47 (m, 2H, C(7)-$\mathbf{H_2}$), 3.33 (d, 1H, *J* = 1.8 Hz, C(16)-**H**), 3.04 (m, 1H, C(10)-**H**), 2.62 (m, 1H, C(9)-**H**), 2.04 (m, 3H, C(22)-$\mathbf{H_2}$, C(18)-**H**), 1.81 (m, 1H, C(18)-**H**), 1.63 (m, 4H, C(25)-$\mathbf{H_3}$, C(17)-**H**), 1.44

(m, 8H, C(19)-$\mathbf{H_2}$, C(20)-$\mathbf{H_2}$, C(21)-$\mathbf{H_2}$, C(8)-$\mathbf{H_2}$), 0.94 (t, 9H, C(11)OSi($CH_2C\mathbf{H_3}$)$_3$) 0.55 (q, 6H, C(11)OSi($C\mathbf{H_2}CH_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 145.5, 138.7, 134.8, 131.8, 127.5, 127.5, 124.9, 122.0, 120.6, 119.1, 117.4, 85.4, 62.9, 61.0, 54.0, 50.1, 40.9, 36.0, 35.4, 33.0, 30.2, 29.9, 29.8, 28.8, 18.1, 7.1, 6.6; IR (thin film) 3445, 2958, 2926, 2875, 2356, 2283, 1872, 1732, 1638, 1602, 1457, 1415, 1332, 1218, 1135, 1005, 969, 927, 824, 741 cm^{-1}. HRMS (FAB+) calculated for $C_{29}H_{46}F_3O_6SSi$: 607.2736, found 607.2747.

Silyl Enol Ether 10 from *Z*-enoltriflate 3: To a solution of 140 mg (0.231 mmol) *Z*-enoltriflate **3** in 10 ml benzonitrile was added 100 μl (0.577 mmol) diisopropylethylamine. The resulting solution was added by cannula (1 mL benzonitrile rinse) to a glass-lined Parr model 4700 pressure vessel under N_2, charged with 27 mg (0.023 mmol) of tetrakis(triphenylphosphine)palladium. The pressure gauge assembly was then attached and the apparatus was charged with 800 psi CO and vented three times. The apparatus was then pressurized to 800 psi CO and was heated at 70 °C (oil bath) for 4 h and then at 110 °C (oil bath) for 1 h. The pressure vessel was cooled and vented and the reaction mixture was concentrated. The residue was purified by flash chromatography on silica gel eluting with 5 - 10% Et_2O/hexanes to afford 51 mg (0.105 mmol, 46% yield) of **10** as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (dd, 1H, *J* = 17.4 and 10.6 Hz, C(28)-**H**), 5.74 (s, 1H, C(16)-**H**), 5.42 (m, 4H, C(29)-$\mathbf{H_2}$, C(24)-**H**, C(23)-**H**), 4.54 (m, 1H, C(12)-**H**), 3.90 (m, 2H, C(7)-$\mathbf{H_2}$), 2.62 (m, 2H, C(13)-**H**, C(10)-**H**), 2.48 (broad s, 1H, C(9)-**H**), 2.37 (d, 1H, C(13)-**H**), 2.16 (broad s, 1H, C(17)-**H**), 1.96 (broad s, 3H, C(22)-$\mathbf{H_2}$, C(8)-**H**), 1.60 (m, 4H, C(25)-$\mathbf{H_3}$, C(8)-**H**), 1.34 (m, 8H, C(18)-$\mathbf{H_2}$, C(19)-$\mathbf{H_2}$, C(20)-$\mathbf{H_2}$, C(21)-$\mathbf{H_2}$,), 0.95 (t, 9H, C(11)OSi($CH_2C\mathbf{H_3}$)$_3$) 0.65 (q, 6H, C(11)OSi($C\mathbf{H_2}CH_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.6, 149.0, 135.2, 133.0, 132.5, 131.3, 124.8, 117.5, 103.5, 61.4, 54.9, 51.0, 46.3, 41.9, 35.9, 33.9, 33.4, 32.5, 29.4, 29.0, 27.7, 17.9, 6.7, 4.9; IR (thin film) 2926, 2885, 2366, 2335, 2252, 1789, 1633, 1462, 1415, 1379, 1301, 1270, 1239, 1176, 1109, 1036, 1010, 974, 912, 839, 803, 735, 647 cm^{-1}. HRMS (FAB+) calculated for $C_{29}H_{45}O_4Si$: 485.3087, found 485.3081.

Silyl Enol Ether 10 from *E*-enoltriflate 4: To a solution of 67 mg (0.110 mmol) *E*-enoltriflate **4** in 10 ml benzonitrile was added 48 μl (0.276 mmol) diisopropylethylamine. The

resulting solution was added by cannula (1 mL benzonitrile rinse) to a glass-lined Parr model 4700 pressure vessel under N_2, charged with 13 mg (0.011 mmol) of tetrakis(triphenylphosphine)palladium. The pressure gauge assembly was then attached and the apparatus was charged with 800 psi CO and vented three times. The apparatus was then pressurized to 800 psi CO and was heated at 70 °C (oil bath) for 4 h and then at 110 °C (oil bath) for 1 h. The pressure vessel was cooled and vented and the reaction mixture was concentrated. The residue was purified by flash chromatography on silica gel eluting with 5 - 10% Et_2O/hexanes to afford 30 mg (0.062 mmol, 56% yield) of **10** as an oil which was spectroscopically identical to **10** formed from the reaction of *Z*-enoltriflate **3**.

Stereochemical Proof: The (*Z*)-geometry of the enoltriflate double bond of **3** was proven by the illustrated selective 1D NOESY experiment (Figure 1).

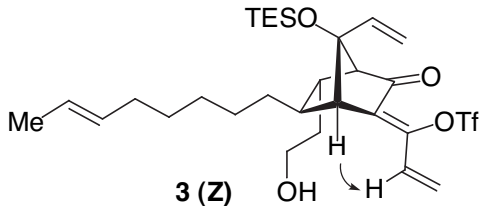

Figure 1. Observed selective 1D NOESY enhancement to establish the *Z* geometry of enoltriflate **3**.