Formation of Homoallyl Stannanes via Palladium Catalyzed Stannylative Cyclization of Enynes.

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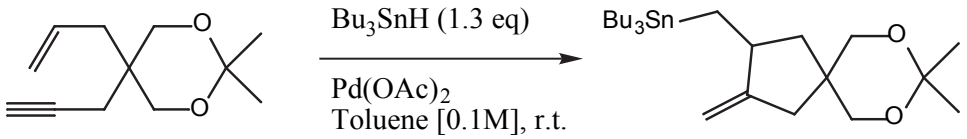
Experimental Procedures and Characterization Data

General Procedure for the Hydrostannation/Carbocyclization of 1,6-Enynes.

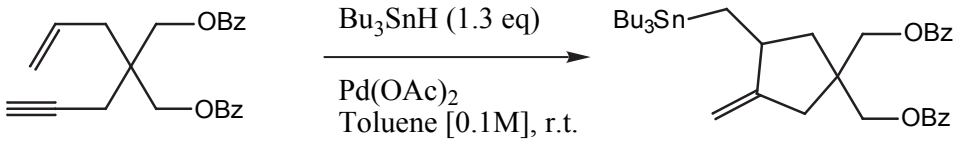
Palladium acetate (5-10 mol%) was added to a 0.1M solution of the enyne in freshly distilled and degassed toluene under argon, followed by dropwise additon of Bu_3SnH (1.3 eq dissolved in 1mL toluene) *via* syringe pump over 90 min. The dark brown solution was stirred a further 2 h before being filtered through a pad of Celite, and washing with diethyl ether. The filtrate was concentrated *in vacuo* and the residue purified by flash chromatography on normal silica gel using a mixture of Et_2O and hexanes as eluent. For NMR studies, 10µl of mesitylene or tetramethyl tin per 0.25 mmol of substrate used was added to the filtered crude residue.

8,8-Dimethyl-3-methylene-7,9-dioxa-spiro[4.5]dec-2-ylmethyl-(tri-*n*-butyl)stannane



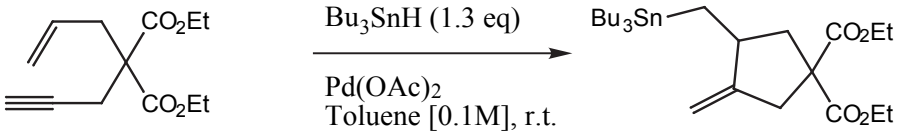
Enyne was treated according to the general procedure and purified by flash chromatography (hexanes, 5% ether/hexanes) to give a colorless oil. R_F = 0.42 (5% ether/hexanes). IR (neat) 2950, 2922, 2838, 1655, 1458, 1380, 1247, 1190, 1152, 1078, 1036, 877, 832, 733, 680 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.82 (2H, dd, *J* = 2.4 Hz, 21.2 Hz), 3.60 (4H, m), 2.64 (1H, m), 2.36 (2H, AB system, *J* = 16.8 Hz, 47.2 Hz), 1.93 (1H, m), 1.46 (7H, m) 1.43 (3H, s), 1.42 (3H, s), 1.26-1.33 (8H, m), 0.8-0.9 (15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 105.4, 97.8, 69.7, 68.4, 42.6, 40.4, 40.2, 39.3, 29.2, 27.4, 24.7, 23.0, 14.0, 13.7, 9.5. HRMS Calcd. for $C_{24}H_{45}O_2{}^{120}Sn$ [M]: 485.2441 Found: 485.2411.

Benzoic acid 1-benzoyloxymethyl-3-methylene-4-(tri-*n*-butylstannylmethyl)-cyclopentylmethyl ester



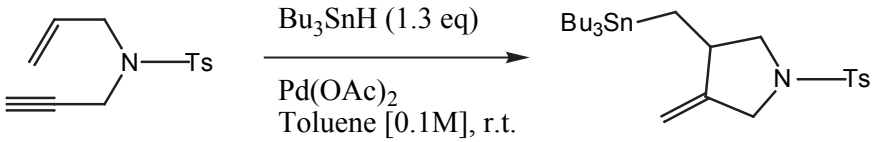
Enyne was treated according to the general procedure and purified by flash chromatography (hexanes, 10% ether/hexanes) to give a colorless oil (50%). R_F = 0.25 (5% ether/hexanes). IR (neat) 3070, 2957, 2922, 1722, 1602, 1451, 1370, 1264, 1176, 1113, 1067, 1025, 972, 906, 874, 737, 705 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (4H, dd, *J* = 1.2 Hz, 7.2 Hz), 7.57 (2H, t, *J* = 7.2 Hz), 7.43 (4H, t, *J* = 8 Hz), 4.92 (2H, dd, *J* =1.6 Hz, 13.2 Hz), 4.36 (4H, m), 2.83 (1H, m), 2.53 (2H, s), 2.12 (1H, dd, *J* = 8 Hz, 4.8 Hz), 1.41-1.5 (6H, m), 1.22-1.3 (10H, m), 0.8-0.9 (15H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 156.1, 133.0, 130.0, 129.9, 129.5, 128.3, 106.0, 68.8, 66.9, 43.8, 41.6, 40.4, 39.5, 29.8, 29.9, 27.3, 13.9, 13.6, 9.4. HRMS Calcd. for $C_{35}H_{50}O_4{}^{120}Sn$ [M]: 654.2731. Found 654.2717. Calcd. for $C_{31}H_{41}O_4{}^{120}Sn$ [M-(C_4H_9)]$^+$: 597.2026. Found 597.2024.

3-Methylene-4-(tri-*n*-butylstannylmethyl)-cyclopentane-1,1-dicarboxylic acid diethyl ester



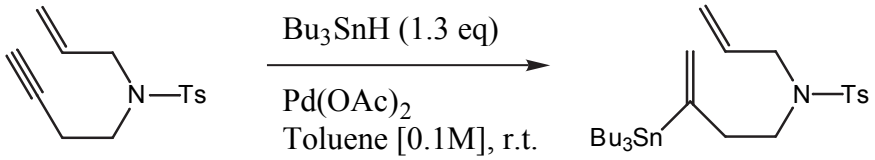
Enyne was treated according to the general procedure and purified by flash chromatography (hexanes, 10% ether/hexanes) to give a colorless oil (50%). R_F = 0.25 (5% ether/hexanes). IR (neat) 2957, 2922, 2859, 1729, 1651, 1458, 1366, 1275, 1250, 1226, 1176, 1092, 1067, 1036, 906, 877, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 4.87 (2H, dd, *J* = 2.4 Hz, 27.6 Hz), 4.18 (4H, m), 3.02 (2H, AB system, *J* = 20 Hz, 32 Hz), 2.68 (1H, m), 2.54 (1H, dd, *J* = 8 Hz, 4 Hz), 1.69 (1H, t, *J* = 12 Hz) 1.43-1.51 (6H, m), 1.22-1.34 (8H, m), 0.82-0.9 (15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 155.0, 105.4, 61.4, 57.8, 43.2, 41.2, 40.3, 29.3, 27.4, 13.7, 12.9, 9.4. HRMS Calcd. for $C_{21}H_{37}O_4{}^{120}Sn$ [M-(C_4H_9)]$^+$: 473.1713. Found 473.1721.

1-*p*-Toluenesulfonyl-3-methylene-4-(tri-*n*-butylstannylmethyl)-pyrrolidine



Enyne was treated according to the general procedure and purified by flash chromatography (hexanes, 10% ether/hexanes) to give a pale yellow oil (41%). R_F = 0.23 (10% ether/hexanes). IR (neat) 2957, 2915, 2852, 1669, 1595, 1489, 1458, 1412, 1342, 1307, 1159, 1092, 1046, 913, 811, 733, 659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (2H, d, *J* = 8.4 Hz), 7.33 (2H, d, *J* = 8 Hz), 4.87 (2H, dd, *J* = 2 Hz, 11.8 Hz), 3.87 (2H, AB system, *J* = 14 Hz, 92.4 Hz), 2.54 (1H, dd, *J* = 7.6 Hz, 1.2 Hz), 2.77 (1H, m), 2.58 (1H, t, *J* = 8 Hz), 2.44 (3H, s) 1.38-1.46 (6H, m), 1.23-1.32 (8H, m), 1.04 (1H, dd, J = 5.2 Hz, 8.4 Hz), 0.76-0.91 (15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.5, 132.8, 129.6, 127.8, 105.9, 56.1, 52.2, 41.3, 29.2, 29.1, 29.0, 27.3, 21.5, 13.7, 10.5, 9.5. HRMS Calcd. for $C_{21}H_{34}NO_2S^{120}Sn$ $[M-(C_4H_9)]^+$: 484.1332. Found 484.1335.

_N_-Allyl-_N_-(3-tri-_n_-butylstannyl-but-3-enyl)-_p_-toluenesulfonamide



Enyne was treated according to the general procedure and purified by flash chromatography (hexanes, 10% ether/hexanes) to give a colorless oil (58%). R_F = 0.32 (10% ether/hexanes). IR (neat) 2957, 2915, 2859, 1595, 1489, 1461, 1416, 1342, 1303, 1282, 1159, 1092, 986, 913, 811, 733, 659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (2H, d, *J* = 8.4 Hz), 7.29 (2H, d, *J* = 7.6 Hz), 5.67 (2H, m), 5.17 (3H, m), 3.83 (2H, d, J = 6 Hz), 3.12 (2H, m), 2.43 (5H, m), 1.41-1.5 (6H, m), 1.22-1.3 (8H, m), 0.8-0.9 (13H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 143.1, 137.3, 133.4, 129.6, 127.4, 127.1, 118.6, 50.7, 47.4, 39.5, 29.7, 29.1, 29.0, 28.9, 27.6, 27.3, 21.4, 13.6, 9.5. HRMS Calcd. for $C_{22}H_{36}NO_2S^{120}Sn$ $[M-(C_4H_9)]^+$: 498.1488. Found 498.1489.