Supporting Information

A stereoselective enyne cross metathesis

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General consideration:

Unless otherwise noted, materials were obtained from commercial supplier and used without further purification. Grubbs 2nd generation catalyst was purchased from Strem. Silica gel column chromatography was performed using Baxter brand silica gel (230-400 mesh ASTM). CH₂Cl₂ was distilled from CaH₂. Infrared (IR) spectra were recorded on a Nicolet 210 FT-IR spectrometer, ν_{max} in cm⁻¹. ¹H NMR and ¹³C NMR spectra were measured at 400MHz/100MHz on a Varian Gemini-400 instrument. Chemical shifts are reported with the solvent resonance as the internal standard (CHCl₃; 7.26 and 77.0). High Resolution Mass Spectral (HRMS) analyses were performed by the Mass Spectrometry Laboratory at Boston College.

General Procedure:

Alkyne (0.1mmol) and olefin (1.0mmol, 10 equivalent) were dissolved in CH₂Cl₂ (0.2ml) under ethylene atmosphere. Grubbs 2nd generation catalyst was added to the reaction mixture at room temperature. The reaction mixture was stirred for 24h at room temperature and concentrated under reduced pressure. Then the residue was purified by flash column chromatography on silica gel to afford the desired product.

(E)-3-Methylene-undec-4-en-1-yl benzoate (**4a**).

¹H NMR (400MHz, CDCl₃): 7.35-7.28 (m, 5H), 6.05 (d, *J* = 15.6Hz, 1H), 5.71 (dt, *J* = 15.6, 7.0Hz, 1H), 4.95 (s, 1H), 4.90 (s, 1H), 4.53 (s, 2H), 3.62 (t, *J* = 7.0Hz, 2H), 2.55 (t, *J* = 7.2Hz, 2H), 2.08 (q, *J* = 6.8Hz, 2H), 1.39-1.28 (m, 8H), 0.87 (t, *J* = 6.8Hz, 3H) ¹³C NMR (100MHz, CDCl₃): 142.8,

138.3, 131.6, 130.6, 128.2, 127.5, 127.4, 114.3, 72.9, 69.3, 32.9, 32.7, 31.8, 29.4, 29.0, 22.7, 14.2 IR (thin film, NaCl, cm^{-1}); 2955, 2920, 2849, 1602, 1454, 1359, 1205, 1104, 1033, 961, 884 **HRMS** (ESI) calcd. for $\text{C}_{19}\text{H}_{28}\text{ONa}$ 295.2033 found 295.2038

(E)-3-Methylene-oct-4-enyloxymethyl-benzene (**4b**).

^1H NMR (400MHz, CDCl_3): 7.35-7.28 (m, 5H), 6.06 (d, $J = 15.6\text{Hz}$, 1H), 5.71 (dt, $J = 16.0$, 7.0Hz, 1H), 4.95 (s, 1H), 4.90 (s, 1H), 4.53 (s, 2H), 3.62 (t, $J = 7.2\text{Hz}$, 2H), 2.55 (t, $J = 6.8\text{Hz}$, 2H), 2.09-2.04 (m, 2H), 1.45-1.36 (m, 2H), 0.89 (t, $J = 7.2\text{Hz}$, 3H) ^{13}C NMR (100MHz, CDCl_3): 142.7, 138.3, 131.8, 130.3, 128.2, 127.5, 127.4, 114.3, 72.9, 69.3, 35.0, 32.6, 22.6, 13.9 IR (thin film, NaCl, cm^{-1}); 3027, 2955, 2919, 2847, 1605, 1497, 1455, 1365, 1203, 1095, 1029, 957, 879 **HRMS** (ESI) calcd. for $\text{C}_{16}\text{H}_{22}\text{ONa}$ 253.1566 found 253.1568

(E)-(7-Bromo-3-methylene-hept-4-enyloxymethyl)-benzene (**4c**).

^1H NMR (400MHz, CDCl_3): 7.36-7.27 (m, 5H), 6.15 (d, $J = 15.6\text{Hz}$, 1H), 5.67 (dt, $J = 15.6$, 6.8Hz, 1H), 5.03 (s, 1H), 5.00 (s, 1H), 4.53 (s, 2H), 3.62 (t, $J = 7.2\text{Hz}$, 2H), 3.38 (t, $J = 7.0\text{Hz}$, 2H), 2.68-2.62 (m, 2H), 2.55 (t, $J = 7.0\text{Hz}$, 2H) ^{13}C NMR (100MHz, CDCl_3): 142.2, 138.2, 134.6, 128.2, 127.5, 127.4, 126.1, 116.1, 72.9, 69.0, 36.1, 32.5, 32.4 IR (thin film, NaCl, cm^{-1}); 3024, 2920, 2859, 1455, 1357, 1259, 1210, 1106, 971, 897 **HRMS** (ESI) calcd. for $\text{C}_{15}\text{H}_{19}\text{ONaBr}$ 317.0517 found 317.0517

(E)-Propionic acid 5-(2-benzyloxy-ethyl)-hexa-3,5-dienyl ester (**4d**)

^1H NMR (400MHz, CDCl_3): 7.35-7.27 (m, 5H), 6.14 (d, $J = 16.4\text{Hz}$, 1H), 5.66 (dt, $J = 16.0$, 7.0Hz, 1H), 5.00 (s, 1H), 4.96 (s, 1H), 4.53 (s, 2H), 4.11 (t, $J = 6.8\text{Hz}$, 2H), 3.61 (t, $J = 7.0\text{Hz}$, 2H), 2.54 (t, $J = 7.0\text{Hz}$, 2H), 2.45-2.40 (m, 2H), 2.32 (q, $J = 7.6\text{Hz}$, 2H), 1.13 (t, $J = 7.6\text{Hz}$, 3H) ^{13}C NMR (100MHz, CDCl_3): 174.2, 142.3, 138.3, 134.3, 128.2, 127.5, 127.4, 124.9, 115.5, 72.9, 69.1, 63.5, 32.5, 32.3, 27.7, 9.3 IR (thin film, NaCl, cm^{-1}); 3031, 2939, 2975, 2859, 1737, 1461, 1388, 1271, 1186, 1100, 1094, 1014, 971, 898 **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}$ 311.1624 found 311.1623

(E)-Toluene-4-sulfonic acid 3-methylene-undec-4-enyl ester (**4e**)

^1H NMR (400MHz, CDCl_3): 7.79 (d, $J = 8.4\text{Hz}$, 2H), 7.34 (d, $J = 8.4\text{Hz}$, 2H), 5.95 (d, $J = 15.6\text{Hz}$, 1H), 5.56 (dt, $J = 15.6, 7.0\text{Hz}$, 1H), 4.94 (s, 1H), 4.83 (s, 1H), 4.12 (t, $J = 7.4\text{Hz}$, 2H), 2.56 (t, $J = 7.2\text{Hz}$, 2H), 2.45 (s, 3H), 2.06-2.00 (m, 2H), 1.35-1.26 (m, 8H), 0.88 (t, $J = 6.8\text{Hz}$, 3H) ^{13}C NMR (100MHz, CDCl_3): 144.5, 140.3, 130.9, 130.8, 129.6, 127.8, 127.8, 115.6, 69.0, 32.8, 31.9, 31.8, 29.3, 29.0, 22.7, 21.8, 14.2 IR (thin film, NaCl, cm^{-1}): 2961, 2924, 2856, 1600, 1458, 1359, 1180, 1093, 963, 902, 815 **HRMS** (ESI) calcd. for $\text{C}_{19}\text{H}_{28}\text{O}_3\text{NaS}$ 359.1654 found 359.1657

(E)-Toluene-4-sulfonic acid 3-methylene-oct-4-enyl ester (**4f**)

^1H NMR (400MHz, CDCl_3): 7.79 (d, $J = 8.4\text{Hz}$, 2H), 7.34 (d, $J = 8.0\text{Hz}$, 2H), 5.96 (d, $J = 15.6\text{Hz}$, 1H), 5.55 (dt, $J = 15.6, 7.0\text{Hz}$, 1H), 4.94 (s, 1H), 4.84 (s, 1H), 4.12 (t, $J = 7.4\text{Hz}$, 2H), 2.56 (t, $J = 7.4\text{Hz}$, 2H), 2.45 (s, 3H), 2.01 (q, $J = 6.8\text{Hz}$, 2H), 1.41-1.32 (m, 2H), 0.87 (t, $J = 7.2\text{Hz}$, 3H) ^{13}C NMR (100MHz, CDCl_3): 144.5, 140.3, 131.0, 130.7, 129.6, 129.6, 127.8, 115.7, 69.0, 34.9, 31.9, 22.5, 21.7, 13.8 IR (thin film, NaCl, cm^{-1}): 2956, 2920, 2871, 1597, 1444, 1365, 1176, 1097, 969, 908, 816 **HRMS** (ESI) calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_3\text{NaS}$ 317.1174 found 317.1187

(E)-Toluene-4-sulfonic acid 7-bromo-3-methylene-hept-4-enyl ester (**4g**)

^1H NMR (400MHz, CDCl_3): 7.80-7.78 (m, 2H), 7.34 (d, $J = 8.0\text{Hz}$, 2H), 6.06 (d, $J = 16.0\text{Hz}$, 1H), 5.54 (dt, $J = 16.0, 6.8\text{Hz}$, 1H), 5.03 (s, 1H), 4.94 (s, 1H), 4.13 (t, $J = 7.4\text{Hz}$, 2H), 3.36 (t, $J = 6.8\text{Hz}$, 2H), 2.64-2.56 (m, 4H), 2.45 (s, 3H) ^{13}C NMR (100MHz, CDCl_3): 144.6, 139.8, 133.7, 133.0, 129.7, 127.8, 126.5, 117.5, 68.7, 35.9, 32.2, 31.8, 21.8 IR (thin film, NaCl, cm^{-1}): 3027, 2965, 2921, 1602, 1367, 1100, 976, 914, 815. **HRMS** (ESI) calcd. for $\text{C}_{15}\text{H}_{19}\text{O}_5\text{NaSBr}$ 381.0131 found 381.0136

(E)-Propionic acid 5-[2-(toluene-4-sulfonyloxy)-2-ethyl]-hexa-3,5-dienyl ester (**4h**)

^1H NMR (400MHz, CDCl_3): 7.78 (d, $J = 8.8\text{Hz}$, 2H), 7.34 (d, $J = 8.0\text{Hz}$, 2H), 6.04 (d, $J = 16.0\text{Hz}$, 1H), 5.59 (dt, $J = 16.0, 7.2\text{Hz}$, 1H), 4.99 (s, 1H), 4.90 (s, 1H), 4.12 (t, $J = 7.2\text{Hz}$, 2H), 4.08 (t, $J = 6.6\text{Hz}$, 2H), 2.54 (t, $J = 7.2\text{Hz}$, 2H), 2.45 (s, 3H), 2.41-2.35 (m, 2H), 2.31 (q, $J = 7.6\text{Hz}$, 2H), 1.12 (t, $J = 7.6\text{Hz}$, 3H) ^{13}C NMR (100MHz, CDCl_3): 174.2, 144.5, 139.9, 133.4, 133.0, 129.7, 127.8, 125.4, 116.9, 68.7, 63.3, 32.2, 31.7, 27.7, 21.7, 9.3 IR (thin film, NaCl, cm^{-1}): 2985, 2953, 2916, 1739, 1602, 1459, 1365, 1272, 1179, 1098, 1023, 973, 917, 817 **HRMS** (ESI) calcd. for $\text{C}_{18}\text{H}_{24}\text{O}_5\text{NaS}$ 375.1246 found 375.1242

(E)-*tert*-Butyl-(2-methylene-dec-3-enyloxy)-diphenylsilane (**4i**)

^1H NMR (400MHz, CDCl_3): 7.71-7.69 (m, 4H), 7.45-7.37 (m, 6H), 6.06 (d, $J = 16.4\text{Hz}$, 1H), 5.54 (dt, $J = 16.0, 6.8\text{Hz}$, 1H), 5.35 (d, $J = 2.0\text{Hz}$, 1H), 5.04 (s, 1H), 4.36 (s, 2H), 2.02 (q, $J = 6.8\text{Hz}$, 2H), 1.34-1.23 (m, 8H), 1.07 (s, 9H), 0.87 (t, $J = 7.2\text{Hz}$, 3H), ^{13}C NMR (100MHz, CDCl_3): 144.3, 135.4, 133.5, 130.1, 129.5, 129.3, 127.5, 112.1, 63.7, 33.2, 31.8, 29.3, 29.0, 26.9, 22.7, 19.4, 14.2 IR (thin film, NaCl, cm^{-1}): 2963, 2926, 2845, 1475, 1426, 1111, 963, 895, 814 **HRMS** (ESI) calcd. for $\text{C}_{27}\text{H}_{38}\text{ONaSi}$ 429.2580 found 429.2590

(E)-(6-Bromo-2-methylene-hex-3-enyloxy)-*tert*-butyl-diphenylsilane (**4j**)

^1H NMR (400MHz, CDCl_3): 7.71-7.68 (m, 4H), 7.45-7.36 (m, 6H), 6.15 (d, $J = 16.0\text{Hz}$, 1H), 5.51 (dt, $J = 16.0, 7.0\text{Hz}$, 1H), 5.41 (d, $J = 1.6\text{Hz}$, 1H), 5.11 (s, 1H), 4.35 (s, 2H), 3.34 (t, $J = 7.2\text{Hz}$, 2H), 2.60 (q, $J = 7.0\text{Hz}$, 2H), 1.07 (s, 9H) ^{13}C NMR (100MHz, CDCl_3): 143.7, 135.4, 133.4, 132.3, 129.5, 127.6, 125.7, 114.1, 63.5, 36.5, 32.1, 26.9, 19.4 IR (thin film, NaCl, cm^{-1}): 2956, 2931, 2895, 2853, 1476, 1427, 1391, 1361, 1264, 1203, 1112, 966, 900, 827 **HRMS** (ESI) calcd. for $\text{C}_{23}\text{H}_{29}\text{ONaSiBr}$ 451.1068 found 451.1069

(E)-Propionic acid 5-(*tert*-butyl-diphenyl-silanyloxymethyl)-hexa-3,5-dienyl ester (**4k**)

^1H NMR (400MHz, CDCl_3): 7.70-7.68 (m, 4H), 7.43-7.37 (m, 6H), 6.14 (d, $J = 16.0\text{Hz}$, 1H), 5.50 (dt, $J = 16, 7.0\text{Hz}$, 1H), 5.40 (d, $J = 1.6\text{Hz}$, 1H), 5.08 (s, 1H), 4.34 (s, 2H), 4.06 (t, $J = 7.0\text{Hz}$, 2H), 2.39-2.34 (m, 2H), 2.28 (q, $J = 7.6\text{Hz}$, 2H), 1.10 (t, $J = 7.8\text{Hz}$, 3H), 1.07 (s, 9H) ^{13}C NMR (100MHz, CDCl_3): 174.2, 143.9, 135.3, 133.4, 132.0, 129.5, 127.6, 124.6, 113.5, 63.5, 63.5, 32.5, 27.7, 26.9, 19.4, 9.3 IR (thin film, NaCl, cm^{-1}): 2956, 2896, 2853, 1737, 1474, 1425, 1388, 1351, 1180, 1112, 1082, 1014, 959, 818 **HRMS** (ESI) calcd. for $\text{C}_{26}\text{H}_{34}\text{O}_3\text{NaSi}$ 445.2179 found 445.2175

(E)-Acetic acid 4-methylene-dodec-5-enyl ester (**4l**)

^1H NMR (400MHz, CDCl_3): 6.05 (d, $J = 16.0\text{Hz}$, 1H), 5.69 (dt, $J = 16.0, 7.0\text{Hz}$, 1H), 4.91 (s, 1H), 4.85 (s, 1H), 4.09 (t, $J = 6.6\text{Hz}$, 2H), 2.28-2.24 (m, 2H), 2.12-2.05 (m, 2H), 2.06 (s, 3H), 1.86-1.78 (m, 2H), 1.41-1.27 (m, 8H), 0.88 (t, $J = 6.8\text{Hz}$, 3H) ^{13}C NMR (100MHz, CDCl_3): 170.9, 144.9, 131.5,

130.5, 113.4, 64.2, 32.9, 31.8, 29.5, 29.0, 28.6, 27.3, 22.7, 21.1, 14.2 IR (thin film, NaCl, cm^{-1}); 2953, 2923, 2849, 1742, 1460, 1393, 1387, 1234, 1038, 965, 891 **HRMS** (ESI) calcd. for $\text{C}_{15}\text{H}_{26}\text{O}_2\text{Na}$ 261.1839 found 261.1831

(E)-Acetic acid 4-methylene-non-5-enyl ester (**4m**)

^1H NMR (400MHz, CDCl_3): 6.05 (d, $J = 15.6\text{Hz}$, 1H), 5.69 (dt, $J = 15.6, 7.0\text{Hz}$, 1H), 4.91 (s, 1H), 4.86 (s, 1H), 4.09 (t, $J = 6.8\text{Hz}$, 2H), 2.27 (t, $J = 7.2\text{Hz}$, 2H), 2.11-2.04 (m, 2H), 1.85 (m, 2H), 1.47-1.38 (m, 2H), 0.91 (t, $J = 7.2\text{Hz}$, 3H) ^{13}C NMR (100MHz, CDCl_3): 170.9, 144.9, 131.7, 130.2, 113.5, 64.2, 35.0, 28.6, 27.3, 22.7, 21.1, 13.9 IR (thin film, NaCl, cm^{-1}); 2945, 2917, 2873, 1741, 1457, 1363, 1237, 1042, 966, 891 **HRMS** (ESI) calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_2\text{Na}$ 219.1358 found 219.1361

(E)-Acetic acid 8-bromo-4-methylene-oct-5-enyl ester (**4n**)

^1H NMR (400MHz, CDCl_3): 6.15 (d, $J = 15.6\text{Hz}$, 1H), 5.67 (dt, $J = 16.0, 7.2\text{Hz}$, 1H), 4.99 (s, 1H), 4.95 (s, 1H), 4.09 (t, $J = 6.6\text{Hz}$, 2H), 3.41 (t, $J = 7.2\text{Hz}$, 2H), 2.69-2.64 (m, 2H), 2.27 (t, $J = 7.2\text{Hz}$, 2H), 2.06 (s, 3H), 1.86-1.79 (m, 2H) ^{13}C NMR (100MHz, CDCl_3): 170.9, 144.3, 134.4, 126.0, 115.2, 64.1, 36.1, 32.5, 28.4, 27.1, 21.1 IR (thin film, NaCl, cm^{-1}); 2963, 1737, 1467, 1394, 1363, 1241, 1044, 971, 897. **HRMS** (ESI) calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_2\text{NaBr}$ 283.0311 found 283.0310

2-(*tert*-Butyl-diphenyl-silanyloxymethyl)-5-trimethylsilanyl-penta-1,3-diene (**4o**)

E isomer: ^1H NMR (400MHz, CDCl_3): 7.72-7.69 (m, 4H), 7.45-7.36 (m, 6H), 5.93 (d, $J = 16.0\text{Hz}$, 1H), 5.59 (dt, $J = 16.0, 8.0\text{Hz}$, 1H), 5.26 (d, $J = 2.0\text{Hz}$, 1H), 4.97 (s, 1H), 4.34 (s, 2H), 1.48 (d, $J = 8.4\text{Hz}$, 2H), 1.08 (s, 9H), -0.02 (s, 9H)

Z isomer: ^1H NMR (400MHz, CDCl_3): 7.72-7.69 (m, 4H), 7.45-7.36 (m, 6H), 5.64 (d, $J = 11.6\text{Hz}$, 1H), 5.52 (dt, $J = 11.6, 9.0\text{Hz}$, 1H), 5.47 (d, $J = 2.0\text{Hz}$, 1H), 5.06 (s, 1H), 4.17 (s, 2H), 1.67 (dd, $J = 8.8, 1.2\text{Hz}$, 2H), 1.07 (s, 9H), -0.04 (s, 9H)

(5-Butoxy-2-methylene-pent-3-enyloxy)-*tert*-butyl-diphenylsilane (**4p**)

E isomer: ^1H NMR (400MHz, CDCl_3): 7.72-7.70 (m, 4H), 7.45-7.36 (m, 6H), 6.27 (d, $J = 16.0\text{Hz}$, 1H),

5.60 (dt, $J = 16.0, 6.2\text{Hz}$, 1H), 5.50 (d, $J = 2.0\text{Hz}$, 1H), 5.16 (s, 1H), 4.37 (s, 2H), 3.95 (dd, $J = 6.0, 1.2\text{Hz}$, 2H), 3.34 (t, $J = 6.8\text{Hz}$, 2H), 1.57-1.51 (m, 2H), 1.40-1.30 (m, 2H), 1.07 (s, 9H), 0.9 (t, $J = 7.4\text{Hz}$, 3H)
 Z isomer (characteristic peaks): ^1H NMR (400MHz, CDCl_3): d, $J = 10.8\text{Hz}$, 1H), 5.71 (dt, $J = 12.0, 6.2\text{Hz}$, 1H), 5.46 (d, $J = 2.0\text{Hz}$, 1H), 4.92 (s, 1H), 4.16 (s, 2H), 4.11 (dd, $J = 6.0, 1.6\text{Hz}$, 2H)

(E)-Acetic acid 4-(tert-butyl-diphenyl-silanyloxymethyl)-penta-2,4-dienyl ester (**4q**)

^1H NMR (400MHz, CDCl_3): 7.70-7.62 (m, 4H), 7.46-7.34 (m, 6H), 6.31 (d, $J = 16.0\text{Hz}$, 1H), 5.61 (dt, $J = 16.0, 6.4\text{Hz}$, 1H), 5.52 (d, $J = 1.6\text{Hz}$, 1H), 5.20 (s, 1H), 4.55 (d, $J = 6.8\text{Hz}$, 2H), 4.36 (s, 2H), 2.05 (s, 3H), 1.07 (s, 9H) ^{13}C NMR (100MHz, CDCl_3): 170.5, 143.2, 135.3, 133.5, 133.3, 129.6, 127.6, 122.3, 115.8, 65.1, 63.3, 26.9, 21.1, 19.4 IR (thin film, NaCl, cm^{-1}): 2960, 2929, 2855, 1736, 1477, 1428, 1366, 1238, 1115, 1035, 967, 832 **HRMS** (ESI) calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_3\text{NaSi}$ 417.1862 found 417.1862

Toluene-4-sulfonic acid 6-butoxy-3-methylene-hex-4-enyl ester (**4r**)

E isomer: ^1H NMR (400MHz, CDCl_3): 7.78 (d, $J = 8.4\text{Hz}$, 2H), 7.34 (d, $J = 8.4\text{Hz}$, 2H), 6.18 (d, $J = 16.4\text{Hz}$, 1H), 5.65 (dt, $J = 16.0, 6.0\text{Hz}$, 1H), 5.06 (s, 1H), 4.96 (s, 1H), 4.14 (t, $J = 7.2\text{Hz}$, 2H), 3.97 (dd, $J = 6.0, 1.2\text{Hz}$, 2H), 3.40 (t, $J = 6.6\text{Hz}$, 2H), 2.57 (t, $J = 5.6\text{Hz}$, 2H), 2.45 (s, 3H), 1.58-1.56 (m, 2H), 1.40-1.32 (m, 2H), 0.92 (t, $J = 7.2\text{Hz}$, 3H)

Z isomer (characteristic peaks): ^1H NMR (400MHz, CDCl_3): 5.81 (d, $J = 11.6\text{Hz}$, 1H), 5.69 (dt, $J = 12.0, 6.4\text{Hz}$, 1H), 5.05 (d, $J = 1.2\text{Hz}$, 1H), 4.84 (s, 1H)

(E)-Acetic acid 4-[2-(toluene-4-sulfonyloxy)-ethyl]-penta-2,4-dienyl ester (**4s**)

^1H NMR (400MHz, CDCl_3): 7.79 (dd, $J = 8.4, 1.6\text{Hz}$, 2H), 7.34 (d, $J = 8.0\text{Hz}$, 2H), 6.22 (d, $J = 16.4\text{Hz}$, 1H), 5.65 (dt, $J = 16.0, 6.4\text{Hz}$, 1H), 5.11 (s, 1H), 5.02 (s, 1H), 4.57 (dd, $J = 6.4, 0.8\text{Hz}$, 2H), 4.14 (t, $J = 7.2\text{Hz}$, 2H), 2.57 (t, $J = 6.4\text{Hz}$, 2H), 2.45 (s, 3H), 2.07 (s, 3H) ^{13}C NMR (100MHz, CDCl_3): 170.5, 144.6, 139.4, 134.9, 132.9, 129.7, 127.8, 123.1, 119.2, 68.4, 64.6, 31.5, 21.8, 21.1 IR (thin film, NaCl, cm^{-1}): 2960, 1739, 1604, 1446, 1360, 1244, 1201, 1183, 1104, 1024, 969, 908, 823 **HRMS** (ESI) calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{NaS}$ 347.0921 found 347.0929

[4-(2-Benzoyloxy-ethyl)-penta-2,4-dienyl]-trimethylsilane (**4u**)

E isomer: ^1H NMR (400MHz, CDCl_3): 7.35-7.74 (m, 3H), 7.30-7.28 (m, 2H), 5.93 (d, $J = 15.6\text{Hz}$, 1H), 5.73 (dt, $J = 15.6, 8.4\text{Hz}$, 1H), 4.88 (d, $J = 1.6\text{Hz}$, 1H), 4.82 (s, 1H), 4.53 (s, 2H), 3.61 (t, $J = 7.4\text{Hz}$, 2H), 2.54 (t, $J = 7.0\text{Hz}$, 2H), 1.53 (d, $J = 8.0\text{Hz}$, 2H), 0.00 (s, 9H)

Z isomer: ^1H NMR (400MHz, CDCl_3): 7.35-7.74 (m, 3H), 7.30-7.28 (m, 2H), 5.70 (d, $J = 11.6\text{Hz}$, 1H), 5.52 (dt, $J = 11.6, 9.0\text{Hz}$, 1H), 5.01 (s, 1H), 4.94 (s, 1H), 4.52 (s, 2H), 3.57 (t, $J = 7.2\text{Hz}$, 2H), 2.45 (t, $J = 7.0\text{Hz}$, 2H), 1.73 (dd, $J = 8.8, 1.6\text{Hz}$, 2H), 0.03 (s, 9H)

Acetic acid 4-methylene-7-trimethylsilanyl-hept-5-enyl ester (**4v**)

E isomer: ^1H NMR (400MHz, CDCl_3): 5.91 (d, $J = 15.6\text{Hz}$, 1H), 5.73 (d, $J = 15.6, 8.0\text{Hz}$, 1H), 4.83 (s, 1H), 4.77 (s, 1H), 4.08 (t, $J = 6.6\text{Hz}$, 2H), 2.25 (t, $J = 7.6\text{Hz}$, 2H), 2.05 (s, 3H), 1.84-1.73 (m, 2H), 1.54 (d, $J = 8.4\text{Hz}$, 2H), 0.00 (s, 9H)

Z isomer: ^1H NMR (400MHz, CDCl_3): 5.67 (d, $J = 11.6\text{Hz}$, 1H), 5.53 (dt, $J = 11.6, 8.8\text{Hz}$, 1H), 4.95 (s, 1H), 4.88 (s, 1H), 4.06 (t, $J = 6.8\text{Hz}$, 2H), 2.16 (t, $J = 7.8\text{Hz}$, 2H), 2.04 (s, 3H), 1.83-1.72 (m, 2H), 1.72 (dd, $J = 8.4, 1.6\text{Hz}$, 2H), 0.02 (s, 9H)

(E)-5-trimethylsilanyl-2-triphenylsilyl-penta-1,3-diene (**4w**)

^1H NMR (400MHz, CDCl_3): 7.62-7.58 (m, 6H), 7.42-7.33 (m, 9H), 6.25 (d, $J = 15.6\text{Hz}$, 1H), 5.94 (d, $J = 3.2\text{Hz}$, 1H), 5.54 (dt, $J = 15.6, 8.0\text{Hz}$, 1H), 5.21 (d, $J = 3.2\text{Hz}$, 1H), 1.40 (dd, $J = 8.0, 1.2\text{Hz}$, 2H), 0.15 (s, 9H) ^{13}C NMR (100MHz, CDCl_3): 143.8, 136.1, 134.4, 133.2, 132.9, 131.1, 129.2, 127.6, 14.6, 1.9 IR (thin film, NaCl, cm^{-1}): 3067, 3037, 2994, 2951, 2891, 1430, 1248, 1144, 1108, 955, 846