

Synthesis of Highly Substituted Allenylsilanes by Alkylidenation of Silylketenes

Stephen P. Marsden* and Pascal C. Ducept

Experimental section

This document contains full experimental protocols for the preparation of silyldiazoketones **2**, silylketenes **1** and all allenylsilanes **6**, **7**, and **14-19**.

Experimental

General procedure for the preparation of silyldiazoketones 2

1-Diazo-1-triethylsilylpropan-2-one 2a

Triethylsilyl trifluoromethanesulfonate (0.35 ml, 1.56 mmol) was added dropwise to a stirred solution of 1-diazopropan-2-one (0.094 g, 1.12 mmol) and dry DIPEA (0.39 ml, 2.24 mmol) in diethyl ether (5 ml) at 0°C. After 30 min, the reaction mixture was allowed to warm to rt, diluted with ether (10 ml) and washed successively with a saturated aqueous sodium hydrogen carbonate solution (2 ml), a saturated ammonium chloride solution (2 x 10 ml) and finally with brine (15 ml) and the combined organics dried (MgSO₄), filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield 1-diazo-1-triethylsilylpropan-2-one **2a** as a yellow liquid (0.181 g, 82 %).

ν_{\max} (KBr/film) 2961 s, 2878 s, 2066 s (C=N₂), 1732 s, 1643 s (C=O), 1464 m, 1359 m, 1270 s, 1203 s, 1018 s, 725 s cm⁻¹; δ_{H} (300 MHz, CDCl₃) 0.74 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.95 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 2.23 (3 H, s, CH₃); δ_{C} (75 MHz, CDCl₃) 2.7 SiCH₂CH₃, 6.8 SiCH₂CH₃, 26.4 CH₃, 53.3 C=N₂, 195.3 C=O; m/z (Cl⁺, NH₃) 199 ([M+H]⁺, 100), 102 (33), 85 ([M-SiEt₃+2H]⁺, 35); HRMS (Cl⁺) Found [M+H]⁺ 199.1267 C₉H₁₉N₂OSi, requires 199.1267

1-Diazo-1-triethylsilylnonan-2-one 2b

Carried out by the general procedure above, with 1-diazononan-2-one (1.36 g, 8.08 mmol), triethylsilyl trifluoromethanesulfonate (2.2 ml, 9.7 mmol) and DIPEA (2.1 ml, 12.1 mmol) in diethyl ether (40 ml). The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield 1-diazo-1-triethylsilylnonan-2-one **2b** as a yellow liquid (2.116 g, 93 %).

ν_{\max} (KBr/film) 2956 s, 2064 s (C=N₂), 1642 s (C=O), 1463 w, 1181 w, 1007 m, 725 w cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.74 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.85 (3 H, t, $J_{9-8} = 7$ Hz, H₉), 0.96 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 1.20-1.36 (8 H, m, H_{5,6,7,8}), 1.61 (2 H, p, $J = 7.5$ Hz, H₄), 2.48 (2 H,

t, $J_{3,4} = 7$ Hz, H₃); δ_C (75 MHz, CDCl₃) 3.0 SiCH₂CH₃, 7.1 SiCH₂CH₃, 14.0 C₉, 22.6 C₈, 24.7, 29.0, 29.2 C_{5,6,7}, 31.7 C₄, 39.2 C₃, 55.0 C=N₂, 198.8 C=O; m/z (Cl⁺, NH₃) 283 ([M+H]⁺, 15), 255 ([M-N₂+H]⁺, 100), 188 (30), 132 ([SiEt₃+NH₃]⁺, 61); HRMS (Cl⁺) Found [M+H]⁺ 283.2252 C₁₅H₃₁N₂OSi, requires 283.2206

1-Diazo-3-phenyl-1-triethylsilylpropan-2-one 2c

Carried out by the general procedure above, with 1-diazo-3-phenylpropan-2-one (0.8 g, 5 mmol), triethylsilyl trifluoromethanesulfonate (1.35 ml, 6 mmol) and DIPEA (1.3 ml, 7.5 mmol) in diethyl ether (20 ml). The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield 1-diazo-3-phenyl-1-triethylsilylpropan-2-one **2c** as a yellow liquid (2.116 g, 93 %).

ν_{\max} (KBr/film) 2955 s, 2910 m, 2876 m, 2066 s (C=N₂), 1637 s (C=O), 1454 w, 1414 w, 1280 m, 1200 m, 1005 m, 725 s, 701 s cm⁻¹; δ_H (300 MHz, CDCl₃) 0.72 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.91 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 3.82 (2 H, s, H₃), 7.20-7.34 (5 H, m, Ph); δ_C (75 MHz, CDCl₃) 2.9 SiCH₂CH₃, 7.0 SiCH₂CH₃, 46.4 PhCH₂, 52.6 C=N₂, 126.9 C_{4'}, 128.6 C_{2'} or C_{3'}, 129.1 C_{3'} or C_{2'}, 134.4 C_{1'}, 195.6 C=O; m/z (Cl⁺, NH₃) 275 ([M+H]⁺, 92), 247 ([M-N₂+H]⁺, 100), 161 ([M-SiEt₃+H]⁺, 49), 132 ([SiEt₃+NH₃]⁺, 55), 104 (40), 91 ([PhCH₂]⁺, 43); HRMS (Cl⁺) Found [M+H]⁺ 275.1575 C₁₅H₂₃N₂OSi, requires 275.1579

1-Cyclohexyl-2-diazo-2-triethylsilylethan-1-one 2d

Carried out by the general procedure above with 1-cyclohexyl-2-diazoethan-1-one (1.05 g, 6.9 mmol), triethylsilyl trifluoromethanesulfonate (1.9 ml, 8.28 mmol) and DIPEA (1.8 ml, 10.35 mmol) in diethyl ether (30 ml). The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield 1-cyclohexyl-2-diazo-2-triethylsilylethan-1-one **2d** as a yellow liquid (1.74 g, 94 %).

ν_{\max} (KBr/film) 2933 s, 2875 m, 2856 m, 2061 s (C=N₂), 1641 s (C=O), 1452 w, 1251 m, 1214 m, 1187 m, 1172 m, 1006 w, 727 m, 700 w cm⁻¹; δ_H (300 MHz, CDCl₃) 0.71 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.92 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 1.13-1.48 (6 H, m, H_{3',4'}), 1.62-1.78 (4 H, m,

H₂), 2.57 (1 H, tt, $J = 11$ Hz, H₁); δ_C (75 MHz, CDCl₃) 2.9 SiCH₂CH₃, 7.0 SiCH₂CH₃, 25.6, 29.0 C_{2,3}, 25.7 C₄, 47.2 C₁, 50.6 C=N₂, 202.0 C=O; m/z (Cl⁺, NH₃) 267 ([M+H]⁺, 100), 256 ([M-N₂+NH₄]⁺, 20), 239 ([M-N₂+H]⁺, 85), 132 ([SiEt₃+NH₃]⁺, 31), 119 (24); HRMS (Cl⁺) Found [M+H]⁺ 267.1880 C₁₄H₂₇N₂OSi, requires 267.1892

2-Diazo-1-phenyl-2-triethylsilylethan-1-one 2e

Carried out by the general procedure above with 2-diazo-1-phenyl-ethan-1-one (0.67 g, 4.58 mmol), triethylsilyl trifluoromethanesulfonate (1.24 ml, 5.5 mmol) and DIPEA (1.2 ml, 6.86 mmol) in diethyl ether (20 ml). The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield 2-diazo-1-phenyl-2-triethylsilyl-ethan-1-one **2e** as a yellow liquid (0.96 g, 80 %).

ν_{\max} (KBr/film) 3064 w, 2955 m, 2910 w, 2876 m, 2067 s (C=N₂), 1621 s (C=O), 1577 m, 1316 m, 1298 m, 1284 m, 1241 w, 1207 w, 1113 w, 1079 w, 1007 w cm⁻¹; δ_H (300 MHz, CDCl₃) 0.84 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 1.00 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 7.38-7.53 (3 H, m, H_{3,4}), 7.57-7.60 (2 H, m, H₂); δ_C (75 MHz, CDCl₃) 3.0 SiCH₂CH₃, 7.1 SiCH₂CH₃, 53.0 C=N₂, 127.0, 128.5 C_{2,3}, 131.3 C₄, 138.6 C₁, 193.6 C=O; m/z (Cl⁺, NH₃) 261 ([M+H]⁺, 30), 250 (11), 234 ([M-N₂+H]⁺, 58), 132 ([SiEt₃+NH₃]⁺, 100); HRMS (Cl⁺) Found [M+H]⁺ 261.1421 C₁₄H₂₁N₂OSi, requires 261.1423

2-Diazo-1-(4-methoxyphenyl)-2-triethylsilylethan-1-one 2f

Carried out by the general procedure above with 2-diazo-1-(4-methoxyphenyl)-ethan-1-one (1.057 g, 6 mmol), triethylsilyl trifluoromethanesulfonate (2 ml, 9 mmol) and DIPEA (2.1 ml, 12 mmol) in diethyl ether (30 ml). The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield 2-diazo-1-(4-methoxyphenyl)-2-triethylsilyl ethan-1-one **2f** as a yellow liquid (0.608 g, 35 %).

ν_{\max} (KBr/film) 2956 s, 2910 m, 2875 m, 2065 s (C=N₂), 1616 s (C=O), 1514 m, 1313 m, 1290 s, 1172 m cm⁻¹; δ_H (270 MHz, CDCl₃) 0.80 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.99 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 3.83 (3 H, s, OCH₃), 6.90 (2 H, d, $J_{3-2} = 9$ Hz, H₃), 7.60 (2 H, d, $J_{2-3} = 9$

Hz, H₂); δ_C (75 MHz, CDCl₃) 3.0 SiCH₂CH₃, 7.1 SiCH₂CH₃, 51.1 C=N₂, 55.4 OCH₃, 113.7 C₃, 129.2 C₂, 131.3 C₁, 162.1 C₄, 192.3 C=O; *m/z* (CI+, NH₃) 291 ([M+H]⁺, 20), 263 ([M-N₂+H]⁺, 100), 252 (42), 235 (52), 132 ([SiEt₃+NH₃]⁺, 59); HRMS (CI+) Found [M+H]⁺ 291.1522 C₁₅H₂₃N₂O₂Si, requires 291.1529

2-Diazo-1-(4-bromophenyl)-2-triethylsilylethan-1-one **2g**

Carried out by the general procedure above with 2-diazo-1-(4-bromophenyl)-ethan-1-one (0.675 g, 3 mmol), triethylsilyl trifluoromethanesulfonate (0.95 ml, 3.6 mmol) and DIPEA (0.78 ml, 4.5 mmol) in diethyl ether (10 ml). The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield 2-diazo-1-(4-bromo phenyl)-2-triethylsilylethan-1-one **2g** as a yellow liquid (0.92 g, 90 %).

*v*_{max} (KBr/film) 2954 s, 2910 m, 2875 s, 2069 s (C=N₂), 1614 s (C=O), 1587 m, 1303 s, 1292 s, 1205 m, 1105 m, 1070 m, 1010 s, 742 s cm⁻¹; δ_H (270 MHz, CDCl₃) 0.79 (6 H, q, *J* = 8 Hz, SiCH₂CH₃), 0.99 (9 H, t, *J* = 8 Hz, SiCH₂CH₃), 7.46 (2 H, d, *J*_{3-2'} = 8.5 Hz, H₃), 7.55 (2 H, d, H₂, *J*_{2-3'} = 8.5 Hz); δ_C (67.5 MHz, CDCl₃) 2.9 SiCH₂CH₃, 7.1 SiCH₂CH₃, 52.3 C=N₂, 125.8 C₄, 128.6, 131.7 C_{2,3}, 137.2 C₁, 192.2 C=O; *m/z* (CI+, NH₃) 341 ([M⁸¹Br+H]⁺, 100), 339 ([M⁷⁹Br+H]⁺, 98), 313 ([M⁸¹Br-N₂+H]⁺, 41), 311 ([M⁷⁹Br-N₂+H]⁺, 42), 244 ([M⁸¹Br-SiEt₃+NH₄]⁺, 84), 242 ([M⁷⁹Br-SiEt₃+NH₄]⁺, 89), 227 (68), 225 (67), 132 ([SiEt₃+NH₃]⁺, 78), 106 (41), 89 (72); HRMS (CI+) Found [M+H]⁺ 341.0503 C₁₄H₂₀⁸¹BrN₂OSi, requires 341.0501

2-Diazo-1-(2-furyl)-2-triethylsilylethan-1-one **2h**

Carried out by the general procedure above with 2-diazo-1-(2-furyl)-ethan-1-one (1.088 g, 8 mmol), triethylsilyl trifluoromethanesulfonate (2.7 ml, 12 mmol) and DIPEA (2.8 ml, 16 mmol) in diethyl ether (40 ml). The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield 2-diazo-1-(2-furyl)-2-triethylsilylethan-1-one **2h** as a yellow liquid (1.486 g, 74 %).

*v*_{max} (KBr/film) 3115 w, 2949 m, 2899 m, 2870 m, 2074 s (C=N₂), 1587 s (C=O), 1468 m, 1326 m, 1217 m, 1160 m cm⁻¹; δ_H (300 MHz, CDCl₃) 0.81 (6 H, q, *J* = 8 Hz, SiCH₂CH₃), 0.98

(9 H, t, $J = 8$ Hz, SiCH₂CH₃), 6.50 (1 H, dd, $J_{4'-3'} = 3.5$ Hz, $J_{4'-5'} = 1.5$ Hz, H_{4'}), 7.07 (1 H, dd, $J_{3'-4'} = 3.5$ Hz, $J_{3'-5'} = 1$ Hz, H_{3'}), 7.47 (1 H, dd, $J_{5'-4'} = 1.5$ Hz, $J_{5'-3'} = 1$ Hz, H_{5'}); δ_C (75 MHz, CDCl₃) 3.0 SiCH₂CH₃, 7.1 SiCH₂CH₃, 51.1 C=N₂, 111.9, 114.8 C_{3',4'}, 143.9 C_{5'}, 153.3 C_{2'}, 178.6 C=O; m/z (CI+, NH₃) 251 ([M+H]⁺, 73), 240 (42), 223 ([M-N₂+H]⁺, 100), 195 (55), 132 ([SiEt₃+NH₃]⁺, 54), 104 (22); HRMS (CI+) Found [M+H]⁺ 251.1222 C₁₂H₁₉N₂O₂Si, requires 251.1216

2-Diazo-1-(2-thiophenyl)-2-triethylsilylethan-1-one 2i

The experiment was carried out by the general procedure for the preparation of silyl diazoketones with 2-diazo-1-(2-thiophenyl)-ethan-1-one (0.43 g, 2.85 mmol), triethylsilyl trifluoromethanesulfonate (0.77 ml, 3.42 mmol) and DIPEA (0.75 ml, 4.275 mmol) in diethyl ether (20 ml). The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield 2-diazo-1-(2-thiophenyl)-2-triethylsilylethan-1-one **2i** as a yellow liquid (0.554 g, 73 %).

ν_{\max} (KBr/film) 2956 m, 2909 w, 2876 w, 2064 s (C=N₂), 1594 s (C=O), 1416 s, 1302 s, 1240 w, 1203 w, 1005 w, 723 s cm⁻¹; δ_H (270 MHz, CDCl₃) 0.81 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.99 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 7.07 (1 H, dd, $J_{4'-3'} = 5$ Hz, $J_{4'-5'} = 4$ Hz, H_{4'}), 7.52 (1 H, dd, $J_{3'-4'} = 5$ Hz, $J_{3'-5'} = 1$ Hz, H_{3'}), 7.55 (1 H, dd, $J_{5'-4'} = 4$ Hz, $J_{5'-3'} = 1$ Hz, H_{5'}); δ_C (67.5 MHz, CDCl₃) 2.8 SiCH₂CH₃, 7.1 SiCH₂CH₃, 50.6 C=N₂, 127.5, 129.1 C_{3',4'}, 131.2 C_{5'}, 143.7 C_{2'}, 182.6 C=O; m/z (CI+, NH₃) 284 ([M+NH₄]⁺, 10), 267 ([M+H]⁺, 100), 256 (36), 239 ([M-N₂+H]⁺, 80), 238 (48), 228 (34), 211 (42), 132 ([SiEt₃+NH₃]⁺, 48); HRMS (CI+) Found [M+H]⁺ 267.0989 C₁₂H₁₉N₂OSSi, requires 267.0987

1-(3-(1-*tert*-Butoxycarbonyl)indolyl)-2-diazo-2-triethylsilylethan-1-one 2j

Carried out by the general procedure above with 1-(3-(1-*tert*-butoxycarbonyl)indolyl)-2-diazo-1-ethanone (0.335 g, 1.235 mmol), triethylsilyl trifluoromethanesulfonate (0.34 ml, 1.48 mmol) and DIPEA (0.32 ml, 1.85 mmol) in diethyl ether (10 ml). The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield 1-(3-(1-*tert*-

butoxycarbonyl)indolyl)-2-diazo-2-triethylsilylethan-1-one **2j** as a yellow liquid (0.229 g, 46 %).

ν_{\max} (KBr/film) 2956 m, 2936 m, 2911 m, 2877 m, 2062 s (C=N₂), 1742 s (C=O Boc), 1608 m (C=O diazo), 1544 m, 1479 m, 1451 s, 1373 m, 1337 w, 1309 w, 1276 m, 1253 m, 1198 m, 1154 s, 1018 s cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.88 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 1.02 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 1.67 (9 H, s, C(CH₃)), 7.27-7.38 (2 H, m, *Ind*H), 8.00-8.13 (2 H, m, *Ind*H), 8.00 (1 H, s, H₂); δ_{C} (75 MHz, CDCl₃) 3.1 SiCH₂CH₃, 7.2 SiCH₂CH₃, 28.1 C(CH₃), 51.8 C=N₂, 85.0 C(CH₃), 114.9, 122.1, 123.9, 125.3, 128.1 C_{2,4,5,6,7}, 119.7, 127.8, 134.9 C_{3,3a,7a}, 149.0 C=O (Boc), 181.6 C=O; m/z (CI+, NH₃) 400 ([M+H]⁺, 6), 389 ([M-N₂+NH₄]⁺, 52), 371 ([M-N₂]⁺, 70), 344 (56), 315 (76), 233 (100), 132 ([SiEt₃+NH₃]⁺, 79), 119 (65); HRMS (CI+) Found [M+H]⁺ 400.2077 C₂₁H₃₀N₃O₃Si, requires 400.2056

General procedure for the preparation of silyl ketenes 1

2-Triethylsilylpropen-2-one 1a

To a stirred solution of 1-diazo-1-triethylsilylpropan-2-one **2a** (1.09 g, 5.5 mmol) in dry benzene (5 ml) was added Rh₂(octanoate)₄ (0.043 g, 0.055 mmol). The resulting solution was stirred at rt for 15 min. Afterwards, the reaction mixture was concentrated under reduced pressure and the residual oil purified by flash chromatography (100 % petroleum ether) to yield 2-triethylsilylpropen-1-one **1a** as a colourless liquid (0.463 g, 50 %).

ν_{\max} (KBr/film) 2955 s, 2911 m, 2877 s, 2088 s (C=O), 1790 w, 1725 w, 1458 w, 1239 w, 1093 w, 1018 w, 1004 w, 954 w, 738 m, 722 m, 710 m cm⁻¹; δ_{H} (300 MHz, CDCl₃) 0.61 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.94 (9 H, t, $J = 8$ Hz, SiCH₂CH₃) 1.54 (3 H, s, CH₃); δ_{C} (67.5 MHz, CDCl₃) 3.3 SiCH₂CH₃, 7.1 SiCH₂CH₃, 11.0 C₂, 53.4 C₃, 181.9 C₁; m/z (CI+, NH₃) 188 ([M+NH₄]⁺, 13), 171 ([M+H]⁺, 100), 132 ([SiEt₃+NH₃]⁺, 49); HRMS (CI+) Found [M+H]⁺ 171.1205 C₉H₁₉OSi, requires 171.1205

2-Triethylsilylnon-1-en-1-one 1b

Carried out by the general procedure above with 1-diazo-1-triethylsilylnonan-2-one **2b** (7.35 g, 26 mmol) and Rh₂(octanoate)₄ (0.2 g, 0.26 mmol) in benzene (50 ml). The crude product was purified by flash chromatography (petroleum ether) to yield 2-triethylsilylnon-1-en-1-one **1b** as a colourless liquid (4.97 g, 75 %).

ν_{\max} (KBr/film) 2956 s, 2928 s, 2876 m, 2083 s (C=O), 1573 w, 1462 w, 1005 w, 720 w cm⁻¹; δ_{H} (300 MHz, CDCl₃) 0.60 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.85 (3 H, t, $J_{9-8} = 7$ Hz, H₉), 0.94 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 1.20-1.32 (8 H, m, H_{5,6,7,8}), 1.46 (2 H, p, $J = 7.5$ Hz, H₄), 1.85 (2 H, t, $J_{3-4} = 7$ Hz, H₃); δ_{C} (75 MHz, CDCl₃) 3.6 SiCH₂CH₃, 7.1 SiCH₂CH₃, 9.4 C₂, 14.0 C₉, 22.6 C₈, 29.0, 29.2 C_{5,6,7}, 31.7, 31.8 C_{3,4}, 181.9 C₁; m/z (Cl⁺, NH₃) 255 ([M+H]⁺, 100), 132 ([SiEt₃+NH₃]⁺, 56); HRMS (Cl⁺) Found [M+H]⁺ 255.2146 C₁₅H₃₁OSi, requires 255.2144

3-Phenyl-2-triethylsilylpropen-1-one **1c**

Carried out by the general procedure above with 1-diazo-3-phenyl-1-triethylsilylpropan-2-one **2c** (0.274 g, 1 mmol) and Rh₂(octanoate)₄ (0.007 g, 0.01 mmol) in benzene (5 ml). The crude product was purified by flash chromatography (petroleum ether) to yield 3-phenyl-2-triethylsilylpropen-1-one **1c** as a colourless liquid (0.158 g, 64 %).

ν_{\max} (KBr/film) 3030 w, 2955 m, 2912 m, 2875 m, 2088 s (C=O), 1494 w, 1454 w, 1414 w, 1239 w, 1007 m, 735 m, 716 m, 700 m cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.65 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.99 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 3.25 (2 H, s, C₃), 7.20-7.39 (5 H, m, Ph); δ_{C} (75 MHz, CDCl₃) 3.5 SiCH₂CH₃, 7.1 SiCH₂CH₃, 11.5 C₂, 28.0 PhCH₂, 126.5 C₄, 128.0, 128.4 C_{2,3}, 141.1 C₁, 181.7 C₁; m/z (Cl⁺, NH₃) 247 ([M+H]⁺, 100), 217 (18), 132 ([SiEt₃+NH₃]⁺, 22); HRMS (Cl⁺) Found [M+H]⁺ 247.1510 C₁₅H₂₃OSi, requires 247.1518

2-Cyclohexyl-2-triethylsilylethen-1-one **1d**

Carried out by the general procedure above with 1-cyclohexyl-2-diazo-2-triethylsilylethan-1-one **2d** (1.74 g, 6.53 mmol) and Rh₂(octanoate)₄ (0.051 g, 0.065 mmol) in benzene (15 ml) at 50°C. The crude product was purified by flash chromatography (petroleum ether) to yield 2-cyclohexyl-2-triethylsilylethen-1-one **1d** as a colourless liquid (1.209 g, 77 %).

ν_{\max} (KBr/film) 2954 s, 2929 s, 2877 m, 2852 m, 2078 s (C=O), 1448 w, 1515 w, 1236 w, 1006 w, 732 m cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.62 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.95 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.17-1.27 (5 H, m), 1.61-1.88 (6 H, m); δ_{C} (75 MHz, CDCl_3) 4.0 SiCH_2CH_3 , 7.1 SiCH_2CH_3 , 17.2 C_2 , 25.9 C_4 , 26.3 C_3 , 33.8 C_1 , 36.4 C_2 , 182.6 C_1 ; m/z (Cl^+ , NH_3) 239 ($[\text{M}+\text{H}]^+$, 100), 132 ($[\text{SiEt}_3+\text{NH}_3]^+$, 17); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 239.1841 $\text{C}_{14}\text{H}_{27}\text{OSi}$, requires 239.1831

2-Phenyl-2-triethylsilylethen-1-one **1e**

Carried out by the general procedure above with 2-diazo-1-phenyl-2-triethylsilylethan-1-one **2e** (0.96 g, 3.68 mmol) and $\text{Rh}_2(\text{octanoate})_4$ (0.029 g, 0.0368 mmol) in benzene (8 ml) at 50°C . The crude product was purified by flash chromatography (petroleum ether) to yield 2-phenyl-2-triethylsilylethen-1-one **1e** as a colourless liquid (0.365 g, 43 %).

ν_{\max} (KBr/film) 3059 w, 2957 m, 2877 m, 2082 s (C=O), 1597 m, 1496 m, 1463 w, 1416 w, 1318 w, 1167 w, 1074 w, 1032 w, 1004 m, 920 m, 752 m, 737 m, 723 m, 706 m, 694 m cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.75 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.97 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 7.07-7.10 (3 H, m, $\text{H}_{3,4}$), 7.21-7.26 (2 H, m, H_2); δ_{C} (75 MHz, CDCl_3) 4.0 SiCH_2CH_3 , 7.1 SiCH_2CH_3 , 20.2 C_2 , 124.6 C_4 , 128.1, 128.9 $\text{C}_{2,3}$, 131.8 C_1 , 181.8 C_1 ; m/z (Cl^+ , NH_3) 250 ($[\text{M}+\text{NH}_4]^+$, 15), 233 ($[\text{M}+\text{H}]^+$, 27), 154 (53), 132 ($[\text{SiEt}_3+\text{NH}_3]^+$, 49), 118 (59); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 233.1367 $\text{C}_{14}\text{H}_{21}\text{OSi}$, requires 233.1362

2-(4-Methoxyphenyl)-2-triethylsilylethen-1-one **1f**

Carried out by the general above with 2-diazo-1-(4-methoxyphenyl)-2-triethylsilylethan-1-one **2f** (0.157 g, 0.54 mmol) and $\text{Rh}_2(\text{octanoate})_4$ (0.004 g, 0.0054 mmol) in benzene (3 ml) at 50°C . The crude product was purified by flash chromatography (petroleum ether) to yield 2-(4-methoxyphenyl)-2-triethylsilylethen-1-one **1f** as a colourless liquid (0.033 g, 23 %).

ν_{\max} (KBr/film) 2956 s, 2912 m, 2877 m, 2085 s (C=O), 1606 w, 1576 w, 1510 s, 1465 w, 1282 m, 1245 s, 1180 w, 1038 m, 1007 w, 913 w, 826 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.71 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.96 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 3.76 (3 H, s, OCH_3), 6.81 (2 H,

d, $J_{3'-2'} = 9$ Hz, $H_{3'}$), 7.01 (2 H, d, $J_{2'-3'} = 9$ Hz, $H_{2'}$), δ_C (62.5 MHz, $CDCl_3$) 3.9 $SiCH_2CH_3$, 7.1 $SiCH_2CH_3$, 18.5 C_2 , 55.3 OCH_3 , 114.5 C_3 , 122.7 $C_{1'}$, 129.6 C_2' , 157.2 C_4' , 182.1 C_1 ; m/z (Cl^+ , NH_3) 263 ($[M+H]^+$, 45), 262 ($[M]^+$, 100), 234 (52), 132 ($[SiEt_3+NH_3]^+$, 39); HRMS (Cl^+) Found $[M+H]^+$ 263.1467 $C_{15}H_{23}O_2Si$, requires 263.1472

2-(4-Bromophenyl)-2-triethylsilylethen-1-one **1g**

Carried out by the general procedure above with 2-diazo-1-(4-bromophenyl)-2-triethylsilylethan-1-one **2g** (0.9 g, 2.65 mmol) and $Rh_2(octanoate)_4$ (0.021 g, 0.0265 mmol) in benzene (10 ml) at 60°C. The crude product was purified by flash chromatography (petroleum ether) to yield 2-(4-bromophenyl)-2-triethylsilylethen-1-one **1g** as a colourless liquid (0.32 g, 40 %).

ν_{max} (KBr/film) 2956 s, 2910 m, 2977 s, 2088 s (C=O), 1486 s, 1166 m, 1076 m, 1008 s, 914 w, 817 s, 736 s, 723 $s\ cm^{-1}$; δ_H (300 MHz, $CDCl_3$) 0.77 (6 H, q, $J = 8$ Hz, $SiCH_2CH_3$), 0.98 (9 H, t, $J = 8$ Hz, $SiCH_2CH_3$), 6.96 (2 H, d, $J_{3'-2'} = 8.5$ Hz, $H_{3'}$), 7.36 (2 H, d, $J_{2'-3'} = 8.5$ Hz, $H_{2'}$); δ_C (75 MHz, $CDCl_3$) 3.9 $SiCH_2CH_3$, 7.1 $SiCH_2CH_3$, 19.9 C_2 , 118.0 C_4' , 129.5, 132.0 $C_{4',2'}$, 131.1 $C_{1'}$, 181.1 C_1 ; m/z (Cl^+ , NH_3) 348 (20), 346 (19), 313 ($[M^{81}Br+H]^+$, 35), 311 ($[M^{79}Br+H]^+$, 33), 244 (14), 242 (15), 233 ($[M-Br+2H]^+$, 12) 227 (20), 225 (19), 132 ($[SiEt_3+NH_3]^+$, 100), 52 (35); HRMS (Cl^+) Found $[M+H]^+$ 313.0437 $C_{14}H_{20}^{81}BrOSi$, requires 313.0446

2-(2-Furyl)-2-triethylsilylethen-1-one **1h**

Carried out by the general procedure above with 2-diazo-1-(2-furyl)-2-triethylsilylethan-1-one **2h** (0.375 g, 1.5 mmol) and $Rh_2(octanoate)_4$ (0.011 g, 0.015 mmol) in benzene (5 ml) at 60°C. The crude product was purified by flash chromatography (petroleum ether) to yield 2-(2-furyl)-2-triethylsilylethen-1-one **1h** as a pale yellow liquid (0.132 g, 40 %).

ν_{max} (KBr/film) 2958 m, 2878 m, 2099 s (C=O), 1587 m, 1510 w, 1500 w, 1462 w, 1416 w, 1217 m, 1181 m, 1074 w, 1015 $s\ cm^{-1}$; δ_H (300 MHz, $CDCl_3$) 0.74 (6 H, q, $J = 8$ Hz, $SiCH_2CH_3$), 0.96 (9 H, t, $J = 8$ Hz, $SiCH_2CH_3$), 5.89 (1 H, dd, $J_{3'-4'} = 3$ Hz, $J_{3'-5'} = 0.5$ Hz, $H_{3'}$), 6.31 (1 H, dd, $J_{4'-3'} = 3$ Hz, $J_{4'-5'} = 2$ Hz, $H_{4'}$), 7.26 (1 H, dd, $J_{5'-4'} = 2$ Hz, $J_{5'-3'} = 0.5$ Hz, $H_{5'}$); δ_C

(75 MHz, CDCl₃) 3.8 SiCH₂CH₃, 7.0 SiCH₂CH₃, 14.0 C₂, 104.7, 111.2 C_{3',4'}, 140.5 C_{5'}, 143.4 C₂, 182.6 C₁; *m/z* (Cl⁺, NH₃) 223 ([M+H]⁺, 100), 132 ([SiEt₃+NH₃]⁺, 26), 104 (40); HRMS (Cl⁺) Found [M+H]⁺ 223.1174 C₁₂H₁₉N₂O₂Si, requires 223.1154

2-(2-Thiophenyl)-2-triethylsilylethen-1-one **1i**

Carried out by the general procedure above with 2-diazo-1-(2-thiophenyl)-2-triethylsilylethan-1-one **2i** (0.55 g, 2.06 mmol) and Rh₂(octanoate)₄ (0.016 g, 0.02 mmol) in benzene (4 ml) at 60°C. The crude product was purified by flash chromatography (petroleum ether) to yield 2-(2-thiophenyl)-2-triethylsilylethen-1-one **1i** as a pale yellow liquid (0.190 g, 39 %).

ν_{\max} (KBr/film) 2956 m, 2911 w, 2877 w, 2089 s (C=O), 1526 w, 1457 w, 1415 w, 1238 w, 1132 w, 1004 m, 864 m, 841 m, 722 s, 687 s cm⁻¹; δ_{H} (300 MHz, CDCl₃) 0.75 (6 H, q, *J* = 8 Hz, SiCH₂CH₃), 0.99 (9 H, t, *J* = 8 Hz, SiCH₂CH₃), 6.70 (1 H, dd, *J*_{5'-4'} = 3.5 Hz, *J*_{5'-3'} = 1 Hz, H_{5'}), 6.95 (1 H, dd, *J*_{4'-3'} = 5 Hz, *J*_{4'-5'} = 3.5 Hz, H_{4'}), 7.11 (1 H, dd, *J*_{3'-4'} = 5 Hz, *J*_{3'-5'} = 1 Hz, H_{3'}); δ_{C} (75 MHz, CDCl₃) 3.7 SiCH₂CH₃, 7.1 SiCH₂CH₃, 14.4 C₂, 123.1, 124.8 C_{3',4'}, 127.3 C_{5'}, 131.4 C₂, 180.3 C₁; *m/z* (Cl⁺, NH₃) 239 ([M+H]⁺, 100), 238 ([M]⁺, 57), 132 ([SiEt₃+NH₃]⁺, 22); HRMS (Cl⁺) Found [M+H]⁺ 239.0920 C₁₂H₁₉OSSi, requires 239.0926

2-(3-(1-*tert*-Butoxycarbonyl)indolyl)-2-triethylsilylethen-1-one **1j**

Carried out by the general procedure above with 1-(3-(1-*tert*-butoxycarbonyl)indolyl)-2-diazo-2-triethylsilylethan-1-one **2j** (0.202 g, 0.5 mmol) and Rh₂(octanoate)₄ (0.004 g, 0.005 mmol) in benzene (3 ml) at 40°C. The crude product was purified by flash chromatography (petroleum ether) to yield 2-(3-(1-*tert*-butoxycarbonyl)indolyl)-2-triethylsilylethen-1-one **1j** as a colourless liquid (0.094 g, 51 %).

ν_{\max} (KBr/film) 3054 w, 2955 m, 2912 m, 2877 m, 2085 s (C=O), 1733 s (C=O Boc), 1476 m, 1456 m, 1418 m, 1373 m, 1298 m, 1246 m, 1215 m, 1158 m, 1123 w, 1096 m, 1042 w, 1021 m cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.77 (6 H, q, *J* = 8 Hz, SiCH₂CH₃), 0.99 (9 H, t, *J* = 8 Hz, SiCH₂CH₃), 1.66 (9 H, s, C(CH₃)), 7.21-7.34 (3 H, m, *IndH*), 7.58 (1 H, dd, *J* = 7 Hz, *J* = 1.5 Hz, *IndH*), 8.07 (1 H, br d, *J* = 7 Hz, *IndH*); δ_{C} (75 MHz, CDCl₃) 3.8 SiCH₂CH₃, 7.1 SiCH₂CH₃,

9.2 C₂, 28.2 C(CH₃), 83.6 C(CH₃), 115.3, 119.1, 121.2, 122.5, 124.7 C_{2',4',5',6',7'}, 108.7, 130.7, 135.0 C_{3',3a',7a'}, 149.6 C=O, Boc, 181.0 C₁; *m/z* (Cl⁺, NH₃) 372 ([M+H]⁺, 100), 344 ([M-N₂+H]⁺, 86), 315 (92), 286 (17), 271 (60), 242 (20), 132 ([SiEt₃+NH₃]⁺, 27), 104 (12); HRMS (Cl⁺) Found [M+H]⁺ 372.1988 C₂₁H₃₀NO₃Si, requires 372.1995

General procedure for the preparation of allenylsilanes from silyl ketenes and stabilised phosphorus ylides

Ethyl 2-methyl-4-triethylsilylpenta-2,3-dienoate 6a

To a solution of 2-triethylsilylpropen-2-one **1a** (0.031 g, 0.18 mmol) in toluene (1.5 ml) under a nitrogen atmosphere was added in one portion (1-ethoxycarbonyl-ethylidene)triphenylphosphorane (**4**, 0.073 g, 0.20 mmol). The mixture was then heated to gentle reflux and monitored by TLC for complete consumption of the silylketene. Hexane (10 ml) was then added and the white precipitate removed by filtration. The filtrate was concentrated under reduced pressure and the residual oil purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield ethyl 2-methyl-4-triethylsilylpenta-2,3-dienoate **6a** as a colourless liquid (0.025 g, 54 %).

ν_{\max} (KBr/film) 2957 s, 2936 m, 2876 m, 1932 s (C=C=C), 1705 s (C=O), 1458 w, 1267 s, 1238 w, 1119 m, 1003 w, 737 m, 719 m, 712 m cm⁻¹; δ_{H} (300 MHz, CDCl₃) 0.59 (6 H, q, *J* = 8 Hz, SiCH₂CH₃), 0.93 (9 H, t, *J* = 8 Hz, SiCH₂CH₃), 1.21 (3 H, t, *J* = 7 Hz, CH₂CH₃), 1.73 (3 H, s, CH₃), 1.78 (3 H, s, CH₃), 4.07 (1 H, dq, *J* = 11 Hz, *J* = 7 Hz, CH₂CH₃), 4.19 (1 H, dq, *J* = 11 Hz, *J* = 7 Hz, CH₂CH₃); δ_{C} (67.5 MHz, CDCl₃) 2.8 SiCH₂CH₃, 7.1 SiCH₂CH₃, 14.3, 14.6, 14.7 CH₂CH₃, 2-CH₃, C₅, 60.3 CH₂CH₃, 88.4 C₂, 90.7 C₄, 160.8 C=O, 208.8 C₃; *m/z* (Cl⁺, NH₃) 272 ([M+NH₄]⁺, 50), 255 ([M+H]⁺, 100); HRMS (Cl⁺) Found [M+H]⁺ 255.1781 C₁₄H₂₇O₂Si, requires 255.1780

Ethyl 4-triethylsilylpenta-2,3-dienoate 7a

Carried out by the general procedure above with 2-triethylsilylpropen-2-one **1a** (0.064 g, 0.375 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (**5**, 0.157 g, 0.45 mmol) in DCM (2 ml) at rt. The crude product was purified by flash chromatography (95:5 petroleum

ether:diethyl ether) to yield ethyl 4-triethylsilylpenta-2,3-dienoate **7a** as a colourless liquid (0.054 g, 60 %).

ν_{\max} (KBr/film) 2956 m, 2914 w, 2877 w, 1933 s (C=C=C), 1714 s (C=O), 1457 w, 1402 w, 1382 w, 1248 s, 1200 s, 1145 s, 1044 w, 1005 w, 817 w, 806 w, 728 m, 723 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.61 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.93 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.21 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.75 (3 H, d, $J_{5-2} = 2.5$ Hz, H_5), 4.06 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, H_a or H_b), 4.16 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, H_b or H_a), 5.16 (1 H, q, $J_{2-5} = 2.5$ Hz, H_2); δ_{C} (75 MHz, CDCl_3) 2.6 SiCH_2CH_3 , 7.0 SiCH_2CH_3 , 14.2, 14.4 CH_2CH_3 , CH_3 , 60.2 CH_2CH_3 , 81.2 C_2 , 91.9 C_4 , 168.1 C=O, 209.1 C_3 ; m/z (Cl^+ , NH_3) 258 ($[\text{M}+\text{NH}_4]^+$, 40), 241 ($[\text{M}+\text{H}]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 241.1619 $\text{C}_{13}\text{H}_{25}\text{O}_2\text{Si}$, requires 241.1624

Ethyl 2-methyl-4-triethylsilylundeca-2,3-dienoate **6b**

Carried out by the general procedure above with 2-triethylsilylnon-1-en-1-one **1b** (0.076 g, 0.3 mmol) and (1-ethoxycarbonyl ethylidene)triphenylphosphorane (**4**, 0.114 g, 0.315 mmol) in refluxing toluene (3 ml). The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield ethyl 2-methyl-4-triethylsilylundeca-2,3-dienoate **6b** as a colourless liquid (0.045 g, 45 %).

ν_{\max} (KBr/film) 2956 s, 2926 s, 2875 s, 2857 m, 1929 s (C=C=C), 1705 s (C=O), 1458 w, 1267 s, 1236 w, 1118 s, 1004 w, 735 m, 720 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.59 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.86 (3 H, t, $J_{11-10} = 6.5$ Hz, H_{11}), 0.92 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.20 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.20-1.32 (8 H, m, $\text{H}_{7,8,9,10}$), 1.44 (2 H, p, $J = 7.5$ Hz, H_6), 1.78 (3 H, s, 2- CH_3), 2.00 (2 H, t, $J_{5-6} = 6.5$ Hz, H_5), 4.09 (1 H, dq, $J = 10.5$ Hz, $J = 7$ Hz, CH_2CH_3), 4.16 (1 H, dq, $J = 10.5$ Hz, $J = 7$ Hz, CH_2CH_3); δ_{C} (75 MHz, CDCl_3) 3.0 SiCH_2CH_3 , 7.1 SiCH_2CH_3 , 14.1, 14.3, 14.5 C_{11} , 2- CH_3 , CH_2CH_3 , 22.6, 29.0, 29.1, 29.2 (2 peaks) $\text{C}_{6,7,8,9,10}$, 31.8 C_5 , 60.2 CH_2CH_3 , 89.8 C_4 , 96.2 C_2 , 169.9 C=O, 208.6 C_3 ; m/z (Cl^+ , NH_3) 339 ($[\text{M}+\text{H}]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 339.2714 $\text{C}_{20}\text{H}_{39}\text{O}_2\text{Si}$, requires 339.2719

Ethyl 4-triethylsilylundeca-2,3-dienoate **7b**

Carried out by the general procedure above with 2-triethylsilylnon-1-en-1-one **1b** (0.382 g, 1.5 mmol) and (ethoxycarbonylmethylene) triphenylphosphorane (**5**, 0.627 g, 1.8 mmol) in refluxing DCM (5 ml). The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 4-triethylsilylundeca-2,3-dienoate **7b** as a colourless liquid (0.375 g, 77 %).

ν_{\max} (KBr/film) 2954 s, 2929 s, 2875 m, 2858 w, 1928 s (C=C=C), 1714 s (C=O), 1463 w, 1405 w, 1380 w, 1245 s, 1193 m, 1143 s, 1045 w, 1004 w, 806 w, 736 m, 723 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.62 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.85 (3 H, t, $J_{11-10} = 6.5$ Hz, H_{11}), 0.94 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.22 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.19-1.36 (8 H, m, $\text{H}_{7,8,9,10}$), 1.47 (2 H, p, $J = 7.5$ Hz, H_6), 2.00 (2 H, m, H_5), 4.10 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, CH_2CH_3), 4.17 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, CH_2CH_3), 5.23 (1 H, t, $J_{2-5} = 3$ Hz, H_2); δ_{C} (75 MHz, CDCl_3) 2.8 SiCH_2CH_3 , 6.9 SiCH_2CH_3 , 13.9, 14.1 C_{11} , CH_2CH_3 , 22.5, 28.5, 28.8, 29.0, 29.1 $\text{C}_{6,7,8,9,10}$, 31.7 C_5 , 60.0 CH_2CH_3 , 82.6 C_4 , 97.2 C_2 , 167.9 C=O, 208.7 C_3 ; m/z (Cl^+ , NH_3) 342 ($[\text{M}+\text{NH}_4]^+$, 24), 325 ($[\text{M}+\text{H}]^+$, 100), 132 ($[\text{SiEt}_3+\text{NH}_3]^+$, 12); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 325.2567 $\text{C}_{19}\text{H}_{37}\text{O}_2\text{Si}$, requires 325.2563

Ethyl 2-methyl-5-phenyl-4-triethylsilylpenta-2,3-dienoate 6c

Carried out by the general procedure above with 3-phenyl-2-triethylsilylpropen-1-one **1c** (0.123 g, 0.5 mmol) and (1-ethoxycarbonyl-ethylidene) triphenylphosphorane (**4**, 0.200 g, 0.55 mmol) in refluxing benzene (3 ml). The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 2-methyl-5-phenyl-4-triethylsilylpenta-2,3-dienoate **6c** as a colourless liquid (0.099 g, 60 %).

ν_{\max} (KBr/film) 3026 w, 2953 m, 2909 m, 2875 m, 1929 s (C=C=C), 1704 s (C=O), 1454 w, 1267 s, 1238 w, 1120 s, 1006 m, 762 w, 736 m, 719 m, 699 m cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.51 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.87 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.25 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.72 (3 H, s, CH_3), 3.32 (1 H, d, $J = 15$ Hz, H_5), 3.43 (1 H, d, $J = 15$ Hz, H_5), 4.13 (2 H, q, $J = 7$ Hz, CH_2CH_3), 7.16-7.25 (5 H, m, Ph); δ_{C} (75 MHz, CDCl_3) 3.0 SiCH_2CH_3 , 7.0 SiCH_2CH_3 , 14.3 CH_2CH_3 and CH_3 (2 peaks overlapped), 36.1 C_5 , 60.3 CH_2CH_3 , 89.8 C_2 , 95.9

C₄, 126.2 C_{4'}, 128.0, 128.8 C_{2,3'}, 139.4 C_{1'}, 169.4 C₁, 210.5 C₃; *m/z* (CI+, NH₃) 348 ([M+NH₄]⁺, 25), 331 ([M+H]⁺, 100); HRMS (CI+) Found [M+H]⁺ 331.2102 C₂₀H₃₁O₂Si, requires 331.2093

Ethyl 5-phenyl-4-triethylsilylpenta-2,3-dienoate 7c

Carried out by the general procedure above with 3-phenyl-2-triethylsilylpropen-1-one **1c** (0.098 g, 0.4 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (**5**, 0.153 g, 0.44 mmol) in DCM (2 ml) at rt. The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 5-phenyl-4-triethylsilylpenta-2,3-dienoate **7c** as a colourless liquid (0.103 g, 81 %).

ν_{\max} (KBr/film) 3062 w, 3029 w, 2954 s, 2912 w, 2877 m, 1928 s (C=C=C), 1711 s (C=O), 1454 w, 1247 s, 1172 m, 1140 m, 1043 m, 1044 m, 804 w, 737 s, 723 s, 700 s cm⁻¹; δ_{H} (300 MHz, CDCl₃) 0.56 (6 H, q, *J* = 8 Hz, SiCH₂CH₃), 0.90 (9 H, t, *J* = 8 Hz, SiCH₂CH₃), 1.26 (3 H, t, *J* = 7 Hz, CH₂CH₃), 3.41 (2 H, m, H₅), 4.15 (2 H, q, *J* = 7 Hz, CH₂CH₃), 5.21 (1 H, t, *J* = 2.5 Hz, H₂), 7.18-7.27 (5 H, m, Ph); δ_{C} (75 MHz, CDCl₃) 2.9 SiCH₂CH₃, 6.9 SiCH₂CH₃, 14.2 CH₂CH₃, 35.7 C₅, 60.2 CH₂CH₃, 82.6 C₂, 96.9 C₄, 126.4 C_{4'}, 128.1, 128.8 C_{2,3'}, 138.8 C_{1'}, 167.7 C₁, 210.6 C₃; *m/z* (CI+, NH₃) 334 ([M+NH₄]⁺, 88), 333 (37), 317 ([M+H]⁺, 100), 316 ([M]⁺, 64); HRMS (CI+) Found [M+H]⁺ 317.1937 C₁₉H₂₉O₂Si, requires 317.1940

Ethyl 4-cyclohexyl-2-methyl-4-triethylsilylbuta-2,3-dienoate 6d

Carried out by the general procedure above with 2-cyclohexyl-2-triethylsilylethen-1-one **1d** (0.072 g, 0.3 mmol) and (1-ethoxycarbonylethylidene)triphenylphosphorane (**4**, 0.120 g, 0.33 mmol) in refluxing toluene (2 ml). After 48 h the crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 4-cyclohexyl-2-methyl-4-triethylsilylbuta-2,3-dienoate **6d** as a colourless liquid (0.021 g, 22 %) and recovered 2-cyclohexyl-2-triethylsilylethen-1-one **1d** (0.043 g, 60 %).

ν_{\max} (KBr/film) 2952 s, 2927 s, 2875 m, 2852 w, 1924 m (C=C=C), 1704 s (C=O), 1448 w, 1267 s, 1240 w, 1118 s, 1006 w, 732 m, 721 m cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.59 (6 H, q, *J* = 8

Hz, SiCH₂CH₃), 0.92 (9 H, t, *J* = 8 Hz, SiCH₂CH₃), 1.11-1.30 (5 H, m), 1.19 (3 H, t, *J* = 7 Hz, CH₂CH₃), 1.56-1.90 (6 H, m), 1.78 (3 H, s, CH₃), 4.11 (2 H, q, *J* = 7 Hz, CH₂CH₃); δ_C (75 MHz, CDCl₃) 3.3 SiCH₂CH₃, 7.2 SiCH₂CH₃, 14.3, 14.5 CH₃, CH₂CH₃, 26.0, 26.6 C_{3',4'}, 34.0, 34.4 C_{2'a,2'e}, 60.1 CH₂CH₃, 90.6 C₂, 101.9 C₄, 169.9 C=O, 209.5 C₃; *m/z* (Cl⁺, NH₃) 323 ([M+H]⁺, 100), 193 (18); HRMS (Cl⁺) Found [M+H]⁺ 323.2410 C₁₉H₃₅O₂Si, requires 323.2406

Ethyl 4-cyclohexyl-4-triethylsilylbuta-2,3-dienoate 7d

Carried out by the general procedure above with 2-cyclohexyl-2-triethylsilylethen-1-one **1d** (0.072 g, 0.3 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (**5**, 0.115 g, 0.33 mmol) in refluxing benzene (2 ml). The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 4-cyclohexyl-4-triethylsilylbuta-2,3-dienoate **7d** as a colourless liquid (0.072 g, 78 %).

*v*_{max} (KBr/film) 2952 s, 2929 s, 2875 m, 2852 m, 1920 s (C=C=C), 1712 s (C=O), 1243 s, 1191 s, 1145 s, 1045 m, 1006 m, 734 m, 721 m, 698 w cm⁻¹; δ_H (270 MHz, CDCl₃) 0.62 (6 H, q, *J* = 8 Hz, SiCH₂CH₃), 0.92 (9 H, t, *J* = 8 Hz, SiCH₂CH₃), 1.10-1.30 (5 H, m), 1.21 (3 H, t, *J* = 7 Hz, CH₂CH₃), 1.55-1.92 (6 H, m), 4.11 (2 H, app dq, *J* = 2 and 7 Hz CH₂CH₃), 5.23 (1 H, d, *J*_{2,1'} = 0.5 Hz, H₂); δ_C (75 MHz, CDCl₃) 2.9 SiCH₂CH₃, 7.1 SiCH₂CH₃, 14.2 CH₂CH₃, 25.9 C_{4'}, 26.6, 26.6, 34.0, 34.1 C_{2',3'}, 38.9 C_{1'}, 60.1 CH₂CH₃, 83.4 C₂, 102.9 C₄, 168.2 C=O, 209.6 C₃; *m/z* (Cl⁺, NH₃) 326 ([M+NH₄]⁺, 24), 309 ([M+H]⁺, 100); HRMS (Cl⁺) Found [M+H]⁺ 309.2245 C₁₈H₃₃O₂Si, requires 309.2250

Ethyl 2-methyl-4-phenyl-4-triethylsilylbuta-2,3-dienoate 6e and ethyl 2-methyl-4-phenylbuta-2,3-dienoate 8e

Carried out by the general procedure above with 2-phenyl-2-triethylsilylethen-1-one **1e** (0.097 g, 0.42 mmol) and (1-ethoxycarbonyl-ethylidene)triphenylphosphorane (**4**, 0.167 g, 0.46 mmol) in refluxing benzene (3 ml). The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield ethyl 2-methyl-4-phenyl-4-triethylsilylbuta-2,3-dienoate **6e** as a colourless liquid (0.072 g, 55 %) and ethyl 2-methyl-4-phenylbuta-2,3-dienoate **8e** as a colourless liquid (0.006 g, 7 %).

6e: ν_{\max} (KBr/film) 2954 s, 2910 m, 2875 m, 1926 s (C=C=C), 1706 s (C=O), 1596 w, 1490 w, 1267 s, 1240 m, 1118 s, 1004 m, 755 m, 734 m, 721 m, 698 m cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.73 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.97 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.28 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.91 (3 H, s, CH_3), 4.15 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, CH_2CH_3), 4.22 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, CH_2CH_3), 7.22-7.34 (5 H, m, Ph); δ_{C} (75 MHz, CDCl_3) 3.6 SiCH_2CH_3 , 7.1 SiCH_2CH_3 , 14.3, 14.4 $\text{CH}_3, \text{CH}_2\text{CH}_3$, 60.6 CH_2CH_3 , 90.6 C_2 , 99.9 C_4 , 126.7 C_4' , 127.9, 128.6 $\text{C}_{3,2'}$, 136.1 C_1 , 169.0 C_1 , 212.3 C_3 ; m/z (Cl⁺, NH_3) 334 ($[\text{M}+\text{NH}_4]^+$, 100), 317 ($[\text{M}+\text{H}]^+$, 22); HRMS (Cl⁺) Found $[\text{M}+\text{H}]^+$ 317.1925 $\text{C}_{19}\text{H}_{29}\text{O}_2\text{Si}$, requires 317.1937

8e: ν_{\max} (KBr/film) 2983 w, 2960 w, 2931 w, 1947 w (C=C=C), 1710 s (C=O), 1459 w, 1367 w, 1268 s, 1189 w, 1120 w, 1027 w, 765 w, 734 w, 692 m cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 1.25 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.99 (3 H, d, $J = 3$ Hz, CH_3), 4.20 (2 H, q, $J = 7$ Hz, CH_2CH_3), 6.46 (1 H, q, $J = 3$ Hz, H_4), 7.21-7.35 (5 H, m, Ph); δ_{C} (75 MHz, CDCl_3) 14.3, 15.1 $\text{CH}_3, \text{CH}_2\text{CH}_3$, 61.1 CH_2CH_3 , 97.2 C_4 , 99.4 C_2 , 127.3, 128.8 $\text{C}_{2,3'}$, 127.6 C_4' , 132.5 C_1 , 167.1 C_1 , 212.3 C_3 ; m/z (Cl⁺, NH_3) 220 ($[\text{M}+\text{NH}_4]^+$, 100), 203 ($[\text{M}+\text{H}]^+$, 21); HRMS (Cl⁺) Found $[\text{M}+\text{H}]^+$ 203.1076 $\text{C}_{13}\text{H}_{15}\text{O}_2$, requires 203.1072

Ethyl 4-(4-methoxyphenyl)-2-methyl-4-triethylsilylbuta-2,3-dienoate 6f and ethyl 4-(4-methoxyphenyl)-2-methyl-buta-2,3-dienoate 8f

Carried out by the general procedure above with 2-(4-methoxyphenyl)-2-triethylsilylethen-1-one **1f** (0.118 g, 0.45 mmol) and (1-ethoxycarbonyl-ethylidene)triphenylphosphorane (**4**, 0.181 g, 0.66 mmol) in benzene (4 ml) at 50 °C. The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 4-(4-methoxyphenyl)-2-methyl-4-triethylsilylbuta-2,3-dienoate **6f** as a colourless liquid (0.068 g, 44 %) and ethyl 4-(4-methoxyphenyl)-2-methyl-buta-2,3-dienoate **8f** as a colourless liquid (0.003 g, 3 %).

6f: ν_{\max} (KBr/film) 2955 s, 2910 m, 2875 m, 1924 s (C=C=C), 1703 s (C=O), 1605 m, 1509 s, 1462 m, 1367 w, 1286 s, 1264 s, 1246 s, 1174 m, 1117 s, 1035 m, 1006 m, 829 m, 735 m, 701 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.70 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.94 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.22 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.88 (3 H, s, CH_3), 3.78 (3 H, s, OCH_3), 4.12 (1

H, dq, $J = 11$ Hz, $J = 7$ Hz, $\underline{\text{CH}_2\text{CH}_3}$), 4.20 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, $\underline{\text{CH}_2\text{CH}_3}$), 6.84 (2 H, d, $J_{3'-2'} = 9$ Hz, $\text{H}_{3'}$), 7.17 (2 H, d, $J_{2'-3'} = 9$ Hz, $\text{H}_{2'}$); δ_{C} (75 MHz, CDCl_3) 3.6 $\text{Si}\underline{\text{CH}_2\text{CH}_3}$, 7.1 $\text{SiCH}_2\underline{\text{CH}_3}$, 14.3, 14.5 CH_3 , $\text{CH}_2\underline{\text{CH}_3}$, 55.2 OCH_3 , 60.5 $\underline{\text{CH}_2\text{CH}_3}$, 90.7 C_2 , 99.1 C_4 , 114.1 C_3 , 127.9 C_1 , 128.9 C_2 , 158.5 C_4 , 169.1 C_1 , 212.2 C_3 ; m/z (CI^+ , NH_3) 364 ($[\text{M}+\text{NH}_4]^+$, 26), 347 ($[\text{M}+\text{H}]^+$, 100); HRMS (CI^+) Found $[\text{M}+\text{H}]^+$ 347.2046 $\text{C}_{20}\text{H}_{31}\text{O}_3\text{Si}$, requires 347.2042

Ehyl 4-(2-furyl)-2-methyl-4-triethylsilylbuta-2,3-dienoate 6h and ethyl 4-(2-furyl)-2-methylbuta-2,3-dienoate 8h

Carried out by the general procedure above with 2-(2-furyl)-2-triethylsilylethen-1-one **1h** (0.132 g, 0.6 mmol) and (1-ethoxycarbonyl-ethylidene)triphenylphosphorane (**4**, 0.236 g, 0.5 mmol) in benzene (3 ml) at 50 °C. The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 4-(2-furyl)-2-methyl-4-triethylsilylbuta-2,3-dienoate **6h** as a colourless liquid (0.012 g, 7 %) and ethyl 4-(2-furyl)-2-methylbuta-2,3-dienoate **8h** as a colourless liquid (0.026 g, 23 %).

6h: ν_{max} (KBr/film) 2957 s, 2912 m, 2877 s, 1926 s ($\text{C}=\text{C}=\text{C}$), 1708 s ($\text{C}=\text{O}$), 1462 m, 1368 m, 1265 s, 1118 s, 1019 s, 959 m, 859 w, 761 w, 735 s, 701 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.73 (6 H, q, $J = 8$ Hz, $\text{Si}\underline{\text{CH}_2\text{CH}_3}$), 0.94 (9 H, t, $J = 8$ Hz, $\text{SiCH}_2\underline{\text{CH}_3}$), 1.20 (3 H, t, $J = 7$ Hz, $\underline{\text{CH}_2\text{CH}_3}$), 1.90 (3 H, s, CH_3), 4.08 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, $\underline{\text{CH}_2\text{CH}_3}$), 4.21 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, $\underline{\text{CH}_2\text{CH}_3}$), 6.23 (1 H, dd, $J_{3'-4'} = 3$ Hz, $J_{3'-5'} = 0.5$ Hz, $\text{H}_{3'}$), 6.36 (1 H, dd, $J_{4'-3'} = 3$ Hz, $J_{4'-5'} = 1.5$ Hz, $\text{H}_{4'}$), 7.36 (1 H, dd, $J_{5'-4'} = 1.5$ Hz, $J_{5'-3'} = 0.5$ Hz, $\text{H}_{5'}$); δ_{C} (75 MHz, CDCl_3) 3.5 $\text{Si}\underline{\text{CH}_2\text{CH}_3}$, 7.1 $\text{SiCH}_2\underline{\text{CH}_3}$, 14.3, 14.6 CH_3 , $\text{CH}_2\underline{\text{CH}_3}$, 60.7 $\underline{\text{CH}_2\text{CH}_3}$, 91.1, 92.5 $\text{C}_{2,4}$, 107.9, 111.3 $\text{C}_{3,4'}$, 142.0 C_5 , 147.9 C_2 , 168.4 C_1 , 212.7 C_3 ; m/z (CI^+ , NH_3) 324 ($[\text{M}+\text{NH}_4]^+$, 35), 307 ($[\text{M}+\text{H}]^+$, 100); HRMS (CI^+) Found $[\text{M}+\text{H}]^+$ 307.1733 $\text{C}_{17}\text{H}_{27}\text{O}_3\text{Si}$, requires 307.1729

8h: ν_{max} (KBr/film) 2983 m, 2930 w, 2907 w, 1948 w ($\text{C}=\text{C}=\text{C}$), 1711 s ($\text{C}=\text{O}$), 1447 w, 1369 m, 1270 s, 1171 m, 1120 s, 1013 m, 926 m, 739 s cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 1.24 (3 H, t, $J = 7$ Hz, $\underline{\text{CH}_2\text{CH}_3}$), 1.97 (3 H, d, $J = 3$ Hz, CH_3), 4.16 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, $\underline{\text{CH}_2\text{CH}_3}$), 4.22 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, $\underline{\text{CH}_2\text{CH}_3}$), 6.28 (1 H, d, $J_{3'-4'} = 3$ Hz, $\text{H}_{3'}$), 6.38 (1 H, dd, $J_{4'-3'}$

$J_{3'} = 3$ Hz, $J_{4'-5'} = 2$ Hz, $H_{4'}$), 6.42 (1 H, q, $J = 3$ Hz, $H_{4'}$), 7.37 (1 H, dd, $J_{5'-4'} = 2$ Hz, $J_{5'-3'} = 0.5$ Hz, $H_{5'}$); δ_C (75 MHz, $CDCl_3$) 14.2, 15.4 CH_3 , CH_2CH_3 , 61.2 CH_2CH_3 , 87.9 C_4 , 100.1 C_2 , 108.9, 111.5 $C_{3',4'}$, 142.7 $C_{5'}$, 146.1 C_2 , 166.6 C_1 , 211.8 C_3 ; m/z (CI+, NH_3) 193 ($[M+H]^+$, 100), 119 (80); HRMS (CI+) Found $[M+H]^+$ 193.0864 $C_{11}H_{13}O_3$, requires 193.0865

Ethyl 2-methyl-4-(2-thiophenyl)-buta-2,3-dienoate 8i

Carried out by the general procedure above with 2-(2-thiophenyl)-2-triethylsilylethen-1-one **1i** (0.036 g, 0.15 mmol) and (1-ethoxycarbonylethylidene)triphenylphosphorane (**4**, 0.060 g, 0.165 mmol) in DCM (1 ml) at rt. The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 2-methyl-4-(2-thiophenyl)-buta-2,3-dienoate **8i** as a colourless liquid (0.021 g, 67 %).

ν_{max} (KBr/film) 2983 m, 2930 w, 2907 w, 1948 w (C=C=C), 1711 s (C=O), 1447 w, 1369 m, 1270 s, 1171 m, 1120 s, 1013 m, 926 m, 739 $s\text{ cm}^{-1}$; δ_H (270 MHz, $CDCl_3$) 1.24 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.97 (3 H, d, $J = 3$ Hz, CH_3), 4.19 (2 H, app dq, $J_{a-b} = 16$ Hz, $J = 7$ Hz, CH_2CH_3), 6.28 (1 H, d, $J_{3'-4'} = 3$ Hz, $H_{3'}$), 6.38 (1 H, dd, $J_{4'-3'} = 3$ Hz, $J_{4'-5'} = 2$ Hz, $H_{4'}$), 6.42 (1 H, q, $J = 3$ Hz, $H_{4'}$), 7.37 (1 H, dd, $J_{5'-4'} = 2$ Hz, $J_{5'-3'} = 0.5$ Hz, $H_{5'}$); δ_C (75 MHz, $CDCl_3$) 14.2, 15.4 CH_3 , CH_2CH_3 , 61.2 CH_2CH_3 , 87.9 C_4 , 100.1 C_2 , 108.9, 111.5 $C_{3',4'}$, 142.7 $C_{5'}$, 146.1 C_2 , 166.6 C_1 , 211.8 C_3 ; m/z (CI+, NH_3) 193 ($[M+H]^+$, 100), 119 (80); HRMS (CI+) Found $[M+H]^+$ 193.0864 $C_{11}H_{13}O_3$, requires 193.0865

Ethyl 4-(2-thiophenyl)-4-triethylsilylbuta-2,3-dienoate 7i

Carried out by the general procedure above with 2-(2-thiophenyl)-2-triethylsilylethen-1-one **1i** (0.036 g, 0.15 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (**5**, 0.058 g, 0.165 mmol) in DCM (1 ml) at rt. The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 4-(2-thiophenyl)-4-triethylsilylbuta-2,3-dienoate **7i** as a colourless liquid (0.045 g, 98 %).

ν_{max} (KBr/film) 2983 m, 2930 w, 2907 w, 1948 w (C=C=C), 1711 s (C=O), 1447 w, 1369 m, 1270 s, 1171 m, 1120 s, 1013 m, 926 m, 739 $s\text{ cm}^{-1}$; δ_H (300 MHz, $CDCl_3$) 0.78 (6 H, q, $J = 8$

Hz, SiCH₂CH₃), 0.97 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 1.23 (3 H, t, $J = 7$ Hz, CH₂CH₃), 4.17 (2 H, app dq, $J_{a-b} = 16$ Hz, $J = 7$ Hz, CH₂CH₃), 5.57 (1 H, s, H₂), 6.92-6.97 (2 H, m, H_{3,4'}), 7.20 (1 H, dd, $J_{5'-4'} = 5$ Hz, $J_{5'-3'} = 1.5$ Hz, H_{5'}); δ_C (75 MHz, CDCl₃) 3.5 SiCH₂CH₃, 7.1 SiCH₂CH₃, 14.2 CH₂CH₃, 60.7 CH₂CH₃, 84.5 C₂, 95.3 C₄, 125.4 C_{3,4'} (2 peaks), 127.3 C_{5'}, 136.2 C_{2'}, 166.5 C=O, 213.1 C₃; m/z (CI+, NH₃) 326 ([M+NH₄]⁺, 17), 309 ([M+H]⁺, 100), 148 (41); HRMS (CI+) Found [M+H]⁺ 309.1341 C₁₆H₂₅O₂SSi, requires 309.1345

Ethyl 2-methyl-4-(3-(1-tert-butoxycarbonyl)indolyl)-4-triethylsilyl buta-2,3-dienoate 6j and ethyl 2-methyl-4-(3-(1-tert-butoxycarbonyl)indolyl)-4-triethylsilylbuta-2,3-dienoate 8j

Carried out by the general procedure above with 2-(3-(1-tert-butoxycarbonyl)indolyl)-2-triethylsilylethen-1-one **1j** (0.074 g, 0.2 mmol) and (1-ethoxycarbonylethylidene)triphenylphosphorane (0.087 g, 0.24 mmol) in refluxing benzene (2 ml). The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield ethyl 2-methyl-4-(3-(1-tert-butoxycarbonyl)indolyl)-4-triethylsilylbuta-2,3-dienoate **6j** as a colourless liquid (0.067 g, 74 %) and ethyl 2-methyl-4-(3-(1-tert-butoxycarbonyl)indolyl)-buta-2,3-dienoate **8j** as a colourless liquid (0.013 g, 19 %).

6j: ν_{max} (KBr/film) 2954 m, 2875 w, 1918 m (C=C=C), 1735 s (C=O Boc), 1706 s (C=O ester), 1452 m, 1376 s, 1251 s, 1157 s, 1118 m, 1093 m, 1022 w, 858 w, 763 w, 746 w cm⁻¹; δ_H (300 MHz, CDCl₃) 0.77 (6 H, q, $J = 8$ Hz, SiCH₂CH₃), 0.98 (9 H, t, $J = 8$ Hz, SiCH₂CH₃), 1.25 (3 H, t, $J = 7$ Hz, CH₂CH₃), 1.67 (9 H, s, C(CH₃)), 1.96 (3 H, s, CH₃), 4.22 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, CH₂CH₃), 4.28 (1 H, dq, $J = 11$ Hz, $J = 7$ Hz, CH₂CH₃), 7.22 (1 H, appar t, $J = 8$ Hz, *IndH*), 7.32 (1 H, appar t, $J = 8$ Hz, *IndH*), 7.52 (1 H, s, H₂), 7.83 (1 H, d, $J = 8$ Hz, *IndH*), 8.08 (1 H, br d, *IndH*); δ_C (75 MHz, CDCl₃) 3.5 SiCH₂CH₃, 7.2 SiCH₂CH₃, 14.3, 15.0 CH₃, CH₂CH₃, 27.9 C(CH₃), 60.7 CH₂CH₃, 83.9 C(CH₃), 90.7, 90.9 C_{2,4}, 115.0, 120.5, 122.8, 122.9, 124.7 C_{2',4',5',6',7'}, 114.2, 130.0, 135.1 C_{3',3a',7a'}, 149.7 C=O, Boc, 169.3 C₁, 212.3 C₃; m/z (CI+, NH₃) 473 ([M+NH₄]⁺, 25), 456 ([M+H]⁺, 100), 399 (24), 356 (18), 218 (20); HRMS (CI+) Found [M+H]⁺ 456.2567 C₂₆H₃₈NO₄Si, requires 456.2570

8j: ν_{\max} (KBr/film) 2979 w, 2933 w, 1945 w (C=C=C), 1735 s (C=O Boc), 1710 s (C=O ester), 1452 m, 1371 m, 1348 s, 1303 w, 1253 s, 1157 s, 1118 m, 1089 s, 1020 w, 763 w, 748 w cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 1.21 (3 H, t, $J = 7$ Hz, CH_2CH_3), 1.65 (9 H, s, $\text{C}(\text{CH}_3)$), 2.04 (3 H, d, $J_{\text{CH}_3-4} = 3$ Hz, CH_3), 4.20 (2 H, q, $J = 7$ Hz, CH_2CH_3), 6.64 (1 H, q, $J_{4-\text{CH}_3} = 3$ Hz, H_4), 7.23 (1 H, appar t, $J = 8$ Hz, *IndH*), 7.33 (1 H, appar t, $J = 8$ Hz, *IndH*), 7.57 (1 H, s, H_2), 7.68 (1 H, d, $J = 8$ Hz, *IndH*), 8.13 (1 H, br d, *IndH*); δ_{C} (75 MHz, CDCl_3) 14.3, 15.7 CH_3 , CH_2CH_3 , 28.2 $\text{C}(\text{CH}_3)$, 61.2 CH_2CH_3 , 84.0 $\text{C}(\text{CH}_3)$, 88.5 C_4 , 98.6 C_2 , 115.3, 119.9, 123.0, 124.3, 124.9 $\text{C}_{2,4,5,6,7}$, 112.3, 128.6, 135.9 $\text{C}_{3,3a,7a}$, 149.4 (C=O, Boc), 167.2 C_1 , 213.1 C_3 ; m/z (Cl^+ , NH_3) 359 ($[\text{M}+\text{NH}_4]^+$, 25), 342 ($[\text{M}+\text{H}]^+$, 100), 242 (77), 218 (88), 120 (24); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 342.1704 $\text{C}_{20}\text{H}_{24}\text{NO}_4$, requires 342.1705

4-Triethylsilylpenta-2,3-dienynitrile **14a**

Carried out by the general procedure above with 2-triethylsilylpropen-2-one **1a** (0.102 g, 0.60 mmol) and (cyanomethylene)triphenylphosphorane (**9**, 0.2 g, 0.66 mmol) in DCM (2 ml) at rt. The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl ether) to yield 4-triethylsilylpenta-2,3-dienynitrile **14a** as a colourless liquid (0.061 g, 53 %).

ν_{\max} (KBr/film) 3012 w, 2956 s, 2912 m, 2877 s, 2218 s (CN), 1934 s (C=C=C), 1457 w, 1414 w, 1238 w, 1004 m, 739 s, 721 s, 710 s cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.64 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.93 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.76 (3 H, d, $J_{5-2} = 3$ Hz, H_5), 4.74 (1 H, q, $J_{2-5} = 3$ Hz, H_2); δ_{C} (75 MHz, CDCl_3) 2.5 SiCH_2CH_3 , 7.0 SiCH_2CH_3 , 14.3 C_5 , 59.3 C_2 , 94.2 C_4 , 115.2 CN, 210.5 C_3 ; m/z (Cl^+ , NH_3) 211 ($[\text{M}+\text{NH}_4]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{NH}_4]^+$ 211.1627 $\text{C}_{11}\text{H}_{23}\text{N}_2\text{Si}$, requires 211.1630

4-Triethylsilylundeca-2,3-dienenitrile **14b**

Carried out by the general procedure above with 2-triethylsilylnon-1-en-1-one **1b** (0.050 g, 0.2 mmol) and (cyanomethylene)triphenylphosphorane (**9**, 0.066 g, 0.22 mmol) in DCM (2 ml) at rt. The crude product was purified by flash chromatography (95:5 petroleum ether:diethyl

ether) to yield 4-triethylsilylundeca-2,3-diene nitrile **14b** as a colourless liquid (0.052 g, 94 %).

ν_{\max} (KBr/film) 2955 s, 2929 s, 2874 s, 2857 s, 2217 w (CN), 1931 w (C=C=C), 1728 m, 1650 w, 1465 w, 1244 w, 1017 w, 737 m, 721 m cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.65 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.86 (3H, t, $J = 7$ Hz, H_{11}), 0.94 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.16-1.30 (8 H, m, $\text{H}_{7,8,9,10}$), 1.46 (2 H, p, $J = 7.5$ Hz, H_6), 2.01 (2 H, m, H_5), 4.80 (1 H, t, $J_{2-5} = 3.5$ Hz, H_2); δ_{C} (75 MHz, CDCl_3) 2.8 SiCH_2CH_3 , 7.0 SiCH_2CH_3 , 14.0 C_{11} , 22.6 C_{10} , 28.5, 28.7, 29.0, 29.2 $\text{C}_{6,7,8,9}$, 31.7 C_5 , 60.8 C_2 , 99.8 C_4 , 115.4 C_1 , 210.2 C_3 ; m/z (Cl^+ , NH_3) 295 ($[\text{M}+\text{NH}_4]^+$, 100), 131 (28), 103 (27); HRMS (Cl^+) Found $[\text{M}+\text{NH}_4]^+$ 295.2565 $\text{C}_{17}\text{H}_{35}\text{N}_2\text{Si}$, requires 295.2569

5-Triethylsilylhexa-3,4-dien-2-one **15a**

Carried out by the general procedure above with 2-triethylsilylpropen-2-one **1a** (0.102 g, 0.6 mmol) and acetylmethylenetriphenylphosphorane (**10**, 0.21 g, 0.66 mmol) in DCM (2 ml) at rt. The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield 5-triethylsilylhexa-3,4-dien-2-one **15a** as a colourless liquid (0.065 g, 52 %).

ν_{\max} (KBr/film) 2955 s, 2912 m, 2876 s, 1919 s (C=C=C), 1677 s (C=O), 1456 w, 1415 w, 1356 w, 1231 s, 1007 m, 939 w, 795 w, 737 m, 722 m, 711 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.64 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.93 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.80 (3 H, d, $J_{6-3} = 3$ Hz, H_6), 2.15 (3 H, s, H_1), 5.38 (1 H, q, $J_{3-6} = 3$ Hz, H_3); δ_{C} (75 MHz, CDCl_3) 2.7 SiCH_2CH_3 , 7.1 SiCH_2CH_3 , 14.6 CH_3 , 26.3 C_1 , 92.0 C_3 , 93.0 C_5 , 200.4 C=O, 210.5 C_4 ; m/z (Cl^+ , NH_3) 228 ($[\text{M}+\text{NH}_4]^+$, 17), 211 ($[\text{M}+\text{H}]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 211.1526 $\text{C}_{12}\text{H}_{23}\text{OSi}$, requires 211.1518

1-Phenyl-4-triethylsilylpenta-2,3-dien-1-one **16a**

Carried out by the general procedure above with 2-triethylsilylpropen-2-one **1a** (0.073 g, 0.43 mmol) and benzoylmethylenetriphenylphosphorane (**11**, 0.18 g, 0.47 mmol) in refluxing DCM (2 ml). The crude product was purified by flash chromatography (90:10 petroleum

ether:diethyl ether) to yield 1-phenyl-4-triethylsilylpenta-2,3-dien-1-one **16a** as a colourless liquid (0.073 g, 62 %).

ν_{\max} (KBr/film) 2956 s, 2911 m, 2876 m, 1918 s (C=C=C), 1647 s (C=O), 1447 w, 1389 w, 1275 m, 1219 m, 1062 w, 1007 m, 710 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.54 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.81 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.83 (3 H, d, $J_{5-2} = 3$ Hz, H_5), 5.97 (1 H, q, $J_{2-5} = 3$ Hz, H_3), 7.35-7.51 (3 H, m, $\text{H}_{3',4'}$), 7.75-7.79 (2 H, m, H_2); δ_{C} (75 MHz, CDCl_3) 2.6 SiCH_2CH_3 , 6.9 SiCH_2CH_3 , 14.4 C_5 , 88.2 C_2 , 91.6 C_4 , 128.0, 128.1 $\text{C}_{2',3'}$, 131.9 $\text{C}_{4'}$, 138.5 $\text{C}_{1'}$, 194.4 C=O, 210.8 C_3 ; m/z (Cl^+ , NH_3) 273 ($[\text{M}+\text{H}]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 273.1667 $\text{C}_{17}\text{H}_{25}\text{OSi}$, requires 273.1675

1-Phenyl-4-triethylsilylundeca-2,3-dien-1-one **16b**

Carried out by the general procedure above with 2-triethylsilylnon-1-en-1-one **1b** (0.382 g, 1.5 mmol) and benzoylmethylenetriphenylphosphorane (**11**, 0.628 g, 1.65 mmol) in refluxing DCM (5 ml). The crude product was purified by flash chromatography (90:10 petroleum ether:diethyl ether) to yield 1-phenyl-4-triethylsilylundeca-2,3-dien-1-one **16b** as a colourless liquid (0.333 g, 62 %).

ν_{\max} (KBr/film) 2954 s, 2927 s, 2875 m, 1914 s (C=C=C), 1644 s (C=O), 1390 w, 1276 m, 1218 m, 1004 m, 971 w, 842 w, 721 m, 696 m cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.57 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.84 (12 H, t, $J = 8$ Hz, SiCH_2CH_3 , H_{11}), 1.22-1.32 (8 H, m, $\text{H}_{7,8,9,10}$), 1.52 (2 H, p, $J = 7.5$ Hz, H_6), 1.94-2.18 (2 H, m, H_5), 6.10 (1 H, t, $J_{2-5} = 3.5$ Hz, H_2), 7.35-7.47 (3 H, m, $\text{H}_{3',4'}$), 7.79-7.82 (2 H, m, H_2); δ_{C} (75 MHz, CDCl_3) 2.9 SiCH_2CH_3 , 7.0 SiCH_2CH_3 , 14.1 C_{11} , 22.6 C_{10} , 28.9, 29.0, 29.1, 29.3 $\text{C}_{6,7,8,9}$, 31.7 C_5 , 89.5 C_2 , 97.0 C_4 , 128.1 $\text{C}_{2',3'}$ (2 peaks overlapped), 131.9 $\text{C}_{4'}$, 138.6 $\text{C}_{1'}$, 193.6 C_1 , 210.0 C_3 ; m/z (Cl^+ , NH_3) 357 ($[\text{M}+\text{H}]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 357.2614 $\text{C}_{23}\text{H}_{37}\text{OSi}$, requires 357.2614

General procedure for the preparation of allenylsilanes from silyl ketenes and semi-stabilised phosphorus ylides

3-Methyl-1-phenyl-3-triethylsilylbuta-1,2-diene **17a**

To a suspension of benzyltriphenylphosphonium chloride (0.238 g, 0.55 mmol) in THF (2 ml) at rt was added dropwise *n*-BuLi (0.275 ml of a 2 M solution in pentane, 0.55 mmol). The resulting red-orange solution was stirred at rt for 0.5 h and then a solution of 2-triethylsilylpropen-2-one **1a** (0.085 g, 0.5 mmol) in THF (2ml) was added dropwise. After 30 min, hexane (10 ml) was then added and the white precipitate removed by filtration. The filtrate was concentrated under reduced pressure and the residual oil purified by flash chromatography (100 % petroleum ether) to yield 3-methyl-1-phenyl-3-triethylsilylbuta-1,2-diene **17a** as a colourless liquid (0.079 g, 65 %).

ν_{\max} (KBr/film) 3029 w, 2953 s, 2911 m, 2874 s, 1923 s (C=C=C), 1598 w, 1496 w, 1456 m, 1414 w, 1238 w, 1009 m, 931 w, 797 m, 737 s, 711 s, 692 s cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.70 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 1.02 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.85 (3 H, d, $J_{4-1} = 3$ Hz, H_4), 5.84 (1 H, q, $J_{1-4} = 3$ Hz, H_1), 7.12-7.18 (1 H, m, H_4'), 7.24-7.33 (4 H, m, $\text{H}_{2',3'}$); δ_{C} (75 MHz, CDCl_3) 3.0 SiCH_2CH_3 , 7.4 SiCH_2CH_3 , 15.8 C_4 , 88.0 C_3 , 92.6 C_1 , 125.7 $\text{C}_{4'}$, 125.9, 128.4 $\text{C}_{2',3'}$, 136.1 $\text{C}_{1'}$, 206.4 C_2 ; m/z (Cl^+ , NH_3) 245 ($[\text{M}+\text{H}]^+$, 41), 132 ($[\text{SiEt}_3+\text{NH}_3]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 245.1717 $\text{C}_{16}\text{H}_{25}\text{Si}$, requires 245.1725

1-Phenyl-3-triethylsilyldeca-1,2-diene **17b**

Carried out by the general procedure above with 2-triethylsilylnon-1-en-1-one **1b** (0.509 g, 2 mmol), benzyltriphenylphosphonium chloride (0.953 g, 2.2 mmol) in THF (15 ml) and *n*-BuLi (1.15 ml of a 2 M solution in pentane, 2.3 mmol). The crude product was purified by flash chromatography (100 % petroleum ether) to yield 1-phenyl-3-triethylsilyldeca-1,2-diene **17b** as a colourless liquid (0.445 g, 68 %).

ν_{\max} (KBr/film) 3028 w, 2953 s, 2927 s, 2873 m, 2854 m, 1918 s (C=C=C), 1599 w, 1495 w, 1456 m, 1414 w, 1377 w, 1005 m, 797 m, 735 s, 718 s, 692 s cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.61 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.82 (3 H, t, $J_{10-9} = 7$ Hz, H_{10}), 0.93 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.19-1.31 (8 H, m, $\text{H}_{6,7,8,9}$), 1.49 (2 H, p, $J = 7.5$ Hz, H_5), 1.99-2.05 (2 H, m, H_4), 5.83 (1 H, t, $J_{1-4} = 3.5$ Hz, H_1), 7.10 (1 H, m, H_4'), 7.19-7.27 (4 H, m, $\text{H}_{2',3'}$); δ_{C} (75 MHz, CDCl_3) 3.2 SiCH_2CH_3 , 7.4 SiCH_2CH_3 , 14.1 C_{10} , 22.6, 27.0, 29.2, 29.5, 29.7 $\text{C}_{5,6,7,8}$, 31.9 C_4 ,

89.7 C₁, 98.3 C₃, 125.6 C₄, 125.8, 128.4 C_{2,3}, 136.4 C₁, 205.8 C₂; *m/z* (Cl⁺, NH₃) 358 ([M+NH₄]⁺, 10), 329 ([M+H]⁺, 31), 132 ([SiEt₃+NH₃]⁺, 100); HRMS (Cl⁺) Found [M+H]⁺ 329.2657 C₂₂H₃₇Si, requires 329.2665

3-(4-Bromophenyl)-1-phenyl-3-triethylsilylpropa-1,2-diene **18g**

Carried out by the general procedure above with 2-triethylsilylnon-1-en-1-one **1g** (0.109 g, 0.35 mmol), benzyltriphenylphosphonium chloride (0.167 g, 0.385 mmol) in THF (2 ml) and *n*-BuLi (0.16 ml of a 2.5 M solution in pentane, 0.402 mmol). The crude product was purified by flash chromatography (100 % petroleum ether) to yield 3-(4-bromophenyl)-1-phenyl-3-triethylsilylpropa-1,2-diene **18g** as a colourless liquid (0.078 g, 58%).

ν_{\max} (KBr/film) 3027 w, 2954 s, 2910 s, 2873 s, 1913 s (C=C=C), 1598 w, 1483 s, 1456 m, 1413 w, 1375 w, 1238 w, 1072 m, 1008 s, 896 m, 825 m, 802 m, 734 s, 719r s cm⁻¹; δ_{H} (300 MHz, CDCl₃) 0.83 (6 H, q, *J* = 8 Hz, SiCH₂CH₃), 1.00 (9 H, t, *J* = 8 Hz, SiCH₂CH₃), 6.24 (1 H, s, H₁), 7.25 (3 H, m, inc. d, *J* = 8.5 Hz, H_{2'}, H_{4'}), 7.33 (4 H, m, H_{2,3'}), 7.45 (2H, d, *J* = 8.5 Hz, H_{3'}); δ_{C} (75 MHz, CDCl₃) 4.0 SiCH₂CH₃, 7.5 SiCH₂CH₃, 91.5 C₁, 101.0, 120.5, 126.3, 126.6, 128.8, 129.3, 131.7, 134.4, 136.63 (8 x ArC), 210.4 C₂; *m/z* (Cl⁺, NH₃) 387 ([⁸¹BrM+H]⁺, 35), 385 ([⁷⁹BrM+H]⁺, 35), 307 (37), 132 ([SiEt₃+NH₃]⁺, 100); HRMS (Cl⁺) Found [M+H]⁺ 387.0967 C₂₁H₂₆⁸¹BrSi, requires 387.0967

1-(4-Bromophenyl)-3-triethylsilyldeca-1,2-diene **18b**

Carried out by the general procedure above with 2-triethylsilylnon-1-en-1-one **1b** (0.051 g, 0.2 mmol), (4-bromobenzyl)triphenylphosphonium chloride (0.107 g, 0.21 mmol) in THF (15 ml) and lithium hexamethyldisilazide (0.22 ml of a 1 M solution in THF, 2.2 mmol). The crude product was purified by flash chromatography (100 % petroleum ether) to yield 3-(4-bromophenyl)-1-phenyl-3-triethylsilyldeca-1,2-diene **18b** as a colourless liquid (0.043 g, 53 %).

ν_{\max} (KBr/film) 2952 s, 2927 s, 2873 s, 2854 m, 1916 s (C=C=C), 1486 m, 1461 w, 1417 w, 1070 w, 1008 m, 833 m, 732 s, 719 s cm⁻¹; δ_{H} (270 MHz, CDCl₃) 0.61 (6 H, q, *J* = 8 Hz), 0.83

(3 H, t, $J_{10-9} = 7$ Hz), 0.93 (9 H, t, $J = 8$ Hz), 1.18-1.31 (8 H, m), 1.42-1.51 (2 H, m), 1.99-2.07 (2 H, m), 5.77 (1 H, t, $J_{1-4} = 3.5$ Hz), 7.06 (2 H, d, $J_{3'-2'}$ = 8.5 Hz), 7.35 (2 H, d, $J_{2'-3'}$ = 8.5 Hz); δ_C (67.5 MHz, $CDCl_3$) 3.2, 7.4, 14.1, 22.6, 29.1 (2 peaks overlapped), 29.5, 29.6, 31.8, 88.9, 98.9, 118.9, 127.3, 131.5, 135.5, 205.6; m/z (CI+, NH_3) 409 ($[M^{81}Br+H]^+$, 43), 407 ($[M^{79}Br+H]^+$, 40), 329 ($[M-Br+H]^+$, 40), 193 (69), 132 ($[SiEt_3+NH_3]^+$, 100); HRMS (CI+) Found $[M+H]^+$ 409.1756 $C_{22}H_{36}^{81}BrSi$, requires 409.1749

General procedure for the preparation of allenylsilanes from silylketenes and Cp_2TiMe_2

Ethyl 4-triethylsilylundeca-2,3-diene **19b**

A solution of Cp_2TiMe_2 (4 ml of a 0.5M solution in THF, 2 mmol) was mixed with 2-triethylsilylnon-1-en-1-one **1b** (0.255 g, 1 mmol). The resulting solution was protected from light and stirred at 65-70 °C with exclusion of moisture and the reaction monitored by TLC for complete consumption of the silylketene. The solution was cooled to rt and diluted with petroleum ether. The resulting precipitate was removed by filtration, the filtrate concentrated under reduced pressure and the residual oil purified by flash chromatography (100 % petroleum ether) to yield 4-triethylsilylundeca-2,3-diene **19b** as a colourless liquid (0.197 g, 78 %).

ν_{max} (KBr/film) 2954 s, 2925 s, 2875 s, 2956 m, 1926 s (C=C=C), 1461 m, 1415 w, 1376 w, 1008 m, 808 m, 719 s cm^{-1} ; δ_H (300 MHz, $CDCl_3$) 0.62 (6 H, q, $J = 8$ Hz, $SiCH_2CH_3$), 0.84-0.97 (12 H, m, $SiCH_2CH_3$, H_{10}), 1.17-1.24 (8 H, m, $H_{6,7,8,9}$), 1.41 (2 H, p, $J = 7.5$ Hz, H_5), 1.83-1.89 (2 H, m, H_4), 4.28 (2 H, t, $J_{1-4} = 3.5$ Hz, H_1); δ_C (75 MHz, $CDCl_3$) 3.1 $SiCH_2CH_3$, 7.3 $SiCH_2CH_3$, 14.1 C_{10} , 22.7, 28.9 (2 peaks overlapped), 29.0, 29.4 $C_{5,6,7,8,9}$, 31.9 C_4 , 68.5 C_1 , 91.6 C_3 , 208.9 C_2 ; m/z (CI+, NH_3) 253 ($[M+H]^+$, 17), 132 ($[SiEt_3+NH_3]^+$, 100), 119 (40), 105 (27); HRMS (CI+) Found $[M+H]^+$ 253.2350 $C_{16}H_{33}Si$, requires 253.2352

3-tert-Butyldimethylsilyldeca-1,2-diene **19b***

Carried out by the general procedure above with Cp_2TiMe_2 (0.6 ml, 0.3 mmol) and 2-*tert*-butyldimethylsilylnon-2-en-1-one **1b*** (0.038 g, 0.15 mmol). The crude product was purified by flash chromatography (100 % petroleum ether) to yield 3-*tert*-butyldimethylsilyldeca-1,2-diene **19b*** as a colourless liquid (0.030 g, 79 %).

ν_{max} (KBr/film) 2956 s, 2928 s, 2857 s, 1925 s (C=C=C), 1464 w, 1250 w, 838 s, 825 s, 809 s, 771 m cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.03 (6 H, s; $\text{Si}(\underline{\text{CH}_3})_2$), 0.86 (3 H, t, $J_{9,8} = 7$ Hz, H_9), 0.88 (9 H, s, $\text{SiC}(\underline{\text{CH}_3})_3$), 1.22-1.33 (8 H, m, $\text{H}_{6,7,8,9}$), 1.44 (2 H, p, $J = 7.5$ Hz, H_5), 1.86-1.94 (2 H, m, H_4), 4.31 (2 H, t, $J_{1-4} = 3.5$ Hz, H_1); δ_{C} (75 MHz, CDCl_3) - 6.2 $\text{Si}(\underline{\text{CH}_3})_2$, 14.1 C_{10} , 18.8 $\text{SiC}(\underline{\text{CH}_3})_3$, 22.7 C_9 , 26.7 $\text{SiC}(\underline{\text{CH}_3})_3$, 28.9, 29.2, 29.3, 29.4 $\text{C}_{5,6,7,8}$, 31.9 C_4 , 69.2 C_1 , 92.6 C_3 , 209.4 C_2 ; m/z (CI+, NH_3) 270 ($[\text{M}+\text{NH}_4]^+$, 10), 253 ($[\text{M}+\text{H}]^+$, 78), 214 (36), 212 (25), 137 (44), 132 ($[\text{TBS}+\text{NH}_3]^+$, 100), 92 (24), 90 (42); HRMS (CI+) Found $[\text{M}+\text{H}]^+$ 253.2356 $\text{C}_{16}\text{H}_{33}\text{Si}$, requires 253.2352

1-Phenyl-2-triethylsilylbuta-2,3-diene **19c**

Carried out by the general procedure above with Cp_2TiMe_2 (3 ml, 1.5 mmol) and 3-phenyl-2-triethylsilylpropen-1-one **1c** (0.123 g, 0.5 mmol). The crude product was purified by flash chromatography (100 % petroleum ether) to yield 1-phenyl-2-triethylsilylbuta-2,3-diene **19c** as a colourless liquid (0.090 g, 75 %).

ν_{max} (KBr/film) 2952 s, 2910 m, 2875 m, 1926 s (C=C=C), 1494 w, 1454 w, 1415 w, 1238 w, 1006 m, 809 m, 755 w, 734 s, 717 s, 698 s cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.55 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.89 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 3.28 (2 H, t, $J_{1-4} = 3$ Hz, H_1), 4.28 (2 H, t, $J_{4-1} = 3$ Hz, H_4), 7.13-7.29 (5 H, m, Ph); δ_{C} (75 MHz, CDCl_3) 3.1 SiCH_2CH_3 , 7.2 SiCH_2CH_3 , 36.4 C_1 , 68.7 C_4 , 91.5 C_2 , 126.0 C_4' , 128.0, 128.9 $\text{C}_{2,3'}$, 140.5 $\text{C}_{1'}$, 210.6 C_3 ; m/z (CI+, NH_3) 245 ($[\text{M}+\text{H}]^+$, 73), 132 ($[\text{SiEt}_3+\text{NH}_3]^+$, 100); HRMS (CI+) Found $[\text{M}+\text{H}]^+$ 245.1718 $\text{C}_{16}\text{H}_{25}\text{Si}$ requires 245.1725

1-Cyclohexyl-1-triethylsilylpropa-1,2-diene **19d**

Carried out by the general procedure above with Cp_2TiMe_2 (12 ml, 6 mmol) and 2-cyclohexyl-2-triethylsilylethen-1-one **1d** (0.477 g, 2 mmol). The crude product was purified by flash chromatography (100 % petroleum ether) to yield 1-cyclohexyl-1-triethylsilylpropa-1,2-diene **19d** as a colourless liquid (0.39 g, 82 %).

ν_{max} (KBr/film) 2942 s, 2925 s, 2879 m, 1920 s (C=C=C), 1448 w, 1415 w, 1238 w, 1074 w, 1016 w, 808 m, 730 s, 717 s cm^{-1} ; δ_{H} (270 MHz, CDCl_3) 0.59 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.91 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 1.10-1.28 (5 H, m), 1.56-1.80 (6 H, m), 4.30 (2 H, d, $J_{3-1} = 1.5$ Hz, H_3); δ_{C} (75 MHz, CDCl_3) 3.4 SiCH_2CH_3 , 7.4 SiCH_2CH_3 , 26.1 $\text{C}_{4'}$, 26.8, 33.9 $\text{C}_{2',3'}$, 37.9 $\text{C}_{1'}$, 69.3 C_3 , 97.2 C_1 , 208.9 C_2 ; m/z (Cl^+ , NH_3) 237 ($[\text{M}+\text{H}]^+$, 52), 226 (14), 172 (14), 132 ($[\text{SiEt}_3+\text{NH}_3]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 237.2032 $\text{C}_{15}\text{H}_{29}\text{Si}$, requires 237.2038

1-Phenyl-1-triethylsilylpropa-1,2-diene 19e

Carried out by the general procedure for the preparation of silyl allenes with Cp_2TiMe_2 (4 ml, 2 mmol) and 2-phenyl-2-triethylsilylethen-1-one **1e** (0.116 g, 0.5 mmol). The crude product was purified by flash chromatography (100 % petroleum ether) to 1-phenyl-1-triethylsilylpropa-1,2-diene **19e** as a colourless liquid (0.044 g, 38 %).

ν_{max} (KBr/film) 2954 s, 2910 m, 2875 s, 1918 s (C=C=C), 1596 w, 1490 w, 1459 w, 1415 w, 1238 w, 1004 m, 813 m, 761 m, 734 s, 721 s, 696 s cm^{-1} ; δ_{H} (300 MHz, CDCl_3) 0.73 (6 H, q, $J = 8$ Hz, SiCH_2CH_3), 0.95 (9 H, t, $J = 8$ Hz, SiCH_2CH_3), 4.64 (2 H, s, H_3), 7.15-7.19 (1 H, m, $\text{H}_{4'}$), 7.24-7.28 (4 H, m, $\text{H}_{2',3'}$); δ_{C} (75 MHz, CDCl_3) 3.5 SiCH_2CH_3 , 7.3 SiCH_2CH_3 , 69.7 C_1 , 95.6 C_3 , 126.1 $\text{C}_{4'}$, 127.6, 128.4 $\text{C}_{2',3'}$, 137.6 $\text{C}_{1'}$, 211.8 C_2 ; m/z (Cl^+ , NH_3) 231 ($[\text{M}+\text{H}]^+$, 74), 132 ($[\text{SiEt}_3+\text{NH}_3]^+$, 100); HRMS (Cl^+) Found $[\text{M}+\text{H}]^+$ 231.1564 $\text{C}_{15}\text{H}_{23}\text{Si}$, requires 231.1569