# The First Intramolecular Silene Diels-Alder Reactions: Supporting Information

**Michal Czyzewski,[a] Jonathan D. Sellars,[a] Tamaz Guliashvili,[c] Julius Tibbelin,[c] Lisa Johnstone,[a] Justin Bower,[b‡] Matthew Box,[b] Robert D. M. Davies,[b] Henrik Ottosson[c*] and Patrick G. Steel[a*]**

[a] *Department of Chemistry, University of Durham, Durham, DH1 3LE, United Kingdom. Fax: (+) 44 (0)1913844737; E-mail: p.g.steel@durham.ac.uk*

[b] *Astra Zeneca, Alderley Park, Alderley Edge, Cheshire, SK10 4TF, UK*

[c] *Department of Biochemistry and Organic Chemistry, Uppsala University, Box 576, S-751 23 Uppsala, Sweden. E-mail: henrik.ottosson@kemi.uu.se*

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## 7.1 General Procedures

All air- and/or moisture-sensitive reactions were carried out under an argon atmosphere in oven-dried glassware. Commercially available reagents were used without further purification, apart from the following: trimethylacetyl chloride was distilled from anhydrous $P_2O_{10}$, $Et_3N$ was distilled over KOH pellets, *t*-BuOK was dried under vacuum at 50 $^{o}$C overnight before use. 40-60 Petroleum ether was redistilled before use and refers to the fraction of light petroleum ether boiling in the range 40-60 $^{o}$C. Benzene was dried over 4 Å molecular sieves. All other solvents were obtained dried using an Innovative Technology Solvent Purification System (SPS).

Analytical thin layer chromatography (TLC) was performed using commercially available aluminium-backed plates coated with silica gel 60 $F_{254}$ ($UV_{254}$) or neutral aluminium oxide 60 $F_{254}$ ($UV_{254}$), and visualised under ultra-violet light (at 254 nm), or through staining with ethanolic phosphomolybdic acid followed by heating. Flash column chromatography was carried out using 200-400 mesh silica gel 40-63 µm or neutral alumina.

Melting points were determined either using Thermo Scientific 9100 or Gallenkamp melting point apparatus and are uncorrected. Gas Chromatography was carried out on a Hewlett-Packard 5890 series II gas chromatograph fitted with a 25 cm column and connected to a flame ionisation detector. Infrared spectra were recorded using a Diamond ATR (attenuated total reflection) accessory (Golden Gate) or as a solution in chloroform via transmission IR cells on a Perkin-Elmer FT-IR 1600 spectrometer. $^{1}$H, $^{13}$C, $^{19}$F, and $^{29}$Si NMR spectra were recorded in $CDCl_3$ (unless otherwise stated) on Varian Mercury-200 ($^{1}$H), Varian Mercury-400 ($^{1}$H, $^{13}$C, $^{19}$F), Bruker Avance-400 ($^{1}$H, $^{13}$C, $^{29}$Si), Varian Inova-500 ($^{1}$H, $^{13}$C, $^{29}$Si) or Varian VNMRS-700 ($^{1}$H, $^{13}$C, $^{29}$Si) spectrometers and reported as follows: chemical shift δ (ppm) (number of protons, multiplicity, coupling constant *J* (Hz), assignment). All $^{13}$C NMR spectra were proton decoupled. The chemical shifts are reported using the residual signal of $CHCl_3$ as the internal reference ($\delta_H$ = 7.27 ppm; $\delta_C$ = 77.0 ppm). All chemical shifts are quoted in parts per million relative to tetramethylsilane ($\delta_H$ = 0.00 ppm) and coupling constants are given in Hertz to the nearest 0.5 Hz. Assignment of spectra was carried out using COSY, NOESY, HSQC, and HMBC experiments. Gas-Chromatography mass spectra (EI) were taken using a Thermo-Finnigan Trace with a 25 cm column connected to a VG Mass Lab Trio 1000. Electrospray mass spectra (ES) were obtained on a Micromass LCT Mass Spectrometer. High resolution mass spectra were obtained using a Thermo-Finnigan LTQFT mass spectrometer or Xevo QToF mass spectrometer (Waters UK, Ltd) by Durham University Mass Spectrometry service, or performed by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea.

**Standard procedure for the Mitsunobu reaction**

THF was added in one portion to triphenylphosphine, and alcohols at 25 $^{o}$C under argon. The reaction vessel was then sonicated for a few minutes (approx. 5 min) giving a homogenous solution. To the sonicated reaction mixture azodicarboxylate ester was added dropwise over the course of 5-15 min. The reaction mixture was sonicated for 15 min and subsequently triturated with hexane to remove the majority of the triphenylphosphine. Flash column chromatography on silica, elution gradient 0 to 30% ethyl acetate in pet. ether, afforded the desired product.

**Standard ester hydrolysis procedure (B)**

To a solution of ester in THF was added a solution of lithium hydroxide (2 eq) in water. The reaction mixture was stirred at 50 $^{o}$C for 30 h. The reaction was then quenched by addition of HCl (5 M, pH = 1) and diluted with $Et_2O$. The aqueous layer was separated and extracted three times with $Et_2O$. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 50% ethyl acetate in pet. ether, afforded the desired carboxylic acid.

**Standard procedure for acylpolysilane synthesis (C)**

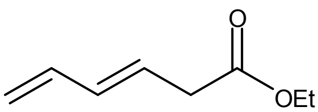
*Stage 1*

Tetrakis(trimethylsilyl)silane and dry potassium *tert*-butoxide were dissolved in THF and stirred for 3 h at room temperature. The resulting solution was used in *Stage 2*.

*Stage 2*

A solution of carboxylic acid in DCM was treated with oxalyl chloride and DMF (one drop) at 0 $^{o}$C. The reaction mixture was stirred at that temperature for 3 h after which time volatiles were evaporated *in vacuo*. The residue was redissolved in THF and treated with silylpotassium (*Stage 1*) at -78 $^{o}$C. After stirring for 3 h at -78 $^{o}$C saturated ammonium chloride solution was added. The organic layer was separated, and the aqueous layer was extracted three times with $Et_2O$. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography, elution gradient 0 to 20% diethyl ether in pet. ether, afforded the desired product.

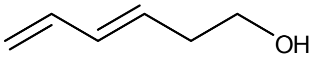
*(E)-Ethyl hexa-3,5-dienoate*[i] **112**




A solution of *n*-butyllithium (134 ml, 214.01 mmol) in hexane was added to a stirred solution of diisopropylamine (30.2 ml, 214.01 mmol) in THF (400 ml) at -78 °C, over a period of 15 minutes under nitrogen. The resulting solution was stirred at -78 °C for 1 h prior to the addition of DMPU (21.50 ml, 178.34 mmol). A room temperature solution of (2*E*,4*E*)-ethyl hexa-2,4-dienoate (27.0 ml, 178.34 mmol) in THF (50 ml) was slowly added to the yellow solution of LDA via cannula. The reaction was stirred at -78 °C for 1 h after which time EtOH (80ml) was added and the mixture was stirred for 5 min. The reaction mixture was poured onto water (200 ml) and EtOAc (100ml). The layers were separated and the aqueous layer was extracted with Et2O (2 x 200ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Distillation gave the title compound as a colourless liquid (14.66 g, 58.6 %). B.p 45 $^{o}$C/10 mbar (lit.[1] 45 $^{o}$C/0.7 mmHg); IR (ATR) 2980, 1732, 1603, 1407, 1368, 1335, 1243, 1177, 1139, 1097, 1025, 1003, 953, 902, 857 cm$^{-1}$; $\delta_H$ (700 MHz) 6.33 (1H, ddd, *J* =

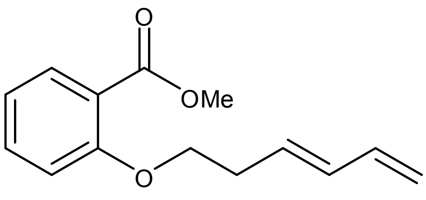
17.0Hz, $J$ = 10.4Hz, $J$ = 10.2Hz, 5-***H***), 6.14 (1H, dd, $J$ = 15.3Hz, $J$ = 10.4Hz, 4-***H***), 5.79 (1H, dt, $J$ = 15.3Hz, $J$ = 7.2Hz, 3-***H***), 5.16 (1H, d, $J$ = 17.0Hz, 6-***H***), 5.06 (1H, d, $J$ = 10.2Hz, 6-***H***), 4.15 (2H, q, $J$ = 7.1Hz, C***H***$_2$CH$_3$), 3.11 (2H, d, $J$ = 7.2Hz, 2-***H***), 1.26 (3H, t, $J$ = 7.1Hz, CH$_2$C***H***$_3$); $\delta_C$ (175 MHz) 171.4 (***C***-1), 136.4 (**C**-5), 134.3 (***C***-4), 125.7 (**C**-3), 116.8 (***C***-6), 60.7 (***C***H$_2$CH$_3$), 38.0 (***C***-2), 14.2 (CH$_2$***C***H$_3$); m/z (EI) 140 ([M]$^{+\cdot}$, 76%), 98 (19), 81 (12), 67 ([M-CO$_2$Et]$^{+\cdot}$, 100), 54 (22), 41(58).

*(E)-Hexa-3,5-dien-1-ol*[1] **10**



To a suspension of $LiAlH_4$ (3.69 g, 97.2 mmol) in diethyl ether (300 ml) was added a solution of (*E*)-ethyl hexa-3,5-dienoate (13.62 g, 97.2 mmol) in diethyl ether (50 ml) at 0 °C, over a period of 15 minutes under nitrogen. The resulting suspension was stirred at RT for 12 h. The reaction mixture was cooled with an ice bath and cautiously quenched sequentially with $H_2O$ (4.0 ml), NaOH (1M, 4.0 ml) and $H_2O$ (8.0 ml). The suspension was then filtered through Celite®. The residue was washed with EtOAc and then the combined filtrate concentrated *in vacuo.* Flash column chromatography on silica, elution gradient 0 to 50% ethyl acetate in hexane, afforded the title dienol **10** as a colourless oil (7.2 g, 76%). $R_f$ 0.4 (pet. ether : ethyl acetate 7:3); IR (ATR) 3326, 2936, 2886, 1654, 1603, 1415, 1042, 1001, 951, 897, 840 cm$^{-1}$; $\delta_H$ (400 MHz) 6.33 (1H, ddd, $J$ = 16.8Hz, $J$ = 10.4Hz, $J$ = 10.1Hz, 5-***H***), 6.16 (1H, dd, $J$ = 15.2Hz, $J$ = 10.4Hz, 4-***H***), 5.69 (1H, dt, $J$ = 15.2Hz, $J$ = 7.2Hz, 3-***H***), 5.14 (1H, d, $J$ = 16.8Hz, 6-***H***), 5.02 (1H, d, $J$ = 10.1Hz, 6-***H***), 3.69 (2H, dt, $J$ = 6.2Hz, $J$ = 5.8Hz , 1-***H***), 2.37 (2H, dt, $J$ = 7.2Hz, $J$ = 6.2Hz, 2-***H***), 1.29 (1H, t, $J$ = 5.8Hz, O***H***); $\delta_C$ (100 MHz) 136.8 (**C**-5), 133.8 (***C***-4), 130.5 (**C**-3), 115.9 (***C***-6), 61.9 (***C***-1), 35.9 (***C***-2); m/z (EI) 98 ([M]$^{+\cdot}$, 35%), 80 ([M-H$_2$O]$^{+\cdot}$, 10), 67 ([M-CH$_2$OH]$^{+\cdot}$, 100), 53 ([M-CH$_2$CH$_2$OH]$^{+\cdot}$, 15), 41 (42).

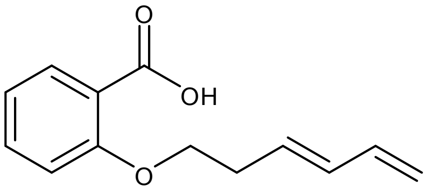
*(E)-methyl 2-(hexa-3,5-dienyloxy)benzoate* **11**



Following standard procedure **A,** a solution of triphenylphosphine (9.48 g, 36.2 mmol), (*E*)-hexa-3,5-dien-1-ol (2.96 g, 30.1 mmol) and methyl 2-hydroxybenzoate (3.91 ml, 30.1 mmol) in THF (10.0 ml) was treated with diisopropyl azodicarboxylate (7.12 ml, 36.2 mmol) to give the title compound as a colourless liquid (3.60 g, 52%). $R_f$ 0.3 (pet. ether : ethyl acetate 7:3); IR (ATR) 2947, 1727, 1599, 1582, 1490, 1452, 1432, 1384, 1302, 1243, 1189, 1163, 1131, 1081, 1048, 1004, 953, 899, 836, 753, 704 cm$^{-1}$; $\delta_H$ (700 MHz) 7.79-7.78 (1H, m, 6-***H***), 7.45-7.43 (1H, m, 4-***H***), 6.99-6.97 (1H, m, 5-***H***), 6.96-6.96 (1H, m, 3-***H***), 6.35 (1H, dt, $J$ = 16.8Hz, $J$ = 10.5Hz, 5'-***H***), 6.20 (1H, dd, $J$ = 15.4Hz, $J$ = 10.5Hz, 4'-***H***), 5.83 (1H, dt, $J$ = 15.4Hz, $J$ = 7.0Hz, 3'-***H***), 5.16 (1H, d, $J$ = 16.8Hz, 6'-***H***), 5.03 (1H, d, $J$ = 10.5Hz, 6'-***H***), 4.09 (2H, t, $J$ = 7.0Hz, 1'-***H***), 3.89 (3H, s, C***H***$_3$), 2.63 (2H, q, $J$ = 7.0Hz, 2'-***H***); $\delta_C$ (175 MHz) 167.0 (***C***O), 158.3 (***C***-2), 136.9 (***C***-5'), 133.33 (***C***-4), 133.27 (***C***-4'), 131.6 (***C***-6), 130.1 (**C**-3'), 120.7 (***C***-1), 120.3 (***C***-5), 115.9 (**C**-6'), 113.4 (***C***-3), 68.3 (C-1'), 51.9 (C***H***$_3$), 32.5 (C-2'); m/z (EI) 201

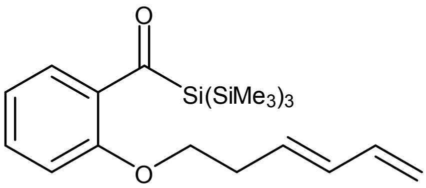
([M-$OCH_3$]$^{+\cdot}$, 14%), 165 (49), 152 (52), 135 (44), 120 (52), 105 (14), 92 (46), 80 (100), 77 (57), 65 (30), 63 (23), 55 (16), 53 (49), 45 (49), 41 (44), 39 (37), 27 (23); HRMS (ES+) found [M+H]$^{+\cdot}$ 233.1175, $C_{14}H_{17}O_3$ requires [M+H]$^{+\cdot}$ 233.1172.

*(E)-2-(Hexa-3,5-dienyloxy)benzoic acid*



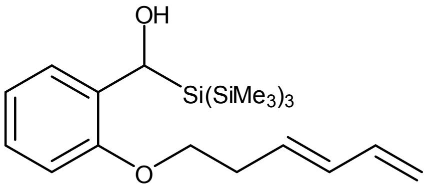
Following standard procedure **B**, a solution of (*E*)-methyl 2-(hexa-3,5-dienyloxy)benzoate (1.30 g, 5.58 mmol) in THF (30 ml) was treated with a solution lithium hydroxide (0.26 g, 11.2 mmol) in water (15 ml) to give the title compound as a white solid (0.95 g, 78%). Mp: 46.0–46.7 $^{o}$C; $R_f$ 0.4 (pet. ether : ethyl acetate 1:1); IR (ATR) 3248, 1726, 1602, 1581, 1488, 1473, 1455, 1399, 1355, 1296, 1237, 1217, 1161, 1123, 1040, 1001, 954, 930, 899, 834, 753, 728 cm$^{-1}$; $\delta_H$ (700 MHz) 10.82 (1H, s, $CO_2$***H***), 8.21-8.20 (1H, m, 6-***H***), 7.57-7.55 (1H, m, 4-***H***), 7.16-7.14 (1H, m, 5-***H***), 7.05-7.04 (1H, m, 3-***H***), 6.34 (1H, ddd, *J* = 16.1Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.26 (1H, dd, *J* = 15.4Hz, *J* = 9.8Hz, 4'-***H***), 5.73 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.22 (1H, d, *J* = 16.1Hz, 6'-***H***), 5.10 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.31 (2H, t, *J* = 7.0Hz , 1'-***H***), 2.72 (2H, q, *J* = 7.0Hz, 2'-***H***); $\delta_C$ (175 MHz) 165.2 (***C***$O_2$H), 157.3 (***C***-2), 136.0 (***C***-5'), 134.94 (***C***-4), 134.90 (***C***-4'), 133.9 (***C***-6), 127.9 (**C**-3'), 122.3 (***C***-5), 117.8 (***C***-1), 117.4 (**C**-6'), 112.4 (***C***-3), 69.1 (C-1'), 32.3 (C-2'); m/z (ES-) 217 ([M-H]$^{-}$ , 15%), 137 (100); HRMS (ES-) found [M-H]$^{-}$ 217.0877, $C_{13}H_{13}O_3$ requires [M-H]$^{-}$ 217.0865.

*(E)-(2-(Hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone* **12**



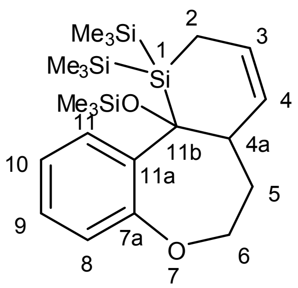
Following standard procedure **C** (page 192), a solution of (*E*)-2-(hexa-3,5-dienyloxy)benzoic acid (2.02 g, 9.24 mmol) in DCM (32.0 ml) was treated with oxalyl chloride (1.03 ml, 12.0 mmol) and DMF (1 drop). The resulting acid chloride was redissolved in THF (32.0 ml) and treated with a solution of silylpotassium in THF (32.0 ml), prepared from tetrakis(trimethylsilyl)silane (2.96g, 9.24 mmol) and potassium *tert*-butoxide (1.09g, 9.70 mmol). Flash column chromatography afforded the title acylpolysilane **12** as a yellow oil (2.20 g, 53%). $R_f$ 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2947, 2891, 1611, 1591, 1484, 1465, 1439, 1393, 1280, 1241, 1188, 1106, 1041, 1020, 999, 950, 895, 828, 747 cm$^{-1}$; $\delta_H$ (700 MHz) 7.29-7.26 (1H, m, 4-***H***), 7.01-7.00 (1H, m, 6-***H***), 6.97-6.94 (1H, m, 5-***H***), 6.88-6.87 (1H, m, 3-***H***), 6.32 (1H, dt, *J* = 17.5Hz, *J* = 10.5Hz, 5'-***H***), 6.15 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.73 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.15 (1H, d, *J* = 17.5Hz, 6'-***H***), 5.02 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.99 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.54 (2H, q, *J* = 7.0Hz, 2'-***H***), 0.19 (27H, s, Si(C$\boldsymbol{H}_3$)$_3$)); $\delta_C$ (175 MHz) 241.6 (***C***O), 153.4 (***C***-2), 139.7 (***C***-1), 136.9 (***C***-5'), 133.3 (***C***-4'), 130.1 (***C***-4), 129.8 (**C**-3'), 125.6 (***C***-6), 120.2 (***C***-5), 115.9 (**C**-6'), 112.8 (***C***-3), 68.1 (**C**-1'), 32.3 (**C**-2'), 1.1 (Si(***C***$H_3$)$_3$); $\delta_{Si}$ (140 MHz) -11.4, -70.4; m/z (EI) 448 ([M]$^{+\cdot}$, 0.2%), 375 ([M-Si($CH_3$)$_3$]$^{+\cdot}$, 4), 147 (12), 73 (100); HRMS (EI) found [M]$^{+\cdot}$ 448.2096, $C_{22}H_{40}O_2Si_4$ requires [M]$^{+\cdot}$ 448.2100.

*(E)-(2-(Hexa-3',5'-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanol* **13**




To a suspension of $LiAlH_4$ (0.029 g, 0.76 mmol) in diethyl ether (4.0 ml) was added a solution of (*E*)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone **14** (0.34 g, 0.76 mmol) in diethyl ether (3.0 ml) at 0 °C, over a period of 3 minutes under nitrogen. The resulting suspension was stirred at RT for 1 h. The reaction mixture was quenched sequentially with $H_2O$ (0.5 ml), NaOH (1M, 0.5 ml) and $H_2O$ (0.5 ml). The mixture was then filtered through Celite®, the precipitate washed with EtOAc and the combined filtrate concentrated *in vacuo.* Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a colourless oil (0.22 g, 65%). $R_f$ 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 3428, 2946, 2891, 1597, 1487, 1471, 1451, 1232, 1161, 1048, 1029, 1001, 951, 827, 745 cm$^{-1}$; $\delta_H$ (700 MHz) 7.42-7.41 (1H, m, Ar-6-***H***), 7.14-7.11 (1H, m, Ar-4-***H***), 6.97-6.95 (1H, m, Ar-5-***H***), 6.79-6.78 (1H, m, Ar-3-***H***), 6.34 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.19 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.76 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.47 (1H, d, *J* = 4.2Hz, C***H***OH), 5.16 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.04 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.10 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 3.97 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 2.63 (1H, dq, *J* = 14.0Hz, *J* = 7.0Hz, 2'-***H***), 2.59 (1H, dq, *J* = 14.0Hz, *J* = 7.0Hz, 2'-***H***), 1.81 (1H, d, *J* = 4.2Hz, O***H***), 0.15 (27H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 153.7 (***C***-2), 136.8 (***C***-5'), 135.8 (***C***-1), 133.5 (***C***-4'), 130.0 (***C***-3'), 127.7 (**C**-6), 126.8 (***C***-4), 120.9 (***C***-5), 116.1 (**C**-6'), 111.2 (***C***-3), 67.3 (**C**-1'), 62.1 (***C***HOH), 32.5 (**C**-2'), 1.5 (Si(***C***$H_3$)$_3$); $\delta_{Si}$ (140 MHz) -12.8, -68.0; m/z compound decomposes under all forms of ionisation.

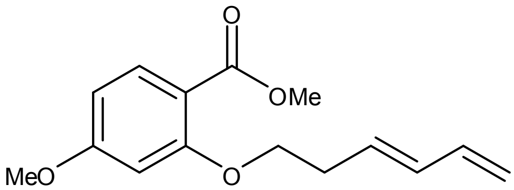
*1,1-Bis(trimethylsilyl)-11b-(trimethylsilyloxy)-1,2,4a,5,6,11b-hexahydrobenzo[b]silino[2,3-d]oxepine* **14**




A solution of (*E*)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone **12** (0.21 g, 0.47 mmol) in dry toluene (2.0 ml) was heated in a microwave tube at 180 °C for 1 h. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the product as a greasy solid (0.17 g, ds 2.7:1, 81%). $R_f$ 0.6 (pet.

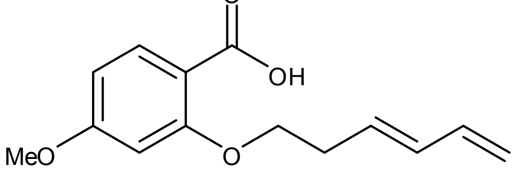
ether : diethyl ether 95:5); IR (ATR) 2951, 2895, 1479, 1441, 1242, 1210, 1059, 1025, 829, 767, 752 $cm^{-1}$; $\delta_H$ (700 MHz) 7.52-7.51 (1H, m, 11-***H***), 7.12-7.08 (2H, m, 9,10-***H***), 6.89-6.87 (1H, m, 8-***H***), 6.09 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 2.8Hz, 3-***H***), 5.73 (1H, ddd, *J* = 10.5Hz, *J* = 6.3Hz, *J* = 2.8Hz, 4-***H***), 4.12 (1H, ddd, *J* = 11.2Hz, *J* = 7.0Hz, *J* = 6.3Hz, 6-***H***), 3.91 (1H, ddd, *J* = 11.2Hz, *J* = 6.3Hz, *J* = 5.6Hz, 6-***H***), 3.21-3.19 (1H, m, 4a-***H***), 2.07-2.03 (1H, m, 5-***H***), 1.88-1.83 (1H, m, 5-***H***), 1.66 (1H, dtd, *J* = 16.1Hz, *J* = 2.8Hz, *J* = 1.4Hz, 2-***H***), 1.40 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.18 (9H, s, $Si(CH_3)_3$), 0.05 (9H, s, $Si(CH_3)_3$), -0.20 (9H, s, $Si(CH_3)_3$); $\delta_C$ (175 MHz) 152.6 (***C***-7a), 140.4 (***C***-11a), 132.9 (***C***-4), 131.0 (***C***-11), 127.8 (***C***-3), 127.4 (***C***-9), 124.0 (**C**-10), 122.6 (***C***-8), 82.4 (***C***-11b), 69.4 (**C**-6), 44.8 (***C***-4a), 30.1 (***C***-5), 8.4 (***C***-2), 2.8 ($Si(CH_3)_3$), 0.5 ($Si(CH_3)_3$), -0.5 ($Si(CH_3)_3$); $\delta_{Si}$ (140 MHz) 10.5, -15.5, -16.8, -26.8; m/z (EI) 448 ($[M]^{+\cdot}$, 0.2%), 433 ($[M-Me]^{+\cdot}$, 0.5%), 375 ($[M-Si(CH_3)_3]^{+\cdot}$, 14), 205 (10), 147 (16), 73 (100); HRMS (EI) found $[M]^{+\cdot}$ 448.2100, $C_{22}H_{40}O_2Si_4$ requires $[M]^{+\cdot}$ 448.2100.

*(E)-Methyl 2-(hexa-3',5'-dienyloxy)-4-methoxybenzoate*



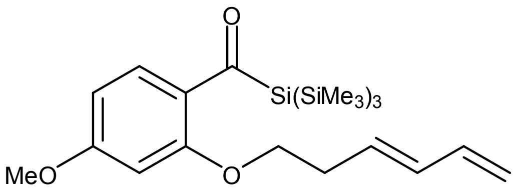

Following standard procedure **A**, a solution of triphenylphosphine (7.59 g, 28.9 mmol), (*E*)-hexa-3,5-dien-1-ol (2.37 g, 24.1 mmol) and methyl 2-hydroxy-4-methoxybenzoate (4.39 g, 24.1 mmol) in THF (8.0 ml) was treated with diethyl azodicarboxylate (4.56 ml, 28.9 mmol) to give the title compound as a colourless liquid (3.61 g, 57%). $R_f$ 0.3 (pet. ether : ethyl acetate 4:1); IR (ATR) 2945, 1720, 1605, 1575, 1503, 1435, 1384, 1249, 1200, 1167, 1136, 1087, 1029, 1007, 954, 904, 829, 768, 731 $cm^{-1}$; $\delta_H$ (700 MHz) 7.85-7.84 (1H, m, 6-***H***), 6.51-6.50 (1H, m, 5-***H***), 6.46-6.45 (1H, m, 3-***H***), 6.35 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.21 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.84 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.16 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.03 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.06 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.86 (3H, s, $CO_2CH_3$), 3.84 (3H, s, $OCH_3$), 2.64 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); $\delta_C$ (175 MHz) 166.4 (***C***O), 164.1 (***C***-4), 160.5 (***C***-2), 136.9 (***C***-5'), 133.8 (***C***-6), 133.4 (**C**-4'), 130.1 (***C***-3'), 115.9 (***C***-6'), 112.8 (**C**-1), 104.9 (***C***-5), 100.1 (***C***-3), 68.4 (***C***-1'), 55.4 ($OCH_3$), 51.6 ($CO_2CH_3$), 32.4 (***C***-2'); m/z (ES+) 548 ($[2M+Na]^{+\cdot}$, 23%), 326 ($[M+Na+MeCN]^{+\cdot}$, 37), 285 ($[M+Na]^{+\cdot}$, 74), 263 ($[M+H]^{+\cdot}$, 100), 122 (61); HRMS (ES+) found $[M+H]^{+\cdot}$ 263.1281, $C_{15}H_{19}O_4$ requires $[M+H]^{+\cdot}$ 263.1283.

*(E)-2-(Hexa-3,5-dienyloxy)-4-methoxybenzoic acid*



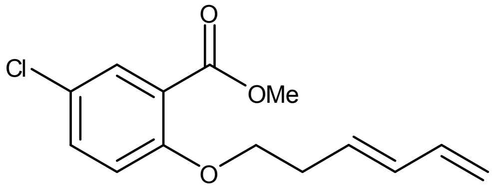

Following standard procedure **B**, a solution of methyl (*E*)-methyl 2-(hexa-3,5-dienyloxy)-4-methoxybenzoate (3.38 g, 12.9 mmol) in THF (60 ml) was treated with a solution lithium hydroxide (0.62g, 25.8 mmol) in water (30 ml) to give the title compound as a white solid (2.69 g, 84%). Mp: 69.3–70.1 $^{o}C$; $R_f$ 0.3 (pet. ether : ethyl acetate 1:1); IR (ATR) 3240, 2954, 2872, 1667, 1608, 1571, 1451, 1387, 1280, 1201, 1164, 1099, 1031, 996, 914, 825, 791 $cm^{-1}$; $\delta_H$ (700 MHz) 10.57 (1H, s, $CO_2$***H***), 8.15-8.13 (1H, m, 6-***H***), 6.66-6.64 (1H, m, 5-***H***), 6.51-6.50 (1H, m, 3-***H***), 6.33 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.25 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.72 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.21 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.09 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.26 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.88 (OC***H***$_3$), 2.70 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); $\delta_C$ (175 MHz) 165.3 (***C***O), 165.2 (***C***-4), 158.9 (***C***-2), 136.2 (***C***-5'), 135.8 (***C***-6), 135.1 (**C**-4'), 128.1 (***C***-3'), 117.6 (***C***-6'), 110.8 (**C**-1), 106.9 (***C***-5), 99.6 (***C***-3), 69.2 (***C***-1'), 55.9 (O***C***H$_3$), 32.4 (***C***-2'); m/z (ES+) 520 ($[2M+Na]^{+\cdot}$, 19%), 498 ($[2M]^{+\cdot}$, 26), 312 ($[M+Na+MeCN]^{+\cdot}$, 25), 271 ($[M+Na]^{+\cdot}$, 25), 249 ($[M+H]^{+\cdot}$, 100), 122 (38); HRMS (ES+) found $[M+H]^{+\cdot}$ 249.1123, $C_{14}H_{17}O_4$ requires $[M+H]^{+\cdot}$ 249.1127.

*(E)-(2-(Hexa-3',5'-dienyloxy)-4-methoxyphenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone* **15**



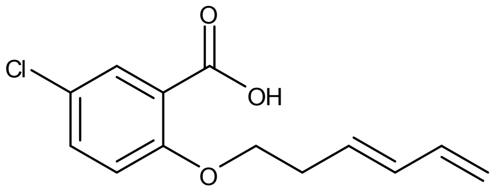

Following standard procedure **C**, a solution of (*E*)-2-(hexa-3,5-dienyloxy)-4-methoxybenzoic acid (2.16 g, 8.69 mmol) in DCM (40.0 ml) was treated with oxalyl chloride (1.43 ml, 11.3 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (40.0 ml) and treated with a solution of silylpotassium in THF (40.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (2.79 g, 8.69 mmol) and potassium *tert*-butoxide (1.02 g, 9.11 mmol). Flash column chromatography afforded the title acylpolysilane **15** as a unstable yellow oil (2.11 g, 51%). $R_f$ 0.3 (pet. ether : diethyl ether 9:1); IR (ATR) 2948, 2892, 1600, 1495, 1421, 1302, 1245, 1198, 1164, 1121, 1028, 1005, 949, 825, 734 $cm^{-1}$; $\delta_H$ (700 MHz) 7.18-7.17 (1H, m, Ar-6-***H***), 6.48-6.47 (1H, m, Ar-5-***H***), 6.42-6.41 (1H, m, Ar-3-***H***), 6.32 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.15 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.75 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.14 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.02 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.98 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.83 (3H, s, OC***H***$_3$), 2.55 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***), 0.21 (27H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 237.5 (***C***O), 162.1 (***C***-4), 155.7 (***C***-2), 136.9 (***C***-5'), 133.3 (***C***-4'), 131.9 (**C**-1), 130.2 (***C***-6), 129.9 (***C***-3'), 115.9 (**C**-6'), 103.8 (***C***-5), 100.2 (***C***-3), 68.2 (***C***-1'), 55.4 (O***C***H$_3$), 32.2 (***C***-2'), 1.3 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) -11.4, -70.2; m/z (EI) 463 ($[M-CH_3]^{+\cdot}$, 3%), 405 ($[M-Si(CH_3)_3]^{+\cdot}$, 43), 263 (62), 214 (83), 189 (30), 175 (40), 147 (39), 131 (26), 117 (33), 73 (100), 45 (11).

*(E)-Methyl 5-chloro-2-(hexa-3,5-dienyloxy)benzoate*



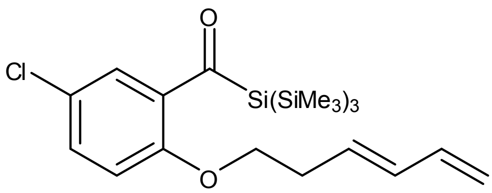

Following standard procedure **A**, a solution of triphenylphosphine (5.27 g, 20.1 mmol), (*E*)-hexa-3,5-dien-1-ol (1.45 g, 14.7 mmol) and methyl 5-chloro-2-hydroxybenzoate (2.50 g, 13.4 mmol) in THF (7.0 ml) was treated with diisopropyl azodicarboxylate (3.17 ml, 16.1 mmol) to give the title ester as a colourless liquid (2.79 g, 78%). $R_f$ 0.4 (hexane : ethyl acetate 9:1); IR (ATR) 2949, 1732, 1598, 1487, 1465, 1435, 1403, 1298, 1273, 1233, 1151, 1113, 1079, 1003, 972, 953, 899, 811, 783, 731 $cm^{-1}$; $\delta_H$ (700 MHz) 7.76-7.75 (1H, m, 6-***H***), 7.40-7.38 (1H, m, 4-***H***), 6.90-6.89 (1H, m, 3-***H***), 6.34 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.20 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.80 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.16 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.04 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.06 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.89 (3H, s, OC***H***$_3$), 2.62 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); $\delta_C$ (175 MHz) 165.6 (***C***O), 156.9 (***C***-2), 136.8 (***C***-5'), 133.5 (***C***-4'), 133.0 (**C**-4), 131.3 (***C***-6), 129.8 (***C***-3'), 125.4 (**C**-5), 121.9 (***C***-1), 116.1 (***C***-6'), 114.8 (***C***-3), 68.8 (***C***-1'), 52.2 (O***C***H$_3$), 32.4 (***C***-2'); m/z (ES+) 289 ($[M+Na]^{+\cdot}$, 100), 555 ($[2M+Na]^{+\cdot}$, 5); HRMS (ES+) found $[M+H]^{+\cdot}$ 267.0778, $C_{14}H_{16}O_3Cl$ requires $[M+H]^{+\cdot}$ 267.0788.

*(E)-5-Chloro-2-(hexa-3',5'-dienyloxy)benzoic acid*



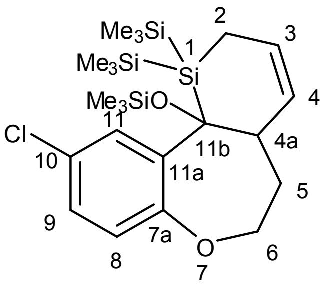
Following standard procedure **B**, a solution of (*E*)-methyl 5-chloro-2-(hexa-3,5-dienyloxy)benzoate (2.73 g, 10.2 mmol) in THF (40 ml) was treated with a solution lithium hydroxide (0.49 g, 20.5 mmol) in water (40 ml) to give the title acid as a white solid (2.20 g, 86%). Mp: 41.3–42.4 °C; $R_f$ 0.4 (pet. ether : ethyl acetate 1:1); IR (ATR) 3258, 2946, 1722, 1655, 1599, 1480, 1456, 1414, 1397, 1274, 1237, 1203, 1149, 1111, 1039, 1004, 951, 899, 855, 826, 782, 767, 706 $cm^{-1}$; $\delta_H$ (700 MHz) 10.70 (1H, s, CO$_2$***H***), 8.161-8.158 (1H, m, 6-***H***), 7.51-7.50 (1H, m, 4-***H***), 7.00-6.99 (1H, m, 3-***H***), 6.33 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.25 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.71 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.22 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.10 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.29 (2H, t, *J* = 6.3Hz, 1'-***H***), 2.71 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); $\delta_C$ (175 MHz) 164.0 (***C***O), 155.8 (***C***-2), 135.9 (***C***-5'), 135.1 (***C***-4'), 134.6 (**C**-4), 133.4 (***C***-6), 127.7 (***C***-5), 127.6 (**C**-3'), 119.2 (***C***-1), 117.6 (***C***-6'), 114.0 (***C***-3), 69.5 (***C***-1'), 32.2 (***C***-2'); m/z (ES+) 275 ($[M+Na]^{+\cdot}$, 100); HRMS (ES+) found $[M+Na]^{+\cdot}$ 275.0434, $C_{13}H_{13}O_3NaCl$ requires $[M+Na]^{+\cdot}$ 275.0451.

*(E)-(5-Chloro-2-(hexa-3',5'-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone* **16**



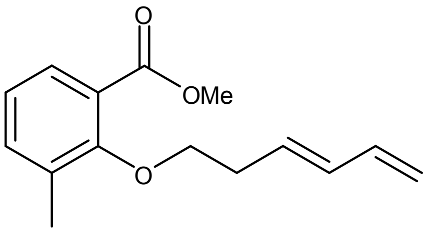
Following standard procedure **C**, a solution of (*E*)-5-chloro-2-(hexa-3',5'-dienyloxy)benzoic acid (2.15 g, 8.53 mmol) in DCM (40.0 ml) was treated with oxalyl chloride (0.88 ml, 10.2 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (45.0 ml) and treated with a solution of silylpotassium in THF (45.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (2.74 g, 8.53 mmol) and potassium *tert*-butoxide (1.01 g, 8.95 mmol). Flash column chromatography afforded the product as a yellow semisolid (0.43 g, 10%). $R_f$ 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2951, 2893, 1609, 1483, 1463, 1388, 1285, 1243, 1181, 1129, 1020, 1001, 952, 929, 901, 823, 750 $cm^{-1}$; $\delta_H$ (700 MHz) 7.24-7.22 (1H, m, 4-***H***), 6.984-6.980 (1H, m, 6-***H***), 6.82-6.81 (1H, m, 3-***H***), 6.32 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.14 (1H, dd, *J* = 14.7Hz, *J* = 10.5Hz, 4'-***H***), 5.71 (1H, dt, *J* = 14.7Hz, *J* = 7.0Hz, 3'-***H***), 5.15 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.03 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.96 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.53 (2H, q, *J* = 7.0Hz, 2'-***H***), 0.21 (27H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 239.7 (***C***O), 152.0 (***C***-2), 140.4 (***C***-5), 136.8 (***C***-5'), 133.5 (**C**-4'), 129.8 (***C***-4), 129.4 (***C***-3'), 125.9 (**C**-6), 125.4 (***C***-1), 116.1 (***C***-6'), 114.4 (***C***-3), 68.6 (***C***-1'), 32.2 (***C***-2') 1.1 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) -11.2, -69.2; m/z (CI) 483 ($[M+H]^{+\cdot}$, 12), 393 (100), 90 (27); HRMS (ES+) found $[M+H]^{+\cdot}$ 483.1787, $C_{22}H_{40}O_2ClSi_4$ requires $[M+H]^{+\cdot}$ 483.1788.

*10-Chloro-1,1-bis(trimethylsilyl)-11b-(trimethylsilyloxy)-1,2,4a,5,6,11b-hexahydrobenzo [b]silino[2,3-d]oxepine* **21**



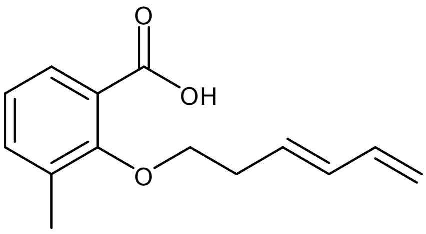

A solution of (*E*)-(5-chloro-2-(hexa-3',5'-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone (0.16 g, 0.33 mmol) in dry toluene (2.0 ml) was heated in a microwave tube at 180 °C for 75 min. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the title silacycle **21** as a greasy colourless solid (0.10 g, ds 3.5:1 (crude ds 2.7:1), 60%). $R_f$ 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2952, 2894, 1477, 1244, 1027, 831, 749 $cm^{-1}$; $\delta_H$ (700 MHz) 7.51-7.50 (1H, m, 11-***H***), 7.06-7.05 (1H, m, 9-***H***), 6.83-6.82 (1H, m, 8-***H***), 6.09 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 2.8Hz, 3-***H***), 5.68 (1H, ddd, *J* = 10.5Hz, *J* = 6.3Hz, *J* = 2.8Hz, 4-***H***), 4.13 (1H, ddd, *J* = 11.2Hz, *J* = 7.0Hz, *J* = 6.3Hz, 6-***H***), 3.86 (1H, ddd, *J* = 11.2Hz, *J* = 6.3Hz, *J* = 5.6Hz, 6-***H***), 3.14-3.12 (1H, m, 4a-***H***), 2.10-2.06 (1H, m, 5-***H***), 1.87-1.82 (1H, m, 5-***H***), 1.64 (1H, dtd, *J* = 16.1Hz, *J* = 2.8Hz, *J* = 1.4Hz, 2-***H***), 1.38 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.19 (9H, s, Si(C***H***$_3$)$_3$), 0.09 (9H, s, Si(C***H***$_3$)$_3$), -0.15 (9H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 151.1 (***C***-7a), 142.5 (***C***-10), 132.5 (***C***-4), 130.5 (***C***-11), 129.2 (***C***-11a), 127.9 (***C***-3), 127.0 (***C***-9), 124.1 (***C***-8), 81.9 (***C***-11b), 69.6 (***C***-6), 45.0 (***C***-4a), 29.9 (***C***-5), 8.2 (***C***-2), 2.9 (Si(***C***H$_3$)$_3$), 0.5 (Si(***C***H$_3$)$_3$), -0.6 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) 11.5, -15.4, -16.6, -26.2; m/z (EI) 482 ($[M]^{+\cdot}$, 0.5%), 467 ($[M-Me]^{+\cdot}$, 2%), 409 ($[M-Si(CH_3)_3]^{+\cdot}$, 19), 293 (12), 263 (34), 243 (15), 205 (56), 191 (27), 175 (25), 147 (76), 133 (48), 117 (47), 73 (100), 59 (23), 45 (31); HRMS (EI) found $[M]^{+\cdot}$ 482.1713, $C_{22}H_{39}O_2ClSi_4$ requires $[M]^{+\cdot}$ 482.1710.

*(E)-Methyl 2-(hexa-3',5'-dienyloxy)-3-methylbenzoate*



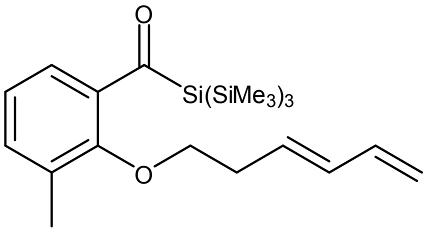
Following standard procedure **A**, a solution of triphenylphosphine (4.23 g, 16.1 mmol), (*E*)-hexa-3,5-dien-1-ol (1.16 g, 11.8 mmol) and methyl 2-hydroxy-3-methylbenzoate (2.00 g, 10.7 mmol) in THF (4.0 ml) was treated with diisopropyl azodicarboxylate (2.54 ml, 12.9 mmol) to give the title ester as a colourless liquid (1.52 g, 58%). $R_f$ 0.5 (pet. ether : ethyl acetate 9:1); IR (ATR) 2949, 1725, 1652, 1592, 1460, 1433, 1377, 1292, 1258, 1221, 1189, 1173, 1137, 1002, 952, 898, 875, 761, 727 cm$^{-1}$; $\delta_H$ (700 MHz) 7.64-7.63 (1H, m, 6-***H***), 7.35-7.33 (1H, m, 4-***H***), 7.06-7.04 (1H, m, 5-***H***), 6.35 (1H, ddd, *J* = 16.1Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.20 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.82 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.45 (1H, d, *J* = 16.1Hz, 6'-***H***), 5.02 (1H, d, *J* = 9.8Hz, 6'-***H***), 3.95 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.91 (3H, s, OC***H***$_3$), 2.62 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***), 2.31 (3H, s, C***H***$_3$); $\delta_C$ (175 MHz) 167.0 (***C***O), 157.1 (***C***-2), 137.0 (***C***-5'), 135.0 (***C***-4), 133.1 (**C**-4'), 132.7 (***C***-3), 130.5 (***C***-3'), 129.1 (**C**-6), 124.7 (***C***-1), 123.4 (***C***-5), 115.7 (***C***-6'), 73.4 (***C***-1'), 52.1 (O***C***H$_3$), 33.4 (***C***-2'), 16.3 (***C***H$_3$); m/z (ES+) 269 ([M+Na]$^{+\cdot}$, 100), 515 ([2M+Na]$^{+\cdot}$, 5); HRMS (ES+) found [M+Na]$^{+\cdot}$ 269.1151, $C_{15}H_{18}O_3Na$ requires [M+Na]$^{+\cdot}$ 269.1154.

*(E)-2-(Hexa-3',5'-dienyloxy)-3-methylbenzoic acid*



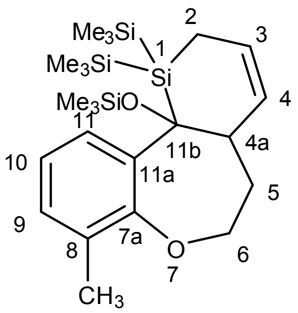
Following standard procedure **B**, a solution of (*E*)-methyl 2-(hexa-3,5-dienyloxy)-3-methylbenzoate (1.47 g, 5.97 mmol) in THF (30 ml) was treated with a solution lithium hydroxide (0.29g, 11.9 mmol) in water (30 ml) to give the title compound as a white solid (1.08 g, 78%). Flash column chromatography on silica, elution gradient 10 to 20% ethyl acetate in hexane, afforded the title acid as a white solid (1.08 g, 78%). Mp: 59.3–60.2 $^oC$; $R_f$ 0.5 (pet. ether : ethyl acetate 1:1); IR (ATR) 3252, 2912, 1700, 1675, 1593, 1407, 1383, 1303, 1276, 1225, 1187, 1165, 1093, 1016, 1000, 949, 912, 898, 865, 796, 747. 763, 719 cm$^{-1}$; $\delta_H$ (700 MHz) 11.21 (1H, s, CO$_2$***H***), 7.98-7.97 (1H, m, 6-***H***), 7.44-7.43 (1H, m, 4-***H***), 7.20-7.18 (1H, m, 5-***H***), 6.36 (1H, ddd, *J* = 16.81Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.24 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.75 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.19 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.08 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.03 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.68 (2H, q, *J* = 7.0Hz, 2'-***H***), 2.36 (3H, s, C***H***$_3$); $\delta_C$ (175 MHz) 165.9 (***C***O), 156.4 (***C***-2), 136.9 (***C***-4), 136.4 (***C***-5'), 134.7 (**C**-4'), 131.5 (***C***-3), 130.8 (***C***-6), 128.2 (**C**-3'), 125.1 (***C***-5), 122.2 (***C***-1), 116.9 (***C***-6'), 74.6 (***C***-1'), 33.1 (***C***-2'), 16.1 (***C***H$_3$); m/z (ES+) 255 ([M+Na]$^{+\cdot}$, 100), 487 ([2M+Na]$^{+\cdot}$, 6); HRMS (ES+) found [M+Na]$^{+\cdot}$ 255.1004, $C_{14}H_{16}O_3Na$ requires [M+Na]$^{+\cdot}$ 255.0997.

*(E)-(2-(Hexa-3',5'-dienyloxy)-3-methylphenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone* **17**




Following standard procedure **C**, a solution of (*E*)-2-(hexa-3',5'-dienyloxy)-3-methylbenzoic acid (0.83 g, 3.57 mmol) in DCM (20.0 ml) was treated with oxalyl chloride (0.37 ml, 4.28 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (25.0 ml) and treated with a solution of silylpotassium in THF (25.0 ml), prepared from tetrakis(trimethylsilyl)silane (1.15 g, 3.57 mmol) and potassium *tert*-butoxide (0.42 g, 3.75 mmol). Flash column chromatography afforded the title acylpolysilane **17** as a yellow oil (0.86 g, 52%). $R_f$ 0.7 (pet. ether : diethyl ether 9:1); IR (ATR) 2948, 2891, 1616, 1376, 1243, 1256, 1211, 1071, 1002, 953, 899, 827, 758 $cm^{-1}$; $\delta_H$ (700 MHz) 7.18-7.16 (1H, m, 6-***H***), 7.03-7.01 (1H, m, 5-***H***), 6.94-6.93 (1H, m, 4-***H***), 6.32 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.14 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.74 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.12 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.00 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.80 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.50 (2H, q, *J* = 7.0Hz, 2'-***H***), 2.26 (3H, s, C***H***$_3$), 0.20 (27H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 242.2 (***C***O), 152.1 (***C***-2), 143.2 (***C***-3), 137.0 (***C***-5'), 133.1 (**C**-4'), 132.3 (***C***-1), 132.1 (***C***-6), 130.5 (**C**-3'), 124.0 (***C***-4), 123.2 (***C***-5), 115.5 (***C***-6'), 74.5 (***C***-1'), 33.3 (***C***-2'), 16.1 (***C***H$_3$), 1.1 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) -11.4, -69.5; m/z (CI) 463 ($[M+H]^{+\cdot}$, 24), 373 (100), 90 (19); HRMS (ES+) found $[M+H]^{+\cdot}$ 463.2333, $C_{23}H_{43}O_2Si_4$ requires $[M+H]^{+\cdot}$ 463.2335.

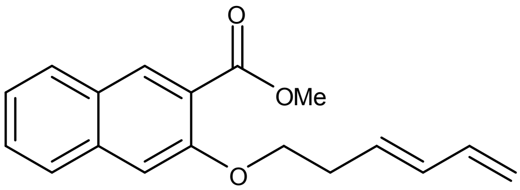
*8-Methyl-1,1-bis(trimethylsilyl)-11b-(trimethylsilyloxy)-1,2,4a,5,6,11b-hexahydrobenzo [b]silino[2,3-d]oxepine* **22**




A solution of (*E*)-(2-(hexa-3',5'-dienyloxy)-3-methylphenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone (0.17 g, 0.36 mmol) in dry toluene (2.0 ml) was heated in a microwave tube at 180 °C for 90 min. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the title silacycle **22** as a greasy colourless solid (0.14 g, ds 4.3:1 (crude ds 3.7:1), 87%). $R_f$ 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2949, 2893, 1469, 1432, 1243, 1193, 1043, 1020, 954, 829, 749 $cm^{-1}$; $\delta_H$ (700 MHz) 7.32-7.31 (1H, m, 10-***H***), 7.00-6.96 (2H, m, 9,11-***H***), 6.13 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 4.2Hz, 3-***H***), 5.68 (1H, ddd, *J* = 10.5Hz, *J* = 6.3Hz, *J* = 2.8Hz, 4-***H***), 4.07 (1H, ddd, *J* = 11.2Hz, *J* = 7.7Hz, *J* = 6.3Hz, 6-***H***), 3.85 (1H, ddd, *J* = 11.2Hz, *J* = 6.3Hz, *J* = 4.2Hz, 6-***H***), 3.16-3.14 (1H, m, 4a-***H***), 2.22 (3H, s, C***H***$_3$), 2.12-2.08 (1H, m, 5-***H***), 1.81-1.75

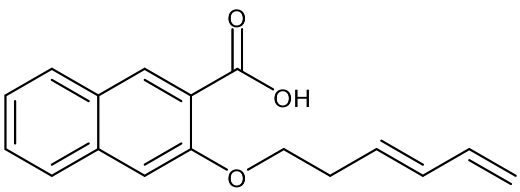
(1H, m, 5-***H***), 1.66 (1H, dddd, $J$ = 16.1Hz, $J$ = 4.2Hz, $J$ = 2.8Hz, $J$ = 1.4Hz, 2-***H***), 1.39 (1H, dd, $J$ = 16.1Hz, $J$ = 7.7Hz, 2-***H***), 0.16 (9H, s, Si(C***H***$_3$)$_3$), 0.08 (9H, s, Si(C***H***$_3$)$_3$), -0.21 (9H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 150.2 (***C***-7a), 140.6 (***C***-11a), 132.6 (***C***-4), 131.0 (***C***-8), 128.6 (***C***-9), 128.2 (***C***-3), 127.9 (***C***-11), 123.5 (***C***-10), 81.9 (***C***-11b), 69.1 (***C***-6), 45.4 (***C***-4a), 29.9 (***C***-5), 16.0 (C***H***$_3$), 8.4 (***C***-2), 2.9 (Si(***C***H$_3$)$_3$), 0.6 (Si(***C***H$_3$)$_3$), -0.5 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) 10.3, -15.6, -16.6, -27.5; m/z (EI) 462 ([M]$^{+\cdot}$, 1%), 447 ([M-Me]$^{+\cdot}$, 3%), 389 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 51), 361 (10), 321 (16), 301 (14), 273 (55), 223 (38), 205 (46), 157 (26), 147 (87), 133 (38), 117 (30), 73 (100), 45 (24); HRMS (EI) found [M]$^{+\cdot}$ 462.2250, $C_{23}H_{42}O_2Si_4$ requires [M]$^{+\cdot}$ 462.2256.

*(E)-Methyl 3-(hexa-3,5-dienyloxy)-2-naphthoate*



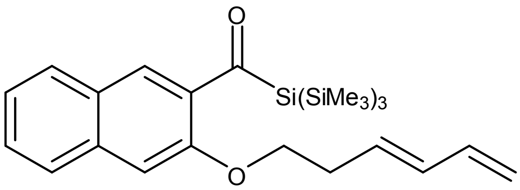
Following standard procedure **A**, a solution of triphenylphosphine (6.23 g, 23.7 mmol), (*E*)-hexa-3,5-dien-1-ol (1.94 g, 19.8 mmol) and methyl 3-hydroxy-2-naphthoate (4.00 g, 19.8 mmol) in THF (7.0 ml) was treated with diethyl azodicarboxylate (3.74 ml, 23.7 mmol) to give the title ether as a white solid (2.88 g, 52%). Mp: 37.9–38.4 $^{o}$C; R$_f$ 0.3 (pet. ether : ethyl acetate 9:1); IR (ATR) 3017, 2913, 1725, 1627, 1595, 1503, 1451, 1431, 1381, 1333, 1273, 1258, 1205, 1183, 1129, 1072, 1005, 951, 896, 861, 831, 780, 739 cm$^{-1}$; $\delta_H$ (700 MHz) 8.29 (1H, s, 1-***H***), 7.83-7.82 (1H, m, 8-***H***), 7.73-7.71 (1H, m, 5-***H***), 7.52-7.50 (1H, m, 6-***H***), 7.39-7.37 (1H, m, 7-***H***), 7.19 (1H, m, 4-***H***), 6.37 (1H, ddd, $J$ = 16.8Hz, $J$ = 10.5Hz, $J$ = 9.8Hz, 5'-***H***), 6.24 (1H, dd, $J$ = 15.4Hz, $J$ = 10.5Hz, 4'-***H***), 5.87 (1H, dt, $J$ = 15.4Hz, $J$ = 7.0Hz, 3'-***H***), 5.17 (1H, d, $J$ = 16.8Hz, 6'-***H***), 5.04 (1H, d, $J$ = 9.8Hz, 6'-***H***), 4.19 (2H, t, $J$ = 6.3Hz, 1'-***H***), 3.95 (3H, s, OC***H***$_3$), 2.70 (2H, dt, $J$ = 7.0Hz, $J$ = 6.3Hz, 2'-***H***); $\delta_C$ (175 MHz) 167.0 (***C***O), 154.8 (***C***-3), 137.0 (***C***-5'), 136.0 (***C***-4a), 133.4 (***C***-4'), 132.6 (***C***-1), 130.2 (***C***-3'), 128.7 (***C***-8), 128.3 (***C***-6), 127.6 (***C***-8a), 126.4 (***C***-5), 124.4 (***C***-7), 122.3 (***C***-2), 115.9 (***C***-6'), 107.9 (***C***-4), 68.1 (***C***-1'), 52.2 (O***C***H$_3$), 32.4 (***C***-2'); m/z (ES+) 283 ([M+H]$^{+\cdot}$, 25%), 305 ([M+Na]$^{+\cdot}$, 100), 587 ([2M+Na]$^{+\cdot}$, 70); HRMS (ES+) found [M+H]$^{+\cdot}$ 283.1326, $C_{18}H_{19}O_3$ requires [M+H]$^{+\cdot}$ 283.1334.

*(E)-3-(Hexa-3',5'-dienyloxy)-2-naphthoic acid*



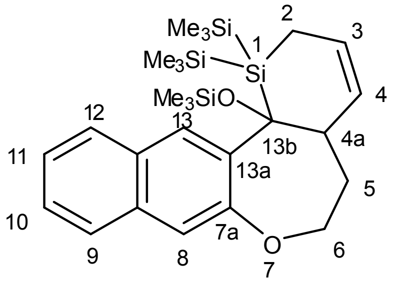
Following standard procedure **B**, a solution of (*E*)-methyl 3-(hexa-3,5-dienyloxy)-2-naphthoate (2.75 g, 9.75 mmol) in THF (45 ml) was treated with a solution lithium hydroxide (0.47g, 19.5 mmol) in water (22 ml) to give the title acid as a white solid (2.27 g, 86%). Mp: 61.9–63.1 $^{o}$C; R$_f$ 0.5 (pet. ether : ethyl acetate 1:1); IR (ATR) 3241, 1737, 1629, 1596, 1451, 1406, 1349, 1243, 1207, 1173, 1059, 1005, 983, 901, 824, 747, 709 cm$^{-1}$; $\delta_H$ (500 MHz) 11.00 (1H, s, CO$_2$***H***), 8.81 (1H, s, 1-***H***), 7.93-7.91 (1H, m, 8-***H***), 7.78-7.76 (1H, m, 5-***H***), 7.61-7.58 (1H, m, 6-***H***), 7.48-7.45 (1H, m, 7-***H***), 7.30 (1H, m, 4-***H***), 6.35 (1H, ddd, *J* = 16.0Hz, *J* = 10.5Hz, *J* = 9.0Hz, 5'-***H***), 6.29 (1H, dd, *J* = 15.0Hz, *J* = 10.5Hz, 4'-***H***), 5.78 (1H, dt, *J* = 15.0Hz, *J* = 7.0Hz, 3'-***H***), 5.24 (1H, d, *J* = 16.0Hz, 6'-***H***), 5.11 (1H, d, *J* = 9.0Hz, 6'-***H***), 4.41 (2H, t, *J* = 6.5Hz, 1'-***H***), 2.79 (2H, dt, *J* = 7.0Hz, *J* = 6.5Hz, 2'-***H***); $\delta_C$ (125 MHz) 165.3 (***C***O), 153.5 (***C***-3), 136.5 (***C***-4a), 136.3 (***C***-1), 136.1 (***C***-5'), 134.9 (***C***-4'), 129.5 (***C***-6, ***C***-8), 128.4 (***C***-8a), 128.1 (***C***-3'), 126.5 (***C***-7), 125.4 (***C***-5), 117.9 (***C***-2), 117.5 (***C***-6'), 107.9 (***C***-4), 69.0 (***C***-1'), 32.2 (***C***-2'); m/z (ES+) 269 ($[M+H]^{+\cdot}$, 49%), 291 ($[M+Na]^{+\cdot}$, 100), 537 ($[2M+H]^{+\cdot}$, 38), 559 ($[2M+Na]^{+\cdot}$, 77); HRMS (ES+) found $[M+H]^{+\cdot}$ 269.1186, $C_{17}H_{17}O_3$ requires $[M+H]^{+\cdot}$ 269.1178.

*(E)-(3-(Hexa-3',5'-dienyloxy)naphthalen-2-yl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone* **18**



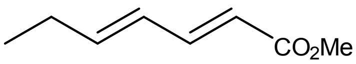

Following standard procedure **C**, a solution of (*E*)-3-(hexa-3',5'-dienyloxy)-2-naphthoic acid (1.93 g, 7.19 mmol) in DCM (35.0 ml) was treated with oxalyl chloride (0.80 ml, 9.34 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (35.0 ml) and treated with a solution of silylpotassium in THF (35.0 ml), prepared from tetrakis(trimethylsilyl)silane (2.31 g, 7.19 mmol) and potassium *tert*-butoxide (0.85 g, 7.54 mmol). Flash column chromatography afforded the title acyl polysilane **18** as a pale yellow solid (1.90 g, 53%). Mp: 112.4–116.8 $^oC$; $R_f$ 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2952, 2891, 1616, 1450, 1389, 1325, 1241, 1183, 1155, 1103, 1005, 949, 827, 743 $cm^{-1}$; $\delta_H$ (700 MHz) 7.77-7.75 (1H, m, 5-***H***), 7.71-7.70 (1H, m, 8-***H***), 7.48 (1H, s, 1-***H***), 7.48-7.46 (1H, m, 6-***H***), 7.38-7.36 (1H, m, 7-***H***), 7.13 (1H, m, 4-***H***), 6.35 (1H, dt, *J* = 17.5Hz, *J* = 10.5Hz, 5'-***H***), 6.19 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.79 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.17 (1H, d, *J* = 17.5Hz, 6'-***H***), 5.04 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.11 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.62 (2H, q, *J* = 7.0Hz, 2'-***H***), 0.22 (27H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 240.6 (***C***O), 152.3 (***C***-3), 140.4 (***C***-4a), 136.9 (***C***-5'), 134.6 (***C***-8a), 133.4 (***C***-4'), 129.8 (***C***-3'), 127.9 (***C***-5), 127.8 (***C***-2), 127.1 (***C***-6), 126.6 (***C***-8), 125.9 (***C***-1), 124.3 (***C***-7), 116.0 (***C***-6'), 107.4 (***C***-4), 67.9 (***C***-1'), 32.2 (***C***-2'), 1.2 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) -11.3, -69.6; m/z (EI) 498 ($[M]^{+\cdot}$, 2%), 425 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 6), 397 (10), 205 (14), 147 (19), 73 (100); HRMS (EI) found $[M]^{+\cdot}$ 498.2256, $C_{26}H_{42}O_2Si_4$ requires $[M]^{+\cdot}$ 498.2256.

*1,1-Bis(trimethylsilyl)-13b-(trimethylsilyloxy)-1,2,4a,5,6,13b-hexahydronaphtho[2,3-b]silino[2,3-d]oxepine* **23**



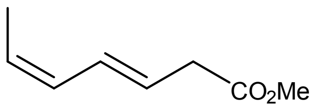
A solution of (*E*)-(3-(hexa-3',5'-dienyloxy)naphthalen-2-yl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone (0.32 g, 0.65 mmol) in dry toluene (3.2 ml) was heated in a microwave tube at 180 °C for 75 min. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the title silacycle **23** as a colourless viscous oil (0.25 g, ds 2.7:1 (crude ds 2.2:1), 75%). $R_f$ 0.5 (pet. ether : diethyl ether 95:5); IR (ATR) 2951, 2891, 1495, 1443, 1398, 1242, 1165, 1093, 1029, 904, 830, 730 cm$^{-1}$; $\delta_H$ (700 MHz) 7.97 (1H, m, 13-***H***), 7.77-7.76 (1H, m, 12-***H***), 7.74-7.71 (1H, m, 9-***H***), 7.41-7.38 (2H, m, 10-***H***, 11-***H***), 6.18 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 4.2Hz, 3-***H***), 5.67 (1H, ddd, *J* = 10.5Hz, *J* = 4.9Hz, *J* = 2.1Hz, 4-***H***), 4.23 (1H, ddd, *J* = 11.2Hz, *J* = 7.0Hz, *J* = 6.3Hz, 6-***H***), 3.91 (1H, ddd, *J* = 11.2Hz, *J* = 5.6Hz, *J* = 4.2Hz, 6-***H***), 3.20-3.18 (1H, m, 4a-***H***), 2.18-2.13 (1H, m, 5-***H***), 1.83-1.78 (1H, m, 5-***H***), 1.72 (1H, dddd, *J* = 16.1Hz, *J* = 4.2Hz, *J* = 2.1Hz, *J* = 1.4Hz, 2-***H***), 1.43 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.18 (9H, s, Si(C***H***$_3$)$_3$), 0.16 (9H, s, Si(C***H***$_3$)$_3$), -0.27 (9H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 151.7 (***C***-7a), 141.9 (***C***-13a), 133.1 (***C***-8a), 132.2 (***C***-4), 130.9 (***C***-12a), 128.4 (***C***-3), 128.2 (**C**-13), 127.3 (**C**-12), 126.5 (***C***-9), 125.4 (***C***-10), 124.9 (***C***-11), 118.8 (***C***-8), 81.9 (***C***-13b), 69.7 (**C**-6), 46.2 (***C***-4a), 30.0 (***C***-5), 8.2 (***C***-2), 3.1 (Si(***C***H$_3$)$_3$), 0.8 (Si(***C***H$_3$)$_3$), -0.4 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) 10.7, -15.6, -16.8, -26.9; m/z (EI) 498 ([M]$^{+\cdot}$, 7%), 470 (12), 425 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 22), 397 (24), 309 (24), 259 (20), 233 (18), 205 (78), 191 (46), 157 (36), 147 (74), 133 (49), 117 (48), 73 (100), 59 (33), 45 (39); HRMS (EI) found [M]$^{+\cdot}$ 498.2252, $C_{26}H_{42}O_2Si_4$ requires [M]$^{+\cdot}$ 498.2256.

*(2E,4E)-Methyl hepta-2,4-dienoate*



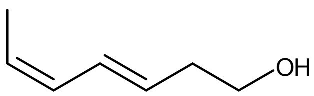
To a solution of methyl (triphenylphosphoranylidene)acetate (19.88 g, 59.4 mmol) in DCM (125 ml) was added (*E*)-pent-2-enal. The reaction mixture was stirred at RT for 6 h after which time the solvent was evaporated under reduced pressure. The residue was than triturated with hexane to remove the majority of the triphenylphosphine oxide. Kugelrohr distillation (95 °C, 0.4 mbar) afforded the product as a colourless liquid (4.50 g, 54%). IR (ATR) 2964, 2879, 1713, 1643, 1617, 1434, 1301, 1259, 1236, 1187, 1139, 1039, 999, 874, 720 cm$^{-1}$; $\delta_H$ (700 MHz) 7.28 (1H, ddd, *J* = 15.4Hz, *J* = 7.0Hz, *J* = 3.5Hz, 3-***H***), 6.18-6.17 (2H, m, 4-***H***, 5-***H***), 5.80 (1H, d, *J* = 15.4Hz, 2-***H***), 3.74 (3H, s, CO$_2$C***H***$_3$), 2.20 (2H, dq, *J* = 7.0Hz, *J* = 4.9Hz, 6-***H***), 1.05 (3H, t, *J* = 7.0Hz, 7-***H***); $\delta_C$ (175 MHz) 167.7 (***C***O), 146.2 (***C***-5), 145.4 (***C***-3), 127.4 (***C***-4), 118.7 (***C***-2), 51.4 (CO$_2$***C***H$_3$), 26.0 (***C***-6), 12.8 (***C***-7); m/z (EI) 140 ([M]$^{+\cdot}$, 48%), 111 (100), 109 ([M-OMe]$^{+\cdot}$, 43), 81 ([M-CO$_2$Me]$^{+\cdot}$, 100), 79 (73), 53 (43), 39 (38), 27 (20).

*(3E,5Z)-Methyl hepta-3,5-dienoate*



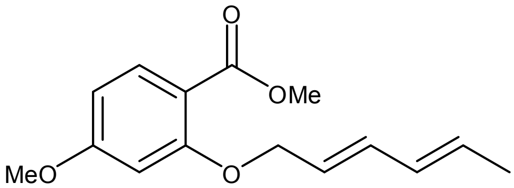
To a solution of sodium bis(trimethylsilyl)amide (61.8 ml, 1M in THF) in THF (90 ml) was added a solution of (2*E*,4*E*)-methyl hepta-2,4-dienoate (4.33 g, 30.9 mmol) in THF (20 ml) at -78 $^oC$. The reaction mixture was stirred at -78 $^oC$ for 4 h after which time a solution of acetic acid (5.0 ml) in THF/$H_2O$ (45 ml, 1:1) was added. The reaction mixture was allowed to reach room temperature and then volatiles were evaporated under reduced pressure. The residue was extracted with $Et_2O$ (3 x 40 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a clear liquid (3.83 g, EZ:EE - 84:16, 88%). $R_f$ 0.4 (pet. ether : diethyl ether 9:1); IR (ATR) 3021, 2952, 1737, 1435, 1339, 1255, 1198, 1161, 985, 945, 827 $cm^{-1}$; $\delta_H$ (500 MHz) 6.45 (1H, dd, *J* = 15.0Hz, *J* = 11.0Hz, 4-***H***), 6.01 (1H, td, *J* = 11.0Hz, *J* = 1.5Hz, 5-***H***), 5.74 (1H, dt, *J* = 15.0Hz, *J* = 7.0Hz, 3-***H***), 5.50 (1H, dq, *J* = 11.0Hz, *J* = 7.0Hz, 6-***H***), 3.70 (3H, s, OC***H***$_3$), 3.16 (2H, d, *J* = 7.0Hz, 2-***H***), 1.75 (3H, dd, *J* = 7.0Hz, *J* = 1.5Hz, 7-***H***); $\delta_C$ (125 MHz) 172.1 (***C***O), 129.0 (***C***-4), 128.6 (***C***-5), 126.3 (***C***-6), 124.4 (***C***-3), 51.9 (O***C***$H_3$), 38.1 (***C***-2), 13.3 (***C***-7); m/z (EI) 140 ($[M]^{+\cdot}$, 56%), 111 (10), 98 (64), 80 (100), 77 (35), 67 (15), 65 (22), 59 (36), 53 (50), 51 (20), 41 (45), 39 (40), 29 (11), 27 (18).

*(3E,5Z)-hepta-3,5-dien-1-ol*



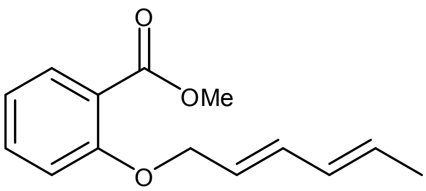
To a suspension of $LiAlH_4$ (0.96 g, 25.4 mmol) in diethyl ether (80 ml) was added a solution of (3*E*,5*Z*)-methyl hepta-3,5-dienoate (3.56 g, 25.4 mmol) in diethyl ether (20 ml) at 0°C, over a period of 15 minutes. The resulting suspension was stirred at RT for 1 h. The reaction mixture was cooled with an ice bath and cautiously quenched sequentially with $H_2O$ (3.0 ml), NaOH (1M, 3.0 ml) and $H_2O$ (6.0 ml). The suspension was then filtered through Celite®, the precipitate washed with EtOAc and the combined filtrate concentrated under reduced preasure. Flash column chromatography on silica, elution gradient 0 to 30% ethyl acetate in hexane, afforded the title product as a clear liquid (2.23 g, *EZ*:*EE* - 84:16, 78%). $R_f$ 0.4 (pet. ether : ethyl acetate 7:3); IR (ATR) 3326, 3018, 2923, 2879, 1432, 1371, 1179, 1041, 982, 945, 911, 839, 729 $cm^{-1}$; $\delta_H$ (500 MHz) 6.46 (1H, dd, *J* = 15.0Hz, *J* = 11.0Hz, 4-***H***), 6.00 (1H, td, *J* = 11.0Hz, *J* = 1.5Hz, 5-***H***), 5.64 (1H, dt, *J* = 15.0Hz, *J* = 7.0Hz, 3-***H***), 5.45 (1H, dq, *J* = 11.0Hz, *J* = 7.0Hz, 6-***H***), 3.70 (2H, q, *J* = 6.0Hz, 1-***H***), 2.40 (2H, dt, *J* = 7.0Hz, *J* = 6.0Hz, 2-***H***), 1.76 (3H, dd, *J* = 7.0Hz, *J* = 1.5Hz, 7-***H***), 1.43 (1H, t, *J* = 6.0Hz, O***H***); $\delta_C$ (125 MHz) 129.4 (***C***-5), 129.0 (***C***-3), 128.5 (***C***-4), 125.3 (***C***-6), 62.0 (***C***-1), 36.3 (***C***-2), 13.3 (***C***-7); m/z (EI) 112 ($[M]^{+\cdot}$, 78%), 94 ($[M-H_2O]^{+\cdot}$, 10), 81 ($[M-CH_2OH]^{+\cdot}$, 100), 79 ($[M-H_2O-CH_3]^{+\cdot}$, 85), 77 (40), 67 (84), 65 (28), 55 (44), 53 (74), 51 (19), 41 (72), 39 (63), 31 (31), 27 (37).

*Methyl 2-((2'E,4'E)-hexa-2',4'-dienyloxy)-4-methoxybenzoate*



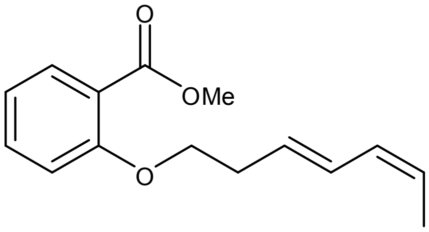
Following standard procedure **A**, a solution of triphenylphosphine (2.45 g, 9.33 mmol), (2*E*,4*E*)-hexa-2,4-dien-1-ol (0.76 g, 7.78 mmol) and methyl 2-hydroxy-4-methoxybenzoate (1.42 g, 7.78 mmol) in THF (2.0 ml) was treated with diisopropyl azodicarboxylate (1.84 ml, 9.33 mmol) to give the title compound as a white solid (0.90 g, 44%). Mp: 59.6–60.5 $^{o}$C; $R_f$ 0.2 (pet. ether : ethyl acetate 9:1); IR (ATR) 3009, 2941, 2842, 1692, 1611, 1570, 1502, 1433, 1385, 1304, 1270, 1200, 1172, 1141, 1099, 1035, 986, 926, 827, 761 cm$^{-1}$; $\delta_H$ (700 MHz) 7.87-7.85 (1H, m, 6-***H***), 6.51-6.50 (1H, m, 5-***H***), 6.481-6.478 (1H, m, 3-***H***), 6.41 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 3'-***H***), 6.10 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.80 (1H, dt, *J* = 15.4Hz, *J* = 5.6Hz, 2'-***H***), 5.76 (1H, dq, *J* = 15.4Hz, *J* = 6.3Hz, 5'-***H***), 4.63 (2H, d, *J* = 5.6Hz, 1'-***H***), 3.87 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.84 (3H, s, $OC\boldsymbol{H}_3$), 1.78 (3H, d, *J* = 6.3Hz, 6'-***H***); $\delta_C$ (175 MHz) 166.2 (***C***O), 164.0 (***C***-4), 160.4 (***C***-2), 133.9 (***C***-6), 133.6 (***C***-3'), 130.7 (***C***-4'), 130.6 (**C**-5'), 124.4 (***C***-2'), 112.8 (***C***-1), 105.0 (**C**-5), 100.5 (***C***-3), 69.4 (***C***-1'), 55.4 (ArO$\boldsymbol{C}H_3$), 51.7 ($CO_2\boldsymbol{C}H_3$), 18.1 (***C***-6'); m/z (ES+) 263 ([M+H]$^+$ , 100%), 285 ([M+Na]$^+$ 45), 547 ([2M+Na]$^+$ 47); Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.80; H, 6.92

*Methyl 2-((2'E,4'E)-hexa-2',4'-dienyloxy)benzoate*



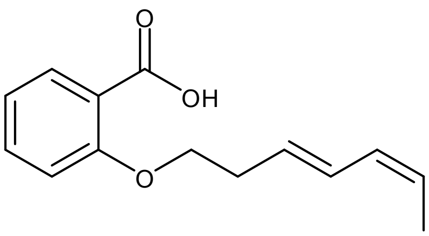
Following standard procedure **A**, a solution of triphenylphosphine (3.25 g, 12.4 mmol), (2*E*,4*E*)-hexa-2,4-dien-1-ol (1.01 g, 10.3 mmol) and methyl 2-hydroxybenzoate (1.57 g, 10.3 mmol) in THF (3.0 ml) was treated with diisopropyl azodicarboxylate (2.44 ml, 12.4 mmol) to give the title compound as a unstable white solid (0.99 g, 41%). Mp: 54.3–53.4 $^{o}$C; $R_f$ 0.4 (pet. ether : ethyl acetate 9:1); IR (ATR) 2911, 2854, 1719, 1595, 1486, 1441, 1374, 1285, 1239, 1188, 1162, 1140, 1077, 996, 957, 923, 833, 762, 706 cm$^{-1}$; $\delta_H$ (700 MHz) 7.81-7.79 (1H, m, 6-***H***), 7.45-7.42 (1H, m, 4-***H***), 6.99-6.97 (2H, m, 3-***H***, 5-***H***), 6.38 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 3'-***H***), 6.10 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.78 (1H, dt, *J* = 15.4Hz, *J* = 6.3Hz, 2'-***H***), 5.75 (1H, dq, *J* = 15.4Hz, *J* = 6.3Hz, 5'-***H***), 4.65 (2H, d, *J* = 6.3Hz, 1'-***H***), 3.91 (3H, s, $CO_2C\boldsymbol{H}_3$), 1.78 (3H, d, *J* = 6.3Hz, 6'-***H***); $\delta_C$ (175 MHz) 166.8 (***C***O), 158.2 (***C***-2), 133.5 (***C***-3'), 133.3 (***C***-4), 131.7 (***C***-6), 130.7 (***C***-4'), 130.6 (**C**-5'), 124.6 (***C***-2'), 120.7 (***C***-1), 120.3 (**C**-5), 113.8 (***C***-3), 69.4 (***C***-1'), 51.9 ($CO_2\boldsymbol{C}H_3$), 18.1 (***C***-6'); m/z compound decomposes under all forms of ionisation.

*Methyl 2-((3E,5Z)-hepta-3',5'-dienyloxy)benzoate*



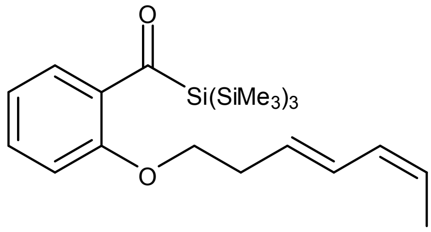

Following standard procedure **A**, a solution of triphenylphosphine (5.79 g, 22.1 mmol), (3*E*,5*Z*)-hepta-3,5-dien-1-ol (2.06 g, 18.4 mmol) and methyl 2-hydroxybenzoate (2.38 ml, 18.4 mmol) in THF (6.0 ml) was treated with diethyl azodicarboxylate (3.47 ml, 22.1 mmol) to give the title compound as a colourless liquid (2.46 g, *EZ*:*EE* - 84:16, 54%). $R_f$ 0.4 (pet. ether : ethyl acetate 7:3); IR (ATR) 3017, 2945, 1725, 1599, 1489, 1450, 1300, 1243, 1163, 1131, 1081, 1044, 1017, 985, 947, 836, 753, 707 $cm^{-1}$; $\delta_H$ (700 MHz) 7.79-7.78 (1H, m, Ar-6-***H***), 7.46-7.43 (1H, m, Ar-4-***H***), 6.99-6.96 (2H, m, Ar-5-***H***, Ar-3-***H***), 6.49 (1H, dd, *J* = 14.7Hz, *J* = 11.2Hz, 4'-***H***), 6.02 (1H, ddd, *J* = 11.2Hz, *J* = 10.5Hz, *J* = 1.4Hz, 5'-***H***), 5.77 (1H, dt, *J* = 14.7Hz, *J* = 7.0Hz, 3'-***H***), 5.45 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, 6'-***H***), 4.09 (2H, t, *J* = 7.0Hz, 1'-***H***), 3.89 (3H, s, OC***H***$_3$), 2.66 (2H, q, *J* = 7.0Hz, 2'-***H***), 1.76 (3H, dd, *J* = 7.0Hz, *J* = 1.4Hz, 7'-***H***); $\delta_C$ (175 MHz) 167.0 (***C***O), 158.3 (***C***-2), 133.3 (***C***-4), 131.6 (***C***-6), 129.2 (***C***-5'), 129.0 (***C***-3'), 127.9 (***C***-4'), 125.2 (***C***-6'), 120.7 (***C***-1), 120.3 (***C***-5), 113.4 (***C***-3), 68.6 (***C***-1'), 51.9 (O***C***H$_3$), 32.8 (***C***-2'), 13.3 (***C***-7'); m/z (EI) 246 ($[M]^{+\cdot}$, 5%), 215 ($[M\text{-}OCH_3]^{+\cdot}$, 8), 185 (61), 135 (10), 120 (12), 94 (100), 79 (86), 67 (40), 55 (22), 45 (33), 41 (20), 39 (14); HRMS (ES+) found $[M+H]^{+\cdot}$ 247.1329, $C_{15}H_{19}O_3$ requires $[M+H]^{+\cdot}$ 247.1329.

*2-((3E,5Z)-Hepta-3,5-dienyloxy)benzoic acid*



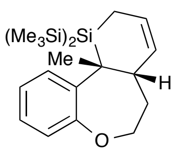

Following standard procedure **B**, a solution of methyl 2-((3*E*,5*Z*)-hepta-3',5'-dienyloxy)benzoate (1.74 g, 7.1 mmol) in THF (35 ml) was treated with a solution lithium hydroxide (0.34g, 14.1 mmol) in water (15 ml) to give the title compound as a colourless liquid (1.43 g, *EZ*:*EE* - 84:16, 87%). $R_f$ 0.5 (pet. ether : ethyl acetate 1:1); IR (ATR) 3276, 3020, 2928, 1728, 1601, 1581, 1486, 1456, 1395, 1295, 1234, 1219, 1163, 1125, 1041, 984, 947, 909, 834, 752 $cm^{-1}$; $\delta_H$ (700 MHz) 10.85 (1H, s, CO$_2$***H***), 8.21-8.19 (1H, m, Ar-6-***H***), 7.57-7.55 (1H, m, Ar-4-***H***), 7.15-7.13 (1H, m, Ar-5-***H***), 7.05-7.04 (1H, m, Ar-3-***H***), 6.55 (1H, dd, *J* = 15.4Hz, *J* = 11.2Hz, 4'-***H***), 6.00 (1H, ddd, *J* = 11.2Hz, *J* = 10.5Hz, *J* = 1.4Hz, 5'-***H***), 5.67 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.51 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, 6'-***H***), 4.31 (2H, t, *J* = 6.3Hz, 1'-***H***), 2.74 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***), 1.77 (3H, dd, *J* = 7.0Hz, *J* = 1.4Hz, 7'-***H***); $\delta_C$ (175 MHz) 165.3 (***C***O), 157.4 (***C***-2), 134.9 (***C***-4), 133.9 (***C***-6), 129.5 (***C***-4'), 128.4 (***C***-5'), 126.8 (***C***-3'), 126.7 (***C***-6'), 122.3 (***C***-5), 117.8 (***C***-1), 112.5 (***C***-3), 69.2 (***C***-1'), 32.6 (***C***-2'), 13.4 (***C***-7'); m/z (ES+) 487 ($[2M+Na]^{+\cdot}$, 24%), 465 ($[2M+H]^{+\cdot}$, 100), 250 ($[M+NH_4]^{+\cdot}$, 28), 233 ($[M+H]^{+\cdot}$, 20); HRMS (ES+) found $[M+NH_4]^{+\cdot}$ 250.1440, $C_{14}H_{20}O_3N$ requires $[M+NH_4]^{+\cdot}$ 250.1438.

*(2-((3E,5Z)-Hepta-3',5'-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone* **19**



Following standard procedure **C**, a solution of 2-((3*E*,5*Z*)-hepta-3,5-dienyloxy)benzoic acid (1.91 g, 8.21 mmol) in DCM (40.0 ml) was treated with oxalyl chloride (0.92 ml, 10.7 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (45.0 ml) and treated with a solution of silylpotassium in THF (45.0 ml), prepared from tetrakis(trimethylsilyl)silane (2.63 g, 8.21 mmol) and potassium *tert*-butoxide (0.97 g, 8.62 mmol). Flash column chromatography afforded the product as a yellow oil (1.90 g, *EZ*:*EE* - 84:16, 50%). $R_f$ 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2948, 2891, 1614, 1591, 1484, 1465, 1441, 1393, 1242, 1188, 1157, 1106, 1040, 1018, 979, 824, 746cm$^{-1}$; $\delta_H$ (700 MHz) 7.29-7.26 (1H, m, 4-***H***), 7.01-6.99 (1H, m, 6-***H***), 6.96-6.94 (1H, m, 5-***H***), 6.88-6.87 (1H, m, 3-***H***), 6.44 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.99 (1H, ddd, *J* = 11.2Hz, *J* = 10.5Hz, *J* = 1.4Hz, 5'-***H***), 5.68 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.44 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, 6'-***H***), 3.99 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.56 (2H, dt, *J* = 7.0Hz, *J* = 7.0Hz, 2'-***H***), 1.76 (3H, dd, *J* = 7.0Hz, *J* = 1.4Hz, 7'-***H***), 0.19 (27H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 241.6 (***C***O), 153.4 (***C***-2), 139.7 (***C***-1), 130.1 (***C***-4), 129.2 (***C***-5'), 128.7 (***C***-3'), 127.9 (***C***-4'), 125.5 (***C***-6), 125.2 (***C***-6'), 120.2 (***C***-5), 112.9 (***C***-3), 68.3 (***C***-1'), 32.7 (***C***-2'), 13.3 (***C***-7'), 1.1 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) -11.4, -70.5; m/z (ES+) 942 ([2M+NH$_4$]$^{+\cdot}$, 100%), 463 ([M+H]$^{+\cdot}$, 75); HRMS (ES+) found [M+H]$^{+\cdot}$ 463.2331, $C_{23}H_{43}O_2Si_4$ requires [M+H]$^{+\cdot}$ 463.2335.

*(4aSR,11bRS)-11b-methyl-1,1-bis(trimethylsilyl)-1,2,4a,5,6,11b-hexahydrobenzo [b]silino[2,3-d]oxepine* **25**

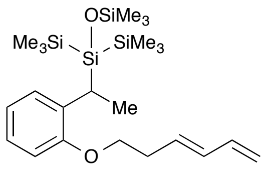


**25**

To a solution of (*E*)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone (0.23 g, 0.52 mmol) in diethyl ether (4.0 ml) was added methyllithium lithium bromide complex (1.5 M in $Et_2O$, 0.34 ml, 0.52 mmol) at -78 $^oC$. The mixture was stirred at -20 $^oC$ for 6 h and then at 10 $^oC$ for 16 h. After that time saturated sodium bicarbonate solution (6.0 ml) was added. The aqueous layer was separated and extracted with diethyl ether (3 x 5 ml), The combined organic extracts were dried over $MgSO_4$, filtered, concentrated and dried under reduced preasure. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the title silacycle **25** as a colourless oil (0.11 g, 57%, ds 2.5:1) and an inseparable mixture of products **27** and **26** as a colourless (28.6 mg, 12%, 25:1). $R_f$ 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2947, 2891, 1481, 1439, 1396, 1241, 1215, 1113, 1069, 1008, 909, 829, 769, 735 cm$^{-1}$; $\delta_H$ (700 MHz) 7.22-7.21

(1H, m, 11-***H***), 7.09-7.07 (2H, m, 9,10-***H***), 6.92-6.90 (1H, m, 8-***H***), 6.15 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 2.1Hz, 3-***H***), 5.63 (1H, ddd, *J* = 10.5Hz, *J* = 4.9Hz, *J* = 2.8Hz, 4-***H***), 4.12 (1H, td, *J* = 10.5Hz, *J* = 6.3Hz, 6-***H***), 3.81 (1H, ddd, *J* = 10.5Hz, *J* = 6.3Hz, *J* = 2.1Hz, 6-***H***), 2.68-2.66 (1H, m, 4a-***H***), 2.09-2.04 (1H, m, 5-***H***), 1.78 (1H, ddt, *J* = 16.1Hz, *J* = 2.8Hz, *J* = 2.1Hz, 2-***H***), 1.69-164 (1H, m, 5-***H***), 1.66 (3H, s, C***H***$_3$), 1.26 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.21 (9H, s, Si(C***H***$_3$)$_3$), -0.23 (9H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 154.6 (***C***-7a), 143.1 (***C***-11a), 133.8 (***C***-4), 128.6 (***C***-11), 128.0 (***C***-3), 126.4 (***C***-9), 124.7 (**C**-10), 123.0 (***C***-8), 68.9 (**C**-6), 44.9 (***C***-4a), 33.4 (***C***-11b), 30.0 (C***H***$_3$), 28.1 (***C***-5), 7.8 (***C***-2), 1.1 (Si(***C***H$_3$)$_3$), -0.6 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) -16.0, -16.8, -27.9; m/z (EI) 374 ([M]$^{+\cdot}$, 8%), 359 ([M-Me]$^{+\cdot}$, 7), 301 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 71), 273 (30), 257 (22), 233 (47), 221 (29), 199 (74), 193 (60), 175 (58), 161 (42), 141 (32), 117 (43), 115 (46), 99 (30), 97 (20), 73 (100), 59 (60), 45 (54), 43 (16); HRMS (ASAP) found [M+H]$^{+\cdot}$ 375.1987, $C_{20}H_{35}OSi_3$ requires [M+H]$^{+\cdot}$ 375.1996.

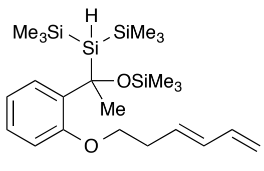
*(E)-2-(1-(2-(Hexa-3',5'-dienyloxy)phenyl)ethyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsiloxy)trisilane* **27**




**27**

R$_f$ 0.7 (pet. ether : diethyl ether 95:5); IR (ATR) 2951, 2893, 1595, 1487, 1447, 1238, 1051, 1002, 831, 743 cm$^{-1}$; $\delta_H$ (700 MHz) 7.19-7.17 (1H, m, Ar-6-***H***), 7.06-7.03 (1H, m, Ar-4-***H***), 6.90-6.88 (1H, m, Ar-5-***H***), 6.79-6.77 (1H, m, Ar-3-***H***), 6.34 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.19 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.80 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.14 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.02 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.03 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 3.93 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 3.06 (1H, q, *J* = 7.7Hz, C***H***CH$_3$), 2.62 (1H, dq, *J* = 14.0Hz, *J* = 7.0Hz, 2'-***H***), 2.59 (1H, dq, *J* = 14.0Hz, *J* = 7.0Hz, 2'-***H***), 1.41 (3H, d, *J* = 7.7Hz, CHC***H***$_3$), 0.11 (9H, s, Si(C***H***$_3$)$_3$), 0.08 (9H, s, OSi(C***H***$_3$)$_3$), -0.10 (9H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 154.9 (Ar-***C***-2), 136.9 (***C***-5'), 135.7 (Ar-***C***-1), 133.2 (***C***-4'), 130.6 (***C***-3'), 128.4 (Ar-**C**-6), 125.1 (Ar-***C***-4), 120.6 (Ar-***C***-5), 115.7 (**C**-6'), 111.2 (Ar-***C***-3), 67.3 (**C**-1'), 32.7 (**C**-2'), 21.6 (C***H***CH$_3$), 17.4 (CHC***H***$_3$), 2.1 (OSi(***C***H$_3$)$_3$), -0.7 (Si(***C***H$_3$)$_3$), -1.2 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) 6.8, 1.9, -19.8, -20.1; m/z (GC-MS, EI) 391 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 28), 323 (20), 309 (12), 263 (46), 207 (25), 189 (42), 175 (44), 147 (45), 117 (42), 81 (100), 73 (64), 53 (32), 41 (24).

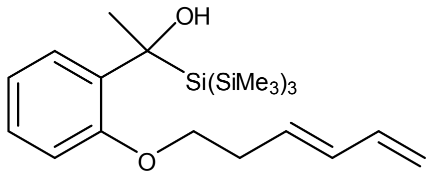
*(E)-2-(1-(2-(Hexa-3',5'-dienyloxy)phenyl)-1-(trimethylsilyloxy)ethyl)-1,1,1,3,3,3-hexamethyltrisilane* **26**




**26**

$^1$H NMR – characteristic peaks: 3.65 (1H, s, Si***H***), 2.02 (3H, s, C***H***$_3$), 0.21 (9H, s, Si(C***H***$_3$)$_3$), 0.17 (9H, s, OSi(C***H***$_3$)$_3$), -0.13 (9H, s, Si(C***H***$_3$)$_3$); m/z (GCMS, EI) 446 ([M-CH$_3$]$^{+\cdot}$, 1%), 147 (22), 81 (100), 73 (60).

*(E)-1-(2-(Hexa-3',5'-dienyloxy)phenyl)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethanol* **28**




To a solution o of (*E*)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone (0.34 g, 0.77 mmol) in diethyl ether (6.0 ml) was added methyllithium lithium bromide complex (1.5 M, 0.51 ml, 0.77 mmol) at -78$^o$C. The mixture was stirred at RT for 16 h after which time saturated sodium bicarbonate solution (6.0 ml) was added. The aqueous layer was separated and extracted with diethyl ether (3 x 5 ml), The combined organic extracts were dried over $MgSO_4$, filtered, concentrated and dried *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a unstable colourless oil (0.15 g, 42%). $R_f$ 0.6 (pet. ether : diethyl ether 9:1); IR (ATR) 3506, 2947, 2892, 1598, 1487, 1443, 1395, 1282, 1241, 1223, 1048, 1020, 1001, 903, 827, 745, 733 cm$^{-1}$; $\delta_H$ (700 MHz) 7.21-7.20 (1H, m, Ar-6-***H***), 7.15-7.12 (1H, m, Ar-4-***H***), 6.92-6.90 (1H, m, Ar-5-***H***), 6.87-6.86 (1H, m, Ar-3-***H***), 6.33 (1H, ddd, *J* = 17.5Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.21 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.73 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.17 (1H, d, *J* = 17.5Hz, 6'-***H***), 5.05 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.89 (1H, s, O***H***), 4.15 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 4.07 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 2.64 (1H, q, *J* = 7.0Hz, 2'-***H***), 1.80 (3H, s, C***H***$_3$), 0.18 (27H, s, Si(C***H***$_3$)$_3$); $\delta_C$ (175 MHz) 155.3 (Ar-***C***-2), 138.3 (Ar-***C***-1), 136.6 (***C***-5'), 134.1 (***C***-4'), 129.3 (***C***-3'), 128.5 (Ar-**C**-6), 126.9 (Ar-***C***-4), 121.0 (Ar-***C***-5), 116.4 (**C**-6'), 113.0 (Ar-***C***-3), 76.0 (**C**OH), 68.0 (***C***-1'), 33.1 (***C***H$_3$), 32.5 (**C**-2'), 2.2 (Si(***C***H$_3$)$_3$); $\delta_{Si}$ (140 MHz) -13.3, -54.7; m/z compound decomposes under all forms of ionisation.

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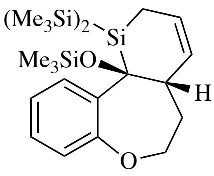
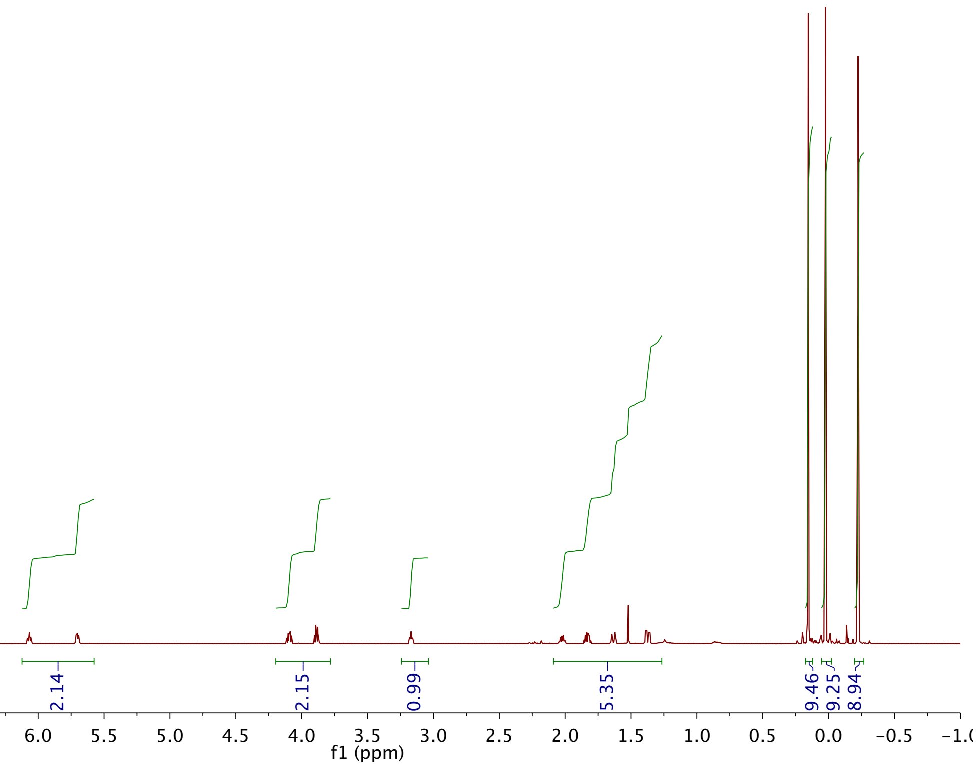
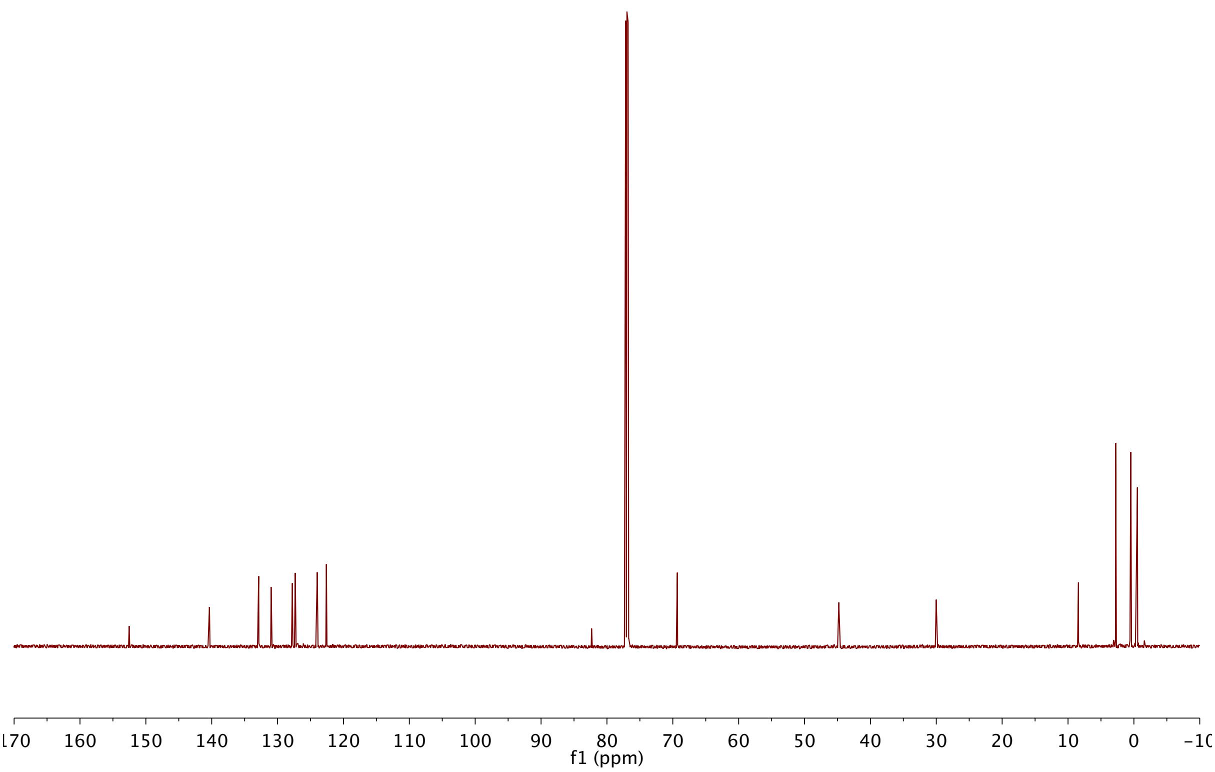
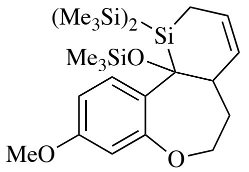
$^{1}H$ & $^{13}C$ NMR of compound **14**

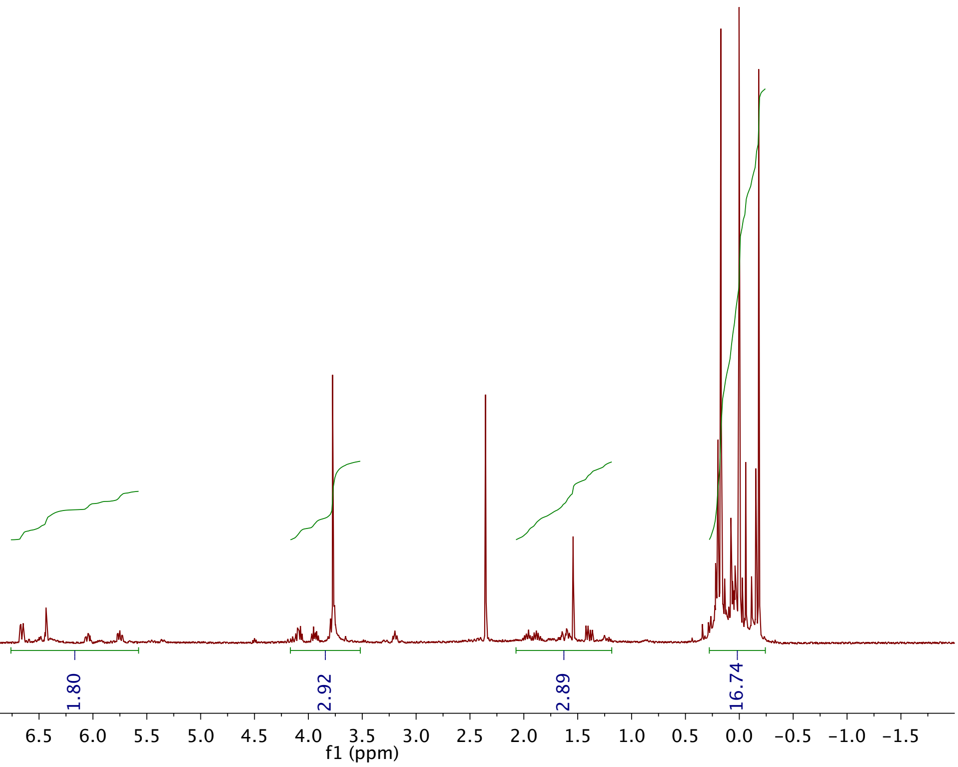


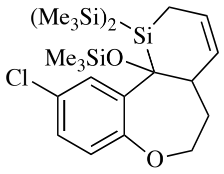



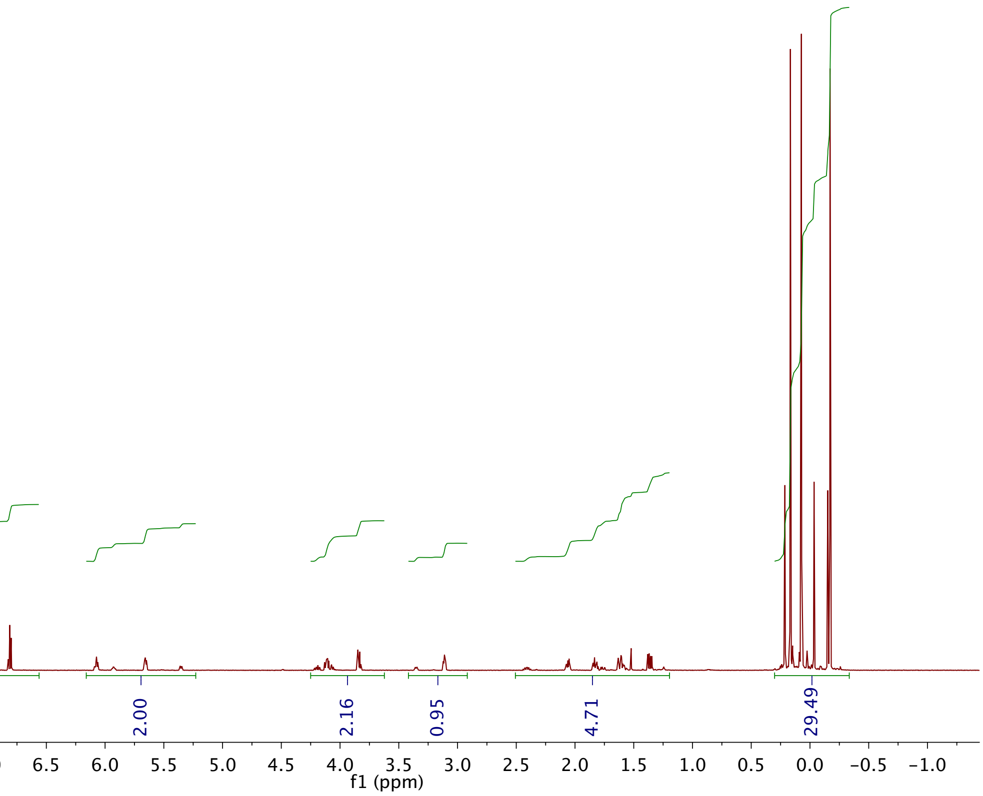
$^{1}$H NMR of compound **20**

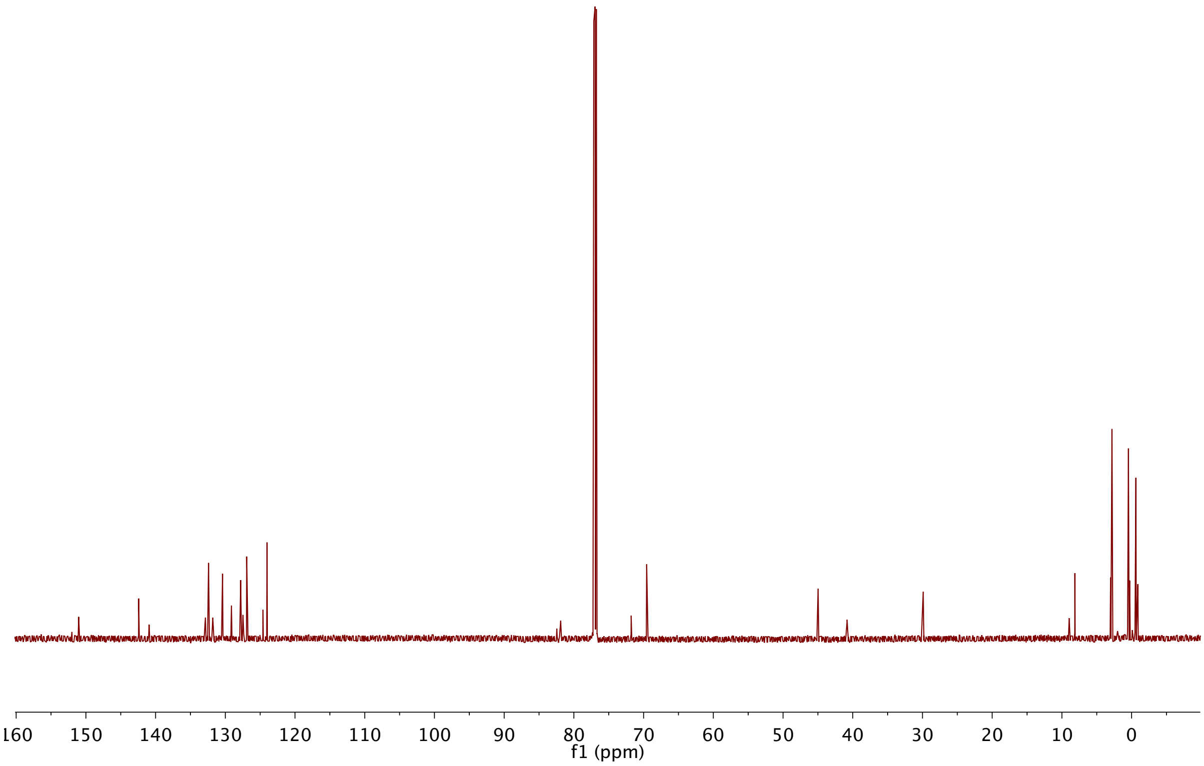




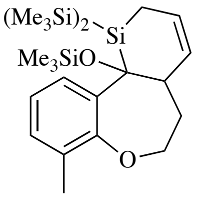
$^1$H & $^{13}$C NMR of compound **21**

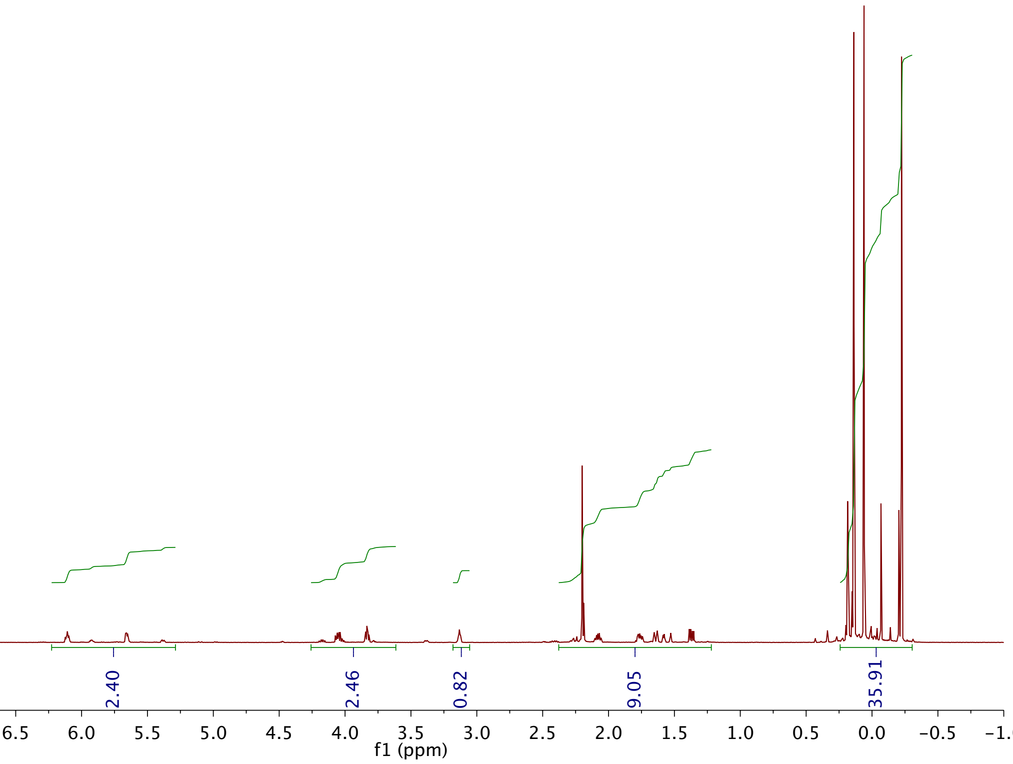


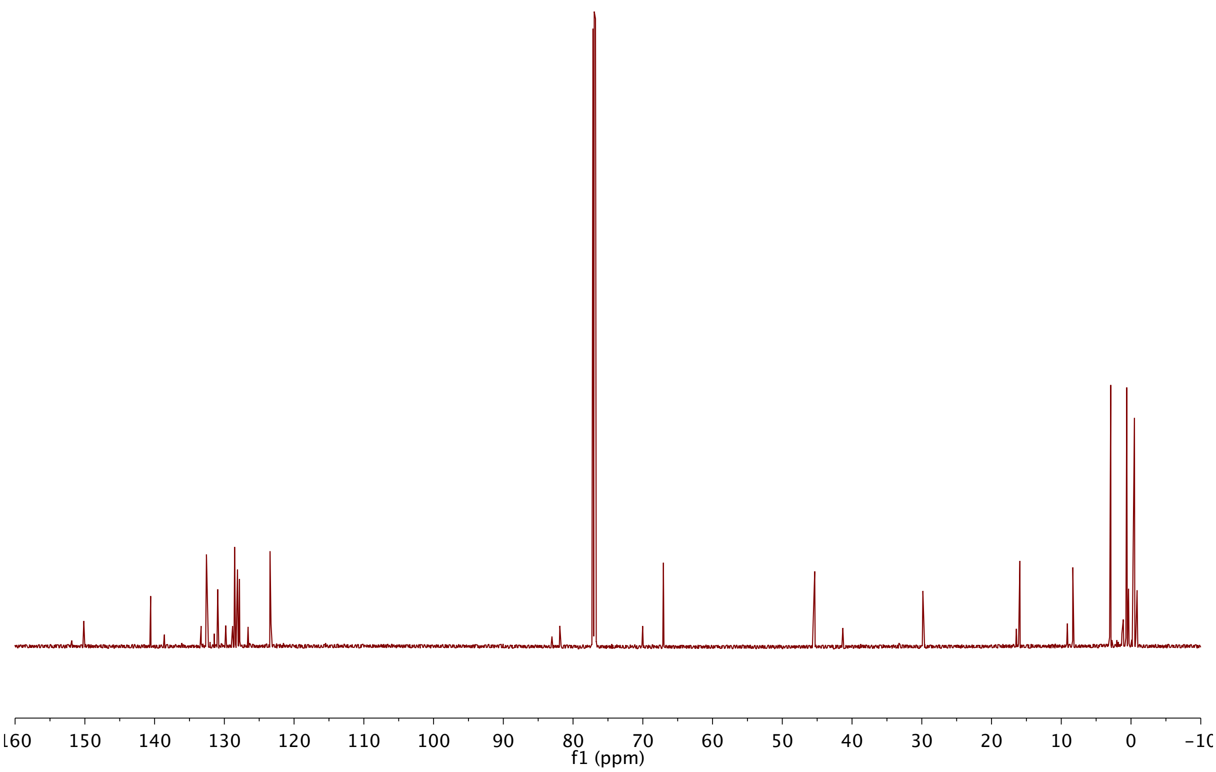



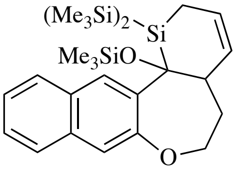
$^{1}H$ & $^{13}C$ NMR of compound **22**

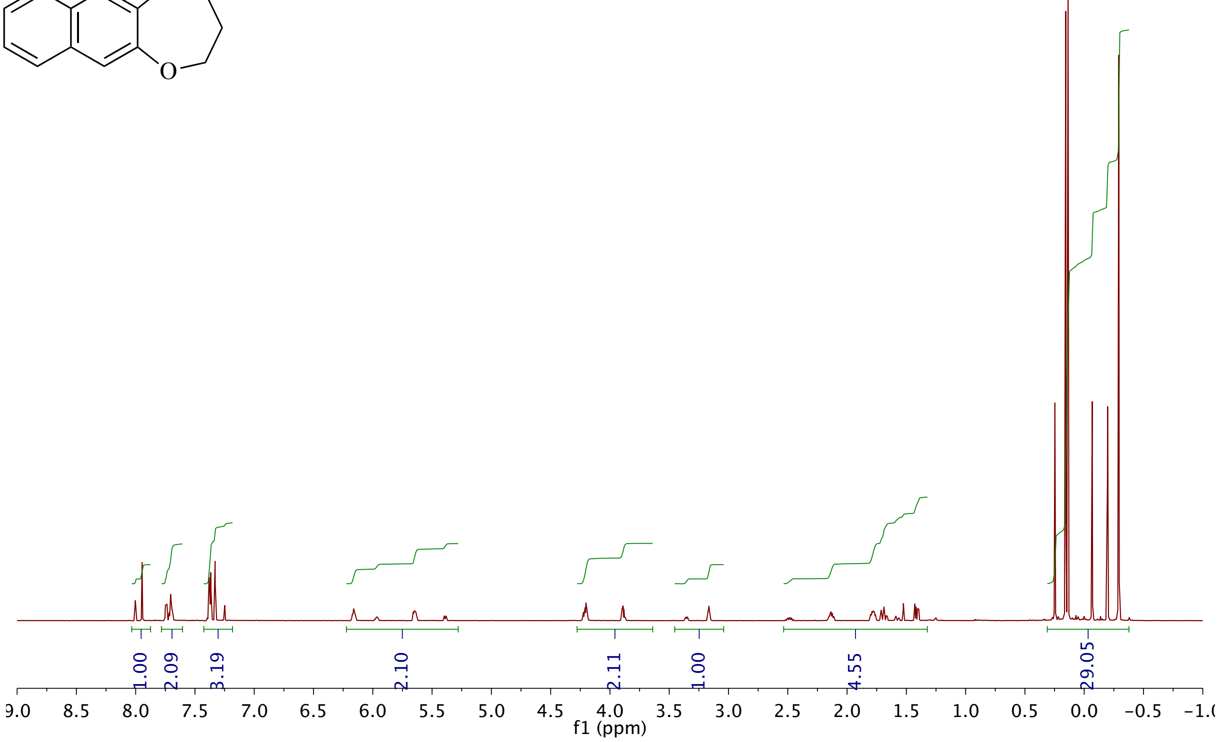


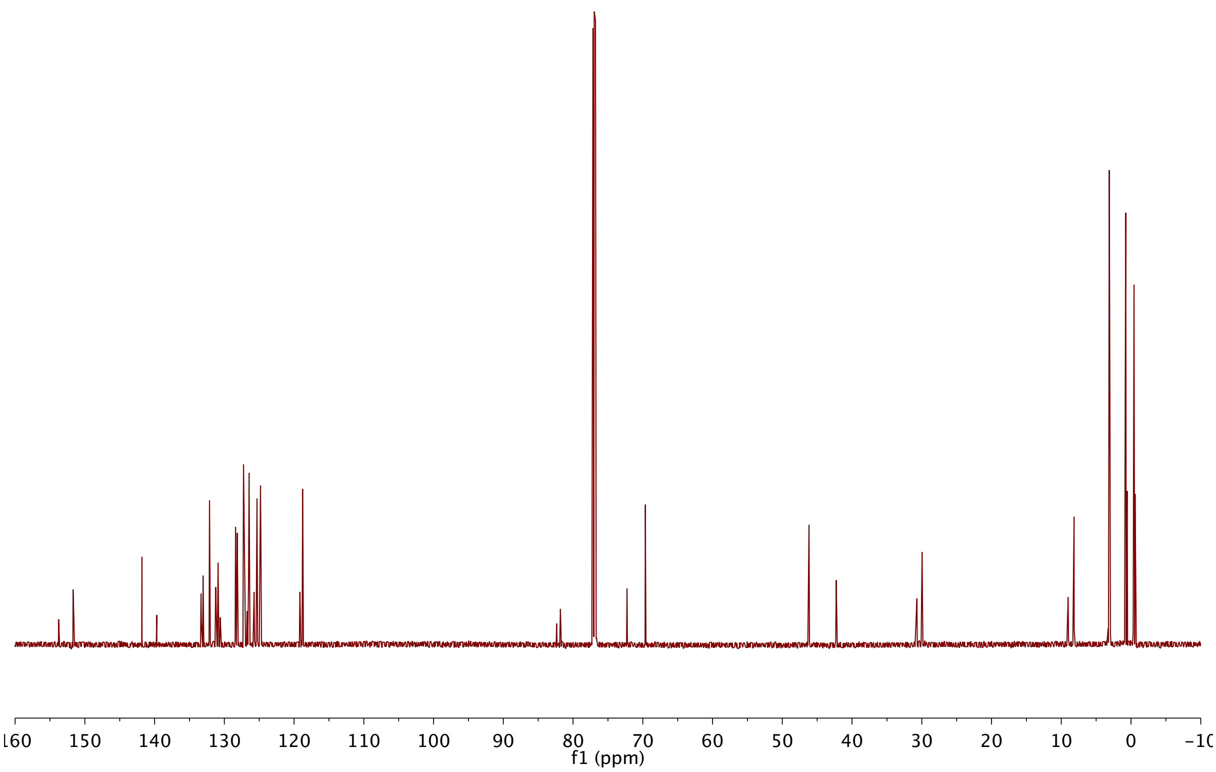



[1]H & [13]C NMR of compound **23**



$^{1}H$ & $^{13}C$ NMR of compound **25**