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INTRAMOLECULAR DIELS-ALDER REACTIONS OF FURANS WITH A MERELY STRAIN-ACTIVATED TETRASUBSTITUTED ALKENE: BICYCLOPROPYLIDENE

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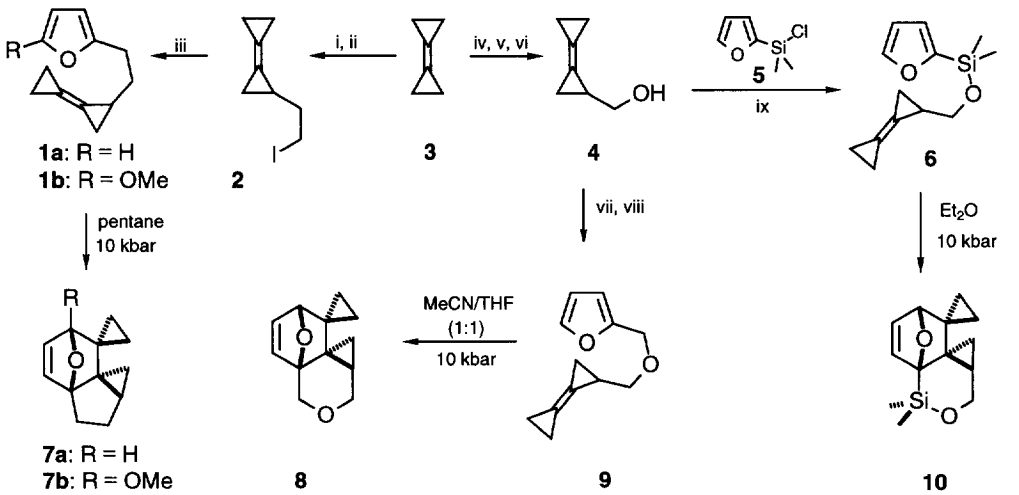
Abstract: Bicyclopropylidene derivatives **1**, **6**, **8** with furan moieties attached on tethers of various length and nature all undergo clean intramolecular Diels-Alder reactions with complete *endo*-diastereoselectivities when heated to 70 – 130 °C, under 10 kbar pressure. The reaction rates are at least as high or higher than those of analogously tethered methylenecyclopropane-furan derivatives **15**, **17**, **20**, in spite of the fact that the reactive double bond in bicyclopropylidene is tetrasubstituted and not activated by any electron withdrawing group. Copyright © 1996 Elsevier Science Ltd

Bicyclopropylidene **3**,[1] with its combined two methylenecyclopropane units, is a uniquely strained tetrasubstituted alkene which unlike other tetrasubstituted alkenes can undergo various cycloadditions and additions[2,3] including palladium-catalyzed coupling reactions.[4] Due to its relatively high HOMO energy,[5] it has a particularly high propensity to participate in 1,3-dipolar cycloadditions,[2,3] but in Diels-Alder reactions only if the diene were electron deficient, i. e. with inverse electron demand. Without any electronically activating substituents attached, **3** has to be referred to as a merely strain-activated tetrasubstituted dienophile, when forced to undergo a Diels-Alder reaction. The release of ring strain during the course of any cycloaddition should contribute to the reaction enthalpy thus rendering the overall process less unfavourable. However, a major incentive would be brought in by the strongly negative entropic contribution to the free enthalpy of activation by tethering bicyclopropylidene as a dienophile to the diene and thereby making the cycloaddition occur intramolecularly.[6] Eventually, high pressure can ensure cycloadditions to occur even in difficult cases as recently demonstrated for an intramolecular reaction of a furan with an unactivated methylenecyclopropane moiety.[7] In order to probe the reactivity of bicyclopropylidene in ordinary Diels-Alder reactions, we prepared a number of bicyclopropylidene derivatives with furan units on a tether and demonstrated their undergoing an intramolecular cycloaddition under high pressure. To our knowledge, these are the first examples for an intramolecular Diels-Alder reaction with a merely strain-activated tetrasubstituted dienophile.

Since bicyclopropylidene **3**, like methylenecyclopropane[8] **13**, can be deprotonated with *n*-butyllithium and the resulting lithium derivative substituted with all sorts of electrophiles,[9] iodoethylbicyclopropylidene **2** was obtained by adding oxirane to lithiated **3**, converting the alcohol to the benzenesulfonate and the sulfonate to the iodide **2**. Treatment of **2** in the presence of HMPA[10] with 2-lithiofuran or 2-lithio-5-methoxyfuran gave the carbon tethered furan derivatives **1a** and **1b**, respectively, in 36 and 15% overall yield. Hydroxymethylbicyclopropylidene **4** was prepared by reduction of ethyl bicyclopropylidenecarboxylate[9,11] with $LiAlH_4$ (97% yield), transformed to its benzenesulfonate and the latter substituted with furfurylalkoxide to yield **9** (21% overall). Reaction of **4** with (2-furyl)dimethylsilyl chloride **5**[12] under basic conditions gave the silicon tethered[13] derivative **6** (Scheme 1).

The carbon tethered furan derivative **1a** underwent a clean intramolecular Diels-Alder reaction (IMDAF), when heated in pentane solution under 10 kbar to 100 °C. The rather low yield (32%) of **7a** after chromatography is due to partial decomposition upon contact with silica gel. The 5-methoxyfuran derivative **1b** reacted cleanly at 85 °C, yet the cycloadduct **7b** is so sensitive that it could not be purified by chromatography.[14] The oxygen tethered derivative **9** underwent IMDAF in acetonitrile/tetrahydrofuran solution at slightly lower temperature (70 °C) (Table 1), while the silicon tethered compound **6** required 130 °C, yet gave a better yield of the isolated product **10**. The IMDAF of all three types of tethered bicyclopropylidene derivatives **1**, **9** and **6** proceeded with complete diastereoselectivity. X-ray crystal structure analyses of the cycloadducts **7a**, **8**, and **10** proved that they were all *endo*-configurated with regard to the orientation of the unsubstituted methylene group of the cyclopropane ring.

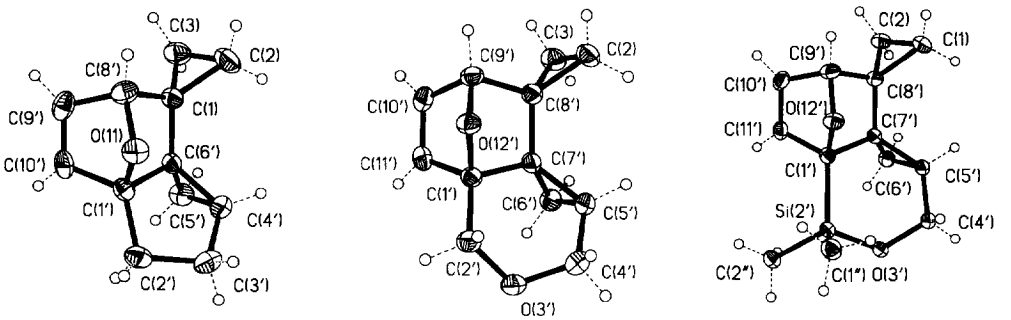


Scheme 1. Synthesis of tethered bicyclopropylidene derivatives with furan units and their intramolecular Diels-Alder reactions. Reaction conditions and yields: i 1) *n*-BuLi, THF; 2) oxirane, 51%; ii Ph_3P, I_2, imidazole, MeCN, Et_2O, 73%; iii for R = H: 2-lithiofuran, HMPA, THF, 95%; for R = OMe: 5-lithio-2-methoxyfuran, HMPA, THF, 40%; iv 1) *n*-BuLi, THF, 2) dry ice, 95%; v BF_3•OEt_2, EtOH, 89%; vi $LiAlH_4$, Et_2O, 97%; vii $PhSO_2Cl$, pyridine, 74%; viii furfuryl alcohol, NaH, THF, 29%; ix Et_3N, Et_2O, >95%. For further details see Table 1.

Table 1. Intramolecular Diels-Alder Reactions of Furans with Tethered Bicyclopropylidene Units at 10 kbar.

Starting Material	Temperature [°C]	Time [h]	Product	Isolated Yield (%)
1a, R = H	90	43	**7a**	32
1b, R = OMe	85	20	**7b**	>95[a]
9	70	48	**8**	46[b]
9	75	70	**8**	42
6	130	20	**10**	83

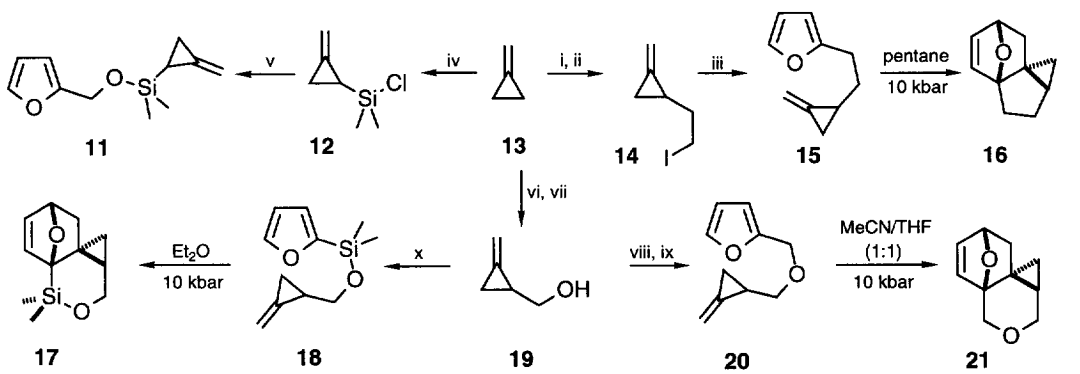
[a] Performed in dry THF, yield of crude product was determined by ^{1}H-NMR spectroscopy. – [b] 28% of starting material **9** recovered.



7a **8** **10**

Figure 1. Structures of intramolecular cycloadducts **7a**, **8**, and **10** in the crystal.[15]

In order to understand, whether the necessary reaction conditions for the IMDAF of compounds **1a,b**, **9**, and **6** in comparison with the previously reported methylenecyclopropane IMDAF[7] are mainly determined by the fact that the dienophile in these new cases is a methylenecyclopropane with a tetrasubstituted double bond or just one that is linked in a different way, the series of furan derivatives **15**, **20**, **18**, and **11** with simple methylenecyclopropane units tethered like bicyclopropylidene above was prepared along analogous routes (see Scheme 2) from methylenecyclopropane **13**. Except for the silicon tethered compound **11** with the dimethylsilyl group directly attached to the cyclopropane ring, all these methylenecyclopropane derivatives underwent intramolecular cycloadditions when heated under 10 kbar pressure (Table 2). It is evident that compounds **15**, **20**, **18** required slightly higher or at least the same temperatures as their bicyclopropylidene counterparts **1a**, **9**, **6**. Apparently, the possible decrease in reactivity due to the tetrasubstitution of the double bond in bicyclopropylidene is overcompensated by the increase in reactivity due to the enhanced strain in the double bond. This is particularly obvious from the fact that the silicon tethered bicyclopropylidene derivative **6** gives a stable crystalline product **10** in 83% yield, while the methylenecyclopropane analogue **18** under totally comparable conditions afforded only 25% of the cycloadduct **17** along with 40% of recovered starting material.



Scheme 2. Synthesis of tethered methylenecyclopropane derivatives with furan units and their IMDAF. Reaction conditions and yields: i 1) *n*-BuLi, THF; 2) oxirane, >95%;[16] ii 1) $PhSO_2Cl$, pyridine; 2) NaI, EtCOMe, 82%; iii 2-lithiofuran, HMPA, THF, 92%; iv 1) *n*-BuLi, THF; 2) Me_2SiCl_2, Et_2O, 36%; v furfuryl alcohol, Et_3N, Et_2O, 96%; vi 1) *n*-BuLi, THF; 2) dry ice, 81%; vii $LiAlH_4$, Et_2O, 83%;[17] viii $PhSO_2Cl$, pyridine, 76%; ix furfuryl alcohol, NaH, THF, 27%; x **5**, Et_3N, Et_2O, >95%. For details of IMDAF see Table 2.

Table 2. Intramolecular Diels-Alder Reactions of Furans with Methylenecyclopropane Units on Tethers at 10 kbar.

Starting Material	Temperature [°C]	Time [h]	Product	Isolated Yield (%)
15	100	17	**16**	82
20	85	45	**21**	47[a]
20	100	20	**21**	50
11	130	20	–[b]	–[b]
18	125	30	**17**	25[c]

[a] 20% of starting material **20** recovered. – [b] Complete decomposition of starting material **11** occurred. – [c] 40% of starting material **18** recovered.

EXPERIMENTAL

THF and Et_2O were distilled from sodium benzophenone ketyl prior to use. MeCN, HMPA and pyridine were freshly distilled from CaH_2. Sodium hydride was washed several times with dry pentane, dried *in vacuo* and stored under argon. All solvents for chromatography and extraction were used distilled. All melting points were determined on a Reichert microscopic hot stage apparatus and are uncorrected. Boiling points were determined upon fractional distillation and are uncorrected. FT-IR spectra were taken on Bruker IFS 66 FT-IR spectrometer. NMR spectra were measured on Bruker AM 250 at 250 (^1H) and 62.9 [^{13}C, additional DEPT (Distortionless Enhancement by Polarization Transfer)] MHz in $CDCl_3$ solution. The signal multiplicities in ^1H NMR spectra are abbreviated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), dq (doublet of quartets), m (multiplet), AB (AB system), and b (broad). Mass spectra were obtained from either Varian MAT CH 7 or Varian MAT 731; HRMS (HR-EI): preselected ion peak matching at R » 10000 to be ± 2 ppm of the exact masses, CI-MS: with NH_3.

Syntheses of Building Blocks

Lithiation of 3 and 13. General Procedure (GP) 1: To a solution of **3** (8.010 g, 9.40 ml, 0.100 mol) or **13** (8.114 g, 9.50 ml 0.150 mol) in THF (100 ml), *n*-butyllithium (44.5 ml, 2.25 M, 0.100 mol, in *n*-hexane) was added at –50 °C. The solution was allowed to warm up to 0 °C and stirred for 1 h.

(2-Hydroxyethyl)bicyclopropylidene: To a solution of lithiobicyclopropylidene, prepared from **3** (8.010 g, 9.40 ml, 0.100 mol) and *n*-butyllithium (44.5 ml of 2.25 M soln in hexane) according to GP 1, 10 ml of oxirane was added in one portion at –50 °C. The mixture was warmed to 0 °C, and the temperature was maintained at 0–8 °C by external cooling for 1 h. After quenching with water (50 ml), the mixture was extracted with Et_2O (2 × 100 ml), washed with brine, dried ($MgSO_4$), concentrated and distilled *in vacuo* to give (2-hydroxyethyl)bicyclopropylidene (6.360 g, 51%), bp 69–72 °C (1 Torr). – IR (film): ν = 3354 cm^{-1}, 2931, 1717, 1445,

1412, 1198, 1056, 960. – ^{1}H NMR: δ = 0.85 (m, 1 H, cpr), 1.14 (m, 4 H, cpr), 1.36 (m, 1 H, cpr), 1.42 (dq, ^2J = 13.0, ^3J = 6.9 Hz, 1 H, CH_2), 1.49 (m, 1 H, cpr), 1.80 (dq, ^2J = 13.0, ^3J = 6.9 Hz, 1 H, CH_2), 2.47 (bs, 1 H, OH), 3.69 ppm (t, ^3J = 6.9 Hz, 2 H, CH_2OH). – ^{13}C NMR: δ = 2.69 ($2CH_2$), 9.35 (CH_2), 12.80 (CH), 35.99, 62.66 (each CH_2), 110.28, 115.10 ppm (each C). – MS (70 eV, EI), *m/z* (%): 124 (1) [M^+], 123 (4) [M^+ – H], 93 (42) [M^+ – CH_2OH], 91 (66) [$C_7H_7^+$], 79 (100) [$C_6H_7^+$], 77 (62) [$C_6H_5^+$]. HRMS calcd for $C_8H_{12}O$ 124.0888. Found 124.0888.

2-(2'-Hydroxyethyl)methylenecyclopropane: To a solution of lithiomethylenecyclopropane, prepared from **13** (8.114 g, 9.50 ml, 0.150 mol) and *n*-butyllithium (44.5 ml of 2.25 M soln in hexane) according to GP1, oxirane (10 ml) was added in one portion at –78 °C. After stirring at this temperature for 1 h, the mixture was allowed to warm to 0 °C. After quenching with ice-cold water (100 ml), the mixture was extracted with Et_2O (2 × 100 ml), washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by bulb-to-bulb distillation (1 Torr) to give 2-(2'-hydroxyethyl)methylenecyclopropane (9.620 g, 98%). – ^{1}H NMR: δ = 0.67 (m, 1 H, cpr), 1.22 (m, 1 H, cpr), 1.45 (m, 1 H, cpr), 1.59 (m, 2 H, CH_2), 2.62 (bs, 1 H, OH), 3.67 (t, ^3J = 6 Hz, 2 H, CH_2OH), 5.32 (bs, 1 H, C=CH), 5.39 ppm (bs, 1 H, C=CH). – ^{13}C NMR: δ = 9.11 (CH_2), 12.44 (CH), 35.90, 62.40, 102.93 (each CH_2), 135.93 ppm (C).

Preparation of Benzenesulfonates. General Procedure (GP) 2: Benzenesulfonyl chloride (11.820 g, 66.90 mmol) was added slowly for 30 min at –10 °C to a solution of the alcohol (66.90 mmol) in pyridine (60 ml). Stirring was continued for 30 min at –10 °C and 3 h at 0 °C. The reaction mixture was diluted with CH_2Cl_2 (200 ml) and quenched with ice-cold water (100 ml). The aqueous layer was extracted with CH_2Cl_2 (3 × 50 ml). The combined organic layers were first washed with ice-cold 5% HCl solution (3 × 40 ml), brine (3 × 50 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Benzenesulfonates thus obtained were used without further purification.

2-[2'-(Benzenesulfonyl)oxyethyl]methylenecyclopropane (15.767 g, 99%) was obtained from 2-(hydroxyethyl)methylenecyclopropane (6.566 g, 66.90 mmol), according to GP 2, as an unstable lilac oil. – IR (film): ν = 2989 cm^{-1}, 1448, 1359, 1187, 1097, 965, 911, 755, 689, 589. – ^{1}H NMR: δ = 0.72 (m, 1 H, cpr), 1.19 (m, 1 H, cpr), 1.38 (m, 1 H, cpr), 1.61 (m, 1 H, CH_2), 1.70 (m, 1 H, CH_2), 4.09 (t, ^3J = 6.5 Hz, 2 H, CH_2O), 5.29 (m, 2 H, C=CH_2), 7.52 (m, 2 H, Ph), 7.64 (m, 1 H, Ph), 7.90 ppm (m, 2 H, Ph). – ^{13}C NMR: δ = 9.17 (CH_2), 11.71 (CH), 32.20, 70.37, 103.62 (each CH_2), 126.59, 127.70, 133.59 (each CH), 134.46, 136.09 ppm (each C). – MS (70 eV, EI), *m/z* (%): 184 (2) [M^+ – C_4H_6], 141 (49) [$PhSO_2^+$], 97 (6) [M^+ – $PhSO_2$], 80 (54), 79 (55), 77 (100) [Ph^+], 67 (22), 51 (34).

2-[2'-(Benzenesulfonyl)oxymethyl]methylenecyclopropane (11.403 g, 76%) was obtained from **19** (5.628 g, 66.90 mmol) according to GP 2, as an unstable yellow oil. – IR (film): ν = 2991 cm^{-1}, 1683, 1448, 1360, 1188, 1097, 1008, 924, 755, 689, 588. – ^{1}H NMR: δ = 0.94 (m, 1 H, cpr), 1.31 (m, 1 H, cpr), 1.75 (m, 1 H, cpr), 3.81 (dd, ^3J = 7.5, ^2J = 11.0 Hz, 1 H, CH_2O), 4.07 (dd, ^3J = 7.5, ^2J = 11.0 Hz, 1 H, CH_2O), 5.39 (m, 2 H, C=CH_2), 7.50 (m, 2 H, Ph), 7.59 (m, 1 H, Ph), 7.86 ppm (m, 2 H, Ph). – ^{13}C NMR: δ = 8.85 (CH_2), 13.90 (CH), 73.48, 105.47 (each CH_2), 127.51, 129.05 (each CH), 130.56 (C), 133.53 (CH), 136.17 ppm (C). – MS (70 eV, EI), *m/z* (%): 224 (< 0.1) [M^+], 141 (48) [$PhSO_2^+$], 83 (20) [M^+ – $PhSO_2$], 77 (100) [Ph^+], 55 (21) [$C_4H_7^+$], 51 (26) [$C_4H_3^+$]. HRMS calcd for $C_{11}H_{12}SO_3$ 224.0507. Found 224.0507.

[(Benzenesulfonyl)oxymethyl]bicyclopropylidene (12.380 g, 74%) was obtained from hydroxymethylbicyclopropylidene **4** (7.369 g, 66.90 mmol) according to GP 2, as a slightly yellow oil. – ^{1}H NMR: δ = 1.06 (m, 4 H, cpr), 1.40 (m, 2 H, cpr), 1.81 (m, 1 H, cpr), 3.77 (m, 1 H, CH_2O), 4.18 (m, 1 H, CH_2O), 7.50 (m, 2 H, Ph), 7.60 (m, 1 H, Ph), 7.88 ppm (m, 2 H, Ph). – ^{13}C NMR: δ = 2.99 (2 CH_2), 9.35 (CH_2), 14.31 (CH), 73.94 (CH_2), 114.29, 114.39 (each C), 127.51, 129.01, 133.46 (each CH), 136.32 ppm (C). – MS (70 eV, EI), *m/z* (%): 250 (4) [M^+], 141 (30) [$PhSO_2^+$], 109 (26) [$M^+ - PhSO_2$], 92 (31) [$M^+ - PhSO_2OH$], 91 (29) [$M^+ - PhSO_2 - H_2O$], 77 (100) [Ph^+]. HRMS calcd for $C_{13}H_{14}SO_3$ 250.0664. Found 250.0663.

2-(2'-Iodoethyl)methylenecyclopropane (**14**): Sodium iodide (24.160 g, 161.20 mmol) was added to a solution of 2-[2'-(benzenesulfonyl)oxyethyl]methylenecyclopropane (19.064 g, 80.00 mmol) in ethyl methyl ketone (160 ml). The solution was heated for 1.5 h at 80 °C, cooled, diluted with ice-cold water (100 ml) and extracted with pentane (3 × 100 ml). The combined organic layers were washed with water (100 ml), brine (3 × 100 ml), dried ($MgSO_4$) and concentrated. The residual oil was purified by bulb-to-bulb distillation (50 °C, 1 Torr) to give **14** (13.650 g, 82%), as a colourless liquid (stench!). – IR (film): ν = 2973 cm^{-1}, 1424, 1237, 1174, 1130, 1022, 889, 757. – ^{1}H NMR: δ = 0.83 (m, 1 H, cpr), 1.29 (m, 1 H, cpr), 1.52 (m, 1 H, cpr), 1.87 (m, 1 H, CH_2), 1.93 (m, 1 H, CH_2), 3.21 (t, ^3J = 7.0 Hz, 2 H, CH_2I), 5.38 (m, 1 H, C=CH), 5.44 ppm (m, 1 H, C=CH). – ^{13}C NMR: δ = 5.10 (2 CH_2), 9.29 (CH), 37.12, 103.55 (each CH_2), 134.73 ppm (C). – MS (70 eV, EI), *m/z* (%): 208 (0.1) [M^+], 128 (32) [HI^+], 127 (100) [I^+], 81 (100) [$M^+ - I$]. HRMS calcd for C_6H_9I 207.9749. Found 207.9748.

(2'-Iodoethyl)bicyclopropylidene (**2**): Iodine (23.632 g, 93.11 mmol) was added in small portions for 30 min to an efficiently cooled (0 °C) solution of hydroxyethylbicyclopropylidene (5.980 g, 48.15 mmol), imidazole (5.995 g, 88.00 mmol) and PPh_3 (21.980 g, 83.30 mmol) in a mixture of Et_2O (100 ml) and MeCN (65 ml). Stirring was continued for 2 h at 0 °C and the reaction mixture was washed with 20% $Na_2S_2O_3$ solution (5 × 20 ml), dried ($MgSO_4$) and concentrated. The residue was purified by bulb-to-bulb distillation (80 °C, 0.1 Torr) to yield **2** (8.236 g, 73%), as a pale yellow oil. – IR (film): ν = 2977 cm^{-1}, 1425, 1224, 1173, 964, 901, 862, 736. – ^{1}H NMR: δ = 0.92 (m, 1 H, cpr), 1.18 (m, 4 H, cpr), 1.39 (m, 1 H, cpr), 1.61 (m, 1 H, cpr), 1.85 (dq, ^2J = 13.0, ^3J = 6.9 Hz, 1 H, CH_2), 2.01 (dq, ^2J = 13.0, ^3J = 6.9 Hz, 1 H, CH_2), 3.24 ppm (t, ^3J = 6.9 Hz, 2 H, CH_2I). – ^{13}C NMR: δ = 2.90, 3.00, 5.26, 9.67 (each CH_2), 16.87 (CH), 37.45 (CH_2), 110.70, 113.70 ppm (each C). – MS (70 eV, EI), *m/z* (%): 234 (0.1) [M^+], 141 (6), 127 (14), 91 (92), 79 (100), 77 (52). HRMS calcd for $C_8H_{11}I$ 233.9906. Found 233.9905.

(2-Furyl)dimethylsilyl chloride (**5**): A suspension of 2-furyllithium (see GP 3) (50 mmol, in hexane/ether = 3 : 1) was added as fast as possible to Me_2SiCl_2 (19.359 g, 150 mmol) in Et_2O (40 ml) at 0 °C. The white suspension was stirred for 1.5 h at 0 °C and filtered under argon to give a colourless solution, which was concentrated *in vacuo* (25 °C, 40 Torr). The residue was fractionated to yield **5** (5.060 g, 63%), as a colourless liquid, bp 35 °C (1 Torr). – IR (film): ν = 2965 cm^{-1}, 1551, 1453, 1257, 1206, 1119, 1009, 902, 796, 750, 680. – ^{1}H NMR: δ = 0.70 (s, 6 H, CH_3), 6.45 (m, 1 H, Fu), 6.86 (m, 1 H, Fu), 7.71 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = 1.56 (2 CH_3), 109.73, 121.80, 147.68 (each CH), 155.40 ppm (C). – MS (70 eV, EI), *m/z* (%): 162/160 (4/13) [M^+], 147/145 (17/49) [$M^+ - Me$].

2-(Chlorodimethylsilyl)methylenecyclopropane (**12**): The solution of lithiomethylenecyclopropane, prepared from **13** (8.114 g, 0.150 mol) and *n*-butyllithium (44.5 ml, 2.25 M, 0.100 mol, in *n*-hexane) in THF (100 ml) according to GP 1, was quickly added to a cooled solution of Me_2SiCl_2 (38.718 g, 0.300 mol) in Et_2O (100 ml) at –10 °C. Stirring was continued at 0 °C for 30 min, then at 25 °C for 10 min. The salts were filtered off under argon and the solvent was removed by bulb-to-bulb distillation (25 °C, from 150 Torr down to 40 Torr). The

residue was fractionated at 25 Torr to yield **12** (5.339 g, 36%), bp 41-45 °C, as a colourless liquid. – IR (film): ν = 2964 cm^{-1}, 1737, 1410, 1255, 1211, 1079, 882, 840, 811, 790, 676, 586. – ^1H NMR: δ = 0.37 (s, 3 H, CH_3Si), 0.41 (s, 3 H, CH_3Si), 0.90 (m, 1 H, cpr), 1.13 (m, 1 H, cpr), 1.40 (m, 1 H, cpr), 5.32 (m, 1 H, $C=CH_2$), 5.39 ppm (m, 1 H, $C=CH_2$). – ^{13}C NMR: δ = 0.09, 0.68 (each CH_3), 5.77 (CH), 6.34, 101.77 (each CH_2), 131.46 ppm (C).

Preparation of Trienes

Coupling of Iodides 2, 14 with 2-Lithiofurans. General Procedure (GP) 3: 2-Furyllithium: To a solution of *n*-butyllithium (13.78 ml, 2.25 M, 39.01 mmol, in *n*-hexane) in THF (70 ml), furan (2.735 g, 40.16 mmol) was given at –78 °C. The solution was allowed to warm up to 25 °C and was stirred for 2 h.
To a solution of HMPA (7.0 ml, 40 mmol) [*caution*] in THF (100 ml), the iodide (38.25 mmol) was added at –78 °C. The solution of furyllithium (39.01 mmol) prepared as described above was dropped to this solution by means of a syringe pump at a rate of 100 ml/h while maintaining the temperature at –78 °C. The reaction mixture was allowed to thaw slowly for over 12 h without removing the cooling bath and then to warm up to 25 °C. Stirring was continued for 30 min at 25 °C, the solution was quenched with sat. NH_4Cl solution (100 ml) and extracted with Et_2O (3 × 40 ml). The combined organic layers were washed with sat. NH_4Cl solution (100 ml), water (100 ml), brine (3 × 50 ml) and dried over molecular sieves (4 Å). The solvent was removed by bulb-to-bulb distillation (20 Torr, 25 °C). The residue was then purified as described detailed below.

2-[(2'-Furyl)ethyl]bicyclopropylidene (**1a**): The residue obtained from **2** (8.950 g, 38.25 mmol) according to GP 3 was purified by bulb-to-bulb distillation (10^{-2} Torr, 30 °C) to yield **1a** (6.327 g, 95%), as a colourless liquid with an intensely offensive smell. – IR (film): ν = 2978 cm^{-1}, 2923, 1597, 1507, 1262, 1146, 1006, 914, 797, 728. – ^1H NMR: δ = 0.90 (m, 1 H, cpr), 1.20 (m, 4 H, 5-H, cpr), 1.39 (m, 1 H, cpr), 1.59 (m, 1 H, cpr), 1.65-1.88 (m, 2 H, CH_2), 2.80 (t, ^3J = 7.3 Hz, 2 H, CH_2), 6.02 (m, 1 H, Fu) 6.29 (m, 1 H, Fu), 7.31 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = 2.76, 2.93, 9.71 (each CH_2), 15.11 (CH), 25.57, 27.98 (each CH_2), 104.70, 110.02 (each CH), 110.02, 115.50 (each C), 140.67 (CH), 156.04 ppm (C). – MS (70 eV, EI), *m/z* (%): 174 (1) [M^+], 173 (3) [M^+ – H], 145 (16) [$M^+ - C_2H_5$], 91 (16), 81 (100) [$FuCH_2^+$]. HRMS calcd for $C_{12}H_{14}O$ 174.1045. Found 174.1044.

2-[2'-(2''-Furyl)ethyl]methylenecyclopropane (**15**): The residue obtained from **14** (7.960 g, 38.25 mmol) according to GP 3 was distilled to yield **15** (5.215 g, 92%), with bp 75–77 °C (18 Torr), a colourless liquid with an offensive smell. – IR (film): ν = 2990 cm^{-1}, 1597, 1508, 1147, 1006, 923, 892, 798, 725. – ^1H NMR: δ = 0.81 (m, 1 H, cpr), 1.27 (m, 1 H, cpr), 1.49 (m, 1 H, cpr), 1.72 (m, 1 H), 1.78 (m, 1 H), 2.80 (t, ^3J = 7.0 Hz, 2 H, Fu–CH_2), 5.43 (m, 2 H, $C=CH_2$), 6.05 (m, 1 H, Fu), 6.30 (m, 1 H, Fu), 7.33 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = 9.26 (CH_2), 15.17 (CH), 27.81, 31.63, 102.72 (each CH_2), 104.82, 110.00 (each CH), 136.28 (C), 140.67 (CH), 155.80 ppm (C). – MS (70 eV, EI), *m/z* (%): 148 (6) [M^+], 133 (10), 111 (10), 91 (10), 81 (100) [$FuCH_2^+$]. HRMS calcd for $C_{10}H_{12}O$ 148.0888. Found 148.0888.

2-[(5'-Methoxy-2'-furyl)ethyl]bicyclopropylidene (**1b**): To a solution of 5-methoxy-2-lithiofuran, prepared according to GP 3 from 2-methoxyfuran (2.694 g, 27.50 mmol) and *n*-butyllithium (17.83 ml, 1.54 M, 27.50 mmol, in *n*-hexane) in THF (90 ml), but with stirring over 15 min at 10 °C, a solution of **2** (7.081 g, 30.25 mmol) and HMPA (5.50 ml, 31.6 mmol) [*caution*] in THF (30 ml) was added slowly at –78 °C. The dark reaction mixture was allowed to thaw slowly for over 16 h without removing the cooling bath and then to warm up to 25 °C, quenched with sat. NH_4Cl solution (100 ml) and extracted with Et_2O (3 × 40 ml). The combined

organic layers were washed with sat. NH_4Cl solution (100 ml), water (100 ml), brine (3 × 50 ml) and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by rapid column chromatography on deactivated neutral alumina (5% water content) (pentane) to yield **1b** (2.247 g, 40%), as a yellow oil, $R_f = 0.17$. – IR (film): ν = 2977 cm^{-1}, 2852, 1618, 1592, 1438, 1375, 1261, 1063, 1011, 963, 737. – ^1H NMR: δ = 0.88 (m, 1 H, cpr), 1.15 (m, 4 H, cpr), 1.36 (m, 1 H, cpr), 1.60 (m, 1 H, cpr), 1.65 (m, 1 H, CH_2), 1.76 (m, 1 H, CH_2), 2.67 (t, ^3J = 7.1 Hz, 2 H, Fu–CH_2), 3.82 (s, 3 H, MeO), 5.01 (d, ^3J = 4.2 Hz, 1 H, Fu), 5.85 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = 2.73, 2.90, 9.70 (each CH_2), 15.49 (CH), 27.86, 31.74 (each CH_2), 57.57 (CH_3), 79.35, 105.45 (each CH), 109.91, 115.58, 145.89, 160.34 ppm (each C). – MS (70 eV, EI), *m/z* (%): 204 (1) [M^+], 203 (1) [$M^+ - H$], 189 (6) [$M^+ - Me$], 145 (15), 111 (100) [5-MeOFuCH_2^+], 91 (14).

Coupling of Benzenesulfonates with Sodium 2-Furylmethoxide. General Procedure (GP) 4: Furfuryl alcohol (6.204 g, 63.25 mmol) was slowly added to a suspension of sodium hydride (1.518 g, 63.25 mmol) in THF (100 ml) at –10 °C and stirred for additional 1 h at 25 °C, then cooled to –30 °C. A solution of the benzenesulfonate (50.50 mmol) in THF (20 ml) was added in one portion, the cooling bath was removed and the reaction mixture was stirred for 16 h at 25 °C. The solution was poured into ice-cold water (100 ml) and extracted with Et_2O (3 × 50 ml). The combined organic phases were washed with brine (3 × 50 ml), dried ($MgSO_4$) and concentrated *in vacuo*.

[(2-Furfuryl)oxymethyl]bicyclopropylidene (**9**): The residual oil obtained from [(benzenesulfonyl)oxymethyl]bicyclopropylidene (12.640 g, 50.50 mmol) according to GP 4 was purified by column chromatography on silica gel with pentane/Et_2O (15 : 1) to give **9** (2.785 g, 29%), $R_f = 0.40$, as a colourless oil. – IR (film): ν = 2979 cm^{-1}, 2847, 1517, 1148, 1080, 1014, 897, 724. – ^1H NMR: δ = 1.04 (m, 1 H, cpr), 1.19 (m, 4 H, cpr), 1.45 (m, 1 H, cpr), 1.89 (m, 1 H, cpr), 3.39 (dd, ^3J = 7.6, ^2J = 10.4 Hz, 1 H, OCH_2), 3.60 (dd, ^3J = 6.2, ^2J = 10.4 Hz, 1 H, OCH_2), 4.49 (d, AB, ^2J = 12.5 Hz, 1 H, FuCH_2O), 4.58 (d, AB, ^2J = 12.5 Hz, 1 H, FuCH_2O), 6.31 (m, 2 H, Fu), 7.40 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = 2.78, 3.00, 8.71 (each CH_2), 15.61 (CH), 64.06, 72.73 (each CH_2), 108.87, 110.13 (each CH), 111.62, 112.50 (each C), 142.55 (CH), 152.04 ppm (C). – MS (70 eV, EI), *m/z* (%): 81 (100) [FuCH_2^+], 53 (17) [$C_4H_5^+$]. DCI calcd for $C_{12}H_{14}O_2$ 190.2. Found 190.2.

2-[(2'-Furfuryl)oxymethyl]methylenecyclopropane (**20**): The residual oil, obtained from 2-[2'-(benzenesulfonyl)oxymethyl]methylenecyclopropane (11.322 g, 50.50 mmol) according to GP 4 was purified by distillation to yield **20** (2.239 g, 27%), with bp 88–91 °C (8 Torr) as a colourless oil. – IR (film): ν = 2857 cm–^{1}, 1503, 1357, 1224, 1151, 1081, 1016, 885, 813, 738. – ^1H NMR: δ = 0.96 (m, 1 H, cpr), 1.34 (m, 1 H, cpr), 1.78 (m, 1 H, cpr), 3.28 (dd, ^3J = 7.6, ^2J = 10.2 Hz, 1 H, CH_2O), 3.52 (dd, ^3J = 5.9, ^2J = 10.2 Hz, 1 H, CH_2O), 4.48 (m, 2 H, FuCH_2), 5.42 (m, 1 H, C=CH), 5.45 (m, 1 H, C=CH), 6.32 (m, 2 H, Fu), 7.39 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = 8.52 (CH_2), 15.30 (CH), 64.20, 72.50, 104.10 (each CH_2), 108.97, 110.12 (each CH), 132.92 (C), 142.57 (CH), 151.86 ppm (C). – MS (70 eV, EI), *m/z* (%): 97 (2) [M^+ – Fu], 81 (100) [FuCH_2^+], 67 (2) [Fu$^+$]. DCI calcd for $C_{10}H_{12}O_2$ 164.2. Gef. 164.2

Reaction of Chlorosilanes with Alcohols. General Procedure (GP) 5: To a solution of the alcohol **4**, **19** or furfuryl alcohol (6.20 mmol) and Et_3N (658 mg, 6.50 mmol) in Et_2O (20 ml), chlorosilane **5**, or **12** (6.20 mmol) in Et_2O (5 ml) was added by means of a syringe pump over 30 min at 0 °C. The white turbid reaction mixture was stirred for 1 h at 0 °C and 30 min at 25 °C, before being filtered through Celite to give a colourless solution. Evaporation of the solvent at 25 °C *in vacuo* gave the pure product.

2'-(Dimethylsilyl)furyl 1-(Bicyclopropylidenyl)methyl Ether (6) (1.422 g, 98%) was obtained from **4** (683 mg, 6.20 mmol) and **5** (996 mg, 6.20 mmol) according to GP 5, as a colourless oil with a pleasant spicy odour. – IR (film): ν = 2981 cm^{-1}, 2864, 1550, 1454, 1255, 1072, 1006, 853, 823, 791, 748, 664. – ^1H NMR: δ = 0.40 (s, 6 H, Me_2Si), 1.00 (m, 1 H, cpr), 1.15 (m, 4 H, cpr), 1.39 (m, 1 H, cpr), 1.84 (m, 1 H, cpr), 3.36 (dd, ^3J = 7.8, ^2J = 11.0 Hz, 1 H, CH_2O), 3.88 (dd, ^3J = 5.5, ^2J = 11.0 Hz, 1 H, CH_2O), 6.39 (m, 1 H, Fu), 6.75 (m, 1 H, Fu), 7.67 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = – 2.02, – 1.94 (each CH_3), 2.80, 3.10, 9.06 (each CH_2), 18.20 (CH), 66.28 (CH_2), 109.26 (CH), 111.37, 112.58 (each C), 120.84, 146.77 (each CH), 157.97 ppm (C). – MS (70 eV, EI), *m/z* (%): 234 (2) [M^+], 219 (10) [M^+ – Me], 205 (10) [M^+ – Me – CH_2], 125 (100) [$FuSiMe_2^+$], 75 (71) [Me_2SiOH^+]. HRMS calcd for $C_{13}H_{18}SiO_2$ 234.1076. Found 234.1076.

2'-Furfuryl (Methylenecycloprop-2-yl)dimethylsilyl Ether (11) (1.239 g, 96%) was obtained from furfuryl alcohol (608 mg, 6.20 mmol) and **12** (909 mg, 6.20 mmol) according to GP 5, as a colourless unstable oil. – IR (film): ν = 2960 cm^{-1}, 2874, 1734, 1504, 1372, 1258, 1209, 1151, 1071, 918, 829, 788, 736. – ^1H NMR: δ = 0.08 (s, 3 H, CH_3Si), 0.10 (s, 3 H, CH_3Si), 0.73 (m, 1 H, cpr), 1.01 (m, 1 H, cpr), 1.30 (m, 1 H, cpr), 4.69 (s, 2 H, $FuCH_2$), 5.24 (m, 1 H, C=CH_2), 5.34 (m, 1 H, C=CH_2), 6.28 (m, 1 H, Fu), 6.32 (m, 1 H, Fu), 7.39 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = – 4.02, – 3.26 (each CH_3), 4.21 (CH), 5.48, 57.62, 100.69 (each CH_2), 107.59, 110.14 (each CH), 131.46 (C), 142.15 (CH), 153.72 ppm (C). – MS (70 eV, EI), *m/z* (%): 208 (2) [M^+], 193 (6) [M^+ – Me], 178 (5) [M^+ – 2 Me], 155 (34) [M^+ – C_4H_5], 111 (6) [$C_6H_{11}Si^+$], 81 (100) [$FuCH_2^+$], 75 (20) [Me_2SiOH^+]. HRMS calcd for $C_{11}H_{16}SiO_2$ 208.0919. Found 208.0919.

2'-(Dimethylsilyl)furyl (Methylenecycloprop-2-yl)methyl Ether (18) (1.277 g, 99%) was obtained from **19** (522 mg, 6.20 mmol) and **5** (996 mg, 6.20 mmol) according to GP 5, as a colourless oil with a pleasant spicy odour. – IR (film): ν = 2962 cm^{-1}, 1550, 1454, 1255, 1078, 1007, 901, 823, 792, 748, 662. – ^1H NMR: δ = 0.40 (s, 6 H, Me_2Si), 0.88 (m, 1 H, cpr), 1.28 (m, 1 H, cpr), 1.72 (m, 1 H, cpr), 3.36 (dd, ^3J = 7.6, ^2J = 10.2 Hz, 1 H, CH_2O), 3.74 (dd, ^3J = 5.9, ^2J = 10.2 Hz, 1 H, CH_2O), 5.37 (m, 1 H, C=CH), 5.40 (m, 1 H, C=CH), 6.40 (m, 1 H, Fu), 6.76 (m, 1 H, Fu), 7.68 ppm (m, 1 H, Fu). – ^{13}C NMR: δ = – 2.03 (2 CH_3), 8.57 (CH_2), 17.78 (CH), 66.05, 103.85 (each CH_2), 109.26, 120.90 (each CH), 133.19 (C), 146.80 (CH), 157.82 ppm (C). – MS (70 eV, EI), *m/z* (%): 208 (1) [M^+], 193 (6) [M^+ – Me], 178 (8) [M^+ – 2 Me], 125 (100) [$FuSiMe_2^+$], 75 (22) [Me_2SiOH^+]. HRMS calcd for $C_{11}H_{16}SiO_2$ 208.0919. Found 208.0919.

Intramolecular Diels-Alder Reactions under High Pressure

***endo*-Spiro[cyclopropane-(1,7')-11'-oxatetracyclo[6.2.1.0^{1,6}0^{4,6}]undec-9'-ene] (7a)**: A solution of **1a** (320 mg, 1.84 mmol) in pentane (8.5 ml) was pressurized to 10 kbar and heated at 90 °C for 43 h. The solvent was evaporated *in vacuo* and the residual oil chromatographed on silica gel with pentane/Et_2O (8 : 1) to yield **7a** (103 mg, 32%), R_f = 0.22, as a colourless oil. – IR (film): ν = 2976 cm^{-1}, 2920, 2863, 1304, 1185, 1067, 1019, 886, 818. – ^1H NMR: δ = 0.11–0.31 (m, 4 H, cpr), 0.47 (m, 1 H, cpr), 0.72 (m, 1 H, cpr), 1.00 (m, 1 H, cpr), 1.75 (m, 1 H), 1.91 (m, 1 H), 2.12 (m, 1 H), 2.21 (m, 1 H), 4.40 (d, ^3J = 1.7 Hz, 1 H, 8'-H), 6.49 (d, ^3J = 5.7 Hz, 1 H, 10'-H), 6.58 ppm (dd, ^3J = 1.7, ^3J = 5.7 Hz, 1 H, 9'-H). – ^{13}C NMR: δ = 5.41, 7.52, 7.63 (each CH_2), 19.10 (CH), 25.55 (CH_2), 28.05 (C), 28.17 (CH_2), 44.07 (C), 85.67 (CH), 98.95 (C), 136.21, 137.02 ppm (each CH). – MS (70 eV, EI), *m/z* (%): 174 (15) [M^+], 159 (30) [M^+ – CH_3], 146 (26) [M^+ – C_2H_4], 145 (47), 131 (48) 117 (90), 105 (34), 91 (100) [$C_7H_7^+$], 81 (50) [$C_5H_5O^+$]. HRMS calcd for $C_{12}H_{14}O$ 174.1044. Found 174.1044.

***endo*-8'-Methoxy[spirocyclopropane-(1,7')-11'-oxatetracyclo[6.2.1.0^{1,6}0^{4,6}]undec-9'-ene] (7b)**: A solution of **1b** (370 mg, 1.81 mmol) in THF (11 ml) was pressurized to 10 kbar and heated at 85 °C for 20 h. The solvent was evaporated *in vacuo* to give the crude product **7b** as a pale yellow oil (370 mg, >95%), which did not contain any more starting material according to its ^{1}H NMR spectrum and was not further purified. – IR (film): ν = 2939 cm^{-1}, 1608, 1446, 1318, 1214, 1141, 1064, 1016, 914, 887, 787, 734. – ^{1}H NMR: δ = 0.06 (m, 2 H, cpr), 0.17 (dd, ^2J = 6.0, $^3J_{cis}$ = 8.0 Hz, 1 H, 5'-H), 0.27 (dd, ^2J = 6.0, $^3J_{trans}$ = 4.2 Hz, 1 H, 5'-H), 0.48 (m, 1 H, cpr), 0.93 (m, 1 H, cpr), 1.04 (m, 1 H, 4'-H), 1.68 (m, 1 H), 1.85 (m, 1 H), 2.08 (m, 1 H), 2.19 (m, 1 H), 3.50 (s, 3 H, MeO), 6.43 ppm (m, 2 H). – ^{13}C NMR: δ = 3.71, 5.37, 7.75 (each CH_2), 19.61 (CH), 25.69, 27.95 (each CH_2), 29.35, 46.33 (each C), 54.00 (CH_3), 92.17, 113.17 (each C), 135.65, 138.90 ppm (each CH). – MS (70 eV, EI), *m/z* (%): 204 (8) [M$^+$], 189 (34) [M$^+$ – Me], 176 (23) [M$^+$ – C_2H_4], 161 (42) [M$^+$ – C_2H_4 – Me], 145 (54) [M$^+$ – C_2H_4 – MeO], 129 (61), 117 (86), 91 (100) [$C_7H_7^+$], 77 (74) [$C_6H_5^+$]. HRMS calcd for $C_{13}H_{16}O_2$ 204.1150. Found 204.1150.

***endo*-Spiro[cyclopropane-(1,8')-3',12'-dioxatetracyclo[7.2.1.0^{1,7}0^{5,7}]dodec-10'-ene] (8)**: A solution of **9** (216 mg, 1.14 mmol) in THF/MeCN (1 : 1) (5 ml) was pressurized to 10 kbar and heated at 70 °C for 48 h. The solvent was evaporated *in vacuo* and the residual oil chromatographed on silica gel with pentane/Et_2O (1 : 1) to yield **8** (100 mg, 46%), R_f = 0.40; along with recovered **9** (60 mg, 28%), R_f = 0.71. – IR (KBr): ν = 3073 cm^{-1}, 2837, 1563, 1302, 1119, 1030, 914, 726, 641, 520. – ^{1}H NMR: δ = 0.04 (m, 1 H, cpr), 0.15 (dd, $^3J_{cis}$ = 8.4, ^2J = 5.8 Hz, 1 H, 6'-H), 0.30 (m, 1 H, cpr), 0.43 (m, 1 H, cpr), 0.57 (dd, $^3J_{trans}$ = 5.8, ^2J = 5.8 Hz, 1 H, 6'-H), 0.66 (m, 1 H, cpr), 0.92 (ddd, $^3J_{trans}$ = 5.8, $^3J_{cis}$ = 8.4, ^3J = 2.4 Hz, 1 H, 5'-H), 3.63 (dd, $^3J_{trans}$ = 2.4, ^2J = 11.5 Hz, 1 H, 4'-H_{exo}), 3.88 (d, AB, ^2J = 12.9 Hz, 1 H, 2'-H), 3.96 (d, AB, ^2J = 12.9 Hz, 1 H, 2'-H), 3.99 (d, ^2J = 11.5 Hz, 1 H, 4'-H), 4.33 (d, ^3J = 1.7 Hz, 1 H, 9'-H), 6.40 (d, ^3J = 5.9 Hz, 1 H, 11'-H), 6.56 ppm (dd, ^3J = 1.7, ^3J = 5.9 Hz, 1 H, 10'-H). – ^{13}C NMR: δ = 4.19, 7.79, 9.55 (each CH_2), 13.65 (CH), 28.72, 29.32 (each C), 66.59, 67.47 (each CH_2), 84.09 (C), 85.23 (CH), 136.82 ppm (2 CH). – MS (70 eV, EI), *m/z* (%):190 (1) [M$^+$], 160 (5) [M$^+$ – CH_2O], 133 (35), 119 (59), 117 (58), 91 (100), 81 (100) [$C_5H_5O^+$]. HRMS calcd for $C_{12}H_{14}O_2$ 190.0994. Found 190.0993

***endo*-Spiro[cyclopropane-(1,8')-3',12'-dioxa-2',2'-dimethyl-2'-silatetracyclo[7.2.1.0^{1,7}0^{5,7}]dodec-10'-ene] (10)**: A solution of **6** (160 mg, 0.68 mmol) in Et_2O (4 ml) was pressurized to 10 kbar and heated at 130 °C for 20 h. The solvent was evaporated *in vacuo* and the residual solid chromatographed on silica gel with pentane/Et_2O (5 : 1) to yield **10** (133 mg, 83%), R_f = 0.33, an ivory-white crystalline solid. – IR (KBr): ν = 3047 cm^{-1}, 2979, 2877, 1252, 1017, 852, 822, 790, 713, 653. – ^{1}H NMR: δ = – 0.03 (m, 1 H, cpr), 0.02 (m, 1 H, cpr), 0.22 (m, 1 H, cpr), 0.27 (s, 3 H, CH_3Si), 0.31 (s, 3 H, CH_3Si), 0.35 (m, 1 H, cpr), 0.58 (m, 2 H, cpr), 0.63 (m, 1 H, cpr), 4.01 (d, AB, ^2J = 11.6 Hz, 1 H, 4' -H), 4.12 (d, AB, ^2J = 11.6 Hz, 1 H, 4'-H), 4.33 (s, 1 H, 9'-H), 6.40 (d, ^3J = 5.5 Hz, 1 H), 6.50 ppm (d, ^3J = 5.5 Hz, 1 H). – ^{13}C NMR: δ = – 4.82, – 2.00 (each CH_3), 3.57, 5.23, 8.25 (each CH_2), 16.16 (CH), 28.73, 32.11 (each C), 59.41 (CH_2), 78.74 (C), 86.68, 135.30, 137.94 ppm (each CH). – MS (70 eV, EI), *m/z* (%): 234 (1) [M$^+$], 219 (5) [M$^+$ – Me], 205 (10) [M$^+$ – Me –CH_2], 191 (10) [M$^+$ – Me –C_2H_4], 177 (13) [M$^+$ – Me –C_3H_6], 163 (17) [M$^+$ – Me – C_4H_8], 117 (46), 115 (57), 91 (100) [$C_7H_7^+$], 75 (89) [Me_2SiOH^+], 59 (44) [Me_2SiH^+]. HRMS calcd for $C_{13}H_{18}SiO_2$ 234.1076. Found 234.1076.

***endo*-11-Oxatetracyclo[6.2.1.0^{1,6}.0^{4,6}]undec-9-ene (16)**: A solution of **15** (310 mg, 2.09 mmol) in pentane (8 ml) was pressurized to 10 kbar and heated at 100 °C for 17 h. The solvent was evaporated *in vacuo* and the residual oil chromatographed on silica gel with pentane/Et_2O (8 : 1) to yield **16** (255 mg, 82%), R_f = 0.27, as a colourless oil. – IR (film): ν = 2936 cm^{-1}, 2863, 1342, 1313, 1068, 972, 909, 848, 779, 699. – ^{1}H NMR: δ = 0.32 (dd, $^3J_{trans}$ = 4.1, ^2J = 5.4 Hz, 1 H, 5-H), 0.65 (dd, $^3J_{cis}$ = 7.8, ^2J = 5.4 Hz, 1 H, 5-H), 1.20 (ddd, $^3J_{trans}$ = 4.1, $^3J_{cis}$ = 7.8, ^3J = 6.5 Hz, 1 H, 4-H), 1.45 (d, ^2J = 11.2 Hz, 1 H, 7-H_{endo}), 1.65 (ddd, ^3J = 8.0, ^3J = 9.0, ^2J =

13.0 Hz, 1 H, 3-H_{endo}), 1.83–2.23 (m, 2 H, 2-H), 2.14 (dd, ^3J = 4.8, ^2J = 11.2 Hz, 7-H_{exo}), 5.02 (dd, ^3J = 4.8, ^3J = 1.5 Hz, 1 H, 8-H), 6.26 (d, ^3J = 5.7 Hz, 1 H, 10-H), 6.44 ppm (dd, ^3J = 5.7, ^3J = 1.5 Hz, 1 H, 9-H). – ^{13}C NMR: δ = 9.90 (CH_2), 19.81 (CH), 24.34, 28.23, 33.43 (each CH_2), 37.09 (C), 79.78 (CH), 97.23 (C), 135.52, 136.67 ppm (each CH). – MS (70 eV, EI), *m/z* (%): 148 (12) [M^+], 120 (28), 119 (27), 93 (42), 92 (30), 91 (74) [$M^+ - C_4H_9$], 81 (100) [$FuCH_2^+$], 79 (30), 77 (25). HRMS calcd for $C_{10}H_{12}O$ 148.0888. Found 148.0888.

***endo* -3,12-Dioxa-2,2-dimethyl-2-silatetracyclo[7.2.1.0^{1,7}0^{5,7}]dodec-10-ene (17)**: A solution of **18** (260 mg, 1.25 mmol) in Et_2O (7 ml) was pressurized to 10 kbar and heated at 125 °C for 30 h. The solvent was evaporated *in vacuo* and the residual oil chromatographed on silica gel with pentane/Et_2O (3 : 1) to yield **17** (65 mg, 25%), R_f = 0.43, as a white, crystalline solid; along with recovered **18** (104 mg, 40%), R_f = 0.74. – IR (KBr): ν = 2959 cm^{-1}, 2859, 1252, 1126, 1005, 850, 792, 735, 644. – ^{1}H NMR: δ = 0.25 (s, 3 H, CH_3Si), 0.31 (s, 3 H, CH_3Si), 0.55 (dd, ^2J = 5.3, $^3J_{cis}$ = 8.4 Hz, 1 H, 6-H), 0.69 (dd, ^2J = 5.3, $^3J_{trans}$ = 6.1 Hz, 1 H, 6-H), 1.07 (m, 1 H, 5-H), 1.29 (d, ^2J = 10.2 Hz, 1 H, 8-H_{endo}), 1.94 (dd, ^2J = 10.2, ^3J = 4.5 Hz, 1 H, 8-H_{exo}), 4.07 (d, AB, ^2J = 11.3 Hz, 1 H, 4-H), 4.18 (d, AB, ^2J = 11.3 Hz, 1 H, 4-H), 4.99 (dd, ^3J = 1.3, ^3J = 6.4 Hz, 1 H, 9-H), 6.39 ppm (m, 2 H). – ^{13}C NMR: δ = – 4.74, – 1.94 (each CH_3), 7.88 (CH_2), 19.67 (CH), 27.12 (C), 37.03, 59.49 (each CH_2), 76.30 (C), 79.93, 135.36, 137.01 ppm (each CH). – MS (70 eV, EI), *m/z* (%): 208 (2) [M^+], 193 (12) [M^+ – Me], 178 (27) [M^+ – 2 Me], 125 (84) [$FuSiMe_2^+$], 115 (42), 91 (31) [$C_7H_7^+$], 75 (100) [Me_2SiOH^+], 59 (20) [Me_2SiH^+]. HRMS calcd for $C_{11}H_{16}SiO_2$ 208.0919. Found 208.0919.

***endo*-3,12-Dioxatetracyclo[7.2.1.0^{1,7}.0^{5,7}]dodec-10-ene (21)**: A solution of **20** (210 mg, 1.28 mmol) in THF/MeCN (1 : 1) (5 ml) was pressurized to 10 kbar and heated at 85 °C for 45 h. The solvent was evaporated *in vacuo* and the residual oil chromatographed on silica gel with pentane/Et_2O (5 : 1) to yield **21** (99 mg, 47%), R_f = 0.17, as a colourless oil; along with recovered **20** (42 mg, 20%), R_f = 0.55. – IR (film): ν = 2958 cm^{-1}, 2853, 1460, 1308, 1247, 1115, 1013, 919, 842, 713, 633. – ^{1}H NMR: δ = 0.61 (m, 1 H, 6-H), 0.64 (m, 1 H, 6-H), 1.31 (m, 1 H, 5-H), 1.41 (d, ^2J = 11.1 Hz, 1 H, 8-H_{endo}), 2.08 (dd, ^3J = 4.4, ^2J = 11.1 Hz, 1 H, 8-H_{exo}), 3.62 (dd, ^3J = 2.3, ^2J = 12.1 Hz, 1 H, 4-H_{endo}), 3.82 (d, AB, ^2J = 12.9 Hz, 1 H, 2-H), 3.90 (d, AB, ^2J = 12.9 Hz, 1 H, 2-H), 3.97 (dd, ^3J = 2.3, ^2J = 12.1 Hz, 1 H, 4-H_{exo}), 4.94 (dd, ^3J = 4.7, ^3J = 1.6 Hz, 1 H, 9-H), 6.26 (d, ^3J = 5.7 Hz, 1 H, 11-H), 6.42 ppm (dd, ^3J = 5.7, ^3J = 1.6 Hz, 1 H, 10-H). – ^{13}C NMR: δ = 12.46 (CH_2), 16.19 (CH), 23.16 (C), 37.03, 66.74, 67.20 (each CH_2), 78.60 (CH), 82.28 (C), 136.08, 136.63 ppm (each CH). – MS (70 eV, EI), *m/z* (%): 164 (2) [M^+], 108 (30), 106 (72), 91 (90), 81 (100) [$FuCH_2^+$], 78 (42). HRMS calcd for $C_{10}H_{12}O_2$ 164.0837. Found 164.0837.

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