DIELS-ALDER REACTION OF 5-TRIISOPROPYLSILYL-2-VINYLFURAN AND 2-TRIETHYLSILYL-4-VINYLFURAN. STERIC SHIELDING BY THE TRIALKYLSILYL GROUP[1]

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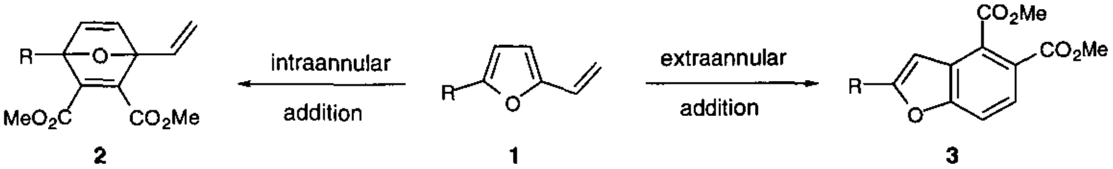
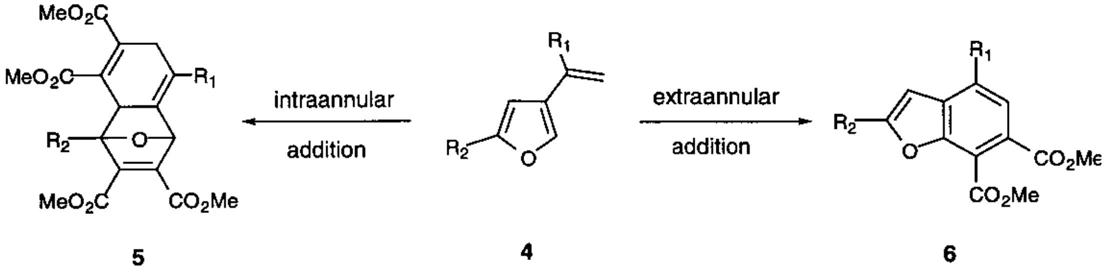
Abstract - The Diels-Alder reaction of 5-triisopropylsilyl-2-vinylfuran (**1b**) and 2-triethylsilyl-4-vinylfuran (**4b**) with acetylenic and olefinic dienophiles occurs with high site specificity in the extraannular mode to produce trialkylsilyl benzofuran derivatives.

It is well known that furans readily function as dienes in [4π + 2π] cycloaddition reactions.[2] 2- and 3-Vinylfurans also participate in such reactions, but two cycloaddition modes are possible, and both types of products have been observed for acetylenic[3-6] and olefinic[5] dienophiles. For example, Davidson and Elix[7] have reported that 2-vinylfuran (**1a**) reacted with dimethyl acetylenedicarboxylate (DMAD) at room temperature (4 days) to give a 1:1 mixture (10% yield) of the intraannular and extraannular cycloaddition products (**2a**) and (**3a**), respectively. We[6] have reported that 3-(1-*tert*-butyldimethylsilyloxyvin-1-yl)furan (**4a**) reacted with DMAD at room temperature (3 days) to give the tricyclic compound (**5a**) (16% yield)



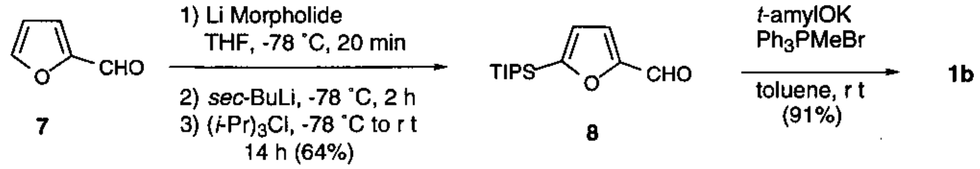
a) R = H, **b**) R = TIPS, **c**) R = *n*-Bu_4Sn

and the benzofuran (**6a**) (39% yield). Compound (**5a**) was formed by the intraannular addition of the dienophile to the furan ring diene system followed by a second addition to the newly formed diene system. In connection with our interest in the synthesis of benzofuran derivatives,[6] we wished to devise methodology which would result in preferential or exclusive extraannular cycloadditions for vinylfurans.

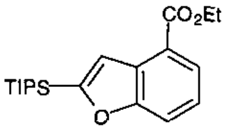


a) R_1 = TBDMSO, R_2 = H b) R_1 = H, R_2 = Et_3Si

In this regard, 2-trimethylsilylfuran undergoes a Diels-Alder reaction with DMAD considerably more slowly (benzene, 80 °C)[8] than does furan (room temperature).[9] On the assumption that this rate difference is mainly a steric phenomenon, we reasoned that [$4\pi + 2\pi$] cycloaddition reactions with 5-triisopropylsilyl-2-vinylfuran (**1b**) would occur exclusively *via* the extraannular mode because of the profound steric screening effect of the triisopropylsilyl (TIPS) moiety.[10] Compound (**1b**), which exhibited considerably greater stability than **1a**, was prepared by a Wittig reaction[11] from the aldehyde (**8**). This aldehyde was in turn synthesized from 2-furaldehyde (**7**) using conditions slightly modified from those reported for the synthesis of 5-trimethylsilyl-2-furaldehyde.[12a]



We were pleased to find that **1b** does indeed react with complete site specificity with DMAD to give **3b** as the only cycloaddition product in 41% yield (oxidant unknown) although at a slower rate (9 days, 50 °C, toluene) than reported[7] for **1a**. The vinylfuran (**1b**) reacted even more slowly (5 days, toluene, reflux) with the less reactive dienophile ethyl propiolate. Nevertheless, the benzofuran derivative (**9**) was the sole cycloaddition product observed, albeit in only 9% yield (40% recovered **1b**). In contrast to the acetylenic dienophile, (**1b**) reacted with *N*-phenylmaleimide at room temperature (9 days, toluene) to give a mixture of the cycloaddition products (**10**) (25%) and (**11**) (35%). The primary product (**10**) precipitated from the reaction mixture and was rapidly isomerized to the more stable furan derivative (**11**) on standing in $CHCl_3$ at room temperature. Dehydrogenation (10% Pd-C, Ph_2O, reflux) of the crude reaction mixture gave the benzofuran derivative (**12**) exclusively (56%). Similarly, reaction of **1b** with benzoquinone (15 days, toluene, room temperature) followed by dehydrogenation gave the furanonaphthoquinone derivative (**13**) as the only cycloaddition derived product (56%).



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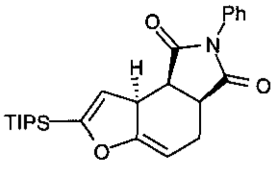

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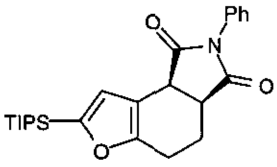

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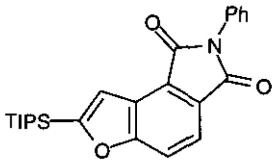

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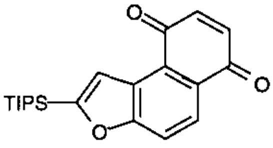

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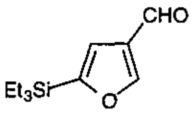
It was of interest to determine if 5-tributylstannyl-2-vinylfuran (**1c**) would also undergo exclusive extraannular cycloaddition reactions. This compound was prepared (54% overall) from 2-furaldehyde in a manner entirely analogous to that used to synthesize **1b**. Reaction of **1c** with DMAD (8 days, 50 °C, toluene) gave three products (**2c**) (13%), (**3a**) (7%), and (**3c**) (7%), which were separated by column chromatography [SiO_2, hexane-EtOAc (95:5), Et_3N (5%)]. The failure of the tributylstannyl moiety to impede intraannular cycloaddition is presumably a consequence of decreased bulkiness and a longer carbon metal bond (214.3 nm for C-Sn *vs.* 187.0 nm for C-Si).[13]

Based on the above results, it seemed quite probable that intraannular cycloaddition reactions of 3-vinylfurans could also be prevented by a suitably placed bulky trialkylsilyl moiety. Therefore, 2-triethylsilyl-4-vinylfuran (**4b**) was synthesized by a Wittig reaction (91% yield) from the corresponding known aldehyde (**14**)[12b]. As expected, cycloaddition of **4b** with DMAD occurred at room temperature (5 days, toluene) affording the extraannular product (**6b**) exclusively (40% yield). *N*-Phenylmaleimide also reacted with **4b** in a site specific manner (room temperature, 3 days, toluene) to produce the tetrahydrobenzofuran derivative (**15**) (29% yield). In contrast, the cycloaddition with diethyl maleate required considerably more rigorous conditions (4 days, 70-80 °C, neat). The extraannular product (**16**) (mixture of isomers) was still, however, the only cycloaddition product observed (22% yield, 50% recovered **4b**).



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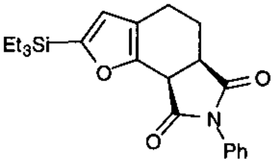

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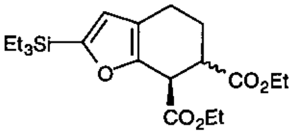

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In conclusion, 5-triisopropylsilyl-2-vinylfuran (**1b**) and 2-triethylsilyl-4-vinylfuran (**4b**) react with dienophiles exclusively *via* the extraannular mode, intraannular cycloaddition being prevented by the sterically demanding trialkylsilyl moieties.

EXPERIMENTAL

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Chromatography was carried out using Merck 60 (230-400 mesh) silica gel. Melting points are uncorrected. IR spectra were recorded as $CHCl_3$ solution using a Perkin-Elmer 1720-X instrument. ^1H NMR measurements were recorded at 200.0 MHz and ^{13}C NMR measurements were recorded at 50.0 MHz using a Varian Gemini-200 instrument. Spectra are reported in ppm downfield from tetramethylsilane as the internal standard. Unless otherwise noted, NMR spectra were measured in $CDCl_3$ solution. Low resolution mass spectra (LRMS) were recorded on a Finnigan MAT-INCOS XL instrument. Elemental analyses were performed using a Fison EA-1108 instrument.

2-Formyl-5-triisopropylsilylfuran (8). Compound (**8**) was prepared from 2-furaldehyde (8.62 mL, 0.1 mol) as described on reference 12a with the only modification of preparing the morpholide anion at -10 °C instead of -78 °C as described by those authors. The crude product was purified by column chromatography (hexane-Et_2O, 95:5) to obtain **8** as an oil (16.8 g, 66%); IR: 1680, 967, 805 cm^{-1}; ^1H NMR: δ 9.71 (s, 1H), 7.25 (d, *J* = 3.5 Hz, 1H), 6.81 (d, *J* = 3.5 Hz, 1H), 1.48-1.25 (m, 3H), 1.25-1.01 (m, 18H); ^{13}C NMR: δ 177.9, 166.0, 156.9, 123.4, 120.1, 18.1, 10.6; MS: (m/z) 252 (M^+, 8.0), 43 (100). Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.60; H, 9.58; Found: C, 66.23; H, 9.72.

2-Vinyl-5-triisopropylsilylfuran (1b). To a suspension of 37% KH/oil (4.3 g, 0.11 mol) in toluene (80 mL) was added *t*-amylic alcohol (4.3 mL, 0.4 mol) and stirred for 20 min at rt under Ar. Methyl triphenylphosphonium bromide (14.1 g, 0.4 mol) was added and after 15 min the aldehyde (**8**) (5.0 g, 0.02 mol) was added. The reaction was stirred for 20 min and diluted with water (8 mL), extracted with CH_2Cl_2 (100 mL) and washed with water (60 mL). The organic phase was dried over $MgSO_4$ and concentrated. The crude product was purified by column (hexane) to obtain the vinyl aldehyde (**1b**) (4.5 g, 91%) as an oil; IR: 1641, 907, 884, cm^{-1}; ^1H NMR: δ 6.63 (d, *J* = 3.3 Hz, 1H), 6.54 (dd, *J* = 17.5, 11.1 Hz, 1H), 6.25 (d, *J* = 3.3 Hz, 1H), 5.66 (dd, *J* = 17.5, 11.1 Hz, 1H) 5.14 (dd, *J* = 11.1, 1.5 Hz, 1H), 1.40-1.16 (m, 3H), 1.16-1.01 (m, 18H); ^{13}C NMR: δ 157.2, 125.4, 123.1, 112.2, 107.9, 18.4, 10.8; MS: (m/z) 250 (M^+, 12), 165 (100). Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.93; H, 10.46; Found: C, 72.06; H, 10.32.

General conditions for the Diels-Alder reaction. A solution of the vinylfuran and the dienophile (2 to 3 equivalents with respect to the vinylfuran) in anh. toluene (degassed by bubbling Ar for 5 min) reacted under the conditions described. The reaction was concentrated and the residue purified by column chromatography. All the crude reaction products were examined by ^1H NMR. The yields are based on the vinylfuran.

Dimethyl 2-triisopropylsilylbenzofuran-4,5-dicarboxylate (3b). Vinylfuran (**1b**) (1.0 g, 4.0 mmol) and dimethyl acetylenedicarboxylate (1.5 mL, 12.0 mmol) in toluene (8 mL) were treated under the general conditions at 50 °C for 9 d to give, after chromatography (hexane-EtOAc, 9:1), **3b** (0.64 g, 41%) as an oil; IR: 1724, 1464, 886 cm^{-1}; ^1H NMR: δ 7.77 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.16 (s, 1H), 4.00 (s, 3H), 3.30 (s, 3H), 1.48-1.26 (m, 3H), 1.26-1.01 (m, 18H); ^{13}C NMR: δ 168.2, 168.0, 164.8, 159.6, 127.5, 126.1, 125.5, 125.2, 117.4, 113.0, 52.6, 52.5, 18.3, 10.7; MS: (m/z) 390 (M^+, 3), 315 (100). Anal. Calcd for $C_{21}H_{30}O_5Si$: C, 64.58; H, 7.74; Found: C, 64.35; H, 7.74.

Ethyl 2-triisopropylsilylbenzofuran-4-carboxylate (9). Vinylfuran (**1b**) (0.5 g, 2.0 mmol) and ethyl propiolate (0.6 g, 6.0 mmol) in toluene (4 mL) were treated under the general conditions at reflux for 5 d to give, after chromatography (hexane-EtOAc, 95:5), **9** (64 mg, 9%) as an oil and **1b** (200 mg, 40%) as an oil; IR: 1709, 1465, 884 cm^{-1}; ^{1}H NMR: δ 7.95 (d, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 0.9 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.54-1.20 (m, 3H), 1.20-1.00 (m, 18H); ^{13}C NMR: δ 166.6, 163.1, 158.4, 128.5, 124.8, 123.3, 122.6, 118.8, 115.5, 60.8, 18.6, 14.4, 11.0 MS: (m/z) 346 (M$^+$, 18), 275 (100).

2-Phenyl-7-triisopropylsilyl-3a, 4, 8a, 8b-tetrahydro-6-oxa-2-azaindecene-1,3-dione (10) and 2-phenyl-7-triisopropylsilyl-3a, 4, 5, 8b-tetrahydro-6-oxa-2-azaindecene-1,3-dione (11). Vinylfuran (**1b**) (1.0 g, 4.0 mmol) and *N*-phenylmaleimide(2.07 g, 10.0 mmol) in toluene (8 mL) were treated under the general conditions at rt for 9 d. Compound (**10**) precipitated from the reaction mixture (420 mg, 25%); mp 122-125 °C (hexane-CH_2Cl_2); IR: 1779, 1712, 889 cm^{-1}; ^{1}H NMR: δ 7.48-7.30 (m, 3H), 7.18-7.05 (m, 2H), 5.92 (dd, *J* = 2.2, 1.3 Hz, 1H), 5.19 (dtd, *J* = 7.8, 3.2, 1.4 Hz, 1H), 3.70-3.58 (m, 1H), 3.63 (q, *J* = 8.2 Hz, 1H), 3.21 (ddd, *J* = 7.8, 5.7, 1.8 Hz, 1H), 3.05 (ddd, *J* = 15.1, 7.9, 2.0 Hz, 1H), 2.09 (ddt, *J* = 15.1, 5.7, 2.6 Hz, 1H), 1.3-1.1 (m, 3H), 1.10-0.90 (m, 18H); ^{13}C NMR: δ 178.5, 174.9, 160.3, 158.6, 131.9, 128.9, 128.5, 126.5, 117.6, 90.9, 43.4, 42.5, 38.9, 24.3, 18.4, 10.6; MS: (m/z) 423 (M$^+$, 11.0), 83 (100). Anal. Calcd for $C_{25}H_{33}NO_3Si$: C, 70.88; H, 7.85; N, 3.33; Found: C, 70.79; H, 7.87; N, 3.44. The crude product was purified on column (CH_2Cl_2-hexane, 8:2) to give compound (**11**) (595 mg, 35%) as a solid; mp 120-123 °C (hexane-CH_2Cl_2); IR: 1783, 1716, 884 cm^{-1}; ^{1}H NMR: δ 7.52-7.35 (m, 3H), 7.28-7.18 (m, 2H), 6.84 (s, 1H), 4.05 (d, *J* = 8.0 Hz, 1H), 3.41 (dt, *J* = 7.7, 5.0 Hz, 1H), 2.77-2.63 (m, 2H), 2.52 (dd, *J* = 9.9, 4.8 Hz, 1H), 2.20-1.98 (m, 1H), 1.37-1.18 (m, 3H), 1.14-1.00 (m, 18H); ^{13}C NMR: δ 177.5, 176.2, 156.5, 154.8, 131.8, 129.0, 128.4, 126.2, 121.5, 111.3, 40.2, 40.1, 21.7, 20.4, 18.5, 10.9; MS: (m/z) 423 (M$^+$, 83), 207 (100). Anal. Calcd for $C_{25}H_{33}NO_3Si$: C, 70.88; H, 7.85; N, 3.33; Found C, 70.99; H, 7.84; N, 3.35.

2-Phenyl-7-triisopropylsilyl-6-oxa-azaindecene-1, 3-dione (**12**). The crude reaction product, obtained using the same reaction conditions described above, and 10% Pd/C (2.52 g) in diphenyl ether (5 mL) were refluxed for 90 min. The reaction cooled to rt, filtered over Celite, the solvent removed and the crude purified by chromatography (CH_2Cl_2-hexane, 7:3) to afford **12** (0.94 g, 56%) as a solid; mp 142-

145 °C (hexane-CH_2Cl_2); IR: 1771, 1716, 836 cm^{-1}; ^1H NMR: δ 7.85 (s, 1H), 7.64-7.36 (m, 4H), 1.61-1.30 (m, 3H), 1.30-1.01 (m, 18H); ^{13}C NMR: δ 168.5, 168.1, 167.5, 162.6, 132.1, 129.2, 127.9, 126.9, 126.7, 124.7, 124.1, 119.1, 116.3, 116.2, 18.3, 10.7; MS: (m/z) 419 (M^+, 8), 376 (100). Anal. Calcd for $C_{25}H_{29}NO_3Si$: C, 71.56; H,6.96; N, 3.33; Found: C, 71.57; H, 7.00; N, 3.32.

2-Triisopropylsilylnaphtho[2,1-*b*]furan-6,9-dione (13). Vinylfuran (**1b**) (1.0 g, 4.0 mmol) and *benzoquinone* (1.26 g, 11.6 mmol) in toluene (8 mL) were treated under the general conditions at rt for 15 d followed by dehydrogenation as described above to give, after chromatography (hexane-Et_2O, 95:5), **13** (0.79 g, 56%) as a solid; mp 203-206 °C (hexane-MeOH); IR: 1666, 1608, 887, 808 cm^{-1}; ^1H NMR: δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.92 (s, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 6.95 (s, 2H), 1.52-1.35 (m, 3H), 1.25-1.01 (m, 18H); ^{13}C NMR: δ 186.6, 185.5, 168.2, 161.8, 139.0, 138.2, 128.1, 126.9, 124.8, 123.2, 118.9, 116.3, 18.3, 10.7; MS: (m/z) 354 (M^+, 4), 311 (100). Anal. Calcd for $C_{21}H_{26}O_3Si$: C, 71.14; H, 7.39; Found: C, 70.99; H, 7.37.

2-Vinyl-5-tributylstannylfuran (1c). 2-Formyl-5-tributylstannylfuran[12a] (5.0 g, 10.0 mmol) was treated under the Wittig conditions described for the preparation of **1b** to give, after chromatography (Florisil, hexane-Et_3N, 97:3), **1c** (3.39 g, 68%, 54% from 2-furaldehyde) as a colorless oil; IR: 3011, 1639, 1000, 908 cm^{-1}; ^1H NMR: δ 6.56 (dd, *J* = 17.6, 11.2 Hz, 1H), 6.52 (d, *J* = 3.1 Hz, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 5.63 (dd, *J* = 17.5, 1.1 Hz, 1H), 5.11 (dd, *J* = 11.2, 1.3 Hz, 1H), 1.80-1.46 (m. 6H), 1.34 (m, 6H), 1.06 (t, *J* = 7.6 Hz, 6H), 0.89 (t, *J* = 7.2 Hz, 9H); ^{13}C NMR: δ 161.4, 157.8, 125.4, 123.0, 111.5, 108.1, 28.8, 27.0, 13.5, 10.0; MS: (m/z) 327 (M^+ - 57, 42), 41 (100). Anal. Calcd for $C_{18}H_{32}OSn$: C, 56.42; H, 8.41; Found: C, 56.46; H, 8.59.

Dimethyl 1-tributylstannyl-4-vinyl-7-oxabicycle[2,2,1]hepta-2,5-diene-2,3-dicarboxylate (2c) and dimethyl 2-tributylstannylbenzofuran-4,5-dicarboxylate (3c). Vinylfuran (**1c**) (1.0 g, 2.6 mmol) and dimethyl acetylenedicarboxylate (0.97 ml, 7.8 mmol) in toluene (5 mL) were treated under the general conditions at 50 °C for 8 d to give, after chromatography (SiO_2, hexane-EtOAc, 95:5 with 3% Et_3N), **3a**[7] (30 mg, 7%), **2c** (131 mg, 13%); **2c**; IR: 1711, 1463, 1025 cm^{-1}; ^1H NMR: δ 6.66 (d, *J* = 3.4 Hz, 1H), 6.44 (dd, *J* = 17.4, 11.0 Hz, 1H), 6.26 (d, *J* = 3.5 Hz, 1H), 5.68 (d, *J* = 16.6 Hz, 1H), 5.20 (d, *J* = 11.9 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 1.60-1.43 (m, 6H), 1.32 (m, 6H), 1.02 (t, *J* = 7.9 Hz, 6H), 0.89 (t, *J* = 7.1 Hz, 9H); ^{13}C NMR: δ 173.5, 167.4, 154.0, 153.8, 148.0, 124.6, 113.8, 113.1, 52.6, 51.8, 28.8, 28.6, 28.0, 27.7, 27.0, 26.49, 26.46, 15.7, 15.6, 13.0, 12.0, 8.6, 8.5; MS: (m/z) 469 (M^+ - 55, 34), 467 (25), 179 (52), 41 (100). Anal. Calcd for $C_{24}H_{38}O_5Sn$: C, 54.87; H, 7.29; Found: C, 54.76; H, 7.69; and **3c** (70 mg, 7%); IR: 1721, 1152 cm^{-1}; ^{1}H NMR: δ 7.72 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.05 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 1.66-1.50 (m, 6H), 1.34 (m, 6H), 1.17 (t, *J* = 7.6 Hz, 6H), 0.90 (t, *J* = 7.1 Hz, 9H); ^{13}C NMR: δ 170.2, 168.4, 168.2, 160.4, 127.8, 125.4, 124.9, 124.8, 117.5, 112.7, 52.5, 52.4, 28.7, 27.0, 13.4, 10.1; MS: (m/z) 465 (M^+ - 57, 12), 203 (67), 41 (100). Anal. Calcd for $C_{24}H_{36}O_5Sn$: C, 55.08; H, 6.93; Found: C, 54.80; H, 7.11.

5-Triethylsilyl-3-vinylfuran (**4b**). 2-Triethylsilyl-4-formylfuran (**14**)[12b] (2.0 g, 9.5 mmol) was treated under the Wittig conditions described for the preparation of **1b** to give, after chromatography (pentane), **4b** (1.8 g, 91%) as a colorless oil; IR: 3015, 1645, 904 cm^{-1}; ^{1}H NMR: δ 7.61 (s, 1H), 6.78 (s, 1H), 6.58 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.45 (dd, *J* = 17.6, 1.4 Hz, 1H), 5.11 (dd, *J* = 11.0, 1.6 Hz, 1H), 1.10-0.65 (m, 15H); MS: (m/z) 208 (M^+, 20), 179 (68), 151 (100).

Dimethyl 2-triethylsilylbenzofuran-6,7-dicarboxylate (**6b**). Vinylfuran (**4b**) (0.5 g, 2.4 mmol) and dimethyl acetylenedicarboxylate (0.88 ml, 7.2 mmol) in toluene (8 mL) were treated under the general conditions at rt for 5 d to give, after chromatography (CH_2Cl_2-EtOAc, 99:1), **6b** (0.33 g, 41%) as an oil; IR: 1721, 1141 cm^{-1}; ^{1}H NMR: δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 4.03 (s, 3H), 3.92 (s, 3H), 1.10-0.75 (m, 15H); ^{13}C NMR: δ 166.9, 166.8, 154.2, 132.5, 124.0, 123.8, 121.7, 119.6, 116.7, 111.0, 52.8, 52.5, 7.2, 3.0; MS: (m/z) 208 (M^+, 15), 319 (100). Anal. Calcd for $C_{18}H_{24}O_5Si$: C, 61.98; H, 6.88; Found: C, 62.18; H, 7.02.

7-Phenyl-2-triethylsilyl-4, 5, 5a, 8a-tetrahydro-1-oxa-7-azaindacene-6,8-dione (**15**). Vinylfuran (**4b**) (0.5 g, 2.4 mmol) and *N*-phenylmaleimide (1.24 g, 7.2 mmol) in toluene (5 mL) were treated under the general conditions at rt for 3 d to give, after chromatography (hexane-EtOAc, 9:1), **15** (0.26 g, 29%) as a solid; mp 159-162 °C; IR: 1785, 1719 cm^{-1}; ^{1}H NMR: δ 7.50-7.34 (m, 3H), 7.30-7.20 (m, 2H), 6.49 (s, 1H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.58-3.47 (m, 1H), 2.60-2.39 (m, 3H), 2.08-1.87 (m, 1H), 1.10-0.70 (m, 15H); ^{13}C NMR: δ 177.2, 173.0, 159.6, 146.4, 131.8, 129.0, 128.4, 126.2, 121.2, 119.5, 41.2, 41.0, 22.3, 19.2, 7.3, 3.2; MS: (m/z) 381 (M^+, 80), 179 (100). Anal. Calcd for $C_{22}H_{27}NO_3Si$: C, 69.19; H, 7.07; N, 3.67; Found: C, 68.81; H, 7.32, N, 3.46.

Diethyl 2-triethylsilyl-4, 5, 6, 7-tetrahydrobenzofuran-6,7-dicarboxylate (16). Vinylfuran (**4b**) (0.5 g, 2.4 mmol) and diethyl maleate (1.16 ml, 7.2 mmol) were treated under the general conditions (neat) at 70-80 °C for 4 d to give, after chromatography (hexane-EtOAc, 95:5), **16** (0.2 g, 22%) as a mixture of isomers and **4b** (0.25 g, 50%). Less polar isomer **16** as an oil; IR: 1734, 1199 cm^{-1}; ^1H NMR: δ 6.46 (s, 1H), 4.28-4.05 (m, 5H), 2.81 (ddd, J = 11.4, 5.4, 3.9 Hz, 1H), 2.59 (ddd, J = 15.3, 5.4, 2.2 Hz, 1H), 2.48 (ddd, J = 10.9, 5.5, 1.5 Hz, 1H), 2.40-2.20 (m, 3H), 1.26 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.0 Hz, 3H), 1.10-0.65 (m, 15H); ^{13}C NMR: δ 172.7, 170.4, 158.1, 149.4, 121.2, 118.9, 60.9, 60.7, 42.9, 41.8, 21.9, 21.0, 14.0, 7.2, 3.2; MS: (m/z) 380 (M^+, 30), 307 (100). Anal. Calcd for $C_{20}H_{32}O_5Si$: C, 63.06; H, 8.40; Found: C, 63.26; H, 8.59. More polar isomer **16** as an oil; IR: 1726, 1031 cm^{-1}; ^1H NMR: δ 6.43 (s, 1H), 4.31-4.05 (m, 4H), 3.20 (ddd, J = 10.6, 8.4, 3.3 Hz, 1H), 2.60-2.46 (m, 3H), 2.30-2.14 (m, 1H), 2.00-1.78 (m, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 1.08-0.64 (m, 15H); ^{13}C NMR: δ 173.4, 171.3, 157.8, 149.3, 121.1, 118.0, 61.2, 60.9, 43.5, 25.1, 20.7, 14.1, 7.3, 3.3; MS: (m/z) 380 (M^+, 20), 307 (100). Anal. Calcd for $C_{20}H_{32}O_5Si$: C, 63.06; H, 8.40; Found: C, 62.85; H, 8.27.

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