Supporting Information

General procedure for the synthesis of {[2-(2,2-Dibutyl-2-stannahexyl)phenyl]methylthio}benzenes: 2-Methylbenzaldehyde was reduced to 2-methylbenzylalcohol by sodium borohydride in methanol. *n*-Butyllithium (2.1 eq.) was added into the solution of the 2-methylbenzylalcohol in anhydrous diethyl ether at 0^{o}C, then the reaction mixture was refluxed under Ar atm for 24 hr. In an ice bath, Bu_3SnCl (2.0 eq.) was added dropwise to the solution, and the solution was allowed to stand at ambient temperature for 3 hr. To the reaction mixture was added aq. NH_4Cl, then extracted by EtOAc. The organic layer was separated, dried over $MgSO_4$ and evaporated *in vacuo* to give crude **4** which was further purified by silica gel column chromatography (hexane:EtOAc 30:1).4) Compound **4** was then dissolved in dichloromethane with thiophenol (1.2 eq.) and ZnI_2 (0.5 eq.).9) After the reaction mixture was stirred for 15 min under Ar at ambient temperature, brine was added and extracted with EtOAc. After dryness and evaporation, the residue was purified by silica gel column chromatograpy to give **3** (yield 51 % from aldehyde). *{[2-(2,2-Dibutyl-2-stannahexyl)phenyl]methylthio}benzene* **3.** ^{1}H-NMR δ ($CDCl_3$) 7.35-7.06(m, 9H), 4.04(s, 2H, $C\underline{H}_2S$), 2.43(s, 2H, $PhC\underline{H}_2Sn$), 1.38(m, 6H), 1.23(m, 6H), 0.83(t, J=7.42 Hz, 9H), 0.79(t, J=8.08 Hz, 6H); ^{13}C-NMR δ($CDCl_3$) 142.6, 137.1, 136.9, 131.5, 129.5, 128.4, 127.5, 127.1, 126.1, 123.3, 37.7($Ph\underline{C}H_2S$), 29.1, 27.4, 15.8 ($Ph\underline{C}H_2Sn$), 13.7, 10.0. *{[2-(2,2-Dibutyl-2-stannahexyl)phenyl]phenylmethylthio}-benzene* **5.** 2-Methylbenzophenone was used in stead of 2-methyl-benzaldehyde for the synthesis of compound **5**. ^{1}H-NMR δ($CDCl_3$) 7.55-6.97 (m, 14H), 5.58 (s, 1H, $Ph_2C\underline{H}S$), 2.46 (d, J=11.87 Hz, 1H, $PhC\underline{H}Sn$), 2.33(d, J=11.87 Hz, 1H, $PhC\underline{H}Sn$), 1.37 (m, 6H), 1.23 (m, 6H), 0.84 (t, J=7.09 Hz, 9H), 0.76 (m, 6H). ^{13}C-NMR δ($CDCl_3$) 141.9, 140.6, 130.0, 129.0, 128.8, 128.7, 128.6, 128.3, 127.4, 127.1, 126.9, 126.3, 123.4, 54.3 ($Ph_2\underline{C}HS$), 29.2, 27.4, 15.8 ($Ph\underline{C}H_2Sn$), 13.9, 10.1.

General procedure for the Diels-Alder reaction of electrogenerated *o*-quinodimethanes with dienophiles. {[2-(2,2-Dibutyl-2-stannahexyl)phenyl]methylthio}benzene (1.0 mmol) and a dienophil (1.2 mmol) were added in 1.0 M dry $LiClO_4$ / CH_3NO_2 (20 ml). To this solution was dissolved AcOH (2.0 mmol) and electrolyzed by using the glassy carbon anode (60 mm x 20 mm) and a Pt cathode (10 mm x 10 mm) at a constant potential (at each oxidation peak potential, see text) under Ar. After the reaction was completed (ca.1.2 F/mol), the reaction mixture was poured into EtOAc and the EtOAc solution was washed successively with 5% aq. $NaHCO_3$ and brine. The organic layer was dried over anhydrous $MgSO_4$. After filtration, and evaporation under reduced pressure, the residue was purified by silica gel column chromatograpy (hexane-AcOEt) to give corresponding cycloadducts.

Selected NMR data.

Methyl-3-(methoxycarbonyl)-1-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate **9a**. ^{1}H-NMR δ($CDCl_3$) 7.32-7.23 (m, 3H), 7.15-7.11 (m, 4H), 7.04 (m, 1H), 6.73 (m, 1H), 4.29 (d, J=11.05 Hz, 1H), 3.71 (s, 3H), 3.45 (s, 3H), 3.28-3.09 (m, 4H). ^{13}C-NMR δ($CDCl_3$) 174.3, 173.9, 142.9, 137.7, 133.8, 129.4, 129.1, 128.5, 128.3, 127.0, 126.4, 52.5, 51.7, 51.5, 49.5, 43.1, 32.3. **9b**. ^{1}H-NMR δ($CDCl_3$) 4.68 (d, J=6.27 Hz). 4-Phenyl-4,9,3a,9a-tetrahydrobenzo[f] isobenzofuran-1,3-dione **12**. ^{1}H-NMR δ($CDCl_3$) 7.34-7.16(m, 9H), 4.55 (d, J=5.61 Hz, 1H), 3.78-3.62 (m, 2H), 3.39 (dd, J=15.83, 4.95 Hz, 1H), 3.21 (dd, J=15.83, 8.57 Hz, 1H); ^{13}C-NMR δ($CDCl_3$) 173.1, 171.0, 136.7, 135.7, 133.9, 129.3, 128.7, 128.6, 127.9, 127.8, 127.7, 46.8, 45.8, 45.7, 40.3. Methyl-3-(methoxycarbonyl)-1-phenyl-1,2,3,4-tetrahydro-naphthalene-2-carboxylate **16a**. ^{1}H-NMR δ($CDCl_3$) 4.81 (d, J=3.13 Hz, 1H), 3.67 (s, 3H), 3.64 (s, 3H). **16b**. ^{1}H-NMR δ($CDCl_3$) 4.48 (d, J=6.43 Hz, 1H), 3.73 (s, 3H), 3.28 (s. 3H).