Synthesis of \( p \)-phenylthio- \( peri \)-hydroxy polyaromatic compounds by strong-base-induced \([4+2]\) cycloaddition of \( 4-(\text{phenylthio}) \)homophthalic anhydrides with phenylsulfinyl-dienophiles

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Dedicated to Professor Keiichiro Fukumoto on the occasion of his 70\textsuperscript{th} birthday
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Abstract
A direct and regioselective synthesis of \( p \)-phenylthio-substituted \( peri \)-hydroxy polyaromatic compounds (9–12) was developed via the strong-base-induced \([4+2]\) cycloaddition of the \( 4-(\text{phenylthio}) \)homophthalic anhydrides (1a–d) to the phenylsulfinyl-substituted dienophiles (5–8). The sulfinyl group in 5–8 is the key to producing the desired reaction under mild conditions (at –20 °C to room temperature) in good yields. A reaction mechanism explaining the remarkable effect of the sulfinyl group is discussed.

Keywords: \( peri \)-Hydroxy polyaromatic compounds, strong-base-induced \([4+2]\) cycloaddition, homophthalic anhydride, sulfinyl-substituted dienophile

Introduction
General and efficient syntheses of \( peri \)-hydroxy polyaromatic \( p \)-quinones (I) and their dihydroquinone derivatives (II) are important in recent synthetic organic- and medicinal chemistry because these compounds are key components of many biologically important natural products such as anthracyclines\textsuperscript{1} and fredericamycin A.\textsuperscript{2} For the synthesis of these quinone compounds, the transformation of phenols into \( p \)-benzoquinones or \( p \)-dihydrobenzoquinone derivatives has been one of the most important steps.\textsuperscript{3} Recently, we reported a new method for the synthesis of I and II from \( p-(\text{phenylthio}) \)phenols (III) via the aromatic Pummerer-type reaction of the derived sulfoxides (IV).\textsuperscript{4} The synthesis of III has been achieved by two methods; \textit{viz}, the \( p \)-specific thiocyanation of phenols (V) using the combination of PhICl\(_2\) and Pb(SCN)\(_2\)
followed by reaction with PhMgBr (method A)\textsuperscript{4d,5} and the oxidative intramolecular [4+2] cycloaddition of \(o-[\omega\text{-phenylthio-ethynyl}acetyl]-phenols (VI)\) (method B).\textsuperscript{6} Recently, we briefly reported a third method, based on the strong-base-induced [4+2] cycloaddition of \(4\text{-}(\text{phenylthio})\text{-homophthalic anhydrides (1a, b)}\) to sulfinyl-substituted dienophiles, in which we found that the sulfinyl groups were essential for producing the desired reaction under mild conditions in good yields (method C) (Scheme 1).\textsuperscript{7} We now give a full account of our studies on method C, with additional examples using the new homophthalic anhydrides (1c and 1d). A reaction mechanism to explain the remarkable effect of the sulfinyl group is also discussed.

**Scheme 1**

**Results and Discussion**
The starting 4-(phenylthio)homophthalic anhydrides (1a–d) were readily prepared from the corresponding homophthalic acid dimethyl esters (2a–d), in good overall yields. That is, the reaction of 2 with lithium bis-(trimethylsilyl)amide followed by treatment with PhSSO₂Ph afforded the phenylthio-substituted diesters (3). Alkaline hydrolysis of 3 and dehydration of the resultant dicarboxylic acids with trimethylsilyl(ethoxy)acetylene affor ded 1. As in our previous study using the related homophthalic anhydrides,⁹ the cycloaddition of 1b, d with acetylenedicarboxylic acid diethyl ester took place in the presence of NaH to give directly the p-phenylthio-substituted adducts (4b and 4d) in 58% and 64% yields, respectively (Scheme 2).

### Scheme 2

In order to establish the regioselective synthesis of the p-phenylthio-substituted peri-hydroxy polyaromatic compounds, we examined the strong-base-induced [4+2] cycloaddition of 1a with naphthoquinones (5a–d) bearing various types of activating groups (X). The reactions of 1a with the known halogen-substituted naphthoquinones (5a,b)¹⁰ took a long time to produce the tetracyclic product (9a), in 65–67 yields (Table 1, runs 1 and 2). The similar reaction with the phenylthio derivative (5c)¹¹ did not proceed at all, even in refluxing THF (run 3). On the other hand, the reaction with the phenylsulfinyl derivative (5d)¹² was very fast at room temperature, to give 9a in 72% yield (run 4).
In a like manner, the reactions of a highly-oxygen-substituted homophthalic anhydride (1d) and the spiro-dienophiles (6a–e) were investigated. The reaction of 1d with the bromide (6a) required refluxing in THF to give a mixture of the desired product 10d and the product lacking the phenylthio group, (10d'), in low yield (run 5). Similar low reactivity and/or the formation of 10d' were also observed in the reactions with the arylthio- (6b, c) and the phenylsulfonyl-derivative (6e) (runs 6, 7 and 9). In contrast, the reaction with the sulfinyl derivative (6d) was again very fast at room temperature, to afford 10d (77% yield) without forming 10d' (run 8). Thus, the sulfinyl group was unique, because other electron-withdrawing substituents, viz., the p-nitrophenylthio- (6c), and the phenylsulfonyl- (6e) groups, were not efficient.

The NaH-induced [4+2] cycloaddition reaction of 1 was found to be generally applicable for a range of sulfinyl-substituted dienophiles (5d, 6d, 7, and 8) as summarized in Table 1. All the reactions were completed at or below room temperature and gave the expected adducts (9–12) in 66–82% yields. The reactions with a set of two regioisomers (5d and 7) afforded the corresponding products (9 and 11) as a single product, and thus, the regiochemistry of each reaction was proved to be controlled exclusively by the position of the sulfinyl group. Some results of the reactions with the corresponding bromo-substituted dienophiles are also given in brackets (runs 10, 14, 17, and 21) to emphasize the general superiority of the phenylsulfinyl group over the halogen substituents.

In order to obtain some insights into the reactivity of dienophiles, the frontier molecular orbital (FMO) energy levels of 5–8 and some related compounds were calculated using the PM3 Hamiltonian in the Spartan (ver. 3.1.2) program (Table 2). The results show that the LUMO levels of the sulfinyl-substituted dienophiles (5d, 6d, 7, and 8) are similar to, or lower than, those of the halogen derivatives (5a, 5b, 6a, etc.) but higher than that of the sulfonyl derivative (6e). Therefore, the LUMO levels are not the only factor that causes the remarkable effect of the sulfinyl group in our case.

The following reaction mechanism seems plausible. First, the δ-oxy-quinodimethanes A, generated by the treatment with NaH, would produce the oxyanion-assisted Diels–Alder type cycloaddition9,13 to dienophiles to provide the adduct B in which the X and H groups are situated syn- to each other. In the case of the sulfinyl-substituted dienophiles [X = S(O)Ph], the easy syn-elimination of PhSOH followed by the oxyanion-assisted retro-Diels–Alder reaction14 of the resultant C would give the cycloadducts (9–12) with CO2 release15 (Scheme 3). These irreversible reactions from B to the final products could proceed at or below room temperature, as reported in the literature.12,14 Thereby, the fast and exclusive formation of 10d from 6d was attained.16 On the other hand, the reactions of the halogen- and sulfonyl-substituted dienophiles must have suffered a slow elimination of the X and H groups in B, which not only retarded the overall reaction but also brought about the side reaction leading to 10d'. This explanation may be consistent with the fact that the reaction of 1d with diethyl acetylenedicarboxylate gave exclusively 4d, in which the intermediate (C') was formed directly from A.

Table 1. Reaction of 4-(phenylthio)homophthalic anhydrides (1a-d) with dienophiles (5-8)
The molar ratio of the reagents is generally as follows: 1 (1.3 equiv), and 5-8 (1.0 equiv).

Isolated yield of the product based on 5-8.

The reaction conditions and the yield of the product of the similar reaction with the corresponding bromo-substituted dienophile are given in the bracket.
Table 2. HOMO and LUMO level values of 5–8 and some related compounds using the PM3 calculation

<table>
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<th>dienophile</th>
<th>HOMO/eV</th>
<th>LUMO/eV</th>
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<td>5b X = Cl</td>
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<td>6a X = H</td>
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<td>8 X = S(O)Ph</td>
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We have applied this anionic cycloaddition to the synthesis of the ABCD-ring analog of fredericamycin A. The tetracyclic compound (10b), obtained in 82% yield from 1b and 6d (Table 1, run 14), was subjected successively to debenzylolation by BCl₃, protection of the diol by silylene formation, and the oxidation of the phenylthio group to give 13 in 97% overall yield. The aromatic Pummerer-type reaction⁴c of 13 followed by sequential deprotection using aqueous NaHCO₃ and Bu₄NF provided the ABCD-ring analog, 15. Since 15 was susceptible to autoxidation during chromatography, to give a mixture of 15 and the p-quinone 16, the product was isolated as either 16 or 17 (Scheme 4).
Scheme 3
Scheme 4

Conclusions

We have succeeded in producing the efficient and versatile synthesis of $p$-phenylthio-substituted peri-hydroxy polyaromatic compounds, whose structure is expected to be capable of various modifications. In this cycloaddition, use of the sulfinyl-substituted dienophile is crucial, and this method offers very mild reaction conditions and the direct formation of the desired compounds in good yields.

Experimental Section

General Procedures. All melting points are uncorrected. The $^1$H NMR spectra were measured using 200–500 MHz spectrometers with SiMe$_4$ as internal standard. Infrared (IR) absorption spectra were recorded in CH$_2$Cl$_2$ solutions or by diffuse reflectance measurement of the samples dispersed in KBr powder. Column chromatographic purification was performed on silica gel BW-300 (200–400 mesh, Fuji Silysia Chemical Co., Ltd., Japan). RT denotes room temperature.

Methyl 6-benzyloxy-2-(methoxycarbonylmethyl)benzoate (2b). was prepared similar to the reported preparation method of substituted homophthalates.$^{2c}$ Under an argon atmosphere, $n$-BuLi (1.6 M in hexane, 33 mL, 56 mmol) was added to a solution of diisopropylamine (2.6 mL, 19 mmol) in anhydrous THF (40 mL) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C, and a solution of dimethyl malonate (4.3 mL, 37 mmol) in anhydrous THF (30 mL) was added. After 1 h, a solution of 3-benzyloxy-1-bromobenzene (4.9 g, 8.6 mmol) in anhydrous THF (30 mL) was added at -78 °C. The reaction mixture was stirred for 30 min at -78 °C, quenched with saturated aqueous NH$_4$Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography (hexane–EtOAc, 10:1 → 3:1) to give 2b (2.2 g, 38%) as a yellow solid, mp 66–67 °C: IR (KBr) cm$^{-1}$: 1736, 1586. $^1$H NMR (CDCl$_3$) $\delta$ 3.69 (5H, s), 3.89 (3H, s), 5.12 (2H, s), 6.92 (2H, d, $J = 8.0$ Hz), 7.27–7.42 (6H, m). Anal. Calcd for C$_{18}$H$_{18}$O$_5$: C, 68.78; H, 5.77. Found: C, 68.97; H, 5.78.

Methyl 6-benzyloxy-3-methoxy-2-(methoxycarbonylmethyl)benzoate (2c). As in the preparation of 2b, methyl 3,6-dimethoxy-2-(methoxycarbonylmethyl)benzoate (2.3 g, 37%) was obtained, but using 2,2,6,6-tetramethylpiperidine (5.4 mL, 32 mmol) as base (instead of diisopropylamine), $n$-BuLi (1.6 M in hexane, 44 mL, 69 mmol), dimethyl malonate (5.3 mL, 46 mmol) and 1-bromo-2,5-dimethoxybenzene (5.0 g, 23 mmol). An orange oil: IR (KBr) cm$^{-1}$:
1740, 1736, 1599. ¹H NMR (CDCl₃) δ 3.65 (2H, s), 3.67 (3H, s), 3.79 (6H, s), 3.88 (3H, s), 6.83 (1H, d, J = 9.0 Hz), 6.89 (1H, d, J = 9.0 Hz). Anal. Caled for C₁₃H₁₆O₆: C, 58.20; H, 6.01. Found: C, 57.95; H, 5.97%. Under a nitrogen atmosphere, BCl₃ (1.0 M in CH₂Cl₂, 9.8 mL, 9.8 mmol) was added to a solution of the methyl 3,6-dimethoxy-2-(methoxycarbonylmethyl)benzoate (2.2 g, 8.2 mmol) in anhydrous CH₂Cl₂ (80 mL) at 0 °C. The reaction mixture was stirred at RT for 10 min, quenched with ice-water and extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (hexane–Et₂O, 2:1) to give methyl 6-hydroxy-3-methoxy-2-(methoxycarbonylmethyl)benzoate (1.9 g, 89%) as a yellow solid, mp 78–79 °C (Et₂O). IR (KBr) cm⁻¹: 1740, 1673, 1607. ¹H NMR (CDCl₃) δ: 3.69 (3H, s), 3.79 (3H, s), 3.90 (3H, s), 4.04 (2H, s), 6.95 (1H, d, J = 9.0 Hz), 7.13 (1H, d, J = 9.0 Hz), 10.56 (1H, s). Anal. Caled for C₁₂H₁₄O₆: C, 56.69; H, 5.55. Found: C, 56.66; H, 5.50%. Under a nitrogen atmosphere, K₂CO₃ (2.1 g, 15 mmol) and benzyl bromide (0.86 mL, 7.2 mmol) were added to a solution of methyl 6-hydroxy-3-methoxy-2-(methoxycarbonylmethyl)benzoate (1.8 g, 6.9 mmol) in anhydrous DMF (25 mL) at 0 °C. The reaction mixture was stirred at RT overnight, quenched with water and extracted with Et₂O. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was recrystallized from hexane–Et₂O to give 2c (2.0 g, 83%) as a colorless solid, mp 96–97 °C. IR (KBr) cm⁻¹: 1732, 1599. ¹H NMR (CDCl₃) δ: 3.67 (2H, s), 3.68 (3H, s), 3.77 (3H, s), 3.87 (3H, s), 5.05 (2H, s), 6.83–6.91 (2H, m), 7.28–7.39 (5H, m). Anal. Caled for C₁₉H₂₀O₆: C, 66.27; H, 5.85. Found: C, 66.29; H, 5.79%.

Methyl 6-benzylxoy-3,4-dimethoxy-2-(methoxycarbonylmethyl)benzoate (2d). As in the preparation of 2c, the reaction of methyl 3,4,6-trimethoxy-2-(methoxycarbonylmethyl)benzoate2c (1.7 g, 5.7 mmol) with BCl₃ (1.0 M in CH₂Cl₂, 6.5 mL, 6.5 mmol) gave methyl 6-hydroxy-3,4-dimethoxy-2-(methoxycarbonylmethyl)benzoate (1.6 g, 96%), a colorless solid, mp 77–78 °C (hexane–Et₂O). IR (KBr) cm⁻¹: 1740, 1661, 1609, 1586. ¹H NMR (CDCl₃) δ: 3.69 (2H, s), 3.68 (3H, s), 3.77 (3H, s), 3.86 (3H, s), 4.04 (2H, s), 6.48 (1H, d, J = 9.0 Hz), 11.49 (1H, s). Anal. Caled for C₁₃H₁₆O₇: C, 54.93; H, 5.67. Found: C, 54.90; H, 5.59%. As in the preparation of 2c, 2d (1.8 g, 96%) was obtained from methyl 6-hydroxy-3,4-dimethoxy-2-(methoxycarbonylmethyl)benzoate (1.4 g, 5.1 mmol), K₂CO₃ (1.7 g, 12 mmol) and benzyl bromide (0.65 mL, 5.5 mmol). A yellow solid, mp 78–79 °C (hexane–Et₂O). IR (KBr) cm⁻¹: 1736, 1600. ¹H NMR (CDCl₃) δ: 3.69 (3H, s), 3.76 (3H, s), 3.77 (2H, s), 3.83 (6H, s), 5.09 (2H, s), 6.50 (1H, s), 7.30 (1H, t, J = 7.5 Hz), 7.35–7.42 (4H, m). Anal. Caled for C₂₀H₂₂O₇: C, 64.16; H, 5.92. Found: C, 64.14; H, 5.88%.

Typical procedure for preparation of 3. Methyl 2-[methoxycarbonyl(phenylthio)methyl]benzoate (3a)
Under a nitrogen atmosphere, LiN(TMS)₂ (1.0 M in THF, 8.0 mL, 8.0 mmol) was added to a solution of 2a (1.4 g, 6.6 mmol) in anhydrous THF (20 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h, and a solution of PhSSO₂Ph (1.7 g, 7.0 mmol) in anhydrous THF
(12 mL) was added. The reaction mixture was stirred at -78 °C for 30 min, quenched with saturated aqueous NH₄Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (hexane–benzene, 2:1) to give 3a (1.9 g, 89%) as a yellow oil: IR (KBr) cm⁻¹: 1740, 1719, 1599, 1578. ¹H NMR (CDCl₃) δ: 3.69 (3H, s), 3.85 (3H, s), 6.15 (1H, s), 7.22–7.26 (3H, m), 7.33 (1H, dd, J = 7.5, 1.5 Hz), 7.37–7.41 (2H, m), 7.49 (1H, dt, J = 7.5, 1.5 Hz), 7.68 (1H, dd, J = 7.5, 1.5 Hz), 7.91 (1H, dd, J = 7.5, 1.5 Hz). Anal. Calcd for C₁₇H₁₆O₄S: C, 64.54; H, 5.16; S, 10.00%.

**Methyl 6-benzyloxy-2-[methoxycarbonyl(phenylthio)methyl]benzoate (3b).** Compound 2b (1.1 g, 3.4 mmol) was converted into 3b (1.4 g, quant.). A yellow oil. IR (KBr) cm⁻¹: 1730, 1584. ¹H NMR (CDCl₃) δ: 3.61 (3H, s), 3.77 (3H, s), 5.04 (3H, s), 6.83–6.86 (1H, m), 7.18–7.36 (12H, m). Anal. Calcd for C₂₄H₂₂O₅S: C, 68.23; H, 5.25; S, 7.59. Found: C, 68.27; H, 5.27; S, 7.60%.

**Methyl 6-benzyloxy-3-methoxy-2-[methoxycarbonyl(phenylthio)methyl]benzoate (3c).** Compound 2c (2.0 g, 5.7 mmol) was converted into 3c (2.4 g, 94%). A colorless solid, mp 91–92 °C (hexane–Et₂O). IR (KBr) cm⁻¹: 1736, 1732, 1595. ¹H NMR (CDCl₃) δ: 3.69 (3H, s), 3.71 (3H, s), 3.72 (3H, s), 5.04 (2H, s), 5.25 (1H, s), 6.81 (1H, d, J = 9.0 Hz), 6.86 (1H, d, J = 9.0 Hz), 7.21–7.46 (10H, m). Anal. Calcd for C₂₅H₂₄O₆S: C, 66.36; H, 5.35; S, 7.08. Found: C, 66.20; H, 5.31; S, 6.87.

**Methyl 6-benzyloxy-3,4-dimethoxy-2-[methoxycarbonyl(phenylthio)methyl]benzoate (3d).** Compound 2d (2.5 g, 6.8 mmol) was converted into 3d (2.7 g, 82%). A colorless solid, mp 124–125 °C (hexane–Et₂O). IR (KBr) cm⁻¹: 1736, 1595. ¹H NMR (CDCl₃) δ: 3.63 (3H, s), 3.73 (3H, s), 3.74 (3H, s), 3.80 (3H, s), 5.08 (2H, s), 5.48 (1H, s), 6.48 (1H, s), 7.20–7.46 (10H, m). Anal. Calcd for C₂₆H₂₆O₇S: C, 64.72; H, 5.43; S, 6.64. Found: C, 64.64; H, 5.45; S, 6.58%.

**Typical procedure for preparation of 1 from 3. 4-(phenylthio)homophthalic anhydride (1a)**

A mixture of 3a (1.4 g, 4.4 mmol) and KOH (4.9 g, 88 mmol) in EtOH (25 mL) and water (5 mL) was heated at reflux for 1 h and concentrated in vacuo to one-fifth of the original volume. The residual aqueous layer was washed with CH₂Cl₂. To the aqueous layer was added CH₂Cl₂, and the mixture cooled to 0 °C and acidified with 10% HCl to pH 2–3 with vigorous stirring. The organic layer was separated, and the aqueous layer extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residual solid was washed with EtOAc to give 2-[carboxy(phenylthio)methyl]benzoic acid (1.3 g, quant.) as a colorless solid, mp 138–140 °C: IR (KBr) cm⁻¹: 3400–2600, 1714, 1599, 1576. ¹H NMR (CDCl₃) δ: 5.87 (1H, s), 7.21–7.26 (3H, m), 7.36–7.44 (3H, m), 7.56 (1H, td, J = 7.5, 1.5 Hz), 7.71 (1H, d, J = 7.0 Hz), 8.09 (1H, dd, J = 8.0, 1.5 Hz), 9.58 (2H, br. s). High resolution FAB-MS Calcd for C₁₅H₁₃O₄S (M⁺+H): 289.0535. Found 289.0555. Similarly to the reported method, a mixture of 2-[carboxy(phenylthio)methyl]benzoic acid (0.43 g, 1.5 mmol) and trimethylsilyl(ethoxy)-
acetylene (0.35 mL, 2.4 mmol) in anhydrous CH₂Cl₂ (10 mL) was stirred at RT for 2.5 h. The reaction mixture was concentrated in vacuo, and the residual solid was washed with hexane–benzene and dried in vacuo to give 1a (0.35 g, 87%) as a colorless solid, mp 144–145 °C (hexane–benzene). IR (CH₂Cl₂) cm⁻¹: 1798, 1757, 1603. ¹H NMR (CDCl₃) δ: 4.99 (1H, s), 7.20–7.43 (5H, m), 7.49 (1H, td, J = 8.0, 1.0 Hz), 7.59 (1H, dd, J = 8.0, 1.0 Hz), 7.76 (1H, td, J = 8.0, 1.0 Hz), 7.95 (1H, dd, J = 8.0, 1.0 Hz). Anal. Calcd for C₁₅H₁₀O₃S: C, 66.65; H, 3.73; S, 11.86. Found: C, 66.30; H, 3.89; S, 11.72%.

8-Benzyloxy-4-(phenylthio)homophthalic anhydride (1b). Compound 3b (1.4 g, 3.4 mmol) was converted into 6-benzyloxy-2-[carboxy(phenylthio)methyl]benzoic acid (1.2 g, 90%);

8-Benzyloxy-2,3-bis-(ethoxycarbonyl)-1-hydroxy-5,6-dimethoxy-4-(phenylthio)naphthalene (4d). As in the preparation of 4b, 1d (36 mg, 0.082 mmol) and diethyl acetylenedicarboxylate (0.040 mL, 0.25 mmol) were converted into 4d (29 mg, 64%). A yellow oil. IR (KBr) cm⁻¹: 1779, 1744, 1653, 1595, 1570. ¹H NMR (CDCl₃) δ: 0.97 (3H, t, J = 7.0 Hz), 1.35 (3H, t, J = 7.0 Hz), 2.52 (1H, br s), 3.85 (3H, s), 3.88 (3H, s), 3.95–4.03 (2H, m), 4.27–4.34 (2H, m), 5.15 (2H, s), 6.50 (1H, s), 7.19–7.23 (5H, m), 7.31–7.34 (1H, m), 7.37–7.40 (3H, m), 7.44 (2H, d, J = 7.5 Hz). High resolution MS Calcd for C₃₁H₃₀O₈S: 562.1161. Found 562.1673.

The known compounds (5a, ¹⁷ 5b, ¹⁸ 5c, ¹¹c ¹⁸ ¹₂,¹⁹) were prepared according to the literature, and new compounds were prepared as follows.

8-Methoxy-2-phenylsulfinyl-1,4-naphthaquinone (5d). A solution of m-CPBA (80% purity, 36 mg, 0.17 mmol) in CH₂Cl₂ (5 mL) was gradually added to an ice-cooled solution of 5c (50 mg, 0.17 mmol) in CH₂Cl₂ (10 mL). The reaction mixture was stirred for 4 h, quenched with saturated aqueous Na₂S₂O₃ and extracted with CH₂Cl₂. The organic layer was washed with saturated aqueous NaHCO₃, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (CH₂Cl₂–MeOH, 50:1) to give 5d (53 mg, quant.) as an orange solid, mp 212–214 °C. IR (KBr) cm⁻¹: 1667, 1586. ¹H NMR (CDCl₃) δ 3.97 (3H, s), 7.29 (1H, d, J = 8.0 Hz), 7.46–7.48 (3H, m), 7.58 (1H, s), 7.68–7.75 (2H, m), 7.86–7.88 (2H, m). High resolution MS Calcd for C₁₇H₁₉O₄S: 562.1161. Found 562.1673.

2-Bromo-spiro-[4,4]-non-2-ene-1,4-dione (6a). Under a nitrogen atmosphere, a solution of phenyltrimethylammonium tribromide (1.4 g, 3.8 mmol) in THF (20 mL) was slowly added to a solution of spiro-[4,4]-nonane-1,4-dione (0.50 g, 3.3 mmol) in THF (20 mL) at RT. The mixture was stirred for 3 h, quenched with saturated aqueous NaHCO₃ and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (hexane:EtOAc, 10:1) to give 6a (0.22 g, 29%) as a yellow solid, mp 74–75 °C (hexane–Et₂O). IR (KBr) cm⁻¹: 1754, 1705, 1561. ¹H NMR (CDCl₃) δ 1.89 (8H, br. s), 7.45 (1H, s). High resolution MS Calcd for C₉H₉O₂Br: 227.9785. Found 227.9811.
2-(Phenylthio)-spiro-[4,4]-on-2-ene-1,4-dione (6b). Under a nitrogen atmosphere, a solution of PhSCl (ca. 4.9 mmol), prepared in situ from PhSSPh (0.54 g, 2.5 mmol) and SO₂Cl₂ (0.20 mL, 2.5 mmol), in CH₃CN (7 mL) was added to a solution of spiro-[4,4]-nonane-1,4-dione (0.30 g, 2.0 mmol) in CH₃CN (8 mL) at 0 °C. The reaction mixture was stirred at RT for 1 day and concentrated in vacuo. The residue was purified by column chromatography (hexane–EtOAc, 8:1) to give 6b (0.42 g, 82%) as a yellow solid, mp 103–104 °C (hexane–Et₂O). IR (KBr) cm⁻¹: 1742, 1694, 1541. ¹H NMR (CDCl₃) δ 1.87 (8H, s), 6.27 (1H, s), 7.46–7.57 (5H, m). Anal. Calcd for C₁₅H₁₄O₂S: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.71; H, 5.54; S, 12.39.

2-(4-Nitrophenylthio)-spiro-[4,4]-non-2-ene-1,4-dione (6c). Under a nitrogen atmosphere, Et₃N (0.050 mL, 0.36 mmol) and 4-nitrothiophenol (55 mg, 0.35 mmol) were added to a solution of 6a (41 mg, 0.18 mmol) in THF (3 mL) at 0 °C. The mixture was stirred at RT for 3 h, quenched with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (hexane–EtOAc, 3:1) to give 6c (46 mg, 86%), a yellow solid, mp 130–132 °C. IR (KBr) cm⁻¹: 1741, 1698, 1541, 1522. ¹H NMR (CDCl₃) δ 1.89 (8H, s), 6.39 (1H, s), 7.76 (2H, d, J = 8.5 Hz), 8.34 (2H, d, J = 8.5 Hz). High resolution MS Calcd for C₁₅H₁₃NO₄S: 303.0565. Found 303.0563.

2-(Phenylsulfinyl)-spiro-[4,4]-non-2-ene-1,4-dione (6d). As in the preparation of 5d, 6b (0.28 g, 1.1 mmol) was converted into 6d (0.29 g, 99%), a yellow solid, mp 102–103 °C (hexane–Et₂O). IR (KBr) cm⁻¹: 1748, 1707. ¹H NMR (CDCl₃) δ 1.46–1.57 (2H, m), 1.65–1.93 (6H, m), 7.51–7.57 (3H, m), 7.64 (1H, s), 7.76–7.83 (2H, m). Anal. Calcd for C₁₅H₁₄O₃S: C, 65.67; H, 5.14; S, 11.69. Found: C, 65.58; H, 5.20; S, 11.55.

2-(Phenylsulfonyl)-spiro-[4,4]-non-2-ene-1,4-dione (6e). To a solution of 6b (49 mg, 0.19 mmol) in CH₂Cl₂ (2 mL) was added dimethylidioxirane (ca. 0.06 M in acetone, 7.3 mL, ca. 0.45 mmol) at RT. The reaction mixture was stirred for 2 h and concentrated in vacuo. The residue was recrystallized from hexane–Et₂O to give 6e (45 mg, 82%) as a yellow solid, mp 148–150 °C (hexane–Et₂O). IR (KBr) cm⁻¹: 1755, 1713. ¹H NMR (CDCl₃) δ 1.79–1.83 (8H, m), 7.62 (2H, t, J = 8.0 Hz), 7.63 (1H, s), 7.74 (1H, t, J = 8.0 Hz), 8.11 (2H, d, J = 8.0 Hz). High resolution MS Calcd for C₁₅H₁₄O₄S: 290.0613. Found 290.0613.

5-Methoxy-2-phenylsulfinyl-1,4-naphthaquinone (7). As in the preparation of 5d, 5-methoxy-2-phenylthio-1,4-naphthaquinone (11c) (160 mg, 0.54 mmol) was converted into 7 (143 mg, 85 %). An orange solid, mp 215–217 °C. IR (KBr) cm⁻¹: 1667, 1584. ¹H NMR (CDCl₃) δ: 4.00 (3H, s), 7.30–7.35 (1H, m), 7.46–7.52 (4H, m), 7.62–7.72 (2H, m), 7.83–7.87 (2H, m). Anal. Calcd for C₁₇H₁₂O₄S: C, 65.37; H, 3.87; S, 10.26. Found: C, 65.19; H, 3.94; S, 10.25%.

Typical procedure for [4+2]-cycloaddition of 1 with the sulfinyl-substituted dienophiles. 5-Benzylxoxy-4-hydroxy-9-phenylthio-2,2-tetramethylenebenz-[f]-indane-1,3-dione (10b) (Table 1, run 14)
Under a nitrogen atmosphere, a solution of 1b (94 mg, 0.25 mmol) in anhydrous THF (4 mL) was added to a suspension of sodium hydride (60% in mineral oil, 11 mg, 0.27 mmol) in THF (4 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1.5 h, and a solution of 6d (53 mg, 0.19 mmol) in anhydrous THF (8 mL) was added. The mixture was stirred at RT for 30 min, then quenched with saturated aqueous NH₄Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (hexane–EtOAc) to give 10b (76 mg, 82%), a yellow solid, mp 164–165 °C (CH₂Cl₂–Et₂O). IR (KBr) cm⁻¹: 1734, 1705, 1671, 1607, 1580. 

¹H NMR (CDCl₃) δ 1.91–2.00 (8H, m), 5.33 (2H, s), 7.04–7.08 (3H, m), 7.13–7.16 (3H, m), 7.39–7.46 (3H, m), 7.55 (2H, d, J = 7.5 Hz), 7.62 (1H, t, J = 8.5 Hz), 8.49 (1H, d, J = 8.5 Hz), 11.26 (1H, s). Anal. Calcd for C₃₀H₂₄O₄S: C, 74.98; H, 5.03; S, 6.67. Found: C, 74.63; H, 5.08; S, 6.59.

5-Benzyloxy-4-hydroxy-7,8-dimethoxy-9-phenylthio-2,2-tetramethylenebenz-[f]-indane-1,3-dione (10d) (run 8). 1d (62 mg, 0.14 mmol) and 6d (33 mg, 0.12 mmol) were converted to 10d (50 mg, 77%), a brown solid, mp 186–187 °C (EtOAc). IR (KBr) cm⁻¹: 1726, 1700, 1663, 1595. 

¹H NMR (CDCl₃) δ 1.52–1.94 (8H, m), 3.94 (3H, s), 3.98 (3H, s), 5.33 (2H, s), 6.90 (1H, s), 7.11–7.16 (4H, m), 7.40–7.48 (4H, m), 7.58 (2H, dd, J = 7.5, 1.5 Hz), 11.15 (1H, s). High resolution MS Calcd for C₃₂H₂₈O₆S: 540.1606. Found 540.1633.
purple solid, mp 218–219 °C (EtOAc). IR (KBr) cm⁻¹: 1617, 1586. ¹H NMR (CDCl₃) δ 3.82 (3H, s), 3.84 (3H, s), 4.06 (3H, s), 6.79 (1H, s), 6.94 (1H, dd, J = 7.5, 6.5 Hz), 7.02 (2H, dd, J = 8.0, 7.5 Hz), 7.07 (2H, d, J = 7.5 Hz), 7.24 (1H, d, J = 8.0 Hz), 7.35 (1H, t, J = 7.5 Hz), 7.43 (2H, t, J = 7.5 Hz), 7.58 (1H, dd, J = 7.5, 8.0 Hz), 7.63–7.64 (3H, m), 16.85 (1H, s). High resolution MS Calcd for C₃₄H₂₆O₇S: 578.1399. Found 578.1418.

4-Hydroxy-9-phenylthio-2,2-tetramethylenebenz-[f]-indane-1,3-dione (10a) (run 13). 1a (37 mg, 0.14 mmol) and 6d (29 mg, 0.11 mmol) were converted into 10a (30 mg, 76%), a yellow solid, mp 172–173 °C. IR (KBr) cm⁻¹: 1736, 1678, 1617, 1595, 1582. ¹H NMR (CDCl₃) δ 1.96–2.05 (8H, m), 7.05–7.18 (5H, m), 7.71 (1H, dd, J = 7.5, 2.0 Hz), 7.77 (1H, dd, J = 7.5, 2.0 Hz), 8.51 (1H, d, J = 9.0 Hz), 8.79 (1H, d, J = 9.0 Hz), 10.46 (1H, br. s). Anal. Calcd for C₂₃H₁₈O₃S: C, 73.78; H, 4.84; S, 8.56. Found: C, 73.62; H, 4.93; S, 8.57.

5-Benzyloxy-4-hydroxy-8-methoxy-9-phenylthio-2,2-tetramethylenebenz-[f]-indane-1,3-dione (10c) (run 15). 1c (65 mg, 0.16 mmol) and 6d (34 mg, 0.12 mmol) were converted into 10c (45 mg, 71%), a yellow solid, mp 163–164 °C (EtOAc). IR (KBr) cm⁻¹: 1728, 1703, 1673, 1605. ¹H NMR (CDCl₃) δ 1.61–1.91 (8H, m), 3.91 (3H, s), 5.28 (2H, s), 7.01 (1H, d, J = 8.0 Hz), 7.03–7.14 (6H, m), 7.39–7.46 (3H, m), 7.53 (2H, d, J = 7.5 Hz), 11.14 (1H, s). Anal. Calcd for C₃₁H₂₆O₅S: C, 72.92; H, 5.13; S, 6.28. Found: C, 73.05; H, 5.19; S, 6.23%.

6-Hydroxy-1-methoxy-11-(phenylthio)naphthacene-5,12-dione (11a) (run 16). 1a (15 mg, 0.056 mmol) and 7 (14 mg, 0.043 mmol) were converted into 11a (13 mg, 73%), an orange solid, mp 235–236 °C (EtOAc). IR (KBr) cm⁻¹: 1676, 1673, 1665, 1619, 1582. ¹H NMR (CDCl₃) δ 4.00 (3H, s), 7.02–7.12 (5H, m), 7.32 (1H, d, J = 8.0 Hz), 7.58–7.60 (2H, m), 7.70 (1H, d, J = 7.5 Hz), 7.97 (1H, d, J = 7.5 Hz), 8.51–8.55 (2H, m), 14.97 (1H, s). Anal. Calcd for C₂₅H₁₆O₄S: C, 72.80; H, 3.91; S, 7.77. Found: C, 72.71; H, 4.03; S, 7.69.

7-Benzyloxy-6-hydroxy-1-methoxy-11-(phenylthio)naphthacene-5,12-dione (11b) (run 17). 1b (35 mg, 0.088 mmol) and 7 (22 mg, 0.071 mmol) were converted into 11b (25 mg, 67%), an orange solid, mp 217–218 °C (EtOAc). IR (KBr) cm⁻¹: 1674, 1622, 1617, 1601, 1576. ¹H NMR (CDCl₃) δ 3.99 (3H, s), 5.31 (2H, s), 7.01–7.10 (5H, m), 7.27–7.51 (6H, m), 7.62–7.72 (3H, m), 7.98 (1H, d, J = 6.5 Hz), 8.23 (1H, d, J = 8.5 Hz), 16.05 (1H, s). Anal. Calcd for C₃₂H₂₂O₅S: C, 74.12; H, 4.28; S, 6.18. Found: C, 74.04; H, 4.39; S, 6.07%.

7-Benzyloxy-6-hydroxy-1,9,10-trimethoxy-11-(phenylthio)naphthacene-5,12-dione (11d) (run 19). 1d (10 mg, 0.024 mmol) and 7 (5.7 mg, 0.018 mmol) were converted into 11d (7.6 mg, 72%), a purple solid, mp 239–240 °C (EtOAc). IR (KBr) cm⁻¹: 1667, 1615, 1574. ¹H NMR
(CDCl$_3$) δ: 3.79 (3H, s), 3.82 (3H, s), 3.90 (3H, s), 5.30 (2H, s), 6.75 (1H, s), 6.95 (1H, t, J = 7.5 Hz), 7.00 (2H, t, J = 7.5 Hz), 7.06 (2H, d, J = 7.5 Hz), 7.19 (1H, d, J = 8.0 Hz), 7.36 (1H, t, J = 7.5 Hz), 7.44 (2H, dd, J = 8.0, 7.5 Hz), 7.61–7.65 (3H, m), 7.93 (1H, d, J = 8.0 Hz), 16.43 (1H, s). High resolution MS Calcd for C$_{34}$H$_{26}$O$_7$S: 578.1399. Found 578.1407.

6-Hydroxy-11-(phenylthio)naphthacene-5,12-dione (12a) (run 20). 1a (30 mg, 0.11 mmol) and 8 (24 mg, 0.086 mmol) were converted into 12a (23 mg, 70%), an orange solid, mp 217–218 °C. IR (KBr) cm$^{-1}$: 1659, 1622, 1592, 1576, 1549. $^1$H NMR (CDCl$_3$) δ: 7.03–7.15 (5H, m), 7.61–7.64 (2H, m), 7.77–7.81 (2H, m), 8.25–8.28 (1H, m), 8.33–8.37 (1H, m), 8.56–8.64 (2H, m), 15.37 (1H, s). Anal. Calcd for C$_{24}$H$_{14}$O$_3$S: C, 75.38; H, 3.69; S, 8.38. Found: C, 75.09; H, 3.87; S, 8.42.

7-Benzyloxy-6-hydroxy-11-(phenylthio)naphthacene-5,12-dione (12b) (run 21). 1b (44 mg, 0.11 mmol) and 8 (25 mg, 0.090 mmol) were converted into 12b (29 mg, 66%), an orange solid, mp 222–223 °C (EtOAc). IR (KBr) cm$^{-1}$: 1669, 1619, 1593, 1578. $^1$H NMR (CDCl$_3$) δ: 5.30 (2H, s), 7.00–7.14 (6H, m), 7.32–7.52 (4H, m), 7.63 (2H, d, J = 7.5 Hz), 7.72–7.75 (2H, m), 8.21–8.37 (3H, m), 16.45 (1H, s). Anal. Calcd for C$_{31}$H$_{20}$O$_4$S: C, 76.21; H, 4.13; S, 6.56. Found: C, 76.14; H, 4.21; S, 6.45.

7-Benzyloxy-6-hydroxy-10-methoxy-11-(phenylthio)naphthacene-5,12-dione (12c) (run 22). 1c (41 mg, 0.10 mmol) and 8 (22 mg, 0.077 mmol) were converted into 12c (27 mg, 68%), a purple solid, mp 194–195 °C (EtOAc). IR (KBr) cm$^{-1}$: 1642, 1619, 1590, 1541. $^1$H NMR (CDCl$_3$) δ: 3.66 (3H, s), 5.26 (2H, s), 6.81 (1H, d, J = 9.0 Hz), 6.96–7.05 (5H, m), 7.35–7.50 (4H, m), 7.62 (2H, d, J = 7.5 Hz), 7.72–7.75 (2H, m), 8.16–8.20 (1H, m), 8.32–8.36 (1H, m), 16.50 (1H, s). Anal. Calcd for C$_{32}$H$_{22}$O$_5$S: C, 74.02; H, 4.44; S, 6.01.

7-Benzyloxy-6-hydroxy-9,10-dimethoxy-11-(phenylthio)naphthacene-5,12-dione (12d) (run 23). 1d (44 mg, 0.10 mmol) and 8 (22 mg, 0.078 mmol) were converted into 12d (30 mg, 70%), a purple solid, mp 184–185 °C (EtOAc). IR (KBr) cm$^{-1}$: 1642, 1619, 1590, 1541. $^1$H NMR (CDCl$_3$) δ: 3.81 (3H, s), 3.82 (3H, s), 5.30 (2H, s), 6.77 (1H, d, J = 9.0 Hz), 6.96–7.05 (5H, m), 7.35–7.50 (4H, m), 7.62 (2H, d, J = 7.5 Hz), 7.72–7.75 (2H, m), 8.16–8.20 (1H, m), 8.32–8.36 (1H, m), 16.50 (1H, s). Anal. Calcd for C$_{33}$H$_{24}$O$_6$S: 548.1293. Found 548.1267.
was stirred at RT overnight, quenched with ice-water and extracted twice with Et\(_2\)O. The organic layer was washed with brine, dried over Na\(_2\)SO\(_4\) and concentrated \textit{in vacuo}. The residue was purified by column chromatography (hexane–EtOAc, 6:1) to give 4,5-(di-tert-butylsilylenedioxy)-9-phenylthio-2,2-tetramethylenebenz-[f]-indane-1,3-dione. This product was dissolved in anhydrous CH\(_2\)Cl\(_2\) (1.5 mL), cooled to -60 °C, and m-CPBA (80% purity, 21 mg, 0.098 mmol) was added, the reaction mixture stirred at -30 °C for 1 h and then at 0 °C for 1 h. The mixture was worked up as in the preparation of 5d, and the product purified by column chromatography (hexane–EtOAc, 2:1) to give 14 (52 mg, 97% from 10b) as a yellow gum, IR (KBr) cm\(^{-1}\) 1736, 1709, 1578. \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.13 (9H, s), 1.15 (9H, s), 1.92–2.13 (8H, m), 7.07 (1H, d, \(J = 8.0\) Hz), 7.37–7.78 (6H, m), 8.69 (1H, d, \(J = 9.0\) Hz). High resolution MS Calcd for C\(_{31}\)H\(_{34}\)O\(_5\)SSi: 546.1893. Found 546.1890.

5-Hydroxy-2,2-tetramethylenebenz-[f]-indane-1,3,4,9-tetra-one (16). Under a nitrogen atmosphere, trifluoroacetic anhydride (0.031 mL, 0.22 mmol) was added to an ice-cooled solution of 13 (12 mg, 0.022 mmol) and styrene (6.7 µl, 0.071 mmol) in anhydrous CH\(_2\)CN (1 mL), and the mixture stirred at 0 °C for 3 h. Ethyl acetate (5 mL) was added, and the whole mixture concentrated \textit{in vacuo}. The residue was dissolved in MeOH (1 mL), and saturated aqueous NaHCO\(_3\) (2 drops) was added. The reaction mixture was stirred at RT for 1 h, then EtOAc (5 mL) added, and saturated aq. NH\(_4\)Cl (2 drops). After stirring for 5 min, the mixture was dried over Na\(_2\)SO\(_4\) and concentrated \textit{in vacuo} to give crude 14. This product was dissolved in THF (0.5 mL) and water (0.1 mL), and Bu\(_4\)NF (1.0 M in THF, 0.010 mL, 0.010 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 2 h, quenched with saturated aq. NH\(_4\)Cl and extracted with CH\(_2\)Cl\(_2\) three times. The combined organic layer was dried over Na\(_2\)SO\(_4\) and concentrated \textit{in vacuo} to give crude 15. Purification by column chromatography (CH\(_2\)Cl\(_2\)–MeOH, 100:1) gave a mixture of 15 and 16, which was dissolved in CH\(_2\)Cl\(_2\) (1 mL), and MnO\(_2\) (95 mg) added. The reaction mixture was stirred overnight, filtered through a Celite pad, concentrated \textit{in vacuo}, and the residue purified by column chromatography (hexane–EtOAc, 5:1) to give 16 (4.8 mg, 75% from 13) as a red–purple solid, mp >300 °C (EtOAc–hexane). IR (KBr) cm\(^{-1}\): 1719, 1634, 1603, 1449. \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.96–1.99 (8H, m), 2.45 (3H, s), 2.55 (3H, s), 2.58 (3H, s), 7.39 (1H, d, \(J = 7.5\) Hz), 7.73 (1H, dd, \(J = 7.5, 8.0\) Hz), 8.16 (1H, d, \(J = 8.0\) Hz). High resolution MS Calcd for C\(_{17}\)H\(_{12}\)O\(_5\): 296.0685. Found 296.0674.

4,5,9-Triacetoxy-2,2-tetramethylenebenz-[f]-indane-1,3-dione (17). As in the preparation of 16, 13 (15 mg, 0.027 mmol) was converted into 15. The crude product was immediately dissolved in pyridine (1.0 mL, 13 mmol), and acetic anhydride (0.40 mL, 4.0 mmol) was added. The reaction mixture was then stirred overnight, filtered through a Celite pad, concentrated \textit{in vacuo}, and the residue purified by column chromatography (hexane–EtOAc, 2:1) to give 17 (9.8 mg, 86% from 13) as a pale yellow solid, mp 245–247 °C (hexane–EtOAc). IR (KBr) cm\(^{-1}\): 1775, 1736, 1711. \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 1.94–1.98 (8H, m), 2.45 (3H, s), 2.55 (3H, s), 2.58 (3H, s), 7.39 (1H, d, \(J = 7.5\) Hz), 7.73 (1H, dd, \(J = 7.5, 8.0\) Hz), 8.16 (1H, d, \(J = 8.0\) Hz). High resolution MS Calcd for C\(_{23}\)H\(_{26}\)O\(_8\)Si: 424.1158. Found 424.1163.
Acknowledgments

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References


14. We also have reported that the similar strong-base-induced [4+2] cycloaddition of homophthalic anhydrides to enolizable enones could be accomplished by using the α-
sulfinyl enones, see: Iio, K.; Ramesh, N. G.; Okajima, A.; Higuchi, K.; Fujioka, H.; Akai, S.;