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# 2-Hydroxybenzocyclobutenone Ethylene Dithioacetals as Precursors of Highly Substituted 1,4-Dihydronaphthalenes

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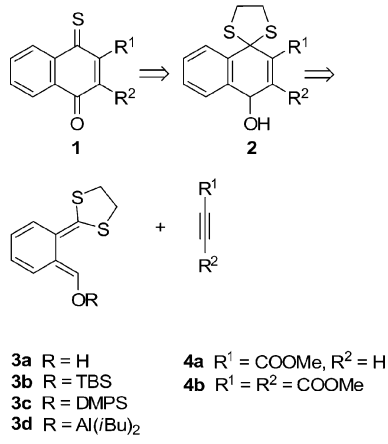
1,4-Dihydronaphthalenes **2**, **9**, and **11** with a spiro-connected 1,3-dithiolane ring as well as tetrahydronaphthalenes **15**, **17**, and **19** have been obtained from *o*-quinodimethanes **3** and alkynes **4**, naphthoquinones **10**, or alkenes **14** and **16**. Benzocyclobutenol **6** is not an appropriate quinodimethane precursor as it readily rearranges to phthalaldehyde derivative **7**. However, silyl ether **8**, silyl ether **13**, obtained by the hydrosilylation of cyclobutenol **5**, or aluminium alkoxide **3d**, generated in situ by DIBAL reduction of **5**, are useful sources of the corresponding quinodimethanes. The use of **3b**,**c** gives a reversal of regioselectivity compared with **3d** in the cycloaddition with propriolate **4a** (product **9a** vs. **2a**). Naphthoquinone **10** reacts in the cycloaddition with **3b**,**c** through its C2=C3 bond or through a C=O unit to give **11** and **12**.


## Introduction

1,4-Dihydronaphthalenes have been called a "privileged" structural class because of their diverse biological activities[1] and thus there is continued interest in their synthesis. The Diels–Alder reaction of dienes with arynes[1] and, in particular, the reaction of *o*-quinodimethanes with alkynes are the most prominent strategies used in the synthesis of 1,4-dihydronaphthalenes.[2] In addition to photoenolization,[3] reactive *o*-quinodimethanes are mostly generated in situ by the electrocyclic ring-opening of benzocyclobutenes.[4] We are interested in 1,4-dihydronaphthalenes because we envisage spiro derivatives **2** as intermediates en route to thionaphthoquinones **1** (Scheme 1). In fact, we have previously shown that 1,3-dithiolane *S*-oxides can be converted into thioaldehydes and -ketones by silylation and subsequent deprotonation.[5] This means that spiro compounds **2** should be only two oxidation steps away from the target molecules **1** and with appropriately chosen substituents, even thio analogues of vitamin K might be available.

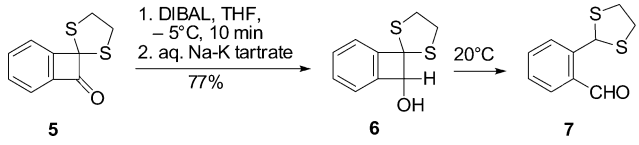
The obvious route to dihydronaphthalenes **2** appears to be the [4+2] cycloaddition of functionalized *o*-quinodimethanes **3** with alkynes **4** (Scheme 1). However, it turns out that dienol **3a** cannot be employed in Diels–Alder chemistry because of its low stability. In contrast, its silyl ether derivative **3b**, the in-situ generated silyl ether **3c**, and the aluminium salt **3d** are useful dienes in cycloaddition reactions with alkynes **4** and also with alkenes.[6]




Scheme 1. A potential route to thionaphthoquinones.

## Results and Discussion

The readily available benzocyclobutenedione monothioketal **5**[7] can be smoothly reduced to alcohol **6** by DIBAL. After work-up **6** is obtained in 77% yield, but within minutes at room temperature it rearranges to aldehyde **7** by electrocyclic ring-opening and a subsequent [1,5] hydrogen shift (Scheme 2). This ready rearrangement prevents the use of benzocyclobutenol **6** in Diels–Alder chemistry.




Scheme 2. Synthesis and rearrangement of benzocyclobutenol **6**.

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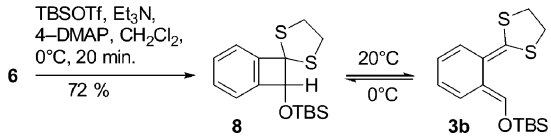
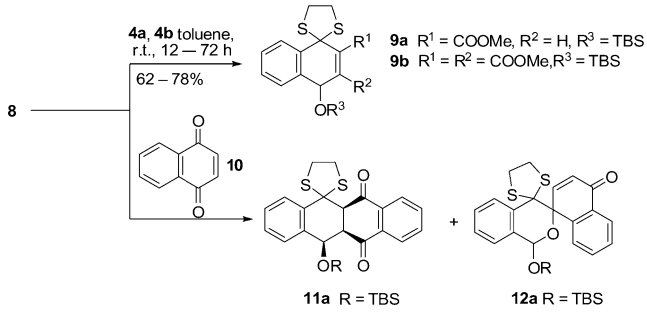
One way to suppress this reaction, at least to some extent, is to trap the alcohol **6** as the silyl ether **8**. This compound is remarkably stable and may be stored at room temperature for at least 3 days. Silyl ether **8** exists in equilibrium with the corresponding ring-opened product **3b** (Scheme 3). Thus, due to the different colors of the two compounds, a color change can be observed on going from **3b** (deep yellow at room temperature) to **8** (colorless at 0 °C) on cooling.




Scheme 3. Stabilization of benzocyclobutenol **6** as the silyl ether **8** and its electrocyclic ring-opening.

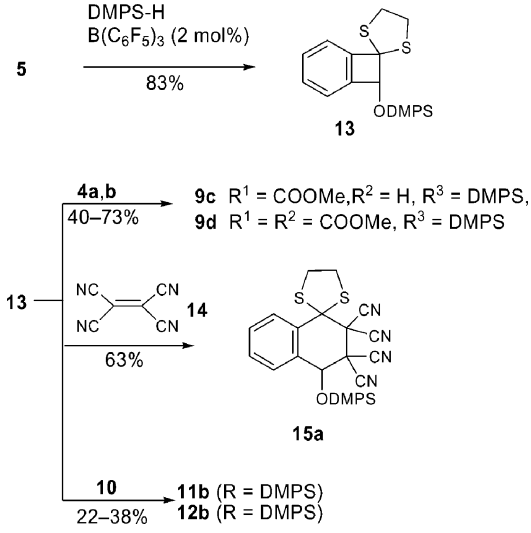
TBS ether **8** undergoes Diels–Alder reactions with electron-deficient alkynes **4** in good yields, clearly reacting in its ring-opened form **3b** (Scheme 4). Thus, stirring **8** with an alkyne **4** at room temperature in toluene leads to naphthalenes **9a**,**b** with the regiochemistry shown in Scheme 4.




Scheme 4. Reaction of silyl ether **8** with alkynes **4** or 1,4-naphthoquinone **10**.

Particularly interesting is the reaction of silyl enol ether **8** with 1,4-naphthoquinone (**10**). Here, the expected tetracyclic silyl enol ether **11a** is only the minor product; the major product is the isochromane **12a** generated by a hetero-Diels–Alder reaction (Scheme 4). The structure of **12a** may be delineated primarily from the NMR spectroscopic data, but it is unambiguously supported by a single-crystal X-ray structure determination (Figure 1). This cycloaddition behavior is typical of light-induced reactions,[8] but several experiments in the dark led to exactly the same product ratio of 1:2. So far, only in one case are thermally induced hetero-Diels–Alder products of benzoquinones described in the literature.[9]

These successful applications of silyl dienol ether **8** called for a more reliable synthesis that would prevent any formation of the rearrangement product **7**. With this in mind, hydrosilylation of the carbonyl unit in **1** seemed promising. Unfortunately, the use of *tert*-butyldimethylsilane in combination with transition-metal catalysts (Re-,[10] Ru-,[11] or Rh-based[12]) or several Lewis acids[13] was not successful. However, the use of dimethyl(phenyl)silane (DMPS-H) and tris(pentafluorophenyl)borane[14] as catalyst led to the successful hydrosilylation of **5**, affording silyl ether **13** in good yield and free from aldehyde **7**. In a convenient one-pot procedure alkyne dienophiles can be added to the crude silyl ether to provide naphthalenes **9c**,**d** directly (Scheme 5). Again, the cycloaddition certainly involves intermediate **3c**, which also reacts with tetracyanoethene (**14**) to give Diels–Alder adduct **15a**. With 1,4-naphthoquinone (**10**), as with the silyl ether **8**/*o*-quinodimethane **3b** system, the competing formation of cycloadducts **11b** and **12b** (cf. Scheme 4) is observed in a similar ratio of 1:1.5 (Scheme 5).




Scheme 5. Reaction of silyl ether **13** with alkynes **4**, 1,4-naphthoquinone (**10**), or tetracyanoethene (**14**).

In an alternate approach, which also excludes the formation of **7**, the alcohol **6** was not isolated after the reaction of **5** with DIBAL, but employed as the aluminium salt **3d** in reactions with alkynes **4**. With acetylenedicarboxylate this gives the [4+2] cycloadduct **2b** in about the same yield as starting from silyl ether **8**, but interestingly a different product **2a** with propiolate. This turned out to be the regioisomer of **9a**. The structure was assigned on the basis of the pattern of proton couplings in the NMR spectra. The decisive feature is the $^1$H NMR signal of the single proton, which is observed as a singlet for **2a** but as a doublet ($J$ =

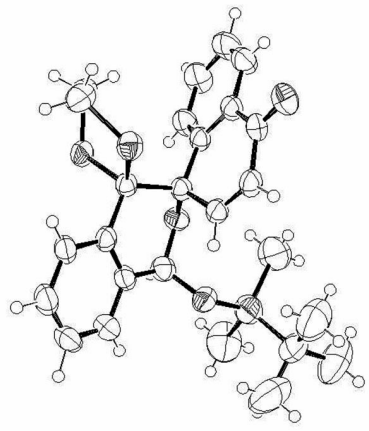
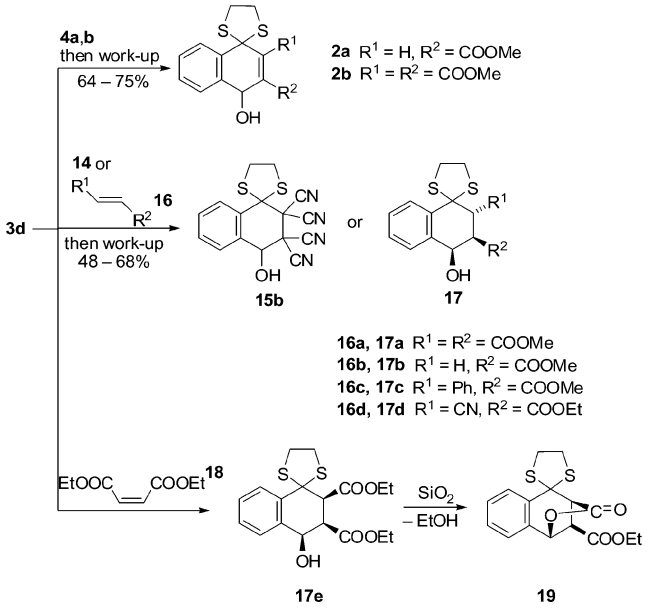


Figure 1. Crystal structure of **12a** (ORTEP plot).

2.9 Hz) for **9a**. The regiochemical dichotomy of these reactions leads us to assume that **9a**,**b** are formed in a classic concerted Diels–Alder reaction, but that in the formation of **2a** a Michael-type pathway with subsequent ring-closure directs the electron-withdrawing group adjacent to the hydroxy group.

Following the successful reactions with alkynes **4**, we investigated the reaction of the aluminium salt **3d** with a wide range of electron-deficient alkenes. Some interesting products are reported in Scheme 6. In all cases, *endo* products with a *cis* arrangement of the alcohol and the neighboring functional group are isolated. The cycloaddition reactions of **3d** all proceed at room temperature, which indicates that the benzo-annulated diene unit in **3d** is more reactive than the corresponding acyclic species, which is generated from cyclobutenyl silyl ethers and requires refluxing toluene for some reaction partners.[15]




Scheme 6. Reaction of the aluminium salt **3d** with dienophiles (only one enantiomer is shown; products after work-up).

Particularly interesting is the reaction of aluminium salt **3d** and diethyl maleate (**18**, Scheme 6). The expected naphthalene **17e** was observed in the crude product, which on flash chromatography was converted into lactone **19** by acid-induced transesterification, clearly under the action of silica gel.

The composition and expected configuration of **19** were confirmed by an X-ray crystal analysis (Figure 2). A similar γ-lactone formation has previously been observed by Sammes and co-workers.[3a,3b]

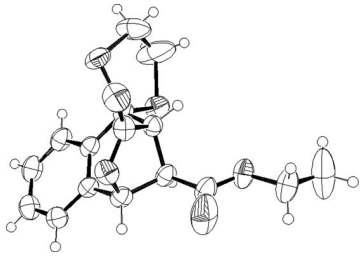


Figure 2. Crystal structure of **19** (ORTEP plot).

## Conclusions

The ring-opening of alcohol **6** to monoprotected phthalaldehyde **7** can be avoided by using silyl ethers **8** and **13** in the Diels–Alder reactions. This approach is complemented by employing aluminium salt **3d** in the cycloaddition reactions, which gives similar yields in the cycloaddition reactions with alkynes **4**. However, a striking feature of these latter reactions is the reversal of the regioselectivity as compared with the use of silyl ethers **8** and **13**. The success of these model reactions is encouraging in the pursuit of spiro compounds **2** as intermediates in thioquinone synthesis.

## Experimental Section

**General:** All reactions were carried out under nitrogen. $^1$H and $^{13}$C NMR spectra were recorded with Bruker DPX-200 and AMX-400 instruments in $CDCl_3$ as solvent. Chemical shifts were measured in $\delta$ (ppm) and coupling constants $J$ in Hz. TMS was used as reference for $^1$H NMR spectra ($\delta$ = 0.00 ppm). The solvent peak was used as the reference for $^{13}$C NMR spectra ($\delta$ = 77.00 ppm). To assign the number of substituents attached to a specified carbon, each carbon is described as + (primary or tertiary carbon), – (secondary carbon) or o (quaternary carbon), as determined by the DEPT method. When necessary, NMR spectroscopic data were assigned by using H–H and C–H correlation spectra. Melting points are uncorrected. MS were recorded with a Hewlett–Packard 5980 GC and a Hewlett–Packard 5989B MS. IR spectra were recorded with a Bruker Vektor 22 FTIR spectrometer. TLC was performed on Merck 60 $F_{254}$ precoated silica plates and spots were detected by spraying with a solution of 10% $KMnO_4$ and 0.5 M $K_2CO_3$ in $H_2O$ and heating. Flash chromatography was performed with silica gel 60 (Merck, 40–63 μm). Petroleum ether (PE) with the boiling range 60–70 °C was used in the separations. All solvents were distilled before use.

**2*H*-Spiro[cyclobutabenzene-1,2′-[1,3]dithiolan]-2-ol (6):** A solution of benzocyclobutenone **5** (208 mg, 1 mmol) in dry THF (5 mL) was treated with diisobutylaluminium hydride (1 M in hexanes, 1.1 mL, 1.1 mmol) at –5 °C. The reaction was complete after 10 min and saturated sodium potassium tartrate (10 mL) and $Et_2O$ (10 mL) were added. The resulting mixture was vigorously stirred for 20 min. The aqueous phase was separated and extracted with $Et_2O$ (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried. Removal of the solvent in vacuo followed by flash chromatography (PE/EtOAc, 10:1) provided the product as a colorless oil (161 mg, 77% yield). IR (film): $\tilde{\nu}$ = 3394, 3064, 2923, 1590, 1450, 1420, 1390, 1274, 1174, 1151, 1103, 1059, 913, 747 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.36 (m, 3 H), 7.26 (m, 1 H), 5.17 (s, 1 H), 3.53 (m, 1 H), 3.40 (m, 2 H), 3.31 (m, 1 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 145.9 (o), 141.6 (o), 130.7 (+), 130.6 (+), 123.5 (+), 123.1 (+), 84.1 (+), 75.7 (o), 40.1 (–), 39.4 (–) ppm. MS (CI): *m*/*z* = 211, 210, 182, 166, 149, 134. HRMS (EI): calcd. for $C_{10}H_{10}OS_2$: 210.0173; found 210.0166.

**2-(1,3-Dithiolan-2-yl)benzaldehyde (7):** On standing at room temperature, product **6** isomerized to phthalaldehyde derivative **7**; this conversion was complete within a few hours. $^1$H NMR (200 MHz): $\delta$ = 10.09 (s, 1 H), 7.80, 7.58, 7.37, 7.28 (each m, 1 H), 6.46 (s, 1

H), 3.23 (m, 4 H) ppm. $^{13}$C NMR (50 MHz): $\delta$ = 192.7 (+), 147.7 (o), 142.9 (o), 133.8 (+), 133.75 (+), 130.3 (+), 129.1 (+), 51.22 (+), 39.8 (–) ppm.

***tert*-Butyldimethylsilyl [6-(1,3-Dithiolan-2-ylidene)cyclohexa-2,4-dienylidene]methyl Ether (8):** A solution of alcohol **6** (210 mg, 1.0 mmol) in dry $CH_2Cl_2$ (4 mL) was treated with $Et_3N$ (0.42 mL, 3.0 mmol), 4-DMAP (12 mg, 0.1 mmol) and TBSOTf (0.25 mL, 1.1 mmol) at 0 °C. The reaction was complete after 1 h and saturated $NaHCO_3$ (10 mL) and $CH_2Cl_2$ were added. The aqueous phase was separated and extracted with $CH_2Cl_2$ (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried. Removal of the solvent in vacuo followed by flash chromatography (PE/EtOAc, 50:1) provided the product as a yellow oil (236 mg, 72% over two steps). IR (film): $\tilde{\nu}$ = 2953, 2927, 2855, 1471, 1459, 1361, 1255, 1205, 1186, 1120, 1080, 882, 837, 779, 738 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.32 (m, 3 H), 7.16 (m, 1 H), 5.43 (s, 1 H), 3.28–3.51 (m, 4 H), 0.99 (s, 9 H), 0.22, 0.21 (each, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 146.2 (o), 145.1 (o), 130.5 (+), 129.8 (+), 122.8 (+), 122.3 (+), 84.3 (+), 75.4 (o), 40.6 (–), 39.4 (–), 25.9 (+, 3 C), 18.5 (o), –4.3 (+), –4.5 (+) ppm. MS (CI): *m*/*z* = 325, 324, 267, 256, 239, 207, 165, 149, 133, 121. HRMS (EI): calcd. for $C_{16}H_{25}OS_2Si$: 324.1037; found 324.1034.

**Cycloaddition Reactions of Silyl Ether 8 with Alkynes 4 or Naphthoquinone 10. General Procedure:** A solution of silyl ether **8** (324 mg, 1 mmol) in toluene (4 mL) was treated with the dienophile **4** or **10** (1.1 mmol) at room temp. The reaction was complete after 36–48 h. The solvent was removed in vacuo and the crude product was purified by flash chromatography.

**Methyl 4′-{[*tert*-Butyl(dimethyl)silyl]oxy}-4′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-2′-carboxylate (9a):** Yield 253 mg (62%). IR (film): $\tilde{\nu}$ = 2953, 2929, 2857, 1732, 1652, 1472, 1434, 1361, 1266, 1230, 1199, 1126, 1085, 1050, 1035, 911, 848, 836, 776, 756 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.99 (d, *J* = 8.1 Hz, 1 H), 7.40 (d, *J* = 7.7 Hz, 1 H), 7.34 (t, *J* = 8.1 Hz, 1 H), 7.26 (m, *J* = 7.7 Hz, 1 H), 6.85 (d, *J* = 2.9 Hz, 1 H), 5.30 (d, *J* = 2.9 Hz, 1 H), 3.91 (m, 2 H), 3.83 (s, 3 H), 3.79 (m, 1 H), 3.67 (m, 1 H), 0.96 (s, 9 H), 0.19 (s, 3 H), 0.11 (s, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 166.4 (o), 140.8 (o), 138.7 (o), 135.2 (o), 135.1 (o), 122.8 (+), 127.9 (+), 127.2 (+), 126.1 (+), 65.2 (+), 62.3 (o), 52.0 (+), 44.3 (–), 43.4 (–), 25.8 (+, 3 C), 18.1 (o), –4.0 (–), –4.3 (–) ppm. MS (CI): *m*/*z* = 409, 408, 377, 351, 316, 277, 259, 245, 218, 186, 158. HRMS (EI): calcd. for $C_{20}H_{28}O_2S_2Si$: 408.1249; found 408.1248.

**Dimethyl 4′-{[*tert*-Butyl(dimethyl)silyl]oxy}-4′-spiro[1,3-dithiolane-2,1′-naphthalene]-2′,3′-dicarboxylate (9b):** Yield 363 mg (78%). IR (film): $\tilde{\nu}$ = 2954, 2928, 2856, 1728, 1643, 1472, 1434, 1260, 1204, 1139, 1086, 1050, 966, 881, 837, 776, 735 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.97 (d, *J* = 8.0 Hz, 1 H), 7.34 (m, 1 H), 7.25 (m, 2 H), 5.69 (s, 1 H), 3.82 (s, 6 H), 3.71 (m, 2 H), 3.62 (m, 1 H), 3.54 (m, 1 H), 0.78 (s, 9 H), 0.08, 0.04 (each s, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 167.3 (o), 165.8 (o), 148.2 (o), 141.2 (o), 135.3 (o), 131.2 (o), 128.5 (+), 128.4 (+), 128.2 (+), 127.4 (+), 65.9 (+), 63.7 (o), 52.4 (+), 52.2 (+), 44.2 (–), 42.4 (–), 25.5 (+, 3 C), 17.9 (o), –4.3 (+), –4.4 (+) ppm. MS (CI): *m*/*z* = 409, 377, 305, 291, 276, 244, 213, 133. HRMS (EI): calcd. for $C_{22}H_{30}O_5S_2Si$ – *t*Bu: 409.0600; found 409.0600.

**12′-{[*tert*-Butyl(dimethyl)silyl]oxy}-11a′,12′-dihydro-5a′*H*-spiro[1,3-dithiolane-2,5′-tetracene]-6′,11′-dione (11a):** Yield 121 mg (25%). IR (film): $\tilde{\nu}$ = 2958, 2927, 2856, 1708, 1688, 1596, 1472, 1327, 1288, 1254, 1215, 1115, 1051, 981, 911, 848, 836, 824, 776, 754, 734 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 8.09 (m, 1 H), 8.05 (dd, *J* = 8.1, 1.0 Hz, 1 H), 7.89 (m, 1 H), 7.68 (m, 2 H), 7.36 (dt, *J* = 1.3, 7.7 Hz, 1 H), 7.20 (dt, *J* = 1.1, 7.7 Hz, 1 H), 7.11 (dd, *J* = 7.7, 1.1 Hz, 1 H), 5.17 (d, *J* = 3.9 Hz, 1 H), 4.22 (dd, *J* = 3.9, 5.1 Hz, 1 H), 4.02 (d, *J* = 5.1 Hz, 1 H), 3.65, 3.49, 3.36, 3.16 (m, 1 H), 0.33 (s, 9 H), –0.07, –0.55 (s, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 197.0 (o), 194.9 (o), 139.0 (o), 138.8 (o), 135.7 (o), 134.5 (o), 134.0 (+), 132.7 (+), 129.6 (+), 129.3 (+), 129.2 (+), 127.5 (+), 127.2 (+), 125.8 (+), 70.0 (+), 67.3 (o), 60.0 (+), 56.1 (+), 43.0 (–), 39.7 (–), 25.3 (+, 3 C), 17.8 (o), –4.5 (+), –4.6 (+) ppm. MS (CI): *m*/*z* = 483, 482, 467, 425, 351, 290, 277, 258, 244, 215, 202. HRMS (EI): calcd. for $C_{26}H_{30}O_3S_2Si$: 482.1405; found 482.1397.

**1′-{[*tert*-Butyl(dimethyl)silyl]oxy}-1′*H*,4′′*H*-dispiro[1,3-dithiolane-2,4′-isochromene-3′,1′′-naphthalen]-4′′-one (12a):** Yield 328 mg (68%); m.p. 114–117 °C (dec.). IR (film): $\tilde{\nu}$ = 2954, 2928, 2885, 2856, 1637, 1598, 1471, 1388, 1360, 1329, 1299, 1253, 1214, 1093, 1028, 1004, 840, 763 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 8.29 (d, *J* = 8.0 Hz, 1 H), 8.05 (dd, *J* = 1.0, 7.7 Hz, 1 H), 7.88 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.57, 7.49 (dt, *J* = 1.0, 7.8 Hz, 1 H), 7.42 (d, *J* = 10.6 Hz, 1 H), 7.33 (m, 3 H), 6.37 (s, 1 H), 6.32 (d, *J* = 10.5 Hz, 1 H), 3.19 (dt, *J* = 4.8, 10.5 Hz, 1 H), 2.93 (dt, *J* = 11.4, 4.1 Hz, 1 H), 2.67 (dt, *J* = 11.0, 4.1 Hz, 1 H), 1.48 (dt, *J* = 4.8, 11.4 Hz, 1 H), 0.90 (s, 9 H), 0.24, 0.04 (s, 3 H) ppm. $^{13}$C NMR (50 MHz, $C_6D_6$): $\delta$ = 183.7 (o), 146.7 (+), 140.7 (o), 138.5 (o), 137.9 (o), 134.6 (o), 133.9 (+), 131.0 (+), 130.0 (+), 129.6 (+), 129.3 (+), 129.1 (+), 126.8 (+), 126.1 (+), 125.1 (+), 91.8 (+), 77.3 (o), 77.4 (o), 41.8 (–), 40.9 (–), 25.8 (+, 3 C), 18.1 (o), –3.9 (+), –5.3 (+) ppm. MS (EI): *m*/*z* = 483, 425, 324, 239, 165, 149, 73. HRMS (EI): calcd. for $C_{26}H_{30}O_3S_2Si$ – *t*Bu: 425.0699; found 425.0701.

**Crystal Data of 12a:** $C_{26}H_{30}O_3S_2Si$ (486.68), crystal size 0.30 × 0.33 × 0.41 mm. The crystal structure was determined by X-ray diffraction analysis using graphite-monochromated Mo-$K_\alpha$ radiation (0.71073 Å) [*T* = 293(2) K]. The scattering intensities were collected with a single-crystal diffractometer (STOE IPDS II). The crystal structure was solved by direct methods using SHELXS-97 and refined by using alternating cycles of least-squares refinements against $F^2$ (SHELXL-97). All non-hydrogen atoms were located in difference Fourier maps and were refined with anisotropic displacement parameters. The hydrogen positions were determined by a final difference Fourier synthesis. The compound crystallized orthorhombic crystals, space group *Pbca*, unit cell dimensions: *a* = 8.608(1), *b* = 16.130(1), *c* = 37.242(1) Å, cell volume *V* = 5170.9(7) Å$^3$, *Z* = 8, *F*(000) = 2064 using 5292 independent reflections and 350 parameters, $R_1$ = 0.0581, $wR_2$ = 0.1497 [$I > 2\sigma(I)$], goodness of fit on $F^2$ = 1.040, residual electron density: 0.271 and –0.514 e Å$^{-3}$.

CCDC-226514 contains the supplementary crystallographic data for **12a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**In situ Reduction of Ketone 5 and Cycloaddition Reactions with Alkynes 4, Quinone 10, or Alkene 14. General Procedure:** A solution of ketone **5** (208 mg, 1 mmol) in dry toluene (5 mL) was treated with tris(pentafluorophenyl)borane solution (0.77 M in toluene, 2 mol-%) and dimethyl(phenyl)silane (1.1 mmol) at room temp. The reaction was complete after 10 min and the appropriate dienophile (1.1 mmol) was added. The resulting mixture was stirred at room temp. for 16–24 h. Saturated $NaHCO_3$ solution (5 mL) was added. The aqueous phase was separated and extracted with toluene (3 × 3 mL). The combined organic layers were washed with brine (10 mL) and dried with $Na_2SO_4$. Removal of the solvent in vacuo followed by flash chromatography (PE/EtOAc, 10:1) gave the products **9c**,**d**, **11b**, **12b**, and **15a**, respectively.

**Methyl 4′-{[Dimethyl(phenyl)silyl]oxy}-4′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-2′-carboxylate (9c):** Yield 312 mg (73%). IR

(film): $\tilde{\nu}$ = 3068, 2956, 1733, 1429, 1252, 1120, 1084, 1021, 871, 829, 701 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.96 (m, 1 H), 7.64 (m, 1 H), 7.60 (m, 1 H), 7.40 (m, 4 H), 7.31 (m, 1 H), 7.22 (m, 1 H), 6.75 (d, $J$ = 3.1 Hz, 1 H), 5.32 (d, $J$ = 3.1 Hz, 1 H), 3.91 (m, 2 H), 3.78 (s, 3 H), 3.67 (m, 2 H), –0.27 (s, 3 H), –1.0 (s, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 166.2 (o), 141.0 (o), 137.9 (+), 137.2 (o), 134.9 (o), 134.4 (o), 133.6 (+), 133.0 (+), 129.9 (+), 128.0 (+), 127.9 (+), 127.3 (+), 126.4 (+), 65.2 (+), 62.2 (o), 51.2 (+), 44.4 (–), 43.6 (–), –0.83 (+), –1.1 (+) ppm. MS (EI): $m/z$ = 428, 393, 367, 335, 307, 290, 262, 233, 202, 135, 107, 91, 51. HRMS (EI): calcd. for $C_{22}H_{24}O_3S_2Si$: 428.0936; found 428.0929.

**Dimethyl 4′-{[Dimethyl(phenyl)silyl]oxy}-4′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-2′,3′-dicarboxylate (9d):** Yield 194 mg (40%); m.p. 107–108 °C. IR (film): $\tilde{\nu}$ = 3070, 2949, 1722, 1427, 1368, 1263, 1119, 1016, 962, 889, 831, 701 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.97 (dd, $J$ = 8.0, 1.2 Hz, 1 H), 7.54 (m, 2 H), 7.35 (m, 4 H), 7.17 (dt, $J$ = 7.6, 1.2 Hz, 1 H), 7.04 (dd, $J$ = 7.6, 1.4 Hz, 1 H), 5.75 (s, 1 H), 3.83 (s, 3 H), 3.71 (m, 2 H), 3.64 (s, 3 H), 3.59 (m, 2 H), 0.36 (s, 3 H), 0.35 (s, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 167.1 (o), 165.5 (o), 147.9 (o), 140.9 (o), 138.0 (o), 134.8 (o), 133.5 (+), 131.0 (o), 129.4 (+), 128.4 (+), 128.3 (+), 128.2 (+), 127.6 (+), 127.4 (+), 65.8 (+), 63.5 (o), 52.2 (+), 52.1 (+), 44.0 (–), 42.4 (–), –0.28 (+), –1.1 (+) ppm. MS (EI): $m/z$ = 486, 471, 458, 408, 398, 367, 348, 334, 316, 262, 233, 195, 135, 107, 61. HRMS (EI): calcd. for $C_{24}H_{26}O_5S_2Si$: 486.0991; found 486.0990.

**12′-{[Dimethyl(phenyl)silyl]oxy}-11a′,12′-dihydro-5′a*H*-spiro[1,3-dithiolane-2,5′-tetracene]-6′,11′-dione (11b):** Yield 108 mg (22%). IR (film): $\tilde{\nu}$ = 3068, 2958, 1771, 1694, 1595, 1427, 1255, 1118, 1051, 982, 832 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 8.11 (m, 1 H), 8.01 (dd, $J$ = 8.0, 1.0 Hz, 1 H), 7.87 (m, 1 H), 7.63 (m, 2 H), 7.25 (m, 4 H), 7.16 (dd, $J$ = 8.0, 1.0 Hz, 2 H), 6.95 (dt, $J$ = 7.5, 1.2 Hz, 1 H), 6.60 (d, $J$ = 7.5 Hz, 1 H), 5.11 (d, $J$ = 3.5 Hz, 1 H), 4.18 (dd, $J$ = 5.0, 3.5 Hz, 1 H), 4.02 (d, $J$ = 5.0 Hz, 1 H), 3.65, 3.48, 3.34, 3.16 (m, 1 H), –0.23, –0.31 (s, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 197.0 (o), 195.1 (o), 139.1 (o), 138.8 (o), 136.6 (o), 135.6 (o), 134.0 (+), 133.8 (o), 133.4 (+), 132.7 (+), 129.7 (+), 129.5 (+), 129.3 (+), 129.0 (+), 127.8 (+), 127.7 (+), 127.4 (+), 126.5 (+), 125.6 (+), 70.1 (+), 67.3 (o), 59.9 (+), 56.3 (+), 42.9 (–), 39.6 (–), –2.1 (+), –2.3 (+) ppm. HRMS (EI): calcd. for $C_{28}H_{26}O_3S_2Si$: 502.1093; found 502.1095.

**1′-{[Dimethyl(phenyl)silyl]oxy}-1′*H*,4′′*H*-dispiro[1,3-dithiolane-2,4′-isochromene-3′,1′′-naphthalen]-4′′-one (12b):** Yield 187 mg (38%); m.p. 145–146 °C. IR (film): $\tilde{\nu}$ = 2917, 1673, 1597, 1429, 1387, 1347, 1254, 1211, 1118, 1020, 957, 834, 699 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 8.32 (dd, $J$ = 0.9, 7.9 Hz, 1 H), 8.10 (dd, $J$ = 1.0, 7.7 Hz, 1 H), 7.91 (m, 1 H), 7.60 (m, 3 H), 7.49 (dt, $J$ = 1.0, 7.7 Hz, 1 H), 7.38 (d, $J$ = 10.6 Hz, 1 H), 7.37 (m, 4 H), 7.28 (m, 2 H), 6.42 (s, 1 H), 6.25 (d, $J$ = 10.6 Hz, 1 H), 3.21 (m, 1 H), 2.93 (m, 1 H), 2.67 (m, 1 H), 1.48 (m, 1 H), 0.51, 0.50 (each s, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 184.7 (o), 146.8 (+), 140.3 (o), 137.6 (o), 136.7 (o), 133.7 (+), 133.6 (o), 133.3 (o), 130.3 (+), 129.8 (+), 129.0 (+), 129.0 (+), 128.8 (+), 128.0 (+), 127.9 (+), 127.7 (+), 126.6 (+), 124.6 (+), 91.4 (+), 77.1 (o), 76.8 (o), 41.9 (–), 40.9 (–), –1.3 (+), –1.4 (+) ppm. MS (ESI): $m/z$ = 525 [M + Na]$^+$. HRMS (EI): calcd. for $C_{28}H_{26}O_3S_2Si$: 502.1093; found 502.1094.

**4′-{[Dimethyl(phenyl)silyl]oxy}-2′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-2′,2′,3′,3′(4*H*)-tetracarbonitrile (15a):** Yield 297 mg (63%). IR (film): $\tilde{\nu}$ = 3072, 2961, 2273, 1774, 1481, 1428, 1259, 1209, 1117, 911, 826, 738 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.70 (d, $J$ = 8.0 Hz, 1 H), 7.67 (m, 2 H), 7.46 (m, 4 H), 7.30 (m, 1 H), 7.13 (d, $J$ = 8.0 Hz, 1 H), 5.49 (s, 1 H), 3.81 (m, 4 H), 0.74 (s, 3 H), 0.67 (s, 3 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 134.1 (o), 133.9 (o), 133.8 (+, 2 C), 131.1 (+), 130.9 (+), 130.8 (o), 130.2 (+), 129.9 (+), 128.4 (+, 2 C), 126.5 (+), 111.4 (o), 110.4 (o), 110.3 (o), 108.6 (o), 72.4 (+), 71.5 (o), 53.6 (o), 44.0 (–), 43.1 (o), –0.86 (+), –1.54 (+) ppm. MS (ESI): $m/z$ = 495 [M + Na]$^+$. HRMS (EI): calcd. for $C_{24}H_{20}N_4OS_2Si$: 472.0848; found 472.0848.

**Cycloaddition Reactions of Alkoxide 3d. General Procedure:** A solution of ketone **5** (208 mg, 1 mmol) in dry THF (5 mL) was treated with diisobutylaluminium hydride (1 M in hexanes, 1.1 mL, 1.1 mmol) at –5 °C. The reaction was complete after 10 min and dienophile **4**, **14**, **16** or **18** (1.1 mmol) was added. The resulting mixture was warmed to room temp. and stirred for 10 h. Saturated sodium potassium tartrate (10 mL) and $Et_2O$ (10 mL) were added and the mixture was vigorously stirred for 20 min. The aqueous phase was separated and extracted with $Et_2O$ (3 × 5 mL). The combined organic layers were washed with brine (10 mL) and dried. Removal of the solvent in vacuo followed by flash chromatography (PE/EtOAc, 2:1) gave products **2a**,**b**, **15b**, **17a**–**d**, or **19**.

**Methyl 4′-Hydroxy-4′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-3′-carboxylate (2a):** Yield 188 mg (64%); m.p. 101–102 °C. IR (film): $\tilde{\nu}$ = 3485, 2950, 2922, 1710, 1650, 1484, 1437, 1278, 1250, 1220, 1126, 1027, 1007, 965, 911, 762, 733 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.97 (d, $J$ = 7.7 Hz, 1 H), 7.55 (d, $J$ = 7.4 Hz, 1 H), 7.34 (m, 2 H), 7.20 (s, 1 H), 5.49 (s, 1 H), 3.87 (s, 3 H), 3.73 (m, 2 H), 3.63 (m, 2 H), 3.47 (br. s, 1 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 167.6 (o), 142.1 (+), 135.3 (o), 135.1 (o), 130.0 (+), 128.6 (+), 128.4 (+), 128.3 (+), 123.6 (o), 63.0 (+), 62.6 (o), 52.2 (+), 42.1 (–), 41.9 (–) ppm. MS (CI): $m/z$ = 294, 276, 245, 219, 187, 145, 128. HRMS (EI): calcd. for $C_{14}H_{14}O_3S_2$: 294.0384; found 294.0388.

**Dimethyl 4′-Hydroxy-4′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-2′,3′-dicarboxylate (2b):** Yield 264 mg (75%); m.p. 135–136 °C. IR (film): $\tilde{\nu}$ = 3483, 2951, 1726, 1639, 1485, 1435, 1266, 1206, 1144, 1086, 922, 961, 912, 732 cm$^{-1}$. $^1$H NMR (400 MHz): $\delta$ = 7.94 (m, 1 H), 7.46 (m, 1 H), 7.34 (m, 2 H), 5.60 (s, 1 H), 3.86, 3.84 (each s, 3 H), 3.69 (m, 4 H), 2.79 (br. s, 1 H) ppm. $^{13}$C NMR (100 MHz): $\delta$ = 167.1 (o), 165.7 (o), 147.5 (o), 139.6 (o), 133.7 (o), 129.6 (o), 128.8 (+), 128.4 (+, 2 C), 128.1 (+), 64.6 (+), 63.6 (o), 52.8 (+), 52.4 (+), 43.9 (–), 42.8 (–) ppm. MS (EI): $m/z$ = 352, 320, 292, 260, 233, 145, 59. HRMS (EI): calcd. for $C_{16}H_{16}O_5S_2$: 352.0440; found 352.0439.

**4′-Hydroxy-2′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-2′,2′,3′,3′(4′*H*)-tetracarbonitrile (15b):** Yield 162 mg (48%); m.p. 142–144 °C. IR (KBr): $\tilde{\nu}$ = 3280, 2917, 2849, 1707, 1483, 1455, 1422, 1374, 1316, 1246, 1207, 1144, 1045, 980, 893, 770, 744, 730 cm$^{-1}$. $^1$H NMR (200 MHz): $\delta$ = 7.93 (d, $J$ = 7.6 Hz, 1 H), 7.61 (dt, $J$ = 1.5, 7.4 Hz, 1 H), 7.43 (dt, $J$ = 7.6, 1.5 Hz, 1 H), 7.21 (d, $J$ = 7.4 Hz, 1 H), 5.31 (s, 1 H), 3.84 (m, 4 H) ppm. $^{13}$C NMR (50 MHz): $\delta$ = 137.6 (o), 137.5 (o), 132.8 (+), 132.5 (+), 129.8 (+), 127.5 (+), 110.4 (o), 110.3 (o), 108.7 (o), 108.6 (o), 80.5 (o), 80.1 (o), 60.4 (o), 53.5 (+), 43.8 (–), 43.2 (–) ppm. MS (EI): $m/z$ = 338, 310, 267, 235, 209, 181, 164, 149, 121. HRMS (EI): calcd. for $C_{16}H_{10}N_4OS_2$: 338.0296; found 338.0297.

**Dimethyl (2′*S**,3′*R**)-4′-Hydroxy-3′,4′-dihydro-2′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-2′,3′-dicarboxylate (17a):** Yield 242 mg (68%); m.p. 126–128 °C. IR (KBr): $\tilde{\nu}$ = 3466, 2954, 1784, 1741, 1484, 1437, 1364, 1286, 1200, 1059, 960, 855, 771, 683 cm$^{-1}$. $^1$H NMR (200 MHz): $\delta$ = 7.92 (d, $J$ = 7.6 Hz, 1 H), 7.32 (m, 3 H), 5.06 (d, $J$ = 3.8 Hz, 1 H), 3.89 (d, $J$ = 10.7 Hz, 1 H), 3.77, 3.76 (each s, 3 H), 3.61 (dd, $J$ = 10.7, 3.8 Hz, 1 H), 3.48 (m, 4 H) ppm. $^{13}$C NMR (50 MHz): $\delta$ = 172.1 (o), 171.9 (o), 140.2 (o), 134.9 (o), 130.3 (+), 129.1 (+), 128.4 (+), 128.3 (+), 68.6 (o), 67.5 (+), 52.3 (+), 52.1 (+), 50.5 (+), 49.2 (+), 42.1 (–), 41.7 (–) ppm. MS (EI): $m/z$ = 354, 322, 294, 276, 262, 250, 234, 217, 202, 186, 149, 115,

77. $C_{16}H_{18}O_5S_2$: C 54.22, H 5.12, S 18.09; found C 54.35, H 5.02, S 18.63.

**Methyl (3′*R**,4′*R**)-4-Hydroxy-3′,4′-dihydro-2′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-3′-carboxylate (17b):** Yield 149 mg (50%); m.p. 135–136 °C. IR (KBr): $\tilde{\nu}$ = 3494, 2924, 1720, 1445, 1393, 1378, 1302, 1290, 1277, 1243, 1226, 1198, 1165, 1126, 1105, 1052, 974, 931, 746, 496 $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ = 7.96 (d, $J$ = 7.3 Hz, 1 H), 7.29 (m, 3 H), 5.04 (d, $J$ = 2.4 Hz, 1 H), 3.78 (s, 3 H), 3.48 (m, 4 H), 3.21 (dt, $J$ = 2.6, 12.5 Hz, 1 H), 2.83 (d, $J$ = 12.5 Hz, 2 H) ppm. $^{13}C$ NMR (50 MHz): $\delta$ = 173.6 (o), 138.2 (o), 136.1 (o), 130.5 (+), 129.7 (+), 128.8 (+), 128.2 (+), 67.9 (o), 67.0 (+), 52.1 (+), 45.3 (+), 41.3 (–), 40.3 (–), 38.6 (–) ppm. MS (EI): *m*/*z* = 296, 278, 232, 218, 187, 173, 159, 115, 75. $C_{14}H_{16}O_3S_2$: C 56.73, H 5.44, S 21.64; found C 56.63, H 5.48, S 21.30.

**Methyl (2′*R**,3′*R**,4*R**)-4′-Hydroxy-2′-phenyl-3′,4′-dihydro-2′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-3′-carboxylate (17c):** Yield 252 mg (68%); m.p. 134–136 °C. IR (film): $\tilde{\nu}$ = 3449, 3030, 1735, 1600, 1494, 1450, 1376, 1238, 1027, 969, 750, 700 $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ = 8.04 (d, $J$ = 7.3 Hz, 1 H), 7.58 (m, 3 H), 7.30 (m, 5 H), 5.00 (d, $J$ = 2.8 Hz, 1 H), 4.21 (d, $J$ = 11.8 Hz, 1 H), 3.66 (dd, $J$ = 2.8, 11.8 Hz, 1 H), 3.49 (s, 3 H), 3.30 (m, 2 H), 3.09, 2.72 (each m, 1 H) ppm. $^{13}C$ NMR (50 MHz): $\delta$ = 173.5 (o), 140.5 (o), 138.1 (o), 136.6 (o), 128.9 (+), 128.7 (+), 128.5 (+), 128.4 (+), 127.9 (+), 127.6 (+), 127.1 (+), 127.0 (+), 126.4 (+), 72.8 (o), 68.0 (+), 51.8 (+), 50.3 (+), 49.9 (+), 41.8 (–), 41.6 (–) ppm. MS (EI): *m*/*z* = 372, 355, 326, 296, 279, 263, 234, 210, 182, 149, 121, 105, 92. $C_{20}H_{20}O_3S_2$: C 64.49, H 5.41, S 17.22; found C 63.87, H 5.39, S 17.70.

**Ethyl (2′*R**,3′*R**,4′*R**)-2′-Cyano-4′-hydroxy-3′,4′-dihydro-2′*H*-spiro[1,3-dithiolane-2,1′-naphthalene]-3′-carboxylate (17d):** Yield 224 mg (67%); m.p. 68 °C. IR (KBr): $\tilde{\nu}$ = 3458, 2979, 2927, 2248, 1733, 1447, 1372, 1296, 1212, 1131, 1042, 755 $cm^{-1}$. $^1H$ NMR (200 MHz): $\delta$ = 8.01 (dd, $J$ = 7.5, 1.7 Hz, 1 H), 7.44 (dd, $J$ = 7.3, 1.9 Hz, 1 H); 7.37 (m, 2 H), 5.21 (d, $J$ = 4.2 Hz, 1 H), 4.37 (d, $J$ = 7.2 Hz, 2 H), 3.67 (m, 4 H), 3.58 (m, 1 H), 3.37 (m, 1 H), 1.38 (t, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (50 MHz): $\delta$ = 169.7 (o), 135.3 (o), 134.6 (o), 130.3 (+), 129.8 (+), 129.5 (+), 129.2 (+), 119.3 (o), 69.5 (o), 66.3 (+), 62.0 (–), 47.4 (+), 41.7 (–), 41.3 (–), 41.2 (+), 14.2 (+) ppm. MS (EI): *m*/*z* = 334, 317, 307, 289, 241, 210, 182, 169, 149, 121, 77, 51. HRMS (EI): calcd. for $C_{16}H_{17}NO_3S_2$: 335.0650; found 335.0647.

**Ethyl (1′*R**,4′*R**,10′*R**)-3′-Oxo-3′,4′-dihydro-1′*H*-spiro[1,3-dithiolane-2,5′-[1,4]methano[2]benzoxepine]-10′-carboxylate (19):** Yield 84 mg (25%); m.p. >185 °C (dec.). IR (film): $\tilde{\nu}$ = 3123, 1776, 1728, 1377, 1333, 1269, 1170, 1143, 1053, 948, 917, 887, 604 $cm^{-1}$. $^1H$ NMR (400 MHz): $\delta$ = 7.94 (d, $J$ = 7.9 Hz, 1 H), 7.42 (dt, $J$ = 7.0, 1.8 Hz, 1 H), 7.22 (m, 2 H), 5.50 (d, $J$ = 1.3 Hz, 1 H), 4.27 (q, $J$ = 7.2 Hz, 2 H), 3.72 (m, 5 H), 5.54 (dd, $J$ = 2.0, 1.3 Hz, 1 H), 1.33 (t, $J$ = 7.2 Hz, 3 H) ppm. $^{13}C$ NMR (100 MHz): $\delta$ = 171.7 (o), 169.3 (o), 136.5 (o), 135.1 (o), 132.0 (+), 130.7 (+), 128.5 (+), 126.9 (+), 79.6 (+), 68.4 (o), 62.2 (–), 54.9 (+), 53.8 (+), 42.4 (–), 40.8 (–), 14.1 (+) ppm. MS (EI): *m*/*z* = 336, 308, 263, 247, 233, 191, 160, 128, 115, 89, 71, 51. HRMS (EI): calcd. for $C_{16}H_{16}O_4S_2$: 336.0490; found 336.0491.

**Crystal Data for 19:** $C_{16}H_{16}O_4S_2$ (336.41), crystal size 0.33 × 0.28 × 0.21 mm. The crystal structure was solved as described above for 12a. The crystal of the compound was triclinic, space group $P\bar{1}$, unit cell dimensions: $a$ = 8.317(1), $b$ = 10.068(1), $c$ = 10.761(1) Å, $\alpha$ = 70.15(1), $\beta$ = 74.34(1), $\gamma$ = 68.52(1)°, $Z$ = 2, cell volume $V$ = 777.69(14) $Å^3$, $F(000)$ = 352 using 3549 independent reflections and 228 parameters, $R_1$ = 0.0540, $wR_2$ = 0.1457 [$I > 2\sigma(I)$], goodness of fit on $F^2$ = 1.155, residual electron density: 0.558 and –0.586 e $Å^{-3}$.

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