[4 + 2] Cycloaddition of thiophene *S*-monoxides to activated methylenecyclopropanes

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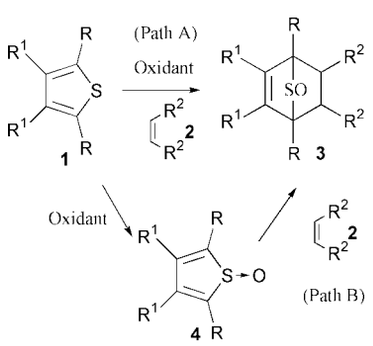
Thiophene *S*-oxides **4** have been shown to undergo [4 + 2] cycloadditions with methylenecyclopropanes **2** with one or two electron acceptor substituents, *i.e.* even the tetrasubstituted 2-chloro-2-cyclopropylideneacetate **2c** reacted well. However, for the tetrasubstituted alkene bi(cyclopropylidene) **2f** high pressure had to be applied to make it react with **4**. Only one diastereoisomer was formed in all the reactions. X-Ray crystal structure analyses of two of the cycloadducts, **3a** and **3f**, have been performed, their relative configuration determined as being *endo*,*syn*. The Wittig olefination of cyclopropanone hemiacetal to generate the methylenecyclopropanes and the subsequent cycloaddition can be carried out in a one-pot operation. This procedure is one of many potential one-pot or multi-component reactions involving stabilized phosphoranes. A further example of this type of reaction is shown in the novel desilylation–Wittig olefination of 1-ethoxy-1-trimethylsilyloxycyclopropane **5** to yield in one step cyclopropylideneacetates, *e.g.* **2a**.

Introduction

While many thiophenes[1] **1** do not undergo cycloaddition reactions, and the cycloadditions of thiophene *S*,*S*-dioxides[2] for the most part necessitate higher reaction temperatures, cycloaddition of dienophiles to thiophene *S*-monoxides **4**, prepared *in situ* by oxidation of thiophenes,[3] (Path A, Scheme 1) is possible at temperatures as low as −20 °C.[4] Recently, thiophene *S*-monoxides have been isolated prior to further reactions[4,5] (Path B, Scheme 1). While a number of differently substituted

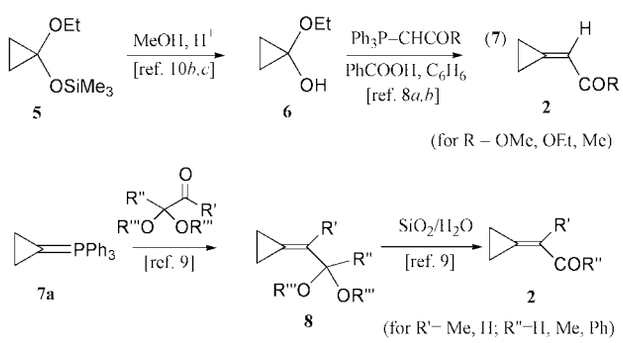


Scheme 1

thiophenes/thiophene *S*-monoxides and dienophiles have been studied,[5] clearly the use of a greater variety of dienophiles would be required in order to assess the scope of the cycloaddition reaction. Especially, the effect of steric hindrance and strain in the dienophile needs to be studied. Suitable candidates for this study are the methylenecyclopropane derivatives **2**.[6] As methylenecyclopropanes are themselves susceptible to oxidation by MCPBA,[7] their cycloaddition reactions can only be carried out with isolated thiophene *S*-monoxides (Path B).

Results and discussion

The unsubstituted and the 2-bromosubstituted cyclopropylideneacetates and certain cyclopropylidenealkanones[6] have been prepared by Wittig olefination either of the cyclopropanone ethyl hemiacetal with the corresponding phosphorane **7** (Scheme 2, reaction 1)[8a,b] or of a suitably protected α,β-



Scheme 2 Known synthetic approaches to methylenecyclopropanes.

diketone or α-ketoaldehyde with cyclopropylidenetriphenylphosphorane **7a**[9] (Scheme 2, reaction 2). The cyclopropanone hemiacetal **6** can be prepared in two steps from ethyl 3-chloropropionate.[10a–c] The second step, the methanolysis of the 1-ethoxy-1-trimethylsilyloxycyclopropane **5**,[10a] requires some care as the separation of the cyclopropanone hemiacetal **6** from the methanol, used in the solvolysis[10b,c] is often time consuming. This is greatly facilitated by applying a one pot procedure to convert 1-ethoxy-1-trimethylsilyloxycyclopropane **5**[11] directly to the cyclopropylideneacetates, *e.g.*, **2a**. The trimethylsilyloxy group is cleaved off by fluoride, the anion formed is protonated by benzoic acid, and the Wittig olefination ensues at

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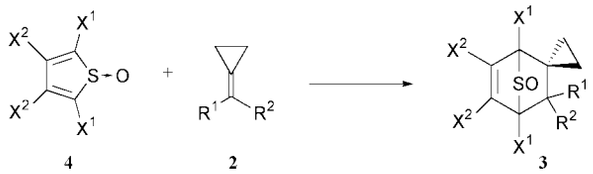
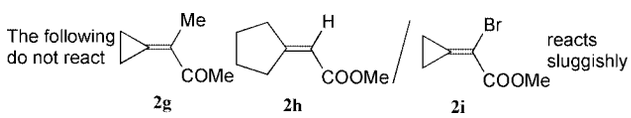
Table 1 Cycloaddition of thiophene *S*-oxides with methylenecyclopropanes

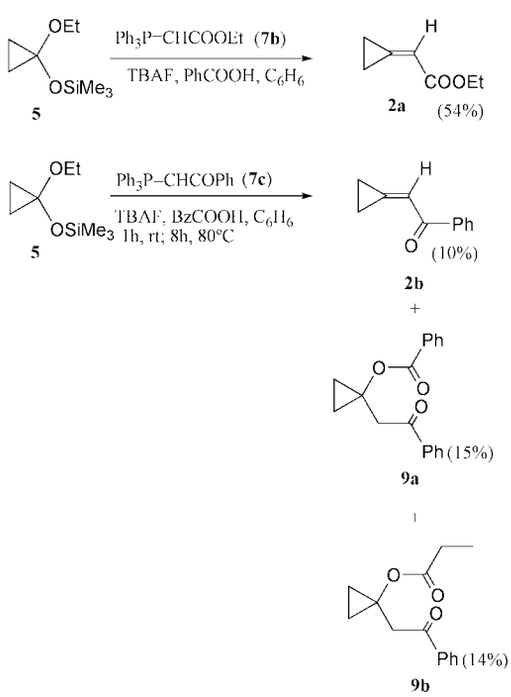


Entry	X^1	X^2	R^1	R^2	Conditions	Yield (%)
1 (**4c**)	Me	Bn	COOMe	Cl (**2c**)	$CHCl_3$, 60 °C, 24 h	60 (**3a**)
2 (**4a**)	Me	*p*-Bu^t–Bn	COOEt	H (**2a**)	$CHCl_3$, 60 °C, 20 h	85 (**3b**)
3 (**4c**)	Me	Bn	COOH	H (**2d**)	$CHCl_3$, 60 °C, 56 h	50 (**3c**)[a]
4 (**4d**)	Me	Br	COOMe	H (**2e**)	$CHCl_3$, 60 °C, 19 h	67 (**3d**)
5 (**4c**)	Me	Bn	COOMe	Cl (**2c**)	CH_3CN, 60 °C, 24 h, 10 kbar	92 (**3a**)
6 (**4a**)	Me	*p*-Bu^t–Bn	–(CH_2CH_2)–	(**2f**)	CH_3CN, 60 °C, 5 d, 10 kbar	48 (**3e**)
7 (**4c**)	Me	Bn	–(CH_2CH_2)–	(**2f**)	CH_3CN, 60 °C, 5 d, 10 kbar	43 (**3f**)
8 (**4a**)	Me	*p*-Bu^t–Bn	–(CH_2CH_2)–	(**2f**)	CH_3CN, 60 °C, 24 h, 10 kbar	31 (**3e**)
9 (**4c**)	Me	Bn	–(CH_2CH_2)–	(**2f**)	CH_3CN, 60 °C, 24 h, 10 kbar	39 (**3f**)

[a] Isolated as its methyl ester, see below.



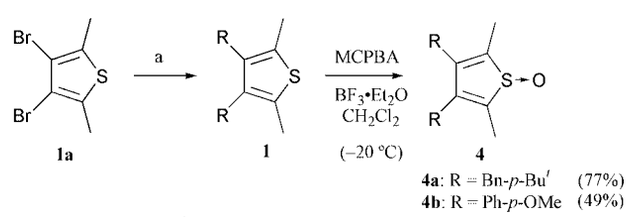
elevated temperature (80 °C) under benzoic acid catalysis as has been described by Spitzner and Swoboda[8b] for the olefination of 1-ethoxy-1-hydroxycyclopropane **6**. 1.3 to 1.4 equivalents of benzoic acid are used for every equivalent of 1-ethoxy-1-silyloxycyclopropane **5** (Scheme 2). It is not possible, however, to use the same procedure to prepare the corresponding cyclopropylidenealkanones, *e.g.*, **2b**, because, although they are formed, they undergo subsequent side reactions (Scheme 3).



Scheme 3 One-pot desilyation–Wittig olefination.

Interestingly, benzoic acid acts as a Michael nucleophile under these conditions to yield the benzoate **9a** as a side product, which has also been observed in the Wittig reaction with the isolated cyclopropanone hemiacetal **6**.[12] Conia *et al.* also reported a similar Michael adduct as a side product with *m*-chlorobenzoic acid acting as a nucleophile in the treatment of a cyclopropylidenealkanone with MCPBA.[7] Furthermore, it is important to adjust the pH of the reaction mixture carefully by addition of benzoic acid, as basic conditions facilitate the ring opening of the intermediate anion of the cyclopropanone hemiacetal **6** to the ethyl propionate homoenolate, which is protonated and cleaved to the propionate anion that subsequently adds to the cyclopropylidenealkanone **2b** to give **9b**. When benzoic acid is substituted by aq. 10% HCl (10% excess with respect to 1-ethoxycyclopropanolate formed), the resulting solution washed with water and the benzene solution after drying used directly for the subsequent Wittig olefination, the product **2b** also is formed in mediocre yields (10%) only. Thus, for the preparation of cyclopropylidenealkanones the two-step procedure with isolated 1-ethoxycyclopropanol **6** is preferable.[8] Methyl 2-chloro-2-cyclopropylideneacetate[8c] and bi(cyclopropylidene)[8d,e] were prepared according to well established literature procedures.

The thiophene *S*-monoxides **4** can be prepared easily by oxidation of the corresponding thiophenes **1** with MCPBA in the presence of a Lewis acid, *e.g.* $BF_3{\cdot}Et_2O$ (Scheme 4). It



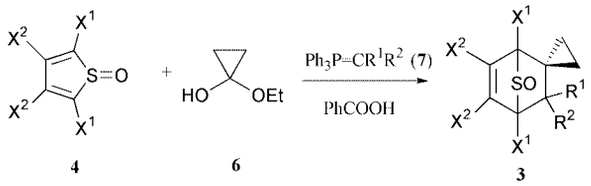
a) for **1b** (R = Bn-*p*-Bu^t):
for **1c** (R = Ph-*p*-0Me), *p*-MeOPhB(OH)$_2$, Pd(PPh$_3$)$_4$, DME, 2M Na_2CO_3 (83%)

Scheme 4 Preparation of thiophene *S*-oxides.

is advantageous for the thiophenes used to possess an electron-donating substituent in positions 2 and 5, *e.g.* alkyl groups. Positions 3 and 4 can accommodate a variety of substituents, such as slightly electron-withdrawing functionalities, as in 3,4-dibromo-2,5-dimethylthiophene *S*-monoxide **4d**.

In general, thiophene *S*-oxides **4** react readily with methylenecyclopropanes **2**, which have one electron-withdrawing group (Table 1). Even the tetrasubstituted alkene, methyl 2-chloro-2-cyclopropylideneacetate **2c**, undergoes the cycloaddition reaction. In this case, the steric hindrance of the substituents is counteracted by the two electron-withdrawing functionalities.[13,14] 3-Cyclopropylidenebutan-2-one **2g**, another

Table 2 Thiabicyclo[2.2.1]heptene *S*-oxides by one-pot Wittig olefination and cycloaddition reaction



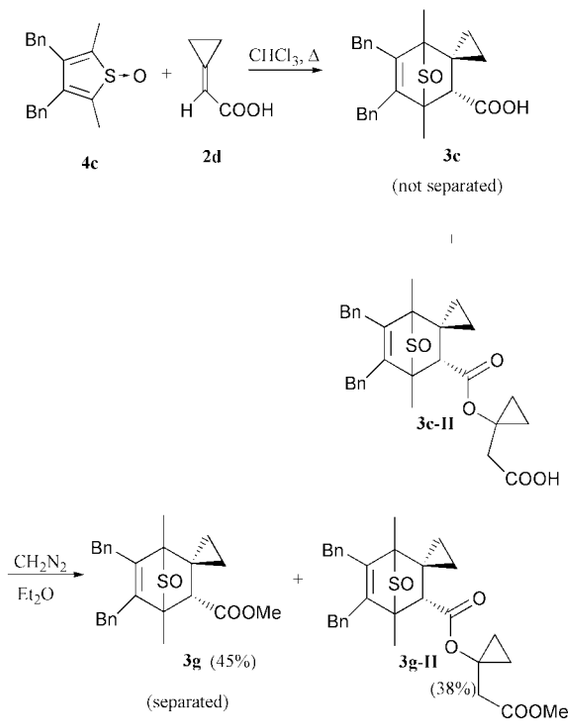
			Phosphorane/equiv. alkene			
Entry	X^1	X^2	R^1	R^2	Conditions	Yield (%)
1 (**4a**)	Me	Bn-*p*-Bu^t	COPh	H **7c/2b**	C_6H_6, 80 °C, 24 h	90 (**3h**)
2 (**4c**)	Me	Bn	COPh-*p*-Cl	H **7d/2j**	C_6H_6, 80 °C, 22 h	91 (**3i**)
3 (**4c**)	Me	Bn	COMe	H **7e/2k**	C_6H_6, 80 °C, 56 h	52 (**3j**)
4 (**4c**)	Me	Bn	CN	H **7f/2m**	C_6H_6, 80 °C, 10 h + 22 h	71 (**3k**)
5 (**4b**)	Me	Ph-*p*-OMe	COOEt	H **7b/2a**	C_6H_6, 80 °C, 2 h + 22 h	67 (**3m**)

tetrasubstituted methylenecyclopropane, but with one electron-withdrawing and one electron-donating substituent, failed to react. The thiophene *S*-monoxides generally are better dienes in the [4 + 2] cycloaddition than the corresponding thiophene *S*,*S*-dioxides as can be seen from the fact that most tetraalkyl-substituted thiophene *S*,*S*-dioxides give no cycloadducts under the conditions used for the monoxides. Thus, no reaction could be observed between 2,3,4,5-tetramethylthiophene *S*,*S*-dioxide (1.7×10^{-1} M in $CDCl_3$) and methyl cyclopropylideneacetate **2c** (5.1×10^{-1} M in $CDCl_3$) at 60 °C even after 48 h. Moreover, it must be noted that the reactivity of the methylenecyclopropanes is due to their inherent strain. Thus, methyl cyclopentylideneacetate **2h** gave no cycloaddition product with 3,4-dibromo-2,5-dimethylthiophene *S*-oxide **4d** after 24 h at 60 °C.

At room temperature and ambient pressure, the reaction of the 2,5-dimethyl-3,4-bis(phenylmethyl)thiophene *S*-oxide **4c** with bi(cyclopropylidene) **2f** proceeds, at best, very slowly. At an early stage of the reaction, however, it is noticeable that a considerable proportion of thiophene *S*-oxide is reduced to the thiophene. Under high pressure (10 kbar) the cycloadduct of **2f** with **4c** can be obtained in good yield.[15,16]

One remarkable example is the cycloaddition of **4c** to cyclopropylideneacetic acid **2d**, as carboxylic acids themselves are rarely used in cycloaddition reactions. Two products were formed, one of which at first could not be identified; the other product was the cycloadduct **3c** (Scheme 5). As the two products could not be separated, they were converted with ethereal diazomethane solution to their respective methyl esters, which could be separated easily by column chromatography. Interestingly, the second product **3g-II** was the Michael adduct of the primary cycloadduct **3c** and a second molecule of cyclopropylideneacetic acid **2d**. The Wittig olefination of cyclopropanone hemiacetal **6** to yield the acceptor-substituted methylenecyclopropane and its subsequent cycloaddition to a thiophene *S*-monoxide **4** can be performed as a one-pot reaction (Table 2). This has been carried out with both the intermediate cyanomethylenecyclopropane (**2m**)[17] and the cyclopropylidenemethyl phenyl ketone (**2b**). The thiophene *S*-monoxide **4** can be added to the reaction mixture after the Wittig olefination has taken place, but it can also be present as a component from the beginning, while the Wittig reaction is going on. The stabilised phosphoranes of type **7** are compatible with a variety of reaction conditions. Thus, in principle, a number of multiple step, one-pot reactions can be devised, which involve Wittig olefination with these conjugated phosphoranes.[18,19]

Competition experiments between different methylenecyclopropanes as dienophiles have been carried out. Thus, one equivalent each of methyl cyclopropylideneacetate **2e** and methyl bromocyclopropylideneacetate **2i** have been reacted as



Scheme 5

a mixture with 3,4-dibromo-2,5-dimethylthiophene *S*-oxide **4d** (Scheme 6). While **2e** as a trisubsubstituted alkene is sterically less congested than the tetrasubstituted **2i**, the latter is more electron-deficient than **2e**. Nevertheless, the thiophene *S*-oxide **4d** reacted exclusively with **2e**. The reaction of **4d** with methyl 2-bromo-2-cyclopropylidenecarboxylate **2i** at 61 °C (refluxing $CHCl_3$) proceeds very sluggishly. When the reaction temperature is raised to 110 °C (refluxing toluene), dimerisation of **4d** and deoxygenation[20] to 3,4-dibromo-2,5-dimethylthiophene become the major competing reactions.

In the cycloadditions of compounds **4** five new stereocenters are formed, yet only a single diastereoisomer could be isolated in all of the cycloadditions. All products have the *endo*-configuration. One of the five stereocenters is located at the sulfur of the 7-thiabicyclo[2.2.1]heptene *S*-oxides **3**. As proven by X-ray crystal structure analyses for two of the cycloadducts (Figs. 1 and 2), the sulfoxide oxygen sits on the side of the attached former dienophile (*i.e.*, formed by *syn*-addition). The stereochemistry is the same as that reported for the oxidative cycloaddition of thiophenes to alkenes.[3b,d,5a,c] The stereochemical outcome can be rationalized by the same effect originally proposed by Cieplak[21] to account for the contribution of remote substituents in cyclohexanones. This was later used to

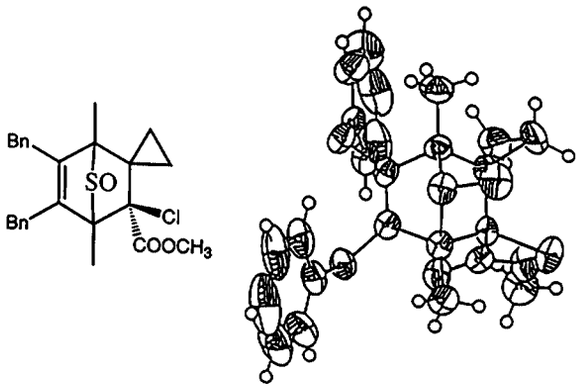


Fig. 1 ORTEP drawing of **3a**.

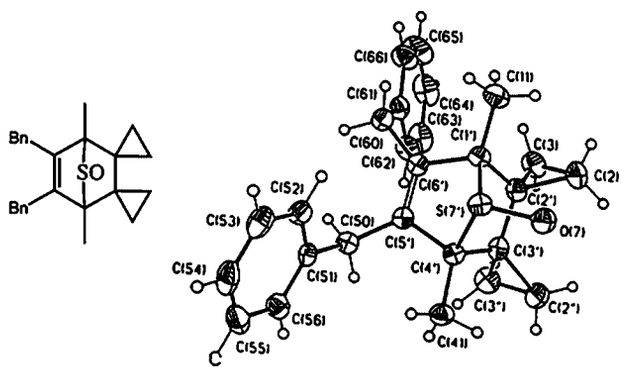
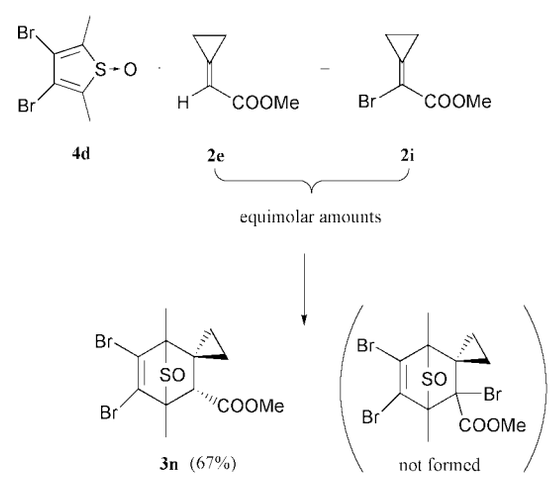


Fig. 2 ORTEP drawing of **3f**.



Scheme 6 Competition of trisubstituted **2e** and tetrasubstituted **2i** in the reaction with **4d**.

account for the π-selectivity of 5-substituted cyclopentadienes in Diels–Alder reactions. According to this rule the stronger σ-electron donor directs the incoming dienophile *anti* to it. In case of the cycloaddition of thiophene *S*-monoxides, the lone electron pair on sulfur should be a stronger σ-donor than the oxygen atom with its lone electron pairs. Thus, because of the better orbital geometry the sulfur can stabilize better the incipient σ*-bonds of the cycloadduct from an *anti* position.

Experimental

General

Melting points were measured on a Reichert microscopic hot stage and are uncorrected. Infrared spectra were measured with JASCO IR-700, Bruker IFS 66 and Nippon Denshi JIR-AQ2OM machines. ^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL EX-270 and a Bruker AM 250 spectrometer. The chemical reported shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). mc refers to a centred multiplet. Mass spectra were measured with a JMS-01-SG-2 spectrometer, a Varian MAT CH7 and a Varian MAT 731 spectrometer (EI, 70 eV).

3,4-Dibenzyl-2,5-dimethylthiophene *S*-monoxide **4c**,[5a] methyl 2-chloro-2-cyclopropylideneacetate **2c**,[8b,c] bi(cyclopropylidene) **2f**,[8d] 2-cyclopropylidenebutanone **2g**,[9] cyclopropylidenepropanone **2k**[9] and 1-ethoxy-1-hydroxycyclopropane **6**[10] were prepared according to literature procedures. Methyl bromocyclopropylideneacetate **2m** was synthesized by a procedure analogous to that reported by Osborne,[8a] from cyclopropanone hemiacetal **6** and methoxycarbonylbromomethylenephosphorane.[22] The phosphoranes **7** were prepared according to a procedure by Ramirez and Dershowitz.[18] Methyl cyclopentylideneacetate **2h** was prepared directly from cyclopentanone by Wittig olefination.

2,5-Dimethyl-3,4-bis(*p*-methoxyphenyl)thiophene 1c

A mixture of 3,4-dibromothiophene **1a** (1.00 g, 3.70 mmol), *p*-methoxyphenylboronic acid (2.26 g, 14.8 mmol) and tetrakis(triphenylphosphine)palladium(0) (25 mg, 2.1×10^{-2} mmol) in 2 M aq. Na_2CO_3 (14 mL) and DME (8 mL) was stirred under an inert atmosphere at 75 °C for 8 h. Then the cooled reaction mixture was poured into a mixture of water (100 mL) and chloroform (100 mL). The separated aq. phase was extracted with chloroform (3 × 30 mL), and the collected organic phase was washed with water (2 × 30 mL), aq. Na_2CO_3 (3 × 30 mL), and dried over anhydrous $MgSO_4$. The filtered solution was concentrated *in vacuo*, and the residue subjected to column chromatography on silica gel (eluting with ether–hexane 1:10) to give a colorless oil (R_f 0.42 [ether–hexane 1:10]). The oil included residual *p*-methoxyphenylboronic acid which crystallized out in hexane. The solution was then filtered and concentrated. Two crystallizations gave pure **1c** from the filtrate as a colorless solid (933 mg, 3.06 mmol, 83%); mp 69–71 °C (decomp.); IR (KBr) *ν* 3034, 2950, 2910, 1609, 1525, 1463, 1440, 1295, 1283, 1246, 1175, 1162, 1034, 832, 592 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) *δ* 2.33 (s, 6H, 2 CH_3), 3.75 (s, 6H, 2 OCH_3), 6.75 (d, 4H, ^3J 8.9 Hz), 6.91 (d, 4H, ^3J 8.9 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) *δ* 13.96 (+, CH_3), 55.04 (+, OCH_3), 113.54 (CH), 129.25 (C_{quat}), 130.73 (C_{quat}), 131.29 (CH), 138.65 (C_{quat}), 157.88 (C_{quat}); MS (70 eV) *m*/*z* (%) 324 (M^+, 100), 309 ($M^+ - CH_3$, 12). HRMS Found: 324.1184; calcd. for $C_{20}H_{20}O_2S$: 324.1183. Anal. calcd. for $C_{20}H_{20}O_2S$ (324.44) C, 74.04; H, 6.21. Found C, 74.03; H, 6.27%.

2,5-Dimethyl-3,4-bis(*p*-*tert*-butylphenylmethyl)thiophene 1b

At 0 °C 2,5-dimethyl-3,4-bis(chloromethyl)thiophene (2.0 g, 9.6 mmol) in anhydrous *p*-*tert*-butylbenzene (40 mL) was added slowly to a solution of titanium tetrachloride (0.75 g, 0.42 mL, 3.9 mmol) in anhydrous *p*-*tert*-butylbenzene (30 mL). The reaction mixture was allowed to warm to rt, stirred for 2 h and then heated under reflux for 1 h. Thereafter it was cooled to rt, and ice water (50 g) was added. The layers were separated, and the aqueous layer was extracted with ether (3 × 30 mL). The combined organic phase was washed with water (3 × 30 mL), brine (2 × 30 mL), and dried over anhydrous $MgSO_4$. The solvent was evaporated *in vacuo*, and the residue subjected to column chromatography on silica gel (eluting with hexane) to give **1b** (1.82 g, 4.5 mmol, 47%) as colorless crystals, mp 95–96 °C (ether); IR (KBr) *ν* 2960, 2910, 2866, 1513, 1413, 1391, 1360, 1285, 815, 546 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) *δ* 1.28 (s, 18H, 6 CH_3), 2.30 (s, 6H, 2 CH_3), 3.70 (s, 4H, 2 PhCH_2), 6.92 (d, 4H, ^3J 8.2 Hz), 7.22 (d, 4H, ^3J 8.2 Hz); ^{13}C NMR (67.9 MHz) *δ* 13.37, 31.39, 32.18, 34.29, 125.16, 127.31, 130.35, 135.70, 137.25, 148.48; MS (70 eV) *m*/*z* (%) 404 (M^+, 100), 389 ($M^+ - CH_3$, 13), 213 (73). HRMS Found: 404.2540; calcd. for

$C_{28}H_{36}S$: 404.2538. Anal. calcd. for $C_{28}H_{36}S$ (404.65) C, 83.11; H, 8.97. Found C, 82.86; H, 8.96%.

Ethyl cyclopropylideneacetate 2a

To a stirred solution of 1-ethoxy-1-trimethylsilyloxycyclopropane **5** (870 mg, 5.0 mmol) in benzene (15 mL) was added in portions a well homogenized melt of tetrabutylammonium fluoride (1.305 g, 5.0 mmol), benzoic acid (730 mg, 6.0 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane **7b** (2.09 g, 6.0 mmol) within 15 min. The mixture was kept at room temperature for 1 h. Afterwards it was stirred at 80 °C for 2.5 h. The cooled mixture was poured into water (50 mL). The phases were separated, the aqueous phase extracted with diethyl ether (2 × 10 mL), and the combined organic phases were dried over anhydrous $MgSO_4$. Careful evaporation of the solvent gave a residue which was chromatographed on silica gel (hexane–ether 2.5:1). Careful evaporation of the solvent gave pure **2a** (330 mg, 54%). The analytical data were identical to those reported.[8b]

Reaction of 1-ethoxy-1-trimethylsilyloxycyclopropane (5) with (benzoylmethylene)triphenylphosphorane (7c) under benzoic acid catalysis (1.2 equiv. PhCOOH)

To a stirred solution of 1-ethoxy-1-trimethylsilyloxycyclopropane **5** (870 mg, 5.0 mmol) in benzene (15 mL) was added in portions a well homogenized melt of tetrabutylammonium fluoride (1.31 g, 5.0 mmol), benzoic acid (730 mg, 6.0 mmol) and (benzoylmethylene)triphenylphosphorane **7c** (2.09 g, 6.0 mmol) within 15 min. The mixture was kept at room temperature for 1 h. Afterwards it was stirred at 80 °C for 3 h. The cooled mixture was poured into water (50 mL). The phases were separated, the aqueous phase extracted with diethyl ether (2 × 10 mL), and the combined phases were dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a residue which was separated on silica gel (hexane–ether 3:1) to give fraction 1 (75 mg, 4%) cyclopropylideneacetophenone **2b**, IR (neat) ν 1723, 1687, 1599, 1450, 1360, 1265, 759, 690 cm^{-1}; all other spectroscopic data match those given in ref. 9*a*; fraction 2 (216 mg, 15%) 1-(1′-benzoyloxycyclopropyl)acetophenone **9a** as a colorless oil, R_f 0.32; IR (neat) ν 3062, 2914, 1722, 1681, 1599, 1283, 1253, 1107, 1025, 713, 690 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.99 (mc, 2H, cyclopr.-H), 1.13 (mc, 2H, cyclopr.-H), 3.62 (s, 2H), 7.35–7.42 (m, 4H), 7.48–7.55 (m, 2H), 7.92–7.97 (m, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 11.97, 42.83, 56.91, 128.27, 128.29, 128.59, 129.59, 130.15, 133.06, 133.17, 137.07, 166.90, 197.20; MS (EI, 70 eV) *m/z* (%) 280 (M^+, 0.6), 175 (M^+ − PhCO, 15), 161 (M^+ − $PhCOCH_2$, 25), 159 (M^+ − PhCOO, 21), 105 (100); MS (FAB, 3-nitrobenzyl alcohol) 281 (MH^+, 39), 159 (57), 105 (23). HRMS Found: 281.1180; calcd. for $C_{18}H_{17}O_3$: 281.1178 (MH^+); and fraction 3 (150 mg, 14%) 1-(1′-propionyloxycyclopropyl)acetophenone **9b** as a colorless solid, R_f 0.25, mp (ether–hexane) 83–84 °C; IR (KBr) ν 2982, 2942, 1735, 1687, 1450, 1420, 1216, 1192, 744, 688 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.87 (mc, 2H, cyclopr.-H), 0.97 (mc, 2H, cyclopr.-H), 1.03 (t, 3H, ^3J 7.6 Hz), 2.18 (q, 2H, ^3J 7.6 Hz), 3.48 (s, 2H), 7.46 (m, 2H), 7.55 (m, 1H), 7.95 (m, 2H); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 8.88, 11.93, 27.76, 42.70, 56.38, 128.36, 128.68, 133.29, 137.22, 174.91, 197.43; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 233 (MH^+, 100), 159 (52), 105 (23).

3,4-Bis(*tert*-butylphenylmethyl)-2,5-dimethylthiophene *S*-monoxide 4a

At −20 °C and under an inert atmosphere, $BF_3{\cdot}Et_2O$ (3.6 mL, 28.5 mmol) was added to a solution of 3,4-bis(*tert*-butylphenylmethyl)-2,5-dimethylthiophene **1b** (1.28 g, 3.17 mmol) in anhydrous CH_2Cl_2 (20 mL). The solution was stirred for 10 min at −20 °C, then a solution of *m*-chloroperbenzoic acid (MCPBA) (716 mg, 4.14 mmol) in anhydrous CH_2Cl_2 (20 mL) was added dropwise. The reaction mixture was stirred at −20 °C for 2 h. Then the suspension was poured into a mixture of conc. aq. $NaHCO_3$ (30 mL) and CH_2Cl_2 (80 mL). The resulting mixture was stirred for 20 min at rt. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with water (2 × 20 mL), brine (20 mL), and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was subjected to flash chromatography on silica gel (eluting with ether) to give **4a** (1.02 mg, 77%) as colorless crystals; mp 153–155 °C; IR (KBr) ν 2960, 1512, 1363, 1269, 1028, 816, 547 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.30 (s, 18H, 2 Bu^t), 2.24 (s, 6H, 2 CH_3), 3.45 (4H, 2 CH_2), 6.96 (d, 4H, *J* 8.3 Hz), 7.29 (d, 4H, *J* 8.3 Hz); ^{13}C NMR (99.5 MHz, $CDCl_3$) δ 10.59, 31.34, 31.76, 34.41, 125.69, 127.62, 134.17, 138.89, 142.64, 149.66; MS (70 eV) *m/z* (%) 420 (M^+, 21), 404 (M^+ − O, 65), 331 (69), 199 (64), 147 (100). Anal. calcd. for $C_{28}H_{36}OS{\cdot}0.5H_2O$ (429.67) C, 78.27; H, 8.67. Found C, 78.77; H, 8.49%.

2,5-Dimethyl-3,4-bis(*p*-methoxyphenyl)thiophene *S*-oxide 4b

At −20 °C and under an inert atmosphere, $BF_3{\cdot}Et_2O$ (1.5 mL, 11.9 mmol) was slowly added to a solution of **1c** (500 mg, 1.54 mmol) in anhydrous CH_2Cl_2 (10 mL). After 10 min, a solution of MCPBA (300 mg, 1.73 mmol) in anhydrous CH_2Cl_2 (10 mL) was slowly added to the reaction mixture. The resulting mixture was stirred for 3 h at −20 °C. Then it was poured into a solution of aq. $NaHCO_3$ (100 mL) and CH_2Cl_2 (50 mL) and the mixture stirred for 20 min at rt. The two phases were separated, the aqueous phase extracted with CH_2Cl_2 (3 × 50 mL), and the collected organic phase was washed with water (2 × 50 mL). The solution was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (eluting with ether) to give **4b** (255 mg, 0.75 mmol, 49%) as colorless crystals, R_f 0.34 (ether), mp (ether) 149–151 °C (decomp.); IR (KBr) ν 3048, 3004, 2960, 2932, 2908, 1606, 1510, 1460, 1289, 1244, 1180, 1031, 842, 802, 750 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.26 (s, 6H, 2 CH_3), 3.78 (s, 6H, 2 OCH_3), 6.77 (d, 4H, ^3J 2.3 Hz, Ar-H), 6.84 (d, 4H, ^3J 2.3 Hz, Ar-H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 11.55, 55.19, 113.53, 125.65, 130.69, 140.90, 141.58, 159.25; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 341 (MH^+, 100), 324 (M^+ − O, 73). HRMS (FAB) Found: 341.1211; calcd. for $C_{20}H_{20}O_3S$: 341.1215 (MH^+). Anal. calcd. for $C_{20}H_{20}O_3S$ (340.12) C, 70.56; H, 5.92. Found C, 70.52; H, 5.96%.

Methyl 7-oxo-3′-chloro-5′,6′-dibenzyl-1′,4′-dimethylspiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene]-3′-carboxylate 3a

2,5-Dimethyl-3,4-bis(phenylmethyl)thiophene *S*-oxide **4c** (188 mg, 0.61 mmol) and methyl 2-chloro-2-cyclopropylideneacetate **2c** (87 mg, 0.81 mmol) in chloroform (1 mL) were stirred at rt for 11 h. After this time no products could be detected in the ^1H NMR spectrum of the reaction mixture.

2,5-Dimethyl-3,4-bis(phenylmethyl)thiophene *S*-oxide **4c** (188 mg, mmol) and methyl 2-chloro-2-cyclopropylideneacetate **2c** (87 mg, mmol) in chloroform (1 mL) were stirred at 60 °C for 24 h. The solution was cooled, concentrated *in vacuo*, and the residue was subjected to column chromatography on silica gel (ether–hexane 1:2) to give dimethyl (*E*)-7,8-dichlorodispiro-[2.0.2.2.]octane-7,8-dicarboxylic acid (10 mg, 11%) as a colorless solid; IR (KBr) ν 3066, 3026, 3002, 2960, 1741, 1510, 1493, 1450, 1263, 1032, 935, 732 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 0.62 (m, 4H, cycloprop.-H), 0.97 (m, 4H, cycloprop.-H), 3.88 (s, 3H, 2 OCH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, INEPT) δ 9.14 (−, CH_2, 2C), 10.70 (−, CH_2, 2C), 33.07 (C_{quat}, 2C), 53.29 (+, OCH_3), 75.75 (C, $2C_{quat}$), 166.83 (C_{quat}, 2C, *C*OOMe) and methyl 7′-oxo-3-chloro-5′,6′-dibenzyl-1′,4′-dimethylspiro-[cyclopropane-1,2′[7]thiabicyclo[2.2.1]hept[5]ene]-3′-carboxylate **3a** (166 mg, 60%), IR (KBr) ν 3060, 3024, 2946, 1736,

1494, 1453, 1248, 1109, 1076, 1028, 729, 697 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ −0.62 (m, 1H, cycloprop.-H), 0.47 (m, 1H, cycloprop.-H), 1.11 (m, 1H, cycloprop.-H), 1.19 (s, 3H, CH_3), 1.34 (m, 1H, cycloprop.-H), 1.74 (s, 3H, CH_3), 3.23 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 3.77 (d, 1H, benzyl-CH, ^2J 12.5 Hz), 3.78 (s, 3H, $COOCH_3$), 3.83 (d, 1H, benzyl-CH, ^2J 12.5 Hz), 4.05 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 7.05 (m, 2H), 7.18–7.34 (m, 8H); ^{13}C NMR (67.9 MHz, $CDCl_3$, DEPT) δ 7.64 (−, CH_2, cycloprop.-C), 9.51 (+, CH_3), 12.47 (−, CH_2, cycloprop.-C), 12.85 (+, CH), 32.96 (−, CH_2, 2C), 37.09 (C_{quat}), 52.80 (+, OCH_3), 72.33 (C_{quat}), 76.10 (C_{quat}), 81.83 (C_{quat}), 126.45 (+, CH), 126.83 (+, CH), 128.05 (+, CH, 2C), 128.48 (+, CH, 2C), 128.68 (+, CH), 129.02 (+, CH), 136.03 (C_{quat}), 137.14 (C_{quat}), 138.53 (C_{quat}), 140.77 (C_{quat}), 168.75 (C_{quat}, *C*OOMe); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 457 ([^{37}ClMH$^+$], 4.6), 455 ([^{35}ClMH$^+$], 10.7). Anal. calcd. for $C_{26}H_{27}ClO_3S$ (455.01) C, 68.63; H, 5.98. Found: C, 68.34; H, 5.88%.

Ethyl 7′-oxo-5′,6′-bis(*p-tert*-butylphenylmethyl)-1′,4′-dimethylspiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene]-3′-carboxylate 3b

A solution of 3,4-bis(*p-tert*-butylphenylmethyl)-2,5-dimethylthiophene *S*-monoxide **4a** (112 mg, 0.265 mmol) and ethyl cyclopropylideneacetate **2a** (67 mg, 0.53 mmol) in $CDCl_3$ (2 mL) were kept at 60 °C. According to an ^1H NMR spectrum of the reaction mixture, complete reaction of the thiophene *S*-oxide had occurred after 19.5 h to give the cycloadduct **3b** as a single stereoisomer. Column chromatography of the mixture on silica gel (ether–hexane 2 : 1) gave **3b** as a colorless solid; R_f 0.5; IR (neat) *ν* 3086, 2962, 1733, 1513, 1181, 1094, 1065, 1030, 910, 732 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ −0.83 (m, 1H, cyclopr.-H), 0.01 (m, 1H, cyclopr.-H), 0.72 (m, 1H, cyclopr.-H), 0.89 (m, 1H, cyclopr.-H), 1.09 (s, 3H, CH_3), 1.29 (s, 9H, Bu^t), 1.31 (t, 3H, CH_3), 1.31 (s, 9H, Bu^t), 1.35 (s, 3H, CH_3), 3.25 (d, 1H, benzyl-CH, ^2J 15.1 Hz), 3.47 (s, 1H), 3.64 (d, 1H, benzyl-CH, ^2J 15.1 Hz), 3.83 (d, 1H, benzyl-CH, ^2J 15.1 Hz), 4.07 (d, 1H, benzyl-CH, ^2J 15.1 Hz), 4.17 (dq, 2H), 7.10 (m, 4H), 7.27 (m, 4H); ^{13}C NMR (67.9 MHz, $CDCl_3$, DEPT) δ 3.42 (−, cyclopr.), 9.09 (+, CH_3), 9.69 (−, cyclopr.), 13.30 (+, CH_3), 14.36 (+, CH_3), 29.45 (C_{quat}), 31.36 (+, CH_3, 6C), 32.08 (−, CH_2), 32.47 (−, CH_2), 34.36 (C_{quat}), 56.62 (+, CH), 60.55 (−, OCH_2), 71.14 (C_{quat}), 73.16 (C_{quat}), 125.10 (+, $CH_{arom.}$), 125.60 (+, $CH_{arom.}$), 127.80 (+, $CH_{arom.}$), 128.84 (+, $CH_{arom.}$), 134.32 (C_{quat}), 135.76 (C_{quat}), 135.94 (C_{quat}), 137.84 (C_{quat}), 149.18 (C_{quat}), 149.45 (C_{quat}), 171.66 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 547 (MH^+, 33), 498 (M^+-SO, 21). Anal. calcd. for $C_{35}H_{46}O_3S$ (546.81) C, 76.88; H, 8.48. Found: C, 76.59; H, 8.45.

7′-Oxo-1′,4′-dimethyl-5′,6′-bis(phenylmethyl)spiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene]-3′-carboxylic acid 3c

A solution of 2,5-dimethyl-3,4-bis(phenylmethyl)thiophene *S*-oxide **4c** (67 mg, 0.21 mmol) and cyclopropylideneacetic acid **2d** (73 mg, 0.74 mmol) in $CDCl_3$ (2 mL) was heated under reflux for 56 h, after which time complete reaction of **4c** had occurred according to the ^1H NMR spectrum. The mixture was concentrated *in vacuo*. Unreacted **2d** was recovered by column chromatography on silica gel (ether). The products **3c/3c-II** (ratio 1 : 1), however, could not be separated and were analysed as a mixture. The NMR signals were assigned to the products by ^1H-COSY in the following way: ^1H NMR (270 MHz, $CDCl_3$) δ **3c**: −0.75 (m, 1H, cyclopr.-H), 0.15 (m, 1H, cyclopr.-H), 0.78 (m, 1H, cyclopr.-H), 1.11 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 3.29 (1H, benzyl-CH, ^2J 16.2 Hz), 3.55 (s, 1H), 3.66 (d, 1H, benzyl-CH, ^2J 12.5 Hz), 3.87 (d, 1H, benzyl-CH, ^2J 12.5 Hz), 4.09 (d, 1H, benzyl-CH, ^2J 16.2 Hz), 7.12–7.33 (m, 10H); **3c-II**: δ −0.87 (m, 1H, cyclopr.-H), −0.07 (m, 1H, cyclopr.-H), 1.08 (s, 3H, CH_3), 2.78 (d, 1H, ^2J 16.5 Hz), 2.90 (d, 1H, ^2J 16.5 Hz), 3.26 (d, 1H, benzyl-CH, ^2J 16.1 Hz), 3.43 (s, 1H), 3.73 (d, 1H, benzyl-CH, ^2J 12.5 Hz), 3.88 (d, 1H, benzyl-CH, ^2J 12.5 Hz), 4.12 (d, 1H, benzyl-CH, ^2J 16.1 Hz), 7.12–7.33 (m, 10H); not all the proton signals are listed. To the mixture **3c/3c-II** in ether (5 mL) was added a solution of diazomethane[23] (prepared from nitrosomethylurea[23a]) in ether at 0 °C. The reaction mixture was kept at rt for 12 h. Afterwards the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether–hexane 3 : 1) to give **3g** and **3g-II**.

Methyl 7′-oxo-1′,4′-dimethyl-5′,6′-bis(phenylmethyl)spiro[cyclopropane-1,2′-[7′]thiabicyclo[2.2.1]hept[5]ene]-3′-carboxylate 3g. 40 mg, 45%; R_f 0.4; mp 180–181 °C; IR (KBr) *ν* 3080, 3022, 2924, 1725, 1602, 1494, 1453, 1427, 1347, 1194, 1092, 1068, 792, 724, 698 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ −0.79 (m, 1H, cyclopr.-H), −0.06 (m, 1H, cyclopr.-H), 0.73 (m, 1H, cyclopr.-H), 0.84 (m, 1H, cyclopr.-H), 1.10 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 3.28 (d, 1H, benzyl-CH, ^2J 15. 2 Hz), 3.51 (s, 1H), 3.68 (d, 1H, benzyl-CH, ^2J 16.5 Hz), 3.70 (s, 3H, $COOCH_3$), 3.87 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 4.12 (d, 1H, benzyl-CH, ^2J 16.5 Hz), 7.15–7.32 (m, 10H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 3.79, 9.09, 9.81, 13.32, 29.59, 32.65, 32.99, 51.71, 56.73, 71.19, 73.24, 126.38, 126.57, 128.16 (2C), 128.37 (2C), 128.62 (2C), 129.20 (2C), 136.03, 137.32, 137.93, 138.81, 172.23; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 421 (MH^+, 100), 372 (M^+ − SO, 87), HRMS Found: 421.1838; calcd. for $C_{26}H_{29}O_3S$: 421.1837.

1-(Methoxycarbonylmethyl)cyclopropyl 7′-oxo-1′,4′-dimethyl-5′,6′-bis(phenylmethyl)spiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5′]ene]-3′-carboxylate 3g-II. 41 mg, 38%, Colorless needles; R_f 0.2; mp 145–146 °C; IR (KBr) *ν* 3064, 3026, 3004, 2924, 1742, 1452, 1439, 1201, 1170, 1143, 1064, 1023, 731, 719, 698 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ −0.84 (m, 1H, cyclopr.-H), −0.04 (m, 1H, cyclopr.-H), 0.66 (m, 1H, cyclopr.-H), 0.86 (m, 1H, cyclopr.-H), 0.97 (m, 4H, cyclopr.-H), 1.09 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 2.76 (d, 1H, H-C2″, ^2J 15.5 Hz), 2.86 (d, 1H, H-C2″, ^2J 15.5 Hz), 3.27 (d, 1H, benzyl-CH, ^2J 15.5 Hz), 3.41 (s, 1H), 3.71 (s, 3H, $COOCH_3$), 3.72 (d, 1H, benzyl-CH, ^2J 16.5 Hz), 3.88 (d, 1H, benzyl-CH, ^2J 15.5 Hz), 4.12 (d, 1H, benzyl-CH, ^2J 16.5 Hz), 7.14–7.33 (m, 10H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 3.22, 9.04, 9.63, 12.09, 12.47, 13.06, 29.51, 32.61, 32.97, 39.94, 51.91, 56.35, 57.11, 71.19, 73.24, 126.38, 126.61, 128.16 (2C), 128.37 (2C), 128.62 (2C), 129.16 (2C), 136.03, 137.32, 138.00, 138.85, 170.67, 171.96; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 519 (MH^+, 61), 470 (M^+ − SO, 38). HRMS Found: 519.2212; calcd. for $C_{31}H_{35}O_5S$: 519.2205.

7′-Oxo-3′-acetyl-5′,6′-dibenzyl-1′,4′-dimethylspiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene] 3j

Variant 1. A solution of 3,4-dibenzyl-2,5-dimethylthiophene *S*-monoxide **4c** (112 mg, 0.265 mmol) and cyclopropylidenepropanone **2k** (51 mg, 0.53 mmol) in $CDCl_3$ (2 mL) was kept at 60 °C. ^1H NMR spectra of the mixture were recorded after 8.5, 17, and 25.5 h. Then the reaction mixture was concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether–hexane 4 : 1) to give **3j** (37 mg, 35%) as a colorless oil; R_f (ether–hexane 4 : 1) 0.2; ^1H NMR (270 MHz, $CDCl_3$) δ 0.81 (m, 1H, cyclopr.-H), −0.07 (m, 1H, cyclopr.-H), 0.60 (m, 1H, cyclopr.-H), 1.10 (m, 1H, cyclopr.-H), 1.16 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 3.12 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 3.32 (s, 1H), 3.48 (d, 1H, benzyl-CH, ^2J 16.7 Hz), 3.80 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 4.06 (d, 1H, benzyl-CH, ^2J 16.7 Hz), 7.01–7.17 (m, 10H); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 405 (MH^+, 10). Anal. calcd. for $C_{26}H_{28}O_2S$ (404.57) C, 77.19; H, 6.98. Found: C, 77.15; H, 6.92%.

Variant 2. A mixture of 1-ethoxycyclopropanol **6** (175 mg, 1.7 mmol), (acetylmethylene)triphenylphosphorane **7e** (2.15

mmol), benzoic acid (12.0 mg, 0.10 mmol) and **4c** (52 mg, 0.17 mmol) in benzene (3 mL) was stirred under reflux for 56 h. The reaction mixture was cooled and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether–hexane 4 : 1) to give **3j** (35 mg, 52%).

7′-Oxo-3′-benzoyl-5′,6′-bis(*p*-*tert*-butylbenzyl)-1′,4′-dimethylspiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene] 3h—one-pot Wittig olefination–cycloaddition reaction

A mixture of 1-ethoxycyclopropanol **6** (175 mg, 1.7 mmol), (benzoylmethylene)triphenylphosphorane (810 mg, 2.13 mmol), benzoic acid (12.7 mg, 0.11 mmol) and **4a** (71.4 mg, 0.17 mmol) in benzene (3 mL) was stirred under reflux for 22 h. The reaction mixture was cooled to rt and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (ether–hexane 3 : 1) to give **3h** (89 mg, 90% based on **4a**); R_f 0.4; ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.86 (m, 1H, cyclopr.-H), −0.32 (m, 1H, cyclopr.-H), 0.67 (m, 1H, cyclopr.-H), 0.84 (m, 1H, cyclopr.-H), 1.11 (s, 3H, CH_3), 1.27 (s, 9H, Bu^t), 1.29 (s, 3H, CH_3), 1.30 (s, 9H, Bu^t), 3.28 (d, 1H, benzyl-CH, ^3J 15.1 Hz), 3.66 (d, 1H, benzyl-CH, ^3J 16.5 Hz), 3.89 (d, 1H, benzyl-CH, ^3J 15.1 Hz), 4.18 (d, 1H, benzyl-CH, ^3J 16.5 Hz), 4.66 (s, 1H), 7.13 (d, 2H, ^3J 8.2 Hz), 7.29 (2d, 4H, ^3J 8.2 Hz), 7.59 (m, 1H), 7.90 (d, 2H, ^3J 8.5 Hz); MS (70 eV) *m*/*z* (%) 574 (M^+, 7). Anal. calcd. for $C_{39}H_{42}O_2S$ (574.82) C, 81.49; H, 7.36. Found: C, 81.24; H, 7.25%.

7′-Oxo-3′-(*p*-chlorobenzoyl)-5′,6′-dibenzyl-1′,4′-dimethylspiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene] 3i

A mixture of 1-ethoxycyclopropanol **6** (204 mg, 2.0 mmol), (*p*-chlorobenzoylmethylene)triphenylphosphorane **7d** (830 mg, 2.0 mmol), benzoic acid (10 mg, 0.095 mmol) and **4c** (50 mg, 0.16 mmol) in benzene (10 mL) were stirred under reflux for 22 h and worked up as described above to give **3i** (75 mg, 91%) as a colorless oil; IR ($CHCl_3$) *v* 3062, 3026, 2970, 1733, 1679, 1588, 1453, 1092 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.87 (m, 1H, cyclopr.-H), −0.34 (m, 1H, cyclopr.-H), 0.65 (m, 1H, cyclopr.-H), 0.83 (m, 1H, cyclopr.-H), 1.11 (3H, s, CH_3), 1.29 (3H, s, CH_3), 3.30 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 3.69 (d, 1H, benzyl-CH, ^2J 16.5 Hz), 3.93 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 4.22 (d, 1H, benzyl-CH, ^2J 16.5 Hz), 4.60 (s, 1H), 7.20–7.27 (m, 10H), 7.45 (d, 2H, ^3J 8.5 Hz), 7.87 (d, 2H, ^3J 8.5 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 4.01 (−, cyclopr.-C), 9.51 (−, cyclopr.-C), 9.58 (CH_3), 14.11 (CH_3), 31.29 (C_{quat}), 33.15 (−, benzyl-C), 33.61 (−, benzyl-C), 56.37 (+, CH), 73.06 (C_{quat}), 74.31 (C_{quat}), 126.79 (+, CH), 126.97 (+, CH), 128.61 (+, CH), 128.81 (+, CH), 129.40 (+, CH), 129.72 (+, CH), 129.76 (+, CH), 136.91 (C_{quat}), 137.30 (C_{quat}), 137.37 (C_{quat}), 137.77 (C_{quat}), 139.34 (C_{quat}), 140.81 (C_{quat}), 199.53 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (%) 503 ([^{37}Cl]MH^+, 5.2), 501 ([^{35}Cl]MH^+, 12), 452 (M^+ − SO, 6.4). HRMS (FAB) Found: 501.1655; calcd. for $C_{31}H_{30}$ [^{35}Cl]O_2S: 501.1655.

7′-Oxo-5′,6′-bis(phenylmethyl)-3′-cyano-1′,4′-dimethylspiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene] 3k

A mixture of 1-ethoxycyclopropanol **6** (350 mg, 3.4 mmol), (cyanomethylene)triphenylphosphorane **7f**[18] (1.28 g, 4.26 mmol) and benzoic acid (10 mg, 9×10^{-2} mmol) in benzene (3 mL) was stirred under reflux for 10 h. Thereafter **4c** (75 mg, 0.24 mmol) was added to the cooled solution, and the mixture was stirred under reflux for an additional 22 h. The reaction mixture was concentrated *in vacuo* and subjected to column chromatography on silica gel (ether–hexane 3 : 1) to afford **3k** (66 mg, 71%) as a colorless solid; R_f 0.37; mp 134–135 °C ($CHCl_3$–hexane 1 : 4); IR (KBr) *v* 3080, 3026, 2924, 2232, 1603, 1494, 1450, 1105, 1076, 1031, 748, 726, 697 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ −0.59 (m, 1H, cyclopr.-H), 0.39 (m, 1H, cyclopr.-H), 0.77 (m, 1H, cyclopr.-H), 0.95 (m, 1H, cyclopr.-H), 1.13 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.35 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 3.40 (s, 1H), 3.64 (d, 1H, benzyl-CH, ^2J 16.2 Hz), 3.92 (d, 1H, benzyl-CH, ^2J 15.2 Hz), 4.15 (d, 1H, benzyl-CH, ^2J 16.2 Hz), 7.15–7.36 (m, 10H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 4.55, 8.89, 10.82, 12.99, 28.84, 32.39, 32.65, 45.26, 71.07, 73.60, 118.52, 126.81, 127.01, 128.05 (2C), 128.59 (2C), 128.84 (2C), 129.02 (2C), 134.28, 136.35, 137.64, 140.81; MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (%) 388 ($M+H^+$, 100), 339 (M^+ − SO, 74). HRMS Found: 388.1731; calcd. for $C_{25}H_{26}ONS$: 388.1735. Anal. calcd. for $C_{25}H_{26}ONS$ (388.55) C, 77.28; H, 6.74; N, 3.60%.

Ethyl 7′-oxo-1′,4′-dimethyl-5′,6′-bis(*p*-methoxyphenyl)spiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene]-3′-carboxylate 3m

A mixture of 1-hydroxy-1-ethoxycyclopropane **6** (175 mg, 1.70 mmol), (ethoxycarbonylmethylene)triphenylphosphorane **7b** (740 mg, 2.13 mmol), 2,5-dimethyl-3,4-bis(*p*-methoxyphenyl)-thiophene *S*-oxide **4b** (77 mg, 0.23 mmol), and benzoic acid (50 mg, 0.41 mmol) in benzene (4 mL) was heated under reflux for 21 h. The reaction mixture was concentrated *in vacuo* and directly submitted to column chromatography on silica gel (eluting with ether–hexane 2 : 1) to give **3m** (91 mg, 85%); R_f 0.25; IR (neat) *v* 2930, 2836, 1735, 1607, 1510, 1246, 1175, 1032 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.54 (m, 1H, cyclopr.-H), 0.62 (m, 1H, cyclopr.-H), 0.95 (m, 1H, cyclopr.-H), 1.03 (s, 3H, CH_3), 1.08 (m, 1H, cyclopr.-H), 1.22 (t, 3H, ^3J 7.2 Hz), 1.49 (s, 3H, CH_3), 3.69 (s, 1H), 3.73 (s, 3H, *p*-OCH_3), 3.74 (s, 3H, *p*-OCH_3), 4.15 (q, 2H, ^3J 7.2 Hz), 6.70 (d, 2H, ^3J 8.9 Hz), 6.72 (d, 2H, ^3J 8.6 Hz), 6.94 (d, 2H, ^3J 8.9 Hz), 7.05 (d, 2H, ^3J 8.6 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 3.88 (−, cyclopr.), 9.18 (−, cyclopr.), 10.20 (CH_3), 14.17 (CH_3), 14.54 (CH_3), 29.70 (C_{quat}, cyclopr.), 50.04 (2 OCH_3), 56.26 (CH), 60.71 (−, OCH_2), 72.24 (C_{quat}), 73.64 (C_{quat}), 113.09 (CH), 113.49 (CH), 113.62 (C_{quat}), 126.79 (C_{quat}), 130.65 (CH), 131.48 (CH), 138.34 (C_{quat}), 140.63 (C_{quat}), 158.56 (C_{quat}, 2C), 171.71 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (%) 467 (MH^+, 23), 418 (M^+ − SO, 88), 390 ([418] − C_2H_4, 25), 345 ([418] − $COOC_2H_5$, 100); MS (FAB, glycerine) *m*/*z* (%) 467 (MH^+, 34), 418 (M^+ − SO, 33), 345 ([418 − $COOC_2H_5$, 40). HRMS Found: 467.1892; calcd. for $C_{27}H_{31}O_5S$: 467.1892.

Attempted cycloaddition of tetramethylthiophene *S*,*S*-dioxide to ethyl cyclopropylideneacetate

A solution of tetramethylthiophene *S*,*S*-dioxide (58 mg, 0.33 mmol) and ethyl cyclopropylideneacetate (130 mg, 1.03 mmol) in $CDCl_3$ (2 mL) was kept at 60 °C. ^{1}H NMR spectra were recorded after 10.5, 24, and 48 h. No reaction products could be detected.

Reactions under high pressure

Ethyl 7′-oxo-5′,6′bis(*p*-*tert*-butylphenylmethyl)-2′-chloro-1′,4′-dimethylspiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept-[5]ene]-3′-carboxylate 3b—cycloaddition reaction under high pressure. A mixture of **4a** (42 mg, 0.1 mmol) and **2c** (29 mg, 0.2 mmol) in acetonitrile (3 mL) was heated at 60 °C under a pressure of 10 kbar for 24 h. After concentration *in vacuo* the residue was chromatographed on silica gel to give **3b** (52 mg, 92%) as colorless crystals; R_f 0.70 (ether). The spectroscopic data were identical with those of **3b**, as listed above.

5′,6′-Dibenzyl-1′,4′-dimethyl-7′-oxodispiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene-3′,1″-cyclopropane] 3f. A mixture of **4c** (62 mg, 0.2 mmol) and **2f** (80 mg, 1.0 mmol) in acetonitrile (3 mL) was heated at 60 °C under a pressure of 10 kbar for 5 d. After concentration of the solution *in vacuo* the residue was subjected to column chromatography on silica gel

to give **3f** (37 mg, 48%) as a colorless solid; mp 120 °C; R_f 0.37 (ether); IR (KBr) ν 3061, 3025, 1601, 1494, 1451, 1123, 1090, 1063, 728, 698 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ −0.31–−0.20 (m, 4H), 0.33 (m, 2H), 0.68 (m, 2H), 1.11 (6H, s, 2 CH_3), 3.64 (s, 4H, 2 CH_2), 7.14–7.32 (m, 10H, arom. H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT) δ 1.77 (−), 6.20 (−), 9.73 (+, CH_3), 29.40 (C_{quat}), 32.40 (−), 72.07 (C_{quat}), 128.50 (+, CH), 128.46 (+,CH), 128.52 (+, CH), 137.52 (C_{quat}), 137.90 (C_{quat}); MS (70 eV) *m*/*z* (%) 388 (M^+, 9), 372 ($M^+ - CH_3$, 9), 340 ($M^+ - SO$, 58), 312 (100). Anal. calcd. for $C_{26}H_{28}SO$ (388.57) C, 80.37; H, 7.26. Found C, 80.20; H, 7.43%.

The same reaction was carried out in acetonitrile (2 mL) for 24 h under otherwise identical conditions to give **3f** (24 mg, 31%).

5′,6′-Bis(*p*-*tert*-butylphenylmethyl)-1′,4′-dimethyl-7′-oxodispiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene-3′,1″-cyclopropane] 3e. A mixture of **4a** (84 mg, 0.2 mmol) and **2f** (80 mg, 1.0 mmol) in acetonitrile (3 mL) was heated at 60 °C under a pressure of 10 kbar for 5 d. After concentration of the solution *in vacuo* the residue was subjected to column chromatography on silica gel to give **3e** (43 mg, 43%) as a colorless solid; mp 93 °C; R_f 0.37 (ether); ^{1}H NMR (250 MHz, $CDCl_3$) δ −0.32–−0.21 (m, 4H), 0.31 (m, 2H), 0.68 (m, 2H), 1.11 (s, 6H, 2 CH_3), 1.31 (s, 18, 2 Bu^t), 3.60 (s, 4H, 2 CH_2), 7.08 (d, 4H, ^3J 8.3 Hz), 7.30 (d, 4H, ^3J 8.3 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT) δ 1.71 (−), 6.17 (−), 9.73 (+), 29.43 (C_{quat}), 31.32 (+), 31.84 (−), 34.35 (C_{quat}), 72.05 (C_{quat}), 125.27 (+), 128.20 (+), 134.86 (C_{quat}), 137.42 (C_{quat}), 149.41 (C_{quat}); MS (70 eV) *m*/*z* (%) 500 (M^+, 16), 485 ($M^+ - CH_3$, 22), 452 ($M^+ - SO$, 56), 424 (100). HRMS Found: 500.3112; calcd. for $C_{34}H_{44}OS$: 500.3113.

The same reaction was carried out in acetonitrile (2 mL) for 24 h under otherwise identical conditions to give **3e** (39 mg, 39%).

Attempted cycloaddition of 3,4-bis(*p*-methoxyphenyl)-2,5-dimethylthiophene *S*-oxide to methyl cyclopentylideneacetate

A mixture of **4b** (50 mg, 0.15 mmol) and **2h** (56 mg, 0.36 mmol) in $CDCl_3$ (2 mL) was heated at 60 °C for 24 h. No product could be detected in the ^{1}H NMR spectrum of the crude reaction mixture.

Competitive cycloaddition of methyl cyclopropylideneacetate 2e and methyl 2-bromo-2-cyclopropylideneacetate 2i with 3,4-dibromo-2,5-dimethylthiophene *S*-oxide 4d

A solution of **4d** (50 mg, 0.175 mmol), **2i** (67 mg, 0.35 mmol) and **2e** (39 mg, 0.35 mmol) in $CHCl_3$ (2 mL) was heated under reflux for 19 h. After the reaction mixture had cooled down to rt, the volatile material was removed *in vacuo*. The residue was subjected to column chromatography to give methyl 5′,6′-dibromo-1′,4′-dimethyl-7-oxospiro[cyclopropane-1,2′-[7]thiabicyclo[2.2.1]hept[5]ene]-3′-carboxylate **3n** (60 mg, 67%) as colorless needles; mp 139.5–140.5 °C (hexane–ether 1:1); IR (KBr) ν 3084, 2954, 1740, 1565, 1454, 1203, 1096, 1072, 1020, 791 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.37 (m, 1H), 0.55 (m, 1H), 0.88–1.05 (m, 2H), 1.21 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 3.66 (s, 1H), 3.69 (s, 3H, $COOCH_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT 90, DEPT 135) δ 2.84 (−), 8.39 (−), 11.66 (+, CH_3), 15.58 (+, CH_3), 29.50 (C_{quat}), 52.16 (+, $COOCH_3$), 55.22 (+, CH), 73.87 (C_{quat}), 76.12 (C_{quat}), 125.55 (C_{quat}), 126.47 (C_{quat}), 170.51 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (%) 401 ($^{81}Br_2MH^+$, 7.9), 399 ($^{79}Br^{81}BrMH^+$, 14.8), 397 ($^{79}Br_2MH^+$, 7.2). HRMS Found: 398.9081; calcd. for $C_{12}H_{15}O_3{}^{79}Br^{81}BrS$: 398.9088 ($MH^+$, FAB). Anal. calcd. for $C_{12}H_{14}O_3Br_2S$ (398.10) C, 36.20; H, 3.54. Found C, 36.30; H, 3.56%.

Methyl 2-bromo-2-cyclopropylideneacetate **2i** (50 mg, 75%) was recovered.

Table 3 Experimental crystallographic details for **3a** and **3f**

Compound	**3a**	**3f**
Formula	$C_{26}H_{27}ClO_3S$	$C_{26}H_{28}OS$
M	454.99	388.54
Crystal system	Orthohombic	Monoclinic
Space group	*Pna*21	$P2_1/c$
a/Å	11.807(2)	13.131(2)
b/Å	20.089(2)	14.125(2)
c/Å	9.866(2)	11.6791(14)
β/°		97.061(12)
V/Å^3	2340.1(7)	2149.8(5)
D_{calc}/g cm^{-3}	1.291	1.200
Z	4	4
μ(Cu-Kα)/Å	μ(Co-Kα) 0.71073	μ(Co-Kα) 0.71073
T/K	296(2)	150(2)
Measured data	11348	2837
Unique data	5791	2817
Observed data	2106	2807
No. of parameters	280	255
R	0.0524	0.0419
R_w	0.1318	0.0930

X-Ray crystallographic structure analysis of 3a †

Intensity data were collected with an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods (SIR-97).[24] All non-hydrogen atoms were located in successive difference Fourier syntheses. Hydrogen atoms were located by calculation with a riding model, weighting scheme $\omega^{-1} = \sigma^2(F_o^2) + (0.0376\ P)^2 + 0.00P$, where $3\ P = (F_o^2 + 2F_c^2)$. All non-hydrogen atoms treated anisotropically were refined by full-matrix least-squares calculation. Hydrogen atoms treated isotropically were refined by full-matrix least-squares calculation. All calculations were performed with an IBM RISC System/6000 380 computer using SHELXL-97.[25] The final cell parameters and specific data collection parameters are summarised in Table 3.

X-Ray crystallographic structure analysis of 3f †

Intensity data were collected at 150(2) K on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-Kα radiation and $\omega/2\theta$ scan mode. The structure was solved by direct methods (SHELXS-86) and refined anisotropically (non-hydrogen atoms) by the full-matrix least-squares method on F^2 (SHELXL-93). Parameters of crystal data collection and structure refinement are presented in Table 3.

† CCDC reference number 207/455. See http://www.rsc.org/suppdata/p1/b0/b003850o for crystallographic files in .cif format.

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