Thiocarbonyl Compounds in [4+2] Cycloadditions: Preparative Aspects☆

Josef Breu[b], Peter Höcht[a], Uwe Rohr[a], Jürgen Schatz[a][+], and Jürgen Sauer*[a]

Institut für Organische Chemie, Universität Regensburg[a],
Universitätsstraße 31, D-93053 Regensburg, Germany
Fax: (internat.) +49(0)941/943-4946
E-mail: elisabeth.liebl@chemie.uni-regensburg.de

Institut für Anorganische Chemie, Universität Regensburg[b],
Universitätsstraße 31, D-93053 Regensburg, Germany

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[4+2] Cycloadditions of thiobenzophenones **1a** and thiofluorenones **2** with cyclic and open-chain dienes gave cycloadducts in high yields. Assignment of the product structure especially the regiochemistry of the cycloadditions involved ^{1}H- and ^{13}C-NMR spectroscopy, and single-crystal structure determination.

The behaviour of hetero double bonds (X=Y with X = C and Y = S, Se, Te, Ge) in cycloaddition reactions have been studied extensively in recent years because of their unique and interesting properties, which are usually quite different from those of the corresponding ketones or alkenes. Stable thioaldehydes[1], telluroketones[2] and germanones[3] are now accessible and their reactivity on the addition to 1,3-dienes or 1,3-dipoles can be studied. Surprisingly little is known about the reactivity of thioketones such as **1**−**9** (Scheme 1) as 2π components in [4+2] cycloaddition reactions. Thioketones, like thiobenzophenone (**1a**),[4][5] thiofluorenone (**2**)[6] or thioadamantone[7] were investigated as dienophiles. Products formed by such cycloaddition processes give rise to 3,6-dihydro-2*H*-thiopyrans (cf. Scheme 1, 2 and 4), which are interesting building blocks in organic synthesis. For example, base-induced ring contraction of such ring systems leads to vinylcyclopropanes or cyclopentenes.[8]

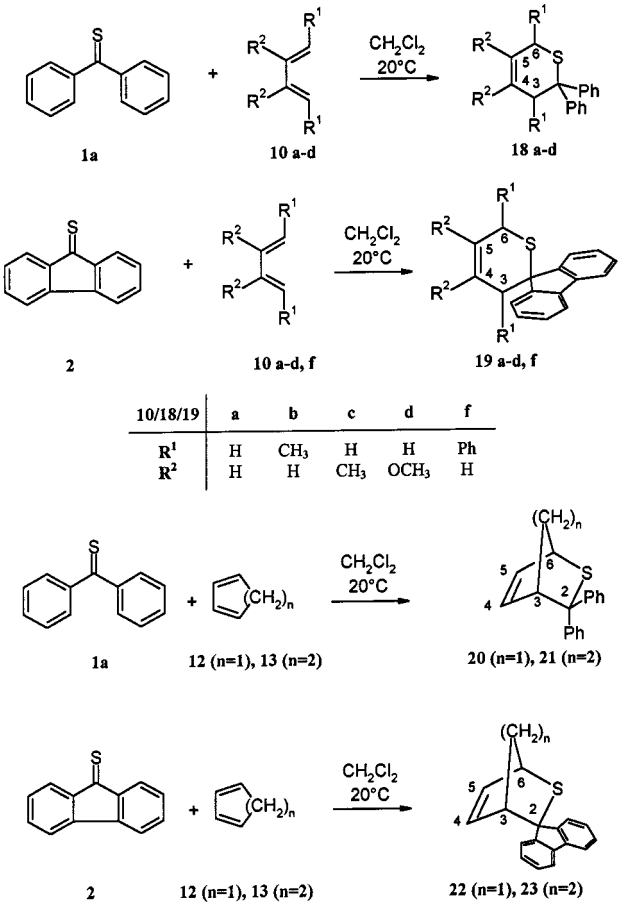
We herein wish to report the preparative results of our investigations concerning the [4+2] cycloadditions of thiocarbonyl compounds **1**−**9** with an extensive range of acyclic and cyclic dienes, which yield a single cycloadduct in good chemical yield. For most of these systems kinetic data will be presented in a subsequent paper.[9]

Results and Discussion

Synthesis of Thioketones and Reaction with Symmetrical and Cyclic Dienes

Thioketones are usually synthesized from the corresponding ketones by reaction with sulfur-donating reagents like S_8,[10][11] H_2S,[12] P_2S_5,[13] or Lawesson's reagent.[14][15] We used Lawesson's reagent for the synthesis of thioketones **1a**−**g** and **3**−**6** starting from the corresponding ketone. However, it was not possible to prepare thiofluorenone (**2**) in a similar manner. Therefore, **2** was obtained in good yields by the reaction of fluorenone with HCl/H_2S in ethanol at low temperatures.[12] The heterocyclic systems **7**,[16]

Scheme 1. [4+2] Cycloadditions of thiones **1a** and **2** with open-chain and cyclic dienes **10**−**13** (CH_2Cl_2, 20°C)



[+] Present address: Abteilung Organische Chemie I, Universität Ulm, Albert-Einstein-Allee 11, D-89069 Ulm, Germany.

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8[17][18] and **9**[19] were readily available by established procedures.

Reactions of thiobenzophenone (**1a**) and thiofluorenone (**2**) as dienophiles with symmetrically substituted open-chain and cyclic dienes **10a−d** and **12−15** in dichloromethane at room temperature gave single cycloadducts in generally high yields (Scheme 1 and Table 1). In all cases completion of the exothermic reaction could be easily detected by the disappearance of the deep blue or green colour of thiobenzophenone or thiofluorenone, respectively. Crude products were usually obtained as colourless or slightly yellow oils with yields higher than 95% as indicated by ^{1}H NMR. Further purification was achieved by recrystallization from suitable solvents or solvent mixtures like ethanol or diethyl ether/petroleum ether. Other potential pathways like ene reactions or the reactions of thioketones[20] as dienes could be excluded in every case.

In general, thiofluorenone (**2**) showed a much higher reactivity towards 1,3-butadienes than thiobenzophenone (**1a**). This could also be proven by extensive kinetic studies for these systems.[9] The structures of the resulting 3,6-dihydro-2*H*-thiopyrans **18** and **19** as well as bicyclic systems **20−24** were established by ^{1}H- and ^{13}C-NMR spectroscopy and by mass spectrometry (EI MS). For the investigation of regiochemical problems (vide infra) in the reaction of unsymmetrically substituted 1,3-butadienes with thiobenzophenone (**1a**) and thiofluorenone (**2**) it was important to assign the protons attached to C-3 and C-6 in the basic 3,6-dihydro-2*H*-thiopyran system. The ^{1}H-NMR data summarized in Table 1 clearly show that the absorptions of methylene or methine protons attached to C-6 (for the numbering of atoms cf. Scheme 1) are strongly influenced by the effect of the neighbouring sulfur ring atom compared to the corresponding C-3 protons. The difference in chemical shift

Table 1. Reactions of thiones **1a** and **2** with open-chain and cyclic dienes **10**, **12** and **13** (CH_2Cl_2, 20°C)

Adduct	R^1	R^2	Yield (%)	δ(3-H)	δ(4-H)	δ(5-H)	δ(6-H)	δ(subst.)
			Reaction of thiobenzophenone (**1a**) with symmetrically substituted 1,3-butadienes					
18a	H	H	53	2.84−2.88	5.76−5.86	5.97−6.03	3.00−3.05	−
18b	CH_3	H	60	2.67	5.55	5.96	3.09	0.84 (C-3−CH_3); 1.24 (C-6−CH_3)
18c	H	CH_3	25	2.72	−	−	2.88	1.64 (C-4−CH_3); 1.78 (C-5−CH_3)
			Reaction of thiofluorenone (**2**) with symmetrically substituted 1,3-butadienes					
19a	H	H	76	2.72−2.74	6.12−6.25	6.12−6.25	3.52−3.54	−
19b	CH_3	H	98	2.83−2.94	5.87−5.93	6.01−6.08	3.81−3.93.	0.75 (C-3−CH_3); 1.45 (C-6−CH_3)
19c	H	CH_3	30	2.64	−	−	3.43	1.77 (C-4−CH_3); 1.95 (C-5−CH_3)
19d	H	OCH_3	83	2.91	−	−	3.54	3.65 (C-4−OCH_3); 3.82 (C-5−OCH_3)
19f	Ph	H	66	3.65	6.34	6.51	5.04	7.18−7.54
			Reaction of thiobenzophenone (**1a**) with cyclic 1,3-butadienes					
20	$-CH_2-$	H	76	4.10	5.57	6.38	4.20	1.92, 2.12
21	$-CH_2CH_2-$	H	84	3.62	6.30	6.51	3.71	1.30, 1.70, 2.10
			Reaction of thiofluorenone (**2**) with cyclic 1,3-butadienes					
22	$-CH_2-$	H	74	3.05−3.07	6.04−6.08	6.80−6.81	4.45−4.47	1.83, 2.65
23	$-CH_2CH_2-$	H	23	2.43−2.50	6.40−6.85	6.85−6.91	3.85−3.89	1.24−1.38, 1.88−1.98, 2.43−2.50

Table 2. [4+2] Cycloaddition reactions of thiobenzophenone (**1a**) with substituted 1,3-butadienes

Adduct	[Diene]/ [C=S]	Yield (%)	M.p. [°C]	Formula [g·mol^{-1}]	C found (calcd.)	H found (calcd.)	UV (CH_2Cl_2) λ_{max} (ε)	IR (KBr) ν̃
18a	1.3	53	95−96	$C_{17}H_{16}S$ (252.4)	80.68 (80.91)	6.32 (6.39)	250 (1300), 233 (2100)	3050, 3000 2960, 2900, 2860, 2840, 1585, 1570
18b	10.3	60	50−51	$C_{19}H_{20}S$ (280.4)	81.34 (81.39)	7.10 (7.19)	218 (1700), 233 (2800)	3080, 3050, 3020, 2960, 2920, 2880, 2860, 1640, 1590
18c	14.5	25	51−52	$C_{19}H_{20}S$ (280.4)	81.40 (81.39)	7.22 (7.19)	253 (1400), 235 (2500)	3070, 3040, 3010, 2890, 2880, 2840, 2800, 1590
20	14.6	76	128−129	$C_{18}H_{16}S$ (264.4)	81.54 (81.80)	5.99 (6.10)	267 (1200), 245 (3200), 235 (400)	3040, 2980, 2950, 2930, 1590
21	10.2	84	195−196	$C_{19}H_{18}S$ (278.4)	81.90 (82.00)	6.44 (6.52)	260 sh, 240 (3600)	3040, 3010, 2950, 2930, 2850, 1590
37a	3.96	64	77−78 (3-Me)	$C_{18}H_{18}S$ (266.4)	81.28 (81.19)	6.61 (6.81)	248 (1800), 235 (2300)	3070, 3050, 3020, 2980, 2930, 2880, 1650, 1590
37b	2.97	64	119−120 (3-OMe)	$C_{18}H_{18}OS$ (282.4)	76.51 (76.58)	6.53 (6.43)	250 (1300), 232 (2100)	3050, 3000, 2980, 2920, 2880, 2850, 1590
40/41a	14.6	54	47−50 (mixture)	$C_{18}H_{18}S$ (266.4)	81.29 (81.19)	6.81 (6.81)		3060, 2990, 2920, 2890, 2860, 1600, 1580
40/41b	4	4		$C_{18}H_{18}OS$ (282.4)				3080, 3050, 3020, 2940, 2920, 2900 1590

Table 3. [4+2] Cycloaddition reactions of thiofluorenone (**2**) with substituted 1,3-butadienes

Adduct	[Diene]/ [C=S]	Yield (%)	M.p. [°C]	Formula [g·mol^{-1}]	C found (calcd.)	H found (calcd.)	UV (CH_2Cl_2) λ_{max} (ε)	IR (KBr)
19a	1.00	76	119−120	$C_{17}H_{14}S$ (250.4)	81.45 (80.54)	5.44 (5.64)	255 (16200), 300 (4340)	3040, 3020, 3000, 2860, 2880, 1460, 1430
19b	4.53	98	oil	$C_{19}H_{18}S$ (278.4)	oil			3040, 3000, 2950, 2900, 2840, 1590, 1570
19c	1.39	30	121	$C_{19}H_{18}S$ (278.4)	81.65 (81.94)	6.51 (6.45)	237 (12600), 275 (26600)	3060, 3040, 3000,2910, 2870, 2800, 1440, 1400
19d	1.23	83	140−141	$C_{18}H_{16}O_2S$ (310.4)	73.54 (73.52)	5.65 (5.85)	230 (13100), 260 (17900), 302 (5000)	3060, 2990, 2940, 2890, 2830, 1580
19f	1.45	66	125	$C_{29}H_{22}S$ (402.6)	86.36 (86.52)	5.72 (5.51)	230 (26500), 330 (33000), 345 (20700)	3060, 3020, 2870, 1590
22	1.89	74	128−130	$C_{18}H_{14}S$ (262.4)	82.25 (82.39)	5.41 (5.39)	280 (6690)	3050, 3025,2995, 2960, 2900, 1435
23	1.23	23	193−195	$C_{19}H_{16}S$ (276.4)	82.43 (82.48)	5.82 (5.94)	312 (3150)	3050, 3020, 2960, 2940, 2860, 1590
39a	1.22	30	125−126	$C_{18}H_{16}S$ (264.4)	81.89 (81.77)	6.04 (6.10)	230 (13700), 260 (27600)	3060, 3040, 3010, 2980, 2930, 2880, 2860, 1470, 1445
39b	2.42	31	153−154	$C_{18}H_{16}OS$ (280.4)	76.41 (77.10)	5.85 (5.75)	230 (13500), 260 (14200), 303 (3200)	3060, 3040, 3000, 2920, 2900, 2840, 2820, 1440
42/43a	1.22	86	97−107 (mixture)	$C_{18}H_{16}S$ (264.4)				3080, 3060, 2990, 2900,
42/43b	1.21	56	128−129	$C_{18}H_{16}OS$ (280.4)	76.30 (7.10)	5.92 (5.75)	230 (12100), 260 (1500), 303 (4200)	3080, 3000, 2970, 2950, 2900, 2840, 1650, 1440

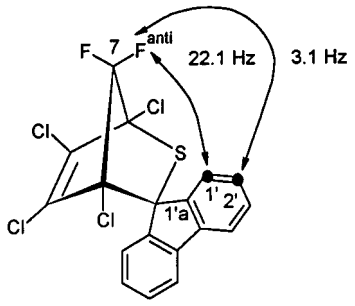
($\delta_{6\text{-H}} - \delta_{3\text{-H}}$) is usually 0.1−1.3 ppm. This assignment of chemical shifts is in full agreement with ^{13}C-NMR data and CH-COSY experiments done on selected cycloadducts. Furthermore, the fluorene ring system exhibits a strong anisotropic effect on substituents attached to C-3. For example, one methyl group of cycloadduct **19b** is shifted by 0.7 ppm upfield to δ = 0.75 relative to δ = 1.45 for the C^6-CH_3 group. In case of the thiobenzophenone adduct **18b** the corresponding difference is 0.4 ppm [$\delta(C^3-CH_3)$ = 0.84 and $\delta(C^6-CH_3)$ = 1.24].

Cycloaddition of Thiofluorenone and Polyhalogenated Cyclopentadienes

Surprisingly, the reactivity of thiofluorenone (**2**) towards 4π systems was so high that cycloadducts could also be isolated during reactions with typical electron-deficient 5,5-substituted 1,2,3,4-tetrachloro-1,3-cyclopentadienes **15**.[21][22] The reaction proceeded smoothly at room temperature in dichloromethane. No heating or Lewis acid catalysts were necessary to speed up the reaction. The cycloadducts could be isolated as colourless crystalline compounds **24** (Scheme 2) which decomposed on melting. The green colour observed during melting of pure material indicated a retro Diels−Alder process yielding thiofluorenone (**2**) and polyhalogenated cyclopentadiene. Compounds **24c** and **24d** with a melting point higher than 150°C showed a strong red colour at the melting point indicating the formation of 9,9′-bifluorenylidene. At those elevated temperatures thiofluorenone (**2**) formed during the retro Diels−Alder reaction underwent the known dimerization and loss of sulfur to yield the red 9,9′-bifluorenylidene.[23][24] The reactivity of hexachloro-1,3-cyclopentadiene was not high enough to form the corresponding cycloadduct. In this case only the decomposition of thiofluorenone (**2**) could be observed.

Cycloadducts **24b** formed by the reaction of thiofluorenone (**2**) and 1,2,3,4-tetrachloro-5,5-difluoro-1,3-cyclopentadiene (**15b**) showed additional splitting of the C-1′ and C-2′ signals in the ^{13}C-NMR spectra (Figure 1). It is assumed that these splittings are transmitted *through space* and therefore coupling constants $J(F_{anti}, C_{1'})$ = 22.1 Hz and $J(F_{anti}, C_{2'})$ = 3.1 Hz can be found. From an optimized geometry obtained by molecular modeling (PM3 semiempirical method,[25] Nimag = 0) of the cycloadduct **24b**, distances between 7-F_{anti} and C-1′ or C-2′ can be determined as 273 and 397 pm, respectively, supporting the assumption that the additional splitting is due to *through-space* interactions. Furthermore, a similar kind of interaction could be found in cycloadducts of 5,5-disubstituted 1,2,3,4-tetrachloro-1,3-cyclopentadienes and styrenes.[21]

Figure 1. Through-space coupling in **24h**

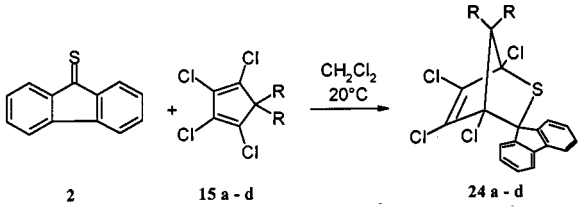


24b

Cycloaddition of Substituted Thiobenzophenones and 1,2,4,5-Tetrazines

The clean reaction between thiofluorenone (**2**) and polyhalogenated cyclopentadienes **15a−15d** also implies the possibility of a reaction of thiocarbonyl compounds with typical electron-deficient 4π systems like 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine **14** (Scheme 3). Since the reactivity towards these dienes was low, thiofluorenone **2** could not be used due to its high tendency for dimerization at elevated temperatures and prolonged reaction times. Therefore, a range of substituted thiobenzophenones **1a−c**, **e−f** easily

Scheme 2. [4+2] Cycloadditions of thiofluorenone (**2**) with polyhalogenated 1,3-cyclopentadienes (CH_2Cl_2, 20°C)

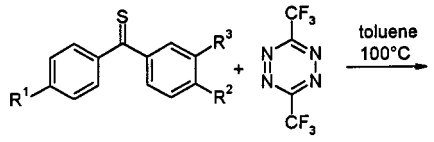


2 15 a - d 24 a - d

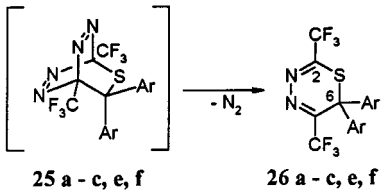
15/24	a	b	c	d
R	H	F	OMe	O-CH_2-

obtainable from the corresponding carbonyl analogue and Lawesson's reagent[23][24] were reacted with 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine (**14**). More strenuous reaction conditions were necessary to yield cycloadducts, but in toluene at 100°C unstable tetraaza intermediates **25** were formed. 6*H*-1,3,4-thiadiazines **26** formed by loss of nitrogen were purified by column chromatography followed by recrystallization from petroleum ether. The mediocre yields (47−75%) were mainly due to this purification protocol. As expected variation of substituents in the aryl moiety of the 6*H*-1,3,4-thiadiazines **26** obtained by Diels−Alder reactions has nearly no influence on the habitus of the NMR spectra. The quaternary spiro carbon atom shows absorption at $\delta \approx 52-53$. Coupling to fluorine is very important for structure elucidation of the basic heterocyclic ring system. Imine positions C-2 and C-5 show additional splitting ($^2J \approx 31.7-39.7$ Hz) as well as the trifluoromethyl groups at ($^1J \approx 276.2-279.2$ Hz) due to coupling with neighbouring fluorine atoms (Scheme 3).

Scheme 3. [4+2] Cycloadditions of substituted thiobenzophenones **1** with 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine (**14**) (toluene, 100°C)



1 a - c, e, f 14



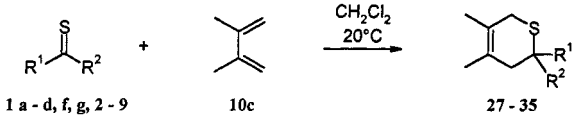
25 a - c, e, f 26 a - c, e, f

1/25/26	a	b	c	e	f
R^1	H	OCH_3	CH_3	H	Cl
R^2	H	OCH_3	CH_3	H	Cl
R^3	H	H	H	F	H

Cycloadditions of Thiocarbonyl Compounds and 2,3-Dimethyl-1,3-butadiene

To shed more light on the reactivity and to determine the scope and limitation of the cycloaddition reactions of thiocarbonyl compounds an extended range of thioketones **1−9** was tested towards their ability to form a cycloadduct with 2,3-dimethyl-1,3-butadiene (Scheme 4). This diene was chosen since the expected products exhibit simple NMR spectra. Furthermore, the low boiling point of this 1,3-diene allows the use of a large excess of the 4π component to accelerate the cycloaddition process. In all cases products derived from Diels−Alder reactions could be isolated and fully characterized (Table 4). The purity of crude products was higher than 90−95% as estimated by ^{1}H-NMR spectroscopy. TLC analysis indicated the presence of the corresponding ketone as the sole impurity. All cycloaddition products **27−35** tend to decompose at elevated temperatures by retro Diels−Alder processes. In case of **35** the loss of sulfinic acid is a possible pathway for decomposition.[26]

Scheme 4. [4+2] Cycloadditions of various thiones **1−9** with 2,3-dimethyl-1,3-butadiene (**10c**) (CH_2Cl_2, 20°C)



1 a - d, f, g, 2 - 9 10c 27 - 35

1/27	a	b	c	d	f	g
R^1 = p-C_6H_4-X; X =	H	OCH_3	CH_3	CH_3	Cl	NO_2
R^2 = p-C_6H_4-Y; Y =	H	OCH_3	CH_3	H	Cl	H

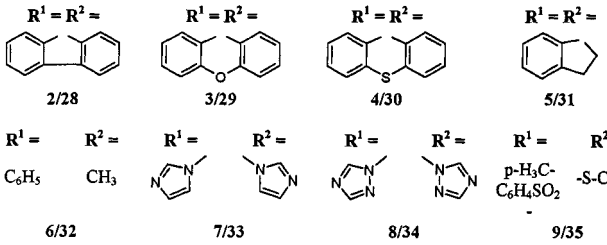


Table 4. [4+2] Cycloadditions of various thiones **1−9** with 2,3-dimethyl-1,3-butadiene (**10c**) (CH_2Cl_2, 20°C)

Thione	Adduct	R^1	R^2	Yield (%)	M.p. [°C]
1a	**27a**	*p*-C_6H_4−H	*p*-C_6H_4−H	25	51−52
1b	**27b**	*p*-C_6H_4−OMe	*p*-C_6H_4−OMe	75	oil
1c	**27c**	*p*-C_6H_4−Me	*p*-C_6H_4−Me	95	oil
1d	**27d**	*p*-C_6H_4−Me	*p*-C_6H_4−H	33	66−68
1f	**27f**	*p*-C_6H_4−Cl	*p*-C_6H_4−Cl	67	68−70
1g	**27g**	*p*-C_6H_4−NO_2	*p*-C_6H_4−H	98	oil
2	**28**	fluorenyl		30	121
3	**29**	xanthyl		97	97
4	**30**	thioxantyl		81	170−171
5	**31**	indenyl		56	50−51
6	**32**	C_6H_5	CH_3	91	oil
7	**33**	1-imidazolyl	1-imidazolyl	no reaction	
8	**34**	1-triazolyl	1-triazolyl	99	121−122
9	**35**	*p*-H_3C−$C_6H_4SO_2$	−S−C_6Cl_5	52	127−128

Nevertheless, all products could be fully characterized by the usual spectroscopic methods (NMR).

Reaction of Thiobenzophenone (1a) and Thiofluorenone (2) with Unsymmetrically Substituted 1,3-Dienes

In case of the Diels−Alder reaction of unsymmetrical butadienes and dienophiles usually one regioisomer is preferred. This can be rationalized by the FMO theory (frontier molecular orbital theory) developed by Sustmann[27] and Fukui[28] for concerted cycloaddition reactions. For the combination of thiobenzophenone (**1a**) and thiofluorenone (**2**) as dienophiles with 1- or 2-substituted 1,3-butadienes the formation of regioisomers is to be expected in principle. Depending on the orientation during the approach of diene and dienophile in the transition state 3/6- or 4/5-substituted 3,6-dihydro-2*H*-thiopyrans can be formed (Scheme 5 and Tables 5−6). Cycloadducts **36/38** can be described as

Scheme 5. [4+2] Cycloadditions of thiones **1a** and **2** with 1- and 2-substituted 1,3-butadienes **11**, **16** and **17** (CH_2Cl_2, 20°C)

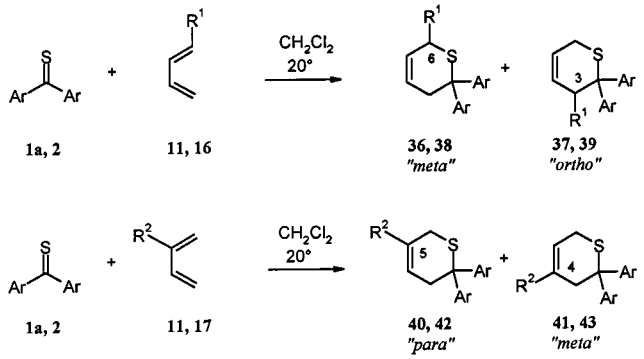


Figure 2. ORTEP plot for spiro compound **40h**

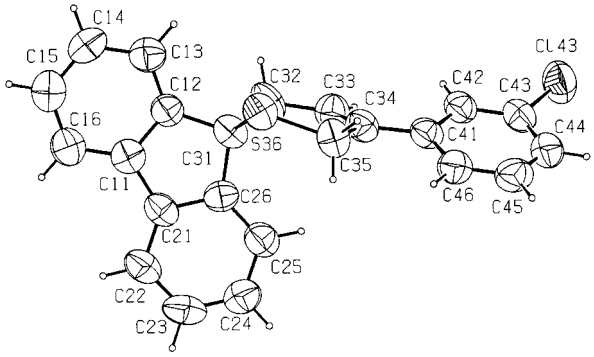
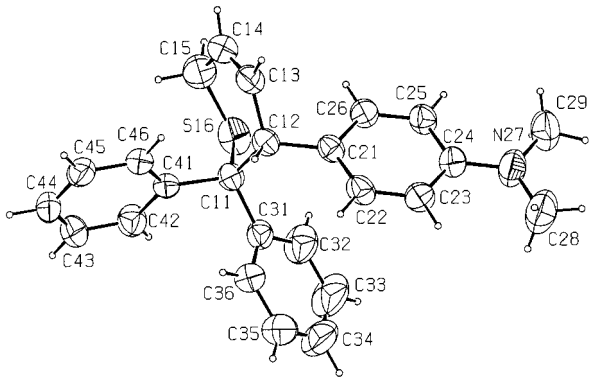


Figure 3. ORTEP plot for spiro compound **37d**



"*meta*"- and **37/39** as "*ortho*"-substituted heterocyclic ring systems. In analogy **40/42** and **41/43** are named "*para*" and "*meta*" adducts. Ratios of regioisomers were detected by ^{1}H-NMR spectroscopy of the crude reaction mixtures. At this stage the assignments made with cycloadducts stemming from symmetric dienes were very helpful to rationalize

Table 5. [4+2] Cycloadditions of thiones **1a** and **2** with 1-substituted 1,3-butadienes **11** and **16** (CH_2Cl_2, 20°C)

Thione	Ar_2	Diene	R^1	No.	Ratio[a]	Yield[b] (%)
1a	Ph_2			**36/37**	**36 37**	
		11b	CH_3	**a**	16 : 84	64[c]
		11e	OCH_3	**b**	10 : 90	64[c]
		16a	Ph	**c**	nd : > 97	60
		16b	*p*-$Me_2N-C_6H_4-$	**d**	nd : > 97	47
		16c	*p*-$MeO-C_6H_4-$	**e**	nd : > 97	62
		16d	*p*-$Me-C_6H_4-$	**f**	− −	−
		16e	*m*-$F-C_6H_4-$	**g**	− −	−
		16f	*m*-$Cl-C_6H_4-$	**h**	− −	
		16g	*m*-$CF_3-C_6H_4-$	**i**	nd : > 97	72
		16h	*p*-$O_2N-C_6H_4-$	**j**	nd : > 97	70
2	2,2′-biphenyldiyl			**38/39**	**38 39**	
		11b	CH_3	**a**	nd : > 97	30
		11e	OCH_3	**b**	nd : > 97	31
		16a	Ph	**c**	nd : > 97	94
		16b	*p*-$Me_2N-C_6H_4-$	**d**	nd : > 97	86
		16c	*p*-$MeO-C_6H_4-$	**e**	nd : > 97	59
		16d	*p*-$Me-C_6H_4-$	**f**	nd : > 97	92
		16e	*m*-$F-C_6H_4-$	**g**	nd : > 97	89
		16f	*m*-$Cl-C_6H_4-$	**h**	nd : > 97	70
		16g	*m*-$CF_3-C_6H_4-$	**i**	nd : > 97	67

[a] Ratio of isomers determined by ^{1}H-NMR spectroscopy of raw materials. − [b] Isolated yield of major isomer. − [c] Yield of mixture of isomers.

Table 6. [4+2] Cycloadditions of thiones **1a** and **2** with 2-substituted 1,3-butadiene **11** and **17** (CH_2Cl_2, 20°C)

Thione	Ar_2	Diene	R^2	No.	Ratio[a]	Yield[b] (%)
1a	Ph_2			**40/41**	**40 41**	
		11c	CH_3	**a**	36 : 64	54[c]
		11d	OCH_3	**b**	35 : 65	56[c]
		17a	Ph	**c**	> 97 : nd	77
		17b	*p*-$Me_2N-C_6H_4-$	**d**	– –	–
		17c	*p*-MeO$-C_6H_4-$	**e**	> 97 : nd	63
		17d	*p*-Me$-C_6H_4-$	**f**	> 97 : nd	84
		17e	*m*-F$-C_6H_4-$	**g**	97 : 3	77
		17f	*m*-Cl$-C_6H_4-$	**h**	97 : 3	89
		17g	*m*-$CF_3-C_6H_4-$	**i**	95 : 5	96
2	2,2′-biphenyldiyl			**42/43**	**42 43**	
		11c	CH_3	**a**	59 : 41	86
		11d	OCH_3	**b**	58 : 42	56[c]
		17a	Ph	**c**	92 : 8	64
		17b	*p*-$Me_2N-C_6H_4-$	**d**	– –	
		17c	*p*-MeO$-C_6H_4-$	**e**	96 : 4	68
		17d	*p*-Me$-C_6H_4-$	**f**	96 : 4	91
		17e	*m*-F$-C_6H_4-$	**g**	– –	–
		17f	*m*-Cl$-C_6H_4-$	**h**	90 : 10	67
		17g	*m*-$CF_3-C_6H_4-$	**i**	91 : 9	47

[a] Ratio of isomers determined by ^{1}H-NMR spectroscopy of raw materials. – [b] Isolated yield of major isomer. – [c] Yield of mixture of isomers.

the corresponding signals of different isomers. The results of this approach are shown in Table 5 and 6. The formation of "*ortho*" products **37/39** is preferred in every case and the known correlation of reactivity and selectivity could be confirmed. The more reactive 1-aryl-1,3-butadienes **16** gave only one regioisomer, namely the "*ortho*" isomer **37/39**, the second possible isomer ("*meta*" isomer **36/38**) could not be detected by ^{1}H-NMR spectroscopy. Stacking effects in the transition state could be a possible explanation for this observation. Similar tendencies could be observed during the reaction of 2-substituted dienes **11** and **17a–g** with thioketones **1a** and **2**. The "*para*" isomers **40** and **42** were the predominant ones but the reactivity–selectivity relationship was much more obvious in this case. With simple 2-methyl- or 2-methoxy-1,3-butadiene about 1:1 mixtures of "*para*" and "*meta*" isomers were obtained. With the much more reactive 2-aryl-1,3-butadienes[29] the proportion is shifted towards the sterically favoured 5-substituted or "*para*" adducts **40** and **42**. All assignments of regioisomers were made on the basis of ^{1}H- and ^{13}C-NMR-spectroscopic data. This rational could be fully confirmed by single-crystal analysis of two representative examples **37d** and **40h** shown in Figure 2 and 3.

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Experimental Section

Solvents were dried according to standard procedures. Melting points (uncorrected): Büchi SMP-20. – UV/Vis: Beckman Modell 24 and Zeiss Specord M 400. The extinctions (lg ε, or ε) are given in brackets. – IR (KBr discs): Beckman Acculab 1. – ^{1}H NMR: Bruker AW 80, Bruker WH 250 and Bruker ARX 400; ^{13}C NMR: Bruker W 250 and Bruker ARX 400; δ values are reported in ppm downfield from internal TMS. – MS: Varian Mat 90 and CH-5 at 70 eV. – Elemental analyses: Heraeus Mikro UE and CHN-Rapid instruments. – All reactions were performed under an inert gas by standard Schlenk techniques in dried solvents. Starting materials, if not commercially available, were prepared in analogy to methods known in the literature: Thiofluorenone (**2**),[12] thioketones,[14] 1- and 2-aryl-1,3-butadienes.[30][31][32][33][34] Reported yields refer to isolated pure materials. Cycloadducts **29**,[35] **30**[36] and **34**[37] have been fully characterized before.

X-ray Structure Analysis: The crystal structures of both compounds were solved by direct methods using SIR92[38] and refined by full-matrix least-squares methods on all F^2 using SHELXL93.[39] Methyl H atoms were placed in idealized positions based on difference electron synthesis and torsion angles were refined with fixed isotropic displacement parameters of 1.5 U_{eq} of the parent C. All other H atoms were placed in idealized positions and refined with fixed isotropic displacement parameters of 1.2 U_{eq} of the parent C. Compound **40h** crystallized in the polar orthorhombic spacegroup $Pn2_1a$ with four molecules in general positions. Straightforward refinement led to unusual bond lengths in the heterocylic six-membered ring [e.g. C31–C32: 1.683(9) Å] and an unrealistic temperature factor for C32. The $wR(F^2)$ is high (0.1460) and the absolute structure cannot be determined reliably with the Flack *x* parameter being 0.49(17).[40] Both, refinement in the monoclinic subgroups and refinement as inversion twin were tried, but did not remedy these shortcomings. Compound **40h** possesses only C_1 symmetry, but aside the chlorophenyl group, which can adjust by rotation around C34–C41, the molecules display a pseudo mirror plane defined by the fluorenyl group with the heterocyclic six-membered ring disordered about this pseudo mirror plane. Final refinement of compound **40h** was therefore performed with a disorder model for the heterocyclic six-membered ring. The bond lengths in the ring were restrained to those found in compound **37d**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101446. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge

CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 7. Crystallographic data for the cycloadducts **37d** and **40h**

Crystal data of compound	**37d**	**40h**
empirical formula	$C_{25}H_{25}NS$	$C_{23}H_{17}ClS$
molecular mass	371.55	360.91
crystal system	monoclinic	orthorhomic
space group symbol	*I*2/*a*	*Pn*2$_1$*a*
a [Å]	12.083(3)	7.3721(9)
b [Å]	9.7390(15)	12.8214(22)
c [Å]	35.054(8)	19.1609(32)
β [°]	98.42(2)	90
V [Å^3]	4080.6(15)	1811.1(5)
T [K]	298(2)	298(2)
Z	8	4
D_x [Mg·m^{-3}]	1.210	1.324
μ [mm^{-1}]	0.17	0.33
size of crystal [mm]	0.68 × 0.38 × 0.11	0.21 × 0.07 × 0.06
	colourless lath	colourless needle
Data collection		
diffractometer	STOE IPDS	STOE IPDS
data collection mode	rotation scans	rotation scans
monochromator	graphite	graphite
radiation, Å	Mo-K_α, 0.71069	Mo-K_α, 0.71069
θ range [°]	2.17−20.52	1.91−20.90
reciprocal lattice segment	*h* = −11→11	*h* = −7→7
	k = −8→9	*k* = −12→12
	l = −34→30	*l* = −18→18
reflections measured	3584	5241
symmetrie independent reflections	1974	1886
observed reflections [*I* > 2σ(*I*)]	1619	1466
R_{int}	0.0198	0.0496
Refinement		
number of variables	246	243
reflections used	1974	1886
R(*F*)	0.0313	0.0404
wR(F^2)	0.0808	0.0973
weighting scheme	$1/\sigma^2(F_o^2)$ + (0.0556*P*)^2 + 0.5978*P*	$1/\sigma^2(F_o^2)$ + (0.0884*P*)^2 + 0.00*P*
[$P = (F_o^2 + 2F_c^2)/3$]		
S	1.106	0.882
(Δ/σ)max$_x$	0.001	< 0.001
$\Delta\rho_{max}$ [e Å^{-3}]	0.139	0.152
$\Delta\rho_{min}$ [e Å^{-3}]	−0.098	−0.182

General Procedure for the Cycloaddition Reactions of Thiones with 1,3-Dienes: A solution of thioketone (1−5 mmol) and a slight excess of 1,3-diene in dichloromethane was stirred at room temp. until the characteristic colour of the thione disappeared. All volatile components were removed at room temp. in vacuo to avoid retro Diels−Alder reactions. The yield of raw cycloadduct was in each case > 95% and the ^{1}H-NMR spectroscopy of the raw materials showed nearly no difference to pure products. Materials were purified by column chromatography on silica gel eluting with mixtures of petroleum ether 40/60 and dichloromethane and/or low-temperature recrystallization from suitable mixtures of petroleum ether 40/60, dichloromethane or ethanol. Reactions of thiobenzophenones with 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine (**14**) were performed at 100°C in toluene.

Cycloaddition Rections of Thiobenzophenone and Thiofluorenone with 1,3-Butadienes. − Thiobenzophenone Adducts

3,6-Dihydro-3-methyl-2,2-diphenyl-2H-thiopyran (**37a**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (d, ^3J = 6.7 Hz, 3 H), 2.53 (ddd, ^4J = 2.3 Hz, ^3J = 4.8 Hz, ^2J = 17.4 Hz, 1 H), 2.83 (dddd, ^5J = 0.6 Hz, ^4J = 1.1 Hz, ^3J = 6.4 Hz, ^2J = 17.4 Hz, 1 H), 3.06−3.16 (ddq, *J* = 1.5 Hz, *J* = 5.8 Hz, *J* = 6.7 Hz, 1 H), 5.72 (dm, ^3J = 10.5 Hz, 1 H), 6.01 (dm, ^3J = 10.5 Hz, 1 H), 7.11−7.28 (m, 8 H), 7.35−7.50 (m, 2 H).

3,6-Dihydro-3-methoxy-2,2-diphenyl-2H-thiopyran (**37b**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.78−2.82 (m, 2 H), 3.01 (s, 3 H), 4.48−4.52 (m, 1 H), 5.72−5.78 (dm, ^3J = 10.6 Hz, 1 H), 6.05−6.12 (dm, ^3J = 10.6 Hz, 1 H), 7.17−7.36 (m, 8 H), 7.61−7.67 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 26.8, 57.3, 59.0, 84.1, 125−130, 141.6, 144.6.

3,6-Dihydro-4-methyl-2,2-diphenyl-2H-thiopyran (**41a**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.67 (asym. t, ^2J = ca. 0.8 Hz, 3 H), 2.72 (d, ^2J = 0.74 Hz, 2 H), 2.99 (ddd, ^2J = 4 Hz, ^3J = 2.0 Hz, ^3J = 2.0 Hz, 2 H) , 5.67−5.69 (m, 1 H), 7.15−7.41 (m, 10 H, 2 × PhH).

3,6-Dihydro-5-methyl-2,2-diphenyl-2H-thiopyran (**40a**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.82 (d, ^2J = 1.4 Hz, 3 H), 2.83 (ddd, ^2J = 3.9 Hz, ^3J = 2.0 Hz, ^3J = 2.0 Hz, 2 H), 2.87 (br. s, 2 H), 5.55−5.66 (m, 1 H), 7.15−7.41 (m, 10 H, 2 × PhH).

Thiofluorenone Adducts

3′,6′-Dihydro-3′-methylspiro(9H-fluorene-9,2′-2H-thiopyran) (**39a**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.46 (d, ^3J = 7.3 Hz), 3.26−3.39 (m, 2 H), 3.64−3.75 (m, 1 H), 5.88−5.95 (dm, ^3J = 10.8 Hz, 1 H), 6.06−6.16 (dm, ^3J = 10.8 Hz, 1 H), 7.21−7.43 (m, 4 H), 7.48−7.52 (m, 2 H), 7.71−7.79 (m, 2 H).

3′,6′-Dihydro-3′-methoxyspiro(9H-fluorene-9,2′-2H-thiopyran) (**39b**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.96 (s, 3 H), 3.20−3.31 (m, 1 H), 3.58−3.68 (m, 1 H), 4.63−4.66 (m, 1 H), 6.08−6.25 (m, 2 H), 7.24−7.45 (m, 4 H), 7.53−7.57 (m, 1 H), 7.60−7.64 (m, 1 H), 7.73−7.79 (m, 2 H).

3′,6′-Dihydro-5′-methylspiro(9H-fluorene-9,2′-2H-thiopyran) (**42a**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.98 (br. s, 3 H), 2.69−2.73 (m, 2 H), 3.39 (d, *J* = 0.9 Hz, 2 H), 5.83−5.87 (m, 1 H), 7.25−7.47 (m, 4 H), 7.49−7.54 (m, 2 H), 7.73−7.76 (m, 2 H).

3′,6′-Dihydro-5′-methoxyspiro(9H-fluorene-9,2′-2H-thiopyran) (**42b**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.87 (m, 2 H), 3.48 (m, 2 H), 3.69 (s, 3 H), 5.02−5.03 (m, 1 H), 7.27−7.34 (m, 2 H), 7.37−7.43 (m, 2 H), 7.54−7.57 (m, 2 H), 7.74−7.77 (m, 2 H).

3′,6′-Dihydro-4′-methylspiro(9H-fluorene-9,2′-2H-thiopyran) (**43a**): ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.83 (d, *J* = 1.4 Hz, 3 H), 2.58 (d, *J* = 0.7 Hz, 2 H), 3.51−3.55 (m, 2 H), 5.94 (m, 1 H), 7.25−7.47 (m, 4 H), 7.49−7.54 (m, 2 H), 7.73−7.76 (m, 2 H).

Cycloaddition Reactions of Thiobenzophenone with 1-Aryl-1,3-butadienes

3-[p-Dimethylaminophenyl]-3,6-dihydro-2,2-diphenyl-2H-thiopyran (**37d**): Yield: 166 mg (47%). − M.p. 147−148°C (decomp.). − UV (CH_2Cl_2): λ_{max} = 265 nm (4.286). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}; 3020 (=C−H, w); 2980, 2900, 2850, 2780 (−CH, w); 1590, 1500 (C=C, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.61−2.64 and 2.68−2.71 (m, 1 H), 2.83 (s, 6 H), 2.97−2.99 and 3.04−3.10 (m, 1 H), 4.12−4.14 (m, 1 H), 5.90−6.10 (m, 2 H), 6.38−6.44 (m, 2 H), 6.73−6.84 (m, 4 H), 6.96−7.02 (m, 3 H), 7.16−7.31 (m, 3 H), 7.58−7.62 (m, 2 H). −^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.01 (DEPT neg.), 40.70 (DEPT pos.), 48.71 (DEPT pos.), 59.20 (DEPT 0), 111.43, 124.05, 125.96, 126.15, 127.23 (2 C), 128.24, 129.47, 131.82, 131.98 (all DEPT pos.), 127.45, 146.05, 146.18, 149.35 (all DEPT 0). − $C_{25}H_{25}NS$ (371.5): calcd. C 80.82, H 6.78, N 3.77; found C 80.71, H 6.81, N 4.05.

Table 8. Bond lengths and angles for the cycloadduct **40h**

Bond lengths [Å]					
Cl43−C43	1.753(6)	C21−C22	1.400(8)	C34−C35	1.539(12)
S36−C31	1.826(6)	C22−C23	1.398(9)	C34−C41	1.497(8)
S36−C35	1.814(10)	C23−C24	1.369(10)	C34−C35′	1.55(3)
C11−C16	1.400(8)	C24−C25	1.395(9)	C41−C42	1.397(8)
C11−C21	1.466(8)	C25−C26	1.396(8)	C41−C46	1.413(8)
C11−C12	1.392(8)	C26−C31	1.526(8)	C42−C43	1.379(7
C12−C13	1.374(8)	C31−C32′	1.65(4)	C43−C44	1.396(8)
C12−C31	1.539(7)	C31−C32	1.593(19)	C44−C45	1.379(9)
C13−C14	1.393(9)	C32−C33	1.51(2)	C45−C46	1.382(9)
C14−C15	1.377(10)	C32′−C33′	1.52(5)		
C15−C16	1.379(10)	C33−C34	1.311(14)		
C21−C26	1.402(7)	C33′−C34	1.28(4)		
Bond angles [°]					
C31−S36−C35	100.2(4)	C33−C34−C41	122.9(7)	S36−C31−C32	109.7(6)
C12−C11−C16	120.0(5)	C35′−C34−C41	113.1(10)	C12−C31−C32	113.6(7)
C12−C11−C21	108.7(5)	C33′−C34−C41	125.7(17)	C12−C31−C32′	111.2(14)
C13−C12−C31	128.7(5)	C42−C41−C46	117.9(5)	C31−C32−C33	111.9(12)
C12−C13−C14	119.1(6)	C41−C42−C43	120.8(5)	C32−C33−C34	131.3(11)
C14−C15−C16	121.2(6)	Cl43−C43−C44	119.7(4)	C33−C34−C35	122.2(7)
C11−C21−C22	130.7(5)	C43−C44−C45	117.8(5)	C33′−C34−C35′	121.2(19)
C22−C21−C26	120.1(5)	C41−C46−C45	119.9(5)	C35−C34−C41	114.9(6)
C22−C23−C24	121.1(6)	C16−C11−C21	131.3(5)	S36−C35−C34	115.2(7)
C24−C25−C26	119.3(6)	C11−C12−C13	120.8(5)	C34−C41−C46	121.1(5)
C21−C26−C31	110.2(5)	C11−C12−C31	110.6(5)	C34−C41−C42	121.0(5)
S36−C31−C26	113.2(4)	C13−C14−C15	120.4(6)	Cl43−C43−C42	118.9(4)
C12−C31−C26	101.3(4)	C11−C16−C15	118.6(6)	C42−C43−C44	121.4(5)
C26−C31−C32	114.7(7)	C11−C21−C26	109.1(5)	C44−C45−C46	122.2(5)
C26−C31−C32′	113(2)	C21−C22−C23	118.9(5)		
S36−C31−C12	103.6(4)	C23−C24−C25	120.7(6)		
C31−C32′−C33′	111(3)	C21−C26−C25	120.0(5)		
C32′−C33′−C34	133(3)	C25−C26−C31	129.7(5)		

Table 9. Bond lengths and angles for the cycloadduct **37d**

Bond lengths [Å]					
S16−C11	1.846(2)	C32−C33	1.377(4)	C14−C15	1.481(4)
N27−C24	1.388(3)	C34−C35	1.371(6)	C21−C26	1.387(3)
N27−C29	1.438(3)	C41−C42	1.392(3)	C23−C24	1.398(3)
C11−C31	1.522(3)	C42−C43	1.373(3)	C25−C26	1.375(3)
C12−C13	1.501(3)	C44−C45	1.369(4)	C31−C36	1.379(3)
C13−C14	1.309(3)	S16−C15	1.795(3)	C33−C34	1.353(6)
C21−C22	1.378(3)	N27−C28	1.412(4)	C35−C36	1.388(4)
C22−C23	1.378(3)	C11−C12	1.568(3)	C41−C46	1.383(3)
C24−C25	1.389(3)	C11−C41	1.537(3)	C43−C44	1.369(3)
C31−C32	1.386(3)	C12−C21	1.520(3)	C45−C46	1.384(3)
Bond angles [°]					
C11−S16−C15	97.70(11)	C32−C31−C36	118.0(2)	S16−C15−C14	114.03(18)
C24−N27−C29	120.7(2)	C32−C33−C34	120.7(3)	C12−C21−C26	121.83(19)
S16−C11−C12	108.49(15)	C34−C35−C36	120.0(3)	C21−C22−C23	122.4(2)
S16−C11−C41	107.63(14)	C11−C41−C42	118.92(19)	N27−C24−C23	121.8(2)
C12−C11−C41	113.48(18)	C42−C41−C46	116.96(19)	C23−C24−C25	116.67(19)
C11−C12−C13	113.78(17)	C42−C43−C44	120.5(2)	C21−C26−C25	122.8(2)
C13−C12−C21	110.19(17)	C44−C45−C46	120.5(2)	C11−C31−C36	118.9(2)
C13−C14−C15	125.3(2)	C24−N27−C28	120.6(2)	C31−C32−C33	120.8(3)
C12−C21−C22	122.2(2)	C28−N27−C29	118.7(2)	C33−C34−C35	119.9(3)
C22−C21−C26	115.93(19)	S16−C11−C31	108.73(16)	C31−C36−C35	120.7(2)
C22−C23−C24	121.2(2)	C12−C11−C31	108.30(16)	C11−C41−C46	124.11(18)
N27−C24−C25	121.6(2)	C31−C11−C41	110.10(17)	C41−C42−C43	121.6(2)
C24−C25−C26	121.0(2)	C11−C12−C21	113.76(18)	C43−C44−C45	119.2(2)
C11−C31−C32	122.7(2)	C12−C13−C14	127.4(2)	C41−C46−C45	121.3(2)

3,6-Dihydro-3-(p-methoxyphenyl)-2,2-diphenyl-2H-thiopyran (**37e**): Yield: 455 mg (62%). − M.p. 127−128°C (decomp.). − UV (CH_2Cl_2): λ_{max} = 255 nm (sh), 276 (sh), 283 (sh). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3060, 3020, 3000 (=C−H, w); 2960, 2930, 2900, 2840 (−CH, w); 1650 (w), 1605 (s), 1575 (m), 1500 (s), 1490 (s, C=C, w). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.61−2.64 and 2.68−2.71 (m, 1 H), 2.97−3.00 and 3.04−3.07 (m, 1 H), 3.70 (s, 3 H), 4.14−4.17 (m, 1 H), 5.93−6.09 (m, 2 H), 6.53−6.57 (m, 2 H), 6.72−6.75 (m, 2 H), 6.86−6.89 (m, 2 H), 6.97−7.01 (m, 3 H), 7.17−7.31 (m, 3 H), 7.57−7.61(m, 2 H). − ^{13}C NMR (63 MHz,

$CDCl_3$): δ = 25.94 (DEPT neg.), 48.74 (DEPT pos.), 55.14 (DEPT pos.), 58.98 (DEPT 0), 112.25, 124.47, 126.11, 126.25, 127.3 (2 C), 128.15, 129.4, 131.68, 132.15 (all DEPT pos.), 131.58, 145.83,145.98, 158.25 (all DEPT 0). − $C_{24}H_{22}OS$ (358.5): calcd. C 80.41, H 6.19; found C 80.35, H 5.90.

3,6-Dihydro-3-(m-trifluoromethylphenyl)-2,2-diphenyl-2H-thiopyran (**37i**): Yield: 417 mg (72%). − M.p. 124−124.5°C (decomp.). − UV (CH_2Cl_2): λ_{max} = 247−278 nm (sh). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3050, 3020 (=C−H, w); 2880, 2800 (−CH, w); 1585, 1570 (C=C, w); 1325, 1310 (C−F, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.63−2.72 (m, 1 H), 3.02−3.11 (m, 1 H), 4.24−4.26 (m, 1 H), 6.05−6.07 (m, 2 H), 6.68−6.74 (m, 2 H), 6.93−7.33 (m, 10 H), 7.55−7.60 (m, 2 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.87 (DEPT neg.), 49.30 (DEPT pos.), 58.59 (DEPT 0), 123.09 (q, DEPT pos., ^3J = 3.8 Hz), 124.18 (q, DEPT 0, CF_3, ^1J = 272 Hz), 128.07 (q, DEPT pos., ^3J = 3.7 Hz), 128.99 (q, DEPT 0, ^2J = 30 Hz), 125.83, 126.49, 126.53, 126.99, 127.43, 127.52, 127.88, 129.23, 130.40, 134.39 (all DEPT pos.), 140.47, 145.14, 145.44 (all DEPT 0). − $C_{24}H_{19}SF_3$ (396.5): calcd. C 72.71, H 4.83; found C 72.38, H 4.81.

3,6-Dihydro-3-(p-nitrophenyl)-2,2-diphenyl-2H-thiopyran (**37j**): Yield: 487 mg (70%), yellow crystals. − M.p. 161−165°C (decomp.). − UV (CH_2Cl_2): λ_{max} = 282 nm (4.021). − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}; 3060, 3040 (=C−H, w); 2900, 2880, 2820 (−CH, w); 1600, 1590 (C=C, w); 1510, 1340, 1335, 1310 (NO_2, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.64−2.67 and 2.72−2.74 (m, 1 H), 3.04−3.06 and 3.11−3.13 (m, 1 H), 4.30−4.33 (m, 1 H), 5.99−6.13 (m, 2 H), 6.72−6.80 (m, 2 H), 6.93−7.05 (m, 3 H), 7.13−7.33 (m, 5 H), 7.53−7.60 (m, 2 H), 7.81−7.87 (m, 2 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.86 (DEPT neg.), 49.36 (DEPT pos.), 58.43 (DEPT 0), 121.70, 126.15, 126.62, 126.74, 127.51, 127.69, 127.87, 129.07,130.05, 131.89 (all DEPT pos.), 144.94, 145.29, 146.61, 147.44 (all DEPT 0). − $C_{23}H_{19}NO_2S$ (373.5): calcd. C 73.97, H 5.13, N 3.75 ; found C 73.95, H 5.23, N 3.90.

Cycloaddition Reactions of Thiobenzophenone with 2-Aryl-1,3-butadienes

3,6-Dihydro-5-(p-methoxyphenyl)-2,2-diphenyl-2H-thiopyran (**40e**): Yield: 586 mg (63%), colourless powder. − M.p. 131.5−132°C. − UV (CH_2Cl_2): λ_{max} = 258 nm (4.269). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3050, 3020, 2995 (=C−H, w); 2960, 2930, 2900, 2860, 2830 (−CH, w); 1595 (m), 1500 (s), 1480 (s, C=C). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.17−3.20 (m, 4 H), 3.78 (s, 3 H), 6.20−6.24 (m, 1 H), 6.79−6.85 (m, 2 H), 7.17−7.31 (m, 8 H), 7.40−7.45 (m, 4 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.52 (DEPT neg.), 40.38 (DEPT neg.), 52.87 (DEPT 0), 55.31 (DEPT pos.), 113.80, 124.10, 126.44, 126.65, 127.81, 128.04 (all DEPT pos.), 134.36, 134.80, 145.68, 158.98 (all DEPT 0). − $C_{24}H_{22}OS$ (358.5): calcd. C 80.41, H 6.19; found C 80.18, H 6.34; C 80.21, H 6.30; C 80.18, H 6.26.

3,6-Dihydro-5-(p-methylphenyl)-2,2-diphenyl-2H- thiopyran (**40f**): Yield: 691 mg (84%), colourless crystals. − M.p. 99−100°C. − UV (CH_2Cl_2): λ_{max} = 252 nm (4.196). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3050, 3020 (=C−H, s); 2920, 2890, 2820 (−CH, s); 1640, 1590, 1570 (C=C, m). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 3.18 (br. s, 4 H), 6.24−6.28 (m, 1 H), 7.07−7.30 (m, 10 H), 7.39−7.40 (m, 4 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.03 (DEPT pos.), 28.52 (DEPT neg.), 40.42 (DEPT neg.), 52.92 (DEPT 0), 124.81, 125.25, 126.68, 127.84, 128.07, 129.07 (all DEPT pos.), 135.24, 136.94, 138.91, 145.70 (all DEPT 0). − $C_{24}H_{22}S$ (342.5): calcd. C 84.16, H 6.47; found C 84.00, H 6.41; C 83.98, H 6.43.

5-(m-Fluorophenyl)-3,6-dihydro-2,2-diphenyl-2H-thiopyran (**40g**): Yield: 495 mg (77%), colourless needles. − M.p. 107−108°C. − UV (CH_2Cl_2): λ_{max} = 247 nm (4.042). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3040, 3020 (=C−H, m); 2900 (−CH, m); 1630 (w), 1595 (s), 1570 (s, C=C). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.15−3.17 (m, 2 H,), 3.19−3.22 (m, 2 H), 6.30−6.34 (m, 1 H), 6.86−7.04 (m, 3 H), 7.17−7.32 (m, 7 H), 7.39−7.44 (m, 4 H). − ^{13}C NMR (63 MHz, $CDCl_3$) δ = 28.38 (DEPT neg.), 40.34 (DEPT neg.), 52.96 (DEPT 0), 112.35 (DEPT pos., ^2J = 21.9 Hz), 113.93 (DEPT pos., ^2J = 21.3 Hz), 120.95 (DEPT pos., ^4J = 2.78 Hz), 126.67, 126.86, 127.77, 128.14 (all DEPT pos.), 129.80 (DEPT pos., ^3J = 8.38 Hz), 134.50 (DEPT 0, ^4J = 2.04 Hz), 143.99 (DEPT 0, ^3J = 7.51 Hz), 145.44 (DEPT 0), 162.95 (DEPT 0, ^1J = 245.6 Hz). − $C_{23}H_{19}FS$ (346.5): calcd. C 79.74, H 5.53; found C 79.75, H 5.60, C 79.80, H 5.58.

5-(m-Chlorophenyl)-3,6-dihydro-2,2-diphenyl-2H-thiopyran (**40h**): Yield: 478 mg (89%). − M.p. 94−95°C. − UV (CH_2Cl_2): λ_{max} = 248 nm (4.253). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3050, 3020 (=C−H, m); 2890 (−CH, m); 1640 (m), 1585(s), 1560 (s, C=C). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.14−3.15 (m, 2 H,), 3.18−3.21 (m, 2 H), 6.29−6.32 (m, 1 H), 7.08−7.31 (m, 10 H), 7.39−7.43 (m, 4 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.33 (DEPT neg., C-6), 40.29 (DEPT neg.), 52.88 (DEPT 0), 123.43, 125.55, 126.77, 127.14, 127.71 (2 C), 128.10, 129.54 (all DEPT pos.), 134.35, 143.50, 145.36 (2 C) (all DEPT 0). − $C_{23}H_{19}ClS$: (362.9): calcd. C 76.12, H 5.28; found C 75.94, H 5.21; C 75.83, H 5.32; C 75.85, H 5.39.

3,6-Dihydro-2,2-diphenyl-5-(m-trifluoromethylphenyl)-2H-thiopyran (**40i**): Yield: 178 mg (96%), colourless oil. − UV (CH_2Cl_2): λ_{max} = 247 nm (4.115). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3050, 3020 (=C−H, w); 2950, 2920, 2860 (−C−H, m); 1590 (C=C, w); 1320 (C−F, s). − ^{1}H NMR (250 MHz, $CDCl_3$) δ = 3.19−3.20 (m, 2 H), 3.21−3.24 (m, 2 H), 6.34−6.37 (m, 1 H, H_y), 7.18−7.50 (m, 14 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.40 (DEPT neg.), 40.34 (DEPT neg.), 52.95 (DEPT 0), 122.10 (DEPT pos., ^3J = 3.8 Hz), 123.81 (DEPT pos., ^3J = 3.7 Hz), 124.12 (DEPT 0, ^1J = 272 Hz, CF_3), 130.87 (DEPT 0, ^2J = 32.1 Hz), 126.83, 127.28, 127.73, 128.15, 128.55, 128.83 (all DEPT pos.), 134.40, 142.44, 145.34 (all DEPT 0).

Cycloaddition Reactions of Thiofluorenone with 1-Aryl-1,3-butadienes

3′,6′-Dihydro-3′-phenylspiro(9H-fluorene-9,2′-2H-thiopyran) (**39c**): Yield: 779 mg (94%). − M.p. 124−125°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}; 3020 (m, =C−H); 2960, 2910, 2880, 2860 (w, −C−H); 1590 (w, C=C); 790 (m), 760, 750, 740, 730, 700, 660, (s), 620 (m, C−H deform.). − UV (CH_2Cl_2): λ_{max} = 305 nm (2950), 262 (13500), 235 (3180). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.72−7.76 (m, 1 H), 7.52−7.57 (m, 2 H), 7.10−7.51 (m, 5 H), 6.85−6.98 (m, 3 H), 6.71−6.75 (m, 2 H), 6.31−6.40 (m, 1 H), 6.23 (ddd, 1 H, *J* = 2.0 Hz, *J* = 4.5 Hz, *J* = 10.9 Hz), 4.35−4.39 (m, 1 H), 3.45−3.56 and 3.75−3.86 (m, 2 H). − $C_{23}H_{18}S$ (326.5): calcd. C 84.62, H 5.57; found C 84.74, H 5.57; C 84.79, H 5.59.

3′-[p-(Dimethylamino)phenyl]-3′,6′-dihydrospiro(9H-fluorene-9,2′-2H-thiopyran) (**39d**). Yield: 409 mg (86%). − M.p. 194−195°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}; 3020 (w, =C−H); 2890, 2860, 2800 (w, −C−H); 1610 (s, C=C); 820 (s), 805, 800 (m), 750, 740, 730 (s), 700, 650, 620 (m, C−H deform.). − UV (CH_2Cl_2): λ_{max} = 305 nm (5200), 262 (28400), 232 (15000). − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.0−7.8 (m, 8 H), 6.48−6.68 (m, 2 H), 6.16−6.36 (m, 4 H), 4.18−4.30 (m, 1 H), 3.45−3.68 (m, 2 H), 2.73 (s, 6 H). − $C_{25}H_{23}NS$ (369.5): calcd. C 81.26, H 6.27, N 3.79; found C 81.17, H 6.22, N 3.84; C 81.11, H 6.20, N 3.86.

3′,6′-Dihydro-3′-(p-methoxyphenyl)spiro(9H-fluorene-9,2′-2H-thiopyran) (**39e**): Yield: 279 mg (59%). − M.p. 153−154°C (de-

comp.). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}; 3040, 3020 (m, =C−H); 2960, 2940, 2910, 2840 (w, −C−H); 1610 (m, C=C); 830 (s), 800, 700 (m), 760, 750, 730 (s), 650, 620 (m, C−H deform.). − UV (CH_2Cl_2): λ_{max} = 305 nm (1970), 263 (8660), 235 (8790). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.70−7.74 (m, 1 H), 7.51−7.58 (m, 2 H), 7.31−7.40 (m, 2 H), 7.21−7.27 (m, 2 H), 7.11−7.17 (m, 1 H), 6.40−6.67 (m, 4 H), 6.29−6.36 (m, 1 H), 6.17−6.23 (m, 1 H), 4.29−4.31 (m, 1 H), 3.61 (s, 3 H), 3.44−3.56 and 3.73−3.90 (m, 2 H). − EI MS: *m/z* (%) = 356 (1), 357 (1) [M^+], 195 (19), 196 (100) [thiofluoreneone (retro-Diels−Alder)], 160 (28), 161 (74) [diene (retro-Diels−Alder)]. − $C_{24}H_{20}OS$ (356.5): calcd. C 80.56, H 5.59; found C 79.74, H 5.97; C 79.95, H 5.57.

3′,6′-Dihydro-3′-(p-methylphenyl)spiro(9H-fluorene-9,2′-2H-thiopyran) (**39f**): Yield: 495 mg (92%). − M.p. 165−166°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}; 3040, 3020 (m, =C−H); 2920, 2890 (w, −C−H); 820 (s), 800, 770 (m), 760, 750, 730 (s), 650, 620 (m, C−H deform.). − UV (CH_2Cl_2): λ_{max} = 270 nm (20300), 257 (19900), 235 (24300). − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 6.95−7.83 (m, 8 H), 6.45−6.80 (m, 4 H), 6.18−6.36 (m, 2 H), 4.25−4.35 (m, 1 H), 3.25−3.95 (m, 2 H), 2.06 (s, 3 H). − EI MS: *m/z* (%) = 340 (2), 341 (1) [M^+], 195 (4), 196 (17) [thiofluoreneone (retro-Diels−Alder)], 143 (5), 144 (58) [diene (retro-Diels−Alder)]. − $C_{24}H_{20}S$ (340.5): calcd. C 84.66, H 5.92; found C 83.41, H 5.85; C 83.51, H 5.70. − High-resolution MS: calcd. 340.1286; found 340.1274; Δ*m* = 3.4 ppm.

3′-(m-Fluorophenyl)-3′,6′-dihydrospiro(9H-fluorene-9,2′-2H-thiopyran) (**39g**): Yield: 645 mg (89%). − M.p. 125−126°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}; 3040 (w, =C−H); 2920, 2890, 2860 (w, −C−H) 1610, 1580 (s, C=C); 890, 870, 860, 800, 790, 780, 740, 720, 700, 695, 670, 630 (s, C−H deform.). − UV (CH_2Cl_2): λ_{max} = 306 nm (5210), 263 (20200), 235 (13200). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.70−7.73 (m, 1 H), 7.51−7.58 (m, 2 H), 7.12−7.41 (m, 5 H), 6.78−6.83 (m, 1 H), 6.60−6.68 (m, 1 H), 6.44−6.48 (m, 2 H), 6.33−6.40 (m, 1 H), 6.23 (ddd, 1 H, *J* = 2.0 Hz, *J* = 4.6 Hz, *J* = 10.8 Hz), 4.36−4.38 (m, 1 H), 3.76−3.86 and 3.44−3.55 (m, 2 H). − $C_{23}H_{17}FS$ (344.5): calcd. C 80.20, H 4.97; found C 80.11, H 5.08; C 80.10, H 5.02.

3′-(m-Chlorophenyl)-3′,6′-dihydrospiro(9H-fluorene-9,2′-2H-thiopyran) (**39h**): Yield: 67.4 mg (70%). − M.p. 131−132°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}; 3040 (m, =C−H); 2920, 2900, 2870 (w, −C−H); 1590, 1560 (m, C=C); 880 (m), 790 (s), 770 (m), 750, 740 (m), 720, 700 (s), 680, 670, 630 (m, C−H deform.). − UV (CH_2Cl_2) λ_{max} = 270 nm (15000), 237 (20000). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.68−7.73 (m, 1 H), 7.51−7.59 (m, 2 H), 7.33−7.42 (m, 2 H), 7.13−7.29 (m, 3 H), 6.92 (ddd, 1 H, *J* = 1.1 Hz, *J* = 2.1 Hz, *J* = 8.0 Hz, aryl-H), 6.79 (dd, 1 H, *J* = 7.8 Hz, *J* = 7.8 Hz), 6.72 (dd, 1 H, *J* = 1.8 Hz, *J* = 1.8 Hz), 6.55 (ddd, 1 H, *J* = 1.2 Hz, *J* = 1.2 Hz, *J* = 7.6 Hz), 6.34−6.42 (m, 1 H), 6.17 (ddd, 1 H, *J* = 2.2 Hz, *J* = 4.8 Hz, *J* = 10.8 Hz), 4.31−4.35 (m, 1 H), 3.77−3.88 and 3.46−3.56 (m, 2 H). − EI MS: *m/z* (%) = 360 (4), 362 (2) [M^+], 195 (16), 196 (100), 197 (15) [thiofluorenone (retro-Diels−Alder)], 164 (20), 165 (4), 165 (7) [diene (retro-Diels−Alder)]. − $C_{23}H_{17}ClS$ (360.9): calcd. C 76.55, H 4.75; found C 75.52, H 4.85; C 75.78, H 4.70. −High-resolution MS: calcd. 360.07395; found 360.07346; Δ*m* = 1.3 ppm.

3′,6′-Dihydro-3′-(m-trifluoromethylphenyl)spiro(9H-fluorene-9,2′-2H-thiopyran) (**39i**): Yield: 322 mg (67%). − M.p. 110−111°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3040 (w, =C−H); 2910 (w, −C−H); 810 (m), 770, 760, 740, 720, 690 (s), 630 (m, C−H deform.). − UV (CH_2Cl_2): λ_{max} = 305 nm (2730), 263 (13900), 235 (10600). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.72−7.75 (m, 1 H), 7.32−7.53 (m, 5 H), 7.13−7.27 (m, 2 H), 7.13−7.27 (m, 1 H), 6.79−6.97 (m, 3 H), 6.37−6.45 (m, 1 H), 6.19 (ddd, 1 H, *J* =, 2.3 Hz, *J* = 4.4 Hz, *J* = 10.8 Hz), 4.42−4.47 (m, 1 H), 3.82−3.93 and 3.47−3.57 , (m, 2 H). − EI MS: *m/z* (%) = 394 (6), 395 (2) [M^+], 195 (12), 196 (100), 197 (12) [thiofluorenone (retro-Diels−Alder)], 198 (23), 199 (3) [diene (retro-Diels−Alder)]. − $C_{24H17}F_3S$ (394.5): calcd. C 73.08, H 4.34; found C 73.37, H 4.60; C 73.43, H 4.70.

Cycloaddition Reactions of Thiofluorenone with 2-Aryl-1,3-butadienes

Spiro Compound **42e**: Yield: 787 mg (68%), colourless powder. − M.p. 248−255°C (decomp.). − UV (CH_2Cl_2): λ_{max} = 259 nm (4.510), 305 (3.686). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3060, 3040 (=C−H, w); 2950, 2930, 2900, 2890, 2880, 2840, 2810 (−CH, w); 1640, 1600, 1540 (C=C, m). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.93−2.96 (m, 2 H), 3.86 (s, 3 H), 3.88 and 3.86 (m, 2 H), 6.37−6.40 (m, 1 H), 6.94−6.98 (m, 2 H), 7.26−7.33 (m, 3 H), 7.38−7.48 (m, 3 H), 7.52−7.55 (m, 2 H), 7.76−7.79 (m, 2 H). − $C_{24}H_{20}OS$ (356.5): calcd. C 80.86, H 5.65; found C 80.45, H 5.79; C 80.31, H 5.70; C 80.40, H 5.84.

Spiro Compound **42f**: Yield: 327 mg (91%), colourless crystals. − M.p. 206−207°C (decomp.). − UV (CH_2Cl_2): λ_{max} = 261 (4.441), 308 (3.691). − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}; 3020 (=C−H, m); 2940, 2910, 2860 (−CH, m) 1630(m), 1500(s, C=C). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 2.91−2.94 (m, 2 H), 3.87 and 3.86 (m, 2 H), 6.40−6.43 (m, 1 H), 7.20−7.42 (m, 8 H), 7.51−7.54 (m, 2 H), 7.73−7.77 (m, 2 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.12 (DEPT pos.), 29.16 (DEPT neg.), 35.95 (DEPT neg.), 49.43 (DEPT 0), 120.32, 123.56, 124.98, 125.54, 127.77, 128.21, 129.40 (all DEPT pos.), 134.77, 137.41, 138.92, 139.20, 149.76 (all DEPT 0). − $C_{24}H_{20}S$ (340.5): calcd. C 84.66, H 5.92; found C 84.46, H 6.01, C 84.34, H 6.01.

Spiro Compound **42h**: Yield: 208 mg (67%), colourless powder. − M.p. 195−196°C. − UV (CH_2Cl_2): λ_{max} = 250 nm (4.451), 305 (3.604). − IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1}; 3020 (=CH, m); 2870, 2795 (−CH, m); 1630 (m), 1580 (s), 1545 (s, C=C, m). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.92−2.95 (m, 2 H), 3.85 and 3.83 (m, 2 H), 6.44−6.48 (m, 1 H), 7.23−7.51 (m, 10 H), 7.75−7.78 (m, 2 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 28.97 (DEPT neg.), 35.91 (DEPT neg.), 49.35 (DEPT 0), 120.37, 123.41, 123.75, 125.89, 127.09, 127.82, 127.59, 128.31, 129.91 (all DEPT pos.), 133.92, 134.73, 139.18, 143.60, 149.50 (all DEPT 0). − $C_{23}H_{17}ClS$ (360.9): calcd. C 76.55, H 4.75; found C 75.19, H 4.87; C 75.19, H 4.88.

Spiro Compound **42i**: Yield: 295 mg (47%), colourless crystals. − M.p. 162−163.5°C (decomp.). − UV (CH_2Cl_2): λ_{max} = 258 nm (4.434), 305 (3.627). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}; 3040 (=C−H, w); 2900, 2880, 2805 (−CH, w); 1640, 1590 (C=C, w); 1320 (C−F, s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.96−2.98 (m, 2 H), 3.90 and 3.88 (m, 2 H), 6.51−6.54 (m, 1 H), 7.23−7.33 (m, 2 H), 7.39−7.43 (m, 2 H), 7.50−7.54 (m, 3 H), 7.58−7.60 (m, 1 H), 7.67−7.69 (m, 1 H), 7.75−7.78 (m, 3 H). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 28.87 (DEPT neg.), 35.75 (DEPT neg.), 49.15 (DEPT 0), 122.34 (q, DEPT pos., ^3J = 3.8 Hz), 124.12 (q, DEPT 0, CF_3, ^1J = 272 Hz), 124.20 (q, DEPT pos., ^3J = 3.7 Hz), 131.06 (q, DEPT 0, ^2J = 32 Hz), 120.38, 123.31, 128.32, 127.56, 127.80, 128.79, 129.15 (all DEPT pos.), 133.73, 139.09, 142.39, 149.30 (all DEPT 0). − $C_{24}H_{17}F_3S$: (394.4) calcd. C 73.08, H 4.34; found C 72.62, H 4.49; C 72.41, H 4.54; C 72.42, H 4.55.

Cycloaddition Reactions of Thiofluorenone (2) *with 5,5-Disubstituted 1,2,3,4-Tetrachloro-1,3-cyclopentadienes*

Spiro Compound **24a**: Yield: 275 mg (72%). − M.p. 111−112°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}; 3030 (w, =C−H); 2820 (w, −C−H); 1585 (m, C=C); 765, 735 (m, C−H deform.); 710 (m,

C−Cl). − UV (CH_2Cl_2): λ_{max} = 262 nm (20700), 268 (26500), 351 (5780). − ^{1}H NMR (60 MHz, $CDCl_3$): δ = 2.87 (d, 1 H, *J* = 9 Hz), 3.85 (d, 1 H, *J* = 9 Hz), 7.15−7.75 (m, 8 H). − $C_{18}H_{10}Cl_4S$ (400.2): calcd. C 54.03, H 2.52; found C 53.99, H 2.59; C 54.12, H 2.92.

Spiro Compound **24b**: Yield: 745 mg (83%). − M.p. 156−159°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}; 3050 (w, =C−H); 1590, 1450 (m, C=C). − UV (CH_2Cl_2): λ_{max} = 245 nm (21200), 278 (8830). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08−7.10 (m, 1 H), 7.20−7.24 (m, 1 H), 7.29−7.33 (m, 1 H), 7.36−7.43 (m, 2 H), 7.59−7.65 (m, 2 H), 7.92−7.95 (m, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.07 (d, $^3J_{FC}$ = 2.0 Hz), 75.08 (dd, $^2J_{FC}$ = 22.5 Hz , and 19.1 Hz,), 79.38 (dd, $^2J_{FC}$ = 19.4 Hz), 123.01 (dd, DEPT 0, $^1J_{FC}$ = 276.6 Hz and 268.7 Hz), 131.48 (d, DEPT 0, J_{FC} = 4.5 Hz), 133.94 (s, DEPT 0), 127.33 (d, DEPT pos., J_{FC} = 22.1 Hz), 127.80 (d, DEPT pos., J_{FC} = 3.1 Hz), 119.81, 119.92, 127.25, 127.36, 129.33, 130.19 (all s and DEPT pos.), 141.01, 141.58, 141.72, 141.99 (all s and DEPT 0). − $C_{18}H_8Cl_4F_2S$: (436.1): calcd. C 49.57, H 1.85; found C 49.37, H 2.02; C 49.38, H 2.06.

Spiro Compound **24c**: Yield: 452 mg (65%). − M.p. 137−138°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}; 3050 (w, =C−H); 2980, 2940, 2830 (m, −C−H); 1590, 1430 (s, C=C). − UV (CH_2Cl_2): λ_{max} = 292 nm (6100), 280 (8230), 252 (17400), 235 (15600). − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 3.57 and 3.77 (2 × s, 6 H), 7.00−7.70 (m, 7 H), 8.08−8.20 (m, 1 H). − $C_{20}H_{14}Cl_4O_2S$ (460.2): calcd. C 52.20, H 3.07; found C 52.18, H 3.07.

Spiro Compound **24d**: Yield: 586 mg (88%). − M.p. 214°C (decomp.). − IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1}; 2910 (w, −C−H); 1585, 1440 (m, C=C). − UV (CH_2Cl_2): λ_{max} = 253 nm (16900), 279 (86800). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.21−4.30 (m, 2 H), 4.49−4.44 (m, 1 H), 4.51−4.56 (m, 1 H), 7.09−7.11 (m, 1 H), 7.19−7.42 (m, 4 H), 7.49−7.59 (m, 2 H), 8.41−8.43 (m, 1 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.36, 68.46, 70.77, 78.31, 82.43, 121.53, 119.48, 119.53, 127.06, 127.17, 127.54, 128.52, 129.27, 129.56, 132.47, 134.02, 140.84, 142.08, 143.34, 143.42. − $C_{20}H_{12}Cl_4O_2S$ (458.2): calcd. C 52.43, H 2.64; found C 52.06, H 2.69; C 52.16, H 2.68.

Cycloaddition Reactions of Substituted Thiobenzophenones with 3,6-Bis(trifluoromethyl)-1,2,4,5-tetrazine (14)

6,6-Diphenyl-2,5-bis(trifluoromethyl)-6H-1,3,4-thiadiazin (**26a**): Yield: 229 mg (48%), yellow cubes. − M.p. 89.5−90.5°C. − UV (hexane): λ_{max} = 200 nm (4.704, end absorption), 254 (3.471). − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}; 3060, 3020 (=C−H, w); 1280, 1190, 1130 (−CF, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.17−7.25 (m, 4 H), 7.30−7.42 (m, 6 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 52.98 (DEPT 0), 118.76 (DEPT 0, q,^1J = 276.3 Hz, CF_3), 119.28 (DEPT 0, q, ^1J = 279.2 Hz, CF_3), 134.98 (DEPT 0), 146.03 (DEPT 0, q, ^2J = 31.7 Hz), 148.54 (DEPT 0, q, ^2J = 38.7 Hz), 128.58, 129.33, 129.49 (all DEPT pos.). − EI MS (T_E = 60°C): *m/z* (%) = 388 (10), 359 (5), 360 (10), 291 (32), 292 (6), 293 (16, 275 (12), 247 (66), 248 (11), 227 (100), 228 (16), 207 (12), 178 (33), 121 (5), 113 (8). − $C_{17}H_{10}F_6N_2S$ (388.3): calcd. C 52.58, H 2.60, N 7.21; found C 52.53, H 2.91, N 7.27; C 52.54, H 2.86, N 7.25; C 52.56, H 2.83, N 7.26.

6,6-Bis(p-methoxyphenyl)-2,5-bis(trifluoromethyl)-6H-1,3,4-thiadiazin (**26b**): Yield: 337 mg (74%), yellow powder. − M.p. 78−79°C. − UV (hexane): λ_{max} = 203 nm (4.678), 236 (4.415), 263 (3.591). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3060, 3040, 3020 (=C−H, w); 2990, 2950, 2940, 2920, 2890, 2820 (−CH, m); 1590, 1530 (C=C, s); 1280, 1240, 1180, 1130 (−CF, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.81 (s, 6 H), 6.81−6.88 and 7.07−7.13 (m, 8 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 52.35 (DEPT 0), 55.32 (DEPT pos), 113.91 (DEPT pos.), 118.76 (DEPT 0, q, ^1J = 276.3 Hz, CF_3), 119.28 (DEPT 0, q, ^1J = 279.2 Hz, CF_3), 126.58 (DEPT 0), 130.61 (DEPT pos.), 146.59 (DEPT 0, q, ^2J = 31.7 Hz), 148.74 (DEPT 0, q, ^2J = 39.7 Hz), 160.24 (DEPT 0). − EI MS (T_E = 90°C): *m/z* (%) = 448 (16), 354 (11), 353 (61), 352 (21), 351 (100), 151 (7), 152 (8). − $C_{17}H_{10}F_6N_2S$ (448.4): calcd. C 50.90, H 3.15, N 6.25; found C 50.77, H 3.18, N 6.20 C 50.86, H 3.40, N 6.29 C 50.78, H 3.45, N 6.19.

6,6-Bis(p-methylphenyl)-2,5-bis(trifluoromethyl)-6H-1,3,4-thiadiazin (**26c**): Yield: 194 mg (47%), yellow crystals. − M.p. 86−87°C. − UV (hexane): λ_{max} = 203 nm (4.662), 222 (4.273, sh), 261 (3.365). − IR (KBr): $\tilde{\nu}$ = 3120 (w) cm^{-1}; 3080 (w), 3040 (m, =C−H); 2950 (w), 2920 (m), 2860 (w, −CH); 1600, 1560 (C=C, m); 1310, 1280, 1270, 1210, 1180, 1150, 1140 (−CF, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.35 (s, 6 H), 7.04−7.07 and 7.12−7.15 (m, 8 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.98 (DEPT pos.), 52.71 (DEPT 0), 118.83 (DEPT 0, q, ^1J = 276.3 Hz, CF_3), 119.34 (DEPT 0, q, ^1J = 279.2 Hz, CF_3), 129.19 (DEPT pos.), 132.04 (DEPT 0), 54b 139.52 (DEPT 0), 146.38 (DEPT 0, q, ^2J = 31.7 Hz), 148.74 (DEPT 0, q, ^2J = 38.2 Hz). − $C_{19}H_{14}F_6N_2S$ (416.4): calcd. C 54.81, H 3.39, N 6.73; found C 54.93, H 3.76, N 6.99; C 54.87, H 3.62, N 6.89.

6-(m-Fluorophenyl)-6-phenyl-2,5-bis(trifluoromethyl)-6H-1,3,4-thiadiazin (**26e**): Yield: 266 mg (59%), yellow crystals. − M.p. 66−67°C. − UV (hexane): λ_{max} = 202 nm (4.521), 265 (3.457). − IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}; 3080, 3040 (=C−H, w); 1600 (m), 1580 (s, C=C); 1300, 1290, 1240, 1180, 1140 (−CF, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.86−7.41 (m, aromatic protons). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 52.45 (DEPT 0), 116.74 (DEPT pos., d, ^2J_F = 21.1 Hz), 116.80 (DEPT pos., d, ^2J_F = 24.2 Hz), 118.69 (DEPT 0, q, ^1J = 276.4 Hz, CF_3), 119.20 (DEPT 0, q, ^1J = 279.2 Hz, CF_3), 125.04 (DEPT pos., d, ^4J_F = 2.9 Hz), 129.73, 129.16, 128.72 (DEPT pos.), 130.09 (DEPT pos., d, ^3J_F = 8.3 Hz), 134.34 (DEPT 0), 137.68 (DEPT 0, d, ^3J_F = 7.1 Hz), 145.57 (DEPT 0, q, ^2J = 31.7 Hz), 148.22 (DEPT 0, q, ^2J = 38.7 Hz), 162.44 (DEPT 0, d, ^1J_F = 248.8 Hz). − $C_{17}H_9F_7N_2S$ (406.3): calcd. C 50.25, H 2.23, N 6.89; found C 50.17, H 2.36, N 6.89; C 50.20, H 2.55, N 6.90; C 50.27, H 2.52, N 6.92.

6,6-Bis(p-chlorophenyl)-2,5-bis(trifluoromethyl)-6H-1,3,4-thiadiazin (**26f**): Yield: 288 mg (56%), yellow crystals. − M.p. 79−80°C. − UV (hexane): λ_{max} = 205 nm (4.565), 227 (4.438), 279 (3.285, sh). − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}; 3060, 3040 (=C−H, w); 1585 (m), 1570 (w, C=C); 1310, 1295, 1220, 1190, 1150 (−CF, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.09−7.14 and 7.32−7.38 (m, 8 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 51.93 (DEPT 0), 118.67 (DEPT 0, q, ^1J = 276.5 Hz, CF_3), 119.19 (DEPT 0, q, ^1J = 279.1 Hz, CF_3), 129.08 (DEPT pos.), 130.56 (DEPT pos.), 133.17 (DEPT 0), 136.19 (DEPT 0), 145.31 (DEPT 0, q, ^2J = 33.3 Hz), 148.04 (DEPT 0, q, ^2J = 38.9 Hz). − EI MS (T_E = 65°C): *m/z* (%) = 456 (3), 458 (2), 393 (5), 315 (19), 316 (4), 317 (13), 280 (100), 281 (17), 282 (33), 245 (23), 246 (19). − $C_{17}H_8Cl_2F_6N_2S$ (457.2): calcd. C 44.66, H 1.76, N 6.13; found C 44.85, H 1.96, N 6.17.

Cycloaddition Reactions of Substituted Thiones with 2,3-Dimethyl-1,3-butadiene (10c)

Spiro Compound **31**: Yield: 501 mg (56%), colourless crystals. − M.p. 50−51°C. − UV (CH_2Cl_2): λ_{max} = 268 nm (3.232), 275 (3.195). − IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1}; 3040, 3000 (=C−H, w); 2950 (m), 2920 (m), 2880 (s), 2860 (s), 2810 (w, −CH,); 1480, 1450 (C=C, s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.75 (s, 3 H), 1.81 (s, 3 H), 2.03−2.15 (m, 1 H), 2.27−2.42 (m, 2 H), 2.58−2.65 (m, 1 H), 2.82−3.22 (m, 4 H), 7.16−7.24 (m, 4 H). − ^{13}C NMR (63 MHz,

$CDCl_3$): δ = 19.37 (DEPT pos.), 20.61 (DEPT pos.), 30.13 (DEPT neg.), 31.62 (DEPT neg.), 40.41 (DEPT neg.), 44.53 (DEPT neg.), 52.28 (DEPT 0.), 122.68, 124.87, 126.52, 127.51, (all DEPT pos.), 123.29 (DEPT 0), 127.11 (DEPT 0), 143.19 (DEPT 0), 147.76 (DEPT 0). − $C_{15}H_8S$ (230.4): calcd. C 78.21, H 7.88; found C 78.23, H 7.86; C 78.22, H 7.82.

3,6-Dihydro-2,4,5-trimethyl-2-phenyl-2H-thiopyran (**32**): Yield: 367 mg (91%), colourless liquid. − B.p.: decomp. 80−130°C. − UV (CH_2Cl_2): λ_{max} = 220 nm (2.966), 243−257 (sh). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3060, 3030 (=C−H, m); 2960, 2920, 2910, 2860 (−CH, s); 1590 (C=C, m); 1490, 1440 (−CH deform., s), 750, 690 (s). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.59 (s, 3 H), 1.65 (br. s, 3 H), 1.76 (br. s, 3 H), 2.44−2.51 (m, 1 H), 2.67−2.89 (m, 3 H), 7.15−7.35 (m, 4 H), 7.43−7.48 (m, 1 H,). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.19 (DEPT pos.), 20.37 (DEPT pos.), 30.48 (DEPT pos.), 31.18 (DEPT neg.), 44.59 (DEPT 0), 45.06 (DEPT neg.), 123.16 (DEPT 0), 126.26 (DEPT 0), 126.35 (2 C), 127.97 (DEPT pos.), 146.15 (DEPT 0). − High-resolution MS: calcd. 218.11292; $C_{14}H_{18}S$: found 218.1124; Δ*m* = 2.5 ppm.

3,6-Dihydro-4,5-dimethyl-2-[(pentachlorophenyl)thio]-2-toluenesulfonyl-2H-thiopyran (**35**): Yield: 76.1 mg (52%), colourless powder. − M.p. 127−128°C (decomp.). − UV (CH_2Cl_2): λ_{max} = 305 nm (3.518). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}; 3040, (=C−H, w); 2960, 2920, 2860 (−CH, w); 1590 (C=C, m); 1340, 1320, 1305, 1310, 1140, (S=O, s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (br. s, 3 H), 1.75 (br. s, 3 H), 2.47 (s, 3 H), 2.80 and 2.89 (AB system, J_{AB} = 16.4 Hz, 2 H), 2.90 and 3.13 (AB system, J_{AB} = 15.2 Hz, 2 H), 7.34−7.36 and 7.95−7.98 (m, 4 H). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 19.08 (DEPT pos.), 20.41 (DEPT pos.), 21.73 (DEPT pos.), 33.16 (DEPT neg.), 39.35 (DEPT neg.), 86.49 (DEPT 0), 125.25 and 126.09 (DEPT 0), 129.14 and 132.01 (DEPT pos.), 130.34, 132.02, 132.14, 136.59, 142.26, 145.31 (all DEPT 0). − EI MS (T_E = 155°C): *m/z* (%) = 404 (25), 156 (41), 139 (22), 92 (46), 91(100). − $C_{20}H_{17}Cl_5O_2S_3$ (562.8): calcd. C 42.68, H 3.04; found C 40.90, H 3.19.

***Cycloaddition Reactions of Substituted Thiobenzophenonenes with 2,3-Dimethyl-1,3-butadiene* (10c)**

3,6-Dihydro-4,5-dimethyl-2,2-diphenyl-2H-thiopyran (**27a**): Yield: 360 mg (25%). − M.p. 51−52°C − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}; 3040, 3010 (w, =C-H); 2898, 2880, 2850, 2800(w, -C-H); 1590 (m, C=C); 760, 740, 700, 690 (s, C−H deform.). − UV (CH_2Cl_2): λ_{max} = 253 nm (1400), 235 (2500). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.64−1.65 (m, 3 H), 1.78 (asym. t, *J* ≈ 0.8 Hz, 3 H), 2.72 (br. s, 1 H), 2.88 (br. s, 1 H), 7.15−7.35 (m, 10 H). − $C_{19}H_{20}S$ (280.4): calcd. C 81.34, H 7.19; found C 81.40, H 7.22; C 81.48, H 7.32.

3,6-Dihydro-2,2-bis(4-methoxyphenyl)-4,5-dimethyl-2H-thiopyran (**27b**): Yield: 212 mg (75%). − IR (neat): $\tilde{\nu}$ = 3080 cm^{-1}; 3050, 3010 (m, =C−H); 2970, 2950, 2920, 2880, 2850 (m, −C−H); 1610, 1510 (s, C=C); 830 (s), 820 (m, C−H deform.). − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.60−1.73 (m, 3 H), 1.73−1.86 (m, 3 H), 2.63−2.77 (m, 2 H), 2.77−2.91 (m, 2 H), 4.78 (s, 6 H), 6.74−6.87 and 7.20−7.33 (m, 8 H). − EI MS: *m/z* (%) = 340 (11), 341 (2), 307 (18), 308 (4), 258 (100), 259 (17), 260 (6) [thioketone (retro Diels−Alder)], 225 (29), 121 (13). − $C_{21}H_{20}O_2S$ (340.5): calcd. C 74.97, H 5.99; found C 71.82, H 7.42; C 72.06, H 7.45.

3,6-Dihydro-4,5-dimethyl-2,2-bis(p-tolyl)-2H-thiopyran (**27c**): Yield:1.06 g (95%). − IR (neat): $\tilde{\nu}$ = 3040 cm^{-1}; 3000 (s, =C−H); 2920, 2860 (s, −C−H); 1500, 1440 (s, C=C); 810, 800, 780, 770 (s), 730, 720 (C−H deform.). − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.77 (s, 3 H), 2.11 (s, 6 H), 2.40−2.76 (m, 2 H), 2.76−2.91 (m, 2 H), 6.93−7.28 (m, 8 H). − EI MS: *m/z* (%) = 308 (26), 209 (6), 275 (5), 226 (91), 227 (14), 228 (5) [thioketone (retro Diels−Alder)], 193 (23). − $C_{21}H_{24}S$ (308.5): calcd. C 81.76, H 7.84; found C 80.60, H 8.04; C 80.42, H 7.91.

3,6-Dihydro-4,5-dimethyl-2-phenyl-2-(p-tolyl)-2H-thiopyran (**27d**): Yield: 258 mg (33%). − M.p. 66−68°C. − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}; 3080, 3040 (w, =C−H); 2990, 2970, 2880 (m, −C−H); 1600, 1510 (m), 1490, 1450 (s, C=C); 820 (m), 810 (s), 790 (m), 780, 760, 710 (s), 670, 640 (m, C−H deform.). − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.61 (s, 3 H) 1.72 (s, 3 H) 2.38 (s, 3 H) 2.68 (br. s, 2 H) 2.83 (br. s, 2 H) 7.0−7.36 (m, 9 H). − $C_{20}H_{22}S$ (294.5): calcd. C 81.56, H 7.53; found C 80.94, H 7.50; C 80.85, H 7.36; C 81.15, H 7.33.

2,2-Bis(4-chlorophenyl)-3,6-dihydro-4,5-dimethyl-2H-thiopyran (**27f**): Yield: 98.2 mg (67%). − M.p. 68−70°C. − IR (KBr): $\tilde{\nu}$ = 3060 (w, =C−H) cm^{-1}; 2980, 2900, 2860 (m, −C−H); 1640 (w), 1480 (s, C=C); 810 (s), 790 (m, C−H deform.). − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.63 (br. s, 3 H), 1.75 (br. s, 3 H), 2.60−2.93 (m, 4 H), 7.00−7.25 (m, 8 H). − $C_{19}H_{18}Cl_2S$ (349.4): calcd. C 65.31, H 5.19, Cl 20.29; found C 64.79, H 5.15, 20.30; C 64.87, H 5.15.

3,6-Dihydro-4,5-dimethyl-2-(p-nitrophenyl)-2-phenyl-2H-thiopyran (**27g**): Yield: 213 mg (98%). − IR (neat): $\tilde{\nu}$ = 3100 cm^{-1}; 3080, 3060, 3020, 3000 (m, =C−H); 2900, 2860 (s), 2980 (w, −C−H); 1600, 1490, 1480 (m, C=C); 1590, 1510 (s, N=O); 740, 740, 710, 690 (s, C−H deform.). − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 1.60−1.70 (m, 3 H), 1.70−1.80 (m, 3 H), 2.66−2.80 (m, 2 H), 2.80−2.94 (m, 2 H), 7.26 (s, 5 H), 7.43−7.63 and 8.03−8.16 (m, 4 H). − EI MS: *m/z* (%) = 325 (38), 326 (8) [M^+] 243 (100), 244 (17), 245 (7) [thioketone (retro Diels−Alder)], 226 (25). − $C_{19}H_{19}NO_2S$ (325.4): calcd. C 70.13, H 5.88, N 4.30; found C 67.41, H 5.81, N 4.15; C 67.28, H 5.70, N 4.17.

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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