DIELS–ALDER REACTIONS OF [1]BENZOTHIENO[3,2-*b*]FURAN

Pavel PIHERA[1], Jaroslav PALECEK[2] and Jiri SVOBODA[3]

Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail: [1] pavel.pihera@vscht.cz, [2] jaroslav.palecek@vscht.cz, [3] jiri.svoboda@vscht.cz

[1]Benzothieno[3,2-*b*]furan reacts with substituted dienes **2** as a dienophile under formation of substituted tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran derivatives **3–14**. The cycloaddition is *endo*-stereoselective. Aromatization of the products leads to a series of new fused [1]benzothieno[3,2-*b*][1]benzofurans **17–24**. The ^{1}H NMR spectra of the new compounds were fully assigned.
Key words: Fused heterocycles; [1]Benzothieno[3,2-*b*]furan; Dienophiles, Diels–Alder reaction; Aromatization; Regioselectivity; NMR spectra.

In our previous papers[1,2] we described the synthesis of [1]benzothieno[2,3-*b*]furan (**1**) and studied its reactions with electrophilic reagents. We have found that under conditions of electrophilic substitution compound **1** shows a lower stability toward acidic reagents, similar to furan or benzo[*b*]furan. Since in some respect the aromatic character of benzo[*b*]furan is compared to vinylbenzene[3], the aromaticity of compound **1** can be, with some probability, related to vinylbenzo[*b*]thiophene; however, the dienophile reactivity of this compound has not been hitherto reported. On the other hand, the effect of the furan moiety on the aromatic system in this compound, and thus on its reactivity, cannot be excluded. We therefore decided to study cycloaddition reactions (Diels–Alder reaction) to assess qualitatively the changes due to the presence of furan moiety in the molecule of compound **1**. In this paper we describe the obtained results together with the synthesis of a series of novel fused heterocyclic systems.

Whereas the diene character of furan and its derivatives is generally known[4,5], there are only scarce reports on its reactivity as a dienophile. Its dienophile reactivity can be enhanced, *e.g.*, by introduction of electron accepting substituents[6,7] or by performing the reaction at higher pressures[8]. More often, the dienophile character of furan manifested itself in inverse cycloadditions (so-called inverse electron demand)[9–12]. On fusion with a benzene ring, the furan system loses its diene activity[13]. Under the above-mentioned conditions, Diels–Alder reactions of benzo[*b*]furan as dienophile proceed better than those of furan itself[7,9,11,14,15].

We tried to prove the dienophile character of compound **1** (representing a model structure for a substituted vinylbenzo[*b*]thiophene) by its reaction with 1,3-butadiene (**2a**). Whereas there was no reaction at room temperature, at 140 °C the components gave a small amount of the desired 5a,6,9,9a-tetrahydro[1]benzothieno[3,2-*b*]benzo-furan (**3**). The cycloaddition reaction was optimized under various reaction conditions (Table I). The results show that higher reaction temperatures and longer reaction times increase the undesired decomposition of compound **1**, and thus full conversion is not economical. Under optimum conditions, *i.e.* 180 °C and 20 h, the reaction proceeds with more than 50% conversion of the starting compound (82% yield of product **3**, corrected for recovery of the starting compound **1**).
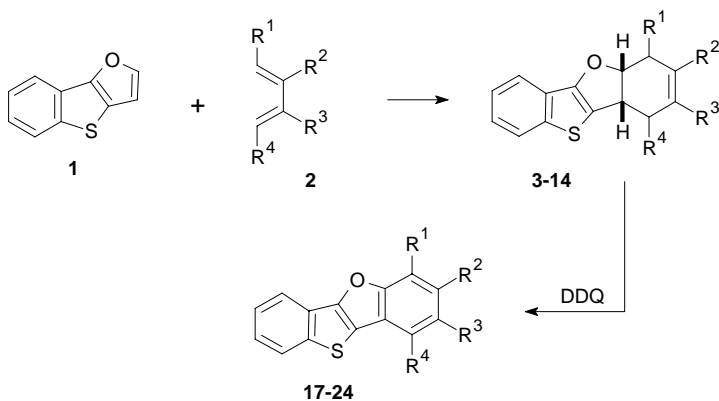
SCHEME 1

Compound **1** was then utilized for the preparation of novel polycondensed hetero-cyclic systems (Scheme 1) by reaction with a series of the following specifically se-lected dienes: 2-methyl-1,3-butadiene (**2b**), 2-trimethylsilyloxy-1,3-butadiene (**2c**),

TABLE I
Optimization of the reaction of **1** with **2a**

Reaction time 20 h			Reaction temperature 180 °C		
temperature °C	yield of **3** %	corrected yield of **3**, %	time h	yield of **3** %	corrected yield of **3**, %
140	25	87	5	32	96
155	37	82	10	46	90
180	53	82	20	53	82
200	58	81	30	55	84
			40	54	80

2,3-dimethyl-1,3-butadiene (**2d**), 2,3-diphenyl-1,3-butadiene (**2e**), 1-vinylcyclohexene (**2f**), *trans*-1,3-pentadiene (**2g**), methyl *trans*-2,4-pentadienoate (**2h**), *trans,trans*-1,4-diphenyl-1,3-butadiene (**2i**), furan (**2j**), 1,1′-bi(cyclopent-1-enyl) (**2k**) and 1,1′-bi(cyclohex-1-enyl) (**2l**). Dienes **2g** and **2h** were mixtures of configurational isomers; however, since the *trans*-isomers of dienes **2g** and **2h** react much faster than the corresponding *cis*-isomers[16–18] and the reaction was performed with a great excess of the diene component, we assume that only the *trans*-isomer participates in the reaction. The reaction conditions and results of the Diels–Alder reactions are given in Table II.

Reaction of compound **1** with isoprene (**2b**) afforded an unseparable mixture of 7-methyl- (**4**) and 8-methyl-5a,6,9,9a-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran (**5**) in the ratio 1.6 : 1 as determined from ¹H NMR signal intensities. Addition to 2,3-disubstituted dienes **2d** and **2e** proceeded smoothly and gave the respective 7,8-dimethyl- (**6**) and 7,8-diphenyl-5a,6,9,9a-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran (**7**).

The reactions with dienes **2f** and **2g** were highly regioselective, affording 1,2,3,4,6,6a,12b,12c-octahydrobenzo[*e*][1]benzothieno[3,2-*b*][1]benzofuran (**8**) and 9-methyl-5a,6,9,9a-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran (**9**), respectively, as the sole products. Surprisingly, the same regioselectivity was observed in the case of diene **2h**, in spite of the different substituent character. The reaction afforded a mixture of two compounds which were separated by column chromatography: methyl 5a,6,9,9a-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-9-carboxylate (**10**) and methyl 5a,6,7,9a-tetrahydro[1]benzothieno[3,2-*b*][1]benzofuran-9-carboxylate (**11**) which arose from **10** by subsequent rearrangement of the double bond into conjugation with the ester functionality and which was the major reaction product (**10** : **11** = 1 : 13).

With the little reactive diene **2i**, the reaction gave only a low yield of 6,9-diphenyl-5a,9,9a-tetrahydro[1]benzothieno-[3,2-*b*][1]benzofuran (**12**). Cycloaddition of diene **2k** with heterocycle **1** was more facile than that of diene **2l**, the yield of 1,2,3,4,5,6,6a,6b,12b,12c-decahydro[1]benzothieno[3,2-*b*]*as*-indaceno[4,5-*d*]furan (**13**) being markedly higher than of 1,2,3,4,5,6,7,8,8a,8b,14b,14c-dodecahydro[1]benzothieno-[3,2-*b*]phenanthro[9,10-*d*]furan (**14**). In addition to the products **7** and **12**, expected in the reaction of the diphenyl-substituted dienes **2e** and **2i**, the reaction mixtures gave also minor amounts of hitherto undescribed 1,2,4-triphenyl-4-(1-phenylvinyl)cyclohexene (**15**) and 3,4,6-triphenyl-5-(2-phenylvinyl)cyclohexene (**16**), respectively, as mixtures of configurational isomers. Their structure was confirmed by elemental analysis and spectra. These compounds are products of mutual cycloaddition reaction of two molecules of the corresponding diene (**2e** or **2i**). Diene **2c** did not react with compound **1** and decomposed under the reaction conditions; in the case of furan (**2j**) only the starting compounds were recovered from the reaction mixture.

Selected cycloadducts were smoothly aromatized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[19] (DDQ) (Table III). Compound **3** thus afforded the parent compound of the series, [1]benzothieno[3,2-*b*][1]benzofuran (**17**) which has been obtained only re-
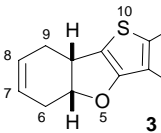
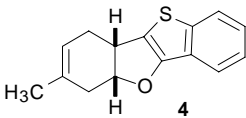TABLE II
Cycloadditions of **1** with dienes **2**
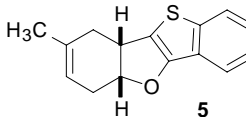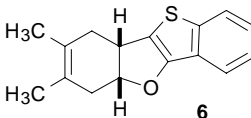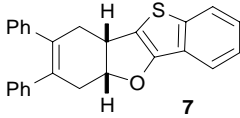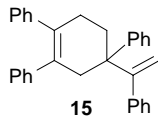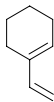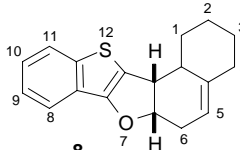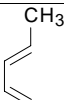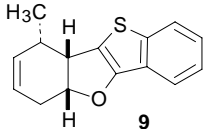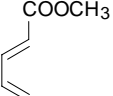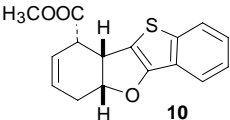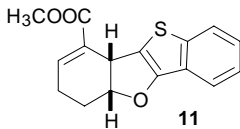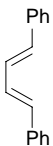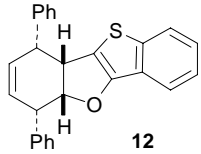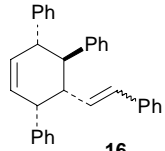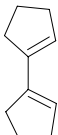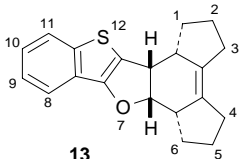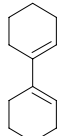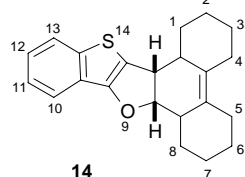
Entry	Diene mg (mmol)	Compound **1** mg (mmol)	Time h	Cycloadduct Yield (corrected yield), %
1	**2a** 620 (11.5)	91 (0.52)	20	**3** 53 (82)
2	H$_3$C **2b** 408 (5.99)	207 (1.19)	26	**4** / **5** 64 (78)
3	H$_3$C H$_3$C **2d** 436 (5.31)	182 (1.04)	25	**6** 75 (85)
4	Ph Ph **2e** 374 (1.81)	113 (0.65)	26	**7** 30 (59)
				15 10[a]
5	**2f** 1 990 (18.4)	605 (3.47)	21	**8** 42 (98)

TABLE II
(*Continued*)

Entry	Diene mg (mmol)	Compound **1** mg (mmol)	Time h	Cycloadduct Yield (corrected yield), %
6	**2g** 801 (11.8)	358 (2.05)	21	**9** 22 (60)
7	**2h** 990 (9.90)	356 (2.04)	20	**10** 3 (6)
				11 38 (78)
8	**2i** 692 (3.35)	232 (1.33)	26	**12** 4 (14)
				16 45[a]
9	**2k** 708 (5.27)	216 (1.24)	26	**13** 49 (75)
10	**2l** 864 (5.32)	235 (1.35)	26	**14** 5 (27)

[a] Based on diene compound.

TABLE III
Reaction conditions and results of aromatization of adducts **3–23**
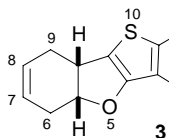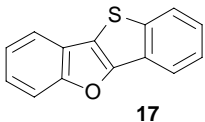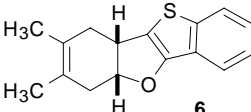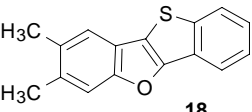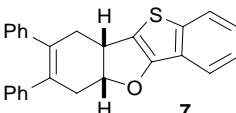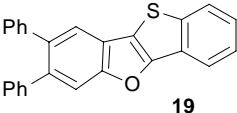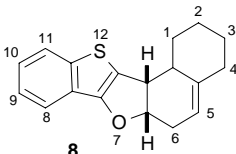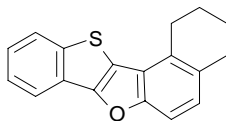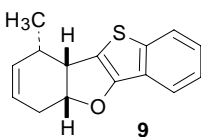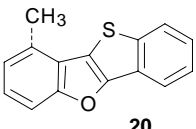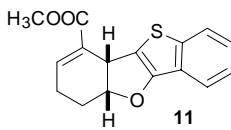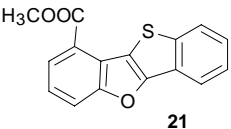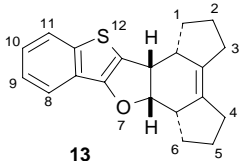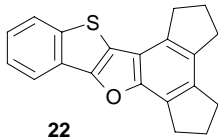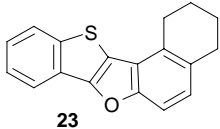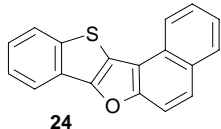
Entry	Cycloadduct mg (mmol)	Time h	Product Yield, %
1	**3** 105 (0.46)	5	**17** 72
2	**6** 89 (0.35)	3	**18** 34
3	**7** 71 (0.19)	1	**19** 70
4	**8** 415 (1.47)	0.5[a]	**23** 59
5	**9** 99 (0.41)	1	**20** 63
6	**11** 104 (0.38)	1	**21** 63

TABLE III
(*Continued*)

Entry	Cycloadduct mg (mmol)	Time h	Product Yield, %
7	**13** 158 (0.51)	1	**22** 59
8	**23** 198 (0.71)	6	**24** 79

[a] Room temperature.

cently as one of the products in flash vacuum pyrolysis of substituted α-oxo ylides[20]. Aromatization of adducts **7**, **8**, **10** and **12** gave 7,8-dimethyl- (**18**), 7,8-diphenyl- (**19**), 9-methyl[1]benzothieno[3,2-*b*][1]benzofuran (**20**) and methyl [1]benzothieno[3,2-*b*]-[1]benzofuran-9-carboxylate (**21**). Adduct **13** was oxidized under formation of 1,2,3,4,5,6-hexahydro[1]benzothieno[3,2-*b*]*as*-indaceno[4,5-*d*]furan (**22**). Attempted aromatization of the indacene grouping in compound **22** with an excess of DDQ was unsuccessful and the reaction mixture contained (according to TLC) only decomposition products. On the other hand, depending on the amount of the reagent, compound **8** could be dehydrogenated either to 1,2,3,4-tetrahydrobenzo[*e*][1]benzothieno[3,2-*b*]-[1]benzofuran (**23**) or to the completely aromatized benzo[*e*][1]benzothieno[3,2-*b*]-[1]benzofuran (**24**), a new parent heteroaromatic system.

The structure of all the newly synthesized compounds was confirmed by elemental analyses and detailed analyses of their NMR, mass and IR spectra (Tables IV–VII). To elucidate the regioselectivity and stereoselectivity of the cycloaddition reaction we made use of detailed assignment of ^{1}H NMR signals. First we assigned completely the ^{1}H and ^{13}C signals for compound **3** (see Tables IV and V and structure **3a**), utilizing our previous finding[2] that the oxygen-bonded quaternary carbon atom C-4b resonates most downfield and the sulfur-bonded quaternary atom C-10a resonates only a little higher. The proton that exhibits a ^3J(C,H) interaction with these two nuclei is then the H-4 proton. Other protons and the corresponding carbon atoms of the aromatic part in compound **3** could be then assigned on the basis of identification of ^3J(H,H) and

[1]J(C,H) couplings by COSY and HMQC experiments. Tertiary carbon atom with the most upfield signal is the C-9a atom. Upon assignment of this atom, we applied analogously the COSY and HMQC experiments to the cyclohexene part of the molecule. The remaining two quaternary carbon atoms, C-4a and C-9b, were assigned on the basis of their interaction with protons H-1 and H-3, and H-9A and H-9B, respectively (coupling

3a
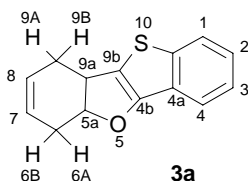
constant [3]J(C,H)). The aromatic part of adduct **3** retains, to certain extent, the character of the benzo[*b*]thiophene system[21,22] but shows a markedly lower chemical shift (–19.2 ppm) of the C-4a carbon atom; this was found[2] also for [1]benzothieno[3,2-*b*]furan (**1**). Smaller changes in the chemical shifts were observed also for the C-4 (–2.9 ppm) and C-10a (+3.9 ppm) carbon atoms. Signals of protons H-1 and H-4 are shifted upfield (for 0.13 ppm and 0.18 ppm, respectively).

NMR spectra of the compounds **4–10** and **12–14** are very similar to that of the parent compound **3** (although some of the compounds are formally derived from other fused heteroaromatic systems) and are characterized by uniform shape in the aromatic region, by relatively constant chemical shifts of protons H-5a and H-9a, and by the value of J(H-5a,H-9a) (9.3–9.7 Hz). This enabled us to assign analogously the ^{1}H NMR signals by COSY (compounds **6**, **8**, **9** and **11**) and NOE (compound **9**) experiments. Compounds **4** and **5**, arising by reaction of compound **1** with isoprene, differ in chemical shifts of the H-9a proton and of the methyl groups. Their structure was determined by comparing chemical shifts of methyl groups with those of protons H-7 and H-8 in compound **3**.

In order to determine the relative configuration of cycloaddition products of 1,3-butadienes carrying substituent(s) in position 1 or 1 and 4, we chose compound **9** as a model. The observed NOE effect of H-9 with H-9a, and also to a lesser extent with H-5a indicates their mutual *cis*-configuration. Since the values of coupling constants in compounds **10**, **12** and **13** are very close to those in the compound **9**, we ascribed to them also the "all-*cis*" structure. This proves that the Diels–Alder reaction of compound **1** with dienes **2g–2j** proceeds as an *endo*-addition. Similarly to compound **3**, also in **9** and **12** we identified long-range interactions ("*W*-interactions") between protons H-5a and H-9.

Somewhat different coupling constants of dihydrofuran ring protons in derivatives **8** and **14** with attached one and two cyclohexane rings (J(H-6a,H-12b) = 7.7 and J(H-8b, H-14b) = 8.1) made impossible to elucidate the relative configuration, and thus to determine the character of the addition. Moreover, the spectrum of compound **8** exhibited a somewhat different value of J(H-12b,H-12c).

TABLE IV
^{1}H NMR chemical shifts in compounds **3–12**

Compound	Proton											
	H-1	H-2	H-3	H-4	H-5a	H-6A	H-6B	H-7	H-8	H-9A	H-9B	H-9a
3	7.75 d	7.29 ddd	7.36 ddd	7.64 d	5.59 ddd	2.55 dddd	2.67 ddd	5.93 ddd	5.98 ddd	2.42 dddd	2.28 ddd	3.83 dddd
4[a]	7.71 d	7.25 dd	7.33 dd	7.59 d	5.56 m	2.57 m		–	5.56 m	2.35 m	2.20 m	3.86 ddd
5[b]	7.71 d	7.25 dd	7.33 dd	7.59 d	5.56 m	2.57 m		5.56 m	–	2.35 m	2.20 m	3.77 ddd
6[c]	7.70 dd	7.24 ddd	7.32 ddd	7.58 dd	5.56 ddd	2.44 dd	2.50 dd	–	–	2.33 dd	2.18 dd	3.83 ddd
7[d]	7.71 d	7.26 dd	7.34 dd	7.61 d	5.87 ddd	2.93 dd	3.14 dd	–	–	2.84 m		4.15 ddd
9[e]	7.67 d	7.23 dd	7.30 ddd	7.57 d	5.75 dddd	2.29 dddd	2.78 ddd	5.92 ddd	5.68 ddd	2.42 m	–	3.93 dd
10[f]	7.71 d	7.27 dd	7.33 dd	7.60 d	5.53 ddd	2.53 dm	2.83 ddd	6.01 m	6.08 dd	3.29 m	–	4.01 dd
12[g]	overlap	7.19 dd	7.23 dd	overlap	5.84 ddd	3.80 m	–	6.32 dm	6.45 ddd	3.73 m	–	4.39 dd

Additional signals: [a] 1.70 s, 3 H (CH$_3$); [b] 1.79 s, 3 H (CH$_3$); [c] 1.73 s, 3 H (CH$_3$); [d] 6.82 m and 6.98–7.12 m, 10 H (Ph); [e] 1.32 d, 3 H (CH$_3$); [f] 3.82 s, 3 H (OCH$_3$); [g] 7.35–7.60 m, 12 H (H-1,H-4 and Ph).

TABLE V
Interaction constants J(H,H) in compounds **3–12**

Compound	1,2	1,3	2,3	2,4	3,4	5a,6A	5a,6B	5a,9a	6A,6B	6A,7	6B,7	7,8	8,9A	8,9B	9A,9B	9A,9a	9B,9a
3[b]	8.1	0.9	7.5	1.2	7.9	5.0	4.6	9.3	16.0	3.8	4.6	9.7	4.2	4.7	15.6	6.7	5.3
4	8.2	n.o.	7.2	n.o.	7.6	n.d.	n.d.	9.3	n.d.	–	–	–	n.d.	n.d.	n.d.	6.4	5.4
5	8.2	n.o.	7.2	n.o.	7.6	n.d.	n.d.	9.3	n.d.	n.d.	n.d.	–	–	–	n.d.	6.6	5.1
6	8.0	1.0	7.2	0.8	7.8	4.8	4.8	9.7	15.1	–	–	–	–	–	15.0	6.3	4.9
7	7.7	n.o.	7.3	n.o.	7.7	4.7	4.2	9.6	15.1	–	–	–	–	–	n.d.	5.1	4.4
9[c]	8.0	0.9	7.3	1.2	7.7	4.9	2.3	9.6	16.1	2.7	6.5	9.4	3.1	–	–	6.0	–
10	7.7	n.o.	7.2	n.o.	7.6	6.1	6.1	9.4	16.5	n.d.	5.5	9.3	4.4	–	–	6.6	–
12[d]	n.d.	n.o.	n.d.	n.o.	n.d.	3.4	–	9.4	–	n.d.	–	9.4	2.9	–	–	6.5	–

[a] n.d. Not determined, n.o. not observed. Additional couplings: [b] J(5a,9A) = 1.2 and J(6A,9a) = 1.5; [c] J(5a,9A) = 1.1 and J(6A,8) = 3.0 and J(9A,CH$_3$) = 7.2; [d] J(5a,9A) = 1.1 and J(6A,8) = 1.8.

TABLE VI
^{1}H NMR chemical shifts in compounds **17–21**

Compound	Proton							
	H-1	H-2	H-3	H-4	H-6	H-7	H-8	H-9
17	7.85 d	7.36 m	7.45 ddd	7.98 d	7.63 dd	7.36 m	7.32 ddd	7.70 dd
18^a	7.87 d	7.36 ddd	7.47 dd	7.98 d	7.44 s	–	–	7.50 s
19^b	7.92 d	7.44 ddd	7.51 ddd	8.06 d	7.72 s	–	–	7.78 s
20^c	7.89 d	7.38 ddd	7.49 ddd	8.02 d	7.48 d	7.28 dd	7.14 d	–
21^d	7.91 d	7.43 ddd	7.49 ddd	8.02 d	7.82 d	7.42 dd	8.05 d	–

Additional signals: ^{a} 2.40 s, 3 H (CH$_3$-8) and 2.43 s, 3 H (CH$_3$-7); ^{b} 7.24 m, 10 H (Ph); ^{c} 2.69 s, 3 H (CH); ^{d} 4.10 s, 3 H (OCH$_3$).

TABLE VII
Interaction constants J(H,H) in compounds **17–21**^{a}

Compound	J(H,H)									
	1,2	1,3	2,3	2,4	3,4	6,7	6,8	7,8	7,9	8,9
17	8.1	0.9	7.1	n.o.	7.9	7.2	1.1	7.2	1.6	7.3
18	8.2	n.o.	7.1	1.0	7.7	–	–	–	–	–
19	8.2	1.1	7.3	1.2	8.0	–	–	–	–	–
20	8.0	1.0	7.1	1.4	7.5	7.5	n.o.	7.1	–	–
21	8.2	1.1	7.2	1.1	7.7	8.2	n.o.	7.7	–	–

^{a} n.o. Not observed.

In addition to the molecular ion M[+], mass spectra of adducts **3**, **6–10** and **12–14** exhibit molecular ion of compound **1** (mostly as the base peak) and, in the case of compounds **13** and **14**, also molecular ion of the corresponding diene **2k** and **2l**. The presence of these ion species can be explained by retro-Diels–Alder reaction, currently occuring during mass spectral measurements of Diels–Alder adducts. The absence of molecular ion of compound **1** in the spectrum of ester **11** indicates a different structure of the cyclohexene moiety due to rearrangement of the double bond in adduct **10**, and thus indirectly confirms the structure of compound **11**.

The structure of compounds **17–24** was determined again by detailed interpretation of their ^{1}H NMR spectra (Tables VI and VII). The proton and carbon atom signals in the parent compound **17** were assigned using the above-mentioned data for compound **1** as well as the fully assigned ^{1}H and ^{13}C NMR spectra of the isomeric system, thieno[3,2-*b*][1]benzofuran[23]. It was thus possible to assign unequivocally the chemical shift of the C-10a carbon atom. We could not distinguish between the C-4b and C-5a carbon atoms whose signals are located most downfield due to direct bonding to the oxygen atom. However, it was possible to decompose the heteroaromatic system into benzo[*b*]thiophene and benzo[*b*]furan parts by COSY and ^{1}H NMR spectra. Protons exhibiting a ^3J(C,H) interaction with the C-10a carbon atom belong to the benzo[*b*]thiophene part; and out of the two of them, that proton which interacts across three bonds with one of the quaternary carbon atoms at the lowest field, *i.e.* C-4b, must be the H-4 proton. The other protons of the benzo[*b*]thiophene part and the corresponding tertiary carbon atoms were assigned on the basis of identification of ^3J(H,H) or ^1J(C,H) using COSY and HETCOR experiments. Chemical shift of the quaternary carbon atom C-4a was determined on the basis of coupling constant ^3J(C,H) with H-1. Analysis of the benzo[*b*]furan part of the spectrum consisted in identification of the ^3J(C,H) interaction of carbon atom C-5a with protons H-7 and H-9. Protons H-6 and H-8 and the corresponding tertiary carbon atoms were again assigned by COSY and HETCOR experiments and the remaining quaternary carbon atoms C-9a and C-9b were assigned on the basis of ^3J(C,H) with the respective H-6 and H-9 protons. The chemical shifts in the spectrum of compound **17** differ only slightly from those for benzo[*b*]thiophene[21,22] or benzo[*b*]furan[22,24]. In the ^{1}H NMR spectrum, the H-4 proton signal is located higher than that of the corresponding proton in benzo[*b*]thiophene and compound **3** (0.16 ppm and 0.34 ppm, respectively), this signal being the lowest field signal. Chemical shifts of the other protons differ from those of the corresponding protons in benzo[*b*]thiophene or benzo[*b*]furan by not more than 0.1 ppm and analogous differences in chemical shifts of the carbon atoms usually do not exceed 2 ppm. An exception is the signals of carbon atoms C-4a and C-10a (–13.7 ppm and +3.0 ppm, respectively), already mentioned for adduct **3**, and also of the C-5a carbon atom (+4.5 ppm).

The coupling constants ^3J(H,H) in the benzo[*b*]thiophene part of compound **17** resemble those in benzo[*b*]thiophene[25]; however, the constants *J*(H-6,H-7) and *J*(H-8,H-9)

are by 1.2 Hz and 0.6 Hz, respectively, lower than in benzo[*b*]furan[26]. ^{1}H NMR spectrum of the new heterocyclic system **24** was assigned on the basis of the above-mentioned findings and of COSY and NOE experiments.

Mass spectra of the aromatized compounds **17–22** and **24** exhibit dominant M^+ ions (100% rel. int.), accompanied by low-intensity fragments formed by loss of substituents from the aromatic nucleus.

Fusion of another aromatic ring with the heterocycle **1** results in significant changes in the UV spectra: whereas the tricyclic system **1** exhibits absorption maxima at about 244 and 282 nm (ref.[1]), similarly to benzo[*b*]thiophene[27] or benzo[*b*]furan[28], the maxima for compound **17** are shifted markedly to longer wavelengths (256, 304 and 318 nm). These data indicate a much greater conjugation in this system than in compound **1**. Fusion with another aromatic ring in compound **24** shifts the maxima further to longer wavelengths (242, 273, 327 and 343 nm).

The studies support our earlier[2] results of the similar reactivity of compound **1** and benzo[*b*]furan. Cycloaddition reactions of heterocycle **1** with dienes can serve for preparation of new condensed heterocyclic compounds derived from thieno[3,2-*b*]furan. The possible "diene" character of compound **1** will be a subject of further studies.

EXPERIMENTAL

Melting points were determined on a Boetius block and are uncorrected. NMR spectra were taken on a Varian Gemini 300 instrument, compounds **3** and **17** were studied on Bruker 400 and Bruker 500 spectrometers. Compounds were measured in deuteriochloroform which was used as internal standard. Chemical shifts are given in δ-scale (ppm) and coupling constants *J* in Hz. The multiplicity of signals in ^{13}C NMR spectra was determined in APT experiments. NOE effects were studied by DPFGSE-NOE spectra. COSY, HETCOR, HMQC, INEPT, COLOC and HMBC experiments were carried out using manufacturer-supplied pulse sequencies. IR spectra were recorded in chloroform on a Nicolet 740 FTIR spectrometer, mass spectra were taken on Jeol DX 300, 2DV.G.ZAP-70 and Finnigan spectrometers. UV spectra of compounds **3** and **17** were obtained in ethanol with an Otsuka MCPD 1100 spectrophotometer whereas compound **24** was measured on a Specord M 40 instrument in methanol.

Chemicals: 2-trimethylsilyloxy-1,3-butadiene (**2c**) was prepared from 3-buten-2-one according to the literature[29], 2,3-dimethyl-1,3-butadiene (**2d**) by dehydration of pinacol[30], 2,3-diphenyl-1,3-butadiene (**2e**) analogously to a published[31] procedure, 1-vinylcyclohexene (**2f**) from 1-vinylcyclohexanol[32] according to ref.[33], 1,3-pentadiene (**2g**) from 1-penten-3-ol (ref.[34]), methyl 2,4-pentadienoate (**2h**) by esterification of 2,4-pentadienoic acid[35], 1,1′-bi(cyclopent-1-enyl) (**2k**) and 1,1′-bi(cyclohex-1-enyl) (**2l**) according to ref.[36].

Optimization of Diels–Alder Reaction of Compound **1** with 1,3-Butadiene (**2a**)

A mixture of compound **1** (100 mg, 0.57 mmol), diene **2a** (620 mg, 11.5 mmol) and 4-(1,1,3,3-tetramethylbutyl)pyrocatechol (about 5 mg) was heated in a glass ampoule under conditions given in Table I. After cooling, the content of the ampoule was dissolved in dichloromethane (25 ml), the solvent was evaporated and the dry residue was chromatographed on silica gel (gradient hexane–hexane/toluene (5 : 1)) to give adduct **3** and the unreacted starting compound **1**. For the results see Table I.

Reaction of Compound **1** with Dienes **2a–2l** (General Procedure)

A mixture of compound **1**, diene **2a–2l** (Table II) and 4-(1,1,3,3-tetramethylbutyl)pyrocatechol (about 5 mg) was heated at 180 °C in a glass ampoule. After cooling, the reaction mixture was worked up as described in the preceding experiment. The reaction conditions and results are summarized in Table II. For ^{1}H NMR spectra of new compounds see Tables IV and V.

5a,6,9,9a-Tetrahydro[1]benzothieno[3,2-b][1]benzofuran (**3**). M.p. 57–59 °C (toluene). For $C_{14}H_{12}OS$ (228.3) calculated: 73.65% C, 5.30% H, 14.04% S; found: 73.66% C, 5.27% H, 13.88% S. IR spectrum: 3 046, 3 012, 2 942, 2 846, 1 601, 1 592, 1 544, 1 475, 1 430, 1 401, 1 285, 1 261, 1 091, 1 062, 1 015. UV spectrum: λ_{max} (log ε): 252 (4.24); 303 (4.46); 312 (3.83). ^{13}C NMR spectrum: 28.6 (C-9); 29.6 (C-6); 41.3 (C-9a); 89.8 (C-5a); 120.2 (C-9b); 120.4 (C-4a); 120.7 (C-4); 124.6 (C-2); 124.8 (C-1); 124.9 (C-3); 126.5 (C-7); 129.2 (C-8); 143.6 (C-10a); 155.3 (C-4b). Mass spectrum: 229 (15), 228 (100) (M$^+$), 227 (10), 213 (15), 187 (25), 176 (15), 175 (30), 174 (100) [retro D.A.], 163 (20), 162 (25), 151 (10), 150 (10), 137 (20), 114 (10), 91 (10), 77 (10).

7-Methyl- (**4**) *and 8-methyl-5a,6,9,9a-tetrahydro[1]benzothieno[3,2-b][1]benzofuran* (**5**). For $C_{15}H_{14}OS$ (242.3) calculated: 74.35% C, 5.82% H, 13.23% S; found: 74.26% C, 5.91% H, 13.11% S.

7,8-Dimethyl-5a,6,9,9a-tetrahydro[1]benzothieno[3,2-b][1]benzofuran (**6**). M.p. 90–92 °C (toluene). For $C_{16}H_{16}OS$ (256.4) calculated: 74.96% C, 6.29% H, 12.51% S; found: 74.77% C, 6.42% H, 12.42% S. IR spectrum: 3 046, 3 011, 2 933, 2 859, 1 594, 1 544, 1 475, 1 431, 1 401, 1 350, 1 288, 1 261, 1 179, 1 112, 1 090, 1 051, 1 016. Mass spectrum: 257 (10), 256 (65) (M$^+$), 241 (15) [M$^+$ – CH$_3$], 174 (100) [retro D.A.], 149 (15), 94 (25), 69 (10), 57 (15), 55 (15), 43 (20), 41 (20).

7,8-Diphenyl-5a,6,9,9a-tetrahydro[1]benzothieno[3,2-b][1]benzofuran (**7**). M.p. 101–104 °C (methanol). For $C_{26}H_{20}OS$ (380.5) calculated: 82.07% C, 5.30% H, 8.43% S; found: 81.45% C, 5.37% H, 7.98% S. IR spectrum: 3 080, 3 060, 3 011, 2 944, 2 842, 1 599, 1 544, 1 494, 1 475, 1 444, 1 431, 1 401, 1 287, 1 251, 1 176, 1 091, 1 070, 1 013. Mass spectrum: 381 (10), 380 (30) [M$^+$], 218 (30), 175 (15), 174 (100) [retro D.A.], 163 (10), 115 (10), 91 (10), 77 (10).

1,2,3,4,6,6a,12b,12c-Octahydrobenzo[e][1]benzothieno[3,2-b][1]benzofuran (**8**). M.p. 75–77 °C (methanol). For $C_{18}H_{18}OS$ (282.4) calculated: 76.56% C, 6.42% H, 11.35% S; found: 75.77% C, 6.79% H, 11.53% S. IR spectrum: 3 013, 2 934, 2 857, 1 705, 1 594, 1 534, 1 430, 1 398, 1 261, 1 163, 1 089, 1 017. ^{1}H NMR spectrum: 1.30–2.50 m, 11 H; 4.00 dd, 1 H, $J(12b,12c) = 8.0$ (H-12b); 5.32 ddd, 1 H, $J(6a,12b) = 7.7$, $J(6A,6a) = 6.3$, $J(6B,6a) = 5.8$ (H-6a); 5.51 bs, 1 H (H-5); 7.25 ddd, 1 H, $J(8,10) = 1.1$ (H-10); 7.32 ddd, 1 H, $J(9,10) = 7.1$, $J(9,11) = 1.1$ (H-9); 7.62 d, 1 H, $J(8,9) = 7.7$ (H-8); 7.69 d, 1 H, $J(10,11) = 8.3$ (H-11). Mass spectrum: 282 (5) [M$^+$], 187 (10), 175 (15), 174 (100) [retro D.A.], 146 (15), 91 (10).

9-Methyl-5a,6,9,9a-tetrahydro[1]benzothieno[3,2-b][1]benzofuran (**9**). M.p. 98–99 °C (methanol). For $C_{15}H_{14}OS$ (242.3) calculated: 74.35% C, 5.82% H, 13.23% S; found: 74.43% C, 5.91% H, 12.98% S. IR spectrum: 3 039, 3 012, 2 965, 2 934, 2 878, 2 837, 1 590, 1 543, 1 476, 1 431, 1 402, 1 376, 1 261, 1 244, 1 167, 1 039, 1 063, 1 035. Mass spectrum: 242 (15) [M$^+$], 175 (10), 174 (100) [retro D.A.], 146 (10), 102 (10).

Methyl 5a,6,9,9a-tetrahydro[1]benzothieno[3,2-b][1]benzofuran-9-carboxylate (**10**). Yellowish oil. For $C_{16}H_{14}O_3S$ (286.4) calculated: 67.11% C, 4.93% H; found: 66.75% C, 5.01% H. IR spectrum: 3 025, 2 955, 2 929, 2 855, 1 732 (non-conjugated COOCH$_3$), 1 591, 1 544, 1 476, 1 435, 1 402, 1 282, 1 259, 1 174, 1 090, 1 031.

Methyl 5a,6,7,9a-tetrahydro[1]benzothieno[3,2-b][1]benzofuran-9-carboxylate (**11**). M.p. 87–89 °C (methanol). For $C_{16}H_{14}O_3S$ (286.4) calculated: 67.11% C, 4.93% H, 11.20% S; found: 67.06% C, 5.15% H, 11.37% S. IR spectrum: 3 014, 2 953, 2 847, 1 708 (conjugated COOCH$_3$), 1 650, 1 588, 1 437, 1 402, 1 306, 1 269, 1 233, 1 168, 1 089, 1 050, 1 030. ^{1}H NMR spectrum: 1.85 m, 1 H and 2.25–2.55 m, 3 H (H-6A, H-6B, H-7A, H-7B); 3.84 s, 3 H (OCH$_3$); 4.35 d, 1 H, $J(5a,9a) = 8.2$ (H-9a); 5.61 ddd, 1 H, $J(5a,6A) = 2.8$, $J(5a,6B) = 2.8$ (H-5a); 7.23 dd, 1 H, $J(7A,8) = 2.7$, $J(7B,8) = 6.1$

(H-8); 7.25 ddd, 1 H, $J(2,4) = 1.7$ (H-2); 7.32 ddd, 1 H, $J(2,3) = 7.2$, $J(1,3) = 1.1$ (H-3); 7.60 d, 1 H, $J(3,4) = 7.7$ (H-4); 7.68 d, 1 H, $J(1,2) = 8.2$ (H-1). Mass spectrum: 287 (20), 286 (100) [M$^+$], 254 (70) [M$^+$ – CH$_3$OH], 253 (25), 227 (35), 226 (80) [M$^+$ – CH$_3$OH – CO], 225 (50), 197 (70), 187 (20), 171 (10), 165 (40), 153 (20), 150 (40), 137 (15), 121 (40), 115 (20), 105 (20), 91 (25), 77 (40).

6,9-Diphenyl-5a,6,9,9a-tetrahydro[1]benzothieno[3,2-b][1]benzofuran (**12**). M.p. 215–217 °C (hexane–toluene). For C$_{26}$H$_{20}$OS (380.5) calculated: 82.07% C, 5.30% H, 8.43% S; found: 81.86% C, 5.33% H, 8.22% S. IR spectrum: 3 089, 3 066, 3 031, 3 012, 2 929, 2 837, 1 593, 1 543, 1 496, 1 476, 1 453, 1 431, 1 404, 1 326, 1 260, 1 170, 1 092, 1 057, 1 033. Mass spectrum: 380 (5) [M$^+$], 207 (15), 206 (100) [retro D.A.], 205 (15), 174 (20) [retro D.A.], 91 (35).

1,2,3,4,5,6,6a,6b,12b,12c-Decahydro[1]benzothieno[3,2-b]as-indaceno[4,5-d]furan (**13**). M.p. 139–141 °C (heptane). For C$_{20}$H$_{20}$OS (308.4) calculated: 77.88% C, 6.54% H, 10.39% S; found: 78.05% C, 6.59% H, 10.19% S. IR spectrum: 3 011, 2 956, 2 869, 2 836, 1 593, 1 543, 1 478, 1 431, 1 404, 1 337, 1 261, 1 175, 1 132, 1 093, 1 063, 1 016. ^{1}H NMR spectrum: 1.58–2.22 m, 12 H; 2.50 m, 2 H (H-6a and H-12c); 4.04 dd, 1 H, $J(12b,12c) = 7.0$ (H-12b); 5.71 dd, 1 H, $J(6b,12b) = 9.4$, $J(6a,6b) = 3.9$ (H-6b); 7.24 ddd, 1 H, $J(8,10) = 1.2$ (H-10); 7.30 ddd, 1 H, $J(9,10) = 7.4$, $J(9,11) = 1.1$ (H-9); 7.57 d, 1 H, $J(8,9) = 7.5$ (H-8); 7.68 d, 1 H, $J(10,11) = 8.4$ (H-11). Mass spectrum: 308 (15) [M$^+$], 175 (15), 174 (100) [retro D.A.], 134 (40) [retro D.A.], 91 (10).

1,2,3,4,5,6,7,8,8a,8b,14b,14c-Dodecahydro[1]benzothieno[3,2-b]fenanthro[9,10-d]furan (**14**). Yellowish oil. For C$_{22}$H$_{24}$OS (336.5) calculated: 78.53% C, 7.19% H; found: 78.32% C, 7.34% H. IR spectrum: 3 001, 2 935, 2 856, 1 713, 1 692, 1 449, 1 404, 1 366, 1 266, 1 147, 1 111. ^{1}H NMR spectrum: 1.10–2.10 m, 16 H; 3.67 dd, 1 H, $J(14b,14c) = 7.0$ (H-14b); 5.31 dd, 1 H, $J(8b,14b) = 8.1$, $J(8a,8b) = 6.0$ (H-8b); 7.24 dd, 1 H (H-12); 7.31 ddd, 1 H, $J(11,12) = 7.5$, $J(11,13) = 1.0$ (H-11); 7.62 d, 1 H, $J(10,11) = 7.6$ (H-10); 7.70 d, 1 H, $J(12,13) = 7.9$ (H-13). Mass spectrum: 336 (20) [M$^+$], 174 (100) [retro D.A.], 162 (95) [retro D.A.], 94 (15).

1,2,4-Triphenyl-4-(1-phenylvinyl)cyclohexene (**15**). M.p. 121–125 °C (methanol). For C$_{32}$H$_{28}$ (412.6) calculated: 93.16% C, 6.84% H; found: 93.20% C, 6.96% H. IR spectrum: 3 082, 3 060, 3 011, 2 942, 2 837, 1 621, 1 598, 1 574, 1 492, 1 444, 1 357, 1 283, 1 183, 1 134, 1 071, 1 030. ^{1}H NMR spectrum: 2.21 m, 2 H (H-5); 2.43 m, 2 H (H-6); 2.82 m, 2 H (H-3); 5.33 s, 1 H (H-2′); 5.51 s, 1 H (H-2′); 6.81–7.56 m, 20 H (Ph). Mass spectrum: 412 (5) [M$^+$], 308 (10), 307 (10), 296 (25), 295 (100), 206 (50) [retro D.A.], 205 (40), 191 (15), 128 (15), 103 (10), 91 (65).

3,4,6-Triphenyl-5-(2-phenylvinyl)cyclohexene (**16**). For C$_{32}$H$_{48}$ (412.6) calculated: 93.16% C, 6.84% H; found: 93.53% C, 6.85% H. ^{1}H NMR spectrum of (*Z*)-17: 2.93 m, 1 H (H-4); 3.54 m, 2 H (H-3 and H-5); 3.77 m, 1 H (H-6); 5.60 m, 2 H (H-1′ and H-2′); 6.08 m, 2 H (H-1 and H-2); 6.87–7.40 m, 20 H (Ph). ^{1}H NMR spectrum of (*E*)-17: 2.88 dd, 1 H, $J(3,4) = 10.4$, $J(4,5) = 11.7$ (H-4); 3.32 ddd, 1 H, $J(5,1′) = 10.1$, $J(5,6) = 5.9$ (H-5); 3.68 dd, 1 H, $J(2,3) = 1.7$ (H-3); 3.83 m, 1 H (H-6); 5.16 dd, 1 H, $J(1′,2′) = 15.8$ (H-1′); 6.09 m, 2 H (H-1 and H-2); 6.25 d, 1 H (H-2′); 6.80–7.42 m, 20 H (Ph).

Aromatization of Compounds **3–13** and **23** (General Procedure)

The adduct (Table III) was dissolved in dry degassed benzene (10 ml). After addition of DDQ (2.1 mol-equivalent), the suspension was refluxed under nitrogen and the reaction course was monitored by TLC. After the starting compound disappeared, the reaction mixture was taken down and the product was isolated by column chromatography on silica gel in hexane. The results of the aromatization are summarized in Table III. For ^{1}H NMR spectra see Tables VI and VII.

[1]Benzothieno[3,2-b][1]benzofuran (**17**). M.p. 130-132 C (hexane) (ref.[20] gives m.p. 126.5–127.5 °C). For C$_{14}$H$_8$OS (224.3) calculated: 74.98% C, 3.60% H, 14.29% S; found: 74.73% C, 3.70% H, 14.53% S. IR spectrum: 3 065, 3 027, 3 012, 1 599, 1 522, 1 474, 1 447, 1 420, 1 395, 1 358, 1 299, 1 263, 1 162, 1 135, 1 088, 1 052, 1 016. UV spectrum: λ_{max} (log ε): 228 (4.32); 240 (4.26); 248

(4.32); 256 (4.43); 304 (4.47); 311 (4.41); 318 (4.38). ^{13}C NMR spectrum: 113.2 (C-6); 119.3 (C-9b); 120.3 (C-9); 120.4 (C-1); 124.0 (C-8); 124.8 (C-9a); 125.0 (C-4); 125.6 (C-7); 125.6 (C-2); 125.6 (C-3); 125.9 (C-4a); 142.7 (C-10a); 153.7 (C-4b); 159.5 (C-5a). Mass spectrum: 225 (15), 224 (100) [M$^+$], 195 (15), 152 (15), 112 (20).

7,8-Dimethyl[1]benzothieno[3,2-b][1]benzofuran (**18**). M.p. 163–165 °C (hexane). For C$_{16}$H$_{12}$OS (252.3) calculated: 76.16% C, 4.79% H, 12.71% S; found: 75.86% C, 4.83% H, 12.22% S. IR spectrum: 3 065, 3 008, 2 9075, 2 926, 2 863, 1 603, 1 518, 1 456, 1 394, 1 292, 1 262, 1 165, 1 108, 1 087, 1 052. Mass spectrum: 253 (20), 252 (100) [M$^+$], 251 (30), 237 (20) [M$^+$ – CH$_3$], 126 (10).

7,8-Diphenyl[1]benzothieno[3,2-b][1]benzofuran (**19**). M.p. 158–160 °C (hexane). For C$_{26}$H$_{16}$OS (376.5) calculated: 82.95% C, 4.28% H, 8.52% S; found: 83.26% C, 4.44% H, 8.56% S. IR spectrum: 3 063, 3 031, 3 011, 1 600, 1 498, 1 458, 1 433, 1 393, 1 346, 1 311, 1 268, 1 243, 1 157, 1 135, 1 087, 1 053, 1 016. Mass spectrum: 377 (30), 376 (100) [M$^+$], 345 (10), 97 (10), 83 (15), 72 (15), 69 (20), 57 (30), 55 (25), 43 (30).

9-Methyl[1]benzothieno[3,2-b][1]benzofuran (**20**). M.p. 90–91 °C (methanol). For C$_{15}$H$_{10}$OS (238.3) calculated: 75.60% C, 4.23% H, 13.45% S; found: 75.42% C, 4.48% H, 13.49% S. IR spectrum: 3 062, 3 013, 2 976, 2 920, 1 594, 1 488, 1 460, 1 426, 1 394, 1 352, 1 291, 1 238, 1 159, 1 136, 1 085, 1 055, 1 029. Mass spectrum: 239 (20), 238 (100) [M$^+$], 237 (50) [M$^+$ – H], 209 (10), 208 (20), 165 (25), 164 (10), 139 (10), 119 (15), 104 (30), 89 (10), 69 (15), 50 (15).

Methyl [1]benzothieno[3,2-b][1]benzofuran-9-carboxylate (**21**). M.p. 116–117 °C (methanol). For C$_{16}$H$_{10}$O$_3$S (282.3) calculated: 68.07% C, 3.57% H, 11.36% S; found: 67.82% C, 3.67% H, 11.42% S. IR spectrum: 3 065, 3 017, 2 954, 1 712 (ArCOOCH$_3$), 1 614, 1 587, 1 515, 1 469, 1 430, 1 396, 1 362, 1 300, 1 275, 1 174, 1 142, 1 097, 1 058. Mass spectrum: 283 (20), 282 (100) [M$^+$], 252 (15), 251 (70) [M$^+$ – CH$_3$O], 224 (15), 223 (55) [M$^+$ – COOCH$_3$], 196 (10), 195 (45), 151 (30), 150 (15), 125 (20), 98 (35).

1,2,3,4,5,6-Hexahydro[1]benzothieno[3,2-b]as-indaceno[4,5-d]furan (**22**). M.p. 151–153 °C (hexane). For C$_{20}$H$_{16}$OS (304.4) calculated: 78.91% C, 5.30% H, 10.53% S; found: 78.60% C, 5.529% H, 10.35% S. IR spectrum: 3 065, 3 011, 2 957, 2 847, 1 516, 1 463, 1 441, 1 422, 1 404, 1 383, 1 333, 1 306, 1 242, 1 158, 1 137, 1 086, 1 069, 1 016. ^{1}H NMR spectrum: 2.28 m, 4 H (H-2A, H-2B, H-5A, H-5B); 2.96 dt, 4 H, J = 7.3 (H-3A, H-3B, H-4A, H-4B); 3.23 dt, 4 H, J = 7.8 (H-1A, H-1B, H-6A, H-6B); 7.36 ddd, 1 H, $J(8,10)$ = 1.1 (H-10); 7.47 ddd, 1 H, $J(8,9)$ = 8.1, $J(9,10)$ = 7.2, $J(9,11)$ = 1.1 (H-9); 7.88 d, 1 H, $J(10,11)$ = 8.2 (H-11); 8.02 d, 1 H (H-8). Mass spectrum: 305 (25), 304 (100) [M$^+$], 275 (10), 138 (10), 69 (15), 57 (10).

1,2,3,4-Tetrahydrobenzo[e][1]benzothieno[3,2-b][1]benzofuran (**23**). M.p. 107–109 °C (methanol). For C$_{18}$H$_{14}$OS (278.4) calculated: 77.67% C, 5.07% H, 11.52% S; found: 77.87% C, 5.35% H, 11.45% S. IR spectrum: 3 065, 2 936, 2 863, 2 840, 1 599, 1 520, 1 467, 1 430, 1 396, 1 289, 1 2663, 1 155, 1 090, 1 052, 1 010. ^{1}H NMR spectrum: 1.94 m, 4 H; 2.89 t, 2 H, $J(3,4)$ = 6.1 (H-4A and H-4B); 3.10 t, 2 H, $J(1,2)$ = 6.0 (H-1A and H-1B); 7.10 d, 1 H (H-5); 7.38 ddd, 1 H, $J(8,10)$ = 1.1 (H-10); 7.39 d, 1 H, $J(5,6)$ = 8.8 (H-6); 7.48 ddd, 1 H, $J(9,10)$ = 7.1, $J(9,11)$ = 1.1 (H-9); 7.89 d, 1 H, $J(10,11)$ = 8.2 (H-11); 8.01 d, 1 H, $J(8,9)$ = 7.7 (H-8).

Benzo[e][1]benzothieno[3,2-b][1]benzofuran (**24**). M.p. 151–153 °C (methanol–ethyl acetate). For C$_{18}$H$_{10}$OS (274.3) calculated: 78.81% C, 3.67% H, 11.69% S; found: 78.71% C, 3.95% H, 11.74% S. IR spectrum: 3 058, 2 921, 1 693, 1 603, 1 576, 1 508, 1 466, 1 423, 1 399, 1 369, 1 343, 1 291, 1 262, 1 162, 1 138, 1 091. UV spectrum: λ_{max} (log ε): 222 (4.57); 242 (4.47); 273 (4.14); 327 (4.52); 343 (4.65). ^{1}H NMR spectrum: 7.43 dd, 1 H (H-9); 7.54 dd, 1 H, $J(8,9)$ = 7.4 (H-8); 7.59 dd, 1 H (H-3); 7.73 dd, 1 H, $J(2,3)$ = 7.4 (H-2); 7.84 m, 2 H (H-5 and H-6); 7.97 d, 1 H, $J(10,9)$ = 8.1 (H-10); 8.03 d, 1 H, $J(4,3)$ = 8.1 (H-4); 8.09 d, 1 H, $J(7,8)$ = 7.9 (H-7); 8.19 d, 1 H, $J(1,2)$ = 8.1 (H-1). Mass spectrum: 275 (20), 274 (100) [M$^+$], 246 (20), 245 (75) [M$^+$ – CHO], 213 (10), 202 (25), 201 (15), 200 (20), 170 (15), 169 (20), 137 (50), 126 (15), 122 (30).

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