A Simple and Efficient Synthesis of Heterocycle-Fused 2*H*-Thiopyrans, Furo-, Benzofuro-, Thieno-, Benzothieno-, Pyrrolo- and Indolo-2*H*-thiopyrans, from Heteroaromatic Thioketones and α-Chloroacrylonitrile or α-Bromoacrylic Esters via a Hetero Diels–Alder Reaction–Dehydrohalogenation Process

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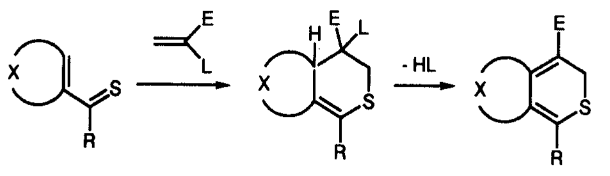
An efficient and convenient procedure is described for the synthesis of heterocycle-fused 2*H*-thiopyrans having ortho-dimethylene structures via a hetero Diels–Alder reaction–dehydrohalogenation process starting from heteroaromatic thioketones and α-chloroacrylonitrile or α-bromoacrylates.

Although various methods for the synthesis of 2*H*-thiopyrans have been reported so far, they are mostly tedious and restricted by availability of starting materials. Moreover, these 2*H*-thiopyrans are, in most cases, limited to the monocyclic or benzo-fused derivatives.[1] Previously we reported that α,β-unsaturated and aromatic thioketones readily underwent hetero Diels–Alder reaction with a variety of dienophiles to give dihydro-2*H*-thiopyrans.[2] For potentially wider applicability, we have now extended this procedure toward facile, straightforward synthesis of heterocycle-fused 2*H*-thiopyrans **D** (Scheme 1) which involves the Diels–Alder reaction of readily available heteroaromatic thioketones **A** as heterodienes with reactive dienophiles **B** bearing an electron-withdrawing group (E) and a leaving group (L), followed by regiospecific 1,2-elimination of the Diels–Alder adducts **C**.

Furthermore, it is noteworthy that the heterocycle-fused 2*H*-thiopyrans **D** obtained in most cases have ortho-



A **B** **C** **D**

Scheme 1

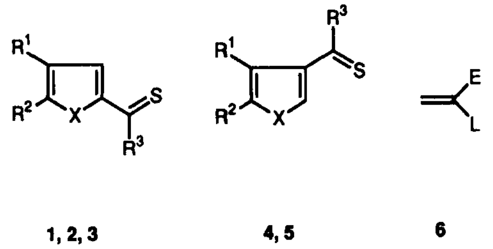
dimethylene (ortho-quinodimethane-type) structures with respect to the fused heterocycles. Compounds with such structures are generally unstable and very reactive,[3,4] thereby being useful intermediates as potent Diels–Alder diene components to provide fused carbo- and heterocyclic compounds.[5]

When the furyl or benzofuryl thioketones **1** were heated with α-chloroacrylonitrile or α-bromoacrylate **6** in benzene, the corresponding Diels–Alder adducts **C** were formed regiospecifically, but they were too labile to be isolated owing to subsequent facile dehydrohalogenation; treatment with triethylamine in one-pot gave red-colored furo-fused 2*H*-thiopyrans **7** (Scheme 2, Table 1).

Table 1. Furo- and Benzofuro-fused 2*H*-Thiopyrans **7** and **7′**

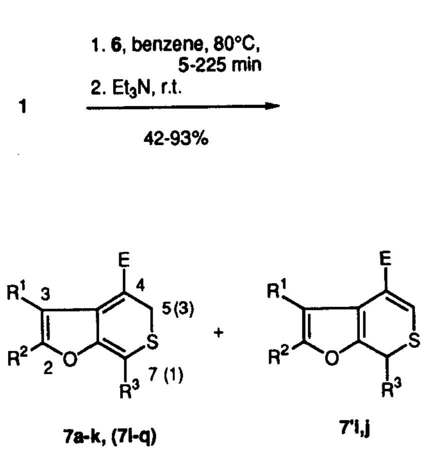
Product	R^1	R^2	R^3	E	Reaction Time (min)	Yield (%)	mp (dec.) (°C)
7a[a,b]	H	H	Ph	CN	10	63	85–87
7b[a,b]	H	H	$2,4,6\text{-}Me_3C_6H_2$	CN	20	93	135–137
7c[c]	H	H	Ph	CO_2Me	10	48	oil
7d[a]	H	H	$2,4,6\text{-}Me_3C_6H_2$	CO_2Me	35	73	87–88
7e[a]	H	H	$2,4,6\text{-}Me_3C_6H_2$	CO_2Et	120	77	101–102
7f[c]	H	H	Ph	$CO_2CH_2C{\equiv}CH$	15	45	132–134
7g[c]	H	H	$4\text{-}MeOC_6H_4$	$CO_2CH_2C{\equiv}CH$	30	42	109–110
7h[a]	H	H	$2,4,6\text{-}Me_3C_6H_2$	$CO_2CH_2C{\equiv}CH$	60	80	113–114
7i[a]	H	H	Ph	$CO_2Bu\text{-}t$	90	8	oil
7′i[a]						50	oil
7j[a]	H	H	$4\text{-}MeOC_6H_4$	$CO_2Bu\text{-}t$	20	17	oil
7′j[a]						29	oil
7k[a]	H	H	$2,4,6\text{-}Me_3C_6H_2$	$CO_2Bu\text{-}t$	225	64	141–142
7l[a]	CH=CH–CH=CH		Ph	CN	5	82	126–128
7m[a]	CH=CH–CH=CH		Ph	CO_2Me	5	83	119–120
7n[a]	CH=CH–CH=CH		Ph	CO_2Et	30	66	94–95
7o[a]	CH=CH–CH=CH		Ph	$CO_2CH_2C{\equiv}CH$	5	84	81–82
7p[c]	CH=CH–CH=CH		Ph	$CO_2Bu\text{-}t$	20	56	132–133
7q[c]	CH=CH–CH=CH		Ph	$CO_2C(Me)_2C{\equiv}CH$	20	40	oil

[a] Satisfactory microanalyses obtained: C ± 0.29, H ± 0.27, N ± 0.28, or high resolution mass spectra obtained: M ± 1.5 ppm.
[b] Reported in literature.[4]
[c] Not analysed due to instability or poor crystallinity.



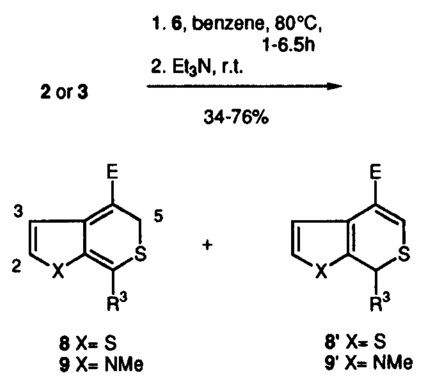
1-5	X	R^1	R^2	R^3
1a	O	H	H	C_6H_5
1b	O	H	H	$4\text{-}MeOC_6H_4$
1c	O	H	H	$2,4,6\text{-}Me_3C_6H_2$
1d	O	CH=CH-CH=CH		C_6H_5
2a	S	H	H	C_6H_5
2b	S	H	H	$4\text{-}MeOC_6H_4$
2c	S	H	H	$2,4,6\text{-}Me_3C_6H_2$
3a	NMe	H	H	C_6H_5
4a	S	CH=CH-CH=CH		C_6H_5
5a	NMe	CH=CH-CH=CH		C_6H_5
5b	NCOPh	CH=CH-CH=CH		C_6H_5

6	E	L
a	CN	Cl
b	CO_2Me	Br
c	CO_2Et	Br
d	$CO_2CH_2C{\equiv}CH$	Br
e	$CO_2Bu\text{-}t$	Br



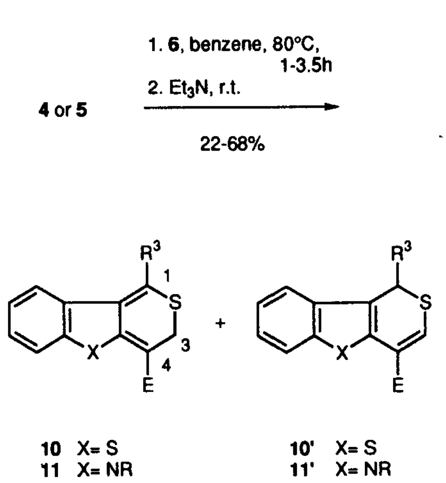
Scheme 2

The use of a stronger base such as sodium alcoholate caused isomerization by way of a proton shift (or 1,5-sigmatropic rearrangement) of the initially formed ortho-dimethylene-type compounds **7** to produce the corresponding rearomatized compounds **7'**. During column-chromatographic purification, compounds **7** also partly isomerized to **7'** in some cases, depending on their instability. The substituent, either E = CN or R^3 = mesityl, or the fused benzene ring at R^1, R^2 tends to stabilize **7**. Indeed, in these cases, compounds **7** were obtained in relatively good yields. Easy isomerization was also observed particularly in the reaction of thienyl **2** or pyrrolyl **3** thioketones with **6**.



Scheme 3

Similarly, benzothienyl and indolyl thioketones **4** and **5** gave, before column chromatographic purification, only 2*H*-thiopyrans **10** and **11**, respectively, having ortho-dimethylene structures (Scheme 4, Table 2).



Scheme 4

Thus, the present work provides a novel, straightforward and general method for the synthesis of, particularly, ortho-quinodimethane-type heterocycle-fused-2*H*-thiopyrans, which are not readily available by other methods. The accessibility of these 2*H*-thiopyrans may reveal new chemistry concerning ortho-dimethylene heterocyclic compounds by further elaboration. For example, it was found that **7q** underwent the intramolecular Diels–Alder reaction, followed by the retro Diels–Alder reaction of the initially formed cycloadduct with concomitant elimination of thioformaldehyde to afford the four fused-ring heterocyclic compound **12** as the final product (Scheme 5).

Table 2. Thieno-, Benzothieno-, Pyrrolo- and Indolo-fused 2*H*-Thiopyrans **8–11** and **8′–11′**

Product	X	R^3	E	Reaction Time (h)	Yield (%)	mp (°C)
8a[a,b]	S	Ph	CN	1	63	103–105
8b[a,b]	S	4-ClC_6H_4	CN	1	69	165–166
8c[a,b]	S	$2,4,6\text{-Me}_3C_6H_2$	CN	2	76	156–158
8′d[a]	S	Ph	CO_2Me	3	49	96–97
8′e[a]	S	4-MeOC_6H_4	CO_2Me	4	53	122–123
8f[a]	S	$2,4,6\text{-Me}_3C_6H_2$	CO_2Me	3	74	136–137
8′g[a]	S	4-MeOC_6H_4	CO_2Et	3.5	43	oil
8h[c]	S	$2,4,6\text{-Me}_3C_6H_2$	CO_2Et	6.5	54	133–134
8′i[a]	S	Ph	$CO_2CH_2C{\equiv}CH$	4	52	oil
8j[a]	S	$2,4,6\text{-Me}_3C_6H_2$	$CO_2CH_2C{\equiv}CH$	3	51	decomp.
8′k[a]	S	Ph	$CO_2Bu\text{-}t$	4.5	34	oil
8l[a]	S	$2,4,6\text{-Me}_3C_6H_2$	$CO_2Bu\text{-}t$	8	73	oil
9′a[c]	NMe	Ph	CN	3	44	152–154
9′b[c]	NMe	4-MeOC_6H_4	CN	3	52	120–123
10a[a]	S	Ph	CN	3.5	68	197–200
10b[c]	S	Ph	CO_2Me	1.5	37	decomp.
10′b[a]					12	oil
10c[a]	S	Ph	CO_2Et	2	13	oil
10′c[a]					9	202–203
10d[a]	S	Ph	$CO_2CH_2C{\equiv}CH$	1.5	28	decomp.
11a[a]	NMe	Ph	CN	3	48	169–171
11b[a]	NCOPh	Ph	CN	1	50	218–220
11′c[c]	NMe	Ph	CO_2Me	0.2	71	decomp.

See footnotes in Table 1.

Table 3. Spectroscopic Data of Compounds **7–11** and **7′–11′**

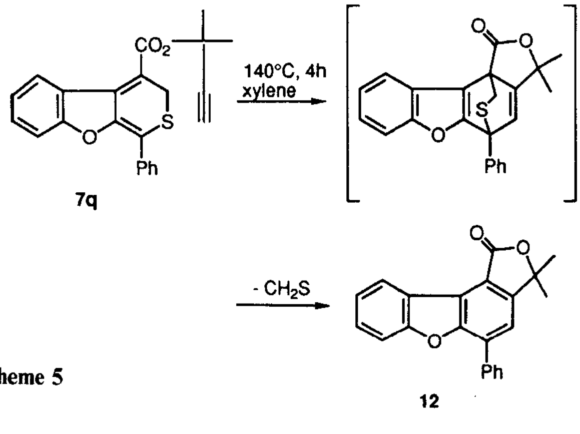
Compound	IR (KBr or neat) ν (CN) or ν (CO) (cm^{-1})	MS (70 eV) m/z (rel. int, %)	^1H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$; DEPT) δ
7a	2190	239 (M^+, 64), 238 (100)	3.68 (s, 2H, H-5), 6.26 (d, 1H, J = 2.7, H-3), 7.22 (d, 1H, J = 2.7, H-2), 7.28–7.48 (m, 3H, PhH), 7.60–7.80 (m, 2H, PhH)	28.2 (C-5), 76.5, 106.0 (C-3), 118.7, 123.5, 128.5, 129.1, 129.9, 132.4, 145.0, 146.5, 153.3
7b	2190	281 (M^+, 100), 266 (42)	2.20 (s, 6H, 2Me), 2.29 (s, 3H, Me), 3.74 (s, 2H, H-5), 6.20 (d, 1H, J = 2.5, H-3), 6.87 (s, 2H, m-H), 7.08 (d, 1H, J = 2.5, H-2)	19.6 (2Me), 21.1 (Me), 28.8 (C-5), 74.6, 105.7, 118.8, 124.9, 127.8, 128.5 (m-C), 137.0, 139.4, 145.7, 153.8
7c	1692		3.83 (s, 3H, OMe), 3.90 (s, 2H, H-5), 7.25–7.47 (m, 5H, H-2,3, PhH), 7.72–7.88 (m, 2H, PhH)	
7d	1692	314 (M^+, 47), 299 (100)	2.20 (s, 6H, 2Me), 2.27 (s, 3H, Me), 3.81 (s, 3H, OMe), 3.92 (s, 2H, H-5), 6.77 (d, 1H, J = 2.6, H-3), 6.88 (s, 2H, m-H), 7.09 (d, 1H, J = 2.6, H-2)	19.6 (2Me), 21.1 (Me), 27.7 (C-5), 51.5 (OMe), 95.0, 107.9, 125.8, 128.3, 128.8, 137.0, 138.9, 142.3, 147.0, 153.4, 166.6 (CO)
7e	1686	328 (M^+, 35), 299 (100)	1.36 (t, 3H, J = 7.3, Me), 2.22 (s, 6H, 2Me), 2.29 (s, 3H, Me), 3.94 (s, 2H, H-5), 4.29 (q, 2H, J = 7.3, OCH_2), 6.81 (d, 1H, J = 2.6, H-3), 6.91 (s, 2H, m-H), 7.12 (d, 1H, J = 2.6, H-2)	14.5 (Me), 19.7 (2Me), 21.2 (Me), 27.7 (C-5), 60.4 (OCH_2), 95.5, 108.0, 125.5, 128.4, 128.8, 137.1, 139.0, 142.1, 147.1, 153.4, 166.3 (CO)
7f	1674		2.50 (t, 1H, J = 2.3, HC≡), 3.89 (s, 2H, H-5), 4.83 (d, 2H, J = 2.3, OCH_2), 6.92 (d, 1H, J = 2.6, H-3), 7.30–7.45 (m, 4H, H-2, PhH), 7.78–7.83 (m, 2H, PhH)	27.1 (C-5), 51.9 (OCH_2), 74.7 (C≡), 78.2 (HC≡), 95.4, 108.3, 125.9, 128.4, 129.2, 129.7, 133.1, 143.9, 146.5, 153.3, 164.0 (CO)
7g	1680	326 (M^+, 100), 293 (85)	2.50 (t, 1H, J = 2.3, HC≡), 3.83 (s, 3H, OMe), 3.86 (s, 2H, H-5), 4.83 (d, 2H, J = 2.3, OCH_2), 6.93 (d, 1H, J = 2.64, H-3), 6.94 (d, 2H, J = 8.91, ArH), 7.33 (d, 1H, H-2), 7.80 (d, 2H, J = 8.91, ArH)	27.2 (C-5), 51.8 (OCH_2), 55.3 (OMe), 74.6 (C≡), 78.3 (HC≡), 94.2, 108.4, 113.9, 125.5, 126.1, 131.1, 144.1, 145.1, 145.7, 153.1, 160.8, 165.0 (CO)
7h	1682	338 (M^+, 79), 299 (100)	2.21 (s, 6H, 2Me), 2.28 (s, 3H, Me), 2.47 (t, 1H, J = 2.2, HC≡), 3.93 (s, 2H, H-3), 4.84 (d, 2H, J = 2.2, OCH_2), 7.18 (d, 1H, J = 2.4, H-3), 7.20 (s, 2H, m-H), 7.49 (d, 1H, J = 2.4, H-2)	19.7 (2Me), 21.2 (Me), 24.7 (C-5), 51.9 (OCH_2), 74.7 (C≡), 78.2 (HC≡), 93.6, 108.2, 128.2, 128.3, 128.4, 128.7, 137.0, 139.2, 143.2, 147.1, 153.9, 165.3 (CO)
7i	1678	314 (M^+, 25), 257 (100)	1.57 (s, 9H, 3Me), 3.84 (s, 2H, H-5), 6.83–7.83 (m, 7H, H-2,3, PhH)	27.2 (C-5), 28.4 (3Me), 80.7 (t-Bu–C), 99.4, 108.2, 123.4, 128.4, 129.1, 129.3, 133.4, 142.0, 146.6, 152.4, 165.4 (CO)
7′i	1704	314 (M^+, 28), 258 (33)	1.56 (s, 9H, 3Me), 5.48 (s, 1H, H-7), 7.00–7.33 (m, 8H, H-2,3,5, PhH)	28.2 (3Me), 41.8 (C-7), 81.1 (t-Bu–C), 109.9, 116.3, 127.1, 128.5, 128.7, 128.9, 129.4, 141.5, 144.0, 148.2, 162.8 (CO)

Table 3. (continued)

Compound	IR (KBr or neat) ν (CN) or ν (CO) (cm^{-1})	MS (70 eV) m/z (rel. int, %)	^1H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$; DEPT) δ
7j	1676	344 (M^+, 50), 287 (100)	1.57 (s, 9H, 3Me), 3.81 (s, 2H, H-5), 3.83 (s, 3H, OMe), 6.85 (d, 1H, J = 2.6, H-3), 6.93 (d, 2H, J = 8.6, ArH), 7.26–7.28 (d, 1H, J = 2.6, H-2), 7.80 (d, 2H, J = 8.6, ArH)	27.3 (C-5), 28.4 (3Me), 55.4 (OMe), 80.5 (t-BuC), 98.3, 108.3, 113.9, 114.0, 123.5, 125.9, 130.9, 142.1, 152.2, 160.5, 165.5 (CO)
7'j	1704	344 (M^+, 83), 288 (87)	1.56 (s, 9H, 3Me), 3.75 (s, 3H, OMe), 5.46 (s, 1H, H-7), 6.82 (d, 2H, J = 8.6, ArH), 7.03 (d, 1H, J = 1.7, H-5), 7.09 (d, 2H, J = 8.6, ArH), 7.20–7.30 (m, 2H, H-2,3)	28.3 (3Me), 41.5 (C-7), 55.2 (OMe), 81.1 (t-Bu–C), 109.9, 114.3, 116.2, 120.8, 128.4, 128.6, 133.4, 141.5, 144.3, 159.4, 162.9 (CO)
7k	1676	356 (M^+, 36), 299 (100)	1.57 (s, 9H, 3Me), 2.22 (s, 6H, 2Me), 2.28 (s, Me), 3.90 (s, 2H, H-5), 6.76 (d, 1H, J = 2.3, H-3), 6.91 (s, 2H, ArH), 7.08 (d, 1H, J = 2.3, H-2)	19.7 (2Me), 21.1 (Me), 27.8 (C-5), 28.4 (3Me), 80.5 (t-Bu–C), 97.9, 107.9, 124.2, 128.3, 128.9, 137.1, 138.9, 141.2, 147.1, 152.9, 165.6 (CO)
7l	2200	289 (M^+, 74), 288 (100)	3.76 (s, 2H, H-3), 7.02–7.25 (m, 2H, ArH), 7.70–7.92 (m, 2H, ArH), 7.96–8.14 (m, 1H, ArH)	28.3 (C-3), 80.5, 111.2, 118.4, 121.6, 123.1, 128.5, 129.7, 130.0, 132.4, 132.7, 140.2, 159.4
7m	1706	322 (M^+, 95), 307 (100)	3.90 (s, 5H, H-3, OMe), 7.03–7.54 (m, 6H, ArH), 7.76–7.94 (m, 2H, ArH), 8.64–8.74 (m, 1H, ArH)	28.1 (C-3), 51.7 (OMe), 101.4, 110.6, 122.4, 122.8, 123.4, 128.4, 128.7, 129.3, 129.6, 131.7, 133.5, 139.8, 160.1, 165.0 (CO)
7n	1698	336 (M^+, 55), 307 (100)	1.40 (t, 3H, Me), 3.90 (s, 2H, H-3), 4.37 (q, 2H, J = 7.3, OCH_2), 7.10–7.47 (m, 6H, ArH), 7.83–8.76 (m, 3H, ArH)	14.3 (Me), 28.1 (C-3), 60.7 (OCH_2), 101.9, 110.6, 122.3, 122.8, 123.0, 128.3, 129.2, 129.6, 131.6, 133.5, 139.5, 147.2, 160.0, 165.4 (CO)
7o	1696	346 (M^+, 49), 313 (63)	2.54 (t, 1H, J = 2.3, HC≡), 3.92 (s, 2H, H-3), 4.91 (d, 2H, J = 2.3, OCH_2), 7.11–7.48 (m, 6H, ArH), 7.84–7.87 (m, 2H, ArH), 8.76–8.79 (m, 1H, ArH)	28.1 (C-3), 52.2 (OCH_2), 75.1 (HC≡), 77.9 (C≡), 99.7, 110.7, 122.4, 122.7, 124.8, 128.4, 128.5, 129.5, 129.7, 132.0, 133.4, 140.8, 147.2, 160.1, 164.5 (CO)
7p	1672	364 (M^+, 40), 307 (100)	1.61 (s, 9H, 3Me), 3.85 (s, 2H, H-3), 7.12–7.46 (m, 6H, ArH), 7.85–8.77 (m, 3H, ArH)	28.3 (3Me), 28.5 (C-3), 81.2 (t-Bu–C), 104.5, 110.6, 121.8, 122.3, 123.0, 128.3, 128.4, 129.1, 129.6, 131.4, 133.7, 138.8, 147.3, 159.9, 164.9 (CO)
7q	1696		1.84 (s, 6H, Me), 2.63 (s, 1H, HC≡), 3.87 (s, 2H, H-3), 7.10–7.47 (m, 6H, ArH), 7.85–7.88 (m, 2H, ArH), 8.80–8.83 (m, 1H, ArH)	28.3 (C-3), 29.1 (2Me), 72.3 (O–C), 72.8 (C≡), 84.9 (HC≡), 102.1, 110.6, 122.3, 122.8, 123.3, 127.2, 128.4, 129.3, 129.7, 131.7, 133.6, 140.0, 147.3, 160.0, 163.8 (CO)
8a	2190	255 (M^+, 80), 254 (100)	3.73 (s, 2H, H-5), 6.68 (d, 1H, J = 7.0, H-3), 7.10 (d, 1H, J = 7.0, H-2), 7.20–7.60 (m, 5H, PhH)	28.2 (C-5), 80.2, 119.1, 121.9, 127.5, 128.5, 128.7, 130.2, 136.6, 136.9, 153.7
8b	2200	291 (M^+, 35), 288 (100)	3.76 (s, 2H, H-3), 6.70 (d, 1H, J = 6.3, H-3), 7.11 (d, 1H, J = 6.3, H-2), 7.20–7.84 (m, 4H, ArH)	28.2 (C-5), 80.8, 122.1, 129.0, 131.0, 134.3, 134.9, 136.3, 136.6, 138.2, 153.6
8c	2190	297 (M^+, 100), 282 (29)	2.19 (s, 6H, 2Me), 2.28 (s, 3H, Me), 3.78 (s, 2H, H-3), 6.63 (d, 1H, J = 5.9, H-3), 6.85 (s, 2H, m-H), 7.02 (d, 1H, J = 5.9, H-2)	19.3 (2Me), 21.1 (Me), 28.6 (C-5), 79.1, 119.1, 122.0, 128.6 (m-C), 130.1, 132.1, 136.0, 137.5, 139.4, 140.6, 152.7
8'd	1704	288 (M^+, 52), 211 (100)	3.82 (s, 3H, OMe), 5.48 (s, 1H, H-7), 7.16 (d, 1H, J = 7.0, H-3), 7.20–7.30 (m, 5H, PhH), 7.53 (s, 1H, H-5), 7.72 (d, 1H, J = 7.0, H-2)	43.4 (C-7), 51.8 (OMe), 122.9, 127.4, 127.7, 128.3, 128.8, 130.7, 131.9, 132.6, 140.6, 164.2 (CO)
8'e	1702	318 (M^+, 90), 211 (100)	3.77 (s, 3H, OMe), 3.83 (s, 3H, OMe), 5.47 (s, 1H, H-7), 6.81 (d, 2H, J = 10.0, ArH), 7.16 (d, 1H, J = 5.7, H-3), 7.22 (d, 2H, J = 10.0, ArH), 7.54 (s, 1H, H-5), 7.70 (d, 1H, J = 5.7, H-2)	43.1 (C-7), 51.8 (OMe), 55.2 (OMe), 114.2, 122.9, 127.4, 129.0, 131.4, 132.0, 132.5, 133.0, 159.6, 164.3 (CO)
8f	1692	330 (M^+, 76), 315 (100)	2.18 (s, 6H, 2Me), 2.29 (s, 3H, Me), 3.83 (s, 3H, OMe), 3.96 (s, 2H, H-5), 6.78 (s, 2H, ArH), 7.05 (d, 1H, J = 5.8, H-3), 7.48 (d, 1H, J = 5.8, H-2)	19.3 (2Me), 21.2 (Me), 28.1 (C-5), 51.6 (OMe), 98.5, 124.4, 128.5, 132.9, 133.2, 136.1, 136.7, 139.0, 142.1, 149.5, 166.4 (CO)
8'g	1706	332 (M^+, 100), 303 (25)	1.36 (t, 3H, J = 7.25, Me), 3.78 (s, 3H, OMe), 4.30 (q, 2H, J = 7.25, OCH_2), 5.49 (s, 1H, H-7), 6.85 (d, 2H, J = 8.90, ArH), 7.18 (d, 1H, J = 5.28, H-3), 7.23 (d, 2H, J = 8.90, ArH), 7.58 (s, 1H, H-5), 7.74 (d, 1H, J = 5.28, H-2)	14.3 (Me), 43.0 (C-7), 55.3 (OMe), 60.8 (OCH_2), 114.0, 114.2, 122.9, 123.1, 129.1, 129.9, 131.4, 132.5, 132.7, 159.6, 163.9 (CO)
8h	1684	344 (M^+, 65), 315 (100)	1.37 (t, 3H, J = 7.26, Me), 2.19 (s, 6H, 2Me), 2.29 (s, 3H, Me), 3.97 (s, 2H, H-5), 4.29 (q, 2H, J = 7.26, OCH_2), 6.91 (s, 2H, m-H), 7.06 (d, 1H, J = 5.30, H-3), 7.52 (d, 1H, J = 5.30, H-2)	14.4 (Me), 19.3 (2Me), 21.1 (Me), 28.1 (C-5), 60.5 (OCH_2), 99.1, 124.4, 128.5, 132.9, 133.2, 136.1, 136.4, 139.0, 141.7, 149.2, 166.1 (CO)
8'i	1714	312 (M^+, 64), 235 (100)	2.51 (t, 1H, J = 2.6, HC≡), 4.83 (d, 2H, J = 2.6, OCH_2), 5.51 (s, 1H, H-7), 7.16–7.29 (m, 6H, H-3, PhH), 7.63–7.78 (m, 2H, H-2, H-5)	43.4 (C-7), 52.2 (OCH_2), 75.1 (C≡), 77.7 (HC≡), 122.0, 123.1, 127.2, 127.4, 127.7, 128.4, 128.8, 130.6, 131.7, 134.1, 140.5, 162.8 (CO)

Table 3. (continued)

Compound	IR (KBr or neat) ν (CN) or ν (CO) (cm^{-1})	MS (70 eV) m/z (rel. int, %)	^{1}H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$; DEPT) δ
8j	1680	354 (M^+, 100), 321 (92)	2.18 (s, 6H, 2Me), 2.30 (s, 3H, Me), 2.50 (t, 1H, J = 2.3, HC≡), 3.99 (s, 2H, H-5), 4.85 (d, 2H, J = 2.3, OCH_2), 6.91 (s, 2H, m-H), 7.13 (d, 1H, J = 6.3, H-3), 7.54 (d, 1H, J = 6.3, H-2)	19.4 (2Me), 21.2 (Me), 28.1 (C-5), 52.0 (OCH_2), 74.8 (C≡), 78.2 (HC≡), 97.1, 124.5, 128.3, 128.5, 133.1, 136.1, 137.5, 139.2, 143.6, 150.4, 165.1 (CO)
8'k	1704	330 (M^+, 15), 274 (39)	1.55 (s, 9H, 3Me), 5.48 (s, 1H, H-7), 7.16 (d, 1H, J = 5.3, H-3), 7.47 (s, 1H, H-5), 7.75 (d, 1H, J = 5.3, H-2)	28.2 (3Me), 43.4 (C-7), 81.1 (t-Bu–C), 122.8, 124.6, 127.5, 127.8, 128.3, 128.8, 130.8, 131.6, 132.3, 140.5, 163.1 (CO)
8l	1692	372 (M^+, 50), 316 (100)	1.58 (s, 9H, 3Me), 2.20 (s, 6H, 2Me), 2.29 (s, Me), 3.93 (2H, H-5), 6.90 (s, 2H, m-H), 7.01 (d, 1H, J = 6.3, H-3), 7.47 (d, 1H, J = 6.3, H-2)	19.4 (2Me), 21.2 (Me), 28.2 (C-5), 28.4 (3Me), 80.8 (t-Bu–C), 101.5, 124.4, 128.5, 132.8, 133.3, 135.7, 136.2, 138.9, 140.6, 148.4, 165.4 (CO)
9'a	2210	252 (M^+, 63), 145 (100)	3.30 (s, 3H, NMe), 5.29 (s, 1H, H-7), 6.31 (d, 1H, J = 3.8, H-3), 6.55 (s, 1H, H-5), 6.57 (d, 1H, J = 3.8, H-2), 6.80–7.00 (m, 2H, PhH), 7.13–7.29 (m, 3H, PhH)	33.3 (NMe), 40.4 (C-7), 110.8, 115.0, 122.8, 125.4, 126.6, 128.1, 128.7, 129.0, 129.5, 129.7, 141.7
9'b	2215	282 (M^+, 71), 175 (100)	3.26 (s, 3H, NMe), 3.76 (s, 3H, OMe), 5.28 (s, 1H, H-7), 6.30 (d, 1H, J = 4.0, H-3), 6.52 (d, 1H, J = 4.0, H-2), 6.57 (s, 1H, H-5), 6.76 (d, 2H, J = 8.0, ArH), 6.88 (d, 2H, J = 8.0, ArH)	33.0 (NMe), 52.0 (OMe), 104.6, 113.5, 114.5, 117.4, 122.2, 122.8, 125.5, 127.9, 133.9, 159.4
10a	2200	305 (M^+, 60), 304 (100)	3.70 (s, 2H, H-3), 6.52–7.27 (m, 4H, ArH), 7.30–7.64 (m, 5H, ArH)	28.3 (C-3), 79.3, 118.9, 122.5, 124.6, 124.8, 125.6, 127.7, 128.4, 128.9, 129.2, 130.3, 130.5, 135.1, 136.6, 145.6
10b			3.84 (s, 2H, H-3), 3.86 (s, 3H, OMe), 6.40–7.77 (m, 9H, ArH)	
10'b	1724	338 (M^+, 38), 261 (100)	3.90 (s, 3H, OMe), 5.44 (s, 1H, H-1), 7.29–7.40 (m, 7H, ArH), 7.51 (s, 1H, H-3), 7.67–7.76 (m, 2H, ArH)	44.1 (C-1), 52.1 (OMe), 122.4, 123.7, 124.4, 124.5, 125.8, 127.6, 128.1, 128.5, 128.8, 128.9, 132.0, 133.9, 136.1, 138.5, 165.3 (CO)
10c	1690	352 (M^+, 55), 323 (10)	1.38 (t, 3H, J = 6.9, Me), 3.86 (s, 2H, H-3), 4.34 (q, 2H, J = 6.9, OCH_2), 6.57–6.80 (m, 1H, ArH), 7.06–7.83 (m, 8H, ArH)	14.5 (Me), 26.8 (C-3), 61.0 (OCH_2), 99.5, 124.0, 124.6, 127.0, 128.3, 128.7, 130.1, 130.6, 134.1, 134.2, 135.9, 140.0, 146.8, 153.1, 165.8 (CO)
10'c	1704	352 (M^+, 50), 275 (100)	1.38 (t, 3H, J = 6.9, Me), 4.36 (q, 2H, J = 6.9, OCH_2), 5.70 (d, 1H, J = 1.3, H-1), 7.15–7.30 (m, 7H, ArH), 7.48 (s, 1H, H-3), 7.71–7.72 (m, 1H, ArH), 7.83–7.86 (m, 1H, ArH)	14.3 (Me), 41.7 (C-1), 61.4 (OCH_2), 120.6, 121.5, 122.2, 124.4, 124.8, 126.8, 128.0, 128.9, 132.2, 134.1, 136.5, 140.9, 142.1, 163.5 (CO)
10d	1680		2.46 (t, 1H, J = 2.5, HC≡), 3.81 (s, 2H, H-3), 4.82 (d, 2H, J = 2.5, OCH_2), 6.51–7.40 (m, 9H, ArH)	26.7 (C-3), 52.3 (OCH_2), 75.1 (C≡), 78.0 (HC≡), 97.9, 122.2, 124.1, 124.6, 127.0, 128.7, 130.2, 130.6, 131.8, 134.0, 135.7, 139.7, 148.0, 154.9, 164.8 (CO)
11a	2210	302 (M^+, 84), 301 (100), 269 (14)	3.72 (s, 3H, NMe), 3.82 (s, 2H, H-3), 6.58–6.96 (m, 3H, ArH), 7.08–7.48 (m, 6H, ArH)	30.1 (C-3), 30.9 (NMe), 107.6, 120.5, 121.4, 122.0, 124.0, 127.5, 128.3, 128.8, 129.2, 129.9, 130.2, 135.5, 145.0, 152.7
11b	2195	392 (M^+, 16), 105 (100)	3.84 (s, 2H, H-3), 6.72–7.04 (m, 4H, ArH), 7.48–7.72 (m, 8H, ArH), 7.90–8.02 (m, 2H, ArH)	29.3 (C-3), 67.2, 113.0, 117.8, 122.6, 123.1, 123.8, 124.8, 127.5, 128.9, 129.0, 129.4, 129.9, 130.0, 130.3, 130.5, 134.0, 135.0, 142.1, 144.9, 168.7 (CO)
11'c	1710	335 (M^+, 35), 258 (100)	3.67 (s, 3H, NMe), 3.84 (s, 3H, OMe), 5.60 (d, 1H, J = 1.32, H-1), 6.98–7.31 (m, 9H, ArH), 7.44 (d, 1H, J = 1.32, H-3)	32.9 (NMe), 42.7 (C-1), 52.1 (OMe), 107.7, 109.6, 118.3, 120.0, 120.6, 122.8, 124.2, 127.4, 127.6, 128.6, 132.6, 134.3, 138.7, 141.6, 164.7 (CO)



7q

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Scheme 5

Melting points were determined on a Yanaco MP-S2 melting point apparatus and are uncorrected. IR spectra were taken on a Hitachi Model 270-30 spectrophotometer. Mass spectra were obtained with a Hitachi Model RMU-7M double focusing mass spectrometer at an ionizing potential of 70 eV. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-EX 270 (270 MHz, 67.5 MHz) and/or JEOL JNM-FX 100 (100 MHz, 25.5 MHz) instruments in deuteriochloroform using tetramethylsilane as an internal standard. Elemental microanalyses were performed using a Yanaco MT-3 CHN recorder.

5*H*- and 7*H*-Furo-, 3*H*- and 1*H*-Benzofuro-, and 5*H*- and 7*H*-Thieno[2,3-*c*]thiopyrans (7, 7', 8 and 8'), 7*H*-Thiopyrano[3,4-*b*]pyrrole (9'), 3*H*- and 1*H*-Benzothieno[3,2-*c*]thiopyrans (10 and 10'), and 3*H*- and 1*H*-Thiopyrano[4,3-*b*]indoles (11 and 11'); General Procedure:

A solution of thioketone **1–5** (2 mmol) and 2-chloroacrylonitrile (**6a**) or 2-bromoacrylates **6b–e** (3 mmol) in benzene (15 mL) was heated under reflux until the thioketone disappears (TLC). Having been cooled, the reaction mixture was treated with Et_3N (1–2 mL) and stirred overnight at r.t. The resulting red-orange reaction mixture was evaporated and the residue was column-chromatographed (silica gel; CH_2Cl_2–hexane, 1:1–50, or EtOAc–hexane, 1:50–90) to give red **7–11** and colorless or yellowish **7′–11′** as crystals (recrystallized from CH_2Cl_2–hexane or EtOH) or oils or glassy solids.

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