Dipolarophilic behaviour of the thiophene ring in intramolecular nitrile imine cycloadditions

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Unprecedented intramolecular nitrile imine cycloadditions onto a thiophene ring are described as a synthetic route to a number of tricyclic pyrazoline derivatives (**5**). Diadducts **6** and **7**, which can be ascribed to a sequential intra–intermolecular cycloaddition pathway, are also formed.

Despite their propensity for substitution rather than addition reactions, various five-membered heteroaromatics can behave as dipolarophiles in intramolecular cycloadditions of 1,3-dipoles.[1] Intramolecular nitrile oxide cycloadditions to furan and thiophene[2–4] have received growing attention, in recent years, owing to the array of latent functionalities presented by the cycloadducts. Little is known, in this respect, about nitrile imines. To the best of our knowledge, only two reports describe intramolecular cycloadditions of a nitrile imine to the furan ring,[5,6] while there is a complete lack of data regarding the thiophene ring.

We present here the first investigation about the intramolecular reactivity of a series of appropriately substituted nitrile imines (**4**) containing the thiophene moiety.

Results and discussion

As precursors of the desired nitrile imines, we first synthesised the hydrazonoyl chlorides **3** according to the reaction sequence outlined in Scheme 1. Cycloaddition reactions of **3** *via* the labile species **4** were carried out in hot dioxane in the presence of a two-fold molar excess of silver carbonate.

entry	a	b	c	d	e	f	g
R	H	Me	OMe	F	Cl	COMe	NO$_2$
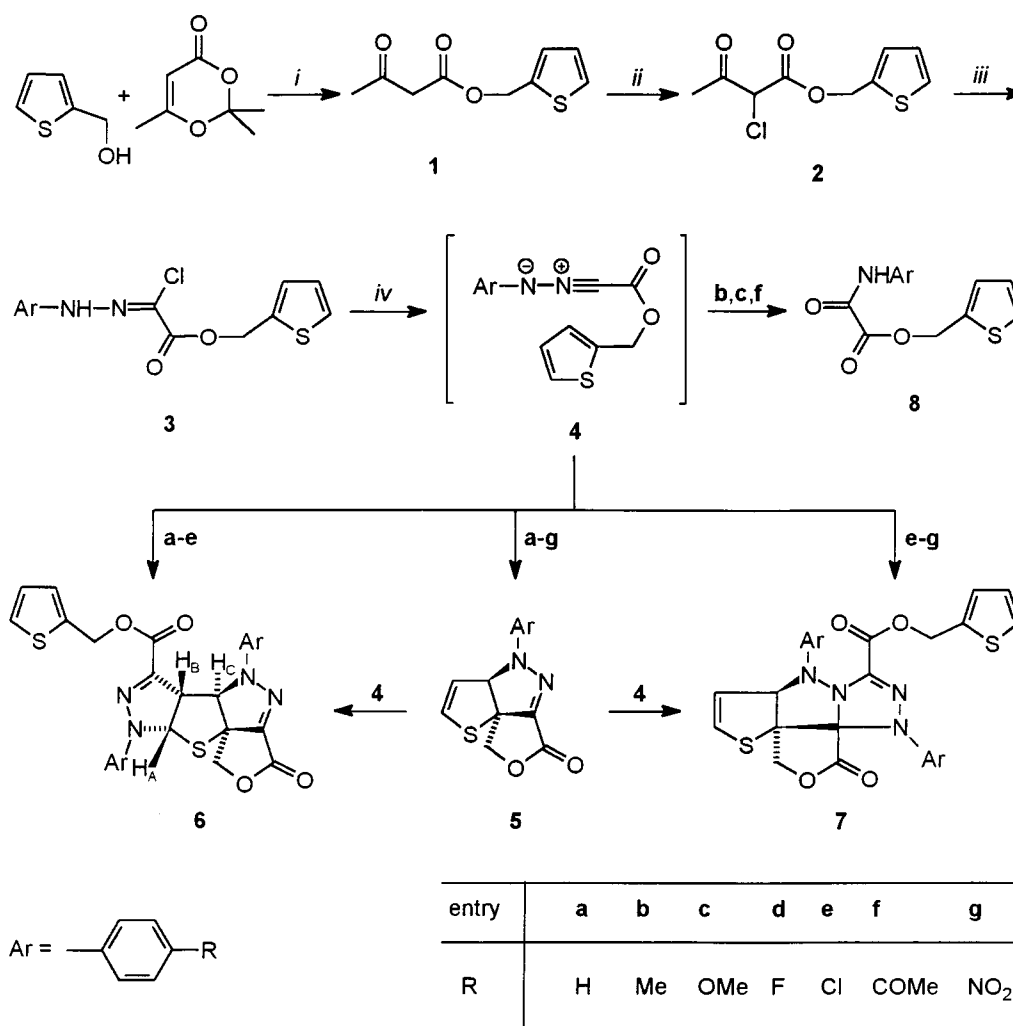
Scheme 1 *Reagents and conditions*: *i*, xylene, Δ; *ii*, SO$_2$Cl$_2$, 0 °C; *iii*, ArN$^+_2$ Cl$^-$, 0 °C; *iv*, Ag$_2$CO$_3$–dioxane, room temp.

Reaction times, products, eluants and yields are summarised in Table 1.

Structures **5**–**7** were firmly established by elemental analyses and spectral data, including ^{1}H NMR, IR, and MS spectrometry (see Table 2). ^{1}H NMR spectra of compounds **5** parallel those reported for some analogous thienoxazolines[7] and furopyrazolines.[8] For diadducts **6**, the relative configuration of the hydrogens H_A and H_B reflects the typical *cis* junction of five-membered rings. On the other hand, the stereochemical relationship between H_B and H_C was proven to be *anti* by the apparent lack of vicinal coupling ($J_{vic} < 1$ Hz), which finds precedents in the literature for such a disposition in strained polycyclic structures.[9,10] Diagnostic evidence also came from the IR spectra, where higher frequencies appeared for the unconjugated lactone carbonyl of **7** in comparison with the conjugated one of both **5** and **6**. Oxalamides **8** are trivial side-products due to a known degradative process of nitrile imines.[11]

The results depicted in Scheme 1 deserve some comments aimed at rationalising the operative reaction paths. First of all, the intramolecular cycloaddition onto the thiophene ring to give the tricyclic pyrazolines **5** merits attention owing to its novelty. Plausibly, the high energy barrier due to the loss of aromaticity is overcome by favourable entropic contributions working in intramolecular reaction.[12,13] However, both geometric constraints and electronic factors must be responsible for the regiochemical trend of the cycloaddition. In fact, experimental results[9,10] as well as theoretical calculations[9,14] dealing with nitrile oxide cycloaddition on thiophene have shown that the preferred orientation involves bond formation between the carbon of the dipole and the α-carbon of the heterocycle. Assuming the same preference in the case of nitrile imines, this explains the formation of **5**. To gain a deeper insight into this point, we synthesised the hydrazonoyl chloride **11** (Scheme 2) and reacted it under the same conditions as **3**; besides tarry material, unchanged **11** (65%) was recovered. No cycloaddition product was formed, which accords with the fact that the molecular geometry precludes the regiochemistry favoured by electronic factors.

The first-formed cycloadducts **5** still contain two double bonds, namely the C=C bond of the 2,3-dihydrothiophenic ring and the C=N bond of the pyrazolinic one, which are potentially susceptible to subsequent dipolar attack. In several cases (entries **a**–**d**), the route **5**→**6** is the only operative one in accord with the usual better dipolarophilicity of carbon–carbon multiple bonds with respect to heterodipolarophiles.[15] The LUMO-dipole control of cycloadditions onto 2,3-dihydrothiophene, as indicated by early calculations,[9] well accounts for the observed

**Table 1** Treatment of hydrazonoyl chlorides **3** with silver carbonate[a]

| Entry | t/h | Products and yields (%)[b] | | | | Eluant[c] |
		5	**6**	**7**	**8**	
a	3	25	16	—	—	CH$_2$Cl$_2$–LP (10:1)
b	30	18	28	—	5	Et$_2$O–LP (2:1)
c	20	14	15	—	18	CH$_2$Cl$_2$
d	11	28	11	—	—	Et$_2$O–hexane (2:1)
e	10	57	10	8	—	CH$_2$Cl$_2$
f	10	23	—	15	30	Et$_2$O–AcOEt (10:1)
g	14	67	—	5	—	Et$_2$O–LP (4:1)

[a] 70 °C in dioxane. [b] Isolated yield by column chromatography. [c] LP = light petroleum bp 40–60 °C.

Table 2 Physical and spectral data of cycloaddition products **5**, **6** and **7**

Compd.	Mp[a]/°C	ν_{max}(Nujol)/cm^{-1}	δ_H (CDCl$_3$)	m/z (M$^+$)
5a	152	1750	4.50 (1H, d, J 9.9), 4.92 (1H, d, J 9.9), 5.84 (1H, d, J 3.2), 5.94 (1H, dd, J 6.1, 3.2), 6.66 (1H, d, J 6.1), 7.15–7.40 (5H, m)	258 (14%)
5b	145	1770	2.30 (3H, s), 4.65 (1H, d, J 9.9), 4.90 (1H, d, J 9.9), 5.82 (1H, d, J 3.2), 5.90 (1H, dd, J 6.1, 3.2), 6.65 (1H, d, J 6.1), 7.05–7.20 (4H, m)	272 (15%)
5c	150	1765	3.80 (3H, s), 4.65 (1H, d, J 9.2), 4.90 (1H, d, J 9.2), 5.80 (1H, d, J 3.7), 5.88 (1H, dd, J 6.4, 3.7), 6.68 (1H, d, J 6.4), 6.85–7.20 (4H, m)	288 (23%)
5d	150	1760	4.60 (1H, d, J 9.9), 4.90 (1H, d, J 9.9), 5.80 (1H, d, J 3.3), 5.90 (1H, dd, J 6.1, 3.3), 6.65 (1H, d, J 6.1), 7.00–7.20 (4H, m)	276 (15%)
5e	162	1760	4.65 (1H, d, J 10.2), 4.75 (1H, d, J 10.2), 5.81 (1H, d, J 3.2), 5.90 (1H, dd, J 6.1, 3.2), 6.69 (1H, d, J 6.1), 7.10–7.35 (4H, m)	292 (19%)
5f	163	1770 1670	2.60 (3H, s), 4.71 (1H, d, J 9.9), 4.95 (1H, d, J 9.9), 5.90 (1H, d, J 3.2), 5.96 (1H, dd, J 6.0, 3.2), 6.70 (1H, d, J 6.0), 7.22–7.78 (4H, m)	300 (18%)
5g	191	1770	4.70 (1H, d, J 10.2), 4.90 (1H, d, J 10.2), 5.72 (1H, d, J 3.1), 5.85 (1H, dd, J 6.1, 3.1), 6.50 (1H, d, J 6.1), 7.20–8.30 (4H, m)	303 (25%)
6a	145	1760 1700	4.55 (1H, d, J 10.2), 4.60 (1H, d, J 10.2), 4.90 (1H, d, J 8.5), 5.54 (1H, d, J 12.7), 5.63 (1H, d, J 12.7), 6.00 (1H, s), 6.28 (1H, d, J 8.5), 7.04 (1H, dd, J 5.2, 3.8), 7.09 (1H, d, J 3.8), 7.23 (1H, d, J 5.2), 7.27–7.43 (10H, m)	516 (12%)
6b	180	1760 1700	2.30 (3H, s), 2.35 (3H, s), 4.52 (1H, d, J 10.1), 4.58 (1H, d, J 10.1), 4.86 (1H, d, J 8.1), 5.52 (1H, d, J 12.2), 5.60 (1H, d, J 12.2), 5.98 (1H, s), 6.25 (1H, d, J 8.1), 7.04 (1H, dd, J 4.7, 3.8), 7.05–7.20 (8H, m), 7.22 (1H, d, J 3.8), 7.38 (1H, d, J 4.7)	544 (23%)
6c	156	1765 1690	3.75 (3H, s), 3.80 (3H, s), 4.50 (1H, d, J 10.1), 4.58 (1H, d, J 10.1), 4.80 (1H, d, J 8.5), 5.50 (1H, d, J 12.3), 5.58 (1H, d, J 12.3), 5.92 (1H, s), 6.25 (1H, d, J 8.5), 7.02 (1H, dd, J 5.0, 3.7), 7.05–7.16 (8H, m), 7.20 (1H, d, J 3.7), 7.36 (1H, d, J 5.0)	576 (18%)
6d	165	1760 1710	4.55 (1H, d, J 10.1), 4.62 (1H, d, J 10.1), 4.85 (1H, d, J 8.3), 5.55 (1H, d, J 12.9), 5.60 (1H, d, J 12.9), 5.95 (1H, s), 6.29 (1H, d, J 8.3), 7.00–7.40 (11H, m)	552 (20%)
6e	125	1760 1720	4.55 (1H, d, J 10.2), 4.60 (1H, d, J 10.2), 4.90 (1H, d, J 8.7), 5.51 (1H, d, J 12.7), 5.62 (1H, d, J 12.7), 5.99 (1H, s), 6.25 (1H, d, J 8.7), 6.90–7.90 (11H, m)	584 (36%)
7e	135	1787 1738	4.41 (1H, d, J 10.8), 4.60 (1H, d, J 10.8), 5.40 (1H, d, J 12.4), 5.47 (1H, dd, J 3.0, 2.0), 5.55 (1H, dd, J 12.4), 5.60 (1H, dd, J 6.2, 3.0), 6.12 (1H, dd, J 6.2, 2.0), 7.00 (1H, dd, J 4.9, 3.9), 7.03–7.25 (8H, m), 7.18 (1H, d, J 3.9), 7.35 (1H, d, J 4.9)	584 (31%)
7f	93	1790 1740 1680	2.50 (3H, s), 2.58 (3H, s), 4.40 (1H, d, J 10.8), 4.62 (1H, d, J 10.8), 5.40 (1H, d, J 12.7), 5.58 (1H, dd, J 6.1, 2.3), 5.60 (1H, d, J 12.7), 5.64 (1H, dd, J 2.3, 2.0), 6.15 (1H, dd, J 6.1, 2.0), 7.00 (1H, dd, J 5.1, 3.5), 7.15–7.75 (10H, m)	600 (36%)
7g	142	1790 1740	4.45 (1H, d, J 10.9), 4.65 (1H, d, J 10.9), 5.42 (1H, d, J 12.7), 5.59 (1H, d, J 12.7), 5.61 (1H, dd, J 6.1, 3.1), 5.64 (1H, dd, J 3.1, 2.2), 6.20 (1H, dd, J 6.1, 2.2), 7.01 (1H, dd, J 5.1, 3.5), 7.20 (1H, d, J 3.5), 7.22–7.33 (4H, m), 7.38 (1H, d, J 5.1), 8.05–8.25 (4H, m)	606 (28%)

[a] From diisopropyl ether.
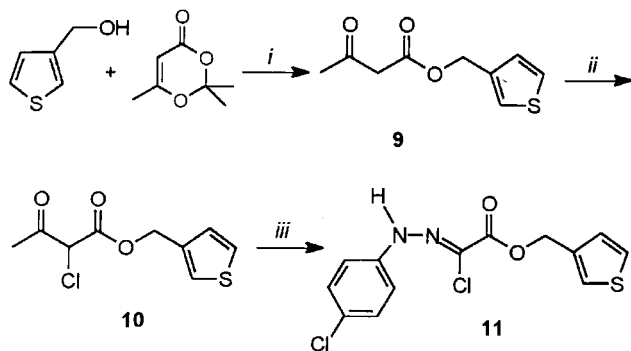
Scheme 2 *Reagents and conditions*: *i*, xylene, Δ; *ii*, SO_2Cl_2, 0 °C; *iii*, 4-Cl-$C_6H_4N^+_2Cl^-$, 0 °C.

regiochemistry. However, strongly electron-withdrawing groups on the phenyl ring of **5** favour selectively the transformation **5→7** (entries **f,g**). This reversal in site preference may tentatively be explained on the basis of the following consideration. 1,3-Dipolar cycloadditions onto heterodipolarophiles[16] are typically governed by the HOMO-dipole–LUMO-dipolarophile interaction; they are consequently facilitated when lowering the LUMO energy of the dipolarophile by means of electron-withdrawing substituents. This may just be the case for the substrates **5f,g**. The behaviour of compound **3e**, containing the chlorine substituent, remains to be noted as a borderline case.

Two conclusions can be drawn from the present work. Primarily, our extension of the intramolecular nitrile imine cycloaddition methodology to the thiophene dipolarophile has provided interesting, strained tricyclic pyrazolines. The observed yields, ranging from fair to good, make this protocol valuable on a preparative scale. As a corollary, the formation of the diadducts **7** is noteworthy, since there is no precedent in the literature concerning the cycloaddition of nitrile imines onto the C=N bond of pyrazolines.

Experimental

Mps were determined on a Büchi apparatus and are uncorrected. IR Spectra were recorded on a FT IR Perkin-Elmer 1725 X spectrophotometer. Mass spectra were determined with a VG-70EQ apparatus. ^{1}H NMR Spectra were taken on a Bruker AC 300 instrument in $CDCl_3$ solutions; chemical shifts are given as ppm from tetramethylsilane; *J* values are given in Hz. Compounds **3**, **5–8** and **11** gave satisfactory elemental analyses, which are given in Table 3.

General procedure for the preparation of thienyl acetoacetates 1 and 9

A solution of 2- or 3-hydroxymethylthiophene (11.4 g, 0.1 mol) in xylene (20 ml) was treated with 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (14.2 g, 0.1 mol). The mixture was refluxed for 1.5 h. Evaporation of the solvent under reduced pressure gave crude **1** or **9** as undistillable oil not analytically pure.

Compound 1. (19.6 g, 99%) ν_{max}/cm^{-1} (neat) 1742, 1716; δ_H 2.17 (3H, s), 3.41 (2H, s), 5.26 (2H, s), 6.86–7.38 (3H, m); *m/z* 198 (M$^+$).

Compound 9. (19.6 g, 99%) ν_{max}/cm^{-1} (neat) 1740, 1716; δ_H 2.18 (3H, s), 3.45 (2H, s), 5.15 (2H, s), 7.02–7.36 (3H, m); *m/z* 198 (M$^+$).

General procedure for the preparation of hydrazonoyl chlorides 3 and 11

A solution of sulfuryl chloride (3.35 g, 25 mmol) in dry chloroform (5 ml) was slowly added (2 h) to a mixture of **1** or **9** (4.95

Table 3 Elemental analyses of compounds **3**, **5**, **6**, **7**, **8** and **11**

Compd. (Molecular Formula)	C(%) found (required)	H(%) found (required)	N(%) found (required)
3a ($C_{13}H_{11}ClN_2O_2S$)	53.11 (53.06)	3.82 (3.77)	9.58 (9.53)
3b ($C_{14}H_{13}ClN_2O_2S$)	54.48 (54.54)	4.30 (4.25)	9.13 (9.09)
3c ($C_{14}H_{13}ClN_2O_3S$)	51.92 (51.85)	4.11 (4.04)	8.70 (8.64)
3d ($C_{13}H_{10}ClFN_2O_2S$)	49.93 (50.00)	3.20 (3.23)	9.05 (8.98)
3e ($C_{13}H_{10}Cl_2N_2O_2S$)	47.58 (47.56)	3.10 (3.07)	8.50 (8.54)
3f ($C_{15}H_{13}ClN_2O_3S$)	53.60 (53.57)	3.94 (3.90)	8.30 (8.33)
3g ($C_{13}H_{10}ClN_3O_4S$)	46.00 (46.02)	3.02 (2.97)	12.44 (12.39)
11 ($C_{13}H_{11}ClN_2O_2S$)	53.05 (53.06)	3.74 (3.77)	9.49 (9.53)
5a ($C_{13}H_{10}N_2O_2S$)	60.50 (60.45)	3.88 (3.91)	10.91 (10.85)
5b ($C_{14}H_{12}N_2O_2S$)	61.69 (61.75)	4.42 (4.45)	10.33 (10.29)
5c ($C_{14}H_{12}N_2O_3S$)	58.27 (58.32)	4.13 (4.20)	9.79 (9.72)
5d ($C_{13}H_9FN_2O_2S$)	56.48 (56.51)	3.31 (3.29)	10.11 (10.15)
5e ($C_{13}H_{10}ClN_2O_2S$)	53.30 (53.24)	3.44 (3.44)	9.62 (9.56)
5f ($C_{15}H_{12}N_2O_3S$)	60.01 (59.99)	4.00 (4.03)	9.38 (9.33)
5g ($C_{13}H_9N_3O_4S$)	51.51 (51.48)	3.04 (2.99)	13.90 (13.86)
6a ($C_{26}H_{20}N_4O_4S_2$)	60.39 (60.45)	3.86 (3.91)	10.83 (10.85)
6b ($C_{28}H_{24}N_4O_4S_2$)	61.77 (61.75)	4.41 (4.45)	10.33 (10.29)
6c ($C_{28}H_{24}N_4O_6S_2$)	58.35 (58.32)	4.16 (4.20)	9.69 (9.72)
6d ($C_{26}H_{18}F_2N_4O_4S_2$)	56.55 (56.51)	3.33 (3.29)	10.08 (10.15)
6e ($C_{26}H_{20}Cl_2N_4O_4S_2$)	53.20 (53.24)	3.48 (3.44)	9.61 (9.56)
7e ($C_{26}H_{20}Cl_2N_4O_4S_2$)	53.21 (53.24)	3.44 (3.44)	9.67 (9.56)
7f ($C_{30}H_{24}N_4O_6S_2$)	59.91 (59.99)	3.98 (4.03)	9.36 (9.33)
7g ($C_{26}H_{18}N_6O_8S_2$)	51.44 (51.48)	3.02 (2.99)	13.95 (13.86)
8b ($C_{14}H_{13}NO_3S$)	61.01 (61.08)	4.80 (4.76)	5.13 (5.09)
8c ($C_{14}H_{13}NO_4S$)	57.70 (57.72)	4.44 (4.50)	4.86 (4.81)
8f ($C_{15}H_{13}NO_4S$)	59.44 (59.39)	4.29 (4.32)	4.58 (4.62)

g, 25 mmol) and sodium hydrogen carbonate (2.10 g, 25 mmol) in dry chloroform (40 ml), on keeping the temperature in the range 0–5 °C. After 1.5 h at room temperature, chloroform (80 ml) was added, and the mixture was washed with water (25 ml). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure to afford **2** or **10** in the crude state.

Compound 2. (3.77 g, 65%) ν_{max}/cm^{-1} (neat) 1755, 1732; δ_H 2.30 (3H, s), 4.75 (1H, s), 5.48 (2H, s), 6.90–7.40 (3H, m).

Compound 10. (4.06 g, 70%) ν_{max}/cm^{-1} (neat) 1760, 1730; δ_H 2.30 (3H, s), 4.77 (1H, s), 5.25 (2H, s), 7.00–7.35 (3H, m).

Crude **2** or **10** was dissolved in cold methanol (45 ml), and sodium acetate (2.72 g, 20 mmol) was added. A cold aqueous solution of the appropriate aryldiazonium chloride (16.3 mmol for **2**, 17.5 mmol for **10**) was added dropwise under vigorous stirring and ice-cooling. The mixture was allowed to stand

overnight under stirring at room temperature. The solvent was partly removed under reduced pressure and the resulting mixture was extracted with diethyl ether (150 ml). The organic layer was washed firstly with 5% aqueous sodium hydrogen carbonate (50 ml), then with water (100 ml), and dried over sodium sulfate. Evaporation of the solvent and subsequent crystallisation of the residue from diisopropyl ether gave the hydrazonoyl chlorides **3** or **11** in the pure state.

Compound 3a. (3.31 g, 45%) Mp 90 °C; v_{max}/cm^{-1} (Nujol) 3276, 1700; δ_H (CDCl$_3$) 5.50 (2H, s), 7.00 (1H, dd, J 5.6, 3.2), 7.13 (1H, d, J 3.2), 7.15–7.30 (5H, m), 7.35 (1H, d, J 5.6), 8.35 (1H, br s); m/z 294 (M$^+$).

Compound 3b. (3.08 g, 40%) Mp 125 °C; v_{max}/cm^{-1} (Nujol) 3270, 1710; δ_H (CDCl$_3$) 2.30 (3H, s), 5.50 (2H, s), 6.95 (1H, dd, J 4.8, 3.7), 7.10 (1H, d, J 3.7), 7.15–7.25 (4H, m), 7.30 (1H, d, J 4.8), 8.30 (1H, br s); m/z 308 (M$^+$).

Compound 3c. (3.24 g, 40%) Mp 90 °C; v_{max}/cm^{-1} (Nujol) 3270, 1700; δ_H (CDCl$_3$) 3.80 (3H, s), 5.50 (2H, s), 6.85 (1H, dd, J 4.9, 3.8), 7.08 (1H, d, J 3.8), 7.10–7.20 (4H, m), 7.31 (1H, d, J 4.9), 8.25 (1H, br s); m/z 324 (M$^+$).

Compound 3d. (2.73 g, 35%) Mp 115 °C; v_{max}/cm^{-1} (Nujol) 3275, 1700; δ_H (CDCl$_3$) 5.50 (2H, s), 6.90–7.30 (6H, m), 7.35 (1H, d, J 5.3), 8.35 (1H, br s); m/z 312 (M$^+$).

Compound 3e. (3.28 g, 40%) Mp 115 °C; v_{max}/cm^{-1} (Nujol) 3270, 1700; δ_H (CDCl$_3$) 5.50 (2H, s), 7.01 (1H, dd, J 5.0, 3.6), 7.10–7.30 (4H, m), 7.19 (1H, d, J 3.6), 7.30 (1H, d, J 5.0), 8.30 (1H, br s); m/z 328 (M$^+$).

Compound 3f. (4.70 g, 56%) Mp 98 °C; v_{max}/cm^{-1} (Nujol) 3260, 1710, 1700; δ_H (CDCl$_3$) 2.95 (3H, s), 5.40 (2H, s), 6.90–7.20 (7H, m), 8.25 (1H, br s); m/z 336 (M$^+$).

Compound 3g. (2.88 g, 34%) Mp 152 °C; v_{max}/cm^{-1} (Nujol) 3270, 1700; δ_H (CDCl$_3$) 5.50 (2H, s), 7.08 (1H, dd, J 5.3, 3.2), 7.18 (1H, d, J 3.2), 7.20–7.35 (4H, m), 7.40 (1H, d, J 5.3), 8.60 (1H, br s); m/z 339 (M$^+$).

Compound 11. (6.47 g, 88%) Mp 110 °C; v_{max}/cm^{-1} (Nujol) 3260, 1720; δ_H (CDCl$_3$) 5.35 (2H, s), 7.12–7.18 (2H, m), 7.20 (1H, s), 7.26–7.31 (2H, m), 7.33 (1H, dd, J 5.0, 2.5), 7.40 (1H, d, J 5.0), 8.30 (1H, br s); m/z 294 (M$^+$).

General procedure for the treatment of hydrazonoyl chlorides 3 or 11 with silver carbonate

A solution of **3** or **11** (5.0 mmol) in dry dioxane (250 ml) was treated with silver carbonate (2.76 g, 10.0 mmol), and the mixture was stirred in the dark at 70 °C for the time indicated in Table 1. The undissolved material was filtered off, the solvent was evaporated and then the residue was chromatographed on a silica gel column. Eluents, products and yields are given in Table 1. Physical and spectral data of compounds **5**–**7** are given in Table 2. Side products **8** had the following characteristic data.

Compound 8b. Mp 136 °C; v_{max}/cm^{-1} (Nujol) 3356, 1710, 1660; δ_H (CDCl$_3$) 2.28 (3H, s), 5.51 (2H, s), 6.89–7.35 (7H, m), 12.60 (1H, br s); m/z 275 (M$^+$).

Compound 8c. Mp 141 °C; v_{max}/cm^{-1} (Nujol) 3352, 1710, 1665; δ_H (CDCl$_3$) 3.80 (3H, s), 5.50 (2H, s), 6.90–7.30 (7H, m), 12.54 (1H, br s); m/z 291 (M$^+$).

Compound 8f. Mp 158 °C; v_{max}/cm^{-1} (Nujol) 3360, 1710, 1670; δ_H (CDCl$_3$) 2.52 (3H, s), 5.52 (2H, s), 7.00–7.90 (7H, m), 12.75 (1H, br s); m/z 303 (M$^+$).

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Paper 8/07441K