Letter

Double 1,4-addition of malonate to 1,2-diaza-1,3-butadienes: a useful route to previously unknown symmetric and unsymmetric 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-dienes†

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In the presence of sodium methoxide in tetrahydrofuran, 1,2-diaza-1,3-butadienes react with dimethyl malonate in a 2 : 1 molar ratio to give symmetric or unsymmetric bishydrazones that in turn produce new 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-dienes, as a consequence of a double ring closure, on treatment with sodium methoxide in methanol.

1,2-Diaza-1,3-butadienes have been demonstrated to be powerful building blocks in organic synthesis.[1–5] Since an extensive bibliographic search showed that 1,6-dioxo-2,7-diazaspiro[4,4]nona-3,8-dienes are unknown molecules,[6] we decided to consider a possible synthetic route starting from 1,2-diaza-1,3-butadienes in view of the potential interest of the aforementioned derivatives as organic, medicinal, and agricultural products. Based on our experience of this chemistry[3,4] and retrosynthetic analysis, we hypothesised a facile two-step protocol to reach smoothly this new class of spiro compounds by unprecedented double 1,4-addition of malonates to two identical or two different 1,2-diaza-1,3-butadienes and double ring closure.

In the presence of a catalytic amount of sodium methoxide in tetrahydrofuran, 1,2-diaza-1,3-butadienes (**1a**–**d**) reacted at room temperature with dimethyl malonate in a molar ratio of 2 : 1 to give the symmetric bishydrazone adducts (**3a**–**d**) as shown in Table 1. With a stoichiometric amount of sodium methoxide in methanol at room temperature, these adducts were converted into symmetric 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-dienes (**4a**–**d**, Table 2) by means of a double five-membered ring closure (Scheme 1) that occurs with loss of two alcohol molecules, as already demonstrated in our previous works.[7]

The ^{1}H-NMR spectrum of compound **4b** shows two signals for the methyl (2.32 and 2.36 ppm), ethyl ester (multiplets at 1.06–1.23 and 3.91–4.14 ppm) and NH (9.06 and 9.09 ppm) groups. This behaviour is probably due to a hindered rotation, as proved by the same spectrum recorded at 60 °C (triplet at 1.14 ppm, singlet at 2.35 ppm, quartet at 4.05 ppm and broad singlet at 8.84 ppm).

In order to obtain unsymmetric 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-dienes, 1,2-diaza-1,3-butadienes (**1e**–**g**) and dimethyl malonate were used in an equimolar ratio. In the presence of a catalytic amount of sodium methoxide in tetrahydrofuran at room temperature, these reagents gave monohydrazone adducts (**2a**–**c**, Table 3). Again in the presence

Table 1 Yield, melting point and reaction time required for bishydrazones **3a**–**d**

1	R^1	R^2	3	Yield^a(%)	mp^b/°C	Time/h
a	Me	NHPh	**a**	61	204–206^c	1.0
b	Et	NH$_2$	**b**	74	142–147	3.0
c	Bz	NH$_2$	**c**	68	157–162	9.0
d	Me	OBu^t	**d**	78	167–171^c	3.0

^{a} Yield of pure isolated products. ^{b} Melting points are uncorrected. ^{c} Melting occurs with decomposition.

Table 2 Yield, melting point and reaction time required for 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-dienes **4a**–**h**

3	R^1	R^2	R^3	R^4	4	Yield^a(%)	mp^b/°C	Time/h
a	Me	NHPh			**a**	62	196–198^c	4.0
b	Et	NH$_2$			**b**	94	236–238	2.0
c	Bz	NH$_2$			**c**	86	238–240^c	2.5
d	Me	OBu^t			**d**	92	201–203	1.0
e	Et	NH(3-FPh)	Me	NH$_2$	**e**	74	169–172^c	1.5
f	Me	NHPh	Et	OBu^t	**f**	65	193–195	4.5
g	Me	NHPh	Et	NH$_2$	**g**	63	171–175	3.0
h	Et	OBu^t	Et	NH$_2$	**h**	86	188–190	3.0

^{a} Yield of pure isolated products. ^{b} Melting points are uncorrected. ^{c} Melting occurs with decomposition.

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† Electronic supplementary information (ESI) available: full characterisation of **2b**, **c**, **3a**, **c**, **d**, **f**–**h**, **4a**, **c**, **d**, **f**–**h**. See http://www.rsc.org/suppdata/nj/b0/b009189h/

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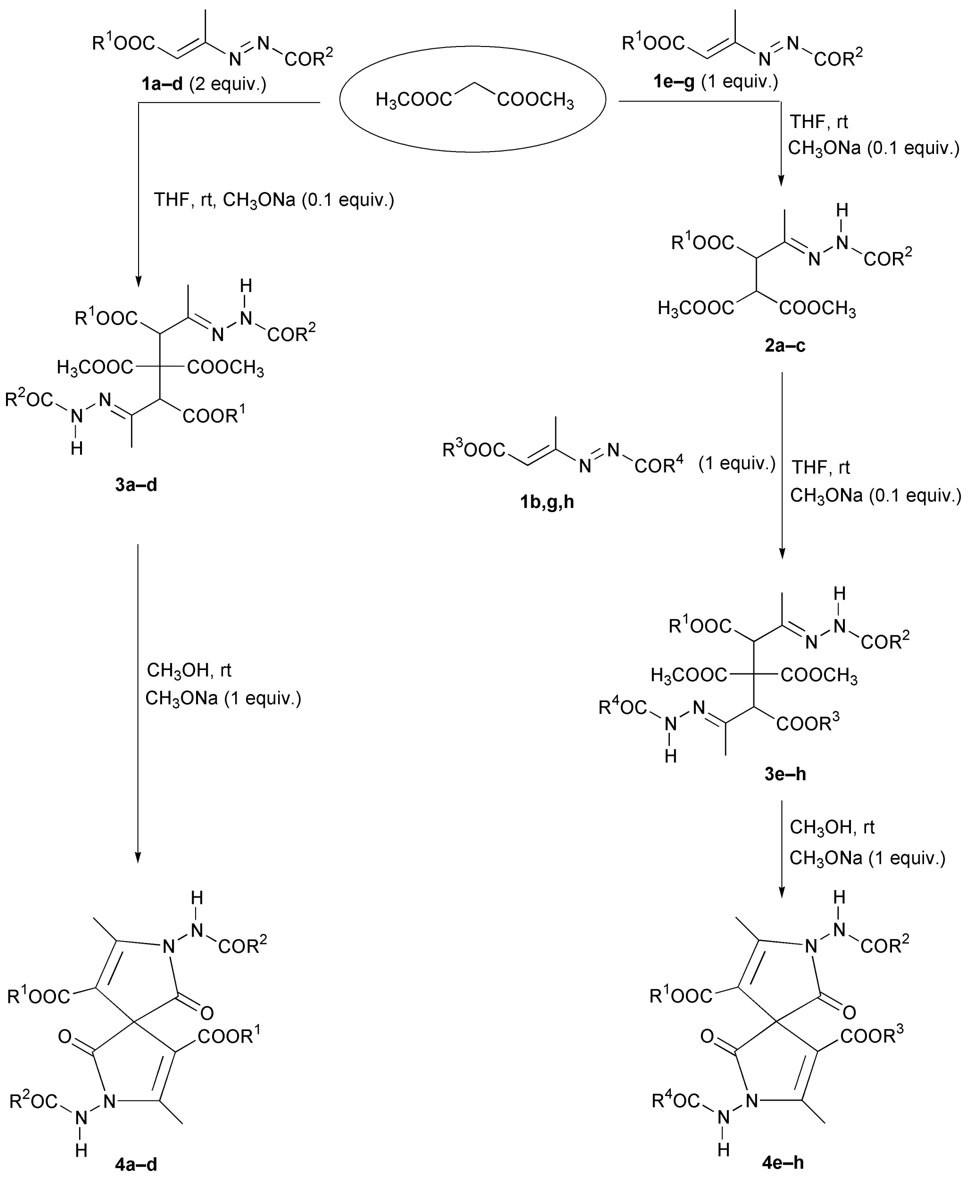

Scheme 1

of a catalytic amount of sodium methoxide in tetrahydrofuran at room temperature, these adducts readily reacted with another equivalent of a different 1,2-diaza-1,3-butadiene (**1b**, **g**, **h**) to afford unsymmetric bishydrazones (**3e**–**h**, Table 4). With a stoichiometric amount of sodium methoxide in methanol at room temperature, these latter adducts were converted into the corresponding asymmetric 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-dienes (**4e**–**h**, Table 2).

Table 3 Yield, melting point and reaction time required for hydrazones **2a**–**c**

1	R^1	R^2	2	Yield^a(%)	mp^b/°C	Time/h
e	Et	NH(3-FPh)	**a**	75	153–155	0.1
f	Me	NHPh	**b**	91	145–147	0.1
g	Et	OBu^t	**c**	89	90–93	0.1

[a] Yield of pure isolated products. [b] Melting points are uncorrected.

Bishydrazones **3a**–**e** were obtained as isomer mixtures and used as such for the subsequent cyclisation.

In conclusion, this method offers simple and high yield access under mild reaction conditions to previously unknown 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-dienes, the chemical, physico-chemical and biological properties of which undoubtedly merit further investigation.

Experimental

Melting points were determined in open capillary tubes and are uncorrected. IR-FT spectra were obtained from Nujol

Table 4 Yield, melting point and reaction time required for bishydrazones **3e**–**h**

2	R^1	R^2	1	R^3	R^4	3	Yield^a(%)	mp^b/°C	Time/h
a	Et	NH(3-FPh)	**h**	Me	NH$_2$	**e**	60	123–125^c	8.5
b	Me	NHPh	**g**	Et	OBu^t	**f**	91	143–148^c	8.0
b	Me	NHPh	**b**	Et	NH$_2$	**g**	58	150–154	3.0
c	Et	OBu^t	**b**	Et	NH$_2$	**h**	61	145–151^c	5.0

[a] Yield of pure isolated products. [b] Melting points are uncorrected. [c] Melting occurs with decomposition.

mulls. ^{1}H-NMR spectra at 25 and 60 °C were recorded at 200 MHz and ^{13}C-NMR spectra at 50.32 MHz. All coupling constants (*J*) are given in Hz. Chemical shifts (δ_C) are reported relative to DMSO-d_6 or CDCl$_3$ as external standards in a broad band decoupled mode. The multiplicities were obtained by using 135 and 90° DEPT experiments to aid in assignment (q = methyl, t = methylene, d = methyne, s = quaternary).

Syntheses

The full characterisation of all products not listed below is given in the electronic supplementary information.

Preparation of 1,2-diaza-1,3-butadienes 1a–g. These compounds were prepared according to methods given in previous papers.[8] **1e**: red powder; mp 71–74 °C; IR (Nujol): 3467, 3203, 1720, 1618 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.29 (t, 3 H, J = 7.1, OCH$_2$C*H*$_3$), 2.25 (s, 3 H, CH$_3$), 4.27 (q, 2 H, J = 7.1, OC*H*$_2$CH$_3$), 6.99–7.05 (m, 1 H$_{ar}$), 7.37–7.66 (m, 4 H, 3 H$_{ar}$ and CH), 11.07 (s, 1 H, NH, D$_2$O exch.); ^{13}C-NMR (DMSO-d_6): δ 10.8 (q), 14.0 (q), 60.8 (t), 106.0 (d, $^{2}J_{CF}$ = 26.0), 111.0 (d, $^{2}J_{CF}$ = 20.0), 115.4 (d), 130.7 (d, $^{3}J_{CF}$ = 9.4), 131.5 (d), 139.4 (s, $^{3}J_{CF}$ = 11.0), 152.3 (s), 162.3 (s, $^{1}J_{CF}$ = 251.0), 165.2 (s); MS *m*/*z* (rel. intensity): 279 (M^{+}, 11), 234 (7), 149 (51), 138 (100). Anal. calc. for C$_{13}$H$_{14}$N$_3$O$_3$F: C, 55.91; H, 5.05; N, 15.05; found: C, 56.01; H, 5.23; N, 15.11%.

Preparation of monohydrazone 2a. To a magnetically stirred solution of 1,2-diaza-1,3-butadiene **1e** (1.0 mmol, 279.3 mg) and dimethyl malonate (1.0 mmol, 132.1 mg) in THF (8 ml), a catalytic amount of sodium methoxide (0.1 mmol, 5.4 mg) was added. The disappearance of the reagents occurred rapidly (0.1 h, monitored by TLC). Product **2a** was purified by chromatography on a silica gel column (cyclohexane–ethyl acetate mixture) and then crystallised from ethyl acetate–petroleum ether (bp 40–60 °C). Methyl 2-methoxycarbonyl-3-ethoxycarbonyl-4-(3-fluoroanilinocarbonylhydrazono)pentanoate (**2a**): white powder; IR (Nujol): 3359, 3201, 3102, 1731, 1705, 1613, 1598 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.18 (t, 3 H, J = 7.1, OCH$_2$C*H*$_3$), 1.95 (s, 3 H, CH$_3$), 3.57 (s, 3 H, OCH$_3$), 3.66 (s, 3 H, OCH$_3$), 4.02 (d, 1 H, J = 10.0, CH), 4.13 (q, 2 H, J = 7.1, OC*H*$_2$CH$_3$), 4.52 (d, 1 H, J = 10.0, CH), 6.82–6.84 (m, 1 H$_{ar}$), 7.31–7.37 (m, 2 H$_{ar}$), 7.57–7.63 (m, 1 H$_{ar}$), 8.66 (s, 1 H, NH, D$_2$O exch.), 9.96 (s, 1 H, NH,D$_2$O exch.); ^{13}C-NMR (DMSO-d_6): δ 13.8 (q), 16.0 (q), 51.1 (d), 52.6 (q and d), 61.2 (t), 105.8 (d, $^{2}J_{CF}$ = 26.3), 108.7 (d, $^{2}J_{CF}$ = 21.0), 114.6 (d), 130.1 (d, $^{3}J_{CF}$ = 14.4), 140.7 (s, $^{3}J_{CF}$ = 11.4), 144.4 (s), 153.0 (s), 162.3 (s, $^{1}J_{CF}$ = 250.0), 186.0 (s), 189.0 (s); MS *m*/*z* (rel. intensity): 411 (M^{+}, 29), 301 (59), 223 (51), 196 (81), 169 (100). Anal. calc. for C$_{18}$H$_{22}$N$_3$O$_7$F: C, 52.55; H, 5.39; N, 10.21; found: C, 52.41; H, 5.44; N, 10.35%.

Preparation of symmetric bishydrazone 3b. To a magnetically stirred solution of 1,2-diaza-1,3-butadiene **1b** (3.0 mmol, 555.6 mg) and sodium methoxide (0.1 mmol, 5.4 mg) in THF (4 ml), was added a solution of dimethyl malonate (1.0 mmol, 132.1 mg) in THF (4 ml). The reaction mixture was allowed to stand at room temperature until complete disappearance of dimethyl malonate (2.0 h, monitored by TLC) had occurred. Product **3b** was purified by chromatography on a silica gel column (cyclohexane–ethyl acetate mixture) and then crystallised from ethyl acetate–petroleum ether (bp 40–60 °C). 3,5-Diethyl-4,4-dimethyl-2,6-bis(2-aminocarbonylhydrazono) heptane-3,4,4,5-tetracarboxylate (**3b**): white powder; IR (Nujol): 3483, 3456, 3218, 1746, 1742, 1699 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 1.25 (t, 6 H, J = 7.1, 2 OCH$_2$C*H*$_3$), 1.93 (s, 6 H, 2 CH$_3$), 3.77 and 3.78 (2 s, 6 H, 2 OCH$_3$), 4.02 and 4.25 (2 s, 2 H, 2 CH), 4.19 (q, 4 H, J = 7.1, 2 OC*H*$_2$CH$_3$), 5.25 and 5.86 (2 br s, 4 H, 2 NH$_2$, D$_2$O exch.), 8.56 and 9.28 (2 s, 2 H, 2 NH, D$_2$O exch.); ^{13}C-NMR (CDCl$_3$): δ 14.0 (q), 16.7 (q), 17.3 (q), 52.7 (q), 52.9 (q), 55.7 (d), 56.4 (d), 60.3 (s), 60.7 (s), 61.7 (t), 61.8 (t), 144.5 (s), 145.1 (s), 158.2 (s), 169.1 (s), 169.4 (s), 170.1 (s), 170.5 (s); MS *m*/*z* (rel. intensity): 502 (M^{+}, 1), 428 (29), 368 (57), 354 (100). Anal. calc. for C$_{19}$H$_{30}$N$_6$O$_{10}$: C, 45.42; H, 6.02; N, 16.73; found: C, 45.31; H, 6.21; N, 16.59%.

Preparation of unsymmetric bishydrazone 3e. To a magnetically stirred solution of 1,2-diaza-1,3-butadiene **1h** (2.0 mmol, 342.3 mg) and sodium methoxide (0.1 mmol, 5.4 mg) in THF (4 ml), was added a solution of monohydrazone **2a** (1.0 mmol, 411.4 mg) in THF (4 ml). The reaction mixture was allowed to stand at room temperature until the total disappearance of **2a** (8.5 h, monitored by TLC) had occurred. Product **3e** was purified by chromatography on a silica gel column (cyclohexane–ethyl acetate mixture) and then crystallised from diethyl ether–petroleum ether (bp 40–60 °C). 3-Ethyl-4,4,5-trimethyl-2(3-fluoroanilinocarbonyl)hydrazono-6-aminocarbonyl-hydrazonoheptane-3,4,4,5-tetracarboxylate (**3e**): white powder; IR (Nujol): 3420, 3380, 3225, 3128, 1738, 1721, 1708, 1599 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.24 (t, 3 H, J = 7.1, OCH$_2$C*H*$_3$), 1.93 and 1.99 (2 s, 6 H, 2 CH$_3$), 3.73, 3.79 and 3.84 (3 s, 9 H, 3 OCH$_3$), 4.05–4.35 (m, 4 H, OC*H*$_2$CH$_3$ and 2 CH), 5.99 (br s, NH$_2$, D$_2$O exch.), 6.66–6.74 (m, 1 H$_{ar}$), 7.16–7.57 (m, 3 H$_{ar}$), 8.04 and 8.14 (2 s, 1 H, NH, D$_2$O exch.), 9.07 and 9.14 (2 s, 1 H, NH, D$_2$O exch.), 9.76 (s, 1 H, NH, D$_2$O exch.); ^{13}C-NMR (DMSO-d_6): δ 14.5 (q), 14.9 (q), 17.5 (q), 17.7 (q), 17.9 (q), 18.1 (q), 52.0 (q), 52.2 (q), 52.4 (q), 52.8 (q), 55.1 (d), 55.5 (d), 56.2 (d), 60.3 (t), 61.8 (s), 106.2 (d, $^{2}J_{CF}$ = 26.7), 109.5 (d, $^{2}J_{CF}$ = 21.4), 114.3 (d), 129.8 (d, $^{3}J_{CF}$ = 9.3), 140.1 (s, $^{3}J_{CF}$ = 11.3), 144.7 (s), 145.1 (s), 145.8 (s), 154.2 (s), 154.3 (s), 158.0 (s), 158.2 (s), 162.9 (s, $^{1}J_{CF}$ = 243.0), 168.7 (s), 168.8 (s), 169.3 (s), 169.6 (s), 170.3 (s), 171.8 (s); MS *m*/*z* (rel. intensity): 582 (M^{+}, 1), 537 (40), 524 (50), 508 (100). Anal. calc. for C$_{24}$H$_{31}$N$_6$O$_{10}$F: C, 49.48; H, 5.36; N, 14.43; found: C, 49.42; H, 5.24; N, 14.51%.

Preparation of symmetric 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-diene 4b and unsymmetric 1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-diene 4e. To a magnetically stirred solution of bishydrazones **3b** (1.0 mmol, 502.5 mg) and **3e** (1.0 mmol, 582.5 mg) in methanol (6 ml), was added sodium methoxide (1 mmol, 54.0 mg). The reaction mixture was allowed to stand at room temperature until the disappearance of **3** (1.5–2.0 h, monitored by TLC) was complete. Products **4b** and **4e** were purified by chromatography on a silica gel column (cyclohexane–ethyl acetate mixture) and then crystallised from ethyl acetate–petroleum ether (bp 40–60 °C). *N*-(7-Aminocarbonylamino-3,8-dimethyl-4,9-diethoxycarbonyl-1,6-dioxo-2,7-diazaspiro[4.4]nona-3,8-dien-2-yl)-*N*′-phenylurea (**4b**): white powder; IR (Nujol): 3482, 3459, 3345, 1755, 1744, 1699, 1693, 1646 cm^{-1}; ^{1}H-NMR (DMSO-d_6) δ 1.06–1.23 (m, 6 H, 2 OCH$_2$C*H*$_3$), 2.32 and 2.36 (2 s, 6 H, 2 CH$_3$), 3.91–4.14 (m, 4 H, 2 OC*H*$_2$CH$_3$), 6.23 (br s, 4 H, 2 NH$_2$, D$_2$O exch.), 8.97 and 8.99 (2 s, 1 H, NH, D$_2$O exch.), 9.06 and 9.09 (2 s, 1 H, NH, D$_2$O exch.); ^{13}C-NMR (DMSO-d_6): δ 11.5 (q), 11.7 (q), 13.9 (q), 59.6 (t), 59.7 (t), 60.2 (s), 103.3 (s), 103.9 (s), 156.7 (s), 158.0 (s), 158.2 (s), 158.8 (s), 161.7 (s), 162.5 (s), 169.4 (s), 169.9 (s); MS *m*/*z* (rel. intensity): 438 (M^{+}, 9), 395 (37), 349 (50), 306 (37), 279 (100). Anal. calc. for C$_{17}$H$_{22}$N$_6$O$_8$: C, 46.58; H, 5.06; N, 19.17; found: C, 46.64; H, 5.12; N, 19.04%. *N*-(7-Aminocarbonylamino-3,8-dimethyl-4-ethoxycarbonyl-9-methoxycarbonyl-1,6-dioxo-2,7-diazaspiro[4.4]-nona-3,8-dien-2-yl)-*N*′-3-fluorophenylurea (**4e**): white powder; IR (Nujol): 3418, 3378, 3218, 1743, 1720, 1700 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 1.26 (t, 3 H, J = 7.1, OCH$_2$C*H*$_3$), 2.47 (s, 6 H, 2 CH$_3$), 3.80 (s, 3 H, OCH$_3$), 4.17 (q, 2 H, J = 7.1, OC*H*$_2$CH$_3$), 5.73 and 6.36 (2 br s, NH$_2$, D$_2$O exch.), 6.70–6.77 (m, 1 H$_{ar}$), 7.00–7.46 (m, 3 H$_{ar}$), 7.97 and 8.05 (2 br s, 2 H, 2 NH, D$_2$O exch.), 8.44 (s, 1 H, NH, D$_2$O exch.); ^{13}C-NMR (DMSO-d_6): δ 12.2 (q), 12.4 (q), 14.1 (q), 52.2 (q), 60.4 (s), 61.4 (t), 104.8 (s), 105.4 (s), 107.2 (d, $^{2}J_{CF}$ = 26.5), 110.2 (d, $^{2}J_{CF}$ = 21.2), 115.1

(d), 129.8 (d, $^3J_{CF} = 9.3$), 139.2 (s, $^3J_{CF} = 10.8$), 154.1 (s), 157.6 (s), 158.1 (s), 160.5 (s), 162.3 (s), 162.9 (s, $^1J_{CF} = 242.1$), 163.3 (s), 163.8 (s), 169.9 (s), 170.4 (s); MS *m*/*z* (rel. intensity): 518 (M^+, 5), 475 (24), 443 (14), 381 (41), 338 (100). Anal. calc. for $C_{22}H_{23}N_6O_8F$: C, 50.97; H, 4.47; N, 16.21; found: C, 50.84; H, 4.53; N, 16.40%.

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References

1 J. G. Schantl, in *Houben-Weyl*, 4th edn., ed. H. Kropf and E. Schaumann, Thieme, Stuttgart, 1990, vol. E15, p. 909; J. G. Schantl, *Farmaco*, 1995, **50**, 379; J. G. Schantl, *Molecules*, 1996, **1**, 212.

2 O. A. Attanasi and L. Caglioti, *Org. Prep. Proced. Int.*, 1986, **18**, 299; O. A. Attanasi and P. Filippone, *Synlett*, 1997, 1128.

3 K. Banert, in *Targets in Heterocyclic Systems—Chemistry and Properties*, ed. O. A. Attanasi and D. Spinelli, Società Chimica Italiana, Roma, 2000, vol. 3, ch. 1, p. 1; S. Polanc, in *Targets in Heterocyclic Systems—Chemistry and Properties*, ed. O. A. Attanasi and D. Spinelli, Società Chimica Italiana, Roma, 2000, vol. 3, ch. 2, p. 33.

4 O. A. Attanasi, L. De Crescentini, P. Filippone, E. Foresti, R. Galeazzi, I. Ghiviriga and A. R. Katritzky, *Tetrahedron*, 1997, **53**, 5617; O. A. Attanasi, L. De Crescentini, E. Foresti, G. Gatti, R. Giorgi, F. R. Perrulli and S. Santeusanio, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1829; O. A. Attanasi, P. Filippone, C. Fiorucci and F. Mantellini, *Synlett*, 1997, 1361; O. A. Attanasi, P. Filippone, C. Fiorucci, E. Foresti and F. Mantellini, *J. Org. Chem.*, 1998, **63**, 9880; O. A. Attanasi, L. De Crescentini, P. Filippone, F. R. Perrulli and S. Santeusanio, *Synlett*, 1999, 339; O. A. Attanasi, P. Filippone, C. Fiorucci and F. Mantellini, *Tetrahedron Lett.*, 1999, **40**, 3891; O. A. Attanasi, L. De Crescentini, P. Filippone, B. Guidi, F. R. Perrulli and S. Santeusanio, *Synlett*, 1999, 1367; O. A. Attanasi, P. Filippone, B. Guidi, T. Hippe, F. Mantellini and L. F. Tietze, *Tetrahedron Lett.*, 1999, **40**, 9277; O. A. Attanasi, R. Ballini, L. De Crescentini, P. Filippone and F. Mantellini, *J. Org. Chem.*, 1999, **64**, 9653; O. A. Attanasi, L. De Crescentini, P. Filippone, E. Foresti and F. Mantellini, *J. Org. Chem.*, 2000, **65**, 2820; O. A. Attanasi, L. De Crescentini, P. Filippone and F. Mantellini, *Synlett*, 2000, 955; O. A. Attanasi, P. Filippone, C. Fiorucci and F. Mantellini, *Chem. Lett.*, 2000, 984.

5 T. L. Gilchrist, O. A. Sanchez Romero and R. C. Wasson, *J. Chem. Soc., Perkin Trans. 1*, 1989, 353; J. Vors, *J. Heterocycl. Chem.*, 1990, **27**, 579; G. Ferguson, A. J. Lough, D. Mackay and G. Weeratunga, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3361; A. J. G. Baxter, J. Fuher and S. J. Teague, *Synthesis*, 1994, 207; G. Baccolini, G. Orsolan and E. Mezzina, *Tetrahedron Lett.*, 1995, **36**, 447; M. S. South, T. L. Jakuboski, M. D. Westmeyer and D. R. Dukesherer, *J. Org. Chem.*, 1996, **61**, 8921; S. Bozzini, F. Felluga, G. Nardin, A. Pizzioli, G. Pitacco and E. Valentin, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1961; V. Buß and L. Eggers, *Tetrahedron: Asymmetry*, 1997, **8**, 1531; Z. V. Todres and G. T. Hovsepyan, *J. Chem. Soc., Perkin Trans. 1*, 1997, 747; C. Joergensen and C. Pedersen, *Carbohydr. Res.*, 1997, **299**, 307; L. J. O. Figueiredo and C. Kasheres, *J. Org. Chem.*, 1997, **62**, 1164; N. Caposcialli, C. Dell'Erba, M. Novi, G. Petrillo and C. Tavani, *Tetrahedron*, 1998, **54**, 5315.

6 Beilstein Commander version 4.0, databases BS0004AB, Chemical Abstract Sci-Finder, Bilstein Institut zur Foerderung der Chemischen Wissenschaften, 1988–2000.

7 O. A. Attanasi, P. Bonifazi, E. Foresti and G. Pradella, *J. Org. Chem.*, 1982, **47**, 684; O. A. Attanasi, P. Filippone, E. Foresti, B. Guidi and S. Santeusanio, *Tetrahedron*, 1999, **55**, 13423.

8 O. A. Attanasi, P. Filippone, A. Mei and S. Santeusanio, *Synthesis*, 1984, 873; S. Sommer, *Tetrahedron Lett.*, 1977, **18**, 117.