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## <sup>1</sup>H and <sup>13</sup>C NMR spectral data of p-nitrobenzenesulfonamides and dansylsulfonamides derived from N-alkylated o-(purinemethyl)anilines

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## Introduction

In recent years, purine bases have been the subject of extensive research that led to the discovery of thousands of biological active compounds, including antineoplastic ones.<sup>[1-6]</sup> We synthesized a novel series of alkylated purines (1-9) with notable in vitro antiproliferative activities, low toxicity and systemic distribution after oral administration in vivo.<sup>[1]</sup> The design of these compounds was based on the modifications of acyclic O,N-acetals, previously described by our research group as anti-proliferative agents.<sup>[7-10]</sup> We have also prepared the 5-fluorouracil (5-FU) derivative (10) as a prototype compound. Finally, the fluorescent analogous (11-14) of the most active compounds were synthesized in order to study the in vitro and in vivo drug distributions.<sup>[1]</sup> The pnitrobenzenesulfonyl group was interchanged with the dansyl group as a chromophore because of its similarity. Moreover, a fluorescence study of some anti-tumour drugs with a dansyl [5-(dimethylamino)naphthalene-1-sulfonyl] group in their structure that present no toxicity in vivo<sup>[11]</sup> confirms the use of this chromophore in the design.

Although the structure of these derivatives was determined by means of standard spectroscopic techniques (<sup>1</sup>H, <sup>13</sup>C NMR and MS), a detailed NMR study has been performed in order to unequivocally corroborate their structures. Herein, we report the <sup>1</sup>H and <sup>13</sup>C NMR unequivocal assignments of a series of anti-proliferative compounds. The spectra of the precursors and intermediate derivatives of the synthesis pathway for their preparation are also included.

### **Experimental**

NMR spectroscopy was carried out at the Centro de Instrumentación Científica, Universidad de Granada (Spain), and the data were recorded at 400 MHz (<sup>1</sup>H) and 100 MHz (<sup>13</sup>C) on a Varian NMR System 400, or at 300 MHz (<sup>1</sup>H) and 75 MHz (<sup>13</sup>C) on a Varian Inova spectrometer at ambient temperature. Chemical shifts  $(\delta)$  are quoted in ppm and are referenced to the residual solvent peak. Spin multiplicities are given as s (singlet), d (doublet), dd (double doublet), ddd (double double doublet), pst (pseudotriplet), t (triplet) and m (multiplet). Coupling constants (J) are given in Hz. The digital resolution of all <sup>13</sup>C spectra recorded is 0.9536 Hz/points. The following parameters were used in DEPT experiments: PW  $(135^{\circ})$ , 9.0 ms; recycle time, 1 s; 1/2 J (CH) = 4 ms; 65 536 data points acquired and transformed from 1024 scans; spectral width, 15 KHz; and line broadening, 1.3 Hz. HMBC spectra were measured with a pulse sequence gc2hmbc (Standard sequence, Agilent Vnmrj\_3.2A software) optimized for 8 Hz (inter-pulse delay for the evolution of long-range couplings: 62.5 ms). The HSQC spectra were measured with a pulse sequence gc2hsqcse (Standard sequence Agilent Vnmrj 3.2A software).

## **Results and discussion**

The N-9-substituted derivatives (isomers 1-8, 11, 13; Scheme 1) and the N-1-5-FU derivative 10 (Scheme 1) were obtained by microwave-assisted Mitsunobu reaction as previously reported.<sup>[1]</sup> We were also able to isolate the N-3-adenine derivative 9 (Scheme 1) and the N-7-2,6-dichloropurine derivatives 12 and 14 (Scheme 1).<sup>[1]</sup> By-products 19 and 20 (Scheme 1) were also obtained when compounds 15 and 16 were treated with tetrabutylammonium fluoride.

<sup>1</sup>H NMR and <sup>13</sup>C NMR data (chemical shifts, multiplicity and coupling constants) for compounds 1-25 are shown in Tables 1-14. Unambiguous assignments for all NMR signals were made through the combined information of onedimensional and two-dimensional NMR experiments such as DEPT, HSQC and HMBC (see Supporting information).

The procedure used to determine the structures of 1-25 from their NMR data is as follows: The identification of N-9-substituted derivatives 1-7 relies on the observation of the correlation of the benzylic hydrogen atoms linked to the purine with the C-4 of the purine moiety in the HMBC spectrum. The C-4 of the purine moiety (C-4<sub>pur</sub>) can be identified because of its 1,3-relationship with the benzylic hydrogen atoms in 1-7 and in addition the H-2 atom of the purine ring in 1, 2, 4-6 (Fig. 1).

The link between the benzylic hydrogen atoms and the quaternary carbons of the 2,6-dichloropurine moiety C-4<sub>pur</sub> and C-5<sub>pur</sub>

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**Scheme 1.** Reagents and conditions: a) *tert*-Butyldimethylsilyl choride (TBDMS-Cl), 4-(dimethylamino)pyridine (DMAP), triethylamine (Et<sub>3</sub>N), anhydrous dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). b) *p*-Nitrobenzenesulfonyl chloride ( $pNO_2-C_6H_4-SO_2Cl$ ), anhydrous CH<sub>2</sub>Cl<sub>2</sub>; dansyl chloride, Et<sub>3</sub>N, anhydrous CH<sub>2</sub>Cl<sub>2</sub> (for **21**). c) 2-Hydroxymethyl-1,3-dioxolane (for **15** and **22**) or 2-(2-hydroxyethyl)-1,3-dioxolane (for **16** and **23**), diisopropylazodicarboxylate (DIAD), triphenylphosphine (PPh<sub>3</sub>), anhydrous tetrahydrofurane (THF). d) TBAF, anhydrous THF. e) DIAD, PPh<sub>3</sub>, anhydrous THF, microwave irradiation.

allows us to distinguish the *N*-9-substituted from the *N*-7-substituted dansyl derivatives (**11**, **13** from **12**, **14**, respectively). The distinction between the C-4<sub>pur</sub> and C-5<sub>pur</sub> signals in the spectrum is based on previously reported data of *N*-7-alkylated and *N*-9-alkylated purines.<sup>[12,13]</sup> C-4<sub>pur</sub> is correlated with the benzylic hydrogen atoms in the *N*-9 isomers, while C-5<sub>pur</sub> is correlated with the benzylic hydrogen atoms in the *N*-9 isomers (Fig. 2).

The discrimination between the *N*-9-substituted and *N*-3-substituted derivatives of adenine (**8** and **9**, respectively) relies on the interaction between the benzylic hydrogen atoms and C-2, C-4 and C-8 atoms of the adenine moiety (Fig. 3). While the benzylic hydrogen atoms are correlated with C-4<sub>pur</sub> and C-8<sub>pur</sub> in the *N*-9 regioisomer **8**, the benzylic hydrogen atoms are correlated with C-2<sub>pur</sub> and C-4<sub>pur</sub> in the *N*-3 regioisomer **9** (Fig. 3). Moreover, the 1,3-relationships between the H-8<sub>pur</sub> (for **8**) and the H-2<sub>pur</sub> (for **9**) with the benzylic carbon atom (Fig. 3) are observed.

The identification of the *N*-1-5-FU regioisomer **10** relies on the 1,3-relationship between the benzylic hydrogen atoms linked to

the 5-FU and the C-6 of 5-FU moiety, and vice versa, the H-6 of 5-FU moiety and the benzylic carbon (Fig. 4).

Some variations are found in the chemical shifts between compounds **15-18** and **19-20**. H-3,5<sub>PhNO2</sub> and H-2,6<sub>PhNO2</sub> resonate at a higher field in **15-18** ( $\delta$  7.83–8.35 ppm) than in **19-20** ( $\delta$  7.08–8.22 ppm). The reverse trend is observed in the case of the benzylic hydrogen atoms where the signals appear at a higher field in **15-18** than in **19-20** (Table 4). The same tendency is shown in their <sup>13</sup>C spectra (Table 12).

Adenine derivatives (4, 8, 9) exhibit different characteristics in their <sup>1</sup>H spectra in relation to those of the purines **1-3**, **5-7**. Pronounced downfield shifts are observed (Table 1) for H-2<sub>pur</sub> ( $\delta$  8.38–8.44 ppm) and H-8<sub>pur</sub> ( $\delta$  8.04–8.13 ppm) signals for the adenine isomers compared with the corresponding signals for purines **1-3**, **5-7** ( $\delta$  8.72–8.80 ppm for H-2<sub>pur</sub>, 8.34–8.42 ppm for H-8<sub>pur</sub>).

The <sup>13</sup>C NMR signals for C-4<sub>5FU</sub>, C-5<sub>5FU</sub> and C-6<sub>5FU</sub> in **10** should be highlighted. The <sup>1</sup>*J* (F,C) and <sup>2</sup>*J* (F,C) give rise to the doublet appearance of the signals (Table 9).

H-2 $_{\mu u}$ H-8 $_{\mu u}$ H-3, 5 $_{5 N NO2}$ H-2, 6 $_{5 N NO2}$ H-3 $_{0 N}$ H-4 $_{0 N}$ H-5 $_{N N}$ H-3 $_{N N}$ H-3 $_{N N}$ H-4 $_{N N}$ H-5 $_{N N}$ H-3 $_{N N}$ H-3} $_{N N}$ H-3 $_{N N}$ H-3 $_{N N}$ H-3 $_{N N}$ H-3 $_{N N}$ H-3} $_{N N}$ H-3} $_{N N}$ H-3} $_{N N}$ H-3}_{N N}         H-3}_{N N}         H-3}_{N N}         H-3} $_{N N}$ H-3}_{N N}         H-	Tab	nle 1. 'H N	VMR data r	or 1-9 (0, pp	(7LL 'C 'III										
1         8.30 (s)         8.33 (s)         8.35 (a)         7.44 (a, 8.8)         6.49 (a, 7.3)         7.17 (m)         7.25 (m)         (d)           2         8.75 (s)         8.38 (s)         8.35 (a, 8.8)         (a, 8.7)         (a, 8.7)         (a, 8.7)         (a, 8.7)         (a, 8.7)         (a, 7.7)         7.26 (a, 7.8)         (a)           3         8.75 (s)         8.38 (s)         8.38         7.84         6.45         7.20 (ad, 7.8, m)         (a)           3         8.24 (s)         8.38 (s)         (a, 8.9)         (a, 8.1)         (a, 7.7)         7.17 (m)         7.26 (m)         (a)           4         8.42 (s)         8.34 (s)         8.33         7.84         6.49         7.17 (m)         7.20         7.30         (a)           4         8.42 (s)         8.34 (s)         8.33         7.86         6.49         7.14 (m)         7.51 (m)         (a)           5         8.34 (s)         8.33         7.86         6.49         (a, 7.7, 1.3)         7.51 (m)         (a)           6         8.78 (d, 7.7, 1.3)         (d, 7.7, 1.3)         7.14 (m)         7.51 (m)         7.51 (m)         6.           7         8.38 (s)         8.33 (s)         8.38         7.88		H-2 <sub>pur</sub>	H-8 <sub>pur</sub>	Н-3, 5 <sub>PhNO2</sub>	H-2, б <sub>РһNO2</sub>	H-3 <sub>Ph</sub>	H-4 <sub>Ph</sub>	H-5 <sub>Ph</sub>	H-6 <sub>Ph</sub>	NH <sub>2pur</sub>	Ph-CH <sub>2</sub>	N-CH <sub>2</sub>	N-CH <sub>2</sub> -CH <sub>2</sub>	CH <sub>2diox</sub>	CH <sub>diox</sub>
2 $8.75$ (s) $8.38$ (s) $8.35$ $7.84$ $6.45$ $7.20$ $7.28^{-1}$ $7.17$ (m) $7.25$ (m) $(d)$ 3 $(d, 8.7)$ $(d, 8.7)$ $(d, 8.7)$ $(d, 7.7)$ $7.17$ (m) $7.20$ $7.30$ $6.6$ 3 $(d, 8.9)$ $(d, 8.9)$ $(d, 8.9)$ $(d, 7.5)$ $7.6$ $6.4$ $7.17^{-1}$ $7.5$ $(d)$ $(d)$ $(d)$ $(d)$ $7.6$ $(d)$	-	8.80 (s)	8.38 (s)	8.35 (d, 8.8)	7.84 (d, 8.8)	6.49 (d, 7.3)	7.21– 7.17 (m)	7.29– 7.25 (m)	7.05 (d, 7.3)		5.92 (d, 16.2) 5.85 (d 16.2)	4.16–4.04 (m) 3.30 (dd, 13.9, 5.6)		4.01–3.82 (m)	5.18–5.15 (m)
3         8.34 (s)         8.38         7.34         6.47         7.20         7.30         5.13)         6.4dd, 7.8,         (ddd, 7.7,         7.19         7.25 (m)         (d         (d)	7	8.75 (s)	8.38 (s)	8.35 (d, 8.7)	7.84 (d, 8.7)	6.45 (d, 7.7)	7.20- 7.17 (m)	7.28– 7.25 (m)	7.05 (d, 7.7)		(d, 16.1) 5.92 5.84 5.84	4.09 (dd, 14.1, 4.0) 3.30		4.00–3.83 (m)	5.16 (dd, 5.6, 4.3)
4 $8.42$ (s) $8.04$ (s) $8.37$ $7.86$ $6.44$ $7.17$ - $725$ (m) $(d)$ 5 $8.78$ (s) $8.38$ (s) $8.38$ $7.85$ $6.49$ $7.14$ (m) $725$ (m) $(d)$ 5 $8.78$ (s) $8.38$ (s) $8.38$ $7.85$ $6.49$ $7.21$ $7.31$ - $6.6$ 6 $(d, 8.9)$ $(d, 8.9)$ $(d, 8.9)$ $(d, 8.9)$ $(d, 7.7, 1.3)$ $(dd, 7.7, 7.13)$ $7.31$ - $6.6$ 6 $(d, 8.9)$ $(d, 8.9)$ $(d, 8.8)$ $(d, 8.8)$ $(d, 7.3)$ $(pst, 7.3)$ $(pst, 7.3)$ $(d, 7.7)$ 6 $8.32$ (s) $8.42$ (s) $8.33$ $7.84$ $6.48$ $7.22$ $7.27$ $7.2$ 7 $8.33$ (s) $8.33$	m		8.34 (s)	8.38 (d, 8.9)	7.84 (d, 8.9)	6.47 (dd, 7.6, 1.3)	7.20 (ddd, 7.8, 7.6, 1.4)	7.30 (ddd, 7.8, 7.6, 1.3)	6.80 (dd, 7.6, 1.4)		(u, 10.1) 5.90 (d, 16.2) 5.80	(dd, 13.8, 4.4) 4.09 (dd, 13.8, 4.4) 3.28		4.00–3.86 (m)	5.15 (dd, 6.0, 4.1)
5         8.78 (s)         8.38 (s)         8.38 (s)         8.38 (s)         8.38 (s)         8.38 (s)         6.49 (d, 7.7, 13) (ddd, 7.7, 7.31)         7.31 (ddd, 7.7, 7.25 (m))         6.46         7.7, 13)         7.7, 13)         7.7, 13)         7.7, 13)         7.7, 13)         7.7, 13)         7.7, 13)         7.7, 13)         7.7, 13)         7.7, 13)         7.7, 13)         7.7         7.25 (m)         (dd, 7.7, 13)         7.7, 13)         7.7         7.7         7.25 (m)         (dd, 7.7, 13)         7.7, 13)         7.7         7.7         7.21         7.7         7.21         7.7         7.21         7.7         7.21         7.7         7.21         7.21         7.21         7.21         7.30         7.4           7         8.31 (s)         8.33 (s)         8.33 (s)         8.34 (s)         (d, 8.2)         (d, 7.5)         (pst, 7.5)         (pst, 7.5)         (d         (d         (d         (d)         (d)	4	8.42 (s)	8.04 (s)	8.37 (d, 8.8)	7.86 (d, 8.8)	6.44 (d, 7.9)	7.17– 7.14 (m)	7.28– 7.25 (m)	7.07 (d, 7.9)	5.98 (s)	(d, 16.2) 5.82 (d, 16.2) 5.77 (d, 16.2)	(dd, 13.8, 4.3) (dd, 13.8, 4.3) 3.33 (dd, 13.8 5.5)		4.01–3.85 (m)	5.17 (pst, 4.9)
6       8.72 (s)       8.42 (s)       8.37       7.84       6.48       7.19       7.27       7.         7       (d, 8.8)       (d, 8.8)       (d, 8.8)       (d, 7.3)       (pst, 7.3)       (pst, 7.3)       (d         7       8.39 (s)       8.36       7.85       6.48       7.22       7.30       7.         8       8.39 (s)       8.36       7.85       6.48       7.22       7.30       7.         8       8.39 (s)       8.36       7.85       6.45       7.19       7.26       7.         8       8.38 (s)       8.04 (s)       8.36       7.86       6.45       7.19       7.25       7.         9       8.44 (s)       8.13 (s)       8.38       7.85       6.47       7.25       7.       7.         9       8.44 (s)       8.13 (s)       8.38       7.85       6.47       7.25       7.33       7.         9       8.44 (s)       8.13 (s)       8.38       7.85       6.47       7.25       7.33       7.       7.0 (m)       7.	20	8.78 (s)	8.38 (s)	8.38 (d, 8.9)	7.85 (d, 8.9)	6.49 (dd, 7.7, 1.3)	7.21 (ddd, 7.7, 7.7, 1.3)	7.31– 7.25 (m)	6.41 (dd, 7.7, 1.3)		(d, 16.2) 5.89 (d, 16.2) 5.79	(	2.07–1.95 (m) 1.89–1.75 (m)	3.99–3.77 (m)	4.92 (pst, 4.1)
<ul> <li>(d, 8.5) (d, 8.5) (d, 8.5) (d, 7.5) (pst, 7.5) (pst, 7.5) (d</li> <li>8 8.38 (s) 8.04 (s) 8.36 7.86 6.45 7.19-7.15 7.28- 7. (d</li> <li>(d, 8.8) (d, 7.9) (m) 7.25 (m) (d</li> <li>9 8.44 (s) 8.13 (s) 8.38 7.85 6.47 7.25- 7.33- 7. (d</li> <li>(d, 8.8) (d, 7.7) 7.20 (m) 7.29 (m) (c</li> </ul>	۲ V	8.72 (s)	8.42 (s) 8.39 (s)	8.37 (d, 8.8) 8.36	7.84 (d, 8.8) 7.85	6.48 (d, 7.3) 6.48	7.19 (pst, 7.3) 7.22	7.27 (pst, 7.3) 7.30	7.05 (d, 7.3) 7.06		(u, 10.2) 5.87 (d, 16.1) 5.78 (d, 16.1) 5.80	4.24–4.08 (m) 3.40–3.25 (m) 4.21–4.09 (m)	2.08–1.94 (m) 1.87–1.74 (m) 2.04–1.93 (m)	4.00–3.75 (m) 3.97–3.72 (m)	4.90 (pst, 4.0) 4.93 (pst, 3.8)
<ul> <li>8.44 (s) 8.13 (s) 8.38 7.85 6.47 7.25- 7.33- 7. (d, 8.8) (d, 8.8) (d, 7.7) 7.20 (m) 7.29 (m) (c)</li> </ul>	œ	8.38 (s)	8.04 (s)	(d, 8.5) 8.36 (d, 8.8)	(d, 8.5) 7.86 (d, 8.8)	(d. 7.9) 6.45 (d, 7.9)	(pst, 7.5) 7.19–7.15 (m)	(pst, /.5) 7.28– 7.25 (m)	(č. / ,b) 7.07 (d, 7.9)		(d, 16.0) 5.70 (d, 16.0) 5.75 (d, 16.2)	3.33–3.21 (m) 4.21–4.14 (m) 3.40–3.28 (m)	1.84–1.71 (m) 2.07–1.99 (m) 1.86–1.75 (m)	3.99–3.77 (m)	4.91 (pst, 4.1)
	6	8.44 (s)	8.13 (s)	8.38 (d, 8.8)	7.85 (d, 8.8)	6.47 (d, 7.7)	7.25– 7.20 (m)	7.33– 7.29 (m)	7.13 (d, 7.7)		5.71 (d, 16.2) 6.05 (d, 15.8) 5.88 (d, 15.8)	4.29–4.11 (m) 3.41–3.24 (m)	2.04–1.90 (m) 1.90–1.74 (m)	4.03–3.73 (m)	4.90 (pst, 3.9)

#### Magn. Reson. Chem. (2016)

	CH <sub>diox</sub>	4.88 5st, 4.1)			N(CH <sub>3</sub> ) <sub>2</sub>	2.89 (s)	2.89 (s)	2.88 (s)		2.89 (s)	ounds.
	×	7 (u			CH <sub>diox</sub>	5.18 (pst, 5.0)	5.17 (dd, 5.8, 4.3)	4.89	(pst, 4.1)	4.88 (pst, 4.1)	or all comp
	CH <sub>2dio</sub>	3.99– 3.74 (r	experiment.		CH <sub>2dio</sub>	4.03– 3.82 (m)	4.02– 3.76 (m)	3.95-	3.76 (m)	3.94– 3.74 (m)	toeriments f
	N-CH <sub>2</sub> -CH <sub>2</sub>	2.04–1.87 (m) 1.79–1.72 (m)	ent in the NMR (		N-CH <sub>2</sub> -CH <sub>2</sub>			1.99–1.90 (m)	1.82–1.73 (m)	1.96–1.85 (m) 1.84–1.74 (m)	nt in the NMR ex
	N-CH <sub>2</sub>	20–4.02 (m) 5–3.23 (m)	vas used as solv		N-CH <sub>2</sub>	4.24 (dd, 13.9, 4.5) 3.26 (dd, 13.9, 5.5)	4.20 (dd, 14.0, 4.3)	3.22 (dd, 14.0, 5.9) 4.21–4.09 (m)	3.47–3.39 (m)	4.15–4.04 (m) 3.51–3.41 (m)	as used as solve
	42	4.2 .0) 3.3 .0)	a. CDCl <sub>3</sub> w		Ph-CH <sub>2</sub>	5.92 (d, 16.1) 5.82 (d, 16.1)	6.12 (s)	5.79	(d, 15.9) 5.73 (d, 15.9)	6.07 (d, 16.7) 5.94	(d, 16.7) 1. CDCl <sub>3</sub> we
	Ph-CF	5.45 (d, 16 5.09 (d, 16	ABC spectr		H-6 <sub>Ph</sub>	6.99 (d, 7.8)	6.43 (d, 8.0)	7.01-	(m) (m)	6.68 (d, 7.6)	BC spectra
	H-6 <sub>Ph</sub>	7.28 (d, 7.2)	QC and HN		H-5 <sub>Ph</sub>	7.19– 7.15 (m)	7.22– 7.14 (m)	7.22-	7.17 (m)	7.21 (pst, 7.6)	DC and HM
	-5 <sub>Ph</sub>	t3– 88 (m)	with the HS		H-4 <sub>Ph</sub>	6.95– 6.91 (m)	7.01– 6.95 (m)	7.01-	(m) (m)	7.03 (pst, 7.6)	with the HS0
	Í	7. 1.7 (n	ı agreement		H-3 <sub>Ph</sub>	6.36 (d, 7.8)	6.74 (d, 8.0)	6.49	(dd, 8.4, 1.0)	6.56 (d, 7.6)	adreement
	H-4 <sub>Ph</sub>	7.24- 7.19 (r	ients are ir		H-8 <sub>pur</sub>	8.34 (s)	8.31 (s)	8.27 (s)		8.28 (s)	ents are in
	H-3 <sub>Ph</sub>	6.44 (d, 7.9)	ft assignm		H-6 <sub>dan</sub>	7.14 (d, 7.6)	7.14 (d, 7.6)	7.13	(d, 7.5)	7.13 (d, 7.6)	t assignme
	2,6 <sub>PhNO2</sub>	7.86 (d, 8.8)	itheses. <sup>1</sup> H shi		H-3 <sub>dan</sub>	7.48 (pst, 7.6)	7.49 (dd, 8.4, 7.5)	7.49	(dd, 8.5, 7.5)	7.49 (dd, 8.4, 7.9)	theses. <sup>1</sup> H shif
/, Hz)	5PhNO2 H-3	3.38 d, 8.8)	given in parer	m; J, Hz)	H-7 <sub>dan</sub>	7.32 (pst, 7.6)	7.33 (dd, 8.7, 7.6)	7.33	(dd, 8.7, 7.5)	7.34 (dd, 8.5, 7.6)	aiven in paren
л <b>10</b> (ð, ррт;.	1-6 <sub>5FU</sub> Н-3	7.62 d, 5.0) (	constants are	or <b>11-14</b> (ð, pp	H-2 <sub>dan</sub>	8.06 (dd, 7.6, 1.2)	8.05 (dd, 7.5, 1.1)	8.09-	8.06 (m)	8.06 (d, 7.9)	constants are o
MR data fc	Ë	(0:	ł coupling	MR data fo	H-8 <sub>dan</sub>	8.01 (d, 7.6)	8.01 (d, 8.7)	8.09-	8.06 (m)	8.06 (d, 8.5)	l coupling o
е <b>2.</b> <sup>1</sup> Н N	H-3 <sub>5F</sub>	8.85 (d, 5.	iplicity anc	e 3. <sup>1</sup> H N	H-4 <sub>dan</sub>	8.60 (d, 7.6)	8.60 (d, 8.4)	8.58	(d, 8.5)	8.59 (d, 8.4)	plicity and
Tabl		10	Multi	Tabl		۲	12	13		14	Multi

## MRC

Table	а <b>4.</b> <sup>1</sup> Н NM	IR data for 1	<b>5-20</b> (δ, ppm; <i>J</i> , I	Hz)										
	H-3,5	H-2,6	H-3 <sub>Ph</sub>	H-4 <sub>Ph</sub>	H-5 <sub>Ph</sub>	H-6 <sub>Ph</sub>	Ph-CH <sub>2</sub>	HN	N-CH <sub>2</sub>	N-CH <sub>2</sub> -CH <sub>2</sub>	CH <sub>2diox</sub>	CH <sub>diox</sub>	CH <sub>3</sub> -C-Si	CH <sub>3</sub> -Si
	PhNO2	PhNO2												
15	8.33	7.85	7.69	7.39	7.11	6.47	5.02		3.91		3.89–	4.96	(s) 76.0	0.12 (s)
	(d, 9.0)	(d, 9.0)	(dd, 7.7, 1.1)	(ddd, 7.7,	(ddd, 7.8,	(dd, 7.8, 1.1)	(d, 14.4)		(dd, 14.1, 5.1)		3.77 (m)	(pst, 4.7)		
				7.4, 1.1)	7.4, 1.1)		4.94		3.48					
							(d, 14.4)		(dd, 14.1, 5.1)					
16	8.32	7.84	7.66	7.35	7.10	6.43	4.94		4.03–3.92 (m)	2.03–1.89 (m)	3.92-	4.80	0.92 (s)	0.02 (s)
	(d, 8.6)	(d, 8.6)	(d, 7.5)	(pst, 7.5)	(pst, 7.5)	(d, 7.5)	(d, 14.3)		3.43–3.30 (m)	1.80–1.65 (m)	3.75 (m)	(pst, 4.4)		
							4.87							
							(d, 14.3)							
17	8.34	7.83	7.64	7.40	7.17	6.40	4.93		3.98		3.95-	5.07		
	(0'6 'P)	(0'6 <sup>(</sup> )	(dd, 7.6, 1.5)	(ddd, 7.6,	(ddd, 7.6,	(dd, 7.6, 1.2)	(d, 12.5)		(dd, 14.0, 4.1)		3.80 (m)	(dd, 5.6, 4.1)		
				7.5, 1.2)	7.5, 1.5)		4.75		3.32					
							(d, 12.5)		(dd, 14.0, 5.7)					
18	8.35	7.84	7.67	7.41	7.18	6.41	4.84		4.05–3.96 (m)	1.96–1.83 (m)	3.91–	4.80		
	(d, 8.8)	(d, 8.8)	(d, 7.7)	(pst, 7.7)	(pst, 7.7)	(d, 7.7)	(d, 12.6)		3.35–3.23 (m)	1.72–1.60 (m)	3.71 (m)	(pst, 4.2)		
							4.63							
							(dd, 12.6, 7.4)							
19	8.21	7.08	7.21	6.80-	7.28	6.80-	5.14 (s)	4.62 (s)	3.39		3.97-	5.15-		
	(d, 9.3)	(d, 9.3)	(dd, 7.7,1.6)	6.72 (m)	(ddd, 7.8,	6.72 (m)			(d, 3.8)		3.86 (m)	5.11 (m)		
					7.6, 1.6)									
20	8.22	7.08	7.21	6.75-	7.30	6.75-	5.14 (s)	4.97 (s)	3.31	2.07–1.99 (m)	3.91–	4.95		
	(d, 9.2)	(d, 9.2)	(dd, 7.3, 1.3)	6.72 (m)	(ddd, 7.9,	6.72 (m)			(t, 6.2)		3.63 (m)	(t, 4.4)		
					7.6, 1.3)									
Multi	plicity and c	oupling con	ıstants are given	in parenthese	s. <sup>1</sup> H shift assiç	gnments are in aç	greement with th	le HSQC and	HMBC spectra. CI	)Cl <sub>3</sub> was used as so	olvent in the	NMR experimen	ts for all com	pounds.

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	H-7 <sub>dan</sub> H-3 <sub>dan</sub> H-6 <sub>dan</sub> H-6 <sub>ph</sub> H-5 <sub>ph</sub> H-4 <sub>ph</sub> H-3 <sub>ph</sub> H-3 <sub>ph</sub> MH Ph-CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> C <u>H</u> <sub>3</sub> -C-Si CH <sub>3</sub> -Si	7.53 7.47- 7.18- 7.47- 7.18- 6.93 6.88 8.66 (s) 4.30 (s) 2.86 (s) 0.94 (s) 0.06 (s) dd, 8.7, 7.7) 7.42 (m) 7.42 (m) 7.42 (m) 7.42 (m) 7.4, 1.1) (ddd, 7.5, (dd, 7.5, 1.4) 7.4, 1.1)	barentheses. <sup>1</sup> H shift assignments are in agreement with the HSQC and HMBC spectra. CDCl <sub>3</sub> was used as solvent in the NMR experiment.	or <b>22-25</b> (ð, ppm; J, Hz)	
H-7 <sub>425</sub> H-3 <sub>4</sub>		7.53 7.47- (dd, 8.7, 7.7) 7.42 (r	in parentheses. <sup>1</sup> H shift as	is for <b>22-25</b> (ô, ppm; J, Hz)	
8 <sub>dan</sub> H-2 <sub>dan</sub> 39 8.22	39 8.22	8.7) (dd, 7.3, 1.2)	ng constants are given i	a of the aromatic group	
H-4 <sub>dan</sub> H-{		<b>21</b> 8.49 8.5 (d, 8.5) (d, 8	Multiplicity and couplin	<b>Table 6.</b> <sup>1</sup> H NMR data	

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7.57 (dd, 7.7, 1.5) 7.60 (dd, 7.6, 1.5)

7.29 (ddd, 7.7, 7.5, 0.8) 7.30 (ddd, 7.6, 7.5, 0.8)

7.56 (d, 7.7) 7.56 (d, 7.4)

7.29 (ddd, 7.6, 7.4, 1.1)

7.30-7.26 (m)

6.96 (ddd, 7.9, 7.5, 1.2) 7.00 (ddd, 8.0, 7.6, 1.5) 6.92 (ddd, 8.0, 7.5, 1.7) 6.95 (ddd, 7.9, 7.5, 1.5)

> 6.67 (dd, 8.0, 0.8) 6.31 (dd, 8.0, 0.8) 6.37 (dd, 7.9, 0.8)

6.64 (d, 7.9)

7.14 (d, 7.6) 7.14 (d, 7.5)

7.42 (dd, 8.4, 7.5)

7.36 (dd, 8.7, 7.6)

8.02 (dd, 7.5, 1.1)

8.15 (d, 8.7) 8.17 (d, 8.7)

8.54 (d, 8.4) 8.54 (d, 8.5) 8.57 (d, 8.4) 8.56 (d, 8.4)

8.05 (dd, 7.5, 1.2) 8.05-8.02 (m)

> 8.05-8.02 (m) 8.08 (d, 8.7)

22 23 23 25 24 25

7.38 (dd, 8.7, 7.5)

Multiplicity and coupling constants are given in parentheses. <sup>1</sup>H shift assignments are in agreement with the HSQC and HMBC spectra. CDCl<sub>3</sub> was used as solvent in the NMR experiments for all compounds.

7.14 (d, 7.6) 7.14 (d, 7.6)

7.44 (dd, 8.5, 7.5) 7.45 (dd, 8.4, 7.5)

> 7.32 (dd, 8.6, 7.6) 7.34 (dd, 8.7, 7.6)

> > 8.05 (dd, 7.5, 1.1)

7.46 (dd, 8.4, 7.5)

Μ	RC

MCH <sub>3</sub> MCH <sub>3</sub> MCH <sub>3</sub> MCH <sub>3</sub> MCH <sub>3</sub> MCH <sub>4</sub> <	Table 7	. <sup>1</sup> H NMR d	ata of the re	emaining s	ignals for	2 <b>2-25</b> (ð, þl	om; J, Hz)													
2         488 (41 Mi + 1/3 V(41 Mi)         395 (61 Mi + 1/3 S)         305 (1/3 Mi + 1/3 Mi + 1/				Ph-CH <sub>2</sub>				N-C	CH <sub>2</sub>			N(CH <sub>3</sub> ) <sub>2</sub>		-	V-CH <sub>2</sub> -CH <sub>2</sub>			C <u>H</u> <sub>3</sub> -C-Si		CH <sub>3</sub> -Si
Multiplicity and coupling constants are given in parentheses. <sup>1</sup> I shift assignments are in agreement with the ISQC and HMBC spectra. CDCl <sub>1</sub> was used as solvent in the NMR experiments for all compounds.           Table 4. <sup>11</sup> C NMR data for 1-9 (k) pm           C-d <sub>ive</sub>	22 23 24	4.85 4.71 4.92 4.89	(d, 14.4) 4.5 (d, 14.1) 4.5 (dd, 12.4, 5. (d, 12.3) 4.6	7 (d, 14.4) 8 (d, 14.1) 2) 4.70 (dc 2–4.53 (m)	, 12.4, 5.3)	_	3.95 (dd, 3.95–3.8{ 4.15 (dd, 4.14–4.02	14.1, 4.9) 3 (m) 3.64- 14.1, 4.3) 2 (m) 3.45-	3.51 (dd, <sup>-</sup> -3.53 (m) 3.25 (dd, 1 -3.36 (m)	14.1, 4.6) 14.1, 5.5)		2.88 (s) 2.88 (s) 2.88 (s) 2.89 (s)		1.95–1.86	(m) 1.81–1. (m) 1.73–1.6	73 (m) 52 (m)		0.92 (s) 0.90 (s)	0 0	.02 (s) .02 (s)
Table S. <sup>1</sup> C MMR data for 19 (s) pm           74m         C <sup>3</sup> m         C <sup>3</sup>	Multipli	city and coul	pling consta	nts are giv	en in pare	ntheses. <sup>1</sup> H	shift assigr	iments are	in agreer	nent with th	he HSQC a	ind HMBC	spectra. C	DCl <sub>3</sub> was i	used as solve	ant in the	NMR expe	eriments for	all compc	unds.
Table 8. <sup>11</sup> C NMR data for 1-9 (A) pm)           C-4Jur         C-3Jur         C-4Jur         C-4																				
To be the total for t																				
Table 8. <sup>13</sup> C NMR data for 1-9 (k) pm)           C-4 <sub>bu</sub> C-2 <sub>pu</sub> C-6 <sub>pu</sub> C-5 <sub>pu</sub> C-4 <sub>pu</sub> C-4 <sub>pu</sub> C-5 <sub>pu</sub> C-4 <sub>pu</sub> C-4 <sub>pu</sub> C-4 <sub>pu</sub> C-4 <sub>pu</sub> C-5 <sub>pu</sub> C-4 <sub>pu</sub> C-4 <sub>pu</sub> C-4 <sub>pu</sub> C-5 <sub>pu</sub> C-4 <sub>pu</sub> C-4 <sub>pu</sub> C-5 <sub>pu</sub> C-4 <sub>pu</sub> C-4 <sub>pu</sub> C-5 <sub>p</sub> C-4 <sub>p</sub> C-4         C-4         C-4         C-4         C-4         C-4 <t< th=""><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th></t<>																				
Table 8. <sup>13</sup> C NMR data for 1-9 (Å pm)           C 4 <sup>pu</sup> C -2 <sup>pu</sup> C -3 <sup>pu</sup> C -1 <sup>pu</sup> C -1 <sup>pu</sup> C -1 <sup>pu</sup> C -3 <sup>pu</sup> C -3 <sup>pu</sup> C -3 <sup>pu</sup> C -3 <sup>puv</sup> C -3 <sup>pu</sup>																				
C-4 <sub>pur</sub> C-3 <sub>pur</sub> C-8 <sub>pur</sub> C-8 <sub>pur</sub> C-8 <sub>pur</sub> C-8 <sub>pur</sub> C-8 <sub>pur</sub> C-1 <sub>pm</sub>	Table 8	• <sup>13</sup> C NMR 6	data for <b>1-9</b>	( <i>i</i> , ppm)																
1         152.69         152.35         151.23         146.49         131.47         150.64         142.77         137.64         137.95         129.30         129.91         124.41         43.41         54.92         65.33         101.96           2         151.48         152.34         153.37         146.37         130.05         137.06         138.00         129.56         127.30         129.95         124.43         43.55         55.19         65.25         101.96           3         153.35         151.99         147.21         130.67         137.56         137.71         137.56         129.56         127.30         129.95         124.45         43.75         55.19         65.28         101.96           4         152.40         152.48         157.35         160.64         137.71         137.56         129.56         124.45         43.75         55.19         65.28         101.86           5         152.20         152.48         157.35         160.64         137.71         137.56         129.56         124.43         43.05         55.13         65.28         102.06           6         152.22         152.48         153.35         164.63         132.61         129.56         129.	Ċ	4 <sub>pur</sub> C-2 <sub>pt</sub>	ur C-6 <sub>pur</sub>	C-8 <sub>pur</sub>	C-5 <sub>pur</sub>	C-4 <sub>PhNO2</sub>	C-1 <sub>PhNO2</sub>	C-2 <sub>Ph</sub>	C-1 <sub>Ph</sub>	C-2,6 <sub>PhNO2</sub>	C-3 <sub>Ph</sub>	C-4 <sub>Ph</sub>	C-5 <sub>Ph</sub>	C-6 <sub>Ph</sub>	C-3,5 <sub>PhNO2</sub>	Ph-CH <sub>2</sub>	N-CH <sub>2</sub> N	-CH <sub>2</sub> -CH <sub>2</sub> (	CH <sub>2diox</sub>	CH <sub>diox</sub>
2         15148         152.34         153.37         146.37         134.09         150.41         142.77         137.66         138.00         129.38         129.33         129.19         124.43         43.55         55.19         65.25         101.96           3         153.97         153.36         151.99         147.21         130.67         150.68         142.71         137.56         129.56         127.32         129.91         129.10         124.46         43.75         55.19         65.28         101.96           4         152.40         152.41         155.08         150.64         137.37         138.76         138.13         129.56         127.30         129.91         129.10         124.46         43.75         55.19         47.78         55.19         40.18         101.89         101.89         102.00           5         152.52         151.20         146.13         134.11         150.64         137.31         129.90         129.46         129.43         44.12         44.12         47.47         32.34         65.25         101.08           5         153.26         131.51         150.64         137.31         129.96         129.43         129.43         44.12         47.47 <th< th=""><th>1 152</th><th>.69 152.3</th><th>5 151.23</th><th>146.49</th><th>131.47</th><th>150.64</th><th>142.77</th><th>137.64</th><th>137.98</th><th>129.56</th><th>127.31</th><th>129.30</th><th>129.92</th><th>129.14</th><th>124.41</th><th>43.41</th><th>54.92</th><th></th><th>65.33 1</th><th>01.88</th></th<>	1 152	.69 152.3	5 151.23	146.49	131.47	150.64	142.77	137.64	137.98	129.56	127.31	129.30	129.92	129.14	124.41	43.41	54.92		65.33 1	01.88
3         153.97         153.36         151.99         147.21         130.67         150.68         142.71         137.56         129.56         127.32         129.49         130.01         129.10         124.46         43.75         55.19         65.28         101.85           4         152.40         152.08         150.64         137.37         150.65         142.13         138.76         138.13         129.58         127.30         129.25         129.39         124.39         43.09         55.13         65.28         101.89           5         152.52         152.48         151.35         146.13         131.12         150.64         142.60         136.93         137.70         129.69         129.44         129.86         129.23         124.42         43.93         47.58         32.34         65.25         102.06           6         151.28         151.20         146.13         134.11         150.64         142.60         137.31         129.96         129.56         129.43         44.12         44.12         47.47         32.34         65.25         102.00           7         153.86         153.36         133.71         129.56         129.56         129.43         43.10         47.43         <	<b>2</b> 15 <sup>-</sup>	1.48 152.3	4 153.37	146.37	134.09	150.41	142.77	137.66	138.00	129.58	127.30	129.33	129.95	129.19	124.43	43.59	55.16		65.25 1	01.96
4       152.40       152.41       155.08       150.64       137.37       150.65       142.13       138.76       138.13       129.58       127.30       129.25       129.91       128.97       124.39       43.09       55.13       65.28       101.89         5       152.52       152.135       146.28       131.12       150.64       142.60       136.99       137.35       129.56       129.44       129.86       129.23       124.42       43.93       47.58       32.44       65.25       102.06         6       151.28       152.25       151.20       146.13       134.11       150.64       142.60       136.99       137.31       129.90       129.46       129.59       124.43       44.12       47.47       32.38       65.25       102.00         7       153.36       152.05       146.05       131.51       150.64       142.60       136.50       137.31       129.90       126.98       129.19       124.43       43.19       47.33       32.22       65.25       102.00         8       150.72       152.05       146.09       137.31       129.59       126.68       129.19       124.43       43.19       47.33       32.22       65.25       101.08       14	<b>3</b> 15:	3.97 153.30	6 151.99	147.21	130.67	150.68	142.71	137.71	137.56	129.56	127.32	129.49	130.01	129.10	124.46	43.75	55.19		65.28 1	01.85
5 $152.52$ $152.48$ $151.35$ $146.28$ $131.12$ $150.67$ $142.73$ $136.93$ $137.70$ $129.65$ $129.44$ $129.86$ $129.42$ $43.93$ $47.58$ $32.44$ $65.25$ $102.06$ 6 $151.28$ $152.52$ $151.20$ $146.13$ $134.11$ $150.64$ $142.60$ $136.99$ $137.31$ $129.96$ $129.65$ $129.43$ $44.12$ $47.47$ $32.38$ $65.24$ $102.00$ 7 $153.86$ $153.33$ $152.05$ $146.05$ $131.51$ $150.64$ $142.60$ $137.31$ $129.90$ $126.98$ $129.61$ $129.19$ $124.43$ $43.19$ $47.73$ $32.38$ $65.24$ $102.00$ 8 $150.72$ $152.05$ $141.57$ $119.15$ $150.64$ $142.62$ $136.55$ $138.51$ $129.59$ $126.18$ $129.79$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $120.10$ 9 $149.80$ $146.09$ $154.43$ $148.90$ $119.15$ $150.64$ $142.62$ $137.11$ $136.62$ $129.79$ $129.79$ $129.99$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $129.19$ $124.43$ $43.19$ $47.54$ $32.42$ $65.24$ $101.06$ 9 $149.80$ $146.09$ $154.43$ $148.90$ $119.15$ $150.80$ $142.42$ $1$	<b>4</b> 15;	2.40 152.4	1 155.08	150.64	137.37	150.65	142.13	138.76	138.13	129.58	127.30	129.25	129.91	128.97	124.39	43.09	55.13		65.28 1	01.89
<ul> <li>6 151.28 152.52 151.20 146.13 134.11 150.64 142.60 136.99 137.35 129.70 126.98 129.65 129.86 129.59 124.43 44.12 47.47 32.38 65.24 102.00</li> <li>7 153.86 153.39 152.05 146.95 131.51 150.64 142.62 136.90 137.31 129.90 126.98 129.61 130.71 129.19 124.43 43.90 47.33 32.22 65.25 101.98</li> <li>8 150.72 152.95 155.56 141.57 119.15 150.54 142.62 136.55 138.51 129.59 126.88 129.28 129.79 129.05 124.38 43.19 47.54 32.42 65.20 102.00</li> <li>9 149.80 146.09 154.43 148.90 119.15 150.80 142.42 137.11 136.62 129.74 127.03 129.67 129.98 129.20 124.45 49.36 47.47 32.21 65.24 101.96</li> <li><sup>13</sup>C shift assignments are in agreement with the HSQC and HMBC spectra. CDCl<sub>3</sub> was used as solvent in the NMR experiments for all compounds.</li> </ul>	<b>5</b> 15.	2.52 152.4	8 151.35	146.28	131.12	150.67	142.73	136.93	137.70	129.65	126.99	129.44	129.86	129.23	124.42	43.93	47.58	32.44	65.25 1	02.06
7         153.86         153.39         152.05         146.95         131.51         150.64         142.62         136.90         137.31         129.90         126.91         130.71         129.19         124.43         43.90         47.33         32.22         65.25         101.98           8         150.72         152.95         141.57         119.15         150.54         142.93         136.55         138.51         129.59         129.79         129.05         124.38         43.19         47.54         32.42         65.20         102.00           9         149.80         146.09         154.43         148.90         119.15         150.80         137.11         136.62         129.74         127.03         129.567         129.20         124.45         49.36         47.47         32.21         65.24         101.96           1 <sup>3</sup> C shift assignments are in agreement with the HSQC and HMBC spectra. CDCl <sub>3</sub> was used as solvent in the NMR experiments for all compounds.         129.36         129.50         124.45         49.36         47.47         32.21         65.24         101.96	<b>6</b> 15 <sup>.</sup>	1.28 152.5.	2 151.20	146.13	134.11	150.64	142.60	136.99	137.35	129.70	126.98	129.65	129.86	129.59	124.43	44.12	47.47	32.38	65.24 1	02.00
8         150.72         152.95         151.55         141.57         119.15         150.54         142.93         136.55         138.51         129.59         126.88         129.79         129.05         124.38         43.19         47.54         32.42         65.20         102.00           9         149.80         146.09         154.43         148.90         119.15         150.80         142.42         137.11         136.62         129.74         127.03         129.67         129.98         129.20         124.45         49.36         47.47         32.21         65.24         101.96 <sup>13</sup> C shift assignments are in agreement with the HSQC and HMBC spectra. CDCl <sub>3</sub> was used as solvent in the NMR experiments for all compounds.         129.36         47.47         32.21         65.24         101.96	7 15:	3.86 153.3	9 152.05	146.95	131.51	150.64	142.62	136.90	137.31	129.90	126.98	129.61	130.71	129.19	124.43	43.90	47.33	32.22	65.25 1	01.98
<b>9</b> 149.80 146.09 154.43 148.90 119.15 150.80 142.42 137.11 136.62 129.74 127.03 129.67 129.98 129.20 124.45 49.36 47.47 32.21 65.24 101.96 <sup>13</sup> C shift assignments are in agreement with the HSQC and HMBC spectra. CDCl <sub>3</sub> was used as solvent in the NMR experiments for all compounds.	<b>8</b> 15(	0.72 152.9.	5 155.56	141.57	119.15	150.54	142.93	136.55	138.51	129.59	126.88	129.28	129.79	129.05	124.38	43.19	47.54	32.42	65.20 1	02.00
<sup>13</sup> C shift assignments are in agreement with the HSQC and HMBC spectra. CDCl <sub>3</sub> was used as solvent in the NMR experiments for all compounds.	9 149	9.80 146.0	9 154.43	148.90	119.15	150.80	142.42	137.11	136.62	129.74	127.03	129.67	129.98	129.20	124.45	49.36	47.47	32.21	65.24 1	01.96
	<sup>13</sup> C shif	: assignment	ts are in agre	ement wi	ith the HSC	QC and HM	BC spectra.	CDCl <sub>3</sub> wa£	s used as s	solvent in th	ne NMR ex	periments:	for all co	mpounds.						

# **/RC**

, CH <sub>diox</sub>	101.90			C-5 <sub>pur</sub>	130.59	122.58	130.66	122.40		
H <sub>2</sub> CH <sub>2dio</sub>	65.19			C-8 <sub>pur</sub>	147.51	151.65	147.12	151.47		
N-CH <sub>2</sub> -CI	32.32			6 <sub>pur</sub>	.33	:29	:22	44.		
N-CH <sub>2</sub>	47.55			Ċ	156	153	153	153		
Ph-CH <sub>2</sub>	47.46			C-2 <sub>pur</sub>	153.24	144.00	151.74	144.00		
C-3,5 <sub>PhNO2</sub>	124.44			C-4 <sub>pur</sub>	154.07	163.52	153.92	163.67		
C-6 <sub>Ph</sub>	129.29			ðdan	.51	.54	.45	.50		
C-5 <sub>Ph</sub>	130.02	t		-C-	115	115	115	115	t	
C-4 <sub>Ph</sub>	129.15	experimen		C-8 <sub>dan</sub>	120.03	119.94	120.01	119.93	experimen	
C-3 <sub>Ph</sub>	127.11	the NMR (		C-3 <sub>dan</sub>	123.25	123.25	123.28	123.29	the NMR (	
C-2,6 <sub>PhNO2</sub>	129.41	as solvent in		C-7 <sub>dan</sub>	127.89	28.26	28.10	128.18	as solvent in	
C-1 <sub>Ph</sub>	137.66	vas used		lan	1	2	8	с ,	vas used	
C-2 <sub>Ph</sub>	137.13	a. CDCl <sub>3</sub> v	(mdc	C-10 <sub>0</sub>	130.1	130.1	130.0	130.1	a. CDCl <sub>3</sub> v	
C-1 <sub>PhNO2</sub>	142.79	IMBC spectr	r <b>11-14</b> (ð, þ	C-2 <sub>dan</sub>	131.50	131.62	131.50	131.59	IMBC spectr	
C-4 <sub>PhNO2</sub>	150.61	ISQC and H	d groups fo	C-9 <sub>dan</sub>	130.65	130.60	130.54	130.62	HSQC and H	
C-6 <sub>5FU</sub>	129.12 (d, 32.9)	t with the F	and dansy	-4 <sub>dan</sub>	1.34	1.48	1.22	1.37	t with the H	
C-5 <sub>5FU</sub>	141.74 (d, 238.2)	agreemen:	f the purine	dan C	19 13	94 13	34 13	18 13	agreemen	
C-2 <sub>5FU</sub>	150.13	nts are in	AR data of	C-1,	133.	132.5	133.5	133.	nts are in	
C-4 <sub>5FU</sub>	157.05 (d, 26.5)	vift assignme	<b>10.</b> <sup>13</sup> C NN	C-5 <sub>dan</sub>	151.80	151.76	151.85	151.84	iift assignme	
	10	13C sh	Table		11	12	13	14	13 C sh	

**Table 9.** <sup>13</sup>C NMR data for **10** ( $\delta$ , ppm)

Table 11.	• <sup>13</sup> C NMR data	of the remain	ing signals for 1.	<b>1-14</b> ( <i>ô</i> , ppm)											
	C-2 <sub>Ph</sub>	C-1 <sub>Ph</sub>	C-3 <sub>Ph</sub>	C-4 <sub>Ph</sub>	E	C-5 <sub>Ph</sub>	C-6 <sub>Ph</sub>	Ph-CH <sub>2</sub>	N(C	CH3)2	N-CH <sub>2</sub>	N-CH <sub>2</sub> -CI	H <sub>2</sub> CH	2diox	CH <sub>diox</sub>
11	138.18	137.52	128.47	128.91		129.26	128.19	43.90	45.	57	55.04		65.	.14	102.46
12	138.08	137.75	129.14	128.97		129.40	127.30	45.56	46.	98	55.16		65.	.25	101.96
13	137.21	137.00	129.12	128.63	~	129.24	129.04	43.93	45.	55	47.14	32.66	65.	.16	102.20
14	137.24	137.14	129.41	129.07		129.45	127.30	47.32	45.	.56	47.15	32.94	65.	20	102.16
<sup>13</sup> C shift ¿	assignments are ii	n agreement	with the HSQC a	and HMBC spe	sctra. CDCl <sub>3</sub>	was used a	as solvent in th	ne NMR experim€	ent						
	(														
Table 12	. <sup>13</sup> C NMR data 1	for <b>15-20</b> ( $\delta$ , $\beta$	(mdd												
L.		ç	, ,			- L	20	100	חר לח			2		:00	Ü

	C-5 <sub>Ph</sub> C-6 <sub>Ph</sub> C-3,5 <sub>PhNO2</sub> Ph-CH <sub>2</sub> N-CH <sub>2</sub> N-CH <sub>2</sub> -CH <sub>2</sub> CH <sub>2</sub> diox CH <sub>3</sub> -C	127.57 127.37 124.05 61.21 54.76 65.14 101.70 26.00	127.64 126.93 124.31 61.37 47.66 32.77 65.18 102.11 26.20	128.86 127.26 124.27 61.30 55.17 65.18 102.06	128.87 126.75 124.32 61.08 47.63 32.42 65.16 102.02	130.41 111.65 126.02 70.46 46.44 65.44 102.41	130.51 111.05 125.99 70.15 39.09 33.00 64.96 104.14	used as solvent in the NMR experiments for all compounds.	
	C-3 <sub>Ph</sub> C-4 <sub>Ph</sub>	29.40 128.46	29.38 128.77	31.99 129.90	31.73 129.75	30.68 117.56	30.76 116.89	spectra. CDCl <sub>3</sub> was	
	C-2,6 <sub>PhNO2</sub>	129.55 1	129.51 1	129.58 1	1 29.50 1	115.23 1	115.09 1	HSQC and HMBC	
(mdd	C-1 <sub>Ph</sub>	135.88	135.38	137.50	136.38	147.45	147.65	: with the	
- <b>15-20</b> (δ,	C-2 <sub>Ph</sub>	143.35	143.43	142.81	142.78	119.83	119.35	agreement	
MR data for	C-1 <sub>PhNO2</sub>	144.27	144.08	143.36	143.28	142.02	141.87	ents are in a	
י <b>12.</b> <sup>13</sup> C N	C-4 <sub>PhNO2</sub>	150.32	150.41	150.50	150.28	163.44	163.84	ift assignm	
Table		15	16	17	18	19	20	13 <sup>C</sup> sh	

Table	13. <sup>13</sup> C NM	R data for th	e purine and	dansyl grou	ps of <b>21-25</b> (	(mqq ,6										
	C-5 <sub>dan</sub>	C-1 <sub>dan</sub>	C-4 <sub>dan</sub>	C-9 <sub>dan</sub>	C-2 <sub>dan</sub>	C-10 <sub>dan</sub>	C-7 <sub>dan</sub>	C-3 <sub>dan</sub>	C-8 <sub>dan</sub>	C-6 <sub>dan</sub>	C-1 <sub>Ph</sub>	C-2 <sub>Ph</sub>	C-5 <sub>Ph</sub>	C-3 <sub>Ph</sub>	C-4 <sub>Ph</sub>	C-6 <sub>Ph</sub>
21	152.03	135.57	130.68	129.97	129.95	129.74	128.36	123.26	118.95	115.31	137.26	130.38	128.78	128.00	124.22	121.46
22	151.47	134.41	130.67	130.55	131.14	129.98	127.88	123.21	120.46	115.32	136.22	143.00	126.93	127.64	128.63	129.51
23	151.60	134.66	130.60	130.52	131.13	130.06	128.07	123.30	120.50	115.34	135.53	142.90	127.15	127.88	128.66	129.49
24	151.59	133.64	130.99	130.61	131.39	130.05	128.00	123.22	120.34	115.40	138.03	142.86	128.36	131.42	129.17	128.80
25	151.63	133.87	130.85	130.52	131.27	130.06	127.94	123.27	120.33	115.37	136.69	142.62	128.36	131.29	129.11	128.82
<sup>13</sup> C shi	ft assignmen	nts are in agr	eement with	the HSQC ar	nd HMBC sp€	ectra. CDCl₃ м	vas used as s	olvent in the	NMR experi	ments for all	compounds					

**/RC** 

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N-CH2-CH2	CH <sub>2diox</sub>	CH <sub>diox</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	<u>C</u> H <sub>3</sub> -C-Si	C-Si	CH <sub>3</sub> -Si
			45.56	25.94	18.33	-5.26
	64.98	102.20	45.54	26.08	18.43	-5.31
33.01	65.01	102.34	45.59	26.10	16.46	-5.26
	65.03	102.54	45.57			
32.75	65.05	102.26	45.57			
	33.01 32.75	33.01 65.01 33.75 65.05 65.03	64.98 102.20 33.01 65.01 102.34 65.03 102.54 32.75 65.05 102.26	45.56 64.98 102.20 45.54 33.01 65.01 102.34 45.59 65.03 102.54 45.57 32.75 65.05 102.26 45.57	45.56         25.94           64.98         102.20         45.54         26.08           33.01         65.01         102.34         45.59         26.10           65.03         102.54         45.57         26.10           32.75         65.05         102.26         45.57	45.56         25.94         18.33           64.98         102.20         45.54         26.08         18.43           33.01         65.01         102.34         45.59         26.10         16.46           65.03         102.54         45.57         26.10         16.46           32.75         65.05         102.26         45.57



Figure 1. The HMBC interactions in the *N*-9 regioisomers 1-7.



Figure 2. The HMBC interactions in the N-9 (11, 13) and N-7 (12, 14) dansyl derivatives.



Figure 3. The HMBC interactions in the N-9 (8) and N-3 (9) adenine regioisomers.

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## **Supporting Information**

Additional supporting information may be found in the online version of this article at the publisher's web site.



Figure 4. The HMBC interactions in the *N*-1-5-FU (10) regioisomer.