NUCLEOPHILIC SUBSTITUTION REACTION OF CHLOROQUINOLINES WITH 1,2,4-TRIAZOLE. II. SYNTHESIS OF 2-(1H-1,2,4-TRIAZOL-1-YL)QUINOLINES

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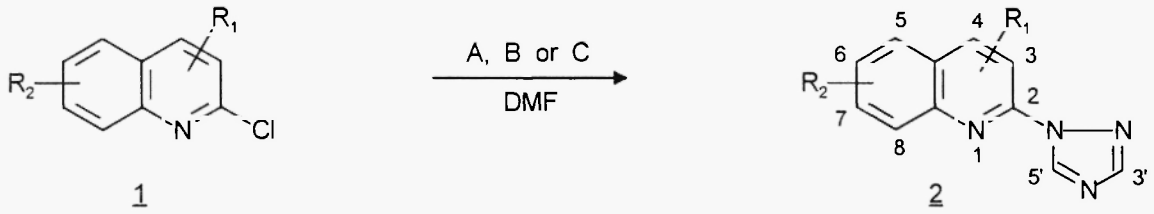
Abstract: Synthesis of 2-(1H-1,2,4-triazol-1-yl)quinolines by the reaction of 2-chloroquinolines with 1,2,4-triazole was studied under neutral, acidic and basic reaction conditions. Significant role of the acid and base catalysis as well as substituent effects on the reactivity of 2-chloroquinolines in these reactions are reported. As a result of this study one can choose the best reaction conditions for the preparation of the title compounds according to the substituents on the quinoline ring.

INTRODUCTION

In the first paper of this series (1) a brief summary of the background and aim of our study has been given and the results related to the 4-chlorquinolines have been reported. In this paper the results concerning the nucleophilic substitution reaction of 2-chloroquinolines with 1,2,4-triazole are reported.

RESULTS AND DISCUSSION

There are some well known differences in behaviour of 2-chloro- and 4-chloroquinoline in nucleophilic substitution reactions. The two major ones are that 2-chloroquinoline has less tendency to show acid catalytic or autocatalytic effect when treated with amines (2, 3), but shows higher reactivity toward methoxide ions (2) than 4-chloroquinoline. The same general methods were used as in our previous work (1) in order to establish the main characteristic features of the reaction of 2-chloroquinolines with 1,2,4-triazole, and to reveal similarities and differences between 4-chloro- and 2-chloro-quinolines in this reaction with special regard to the role of acid and base catalysis and effect of the substituents on the reactivity. Accordingly, 2-chloroquinolines were reacted with 1,2,4-triazole (method A), or with 1,2,4-triazole in the presence of hydrochloric acid (method B), or with sodium salt of 1,2,4-triazole (method C).



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A: 1,2,4-triazole; B: 1,2,4-triazole, HCl; C: 1,2,4-triazole-Na

The substituents of the 2-chloroquinolines investigated herein were chosen with sufficiently different electronic character ranging from the electron-releasing to strong electron-withdrawing groups to illustrate their large effect on the reactivity. The reactions were carried out in dimethylformamide solution at a temperature chosen in accordance with the reactivity of the substrate, and the progress of the reactions was monitored by tic generally until all the starting 2-chloroquinoline derivative had been consumed. The reaction time and the temperature data together with the product yields are gathered in Table1.

Table 1. Preparation of 2-(1H-1,2,4-triazol-1-yl)quinolines (2a - 2s)

Com-pound	R_1	R_2	Method	Temperature (°C)	Time[a] (h)	Yield[b] (%)	mp (°C) /Cryst. solv./	$k \cdot 10^5$ ($l \cdot mol^{-1} \cdot s^{-1}$)
2a	H	H	A	100	16	53	108 - 110	
			B	100	2.5	54	/ethanol -	
			C	100	12	73	hexane/	13.9
2b	4-Me	H	A	100	8	72	118 - 119	
			B	100	1.5	81	/ethanol/	
			C	100	25	67		7.31
2c	3-Me	H	A	100	12	63	87 - 89	
			B	100	1	69	/ethanol -	
			C	100	22	74	water/	9.32
2d	3-Et	H	A	100	18	68	69 - 70	
			B	100	3	66	/ethanol -	
			C	100	30	79	water/	5.53
2e	3-Ph	H	A	100	40	75	172 - 173	
			B	100	7	81	/ethanol/	
			C	100	15	85		14.7
2f	3-Me	6-Me	A	100	15	64	93 - 95	
			B	100	3	74	/ethanol/	
			C	100	40	78		2.69
2g	3-Me	7-Me	A	100	18	66	80 - 82	
			B	100	2	76	/ethanol/	
			C	100	25	82		7.8
2h	3-Me	8-Me	A	100	>50	—	95 - 97	
			B	100	12	67	/ethanol/	
			C	100	45	82		2.32
2i	3-Me	8-Et	A	100	>50	—	82 - 84	
			B	100	22	72	/ethanol/	
			C	100	45	76		2.24
2j	3-Me	6-MeO	A	100	25	70	150 - 152	
			B	100	5	71	/chloroform -	
			C	100	>50	—	ethanol/	1.22
2k	3-Me	6-Cl	A	100	16	78	154 - 155	
			B	100	3	82	/chloroform -	
			C	100	4	86	ethanol/	69.1

Table 1 (continued)

Compound	R_1	R_2	Method	Temperature (°C)	Time[a] (h)	Yield[b] (%)	mp (°C) /Cryst. solv./	$k \cdot 10^5$ ($l \cdot mol^{-1} \cdot s^{-1}$)
2l	3-Me	7-Cl	A	100	14	75	137 - 138	
			B	100	3	76	/chloroform -	
			C	100	3	86	ethanol/	79.0
2m	3-Me	6-F	A	100	18	70	168 - 170	
			B	100	4	72	/chloroform -	
			C	100	20	72	ethanol/	10.6
2n	3-Me	7-F	A	100	12	67	133 - 134	
			B	100	2	70	/ethanol/	
			C	100	4	69		47.9
2o	3-Me	5,6-Cl_2	A	100	>50	52[c]	182 - 183	
			B	100	5	81	/chloroform -	
			C	100	0.5	82	ethanol/	398.3
			C	90	1	82		153.1
2p	3-Me	6-NO_2	A	100	9	83	186 - 187	
			B	100	2	82	/DMSO -	
			C	50	1	87	ethanol/	169.5
			C	60	0.5	86		312.2
			C	100	—	—		(2591.1)[d]
2r	3-CN	H	A	100	24	78	228 - 229	
			B	100	3	81	/DMSO -	
			C	25	4	83	ethanol/	41.3
2s	4-CCl_3	7-Cl	A	100	15	69	181 - 183	
			B	100	3	75	/chloroform -	
			C	25	9	76	ethanol/	21.7

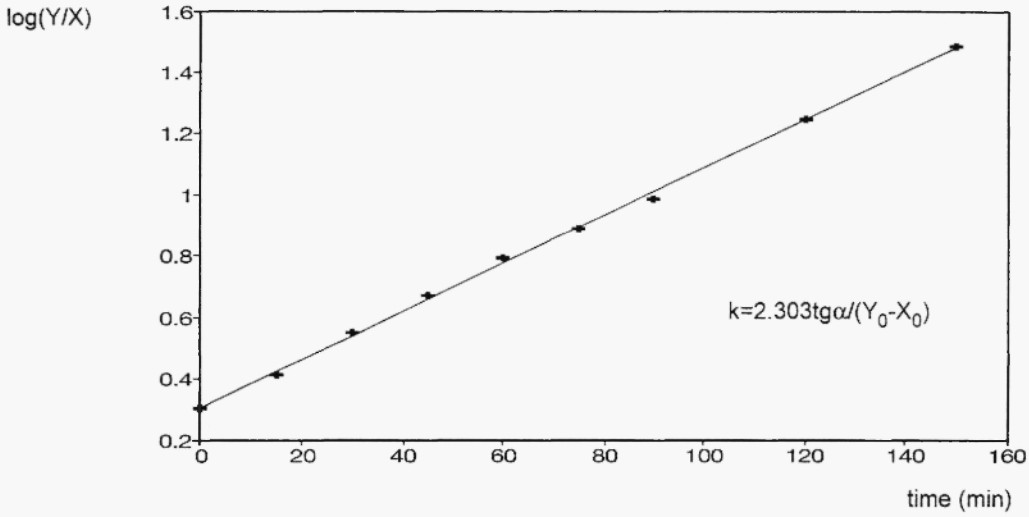
a) Time required to the consumption of the starting chloroquinoline (tlc); b) Yield of recrystallized product; c) Separation from the starting matrial was performed by column chromatography; d)The value in parentheses was calculated by Arrhenius equation

In case of acid catalytic (method B) and autocatalytic (method A) conditions the rate constants could not be determined because the reaction follows a complex kinetic due to increase of hydrochloric acid concentration as the reaction proceeds. Consequently, the reactivity of differently substituted 2-chloroquinolines in these conditions may be characterized only qualitatively by comparison of the reaction time data required to the consumption of the starting 2-chloroquinoline at the same temperature.

In case of method C, when 2-chloroquinolines were treated with the sodium salt of 1,2,4-triazole, the absence of the autocatalytic effect provided an opportunity for the determination of the rate constants. It was carried out by gc determination of the 2-chloroquinoline concentration during the reaction. As expected (4), the reaction follows a second order kinetic because the second order diagrams were found to be linear in the investigated ranges (Figure 1) and the rate constants independent of the initial reactant concentrations. The second-order rate constants (Table 1) are useful for precise characterization of the reactivity of 2-chloroquinolines toward triazole anion.

From the data shown in Table 1 some interesting conclusions can be drawn regarding the characteristic features of the reaction of 2-chloroquinolines with 1,2,4-triazole both in neutral or acidic and in basic conditions. First of all, comparing the reaction time and temperature data for 2-chloroquinoline and 4-chloroquinoline (data were given in the previous paper) (1), it can be seen that the former has a lower reactivity toward 1,2,4-triazole than the latter both in autocatalytic (method A) and in acid catalytic (method B) conditions. On the contrary, 2-chloroquinoline shows higher reactivity toward triazole anion than its 4-chloro isomer. These differences in the reactivity are consistent with the earlier observations (2, 3) and can be attributed to their structural differences. Due to the much stronger base-weakening effect of chlorine in the 2-position than in the 4-position, 2-chloroquinoline is a much weaker base (5) and hence shoud have lower reactivity under acid catalytic or autocatalytic conditions than its 4-chloro isomer. On the other hand, owing to the adjacent nitrogen atom, the reacting carbon centre in 2-chloroquinoline should have a higher electron defficiency than in 4-chloroquinoline, and this difference can account for the higher reactivity of the former toward triazole anion.

Figure 1: Determination of the rate constant for 2,7-dichloro-3-methylquinoline (11) in method C



It is a bit surprising that in spite of the fact discussed above, acid catalysis is still generally effective in the reaction of 2-chloroquinolines with 1,2,4-triazole even in the presence of strong electron-withdrawing substituents. Although, basicity data are not available, it seems to be probable that CN and CCl_3 groups at 3- and 4-positions do not lower the basicity of 2-chloroquinoline in such an extent than 2-CCl_3 group of 4-chloroquinoline (1).

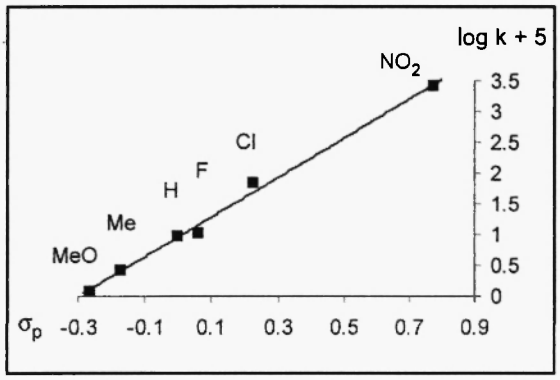
From the data related to autocatalytic (method A) or acid catalytic (method B) conditions no simple relationship can be set up between the known electronic properties and the observed activating effect of the substituents investigated because they exert their effect on the reactivity in two opposite ways. Electron-withdrawing groups, though, increase the electron deficincy at the reacting carbon centre so that they should enhance the reactivity, but at the same time they lower the basicity and hence the concentration of the reactive quinolinium ion, decreasing hereby the rate of the reaction. Electron-releasing groups exert the opposite effects. The opposing factors nearly balance each other, so it is possible that 2-chloroquinolines having so widely different substituents such as CH_3 Cl, CH_3O, F, NO_2 at 6-position or CH_3 and CCl_3 at 4-position show nearly the same reactivity in method A or in method B.

In addition to the electronic effect of the substituents their steric effects also influence the reactivity. Thus, steric hindrance can be partly accounted for the decrease in reactivity when introducing a more bulky (Et, Ph) group instead of methyl to the 3-position. Then again, the well known effect of steric inhibition of solvation (6,1) should be responsible for the much lower reactivity of 2-chloro-6,8-dimethylquinoline than its 6-methyl isomer.

In case of method C the reactivity of differently substituted 2-chloroquinolines can be precisely characterised using the rate constants (Table 1) and the effects of the substituents on the reactivity can be interpreted on the basis of electronic theory of substituent effects in aromatic systems. Alkyl and methoxy groups at all the positions investigated decrease the reactivity because of their electron-releasing property. Conversely, electron-withdrawing groups (Cl, F, NO_2, CN, CCl_3) facilitate the reaction by means of increasing the electron defficiency at the site of displacement. For quantitative treatments we investigated the correlation of the reactivity data (log k) at 100 °C for 6- and 7-substituted 2-chloroquinolines with the known (7) Hammett's σ parameters (Figure 2). For the substituents at 7-position the correlation was found to be much better with σ_m than with σ_p, but the log k data for the 6-substituted 2-chloroquinolines correlate well only with the σ_p parameters. This result is in a good agreement with the earlier observations concerning the substituent effects in the methoxy-dechlorination reaction of 2-chloroquinolines where 6-position was found to be "conjugative" contrarily to the "non-conjugative" 7-position (5).

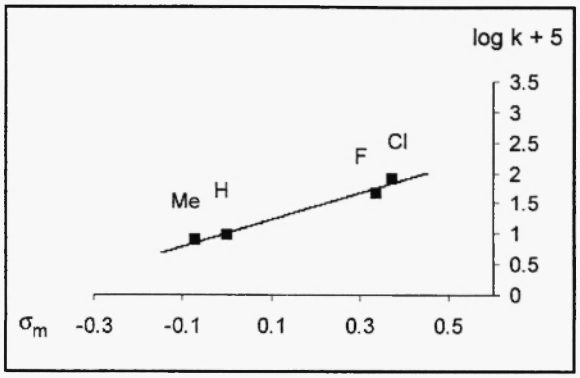
Figure 2: Correlation of reactivity data (log k) with Hammett's σ parameters for the reaction of 2-chloro-3-methyl-quinolines with the sodium salt of 1,2,4-triazole at 100 °C

2-chloro-3-methyl-6-substituted-quinolines



log k = 3.20 σ_p - 4.04 (r = 0.997)

2-chloro-3-methyl-7-substituted-quinolines



log k = 2.20 σ_m - 3.99 (r = 0.992)

To summarize our observations with respect to preparative efficacy of the three general methods described here, we can say that acid catalysis is generally effective in case of wide variety of substituents investigated, but 2-chloroquinolines having strong electron-withdrawing substituents react usually faster and give better yields when treated with the sodium salt of 1,2,4-triazole. As a result of our investigation one can choose the best reaction conditions for the preparation of the title products according to the substituent(s) on the quinoline ring.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. The ^{1}H-nmr spectra were recorded on a Varian Gemini-200 instrument at 200 MHz in deuteriochloroform solution using TMS as internal standard and chemical shifts are expressed in ppm. Mass spectra were scanned on a VG TRIO-2 spectrometer in EI mode at 70 eV.

Materials: 1H-1,2,4-triazole was purchased from Fluka Chemie AG; 2-chloroquinoline derivatives were prepared according to previously described procedures: 1a (8), 1b (9), 1c-p (10, 11), 1r (12), 1s (13). Preparation of 1,2,4-triazole hydrochloride and sodium salt of 1,2,4-triazole was described in our previous paper (1).

Preparation of 2-(1H-1,2,4-triazol-1-yl)quinolines (2a - s). General Procedures.

The corresponding 2-chloroquinoline derivative (1) (0.01 mol) was treated in dimethylformamide (10 ml) with 1.38 g (0.02 mol) of 1,2,4-triazole (method A), or with the mixture of 0.69 g (0.01 mol) of 1,2,4-triazole and 1.06 g (0.01 mol) of 1H-1,2,4-triazole hydrochloride (method B), or with 1.82 g (0.02 mol) of sodium salt of 1,2,4-triazole (method C) at a temperature given in Table 1. The reaction mixture was worked up by pouring into water (50 ml) and neutralization with aqueous sodium hydroxide solution (method A and B) or hydrochloric acid solution (method C). The precipitated product was collected, washed with water and dried. The crude product was recrystallized from the solvent or solvent mixture given in Table 1.

Kinetic experiments - The corresponding 2-chloroquinoline derivative (1) (0.01 mol) was dissolved in dimethylformamide (20 ml) and 1.0 g of N-methylformanilide (internal standard) was added to this solution. The mixture was immersed into a constant temperature bath regulated by a thermostat, and the internal temperature was adjusted to the desired value (Table 1). Sodium salt of 1,2,4-triazole (1.82 g, 0.02 mol) was then added and the reaction was followed by gc. The first sample (1 ml) was taken immediately after addition of sodium salt of 1,2,4-triazole. This sample was added into a 25 ml volumetric flask containing 15 ml of ethanol, then the flask was filled up with ethanol to the mark. The initial concentration of the chloroquinoline (X_o) was determined by gc using calibration curve. Further samples (ca. 0.1 ml) were withdrawn at appropriate time intervals, diluted with ethanol, and the actual concentration of the chloroquinoline (X) was calculated on the basis of the peak area of the chloroquinoline and the internal standard.

The calculation of the rate constants was based upon the equation: $\ln(X_oY/Y_oX)=(Y_o-X_o)kt$, in which X_o and Y_o mean the concentration of the chloroquinoline and the sodium salt of 1,2,4-triazole at the zero time ($Y_o=2X_o$), X and Y mean their concentration in time t ($Y=X_o+X$).

The second order rate constants were determined from the plots log(Y/X) vs. time by the method of least squares (Figure 1) and are given in Table 1.

Table 2. ^{1}H-nmr and Mass Spectral Data of Compounds 2a - s

Compound	^{1}H-nmr δ (ppm), J (Hz)	MS[a] m/e (%)
2a	7.56 (td, 1H, J_1=8.0, J_2=6.9, J_3=1.1, 6-H), 7.76 (td, 1H, J_1=8.4, J_2=6.9, J_3=1.5, 7-H), 7.85 (dd, 1H, J_1=8.0, J_2=1.5, 5-H), 8.03 (dd, 1H, J_1=8.4, J_2=1.1, 8-H), 8.06 (d,1H, J= 8.8, 3-H), 8.14 (s, 1H, 3'-H), 8.35 (d, 1H, J=8.8, 4-H), 9.37 (s, 1H, 5'-H)	196 (M^+, 100)
2b	2.77 (s, 3H, 4-CH_3), 7.57 (td,1H, J_1=8.1, J_2=7.1, J_3=1.1, 6-H), 7.74 (td, 1H, J_1=8.3, J_2=7.0, J_3=1.4, 7-H), 7.91 (s, 1H, 3H), 8.00 (dd, 1H, J_1=8.1, J_2=1.4, 5-H), 8.02 (dd, 1H, J_1=8.3, J_2=1.1, 8-H), 8.13 (s, 1H, 3'-H), 9.35 (s, 1H, 5'-H)	210 (M^+, 100)
2c	2.67 (s, 3H, 3-CH_3), 7.57 (td, 1H, J_1=8.1, J_2=6.9, J_3=1.3, 6-H), 7.72 (td, 1H, J_1=8.5, J_2=6.9, J_3=1.6, 7-H), 7.81 (dd, 1H, J_1=8.1, J_2=1.5, 5-H), 8.02 (dd, 1H, J_1=8.5, J_2= 1.2, 8-H), 8.14 (s, 1H, 4-H), 8.15 (s, 1H, 3'-H), 9.02 (s,1H, 5'-H)	210 (M^+, 100)

Table 2 (continued)

Compound	^{1}H-nmr δ (ppm), J (Hz)	MS[a] m/e (%)
2d	1.25 (t, 3H, J=7.4, CH_3), 3.10 (q, 2H, J=7.4, CH_2), 7.59 (td, 1H, J_1=8.1, J_2=7.0, J_3= 1.1, 6-H), 7.73 (td, 1H, J_1=8.4, J_2=7.0, J_3=1.5, 7-H), 7.85 (dd, 1H, J_1=8.1, J_2=1.5, 5-H), 8.04 (dd, 1H, J_1=8.4, J_2=1.1, 8-H), 8.16 (s, 1H, 4-H), 8.18 (s, 1H, 3'-H), 8.97 (s, 1H, 5'-H)	224 (M^+,74) 154 (100)
2e	7.18 - 7.28 (m, 3H, Ph-H), 7.35 - 7.42 (m, 2H, Ph-H), 7.66 (td, 1H, J_1=8.1, J_2=7.0, J_3=1.2, 6-H), 7.82 (td, 1H, J_1=8.4, J_2=7.0, J_3=1.5, 7-H), 7.94 (dd, 1H, J_1=8.1, J_2= 1.5, 5-H), 8.00 (s, 1H, 3'-H), 8.18 (dd, 1H, J_1=8.4, J_2=1.2, 8-H), 8.34 (s, 1H, 4-H), 8.45 (s, 1H, 5'-H)	271 (M^+, 100)
2f	2.52 (s, 3H, 6-CH_3), 2.62 (s, 3H, 3-CH_3), 7.50 (dd, 1H, J_1=9.1, J_2=1.6, 7-H), 7.53 (d, 1H, J=1.6, 5-H), 7.85 (d, 1H, J=9.1, 8-H), 7.95 (s, 1H, 4-H), 8.15 (s, 1H, 3'-H), 8.97 (s, 1H, 5'-H)	224 (M^+, 100)
2g	2.55 (s, 3H, 7-CH_3), 2.65 (s, 3H, 3-CH_3), 7.37 (dd, 1H, J_1=8.5, J_2=1.4, 6-H), 7.67 (d, 1H, J=8.5, 5-H), 7.77 (d, 1H, J=1.4, 8-H), 8.05 (s, 1H, 4-H), 8.15 (s, 1H, 3'-H), 9.00 (s, 1H, 5'-H)	224 (M^+, 100)
2h	2.69 (s, 3H, 3-CH_3), 2.73 (s, 3H, 8-CH_3), 7.43 (dd, 1H, J_1=8.1, J_2=6.5, 6-H), 7.53 (dd, 1H, J_1=6.5, J_2=1.7, 7-H), 7.62 (dd, 1H, J_1=8.1, J_2=1.7, 5-H), 8.08 (s, 1H, 4-H), 8.14 (s, 1H, 3'-H), 9.07 (s, 1H, 5'-H)	224 (M^+, 85)
2i	1.36 (t, 3H, J=7.5, CH_3), 2.70 (s, 3H, 3-CH_3), 3.23 (q, 2H, J=7.5, CH_2), 7.47 (dd, 1H, J_1=7.7, J_2=7.0, 6-H), 7.54 (dd,1H, J_1=7.0 J_2=1.8, 7-H), 7.62 (dd, 1H, J_1=7.7, J_2=1.8, 5-H9, 8.10 (s, 1H, 4-H), 8.14 (s, 1H, 3'-H), 9.07 (s, 1H, 5'-H)	238 (M^+, 100)
2j	2.64 (s, 3H, 3-CH_3), 3.94 (s, 3H, 6-OCH_3), 7.06 (d, 1H, J=2.8, 5-H), 7.37 (dd, 1H, J_1=9.2, J_2=2.8, 7-H), 7.92 (d, 1H, J=9.2, 8-H), 8.03 (s, 1H, 4-H), 8.14 (s, 1H, 3'-H), 8.93 (s, 1H, 5'-H)	240 (M^+, 100)
2k	2.72 (s, 3H, 3-CH_3), 7.65 (dd, 1H, J_1=9.1, J_2=2.2), 7-H), 7.80 (d, 1H, J=2.2, 5-H), 7.95 (d, 1H, J=9.1, 8-H), 8.05 (s, 1H, 4-H), 8.15 (s, 1H, 3'-H), 9.06 (s, 1H, 5'-H)	244 (M^+, 63) 140 (100)
2l	2.70 (s, 3H, 3-CH_3), 7.52 (dd, 1H, J_1=8.9, J_2=2.0, 6-H), 7.75 (d, 1H, J=8.9, 5-H), 8.02 (d, 1H, J=2.0, 8-H), 8.13 (s, 1H, 4-H), 8.16 (s,1H, 3'-H), 9.06 (s, 1H, 5'-H)	244 (M^+, 52) 140 (100)
2m	2.68 (s, 3H, CH_3), 7.38 - 7.54 (m, 2H, 5-H +7-H), 8.02 (dd, 1H, J_1=9.1, J_2=5.3, 8-H), 8.09 (s, 1H, 4-H), 8.16 (s, 1H, 3'-H), 9.00 (s, 1H, 5'-H)	228 (M^+, 100)
2n	2.68 (s, 3H, CH_3), 7.35 (ddd, 1H, J_1=9.3, J_2=9.0, J_3=2.5, 6-H), 7.63 (dd, 1H, J_1= 9.8, J_2=2.5, 8-H), 7.80 (dd, 1H, J_1=9.0, J_2=6.0, 5-H), 8.13 (s, 1H, 4-H), 8.16 (s, 1H, 3'-H), 9.05 (s, 1H, 5'-H)	228 (M^+, 100)
2o	2.80 (s, 3H, CH_3), 7.75 (d, 1H, J=9.1, 7-H), 7.90 (d, 1H, J=9.1, 8-H), 8.17 (s,1H, 3'-H), 8.56 (s, 1H, 4-H), 9.11 (s, 1H, 5'-H)	278 (M^+, 88) 174 (100)
2p	2.83 (s, 3H, 3-CH_3), 8.15 (d, 1H, J=9.2, 8-H), 8.19 (s, 1H, 3'-H), 8.35 (s, 1H, 4-H), 8.48 (dd, 1H, J_1=9.2, J_2=2.2, 7-H), 8.78 (d, 1H, J=2.2, 5-H), 9.19 (s, 1H, 5'-H)	255 (M^+, 81) 225(100)
2r	7.73 (td, 1H, J_1=8.0, J_2=6.7, J_3=1.0, 6-H), 7.92 - 8.01 (m, 2H, 5-H+7-H), 8.11 (dd, 1H, J_1=8.4, J_2=1.0, 8-H), 8.26 (s, 1H, 3'-H), 8.81(s, 1H, 4-H), 9.30 (s, 1H, 5'-H)	221 (M^+, 100)
2s	7.66 (dd, 1H, J_1=9.2, J_2=2.2, 6-H), 8.16 (d, 1H, J=2.2, 8-H), 8.20 (s, 1H, 3'-H), 8.70 (d, 1H, J=9.2, 5-H), 8.82 (s, 1H, 3'-H), 9.38 (s, 1H, 5'-H)	346 (M^+, 35) 313 (100)

a) The elemental analyses for C, H and N were within +/- 0.4 % of the theoretical values for all new compounds.

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