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# Spectral Assignments and Reference Data

## Synthesis and structure elucidation of five series of aminoflavones using 1D and 2D NMR spectroscopy

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**Twenty-six new aminoflavones have been synthesised by two different methods and the structure elucidation was accomplished using extensive 1D ($^1$H, $^{13}$C) and 2D NMR spectroscopic studies (COSY, HSQC and HMBC experiments). Copyright © 2006 John Wiley & Sons, Ltd.**

**KEYWORDS:** NMR; $^1$H NMR; $^{13}$C NMR; HMBC; nitroflavones; aminoflavones

## INTRODUCTION

During the past decades, there has been a growing interest in the search for biologically active compounds. Synthesis of flavones and their derivatives have attracted considerable attention owing to their significant pharmaceutical,[1–4] biocidal[5–7] and antioxidant[8,9] activities.

Flavones (2-phenylchromones) are one of the most important classes of natural compounds belonging to the flavonoid family.[10] Recently, it has been reported that some synthetic aminoflavones are potential antineoplastic agents[11] and have been proved to be antimutagenic in the Ames test using different species of mutagens.[12] They also exhibit potent cytotoxicity against human breast cancer.[13]

Taking into account the potential biological applications of flavones, especially those having amino-substituents, we decided to devote some attention to the reduction of five series of nitroflavones once synthesised.[14] Compounds **2a–z** were prepared by two different methods: (i) ammonium formate, Pd/C, using methanol as solvent; (ii) $SnCl_2.2H_2O$/HCl, using acetic acid as solvent.

In this paper, we present the synthesis of aminoflavones, and unambiguous structural elucidation of compounds **2a–z** by one-dimensional (1D) and two-dimensional (2D) NMR experiments.

## EXPERIMENTAL

The $^1$H and $^{13}$C NMR spectra were recorded at 25 °C for ~5-mg samples dissolved in 0.5 ml of $CDCl_3$ or DMSO-$d_6$ in 5-mm NMR tubes, using a Bruker DRX 300 spectrometer (300.13 for $^1$H and 75.47 for $^{13}$C). Chemical shifts ($\delta$) were reported in ppm and coupling constants ($J$) in Hz. The internal standard was TMS. The Fourier transform NMR measurement conditions were as follows: for 1H NMR, pulse with 3.4 μs, acquisition time 2.7 s, pulse angle 30° and number of scans 80; for $^{13}$C NMR, pulse with 1.7 ms, acquisition time 0.8 s, pulse angle 30°, number of scans 6144 and number of data points 16 384. Unequivocal $^{13}$C assignments were made with the aid of 2D *g*HSQC and *g*HMBC (delays for one bond and long-range $J$ C/H couplings were optimised for 147 and 7 Hz, respectively) experiments.

### Materials

The syntheses for compounds **1a–z** have been published elsewhere.[14]

Once the nitroflavones **1a–z** were obtained, the two reduction methods were applied in the synthesis of new derivatives of flavones, with amino substituents on the B ring, with the purpose of verifying which of them was more adequate in terms of yields and practical execution (Table 1).

Comparing the two synthetic pathways to obtain aminoflavones **2a–z**, one can conclude that: (i) the approach involving ammonium formate, Pd/C, is generally more favourable, in terms of yields and practical execution; for these reasons, it was the method applied to all compounds, and the method using stannous chloride only applied to the first series of compounds (without substituents on the A ring); (ii) the diamino derivatives were obtained in lower yields than the other derivatives (49–58%); (iii) *orto*-aminoflavones were obtained in moderate yields (59–69%), with the exception of 2′-amino-6-bromoflavone **2x**, which was obtained in 80% of the yield; all the other derivatives were obtained in similar yields; *meta*-aminoflavones **2b, 2e, 2h** and **2k** (68–79%); *para*-aminoflavones **2c, 2f, 2i** and **2l** (64–76%); 3′-amino-2′-methylflavones **2m, 2r** (64–70%); 3′-amino-4′-methylflavones **2p, 2n, 2s** and **2u** (65–79%).

## RESULTS AND DISCUSSION

The full characterisation of compounds **2a–z** is presented in Tables 2–5. The compounds are grouped in five different series.

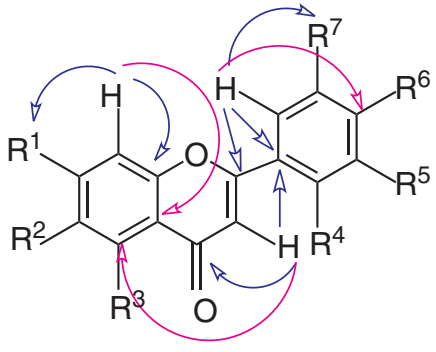
The $^1$H NMR spectra of the compounds were well resolved and the unambiguous proton chemical-shift assignments were based on the multiplicity pattern of proton resonances and also on the use of homonuclear $^1$H–$^1$H COSY spectra. From the NMR spectra of flavones **2a–z,** one can find some typical proton and carbon resonances, namely, those of H-3 (singlet at $\delta$ 6.36–6.86 ppm), C-3 ($\delta$ 160.9–167.0 ppm) and C-4 ($\delta$ 175.6–178.6 ppm). The C-4 assignment was based on their high-frequency value, since it is the most deshielded carbon atom of flavones **2a–z**, while that of C-3 was based on the correlation with H-3 in the HSQC of **2a–z**. The assignments of all carbon resonances of flavones **2a–z** were based on the analysis of the HSQC and HMBC spectra (Fig. 1, shows some of the typical connectivities found in their HMBC spectra).

Taking **2r** (3′-amino-2′-methyl-5-methoxyflavone) (Fig. 2(a)) as an example, we can identify in $^1$H NMR spectra, four singlets at $\delta$ 2.21, $\delta$ 3.81, $\delta$ 4.01 and $\delta$ 6.36 ppm, corresponding to $CH_3$, $NH_2$, $OCH_3$ and H-3, respectively (Fig. 2(b)).

To confirm the assignments made from HSQC and COSY spectra and to deduce more information about the structure of flavone **2r**, a 2D HMBC spectrum was recorded (Fig. 3).

From this spectrum we can conclude that:

(i) the protons from the methoxyl group at $\delta$ 4.01 ppm show long-range correlation with the carbon resonance for C-5 at $\delta$ 159.8 ppm; (ii) the protons from the methyl group at $\delta$ 2.21 ppm show long-range correlations with the carbon resonances for C-3′ at $\delta$ 145.4 ppm, C-1′ at $\delta$ 130.3 ppm and C-2′ at $\delta$ 120.5 ppm; (iii) H-3 signal at $\delta_{H-3}$ 6.36 ppm is correlated with the carbon resonances for C-2, C-1′ and C-10, at $\delta$ 164.2 ppm, 130.3 ppm and 114.5 ppm, respectively. The C-10 signal is also correlated with the H-6 and H-8 resonances at $\delta$ 6.84 and 7.04 ppm. Unambiguous conectivities from these signals




**2 a-z**

**Figure 1.** Typical connectivities found in the flavones HMBC spectra.

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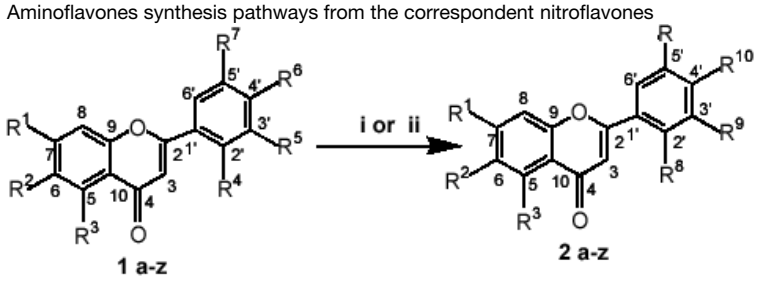
**Table 1.** Aminoflavones synthesis pathways from the correspondent nitroflavones




i) $SnCl_2.2H_2O$, HCl (Conc); AcOH; 90 °C
ii) $HCO_2NH_4$; Pd/C, MeOH, room temp.

| | | | | 1 | | | | 2 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | $R^7$ | $R^8$ | $R^9$ | $R^{10}$ | $R^{11}$ |
| a) | H | H | H | $NO_2$ | H | H | H | $NH_2$ | H | H | H |
| b) | H | H | H | H | $NO_2$ | H | H | H | $NH_2$ | H | H |
| c) | H | H | H | H | H | $NO_2$ | H | H | H | $NH_2$ | H |
| m) | H | H | H | Me | $NO_2$ | H | H | Me | $NH_2$ | H | H |
| n) | H | H | H | H | $NO_2$ | Me | H | H | $NH_2$ | Me | H |
| o) | H | H | H | H | $NO_2$ | H | $NO_2$ | H | $NH_2$ | H | $NH_2$ |
| d) | OMe | H | H | $NO_2$ | H | H | H | $NH_2$ | H | H | H |
| e) | OMe | H | H | H | $NO_2$ | H | H | H | $NH_2$ | H | H |
| f) | OMe | H | H | H | H | $NO_2$ | H | H | H | $NH_2$ | H |
| p) | OMe | H | H | H | $NO_2$ | Me | H | H | $NH_2$ | Me | H |
| q) | OMe | H | H | H | $NO_2$ | H | $NO_2$ | H | $NH_2$ | H | $NH_2$ |
| g) | H | OMe | $NO_2$ | H | H | H | H | $NH_2$ | H | H | H |
| h) | H | OMe | H | $NO_2$ | H | H | H | H | $NH_2$ | H | H |
| i) | H | OMe | H | H | $NO_2$ | H | H | H | H | $NH_2$ | H |
| r) | H | H | OMe | Me | $NO_2$ | H | H | Me | $NH_2$ | H | H |
| s) | H | H | OMe | H | $NO_2$ | Me | H | H | $NH_2$ | Me | H |
| t) | H | H | OMe | H | $NO_2$ | H | $NO_2$ | H | $NH_2$ | H | $NH_2$ |
| j) | OMe | H | OMe | $NO_2$ | H | H | H | $NH_2$ | H | H | H |
| k) | OMe | H | OMe | H | $NO_2$ | H | H | H | $NH_2$ | H | H |
| l) | OMe | H | OMe | H | H | $NO_2$ | H | H | H | $NH_2$ | H |
| u) | OMe | H | OMe | H | $NO_2$ | Me | H | H | $NH_2$ | Me | H |
| v) | OMe | H | OMe | H | $NO_2$ | H | $NO_2$ | H | $NH_2$ | H | $NH_2$ |
| x) | H | Br | H | $NO_2$ | H | H | H | $NH_2$ | H | H | H |
| y) | H | Br | H | H | $NO_2$ | H | H | H | $NH_2$ | H | H |
| w) | H | Br | H | H | H | $NO_2$ | H | H | H | $NH_2$ | H |
| z) | H | Br | H | H | $NO_2$ | H | $NO_2$ | H | $NH_2$ | H | $NH_2$ |




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**Table 2.** $^1$H NMR chemical shifts ($\delta$, ppm), multiplicities and coupling constants ($J$, Hz) for compounds **2a–f** and **2m–q**

| | H-3 | H-5 | H-6 | H-7 | H-8 | H-2′ | H-3′ | H-4′ | H-5′ | H-6′ | $CH_3$ | $OCH_3$ | $NH_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **a** | 6.79 s | 8.23 dd | 7.42 dt | 7.70 dt | 7.56 dd | – | 7.23–7.26 m | 7.29–7.31 m | 6.83–6.87 m | 7.29–7.31 m | – | – | 3.92 s |
| | – | $J$ = 1.7; 8.0 | $J$ = 1.0; 8.0 | $J$ = 1.7; 8.0 | $J$ = 1.0; 8.0 | – | – | – | – | – | – | – | – |
| **b** | 6.81 s | 8.05 dd | 7.50 dt | 7.83 dt | 7.72 dt | 7.24 s | – | 6.77–6.80 m | 7.20–7.22 m | 7.20–7.22 m | – | – | 5.43 s |
| | – | $J$ = 1.6; 7.8 | $J$ = 1.0; 7.8 | $J$ = 1.6; 7.8 | $J$ = 1.0; 7.8 | – | – | – | – | – | – | – | – |
| **c** | 6.74 s | 8.00 dd | 7.45 dt | 7.76 ddd | 7.71 dt | 7.81 d | 6.68 d | – | 6.68 d | 7.81 d | – | – | 6.05 s |
| | – | $J$ = 1.5; 7.7 | $J$ = 1.0; 7.7 | $J$ = 1.5; 7.7; 8.3 | $J$ = 1.0; 8.3 | $J$ = 8.7 | $J$ = 8.7 | – | $J$ = 8.7 | $J$ = 8.7 | – | – | – |
| **m** | 6.36 s | 8.10 dd | 7.50 t | 7.80 dt | 7.63 d | – | – | 6.85 d | 7.05 d | 6.77 d | 2.12 s | – | 6.05 s |
| | – | $J$ = 1.6; 7.8 | $J$ = 7.8 | $J$ = 1.6; 7.8 | $J$ = 7.8 | – | – | $J$ = 7.9 | $J$ = 7.9 | $J$ = 7.9 | – | – | – |
| **n** | 6.77 s | 8.23 dd | 7.41 t | 7.69 ddd | 7.55 d | 7.23 s | – | – | 7.18 d | 7.27 d | 2.24 s | – | 3.83 s |
| | – | $J$ = 1.4; 7.9 | $J$ = 7.9 | $J$ = 1.4; 7.9; 8.3 | $J$ = 8.3 | – | – | – | $J$ = 7.7 | $J$ = 7.7 | – | – | – |
| **o** | 6.58 s | 8.04 dd | 7.46–7.51 m | 7.81 ddd | 7.65 d | 6.45 d | – | 6.04 t | – | 6.45 d | – | – | 5.07 s |
| | – | $J$ = 1.6; 7.7 | – | $J$ = 1.6; 7.7; 8.2 | $J$ = 8.2 | $J$ = 1.8 | – | $J$ = 1.8 | – | $J$ = 1.8 | – | – | – |
| **d** | 6.70 s | 8.12 d | 7.19 dd | – | 6.97 d | – | 7.00 d | 7.31 t | 6.84–6.90 m | 7.28 d | – | 3.29 s | – |
| | – | $J$ = 8.8 | $J$ = 1.0; 8.8 | – | $J$ = 1.0 | – | $J$ = 7.0 | $J$ = 7.0 | – | $J$ = 7.9 | – | – | – |
| **e** | 6.71 s | 8.13 d | 7.00 dd | – | 6.95 d | 7.20 s | – | 6.81–6.85 m | 7.27–7.29 m | 7.27–7.29 m | – | 3.93 s | – |
| | – | $J$ = 8.7 | $J$ = 2.3; 8.8 | – | $J$ = 2.3 | – | – | – | – | – | – | – | – |
| **f** | 6.63 s | 7.89 d | 7.00 d | – | 7.23 s | 7.77 d | 6.67 d | – | 6.67 d | 7.77 d | – | 3.89 s | 6.00 s |
| | – | $J$ = 8.3 | $J$ = 8.3 | – | – | $J$ = 8.0 | $J$ = 8.0 | – | $J$ = 8.0 | $J$ = 8.0 | – | – | – |
| **p** | 6.67 s | 8.09 d | 6.94 dt | – | 6.90 d | 7.14 s | – | – | 7.13 d | 7.19 dd | 2.21 s | 3.90 s | – |
| | – | $J$ = 8.7 | $J$ = 2.3; 8.7 | – | $J$ = 2.3 | – | – | – | $J$ = 7.8 | $J$ = 1.8; 7.8 | – | – | – |
| **q** | 6.52 s | 7.95 d | 7.08 dd | – | 7.15 d | 6.45 d | – | 6.04 t | – | 6.45 d | – | 3.93 s | 5.07 s |
| | – | $J$ = 8.8 | $J$ = 2.4; 8.8 | – | $J$ = 2.4 | $J$ = 1.8 | – | $J$ = 1.8 | – | $J$ = 1.8 | – | – | – |




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**Table 3.** $^1$H NMR chemical shifts ($\delta$, ppm), multiplicities and coupling constants ($J$, Hz) for compounds **2g–l** and **2r–v**

| | H-3 | H-6 | H-7 | H-8 | H-2′ | H-3′ | H-4′ | H-5′ | H-6′ | $CH_3$ | $OCH_3$ | $OCH_3$ | $NH_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **g** | 6.36 s | 6.99 d | 7.66 t | 7.19 d | – | 6.81 d | 7.20 t | 6.65 t | 7.38 | – | 3.87 s | – | 5.61 s |
| | – | $J = 8.3$ | $J = 8.3$ | $J = 8.3$ | – | $J = 7.8$ | $J = 7.8$ | $J = 7.8$ | $J = 7.8$ | – | – | – | – |
| **h** | 6.74 s | 6.86 d | 7.61 t | 7.16 dd | 7.24 t | – | 7.30–7.32 m | 6.85–6.87 m | 7.30–7.32 m | – | 4.04 s | – | – |
| | – | $J = 8.4$ | $J = 8.4$ | $J = 0.8; 8.4$ | $J = 1.5$ | – | – | – | – | – | – | – | – |
| **i** | 6.55 s | 6.95 d | 7.65 t | 7.22 dd | 7.74 d | 6.67 d | – | 6.67 d | 7.74 d | – | 3.86 s | – | 5.97 s |
| | – | $J = 8.2$ | $J = 8.2$ | $J = 0.6; 8.2$ | $J = 8.7$ | $J = 8.7$ | – | $J = 8.7$ | $J = 8.7$ | – | – | – | – |
| **r** | 6.36 s | 6.84 d | 7.56 t | 7.04 dd | – | – | 6.83 dd | 7.13 t | 6.93 dd | 2.21 s | 4.01 s | – | 3.81 s |
| | – | $J = 8.3$ | $J = 8.3$ | $J = 1.0; 8.3$ | – | – | $J = 1.2; 7.6$ | $J = 7.6$ | $J = 1.2; 7.6$ | – | – | – | – |
| **s** | 6.67 s | 6.81 d | 7.56 t | 7.12 dd | 7.19 d | – | – | 7.16 d | 7.23 dd | 2.23 s | 4.00 s | – | 3.80 s |
| | – | $J = 8.4$ | $J = 8.4$ | $J = 0.6; 8.4$ | $J = 1.5$ | – | – | $J = 7.8$ | $J = 1.5; 7.8$ | – | – | – | – |
| **t** | 6.39 s | 6.99 d | 7.69 t | 7.15 d | 6.40 d | – | 6.02 t | – | 6.40 d | – | 3.87 s | – | 5.05 s |
| | – | $J = 8.3$ | $J = 8.3$ | $J = 8.3$ | $J = 1.8$ | – | $J = 1.8$ | – | $J = 1.8$ | – | – | – | – |
| **j** | 6.51 s | 6.38 s | – | 6.49 d | – | 6.77 d | 7.24–7.29 m | 6.83 t | 7.45 dd | – | 3.89 s | 3.95 s | – |
| | – | – | – | $J = 1.7$ | – | $J = 8.2$ | – | $J = 7.6$ | $J = 1.0; 7.6$ | – | – | – | – |
| **k** | 6.63 s | 6.37 d | – | 6.56 d | 7.16 s | – | 6.81 dt | 7.26 d | 7.26 d | – | 3.91 s | 3.96 s | – |
| | – | $J = 2.2$ | – | $J = 2.2$ | – | – | $J = 2.0; 6.8$ | $J = 6.8$ | $J = 6.8$ | – | – | – | – |
| **l** | 6.46 s | 6.45 d | – | 6.80 d | 7.72 d | 6.66 d | – | 6.66 d | 7.72 d | – | 3.81 s | 3.88 s | 5.93 s |
| | – | $J = 1.9$ | – | $J = 1.9$ | $J = 8.6$ | $J = 8.6$ | – | $J = 8.6$ | $J = 8.6$ | – | – | – | – |
| **u** | 6.60 s | 6.36 d | – | 6.55 d | 7.16 s | – | – | 7.14 d | 7.20 dd | 2.22 s | 3.90 s | 3.95 s | – |
| | – | $J = 2.3$ | – | $J = 2.3$ | – | – | – | $J = 7.9$ | $J = 1.6; 7.9$ | – | – | – | – |
| **v** | 6.30 s | 6.51 d | – | 6.67 d | 6.38 d | – | 6.00 t | – | 6.38 d | – | 3.83 s | 3.90 | 5.04 s |
| | – | $J = 2.3$ | – | $J = 2.3$ | $J = 1.8$ | – | $J = 1.8$ | – | $J = 1.8$ | – | – | – | – |

**Table 4.** $^1$H NMR chemical shifts ($\delta$, ppm), multiplicities and coupling constants ($J$, Hz) for compounds **2x–z**

| | H-3 | H-5 | H-7 | H-8 | H-2′ | H-3′ | H-4′ | H-5′ | H-6′ | $NH_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **x** | 6.68 s | 8.36 d | 7.78 dd | 7.41 d | – | 6.79 dd | 7.30 dt | 6.86 dt | 7.48 dd | 4.39 s |
| | – | $J = 2.5$ | $J = 2.5; 8.9$ | $J = 8.9$ | – | $J = 1.0; 7.8$ | $J = 1.5; 7.8$ | $J = 1.0; 7.8$ | $J = 1.5; 7.8$ | – |
| **y** | 6.86 s | 8.10 d | 7.98 dd | 7.72 d | 7.22 d | – | 7.20–7.22 m | 6.78–6.80 m | 7.20–7.22 m | 5.43 s |
| | – | $J = 2.6$ | $J = 2.5; 8.9$ | $J = 8.9$ | $J = 1.1$ | – | – | – | – | – |
| **w** | 6.70 s | 8.34 d | 7.75 dd | 7.43 d | 7.74 d | 6.76 d | – | 6.76d | 7.74 d | 4.14 s |
| | – | $J = 2.5$ | $J = 2.5; 8.9$ | $J = 8.9$ | $J = 8.7$ | $J = 8.7$ | – | $J = 8.7$ | $J = 8.7$ | – |
| **z** | 6.63 s | 8.10 d | 7.98 t | 7.67 d | 6.45 s | – | 6.05 s | – | 6.45 s | 5.10 s |
| | – | $J = 1.6$ | $J = 8.8$ | $J = 8.8$ | – | – | – | – | – | – |

**Table 5.** $^{13}$C NMR chemical shifts ($\delta$, ppm) for compounds **2a–i** and **2m–s**

| | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 | C-10 | C-1′ | C-2′ | C-3′ | C-4′ | C-5′ | C-6′ | $CH_3$ | $OCH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **a** | 163.7 | 107.5 | 178.6 | 125.6 | 125.1 | 133.7 | 118.0 | 156.2 | 123.9 | 132.7 | 147.0 | 112.3 | 130.0 | 118.1 | 116.5 | – | – |
| **b** | 163.7 | 106.5 | 177.1 | 124.9 | 125.5 | 134.4 | 118.4 | 155.7 | 123.4 | 131.7 | 110.9 | 149.4 | 117.3 | 129.7 | 113.9 | – | – |
| **c** | 163.8 | 102.9 | 176.6 | 124.7 | 125.1 | 133.7 | 118.2 | 155.5 | 116.9 | 123.4 | 128.0 | 113.5 | 152.7 | 113.5 | 128.0 | – | – |
| **m** | 166.5 | 111.0 | 176.5 | 124.6 | 125.1 | 133.8 | 118.1 | 155.8 | 123.1 | 132.9 | 119.0 | 147.1 | 116.2 | 126.0 | 117.0 | 13.9 | – |
| **n** | 163.2 | 106.3 | 177.8 | 124.9 | 124.3 | 132.9 | 117.3 | 155.5 | 123.3 | 129.1 | 111.3 | 125.5 | 144.4 | 130.3 | 115.9 | 16.8 | – |
| **o** | 164.6 | 106.0 | 176.9 | 124.8 | 125.4 | 134.2 | 118.2 | 155.6 | 123.4 | 132.0 | 100.7 | 149.8 | 102.8 | 149.8 | 100.7 | – | – |
| **d** | 163.3 | 107.4 | 177.9 | 127.0 | 114.3 | 164.0 | 100.3 | 158.0 | 117.5 | 132.8 | 146.9 | 112.2 | 129.9 | 118.0 | 116.4 | – | 55.8 |
| **e** | 162.6 | 106.8 | 177.2 | 126.3 | 113.6 | 163.4 | 99.7 | 157.3 | 117.1 | 132.2 | 111.5 | 146.2 | 117.2 | 129.2 | 115.7 | – | 55.1 |
| **f** | 163.5 | 100.8 | 176.1 | 126.0 | 114.1 | 163.5 | 102.7 | 157.3 | 117.2 | 117.2 | 127.8 | 113.5 | 152.5 | 113.5 | 127.8 | – | 55.1 |
| **p** | 163.4 | 106.6 | 177.8 | 126.7 | 114.1 | 163.9 | 100.2 | 157.8 | 117.7 | 130.3 | 111.8 | 126.1 | 145.1 | 130.8 | 116.2 | 17.4 | 55.7 |
| **q** | 164.3 | 105.9 | 176.4 | 126.3 | 114.7 | 163.9 | 100.6 | 157.5 | 117.2 | 132.1 | 100.6 | 149.9 | 102.7 | 149.9 | 100.6 | – | – |
| **g** | 162.2 | 111.1 | 176.4 | 159.1 | 107.1 | 134.0 | 110.2 | 157.9 | 113.8 | 115.0 | 147.1 | 116.7 | 131.7 | 116.2 | 129.3 | – | 56.2 |
| **h** | 161.3 | 109.0 | 178.4 | 159.5 | 106.3 | 133.6 | 110.1 | 158.3 | 114.6 | 132.4 | 112.1 | 146.9 | 116.3 | 117.9 | 129.9 | – | 56.5 |
| **i** | 161.7 | 104.9 | 176.7 | 159.4 | 107.4 | 134.2 | 110.3 | 157.9 | 114.1 | 117.1 | 128.1 | 113.9 | 152.8 | 113.9 | 128.1 | – | 56.5 |
| **r** | 164.2 | 113.7 | 178.2 | 159.8 | 106.3 | 133.7 | 110.2 | 158.6 | 114.5 | 130.3 | 120.5 | 145.4 | 117.1 | 120.7 | 119.6 | 14.3 | 56.5 |
| **s** | 161.5 | 108.5 | 178.5 | 159.7 | 106.3 | 133.5 | 110.2 | 158.3 | 114.6 | 130.1 | 111.9 | 145.0 | 126.1 | 131.0 | 116.4 | 17.7 | 56.5 |




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# Spectral Assignments and Reference Data

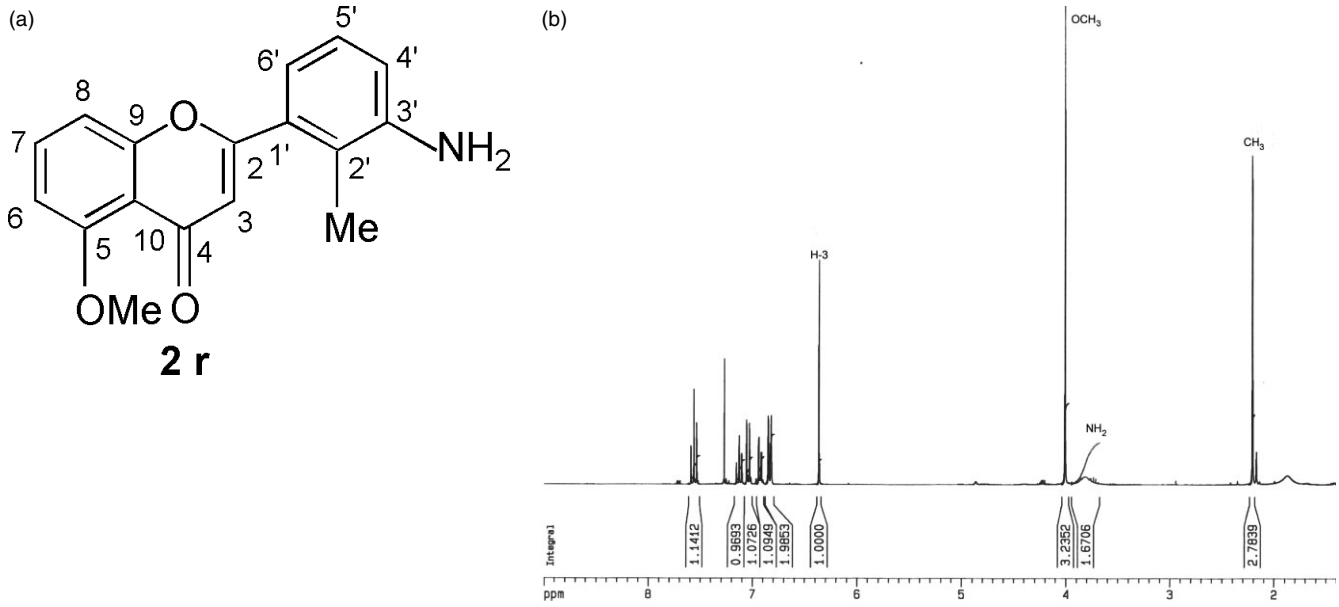


**Figure 2.** 1H NMR spectra of 3′-amino-2′-methyl-5-methoxyflavone (**2r**) in CDCl3.

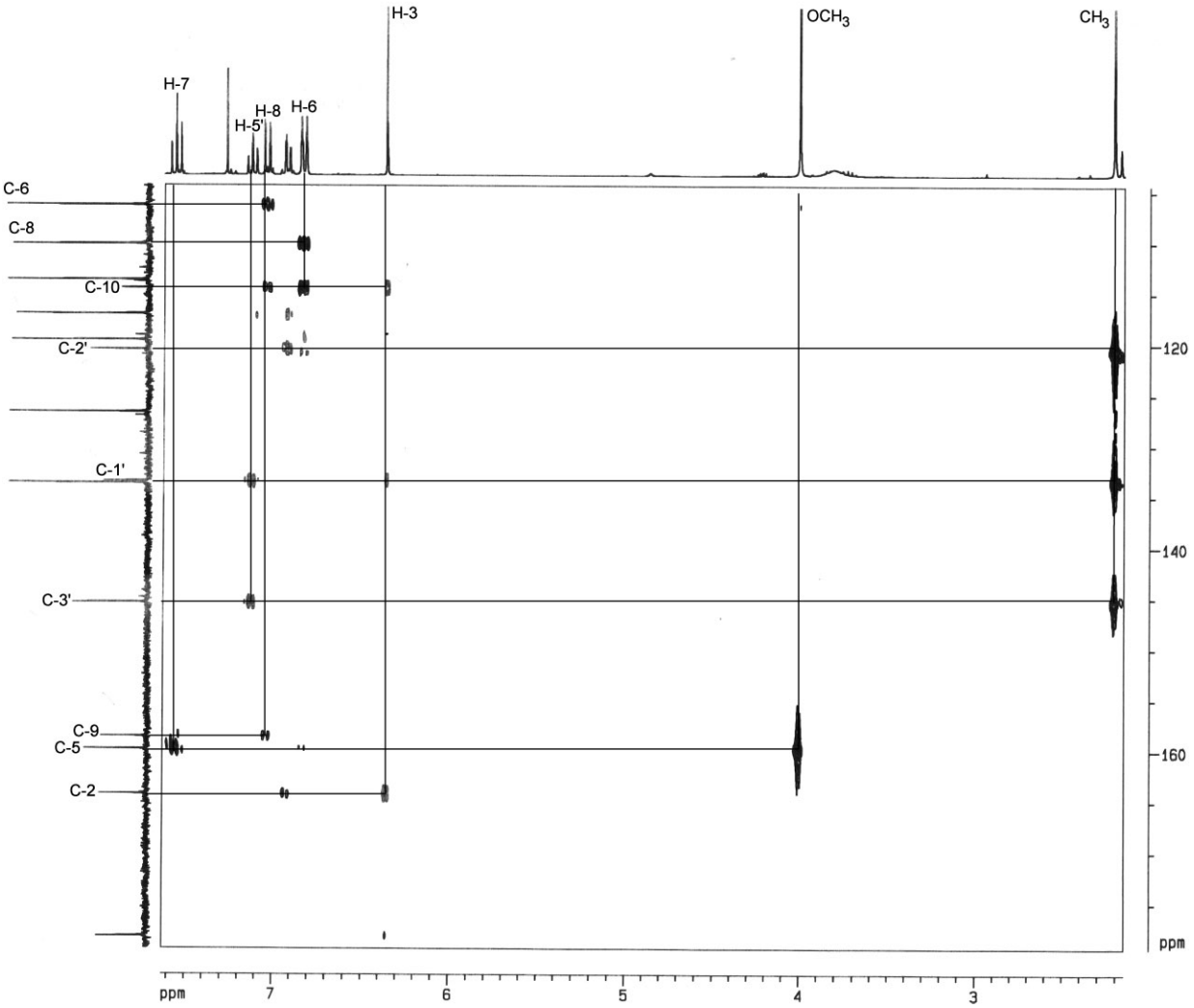


**Figure 3.** HMBC NMR spectra of 3′-amino-2′-methyl-5-methoxyflavone (**2r**) in CDCl3.




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were also demonstrated by the HMBC spectra, as the signal that appears as a double doublet at $\delta$ 7.04 ppm is correlated with the carbon resonance for C-9 at $\delta$ 158.6 ppm. The correlation involved in the exchangeable proton H-8 provides the correct attribution of this signal ($^3J_{H7-H8}$ 8.3 Hz, $^4J_{H6-H8}$ 1.0 Hz); (iv) H-6′ signal at $\delta$ 6.93 ppm shows a long-range correlation with the carbon resonance for C-2′ at $\delta$ 120.5 ppm and C-2 at $\delta$ 164.2 ppm.

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