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# Tautomeric behaviors of 5-arylazobarbituric acids in different concentrations

Nader Noroozi Pesyan *, Jabbar Khalafy, Karim Akbari Dilmaghani, Saeed Rastgar, Zahra Malekpoor, Mina Mohammadzadeh

*Department of Chemistry, Faculty of Science, Urmia University, 57159, Urmia, Iran*

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## Abstract

The NMR spectra of azo dyes, 5-arylazobarbituric (5a-g), 5-arylazo-1,3-dimethylbarbituric (6a-g) and 5-arylazothiobarbituric acids (7a-g) were studied in DMSO-$d_6$ in different concentrations. An intramolecular hydrogen bond was observed and indicating that the hydrazone forms is mostly predominant. The peak of the hydrazone proton was severely broadened and its chemical shift appeared at down field due to intramolecular hydrogen bond. Existence of nitro group at *ortho*-position on phenyl ring caused the chemical shift value of the proton of hydrazone form in 5a-7a to be more deshielded than other hydrazone protons in 5b-g−7b-g due to bifurcated intramolecular hydrogen bond and anisotropic ring-current effect. Dyes 6 shows two tautomers in NMR time scale at low concentration in DMSO-$d_6$.

***Keywords:*** Azo-hydrazone tautomerism; Solvatochromic dyes; 5-Arylazobarbituric acids; Bifurcated intramolecular hydrogen bond

## 1. Introduction

In recent decades, organic colour chemistry is undergoing very exciting development as a result of the opportunities presented by dye applications in high technology fields: electronic devices, linear and non linear optics, reprography, sensors, biomedical uses [1-4]. Some azo dyes as Prontosil [5], the first commercially available antibiotic, were developed by a research team at the Bayer Laboratories in Germany.

If a C–H bond is acidic enough, it couples with diazonium salts in the presence of a base, most often aqueous sodium acetate [6]. Azo colourants containing hydroxyl and amino substituents *ortho* or *para* to the azo groups in principle can exist as a mixtures of azo and hydrazone tautomers. While azo–hydrazone tautomerism is quite interesting from a theoretical viewpoint, it is also important from a practical standpoint, as the two tautomers have different technical properties [7]. Although quantitative evaluation of the tautomeric equilibria associated with arylazonaphthol dyes has been conducted in the past using UV–visible [8] and NMR [9] spectroscopy, these methods have key limitations. The solvent effect on the azo-hydrazone tautomerism, or on the monomer-dimer equilibrium was found not to correlate with any of the physical parameters of the solvent (polarity, dielectric constant and refractive index); it depends on the solvent structure and the microscopic environment of the dye in the solvent matrix [10,

* Corresponding author. Tel.: +98 4412780952; fax: +98 4412776707.
*E-mail address:* n.noroozi@mail.urmia.ac.ir (N. Noroozi)

11]. In the case of NMR spectroscopy, the equilibrium between the azo and hydrazone tautomers is rapidly established on the NMR time scale [12], which renders $^{1}$H NMR unsuitable for establishing the position of the tautomeric equilibrium. However, $^{15}$N, $^{14}$N and $^{13}$C NMR chemical shift data can readily be employed to study quantitatively the tautomer equilibrium [13-19]. The aggregation behavior of some ozo dyes in water and other solvents was recently studied by spectroscopic methods [20-23].

As part of investigations of mono azo pigment-functionalized barbituric, 1,3-dimethylbarbituric and thiobarbituric acids based on 5-arylazo derivatives, we report herein a qualitative study of the tautomeric behaviour of model azo dyes containing an acceptor and a donor substituents in different concentrations. The results of these studies provide the basis for describing the effect and position of the substituent and concentration on the tautomerism of the barbiturate azo dyes.

## 2. Experimental

### *2.1. General*

Melting points were taken with a digital melting point apparatus (Electrothermal) and were uncorrected. IR spectra were determined in the region 4000- 400 cm$^{-1}$ on a NEXUS 670 FT IR spectrometer by preparing KBr pellets. The $^{1}$H NMR spectra were measured in DMSO-$d_6$ at 300 MHz, using Bruker 300 FT-NMR spectrometer and using tetramethylsilane as internal standard. All substituted anilines and deuterated solvent (DMSO-$d_6$) were obtained from Merck and Aldrich and used without further purification.

### *2.2. Typical procedure: Representative procedure for the Synthesis of 5-(2-Nitrophenylazo) pyrimidine (1H,3H,5H)-2,4,6-trion (**5a**)*

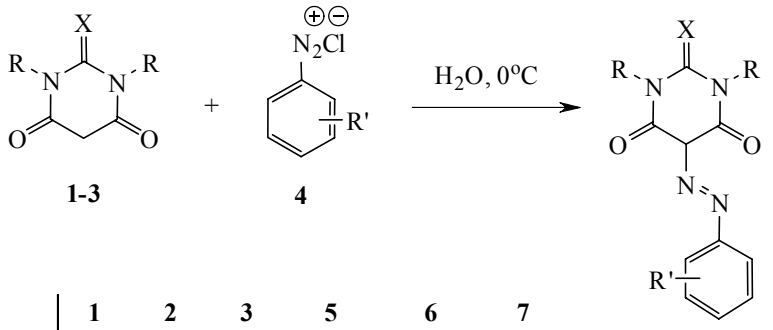
According to the literature procedure, [24], 2-nitroaniline (0.27 g, 1.95 mmol) was dissolved in acidic solution of water (50 mL) and concentrated HCl (5 mL) in a 100 mL beaker. Then a solution of sodium nitrite (0.143 g, 1.95 mmol) in water (10 mL) was added to the reaction mixture. The resulting diazonium salt (**4a**) was added into a solution of barbituric acid **1** (0.25 g, 1.95 mmol) in water (20 mL) with stirring at 0 °C. The desired azo dye was obtained as a yellow crystalline solid (90%). All IR and NMR spectral data of azo dyes are summarized in an Appendix.

## 3. Results and discussion

All azo dyes based on barbituric acids (**5a-g**), 1,3-dimethyl barbituric acids (**6a-g**) and thiobarbituric acid (**7a-g**) were synthesized according to known and regular methods (Scheme 1). All dyes were insoluble in water except **5d**, **6d** and **7d**. Many of these dyes, have an intramolecular hydrogen bond between carbonyl groups and NH/OH proton of azo and/or hydrazone forms (Scheme 2). The significant broad single peak at low-field is due to this phenomenon.

5-(2-Nitrophenylazo) pyrimidine (1*H*,3*H*,5*H*)-2,4,6-trion (**5a**), 5-(3-nitrophenylazo) pyrimidine (1*H*,3*H*,5*H*)-2,4,6-trion (**5b**), 5-(4-nitrophenylazo) pyrimidine (1*H*,3*H*,5*H*)-2,4,6-trion (**5c**), Sodium 4-(2,4,6-trioxo-hexahydro-pyrimidin-5-ylazo)-benzenesulfonate (**5d**) and 5-phenylazo pyrimidine (1*H*,3*H*,5*H*)-2,4,6-trion (**5e**) showed following peaks in down field in DMSO-$d_6$, respectively; two sharp peaks of amidic protons at δ 11.47 and 11.70 ppm and a sharp peak (-NH/-OH) at δ 15.18 ppm for **5a**, only two peaks in down field, a broad peak of amidic protons at δ 11.39 ppm and a severely broadened peak at δ 13.92 ppm for **5b**, three peaks in down field, two peaks of amidic protons in which one is sharp at δ 11.42 ppm, other broad at 11.65 ppm and a broadened peak of hydrazone's proton at 13.95 ppm for **5c** (Fig. 1), three

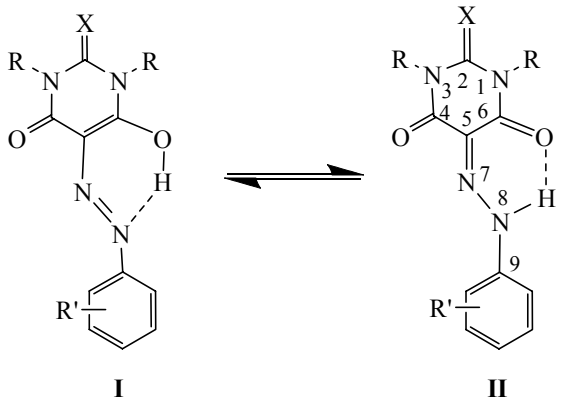
distinct peaks in down field at δ 14.14, 11.49 and δ 11.27 ppm for **5d** and two broadened peaks of amidic and hydrazone protons at δ 11.30 and 14.13 ppm for **5e**. The azo dyes with electron donating substituents on phenyl ring, e.g. 5-(4-tolylazo) pyrimidine (1*H*,3*H*,5*H*)-2,4,6-trion (**5f**) and 5-(4-anisidylazo) pyrimidine (1*H*,3*H*,5*H*)-2,4,6-trion (**5g**) showed two slightly overlapped peaks at δ 11.23 and δ 14.18 ppm for **5f** and two slightly overlapped peaks at δ 11.19 and δ 14.27 ppm for **5g** in down field respectively. All IR and $^1$H NMR spectral data are summarized in Appendix.




| | 1 | 2 | 3 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| R | H | $CH_3$ | H | H | $CH_3$ | H |
| X | O | O | S | O | O | S |

| 4-7 | a | b | c | d | e | f | g |
|---|---|---|---|---|---|---|---|
| R' | *o*-$NO_2$ | *m*-$NO_2$ | *p*-$NO_2$ | *p*-$SO_3Na$ | H | *p*-$CH_3$ | *p*-$OCH_3$ |

**Scheme 1** Synthesis of azo dyes.




**Scheme 2** Azo-hydrazone tautomerism of azo dyes.

In comparison of dyes **5a-c**, these questions arose that; a) Why **5a** with *ortho*-$NO_2$ substituent on phenyl ring showed three distinct sharp peaks in low-field where **5b** and **5c** did not? b) Why the peak of one of amidic protons is severely broadened in comparison with the other one in **5c**.

Dyes **5a-7a** have bifurcated intramolecular hydrogen bond and are of examples of hydrogen bonds involving one proton and two acceptors [7,25] (Scheme 3). Among dyes of **5**, the peak of proton at δ 15.18 ppm in **5a** appeared at lowest field than other dyes without bifurcated hydrogen bond. It seems the bifurcated hydrogen bond restricted the rotation of phenyl ring about carbon-nitrogen single bond ($C_9$–$N_8$) and also carbon-nitrogen double bond ($C_5$=$N_7$), (Scheme 4). To this evidence, the aryl-amide bond rotation may be restricted through specific attractive such as; intramolecular hydrogen bond and repulsive interactions between the amide and the other functional groups at the *ortho* position on the aryl moiety [26]. Therefore, the restricted rotation

about carbon-nitrogen single bond ($C_9$-$N_8$) and double bond ($C_5$=$N_7$) by the bifurcated intramolecular hydrogen bond in **5a** is not improbable and because of this the chemical shift values of two amidic protons are different (Scheme 4).

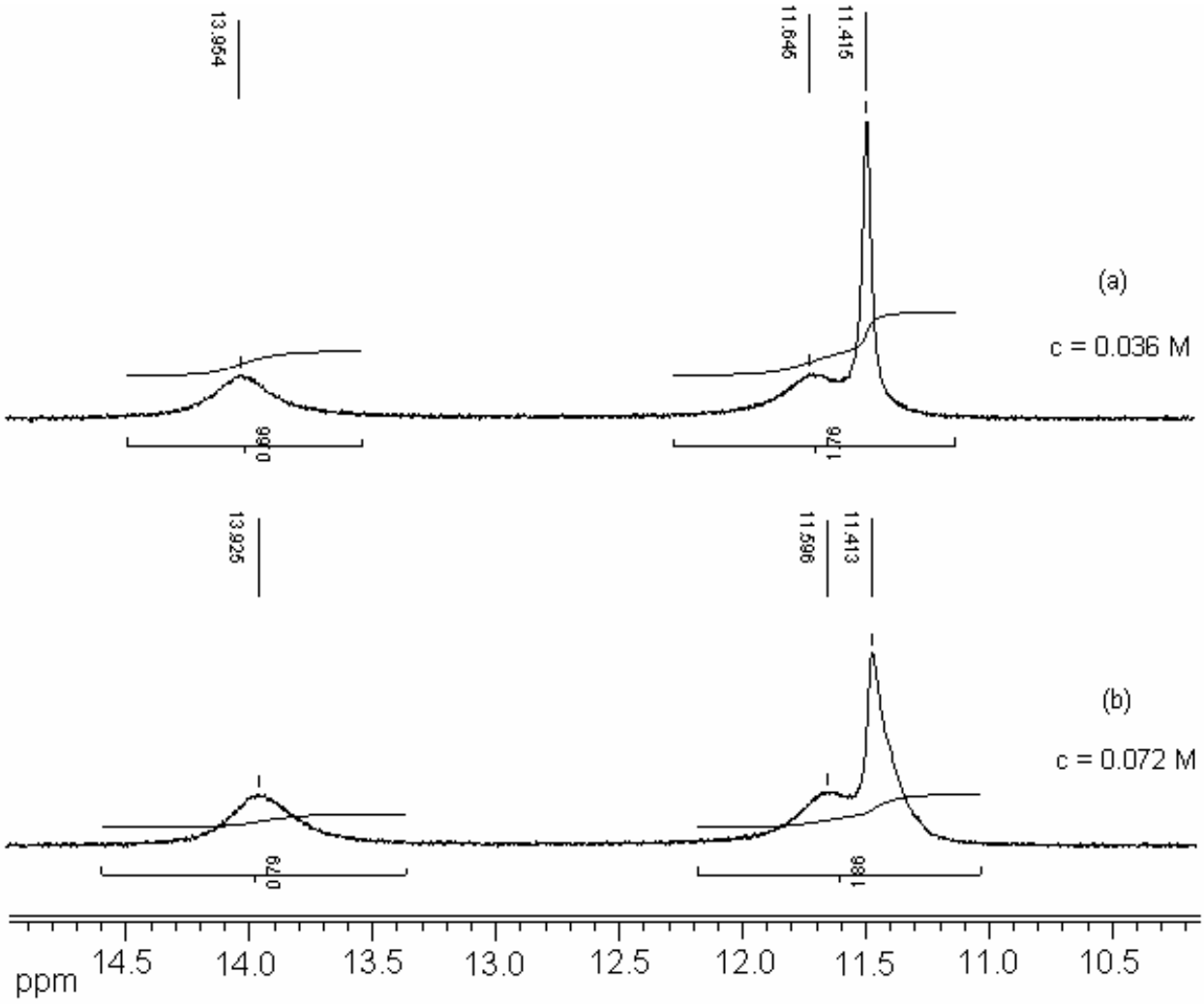
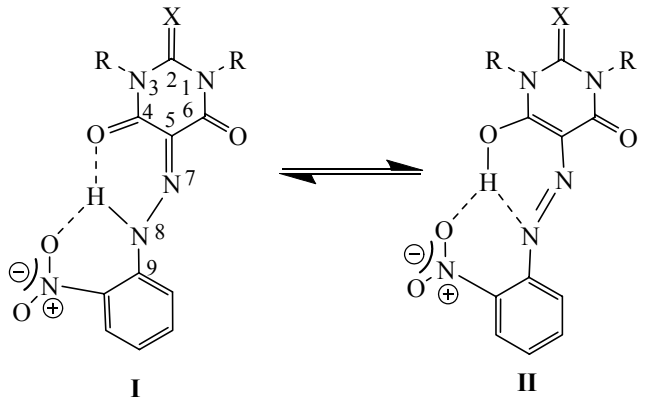


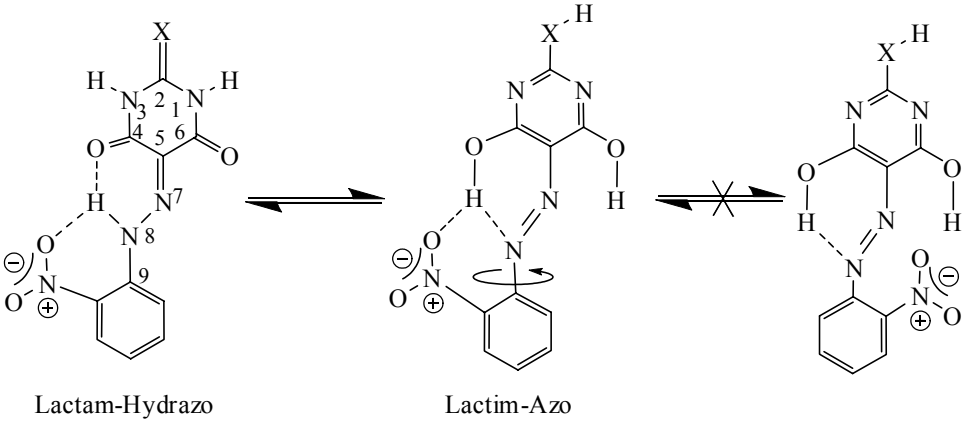

**Fig. 1.** Expanded $^1$H NMR spectra of two amidic and hydrazone protons of **5c** (a) 0.036 M and (b) 0.072 M in DMSO-$d_6$.




**Scheme 3** Bifurcated intramolecular hydrogen bond in **5a-7a.**

These two protons showed sharp peaks at δ 11.47 and 11.70 ppm and other deshielded proton at δ 15.18 ppm (not severely broadened) so that the lactim form of **5a** was predominant in two

different concentrations in DMSO-$d_6$ and demonstrated that hydrogen atoms bonded to oxygen atoms in versus nitrogen atoms (Scheme 4). All tautomeric forms of **5** and **7** are summarized in Table 1.




**Scheme 4** Restricted rotation around the bond between $C_5$-$N_7$ and $N_8$-$C_9$ by means of bifurcated intramolecular hydrogen bond in **5a-7a**.

**Table 1**
Predominant forms of **5a-g** and **7a-g** in DMSO-$d_6$.

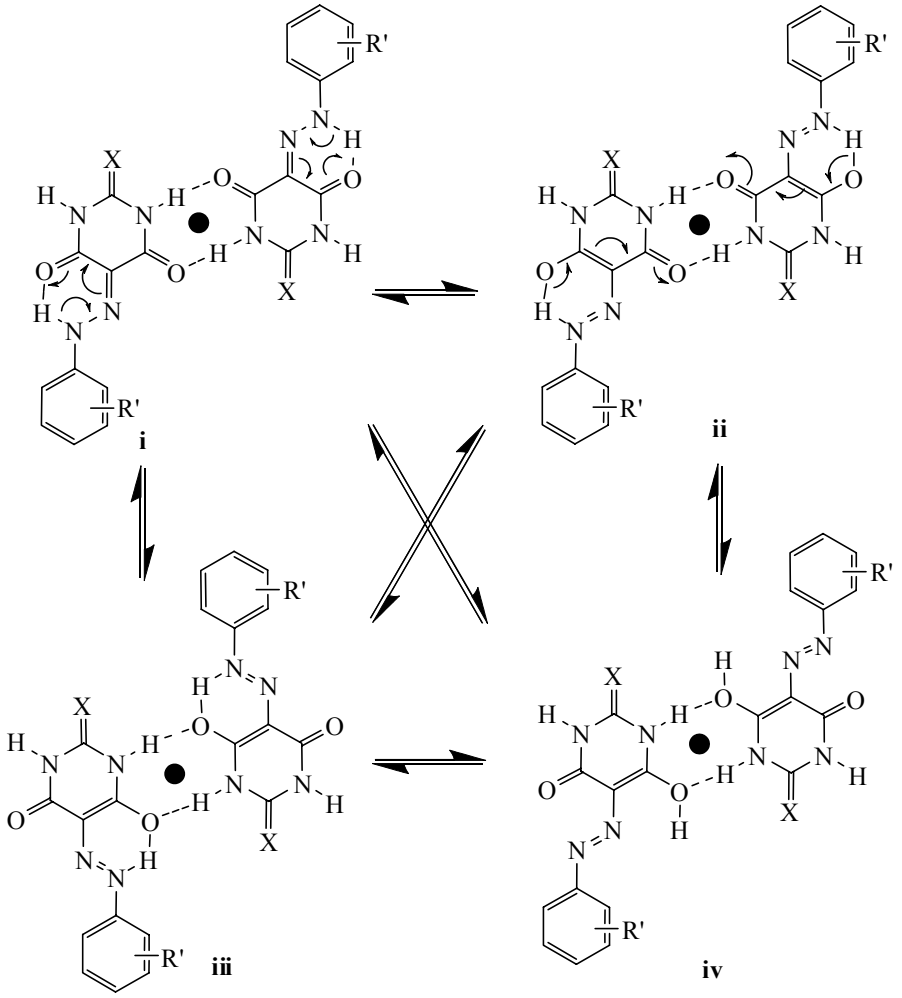
| Dye | Predominant Lactam/Lactim-Azo/Hydrazone forms of **5** in DMSO-$d_6$ | Predominant Lactam/Lactim-Azo/Hydrazone forms of **7** in DMSO-$d_6$ |
|---|---|---|
| **a** | Lactim - Azo | Lactim - Azo |
| **b** | Lactam - Hydrazone | Lactam - Hydrazone |
| **c** | Lactam/Lactim[a] - Hydrazone | Lactam/Lactim[b] – Hydrazone/ Azo |
| **d** | Lactim - Hydrazone | Lactim - Hydrazone |
| **e** | Lactam - hydrazone | Lactam[c] - hydrazone |
| **f** | Lactam/Lactim[d] - Hydrazone | Lactam/Lactim[e] - Hydrazone |
| **g** | Lactam/Lactim[f] - Hydrazone | Lactam/Lactim[g] – Hydrazone |

[a] Lactim form in DMSO-$d_6$ and both lactam-lactim forms in DMSO-$d_6$ added few drops $CD_3OD$ in two different concentrations, respectively
[b] Dependence on concentration, Lactim−Azo form (0.072 M), both lactam/lactim−Hydrazone/Azo forms (0.036 M) and Lactim−Azo form (0.016 M) in DMSO-$d_6$, respectively
[c] Two amidic and hydrazone protons to be overlapped
[d,e,f,g] Both lactam-lactim forms are exist in barbituric acid moiety

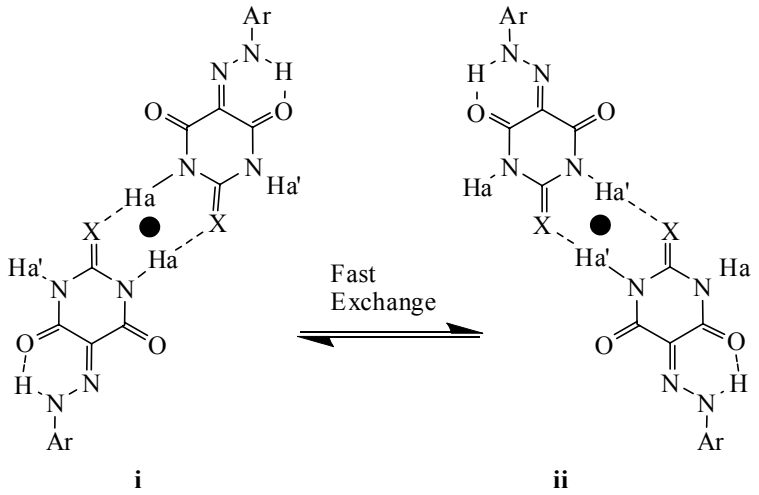
In contrast, dyes **5b** and **5c** did not show distinct three sharp peaks. The compound **5b** showed a broad peak for two amidic protons so they have same chemical environment and a severely broadened peak for NH proton in hydrazone form due to quadrupolar interaction. It seems that **5b** either has intramolecular hydrogen bond or has intermolecular hydrogen bond between carbonyl group in each molecule and amidic proton of the other one (C=O···H−N) in dimeric configuration as shown in Scheme 5.

It is well-known that many barbiturates are in different configurations due to intermolecular hydrogen bond by C=O···H−N functional groups [11, 27-29]. The $C_9$-$N_8$ and $C_5$-$N_7$ in **5b** can rotate *via* enol-keto and azo-hydrazone tautomerism and causes two amidic protons to be equivalent in chemical shift values (Scheme 5 (a)). Other possibility of these chemical shifts equivalent may be fast exchangeability of monomer with each other in dimer form (Scheme 5 (b)). We examined its $^1$H NMR spectra in different concentrations, 0.014, 0.036 and 0.072 M in DMSO-$d_6$. This experiment showed no significant difference in their chemical shifts and only differed in peak intensity. The peak intensity increased with increasing the concentration. Scheme 5 indicated that two amidic protons of **5b** are chemically equivalent. On the other hand, the broadness of signals at δ 11.38 and 13.88 ppm indicated the lactam-hydrazone form is

favoured in **5b**. The dye **5c** indicated three signals in down field; two signals of amidic protons in which one is sharp at δ 11.42 ppm, the two others appeared at δ 11.65 ppm and 13.95 ppm as broad peaks (Figure 1).



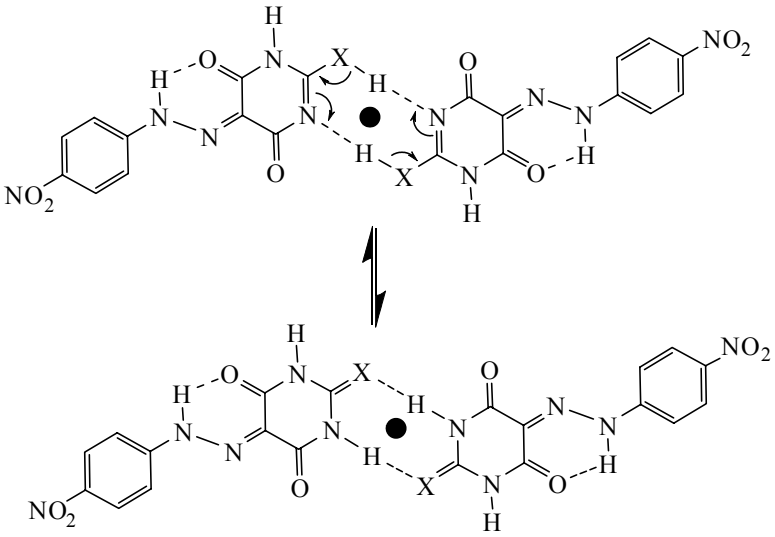

(a)




(b)

**Scheme 5** Two possibilities of equalizing two amidic protons; (a) Enol-azo, keto-hydrazone tautomerism through inter and intramolecular hydrogen bond and rotation about C−N bond, (b) Fast-exchanging between two barbiturate moieties in **5b**,**e** (X= O) and **7b**,**e**,**f** (X= S) in 0.072 M. Dimers with centrosymmetric configuration are indicated by a dot (●) at the centre of symmetry.

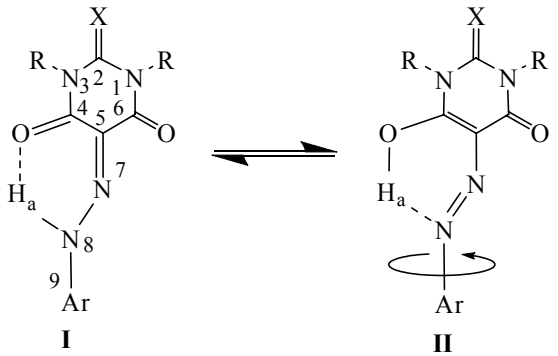
A logical answer to the question mentioned in b is; it seems that the sharp peak of amidic proton at δ 11.42 ppm is due to tautomerisation to lactim form and participation in intermolecular hydrogen bond in centrosymmetric dimer form. This proton is mostly remained on oxygen atom and is of lactim form whereas the other amidic proton at δ 11.65 ppm remained on nitrogen atom and exists as lactam form in barbituric acid moieties (Scheme 6).



**Scheme 6** Lactam-lactim tautomerism in **5c** (X= O).

The broadening of the peak at δ 13.95 ppm depends on hydrazone form involved in intramolecular hydrogen bond and because of slow exchanging, it is mostly remained on nitrogen atom. On the other hand, the aggregation occurring at relatively high dye concentration was found to have a remarkable effect on the azo-hydrazone tautomers in solution, through the existence of monomer-dimer equilibrium [29]. Dakiky *et al* reported about some other azo dyes, the effect of azo dye concentration [11] and solvent [29] on the hydrazo monomer-dimer equilibrium by means of electronic absorption, in DMSO. At a critical concentration, dimerization between the hydrazo species takes place. Dimethyl sulfoxide and water stabilize the intermolecular hydrogen bonding in the dimer more than the intramolecular one in the monomer form [29].

In dyes **6a-g** (except **6b**), two methyl protons are different in chemical environment at room temperature. Thus, the rotation about $C_5$–$N_7$ to be restricted in **6** (R= $CH_3$, X= O). Dyes **6** could not be in lactim form because of no amidic protons on barbituric acid ring so lactam-hydrazone forms are favoured. Presumably the enol-azo forms exist by means of keto-hydrazone and enol-azo intramolecular tautomerisation (Scheme 7).



**Scheme 7** Keto-hydrazone (**I**) and enol-azo (**II**) tautomerism and their restricted rotation about $C_5$–$N_7$ in two forms in **6** (R= $CH_3$, X= O).

The dye **6c** has complicated $^1$H NMR spectrum in 0.013 M in comparison with its spectrum in 0.033 M in DMSO-$d_6$ (Figure 2).

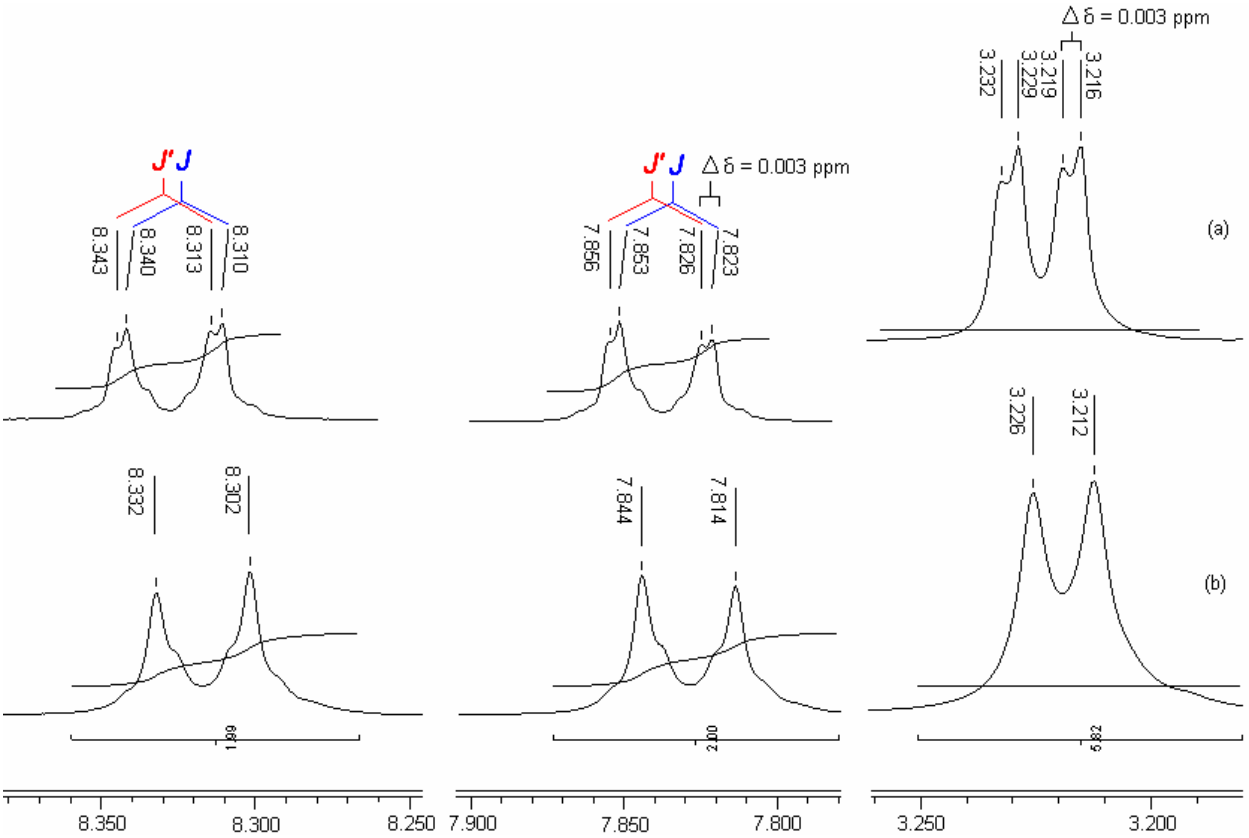



**Fig. 2.** Expanded $^1$H NMR spectra of aromatic and aliphatic regions of **6c** in 0.013 M (a) and 0.033 M (b) in DMSO-$d_6$.

Interestingly, in 0.033 M, the two methyl protons show two signals at δ 3.212 and 3.226 ppm (see Appendix). Whereas, in 0.013 M show two signals at δ 3.216 and 3.229 ppm and two others at δ 3.219 and 3.232 ppm (Δδ= 0.003 ppm). And also aromatic protons show two doublets at δ 7.83 and 8.32 ppm (J= 9 Hz) in high concentration. Instead, in low concentration, it shows two doublets at δ 8.328, 7.841 ppm and two others at δ 8.325, 7.838 ppm (J= 9 Hz) and Δδ= 0.003 ppm. The signal of hydrazone proton of **6c** appeared at δ 13.99 and 14.00 ppm in 0.033 and 0.013 M, respectively. These experiments indicated that one can unambiguously identify the signals of two favoured isomeric forms of **6c** in 0.013 M, so that separate signals are obtained for **6c** in the keto-hydrazone (**6cI**) and enol-azo forms (**6cII**) (Scheme 7), and comparison of their intensities shows that the equilibrium mixture contains both forms in equal approximately. The ratio of each tautomer is determined unsuccessfully since the signal overlapping (Figure 2). The **6c** slowly tautomerized in two forms, **6cI** and **6cII** in 0.013 M *via* solvent intervention that caused each tautomer having enough lifetimes in NMR time scale (Scheme 7 and Figure 2). It seems that the solvent has formed new intermolecular hydrogen bond with deshielded exchangeable hydrogen ($H_a$) and prevented the rapid tautomerisation between keto-hydrazone, **6cI** and enol-azo, **6cII** forms in 0.013 M. The **6c** has rapid tautomerization in 0.033 mol $L^{-1}$ caused two isomeric forms have not enough lifetimes in NMR time scale.

Dyes **6** can not be in dimer form due to absence of their amidic protons. Therefore, these dyes are in monomer forms in solution and only have donor-acceptor interaction in crystal form [28]. Two methyl protons have different chemical shifts values in dyes **6a-g** in 0.033 M except **6b**. In **6b**, the chemical shift of the two methyl protons are equivalent in 0.033 M whereas it has shown two methyl protons with different chemical shift that slightly overlapped in 0.013 M (Figure 3). Probably, the chemical shift of two methyl protons are equivalent by chance in **6b** in

0.033 M. Two methyl protons shows two distinct singlet peaks even consisting electron-donating substituents on phenyl ring (see Appendix).

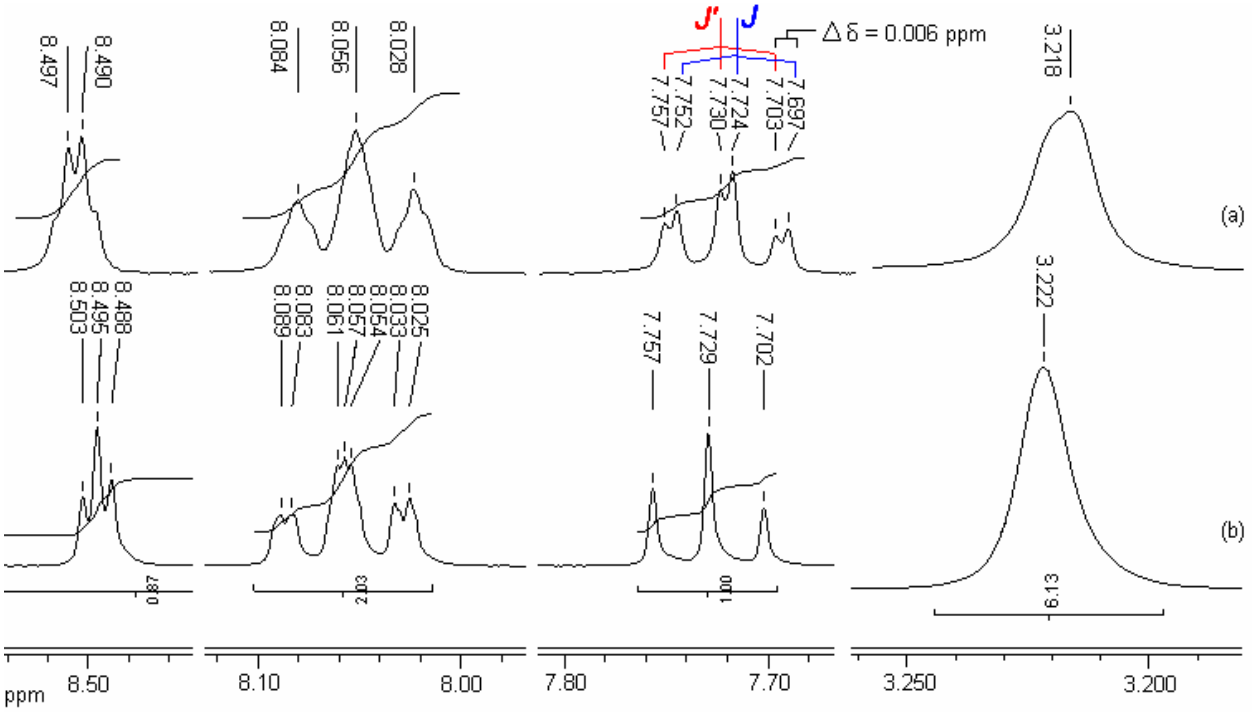



**Fig. 3.** Expanded $^1$H NMR spectra of aromatic and aliphatic regions of **6b** in 0.013 M (a) and 0.033 M (b) in DMSO-$d_6$.

The $^1$H NMR and FT-IR data of azo dyes **7a-g** were similar to **5a-g** and all spectral data and tautomeric forms are summarized in Appendix and Table 1, respectively. Surprisingly, in **7e**, the chemical shift values of two amidic and hydrazone protons are quite equivalent (12.92 ppm) and show a severely broadened singlet. The broadening of that signal arises from the rapid exchange between the two amidic and hydrazone protons in solution.

## 4. Conclusion

In summary, the azo dyes **5a-g**−**7a-g** have been synthesized according to the literature and characterized. The tautomeric forms of these dyes in DMSO-$d_6$ in two or three different concentrations have been studied in detail. Mostly, the dyes **5** and **7** show the same tautomeric forms as shown in Table 1. Indeed, the dyes **6** have two distinct tautomeric forms in lower concentration. Dyes **5a**, **6a** and **7a** have bifurcated intramolecular hydrogen bond.

## Appendix

**(5a)** 3447.85 (m), 3072.32 (s), 1747.31 (s), 1679.78 (s), 1643.32 (m), 1488.16 (s), 1328.62 (s), 1229.67 (s), 813.81 (s). 15.18 (s, 1H), 11.70 (s, 1H), 11.48 (s, 1H), 8.26 (dd, $J_3$= 8.4 Hz, $J_4$= 1.2 Hz 1H), 8.08 (d, J= 7.8 Hz, 1H), 7.88 (t, J= 7.5 Hz, 1H), 7.38 (td, $J_3$= 7.8 Hz, $J_4$= 1.2 Hz). 161.85, 159.86, 150.17, 138.00, 137.03, 135.93, 126.48, 125.17, 122.69, 117.60.

**(5b)** 3194.63 (s), 3074.07 (s), 1755.13 (s), 1729.67 (s), 1665.42 (s), 1519.42 (s), 1355.94 (s), 1249.74 (s), 814.03 (s). 13.92 (bs, 1H), 11.39 (bs, 2H), 8.44 (t, J= 2.1 Hz, 1H), 8.03 (d, J= 2.1 Hz, 1H), 8.00 (d, J= 2.1, 1H), 7.71 (t, J= 8.4). 162.02, 160.09, 150.20, 149.11, 143.42, 131.44, 123.32, 120.10, 119.88, 111.40.

**(5c)** 3569.85 (s), 3461.67 (s), 3202.87 (s), 1711.21 (s), 1670.0 (s), 1611.23, (m), 1509.97 (s), 1446.35 (s), 1336.68 (s), 1246.88 (s).13.95 (bs, 1H), 11.65 (bs, 1H), 11.42 (s, 1H), 8.32 (d, J= 9.3 Hz, 2H ), 7.79 (d, J= 9.3 Hz, 2H). 162.00, 159.97, 150.20, 147.44, 144.29, 126.07, 121.29, 117.17.

**(5d)** 3413.57 (s), 3257.20 (s), 3096.67 (s), 2831.50 (w), 1738.83 (s), 1712.20 (s), 1668.12 (s), 1513.53 (s), 1433.56 (s), 1263.18 (s), 1196.93 (s), 1042.98 (s). 14.14 (s, 1H), 11.49 (s, 1H), 11.27 (s, 1H), 7.65 (d, J= 7.2 Hz, 2H), 7.50 (d, J= 7.2 Hz, 2H). 162.40, 160.47, 150.17, 145.24, 141.92, 127.48, 118.34, 116.35.

**(5e)** 3253.96 (s), 3091.75 (s), 1754.51 (s), 1708.22 (s), 1655.15 (s), 1512.04 (s), 1472.81 (m), 1434.31 (s), 1258.92 (s). 14.13 (bs, 1H), 11.30 (bs, 2H), 7.57 (d, J= 8.1, 2H), 7.45 (t, J= 7.8 Hz, 2H), 7.23 (td, $J_3$= 7.35 Hz, $J_4$= 0.9 Hz).

**(5f)** 3253.55 (s), 3085.31 (s), 2853.08 (w), 1755.17 (s), 1706.80 (s), 1654.86 (s), 1514.68 (s), 1433.10 (s), 1351.68 (m), 1259.44 (s). 14.18 (bs, 1H), 11.23 (bs, 2H), 7.47 (d, J= 8.4 Hz, 2H), 7.26 (d, J= 8.7 Hz, 2H), 2.31 (s, 3H).

**(5g)** 3242.54 (s), 3079.21 (s), 2835.00 (w), 1755.15 (s), 1704.73 (s), 1653.40 (s), 1513.34 (s), 1433.27 (m), 1352.29 (m), 1249.55 (s). 14.27 (bs, 1H), 11.19 (bs, 2H), 7.54 (d, J= 9.0 Hz, 2H), 7.03 (d, J= 8.7 Hz, 2H), 3.78 (s, 3H).

**(6a)** 3440.00 (bm), 3088.92 (m), 2950.00 (w), 2925.00 (w), 1736.95 (s), 1680.80 (s), 1647.45 (s), 1491.56 (s), 1337.86 (s), 1230.70 (s), 747.16 (s). 15.23 (s, 1H), 8.29 (d, J= 8.4 Hz, 1H), 8.10 (d, J= 8.1 Hz, 1H), 7.91 (t, J= 7.8 Hz, 1H), 7.41 (t, J= 8.1 Hz, 1H), 3.24 (s, 3H), 3.23 (s, 3H). 160.31, 158.75, 150.92, 137.82, 137.08, 136.10, 126.51, 125.44, 121.90, 117.66, 28.74, 27.93.

**(6b)** 3436.00 (bs), 3100.00 (w), 2920.00 (w), 2960.00 (w), 1727.63 (s), 1677.71 (s), 1648.60 (s), 1516.46 (s) 1451.76 (s), 1352.64 (s), 1245.80 (s), 750.75 (s). 14.02 (s, 1H), 8.50 (t, J= 2.1 Hz, 1H), 8.06 (m, J= 8.4 Hz, 2H), 7.73 (t, J= 8.4, 1H), 3.22 (s, 3H), 3.21 (s, 3H). 160.32, 158.96, 151.01, 149.12, 143.43, 131.48, 123.46, 120.29, 119.26, 111.65, 28.64, 27.73.

**(6c)** 3399.72 (bw), 3082.44 (m), 2943.78 (w), 2900.0 (w), 1730.66 (s), 1681.01 (s), 1643.49 (s), 1517.90 (s), 1455.18 (s), 1343.52 (s), 1248.28 (s), 746.58 (s). 13.99 (s, 1H), 8.32 (d, J= 9.0 Hz, 2H), 7.83 (d, J= 9.0 Hz, 2H), 3.23 (s, 3H), 3.21 (s, 3H).

**(6d)** 2600-3600 (bs), 1731.13 (s), 1682.62 (s), 1647.57 (s), 1525.84 (s), 1450.42 (s), 1384.66 (s), 1201.24 (s), 1123.72 (s), 651.38 (s). 7.65 (d, J= 8.7 Hz, 2H), 7.21 (d, J= 8.7 Hz, 2H), 2.60-4.60 (bs, $H_2O$), 3.22 (s, 3H), 3.21 (s, 3H). 160.80, 159.29, 164.23, 134.16, 127.42, 122.81, 116.53, 28.46, 27.53.

**(6e)** 3400.00 (bw), 3064.26 (m), 2950.00 (w), 1725.30 (s), 1716.05 (s), 1676.05 (s), 1513.07 (s), 1463.15 (s), 1365.11 (s), 1277.71 (s), 749.98 (s). 14.16 (s, 1H), 7.62 (d, J= 7.8 Hz, 2H), 7.47 (t, J= 8.1 Hz, 2H), 7.25 (t, J= 7.5 Hz, 1H), 3.217 (s, 3H), 3.205 (s, 3H).

**(6f)** 3436.46 (bw), 3100.00 (w), 2950.00 (w), 2922.02 (w), 1716.91 (s), 1676.38 (s), 1633.00 (s), 1514.15 (s), 1438.47 (s), 1364.59 (m), 1283.28 (s), 751.36 (s). 14.21 (s, 1H), 7.52 (d, J= 7.8 Hz, 2H), 7.27 (d, J= 7.8 Hz, 2H), 3.21 (s, 3H), 3.20 (s, 3H), 2.31 (s, 3H).

**(6g)** 3428.52 (bw), 3100.00 (w), 2965.30 (w), 2835.57 (w), 1718.32 (s), 1671.06 (s), 1633.51 (s), 1525.00 (s), 1443.46 (s), 1314.95 (m), 1250.86 (s), 748.46 (s). 14.31 (s, 1H), 7.59 (d, J= 9.0 Hz, 2H), 7.05 (d, J= 9.0 Hz, 2H), 3.21 (s, 3H), 3.20 (s, 3H).

**(7a)** 3633.07 (m), 3504.99 (m), 3137.79 (s), 1720 (s), 1700 (s), 1668.53 (s), 1606.06 (s), 1583.33 (s), 1467.49 (s), 1217.17 (s). 15.23 (s, 1H), 12.76 (s, 1H), 12.59 (s, 1H), 8.27 (dd, J3= 8.4 Hz, $J_4$= 0.9 Hz 1H), 8.08 (d, J= 8.4 Hz, 1H), 7.90 (t, J= 7.2 Hz, 1H), 7.41 (td, $J_3$= 7.8 Hz, $J_4$= 1.2 Hz). 178.28, 159.78, 158.31, 137.73, 137.06, 136.15, 126.52, 125.58, 123.19, 117.80.

**(7b)** 3122.89 (bs), 1720 (s), 1700 (s), 1693.04 (s), 1661.69 (s), 1590.45 (s), 1510.32 (m), 1424.05 (s), 1230.90 (s). 14.04 (bs, 1H), 12.52 (bs, 2H), 8.46 (s, 1H), 8.05 (d, J= 8.1 Hz, 1H), 8.04 (d, J= 8.4, 1H), 7.72 (t, J= 8.1). 178.16, 159.83, 158.55, 149.09, 143.23, 131.49, 123.61, 120.58, 120.49, 111.78.

**(7c)** 3524.00 (s), 3434.03 (s), 3257.04 (s), 3088.14 (s), 1705.60 (s), 1664.05 (s), 1609.92 (s), 1494.20 (s), 1339.63 (s), 1240.07 (s). 14.03 (s, 1H), 12.69 (s, 1H), 12.53 (s, 1H), 8.32 (d, J= 9.3 Hz, 2H), 7.81 (d, J= 9.3 Hz, 2H). 178.23, 159.85, 158.42, 147.17, 144.56, 127.23, 126.05, 125.01, 121.86, 117.54.

**(7d)** 3428.04 (s), 3257.76 (s), 3096.46 (s), 1738.76 (s), 1710.24 (s), 1665.54 (s), 1509.09 (s), 1433.80 (s), 1261.14 (s), 1203.30 (s), 818.91 (m), 618.76 (m). 14.24 (s, 1H), 14.14 (s, 1H), 12.58 (s, 1H), 12.41 (s, 1H), 11.50 (s, 1H), 11.28 (s, 1H), 7.68 (d, J= 8.7 Hz, 2H), 7.67 (d, J= 8.7 Hz, 2H), 7.55 (d, J= 8.7 Hz, 2H), 7.52 (d, J= 8.7 Hz, 2H). 177.87, 162.48, 160.46, 160.33, 158.86, 150.21, 145.76, 145.31, 141.90, 141.74, 127.53, 127.49, 119.24, 118.38, 116.80, 116.37.

**(7e)** 3260.36 (m), 3104.51 (m), 1705.32 (s), 1662.96 (s), 1592.46 (m), 1497.59 (s), 1462.91 (s), 1429.19 (s), 1239.39 (s). 12.92 (bs, 3H), 7.61 (d, 2H), 7.47 (t, 2H), 7.27 (t, 1H). 177.79, 159.55, 141.56, 130.09, 126.98, 118.93, 117.40.

**(7f)** 3433.98 (m), 3257.69 (m), 3103.60 (m), 1706.78 (s), 1659.51 (s), 1499.28 (s), 1435.27 (s), 1349.30 (w), 1247.92 (s). 14.28 (bs, 1H), 12.40 (bs, 2H), 7.51 (d, J= 8.7 Hz, 2H), 7.28 (d, J= 8.7 Hz, 2H), 2.32 (s, 3H). 177.69, 139.26, 136.90, 130.56, 118.41, 117.42, 30.84.

**(7g)** 3421.46 (m), 3254.20 (m), 3079.86 (m), 1700.65 (s), 1654.05 (s), 1505.89 (s), 1437.52 (s), 1416.95 (s), 1349.22 (w), 1242.32 (s). 14.41 (s, 1H), 12.51 (s, 1H), 12.34 (s, 1H), 7.58 (d, J= 9.0 Hz, 2H), 7.05 (d, J= 9.0 Hz, 2H), 3.79 (s, 3H). 177.54, 158.84, 134.90, 119.12, 117.79, 115.36, 55.76.

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