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Short Report

Solid-Phase Synthesis of Isoalloxazines using Merrifield Resin

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A reação da resina de Merrifield ligada a compostos diamino com aloxan monohidrato, resultou em uma resina ligada a isoaloxazinas 10-substituídas, que foram caracterizadas por fluorescência em fase sólida e espectroscopia de IV. A resina foi segmentada por solução aquosa de HF/DMF a 40%, obtendo-se isoaloxazinas 7-carboxi-10-substituídas, que foram caracterizadas por UV-Vis., IV, ^{1}H RMN, fluorescência e análise elementar.

The reaction of Merrifield resin bound diamino compounds with alloxan monohydrate gave 7-resin bound 10-substituted isoalloxazines that were characterized by solid phase fluorescence and IR spectroscopy. The resin was cleaved by 40% aqueous HF/DMF to give 7-carboxy-10-substituted isoalloxazines that were characterized by UV-vis., IR, ^{1}H NMR, fluorescence and elemental analysis.

Keywords: isoalloxazines (or flavins), merrifield resin, polymer-supported synthesis, cyclocondensation, alloxan monohydrate, solid-state fluorescence

Introduction

Polymer-supported synthesis is an important tool in the synthesis of biologically active compounds including peptides, oligonucleotides and oligosaccharides.[1,2] Further, the polymer-supported synthesis has also been applied in a variety of organic reactions including the synthesis of natural products, heterocycles and in medicinal chemistry.[3-10]

Synthesis of 10-substituted isoalloxazines by the acidic cyclocondensation of 2-substituted aminoanilines with alloxan monohydrate in aqueous and organic solvents has been reported by us.[11-15] Now, we report an improved synthesis of selected novel 10-substituted isoalloxazine-7-carboxylic acids via polymer-support to examine the feasibility of polymer-support synthesis in the synthesis of biologically active isoalloxazines. The isoalloxazines being a cofactor of flavoproteins, are involved in the catalysis of a wide variety of biological redox reactions, mediate electron transfer processes and in the regulation of neurotransmitters and detoxification of xenobiotics.[15-19] The isoalloxazines are also found to possess anti-malarial activity and are potent inhibitors of both human and plasmodium glutathione reductase.[20,21]

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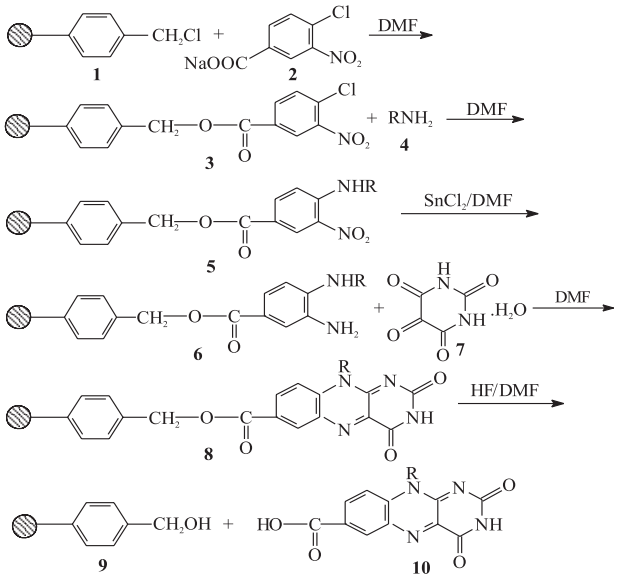
Results and Discussion

The reaction of chloromethylated polystyrene resin (**1**) with sodium salt of the 4-chloro-3-nitrobenzoic acid (**2**) gives the resin bound 4-chloro-3-nitrobenzoate (**3**). The reaction of substituted amines/anilines **4a**-**l** with **3** was carried out in DMF to get 4-(N-substituted amino)-3-nitrobenzoate (**5a**-**l**).[22] The reduction of **5a**-**l** with $SnCl_2.H_2O$ gave resin bound diamines **6a**-**l**.[22] The each nucleophilic substitution products and the diamino products were cleaved with hydrofluoric acid (HF) in DMF and show satisfactory elemental analysis. The cyclocondensation of **6a**-**l** with alloxan monohydrate (**7**) in the presence of boric acid/acetic acid and DMF gave the resin bound isoalloxazines **8a**-**l** (Scheme 1). The appearance of strong peaks in the region 1640-1660 and 1710-1730 cm^{-1} for the presence of carbonyl groups (C=O) at positions 2 and 4 respectively, and in the region 3460-3420 cm^{-1} for -NH group at position 3 in IR spectra is characteristic of the isoalloxazine ring.[23] For example, the IR spectra of **8a** shows peaks at 1729, 1713 and 1661 cm^{-1} for three C=O groups and at 3432 cm^{-1} for –NH group (Table 1) of the resin linked isoalloxazine. Further, the solid phase fluorescence[24-27] of **8a**-**l** shows emission spectra in the region 510-563



a. $CH_2CH_2CH_3$; **b.** $CH_2(CH_2)_2CH_3$; **c.** $CH_2(CH_2)_8CH_3$; **d.** $CH_2(CH_2)_{10}CH_3$; **e.** C_6H_{11}; **f.** $CH_2CH{=}CH_2$; **g.** $CH_2C_6H_5$; **h.** C_6H_5; **i.** 4'-ClC_6H_4; **j.** 4'-BrC_6H_4; **k.** 4'-$OCH_3C_6H_4$ and **l.** 2',6'-$CH_3C_6H_3$

Scheme 1.

and 659-662 nm when excited at 420 nm, which are very similar to their solution phase fluorescence spectra taken after cleavage at same excitation wavelength (Table 1, Experimental section). The reaction of **8a**-**l** with 40% aqueous HF/DMF gave 10-substituted isoalloxazine-7-carboxylic acids (**10a**-**l**) in 74-81% yields. The structure of **10a**-**l** was confirmed by different spectroscopic data, including IR, UV-Visible, ^{1}H NMR, fluorescence and analytical data (experimental section).

In summary, the present polymer-supported synthesis is an attractive, clean, easy and efficient method in comparison to their solution phase synthesis where each synthetic step requires tedious purification process including column chromatography, for the synthesis of 7-carboxy-10-substituted isoalloxazines in good yields.

Experimental

All melting points are uncorrected and were recorded on Thomas Hoover Unimelt Capillary melting point Apparatus. IR spectra were recorded on Shimadzu TR-435 spectrophotometer (ν_{max} in cm^{-1}). The absorption spectra were recorded on Shimadzu UV-260 spectrophotometer and absorption maxima were expressed in nm. ^{1}H NMR was recorded on Bruker Avance 300 spectrometer using TMS as an internal reference (chemical shift in ppm). Fluorescence spectra were recorded at the excitation value 420 nm on a Jobin Youn JY-3CS spectrofluorimeter and emission maxima were expressed in nm. Elemental analysis was carried out in a Heraeus CHN analyzer.

Merrifield resin, Alloxan monohydrate and 4-chlorobenzoic acid were obtained from Across, Germany and used without further purifications.

*Coupling of merrifield resin (**1**) with sodium salt of 4-chloro-3-nitrobenzoic acid (**2**)*

1 (15 g) (chloromethylated styrene-divinylbenzene copolymer, 2% cross-linked, 2.50 mequiv of Cl/g), **2** (11.175 g, 50 mmol) and DMF (100 mL) was taken and stirred for 24 h. The suspension was filtered, washed subsequently with H_2O, DMF, CH_2Cl_2 and MeOH (2×100 mL each) and dried in vacuum to get the resin **3** (20.372 g). 2.906 g (13 mmol) of the sodium salt was recovered after the reaction, which shows that approximately 36 mmol is the theoretical loading capacity of the resin **3**. 15.372 g of the resin **3** has been taken and divided into 12 equal parts to perform further reactions. The yields of the final compounds were calculated based on the theoretical loading.

*General method for the synthesis of merrifield resin bound N-substituted-2-nitroanilines (**5a**-**l**).* Substituted amines/anilines (**4a**-**l**) (3.00 mmol) and DMF (75 mL) were added

Table 1.

Compound	Yield / (g)	Fluorescence λ emission[a] / nm (counts)	IR (KBr) / cm^{-1} NH and C=O
8a	1.358	510.0 (3.15), 660.0 (0.63)	3432 and 1729, 1713, 1661
8b	1.356	521.0 (7.78), 660.1 (1.62)	3442 and 1722, 1709, 1663
8c	1.551	517.9 (4.49), 660.4 (0.91)	3432 and 1720, 1710, 1670
8d	1.613	513.8 (2.29), 659.9 (0.80)	3436 and 1734, 1702, 1650
8e	1.529	523.2 (7.79), 653.0 (0.62)	3460 and 1729, 1711, 1680
8f	1.341	518.8 (3.39), 660.0 (0.67)	3425 and 1733, 1715, 1670
8g	1.439	518.4 (0.99), 661.0 (0.19)	3445 and 1729, 1715, 1660
8h	1.388	560.6 (6.69), 660.0 (2.28)	3455 and 1726, 1713, 1672
8i	1.415	563.4 (9.97), 660.9 (2.77)	3442 and 1725, 1715, 1660
8j	1.571	513.0 (2.59), 652.8 (0.32)	3425 and 1728, 1712, 1670
8k	1.411	559.0 (12.97), 662.9 (3.42)	3428 and 1727, 1711, 1670
8l	1.476	510.9 (3.29), 660.7 (0.69)	3432 and 1728, 1718, 1664

[a] (Exc: 420 nm).

to each part of the resin (**3**) (1.281 g) at room temperature and the suspension was stirred at room temperature for 12 h. It was filtered and washed subsequently with DMF, CH_2Cl_2 and MeOH (2×50 mL each) and dried in vacuo to get resin bound compounds (**5a-l**).

*General method for the synthesis of merrifield resin bound N-substituted-2-aminoanilines (**6a-l**).* To each part of the resin bound nitro compounds (**5**-0.01 g) were added $SnCl_2.H_2O$ (3.50 mmol) and DMF (75 mL) at room temperature. The suspensions was stirred at room temperature for 12 h, filtered and washed subsequently with DMF, H_2O, CH_2Cl_2 and MeOH (2×50 mL each) and dried in vacuo to get resin bound diamino compounds (**6a-l**).

*General method for the synthesis of 7-Merrifield resin bound 10-substituted isoalloxazines (**8a-l**).* To each part of the resin **6a-l**, alloxan monohydrate (**7**) (3.00 mmol), boric acid (3.00 mmol), glacial acetic acid (1.0 mL) and DMF (75 mL) were added. The suspension was stirred at room temperature for 12 h, filtered and washed with H_2O, CH_2Cl_2 and MeOH (2×50 mL each) and dried in vacuo to get the resin (**8a-l**).

Cleavage of resin bound isoalloxazines. To each part of the resin **8a-l**, aqueous HF (40%) and DMF (1:1) (75 mL) were added at 0 °C and stirred for 1 h at room temperature. The suspension was filtered and washed with DMF (2×50 mL). The combined filtrate was concentrated under reduced pressure to get the desired products (**10a-l**) which was recrystallized from AcOH/H_2O.

*10-propylisoalloxazine-7-carboxylic acid (**10a**).* Yield: 0.520 g (77%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm ($\varepsilon_{max}/10^{-3}$ L mol^{-1} cm^{-1}): 429 (0.192), 346 (0.077), 285 (0.733); IR (KBr) ν_{max}/ cm^{-1}: 3404, 3027, 2846, 2362, 1713, 1706, 1659, 1624, 1586, 1551, 1512, 1429, 1256, 1181, 1098, 884, 839, 774; ^{1}H NMR (DMSO-d_6), δ 1.26 (3H, t, *J* 6.3 Hz, CH_3), 1.82-1.89 (2H, m, CH_2), 4.67 (2H, t, $N^{10}CH_2$, *J* 6.5 Hz), 7.78 (1H, d, H-9, *J* 8.7 Hz), 8.06 (1H, bs, H-3), 8.48 (1H, d, H-8, *J* 9.0 Hz), 8.86 (1H, d, H-6, *J* 1.5 Hz), 11.67 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 512.7 (4.32), 662.0 (0.77) nm; Elemental Analysis: Found,%: C 56.05; H 4.09; N 18.79. $C_{14}H_{12}N_4O_4$. Calculated,%: C 56.00; H 4.03; N 18.66.

*10-butylisoalloxazine-7-carboxylic acid (**10b**).* Yield: 0.543 g (77%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm ($\varepsilon_{max}/10^{-3}$ L mol^{-1} cm^{-1}): 431 (0.014), 334 (0.005), 288 (0.289); IR (KBr) ν_{max}/ cm^{-1}: 3474, 3169, 2951, 1720, 1680, 1660, 1591, 1556, 1519, 1405, 1345, 1250, 1236, 1099, 842, 771; ^{1}H NMR (DMSO-d_6), δ 1.00 (3H, t, *J* 6.7 Hz, CH_3), 1.52-1.79 (4H, m, $(CH_2)_2$), 4.61 (2H, t, $N^{10}CH_2$, *J* 6.6 Hz), 7.94 (1H, d, H-9, *J* 9.0 Hz), 8.09 (1H, bs, H-3), 8.40 (1H, d, H-8, *J* 8.7 Hz), 8.68 (1H, s, H-6), 11.60 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 524.0 (9.90), 662.0 (2.23) nm.; Elemental Analysis: Found,%: C 57.55; H 4.59; N 17.83. $C_{15}H_{14}N_4O_4$. Calculated,%: C 57.50; H 4.50; N 17.88.

*10-Decylisoalloxazine-7-carboxylic acid (**10c**).* Yield: 0.700 g (78%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/ nm ($\varepsilon_{max}/10^{-3}$ L mol^{-1} cm^{-1}): 429 (1.533), 337 (0.790), 289 (2.385); IR (KBr) ν_{max}/ cm^{-1}: 3404, 3027, 2846, 2362, 1713, 1706, 1659, 1624, 1586, 1551, 1512, 1429, 1256, 1181, 1098, 884, 839, 774; ^{1}H NMR (DMSO-d_6), δ 0.87 (3H, t, *J* 6.1 Hz, CH_3), 1.61-2.01 (16H, m, $(CH_2)_8$), 4.69 (2H, t, $N^{10}CH_2$, *J* 6.3 Hz), 7.65 (1H, d, H-9, *J* 9.1 Hz), 8.55 (1H, d, H-8, *J* 8.9 Hz), 8.98 (1H, s, H-6), 11.80 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 519.0 (5.73), 662.7 (0.99) nm; Elemental Analysis: Found,%: C 63.40; H 6.59; N 14.03. $C_{21}H_{26}N_4O_4$. Calculated,%: C 63.30; H 6.58; N 14.06.

*10-Dodecylisoalloxazine-7-carboxylic acid (**10d**).* Yield: 0.759 g (79%); mp.: >300 °C; UV-Vis (DMSO) λ_{max} / nm ($\varepsilon_{max}/10^{-3}$ L mol^{-1} cm^{-1}): 430 (1.283), 347 (0.587), 285 (4.900); IR (KBr) ν_{max}/ cm^{-1}: 3404, 3027, 2846, 2362, 1713, 1706, 1659, 1624, 1586, 1551, 1512, 1429, 1256, 1181, 1098, 884, 839, 774; ^{1}H NMR (DMSO-d_6): 0.88 (3H, t, *J* 6.8 Hz, CH_3), 1.87-2.11 (20H, m, $(CH_2)_{10}$), 4.73 (2H, t, $N^{10}CH_2$, *J* 6.7 Hz), 7.69 (1H, d, H-9, *J* 9.1 Hz), 8.58 (1H, d, H-8, *J* 8.0 Hz), 8.99 (1H, s, H-6), 11.89 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 515.9 (3.70), 661.9 (1.14) nm; Elemental Analysis: Found,%: C 64.72; H 7.07; N 13.18. $C_{23}H_{30}N_4O_4$. Calculated,%: C 64.77; H 7.09; N 13.14.

*10-Cyclohexylisoalloxazine-7-carboxylic acid (**10e**).* Yield: 0.614 g (80%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm ($\varepsilon_{max}/10^{-3}$ L mol^{-1} cm^{-1}): 432 (1.787), 338 (0.812), 286 (9.454); IR (KBr) ν_{max}/ cm^{-1}: 3404, 3027, 2846, 2362, 1713, 1706, 1659, 1624, 1586, 1551, 1512, 1429, 1256, 1181, 1098, 884, 839, 774; ^{1}H NMR (DMSO-d_6), δ 1.25-2.00 (10H, m, cyclohexyl-H), 4.15-4.17 (1H, m, $N^{10}CH$) 7.79 (1H, d, H-9, *J* 8.9 Hz), 8.21 (1H, bs, H-3), 8.56 (1H, d, H-8, *J* 8.9 Hz), 8.98 (1H, s, H-6), 11.86 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 527.8 (8.63), 657.9 (0.65) nm; Elemental Analysis: Found,%: C 59.91; H 4.70; N 16.42. $C_{17}H_{16}N_4O_4$. Calculated,%: C 59.99; H 4.74; N 16.46.

*10-Allylisoalloxazine-7-carboxylic acid (**10f**).* Yield: 0.538 g (80%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm ($\varepsilon_{max}/10^{-3}$ L mol^{-1} cm^{-1}): 432 (0.187), 344 (0.067), 286 (0.632); IR (KBr) ν_{max}/ cm^{-1}: 3412, 3029, 2846, 2362, 1720, 1706,

1680, 1628, 1586, 1551, 1512, 1429, 1256, 1181, 1098, 884, 839 and 774; ^{1}H NMR (DMSO-d_6), δ 4.26-4.29 (2H, m, $N^{10}CH_2$), 5.12-5.27 (3H, m, CH=CH_2), 7.78 (1H, d, H-9, *J* 8.7 Hz), 8.48 (1H, d, H-8, *J* 9.0 Hz), 8.86 (1H, s, H-6), 11.67 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 518.0 (4.38), 660.0 (0.79) nm; Elemental Analysis: Found,%: C 56.42; H 3.40; N 18.71. $C_{14}H_{10}N_4O_4$. Calculated,%: C 56.38; H 3.38; N 18.79.

10-Benzylisoalloxazine-7-carboxylic acid (***10g***). Yield: 0.620 g (79%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm (ε_{max}/10^{-3} L mol^{-1} cm^{-1}): 422 (0.977), 342 (0.484), 268 (3.283); IR (KBr) ν_{max}/cm^{-1}: 3414, 3182, 3101, 2924, 2852, 2570, 2364, 1729, 1701, 1623, 1589, 1457, 1395, 1363, 1321, 1273, 1195, 1148, 872, 758; ^{1}H NMR (DMSO-d_6), δ 5.94 (2H, s, $N^{10}CH_2$), 7.26-7.54 (5H, m, Ar-H), 8.00 (1H, d, H-9, *J* 8.9 Hz), 8.25 (1H, bs, H-3), 8.38 (1H, d, H-8, *J* 8.4 Hz), 8.84 (1H, s, H-6), 12.01 (1H, s, COOH); Flourescence (DMSO) λ emission (intensity): 521.4 (1.78), 664.3 (0.35) nm; Elemental Analysis: Found,%: C 62.09; H 3.42; N 16.05. $C_{18}H_{12}N_4O_4$. Calculated,%: C 62.07; H 3.47; N 16.08.

10-Phenylisoalloxazine-7-carboxylic acid (***10h***). Yield: 0.609 g (81%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm (ε_{max}/10^{-3} L mol^{-1} cm^{-1}): 435 (0.113), 334 (0.052), 285 (2.990); IR (KBr) ν_{max}/cm^{-1}: 3452, 3220, 3016, 2926, 1718, 1654, 1589, 1545, 1430, 1390, 1279, 1181, 907, 806, 767; ^{1}H NMR (DMSO-d_6), δ 6.99 (1H, d, H-9, *J* 8.2 Hz), 7.25-7.69 (5H, m, 10-phenyl H), 7.81 (1H, d, H-8, *J* 8.1 Hz), 8.21 (1H, d, H-6, *J* 1.9 Hz), 11.01 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 567.0 (7.27), 662.0 (2.68) nm; Elemental Analysis: Found,%: C 61.03; H 2.99; N 16.77. $C_{17}H_{10}N_4O_4$. Calculated,%: C 61.08; H 3.01; N 16.76.

10-(4'-chlorophenyl)isoalloxazine-7-carboxylic acid (***10i***). Yield: 0.615 g (74%); mp.: >300 °C; UV-Vis (DMSO) λ_{max} / nm (ε_{max}/10^{-3} L mol^{-1} cm^{-1}): 432 (0.342), 338 (0.284), 286 (10.420); IR (KBr) ν_{max}/cm^{-1}: 3399, 3173, 3065, 2936, 1725, 1665, 1585, 1544, 1399, 1289, 1192, 846 and; ^{1}H NMR (DMSO-d_6), δ 7.62 (1H, d, H-9, *J* 9.0 Hz), 7.74 (2H, d, H-2', H-6', *J* 9.0 Hz), 7.93 (2H, d, H-3', H-5', *J* 9.0 Hz), 8.31 (1H, dd, H-8, *J* 2.1 and 9.0 Hz), 8.69 (1H, bs, H-3), 8.92 (1H, d, H-6, *J* 2.1 Hz), 11.90 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 567.0 (12.29), 663.9 (3.56) nm; Elemental Analysis: Found,%: C 55.39; H 2.41; N 15.12. $C_{17}H_9N_4O_4Cl$. Calculated,%: C 55.37; H 2.46; N 15.19.

10-(4'-Bromophenyl)isoalloxazine-7-carboxylic acid (***10j***). Yield: 0.689 g (74%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm (ε_{max}/10^{-3} L mol^{-1} cm^{-1}): 431 (0.857), 332 (0.289), 286 (1.246); IR (KBr) ν_{max}/cm^{-1}: 3404, 3027, 2846, 2362, 1713, 1706, 1659, 1624, 1586, 1551, 1512, 1429, 1256, 1181, 1098, 884, 839, 774; ^{1}H NMR (DMSO-d_6), δ 7.64 (1H, d, H-9, *J* 9.0 Hz), 7.76 (2H, d, H-2', H-6', *J* 9.0 Hz), 7.92 (2H, d, H-3', H-5', *J* 9.0 Hz), 8.35 (1H, dd, H-8, *J* 2.1 and 9.0 Hz), 8.72 (1H, bs, H-3), 8.95 (1H, d, 6-H, *J* 2.1 Hz), 11.89 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 516.7 (3.11), 658.7 (0.41) nm; Elemental Analysis: Found,%: C 49.45; H 2.16; N 13.55. $C_{17}H_9N_4O_4Br$. Calculated,%: C 49.42; H 2.19; N 13.56.

10-(4'-Methoxyphenyl)isoalloxazine-7-carboxylic acid (***10k***). Yield: 0.628 g (77%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm (ε_{max}/10^{-3} L mol^{-1} cm^{-1}): 434 (0.419), 340 (0.316), 282 (7.499); IR (KBr) ν_{max}/cm^{-1}: 3424, 2925, 1728, 1662, 1640, 1607, 1490, 1459, 1299, 1219, 1176, 1040, 1017, 833, 757; ^{1}H NMR (DMSO-d_6), δ 4.06 (3H, s, OCH_3), 7.60 (1H, d, H-9, *J* 9.6 Hz), 8.11 (2H, d, H-3', H-5', *J* 9.3 Hz), 8.21 (2H, d, H-2', H-6', *J* 9.0 Hz), 8.29 (1H, d, H-8, *J* 9.0 Hz), 8.80 (1H, s, H-6), 11.92 (1H, s, COOH); Fluorescence (DMSO) λ emission (intensity): 562.0 (15.97), 664.6 (4.02) nm; Elemental Analysis: Found,%: C 59.37; H 3.35; N 15.41. $C_{18}H_{12}N_4O_5$. Calculated,%: C 59.34; H 3.32; N 15.38.

10-(2, 6'-Dimethylphenyl)isoalloxazine-7-carboxylic acid (***10l***). Yield: 0.604 g (74%); mp.: >300 °C; UV-Vis (DMSO) λ_{max}/nm (ε_{max}/10^{-3} L mol^{-1} cm^{-1}): 431 (0.038), 338 (0.023), 266 (0.130); IR (KBr) ν_{max}/cm^{-1}: 3422, 3182, 2926, 1724, 1664, 1613, 1588, 1548, 1460, 1392, 1272, 1210, 1187, 1025, 876, 796 and 745; ^{1}H NMR (DMSO-d_6), δ 1.86 (6H, s, 2×CH_3), 6.98 (1H, d, H-9, *J* 8.0 Hz), 7.23-7.29 (2H, m, 3'-H, 5'-H), 7.36-7.77 (2H, m, H-8, H-4'), 8.31 (1H, d, H-6, *J* 2.1 Hz), 11.88 (1H, s, COOH); Flourescence (DMSO) λ emission (intensity): 513.6 (4.68), 662.0 (0.96) nm; Elemental Analysis: Found,%: C 62.95; H 3.85; N 15.47. $C_{19}H_{14}N_4O_4$ Calculated,%: C 62.98; H 3.89; N 15.46.

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