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Green Synthesis of Schiff Bases Derived from 4,5-Diazafluorene-9-one in Aqueous Medium Under Microwave Irradiation

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A series of Schiff bases were successfully synthesized with satisfactory yield from various amines and 4,5-diazafluorene-9-one in water by using polystyrene sulfonic acid as a catalyst under microwave irradiation.

Key Words: Schiff base, 4,5-Diazafluorene-9-one, Microwave irradiation, Aqueous medium.

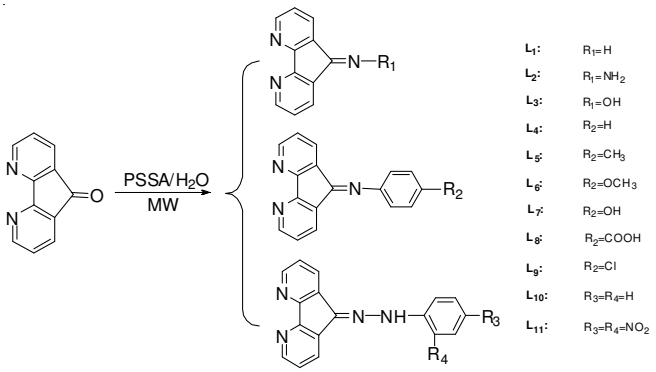
INTRODUCTION

4,5-Diazafluoren-9-one and their derivatives are also strong bidentate chelating and bridging agents[1], which have been widely explored due to their easy accessibility, easy modification and relative air stability[2]. Synthesis of Schiff bases containing a bipyridine type metal receptor[3], has attracted considerable attention due to their many applications in the fields of catalyst[4], conducting and photoresponsive materials[5] and anion sensor[6] *etc*. But, higher temperatures, increased reaction times, plenty of organic solvent and the use of a catalyst were generally required in previous synthesis of Schiff bases from 4,5-diazafluorene-9-one[7,8].

In recent years, microwave irradiation was demonstrated to be a valuable tool in organic synthesis resulting in faster and cleaner reactions that sometimes exhibit different reactivates due to specific microwave absorption[9]. From an environmental view point, we report herein, for the first time, the reaction (**Scheme-I**) can be successfully accomplished with satisfactory yield in water by using polystyrene sulfonic acid (PSSA) as a catalyst under microwave irradiation (MW), which is a rapid and environmentally friendly preparation of schiff bases from 4,5-diazafluorene-9-one compared to conventional heating method.

EXPERIMENTAL

All reagents and solvents were purchased commercially as AC grade and were used without further purification unless noted. The molecular weight of polystyrene sulfonic acid is 70,000. Organic solvents were dried over 4 Å activated molecular sieves prior to use. 4,5-diazafluoren-9-one was obtained as light yellow needle by oxidation of 1,10-phenanthroline with $KMnO_4$ in a KOH solution following a literature method[10]. The microwave reaction was carried out in the WF-4000M closed type microwave synthesis system with the refluxing equipment. Melting points were determined in open capillaries and uncorrected. ^{1}H NMR spectra were obtained using Bruker DRX300 spectrometer with TMS. The IR spectra were determined as potassium bromide pellet on a Bruker Equinox55 FT-IR spectrophotometer. UV-VIS spectra were performed with a UV-2501PC spectrophotometer. Mass spectra and element analysis were done with LC-MSD-Trap-SL and Elementar Vario EL III.



Scheme-I: Synthesis of schiff bases derived from 4,5-diazafluorene-9-one

General procedure for preparation of L_1-L_{11}: All the Schiff bases derived from 4,5-diazafluorene-9-one were synthesized by modification of a literature procedure[11]. A mixture of 4,5-diazafluorene-9-one (455 mg, 2.5 mmol) and amines (3 mmol) were dissolved in 20 % polystyrene sulfonic acid solution in water (5 mL) and then were exposed to microwave irradiation (700 W, 100 ºC) for 7 min. The desired

precipitate was filtered after cooling, washed with ethanol 3 times and dried in vacuum oven at 50 ºC. The results of yield, melt point and UV-visible spectra were listed in Table-1.

9-Imine-4,5-diazafluorene (L_1): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.82 (dd, 2H, J_1 = 5.1, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.05 (dd, 2H, J_1 = 5.1, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.38 (t, 2H, J_1 = 7.6, J_2 = 5.1 Hz, pyridyl H *meta* to N), 5.45 (s, 1H, =NH). IR (KBr, ν_{max}, cm^{-1}): 3314, 3058, 1655, 1590, 1555, 1420, 1200, 801, 726. Elemental analysis calcd. (%) for $C_{11}H_7N_3$: C, 72.92; H, 3.89; N, 23.19. Found (%): C, 72.89; H, 3.92; N, 23.15. MS: m/z = 181.01 (Calcd.: 181.06).

9-Hydrazone-4,5-diazafluorene (L_2): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.75 (dd, 1H, J_1 = 5.1, J_2 = 1.6 Hz, pyridyl H *ortho* to N), 8.65 (dd, 1H, J_1 = 5.0, J_2 = 1.6Hz, pyridyl H *ortho* to N), 8.27 (dd, 1H, J_1 = 7.7, J_2 = 1.6 Hz, pyridyl H *para* to N), 8.16 (dd, 1H, J_1 = 7.8, J_2 = 1.6 Hz, pyridyl H *para* to N), 7.50 (t, 1H, J_1 = 7.7, J_2 = 5.1 Hz, pyridyl H *meta* to N), 7.39 (t, 1H, J_1 = 7.7, J_2 = 5.0 Hz, pyridyl H *meta* to N), 6.65 (s, 2H, -NH_2). IR (KBr, ν_{max}, cm^{-1}): 3376, 3320, 3058, 1646, 1593, 1561, 1206, 799, 723. Elemental analysis calcd. (%) for $C_{12}H_9N_3$: C, 67.34; H, 4.11; N, 28.55. Found (%): C, 67.30; H, 4.10; N, 28.52. MS: m/z = 196.01 (calcd.: 196.06).

9-Oxime-4,5-diazafluorene (L_3): Sodium carbonate (0.016 g, 1.5 mmol) was used as a neutralizer in the reaction. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 13.14 (s, 1H, -OH), 8.73 (dd, 1H, J_1 = 5.1, J_2 = 1.6 Hz, pyridyl H *ortho* to N), 8.67 (dd, 1H, J_1 = 5.0, J_2 = 1.6 Hz, pyridyl H *ortho* to N), 8.27 (dd, 1H, J_1 = 7.7, J_2 = 1.6 Hz, pyridyl H *para* to N), 8.17 (dd, 1H, J_1 = 7.8, J_2 = 1.6 Hz, pyridyl H *para* to N), 7.53 (t, 1H, J_1 = 7.7, J_2 = 5.1 Hz, pyridyl H *meta* to N), 7.46 (t, 1H, J_1 = 7.7, J_2 = 5.0 Hz, pyridyl H *meta* to N). IR (KBr, ν_{max}, cm^{-1}): 3141, 3036, 1627, 1593, 1564, 1495, 1399, 1008, 949, 748. Elemental analysis calcd. (%) for $C_{11}H_7N_3O$: C, 67.00; H, 3.58; N, 21.31. Found (%): C, 69.92.; H, 3.56; N, 21.36. MS: m/z = 197.10 (calcd.: 197.06).

9-Anilino-4,5-diazafluorene (L_4): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.81 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.65 (dd, 1H, J_1 = 4.9, J_2 = 1.6 Hz, pyridyl H *ortho* to N), 8.26 (dd, 1H, J_1 = 7.8, J_2 = 1.6 Hz, pyridyl H *para* to N), 7.43 (m, 3H, pyridyl H *meta* to N and Ar-H), 7.28 (t, 1H, J_1 = 7.7, J_2 = 5.1 Hz, pyridyl H *meta* to N), 7.02 (m, 3H, Ar-H), 6.87 (dd, 1H, J_1 = 7.8, J_2 = 1.5 Hz, pyridyl H *para* to N). IR (KBr, ν_{max}, cm^{-1}): 3045, 1656, 1592, 1561, 1401, 748, 710. Elemental analysis calcd. (%) for $C_{17}H_{11}N_3$: C, 79.36; H, 4.31; N, 16.33. Found (%): C, 79.30; H, 4.35; N, 16.36. MS: m/z = 257.13 (calcd.: 257.10).

9-(4-Methyanilino)-4,5-diazafluorene (L_5): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.80 (dd, 1H, J_1 = 5.0, J_2 = 1.6Hz, pyridyl H *ortho* to N), 8.64 (dd, 1H, J_1 = 4.9, J_2 = 1.6 Hz, pyridyl H *ortho* to N), 8.25 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.39 (t, 1H, J_1 = 7.6, J_2 = 5.1 Hz, pyridyl H *meta* to N), 7.25 (m, 2H, pyridyl H *meta* to N and Ar-H), 6.98 (m, 2H, pyridyl H *para* to N and Ar-H), 6.90 (d, 2H, J = 8.2Hz, Ar-H), 2.43 (s, 3H, -CH_3). IR (KBr, ν_{max}, cm^{-1}): 3046, 2954, 2869, 1642, 1590, 1557, 1399, 752, 729. Elemental analysis calcd. (%) for $C_{18}H_{13}N_3$: C, 79.68; H, 4.83; N, 15.49. Found (%): C, 79.62; H, 4.85; N, 15.46. MS: m/z = 271.13 (calcd.: 271.11).

9-(4-Methoxyanilino)-4,5-diazafluorene (L_6): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.80 (dd, 1H, J_1 = 5.0, J_2 = 1.6 Hz, pyridyl H *ortho* to N), 8.65 (dd, 1H, J_1 = 5.0, J_2 = 1.6 Hz, pyridyl H *ortho* to N), 8.23 (dd, 1H, J_1 = 7.7, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.38 (t, 1H, J_1 = 7.7, J_2 = 5.0 Hz, pyridyl H *meta* to N), 7.09 (dd, 1H, J_1 = 7.8, J_2 = 1.7 Hz, pyridyl H *para* to N), 6.98 (m, 5H, pyridyl H *meta* to N and Ar-H), 3.92 (s, 3H, -OCH_3). IR (KBr, ν_{max}, cm^{-1}): 3043, 2999, 2837, 1634, 1590, 1559, 1497, 1400, 1234, 1023, 845, 757. Elemental analysis calcd. (%) for $C_{18}H_{13}N_3O$: C, 75.25; H, 4.56; N, 13.95. Found (%): C, 75.20; H, 4.58; N, 13.97. MS: m/z = 287.07 (calcd.: 287.11).

9-(4-Hydroxyanilino)-4,5-diazafluorene (L_7): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.53 (s, 1H, -OH), 8.79 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.67 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.27 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.54 (t, 1H, J_1 = 7.6, J_2 = 4.9 Hz, pyridyl H *meta* to N), 7.27 (t, 1H, J_1 = 7.6, J_2 = 4.9 Hz, pyridyl H *meta* to N), 7.13 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 6.90 (m, 4H, Ar-H). IR (KBr, ν_{max}, cm^{-1}): 3144, 3037, 1638, 1592, 1561, 1504, 1401, 1276, 1230, 1165, 758, 708. Elemental analysis calcd. (%) for $C_{17}H_{11}N_3O$: C, 74.71; H, 4.06; N, 15.38. Found (%): C, 74.65; H, 4.00; N, 15.42. MS: m/z = 272.85 (calcd.: 273.09).

9-(4-Carboxyanilino)-4,5-diazafluorene (L_8): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 12.93 (s, 1H, -COOH), 8.82 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.68 (dd, 1H, J_1 = 4.9, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.29 (dd, 1H, J_1 = 7.7, J_2 = 1.5 Hz, pyridyl H *para* to N), 8.02 (d, 2H, J = 8.6 Hz, Ar-H), 7.56 (t, 1H, J_1 = 7.7, J_2 = 4.9 Hz, pyridyl H *meta* to N),

TABLE-1
RESULTS OF YIELD, MELTING POINT AND UV-VISIBLE SPECTRA OF L_{1-11}

No.	Yield (%)	m.p. (ºC)	UV-VIS λ_{max} (> 235 nm, $\varepsilon \times 10^4$)[a]
L_1	78	195-196	249 (2.40), 304 (0.99), 317 (1.01).
L_2	82	208-210	245 (2.45), 303 (0.98), 313 (1.13).
L_3	80	>300	242 (2.41), 308 (1.00), 315 (0.96).
L_4	87	188-189	240 (2.40), 302 (0.95), 315 (1.02).
L_5	89	225-226	244 (2.56, 302 (0.98), 314 (1.13), 416 (0.20).
L_6	85	202-203.	252 (3.80), 300 (1.44), 314 (1.04), 435 (0.29).
L_7	90	>300	244 (2.69), 302 (1.15), 314 (0.97), 433 (0.26)
L_8	81	>300	245 (2.73), 265 (2.51), 302 (1.01), 314 (0.91), 394 (0.16)
L_9	93	216-217	246 (3.24), 302 (1.15), 314 (1.01), 405 (0.20)
L_{10}	85	188-189	242 (2.03), 303 (1.22), 314 (1.18), 396 (2.50)
L_{11}	83	>300	CH_3CN: 303 (0.58), 385 (1.30), 406 (1.27), 562 (0.32)

[a]L_1-L_{10} in $CHCl_3$ and L_{11} in CH_3CN.

7.24 (t, 1H, J_1 = 7.7, J_2 = 4.9 Hz, pyridyl H *meta* to N), 7.17 (d, 2H, *J* = 8.6 Hz, Ar-H), 6.83 (dd, 1H, J_1 = 7.7, J_2 = 1.5 Hz, pyridyl H *para* to N). IR (KBr, ν_{max}, cm^{-1}): 3098, 3032, 1702, 1702, 1663, 1598, 1566, 1398, 1259, 1164, 752, 723. Elemental analysis: calcd. (%) for $C_{18}H_{11}N_3O_2$: C, 71.75; H, 3.68; N, 13.95. Found (%): C, 71.70; H, 3.63; N, 13.89. MS: m/z = 300.99 (calcd.: 301.09).

9-(4-Chloroanilino)-4,5-diazafluorene (L_9): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.83 (dd, 1H, J_1 = 5.0, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.70 (dd, 1H, J_1 = 5.0, J_2 = 1.5 Hz, pyridyl H *ortho* to N), 8.26 (dd, 1H, J_1 = 7.6, J_2 = 1.5 Hz, pyridyl H *para* to N), 7.43 (m, 3H, pyridyl H *meta* to N and Ar-H), 7.07 (t, 1H, J_1 = 7.7, J_2 = 5.0 Hz, pyridyl H *meta* to N), 7.03 (dd, 1H, J_1 = 7.8, J_2 = 1.5 Hz, pyridyl H *para* to N), 6.95 (d, 2H, *J* = 8.2 Hz, Ar-H). IR (KBr, ν_{max}, cm^{-1}): 3046, 1656, 1592, 1561, 1400, 1087, 839, 749, 730. Elemental analysis calcd. (%) for $C_{18}H_{10}N_3Cl$: C, 69.99; H, 3.45; N, 14.40. Found (%): C, 69.93; H, 3.46; N, 14.45. MS: m/z = 291.01 (calcd.: 291.06).

9-Phenylhydrazone-4,5-diazafluorene (L_{10}): ^{1}H NMR (DMSO, 300 MHz): δ 10.72 (s, 1H, -NH), 8.90 (d, 1H, *J* = 7.7 Hz, pyridyl H *para* to N), 8.70 (dd, 2H, *J* = 4.6Hz, pyridyl H *ortho* to N), 8.29 (dd, 1H, *J* = 7.7Hz, pyridyl H *para* to N), 7.59 (m, 3H, pyridyl H *meta* to N and Ar-H), 7.45 (m, 3H, pyridyl H *meta* to N and Ar-H), 7.10 (m, 1H, Ar-H). IR (KBr, n_{max}, cm^{-1}): 3385, 3047, 1652, 1591, 1560, 1404, 750, 713. Elemental analysis: calcd. (%) for $C_{17}H_{12}N_4$: C, 74.98; H, 4.44; N, 20.58. Found (%): C, 74.92; H, 4.41; N, 20.64. MS: m/z = 272.14 (calcd.: 272.11).

9-(2,4-Dinitrophenylhydrazone)-4,5-diazafluorene (L_{11}): ^{1}H NMR (DMSO, 300 MHz): δ 12.01 (s, 1H, -NH), 8.96 (s, 1H, Ar-H), 8.84 (d, 1H, *J* = 5.0Hz, pyridyl H *ortho* to N), 8.76 (d, 1H, *J* = 4.9, Hz, pyridyl H *ortho* to N), 8.59 (d, 1H, *J* = 7.8Hz, pyridyl H *para* to N), 8.53 (d, 1H, *J* = 7.8 Hz, pyridyl H *para* to N), 8.42 (m, 2H, Ar-H), 7.73 (t, 1H, J_1 = 7.7, J_2 = 5.0 Hz, pyridyl H *meta* to N), 7.56 (t, 1H, J_1 = 7.8, J_2 = 5.0 Hz, pyridyl H *meta* to N). IR (KBr, ν_{max}, cm^{-1}): 3414, 3100, 1616, 1594, 1557, 1496, 1404, 1334, 1095, 754, 740, λ_{max} (> 235 nm, ε): Elemental analysis: calcd. (%) for $C_{17}H_{10}N_6O_4$: C, 56.36; H, 2.78; N, 23.20. Found. (%): C, 56.32; H, 2.74; N, 23.25. MS: m/z = 362.14 (calcd.: 362.08).

Conclusion

This work has demonstrated an efficient and general microwave irradiation protocol for the synthesis of schiff bases derived from 4,5-diazafluorene-9-one under microwave irradiation using polystyrene sulfonic acid as a catalyst in aqueous medium. The simple product isolation *via* filtration precludes the use of a organic solvent thus culminating in an environmentally benign aqueous protocol for the synthesis of schiff bases derived from 4,5-diazafluorene-9-one.

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