A New Route for Synthesis of 2-Substituted-3-amino-5-phenyl-7-*N*,*N*-dimethylamino Phenazinium Chloride Salts

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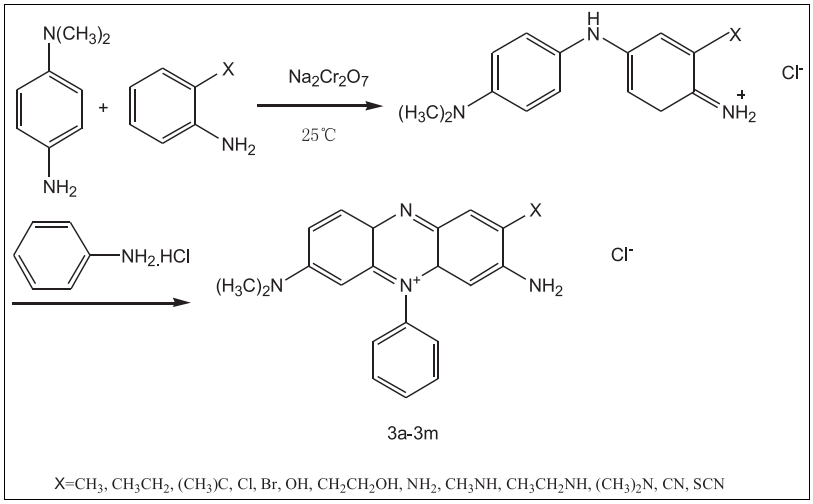

2-Methyl-3-amino-5-phenyl-7-*N*, *N*-dimethylamino phenazinium chloride salts were synthesized in better yields via the cyclization of 4-amino-*N*,*N*-dimethylaniline with toluidine derivatives and aminobenzene under the oxidation of sodium bicarbonate.

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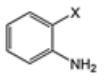
Phenazines are present in natural and synthetic products showing a variety of biological functions [1–6]. Because phenazines have interesting pharmacological activities naturally, they have attracted considerable attention [7]. In addition, their favorable properties are found wide uses in semi-conductor, optical devices, and renewable energy applications [8–16]. Furthermore, phenazines present a great structural diversity that justifies the development of new synthetic methods to prepare these complex substances. The preparation of the simpler phenazines, as distinguished from the numerous more complex phenazines developed by the dye industry, has hitherto been hampered by cumbersome methods of synthesis and relatively poor yields. It is well known that phenazinols may be readily obtained from phenazine ethers by hydrolysis, usually with hydrobromic acid [17] or with aluminum chloride [18]. Bahnmüller *et al.* have applied the Wohl–Aue procedure for the synthesis of ketal-protected natural product saphenic acid but afforded very low yield. [19] *N*-arylation has become more accessible owing to the advent of a new methodology developed by Hartwig and Buchwald [20]. Indeed, the development of biosynthetic studies on naturally occurring phenazines as well as the synthesis of analogs with similar or enhanced properties and a wealth of other research work are still limited by serious obstacles such as harsh experimental conditions, low yields, and incompatibility with the presence of functional groups [21–23]. Recently, a new series of alkylamine or arylamine-substituted benzo-phenazines have been synthesized from 1, 2-naphthoquinones by employing simple sequential Michael-type addition [24]. Jonathan *et al.* have synthesized a series of ethynylated phenazines and their bis-triazolyl cycloadducts to serve as metal ion sensors [25]. Here, we report on the use of the new method to synthesize 2-substituted-3-amino-5-phenyl-7-*N*, *N*-dimethylamino phenazinium chloride salts using sequential aniline arylation. Following the result, further optimization studies were carried out by altering reaction parameters, such as reaction time, temperature, and pH (Tables 1–3). Among the react time studied, best result was obtained in 8 h, which afforded better yield of 2-methyl-3-amino-5-phenyl-7-N, N-dimethylamino phenazinium chloride within 8 h at 105°C, pH 4.5 (Table 1, entry 3a). However, a significant decrease in the product yield was observed for the reaction of *o*-substituted aniline carried out with X = CN, SCN; Table 1, entry 3 l, 3 m which clearly shows that the oxidize cyclization of 4-amino-*N*,*N*-dimethyamine and *o*-substituted aniline with electron-

Table 1

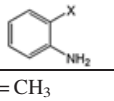
Reaction of 4-Amino-*N*,*N*-dimethylaniline with *o*-toluidine and aniline using $Na_2Cr_2O_7$ oxidation at different react time.[a]

Entry		React Time (h)	Product	Yield[b] (%)
3	X = CH_3	1	3	30
3a	X = CH_3	8	3a	73
3b	X = CH_2CH_3	8	3b	77
3c	X = $C(CH_3)_3$	8	3c	69
3d	X = Cl	8	3d	56
3e	X = Br	8	3e	58
3f	X = OH	8	3f	66
3g	X = CH_2CH_2OH	9	3g	63
3h	X = NH_2	8	3h	69
3i	X = CH_3NH	8	3i	70
3j	X = CH_3CH_2NH	9	3j	69
3k	X = $(CH_3)_2N$	10	3k	65
3l	X = CN	8	3l	39
3m	X = SCN	12	3m	41

[a]Reactions (entries 3–3 m) performed with *o*-toluidine (10 mmol) and aniline (11.5 mmol) using $Na_2Cr_2O_7$ (5.9 g,20 mmol) oxidation: pH 4.5; temperature: 105°C.
[b]Isolated yield.

Table 2

Reaction of 4-Amino-*N*,*N*-dimethylaniline with *o*-toluidine derivant and aniline using $Na_2Cr_2O_7$ oxidation at different temperature.[a]

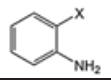
Entry		Temperature (°C)	Product	Yield[b] (%)
3	X = CH_3	25	3	6
3a	X = CH_3	35	3a	13
3b	X = CH_2CH_3	45	3b	27
3c	X = $C(CH_3)_3$	55	3c	32
3d	X = Cl	65	3d	35
3e	X = Br	75	3e	40
3f	X = OH	85	3f	58
3g	X = CH_2CH_2OH	105	3g	63
3h	X = NH_2	50	3h	39
3i	X = CH_3NH	60	3i	39
3j	X = CH_3CH_2NH	70	3g	45
3k	X = $(CH_3)_2N$	80	3k	51
3l	X = CN	90	3l	39
3m	X = SCN	105	3m	42

[a]Reactions (entries 3–3 m) performed with *o*-toluidine (10 mmol) and aniline (11.5 mmol) using $Na_2Cr_2O_7$ (5.9 g,20 mmol) oxidation: pH 4.5; react time:8 h.
[b]Isolated yield.

donating group can be cyclized much easier than the *o*-substituted aniline with electron-withdrawing group. When the large size substituent is on aniline, the yield of the corresponding oxidize cyclization products decreased. It is due to the steric exclusion existed between *o*-substituted aniline and 4-amino-*N*,*N*-dimethyamine (Table 2, entries 3c, 3k).With the temperature increased, the yield of the corresponding oxidize cyclization products increased (Table 2). In addition to that, the effect of temperature on the yield is obvious irrespective of the *o*-substituted aniline with electron-withdrawing group or with electron-donating group on the aromatic ring. The effect of pH on the yield is strong. When pH was below 4.5 with the pH of the reaction medium increased, the yield of the corresponding oxidize cyclization products increased. When pH was over 4.5, the yield decreased with pH increased (Table 3).

Table 3

Reaction of 4-Amino-*N*,*N*-dimethylaniline with *o*-toluidine and aniline using $Na_2Cr_2O_7$ oxidation at different pH.[a]

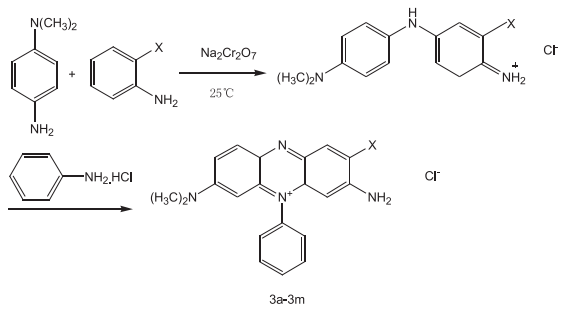
Entry		pH	Product	Yield[b] (%)
3	X = CH_3	1	3	25
3a	X = CH_3	1.5	3a	33
3b	X = CH_2CH_3	2	3b	37
3c	X = $C(CH_3)_3$	2.5	3c	49
3d	X = Cl	3	3d	36
3e	X = Br	3.5	3e	48
3f	X = OH	4	3f	59
3g	X = CH_2CH_2OH	4.5	3g	63
3h	X = NH_2	5	3h	59
3i	X = CH_3NH	5.5	3i	59
3g	X = CH_3CH_2NH	6	3g	42
3k	X = $(CH_3)_2N$	6.5	3k	38
3l	X = CN	7	3l	13
3m	X = SCN	7.5	3m	16

[a]Reactions (entries 3–3 m) performed with *o*-toluidine (10 mmol) and aniline (11.5 mmol) using $Na_2Cr_2O_7$ (5.9 g,20 mmol) oxidation for 8 h: temperature: 90°C.
[b]Isolated yield.

The reaction procedure was seen as same as Scheme 1.

Thus, a simple and efficient method have been developed for the synthesis of 2-substituted-3-amino-5-phenyl-7-*N*,*N*-dimethylamino phenazinium chloride salts via the oxidative cyclization of 4-amino-*N*,*N*-dimethylaniline with 2-substituted aniline and aniline using sodium dichromate as an oxidant. Various structurally divergent aliphatic, primary/secondary amines, and 2-substituted aniline were reacted with 4-amino-N,N-dimethylamine to produce the corresponding 2-substituted-3-amino-5-phenyl-7-*N*,*N*-dimethylamino phenazinium chloride in better yields. Moreover, 2-substituted phenazinium with electron-withdrawing group can be synthesized in good yield. This methodology may find widespread use in the synthesis of

Scheme 1



3a-3m

2-substituted-3-amino-5-phenyl-7-*N*,*N*-dimethylamino phenazinium chloride.

EXPERIMENTAL

Reagent grade ferric chloride, aluminum chloride, hydrazine hydrate, sodium bichromate, sodium acetate, dimethylamine hydrochloride, sodium hydroxide, sodium bicarbonate, 4-nitrobromobenzene, aniline, and 2-substituted aniline were purchased form National Medicines Corporation Ltd (China) and used without any further purification. All solvents used were analytical grade and were used as purchase from Merck Chemicals (Shanghai) Co., Ltd. Routine monitoring of the reactions were performed by thin-layer chromatography studies using Merck silica gel 60 f254 (Merck CO, Germany). Purification of products was carried out by flash column chromatography using neutral alumina and a mixture of ethyl acetate and hexanes as eluting agent. Infrared (IR) absorption data were acquired on a Thermo Nicolet Nexus 670 FT-IR spectrometer (Thermo Nicolet Corp., Madison, WI) with DTGS KBr detector (Thermo Nicolet Corp., Madison, WI). All the products were characterized by mass, ^{1}H and ^{13}C NMR spectroscopy. The NMR spectra of samples were acquired on a Varian Unity Inova 500 MHz spectrometer (Varian Inova Co. Ltd., Palo Alto, CA) using tetramethylslane as an internal standard in $CDCl_3$ or DMSO-d_6. Mass spectra were acquired on a Thermo LCQ fleet ion trap mass spectrometer (Waters, MT).

In a typical experiment, 10 mmol of 4-amino-*N*,*N*-dimethylaniline chloride aniline, 10 mmol of *o*-toluidine hydrochloride in 200 mL of water, and stirred at 25°C, then 20 mmol (5.9 g) of sodium bichromate in 90 mL of water was slowly dropped in 1 h. A precipitate appears within a few minutes, the suspension is filtered through a Büchner funnel. The precipitate is washed with 500 mL of water, suspended in 50 mL of H_2O in a 2-L Erlenmeyer flask; a solution of 11.5 mmol aniline in 700-mL water is added. The pH is adjusted to pH 4–5 by sodium acetate, then heat slowly to 75°C. The reaction was carried to 1h, then the reaction solution was concentrated and kept in the refrigeration overnight. The product is collected on a filter and dried in an oven at 40°C in vacuum until constant weight to afford 1.1–1.5 g (28–32%) of greenish, glittering crystalline solid. (Table 1, entry 3 and 3a).

General procedure for the synthesis of N,N-dimethyl-4-nitroaniline (1). A 500-mL, three-necked, round-bottomed flask equipped with a thermometer, a reflux condenser, and a Teflon-coated mechanical stirring bar is charged with a solution of 20.20 g (100 mmol) 4-nitrobromobenzene, 32.60 g (400 mmol) of dimethylamine hydrochloride, and 33.16 g (400 mmol) of sodium bicarbonate in 750 mL of n-butyl alcohol. The mechanical stirred reaction mixture is heated to 105°C and maintained it in this temperature for 10 h. The reaction mixture is then filtrated, and the residue is rinsed with 500 mL of n-butyl alcohol; the solvent of n-butyl alcohol is removed by rotary evaporation (70°C, 40 mmHg). The residue is added 50 mL of water and then cooled to room temperature to give yellow crystalline solid, filtered and dried it at 110°C for 3 h to afford 12.65–13.71 g (76–81%) of crude 4-nitro-N, N-dimethylaniline, mp 162–164°C. This material is suitable for the next reaction without purifications.

***N*,*N*-dimethyl-4-nitroaniline (1)**. IR (KBr): 3088, 2831, 1914, 1602, 1594, 1583, 1531, 1455, 821, 752 cm^{-1}; UV(MeOH): $\lambda max = 390.00$ nm . ^{1}HNMR (500 MHz 0.030 g : 0.5 mL $CDCl_3$) δ:8.25(-aryl CH),6.51 (-aryl CH),3.02 (-$(CH_3)_2$N); ^{13}C NMR (75 MHz saturated in $CDCl_3$) δ: 156.3, 135.1, 127.4, 112.5, 41.6;MS (ESI): m/z 167 $(M+H)^+$ (These date are consistent with the Japan Spectral Database for Organic Compounds SDBS); *Anal.* Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.06; N, 16.86; O, 19.26. Found: C, 57.91; H, 6.11; N, 16.92; O, 19.06.

General procedure for the synthesis of 4-amino-*N*,*N*-dimethylaniline (2). A 250-mL, three-necked, round-bottomed flask charged with 4-nitro-*N*,*N*-dimethylaniline (1.66 g, 10 mmol) and hydrochloric acid (0.75 g, 20 mmol) equipped with a 125-mL, pressure-equalizing addition funnel, a reflux condenser, Teflon-coated mechanical stirring. The stirred solution is heated to 4-nitro-*N*,*N*-dimethylaniline dissolving, then 0.5 g of active carbon, 10 mL of solution of ferric chloride (0.01 mol), and 1 mL of aluminum chloride solution (0.01 mol) are added in flask. The reaction mixture is stirred at 80°C for 2 h. Next, hydrazine hydrate (60 mmol) is added dropwised at a rate such that the internal temperature remains between 80–85°C which took 4 h. When the addition is complete, the reaction mixture is heat at reflux and stirring at 100°C for 4 h, cooled it to ambient temperature, and then the mixture is transferred to a 250-mL separatory funnel. The organic phase is separated and crystallized from ethanol to give the product 1.20–1.27 g (90–95%) as a black needless solid.

4-Amino-*N*,*N*-dimethylaniline (2). IR (KBr) cm^{-1}: 3420, 3335, 2832, 2791, 2319, 2013, 1848, 1622, 1585, 1513, 1338, 1267, 1053, 944, 818, 690, 533; V(MeOH): $\lambda max = 512$ nm. ^{1}HNMR(500 MHz 0.041 g : 0.5 mL DMSO-d_6) δ: 6.72(-aryl CH), 6.51(-aryl CH), 4.47(-NH_2), 2.75(-$(CH_3)_2$N);^{13}C NMR (75 MHz 0.045 g : 0.5 mL DMSO-d_6) δ: 143.2, 141.6, 115.8, 114.2, 42.2; MS (ESI): m/z 137$(M+H)^+$ (These date are consistent with the Japan Spectral Database for Organic Compounds SDBS); *Anal.* Calcd for $C_8H_{12}N_2$: C, 70.59; H, 8.82; N, 20.59. Found: C, 70.66; H, 8.71; N, 20.63.

General procedure for the optimization of the synthesis of 2-substituted-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride*. A 1-L round-bottomed flask equipped with a mechanical stirring bar is charged with a

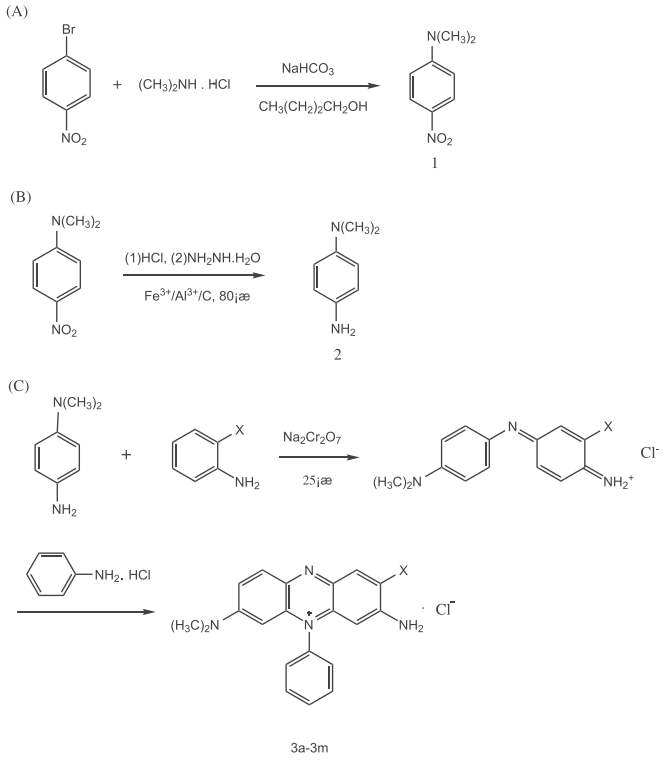
solution of 4-amino-*N*,*N*-dimethylaniline chloride (2.1 g, 10 mmol), *o*-toluidine hydrochloride (1.44 g, 10 mmol) in 200 mL of H_2O. The mixture is stirred uniformly, and a pre-made solution of 5.9 g (20 mmol) sodium bichromate dissolved in 90 mL of water is slowly added at 25°C. A precipitate appears within a minute, the suspension is filtered though a Büchner funnel. The precipitate is washed with 500 mL of water, suspended in 50 mL of water in a 2-L Erlenmeyer flask; a solution of 11.5 mmol of aniline and 700 mL of water are added. The pH is adjusted to pH 4–5 by sodium acetate solution and then heat it slowly to boiling. After 1 hr, the obtained hot solution was concentrated, and then kept under refrigeration overnight. The product is collected on a filter and neutralized with 1 mol/L of NaOH solution, kept it under refrigeration over 12 h, filtered and dried it in an oven at 40°C in vacuum until constant weight to afford 1.1–1.5 g (28–32%) of greenish, glittering crystalline solid (Scheme 2). The results were listed in Tables 1, 2, and 3.

2-Methyl-3-amino-5-phenyl-7-*N*,*N*-dimethylamino phenazinium chloride (3a). IR (KBr thin film): 3400, 2838, 2717, 2160, 1630, 1598, 1521, 1438, 1384, 1135, 775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm. ^{1}HNMR (500 MHz, DMSO-d_6) δ:2.30 (-CH_3Ar), 3.04 (-$(CH_3)_2$N), 3.51(-H_2NAr), 6.37(-aryl CH), 6.52(-aryl CH), 6.92(-aryl CH), 7.75 ~ 8.24 (-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 146.2, 145.1, 144.2, 143.0, 142.5, 141.6, 140.7, 140.2, 129.8, 129.2, 128.9, 128.3, 127.8, 126.2, 118.8, 114.9, 32.5, 15.6; MS (ESI): m/z 330 $(M+H)^+$; *Anal.* Calcd for $C_{21}H_{21}N_4Cl$: C, 69.14 H, 5.76; N, 15.36. Found: C, 69.37; H, 5.65; N, 15.22.

2-ethyl-3-amino-5-phenyl-7-N,N-dimethylamino phenazinium chloride (3b). IR(KBr thin film): 3410, 2858, 2731, 2175, 1635, 1595, 1518, 1465, 1138, 785, 726, 625 cm^{-1}; ^{1}HNMR(500 MHz, DMSO-d_6) δ:1.35 (-CH_3CH_2Ar), 2.81 (-CH_3CH_2Ar), 3.08((CH_3)$_2$N), 3.53(-H_2NAr),6.25 (-aryl CH), 6.56 (-aryl CH), 6.64(-aryl CH),7.72 ~ 8.48(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 146.7, 145.5, 143.7, 142.8, 142.2, 141.7, 141.1, 140.6, 131.1, 130.8, 130.2, 129.8, 129.5, 128.7, 126.5, 119.8, 32.9, 29.2, 15.7; MS (ESI): m/z 344$(M+H)^+$; *Anal.* Calcd for $C_{22}H_{23}N_4Cl$: C, 69.75; H, 6.08; N, 14.80. Found: C, 69.97; H, 6.13; N, 14.69.

2-tertiary-butyl-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3c)*. IR (KBr thin film): 3400, 2838, 2717, 2160, 1630, 1598, 1521, 1392, 1368, 1135, 775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm. ^{1}HNMR (500 MHz, DMSO-d_6) δ:2.30 (-CH_3Ar), 3.04 (-$(CH_3)_2$N), 3.56(-H_2NAr),6.62 (-aryl CH), 6.75(-aryl CH), 7.01(-aryl CH), 7.75 ~ 8.32(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 146.5, 146.2, 145.8, 145.3, 144.9,

Scheme 2



143.8, 142.6, 141.9, 131.5, 131.2, 130.7, 130.2, 129.1, 128.8, 127.5, 120.8, 36.5, 34.5, 31.2; MS (ESI): m/z 372(M + H)$^+$; *Anal.* Calcd for $C_{24}H_{27}N_4Cl$: C, 70.85; H, 6.64; N, 13.78. Found: C, 70.70; H,6.57; N, 13.67.

2-Chloro-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3d)*. IR (KBr thin film): 3400, 2838, 2717, 2160, 1630, 1598, 1521, 1135, 1095,775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm. ^{1}HNMR (500 MHz, DMSO-d_6) 2.85(-$(CH_3)_2$N), 3.47(H_2NAr),5.12 (-aryl CH), 5.52 (-aryl CH), 6.24(-aryl CH),7.84 ~ 8.72(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 147.1, 146.6, 145.3, 144.8, 144.2, 143.6, 142.5, 131.8, 130.2, 129.9, 129.2, 128.4, 127.3, 126.6, 125.4, 124.7, 32.5; MS (ESI): m/z 350.5 (M + H)$^+$; *Anal.* Calcd for $C_{20}H_{18}N_4Cl_2$: C, 62.33; H, 4.93; N, 14.55. Found: C, 62.61; H, 5.08;N, 14.4016.10; Cl, 10.21.

2-bromo-3-amino-5-phenyl- 7-*N*,N-*dimethylamino phenazinium chloride (3e)*. IR(KBr thin film): 3400, 2838, 2717, 2160, 1630, 1598, 1521, 1135, 775, 624,575 cm^{-1}; UV(MeOH): λmax = 542.00 nm. ^{1}HNMR(500 MHz, DMSO-d_6) 3.02 (-$(CH_3)_2$N), 3.41(-H_2NAr),5.55 (-aryl CH), 5.83 6.28(-aryl CH), (-aryl CH),7.75 ~ 8.73(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 147.6, 147.1, 146.8, 146.2, 145.3, 144.8, 143.9, 141.9, 131.3, 130.8, 130.1, 129.7, 128.4, 127.8, 127.1, 126.6, 35.5; MS (ESI): m/z 395(M + H)$^+$; *Anal.* Calcd for $C_{20}H_{18}N_4BrCl$: C, 55.88; H, 4.19; N, 13.04. Found: C, 55.91; H, 4.25; N, 12.89.

2-hydroxy-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3f)*. IR (KBr thin film):3610,3400, 2838, 2717, 2160, 1630, 1598, 1521, 1200, 1135, 775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm. ^{1}HNMR (500 MHz, DMSO-d_6) δ: 3.05 (-$(CH_3)_2$N), 3.37 (-H_2NAr), 5.23 (-aryl OH), 5.67 (-aryl CH), 5.95 (-aryl CH), 6.24(-aryl CH),7.59 ~ 8.56 (-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 149.5, 148.8, 147.4, 146.6, 145.2, 143.5, 142.1, 141.3, 133.2, 132.0, 131.3, 130.4, 129.8, 128.3, 127.9, 127.2, 35.8; MS (ESI): m/z 332(M + H)$^+$; *Anal.* Calcd for $C_{20}H_{19}N_4OCl$: C, 65.48; H, 5.18; N, 15.28; O,4.37. Found: C, 65.65; H, 5.01;N, 15.08; O,4.26.

2-hydroxyethyl-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3 g)*. IR (KBr thin film): 3400, 2838, 2717, 2160, 1630, 1598, 1521, 1135, 1050,775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm. ^{1}HNMR (500 MHz, DMSO-d_6) δ:2.05 ($HOCH_2CH_2$-), 2.89(-CH_2CH_2), 3.06 (-$(CH_3)_2$N), 3.31(-H_2NAr), 3.84(-CH_2CH_2)5.62 (-aryl CH), 5.92(-aryl CH), 6.15 (-aryl CH), 7.67 ~ 8.55(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 146.7, 146.4, 145.9, 145.1, 144.8, 143.2, 142.7, 141.5, 133.4, 132.5, 131.2, 130.8, 129.9, 128.8, 127.8, 126.4, 64.2, 41.3, 32.5; MS (ESI): m/z 360 (M + H)$^+$; *Anal.* Calcd for $C_{22}H_{23}N_4OCl$: C, 66.92; H, 5.83; N, 14.20; O, 4.06. Found: C, 66.79; H, 5.62; N, 14.01; O, 4.13.

2-amino-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3 h)*. IR (KBr thin film): 3400, 2838, 2717, 2160, 1635, 1598, 1521, 1235, 1515, 1135, 775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm.^{1}HNMR (500 MHz, DMSO-d_6) 3.04 (-$(CH_3)_2$N), 3.26(-H_2NAr), 3.31(-H_2NAr), 6.62(-aryl CH), 6.92(-aryl CH), 7.02(-aryl CH),7.65 ~ 8.50(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 144.8, 143.2, 142.9, 142.2, 141.9, 141.3, 140.5, 139.8, 130.7, 129.4, 127.9, 126.6, 124.2, 123.6, 122.7, 118.8, 33.9; MS (ESI): m/z 331 (M + H)$^+$; *Anal.* Calcd for $C_{20}H_{20}N_5Cl$: C, 65.66; H, 5.47; N, 19.15. Found: C, 65.77; H, 5.39;N, 19.12.

2-methylamino-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3i)*. IR (KBr thin film): 3450, 2838, 2717, 2160, 1635, 1598, 1521, 1450, 1375, 1135, 775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm.^{1}HNMR (500 MHz, DMSO-d_6), 2.63(-CH_3NH), 3.04(-$(CH_3)_2$N), 3.25(-H_2NAr),3.56(-$NHCH_3$), 6.49(-aryl CH), 6.58(aryl CH), 7.12(-aryl CH), 7.75 ~ 8.50(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 145.5, 145.1, 144.7, 143.8, 142.6, 141.9, 141.3, 140.8, 132.5, 131.9, 130.6, 128.2, 127.6, 125.7, 122.4, 117.3, 37.9, 32.2; MS (ESI): m/z 345(M + H) $^+$; *Anal.* Calcd for $C_{21}H_{22}N_5Cl$: C, 66.40; H, 5.80; N, 18.45. Found: C, 66.29; H, 5.86; N, 18.25.

2-ethylamino-3-amino-5-phenyl- 7-*N*,N-*dimethylamino phenazinium chloride (3j)*. Greenish solid, mp > 300°C; IR(KBr thin film): 3400, 2838, 2717, 2160, 1630, 1598, 1521, 1465, 1450, 1375, 1250, 1135, 775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm.^{1}HNMR(500 MHz, DMSO-d_6) δ:1.19(-CH_3CH_2NH), 3.04 (-$(CH_3)_2$N), 3.09(-CH_3CH_2NH), 3.22(-H_2NAr), 3.35-$NHCH_2CH_3$), 6.63 (-aryl CH), 6.91(-aryl CH),7.19(-aryl CH), 7.45 ~ 8.20 (-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 148.2, 147.3, 146.7, 145.8, 145.2, 144.5, 143.8, 142.1, 130.7, 128.8, 127.6, 126.9, 125.8., 118.3, 117.8, 116.8, 38.2, 31.7, 15.6; MS (ESI): m/z 359(M + H)$^+$; *Anal.* Calcd for $C_{22}H_{24}N_5Cl$: C, 67.09; H, 6.10; N, 17.79. Found: C, 67.21; H, 6.02; N, 17.85.

2-dimethylamino-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3 k)*. IR (KBr thin film):3400, 3325, 2838, 2717, 2160, 1630, 1598, 1521, 1450, 1375, 1135, 775, 624 cm^{-1}; UV (MeOH): λmax = 542.00 nm. ^{1}HNMR(500 MHz, DMSO-d_6) δ: 2.65 ~ 3.04 (-$(CH_3)_2$N), 3.24(-H_2NAr), 6.50 (-aryl CH), 6.85(-aryl CH), 7.25(-aryl CH),7.37 ~ 8.43(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 147.2, 146.3, 145.8, 144.6, 143.9, 143.2, 142.6, 141.3, 132.6, 130.9, 127.2, 125.1, 124.4, 122.7, 119.5, 112.6, 31.8, 30.6;MS (ESI): m/z 359(M + H)$^+$; *Anal.* Calcd for $C_{22}H_{24}N_5Cl$: C, 67.09; H, 6.10; N, 17.79. Found: C, 66.91; H, 6.22; N, 17.55.

2-cyano-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3 l)*. IR (KBr thin film): 3400, 2838, 2717, 2230, 2160, 1630, 1598, 1521, 1135, 775, 624 cm^{-1}; UV(MeOH): λmax = 542.00 nm. ^{1}HNMR

(500 MHz, DMSO-d_6) δ: 2.94 (-$(CH_3)_2$N), 3.23(-H_2NAr), 6.62 (-aryl CH),6.84 (-aryl CH), 7.12(-aryl CH), 7.36 ~ 8.42(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 145.8, 144.5, 143.8, 143.1, 142.6, 141.9, 141.2, 140.7, 132.6, 129.3, 125.6, 124.5, 122.8, 118.6, 115.3, 112.9, 110.6, 32.1; MS (ESI): m/z 341 $(M+H)^+$; *Anal.* Calcd for $C_{21}H_{18}N_5Cl$: C, 67.11; H, 4.79; N, 18.64. Found: C, 67.32; H, 4.64; N, 18.59.

2-thiocyanate-3-amino-5-phenyl-7-*N*,N-*dimethylamino phenazinium chloride (3 m)*. IR (KBr thin film): 3400, 2838, 2717, 2160, 1630, 1598, 1521, 1135, 775, 624,367 cm^{-1}; UV(MeOH): λmax = 542.00 nm. ^{1}HNMR (500 MHz, DMSO-d_6) δ: 3.04 (-$(CH_3)_2$N), 3.20(-H_2NAr), 6.52 (-aryl CH), 6.58(-aryl CH), 6.89(-aryl CH), 7.55 ~ 8.68(-aryl CH); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ: 146.2, 145.5, 144.8, 144.1, 143.6, 142.9, 141.8, 141.1, 137.6, 131.9, 130.6, 129.2, 128.4, 126.7, 125.8, 122.8, 118.5, 31.9; MS (ESI): m/z 373 $(M+H)^+$; *Anal.* Calcd for $C_{21}H_{18}N_5SCl$: C, 61.84; H, 4.42 N, 17.18; Found: C, 61.62; H, 4.61; N, 17.02.

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