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Abstract: A series of novel tetracyclic 6-thia-5a-aza-acephenanthrylene derivatives **7** were synthesized by rigidization of the arylsulfonyl/carbonyl/methyl moiety through C7 of indole, which was achieved under Heck conditions. The strategy of altering the palladium–bromine exchange site produced target products.

Keywords: Heck reaction; Tetracyclic 6-thia-5a-aza-acephenanthrylene; Tryptamine

INTRODUCTION

Diaryl coupling using the Heck reaction is one of the best-known methodologies in organic chemistry.[1–4] There are several reports on use of intramolecular Heck reaction for the preparation of polycyclic ring systems.[5] In our efforts to synthesize the compound **7** for the ongoing serotonin receptor ligands[6] program, we largely used route 1 of Scheme 1.

However, to get the potent serotonin ligands, we were more interested in a compound with appropriate substituents in the D-ring and unsubstituted C2 of indole. We realized that the site for palladium bromine exchange, which was the ortho bromo on the aryl sulfonyl/carbonyl/methyl ring, could be changed to C7 of indole. This strategy

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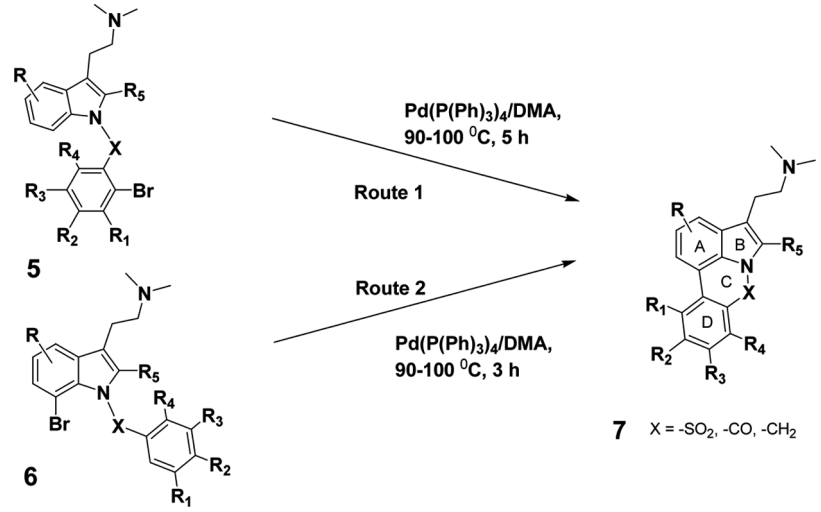
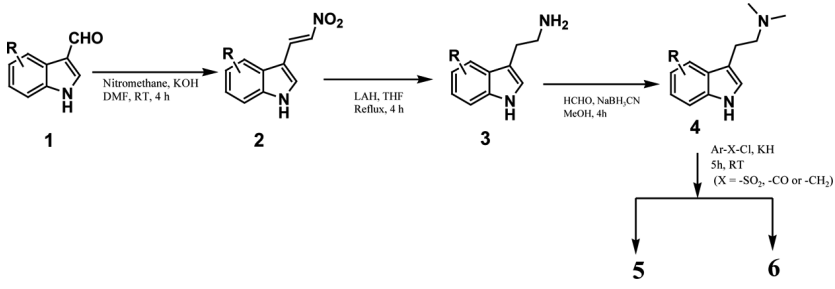


Scheme 1. Synthesis of rigid analogs of tryptamine.

would not only eliminate the need for multiply substituted aryl sulfonyl chlorides but also give the required product unambiguously. When N-(substituted) arylsulfonyl-7-bromotryptamines were subjected to the Heck cyclization under similar conditions, derivatives **7** were obtained in better yields and purities. Possible steric instability of the intermediate palladium complex could be one of the reasons for the better reaction rates.

RESULTS AND CONCLUSIONS

The general synthetic strategy used for the synthesis of title compounds **7** has been summarized in Scheme 1. Various substituted tryptamines **4** were either obtained commercially or synthesized using various literature



Scheme 2. Synthesis of substituted tryptamines.

methods.[7] Treatment of substituted tryptamines **4** with the base and the desired substituted aryl sulfonyl/carbonyl/methyl chlorides in tetrahydrofuran (THF) at rt yielded the intermediates **5** and **6**, which were isolated and fully characterized. The IR spectrum of these products generally showed absorption bands at 1350 and 1175 cm^{-1} for $-SO_2$ and at 1670 cm^{-1} for $-CO$. They were cyclized using the various palladium catalysts to get the desired compounds **7**, which were confirmed with spectral data.

Synthesis of tryptamines was achieved by the route depicted in Scheme 2. The appropriately substituted indoles were converted to their 3-formyl analogs **1**. Its IR spectrum showed the presence of a $-CHO$ peak at 1710 cm^{-1}. 3-Formyl indoles were then condensed with nitromethane under alkaline conditions. The product **2** was reduced using lithium aluminium hydride to the corresponding tryptamines, **3**, which were further dimethylated using formaldehyde and sodium cyanoborohydride to the substituted tryptamines **4**.

Most of the compounds showed relatively better yields and purities when synthesized by route 2, and the reaction times were also relatively lower, mainly because of the better impurity profile of the compounds obtained. Some of the compounds for which the respective sulfonyl chlorides were either unavailable or very costly were also possible by route 2. For example, the compounds, **7d** and **7i**–**7m** would require trisubstituted benzenesulfonyl chlorides by route 1, which were not readily available. However, these compounds were easily possible by route 2 through simple disubstituted benzenesulfonyl chlorides. As can be envisaged, route 1 also offered the possibility of the formation of other Heck products by cyclization through C2 of indole and in fact that is the most favored end product thermodynamically as well as sterically. It was therefore not possible to synthesize the compounds **7** by route 1 without any substitution at C2 of indole. However, these compounds were easily possible by route 2. The Heck reaction was carried out using various palladium(0) catalysts; however, the Tetrakis triphenyl phosphine palladium(0) was found to be best suited for this intramolecular cyclization. Typically, the reactions were carried out with 0.03 to 0.05 mol% of the catalyst. The reaction was also tried in various polar aprotic solvents in combination with a variety of bases. However, the combination of potassium acetate as base and N,N-dimethyl acetamide as solvent was found to be the best. Typically, with this combination, the reactions were completed at 90–100 °C within 3 to 5 h. The better reaction yields and the improved rate of reaction could be due to the difference in the stability of intermediate palladium complex. The palladium complex at C7 could be sterically unstable as compared to the one at *ortho* position of the arylsulfonyl moiety.

EXPERIMENTAL

Commercial reagents were utilized without further purification. Room temperature refers to 25–30 °C. Melting points are uncorrected. IR spectra were taken using KBr and in solid state. All mass spectra were carried out using ESI conditions. ^{1}H NMR spectra were recorded at 400 MHz on a Bruker instrument in $CDCl_3$ using TMS as internal reference standard, and chemical shifts are expressed in δ (ppm) values. CHN analysis was carried out on an Elementar, Vario EL model. Chromatography refers to column chromatography performed using 60- to 120-mesh silica gel executed under nitrogen pressure (flash chromatography) conditions.

Reaction of 4 with Aromatic Sulfonyl/Carbonyl/Methyl Chlorides (General Procedure)

A THF solution of **4** (0.01 mol) was added dropwise to a cooled suspension of KH (0.011 mol, washed with n-hexane before use) in dry THF. The reaction mixture was brought to rt and stirred for 2 h. It was cooled once again, and an appropriate sulfonyl/carbonyl/methyl chloride (0.011 mol, dissolved in THF) was added dropwise. After completion of the reaction (TLC, 5 h), it was poured on ice-cold water and extracted with ethyl acetate. The combined organic layer was washed with water, dried over sodium sulphate, and concentrated under vacuum afford **5** or **6** after purification over silica gel. All the synthesized compounds were purified and fully characterized. Spectral data of some of the selected compounds are given here.

Data

1-Benzene sulfonyl-7-bromo-3-(N,N-dimethylamino ethyl)-1H-indole (6a): IR (KBr, cm^{-1}): 2942, 2768, 1447, 1360, 1265, 1173, 1124, 965, 685; mass (m/z): 407.3, 409.2 $(M+H)^+$; ^{1}H NMR (δ ppm): 2.35 (6H, s), 2.63–2.67 (2H, m), 2.85–2.89 (2H, m), 7.07–7.09 (1H, t, $J = 7.74$ Hz), 7.43–7.49 (4H, m), 7.55–7.60 (1H, m), 7.71 (1H, s), 7.70–7.82 (2H, m). Anal. calcd. for $C_{18}H_{19}BrN_2O_2S$: C, 53.08; H, 4.70; N, 6.88. Found: C, 53.19; H, 4.78; N, 6.99.

1-Benzyl-7-bromo-3-(N,N-dimethylamino ethyl)-2-methyl-5-methoxy-1H-indole (6n): IR (KBr, cm^{-1}): 2951, 2733, 1606, 1489, 1375, 1288, 1033, 790, 679; mass (m/z): 401.2, 403.2 $(M+H)^+$; ^{1}H NMR (δ ppm): 2.27 (3H, s), 2.37 (6H, s), 2.52–2.56 (2H, m), 2.93–2.97 (2H, m), 3.91 (3H, s), 5.1 (2H, s), 7.2–7.4 (5H, m), 7.55–7.69 (2H, m). Anal. calcd. for $C_{21}H_{25}BrN_2O$: C, 62.85; H, 6.28; N, 6.98. Found: C, 62.97; H, 6.37; N, 6.91.

1-Benzoyl-7-bromo-3-(N,N-dimethylamino ethyl)-2-methyl-5-methoxy-1H-indole (6t): IR (KBr, cm^{-1}): 2945, 1668, 1428, 1330, 1151, 960, 795, 680; mass (m/z): 415.3, 417.3 $(M+H)^+$; ^1H NMR (δ ppm): 2.3 (3H, s), 2.44 (6H, s), 2.44–2.59 (2H, m), 2.77–2.88 (2H, m), 3.93 (3H, s), 7.29–7.52 (5H, m), 7.58–7.83 (2H, m). Anal. calcd. for $C_{21}H_{23}BrN_2O_2$: C, 60.73; H, 5.58; N, 6.74. Found: C, 60.65; H, 5.67; N, 6.83.

General Procedure for Synthesis of Compounds 7

A mixture of 1-(substituted benzene sulfonyl/carbonyl/methyl)-7-bromo indole derivative (0.368 mmol), tetrakis triphenylphosphine palladium(0) (0.022 mmol), and potassium acetate (0.55 mmol) in dimethyl acetamide (4 mL) was heated to 90–100 °C under a nitrogen atmosphere. After completion of the reaction (3 h, TLC), it was cooled to 25 °C and filtered over hyflow. The filtrate was diluted with ice water, pH was adjusted to 9–10 with aqueous potassium hydroxide solution, and the product was extracted with (2 × 50 mL) ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under vacuum. The crude residue was purified by column chromatography using silica gel (100–200 mesh), the eluent system being ethyl acetate and triethylamine in 99.5 : 0.5 ratio, to obtain the desired product.

Data

3-(N,N-Dimethylaminoethyl)-1,2-benzothiazino[2,3,4-ab]indole-S,S-dioxide (7a): IR (KBr, cm^{-1}): 2982, 1594, 1328, 1173, 1128, 756; mass (m/z): 327.2 $(M+H)^+$; ^1H NMR (δ ppm): 2.35 (6H, s), 2.69–2.72 (2H, m), 2.97–3.01 (2H, m), 7.46–7.5 (1H, m), 7.59–7.64 (2H, m), 7.71–7.73 (1H, d, $J = 7.72$ Hz), 7.77 (1H, bm), 7.95–7.97 (1H, d, $J = 7.68$ Hz), 8.17–8.19 (1H, d, $J = 7.92$ Hz), 8.22–8.24 (1H, dd, $J = 8.0$, 0.96 Hz). Anal. calcd. for $C_{18}H_{18}N_2O_2S$: C, 66.23; H, 5.56; N, 8.58. Found: C, 66.33; H, 5.63; N, 8.52.

5-Chloro-8-fluoro-3-(N,N-dimethylaminoethyl)-1,2-benzothiazino[2,3,4-ab]indole-S,S-dioxide (7b): IR (KBr, cm^{-1}): 2763, 1603, 1330, 1174, 1126, 865, 551; mass (m/z): 379.2 $(M+H)^+$; ^1H NMR (δ ppm): 2.34 (6H, s), 2.66–2.7 (2H, t), 2.93–2.96 (2H, m), 7.34–7.38 (1H, m), 7.63 (1H, s), 7.72 (1H, d, $J = 1.52$ Hz), 7.77–7.8 (1H, dd, $J = 9.4$ Hz), 7.863–7.866 (1H, d, $J = 1.28$ Hz), 8.22–8.26 (1H, dd, $J = 8.6$ Hz). Anal. calcd. for $C_{18}H_{16}ClFN_2O_2S$: C, 57.07; H, 4.26; N, 7.39. Found: C, 57.19; H, 4.37; N, 7.47.

3-(N,N-Dimethylaminoethyl)-5,8-difluoro-1,2-benzothiazino-[2,3,4-ab]-indole-S,S-dioxide (7c): Melting range (°C): 150–152.5; IR (KBr, cm^{-1}): 2976, 1602, 1474, 1336, 1173, 1134, 860, 662, 539; mass (m/z): 363.3 $(M+H)^+$; ^1H NMR (δ ppm): 2.34 (6H, s), 2.66–2.7 (2H, m), 2.92–2.96 (2H, m), 7.35 (1H, m), 7.43–7.45 (1H, dd, $J = 8.52$ Hz), 7.59–7.62 (1H, dd, $J = 9.6$ Hz), 7.64 (1H, s), 7.72–7.75 (1H, dd, $J = 9.4$ Hz), 8.22–8.26 (dd, 1H, $J = 8.8$ Hz). Anal. calcd. for $C_{18}H_{16}F_2N_2O_2S$: C, 59.66; H, 4.45; N, 7.73. Found: C, 59.81; H, 4.51; N, 7.84.

3-(N,N-Dimethylaminoethyl)-9,10-dichloro-1,2-benzothiazino-[2,3,4-ab]-indole-S,S-dioxide (7d): Melting range (°C): >240; IR (KBr, cm^{-1}): 2940, 1448, 1329, 1165, 793, 600; mass (m/z): 394.9, 397 $(M+H)^+$; ^1H NMR (δ ppm): 2.37 (6H, s), 2.71–2.75 (2H, m), 3.00–3.03 (2H, m), 7.45–7.49 (1H, t), 7.74–7.76 (1H, d, $J = 7.72$ Hz), 7.81–7.83 (1H, d, $J = 8.76$ Hz), 7.89–7.91 (1H, d, $J = 7.76$ Hz), 8.08–8.10 (1H, d, $J = 8.72$ Hz). Anal. calcd. for $C_{18}H_{16}Cl_2N_2O_2S$: C, 54.69; H, 4.08; N, 7.09. Found: C, 54.58; H, 4.16; N, 6.99.

8-Methyl-3-(N,N-dimethylaminoethyl)-1,2-benzothiazino[2,3,4-ab]indole-S,S-dioxide (7e): Mass (m/z): 341.2 $(M+H)^+$; ^1H NMR (δ ppm): 2.36 (6H, s), 2.56 (3H, s), 2.69–2.73 (2H, t), 2.97–3.01 (2H, t), 7.41–7.49 (2H, m), 7.58 (1H, s), 7.7–7.72 (d, 1H, $J = 7.8$ Hz), 7.94–7.96 (d, 1H, $J = 7.68$ Hz), 7.981 (1H, s), 8.1–8.12 (d, 1H, $J = 8.12$ Hz). Anal. calcd. for $C_{19}H_{20}N_2O_2S$: C, 67.03; H, 5.92; N, 8.23. Found: C, 67.19; H, 5.85; N, 8.16.

8-Isopropyl-3-(N,N-dimethylaminoethyl)-1,2-benzothiazino[2,3,4-ab]-indole-S,S-dioxide (7f): Mass (m/z): 369.4 $(M+H)^+$; ^1H NMR (δ ppm): 1.355–1.372 (6H, d, $J = 6.96$ Hz), 2.35 (6H, s), 2.69–2.73 (2H, m), 2.97–3.01 (2H, m), 3.09–3.12 (1H, septet, $J = 6.92$ Hz), 7.45–7.49 (2H, m), 7.58 (1H, s), 7.7–7.72 (dd, 1H, $J = 7.8$ Hz), 7.98–7.99 (1H, d, $J = 7.64$ Hz), 8.00–8.01 (1H, d, $J = 1.52$ Hz), 8.13–8.16 (1H, d, $J = 8.24$ Hz). Anal. calcd. for $C_{21}H_{24}N_2O_2S$: C, 68.45; H, 6.56; N, 7.60. Found: C, 68.59; H, 6.71; N, 7.67.

3-(N,N-Dimethylaminoethyl)-5-chloro-8-methoxy-1,2-benzothiazino-[2,3,4-ab]indole-S,S-dioxide (7g): Melting range (°C): 176.6–183; IR (KBr, cm^{-1}): 2980, 1596, 1311, 1167, 850, 573, 534; mass (m/z): 391.1 $(M+H)^+$; ^1H NMR (δ ppm): 2.36 (6H, s), 2.67–2.71 (2H, m), 2.93–2.97 (2H, m), 4.0 (3H, s), 7.13–7.16 (1H, dd, $J = 8.84$, 2.36 Hz), 7.52–7.53 (1H, d, $J = 2.36$ Hz), 7.61 (1H, s), 7.68 (1H, d, $J = 1.56$ Hz), 7.86–7.87 (1H, d, $J = 1.56$ Hz), 8.13–8.16 (1H, d, $J = 8.84$ Hz). Anal. calcd. for $C_{19}H_{19}ClN_2O_3S$: C, 58.38; H, 4.90; N, 7.17. Found: C, 58.32; H, 4.99; N, 7.28.

3-(N,N-Dimethylaminoethyl)-5-fluoro-8-isopropyl-1,2-benzothiazino-[2,3,4-ab]indole-S,S-dioxide (7h): Melting range (°C): 117–124; IR (KBr, cm^{-1}): 2917, 1598, 1344, 1178, 1128, 796, 661; mass (m/z): 387 $(M+H)^+$;

; ^{1}H NMR (δ ppm): 1.35–1.37 (6H, d), 2.36 (6H, s), 2.68–2.72 (2H, m), 2.93–2.97 (2H, m), 3.1–3.13 (1H, sep), 7.38–7.4 (1H, dd, $J = 8.56$, 2.1 Hz), 7.51–7.53 (1H, dd, $J = 8.28$, 1.56 Hz), 7.63 (1H, s), 7.68–7.71 (1H, dd, $J = 9.9$, 2.08 Hz), 7.914–7.918 (1H, d, $J = 1.48$ Hz), 8.14–8.16 (1H, d, $J = 8.28$ Hz). Anal. calcd. for $C_{21}H_{23}FN_2O_2S$: C, 65.26; H, 6.00; N, 7.25. Found: C, 65.34; H, 5.93; N, 7.37.

3-(N,N-Dimethylaminoethyl)-8,10-difluoro-1,2-benzothiazino-[2,3,4-ab]-indole-S,S-dioxide (7i): Melting range (°C): 155–160; IR (KBr, cm^{-1}): 2963, 1612, 1331, 1261, 1173, 1111, 855, 797, 512; mass (m/z): 363.1 $(M + H)^+$; ^{1}H NMR (δ ppm): 2.41 (6H, s), 2.74–2.78 (2H, m), 3.02–3.06 (2H, m), 7.04–7.1 (1H, m), 7.47–7.53 (1H, t), 7.62 (1H, s), 7.67–7.71 (1H, m), 7.8–7.82 (1H, d, $J = 7.76$ Hz), 7.87–7.89 (1H, d, $J = 7.72$ Hz). Anal. Calcd. for $C_{18}H_{16}F_2N_2O_2S$: C, 59.66; H, 4.45; N, 7.73. Found: C, 59.79; H, 4.57; N, 7.81.

3-(N,N-Dimethylaminoethyl)-7-trifluoromethyl-10-chloro-1,2-benzothiazino-[2,3,4-ab]indole-S,S-dioxide (7j): IR (KBr, cm^{-1}): 2917, 1348, 1297, 1170, 1142, 753; mass (m/z): 429.1, 431 $(M + H)^+$; ^{1}H NMR (δ ppm): 2.37 (6H, s), 2.72–2.76 (2H, m), 2.99–3.04 (2H, m), 7.48–7.58 (2H, m), 7.72–7.82 (2H, m), 8.20–8.60 (2H, m). Anal. calcd. for $C_{19}H_{16}ClF_3N_2O_2S$: C, 53.21; H, 3.76; N, 6.53. Found: C, 53.27; H, 3.85; N, 6.61.

3-(N,N-Dimethylaminoethyl)-5-fluoro-7-trifluoromethyl-10-chloro-1,2-benzothiazino-[2,3,4-ab]indole-S,S-dioxide (7k): IR (KBr, cm^{-1}): 2943, 1435, 1349, 1298, 1170, 868; mass (m/z): 447.2, 449.2 $(M + H)^+$; ^{1}H NMR (δ ppm): 2.36 (6H, s), 2.69–2.73 (2H, m), 2.94–2.98 (2H, m), 7.46–7.49 (1H, dd, $J = 8.0$, 2.1 Hz), 7.54 (1H, s), 7.76–7.78 (1H, d, $J = 8.72$ Hz), 7.79–7.82 (1H, dd), 8.04–8.07 (1H, d, $J = 8.60$ Hz). Anal. calcd. for $C_{19}H_{15}ClF_4N_2O_2S$: C, 51.07; H, 3.38; N, 6.27. Found: C, 51.19; H, 3.33; N, 6.38.

3-(N,N-Dimethylaminoethyl)-5,9,10-trichloro-1,2-benzothiazino-[2,3,4-ab]indole-S,S-dioxide (7l): Melting range (°C): 210.4–214.9; IR (KBr, cm^{-1}): 2946, 1445, 1339, 1163, 838, 594, 568; mass (m/z): 429.1, 431.1, 432.9 $(M + H)^+$; ^{1}H NMR (δ ppm): 2.35 (6H, s), 2.67–2.71 (2H, m), 2.93–2.97 (2H, m), 7.66 (1H, s), 7.70–7.71 (1H, d, $J = 1.48$ Hz), Hz), 7.83–7.86 (2H, m), 8.01–8.03 (1H, d, $J = 8.76$ Hz). Anal. calcd. for $C_{18}H_{15}Cl_3N_2O_2S$: C, 50.31; H, 3.52; N, 6.52. Found: C, 50.19; H, 3.59; N, 6.43.

3-(N,N-Dimethylaminoethyl)-5-fluoro-9,10-dichloro-1,2-benzothiazino-[2,3,4-ab]indole-S,S-dioxide (7m): Melting range (°C): 207–210; IR (KBr, cm^{-1}): 2918, 1454, 1340, 1175, 1163, 838, 581; mass (m/z): 413.2, 415.2 $(M + H)^+$; ^{1}H NMR (δ ppm): 2.35 (6H, s), 2.66–2.70 (2H, m), 2.92–2.96 (2H, m), 7.41–7.44 (1H, dd, $J = 8.4$, 2.12 Hz), 7.59–7.62 (1H, dd, $J = 9.98$, 2.0 Hz), 7.68 (1H, s), 7.83–7.85 (1H, d, $J = 8.78$ Hz),

7.97–7.99 (1H, d, $J = 8.78$ Hz). Anal. calcd. for $C_{18}H_{15}Cl_2FN_2O_2S$: C, 52.31; H, 3.66; N, 6.78. Found: C, 52.45; H, 3.73; N, 6.71.

[2-(2-Methoxy-5-methyl-7H-pyrrolo[3,2,1-de]phenanthridin-4-yl)ethyl] dimethylamine (7n): IR (KBr, cm^{-1}): 2942, 2761, 1601, 1498, 1486, 1375, 1294, 1029; mass (m/z): 321.2 $(M + H)^+$; ^1H NMR (δ ppm): 2.37 (6H, s), 2.52–2.60 (2H, m), 2.84–2.96 (5H, m), 3.97 (3H, s), 5.35 (2H, s), 7.2–7.6 (5H, m), 7.64–7.77 (1H, m). Anal. calcd. for $C_{21}H_{24}N_2O$: C, 78.71; H, 7.55; N, 8.74. Found: C, 78.83; H, 7.67; N, 8.67.

[2-(2-Chloro-5-methyl-7H-pyrrolo[3,2,1-de]phenanthridin-4-yl)ethyl]-dimethylamine (7o): IR (KBr, cm^{-1}): 2939, 2763, 1494, 1449, 1376, 1263, 834, 770; mass (m/z): 325.2, 327.1 $(M + H)^+$; ^{1}HNMR (δ ppm): 2.35 (9H, bs), 2.45–2.53 (2H, m), 2.81–2.89 (2H, m), 5.36 (2H, s), 7.19–7.35 (5H, m), 7.81–7.84 (1H, m). Anal. calcd. for $C_{20}H_{21}ClN_2$: C, 73.95; H, 6.52; N, 8.62. Found: C, 74.12; H, 6.61; N, 8.69.

3-(N,N-Dimethylaminoethyl)-5,8-dichloro-1,2-benzothiazino-[2,3,4-ab]-indole-S,S-dioxide (7p): Melting range (°C): 101–108; IR (KBr, cm^{-1}): 2982, 2769, 1329, 1178, 1150, 851, 791, 619, 529; mass (m/z): 395, 397, 399 $(M + H)^+$; ^1H NMR (δ ppm): 2.35 (6H, s), 2.67–2.71 (2H, m), 2.93–2.97 (2H, m), 7.61–7.64 (2H, m), 7.72 (1H, s), 7.89–7.90 (1H, d, $J = 1.52$ Hz), 8.09–8.10 (1H, d, $J = 1.56$ Hz), 8.15–8.17 (1H, d, $J = 8.56$ Hz). Anal. calcd. for $C_{18}H_{16}Cl_2N_2O_2S$: C, 54.69; H, 4.08; N, 7.09. Found: C, 54.81; H, 4.16; N, 7.13.

3-(N,N-Dimethylaminoethyl)-5-fluoro-1,2-benzothiazino-[2,3,4-ab]-indole-S,S-dioxide (7q): Melting range (°C): 126–129; IR (KBr, cm^{-1}): 2953, 1461, 1333, 1173, 1138, 765, 561; mass (m/z): 345.3 $(M + H)^+$; ^1H NMR (δ ppm): 2.35 (6H, s), 2.67–2.71 (2H, m), 2.92–2.96 (2H, m), 7.38–7.41 (1H, dd, $J = 8.56$, 2.08 Hz), 7.64–7.69 (3H, m), 7.78–7.8 (1H, m), 8.09–8.11 (1H, d, $J = 7.92$ Hz), 8.22–8.25 (1H, dd, $J = 7.92$, 1 Hz). Anal. calcd. for $C_{18}H_{17}FN_2O_2S$: C, 62.77; H, 4.98; N, 8.13. Found: C, 62.89; H, 5.07; N, 8.21.

5-Chloro-3-(N,N-dimethylaminoethyl)-1,2-benzothiazino-[2,3,4-ab]-indole-S,S-dioxide (7r): Melting range (°C): 133–136.3; IR (KBr, cm^{-1}) : 2962, 1331, 1169, 1124, 826, 766, 749; mass (m/z): 361, 363 $(M + H)^+$; ^1H NMR (δ ppm): 2.35 (6H, s), 2.67–2.71 (2H, m), 2.93–2.97 (2H, m), 7.62–7.69 (3H, m), 7.78–7.80 (1H, m), 7.92–7.93 (1H, d, $J = 1.56$ Hz), 8.12–8.14 (1H, d), 8.22–8.24 (1H, dd, $J = 8.0$, 1.08 Hz). Anal. calcd. for $C_{18}H_{17}ClN_2O_2S$: C, 59.91; H, 4.75; N, 7.76. Found: C, 59.83; H, 4.86; N, 7.67.

4-(2-Dimethylamino ethyl)-2-fluoro-5-methyl pyrrolo[3,2,1-de]phenanthridin-7-one (7s): IR (KBr, cm^{-1}): 2945, 1688, 1463, 1353, 1143, 1118, 765; mass (m/z): 323.3 $(M + H)^+$; ^1H NMR (δ ppm): 1.68 (3H, s), 2.25 (6H, s), 3.0–3.2 (2H, m), 3.3–3.43 (2H, m), 6.9–7.48 (4H, m), 7.54–7.66

(2H, m). Anal. calcd. for $C_{20}H_{19}FN_2O$: C, 74.51; H, 5.94; N, 8.69. Found: C, 74.65; H, 6.03; N, 8.81.

4-(2-Dimethylamino ethyl)-2-methoxy-5-methyl pyrrolo[3,2,1-de]phenanthridin-7-one (7t): IR (KBr, cm^{-1}): 2933, 1662, 1461, 1333, 1151, 1157, 795; mass (m/z): 335.3 $(M+H)^+$; ^1H NMR (δ ppm): 2.36 (3H, s), 2.41 (6H, s), 2.41–2.6 (2H, m), 2.81–2.93 (2H, m), 3.85 (3H, s), 7.23–7.66 (5H, m), 7.68–7.74 (1H, m). Anal. calcd. for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.59; H, 6.72; N, 8.47.

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