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Synthesis of fluorescence properties of Di-pyrazolo pyridine (DPP) derivatives and spiro heterocycles.

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ABSTRACT

The present chapter deals with the synthesis of di-pyrazolo pyridine (DPP) derivatives, Spiro heterocycles by *Friedlander* condensation reactions with different substituted acetophenones and cyclic ketones. We have measured the absorbance and emission properties of the synthesized compounds and analogously calculated their quantum yields by comparative method.

Keywords: di-pyrazolo pyridine (DPP), Pyrazolo[4,3:5,6]pyrido[2,3-d]pyrimidines, absorbance and emission.

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INTRODUCTION

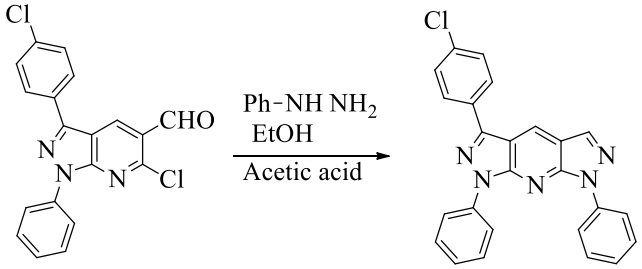
Spiro heterocycles having one quaternary carbon atom and two fused rings are structurally interesting. Spiro heterocycles were organic substances isolated from natural sourses [1-7]. Compounds which have spiro moiety show pronounced biological & pharmacological properties [8-12]. Spiro compounds exhibit high thermal stability as well as photochemical properties due to their structural rigidity [13, 14]. The synthesis of spiro compounds from o-amino carboxamide as a starting material has wide applicability for the annulations of heterocyclic systems. Pyrazolo[4,3:5,6]pyrido[2,3-d]pyrimidines have wide importance as coloreants [15] heat and moisture repellents, thermal transfer printing agents [16], as well as photographic couplers [17]. Spiro compounds display wide range of pharmacological activities such as anticonvulsants [18], anti-malerial agents [19], antacidic agents and central nervous system depressants [20]. Spiro compounds are inhibitors of cyclic-3,5-monophosphate phosphodiestarase and acts agents against erectile disfunction [21]. They also act as antiproliferavive agents [22]. Spirocyclic compounds have found use in the fields of organic optoelectronics [23-25], photochromism [26, 27], and medicinal chemistry [28-30].

Dipyrazolopyridine (DPP) have attracted a wide interest in the last ten years due to a number of optoelectronic applications among which organic light emitting diodes and electroluminescent displays (OLEDs) may be considered as dominant. Releted technologies have already been moved from laboratories to the industry [31, 32] and due to number of advantages OLEDs over the traditional LCD/LED displays they are observed to become competitive on the world markets in nearest perspective.

EXPERIMENTAL SECTION

Experimental No. 1

Synthesis of N,N-Diphenyl-3-(4-chlorophenyl)-dipyrazolo (3,4-b)pyridine 3



1 **3**

Procedure

To a solution of 6-Chloro-1-phenyl -3-(4-Chloro)phenyl pyrazolo (3,4-b) pyridine **1** (4.20 gm, 0.01mole) and phenyl hydrazine (2.2ml, 0.02mole) in ethanol (25ml) & catalytic amount of acetic acid (0.1ml) was added .The Reaction mixture was refluxed for two hours.The completion of reaction mixture was checked by (TLC ethyl acetate /n-hexane 1:1). The mixture was poured in ice cold water to get colorless solid. The solid then dried and re-crystallised from ethanol to furnished a colorless solid and characterized by spectral and analytical data.

Yield: 80%; mp 138°C; IR (KBr): 1274 cm^{-1} (C-N), 1598 (C=C) cm^{-1};^{1}H NMR (DMSO-d_6) δ:8.40 (s, 1H, C_{16}H), 7.7 (s, 1H, C_{25}H), 7.3-7.7 (m, 10H, Ar-H), 8.24 (d, 2H, *J* = 7.6 Hz Ar-H), 7.80 (d, 2H, *J* = 7.6 Hz Ar-H), ^{13}C NMR (DMSO-d_6) δ: 134.3 ,129.3 (2C) , 128.7 (2C) , 131.1 , 144.9 ,113.9, 139.1 ,191.1 ,132.1 ,150.9 ,148.9 ,139.6(2C) ,120.1(4c) ,128.4 (2c) , 129.3(2C), 125.9, 126.0; MS (EI): m/z=422 (M^{+1}). Anal. Calcd. for $C_{25}H_{16}ClN_5$: C: 71.17; H: 3.82; N: 16.60. Found: C: 71.10; H: 3.50; N: 16.40.

Synthesis of N-Phenyl-3-(4-chlorophenyl)-dipyrazolo (3,4-b)pyridine 2

Recrystallised from ethanol to afford colourless needles; Yield: 78%; mp 117°C; IR (KBr): 2974, 1598 cm^{-1};^{1}H NMR (DMSO-d_6) δ:8.78 (s, 1H, C_{16}H), 6.9 (s, 1H, NH), 7.70 (s, 1H, CH), 7.3-7.8 (m, 5H, Ar-H), 8.22 (d, 2H, *J* = 7.7 Hz Ar-H), 8.33 (d, 2H, *J* = 7.7 Hz Ar-H), ^{13}C NMR (DMSO-d_6) δ: 134.3 ,129.4(2C), 127.9(2C) ,

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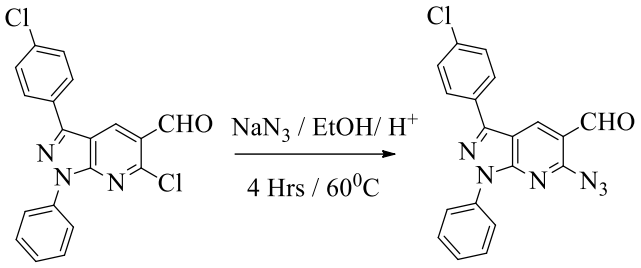
131.1 , 144.8 , 114.9 ,135.6 ,114.6 ,132.4 , 153.9 ,149.2 ,139.6, 120.2 (2C),128.9(2C) ,126.4(2C); MS (EI): m/z=346 (M^{+1}). Anal. Calcd. for $C_{19}H_{12}ClN_5$: C: 66.00; H: 3.50; N: 20.25 . Found: C:66.10 ; H: 3.90; N: 20.50

Experimental No. 2

Synthesis of 6-Azido-1-phenyl -3-(4-Chlorophenyl) pyrazolo (3,4-b) pyridine



1 **4**

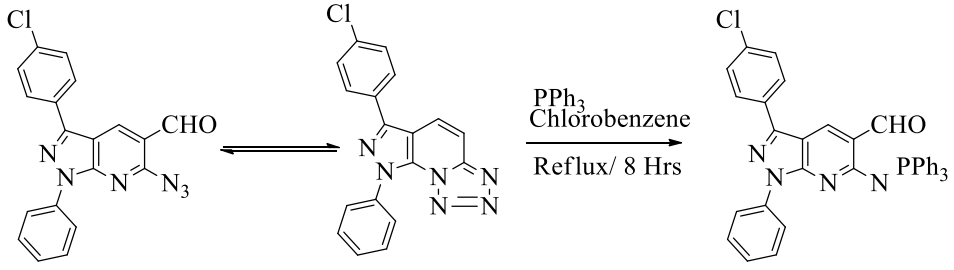
Procedure

To a solution of 6-chloro-3-(4-Chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde **1** (3.75 gm, 0.01mole) and sodium azide (0.65 gm, 0.01 mole) in 20 ml of ethanol using catalytic amount of acetic acid (0.1ml) was added and heated to 60°c for 4 hours. The completion of reaction was checked by (TLC, ethyl acetate /n-hexane 1:1). Then the reaction mixture was poured in ice cold water (150 ml)and stirred for 50 minute, the precipitate product was filtered, washed with water, dried and re-crystalized from ethanol to furnish 6-Azido-1-phenyl -3-(4-Chlorophenyl) pyrazolo (3,4-b) pyridine, **4**

Silvery solid; (Yield= 82%); mp 240-244°C; IR (KBr): 1657,(-CHO) 1506 (C=C)cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 9.40 (s, 1H, CHO), 8.76 (s, 1H, C_{22}H), 7.50 (t, 2H, *J* = 7.68 Hz, Ar-H), 8.1 (d, 2H, *J* =8.84 Hz, Ar-H), 7.60 (m, 2H, *J* = 7.68), 7.62 (d, 1H, *J* = 7.40 Hz Ar-H), 8.4 (d, 2H, *J* = 8.84 Ar-H), ^{13}C NMR (DMSO-d_6) δ: 190.77, 162.91, 146.91, 143.91, 139.71, 137.25, 135.18, 132.02, 129.60 (2C), 129.05 (2C), 128.21 (2C), 126.31, 120.17, 120.97, 116.74, 113.89; MS (EI): m/z=375 (M^{+1}).Anal. Calcd. for $C_{19}H_{11}ClN_6O$: C, 60.89; H, 2.96; N, 22.42.
Found: C, 60.55; H, 3.13; N, 12.15.

Experimental No. 3

Synthesis of 3-Formyl -2-(Triphenylphospharanylideneamino) –pyrazolo (3,4-b) pyridine, 6



4 **5** **6**

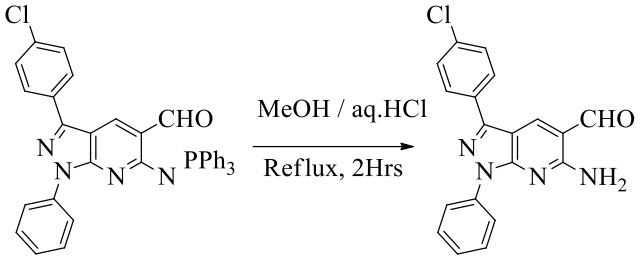
Procedure

To solution of 6-Azido-1-phenyl -3-(4-Chlorophenyl) pyrazolo (3,4-b) pyridine, **4** (3.74 gm, 0.01mole) and triphenyl phosphine (2.62ml, 0.01 mole) in chlorobenzene (30 ml) was stirred and heated for 9 hours. The completion of reaction was monitored by (TLC ethyl acetate /n-hexane 1:1). The excess of Triphenyl phosphine was removed by triturated with cyclohexane (60 ml). The reaction mixture was kept for 20 hours and filtered by suction. The precipitate was washed with water, dried and re-crystallized from dimethyl formamide to afforded pale yellow solid of 6-Triphenylphosphine-1-phenyl -3-(4-Chlorophenyl) pyrazolo (3,4-b) pyridine, **6.**

Pale yellow solid; (Yield= 80%); mp 230-232°C; IR (KBr): 1670 (-CHO), 1530 (C=C)cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 10.50 (s, 1H, CHO), 9.10 (s, 1H, C_{22}H), 7.30-8.20 (m, 24H, Ar-H), MS (EI): m/z=610 (M^{+1}).Anal. Calcd. for $C_{37}H_{26}ClN_4OP$: C, 72.96; H, 4.30; N, 9.20.
Found: C, 72.88; H, 4.53; N, 9.15.

Experimental No. 4

Synthesis of 6-amino-3-(4-chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde, 7



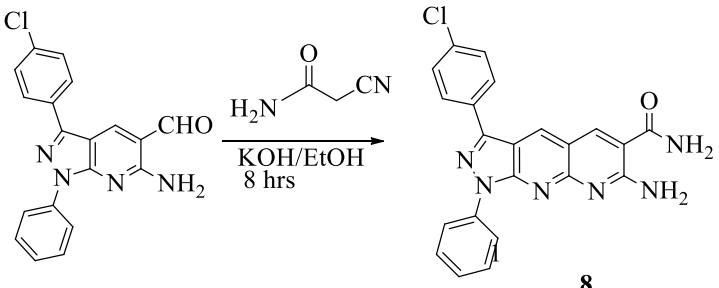
6 **7**

Procedure

A mixture of compound 6-Triphenylphosphine-1-phenyl -3-(4-Chlorophenyl) pyrazolo (3,4-b) pyridine, **6** (3.49 gm, 0.01mole) and hydrochloric acid (20ml) and small amount of methanol (6ml) was refluxed for two hour. The reaction progress was monitored by TLC check, (Toluene : acetone, 8:2). The excess of triphenylphosphineoxide (Ph_3PO) was removed by filtration. The pH of solution (filtrate) was maintained to about 11 with the help of 2N sodium hydroxide (15 ml). The resulting reaction mixture was filtered, the precipitate was washed with water, dried and crystallized from Ethanol to furnish pale yellow needles of 6-amino-3-(4-Chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde**, 7**.
Pale yellow solid; (Yield= 89%); mp 196-197°C;.

Experimental No. 5

Synthesis of 7-Amino-3-(4-chlorophenyl)-1-phenyl 1-H-pyrazolo(3,4-b) (1,8) naphthiridine-6-carboxamide, 8



7 **8**

Procedure

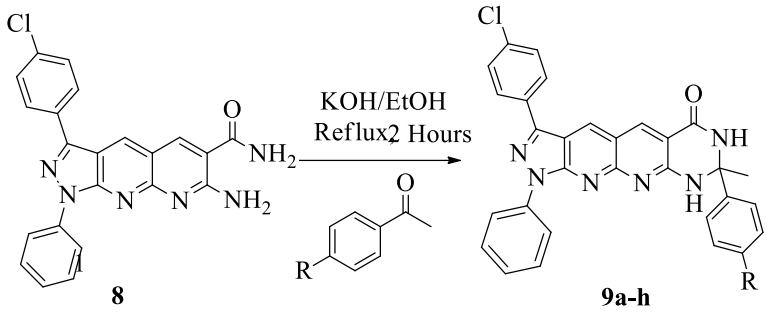
A mixture of 6-amino-3-(4-Chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde**, 7** (10.3 gm, 2.5 mmole) and cyanoacetamide (2.1 gm, 2.5 mmole) in ethanolic potassium hydroxide [8 ml (3%)] was heated under refluxed condition for 8 hours. The reaction completion was monitored by (TLC ethyl acetate /n-hexane 1:1). After cooling the reaction mixture was cooled to room temperature and precipitated obtained was filtered and washed with ethanol, dried and purified by crystallization from methanol to obtain 7-Amino-3-(4-Chlorophenyl)-1-phenyl 1-H-pyrazolo(3,4-b) (1,8) naphthiridine-6-carboxamide, **8**

Recrystallised from methanol to afford yellow needles; (Yield= 78%); mp 311-315°C;IR (KBr): 3417 (–NH_2), 1660 (amide), 1552 (C=C) cm^{-1};^{1}H NMR (DMSO-d_6) δ:9.10 (s, 1H, C_{17}H), 8.70 (s, 1H, C_{26}H), 8.51 (d, 2H, *J* = 7.76 Hz Ar-H), 8.26 (s, 1H), 8.11 (d, 2H, *J* = 8.76 Hz), 7.87 (s, 2H, NH_2), 7.69 (s, 2H, $CONH_2$), 7.58 (t, 2H, *J* = 8.28 Hz Ar-H), 7.31 (t, 1H, *J* = 7.36 Hz Ar-H), 7.17 (d, 1H, *J* = 8.80 Hz Ar-H), ^{13}C NMR (DMSO-d_6) δ:

168.34, 161.44, 155.65, 149.84, 145.81, 139.82, 139.31, 135.65, 133.92, 133.24, 129.41 (2C), 128.74, 128.32, 127.51 (2C), 126.42, 120.24 (2C), 115.54, 114.84, 111.43, MS (EI): m/z=415 (M^{+1}). Anal. Calcd. for $C_{22}H_{15}ClN_6O$: C, 63.69; H, 3.64; N, 20.26. Found: C, 63.80; H, 3.75; N, 20.36

Experimental No. 6

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6- substituted-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9a-h



8 **9a-h**

Procedure

Mixture of compound 7-Amino-3-(4-chlorophenyl)-1-phenyl 1-H-pyrazolo(3,4-b) (1,8) naphthiridine-6-carboxamide, **8** (2 mmole) and acetophenone (2 mmole) were dissolved in 15 ml of ethanolic potassium hydroxide (2%). The mixture was heated under refluxed condition for 2 hours. The progress of reaction mixture was tested by taking (TLC ethyl acetate /n-hexane 1:1). The reaction mixture was cooled at room temperature . The precipitate solid was obtained, filtered and washed five times with ethanol, dried and re-crystallised from methanol to furnished **9** in good yields.

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido [2,3-d]pyrimidin-6(5H)-one, 9a

Recrystallised from methanol to afford pale yellow needles; Yield: 68%; mp 310-312°C; IR (KBr): 3438 cm^{-1} (O=C-NH), 3172 cm^{-1} (-NH), 1646 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ:8.70 (s, 1H, C_{17}H), 9.20 (s, 1H,C_{26}H), 8.10 (s, 1H, NH), 7.12-7.7 (m, 14H, Ar-H), 8.00 (s,1H, NH), 2.30 (s, 3H, CH_3), ^{13}C NMR (DMSO-d_6) δ: 134.3 ,129.4 (2C) , 127.7 (2C) , 131.2 , 144.9 ,114.9, 136.1 ,115.1 ,138.1 ,164.9,66.2, 28.2, 142.9 ,129.6 (2C) ,128.1(2c) ,127.4, 126.3, 164.0, 155.2, 150.0, 120.0 (2C), 129.3(2C), 139.0, 126.2; MS (EI): m/z=517 (M^{+1}). Anal. Calcd. for $C_{30}H_{21}ClN_6O$: C: 69.70; H: 4.09; N: 16.26. Found: C: 69.10 ; H: 4.70; N: 16.50.

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6- methoxy-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9b

Recrystallised from methanol to afford yellow needles; Yield: 88%; mp 303-306°C; IR (KBr): 3450 cm^{-1} (O=C-NH), 3160 cm^{-1} (-NH), 1640 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ:8.20 (s, 1H, C_{17}H), 8.45 (s, 1H, C_{26}H), 8.11 (s, 1H), 7.21 (s, 1H), 3.8 (s, 3H), 1.80 (s, 3H), 7.4-7.6 (m, 5H, Ar-H), 7.62 (d, 2H, *J* = 7.6 Hz, C_9H, C_{11}H), 7.70 (d, 2H, *J* = 7.6 Hz C_8H, C_{12}H), 7.10 (d, 2H, *J* = 7.0 Hz Ar-H), 7.04 (d, 2H, *J* = 7.0 Hz Ar-H), ^{13}C NMR (DMSO-d_6) δ: ^{13}C NMR (DMSO-d_6) δ: 134.3 ,129.4 (2C) , 127.7 (2C) , 131.2 , 144.9 ,114.9, 136.1 ,115.1 ,138.1 ,164.9,66.2, 28.2, 142.9 ,129.6 (2C) ,128.1(2c) ,127.4, 158.0,55.3, 163.0, 155.2, 150.0, 120.0 (2C), 129.3(2C), 139.0, 126.2;; MS (EI): m/z=547 (M^{+1}). Anal. Calcd. for $C_{31}H_{23}ClN_6O_2$: C: 68.07; H: 4.24; N: 15.36. Found: C: 68.10 ; H: 4.90; N: 15.50.

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6- hydroxy-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9c

Recrystallised from methanol to afford pale yellow needles; Yield: 80%; mp 328-330°C; IR (KBr): 3452 cm^{-1} (O=C-NH), 3157 cm^{-1} (-NH), 1639 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ:8.16 (s, 1H, C_{17}H), 8.40 (s, 1H, C_{26}H), 8.20 (s, 1H), 7.24 (s, 1H), 3.80 (s, 3H, CH_3), 1.79 (s, 3H, $C_{38}H_3$), 7.4-7.6 (m, 5H, Ar-H), 7.64 (d, 2H, *J* = 7.4 Hz, C_9H, C_{11}H), 7.73 (d, 2H, *J* = 7.4 Hz, C_8H, C_{12}H), 7.12 (d, 2H, *J* = 7.0 Hz Ar-H), 7.04 (d, 2H, *J* =

7.0 Hz Ar-H), ^{13}C NMR (DMSO-d_6) δ: ^{13}C NMR (DMSO-d_6) δ: 134.2 ,131.4 (2C) , 127.7 (2C) , 127.2 , 164.9 ,114.9, 136.1 ,115.1 ,138.1 ,144.9, 66.2, 28.2, 142.9 ,129.6 (2C) ,128.1(2c) ,127.4, 158.0, 55.3, 162.0, 156.4, 150.0, 120.0 (2C), 129.3, 139.0, 126.2;; MS (EI): m/z=547 (M^{+1}). Anal. Calcd. for $C_{30}H_{20}ClN_6O_2$: C: 67.61; H: 3.97; N: 15.77. Found: C: 67.60 ; H: 3.90; N: 15.72.

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-methyl-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido [2,3-d]pyrimidin-6(5H)-one, 9d

Recrystallised from methanol to afford pale yellow needles; Yield: 82%; mp 310-312°C; IR (KBr): 3449 cm^{-1} (O=C-NH), 3156 cm^{-1} (-NH), 1655 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ 8.13 (s, 1H, C_{17}H), 8.40 (s, 1H, C_{26}H), 8.21 (s, 1H, NH), 7.21 (s, 1H, NH), 1.81 (s, 3H, CH_3), 1.78 (s, 3H, $C_{38}H_3$), 7.3-7.7 (m, 5H, Ar-H), 7.84 (d, 2H, *J* = 7.6 Hz, C_9H, C_{11}H), 7.70 (d, 2H, *J* = 7.6 Hz, C_8H, C_{12}H), 7.13 (d, 2H, *J* = 7.0 Hz Ar-H), 7.14 (d, 2H, *J* = 7.0 Hz Ar-H),^{13}C NMR (DMSO-d_6) δ: ^{13}C NMR (DMSO-d_6) δ: 134.3 ,129.4 (2C) , 127.7 (2C) , 131.2 , 144.9 ,114.9, 136.1 ,115.1 ,138.1 ,164.9,66.2, 28.2, 142.9 ,129.6 (2C) ,128.1(2c) ,127.4, 136.8, 24.4, 163.0, 155.2, 150.0, 120.0 (2C), 129.3(2C), 139.0, 126.2; MS (EI): m/z=530 (M^{+1}). Anal. Calcd. for $C_{31}H_{23}ClN_6O$: C: 70.12; H: 4.37; N: 15.83. Found: C:70.15 ; H: 4.37; N: 15.50.

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-nitro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9e

Recrystallised from methanol to afford pale yellow needles; Yield: 79%; mp 342-348°C; IR (KBr): 3437 cm^{-1} (O=C-NH), 3170 cm^{-1} (-NH), 1646 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ 8.17 (s, 1H, C_{17}H), 8.40 (s, 1H, C_{26}H), 8.11 (s, 1H, NH), 7.21 (s, 1H, NH), 1.80 (s, 3H, CH_3), 7.5-7.7 (m, 5H, Ar-H), 7.34 (d, 2H, *J* = 7.6 Hz, C_8H, C_{12}H), 7.40 (d, 2H, *J* = 7.6 Hz, C_9H, C_{11}H), 7.10 (d, 2H, *J* = 7.0 Hz Ar-H), 7.07 (d, 2H, *J* = 7.0 Hz Ar-H), ^{13}C NMR (DMSO-d_6) δ: ^{13}C NMR (DMSO-d_6) δ: 134.3 ,129.4 (2C) , 127.7 (2C) , 131.2 , 144.9 ,114.9, 136.1 ,115.1 ,138.1 ,164.9,66.2, 28.2, 142.9 ,129.6 (2C) ,128.1(2c) ,127.4, 146.3, 163.0, 155.2, 150.0, 120.0 (2C), 129.3(2C), 139.0, 126.2; MS (EI): m/z=547 (M^{+1}). Anal. Calcd. for $C_{30}H_{20}ClN_6O_2$: C: 68.07; H: 4.24; N: 15.36. Found: C:68.10 ; H: 4.90; N: 15.50.

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9f

Recrystallised from methanol to afford pale yellow needles; Yield: 80%; mp 330-327°C; IR (KBr): 3388 cm^{-1} (O=C-NH), 3210 cm^{-1} (-NH), 1650 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ:9.26 (s, 1H, C_{17}H), 8.73 (s, 1H,C_{26}H), 6.90 (s, 1H, NH), 8.60 (s, 1H, NH), 2.30 (s, 3H, CH_3), 7.4-7.7 (m, 5H, Ar-H), 7.35 (d, 2H, *J* = 7.6 Hz, C_8H, C_{12}H), 7.39 (d, 2H, *J* = 7.6 Hz, C_9H, C_{11}H), 7.12 (d, 2H, *J* = 7.0 Hz Ar-H), 7.14 (d, 2H, *J* = 7.0 Hz), ^{13}C NMR (DMSO-d_6) δ: ^{13}C NMR (DMSO-d_6) δ: 134.3 ,129.4 (2C) , 127.7 (2C) , 131.2 , 144.9 ,114.9, 136.1 ,115.1 ,138.1 ,164.9,66.2, 28.2, 142.9 ,129.6 (2C) ,128.1(2c) ,127.4, 133.0, 163.0, 155.2, 150.0, 120.0 (2C), 129.3(2C), 139.0, 126.2;; MS (EI): m/z=552 (M^{+1}). Anal. Calcd. for $C_{30}H_{20}Cl_2N_6O$: C: 65.34; H: 3.66; N: 15.24. Found: C:65.10 ; H: 3.90; N: 14.70.

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-fluoro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9g

Recrystallised from methanol to afford pale yellow needles; Yield: 84%; mp 335-337°C; IR (KBr): 3440 cm^{-1} (O=C-NH), 3156 cm^{-1} (-NH), 1666 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ:8.12 (s, 1H, C_{17}H), 8.49 (s, 1H, C_{26}H), 8.10 (s, 1H), 7.24 (s, 1H), 1.80 (s, 3H, CH_3), 7.4-7.7 (m, 5H, Ar-H), 7.35 (d, 2H, *J* = 7.6 Hz, C_8H, C_{12}H), 7.40 (d, 2H, *J* = 7.6 Hz, C_9H, C_{11}H), 7.10 (d, 2H, *J* = 7.0 Hz Ar-H), 7.04 (d, 2H, *J* = 7.0 Hz Ar-H),^{13}C NMR (DMSO-d_6) δ: δ: 134.3 ,129.4 (2C) , 127.7 (2C) , 131.2 , 144.9 ,114.9, 136.1 ,115.1 ,138.1 ,164.9,66.2, 28.2, 142.9 ,129.6 (2C) ,128.1(2c) ,127.4, 161.0, 163.0, 155.2, 150.0, 120.0 (2C), 129.3(2C), 139.0, 126.2; MS (EI): m/z=535 (M^{+1}). Anal. Calcd. for $C_{30}H_{20}ClFN_6O$: C: 67.35; H: 3.77; N: 15.71. Found: C:67.10 ; H: 3.90; N: 15.50.

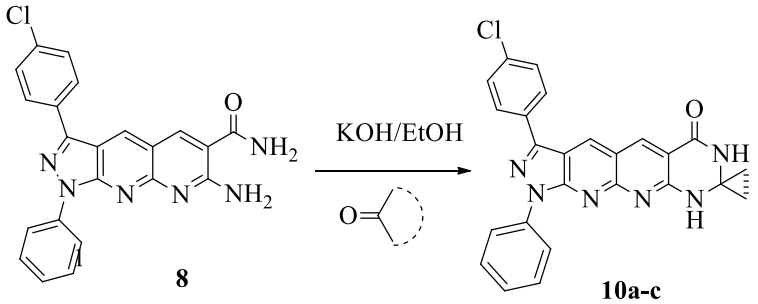
Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-bromo-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9h

Recrystallised from methanol to afford pale yellow needles; Yield: 82%; mp 324-327°C; IR (KBr): 3439 cm^{-1} (O=C-NH), 3180 cm^{-1} (-NH), 1652 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ:8.10 (s, 1H, C_{17}H), 8.39 (s, 1H, C_{26}H), 8.18 (s, 1H, NH), 7.21 (s, 1H, NH), 1.79 (s, 3H, CH_3), 7.5-7.8 (m, 5H, Ar-H), 7.37 (d, 2H, *J* = 7.6 Hz,

C_8H, $C_{12}H$), 7.50 (d, 2H, *J* = 7.6 Hz, C_9H, $C_{11}H$), 7.14 (d, 2H, *J* = 7.0 Hz, Ar-H), 7.04 (d, 2H, *J* = 7.0 Hz, Ar-H),^{13}C NMR (DMSO-d_6) δ: ^{13}C NMR (DMSO-d_6) δ: 134.3 ,129.4 (2C) , 127.7 (2C) , 131.2 , 144.9 ,114.9, 136.1 ,115.1 ,138.1 ,164.9,66.2, 28.2, 142.9 ,129.6 (2C) ,128.1(2c) ,127.4, 121.3, 163.0, 155.2, 150.0, 120.0 (2C), 129.3(2C), 139.0, 126.2; MS (EI): m/z=596 (M^{+1}). Anal. Calcd. for $C_{30}H_{20}BrClN_6O$: C: 60.47; H: 3.38 ; N: 14.10. Found: C:60.10 ; H: 3.30; N: 14.50.

Experimental No. 7

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-spiro[cycloketones-1-H-pyrazolo] naphthyrido[2,3-d]pyrimidin-6(5H)-one, 10a-c



8 **10a-c**

General procedure

To a solution of compound **8** (2 mmol) in 15 ml of ethanolic potassium hydroxide (2%), cyclic ketone (2 mmol) was added. The reaction mixture was refluxed for two hours, the progress of the reaction was monitored by (TLC ethyl acetate/ n-hexane 1:1). The reaction mixture was filtered, washed three times with water, dried and purified from methanol to furnished **10** in good yields.

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-spiro[cyclopentanon-1-H-pyrazolo]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 10a

Recrystallised from methanol to afford yellow needles; (Yield= 78%); mp 311-315°C;IR (KBr): 3448 cm^{-1} (O=C-NH), 3210 cm^{-1} (-NH), 1652 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ:9.00 (s, 1H, $C_{17}H$), 8.43 (s, 1H, $C_{26}H$), 7.40-7.78(m, 5H, Ar-H), 7.14 (d, 2H, *J* = 7.76 Hz, Ar-H), 7.30 (d, 2H, *J* = 7.76 Hz, Ar-H), 6.2 (s, 1H, $N_{26}H$), 8.0 (s, 1H, $N_{30}H$), 2.90 (t, 2H, CH_2), 2.52 (t, 2H, CH_2), 1.94 (q, 4H, 2 X CH_2);^{13}C NMR (DMSO-d_6) δ: 134.2, 129.3(2C), 128.6 (2C), 131.2, 145.2, 114.0, 135.2, 115.2, 139.2, 111.0, 164.2, 163.8, 155.3, 149.2, 120.5 (2C), 129.4(2C), 139.8, 126.4, 68.3, 42.4 (2C), 20.3(2C); MS (EI): m/z=481 (M^{+1}). Anal. Calcd. for $C_{27}H_{21}ClN_6O$: C, 67.43; H, 4.43; N, 17.47. Found: C, 67.80; H, 4.35; N, 17.36

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-spiro[cyclohexanon-1-H-pyrazolo]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 10b

Recrystallised from methanol to afford yellow needles; (Yield= 72%); mp 328-330°C;IR (KBr): 3438 cm^{-1} (O=C-NH), 3172 cm^{-1} (-NH), 1646 cm^{-1} (carbonyl) 1504 cm^{-1} (C=C);^{1}H NMR (DMSO-d_6) δ:9.10 (s, 1H, $C_{17}H$), 8.80 (s, 1H, $C_{26}H$), 7.40-7.78(m, 5H, Ar-H), 7.16 (d, 2H, *J* = 7.7 Hz Ar-H), 7.36 (d, 2H, *J* = 7.7 Hz Ar-H), 6.2 (s, 1H, $N_{26}H$), 8.0 (s, 1H, $N_{30}H$), 2.98 (m, 4H), 1.84 (m, 4H), 1.43 (q, 2H);^{13}C NMR (DMSO-d_6) δ: 134.1, 129.4(2C), 128.5 (2C), 131.3, 144.2, 115.2, 134.2, 114.2, 139.2, 111.7, 164.1, 163.3, 155.5, 149.6, 120.1 (2C), 129.8(2C), 139.4, 126.2, 68.9, 35.4 (2C), 18.3(2C), 28.0; MS (EI): m/z=495 (M^{+1}). Anal. Calcd. for $C_{28}H_{23}ClN_6O$: C, 67.94; H, 4.68; N, 16.98. Found: C, 67.80; H, 4.35; N, 16.36

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-spiro[indanon-1-H-pyrazolo] naphthyrido[2,3-d]pyrimidin-6(5H)-one, 10c

Recrystallised from methanol to afford pale yellow needles; (Yield= 81%); mp 345-348°C;IR (KBr): 3448 cm^{-1} (O=C-NH), 3181 cm^{-1} (-NH), 1656 cm^{-1} (carbonyl);^{1}H NMR (DMSO-d_6) δ:8.80 (s, 1H, $C_{17}H$), 8.44 (s, 1H, $C_{26}H$), 7.32-7.70(m, 9H, Ar-H), 7.14 (d, 2H, *J* = 7.7 Hz Ar-H), 7.30 (d, 2H, *J* = 7.7 Hz Ar-H), 6.30 (s, 1H,

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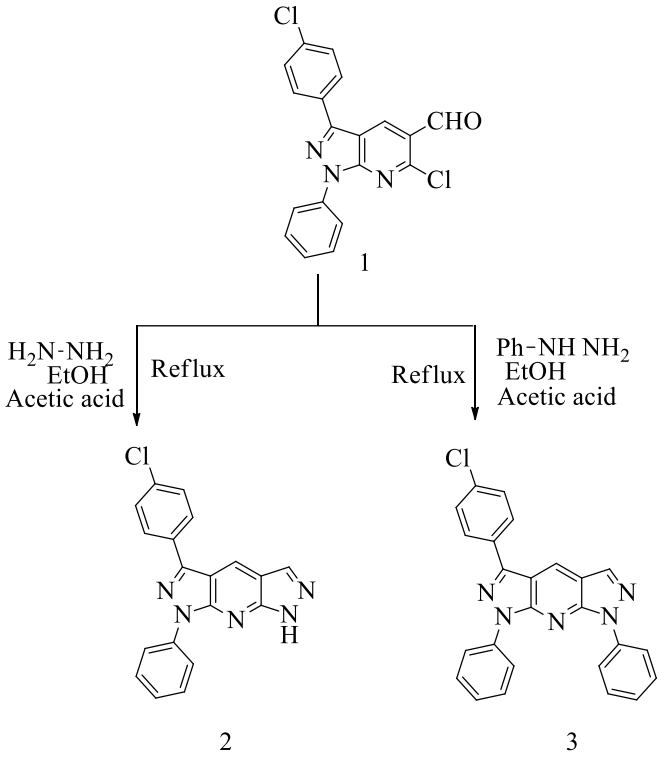
$N_{26}H$), 8.10 (s, 1H, $N_{30}H$), 2.52 (t, 2H, CH_2), 2.92 (t, 2H, CH_2); ^{13}C NMR (DMSO-d_6) δ: 134.2, 129.3(2C), 128.6 (2C), 131.2, 145.2, 114.0, 135.2, 115.2, 139.2, 111.0, 164.2, 163.8, 155.3, 149.2, 120.5 (2C), 129.4(2C), 139.8, 126.4,76.4, 38.3, 23.4, 128.3(2C), 126.4 (2C), 138.2, 143.2; MS (EI): m/z=529 (M^{+1}). Anal. Calcd. for $C_{31}H_{21}ClN_6O$: C, 70.39; H, 4.00; N, 15.89. Found: C, 70.19; H, 4.21; N, 15.90

RESULT AND DISCUSSION

The compound **35** which was synthesized by modified literature method Litt. [42], M.P. 136°C, has two active functionalities ortho chloro carbaldehyde hence compound **1** was utilized to synthesize dipyrazolo pyridine derivatives and further these were studied for photophysical properties.

Synthesis of Dipyrazolo pyrido pyrimidine

1) The compound **3** was synthesized by refluxing 6-chloro-3-(4-chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde **1** with phenyl hydrazine using catalytic amount of acetic acid in ethanol for two hours as depicted in Scheme **1**. The colorless solid thus obtained was characterized by spectral and analytical data.



Scheme-1

In ^1H- NMR (DMSO-*d6*) spectrum of this solid showed the sharp singlet corresponding to pyridine proton of (C_{22}) was appeared at δ 8.40 ppm and all ten aromatic protons were appeared as multiplet in between δ 7.3 to 7.6 ppm. The four protons corresponded to chloro substituted phenyl ring were appeared at δ 7.8-8.2 ppm. The singlet corresponded to one pyrazole proton was appeared at δ 7.7 ppm. The mass spectrum of the compound **3** showed [M^{+1}] peak at 422. The elemental analysis was in agreement with the molecular formula $C_{25}H_{16}ClN_5$ on the basis of these data, structure of compound **3** was assigned to the solid i.e 6-chloro-3-(4-chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde **3.** Analogously compound **2** was synthesized by refluxing compound **1** with hydrazine in ethanol which was characterized by spectral and analytical data. (Fig. S2)

Synthesis of 7-amino-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*][1,8]naphthyridine-6-carboxamide, 8

The 7-amino-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazolo[3,4-*b*][1,8]naphthyridine-6-carboxamide **8** was synthesized from 6-chloro-3-(4-chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde **1** in five steps.

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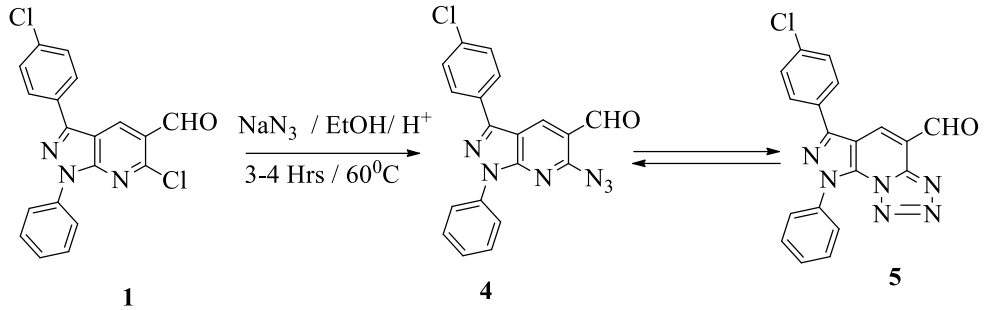
The compound **1** has a chloro functional group which was displaced by the nucleophilic attack of the azido group by (*SN*Ar reaction). The reaction was performed in ethanol using catalytic amount of hydrochloric acid which yielded azido substituted carbaldehyde **4,** a silvery solid in 82% yield which was characterized by spectral and analytical methods. (Fig. S4)

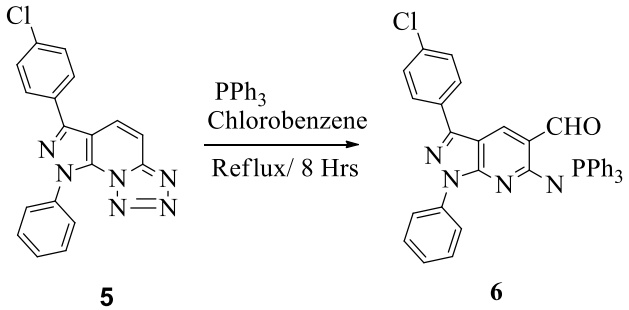


Scheme-2

For instance, The IR (KBr) spectrum showed the absorption band at 1657 cm^{-1} corresponded to carbonyl stretching frequency of aldehyde group. The stretching frequency at 1506 cm^{-1} corresponded to C=C. In ^1H NMR spectrum (DMSO-*d6*) showed the singlet corresponds to the aldehydic proton at δ 9.4 ppm, the five aromatic protons were appeared as multiplet in between δ 7.5 to 7.6 ppm. The four aromatic protons of the chloro substituted phenyl ring were appeared at δ 8.1 & 8.4 ppm. The sharp singlet correspond to pyridine proton of (C_{22}) was appeared at 8.76 ppm. The molecular ion peak [M^{+1}] at 347 exactly matches with the molecular mass of the **5**. The elemental analysis was in agreement with the molecular formula of $C_{18}H_{11}ClN_6$. On the basis of this data, structure of **5** was assigned to the compound that is Tetrazole-3-(4-chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde, **5** (Fig. S5)

Synthesis of Triphenylphosphoranylideniamino-pyrazole, 6.

For the reduction of tetrazole moiety into amino compound, we have tried different methods such as catalytic hydrogenation, sodium dithionate and zinc dust but the problem was associated with the isolation and time required for the completion of reaction. Here, we have performed the *Staudinger* reaction for the reduction of tetrazole moiety into amino compound i.e. with the tertiary phosphine followed by acidic or basic hydrolysis. The redction was achieved in two steps. In first step, the tetrazole moiety reacted with triphenyl phosphine in chlorobenzene. Here we have tried different solvents for the reaction such as 1,2- di-chlorobenzene, bromobenzene, toluene and di-phenyl ether. We observed that the yield associated with the chlorobenzene solvent was 88% which was good as compared to the yields associated with the other solvents. The data of solvents and their yields is given in **Table 1**. Thus the reaction with triphenyl phosphine in chlobenzene afforded open chain compound **6** in 88% which was characterized by spectral and analytical methods.



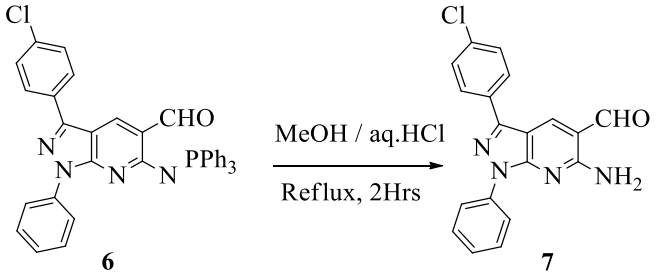
Scheme-3

For instance, the IR (KBr) spectrum of this solid **6** showed peak at 1670 cm^{-1} corresponds to the carbonyl stretching frequency of aldehyde. The stretching frequency at 1530 cm^{-1} corresponded to the C=C. In ^1H NMR spectrum (DMSO-*d6*) of compound **6** showed the crowding of aromatic protons in the range of δ 7.30 to 8.20 ppm corresponds to the twenty four protons of phenyl ring. The pyridine proton of (C_{22}) was appeared as singlet at δ 9.10 ppm. The singlet corresponded to the one proton of aldehyde group appeared at 10.5 ppm.The molecular ion peak [M^{+1}] at 610 exactly matches with the molecular

mass of the compound **6**. The elemental analysis was in agreement with the molecular formula of $C_{37}H_{26}ClN_4OP$. On the basis of this data, structure of **6** was assigned to the compound that is Triphenylphosphoranylideniamino-pyrazole. (Fig. S7)

Synthesis of 6-amino-3-(4-chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde, 7

The oxidative transformation of triphenylphosphoranylideniamino to amino group, several methods are known in organic chemistry. We have performed the reaction in hydrochloric acid and methanol. Thus compound **6** was refluxed in hydrochloric acid and methanol yielded a pale yellow solid in 89 % yield which was characterized by spectral and analytical methods.



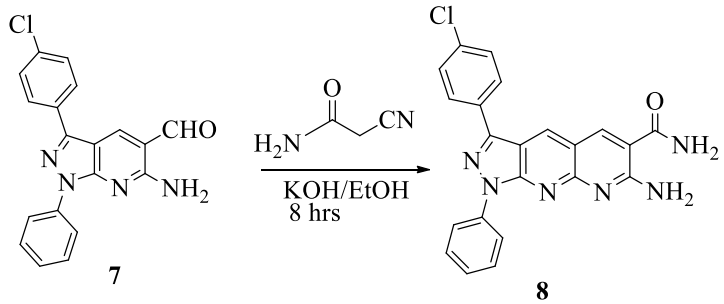
6 **7**

Scheme-4

The compound **7** was previously synthesized in chapter first; hence the confirmation of the structure was performed by physical constant method. (M.P. 196°C)

Synthesis of 7-amino-3-(4-chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b][1,8]naphthyridine-6-carboxamide, 8

The required synthon **8** was synthesized by condensation of amino carbaldehyde **7** with cyanoacetamide. Thus the compound **7** on condensation with cyanoacetamide in ethanolic potassium hydroxide yielded **8** in 78% yields. (Fig. S8)



7 **8**

The confirmation of the solid was performed by physical constant method. (M.P. 312°C)

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6- substituted-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9 a-h

The ortho amino carboxamide **8** which has fascinating potentiality for annulations of heterocyclic ring structures, which supplied synthetic entry in heterocyclic systems fused to a carboxamide nucleus by *Friedlander* condensation reactions. Our approach to synthesize pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one **9** based on *Friedlander* condensation stratergy. Thus we have studied the annulations of pyridine ring on compound **8** with substituted acetophenones and cyclic ketones under basic conditions. Initially, we have performed the condensation with chloro substituted acetophenone because of its better solubility in ethanol.

Thus the ortho amino carboxamide **8** on *Friedlander* condensation with p-chloroacetophenone in ethanolic potassium hydroxide yielded the pale yellow solid in 80% yield which was characterized by spectral and analytical data.

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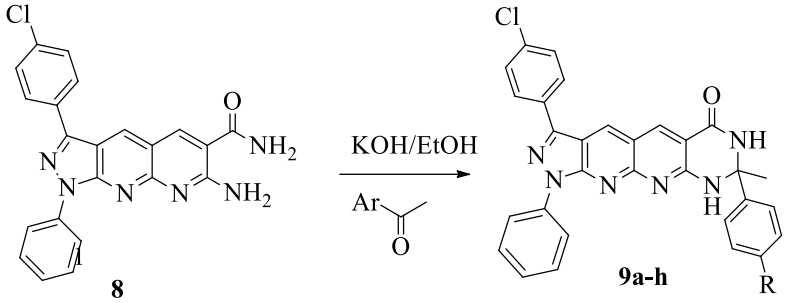
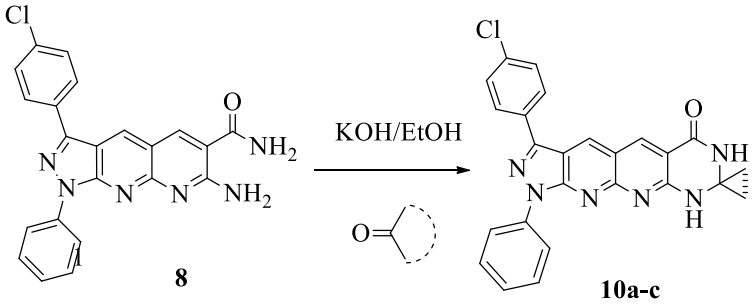


Scheme-5

For instance, the ^{1}H- NMR (DMSO-*d6*) spectrum of compound **9f** showed the two pyridine protons of (C_{17}& C_{26}) at δ 9.2 and 8.7 ppm. The three protons of the methyl group (C_{35}) appeared as singlet at δ 2.30 ppm. All thirteen aromatic protons are appeared as multiplet in between δ 7.3 to 8.2 ppm. The two protons of NH group appeared at δ 7.3 & 8.8 ppm. In ^{13}C NMR spectrum, the carbon of amide functional group appeared at 164 ppm. The three carbons of pyrazole ring was appeared at 145-149 ppm. The two pyridine carbons were appeared at 135 & 137 ppm. The one aliphatic carbon was appeared at 67 ppm. The eighteen aromatic carbons of phenyl ring were appeared in between 120-145 ppm. The mass spectrum showed the [M^{+1}] peak at **516** which exactly matches with the molecular formula $C_{30}H_{20}ClN_6O$. The elemental analysis was in agreement with the molecular formula of the synthesized compound **9f**, on the basis of these data, we confirmed that the synthesized solid was 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, **9f.** Analogously, we have synthesized remaining of derivatives by *Friedlander* reaction under similar reaction conditions. (Fig. S15,16)

Synthesis of 3-(4-chlorophenyl)-7,9-dihydro-spiro[cycloketones-1-H-pyrazolo] naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9a-c

The synthesis of pyrazolo[3,4-b][1,8]naphthyridine-6-carboxamide **9** was achieved by *Friedlander* condensation of carboxamide **8** with cyclic ketones such as cyclohexanone in ethanolic potassium hydroxide. Thus the compound **8** on refluxing with cyclohexanone in ethanolic potassium hydroxide yielded a pale yellow solid in 72% yield which was characterized by spectral and analytical data.



Scheme-6

In ^{1}H- NMR (DMSO-d_6, 400 MHz) spectrum of compound **10b** showed the two pyridine protons of (C_{26} & C_{17}) at δ 9.1 and 8.8 ppm. Aliphatic protons of cyclohexyl group were appeared in between δ 1.41-2.98 ppm. The nine aromatic protons are appeared as multiplet in between δ 7.2 to 8.3 ppm. The mass spectrum showed the [M^{+1}] peak at **495** which exactly matches with the molecular formula $C_{28}H_{23}ClN_6O$. The elemental analysis was in agreement with the molecular formula of the synthesized compound **10b**, on the basis of these data, we confirmed that the synthesized solid was 3-(4-chlorophenyl)-7,9-dihydro-spiro[cyclohexanon-1-H-pyrazolo] naphthyrido[2,3-d]pyrimidin-6(5H)-one **10b,** Analogously remaining derivatives were synthesized under similar reaction condition and characterized by spectral and analytical methods. (Fig. S18,19)

Section –II: Study of photophysical properties.

The number of environmental factors that affect the fluorescence emission including binding action between the fluorophore and solvents polarity, other dissolved organic and inorganic compounds, acidic and basic nature, temperature and the concentration of the fluorophore compound. The effect of these properties are different for different compounds. Due to the interaction in the environment of the fluorophre, the high degree of sensitivity occurs in the emission properties of the compound. Solvents and their polaririte plays important role in the physical and chemical processes, we have studied the effect of polarities of solvent on the fluorophore. There are three types of interactions are present between solute and solvent such as solte-solute, solute–solvent and solvent-solvent interaction but out of them solute-solvent interaction predominates [43]. Liquid chromatography, capillary electrophoresis as a reaction medium, mixture of organic solvents are widely used as mobile phase [44]. The extent of the solute dissolved, is decided by the polarities of the solvent which affects the fluorescence emission and absorption properties of the fluorophore [45]. This phenomenon is called as solvate chromism. One of the major contributor to the salvation effect, is the hydrogen bonding and has been widely investigated as it is present in large varities of chemical, biochemical and pharmacological processes [46].

Mechanism of solvent polarity on the fluorophore emission

The distribution of the solvent molecules surrounding to the fluorophore decided by the interaction between the dipole moments of the solvent molecules with the fluorophore. The change in the molecular dipole moments can occur due to the differenct in the energy levels between ground states and excited states in the fluorophore moiety.

According to the Frank-Condon principle, the fluorophore excited to the higher energy level in a short timeframe as compared to the time for interaction occurs between solute and solvent molecules to reorient themselves which is shown in figure 1. After the excitation of the fluorophore to the higher energy vibrational levels, fluorophore losses their energy and then it relaxes to the lower energy levels which occurs in the 1 to 100 picoseconds. Solvent molecules helps to stabilize and lower the energy level of the excited state and hence solvent molecules shifts the fluorophore to the higher wavelength (red shift) of the fluorescent emission.

It is observed that on increasing the solvent polarity, the emission wavelength increases consequently lowers the energy gap between ground state and excited state. It is observed that the polarity of the fluorophore also affects the absorption and emission wavelengths. (Fig. S20)

On the basis of above discussion, it was observed that the fluorescence emission was influenced by the polarity of the solvent. The interaction between solvent and the fluorophore was exmined by ultra-violet/ visible and fluorescence spectroscopy.

In this section we have investigated the absorption and emission properties of the compound **2** and **3** in homogeneous organic media with different solvent polarities. The ultra-violet absorption and fluorescence emission data in organic solvents of different polarities are given in Table 2.

Photophysical properties study of pyrazolo naphthyridine derivatives

Fluorescence often considered as physical and physic-chemical phenomenon to study light emission properties of organic and inorganic molecules. In last 30 years, an interest and applications of the fluorescent molecules has been steadily and sometimes dramatically increased, now fluorescent dyes play important role in many aspects of modern life. In 1927, Water low & Sons applied the fluorescent compounds to cease forgoing of bank-notes and other securities [47,48]. Fluorescent brighters are mainly applied for in textile finishing and as additives for washing purpose of clothes, in detergents, for brightening of pulp and paper and also in laser-dye technology. Such molecules absorbs in the UV, especially around 370 nm wavelength and also fluoresces in visible region with a typical maxima 440-450 nm and increasing number of commercial brighteners are mixtute of two fluorescent compounds which in some cases give rise to synergetic effects [49,50]. The organic compounds which used as fluorescent brighteners must have the high extinction coefficient, large stock shifts and their quantum yields near to one.

Influence of substituent positions on the absorption and emission spectra of aromatic compounds.

The UV-visible and emission properties (spectrophotometer RF-3100) compounds **9a-h** are studied in polar solvent dimethyl sulphoxide (DMSO) and results are summarized in Table 2 It was observed that fluorescence maxima of the compound **9b** are larger may be due to the presence of strong electron donor group i. e. methoxy group on the ring at C_{38}. This is due to increase in the pi-electron density on the C_{38} ring by methoxy group. On the other hand fluorescence minima of the compound **9e** was observed due to the presence of strong electron withdrawing group at C_{38} in the ring. Another interesting feature noted that halo substitution at para position in compounds **9g** show less fluorescence emission (**0.31 To 0.54**) may be due to the quenching of fluorescence with halogen atoms as the substituent. In this measurement we have used anthracene as reference standard whose quantum yield was 0.26. The comparative absorption and emission data is given in **Table 3** and Fig. 2

Calculation of quantum yield by comparative method.

The quantum yields of the synthesized compounds were calculated by comparative method. In this section, we calculated quantum yield using following equation as shown in figure S22 and S23.

CONCLUSION

In conclusion, we have mentioned the efficient method for the synthesis of dipyrazolo pyridine **2** & **3** and thiophene substituted naphthyrido carboxamide derivatives **9a-h** by *Friedlander* condensation of 7-Amino-3-(4-Chlorophenyl)-1-phenyl 1-H-pyrazolo(3,4-b) (1,8) naphthiridine-6-carboxamide, **8** with acetophenones and cyclic ketones. The synthesis of synthon 42 was performed in four steps which involved nucleophilic aromatic nucleophilic substitution of azido ion, reduction of triphenylphospharanylideneamino into amino compound and condensation with cyanoacetamide. All synthesized compounds were characterized by spectral and analytical methods. We further studied absorption and emission properties of synthesized compounds in different solvents.

From the data given in table 1, it was observed that, absorption and emission properties of these compounds greatly influence by solvent polarities. A red shift in the fluorescence emission was observed from non-polar n-hexane to polar acetonitrile. We observed that the fluorescence intensities of these compounds are low in n-hexane as compared to the polar aprotic and polar protic solvents. The quantum yield of the compound **2** and **3** also influenced by the polarities of the solvents. In non-polar solvents like n-hexane, the fluorescent excited state can be Ag nature, since Ag* to Ag transition is symmetry forbidden hence resulting emission is relatively weak but in case of polar solvents, the transition Bg* to Ag is symmetry allowed which responsible for the enhancement in the quantum yields of the fluorophores **2** & **3**.

All these synthesized compounds **9a-h** and **10a-c** showed the emission in visible region. Absorption and emission maxima are strongly dependent on the aryl substituent i. e. presence of electron donating group such as methoxy group, shifts the absorption as well as emission wavelength to a longer wavelength where electron withdrawing group such as nitro group present on the phenyl ring shifts the absorption and emission wavelength to shorter wavelength. The fluorescent emission wavelengths of all synthesized compounds ranging between 544 nm to 513 nm. No overlapping in absorption and emission region, makes these compounds eligible for biological and material applications.

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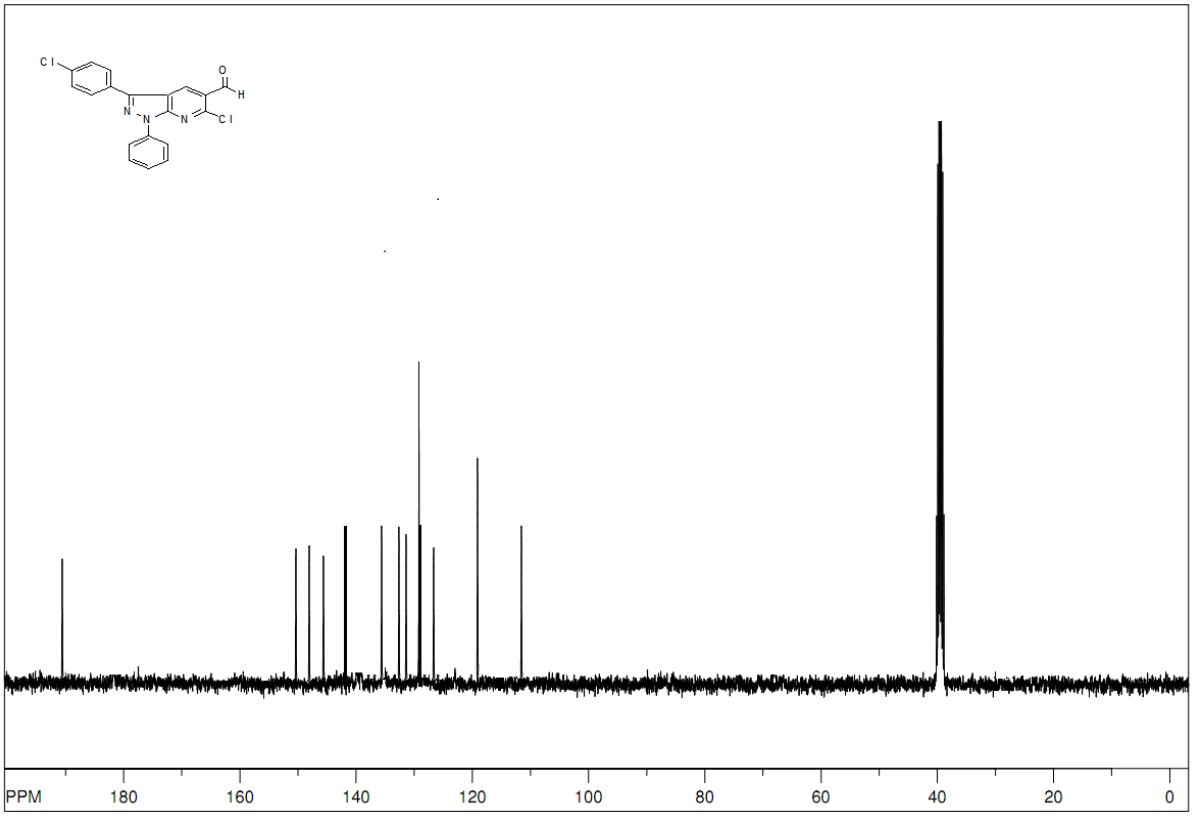

Fig. S1: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 1

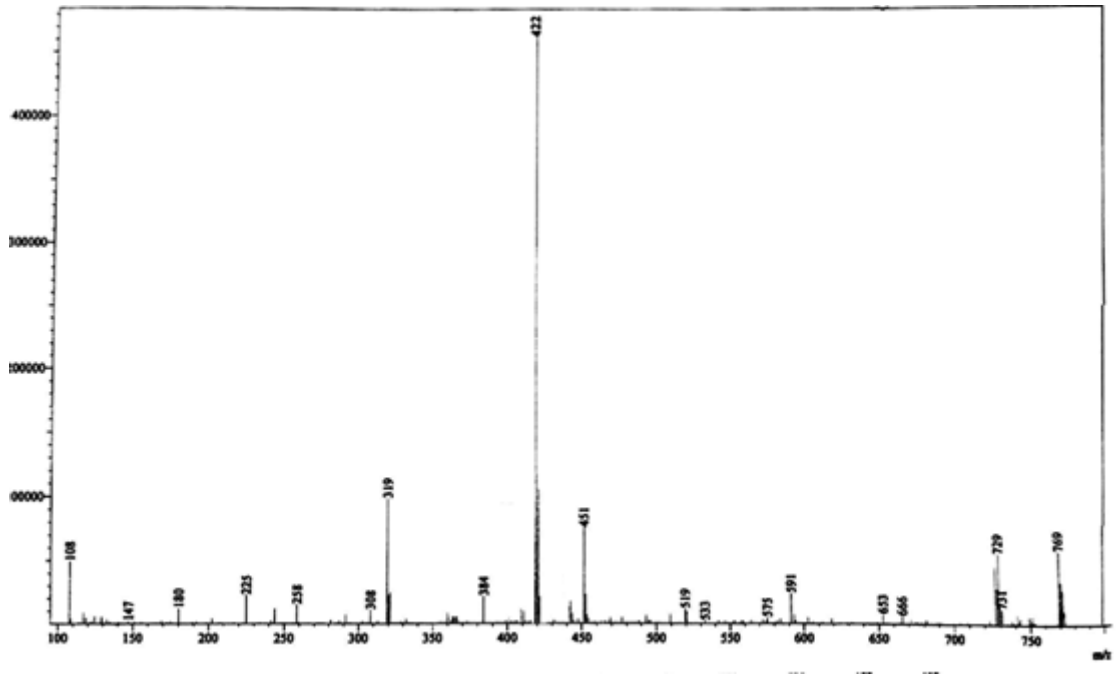

Fig. S2 : Mass Spectrum of N,N-Diphenyl-3-(4-chlorophenyl)-dipyrazolo (3,4-b)pyridine, 3

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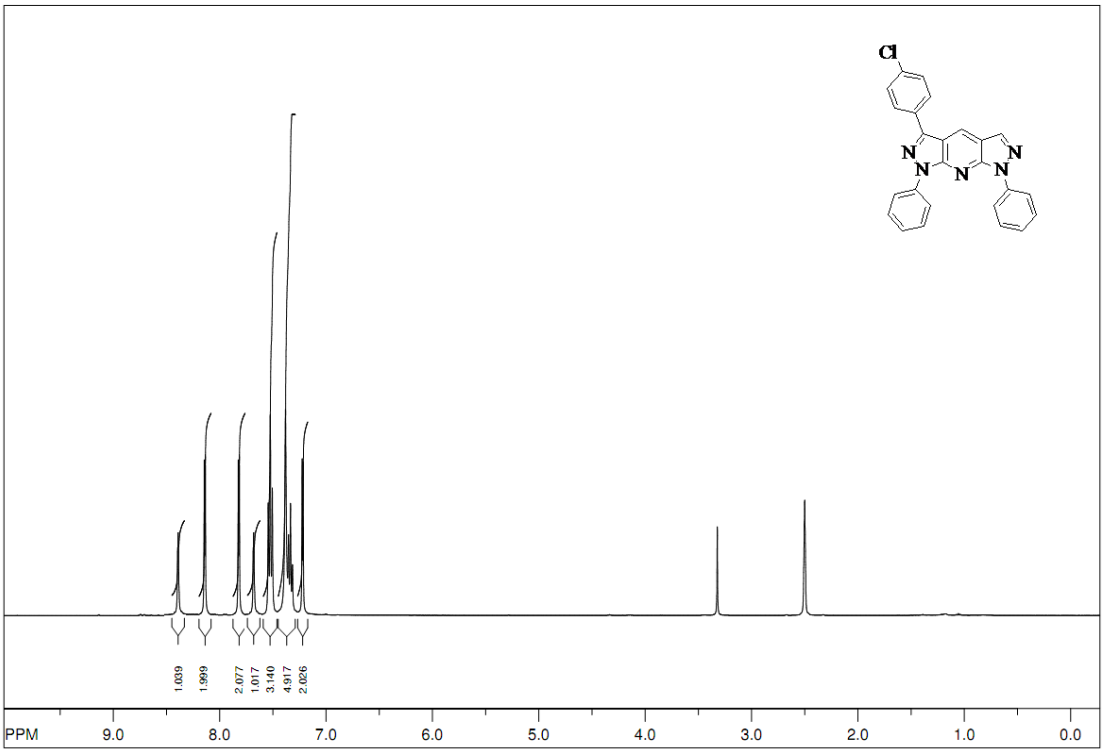

Fig. S3: ^{1}H NMR Spectrum of N,N-Diphenyl-3-(4-chlorophenyl)-dipyrazolo (3,4-b)pyridine, 3

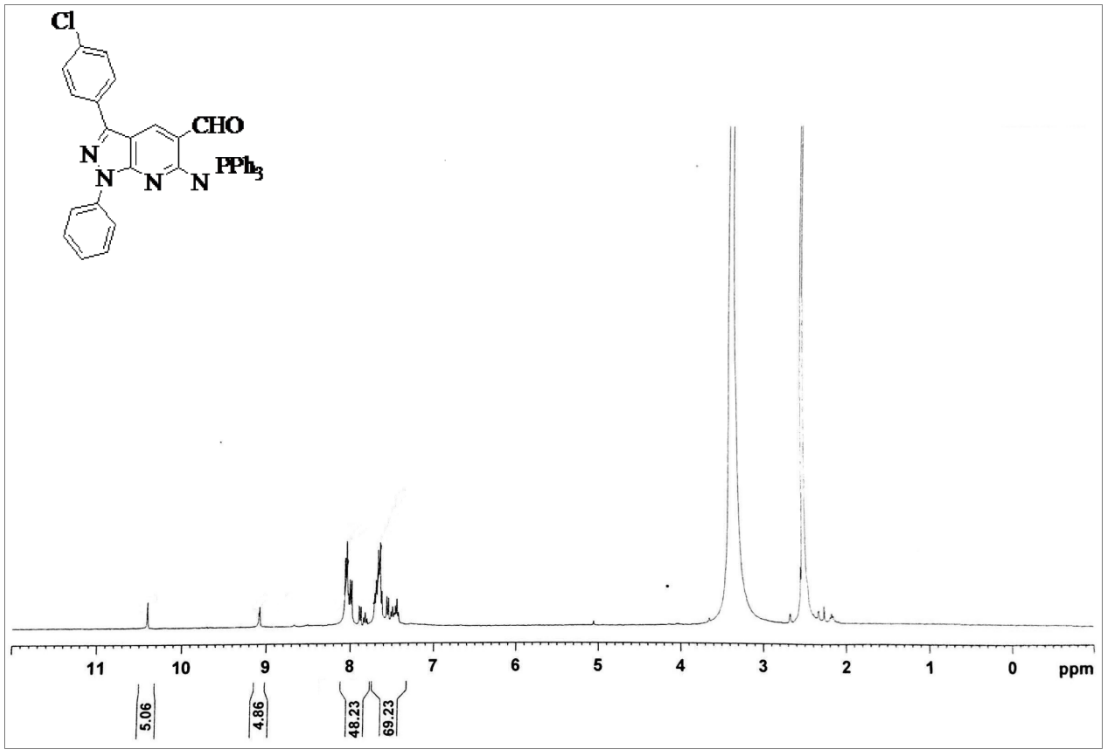

Fig. S4: ^{1}H NMR Spectrum Triphenylphosphoranylideniamino-pyrazole, 4

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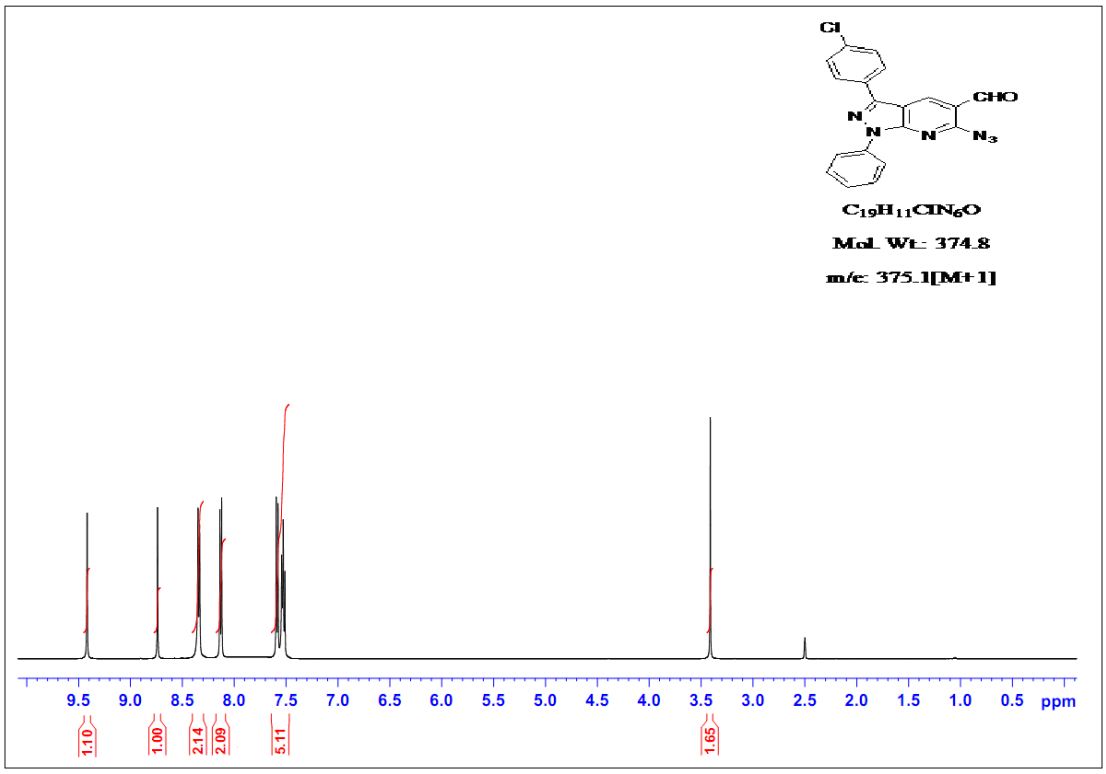

Fig. S5: ^{1}H NMR Spectrum 6-azido-3-(4-chlorophenyl)-1-phenyl-1H-pyrazolo[3,4-b]pyridine-5-carbaldehyde, 5

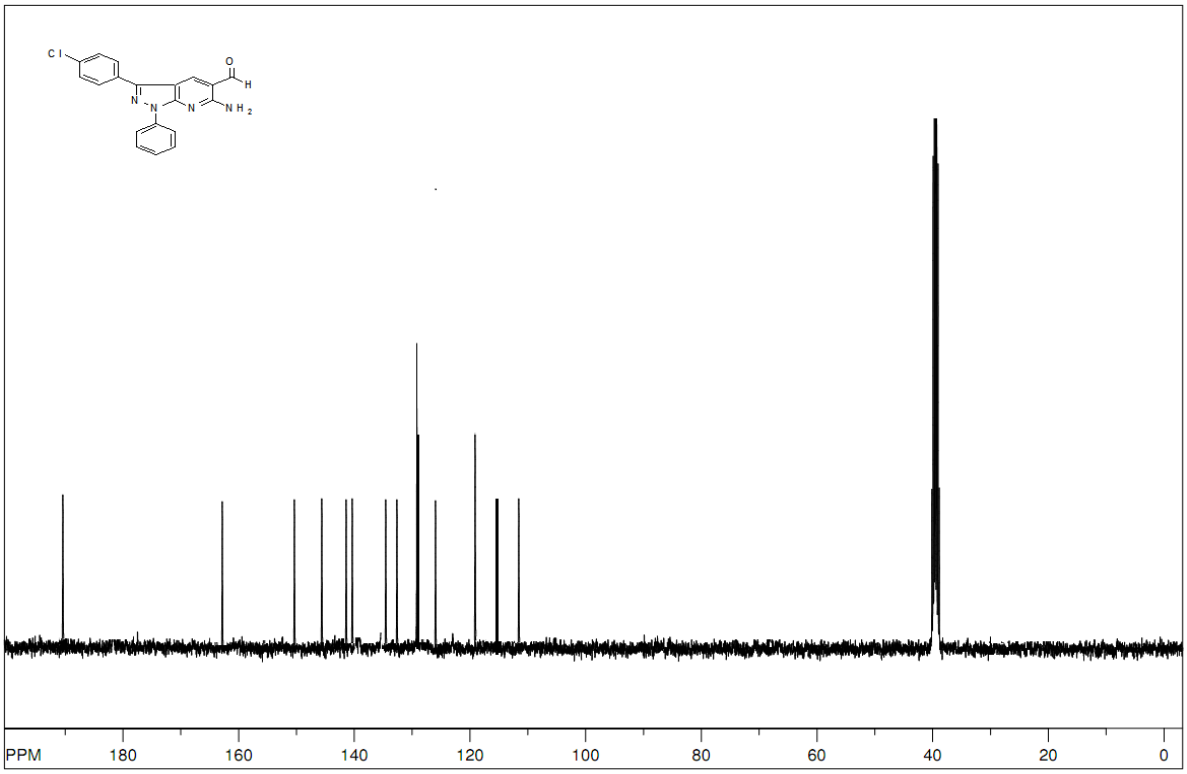

Fig. S6: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 4

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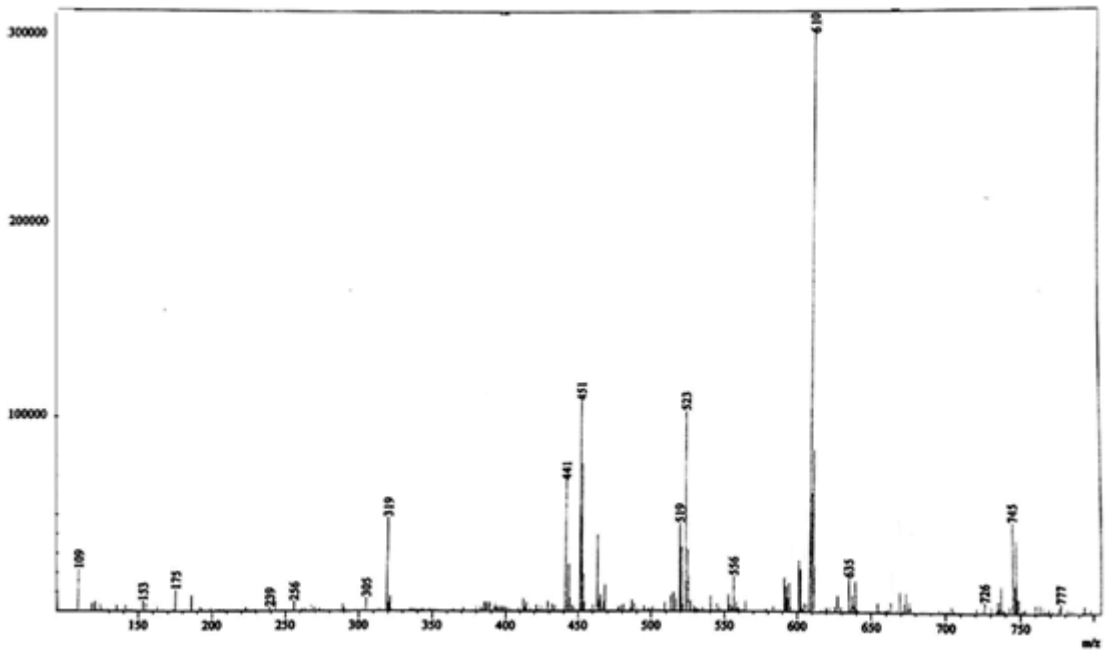

Fig. S7: Mass Spectrum Triphenylphosphoranylideniamino-pyrazole, 6

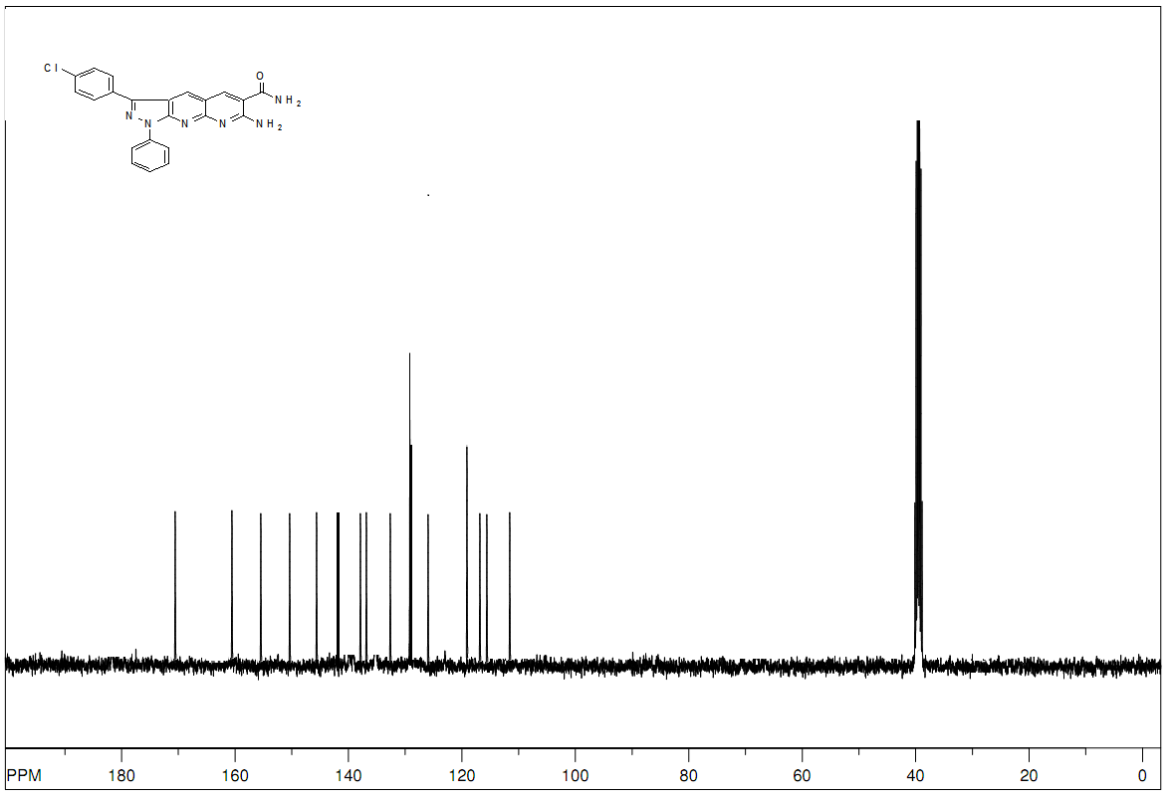

Fig. S8: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 8

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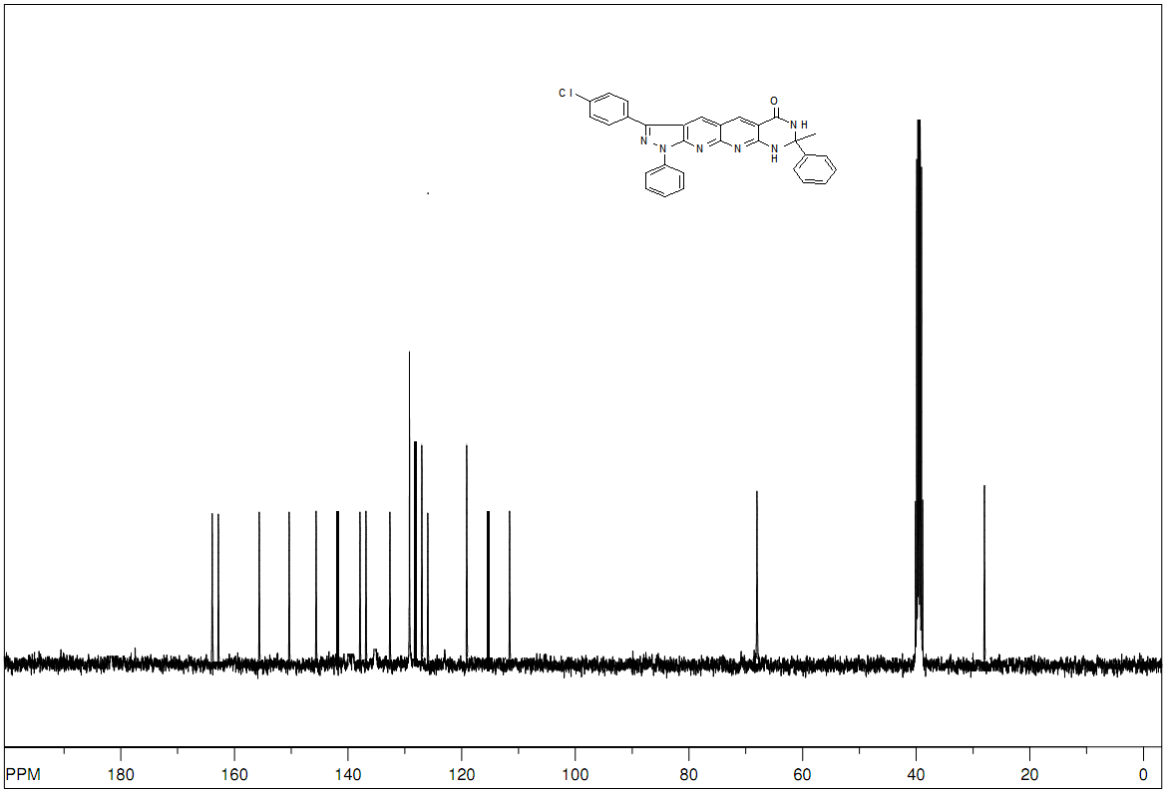
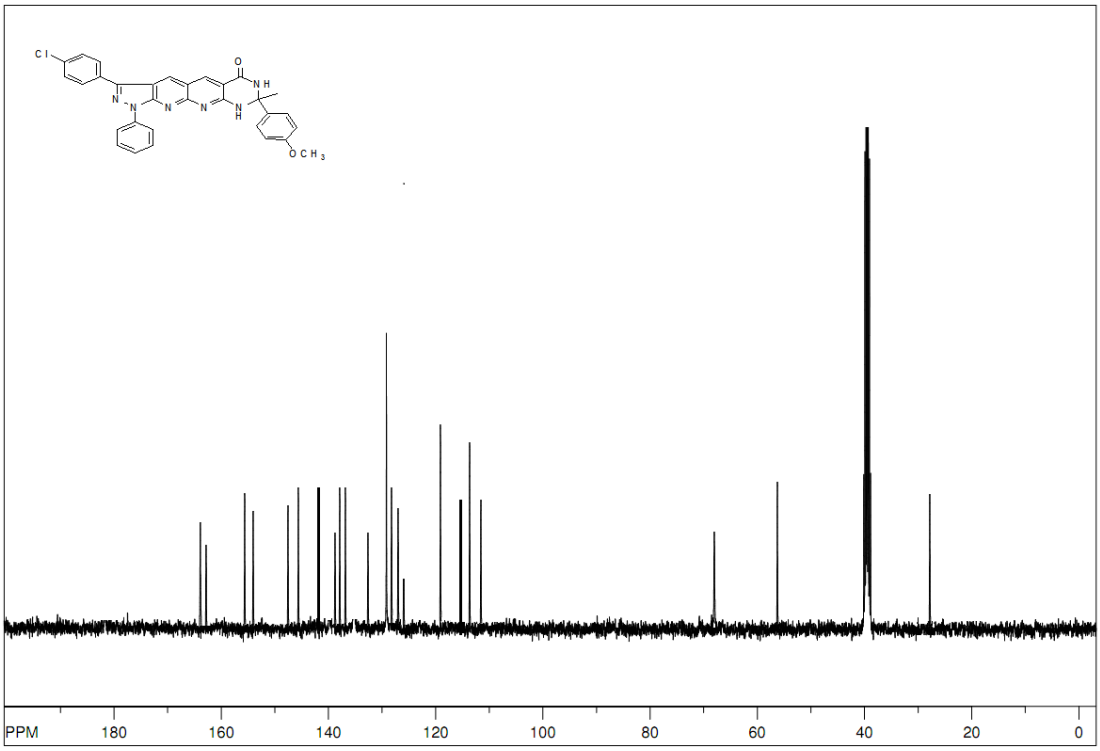


Fig. S9: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 9a



Fg. S10: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one, 9b

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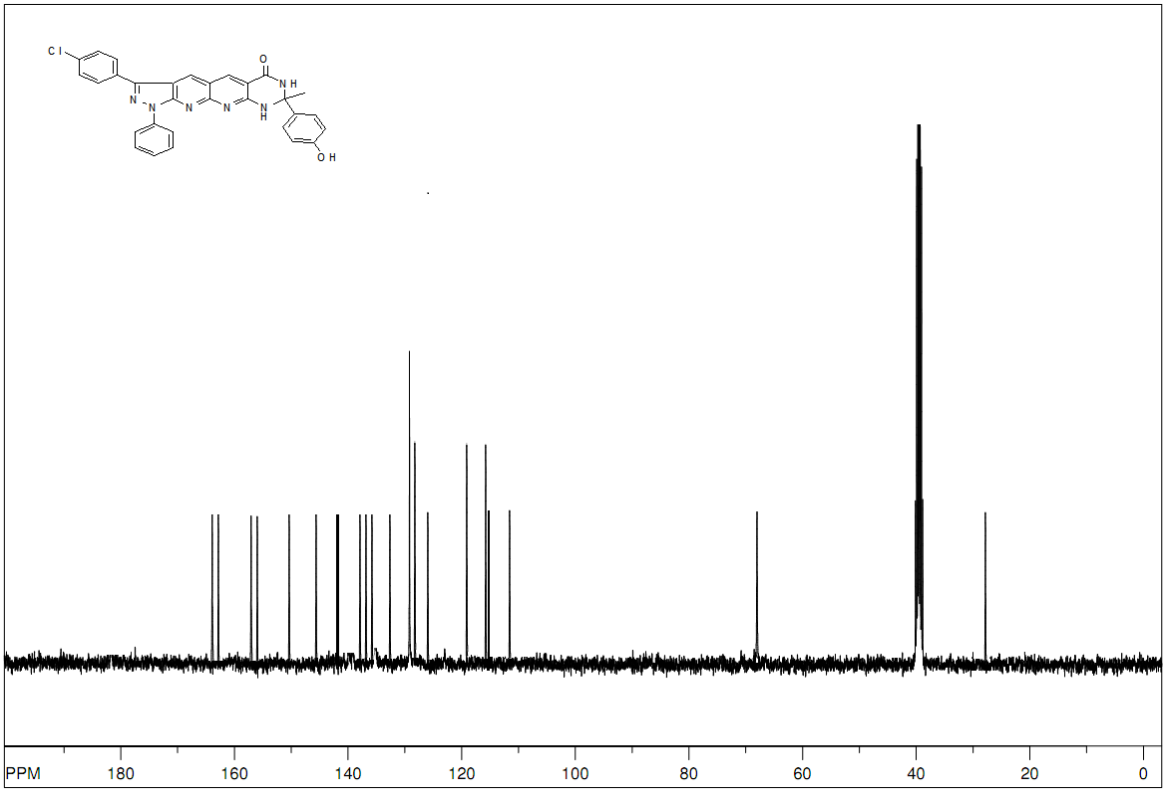

Fig. S11: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 9c

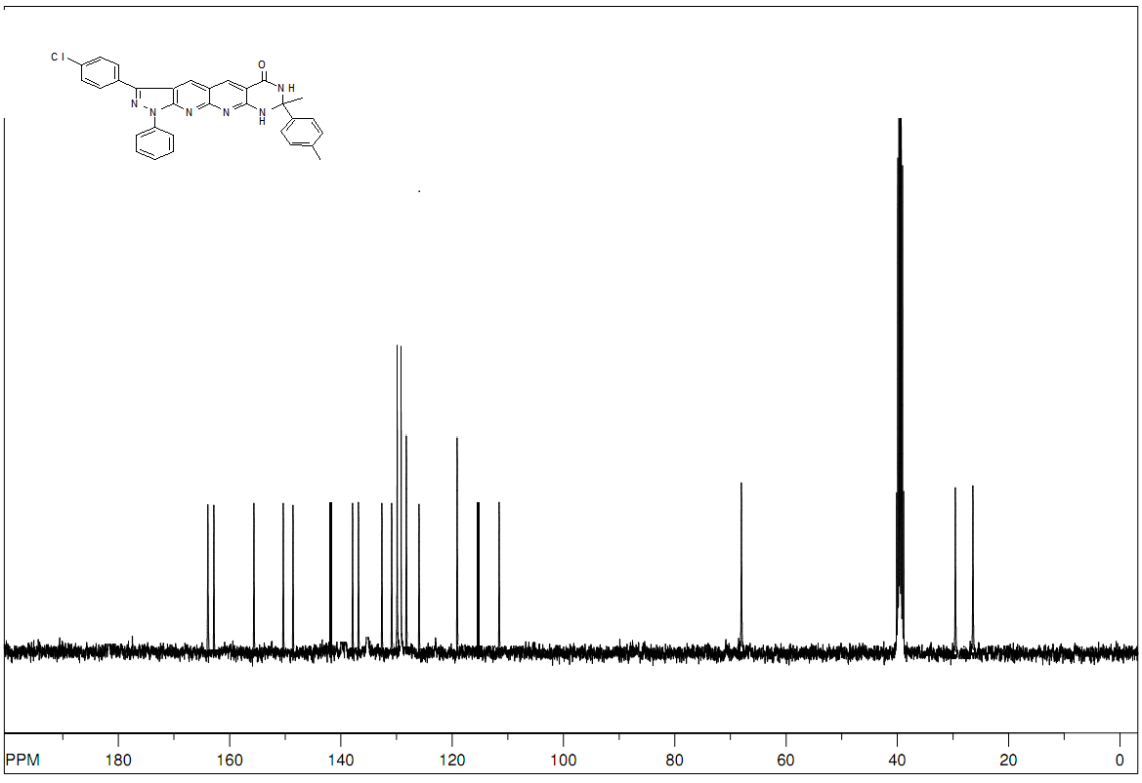

Fig. S12: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 9d

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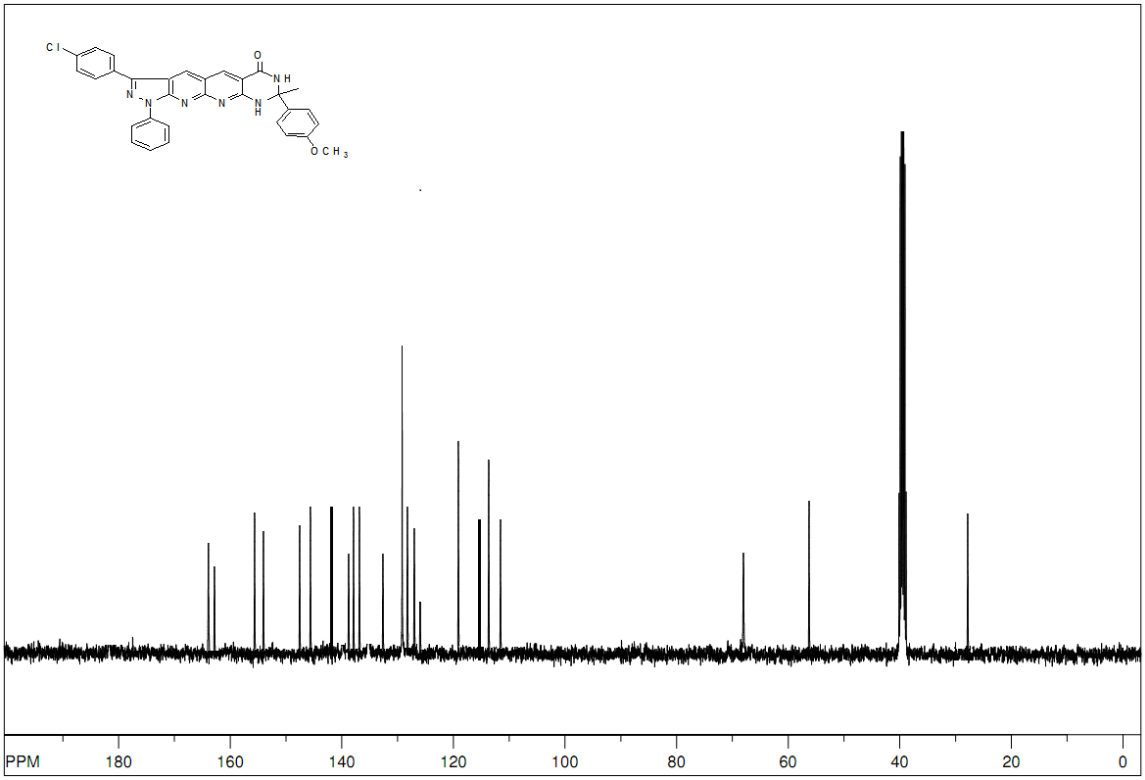

Fig. S13: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 9b

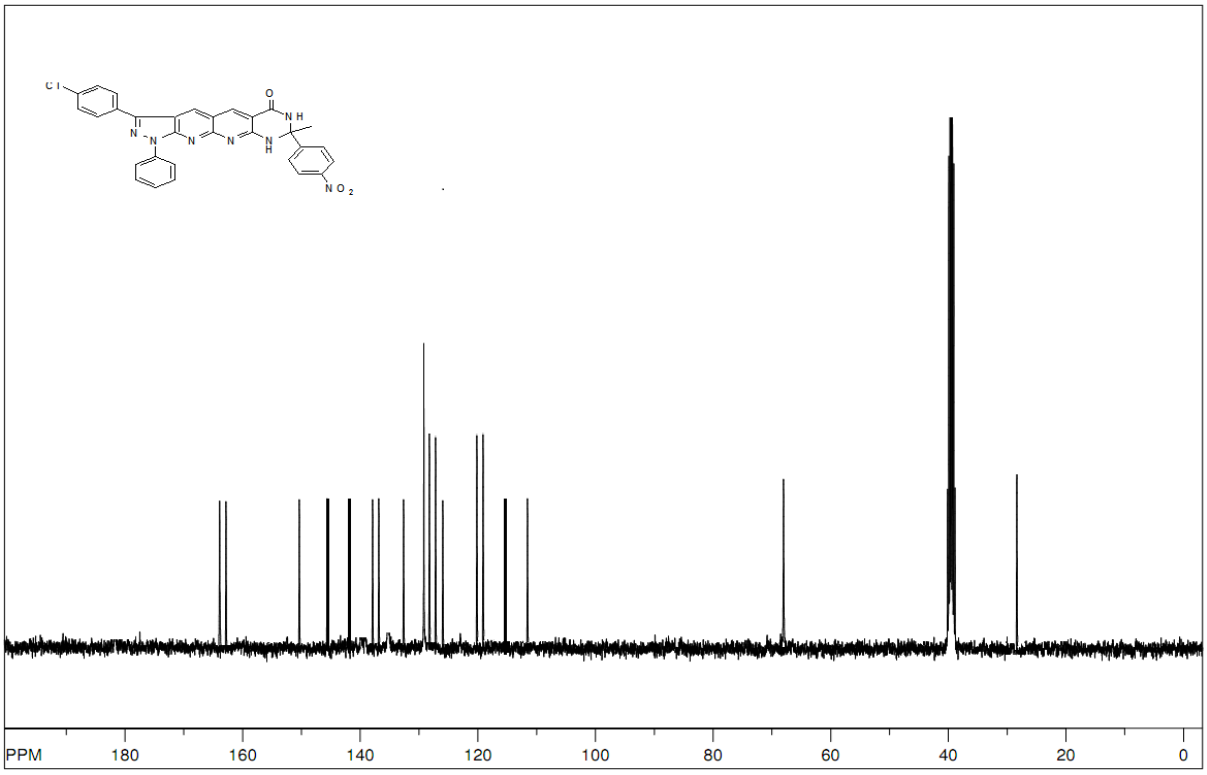

Fig. S14: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 9e

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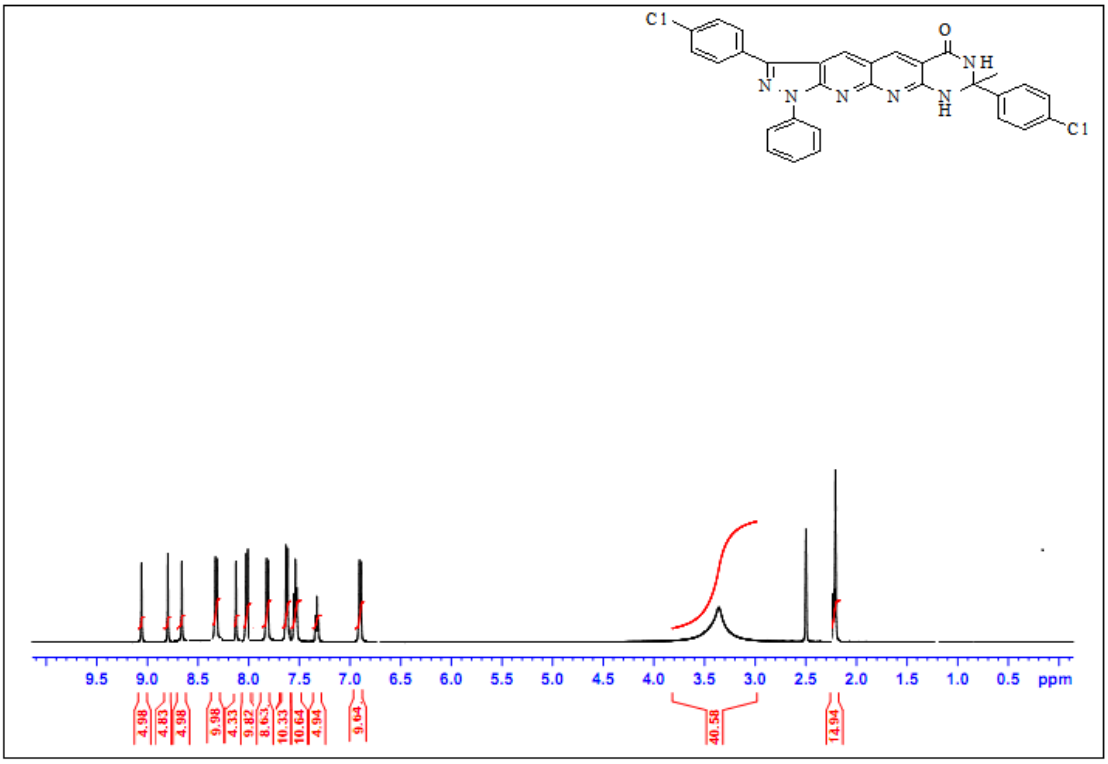

Fig. S15: ^{1}H NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 9f

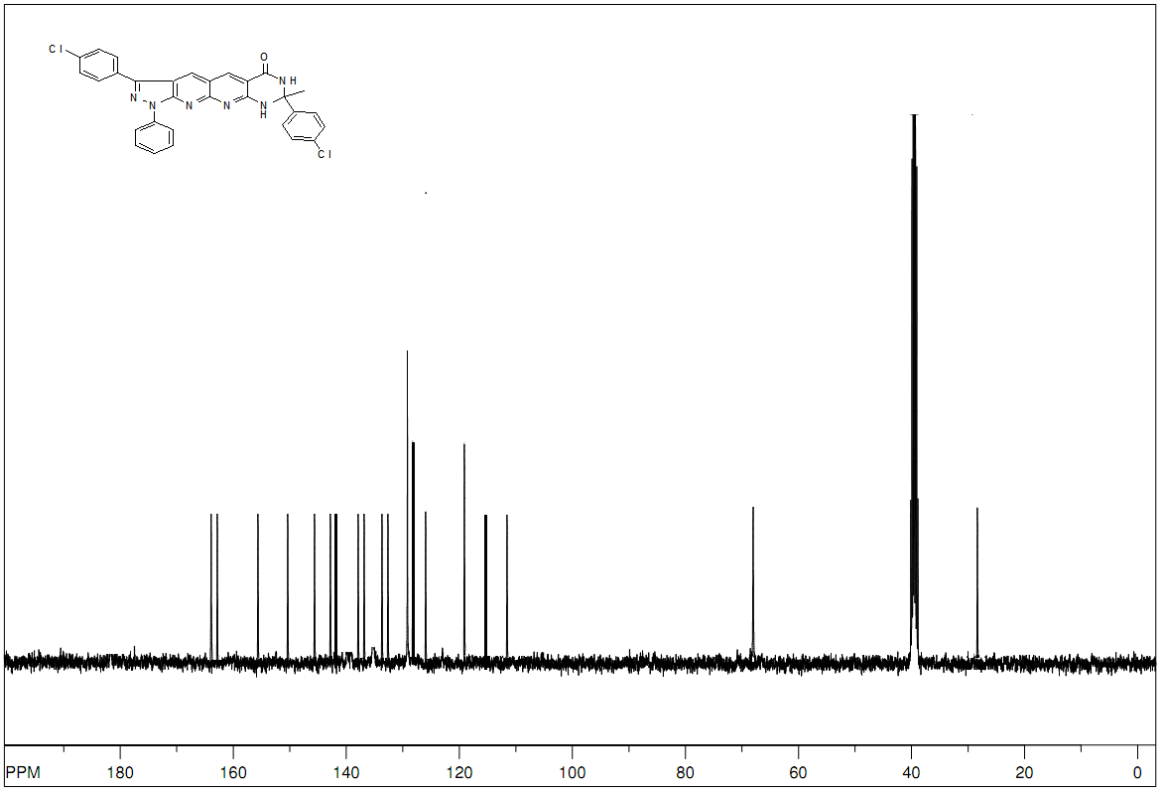

Fig. S16: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 9f

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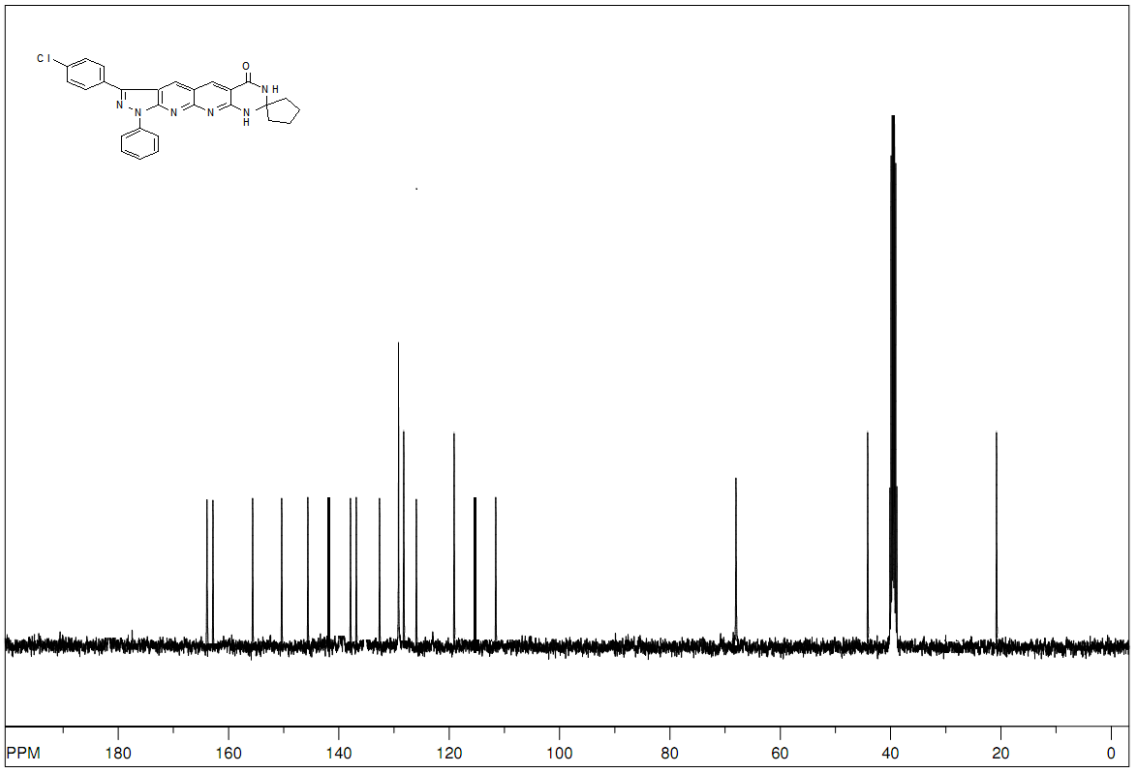

Fig. S17: ^{13}C NMR Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-8-methyl-6-chloro-1-phenyl-5H-pyrazolo[3,4-d]naphthyrido[2,3-d]pyrimidin-6(5H)-one 10a

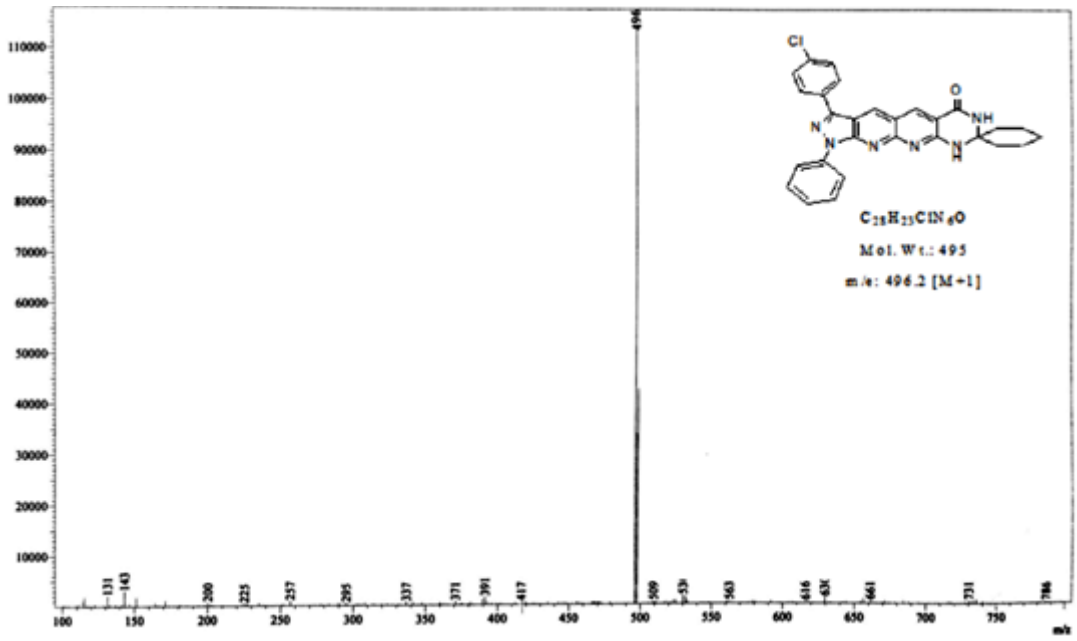

Fig. S18: Mass analysis Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-spiro[cyclohexanon-1-H-pyrazolo] naphthyrido[2,3-d]pyrimidin-6(5H)-one, 10b

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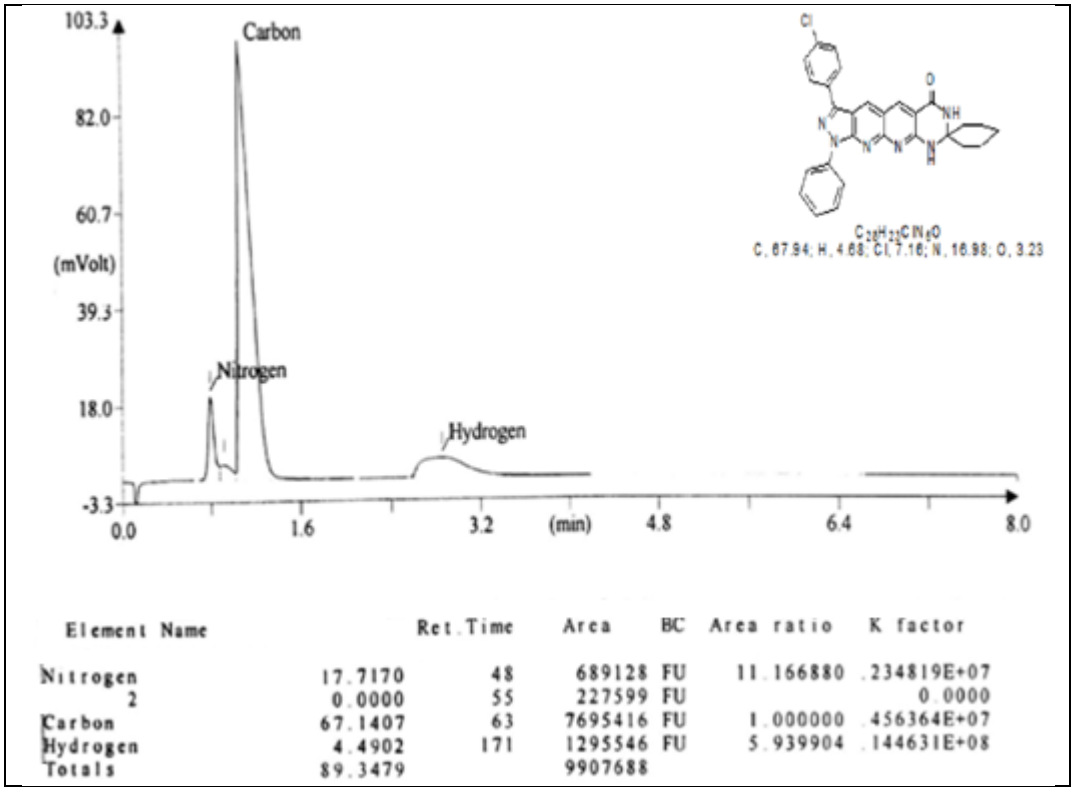

Fig. S19: Elemental analysis Spectrum of 3-(4-chlorophenyl)-7,9-dihydro-spiro[cyclohexanon-1-H-pyrazolo] naphthyrido[2,3-d]pyrimidin-6(5H)-one, 10b

Table-S1: Effect of the solvent on the yield of the product

Sr. No.	Solvent	Yield in %	Time in hours
1	1,2-Dichlorobenzene	48	8-9
2	Chlorobenzene	88	3-4
3	Bromobenzene	68	05
4	Toluene	63	07
5	Diphenyl ether	65	5-6

Table-S2. The Photophysical data for UV-Visible absorption and fluorescence emission and their quantum yields for compound 2 and 3.

Compound	Solvent	$\lambda_{abs.max.}$(nm)	$\lambda_{em.max.}$(nm)	Quantum yield (Φ_f)
2	n-Hexane	358	456	0.24
	Di-oxane	362	464	0.28
	THF	365	476	0.32
	DMF	375	502	0.42
	CH_3CN	368	490	0.37
	CH_3OH	366	486	0.36
3	n-Hexane	378	460	0.27
	Di-oxane	382	469	0.30
	THF	385	482	0.35
	DMF	398	513	0.43
	CH_3CN	388	502	0.40
	CH_3OH	384	498	0.38

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Table-S3.The Photophysical data for electronic absorption ($\lambda_{abs.\,max.}$), Fluorescence ($\lambda_{em.\,max.}$) and quantum yield (Φ_f)

Comp.	$\lambda_{abs.max.}$(nm)	$\lambda_{em.max.}$(nm)	Quantum yield(Φ_f)
9a	422.00	522.00	0.29
9b	**474.00**	**538.00**	**0.44**
9c	449.00	526.00	0.36
9d	449.00	525.00	0.31
9e	**413.00**	**516.00**	**0.21**
9f	415.00	517.00	0.24
9g	415.00	511.00	0.22
9h	411.00	519.00	0.25
10a	480.00	521.00	0.38
10b	474.00	519.00	0.32
10c	482.00	539.00	0.30

9a-h	a	B	c	d	E	f	g	h
R	-H	-OMe	-OH	$-CH_3$	$-NO_2$	-Cl	-F	-Br

10	Cyclic ketones
a	Cyclopentanone
b	Cyclohexanone
c	Indanone

Figure-S20: Fluorophore-solvent excited state interaction

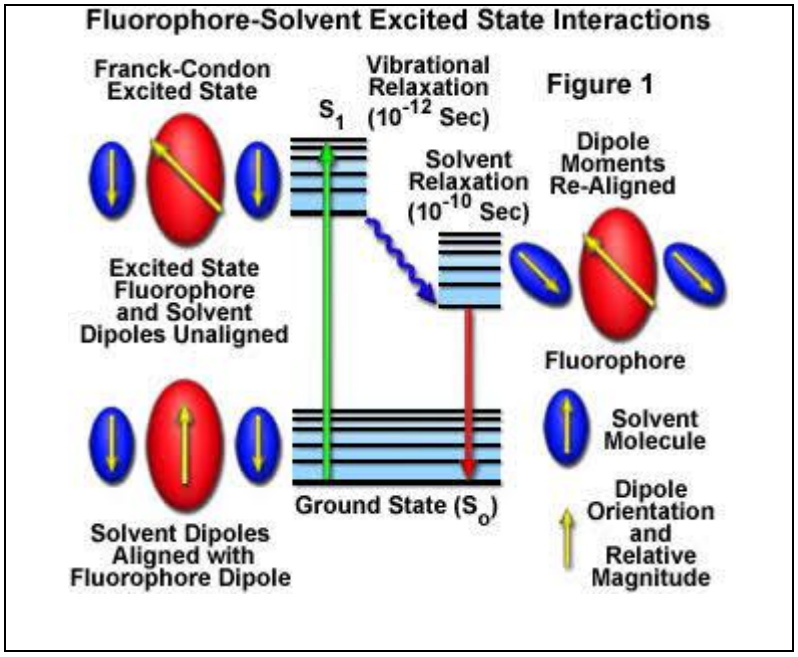

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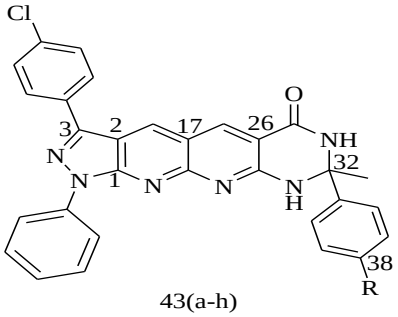
Fig. S21: Representative structure of compounds 9a-h



43(a-h)

Figure-S22 : Graph of emission intensity Vs absorption intensity, calculation of gradient and quantum yield for compound 9b

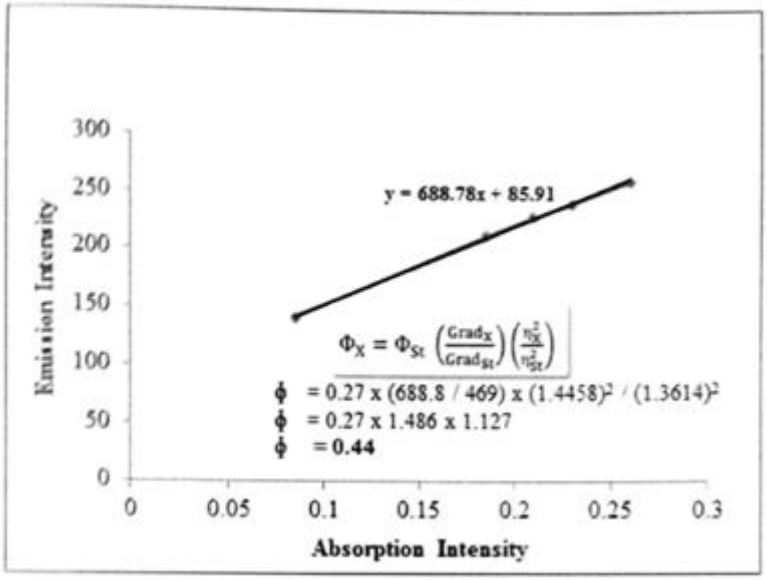
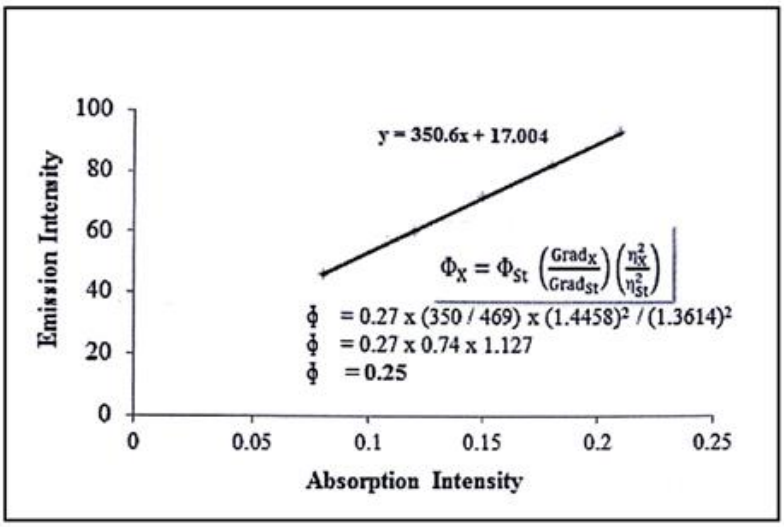


Figure-S23: Graph of emission intensity Vs absorption intensity, calculation of gradient and quantum yield for compound 9h



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