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SHORT COMMUNICATION

Synthesis and Study the Effect of Donor-Acceptor Substituent on Fluorescence Behavior of Thieno[3, 2-*c*]pyridine Derivatives

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Abstract 4-Hetero-1-yl-2-bromothieno[3,2-c]pyridines **3(a–d)** were synthesized by the reaction of 2-bromo-4-chlorothieno[3,2-c]pyridine **(1)** and cyclic amine **2(a–d)**, which on *Suzuki coupling* with substituted boronic acids **4(a–f)** exclusively converted to corresponding 4-hetero -1-yl-2-arylthieno*[3,2-c]* pyridine **5(a–x)** in good yields. The effect of donor-acceptor substituent on absorption emission properties and fluorescent quantum yield of new thienopyridine derivatives **5(a-x)** were studied.

Keywords Thieno[3, 2-*c*]pyridine · 4-Hetero-1-yl-2-bromothieno[3,2-c]pyridines · Fluorescence · HOMO- LUMO · Quantum yield

Introduction

Flurophores play important role in many applications such as in nonlinear optics [1], emitting devices [2], lasers [3], photovoltaic cells [4–11] etc. The interest in the fluorescent molecules has steadily increasing in last half century and today. The fluorescent dyes are playing central role in a modern life [12]. Organic fluorescent heterocyclic chromophores have a wide range of applications in biochemistry [13]. Fluorescent biomarkers and probes are extremely important in modern medicinal chemistry research; provide in-depth knowledge about biological system, which is important part in new drug discovery research. The design and synthesis of organic chromophores as non-linear optical (NLO) materials has got much attention in recent years and have great potential especially for use in optical communication, information processing, frequency doubling and integrated optics [14–17]. Also dye-sensitized solar cells (DSSCs) are one of the most promising alternative to crystalline Si-based photovoltaic's for converting clean, inexhaustible sunlight to electricity and have received significant research interest due to their low fabrication cost and relatively high power conversion efficiency (η).

In recent years emphasis was given on the synthesis and photo physical properties of thiophene and related heterocycles to find their applications in Nonlinear optics [18] and photovoltaic cells technology [19]. This felicitated us to synthesize and study the photo physical properties of novel thinopyridine compounds.

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Results and Discussion

Chemistry

The synthesis of 2-bromo-4-chlorothieno[3,2-c]pyridine **1** is reported in literature [20–23]. 4-Hetero-1-yl-2-bromothieno[3, 2-c]pyridines **3(a–d)** were synthesized by nucleophilic substitution of the cyclic amines **2(a–d)** on 2-bromo-4-chlorothieno[3,2-c] pyridine **1** in presence of K_2CO_3 at 90 °C using 1,4-dioxane and acetone (1:1) as solvent (Scheme 1).

The HCl librated during the reaction was quenched by K_2CO_3. After aqueous workup and column chromatography the desired product **3(a–d)** was obtained in 75–85 % yield were characterized by LCMS,^{1}H NMR, ^{13}C NMR.

Further compound **3(a–d)** on *Suzuki coupling with* substituted boronic acids **4(a–f)** were exclusively yield corresponding 4-hetero -1-yl-2-arylthieno*[3,2-c]* pyridines **5(a–x)** in 70–80 % yields (Scheme 2). The compounds **5(a–x)** were also characterized by LCMS,^{1}H-NMR, ^{13}C-NMR and elemental analysis.

Scheme 1 Synthesis of 4-Hetero-1-yl-2-bromothieno [3,2-c]pyridines 3(a-d)

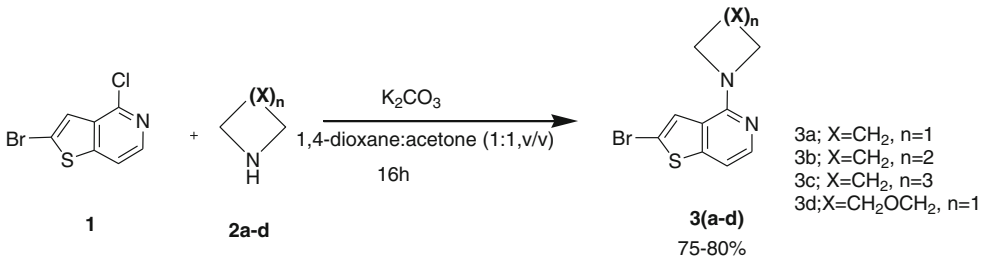


Photo Physical Properties

UV-visible and fluorescence spectra of compounds **5(a–x)** were recorded in DMF at 1.0×10^{-3} M concentration (Table 1). Fluorescence quantum yields of synthesized compounds were determined by standard literature procedure using quinine sulfate [24, 25] as reference standard (Table 1). It was observed that the compounds **5e, 5f, 5k, 5l, 5q,5r, 5w,5x** having electron withdrawing *p*-amido/*p*-nitro group on aromatic ring showed absorption λ_{max} 290–460 nm, while these compounds showed emission λ_{max} 421–577 nm and hence showed high quantum yields Φ_f, (Figs. 1, 2, 3, and 4) as well as high quantum yields compared to other compounds in the series. These results are in competence with semi empirical study. Also, it was observed that compounds **5k, 5l, 5q, 5r, 5w, 5x** having C_4-pyrolidine, piperidine, morpholine showed higher fluorescence emission and high quantum yields compared to C_4-azitidine in **5e, 5f** (Table 1).

Semi Empirical Study

To understand atomic contribution on the basis of frontier molecular orbital, we analyzed the three-dimensional contribution of HOMO and LUMO coefficient by MOPAC-2009 (Version 8.331) [26, 27] (Table 2). It was observed that in the series of compounds **5(a–x)**, having electron withdrawing group (−M effect) e.g. C_4-amido, nitro group of aromatic ring shows low electron hole GAP and these compounds fluoresces at longer wavelength with high quantum yield as compared C_4-electron donating group (+M effect) e.g. methoxy, hydroxy, fluro group in aromatic ring. This is because the electron withdrawing group at C_4- increases electron density and hence lower the electron hole GAP. The compounds **5e** and **5f**, **5k** and **5l**, **5q** and **5r**, **5w** and **5x** showes low GAP indicate higher overlapping of HOMO or LUMO orbital which shift emission to red shift and show high quantum yields. The high heat of formation and ionization potential showed high thermal stability, which indicate that these compounds are suitable candidates for photo electronic devices (Table 2).

Conclusion

The above study proves that,

1. The thienopyridines substituted with different electron donating and electron withdrawing groups in aryl and pyridine ring using S_NAr and Suzuli coupling recation.
2. The new thienopyridines shows considerable absorption (λ_{abs} max) and fluorescence emission (λ_f max) e.g. compounds **5e, 5f, 5k, 5l, 5q, 5r, 5w, 5x** shows maximum fluorescence emission.
3. The empirical calculations reveals that thienopyridines with low electron GAP e.g. compounds **5e,5f, 5k, 5l, 5q, 5r, 5w** and **5x** have high fluorescence emission with high quantum yields.

Experimental

General

Melting points were determined on a Gallenkamp Melting Point Apparatus Mod. MFB-595 in open capillary tube and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker XL 300 spectrometer (300 MHz). Chemical shifts were reported in parts per million using tetramethylsilane as an internal standard and were given in δ units. The solvent for NMR spectra was DMSO-d_6 unless otherwise stated. Infrared spectra were taken on Shimadzu FTIR instrument in potassium

Scheme 2 Synthetic route of 4-hetero-1-yl-2-arylthieno [3,2-c]pyridines 5(a-x)

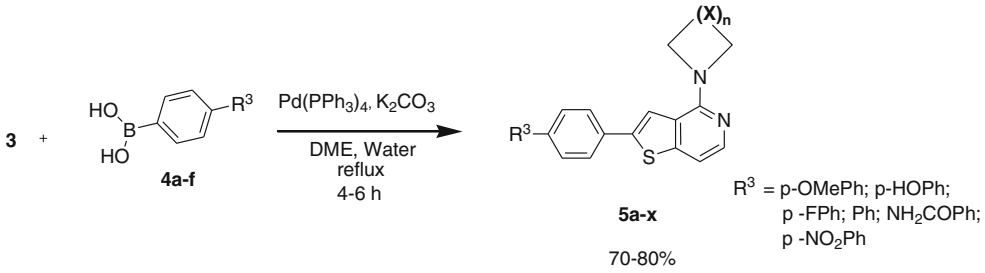
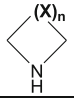
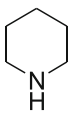
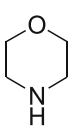


Table 1 The photo physical data for electronic Absorption (λ_{abs}) and Emission (λ_f) of Thieno[3, 2-*c*]pyridine **5(a–x)** in DMF as the solvent (ca. 10^{-3}) at room temp

Compd.		R^3	λ_{abs} nm	λ_f nm	Φ_f
5a	X=CH_2, n=1	*p*-OMePh	351	423	0.152
5b		*p* –HOPh	347	418	0.155
5c		*p* –FPh	362	436	0.142
5d	Azitidine	Ph	351	438	0.193
5e		*p*-NH_2COPh	366	483	0.357
5f		*p* -NO_2Ph	418	478	0.384
5g	X=CH_2, n=2	*p*-OMePh	359	440	0.154
5h		*p* -HOPh	358	496	0.194
5i	Pyrolidine	*p* -FPh	316	432	0.151
5j		Ph	350	435	0.204
5k		*p*-NH_2COPh	378	480	0.399
5l		*p* -NO_2Ph	333	506	0.417
5m	X=CH_2, n=3	*p*-OMePh	337	426	0.187
5n		*p* -HOPh	336	421	0.186
5o		*p* -FPh	337	436	0.148
5p		Ph	344	440	0.170
5q	Piperidine	*p*-NH_2COPh	353	481	0.393
5r		*p* -NO_2Ph	290	532	0.403
5s	X=CH_2OCH_2, n=1	*p*-OMePh	293	428	0.142
5t		*p* -HOPh	333	458	0.130
5u		*p* -FPh	286	456	0.131
5v		Ph	312	476	0.194
5w		*p*-NH_2COPh	346	577	0.395
5x	Morpholine	*p* -NO_2Ph	460	515	0.418

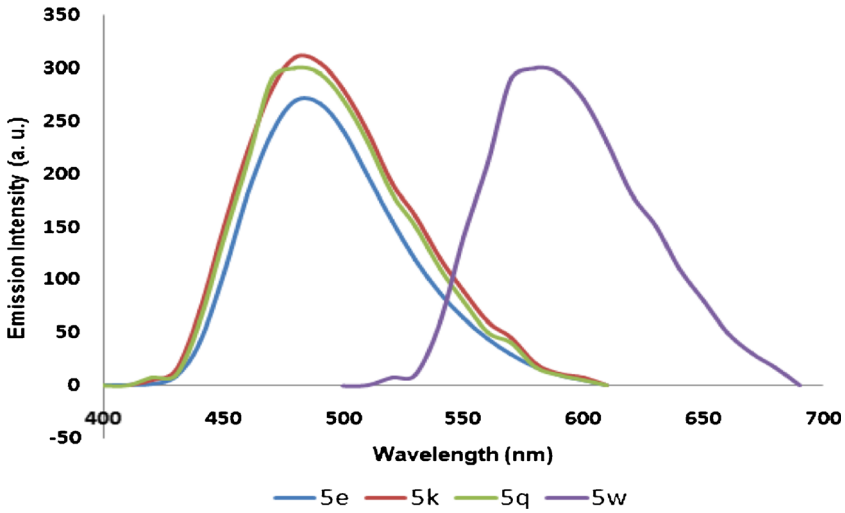


Fig. 1 Fluorescence spectra of compounds **5e, 5k, 5q, 5w**

bromide pellets unless otherwise stated. UV spectra were recorded on a Shimadzu UV-1601 UV–vis Spectrometer. Compounds for UV scan were dissolved in DMSO. Fluorescence spectra were recorded using RF-5301 PC Spectrofluorophotometer. Compounds for fluorescence measurement were dissolved in DMF. All UV and fluorescence spectra were recorded from 200 to 600 nm. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel $60F_{254}$ (Merk) plates using UV light (254 and 366 nm) for detection. Common reagent grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

General Procedure for Synthesis of 4-hetero-1-yl-2-bromo Thieno [3, 2-C] pyridine 3(a-d)

In a 250 mL reaction flask containing 2-bromo-4-chlorothieno[3,2-c]pyridine **1** (10 mmol, 2.48 g), amine **2(a–d)** (20 mmol), K_2CO_3 (25 mmol, 3.45 g), in 1,4-dioxane and acetone (80 ml: 80 ml) was heated at 90 °C for 16 h, (TLC check, 35 % ethyl acetate/hexane). The solvent was removed under vacuum; the residue was added in water (100 ml) and stirred. The product was extracted with ethyl acetate (3×12 ml) and the organic layer was dried over anhydrous sodium sulfate and concentrated under vacuum. The crude product was purified by flash column chromatography eluting with ethyl acetate/hexane with yields 75–85 %.

4-Azetidin-1-yl-2-bromo-thieno[3,2-c]pyridine (3a)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 114 °C; yield 2.01 g, 75 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.80(d, J=5.7 Hz, 1H,C_6H), 7.48(s, 1H, C_3H), 7.14(d, J=5.7 Hz, 1H, C_7H), 4.17 & 4.20(t, J=7.6 Hz, 4H, 2xCH_2), 2.25–2.40(m, 2H, CH_2). ^{13}C NMR (300 MHz,

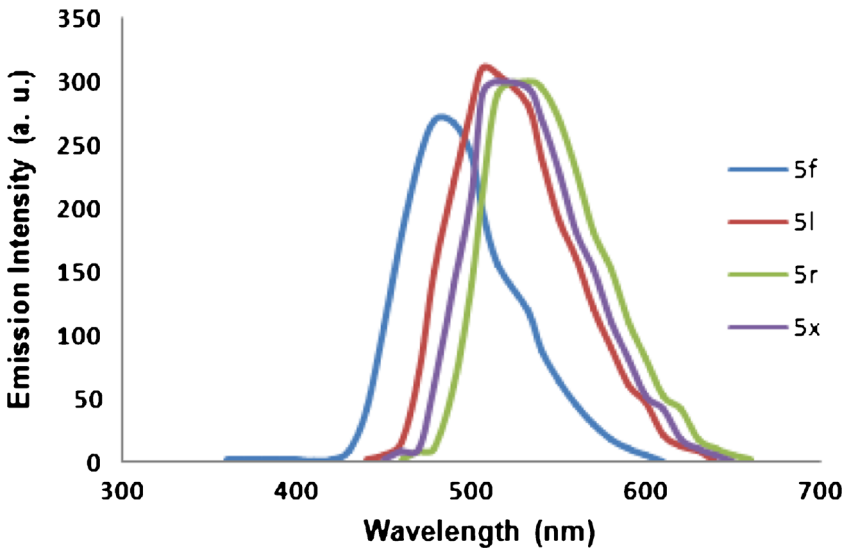


Fig. 2 Fluorescence spectra of compounds **5f, 5l, 5r, 5x**

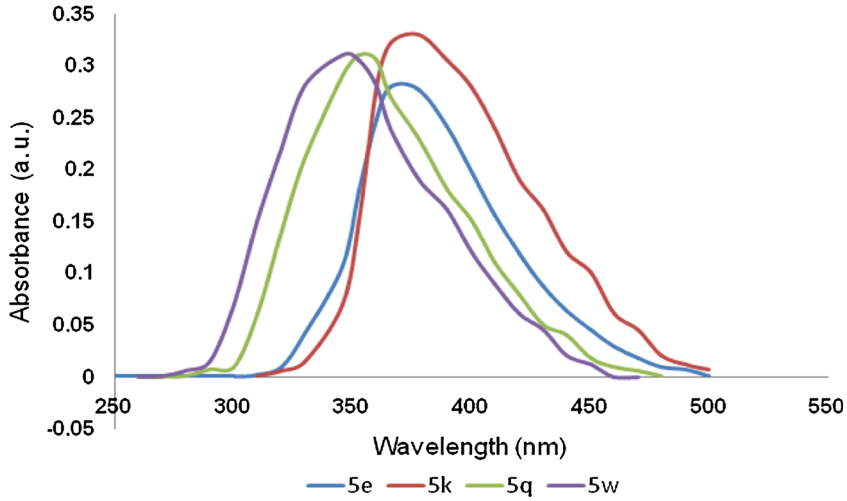


Fig. 3 Absorption spectra of compounds **5e, 5k, 5q, 5w**

DMSO-d_6) δ 16.85, 52.63, 106.96, 111.83, 121.32, 124.72, 142.19, 149.86, 154.85. MS; m/z : 269.16, 271.16 (M^{+1}).

2-Bromo-4-pyrrolidin-1-yl-thieno[3,2-c]pyridine (3b)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 74 °C; yield 2.40 g, 85 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87(d J=5.7 Hz, 1H, C_6H), 7.79(s, 1H, C_3H), 7.11(d J=5.7 Hz, 1H, C_7H), 3.63–3.73(m, 4H, 2xCH_2), 1.90–2.00(m, 4H, 2xCH_2). ^{13}C NMR (300 MHz, DMSO- d_6) δ 24.39, 52.06, 105.03, 111.78, 122.80, 125.06, 141.26, 149.09, 156.91. MS; m/z :283.19, 285.19 (M^{+1}).

2-Bromo-4-piperidin-1-yl-thieno[3,2-c]pyridine (3c)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 68 °C; yield 2.32 g, 78 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.99(d J=5.7 Hz., 1H, C_6H), 7.56(s, 1H, C_3H), 7.41(d J=5.7 Hz, 1H, C_7H), 3.30–3.41(m, 4H, 2xCH_2), 1.56–1.71(m, 6H, 3xCH_2). ^{13}C NMR (300 MHz, DMSO- d_6) δ 24.68, 25.94, 50.74, 110.09, 113.24, 125.63, 125.64, 141.80, 149.86, 156.85. MS; m/z :297.22, 299.22 (M^{+1}).

2-Bromo-4-morpholin-4-yl-thieno[3,2-c]pyridine (3d)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 88 °C; yield 2.39 g,80 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.02(d J=5.7 Hz, 1H, C_6H), 7.74(s, 1H, C_3H), 7.49(d J=5.7 Hz., 1H, C_7H), 3.72–3.82(m, 4H, 2xCH_2), 3.28–3.44(m, 4H, 2xCH_2). ^{13}C NMR (300 MHz, DMSO-d_6) δ 50.10, 66.61, 110.86, 113.80, 125.61, 141.68, 150.09, 156.19. MS; m/z : 299.19, 301.19(M^{+1}).

General Procedure for Suzuki Reaction: Synthesis of 4-hetero -1-yl-2arylthieno [3,2-c]pyridine 5(a–x)

In a 50 ml reaction flask containing compound **3a** (1 mmol, 250 mg), boronic acid **4a** (1.5 mmol),

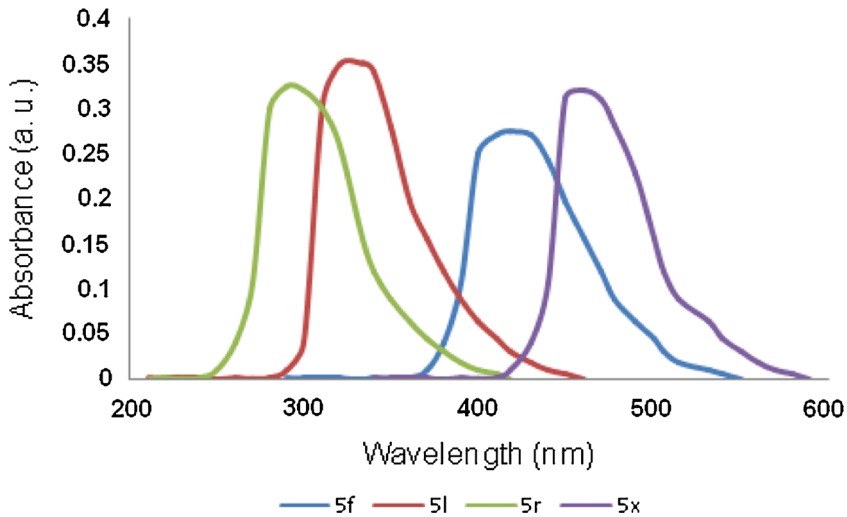


Fig. 4 Absorption spectra of compounds **5f, 5l, 5r, 5x**

Table 2 The molecular electronic properties (Ionization Potential, HOMO-LUMO energy, Gap) of thieno[3, 2-*c*]pyridine **5(a–x)**

Comp.	Heat of Formation (K CAL.)	Ionization Potential (eV)	HOMO (eV)	LUMO (eV)	GAP (eV)
5a	44.458	8.285	−8.285	−0.550	7.735
5b	41.395	8.252	−8.252	−0.819	7.433
5c	37.454	8.461	−8.461	−0.779	7.682
5d	85.530	8.366	−8.366	−0.675	7.691
5e	43.070	8.516	−8.316	−0.964	7.352
5f	80.711	8.712	−8.712	−1.715	6.997
5g	26.602	8.133	−8.133	−0.482	7.651
5h	22.331	8.177	−8.177	−0.486	7.691
5i	19.368	8.278	−8.278	−0.623	7.655
5j	67.827	8.140	−8.140	−0.614	7.526
5k	25.804	8.177	−8.179	−1.014	7.165
5l	62.381	8.360	−8.360	−1.594	6.766
5m	25.186	7.828	−7.828	−0.549	7.279
5n	18.817	8.213	−8.213	−0.597	7.616
5o	15.872	8.310	−8.310	−0.720	7.590
5p	63.846	8.226	−8.227	−0.584	7.643
5q	21.313	8.360	−8.360	−0.927	7.433
5r	58.216	8.546	−8.546	−1.566	6.980
5s	−5.466	8.459	−8.459	−0.632	7.827
5t	−9.480	8.518	−8.518	−0.688	7.830
5u	−12.308	8.610	−8.610	−0.886	7.724
5v	35.697	8.519	−8.519	−0.785	7.734
5w	−6.880	8.658	−8.658	−1.028	7.630
5x	30.576	8.850	−8.850	−1.687	7.163

GAP = *E*LUMO-*E*HOMO

K_2CO_3 (3 mmol, 415 mg), tetrakistriphenylphosphine palladium (0) (60 mg, 5 mol%) was taken in dimethoxy ethane and H_2O (each 10 ml). The reaction mixture was heated at 90 °C for 4–6 h (TLC check give solvent system). The reaction mixture after cooling to room temperature was added in 20 ml water, stirred and the product was extracted with ethyl acetate (3× 15). The organic layer was dried over anhydrous sodium sulphate and concentrated under vacuum. The crude product obtained was purified by flash column chromatography eluting with ethyl acetate/hexane with yields 65–80 %.

4-Azetidin-1-yl-2-(4-methoxy -phenyl)-thieno[3,2-c] pyridine(5a)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 138 °C; yield 201.5 mg, 68 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.86(d, J=5.7 Hz, 1H, C_6H), 7.54–7.73(m, 3H, ArH), 7.21(d, J=5.7 Hz., 1H, C_7H), 7.02(d, J=8.7 Hz., 2H, ArH), 4.29(t, J=7.6 Hz., 4H, 2xCH_2), 3.80(s,3H, OMe), 2.32–2.40(m, 2H, CH_2). MS; m/z : 297.30 (M^{+1}).

4-(4-Azetidin-1-yl-thieno[3,2-c]pyridine-2-yl)phenol (5b)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 242 °C; yield 183.5 mg, 65 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.87(s,1H, OH),7.82(d, J= 5.7 Hz,1H, C_6H) 7.51–7.64(m, 3H, ArH), 7.18(d, J= 5.7 Hz., 1H, C_7H), 6.83(d, J=8.7 Hz., 2H, ArH), 4.29(t, J=7.6 Hz, 4H, 2xCH_2), 2.45–2.50(m, 2H, CH_2).MS; m/z : 283.33 (M^{+1}).

4-Azetidin-1-yl-2-(4-Fluoro -phenyl)-thieno[3,2-c]pyridine (5c)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 120 °C; yield 199 mg, 70 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.57–7.90(m, 4H, ArH), 7.17–7.34(m, 3H, ArH), 4.30(t, J=7.4 Hz,4H, 2xCH_2), 2.32–2.37(m, 2H, CH_2). MS; m/z : 285.33 (M^{+1}).

4-Azetidin-1-yl-2-phenyl-thieno[3,2-c]pyridine (5d)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 148 °C; yield 210 mg, 79 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.01(s, 1H, ArH),7.89(d, J=5.7 Hz, 1H, C_6H)

7.62–7.80(m, 2H, ArH), 7.18–7.49(m, 4H, ArH), 4.31(t, J= 7.4 Hz, 4H, 2xCH_2), 2.30–2.45(m, 2H, CH_2). MS; m/z : 267.35 (M^{+1}).

4-(4-Azetidin-1-yl-thieno[3,2-c]pyridine-2-yl)benzamide (5e)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 218 °C; yield 201 mg, 65 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.31(s, 1H,NH), 8.05(s, 1H,NH), 7.84–8.00(m, 5H, ArH), 7.45(s, 1H, C_3H), 7.25(d, J=5.7 Hz, 1H, C_7H), 4.32(t, J=7.6 Hz, 4H, 2xCH_2), 2.30–2.40(m, 2H, CH_2). MS; m/z : 310.31 (M^{+1}).

4-Azetidin-1-yl-2-(4-Nitro -phenyl)-thieno[3,2-c]pyridine (5f)

Recrystallized from dichloromethane/hexane (7:3), red colour needles; mp 208 °C; yield 208 mg, 67 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.27(d, J=8.7 Hz, 2H, ArH), 8.06(d, J=8.7 Hz, 2H,ArH), 8.04(s, 1H, C_3H), 7.96(d, J=5.7 Hz, 1H, C_6H), 7.27(d, J=5.7 Hz, 1H, C_7H), 4.34(t, J=7.6 Hz, 4H, 2xCH_2), 2.39(m, 2H,CH_2). MS; m/z : 312.34 (M^{+1}).

2-(4-Methoxy -phenyl)-4-pyrrolidin-1-yl-thieno[3,2-c]pyridine (5g)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 108 °C; yield 248 mg, 80 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.80–7.90(m, 2H,ArH), 7.70(d, J=8.7 Hz, 2H,ArH), 7.12(d, J=5.3 Hz, 1H, C_7H), 7.00(m, 2H, ArH), 3.70–3.80(m, 7H, OMe & 2xCH_2), 1.90–1.99(m, 4H, 2xCH_2). MS; m/z : 311.33 (M^{+1}).

4-(4-pyrrolidin-1-yl-thieno[3,2-c]pyridine-2-yl)phenol (5h)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 222 °C; yield 183 mg, 68 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.80–7.86(m, 2H, C_7H & C_3H), 7.58(d, J=8.7 Hz, 2H, ArH), 7.12(d, J= 5.3 Hz, 1H, C_6H), 6.82(d, J=8.7 Hz, 2H, ArH), 3.70–3.80(m, 4H, 2xCH_2), 1.90–1.98(m, 4H, 2xCH_2). MS; m/z : 297.33 (M^{+1}).

2-(4-Fluoro -phenyl)-4-pyrrolidin-1-yl-thieno[3,2-c]pyridine (5i)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 124 °C; yield 232 mg, 78 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.98(s, 1H, ArH), 7.78–7.89(m, 3H, ArH) 7.25–7.34(m, 2H, ArH), 7.11(d, J= 5.3 Hz, 1H, C_7H), 3.72–3.82(m, 4H, 2xCH_2), 1.90–2.00(m, 4H, 2xCH_2). MS; m/z : 299.33 (M^{+1}).

2-Phenyl-4-pyrrolidin-1-yl-thieno[3,2-c]pyridine (5j)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 127 °C; yield 224 mg, 80 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ δ 7.99(d, J=5.7 Hz, 1H, C_6H), 7.70–7.84(m, 3H, ArH), 7.36–7.51(m, 4H, ArH), 3.70–3.83(m, 4H, 2xCH_2), 1.89–2.13(m, 4H, 2xCH_2). MS; m/z : 281.08 (M^{+1}).

4-(4-Pyrrolidin-1-yl-thieno[3,2-c]pyridine-2-yl)benzamide (5k)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 255 °C; yield 223 mg, 69 %;^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15(s, 1H, NH), 8.05(s, 1H, C_3H), 7.80–8.00 (m, 5H, ArH), 7.42(bs, 1H, NH), 7.17(d, J=5.7 Hz., 1H, C_7H) 3.74–3.84(m, 4H, 2xCH_2), 1.88–2.08(m, 4H, 2xCH_2). MS; m/z : 324.25 (M^{+1}).

2-(4-Nitro -phenyl)-4-pyrrolidin-1-yl-thieno[3,2-c]pyridine (5l)

Recrystallized from dichloromethane/hexane (7:3), red colour needles; mp 232 °C; yield 250 mg,79 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.30(d, J=8.7 Hz, 2H,ArH), 8.10(d, J=8.7 Hz, 2H, ArH), 7.93(d, J=5.7 Hz 1H, C_6H), 7.21(d, J=5.7 Hz, 1H, C_7H), 3.77–3.84(m, 4H, 2xCH_2), 1.93–2.03(m, 4H, 2xCH_2). MS; m/z : 326.20 (M^{+1}).

2-(4-Methoxy -phenyl)-4-Piperidin-1-yl-thieno[3,2-c]pyridine (5m)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 98 °C; yield 250 mg, 77 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.96(d, J=5.7 Hz, 1H, C_6H), 7.71–7.77(m, 2H, ArH), 7.59(s, 1H, C_3H), 7.42(d, J= 5.7 Hz, 1H, C_7H), 7.03(d, J=8.7 Hz, 2H, ArH), 3.80(s, 3H, OMe), 3.38–3.47(m, 4H, 2xCH_2), 1.58–1.75(m, 6H, 3xCH_2). MS; m/z : 325.00 (M^{+1}).

4-(4-Piperidin-1-yl-thieno[3,2-c]pyridine-2-yl)phenol (5n)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 184 °C; yield 202 mg, 65 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.81(s, 1H, OH), 7.95(d, J=5.3 Hz, 1H, C_6H), 7.50–7.65(m, 2H, ArH), 7.42(d,, J=5.3 Hz, 1H, C_7H), 6.85(d, J=8.3 Hz, 2H, ArH), 6.54(s, 2H, ArH), 3.38–3.47(m, 4H, 2xCH_2), 1.59–1.76(m, 6H, 3xCH_2). MS; m/z : 311.25 (M^{+1}).

2-(4-Fluoro -phenyl)-4-Piperidin-1-yl-thieno[3,2-c]pyridine (5o)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 98 °C; yield 225 mg, 72 %**;** ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.99(d, J=5.7 Hz, 1H, C_6H),

7.83–7.90(m, 2H, ArH), 7.72(s, 1H, C_3H), 7.45(d, J=6.0 Hz, 1H, C_7H), 7.27–7.35(m, 2H, ArH), 3.40–3.47(m, 4H, 2xCH_2), 1.59–1.75(m, 6H, 3xCH_2). MS; m/z : 313.00 (M^{+1}).

2-phenyl-4-Piperidin-1-yl-thieno[3,2-c]pyridine (5p)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 65 °C; yield 230 mg, 78 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.99(d, J=5.7 Hz, 1H, C_6H), 7.70–7.84(m, 3H, ArH), 7.36–7.51(m, 4H, ArH), 3.40–3.47(m, 4H, 2xCH_2), 1.55–1.80(m, 6H, 3xCH_2). MS; m/z : 295.00 (M^{+1}).

4-(4-Piperidin-1-yl-thieno[3,2-c]pyridine-2-yl)benzamide (5q)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 218 °C; yield 222 mg, 66 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.10(brs, 1H, NH), 7.85–8.00(m, 6H, ArH), 7.42–7.50(m, 2H, ArH), 3.38–3.50(m, 4H, 2xCH_2), 1.60–1.76(m, 6H, 3xCH_2). MS; m/z : 338.27 (M^{+1}).

2-(4-Nitro -phenyl)-4-Piperidin-1-yl-thieno[3,2-c]pyridine (5r)

Recrystallized from dichloromethane/hexane (7:3), red colour needles; mp 125 °C; yield 258 mg, 76 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.31(d, J=8.7 Hz, 2H, ArH), 8.00–8.15(m, 4H, ArH), 7.47(d, J=5.3 Hz, 1H, C_7H), 3.45–3.55(m, 4H, 2xCH_2), 1.60–1.80(m, 6H, 3xCH_2). MS; m/z : 340.20 (M^{+1}).

2-(4-Methoxy -phenyl)-4-Morpholin-1-yl-thieno[3,2-c]pyridine (5s)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 125 °C; yield 241 mg, 74 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.00(d, J=5.7 Hz., 1H, C_6H), 7.73–7.81(m, 3H, ArH), 7.49–7.57(d, J=5.7 Hz., 1H, C_7H) 6.96–7.06(d, J=8.7 Hz., 2H, ArH), 3.76–3.84(m, 7H, OMe & 2xCH_2), 3.37–3.47(m, 4H, 2xCH_2). MS; m/z : 327.33 (M^{+1}).

4-(4-Morpholin-1-yl-thieno[3,2-c]pyridine-2-yl)phenol (5t)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 224 °C; yield 206 mg, 66 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.83(s, 1H, OH), 7.99(d, J=5.7 Hz., 1H, C_6H), 7.64–7.69(m, 3H, ArH), 7.50(d, J=5.3Hz, 1H, C_7H), 6.85(d, J=8.7 Hz, 2H, ArH), 3.78–3.84(m, 4H, 2xCH_2), 3.37–3.47(m, 4H, 2xCH_2). MS; m/z : 313.27 (M^{+1}).

2-(4-Fluoro -phenyl)-4-Morpholin-1-yl-thieno[3,2-c]pyridine (5u)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 116 °C; yield 251 mg, 80 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03(d, J=5.7 Hz., 1H, C_7H), 7.86–7.94(m,3H, ArH), 7.53(d, J=4.9 Hz, 1H,ArH), 7.29–7.36(m, 2H, ArH), 3.78–3.84(m, 4H, 2xCH_2), 3.39–3.48(m, 4H, 2xCH_2). MS; m/z : 315.27 (M^{+1}).

2-Phenyl-4-Morpholin-1-yl-thieno[3,2-c]pyridine (5v)

Recrystallized from dichloromethane/hexane (7:3), pale yellow needles; mp 104 °C; yield 234 mg, 79 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03(d, J=5.7 Hz, 1H, C_7H), 7.83–7.90(m, 3H, ArH), 7.37–7.55(m, 4H, ArH), 3.79–3.85(m, 4H, 2xCH_2), 3.40–3.48(m, 4H, 2xCH_2). MS; m/z : 297.27(M^{+1}).

4-(4-Morpholin-1-yl-thieno[3,2-c]pyridine-2-yl)benzamide (5w)

Recrystallized from dichloromethane/hexane (7:3), colourless needles; mp 231 °C; yield 231 mg, 68 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.92–8.10(m, 7H, ArH &NH), 7.55(d, J= 5.7 Hz, 1H, C_7H), 7.45(s,1H, C_3H), 3.79–3.86(m, 4H, 2xCH_2), 3.40–3.50(m, 4H, 2xCH_2). MS; m/z : 340.27 (M^{+1}).

2-(4-Nitro -phenyl)-4-Morpholin-1-yl-thieno[3,2-c]pyridine (5x)

Recrystallized from dichloromethane/hexane (7:3), red colour needles; mp 180 °C; yield 260 mg, 76 %; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.28–8.36(m, 2H, ArH), 8.06–8.19(m, 4H, ArH), 7.58(d, J=5.7 Hz, 1H,), 3.79–3.85(m, 4H, 2xCH_2), 3.38–3.51(m, 4H,2xCH_2). MS; m/z : 342.21(M^{+1}).

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