

SUPPORTING INFORMATION

Novel 1*H*-pyrrolo[2,3-*b*]pyridine derivatives nortopsentin analogues: synthesis and antitumor activity in peritoneal mesothelioma experimental models

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Supporting Table 1. *In vitro* inhibition of cancer cell lines growth by compounds **1a**, **1d**, **1f**, **1g**, **1l-n**, **2f**, **3b-f**.

Cell lines	pGI ₅₀ ^[a]												
	1a	1d	1f	1g	1l	1m	1n	2f	3b	3c	3d	3e	3f
Leukemia													
CCRF-CEM	4.62	5.26	5.57	5.53	5.62		5.50	5.41	<4.00	5.39	5.38	5.40	6.32
HL-60(TB)	4.97	5.23	5.48	5.72	5.78		5.71	5.58	<4.00	5.74	5.54	5.37	6.50
K-562	5.35	5.56	5.71	6.39	6.45	5.30	6.44	5.69		5.57	5.62	5.57	6.61
MOLT-4	4.64	5.37	5.50	5.33	5.50		5.27	5.05	<4.00	5.50	5.56	5.53	6.11
RPMI-8226	5.34	5.31	5.59	5.43	5.44		5.19	5.12	<4.00	5.32	5.48	5.32	5.33
SR	5.43	5.16	5.67	6.15	6.25	5.56	6.23	5.29		5.54	5.53	5.49	6.38
Non-Small Cell Lung Cancer													
A549/ATCC	4.58	5.40	5.65	5.84	5.76	5.58	5.84	5.22	<4.00	5.47	5.53	5.50	6.24
EKVX	6.43	6.17	6.16	5.75	5.72	5.48	5.52	5.15		5.24	5.66	5.67	5.75
HOP-62	4.71	4.60	5.51	5.70	5.57		5.45	4.92	<4.00	5.28	5.28	5.42	6.07
HOP-92	5.57	5.53	5.78	5.78	5.64		5.76	5.42		5.67	5.65	5.70	6.22
NCI-H226	4.85	4.93	5.29	5.64	5.58		5.45	5.51	<4.00	5.41	5.43	5.30	5.00
NCI-H23	5.35	5.30	5.64	5.50	5.56		4.97	4.95	<4.00	5.36	5.48	5.45	6.16
NCI-H322M	5.89	5.58	5.65	5.56			5.06	4.85	<4.00	5.12	5.37	5.38	6.18
NCI-H460	5.90	5.49	5.80	6.07	5.95	5.68	6.15	5.41		5.49	5.59	5.51	6.45
NCI-H522	4.91	5.26	5.68	6.40	6.44		6.24	5.42	<4.00	5.10	5.56	5.45	6.72
Colon Cancer													
COLO 205	4.62	5.43	5.66	5.77	5.84	5.77	6.11	5.53	6.46	6.18	5.76	5.95	6.23
HCC-2998	5.94	5.46	5.76	5.69	6.02	<4.00	5.15	4.99	<4.00	4.17	5.33	5.45	5.84
HCT-116	4.62	5.36	5.70	6.10	6.11		6.15	5.33	<4.00	5.54	5.49	5.51	6.46
HCT-15	5.83	5.63	5.56	5.83	5.82		6.06	5.20	<4.00	5.58	5.58	5.62	6.35
HT29			5.68										6.49
KM12	6.01	5.65	6.40	6.21	6.21	5.33	6.14	5.56	<4.00	5.45	5.50	5.54	6.41
SW-620	4.45	5.28	5.72	5.91	5.91	<4.00	6.01	5.34	<4.00	5.46	5.51	5.42	6.51
CNS Cancer													
SF-268	4.05	5.28	5.52	5.32	5.47		5.24	5.10	<4.00	5.18	5.30	5.26	6.12
SF-295	4.57	5.63	5.75	5.92	6.15		6.06	5.47	<4.00	5.57	5.56	5.56	6.53
SF-539	4.31	4.92	5.46	5.76	5.74		5.51	5.45	<4.00	5.31	5.30	5.27	6.10
SNB-19	4.15	5.18	5.46	5.43	5.54		5.44	4.98	<4.00		5.22	5.28	6.04
SNB-75	4.73	5.45	5.46	5.84	5.90	5.80	5.76	5.77	<4.00	5.64	5.49	5.68	5.93
U251	4.61	5.41	5.73	5.81	5.81		5.90	5.37	<4.00	5.42	5.50	5.47	6.39
Melanoma													
LOX IMVI	4.61	5.44	5.70	5.90	5.94		6.09	5.45	<4.00	5.55	5.57	5.61	6.24
MALME-3M	4.50	4.90	5.81	6.33				4.84	<4.00	5.31	5.29	5.35	6.67
M14	4.72	5.31	5.57	6.02	6.11		6.19	5.13	<4.00	5.52	5.50	5.57	6.43
MDA-MB-435	5.42	5.46	6.08	6.54	6.62	4.90	6.64	5.78	<4.00	5.23	5.46	5.39	7.24
SK-MEL-2	4.26	4.88	5.58	5.35	5.40	<4.00	5.20	4.86	<4.00	5.08	5.19	5.15	6.51
SK-MEL-28	4.31	5.13	5.21	5.68	5.62	<4.00	5.33	4.99	<4.00	5.19	5.19	5.37	5.45
SK-MEL-5	6.23	5.13	5.52	6.07	6.07		6.03	5.59	<4.00	5.54	5.53	5.53	6.30
UACC-257	4.18	5.49	5.67	5.44	5.20	<4.00	5.13	5.05	<4.00	5.69	5.59	5.60	6.28
UACC-62	4.52	5.06	5.49	5.87	5.88	<4.00	5.63	5.11	<4.00	5.44	5.40	5.44	6.35

Ovarian Cancer													
IGROV1	5.18	5.34	5.77	5.86		5.35	5.73	5.19	<4.00	5.26	5.52	5.50	6.83
OVCAR-3	5.35	5.13	5.65	6.38	6.42		6.30	5.65	<4.00	5.22	5.17	5.26	6.50
OVCAR-4	6.93	6.43	7.23		6.13		5.19	5.17	<4.00	5.16	5.54	5.48	5.58
OVCAR-5	6.12	5.79	5.84	5.31	5.45	<4.00	4.32	4.84	<4.00	<4.00	5.25	5.35	5.11
										0			
OVCAR-8	4.42	5.22	5.64	5.47	5.49		5.48	5.22	<4.00	5.33	5.41	5.39	6.13
NCI/ADR-RES	4.70	5.40	5.61	6.21	6.29		6.39	5.63	<4.00	5.43	5.51	5.47	6.56
SK-OV-3	4.19	4.79	5.52	5.70	5.62		5.20	4.99	<4.00	5.36	5.21	5.24	5.93
Renal Cancer													
786-0	4.04	5.34	5.59	5.57	5.59		5.11	5.31	5.51	5.70	5.63	5.72	5.50
A498	4.46	5.58	5.67	5.82	5.72	5.68	5.21	5.41	<4.00	5.94	5.68	5.71	6.11
ACHN	4.50	5.44	5.51	5.44	5.53		5.20	5.13		5.54	5.55	5.58	6.06
CAKI-1	4.59	5.58	5.65	6.01	6.11		5.98	5.51		5.69	5.76	5.78	6.53
RXF 393	4.75	5.33	5.60	5.82	5.82	<4.00	5.61	5.65		5.83	5.57	5.78	5.79
SN12C	<4.00	5.33	5.49	5.32	5.44		5.27	5.19	<4.00	5.30	5.32	5.39	5.43
TK-10	5.24	5.24	5.71	5.62	5.52	<4.00	5.28	4.80	<4.00	5.26	5.33	5.28	5.82
UO-31	<4.00	5.55	5.79	5.31		6.32	5.36	5.46	6.61	5.85	5.87	5.94	6.49
Prostate Cancer													
PC-3	4.79	5.44	5.61	5.72	5.67		5.51	5.31		5.36	5.46	5.52	6.09
DU-145	4.20	5.25	5.45	5.65	5.55		5.18	5.29		5.24	5.37	5.38	6.09
Breast Cancer													
MCF7	6.40	5.94	6.00	6.43	6.28	5.52	5.97	5.54	<4.00	5.48	5.61	5.59	5.67
MDA-MB-231/ATCC	5.99	5.58	5.66	5.50	5.52		5.49	5.28		5.65	5.66	5.80	5.66
HS 578T	<4.00	5.38	5.41	5.38	5.29	5.50	4.50	5.41	<4.00	5.38	5.12	4.97	5.11
BT-549	4.62	4.56	5.40	5.63	5.66		5.52	5.16	<4.00	5.27	5.31	5.22	5.82
T-47D	6.38	7.04	7.38	5.53	6.19		5.66	5.43	<4.00	5.19	5.31	5.30	6.23
MDA-MB-468	6.50	6.50	7.21	6.77	6.64		5.99	6.06	<4.00	5.57	5.58	5.58	5.76

[a] pGI₅₀ is the -log of the molar concentration that inhibits 50% net cell growth.

5-Fluoro-1-methyl-1*H*-indole (**5f**). Also reported with a different method.¹

Conditions: rt for 5 h and then rt for 1 h. Work-up: extraction. Yellow solid; yield: 98%; mp: 55-56 °C. ¹H NMR (200 MHz, CDCl₃) δ: 3.72 (s, 3H, CH₃), 6.41 (d, 1H, *J* = 3.2 Hz, H-3), 6.89-7.05 (m, 2H, H-4 and H-6), 7.15-7.28 (m, 2H, H-2 and H-7); ¹³C NMR (50 MHz, CDCl₃) δ: 33.0 (q), 100.7 (d, *J*_{C3-F} = 4.9 Hz), 105.4 (d, *J*_{C7-F} = 5.6 Hz), 109.6 (d, *J*_{C4-F} = 23.3 Hz), 109.9 (d, *J*_{C6-F} = 10.8 Hz), 130.3 (d), 130.4 (2xs), 157.8 (d, *J*_{C5-F} = 233.0 Hz). Anal. Calcd for C₉H₈FN: C, 72.47; H, 5.41; N, 9.39. Found: C, 72.82; H, 5.21; N, 9.12.

tert-Butyl 1*H*-indole-1-carboxylate (**6a**). Also reported with a different method.²

Conditions: 24 h at reflux. Column chromatography: dichloromethane. Oil; yield: 93%; IR (cm⁻¹) 1732; ¹H NMR (200 MHz, CDCl₃) δ: 1.66 (s, 9H, 3xCH₃), 6.55 (d, 1H, *J* = 3.7 Hz, H-3), 7.17-

7.34 (m, 2H, H-5 and H-6), 7.53-7.59 (m, 2H, H-2 and H-7), 8.15 (d, 1H, $J = 7.8$ Hz, H-4); ^{13}C NMR (50 MHz, CDCl_3) δ : 28.1 (3xq), 83.5 (s), 107.2 (d), 115.1 (d), 120.9 (d), 122.6 (d), 124.1 (d), 125.8 (d), 130.5 (s), 135.1 (s), 149.7 (s). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.61; H, 7.32; N, 6.07.

***tert*-Butyl 5-methoxy-1*H*-indole-1-carboxylate (6c).** Conditions: 48 h at reflux. Column chromatography: dichloromethane/petroleum ether (9/1). Brown solid; yield: 90%; mp: 76°C; IR (cm^{-1}) 1730; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ : 1.66 (s, 9H, 3x CH_3), 3.79 (s, 3H, CH_3), 6.64 (d, 1H, $J = 3.6$ Hz, H-3), 6.93 (d, 1H, $J = 9.0$ Hz, H-6), 7.14 (s, 1H, H-4), 7.63 (d, 1H, $J = 3.6$ Hz, H-2) 7.93 (d, 1H, $J = 9.0$ Hz, H-7); ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) δ : 27.6 (3xq), 55.2 (q), 83.5 (s), 103.5 (d), 107.4 (d), 112.9 (d), 115.3 (d), 126.5 (d), 129.1 (s), 131.0 (s), 149.0 (s), 155.4 (s). Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.64; H, 6.66; N, 5.87.

***tert*-Butyl 5-chloro-1*H*-indole-1-carboxylate (6d).** Also reported with a different method.³ Conditions: 24 h at reflux. Oil; yield: 100%; IR (cm^{-1}) 1738; ^1H NMR (200 MHz, CDCl_3) δ : 1.66 (s, 9H, 3x CH_3), 6.49 (d, 1H, $J = 3.7$ Hz, H-3), 7.25 (dd, 1H, $J = 8.8, 2.1$ Hz, H-6), 7.51 (d, 1H, $J = 2.1$ Hz, H-4), 7.60 (d, 1H, $J = 3.7$ Hz, H-2), 8.06 (d, 1H, $J = 8.8$ Hz, H-7); ^{13}C NMR (50 MHz, CDCl_3) δ : 28.0 (3xq), 83.9 (s), 106.4 (d), 116.0 (d), 120.3 (d), 124.2 (d), 127.0 (d), 128.1 (s), 131.6 (s), 133.5 (s), 149.3 (s). Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{ClNO}_2$: C, 62.03; H, 5.61; N, 5.56. Found: C, 61.74; H, 5.97; N, 5.85.

***tert*-Butyl 5-bromo-1*H*-indole-1-carboxylate (6e).** Conditions: 24 h at reflux. Oil; yield: 100%; IR, (cm^{-1}) 1732; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ : 1.63 (s, 9H, 3x CH_3), 6.70 (d, 1H, $J = 3.7$ Hz, H-3), 7.47 (dd, 1H, $J = 8.8, 2.0$ Hz, H-6), 7.72 (d, 1H, $J = 3.7$ Hz, H-2), 7.85 (d, 1H, $J = 2.0$ Hz, H-4), 8.00 (d, 1H, $J = 8.8$ Hz, H-7); ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) δ : 27.6 (3xq), 84.2 (s), 106.7 (d), 115.2 (s), 116.4 (d), 123.5 (d), 126.7 (d), 127.5 (d), 132.1 (s), 133.3 (s), 148.7 (s). Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{BrNO}_2$: C, 52.72; H, 4.76; N, 4.73. Found: C, 53.03; H, 5.03; N, 5.08.

5-Fluoro-1-methyl-1*H*-indole-3-carboxamide (7f). Conditions: 1 h rt after CSI addition. White solid; yield: 40%; mp: 174-175°C; IR (cm^{-1}) 3369, 3178, 1626; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ : 3.82 (s, 3H, CH_3), 6.88 (bs, 2H, NH_2), 7.06 (td, 1H, $J = 10.3, 8.9, 2.5$ Hz, H-6), 7.51 (dd, 1H, $J = 8.9, 4.6$ Hz, H-7), 7.84 (dd, 1H, $J = 10.3, 2.5$ Hz, H-4) 8.05 (s, 1H, H-2); ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) δ : 33.3 (q), 105.8 (d, $J_{\text{C4-F}} = 24.5$ Hz), 110.0 (d, $J_{\text{C6-F}} = 26.5$ Hz), 111.5 (d, $J_{\text{C7-F}} = 10.0$ Hz), 109.4 (s), 127.2 (s), 133.5 (s), 133.9 (d), 158.0 (d, $J_{\text{C5-F}} = 234$ Hz), 165.8 (s). Anal. Calcd for $\text{C}_{10}\text{H}_9\text{FN}_2\text{O}$: C, 62.49; H, 4.72; N, 14.58. Found: C, 62.20; H, 4.64; N, 14.32.

1-Methyl-1*H*-indole-3-carboxamide (8a). Also reported with a different method.⁴ Conditions: 1 h rt after CSI addition. White solid; yield: 50%; mp: 185-186°C; IR (cm^{-1}) 3392, 3178, 1603; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ : 3.81 (s, 3H, CH_3), 6.92 (bs, 2H, NH_2), 7.10-7.25 (m, 2H, H-5 and H-6), 7.47 (d, 1H, $J = 7.9$ Hz, H-7), 7.99 (s, 1H, H-2), 8.17 (d, 1H, $J = 7.9$ Hz, H-4); ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) δ : 32.9 (q), 109.5 (s), 110.1 (d), 120.6 (d), 121.2 (d), 121.8 (d), 126.6 (s), 132.3 (d), 136.8 (s), 166.2 (s). Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.74; H, 6.05; N, 15.99.

1,5-Dimethyl-1*H*-indole-3-carboxamide (8b). Conditions: 1 h rt after CSI addition. White solid; yield: 70%; mp: 205-206°C; IR (cm^{-1}) 3377, 3182, 1606; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ : 2.40 (s, 3H, CH_3), 3.77 (s, 3H, CH_3), 6.98 (bs, 2H, NH_2), 7.02 (d, 1H, $J = 8.6$ Hz, H-6), 7.34 (d, 1H, $J = 8.6$ Hz, H-7), 7.92 (s, 1H, H-4), 7.96 (s, 1H, H-2); ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) δ : 21.3 (q), 32.9 (q), 109.0 (s), 109.8 (d), 120.9 (d), 123.4 (d), 126.8 (s), 129.2 (s), 132.3 (d), 135.2 (s), 166.3 (s). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$: C, 70.19; H, 6.43; N, 14.88. Found: C, 70.14; H, 6.70;

N, 15.17.

5-Methoxy-1-methyl-1*H*-indole-3-carboxamide (8c). Conditions: 1 h rt after CSI addition.

White solid; yield: 55%; mp: 169-170°C; IR (cm⁻¹) 3383, 3182, 1605; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.77 (s, 3H, CH₃), 3.78 (s, 3H, CH₃), 6.84 (d, 1H, *J* = 8.9 Hz, H-6), 7.10 (bs, 2H, NH₂), 7.37 (d, 1H, *J* = 8.9 Hz, H-7), 7.67 (s, 1H, H-4), 7.94 (s, 1H, H-2); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.0 (q), 55.2 (q), 102.7 (d), 109.0 (s), 110.9 (d), 112.0 (d), 127.2 (s), 131.9 (s), 132.5 (d), 154.6 (s), 166.3 (s). Anal. Calcd for C₁₁H₁₂N₂O₂: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.39; H, 5.72; N, 13.45.

5-Chloro-1-methyl-1*H*-indole-3-carboxamide (8d). Conditions: 0.5 h rt after CSI addition.

White solid; yield: 60%; mp: 209°C; IR (cm⁻¹) 3373, 3180, 1608; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.83 (s, 3H, CH₃), 6.99 (bs, 2H, NH₂), 7.23 (d, 1H, *J* = 8.8 Hz, H-6), 7.53 (d, 1H, *J* = 8.8 Hz, H-7), 8.06 (s, 1H, H-4), 8.18 (s, 1H, H-2); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.2 (q), 109.2 (s), 111.9 (d), 120.3 (d), 121.8 (d), 125.5 (s), 127.7 (s), 133.7 (d), 135.3 (s), 165.7 (s). Anal. Calcd for C₁₀H₉ClN₂O: C, 57.57; H, 4.35; N, 13.43. Found: C, 57.35; H, 4.26; N, 13.70.

5-Bromo-1-methyl-1*H*-indole-3-carboxamide (8e). Conditions: 0.5 h rt after CSI addition.

White solid; yield: 60%; mp: 235°C; IR (cm⁻¹) 3373, 3172, 1608; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.83 (s, 3H, CH₃), 7.00 (bs, 2H, NH₂), 7.34 (d, 1H, *J* = 8.4 Hz, H-6), 7.49 (d, 1H, *J* = 8.4 Hz, H-7), 8.06 (s, 1H, H-4), 8.35 (s, 1H, H-2); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.2 (q), 109.1 (s), 112.4 (d), 113.6 (s), 123.4 (d), 124.4 (d), 128.3 (s), 133.5 (d), 135.5 (s), 165.7 (s). Anal. Calcd for C₁₀H₉BrN₂O: C, 47.46; H, 3.58; N, 11.07. Found: C, 47.17; H, 3.52; N, 11.34.

***tert*-Butyl 3-carbamoyl-1*H*-indole-1-carboxylate (9a).** Analytical and spectroscopic data are previously reported.⁵

***tert*-Butyl 3-carbamoyl-5-methoxy-1*H*-indole-1-carboxylate (9c).** Conditions: 1 h after CSI addition. White solid; yield: 48%; mp: 168-169°C; IR (cm⁻¹) 3343, 3215, 1728, 1660; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 1.65 (s, 9H, 3xCH₃), 3.81 (s, 3H, CH₃), 6.98 (dd, 1H, *J* = 8.9, 2.0 Hz, H-6), 7.20 (s, 1H, NH), 7.77 (d, 1H, *J* = 2.0 Hz, H-4), 7.89 (s, 1H, NH), 7.96 (d, 1H, *J* = 8.9 Hz, H-7), 8.44 (s, 1H, H-2); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 27.6 (3xq), 55.2 (q), 84.5 (s), 104.1 (d), 113.7 (d), 114.7 (s), 115.3 (d), 128.8 (d), 128.9 (s), 129.3 (s), 148.8 (s), 155.9 (s), 165.2 (s). Anal. Calcd for C₁₅H₁₈N₂O₄: C, 62.06; H, 6.25; N, 9.65. Found: C, 62.35; H, 6.19; N, 9.99.

***tert*-Butyl 3-carbamoyl-5-chloro-1*H*-indole-1-carboxylate (9d).** Conditions: 2 h after CSI addition. White solid; yield: 40%; mp: 169-170°C; IR (cm⁻¹) 3338, 3298, 1664, 1720; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 1.66 (s, 9H, 3xCH₃), 7.30 (s, 1H, NH), 7.41 (d, 1H, *J* = 8.8 Hz, H-6), 7.97 (s, 1H, NH), 8.07 (d, 1H, *J* = 8.8 Hz, H-7), 8.26 (s, 1H, H-4), 8.55 (s, 1H, H-2); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 27.5 (3xq), 85.1 (s), 144.1 (s), 116.0 (s), 116.2 (d), 121.1 (d), 124.6 (d), 128.0 (s), 129.7 (d), 133.3 (s), 148.5 (s), 164.6 (s). Anal. Calcd for C₁₄H₁₅ClN₂O₃: C, 57.05; H, 5.13; N, 9.50. Found: C, 56.79; H, 5.08; N, 9.23.

***tert*-Butyl 5-bromo-3-carbamoyl-1*H*-indole-1-carboxylate (9e).** Conditions: 2 h after CSI addition. White solid; yield: 45%; mp: 170-171°C; IR (cm⁻¹) 3352, 3233, 1662, 1720; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 1.65 (s, 9H, 3xCH₃), 7.29 (s, 1H, NH), 7.52 (dd, 1H, *J* = 8.8, 1.9 Hz, H-6), 7.96 (s, 1H, NH), 8.02 (d, 1H, *J* = 8.8 Hz, H-7), 8.41 (d, 1H, *J* = 1.9 Hz, H-4), 8.53 (s, 1H, H-2); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 27.6 (3xq), 85.2 (s), 114.0 (s), 116.1 (s), 116.6 (d), 124.2 (d), 127.3 (d), 129.6 (d), 130.2 (s), 133.6 (s), 146.6 (s), 148.4 (s). Anal. Calcd for C₁₄H₁₅BrN₂O₃: C, 49.57; H, 4.46; N, 8.26. Found: C, 49.34; H, 4.41; N, 7.99.

5-Fluoro-1*H*-indole-3-carbothioamide (10f). Conditions: toluene as solvent, 24 h at reflux.

Orange solid; yield: 90%; mp: 175-176°C; IR (cm⁻¹) 1626; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 7.03 (td, 1H, *J* = 9.0, 8.7, 2.4 Hz, H-6), 7.60 (dd, 1H, *J* = 8.7, 4.9 Hz, H-7), 8.19 (d, 1H, *J* = 2.8 Hz, H-2), 8.47 (dd, 1H, *J* = 9.0, 2.4 Hz, H-4), 8.89 (s, 1H, SH), 9.00 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 106.8 (d, *J*_{C4-F} = 25.7 Hz), 110.3 (d, *J*_{C6-F} = 26.5 Hz), 113.1 (d, *J*_{C7-F} = 9.6 Hz, H-7), 116.0 (d, *J*_{C7a-F} = 4.6 Hz), 126.8 (d, *J*_{C3a-F} = 11.1 Hz), 129.4 (d), 133.4 (s), 157.9 (d, *J*_{C5-F} = 232.6 Hz), 193.2 (s). Anal. Calcd for C₉H₇FN₂S: C, 55.65; H, 3.63; N, 14.42. Found: C, 55.90; H, 3.40; N, 14.13.

1-Methyl-1*H*-indole-3-carbothioamide (11a). Analytical and spectroscopic data are previously reported.⁶

1,5-Dimethyl-1*H*-indole-3-carbothioamide (11b). Conditions: benzene as solvent, 2 h at reflux. Orange solid; yield: 93%; mp: 126°C; IR (cm⁻¹) 3491, 3373, 1595; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 2.41 (s, 3H, CH₃), 2.50 (s, 3H, CH₃), 7.05 (d, 1H, *J* = 8.5 Hz, H-6), 7.36 (d, 1H, *J* = 8.5 Hz, H-7), 8.03 (s, 1H, H-2), 8.37 (s, 1H, H-4), 8.71 (s, 1H, SH), 8.94 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 21.4 (q), 33.0 (q), 110.1 (d), 115.0 (s), 121.4 (d), 123.6 (d), 126.0 (s), 129.9 (s), 132.9 (d), 135.8 (s), 193.1 (s). Anal. Calcd for C₁₁H₁₂N₂S: C, 64.67; H, 5.92; N, 13.71. Found: C, 64.41; H, 6.13; N, 13.67.

5-Methoxy-1-methyl-1*H*-indole-3-carbothioamide (11c). Conditions: benzene as solvent, 1 h at reflux. Orange solid; yield: 95%; mp: 176-177°C; IR (cm⁻¹) 3354, 3273, 1626; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.79 (s, 6H, CH₃), 6.87 (dd, 1H, *J* = 8.9, 1.8 Hz, H-6), 7.39 (d, 1H, *J* = 8.9 Hz, H-7), 8.05 (s, 1H, H-2), 8.17 (d, 1H, *J* = 1.8 Hz, H-4), 8.72 (s, 1H, SH), 8.90 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.2 (q), 55.3 (q), 103.9 (d), 111.2 (d), 111.8 (d), 114.9 (s), 126.7 (s), 132.4 (s), 132.8 (d), 155.0 (s), 192.9 (s). Anal. Calcd for C₁₁H₁₂N₂OS: C, 59.97; H, 5.49; N, 12.72. Found: C, 59.69; H, 5.28; N, 13.10.

5-Chloro-1-methyl-1*H*-indole-3-carbothioamide (11d). Conditions: toluene as solvent, 0.5 h at reflux. Orange solid; yield: 92%; mp: 192-193°C; IR (cm⁻¹) 3278, 3157, 1627; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.83 (s, 3H, CH₃), 7.26 (dd, 1H, *J* = 8.7, 1.9 Hz, H-6), 7.55 (d, 1H, *J* = 8.7 Hz, H-7), 8.14 (s, 1H, H-2), 8.71 (d, 1H, *J* = 1.9 Hz, H-4), 8.90 (s, 1H, SH), 9.06 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.3 (q), 112.2 (d), 114.7 (s), 121.1 (d), 122.1 (d), 126.0 (s), 127.4 (s), 133.2 (d), 135.9 (s), 192.5 (s). Anal. Calcd for C₁₀H₉ClN₂S: C, 53.45; H, 4.04; N, 12.47. Found: C, 53.24; H, 3.77; N, 12.18.

5-Bromo-1-methyl-1*H*-indole-3-carbothioamide (11e). Conditions: toluene as solvent, 1 h at reflux. Orange solid; yield: 93%; mp: 206-207°C; IR (cm⁻¹) 3276, 3157, 1628; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.83 (s, 3H, CH₃), 7.37 (dd, 1H, *J* = 8.7, 1.8 Hz, H-6), 7.50 (d, 1H, *J* = 8.7 Hz, H-7), 8.12 (s, 1H, H-2), 8.86 (d, 1H, *J* = 1.8 Hz, H-4), 8.90 (s, 1H, SH), 9.06 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.3 (q), 112.6 (d), 114.2 (s), 114.6 (s), 124.1 (d), 124.7 (d), 128.0 (s), 133.0 (d), 136.1 (s), 192.5 (s). Anal. Calcd for C₁₀H₉BrN₂S: C, 44.62; H, 3.37; N, 10.41. Found: C, 44.87; H, 3.30; N, 10.34.

5-Fluoro-1-methyl-1*H*-indole-3-carbothioamide (11f). Conditions: toluene as solvent, 0.5 h at reflux. Orange solid; yield: 93%; mp: 159-160°C; IR (cm⁻¹) 3375, 3489, 1626; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.84 (s, 3H, CH₃), 7.11 (td, 1H, *J* = 11.0, 9.0, 2.6 Hz, H-6), 7.60 (dd, 1H, *J* = 9.0, 4.6 Hz, H-7), 8.16 (s, 1H, H-2), 8.43 (dd, 1H, *J* = 11.0, 2.6 Hz, H-4), 8.86 (s, 1H, SH), 9.04 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.3 (q), 106.8 (d, *J*_{C4-F} = 26.0 Hz), 110.3 (d, *J*_{C6-F} = 26.0 Hz), 111.8 (d, *J*_{C7-F} = 10.0 Hz, H-7), 115.0 (d, *J*_{C7a-F} = 4.8 Hz), 126.8 (d, *J*_{C3a-F} = 11.0 Hz), 133.6 (d), 134.0 (s), 158.21 (d, *J*_{C5-F} = 233.1 Hz), 192.6 (s). Anal. Calcd for C₁₀H₉FN₂S: C,

57.67; H, 4.36; N, 13.45. Found: C, 57.29; H, 4.28; N, 13.22.

***tert*-Butyl 3-carbamothioyl-1*H*-indole-1-carboxylate (12a).** Analytical and spectroscopic data are reported elsewhere.⁵

***tert*-Butyl 3-carbamothioyl-5-methoxy-1*H*-indole-1-carboxylate (12c).** Conditions: benzene as solvent, 1 h at reflux. Orange solid; yield: 98%; mp: 153-154°C; IR (cm⁻¹) 3415, 3365, 1738, 1597; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 1.65 (s, 9H, 3xCH₃), 3.80 (s, 3H, CH₃), 7.00 (dd, 1H, *J* = 9.1, 2.6, Hz, H-6), 7.99 (d, 1H, *J* = 9.1 Hz, H-7), 8.21 (d, 1H, *J* = 2.6 Hz, H-4), 8.32 (s, 1H, H-2), 9.34 (s, 1H, SH), 9.52 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 27.6 (3xq), 55.3 (q), 84.8 (s), 105.1 (d), 113.5 (d), 115.3 (d), 119.8 (s), 126.8 (d), 128.8 (s), 129.6 (s), 148.7 (s), 155.7 (s), 192.8 (s). Anal. Calcd for C₁₅H₁₈N₂O₃S: C, 58.80; H, 5.92; N, 9.14. Found: C, 58.51; H, 5.86; N, 9.44.

***tert*-Butyl 3-carbamothioyl-5-chloro-1*H*-indole-1-carboxylate (12d).** Conditions: benzene as solvent, 1 h at reflux. Orange solid; yield: 97%; mp: 154-155°C; IR (cm⁻¹) 3480, 3367, 1741, 1597; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 1.66 (s, 9H, 3xCH₃), 7.42 (dd, 1H, *J* = 8.8, 2.1 Hz, H-6), 8.10 (d, 1H, *J* = 8.8 Hz, H-7), 8.44 (s, 1H, H-2), 8.75 (d, 1H, *J* = 2.1 Hz, H-4), 9.43 (s, 1H, SH), 9.59 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 27.5 (3xq), 85.4 (s), 116.2 (d), 119.0 (s), 121.9 (d), 124.8 (d), 127.4 (d), 127.9 (s), 129.4 (s), 133.7 (s), 148.4 (s), 192.1 (s). Anal. Calcd for C₁₄H₁₅ClN₂O₂S: C, 54.10; H, 4.86; N, 9.01. Found: C, 54.08; H, 5.22; N, 9.07.

***tert*-Butyl 5-bromo-3-carbamothioyl-1*H*-indole-1-carboxylate (12e).** Conditions: benzene as solvent, 1 h at reflux. Orange solid; yield: 96%; mp: 150-151°C; IR (cm⁻¹) 3380, 3284, 1720, 1633; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 1.66 (s, 9H, 3xCH₃), 7.54 (dd, 1H, *J* = 8.8, 2.0 Hz, H-6), 8.05 (d, 1H, *J* = 8.8 Hz, H-7), 8.42 (s, 1H, H-2), 8.90 (d, 1H, *J* = 2.0 Hz, H-4), 9.44 (s, 1H, SH), 9.60 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 27.5 (3xq), 85.4 (s), 116.1 (s), 116.5 (d), 118.9 (s), 124.9 (d), 127.3 (d), 127.4 (d), 129.8 (s), 134.0 (s), 148.4 (s), 192.1 (s). Anal. Calcd for C₁₄H₁₅BrN₂O₂S: C, 47.33; H, 4.26; N, 7.89. Found: C, 47.12; H, 4.24; N, 8.27.

3-[2-(1-Methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[2,3-*b*]pyridine (1a). Yellow solid; yield: 85%; mp: 298-299 °C; IR (cm⁻¹) 3385 ; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.90 (s, 3H, CH₃), 7.29-7.32 (m, 2H, H-5' and H-6'), 7.46 (dd, 1H, *J* = 7.7, 5.2, H-5''), 7.56-7.60 (m, 1H, H-7'), 8.12-8.17 (m, 1H, H-4'), 8.25 (s, 1H, H-2), 8.32 (s, 1H, H-2''), 8.49 (s, 1H, H-5), 8.50 (d, 1H, *J* = 5.2 Hz, H-6''), 8.97 (d, 1H, *J* = 7.7 Hz, H-4''), 12.80 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 32.9 (q), 108.2 (d), 109.0 (s), 110.7 (d), 110.9 (s), 116.2 (d), 116.4 (s), 119.9 (s), 120.3 (d), 121.1 (d), 121.4 (s), 122.6 (d), 124.3 (s), 124.5 (s), 126.2 (d), 131.1 (d), 133.5 (d), 137.1 (d), 162.4(s) Anal. Calcd for C₁₉H₁₄N₄S: C, 69.07; H, 4.27; N, 16.96. Found: C, 68.83; H, 3.98; N, 16.68.

3-[2-(1,5-Dimethyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[2,3-*b*]pyridine (1b.) Yellow solid; yield: 70%; mp: 344-345° C; IR (cm⁻¹) 3364; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 2.61 (s, 3H, CH₃), 3.88 (s, 3H, CH₃), 6.95 (dd, 1H, *J* = 8.5, 2.3 Hz, H-6'). 7.48 (d, 1H, *J* = 8.5 Hz, H-7'), 7.59 (dd, 1H, *J* = 7.9, 4.7 Hz, H-5''), 7.81 (d, 1H, *J* = 2.3 Hz, H-4'), 7.91 (s, 1H, H-2'), 8.21 (s, 1H, H-2''), 8.37 (s, 1H, H-5), 8.48 (d, 1H, *J* = 4.7 Hz, H-6''), 9.03 (d, 1H, *J* = 7.9 Hz, H-4''), 12.60 (s, 1H, NH) ; ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 21.4 (q), 32.9 (q), 108.4 (d), 108.7 (s), 110.4 (d), 116.1 (d), 116.3 (s), 119.6 (s), 119.9 (d), 124.0 (s), 124.1 (d), 124.5 (s), 124.7 (s), 126.6 (d), 129.9 (s), 130.2 (d), 131.0 (s), 134.6 (d), 137.4 (d), 162.3 (s). Anal. Calcd for C₂₀H₁₆N₄S: C, 69.74; H, 4.68; N, 16.27. Found: C, 69.47; H, 4.42; N, 16.01.

3-[2-(5-Methoxy-1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[2,3-*b*]pyridine (1c).

Yellow solid; yield: 90%; mp 261 °C; IR (cm⁻¹) 3360; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.88 (s, 3H, CH₃), 3.91 (s, 3H, CH₃), 7.16 (dd, 1H, *J* = 8.0, 2.1 Hz, H-6'), 7.48 (d, 1H, *J* = 8.0 Hz, H-7'), 7.59 (dd, 1H, *J* = 7.0, 4.0 Hz, H-5''), 7.84 (s, 1H, H-2'), 8.08 (s, 1H, H-2''), 8.20 (s, 1H, H-5), 8.27 (d, 1H, *J* = 2.1, H-4'), 8.48 (d, 1H, *J* = 4.0 Hz, H-6''), 9.03 (d, 1H, *J* = 7.0 Hz, H-4''), 12.60 (s, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.1 (q), 55.2 (q), 101.9 (d), 108.6 (d), 108.8 (s), 111.4 (s), 111.6 (d), 112.6 (d), 116.1 (d), 121.6 (s), 125.1 (s), 126.9 (d), 131.2 (d), 132.2 (s), 135.8 (d), 136.4 (d), 140.9 (s), 147.5 (s), 155.0 (s), 162.7 (s). Anal. Calcd for C₂₀H₁₆N₄OS: C, 66.65; H, 4.47; N, 15.54. Found: C, 66.41; H, 4.26; N, 15.20.

3-[2-(5-Chloro-1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[2,3-*b*]pyridine (1d). Yellow solid; yield: 78%; mp: 297-298 °C; IR (cm⁻¹) 3369; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.91 (s, 3H, CH₃), 7.22 (dd, 1H, *J* = 7.9, 4.7 Hz, H-5''), 7.34 (dd, 1H, *J* = 8.7, 1.8 Hz, H-6'), 7.63 (d, 1H, *J* = 8.7 Hz, H-7'), 7.71 (s, 1H, H-2'), 8.08 (d, 1H, *J* = 2.5 Hz, H-2''), 8.27 (s, 1H, H-5), 8.31 (d, 1H, *J* = 4.7 Hz, H-6''), 8.37 (d, 1H, *J* = 1.8 Hz, H-4'), 8.62 (d, 1H, *J* = 7.9 Hz, H-4''), 12.01 (bs, 1H, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.1 (q), 106.9 (d), 109.3 (s), 109.9 (s), 112.4 (d), 116.1 (d), 117.1 (s), 119.8 (d), 122.4 (d), 124.7 (d), 125.6 (s), 125.7 (s), 128.4 (d), 132.0 (d), 135.6 (s), 143.1 (d), 148.7 (s), 149.9 (s), 161.2 (s). Anal. Calcd for C₁₉H₁₃ClN₄S: C, 62.55; H, 3.59; N, 15.26. Found: C, 62.28; H, 3.32; N, 14.98.

3-[2-(5-Bromo-1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[2,3-*b*]pyridine (1e). Yellow solid; yield: 60%; mp: 290-292 °C; IR (cm⁻¹) 3374; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.90 (s, 1H, CH₃), 7.43 (dd, 1H, *J* = 8.6, 2.5 Hz, H-6'), 7.56-7.65 (m, 2H, H-5'' and H-7'), 7.95 (s, 1H, H-2'), 8.32-8.43 (m, 3H, H-2'', H-4' and H-5), 8.60 (d, 1H, *J* = 5.1 Hz, H-6''), 9.19 (d, 1H, *J* = 7.4 Hz, H-4''), 13.00 (1H, bs, NH); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 33.2 (q), 108.8 (s), 109.4 (d), 111.6 (s), 112.9 (d), 113.8 (s), 116.1 (d), 121.8 (s), 122.6 (d), 125.0 (d), 126.1 (d), 127.1 (s), 132.1 (d), 135.8 (d), 136.0 (s), 136.1 (d), 140.6 (s), 147.8 (s), 161.8 (s). Anal. Calcd for C₁₉H₁₃BrN₄S: C, 55.75; H, 3.20; N, 13.69. Found: C, 55.52; H, 2.96; N, 13.48.

3-[2-(5-Fluoro-1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[2,3-*b*]pyridine (1f). Yellow solid; yield: 95%; mp: 293-294 °C; IR (cm⁻¹) 3103 (IR cm⁻¹); ¹H NMR (DMSO) δ: 3.92 (s, 3H, CH₃), 7.19 (td, 1H, *J* = 9.2, 7.9, 2.5 Hz, H-6'), 7.48 (dd, 1H, *J* = 7.9, 4.8 Hz, H-5''), 7.62 (dd, 1H, *J* = 7.9, 4.5 Hz, H-7'), 7.85 (1H, s, H-2'), 8.02 (dd, 1H, *J* = 9.2, 2.5 Hz, H-4'), 8.26 (d, 1H, *J* = 1.7 Hz, H-2''), 8.31 (s, 1H, H-5), 8.47 (dd, 1H, *J* = 4.8, 1.2 Hz, H-6''), 8.96 (dd, 1H, *J* = 7.9, 1.2 Hz, H-4''), 12.60 (bs, 1H, NH). Anal. Calcd for C₁₉H₁₃FN₄S: C, 65.50; H, 3.76; N, 16.08. Found: C, 65.29; H, 3.49; N, 15.94.

1-Methyl -3-[2-(1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[2,3-*b*]pyridine (1g). Yellow solid; yield: 75%; mp: 286-287 °C; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.91 (s, 3H, CH₃), 3.98 (s, 3H, CH₃), 7.34-7.42 (m, 3H, H-5', H-5'' and H-6'), 7.58 (d, 1H, *J* = 2.0 Hz, H-4'), 7.76 (s, 1H, H-2'), 8.25 (d, 1H, *J* = 8.3 Hz, H-7'), 8.34 (s, 1H, H-2''), 8.37 (s, 1H, H-5), 8.46 (d, 1H, *J* = 4.2 Hz, H-6''), 8.80 (d, 1H, *J* = 7.7 Hz, H-4''); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 31.7 (q), 32.9 (q), 107.5 (d), 109.3 (s), 109.4 (s), 110.6 (d), 116.2 (d), 118.8 (s), 120.5 (d), 121.1 (d), 122.5 (d), 124.6 (s), 129.6 (d), 130.7 (d), 131.0 (d), 137.1 (s), 140.6 (d), 145.4 (s), 148.5 (s), 162.1 (s). Anal. Calcd for C₂₀H₁₆N₄S: C, 69.74; H, 4.68; N, 16.27. Found: C, 69.46; H, 4.39; N, 16.19.

3-[2-(1,5-Dimethyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (1h). Yellow solid; yield: 60%; mp: 299-300 °C; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 2.52 (s, 3H, CH₃), 3.88 (s, 3H, CH₃), 3.97 (s, 3H, CH₃), 7.15 (d, 1H, *J* = 8.2 Hz, H-6'), 7.37 (dd, 1H, *J* = 7.4, 4.1 Hz, H-5''), 7.47 (d, 1H, *J* = 8.2 Hz, H-7'), 7.74 (s, 1H, H-2'), 8.10-8.25 (m, 3H, H-2'', H-4' and H-5), 8.44 (d, 1H, *J* = 4.1 Hz, H-6''), 8.80 (d, 1H, *J* = 7.4 Hz, H-4''); ¹³C NMR (50MHz, DMSO-*d*₆) δ: 21.4 (q), 31.6 (q), 32.9 (q), 107.3 (d), 108.8 (s), 109.3 (s), 107.3 (d), 110.4 (d),

116.1 (d), 118.6 (s), 120.0 (d), 123.9 (s), 124.0 (d), 124.7 (s), 129.4 (d), 129.9 (s), 130.7 (d), 135.5 (s), 140.8 (d), 148.4 (s), 162.1 (s). Anal. Calcd for C₂₁H₁₈N₄S: C, 70.36; H, 5.06; N, 15.63. Found: C, 70.09; H, 4.79; N, 15.34.

3-[2-(5-Methoxy-1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]

pyridine (1i). Yellow solid; yield: 85%; mp: 264 °C; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.89 (s, 3H, CH₃), 3.91 (s, 3H, CH₃), 3.93 (s, 3H, CH₃), 6.96 (dd, 1H, *J* = 8.8, 2.4 Hz, H-6'), 7.27 (dd, 1H, *J* = 7.7, 4.7 Hz, H-5''), 7.49 (d, 1H, *J* = 8.8 Hz, H-7'), 7.66 (s, 1H, H-2'), 7.90 (d, 1H, *J* = 2.4 Hz, H-4'), 8.14 (s, 1H, H-2''), 8.16 (s, 1H, H-5), 8.38 (d, 1H, *J* = 4.7 Hz, H-6''), 8.75 (d, 1H, *J* = 7.7 Hz, H-4''); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 31.4 (q), 33.0 (q), 55.2 (q), 101.3 (s), 102.1 (d), 106.7 (d), 109.1 (s), 111.5 (d), 112.4 (d), 116.0 (d), 124.8 (s), 125.1 (s), 128.8 (d), 130.2 (d), 130.9 (d), 131.4 (s), 132.2 (s), 141.6 (d), 154.9 (s), 155.1 (s), 162.2 (s). Anal. Calcd for C₂₁H₁₈N₄OS: C, 67.36; H, 4.85; N, 14.96. Found: C, 67.31; H, 4.57; N, 14.90.

3-[2-(5-Chloro-1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]

pyridine (1j). Yellow solid; yield: 57%; mp: 160-162 °C; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.91 (s, 3H, CH₃), 3.93 (s, 3H, CH₃), 7.25 (dd, 1H, *J* = 7.7, 4.6 Hz, H-5''), 7.33 (dd, 1H, *J* = 8.9, 1.9 Hz, H-6'), 7.62 (d, 1H, *J* = 8.9 Hz, H-7'), 7.70 (s, 1H, H-2'), 8.15 (s, 1H, H-2''), 8.26 (s, 1H, H-5), 8.33-8.36 (m, 2H, H-4' and H-6''), 8.61 (d, 1H, *J* = 7.7 Hz, H-4''); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 30.9 (q), 33.1 (q), 107.0 (d), 108.8 (s), 109.3 (s), 112.3 (d), 116.1 (d), 117.3 (s), 119.7 (d), 122.4 (d), 125.5 (s), 125.7 (s), 128.5 (2xd), 132.0 (d), 135.6 (s), 142.9 (d), 147.6 (s), 149.5 (s), 161.2 (s). Anal. Calcd for C₂₀H₁₅ClN₄S: C, 63.40; H, 3.99; N, 14.79. Found: C, 63.15; H, 3.94; N, 14.50.

3-[2-(5-Bromo-1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]

pyridine (1k). Yellow solid; yield: 55%; mp: 296-298 °C; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.91 (s, 3H, CH₃), 3.97 (s, 3H, CH₃), 7.36-7.47 (m, 2H, H-5'' and H-6'), 7.59 (d, 1H, *J* = 8.0 Hz, H-7'), 7.76 (s, 1H, H-2'), 8.21 (1H, s, H-2''), 8.27 (s, 1H, H-5), 8.45-8.49 (m, 2H, H-4' and H-6''), 8.77 (d, 1H, *J* = 7.4 Hz, H-4''); ¹³C NMR (50 MHz, DMSO-*d*₆) δ: 31.5 (q), 33.1 (q), 107.7 (d), 109.0 (s), 109.2 (s), 112.8 (d), 113.8 (s), 116.1 (d), 118.4 (s), 122.7 (d), 125.0 (d), 126.0 (s), 126.1 (s), 129.1 (d), 130.4 (d), 131.9 (d), 135.8 (s), 141.2 (d), 149.0 (s), 161.4 (s). Anal. Calcd for C₂₀H₁₅BrN₄S: C, 56.74; H, 3.57; N, 13.23. Found: C, 56.54; H, 3.48; N, 12.88.

3-[2-(5-Fluoro-1-methyl-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]

pyridine (1l). Yellow solid; yield: 91%; mp: 234 °C; ¹H NMR (200 MHz, DMSO-*d*₆) δ: ¹H NMR (DMSO) δ: 3.91 (s, 3H, CH₃), 3.96 (s, 3H, CH₃), 7.19 (td, 1H, *J* = 9.2, 8.9, 2.6 Hz, H-6'), 7.32 (dd, 1H, *J* = 8.0, 5.2 Hz, H-5''), 7.63 (dd, 1H, *J* = 8.9, 4.4 Hz, H-7'), 7.73 (s, 1H, H-2'), 8.07 (dd, 1H, *J* = 9.2, 2.6 Hz, H-4'), 8.24 (s, 1H, H-2''), 8.28 (s, 1H, H-5), 8.41 (dd, 1H, *J* = 5.2, 1.4 Hz, H-6''), 8.69 (dd, 1H, *J* = 8.0, 1.4 Hz, H-4''). Anal. Calcd for C₂₀H₁₅FN₄S: C, 66.28; H, 4.17; N, 15.46. Found: C, 66.03; H, 3.88; N, 15.19.

3-[2-(5-Fluoro-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1*H*-pyrrolo[2,3-*b*]pyridine (1m).

Yellow solid; yield: 87%; mp: 227-228 °C; IR (cm⁻¹) 3389, 3267; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 7.12 (td, 1H, *J* = 9.1, 8.0, 2.5 Hz, H-6'), 7.44-7.58 (m, 2H, H-5'' and H-7'), 7.85 (s, 1H, H-2'), 8.02 (dd, 1H, *J* = 8.0, 2.5 Hz, H-4'), 8.25 (s, 1H, H-2''), 8.29 (s, 1H, H-5), 8.48 (dd, 1H, *J* = 5.1, 1.2 Hz, H-6''), 8.96 (dd, 1H, *J* = 7.9, 1.2 Hz, H-4''), 12.01 (s, 1H, NH), 12.60 (s, 1H, NH). Anal. Calcd for C₁₈H₁₁FN₄S: C, 64.66; H, 3.22; N, 16.76. Found: C, 64.39; H, 2.93; N, 17.03.

3-[2-(5-Fluoro-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (1n).

Yellow solid; yield: 60%; mp: 256-257 °C; IR (cm⁻¹) 3336; ¹H NMR (200 MHz, DMSO-*d*₆) δ: 3.96 (s, 3H, CH₃), 7.12 (td, 1H, *J* = 9.2, 8.0, 2.5 Hz, H-6'), 7.33 (dd, 1H, *J* = 8.0, 4.8 Hz, H-5''), 7.53 (dd, 1H, *J* = 8.0, 4.8 Hz, H-7'), 7.74 (s, 1H, H-2'), 8.06 (dd, 1H, *J* = 9.2, 2.5 Hz, H-4''), 8.25

(s, 1H, H-2''), 8.26 (s, 1H, H-5), 8.41 (dd, 1H, $J = 4.8, 1.4$ Hz, H-6''), 8.70 (dd, 1H, $J = 8.0, 1.4$ Hz, H-4''), 11.90 (s, 1H, NH). Anal. Calcd for $C_{19}H_{13}FN_4S$: C, 65.50; H, 3.76; N, 16.08. Found: C, 65.79; H, 3.48; N, 15.79.

tert-Butyl 3-[4-(1H-pyrrolo[2,3-b]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2a). Yellow solid; yield: 85%, mp: 202 °C; IR (cm^{-1}) 3356, 1728; 1H NMR (200 MHz, DMSO- d_6) δ : (s, 9H, 3xCH₃), 7.47-7.51 (m, 2H, H-5' and H-6'), 7.57 (dd, 1H, $J = 7.6, 5.7$ Hz, H-5''), 8.10 (s, 1H, H-2'), 8.18 (dd, 1H, $J = 8.6, 2.0$ Hz, H-7'), 8.35 (s, 1H, H-2''), 8.36 (s, 1H, H-5), 8.45 (dd, 1H, $J = 8.6, 2.0$ Hz, H-4'), 8.55 (d, 1H, $J = 5.7$ Hz, H-6''), 9.04 (d, 1H, $J = 7.6$ Hz, H-4''), 12.8 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 27.6 (3xq), 85.0 (s), 110.8 (s), 110.9 (d), 115.0 (s), 115.1 (d), 116.3 (d), 120.3 (s), 121.3 (d), 123.9 (d), 125.5 (d), 125.7 (d), 126.7 (s), 126.8 (d), 133.7 (s), 135.0 (d), 138.2 (d), 143.1 (s), 148.7 (s), 149.0 (s), 160.0 (s). Anal. Calcd for $C_{23}H_{20}N_4O_2S$: C, 66.33; H, 4.84; N, 13.45. Found: C, 66.12; H, 4.56; N, 13.18.

tert-Butyl 5-methoxy-3-[4-(1H-pyrrolo[2,3-b]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2c).

Yellow solid; yield: 90%; mp: 234-235 °C; IR (cm^{-1}) 3307, 1736; 1H NMR (200 MHz, DMSO- d_6) δ : 1.68 (s, 9H, 3xCH₃), 3.91 (s, 3H, CH₃), 7.07 (dd, 1H, $J = 9.0, 2.4$ Hz, H-6'), 7.51 (dd, 1H, $J = 7.7, 5.7$ Hz, H-5''), 7.96 (d, 1H, $J = 2.4$ Hz, H-4'), 8.01 (d, 1H, $J = 9.0$ Hz, H-7'), 8.05 (s, 1H, H-2'), 8.26 (s, 1H, H-2''), 8.32 (s, 1H, H-5), 8.53 (d, 1H, $J = 5.7$ Hz, H-6''), 9.07 (d, 1H, $J = 7.7$ Hz, H-4''), 12.80 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 27.6 (3xq), 55.2 (q), 84.7 (s), 103.2 (d), 110.7 (d), 111.0 (s), 114.5 (d), 114.7 (s), 115.8 (d), 116.1 (d), 120.7 (s), 126.0 (d), 126.6 (d), 127.5 (s), 129.5 (s), 134.2 (d), 137.7 (d), 142.4 (s), 148.6 (s), 148.9 (s), 156.2 (s), 160.3 (s). Anal. Calcd for $C_{24}H_{22}N_4O_3S$: C, 64.56; H, 4.97; N, 12.55. Found: C, 64.84; H, 5.26; N, 12.76.

tert-Butyl 5-chloro-3-[4-(1H-pyrrolo[2,3-b]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2d). Yellow solid; yield: 90%; mp: 241-243 °C; IR 3389, 1734 cm^{-1} ; 1H NMR (200 MHz, DMSO- d_6) δ : 1.68 (s, 9H, 3xCH₃), 7.42-7.52 (m, 2H, H-6' and H-5''), 8.01 (s, 1H, H-2'), 8.07 (d, 1H, $J = 8.7$ Hz, H-7'), 8.23 (s, 1H, H-2''), 8.30 (s, 1H, H-5), 8.38 (d, 1H, $J = 1.5$ Hz, H-4'), 8.51 (d, 1H, $J = 4.9$ Hz, H-6''), 8.92 (d, 1H, $J = 7.2$ Hz, H-4''), 12.70 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 27.6 (3xq), 85.3 (s), 110.8 (d), 114.1 (s), 116.1 (d), 116.4 (d), 120.2 (s), 120.7 (d), 125.3 (d), 126.6 (d), 126.9 (d), 127.8 (s), 128.1 (s), 128.2 (s), 133.4 (d), 133.5 (s), 138.2 (d), 143.0 (s), 148.3 (s), 148.9 (s), 159.5 (s). Anal. Calcd for $C_{23}H_{19}ClN_4O_2S$: C, 61.26; H, 4.15; N, 12.42. Found: C, 61.01; H, 3.87; N, 12.15.

tert-Butyl 5-bromo-3-[4-(1H-pyrrolo[2,3-b]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2e).

Yellow solid; yield: 80%; mp: 203-204 °C; IR (cm^{-1}) 3387, 1734; 1H NMR (200 MHz, DMSO- d_6) δ : 1.68 (s, 9H, 3xCH₃), 7.44 (dd, 1H, $J = 7.7, 5.5$ Hz, H-5''), 7.61 (dd, 1H, $J = 8.8, 1.8$ Hz, H-6'), 8.00 (s, 1H, H-2'), 8.07 (d, 1H, $J = 8.8$ Hz, H-7'), 8.22 (s, 1H, H-2''), 8.34 (s, 1H, H-5), 8.47 (d, 1H, $J = 5.5$ Hz, H-6''), 8.62 (d, 1H, $J = 1.8$ Hz, H-4'), 8.87 (d, 1H, $J = 7.7$ Hz, H-4''), 12.60 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 27.6 (3xq), 85.4 (s), 110.5 (d), 110.6 (s), 114.1 (s), 116.1 (d), 116.4 (s), 116.9 (d), 119.6 (s), 123.8 (d), 126.2 (d), 126.9 (d), 128.0 (d), 128.4 (s), 132.4 (d), 133.9 (s), 139.3 (d), 144.2 (s), 148.3 (s), 149.3 (s), 159.5 (s). Anal. Calcd for $C_{23}H_{19}BrN_4O_2S$: C, 55.76; H, 3.87; N, 11.31. Found: C, 55.49; H, 3.63; N, 11.04.

tert-Butyl 3-[4-(1-methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2f). Yellow solid; yield: 92%; mp: 205-206 °C; IR (cm^{-1}) 1726; 1H NMR (200 MHz, DMSO- d_6) δ : 1.69 (s, 9H, 3xCH₃), 3.98 (s, 3H, CH₃), 7.41 (dd, 1H, $J = 7.9, 5.0$ Hz, H-5''), 7.46-7.51 (m, 2H, H-5' and H-6'), 7.96 (s, 1H, H-2'), 8.16-8.20 (m, 1H, H-7'), 8.29 (s, 1H, H-

2''), 8.32 (s, 1H, H-5), 8.45-8.51 (m, 2H, H-4' and H-6''), 8.76 (d, 1H, $J = 7.7$ Hz, H-4''); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 27.6 (3xq), 31.7 (q), 84.9 (s), 109.3 (s), 109.9 (d), 115.0 (d), 116.2 (d), 118.7 (s), 121.4 (d), 123.9 (d), 125.5 (d), 125.6 (d), 126.7 (s), 128.5 (s), 129.9 (d), 130.9 (d), 135.1 (s), 140.6 (d), 144.3 (s), 148.7 (s), 149.3 (s), 159.8 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_2\text{S}$: C, 66.96; H, 5.15; N, 13.01. Found: C, 67.20; H, 4.96; N, 12.74.

tert-Butyl 5-methyl-3-[4-(1-methyl-1H-pyrrolo[2,3-*b*]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2g). Yellow solid; yield: 53%; mp: 206-207 °C; IR (cm^{-1}) 1732; ^1H NMR (200 MHz, DMSO- d_6) δ : 1.68 (s, 9H, 3xCH $_3$), 2.50 (s, 3H, CH $_3$), 3.95 (s, 3H, CH $_3$), 7.28-7.35 (m, 2H, H-5'' and H-6'), 7.91 (s, 1H, H-2'), 8.06 (d, 1H, $J = 8.5$ Hz, H-7'), 8.25-8.28 (m, 3H, H-2'', H-4' and H-5), 8.40 (d, 1H, $J = 4.7, 1.3$ Hz, H-6''), 8.68 (d, 1H, $J = 7.9, 1.3$ Hz, H-4''); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 21.2 (q), 27.6 (3xq), 31.5 (q), 84.8 (s), 109.7 (d), 110.9 (s), 114.6 (d), 116.0 (d), 118.7 (d), 121.0 (d), 124.3 (s), 125.3 (d), 126.6 (d), 126.7 (s), 129.5 (d), 130.5 (d), 132.9 (s), 133.2 (s), 134.9 (s), 144.2 (s), 148.7 (s), 149.6 (s), 158.5 (s). Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_2\text{S}$: C, 67.54; H, 5.44; N, 12.60. Found: C, 67.27; H, 5.15; N, 12.30.

tert-Butyl 5-methoxy-3-[4-(1-methyl-1H-pyrrolo[2,3-*b*]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2h). Yellow solid; yield: 90%; mp: 208-209 °C; IR (cm^{-1}) 1726; ^1H NMR (200 MHz, DMSO- d_6) δ : 1.68 (s, 9H, 3xCH $_3$), 3.92 (s, 3H, CH $_3$), 3.94 (s, 3H, CH $_3$), 7.10 (dd, 1H, $J = 8.9, 2.2$ Hz, H-6'), 7.31 (dd, 1H, $J = 7.8, 5.0$ Hz, H-5''), 7.90 (s, 1H, H-2'), 8.02 (d, 1H, $J = 2.2$ Hz, H-4'), 8.05 (d, 1H, $J = 8.9$ Hz, H-7'), 8.22 (s, 1H, H-2''), 8.29 (s, 1H, H-5), 8.41 (d, 1H, $J = 5.0$ Hz, H-6''), 8.75 (d, 1H, $J = 7.8$ Hz, H-4''); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 27.6 (3xq), 31.4 (q), 55.3 (q), 84.8 (s), 103.5 (d), 108.9 (s), 109.3 (d), 114.4 (d), 114.9 (s), 115.8 (d), 116.4 (d), 118.1 (s), 126.0 (d), 127.6 (s), 129.1 (d), 129.6 (d), 129.8 (s), 141.9 (d), 146.4 (s), 148.6 (s), 149.8 (s), 156.2 (s), 160.0 (s). Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_3\text{S}$: C, 65.20; H, 5.25; N, 12.17. Found: C, 64.92; H, 5.17; N, 11.90.

tert-Butyl 5-chloro-3-[4-(1-methyl-1H-pyrrolo[2,3-*b*]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2i). Yellow solid; yield: 90%; mp: 173-174 °C; IR (cm^{-1}) 1736; ^1H NMR (200 MHz, DMSO- d_6) δ : 1.68 (s, 9H, 3xCH $_3$), 3.92 (s, 3H, CH $_3$), 7.26 (dd, 1H, $J = 7.8, 5.1$ Hz, H-5''), 7.51 (dd, 1H, $J = 8.8, 1.8$ Hz, H-6'), 7.88 (s, 1H, H-2'), 8.15 (s, 1H, $J = 8.8$ Hz, H-7'), 8.18 (s, 1H, H-2''), 8.37 (s, 1H, H-5), 8.38 (d, 1H, $J = 1.8$ Hz, H-4'), 8.49 (d, 1H, $J = 5.1$ Hz, H-6''), 8.57 (d, 1H, $J = 7.8$ Hz, H-4''); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 27.5 (3xq), 30.9 (q), 85.6 (s), 103.8 (d), 110.0 (s), 109.5 (d), 113.9 (d), 115.0 (s), 116.1 (d), 116.7 (d), 118.5 (s), 126.9 (d), 127.3 (s), 128.0 (d), 131.0 (d), 129.0 (s), 143.0 (d), 145.8 (s), 148.5 (s), 148.1 (s), 157.1 (s), 159.9 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{ClN}_4\text{O}_2\text{S}$: C, 62.00; H, 4.55; N, 12.05. Found: C, 62.28; H, 4.79; N, 11.70.

tert-Butyl 5-bromo-3-[4-(1-methyl-1H-pyrrolo[2,3-*b*]pyridin-3-yl)-1,3-thiazol-2-yl]-1H-indole-1-carboxylate (2j). Yellow solid; yield: 72%; mp: 177-179 °C; IR (cm^{-1}) 1734; ^1H NMR (200 MHz, DMSO- d_6) δ : 1.68 (s, 9H, 3xCH $_3$), 3.93 (s, 3H, CH $_3$), 7.32 (dd, 1H, $J = 7.7, 4.9$ Hz, H-5''), 7.54 (dd, 1H, $J = 8.9, 1.6$ Hz, H-6'), 7.83 (s, 1H, H-2'), 7.98 (d, 1H, $J = 8.9$ Hz, H-7'), 8.10 (s, 1H, H-2''), 8.18 (s, 1H, H-5), 8.41 (d, 1H, $J = 4.9$ Hz, H-6''), 8.47 (d, 1H, $J = 1.6$ Hz, H-4'), 8.65 (d, 1H, $J = 7.7$ Hz, H-4''); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 27.8 (3xq), 31.1 (q), 85.8 (s), 103.9 (d), 110.3 (s), 109.7 (d), 114.1 (d), 115.6 (s), 116.7 (d), 117.1 (d), 118.8 (s), 127.0 (d), 127.7 (s), 128.4 (d), 131.7 (d), 129.5 (s), 143.7 (d), 145.9 (s), 148.7 (s), 148.6 (s), 157.4 (s), 159.8 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{21}\text{BrN}_4\text{O}_2\text{S}$: C, 56.59; H, 4.16; N, 11.17. Found: C, 56.86; H, 4.08; N, 11.37.

3-[2-(1H-Indol-3-yl)-1,3-thiazol-4-yl]-1H-pyrrolo[2,3-*b*]pyridine (3a). Green solid; yield: 99%; mp: 266-267 °C; IR (cm^{-1}) 3307, 3327; ^1H NMR (200 MHz, DMSO- d_6) δ : 7.26-7.30 (m,

2H, H-5' and H-6'), 7.54-7.58 (m, 1H, H-7'), 7.65 (dd, 1H, $J = 7.7, 5.1$ Hz, H-5''), 7.97 (s, 1H, H-2''), 8.28 (s, 1H, H-2''), 8.29 (s, 1H, H-5), 8.40 (d, 1H, $J = 1.4$ Hz, H-4'), 8.60 (d, 1H, $J = 5.1$ Hz, H-6''), 9.22 (d, 1H, $J = 7.7$ Hz, H-4''), 11.90 (s, 1H, NH), 13.50 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 109.1 (d), 110.1 (s), 111.4 (s), 112.4 (d), 116.3 (d), 120.1 (d), 121.0 (d), 121.5 (s), 122.5 (d), 124.1 (s), 127.1 (d), 127.2 (d), 135.8 (d), 136.5 (d), 136.7 (s), 141.1 (s), 147.4 (s), 162.9 (s). Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{N}_4\text{S}$: C, 68.33; H, 3.82; N, 17.71. Found: C, 68.61; H, 4.11; N, 17.42.

3-[2-(5-Methoxy-1H-indol-3-yl)-1,3-thiazol-4-yl]-1H-pyrrolo[2,3-*b*]pyridine (3c). Green solid; yield: 99%; mp: 192-193 °C; IR (cm^{-1}) 3316, 3344; ^1H NMR (200 MHz, DMSO- d_6) δ : 3.91 (s, 3H, CH_3), 6.92 (dd, 1H, $J = 8.8, 2.1$ Hz, H-6'), 7.45 (d, 1H, $J = 8.8$ Hz, H-7'), 7.55 (dd, 1H, $J = 7.7, 5.6$ Hz, H-5''), 7.87 (s, 1H, H-2'), 8.13 (s, 1H, H-2''), 8.18 (d, 1H, $J = 2.1$ Hz, H-4'), 8.33 (s, 1H, H-5), 8.54 (d, 1H, $J = 5.6$ Hz, H-6''), 9.16 (d, 1H, $J = 7.7$ Hz, H-4''), 11.80 (s, 1H, NH), 12.80 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 55.2 (q), 101.7 (d), 108.2 (d), 110.1 (s), 111.2 (s), 112.7 (d), 113.1 (d), 116.1 (d), 120.8 (s), 124.8 (s), 126.4 (d), 127.3 (d), 131.6 (s), 134.4 (d), 137.8 (d), 142.6 (s), 147.9 (s), 154.8 (s), 163.1 (s). Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{N}_4\text{OS}$: C, 65.88; H, 4.17; N, 16.17. Found: C, 66.14; H, 4.43; N, 15.88.

3-[2-(5-Chloro-1H-indol-3-yl)-1,3-thiazol-4-yl]-1H-pyrrolo[2,3-*b*]pyridine (3d). Green solid; yield: 99%; mp: 277-278 °C; IR (cm^{-1}) 3851, 3388; ^1H NMR (200 MHz, DMSO- d_6) δ : 7.28 (dd, 1H, $J = 8.6, 2.1$ Hz, H-6'), 7.47 (dd, 1H, $J = 7.6, 5.0$ Hz, H-5''), 7.57 (d, 1H, $J = 8.6$ Hz, H-7'), 7.85 (s, 1H, H-2'), 8.25 (s, 1H, H-2''), 8.30 (d, 1H, $J = 2.1$ Hz, H-4'), 8.35 (s, 1H, H-5), 8.49 (d, 1H, $J = 5.0$ Hz, H-6''), 8.97 (d, 1H, $J = 7.6$ Hz, H-4''), 12.0 (s, 1H, NH), 12.6 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 108.4 (d), 110.2 (s), 111.0 (s), 113.9 (d), 116.1 (d), 119.5 (d), 119.8 (s), 122.5 (d), 125.4 (s), 125.6 (s), 126.1 (d), 128.4 (d), 132.8 (d), 135.1 (s), 139.1 (d), 144.2 (s), 148.7 (s), 162.0 (s). Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{ClN}_4\text{S}$: C, 61.62; H, 3.16; N, 15.97. Found: C, 61.35; H, 3.45; N, 16.24.

3-[2-(5-Bromo-1H-indol-3-yl)-1,3-thiazol-4-yl]-1H-pyrrolo[2,3-*b*]pyridine (3e). Green solid; yield: 54%; mp: 247° C; IR (cm^{-1}) 3347, 3367; ^1H NMR (200 MHz, DMSO- d_6) δ : 7.29 (m, 2H, H-5' and H-6'), 7.51 (d, 1H, $J = 8.6$ Hz, H-7'), 7.77 (s, 1H, H-2'), 8.15 (s, 1H, H-2''), 8.26 (d, 1H, $J = 2.2$ Hz, H-4'), 8.35 (d, 1H, $J = 4.9$ Hz, H-6''), 8.55 (s, 1H, H-5), 8.77 (d, 1H, $J = 7.7$ Hz, H-4''), 12.00 (s, 1H, NH), 12.20 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 107.5 (d), 110.2 (s), 110.4 (s), 113.4 (s), 114.3 (d), 116.1 (d), 118.2 (s), 122.8 (d), 125.0 (d), 125.2 (d), 126.1 (s), 128.1 (d), 130.1 (d), 135.4 (s), 141.6 (d), 147.0 (s), 149.4 (s), 161.8 (s). Anal. Calcd for $\text{C}_{18}\text{H}_{11}\text{BrN}_4\text{S}$: C, 54.69; H, 2.80; N, 14.17. Found: C, 54.91; H, 2.59; N, 13.90.

3-[2-(1H-Indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1H-pyrrolo[2,3-*b*]pyridine (3f). Green solid; yield: 71%; mp: 279-281 °C; IR (cm^{-1}) 3399; ^1H NMR (200 MHz, DMSO- d_6) δ : 3.97 (s, 3H, CH_3), 7.24-7.29 (m, 2H, H-5' and H-6'), 7.39 (dd, 1H, $J = 7.8, 4.9$ Hz, H-5''), 7.51-7.56 (m, 1H, H-7'), 7.77 (s, 1H, H-2''), 8.21 (d, 1H, $J = 2.0$ Hz, H-2'), 8.28 (s, 1H, H-5), 8.32-8.37 (m, 1H, H-4'), 8.45 (d, 1H, $J = 4.9$ Hz, H-6''), 8.79 (d, 1H, $J = 7.8$ Hz, H-4''), 11.84 (bs, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 31.6 (q), 107.5 (d), 109.4 (s), 110.3 (s), 112.3 (d), 116.2 (d), 118.7 (s), 120.4 (d), 122.5 (d), 124.3 (s), 126.9 (d), 129.6 (d), 130.9 (d), 136.6 (s), 140.9 (d), 145.5 (s), 145.6 (d), 148.4 (s), 162.5 (s). Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{N}_4\text{S}$: C, 69.07; H, 4.27; N, 16.96. Found: C, 68.80; H, 4.22; N, 16.72.

1-Methyl-3-[2-(5-methyl-1H-indol-3-yl)-1,3-thiazol-4-yl]-1H-pyrrolo[2,3-*b*]pyridine (3g). Green solid; yield: 99%; mp: 172°C; IR (cm^{-1}) 3361; ^1H NMR (200 MHz, DMSO- d_6) δ : 2.50 (3H, s, CH_3), 3.94 (s, 3H, CH_3), 7.08 (dd, 1H, $J = 8.3, 1.6$ Hz, H-6'), 7.27 (dd, 1H, $J = 7.9, 4.7$ Hz, H-5''), 7.40 (d, 1H, $J = 8.3$ Hz, H-7'), 7.68 (s, 1H, H-2'), 8.09-8.11 (m, 2H, H-2' and H-5),

8.18 (d, 1H, $J = 1.6$ Hz, H-4'), 8.37 (dd, 1H, $J = 4.7, 1.5$ Hz, H-6''), 8.68 (dd, 1H, $J = 7.9, 1.5$ Hz, H-4''), 11.7 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 21.6 (q), 31.7 (q), 107.3 (d), 109.4 (s), 110.3 (s), 112.8 (d), 116.9 (d), 118.7 (s), 120.3 (d), 122.7 (d), 124.3 (s), 125.9 (d), 129.8 (d), 131.3 (d), 136.6 (s), 140.5 (d), 145.6 (s), 146.0 (s), 148.4 (s), 162.5 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{S}$: C, 69.74; H, 4.68; N, 16.27. Found: C, 69.95; H, 4.39; N, 16.48.

3-[2-(5-Methoxy-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (3h). Green solid; yield: 90%; mp: 253-254° C; IR (cm^{-1}) 3369; ^1H NMR (200 MHz, DMSO- d_6) δ : 3.91 (s, 3H, CH_3), 3.98 (s, 3H, CH_3), 6.92 (dd, 1H, $J = 8.7, 2.2$ Hz, H-6'), 7.39 (dd, 1H, $J = 7.9, 5.2$ Hz, H-5''), 7.41 (d, 1H, $J = 8.7$ Hz, H-7'), 7.75 (s, 1H, H-2''), 7.85 (d, 1H, $J = 1.8$ Hz, H-2'), 8.17 (1H, d, $J = 2.2$ Hz, H-4'), 8.25 (1H, s, H-5), 8.48 (1H, d $J = 5.2$ Hz, H-6''), 8.92 (d, 1H, $J = 7.9$ Hz, H-4''), 11.70 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 31.9 (q), 55.3 (q), 101.9 (d), 107.5 (d), 109.4 (s), 110.0 (s), 112.6 (d), 113.1 (d), 116.1 (d), 119.3 (s), 124.8 (s), 127.4 (d), 129.5 (d), 131.6 (s), 131.8 (d), 140.3 (d), 144.8 (s), 148.1 (s), 154.8 (s), 163.0 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{OS}$: C, 66.65; H, 4.47; N, 15.54. Found: C, 66.89; H, 4.26; N, 15.49.

3-[2-(5-Chloro-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (3i). Green solid; yield: 99%; mp: 257-258°C; IR (cm^{-1}) 3315; ^1H NMR (200 MHz, DMSO- d_6) δ : 3.98 (s, 3H, CH_3), 7.28 (dd, 1H, $J = 8.6, 1.8$ Hz, H-6'), 7.36 (dd, 1H, $J = 7.9, 5.0$ Hz, H-5''), 7.56 (d, 1H, $J = 8.6$ Hz, H-7'), 7.77 (s, 1H, H-2''), 8.24 (s, 1H, H-5), 8.28 (d, 1H, $J = 2.5$ Hz, H-2'), 8.35 (d, 1H, $J = 1.8$ Hz, H-4'), 8.46 (d, 1H, $J = 5.0$ Hz, H-6''), 8.75 (d, 1H, $J = 7.9$ Hz, H-4''), 12.00 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 31.6 (q), 107.8 (d), 109.4 (s), 110.2 (s), 113.9 (d), 116.1 (d), 118.7 (s), 119.6 (d), 122.5 (d), 125.3 (s), 125.5 (s), 128.4 (d), 129.4 (d), 130.8 (d), 135.1 (s), 140.9 (d), 145.5 (s), 148.8 (s), 162.0 (s). Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{ClN}_4\text{S}$: C, 62.55; H, 3.59; N, 15.46. Found: C, 62.81; H, 3.33; N, 15.72.

3-[2-(5-Bromo-1*H*-indol-3-yl)-1,3-thiazol-4-yl]-1-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (3j). Green solid; yield: 90%; mp: 310-311°C; IR (cm^{-1}) 3317; ^1H NMR (200 MHz, DMSO- d_6) δ : 4.03 (s, 3H, CH_3), 7.37-7.56 (m, 3H, H-5'', H-6' and H-7'), 7.85 (bs, 1H, H-2'), 8.30-8.32 (m, 2H, H-2'' and H-5), 8.45 (s, 1H, H-4'), 8.56 (d, 1H, $J = 4.8$ Hz, H-6''), 9.00 (d, 1H, $J = 7.8$ Hz, H-4''), 12.10 (s, 1H, NH); ^{13}C NMR (50 MHz, DMSO- d_6) δ : 32.5 (q), 108.8 (d), 109.8 (s), 110.0 (s), 113.5 (s), 114.4 (d), 116.0 (d), 116.2 (s), 120.3 (s), 122.5 (d), 125.1 (d), 125.9 (s), 128.4 (d), 130.2 (d), 133.5 (d), 135.4 (s), 138.5 (d), 147.8 (s), 162.2 (s). Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{BrN}_4\text{S}$: C, 55.75; H, 3.20; N, 13.69. Found: C, 56.03; H, 3.11; N, 13.96.

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