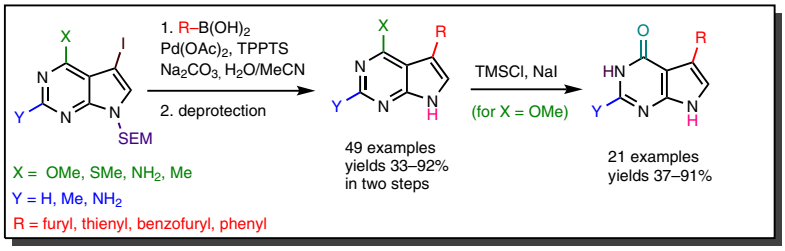
Synthesis N. Sabat et al. Special Topic

Synthesis of 2,6-Substituted 7-(Het)aryl-7-deazapurine Nucleobases (2,4-Disubstituted 5-(Het)aryl-pyrrolo[2,3-*d*]pyrimidines)

Nazarii Sabat[a,b]
Sabina Smoleń[a]
Petr Nauš[a]
Pavla Perlíková[a]
Magdaléna Cebová[a]
Lenka Poštová Slavětínská[a]
Michal Hocek*[a,b]

[a] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 16610 Prague 6, Czech Republic
[b] Department of Organic Chemistry, Faculty of Science, Charles University, Hlavova 8, 12843 Prague 2, Czech Republic
hocek@uochb.cas.cz



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Abstract A series of 7-(het)aryl-7-deazapurine nucleobases (5-[(het)aryl]-2,4-disubstituted 7*H*-pyrrolo[2,3-*d*]pyrimidines) bearing NH_2, OMe, SMe, or Me groups at position 6 and H, NH_2, or Me at position 2 were prepared by the aqueous Suzuki–Miyaura cross-coupling reactions from SEM-protected 7-iodo-7-deazapurines with (het)arylboronic acids followed by deprotection. The 6-methoxy derivatives were further transformed into 7-deazahypoxanthines or 7-deazaguanines by *O*-demethylation reactions. Unlike their ribonucleoside counterparts, the 7-deazapurine nucleobases did not exert any significant cytostatic or antiviral effects.

Key words deazapurines, pyrrolo[2,3-*d*]pyrimidines, nucleobases, Suzuki–Miyaura cross-coupling, deprotection, demethylation

Pyrrolo[2,3-*d*]pyrimidines (7-deazapurines)[1] are important carba-analogues of biogenic purine bases and possess diverse biological activities. [For clarity and as a reference to purines, the (7-deaza)purine nomenclature is used in the discussion, but IUPAC names are given in the experimental part.] Most importantly, some substituted 7-deazapurine bases are potent inhibitors of several protein kinases,[2] which results in diverse therapeutically relevant biological effects. Therefore, many approaches have been reported of the regioselective preparation of mono-, di-, and triaryl-substituted 7-deazapurines[3,4] The synthesis and biological profiling of simple 6-substituted or 2,6-disubstituted 7-hetaryl-7-deazapurine bases have not been reported yet.

In our laboratory, we discovered that the 7-hetaryl-7-deazaadenosines **1a–g** (see Figure 1) are potent cytostatics[5] and/or inhibitors[6] of mycobacterial adenosine kinase. The mechanism of their cytostatic effect involves activation as nucleoside triphosphates, and incorporation in RNA and DNA.[7] We also found that 7-hetaryl-7-deazapurine ribonucleosides bearing other substituents at position 6 (OMe, SMe, Me), compounds **2–4** (Figure 1), exert cytostatic activities comparable to the parent 7-deazaadenosines **1**, whereas the 6-oxo- **7** and 2-substituted derivatives **5**, **6**, and **8** were inactive.[8] On the other hand, the biological activity of the parent 7-hetaryl-7-deazapurine nucleobases with the same substitution patterns is not known yet, though it is important for mechanistic considerations, because the nucleobases could be converted into nucleotides by phosphoribosyl transferases of the salvage pathway. Therefore, we set up the synthesis and profiling of several new types of 7-(het)aryl-7-deazapurine bases (Figure 1).

At first, we intended to synthesize the target 7-hetaryl-7-deazapurine bases through aqueous phase Suzuki–Miyaura cross-coupling reactions[9] of the corresponding 7-iodo-7-deazapurines with hetarylboronic acids (in analogy to our previous works using this approach for the synthesis of 6-arylpurines[10] or 6-aryl-7-deazapurine bases[4]). However, we found that the aqueous Suzuki reactions of 9-unsubstituted 7-iodo-7-deazapurine bases proceeded less efficiently and were accompanied by significant deiodination of the starting heterocycles which lowered the yields and complicated isolation of the products. Therefore, we changed the strategy and decided to introduce a suitable protecting group at position 9. Our previous experience suggested that the 2-[(trimethylsilyl)ethoxy]methyl (SEM) group[11] would be suitable for the Suzuki reactions and be easily removable at the end.

Therefore, the first goal was the synthesis of the 9-SEM-protected 7-iodo-7-deazapurine intermediates **9–15**. They were prepared from the corresponding 6-chloro-7-iodo-7-

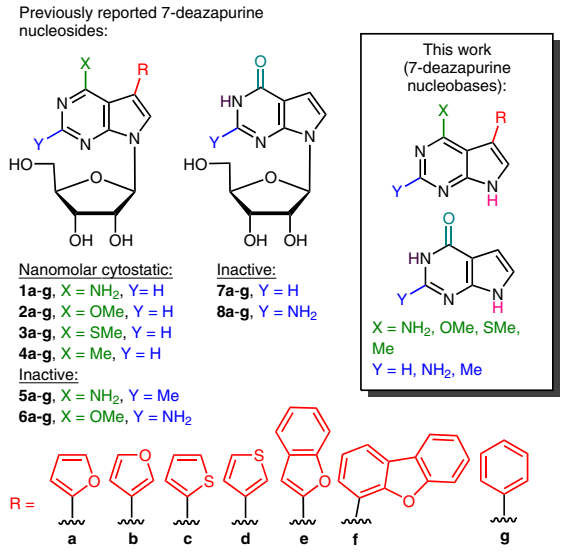
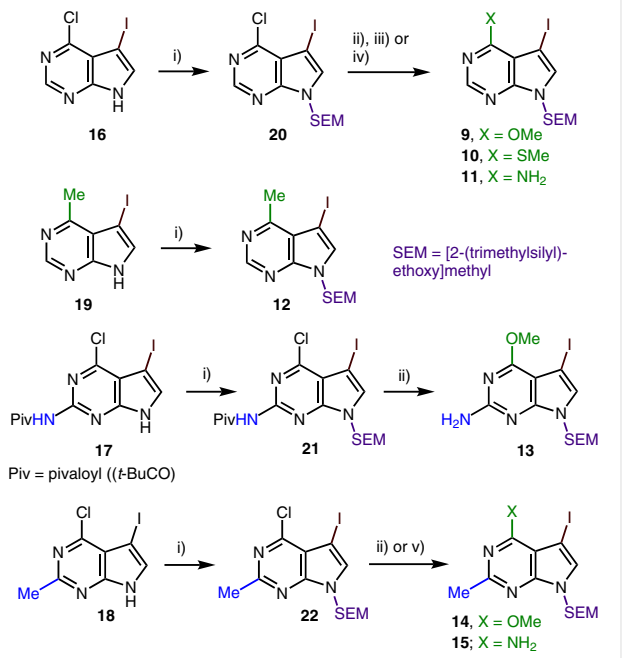


Figure 1 Previously reported biologically active 7-deazapurine nucleosides and the 7-deazapurine nucleobases under study



Scheme 1 Preparation of starting deazapurine bases. *Reagents and conditions*: i) NaH, SEM-Cl, DMF, 0 °C to r.t.; for **12**: 71%; for **20**: 75%; for **21**: 88%; for **22**: 89%; ii) MeONa, MeOH, reflux, 1–2 h, for **9**: 96%; for **13**: 90%; for **14**: 79%; iii) MeSNa, EtOH, r.t., overnight, 81% of **10**; iv) NH_3, MeOH, 130 °C, quant. of **11**; v) aq NH_3 (26% w/w), dioxane, 120 °C, 16 h, 94% of **15**.

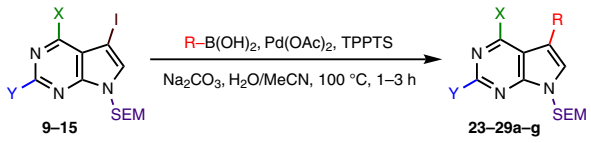
deazapurine bases **16–18** (known compounds prepared according to literature procedures[12–16]) by alkylation with 2-[(trimethylsilyl)ethoxy]methyl chloride (SEM-Cl) under basic conditions,[11] followed by nucleophilic substitution at position 6 with NaOMe, NaSMe, or NH_3 (Scheme 1). In case of 2-amino derivative **13**, orthogonal protection of the amino function by the pivaloyl group was introduced to avoid alkylation at the amino group. All of these reactions proceeded smoothly to give the key intermediates **9–15** in good overall yields on a multigram scale. The SEM-protected 6-methyl derivative **12** was prepared by alkylation of the known 6-methyl-7-iodo-7-deazapurine **19**.[17]

The 9-SEM-protected 6-substituted or 2,6-disubstituted 7-iodo-7-deazapurines **9–15** were then used in aqueous Suzuki–Miyaura reactions with a series of (het)arylboronic acids (Table 1). The choice of the (het)aryl substituents was based on our previous experience with cytostatic nucleosides **1–4** and involved small furyl or thienyl groups (their corresponding nucleosides **1–4a–d** were nanomolar cytostatics) and bulkier benzofuryl, dibenzofuryl, and phenyl groups (their nucleosides **1–4e–g** were non-cytotoxic but some showed inhibition of adenosine kinases).

The aqueous Suzuki–Miyaura cross-couplings of all the SEM-protected 7-iodo-7-deazapurines **9–15** with the (het)aryl boronic acids were performed under standard reaction conditions in the presence of Na_2CO_3 (3 equiv) as a base and $Pd(OAc)_2$ (0.05 equiv) and water soluble triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt ligand (TPPTS) (0.125 equiv) in a mixture of water/acetonitrile (2:1) at 100 °C for 3 hours. The reactions proceeded generally very well and gave the desired SEM-protected 7-(het)aryl-7-deazapurines **23–29a–g** in good to excellent yields (Table 1). The reactions worked nicely even with 2-thienyl- and 2-furylboronic acids which are rather unstable and prone to protodeboronation during the cross-couplings. Exceptionally, in several cases 2-thienyl- and 2-furyltributylstannanes were used in an alternative Stille coupling with deazapurines **9** and **10** in order to get the corresponding 7-thienyl- or 7-furyl derivatives **25a,c** and **26a,c** in slightly higher yields (compared to the Suzuki coupling).

The SEM-protected 7-(het)aryl-7-deazapurine intermediates **23–29a–g** were deprotected yielding the target free deazapurine bases **30–36a–g** (Table 2). The cleavage of the 2-(trimethylsilyl)ethoxy]methyl (SEM) group was performed in two steps. In the first step, the SEM-deazapurine derivatives were treated with trifluoroacetic acid resulting in *N*-hydroxymethyl intermediates which were subsequently cleaved in the second step by treatment with aqueous ammonia (urotropine formation). Alternatively, the SEM group was removed using tetrabutylammonium fluoride (TBAF) in the presence of ethylenediamine (to trap the liberated formaldehyde). This procedure was used in several cases where the target deazapurines were insufficiently stable under strong acidic conditions. Deprotection reactions gave the library of desired 7-(het)aryl-7-deazaadenines **30a–g**, 6-amino-2-methyl-7-deazapurines **31a–g**, 6-methoxy-7-deazapurines **32a–g**, 6-(methylsulfanyl)-7-

Table 1 Synthesis of SEM-Protected Deazapurines **23–29**



R	Product (yield)						
	X = NH_2 Y = H	X = NH_2 Y = Me	X = OMe Y = H	X = SMe Y = H	X = Me Y = H	X = OMe Y = NH_2	X = OMe Y = Me
furan-2-yl	**23a** (72%)	**24a** (78%)	**25a** (80%)[a]	**26a** (82%)[a]	**27a** (91%)	**28a** (71%)	**29a** (68%)
furan-3-yl	**23b** (93%)	**24b** (88%)	**25b** (89%)	**26b** (93%)	**27b** (99%)	**28b** (73%)	**29b** (76%)
thiophen-2-yl	**23c** (78%)	**24c** (97%)	**25c** (83%)[a]	**26c** (76%)[a]	**27c** (98%)	**28c** (73%)	**29c** (80%)
thiophen-3-yl	**23d** (92%)	**24d** (99%)	**25d** (98%)	**26d** (93%)	**27d** (94%)	**28d** (76%)	**29d** (88%)
benzofuran-2-yl	**23e** (82%)	**24e** (90%)	**25e** (92%)	**26e** (87%)	**27e** (84%)	**28e** (70%)	**29e** (76%)
dibenzofuran-4-yl	**23f** (95%)	**24f** (92%)	**25f** (94%)	**26f** (99%)	**27f** (79%)	**28f** (65%)	**29f** (71%)
phenyl	**23g** (99%)	**24g** (98%)	**25g** (84%)	**26g** (94%)[b]	**27g** (85%)	**28g** (68%)	**29g** (64%)

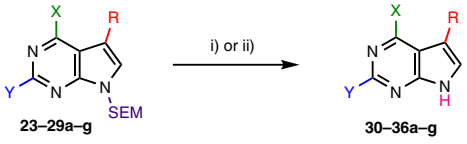
[a] Reaction conditions: $RSnBu_3$, $PdCl_2(PPh_3)_2$, DMF, 100 °C, 1 h.
[b] Estimated yield of crude product used directly in the next step.

deazapurines **33a–g**, 6-methyl-7-deazapurines **34a–g**, 2-amino-6-methoxy- and 6-methoxy-2-methyl-7-deazapurines **35a–g**, **36a–g** in good to excellent yields (Table 2).

In order to get the 6-oxo derivatives, we could not use direct cross-coupling reactions (which did not proceed efficiently). Therefore, we prepared the 6-oxo derivatives by demethylation of 6-methoxy-7-deazapurines. Thus the 6-methoxy-7-deazapurines **32a–g**, **35a–g**, and **36a–g** were transformed into 7-substituted 7-deazaguanines **38a–g** and 7-deazahypoxanthines **37a–g**, **39a–g** (Table 3) which are 7-substituted 7-deaza analogues of natural purine bases guanine or hypoxanthine. The *O*-demethylation reaction[18] was performed by treatment with iodotrimethylsilane generated in situ from TMSCl and NaI in acetonitrile furnishing the desired products **37–39a–g** in good yields (Table 3).

In 7-substituted 7-deazaadenines **30a–g**, 7-deazahypoxanthines **37a–g**, and 7-deazaguanines **38a–g**, which are the closest analogues of natural nucleobases, we also performed UV-vis and fluorescence spectroscopy characteriza-

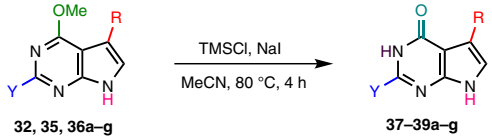
Table 2 Synthesis of Free Deazapurine Bases **30–36**[a]



R	Product (yield)						
	X = NH_2 Y = H	X = NH_2 Y = Me	X = OMe Y = H	X = SMe Y = H	X = Me Y = H	X = OMe Y = NH_2	X = OMe Y = Me
furan-2-yl	**30a** (39%)	**31a** (59%)[b]	**32a** (52%)	**33a** (71%)	**34a** (85%)[b]	**35a** (69%)[b]	**36a** (91%)
furan-3-yl	**30b** (66%)	**31b** (83%)	**32b** (77%)	**33b** (79%)	**34b** (57%)[b]	**35b** (78%)[b]	**36b** (61%)[b]
thiophen-2-yl	**30c** (73%)	**31c** (91%)	**32c** (68%)	**33c** (83%)	**34c** (71%)[b]	**35c** (72%)[b]	**36c** (87%)
thiophen-3-yl	**30d** (96%)	**31d** (72%)	**32d** (85%)	**33d** (98%)	**34d** (44%)[b]	**35d** (61%)[b]	**36d** (58%)[b]
benzofuran-2-yl	**30e** (81%)	**31e** (98%)	**32e** (98%)	**33e** (83%)	**34e** (59%)[b]	**35e** (56%)[b]	**36e** (77%)
dibenzofuran-4-yl	**30f** (80%)	**31f** (85%)	**32f** (98%)	**33f** (93%)	**34f** (84%)[b]	**35f** (51%)[b]	**36f** (83%)
phenyl	**30g** (90%)	**31g** (80%)	**32g** (74%)	**33g** (82%)	**34g** (90%)[b]	**35g** (54%)[b]	**36g** (62%)[b]

[a] Reactions conditions: (i) 1. TFA, CH_2Cl_2, r.t., 4 h; 2. aq NH_3 (25% [w/w]), r.t., 12 h; (ii) TBAF, ethylenediamine, DMF, 45–50 °C, 2–7 d.
[b] Reaction conditions (ii) used instead of (i).

Table 3 Synthesis of 7-Deazahypoxanthines **37**, **39** and 7-Deazaguanines **38**



32, 35, 36a–g **37–39a–g**

R	Product (yield)		
	Y = H	Y = NH_2	Y = Me
furan-2-yl	**37a** (82%)	**38a** (64%)	**39a** (91%)
furan-3-yl	**37b** (37%)	**38b** (58%)	**39b** (61%)
thiophen-2-yl	**37c** (76%)	**38c** (65%)	**39c** (87%)
thiophen-3-yl	**37d** (73%)	**38d** (68%)	**39d** (58%)
benzofuran-2-yl	**37e** (89%)	**38e** (77%)	**39e** (77%)
dibenzofuran-4-yl	**37f** (63%)	**38f** (73%)	**39f** (83%)
phenyl	**37g** (90%)	**38g** (62%)	**39g** (52%)

tion (Table 4). They generally exerted absorption maxima at 277–326 nm and some of them showed rather weak fluorescence. The only brighter fluorophores were 7-(dibenzofuryl)-7-deazaadenine and 7-deazaguanine **30f** and **38f**, respectively, which might have potential for fluorescent labelling of nucleic acids.

All final free 7-substituted 7-deazapurine bases **30–39a–g** were evaluated against six cell lines derived from human solid tumors including lung (A549 cells) and colon (HCT116 and HCT116p53–/–) carcinomas, as well as leukemia cell lines (CCRF-CEM, CEM-DNR, K562, and K562-TAX) and, for comparison, non-malignant BJ and MRC-5 fibroblasts (in analogy to previous work[5]). None of the compounds showed any considerable cytotoxic or cytostatic activity at concentrations up to 15 µM. This is an important result in comparison with the corresponding ribonucleosides **1–4** having the same substituents at the heterocyclic aglycon. This indicates that the salvage pathway (which would allow formation of the cytotoxic nucleosides from these nucleobases) does not play a role in the metabolism of nucleosides **1–4**.

In conclusion, a library of 70 new 7-(het)aryl-7-deazapurine bases bearing different substituents at position 2 and 6 were synthesized through aqueous phase Suzuki–Miyaura cross coupling reactions of 9-SEM-protected 7-iodo-7-deazapurines with diverse (het)arylboronic acids followed by the cleavage of SEM-protecting group and *O*-demethylation. The title 7-deazapurine nucleobases did not exert a cytostatic effect which is important for the mechanism of action of the corresponding cytostatic nucleosides.

Table 4 UV Absorption Spectra and Fluorescence Properties of Selected 7-(Het)aryl-7-deazapurine Bases

Compound	λ_{abs} (nm) (ε, 10^4)[a]	λ_{em} (nm)[b]	Φ_f[c]
30a	287 (1.5)	402	0.03
30b	277 (0.8)	–	–
30c	283 (1.3)	425	0.01
30d	280 (1.2)	415	0.01
30e	305 (2.0)	390	0.11
30f	286 (2.0)	393	0.17
30g	281 (1.8)	368	0.02
37a	291 (1.2)	424	0.01
37b	282 (0.6)	–	–
37c	298 (1.3)	–	–
37d	285 (1.0)	–	–
37e	312 (2.5), 326 (1.9)	397	0.01
37f	288 (2.3), 313 (1.0)	–	–
37g	284 (1.1)	–	–
38a	304 (1.1)	–	–
38b	292 (1.6)	–	–
38c	310 (1.1)	380	0.03
38d	300 (1.6)	–	–
38e	318 (3.0), 332 (2.6)	360	0.13
38f	289 (2.4)	430	0.36
38g	293 (0.9)	–	–

[a] Absorption maxima [absorption coefficient ε (M^{-1} cm^{-1})] measured in EtOH.
[b] Emission maximum in EtOH.
[c] Fluorescence quantum yield in EtOH measured using quinine sulfate in 0.5 M H_2SO_4 (Φ_f = 0.55) as reference.

Since the title 7-substituted 7-deazapurines are direct analogues of biogenic purine bases, they also have potential in fragment-based screening of ligands of new proteins.

NMR spectra were recorded on 400 MHz (^{1}H at 400 MHz, ^{13}C at 100.6 MHz) or 500 MHz (^{1}H at 500 MHz, ^{13}C at 125.7 MHz, ^{19}F at 470.3 MHz) Bruker Avance spectrometers. Melting points were determined on a Kofler block and are uncorrected. Mass spectra were measured using electrospray ionization (ESI) on a LTQ Orbitrap XL (Thermo) for high resolution and on a Qtof micro (Waters) for low resolution. Electron impact (EI) mass spectra were recorded on a GCT Premier (Waters). FT IR spectra were measured on a Nicolet Avatar 370 FT-IR using KBr method. 4-Chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine and 2-amino-4-chloro-7*H*-pyrrolo[2,3-*d*]pyrimidine were purchased from commercial suppliers and used without any further purifications. Petroleum ether = PE.

Compounds **11**,[12] **16**,[13] **17**,[14] **18**,[15] **19**,[17] **20**,[16] were prepared according to the reported procedures.

5-Iodo-4-methoxy-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (9)

Deazapurine **20** (2.5 g, 6 mmol) was suspended in dry MeOH (17 mL) then MeONa (1.65 g, 50 mmol) was added. The mixture was refluxed for 1 h. After cooling the mixture was poured into EtOAc and washed with H_2O and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated. The crude product was purified using column chromatography (silica gel, 0–5% EtOAc/PE). Recrystallization (hexane/EtOAc 2:1) afforded **9** (2.47 g, 96%) as a white solid; mp 80–82 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.11 (s, 9 H, CH_3Si), 0.80 (m, 2 H, OCH_2CH_2Si), 3.49 (m, 2 H, OCH_2CH_2Si), 4.03 (s, 3 H, CH_3O), 5.53 (s, 2 H, NCH_2O), 7.75 (s, 1 H, H-6), 8.45 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.25 (CH_3Si), 17.25 (OCH_2CH_2Si), 51.05 (C-5), 53.91 (CH_3O), 65.90 (OCH_2CH_2Si), 72.70 (NCH_2O), 106.49 (C-4a), 132.42 (CH-6), 151.44 (CH-2), 152.04 (C-7a), 162.48 (C-4).

MS (EI): *m*/*z* (%) = 405.0 (100) [M].

HRMS (EI): *m*/*z* [M] calcd for $C_{13}H_{20}N_3O_2SiI$: 405.0370; found: 405.0366.

5-Iodo-4-(methylsulfanyl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (10)

MeSNa (630 mg, 8.9 mmol) was added to a suspension of **20** (1.8 g, 4.4 mmol) in abs EtOH (80 mL), and mixture was stirred at r.t. overnight. Solvent was evaporated under reduced pressure and crude mixture was purified by flash column chromatography (silica gel, 0–5% EtOAc/PE). Recrystallization (hexane/EtOAc 3:1) furnished **10** (1.42 g, 81%) as a white solid; mp 94–96 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.10 (s, 9 H, CH_3Si), 0.81 (m, 2 H, OCH_2CH_2Si), 2.63 (s, 3 H, CH_3S), 3.49 (m, 2 H, OCH_2CH_2Si), 5.55 (s, 2 H, NCH_2O), 7.87 (s, 1 H, H-6), 8.64 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.23 (CH_3Si), 12.10 (CH_3S), 17.24 (OCH_2CH_2Si), 52.53 (C-5), 66.01 (OCH_2CH_2Si), 72.57 (NCH_2O), 116.78 (C-4a), 133.80 (CH-6), 148.73 (C-7a), 151.05 (CH-2), 161.81 (C-4).

MS (EI): *m*/*z* (%) = 421.0 (100) [M].

HRMS (EI): *m*/*z* [M] calcd for $C_{13}H_{20}N_3OSiSI$: 421.0141; found: 421.0143.

4-Chloro-5-iodo-2-pivalamido-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (21)

Deazapurine **17** (5 g, 13.2 mmol) was added in portions to a stirred suspension of NaH (0.58 g, 60% dispersion, 44 mmol) in dry DMF (50 mL) at 0 °C. After effervescence ceased, SEM-Cl (2.5 mL, 14.1 mmol) was added at 0 °C and the mixture was stirred overnight at r.t.. The mixture was then diluted with EtOAc (250 mL) and washed with H_2O (200 mL), and the organic phase was washed with 10% brine (4 × 100 mL), dried ($MgSO_4$), and evaporated. The residue was recrystallized (MeCN) to afford the product (5.92 g, 88%) as a pinkish solid; mp 145–146 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.1 (s, 9 H, $Si(CH_3)_3$), 0.87 (m, 2 H, CH_2-3′), 1.22 (s, 9 H, CH_3-*t*Bu), 3.52 (m, 2 H, CH_2-2′), 5.52 (s, 2 H, CH_2-1′), 7.93 (s, 1 H, CH-6), 10.24 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.31 ($Si(CH_3)_3$), 17.16 (CH_2-3′), 26.98 (CH_3-*t*Bu), 39.84 (C-2″), 53.20 (C-5), 66.24 (CH_2-2′), 72.46 (CH_2-1′), 112.60 (C-4a), 135.50 (CH-6), 151.30 (C-2/4), 152.15 (C-2/4), 152.44 (C-7a), 175.88 (C-1″).

MS (ESI): *m*/*z* (%) = 509.0 (100) [M + H], 530.9 (85) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{17}H_{26}N_4O_2ClISiNa$: 531.0450; found: 531.0450.

2-Amino-5-iodo-4-methoxy-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (13)

A mixture of **21** (4.585 g, 9 mmol) and MeONa (6.2 mL, 25% w/w soln, 27 mmol) in MeOH (20 mL) was stirred at 100 °C for 1 h. After cooling, the volatiles were evaporated and the residue was partitioned between EtOAc (50 mL) and H_2O (50 mL). The organic phase was dried ($MgSO_4$) and evaporated. The residue was recrystallized (hexane) to furnish the product (3.42 g, 90%) as a white solid; mp 92–93 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.08 (s, 9 H, $Si(CH_3)_3$), 0.80 (t, $J_{3',2'}$ = 8.1 Hz, 2 H, CH_2-3′), 3.46 (t, $J_{2',3'}$ = 8.1 Hz, 2 H, CH_2-2′), 3.93 (s, 3 H, CH_3O-4), 5.30 (s, 2 H, CH_2-1′), 6.37 (bs, 2 H, NH_2), 7.18 (s, 1 H, CH-6).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.18 ($Si(CH_3)_3$), 17.32 (CH_2-3′), 51.28 (C-5), 53.24 (CH_3O-4), 65.45 (CH_2-2′), 72.15 (CH_2-1′), 98.76 (C-4a), 127.78 (CH-6), 154.74 (C-7a), 159.85 (C-2), 163.10 (C-4).

MS (ESI): *m*/*z* (%) = 421.0 (100) [M + H], 443.0 (45) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{22}N_4O_2ISi$: 421.0551; found: 421.0551.

4-Chloro-5-iodo-2-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (22)

Deazapurine **18** (11.74 g, 40 mmol) was added in portions to a stirred suspension of NaH (1.76 g, 60% dispersion, 44 mmol) in dry DMF (100 mL) at 0 °C. After effervescence ceased, SEM-Cl (7.82 mL, 44 mmol) was added at 0 °C and the mixture was stirred overnight at r.t. The mixture was then diluted with EtOAc (250 mL) and washed with H_2O (200 mL), and the organic phase was washed with 10% brine (4 × 100 mL) and dried ($MgSO_4$). Purification by column chromatography (silica gel, hexane/CH_2Cl_2 1:1) provided the product (15.08 g, 89%) as a redish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.05 (s, 9 H, CH_3Si), 0.92 (m, 2 H, OCH_2CH_2Si), 2.73 (s, 3 H, CH_3-2), 3.52 (m, 2 H, OCH_2CH_2Si), 5.57 (s, 2 H, NCH_2O), 7.43 (s, 1 H, H-6).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.49 (CH_3Si), 17.63 (OCH_2CH_2Si), 25.51 (CH_3-2), 52.30 (C-5), 66.89 (OCH_2CH_2Si), 72.90 (NCH_2O), 114.28 (C-4a), 133.54 (CH-6), 152.10 (C-7a), 152.34 (C-4), 161.49 (C-2).

MS (ESI): *m*/*z* (%) = 424.0 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{20}N_3OClISi$: 424.0103; found: 424.0104.

5-Iodo-4-methoxy-2-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (14)

A mixture of **22** (15 g, 35.4 mmol) and MeONa (16 mL, 25% w/w soln, 70 mmol) in MeOH (30 mL) was stirred at 100 °C for 2 h. After cooling the volatiles were evaporated and the residue was partitioned between EtOAc (100 mL) and 10% brine (100 mL). The organic phase was dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography (silica gel, CH_2Cl_2/hexane 1:1) to give the product (11.74 g, 79%) as an orange oil.

IR (KBr): 3119, 2950, 2895, 1673, 1595, 1340, 1250, 1085, 918, 861, 696 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.11 (s, 9 H, CH_3Si), 0.81 (m, 2 H, OCH_2CH_2Si), 2.54 (s, 3 H, CH_3-2), 3.48 (m, 2 H, OCH_2CH_2Si), 4.01 (s, 3 H, CH_3O-4), 5.47 (s, 2 H, NCH_2O), 7.60 (s, 1 H, H-6).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.32 (CH_3Si), 17.21 (OCH_2CH_2-Si), 25.73 (CH_3-2), 50.88 (C-5), 53.60 (CH_3O-4), 65.76 (OCH_2CH_2Si), 72.44 (NCH_2O), 104.16 (C-4a), 131.60 (CH-6), 152.75 (C-7a), 160.53 (C-2), 162.17 (C-4).

MS (ESI): *m*/*z* (%) = 420.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{14}H_{23}N_3O_2ISi$: 420.0599; found: 420.0600.

4-Amino-5-iodo-2-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (15)

Compound **22** (4.24 g, 10.0 mmol) was dissolved in aq NH_3 (26% w/w, 40 mL) and dioxane (40 mL) and heated in a steel bomb at 120 °C for 16 h. The volatiles were removed in vacuo and the residue was recrystallized (H_2O) to give the product (3.80 g, 94%) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.82 (m, 2 H, OCH_2CH_2Si), 2.37 (s, 3 H, CH_3-2), 3.48 (m, 2 H, OCH_2CH_2Si), 5.40 (s, 2 H, NCH_2O), 6.56 (bs, 2 H, NH_2), 7.45 (s, 1 H, H-6).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.23 (CH_3Si), 17.26 (OCH_2CH_2-Si), 25.61 (CH_3-2), 51.61 (C-5), 65.61 (OCH_2CH_2Si), 72.07 (NCH_2O), 100.86 (C-4a), 129.25 (CH-6), 151.45 (C-7a), 157.24 (C-4), 161.02 (C-2).

MS (ESI): *m*/*z* (%) = 405.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{22}N_4OISi$: 405.0602; found: 405.0602.

5-Iodo-4-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (12)

Nucleobase **19** (1.0 g, 3.86 mmol) was added to a suspension of NaH (201 mg, 60% dispersion, 5.02 mmol) in anhyd DMF (15 ml) under an argon atmosphere and the mixture was stirred at r.t. for 15 min. Then the mixture was cooled to 0 °C, SEM-Cl (717 µL, 4.05 mmol) was added and the mixture was stirred at 0 °C for a further 1.5 h. The mixture was diluted with EtOAc and washed with brine. The organic layer was dried ($MgSO_4$) and evaporated under reduced pressure. After column chromatography (silica gel, hexane/EtOAc 10:1) protected nucleobase **12** (1.06 g, 71%) was obtained as a white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.06 (s, 9 H, CH_3Si), 0.91 (m, 2 H, OCH_2CH_2Si), 2.99 (s, 3 H, CH_3-4), 3.51 (m, 2 H, OCH_2CH_2Si), 5.49 (s, 2 H, NCH_2O), 7.44 (s, 1 H, H-6), 8.74 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.48 (CH_3Si), 17.66 (OCH_2CH_2Si), 20.90 (CH_3-4), 52.74 (C-5), 66.74 (OCH_2CH_2Si), 72.64 (NCH_2O), 117.99 (C-4a), 132.76 (CH-6), 150.49 (C-7a), 151.72 (CH-2), 160.61 (C-4).

MS (ESI): *m*/*z* (%) = 390.1 (100) [M + H], 412.1 (8) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{21}ON_3ISi$: 390.04931; found: 390.04941.

Suzuki–Miyaura Cross-Coupling Reaction; General Procedure A (GPA)

An argon-purged mixture of SEM-protected 7-iodo-7-deazapurine derivative **9**–**15** (1 mmol), boronic acid (1.5 mmol), Na_2CO_3 (318 mg, 3 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and TPPTS (71 mg, 0.125 mmol) in H_2O/MeCN (2:1, 5 mL) was stirred at 100 °C for 3 h. After cooling, the mixture was diluted with H_2O and extracted with $CHCl_3$. The organic phase was dried ($MgSO_4$), filtered, and evaporated and the residue was purified by column chromatography (silica gel). Alternatively, after cooling the mixture was directly loaded onto silica gel by co-evaporation without aqueous work-up.

Variations: In **General Procedure A′** (GPA′), a reduced amount of catalyst and ligand were used: $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 2 mol%) and TPPTS (28 mg, 0.05 mmol, 5 mol%) for 1 mmol of starting compound. In **General Procedure A″** (GPA″), boronic acid (1.1 equiv) was used. In **General Procedure A‴** (GPA‴), boronic acid (1.25 equiv) and TPPTS (0.15 equiv) were used and the mixture was stirred for 1 h.

Stille Coupling; General Procedure B (GPB)

An argon-purged mixture of SEM-protected 7-iodo-7-deazapurine derivative **9**–**10**, $RSnBu_3$ (1.2 equiv), and $PdCl_2(PPh_3)_2$ (0.1 equiv) was dissolved in dry DMF, heated to 100 °C and stirred for 1 h. After cooling the volatiles were removed under reduced pressure and the mixture was purified by flash column chromatography (silica gel, EtOAc 0–5%/PE).

Acidic SEM Cleavage; General Procedure C (GPC)

A SEM-protected deazapurine derivative **23**–**29a**–**g** (1 mmol) was dissolved in CH_2Cl_2 (2 mL) and TFA (4 mL). After 4 h at r.t. (TLC usually revealed full conversion of starting material), the volatiles were removed by evaporation and co-evaporation with MeOH (3 ×). The residue was stirred with MeOH (2 mL) and aq NH_3 (25% w/w, 4 mL) for an additional 12 h. The mixture then was evaporated to dryness and the crude product was recrystallized or purified by flash column chromatography (silica gel) prior to final crystallization.

TBAF SEM Cleavage; General Procedure D (GPD)

A mixture of a SEM-protected deazapurine derivative **23**–**29a**–**g** (1 mmol), TBAF (3 equiv), and ethylenediamine (6 equiv) in DMF (0.5 mL) was stirred at 50 °C for 96 h. After cooling the volatiles were removed by evaporation in vacuo and co-evaporation with toluene (3 ×). The residue was purified by flash column chromatography.

Variations: In **General Procedure D′** (GPD′), TBAF (4 equiv), ethylenediamine (8 equiv), and DMF (5.5 mL per 1 mmol of starting compound) were used. The mixture was stirred at 45 °C. In **General Procedure D″** (GPD″), TBAF (8 equiv), ethylenediamine (16 equiv), and DMF (5.5 mL per 1 mmol of starting compound) were used. The mixture was stirred at 45 °C.

O-Demethylation Reaction; General Procedure E (GPE)

To a stirred mixture of 6-methoxy-7-deazapurine derivative **32a**–**g**, **35a**–**g**, **36a**–**g** and NaI (5 equiv) in anhyd MeCN, TMSCl (5 equiv) was added slowly and the mixture was stirred at 80 °C for 4 h. The precipitate was filtered off, washed carefully with MeCN, dissolved in H_2O and the pH was adjusted to 7 using solid K_2CO_3. The product precipitated and was filtered off. The product was repurified by flash column chromatography if needed.

4-Amino-5-(furan-2-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (23a)

Compound **23a** was prepared from **11** (390 mg, 1.0 mmol) and furan-2-boronic acid (168 mg, 1.5 mmol) by GPA. Column chromatography (0.5% MeOH/$CHCl_3$) gave the product (233 mg, 72%) as a yellowish oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.83 (m, 2 H, OCH_2CH_2Si), 3.52 (m, 2 H, OCH_2CH_2Si), 5.52 (s, 2 H, NCH_2O), 6.60 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 6.69 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 6.93 (bs, 2 H, NH_2), 7.75 (s, 1 H, H-6), 7.78 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 8.16 (H-2).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.21 (CH_3Si), 17.29 (OCH_2CH_2Si), 65.71 (OCH_2CH_2Si), 72.45 (NCH_2O), 98.91 (C-4a), 105.33 (CH-3-furyl), 106.27 (C-5), 112.13 (CH-4-furyl), 122.94 (CH-6), 142.09 (CH-5-furyl), 148.76 (C-2-furyl), 151.26 (C-7a), 152.60 (CH-2), 157.46 (C-4).

MS (ESI): *m*/*z* (%) = 331.2 (100) [M + H], 353.2 (20) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{16}H_{23}O_2N_4Si$: 331.1585; found: 331.1586.

4-Amino-5-(furan-3-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (23b)

Compound **23b** was prepared from **11** (390 mg, 1.0 mmol) and furan-3-boronic acid (168 mg, 1.5 mmol) by GPA. Column chromatography (hexanes/EtOAc 2:1) gave the product (308 mg, 93%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.93 (m, 2 H, OCH_2CH_2Si), 3.57 (m, 2 H, OCH_2CH_2Si), 5.46 (bs, 2 H, NH_2), 5.58 (s, 2 H, NCH_2O), 6.58 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.08 (s, 1 H, H-6), 7.56 (t, $J_{5,2}$ = $J_{5,4}$ = 1.7 Hz, 1 H, H-5-furyl), 7.58 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 8.32 (H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.71 (OCH_2CH_2Si), 66.45 (OCH_2CH_2Si), 72.75 (NCH_2O), 101.55 (C-4a), 107.13 (C-5), 111.52 (CH-4-furyl), 118.63 (C-3-furyl), 122.71 (CH-6), 139.70 (CH-2-furyl), 144.03 (CH-5-furyl), 151.28 (C-7a), 151.89 (CH-2), 156.87 (C-4).

MS (ESI): *m*/*z* (%) = 331.2 (100) [M + H], 353.1 (5) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{16}H_{23}O_2N_4Si$: 331.1585; found: 331.1585.

4-Amino-5-(thiophen-2-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (23c)

Compound **23c** was prepared from **11** (390 mg, 1.0 mmol) and thiophene-2-boronic acid (192 mg, 1.5 mmol) by GPA. Column chromatography (hexanes/EtOAc 2:1) gave the product (269 mg, 78%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.93 (m, 2 H, OCH_2CH_2Si), 3.58 (m, 2 H, OCH_2CH_2Si), 5.52 (bs, 2 H, NH_2), 5.59 (s, 2 H, NCH_2O), 7.11–7.15 (m, 2 H, H-3,5-thienyl), 7.18 (s, 1 H, H-6), 7.34 (m, 1 H, H-4-thienyl), 8.33 (H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.45 (CH_3Si), 17.72 (OCH_2CH_2Si), 66.54 (OCH_2CH_2Si), 72.83 (NCH_2O), 101.25 (C-4a), 109.53 (C-5), 123.86 (CH-6), 125.65 (CH-4-thienyl), 126.38 and 127.99 (CH-3,5-thienyl), 135.76 (C-2-thienyl), 151.22 (C-7a), 152.16 (CH-2), 156.84 (C-4).

MS (ESI): *m*/*z* (%) = 347.1 (100) [M + H], 369.1 (10) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{16}H_{23}ON_4SSi$: 347.1356; found: 347.1356.

4-Amino-5-(thiophen-3-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (23d)

Compound **23d** was prepared from **11** (390 mg, 1.0 mmol) and thiophene-3-boronic acid (192 mg, 1.5 mmol) by GPA. Column chromatography (0.5% MeOH/$CHCl_3$) gave the product (319 mg, 92%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.93 (m, 2 H, OCH_2CH_2Si), 3.58 (m, 2 H, OCH_2CH_2Si), 5.39 (bs, 2 H, NH_2), 5.60 (s, 2 H, NCH_2O), 7.12 (s, 1 H, H-6), 7.23 (dd, $J_{4,5}$ = 4.9 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.32 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 7.47 (dd, $J_{5,4}$ = 4.9 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 8.33 (H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.45 (CH_3Si), 17.72 (OCH_2CH_2Si), 66.45 (OCH_2CH_2Si), 72.79 (NCH_2O), 101.30 (C-4a), 111.93 (C-5), 122.15 (CH-2-thienyl), 122.65 (CH-6), 127.02 (CH-5-thienyl), 128.45 (CH-4-thienyl), 134.77 (C-3-thienyl), 151.20 (C-7a), 151.99 (CH-2), 156.89 (C-4).

MS (ESI): *m*/*z* (%) = 347.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{16}H_{23}ON_4SSi$: 347.1356; found: 347.1356.

4-Amino-5-(benzofuran-2-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (23e)

Compound **23e** was prepared from **11** (390 mg, 1.0 mmol) and benzofuran-2-boronic acid (243 mg, 1.5 mmol) by GPA. Column chromatography (0.5% MeOH/$CHCl_3$) gave the product (313 mg, 82%) as a pinkish solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.94 (m, 2 H, OCH_2CH_2Si), 3.59 (m, 2 H, OCH_2CH_2Si), 5.63 (s, 2 H, NCH_2O), 6.37 (bs, 2 H, NH_2), 6.88 (d, $J_{3,7a}$= 1.0 Hz, 1 H, H-3-benzofuryl), 7.28 (m, 1 H, H-5-benzofuryl), 7.30 (m, 1 H, H-6-benzofuryl), 7.52 (m, 1 H, H-7-benzofuryl), 7.54 (s, 1 H, H-6), 7.58 (m, 1 H, H-4-benzofuryl), 8.35 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.45 (CH_3Si), 17.74 (OCH_2CH_2Si), 66.70 (OCH_2CH_2Si), 73.02 (NCH_2O), 99.96 (C-4a), 101.80 (CH-3-benzofuryl), 107.09 (C-5), 110.82 (CH-7-benzofuryl), 120.73 (CH-4-benzofuryl), 123.47 (CH-6), 123.60 (CH-5-benzofuryl), 124.12 (CH-6-benzofuryl), 128.91 (C-3a-benzofuryl), 150.85 (C-2-benzofuryl), 151.67 (C-7a), 152.15 (CH-2), 154.25 (C-7a-benzofuryl), 156.83 (C-4).

MS (ESI): *m*/*z* (%) = 381.2 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{20}H_{25}O_2N_4Si$: 381.1741; found: 381.1742.

4-Amino-5-(dibenzo[*b*,*d*]furan-4-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (23f)

Compound **23f** was prepared from **11** (390 mg, 1.0 mmol) and dibenzo[*b*,*d*]furan-4-boronic acid (318 mg, 1.5 mmol) by GPA. Column chromatography (0.5% MeOH/$CHCl_3$) gave the product (409 mg, 95%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.01 (s, 9 H, CH_3Si), 0.98 (m, 2 H, OCH_2CH_2Si), 3.67 (m, 2 H, OCH_2CH_2Si), 5.31 (bs, 2 H, NH_2), 5.70 (s, 2 H, NCH_2O), 7.39 (btd, $J_{8,7}$ = $J_{8,9}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{12}H_7O$), 7.47 (t, $J_{2,3}$ = $J_{2,1}$ = 7.6 Hz, 1 H, H-2-$C_{12}H_7O$), 7.48 (ddd, $J_{7,6}$ = 8.2 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{12}H_7O$), 7.48 (s, 1 H, H-6), 7.54 (dd, $J_{3,2}$ = 7.5 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{12}H_7O$), 7.56 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{12}H_7O$), 7.98 (dd, $J_{1,2}$ = 7.6 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{12}H_7O$), 8.01 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{12}H_7O$), 8.38 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.40 (CH_3Si), 17.78 (OCH_2CH_2Si), 66.64 (OCH_2CH_2Si), 73.09 (NCH_2O), 101.75 (C-4a), 110.62 (C-5), 111.92 (CH-6-$C_{12}H_7O$), 118.82 (C-4-$C_{12}H_7O$), 119.90 (CH-1-$C_{12}H_7O$), 120.90 (CH-9-$C_{12}H_7O$), 123.11 (CH-8-$C_{12}H_7O$), 123.41 (CH-2-$C_{12}H_7O$), 124.14 (C-9a-$C_{12}H_7O$), 124.73 (CH-6), 125.05 (C-9b-$C_{12}H_7O$), 127.62 (CH-7-$C_{12}H_7O$), 127.90 (CH-3-$C_{12}H_7O$), 151.42 (C-7a), 151.66 (CH-2), 153.63 (C-4a-$C_{12}H_7O$), 156.17 (C-5a-$C_{12}H_7O$), 156.81 (C-4).

MS (ESI): *m*/*z* (%) = 431.2 (100) [M + H], 453.2 (10) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{24}H_{27}O_2N_4Si$: 431.1898; found: 431.1898.

4-Amino-5-phenyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (23g)

Compound **23g** was prepared from **11** (390 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) by GPA. Column chromatography (hexanes/EtOAc 3:1) gave the product (340 mg, 99%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.94 (m, 2 H, OCH_2CH_2Si), 3.59 (m, 2 H, OCH_2CH_2Si), 5.41 (bs, 2 H, NH_2), 5.62 (s, 2 H, NCH_2O), 7.11 (s, 1 H, H-6), 7.39 (m, 1 H, H-*p*-Ph), 7.44–7.51 (m, 2 × 2 H, H-*m*,*o*-Ph), 8.43 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.45 (CH_3Si), 17.74 (OCH_2CH_2Si), 66.50 (OCH_2CH_2Si), 72.88 (NCH_2O), 101.05 (C-4a), 117.60 (C-5), 122.72 (CH-6), 127.46 (CH-*p*-Ph), 128.83 and 129.10 (CH-*o*,*m*-Ph), 134.37 (C-*i*-Ph), 151.24 (C-7a), 151.77 (CH-2), 156.70 (C-4).

MS (ESI): *m*/*z* (%) = 341.2 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{25}ON_4Si$: 341.1792; found: 341.1792.

4-Amino-5-(furan-2-yl)-2-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (24a)

Compound **24a** was prepared from **15** (404 mg, 1.0 mmol) and furan-2-boronic acid (168 mg, 1.5 mmol) by GPA′. Column chromatography (hexanes/EtOAc 2:1) gave the product (269 mg, 78%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.05 (s, 9 H, CH_3Si), 0.93 (m, 2 H, OCH_2CH_2Si), 2.56 (s, 3 H, CH_3-2), 3.55 (m, 2 H, OCH_2CH_2Si), 5.56 (s, 2 H, NCH_2O), 6.11 (bs, 2 H, NH_2), 6.48 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.8 Hz, 1 H, H-3-furyl), 6.51 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 7.26 (s, 1 H, H-6), 7.49 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.8 Hz, 1 H, H-5-furyl).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.48 (CH_3Si), 17.67 (OCH_2CH_2Si), 25.48 (CH_3-2), 66.37 (OCH_2CH_2Si), 72.55 (NCH_2O), 97.58 (C-4a), 105.00 (CH-3-furyl), 107.29 (C-5), 111.96 (CH-4-furyl), 121.07 (CH-6), 141.01 (CH-5-furyl), 149.31 (C-2-furyl), 152.53 (C-7a), 156.81 (C-4), 161.57 (C-2).

MS (ESI): *m*/*z* (%) = 345.2 (100) [M + H], 367.2 (10) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{25}O_2N_4Si$: 345.1741; found: 345.1742.

4-Amino-5-(furan-3-yl)-2-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (24b)

Compound **24b** was prepared from **15** (404 mg, 1.0 mmol) and furan-3-boronic acid (168 mg, 1.5 mmol) by GPA′. Column chromatography (hexanes/EtOAc 2:1) gave the product (302 mg, 88%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.94 (m, 2 H, OCH_2CH_2Si), 2.56 (s, 3 H, CH_3-2), 3.57 (m, 2 H, OCH_2CH_2Si), 5.55 (s, 2 H, NCH_2O), 6.57 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.00 (s, 1 H, H-6), 7.54 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 7.57 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.47 (CH_3Si), 17.67 (OCH_2CH_2Si), 25.57 (CH_3-2), 66.29 (OCH_2CH_2Si), 72.44 (NCH_2O), 99.28 (C-4a), 106.88 (C-5), 111.52 (CH-4-furyl), 118.94 (C-3-furyl), 121.97 (CH-6), 139.55 (CH-2-furyl), 143.90 (CH-5-furyl), 152.40 (C-7a), 156.81 (C-4), 161.42 (C-2).

MS (EI): *m*/*z* (%) = 344.2 (100).

HRMS (EI): *m*/*z* [M] calcd for $C_{17}H_{24}N_4O_2Si$: 344.1671; found: 344.1669.

4-Amino-5-(thiophen-2-yl)-2-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (24c)

Compound **24c** was prepared from **15** (404 mg, 1.0 mmol) and thiophene-2-boronic acid (192 mg, 1.5 mmol) by GPA′. Column chromatography (hexanes/EtOAc 2:1) gave the product (348 mg, 97%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.94 (m, 2 H, OCH_2CH_2Si), 2.57 (s, 3 H, CH_3-2), 3.58 (m, 2 H, OCH_2CH_2Si), 5.38 (bs, 2 H, NH_2), 5.57 (s, 2 H, NCH_2O), 7.10 (s, 1 H, H-6), 7.10–7.13 (m, 2 H, H-3,5-thienyl), 7.31 (m, 1 H, H-4-thienyl).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.69 (OCH_2CH_2Si), 25.63 (CH_3-2), 66.40 (OCH_2CH_2Si), 72.53 (NCH_2O), 98.99 (C-4a), 109.35 (C-5), 123.12 (CH-6), 125.35 (CH-4-thienyl), 126.10 and 127.93 (CH-3,5-thienyl), 136.24 (C-2-thienyl), 152.33 (C-7a), 156.71 (C-4), 161.65 (C-2).

MS (ESI): *m*/*z* (%) = 361.2 (100) [M + H], 383.1 (10) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{25}ON_4SSi$: 361.1513; found: 361.1514.

4-Amino-5-(thiophen-3-yl)-2-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (24d)

Compound **24d** was prepared from **15** (404 mg, 1.0 mmol) and thiophene-3-boronic acid (192 mg, 1.5 mmol) by GPA′. Column chromatography (hexanes/EtOAc 2:1) gave the product (358 mg, 99%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.94 (m, 2 H, OCH_2CH_2Si), 2.58 (s, 3 H, CH_3-2), 3.58 (m, 2 H, OCH_2CH_2Si), 5.57 (s, 2 H, NCH_2O), 5.63 (bs, 2 H, NH_2), 7.06 (s, 1 H, H-6), 7.22 (dd, $J_{4,5}$ = 4.9 Hz, $J_{4,5}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.31 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 7.46 (dd, $J_{5,4}$ = 4.9 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.69 (OCH_2CH_2Si), 25.05 (CH_3-2), 66.41 (OCH_2CH_2Si), 72.58 (NCH_2O), 98.90 (C-4a), 112.06 (C-5), 122.03 (CH-2-thienyl), 122.21 (CH-6), 127.04 (CH-5-thienyl), 128.37 (CH-4-thienyl), 134.78 (C-3-thienyl), 151.87 (C-7a), 156.26 (C-4), 160.40 (C-2).

MS (ESI): *m*/*z* (%) = 361.2 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{25}ON_4SSi$: 361.1513; found: 361.1514.

4-Amino-5-(benzofuran-2-yl)-2-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (24e)

Compound **24e** was prepared from **15** (404 mg, 1.0 mmol) and benzofuran-2-boronic acid (243 mg, 1.5 mmol) by GPA′. Column chromatography (hexanes/EtOAc 2:1) gave the product (355 mg, 90%) as a white needles.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.03 (s, 9 H, CH_3Si), 0.95 (m, 2 H, OCH_2CH_2Si), 2.59 (s, 3 H, CH_3-2), 3.59 (m, 2 H, OCH_2CH_2Si), 5.60 (s, 2 H, NCH_2O), 6.16 (bs, 2 H, NH_2), 6.85 (d, $J_{3,7}$ = 0.9 Hz, 1 H, H-3-benzofuryl), 7.24–7.31 (m, 2 H, H-5,6-benzofuryl), 7.45 (s, 1 H, H-6), 7.52 (m, 1 H, H-7-benzofuryl), 7.57 (m, 1 H, H-4-benzofuryl).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.47 (CH_3Si), 17.69 (OCH_2CH_2Si), 25.66 (CH_3-2), 66.51 (OCH_2CH_2Si), 72.67 (NCH_2O), 97.72 (C-4a), 101.36 (CH-3-benzofuryl), 106.74 (C-5), 110.79 (CH-7-benzofuryl), 120.60 (CH-4-benzofuryl), 122.81 (CH-6), 123.47 and 123.88 (CH-5,6-benzofuryl), 129.02 (C-3a-benzofuryl), 151.38 (C-2-benzofuryl), 152.88 (C-7a), 154.21 (C-7a-benzofuryl), 156.92 (C-4), 162.05 (C-2).

MS (EI): *m*/*z* (%) = 394.2 (100).

HRMS (EI): *m*/*z* [M] calcd for $C_{21}H_{26}N_4O_2Si$: 394.1824; found: 394.1825.

4-Amino-5-(dibenzo[*b*,*d*]furan-4-yl)-2-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (24f)

Compound **24f** was prepared from **15** (404 mg, 1.0 mmol) and dibenzo[*b*,*d*]furan-4-boronic acid (318 mg, 1.5 mmol) by GPA′. Column chromatography (hexanes/EtOAc 2:1) gave the product (409 mg, 92%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.01 (s, 9 H, CH_3Si), 0.99 (m, 2 H, OCH_2CH_2Si), 2.61 (s, 3 H, CH_3-2), 3.67 (m, 2 H, OCH_2CH_2Si), 5.08 (bs, 2 H, NH_2), 5.67 (s, 2 H, NCH_2O), 7.38 (btd, $J_{8,7}$ = $J_{8,9}$ = 7.5 Hz, $J_{8,6}$ = 1.1 Hz, 1 H, H-8-$C_{12}H_7O$), 7.40 (s, 1 H, H-6), 7.45 (t, $J_{2,3}$ = $J_{2,1}$ = 7.6 Hz, 1 H, H-2-$C_{12}H_7O$), 7.48 (ddd, $J_{7,6}$ = 8.3 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.3 Hz, 1 H, H-7-$C_{12}H_7O$), 7.54 (dd, $J_{3,2}$ = 7.5 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{12}H_7O$), 7.57 (dt, $J_{6,7}$ = 8.3 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{12}H_7O$), 7.95 (dd, $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{12}H_7O$), 8.00 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{12}H_7O$).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.42 (CH_3Si), 17.76 (OCH_2CH_2Si), 25.73 (CH_3-2), 66.46 (OCH_2CH_2Si), 72.75 (NCH_2O), 99.52 (C-4a), 110.26 (C-5), 111.91 (CH-6-$C_{12}H_7O$), 119.33 (C-4-$C_{12}H_7O$), 119.58 (CH-1-$C_{12}H_7O$), 120.85 (CH-9-$C_{12}H_7O$), 123.01 (CH-8-$C_{12}H_7O$), 123.34 (CH-2-$C_{12}H_7O$), 123.96 (CH-6), 124.21 (C-9a-$C_{12}H_7O$), 124.94 (C-9b-$C_{12}H_7O$), 127.50 (CH-7-$C_{12}H_7O$), 127.90 (CH-3-$C_{12}H_7O$), 152.70 (C-7a), 153.64 (C-4a-$C_{12}H_7O$), 156.16 (C-5a-$C_{12}H_7O$), 156.93 (C-4), 161.57 (C-2).

MS (ESI): *m*/*z* (%) = 445.2 (100) [M + H], 467.2 (5) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{25}H_{29}O_2N_4Si$: 445.2054; found: 445.2055.

4-Amino-2-methyl-5-phenyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (24g)

Compound **24g** was prepared from **15** (404 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) by GPA′. Column chromatography (hexanes/EtOAc 2:1) gave the product (350 mg, 98%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.03 (s, 9 H, CH_3Si), 0.95 (m, 2 H, OCH_2CH_2Si), 2.59 (s, 3 H, CH_3-2), 3.59 (m, 2 H, OCH_2CH_2Si), 5.16 (bs, 2 H, NH_2), 5.59 (s, 2 H, NCH_2O), 7.03 (s, 1 H, H-6), 7.36 (m, 1 H, H-*p*-Ph), 7.45 (m, 2 H, H-*m*-Ph), 7.49 (m, 2 H, H-*o*-Ph).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.71 (OCH_2CH_2Si), 25.55 (CH_3-2), 66.34 (OCH_2CH_2Si), 72.58 (NCH_2O), 98.80 (C-4a), 117.35 (C-5), 121.97 (CH-6), 127.23 (CH-*p*-Ph), 128.71 (CH-*o*-Ph), 129.02 (CH-*m*-Ph), 134.77 (C-*i*-Ph), 152.48 (C-7a), 156.68 (C-4), 161.29 (C-2).

MS (ESI): *m*/*z* (%) = 355.2 (100) [M + H], 377.2 (5) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{27}ON_4Si$: 355.1949; found: 355.1950.

5-(Furan-2-yl)-4-methoxy-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (25a)

Compound **25a** was prepared from **9** (500 mg, 1.23 mmol) and 2-(tributylstannyl)furan (0.32 mL, 1.48 mmol) by GPB. Flash column chromatography (0–5% EtOAc/PE) gave the product (338 mg, 80%) as a greenish oil.

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 3.54 (m, 2 H, OCH_2CH_2Si), 4.12 (s, 3 H, CH_3O), 5.62 (s, 2 H, NCH_2O), 6.57 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.8 Hz, 1 H, H-4-furyl), 6.94 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.67 (dd, $J_{5,4}$ = 1.8 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 7.84 (s, 1 H, H-6), 8.50 (s, 1 H, H-2).

^{13}C NMR (101 MHz, $CDCl_3$): δ = –1.45 (CH_3Si), 17.72 (OCH_2CH_2Si), 53.80 (CH_3O), 66.50 (OCH_2CH_2Si), 73.15 (NCH_2O), 101.87 (C-4a), 107.34 (C-5), 108.34 (CH-3-furyl), 111.45 (CH-4-furyl), 122.20 (CH-6), 140.91 (CH-5-furyl), 148.70 (C-2-furyl), 151.61 (CH-2), 152.79 (C-7a), 163.27 (C-4).

MS (EI): *m*/*z* (%) = 345.2 (100) [M].

HRMS (EI): *m*/*z* [M] calcd for $C_{17}H_{23}N_3O_3Si$: 345.1509; found: 345.1512.

5-(Furan-3-yl)-4-methoxy-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (25b)

Compound **25b** was prepared from **9** (600 mg, 1.48 mmol) and furan-3-boronic acid (183 mg, 1.63 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (455 mg, 89%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.06 (s, 9 H, CH_3Si), 0.92 (m, 2 H, OCH_2CH_2Si), 3.54 (m, 2 H, OCH_2CH_2Si), 4.16 (s, 3 H, CH_3O), 5.62 (s, 2 H, NCH_2O), 6.70 (dd, $J_{4,5}$ = 1.9 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.30 (s, 1 H, H-6), 7.46 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 8.00 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 8.48 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.71 (OCH_2CH_2Si), 53.72 (CH_3O), 66.44 (OCH_2CH_2Si), 72.94 (NCH_2O), 103.08 (C-4a), 108.43 (C-5), 109.80 (CH-4-furyl), 118.20 (C-3-furyl), 122.36 (CH-6), 140.45 (CH-2-furyl), 142.83 (CH-5-furyl), 151.45 (CH-2), 152.98 (C-7a), 163.30 (C-4).

MS (ESI): *m*/*z* (%) = 346.2 (23) [M + H], 368.1 (77) [M + Na].

HRMS (EI): *m*/*z* [M + Na] calcd for $C_{17}H_{23}O_3N_3NaSi$: 368.1400; found: 368.1399.

4-Methoxy-5-(thiophen-2-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (25c)

Compound **25c** was prepared from **9** (500 mg, 1.23 mmol) and 2-(tributylstannyl)thiophene (0.46 mL, 1.48 mmol) by GPB. Flash column chromatography (0–5% EtOAc/PE) provided a brownish oil (369 mg, 83%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 3.55 (m, 2 H, OCH_2CH_2Si), 4.08 (s, 3 H, CH_3O), 5.61 (s, 2 H, NCH_2O), 7.11 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, H-4-thienyl), 7.45 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.48 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.84 (s, 1 H, H-6), 8.50 (s, 1 H, H-2).

^{13}C NMR (101 MHz, DMSO-d_6): δ = –0.94 (CH_3Si), 17.55 (OCH_2CH_2Si), 54.11 (CH_3O) , 66.18 (OCH_2CH_2Si), 73.07 (NCH_2O), 102.38 (C-4a), 109.88 (C-5), 124.88 (CH-6), 125.46 (CH-5-thienyl), 126.17 (CH-3-thienyl), 128.18 (CH-4-thienyl), 135.86 (C-2-thienyl), 151.78 (CH-2), 152.84 (C-7a), 163.10 (C-4).

MS (EI): *m*/*z* (%) = 361.1 (100) [M].

HRMS (EI): *m*/*z* [M] calcd for $C_{17}H_{23}N_3O_2SiS$: 361.1280; found: 361.1284.

4-Methoxy-5-(thiophen-3-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (25d)

Compound **25d** was prepared from **9** (700 mg, 1.73 mmol) and thiophene-3-boronic acid (245 mg, 1.90 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (612 mg, 98%) as a yellowish oil.

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.85 (m, 2 H, OCH_2CH_2Si), 3.54 (m, 2 H, OCH_2CH_2Si), 4.10 (s, 3 H, CH_3O), 5.61 (s, 2 H, NCH_2O), 7.54 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.58 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 2.9 Hz, 1 H, H-5-thienyl), 7.87 (dd, $J_{2,5}$ = 2.7 Hz, $J_{2,4}$ = 1.5 Hz, 1 H, H-2-thienyl), 7.92 (s, 1 H, H-6), 8.48 (s, 1 H, H-2).

^{13}C NMR (101 MHz, DMSO-d_6): δ = –0.94 (CH_3Si), 17.55 (OCH_2CH_2Si), 54.16 (CH_3O), 66.13 (OCH_2CH_2Si), 73.05 (NCH_2O), 102.58 (C-4a), 111.70 (C-5), 121.71 (CH-2-thienyl), 125.62 (CH-6), 126.25 (CH-5-thienyl), 128.20 (CH-4-thienyl), 134.27 (C-3-thienyl), 151.49 (CH-2), 152.93 (C-7a), 163.10 (C-4).

MS (EI): *m*/*z* (%) = 361.1 (100) [M].

HRMS (EI): *m*/*z* [M] calcd for $C_{17}H_{23}N_3O_2SiS$: 361.1280; found: 361.1281.

5-(Benzofuran-2-yl)-4-methoxy-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (25e)

Compound **25e** was prepared from **9** (700 mg, 1.73 mmol) and benzofuran-2-boronic acid (308 mg, 1.90 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (627 mg, 92%) as a yellowish powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 3.58 (m, 2 H, OCH_2CH_2Si), 4.19 (s, 3 H, CH_3O), 5.67 (s, 2 H, NCH_2O), 7.27 (m, 2 H, H-5-benzofuryl, H-6-benzofuryl), 7.43 (d, $J_{3,7}$ = 0.8 Hz, 1 H, H-3-benzofuryl), 7.56 (m, 1 H, H-7-benzofuryl), 7.66 (ddd, $J_{4,5}$= 7.3 Hz, $J_{4,6}$ = 1.6 Hz, $J_{4,7}$ = 0.7 Hz, 1 H, H-4-benzofuryl), 8.13 (s, 1 H, H-6), 8.55 (s, 1 H, H-2).

^{13}C NMR (101 MHz, DMSO-d_6): δ = –0.94 (CH_3Si), 17.58 (OCH_2CH_2Si), 54.49 (CH_3O), 66.30 (OCH_2CH_2Si), 73.37 (NCH_2O), 101.73 (C-4a), 103.56 (CH-3-benzofuryl), 106.36 (C-5), 110.98 (CH-7-benzofuryl), 121.32 (CH-4-benzofuryl), 123.46 (CH-6-benzofuryl), 124.53 (CH-6), 126.28 (CH-5-benzofuryl), 129.67 (C-3a-benzofuryl), 150.91 (C-2-benzofuryl), 152.31 (CH-2), 153.22 (C-7a), 154.05 (C-7a-benzofuryl), 163.09 (C-4).

MS (EI): *m*/*z* (%) = 395.2 (100) [M], 396.2 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{21}H_{25}N_3O_3Si$: 395.1665; found: 395.1663.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-methoxy-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (25f)

Compound **25f** was prepared from **9** (700 mg, 1.73 mmol) and dibenzo[*b*,*d*]furan-4-boronic acid (405 mg, 1.90 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (725 mg, 94%) as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.01 (s, 9 H, CH_3Si), 1.04–0.98 (m, 2 H, OCH_2CH_2Si), 3.72–3.66 (m, 2 H, OCH_2CH_2Si), 4.09 (s, 3 H, CH_3O), 5.78 (s, 2 H, NCH_2O), 7.39 (btd, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{10}H_7O$), 7.51–7.43 (m, 2 H, H-2-$C_{10}H_7O$, H-7-$C_{10}H_7O$), 7.61 (dt, J = 8.3, 0.9 Hz, $J_{6,7}$ = 8.3 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{10}H_7O$), 7.91 (s, 1 H, H-6), 7.94 (m, 2 H, H-1-$C_{10}H_7O$, H-3-$C_{10}H_7O$), 8.01 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz , $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{10}H_7O$), 8.59 (s, 1 H, H-2).

^{13}C NMR (101 MHz, DMSO-d_6): δ = –0.91 (CH_3Si), 17.64 (OCH_2CH_2Si), 54.09 (CH_3O), 66.31 (OCH_2CH_2Si), 73.28 (NCH_2O), 103.67 (C-4a), 109.89 (C-5), 112.02 (CH-6-$C_{10}H_7O$), 118.86 (CH-1-$C_{10}H_7O$), 119.86 (C-4-$C_{10}H_7O$), 121.68 (CH-9-$C_{10}H_7O$), 123.42 (CH-2-$C_{10}H_7O$), 123.55 (CH-8-$C_{10}H_7O$), 124.09 (C-9b-$C_{10}H_7O$), 124.23 (C-9a-$C_{10}H_7O$), 127.80 (CH-6), 128.00 (CH-7-$C_{10}H_7O$), 129.19 (CH-3-$C_{10}H_7O$), 151.64 (CH-2), 152.85 (C-7a), 153.52 (C-4a-$C_{10}H_7O$), 155.85 (C-5a-$C_{10}H_7O$), 163.26 (C-4).

MS (ESI): *m*/*z* (%) = 446.2 (53) [M + H], 468.2 (47) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{25}H_{27}O_3N_3NaSi$: 468.1713; found: 468.1714.

4-Methoxy-5-phenyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (25g)

Compound **25g** was prepared from **9** (450 mg, 1.11 mmol) and phenylboronic acid (154 mg, 1.26 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (330 mg, 84%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.02 (s, 9 H, CH_3Si), 0.97 (m, 2 H, OCH_2CH_2Si), 3.61 (m, 2 H, OCH_2CH_2Si), 4.12 (s, 3 H, CH_3O), 5.69 (s, 2 H, NCH_2O), 7.31 (s, 1 H, H-6), 7.35 (m, 1 H, H-*p*-Ph), 7.44 (m, 2 H, H-*m*-Ph), 7.69 (m, 2 H, H-*o*-Ph), 8.54 (s, 1 H, H-2).

^{13}C NMR (101 MHz, $CDCl_3$): δ = –1.42 (CH_3Si), 17.76 (OCH_2CH_2Si), 53.71 (CH_3O), 66.53 (OCH_2CH_2Si), 73.09 (NCH_2O), 103.38 (C-4a), 117.98 (C-5), 123.56 (CH-6), 126.70 (CH-*p*-Ph), 128.20 (CH-*m*-Ph), 128.80 CH-*o*-Ph), 133.89 (C-*i*-Ph), 151.29 (CH-2), 153.03 (C-7a), 163.51 (C-4).

MS (EI): *m*/*z* (%) = 355.2 (100) [M], 356.2 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{19}H_{25}N_3O_2Si$: 355.1716; found: 355.1718.

5-(Furan-2-yl)-4-(methylsulfanyl)-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (26a)

Compound **26a** was prepared from **10** (700 mg, 1.66 mmol) and 2-(tributylstannyl)furan (0.43 mL, 1.99 mmol) by GPB. Flash column chromatography (0–5% EtOAc/PE) gave the product (492 mg, 82%) as a brown oil.

^{1}H NMR (401 MHz, $CDCl_3$): δ = –0.02 (s, 9 H, CH_3Si), 0.95 (m, 2 H, OCH_2CH_2Si), 2.68 (s, 3 H, CH_3S), 3.59 (m, 2 H, OCH_2CH_2Si), 5.66 (s, 2 H, NCH_2O), 6.54 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 6.74 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.7 Hz, 1 H, H-3-furyl), 7.46 (s, 1 H, H-6), 7.56 (dd, $J_{5,4}$ = 1.8 Hz, $J_{5,3}$ = 0.8 Hz, 1 H, H-5-furyl), 8.71 (s, 1 H, H-2).

^{13}C NMR (101 MHz, $CDCl_3$): δ = –1.42 (CH_3Si), 12.63 (CH_3S), 17.74 (OCH_2CH_2Si), 66.68 (OCH_2CH_2Si), 72.95 (NCH_2O), 107.87 (C-5), 109.05 (CH-3-furyl), 111.27 (CH-4-furyl), 113.82 (C-4a), 125.73 (CH-6), 142.06 (CH-5-furyl), 147.13 (C-2-furyl), 149.29 (C-7a), 151.14 (CH-2), 162.62 (C-4).

MS (EI): *m*/*z* (%) = 361.1 (100) [M], 362.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{17}H_{23}N_3O_2SiS$: 361.1280; found: 361.1281.

5-(Furan-3-yl)-4-(methylsulfanyl)-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (26b)

Compound **26b** was prepared from **10** (500 mg, 1.19 mmol) and furan-3-boronic acid (147 mg, 1.35 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (395 mg, 93%) as a yellowish oil.

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.08 (s, 9 H, CH_3Si), 0.85 (m, 2 H, OCH_2CH_2Si), 2.59 (s, 3 H, CH_3S), 3.55 (m, 2 H, OCH_2CH_2Si), 5.61 (s, 2 H, NCH_2O), 7.69 (s, 1 H, H-6), 6.73 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.77 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 7.88 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.8 Hz, 1 H, H-2-furyl), 8.68 (s, 1 H, H-2).

^{13}C NMR (101 MHz, DMSO-d_6): δ = –0.93 (CH_3Si), 12.31 (CH_3S), 17.56 (OCH_2CH_2Si), 66.22 (OCH_2CH_2Si), 72.82 (NCH_2O), 106.98 (C-5), 113.27 (CH-4-furyl), 114.34 (C-4a), 117.88 (C-3-furyl), 127.50 (CH-6), 141.14 (CH-2-furyl), 143.53 (CH-5-furyl), 149.29 (C-7a), 151.08 (CH-2), 161.62 (C-4).

MS (EI): *m*/*z* (%) = 361.1 (100) [M], 362.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{17}H_{23}N_3O_2SiS$: 361.1280; found: 361.1281.

4-(Methylsulfanyl)-5-(thiophen-2-yl)-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (26c)

Compound **26c** was prepared from **10** (700 mg, 1.66 mmol) and 2-(tributylstannyl)thiophene (0.62 mL, 1.99 mmol) by GPB. Flash column chromatography (0–5% EtOAc/PE) gave the product (474 mg, 76%) as a brown oil.

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.08 (s, 9 H, CH_3Si), 0.85 (m, 2 H, OCH_2CH_2Si), 2.56 (s, 3 H, CH_3S), 3.59 (m, 2 H, OCH_2CH_2Si), 5.63 (s, 2 H, NCH_2O), 7.16 (dd, $J_{4,5}$ = 5.2 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.23 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.59 (dd, $J_{5,4}$ = 5.2 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.79 (s, 1 H, H-6), 8.71 (s, 1 H, H-2).

^{13}C NMR (101 MHz, DMSO-d_6): δ = –0.92 (CH_3Si), 12.32 (CH_3S), 17.57 (OCH_2CH_2Si), 66.32 (OCH_2CH_2Si), 72.96 (NCH_2O), 108.87 (C-4a), 114.34 (C-5), 126.72 (CH-6), 127.93 (CH-5-thienyl), 128.71 (CH-3-thienyl), 128.99 (CH-4-thienyl), 134.16 (C-2-thienyl), 149.08 (CH-2), 151.30 (C-7a), 161.88 (C-4).

MS (EI): *m*/*z* (%) = 377.1 (100) [M], 378.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{17}H_{23}N_3OSiS_2$: 377.1052; found: 377.1053.

4-(Methylsulfanyl)-5-(thiophen-3-yl)-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (26d)

Compound **26d** was prepared from **10** (700 mg, 1.66 mmol) and thiophene-3-boronic acid (255 mg, 1.82 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (584 mg, 93%) as a straw oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 2.56 (s, 3 H, CH_3S), 3.55 (m, 2 H, OCH_2CH_2Si), 5.61 (s, 2 H, NCH_2O), 7.28 (dd, $J_{4,5}$ = 4.9 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.56 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 7.62 (dd, $J_{5,4}$ = 4.9 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 7.70 (s, 1 H, H-6), 8.67 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.17 (CH_3Si), 12.12 (CH_3S), 17.32 (OCH_2CH_2Si), 66.00 (OCH_2CH_2Si), 72.63 (NCH_2O), 111.33 (C-5), 114.01 (C-4a), 124.02 (CH-2-thienyl), 125.79 (CH-5-thienyl), 127.31 (CH-6), 130.01 (CH-4-thienyl), 133.48 (C-3-thienyl), 148.84 (C-7a), 150.80 (CH-2), 161.41 (C-4).

MS (EI): *m*/*z* (%) = 377.1 (100) [M], 378.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{17}H_{23}N_3OSiS_2$: 377.1052; found: 377.1058.

5-(Benzofuran-2-yl)-4-(methylsulfanyl)-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (26e)

Compound **26e** was prepared from **10** (500 mg, 1.19 mmol) and benzofuran-2-boronic acid (218 mg, 1.35 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (425 mg, 87%) as a yellow oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.10 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 2.61 (s, 3 H, CH_3S), 3.57 (m, 2 H, OCH_2CH_2Si), 5.67 (s, 2 H, NCH_2O), 7.23 (d, $J_{3,7}$ = 0.9 Hz, 1 H, H-3-benzofuryl), 7.26 (btd, $J_{5,6}$ = $J_{5,4}$ = 7.4 Hz, $J_{5,7}$ = 1.1 Hz, 1 H, H-5-benzofuryl), 7.31 (bddd, $J_{6,7}$ = 8.1 Hz, $J_{6,5}$ = 7.2 Hz, $J_{6,4}$ = 1.5 Hz, 1 H, H-6-benzofuryl), 7.59 (m, 1 H, H-7-benzofuryl), 7.68 (m, 1 H, H-4-benzofuryl), 8.13 (s, 1 H, H-6), 8.73 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.20 (CH_3Si), 12.44 (CH_3S), 17.33 (OCH_2CH_2Si), 66.18 (OCH_2CH_2Si), 72.97 (NCH_2O), 104.98 (CH-3-benzofuryl), 105.81 (C-5), 111.12 (CH-7-benzofuryl), 113.12 (C-4a), 121.17 (CH-4-benzofuryl), 123.27 (CH-5-benzofuryl), 124.45 (CH-6-benzofuryl), 129.00 (C-3a-benzofuryl), 129.18 (CH-6), 149.31 (C-7a), 149.74 (C-2-benzofuryl), 151.33 (CH-2), 154.29 (C-7a-benzofuryl), 161.93 (C-4).

MS (EI): *m*/*z* (%) = 411.1 (100) [M], 412.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{21}H_{25}N_3O_2SiS$: 411.1437; found: 411.1440.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-(methylsulfanyl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (26f)

Compound **26f** was prepared from **10** (550 mg, 1.30 mmol) and dibenzo[*b*,*d*]furan-4-boronic acid (303 mg, 1.43 mmol) by GPA″. Flash column chromatography (0–5% EtOAc/PE) gave the product (598 mg, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.02 (s, 9 H, CH_3Si), 1.01 (m, 2 H, OCH_2CH_2Si), 2.53 (s, 3 H, CH_3S), 3.69 (m, 2 H, OCH_2CH_2Si), 7.39 (btd, $J_{8,9}$ = $J_{8,7}$ = 7.6 Hz, $J_{8,6}$ = 0.9 Hz, 1 H, H-8-$C_{10}H_7O$), 7.47 (m, 2 H, H-2-$C_{10}H_7O$ and H-7-$C_{10}H_7O$), 7.53 (s, 1 H, H-6), 7.61 (bdt, $J_{6,7}$ = 8.0 Hz, $J_{6,8}$ = $J_{6,9}$ = 1.0 Hz, 1 H, H-6-$C_{10}H_7O$), 7.61 (dd, $J_{3,2}$ = 7.7 Hz, $J_{3,1}$ = 1.4 Hz, 1 H, H-3-$C_{10}H_7O$), 8.03 (m, 2 H, H-1-$C_{10}H_7O$, H-9-$C_{10}H_7O$), 8.78 (s, 1 H, H-2).

^{13}C NMR (101 MHz, $CDCl_3$): δ = –1.35 (CH_3Si), 12.43 (CH_3S), 17.82 (OCH_2CH_2Si), 66.77 (OCH_2CH_2Si), 73.11 (NCH_2O), 111.33 (C-5), 111.87 (CH-6-$C_{10}H_7O$), 115.45 (C-4a), 118.31 (C-4-$C_{10}H_7O$), 120.09 (CH-1-$C_{10}H_7O$), 120.79 (CH-9-$C_{10}H_7O$), 122.44 (CH-2-$C_{10}H_7O$), 122.81 (CH-8-$C_{10}H_7O$), 124.25 (C-9b-$C_{10}H_7O$), 124.45 (C-9a-$C_{10}H_7O$), 126.42 (CH-6), 127.20 (CH-7-$C_{10}H_7O$), 129.88 (CH-3-$C_{10}H_7O$), 149.27 (C-7a), 151.07 (CH-2), 154.63 (C-4a-$C_{10}H_7O$), 156.20 (C-5a-$C_{10}H_7O$), 162.84 (C-4).

MS (EI): *m*/*z* (%) = 461.1 (100) [M], 462.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{25}H_{27}N_3O_2SSi$: 461.1593; found: 461.1595.

4-(Methylsulfanyl)-5-phenyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (26g)

Compound **26g** was prepared from **10** (300 mg, 0.72 mmol) and phenylboronic acid (154 mg, 1.08 mmol) by GPA″. Thecrude yellowish oil (251 mg, 94%) obtained was used in the next step without additional purification.

MS (ESI): *m*/*z* (%) = 394.1 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{19}H_{25}ON_3NaSSi$: 394.1379; found: 394.1380.

5-(Furan-2-yl)-4-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (27a)

Compound **27a** was prepared from **12** (200 mg, 0.51 mmol) and furan-2-boronic acid (72 mg, 0.64 mmol) by GPA‴. Column chromatography (silica gel, hexane/EtOAc 10:1) gave the product (153 mg, 91%) as a yellowish amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.05 (s, 9 H, CH_3Si), 0.93 (m, 2 H, OCH_2CH_2Si), 2.76 (s, 3 H, CH_3-4), 3.56 (m, 2 H, OCH_2CH_2Si), 5.66 (s, 2 H, NCH_2O), 6.49 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 6.51 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 7.47 (s, 1 H, H-6), 7.54 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 8.79 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.47 (CH_3Si), 17.70 (OCH_2CH_2Si), 23.22 (CH_3-4), 66.69 (OCH_2CH_2Si), 72.77 (NCH_2O), 107.89 (C-5), 108.10 (CH-3-furyl), 111.25 (CH-4-furyl), 115.59 (C-4a), 126.58 (CH-6), 142.18 (CH-5-furyl), 147.82 (C-2-furyl), 151.24 (C-7a), 151.87 (CH-2), 160.56 (C-4).

MS (ESI): *m*/*z* (%) = 330.2 (100) [M + H], 352.2 (13) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{24}O_2N_3Si$: 330.16323; found: 330.16336.

5-(Furan-3-yl)-4-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (27b)

Compound **27b** was prepared from **12** (200 mg, 0.51 mmol) and furan-3-boronic acid (72 mg, 0.64 mmol) by GPA‴. Column chromatography (silica gel, hexane/EtOAc 10:1) gave the product (167 mg, 99%) as a white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.05 (s, 9 H, CH_3Si), 0.93 (m, 2 H, OCH_2CH_2Si), 2.66 (s, 3 H, CH_3-4), 3.56 (m, 2 H, OCH_2CH_2Si), 5.65 (s, 2 H, NCH_2O), 7.55 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 1.0 Hz, 1 H, H-4-furyl), 7.26 (s, 1 H, H-6), 7.52–7.54 (m, 2 H, H-2,5-furyl), 8.78 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.47 (CH_3Si), 17.69 (OCH_2CH_2Si), 22.65 (CH_3-4), 66.60 (OCH_2CH_2Si), 72.62 (NCH_2O), 108.10 (C-5), 112.69 (CH-4-furyl), 116.51 (C-4a), 118.27 (C-3-furyl), 126.10 (CH-6), 140.29 (CH-2-furyl), 143.07 (CH-5-furyl), 151.31 (C-7a), 151.60 (CH-2), 160.04 (C-4).

MS (ESI): *m*/*z* (%) = 330.0 (100) [M + H], 352.2 (12) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{24}O_2N_3Si$: 330.16323; found: 330.16330.

4-Methyl-5-(thiophen-2-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (27c)

Compound **27c** was prepared from **12** (200 mg, 0.51 mmol) and thiophene-2-boronic acid (82 mg, 0.64 mmol) by GPA‴. Column chromatography (silica gel, hexane/EtOAc 10:1) gave the product (172 mg, 98%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.94 (m, 2 H, OCH_2CH_2Si), 2.63 (s, 3 H, CH_3-4), 3.58 (m, 2 H, OCH_2CH_2Si), 5.66 (s, 2 H, NCH_2O), 7.10 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.3 Hz, 1 H, H-3-thienyl), 7.11 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.36 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.3 Hz, 1 H, H-5-thienyl), 7.36 (s, 1 H, H-6), 8.80 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.70 (OCH_2CH_2Si), 22.78 (CH_3-4), 66.71 (OCH_2CH_2Si), 72.72 (NCH_2O), 110.14 (C-5), 116.49 (C-4a), 125.66 (CH-5-thienyl), 127.29 (CH-6, CH-4-thienyl), 127.94 (CH-3-thienyl), 134.97 (C-2-thienyl), 151.05 (C-7a), 151.80 (CH-2), 160.34 (C-4).

MS (ESI): *m*/*z* (%) = 346.0 (100) [M + H], 368.0 (17) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{24}ON_3SSi$: 346.14039; found: 346.14045.

4-Methyl-5-(thiophen-3-yl)-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (27d)

Compound **27d** was prepared from **12** (200 mg, 0.51 mmol) and thiophene-3-boronic acid (82 mg, 0.64 mmol) by GPA‴. Column chromatography (silica gel, hexane/EtOAc 10:1) gave the product (168 mg, 94%) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.05 (s, 9 H, CH_3Si), 0.93 (m, 2 H, OCH_2CH_2Si), 2.58 (s, 3 H, CH_3-4), 3.57 (m, 2 H, OCH_2CH_2Si), 5.66 (s, 2 H, NCH_2O), 7.18 (dd, $J_{4,5}$ = 4.9 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.28 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 7.29 (s, 1 H, H-6), 7.42 (dd, $J_{5,4}$ = 4.9 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 8.78 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.70 (OCH_2CH_2Si), 22.79 (CH_3-4), 66.61 (OCH_2CH_2Si), 72.65 (NCH_2O), 112.71 (C-5), 116.42 (C-4a), 123.29 (CH-2-thienyl), 125.51 (CH-5-thienyl), 126.00 (CH-6), 129.57 (CH-4-thienyl), 134.30 (C-3-thienyl), 151.10 (C-7a), 151.65 (CH-2), 160.11 (C-4).

MS (ESI): *m*/*z* (%) = 346.1 (100) [M + H], 368.1 (9) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{24}ON_3SSi$: 346.14039; found: 346.14044.

5-(Benzofuran-2-yl)-4-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (27e)

Compound **27e** was prepared from **12** (200 mg, 0.51 mmol) and benzofuran-2-boronic acid (104 mg, 0.64 mmol) by GPA‴. Purification by HPFC (silica gel, gradient 0–100% EtOAc/hexane) gave the product (164 mg, 84%) as a beige amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.04 (s, 9 H, CH_3Si), 0.95 (m, 2 H, OCH_2CH_2Si), 2.88 (s, 3 H, CH_3-4), 3.59 (m, 2 H, OCH_2CH_2Si), 5.71 (s, 2 H, NCH_2O), 6.88 (d, $J_{3,7}$ = 1.0 Hz, 1 H, H-3-benzofuryl), 7.27 (td, $J_{5,6}$ = $J_{5,4}$ = 7.4 Hz, $J_{5,7}$ = 1.1 Hz, 1 H, H-5-benzofuryl), 7.21 (bddd, $J_{6,7}$ = 8.0 Hz, $J_{6,5}$ = 7.2 Hz, $J_{6,4}$ = 1.5 Hz, 1 H, H-6-benzofuryl), 7.53 (dq, $J_{7,6}$ = 8.0 Hz, $J_{7,5}$ = $J_{7,4}$ = $J_{7,3}$ = 1.0 Hz, 1 H, H-7-benzofuryl), 7.62 (ddd, $J_{4,5}$ = 7.5 Hz, $J_{4,6}$ = 1.5 Hz, $J_{4,7}$ = 0.8 Hz, 1 H, H-4-benzofuryl), 7.67 (s, 1 H, H-6), 8.83 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.71 (OCH_2CH_2Si), 23.69 (CH_3-4), 66.82 (OCH_2CH_2Si), 72.90 (NCH_2O), 104.30 (CH-3-benzofuryl), 107.60 (C-5), 111.02 (CH-7-benzofuryl), 115.46 (C-4a), 120.73 (CH-4-benzofuryl), 123.03 (CH-5-benzofuryl), 124.16 (CH-6-benzofuryl), 127.71 (CH-6), 128.93 (C-3a-benzofuryl), 150.36 (C-2-benzofuryl), 151.49 (C-7a), 152.06 (CH-2), 154.80 (C-7a-benzofuryl), 160.67 (C-4).

MS (ESI): *m*/*z* (%) = 380.2 (100) [M + H], 402.1 (66) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{21}H_{26}O_2N_3Si$: 380.17888; found: 380.17902.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (27f)

Compound **27f** was prepared from **12** (200 mg, 0.51 mmol) and dibenzo[*b*,*d*]furan-4-boronic acid (136 mg, 0.64 mmol) by GPA‴. Purification by HPFC (silica gel, gradient 0–100% EtOAc/hexane) gave the product (174 mg, 79%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.02 (s, 9 H, CH_3Si), 0.97 (m, 2 H, OCH_2CH_2Si), 2.40 (s, 3 H, CH_3-4), 3.66 (m, 2 H, OCH_2CH_2Si), 5.75 (s, 2 H, NCH_2O), 7.38 (ddd, $J_{8,9}$ = 7.7 Hz, $J_{8,7}$ = 7.1 Hz, $J_{8,6}$ = 1.2 Hz, 1 H, H-8-$C_{10}H_7O$), 7.44 (t, $J_{2,1}$ = $J_{2,3}$ = 7.5 Hz, 1 H, H-2-$C_{10}H_7O$), 7.46 (ddd, $J_{7,6}$ = 8.2 Hz, $J_{7,8}$ = 7.1 Hz, $J_{7,9}$ = 1.3 Hz, 1 H, H-7-$C_{10}H_7O$), 7.49 (dd, $J_{3,2}$ = 7.4 Hz, $J_{3,1}$ = 1.4 Hz, 1 H, H-3-$C_{10}H_7O$), 7.51 (bdt, $J_{6,7}$ = 8.3 Hz, $J_{6,8}$ = $J_{6,9}$ = 1.0 Hz, 1 H, H-6-$C_{10}H_7O$), 7.51 (s, 1 H, H-6), 8.00 (dd, $J_{1,2}$ = 7.6 Hz, $J_{1,3}$ = 1.4 Hz, 1 H, H-1-$C_{10}H_7O$), 8.01 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{10}H_7O$), 8.55 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.42 (CH_3Si), 17.77 (OCH_2CH_2Si), 22.04 (CH_3-4), 66.76 (OCH_2CH_2Si), 72.92 (NCH_2O), 111.77 (C-5), 111.77 (CH-6-$C_{10}H_7O$), 116.96 (C-4a), 119.04 (C-4-$C_{10}H_7O$), 120.08 (CH-1-$C_{10}H_7O$), 120.83 (CH-9-$C_{10}H_7O$), 122.87 (CH-2-$C_{10}H_7O$), 122.98 (CH-8-$C_{10}H_7O$), 124.27 (C-9a-$C_{10}H_7O$), 124.42 (C-9b-$C_{10}H_7O$), 127.02 (CH-6), 127.41 (CH-7-$C_{10}H_7O$), 129.03 (CH-3-$C_{10}H_7O$), 151.32 (C-7a), 151.74 (CH-2), 154.33 (C-4a-$C_{10}H_7O$), 156.04 (C-5a-$C_{10}H_7O$), 160.60 (C-4).

MS (ESI): *m*/*z* (%) = 430.1 (100) [M + H], 452.1 (38) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{25}H_{28}O_2N_3Si$: 430.19453; found: 430.19450.

4-Methyl-5-phenyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidine (27g)

Compound **27g** was prepared from **12** (250 mg, 0.64 mmol) and phenylboronic acid (98 mg, 0.80 mmol) by GPA‴. Purification by HPFC (silica gel, gradient 0–100% EtOAc/hexane) gave the product (186 mg, 85%) as a white glassy solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = –0.05 (s, 9 H, CH_3Si), 0.94 (m, 2 H, OCH_2CH_2Si), 2.54 (s, 3 H, CH_3-4), 3.59 (m, 2 H, OCH_2CH_2Si), 5.68 (s, 2 H, NCH_2O), 7.27 (s, 1 H, H-6), 7.39 (m, 1 H, H-*p*-Ph), 7.41–7.47 (m, 4 H, H-*o*,*m*-Ph), 8.79 (s, 1 H, H-2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = –1.46 (CH_3Si), 17.71 (OCH_2CH_2Si), 23.08 (CH_3-4), 66.61 (OCH_2CH_2Si), 72.71 (NCH_2O), 116.23 (C-4a), 118.29 (C-5), 125.82 (CH-6), 127.33 (CH-*p*-Ph), 128.24 (CH-*m*-Ph), 129.96 (CH-*o*-Ph), 134.37 (C-*i*-Ph), 151.19 (C-7a), 151.59 (CH-2), 160.13 (C-4).

MS (ESI): *m*/*z* (%) = 340.2 (100) [M + H], 362.2 (20) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{26}ON_3Si$: 340.18397; found: 340.18398.

5-(Furan-2-yl)-4-methoxy-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (28a)

Compound **28a** was prepared from **13** (420 mg, 1.0 mmol) and furan-2-boronic acid (168 mg, 1.5 mmol) by GPA′. Flash column chromatography (30–40% EtOAc/hexanes) gave the product (256 mg, 71%) as a yellowish oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.08 (s, 9 H, CH_3Si), 0.83 (m, 2 H, OCH_2CH_2Si), 3.50 (m, 2 H, OCH_2CH_2Si), 3.99 (s, 3 H, CH_3O-4), 5.38 (s, 2 H, NCH_2O), 6.37 (bs, 2 H, NH_2), 6.50 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 6.82 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.30 (s, 1 H, H-6), 7.58 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.16 (CH_3Si), 17.35 (OCH_2CH_2Si), 53.27 (CH_3O-4), 65.43 (OCH_2CH_2Si), 72.37 (NCH_2O), 93.54 (C-4a), 106.49 (CH-3-furyl), 107.13 (C-5), 111.69 (CH-4-furyl), 119.55 (CH-6), 141.15 (CH-5-furyl), 149.16 (C-2-furyl), 155.37 (C-7a), 160.10 (C-2), 163.37 (C-4).

MS (ESI): *m*/*z* (%) = 361.2 (100) [M + H], 383.2 (40) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{25}N_4O_3Si$: 361.1690; found: 361.1691.

5-(Furan-3-yl)-4-methoxy-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (28b)

Compound **28b** was prepared from **13** (420 mg, 1.0 mmol) and furan-3-boronic acid (168 mg, 1.5 mmol) by GPA′. Flash column chromatography (30–40% EtOAc/hexanes) gave the product (263 mg, 73%) as a yellowish oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.07 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 3.49 (m, 2 H, OCH_2CH_2Si), 3.98 (s, 3 H, CH_3O-4), 5.35 (s, 2 H, NCH_2O), 6.30 (bs, 2 H, NH_2), 6.84 (dd, $J_{4,5}$ = 1.9 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.31 (s, 1 H, H-6), 7.64 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 8.02 (m, 1 H, H-2-furyl).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.16 (CH_3Si), 17.33 (OCH_2CH_2Si), 53.19 (CH_3O-4), 65.34 (OCH_2CH_2Si), 72.21 (NCH_2O), 94.74 (C-4a), 107.21 (C-5), 109.97 (CH-4-furyl), 119.14 (C-3-furyl), 120.36 (CH-6), 139.53 (CH-2-furyl), 143.51 (CH-5-furyl), 155.57 (C-7a), 159.93 (C-2), 163.37 (C-4).

MS (ESI): *m*/*z* (%) = 361.2 (100) [M + H], 383.2 (30) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{25}N_4O_3Si$: 361.1690; found: 361.1691.

5-(Thiophen-2-yl)-4-methoxy-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (28c)

Compound **28c** was prepared from **13** (420 mg, 1.0 mmol) and thiophene-2-boronic acid (192 mg, 1.5 mmol) by GPA′. Flash column chromatography (30–40% EtOAc/hexanes) gave the product (275 mg, 73%) as a yellowish oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.07 (s, 9 H, CH_3Si), 0.83 (m, 2 H, OCH_2CH_2Si), 3.51 (m, 2 H, OCH_2CH_2Si), 3.96 (s, 3 H, CH_3O-4), 5.37 (s, 2 H, NCH_2O), 6.36 (bs, 2 H, NH_2), 7.04 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, H-4-thienyl), 7.27 (s, 1 H, H-6), 7.34 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.40 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.17 (CH_3Si), 17.34 (OCH_2CH_2Si), 53.13 (CH_3O-4), 65.43 (OCH_2CH_2Si), 72.25 (NCH_2O), 94.70 (C-4a), 110.01 (C-5), 120.74 (CH-6), 123.57 (CH-5-thienyl), 125.02 (CH-3-thienyl), 127.76 (CH-4-thienyl), 136.79 (C-2-thienyl), 155.42 (C-7a), 159.95 (C-2), 163.44 (C-4).

MS (ESI): *m*/*z* (%) = 377.2 (100) [M + H], 399.2 (50) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{25}N_4O_2SSi$: 377.1462; found: 377.1462.

5-(Thiophen-3-yl)-4-methoxy-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (28d)

Compound **28d** was prepared from **13** (420 mg, 1.0 mmol) and thiophene-3-boronic acid (192 mg, 1.5 mmol) by GPA′. Flash column chromatography (30–40% EtOAc/hexanes) gave the product (286 mg, 76%) as a yellowish oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.07 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 3.51 (m, 2 H, OCH_2CH_2Si), 3.98 (s, 3 H, CH_3O-4), 5.37 (s, 2 H, NCH_2O), 6.31 (bs, 2 H, NH_2), 7.37 (s, 1 H, H-6), 7.45 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.50 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 7.77 (dd, $J_{2,5}$ = 2.9 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.16 (CH_3Si), 17.35 (OCH_2CH_2Si), 53.19 (CH_3O-4), 65.39 (OCH_2CH_2Si), 72.27 (NCH_2O), 94.86 (C-4a), 111.76 (C-5), 120.32 (CH-2-thienyl), 121.06 (CH-6), 125.58 (CH-5-thienyl), 127.71 (CH-4-thienyl), 134.93 (C-3-thienyl), 155.53 (C-7a), 159.79 (C-2), 163.43 (C-4).

MS (ESI): *m*/*z* (%) = 377.2 (100) [M + H], 399.2 (20) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{17}H_{25}N_4O_2SSi$: 377.1462; found: 377.1463.

5-(Benzofuran-2-yl)-4-methoxy-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (28e)

Compound **28e** was prepared from **13** (420 mg, 1.0 mmol) and benzofuran-2-boronic acid (243 mg, 1.5 mmol) by GPA′. Flash column chromatography (40–50% EtOAc/hexanes) gave the product (287 mg, 70%) as a yellowish oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.07 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 3.54 (m, 2 H, OCH_2CH_2Si), 4.07 (s, 3 H, CH_3O-4), 5.43 (s, 2 H, NCH_2O), 6.46 (bs, 2 H, NH_2), 7.21 (btd, $J_{5,4}$ = $J_{5,6}$ = 7.2 Hz, $J_{5,7}$ = 1.2 Hz, 1 H, H-5-benzofuryl), 7.24 (bddd, $J_{6,7}$ = 8.2 Hz, $J_{6,5}$ = 7.3 Hz, $J_{6,4}$ = 1.5 Hz,

1 H, H-6-benzofuryl), 7.31 (d, $J_{3,7}$ = 1.1 Hz, 1 H, H-3-benzofuryl), 7.50 (dm, $J_{7,6}$ = 8.2 Hz, 1 H, H-7-benzofuryl), 7.60 (s, 1 H, H-6), 7.61 (dm, $J_{4,5}$ = 7.3 Hz, 1 H, H-4-benzofuryl).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.16 (CH_3Si), 17.37 (OCH_2CH_2Si), 53.47 (CH_3O-4), 65.57 (OCH_2CH_2Si), 72.56 (NCH_2O), 93.74 (C-4a), 102.39 (CH-3-benzofuryl), 106.39 (C-5), 110.55 (CH-7-benzofuryl), 120.78 (CH-4-benzofuryl), 121.96 (CH-6), 123.04 (CH-5-benzofuryl), 123.89 (CH-6-benzofuryl), 129.60 (C-3a-benzofuryl), 151.62 (C-2-benzofuryl), 153.65 (C-7a-benzofuryl), 155.81 (C-7a), 160.33 (C-2), 163.40 (C-4).

MS (ESI): *m*/*z* (%) = 411.2 (100) [M + H], 433.1 (50) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{21}H_{27}N_4O_3Si$: 411.1846; found: 411.1848.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-methoxy-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (28f)

Compound **28f** was prepared from **13** (420 mg, 1.0 mmol) and dibenzo[*b*,*d*]furan-4-boronic acid (318 mg, 1.5 mmol) by GPA′. Flash column chromatography (40–50% EtOAc/hexanes) gave the product (299 mg, 65%) as a colorless oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.05 (s, 9 H, $(CH_3)_3Si$), 0.87 (m, 2 H, CH_2-3″), 3.60 (m, 2 H, CH_2-2″), 3.84 (s, 3 H, CH_3O-4), 5.49 (s, 2 H, CH_2-1″), 6.38 (bs, 2 H, NH_2-2), 7.40 (m, 1 H, CH-8′), 7.42 (t, $J_{2',1'}$ = $J_{2',3'}$ = 7.7 Hz, 1 H, CH-2′), 7.52 (ddd, $J_{7',6'}$ = 8.3 Hz, $J_{7',8'}$ = 7.3 Hz, $J_{7',9'}$ = 1.4 Hz, 1 H, CH-7′), 7.59 (s, 1 H, CH-6), 7.67 (dt, $J_{6',7'}$ = 8.3 Hz, $J_{6',8'}$ = $J_{6',9'}$ = 0.8 Hz, 1 H, CH-6′), 7.80 (dd, $J_{3',2'}$ = 7.7 Hz, $J_{3',1'}$ = 1.3 Hz, 1 H, CH-3′), 8.01 (dd, $J_{1',2'}$ = 7.7 Hz, $J_{1',3'}$ = 1.3 Hz, 1 H, CH-1′), 8.16 (ddd, $J_{9',8'}$ = 7.7 Hz, $J_{9',7'}$ = 1.3 Hz, $J_{9',6'}$ = 0.8 Hz, 1 H, CH-9′).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.12 (($CH_3)_3Si$), 17.46 (CH_2-3″), 53.20 (CH_3O-4), 65.59 (CH_2-2″), 72.53 (CH_2-1″), 95.81 (C-4a), 110.02 (C-5), 111.75 (CH-6′), 118.92 (CH-1′), 119.54 (C-4′), 121.36 (CH-9′), 123.11 (CH-2′/8′), 123.24 (CH-2′/8′), 123.44 (CH-6), 123.72 (C-9a′/9b′), 124.07 (C-9a′/9b′), 127.66 (CH-7′), 128.55 (CH-3′), 153.12 (C-4a′), 155.46 (C-5a′/7a), 155.56 (C-5a′/7a), 159.97 (C-2), 163.63 (C-4).

MS (ESI): *m*/*z* (%) = 461.2 (65) [M + H], 483.2 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{25}H_{28}N_4O_3NaSi$: 483.1822; found: 483.1821.

4-Methoxy-5-phenyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (28g)

Compound **28g** was prepared from **13** (420 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) by GPA′. Flash column chromatography (40–50% EtOAc/hexanes) gave the product (252 mg, 68%) as a yellowish oil.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.07 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 3.53 (m, 2 H, OCH_2CH_2Si), 3.90 (s, 3 H, CH_3O-4), 5.39 (s, 2 H, NCH_2O), 6.31 (s, 2 H, NH_2), 7.22 (s, 1 H, H-6), 7.23 (m, 1 H, H-*p*-Ph), 7.36 (m, 2 H, H-*m*-Ph), 7.60 (m, 2 H, H-*o*-Ph).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.16 (CH_3Si), 17.37 (OCH_2CH_2Si), 53.12 (CH_3O-4), 65.45 (OCH_2CH_2Si), 72.35 (NCH_2O), 95.12 (C-4a), 116.68 (C-5), 121.20 (CH-6), 126.12 (CH-*p*-Ph), 128.11 and 128.25 (CH-*m*,*o*-Ph), 134.72 (C-*i*-Ph), 155.69 (C-7a), 159.77 (C-2), 163.55 (C-4).

MS (ESI): *m*/*z* (%) = 371.2 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{27}N_4O_2Si$: 371.1897; found: 371.1899.

5-(Furan-2-yl)-4-methoxy-2-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (29a)

Compound **29a** was prepared from **14** (419 mg, 1.0 mmol) and furan-2-boronic acid (168 mg, 1.5 mmol) by GPA′. Flash column chromatography (0–5% EtOAc/hexanes) gave the product (246 mg, 68%) as a colorless oil.

IR (KBr): 3119, 2954, 1743, 1590, 1424, 1249, 1084, 920, 837, 697 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.10 (s, 9 H, CH_3Si), 0.83 (m, 2 H, OCH_2CH_2Si), 2.56 (s, 3 H, CH_3-2), 3.53 (m, 2 H, OCH_2CH_2Si), 4.07 (s, 3 H, CH_3O-4), 5.56 (s, 2 H, NCH_2O), 6.54 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 6.90 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.64 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 7.71 (s, 1 H, H-6).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.26 (CH_3Si), 17.27 (OCH_2CH_2Si), 25.69 (CH_3-2), 53.70 (CH_3O-4), 65.76 (OCH_2CH_2Si), 72.67 (NCH_2O), 98.78 (C-4a), 106.71 (C-5), 107.12 (CH-3-furyl), 111.81 (CH-4-furyl), 123.00 (CH-6), 141.60 (CH-5-furyl), 148.46 (C-2-furyl), 153.31 (C-7a), 160.76 (C-2), 162.49 (C-4).

MS (ESI): *m*/*z* (%) = 360.2 (100) [M + H], 382.2 (40) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{26}N_3O_3Si$: 360.1738; found: 360.1738.

5-(Furan-3-yl)-4-methoxy-2-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (29b)

Compound **29b** was prepared from **14** (419 mg, 1.0 mmol) and furan-3-boronic acid (168 mg, 1.5 mmol) by GPA′. Flash column chromatography (0–5% EtOAc/hexanes) gave the product (274 mg, 76%) as a yellowish oil.

IR (KBr): 3115, 2951, 1756, 1591, 1462, 1253, 1097, 932, 851, 700 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.10 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 2.56 (s, 3 H, CH_3-2), 3.52 (m, 2 H, OCH_2CH_2Si), 4.06 (s, 3 H, CH_3O-4), 5.53 (s, 2 H, NCH_2O), 6.91 (dd, $J_{4,5}$ = 1.9 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.68 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 7.73 (s, 1 H, H-6), 8.09 (m, 1 H, H-2-furyl).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.23 (CH_3Si), 17.27 (OCH_2CH_2Si), 25.72 (CH_3-2), 53.65 (CH_3O-4), 65.70 (OCH_2CH_2Si), 72.51 (NCH_2O), 99.92 (C-4a), 106.90 (C-5), 110.10 (CH-4-furyl), 118.63 (C-3-furyl), 123.90 (CH-6), 139.93 (CH-2-furyl), 143.48 (CH-5-furyl), 153.54 (C-7a), 160.42 (C-2), 162.52 (C-4).

MS (ESI): *m*/*z* (%) = 360.2 (100) [M + H], 382.2 (90) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{26}N_3O_3Si$: 360.1738; found: 360.1739.

4-Methoxy-2-methyl-5-(thiophen-2-yl)-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (29c)

Compound **29c** was prepared from **14** (419 mg, 1.0 mmol) and thiophen-2-boronic acid (192 mg, 1.5 mmol) by GPA′. Flash column chromatography (0–5% EtOAc/hexanes) gave the product (301 mg, 80%) as a pinkish oil.

IR (KBr): 3107, 2950, 1747, 1556, 1414, 1277, 1086, 978, 838, 697 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 2.57 (s, 3 H, CH_3-2), 3.54 (m, 2 H, OCH_2CH_2Si), 4.01 (s, 3 H, CH_3O-4), 5.55 (s, 2 H, NCH_2O), 7.08 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, H-4-thienyl), 7.41 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.46 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.70 (s, 1 H, H-6).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.27 (CH_3Si), 17.25 (OCH_2CH_2Si), 25.68 (CH_3-2), 53.54 (CH_3O-4), 65.77 (OCH_2CH_2Si), 72.54 (NCH_2O), 99.80 (C-4a), 109.52 (C-5), 124.30 (CH-6, CH-5-thienyl), 125.65 (CH-3-thienyl), 127.86 (CH-4-thienyl), 135.90 (C-2-thienyl), 153.34 (C-7a), 160.55 (C-2), 162.53 (C-4).

MS (ESI): *m*/*z* (%) = 376.1 (100) [M + H], 398.1 (40) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{26}N_3O_2SSi$: 376.1509; found: 376.1510.

4-Methoxy-2-methyl-5-(thiophen-3-yl)-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (29d)

Compound **29d** was prepared from **14** (419 mg, 1.0 mmol) and thiophen-3-boronic acid (192 mg, 1.5 mmol) by GPA′. Flash column chromatography (0–5% EtOAc/hexanes) gave the product (331 mg, 88%) as a greenish oil.

IR (KBr): 3130, 2951, 1599, 1556, 1344, 1209, 1089, 926, 776, 697 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.10 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 2.56 (s, 3 H, CH_3-2), 3.53 (m, 2 H, OCH_2CH_2Si), 4.05 (s, 3 H, CH_3O-4), 5.54 (s, 2 H, NCH_2O), 7.51 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.54 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 2.9 Hz, 1 H, H-5-thienyl), 7.77 (s, 1 H, H-6), 7.84 (dd, $J_{2,5}$ = 2.9 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.27 (CH_3Si), 17.25 (OCH_2CH_2-Si), 25.68 (CH_3-2), 53.54 (CH_3O-4), 65.77 (OCH_2CH_2Si), 72.54 (NCH_2O), 99.80 (C-4a), 109.52 (C-5), 124.30 (CH-6, CH-5-thienyl), 125.65 (CH-3-thienyl), 127.86 (CH-4-thienyl), 135.90 (C-2-thienyl), 153.34 (C-7a), 160.55 (C-2), 162.53 (C-4).

MS (ESI): *m*/*z* (%) = 376.2 (100) [M + H], 398.1 (40) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{26}N_3O_2SSi$: 376.1509; found: 376.1510.

5-(Benzofuran-2-yl)-4-methoxy-2-methyl-7-{[2-(trimethylsilyl)-ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (29e)

Compound **29e** was prepared from **14** (419 mg, 1.0 mmol) and benzofuran-2-boronic acid (243 mg, 1.5 mmol) by GPA′. Flash column chromatography (5–10% EtOAc/hexanes) gave the product (312 mg, 76%) as a colorless oil.

IR (KBr): 3059, 2950, 1593, 1463, 1347, 1249, 1093, 862, 750, 696 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.09 (s, 9 H, CH_3Si), 0.85 (m, 2 H, OCH_2CH_2Si), 2.59 (s, 3 H, CH_3-2), 3.57 (m, 2 H, OCH_2CH_2Si), 4.15 (s, 3 H, CH_3O-4), 5.61 (s, 2 H, NCH_2O), 7.23 (btd, $J_{5,6}$ = $J_{5,4}$ = 7.4 Hz, $J_{5,7}$ = 1.3 Hz, 1 H, H-5-benzofuryl), 7.27 (ddd, $J_{6,7}$ = 7.9 Hz, $J_{6,5}$ = 7.3 Hz, $J_{6,4}$ = 1.5 Hz, 1 H, H-6-benzofuryl), 7.39 (d, $J_{3,7}$ = 1.0 Hz, 1 H, H-3-benzofuryl), 7.54 (dq, $J_{7,6}$ = 7.9 Hz, $J_{7,5}$ = $J_{7,4}$ = $J_{7,3}$ = 1.0 Hz, 1 H, H-7-benzofuryl), 7.64 (dm, $J_{4,5}$ = 7.4 Hz, 1 H, H-4-benzofuryl), 8.00 (s, 1 H, H-6).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.23 (CH_3Si), 17.30 (OCH_2CH_2-Si), 25.74 (CH_3-2), 53.96 (CH_3O-4), 65.92 (OCH_2CH_2Si), 72.90 (NCH_2O), 99.15 (C-4a), 103.08 (CH-3-benzofuryl), 105.95 (C-5), 110.68 (CH-7-benzofuryl), 121.00 (CH-4-benzofuryl), 123.18 (CH-5-benzofuryl), 124.19 (CH-6-benzofuryl), 125.32 (CH-6), 129.44 (C-3a-benzofuryl), 150.87 (C-2-benzofuryl), 153.73 and 153.75 (C-7a, C-7a-benzofuryl), 161.21 (C-2), 162.55 (C-4).

MS (ESI): *m*/*z* (%) = 410.2 (100) [M + H], 432.2 (90) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{22}H_{28}N_3O_3Si$: 410.1894; found: 410.1898.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-methoxy-2-methyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (29f)

Compound **29f** was prepared from **14** (419 mg, 1.0 mmol) and dibenzo[*b*,*d*]furan-4-boronic acid (318 mg, 1.5 mmol) by GPA′. Flash column chromatography (5–10% EtOAc/hexanes) gave the product (327 mg, 71%) as a colorless oil.

IR (KBr): 3055, 2951, 1591, 1450, 1347, 1207, 1090, 923, 757, 697 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.06 (s, 9 H, CH_3Si), 0.89 (m, 2 H, OCH_2CH_2Si), 2.61 (s, 3 H, CH_3-2), 3.63 (m, 2 H, OCH_2CH_2Si), 3.91 (s, 3 H, CH_3O-4), 5.67 (s, 2 H, NCH_2O), 7.41 (td, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{12}H_7O$), 7.46 (t, $J_{2,1}$ = $J_{2,3}$ = 7.7 Hz, 1 H, H-2-$C_{12}H_7O$), 7.52 (ddd, $J_{7,6}$ = 8.2 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{12}H_7O$), 7.67 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{12}H_7O$), 7.81 (dd, $J_{3,2}$ = 7.6 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{12}H_7O$), 7.97 (s, 1 H, H-6), 8.07 (dd, $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{12}H_7O$), 8.18 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{12}H_7O$).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.22 (CH_3Si), 17.36 (OCH_2CH_2-Si), 25.74 (CH_3-2), 53.55 (CH_3O-4), 65.92 (OCH_2CH_2Si), 72.79 (NCH_2O), 101.03 (C-4a), 109.51 (C-5), 111.75 (CH-6-$C_{12}H_7O$), 118.80 (C-4-$C_{12}H_7O$), 119.40 (CH-1-$C_{12}H_7O$), 121.38 (CH-9-$C_{12}H_7O$), 123.13 (CH-2-$C_{12}H_7O$), 123.26 (CH-8-$C_{12}H_7O$), 123.79 (C-9b-$C_{12}H_7O$), 123.97 (C-9a-$C_{12}H_7O$), 126.79 (CH-6), 127.70 (CH-7-$C_{12}H_7O$), 128.79 (CH-3-$C_{12}H_7O$), 153.18 (C-4a-$C_{12}H_7O$), 153.37 (C-7a), 155.56 (C-5a-$C_{12}H_7O$), 160.40 (C-2), 162.70 (C-4).

MS (ESI): *m*/*z* (%) = 460.3 (100) [M + H], 483.2 (30) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{26}H_{30}N_3O_3Si$: 460.2051; found: 460.2052.

4-Methoxy-2-methyl-5-phenyl-7-{[2-(trimethylsilyl)ethoxy]methyl}-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (29g)

Compound **29g** was prepared from **14** (419 mg, 1.0 mmol) and phenylboronic acid (183 mg, 1.5 mmol) by GPA′. Flash column chromatography (0–5% EtOAc/hexanes) gave the product (237 mg, 64%) as a yellowish oil.

IR (KBr): 2951, 2895, 1590, 1347, 1201, 1090, 919, 838, 763, 697 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = –0.10 (s, 9 H, CH_3Si), 0.84 (m, 2 H, OCH_2CH_2Si), 2.58 (s, 3 H, CH_3-2), 3.56 (m, 2 H, OCH_2CH_2Si), 3.98 (s, 3 H, CH_3O-4), 5.57 (s, 2 H, NCH_2O), 7.26 (m, 1 H, H-*p*-Ph), 7.39 (m, 2 H, H-*m*-Ph), 7.63 (s, 1 H, H-6), 7.64 (m, 2 H, H-*o*-Ph).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = –1.29 (CH_3Si), 17.28 (OCH_2CH_2Si), 25.66 (CH_3-2), 53.47 (CH_3O-4), 65.77 (OCH_2CH_2Si), 72.59 (NCH_2O), 100.23 (C-4a), 116.20 (C-5), 124.73 (CH-6), 126.44 (CH-*p*-Ph), 128.31 (CH-*m*-Ph), 128.43 (CH-*o*-Ph), 134.04 (C-*i*-Ph), 153.63 (C-7a), 160.12 (C-2), 162.61 (C-4).

MS (ESI): *m*/*z* (%) = 370.2 (100) [M + H], 392.2 (60) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{20}H_{28}N_3O_2Si$: 370.1945; found: 370.1947.

4-Amino-5-(furan-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (30a)

Compound **30a** was prepared from **23a** (220 mg, 0.66 mmol) by GPC. Column chromatography (0.5% MeOH/$CHCl_3$) then recrystallization (MeOH) gave the product (52 mg, 39%) as an orange solid; mp 271–272 °C.

IR (KBr): 1643, 1574, 1320, 1158, 870, 790 cm^{-1}.

^{1}H NMR (499.8 MHz, DMSO-d_6): δ = 6.58 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 6.64 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.8 Hz, 1 H, H-3-furyl), 6.79 (bs, 2 H, NH_2), 7.56 (s, 1 H, H-6), 7.75 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.8 Hz, 1 H, H-5-furyl), 8.09 (s, 1 H, H-2), 11.92 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 98.85 (C-4a), 104.74 (CH-3-furyl), 108.32 (C-5), 105.75 (CH-4-furyl), 120.18 (CH-6), 141.69 (CH-5-furyl), 149.52 (C-2-furyl), 151.66 (C-7a), 152.29 (CH-2), 157.34 (C-4).

MS (ESI): *m*/*z* (%) = 201.1 (100) [M + H], 223.0 (5) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_9ON_4$: 201.0771; found: 201.0771.

4-Amino-5-(furan-3-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (30b)

Compound **30b** was prepared from **23b** (220 mg, 0.66 mmol) by GPC. Column chromatography (0.5% MeOH/$CHCl_3$) then recrystallization (MeOH) gave the product (119 mg, 66%) as a white solid; mp 158 °C.

IR (KBr): 1643, 1576, 1325, 1158, 873, 792 cm^{-1}.

^{1}H NMR (499.8 MHz, DMSO-d_6): δ = 6.13 (bs, 2 H, NH_2), 6.70 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.20 (d, $J_{6,NH}$ = 1.8 Hz, 1 H, H-6), 7.78 (dd, $J_{5,4}$ = 1.8 Hz, $J_{5,2}$ = 1.6 Hz, 1 H, H-5-furyl), 7.80 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 8.09 (s, 1 H, H-2), 11.73 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 100.50 (C-4a), 105.64 (C-5), 111.84 (CH-4-furyl), 119.43 (C-3-furyl), 120.41 (CH-6), 139.47 (CH-2-furyl), 144.20 (CH-5-furyl), 151.52 (C-7a), 151.97 (CH-2), 157.54 (C-4).

MS (ESI): *m*/*z* (%) = 201.1 (100) [M + H], 223.0 (5) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_9ON_4$: 201.0771; found: 201.0771.

4-Amino-5-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (30c)

Compound **30c** was prepared from **23c** (203 mg, 0.59 mmol) by GPC. Recrystallization (MeOH) gave the product (94 mg, 73%) as a white solid; mp 279 °C.

IR (KBr): 1654, 1601, 1576, 1468, 1328, 806, 710 cm^{-1}.

^{1}H NMR (499.8 MHz, DMSO-d_6): δ = 6.21 (bs, 2 H, NH_2), 7.12 (dd, $J_{3,4}$ = 3.4 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.16 (dd, $J_{4,5}$ = 5.2 Hz, $J_{4,3}$ = 3.4 Hz, 1 H, H-4-thienyl), 7.30 (s, 1 H, H-6), 7.53 (dd, $J_{5,4}$ = 5.2 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 8.12 (s, 1 H, H-2), 11.91 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 100.19 (C-4a), 107.90 (C-5), 121.65 (CH-6), 125.60 (CH-5-thienyl), 126.11 (CH-3-thienyl), 128.39 (CH-4-thienyl), 136.65 (C-2-thienyl), 151.43 (C-7a), 152.24 (CH-2), 157.34 (C-4).

MS (ESI): *m*/*z* (%) = 217.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_9N_4S$: 217.05424; found: 217.05425.

4-Amino-5-(thiophen-3-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (30d)

Compound **30d** was prepared from **23d** (305 mg, 0.88 mmol) by GPC. Recrystallization (H_2O) gave the product (182 mg, 96%) as a white solid; mp 283 °C.

IR (KBr): 1647, 1575, 1553, 1471, 854, 810, 783, 718 cm^{-1}.

^{1}H NMR (499.8 MHz, DMSO-d_6): δ = 6.10 (bs, 2 H, NH_2), 7.26 (s, 1 H, H-6), 7.275 (dd, $J_{4,5}$ = 4.9 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.47 (dd, $J_{2,5}$ = 2.9 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 7.68 (dd, $J_{5,4}$ = 4.9 Hz, $J_{5,2}$ = 2.9 Hz, 1 H, H-5-thienyl), 8.11 (s, 1 H, H-2), 11.77 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 100.28 (C-4a), 110.51 (C-5), 120.55 (CH-6), 121.56 (CH-2-thienyl), 127.32 (CH-5-thienyl), 128.83 (CH-4-thienyl), 135.72 (C-3-thienyl), 151.38 (C-7a), 151.96 (CH-2), 157.47 (C-4).

MS (ESI): *m*/*z* (%) = 217.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_9N_4S$: 217.0542; found: 217.0543.

4-Amino-5-(benzofuran-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (30e)

Compound **30e** was prepared from **23e** (294 mg, 0.77 mmol) by GPC. Recrystallization (MeOH) gave the product (156 mg, 81%) as a white solid; mp 328 °C.

IR (KBr): 1656, 1577, 1464, 1325, 809, 750 cm^{-1}.

^{1}H NMR (499.8 MHz, DMSO-d_6): δ = 6.93 (bs, 2 H, NH_2), 7.11 (d, $J_{3,7}$ = 0.9 Hz, 1 H, H-3-benzofuryl), 7.25 (ddd, $J_{6,7}$ = 8.9 Hz, $J_{6,5}$ = 7.3 Hz, $J_{6,4}$ = 1.8 Hz, 1 H, H-6-benzofuryl), 7.27 (ddd, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 7.3 Hz, $J_{5,7}$ = 2.1 Hz, 1 H, H-5-benzofuryl), 7.61 (m, 1 H, H-4-benzofuryl), 7.65 (m, 1 H, H-7-benzofuryl), 7.84 (s, 1 H, H-6), 8.16 (s, 1 H, H-2), 12.19 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 98.98 (C-4a), 100.99 (CH-3-benzofuryl), 105.09 (C-5), 111.16 (CH-7-benzofuryl), 120.62 (CH-4-benzofuryl), 122.67 (CH-6), 123.60, 123.75 (CH-5,6-benzofuryl), 129.17 (C-3a-benzofuryl), 151.99, 152.03 (C-7a, C-2-benzofuryl), 152.41 (CH-2), 153.84 (C-7a-benzofuryl), 157.30 (C-4).

MS (ESI): *m*/*z* (%) = 251.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{14}H_{11}ON_4$: 251.0927; found: 251.0928.

4-Amino-5-(dibenzo[*b*,*d*]furan-4-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (30f)

Compound **30f** was prepared from **23f** (396 mg, 0.92 mmol) by GPC. Recrystallization (MeOH) gave the product (222 mg, 80%) as a yellowish solid; mp 313 °C.

IR (KBr): 1639, 1570, 1474, 1456, 1187, 801, 755 cm^{-1}.

^{1}H NMR (499.8 MHz, DMSO-d_6): δ = 5.95 (bs, 2 H, NH_2), 7.42 (ddd, $J_{8,9}$ = 8.2 Hz, $J_{8,9}$ = 7.7 Hz, $J_{8,6}$ = 0.8 Hz, 1 H, H-8-dibenzofuryl), 7.49 (s, 1 H, H-6), 7.50–7.55 (m, 3 H, H-2,3,7-dibenzofuryl), 7.70 (d, $J_{6,7}$ = 8.2 Hz, 1 H, H-6-dibenzofuryl), 8.13 (dd, $J_{1,2}$ = 7.0 Hz, $J_{1,2}$ = 2.0 Hz, 1 H, H-1-dibenzofuryl), 8.16 (s, 1 H, H-2), 8.19 (d, $J_{9,8}$ = 7.7 Hz, 1 H, H-9-dibenzofuryl), 11.98 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 100.95 (C-4a), 108.96 (C-5, C-4-dibenzofuryl), 112.03 (CH-6-dibenzofuryl), 119.86 (CH-1-dibenzofuryl), 121.50 (CH-9-dibenzofuryl), 122.20 (CH-6), 123.37 (CH-8-dibenzofuryl), 123.77 (CH-2-dibenzofuryl), 124.07 (C-9a-dibenzofuryl), 124.29 (C-9b-dibenzofuryl), 127.83 (CH-7-dibenzofuryl), 128.60 (CH-3-dibenzofuryl), 151.62 (C-7a), 152.06 (CH-2), 153.44 (C-4a-dibenzofuryl), 155.70 (C-5a-dibenzofuryl), 157.55 (C-4).

MS (ESI): *m*/*z* (%) = 301.1 (100) [M + H], 323.1 (10) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{13}ON_4$: 301.1084; found: 301.1084.

4-Amino-5-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (30g)

Compound **30g** was prepared from **23g** (320 mg, 0.94 mmol) by GPC. Recrystallization (MeOH) gave the product (178 mg, 90%) as a white solid; mp 258 °C.

IR (KBr): 1652, 1580, 1529, 1459, 1326, 964, 764, 756 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.01 (bs, 2 H, NH_2), 7.25 (d, $J_{6,NH}$ = 1.8 Hz, 1 H, H-6), 7.34 (m, 1 H, H-*p*-Ph), 7.44–7.49 (m, 2 × 2 H, H-*m*,*o*-Ph), 8.12 (s, 1 H, H-2), 11.82 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 99.98 (C-4a), 115.92 (C-5), 120.59 (CH-6), 126.72 (CH-*p*-Ph), 128.65 (CH-*o*-Ph), 129.12 (CH-*m*-Ph), 135.39 (C-*i*-Ph), 151.68 (C-7a), 151.91 (CH-2), 157.36 (C-4).

MS (ESI): *m*/*z* (%) = 211.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{12}H_{11}N_4$: 211.0978; found: 211.0978.

4-Amino-5-(furan-2-yl)-2-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (31a)

Compound **31a** was prepared from **24a** (255 mg, 0.74 mmol) by GPD. Recrystallization (MeOH/H_2O) gave the product (94 mg, 59%) as a brownish solid; mp >200 °C (dec).

IR (KBr): 1652, 1566, 1526, 1493, 1014, 815, 791, 717 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, CH_3-2), 5.67 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 6.61 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 6.72 (bs, 2 H, NH_2), 7.46 (s, 1 H, H-6), 7.73 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 11.70 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.40 (CH_3-2), 96.64 (C-4a), 104.41 (CH-3-furyl), 105.65 (C-5), 112.03 (CH-4-furyl), 119.42 (CH-6), 141.51 (CH-5-furyl), 149.76 (C-2-furyl), 152.70 (C-7a), 157.15 (C-4), 160.52 (C-2).

MS (ESI): *m*/*z* (%) = 215.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{11}ON_4$: 215.0927; found: 215.0927.

4-Amino-5-(furan-3-yl)-2-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (31b)

Compound **31b** was prepared from **24b** (290 mg, 0.84 mmol) by GPC. Recrystallization (MeOH/H_2O) gave the product (149 mg, 83%) as a brownish solid; mp >200 °C (dec).

IR (KBr): 1645, 1572, 1460, 1310, 1157, 1033, 872, 784 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, CH_3-2), 6.08 (bs, 2 H, NH_2), 6.68 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.12 (d, $J_{6,NH}$ = 1.8 Hz, 1 H, H-6), 7.77 (t, $J_{5,2}$ = $J_{5,4}$ = 1.7 Hz, 1 H, H-5-furyl), 7.78 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 11.54 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.37 (CH_3-2), 98.26 (C-4a), 105.58 (C-5), 111.74 (CH-4-furyl), 119.57 (C-3-furyl), 119.71 (CH-6), 139.29 (CH-2-furyl), 144.15 (CH-5-furyl), 152.50 (C-7a), 157.23 (C-4), 159.97 (C-2).

MS (ESI): *m*/*z* (%) = 215.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{11}ON_4$: 215.0927; found: 215.0927.

4-Amino-2-methyl-5-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (31c)

Compound **31c** was prepared from **24c** (334 mg, 0.93 mmol) by GPC. Recrystallization (MeOH/H_2O) gave the product (195 mg, 91%) as a white solid; mp 137 °C.

IR (KBr): 1651, 1612, 1574, 1326, 1300, 844, 818, 791, 775 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.38 (s, 3 H, CH_3-2), 6.15 (bs, 2 H, NH_2), 7.10 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.14 (dd, $J_{4,5}$ = 5.2 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.21 (s, 1 H, H-6), 7.50 (dd, $J_{5,4}$ = 5.2 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 11.71 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.42 (CH_3-2), 97.99 (C-4a), 107.86 (C-5), 120.89 (CH-6), 125.36 (CH-5-thienyl), 125.81 (CH-3-thienyl), 128.36 (CH-4-thienyl), 136.92 (C-2-thienyl), 152.45 (C-7a), 157.10 (C-4), 160.43 (C-2).

MS (ESI): *m*/*z* (%) = 231.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{11}N_4S$: 231.0699; found: 231.0699.

4-Amino-2-methyl-5-(thiophen-3-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (31d)

Compound **31d** was prepared from **24d** (350 mg, 0.97 mmol) by GPC. Recrystallization (MeOH/H_2O) gave the product (161 mg, 72%) as a white solid; mp 336 °C.

IR (KBr): 1653, 1609, 1573, 1397, 1327, 818, 784 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.38 (s, 3 H, CH_3-2), 6.04 (bs, 2 H, NH_2), 7.17 (d, $J_{6,NH}$ = 2.3 Hz, 1 H, H-6), 7.26 (dd, $J_{4,5}$ = 4.9 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.44 (dd, $J_{2,5}$ = 2.9 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 7.67 (dd, $J_{5,4}$ = 4.9 Hz, $J_{5,2}$ = 2.9 Hz, 1 H, H-5-thienyl), 11.57 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.34 (CH_3-2), 98.05 (C-4a), 110.50 (C-5), 119.89 (CH-6), 121.29 (CH-2-thienyl), 127.29 (CH-5-thienyl), 128.73 (CH-4-thienyl), 135.87 (C-3-thienyl), 152.33 (C-7a), 157.11 (C-4), 159.91 (C-2).

MS (ESI): *m*/*z* (%) = 231.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{11}N_4S$: 231.0699; found: 231.0699.

4-Amino-5-(benzofuran-2-yl)-2-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (31e)

Compound **31e** was prepared from **24e** (343 mg, 0.87 mmol) by GPC. Recrystallization (MeOH/H_2O) gave the product (225 mg, 98%) as a white solid; mp >200 °C (dec).

IR (KBr): 1645, 1595, 1567, 1455, 1320, 1256, 817, 791, 745 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.40 (s, 3 H, CH_3-2), 6.84 (bs, 2 H, NH_2), 7.08 (d, $J_{3,7}$ = 1.0 Hz, 1 H, H-3-benzofuryl), 7.22–7.29 (m, 2 H, H-5,6-benzofuryl), 7.57–7.67 (m, 2 H, H-4,7-benzofuryl), 7.75 (s, 1 H, H-6), 11.96 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.41 (CH_3-2), 96.77 (C-4a), 100.64 (CH-3-benzofuryl), 104.93 (C-5), 111.10 (CH-7-benzofuryl), 120.53 (CH-4-benzofuryl), 121.93 (CH-6), 123.56 and 123.65 (CH-5,6-benzofuryl), 129.20 (C-3a-benzofuryl), 152.30 (C-2-benzofuryl), 153.05 (C-7a), 153.77 (C-7a-benzofuryl), 157.16 (C-4), 160.81 (C-2).

MS (ESI): *m*/*z* (%) = 265.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{15}H_{13}ON_4$: 265.1084; found: 265.1084.

4-Amino-5-(dibenzo[*b*,*d*]furan-4-yl)-2-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (31f)

Compound **31f** was prepared from **24f** (356 mg, 0.8 mmol) by GPC. Recrystallization (MeOH/H_2O) gave the product (214 mg, 85%) as a white solid; mp 160–161 °C.

IR (KBr): 1640, 1569, 1451, 1191, 841, 753 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.42 (s, 3 H, CH_3-2), 5.88 (bs, 2 H, NH_2), 7.40 (d, $J_{6,NH}$ = 2.1 Hz, 1 H, H-6), 7.42 (btd, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{12}H_7O$), 7.47–7.52 (m, 2 H, H-2,3-$C_{12}H_7O$), 7.52 (ddd, $J_{7,6}$ = 8.3 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{12}H_7O$), 7.70 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.8 Hz, 1 H, H-6-$C_{12}H_7O$), 8.11 (m, 1 H, H-1-$C_{12}H_7O$), 8.19 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{12}H_7O$), 11.79 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.46 (CH_3-2), 98.74 (C-4a), 108.87 (C-5), 112.01 (CH-6-$C_{12}H_7O$), 119.71 (CH-1-$C_{12}H_7O$), 120.07 (C-4-$C_{12}H_7O$), 121.49 and 121.51 (CH-6, CH-9-$C_{12}H_7O$), 123.36 (CH-8-$C_{12}H_7O$), 123.77 (CH-2-$C_{12}H_7O$), 124.08 and 124.27 (C-9a,9b-$C_{12}H_7O$), 127.82 (CH-7-$C_{12}H_7O$), 128.43 (CH-3-$C_{12}H_7O$), 152.65 (C-7a), 153.36 (C-4a-$C_{12}H_7O$), 155.68 (C-5a-$C_{12}H_7O$), 157.33 (C-4), 160.22 (C-2).

MS (ESI): *m*/*z* (%) = 315.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{15}ON_4$: 315.1240; found: 315.1241.

4-Amino-2-methyl-5-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (31g)

Compound **31g** was prepared from **24g** (335 mg, 0.95 mmol) by GPC. Recrystallization ($MeOH/H_2O$) gave the product (171 mg, 80%) as a white solid; mp 322 °C.

IR (KBr): 1652, 1597, 1563, 1531, 1484, 1318, 814, 754 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.39 (s, 3 H, CH_3-2), 5.93 (bs, 2 H, NH_2), 7.15 (d, $J_{6,NH}$ = 1.4 Hz, 1 H, H-6), 7.32 (m, 1 H, H-*p*-Ph), 7.42–7.48 (m, 2 × 2 H, H-*m*,*o*-Ph), 11.60 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.47 (CH_3-2), 97.81 (C-4a), 115.83 (C-5), 119.85 (CH-6), 126.62 (CH-*p*-Ph), 128.51 and 129.12 (CH-*o*,*m*-Ph), 135.61 (C-*i*-Ph), 152.78 (C-7a), 157.23 (C-4), 160.18 (C-2).

MS (ESI): *m*/*z* (%) = 225.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{13}N_4$: 225.1135; found: 225.1135.

5-(Furan-2-yl)-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidine (32a)

Compound **32a** was prepared from **25a** (270 mg, 0.78 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (87 mg, 52%) as a brownish solid; mp >200 °C (dec).

^1H NMR (500 MHz, DMSO-d_6): δ = 4.09 (s, 3 H, CH_3O), 6.53 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.8 Hz, 1 H, H-4-furyl), 6.88 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.62 (dd, $J_{5,4}$ = 1.8 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 7.63 (d, $J_{6,NH}$ = 2.6 Hz, 1 H, H-6), 8.40 (s, 1 H, H-2), 12.32 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 54.18 (CH_3O), 101.08 (C-4a), 106.90 (C-5), 107.03 (CH-3-furyl), 112.20 (CH-4-furyl), 121.22 (CH-6), 141.73 (CH-5-furyl), 149.13 (C-2-furyl), 151.65 (CH-2), 153.26 (C-7a), 163.07 (C-4).

MS (ESI): *m*/*z* (%) = 216.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{10}O_2N_3$: 216.0767; found: 216.0768.

5-(Furan-3-yl)-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidine (32b)

Compound **32b** was prepared from **25b** (250 mg, 0.72 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (120 mg, 77%) as a white solid; mp >200 °C (dec).

^1H NMR (500 MHz, DMSO-d_6): δ = 4.08 (s, 3 H, CH_3O), 6.94 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.65 (d, $J_{6,NH}$ = 2.5 Hz, 1 H, H-6), 7.67 (t, $J_{5,2}$ = $J_{5,4}$ = 1.7 Hz, 1 H, H-5-furyl), 8.07 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 8.37 (s, 1 H, H-2), 12.16 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 54.09 (CH_3O), 102.24 (C-4a), 106.86 (C-5), 110.67 (CH-4-furyl), 119.32 (C-3-furyl), 121.98 (CH-6), 139.94 (CH-2-furyl), 143.68 (CH-5-furyl), 151.29 (CH-2), 153.41 (C-7a), 163.05 (C-4).

MS (ESI): *m*/*z* (%) = 216.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{10}O_2N_3$: 216.0767; found: 216.0768.

4-Methoxy-5-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (32c)

Compound **32c** was prepared from **25c** (180 mg, 0.50 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (78 mg, 68%) as a yellowish solid; mp >200 °C (dec).

^1H NMR (500 MHz, DMSO-d_6): δ = 4.06 (s, 3 H, CH_3O), 7.07 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.40 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.44 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.63 (d, $J_{6,NH}$ = 2.6 Hz, 1 H, H-6), 8.40 (s, 1 H, H-2), 12.32 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 53.57 (CH_3O), 101.75 (C-4a), 109.17 (C-5), 122.26 (CH-6), 124.13 (CH-5-thienyl), 125.35 (CH-3-thienyl), 127.76 (CH-4-thienyl), 136.45 (C-2-thienyl), 151.09 (CH-2), 153.08 (C-7a), 162.69 (C-4).

MS (ESI): *m*/*z* (%) = 230.0 (100) [M – H].

HRMS (ESI): *m*/*z* [M – H] calcd for $C_{11}H_8ON_3S$: 230.03936; found: 230.03936.

4-Methoxy-5-(thiophen-3-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (32d)

Compound **32d** was prepared from **25d** (400 mg, 1.16 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (217 mg, 85%) as a white solid; mp 250–251 °C.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.07 (s, 3 H, CH_3O), 7.45 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 2.7 Hz, 1 H, H-5-thienyl), 7.55 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.5 Hz, 1 H, H-4-thienyl), 7.72 (s, 1 H, H-6), 7.82 (dd, $J_{2,5}$ = 2.7 Hz, $J_{2,4}$ = 1.5 Hz, 1 H, H-2-thienyl), 8.39 (s, 1 H, H-2), 12.22 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 53.65 (CH_3O), 101.94 (C-4a), 111.03 (C-5), 120.71 (CH-2-thienyl), 122.37 (CH-6), 125.70 (CH-5-thienyl), 128.14 (CH-4-thienyl), 134.82 (C-3-thienyl), 150.82 (CH-2), 153.19 (C-7a), 162.70 (C-4).

MS (EI): *m*/*z* (%) = 231.0 (100) [M], 232.0 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{11}H_9N_3OS$: 231.0466; found: 231.0467.

5-(Benzofuran-2-yl)-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidine (32e)

Compound **32e** was prepared from **25e** (350 mg, 0.89 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (228 mg, 98%) as a yellowish solid; mp 276–277 °C.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.16 (s, 3 H, CH_3O), 7.22 (td, $J_{5,6}$ = $J_{5,4}$ = 7.3 Hz, $J_{5,7}$ = 1.2 Hz, 1 H, H-5-benzofuryl), 7.25 (bddd, $J_{6,7}$ = 8.0 Hz, $J_{6,5}$ = 7.3 Hz, $J_{6,4}$ = 1.5 Hz, 1 H, H-6-benzofuryl), 7.37 (d, $J_{3,7}$ = 1.1 Hz, 1 H, H-3-benzofuryl), 7.53 (bdq, $J_{7,6}$ = 8.0 Hz, $J_{7,5}$ = $J_{7,4}$ = $J_{7,3}$ = 1.0 Hz, 1 H, H-7-benzofuryl), 7.63 (ddd, $J_{4,5}$= 7.3 Hz, $J_{4,6}$ = 1.5 Hz, $J_{4,7}$ = 0.7 Hz, 1 H, H-4-benzofuryl), 7.91 (d, $J_{6,NH}$ = 2.7 Hz, 1 H, H-6), 8.46 (s, 1 H, H-2), 12.56 (bd, $J_{NH,6}$ = 2.2 Hz, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 54.02 (CH_3O), 101.17 (C-4a), 102.54 (CH-3-benzofuryl), 105.87 (C-5), 110.72 (CH-7-benzofuryl), 120.92 (CH-4-benzofuryl), 123.15 (CH-6, CH-6-benzofuryl), 124.02 (CH-5-benzofuryl), 129.61 (C-3a-benzofuryl), 151.44 (C-2-benzofuryl), 151.72 (CH-2), 153.59 (C-7a), 153.76 (C-7a-benzofuryl), 162.75 (C-4).

MS (EI): *m*/*z* (%) = 265.1 (100) [M], 266.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{15}H_{11}N_3O_2$: 265.0851; found: 265.0851.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidine (32f)

Compound **32f** was prepared from **25f** (500 mg, 1.12 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (347 mg, 98%) as a white solid; mp >250 °C (dec).

^1H NMR (500 MHz, DMSO-d_6): δ = 3.92 (s, 3 H, CH_3O), 7.41 (btd, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{10}H_7O$), 7.45 (t, $J_{2,1}$ = $J_{2,3}$ = 7.6 Hz, 1 H, H-2-$C_{10}H_7O$), 7.52 (ddd, $J_{7,6}$ = 8.2 Hz, $J_{7,8}$ = 7.2 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{10}H_7O$), 7.71 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{10}H_7O$),

7.80 (dd, $J_{3,2}$ = 7.6 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{10}H_7O$), 7.87 (d, $J_{6,NH}$ = 2.5 Hz, 1 H, H-6), 8.06 (dd, $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{10}H_7O$), 8.18 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{10}H_7O$), 8.46 (s, 1 H, H-2), 12.47 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 53.65 (CH_3O), 103.05 (C-4a), 109.24 (C-5), 111.94 (CH-6-$C_{10}H_7O$), 119.27 (CH-1-$C_{10}H_7O$), 119.38 (C-4-$C_{10}H_7O$), 121.39 (CH-9-$C_{10}H_7O$), 123.18 (CH-2-$C_{10}H_7O$), 123.30 (CH-8-$C_{10}H_7O$), 123.79 (C-9b-$C_{10}H_7O$), 124.05 (C-9a-$C_{10}H_7O$), 124.58 (CH-6), 127.72 (CH-7-$C_{10}H_7O$), 128.94 (CH-3-$C_{10}H_7O$), 151.03 (CH-2), 153.15 (C-7a), 153.37 (C-4a-$C_{10}H_7O$), 155.64 (C-5a-$C_{10}H_7O$), 162.93 (C-4).

MS (EI): *m*/*z* (%) = 315.1 (100) [M], 316.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{19}H_{13}N_3O_2$: 315.1008; found: 315.1008.

4-Methoxy-5-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (32g)

Compound **32g** was prepared from **25g** (300 mg, 0.85 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (140 mg, 74%) as a white solid; mp 197–198 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.01 (s, 3 H, CH_3O), 7.26 (m, 1 H, H-*p*-Ph), 7.39 (m, 2 H, H-*m*-Ph), 7.58 (s, 1 H, H-6), 7.67 (m, 2 H, H-*o*-Ph), 8.41 (s, 1 H, H-2), 12.27 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 53.54 (CH_3O), 102.14 (C-4a), 115.91 (C-5), 122.54 (CH-6), 126.19 (CH-*p*-Ph), 128.26 (CH-*m*-Ph), 128.57 (CH-*o*-Ph), 134.54 (C-*i*-Ph), 150.71 (CH-2), 153.35 (C-7a), 162.76 (C-4).

MS (ESI): *m*/*z* (%) = 226.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{12}ON_3$: 226.0974; found: 226.0974.

5-(Furan-2-yl)-4-(methylsulfanyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (33a)

Compound **33a** was prepared from **26a** (250 mg, 0.69 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (157 mg, 71%) as a white solid; mp 221–222 °C.

^{1}H NMR (401 MHz, DMSO-d_6): δ = 2.58 (s, 3 H, CH_3S), 6.58 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 6.67 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.8 Hz, 1 H, H-3-furyl), 7.69 (S, 1 H, H-6), 7.74 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.8 Hz, 1 H, H-5-furyl), 8.62 (s, 1 H, H-2), 12.47 (bs, 1 H, NH).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 12.38 (CH_3S), 106.16 (C-5), 108.77 (CH-3-furyl), 111.82 (CH-4-furyl), 113.16 (C-4a), 125.35 (CH-6), 142.73 (CH-5-furyl), 147.82 (C-2-furyl), 149.71 (C-7a), 151.06 (CH-2), 161.25 (C-4).

MS (ESI): *m*/*z* (%) = 232.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{10}ON_3S$: 232.05391; found: 232.05392.

5-(Furan-3-yl)-4-(methylsulfanyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (33b)

Compound **33b** was prepared from **26b** (250 mg, 0.69 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (130 mg, 79%) as a white solid; mp 192–193 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.57 (s, 3 H, CH_3S), 6.73 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.49 (d, $J_{6,NH}$ = 2.5 Hz, 1 H, H-6), 7.74 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 7.84 (dd, $J_{2,5}$ = 1.7 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 8.59 (s, 1 H, H-2), 12.27 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 11.95 (CH_3S), 106.15 (C-5), 113.17 (CH-4-furyl), 113.72 (C-4a), 118.24 (C-3-furyl), 124.32 (CH-6), 140.62 (CH-2-furyl), 143.05 (CH-5-furyl), 149.49 (C-7a), 150.50 (CH-2), 160.62 (C-4).

MS (ESI): *m*/*z* (%) = 232.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{10}ON_3S$: 232.0539; found: 232.0538.

4-(Methylsulfanyl)-5-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (33c)

Compound **33c** was prepared from **26c** (300 mg, 0.80 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (163 mg, 83%) as a white solid; mp 234–235 °C.

^{1}H NMR (401 MHz, DMSO-d_6): δ = 2.55 (s, 3 H, CH_3S), 7.14 (dd, $J_{4,5}$ = 5.2 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.20 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.55 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.58 (s, 1 H, H-6), 8.62 (s, 1 H, H-2), 12.42 (bs, 1 H, NH).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 12.21 (CH_3S), 108.38 (C-5), 114.01 (C-4a), 125.86 (CH-6), 126.30 (CH-5-thienyl), 127.78 (CH-3-thienyl), 128.66 (CH-4-thienyl), 135.06 (C-2-thienyl), 149.55 (C-7a), 150.97 (CH-2), 161.15 (C-4).

MS (ESI): *m*/*z* (%) = 248.0 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{10}N_3S_2$: 248.0310; found: 248.0310.

4-(Methylsulfanyl)-5-(thiophen-3-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (33d)

Compound **33d** was prepared from **26d** (300 mg, 0.80 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (192 mg, 98%) as a white solid; mp 222–223 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.45 (s, 3 H, CH_3S), 7.29 (dd, $J_{4,5}$ = 4.9 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.51 (d, $J_{6,NH}$ = 2.4 Hz, 1 H, H-6), 7.53 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 7.59 (dd, $J_{5,4}$ = 4.9 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 8.60 (s, 1 H, H-2), 12.29 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 12.01 (CH_3S), 110.88 (C-5), 113.61 (C-4a), 123.48 (CH-2-thienyl), 124.37 (CH-6), 125.44 (CH-5-thienyl), 130.19 (CH-4-thienyl), 134.27 (C-3-thienyl), 149.29 (C-7a), 150.45 (CH-2), 160.65 (C-4).

MS (EI): *m*/*z* (%) = 247.0 (100) [M], 248.0 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{11}H_9N_3S_2$: 247.0238; found: 247.0236.

5-(Benzofuran-2-yl)-4-(methylsulfanyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (33e)

Compound **33e** was prepared from **26e** (300 mg, 0.73 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (170 mg, 83%) as a white solid; mp 230–231 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.60 (s, 3 H, CH_3O), 7.18 (d, $J_{3,7}$ = 1.0 Hz, 1 H, H-3-benzofuryl), 7.26 (td, $J_{5,6}$ = $J_{5,4}$ = 7.4 Hz, $J_{5,7}$ = 1.2 Hz, 1 H, H-5-benzofuryl), 7.30 (bddd, $J_{6,7}$ = 8.1 Hz, $J_{6,5}$ = 7.2 Hz, $J_{6,4}$ = 1.5 Hz, 1 H, H-6-benzofuryl), 7.59 (bdq, $J_{7,6}$ = 8.1 Hz, $J_{7,5}$ = $J_{7,4}$ = $J_{7,3}$ = 1.0 Hz, 1 H, H-7-benzofuryl), 7.67 (ddd, $J_{4,5}$= 7.5 Hz, $J_{4,6}$ = 1.5 Hz, $J_{4,7}$ = 0.7 Hz, 1 H, H-4-benzofuryl), 7.95 (d, $J_{6,NH}$ = 2.4 Hz, 1 H, H-6), 8.67 (s, 1 H, H-2), 12.68 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 12.31 (CH_3S), 104.42 (CH-3-benzofuryl), 105.35 (C-5), 111.07 (CH-7-benzofuryl), 112.82 (C-4a), 120.97 (CH-4-benzofuryl), 123.15 (CH-5-benzofuryl), 124.16 (CH-6-

benzofuryl), 126.55 (CH-6), 129.10 (C-3a-benzofuryl), 149.82 (C-7a), 150.51 (C-2-benzofuryl), 151.05 (CH-2), 154.21 (C-7a-benzofuryl), 161.20 (C-4).

MS (EI): *m*/*z* (%) = 282.1 (100) [M + H].

HRMS (EI): *m*/*z* [M + H] calcd for $C_{15}H_{12}ON_3S$: 282.0695; found: 282.0696.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-(methylsulfanyl)-7*H*-pyrrolo[2,3-*d*]-pyrimidine (33f)

Compound **33f** was prepared from **26f** (500 mg, 1.08 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (330 mg, 93%) as a white solid; mp 280–281 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.39 (s, 3 H, CH_3S), 7.41 (btd, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{10}H_7O$), 7.46 (t, $J_{2,1}$ = $J_{2,3}$ = 7.5 Hz, 1 H, H-2-$C_{10}H_7O$), 7.49 (ddd, $J_{7,6}$ = 8.3 Hz, $J_{7,8}$ = 7.2 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{10}H_7O$), 7.53 (dd, $J_{3,2}$ = 7.4 Hz, $J_{3,1}$ = 1.4 Hz, 1 H, H-3-$C_{10}H_7O$), 7.63 (bdt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.8 Hz, 1 H, H-6-$C_{10}H_7O$), 7.68 (d, $J_{6,NH}$ = 2.5 Hz, 1 H, H-6), 8.15 (dd, $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 1.4 Hz, 1 H, H-1-$C_{10}H_7O$), 8.18 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.5 Hz, $J_{9,6}$ = 0.8 Hz, 1 H, H-9-$C_{10}H_7O$), 8.64 (s, 1 H, H-2), 12.46 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 11.86 (CH_3S), 109.58 (C-5), 112.10 (CH-6-$C_{10}H_7O$), 114.86 (C-4a), 119.24 (C-4-$C_{10}H_7O$), 120.61 (CH-1-$C_{10}H_7O$), 121.55 (CH-9-$C_{10}H_7O$), 123.11 (CH-2-$C_{10}H_7O$), 123.42 (CH-8-$C_{10}H_7O$), 123.76 (C-9b-$C_{10}H_7O$), 124.16 (C-9a-$C_{10}H_7O$), 125.31 (CH-6), 127.88 (CH-7-$C_{10}H_7O$), 130.19 (CH-3-$C_{10}H_7O$), 149.41 (C-7a), 150.81 (CH-2), 154.54 (C-4a-$C_{10}H_7O$), 155.75 (C-5a-$C_{10}H_7O$), 161.21 (C-4).

MS (EI): *m*/*z* (%) = 331.1 (100) [M], 332.1 (10) [M + H].

HRMS (EI): *m*/*z* [M] calcd for $C_{19}H_{13}N_3OS$: 331.0779; found: 331.0778.

4-(Methylsulfanyl)-5-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (33g)

Compound **33g** was prepared from **26g** (256 mg, 0.70 mmol) by GPC. Flash column chromatography (0–25% EtOAc/hexanes) gave the product (140 mg, 82%) as a white solid; mp 237–239 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.53 (s, 3 H, CH_3S), 7.36 (m, 1 H, H-*p*-Ph), 7.43 (m, 2 H, H-*m*-Ph), 7.50 (m, 3 H, H-6 and H-*o*-Ph), 8.62 (s, 1 H, H-2), 12.34 (bs, 1 H, NH).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 12.31 (CH_3S), 113.76 (C-4a), 116.59 (C-5), 124.53 (CH-6), 127.30 (CH-*p*-Ph), 128.29 (CH-*m*-Ph), 130.47 (CH-*o*-Ph), 134.60 (C-*i*-Ph), 149.71 (CH-2), 150.69 (C-7a), 160.91 (C-4).

MS (ESI): *m*/*z* (%) = 242.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{12}N_3S$: 242.0746; found: 242.0746.

5-(Furan-2-yl)-4-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (34a)

Compound **34a** was prepared from **27a** (119 mg, 0.36 mmol) by GPD″. Reaction time: 48 h. Column chromatography (silica gel, 0–1.5% MeOH/$CHCl_3$) then recrystallization (H_2O/MeOH 2:1) gave the product (61 mg, 85%) as a white crystalline solid; mp 206–208 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.64 (s, 3 H, CH_3-4), 6.59 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.8 Hz, 1 H, H-4-furyl), 6.61 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.75 (s, 1 H, H-6), 7.76 (dd, $J_{5,4}$ = 1.8 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 8.64 (s, 1 H, H-2), 12.38 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 23.14 (CH_3-4), 106.00 (C-5), 107.83 (CH-3-furyl), 111.66 (CH-4-furyl), 114.51 (C-4a), 125.75 (CH-6), 142.52 (CH-5-furyl), 148.52 (C-2-furyl), 151.33 (CH-2), 151.39 (C-7a), 159.08 (C-4).

MS (CI): *m*/*z* (%) = 199.1 (25) [M], 200.1 (100) [M + H].

HRMS (CI): *m*/*z* [M + H] calcd for $C_{11}H_{10}ON_3$: 200.0824; found: 200.0816.

5-(Furan-3-yl)-4-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (34b)

Compound **34b** was prepared from **27b** (143 mg, 0.43 mmol) by GPD′. Reaction time: 48 h. Column chromatography (silica gel, 0–1% MeOH/$CHCl_3$) then recrystallization (H_2O/MeOH 2:1) gave the products (49 mg, 57%) as a white crystalline solid; mp 229–230 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.60 (s, 3 H, CH_3-4), 6.76 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.51 (s, 1 H, H-6), 7.77 (dd, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 7.84 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 8.61 (s, 1 H, H-2), 12.17 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 22.93 (CH_3-4), 106.35 (C-5), 113.05 (CH-4-furyl), 115.35 (C-4a), 118.99 (C-3-furyl), 124.73 (CH-6), 140.42 (CH-2-furyl), 143.46 (CH-5-furyl), 151.01 (CH-2), 151.43 (C-7a), 158.91 (C-4).

MS (CI): *m*/*z* (%) = 199.1 (24) [M], 200.1 (100) [M + H].

HRMS (CI): *m*/*z* [M + H] calcd for $C_{11}H_{10}ON_3$: 200.0824; found: 200.0818.

4-Methyl-5-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (34c)

Compound **34c** was prepared from **27c** (136 mg, 0.39 mmol) by GPD′. Reaction time: 96 h. Column chromatography (silica gel, 0–1% MeOH/$CHCl_3$) then recrystallization (H_2O/MeOH 2:1) gave the product (60 mg, 71%) as a white crystalline solid; mp 210–212 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.53 (s, 3 H, CH_3-4), 7.15 (dd, $J_{4,5}$ = 5.2 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.19 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.56 (dd, $J_{5,4}$ = 5.2 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.26 (s, 1 H, H-6), 8.64 (s, 1 H, H-2), 12.35 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 22.81 (CH_3-4), 108.23 (C-5), 115.38 (C-4a), 125.94 (CH-5-thienyl), 126.15 (CH-6), 127.75 (CH-4-thienyl), 127.93 (CH-3-thienyl), 135.76 (C-2-thienyl), 151.23 (C-7a), 151.26 (CH-2), 158.87 (C-4).

MS (CI): *m*/*z* (%) = 215.1 (22) [M], 216.1 (100) [M + H].

HRMS (CI): *m*/*z* [M + H] calcd for $C_{11}H_{10}N_3S$: 216.0595; found: 216.0586.

4-Methyl-5-(thiophen-3-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (34d)

Compound **34d** was prepared from **27d** (202 mg, 0.59 mmol) by GPD′. Reaction time: 7 d. Column chromatography (silica gel, 0–1% MeOH/$CHCl_3$) then recrystallization (H_2O/MeOH 2:1) gave the product (55 mg, 44%) as a white crystalline solid; mp 254–255 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.52 (s, 3 H, CH_3-4), 7.30 (dd, $J_{4,5}$ = 4.9 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.54 (s, 1 H, H-6), 7.54 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 7.63 (dd, $J_{5,4}$ = 4.9 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 8.62 (s, 1 H, H-2), 12.19 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 23.01 (CH_3-4), 111.07 (C-5), 115.29 (C-4a), 123.19 (CH-2-thienyl), 124.80 (CH-6), 125.99 (CH-5-thienyl), 130.08 (CH-4-thienyl), 135.13 (C-3-thienyl), 150.98 (CH-2), 151.23 (C-7a), 158.92 (C-4).

MS (CI): *m*/*z* (%) = 215.1 (24) [M], 216.1 (100) [M + H].

HRMS (CI): *m*/*z* [M + H] calcd for $C_{11}H_{10}N_3S$: 216.0595; found: 216.0594.

5-(Benzofuran-2-yl)-4-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (34e)

Compound **34e** was prepared from **27e** (164 mg, 0.43 mmol) by GPD′. Reaction time: 72 h. Purification by reverse-phase HPFC (C-18, 0–100% MeOH/H_2O) then recrystallization (H_2O/MeOH 2:1) gave the product (86 mg, 59%) as a white crystalline solid; mp 257–258 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.77 (s, 3 H, CH_3-4), 7.10 (d, $J_{3,7}$ = 1.0 Hz, 1 H, H-3-benzofuryl), 7.26 (td, $J_{5,6}$ = $J_{5,4}$ = 7.3 Hz, $J_{5,7}$ = 1.3 Hz, 1 H, H-5-benzofuryl), 7.30 (bddd, $J_{6,7}$ = 8.0 Hz, $J_{6,5}$ = 7.3 Hz, $J_{6,4}$ = 1.5 Hz, 1 H, H-6-benzofuryl), 7.61 (bdq, $J_{7,6}$ = 8.0 Hz, $J_{7,5}$ = $J_{7,4}$ = $J_{7,3}$ = 0.8 Hz, 1 H, H-7-benzofuryl), 7.65 (ddd, $J_{4,5}$ = 7.3 Hz, $J_{4,6}$ = 1.6 Hz, $J_{4,7}$ = 0.8 Hz, 1 H, H-4-benzofuryl), 8.01 (s, 1 H, H-6), 8.69 (s, 1 H, H-2), 12.59 (vbs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 23.67 (CH_3-4), 103.66 (CH-3-benzofuryl), 105.48 (C-5), 111.06 (CH-7-benzofuryl), 114.39 (C-4a), 120.88 (CH-4-benzofuryl), 123.25 (CH-5-benzofuryl), 124.07 (CH-6-benzofuryl), 127.31 (CH-6), 129.10 (C-3a-benzofuryl), 151.33 (C-2-benzofuryl), 151.55 (CH-2), 151.72 (C-7a), 154.28 (C-7a-benzofuryl), 159.29 (C-4).

MS (CI): *m*/*z* (%) = 249.1 (98) [M], 250.1 (100) [M + H].

HRMS (CI): *m*/*z* [M + H] calcd for $C_{15}H_{12}N_3O$: 250.0980; found: 250.0981.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (34f)

Compound **34f** was prepared from **27f** (174 mg, 0.41 mmol) by GPD″. Reaction time: 7 d. Column chromatography (silica gel, 0–1.5% MeOH/$CHCl_3$) then recrystallization (H_2O/MeOH 2:1) gave the product (102 mg, 84%) as a white crystalline solid; mp 304–306 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.24 (s, 3 H, CH_3-4), 7.42 (btd, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{10}H_7O$), 7.49 (t, $J_{2,1}$ = $J_{2,3}$ = 7.6 Hz, 1 H, H-2-$C_{10}H_7O$), 7.51 (ddd, $J_{7,6}$ = 8.3 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{10}H_7O$), 7.57 (dd, $J_{3,2}$ = 7.4 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{10}H_7O$), 7.66 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{10}H_7O$), 7.75 (s, 1 H, H-6), 8.19 (dd, $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{10}H_7O$), 8.20 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{10}H_7O$), 8.69 (s, 1 H, H-2), 12.43 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 21.99 (CH_3-4), 110.00 (C-5), 112.22 (CH-6-$C_{10}H_7O$), 116.29 (C-4a), 120.14 (C-4-$C_{10}H_7O$), 120.65 (CH-1-$C_{10}H_7O$), 121.79 (CH-9-$C_{10}H_7O$), 123.69 (CH-2,8-$C_{10}H_7O$), 124.08 (C-9a-$C_{10}H_7O$), 124.24 (C-9b-$C_{10}H_7O$), 126.19 (CH-6), 128.15 (CH-7-$C_{10}H_7O$), 129.88 (CH-3-$C_{10}H_7O$), 151.42 (CH-2), 151.69 (C-7a), 154.26 (C-4a-$C_{10}H_7O$), 155.82 (C-5a-$C_{10}H_7O$), 159.28 (C-4).

MS (ESI): *m*/*z* (%) = 300.2 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{14}N_3O$: 300.11314; found: 300.11318.

4-Methyl-5-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (34g)

Compound **34g** was prepared from **27g** (350 mg, 0.90 mmol) by GPD″. Reaction time: 5 d. Column chromatography (silica gel, 0–1.5% MeOH/$CHCl_3$) then recrystallization (H_2O/MeOH 2:1) gave the product (171 mg, 90%) as a white crystalline solid; mp 240–242 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.45 (s, 3 H, CH_3-4), 7.35 (m, 1 H, H-*p*-Ph), 7.43 (m, 2 H, H-*m*-Ph), 7.49 (m, 2 H, H-*o*-Ph), 7.53 (s, 1 H, H-6), 8.63 (s, 1 H, H-2), 12.24 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 23.20 (CH_3-4), 115.12 (C-4a), 116.47 (C-5), 124.69 (CH-6), 126.95 (CH-*p*-Ph), 128.36 (CH-*m*-Ph), 130.07 (CH-*o*-Ph), 135.13 (C-*i*-Ph), 150.96 (CH-2), 151.41 (C-7a), 158.81 (C-4).

MS (CI): *m*/*z* (%) = 209.1 (77) [M], 210.1 (100) [M + H].

HRMS (CI): *m*/*z* [M + H] calcd for $C_{13}H_{12}N_3$: 210.1031; found: 210.1034.

5-(Furan-2-yl)-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (35a)

Compound **35a** was prepared from **28a** (270 mg, 0.75 mmol) by GPD. Flash column chromatography (70–80% EtOAc/hexanes) then recrystallization (MeOH, gave the product (120 mg, 69%) as a yellowish solid; mp 208–209 °C.

IR (KBr): 3342, 3138, 1617, 1576, 1392, 1093, 968, 794, 700, 551 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.97 (s, 3 H, CH_3O-4), 6.15 (bs, 2 H, NH_2), 6.48 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 6.77 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.12 (d, $J_{6,NH}$ = 2.4 Hz, 1 H, H-6), 7.54 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 11.30 (bd, $J_{NH,6}$ = 2.3 Hz, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 53.07 (CH_3O-4), 93.51 (C-4a), 105.64 (CH-3-furyl), 106.72 (C-5), 111.60 (CH-4-furyl), 116.47 (CH-6), 140.69 (CH-5-furyl), 149.85 (C-2-furyl), 155.79 (C-7a), 159.88 (C-2), 163.26 (C-4).

MS (ESI): *m*/*z* (%) = 231.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{11}N_4O_2$: 231.0876; found: 231.0876.

5-(Furan-3-yl)-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (35b)

Compound **35b** was prepared from **28b** (340 mg, 0.94 mmol) by GPD. Flash column chromatography (70–80% EtOAc/hexanes) then recrystallization (MeOH) gave the product (169 mg, 78%) as an orange solid; mp 223–224 °C.

IR (KBr): 3316, 3102, 1629, 1575, 1391, 1316, 1098, 1013, 776, 595 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.96 (s, 3 H, CH_3O), 6.08 (bs, 2 H, NH_2), 6.84 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.14 (d, $J_{6,NH}$ = 2.3 Hz, 1 H, H-6), 7.61 (t, $J_{5,2}$ = $J_{5,4}$ = 1.7 Hz, 1 H, H-5-furyl), 7.98 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 11.14 (d, $J_{NH,6}$ = 2.3 Hz, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 52.99 (CH_3O-4), 94.72 (C-4a), 106.53 (C-5), 110.11 (CH-4-furyl), 117.25 (CH-6), 119.74 (C-3-furyl), 139.03 (CH-2-furyl), 142.99 (CH-5-furyl), 155.89 (C-7a), 159.64 (C-2), 163.26 (C-4).

MS (ESI): *m*/*z* (%) = 231.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{11}N_4O_2$: 231.0876; found: 231.0876.

4-Methoxy-5-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (35c)

Compound **35c** was prepared from **28c** (508 mg, 1.35 mmol) by GPD. Flash column chromatography (70–80% EtOAc/hexanes) then recrystallization (MeOH, gave the product (239 mg, 72%) as a white solid; mp 266–267 °C.

IR (KBr): 3337, 3103, 1624, 1575, 1393, 1316, 1093, 826, 697, 568 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.94 (s, 3 H, CH_3O-4), 6.14 (bs, 2 H, NH_2), 7.02 (dd, $J_{4,5}$ = 5.2 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, H-4-thienyl), 7.09 (s, 1 H, H-6), 7.30 (dd, $J_{5,4}$ = 5.2 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.36 (dd, $J_{3,4}$ = 3.5 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-3-thienyl), 11.30 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 52.93 (CH_3O-4), 94.64 (C-4a), 109.47 (C-5), 117.69 (CH-6), 123.04 (CH-5-thienyl), 124.41 (CH-3-thienyl), 127.63 (CH-4-thienyl), 137.63 (C-2-thienyl), 155.83 (C-7a), 159.72 (C-2), 163.31 (C-4).

MS (ESI): *m*/*z* (%) = 247.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{11}N_4OS$: 247.0648; found: 247.0647.

4-Methoxy-5-(thiophen-3-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (35d)

Compound **35d** was prepared from **28d** (480 mg, 1.27 mmol) by GPD. Flash column chromatography (70–80% EtOAc/hexanes) then recrystallization (MeOH) gave the product (190 mg, 61%) as a brownish solid; mp 260–261 °C.

IR (KBr): 3336, 3099, 1624, 1570, 1389, 1307, 1095, 854, 772, 571 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.96 (s, 3 H, CH_3O), 6.10 (bs, 2 H, NH_2), 7.20 (d, $J_{6,NH}$ = 2.3 Hz, 1 H, H-6), 7.46 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.6 Hz, 1 H, H-4-thienyl), 7.47 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 2.7 Hz, 1 H, H-5-thienyl), 7.72 (dd, $J_{2,5}$ = 2.7 Hz, $J_{2,4}$ = 1.6 Hz, 1 H, H-2-thienyl), 11.21 (d, $J_{NH,6}$ = 2.2 Hz, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 53.07 (CH_3O-4), 94.85 (C-4a), 111.32 (C-5), 118.01 (CH-6), 1119.57 (CH-2-thienyl), 125.35 and 127.90 (CH-4,5-thienyl), 135.68 (C-3-thienyl), 155.75 (C-7a), 159.49 (C-2), 163.40 (C-4).

MS (ESI): *m*/*z* (%) = 247.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{11}H_{11}N_4OS$: 247.0648; found: 247.0648.

5-(Benzofuran-2-yl)-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (35e)

Compound **35e** was prepared from **28e** (400 mg, 0.97 mmol) by GPD. Flash column chromatography (80–90% EtOAc/hexanes) then recrystallization (MeOH) gave the product (145 mg, 56%) as a yellowish solid; mp 238–239 °C.

IR (KBr): 3344, 3117, 1612, 1579, 1452, 1321, 1092, 791, 739, 557 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.06 (s, 3 H, CH_3O-4), 6.25 (bs, 2 H, NH_2), 7.19 (btd, $J_{5,6}$ = $J_{5,4}$ = 7.3 Hz, $J_{5,7}$ = 1.4 Hz, 1 H, H-5-benzofuryl), 7.22 (btd, $J_{6,7}$ = $J_{6,5}$ = 7.2 Hz, $J_{6,4}$ = 1.7 Hz, 1 H, H-6-benzofuryl), 7.26 (d, $J_{3,7}$ = 1.1 Hz, 1 H, H-3-benzofuryl), 7.42 (d, $J_{6,NH}$ = 2.5 Hz, 1 H, H-6), 7.49 (m, 1 H, H-7-benzofuryl), 7.59 (m, 1 H, H-4-benzofuryl), 11.55 (d, $J_{NH,6}$ = 2.5 Hz, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 53.29 (CH_3O-4), 93.71 (C-4a), 101.52 (CH-3-benzofuryl), 106.01 (C-5), 110.51 (CH-7-benzofuryl), 118.97 (CH-6), 120.60 (CH-4-benzofuryl), 122.96 (CH-5-benzofuryl), 123.60 (CH-6-benzofuryl), 129.77 (C-3a-benzofuryl), 152.35 (C-2-benzofuryl), 153.59 (C-7a-benzofuryl), 156.31 (C-7a), 160.15 (C-2), 163.30 (C-4).

MS (ESI): *m*/*z* (%) = 281.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{15}H_{13}N_4O_2$: 281.1033; found: 281.1033.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-methoxy-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (35f)

Compound **35f** was prepared from **28f** (540 mg, 1.17 mmol) by GPD. Flash column chromatography (80–90% EtOAc/hexanes) then recrystallization (MeOH) gave the product (190 mg, 51%) as a brownish solid; mp 257–258 °C.

IR (KBr): 3362, 3122, 1634, 1576, 1450, 1302, 1197, 1096, 734, 631 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.84 (s, 3 H, CH_3O), 6.15 (bs, 2 H, NH_2), 7.40 (btd, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{12}H_7O$), 7.41 (t, $J_{2,1}$ = $J_{2,3}$ = 7.7 Hz, 1 H, H-2-$C_{12}H_7O$), 7.43 (d, $J_{6,NH}$ = 2.4 Hz, 1 H, H-6), 7.51 (ddd, $J_{7,6}$ = 8.2 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{12}H_7O$), 7.72 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{12}H_7O$), 7.81 (dd, $J_{3,2}$ = 7.6 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{12}H_7O$), 7.99 (dd, $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{12}H_7O$), 8.15 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{12}H_7O$), 11.47 (d, $J_{NH,6}$ = 2.4 Hz, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 52.96 (CH_3O-4), 95.64 (C-4a), 109.42 (C-5), 111.86 (CH-6-$C_{12}H_7O$), 118.43 (CH-1-$C_{12}H_7O$), 120.23 (C-4-$C_{12}H_7O$), 120.35 (CH-6), 121.24 (CH-9-$C_{12}H_7O$), 123.02 and 123.14 (CH-2,8-$C_{12}H_7O$), 123.61 (C-9b-$C_{12}H_7O$), 124.08 (C-9a-$C_{12}H_7O$), 127.51 (CH-7-$C_{12}H_7O$), 128.41 (CH-3-$C_{12}H_7O$), 153.12 (C-4a-$C_{12}H_7O$), 155.52 (C-5a-$C_{12}H_7O$), 155.88 (C-7a), 159.70 (C-2), 163.46 (C-4)..

MS (ESI): *m*/*z* (%) = 331.1 (100) [M + H], 353.1 (10) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{15}N_4O_2$: 331.1189; found: 331.1191.

4-Methoxy-5-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidin-2-amine (35g)

Compound **35g** was prepared from **28g** (185 mg, 0.50 mmol) by GPD. Flash column chromatography (70–80% EtOAc/hexanes) then recrystallization (MeOH) gave the product (65 mg, 54%) as a white solid; mp 226–227 °C.

IR (KBr): 3312, 3118, 1630, 1574, 1379, 1314, 1091, 971, 785, 608 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.89 (s, 3 H, CH_3O-4), 6.08 (bs, 2 H, NH_2), 7.05 (d, $J_{6,NH}$ = 2.4 Hz, 1 H, H-6), 7.19 (m, 1 H, H-*p*-Ph), 7.33 (m, 2 H, H-*m*-Ph), 7.61 (m, 2 H, H-*o*-Ph), 11.26 (bd, $J_{NH,6}$ = 2.3 Hz, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 52.92 (CH_3O-4), 94.99 (C-4a), 116.16 (C-5), 118.01 (CH-6), 125.66 (CH-*p*-Ph), 128.04 and 128.14 (CH-*o*,*m*-Ph), 135.40 (C-*i*-Ph), 156.12 (C-7a), 159.51 (C-2), 163.41 (C-4).

MS (ESI): *m*/*z* (%) = 241.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{13}H_{13}N_4O$: 241.1083; found: 241.1084.

5-(Furan-2-yl)-4-methoxy-2-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (36a)

Compound **36a** was prepared from **29a** (240 mg, 0.67 mmol) by GPC. Flash column chromatography (0–5% MeOH/CH_2Cl_2) then recrystallization (MeOH) gave the product (140 mg, 91%) as a white solid; mp 246–247 °C.

IR (KBr): 3115, 2949, 1569, 1347, 1288, 1207, 1102, 820, 772, 604 cm^{-1}.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 2.53 (s, 3 H, CH_3-2), 4.06 (s, 3 H, CH_3O-4), 6.52 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.8 Hz, 1 H, H-4-furyl), 6.85 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.52 (d, $J_{6,NH}$ = 2.5 Hz, 1 H, H-6), 7.60 (dd, $J_{5,4}$ = 1.8 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 12.06 (bs, 1 H, NH).

^{13}C NMR (150.9 MHz, DMSO-d_6): δ = 25.58 (CH_3-2), 53.41 (CH_3O-4), 98.41 (C-4a), 106.34 (CH-3-furyl), 106.41 (C-5), 111.75 (CH-4-furyl), 119.99 (CH-6), 141.19 (CH-5-furyl), 149.19 (C-2-furyl), 153.93 (C-7a), 160.22 (C-2), 162.43 (C-4).

MS (ESI): *m*/*z* (%) = 230.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{12}H_{12}N_3O_2$: 230.0924; found: 230.0924.

5-(Furan-3-yl)-4-methoxy-2-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (36b)

Compound **36b** was prepared from **29b** (310 mg, 0.86 mmol) by GPD. Flash column chromatography (0–5% MeOH/CH_2Cl_2) then recrystallization (MeOH) gave the product (125 mg, 61%) as a yellowish solid; mp 242–243 °C.

IR (KBr): 3101, 2947, 1570, 1348, 1296, 1105, 1035, 817, 777, 592 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.53 (s, 3 H, CH_3-2), 4.05 (s, 3 H, CH_3O-4), 6.92 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.9 Hz, 1 H, H-4-furyl), 7.55 (d, $J_{6,NH}$ = 2.4 Hz, 1 H, H-6), 7.66 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 8.06 (dd, $J_{2,5}$ = 1.6 Hz, $J_{2,4}$ = 0.9 Hz, 1 H, H-2-furyl), 11.90 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.58 (CH_3-2), 53.36 (CH_3O-4), 99.49 (C-4a), 106.28 (C-5), 110.23 (CH-4-furyl), 119.25 (C-3-furyl), 120.76 (CH-6), 139.43 (CH-2-furyl), 143.22 (CH-5-furyl), 154.08 (C-7a), 159.76 (C-2), 162.38 (C-4).

MS (ESI): *m*/*z* (%) = 230.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{12}H_{12}N_3O_2$: 230.0924; found: 230.0924.

4-Methoxy-2-methyl-5-(thiophen-2-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (36c)

Compound **36c** was prepared from **29c** (350 mg, 0.93 mmol) by GPC. Flash column chromatography (0–5% MeOH/CH_2Cl_2) then recrystallization (MeOH) gave the product (208 mg, 87%) as a white solid; mp 219–220 °C.

IR (KBr): 3101, 2945, 1568, 1351, 1289, 1100, 1021, 792, 710, 615 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.54 (s, 3 H, CH_3-2), 4.03 (s, 3 H, CH_3O-4), 7.06 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.37 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.42 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 7.51 (s, 1 H, H-6), 12.06 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.56 (CH_3-2), 53.30 (CH_3O-4), 99.40 (C-4a), 109.07 (C-5), 121.31 (CH-6), 123.84 (CH-5-thienyl), 125.09 (CH-3-thienyl), 127.72 (CH-4-thienyl), 136.76 (C-2-thienyl), 153.93 (C-7a), 159.96 (C-2), 162.43 (C-4).

MS (ESI): *m*/*z* (%) = 246.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{12}H_{12}N_3OS$: 246.0696; found: 246.0696.

4-Methoxy-2-methyl-5-(thiophen-3-yl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (36d)

Compound **36d** was prepared from **29d** (450 mg, 1.20 mmol) by GPD. Flash column chromatography (0–5% MeOH/CH_2Cl_2) then recrystallization (MeOH) gave the product (171 mg, 58%) as a white solid; mp 312–313 °C.

IR (KBr): 3099, 2950, 2828, 1570, 1347, 1288, 1102, 1006, 777, 605 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.54 (s, 3 H, CH_3-2), 4.04 (s, 3 H, CH_3O-4), 7.52 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 2.7 Hz, 1 H, H-5-thienyl), 7.54 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.6 Hz, 1 H, H-4-thienyl), 7.61 (s, 1 H, H-6), 7.81 (dd, $J_{2,5}$ = 2.7 Hz, $J_{2,4}$ = 1.6 Hz, 1 H, H-2-thienyl), 11.96 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.35 (CH_3-2), 53.35 (CH_3O-4), 99.53 (C-4a), 110.86 (C-5), 120.34 (CH-2-thienyl), 121.44 (CH-6), 125.58 (CH-4-thienyl), 128.00 (CH-5-thienyl), 135.03 (C-3-thienyl), 154.04 (C-7a), 159.59 (C-2), 162.41 (C-4).

MS (ESI): *m*/*z* (%) = 246.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{12}H_{12}N_3OS$: 246.0696; found: 246.0696.

5-(Benzofuran-2-yl)-4-methoxy-2-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (36e)

Compound **36e** was prepared from **29e** (300 mg, 0.81 mmol) by GPC. Flash column chromatography (0–5% MeOH/CH_2Cl_2) then recrystallization (MeOH) gave the product (174 mg, 77%) as a yellowish solid; mp 111–112 °C.

IR (KBr): 3099, 2940, 1571, 1344, 1272, 1099, 1017, 798, 707, 614 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.56 (s, 3 H, CH_3-2), 4.14 (s, 3 H, CH_3O-4), 7.21 (btd, $J_{5,6}$ = $J_{5,4}$ = 7.2 Hz, $J_{5,7}$ = 1.3 Hz, 1 H, H-5-benzofuryl), 7.25 (btd, $J_{6,7}$ = $J_{6,5}$ = 7.6 Hz, $J_{6,4}$ = 1.5 Hz, 1 H, H-6-benzofuryl), 7.35 (d, $J_{3,7}$ = 1.1 Hz, 1 H, H-3-benzofuryl), 7.53 (bdq, $J_{7,6}$ = 7.6 Hz, $J_{7,5}$ = $J_{7,4}$ = $J_{7,3}$ = 1.1 Hz, 1 H, H-7-benzofuryl), 7.62 (bd, $J_{4,5}$ = 7.4 Hz, 1 H, H-4-benzofuryl), 7.81 (s, 1 H, H-6), 12.31 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.60 (CH_3-2), 53.70 (CH_3O-4), 98.76 (C-4a), 102.24 (CH-3-benzofuryl), 105.67 (C-5), 110.63 (CH-7-benzofuryl), 120.80 (CH-4-benzofuryl), 122.30 (CH-6), 123.07 (CH-5-benzofuryl), 123.88 (CH-6-benzofuryl), 129.61 (C-3a-benzofuryl), 151.66 (C-2-benzofuryl), 153.69 (C-7a-benzofuryl), 154.41 (C-7a), 160.66 (C-2), 162.44 (C-4).

MS (ESI): *m*/*z* (%) = 280.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{16}H_{14}N_3O_2$: 280.1081; found: 280.1082.

5-(Dibenzo[*b*,*d*]furan-4-yl)-4-methoxy-2-methyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (36f)

Compound **36f** was prepared from **29f** (496 mg, 1.08 mmol) by GPC. Flash column chromatography (0–5% MeOH/CH_2Cl_2) then recrystallization (MeOH) gave the product (295 mg, 83%) as a white solid; mp 290–291 °C.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.58 (s, 3 H, CH_3-2), 3.90 (s, 3 H, CH_3O-4), 7.41 (td, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{12}H_7O$), 7.44 (t, $J_{2,1}$ = $J_{2,3}$ = 7.6 Hz, 1 H, H-2-$C_{12}H_7O$), 7.52 (ddd, $J_{7,6}$ = 8.2 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{12}H_7O$), 7.72 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{12}H_7O$), 7.79 (s, 1 H, H-6), 7.81 (dd, $J_{3,2}$ = 7.6 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{12}H_7O$), 8.04 (dd, $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{12}H_7O$), 8.17 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{12}H_7O$), 12.21 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.63 (CH_3-2), 53.35 (CH_3O-4), 100.59 (C-4a), 109.09 (C-5), 111.91 (CH-6-$C_{12}H_7O$), 119.03 (C-4-$C_{12}H_7O$), 121.33 (CH-9-$C_{12}H_7O$), 123.12 and 123.23 (CH-2,8-$C_{12}H_7O$), 123.72 (CH-6), 123.73 (C-9b-$C_{12}H_7O$), 124.03 (C-9a-$C_{12}H_7O$), 127.64 (C-7-$C_{12}H_7O$), 128.75 (CH-3-$C_{12}H_7O$), 153.25 (C-4a-$C_{12}H_7O$), 154.00 (C-7a), 155.59 (C-5a-$C_{12}H_7O$), 159.85 (C-2), 162.63 (C-4).

MS (ESI): *m*/*z* (%) = 330.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{20}H_{16}N_3O_2$: 330.1237; found: 330.1238.

4-Methoxy-2-methyl-5-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (36g)

Compound **36g** was prepared from **29g** (368 mg, 0.90 mmol) by GPD. Flash column chromatography (0–5% MeOH/CH_2Cl_2) then recrystallization (MeOH) gave the product (134 mg, 62%) as a white solid; mp 227–228 °C.

IR (KBr): 3111, 2948, 2840, 1560, 1335, 1188, 1007, 835, 728, 616 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.55 (s, 3 H, CH_3-2), 3.98 (s, 3 H, CH_3O-4), 7.24 (m, 1 H, H-*p*-Ph), 7.37 (m, 2 H, H-*m*-Ph), 7.47 (s, 1 H, H-6), 7.66 (m, 2 H, H-*o*-Ph), 12.02 (bs, 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 25.23 (CH_3-2), 53.27 (CH_3O-4), 99.75 (C-4a), 115.75 (C-5), 121.62 (CH-6), 126.04 (CH-*p*-Ph), 128.24 (CH-*m*-Ph), 128.40 (CH-*o*-Ph), 134.75 (C-*i*-Ph), 154.24 (C-7a), 159.51 (C-2), 162.49 (C-4).

MS (ESI): *m*/*z* (%) = 240.1 (100) [M + H].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{14}H_{14}N_3O$: 240.1131; found: 240.1132.

5-(Furan-2-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (37a)

Compound **37a** was prepared from **32a** (40 mg, 0.18 mmol) by GPE. Flash column chromatography (0–5% MeOH/CH_2Cl_2) gave the product (30 mg, 82%) as a white solid; mp >200 °C (dec).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.48 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.9 Hz, 1 H, H-4-furyl), 7.31 (d, $J_{6,NH}$ = 2.6 Hz, 1 H, H-6), 7.33 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 1.0 Hz, 1 H, H-3-furyl), 7.56 (dd, $J_{5,4}$ = 1.9 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 7.86 (d, $J_{2,NH}$ = 3.8 Hz, 1 H, H-2), 11.88 (bs, 1 H, NH-1), 12.10 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 103.50 (C-4a), 107.62 (CH-3-furyl), 110.89 (C-5), 111.64 (CH-4-furyl), 116.49 (CH-6), 141.00 (CH-5-furyl), 144.46 (CH-2), 149.16 (C-7a), 149.30 (C-2-furyl), 158.66 (C-4).

MS (ESI): *m*/*z* (%) = 224.04 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{10}H_7O_2N_3Na$: 224.0430; found: 224.0430.

5-(Furan-3-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (37b)

Compound **37b** was prepared from **32b** (92 mg, 0.43 mmol) by GPE. Flash column chromatography (0–5% MeOH/CH_2Cl_2) gave the product (32 mg, 37%) as a white solid; mp >250 °C (dec).

^{1}H NMR (401 MHz, DMSO-d_6): δ = 6.97 (dd, $J_{4,5}$ = 1.9 Hz, $J_{4,2}$ = 0.8 Hz, 1 H, H-4-furyl), 7.40 (s, 1 H, H-6), 7.62 (t, $J_{5,2}$ = $J_{5,4}$ = 1.7 Hz, 1 H, H-5-furyl), 7.84 (s, 1 H, H-2), 8.50 (bd, $J_{2,5}$ = 1.7 Hz, 1 H, H-2-furyl), 11.82 and 11.95 (2 bs, 2 × 1 H, NH).

^{13}C NMR (101 MHz, DMSO-d_6): δ = 104.91 (C-4a), 109.94 (CH-4-furyl), 111.19 (C-5), 117.89 (CH-6), 119.44 (C-3-furyl), 140.95 (CH-2-furyl), 143.29 (CH-5-furyl), 144.27 (CH-2), 149.42 (C-7a), 159.28 (C-4).

MS (ESI): *m*/*z* (%) = 224.04 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{10}H_7O_2N_3Na$: 224.0430; found: 224.0430.

5-(Thiophen-2-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (37c)

Compound **37c** was prepared from **32c** (70 mg, 0.33 mmol) by GPE. Flash column chromatography (0–5% MeOH/CH_2Cl_2) gave the product (50 mg, 76%) as a white solid; mp >200 °C (dec).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.02 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.6 Hz, 1 H, H-4-thienyl), 7.31 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.34 (s, 1 H, H-6), 7.85 (s, 1 H, H-2), 7.90 (dd, $J_{3,4}$ = 3.6 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 11.66–12.36 (m, 2 H, NH-1,7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 104.32 (C-4a), 113.95 (C-5), 117.94 (CH-6), 123.41 (CH-5-thienyl), 126.13 (CH-3-thienyl), 127.71 (CH-4-thienyl), 136.73 (C-2-thienyl), 144.27 (CH-2), 149.26 (C-7a), 158.76 (C-4).

MS (ESI): *m*/*z* (%) = 240.0 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{10}H_7ON_3NaS$: 240.0202; found: 240.0202.

5-(Thiophen-3-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (37d)

Compound **37d** was prepared from **32d** (80 mg, 0.35 mmol) by GPE. Flash column chromatography (0–5% MeOH/CH_2Cl_2) gave the product (55 mg, 73%) as a white solid; mp >300 °C (dec).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.47 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 7.50 (d, $J_{6,NH}$ = 2.6 Hz, 1 H, H-6), 7.66 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.3 Hz, 1 H, H-4-thienyl), 7.85 (d, $J_{2,NH}$ = 3.4 Hz, 1 H, H-2), 8.43 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.3 Hz, 1 H, H-2-thienyl), 11.86 (bs, 1 H, NH-1), 12.01 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 104.61 (C-4a), 115.59 (C-5), 118.39 (CH-6), 121.17 (CH-2-thienyl), 125.41 (CH-5-thienyl), 127.48 (CH-4-thienyl), 135.05 (C-3-thienyl), 143.36 (CH-2), 149.29 (C-7a), 159.14 (C-4).

MS (ESI): *m*/*z* (%) = 218.2 (11) [M + H], 240.2 (89) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_8ON_3S$: 218.0382; found: 218.0382.

5-(Benzofuran-2-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (37e)

Compound **37e** was prepared from **32e** (80 mg, 0.30 mmol) by GPE. Flash column chromatography (0–5% MeOH/CH_2Cl_2) gave the product (67 mg, 89%) as a white solid; mp >250 °C (dec).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.20 (td, $J_{5,6}$ = $J_{5,4}$ = 7.3 Hz, $J_{5,7}$ = 1.2 Hz, 1 H, H-5-benzofuryl), 7.23 (bddd, $J_{6,7}$ = 8.0 Hz, $J_{6,5}$ = 7.2 Hz, $J_{6,4}$ = 1.5 Hz, 1 H, H-6-benzofuryl), 7.51 (bdq, $J_{7,6}$ = 8.0 Hz, $J_{7,5}$ = $J_{7,4}$ = $J_{7,3}$ = 1.0 Hz, 1 H, H-7-benzofuryl), 7.60 (d, $J_{6,NH}$ = 2.7 Hz, 1 H, H-6), 7.62 (dm, $J_{4,5}$= 7.5 Hz, 1 H, H-4-benzofuryl), 7.38 (d, $J_{3,7}$ = 1.1 Hz, 1 H, H-3-benzofuryl), 7.92 (d, $J_{2,NH}$ = 3.7 Hz, 1 H, H-2), 12.06 (bd, $J_{NH,2}$ = 3.3 Hz, 1 H, NH-1), 13.34 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 103.54 (CH-3-benzofuryl), 104.12 (C-4a), 110.10 (C-5), 110.61 (CH-7-benzofuryl), 118.84 (CH-6), 120.86 (CH-4-benzofuryl), 123.02 (CH-5-benzofuryl), 123.83 (CH-6-benzofuryl), 129.60 (C-3a-benzofuryl), 144.92 (CH-2), 149.80 (C-7a), 151.76 (C-2-benzofuryl), 153.74 (C-7a-benzofuryl), 158.73 (C-4).

MS (ESI): *m*/*z* (%) = 252.2 (50.8) [M + H], 274.2 (49.2) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{14}H_{10}O_2N_3$: 252.0767; found: 252.0768.

5-(Dibenzo[*b*,*d*]furan-4-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (37f)

Compound **37f** was prepared from **32f** (290 mg, 0.92 mmol) by GPE. Flash column chromatography (0–5% MeOH/CH_2Cl_2) gave the product (175 mg, 63%) as a white solid; mp >200 °C (dec).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.41 (t, $J_{2,1}$ = $J_{2,3}$ = 7.7 Hz, 1 H, H-2-$C_{10}H_7O$), 7.41 (td, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 0.9 Hz, 1 H, H-8-$C_{10}H_7O$), 7.52 (ddd, $J_{7,6}$ = 8.3 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{10}H_7O$), 7.76 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.9 Hz, 1 H, H-6-$C_{10}H_7O$), 7.85 (s, 1 H, H-6), 7.93 (s, 1 H, H-2), 7.99 (dd, $J_{1,2}$ = 7.6 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{10}H_7O$), 8.16 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{10}H_7O$), 8.50 (dd, $J_{3,2}$ = 7.7 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{10}H_7O$), 11.94 and 12.32 (2 bs, 2 × 1 H, NH).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 105.25 (C-4a), 112.03 (CH-6-$C_{10}H_7O$), 114.02 (C-5), 118.75 (CH-1-$C_{10}H_7O$), 119.28 (C-4-$C_{10}H_7O$), 121.26 (CH-9-$C_{10}H_7O$), 121.51 (CH-6), 123.11 and 123.31 (CH-2,8-$C_{10}H_7O$), 123.63 (C-9b-$C_{10}H_7O$), 124.08 (C-9a-$C_{10}H_7O$), 127.55 (CH-7-$C_{10}H_7O$), 129.37 (CH-3-$C_{10}H_7O$), 144.29 (CH-2), 149.43 (C-7a), 152.82 (C-4a-$C_{10}H_7O$), 155.47 (C-5a-$C_{10}H_7O$), 158.87 (C-4).

MS (ESI): *m*/*z* (%) = 302.3 (61) [M + H], 324.3 (39) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{12}O_2N_3$: 302.0924; found: 302.0925.

5-Phenyl-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (37g)

Compound **37g** was prepared from **32g** (75 mg, 0.33 mmol) by GPE. Flash column chromatography (0–5% MeOH/CH_2Cl_2) gave the product (63 mg, 90%) as a white solid; mp >250 °C (dec).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.19 (m, 1 H, H-*p*-Ph), 7.32 (m, 2 H, H-*m*-Ph), 7.39 (d, $J_{6,NH}$ = 2.6 Hz, 1 H, H-6), 7.86 (d, $J_{2,NH}$ = 3.4 Hz, 1 H, H-2), 7.94 (m, 2 H, H-*o*-Ph), 11.84 (bs, 1 H, NH-1), 12.08 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 104.66 (C-4a), 118.74 (CH-6), 120.24 (C-5), 125.92 (CH-*p*-Ph), 128.10 and 128.11 (CH-*m*,*o*-Ph), 134.44 (C-*i*-Ph), 143.85 (CH-2), 149.54 (C-7a), 158.86 (C-4).

MS (ESI): *m*/*z* (%) = 212.1 (49) [M + H], 234.1 (51) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{12}H_9ON_3Na$: calcd 234.0637; found: 234.0637.

2-Amino-5-(furan-2-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (38a)

Compound **38a** (56 mg, 64%) was obtained as a brownish solid from **35a** (86 mg, 0.40 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3198, 3006, 2887, 1686, 1570, 1405, 1139, 774, 516 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.19 (bs, 2 H, NH_2), 6.44 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.8 Hz, 1 H, H-4-furyl), 6.91 (bs, 1 H, H-6), 7.25 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.49 (dd, $J_{5,4}$ = 1.8 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 10.39 (bs, 1 H, NH-3), 11.20 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 96.08 (C-4a), 106.87 (CH-3-furyl), 110.52 (C-5), 111.51 (CH-4-furyl), 113.17 (CH-6), 140.46 (CH-5-furyl), 150.04 (C-2-furyl), 152.40 (C-7a), 152.98 (C-2), 159.12 (C-4).

MS (ESI): *m*/*z* (%) = 217.0 (70) [M + H], 239.0 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_9N_4O_2$: 217.0720; found: 217.0719.

2-Amino-5-(furan-3-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (38b)

Compound **38b** (50 mg, 58%) was obtained as a brownish solid from **35b** (93 mg, 0.40 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3202, 2879, 2758, 1667, 1570, 1388, 1152, 1020, 777, 486 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.11 (bs, 2 H, NH_2), 6.86 (dd, $J_{4,5}$ = 1.9 Hz, $J_{4,2}$ = 0.8 Hz, 1 H, H-4-furyl), 6.97 (d, $J_{6,NH}$ = 2.4 Hz, 1 H, H-6), 7.56 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 8.44 (bd, $J_{2,5}$ = 1.6 Hz, 1 H, H-2-furyl), 10.23 (bs, 1 H, NH-3), 11.05 (bd, $J_{NH,6}$ = 1.8 Hz, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 97.29 (C-4a), 109.50 (CH-4-furyl), 110.44 (C-5), 114.26 (CH-6), 119.73 (C-3-furyl), 140.36 (CH-2-furyl), 142.83 (CH-5-furyl), 152.44 (C-7a), 152.71 (C-2), 159.45 (C-4).

MS (ESI): *m*/*z* (%) = 217.1 (30) [M + H], 239.1 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_9N_4O_2$: 217.0720; found: 217.0720.

2-Amino-5-(thiophen-2-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (38c)

Compound **38c** (54 mg, 65%) was obtained as a yellowish solid from **35c** (90 mg, 0.36 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3187, 3021, 2869, 1690, 1573, 1400, 1137, 770, 686, 506 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.17 (bs, 2 H, NH_2), 6.93 (s, 1 H, H-6), 6.97 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.22 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.88 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 10.38 (bs, 1 H, NH-3), 11.19 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 97.02 (C-4a), 113.63 (C-5), 114.43 (CH-6), 122.40 (CH-5-thienyl), 125.50 (CH-3-thienyl), 127.56 (CH-4-thienyl), 137.63 (C-2-thienyl), 152.53 (C-7a), 152.81 (C-2), 159.19 (C-4).

MS (ESI): *m*/*z* (%) = 233.0 (40) [M + H], 255.0 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_9N_4OS$: 233.0491; found: 233.0491.

2-Amino-5-(thiophen-3-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (38d)

Compound **38d** (63 mg, 68%) was obtained as a white solid from **35d** (98 mg, 0.40 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3181, 3020, 2858, 1691, 1574, 1402, 1130, 777, 684, 507 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.12 (bs, 2 H, NH_2), 7.08 (d, $J_{6,NH}$ = 2.4 Hz, 1 H, H-6), 7.41 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.2 Hz, 1 H, H-4-thienyl), 7.55 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 8.37 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.2 Hz, 1 H, H-2-thienyl), 10.33 (bs, 1 H, NH-3), 11.10 (bd, $J_{NH,6}$ = 2.3 Hz, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 97.36 (C-4a), 115.22 (CH-6), 115.35 (C-5), 120.46 (CH-2-thienyl), 125.30 (CH-5-thienyl), 127.30 (CH-4-thienyl), 135.81 (C-3-thienyl), 152.68 and 152.74 (C-7a, 2), 159.73 (C-4).

MS (ESI): *m*/*z* (%) = 233.1 (30) [M + H], 255.1 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{10}H_9N_4OS$: 233.0491; found: 233.0491.

2-Amino-5-(benzofuran-2-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (38e)

Compound **38e** (82 mg, 77%) was obtained as a greenish solid from **35e** (101 mg, 0.36 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3349, 3123, 1624, 1577, 1345, 1257, 1175, 783, 684, 547 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.25 (bs, 2 H, NH_2), 7.17 (m, 1 H, H-5-benzofuryl), 7.17–7.22 (m, 2 H, H-6-benzofuryl, H-6), 7.47 (dm, $J_{7,6}$ = 7.4 Hz, 1 H, H-7-benzofuryl), 7.56 (dm, $J_{4,5}$ = 7.0 Hz, 1 H, H-4-benzofuryl), 7.78 (d, $J_{3,7}$ = 1.1 Hz, 1 H, H-3-benzofuryl), 10.52 (bs, 1 H, NH-3), 11.45 (d, $J_{NH,6}$ = 2.0 Hz, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 96.55 (C-4a), 102.86 (CH-3-benzofuryl), 109.79 (C-5), 110.57 (CH-7-benzofuryl), 115.86 (CH-6), 120.69 (CH-4-benzofuryl), 123.00 (CH-5-benzofuryl), 123.62 (CH-6-benzofuryl), 129.85 (C-3a-benzofuryl), 152.55 (C-2-benzofuryl), 153.12 and 153.32 (C-7a, 2), 153.73 (C-7a-benzofuryl), 159.26 (C-4).

MS (ESI): *m*/*z* (%) = 267.2 (40) [M + H], 289.2 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{14}H_{11}N_4O_2$: 267.0876; found: 267.0877.

2-Amino-5-(dibenzo[*b*,*d*]furan-4-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (38f)

Compound **38f** (62 mg, 73%) was obtained as a brownish solid from **35f** (90 mg, 0.27 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3324, 3257, 1643, 1451, 1195, 842, 783, 750, 631 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.21 (bs, 2 H, NH_2), 7.37 (t, $J_{2,1}$ = $J_{2,3}$ = 7.6 Hz, 1 H, H-2-$C_{12}H_7O$), 7.40 (btd, $J_{8,9}$ = $J_{8,7}$ = 7.5 Hz, $J_{8,6}$ = 1.0 Hz, 1 H, H-8-$C_{12}H_7O$), 7.51 (ddd, $J_{7,6}$ = 8.2 Hz, $J_{7,8}$ = 7.3 Hz, $J_{7,9}$ = 1.4 Hz, 1 H, H-7-$C_{12}H_7O$), 7.58 (d, $J_{6,NH}$ = 2.2 Hz, 1 H, H-6), 7.76 (dt, $J_{6,7}$ = 8.2 Hz, $J_{6,8}$ = $J_{6,9}$ = 0.8 Hz, 1 H, H-6-$C_{12}H_7O$), 7.92 (dd, $J_{1,2}$ = 7.6 Hz, $J_{1,3}$ = 1.3 Hz, 1 H, H-1-$C_{12}H_7O$), 8.13 (ddd, $J_{9,8}$ = 7.7 Hz, $J_{9,7}$ = 1.4 Hz, $J_{9,6}$ = 0.7 Hz, 1 H, H-9-$C_{12}H_7O$), 8.67 (dd, $J_{3,2}$ = 7.7 Hz, $J_{3,1}$ = 1.3 Hz, 1 H, H-3-$C_{12}H_7O$), 10.45 (bs, 1 H, NH-3), 11.45 (bd, $J_{NH,6}$ = 2.1 Hz, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 97.86 (C-4a), 112.20 (CH-6-$C_{12}H_7O$), 113.95 (C-5), 118.24 (CH-1-$C_{12}H_7O$), 118.90 (CH-6), 120.18 (C-4-$C_{12}H_7O$), 121.39 (CH-9-$C_{12}H_7O$), 123.30 and 123.48 (CH-2,8-$C_{12}H_7O$), 123.70 (C-9b-$C_{12}H_7O$), 124.35 (C-9a-$C_{12}H_7O$), 127.65 (CH-7-$C_{12}H_7O$), 129.19 (CH-3-$C_{12}H_7O$), 152.79 (C-4a-$C_{12}H_7O$), 153.03 and 153.07 (C-2,7a), 155.60 (C-5a-$C_{12}H_7O$), 159.63 (C-4).

MS (ESI): *m*/*z* (%) = 317.1 (95) [M + H], 339.1 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{18}H_{13}N_4O_2$: 317.1033; found: 317.1034.

2-Amino-5-phenyl-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (38g)

Compound **38g** (68 mg, 62%) was obtained as a white solid from **35g** (116 mg, 0.48 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3180, 3017, 2859, 1688, 1573, 1401, 1130, 779, 683, 506 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.13 (bs, 2 H, NH_2), 7.02 (m, 1 H, H-*p*-Ph), 7.18 (m, 2 H, H-*m*-Ph), 7.29 (s, 1 H, H-6), 7.94 (m, 2 H, H-*o*-Ph), 10.36 (bs, 1 H, NH-3), 11.19 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 97.29 (C-4a), 115.33 (CH-6), 119.81 (C-5), 125.50 (CH-*p*-Ph), 127.60 (CH-*o*-Ph), 128.03 (CH-*m*-Ph), 135.12 (C-*i*-Ph), 151.66 (C-7a), 152.60 (C-2), 159.36 (C-4).

MS (ESI): *m*/*z* (%) = 227.1 (50) [M + H], 249.0 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{12}H_{11}N_4O$: 227.0927; found: 227.0927.

5-(Furan-2-yl)-2-methyl-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (39a)

Compound **39a** (78 mg, 91%) was obtained as a yellowish solid from **36a** (98 mg, 0.40 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3099, 2912, 1664, 1600, 1452, 1301, 911, 816, 775, 673 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.30 (s, 3 H, CH_3-2), 6.47 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ = 1.8 Hz, 1 H, H-4-furyl), 7.22 (d, $J_{6,NH}$ = 2.6 Hz, 1 H, H-6), 7.32 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, H-3-furyl), 7.54 (dd, $J_{5,4}$ = 1.8 Hz, $J_{5,3}$ = 0.9 Hz, 1 H, H-5-furyl), 11.78 (bs, 1 H, NH-3), 11.87 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 20.96 (CH_3-2), 101.19 (C-4a), 107.46 (CH-3-furyl), 110.64 (C-5), 111.60 (CH-4-furyl), 115.82 (CH-6), 140.87 (CH-5-furyl), 149.48 (C-2-furyl), 149.83 (C-7a), 153.66 (C-2), 159.37 (C-4).

MS (ESI): *m*/*z* (%) = 214.1 (100) [M – H].

HRMS (ESI): *m*/*z* [M – H] for $C_{11}H_8N_3O_2$: 214.0622; found: 214.0618.

5-(Furan-3-yl)-2-methyl-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (39b)

Compound **39b** (53 mg, 61%) was obtained as a yellowish solid from **36b** (100 mg, 0.40 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3100, 2922, 1662, 1604, 1448, 1307, 1035, 814, 787, 673 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.30 (s, 3 H, CH_3-2), 6.94 (dd, $J_{4,5}$ = 1.8 Hz, $J_{4,2}$ = 0.8 Hz, 1 H, H-4-furyl), 7.29 (s, 1 H, H-6), 7.60 (t, $J_{5,4}$ = $J_{5,2}$ = 1.7 Hz, 1 H, H-5-furyl), 8.49 (bd, $J_{2,5}$ = 1.7 Hz, 1 H, H-2-furyl), 11.27–12.11 (m, 2 H, NH-1,7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 20.92 (CH_3-2), 102.29 (C-4a), 109.60 (CH-4-furyl), 110.60 (C-5), 116.92 (CH-6), 119.31 (C-3-furyl), 140.59 (CH-2-furyl), 142.98 (CH-5-furyl), 149.87 (C-7a), 153.13 (C-2), 159.73 (C-4).

MS (ESI): *m*/*z* (%) = 214.1 (100) [M – H].

HRMS (ESI): *m*/*z* [M – H] for $C_{11}H_8N_3O_2$: 214.0622; found: 214.0619.

2-Methyl-5-(thiophen-2-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (39c)

Compound **39c** (56 mg, 87%) was obtained as a yellowish solid from **36c** (69 mg, 0.30 mmol) by GPE; mp 409–410 °C.

IR (KBr): 3093, 2923, 1651, 1600, 1551, 1297, 1099, 808, 787, 681 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.30 (s, 3 H, CH_3-2), 7.01 (dd, $J_{4,5}$ = 5.1 Hz, $J_{4,3}$ = 3.5 Hz, 1 H, H-4-thienyl), 7.25 (d, $J_{6,NH}$ = 2.5 Hz, 1 H, H-6), 7.29 (dd, $J_{5,4}$ = 5.1 Hz, $J_{5,3}$ = 1.2 Hz, 1 H, H-5-thienyl), 7.91 (dd, $J_{3,4}$ = 3.5 Hz, $J_{3,5}$ = 1.2 Hz, 1 H, H-3-thienyl), 11.78 (bs, 1 H, NH-1), 11.86 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 20.89 (CH_3-2), 101.98 (C-4a), 113.68 (C-5), 117.15 (CH-6), 123.09 (CH-5-thienyl), 125.97 (CH-3-thienyl), 127.64 (CH-4-thienyl), 136.92 (C-2-thienyl), 149.93 (C-7a), 153.40 (C-2), 159.41 (C-4).

MS (ESI): *m*/*z* (%) = 232.1 (15) [M + H], 254.0 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + Na] calcd for $C_{11}H_9N_3ONaS$: 254.0359; found: 254.0359.

2-Methyl-5-(thiophen-3-yl)-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (39d)

Compound **39d** (54 mg, 58%) was obtained as a white solid from **36d** (100 mg, 0.40 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3091, 2920, 1647, 1601, 1548, 1288, 1082, 809, 787, 672 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.31 (s, 3 H, CH_3-2), 7.41 (s, 1 H, H-6), 7.47 (dd, $J_{5,4}$ = 5.0 Hz, $J_{5,2}$ = 3.0 Hz, 1 H, H-5-thienyl), 7.64 (dd, $J_{4,5}$ = 5.0 Hz, $J_{4,2}$ = 1.2 Hz, 1 H, H-4-thienyl), 8.43 (dd, $J_{2,5}$ = 3.0 Hz, $J_{2,4}$ = 1.2 Hz, 1 H, H-2-thienyl), 11.43–12.00 (m, 2 H, NH-1,7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 20.86 (CH_3-2), 102.25 (C-4a), 115.30 (C-5), 117.66 (CH-6), 120.93 (CH-2-thienyl), 125.35 (CH-5-thienyl), 127.36 (CH-4-thienyl), 135.22 (C-3-thienyl), 149.99 (C-7a), 153.08 (C-2), 159.82 (C-4).

MS (ESI): *m*/*z* (%) = 230.1 (100) [M – H].

HRMS (ESI): *m*/*z* [M – H] for $C_{11}H_8N_3OS$: 230.0394; found: 230.0390.

5-(Benzofuran-2-yl)-2-methyl-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (39e)

Compound **39e** (70 mg, 77%) was obtained as a yellowish solid from **36e** (96 mg, 0.40 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3094, 2928, 1643, 1599, 1452, 1255, 1115, 818, 792, 742 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.33 (s, 3 H, CH_3-2), 7.19 (td, $J_{5,6}$ = $J_{5,4}$ = 7.3 Hz, $J_{5,7}$ = 1.2 Hz, 1 H, H-5-benzofuryl), 7.23 (m, 1 H, H-6-benzofuryl), 7.50 (m, 1 H, H-7-benzofuryl), 7.51 (d, $J_{6,NH}$ = 2.5 Hz, 1 H, H-6), 7.61 (m, 1 H, H-4-benzofuryl), 7.86 (d, $J_{3,7}$ = 1.1 Hz, 1 H, H-3-benzofuryl), 11.94 (bs, 1 H, NH-1), 12.11 (bs, 1 H, NH-7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 20.97 (CH_3-2), 101.76 (C-4a), 103.34 (CH-3-benzofuryl), 109.82 (C-5), 110.56 (CH-7-benzofuryl), 118.18 (CH-6), 120.79 (CH-4-benzofuryl), 122.97 (CH-5-benzofuryl), 123.73 (CH-6-benzofuryl), 129.62 (C-3a-benzofuryl), 150.46 (C-7a), 151.93 (C-2-benzofuryl), 153.71 (C-7a-benzofuryl), 154.17 (C-2), 159.40 (C-4).

MS (ESI): *m*/*z* (%) = 264.1 (100) [M – H].

HRMS (ESI): *m*/*z* [M – H] for $C_{15}H_{10}N_3O_2$: 264.0779; found: 264.0773.

5-(Dibenzo[*b*,*d*]furan-4-yl)-2-methyl-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (39f)

Compound **39f** (79 mg, 83%) was obtained as a yellowish solid from **36f** (99 mg, 0.30 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3055, 2911, 2826, 1650, 1613, 1452, 1196, 933, 819, 743 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.63 (s, 3 H, CH_3-2), 7.38–7.44 (m, 2 H, H-2,8-$C_{12}H_7O$), 7.52 (bt, $J_{7,6}$ = $J_{7,8}$ = 7.8 Hz, 1 H, H-7-$C_{12}H_7O$), 7.77 (bd, $J_{6,7}$ = 8.2 Hz, 1 H, H-6-$C_{12}H_7O$), 7.81 (s, 1 H, H-6), 7.98 (bd, $J_{1,2}$ = 7.5 Hz, 1 H, H-1-$C_{12}H_7O$), 8.16 (bd, $J_{9,8}$ = 7.7 Hz, 1 H, H-9-$C_{12}H_7O$), 8.58 (bd, $J_{3,2}$ = 7.6 Hz, 1 H, H-3-$C_{12}H_7O$), 11.10–12.68 (m, 2 H, NH-1,7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 20.91 (CH_3-2), 102.83 (C-4a), 111.98 (CH-6-$C_{12}H_7O$), 113.76 (C-5), 118.51 (CH-1-$C_{12}H_7O$), 119.44 (C-4-$C_{12}H_7O$), 120.93 (CH-6), 121.19 (CH-9-$C_{12}H_7O$), 123.08 and 123.24 (CH-2,8-$C_{12}H_7O$), 123.56 (C-9b-$C_{12}H_7O$), 124.05 (C-9a-$C_{12}H_7O$), 127.46 (C-7-$C_{12}H_7O$), 129.20 (CH-3-$C_{12}H_7O$), 150.16 (C-7a), 152.69 (C-4a-$C_{12}H_7O$), 153.45 (C-2), 155.41 (C-5a-$C_{12}H_7O$), 159.58 (C-4).

MS (ESI): *m*/*z* (%) = 316.1 (100) [M + H], 338.1 (100) [M + Na].

HRMS (ESI): *m*/*z* [M + H] calcd for $C_{19}H_{14}N_3O_2$: 316.1081; found: 316.1081.

2-Methyl-5-phenyl-3,7-dihydro-4*H*-pyrrolo[2,3-*d*]pyrimidin-4-one (39g)

Compound **39g** (55 mg, 52%) was obtained as a white solid from **36g** (102 mg, 0.40 mmol) by GPE; mp >300 °C (dec).

IR (KBr): 3090, 2919, 1648, 1600, 1548, 1288, 1086, 802, 785, 677 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.32 (s, 3 H, CH_3-2), 7.17 (m, 1 H, H-*p*-Ph), 7.32 (s, 1 H, H-6), 7.32 (m, 2 H, H-*m*-Ph), 7.96 (m, 2 H, H-*o*-Ph), 11.50–12.10 (m, 2 H, NH-1,7).

^{13}C NMR (125.7 MHz, DMSO-d_6): δ = 20.84 (CH_3-2), 102.31 (C-4a), 118.03 (CH-6), 119.93 (C-5), 125.79 (CH-*p*-Ph), 127.92 (CH-*o*-Ph), 128.10 (CH-*m*-Ph), 134.60 (C-*i*-Ph), 150.29 (C-7a), 153.00 (C-2), 159.59 (C-4).

MS (ESI): *m*/*z* (%) = 224.1 (100) [M – H].

HRMS (ESI): *m*/*z* [M – H] calcd for $C_{13}H_{10}N_3O$: 224.0829; found: 224.0827.

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Supporting Information

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