Electronic Supporting Information

for

Direct C-H sulfenylation of purines and deazapurines

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1. Experimental Section

General
Deazapurines (3 and 9), disulfides, boronic acid and stannanes were purchased from commercial suppliers and used without any further purification. Dry DMF and THF were used as received from supplier. All compounds were fully characterized by NMR and spectra were recorded on a Bruker Avance II 600 (¹H at 600.1 MHz, ¹³C at 150.9 MHz) or on a Bruker Avance II 500 (499.8 or 500.0 MHz for ¹H and 125.7 MHz for ¹³C) spectrometer. ¹H and ¹³C resonances were assigned using H,C-HSQC and H,C-HMBC spectra. The samples were measured in CDCl₃ and chemical shifts (in ppm, δ-scale) were referenced to solvent signal (δ(¹H) = 7.26 ppm, δ(¹H) = 77.0 ppm) or in or DMSO (δ(¹H) = 2.50 ppm, δ(¹H) = 39.43 ppm) Coupling constants (J) are given in Hz. IR spectra (wavenumbers in cm⁻¹) were recorded on Bruker Alpha FT-IR spectrometer using ATR technique. High resolution mass spectra were measured on a LTQ Orbitrap XL (Thermo Fisher Scientific) spectrometer using EI ionization technique. Melting points were determined on a Kofler block and are uncorrected. Elemental analyses were measured on PE 2400 Series II CHNS/O (Perkin Elmer, USA, 1999). X-ray diffraction experiment of single crystals was carried out on an X-ray diffractometer using CuKα radiation (λ=1.54180 Å).
Preparation of starting compounds:

7-Deazapurines

4-Phenyl-7H-pyrrolo[2,3-d]pyrimidine

(6-Phenyl-7-deazapurine) (1)

Dry toluene (250 ml) was added to a stirred solution of potassium carbonate (27.64 g, 200 mmol), 6-chloro-7-deazapurine 3 (15.36 g, 100 mmol), phenylboronic acid (18.29 g, 150 mmol) and Pd(PPh₃)₄ (4.62 g, 4 mmol) under Ar. The mixture was stirred for 18 h at temperature 100°C. After cooling to rt a brine was added and mixture were extracted with EtOAc 5x 250 mL and dried over Na₂SO₄. The crude mixture was separated by flash chromatography (gradient elution hexanes → hexanes/ethyl acetate 6:4) to give product 1 (17.57 g, 90 %) as white crystals.

M.p. 220-221 °C. ¹H NMR (500.0 MHz, CDCl₃): 6.89 (d, 1H, J₅,₆ = 3.6, H-5); 7.55 (m, 1H, H-p-Ph); 7.59 (m, 2H, H-m-Ph); 7.66 (d, 1H, J₆,₅ = 3.5, H-6); 8.18 (m, 2H, H-o-Ph); 8.84 (s, 1H, H-2); 12.27 (bs, 1H, NH). ¹³C NMR (125.7 MHz, CDCl₃): 100.17 (CH-5); 114.71 (C-4a); 127.93 (CH-6); 128.76 (CH-o-Ph); 129.05 (CH-m-Ph); 130.23 (CH-p-Ph); 138.14 (C-i-Ph); 151.14 (CH-2); 152.80 (C-7a); 155.73 (C-4). IR (KBr): 3205, 3133, 3006, 2865, 1598, 1581, 1563, 1503, 1412, 1349. HRMS (ESI) calculated for C₁₂H₁₀N₃: 196.0869; found: 196.0869. Anal. calculated for C₁₂H₉N₃ (195.08): C 73.83%, H 4.65%, N 21.52%; found: C 73.59%, H 4.63%, N 21.19%.
4-Amino-7H-pyrrolo[2,3-d]pyrimidine
(6-Amino-7-deazapurine) (4)

6-chloro-7-deazapurine 3 (5 g; 31.73 mmol) was dissolved in 70 mL of mixture 1,4-dioxane/aqueous ammonia (1:1) in a steel bomb and was heated at 130 °C for 19 h. After cooling, the mixture was evaporated. The crude mixture was separated by flash chromatography (gradient elution chloroform → chloroform/methanol 95:5) to give product 4 (4.25 g, 91 %) as white crystals.

7-Benzyl-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine
(9-Benzyl-6-phenyl-7-deazapurine) (2)

Dry toluene (250 ml) was added to a stirred solution of potassium carbonate (27.64 g, 200 mmol), 9-benzyl-6-chloro-7-deazapurine (23.4 g, 100 mmol), phenylboronic acid (18.29 g, 150 mmol) and Pd(PPh₃)₄ (4.62 g, 4 mmol) under Ar. The mixture was stirred for 18 h at temperature 100°C. After cooling to rt a brine was added and mixture were extracted with EtOAc 3x 250 mL and dried over Na₂SO₄. The crude mixture was separated by flash chromatography (gradient elution hexanes → hexanes/ethyl acetate 8:2) to give product 2 (25.9 g, 91 %) as white crystals.
9-Deazapurines

4-Phenyl-5H-pyrrolo[3,2-d]pyrimidine

(6-Phenyl-9-deazapurine) (7)

Dry tolue (250 ml) was added to a stirred solution of potassium carbonate (27.64 g, 200 mmol), 6-chloro-9-deazapurine 9 (15.36 g, 100 mmol), phenylboronic acid (18.29 g, 150 mmol) and Pd(PPh₃)₄ (4.62 g, 4 mmol) under Ar. The mixture was stirred for 18 h at temperature 100°C. After cooling to rt a brine was added and mixture were extracted with EtOAc 5x 250 mL and dried over Na₂SO₄. The crude mixture was separated by flash chromatography (gradient elution hexanes → hexanes/ethyl acetate 6:4) to give product 7 (16.59 g, 85%) as yellowish crystals.

M.p. 136-142 °C. ¹H NMR (499.8 MHz, DMSO-d₆): 6.71 (dd, 1H, J₇,6 = 3.1, J₇,NH = 1.5, H-7); 7.58 (m, 1H, H-p-Ph); 7.62 (m, 2H, H-m-Ph); 7.91 (dd, 1H, J₆,7 = J₆,NH = 3.1, H-6); 8.09 (m, 2H, H-o-Ph); 8.90 (s, 1H, H-2); 11.99 (bs, 1H, NH). ¹³C NMR (125.7 MHz, DMSO-d₆): 101.82 (CH-7); 123.70 (C-4a); 128.79 (CH-o-Ph); 129.11 (CH-m-Ph); 130.32 (CH-p-Ph); 134.20 (CH-6); 136.34 (C-i-Ph); 147.64 (C-4); 150.38 (CH-2); 151.45 (C-7a). IR (KBr): 3205, 3135, 3081, 3007, 2867, 1599, 1582, 1563, 1503, 1438, 1412, 1350. HRMS (ESI) calculated for C₁₂H₁₁N₃: 196.0796; found: 196.0869. Anal. calculated for C₁₂H₉N₃ (195.08): C 73.83%, H 4.65%, N 21.52%; found: C 73.68%, H 4.54%, N 21.12%.

5-Benzyl-4-chloro-5H-pyrrolo[3,2-d]pyrimidine

(7-Benzyl-6-chloro-9-deazapurine)

Dry DMF (150 ml) was added to a stirred solution of potassium carbonate (11.4 g, 82.5 mmol) and 6-chloro-9-deazapurine 9 (11.5 g, 75 mmol) under Ar. After 20 min, benzyl chloride (9.2 ml, 78.75 mmol) was added and the resulting mixture was stirred overnight at rt.
After that brine was added and mixture were extracted with EtOAc 3x 250 mL and dried over Na₂SO₄. The crude mixture was separated by flash chromatography (gradient elution hexanes → hexanes/ethyl acetate 8:2) to give product 7-benzyl-6-chloro-9-deazapurine (16.63 g, 91 %) as yellowish crystals.

M.p. 122-126 °C. ¹H NMR (600.1 MHz, DMSO-d₆): 5.51 (s, 2H, CH₂Ph); 6.69 (d, 1H, J₇,₆ = 3.6, H-7); 7.27 (m, 3H, H-o,p-Ph); 7.32 (m, 2H, H-m-Ph); 7.85 (d, 1H, J₆,₇ = 3.6, H-6); 8.66 (s, 1H, H-2). ¹³C NMR (150.9 MHz, DMSO-d₆): 47.99 (CH₂Ph); 99.01 (CH-7); 116.91 (C-4a); 127.54 (CH-o-Ph); 127.87 (CH-p-Ph); 128.84 (CH-m-Ph); 131.66 (CH-6); 137.33 (C-i-Ph); 150.65 (CH-2); 150.72, 150.90 (C-4,7a). IR(KBr): 3113, 3070, 3032, 1593, 1522, 1496, 1460, 1452, 1444, 1409, 1399, 1350. HRMS (ESI) calculated for C₁₈H₁₄N₃S: 243.0563; found: 243.0569.

5-Benzyl-4-phenyl-5H-pyrrolo[3,2-d]pyrimidine
(7-Benzyl-6-phenyl-9-deazapurine) (8)

Dry toluene (100 ml) was added to a stirred solution of potassium carbonate (11.06 g, 80 mmol), 7-benzyl-6-chloro-9-deazapurine (9.72 g, 40 mmol), phenylboronic acid (7.32 g, 60 mmol) and Pd(PPh₃)₄ (1.85 g, 1.6 mmol) under Ar. The mixture was stirred for 18 h at temperature 110°C. After cooling to rt a brine was added and mixture were extracted with EtOAc 5x 250 mL and dried over Na₂SO₄. The crude mixture was separated by flash chromatography (gradient elution hexanes → hexanes/ethyl acetate 7:3) to give product 8 (11.07 g, 97 %) as white crystals.

M.p. 110-111 °C. ¹H NMR (499.8 MHz, DMSO-d₆): 5.21 (s, 2H, CH₂Ph); 6.37 (m, 2H, H-o-Bn); 6.81 (d, 1H, J₇,₆ = 3.2, H-7); 7.07 (m, 2H, H-m-Bn); 7.10 (m, 1H, H-p-Bn); 7.41 (m, 2H, H-o-Ph); 7.45 (m, 2H, H-m-Ph); 7.53 (m, 1H, H-p-Ph); 8.10 (d, 1H, J₆,₇ = 3.2, H-6); 8.85 (s, 1H, H-2). ¹³C NMR (125.7 MHz, DMSO-d₆): 51.85 (CH₂Ph); 101.83 (CH-7); 124.45 (C-4a);
12.97 (CH-o-Bn); 127.45 (CH-p-Bn); 128.21 (CH-m-Ph); 128.47 (CH-m-Bn); 129.32 (CH-o-Ph); 129.38 (CH-p-Ph); 137.35 (C-i-Ph); 137.44 (C-i-Bn); 138.99 (CH-6); 150.02 (CH-2); 150.37 (C-4); 152.14 (C-7a). IR(KBr): 3436, 3062, 3030, 1583, 1575, 1537, 1510, 1490, 1454, 1443, 1394, 1360. HRMS (ESI) calculated for C_{19}H_{16}N_{3}: 286.1339; found: 286.1339.

**Sulfenylation of 7-deazapurines. General Procedure:**

A mixture of 7-deazapurines 1-4 (2 mmol), disulphides (1.5 mmol), and CuI (0.2 mmol, 10 mol %) in DMF (20 mL) was stirred at 110°C under air atmosphere for 18 hours until complete consumption of starting material as monitored by TLC. The solution was then cooled to room temperature, diluted with EtOAc (30 mL), washed with 1M solution of sodium salt of EDTA (20 mL). Aqueous solution was then extracted three times with EtOAc and combitated organic layers were dried over Na_{2}SO_{4}, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel.

**4-Phenyl-5-(phenylsulfanyl)-7H-pyrrolo[2,3-d]pyrimidine (6-Phenyl-7-(phenylsulfanyl)-7-deazapurine) (**5a**)

![Chemical structure of 5a](image)

6-phenyl-7-deazapurine 1 (390 mg, 2 mmol) and diphenylidisulfide (328 mg, 1.5 mmol) were used as starting compounds to give products 5a (582 mg, 96%) and 6a (25 mg, 3%) as white solids after chromatography eluting with hexane/EtOAc 5:1 to 1:1. Crystalization in hexan/EtOAc gave white needles.

M.p. 184-186°C. \(^1\)H NMR (499.8 MHz, DMSO-\(d_6\)): 6.70 (m, 2H, H-o-SPh); 6.99 (m, 1H, H-p-SPh); 7.06 (m, 2H, H-m-SPh); 7.27 (m, 2H, H-m-Ph); 7.38 (m, 1H, H-p-Ph); 7.53 (m, 2H, H-o-Ph); 8.05 (d, 1H, \(J_{6,NH}=2.5\), H-6); 8.88 (s, 1H, H-2); 12.86 (bs, 1H, NH). \(^{13}\)C NMR (125.7 MHz, DMSO-\(d_6\)): 99.90 (C-5); 115.26 (C-4a); 125.25 (CH-p-SPh); 126.04 (CH-o-SPh); 127.29 (CH-m-Ph); 128.80 (CH-m-SPh); 129.23 (CH-p-Ph); 129.86 (CH-o-Ph); 135.69 (CH-6); 137.04 (C-i-Ph); 138.47 (C-i-SPh); 151.53 (CH-2); 153.55 (C-7a); 159.40 (C-4).
IR(KBr): 3104, 3059, 2988, 2862, 2818, 1598, 1581, 1551, 1478, 1435, 1322. HRMS (ESI) calculated for C_{18}H_{14}N_{3}S: 304.0902; found: 304.0901. Anal. calculated for C_{18}H_{13}N_{3}S (303.08): C 71.26%, H 4.32%, N 13.85%, S 10.57%; found: C 71.07%, H 4.15%, N 13.57%, S 10.47%.

4-Phenyl-5,6-bis(phenylsulfanyl)-7H-pyrrolo[2,3-d]pyrimidine
(6-Phenyl-7,8-bis(phenylsulfanyl)-7-deazapurine) (6a)

M.p. 231-233 °C. \(^1^H\) NMR (500.0 MHz, CDCl\(_3\)): 6.68 (m, 2H, H-\(o\)-Ph); 6.95 (m, 1H, H-\(p\)-SPh-5); 6.98 (m, 2H, H-\(m\)-SPh-5); 7.23 (m, 2H, H-\(m\)-Ph); 7.28-7.365 (m, 3H, H-\(p\)-Ph, H-\(m,p\)-SPh-6); 7.45 (m, 2H, H-\(o\)-SPh-6); 7.49 (m, 2H, H-\(o\)-Ph); 8.62 (s, 1H, H-2); 10.33 (bs, 1H, NH). \(^{13}\)C NMR (125.7 MHz, CDCl\(_3\)): 104.40 (C-5); 117.30 (C-4a); 125.40 (CH-\(p\)-SPh-5); 126.82 (CH-\(o\)-SPh-5); 127.46 (CH-\(m\)-Ph); 128.61 (CH-\(m\)-SPh-5); 129.04 (CH-\(p\)-Ph); 129.39 (CH-\(p\)-SPh-6); 129.87 (CH-\(o\)-Ph); 130.09 (CH-\(m\)-SPh-6); 131.02 (C-\(i\)-SPh-6); 132.24 (CH-\(o\)-SPh-6); 136.50 (C-\(i\)-Ph); 137.17 (C-\(i\)-SPh-5); 140.40 (C-6); 151.31 (CH-2); 153.27 (C-7a); 159.77 (C-4). IR(KBr): 3430, 3073, 2489, 1581, 1559, 1477, 1327. HRMS (ESI) calculated for C\(_{24}\)H\(_{18}\)N\(_{3}\)S\(_{2}\): 412.0935; found: 412.0936.

5-(Methylsulfanyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine
(7-(Methylsulfanyl)-6-phenyl-7-deazapurine) (5b)
6-phenyl-7-deazapurine 1 (390 mg, 2 mmol) and dimethyl disulfide (0.9 mL, 10 mmol) were used as starting compounds to give products 5b (343 mg, 71%) and 6b (86 mg, 15%) as yellow solids after chromatography with hexane/EtOAc 5:1 to 1:1.

M.p. 174-175 °C. $^1$H NMR (600.1 MHz, CDCl$_3$): 1.92 (s, 3H, CH$_3$S); 7.37 (d, 1H, J = 2.1, H-6); 7.53 (m, 3H, H-m,p-Ph); 7.91 (m, 2H, H-o-Ph); 9.01 (s, 1H, H-2); 11.12 (bs, 1H, NH).

$^{13}$C NMR (150.9 MHz, CDCl$_3$): 18.99 (CH$_3$S); 108.89 (C-5); 115.85 (C-4a); 126.78 (CH-6); 127.84 (CH-m-Ph); 129.76 (CH-p-Ph); 129.93 (CH-o-Ph); 137.27 (C-i-Ph); 151.29 (CH-2); 153.17 (C-7a); 160.54 (C-4). IR(CDCl$_3$): 3452, 3114, 2924, 2855, 1579, 1553, 1453, 1442, 1325. HRMS (ESI) calculated for C$_{13}$H$_{12}$N$_3$S: 242.0746; found: 242.0746.

5,6-Bis(methylsulfanyl)-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine (7,8-Bis(methylsulfanyl)-6-phenyl-7-deazapurine) (6b)

M.p. 139-141 °C. $^1$H NMR (499.8 MHz, DMSO-d$_6$): 1.70 (s, 3H, CH$_3$S-5); 2.66 (s, 3H, CH$_3$S-6); 7.48-7.55 (m, 3H, H-m,p-Ph); 7.80 (m, 2H, H-o-Ph); 8.81 (s, 1H, H-2); 12.86 (bs, 1H, NH). $^{13}$C NMR (125.7 MHz, DMSO-d$_6$): 15.74 (CH$_3$S-6); 19.33 (CH$_3$S-5); 103.91 (C-5); 116.72 (C-4a); 127.51 (CH-m-Ph); 129.49 (CH-p-Ph); 129.95 (CH-m-Ph); 136.69 (C-i-Ph); 142.14 (C-6); 149.87 (CH-2); 153.67 (C-7a); 156.20 (C-4). IR(KBr): 2920, 2857, 1739, 1577, 1550, 1464, 1458, 1437, 1317, 1254, 770, 704. HRMS (ESI) calculated for C$_{14}$H$_{14}$N$_3$S$_2$: 288.0624; found: 288.0624.
5-[(4-Methoxyphenyl)sulfanyl]-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine
(7-[(4-Methoxyphenyl)sulfanyl]-6-phenyl-7-deazapurine) (5c)

6-phenyl-7-deazapurine 1 (390 mg, 2 mmol) and bis(4-methoxyphenyl) disulfide (418 mg, 1.5 mmol) were used as starting compounds to give product 5c (608 mg, 91%) as white solids after chromatography eluting with hexane/EtOAc 5:1 to 1:1. Crystalization from hexan/EtOAc gave white needles.

M.p. 192-196 °C. ¹H NMR (499.8 MHz, CDCl₃): 3.71 (s, 3H, CH₃O); 6.59 (m, 2H, H-m-SC₆H₄OMe); 6.74 (m, 2H, H-o-SC₆H₄OMe); 7.42 (m, 2H, H-m-Ph); 7.47 (m, 1H, H-p-Ph); 7.54(s, 1H, H-6); 7.68 (m, 2H, H-o-Ph); 9.00 (s, 1H, H-2); 11.13 (bs, 1H, NH). ¹³C NMR (125.7 MHz, CDCl₃): 55.29 (CH₃O); 106.46 (C-5); 114.30 (CH-m-SC₆H₄OMe); 115.56 (C-4a); 127.29 (C-i-SC₆H₄OMe); 127.61 (CH-m-Ph); 129.53 (CH-p-Ph); 130.09 (CH-o-Ph); 130.67 (CH-o-SC₆H₄OMe); 131.02 (CH-6); 136.82 (C-i-Ph); 151.35 (CH-2); 153.33 (C-7a); 158.39 (C-p-SC₆H₄OMe); 160.94 (C-4). IR(KBr): 3099, 2982, 2959, 2835, 1595, 1552, 1493, 1249, 1026. HRMS (ESI) calculated for C₁₉H₁₆ON₃S: 334.1009; found: 334.1008.

5-[(4-Nitrophenyl)sulfanyl]-4-phenyl-7H-pyrrolo[2,3-d]pyrimidine
(7-[(4-Nitrophenyl)sulfanyl]-6-phenyl-7-deazapurine) (5d)

6-phenyl-7-deazapurine 1 (390 mg, 2 mmol) and 4-nitrophenyl disulfide (463 mg, 1.5 mmol) were used as starting compounds to give product 5d (328 mg, 47%) as green solids after chromatography eluting with hexane/EtOAc 5:1 to 1:1.
M.p. 253-261 °C. 1H NMR (499.8 MHz, DMSO-d6): 6.88 (m, 2H, H-ο-SC6H4NO2); 7.22 (m, 2H, H-m-Ph); 7.32 (m, 1H, H-p-Ph); 7.47 (m, 2H, H-ο-Ph); 7.88 (m, 2H, H-m-SC6H4NO2); 8.16 (s, 1H, H-6); 8.92 (s, 1H, H-2); 13.03 (bs, 1H, NH). 13C NMR (125.7 MHz, DMSO-d6): 97.21 (C-5); 115.06 (C-4a); 123.79 (CH-m-SC6H4NO2); 125.47 (CH-ο-SC6H4NO2); 127.29 (CH-m-Ph); 129.28 (CH-p-Ph); 129.63 (CH-ο-Ph); 136.31 (CH-6); 136.71 (C-ι-Ph); 144.53 (C-p-SC6H4NO2); 149.10 (C-ι-SC6H4NO2); 151.84 (CH-2); 153.69 (C-7a); 159.56 (C-4). IR(KBr): 2986, 2862, 2821, 1600, 1580, 1553, 1502, 1342, 1320, 1085. HRMS (ESI) calculated for C18H13O2N4S: 349.0754; found: 349.0753.

7-Benzyl-4-phenyl-5-(phenylsulfanyl)-7H-pyrrolo[2,3-d]pyrimidine
(9-Benzyl-6-phenyl-7-(phenylsulfanyl)-7-deazapurine) (5e)

7-benzyl-6-phenyl-7-deazapurine 2 (570 mg, 2 mmol) and diphenyldisulfide (1.1 g, 5 mmol) was used as starting compound to give product 5e (157 mg, 20%) as white solids after chromatography eluting with hexane/EtOAc 10:1 to 4:1. Crystalization in hexan/EtOAc gave white crystals. Recovery of starting compound 2 (405 mg, 71%).

M.p. 91-94 °C 1H NMR (500.0 MHz, CDCl3): 5.55 (s, 2H, CH2Ph); 6.71 (m, 2H, H-ο-SPh); 6.98 (m, 1H, H-p-SPh); 6.99 (m, 2H, H-m-SPh); 7.29 (m, 2H, H-m-Bn); 7.33 (m, 2H, H-ο-Bn); 7.35-7.40 (m, 4H, H-m,p-Ph, H-p-Bn); 7.48 (s, 1H, H-6); 7.52 (m, 2H, H-ο-Ph); 9.01 (s, 1H, H-2). 13C NMR (125.7 MHz, CDCl3): 48.23 (CH2Ph); 102.82 (C-5); 115.90 (C-4a); 125.25 (CH-p-SPh); 126.80 (CH-ο-SPh); 127.38 (CH-m-Bn); 127.85 (CH-ο-Bn); 128.28 (CH-p-Bn); 128.45 (CH-m-SPh); 129.03 (CH-m-Ph); 129.20 (CH-p-Ph); 129.80 (CH-ο-Ph); 135.25 (CH-6); 136.14 (C-ι-Ph); 136.78 (C-ι-Bn); 137.81 (C-ι-SPh); 151.93 (CH-2); 152.66 (C-7a); 160.93 (C-4). IR(KBr): 1552, 1451, 1414, 1330, 983. HRMS (ESI) calculated for
C\textsubscript{25}H\textsubscript{20}N\textsubscript{3}S: 394.1372; found: 394.1371. Anal. calculated for C\textsubscript{25}H\textsubscript{19}N\textsubscript{3}S (393.13): C 76.31%, H 4.87%, N 10.68%, S 8.15%; found: C 76.13%, H 4.69%, N 10.43%, S 8.02%.

4-Chloro-5-(phenylsulfanyl)-7H-pyrrolo[2,3-d]pyrimidine
(6-Chloro-7-(phenylsulfanyl)-7-deazapurine) (5f)

6-chloro-7-deazapurine 3 (307 mg, 2 mmol) and diphenyldisulfide (2.2 g, 10 mmol) were used as starting compounds to give product 5f (472 mg, 90%) as white solids. Diphenyldisulfide was divided into five portions and each one was added every 10 hours until complete consumption of starting material as monitored by TLC. Chromatography was started with pure hexane (to remove excess of diphenyldisulfide) and followed by hexane/EtOAc 5:1 to 1:1. Crystalization in hexan/EtOAc gave white crystals.

M.p. 184-186 °C \textsuperscript{1}H NMR (499.8 MHz, DMSO-\textit{d}_6): 7.06 (m, 2H, H-o-Ph); 7.12 (m, 1H, H-p-Ph); 7.24 (m, 2H, H-m-Ph); 8.12 (d, 1H, J = 2.6, H-6); 8.65 (s, 1H, H-2); 13.11 (bs, 1H, NH).
\textsuperscript{13}C NMR (125.7 MHz, DMSO-\textit{d}_6): 99.70 (C-5); 116.29 (C-4a); 125.49 (CH-p-Ph); 125.90 (CH-o-Ph); 129.25 (CH-m-Ph); 136.32 (CH-6); 139.13 (C-i-Ph); 150.98 (C-4); 151.44 (CH-2); 153.31 (C-7a). IR(KBr): 3072, 2963, 2813, 1596, 1551, 1478, 1439, 1338, 1228, 975, 844, 734. HRMS (ESI) calculated for C\textsubscript{12}H\textsubscript{9}N\textsubscript{3}ClS: 262.0200; found: 262.0200.

5-(Phenylsulfanyl)-7H-pyrrolo[2,3-d]pyrimidin-4-amine
(6-Amino-7-(phenylsulfanyl)-7-deazapurine) (5g)
6-amino-7-deazapurine 4 (268 mg, 2 mmol) and diphenyldisulfide (1.1 g, 5 mmol) were used as starting compounds to give product 5g (384 mg, 79%) as white solids after chromatography eluting DCM/MeOH 10:0 to 7:3 with 1% Et₃N.

M.p. 268-299 °C ¹H NMR (500.0 MHz, DMSO-d⁶): 6.52 (bs, 2H, NH₂); 7.09 (m, 2H, H-o-Ph); 7.13 (m, 1H, H-p-Ph); 7.27 (m, 2H, H-m-Ph); 7.58 (s, 1H, H-8); 8.10 (s, 1H, H-2); 12.16 (bs, 1H, NH). ¹³C NMR (125.7 MHz, DMSO-d⁶): 98.03 (C-7); 102.87 (C-5); 125.67 (CH-p-Ph); 125.79 (CH-o-Ph); 129.35 (CH-m-Ph); 129.91 (CH-8); 138.94 (C-i-Ph); 151.83 (C-4); 152.79 (CH-2); 157.52 (C-6). IR(KBr):3456, 3100, 3066, 1644, 1611, 1597, 1582, 1479, 1318. HRMS (ESI) calculated for C₁₂H₁₁N₄S: 243.0699; found: 243.0699

**Sulfenylation of 9-deazapurines. General Procedure:**

A mixture of CuI (0.2 mmol, 10 mol %) and 2,2’-bipyridine (0.4 mmol, 20 mol %) in DMF (10 mL) was stirred at rt for 15 minutes and then was added to mixture of 9-deazapurines 7-9 (2 mmol), disulphides (3 mmol) in DMF (20 mL) and then was stirred at 110°C under air atmosphere for 48 hours until complete consumption of starting material as monitored by TLC. The solution was then cooled to room temperature, diluted with EtOAc (30 mL), washed with 1M solution of sodium salt of EDTA (20 mL). Aqueous solution was then extracted three times with EtOAc and combinated organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel.

**4-Phenyl-7-(phenylsulfanyl)-5H-pyrrolo[3,2-d]pyrimidine**

(6-Phenyl-9-(phenylsulfanyl)-9-deazapurine) (10a)

![Chemical Structure](image-url)
6-phenyl-9-deazapurine 7 (390 mg, 2 mmol) and diphenyldisulfide (656 mg, 3 mmol) were used as starting compounds to give product 10a (595 mg, 96%) as white solids after chromatography eluting with hexane/EtOAc 5:1 to 1:2. Crystalization in hexan/EtOAc gave white needles. M.p. 210-216 °C. $^1$H NMR (499.8 MHz, DMSO-$d_6$): 7.10 (m, 3H, H-o,p-SPh); 7.22 (m, 2H, H-m-SPh); 7.61 (m, 1H, H-p-Ph); 7.63 (m, 2H, H-m-Ph); 8.11 (m, 2H, H-o-Ph); 8.29 (s, 1H, H-6); 8.95 (s, 1H, H-2); 12.56 (bs, 1H, NH). $^{13}$C NMR (125.7 MHz, DMSO-$d_6$): 101.28 (C-7); 124.83 (C-4a); 125.30 (CH-p-SPh); 126.02 (CH-o-SPh); 128.99 (CH-o-Ph); 129.10, 129.15 (CH-m-Ph, CH-m-SPh); 130.61 (CH-p-Ph); 135.77 (C-i-Ph); 138.63 (C-i-SPh); 140.37 (CH-6); 148.88 (C-4); 151.29 (CH-2); 151.43 (C-7a). IR(KBr): 3066, 2835, 1594, 1542, 1505, 1490, 1480, 1429. HRMS (ESI) calculated for C$_{18}$H$_{14}$N$_3$S: 304.0902; found: 304.0902.

7-(Methylsulfanyl)-4-phenyl-5H-pyrrolo[3,2-d]pyrimidine (9-(Methylsulfanyl)-6-phenyl-9-deazapurine) (10b)

6-phenyl-9-deazapurine 7 (390 mg, 2 mmol) and dimethyldisulfide (1.26 mL, 14 mmol) was used as starting compounds to give product 10b (208 mg, 43%) as yellow solids after chromatography with hexane/EtOAc 5:1 to 1:2. M.p. 196-206 °C. $^1$H NMR (499.8 MHz, DMSO-$d_6$): 2.46 (s, 3H, CH$_3$S); 7.59 (m, 1H, H-p-Ph); 7.61 (m, 2H, H-m-Ph); 7.94 (s, 1H, H-6); 8.07 (m, 2H, H-o-Ph); 8.94 (s, 1H, H-2); 12.15 (bs, 1H, NH). $^{13}$C NMR (125.7 MHz, DMSO-$d_6$): 18.12 (CH$_3$S); 107.46 (C-7); 124.55 (C-4a); 128.88 (CH-o-Ph); 129.17 (CH-m-Ph); 130.54 (CH-p-Ph); 135.06 (CH-6); 135.99 (C-i-Ph); 148.42 (C-4); 150.50 (CH-2); 150.54 (C-7a). IR(KBr): 3053, 2988, 2924, 2824, 1604, 1592, 1537, 1502, 1486, 1471, 1421, 1115, 866, 771. HRMS (ESI) calculated for C$_{13}$H$_{12}$N$_3$S: 242.0746; found: 242.0746.
7-[(4-Methoxyphenyl)sulfanyl]-4-phenyl-5H-pyrrolo[3,2-d]pyrimidine
(9-[(4-Methoxyphenyl)sulfanyl]-6-phenyl-9-deazapurine) (10c)

6-phenyl-9-deazapurine 7 (390 mg, 2 mmol) and bis(4-methoxyphenyl) disulfide (836 mg, 3 mmol) were used as starting compounds to give product 10c (566 mg, 85%) as yellow crystals after chromatography eluting with hexane/EtOAc 5:1 to 1:2.

M.p. 175-177 °C. \(^1\)H NMR (600.1 MHz, CDCl\(_3\)):
- 3.63 (s, 3H, CH\(_3\)O);
- 6.63 (m, 2H, H-\(m\)-SC\(_6\)H\(_4\)OMe);
- 7.03 (m, 2H, H-\(m\)-SC\(_6\)H\(_4\)OMe);
- 7.20 (m, 2H, H-\(m\)-Ph);
- 7.26 (m, 1H, H-\(p\)-Ph);
- 7.72 (d, 1H, \(J = 3.0\), H-6);
- 7.86 (m, 2H, H-\(o\)-Ph);
- 8.66 (s, 1H, H-2);
- 12.59 (bs, 1H, NH).

\(^{13}\)C NMR (150.9 MHz, CDCl\(_3\)):
- 55.10 (CH\(_3\)O);
- 104.13 (C-7);
- 114.33 (CH-\(m\)-SC\(_6\)H\(_4\)OMe);
- 125.56 (C-4a);
- 128.15 (C-\(i\)-SC\(_6\)H\(_4\)OMe);
- 128.50 (CH-\(o\)-Ph);
- 128.60 (CH-\(m\)-Ph);
- 128.71 (CH-\(o\)-SC\(_6\)H\(_4\)OMe);
- 130.16 (CH-\(p\)-Ph);
- 135.34 (C-\(i\)-Ph);
- 139.05 (CH-6);
- 149.91 (C-4);
- 150.56 (C-7a);
- 150.77 (CH-2);
- 157.91 (C-\(p\)-SC\(_6\)H\(_4\)OMe).

IR (CDCl\(_3\)):
- 3453, 3066, 2838, 2231, 1671, 1595, 1537, 1493, 1464, 1287, 1244, 1182, 1034.

HRMS (ESI) calculated for C\(_{19}\)H\(_{16}\)ON\(_3\)S: 334.1009; found: 334.1008.

7-[(4-Nitrophenyl)sulfanyl]-4-phenyl-5H-pyrrolo[3,2-d]pyrimidine
(9-[(4-Nitrophenyl)sulfanyl]-6-phenyl-9-deazapurine) (10d)
6-phenyl-9-deazapurine 7 (390 mg, 2 mmol) and 4-nitrophenyl disulfide (926 mg, 3 mmol) were used as starting compounds to give product 10d (348 mg, 50%) as yellow crystals after chromatography eluting with hexane/EtOAc 5:1 to 1:2.

M.p. 114-118 °C. $^1$H NMR (600.1 MHz, DMSO-$d_6$): 7.25 (m, 2H, H-o-SC$_6$H$_4$NO$_2$); 7.64 (m, 1H, H-p-Ph); 7.65 (m, 2H, H-m-Ph); 8.07 (m, 2H, H-m-SC$_6$H$_4$NO$_2$); 8.13 (m, 2H, H-o-Ph); 8.41 (s, 1H, H-6); 8.96 (s, 1H, H-2); 12.75 (bs, 1H, NH). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$): 98.61 (C-7); 124.20 (CH-m-SC$_6$H$_4$NO$_2$); 125.11 (C-4a); 125.56 (CH-o-SC$_6$H$_4$NO$_2$); 129.01 (CH-o-Ph); 129.18 (CH-m-Ph); 130.72 (CH-p-Ph); 135.65 (C-i-Ph); 140.90 (CH-6); 144.80 (C-p-SC$_6$H$_4$NO$_2$); 149.09 (C-i-SC$_6$H$_4$NO$_2$); 149.17 (C-4); 151.18 (C-7a); 151.49 (CH-2). IR(KBr): 3095, 3065, 1596, 1580, 1540, 1506, 1322, 1115, 1089, 854. HRMS (ESI) calculated for C$_{18}$H$_{13}$O$_2$N$_4$S:349.0754; found: 349.0753.

4-Chloro-7-(phenylsulfanyl)-5H-pyrrolo[3,2-d]pyrimidine

(6-Chloro-9-(phenylsulfanyl)-9-deazapurine) (10e)

6-chloro-9-deazapurine 9 (307 mg, 2 mmol) and diphenyldisulfide (3.1 g, 14 mmol) were used as starting compounds to give product 10e (471 mg, 90%) as white solids.
Diphenyldisulfide was divided into seven portions and each one was added every 10 hours until complete consumption of starting material as monitored by TLC. Chromatography was started with hexane (to remove excess of diphenyldisulfide) and followed by hexane/EtOAc 5:1 to 1:2. Crystalization in hexan/EtOAc gave white crystals.

[Do not exceed the reaction time (80 hours) to avoid forming mixture of products.]

M.p. 224-226 °C ¹H NMR (499.8 MHz, DMSO-d₆): 7.06 (m, 2H, H-o-Ph); 7.10 (m, 1H, H-p-Ph); 7.21 (m, 2H, H-m-Ph); 8.39 (s, 1H, H-6); 8.69 (s, 1H, H-2); 13.08 (bs, 1H, NH). ¹³C NMR (125.7 MHz, DMSO-d₆): 102.28 (C-7); 125.36 (C-4a); 125.48 (CH-p-Ph); 126.11 (CH-o-Ph); 129.16 (CH-m-Ph); 138.12 (C-i-Ph); 140.98 (CH-6); 142.99 (CH-4); 150.43 (CH-2); 151.38 (C-7a). IR(KBr): 3072, 1796, 1612, 1584, 1524, 1494, 1478, 1422, 1393, 1215, 868. HRMS (ESI) calculated for C₁₂H₉N₃ClS: 262.0200; found: 262.0200.

Optimization of bypyriddyne ligand

A mixture of CuI (0.1 mmol, 10 mol %) and bipyridine ligand (10-100 mol%) in DMF (5 mL) was stirred at rt for 15 minutes and then was added to mixture of 9-deazapurines 7 (195 mg, 1 mmol) and diphenyldisulphides (110 mg, 0.5 mmol) in DMF (5 mL) and then was stirred at 110°C under air atmosphere for 18 hours. The solution was then cooled to room temperature, diluted with EtOAc (10 mL), washed with 1M solution of sodium salt of EDTA (5 mL). Aqueous solution was then extracted three times with EtOAc and combitated organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum and NMR of reaction mixture was measured.

![Chemical Structure](image)

NMR conversion

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As the most economical ligand was chosen bpy (20 mol%) for the synthesis of 10a-d and the time was prolonged until complete conversion (generally 48 hours). To avoid mixture of products in the synthesis of 10e, we used dtbpy (20 mol%) as a more effective ligand and prolonged reaction time up to 80 hours.

**Halogenation of 9-deazapurines. General Procedure:**

A mixture of 9-deazapurine 7 or 9 (0.5 mmol) and CuX, (I, Br2) (0.6 mmol) in DMF (5 mL) was stirred at 110°C under air atmosphere for 18 hours until complete consumption of starting material as monitored by TLC. The solution was then cooled to room temperature, diluted with EtOAc (15 mL), washed with 1M solution of sodium salt of EDTA (10 mL). Aqueous solution was then extracted three times with EtOAc and combinated organic layers were dried over Na2SO4, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel.

**7-Iodo-4-phenyl-5H-pyrrolo[3,2-d]pyrimidine**

(6-Phenyl-9-iodo-9-deazapurine) (11a)

6-phenyl-9-deazapurine 7 (98 mg, 0.5 mmol) and CuI (115 mg, 0.6 mmol) were used as starting compound to give product 11a (130 mg, 81%) as white solid after chromatography eluting with hexane/EtOAc 5:1 to 1:2.

1H NMR (500.0 MHz, DMSO-d6): 7.60 (m, 3H, H-m,p-Ph); 8.09 (m, 2H, H-o-Ph); 8.11 (s, 1H, H-6); 8.97 (s, 1H, H-2); 12.43 (bs, 1H, NH). 13C NMR (125.7 MHz, DMSO-d6): 58.43 (C-7); 124.08 (C-4a); 128.90 (CH-o-Ph); 129.07 (CH-m-Ph); 130.54 (CH-p-Ph); 135.57 (C-i-Ph); 137.73 (CH-6); 148.48 (C-4); 150.95 (CH-2); 151.19 (C-7a). IR(KBr): 3434, 1605, 1595, 1539, 1504. HRMS (ESI) calculated for C12H9N3I: 321.9836; found: 321.9835

**7-Bromo-4-phenyl-5H-pyrrolo[3,2-d]pyrimidine**
(6-Phenyl-9-bromo-9-deazapurine) (11b)

6-phenyl-9-deazapurine 7 (98 mg, 0.5 mmol) and CuBr$_2$ (134 mg, 0.6 mmol) were used as starting compound to give product 11b (123 mg, 75%) as white solid after chromatography eluting with hexane/EtOAc 5:1 to 1:2.

M.p. 264 - 294 °C. $^1$H NMR (499.8 MHz, DMSO-$d_6$): 7.59 (m, 1H, H-p-Ph); 7.62 (m, 2H, H-m-Ph); 8.08 (m, 2H, H-o-Ph); 8.15 (d, 1H, $J = 3.1$, H-6); 8.98 (s, 1H, H-2); 12.40 (bs, 1H, NH). $^{13}$C NMR (125.7 MHz, DMSO-$d_6$): 89.68 (C-7); 123.66 (C-4a); 128.96 (CH-o-Ph); 129.14 (CH-m-Ph); 130.68 (CH-p-Ph); 133.44 (CH-6); 135.53 (C-i-Ph); 147.88 (C-7a); 148.77 (C-4); 150.98 (CH-2).

IR(KBr): 3438, 3054, 2929, 2788, 1607, 1597, 1545, 1508, 1490, 1184. HRMS (ESI) calculated for C$_{12}$H$_9$N$_3$Br: 273.9974; found: 273.9974

4-Chloro-7-iodo-5H-pyrrolo[3,2-d]pyrimidine

(6-Chloro-9-iodo-9-deazapurine) (11c)

6-chloro-9-deazapurine 7 (77 mg, 0.5 mmol) and CuI (115 mg, 0.6 mmol) were used as starting compound to give product 11c (91 mg, 65%) as white solid after chromatography eluting with hexane/EtOAc 5:1 to 1:2.
\(^1\)H NMR (499.8 MHz, DMSO-\(d_6\)): 8.20 (s, 1H, H-6); 8.71 (s, 1H, H-2); 12.95 (bs, 1H, NH).

\(^13\)C NMR (125.7 MHz, DMSO-\(d_6\)): 58.68 (C-7); 124.59 (C-4a); 138.45 (CH-6); 142.30 (C-4); 150.00 (CH-2); 151.13 (C-7a).

IR (KBr): 3436, 3120, 3092, 2972, 1609, 1527, 1494, 1417, 1354, 1245, 1177, 898, 860.

HRMS (ESI) calculated for C\(_6\)H\(_4\)N\(_3\)ClI: 279.9133; found: 279.9133

**Sulfenytion of 9-benzyl-6-phenyl-9H-purine. General procedure**

A 20 mL sealable tube equipped with a magnetic stirring bar was charged with all solid reaction components, 9-benzyl-6-phenyl-9H-purine 12 (286 mg, 1 mmol), disulfide (2.5 mmol), \(t\)BuOLi (240 mg, 3 mmol) and 1,4-dioxane (2 mL) via a syringe. The vessel was close by teflon-coated screw cap under Ar and was placed in a pre-heated oil bath at 130 °C and stirred until complete consumption of starting material as monitored by TLC, approx. 130 hours. It was cooled to room temperature and diluted with ethyl acetate (15 mL). The resulting solution was directly filtered through a filter paper and concentrated under reduced pressure.

**9-Benzyl-6-phenyl-8-(phenylsulfanyl)-9H-purine (13a)**

Diphenyldisulfide (546 mg, 2.5 mmol) was used as starting compound to give product 13a (237 mg, 60%) as white crystals after chromatography eluting with hexane/EtOAc 5:1 to 1:2.
9-Benzyl-8-[(4-methoxyphenyl)sulfanyl]-6-phenyl-9H-purine (13b)

Bis(4-methoxyphenyl) disulfide (696 mg, 2.5 mmol) was used as starting compound to give product 13b (238 mg, 56%) as white crystals after chromatography eluting with hexane/EtOAc 5:1 to 1:2.

M.p. 101 - 104 °C. \(^1\)H NMR (499.8 MHz, CDCl\(_3\)): 5.50 (s, 2H, CH\(_2\)Ph); 7.27-7.35 (m, 5H, H-o,m,p-Bn); 7.37-7.41 (m, 5H, H-m,p-PhS); 7.45-7.50 (m, 3H, H-m,p-Ph); 7.59 (m, 2H, H-o-PhS); 8.74 (m, 2H, H-o-Ph); 8.96 (s, 1H, H-2). \(^{13}\)C NMR (125.7 MHz, CDCl\(_3\)): 46.59 (CH\(_2\)Ph); 127.75 (CH-o-Bn); 128.18 (CH-p-Bn); 128.50 (CH-m-Ph); 128.68 (C-i-PhS); 128.82 (CH-m-Bn); 129.03 (CH-p-PhS); 129.37 (CH-m-PhS); 129.68 (CH-o-Ph); 130.78 (CH-p-Ph); 131.16 (C-5); 132.91 (CH-o-PhS); 135.24 (C-i-Bn); 135.54 (C-i-Ph); 151.95 (CH-2); 152.37 (C-6); 152.92 (C-8); 154.46 (C-4). IR(KBr): 2921, 2851, 1580, 1561, 1495, 1459, 1429, 1258, 764. HRMS (ESI) calculated for C\(_{24}\)H\(_{19}\)N\(_4\)S: 395.1325; found: 395.1323.

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M.p. 124-127 °C. \(^1\)H NMR (500.0 MHz, CDCl\(_3\)): 3.85 (s, 3H, CH\(_3\)O); 5.49 (s, 2H, CH\(_2\)Ph); 6.94 (m, 2H, H-m-SC\(_6\)H\(_4\)OMe); 7.28-7.36 (m, 5H, H-o,m,p-Bn); 7.45-7.50 (m, 3H, H-m,p-Ph); 7.56 (m, 2H, H-o-SC\(_6\)H\(_4\)OMe); 8.73 (m, 2H, H-o-Ph); 8.95 (s, 1H, H-2).

\(^{13}\)C NMR (125.7 MHz, CDCl\(_3\)): 46.47 (CH\(_2\)Ph); 55.43 (CH\(_3\)O); 114.96 (CH-m-SC\(_6\)H\(_4\)OMe); 118.00 (C-i-SC\(_6\)H\(_4\)OMe); 127.73 (CH-o-Bn); 128.16 (CH-p-Bn); 128.47 (CH-m-Ph); 128.81 (CH-m-Bn); 129.65 (CH-o-Ph); 130.73 (CH-p-Ph); 131.10 (C-5); 135.21 (C-i-Bn); 135.39 (C-i-Ph); 135.84 (CH-o-SC\(_6\)H\(_4\)OMe); 151.47 (CH-2); 151.61 (C-6); 154.67 (C-4,8); 160.76 (C-p-SC\(_6\)H\(_4\)OMe). IR (KBr): 3066, 3022, 2953, 2923, 2854, 1586, 1559, 1494, 1542, 1443, 1323, 1302, 1245, 1171, 1030, 833, 770, 725, 692. HRMS (ESI) calculated for C\(_{25}\)H\(_{21}\)ON\(_4\)S: 425.1431; found: 425.1429.
Liebeskind-Srogl cross-coupling of 9-benzyl-6-phenyl-8-(phenylsulfanyl)-9H-purine

a) Reaction with stannanes
To the mixture of CuMeSal (47 mg, 0.22 mmol, 2.2 equiv), Pd(PPh₃)₄ (5.8 mg, 0.005 mmol, 0.05 equiv) and 9-benzyl-6-phenyl-8-(phenylthio)-9H-purine 13a (39 mg, 0.1 mmol, 1.0 equiv) and stannane (0.12 mmol, 1.2 equiv) in THF (2 mL). The reaction mixture was stirred under nitrogen at 50 °C for 18 h, and then 10% aqueous NH₄OH (10 mL) was added and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with ethylacetate (3 × 15 mL). The organic layer was washed with brine (5 mL), dried over Na₂SO₄, and evaporated. The crude product was purified by column chromatography on silica gel.

9-Benzyl-8-(furan-2-yl)-6-phenyl-9H-purine (14a)

2-(tri-n-butylstannyl)furan (38 µL, 0.12 mmol, 1.2 equiv) was used as starting compound to give product 14a (25 mg, 70%) as white crystals after chromatography eluting with hexane/EtOAc 5:1 to 2:1.

M.p. 135 - 141 °C. ¹H NMR (500.0 MHz, CDCl₃): 5.86 (s, 2H, CH₂Ph); 6.59 (dd, 1H, J₄,3 = 3.6, J₄,5 = 1.8, H-4-furyl); 7.22 (m, 2H, H-o-Bn); 7.26 (m, 1H, H-p-Bn); 7.28 (m, 2H, H-m-Bn); 7.29 (dd, 1H, J₅,4 = 3.6, J₅,5 = 0.8, H-3-furyl); 7.52 (m, 1H, H-p-Ph); 7.58 (m, 2H, H-m-Ph); 7.64 (dd, 1H, J₅,4 = 1.8, J₅,5 = 0.8, H-5-furyl); 8.88 (m, 2H, H-o-Ph); 9.02 (s, 1H, H-2).

¹³C NMR (125.7 MHz, CDCl₃): 46.96 (CH₂Ph); 112.34 (CH4-furyl); 114.88 (CH3-furyl);126.85 (CH-o-Bn); 127.84 (CH-p-Bn); 128.62 (CH-m-Ph); 128.76 (CH-m-Bn); 129.79 (CH-o-Ph); 130.82 (CH-p-Ph); 131.05 (C-5); 135.75 (C-i-Ph); 136.16 (C-i-Bn); 144.70 (C-2-
furyl); 144.93 (CH-5-furyl); 145.47 (C-8); 152.27 (CH-2); 153.64 (C-6); 154.18 (C-4).

IR(KBr): 3068, 1605, 1603, 1562, 1497, 1454, 1334, 1321, 1016. HRMS (ESI) calculated for C_{22}H_{17}O_{3}N_{4}: 353.1397; found: 353.1397

9-Benzyl-6,8-diphenyl-9H-purine (14b)

Tributylphenylstannane (39 \mu L, 0.12 mmol, 1.2 equiv) was used as starting compound to give product 14b (30 mg, 83%) as white crystals after chromatography eluting with hexane/EtOAc 5:1 to 2:1. \(^1\)H NMR was compared with published data\(^1\).

\(^1\)H NMR (300 MHz, CDCl\(_3\)): 5.61 (s, 2H, CH\(_2\)Ph); 7.10 (m, 2H, H-o-Bn); 7.25-7.33 (m, 3H, H-m,p-Bn); 7.46-7.60 (m, 6H, H-m,p-Ph-6 and H-m,p-Ph-8); 7.73 (m, 2H, H-o-Ph-8); 8.92 (m, 2H, H-o-Ph-6); 9.05 (s, 1H, H-2).

b) Reaction with boronic acid

9-benzyl-6-phenyl-8-(phenylsulfanyl)-9H-purine 13a (39 mg, 0.1 mmol), Cu (I) thiophene-2-carboxylate (23 mg, 0.12 mmol), \(p\)-tolyboronic acid (21 mg, 0.15 mmol), Pd\(_2\)dba\(_3\) (4 mg, 0.004 mmol) and tris-2-furylphosphine (4 mg, 0.016 mmol) were placed in reaction vessel that was flushed with argon. THF (1 mL) was added and the mixture was stirred for 18 h at 50 °C. EtOAc (5 mL) was added and the suspension was washed with 10% aq. NH\(_4\)OH (10 mL). The aqueous layer was extracted with ethyl acetate (3 \times 15 mL). The combined organic phase was dried over anhydrous Na\(_2\)SO\(_4\) and filtered, and all of the volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel to give product 14c (20 mg, 54%) as white crystals after chromatography eluting with hexane/EtOAc 5:1 to 2:1. \(^1\)H NMR was compared with published data\(^1\).
9-Benzyl-6-phenyl-8-(p-tolyl)-9H-purine (14c)

$^1$H NMR (300 MHz, CDCl$_3$): 2.43 (s, 3H, CH$_3$); 5.59 (s, 2H, CH$_2$Ph); 7.11 (m, 2H, H-o-Bn); 7.25-7.34 (m, 5H, H-m-Tol and H-m,p-Bn); 7.51 (m, 1H, H-p-Ph); 7.57 (m, 2H, H-m-Ph); 7.64 (m, 2H, H-o-Tol); 8.92 (m, 2H, H-o-Ph); 9.03 (s, 1H, H-2).
2. Copies of NMR spectra
3. Single crystal X-ray structure analysis

Crystallographic data for 5e and 10a were obtained from Xcalibur X-ray diffractometer by monochromatized CuKα radiation (λ=1.54180 Å) at 190 K. The structures were solved by direct methods (SIR92)\(^2\) and refined by full-matrix least-squares based on F with (CRYSTALS)\(^3\). The hydrogen atoms were found on difference Fourier map, those on carbon atoms were recalculated into idealized positions. All hydrogen atoms were refined with riding constraints, while all other atoms were refined anisotropically in both cases.

**Crystal data for 5e** (0.05 x 0.13 x 0.21 mm):

C\(_{25}\)H\(_{19}\)N\(_3\)S\(_1\), monoclinic, space group \(P2_1/n\), \(a = 5.9059(3)\) Å, \(b = 13.5680(5)\) Å, \(c = 24.5309(9)\) Å, \(β = 91.499(4)^\circ\), \(V = 1965.01(13)\) Å\(^3\), \(Z = 4\), \(M = 393.51\), 9133 reflections measured, 4031 independent reflections. Final \(R = 0.039\), \(wR = 0.050\), \(GoF = 1.089\) for 3473 reflections with \(I > 2σ(I)\) and 263 parameters. CCDC 926544.

**Crystal data for 10a**:

C\(_{18}\)H\(_{13}\)N\(_3\)S\(_1\), monoclinic, space group \(P2_1/n\), \(a = 6.8659(2)\) Å, \(b = 18.4844(5)\) Å, \(c = 11.9993(4)\) Å, \(β = 103.118(3)^\circ\), \(V = 1483.11(8)\) Å\(^3\), \(Z = 4\), \(M = 303.39\), 6709 reflections measured, 3014 independent reflections. Final \(R = 0.037\), \(wR = 0.047\), \(GoF = 1.004\) for 2707 reflections with \(I > 2σ(I)\) and 200 parameters. CCDC 926543.

**References:**