Electronic Supplementary Information

A Concise, Efficient Synthesis of Sugar-Based Benzothiazoles through Chemoselective Intramolecular C–S Coupling

Chao Shen,[1,2] Haijun Xia,[1] Hua Yan,[1] Xinzhi Chen,[2] Sadananda Ranjit,[3] Xiaoji Xie,[3] Davin Tan,[4] Richmond Lee,[4] Yanmei Yang,[5] Bengang Xing,[5] Kuo-Wei Huang,[4] Pengfei Zhang[1*] and Xiaogang Liu[3,6*]

[1]College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, China. [2]Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China. [3]Department of Chemistry, National University of Singapore, Singapore 117543. [4]KAUST Catalysis Center and Division of Chemical and Life Sciences and Engineering,King Abdullah University of Science and Technology, Thuwal 23955- 6900, Kingdom of Saudi Arabia. [5]Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore 637371. [6]Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602.

1. General Information

a. Materials

Unless otherwise noted, all reactions were carried out without taking precautions to exclude air and moisture. Toluene was dried over sodium in the presence of benzophenone indicator and CH_2Cl_2 was distilled from CaH_2 freshly prior to use. Other commercially available reagents and solvents were used without additional purification unless otherwise stated. The pivaloylated sugar substrates were prepared according to our previous reports[1]. All thiourea derivatives were prepared according to the literature[2,3].

b. Methods

Melting points were determined on an X-5 Data microscopic melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature with $CDCl_3$ or DMSO-d_6 as solvent unless otherwise noted and tetramethylsilane (TMS) as the internal standard. ^{1}H NMR data were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, m = multiplet and br = broad), coupling constant (*J* values, Hz). ^{13}C NMR data were reported in terms of chemical shift (δ ppm). Mass spectra (EI-MS) were acquired on an Agilent 5975 spectrometer. Elemental analyses were performed on Carlo-Erba 1106. Analytical thin layer chromatography (TLC) was performed on Merk precoated TLC (silica gel 60 F254) plates. X-ray measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Ka. All calculations were performed with the density functional theory in Gaussian 09 programs.

2. Experimental Section

a. General procedure for the synthesis of glycosyl thiourea derivative (4a-o).

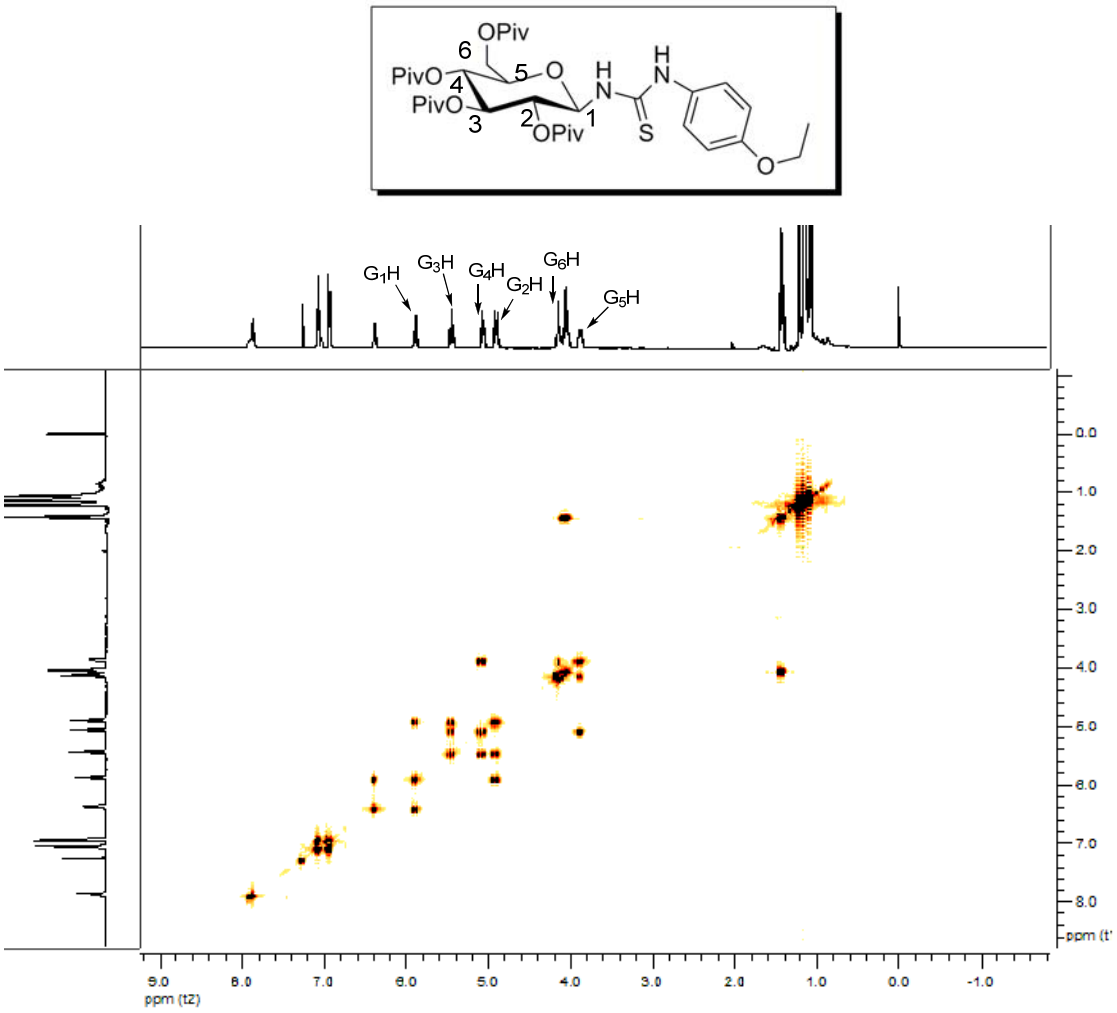
To a glass vial charged with acetonitrile (8 mL) was added glycosyl isothiocyanate (2.00 mmol) and substituted aromatic amine (2.20 mmol). The resulting mixture was stirred at room temperature and monitored by TLC. Upon completion of the reaction after 3 h, the mixture was poured into water (10 mL), and extracted three times with dichloromethane (10 mL x 3). The combined organic layers were washed with water, dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo* rotary evaporation and the product was isolated by recrystallization from dichloromethane and hexane (v/v; 1:10).

b. General procedure for the synthesis of glycosyl sugar-based benzothiazoles (5a-o).

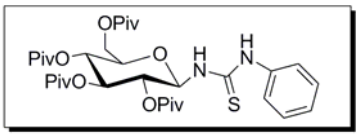
A mixture of **4** (0.14 mmol), $Pd(COD)Cl_2$ (3.99 mg, 0.014 mmol), and Bu_4NBr (46.1 mg, 0.28 mmol) in DMSO (3 mL) was stirred at 100 ^oC under O_2 (balloon pressure) and the reaction progress was monitored by TLC. Upon completion of the reaction after 12 h, the mixture was cooled to room temperature and poured into 10 mL of water. The mixture was extracted with AcOEt (5 mL x 3) and the combined organic layer was washed with brine (10 mL), and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane-AcOEt (v/v; 10:1) as an eluent to afford sugar-based benzothiazole **5.**

3. Characterization of the Products

^{1}H-^{1}H COSY spectrum of **4d**



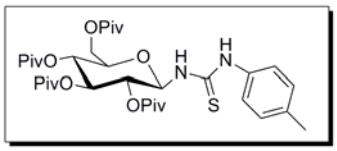
***N*-(2,3,4,6-Tetra-*O*-pivaloyl-*β*-D-glucopyranosyl)-*N'*-phenylthiourea (4a)**



Obtained as a white solid in 96% yield; M.p. 155-157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (br, 1H, NH), 7.44 (m, 2H, ArH), 7.36 (m, 1H, ArH), 7.18 (d, J = 7.6 Hz, 2H, ArH), 6.61 (d, J = 9.2 Hz, 1H, NH), 5.89 (t, J = 9.2 Hz, 1H, G_1H), 5.45 (t, J = 9.2 Hz, 1H, G_3H), 5.09 (t, J = 9.2 Hz, 1H, G_4H), 4.94 (t, J = 9.2 Hz, 1H, G_2H), 4.18-4.13 (m, 2H, G_6H), 3.88-3.86 (m, 1H, G_5H), 1.21-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

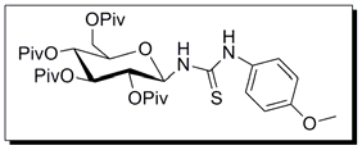
181.9, 178.4, 178.1, 176.7, 176.5, 135.1, 130.1, 127.9, 125.4, 83.2, 74.1, 72.1, 70.5, 67.6, 61.6, 38.9, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{50}N_2O_9S$: *m/z* 650.32 (M^+), found: *m/z* 650 (M^+). Anal. calcd. for $C_{33}H_{50}N_2O_9S$: C, 60.90; H, 7.74; N, 4.30; found: C, 60.63; H, 7.76; N, 4.31.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-_p_-tolythiourea (4b)



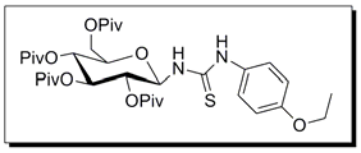
Obtained as a white solid in 86% yield; M.p. 181-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (br, 1H, NH), 7.25 (d, J = 8.0 Hz, 2H, ArH), 7.04 (d, J = 8.0 Hz, 2H, ArH), 6.49 (d, J = 9.2 Hz, 1H, NH), 5.89 (t, J = 9.2 Hz, 1H, G_1H), 5.45 (t, J = 9.2 Hz, 1H, G_3H), 5.08 (t, J = 9.2 Hz, 1H, G_4H), 4.93 (t, J = 9.2 Hz, 1H, G_2H), 4.18-4.09 (m, 2H, G_6H), 3.89-3.87 (m, 1H, G_5H), 2.38 (s, 3H, OCH_3), 1.21-1.08 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.1, 178.4, 178.1, 176.7, 176.5, 138.3, 132.3, 130.7, 125.6, 83.2, 74.0, 72.1, 70.5, 67.7, 61.6, 39.0, 38.9, 38.7, 27.1, 27.0, 21.1. MS (EI) calcd. for $C_{34}H_{52}N_2O_9S$: *m/z* 664.34 (M^+), found: *m/z* 664 (M^+). Anal. calcd. for $C_{34}H_{52}N_2O_9S$: C, 61.42; H, 7.88; N, 4.21; found: C, 61.43; H, 7.91; N, 4.22.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(4-methoxyphenyl)thiourea (4c)



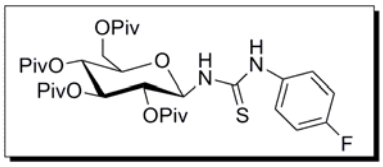
Obtained as a white solid in 91% yield; M.p. 177-179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (br, 1H, NH), 7.09 (d, J = 8.8 Hz, 2H, ArH), 6.95 (d, J = 8.8 Hz, 2H, ArH), 6.42 (d, J = 9.2 Hz, 1H, NH), 5.88 (t, J = 9.2 Hz, 1H, G_1H), 5.44 (t, J = 9.2 Hz, 1H, G_3H), 5.08 (t, J = 9.2 Hz, 1H, G_4H), 4.92 (t, J = 9.2 Hz, 1H, G_2H), 4.18-4.07 (m, 2H, G_6H), 3.86-3.83 (m, 1H, G_5H), 3.83 (s, 3H, CH_3), 1.21-1.08 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.3, 178.3, 178.0, 176.7, 176.4, 159.3, 127.6, 115.2, 83.2, 74.0, 72.1, 70.6, 67.6, 61.6, 55.5, 38.9, 38.8, 38.7, 38.6, 27.1, 27.0. MS (EI) calcd. for $C_{34}H_{52}N_2O_{10}S$: *m/z* 680.33 (M^+), found: *m/z* 680 (M^+). Anal. calcd. for $C_{34}H_{52}N_2O_{10}S$: C, 59.98; H, 7.70; N, 4.11; found: C, 59.60; H, 7.68; N, 4.10.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl-*β*-D-glucopyranosyl)-*N'*-(4-ethoxyphenyl)thiourea (4d)**



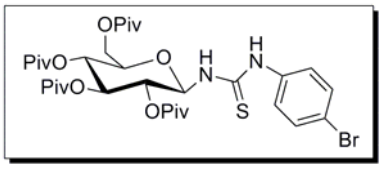
Obtained as a white solid in 84% yield; M.p. 180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (br, 1H, NH), 7.06 (d, J = 8.4 Hz, 2H, ArH), 6.93 (d, J = 8.4 Hz, 2H, ArH), 6.38 (d, J = 9.2 Hz, 1H, NH), 5.88 (t, J = 9.2 Hz, 1H, G_1H), 5.44 (t, J = 9.2 Hz, 1H, G_3H), 5.07 (t, J = 9.6 Hz, 1H, G_4H), 4.91 (t, J = 9.2 Hz, 1H, G_2H), 4.18-4.09 (m, 2H, G_6H), 4.05 (q, 2H, CH_2), 3.89-3.86 (m, 1H, G_5H), 1.43 (t, J =7.2 Hz, 3H, CH_3), 1.22-1.08 (m, 36 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.3, 178.3, 178.0, 176.7, 176.4, 158.7, 127.6, 115.7, 83.2, 74.0, 72.2, 70.5, 67.7, 63.8, 61.6, 38.9, 38.8, 38.7, 38.6, 27.1, 27.0, 14.7. MS (EI) calcd. for $C_{35}H_{54}N_2O_{10}S$: *m/z* 694.35 $(M]^+$), found: *m/z* 694 (M^+). Anal. calcd. for $C_{35}H_{54}N_2O_{10}S$: C, 60.50; H, 7.83; N, 4.03; found: C, 60.55; H, 7.84; N, 4.06;

***N*-(2,3,4,6-Tetra-*O*-pivaloyl-*β*-D-glucopyranosyl)-*N'*-(4-fluorophenyl)thiourea (4e)**



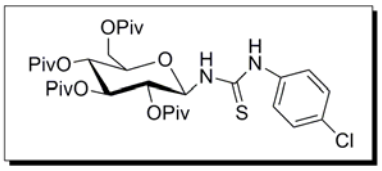
Obtained as a white solid in 92% yield; M.p. 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (br, 1H, NH), 7.16-7.14 (m, 4H, ArH), 6.52 (d, J = 9.2 Hz, 1H, NH), 5.86 (t, J = 9.2 Hz, 1H, G_1H), 5.46 (t, J = 9.2 Hz, 1H, G_3H), 5.09 (t, J = 9.6 Hz, 1H, G_4H), 4.93 (t, J = 9.2 Hz, 1H, G_2H), 4.18-4.11 (m, 2H, G_6H), 3.88-3.87 (m, 1H, G_5H), 1.21-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.2, 178.6, 178.1, 176.7, 176.5, 131.2 (d, J_{CF} = 16 Hz), 127.9 (d, J_{CF} = 88 Hz), 117.0 (d, J_{CF} = 223 Hz), 83.2, 74.1, 72.0, 70.7, 67.6, 61.6, 39.0, 38.8, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{49}FN_2O_9S$: *m/z* 668.31 (M^+), found: *m/z* 668 (M^+). Anal. calcd. for $C_{33}H_{49}FN_2O_9S$: C, 59.26; H, 7.38; N, 4.19; found: C, 59.28; H, 7.40; N, 4.21.

***N*-(2,3,4,6-Tetra-*O*-pivaloyl-*β*-D-glucopyranosyl)-*N'*-(4-bromophenyl) thiourea (4f)**



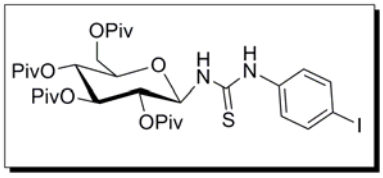
Obtained as a white solid in 92% yield; M.p. 165-167 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (br, 1H, NH), 7.56 (d, J = 8.0 Hz, 2H, ArH), 7.08 (d, J = 8.0 Hz, 2H, ArH), 6.60 (d, J = 9.2 Hz, 1H, NH), 5.87 (t, J = 9.2 Hz, 1H, G_1H), 5.47 (t, J = 9.2 Hz, 1H, G_3H), 5.10 (t, J = 9.2 Hz, 1H, G_4H), 4.96 (t, J = 9.2 Hz, 1H, G_2H), 4.16-4.13 (m, 2H, G_6H), 3.87 (m, G_5H), 1.20-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.9, 178.7, 178.0, 176.7, 176.4, 134.4, 133.1, 126.9, 121.3, 83.2, 74.2, 72.0, 70.7, 67.6, 61.6, 38.9, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{49}BrN_2O_9S$: *m/z* 728.23 (M^+), found: *m/z* 728 (M^+). Anal. calcd. for $C_{33}H_{49}BrN_2O_9S$: C, 54.32; H, 6.77; N, 3.84; found: C, 54.35; H, 6.75; N, 3.81.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(4-chlorophenyl)thiourea (4g)



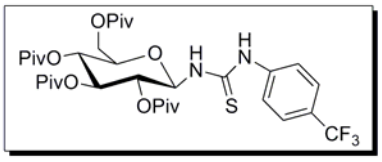
Obtained as a poor yellow solid in 95% yield; M.p. 143-145 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (br, 1H, NH), 7.38 (d, J = 8.4 Hz, 2H, ArH), 7.12 (d, J = 8.4 Hz, 2H, ArH), 6.60 (d, J = 9.2 Hz, 1H, NH), 5.85 (t, J = 9.2 Hz, 1H, G_1H), 5.44 (t, J = 9.2 Hz, 1H, G_3H), 5.07 (t, J = 9.2 Hz, 1H, G_4H), 4.94 (t, J = 9.2 Hz, 1H, G_2H), 4.16-4.08 (m, 2H, G_6H), 3.87-3.84 (m, 1H, G_5H), 1.18-1.07 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.9, 178.7, 178.1, 176.8, 176.5, 134.0, 130.1, 126.7, 125.9, 83.1, 74.1, 72.0, 70.7, 67.6, 61.6, 39.0, 38.8, 38.7, 38.6, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{49}ClN_2O_9S$: *m/z* 684.28 (M^+), found: *m/z* 684 (M^+). Anal. calcd. for $C_{33}H_{49}ClN_2O_9S$: C, 57.84; H, 7.21; N, 4.09; found: C, 57.86; H, 7.23; N, 4.11.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(4-iodophenyl) thiourea (4h)



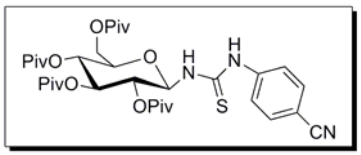
Obtained as a yellow solid in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (br, 1H, NH), 7.76 (d, J = 8.4 Hz, 2H, ArH), 6.94 (d, J = 8.4 Hz, 2H, ArH), 6.60 (d, J = 9.2 Hz, 1H, NH), 5.87 (t, J = 9.2 Hz, 1H, G_1H), 5.47 (t, J = 9.2 Hz, 1H, G_3H), 5.09 (t, J = 9.6 Hz, 1H, G_4H), 4.97 (t, J = 9.2 Hz, 1H, G_2H), 4.16-4.11 (m, 2H, G_6H), 3.88 (m, 1H, G_5H), 1.21-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.6, 178.7, 178.0, 176.7, 176.4, 139.0, 135.2, 126.9, 92.4, 83.1, 74.2, 72.0, 70.7, 67.6, 61.6, 39.0, 38.8, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{49}IN_2O_9S$: *m/z* 776.22 (M^+), found: *m/z* 776 (M^+). Anal. calcd. for $C_{33}H_{49}IN_2O_9S$: C, 51.03; H, 6.36; N, 3.61; found: C, 51.06; H, 6.31; N, 3.68.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(4-(trifluoromethyl)phenyl)thioure a (4i)



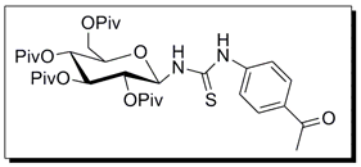
Obtained as a white solid in 86% yield; M.p. 195-197 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (br, 1H, NH), 7.68 (d, J = 8.0 Hz, 2H, ArH), 7.36 (d, J = 8.0 Hz, 2H, ArH), 6.83 (s, 1H, NH), 5.89 (t, J = 9.2 Hz, 1H, G_1H), 5.49 (t, J = 9.2 Hz, 1H, G_3H), 5.12 (t, J = 9.2 Hz, 1H, G_4H), 5.01 (t, J = 9.2 Hz, 1H, G_2H), 4.20-4.12 (m, 2H, G_6H), 3.90 (d, J = 9.6 Hz, 1H, G_5H), 1.20-1.11 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.7, 178.9, 178.1, 176.8, 176.5, 139.0, 127.0, 125.0, 124.6, 122.3, 83.1, 74.3, 72.0, 70.7, 67.6, 61.7, 39.0, 38.8, 38.7, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{34}H_{49}F_3N_2O_9S$: *m/z* 718.31 (M^+), found: *m/z* 718 (M^+). Anal. calcd. for $C_{34}H_{49}F_3N_2O_9S$: C, 56.81; H, 6.87; N, 3.90; found: C, 56.82; H, 6.88; N, 3.92.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(4-cyanophenyl)thiourea (4j)



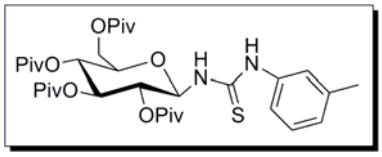
Obtained as a white solid in 88% yield; M.p.167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (br, 1H, NH), 6.98 (d, J = 8.0 Hz, 2H, ArH), 6.87 (d, J = 8.0 Hz, 2H, ArH), 6.47 (d, J = 9.2 Hz, 1H, NH), 5.88 (t, J = 9.2 Hz, 1H, G_1H), 5.42 (t, J = 9.2 Hz, 1H, G_3H), 5.07 (t, J = 9.6 Hz, 1H, G_4H), 4.91 (t, J = 9.2 Hz, 1H, G_2H), 4.19-4.12 (m, 2H, G_6H), 3.88 (m, 1H, G_5H), 1.22-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.3, 178.6, 176.9, 176.6, 156.2, 127.9, 127.0, 116.9, 83.2, 74.0, 72.1, 70.5, 67.7, 61.7, 39.0, 38.9, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{34}H_{49}N_3O_9S$: *m/z* 675.32 (M^+), found: *m/z* 675 (M^+). Anal. calcd. for $C_{34}H_{49}N_3O_9S$: C, 60.42; H, 7.31; N, 6.22; found: C, 60.43; H, 7.38; N, 6.27.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(acetylphenyl)thiourea (4k)



Obtained as a white solid in 78% yield; M.p. 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (br, 1H, NH), 7.84 (d, J = 8.8 Hz, 2H, ArH), 7.41(d, J = 8.8 Hz, 2H, ArH), 6.13 (d, J = 9.6 Hz, 1H, NH), 5.39 (t, J = 9.6 Hz, 1H, G_1H), 5.28 (t, J = 9.6 Hz, 1H, G_3H), 5.09 (t, J = 9.6 Hz, 1H, G_4H), 4.86 (t, J = 9.6 Hz, 1H, G_2H), 4.15-4.11 (m, 2H, G_6H), 3.87 (m, 1H, G_5H), 2.54 (s, 3H, $COCH_3$), 1.16-1.07 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 181.6, 178.8, 178.1, 176.7, 176.5, 140.5, 134.9, 130.1, 123.6, 83.0, 74.2, 72.0, 70.7, 67.6, 61.7, 39.0, 38.8, 38.7, 27.1, 27.0, 26.6. MS (EI) calcd. for $C_{35}H_{52}N_2O_{10}S$: *m/z* 692.33 (M^+), found: *m/z* 692 (M^+). Anal. calcd. for $C_{35}H_{52}N_2O_{10}S$: C, 60.67; H, 7.56; N, 4.04; found: C, 60.65; H, 7.59; N, 4.05.

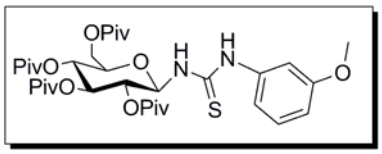
_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-_m_-tolylthiourea (4l)



Obtained as a white solid in 95% yield; M.p.173-174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (br, 1H, NH), 7.18 (t, J = 7.6 Hz, 1H, ArH), 7.10 (s, 1H, ArH), 7.03 (d, J = 7.6 Hz, 1H, ArH), 6.91 (d, J = 7.6 Hz, 1H, ArH), 5.89 (d, J = 9.6 Hz, 1H,

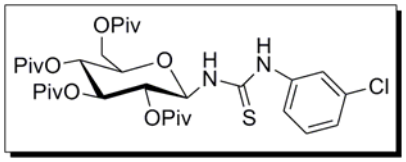
NH), 5.39 (t, J = 9.6 Hz, 1H, G_1H), 5.29 (t, J = 9.6 Hz, 1H, G_3H), 5.11 (t, J = 9.6 Hz, 1H, G_4H), 4.91 (t, J = 9.6 Hz, 1H, G_2H), 4.16-4.03 (m, 2H, G_6H), 3.82 (m, 1H, G_5H), 2.32 (s, 3H, CH_3), 1.24-1.11 (m, 36H).. ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.8, 178.2, 178.0, 176.7, 176.4, 140.4, 134.9, 129.9, 128.7, 125.9, 122.4, 83.2, 74.0, 72.1, 70.4, 67.6, 61.6, 38.9, 38.8, 38.7, 38.6, 27.1, 27.0, 21.2. MS (EI) calcd. for $C_{34}H_{52}N_2O_9S$: *m/z* 664.34 (M^+), found: *m/z* 664 (M^+). Anal. calcd. for $C_{34}H_{52}N_2O_9S$: C, 61.42; H, 7.88; N, 4.21; found: C, 61.45; H, 7.88; N, 4.20.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(3-methoxyphenyl)thiourea (4m)



Obtained as a white solid in 90% yield; M.p.190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.8 Hz, 1H, ArH), 7.29 (m, 1H, ArH), 7.19 (m, ArH), 6.82 (dd, J = 8.8, 2.4 Hz, 1H, ArH), 6.09 (s, 1H, NH), 5.59 (d, J = 8.8 Hz, 1H, G_1H), 5.52 (m, 1H, G_3H), 5.23-5.18 (m, 2H, G_4H, G_2H), 4.18 (m, 1H, G_5H), 4.12-4.08 (m, 2H, G_6H), 3.83 (s, 3H, CH_3), 1.25-1.15 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 178.0, 176.9, 176.4, 165.9, 159.0, 152.8, 121.0, 111.3, 104.2, 83.8, 74.0, 72.0, 70.7, 67.8, 61.8, 55.5, 38.9, 38.8, 38.7, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{34}H_{52}N_2O_{10}S$: *m/z* 680.33(M^+), found: *m/z* 680 (M^+). Anal. calcd. for $C_{34}H_{52}N_2O_{10}S$: C, 59.98; H, 7.70; N, 4.11; found: C, 59.63; H, 7.70; N, 4.13.

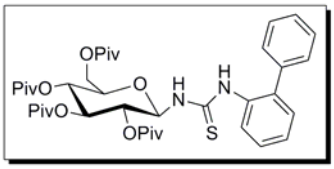
_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(3-chlorophenyl)thiourea (4n)



Obtained as a white solid in 90% yield; M.p. 160-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (br, 1H, NH), 7.36 (t, J = 8.0 Hz, 1H, ArH), 7.29-7.22 (m, 2H, ArH), 7.10 (t, J = 8.0 Hz, 1H, ArH), 6.67 (d, J = 9.2 Hz, 1H, NH), 5.85 (t, J = 9.2 Hz, 1H, G_1H), 5.45 (t, J = 9.2 Hz, 1H, G_3H), 5.08 (t, J = 9.2 Hz, 1H, G_4H), 4.96 (t, J = 9.2 Hz, 1H, G_2H), 4.14-4.11 (m, 2H, G_6H), 3.88-3.86 (m, 1H, G_5H), 1.19-1.07 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.9, 178.7, 178.0, 176.7, 176.4, 136.7, 135.5, 130.8, 127.8, 125.4, 123.4,

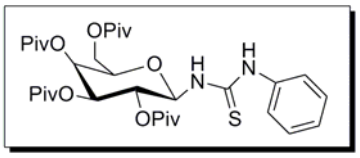
83.1, 74.2, 72.0, 70.6, 67.6, 61.6, 38.9, 38.8, 38.7, 38.6, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{49}ClN_2O_9S$: *m/z* 684.28 (M^+), found: *m/z* 684 (M^+). Anal. calcd. for $C_{33}H_{49}ClN_2O_9S$: C, 57.84; H, 7.21; N, 4.09; found: C, 57.87; H, 7.20; N, 4.11.

_N_-(2,3,4,6-Tetra-_O_-pivaloyl-_β_-D-glucopyranosyl)-_N'_-(2-phenyphenyl)thiourea (4o)



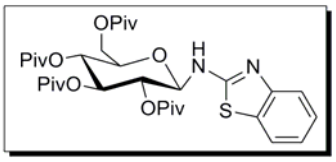
Obtained as a white solid in 82% yield; M.p. 81-83 °C. ^{1}H NMR (400 MHz, $CDCl_3$)：δ 7.59 (br, 1H, NH), 7.44-7.40 (m, 6H, ArH), 7.29-7.27 (m, 3H, ArH), 6.63 (d, J = 9.2 Hz, 1H, NH), 5.83 (t, J = 9.2 Hz, 1H, G_1H), 5.46 (t, J = 9.6 Hz, 1H, G_3H), 5.08 (t, J = 9.6 Hz, 1H, G_4H), 4.94 (t, J = 9.2 Hz, 1H, G_2H), 4.13-4.09 (m, 2H, G_6H), 3.85 (m, 1H, G_5H), 1.22-1.10 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 178.4, 177.9, 176.6, 176.4, 138.0, 137.2, 132.6, 131.5, 130.3, 128.8, 128.0, 126.7, 118.5, 115.5, 83.0, 73.9, 72.0, 70.5, 67.8, 61.6, 38.8, 38.6, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{39}H_{54}N_2O_9S$: *m/z* 726.36 (M^+), found: *m/z* 726 (M^+). Anal. calcd. for $C_{39}H_{54}N_2O_9S$: C, 64.44; H, 7.49; N, 3.85; found: C, 64.46; H, 7.45; N, 3.88.

_N_-(2,3,4,6-Tetra-O-pivaloyl-_β_-D-galacopyranosyl)-_N'_-phenylthiourea (12)



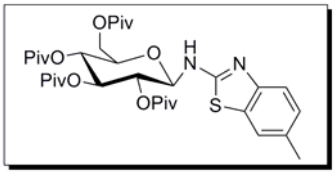
Obtained as a white solid in 95% yield; M.p. 152-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$)：δ 8.49 (br, 1H, NH), 7.45 (m, 2H, ArH), 7.36 (m, 1H, ArH), 7.18 (d, J = 7.6 Hz, 2H, ArH), 6.58 (d, J = 9.2 Hz, 1H, NH), 5.86 (t, J = 9.2 Hz, 1H, G_1H), 5.42 (t, J = 9.2 Hz, 1H, G_3H), 5.06 (t, J = 9.2 Hz, 1H, G_4H), 4.91 (t, J = 9.2 Hz, 1H, G_2H), 4.15-4.14 (m, 2H, G_6H), 3.89 (m, 1H, G_5H), 1.21-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.9, 178.4, 178.1, 176.7, 176.5, 135.1, 130.1, 127.9, 125.4, 83.2, 74.1, 72.1, 70.5, 67.6, 61.6, 38.9, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{50}N_2O_9S$: *m/z* 650.32 (M^+), found: *m/z* 650 (M^+). Anal. calcd. for $C_{33}H_{50}N_2O_9S$: C, 60.90; H, 7.74; N, 4.30; found: C, 60.65; H, 7.76; N, 4.34.

_N_-(2,3,4,6-Tetra-O-pivaloyl-_β_-D-glucopyranosyl)benzo[_d_]thiazol-2-amine (5a):



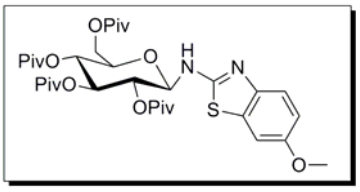
Obtained as a white solid in 85% yield; M.p. 196-198 °C. ^{1}H NMR (400 MHz, $CDCl_3$)：7.30 (t, J = 7.6 Hz, 1H, ArH), 7.12 (t, J = 7.6 Hz, 1H, ArH), 6.89 (d, J = 7.6 Hz, 2H, ArH), 6.21 (br, 1H, NH), 5.41 (t, J = 9.2 Hz, 1H, G_1H), 5.13 (t, J = 9.2 Hz, 1H, G_3H), 5.05 (t, J = 9.6 Hz, 1H, G_4H), 4.91 (t, J = 9.2 Hz, 1H, G_2H), 4.15-4.12 (m, 2H, G_6H), 3.85-3.82 (m, 1H, G_5H), 1.24-1.08 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 178.0, 176.9, 176.5, 164.7, 151.6, 130.8, 126.0, 122.6, 120.8, 120.0, 83.7, 73.9, 72.1, 70.7, 67.9, 61.8, 38.9, 38.8, 38.7, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{33}H_{48}N_2O_9S$: m/z 648.31 (M^+), found: m/z 648 (M^+). Anal. calcd. for $C_{33}H_{48}N_2O_9S$: C, 61.09; H, 7.46; N, 4.32; found: C, 61.10; H, 7.45; N, 4.13.

6-Methyl-_N_-(2,3,4,6-tetra-O-pivaloyl-_β_-D-glucopyranosyl)benzo[_d_]thiazol-2-amine (5b):



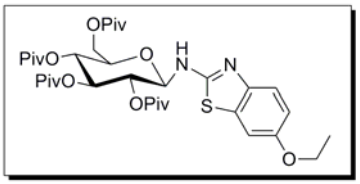
Obtained as a white solid in 78% yield; M.p.245-247 °C. ^{1}H NMR (400 MHz, $CDCl_3$)：δ 7.45 (d, J = 8.0 Hz, 1H, ArH), 7.39 (s, 1H, ArH), 7.11 (d, J = 8.0 Hz, 1H, ArH), 5.84 (br, 1H, NH), 5.49 (t, J = 9.6 Hz, 1H, G_1H), 5.31 (m, 1H, G_3H), 5.15 (t, J = 9.6 Hz, 1H, G_4H), 5.08 (t, J = 9.6 Hz, 1H, G_2H), 4.21-4.11 (m, 2H, G_6H), 3.97-3.93 (m, 1H, G_5H), 2.39 (s, 3H, CH_3), 1.17-1.08 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 178.0, 176.8, 176.4, 163.7, 149.4, 132.4, 130.9, 127.2, 120.8, 119.5, 83.7, 73.8, 72.0, 70.6, 67.8, 61.7, 38.8, 38.7, 38.6, 27.0, 26.8, 21.2. MS (EI) calcd. for $C_{34}H_{50}N_2O_9S$: m/z 662.32 (M^+), found: m/z 662 (M^+). Anal. calcd. for $C_{34}H_{50}N_2O_9S$: C, 61.61; H, 7.60; N, 4.23; found: C, 61.60; H, 7.65; N, 4.24.

6-Methoxyl-_N_-(2,3,4,6-tetra-O-pivaloyl-_β_-D-glucopyranosyl)benzo[_d_]thiazol-2-amine (5c):



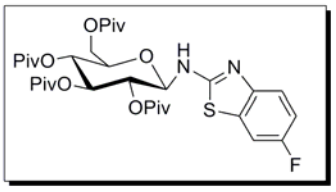
Obtained as a white solid in 80% yield; M.p. 198-200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.8 Hz, 1H, ArH), 7.13 (s, 1H, ArH), 6.94 (m, 1H, ArH), 5.95 (br, 1H, NH), 5.49 (t, J = 9.2 Hz, 1H, G_1H), 5.29 (t, J = 9.2 Hz, 1H, G_3H), 5.18-5.08 (m, 2H, G_4H, G_2H), 4.21-4.11 (m, 2H, G_6H), 3.96-3.91 (m, 1H, G_5H), 3.82 (s, 3H, OCH_3), 1.16-1.14 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 177.1, 176.7, 176.3, 162.7, 155.9, 145.3, 132.2, 120.4, 114.1, 105.0, 79.8, 69.4, 67.8, 67.4, 61.6, 55.8, 38.8, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{34}H_{50}N_2O_{10}S$: *m/z* 678.32 (M^+), found: *m/z* 678 (M^+). Anal. calcd. for $C_{34}H_{50}N_2O_{10}S$: C, 60.16; H, 7.42; N, 4.13; found: C, 60.19; H, 7.42; N, 4.15.

6-Ethoxyl-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl)benzo[*d*]thiazol-2-amine (5d):



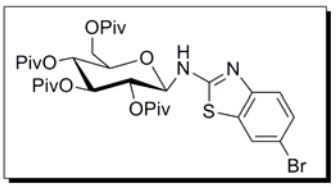
Obtained as a white solid in 81% yield; M.p. 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.8 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 6.89 (m, 1H, ArH), 6.04 (br, 1H, NH), 5.50 (t, J = 9.2 Hz, 1H, G_1H), 5.30 (d, J = 9.2 Hz, 1H, G_3H), 5.15 (t, J = 9.6 Hz, 1H, G_4H), 5.09 (t, J = 9.2 Hz, 1H, G_2H), 4.18-4.15 (m, 2H, G_6H), 4.03 (q, 2H, CH_2), 3.96 (m, 1H, G_5H), 1.39 (t, J = 6.8 Hz, 3H, CH_3), 1.17-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 178.0, 176.9, 176.4, 162.8, 155.1, 145.7, 131.8, 120.3, 114.4, 105.8, 83.8, 73.9, 72.1, 70.7, 67.9, 64.1, 61.8, 38.9, 38.7, 38.6, 27.1, 27.0, 26.9, 14.8. MS (EI) calcd. for $C_{35}H_{52}N_2O_{10}S$: *m/z* 692.33 (M^+), found: *m/z* 692 (M^+). Anal. calcd. for $C_{35}H_{52}N_2O_{10}S$: C, 60.67; H, 7.56; N, 4.04; found: C, 60.69; H, 7.53; N, 4.02.

6-Fluoro-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-Dglucopyranosyl) benzo[*d*]thiazol-2-amine (5e):



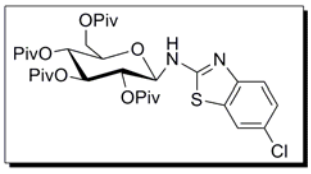
Obtained as a white solid in 70% yield; M.p. 196-198 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46（s, 1H, ArH）7.20 (d, J = 9.2 Hz, 2H, ArH), 5.87 (d, J = 9.2 Hz, 1H, NH), 5.41 (t, J = 9.2 Hz, 1H, G_1H), 5.28 (t, J = 9.6 Hz, 1H, G_3H), 5.11 (t, J = 9.6 Hz, 1H, G_4H), 4.92 (t, J = 9.2 Hz, 1H, G_2H), 4.17-4.05 (m, 2H, G_6H), 3.85 (m, 1H, G_5H), 1.19-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.4, 178.0, 176.9, 176.4, 164.1, 154.8, 148.0, 131.5 (d, J_{CF} = 107 Hz), 120.5 (d, J_{CF} = 89 Hz), 113.9 (d, J_{CF} = 268 Hz), 107.6, 107.4, 83.7, 73.9, 72.0, 70.7, 67.8, 61.8, 38.9, 38.8, 38.7, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{33}H_{47}FN_2O_9S$: *m/z* 666.30 (M^+), found: *m/z* 666 (M^+). Anal. calcd. for $C_{33}H_{47}FN_2O_9S$: C, 59.44; H, 7.10; N, 4.20; found: C, 59.40; H, 7.18; N, 4.33.

6-Bromo-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl) benzo[*d*]thiazol-2-amine (5f):



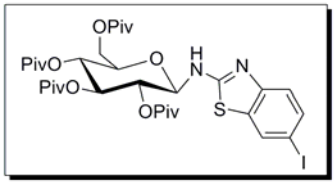
Obtained as a white solid in 73% yield; M.p. 218-220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H, ArH), 7.42 (d, J = 1.6 Hz, 2H, ArH), 6.09 (s, 1H, NH), 5.52 (t, J = 9.2 Hz, 1H, G_1H), 5.33 (d, J = 9.2 Hz, 1H, G_3H), 5.17 (t J = 9.6 Hz, 1H, G_4H), 5.10 (t, J = 9.2 Hz, 1H, G_2H), 4.23-4.12 (m, 2H, G_6H), 3.98-3.95 (m, 1H, G_5H), 1.18-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 178.0, 176.9, 176.4, 164.8, 150.6, 132.5, 129.3, 123.3, 121.1, 115.1, 83.6, 74.0, 72.0, 70.7, 67.8, 61.8, 38.9, 38.8, 38.7, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{33}H_{47}BrN_2O_9S$: *m/z* 726.22 (M^+), found: *m/z* 726 (M^+). Anal. calcd. for $C_{33}H_{47}BrN_2O_9S$: C, 54.47; H, 6.51; N, 3.85; found: C, 54.52; H, 6.58; N, 3.86.

6-Chloro-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl)benzo[*d*]thiazol-2-amine (5g):



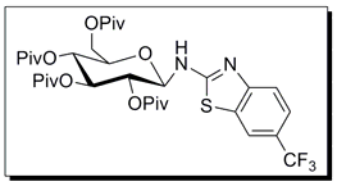
Obtained as a white solid in 75% yield; M.p. 195-197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H, ArH), 7.47 (d, J = 8.8 Hz, 1H, ArH), 7.28 (d, J = 8.8 Hz, 1H, ArH), 5.99 (br, 1H, NH), 5.51 (t, J = 9.2 Hz, 1H, G_1H), 5.33 (d, J = 9.2 Hz, 1H, G_3H), 5.16 (t, J = 9.6 Hz, 1H, G_4H), 5.09 (t, J = 9.2 Hz, 1H, G_2H), 4.22-4.11 (m, 2H, G_6H), 3.96 (m, 1H, G_5H), 1.17-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 177.1, 176.7, 176.3, 164.7, 149.9, 132.5, 128.0, 126.7, 120.5, 83.6, 74.0, 72.0, 69.3, 67.4, 61.6, 38.9, 38.8, 38.7, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{33}H_{47}ClN_2O_9S$: *m/z* 682.27 (M^+), found: *m/z* 682 (M^+). Anal. calcd. for $C_{33}H_{47}ClN_2O_9S$: C, 58.01; H, 6.93; N, 4.10; found: C, 58.03; H, 6.95; N, 4.12.

6-Iodo-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl)benzo[*d*]thiazol-2-amine (5h):



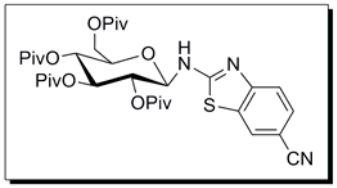
Obtained as a white solid in 66% yield; M.p. 212-214 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H, ArH), 7.62 (m, 1H, ArH), 7.37 (d, J = 8.8 Hz, 1H, ArH), 6.13 (br, 1H, NH), 5.51 (d, J = 9.2 Hz, 1H, G_1H), 5.60 (d, J = 9.2 Hz, 1H, G_3H), 5.22-5.17 (m, 2H, G_4, G_2H), 4.15 (m, 1H, G_5H), 4.09-4.07 (m, 2H, G_6H), 1.25-1.14 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 177.0, 176.7, 176.3, 164.7, 150.7, 135.2, 133.4, 129.2, 121.7, 85.2, 79.7, 69.3, 68.1, 67.4, 61.5, 38.8, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{47}IN_2O_9S$: *m/z* 774.20 (M^+), found: *m/z* 774 (M^+). Anal. calcd. for $C_{33}H_{47}IN_2O_9S$: C, 51.16; H, 6.12; N, 3.62; found: C, 51.10; H, 6.15; N, 3.61.

6-Trifluoromethyl-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl)benzo[*d*]thiazol-2-amine (5i):



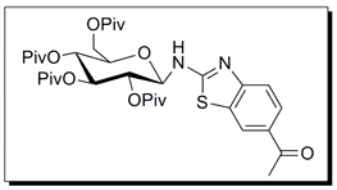
Obtained as a white solid in 66% yield; M.p. 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H, ArH), 7.60 (d, J = 8.4 Hz, 1H, ArH), 7.54 (d, J = 8.8 Hz, 1H, ArH), 6.19 (br, 1H, NH), 5.50 (t, J = 9.2 Hz, 1H, G_1H), 5.34 (m, 1H, G_3H), 5.14 (t, J = 9.2 Hz, 1H, G_4H), 5.09 (t, J = 9.2 Hz, 1H, G_2H), 4.17-4.13 (m, 2H, G_6H), 3.96-3.93 (m, 1H, G_5H), 1.16-1.07 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 177.9, 176.9, 176.3, 166.8, 154.1, 131.0, 123.3, 122.9, 120.0, 118.3, 83.5, 74.1, 72.0, 70.7, 67.8, 61.7, 38.9, 38.7, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{34}H_{47}F_3N_2O_9S$: *m/z* 716.30 (M^+), found: *m/z* 716 (M^+). Anal. calcd. for $C_{34}H_{47}F_3N_2O_9S$: C, 56.97; H, 6.61; N, 3.91; found: C, 56.95; H, 6.63; N, 3.95.

6-Cyano-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl)benzo[*d*]thiazol-2-amine (5j)



Obtained as a yellow solid in 63% yield; M.p. 139-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 2H, ArH), 7.11 (d, J = 8.8 Hz, 1H, ArH), 6.07 (br, 1H, NH), 5.51 (t, J = 9.2 Hz, 1H, G_1H), 5.33 (d, J = 9.2 Hz, 1H, G_3H), 5.18-5.06 (m, 2H, G_4H, G_2H), 4.18-4.14 (m, 2H, G_6H), 3.98-3.94 (m, 1H, G_5H), 1.17-1.08 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 178.2, 177.2, 176.7, 164.1, 160.2, 148.8, 142.2, 124.5, 122.1, 117.5, 109.4, 83.0, 74.2, 72.4, 70.8, 68.0, 61.9, 39.1, 39.0, 27.4, 27.3, 27.1. MS (EI) calcd. for $C_{34}H_{47}N_3O_9S$: *m/z* 679.30 (M^+), found: *m/z* 673 (M^+). Anal. calcd. for $C_{34}H_{47}N_3O_9S$: C, 60.60; H, 7.03; N, 6.24; found: C, 60.60; H, 7.04; N, 6.22.

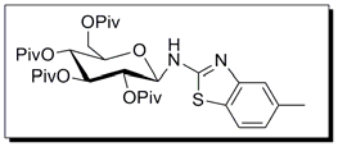
6-Acetyl-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl)benzo[*d*]thiazol-2-amine (5k):



Obtained as a white solid in 65% yield; M.p. 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H, ArH), 7.90 (m, 1H, ArH), 7.56 (d, J = 8.8 Hz, 1H, ArH), 6.63 (br, 1H, NH), 5.49 (t, J = 9.2 Hz, 1H, G_1H), 5.38 (d, J = 9.2 Hz, 1H, G_3H),

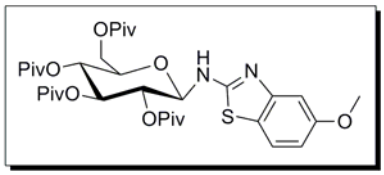
5.16-5.07 (m, 2H, G_4H, G_2H), 4.16-4.12 (m, 2H, G_6H), 3.97-3.94 (m, 1H, G_5H), 2.58 (s, 3H), 1.14-1.05 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 177.9, 176.8, 176.4, 167.8, 155.4, 131.8, 131.2, 127.0, 121.6, 119.4, 83.5, 74.1, 72.0, 70.7, 67.8, 61.7, 38.9, 38.7, 27.1, 27.0, 26.8, 26.5. MS (EI) calcd. for $C_{35}H_{50}N_2O_{10}S$: *m/z* 690.32 (M^+), found: *m/z* 690 (M^+). Anal. calcd. for $C_{35}H_{50}N_2O_{10}S$: C, 60.85; H, 7.29; N, 4.05; found: C, 60.82; H, 7.24; N, 4.08.

5-Methyl-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl) benzo[*d*]thiazol-2-amine (5l):



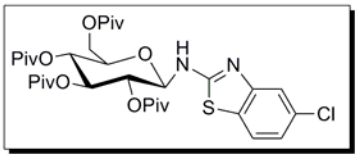
Obtained as a white solid in 77% yield; M.p. 185-187 °C. ^1H NMR (400 MHz, $CDCl_3$)：δ 7.51 (d, J = 8.0 Hz, 1H, ArH), 7.46 (s, 1H, ArH), 7.01 (d, J = 8.0 Hz, 1H, ArH), 6.04 (br, 1H, NH), 5.59-5.50 (m, 2H, G_1H, G_3H), 5.12-5.19 (m, 2H, G_4H, G_2H), 4.16-4.10 (m, 3H), 2.44 (s, 3H, CH_3), 1.26-1.15 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3, 177.9, 176.9, 176.4, 164.8, 151.8, 135.9, 127.6, 123.8, 120.3, 117.4, 83.7, 73.9, 72.1, 70.7, 67.9, 61.8, 38.9, 38.7, 27.1, 27.0, 26.9, 21.4. MS (EI) calcd. for $C_{34}H_{50}N_2O_9S$: *m/z* 662.32 (M^+), found: *m/z* 662 (M^+). Anal. calcd. for $C_{34}H_{50}N_2O_9S$: C, 60.61; H, 7.60; N, 4.23; found: C, 60.33; H, 7.62; N, 4.15.

5-Methoxyl-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl)benzo[*d*]thiazol-2-amine (5m):



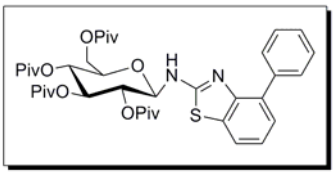
Obtained as a white solid in 72% yield; M.p. 193-195 °C. ^1H NMR (400 MHz, $CDCl_3$)：δ 7.43 (d, J = 8.8 Hz, 1H, ArH), 7.14 (s, 1H, ArH), 6.78 (m, 1H, ArH), 5.95 (br, 1H, NH), 5.49 (t, J = 9.2 Hz, 1H, G_1H), 5.17 (d, J = 9.2 Hz, 1H, G_3H), 5.13-5.09 (m, 2H, G_4H, G_2H), 4.21-4.11 (m, 2H, G_6H), 3.96-3.93 (m, 1H, G_5H), 3.82 (s, 3H, CH_3), 1.17-1.08 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.0, 177.0, 176.7, 176.3, 165.8, 159.1, 122.7, 121.1, 111.6, 104.1, 79.7, 69.4, 67.9, 67.4, 61.6, 55.5, 38.8, 38.7, 27.1, 27.0. MS (EI) calcd. for $C_{34}H_{50}N_2O_{10}S$: *m/z* 678.32 (M^+), found: *m/z* 678 (M^+). Anal. calcd. for $C_{34}H_{50}N_2O_{10}S$: C, 60.16; H, 7.42; N, 4.13; found: C, 60.13; H, 7.40; N, 4.18.

5-Chloro-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl) benzo[*d*]thiazol-2-amine (5n):



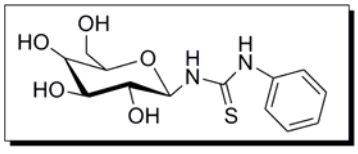
Obtained as a white solid in 69% yield; M.p. 189-192 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H, ArH), 7.49 (d, J = 8.8 Hz, 1H, ArH), 7.12 (m, 1H, ArH), 5.97 (br, 1H, NH), 5.51 (t, J = 9.2 Hz, 1H, G_1H), 5.32 (t, J = 9.6 Hz, 1H, G_3H), 5.18-5.06 (m, 2H, G_4H, G_2H), 4.21-4.11 (m, 2H, G_6H), 3.98-3.94 (m, 1H, G_5H), 1.17-1.08 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 177.4, 176.7, 176.3, 168.8, 143.3, 135.1, 130.5, 125.7, 123.0, 121.4, 79.4, 73.2, 70.0, 67.3, 61.4, 38.9, 38.8, 38.7, 38.6, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{33}H_{47}ClN_2O_9S$: *m/z* 682.27 (M^+), found: *m/z* 682 (M^+). Anal. calcd. for $C_{33}H_{47}ClN_2O_9S$: C, 58.01; H, 6.93; N, 4.10; found: C, 58.06; H, 6.91; N, 4.09.

4-Phenyl-*N*-(2,3,4,6-tetra-O-pivaloyl-*β*-D-glucopyranosyl)benzo[*d*]thiazol-2-amine (5o):



Obtained as a yellow solid in 66% yield; M.p. 103-105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 7.6 Hz, 2H, ArH), 7.59 (d, J = 7.6 Hz, 1H, ArH), 7.47-7.43 (m, 3H, ArH), 7.38 (t, J = 7.6 Hz, 1H, ArH), 7.23 (t, J = 7.6 Hz, 1H, ArH), 5.94 (s, 1H, NH), 5.49 (t, J = 9.2 Hz, 1H, G_1H), 5.25-5.18 (m, 2H, G_3H, G_4H), 5.10 (t, J = 9.2 Hz, 1H, G_2H), 4.17-4.16 (m, 2H, G_6H), 3.88 (m, 1H, G_5H), 1.18-1.10 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.2, 178.0, 176.9, 176.3, 164.0, 149.0, 139.2, 133.2, 132.0, 129.3, 128.0, 127.2, 126.4, 122.8, 119.8, 84.1, 73.9, 72.1, 70.5, 67.7, 61.7, 38.8, 38.7, 38.6, 27.1, 27.0, 26.9. MS (EI) calcd. for $C_{39}H_{52}N_2O_9S$: *m/z* 724.34 (M^+), found: *m/z* 724 (M^+). Anal. calcd. for $C_{39}H_{52}N_2O_9S$: C, 64.62; H, 7.23; N, 3.86; found: C, 64.60; H, 7.26; N, 3.88.

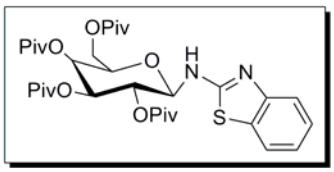
***N*-*β*-D-galacopyranosyl-*N*'-phenylthiourea(11)[2]:**



Obtained as a white solid in 75% yield; M.p.153-155 ^{o}C. ^{1}H

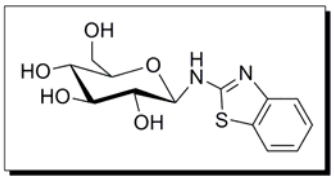
NMR (400 MHz, DMSO-d_6): δ 8.30 (d, J = 8.0 Hz, 1H, NH), 7.52 (m, 2H, ArH), 7.31 (d, J = 7.2 Hz, 2H, ArH), 7.11 (t, J = 7.2 Hz, 1H, ArH), 5.28-4.95 (m, 3H), 4.52 (s, 1H, GH), 3.64 (d, J = 8.4 Hz, 1H, GH), 3.23 (t, J = 8.4 Hz, 1H, GH), 3.14 (t, J = 8.4 Hz, 2H, GH). ^{13}C NMR (100 MHz, DMSO-d_6): 183.4, 138.2, 132.5, 128.0, 124.9, 84.5, 79.3, 77.1, 75.6, 71.4, 62.9.

_N_-(2,3,4,6-Tetra-O-pivaloyl-_β_-D-galacopyranosyl)benzo[_d_]thiazol-2-amine (13):



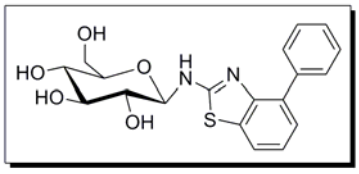
Obtained as a white solid in 80% yield; M.p. 146-148 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.57 (m, 2H, ArH), 7.32 (m, 1H, ArH), 7.15 (t, J = 7.6 Hz, 1H), 5.52 (t, J = 9.6 Hz, 1H, G_1H), 5.34 (t, J = 9.6 Hz, 1H, G_3H), 5.19-5.08 (m, 2H, G_4H, G_2H), 4.19-4.15 (m, 2H, G_6H), 3.99-3.95 (m, 1H, G_5H), 1.18-1.09 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.3 178.0, 176.7, 176.3, 164.3, 142.1, 129.4, 129.0, 125.5, 123.4, 122.9, 79.4, 74.1, 71.9, 69.9, 67.5, 61.6, 38.9, 38.8, 38.7, 38.6, 27.1, 27.0. MS (EI) calcd. for $C_{33}H_{48}N_2O_9S$: m/z 648.31 (M^+), found: m/z 648 (M^+). Anal. calcd. for $C_{33}H_{48}N_2O_9S$: C, 61.09; H, 7.46; N, 4.32; found: C, 61.13; H, 7.44; N, 4.15.

_N_-(_β_-D-glucopyranosyl)benzo[_d_]thiazol-2-amine (5a'):



Obtained as a white solid in 78% yield; M.p.196-198 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.71 (d, J = 8.0 Hz, 1H, ArH), 7.45 (d, J = 7.6 Hz, 1H, ArH), 7.25 (t, J = 8.0 Hz, 1H, ArH), 7.06 (t, J = 7.6 Hz, 1H, ArH), 4.89 (d, J = 8.8 Hz, 1H), 3.64 (m, 1H), 3.27-3.11 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): 171.4, 157.2, 135.5, 130.8, 126.6, 126.2, 123.6, 89.6, 83.5, 82.6, 77.9, 75.0, 65.9. MS (EI) calcd. for $C_{13}H_{16}N_2O_5S$: m/z 312.08 (M^+), found: m/z 312 (M^+). Anal. calcd. for $C_{13}H_{16}N_2O_5S$: C, 49.99; H, 5.16; N, 8.97; found: C, 49.93; H, 5.10; N, 8.96.

4-Phenyl-_N_-(_β_-D-glucopyranosyl)benzo[_d_]thiazol-2-amine (5o'):



Obtained as a white solid in 72% yield; M.p.203-205 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6)：δ 7.80 (d, J = 7.6 Hz, 2H, ArH), 7.66 (d, J = 7.6 Hz, 1H, ArH), 7.37 (m, 3H, ArH), 7.27 (d, J = 8.0 Hz, 1H, ArH), 7.10 (t, J = 7.6 Hz, 1H, ArH), 4.66 (m, 1H), 3.60 (m, 1H), 3.40 (m, 1H), 3.17-3.07 (m, 4H). MS (EI) calcd. for $C_{19}H_{20}N_2O_5S$: *m/z* 388.11 (M^+), found: *m/z* 388 (M^+). Anal. calcd. for $C_{19}H_{20}N_2O_5S$: C, 58.75; H, 5.19; N, 7.21; found: C, 58.77; H, 5.10; N, 7.25.

4. Computational Studies:

Computational details. Density Functional Theory (DFT) was performed by employing the Gaussian 09 program[4]. Becke three parameter functional[5] with the nonlocal Lee-Yang-Parr correlation functional (B3LYP) theory[6] was applied. LANL2DZ basis set including double-ζ valence basis set with the Hay and Wadt effective core potential (ECP) was used for Pd atom[7], and 6-31+G* Pople basis set[8] for the rest of the atoms.

a. Cartesian coordinates of calculated structures

B3LYP/6-31+G(d) optimized geometries, given in standard XYZ format: coordinates are Cartesian coordinates in the usual order (units are in ångstroms). Energies of the various structures (in Hartree/Particle) are also provided.

Complex 5-S-B:

Zero-point correction = 0.796137 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -3057.973207
Sum of electronic and thermal Free Energies = -3058.119436

	X	Y	Z
O	0.16610500	-0.58059900	-0.17618300
O	-0.53929800	0.68095200	-3.16731000
O	2.77968000	1.62719200	-1.43006500
O	3.98082700	0.23804800	-2.75528800
O	3.73609600	0.64088200	1.16809900
O	4.02342900	2.79493400	1.81682600
O	1.49356300	0.61476000	3.01648500
O	1.39932100	-1.40739800	4.02618300
N	-2.39853700	-2.55714900	1.56437700
N	-0.79391500	-0.96874000	1.90860500
H	-0.32849800	-1.75734700	2.35372100
C	-2.02754400	-1.31606400	1.38407800
C	0.06001000	-0.08238900	1.15956500
H	-0.38730000	0.91936000	1.13233800
C	0.72591600	0.37015400	-1.07039400
H	0.22532700	1.34383300	-0.94756500
C	2.21206900	0.52574800	-0.69300500
H	2.76115400	-0.38898300	-0.93104700
C	2.36206300	0.86406200	0.80210600

H	2.12375800	1.91971800	0.96304200
C	1.48615100	-0.00648000	1.71968300
H	1.90333300	-1.01462300	1.79471300
C	0.46757300	-0.12416500	-2.50264500
H	1.35093000	-0.02005800	-3.13235900
H	0.14941300	-1.16817100	-2.47484500
C	-1.84110300	0.33834600	-3.09018500
C	-2.73802400	1.33522500	-3.83020000
C	-4.20933400	0.90608200	-3.71432300
H	-4.37635100	-0.09977500	-4.11008200
H	-4.83407600	1.61066100	-4.27573500
H	-4.55207700	0.91229200	-2.67314300
C	-2.31661000	1.35483600	-5.32032500
H	-2.43239900	0.36572500	-5.77844500
H	-1.27750500	1.67500100	-5.44138900
H	-2.95969400	2.05495900	-5.86618500
C	-2.54381800	2.73953100	-3.21051800
H	-1.51182800	3.08773900	-3.31378900
H	-2.80780100	2.74427300	-2.14620200
C	3.65871600	1.36503500	-2.44110100
C	4.14068500	2.65507300	-3.11569700
C	2.91721900	3.39496300	-3.70768900
H	2.38615700	2.77138900	-4.43702300
H	3.25761500	4.29926500	-4.22568800
H	2.21096200	3.69248800	-2.92707900
C	5.12740900	2.29045900	-4.23754400
H	5.99799800	1.75481100	-3.84563100
H	5.47737400	3.20630000	-4.72797900
H	4.65878200	1.65204000	-4.99333600
C	4.83573400	3.55713700	-2.07011200
H	4.16616900	3.81597400	-1.24512800
H	5.16436500	4.48492400	-2.55335800
H	5.72327500	3.06741000	-1.65280300
C	4.47012600	1.67766400	1.67020400
C	5.89998600	1.23179300	2.00609100
C	6.59087200	0.72262300	0.71944700
H	6.06848600	-0.13745300	0.29081500
H	7.61756300	0.41873900	0.95566900
H	6.64293200	1.50923600	-0.04217100
C	6.67303500	2.43244100	2.57713300
H	6.72017400	3.25651600	1.85810800
H	7.69745900	2.12622800	2.81932600
H	6.20293800	2.81492900	3.48879800
C	5.84849600	0.09112100	3.04887700

H	5.35717900	0.41795000	3.97256700
H	6.87034800	-0.21405000	3.30364700
H	5.31557800	-0.78355200	2.66484800
C	1.42666100	-0.19626700	4.11208700
C	1.37244100	0.61117000	5.41221600
C	0.09069500	1.47910400	5.39712300
H	0.10957400	2.20801000	4.58155600
H	0.01356100	2.02532900	6.34467400
H	-0.80853700	0.86153400	5.28887600
C	1.33376200	-0.36384800	6.60109600
H	0.45747000	-1.01804600	6.55448700
H	1.29169400	0.20454800	7.53750800
H	2.22327200	-1.00184900	6.62480400
C	2.61699000	1.52248700	5.51145500
H	3.53960400	0.93020900	5.53467900
H	2.56936600	2.10030100	6.44207900
H	2.67525200	2.22341900	4.67372800
O	-2.20551300	-0.66798200	-2.49936700
S	-2.88622200	-0.03245100	0.52580800
Pd	-3.86554800	-1.45829400	-1.10099700
Cl	-4.75288600	-2.83409100	-2.81048400
C	-3.63692400	-4.49413700	1.02318400
H	-2.75963200	-5.05226000	1.33408700
C	-4.77677400	-5.14336800	0.57567300
H	-4.77901100	-6.23004000	0.53110200
C	-5.93068200	-4.43524600	0.16904200
H	-6.80218900	-4.97130200	-0.19280000
C	-5.92416300	-3.06150300	0.23443200
H	-6.80593000	-2.49063100	-0.04104000
C	-4.75932000	-2.33482300	0.66611100
C	-3.57499800	-3.08238000	1.08967800
H	-3.20078600	3.45278100	-3.72177200
H	-4.95259400	-1.38621000	1.16872000

Complex 5-S-C:

Zero-point correction = 0.783231 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2597.162597
Sum of electronic and thermal Free Energies = -2597.303532

	X	**Y**	**Z**
O	-0.02460200	-0.88168200	-0.33691900
O	-0.89599100	0.48400000	-3.24151500
O	2.64136300	1.03737700	-1.93102700
O	3.49119800	-0.47004900	-3.39147200

O	3.79912400	0.00325100	0.56394600
O	4.37495000	2.14777600	1.02545000
O	1.79360300	0.20588500	2.65227100
O	1.78055600	-1.80494900	3.69122900
N	-2.66291200	-2.31854700	2.16908700
N	-0.72250400	-1.12564300	1.89402200
H	-0.30835500	-1.97726600	2.26537500
C	-2.09976700	-1.25599100	1.70407100
C	0.08685700	-0.36438700	1.00171800
H	-0.26241100	0.67642000	0.99294700
C	0.53125500	0.00079800	-1.29944700
H	0.15620200	1.02363900	-1.13424600
C	2.06027000	0.00619500	-1.10541100
H	2.48313800	-0.96256000	-1.38360600
C	2.41753000	0.34995300	0.35006900
H	2.29898200	1.42570300	0.51056900
C	1.57613600	-0.42153000	1.37742400
H	1.90083400	-1.46467700	1.42573200
C	0.06165100	-0.45896700	-2.68754000
H	0.87451700	-0.47917100	-3.41271900
H	-0.39582100	-1.44644200	-2.60924300
C	-2.21218000	0.27002900	-3.09812000
C	-3.05111300	1.41878200	-3.66784400
C	-4.54406800	1.06234800	-3.57057200
H	-4.77936900	0.15744000	-4.14112600
H	-5.14131700	1.88662900	-3.97664700
H	-4.85327800	0.89835100	-2.53237600
C	-2.66046600	1.64818300	-5.14691400
H	-2.83683000	0.74963500	-5.75046600
H	-1.60829500	1.92928500	-5.24635800
H	-3.27422500	2.45633000	-5.56144500
C	-2.75789700	2.69612900	-2.84338300
H	-1.70794300	2.99297600	-2.92624400
H	-2.99610400	2.55189600	-1.78337200
C	3.34235900	0.68417100	-3.04558800
C	3.87767100	1.91637000	-3.78599000
C	2.68603900	2.81862600	-4.18573100
H	1.97465900	2.28203600	-4.82527900
H	3.05890000	3.68151000	-4.75004500
H	2.15040000	3.18946300	-3.30706100
C	4.63087400	1.45305500	-5.04414200
H	5.47052600	0.79848500	-4.78979900
H	5.02318000	2.32712600	-5.57710300
H	3.97496300	0.90026900	-5.72461200

C	4.83120300	2.70069700	-2.85518400
H	4.32965400	3.02853900	-1.94036400
H	5.20388100	3.58692200	-3.38251900
H	5.69852200	2.09202800	-2.57355200
C	4.68563400	0.98154400	0.91032300
C	6.09142300	0.40374200	1.12471300
C	6.56887300	-0.27779700	-0.17878800
H	5.91096700	-1.10156400	-0.47013400
H	7.57812000	-0.67974500	-0.02957800
H	6.61401800	0.43706300	-1.00872300
C	7.04755900	1.54766600	1.50152800
H	7.10128500	2.30215500	0.71012900
H	8.05398200	1.14429200	1.66343500
H	6.72573600	2.05178600	2.41832600
C	6.04294500	-0.64022300	2.26482200
H	5.70366600	-0.18739900	3.20358500
H	7.04932900	-1.04225600	2.43200800
H	5.37683200	-1.47357200	2.02338900
C	1.84005800	-0.59426400	3.75725000
C	1.94706600	0.22637500	5.04609100
C	0.64055800	1.04240400	5.20590600
H	0.51381200	1.76042900	4.39013600
H	0.67547400	1.59766900	6.15082600
H	-0.23849000	0.38837800	5.22871900
C	2.11311300	-0.73515600	6.23483300
H	1.26328000	-1.41962400	6.31675500
H	2.18462000	-0.15787700	7.16407100
H	3.01973300	-1.34144400	6.13560500
C	3.15434600	1.18710100	4.96571900
H	4.09533700	0.63344300	4.86220500
H	3.21325000	1.77265000	5.89098700
H	3.06833800	1.88050300	4.12432400
O	-2.66128700	-0.74296600	-2.57526600
S	-2.93559800	0.09631400	0.88199200
C	-4.79034700	-2.04737400	0.89971400
C	-6.17124900	-2.25463700	0.83867500
H	-6.75753300	-1.80568400	0.03898100
C	-6.80351000	-3.07041000	1.78636500
H	-7.87091900	-3.26221400	1.71092400
C	-6.04854800	-3.63250400	2.82132000
H	-6.52946900	-4.26316200	3.56501500
C	-4.68208300	-3.37395100	2.91855300
H	-4.09204200	-3.78631400	3.73238900
C	-4.02436500	-2.54411700	1.98725600

Pd	-3.93102900	-1.27336300	-0.69252000
H	-3.37739800	3.51853100	-3.21986800

Complex N-2-B:

Zero-point correction = 0.796867 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -3057.977791
Sum of electronic and thermal Free Energies = -3058.124846

	X	**Y**	**Z**
S	-3.09949800	2.01364500	1.34782100
O	-0.97749600	0.22102500	-0.96897000
O	-2.49149200	1.05049300	-3.28152200
O	1.65672300	1.90696300	-2.83619000
O	2.79483700	0.47439200	-4.17000300
O	3.13128800	0.53574000	-0.66153700
O	2.66234800	-1.62780000	-1.14541900
O	1.49626200	0.69171900	1.70293500
O	0.97743100	-1.18792700	2.86148200
N	-3.44834800	-0.44484600	2.24549900
N	-1.36600900	-0.10772800	1.30069500
C	-2.56351800	0.42693100	1.59938900
C	-0.54726700	0.58315900	0.34820600
C	-0.42078400	1.05931400	-1.97598200
H	-0.61824700	2.11441700	-1.73688100
C	1.10304200	0.83418700	-2.04533600
H	1.33331400	-0.12367600	-2.51340000
C	1.73881500	0.92189100	-0.64614800
H	1.79033600	1.98119000	-0.37506100
C	0.93731300	0.20365400	0.45127600
H	1.06349300	-0.87678100	0.38760300
C	-1.09568600	0.70240500	-3.29485100
H	-0.59825300	1.20904600	-4.12418700
H	-1.07388100	-0.37990800	-3.44183500
C	-2.81257900	2.32646500	-3.60483200
C	-4.31968800	2.60757700	-3.54949300
C	-5.12194500	1.44802300	-2.93314700
H	-5.01733700	0.52668900	-3.51510200
H	-6.18485000	1.71840800	-2.91091300
H	-4.80218900	1.24104900	-1.90680100
C	-4.78131700	2.85879400	-5.00557500
H	-4.64783600	1.96470400	-5.62701300
H	-4.22120300	3.68265300	-5.45941700
H	-5.84686800	3.11764100	-5.01212000
C	-4.52249600	3.89084900	-2.71271000

H	-5.58466400	4.16356100	-2.71299000
H	-3.94761700	4.72494500	-3.12606900
H	-4.21278600	3.73734700	-1.67243600
C	2.47657300	1.61001700	-3.88367100
C	2.88551100	2.87275800	-4.65124400
C	1.65145800	3.34933900	-5.45855400
H	1.33293500	2.58696700	-6.17968800
H	1.91542500	4.25240600	-6.02205700
H	0.80382800	3.58598700	-4.80811900
C	4.03536800	2.52082100	-5.61053500
H	4.92309000	2.18269300	-5.06432500
H	4.31009800	3.40787500	-6.19324500
H	3.74797000	1.72506800	-6.30402700
C	3.32893100	3.98381300	-3.67471400
H	2.51237600	4.29153600	-3.01600100
H	3.65626600	4.85937500	-4.24791000
H	4.17053200	3.65745600	-3.05163100
C	3.48034500	-0.75556500	-0.94151600
C	5.00140200	-0.94654400	-0.93056900
C	5.66487500	0.05797900	-1.89938800
H	5.28234000	-0.06363700	-2.91857000
H	6.74716400	-0.11819800	-1.91708700
H	5.49159000	1.09200100	-1.58576900
C	5.51505300	-0.70431000	0.50890800
H	5.30841800	0.31813200	0.84094800
H	6.59977300	-0.86220800	0.54019400
H	5.05511600	-1.40336300	1.21797900
C	5.31875900	-2.38726700	-1.36597000
H	4.85310100	-3.11939000	-0.69919300
H	6.40392400	-2.54264800	-1.34937300
H	4.95721200	-2.58328400	-2.38045200
C	1.50170800	-0.07586200	2.79092300
C	2.23155600	0.52750900	3.99341900
C	1.18939400	0.66448100	5.13075000
H	0.38511200	1.35672200	4.85540100
H	1.68365800	1.05921900	6.02580000
H	0.74596300	-0.30462900	5.37709700
C	3.33047800	-0.47607500	4.41828500
H	2.90528100	-1.46009200	4.63467000
H	3.82853700	-0.10247800	5.32021500
H	4.09027300	-0.59067100	3.63636800
C	2.85401000	1.89859100	3.67925100
H	3.59148700	1.83677400	2.87247600
H	3.36287500	2.27199200	4.57544900

H	2.09562400	2.63318700	3.39002700
O	-1.97653000	3.15136600	-3.92544500
H	-4.20483500	0.01858600	2.73488100
Pd	-0.82868400	-2.01286200	1.94340200
Cl	-0.18808600	-4.12917300	2.72061800
C	-2.91901200	-3.95841400	1.06013000
H	-2.40731400	-4.48507100	0.26116600
C	-2.76617700	-2.53385200	1.13135300
H	-0.67028200	1.66753200	0.48531300
C	-3.68717200	-4.64215400	1.97388400
H	-3.77635200	-5.72239600	1.92584200
C	-4.35112000	-3.92079500	2.99296100
H	-4.95220200	-4.46054600	3.72050500
C	-4.24166800	-2.54552800	3.10694500
H	-4.74697400	-2.01488500	3.90962200
C	-3.46286800	-1.82095900	2.17619600
H	-2.57177900	-2.00580400	0.19750700

Complex N-2-C:

Zero-point correction = 0.783556 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2597.152013
Sum of electronic and thermal Free Energies = -2597.295252

	X	**Y**	**Z**
S	-2.69416300	2.02337500	2.06465800
O	-0.90344600	0.06432600	-0.59261400
O	-2.49633300	0.88402700	-2.90094500
O	1.63218200	1.71788500	-2.62195300
O	2.80825700	0.25838800	-3.89142500
O	3.22024800	0.47099800	-0.46669100
O	2.83298700	-1.73127600	-0.84146400
O	1.69125800	0.54567200	1.96063600
O	1.47430600	-1.46463200	2.96300700
N	-3.33299400	-0.47254400	2.61472900
N	-1.19939700	-0.22352600	1.70139900
C	-2.35763400	0.35263000	2.10266800
C	-0.41459800	0.44158200	0.70206800
C	-0.39622700	0.88225200	-1.63972600
H	-0.59236500	1.94300200	-1.42168500
C	1.12647300	0.66941600	-1.76919500
H	1.34689700	-0.30316800	-2.21220900
C	1.81500800	0.80915300	-0.40127300
H	1.84145500	1.87388500	-0.14845500
C	1.07769800	0.07469700	0.72834100

H	1.21173900	-1.00176900	0.63843000
C	-1.11677400	0.48182500	-2.92211800
H	-0.62270900	0.92283200	-3.78972000
H	-1.13492400	-0.60746900	-3.00540100
C	-2.79910200	2.10673500	-3.40608600
C	-4.29196400	2.42643100	-3.27454300
C	-5.14916600	1.20660200	-3.67516800
H	-4.95479900	0.90420700	-4.71167100
H	-6.21131900	1.46811100	-3.59583900
H	-4.95664100	0.34789300	-3.02644700
C	-4.62636500	3.62768400	-4.17590000
H	-4.43818900	3.40046900	-5.23149000
H	-4.02737800	4.50414100	-3.91191200
H	-5.68657600	3.88440200	-4.06477500
C	-4.55723500	2.78948000	-1.79192500
H	-5.62020100	3.02657600	-1.66088400
H	-3.97667800	3.66808400	-1.48808400
H	-4.30284100	1.96588700	-1.11799000
C	2.44643100	1.39502500	-3.66536000
C	2.78709500	2.62412800	-4.51640100
C	1.53494300	2.95878000	-5.36653500
H	1.27372500	2.12425600	-6.02829600
H	1.74929300	3.83067700	-5.99643400
H	0.66642000	3.19124300	-4.74279700
C	3.96846200	2.27786100	-5.43924000
H	4.87019000	2.03973400	-4.86367000
H	4.19218300	3.13600000	-6.08376500
H	3.74049600	1.41682700	-6.07424900
C	3.14708000	3.82988100	-3.62216100
H	2.30510300	4.13291000	-2.99418400
H	3.42528500	4.67982600	-4.25659000
H	4.00012500	3.60441400	-2.97051500
C	3.61440200	-0.81136700	-0.71252300
C	5.14280700	-0.93248600	-0.75978300
C	5.72577100	0.08685700	-1.76355100
H	5.31281700	-0.06636200	-2.76613200
H	6.81383500	-0.03982900	-1.81687700
H	5.51557000	1.11603400	-1.45701900
C	5.69555600	-0.64614500	0.65723100
H	5.44963300	0.36923200	0.98419700
H	6.78729000	-0.74898300	0.65084100
H	5.29694000	-1.35713400	1.39154600
C	5.51104000	-2.36316900	-1.18766300
H	5.10475400	-3.10612600	-0.49435300

H	6.60214500	-2.46855900	-1.20936100
H	5.12213900	-2.59024500	-2.18540800
C	1.86782800	-0.29534200	2.97710600
C	2.55229100	0.32855800	4.19279900
C	1.41094200	0.69596000	5.17969600
H	0.71771300	1.42217000	4.74137700
H	1.84786100	1.14157200	6.08080400
H	0.84177100	-0.19099800	5.47646700
C	3.47730800	-0.72518700	4.83588700
H	2.92796400	-1.63360700	5.09741000
H	3.91818000	-0.31001100	5.74913000
H	4.29622100	-1.00208400	4.16154000
C	3.35262200	1.59249000	3.82889700
H	4.14082700	1.37501300	3.09973400
H	3.82924700	1.98623100	4.73392200
H	2.71182200	2.37537500	3.41401400
O	-1.95799300	2.85030400	-3.87563600
H	-4.14801800	0.04334600	2.92316200
Pd	-0.59832200	-2.07830000	2.28600600
C	-2.64075200	-4.04803500	1.82788900
H	-1.80709200	-4.68738200	1.53903500
C	-2.43171300	-2.69324800	2.09034800
H	-0.53511100	1.52535800	0.83361000
C	-3.92549100	-4.59701000	1.94282200
H	-4.08502900	-5.65388600	1.74757500
C	-4.99364600	-3.76848300	2.29919800
H	-5.99595500	-4.17893800	2.38824500
C	-4.79049500	-2.40605300	2.52226300
H	-5.63049200	-1.76403900	2.78074900
C	-3.50442800	-1.84961500	2.40225200

Complex N-5-B:

Zero-point correction = 0.795368 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -3057.952163
Sum of electronic and thermal Free Energies = -3058.100713

	X	**Y**	**Z**
S	1.07653800	-1.21131200	4.82719900
O	-0.18448800	1.31420000	1.56045100
O	-1.06816700	3.03968300	-1.15156900
O	2.25772100	2.44631500	-0.87888800
O	1.91068400	1.94035400	-3.05956800
O	2.40130800	-0.58504400	-1.04738400
O	4.58068900	-0.02141000	-0.80499100

O	1.81568100	-1.75535100	1.42323900
N	-1.53123900	-1.64004200	4.58242200
N	-0.58837800	-0.50302300	2.79855700
C	-0.39386000	-1.05686000	4.00414700
C	0.49834500	0.16836900	2.10018900
C	0.50970400	2.20363400	0.68044000
H	1.23838800	2.75240900	1.29597700
C	1.29262900	1.47302800	-0.42858900
H	0.64983100	1.19430900	-1.26142100
C	2.00256500	0.21291100	0.08299700
H	2.89283900	0.48025100	0.66066100
C	1.05275600	-0.65249400	0.92078300
H	0.22131400	-1.02328100	0.31612900
C	-0.51195400	3.23377000	0.16432100
H	-1.33035300	3.30428900	0.88772800
H	-0.02435100	4.20586500	0.07929500
C	-1.81548700	1.94002800	-1.43850400
C	-2.60768100	2.11195900	-2.73793300
C	-3.17829600	0.74551600	-3.15506800
H	-2.37910500	0.02569600	-3.36353500
H	-3.77855100	0.86392300	-4.06491200
H	-3.81336100	0.32278400	-2.37111400
C	-1.70886500	2.67877100	-3.85823800
H	-0.84507300	2.03237700	-4.04945600
H	-1.33641000	3.67653700	-3.60901500
H	-2.29224900	2.75196900	-4.78409200
C	-3.76604600	3.09754000	-2.44102600
H	-4.38722400	3.20486700	-3.33853700
H	-3.38602900	4.08720900	-2.16697600
H	-4.39936900	2.73422300	-1.62419800
C	2.46213300	2.61631900	-2.21730100
C	3.43864700	3.76735400	-2.48988100
C	2.74188100	5.09243500	-2.09478200
H	1.81457400	5.24202400	-2.66058900
H	3.41009300	5.93370000	-2.31398000
H	2.50612700	5.11705200	-1.02593700
C	3.77842900	3.78631200	-3.98996600
H	4.27333800	2.85955500	-4.29859100
H	4.45659200	4.62175500	-4.19964300
H	2.88046800	3.90578700	-4.60397900
C	4.72577600	3.58498900	-1.65448400
H	4.51901800	3.62467800	-0.58147000
H	5.43119400	4.38777700	-1.90059000
H	5.21034100	2.62576300	-1.86539900

C	3.71457100	-0.63788000	-1.39287300
C	3.97930800	-1.54536800	-2.60379900
C	2.71846800	-2.27334200	-3.10141600
H	2.28091800	-2.91137500	-2.32686700
H	2.98538900	-2.90945700	-3.95421100
H	1.94918600	-1.56795800	-3.42972800
C	4.54148100	-0.64510100	-3.73038500
H	3.80321200	0.10007500	-4.04658300
H	4.79390400	-1.26470600	-4.59922300
H	5.44769500	-0.12586500	-3.40183300
C	5.05735500	-2.56967500	-2.18142000
H	5.95921300	-2.06585000	-1.82105400
H	5.32526600	-3.19544200	-3.04101000
H	4.69258700	-3.23035900	-1.38589000
C	1.35136100	-3.01958300	1.21304600
C	2.26804800	-4.10026600	1.80584000
C	1.46929100	-4.79860800	2.93354500
H	1.25242700	-4.10066400	3.74987900
H	2.06394400	-5.62552100	3.34032500
H	0.52686500	-5.20490200	2.55114900
C	2.56398500	-5.12059000	0.68364500
H	1.63819300	-5.52634300	0.26486600
H	3.15828400	-5.94805400	1.08903400
H	3.13740300	-4.66360400	-0.13177800
C	3.58154200	-3.53516000	2.37364000
H	4.17668100	-3.03470300	1.60217300
H	4.18053700	-4.35953900	2.78007100
H	3.39356600	-2.81740300	3.17702100
O	-1.83556000	0.95392700	-0.72951100
H	-1.28908100	-2.33434100	5.27941200
H	1.30091600	0.47613500	2.78295000
O	0.31754800	-3.25711900	0.62417800
Pd	-2.23533800	0.57453100	2.24643600
C	-4.83008500	-0.64938900	3.10890500
H	-5.35277700	0.25707500	2.82690400
C	-3.51171400	-0.52492900	3.64354100
C	-5.42517100	-1.89128600	2.97112700
H	-6.42296400	-1.97959200	2.55272800
C	-4.73479800	-3.03883000	3.40197500
H	-5.20292100	-4.01520300	3.30410800
C	-3.44814300	-2.95815600	3.92989900
H	-2.91713900	-3.85975600	4.22244200
C	-2.81003500	-1.71447000	4.03644500
Cl	-3.89539900	2.17057500	1.68666800

H	-3.27816300	0.38896600	4.21204300

Complex N-5-C:

Zero-point correction = 0.783268 (Hartree/Particle)
Sum of electronic and thermal Enthalpies = -2597.153893
Sum of electronic and thermal Free Energies = -2597.295632

	X	Y	Z
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O	-1.35718700	2.94288600	-1.24536600
O	2.16998600	2.68165900	-0.93384300
O	1.71060300	2.35172500	-3.12943000
O	2.47354800	-0.26109400	-1.00628100
O	4.57844600	0.14280800	-0.27081300
O	1.56919700	-1.52390600	1.36748300
N	-2.22531100	-1.44849600	4.06049700
N	-1.02607200	-0.36605900	2.40566300
C	-1.03879000	-0.89102300	3.64059100
C	0.11857300	0.34087900	1.87442600
C	0.30249500	2.41831600	0.52325100
H	0.95090000	2.95508000	1.23417500
C	1.18786400	1.71182800	-0.51993000
H	0.60144200	1.40781500	-1.38889900
C	1.88495000	0.48221000	0.07508900
H	2.67521900	0.78084500	0.77080800
C	0.86533100	-0.43396500	0.77187400
H	0.14294700	-0.82436400	0.04943400
C	-0.66413000	3.44219400	-0.07639100
H	-1.38864000	3.74813600	0.68174700
H	-0.11043100	4.31048800	-0.43752800
C	-2.57566300	2.37909600	-1.15496200
C	-3.13453500	2.00453100	-2.52960900
C	-4.50731700	1.33411800	-2.35466000
H	-4.43046200	0.40835200	-1.77486000
H	-4.91559100	1.08294700	-3.34000100
H	-5.21729100	1.99459200	-1.84643800
C	-2.15232600	1.03245300	-3.22782000
H	-2.02220900	0.11183200	-2.64651900
H	-1.17062500	1.48818900	-3.38472000
H	-2.56091300	0.75257200	-4.20569400
C	-3.27867200	3.29632300	-3.37083100
H	-3.69829300	3.04216100	-4.35088100
H	-2.31101300	3.78152300	-3.52798300

H	-3.95654600	4.01283500	-2.89114000
C	2.33561300	2.93142100	-2.26739400
C	3.36186600	4.04695600	-2.50399300
C	2.73251700	5.37917100	-2.02574800
H	1.79981200	5.59680700	-2.56069500
H	3.42987900	6.20205300	-2.22211500
H	2.52602200	5.36168600	-0.95047100
C	3.66865100	4.12868500	-4.00919800
H	4.11260000	3.19740200	-4.37654500
H	4.38042000	4.94179900	-4.19311600
H	2.76418100	4.31947500	-4.59478300
C	4.65696900	3.76986100	-1.70950000
H	4.47303400	3.73420900	-0.63259900
H	5.38162600	4.56755100	-1.91163900
H	5.11156700	2.81794800	-2.00356700
C	3.82838200	-0.38015300	-1.06891800
C	4.29671500	-1.22007100	-2.26749800
C	3.13997100	-1.90517400	-3.01641600
H	2.57195000	-2.57787200	-2.36607500
H	3.55076900	-2.49708500	-3.84358800
H	2.44179900	-1.17423400	-3.43532900
C	5.04174700	-0.25873400	-3.22547100
H	4.36334400	0.49888400	-3.63528500
H	5.45312800	-0.82916400	-4.06669900
H	5.86752100	0.24636200	-2.71380400
C	5.28850400	-2.27708600	-1.73236900
H	6.11249400	-1.80649000	-1.18803300
H	5.70253000	-2.84860900	-2.57126100
H	4.79127300	-2.98333000	-1.05723100
C	1.28823300	-2.78993700	0.93784000
C	2.02617600	-3.86522900	1.74550000
C	0.98711400	-4.46463200	2.72784200
H	0.63520700	-3.71021200	3.43931000
H	1.45784400	-5.27605800	3.29641900
H	0.12721100	-4.87485800	2.18732900
C	2.49695600	-4.96036800	0.76589400
H	1.66029600	-5.36061100	0.18618800
H	2.95734800	-5.78013800	1.32973300
H	3.24547800	-4.57476000	0.06281500
C	3.22188700	-3.30347500	2.53636300
H	3.96357700	-2.83839000	1.87670000
H	3.71469400	-4.12532300	3.07026700
H	2.90439700	-2.55874400	3.27096300
O	-3.15856500	2.21006700	-0.08857600

H	-2.14694300	-1.87945100	4.97289500
H	0.79962800	0.66041600	2.67300800
O	0.51453800	-3.02162500	0.03232800
Pd	-2.60476100	0.48355800	1.48479600
C	-5.09853700	-0.93199600	1.72246500
H	-5.35523700	-0.36396800	0.82917900
C	-3.82934400	-0.79860600	2.28779700
C	-6.05442600	-1.77273300	2.30454200
H	-7.04405400	-1.86039500	1.86454400
C	-5.71700000	-2.49284200	3.45504100
H	-6.44390000	-3.15379800	3.91959800
C	-4.44503900	-2.37749500	4.01086600
H	-4.18619500	-2.95003100	4.89978700
C	-3.47577900	-1.53208400	3.43293700

b. Optimized structures showing different coordination modes to Pd

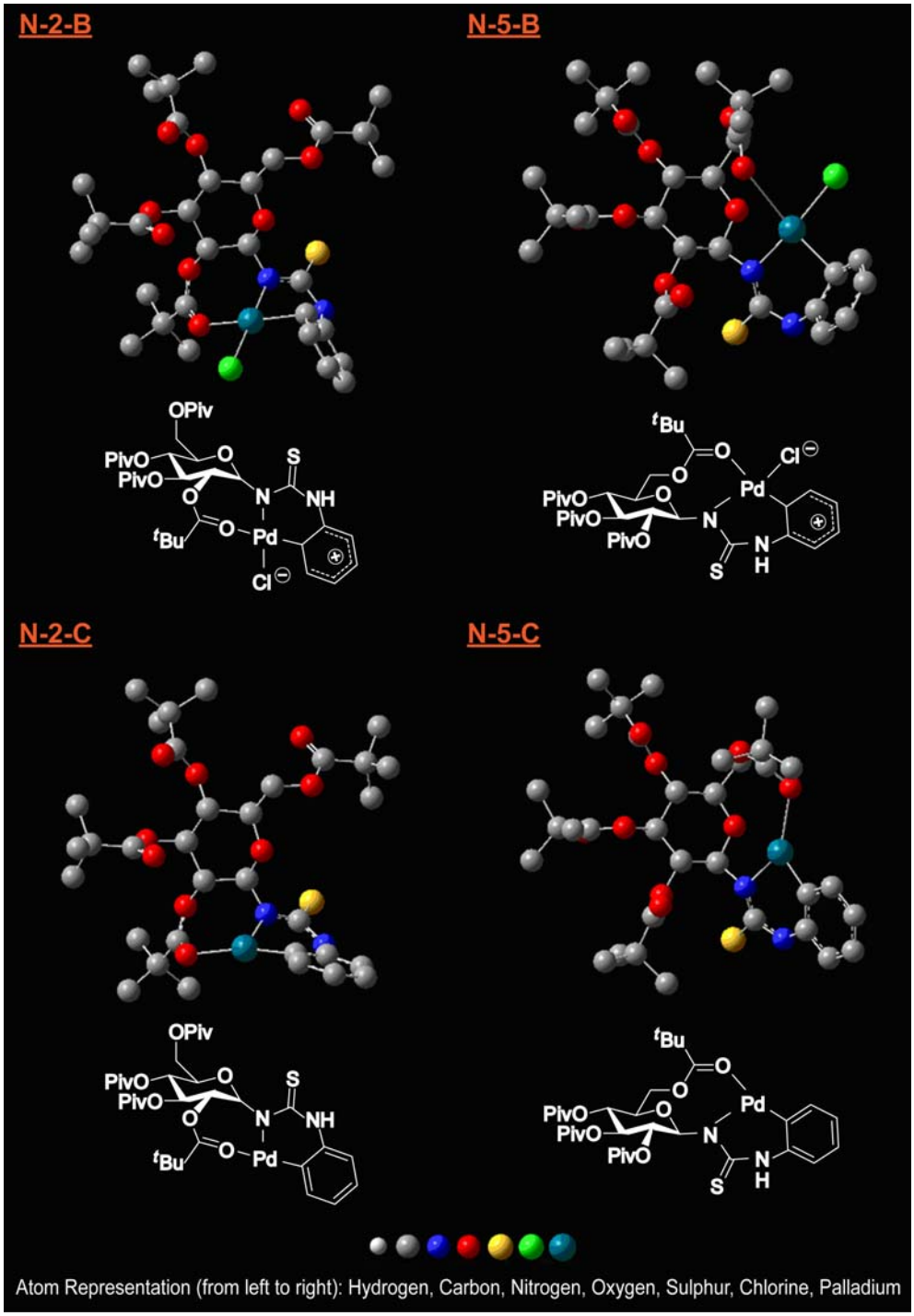

Fig. S1 Optimized geometrical structures showing nitrogen coordination to Pd. The pivolate groups can also be coordinated to Pd via 2-*O*-pivaloyl or 5-*O*-pivaloyl carbonyl group for each of the intermediate types **B** and **C**, giving rise to **N-2-B/C** and **N-5-B/C** respectively. These coordination modes were found to be disfavored by 5-16 kcal/mol. Hydrogen atoms were omitted for visual clarity.

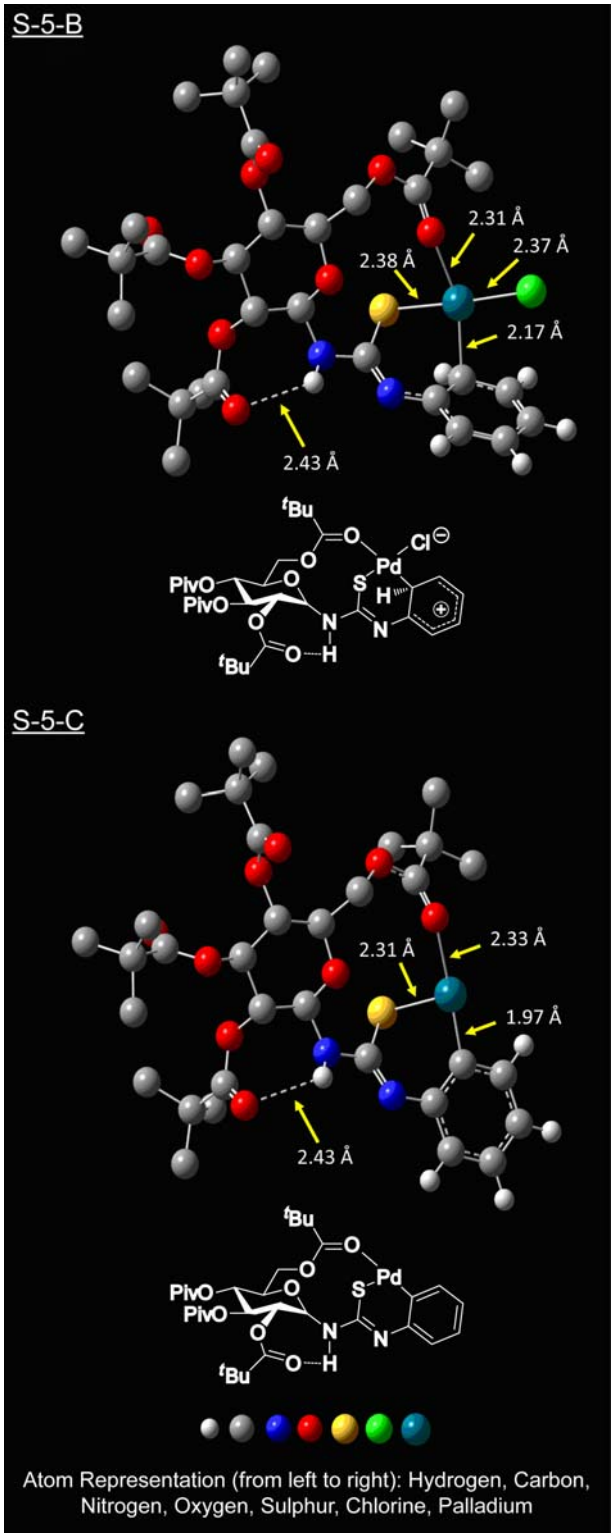

Fig. S2 Optimized geometrical structures showing sulfur coordination to Pd for intermediates **B** and **C** shown in Figure 4. The coordination of the 3-*O*-pivaloyl or 4-*O*-pivaloyl carbonyl group to the Pd metal center is physically impossible because of large Pd-O distances (8.196 and 9.425 Å, respectively). Presence of the intramolecular H-bond (2.43Å) was also depicted. Redundant hydrogen atoms were omitted for visual clarity.

5. X-ray Crystal Data for Glycosyl Benzothiazoles (5a)

Crystals of **5a** ($C_{33}H_{48}N_2O_9S$) were recrystallized from methanol. A single yellow needle crystal which was suitable for X-ray diffraction measurements was mounted on a glass fiber. Unit cell measurements and intensity data collections were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo Ka. The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL-97 program suite[9]. Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. The two oxygen atoms (O9 and O10) of the pivaloyl group on sugar moieties were disordered and treated with a disorder model and all the date were refined. The reflection data were consistent with a monoclinic system: P2(1)/c. The obtained crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 790566 (CCDC NO). The crystallographic data and refinement parameters of **5a** are listed in Table S1.

Table S1 Crystallographic data and structure refinement for **5a.**

Identification code	100422_wanggp_2_2
Empirical formula	$C_{33}H_{48}N_2O_9S$
Formula weight	648.79
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	P 21
Cell dimensions	
a, *b*, *c*, Å	13.6507(6), 10.3032(3), 13.9805(6)
α, β, γ, °	90, 109.803(5), 90
Volume, Å^3	1850.03(12)
Z	2
Calculated density, g/cm^3	1.165
Absorption coefficient, mm^{-1}	0.138
F (000)	696
Crystal size, mm	0.36 × 0.30 × 0.26
Theta range for data collection, °	3.56 to 25.35
Limiting indices	-12<= *h* <=16, -9<= *k* <=12, -16<= *l* <=13
Completeness to theta = 25.35 °	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.965 and 0.952
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5221 / 73 / 416
Goodness of fit on F^2	0.904
R indices [$I > 2\sigma(I)$]	R_1 = 0.0631, wR_2 = 0.1650
R indices (all data)	R_1 = 0.1120, wR_2 = 0.1837
Absolute structure parameter	0.0(2)
Largest diff. peak and hole, e Å^{-3}	0.658 and -0.251

6. Biological Activity Assays

a. Cell culture

Four different human carcinoma cell lines: HL-60, Bel-7402, BGC-823 and KB were cultured in RPMI-1640 medium supplemented with 10% fetal bovine serum, 100 units/mL of penicillin and 100 μg/mL of streptomycin. Cells were maintained at 37 ^{o}C in a humidified atmosphere of 5% CO_2 in air.

C6 glioma cell line was bought from American Type Culture Collection (ATCC Cat No: CCL-107, Manassas, VA) and maintained in Dulbecco's Modified Eagle Medium cell lines (DMEM) containing 10% FBS (Invitrogen, Burlington, Canada). C6 cell line were seeded at a density of 2×10^5 in a 35 mm diameter μ-dish plastic bottom (ibidi GmbH, Germany) and cultured for 24 h in DMEM. Human dermal fibroblast cells were purchased from Genlantis.

b. Solutions

The compound **5a'-5o'** can be prepared according to previous procedure[10]**.** Then the selected compounds (**5a', 5b', 5e', 5f' and 5g'**) were dissolved in DMSO at a concentration of 5 mM as stock solution, and diluted in culture medium at concentrations of 1.0, 10, 100, and 500 μM as working-solution. To avoid DMSO toxicity, the concentration of DMSO was less than 0.1% (v/v) in all experiments.

c. Cytotoxicity analysis

The cells harvested in the exponential phase were seeded equivalently into a 96-well plate, and then selected compounds were added to the wells to achieve final concentrations. Control wells were prepared by addition of culture medium. Wells containing culture medium without cells were used as blanks. All experiments were performed in quintuplicate. The MTT assay was performed as described by Mosmann for HL-60[11]. Upon completion of the incubation for 44 h, stock MTT dye solution (20 mL, 5 mg/mL) was added to each well. After 4 h incubation, 2-propanol (100 mL) was added to solubilize the MTT formazan. The OD of each well was measured on a microplate spectrophotometer at a wavelength of 570 nm.

The SRB assay was performed as previously described for Bel-7402, BGC-823, and KB[12]. Upon completion of the incubation for 44 h, the cells were fixed in 10% trichloroacetic acid (100 mL) for 30 min at 4 ^{o}C, washed five times and stained with 0.1% SRB in 1% acetic acid (100 mL) for 15 min. The cells were then washed four times in 1% acetic acid and air-dried. The stain was solubilized in 10 mM unbuffered Tris base (100 mL) and the OD was measured at 540 nm as above. The IC_{50} value was determined from plot of % viability against dose of compounds added.

Table S2 The cytotoxicity of the selected compounds against various human carcinomas.

Compound	**IC_{50} (μM)**			
	HL-60	BGC-823	Bel-7402	KB
5a	17.84	40.35	18.58	24.87
5a'	11.02	32.01	37.20	15.92
5b'	32.03	35.47	37.45	73.52
5e'	19.44	33.29	25.69	25.97
5f'	17.31	38.24	21.48	25.01
5g'	22.43	30.01	23.45	26.41

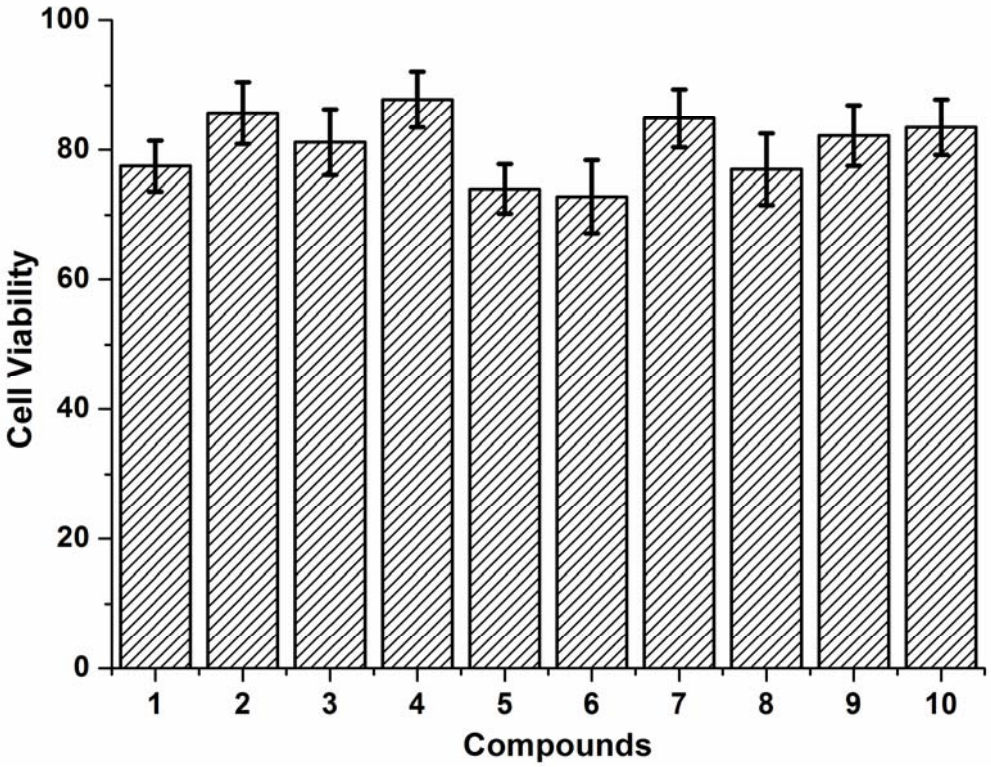

Fig. S3 The cytotoxicity of the selected compounds to HDF cells. HDF cells were treated with 8 μM of compounds and incubated at 37 ^{o}C for 4 h. Compound No. 1: **5a**; 2: **5a'**; 3: **5k**; 4: **5e**; 5: **5d**; 6: **5c**; 7: **5f**; 8: **5g**; 9: **5o**; 10: **5o'**.

d. Fluorescence imaging of C6 glioma cells.

The medium was removed and the cells were washed twice with phosphate buffered saline (PBS) and fixed with 4% paraformaldehyde in PBS for 10 min at room temperature. The fixed cells were washed with PBS and incubated with the DMEM (1 mL) solution containing 80 μM compounds (NO. G1-G10) for 1 h at 37 ^{o}C. After washing twice with Hank's Balanced Salt solution (HBSS), the cell imaging was conducted under confocal fluorescence microscope (Nikon, Eclipse TE2000-E) with excitation filter: 350/40 nm; emission filter: 460/50 nm.

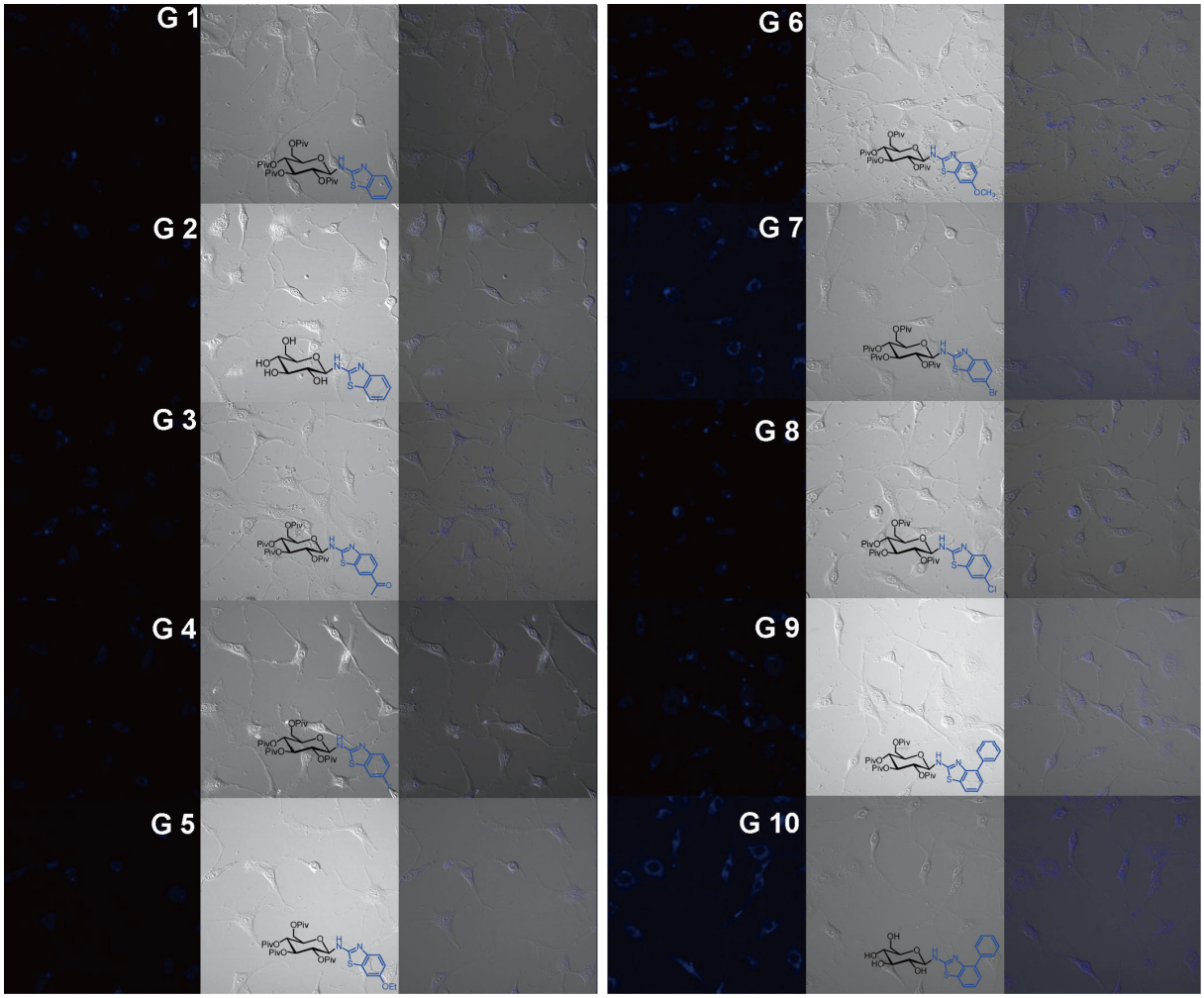

Fig. S4 Evaluation of cell uptake based on fluorescence microscopy. Representative normal light and fluorescence contrast images of C6 Glioma Cells treated with 80 μM substrate (NO. G1-G10) and incubated at 37 ^{o}C for 1 h. Substrate NO. G1: **5a**; G2: **5a'**; G3: **5k**; G4: **5e**; G5: **5d**; G6: **5c**; G7: **5f**; G8: **5g**; G9: **5o**; G10: **5o'**.

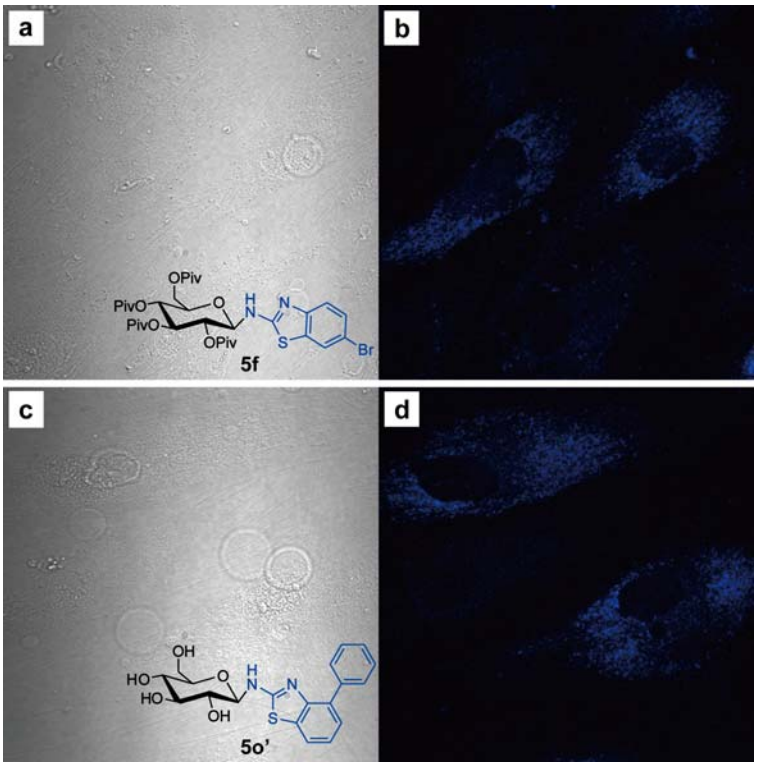

Fig. S5 Evaluation of cell staining of the cross-coupled products by fluorescence microscopy. (**a** and **c**) Representative normal light contrast images of HDF cells loaded with **5f** and **5o'** (80 μM each) in Hank's Balanced Salts Solution for 1 h at 37 ^{o}C. (**b** and **d**) The corresponding fluorescence images of the cells loaded with **5f** and **5o'**, respectively.

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