Supporting Information

Design and Synthesis of Covalently Tethered "IsoG-Star" as Recyclable Host for Selective Cesium Separation

Mengjia Liu,[a] Ying He,[a] Lukasz Wojtas,[a] and Xiaodong Shi*[a]

[a] Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States

I. Self-assembly NMR Study

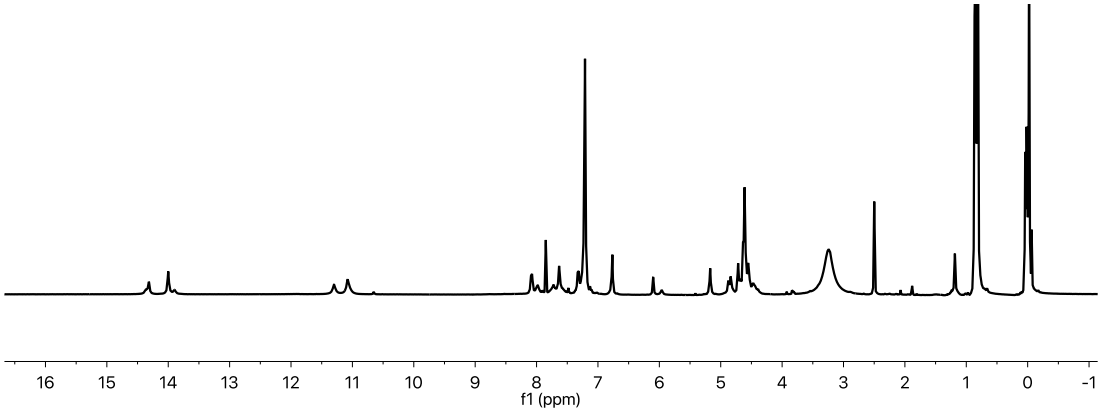


Figure S1. Self-assembly experiments of **1c** with CsCl in$CDCl_3$.

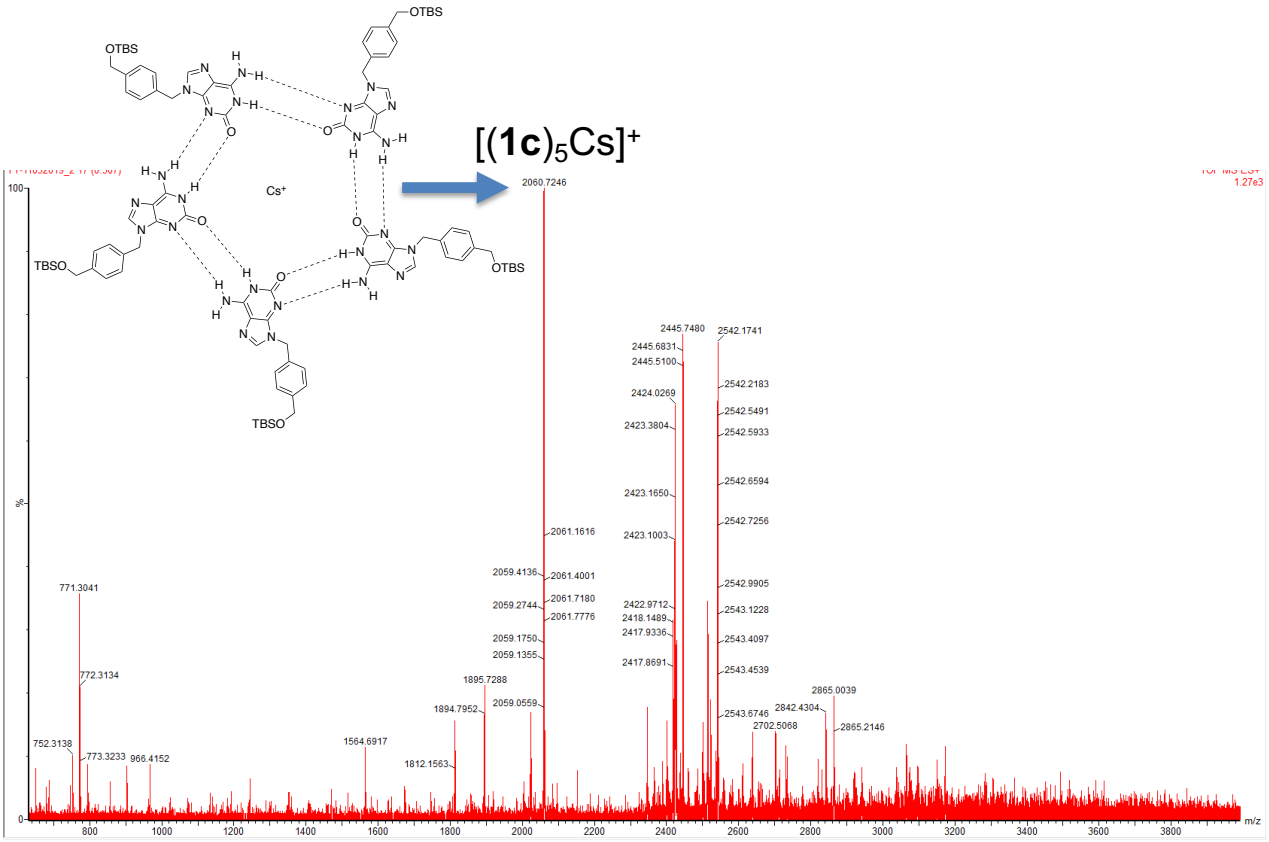


Figure S2. ESI-MS of Self-assembly experiments of **1c**

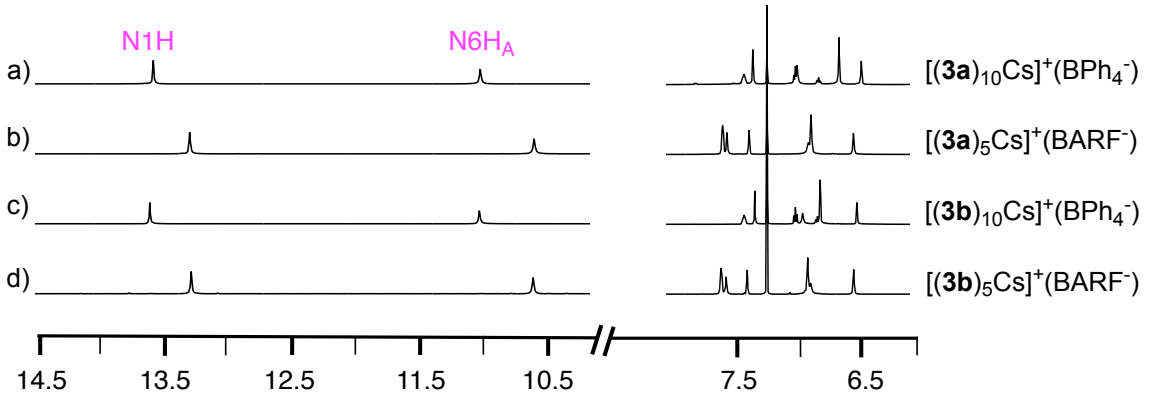


Figure S3. Self-assembly experiments of **3a** and **3b**: a) ^{1}H NMR spectrum of [(**3a**)$_{10}$Cs]$^+$(BPh$_4^-$) in $CDCl_3$; b) ^{1}H NMR spectrum of [(**3a**)$_5$Cs]$^+$(BARF$^-$) in $CDCl_3$, c) ^{1}H NMR spectrum of [(**3b**)$_{10}$Cs]$^+$(BPh$_4^-$) in $CDCl_3$, d) ^{1}H NMR spectrum of [(**3b**)$_5$Cs]$^+$(BARF$^-$) in $CDCl_3$. The portion of the spectra shows the region of the N1H and N6HA peaks.

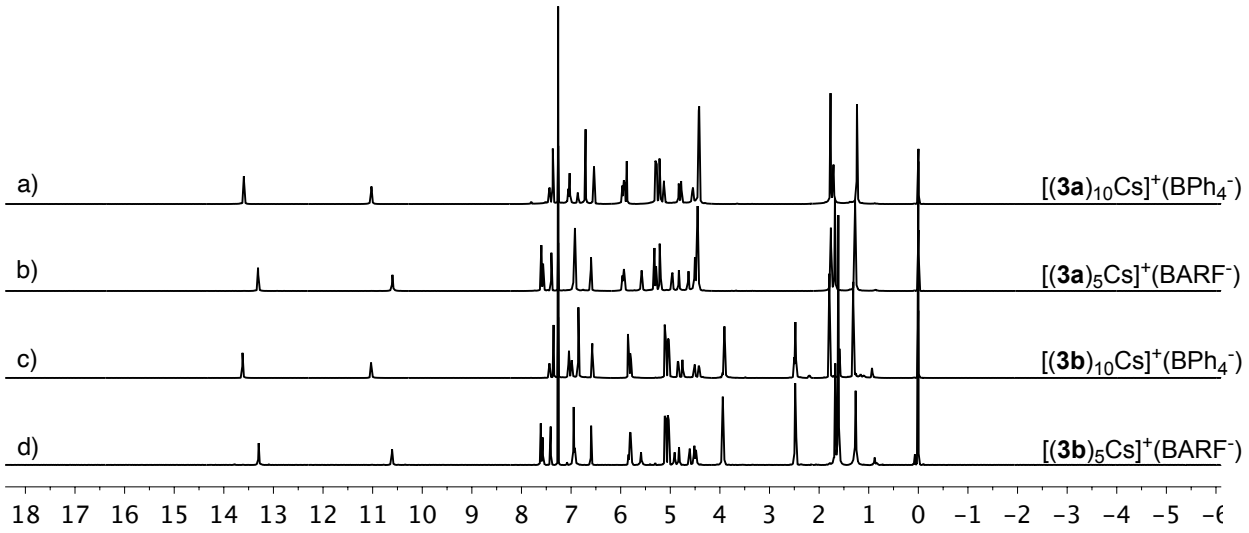


Figure S4. Self-assembly experiments of **3a** and **3b**: a) ^{1}H NMR spectrum of [(**3a**)$_{10}$Cs]$^+$(BPh$_4^-$) in $CDCl_3$; b) ^{1}H NMR spectrum of [(**3a**)$_5$Cs]$^+$(BARF$^-$) in $CDCl_3$, c) ^{1}H NMR spectrum of [(**3b**)$_{10}$Cs]$^+$(BPh$_4^-$) in $CDCl_3$, d) ^{1}H NMR spectrum of [(**3b**)$_5$Cs]$^+$(BARF$^-$) in $CDCl_3$.

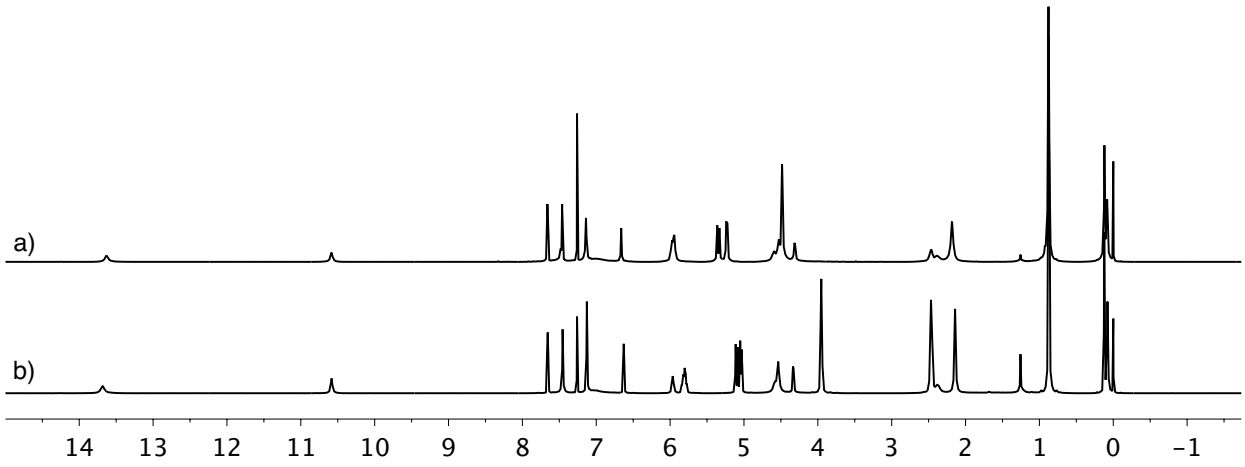


Figure S5. Self-assembly experiments of **4a** and **4b**: a) ^{1}H NMR spectrum of $[(\mathbf{4a})_{10}Cs_2]^{2+}(BARF^-)_2$ in $CDCl_3$; b) ^{1}H NMR spectrum of $[(\mathbf{4b})_{10}Cs_2]^{2+}(BARF^-)_2$ in $CDCl_3$.

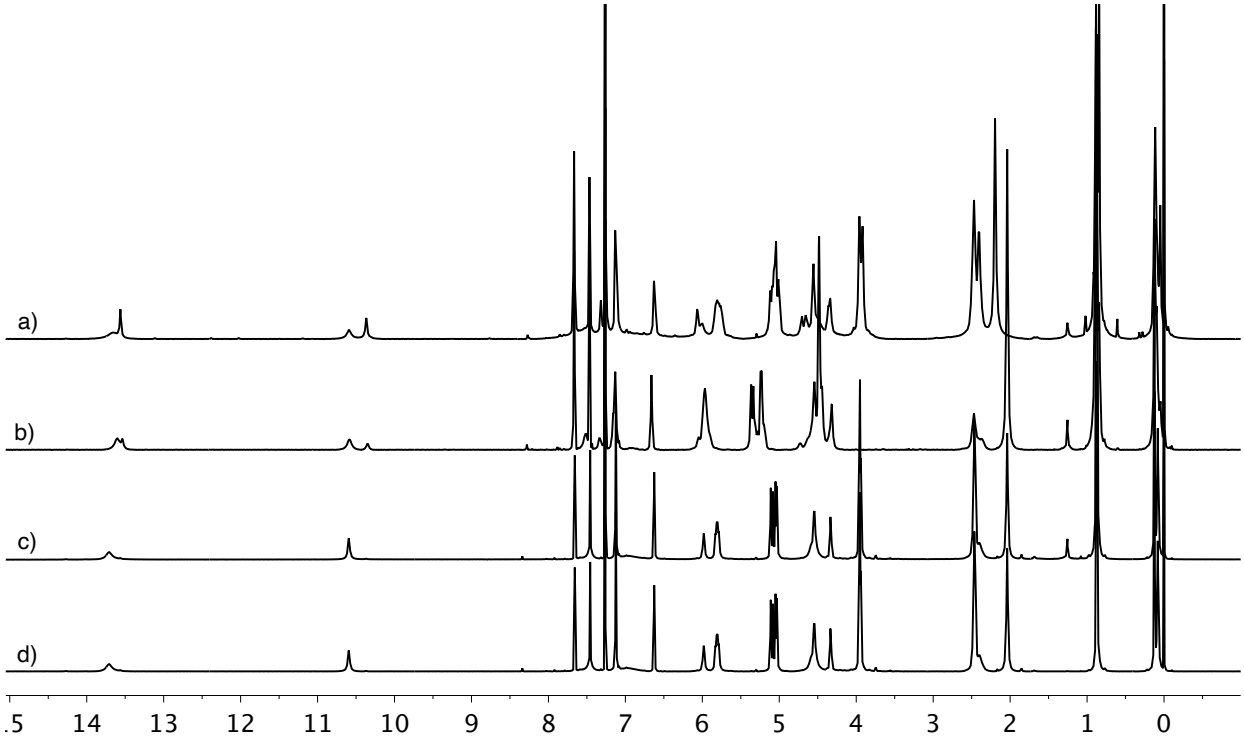


Figure S6. ^{1}H NMR experiments of **4b** with Cs^+ and Na^+ mixture at 25°C in $CDCl_3$, Cs^+ : Na^+ molar ratio of : (a) 1:150, (b) 1:100, (c) 1:50, (d) $[(\mathbf{4b})_{10}Cs_2]^{2+}(BARF^-)_2$. The concentrations of Cs^+ in aqueous solution are the same in all cases.

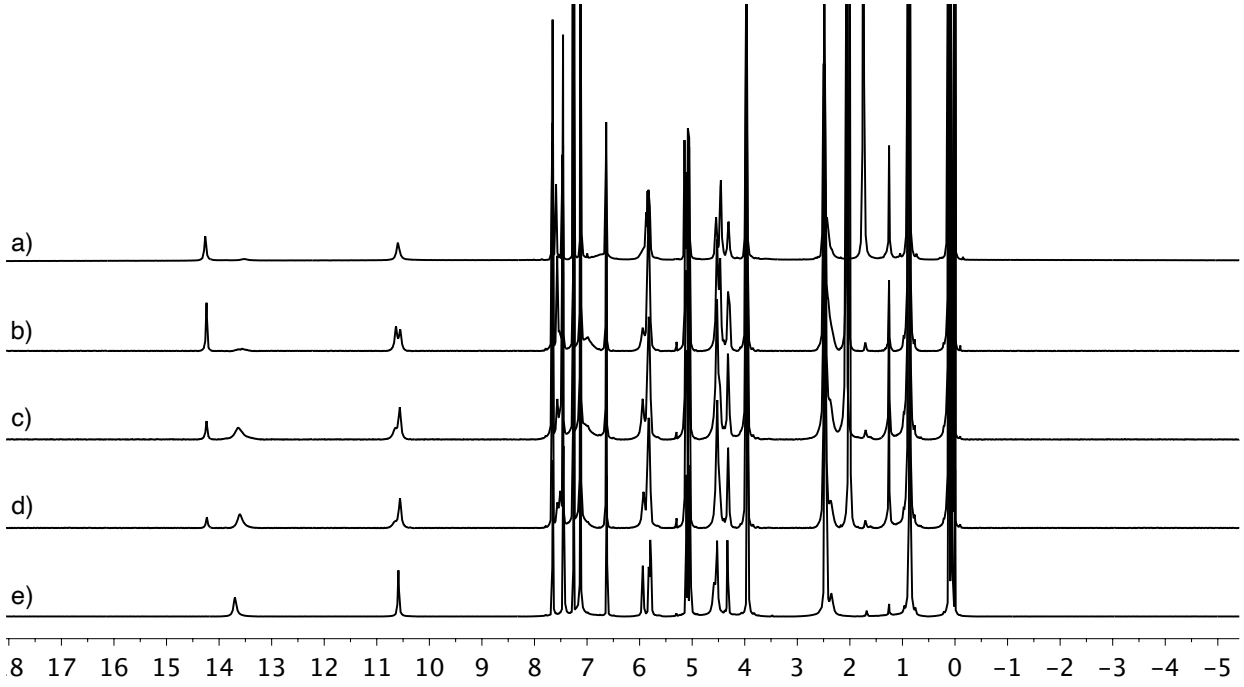


Figure S7. ^{1}H NMR experiments of **4b** with Cs^{+} and K^{+} mixture at 25°C in $CDCl_3$, (a) $[(\mathbf{4b})_{10}K_2]^{2+}(BARF^{-})_2$, Cs^{+} : K^{+} molar ratio of (b) 1:150, (c) 1:100, (d) 1:50, (e) $[(\mathbf{4b})_{10}Cs_2]^{2+}(BARF^{-})_2$. The concentrations of Cs^{+} in aqueous solution are the same in all cases.

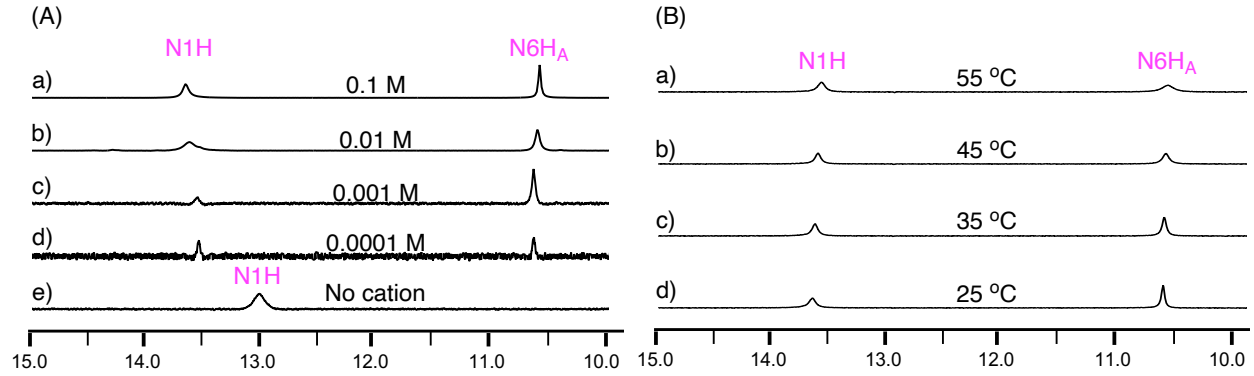


Figure S8. (A) ^{1}H NMR spectra of $[(\mathbf{4b})_{10}Cs_2]^{2+}(BARF^{-})_2$ in $CDCl_3$ at different concentrations; (B) VT-^{1}H NMR spectra of $[(\mathbf{4b})_{10}Cs_2]^{2+}(BARF^{-})_2$ in $CDCl_3$ from 25 °C to 55 °C The portion of the spectra shows the region of the N1H and N6H$_A$ peaks.

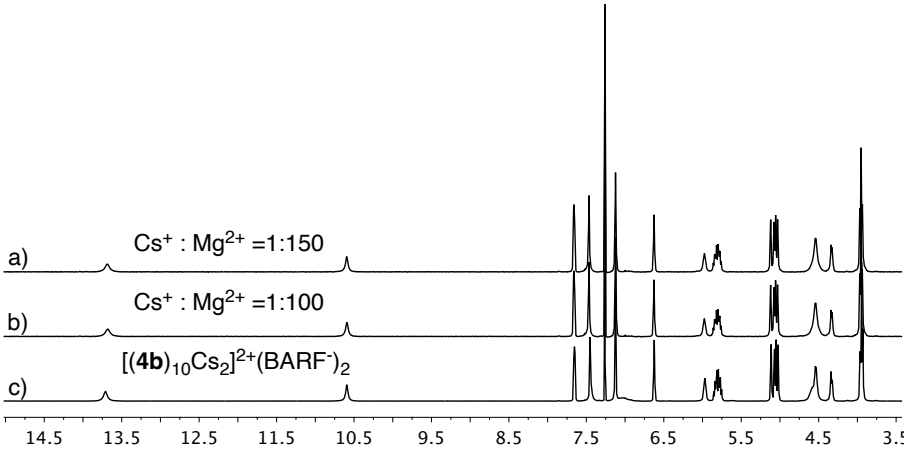


Figure S9. ^{1}H NMR experiments of **4b** with Cs^+ and Mg^{2+} mixture at 25°C in $CDCl_3$, Cs^+ : Mg^{2+} molar ratio of (a) 1:150, (b) 1:100, (c) $[(\mathbf{4b})_{10}Cs_2]^{2+}(BARF^-)_2$. The concentrations of Cs^+ in aqueous solution are the same in all cases.

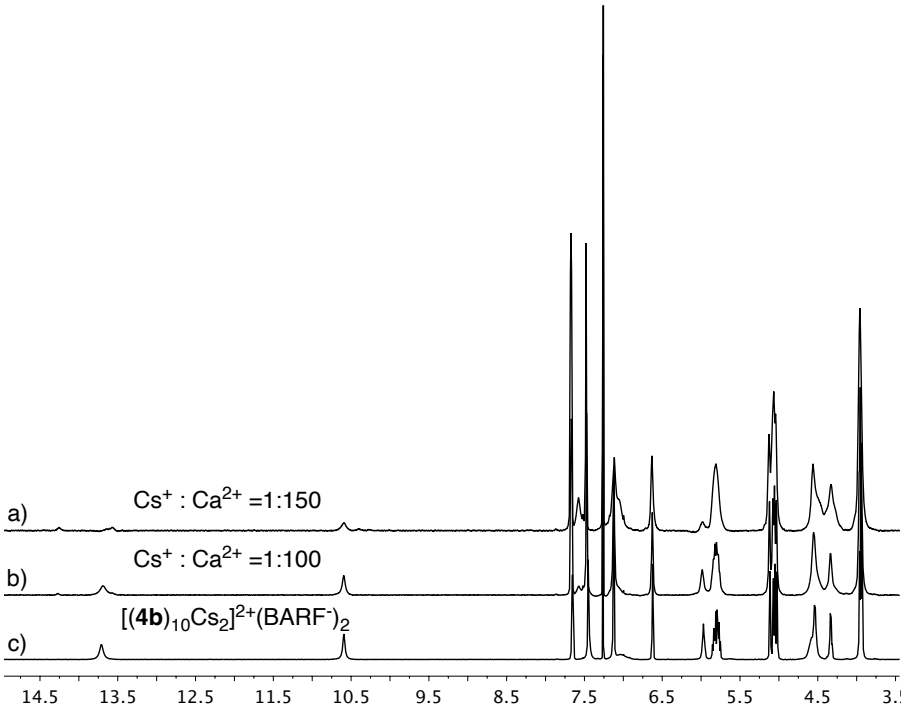


Figure S10. ^{1}H NMR experiments of **4b** with Cs^+ and Ca^{2+} mixture at 25°C in $CDCl_3$, Cs^+ : Ca^{2+} molar ratio of (a) 1:150, (b) 1:100, (c) $[(\mathbf{4b})_{10}Cs_2]^{2+}(BARF^-)_2$. The concentrations of Cs^+ in aqueous solution are the same in all cases.

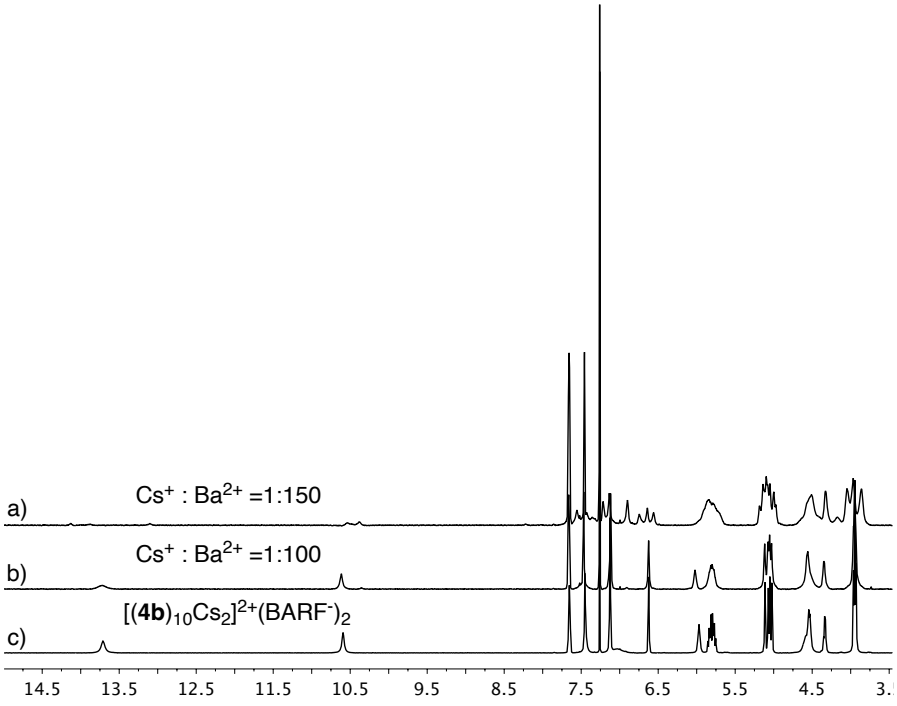


Figure S11. ^{1}H NMR experiments of **4b** with Cs^+ and Ba^{2+} mixture at 25°C in $CDCl_3$, Cs^+ : Ba^{2+} molar ratio of (a) 1:150, (b) 1:100, (c) $[(\mathbf{4b})_{10}Cs_2]^{2+}(BARF^-)_2$. The concentrations of Cs^+ in aqueous solution are the same in all cases.

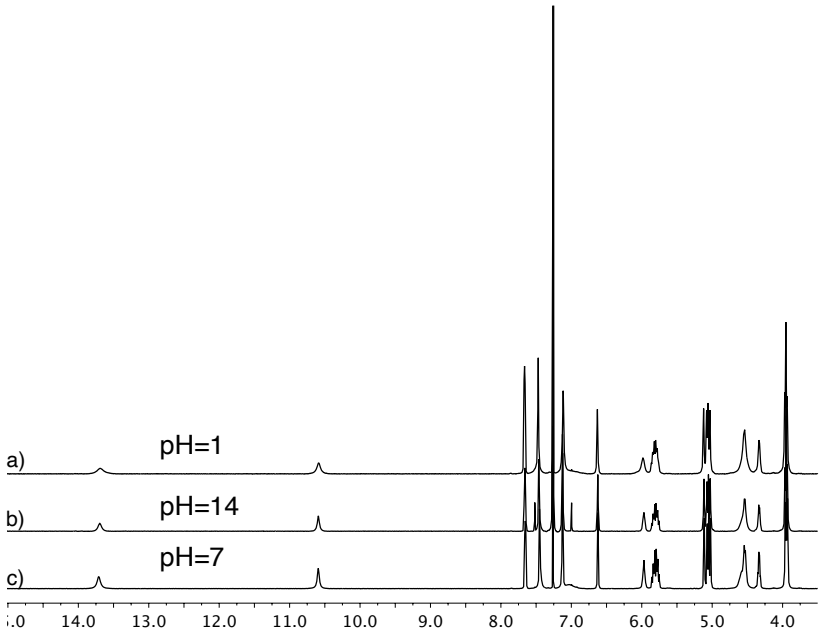


Figure S12. ^{1}H NMR experiments of **4b** with 1:50 Cs^+/ Na^+ ratio in $CDCl_3$ at (a) pH=1; (b) pH=14; (c) pH=7.

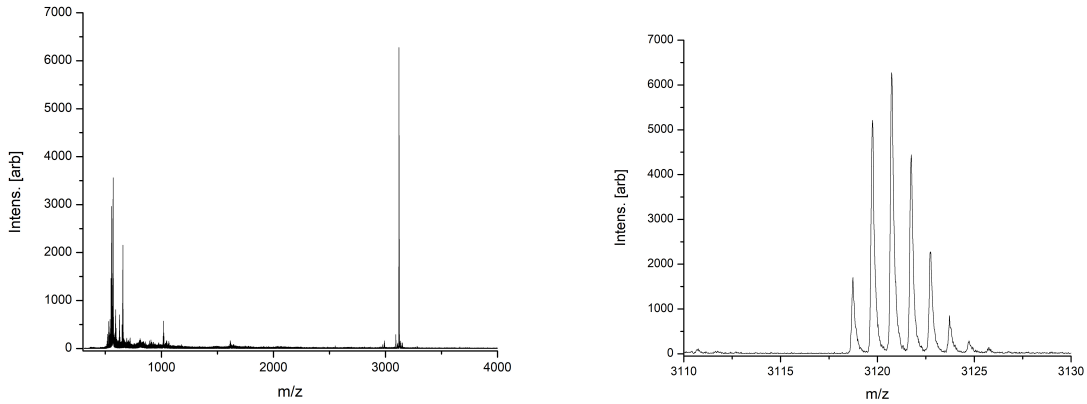


Figure S13. MALDI-TOF spectra of cyclic pentamer **5a**

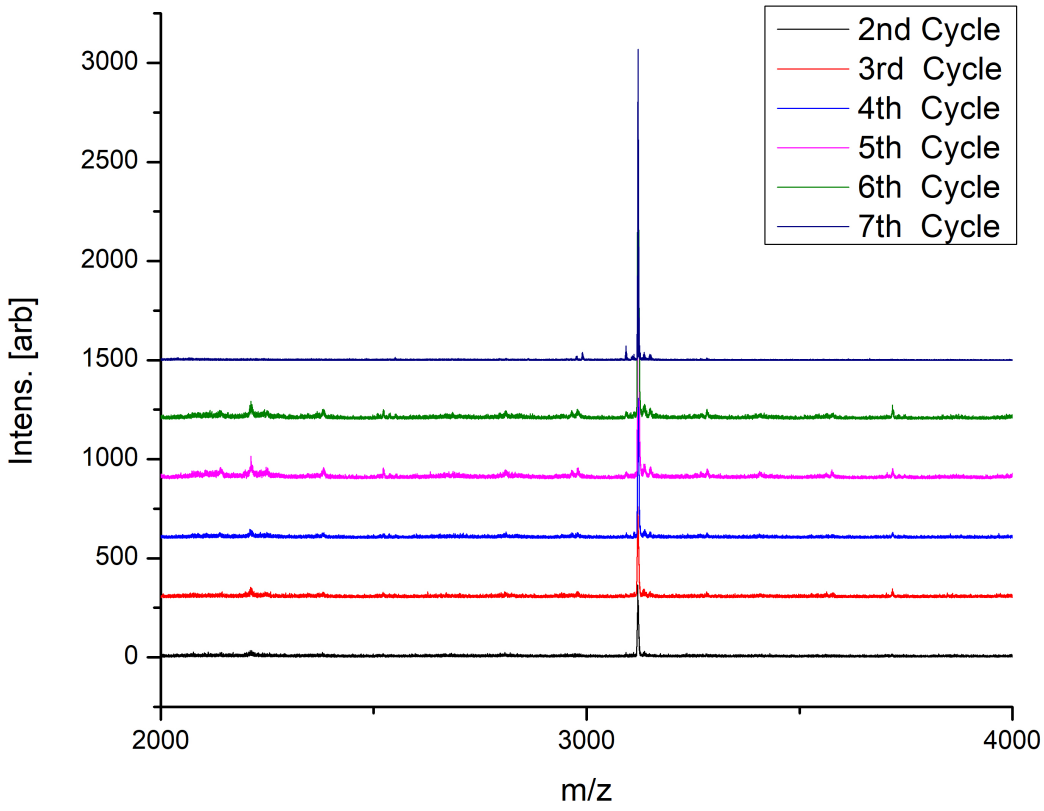


Figure S14. MALDI-TOF spectra after each cycle extraction experiments of cyclic pentamer **5a**.

II. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^{1}H NMR, ^{13}C NMR, spectra were recorded on Bruker Avance NEO-600 MHz spectrometers and Bruker Avance NEO-400 MHz spectrometers. Chemical shifts were reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H, DMSO (δ 2.50 ppm) for ^{1}H and DMSO (δ 39.52 ppm) for ^{13}C. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS were recorded on Agilent 6320 TOF MS/Agilent 1200 HPLC spectrometer. MALDI-TOF spectra were recorded on Bruker UltraFlexXtreme MALDI-TOF/TOF.

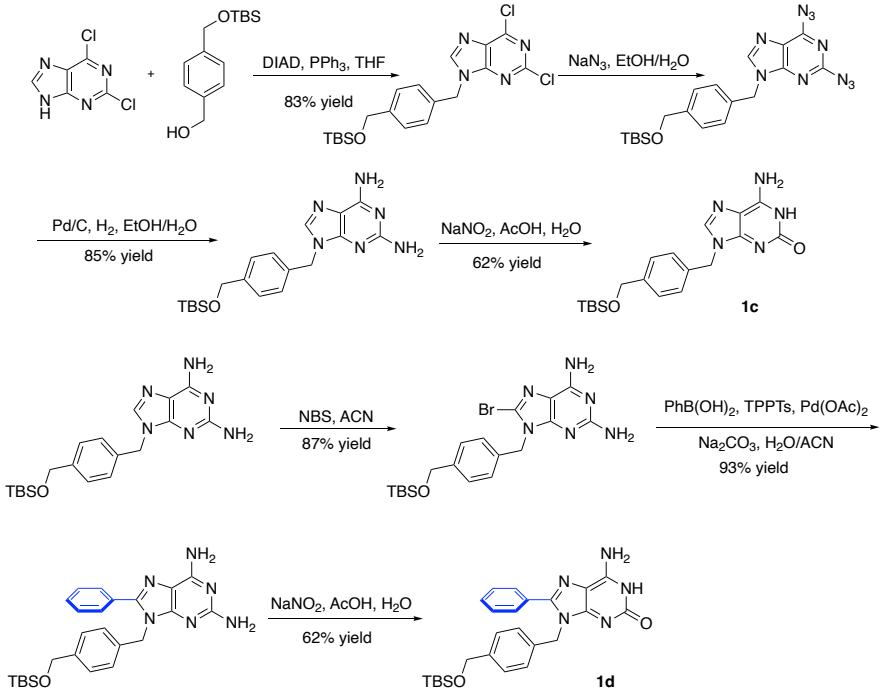
III. Procedures and NMR Spectra

1. Synthesis Procedures

(1) Synthesis of 6-amino-9-(4-(((tert-butyldimethylsilyl)oxy)methyl)benzyl)-1,9-dihydro-2H-purin-2-one (**1c**) and 6-amino-9-(4-(((tert-butyldimethylsilyl)oxy)methyl)benzyl)-8-phenyl-1,9-dihydro-2H-purin-2-one (**1d**)

Standard procedure for Mitsunobu coupling: The dichloropurine (1.0 eq.) was added to a solution of alcohol (1.05 eq.) and PPh_3 (1.05 eq.) in anhydrous THF under a N_2 atmosphere at 0 °C. The resulting solution was treated with diisopropylazodicarboxylate (DIAD, 1.05 eq.). The reaction mixture was stirred at room temperature for 6 h. The reaction was treated with saturated sodium chloride, and the mixture was extracted with dichloromethane. The combined organic layer was then washed with water and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The pure product was obtained by flash silica gel chromatography.[1]

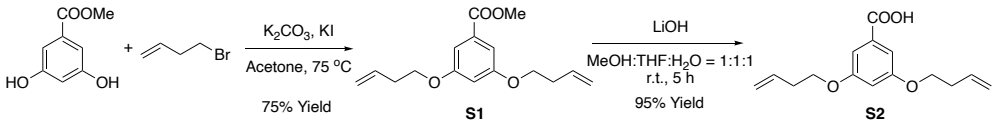
Standard procedure for the synthesis of diaminopurine: A solution of resulting dichloropurine (1.0 eq.) and NaN_3 (2.5 eq.) in EtOH/H_2O (5/1 volume ratio) was refluxed for 2 h. The solvent was then removed under reduced pressure, yielding the crude product. This crude product was subjected to hydrogenation in EtOH with the presence of Pd/C (10 mol %). The resulting mixture was passed through celite, concentrated, and subsequently purified using flash silica column chromatography.



^{1}H NMR of 1c (400 MHz, DMSO-d_6) δ 7.83 (s, 1H), 7.26 (d, J = 2.2 Hz, 4H), 5.10 (s, 2H), 4.67 (s, 2H), 0.88 (s, 9H), 0.06 (s, 6H).

^{1}H NMR of 1d (400 MHz, Chloroform-*d*) δ 7.50 – 7.34 (m, 5H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 5.21 (s, 2H), 4.65 (s, 2H), 0.85 (s, 9H), 0.02 (d, *J* = 55.1 Hz, 6H).

(2) Synthesis of methyl 3,5-bis(but-3-en-1-yloxy)benzoate (**S1**)



A solution consisting of 10.00 g (59.5 mmol) of Methyl 3,5-dihydroxybenzoate, 32.4 g (240.0 mmol) of 4-Bromo-1-butene, and 55.69 g (238.4 mmol) of K_2CO_3 in 120 mL of acetone was refluxed for 24 hours. The acetone was then removed under reduced pressure. To the resulting solid, 100 mL of water was added, and the aqueous layer was subsequently extracted with EA (ethyl acetate). The organic layers were combined and washed with 1 M HCl, followed by a brine extraction. The organic layer was dried over sodium sulfate, filtered, and evaporated. The crude product was purified using column chromatography (Hexane: EA = 10:1), yielding methyl 3,5-bis(but-3-en-1-yloxy)benzoate (**S1**) as an oil (12.32 g, 75% yield).

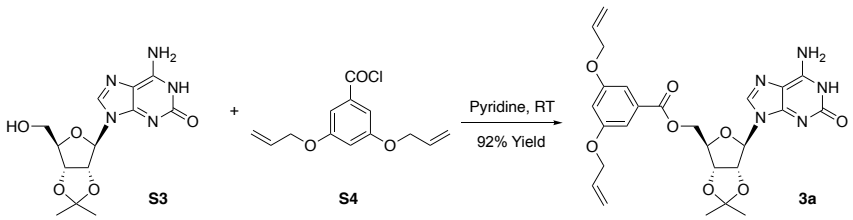
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 2.4 Hz, 2H), 6.65 (t, *J* = 2.3 Hz, 1H), 5.89 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 2H), 5.21 – 5.06 (m, 4H), 4.03 (t, *J* = 6.7 Hz, 4H), 3.89 (s, 3H), 2.54 (qt, *J* = 6.7, 1.4 Hz, 4H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.37, 160.40, 134.74, 132.39, 117.64, 108.34, 107.23, 67.99, 52.69, 34.01.
HRMS m/z (ESI) calcd. for $C_{16}H_{21}O_4^+$ $(M+H)^+$ 277.1434, found 277.1453.

(3) Synthesis of 3,5-bis(but-3-en-1-yloxy)benzoic acid (**S2**)

This methyl 3,5-bis(but-3-en-1-yloxy)benzoate was then subjected to direct hydrolysis using LiOH (2.14 g, 89.25 mmol) in a mixture of methanol, THF, and water in a 1:1:1 ratio (120 mL) at room temperature for 5 hours. The organic solvent was removed under reduced pressure, and the solution was diluted with 80 mL of water. The aqueous layer was extracted with EA, and the combined aqueous layers were acidified with a 10% HCl solution until the pH reached 2. The resulting crystals were collected via vacuum filtration, yielding white solid 3,5-bis(but-3-en-1-yloxy)benzoic acid (**S2**) with a yield of 11.10 g (95%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 2.4 Hz, 2H), 6.71 (t, *J* = 2.3 Hz, 1H), 5.90 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 2H), 5.25 – 5.08 (m, 4H), 4.05 (t, *J* = 6.7 Hz, 4H), 2.55 (qt, *J* = 6.7, 1.5 Hz, 4H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.27, 160.47, 134.69, 131.47, 117.70, 108.87, 108.13, 68.04, 33.99.
HRMS m/z (ESI) calcd. for $C_{16}H_{21}O_4^+$ $(M+H)^+$ 263.1278, found 263.1298.

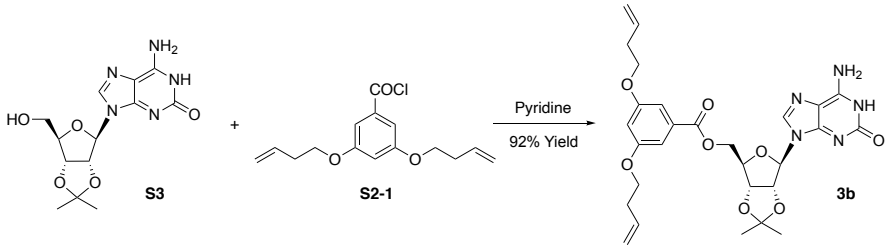
(4) Synthesis of ((3aR,4R,6R,6aR)-6-(6-amino-2-oxo-1,2-dihydro-9H-purin-9-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methyl 3,5-bis(allyloxy)benzoate (**3a**)



A mixture of 3,5-bis(allyloxy)benzoic acid (1 g, 4.27 mmol) and DMF (1 drop) in DCM (10 mL) was combined with $(COCl)_2$ (1.08 g, 8.54 mmol) at room temperature. The reaction mixture was stirred for 2 hours at room temperature, followed by concentration to yield a yellow solid, **S4**, which was directly used in the subsequent step without purification. **S3**(1 g, 3.09 mmol) was dissolved in 10 mL of anhydrous pyridine at room temperature. Then, a solution of acid chloride **S4** (3.14 mmol) in anhydrous pyridine (10 mL) was added dropwise. The resulting mixture was stirred for 2 hours, poured into 30 mL of cold water, and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel using a DCM: MeOH eluent in a 10:1 ratio. This procedure afforded the desired white solid (**3a**), with a yield of 1.53 g (92%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.89 (s, 1H), 7.02 (d, J = 2.2 Hz, 2H), 6.82 (d, J = 2.4 Hz, 1H), 6.02 (dt, J = 17.0, 5.3 Hz, 3H), 5.41 (d, J = 2.0 Hz, 1H), 5.39 – 5.30 (m, 2H), 5.26 (dd, J = 10.6, 1.8 Hz, 2H), 5.12 (d, J = 6.3 Hz, 1H), 4.59 (d, J = 5.2 Hz, 4H), 4.53 – 4.39 (m, 3H), 1.54 (s, 3H), 1.34 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 165.01, 159.31, 137.83, 133.32, 131.19, 117.69, 113.43, 107.78, 106.68, 88.53, 83.68, 83.37, 81.29, 68.54, 64.85, 26.98, 25.27.
HRMS m/z (ESI) calcd. for $C_{26}H_{30}N_5O_8^+$ $(M+H)^+$ 540.2089, found 540.2172.

(5) Synthesis of ((3aR,4R,6R,6aR)-6-(6-amino-2-oxo-1,2-dihydro-9H-purin-9-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methyl 3,5-bis(but-3-en-1-yloxy)benzoate (**3b**)

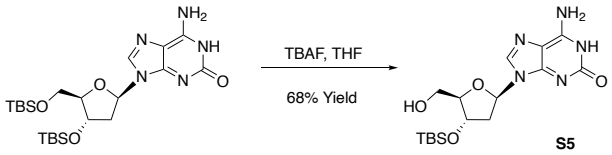


To a mixture of the **S3** (1 g, 3.82 mmol) and DMF (1 drop) in DCM (10 mL) was added $(COCl)_2$ (970 mg, 7.64 mmol) at room temperature. The reaction mixture was stirred for 2 hours at room temperature and then concentrated, resulting in the formation of a yellow solid, **S2-1**, which was directly used in the subsequent step without purification. **S3** (1 g, 3.09 mmol) was dissolved in 10 mL of anhydrous pyridine at room temperature. A solution of acid chloride **S2-1** (3.14 mmol) in anhydrous pyridine (10 mL) was added dropwise to the mixture. The resulting mixture was stirred for 2 hours, then poured into 30 mL of cold water and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4. After removing the solvent under reduced pressure, the residue was separated using silica gel column chromatography eluted with a DCM:

MeOH ratio of 10:1. This procedure yielded the desired white solid (**3b**), with a total mass of 1.61 g (92% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 7.89 (s, 1H), 6.99 (d, J = 2.2 Hz, 2H), 6.76 (d, J = 2.6 Hz, 1H), 6.00 (d, J = 2.2 Hz, 1H), 5.87 (ddt, J = 17.0, 10.2, 6.6 Hz, 2H), 5.33 (dd, J = 6.3, 2.2 Hz, 1H), 5.18 (t, J = 1.6 Hz, 1H), 5.16 – 5.09 (m, 2H), 5.08 (d, J = 10.3 Hz, 2H), 4.48 – 4.41 (m, 3H), 4.04 (t, J = 6.6 Hz, 4H), 2.47 (dt, J = 13.1, 5.8 Hz, 4H), 1.54 (s, 3H), 1.34 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 165.04, 159.69, 137.85, 134.77, 131.17, 117.09, 113.41, 107.50, 106.10, 88.52, 83.70, 83.37, 81.33, 67.08, 64.88, 32.93, 26.98, 25.27.
HRMS m/z (ESI) calcd. for $C_{28}H_{34}N_5O_8^+$ $(M+H)^+$ 568.2402, found 568.2498.

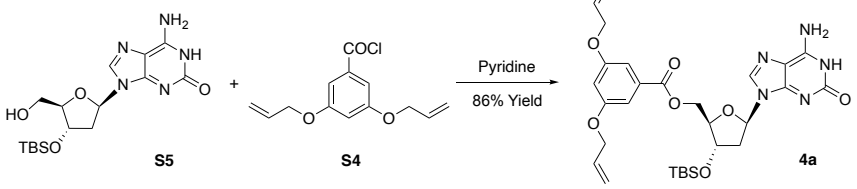
(6) Synthesis of 6-amino-9-((2R,4S,5R)-4-((tert-butyldimethylsilyl)oxy)-5 (hydroxymethyl)tetrahydrofuran-2-yl)-1,9-dihydro-2H-purin-2-one (**S5**)



A cold solution (0 ºC) of 6-amino-9-((2R,4S,5R)-4-((tert-butyldimethylsilyl)oxy)-5-(((tert-butyldimethylsilyl)oxy)methyl)tetrahydrofuran-2-yl)-1,9-dihydro-2H-purin-2-one (1 g, 2.02 mmol, 1 equiv.) in dry tetrahydrofuran (20 mL) was prepared. To this solution, tetra-n-butylammonium fluoride (TBAF) (2 mL of a 1 M solution in tetrahydrofuran, 2.02 mmol, 1 equiv.) was added, and the resulting solution was stirred for 45 minutes, allowing it to warm to room temperature. The resulting solution was then diluted with dichloromethane (20 mL) and quenched with water (5 mL). The organic layer was extracted with brine (5 mL), dried over sodium sulfate, and the solvent was subsequently reduced under vacuum. The crude product was purified by flash column chromatography (DCM: MeOH = 5:1), resulting in the isolation of **S5** as a white powder (523 mg, 68%).[2]

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (s, 1H), 6.11 (dd, J = 8.3, 5.8 Hz, 1H), 4.51 (dt, J = 5.0, 2.3 Hz, 1H), 3.84 (q, J = 3.3 Hz, 1H), 3.69 – 3.45 (m, 2H), 2.65 (ddd, J = 13.5, 8.4, 5.5 Hz, 1H), 2.14 (ddd, J = 13.1, 5.9, 2.3 Hz, 1H), 0.89 (s, 9H), 0.10 (s, 6H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 156.26, 138.22, 88.63, 83.98, 73.44, 62.09, 39.85, 26.20, 18.22, -4.33, -4.39.
HRMS m/z (ESI) calcd. for $C_{16}H_{28}N_5O_4Si^+$ $(M+H)^+$ 382.1905, found 382.1939.

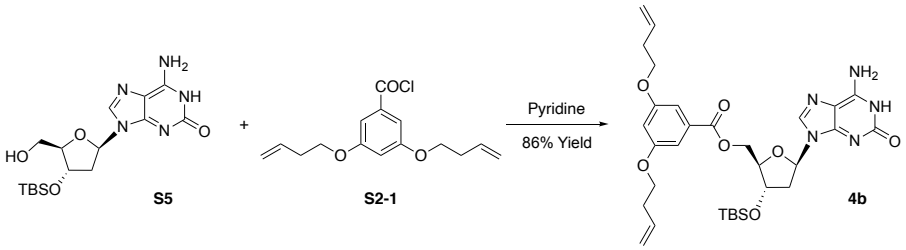
(7) Synthesis of ((2R,3S,5R)-5-(6-amino-2-oxo-1,2-dihydro-9H-purin-9-yl)-3-((tert-butyldimethylsilyl)oxy)tetrahydrofuran-2-yl)methyl 3,5-bis(allyloxy)benzoate (**4a**)



To a mixture of the 3,5-bis(allyloxy)benzoic acid (1 g, 4.27 mmol) and DMF (1 drop) in DCM (10 mL) was added $(COCl)_2$ (1.08 g, 8.54 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 hours. Afterward, the mixture was concentrated to yield a yellow solid, which was used in the subsequent step without undergoing further purification. **S5** (1 g, 2.62 mmol) was dissolved in 10 mL of anhydrous pyridine at room temperature. Subsequently, a solution of acid chloride **S4** (3.14 mmol) in anhydrous pyridine (10 mL) was added dropwise to the mixture. The resulting solution was stirred for two hours, poured into 30 mL of cold water, and then extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was separated on a silica gel column using a DCM: MeOH eluent ratio of 10:1. This process afforded the desired white solid **4a** with a mass of 1.35 g (86% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.51 (s, 1H), 7.93 (s, 1H), 7.07 (d, J = 2.3 Hz, 2H), 6.83 (t, J = 2.3 Hz, 1H), 6.15 (t, J = 6.9 Hz, 1H), 6.02 (ddt, J = 17.2, 10.4, 5.1 Hz, 2H), 5.39 (dq, J = 17.3, 1.7 Hz, 2H), 5.26 (dq, J = 10.6, 1.5 Hz, 2H), 4.67 (dt, J = 6.0, 3.1 Hz, 1H), 4.60 (dt, J = 5.2, 1.6 Hz, 4H), 4.48 (dd, J = 11.7, 5.8 Hz, 1H), 4.38 (dd, J = 11.7, 5.7 Hz, 1H), 4.11 (td, J = 5.7, 2.9 Hz, 1H), 3.33 (s, 6H), 2.80 (ddd, J = 13.3, 7.7, 5.8 Hz, 1H), 2.27 (ddd, J = 13.3, 6.3, 3.3 Hz, 1H), 0.88 (s, 9H), 0.11 (d, J = 2.8 Hz, 6H).
^{13}C NMR (151 MHz, DMSO-d_6) δ 165.10, 159.35, 133.28, 131.26, 117.54, 107.76, 106.76, 83.93, 82.51, 72.63, 68.52, 64.40, 38.57, 25.68, 17.67, -4.81, -4.99.
HRMS m/z (ESI) calcd. for $C_{29}H_{40}N_5O_7Si^+$ $(M+H)^+$ 598.2692, found 598.2788.

(8) Synthesis of ((2R,3S,5R)-5-(6-amino-2-oxo-1,2-dihydro-9H-purin-9-yl)-3-((tert-butyldimethylsilyl)oxy)tetrahydrofuran-2-yl)methyl 3,5-bis(but-3-en-1-yloxy)benzoate (**4b**)



To a mixture of the **S2** (1 g, 3.82mmol) and DMF (1 drop) in DCM (10 mL) was added $(COCl)_2$ (970 mg, 7.64 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 hours. Upon concentration, the product was obtained as a yellow solid, **S2-1**, which was utilized in the subsequent step without undergoing further purification. **S5** (1 g, 2.62 mmol) was dissolved in 10 mL of anhydrous pyridine at room temperature. Subsequently, a solution of acid chloride **S2-1** (3.14 mmol) in anhydrous pyridine (10 mL) was added dropwise. The resulting mixture was stirred for two hours, then poured into 30 mL of cold water and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting residue was separated on a silica gel column eluted with DCM: MeOH = 10:1. This procedure yielded the desired white solid **4b** with a mass of 1.41 g (86% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.94 (s, 1H), 7.03 (d, J = 2.3 Hz, 2H), 6.78 (t, J = 2.3 Hz, 1H), 6.14 (t, J = 7.1 Hz, 1H), 5.87 (ddt, J = 17.0, 10.3, 6.6 Hz, 2H), 5.16 (dq, J = 17.2, 1.7 Hz, 2H),

5.07 (ddt, J = 10.2, 2.2, 1.3 Hz, 2H), 4.67 (dt, J = 5.9, 3.0 Hz, 1H), 4.46 (dd, J = 11.6, 6.2 Hz, 1H), 4.36 (dd, J = 11.6, 5.7 Hz, 1H), 4.11 (td, J = 5.8, 2.7 Hz, 1H), 4.04 (t, J = 6.5 Hz, 4H), 2.80 (dt, J = 13.5, 6.9 Hz, 1H), 2.46 (qt, J = 6.6, 1.4 Hz, 4H), 2.25 (ddd, J = 13.4, 6.1, 2.9 Hz, 1H), 0.88 (s, 9H), 0.10 (d, J = 2.1 Hz, 6H).
^{13}C NMR (151 MHz, DMSO-d_6) δ 165.60, 160.20, 137.85, 135.22, 131.70, 117.57, 107.96, 84.42, 83.03, 73.20, 67.59, 64.85, 40.02, 39.88, 39.74, 39.60, 33.39, 26.14, 18.15, -4.34, -4.52.
HRMS m/z (ESI) calcd. for $C_{31}H_{44}N_5O_7Si^+$ $(M+H)^+$ 626.3005, found 626.3089.

2. General procedure for complex preparation

To a solution of isoguanosine derivatives (10 mg) in $CDCl_3$ (1 mL) was added the MCl_n (0.25 equiv.) and NaX (equivalents depend on the cation M^{n+} charge) in deionized H_2O (1 mL). After stirring for 2 h, the organic layer was separated and washed with deionized H_2O (2*1 mL) giving the desired complexes.

3. General procedure for competitive experiments

(1) Cs^+ Extraction Procedures of **4b**: In an aqueous phase, the competing MCl (M = Na^+ and K^+) salt concentration was altered based on the ratio to CsCl salt (2.5×10^{-5} M) in aqueous phase. Deoxy isoG 4b concentration was 10^{-4} M in the 1 mL organic phase $CDCl_3$. After 1 h, the organic layer was separated and washed with deionized H_2O (2 × 1 mL) giving the desired complexes and characterized by ^{1}H NMR."

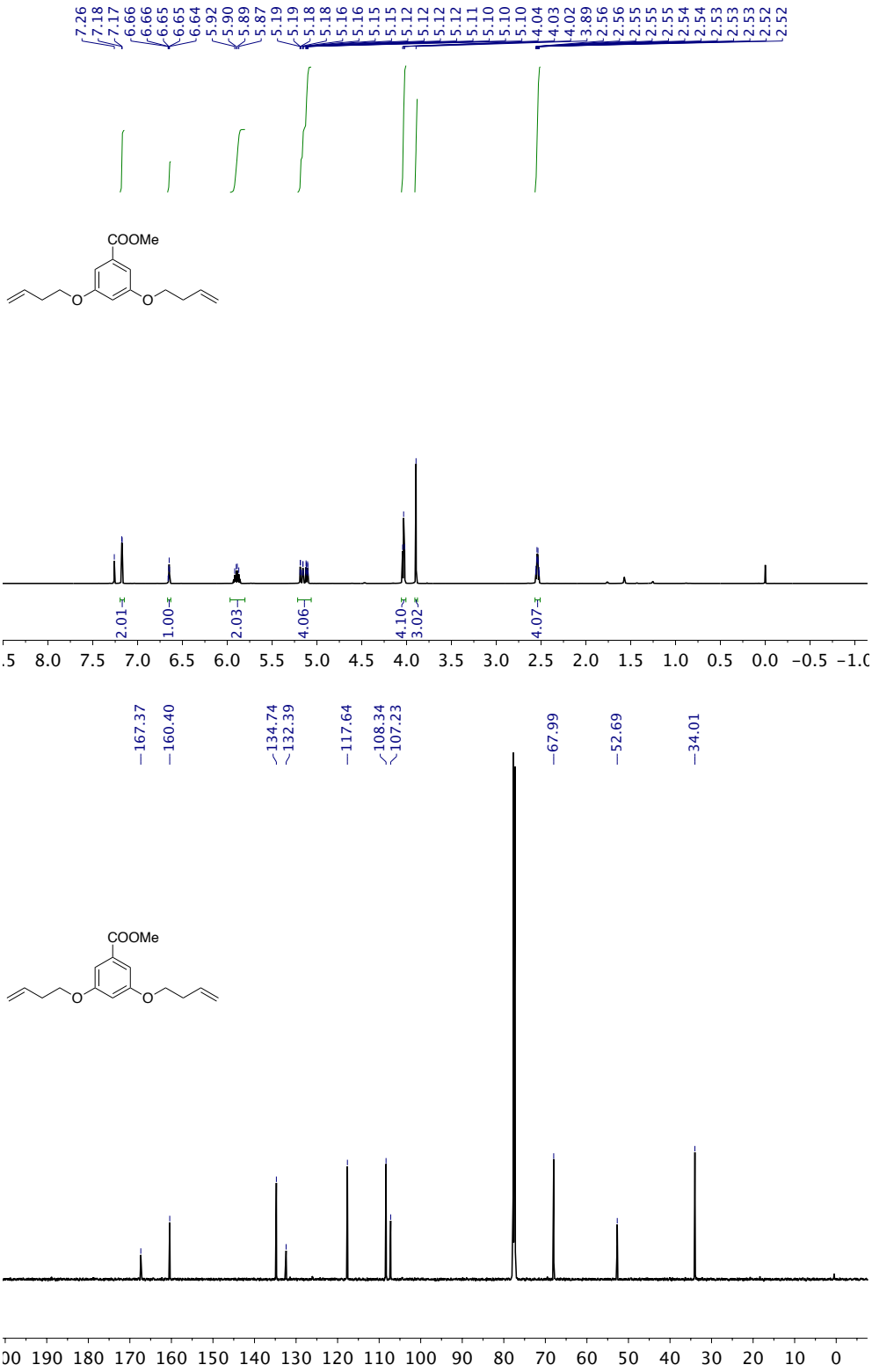
(2) Cs^+ Extraction Procedures of **5a**: In the competitive extraction experiment, the aqueous phase consisted of Cs^+ (2.5×10^{-5} M) and MCl (M = Na^+ and K^+) (1.25×10^{-3} M) in 1 mL. Cyclic pentamer **5a** concentration was 10^{-4} M in the 1 mL organic phase $CHCl_3$. After 1 h, the organic layer was separated and washed with deionized H_2O (2 × 1 mL) giving the desired complexes and characterized by MALDI-TOF."

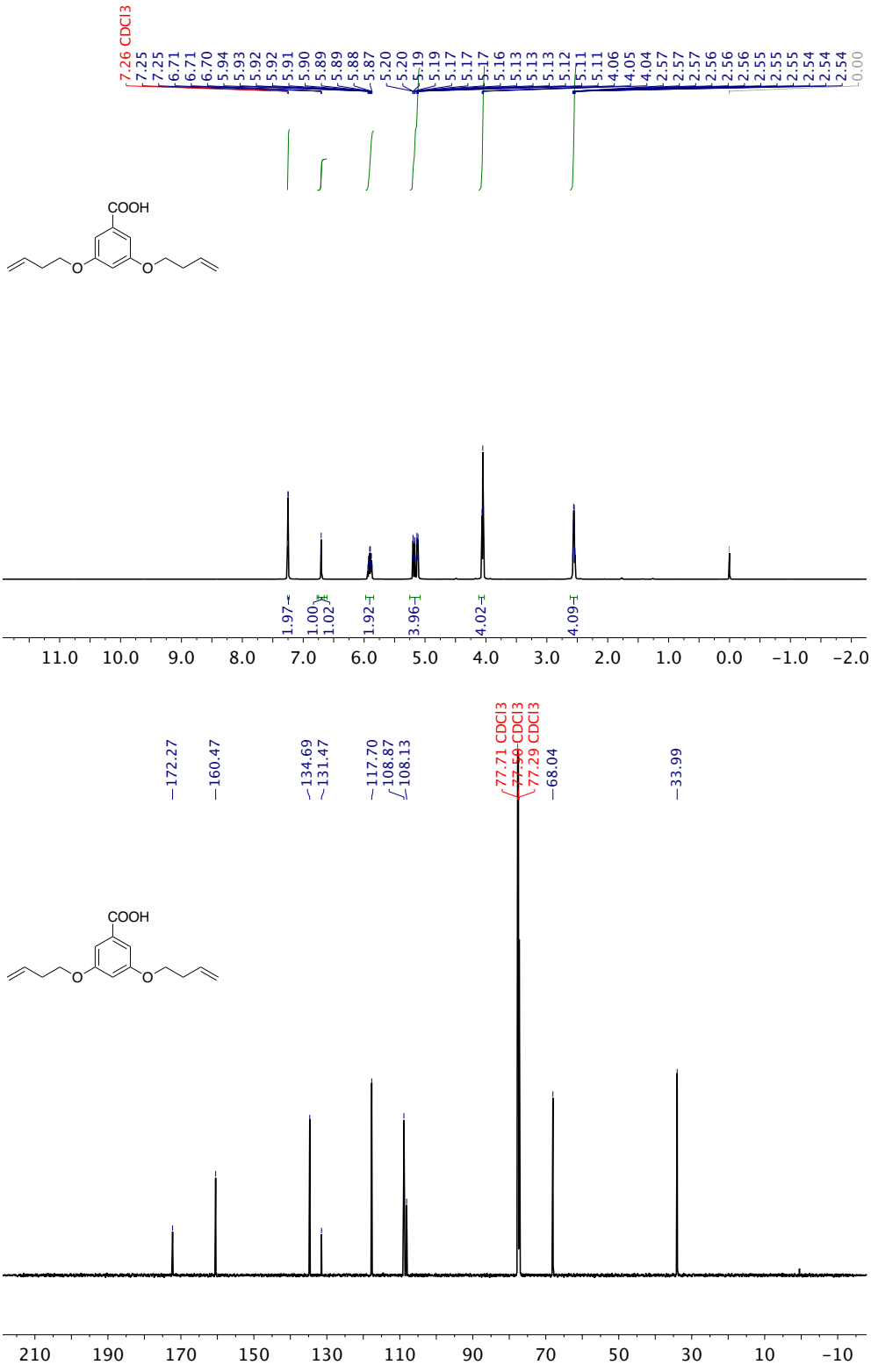
4. Procedure for metathesis: To a solution of precursor isoG complex (0.08 mmol) in distilled, degassed $CHCl_3$ (10 mL) was added Hoveyda-Grubbs-II catalyst (2.5 mg, 0.05 mmol, 5 mol% per alkene). The resulting solution was stirred at 55 ºC under an Ar atmosphere for 8 h. The resulting solution was then washed with 0.1 M HCl (10 mL), saturated $NaHCO_3$ (3 x 10 mL), and H_2O (3 x 10 mL). After removal of the solvent, the black solid was purified by flash chromatography (5 % MeOH in CH_2Cl_2) to give metathesis product as an off-white solid.

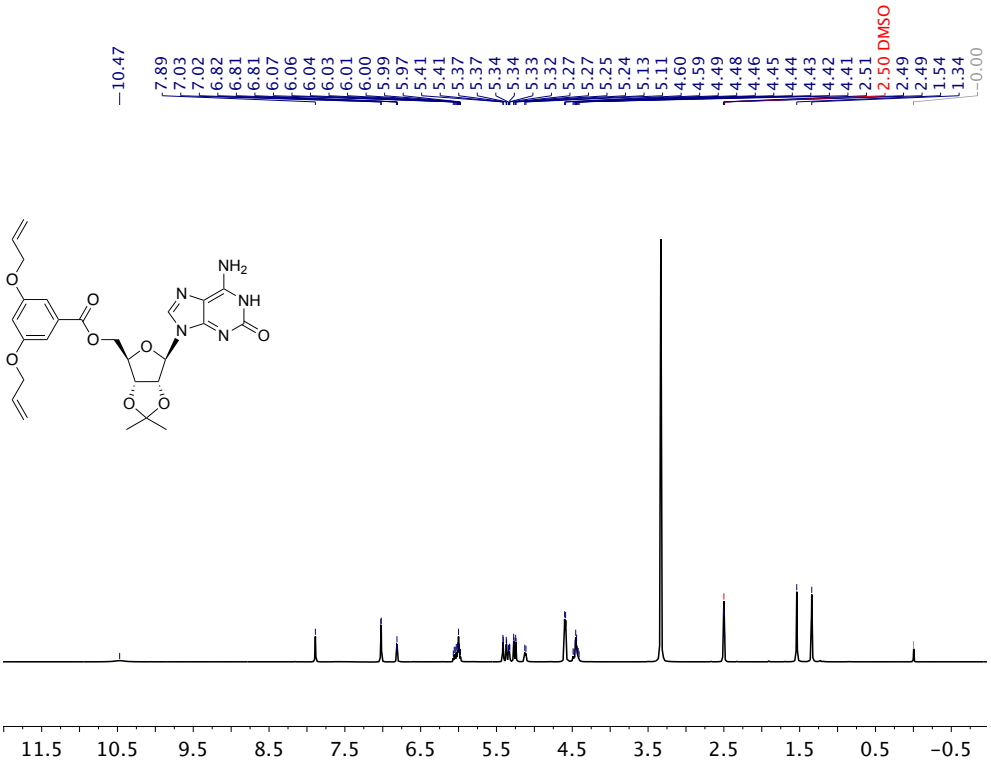
5. Procedure for recycle experiment

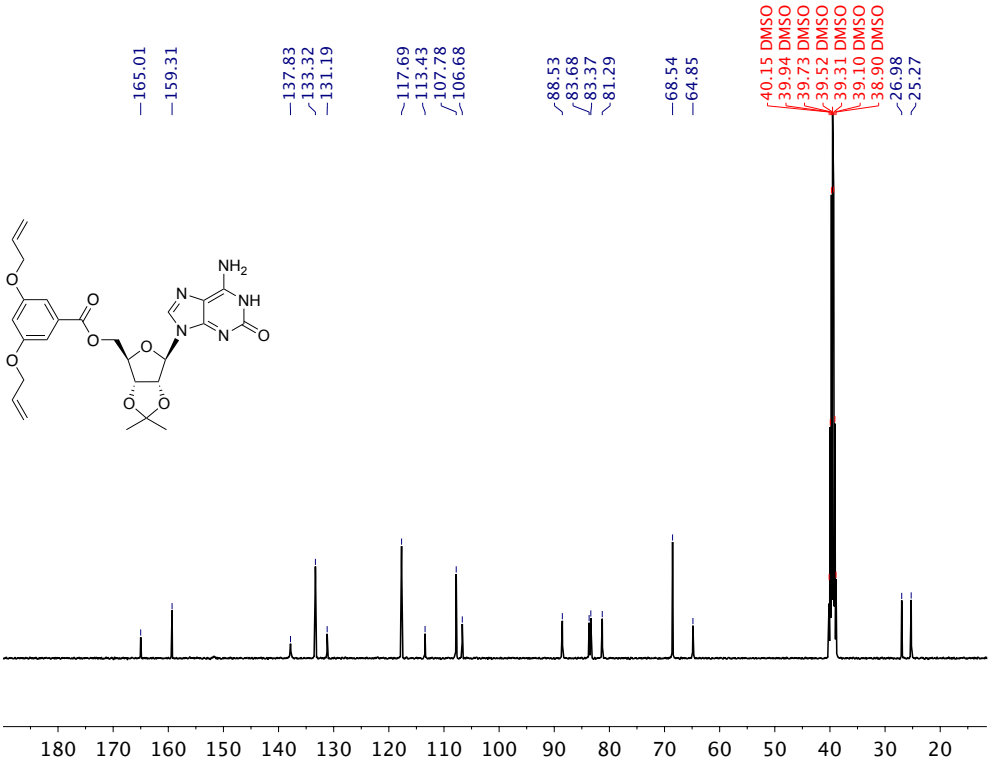
Each cycle extraction experiments were performed under competitive conditions. In an aqueous phase, the molar ratio of competing MCl_n (M = Na^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}) to CsCl salt (2.5×10^{-5} M) 100: 1 in aqueous phase. Cyclic pentamer **5a** concentration was 10^{-4} M in the organic phase $CHCl_3$. After stirring for 1 h, the organic layer gave the desired complexes and characterized by MALDI-TOF. The resulting cyclic isoG **5a** Cs^+ complex solution was concentrated, and MeOH

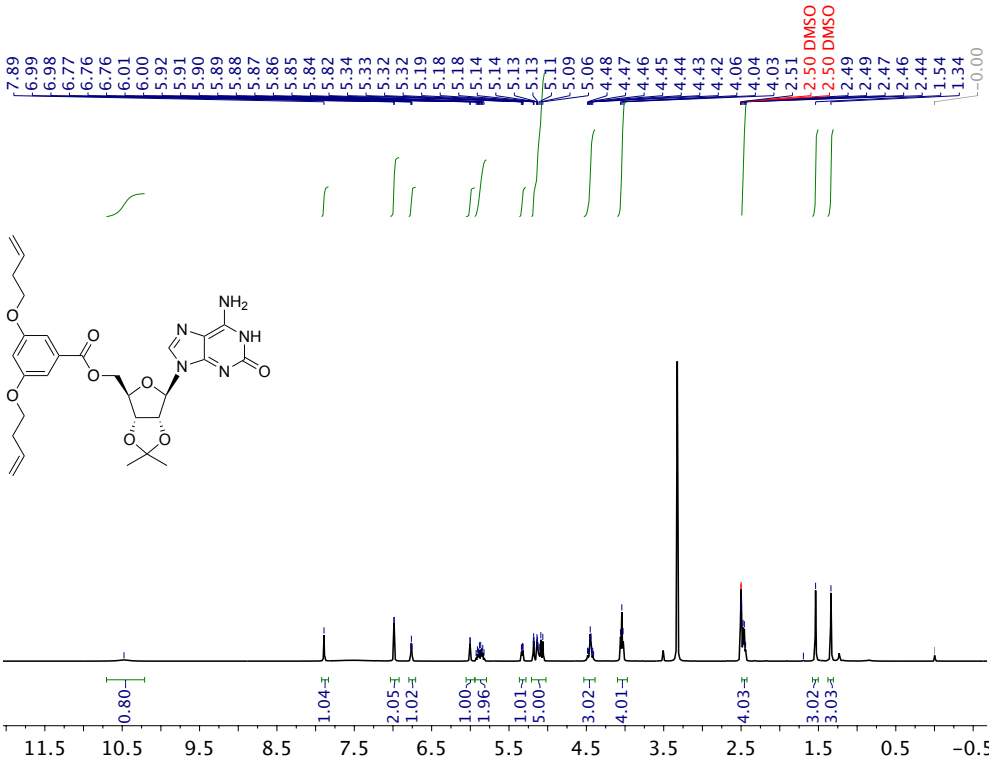
was added. After filtration, solid **5a** was collected, which was reapplied for Cs^+ extraction by dissolving it in $CHCl_3$ and reacting it with Cs^+ containing aqueous solution under competitive conditions. m/z = 3120.937, 3120.866, 3120.834, 3120.854, 3120.767, 3120.800 and 3120.868 were observed after each cycle separately (**Figure S14).** The properties were characterized by MALDI-TOF, showing the effective extraction of Cs^+ after 7 cycles.

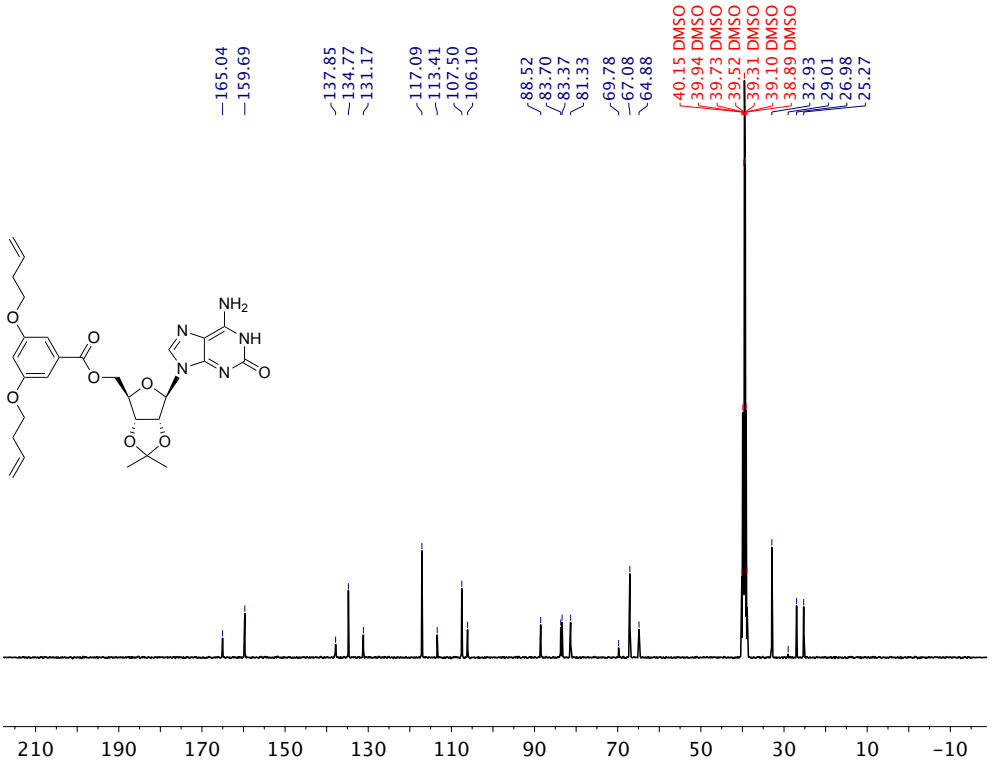

7.26
7.18
7.17
6.66
6.66
6.65
6.65
6.64
5.92
5.90
5.89
5.87
5.19
5.19
5.18
5.18
5.16
5.15
5.15
5.12
5.12
5.12
5.12
5.11
5.10
5.10
5.10
4.04
4.03
4.02
3.89
2.56
2.56
2.55
2.55
2.55
2.54
2.54
2.53
2.53
2.53
2.52
2.52
COOMe
O
O
2.01
1.00
2.03
4.06
4.10
3.02
4.07
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
167.37
160.40
134.74
132.39
117.64
108.34
107.23
67.99
52.69
34.01
COOMe
O
O
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

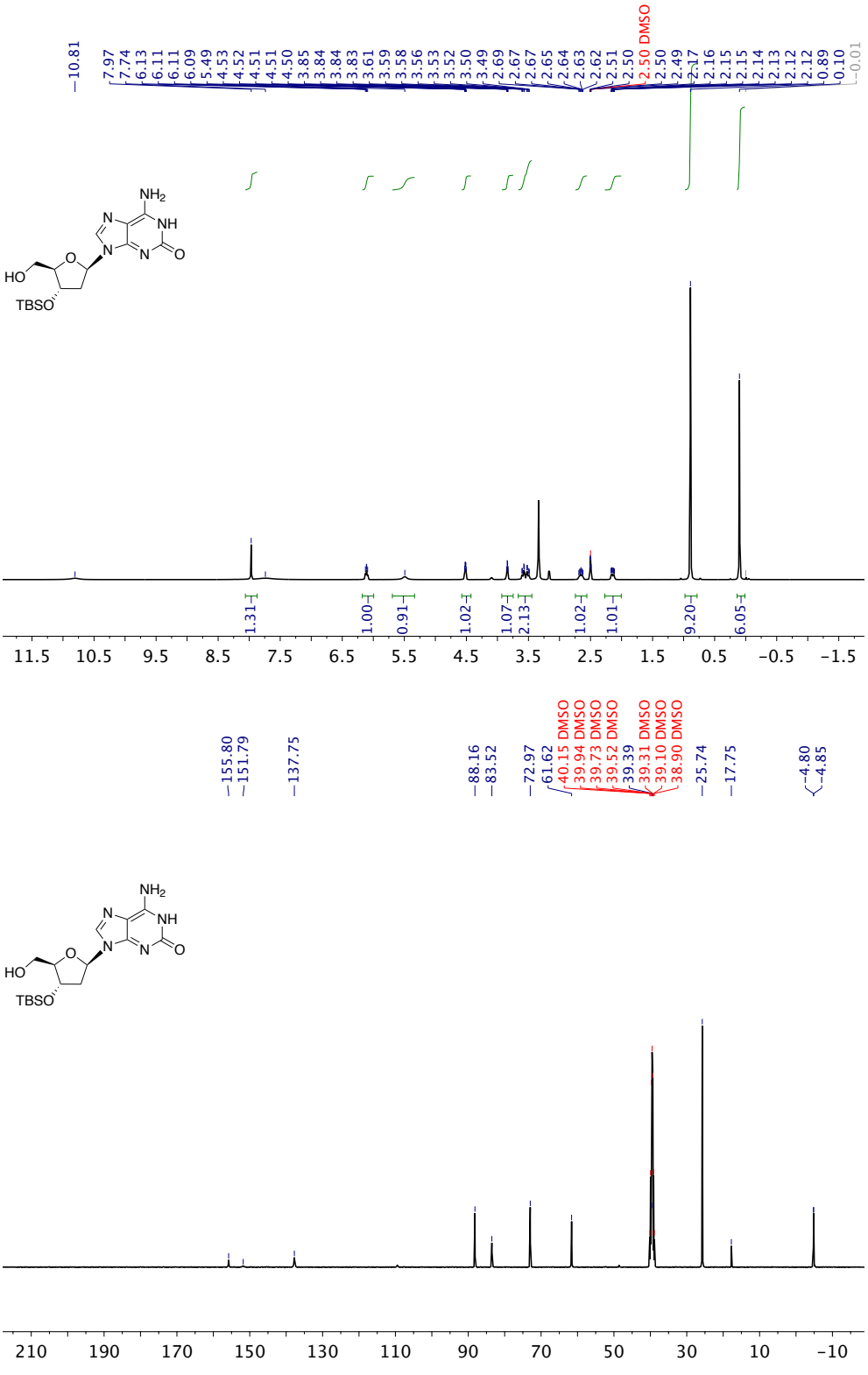

7.26 CDCl3
7.25
7.25
6.71
6.71
6.70
5.94
5.93
5.92
5.92
5.91
5.90
5.89
5.89
5.88
5.87
5.20
5.20
5.19
5.19
5.17
5.17
5.17
5.16
5.13
5.13
5.13
5.12
5.11
5.11
4.06
4.05
4.04
2.57
2.57
2.57
2.56
2.56
2.56
2.55
2.55
2.55
2.54
2.54
2.54
0.00
COOH
O
O
1.97
1.00
1.02
1.92
3.96
4.02
4.09
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
172.27
160.47
134.69
131.47
117.70
108.87
108.13
77.71 CDCl3
77.50 CDCl3
77.29 CDCl3
68.04
33.99
COOH
O
O
210
190
170
150
130
110
90
70
50
30
10
-10

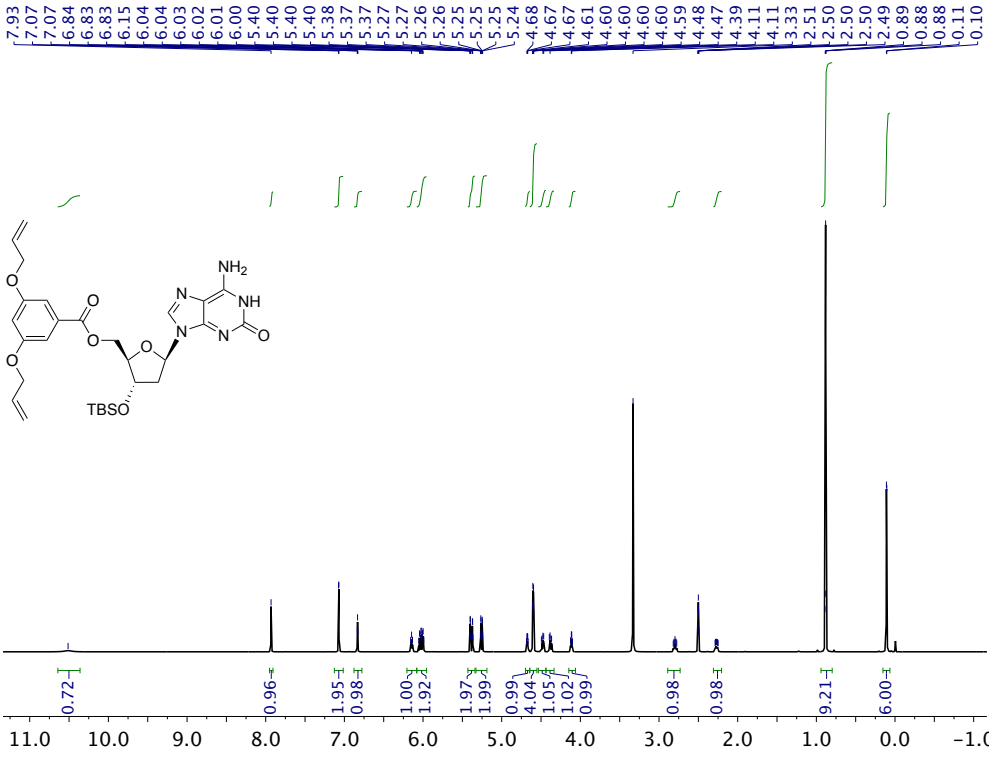

10.47
7.89
7.03
7.02
6.82
6.81
6.81
6.07
6.06
6.04
6.03
6.01
6.00
5.99
5.97
5.41
5.41
5.37
5.37
5.34
5.34
5.33
5.32
5.27
5.27
5.25
5.24
5.13
5.11
4.60
4.59
4.49
4.48
4.46
4.45
4.44
4.43
4.42
4.41
2.51
2.50 DMSO
2.49
2.49
1.54
1.34
0.00
NH2
NH
O
N
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

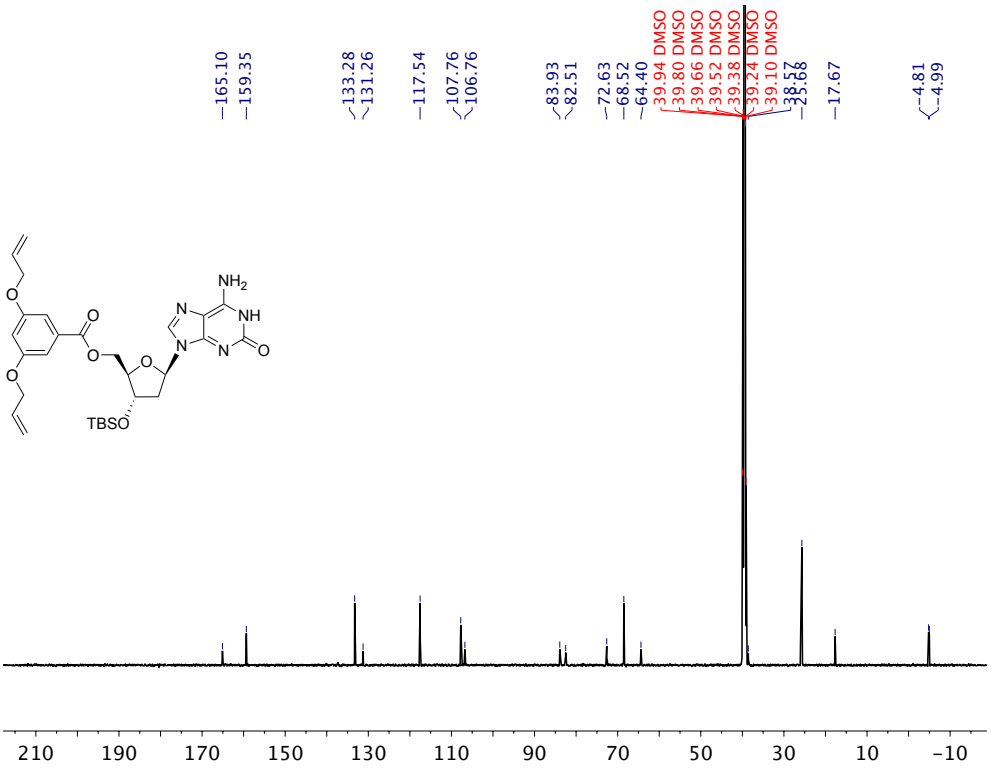

165.01
159.31
137.83
133.32
131.19
117.69
113.43
107.78
106.68
88.53
83.68
83.37
81.29
68.54
64.85
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.90 DMSO
26.98
25.27
NH2
NH
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

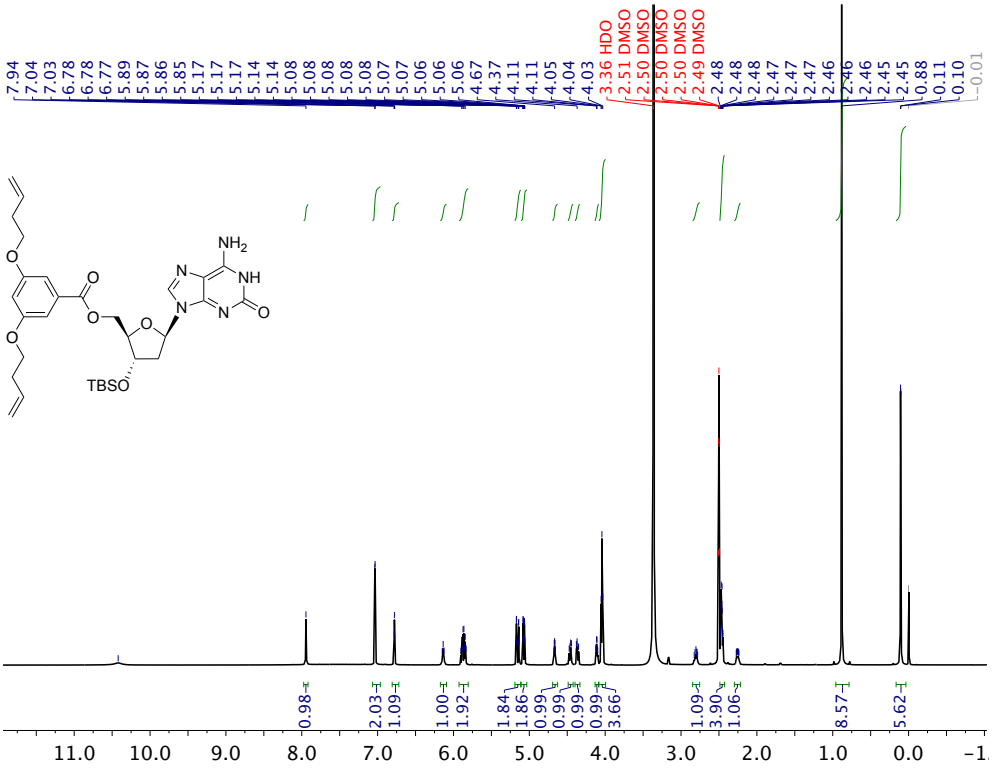

7.89
6.99
6.98
6.77
6.76
6.76
6.01
6.00
5.92
5.91
5.90
5.89
5.88
5.87
5.86
5.85
5.84
5.82
5.34
5.33
5.32
5.32
5.19
5.18
5.18
5.14
5.14
5.13
5.13
5.11
5.09
5.06
4.48
4.47
4.46
4.45
4.44
4.43
4.42
4.06
4.04
4.03
2.51
2.50 DMSO
2.50 DMSO
2.49
2.49
2.47
2.46
2.44
1.54
1.34
0.00
NH2
NH
0.80
1.04
2.05
1.02
1.00
1.96
1.01
5.00
3.02
4.01
4.03
3.02
3.03
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

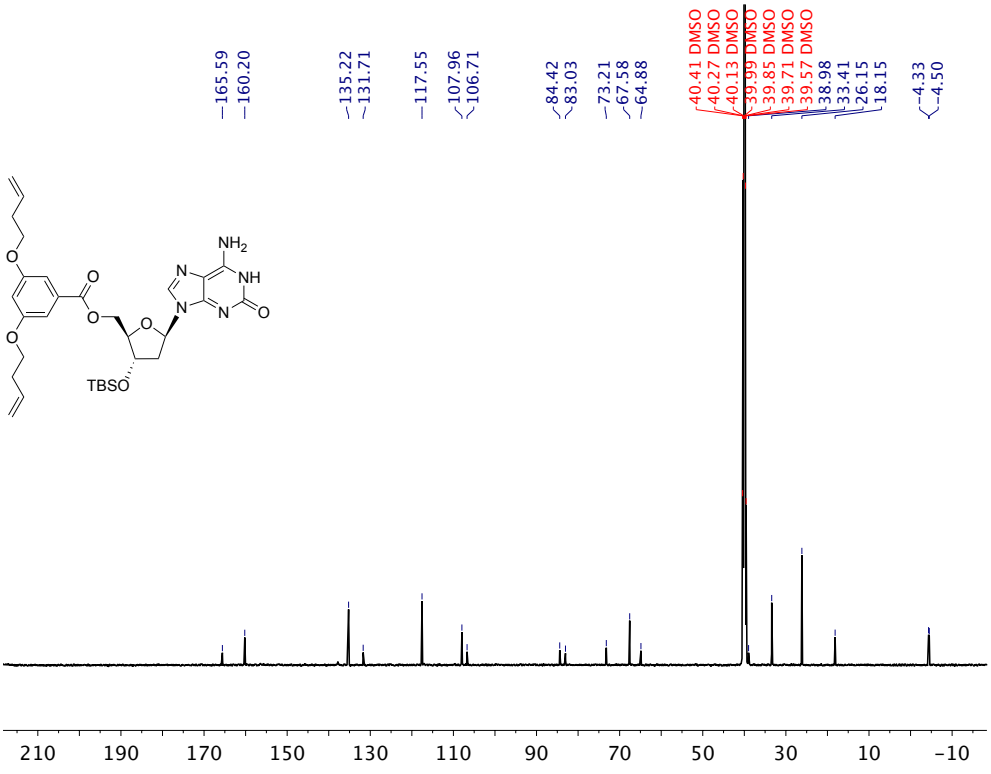

165.04
159.69
137.85
134.77
131.17
117.09
113.41
107.50
106.10
88.52
83.70
83.37
81.33
69.78
67.08
64.88
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
32.93
29.01
26.98
25.27
NH2
NH
210
190
170
150
130
110
90
70
50
30
10
-10

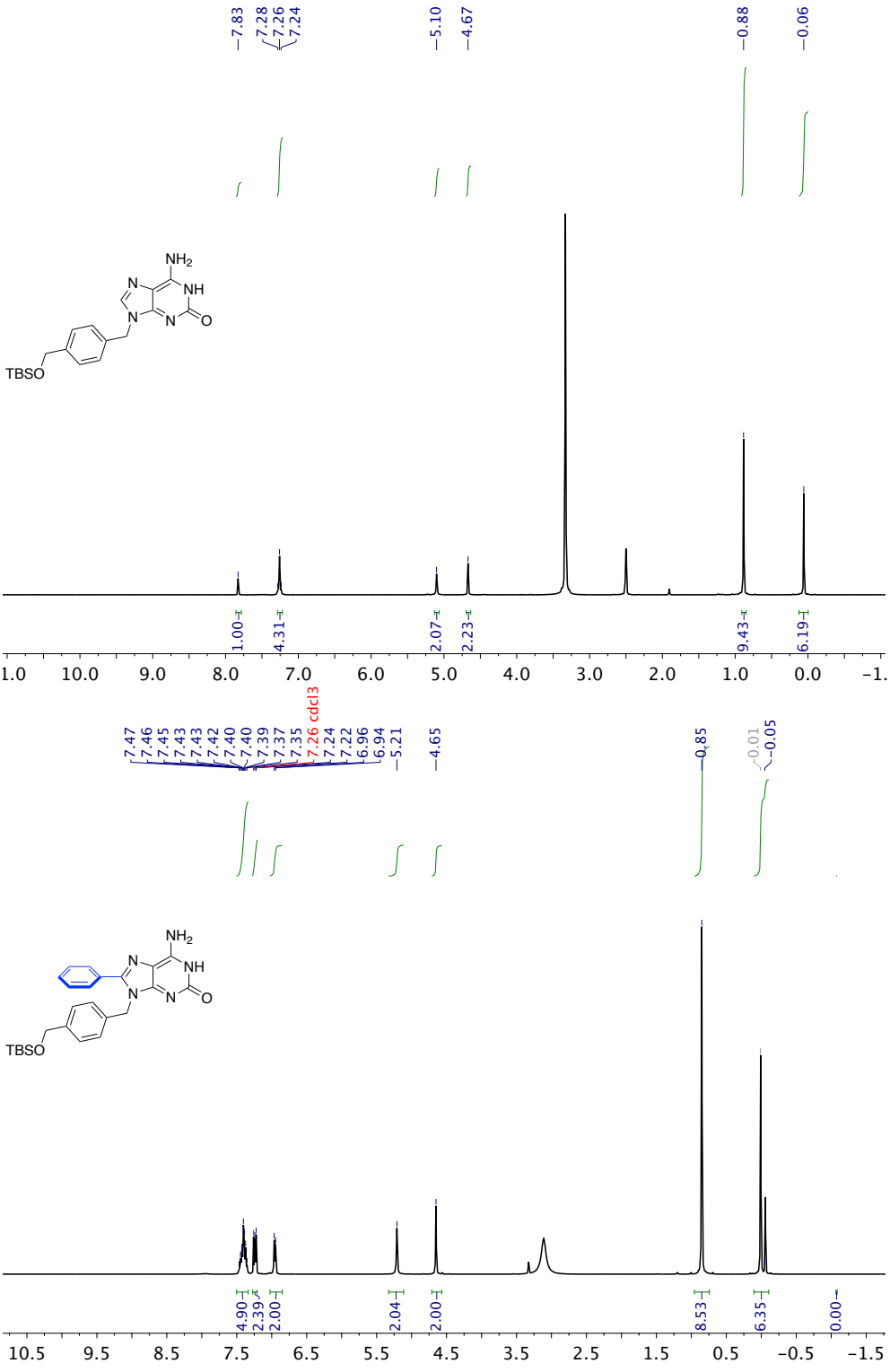

10.81
7.97
7.74
6.13
6.11
6.11
6.09
5.49
4.53
4.52
4.51
4.51
4.50
3.85
3.84
3.84
3.83
3.61
3.59
3.58
3.56
3.53
3.52
3.50
3.49
2.69
2.67
2.67
2.65
2.64
2.63
2.62
2.51
2.50
2.50 DMSO
2.50
2.49
2.17
2.16
2.15
2.15
2.14
2.13
2.12
2.12
0.89
0.10
0.01
NH2
NH
N
N
N
O
HO
O
TBSO
1.31
1.00
0.91
1.02
1.07
2.13
1.02
1.01
9.20
6.05
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
155.80
151.79
137.75
88.16
83.52
72.97
61.62
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.39
39.31 DMSO
39.10 DMSO
38.90 DMSO
25.74
17.75
4.80
4.85
NH2
NH
N
N
N
O
HO
O
TBSO
210
190
170
150
130
110
90
70
50
30
10
-10

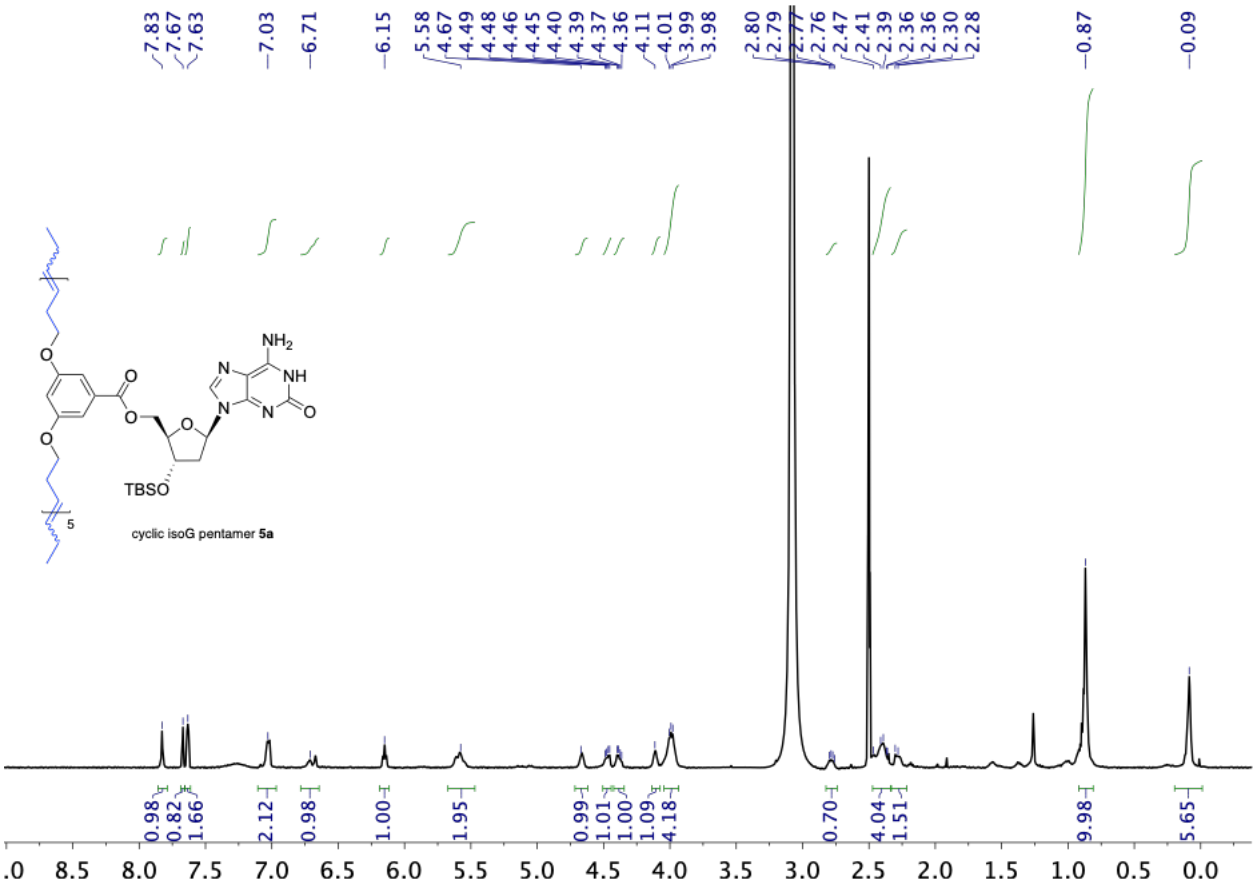

7.93
7.07
7.07
6.84
6.83
6.15
6.04
6.04
6.03
6.02
6.01
6.00
5.40
5.40
5.40
5.40
5.38
5.37
5.37
5.27
5.27
5.26
5.26
5.25
5.25
5.24
4.68
4.67
4.67
4.61
4.60
4.60
4.60
4.60
4.59
4.48
4.47
4.39
4.11
4.11
3.33
2.51
2.50
2.50
2.50
2.49
0.89
0.88
0.88
0.11
0.10
NH2
NH
O
N
TBSO
0.72
0.96
1.95
0.98
1.00
1.92
1.97
1.99
0.99
4.04
1.05
1.02
0.99
0.98
0.98
9.21
6.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


165.10
159.35
133.28
131.26
117.54
107.76
106.76
83.93
82.51
72.63
68.52
64.40
39.94 DMSO
39.80 DMSO
39.66 DMSO
39.52 DMSO
39.38 DMSO
39.24 DMSO
39.10 DMSO
38.57
25.68
17.67
4.81
-4.99
NH2
NH
O
N
TBSO
210
190
170
150
130
110
90
70
50
30
10
-10


7.94
7.04
7.03
6.78
6.78
6.77
5.89
5.87
5.86
5.85
5.17
5.17
5.17
5.14
5.14
5.08
5.08
5.08
5.08
5.08
5.07
5.07
5.06
5.06
5.06
4.67
4.37
4.11
4.11
4.05
4.04
4.03
3.36 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.48
2.48
2.48
2.47
2.47
2.47
2.46
2.46
2.46
2.45
2.45
0.88
0.11
0.10
-0.01
NH2
NH
N
N
O
O
O
O
O
O
O
TBSO
0.98
2.03
1.09
1.00
1.92
1.84
1.86
0.99
0.99
0.99
3.66
1.09
3.90
1.06
8.57
5.62
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


165.59
160.20
135.22
131.71
117.55
107.96
106.71
84.42
83.03
73.21
67.58
64.88
40.41 DMSO
40.27 DMSO
40.13 DMSO
39.99 DMSO
39.85 DMSO
39.71 DMSO
39.57 DMSO
38.98
33.41
26.15
18.15
-4.33
-4.50
NH2
NH
N
N
O
O
O
O
O
O
O
TBSO
210
190
170
150
130
110
90
70
50
30
10
-10


7.83
7.28
7.26
7.24
5.10
4.67
0.88
0.06
NH2
NH
N
N
N
O
TBSO
1.00
4.31
2.07
2.23
9.43
6.19
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.47
7.46
7.45
7.43
7.43
7.42
7.40
7.40
7.39
7.37
7.35
7.26 cdcl3
7.24
7.22
6.96
6.94
5.21
4.65
0.85
0.01
0.05
4.90
2.39
2.00
2.04
2.00
8.53
6.35
0.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5


7.83
7.67
7.63
7.03
6.71
6.15
5.58
4.67
4.49
4.48
4.46
4.45
4.40
4.39
4.37
4.36
4.11
4.01
3.99
3.98
2.80
2.79
2.77
2.76
2.47
2.41
2.39
2.36
2.36
2.30
2.28
0.87
0.09
NH2
NH
N
O
TBSO
5
cyclic isoG pentamer 5a
0.98
0.82
1.66
2.12
0.98
1.00
1.95
0.99
1.01
1.00
1.09
4.18
0.70
4.04
1.51
9.98
5.65
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

IV. Single-Crystal X-Ray Diffraction

X-ray diffraction data were measured on Bruker D8 Venture PHOTON II CMOS diffractometer equipped with a Cu Kα INCOATEC ImuS micro-focus source (λ = 1.54178 Å). Indexing was performed using APEX4 [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space group was determined using XPREP implemented in APEX3 [1]. Structure was solved using SHELXT [4] and refined using SHELXL-2019/1 [5] (full-matrix least-squares on F2) through OLEX2 interface program [6]. Ellipsoid plot was made with Platon [7].

Data and refinement conditions of **1d** are shown in **Table 1**.

4b: Disordered parts were refined with restraints. There are four symmetrically independent molecules in asymmetric unit. Data and refinement conditions are shown in **Table 2**.

[1] Bruker (2022). APEX4. Bruker AXS LLC, Madison, Wisconsin, USA.
[2] Bruker SAINT. Bruker AXS LLC, Madison, Wisconsin, USA.
[3] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. (2015).
"Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination" J. Appl. Cryst. 48, 3-10.
[4] Sheldrick, G. M. (2015). "SHELXT - Integrated space-group and crystal-structure determination", Acta Cryst. A71, 3-8.
[5] Sheldrick, G. M. (2015) "Crystal structure refinement with SHELXL",
Acta Cryst., C71, 3-8
[6] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341
[7] A.L.Spek, The Program PLATON is designed as a Multipurpose Crystallographic Tool.
1980-2021 A.L.Spek, Utrecht University, Utrecht, The Netherlands. Acta Cryst. 2020, E76, 1-11

Table 1 Crystal data and structure refinement for 1d.	
Identification code	**1d**
Empirical formula	$C_{20}H_{23}N_5O_4$
Moiety formula	$C_{19}H_{17}N_5O_2$, CH_3OH, H_2O
Formula weight	397.43
Temperature/K	134.68
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.4448(3)
b/Å	8.3202(2)
c/Å	20.9237(6)
α/°	90
β/°	104.7380(10)
γ/°	90
Volume/Å^3	1926.87(9)
Z	4
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	0.808
F(000)	840.0
Crystal size/mm^3	0.28 × 0.05 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.07 to 159.964
Index ranges	$-12 \le h \le 13$, $-10 \le k \le 10$, $-25 \le l \le 26$
Reflections collected	27244
Independent reflections	4101 [R_{int} = 0.0563, R_{sigma} = 0.0325]
Data/restraints/parameters	4101/2/294
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0491, wR_2 = 0.1279
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.1358
Largest diff. peak/hole / e Å^{-3}	0.32/-0.28

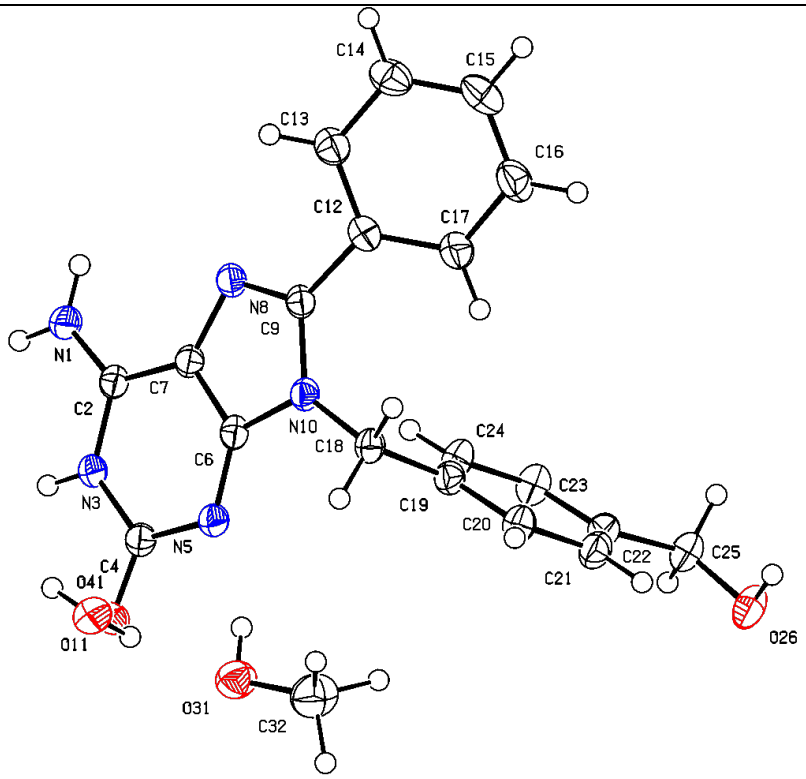


Figure S15. Ellipsoid plot of **1d**. Anisotropic displacement parameters were drawn at 50% probability level.

Table 2 Crystal data and structure refinement for 4b.	
Identification code	**4b**
Empirical formula	$C_{32.05}H_{47.58}N_5O_{8.68}Si$
Moiety formula	$C_{31}H_{43}N_5O_7$ Si, 1.052(CH_3OH), 0.185(H_2O), 0.293$(O1.5)_{solv}$
Formula weight	669.87
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2
a/Å	44.2430(10)
b/Å	19.9018(6)
c/Å	17.7791(6)
α/°	90
β/°	110.985(2)
γ/°	90
Volume/$Å^3$	14616.4(8)
Z	16
$\rho_{calc}g/cm^3$	1.218
μ/mm^{-1}	1.027
F(000)	5733.0
Crystal size/mm^3	0.16 × 0.13 × 0.04
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.928 to 159.604
Index ranges	$-53 \leq h \leq 55$, $-25 \leq k \leq 25$, $-22 \leq l \leq 21$
Reflections collected	102233
Independent reflections	29057 [R_{int} = 0.0671, R_{sigma} = 0.0559]
Data/restraints/parameters	29057/462/1838
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0569, wR_2 = 0.1498
Final R indexes [all data]	R_1 = 0.0799, wR_2 = 0.1661
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.32
Flack parameter	0.030(12)

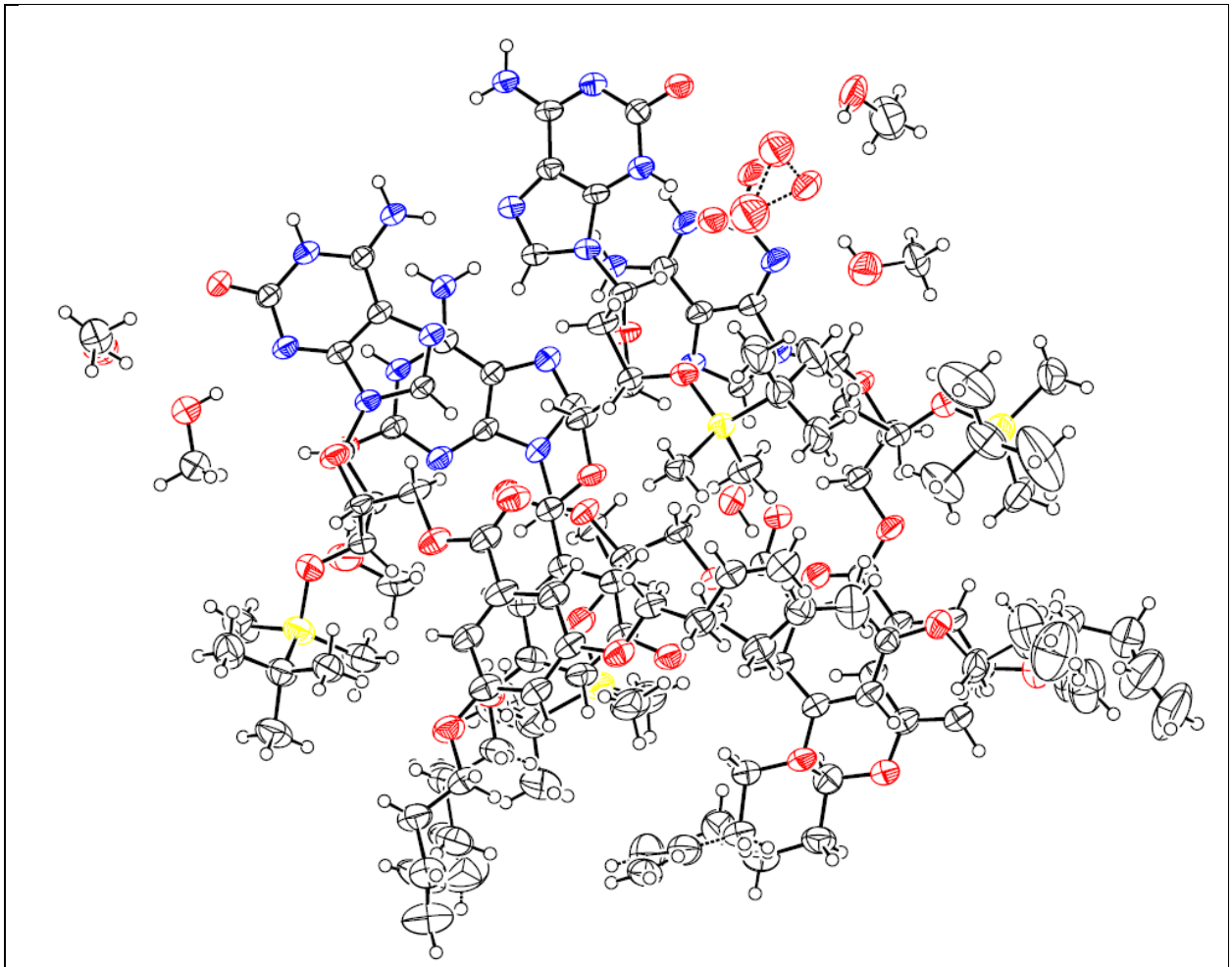


Figure S16. Ellipsoid plot of **4b**. Anisotropic displacement parameters were drawn at 50% probability level.

V. References

1. W. Lu, S. Sengupta, J. L. Petersen, N. G. Akhmedov and X. Shi, *J. Org. Chem.*, **2007**, 72, 5012-5015.
2. M. Liu, Y. He, C. Shan, L. Wojtas, I. Ghiviriga, O. Fathalla, Y. Yan, X. Li and X. Shi, *Chem. Sci.*, **2021**, 12, 7569-7574.