Supporting information

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General methods

All chemicals were purchased from Sigma-Aldrich unless otherwise noted. The cap analogue and the *Vaccinia* capping system were purchased from NEB.

Electroporation was performed on an Eppendorf Eporator® (Eppendorf, Hamburg). Sonication was carried out using a Sonoplus GM3100 (Bandelin, Berlin). Protein purification was performed by affinity chromatography (Ni-NTA, GE Healthcare) on an ÄKTA Prime purifier system (GE Healthcare). For RNase-free preparation of proteins, additional gel filtration was performed using a Superdex 200 Increase 10/300 GL (GE Healthcare).

HPLC analysis and purification of ^{7m}G-capped RNAs were performed on a Dionex Ultimate 3000 titanium system equipped with anion-exchange DNAPac PA200 columns (4×250 mm or 9×250 mm) and a diode array detector (DAD-3000) (190-800 nm). The elution was performed with a mixture of 5 % CH_3CN in 25 mM Tris-HCl buffer, pH 8 (buffer A) and 5 % CH_3CN containing 400 mM $NaClO_4$ in 25 mM Tris-HCl buffer, pH 8 (buffer B). Flow rates were 1 mL/min and 2.5 mL/min for analysis and semi-preparative purposes, respectively.

Monitoring of enzymatic reactions on ^{7m}G-capped RNAs were performed on a Thermoscientific Ultimate 3000 system equipped with a diode array detector (DAD-3000) (190-800 nm) and with a Nucleodur reverse-phase ec column (Macherey Nagel EC 75/4.5, 100-3 C_{18}). Elution was performed at a 1 mL/min flow rate with a 20 min linear gradient of 0-24 % acetonitrile in 50 mM triethylammonium acetate buffer, pH 7.

HPLC analysis of digested nucleotides was performed on an Agilent 1260 Infinity HPLC equipped with a diode array detector (DAD) (190-640 nm).

The $m_2^{7,3\text{-}O}GP_3G$ (ARCA) cap analog was purchased from *Jena Bioscience*.

MALDI-TOF mass spectra were recorded on a Voyager-DE spectrometer equipped with a N_2 laser (337 nm) (Perseptive Biosystems, USA) or a Axima assurance spectrometer equipped with a N_2 laser (337 nm) (Shimadzu Biotech) using 2,4,6-trihydroxyacetophenone as a saturated solution in a mixture of acetonitrile/0.1 M ammonium citrate solution (1:1, v/v) for the matrix. Analytical samples were mixed with the matrix in a 1:5 (v/v) ratio, crystallized on a stainless steel plate and analyzed.

UV quantitation of RNAs was performed on a Varian Cary 300 Bio UV/Visible spectrometer by measuring absorbance at 260 nm.

Human (guanine N^7)- Methyltransferase (N^7-hMTase) was a kind gift from Etienne Decroly (AFMB, University of Aix-Marseille, Luminy, France).[1]

Experimental procedures

Synthesis of ^{7m}G-capped RNAs

RNA oligonucleotides were synthesized using an ABI 394 DNA/RNA synthesizer (Applied Biosystems) on a 1 µmol scale in Twist oligonucleotide synthesis columns (Glen research) filled with commercially available (Link Technologies) long chain alkylamine controlled-pore glass (LCAA-CPG) solid support with a pore size of 1000 Å derivatized through the succinyl linker with 5′-*O*-dimethoxytrityl-2′-*O*-acetyl-[uridine, N^6-phenoxyacetyl adenosine or N^2-dimethylformamide guanosine]. RNA sequences were assembled with commercially available 2′-*O*-pivaloyloxymethyl (PivOM) phosphoramidites (5′-*O*-DMTr-2′-*O*-PivOM-[U, C^{Ac}, A^{Pac} or G^{Pac}]-3′-*O*-(*O*-cyanoethyl-*N,N*-diisopropyl-phosphoramidite) from Chemgenes.[2] The 5′-terminal adenosine can be unmodified A, or methylated at 2′-OH (A_m), or at *N*-6 position (m^6A) or at both positions (m^6A_m). The 5′-*O*-DMTr-2′-*O*-Me-A^{Pac}-3′-*O*-(*O*-cyanoethyl-*N,N*-diisopropylphosphoramidite) (Chemgenes) was used to introduce A_m at the 5′-end of RNA. For the synthesis of m^6A-RNAs or m^6A_m-RNAs, the preparation of m^6A and m^6A_m phosphoramidite synthons was performed by a selective one-step methylation of the commercially available 2′-*O*-PivOM-Pac-A-CE phosphoramidite or 2′-*O*-Me-Pac-A-CE phosphoramidite, respectively.[3] All RNAs were synthesized using standard protocols for solid-phase RNA synthesis with the PivOM methodology.[4] Phosphoramidites were vacuum dried prior to their dissolution in extra dry acetonitrile (Glen Research) at 0.1 M. For the coupling reaction, the activator was 5-benzylmercaptotetrazole (BMT, Chemgenes) used at 0.3 M concentration. Dichloroacetic acid (3 % in CH_2Cl_2) (Glen research) was the detritylation reagent. The capping step was performed with a mixture of 5 % phenoxyacetic anhydride (Pac_2O) in THF and 10 % *N*-methylimidazole in THF (Link Technologies). The oxidizing solution was 0.1 M iodine in THF/pyridine/H_2O (78:20:2; v/v/v) (Link Technologies). After RNA assembly completion, the column was removed from the synthesizer and dried under a stream of argon.

A solution (2 mL) of 0.1 M diphenyl phosphite in dry pyridine was manually passed with a glass syringe containing activated 3 Å molecular sieves (5 beads), through a column with RNA still attached to the solid support. Using another syringe, the solution was pushed back and forth for 5 minutes and left to stand for 30 minutes at room temperature. The support was washed with CH_3CN (4×2 mL) then a 0.1 M solution of TEAB, pH 7.5 (2 mL) was pushed back and forth for 5 minutes and left to react for 120 minutes at 30 °C. The solution was removed from the column, the support was washed with dry CH_3CN (3×3 mL) and then dried under a stream of argon.

The column containing the 5′*H*-phosphonate oligonucleotide was flushed with argon and activated 3 Å molecular sieves (5 beads) were added to the glass syringes. An oxidation solution containing imidazole (150 mg, 2 mmol) in *N,O*-bis-trimethylsilylacetamide (0.4 mL, 1.64 mmol), CH_3CN (0.75 mL), CCl_4 (0.75 mL) and triethylamine (0.1 mL) was pushed back and forth through the synthesis column for 5 min, then left to react for 5 h at 30 °C. The solution

was removed from the column and the support was washed twice with anhydrous CH_3CN (2×2 mL), followed by a 1 min flush with argon.[5]
Guanosine-5′-diphosphate, bis(tri-*n*-butylammonium) salt, suitable for phosphorylation reactions was prepared from the commercially available guanosine-5′-diphosphate, disodium salt (Carbosynth). GDP disodium salt (0.5 g, 1.2 mmol) was dissolved in milliQ water (25 mL), the solution was passed through a glass column filled with 20 mL of wet DOWEX-50W X 8 resin, H^+ form, then was collected in a 250 mL round flask containing absolute ethanol (12 mL) and tri-*n*-butylamine (0.72 mL), stirred at 0 °C. The Dowex column was rinsed with water (80 mL) to reach pH 5 to 6. The solvents were evaporated from the collected solution and the residue was coevaporated four times with absolute ethanol then was lyophilized from water to afford a white hygroscopic powder (0.938 g, 1.15 mmol, 96 %). The desired GDP, tri-*n*-butylammonium salt was characterized by two doublets at -10.55 and -11.20 ppm (^{31}P-NMR, 121 MHz, D_2O). It can be stored as a solid for several weeks at -20 °C.
In a dry 4 mL screw-capped glass vial, bis (tri-*n*-butylammonium) guanosine diphosphate (103 mg, 0.14 mmol), zinc chloride (28 mg, 0.2 mmol, Alfa Aesar) and activated 4 Å molecular sieves (5 beads) were mixed in anhydrous DMF (0.5 mL). The Twist column containing the 5′-phosphoroimidazolidate RNA was flushed with argon and activated 4Å molecular sieves (5 beads) were added to the glass syringes. The GDP solution (0.28 M) was applied to the column and left to react for 18 h at 30 °C. The solution was removed and the support was washed with water (2×2 mL), a 0.1 M aqueous solution of EDTA (pH 7, 2×2 mL), and dry CH_3CN (4×2 mL). The column was dried by blowing argon through it during 1 min.[1]
The solid support was treated with a 30 % aqueous ammonia solution for 3 h at 30 °C. The deprotection solution was evaporated in the presence of isopropylamine (13 % of total volume) under reduced pressure. The residue was dissolved in 1.5 mL of water and transferred to a 2 mL Eppendorf-vial and lyophilized.
The crude G-capped RNAs were analyzed and purified by anion-exchange HPLC using a 0-30 % or 0-40 % linear gradient of buffer B in buffer A and they were characterized by MALDI-TOF spectrometry. The pure fractions of the G-capped RNAs were pooled in 100 mL round-bottomed flasks and were concentrated to 0.5 mL under reduced pressure with a bath at maximum 30 °C. The mixtures were dissolved in 3 mL of 50 mM TEAAc buffer and loaded on a Sep Pak C_{18} cartridge. Elution was performed with 10 mL of 50 mM TEAAc, pH 7 then with 10 mL of 50 % CH_3CN in 12.5 mM TEAAc, pH 7. The second fraction containing the desired RNA was collected and lyophilized from water.
Methylation of purified G-capped RNAs (~70 nmol) to give ^{7m}G-capped RNAs were carried out using 0.25 µM *N*7-hMTase and 0.4 mM *S*-adenosyl-L-methionine (New England Biolabs) in 40 mM Tris-HCl pH 8 with 5 mM dithiothreitol in a 1725 µL reaction volume (G-capped RNAs at a final concentration of 40 µM) at 30 °C. *N*7-methylation was monitored using IEX-HPLC analysis of an aliquot from the reaction mixture and passed through ZipTip C_{18} prior analysis to remove the enzyme.[1] After 5 h incubation, the reaction was complete. The mixture was subsequently redissolved in 2 mL of 50 mM TEAAc, pH 7 and the solution was loaded onto a Sep Pak C_{18} cartridge (Waters) following the same desalting procedure as described above. Remaining AdoMet and the *S*-adenosyl-L-homocysteine (AdoHcy) by-product were then removed as follows: the residue was dissolved with 1 mL of 12.5 mM TEAAc pH 7 and loaded onto a Sephadex G-25 gel filtration NAP 10 cartridge (GE Healthcare Life Sciences). ^{7m}G-capped RNAs are eluted in the second 1 mL-fraction using 12.5 mM TEAAc and they are lyophilized three times from water.

Enzymatic N^2 mono-and di-methylation of ^{7m}G-capped RNAs

The ^{7m}G-capped RNAs (150 µM) were incubated with purified GlaTgS or HTgS (2.5 µM or 5 µM depending on the assay) for N^2 mono or di-methylation respectively, and SAM (0.5 mM or 1 mM) in reaction buffer (50 mM Tris-HCl, 5 mM DTT, 50 mM NaCl, pH 8) at 37 °C. The enzymatic reactions were monitored at 260 nm by RP-HPLC analysis. A large excess of SAM (1 mM) is required to drive the reaction to completion after 8 h incubation time. MALDI-TOF mass analyses were performed for characterization of di- or tri-methylated G-capped RNAs.

Production and purification of CMTR1:

For recombinant production, *E. coli* BL(21)DE3 Gold cells were transformed with the plasmid pET28a_his_CMTR1_126-549. Overnight cultures were grown in 2×YT-medium supplemented with kanamycin (c_{final}= 25 µg/mL). After inoculation with 2.5 % (v/v) overnight culture, cells supplemented as described above were grown to an OD_{600}= 0.6, placed on ice for 30 min and induced with 0.5 mM IPTG and 2 %(*v*/*v*) EtOH. Cultures were shaken overnight at 12 °C, harvested by centrifugation and stored at −20 °C. For purification, thawed bacteria were resuspended in 10 mL lysis buffer (30 mM Tris-buffer, 500 mM NaCl, 1 mM DTT, 10 mM imidazole, 10 %(v/v) glycerol, pH 7.8), phenylmethylsulfonyl fluoride (300 µM) was added and cells were sonicated on ice. The His-tagged enzyme was purified via IMAC using a HisTrap™ FF 1 mL column in a linear gradient up to 500 mM imidazole. Fractions containing the enzyme were concentrated using Amicon® Ultra-15 centrifugal units (regenerated cellulose, MWCO 10,000) and purified via size exclusion chromatography on a Superdex™ 200 Inc column in dialysis buffer (30 mM Tris-buffer, 100 mM NaCl, 3 mM TCEP, 10 %(*v*/*v*) glycerol, pH 7.8). CMTR1 was aliquoted, frozen in liquid nitrogen and stored at −80 °C. The concentration was determined *via* BSA-standard. Chromatograms of the purification and SDS-PAGE analysis of the purified protein are shown in Figure S8. To assess the absence of nuclease in the concentrated protein, CMTR1 was incubated with a model RNA at 37 °C for 1 h and then analyzed on a 15 % TBE-gel for degradation.

Production and purification of hTgs1, GlaTgs2 and MTAN:

The enzymes hTgS1, GlaTgs2 and MTAN were produced and purified as previously described.[6]

CMTR1$_{126-549}$ methyltransferase assay

Typically, RNA was incubated with 20 mol% CMTR1$_{126-549}$, a 10-fold excess of AdoMet or a corresponding AdoMet analog, 4 µM MTAN in 1×reaction buffer (10×reaction buffer: 500 mM HEPES, 50 mM $MgCl_2$, 5 mM TCEP, pH 7 at 20 °C) in a total volume of 10 µL ddH_2O. Reactions were incubated at 37 °C for 90 min. For RNAs to short for EtOH precipitation (<20 nt), the reaction was stopped by heating to 95 °C for 2 min, followed by centrifugation at 21,000 ×g for 10 min. The supernatant was dialyzed against ddH_2O for 10 min on Merck-Millipore™ Membrane Filter (0.025 µm pore size). RNAs longer than 20 nt were precipitated from the reaction mixture by EtOH precipitation and redissolved in ddH_2O. For HPLC or LC-MS analysis, RNA was digested with 0.5 U SnakeVenom phosphodiesterase in 55 µM Tris-buffer with 55 mM NaCl and 7.5 mM $MgCl_2$, pH 8.9 at 20 °C) for 16 h at 37 °C. 1 U fast AP was added and incubated for 1 additional hour at 37 °C. Proteins were then precipitated by addition of 0.1 volumes of $HClO_4$ (1 M) followed by centrifugation at 21,000 ×g for 10 min at 4 °C. The supernatant was then analyzed by HPLC or LC-MS.

Enzymatic preparation of RNA substrates

<u>24-nt model RNA:</u>

RNA synthesis and purification: A 24 nt model RNA was prepared by T7 in vitro transcription from a dsDNA template:
DNA-Templat: 5′-GAAATTAATACGACTCACTATAGGAGCCAGCCTACGAGCCTGAGCC-3′
transcribed RNA: 5′-GGAGCCAGCCUACGAGCCUGAGCC-3′

Transcribed RNA was purified via dPAGE, corresponding bands were excised and eluted by crush-elution for 2 h in 0.3 M NaOAc buffer. RNA was then precipitated by EtOH precipitation and stored at -20 °C for further use. Concentration of RNA was determined via absorbance at 260 nm. To obtain cap0-RNA, RNA was capped using the *Vaccinia* Capping Enzyme (NEB) according to manufacturers' instructions. Success of the capping reaction was assessed via dPAGE on a 15 % TAE gel with 0.5 % copolymerized acryloylaminophenyl boronic acid.[7] Acryloylaminophenyl boronic acid was synthesized as described by Igloi et al.(4) Identity was confirmed by 1H-NMR and mass spectrometry.

<u>*Renilla* luciferase RNA:</u>

ARCA-capped rLUC-RNA: rLUC-RNA was produced from a dsDNA template *via in vitro* run-off transcription. The dsDNA template was generated via PCR from the corresponding pMRNA-RLuc plasmid. For IVT, 100 ng template DNA, 50 U T7 RNA polymerase (Thermo Scientific), 0.1 U pyrophosphatase (Thermo Scientific), 0.5 mM of each ATP, CTP, UTP, 0.1 mM GTP and 1 mM of the ARCA-cap analog were incubated in 1×T7 buffer (Thermo Scientific) in a total volume of 25 µL for 4 h at 37 °C. The template was digested by addition of 1 U DNase I for 60 min at 37 °C. RNAs were purified using the RNA Clean & ConcentratorTM-5 Kit (Zymo Research). Uncapped pppRNAs were digested using 20 U of 5′-polyphosphatase (Biozym) in 1×5′-polyphosphatse reaction buffer for 30 min at 37 °C. Then, 5′→3′ exoribonuclease XRN1 (1 U) and $MgCl_2$ (5 mM) were added to the reaction mixture and incubated for 30 min at 37 °C. RNA was purified using the RNA Clean & ConcentratorTM-5 Kit (Zymo Research). Concentration of RNA was determined via absorbance at 260 nm.

Luminescence measurements:

Renilla luciferase luminescence measurements were performed using the *Gaussia*-Juice Luciferase Assay Kit (pjk). Luciferase activity experiments were performed using 5, 10, 20 and 40 ng of the corresponding mRNAs. Samples were incubated with 1×translation mix, 0.05 mM L-methionine and 8.5 µL reticulocyte lysate at 30 °C for 90 min. Luciferase activity was determined by pipetting 2 µL of each reaction into a 96-well plate followed by injection of 50 µL of the substrate mixture using the Tecan Infinite M1000 PRO® (TECAN, Salzburg, Austria). Upon injection, the signal was integrated for 3000 ms.

HPLC and LC-MS analysis of nucleosides

Nucleosides were separated by reversed phase chromatography on a NUCLEODUR C_{18} Pyramid (125×4 mm) column (Macherey Nagel) in linear gradient from buffer A to buffer B. Buffer A: 20 mM HCO_2NH_4 (pH 3.5), buffer B: methanol LC-MS grade, flow rate: 1 mL/min. For LC-MS measurements, ultra-performance reversed-phase chromatography was performed on a NUCLEODUR C_{18} Pyramid (125×2 mm) column (MN) with mass spectrometric detection using maXis II ultra-high resolution QTOF (Bruker, Bremen) in positive electrospray ionization mode (identical buffers as for HPLC-analysis, flow rate: 0.6 mL/min).

Synthesis of AdoMet analogs

AdoMet analogs SeAoYn and AdoEnYn were prepared as previously described.[8,9]

Supplementary Figures

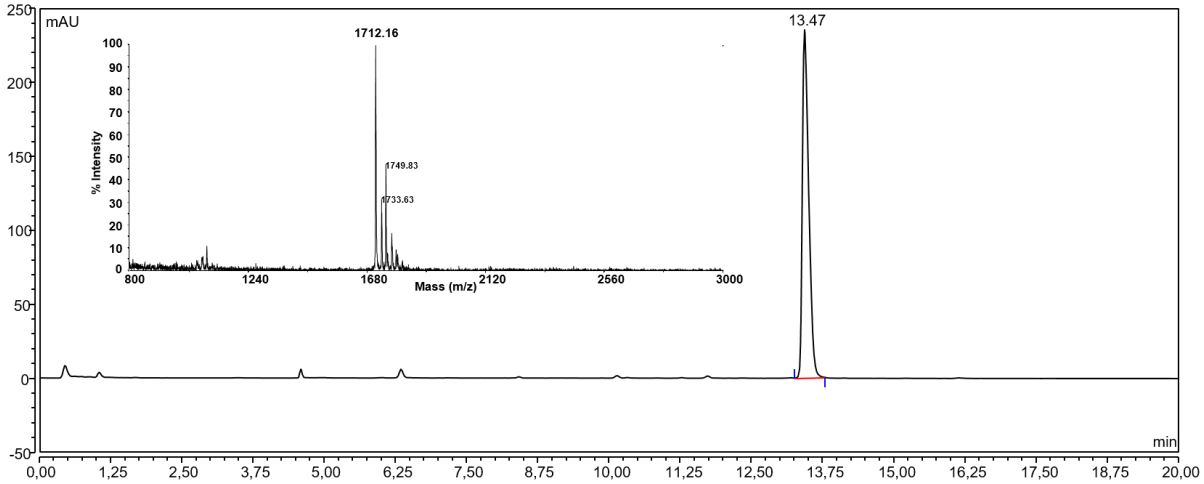

Figure S1: Purification of GpppAUAU *via* ion-exchange chromatography in a linear gradient of 0-30 % buffer B in buffer A for 20 min at 1.5 mL/min. MALDI-TOF-analysis is shown as inset.

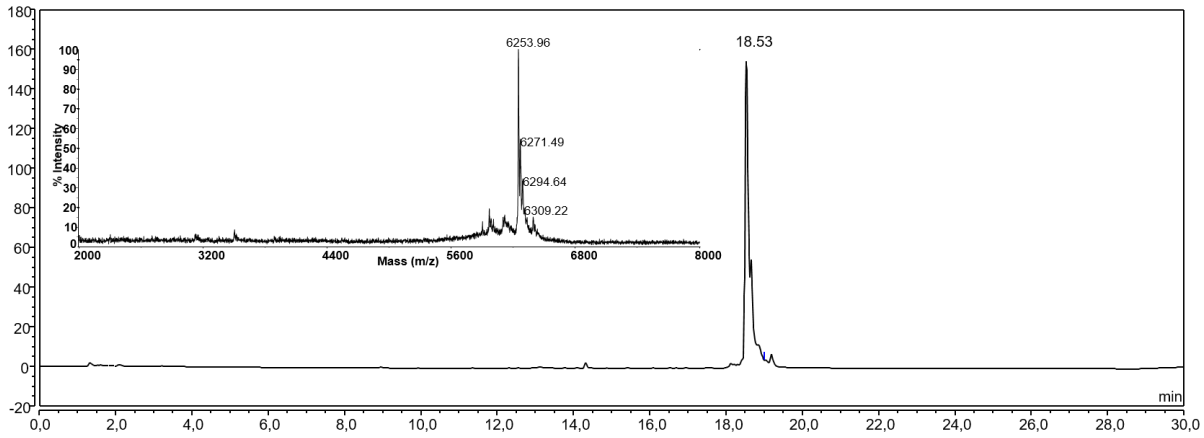

Figure S2: Purification of GpppAGUUGUUAGUCUACGUGG *via* ion-exchange chromatography in a linear gradient of 0-75 % buffer B in buffer A for 20 min at 1.5 mL/min. MALDI-TOF-analysis is shown as inset.

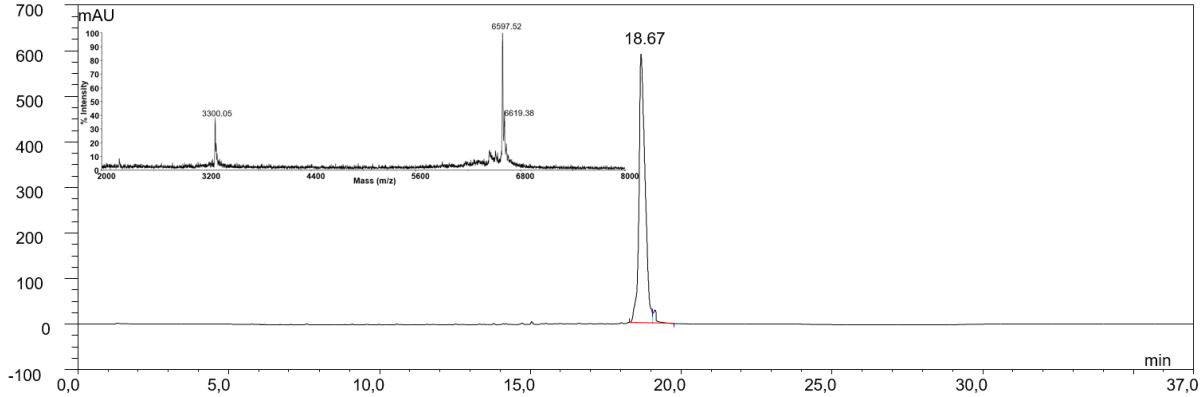

Figure S3: Purification of GpppAmGUUGUUAGUCUACGUGGA *via* ion-exchange chromatography in a linear gradient of 0-75 % buffer B in buffer A for 20 min at 1.5 mL/min. MALDI-TOF-analysis is shown as inset.

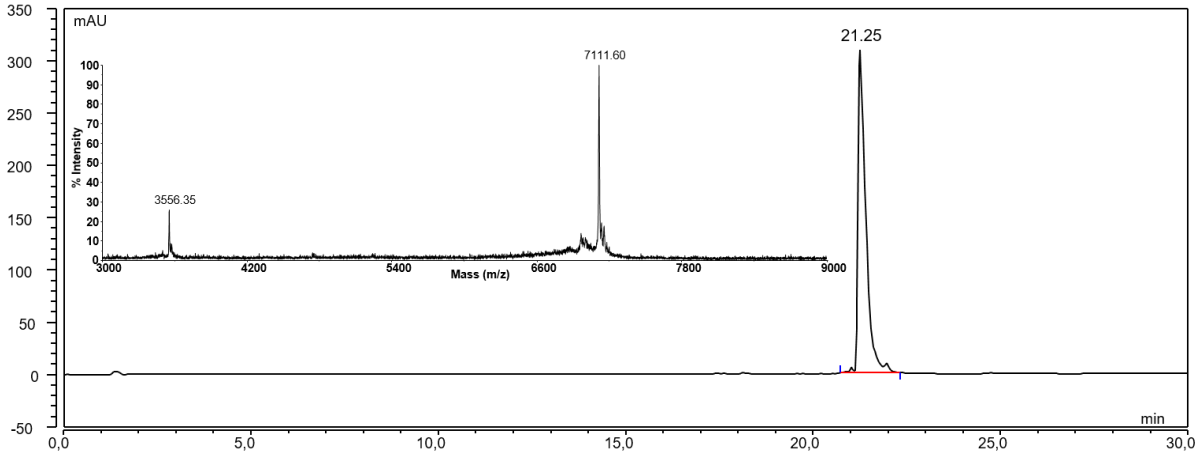

Figure S4: Purification of Gppp^{6m}AmCACUUGCUUUUGACACAACU *via* ion-exchange chromatography in a linear gradient of 10-45 % buffer B in buffer A for 22.5 min at 1.2 mL/min. MALDI-TOF-analysis is shown as inset.

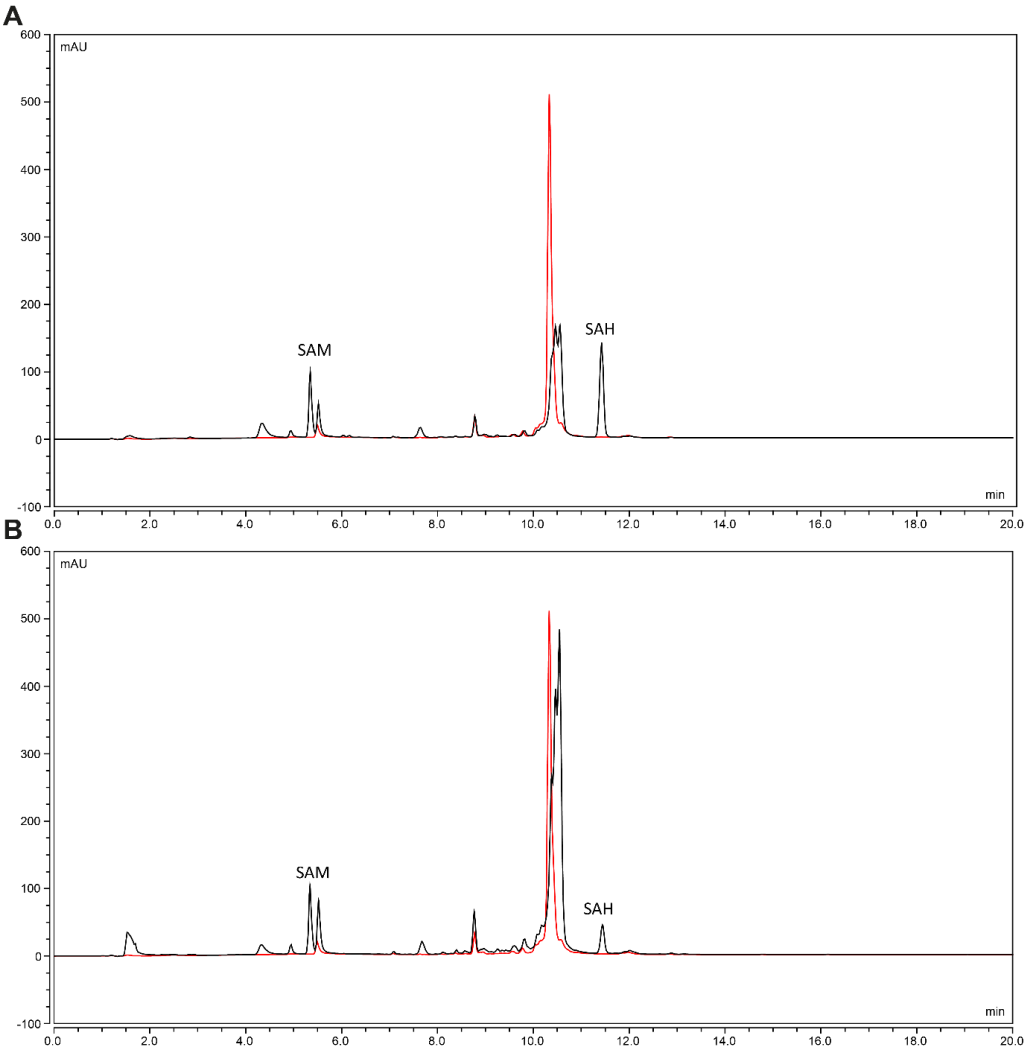

Figure 5: **A)** RP-HPLC analysis of the double N^2-methylation reaction of ^{7m}Gppp 19-mer **3** with A_m as the first nucleotide after 15 h incubation with hTgs1 at 2.5 μM (black trace) in comparison with the N^7-methylated substrate **3** (red trace). The reaction was not complete due to hTgs1 inhibition by excess SAH remaining from the previous N^7-methylation by hMTase (ratio SAH/SAM >1). **B)** RP-HPLC analysis of double N^2-methylation reaction of ^{7m}Gppp 19-mer **3** with A_m as the first nucleotide after 6 h incubation with hTgs1 at 2.5 μM (black trace) in comparison with the N^7-methylated substrate **3** (red trace). Although the reaction was not complete, the conversion is higher compared to **A)**. In this case, the remaining SAH from the N^7-methylation was previously removed through a NAP-cartridge.

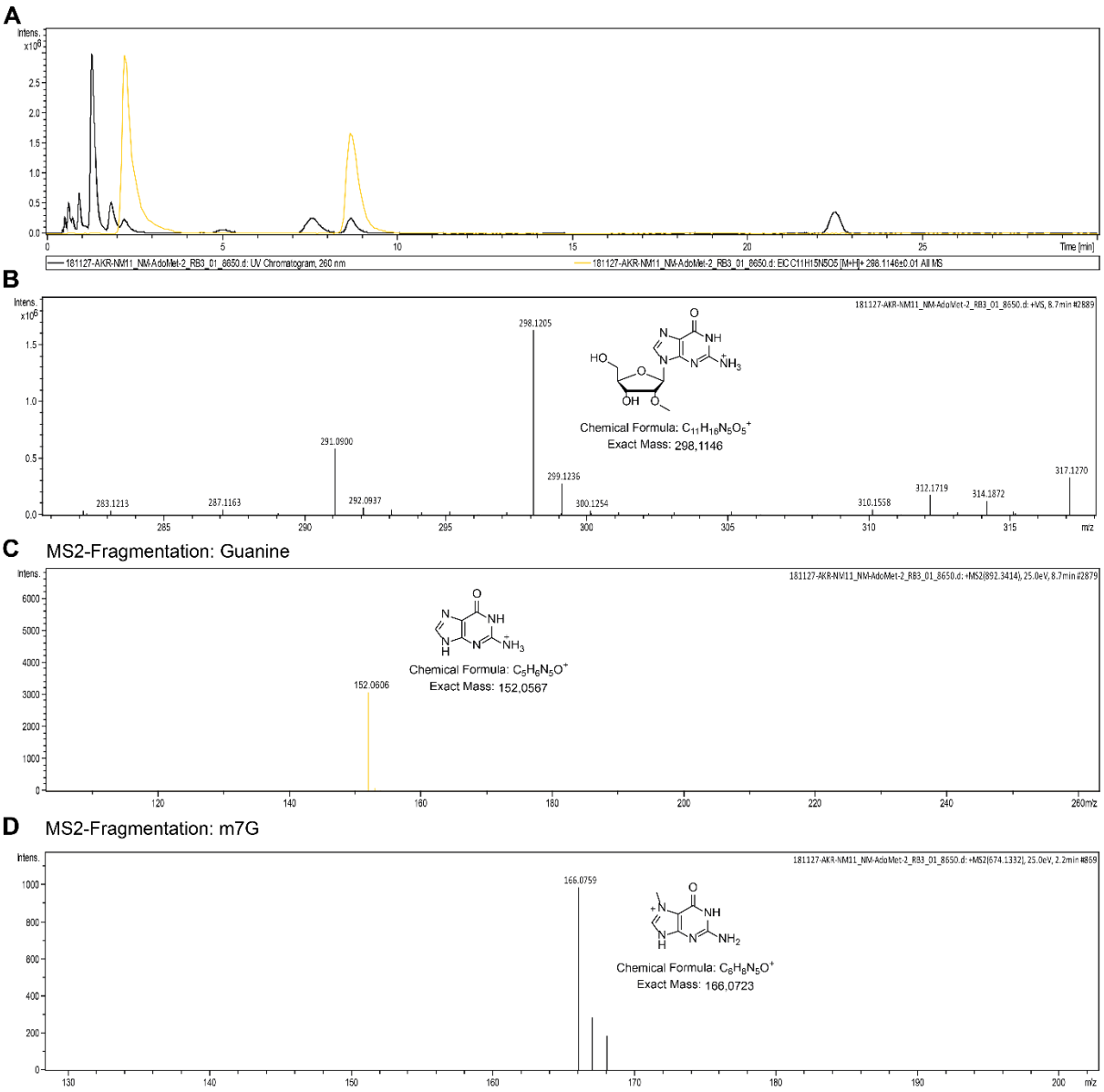

Figure S6: LC-MS analysis of the 2′-*O*-methylation by CMTR1 of ^{7m}GpppGAUC **8**. **A)** Absorbance at 260 nm (yellow curve) and the EIC (black curve) for 2′-*O*Me-guanosine. **B)** Mass-spectrum of 2′-*O*Me-guanosine at a retention time of 8.6-8.7 min (expected mass for $C_{11}H_{16}N_5O_5^+$ $[M+H]^+$=298.1146, found=298.1205) **C)** MS2-fragmentation at a retention time of 8.7 min. Expected mass for guanosine: $C_5H_6N_5O^+$ $[M+H]^+$=152.0567, found=152.0606. **D)** MS2-fragmentation at a retention time of 2.2 min. Expected mass for *N*7-methyl-guanosine: $C_6H_8N_5O^+$ $[M+H]^+$=166.0723, found=166.0759.

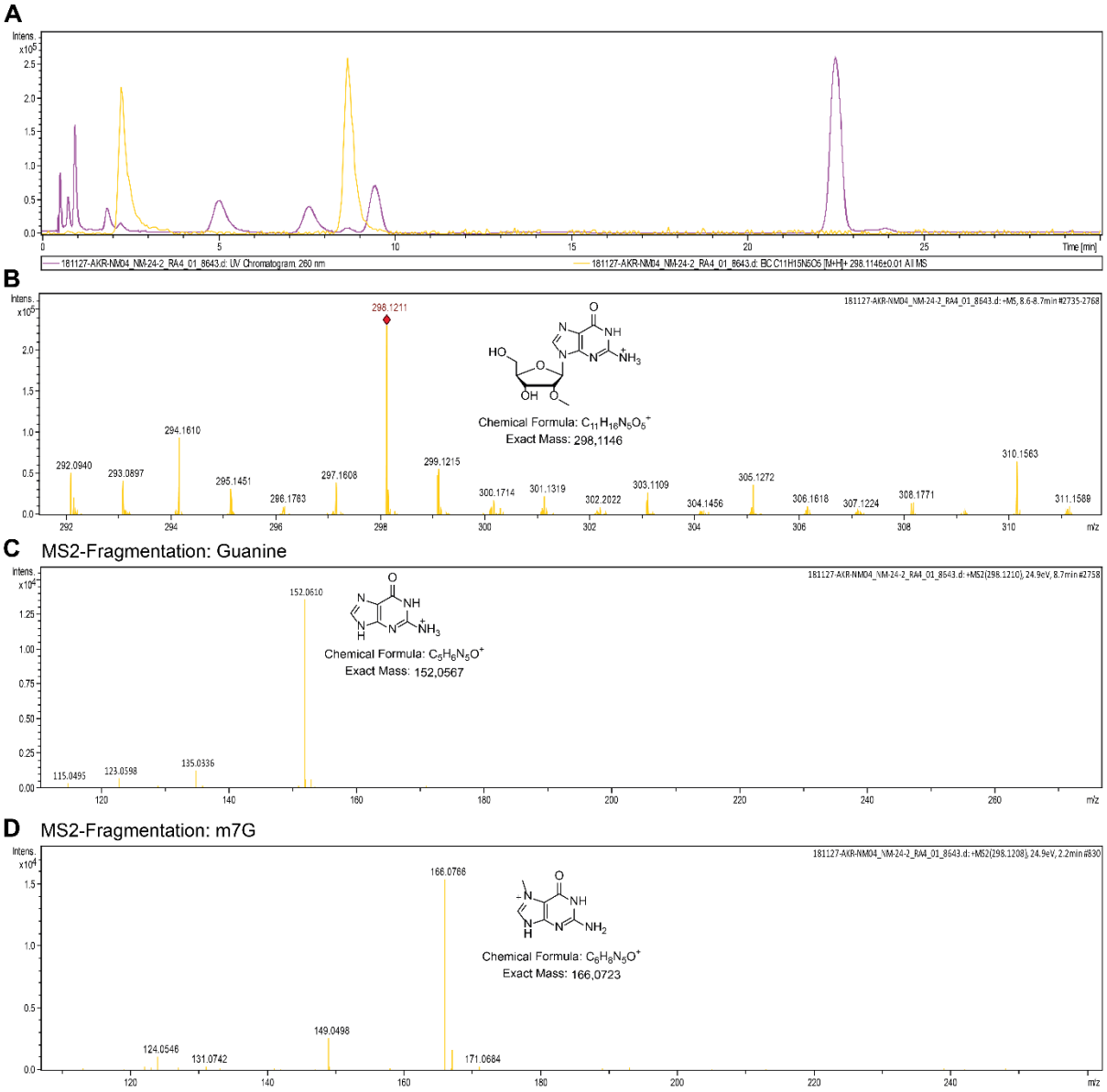

Figure S7: LC-MS analysis of the 2′-O-methylation by CMTR1 of a ^{7m}G capped 24 nucleotide long RNA. **A)** Absorbance at 260 nm (yellow curve) and the EIC (purple curve) for 2′-OMe-guanosine. **B)** Mass-spectrum of 2′-OMe-guanosine at a retention time of 8.6-8.7 min (expected mass for $C_{11}H_{16}N_5O_5^+$ $[M+H]^+$=298.1146, found=298.1211) **C)** MS2-fragmentation at a retention time of 8.7 min. Expected mass for guanosine: $C_5H_6N_5O^+$ $[M+H]^+$=152.0567, found=152.0610. **D)** MS2-fragmentation at a retention time of 2.2 min. Expected mass for N7-methyl-guanosine: $C_6H_8N_5O^+$ $[M+H]^+$=166.0723, found=166.0766.

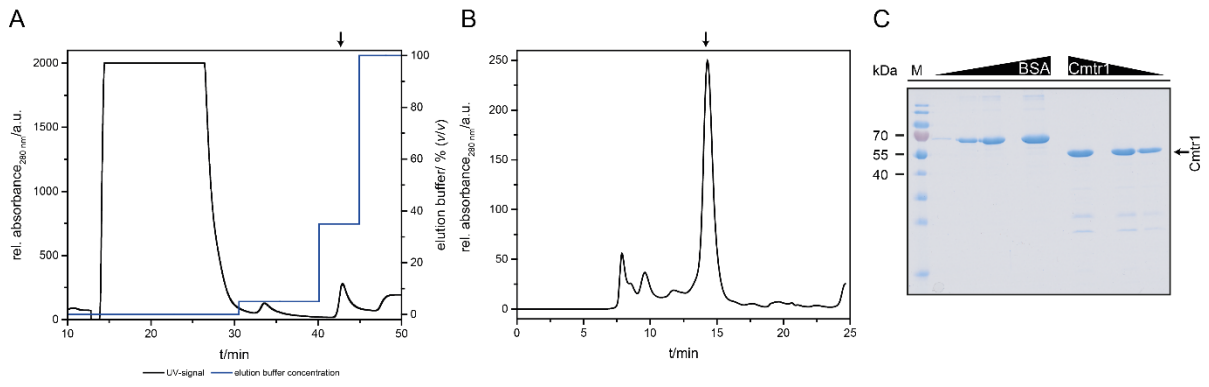

Figure S8: Purification and analysis of CMTR1. **A)** UV-chromatogram (280 nm, black line) of the CMTR1 purification via IMAC on a Ni-NTA column using gradient steps (blue line). The arrow indicates the peak collected for

subsequent experiments. **B)** UV-chromatogram (280 nm) of the size-exclusion purification on a Superdex^{TM}200 Increase 10/300 GL column. The arrow indicates the collected peak. **C)** Gel analysis (SDS-PAGE) of purified and concentrated CMTR1 (~54 kDa), quantified by a BSA-standard (lanes 2-6). Ladder: PageRulerTM Prestained Protein Ladder, 10 to 180 kDa.

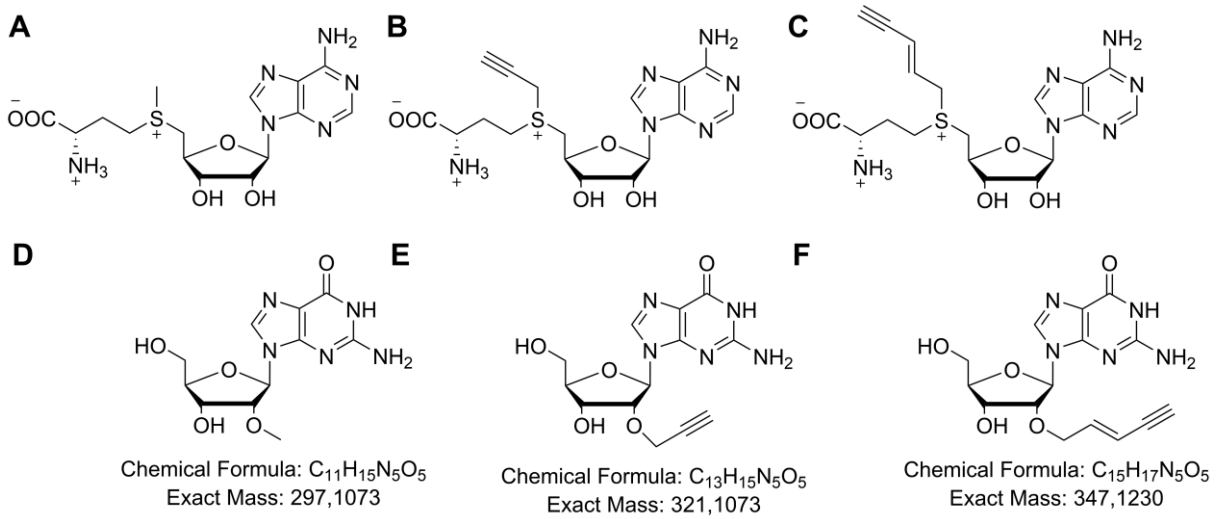

Figure S9: Chemical structures of AdoMet analogs and corresponding 2′-*O*-modified guanosine nucleosides. **A)** *S*-adenoysl-L-homocysteine (AdoMet) **B)** SeAdoYn **C)** AdoEnYn **D)** 2′-*O*-Methylguanosine **E)** 2′-*O*-Propargylguanosine **F)** 2′-*O*-Hexenynylguanosine.

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