# Synthesis of 2′-Deoxyuridine and 2′-Deoxycytidine Nucleosides Bearing Bipyridine and Terpyridine Ligands at Position 5

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**Abstract:** A methodology for the syntheses of pyrimidine (C or U) 2-deoxyribonucleosides bearing bipyridine or terpyridine ligands attached via acetylene or phenylene linkers was developed based on single step cross-coupling reactions of unprotected 5-iodopyrimidine nucleosides with bipyridine or terpyridine acetylenes of phenyl boronates. The Sonogashira reactions with acetylenes were performed in DMF, while the Suzuki reactions with boronates in water–acetonitrile mixtures. Photophysical properties of the title modified nucleosides have been studied and (2,2′-bipyridin-5-yl)ethynyl or (2,2′-bipyridin-5-yl)phenyl derivatives exerting absorption at >300 nm and bright emission at 421–451 nm were selected as the best candidates for luminescent DNA labeling.

**Key words:** nucleosides, pyrimidines, bipyridines, N-ligands, cross-coupling reactions

Complexes of 2,2′-bipyridine (bpy) and related ligands with transition metals possess[1] unique electrochemical and photophysical properties and thus could be used for electrochemical or luminescent labeling of biomolecules. Covalently bound conjugates of pyrimidine nucleotides with bipyridine or phenanthroline complexes of Ru and Os have been extensively studied as luminescence probes for DNA hybridization and charge transfer through DNA.[2] Recently, we have reported on the synthesis of purine[3] and 7-deazapurine[4] nucleosides and nucleoside triphosphates bearing Ru(II)bpy$_3$ and Os(II)bpy$_3$ and their enzymatic incorporation to DNA by polymerase primer extension.[5] Considerably less attention has been paid to conjugates of nucleosides with free (nonchelated) bpy-type ligands, which could be very useful in post synthetic complexations of nucleosides, nucleotides or nucleic acids with metals, self assembly and/or catalysis. In purine bases[6] and nucleosides[3] and 7-deazapurine nucleosides,[4] we have reported all the bipyridine, phenanthroline, and terpyridine conjugates linked via acetylene or phenylene tether. However, only two isolated examples of pyrimidine nucleosides bearing N-ligands have been reported so far: synthesis of 5-[(phenanthrolin-3-yl)ethynyl]-2′-deoxyuridine (including chemical incorporation of its phosphoramidite to oligonucleotides)[7] and 5-[(bipyridin-6-yl)ethynyl]-2′-deoxyuridine.[8] To complement the series of bpy-nucleoside conjugates, we report here on the synthesis of 2′-deoxyuridine and 2′-deoxycytidine nucleosides bearing bpy or terpyridine (tpy) ligands linked via acetylene or phenylene linkers.

Our selected approach of choice for the synthesis of the target modified nucleosides consists in the application of cross-coupling reactions of unprotected 5-iodopyrimidine nucleosides. Both Sonogashira[9–11] and Suzuki[12] cross-coupling of 5-iodopyrimidines with diverse terminal acetylenes or boronic acids have been extensively used in the synthesis of 5-modified pyrimidine nucleosides. In recent years, unprotected nucleosides[11–13] are preferentially used for the cross-couplings in DMF or in aqueous solutions to save two steps (protection and deprotection). Our goal to attach bpy or tpy ligands via the cross-coupling reaction is more challenging due to possible chelation of the Pd catalyst to the bpy/tpy ligand which can terminate the catalytic cycle. Therefore in some cases, a thorough optimization of the catalytic system, solvent, and conditions must have been performed to achieve good conversions.

Terminal acetylenes **1a–c** bearing bpy ligand attached via positions 6 or 5, as well as tpy ligand were the reagents of choice for the Sonogashira coupling, while the corresponding 4-(pinacolboronato)phenyl derivatives of the same ligands (compounds **2a–c**) were used for the Suzuki–Miyaura coupling. The synthesis of these starting building blocks have been reported previously.[6] The cross-coupling partners for these reagents were commercially available unprotected 5-iodo-2′-deoxycytidine (**3**) and -deoxyuridine (**4**).

The Sonogashira reactions of iodinated pyrimidine nucleosides **3** and **4** with terminal acetylenes **1a–c** (Scheme 1, Table 1) were performed under previously developed[6,4] conditions using 5 mol% of Pd(OAc)$_2$, water-soluble tris(3-sulfonatophenyl)phosphane (TPPTS) ligand, CuI, and Hünig's base in DMF (which in the Sonogashira reactions of purine bases and nucleosides worked better[6,4] than the aqueous-phase conditions[13] using water–acetonitrile mixtures). All the reactions proceeded reasonably well at 75 °C to reach full conversion in 2 hours. The products **5a–c** and **6a–c** were isolated in acceptable yields of 63–75% after column chromatography. Minor parts of the products were probably lost on chromatography as complexes with Cu and/or Pd, but also some minor products of decomposition of rather labile 2′-deoxyribonucleosides have also been observed. Taking into consideration that the synthesis of the target bpy-

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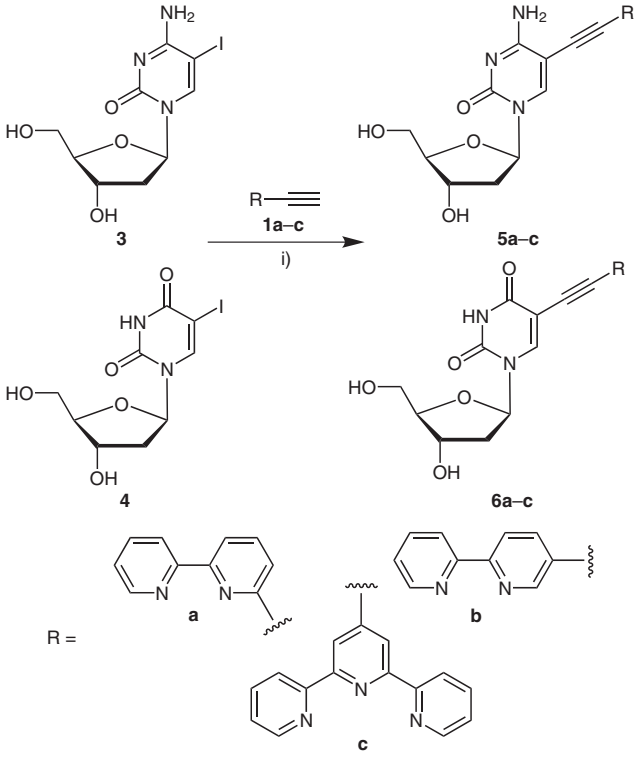


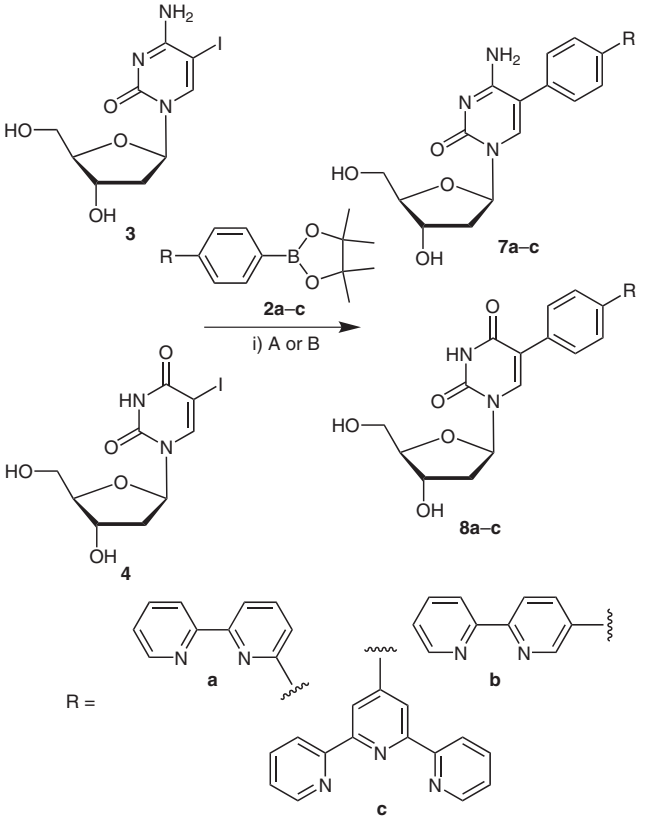

**Scheme 1** *Reagents and conditions*: i) $Pd(OAc)_2$ (5 mol%), TPPTS (2.5 equiv to Pd), CuI (10 mol%), $(i\text{-Pr})_2NEt$ (10 equiv), DMF, 75 °C, 2 h.

**Table 1** The Sonogashira Reactions of Nucleosides **3** and **4** with Alkynes **1a–c**

| Entry | Nucleoside | Alkyne | Product | Yield (%) |
|---|---|---|---|---|
| 1 | **3** | **1a** | **5a** | 70 |
| 2 | **4** | **1a** | **6a** | 75 |
| 3 | **3** | **1b** | **5b** | 67 |
| 4 | **4** | **1b** | **6b** | 70 |
| 5 | **3** | **1c** | **5c** | 63 |
| 6 | **4** | **1c** | **6c** | 67 |

modified nucleosides **5** and **6** is just a single-step procedure without any use of protecting groups, the yields were satisfactory.

The second class of target compounds were the corresponding phenylene linked conjugates **7** and **8**. At first the Suzuki–Miyaura reactions of boronates **2a–c** with nucleosides **3** and **4** were performed under previously developed[3,6,13] aqueous-phase conditions using 5 mol% of $Pd(OAc)_2$, TPPTS, and $Cs_2CO_3$ in water–acetonitrile 2:1 at 80 °C (Scheme 2, Table 2, conditions A). While the reactions of 6-(4-boronatophenyl)bpy **2a** with **3** and **4** gave good conversions and the products **7a** and **8a** were isolated in acceptable 60–65% yields (entries 1,2), the other boronates **2b** and **2c** reacted very slowly and even after




**Scheme 2** *Reagents and conditions*: i) A: $Pd(OAc)_2$ (5 mol%), TPPTS (2.5 equiv to Pd), $Cs_2CO_3$ (3 equiv), $H_2O$–MeCN (2:1), 80 °C; B: $Pd(OAc)_2$ (10 mol%), TPPTS (5 equiv to Pd), $Cs_2CO_3$ (3 equiv), $H_2O$–MeCN (1:2), 90 °C.

**Table 2** The Suzuki Reactions of Nucleosides **3** and **4** with Boronates **2a–c**

| Entry | Nucleoside | Boronate | Product | Yield A (%)[a] | Yield B (%)[b] |
|---|---|---|---|---|---|
| 1 | **3** | **2a** | **7a** | 65 | 75 |
| 2 | **4** | **2a** | **8a** | 60 | 75 |
| 3 | **3** | **2b** | **7b** | 12 | 55 |
| 4 | **4** | **2b** | **8b** | 7 | 35 |
| 5 | **3** | **2c** | **7c** | 28 | 70 |
| 6 | **4** | **2c** | **8c** | 24 | 70 |

[a] Conditions A (see Scheme 2).
[b] Conditions B (see Scheme 2).

prolonged reaction time, the conversions were incomplete and only very low yields of products **7b**,**c** and **8b**,**c** were obtained (entries 3–6).

Therefore, the conditions of the Suzuki reaction were further optimized for the reaction of **3** with boronates **2b** or **2c**. At first several sources of Pd and several ligands successful in other aqueous Suzuki reactions with different boronic acids/boronates have been tested. The reactions using $Pd(PPh_3)_4$ or $Pd(OAc)_2$ in combination with

Buchwald's ligands (S-Phos,[14] dicyclohexylphosphinobiphenyl[15]) or catalytic system prepared from $Na_2PdCl_4$ and disulfonated fluorenyldialkylphosphine[16] using different bases ($Cs_2CO_3$, NaOH, $K_2CO_3$, $K_3PO_4$) did not bring any improvement (the yields varied from 0 to 15%). Further optimization experiments were performed using the original $Pd(OAc)_2$/TPPTS catalytic system and focused on changing the ratio of the reagents and catalyst and solvent mixtures. These experiments showed that using 10 mol% of the catalyst and higher amount of the TPPTS ligand (5 equiv to Pd), as well as changing the solvent mixture to water–acetonitrile (1:2) had a beneficial effect on the conversion.

The final optimized conditions (Scheme 2, Table 2, conditions B) then involved the use of 10 mol% of $Pd(OAc)_2$, 50 mol% of TPPTS and $Cs_2CO_3$ in water–acetonitrile (1:2) at 90 °C. In all cases, the yields of the products **7** and **8** were substantially improved compared to the conditions A. The reactions of 6-linked bpy boronate **2a** and tpy-boronate **2c** gave full conversions and satisfactory isolated yields of products **7a**,**c** and **8a**,**c** (70–75%). Only in the case of 5-linked bpy-boronate **2b**, the conversions were incomplete and the products **7b** and **8b** were isolated in moderate yields of 55 or 35%, respectively.

Preliminary study of photophysical properties of the modified nucleosides has been performed. The UV-VIS absorption spectra of the compounds revealed absorption maxima at 282–329 nm. All compounds showed some luminescence with emission maxima at 389–451 nm (Table 3). The 6-linked bpy-nucleosides **5a**–**8a** exerted very low luminescence with negligible quantum yields and the shortest wavelengths of emission (<400 nm). The tpy-linked nucleosides **5c**–**8c** gave moderately bright ($\phi$ = 1–8%) emission in VIS region. The most interesting class of compounds were the 5-linked bpy-nucleosides **5b**–**8b** that absorbed at 306–329 nm (and thus in principle could be selectively excited in DNA) and provided very bright emission at 421–451 with quantum yields of 11–29%.

In conclusion, aqueous-phase cross-coupling methodology for attachment of bpy and tpy ligands to position 5 of 2′-deoxyuridine and 2′-deoxycytidine via acetylene or phenylene spacer has been developed. While the Sonogashira reactions worked reasonably well with bpy- or tpy-acetylenes under standard conditions in DMF, the aqueous-phase Suzuki reactions were much more problematic and only after thorough optimization, efficient procedure has been developed using higher catalyst loading, higher temperature and different ratio of solvents. Most importantly, at least the Sonogashira protocol is suitable for the use in modification of nucleoside triphosphates.[17] All the nucleoside-bpy/tpy conjugates are luminescent and in particular the 5-linked bpy derivatives exert very high level of luminescence. We will further prepare the corresponding dNTPs, study their polymerase incorporation to DNA[17] and use these building blocks for fluorescent labeling of DNA, for complexation with metals, self-assembly and catalysis.

**Table 3** Absorption and Emission Band Positions in Methanol

| Compd | Absorption | | Emission | |
|---|---|---|---|---|
| | $\lambda_{max}$ (nm) | $\varepsilon$ (L·mol$^{-1}$·cm$^{-1}$) | $\lambda_{max}$ (nm) | $\phi$ |
| **5a** | 326 | $2.1 \times 10^{-4}$ | 397 | <0.01 |
| **5b** | 329 | $5.4 \times 10^{-4}$ | 435 | 0.11 |
| **5c** | 283 | $3.7 \times 10^{-4}$ | 445 | 0.02 |
| **6a** | 316 | $3.1 \times 10^{-4}$ | 389 | <0.01 |
| **6b** | 327 | $3.9 \times 10^{-4}$ | 421 | 0.16 |
| **6c** | 282 | $4.4 \times 10^{-4}$ | 408 | 0.01 |
| **7a** | 286 | $3.9 \times 10^{-4}$ | 389 | <0.01 |
| **7b** | 306 | $3.7 \times 10^{-4}$ | 451 | 0.18 |
| **7c** | 286 | $1.2 \times 10^{-4}$ | 444 | 0.04 |
| **8a** | 309 | $3.6 \times 10^{-4}$ | 399 | <0.01 |
| **8b** | 315 | $5.3 \times 10^{-4}$ | 437 | 0.29 |
| **8c** | 285 | $3.4 \times 10^{-4}$ | 427 | 0.08 |

Melting points were determined on a Kofler block. NMR spectra were measured at 500 MHz for $^1$H and 125.7 MHz for $^{13}$C, or at 600 MHz for $^1$H and 151 MHz for $^{13}$C in DMSO-$d_6$ (referenced to the residual solvent signal: $\delta$ = 2.50 for $^1$H NMR and 39.7 for $^{13}$C NMR). Chemical shifts are given in ppm ($\delta$-scale) and coupling constants ($J$) in Hz. Complete assignments of all NMR signals (see Figure 1 for numbering) were performed using a combination of H,H-COSY, H,C-HSQC, and H,C-HMBC experiments. Preparative flash chromatography on reverse phase was performed on Biotage SP1 flash purification system.

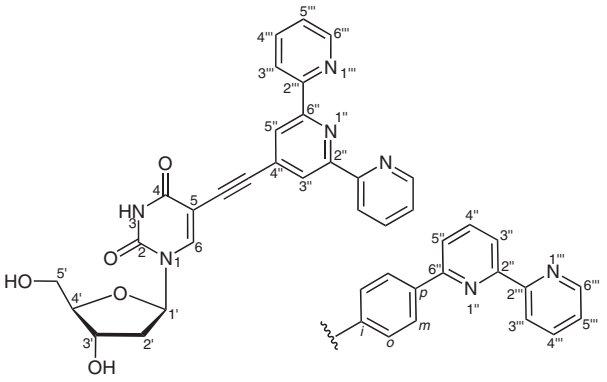


**Figure 1** Numbering scheme for NMR assignment

**Sonogashira Cross-Coupling Reactions; General Procedure**

DMF (1 mL) and (*i*-Pr)$_2$NEt (0.22 mL, 1.25 mmol, 10 equiv) were added to an argon-purged flask containing nucleoside **3** or **4** (44 mg, 0.125 mmol), an alkyne **1a–c** (0.188 mmol, 1.5 equiv), and CuI (2.4 mg, 0.0125 mmol, 10 mol%). In a separate flask, $Pd(OAc)_2$ (1.4 mg, 6.25 μmol, 5 mol%) and TPPTS (8.9 mg, 0.0156 mmol, 2.5 equiv to Pd) were combined, evacuated and purged with argon followed by addition of DMF (0.5 mL). The mixture of catalyst was then in-

jected into the reaction mixture and the resulting mixture was stirred at 75 °C for 2 h. The solvent was then evaporated in vacuo. Products were directly purified by flash chromatography on reverse phase using $H_2O$–MeOH (0 to 100%) as an eluent.

**5-[(2,2′-Bipyridin-6-yl)ethynyl]-2′-deoxycytidine (5a)**
Prepared from deoxycytidine **3** and bipyridinyl acetylene **1a**. It was isolated as a brown powder in a yield of 70% (35 mg), which was then crystallized from a mixture of MeOH–$H_2O$; mp 139–146 °C.

IR (KBr): 3392, 1645, 1500, 1094, 780 $cm^{-1}$.

$^1H$ NMR (500 MHz, DMSO-$d_6$): δ = 2.07 (ddd, $J_{gem}$ = 13.2 Hz, $J_{2'b,1'}$ = 7.0 Hz, $J_{2'b,3'}$ = 6.1 Hz, 1 H, H-2′b), 2.19 (ddd, $J_{gem}$ = 13.2 Hz, $J_{2'a,1'}$ = 6.1 Hz, $J_{2'a,3'}$ = 3.7 Hz, 1 H, H-2′a), 3.59 (ddd, $J_{gem}$ = 11.9 Hz, $J_{5'b,OH}$ = 5.1 Hz, $J_{5'b,4'}$ = 3.7 Hz, 1 H, H-5′b), 3.67 (ddd, $J_{gem}$ = 11.9 Hz, $J_{5'a,OH}$ = 5.1 Hz, $J_{5'a,4'}$ = 3.5 Hz, 1 H, H-5′a), 3.82 (ddd, $J_{4',5'}$ = 3.7, 3.5 Hz, $J_{4',3'}$ = 3.3 Hz, 1 H, H-4′), 4.24 (dddd, $J_{3',2'}$ = 6.1, 3.7 Hz, $J_{3',OH}$ = 4.3 Hz, $J_{3',4'}$ = 3.3 Hz, 1 H, H-3′), 5.17 (t, $J_{OH,5'}$ = 5.1 Hz, 1 H, OH-5′), 5.26 (d, $J_{3',OH}$ = 4.3 Hz, 1 H, OH-3′), 6.15 (dd, $J_{1',2'}$ = 7.0, 6.1 Hz, 1 H, H-1′), 7.17 (br s, 1 H, $NH_aH_b$), 7.49 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.7 Hz, $J_{5''',3'''}$ = 1.2 Hz, 1 H, H-5‴), 7.87 (dd, $J_{5'',4''}$ = 7.7 Hz, $J_{5'',3''}$ = 1.1 Hz, 1 H, H-5″), 7.90 (br s, 1 H, $NH_aH_b$), 7.97 (ddd, $J_{4''',3'''}$ = 8.0 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 1 H, H-4‴), 8.00 (dd, $J_{4'',3''}$ = 8.0 Hz, $J_{4'',5''}$ = 7.7 Hz, 1 H, H-4″), 8.36 (dd, $J_{3'',4''}$ = 8.0 Hz, $J_{3'',5''}$ = 1.1 Hz, 1 H, H-3″), 8.38 (ddd, $J_{3''',4'''}$ = 8.0 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 1.0 Hz, 1 H, H-3‴), 8.43 (s, 1 H, H-6), 8.71 (ddd, $J_{6''',5'''}$ = 4.7 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 1.0 Hz, 1 H, H-6‴).

$^{13}C$ NMR (125.7 MHz, DMSO-$d_6$): δ = 41.10 ($CH_2$-2′), 61.13 ($CH_2$-5′), 70.21 (CH-3′), 81.62 (C5-*C*≡C–C6″), 85.76 (CH-1′), 87.75 (CH-4′), 88.79 (C-5), 93.86 (C5–C≡*C*–C6″), 120.10 (CH-3″), 120.90 (CH-3‴), 124.79 (CH-5‴), 128.05 (CH-5″), 137.67 (CH-4‴), 137.95 (CH-4″), 142.42 (C-6″), 146.22 (CH-6), 149.61 (CH-6‴), 153.53 (C-2), 154.72 (C-2‴), 155.70 (C-2″), 164.05 (C-4).

MS (ESI): *m*/*z* (%) = 428 (15, [$M^+$ + Na]), 833 (100, [2 $M^+$ + Na]).

HRMS-ESI: *m*/*z* [$M^+$ + H] calcd for $C_{21}H_{20}N_5O_4$: 406.1510; found: 406.1514.

Anal. Calcd for $C_{21}H_{19}N_5O_4 \cdot 1H_2O \cdot 1MeOH$: C, 58.01; H, 5.53; N, 15.38. Found: C, 57.97; H, 5.13; N, 15.20.

**5-[(2,2′-Bipyridin-5-yl)ethynyl]-2′-deoxycytidine (5b)**
Prepared from deoxycytidine **3** and bipyridinyl acetylene **1b**. It was isolated as a slightly yellow powder in a yield of 67% (34 mg), and was then crystallized from a mixture of EtOH–$H_2O$; mp >300 °C.

IR (KBr): 3448, 1656, 1634, 1501, 1462, 1101, 794, 781, 742 $cm^{-1}$.

$^1H$ NMR (500 MHz, DMSO-$d_6$): δ = 2.05 (dt, $J_{gem}$ = 13.3 Hz, $J_{2'b,1'}$ = $J_{2'b,3'}$ = 6.4 Hz, 1 H, H-2′b), 2.20 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'a,1'}$ = 6.1 Hz, $J_{2'a,3'}$ = 3.9 Hz, 1 H, H-2′a), 3.60 and 3.68 (2 br dt, $J_{gem}$ = 11.9 Hz, $J_{5',OH}$ = $J_{5',4'}$ = 3.5 Hz, 2 H, H-5′), 3.82 (q, $J_{4',5'}$ = $J_{4',3'}$ = 3.5 Hz, 1 H, H-4′), 4.25 (br m, $J_{3',2'}$ = 6.4, 3.9 Hz, $J_{3',OH}$ = 4.3 Hz, $J_{3',4'}$ = 3.5 Hz, 1 H, H-3′), 5.17 (br t, $J_{OH,5'}$ = 3.5 Hz, 1 H, OH-5′), 5.26 (br d, $J_{3',OH}$ = 4.3 Hz, 1 H, OH-3′), 6.13 (dd, $J_{1',2'}$ = 6.4, 6.1 Hz, 1 H, H-1′), 7.21 (br s, 1 H, $NH_aH_b$), 7.47 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.8 Hz, $J_{5''',3'''}$ = 1.2 Hz, 1 H, H-5‴), 7.85 (br s, 1 H, $NH_aH_b$), 7.97 (ddd, $J_{4''',3'''}$ = 7.9 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 1 H, H-4‴), 8.14 (dd, $J_{4'',3''}$ = 8.3 Hz, $J_{4'',6''}$ = 2.1 Hz, 1 H, H-4″), 8.40 (ddd, $J_{3''',4'''}$ = 7.9 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 1.0 Hz, 1 H, H-3‴), 8.41 (dd, $J_{3'',4''}$ = 8.4 Hz, $J_{3'',6''}$ = 0.9 Hz, 1 H, H-3″), 8.42 (s, 1 H, H-6), 8.70 (ddd, $J_{6''',5'''}$ = 4.8 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 1.0 Hz, 1 H, H-6‴), 8.88 (dd, $J_{6'',4''}$ = 2.1 Hz, $J_{6'',3''}$ = 0.9 Hz, 1 H, H-6″).

$^{13}C$ NMR (125.7 MHz, DMSO-$d_6$): δ = 41.12 ($CH_2$-2′), 61.06 ($CH_2$-5′), 70.09 (CH-3′), 85.77 (CH-1′), 86.36 (C5–*C*≡C–C5″)), 87.70 (CH-4′), 89.22 (C-5), 91.18 (C5–C≡*C*–C5″), 120.05 (CH-3″), 120.09 (C-5″), 121.00 (CH-3‴), 124.71 (CH-5‴), 137.68 (CH-4‴), 139.58 (CH-4″), 145.79 (CH-6), 149.68 (CH-6‴), 151.46 (CH-6″), 153.57 (C-2), 154.11 (C-2″), 154.69 (C-2‴), 163.93 (C-4).

MS (ESI): *m*/*z* (%) = 405 (3, [$M^+$]), 428 (16, [$M^+$ + Na]), 833 (100, [2 $M^+$ + Na]).

HRMS-ESI: *m*/*z* [$M^+$ + H] calcd for $C_{21}H_{20}N_5O_4$: 406.1510; found: 406.1512.

Anal. Calcd for $C_{21}H_{19}N_5O_4 \cdot 0.5H_2O$: C, 60.86; H, 4.86; N, 16.90; Found C, 61.13; H, 4.67; N, 16.60.

**5-[(2,2′:6′,2″-Terpyridin-4′-yl)ethynyl]-2′-deoxycytidine (5c)**
Prepared from deoxycytidine **3** and terpyridinyl acetylene **1c**. It was isolated as a slightly brownish powder in a yield of 63% (38 mg), which was then crystallized from a mixture of DMSO–$H_2O$; mp 284–295 °C.

IR (KBr): 3422, 2214, 1645, 1602, 1583, 1567, 1502, 1468, 1393, 1264, 1097, 792 $cm^{-1}$.

$^1H$ NMR (500 MHz, DMSO-$d_6$): δ = 2.09 (dt, $J_{gem}$ = 13.1 Hz, $J_{2'b,1'}$ = $J_{2'b,3'}$ = 6.4 Hz, 1 H, H-2′b), 2.21 (ddd, $J_{gem}$ = 13.1 Hz, $J_{2'a,1'}$ = 5.9 Hz, $J_{2'a,3'}$ = 3.6 Hz, 1 H, H-2′a), 3.62 (ddd, $J_{gem}$ = 11.9 Hz, $J_{5'b,OH}$ = 4.9 Hz, $J_{5'b,4'}$ = 3.9 Hz, 1 H, H-5′b), 3.70 (ddd, $J_{gem}$ = 11.9 Hz, $J_{5'a,OH}$ = 5.4 Hz, $J_{5'a,4'}$ = 3.7 Hz, 1 H, H-5′a), 3.83 (ddd, $J_{4',5'}$ = 3.9, 3.7 Hz, $J_{4',3'}$ = 3.1 Hz, 1 H, H-4′), 4.26 (m, $J_{3',2'}$ = 6.4, 3.6 Hz, $J_{3',OH}$ = 4.3 Hz, $J_{3',4'}$ = 3.1 Hz, 1 H, H-3′), 5.19 (dd, $J_{OH,5'}$ = 5.4, 4.9 Hz, 1 H, OH-5′), 5.24 (d, $J_{3',OH}$ = 4.3 Hz, 1 H, OH-3′), 6.15 (dd, $J_{1',2'}$ = 6.4, 5.9 Hz, 1 H, H-1′), 7.52 (br s, 1 H, $NH_aH_b$), 7.53 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.7 Hz, $J_{5''',3'''}$ = 1.2 Hz, 2 H, H-5‴), 7.82 (br s, 1 H, $NH_aH_b$), 8.03 (ddd, $J_{4''',3'''}$ = 8.0 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 2 H, H-4‴), 8.49 (s, 1 H, H-6), 8.62 (s, 2 H, H-3″,5″), 8.63 (ddd, $J_{3''',4'''}$ = 8.0 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 0.9 Hz, 2 H, H-3‴), 8.74 (ddd, $J_{6''',5'''}$ = 4.7 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 0.9 Hz, 2 H, H-6‴).

$^{13}C$ NMR (125.7 MHz, DMSO-$d_6$): δ = 41.02 ($CH_2$-2′), 61.09 ($CH_2$-5′), 70.10 (CH-3′), 85.78 (CH-1′), 87.27 (C5–*C*≡C–C4″), 87.75 (CH-4′), 88.85 (C-5), 92.15 (C5–C≡*C*–C4″), 121.10 (CH-3‴), 121.99 (CH-3″,5″), 124.89 (CH-5‴), 133.13 (C-4″), 137.74 (CH-4‴), 146.85 (CH-6), 149.51 (CH-6‴), 153.52 (C-2), 154.78 (C-2‴), 155.30 (C-2″,6″), 163.93 (C-4).

MS (ESI): *m*/*z* (%) = 483 (37, [$M^+$ + H]), 505 (100, [$M^+$ + Na]), 982 (86, [2 $M^+$ + Na]).

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{23}N_6O_4$: 483.1775; found: 483.1780.

**5-[(2,2′-Bipyridin-6-yl)ethynyl]-2′-deoxyuridine (6a)**
Prepared from deoxyuridine **4** and bipyridinyl acetylene **1a**. Product was isolated as yellow crystals in a yield of 75% (38 mg) and crystallized from a mixture of MeOH–$H_2O$; mp 129–136 °C.

IR (KBr): 3424, 3061, 1699, 1626, 1454, 1429, 1274, 1094, 1056, 778 $cm^{-1}$.

$^1H$ NMR (500 MHz, DMSO-$d_6$): δ = 2.17 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'b,1'}$ = 6.2 Hz, $J_{2'b,3'}$ = 3.9 Hz, 1 H, H-2′b), 2.21 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'a,1'}$ = 6.9 Hz, $J_{2'a,3'}$ = 5.9 Hz, 1 H, H-2′a), 3.60 (ddd, $J_{gem}$ = 12.1 Hz, $J_{5'b,OH}$ = 4.5 Hz, $J_{5'b,4'}$ = 3.6 Hz, 1 H, H-5′b), 3.68 (ddd, $J_{gem}$ = 12.1 Hz, $J_{5'a,OH}$ = 4.8 Hz, $J_{5'a,4'}$ = 3.6 Hz, 1 H, H-5′a), 3.83 (td, $J_{4',5'}$ = 3.6 Hz, $J_{4',3'}$ = 3.0 Hz, 1 H, H-4′), 4.27 (m, $J_{3',2'}$ = 5.9, 3.9 Hz, $J_{3',OH}$ = 4.3 Hz, $J_{3',4'}$ = 3.0 Hz, 1 H, H-3′), 5.21 (br dd, $J_{OH,5'}$ = 4.8, 4.5 Hz, 1 H, OH-5′), 5.30 (br d, $J_{3',OH}$ = 4.3 Hz, 1 H, OH-3′), 6.14 (dd, $J_{1',2'}$ = 6.9, 6.2 Hz, 1 H, H-1′), 7.49 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.8 Hz, $J_{5''',3'''}$ = 1.2 Hz, 1 H, H-5‴), 7.61 (dd, $J_{5'',4''}$ = 7.7 Hz, $J_{5'',3''}$ = 1.0 Hz, 1 H, H-5″), 7.97 (ddd, $J_{4''',3'''}$ = 8.0 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 1 H, H-4‴), 7.99 (dd, $J_{4'',3''}$ = 8.0 Hz, $J_{4'',5''}$ = 7.7 Hz, 1 H, H-4″), 8.36 (ddd, $J_{3''',4'''}$ = 8.0 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 1.0 Hz, 1 H, H-3‴), 8.37 (dd, $J_{3'',4''}$ = 8.0 Hz, $J_{3'',5''}$ = 1.0 Hz, 1 H, H-3″), 8.50 (s, 1 H, H-6),

8.70 (ddd, $J_{6''',5'''}$ = 4.8 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 1.0 Hz, 1 H, H-6‴).

$^{13}$C NMR (125.7 MHz, DMSO-$d_6$): δ = 40.48 ($CH_2$-2′), 61.02 ($CH_2$-5′), 70.11 (CH-3′), 82.52 (C5–*C*≡C–C6″), 85.24 (CH-1′), 87.86 (CH-4′), 91.76 (C5–C≡*C*–C6″), 97.51 (C-5), 120.27 (CH-3″), 120.95 (CH-3‴), 124.83 (CH-5‴), 127.66 (CH-5″), 137.70 (CH-4‴), 138.25 (CH-4″), 142.24 (C-6″), 145.31 (CH-6), 149.62 (CH-6‴), 149.68 (C-2), 154.67 (C-2‴), 155.97 (C-2″), 161.70 (C-4).

MS (ESI): *m*/*z* (%) = 406 (9, [M$^+$]), 429 (100, [M$^+$ + Na]), 835 (21, [2 M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{19}N_5O_4$: 407.1350; found: 407.1357.

Anal. Calcd for $C_{21}H_{18}N_5O_4 \cdot 1H_2O$: C, 59.43; H, 4.75; N, 13.20. Found: C, 59.73; H, 4.67; N, 13.12.

**5-[(2,2′-Bipyridin-5-yl)ethynyl]-2′-deoxyuridine (6b)**

Prepared from deoxyuridine **4** and acetylene **1b** and isolated as a yellowish solid in a yield of 70% (35 mg) and crystallized from a mixture of $CHCl_3$–MeOH–heptane; mp 134–139 °C.

IR (KBr): 3419, 3056, 2974, 1716, 1697, 1624, 1458, 1306, 1274, 1092, 1051, 795, 747 cm$^{-1}$.

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 2.16 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'b,1'}$ = 6.3 Hz, $J_{2'b,3'}$ = 4.3 Hz, 1 H, H-2′b), 2.20 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'a,1'}$ = 6.8 Hz, $J_{2'a,3'}$ = 5.8 Hz, 1 H, H-2′a), 3.60 (br ddd, $J_{gem}$ = 12.1 Hz, $J_{5'b,OH}$ = 4.0 Hz, $J_{5'b,4'}$ = 3.5 Hz, 1 H, H-5′b), 3.68 (br ddd, $J_{gem}$ = 12.1 Hz, $J_{5'a,OH}$ = 4.4 Hz, $J_{5'a,4'}$ = 3.5 Hz, 1 H, H-5′a), 3.82 (td, $J_{4',5'}$ = 3.5 Hz, $J_{4',3'}$ = 3.2 Hz, 1 H, H-4′), 4.27 (br m, $J_{3',2'}$ = 5.8, 4.3 Hz, $J_{3',OH}$ = 4.2 Hz, $J_{3',4'}$ = 3.2 Hz, 1 H, H-3′), 5.23 (br dd, $J_{OH,5'}$ = 4.4, 4.0 Hz, 1 H, OH-5′), 5.31 (br d, $J_{3',OH}$ = 4.2 Hz, 1 H, OH-3′), 6.13 (dd, $J_{1',2'}$ = 6.8, 6.3 Hz, 1 H, H-1′), 7.48 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.8 Hz, $J_{5''',3'''}$ = 1.2 Hz, 1 H, H-5‴), 7.97 (ddd, $J_{4''',3'''}$ = 8.0 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 1 H, H-4‴), 8.03 (dd, $J_{4'',3''}$ = 8.3 Hz, $J_{4'',6''}$ = 2.2 Hz, 1 H, H-4″), 8.39 (ddd, $J_{3''',4'''}$ = 8.0 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 0.9 Hz, 1 H, H-3‴), 8.42 (dd, $J_{3'',4''}$ = 8.3 Hz, $J_{3'',6''}$ = 1.0 Hz, 1 H, H-3″), 8.50 (s, 1 H, H-6), 8.71 (ddd, $J_{6''',5'''}$ = 4.8 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 0.9 Hz, 1 H, H-6‴), 8.76 (dd, $J_{6'',4''}$ = 2.2 Hz, $J_{6'',3''}$ = 1.0 Hz, 1 H, H-6″).

$^{13}$C NMR (125.7 MHz, DMSO-$d_6$): δ = 40.51 ($CH_2$-2′), 60.99 ($CH_2$-5′), 70.06 (CH-3′), 85.23 (CH-1′), 87.17 (C5–*C*≡C–C5″), 87.84 (CH-4′), 89.04 (C5–C≡*C*–C5″), 97.85 (C-5), 119.94 (C-5″), 120.34 (CH-3″), 121.05 (CH-3‴), 124.80 (CH-5‴), 137.73 (CH-4‴), 139.68 (CH-4″), 144.97 (CH-6), 149.66 (C-2), 149.73 (CH-6‴), 151.32 (CH-6″), 154.39 (C-2″), 154.60 (C-2‴), 161.61 (C-4).

MS (ESI): *m*/*z* (%) = 407 (17, [M$^+$ + H]), 429 (19, [M$^+$ + Na]), 835 (21, [2 M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{19}N_4O_5$: 407.1350; found: 407.1358

Anal. Calcd for $C_{21}H_{18}N_4O_5 \cdot 3H_2O$: C, 54.78; H, 5.25; N, 12.17. Found: C, 54.72; H, 5.19; N, 12.04.

**5-[(2,2′:6′,2″-Terpyridin-4′-yl)ethynyl]-2′-deoxyuridine (6c)**

Prepared from deoxyuridine **4** and bipyridinyl acetylene **1c** and isolated as a yellowish powder in a yield of 67% (40 mg) and crystallized from a mixture of MeOH–$H_2O$; mp 234–242 °C.

IR (KBr): 3405, 2923, 2228, 1704, 1586, 1568, 1462, 1396, 1282, 1054, 790 cm$^{-1}$.

$^1$H NMR (600 MHz, DMSO-$d_6$): δ = 2.18 (ddd, $J_{gem}$ = 13.4 Hz, $J_{2'b,1'}$ = 6.2 Hz, $J_{2'b,3'}$ = 4.0 Hz, 1 H, H-2′b), 2.23 (ddd, $J_{gem}$ = 13.4 Hz, $J_{2'a,1'}$ = 6.8 Hz, $J_{2'a,3'}$ = 5.8 Hz, 1 H, H-2′a), 3.62 (ddd, $J_{gem}$ = 12.0 Hz, $J_{5'b,OH}$ = 4.6 Hz, $J_{5'b,4'}$ = 3.7 Hz, 1 H, H-5′b), 3.70 (ddd, $J_{gem}$ = 12.0 Hz, $J_{5'a,OH}$ = 5.1 Hz, $J_{5'a,4'}$ = 3.5 Hz, 1 H, H-5′a), 3.84 (ddd, $J_{4',5'}$ = 3.7, 3.5 Hz, $J_{4',3'}$ = 3.2 Hz, 1 H, H-4′), 4.28 (m, $J_{3',2'}$ = 5.8, 4.0 Hz, $J_{3',OH}$ = 4.4 Hz, $J_{3',4'}$ = 3.2 Hz, 1 H, H-3′), 5.29 (dd, $J_{OH,5'}$ = 5.1, 4.6 Hz, 1 H, OH-5′), 5.33 (d, $J_{3',OH}$ = 4.4 Hz, 1 H, OH-3′), 6.14 (dd, $J_{1',2'}$ = 6.8, 6.2 Hz, 1 H, H-1′), 7.53 (ddd, $J_{5''',4'''}$ = 7.4 Hz, $J_{5''',6'''}$ = 4.7 Hz, $J_{5''',3'''}$ = 1.2 Hz, 2 H, H-5‴), 8.03 (ddd, $J_{4''',3'''}$ = 7.9 Hz, $J_{4''',5'''}$ = 7.4 Hz, $J_{4''',6'''}$ = 1.8 Hz, 2 H, H-4‴), 8.41 (s, 2 H, H-3″,5″), 8.58 (s, 1 H, H-6), 8.63 (ddd, $J_{3''',4'''}$ = 7.9 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 1.0 Hz, 2 H, H-3‴), 8.74 (ddd, $J_{6''',5'''}$ = 4.7 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 1.0 Hz, 2 H, H-6‴), 11.83 (br s, 1 H, NH).

$^{13}$C NMR (151 MHz, DMSO-$d_6$): δ = 40.49 ($CH_2$-2′), 61.02 ($CH_2$-5′), 70.09 (CH-3′), 85.34 (CH-1′), 87.93 (CH-4′), 88.10 (C5–*C*≡C–C4″), 90.20 (C5–C≡*C*–C4″), 97.40 (C-5), 121.15 (CH-3‴), 121.66 (CH-3″,5″), 125.13 (CH-5‴), 132.87 (C-4″), 137.90 (CH-4‴), 145.79 (CH-6), 149.70 (C-2), 149.74 (CH-6‴), 154.48 (C-2‴), 155.62 (C-2″,6″), 161.68 (C-4).

MS (ESI): *m*/*z* (%) = 483 (57, [M$^+$]), 506 (100, [M$^+$ + Na]), 989 (77, [2 M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{22}N_5O_5$: 484.1615; found: 484.1614.

Anal. Calcd for $C_{26}H_{21}N_5O_5 \cdot 0.5H_2O$: C, 63.41; H, 4.5; N, 14.22. Found: C, 63.49; H, 4.36; N, 14.07.

**Suzuki–Miyaura Cross-Coupling Reactions; General Procedure**

*Conditions A*: A mixture of $H_2O$–MeCN (2:1) (1 mL) was added to an argon-purged flask containing nucleoside **3** or **4** (44 mg, 0.125 mmol), a boronate **2a–c** (0.15 mmol, 1.2 equiv), and $Cs_2CO_3$ (122 mg, 0.38 mmol, 3 equiv). In a separate flask, $Pd(OAc)_2$ (1.4 mg, 6.3 μmol, 5 mol%) and TPPTS (8.9 mg, 15.6 μmol, 2.5 equiv to Pd) were combined, evacuated and purged with argon followed by the addition of $H_2O$–MeCN (2:1, 0.5 mL). The mixture of catalyst was then injected into the reaction mixture and the resulting mixture was heated at 80 °C for appropriate time. The solvent was then evaporated in vacuo. Products **7a**,**b** and **8a–c** were directly purified by flash chromatography on reverse phase using $H_2O$–MeOH (0 to 100%) as an eluent. Product **7c** was purified by column chromatography on silica gel using $CHCl_3$–MeOH (10 to 100%) as an eluent. Products were crystallized from a mixture MeOH–$H_2O$, unless otherwise stated.

*Conditions B*: A mixture of $H_2O$–MeCN (1:2) (1 mL) was added to an argon-purged flask containing nucleoside **3** or **4** (44 mg, 0.125 mmol), a boronate **2a–c** (0.15 mmol, 1.2 equiv), and $Cs_2CO_3$ (122 mg, 0.38 mmol, 3 equiv). In a separate flask, $Pd(OAc)_2$ (2.8 mg, 12.5 μmol, 10 mol%) and TPPTS (35.5 mg, 62.5 μmol, 5 equiv to Pd) were combined, evacuated and purged with argon followed by the addition of $H_2O$–MeCN (1:2, 0.5 mL). The mixture of catalyst was then injected into the reaction mixture and the resulting mixture was heated at 90 °C until complete consumption of the starting material. The reaction was monitored by TLC, and at the end of the reaction the solvent was evaporated in vacuo. Products **7a**,**b** and **8a–c** were directly purified by flash chromatography on reverse phase using $H_2O$–MeOH (0 to 100%) as an eluent. Product **7c** was purified by column chromatography on silica gel using $CHCl_3$–MeOH (10 to 100%) as an eluent. Products were crystallized from a mixture MeOH–$H_2O$, unless otherwise stated.

**5-[4-(2,2′-Bipyridin-6-yl)phenyl]-2′-deoxycytidine (7a)**

Prepared from deoxycytidine **3** and bipyridinyl boronate **2a**.

*Conditions A*: Reaction was heated for 2 h and the product was then isolated as a white powder in a yield of 65% (37 mg).

*Conditions B*: Reaction mixture was heated for 1 h and **7a** was isolated as a white powder in a yield of 75% (43 mg).

Mp >300 °C.

IR (KBr): 3462, 3370, 1649, 1599, 1581, 1470, 1456, 1429, 1097, 778 cm$^{-1}$.

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 2.11 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'b,1'}$ = 6.9 Hz, $J_{2'b,3'}$ = 6.0 Hz, 1 H, H-2′b), 2.18 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'a,1'}$ = 6.7 Hz, $J_{2'a,3'}$ = 3.7 Hz, 1 H, H-2′a), 3.54 and 3.60 (2 ddd, $J_{gem}$ = 11.8 Hz, $J_{5',OH}$ = 4.8 Hz, $J_{5',4'}$ = 3.6 Hz, 2 H, H-5′), 3.80 (td, $J_{4',5'}$ = 3.6 Hz, $J_{4',3'}$ = 3.1 Hz, 1 H, H-4′), 4.25 (m, $J_{3',2'}$ = 6.0, 3.7 Hz, $J_{3',OH}$ = 4.2 Hz, $J_{3',4'}$ = 3.1 Hz, 1 H, H-3′), 5.02 (t, $J_{OH,5'}$ = 4.8 Hz, 1 H, OH-5′), 5.24 (br d, $J_{3',OH}$ = 4.2 Hz, 1 H, OH-3′), 6.23 (dd, $J_{1',2'}$ = 6.9, 6.2 Hz, 1 H, H-1′), 6.54 and 7.42 (2 br s, 2 H, $NH_2$), 7.49 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.8 Hz, $J_{5''',3'''}$ = 1.2 Hz, 1 H, H-5‴), 7.51 (m, 2 H, H-*o*-phenylene), 7.99 (s, 1 H, H-6), 8.01 (ddd, $J_{4''',3'''}$ = 7.9 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 1 H, H-4‴), 8.07 (dd, $J_{4'',5''}$ = 7.9 Hz, $J_{4'',3''}$ = 6.8 Hz, 1 H, H-4″), 8.08 (dd, $J_{5'',4''}$ = 7.9 Hz, $J_{5'',3''}$ = 1.9 Hz, 1 H, H-5″), 8.30 (m, 2 H, H-*m*-phenylene), 8.36 (dd, $J_{3'',4''}$ = 6.8 Hz, $J_{3'',5''}$ = 1.9 Hz, 1 H, H-3″), 8.59 (ddd, $J_{3''',4'''}$ = 7.9 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 0.9 Hz, 1 H, H-3‴), 8.72 (ddd, $J_{6''',5'''}$ = 4.8 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 0.9 Hz, 1 H, H-6‴).

$^{13}$C NMR (125.7 MHz, DMSO-$d_6$): δ = 40.90 ($CH_2$-2′), 61.24 ($CH_2$-5′), 70.35 (CH-3′), 85.37 (CH-1′), 87.51 (CH-4′), 107.45 (C-5), 119.40 (CH-3″), 120.60 (CH-5″), 120.85 (CH-3‴), 124.57 (CH-5‴), 127.41 (CH-*m*-phenylene), 129.42 (CH-*o*-phenylene), 135.10 (C-*i*-phenylene), 137.64 (CH-4‴), 137.69 (C-*p*-phenylene), 138.77 (CH-4″), 140.51 (CH-6), 149.54 (CH-6‴), 154.65 (C-2), 155.24 and 155.27 (C-2″,6″), 155.50 (C-2‴), 163.49 (C-4).

MS (ESI): *m*/*z* (%) = 457 (20, [M$^+$]), 915 (100, [2 M$^+$]), 937 (87, [2 M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{24}N_5O_4$: 458.1823; found: 458.1831.

Anal. Calcd for $C_{25}H_{23}N_5O_4 \cdot 1/3H_2O$: C, 64.78; H, 5.15; N, 15.11. Found: C, 64.97; H, 5.04; N, 14.88.

**5-[4-(2,2′-Bipyridin-5-yl)phenyl]-2′-deoxycytidine (7b)**
Prepared from 2′-deoxycytidine **3** and bipyridinyl boronate **2b**.

*Conditions A*: Reaction mixture was heated for 6 h. Even if the starting material was not fully converted, the product **7b** was isolated as a white powder in a yield of 12% (7 mg).

*Conditions B*: Reaction mixture was heated for 3 h. Product was isolated as a white powder in a yield of 55% (31 mg).

Mp >300 °C.

IR (KBr): 3389, 3176, 3068, 2932, 1661, 1631, 1503, 1459, 1263, 1196, 1082, 798, 750 cm$^{-1}$.

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 2.11 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'b,1'}$ = 6.9 Hz, $J_{2'b,3'}$ = 6.0 Hz, 1 H, H-2′b), 2.18 (ddd, $J_{gem}$ = 13.3 Hz, $J_{2'a,1'}$ = 6.7 Hz, $J_{2'a,3'}$ = 3.7 Hz, 1 H, H-2′a), 3.54 and 3.60 (2 ddd, $J_{gem}$ = 11.8 Hz, $J_{5',OH}$ = 4.8 Hz, $J_{5',4'}$ = 3.6 Hz, 2 H, H-5′), 3.80 (td, $J_{4',5'}$ = 3.6 Hz, $J_{4',3'}$ = 3.1 Hz, 1 H, H-4′), 4.25 (m, $J_{3',2'}$ = 6.0, 3.7 Hz, $J_{3',OH}$ = 4.2 Hz, $J_{3',4'}$ = 3.1 Hz, 1 H, H-3′), 5.02 (t, $J_{OH,5'}$ = 4.8 Hz, 1 H, OH-5′), 5.24 (br d, $J_{3',OH}$ = 4.2 Hz, 1 H, OH-3′), 6.23 (dd, $J_{1',2'}$ = 6.9, 6.2 Hz, 1 H, H-1′), 6.54 and 7.42 (2 br s, 2 H, $NH_2$), 7.49 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.8 Hz, $J_{5''',3'''}$ = 1.2 Hz, 1 H, H-5‴), 7.51 (m, 2 H, H-*o*-phenylene), 7.99 (s, 1 H, H-6), 8.01 (ddd, $J_{4''',3'''}$ = 7.9 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 1 H, H-4‴), 8.07 (dd, $J_{4'',5''}$ = 7.9 Hz, $J_{4'',3''}$ = 6.8 Hz, 1 H, H-4″), 8.08 (dd, $J_{5'',4''}$ = 7.9 Hz, $J_{5'',3''}$ = 1.9 Hz, 1 H, H-5″), 8.30 (m, 2 H, H-*m*-phenylene), 8.36 (dd, $J_{3'',4''}$ = 6.8 Hz, $J_{3'',5''}$ = 1.9 Hz, 1 H, H-3″), 8.59 (ddd, $J_{3''',4'''}$ = 7.9 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 0.9 Hz, 1 H, H-3‴), 8.72 (ddd, $J_{6''',5'''}$ = 4.8 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 0.9 Hz, 1 H, H-6‴).

$^{13}$C NMR (125.7 MHz, DMSO-$d_6$): δ = 40.90 ($CH_2$-2′), 61.24 ($CH_2$-5′), 70.35 (CH-3′), 85.37 (CH-1′), 87.51 (CH-4′), 107.45 (C-5), 119.40 (CH-3″), 120.60 (CH-5″), 120.85 (CH-3‴), 124.57 (CH-5‴), 127.41 (CH-*m*-phenylene), 129.42 (CH-*o*-phenylene), 135.10 (C-*i*-phenylene), 137.64 (CH-4‴), 137.69 (C-*p*-phenylene), 138.77 (CH-4″), 140.51 (CH-6), 149.54 (CH-6‴), 154.65 (C-2), 155.24 and 155.27 (C-2″,6″), 155.50 (C-2‴), 163.49 (C-4).

MS (ESI): *m*/*z* (%) = 457 (48, [M$^+$]), 480 (100, [M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{24}N_5O_4$: 458.1823; found: 458.1821.

Anal. Calcd for $C_{25}H_{23}N_5O_4$: C, 65.63; H, 5.07; N, 15.31. Found: C, 65.34; H, 5.09; N, 15.05.

**5-[4-(2,2′:6′,2″-Terpyridin-4′-yl)phenyl]-2′-deoxycytidine (7c)**
Prepared from deoxycytidine **3** and terpyridinyl boronate **2c** and after chromatography was crystallized from a mixture of DMSO–$H_2O$.

*Conditions A*: Reaction mixture was heated for 5 h. Even if the starting material was not fully consumed, product **7c** was isolated as a white solid in a yield of 28% (19 mg).

*Conditions B*: Reaction mixture was heated for 3 h. Product **7c** was isolated as a white solid in a yield of 70% (47 mg).

Mp >300 °C.

IR (KBr): 3464, 3382, 2919, 2852, 1648, 1602, 1587, 1566, 1468, 1392, 1268, 1096, 1063, 1040, 788, 744, 517 cm$^{-1}$.

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 2.11 (ddd, $J_{gem}$ = 13.5 Hz, $J_{2'b,1'}$ = 6.7 Hz, $J_{2'b,3'}$ = 6.0 Hz, 1 H, H-2′b), 2.19 (ddd, $J_{gem}$ = 13.5 Hz, $J_{2'a,1'}$ = 6.3 Hz, $J_{2'a,3'}$ = 4.0 Hz, 1 H, H-2′a), 3.55 and 3.62 (2 ddd, $J_{gem}$ = 11.9 Hz, $J_{5',OH}$ = 5.0 Hz, $J_{5',4'}$ = 3.7 Hz, 2 × 1 H, H-5′), 3.80 (td, $J_{4',5'}$ = 3.7 Hz, $J_{4',3'}$ = 2.8 Hz, 1 H, H-4′), 4.26 (m, $J_{3',2'}$ = 6.0, 4.0 Hz, $J_{3',OH}$ = 4.2 Hz, $J_{3',4'}$ = 2.8 Hz, 1 H, H-3′), 5.02 (t, $J_{OH,5'}$ = 5.0 Hz, 1 H, OH-5′), 5.22 (d, $J_{3',OH}$ = 4.2 Hz, 1 H, OH-3′), 6.25 (dd, $J_{1',2'}$ = 6.7, 6.3 Hz, 1 H, H-1′), 6.56 and 7.44 (2 br s, 2 × 1 H, $NH_2$), 7.54 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.7 Hz, $J_{5''',3'''}$ = 1.1 Hz, 2 H, H-5‴), 7.57 (m, 2 H, H-*o*-phenylene), 7.99 (m, 2 H, H-*m*-phenylene), 8.04 (s, 1 H, H-6), 8.05 (ddd, $J_{4''',3'''}$ = 7.9 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 2 H, H-4‴), 8.69 (ddd, $J_{3''',4'''}$ = 7.9 Hz, $J_{3''',5'''}$ = 1.1 Hz, $J_{3''',6'''}$ = 0.9 Hz, 2 H, H-3‴), 8.76 (s, 2 H, H-3″,5″), 8.78 (ddd, $J_{6''',5'''}$ = 4.7 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 0.9 Hz, 2 H, H-6‴).

$^{13}$C NMR (125.7 MHz, DMSO-$d_6$): δ = 40.93 ($CH_2$-2′), 61.15 ($CH_2$-5′), 70.25 (CH-3′), 85.36 (CH-1′), 87.46 (CH-4′), 107.13 (C-5), 117.98 (CH-3″,5″), 121.16 (CH-3‴), 124.81 (CH-5‴), 127.68 (CH-*m*-phenylene), 129.91 (CH-*o*-phenylene), 135.45 (C-*i*-phenylene), 136.60 (C-*p*-phenylene), 137.73 (CH-4‴), 140.68 (CH-6), 149.24 (C-4″), 149.61 (CH-6‴), 154.57 (C-2), 155.11 (C-2‴), 155.99 (C-2″,6″), 163.41 (C-4).

MS (ESI): *m*/*z* (%) = 534 (3, [M$^+$]), 535 (20, [M$^+$ + H]), 557 (100, [M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M$^+$ + H] calcd for $C_{30}H_{27}N_5O_4$: 353.2088; found: 353.2090.

**5-[4-(2,2′-Bipyridin-6-yl)phenyl]-2′-deoxyuridine (8a)**
Prepared from deoxyuridine **4** and boronate **2a**.

*Conditions A*: The reaction mixture was heated for 2 h and then the product was isolated as a white solid in a yield of 60% (34 mg).

*Conditions B*: The reaction mixture was heated for 1 h and then the product was isolated as a white compound in a yield of 75% (43 mg).

Mp 145–150 °C.

IR (KBr): 3385, 3185, 3059, 1707, 1581, 1457, 1434, 1288, 1093, 783, 599 cm$^{-1}$.

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 2.19 (ddd, $J_{gem}$ = 13.5 Hz, $J_{2'b,1'}$ = 6.4 Hz, $J_{2'b,3'}$ = 3.8 Hz, 1 H, H-2′b), 2.28 (ddd, $J_{gem}$ = 13.5 Hz, $J_{2'a,1'}$ = 6.9, $J_{2'a,3'}$ = 6.0 Hz, 1 H, H-2′a), 3.62 (ddd, $J_{gem}$ = 11.9 Hz, $J_{5'b,OH}$ = 4.7 Hz, $J_{5'b,4'}$ = 3.3 Hz, 1 H, H-5′b), 3.67 (ddd, $J_{gem}$ = 11.9 Hz, $J_{5'a,OH}$ = 5.0 Hz, $J_{5'a,4'}$ = 3.3 Hz, 1 H, H-5′a), 3.85 (td, $J_{4',5'}$ = 3.3 Hz, $J_{4',3'}$ = 2.9 Hz, 1 H, H-4′), 4.32 (m, $J_{3',2'}$ = 6.0, 3.8 Hz, $J_{3',OH}$ = 4.3 Hz, $J_{3',4'}$ = 2.9 Hz, 1 H, H-3′), 5.21 (dd, $J_{OH,5'}$ = 5.0, 4.7 Hz, 1 H, OH-5′), 5.30 (br d, $J_{3',OH}$ = 4.3 Hz, 1 H, OH-3′), 6.26 (dd,

$J_{1',2'}$ = 6.9, 6.4 Hz, 1 H, H-1′), 7.49 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.7 Hz, $J_{5''',3'''}$ = 1.2 Hz, 1 H, H-5‴), 7.76 (m, 2 H, H-*o*-phenylene), 8.01 (ddd, $J_{4''',3'''}$ = 8.0 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.9 Hz, 1 H, H-4‴), 8.04 (dd, $J_{4'',5''}$ = 7.9 Hz, $J_{4'',3''}$ = 7.2 Hz, 1 H, H-4″), 8.07 (dd, $J_{5'',4''}$ = 7.9 Hz, $J_{5'',3''}$ = 1.5 Hz, 1 H, H-5″), 8.25 (m, 2 H, H-*m*-phenylene), 8.35 (dd, $J_{3'',4''}$ = 7.2 Hz, $J_{3'',5''}$ = 1.5 Hz, 1 H, H-3″), 8.37 (s, 1 H, H-6), 8.60 (ddd, $J_{3''',4'''}$ = 8.0 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 1.0 Hz, 1 H, H-3‴), 8.72 (ddd, $J_{6''',5'''}$ = 4.7 Hz, $J_{6''',4'''}$ = 1.9 Hz, $J_{6''',3'''}$ = 1.0 Hz, 1 H, H-6‴).

$^{13}$C NMR (125.7 MHz, DMSO-$d_6$): δ = 40.42 ($CH_2$-2′), 61.14 ($CH_2$-5′), 70.37 (CH-3′), 84.81 (CH-1′), 87.75 (CH-4′), 113.01 (C-5), 119.29 (CH-3″), 120.54 (CH-5″), 120.87 (CH-3‴), 124.56 (CH-5‴), 126.57 (CH-*m*-phenylene), 128.33 (CH-*o*-phenylene), 134.40 (C-*i*-phenylene), 137.23 (C-*p*-phenylene), 137.63 (CH-4‴), 138.54 (CH-6), 138.70 (CH-4″), 149.53 (CH-6‴), 150.10 (C-2), 155.19 and 155.27 (C-2″,6″), 155.50 (C-2‴), 162.31 (C-4).

MS (ESI): *m*/*z* (%) = 459 (100, [M$^+$ + H]), 481 (33, [M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M$^+$ + H] calcd for $C_{25}H_{23}N_4O_5$: 459.1663; found: 459.1660.

Anal. Calcd for $C_{25}H_{22}N_4O_5 \cdot 3/2H_2O$: C, 61.85; H, 5.19; N, 11.54. Found: C, 61.90; H, 5.04; N, 11.35.

**5-[4-(2,2′-Bipyridin-5-yl)phenyl]-2″-deoxyuridine (8b)**
Prepared from deoxyuridine **4** and boronate **2b**.

*Conditions A*: The reaction mixture was heated for 6 h and even if the starting material was not fully consumed, the product was isolated as a white compound in a yield of 7% (4 mg).

*Conditions B*: The reaction mixture was heated for 3 h. The product was isolated as a white compound in a yield of 35% (20 mg).

Mp 188–193 °C.

IR (KBr): 3427, 2923, 1694, 1589, 1464, 1289, 1265, 1088, 873, 796, 751, 603, 463 cm$^{-1}$.

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 2.19 (ddd, $J_{gem}$ = 13.5 Hz, $J_{2'b,1'}$ = 6.4 Hz, $J_{2'b,3'}$ = 3.7 Hz, 1 H, H-2′b), 2.29 (ddd, $J_{gem}$ = 13.5 Hz, $J_{2'a,1'}$ = 6.9 Hz, $J_{2'a,3'}$ = 6.0 Hz, 1 H, H-2′a), 3.61 and 3.66 (2 br ddd, $J_{gem}$ = 11.8 Hz, $J_{5',OH}$ = 4.4 Hz, $J_{5',4'}$ = 3.3 Hz, 2 H, H-5′), 3.84 (td, $J_{4',5'}$ = 3.3 Hz, $J_{4',3'}$ = 3.1 Hz, 1 H, H-4′), 4.32 (br m, $J_{3',2'}$ = 6.0, 3.7 Hz, $J_{3',OH}$ = 4.2 Hz, $J_{3',4'}$ = 3.1 Hz, 1 H, H-3′), 5.18 (br t, $J_{OH,5'}$ = 4.4 Hz, 1 H, OH-5′), 5.29 (br d, $J_{3',OH}$ = 4.2 Hz, 1 H, OH-3′), 6.26 (dd, $J_{1',2'}$ = 6.9, 6.4 Hz, 1 H, H-1′), 7.47 (ddd, $J_{5''',4'''}$ = 7.5 Hz, $J_{5''',6'''}$ = 4.7 Hz, $J_{5''',3'''}$ = 1.2 Hz, 1 H, H-5‴), 7.73 (m, 2 H, H-*o*-phenylene), 7.83 (m, 2 H, H-*m*-phenylene), 7.97 (ddd, $J_{4''',3'''}$ = 7.9 Hz, $J_{4''',5'''}$ = 7.5 Hz, $J_{4''',6'''}$ = 1.8 Hz, 1 H, H-4‴), 8.27 (dd, $J_{4'',3''}$ = 8.3 Hz, $J_{4'',6''}$ = 2.4 Hz, 1 H, H-4″), 8.32 (s, 1 H, H-6), 8.43 (ddd, $J_{3''',4'''}$ = 7.9 Hz, $J_{3''',5'''}$ = 1.2 Hz, $J_{3''',6'''}$ = 0.9 Hz, 1 H, H-3‴), 8.48 (dd, $J_{3'',4''}$ = 8.3 Hz, $J_{3'',6''}$ = 0.9 Hz, 1 H, H-3″), 8.72 (ddd, $J_{6''',5'''}$ = 4.7 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 0.9 Hz, 1 H, H-6‴), 9.05 (dd, $J_{6'',4''}$ = 2.4 Hz, $J_{6'',3''}$ = 0.9 Hz, 1 H, H-6″).

$^{13}$C NMR (125.7 MHz, DMSO-$d_6$): δ = 40.32 ($CH_2$-2′), 61.15 ($CH_2$-5′), 70.37 (CH-3′), 84.78 (CH-1′), 87.74 (CH-4′), 112.94 (C-5), 120.60 (CH-3‴), 120.69 (CH-3″), 124.40 (CH-5‴), 126.69 (CH-*m*-phenylene), 128.73 (CH-*o*-phenylene), 133.52 (C-*i*-phenylene), 135.13 (CH-4″), 135.39 (C-5″), 135.44 (C-*p*-phenylene), 137.56 (CH-4‴), 138.43 (CH-6), 147.39 (CH-6″), 149.59 (CH-6‴), 150.08 (C-2), 154.32 (C-2″), 155.11 (C-2‴), 162.29 (C-4).

MS (ESI): *m*/*z* (%) = 459 (100, [M$^+$ + H]), 481 (96, [M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M$^+$ + H] calcd for $C_{25}H_{23}N_4O_5$: 459.1663; found: 459.1661.

Anal. Calcd for $C_{25}H_{22}N_4O_5 \cdot 1H_2O$: C, 63.02; H, 5.08; N, 11.76. Found: C, 63.32; H, 4.92; N, 11.64.

**5-[4-(2,2′:6′,2″-Terpyridin-4′-yl)phenyl]-2′-deoxyuridine (8c)**
Prepared from deoxyuridine **4** and boronate **2c**.

*Conditions A*: The reaction mixture was heated for 7 h and even if the starting material was not fully consumed, the product **8c** was then isolated as a brownish compound in a yield of 24% (16 mg).

*Conditions B*: The reaction mixture was heated for 3 h. The product was isolated as a brownish solid in a yield of 70% (47 mg).

Mp 240–249 °C.

IR (KBr): 3426, 3055, 2925, 1687, 1583, 1467, 1390, 1292, 1096, 840, 791, 749, 659, 595 cm$^{-1}$.

$^1$H NMR (500 MHz, DMSO-$d_6$): δ = 2.20 (ddd, $J_{gem}$ = 13.4 Hz, $J_{2'b,1'}$ = 6.3 Hz, $J_{2'b,3'}$ = 4.0 Hz, 1 H, H-2′b), 2.29 (ddd, $J_{gem}$ = 13.4 Hz, $J_{2'a,1'}$ = 6.7 Hz, $J_{2'a,3'}$ = 6.0 Hz, 1 H, H-2′a), 3.63 (ddd, $J_{gem}$ = 11.8 Hz, $J_{5'b,OH}$ = 4.3 Hz, $J_{5'b,4'}$ = 3.3 Hz, 1 H, H-5′b), 3.70 (ddd, $J_{gem}$ = 11.8 Hz, $J_{5'a,OH}$ = 4.3 Hz, $J_{5'a,4'}$ = 3.1 Hz, 1 H, H-5′b), 3.86 (dt, $J_{4',5'}$ = 3.3, 3.1 Hz, $J_{4',3'}$ = 3.1 Hz, 1 H, H-4′), 4.33 (m, $J_{3',2'}$ = 6.0, 4.0 Hz, $J_{3',OH}$ = 4.2 Hz, $J_{3',4'}$ = 3.1 Hz, 1 H, H-3′), 5.24 (br t, $J_{OH,5'}$ = 4.3 Hz, 1 H, OH-5′), 5.30 (br d, $J_{3',OH}$ = 4.2 Hz, 1 H, OH-3′), 6.26 (dd, $J_{1',2'}$ = 6.7, 6.3 Hz, 1 H, H-1′), 7.54 (ddd, $J_{5''',4'''}$ = 7.4 Hz, $J_{5''',6'''}$ = 4.7 Hz, $J_{5'''3'''}$ = 1.1 Hz, 2 H, H-5‴), 7.82 (m, 2 H, H-*o*-phenylene), 7.94 (m, 2 H, H-*m*-phenylene), 8.05 (s, 1 H, H-6), 8.05 (ddd, $J_{4''',3'''}$ = 7.9 Hz, $J_{4''',5'''}$ = 7.4 Hz, $J_{4''',6'''}$ = 1.8 Hz, 2 H, H-4‴), 8.68 (ddd, $J_{3''',4'''}$ = 7.9 Hz, $J_{3''',5'''}$ = 1.1 Hz, $J_{3''',6'''}$ = 0.9 Hz, 2 H, H-3‴), 8.74 (s, 2 H, H-3″,5″), 8.77 (ddd, $J_{6''',5'''}$ = 4.7 Hz, $J_{6''',4'''}$ = 1.8 Hz, $J_{6''',3'''}$ = 0.9 Hz, 2 H, H-6‴).

$^{13}$C NMR (125.7 MHz, DMSO-$d_6$): δ = 40.49 ($CH_2$-2′), 61.06 ($CH_2$-5′), 70.26 (CH-3′), 84.87 (CH-1′), 87.71 (CH-4′), 112.69 (C-5), 117.89 (CH-3″,5″), 121.15 (CH-3‴), 124.76 (CH-5‴), 126.84 (CH-*m*-phenylene), 128.80 (CH-*o*-phenylene), 134.76 (C-*i*-phenylene), 136.17 (C-*p*-phenylene), 137.69 (CH-4‴), 138.80 (CH-6), 149.25 (C-4″), 149.57 (CH-6‴), 150.05 (C-2), 155.14 (C-2‴), 155.92 (C-2″,6″), 162.26 (C-4).

MS (ESI): *m*/*z* (%) = 536 (96, [M$^+$ + H]), 558 (100, [M$^+$ + Na]).

HRMS-ESI: *m*/*z* [M$^+$ + H] calcd for $C_{30}H_{26}N_5O_5$: 536.1928; found: 536.1925.

**Fluorescence and UV-Vis Spectroscopy**

The UV-Vis spectra were measured on Varian CARY 100 Bio Spectrophotometer (ε is the molar extinction coefficient in L·mol$^{-1}$·cm$^{-1}$). The fluorescence measurements were performed on a spectrofluorometer Aminco Bowman series 2 in 220–850 nm range with Xenon source, excitation and emission wavelength scans, spectral bandwidth 1–16 nm, PMT detector, scan rate 3–6000 nm/min, and Seya-Namioka grating monochromator. We used the comparative method of Williams et al.[18] for recording fluorescence quantum yield of a sample $\phi_{SA}$ [a 10 μM solution of quinine sulfate in 0.1 M $H_2SO_4$ (in $H_2O$) was chosen as a standard: $\phi_{ST}$ = 0.54].[19] Thus, the fluorescence quantum yield of a sample $\phi_{SA}$ is calculated by the formula of Equation 1, where the subscripts ST and SA denote standard and sample respectively, ϕ is the fluorescent quantum yield, IFI the integrated fluorescence intensity, *Grad* the gradient from the plot of IFI versus absorbance A, and η the refractive index of the solvent.

$$\phi_{SA} = \phi_{ST}\left(\frac{\eta SA}{\eta ST}\right)^2\left(\frac{Grad_{SA}}{Grad_{ST}}\right) \text{ where } Grad = \frac{IFI}{A}$$

**Equation 1** Fluorescence quantum yields calculation

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