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Purine-Furan and Purine-Thiophene Conjugates

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Abstract: Furyl and thienyl moieties were introduced into a purine structure to elevate its fluorescence properties, while a trityl group was used to increase the amorphous properties of the purine compounds. The title compounds were prepared by a sequence involving a Mitsunobu, a S_NAr and a Suzuki–Miyaura reaction and their photophysical properties were studied. Quantum yields in the solution reached up to 88% but only up to 5% in the thin layer.

Keywords: purine; furan conjugates; thiophene conjugates; fluorescence; Suzuki–Miyaura reaction

1. Introduction

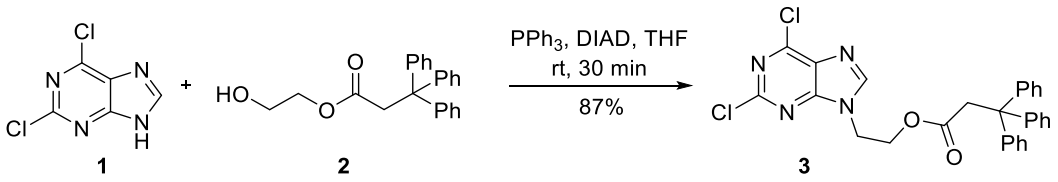
The synthesis and development of novel push–pull purine derivatives with potential as new materials and/or heavy metal sensors are currently in high demand [1]. Purines containing five-membered heterocycles in their structure show fluorescence with good quantum yields in the solution [2,3]. In 2017, functionalized purine chromophores were developed using a Stille cross-coupling between 6-bromopurine and distannyl π-linkers of benzodithiophene, thiophene, or dithienylbenzothiadiazole [4]. These chromophores showed high thermal stability, long excited state lifetimes and high quantum yields, which will permit the use of such purine derivatives in material chemistry in the future.

We have developed novel purine derivatives, containing a group at N(9) to enhance their amorphous properties [5], for study a fluorescent materials in thin films. Our approach for building push–pull structures is based on the introduction of electron donating piperidinyl groups at C(2) and C(6) of the purine cycle and by extending the conjugation through introduction of a furan or thiophene at C(8).

Various approaches have been used for the introduction of thienyl and furyl substituents at the purine C(8) position. Ozola and co-workers used palladium-catalyzed Stille cross-coupling reactions in the presence of CuO to install the 2- and 3-furanyl rings [6]. The Sedlaček group also successfully introduced a 2-thienyl group to the 9-substituted 2,6-diaminopurine using a Stille cross-coupling and a 3-thienyl group using a Suzuki–Miyaura reaction [7]. 2-Iodothiophene was used for direct cross-coupling at the purine C(8) position in the presence of CuI and $Pd(OAc)_2$ giving the 8-substitued product in 15% yield [8].

2. Results and Discussion

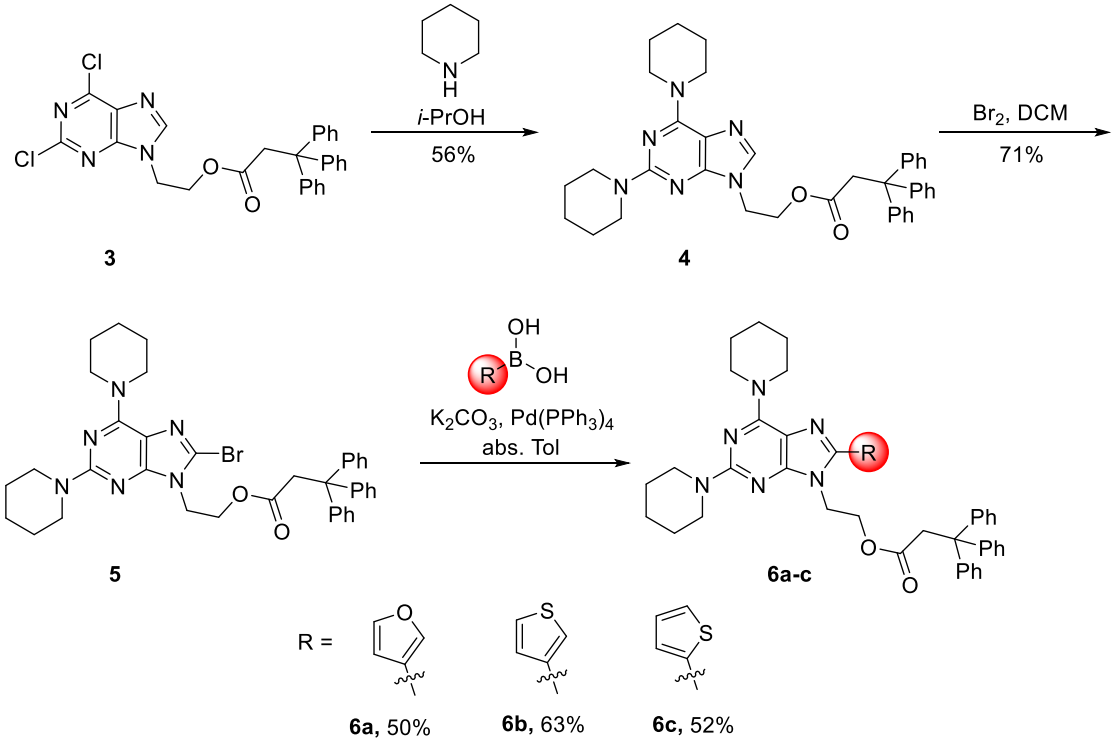
The Mitsunobu reaction between 2,6-dichloropurine **1** and 2-hydroxyethyl 3,3,3-triphenylpropanoate **2** led to the C(9)-substituted 2,6-dichloropurine **3** (Scheme 1) which was used as a starting material in subsequent steps.



Scheme 1. The Mitsunobu reaction.

In the S_NAr reaction of 2,6-dichloropurine **3** with piperidine, the most reactive chlorine atom at C(6) was replaced followed by the less active C(2) chlorine. A complete conversion to 2-chloro-6-piperidinylpurine derivative was observed by HPLC over a period of 15 min, followed by the slower substitution at C(2) of the purine giving product **4** in 56% yield. In isopropanol, this reaction runs without any significant formation of side-products.

The 8-bromo derivative **5** was obtained by bromination of the 8-position of the purine ring in 71% yield. Subsequently, the Suzuki–Miyaura reaction with the furyl- and thienylboronic acids resulted in the 2,6,8-tri-substituted purine derivatives **6a–c** in 50–63% yields (Scheme 2).

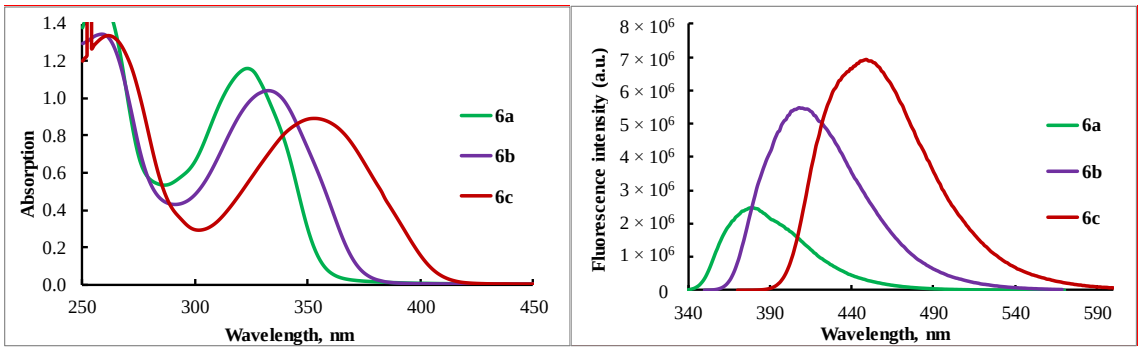


Scheme 2. Synthesis of 8-furyl- and 8-thienylpurine derivatives.

Fluorescence quantum yields were measured for compounds **6a–c** in solution (DCM) and as thin films. The quantum yields were much lower in the films than in solution. Compound **6c** exhibited the highest quantum yield (0.88, solution) among the three synthesized compounds. In the case of compounds **6b** and **6c**, there is a significant drop in fluorescence quantum yields in the thin film in comparison to the solution, from 0.60 and 0.88 to 0.04 and 0.05, respectively (Table 1). Typically, amorphous thin films are characterized by a significant degree of disorder which might result in the concentration induced or aggregation induced fluorescence self-quenching [9–16]. Compounds **6a–c** exhibited an absorption maximum around 320–350 nm and an emission maximum around 380–450 nm when excited at 320–350 nm (Figure 1).

Table 1. Photophysical properties of target compounds **6a–c**.

Compound	Solvent/Thin Layer	λ_{abs}, nm	log ε	λ_{em}, nm	QY
6a	DCM	323	4.4	380	0.18
	Thin layer	326	-	382	<0.01
6b	DCM	333	4.3	408	0.60
	Thin layer	336	-	415	0.04
6c	DCM	353	4.3	449	0.88
	Thin layer	356	-	445	0.05

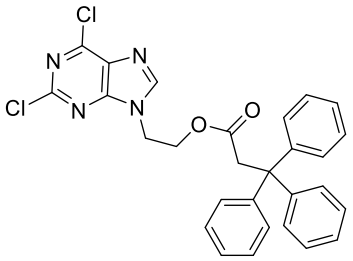


(a) (b)

Figure 1. (**a**) Absorption and (**b**) emission spectra for 0.5 × 10^{-5} M **6a–c** in DCM.

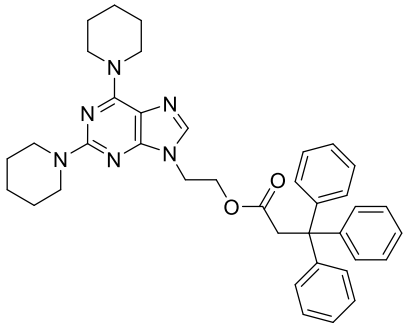
3. Materials and Methods

^{1}H- and ^{13}C-NMR spectra were recorded at 300 and 75.5 MHz, respectively. The proton signals for residual non-deuterated solvents (δ 7.26 for $CDCl_3$ and δ 2.50 for DMSO-d_6) and carbon signals (δ 77.1 for $CDCl_3$ and δ 39.5 for DMSO-d_6) were used as internal references for ^{1}H- and ^{13}C-NMR spectra, respectively (see Supplementary Materials). Coupling constants are reported in Hz. Infrared spectra were recorded using a Perkin Elmer Spectrum BX spectrometer (PerkinElmer, Inc., Hebron, KY, USA). Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} aluminum plates precoated with a 0.25 mm layer of silica gel. For HPLC analyses Agilent Technologies 1200 Series system (Agilent Technologies, Foster City, CA, USA) was used (XBridge C18 column, 4.6 × 150 mm, particle size 3.5 µm) with a flow rate of 1 mL/min; eluent system: 0.01% TFA water solution/MeCN (95:5, *v/v*). The content of MeCN was changed as follows: 20–95–95–20% (0–5–10–12 min). The wavelength of detection was 260 nm. The UV–vis absorption spectra of compounds were acquired using a Perkin-Elmer 35 UV–vis spectrometer. Emission spectra were measured on a QuantaMaster 40 steady state spectrofluorometer (Photon Technology International, Inc., Ford, West Sussex, UK). Absolute photoluminescence quantum yields were determined using a QuantaMaster 40 steady state spectrofluorometer (Photon Technology International, Inc.) equipped with a 6-inch integrating sphere by LabSphere, using a florescence standard of quinine sulfate in 0.1 M H_2SO_4 as the reference.

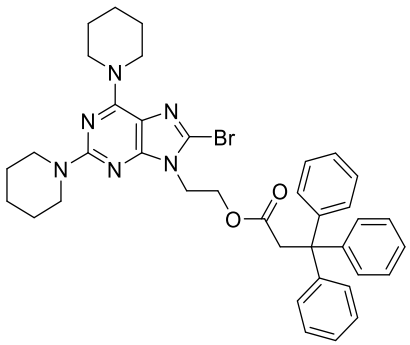


2-(2,6-Dichloro-9H-purin-9-yl)ethyl 3,3,3-triphenylpropanoate (**3**); To a solution of 2,6-dichloropurine **1** (1.00 g, 5.26 mmol) in THF (15 mL), compound **2** (2.00 g, 5.78 mmol), Ph_3P (1.66 g, 6.31 mmol) and

DIAD (0.41 mL, ρ = 1.03 g/cm^3, 6.31 mmol) were added. The resulting solution was stirred at 20 °C for 12 h. The reaction mixture was filtered, washed with cold MeOH (2 × 5 mL) and dried under reduced pressure. Yield: 2.39 g, 87%. Colorless powder, R_f = 0.28 (DCM/MeCN = 20:1). HPLC: t_R = 7.31 min, purity 93%. IR (KBr) ν (cm^{-1}): 2928, 1746, 1593, 1551, 1343, 1232, 1142. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.68 (s, 1H, H-C(8)), 7.30–7.12 (m, 15H, 15 × H-C(Ph)), 4.22–4.10 (m, 4H, 2 × (-CH_2-)), 3.71 (s, 2H, (-CH_2-)). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm): 170.4, 153.2, 153.1, 152.0, 146.2, 146.1, 130.8, 129.1, 128.1, 126.6, 61.7, 55.9, 46.0, 43.3. HRMS (ESI): calcd for [$C_{28}H_{22}Cl_2N_4O_2$ + H]$^+$ 517.1193, found 517.1197.

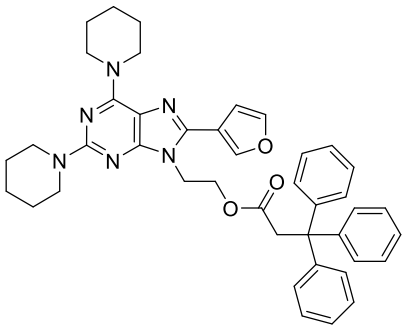


2-[2,6-Di(piperidin-1-yl)-9H-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**4**); To a solution of compound **3** (1.50 g, 3.25 mmol) in *i*-PrOH (8 mL) piperidine (1.52 mL, 15.60 mmol) was added. The resulting reaction mixture was stirred at 100 °C for 48 h, evaporated under reduced pressure and purified by silica gel column chromatography (DCM/MeCN, gradient 0–3%). Yield: 300 mg, 42%. Colorless powder, R_f = 0.56 (DCM/MeCN = 20:1). HPLC: t_R = 7.93 min, purity 90%. IR (KBr) ν (cm^{-1}): 2931, 2851, 1742, 1595, 1567, 1482, 1444, 1316, 1245, 1206, 1142, 1022. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.31–7.16 (m, 16H, 15 × H-C(Ph), H-C(8)), 4.27–4.06 (m, 6H, 3 × (-CH_2-)), 4.02–3.94 (m, 2H, (-CH_2-)), 3.79–3.68 (m, 6H, 3 × (-CH_2-)), 1.78–1.54 (m, 12H, 6 × (-CH_2-)). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm): 170.7, 158.9, 154.0, 153.1, 146.4, 135.8, 129.2, 127.8, 126.4, 113.7, 62.3, 55.9, 46.3, 46.2, 45.6, 41.9, 26.2, 25.9, 25.1, 25.0. HRMS (ESI): calcd for [$C_{38}H_{42}N_6O_2$ + H]$^+$ 615.3442, found 615.3426.

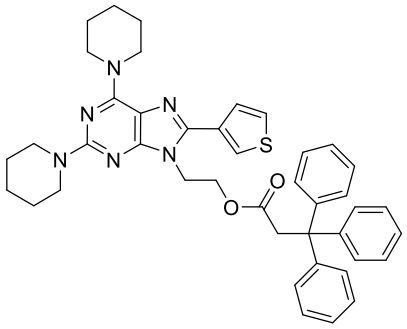


2-[8-Bromo-2,6-di(piperidin-1-yl)-9H-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**5**); To a solution of compound **4** (1.50 g, 3.25 mmol) in DCM (10 mL) bromine was added (2.60 mL, 32.50 mmol). The resulting reaction mixture was stirred at 23 °C for 1 h, evaporated under reduced pressure and purified by silica gel column chromatography (DCM/MeCN, gradient 0–2%). Yield: 200 mg, 71%. Colorless powder, R_f = 0.56 (DCM/MeCN = 20:1). HPLC: t_R = 11.79 min, purity 97%. IR (KBr) ν (cm^{-1}): 2931, 2851, 1743, 1596, 1568, 1482, 1444, 1311, 1245, 1213, 1142, 1023. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.33–7.17 (m, 15H, 15 × H-C(Ph)), 4.22–3.98 (m, 8H, 4 × (-CH_2-)), 3.77–3.63 (m, 6H, 3 × (-CH_2-)), 1.77–1.51 (m, 12H, 6 × (-CH_2-)). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm): 170.7, 158.2, 152.8, 146.5, 129.3, 127.9, 126.4, 120.4, 114.3, 67.2, 61.6, 55.9, 46.3 (2C) (determined by the H-C HSQC spectrum), 45.7, 42.7, 29.8, 26.2, 25.9, 25.1, 25.0. HRMS (ESI): calcd for [$C_{38}H_{41}N_6O_2Br$ + H]$^+$ 695.2534, found 695.2527.

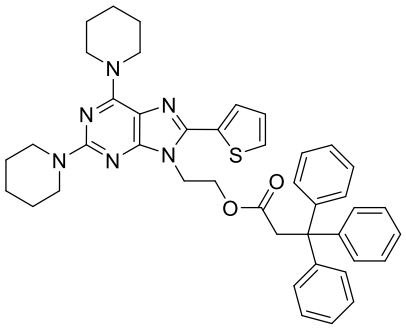
General Procedure for the Suzuki–Miyaura Reaction



2-[8-(Furan-3-yl)-2,6-di(piperidin-1-yl)-9H-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**6a**); To a solution of compound **5** (500 mg, 0.72 mmol) in anhydrous toluene (10 mL) 3-furanylboronic acid (161 mg, 1.40 mmol), K_2CO_3 (200 mg, 1.40 mmol), and $Pd(PPh_3)_4$ (41 mg, 0.08 mmol) were added. The resulting reaction mixture was stirred for 4 h at 110 °C, then evaporated to dryness. The residue was dissolved in DCM (20 mL), washed with saturated aqueous $NaHCO_3$ (5 mL) and water (5 mL). The organic layer was dried over anhyd. Na_2SO_4, evaporated under reduced pressure and purified by silica gel column chromatography (DCM/MeCN, gradient 0–2%). Yield: 300 mg, 52%. Yellow powder, R_f = 0.55 (DCM/MeCN = 9:1). HPLC: t_R = 8.83 min, purity 91%. IR (KBr) ν (cm^{-1}): 2929, 2850, 1743, 1596, 1563, 1480, 1443, 1314, 1208, 1142, 1022. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.79 (s, 1H, H-C(furyl)), 7.49 (s, 1H, H-C(furyl)), 7.34–7.11 (m, 15H, H-C(Ph)), 6.84 (s, 1H, H-C(furyl)), 4.29–4.02 (m, 8H, 4 × (-CH_2-)), 3.82–3.65 (m, 4H, 2 × (-CH_2-)), 3.63 (s, 2H, (-CH_2-)), 1.80–1.52 (m, 12H, 6 × (-CH_2-)). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm): 170.7, 158.7, 154.8, 153.6, 146.3, 143.3, 141.1, 139.1, 129.2, 127.9, 126.3, 117.2, 113.7, 110.7, 61.7, 55.9, 46.2, 46.1, 45.6, 41.3, 26.2, 25.9, 25.2, 25.1. HRMS (ESI): calcd for [$C_{42}H_{44}N_6O_3$ + H]$^+$ 681.3548, found 681.3545.



2-[2,6-Di(piperidin-1-yl)-8-(3-thienyl)-9H-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**6b**); Product **6b** was obtained by the general synthetic procedure for the Suzuki–Miyaura reaction: compound **5** (500 mg, 0.96 mmol), 3-thienylboronic acid (113 mg, 1.00 mmol), K_2CO_3 (200 mg, 1.40 mmol) and $Pd(PPh_3)_4$ (55 mg, 0.05 mmol). The reaction mixture was stirred for 4 h at 110 °C and the crude product was purified by silica gel column chromatography (DCM/MeCN, gradient 0–3%). Yield: 320 mg, 63%. Colorless powder, R_f = 0.62 (DCM/MeCN = 20:1). HPLC: t_R = 9.14 min, purity 95%. IR (KBr) ν (cm^{-1}): 2930, 2850, 1743, 1595, 1580, 1548, 1480, 1443, 1313, 1209, 1142, 1087. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.59 (d, 1H, ^4J = 2.8 Hz, H-C(thienyl)), 7.53 (d, 1H, ^3J = 4.6 Hz, H-C(thienyl)), 7.39 (dd, 1H, ^4J = 2.8 Hz, ^3J = 4.6 Hz H-C(thienyl)), 7.30–7.13 (m, 15H, 15 × H-C(Ph)), 4.30–4.09 (m, 8H, 4 × (-CH_2-)), 3.83–3.71 (m, 4H, 2 × (-CH_2-)), 3.59 (s, 2H, (-CH_2-)), 1.79–1.56 (m, 12H, 6 × (-CH_2-)). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm): 170.7, 158.7, 154.8, 153.8, 146.4, 141.8, 131.7, 129.2, 128.5, 127.9, 126.4, 126.0, 124.5, 113.6, 61.9, 55.9, 46.1, 46.1, 45.7, 41.6, 26.3, 25.9, 25.2, 25.1. HRMS (ESI): calcd for [$C_{42}H_{44}N_6O_2S$ + H]$^+$ 697.3319, found 697.3332.



2-[2,6-Di(piperidin-1-yl)-8-(2-thienyl)-9H-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**6c**); Product **6c** was obtained by the general synthetic procedure for the Suzuki–Miyaura reaction: compound **5** (600 mg, 0.86 mmol), 2-thienylboronic acid (220 mg, 1.70 mmol), K_2CO_3 (238 mg, 1.70 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.08 mmol). The reaction mixture was stirred for 4 h at 110 °C and the crude product was purified by silica gel column chromatography (DCM/MeCN, gradient 0–1%). Yield: 300 mg, 50%. Colorless powder, R_f = 0.60 (DCM/MeCN = 9:1). HPLC: t_R = 9.63 min, purity 94%. IR (KBr) ν (cm^{-1}): 2928, 2842, 1742, 1594, 1577, 1545, 1481, 1442, 1314, 1243, 1206, 1141, 1023. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.39–7.32 (m, 2H, H-C(thienyl)), 7.30–7.13 (m, 15H, 15 × H-C(Ph),), 7.41–7.35 (m, 1H, H-C(thienyl)), 4.35–4.10 (m, 8H, 4 × (-CH_2-)), 3.82–4.69 (m, 4H, 2 × (-CH_2-)), 3.59 (s, 2H, (-CH_2-)), 1.79–1.53 (m, 12H, 6 × (-CH_2-)). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ (ppm): 170.6, 158.7, 155.0, 153.6, 146.4, 140.0, 133.3, 129.2, 127.8, 127.7, 127.1, 126.4, 126.3, 113.8, 61.8, 55.8, 46.2, 46.1, 45.6, 41.6, 26.2, 25.9, 25.1, 25.1. HRMS (ESI): calcd for $[C_{42}H_{44}N_6O_2S + H]^+$ 697.3319, found 697.3319.

4. Conclusions

A method for the synthesis of purine derivatives modified with furan and thiophene heterocycles at C(8) has been developed. The key step was a Suzuki–Miyaura reaction and the products were obtained in 50–63% yields.

Target compounds exhibited strong fluorescence in solution with emission maxima at 380–480 nm. The fluorescence quantum yields in DCM solution reached up to 88% and in the thin layer films up to 5%.

Supplementary Materials: The following are available online at http://www.mdpi.com/1422-8599/2018/4/M1024/s1. ^{1}H- and ^{13}C-NMR spectra of 2-(2,6-dichloro-9*H*-purin-9-yl)ethyl 3,3,3-triphenylpropanoate (**3**), 2-[2,6- di(piperidin-1-yl)-9*H*-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**4**), 2-[8-bromo-2,6-di(piperidin-1-yl)-9*H*-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**5**), 2-[8-(furan-3-yl)-2,6-di(piperidin-1-yl)-9*H*-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**6a**), 2-[2,6-di(piperidin-1-yl)-8-(3-thienyl)-9*H*-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**6b**) and 2-[2,6-di(piperidin-1-yl)-8-(2-thienyl)-9*H*-purin-9-yl]ethyl 3,3,3-triphenylpropanoate (**6c**); IR spectra of compounds **3**, **4**, **5**, **6a**, **6b**, and **6c**; results tables of absorption and emission spectra of compounds **6a**, **6b**, and **6c** in DCM solution and in thin film.

Author Contributions: M.T. designed the experiments; Z.K. performed the experiments; Z.K., I.N., and M.T. analyzed the IR, HRMS, and NMR spectral data and wrote the manuscript. All authors read and approved the final manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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