Sulfuric Acid Functionalized Silica-Coated Magnetic Nanoparticles: Preparation and Application in Synthesis of Mono-, Di- and Tri[bis(6-aminopyrimidinyl)methanes]

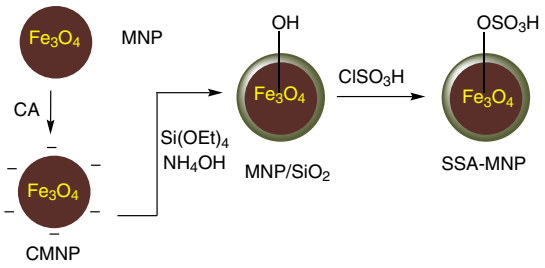
Ali Reza Karimi,* Zeinab Dalirnasab, Marzie Karimi, Fatemeh Bagherian

Department of Chemistry, Faculty of Science, Arak University, Arak 38156-8-8349, Iran
Fax +98(861)4173406; E-mail: a-karimi@araku.ac.ir

Received: 24.06.2013; Accepted after revision: 16.08.2013

Abstract: Sulfuric acid functionalized silica-coated magnetic nanoparticles (SSA-MNPs) were prepared by a simple method and evaluated as efficient catalysts for the condensation reaction of 6-amino-1,3-dimethyluracil with mono-, di-, or trialdehydes to give the corresponding mono-, di- and tri[bis(6-aminopyrimidinyl)methanes]. The catalyst was simply recycled by the use of an external magnetic field and could be reused five times without significant loss of activity or mass.

Key words: nanostructures, catalysis, condensation, aldehydes, heterocycles, ultrasound



Scheme 1 Preparation of sulfuric acid functionalized silica-coated magnetic nanoparticles (SSA-MNPs); CA = citric acid; CMNP = citrate-functionalized MNP.

Recently, much attention has been focused on the preparation of acid-functionalized catalysts. Zolfigol prepared sulfuric acid functionalized silica (SSA) by treatment of silica gel with chlorosulfonic acid,[1] and SSA has since been shown to be an extremely useful catalyst in various organic transformations.[2] The preparation of acid-functionalized magnetic nanoparticle (MNP) catalysts has also become a significant area of research that has attracted worldwide attention.[3–6] As acid catalysts, magnetic nanoparticles have many advantages, such as a large surface area, low mass-transfer resistance, and ease of recovery by the use of a magnetic field. The surfaces of silica-coated MNPs can be functionalized to accommodate a wide variety of acid catalysts, for example, by oxidation of immobilized thiols to form sulfonic acids, hydrolysis of immobilized sulfonic acid chlorides, sulfonation of supported phenyl groups, ring opening of perfluorosulfonic acid sulfones, immobilization of perfluorosulfonic acid triethoxysilanes,[3] grafting of chlorosulfuric acid onto amino-functionalized Fe_3O_4 nanoparticles,[6] or reaction of silica-coated γ-Fe_2O_3 with chlorosulfonic acid.[7]

We synthesized sulfuric acid functionalized silica-coated magnetic nanoparticles (SSA-MNPs) by functionalization of silica-coated magnetic nanoparticles with chlorosulfonic acid (Scheme 1), and we examined their catalytic behavior in the reaction of 6-amino-1,3-dimethyluracil with various aldehydes.

6-Amino-1,3-dimethyluracil and its fused derivatives[8] are versatile building blocks for the synthesis of several bioactive nitrogen-containing heterocycles.[9] 6-Aminouracils are key intermediates in the synthesis of purines, which constitute the basic nuclei of many drugs, such as caffeine, penciclovir, theobromine, and theophylline.[10] Organic compounds containing pyrimidine scaffolds are important targets and are known to show diverse biological and pharmaceutical activities.[11] Heterocyclic structures bearing a pyrimidine moiety, such as dihydropyrimidines,[12] furopyrimidines,[13] and pyrazolopyrimidines,[14] have long been important in the pharmaceutical industry.

The reaction of 6-amino-1,3-dimethyluracil with aldehydes affords the corresponding bis(6-aminopyrimidinyl)methanes, a useful class of organic compounds. Because of the pharmacological interest in pyrimidinones, synthesis of such compounds has become very important, and was initially achieved by the reaction of 6-aminouracils with aldehydes.[15]

2,4,6-Trisubstituted 1,3,5-triazine derivatives have found widespread applications in diverse fields, such as textiles, plastics, rubber,[16] and electroluminescent devices.[17] The compounds have been used in the development of organic light-emitting diodes,[18] liquid crystalline materials,[19] and nonlinear optical materials.[20] Therefore, the development of techniques for the synthesis and functionalization of 2,4,6-trisubstituted 1,3,5-triazines has been a focus of research over many years.[16,21]

Although the pseudo three-component reaction of 6-aminouracil with monoaldehydes has been previously investigated,[15] surprisingly there are no reports on the reaction of 6-aminouracils with di- or trialdehydes to give di- and tri[bis(6-aminopyrimidinyl)methanes], respectively. Because of the biological activity of bis(6-aminopyrimidi-

SYNTHESIS 2013, 45, 3300–3304
Advanced online publication: 27.09.2013
DOI: 10.1055/s-0033-1339761; Art ID: SS-2013-Z0436-OP

nyl)methanes and our interest in the synthesis of heterocyclic compounds,[22] we have developed a simple and efficient method for the preparation of mono-, di-, and tri[bis(6-aminopyrimidinyl)methanes] by using SSA-MNPs as efficient catalysts for the pseudo three-, five- and seven-component reactions of 6-amino-1,3-dimethyluracil with mono-, di- and trialdehydes, respectively, in the presence of ultrasound at 50 °C (Scheme 2).

To optimize the reaction conditions, we investigated the typical reaction of 4-chlorobenzaldehyde (**2a**; 1 mmol) with 6-amino-1,3-dimethyluracil (2 mmol) under various conditions (Table 1).

Initially, we examined the effect of the catalyst concentration on the yield by varying the amount of catalyst from 0 to 0.15 g in the presence of ultrasound at 50 °C. After one hour, with 0, 0.03, 0.06, 0.1, or 0.15 gram of SSA-MNP, we obtained yields of 10, 65, 75, 95, and 83%, respectively (Table 1, entries 1–5). Next we examined the role of the solvent (entries 4 and 6–10). The reaction barely proceeded in tetrahydrofuran (entry 9), whereas the reaction in ethanol (entry 4) gave the product in high yield with nearly complete conversion. We therefore selected ethanol as the reaction solvent for subsequent investigations. The optimal reaction conditions involve the use of 0.1 gram of SSA-MNP in ethanol at 50 °C.

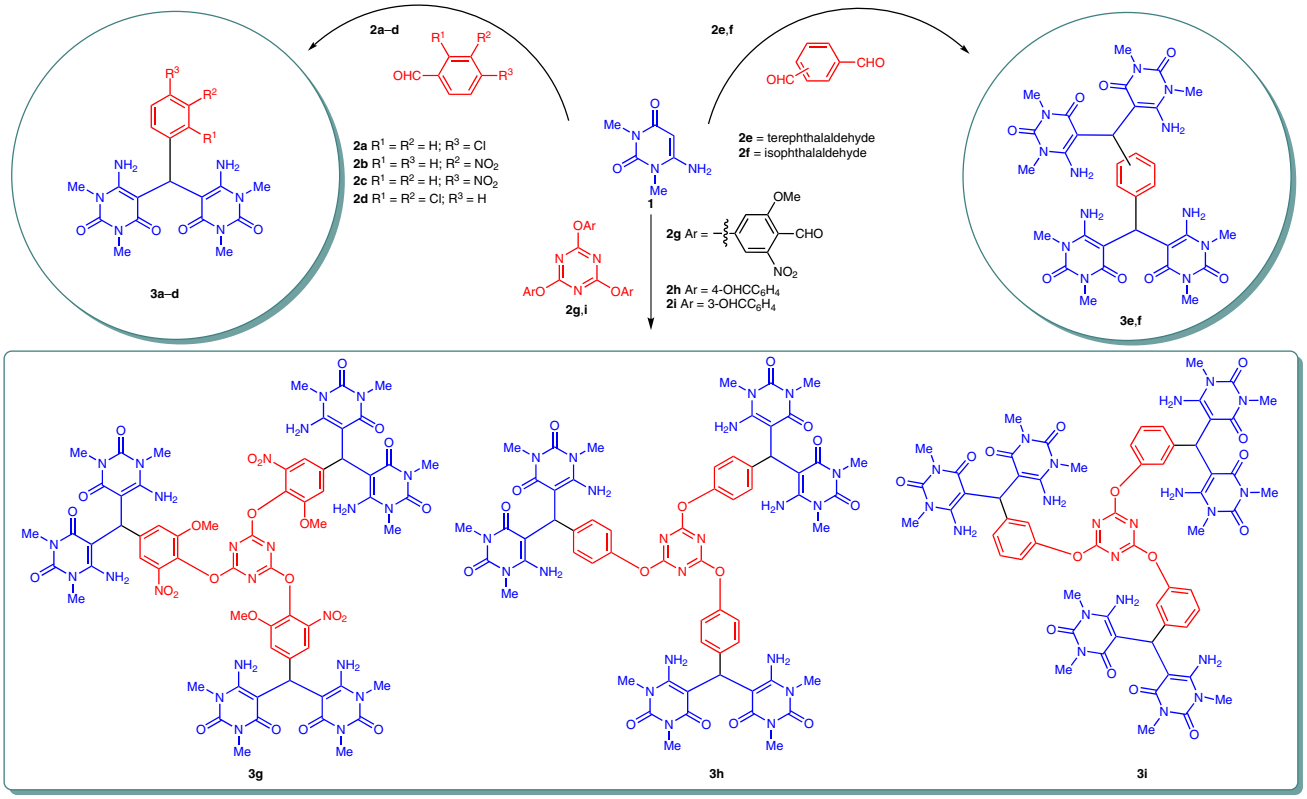
We next examined the reactions of a wide range of monoaldehydes **2a–d**, dialdehydes **2e**,**f**, and trialdehydes **2g–i** to establish the scope of the catalytic transformation (Scheme 2 and Table 2)

Table 1 Optimization of the Synthesis of **3a**[a]

Entry	SSA-MNPs (g)	Solvent	Yield (%)
1	–	EtOH	10
2	0.03	EtOH	65
3	0.06	EtOH	75
4	0.10	EtOH	95
5	0.15	EtOH	79
6	0.10	H_2O	30
7	0.10	MeCN	85
8	0.10	DMF	55
9	0.10	THF	20
10	0.10	DMSO	40

[a] Reaction conditions: 4-ClC_6H_4CHO (1 mmol), 6-amino-1,3-dimethyluracil (2 mmol), 50 °C, 1 h, ultrasound.

The mono[bis(6-aminopyrimidinyl)methanes] **3a–d** were obtained in high yields by the pseudo-three-component condensation of 6-amino-1,3-dimethyluracil (2 mmol) with monoaldehydes **2a–d** (1 mmol), respectively, in the



Scheme 2 Synthesis of mono-, di- and tri[bis(6-aminopyrimidinyl)methanes] **3a–i** catalyzed by SSA-MNPs

Table 2 SSA-MNP-Catalyzed Synthesis of Mono-, Di- and Tri[bis(6-aminopyrimidinyl)methanes][a]

Entry	Aldehyde	Product	Time (h)	Yield (%)	mp (°C)
1	**2a**	**3a**	1	95	<300[b]
2	**2b**	**3b**	1	90	248–250
3	**2c**	**3c**	1	92	<300[b]
4	**2d**	**3d**	1	87	275–277
5	**2e**	**3e**	4	83	<300
6	**2f**	**3f**	4	80	284–286
7	**2g**	**3g**	5	87	291–294
8	**2h**	**3h**	5	88	285–288
9	**2i**	**3i**	5	85	265–268

[a] Reaction conditions: EtOH, 50 °C, ultrasound.
[b] Lit.15 >300 °C.

presence of SSA-MNPs (0.1 g) as heterogeneous catalyst in ethanol (8 mL) at 50 °C with ultrasound irradiation. The di[bis(6-aminopyrimidinyl)methanes] **3e–f** were similarly prepared by pseudo-five-component reaction of 6-amino-1,3-dimethyluracil (5 mmol) with terephthalaldehyde (**2e**; 1 mmol) or isophthalaldehyde (**2f**; 1 mmol) in the presence of SSA-MNPs (0.1 g) in ethanol (15 mL). The same procedure was used to prepare the tri[bis(6-aminopyrimidinyl)methanes] **3g–i** by pseudo-seven-component reaction of trialdehydes **2g–i** (1 mmol), respectively, with 6-amino-1,3-dimethyluracil (7 mmol). All products were characterized by means of melting point measurements and by Fourier-transform IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. No byproducts were formed, and the time required for the reactions was reduced from four hours to one hour by the use of SSA-MNP catalysts.

The sulfuric acid functionalized silica magnetic nanoparticles (SSA-MNPs) were prepared by a simple one-step procedure through direct reaction of chlorosulfonic acid with silica-coated magnetite (Fe_3O_4) MNPs. The silica-coated MNPs were prepared by modifying the surfaces of the magnetite nanoparticles with negatively charged citrate groups, then coating with silica by reaction with tetraethyl orthosilicate.

The Fourier-transform IR spectra of the bare MNPs, citrate-functionalized MNPs, silica-coated MNPs, and SSA-MNPs all showed peaks at 3300, 561, and 578 cm^{-1}, which are assigned to –OH groups and Fe–O groups, respectively. Absorptions at 1558 and 1396 cm^{-1} were assigned to binding of citric acid to the iron oxide nanoparticle surfaces.[23] Peaks at 1091 and 1087 cm^{-1} corresponded to the Si–O stretch, and the peak at 945 cm^{-1} corresponded to the Si–OH stretch in the amorphous silica shell. The formation of SSA-MNPs was confirmed by the presence of SO_2 peaks at 1039 and 1138 cm^{-1}. In addition, the intensity of the peak corresponding to the Fe–O group in SSA-MNPs decreased and a broad bond corresponding to O–H stretching of the SO_3H group appeared at 3300–3600 cm^{-1}.

The sizes of nanoparticles were determined by scanning electron microscopy (SEM). The average size was about 39 nm. The thermal properties of the SSA-MNPs were analyzed by thermogravimetry at 20–850 °C under nitrogen. The primary weight loss at temperatures up to 160 °C was related to the removal of physically adsorbed solvent. The rate of weight loss between 160 and 540 °C was relatively slow, showing that SSA-MNPs have a high thermal stability. The maximum rate of lost weight of the SSA-MNPs began at 540 °C. There was a well-defined mass weight loss of 39% between 160 and 670 °C; this was ascribed to the breakdown of the sulfuric acid moieties, in agreement with the results of elemental analysis of SSA-MNPs (S, 14.88%).

X-ray diffraction patterns of the SSA-MNPs showed that the cubic structure of the magnetite was well preserved after introduction of the silica and sulfuric acid functionality.[24] The intensity of the 35.7° reflection of the SSA-MNPs was decreased after introduction of the sulfuric acid group.

The SSA-MNPs showed a high catalytic activity and could be recovered and recycled several times without significant loss of activity. In conclusion, we prepared magnetically recyclable sulfuric acid functionalized silica magnetic nanoparticles (SSA-MNPs) and examined their catalytic activity. The SSA-MNPs were prepared by a simple procedure through direct functionalization of silica-coated iron(III) oxide nanoparticles with chlorosulfonic acid. The SSA-MNPs are nontoxic, can be dispersed in various solvents, and can be readily recovered by using a magnet. In the condensation reaction of 6-amino-1,3-dimethyluracil with aldehydes, the SSA-MNP catalysts gave a short reaction time coupled with a simple reaction procedure; the use of SSA-MNPs as inexpensive and re-

usable catalysts make this method one of the most efficient for the synthesis of bis(6-aminopyrimidinyl)methanes.

All reagents were of the best available purity and were used without further purification. Fe_3O_4 nanoparticles (MNP), citric acid modified nanoparticles (CMNPs), and silica-coated magnetic nanoparticles (Fe_3O_4/SiO_2 MNPs) were prepared according to the literature procedure.[25] Trialdehydes **2g–i** were prepared according to the literature procedure.[26] The products **3a** and **3c** are known compounds and their structures were deduced by comparison of their physical and spectroscopic data (IR and ^{1}H NMR) with previously reported values.[15] New products were characterized by elemental analysis and by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Fourier-transform IR spectra were recorded on a Unicom Galaxy Series FTIR 5000 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts (δ) are reported relative to TMS as an internal standard. Mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer operated in the EI mode. Elemental analyses were carried out on a Vario EL III elemental analyzer. Sonication was performed in a Struers Metason 200 HT ultrasonic cleaner with a frequency of 50–60 Hz and an output power of 140 W.

^{13}C NMR spectra of products **3e**, **3g**, and **3i** are not reported because these compounds were insoluble in common organic solvents.

Sulfuric Acid Functionalized Silica-Coated Magnetic Nanoparticles (SSA-MNPs)

Silica-coated magnetic nanoparticles (1 g) were added to a two-necked flask fitted with a constant-pressure dropping funnel and a tube to remove the HCl gas that formed, by conducting it to an adsorbent solution. $ClSO_3H$ (1.5 mL) was added dropwise over 30 min at r.t. and the mixture was mechanically stirring slowly. HCl gas immediately evolved, and the mixture was shaken well for 30 min. The resulting SSA-MNPs were washed with acetone (10 mL) and distilled H_2O (20 mL) to remove excess $ClSO_3H$ and finally dried in an oven at 60 °C for 6 h.

Di- and Tri[bis(6-aminopyrimidinyl)methanes] 3e–i; General Procedure

A mixture of dialdehyde **2e–f** or trialdehyde **2g–i** (1 mmol), 6-amino-1,3-dimethyluracil (5 mmol for **2e–f** or 7 mmol for **2g–i**) and SSA-MNPs (0.1 g) in EtOH (8 mL) was irradiated with ultrasound (50–60 Hz, 140 W) at 50 °C for an appropriate time (see Table 2). When the reaction was complete (TLC), the SSA-MNPs were removed by using an external magnetic field. The solution was then concentrated and left to evaporate slowly. H_2O–EtOH (5:1; 30 mL) was added and the resulting solid products were collected by filtration, washed with H_2O–EtOH (5:1, 30 mL) to remove excess 6-amino-1,3-dimethyluracil.

5,5′-[(3-Nitrophenyl)methylene]bis[6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione] (3b)

White solid; yield: 398 mg (90%); mp 248–250 °C.

IR (KBr): 3352, 3119, 2955, 2831, 1689, 1662, 1606, 1591, 1502, 1344 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.34 (s, 6 H, N–CH_3), 3.36 (s, 6 H, N–CH_3), 5.66 (s, 1 H, $CH_{methine}$), 7.30 (br s, 2 H, NH_2), 7.51 (t, J = 7.8 Hz, 2 H, H_{arom}), 7.59 (d, J = 7.6 Hz, 1 H, H_{arom}), 7.86 (s, 2 H, NH_2), 7.99 (d, J = 7.8 Hz, 1 H, H_{arom}).

Anal. Calcd for $C_{19}H_{21}N_7O_6$: C, 51.47; H, 4.77; N, 22.11. Found: C, 51.22; H, 4.69; N, 22.34.

5,5′-[(2,4-Dichlorophenyl)methylene]bis[6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione] (3d)

White solid; yield: 407 mg (87%); mp 275–277 °C.

IR (KBr): 3358, 3159, 3049, 2955, 1689, 1678, 1595, 1500 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.33 (s, 6 H, N–CH_3), 3.36 (s, 6 H, N–CH_3), 5.49 (s, 1 H, $CH_{methine}$), 6.97 (br s, 2 H, NH_2), 7.28 (d, J = 8.4 Hz, 1 H, H_{arom}), 7.34 (d, J = 8.4 Hz, 1 H, H_{arom}), 7.43 (s, 1 H, H_{arom}), 7.48 (br s, 2 H, NH_2).

MS (EI, 70 eV): m/z = 466 [M$^+$].

Anal. Calcd for $C_{19}H_{20}C_{l2}N_6O_4$: C, 48.83; H, 4.31; Cl, 15.17; N, 17.98. Found: C, 48.97; H, 4.44; Cl, 15.06; N, 18.11.

5,5′,5″,5‴-[1,4-Phenylenedi(methanetriyl)]tetrakis[6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione] (3e)

White solid; yield: 595 mg (83%); mp >300 °C

IR (KBr): 3396, 3167, 2953, 1666, 1608, 1589, 1494 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.31 (s, 12 H, N–CH_3), 3.34 (s, 12 H, N–CH_3), 5.53 (s, 2 H, $CH_{methine}$), 6.90 (s, 4 H, H_{arom}), 7.33 (br s, 4 H, NH_2), 7.56 (br s, 4 H, NH_2).

MS (EI, 70 eV)): m/z = 718 [M$^+$].

Anal. Calcd for $C_{32}H_{38}N_{12}O_8$: C, 53.48; H, 5.33; N, 23.39. Found: C, 53.35; H, 5.21; N, 23.44.

5,5′,5″,5‴-[1,3-Phenylenedi(methanetriyl)]tetrakis[6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione] (3f)

White solid; yield: 574 mg (80%); mp 284–286 °C.

IR (KBr): 3454, 3360, 3111, 2962, 1683, 1601, 1496 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.33 (s, 12 H, N–CH_3), 3.35 (s, 12 H, N–CH_3), 5.52 (s, 2 H, $CH_{methine}$), 6.74 (s, 1 H, H_{arom}), 6.81 (d, J = 7.7 Hz, 2 H, H_{arom}), 7.02 (t, J = 7.5 Hz, 1 H, H_{arom}), 7.31 (br s, 4 H, NH_2), 7.56 (br s, 4 H, NH_2).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 28.0, 28.6, 29.9, 30.4, 35.7, 85.4, 87.1, 123.9, 127.7, 139.0, 150.7, 153.9, 155.1, 162.4, 164.0.

Anal. Calcd for $C_{32}H_{38}N_{12}O_8$: C, 53.48; H, 5.33; N, 23.39. Found: C, 53.55; H, 5.40; N, 23.28.

5,5′,5″,5‴,5⁗,5′′′′′-{1,3,5-Triazine-2,4,6-triyltris[oxy(3-methoxy-5-nitro-4,1-phenylene)methanetriyl]}hexakis(6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione) (3g)

Pale-yellow solid; yield: 1310 mg (85%); mp 265–268 °C.

IR (KBr): 3398, 3119, 2953, 1691, 1614, 1537, 1498, 1452, 1344 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.34 (s, 36 H, N–CH_3), 3.75 (s, 9 H, O–CH_3), 5.66 (s, 3 H, $CH_{methine}$), 7.25 (s, 3 H, H_{arom}), 7.39 (s, 3 H, H_{arom}), 7.2–7.9 (br s, 12 H, NH_2).

Anal. Calcd for $C_{60}H_{63}N_{21}O_{15}$: C, 54.67; H, 4.82; N, 22.31. Found: C, 54.75; H, 4.90; N, 22.22.

5,5′,5″,5‴,5⁗,5′′′′′-[1,3,5-Triazine-2,4,6-triyltris(oxy-4,1-phenylenemethanetriyl)]hexakis[6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione](3h)

White solid; yield: 1160 mg (88%); mp 285–288 °C.

IR (KBr): 3377, 3119, 2953, 2829, 1689, 1606, 1562, 1496, 1456 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.30 (s, 18 H, N–CH_3), 3.33 (s, 18 H, N–CH_3), 5.61 (s, 3 H, $CH_{methine}$), 6.92–7.02 (m, 9 H, H_{arom}), 7.25 (t, J = 7.8 Hz, 3 H, H_{arom}), 7.34 (br s, 12 H, NH_2).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 28.7, 30.4, 35.7, 85.2, 118.7, 119.8, 124.7, 129.1, 142.5, 150.9, 151.7, 153.9, 164.1, 173.4.

Anal. Calcd for $C_{60}H_{63}N_{21}O_{15}$: C, 54.67; H, 4.82; N, 22.31. Found: C, 54.50; H, 4.88; N, 22.43.

5,5′,5″,5‴,5⁗,5′′′′′-[1,3,5-Triazine-2,4,6-triyltris(oxy-3,1-phenylenemethanetriyl)]hexakis[6-amino-1,3-dimethylpyrimidine-2,4(1*H*,3*H*)-dione](3i)

White solid; yield: 1146 mg (87%); mp 291–294 °C.

IR (KBr): 3379, 3130, 2955, 2810, 1687, 1610, 1564, 1500, 1456 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.29 (s, 18 H, N–CH_3), 3.33 (s, 18 H, N–CH_3), 5.59 (s, 3 H, $CH_{methine}$), 7.06 (d, J = 8.4 Hz, 6 H, H_{arom}), 7.16 (d, J = 8.4 Hz, 6 H, H_{arom}), 7.45 (br s, 12 H, NH_2).

Anal. Calcd for $C_{63}H_{66}N_{24}O_{24}$: C, 49.03; H, 4.31; N, 21.78. Found: C, 48.90; H, 4.40; N, 21.90.

Acknowledgment

We gratefully acknowledge financial support from the Research Council of Arak University.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

References

(1) Zolfigol, M. A. *Tetrahedron* **2001**, *57*, 9509.
(2) Salehi, P.; Zolfigol, M. A.; Shirini, F.; Baghbanzadeh, M. *Curr. Org. Chem.* **2006**, *10*, 2171.
(3) Gill, C. S.; Price, B. A.; Jones, C. W. *J. Catal.* **2007**, *251*, 145.
(4) Kooti, M.; Afshari, M. *Mater. Res. Bull.* **2012**, *47*, 3473.
(5) Sheykhan, M.; Ma'mani, L.; Ebrahimi, A.; Heydari, A. *J. Mol. Catal. A: Chem.* **2011**, *335*, 253.
(6) Kassaee, M. Z.; Masrouri, H.; Movahedi, F. *Appl. Catal., A* **2011**, *395*, 28.
(7) Rostamnia, S.; Lamei, K.; Mohammadquli, M.; Sheykhan, M.; Heydari, A. *Tetrahedron Lett.* **2012**, *53*, 5257.
(8) (a) Hirota, K.; Kuki, H.; Maki, Y. *Heterocycles* **1994**, *37*, 563. (b) Griengl, H.; Wanek, E.; Schwarz, W.; Streicher, W.; Rosenwirth, B.; De Clercq, E. *J. Med. Chem.* **1987**, *30*, 1199. (c) Srivastava, P.; Saxena, A. S.; Ram, V. J. *Synthesis* **2000**, 541. (d) Mitsuya, H.; Yarchoan, R.; Broder, S. *Science (Washington D. C.)* **1990**, *249*, 1533. (e) Pontikis, R.; Monneret, C. *Tetrahedron Lett.* **1994**, *35*, 4351. (f) Wamhoff, H.; Schupp, W. *J. Org. Chem.* **1986**, *51*, 2787. (g) Walsh, E. B.; Wamhoff, H. *Chem. Ber.* **1989**, *122*, 1673.
(9) (a) Lunt, E.; Newton, C. G. In *Comprehensive Heterocyclic Chemistry*; Vol. 3; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon: Oxford, **1984**, 199. (b) Bradshaw, T. K.; Hutchinson, D. W. *Chem. Soc. Rev.* **1977**, *6*, 43.
(10) (a) Zhi, C.; Long, Z.-Y.; Gambino, J.; Xu, W.-C.; Brown, N. C.; Barnes, M.; Butler, M.; LaMarr, W.; Wright, G. E. *J. Med. Chem.* **2003**, *46*, 2731. (b) Devi, I.; Bhuyan, P. J. *Tetrahedron Lett.* **2005**, *46*, 5727.
(11) (a) Kappe, C. O. *Tetrahedron* **1993**, *49*, 6937. (b) Ibrahim, D. A.; El-Metwally, A. M. *Eur. J. Med. Chem.* **2010**, *45*, 1158. (c) Deshmukh, M. B.; Salunkhe, S. M.; Patil, D. R.; Anbhule, P. V. *Eur. J. Med. Chem.* **2009**, *44*, 2651.
(12) Singh, K.; Singh, S.; Mahajan, A. *J. Org. Chem.* **2005**, *70*, 6114.
(13) Petricci, E.; Radi, M.; Corelli, F.; Botta, M. *Tetrahedron Lett.* **2003**, *44*, 9181.
(14) Makarov, V. A.; Riabova, O. B.; Granik, V. G.; Dahse, H.-M.; Stelzner, A.; Wutzlerc, P.; Schmidtke, M. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 37.
(15) Azizian, J.; Mohammadizadeh, M. R.; Teimouri, F.; Mohammadi, A. A.; Karimi, A. R. *Synth. Commun.* **2006**, *23*, 3631.
(16) Blotny, G. *Tetrahedron* **2006**, *62*, 9507.
(17) Bock, H. R.; Anderson, S.; Fujita, Y.; Hudson, A. J.; Rorison, J. M.; Weaver, M. S. US 6437123, **2002**.
(18) Shu, W.; Valiyaveettil, S. *Chem. Commun. (Cambridge)* **2002**, 1350.
(19) Holst, H. C.; Pakula, T.; Meier, H. *Tetrahedron* **2004**, *60*, 6765.
(20) Xu, F.; Wang, Z.; Gong, Q. *Opt. Mater. (Amsterdam, Neth.)* **2007**, *29*, 723.
(21) Mooibroek, T. J.; Gamez, P. *Inorg. Chim. Acta* **2007**, *360*, 381.
(22) (a) Karimi, A. R.; Alimohammadi, Z.; Amini, M. M. *Mol. Diversity* **2010**, *14*, 635. (b) Karimi, A. R.; Alimohammadi, Z.; Azizian, J.; Mohammadi, A. A.; Mohammadizadeh, M. R. *Catal. Commun.* **2006**, *7*, 728. (c) Karimi, A. R.; Pashazadeh, R. *Synthesis* **2010**, 437.
(23) (a) Peng, Z. G.; Hidajat, K.; Uddin, M. S. *J. Colloid Interface Sci.* **2004**, *271*, 277. (b) Chen, F. H.; Gao, Q.; Ni, J. Z. *Nanotechnology* **2008**, *19*, 165103.
(24) Tsukimura, K.; Sasaki, S.; Kimizuka, N. *Jpn. J. Appl. Phys.* **1997**, *36*, 3609.
(25) Ghosh, S.; Badruddoza, A. Z. M.; Uddin, M. S. *J. Colloid Interface Sci.* **2011**, *354*, 483.
(26) Tahmassebi, D. C.; Sasaki, T. *J. Org. Chem.* **1994**, *59*, 679.

