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Synthesis of a Functionalized Polymer Based on a Calix[4]resorcinarene via Covalently Anchored Cationic Moieties: A Reactive Solid Support for Ring Transformation and Expansion of Thiopyrylium Salts

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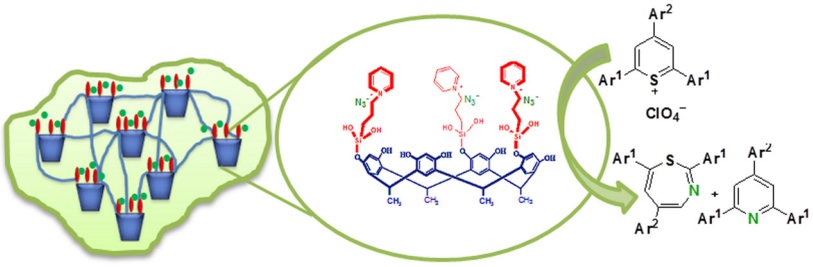

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Abstract In this work, for the first time, a cationic polymer containing pendant pyridinium groups was synthesized via post-functionalization of the polymeric backbone based on a calix[4]resorcinarene, and characterized by AFM, TEM, analytical CHN, TGA, and DTG techniques. The functionalized polymer is conveniently loaded with desired anions, thereby providing novel and recyclable polymer-supported reagents for achieving synthetic goals. The thermal stability of this cationic polymer (up to 250 °C by TGA) allows thermally demanding ring transformation and expansion of 2,4,6-triarylthiopyrylium salts on its side chains and polymeric backbone without decomposition and leaching of active species in the reaction media. This green method furnished a straightforward route for the synthesis of valuable 2,4,6-triarylpyridines, along with novel 2,5,7-triaryl-1,3-thiazepine derivatives, which are widely present as motifs in an assortment of biologically active molecules.

Key words azide, green chemistry, heterocycles, nucleophilic addition, polymers, ring expansion

Functionalization of polymers has been regarded as an effective method to improve polymer performance for various applications. In this context, covalently anchored cationic moieties on the polymeric backbone have received considerable interest due to their utilization as solid-supported reagents and catalysts,[1] anion-exchange membranes for alkaline fuel cells,[2] and adsorbents for anionic azo dyes.[3] Moreover, cationic polymers have been applied in various industries for different purposes (e.g., as strength agents in papermaking).[4]

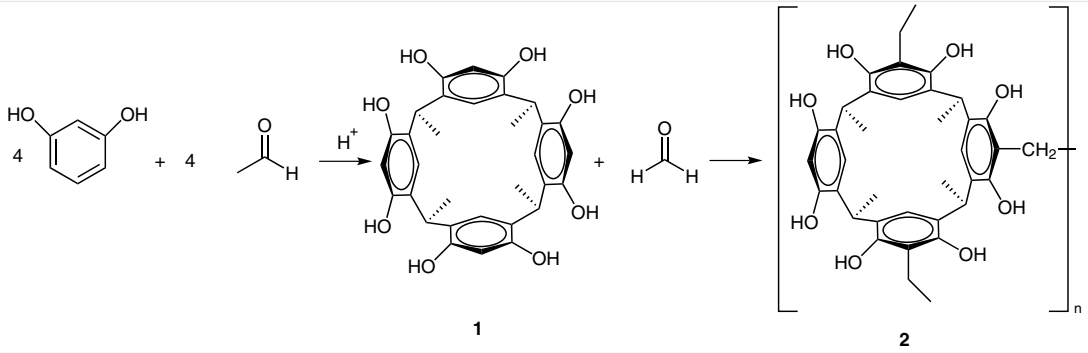
Over the past two decades, a major problem in the field of organic synthetic chemistry has been a lack of more environmentally friendly processes using safer reagents and generating fewer side products. In response to such concerns, a strategy of modern chemistry has been to exploit the advantages of polymer-supported reagents, and this has proven to be an important tool to accommodate the principles of green chemistry in the synthesis of desired products.[5]

The majority of studies in this area have been performed using porous polymers as carriers to achieve highly selective and mild chemical reactions. Some of the key advantages of porous supported reagents, such as the good dispersion of active sites, the concentration of sites within small pores, the presence of molecular dimension pores, and the adsorption of reactant molecules on the material surface, can lead to significant improvements in activity and reaction selectivity. These coupled with the normal advantages of a solid support (e.g., easier recovery and reuse, easier and safer handling) make porous supported reagents attractive materials to organic and industrial chemists.

Although a variety of polymeric supports have been reported, some of them suffer from one or more defects in their synthetic routes or properties, including long reaction times, multiple steps for synthesis, the use of expensive catalysts and harsh reaction conditions, solubility in various solvents, and low thermal and/or chemical stability.

Considering the ease of preparation and unique properties of the 3D-network polymer based on calix[4]resorcinarenes, such as significant potential for functionalization, high thermal and chemical stability, and porous surface (pore radius from approximately 100 to 500 nm),[6] it would be reasonable to consider this polymeric structure as a promising starting material for the synthesis of a novel and efficient polymer-supported reagent.

The synthesis of heterocyclic moieties has attracted tremendous attention due to the utilization of heterocyclic compounds in biological, biochemical, pharmaceutical, and asymmetric chemical investigations. In this context, six-



Scheme 1 Synthesis of calix[4]resorcinarene **1** and the 3D-network polymer **2**

and seven-membered rings containing nitrogen and/or sulfur atoms are essential constituents of a range of products, from pharmacologically active substances to natural products and various materials.[7]

A possible route for the synthesis of triarylpyridine and triarylthiazepine derivatives is the nucleophilic reaction of triarylthiopyrylium salts with azide anion.

Previous studies have revealed that the reactivity of azide anion with thiopyrylium cations at room temperature depends on the substitution of the heterocyclic cation. Only sterically hindered thiopyrylium cations lead to the formation of covalent azide, and trisubstituted examples give only a donor–acceptor complex.[8] The formation of this complex constitutes a dead-end reaction on the normal pathway to covalent azide.

In this vein and as a part of our continuing efforts to develop efficient and environmentally friendly transformations,[9] we report herein, for the first time, the functionalization of a porous polymeric calix[4]resorcinarene via covalently anchored pyridinium moieties, and its application as a reactive polymer-supported reagent for the synthesis of triarylpyridine and triaryl-1,3-thiazepine derivatives through ring transformation and expansion of trisubstituted thiopyrylium salts.

Starting from resorcinol and acetaldehyde, the calix[4]resorcinarene **1** was prepared according to a literature procedure[10] (Scheme 1). The structure of compound **1** was established unambiguously from spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR; see Supporting Information). Subsequently, 3D-network polymer **2** was prepared by polycondensation of **1** with formaldehyde (Scheme 1).[6,11] The formation of polymer **2** was confirmed and characterized by atomic force microscopy (AFM), X-ray diffraction, and scanning electron microscopy (data available in the Supporting Information).

Following the characterization of polymer **2**, due to the possibility to obtain new functional materials for diverse applications, we shifted our attention to the functionalization of the polymer through covalently anchored cationic moieties.

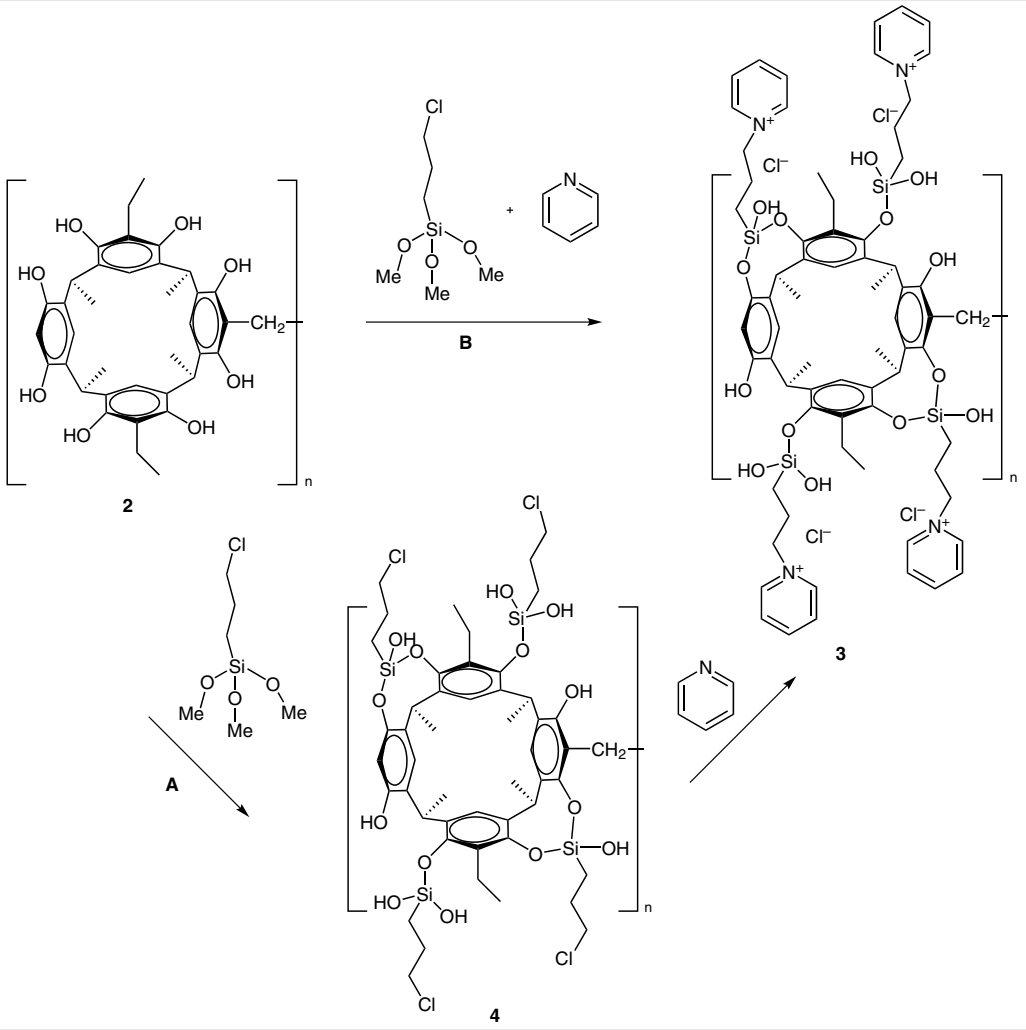
Cationic heterocyclic moieties are a class of valuable headgroups that can be used for the functionalization of solid supports. Among them, in recent years, the chemically and thermally stable pyridinium moiety and its derivatives[12] have been extensively incorporated into various supports to achieve desired goals.[13]

Considering the above point, this part of our study commenced with the synthesis of pyridinium-grafted polymer.

Initially, the cationic polymer **3** was synthesized via two chemical modification steps (Scheme 2, A). Starting from 3D-network polymer **2** and (3-chloropropyl)trimethoxysilane, the chloropropyl-grafted polymer **4** was prepared and subsequently converted into ionic form **3** by a simple nucleophilic substitution reaction. According to elemental analysis data, the amount of grafted pyridinium moieties obtained was 2.4 mmol per gram of polymer **3** (Table 1, entry 2).

Table 1 Elemental Analysis Data for Polymer **2** and the Cationic Polymer **3** Bearing Pyridinium Moieties

Entry	Material	Method	Solvent	Time (h)	C (wt %)	H (wt %)	N (wt %)
1	polymer **2**	–	–	–	45.72	4.96	0.03
2	cationic polymer **3**	two-step	H_2O–EtOH + toluene	48	56.38	5.36	3.37
3	cationic polymer **3**	one-step	toluene	24	48.94	5.25	1.74
4	cationic polymer **3**	one-step	H_2O–EtOH	24	56.38	5.36	3.37



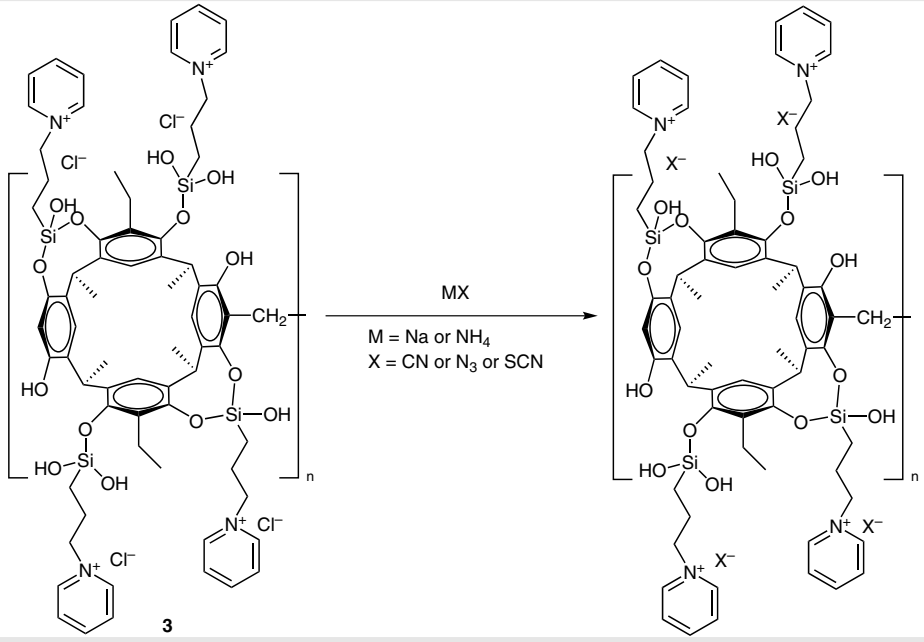
Scheme 2 Synthesis of the cationic polymer **3** containing pyridinium moieties via two pathways

The pyridinium-functionalized polymer **3** was also prepared following a one-step procedure (Scheme 2, B). Surprisingly, similar elemental analysis data were obtained via the one-step chemical modification of polymer in aqueous ethanol as solvent (Table 1, entry 4; cf. entry 2).

It is noteworthy that this polymeric support showed more potential for covalently anchored moieties than some previously reported solid supports.[14] Moreover, the cationic polymer **3** is effectively insoluble in various solvents, including water, methanol, ethanol, dimethyl sulfoxide, *N*,*N*-dimethylformamide, acetonitrile, dichloromethane, and chloroform. These features render polymer **3** suitable for use as a solid-supported reagent or catalyst in various reaction media.

With the above results in hand, in the next step, we investigated the ability of the functionalized polymer **3** in anion-exchange mode. In this regard, cationic polymer **3** was treated with aqueous sodium azide, ammonium thiocyanate, or sodium cyanide for 12 hours (Scheme 3).

The typical loading of the anions onto the support was determined by elemental analysis and the potentiometric method. As shown in Table 2, polymer **3** conveniently loaded with the desired anions. This result gave us confidence that the pyridinium side chain would be tolerated under the alkali conditions which are produced by sodium azide, sodium cyanide, or ammonium thiocyanate dissolved in water.



Scheme 3 Preparation of polymer-supported reagents

Table 2 Elemental Analysis Data for Polymer **3** and the Polymer-Supported Reagents

Entry	Polymer	X	N (wt %)	S (wt %)
1	**3**	Cl	3.37	–
2	supported reagent	N_3	4.99	–
3	supported reagent	CN	3.96	–
4	supported reagent	SCN	1.14	3.81

These significant properties of cationic polymer **3** encouraged us to characterize its structure. In order to gain an insight into the topography of the surface, AFM was utilized (Figure 1, a, b). All of the AFM scans were taken in ambient air in tapping mode, which is ideal for this kind of polymer.[15] More details could be obtained from the 3D height and phase plots (Figure 1, b).

Representative 1.5 μm × 1.5 μm AFM height images of polymer **2** and cationic polymer **3** suggest a series of pores which have an average surface diameter of about 300 nm[6] (see Supporting Information) and 70 nm (Figure 2), respectively. It can be concluded that the introduction of pyridinium moieties into the polymer shifted the pores to smaller diameter.

On the whole, AFM revealed that the 3D-network cationic polymer **3** exhibits a nanoporous surface that has the ability for the inclusion of an organic guest.

Transmission electron microscopy (TEM) of the functionalized polymer **3** was undertaken on a LEO 906E instrument operated at the accelerating voltage of 80 KV (Figure 3). The TEM images show that there are some pores which have a diameter in the nanometer range.

The thermal stability of cationic polymer **3** was investigated by thermogravimetric analysis (TGA, Figure 4) at a heating rate of 10 °C per minute under nitrogen atmosphere.

The TGA of polymer **3** demonstrated high thermal stability, with decomposition starting at around 250 °C. The thermal stability of this cationic polymer allows heat-demanding chemical transformations along its backbone and side chains without leaching of the active species, thereby providing an excellent means of polymer support for conducting chemical transformations.

Along this line, we decided to investigate the application of this cationic polymer as a solid-supported reagent for efficient construction of heterocyclic compounds through ring transformation and expansion of triarylthiopyrylium salts.

In the preliminary stage of the investigation, the reaction of 2,4,6-triphenylthiopyrylium perchlorate (**5A**, 0.1 mmol) with azide anion (0.2 mmol) was selected as the model reaction to survey the requisite reaction conditions. After some experimentation (Table 3), it was found that the use of 0.1 mmol of the triphenylthiopyrylium salt in the presence of polymer-supported azide (0.5 g polymer containing 0.2 mmol azide anion) in boiling acetonitrile were the best conditions (Table 3, entry 7).

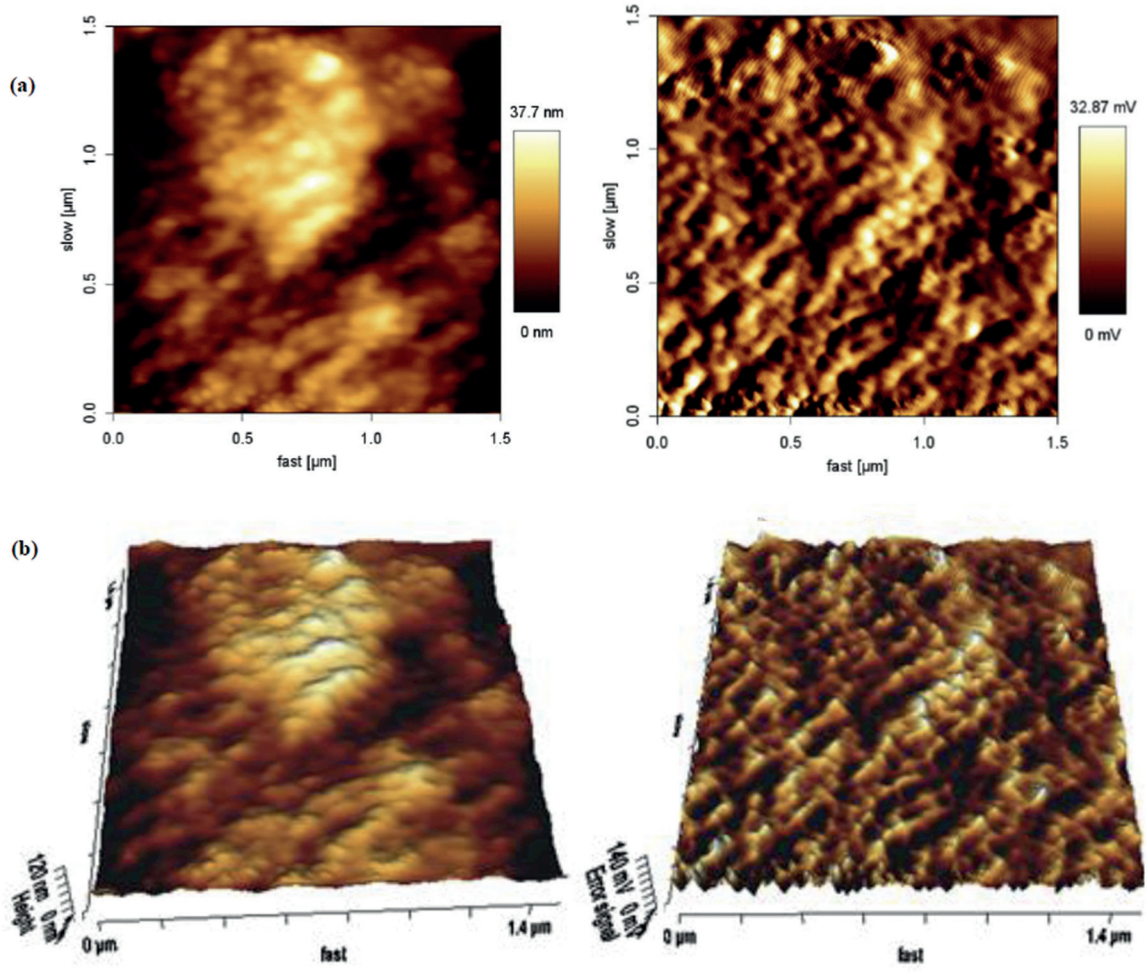


Figure 1 AFM images (1.5 µm × 1.5 µm) of cationic polymer **3**: (a) 2D and (b) 3D height and phase plots

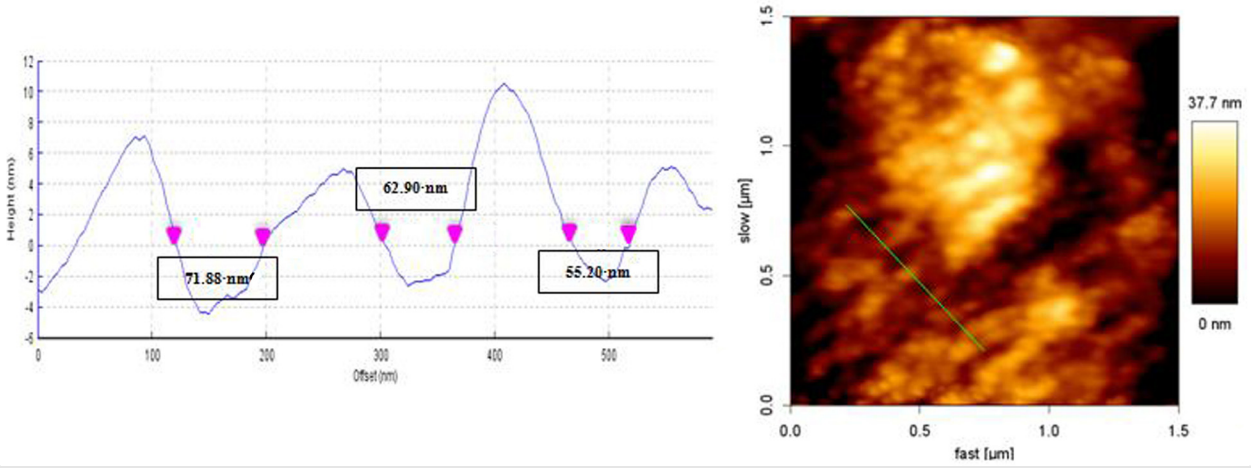


Figure 2 Image profile (the analysis of height along a linear path) of cationic polymer **3**

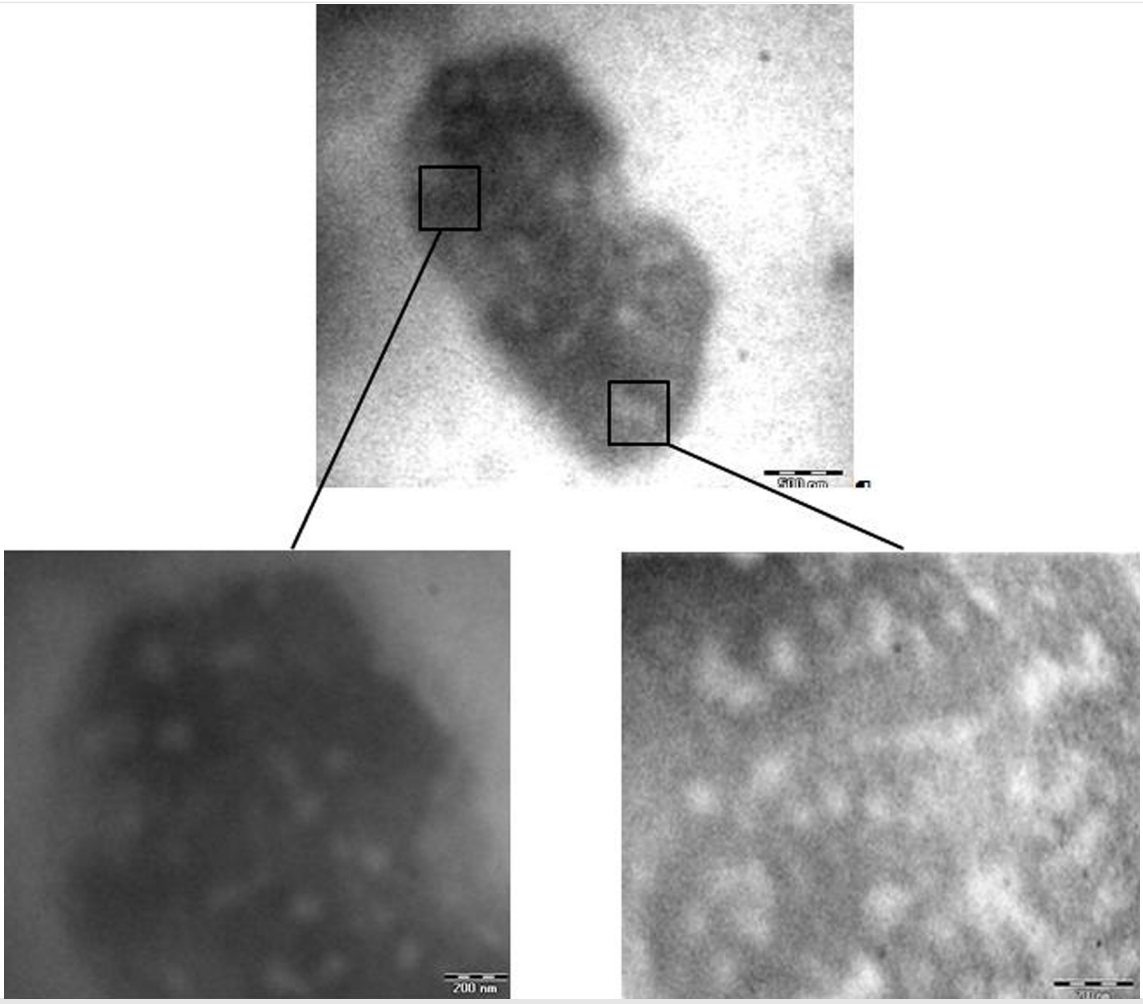


Figure 3 TEM images of cationic polymer **3**

Table 3 Reaction of Triphenylthiopyrylium Salt **5A** with Azide Anion under Various Conditions

Entry	Azide source	Solvent	Temp (°C)	Time	Result	Total yield (%) of **7A** + **8A**
1	NaN_3	CH_2Cl_2	r.t.	24 h	starting material + byproduct **6A**	0
2	NaN_3	EtOH	r.t.	24 h	starting material + byproduct **6A**	0
3	NaN_3	MeCN	r.t.	24 h	starting material + byproduct **6A**	0
4	NaN_3	CH_2Cl_2	reflux	24 h	starting material + byproduct **6A**	0
5	NaN_3	EtOH	reflux	24 h	starting material + byproduct **6A**	0
6	NaN_3	MeCN	reflux	24 h	starting material + byproduct **6A** + desired products **7A** and **8A**	8
7	polymer-supported azide	MeCN	reflux	90 min	desired products **7A** and **8A**	65

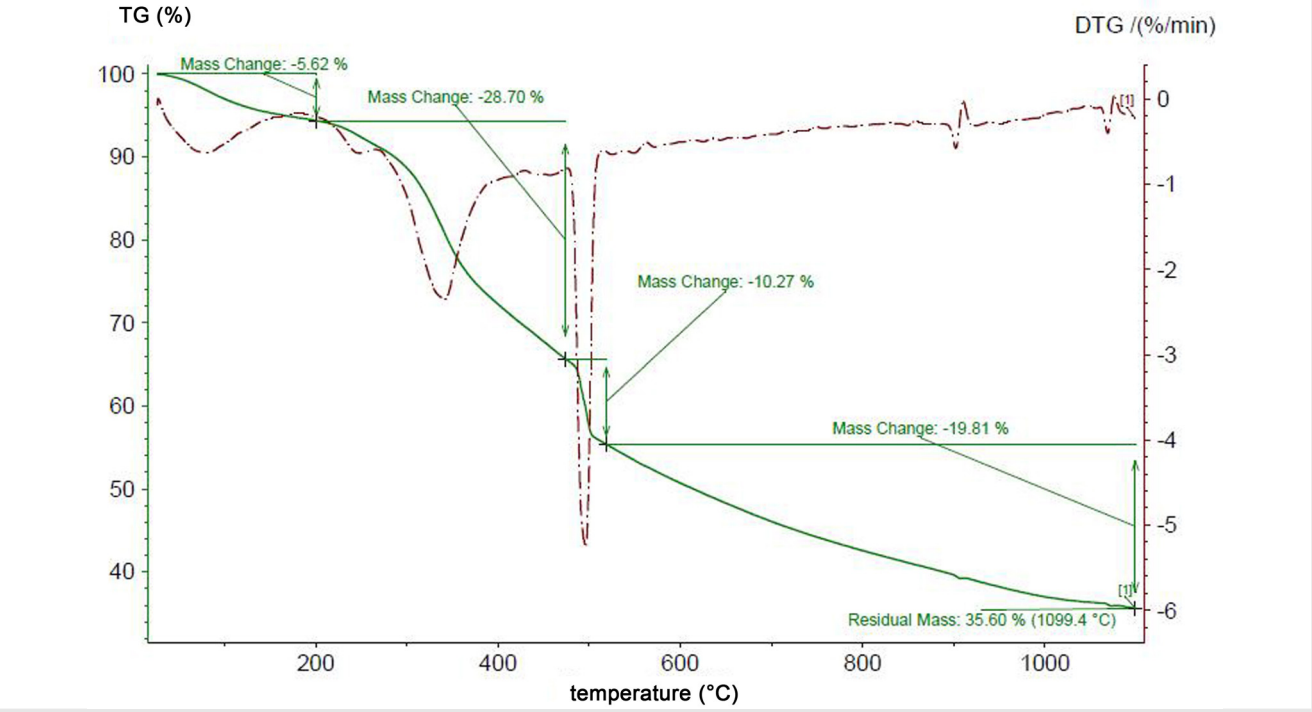


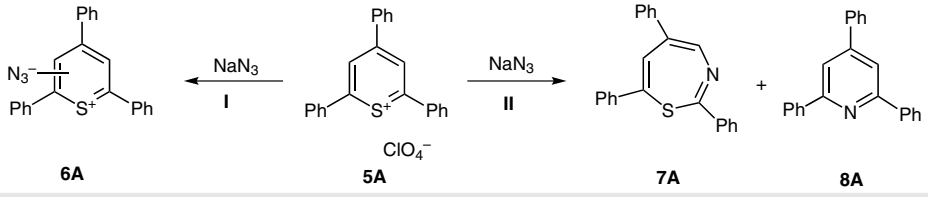
Figure 4 TGA and differential thermogravimetric (DTG) profile of cationic polymer **3**

Briefly, in our optimization studies, when the reaction of triphenylthiopyrylium salt **5A** with sodium azide was carried out in different solvents at room temperature, charge-transfer complex **6A** was obtained as the sole product (Table 3, entries 1–3). According to TLC analysis, there was no evidence of the transformation of **6A** into the desired products **7A** and **8A**, even after 24 hours, which is completely in agreement with the previously reported data.[8] Raising the temperature led to the formation of a small amount of products **7A** and **8A**, along with a considerable amount of charge-transfer complex **6A** as byproduct, in boiling acetonitrile after 24 hours (Table 3, entry 6).

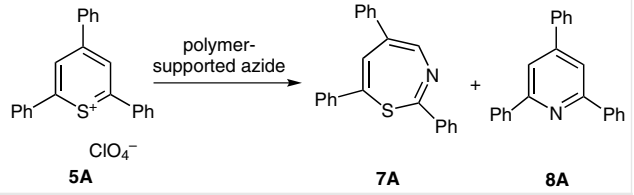
As stated earlier, the formation of a charge-transfer complex constitutes a dead-end reaction on the normal pathway to covalent azide, and prevents the formation of the desired products. Under this light, it could be concluded that the byproduct **6A** produced as a consequence of the competing side reaction I occurs in parallel to the intended reaction II; the two pathways are summarized in Scheme 4.

Surprisingly, as illustrated in Table 3 (entry 7), using polymer-supported azide as the nucleophile source dramatically reduced the reaction time and considerably increased the yield of the desired products **7A** and **8A** without any concentration of unreacted starting material **5A** and byproduct **6A** (Scheme 5).

A weak interaction between azide anion and the pyridinium moieties on the cationic polymer, which increases the nucleophilicity of the azide anion, might contribute to the suppression of byproduct formation and to the rapid progress of the nucleophilic reaction. Furthermore, the adsorption of thiopyrylium salt onto the surface of the functionalized polymer based on hydrophobic interactions between the aromatic substrate and the polymeric backbone



Scheme 4 Two pathways for the reaction of model compound **5A** with sodium azide in boiling acetonitrile



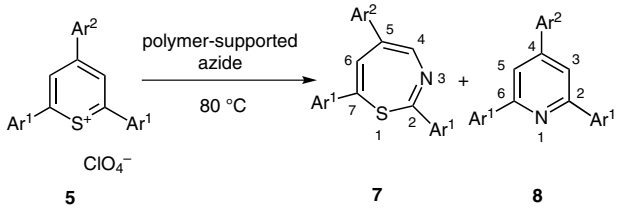
Scheme 5 Reaction of model compound **5A** with polymer-supported azide

could increase local concentration of the substrate around the active sites of the polymer and effectively promote the nucleophilic reaction.

It is noteworthy that the formation of **7** and **8** by this method is of considerable interest, since this is the first report of the synthesis of these privileged heterocyclic compounds via ring expansion and transformation of triarylthiopyrylium salts.

These results encouraged us to demonstrate the efficiency and the applicability of the present method. We performed the reaction of a variety of 2,4,6-triarylthiopyrylium salts containing electron-withdrawing or electron-donating groups with azide anion under the optimized reaction conditions. Representative results for this synthetic modification are listed in Table 4.

Table 4 Conversion of Various 2,4,6-Triarylthiopyrylium Salts **5** into the Corresponding 2,5,7-Triaryl-1,3-thiazepine **7** and 2,4,6-Triarylpyridine **8** Derivatives Using Polymer-Supported Azide under Optimized Conditions



Entry	5/7/8	Ar^1	Ar^2	Time	Yield (%) of 7/8
1	**A**	Ph	Ph	90 min	30/35
2	**B**	Ph	4-MeC_6H_4	2 h	15/40
3	**C**	Ph	4-$MeOC_6H_4$	3 h	30/35
4	**D**	4-$MeOC_6H_4$	Ph	20 h	30/35
5	**E**	Ph	4-ClC_6H_4	13 min	25/33
6	**F**	Ph	4-BrC_6H_4	15 min	27/30

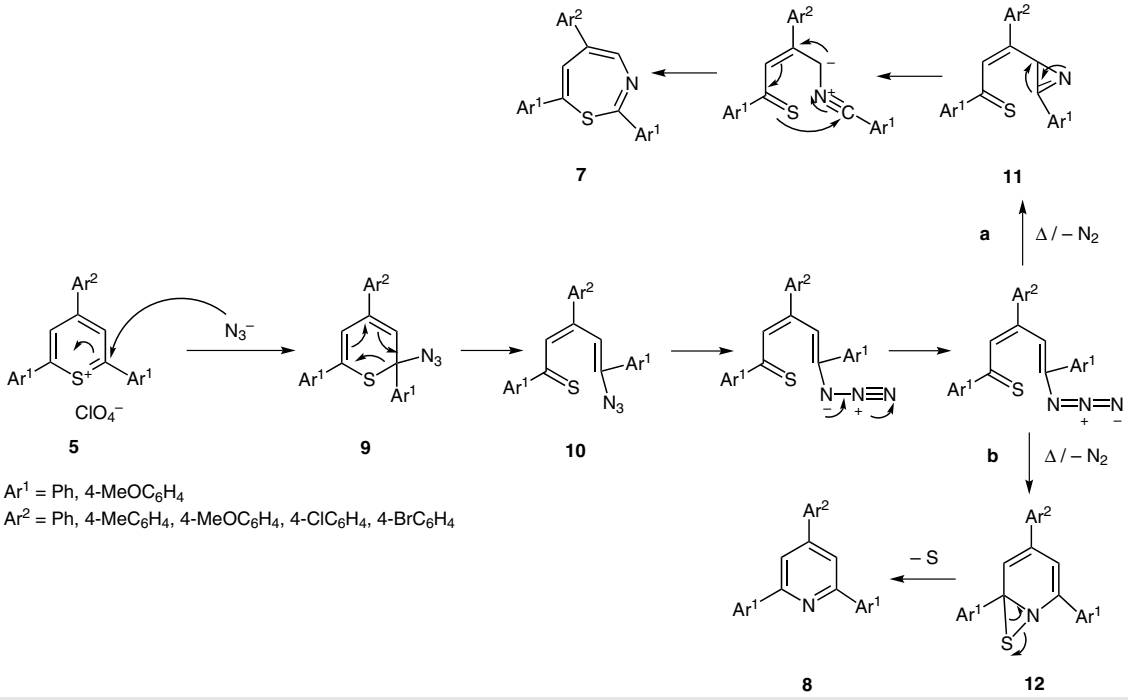
Electron-donating substituents resulted in a decreased reaction rate (Table 4, entries 2–4), possibly because these groups decrease the positive charge at the α-position of the heterocyclic ring. The presence of more strongly electron-donating groups led to longer reaction time (Table 4, entry 4). In contrast, the presence of an electron-withdrawing group (Table 4, entries 5 and 6) accelerated the reaction.

A conceivable mechanism for the synthesis of 2,5,7-triaryl-1,3-thiazepine **7** and 2,4,6-triarylpyridine **8** derivatives via a nucleophilic attack route is outlined in Scheme 6. The first step of the reaction affords the 2-azidothiopyran **9** which undergoes electrocyclic ring opening to form the acyclic valence tautomer **10**. Subsequently, thermal elimination of an N_2 molecule from compound **10** followed by intramolecular nitrogen insertion into the adjacent C–C double bond (path **a**) yields azirine **11** which readily rearranges to the stable 2,5,7-triaryl-1,3-thiazepine **7**. Another plausible pathway which can occur after release of the N_2 molecule from compound **10** is the insertion of the nitrogen atom into the C–S double bond (path **b**) which affords bicyclic thiaziridine **12**. Finally, extrusion of the sulfur atom from compound **12** leads to the formation of 2,4,6-triarylpyridine **8**.

The structures of all known products (the 2,4,6-triarylpyridine derivatives) were established unambiguously from their physical (mp) and spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR), and by direct comparison with authentic samples.[16] Moreover, the structures of all novel products (the 2,5,7-triaryl-1,3-thiazepine derivatives) were settled unambiguously from spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR, MS) (all physical and spectroscopic data are available in the Supporting Information).

Overall, the use of the polymer-supported reagent therefore offers the possibility of considerably decreasing the reaction times and improving the yields of desired products relative to conventional conditions. Furthermore, the immobilized reagent is generally more stable and easy to handle, and can easily be separated by filtration after the reaction. Even in a large excess of solid-supported reagent used to drive the reaction to completion, products require no further purification which has driven continued interest in solid-supported reagents. Finally, the polymer-supported reagents are much less hazardous to use, because the reagent residues (such as azide, cyanide, and thiocyanate) are retained on the cationic polymer and are not extracted into the reaction media.

In conclusion, by combining the advantages of 3D-network polymer **2** with pyridinium moieties, the first pyridinium-functionalized polymer based on a calix[4]resorcinarene as a novel and thermally stable solid support was developed. The remarkable advantages offered by this approach are operational simplicity, a one-pot one-step procedure, no use of an acidic or basic catalyst, ease of isolation and purification of the functionalized polymer, and a high amount of grafted cationic moieties. We believe that this method is a useful alternative to the existing methodologies for the synthesis of functionalized polymers. Following the characterization of functionalized polymer **3**, azide-impregnated cationic polymer was prepared and used as a



Scheme 6 Plausible mechanism for the reaction of 2,4,6-triarylthiopyrylium salts **5** with azide nucleophile

reactive reagent for the clean and efficient synthesis of bioactive 2,4,6-triarylpyridine and novel 2,5,7-triaryl-1,3-thiazepine derivatives, starting from 2,4,6-triarylthiopyrylium salts as simple and readily available starting materials. The cationic polymer as solid support has the potential to be recycled, thereby offering both a green and economical approach for many chemical transformations. Currently, work on developing a variety of functionalized polymers derived from polymeric calix[4]resorcinarenes is in progress in our laboratory.

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies and used without further purification. Products were characterized by physical data, IR, ^{1}H NMR, ^{13}C NMR and HRMS spectra. Melting points were determined on a Thermo Scientific 9200 apparatus. IR spectra were obtained on a Bomen MB:102 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 400 and 100 MHz, respectively, in $CDCl_3$ or DMSO with tetramethylsilane as an internal standard. HRMS spectra were measured on an Agilent 5975 mass spectrometer and elemental analyses were performed on a Thermo Finnigan Flash EA 1112 CHNS-Analyzer. The polymer morphology was examined by AFM (Nano Wizard II) and TEM (LEO-906E). The thermal stability of functionalized polymers was investigated by NETZSCH STA 409 PC/PG.

Monitoring of the reactions and the purity determination of the products were accomplished by TLC on PolyGram SILG/UV 254 silica gel plates.

Novel Functionalized Polymer 3 via a Two-Step Chemical Modification (Scheme 2, A)

Chloropropyl-Grafted Polymer 4

Polymer **2** (1 g) was added to a flask containing H_2O–EtOH (1:1, 10 mL) and (3-chloropropyl)trimethoxysilane (3.4 g, 16 mmol). The reaction mixture was heated at 90 °C with stirring for 20 h. Then, the material was collected by filtration, washed several times with deionized water, and dried at 80 °C.

Functionalized Polymer 3 Bearing Cationic Moieties

Chloropropyl-grafted polymer **4** (1 g) and an excess of pyridine (25 mmol) were stirred in toluene (10 mL) at 90 °C for 20 h. Then, the solid product was recovered by filtration and washed with deionized water several times before being dried at 80 °C.

Novel Functionalized Polymer 3 via a One-Step Chemical Modification (Scheme 2, B)

Polymer **2** (1 g), (3-chloropropyl)trimethoxysilane (3.4 g, 16 mmol), and an excess of pyridine (25 mmol) were added to a flask containing H_2O–EtOH (1:1, 10 mL) or toluene (10 mL). The reaction mixture was heated at 90 °C for 20 h. The desired cationic polymer **3** was collected by filtration and washed with deionized water several times before being dried at 80 °C.

Preparation of Polymer-Supported Reagents as Novel and Efficient Reagents (Scheme 3)

The dried cationic polymer **3** (1 g) was stirred with NaN_3 (15 g), NH_4SCN (10 g), or NaCN (2.8 g) in H_2O (40 mL) for 12 h. The azide, thiocyanate, or cyanide solution was decanted, and the polymer was washed with distilled water several times.

Determination of the Capacity of the Polymer-Supported Reagents

The capacity of the polymer-supported azide or thiocyanate was determined by elemental analysis. The capacity was generally found to be 0.4 and 1.19 mmol per gram of dried cationic polymer **3** for azide and thiocyanate anion, respectively.

The capacity of the polymer-supported cyanide was determined by the potentiometric method. Briefly, a sample of polymer-supported cyanide anion (0.10 g) was stirred for 12 h with KI (8.3 mg) in H_2O (10 mL). The polymer was collected by filtration and washed several times with distilled H_2O. The combined filtrate and washings were titrated against 0.01 M aq $AgNO_3$ using a potentiometer. The capacity was generally found to be 0.4 mmol per gram of dried cationic polymer **3**. Used polymer could be readily regenerated by sequential washing with 1 M aq NaCl and NaCN.

2,5,7-Triaryl-1,3-thiazepine 7 and 2,4,6-Triarylpyridine 8 Derivatives from the Reaction of 2,4,6-Triarylthiopyrylium Perchlorates 5 with Azide-Impregnated Cationic Polymer (Table 4); General Procedure

The 2,4,6-triarylthiopyrylium salt **5** (0.1 mmol) was stirred with the azide-impregnated cationic polymer (0.5 g polymer containing 0.2 mmol azide anion) in refluxing MeCN (5 mL) until the reaction was complete (TLC). The polymer was then removed by filtration, the solvent was evaporated under vacuum and the residue was adsorbed onto silica gel, transferred to a silica gel column and eluted with a mixture of *n*-hexane–ether (4:1). Thereby, the first and second parts containing the corresponding 2,4,6-triarylpyridine **8** and 2,5,7-triaryl-1,3-thiazepine **7**, respectively, were obtained. The sampled parts were concentrated and analyzed by IR and NMR spectroscopy, and mass spectrometry (see Supporting Information).

2,5,7-Triphenyl-1,3-thiazepine (7A)

Yield: 10.17 mg (30%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.75 (m, 17 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.22, 126.72, 127.76, 127.82, 128.09, 128.98, 129.19, 129.25, 129.67 (ArC), 132.17 (C-6), 133.23, 135.11, 136.01 (ArC_q), 137.71 (C-4), 149.30 (C-5), 149.94 (C-7), 189.92 (C-2).

MS: *m*/*z* = 339 [M$^{+\bullet}$].

2,4,6-Triphenylpyridine (8A)

Yield: 10.74 mg (35%); white crystals; mp 132–134 °C (from EtOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.77, 8.22–8.24 (m, 15 H, Ar-H), 7.92 (s, 2 H, H-3, H-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.23 (C-3, C-5), 127.20, 128.72, 129.04, 129.14 (ArC), 139.10, 139.50 (ArC_q), 150.13 (C-4), 157.49 (C-2, C-6).

5-(4-Methylphenyl)-2,7-diphenyl-1,3-thiazepine (7B)

Yield: 5.29 mg (15%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, CH_3), 6.98–7.73 (m, 16 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.71 (CH_3), 126.19, 126.74, 127.80, 128.77, 128.89, 129.09, 129.14 (ArC), 129.67 (C-6), 132.05, 132.86, 133.28, 137.60 (ArC_q), 137.84 (C-4), 148.06 (C-5), 149.08 (C-7), 189.89 (C-2).

MS: *m*/*z* = 353.2 [M$^{+\bullet}$].

4-(4-Methylphenyl)-2,6-diphenylpyridine (8B)

Yield: 12.84 mg (40%); white crystals; mp 114–116 °C (from EtOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 7.33–7.91, 8.21–8.22 (m, 14 H, Ar-H), 7.92 (s, 2 H, H-3, H-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.30 (CH_3), 117.10 (C-3, C-5), 127.08, 127.41, 128.74, 129.31, 129.92 (ArC), 135.68, 136.42, 138.98 (ArC_q), 149.29 (C-4), 157.54 (C-2, C-6).

5-(4-Methoxyphenyl)-2,7-diphenyl-1,3-thiazepine (7C)

Yield: 11.07 mg (30%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3 H, OCH_3), 6.69–7.73 (m, 16 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.27 (OCH_3), 113.54 (C_3 of C_6H_4-OCH_3), 126.18, 126.68, 127.83, 128.28, 128.91, 129.14 (ArC), 129.65 (C-6), 130.48, 132.09, 133.28 (ArC_q), 137.81 (C-4), 147.70 (C-5), 149.15 (C-7), 159.24 (*C*-OCH_3), 189.89 (C-2).

MS: *m*/*z* = 369 [M$^{+\bullet}$].

4-(4-Methoxyphenyl)-2,6-diphenylpyridine (8C)

Yield: 11.79 mg (35%); white crystals; mp 130–132 °C (from EtOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3 H, OCH_3), 7.03–7.74, 8.19–8.21 (m, 14 H, Ar-H), 7.88 (s, 2 H, H-3, H-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.50 (OCH_3), 114.70 (C_3 of C_6H_4-OCH_3), 117.24 (C-3, C-5), 127.53, 128.58, 128.78, 129.53, 130.50 (ArC), 138.31, 150.21 (ArC_q), 150.23 (C-4), 156.93 (C-2, C-6), 160.92 (ArC_q).

2,7-Bis(4-methoxyphenyl)-5-phenyl-1,3-thiazepine (7D)

Yield: 11.97 mg (30%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79, 3.88 (s, 6 H, OCH_3), 6.68–7.69 (m, 15 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.37, 55.42 (OCH_3), 113.09, 114.51 (C_3 of C_6H_4-OCH_3), 125.44, 126.08, 127.49, 127.60, 128.12 (ArC), 129.17 (C-6), 130.43, 132.12 (ArC_q), 135.99 (C-4), 147.15 (C-5), 148.56 (C-7), 160.20, 162.87 (*C*-OCH_3), 188.50 (C-2).

MS: *m*/*z* = 339 [M$^{+\bullet}$].

2,6-Bis(4-methoxyphenyl)-4-phenylpyridine (8D)

Yield: 12.84 mg (35%); white crystals; mp 133–135 °C (from EtOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 6 H, OCH_3), 7.05–7.83, 8.14–8.17 (m, 13 H, Ar-H), 7.85 (s, 2 H, H-3, H-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.43 (OCH_3), 113.29 (C_3 of C_6H_4-OCH_3), 116.92 (C-3, C-5), 127.31, 128.53, 129.06 (ArC), 136.25, 139.15 (ArC_q), 151.21 (C-4), 159.33 (ArC_q), 159.60 (C-2, C-6).

5-(4-Chlorophenyl)-2,7-diphenyl-1,3-thiazepine (7E)

Yield: 9.32 mg (25%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.73 (m, 16 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.17, 123.95, 124.44, 126.18, 126.41, 127.95, 128.24, 129.06, 129.17 (ArC), 129.58 (C-6), 130.38, 132.36, 138.07, 140.24 (ArC_q), 144.26 (C-4), 145.37 (C-5), 158.68 (C-7), 190.15 (C-2).

MS: *m*/*z* = 373.5 [M$^{+\bullet}$].

4-(4-Chlorophenyl)-2,6-diphenylpyridine (8E)

Yield: 15.14 mg (33%); white crystals; mp 121–123 °C (from EtOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.70, 8.21–8.23 (m, 14 H, Ar-H), 7.87 (s, 2 H, H-3, H-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.78 (C-3, C-5), 127.13, 128.76, 129.19, 132.31 (ArC), 123.42, 137.97, 139.38 (ArC_q), 149.00 (C-4), 157.71 (C-2, C-6).

5-(4-Bromophenyl)-2,7-diphenyl-1,3-thiazepine (7F)

Yield: 11.28 mg (27%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.73 (m, 16 H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 118.85 (C-6), 119.09 (C-Br), 122.06, 123.49, 124.00, 124.38, 124.47, 126.21, 126.38, 127.14, 128.72, 128.81, 129.11, 129.20, 129.61, 130.70 (ArC), 130.90, 131.22, 132.99, 134.69, 137.71 (ArC_q), 146.60 (C-4), 147.06 (C-5), 149.60 (C-7), 189.50 (C-2).

MS: m/z = 419 [$M^{+\bullet}$].

4-(4-Bromophenyl)-2,6-diphenylpyridine (8F)

Yield: 15.09 mg (30%); white crystals; mp 104–106 °C (from EtOH).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.70, 8.21–8.23 (m, 14 H, Ar-H), 7.87 (s, 2 H, H-3, H-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.78 (C-3, C-5), 127.13, 128.76, 129.19, 132.31 (ArC), 123.42, 137.97, 139.38 (ArC_q), 149.00 (C-4), 157.71 (C-2, C-6).

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Supporting Information

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