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A convenient method for synthesis of terpyridines via a cooperative vinylogous anomeric based oxidation†

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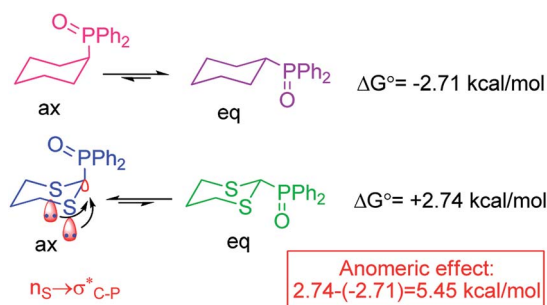
The presented study is the first report of the synthesis of terpyridines in the presence of a nanomagnetic catalyst instead of harmful reagents. Herein, $\text{Fe}_3\text{O}_4@\text{O}_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ as a retrievable nanocatalyst with magnetic properties was applied for the multi-component reaction between acetylpyridine derivatives (2 or 3 or 4-isomer), aryl aldehydes and ammonium acetate under conventional heating conditions in the absence of any solvent. The derived terpyridines were obtained with acceptable yields and brief reaction times via a cooperative vinylogous anomeric based oxidation route. $\text{Fe}_3\text{O}_4@\text{O}_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ showed a high capability for recovery and reuse in the mentioned reaction.

Introduction

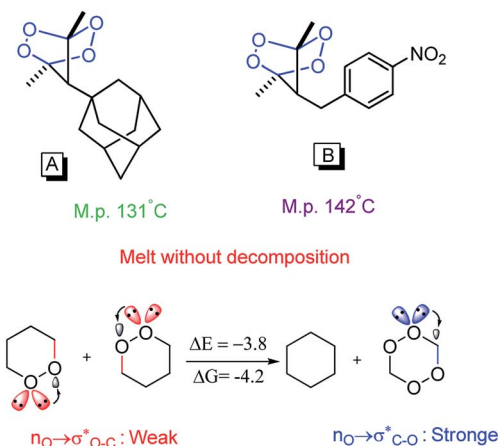
Nowadays, immobilizing catalytically homogeneous species onto the surface of core-shell materials with magnetic cores for the preparation of nanomagnetic heterogeneous catalysts has attracted enormous interest. The insoluble and paramagnetic natures of these kinds of catalysts,^{1–6} provide efficient and simple isolation of them from the reaction mixture with an externally applied magnetic field. Because of their retrievability, high surface area, biocompatibility and possibility of modification of the surface of the magnetic nanoparticles with both organic and inorganic compounds, these catalysts have found comprehensive and significant uses among academic and industrial scientists.^{7–11} They are robust catalysts which have been applied in various kinds of organic synthesis.^{12–23}

In conformity with the principles of green chemistry, such as increase the efficiency of chemical reactions, the atomic economy, reduce derivatives, decrease the utilization of organic solvents and waste production, simplify processes and design for energy efficiency, multi-component reactions (MCRs) have been presented and extended as a powerful method for the preparation of structurally diverse drug-like compounds (expansion of large chemical libraries of drug-like compounds).^{24–32}

Anomeric effect is an important stereoelectronic phenomenon which had been described as the axial superiority for an electronegative substituent (acceptor group) positioned adjacent to a donor group (lone pairs) rather than equatorial



Scheme 1 Anomeric effect leads to more stability axial conformer 2-diphenylphosphinoyl 1,3-dithiane.^{42,43}

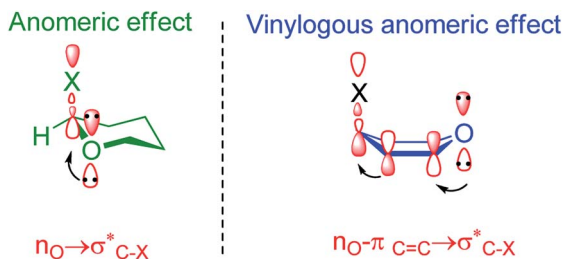


Scheme 2 Stability of bis-peroxides due to the anomeric effect.

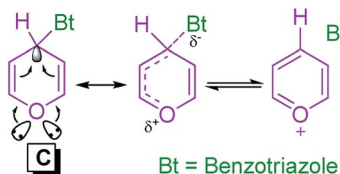
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Scheme 3 Anomeric effect in tetrahydropyran versus a vinylogous anomeric effect in pyran.⁵⁴



Scheme 4 VAE causes facile C–N bond dissociation of the benzotriazole residue.

position.^{33–39} In the other hand, this concept is a kind of negative hyperconjugation can lead sharing of the electron density from lone-pair orbital to a vacant anti-bonding sigma orbital ($n \rightarrow \sigma^*$) (Scheme 1).^{40,41}

Anomeric effect has a potent role to explain some eccentric phenomena in the chemistry knowledge. For instance, anomeric effect justifies why bis-peroxides **A** and **B** can be more thermodynamically stable than mono-peroxides, and can even melt without decomposition at 131 and 142 °C, respectively. Anomalous stability of these compounds is associated with strong anomeric $n_O \rightarrow \sigma_{C-O}^*$ interactions in two peroxide groups which separated by a one-atom bridge (Scheme 2).⁴⁴

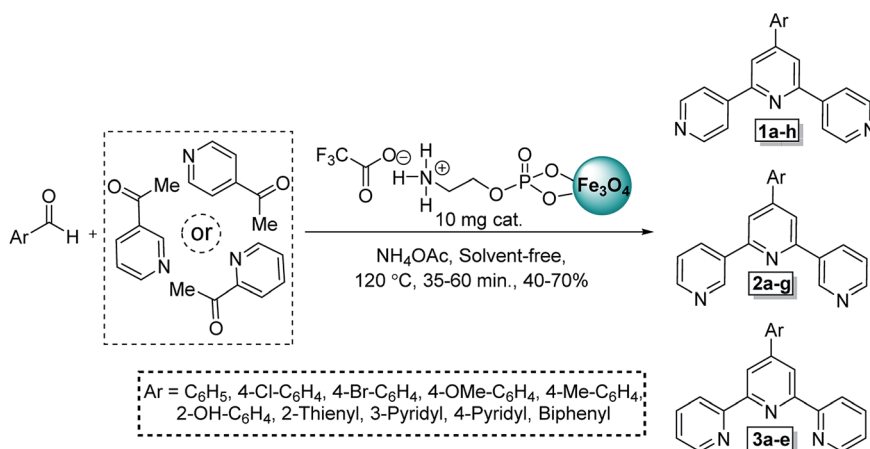
The anomeric effect can also be extended through double bonds in what has been named the vinylogous anomeric effect (VAE). The VAE had been applied for the stereoelectronic supported interactions of unshared electron pairs to vacant anti-bonding sigma orbitals ($n \rightarrow \sigma^*$) over four bonds (Scheme 3).^{45–53}

Katritzky *et al.* by low temperature X-ray crystallography have been shown that facile C–N bond dissociation of the benzotriazole residue in compound **C**, have been related to a vinylogous anomeric effect (VAE) (Scheme 4).⁵⁴

Based on above mentioned facts, “cooperative anomeric and/or vinylogous anomeric based oxidation” terms represent a new mechanistic vision and major driving force for the oxidative aromatization of some susceptible heterocyclic molecules. Recently, these concepts have been reviewed.^{55,56}

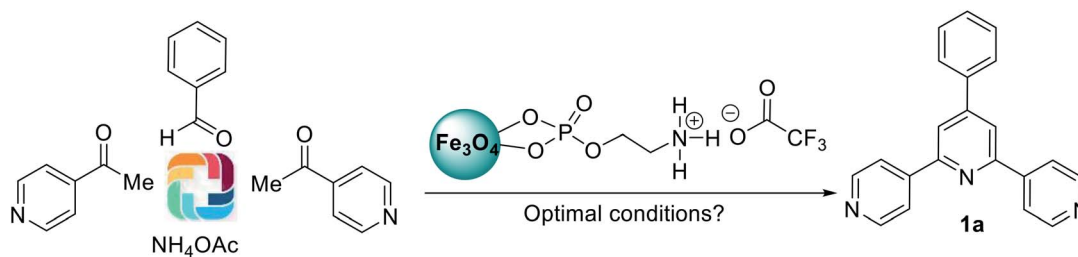
Pyridines are a privileged category of N-heteroaromatics found in numerous natural and synthetic compounds with a wide range of biological, pharmaceutical, agrochemical and physiological applications such as anti-ulcer,⁵⁷ antineoplastic,⁵⁸ antimicrobial,^{59–62} antiviral,⁶³ antitubercular,⁶⁴ antitumor,^{65–69} and cardiotoxic⁷⁰ properties. Among these compounds, terpyridines (tpys) by reason of their π -stacking ability, directional H-bonding and coordination properties are outstanding building blocks in supramolecular chemistry.⁷¹ In addition, terpyridines (tpys) have been applied broadly in various fields such as molecular biology,^{72,73} antitumor chemo-therapeutics,⁷⁴ photosensitization,⁷⁵ and asymmetric catalysis.⁷⁶ Also, they are able to coordinate to a variety of transition-metal ions as ligands and form the corresponding complexes.^{77–79} A class of these ligands is becoming popular as a building block for the assembly of coordination polymers and networks.^{80–95} Therefore, the construction of novel terpyridines and/or methodologies has attracted many attentions. So far many protocols were reported for the synthesis of these valuable compounds.^{96–104} Traditional protocols for synthesis of tpys have many drawbacks such as multi-step procedure, the use of microwave irradiation, a long reaction time, low yield, utilization of organic solvents like glycol and harmful reagents for environment such as sodium or potassium hydroxide and acetic acid. Therefore, the presentation of more efficient and greener methods for the synthesis of tpys is highly desirable.

For overcome to these demerits, for the first time we applied a recoverable nanocatalyst with magnetic properties instead of harmful reagent for one-pot synthesis of tpys under conventional heating conditions in the absence of any solvent. Also, we



Scheme 5 Construction of terpyridines in the presence a catalytic amount of $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$.



Table 1 Influence of the different parameters on construction of terpyridine **1a**^a

Entry	Solvent	Temperature (°C)	Load of catalyst (mg)	Time (min)	Yield ^b (%)
1	—	80	10	90	60
2	—	100	10	60	75
3 ^c	—	120	10	50	80
4	—	140	10	50	78
5	—	120	15	50	80
6	—	120	5	60	65
7	—	120	—	90	30
8	H ₂ O	Reflux	10	90	40
9	EtOH	Reflux	10	90	40
10	CH ₃ CN	Reflux	10	90	43
11	EtOAc	Reflux	10	90	35
12	CH ₂ Cl ₂	Reflux	10	90	Trace
13	<i>n</i> -Hexane	Reflux	10	90	Trace

^a Reaction conditions: benzaldehyde (1.0 mmol, 0.106 g), 4-acetylpyridine (2.0 mmol, 0.242 g) and ammonium acetate (2.0 mmol, 0.154 g).

^b Reported yields are referred to isolated yields. ^c The achieved data for testing the model reaction under air, nitrogen and argon atmospheres are similar.

generalize the presented protocol by applying various isomer of acetylpyridine (2 or 3 or 4-isomer) and introduce a new mechanistic route (CVABO) for the synthesis of tpys. In this paper, to develop the concept of “cooperative vinylogous anomeric based oxidation (CVABO)”^{105–110} and in continuation of our efforts to develop new protocols for the synthesis of pyridine derivatives,^{106–110} we investigated the catalytic performance of $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ in construction of terpyridins (Scheme 5).

Results and discussion

The reusable nano magnetic catalyst with ionic liquid tags namely $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ was synthesized according to our recently reported procedure.¹⁰⁶

In first step, for determine the optimal reaction conditions, we chose condensation between of benzaldehyde, 4-acetylpyridine and ammonium acetate as a model reaction. For obtaining the appropriate conditions, effective parameters including various solvents, temperature and amount of catalyst were exactly probed. Based on the obtained data as summarized in Table 1, the highest experimental yield and lowest reaction time was achieved in the presence of 10 mg catalyst at 120 °C in the absence of any solvent (Table 1, entry 3). In addition to, for demonstration of the last step of the proposed mechanism, the optimized reaction conditions were performed under nitrogen

and argon atmospheres. The results under air, nitrogen and argon atmospheres are same (Table 1, entry 3).

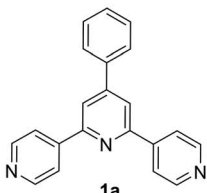
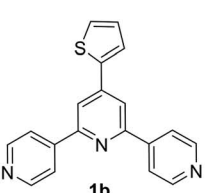
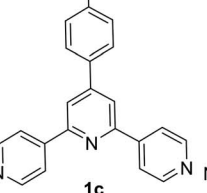
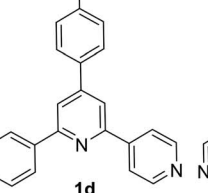
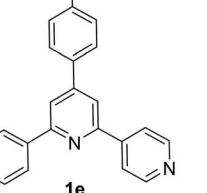
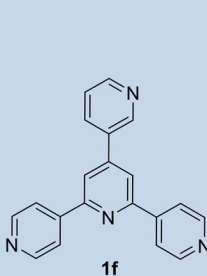
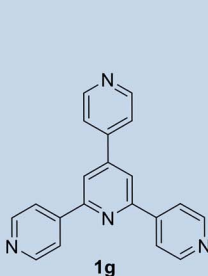
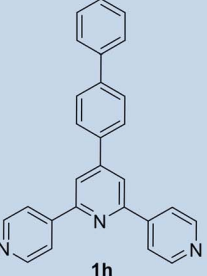
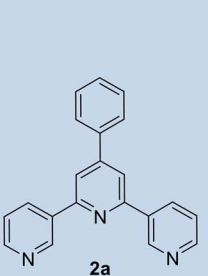
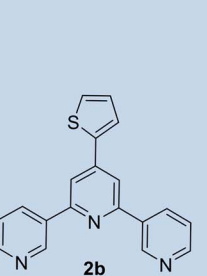
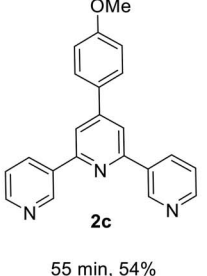
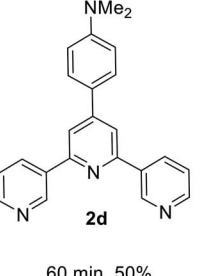
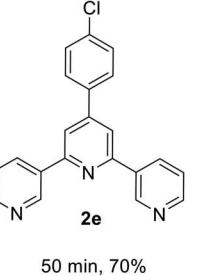
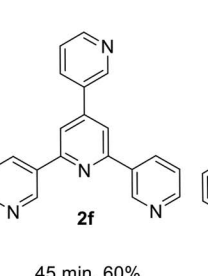
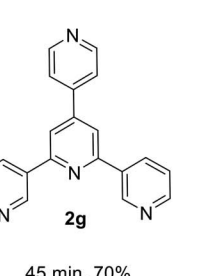
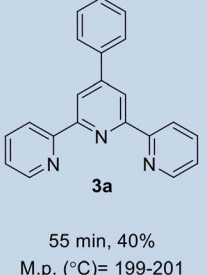
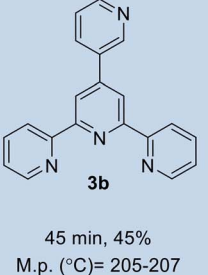


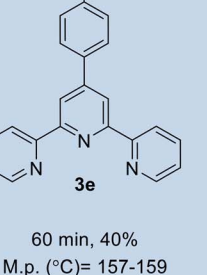
Afterwards, the scope, limitations and generality of the presented protocol developed by applying different aryl aldehydes, acetylpyridine (2, 3 and 4-isomers) and ammonium acetate using of $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ as a recoverable catalyst under the optimal qualifications. As disclose in Table 2, all desired molecules were synthesized in brief times with acceptable yields.

In a separate study, the possibility of recycling $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ was probed by the model reaction between benzaldehyde, 4-acetylpyridine and ammonium acetate in 50 minute. After each individual run, hot ethanol was added to the reaction mixture to dissolve unreacted starting materials and target product. Thus the insoluble nanocatalyst conveniently isolated from the reaction mixture utilizing a magnet bar. Then, the reusable catalyst was utilizable after washing with ethanol and drying for subsequent run. As depicted in Fig. 1, it can be inferred that the catalyst has good recovery capability for reusing test.

A suggested plausible reaction mechanism for the preparation of desirable molecule **2a** via a cooperative vinylogous anomeric based oxidation mechanism is portrayed in Scheme 6. Initially, in the presence of $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$, enolic form of 3-acetylpyridine attacked to activated benzaldehyde to produce intermediate **A**. In continuation, chalcone intermediate **A** is attacked by second molecule of 3-



Table 2 Fe₃O₄@O₂PO₂(CH₂)₂NH₃⁺CF₃CO₂⁻ catalyzed synthesis of terpyridines^a

				
50 min, 70% M.p. (°C)= 275-278 Rep. [283-284] ¹¹¹	35 min, 70% M.p. (°C)= 242-244 New	55 min, 55% M.p. (°C)= 193-195 Rep. [203.5] ¹¹²	50 min, 60% M.p. (°C)= 265-267 [Not reported] ¹⁰⁴	45 min, 68% M.p. (°C)= 260-262 New
				
40 min, 58 % M.p. (°C)= 309-311 [Not reported] ¹¹³	40 min, 68% M.p. (°C)= > 340 Rep.[324] ¹¹⁴	45 min, 50% M.p. (°C)= 201-203 Rep. [230.4] ¹¹⁵	60 min, 68% M.p. (°C)= 205-207 Rep. [220-221] ¹¹⁶	45 min, 68% M.p. (°C)= 194-195 New
				
55 min, 54% M.p. (°C)= 128-130 New	60 min, 50% M.p. (°C)= 120-124 Rep. [112-113] ¹¹⁷	50 min, 70% M.p. (°C)= 202-204 New	45 min, 60% M.p. (°C)= 276-278 Rep. [273.5-274.5] ¹¹⁸	45 min, 70% M.p. (°C)= 319-321 [Not reported] ¹¹⁹
				
55 min, 40% M.p. (°C)= 199-201 Rep. [202-208] ¹²⁰	45 min, 45% M.p. (°C)= 205-207 Rep. [207.5-209.7] ¹²¹	60 min, 41% M.p. (°C)= 288-290 Rep. [260-264] ¹²²	50 min, 50% M.p. (°C)= 155-157 Rep. [154-156] ⁹⁵	60 min, 40% M.p. (°C)= 157-159 Rep. [159] ¹²³

^a Reaction condition: aryl aldehyde (1.0 mmol), acetylpyridine derivatives (2.0 mmol, 0.242 g) and ammonium acetate (2.0 mmol, 0.154 g), solvent free, 120 °C, catalyst = 10 mg. Reported yields are referred to isolated yields.



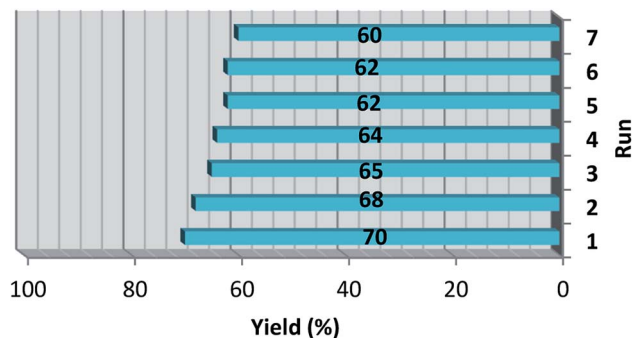


Fig. 1 The reusing test of $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$

acetylpyridine in enolic form to afford intermediate **B**. Afterwards, the enamine intermediate **C** is produced from the reaction of ammonium acetate and intermediate **B**. In the next step, through intramolecular nucleophilic attack, intermediate **C** converted to intermediate **D**. In the last step, lone pair electrons of N atom through C–C double bonds interact with a vacant anti-bonding orbital of C–H bond ($n_{\text{N}} \rightarrow \sigma_{\text{C-H}}^*$ and $\pi_{\text{C=C}} \rightarrow \sigma_{\text{C-H}}^*$) and weaken it which favored hydride transfer and H_2 releasing from intermediate **D** to generate the aromatized molecule **2a**. The achieved data from optimization of reaction under argon and nitrogen atmospheres verified our suggestion for oxidation and aromatization of intermediate **D**.

Experimental

General

The commercially available chemicals were obtained from Fluka and Merck chemical companies and used as received

without further purification. The reaction progress and purity of the prepared structures were monitored by TLC performed with silica gel SIL G/UV 254 plates. FT-IR spectra were recorded on a PerkinElmer Spectrum Version 10.02.00 using KBr pellets. The ^1H NMR (301 MHz) and ^{13}C NMR (76 MHz) spectra were recorded on a Bruker spectrometer (δ in ppm) using DMSO-d_6 as solvent with chemical shifts measured relative to $\text{Si}(\text{CH}_3)_4$ as internal standard. Melting points were determined with a Buchi B-545 melting point apparatus in open capillary tubes.

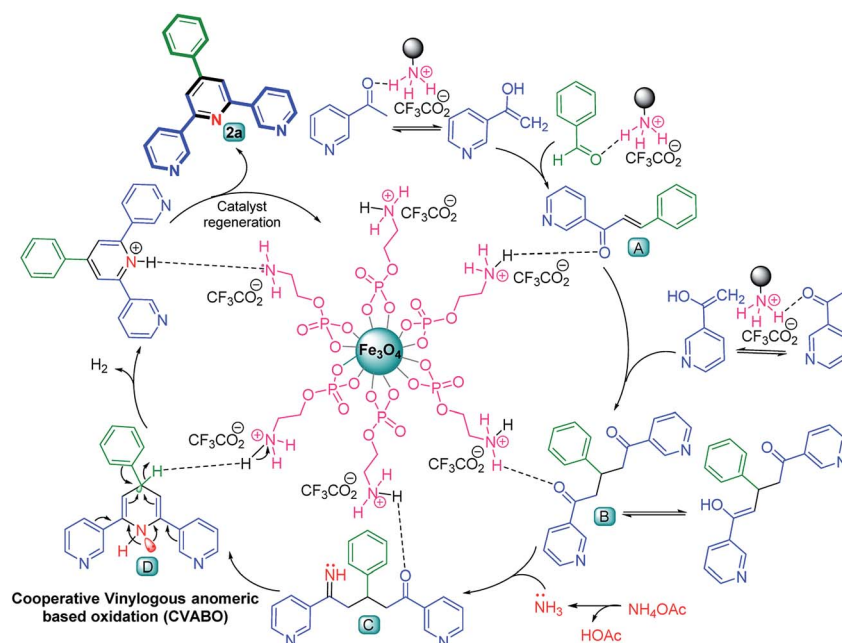
General procedure for synthesis of

$\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$

The reusable nano magnetic catalyst with ionic liquid tags namely $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ was synthesized according to our recently reported protocol.¹⁰⁶

General procedure for the synthesis of terpyridines

To a mixture of aromatic aldehydes (1.0 mmol), acetylpyridine derivatives (2.0 mmol, 0.242 g) and ammonium acetate (2.0 mmol, 0.154 g), 10 mg of $\text{Fe}_3\text{O}_4@O_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ was added. The result mixture was stirred in the absence of any solvent at 120 °C for suitable times (Table 2). The progress of reaction was checked by TLC (*n*-hexane/ethylacetate as eluent). After completions of reactions, for separation of the catalyst, hot ethanol was added to the reaction mixtures. Then, insoluble nanocatalyst conveniently isolated from the reaction mixture utilizing a magnet bar. It was washed with ethanol and reused for subsequent reaction. Finally, the solvent was removed and the crude solids obtained were purified using ethanol. The desired products were obtained in acceptable isolated yields as presented in Table 2.



Scheme 6 A proposed reaction mechanism for preparation of target molecule **2a** via a cooperative vinylogous anomeric based oxidation mechanism.



Selected spectral data

4'-(2-Thiophenyl)-4,2':6',4''-terpyridine (1b). A light green solid, mp = 242–244 °C. FT-IR (KBr, ν , cm^{-1}): 3035, 1592, 1557, 1538, 1403, 828. ^1H NMR (301 MHz, DMSO) δ_{ppm} : 8.80 (d, 4H, J = 6 Hz, pyridine), 8.40 (s, 2H, pyridine), 8.32 (d, 4H, J = 6 Hz, pyridine), 8.20 (d, 1H, J = 3 Hz, thiophene), 7.88 (d, 1H, J = 3 Hz, thiophene), 7.34 (t, 1H, J = 3 Hz, thiophene). ^{13}C NMR (76 MHz, DMSO) δ_{ppm} : 155.1, 150.9, 145.5, 144.3, 140.4, 129.7, 129.4, 128.4, 121.6, 117.5.

4'-(4-Chlorophenyl)-4,2':6',4''-terpyridine (1e). A white solid, mp = 260–262 °C. FT-IR (KBr, ν , cm^{-1}): 3035, 1592, 1559, 1493, 1389, 1092, 812. ^1H NMR (301 MHz, DMSO) δ_{ppm} : 8.80 (d, 4H, J = 6 Hz, pyridine), 8.53 (s, 2H, pyridine), 8.36 (d, 4H, J = 6 Hz, pyridine), 8.20 (d, 2H, J = 6 Hz, aromatic), 7.69 (d, 2H, J = 6 Hz, aromatic). ^{13}C NMR (76 MHz, DMSO) δ_{ppm} : 155.0, 150.9, 149.4, 145.7, 136.1, 135.2, 129.9, 129.6, 121.7, 119.4.

4'-Phenyl-3,2':6',3''-terpyridine (2a). A white solid, mp = 205–207 °C. FT-IR (KBr, ν , cm^{-1}): 3034, 1595, 1558, 1483, 1390, 803. ^1H NMR (301 MHz, DMSO) δ_{ppm} : 9.55–9.54 (m, 2H, pyridine), 8.75–8.71 (m, 4H, pyridine), 8.40 (s, 2H, pyridine), 8.15–8.12 (m, 2H, aromatic), 7.64–7.56 (m, 5H, aromatic). ^{13}C NMR (76 MHz, DMSO) δ_{ppm} : 155.2, 150.6, 150.4, 148.8, 137.6, 135.0, 134.5, 130.1, 129.6, 128.0, 124.3, 118.0.

4'-(2-Thiophenyl)-3,2':6',3''-terpyridine (2b). A white solid, mp = 194–195 °C. FT-IR (KBr, ν , cm^{-1}): 3055, 1603, 1547, 1428, 1024, 805, 695. ^1H NMR (301 MHz, DMSO) δ_{ppm} : 9.50 (s, 2H, pyridine), 8.73–8.67 (m, 4H, pyridine), 8.30 (s, 2H, pyridine), 8.17 (dd, 1H, J_1 = 3.6 Hz, J_2 = 0.9 Hz, thiophene), 7.85 (dd, 1H, J_1 = 4.8 Hz, J_2 = 0.6 Hz, thiophene), 7.60 (dd, 2H, J_1 = 7.8 Hz, J_2 = 4.8 Hz, pyridine), 7.33 (dd, 1H, J_1 = 5.1 Hz, J_2 = 3.9 Hz, thiophene). ^{13}C NMR (76 MHz, DMSO) δ_{ppm} : 155.3, 150.7, 148.7, 143.9, 140.7, 134.9, 134.19, 129.4, 129.3, 128.2, 124.3, 116.1.

4'-(4-Methoxyphenyl)-3,2':6',3''-terpyridine (2c). A white solid, mp = 128–130 °C. FT-IR (KBr, ν , cm^{-1}): 3031, 1597, 1541, 1489, 812. ^1H NMR (301 MHz, DMSO) δ_{ppm} : 9.53 (s, 2H, pyridine), 8.71 (s, 4H, pyridine), 8.35 (s, 2H, pyridine), 8.11 (d, 2H, J = 6 Hz, aromatic), 7.59 (s, 2H, aromatic), 7.15 (d, 2H, J = 3 Hz, aromatic), 3.88 (s, 3H, OMe). ^{13}C NMR (76 MHz, DMSO) δ_{ppm} : 161.1, 155.0, 150.5, 149.9, 148.7, 134.9, 134.6, 129.7, 129.3, 124.2, 117.3, 115.0, 55.9.

4'-(4-Chlorophenyl)-3,2':6',3''-terpyridine (2e). A white solid, mp = 202–204 °C. FT-IR (KBr, ν , cm^{-1}): 3044, 1609, 1577, 1545, 1497, 1420, 1024, 803, 701. ^1H NMR (301 MHz, DMSO) δ_{ppm} : 9.53 (s, 2H, pyridine), 8.73–8.70 (m, 4H, pyridine), 8.40 (s, 2H, pyridine), 8.17 (d, 2H, J = 9 Hz, aromatic), 7.65 (d, 2H, J = 9 Hz, aromatic), 7.60 (dd, 2H, J_1 = 9 Hz, J_2 = 6 Hz, aromatic). ^{13}C NMR (76 MHz, DMSO) δ_{ppm} : 155.2, 150.7, 149.0, 148.8, 136.4, 135.0, 134.94, 134.4, 129.8, 129.5, 124.3, 117.9.

4'-(4-Methylphenyl)-2,2':6',2''-terpyridine (3e). A white solid, mp = 157–159 °C. FT-IR (KBr, ν , cm^{-1}): 3050, 1602, 1584, 1551, 1467, 1386, 780. ^1H NMR (301 MHz, DMSO) δ_{ppm} : 8.85–8.83 (m, 2H, pyridine), 8.79 (s, 2H, pyridine), 8.76–8.74 (m, 2H, pyridine), 8.12 (td, 2H, J_1 = 6 Hz, J_2 = 1.2 Hz), 8.01–7.99 (m, 2H, aromatic), 7.70–7.66 (m, 2H, aromatic), 7.64–7.59 (m, 2H, aromatic), 1.68 (s, 3H, Me). ^{13}C NMR (76 MHz, DMSO) δ_{ppm} :

155.7, 154.9, 149.5, 149.3, 137.5, 137.5, 129.49, 129.4, 126.9, 124.5, 120.9, 118.0, 25.5.

Conclusions

In conclusions, for the first time a nanomagnetic catalyst was applied for one-pot preparation of terpyridines. In this study, the catalytic performance of $\text{Fe}_3\text{O}_4@\text{O}_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ as a retrievable nanocatalyst with magnetic properties was investigated for the synthesis of terpyridines through a multi-component reaction between various isomer of acetylpyridine, aryl aldehyds and ammonium acetate under conventional heating and solvent-free reaction conditions with acceptable yields and brief times. For final step of the mechanistic route for the synthesis of target molecules we suggested a cooperative vinylogous anomeric based oxidation mechanism as a new mechanistic route. Also, $\text{Fe}_3\text{O}_4@\text{O}_2\text{PO}_2(\text{CH}_2)_2\text{NH}_3^+\text{CF}_3\text{CO}_2^-$ showed excellent reusability in the investigated multi-component reactions. Other advantage of presented protocol are overcoming to drawbacks of traditional procedures such as multi-step procedure, use of microwave irradiation, long reaction time, low yield, utilization of organic solvents like glycol and harmful reagents for environment such as sodium or potassium hydroxide and acetic acid.

Conflicts of interest

There are no conflicts to declare.

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