Scientific paper

A Novel, Heterogeneous and Recyclable Polymeric Catalyst for the One-Pot Synthesis of Polyhydroquinoline and 1,8-Dioxohexahydroacridine Derivatives Under Solvent-Free Conditions

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Abstract

An efficient, recyclable and environmental-friendly synthetic route to polyhdroquinoline and 1,8-dioxohexahydroacridine derivatives have been developed via multi-component one-pot Hantzsch reaction of various aldehydes and ammonium acetate with *(a)* cyclic 1,3-dicarbonyl compounds and ethyl acetoacetate, and *(b)* 2 equivalents of cyclic 1,3-dicarbonyl compounds in the presence of novel polymeric catalyst [poly(AMPS-co-AA)] under solvent-free conditions. The present approach offers several advantages such as short reaction times, easy isolation and purification of product, and safe, non-toxic, recyclable and economic use of catalyst.

Keywords: Aldehydes, cyclic 1,3-dicarbonyl compounds, ammonium acetate, ethyl acetoacetate, crosslinked poly(AMPS-co-AA) catalyst, solvent-free, one-pot synthesis

1. Introduction

Development of novel synthetic methodologies to facilitate the preparation of compound libraries based on privileged structures is an intense area of research. One approach to address this challenge involves the development of multicomponent reactions (MCRs), in which three or more reactants are combined together in a single reaction flask to generate a product incorporating most of the atoms contained in the starting materials. In addition to the intrinsic atom economy and selectivity underlying such reactions, simpler procedures, equipment, time, and energy savings, as well as environmental friendliness have all led to a sizable effort to de sign and implement MCRs in both academia and industry.[1–7]

Compounds containing the 4-substituted 1,4-dihydropyridine (DHP) nucleus comprise a large family of medicinally important compounds. They can cure the disordered heart ratio as a chain-cutting agent of factor IV channel, posses the calcium channel agonist-antagonist modulation activities[8–11] and also behave as neuroprotectants, cerebral antiischaemic agents and chemosensitizer.[12–13] They are also common features of various bioactive compounds such as vasodilator, bronchodilator, antiatheroselerotic, antitumor, geroprotective, hepatoprotective and n idiabetic agents.[14–17]

Despite their importance from a pharmacological, industrial, and synthetic point of view, comparatively few methods on their preparation have been reported. In 1822, Arthur Hantzsch reported first synthesis of symmetrically substituted 1,4-dihydropyridine by the one-pot, four-component condensation of two molecules of ethyl acetoacetate, aromatic aldehyde and ammonia.[18] The standard Hantzsch procedure does not need the intervention of any additive or reagent and the reaction was originally conducted either in acetic acid or at reflux in alcohol for rather long periods, resulting in low or modest yields of condensation products.[19] Replacement of ammonia by ammonium acetate allowed the efficient synthesis of Hantzsch compounds in a aqueous medium as well as under solvent-free conditions.[20–21]

The utilization of cyclic 1,3-diketone in Hantzsch reaction for the synthesis of polyhydroquinoline and 1,8-dioxohexahydroacridine was recently demonstrated by

using $HClO_4$ SiO_2,[22] molecular iodine,[23] ionic liquids,[24–25] iodotrimethylsilane (TMSI),[26] organocatalysts,[27–29] microwave irradiation,[30] HY-zeolite,[31] *p*-TSA,[32] montmorillonite K10 clay,[33] hafnium (IV) bis(perfluorooctanesulfonyl)imide complex $[Hf(NPf_2)_4]$,[34] scolecite,[35] 5-pyrrolidine-2-yltetrazole,[36] ceric ammonium nitrate (CAN),[37–38] silica sulfuric acid,[39] scandium triflate $[Sc(oTf)_3]$,[40] $K_7[PW_{11}CoO_{40}]$,[41] sulfamic acid,[42] solar thermal energy,[43] NH_4Cl or $Zn(OAc)_2$,[44] carbon-based solid acid (CBSA),[45] ZnO,[46] HCM-41,[47] fluoro alcohols (TFE or HFIP),[48] nickel nanoparticle, [49] silica-gel supported polyphosphoric acid (PPA-SiO_2),[50] FeF_3,[51] and aluminum phosphate ($AlPO_4$).[52] However, these methods suffer from several drawbacks such as long reaction times, use of large quantities of volatile organic solvents, unsatisfactory yields, the use of expensive reagents, difficult workup, catalysts that are harmful to environment and harsh reaction conditions. Therefore, it is of great interest to develop an efficient and heterogeneous method for the synthesis of polyhydroquinoline and 1,8-dioxohexahydroacridine derivatives.

2. Experimental

IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr pellets). ^1H and ^{13}C NMR spectra were obtained using Bruker DRX-300 Avance spectrometer in DMSO-d_6 or $CDCl_3$ using TMS as an internal reference. Melting points were determined in open capillary tubes in a Stuart BI Branstead Electrothermal apparatus and are uncorrected. All products were characterized by comparing their spectral (IR, ^1H and ^{13}C NMR), TLC, and physical data with those reported in the literature. A simultaneous thermal analyzer (STA-625, Geometric Scientific) was used for thermo gravimetric analysis of AMPS-co-AA polymer under nitrogen atmosphere. The heating rate was 20 °C/min. The sample weight taken for TG was 10.0 mg.

2. 1. Catalyst Preparation

Crosslinked *N,N* -methylene bisacrylamide (MBA, 2 g) was added to the mixture of 2-acrylamido-2-methylpropane sulphonic acid (AMPS, 10 g) and acrylic acid (AA, 10 ml) in 100 ml distilled water. The solution was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type). The reactor was immersed in a thermostated water bath at 70 °C. An inert gas (nitrogen) was gently bubbled into the reactor to remove the oxygen. After 15 min, the ammonium persulphate solution (APS, 0.2 g in 2 ml H_2O) was added to the mixture, and the mixture was allowed to stir (200 rpm) for 20 min. To remove probably unreacted monomer, 1 g of polymer was added and the mixture allowed to stir gently for 72 hours. The polymer was filtered and poured to methanol for 48 hours. Methanol was decanted and the product divided to small pieces. Finally, the polymer was dried in oven. After grinding, the powdered polymer was kept away from moisture, heat and light.

2. 2. Typical Procedure for the Synthesis of Polyhydroquinoline and 1,8-dioxohexahyDroacridine Derivatives

Synthesis of 3-acetyl-4-(4-chlorophenyl)-2,7,7-trimethyl-4,6,7,8-tetrahydroquinolin-5(1H)-one (4b)

A mixture of 4-chlorobenzaldehyde (**1b**, 1mmol), dimedone (**2**, 1 mmol), ethyl acetoacetate (**3**, 1 mmol), ammonium acetate (1.2 mmol) and crosslinked poly (AMPS-co-AA) (0.03 g) was heated on an oil bath at 120 °C for 20 min. Completion of the reaction was indicated by TLC (hexane:ethyl acetate, 2:1). After completion, appropriate amount of hot EtOH (96%) was added and the mixture stirred for 10 min. After that, the catalyst was separated by filtration. The filtrate was poured into crushed ice and the separated solid product was filtered and recrystallized from ethanol to get pure compound **4b**.

Synthesis of 9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (5w)

To mixture of 4-chlorobenzaldehyde (**1b**, 1mmol), dimedone (**2**, 1 mmol), ethyl acetoacetate (**3**, 1 mmol) and ammonium acetate (1 mmol) was added crosslinked poly(AMPS-co-AA) (0.03 g) and the mixture was heated on an oil bath at 120 °C for 10 min. The isolation procedure was the same as described above for **4b**.

The results of all copounds obtained are collected in Table **2**.

Spectral data of the new compound ethyl 4-(2-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (4k)

Mp. 249–251 °C; IR (KBr): 3230, 3080, 2985, 1690, 1610, 1490, 1382, 1280, 1228, 710 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 0.88 (s, 3H), 1.01 (s, 3H), 1.15 (t, 3H), 1.96–2.48 (m, 7H), 3.85 (s, 3H), 4.00 (q, 2H), 4.89 (s, 1H), 6.52–7.45 (m, 4H), 9.05 (s, 1H, NH). ^1H NMR (300 MHz, DMSO-d_6 + D_2O): δ 0.88 (s, 3H), 1.01 (s, 3H), 1.15 (t, 3H), 1.96–2.48 (m, 7H), 3.85 (s, 3H), 4.00 (q, 2H), 4.89 (s, 1H), 6.52–7.45 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.61, 18.57, 26.78, 29.59, 26.19, 50.58, 55.17, 55.26, 59.42, 104.16, 110.15, 111.10, 114.06, 120.23, 129.40, 145.37, 149.49, 150.65, 159.28, 167.55, 195.60.

3. Results and Discussion

In recent years heterogeneous catalysts have attracted a great attention due to efficiency, and for economic and environmental reasons. In the green chemistry context, replacement of homogeneous catalysts with hetero-

geneous ones for the productions of fine chemicals in industrial processes appears as expansive research area.[53–57] Polymer supported reagents have been in use since 1946 and have been the subject of many review articles.[58–60] These catalysts have been recognized as environmentally benign and economically feasible catalysts owing to their high catalytic activities, ease of handling, non-toxicity and experimental simplicity in comparison to conventional catalysts.

Results of thermogravimetric analysis of our polymer catalyst are shown in Figure 1. The crosslinked poly(AMPS-co-AA) catalyst exhibits three distinct weight loss regions. The first one is in the range of 38–181 °C attributed to loss of water (8.3%), and the second is in the range of 183–335 °C with maximum decomposition rate (31% weight loss) at 297 °C. Finally, the third one is in the range of 187–496 °C with maximum decomposition rate (60.7% weight loss) at 416 °C.

The IR spectrum of the polymer showed the characteristic absorption of acid (O–H) groups at 3444 cm^{-1}, carbonyl groups at 1654 cm^{-1} and R_2CH_2-SO_3^- (AMPS) groups at 1206 cm^{-1}.

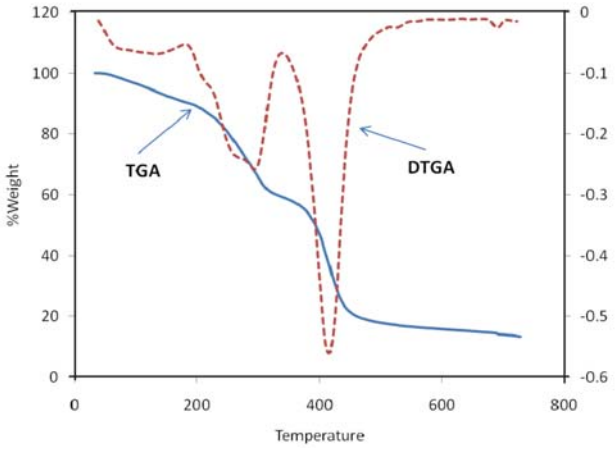
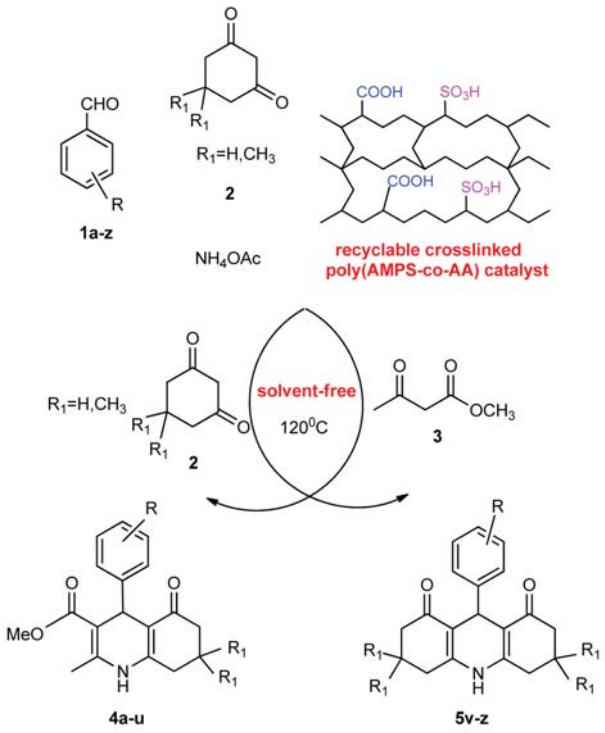


Figure 1. Thermogravimetric analysis of prepared crosslinked poly(AMPS-co-AA) catalyst.

According to our previous studies directed towards the development of practical, and environmentally friendly procedures for some important transformations,[61–68] we investigated poly(AMPS-co-AA) catalyzed reactions for the development of novel synthetic methodology.[69–70] In the present research, poly(AMPS-co-AA) catalysis of the Hantzsch reaction was investigated under solvent-free conditions (**Scheme 1**). To the best of our knowledge, there are no examples of the use of crosslinked poly(AMPS-co-AA) as catalyst for the synthesis of polyhydroquinoline and 1,8-dioxohexahydroacridine derivatives.

Initially, the condensation of 4-chlorobenzaldehyde (**1b**, 1 mmol), dimedone (2, 1 mmol), ethyl acetoacetate (**3**, 1 mmol), and ammonium acetate (1.2 mmol) in the presence of a catalytic amount of crosslinked poly



Scheme 1. Hantzsch synthesis of polyhydroquinoline and 1,8-dioxohexahydroacridine derivatives using crosslinked poly(AMPS-coAA) catalyst under solvent-free conditions.

(AMPS-co-AA) and under solvent-free conditions at 100–120 °C was examined as a model reaction (**Table 1**, entry 1-3). The best results have been obtained at 120 °C (entry 3). The efficiency of the reaction is mainly affected by the amount of catalyst and temperature. Increasing the amount of crosslinked poly(AMPS-co-AA) catalyst and temperature did not increase the yield of the reaction (entry 4-6). It was found that at lower amount of catalyst with the prolonged reaction time, the yield of reaction decreased (entry 7). Furthermore, in absence of the catalyst no products could be detected even after 1h of reaction.

Table 1. Screening of the reaction conditions for the synthesis 3-acetyl-4-(4-chlorophenyl)-2,7,7-trimethyl-4,6,7,8-tetrahydroquinolin-5(1H)-one (**4b**).

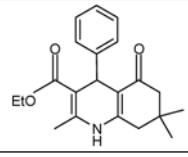
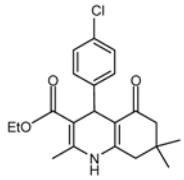
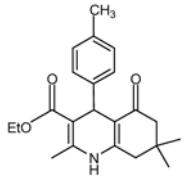
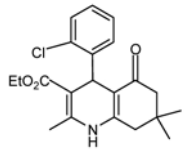
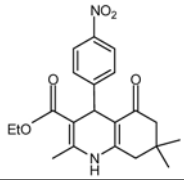
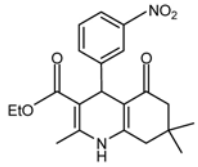
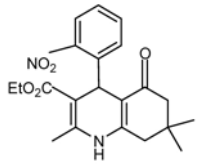
Entry	Amount of poly-(AMPS-co-AA), g	Temperature, C	Time, min	Yield, [a] %
1	0.03	100	20	72
2	0.03	110	20	77
3	0.03	120	20	89
4	0.04	120	20	83
5	0.05	120	20	83
6	0.03	130	20	83
7	0.02	120	30	74
8	–	120	60	– [b]

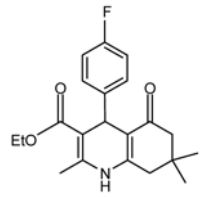
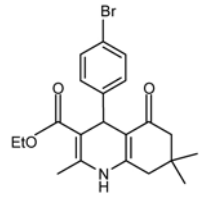
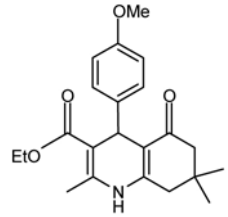
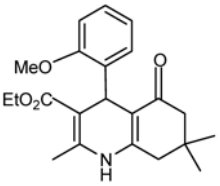
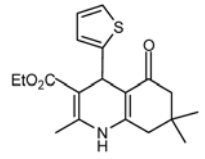
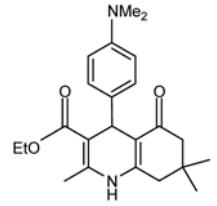
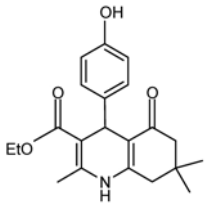
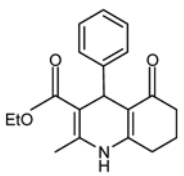
[a] Isolated yields. [b] No reaction.

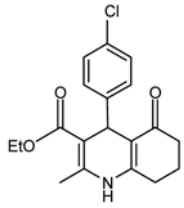
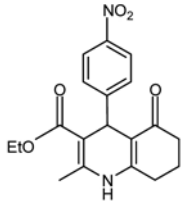
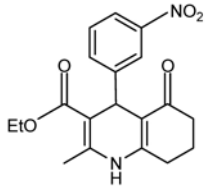
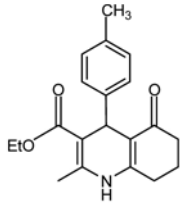
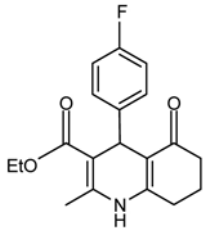
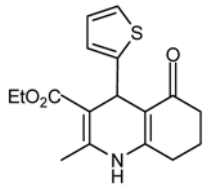
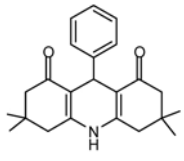
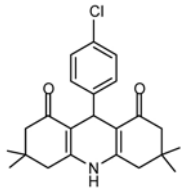
The scope and generality of this four-component one-pot Hantzsch synthesis of polyhydroquinoline derivatives is illustrated with different aldehydes (**Table 2**). All reactions proceeded efficiently within 20–35 minutes at 120 °C to provide the corresponding polyhydroquinoline derivatives in good yields ranging from 68–89%. This method has the ability to tolerate a variety of functional groups such as methoxy, methyl, nitro, hydroxy, halo, etc., under given reaction conditions. Both, the electron-rich and electron-deficient aldehydes as well as heterocyclic aldehyde worked well leading to high yields of products. The structures of all products were established from their spectral data.

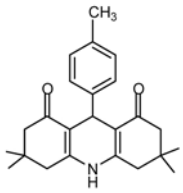
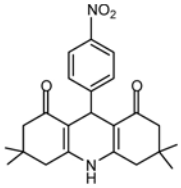
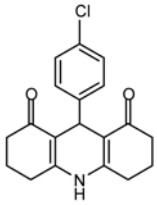
Encouraged by these results, we continued to study the reaction using 2 equivalents of cyclic 1,3-dicarbonyl compounds (1,3-cyclichexadione), various aldehydes and ammonium acetate (**Scheme 1**). Reaction was carried out under solvent-free conditions at 120 C using crosslinked poly (AMPS-co-AA) as catalyst (0.03 g) to give products in good to high yields (**Table 2**). Clearly, the nature of the substitutes on the aromatic ring showed no influence on reaction yield.

Table 2. Preparation of polyhydroquinoline and 1,8-dioxohexahydroacridine derivatives using crosslinked poly(AMPS-co-AA) catalyst.

Product (4 or 5)		R	R^1	Time, min	Yield,[a] %	Mp, °C	
						Found	Reported
(4a)		C_6H_5	CH_3	20	85	200–202	203–204[22]
(4b)		4-Cl-C_6H_4	CH_3	20	89	241–243	245–246[22]
(4c)		4-CH_3-C_6H_4	CH_3	20	86	260–262	260–261[22]
(4d)		2-Cl-C_6H_4	CH_3	25	82	210–212	208–210[22]
(4e)		4-NO_2-C_6H_4	CH_3	30	84	239–241	242–244[22]
(4f)		3-NO_2-C_6H_4	CH_3	30	86	174–177	178–179[22]
(4g)		2-NO_2-C_6H_4	CH_3	25	80	205–207	206–207[22]

Product (4 or 5)		R	R^1	Time, min	Yield,[a] %	Mp, °C	
						Found	Reported
(4h)		4-F-C_6H_4	CH_3	25	85	186–187	185–186[22]
(4i)		4-Br-C_6H_4	CH_3	20	84	248–250	252–253[22]
(4j)		4-CH_3O-C_6H_4	CH_3	25	82	253–255	256–257[22]
(4k)		2-CH_3O-C_6H_4	CH_3	20	88	249–251	204–208[22]
(4l)		2-Thienyl	CH_3	35	78	239–241	238–240[22]
(4m)		4-Me_2N-C_6H_4	CH_3	25	81	260–262	262–263[22]
(4n)		4-HO-C_6H_4	CH_3	25	76	230–232	230–231[22]
(4o)		C_6H_5	H	20	80	244–246	240–241[23]

Product (4 or 5)		R	R^1	Time, min	Yield,[a] %	Mp, °C	
						Found	Reported
(4p)		4-Cl-C_6H_4	H	25	78	237–239	234–235[23]
(4q)		4-NO_2-C_6H_4	H	25	80	207–209	204–205[23]
(4r)		3-NO_2-C_6H_4	H	25	82	202–204	198–200[23]
(4s)		4-CH_3-C_6H_4	H	25	86	242–244	240–241[23]
(4t)		4-F-C_6H_4	H	25	84	243–245	243–244[36]
(4u)		2-Thienyl	H	30	68	230–232	233–234[36]
(5v)		C_6H_5	CH_3	15	86	191–193	190–192[45]
(5w)		4-Cl-C_6H_4	CH_3	10	90	297–300	299–301[45]

Product (4 or 5)		R	R^1	Time, min	Yield,[a] %	Mp, °C	
						Found	Reported
(5x)		4-CH_3-C_6H_4	CH_3	15	86	269–271	269–270[45]
(5y)		4-NO_2-C_6H_4	CH_3	10	88	286–289	286–289[45]
(5z)		4-Cl-C_6H_4	H	15	89	266–268	268–270[48]

[a] Isolated yields.

A tentative mechanism to rationalize the product formation is shown in (**Scheme 2**). Polyhydroquinolines **4a-u** may be formed either through steps **I-III** or through steps **IV-VI**.[31–33,39,41–42] The poly(AMPS-co-AA) catalyst[69–70] is involved in steps **I** and **IV**, where it catalyzes the Knoevenagel type coupling of aldehydes with active methylene compounds and in steps **III** and **VI**, where it catalyzes the Michael type addition of intermediates **6**, **7**, and **8**, **9** to give products **4a-u**. The formation of **5v-z** takes place through a Hantzsch-like mechanism via conjugate addition of the enamine intermediate (obtained from dimedone and ammonium acetate, step **V**) to the Knoevenagel product (obtained from dimedone and aldehydes **1a-z**, step **I**), followed by imino-enamino tautomerism and subsequent cyclization.[44–45]

Furthermore, we investigated the reusability and recycling ability of crosslinked poly(AMPS-co-AA) catalyst. At first, we put 4-chlorobenzaldehyde (**1b**, 1 mmol), dimedone (**2**, 1 mmol), ethyl acetoacetate (**3**, 1 mmol), ammonium acetate (1.2 mmol) and 0.03 g of poly(AMPS-co-AA) catalyst together, and then the mixture was stirred at 120 °C for 20 min without any solvent. When the reaction was completed, the poly(AMPS-co-AA) catalyst was separated by simple filtration and by diluting with hot ethnol. Finally, the catalyst was dried in oven 120 °C for 24 h. Recovered catalyst was reused in subsequent reactions (**Table 3**).

Table 3. Reuse of the crosslinked poly(AMPS-co-AA) catalyst for the synthesis of 3-acetyl-4-(4-chlorophenyl)-2,7,7-trimethyl-4,6,7,8-tetrahydroquinolin-5(1H)-one (**4b**).

Entry	Time, min	Yield,[a] %
0	20	89
1	20	82
2	30	76

[a] Isolated yields.

4. Conclusion

In conclusion, this paper describes an efficient, heterogeneous, simple and safe procedure for the preparation of the polyhydroquinoline and 1,8-dioxohexahydroacridine derivatives. Present methodology offers very attractive features such as reduced reaction times, high yields, non-corrosiveness, generality, easy and safe work-up, recycability of catalyst and environmental acceptability.

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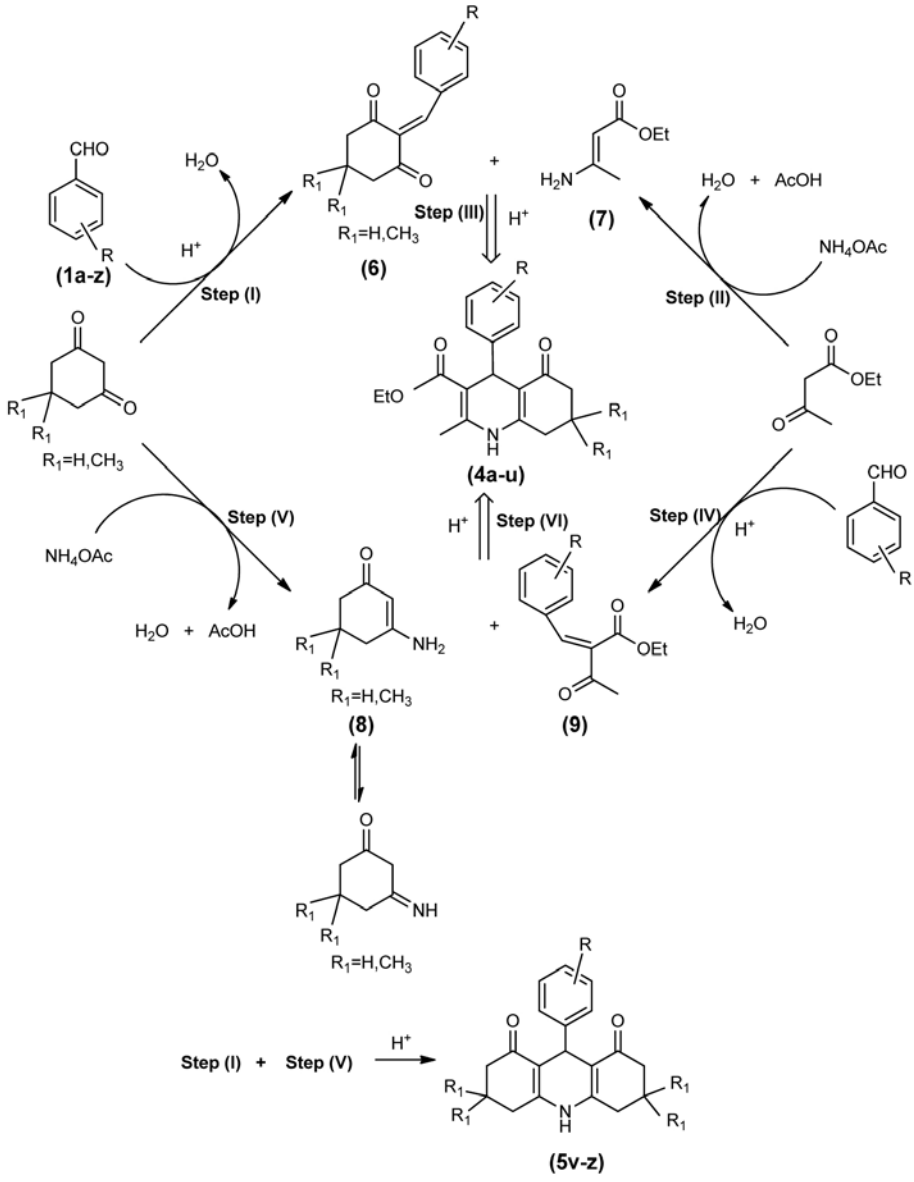
Authors wish to dedicate the present work to Professor M. A. Zolfigol, of Bu-Ali Sina University, Hamadan, Iran, for his remarkable lifetime contributions to research in chemistry and his constant inspirations given to his students.



Scheme 2. The proposed mechanism for the formation of polyhydroquinoline (**4a-u**) and 1,8-dioxohexahydroacridine (**5v-z**) derivatives using crosslinked poly(AMPS-co-AA) catalyst.

6. References

1. L. Nagarapu, M. D. Kumari, N. V. Kumari, S. Kantevari, *Catal. Commun*. **2007**, *8,* 1871–1875.
2. S. Asghari, M. Ahmadipour, *Acta Chim. Slov.* **2010**, *57,* 953–956.
3. S. Ghassamipour, A. R. Sardarian, *J. Iran. Chem. Soc*. **2010**, *7,* 237–242.
4. R. Tayebee, M. Ghadamghae, B. Maleki, *Chin. J. Catal.* **2012**, *33,* 659–665.
5. F. Shirini, M. A. Zolfigol, A. R. Abri, *J. Iran. Chem. Soc.* **2008**, *5,* 96–99.
6. B. Maleki, H. Keshvari-Shirvan, F. Taimazi, E. Akbarzadeh, *Int. J. Org. Chem.* **2012**, *2,* 93–99.
7. A. Dandia, A. K. Jain, D. S. Bhati, *Synth. Commun.* **2011**, *41,* 2905–2919.
8. M. Kawase, A. Shah, A. Gaveriya, N. Motohashi, H. Sakagami, A. Varga, J. Molnar, *Bioorg. Med. Chem*. **2002**, *10,* 1051–1055.
9. U. Eisner, J. Kuthan, *Chem. Rev*. **1972**, *72,* 1–42.
10. R. Shan, C. Velazquez, E. E. Knaus, *J. Med. Chem*. **2004**, *47,* 254–261.
11. Y. Sawada, H. Kayakiri, Y. Abe, T. Mizutani, N. Inamura, M. Asano, C. Hatori, I. Aramori, T. Oku, H. Tanaka, *J. Med. Chem*. **2004**, *47,* 2853–2863.
12. V. Klusa, *Drugs Future* **1995**, *20,* 135–138.
13. R. Boer, V. Gekeler, *Drugs Future* **1995**, *20,* 499–509.
14. A. Sausins, G. Duburs, *Heterocycles* **1988**, *27,* 269–289.

15. R. Mannhold, B. Jablonka, B. Voigdt, K. Schoenafinger, K. Schraven, *Eur. J. Med. Chem*. **1992**, *27,* 229–235.
16. F. Bossert, H. Meyer, E. Wehinger, *Angew. Chem. Int. Ed. Engl*. **1981**, *20,* 762–769.
17. H. Nakayam, Y. Kanaoka, *Heterocycles* **1996**, *42,* 901–909.
18. A. Hantzsch, Lieb. *Ann. Chem*. **1882**, *215,* 1–82.
19. B. Leov, K. M. Snader, *J. Org. Chem.* **1965**, *30,* 1914–1916.
20. G. W. Wang, J. J. Xiu, C. B. Miao, X. L. Wu, *Bull. Chem. Soc. Jpn*. **2006**, *3,* 454–456.
21. M. A. Zolfigol, M. Safaiee, *Synlett* **2004**, 827–829.
22. M. Maheswara, V. Siddaiah, G. L. V. Damu, C. V. Rao, *Arkivoc* **2006**, *ii,* 201–206.
23. S. Ko. M. N. V. Sastry, C. Lin, C. F. Yao, *Tetrahedron Lett*. **2005**, *46,* 5771–5774.
24. S. J. Ji, Z. Q. Jiang, J. Lu, T. P. Loa, *Synlett* **2004**, 831–835.
25. R. Sridhar, P. T. Perumal, *Tetrahedron* **2005**, *61,* 2665–2670.
26. G. Sabitha, G. S. K. K. Reddy, C. S. Reddy, J. S. Yadav, *Tetrahedron Lett.* **2003**, *44,* 4129–4131.
27. A. Kumar, R. A. Maurya, *Tetrahedron* **2007**, *63,* 1946–1952.
28. N. N. Karade, V. H. Budhewar, A. V. Shinde, W. N. Jadhav, *Lett. Org. Chem*. **2007**, *4,* 16–19.
29. A. Kumar, R. A. Maurya, *Tetrahedron Lett*. **2007**, *48,* 3887–3890.
30. S. J. Tu, J. F. Zhou, X. Deng, P. J. Cai, H. Wang, F. C. Feng, *Chin. J. Org. Chem*. **2001**, *21,* 313–316.
31. B. Das, B. Ravikanth, R. Ramu, B. V. Rao, *Chem. Pharm. Bull*. **2006**, *54,* 1044–1045.
32. S. R. Cherkupally, R. Mekala, *Chem. Pharm. Bull*. **2008**, *56,* 1002–1004.
33. G. Song, B. Wang, X. Wu, Y. Kang, L. Yang, *Synth. Commun*. **2005**, *35,* 2875–2880.
34. M. Hong, C. Cai, W. B. Yi, *J. Fluorine Chem*. **2010**, *131,* 111–114.
35. L. S. Gadekar, S. S. Katkar, S. R. Mane, B. R. Arbad, M. K. Lande, *Bull. Korean Chem. Soc*. **2009**, *30,* 2532–2534.
36. W. Su, J. Li, J. Li, *Aust. J. Chem*. **2008**, *61,* 860–863.
37. S. Ko, C. F. Yao, *Tetrahedron* **2006**, *62,* 7293–7299.
38. C. S. Reddy, M. Raghu, *Chin. Chem. Lett*. **2008**, *19,* 775–779.
39. A. Mobinikhaledi, N. Foroughifar, M. A. Bodaghifard, H. Moghanian, S. Ebrahimi, M. Kalhor, *Synth. Commun*. **2009**, *39,* 1166–1174.
40. J. L. Donelson, R. A. Gibbs, S. K. De, *J. Mol. Catal. A: Chem*. **2006**, *256,* 309–311.
41. M. M. Heravi, K. Bakhtiari, N. M. Javadi, F. F. Bamoharram, M. Saeedi, H. A. Oskooie, *J. Mol. Catal. A: Chem*. **2007**, *264,* 50–52.
42. N. Foroughifar, A. Mobinikhaledi, M. A. Bodaghifard, H. Moghanian, S. Ebrahimi, *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.* **2009**, *39,* 161–163.
43. R. A. Mekheimer, A. A. Hameed, K. U. Sadek, *Green. Chem*. **2008**, *10,* 592–593.
44. S. Balalaie, F. Chadegani, F. Darvich, H. R. Bijanazadeh, *Chin. J. Chem*. **2009**, *27,* 1953–1956.
45. A. Davoodnia, A. Khojastehnezhad, N. Tavakoli-Hoseini, *Bull. Korean. Chem. Soc*. **2011**, *32,* 2243–2248.
46. F. Matloubi Moghaddam, H. Saeidian, Z. Mirjafary, A. Sadeghi, *J. Iran. Chem. Soc*. **2009**, *6,* 317–324.
47. L. Nagarapu, M. D. Kumari, N. V. Kumari, S. Kantevari, *Catal. Commun*. **2007**, *8,* 1871–1875.
48. A. Heydari, S. Khaksar, M. Tajbakhsh, H. R. Bijanzadeh, *J. Fluorine Chem*. **2009**, *130,* 609–614.
49. S. B. Sapkal, K. F. Shelke, B. B. Shingate, M. S. Shingare, *Tetrahedron Lett.* **2009**, *50,* 1754–1756.
50. A. Khojastehnezhad, F. Moeinpour, A. Davoodnia, *Chin. Chem. Lett.* **2011**, *22,* 807–810.
51. R. Surasani, D. Kalita, A. V. D. Rao, K. Yarbagi, K. B. Chandrasekhar, *J. Fluorine Chem.* **2012**, *135,* 91–96.
52. P. Reddy, M. A. Chari, K. Mukkanti, *J. Het. Chem*. **2012**, *49,* 232–236.
53. S. Farhadi, Z. Babazadeh, M. Maleki, *Acta Chim. Slov.* **2006,** *53,* 72–76.
54. M. M. Hashemi, A. Rahimi, Z. Karimi-Jaberi, Y. Ahmadibeni, *Acta Chim. Slov.* **2005,** *52,* 86–87.
55. A. Zali, A. Shokrolahi, M. H. Keshavarz, M. A. Zarei, *Acta Chim. Slov.* **2008,** *55,* 257–260.
56. R. S. Vrama, *Green Chem.* **1999,** *1,* 43–55.
57. M. A. Zolfigol, P. Salehi, M. Shiri, T. Fall Rastegar, A. Ghaderi, *J. Iran. Chem. Soc.* **2008,** *5,* 490–497.
58. S. V. Ley, I. R. Baxendale, R. N. Bream, P. S. Jackson, A. G. Leach, D. A. Longbottom, M. Nesi, J. S. Scott, R. I. Storer, S. J. Taylor, *J. Chem. Soc. Perkin Trans 1.* **2000**, *23,* 3815–4195.
59. A. Kirschning, H. Monenschein, R. Wittenberg, *Angw. Chem. Int. Ed*. **2001**, *40,* 650–679.
60. A. Pourjavadi, H. Salimi, S. Barzegar, B. Eftekhari-Sis, *Acta Chim. Slov*. **2007**, *54,* 140–143.
61. B. Maleki, H. Salahabadi, M. Khodaverdian-Moghaddam, *Acta Chim. Slov.* **2010**, *3,* 741–745.
62. B. Maleki, *Coll. Czech. Chem. Commun.* **2011**, *76,* 27–37.
63. B. Maleki, D. Azarifar, R. Ghorbani-Vaghei, H. Veisi, S. F. Hojati, M. Gholizadeh, H. Saleabadi, M. Khodaverdian Moghaddam, *Monatsh. Chem.* **2009**, *140,* 1485–1488.
64. R. Tayebee, E. Rezaei-Seresht, B. Maleki, *Lett. Org. Chem.* **2012**, *9,* 183–191.
65. B. Maleki, H. Veisi, *Bull. Korean Chem. Soc.* **2011**, *32,* 4366–4370.
66. B. Maleki, H. Saleabadi, Z. Sepehr, M. Kermanian, *Coll. Czech. Chem. Commun.* **2011**, *76,* 1307–1315.
67. B. Maleki, D. Azarifar, S. F. Hojati, M. Gholizadeh, H. Veisi, H. Salehabadi, M. Khodaverdian Moghadam, M. *J. Het. Chem*. **2011**, *48,* 449–453.
68. B. Maleki, M. Gholizadeh, Z. Sepehr, *Bull. Korean Chem. Soc.* **2011**, *32,* 1697–1702.
69. A. Mohammadi, H. Keshvari, R. Sandaroos, B. Maleki, H. Rouhi, H. Moradi, Z. Sepehr, S. Damavandi, *Appl. Catal. A: Gen.* **2012**, *429–430,* 73–78.
70. B. Maleki, S. Barzegar, Z. Sepehr, M. Kermanian, R. Tayebee, *J. Iran. Chem. Soc.* **2012**, DOI: 10.1007/s13738-012-0092-5.

Povzetek

V prispevku je predstavljena učinkovita, obnovljiva in okolju prijazna Hantzscheva sinteza polihidrokinolinskih in 1,8-dioksoheksahidroakridinskih derivatov z večkomponentno enostopenjsko reakcijo med različnimi aldehidi, amonijevim acetatom in *(a)* cikličnimi 1,3-dikarbonilnimi spojinami ter etil acetoacetatom, oziroma *(b)* z dvemi ekvivalenti cikličnih 1,3-dikarbonilnih spojin v prisotnosti novega polimernega katalizatorja [poly(AMPS-co-AA)] in brez topila. Postopek ponuja več prednosti, kot so kratki reakcijski časi, enostavna izolacija in čiščenje produkta, ter varen, netoksičen, obnovljiv in ekonomsko učinkovit katalizator.