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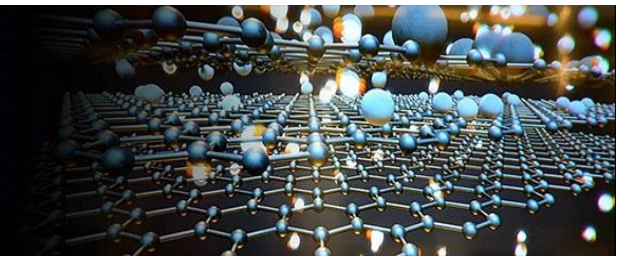

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Synthesis of 4, 5-Diarylidene-1, 2, 3, 4, 5, 6, 7, 8-octahydro-9-arylacridine using cellulose sulfuric acid catalyst: Green approach

Prajakta More, Rupali L Magar and Prashant B Thorat

Abstract
Method describe an efficient synthesis of cycloalkenopyridine derivatives using aromatic aldehyde, cyclic ketone and ammonium acetate in presence of heterogeneous catalyst cellulose sulfuric acid under solvent free conditions. The catalyst was able to catalyze reaction for various aromatic aldehydes to provide excellent yields for products. The present protocol gives several advantages such as green reaction conditions, easy work-up, easy separation of catalyst and reusability of catalyst.

Keywords: Dicycloalkenopyridine, heterogeneous catalysts, cellulose sulfuric acid, solvent free, reusable catalyst, aromatic aldehydes, cyclohexanol

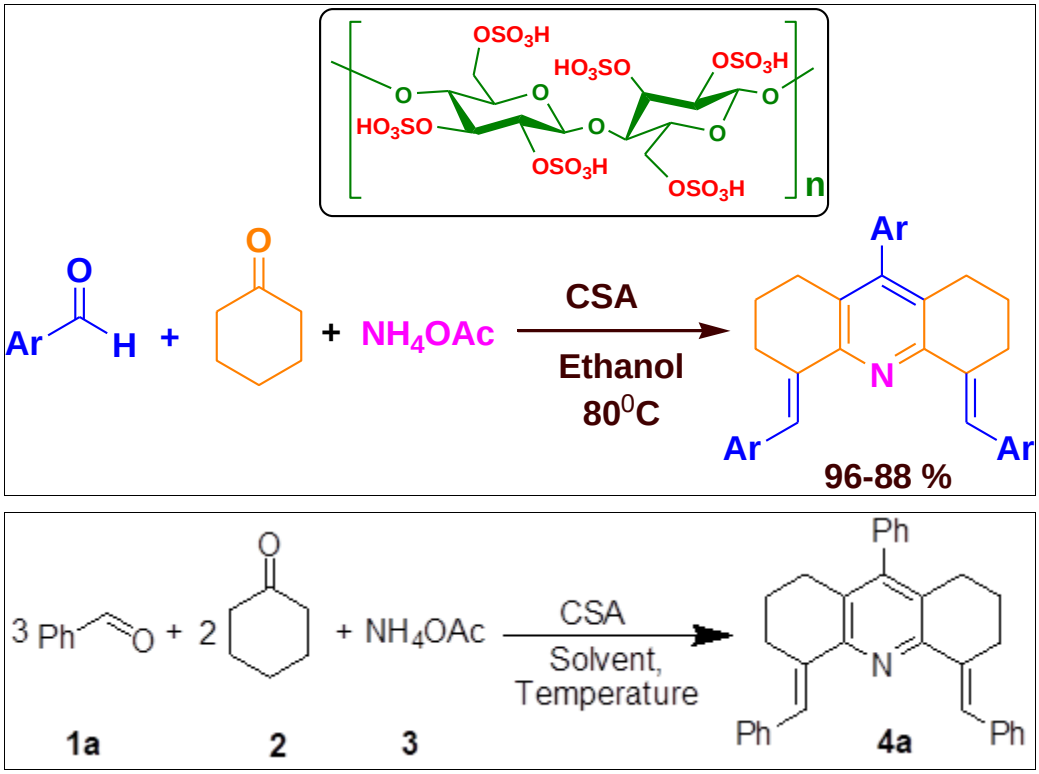
Introduction

Pyridine nucleus is unambiguous skeleton found in plethora of natural and synthetic structures. Small heterocyclic molecules containing pyridine ring are useful building blocks for the construction of many bioactive compounds and pharmaceutical agents in combinatorial chemistry [1]. Compound which serve as high-potency agonists for the human adenosine receptors contain pyridine framework and used as therapeutic agents for the treatment of Parkinson's disease and Prion disease [2]. In addition, due to π-stacking and directional H-bonding ability of pyridine ring they have been used as chelating ligands in coordination and supramolecular chemistry [3].

4, 5-Diarylidene-1, 2, 3, 4, 5, 6, 7, 8-octahydro-9-arylacridine (cycloalkenopyridine) ring is division of nitrogen containing compounds, present in naturally biologically active structures as framework. This scrutiny prompted us to develop new synthetic protocol to prepare cycloalkenopyridines which serves as significant intermediate for pharmaceuticals and agrochemicals [4]. Cycloalkenopyridine are important and useful intermediates in preparing variety of heterocyclic compounds, despite of that the synthesis of cycloalkenopyridine derivatives is unnoticed. While reviewing literature we observed that very few reports have been documented for actual synthesis of cycloalkenopyridine derivatives.[5] Out of these, one report has been reported by our colleagues previously [6].

Nowadays, the stress of synthetic and organic chemistry is focusing more on environmentally friendly processes; in this consideration, carbohydrates are attractive tools to be used as supporting material for heterogeneous catalysis [7, 8]. In recent years many carbohydrates such as alginate [9] gelatin [10, 11] starch [12] and chistosan [13] derivatives have been utilized as a support for catalytic studies. Particularly cellulose sulfuric acid, have been used more popularly [14]. They are extremely inert, inexpensive, biodegradable and environmentally benign which give freedom to employ various reaction conditions. Due to these attractive features it has been studied extensively for last few years.

In our earlier communications we have reported the synthesis of chromenes and pyrimidine molecules using polyamine base and sulfated tin oxide catalysts respectively [15]. Continuing our work on heterogeneous catalysts [15], in this letter, we have explored catalytic ability of cellulose sulfuric acid (CSA) for the synthesis of 4, 5-Diarylidene-1, 2, 3, 4, 5, 6, 7, 8-octahydro-9-arylacridine derivatives. We started with the synthesis of cellulose sulfuric acid. The acid catalyst was easily synthesized using known synthetic route described in the literature[14] and employed in the synthesis of 4,5-dibenzylidene-1, 2, 3, 4, 5, 6, 7, 8-octahydro-9-phenylacridine 4a as model compound. For this synthesis, a mixture of benzaldehyde, cyclohexanone, and ammonium acetate were reacted in presence of CSA as catalyst at room temperature condition (Scheme 1). Based on our previous studies we have chosen ethanol as reaction medium.



Scheme 1: Optimization of synthesis of cycloalkenopyridine 4a

Initially, the reaction was optimized to find suitable catalytic loading of CSA. Table 1 shows the results obtained for the reactions at various catalytic quantities. When the reaction was studied using 10 mol% of catalyst, it offered 57% product for 4a in 12 h (Table 1, Entry 1). At increased catalytic loading 15%, yield of 4a was also improved (61%) with drop in the reaction time (Table 1, Entry 2). The optimum catalytic loading for the reaction was achieved at 20 mol%. Maximum 78% yield for product 4a was obtained and rate of reaction (6h) was also highest (Table 1, Entry 3). More increase in catalytic amount lowered the reaction performance (Table 1, Entries 4 and 5). The decrease in the catalytic activity was may be due to agglomeration of sulfate species which reduce the acid strength [11]. To ensure the essence of catalyst CSA, the reaction was performed under catalytic free conditions. In absence of CSA reaction could yield only 31% product 4a even at extended reaction time (Table 1, Entry 6) which clearly demonstrates the requirement of catalyst CSA.

Table 1: The effect of catalytic loading on the synthesis of **4a**

Entry	Catalytic loading (Wt mol %)	Time (h)	Yield[b] (%)
1	10	12	57
2	15	10	61
3	20	6	78
4	25	6	72
5	30	8	68
6[c]	0	24	31

[a] Conditions: Benzaldehyde (3 mmol) 1a, cyclohexanone (2 mmol) 2, Ammonium acetate (3 g), cellulose ulfuric acid were reacted at room temperature in ethanol solvent. The progress of reaction was monitored by thin layer chromatography.
[b] Isolated yield.
[c] The reaction was performed in absence of catalyst.

Next, to improve and optimize the catalytic activity of catalyst CSA, the reaction was screened with various solvents and temperature along with using 20 mol % of the catalyst. At first, we used polar aprotic solvents acetonitrile and *N*, *N*-dimethylformamide which yielded moderate 57% and 61% products respectively and reaction rate was lowered (Table 2, Entries 1 and 2). The reaction was faster in protic solvents, however methanol was superior to water and reactions in theses solvents offered desired yield 71% and 69% 4a respectively (Table 2, Entries 3 and 4). In non-polar solvent chloroform and dichloromethane the reaction was sluggish and yielded least products 44% and 38% respectively (Table 2, Entries 5 and 6). When reaction was carried out with ethanol as solvent, up to 78% yield was obtained for corresponding product 4a with maximum reaction rate (Table 2, Entry 7). Above result demonstrated that ethanol at optimized conditions were indispensable for achieving excellent yield for product 4a.

Next in order to see the influence of temperature, the reaction was examined over a range of temperature using 20 mol % CSA catalyst optimized condition. The reaction performance was found to be enhanced with increasing temperature. When temperature was raised to 60 °C, the reaction rate was increased giving 80% yield for product 4a (Table 2, Entry 8). The best conditions were arrived at 80 °C, the reaction was completed in fastest time to furnish maximum 89% yield for 4a (Table 2, Entry 9). More increase in temperature did not show progressive change in the reaction. To confirm this, we carried out reactions at elevated temperatures 90 °C and 100 °C which gave 90% and 89% yields respectively for particular desired products without any change in reaction rate (Table 2, Entries 10 and 11).

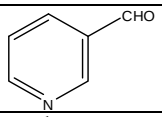
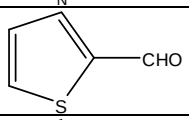
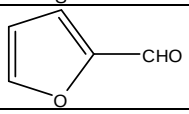
Table 2: The effect of various solvents and temperature on the synthesis of 4a.[a]

Entry	Solvent	Temperature °C	Time (h)	Yield[b] (%)
1	Acetonitrile	RT	18	57
2	DMF	RT	14	61
3	Methanol	RT	8	71
4	Water	RT	14	69
5	Chloroform	RT	24	44
6	Dichloromethane	RT	24	38
7	Ethanol	RT	6	78
8	Ethanol	60	4	80
9	Ethanol	80	2	89
10	Ethanol	90	2	90
11	Ethanol	100	2	89

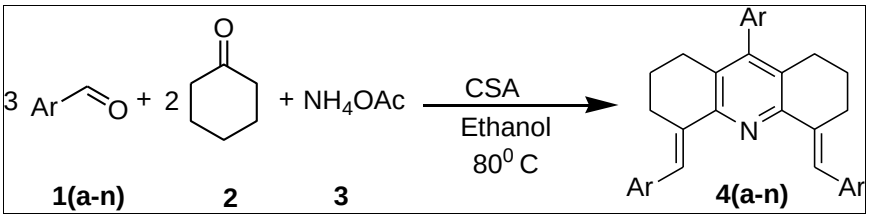
[a] Conditions: Benzaldehyde (3 mmol) 1a, cyclohexanone (2 mmol) 2, Ammonium acetate (3 g), cellulose surfuric acid (20 mol%) were reacted at specified temperature. The progress of reaction was monitored by thin layer chromatography.
[b] Isolated yield.

In order to establish the substrate generality of this reaction, the reactions of various aromatic aldehydes with cyclohexanone using ammonium acetate as nitrogen source were studied under the optimized conditions [16]. It is evident from Table 3, all reactions proceeded well irrespective of type of substituent present on the aromatic ring to furnish excellent to good yields for respective products.

Table 3: Synthesis of dicycloalkenopyridines[a]

Entry	Ar	Product (4)	Time (h)	Yield (%)	MP
1	Ph	a	2.0	95	158-160[5,6]
2	4-F	b	2.0	96	130-132[6]
3	2-Cl	c	2.0	90	180-182[6]
4	4-Cl	d	2.0	91	195-197[5, 6]
5	4-Br	e	3.0	93	200-202[6]
6	3-Br	f	2.5	90	236-238[6]
7	2, 4-(OCH3)	g	2.0	92	230-232[6]
8	4-OCH3	h	2.0	94	222-224[5, 6]
9	4-N(CH3)2	i	2.5	88	>250[6]
10	4-NO_2	j	3.0	90	190-192[6]
11	3-NO_2	k	3.0	88	191-193[6]
12		l	3.0	93	167-168
13		m	3.0	89	159-161
14		n	2.5	92	187-189

[a] Conditions: Aromatic aldehyde (3 mmol) 1a, cyclohexanone (2 mmol) 2, Ammonium acetate (3 g), sulfated tin oxide (20 mol%) were reacted at 110 °C temperature. The progress of reaction was monitored by thin layer chromatography.
[b] Isolated yield.



Based on obtained results and literature[14, 6] the probable mechanistic pathway is shown in Figure 1. It is assumed that the reaction proceeds via acid catalyzed aldol condensation. The reaction starts with proton transfer to a cyclohexanone from Bronsted acid sites of the catalyst which form nucleophile as enol form of cyclohexanone (Intermediate I). Simultaneously, proton transfer to aldehyde formed electrophile which is attacked by intermediate I followed by dehydration to give intermediate II. The intermediate II again react with another molecule of aldehyde to form intermediate III. Further, Michael addition reaction of intermediate II and III gives intermediate IV, which on cyclo-condensation with ammonium acetate furnishes the desired product 4a.

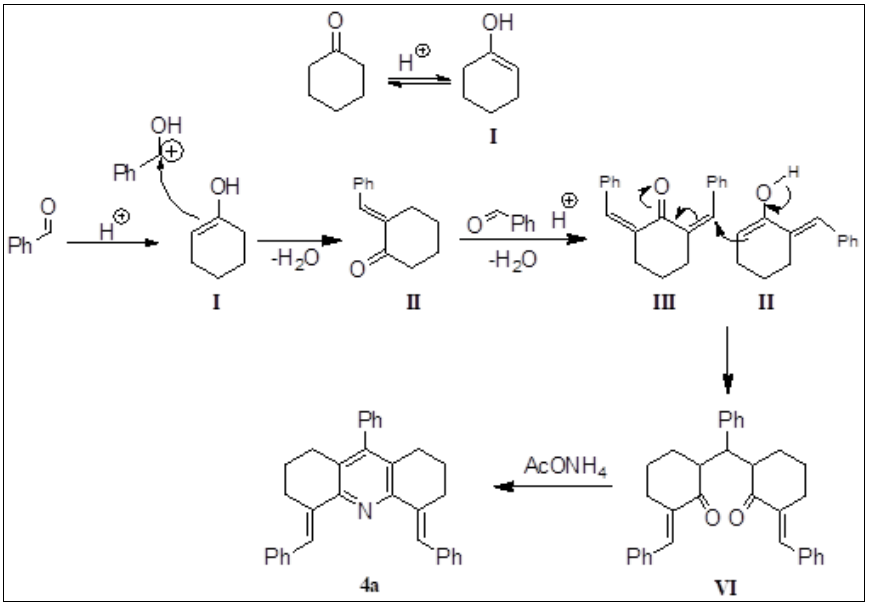


Fig 1: Mechanistic pathway for synthesis of 4a

Reusability of catalyst

To check the reusability of catalyst, it was recovered from the reaction medium by simple filtration and washed with water several times followed by chloroform washing and dried in vacuum at 60 °C for 5-6 h. The recovered catalyst was reused in the synthesis of 4a in the next cycles. Table 4 reveals that catalyst exhibited good activity up to three runs.

Table 4: Reusability of catalyst cellulose sulfuric acid.[a]

No of runs	Time (h)	Yield[b] (%)
1	2	95
2	3	92
3	4	88
4	6	69
5	6	53

[a] Conditions: Aromatic aldehyde (3 mmol) 1a, cyclohexanone (2 mmol) 2, Ammonium acetate (3 g), sulfated tin oxide (20 mol%) were reacted at 80 °C temperature in ethanol as solvent. The progress of reaction was monitored by thin layer chromatography.
[b] Isolated yield.

In summary, we have developed a simple and efficient method for the synthesis of diclycloalkenopyridines using aromatic aldehyde, cyclic ketone and ammonium acetate in presence of heterogeneous catalyst cellulose sulfuric acid under solvent free conditions. The catalyst was able to catalyze reaction successfully and efficiently. The reaction proceeded well for all kinds of aromatic aldehydes. Additionally, catalyst was reused for the reaction and catalyzed reaction up to 3 cycles. The highlighting aspects of the method comprise green reaction conditions, easy work-up, easy separation of catalyst, a broad utility of substrate and high yields of products.

Experimental

General details: All solvents were used as commercial anhydrous grade without further purification. Aluminium sheets 20 x 20cm, Silica gel 60 F_{254}, Merck grade was used for thin layer chromatography to determine progress of reaction. The column chromatography was carried out over silica gel (80–120 mesh). Melting points were determined in open capillary tube and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$ solvent. Mass spectra were taken on Polaris-Q Thermoscintific GC-MS. Entiomeric purity is determined on PerkinElmer Series 200 HPLC Systems.

General Procedure for the Synthesis of catalyst Cellulose sulfuric acid: The catalyst cellulose sulfuric acid was synthesis by pathways described in literature documents.[14]

General Procedure for synthesis of cycloalkenopyridine

To a mixture of aromatic aldehyde (3.0 mmol), cyclohexanone (2.0 mmol), and ammonium acetate (3.0 g) was added catalyst cellulose sulfuric acid (20 wt mol %) in the solvent ethanol.

The reaction was performed under solvent free conditions. The reaction mixture was heated at 80 °C temperature for specified time (Table 3). The progress of the reaction was checked using thin layer chromatography. On completion of the reaction as indicated by TLC, the reaction mixture was allowed to cool. The cooled reaction mixture was diluted with 50 ml of water followed by extraction in chloroform. The solid catalyst was filtered and organic layer was collected and dried over anhydrous Na_2SO_4. The organic solvent was removed under vacuum to give crude product. The crude product was further purified by column chromatography using silica gel to obtain the pure product (4a-n).

Characterization of compounds

4,5-Dibenzylidene-9-phenyl-1,2,3,4,5,6,7,8-octahydroacridine (4a) [5, 6]

M.P.= 158-160 C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 2H), 7.70-7.89 (m, 4H), 7.52-7.68 (d, *J* = 7.3 Hz, 2H), 7.39-7.51(d, *J* = 7.4 Hz, 2H), 7.16-7.31 (m, 5H), 7.06-7.14 (d, *J* = 7.9 Hz, 2H), 2.78-2.90 (t, *J* = 5.9 Hz, 4H), 2.31-2.39 (t, *J* = 6.0 Hz, 4H), 1.72-1.92 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.8, 153.7, 144.9, 143.0, 133.2, 128.8, 126.5, 125.7, 124.4, 124.0, 31.0, 27.9, 25.0; GC-MS: *m/z* 439 (M+); Elemental Analysis: Calcd. $C_{33}H_{29}N$: C, 90.16; H, 6.65; N, 3.19; Found C, 90.14; H, 6.68; N, 3.21.

4,5-bis(4-fluorobenzylidene)-9-(4-fluorophenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4b)

The titled compound was confirmed by comparing melting

point to those reported in literature [5, 6]. M.P.=130-132 °C.

4,5-bis(2-chlorobenzylidene)-9-(2-chlorophenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4c)
The titled compound was confirmed by comparing melting point to those reported in literature [6]. M.P.=180-182 °C.

4,5-Bis(4-chlorobenzylidene)-9-(4-chlorophenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4d) [3, 4]
M.P.= 195-197 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (s, 2H), 7.66-7.89 (m, 6H), 7.39-7.51 (d, *J* = 7.2 Hz, 2H), 7.16-7.30 (m, 4H), 2.73-2.90 (t, *J* = 6.2 Hz, 4H), 2.29-2.41 (t, *J* = 6.2 Hz, 4H), 1.61-1.75 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 153.0, 149.9, 142.1, 138.9, 132.2, 132.0, 131.8, 129.0, 127.6, 126.1, 121.3, 121.0, 29.9, 28.0, 24.1,; GC-MS: *m*/*z* 541 (M+); Elemental Analysis: Calcd. $C_{33}H_{26}Cl_3N$: C, 73.00; H, 4.83; N, 2.58; Found C, 72.97; H, 4.85; N, 2.60.

4,5-bis(4-bromobenzylidene)-9-(4-bromophenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4e)
The titled compound was confirmed by comparing melting point to those reported in literature [6]. M.P. = 200-202 °C.

4,5-bis(3-bromobenzylidene)-9-(3-bromophenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4f)
The titled compound was confirmed by comparing melting point to those reported in literature [6]. M.P.=236-238 °C.

4,5-bis(2,4-dimethoxybenzylidene)-9-(2,4-dimethoxyphenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4g)
The titled compound was confirmed by comparing melting point to those reported in literature [6]. M.P.=230-232 °C.

4,5-bis(4-methoxybenzylidene)-9-(4-methoxyphenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4h)
The titled compound was confirmed by comparing melting point to those reported in literature [6]. M.P.=222-224 °C.

4,4'-(9-(4-(dimethylamino)phenyl)-2,3,7,8-tetrahydroacridine-4,5(1*H*,6*H*)-diylidene)bis(methan-1-yl-1-ylidene)bis(N,N-dimethylaniline) (4i)
The titled compound was confirmed by comparing melting point to those reported in literature [6]. M.P.= >250 °C.

4,5-bis(4-nitrobenzylidene)-9-(4-nitrophenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4j)
The titled compound was confirmed by comparing melting point to those reported in literature [6]. M.P. =190-192 °C.

4,5-bis(3-nitrobenzylidene)-9-(3-nitrophenyl)-1,2,3,4,5,6,7,8-octahydroacridine (4k)
The titled compound was confirmed by comparing melting point to those reported in literature [6]. M.P. =191-193 °C.

9-(Pyridin-3-yl)-4,5-bis(pyridin-3-ylmethylene)-1,2,3,4,5,6,7,8-octahydroacridine (4l)
M.P.= 167-169 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.29 (s, 1H), 8.81 (s, 2H), 8.52-8.66 (d, *J* = 7.3 Hz, 1H), 8.30-8.41 (d, *J* = 7.0 Hz, 1H), 8.10-8.24 (d, *J* = 7.9 Hz, 2H), 7.99 (s, 2H),7.71-7.89 (d, *J* = 6.9 Hz, 2H), 7.17-7.37 (m, 3H), 2.74-2.89 (t, *J* = 6.7 Hz, 4H), 2.44-2.59 (t, *J* = 6.5 Hz, 4H), 1.68-1.89 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 153.1, 151.1, 149.8, 148.1, 144.6, 143.4, 135.8, 129.1, 128.0, 124.5, 122.0, 120.9, 30.9, 28.0, 22.1; GC-MS: *m*/*z* 442 (M+); Elemental Analysis: Calcd. $C_{30}H_{26}N_4$: C, 81.42; H, 5.92; N, 12.66; Found C, 81.39; H, 5.90; N, 12.64.

9-(thiophen-2-yl)-4,5-bis(thiophen-2-ylmethylene)-1,2,3,4,5,6,7,8-octahydroacridine (4m)
M.P.= 159-161 °C;^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71-7.77 (d, *J* = 8.1 Hz 3H), 7.51-7.59 (d, *J* = 7.9 Hz, 1H),7.31 (s, 1H), 6.91-7.11 (m, 3H), 7.77-7.90 (d, *J* = 7.6 Hz, 2H), 2.71-2.88 (t, *J* = 6.1 Hz, 4H), 2.22-2.35 (t, *J* = 6.2 Hz, 4H), 1.60-1.80 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.0, 149.1, 145.9, 138.7, 136.3, 133.0, 132.1, 130.9, 125.8, 125.2, 124.9, 120.0, 30.9, 28.2, 23.6; GC-MS: *m*/*z* 457 (M+); Elemental Analysis: Calcd. $C_{27}H_{23}NS_3$: C, 70.86; H, 5.07; N, 3.06; Found C, 70.89; H, 5.11; N, 3.03.

9-(furan-2-yl)-4,5-bis(furan-2-ylmethylene)-1,2,3,4,5,6,7,8-octahydroacridine (4n)
M.P.= 187-189°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12-8.28 (d, *J* = 7.8 Hz 1H), 7.89-7.99 (d, *J* = 8.1 Hz, 2H),7.58 (s, 1H), 7.20-7.29 (d, *J* = 7.8 Hz, 1H), 6.87-7.03 (d, *J* = 8.3 Hz, 2H),6.62-6.78 (m, 1H), 6.21-6.40 (m, 2H), 2.68-2.81 (t, *J* = 5.9 Hz, 4H), 2.30-2.48 (t, *J* = 6.0 Hz, 4H), 1.61-1.82 (m, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 154.1, 150.4, 149.4, 147.1, 145.8, 143.1, 141.5, 132.3, 121.0, 114.2, 113.4, 107.5, 106.0, 29.2, 27.8, 22.8; GC-MS: *m*/*z* 409 (M+); Elemental Analysis: Calcd. $C_{27}H_{23}NO_3$: C, 79.20; H, 5.66; N, 3.42; Found C, 79.23; H, 5.65; N, 3.45.

Supporting Information
Includes experimental procedure for catalysts synthesis and characterization of compounds

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