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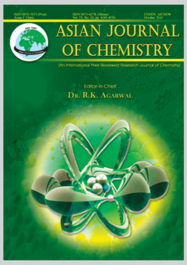

Sulfonic-Acid-Functionalized Silica: An Efficient, Heterogeneous and Reusable Catalyst for the Synthesis of 8-Aryl-7,8-dihydro-[1,3]dioxolo [4,5-g]chromen-6-ones

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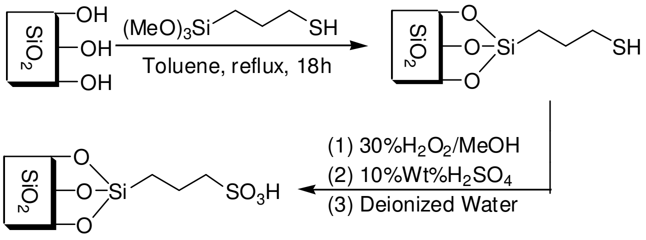
Sulfonic-acid-functionalized silica was used as an efficient and recyclable catalyst for the one-pot synthesis of 8-aryl-7,8-dihydro-[1,3]dioxolo[4,5-g]chromen-6-ones with the help of 3,4-methylenedioxyphenol, aldehydes and Meldrums' acid. Different types of aromatic aldehydes are used in the reaction and in all cases the products were obtained in good to excellent yields.

Key Words: [1,3]Dioxolo[4,5-g]chromen, 3,4-Methylenedioxyphenol, Meldrums'acid, Sulfonic-acid-functionalized silica, Solvent-free.

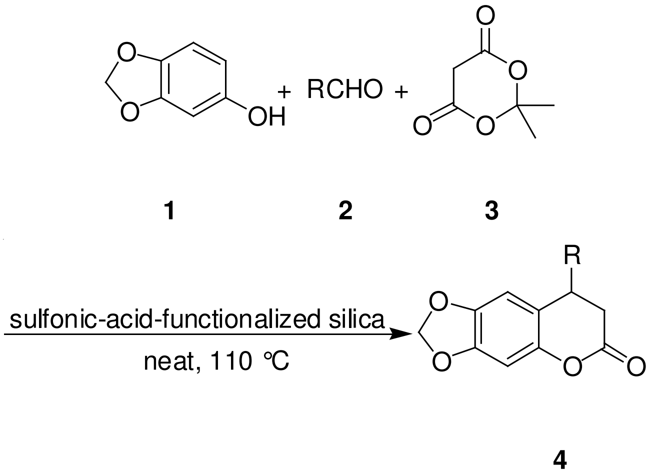
INTRODUCTION

Benzo[1,3]dioxoles constitute a major class of naturally occurring compounds[1] and interest in their chemistry continues unabated because of their wide range of biological and therapeutic properties such as spasm[2], synergistic[3], antitumour[4], antimicrobial[4a], antiproliferative[5], antioxidant[6], antiinflammatory[6], anti HIV[7], antineoplastic and antiviral activities[8]. Considering the above reports, the development of new and simple synthetic methods for the efficient preparation of new benzo[1,3]dioxoles is therefore an interesting challenge.

In recent years, the use of heterogeneous catalysts has received considerable interest in various disciplines including organic synthesis. They are advantageous over their homogeneous counterparts due to the prime advantage that in most of the cases the catalyst can be recovered easily and reused. Sulfonic-acid-functionalized silica has been used as an effcient heterogeneous catalyst for many organic transformations because of its low cost, ease of preparation, catalyst recycling and ease of handling[9]. The catalyst was prepared by the immobilization of propyl thiol on silica using 3-mercaptopropyltrimethoxysilane, followed by the selective oxidation of the thiol groups by aqueous H_2O_2 to the sulfonic acid groups (**Scheme-I**). The catalyst shows high thermal stability (up to 300 ºC). We now report a simple and efficient route to synthesis of 8-aryl-7,8-dihydro-[1,3]dioxolo[4,5-g] chromen-6-ones using sulfonic-acid-functionalized silica an efficient catalyst under solvent-free conditions (**Scheme-II**). To the best of our knowledge, there are no reports on three-component coupling of aldehyde, 3,4-methylenedioxyphenol and Meldrums' acid to produce a new class of 8-aryl-7,8-dihydro-[1,3]dioxolo[4,5-g]chromen-6-ones.



Scheme-I



Scheme-II

EXPERIMENTAL

NMR spectra were determined on Bruker AV-400 instrument at room temperature using TMS as internal standard, coupling constants (*J*) were measured in Hz; IR spectra were determined on FTS-40 infrared spectrometer; Elemental analysis were performed by a Vario-III elemental analyzer; mass spectra were taken on a Macro mass spectrometer (Waters) by electro-spray method (ES); melting points were determined on a XT-4 binocular microscope and were uncorrected; sulfonic-acid-functionalized silica was prepared according to literature[9e]; commercially available reagents were used throughout without further purification unless otherwise stated.

General procedure for the preparation of compound 4: A mixture of 3,4-methylenedioxyphenol (10 mmol), corresponding aromatic aldehyde (10 mmol), Meldrums'acid (10 mmol) and sulfonic-acid-functionalized silica (500 mg) was heated at 110 ºC for an appropriate time and monitored by thin-layer chromatography (TLC) until the final conversion. After cooling, the reaction mixture was washed with $CHCl_3$ and filtered to recover the catalyst. The solvent was evaporated and the crude product purified by silica gel column chromatography using CH_2Cl_2 as eluent to afford the pure product.

Spectral data of compounds

8- Phenyl -7,8-dihydro-[1,3]dioxolo[4,5-g]chromen-6-one (4a): White powder, m.p. 133-134 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37-7.26 (m, 3H), 7.16-7.14 (m, 2H) 6.68 (s, 1H), 6.39 (s, 1H), 5.95 (d, 1H, *J* = 1.2 Hz), 5.94 (d, 1H, *J* = 1.2 Hz), 4.22 (t, *J* = 7.2 Hz, 1H), 3.07-2.93 ppm (m, 2H) ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.7, 147.5, 146.2, 144.4, 140.4, 129.2, 128.6, 127.7, 127.5, 117.9, 107.3, 101.7, 99.1, 40.6, 37.0 ppm; MS (ESI): m/z 269 [M + H]$^+$; anal. calcd. (%) for $C_{16}H_{12}O_4$: C 71.64, H 4.51; found (%): C 71.60, H 4.36.

8-(4-Chlorophenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]-chromen-6-one (4b): White powder, m.p. 133-134 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32 (d, 2H, *J* = 8.4 Hz), 7.08 (d, 2H, *J* = 8.4 Hz), 6.66 (s, 1H), 6.38 (s, 1H), 5.97 (d, 1H, *J* = 0.8 Hz), 5.96 (d, 1H, *J* =0.8 Hz), 4.21 (t, *J* = 6.8 Hz, 1H), 3.06-2.89 ppm (m, 2H) ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.8, 148.1, 146.7, 144.8, 136.4, 134.2, 134.1, 130.0, 129.4, 127.9, 115.7, 107.1, 101.9, 99.3, 37.0, 35.3 ppm; MS (ESI): m/z 303 [M + H]$^+$; anal. calcd. (%) for $C_{16}H_{11}O_4Cl$: C 63.48, H 3.66; found (%): C 63.39, H 3.71.

8-(4-Fluorophenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]-chromen-6-one (4c): White semi-solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.13-7.09 (m, 2H), 7.05-7.01 (m, 2H), 6.66 (s, 1H), 6.38 (s, 1H), 5.96 (d, 2H, *J* = 1.2 Hz), 4.22 (t, *J* = 6.8 Hz, 1H), 3.06-2.89 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ:167.3, 147.7, 146.2, 144.5, 136.2, 136.1, 129.1, 129.0, 117.6, 116.2, 116.0, 107.1, 101.8, 99.2, 39.9, 37.2 ppm; MS (ESI): m/z 287 [M + H]$^+$; anal. calcd. (%) for $C_{16}H_{11}O_4F$: C 67.13, H 3.87; found (%): C 67.09, H 3.92.

8-(4-Methylphenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]-chromen-6-one (4d): White powder, m.p. 143-144 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.15 (d, 2H, *J* = 7.6 Hz), 7.03 (d, 2H, *J* = 8.0 Hz), 6.65 (s, 1H), 6.39 (s, 1H), 5.95 (d, 1H, *J* = 1.2 Hz), 5.94 (d, 1H, *J* = 1.2 Hz), 4.08 (t, *J* = 7.6 Hz, 1H), 3.05-2.91 ppm (m, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.7, 147.4, 146.1, 144.4, 137.4, 129.8, 127.3, 118.2, 107.3, 101.7, 99.1, 40.2, 37.0, 31.0 ppm; MS (ESI): m/z 283 [M + H]$^+$; anal. calcd. (%) for $C_{17}H_{14}O_4$: C 72.33, H 5.00; found (%): C 72.40, H 4.97.

8-(4-Nitrophenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]-chromen-6-one (4e): White powder, m.p. 225-226 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.21 (d, 2H, *J* = 8.8 Hz), 7.33 (d, 2H, *J* = 8.8 Hz), 6.69 (s, 1H), 6.40 (s, 1H), 5.99 (d, 1H, *J* = 1.2 Hz), 5.98 (d, 1H, *J* = 1.2 Hz), 4.30 (t, *J* = 6.0 Hz, 1H), 3.14-2.95 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ:166.4, 148.2, 147.9, 147.4, 146.3, 144.8, 128.4, 124.4, 115.8, 107.0, 102.0, 99.5, 40.5, 36.7 ppm; MS (ESI): m/z 314 [M + H]$^+$; anal. calcd. (%) for $C_{16}H_{11}NO_6$: C 61.35, H 3.54, N 4.47; found (%): C 61.28, H 3.60, N 4.52.

8-(3-Nitrophenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]-chromen-6-one (4f): White powder, m.p. 142-143 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.17-8.15 (m, 1H), 8.03 (s, 1H), 7.56-7.46 (m, 2H), 6.69 (s, 1H), 6.40 (s, 1H), 5.99 (d, 2H, *J* = 0.8 Hz), 4.37 (t, *J* = 6.4 Hz, 1H), 3.14-2.97 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ:166.6, 148.7, 148.2, 146.3, 144.8, 142.7, 133.5, 130.3, 122.9, 122.6, 115.9, 107.0, 102.0, 99.5, 40.4, 36.9 ppm; MS (ESI): m/z 314 [M + H]$^+$; anal. calcd. (%) for $C_{16}H_{11}NO_6$: C 61.35, H 3.54, N 4.47; found (%): C 61.33, H 3.59, N 4.49.

8-(2,4-Dichlorophenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]-chromen-6-one (4g): White powder, m.p. 179-180 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.45 (d, 1H, *J* = 2.0 Hz), 7.16 (dd, 1H, *J* = 2.0, 8.4 Hz), 6.81 (d, 1H, *J* = 8.4 Hz), 6.69 (s, 1H), 6.44 (s, 1H), 5.98 (d, 2H, *J* = 1.2 Hz), 4.68 (t, *J* = 6.0 Hz, 1H), 3.02-2.97 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ:166.5, 148.7, 148.2, 146.3, 144.8, 142.7, 136.4, 133.5, 130.3, 122.6, 115.7, 106.9, 101.9, 99.3, 40.4, 36.9 ppm; MS (ESI): m/z 337 [M + H]$^+$; anal. calcd. (%) for $C_{16}H_{10}O_4Cl_2$: C 57.00, H 2.99; found (%): C 57.03, H 3.02.

8-(4-Methoxyphenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]-chromen-6-one (4h): White powder, m.p. 129-130 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.06 (d, 2H, *J* = 8.8 Hz), 6.87 (d, 2H,*J* = 8.8 Hz), 6.65 (s, 1H), 6.40 (s, 1H), 5.95 (d, 2H, *J* = 1.2 Hz), 4.17 (t, *J* = 6.0 Hz, 1H), 3.80 (s, 3H) 3.00-2.93 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.8, 159.0, 147.4, 146.1, 144.4, 132.3, 128.5, 118.4, 114.5, 107.2, 101.7, 99.1, 55.3, 39.8, 37.2 ppm; MS (ESI): m/z 299 [M + H]$^+$; anal. calcd. (%) for $C_{17}H_{14}O_5$: C 68.45, H 4.73; found (%): C 68.51, H 4.77.

8-(2,5-Dimethoxyphenyl)-7,8-dihydro-[1,3]dioxolo-[4,5-g]chromen-6-one (4i): White powder, m.p. 121-122 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.82 (d, 1H, *J* = 8.8 Hz), 6.76 (d, 1H, *J* = 3.2 Hz), 6.64 (s, 1H), 6.46 (s, 1H), 6.43 (d, 1H, *J* = 3.2 Hz), 5.95 (d, 1H, *J* = 1.2 Hz), 5.94 (d, 1H, *J* = 1.2 Hz), 4.51 (t, *J* = 6.0 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.03-2.95 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.0, 153.6, 150.9, 147.4, 146.5, 144.4, 129.9, 116.8, 115.2, 112.1, 116.7, 107.3, 101.6, 99.0, 55.6, 55.6, 35.4, 35.0 ppm; MS (ESI): m/z 329 [M + H]$^+$; anal. calcd. (%) for $C_{18}H_{16}O_6$: C 65.85, H 4.91; found (%): C 65.88, H 4.87.

8-(Chorophenyl)-7,8-dihydro-[1,3]dioxolo[4,5-g]-chromen-6-one (4j): White powder, m.p. 160-161 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.43 (dd, 1H, *J* = 0.8, 7.6 Hz), 7.25-7.17 (m, 2H), 6.88 (dd, 1H, *J* = 0.8, 7.2 Hz), 6.69 (s, 1H), 6.45 (s, 1H), 5.98 (d, 1H, *J* = 1.2 Hz), 5.97 (d, 1H, *J* = 1.2 Hz), 4.74 (t, *J* = 6.4 Hz, 1H), 3.05-3.02 ppm (m, 2H); ^{13}C NMR (CDCl$_3$, 100 MHz) δ: 167.2, 147.8, 146.7, 144.7, 137.7, 133.4, 130.1, 129.0, 128.5, 127.6, 116.3, 107.2, 101.8, 99.2, 37.3, 35.4 ppm; MS (ESI): m/z 303 [M + H]$^+$; anal. calcd. (%) for $C_{16}H_{11}O_4Cl$: C 63.48, H 3.66; found (%): C 63.44, H 3.70.

RESULTS AND DISCUSSION

Initially, we conducted the reaction of 3,4-methylenedioxyphenol, benzaldehyde and Meldrums'acid in the presence of various catalysts such as H_2SO_4, $NaHSO_4$, $NaHSO_3$, *p*-TsOH, sulfamic acid, $HClO_4$-SiO_2 and sulfonic-acid-functionalized silica separately at 110 ºC under solvent-free conditions. The corresponding 8-phenyl-7,8-dihydro[1,3]dioxolo[4,5-g]chromen-6-one was formed in 5, 49, 27, 74, 65, 82 and 91 % yield (Table-1). Sulfonic-acid-functionalized silica was thus selected as the most effective catalyst to carry out this reaction.

TABLE-1
SYNTHESIS OF 8-PHENYL-7,8-DIHYDRO-[1,3]DIOXOLO [4,5-g]CHROMEN-6-ONE USING VARIOUS CATALYSTS

Entry	Catalysts	Time (h)	Yield (%)**
1	–	6.0	0
2	H_2SO_4 (0.1 mmol)	4.0	5
3	$NaHSO_4$ (0.1 mmol)	2.0	49
4	$NaHSO_3$ (0.1 mmol)	3.0	27
5	*p*-TsOH (0.1 mmol)	1.5	74
6	sulfamic Acid (0.1 mmol)	2.0	65
7	$HClO_4$-SiO_2 (50 mg)	1.5	82
8	Sulfonic-acid-functionalized silica (50 mg)	1.5	91

*Reaction conditions: 3,4-methylenedioxyphenol (1 mmol), benzaldehyde (1 mmol); Meldrums' acid (1 mmol); neat; 110 ºC. ^{b}Isolated yield.

Next, to optimize the amount of catalyst and the reaction temperature, the reaction of 3,4-methylenedioxyphenol, benzaldehyde and Meldrums' acid was studied under solvent-free conditions in the presence of sulfonic acid-functionalized silica at different temperatures. The results were summarized in Table-2 and showed that the reaction using 50 mg/mmol sulfonic acid-functionalized silica at 110 ºC proceeded in highest yield.

With this optimized procedure in hand, the scope of application of this three-component reaction was examined using different aldehydes as staring materials. As seen from Table-3, aromatic aldehydes having electron-donating as well as electron-withdrawing groups were uniformly transformed into the corresponding 8-aryl-7,8-dihydro-[1,3]dioxolo[4,5-g]chromen-6-ones in high to excellent yields within 2.5 h. Substituents on the aromatic ring and the scalability of the reactions (1-10 mmol) had no obvious effect on yield or reaction time under the above optimal conditions (Table-3). All of the products **4** exhibited a triplet in their ^{1}H NMR spectra at δ = 4.08-4.74 ppm for H-8, two doublets at δ = 5.94-5.99 ppm for -OCH$_2$O-, two singlets at δ = 6.38-6.69 ppm for H-4, 9. a clear peak at δ = 37.0-40.6 ppm for C-8 in their ^{13}C NMR spectra, a peak at δ = 166.4-168.0 ppm due to carbonyl group and a peak at δ = 99.1-99.5 ppm for -OCH$_2$O-.

TABLE-2
SYNTHESIS OF 8-PHENYL-7,8-DIHYDRO-[1,3]DIOXOLO[4,5-g]CHROMEN-6-ONE UNDER DIFFERENT CONDITIONS*

Entry	Sulfonic-acid functionalizedsilica (mol %)	Temp. (ºC)	Time (h)	Yield (%)**
1	0	110	6.0	0
2	10	110	3.0	49
3	20	110	3.0	59
4	30	110	2.5	75
5	40	100	2.0	72
6	40	110	2.0	85
7	50	25	6.0	0
8	50	50	6.0	15
9	50	90	3.0	58
10	50	100	2.0	82
11	50	110	1.5	91
12	50	120	1.5	90
13	50	130	1.0	88
14	60	110	1.0	87
15	70	110	1.0	86
16	80	110	1.0	89

*Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); benzaldehyde (1 mmol); Meldrums'acid (1 mmol); neat. **Isolated yield.

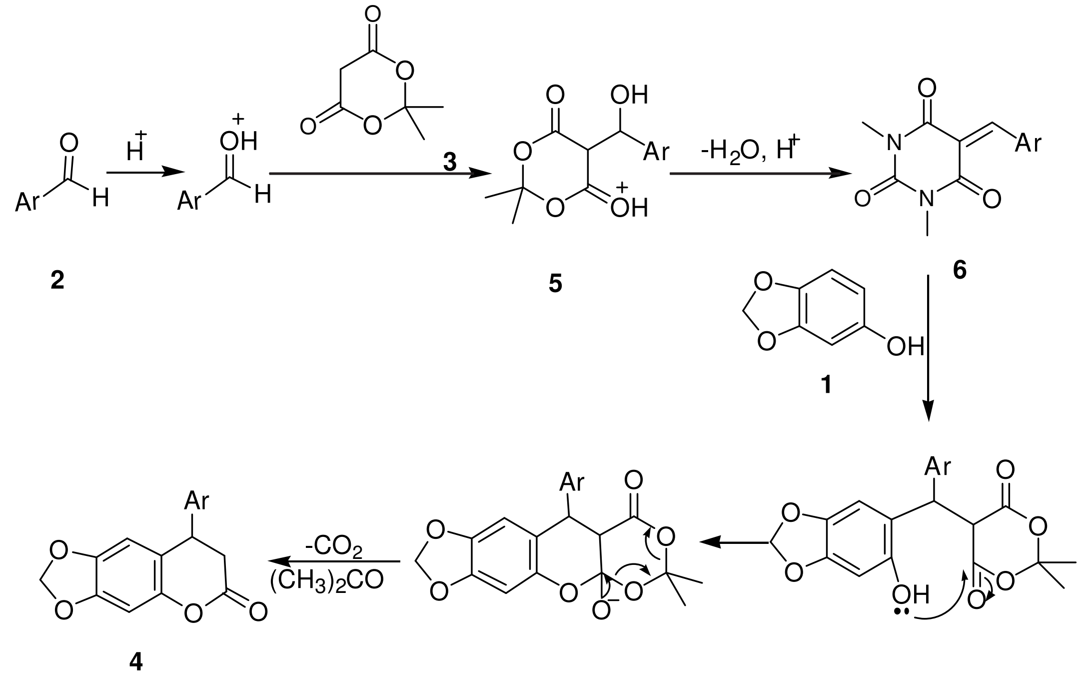
TABLE-3
PREPARATION OF 8-ARYL-7,8-DIHYDRO-[1,3]DIOXOLO [4,5-g]CHROMEN-6-ONES*

Entry	R	Time (h)	Product	Yield (%)**
1	C_6H_5	1.5	**4a**	91 (85)***
2	4-Cl-C_6H_4	1.0	**4b**	92
3	4-F-C_6H_4	1.0	**4c**	89
4	4-Me-C_6H_4	2.0	**4d**	86
5	4-NO_2-C_6H_4	1.0	**4e**	95
6	3-NO_2-C_6H_4	1.5	**4f**	90
7	2,4-Cl_2-C_6H_3	2.0	**4g**	87
8	4-MeO-C_6H_4	2.0	**4h**	85
9	2,5-MeO_2-C_6H_3	2.5	**4i**	86
10	2-Cl-C_6H_4	2.0	**4j**	89

*Reaction conditions: 3,4-methylenedioxyphenol (10 mmol); aldehyde (10 mmol); Meldrums' acid (10 mmol); silica-based sulfonic acid (500 mg); 110 °C; neat. **Isolated yield. ***Yield after the fifth cycle.

Sulfonic acid-functionalized silica works under heterogeneous conditions, but its reaction centers are highly mobile, as in a homogeneous catalyst. It is an inexpensive and non-hazardous solid acid catalyst. It can easily be handled and removed from the reaction mixture by simple filteration. The recovered catalyst was reused consecutively 5 times with a minimum of variation of the yields of the products (Table-3, entry 1). This reusability demonstrates the high stability and turnover of solid silica-based sulfonic acid under operating conditions. The simplicity, together with the use of an inexpensive, nontoxic and environmentally benign catalyst under solvent-free conditions, is another remarkable feature of the procedure.

A tentative mechanism for this transformation is proposed in **Scheme-III**. It is conceivable that sulfonic acid-functionalized silica catalyzes the formation of a carbocation in a reversible reaction with the aromatic aldehyde. The higher reactivity of the carbocation compared with the carbonyl species is utilized to facilitate Knoevenagel condensation between arylaldehyde **2** and Meldrums'acid **3** *via* intermediate **5** and after dehydration olefin **6** is produced. Subsequent Michael type addition of 3,4-



Scheme-III

methylenedioxyphenol **1** to the olefin followed by cyclization and dehydration affords the corresponding products **4a-4h**.

Conclusion

We have developed a novel and highly efficient method for the synthesis of 8-aryl-7,8-dihydro[1,3]dioxolo[4,5-g]chromen-6-ones by treatment of aromatic aldehydes, 3,4-methylenedioxyphenol with Meldrums' acid in the presence of silica solid sulfonic acid as a catalyst. The significant advantages of this methodology are high yields, a simple work-up procedure, cleaner reaction and easy preparation and handling of the catalyst. The catalyst can be recovered by filtration and reused.

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