

A green synthetic route to some supramolecules using molybdate sulfuric acid (MSA) as a highly efficient heterogeneous catalyst

A. Arami¹, B. Karami¹, S. Khodabakhshi*²

¹Department of Chemistry, Yasouj University, Yasouj, Zip Code: 75918-74831 P.O.Box 353, Iran

²Young Researchers and Elite Club, Robotkarim Branch, Islamic Azad University, Robotkarim, Iran

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A facile and simple procedure for the synthesis of some calix[4]resorcinarene derivatives was developed via reaction of aryl aldehydes with resorcinol in the presence of catalytic amounts of molybdate sulfuric acid under solvent-free conditions. This eco-friendly method has many appealing attributes, such as excellent yields, short reactions times, use of a green and recoverable catalyst, and simple work-up procedures.

Key words: Calix[4]resorcinarene; Aryl aldehyde; Molybdate sulfuric acid, Resorcinol.

INTRODUCTION

Supramolecular chemistry has attracted the attention of many chemists in recent years. Calix[4]resorcinarenes, a subclass of calixarenes, are large cyclic tetramers which have found many applications, as solid phases immobilising uranyl cations [1], macrocyclic receptors [2], dendrimers in biological systems [3], nanoparticles [4], nano-capsules [5], supramolecular tectons [6], optical chemosensors [7], host molecules or host-guest complexes [8,9], components in liquid crystals [10], photoresists [11], selective membranes [12], HPLC stationary phases [13], surface reforming agents [14] ion channel mimics [15], and metal ion extraction agents [16].

Although different synthetic methods have been used for the synthesis of calix[4]resorcinarene derivatives by employing some Lewis acid catalysts, however, some of them suffer from disadvantages such as low product yield, cumbersome isolation of the product and long reaction time. In the past few years, we have been involved in a program directed towards developing novel, simple and facile methods for the preparation of organic compounds using various catalysts and readily available starting materials [17-21]. For example, we used molybdate sulfuric acid (MSA) as an efficient catalyst for the synthesis of quinoxalines. In this case, the catalyst showed good recyclability [19]. The challenge in chemistry to develop practical methods, reaction media, conditions and/or materials based on the idea of green chemistry is one of the important issues in the

scientific community. However, preparing and employing a green catalyst in organic synthesis can be extremely valuable [22].

EXPERIMENTAL

Preparation of Catalyst

Firstly 25 mL of dry *n*-hexane was taken in a 100 mL round bottom flask, equipped with ice bath and overhead stirrer, and 4.118 g (20 mmol) of anhydrous sodium molybdate was added to the flask, then 0.266 mL (40 mmol) of chlorosulfonic acid was added dropwise to the flask for 30 min. The solution was stirred for 1.5 h. Afterwards the reaction mixture was gradually poured into 25 mL of chilled distilled water under agitation. The bluish solid which separated out was filtered. Then the catalyst was washed with distilled water five times till the filtrate showed negative test for chloride ions, and was dried at 120 °C for 5 h. The catalyst was obtained in a 90% yield as a bluish solid, which decomposed at 354 °C.

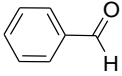
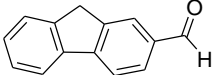
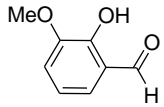
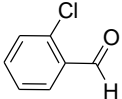
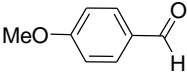
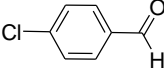
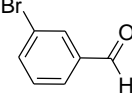
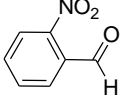
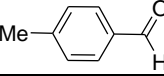
Preparation of calix[4]resorcinarene derivatives 4

A mixture of resorcinol 1 (1 mmol), aryl aldehyde 2 (1 mmol), and MSA (10 mol%) was stirred and heated at 120°C in a preheated oil bath for an appropriate time (Table 1). After completion of the reaction as indicated by TLC (AcOEt/hexane 7:3), the reaction mixture was dissolved in hot MeOH, then filtered to separate the catalyst and afford the pure product 4. At the end of the reaction, the catalyst was filtered, washed with ethanol, dried at 120 °C for 1 h, and reused in another reaction.

* To whom all correspondence should be sent:

E-mail: saeidkhm@yahoo.com

Table 1. Synthesis of calix[4]resorcinarene derivatives catalyzed with MSA 1 at 120 °C under solvent-free conditions.

Entry	Product	Aldehyde	Time (min)	Yield ^a (%)	Melting point (°C) (decompose)
1	4a		150	84	297
2	4b		230	82	298
3	4c		180	82	264
4	4d		45	83	270
5	4e		155	94	262
6	4f		90	85	264
7	4g		70	95	269
8	4h		50	90	225
9	4i		150	88	240

^a Isolated yields.*Spectral Data*

Phenyl-calix[4]resorcinarene (4a): IR (KBr), cm^{-1} : 3400, 3022, 1611, 1510, 1230, 1090; ^1H NMR (400 MHz, DMSO), δ : 8.93-8.88; (m, 2H), 7.17-5.74 (m, 6H), 5.70 (s, 1H); ^{13}C NMR (100 MHz), δ : 156.68, 155.85, 153.42, 146.02, 130.53-125.29 (8c), 106.67, 105.83, 63.27; MS (m/z): 792).

2-Fluorenyl-phenyl-calix[4]resorcinarene (4b): IR (KBr), cm^{-1} : 3436, 2923, 1613, 1503, 1424, 1191, 1062, 767, 731; ^1H NMR (400 MHz, DMSO), δ : 8.68 (s, 1H), 8.50 (s, 1H), 7.05-7.17 (s, 4H), 6.50-6.64 (s, 3H), 6.10 (s, 1H), 5.97 (s, 1H), 5.60 (s, 1H), 3.50 (s, 2H).

2-Hydroxy-3-methoxy-phenyl-calix[4]resorcinarene (4c): IR (KBr), cm^{-1} : 3474, 2938, 2840, 1640, 1477, 1272, 1062, 778, 728; ^1H NMR(400 MHz, DMSO), δ : 8.17 (s, 1H), 8.14 (s, 1H), 8.13(s, 1H), 7.51(s, 1H), 7.49 (s, 1H), 6.43-6.25 (s, 3H), 6.01 (s, 1H), 5.96(s, 1H), 5.85 (s, 1H), 3.65 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz), δ : 153.16, 152.81, 152.72, 152.48, 146.91, 146.65, 143.42, 143.26, 132.81, 131.41, 123.51, 122.83, 122.25, 122.14, 120.26, 119.50, 117.67, 117.45,

108.84, 101.98, 56.28, 35.00, 34.43; MS (m/z): 974.8).

2-Chloro-phenyl-calix[4]resorcinarene (4d): IR (KBr), cm^{-1} : 3446, 2922, 2852, 1617, 1508, 1424, 1272, 1062, 731; ^1H NMR (400 MHz, DMSO), δ : 8.63 (s, 1H), 8.59 (s, 1H), 8.55 (s, 1H), 6.96-6.88 (s, 4H), 6.12 (s, 1H), 5.96 (s, 1H); ^{13}C NMR (100 MHz), δ : 153.59, 153.33, 143.96, 133.74, 130.02, 129.23, 128.85, 126.83, 125.94, 120.39, 118.34, 102.23; MS (m/z): 929.1).

4-Methoxy-phenyl-calix[4]resorcinarene (4e): IR (KBr) cm^{-1} : 3391, 3027, 3001, 1608, 1509, 824; ^1H NMR (400 Hz, DMSO) δ : 8.34 (s, 2H), 6.54 (s, 4H), 6.33 (s, 1H), 5.85 (s, 1H), 5.28 (s, 1H), 4.07 (s, 3H); MS (m/z): 912.4).

4-Chloro-phenyl-calix[4]resorcinarene (4f): IR (KBr) cm^{-1} : 3410, 3036, 2942, 1617, 1487, 1076; ^1H NMR(400 Hz, DMSO) δ : 8.48 (s, 2H), 6.79 (d, 2H, $J = 12$ Hz), 6.41 (d, 2H, $J = 12$ Hz), 5.98 (s, 2H), 5.39 (s, 1H); ^{13}C NMR (100 MHz) δ : 154.31, 146.15, 131.88, 131.25, 128.43, 121.46, 103.25, 42.56; MS (m/z): 929.1).

3-Bromo-phenyl-calix[4]resorcinarene (4g): IR (KBr) cm^{-1} : 3445, 2940, 1595, 1488, 1260, 1092,

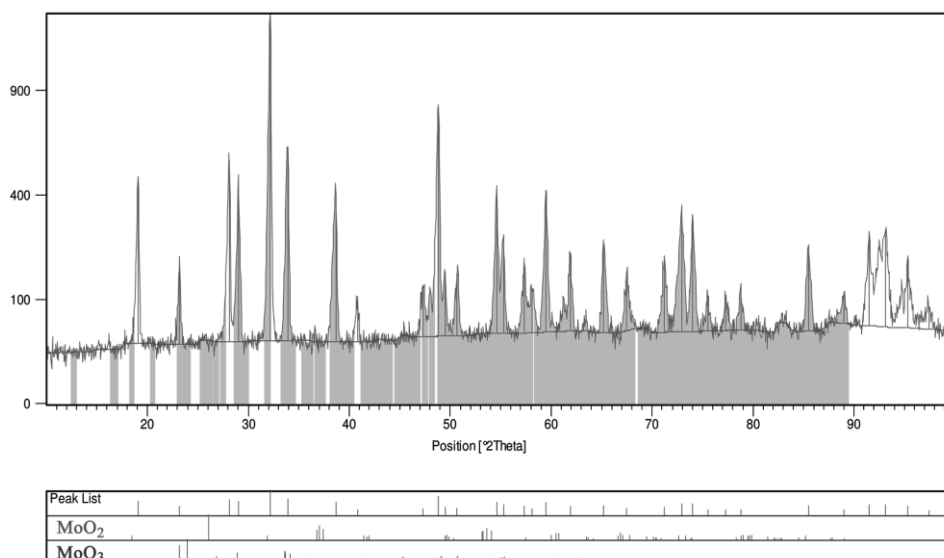


Fig. 1. XRD pattern for MSA 1.

880, 780, 690; ¹H NMR (400 MHz, DMSO) δ: 9.12-8.92 (m, 2H), 7.14-6.56 (m, 4H), 6.25-6.02 (m, 2H), 5.67 (s, 1H); ¹³C NMR (100 MHz) δ: 156.63, 155.80, 131.49, 129.93, 128.09, 121.50, 105.92, 102.64;

2-Nitro-phenyl-calix[4]resorcinarene (4h): IR (KBr) cm⁻¹: 3410, 3080, 2910, 1681, 1605, 1520, 1335, 1150, 730; ¹H NMR (400 MHz, DMSO) δ: 9.10-8.96 (m, 2H), 7.76-5.96 (m, 6H), 4.76 (s, 1H); ¹³C NMR (100 MHz) δ: 170.20, 157.13, 155.91, 154.07, 150.13, 149.30, 139.45, 132.40-124.23 (8C), 119.94, 106.66, 105.93, 102.69, 67.43; MS (*m/z*: 973.1).

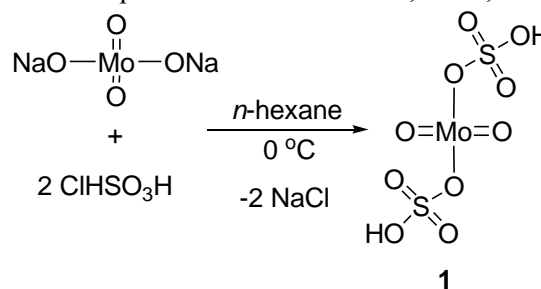
4-Methyl-phenyl-calix[4]resorcinarene (4i): IR (KBr) cm⁻¹: 3405, 3010, 2910, 1600, 1505, 1125.840; ¹H NMR (400 MHz, DMSO) δ: 9.10-8.88 (m, 2H), 7.10-6.20 (m, 6H), 5.67 (s, 1H), 2.19 (s, 3H); ¹³C NMR (100 MHz) δ: 158.91, 156.60, 130.16, 128.99, 128.37, 106.66, 105.81, 102.79, 21.04; MS (*m/z*: 854.7).

RESULTS AND DISCUSSION

The concept of “Green Chemistry” has emerged as one of the guiding principles of the environmentally safe organic synthesis. We found that anhydrous sodium molybdate reacts with chlorosulfonic acid (1:2 mole ratio) to give molybdate sulfuric acid (MSA **1**). The reaction is easy and clean and there is no gas production during the reaction (Scheme 1). The MSA **1** was characterized by X-ray diffraction, transmission electron microscopy, and Fourier transform infrared spectroscopy [23-25]. Figure 1 shows the XRD patterns for molybdate sulfuric acid (MSA **1**). It was reported that high degree mixing of Mo–S in chlorosulfonic acid often

led to the absence of XRD pattern for anhydrous sodium molybdate.

XRD patterns of sodium molybdate (Na₂MoO₄) show broad peaks at around 2θ 17.0°, 27.0°, 32.0°,



Scheme 1. Synthesis of molybdate sulfuric acid (MSA).

48.0°, 53.0°, 57.5°, 78.5°, 82.0° [26], some of which are absent in the XRD pattern of MSA due to high-degree mixing of Mo with sulfonic acid. The broad peaks around 2θ 23°, 29°, and 34° from the smaller inset can be attributed to the linking of Mo to sulfonic acid. The FT-IR spectra for anhydrous sodium molybdate and molybdosulfuric acid (MSA **1**) are shown in Figure 2.

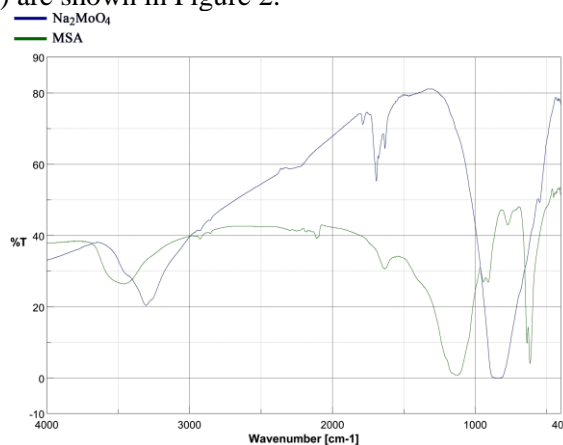


Fig. 2. FT-IR spectrum for MSA 1.

The spectrum of MSA **1** shows the characteristic bonds of anhydrous sodium molybdate and chlorosulfonic acid. The absorbance bands at 3459, 2110, 1635, 1129, 909, 771, 637, 616 and 451 cm^{-1} in the catalyst spectrum reveal both bonds in anhydrous sodium molybdate and $-\text{OSO}_3\text{H}$ group. Hence titration of the catalyst with NaOH (0.1 N) was done. Firstly, 1 mmol of the catalyst was dissolved in 100 mL of water. Then it was titrated with NaOH (0.1 N) in the presence of phenolphthalein as an indicator. In the equivalent point, 2 mmol of NaOH were utilized for 1 mmol of catalyst, which pointed to two acidic valences.

The XRF data of molybdate sulfuric acid (MSA **1**) indicate the presence of MoO_3 and SO_3 in the catalyst (Table 2). In this work, we describe a simple and green strategy based on the condensation of resorcinol **2** with aryl aldehyde **3** using MSA **1** as a powerful, recyclable and safe catalyst under solvent-free conditions for the preparation of calix[4]resorcinarene derivatives **4** (Scheme 2).

Table 2. XRF data of MSA **1**.

Entry	Compound	Concentration (% w/w)
1	SO_3	49.52
2	Na_2O	1.15
3	MoO_3	39.02
4	Cl	0.150
5	K_2O	0.064
6	Nb_2O_5	0.019
7	Fe_2O_3	0.012
8	CuO	0.010
9	LOI ^a	10.03
10	Total	99.98

^aLoss on Ignition.

The need to implement green chemistry principles (e.g. safer solvents, less hazardous chemical synthesis, atom economy and catalysis) is a driving force towards avoiding the use of toxic organic solvents. A solvent-free or solid-state reaction obviously reduces pollution, and brings down handling costs due to simplification of experimental procedure, work up technique and saving in labour. Interest in the environmental control of chemical processes has remarkably increased during the last three decades as a response to the public concern about the use of hazardous chemicals. Therefore, to improve the effectiveness of this method in

preventing chemical waste, it is important to optimize the reaction conditions. To determine the suitable reaction conditions, the reaction of benzaldehyde with resorcinol was taken as a model reaction. At first, we found that in the absence of MSA **1**, the reaction did not complete in a long reaction time (650 min). After examining the reaction using various amounts of MSA **1** at 120 °C, it was found that the reaction can be efficiently carried out by adding 10 mol% of the catalyst under solvent-free conditions for 150 min. The use of higher amounts of the catalyst does not increase the yield and reaction rate. According to Table 1, under the optimized reaction conditions, a number of aromatic aldehydes reacted with resorcinol in a molar ratio of 1:1 with the catalyst affording calix[4]resorcinarenes **4a-4i** in good to excellent yields.

Not only the ecological profile (through decreasing hazardous industrial waste), but also the economic profile (through eliminating expensive organic solvents) are further improved using a recyclable catalyst and solvent-free reaction conditions. In this process, as indicated in Figure 3, the recycled catalyst was used for four cycles of 150 min each. Actually, the catalyst showed an appreciable loss in catalytic activity after reusing. During catalyst recovery, as mentioned in previous studies, sometimes catalyst decomposition and/or leaching occurs [27,28].

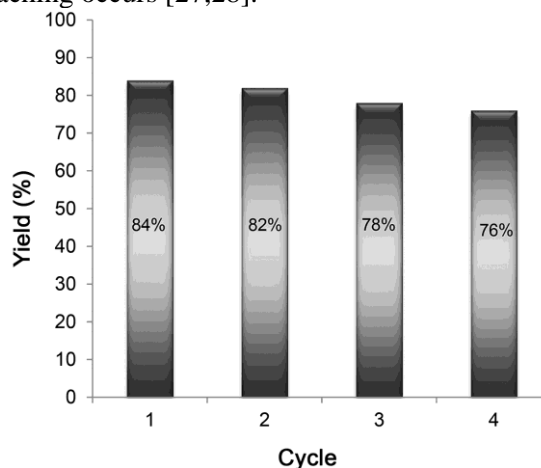
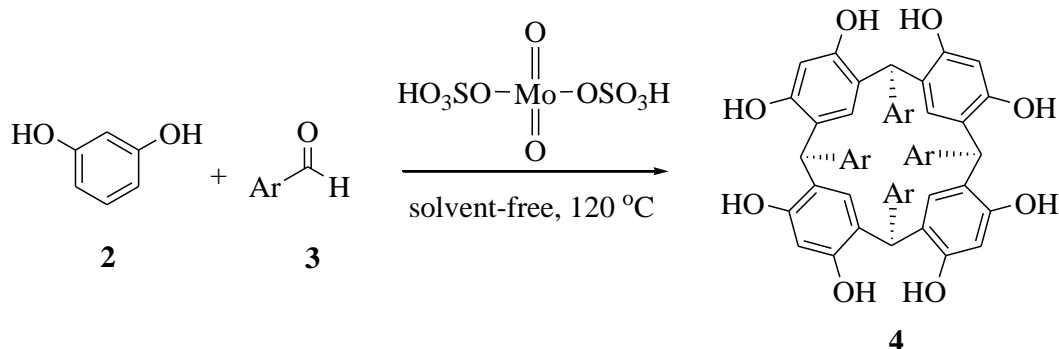


Fig. 3. Recyclability of MSA **1** catalyst in the synthesis of **4a** at 120 °C under solvent-free conditions (reaction time = 150 min).



Scheme 2. Synthesis of calix[4]resorcinarene derivatives using MSA 1.

CONCLUSION

In summary, a green synthetic route to some calix[4]resorcinarene derivatives using MSA 1 under solvent-free conditions is presented. This method not only gives high yield and purity but also is cheap, speedy, facile, and eco-friendly throughout the course of the reaction.

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**“ЗЕЛЕН” СИНТЕТИЧЕН ПЪТ КЪМ НЯКОИ СУПРА-МОЛЕКУЛИ С ИЗПОЛЗВАНЕТО
НА МОЛИБДАТ-СЯРНА КИСЕЛИНА (MSA) КАТО ВИСОКО-ЕФЕКТИВЕН
КАТАЛИЗАТОР**

А. Арами¹, Б. Карами¹, С. Ходабахши ^{*2}

¹*Департамент по химия, Университет в Ясудж, Ясудж, Иран*

²*Младежки изследователски и елитен клуб, Клон Робаткарим, Ислямски университет «Азад»,
Робаткарим, Иран*

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(Резюме)

Разработена е лесна и проста процедура за синтезата на някои каликс [4] резорцин-аренови производни чрез реакцията на арилови алдехиди с резорцинол в присъствие на катализатор от молибдат-сярна киселина в отсъствие на разтворител. Този екологично чист метод показва много примамливи качества, като отлични добиви, кратко време за реакция, “зелен” и възстановим катализатор и проста работна процедура.