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ARTICLE

A facile 2*H*-chromene dimerization through an *ortho*-quinone methide intermediate catalyzed by a sulfonyl derived MIL-101 MOF

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A MIL-101-SO_3H MOF was synthesized using commercially available materials. The as-synthesized MIL-101-SO_3H was characterized by SEM, XRD, FTIR, BET and TGA. An efficient and diastereoselective homo-dimerization of 2*H*-chromenes catalysis was achieved using the sulfonyl derived MIL-101 MOF as a catalyst. Benzopyranobenzopyran polycyclic structure were generated in high yield and diastereoselectivity under mild catalytic reaction conditions. Furthermore, a regio- isomer was observed when 2*H*-chromene bears different substitution group, furnished chromeno[2,3-b]chromene dimer in high yield and good diastereoselectivity. A mechanism is proposed with a tandem rearrangement/hetero-Diels-Alder reaction sequence is supported by evidence. In addition, the acid MIL-101 MOF catalyst can be recycled ten times without compromising the yield and selectivity.

1 Introduction

Ortho-quinone methides (*o*QM)[1] are composed of a cyclohexadiene motif in conjugation with a carbonyl and a methylene group, are highly polarized and are versatile intermediates in organic synthesis,[2] material chemistry[3] and biology.[4] An *ortho*-quinone methide intermediate can undergo 1,4-conjugate addition reactions with nucleophiles and [4 + 2] cycloaddition reactions with various dienophiles.[5] Due to broad range of applications of *ortho*-quinone methide intermediates, numerous methods have been established for the their synthesis.[6] However, a methodology for quick *in-situ* generation from 2*H*-chromene would allow practical, rapid access to a variety of complex synthetic intermediates.[7] The dimeric flavonoid dependensin, which can be isolated from the antimalarial *uvarza dependens*, contains a benzopyranobenzopyran polycyclic ring structure.[8] We envisaged synthetic access to these natural product core structures via benzopyran based starting materials. A rearrangement of 2*H*-chromene is expected to generate an *ortho*-quinone methide intermediate, followed by hetero-Diels-Alder reaction with dienophiles to prepare these unique heterocyclic structures.[9]

In the past decade, metal-organic frameworks (MOFs) have emerged as a new class of solid catalysts, by virtue of their highly tailorable nature, porous structure and large surface area.[10] Brønsted acid MOFs have been developed to serve as the efficient catalysts for acid catalysis.[11] A MOF structure bearing sulfonyl groups can serve as a low pKa catalytic material.[12] Among several choices of -SO_3H derived MOF materials, the synthesis of chemically stable MIL-101-SO_3H MOF has been reported in the literature.[13] Moreover, MIL-101-SO_3H has been utilized as an efficient catalyst for several organic reactions, thanks to its chemical and physical stabilities.[14]

With this communication, we wish to report a novel synthetic utilization of MIL-101-SO_3H MOF catalyst. This newly synthesized MIL-101-SO_3H catalyst, bearing aromatic sulfonic acid groups, was obtained using commercially available monosodium 2-sulfoterephthalate. An efficient homo-dimerization of electron-rich 2*H*-chromene allows rapid access to the benzopyranobenzopyran polycyclic and chromeno[2,3-b]chromene core structure. The achievement of extremely high diastereoselectivity using MIL-101-SO_3H as a strong Brønsted acid solid catalyst is unprecedented in literature. A variety of electron-rich 2*H*-chromenes were tolerated under the optimal reaction conditions for the homo and hetero- dimerization reactions. Furthermore, the as-synthesized MIL-101-SO_3H catalyst can be readily filtered and separated from the reaction solution; our study showed that recycling the catalyst up to ten times doesn't compromise yield or selectivity.

2 Experimental section

2.1 Preparations of MIL-101-SO_3H support

MIL-101 and MIL-101-SO_3H were prepared according to the literature.[15]

2.2 Procedure of 2*H*-chromene homodimerization

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

2*H*-chromenes were prepared according to the published procedure.[16] To a reaction vessel equipped with stir bar in air, 7-methoxy-2-(4-methoxyphenyl)-2*H*-chromene **1a** (0.25 mmol) and 1 mol% catalyst in 1.25 mL dichloromethane were added. The mixture was stirred at room temperature for 12 hours. The crude product was then subjected to ^{1}H NMR analysis for the determination of diastereoselectivity. The product was purified by flash chromatography over silica gel column. The reported yields were calculated based on the isolated amount of product.

2.3 Procedure of 2*H*-chromene heterodimerization

To a reaction vessel equipped with stir bar in air, 7-methoxy-2-(4-methoxyphenyl)-2*H*-chromene **1a** (0.25 mmol), 3,4-dihydro-2*H*-pyran **8a** (1.5 equiv., 89.2 mg, 0.375 mmol) and catalyst (0.1 mmol) in 2.5 mL dichloromethane were added. The mixture was stirred at room temperature for 12 hours. The crude product was then subjected to ^{1}H NMR analysis for the determination of diastereoselectivity. The reaction mixture was purified without work-up by flash chromatography over silica gel column to afford the heterodimer.

2.4 Reusability of the MIL-101-SO_3H catalyst

For the recyclability test of the MIL-101-SO_3H catalyst, the catalytic reactions were performed under the same optimized conditions in dichloromethane for 12 h using the recovered MIL-101-SO_3H catalyst. A leaching study of the MIL-101-SO_3H catalyst was conducted; the mother liquor was filtered and the supernatant was re-evaluated using fresh starting material under optimized catalytic conditions.

3. Results and discussion

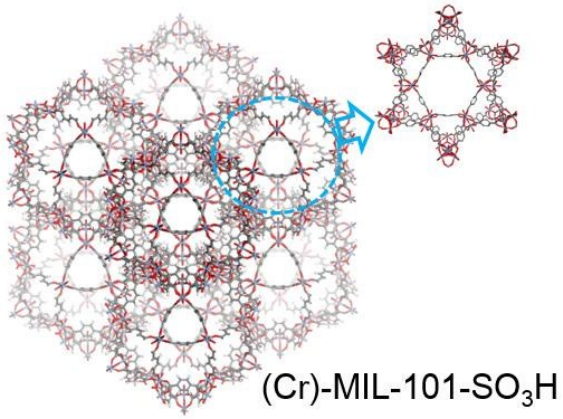


Fig. 1 The detailed structure of MIL-101-SO_3H.

MIL-101-SO_3H can be readily synthesized and purified according to the reported methods as a crystalline powder.[15] It is iso-structural to MIL-101, and thus has the same pore structures (Fig. 1).

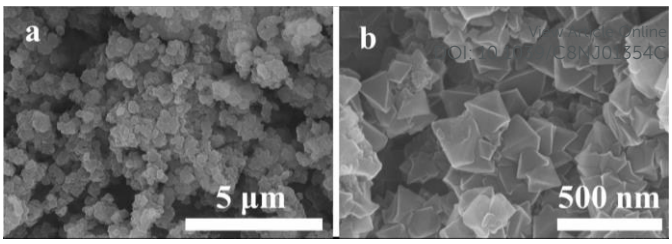


Fig. 2 SEM images of MIL-101-SO_3H.

MIL-101-SO_3H particles were synthesized via hydrothermal method, in order to obtain particles very monodisperse in size. SEM images of MIL-101-SO_3H were acquired (Fig. 2). The rectangular crystals of MIL-101-SO_3H are evenly distributed with a size of 200 nm.

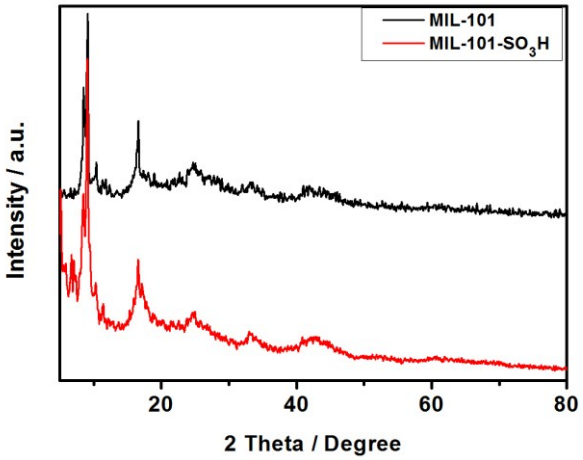


Fig. 3 Powder XRD patterns of (a) MIL-101 and (b) MIL-101-SO_3H.

Additionally, powder X-ray diffraction (PXRD) studies were conducted as part of the characterization process (Fig. 3) and the data were compared with literature values.[17] The laboratory XRD data were not sufficient to refine the structural difference of the MIL-101 and MIL-101-SO_3H composites. MIL-101-SO_3H crystalline structure was highly similar to MIL-101 according to the PXRD patterns.

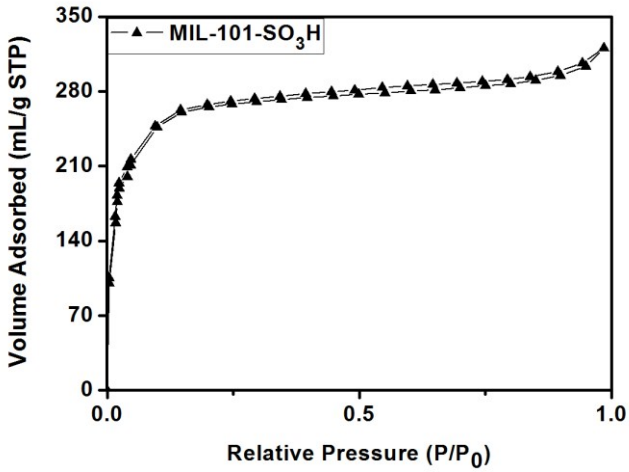


Fig. 4 N_2 adsorption-desorption isotherm of MIL-101-SO_3H.

The specific surface areas of the products were analyzed by N_2 adsorption-desorption measurements at 77 K. As shown in Fig. 4, the trace of the MIL-101-SO_3H showed a type-I isotherm. N_2 gas sorption isotherms reveal a Brunauer–Emmett–Teller (BET) surface area of 1266 m^2/g.

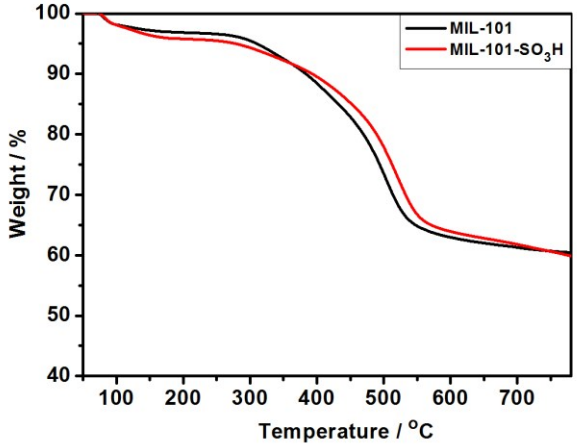
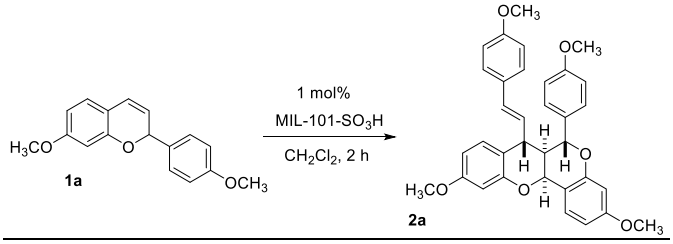


Fig. 5 TGA of MIL-101 and MIL-101-SO_3H.

Additionally, the thermal and structural stabilities of MIL-101 and MIL-101-SO_3H were examined by thermal gravimetric analysis (TGA). A weight loss at about 300 °C was observed during the TGA of MIL-101-SO_3H. The weight loss of the modified samples MIL-101 showed similar thermal curves.[18] The TGA results are evidence of high thermal stability of the acid derived MIL-101-SO_3H sample, which ensures its stability in the catalytic reaction temperature range.

Table 1. Optimization of dimerization using 2*H*-chromene precursor.[a]

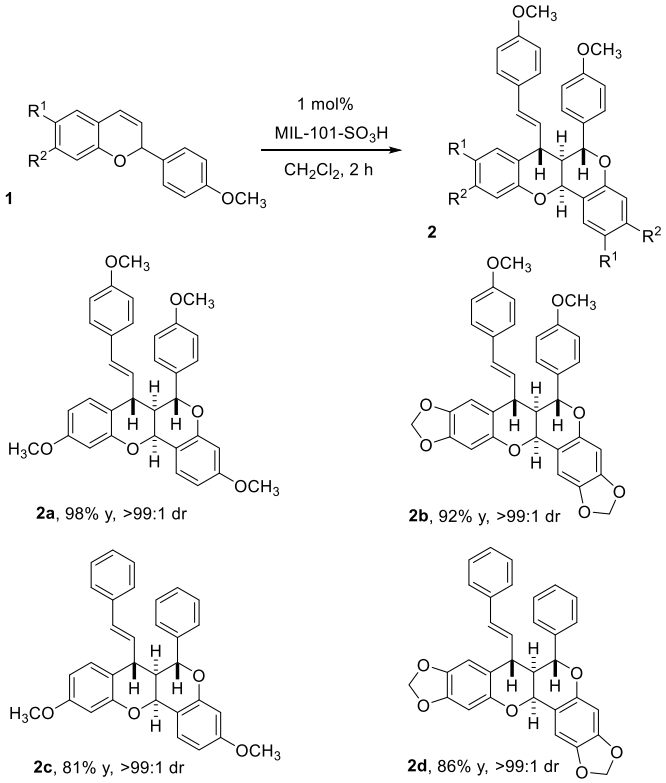


Entry	Catalyst	Solvent	Yield[b]	Dr[c]
1	-	CH_2Cl_2	<5%	n.a.
2	HCl(aq)	CH_2Cl_2	41%	>95:5
3	$FeCl_3·6H_2O$	CH_2Cl_2	53%	>95:5
4	MIL-101	CH_2Cl_2	<10%	n.a.
5	MIL-101-SO_3H	CH_2Cl_2	98%	>99:1
6	MIL-101-SO_3H	$PhCH_3$	67%	>99:1
7	MIL-101-SO_3H	CH_3CN	71%	>99:1
8	MIL-101-SO_3H	THF	59%	>99:1

[a] Reaction condition: 0.20 mmol of **1a**, 1 mol % catalyst, 0.2 M in the solvent for 2 h at room temperature, [b] Isolated yield, [c] Ratio was determined by ^1H NMR analysis.

Several reaction factors such as nature of the catalyst, temperature and solvent, were tested in order to reveal the most suitable parameters for the dimerization reaction (Table 1). Firstly, a control experiment was performed to study the background rate in the dimerization reaction of 7-methoxy-2-(4-methoxyphenyl)-2*H*-chromene **1a** (Table 1, entry 1). No conversion was observed for 2*H*-chromene **1a** in the absence of catalyst. HCl and $FeCl_3·6H_2O$ showed modest yield at 1 mol% catalyst loading and the reaction was slow due to the small amount of catalyst (Table 1, entries 2-3). As expected, MIL-101 bearing no acidic functional group provided only traces of product at 23 ºC in CH_2Cl_2 solvent (Table 1, entry 4). 1 mol% MIL-101-SO_3H showed almost quantitative conversion and over 99:1 diastereoselectivity for the dimerization of 2*H*-chromene **1a**. The greatly enhanced acidity could allow the rearrangement of 2*H*-chromene, followed by the [4 + 2] cycloaddition to provide the desired dimer **2a** in excellent yield (Table 1, entry 5). Toluene and acetonitrile gave comparable, but still lower yields. Further solvent evaluation indicated that dichloromethane is the most suitable reaction solvent for further dimerization reaction studies (Table 1, entries 5-7). Oxygen-containing solvents, such as ether and THF, gave decent yields of the desired dimerization product. However, the yields were not satisfying (Table 1, entry 8). It was noticed that the 7-methoxy functional group on 7-methoxy-2-(4-methoxyphenyl)-2*H*-chromene **1a** is essential for the promotion of the dimerization reaction. A 2*H*-chromene without the 7-methoxy group failed to provide benzopyranobenzopyran product under the several catalytic reaction condition we tested.

Table 2. Homodimerization substrate scope.



Reaction condition: 1 mol% MIL-101-SO_3H, 0.2 M in the CH_2Cl_2 solvent for 2 h at room temperature. For product **2c** and **2d**, 12 h reaction time was required.

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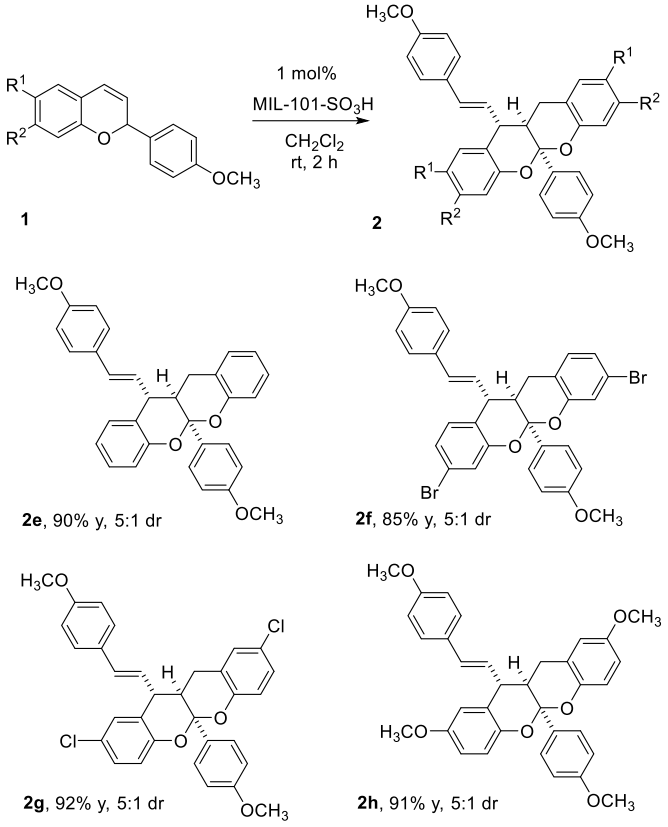
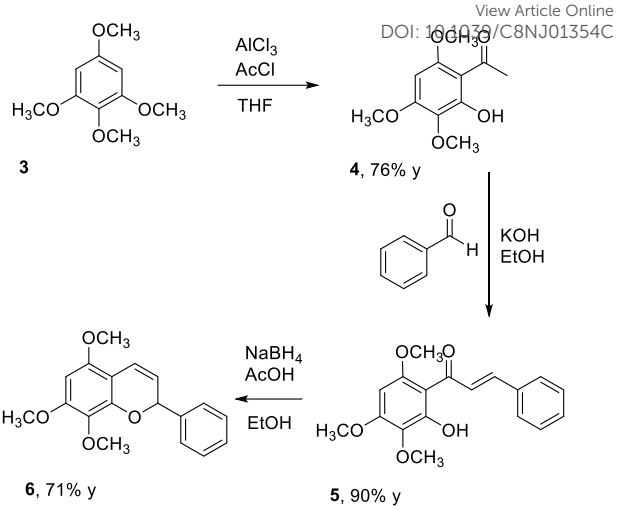
The optimized reaction conditions were employed in the reaction of substituted chromene compounds to widen the substrate scope. Based on our preliminary studies of the reaction, we expected the cyloaddition process to occur in presence of electron-rich dienophiles utilizing 2*H*-chromenes as *o*QM precursors.[19] The reaction proceeded well with 1,3-benzodioxol substituted chromenes **1b** (Table 2, compound **2b**). Less electron rich 2*H*-chromenes **1c** was also able to participate, but at a slower rate (Table 2, compound **2c**). Similar yield was observed for 1,3-benzodioxol substituted chromenes **1d**, despite the presence of a less electron-donating group installed at C2 position (Table 2, compound **2d**).

Table 3. Chromeno[2,3-b]chromene dimer formation.



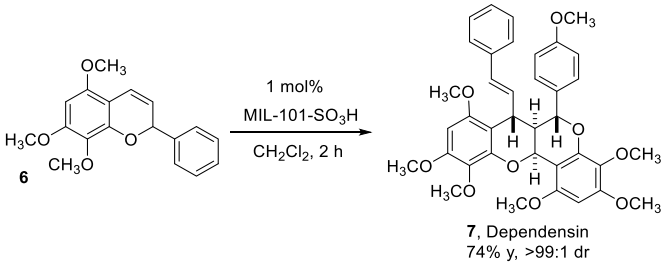
Reaction condition: 1 mol% MIL-101-SO_3H, 0.2 M in the CH_2Cl_2 solvent for 2 h at room temperature.

To broaden the scope of this methodology, the optimized reaction conditions was employed in the dimerization of other substituted 2*H*-chromenes. Interestingly, unexpected chromeno[2,3-b]chromene dimer was isolated as the only product when less electron-rich chromenes were utilized. The reaction proceeded smoothly with non-substituted chromene **1e**, affording chromeno[2,3-b]chromene dimers **2e** in good yields (Table 3, **2e**). Electron-deficient chromenes, such as **1f** and **1g**, underwent dimerization in a similar fashion, providing compounds **2f** and **2g** in good yields (Table 3, **2f** and **2g**). The electron-rich chromene **1h** bearing a –CH_3O group at the C-6 position instead of C-7 position appeared to have the appropriate reactivity profile (Table 3, **2h**).



Scheme 1. Synthesis of 5,7,8-trimethoxyflav-3-ene **6**.

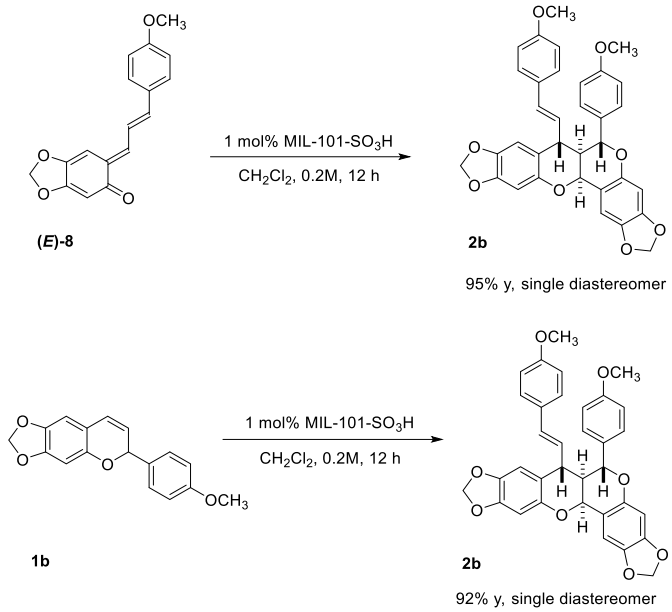
5,7,8-trimethoxyflav-3-ene **6** is the essential starting material for the rapid synthesis of natural product dependensin (Scheme 1), and can be easily prepared in three steps from commercially available starting materials. Potentially, the dimerization of 2*H*-chromene could access the dimeric flavonoid dependensin. Isolated from the antimalarial *uvarza dependens*, dependensin also contains a benzopyranobenzopyran polycyclic ring structure.[8] 5,7,8-trimethoxyflav-3-ene **6** was synthesized from 1,2,3,5-tetramethoxybenzenein **3**, which is commercial available at low price. To a solution of 1,2,3,5-tetramethoxybenzene in dry THF, $AlCl_3$ was added. Acetyl chloride wasthen slowly added to the mixture. The crude product was purified by silica gel column chromatography to give 2-hydroxy-3,4,6-trimethoxyacetophenone **4** in 76% yield. To a stirred mixture of 2-hydroxy-3,4,6-trimethoxyacetophenone **4** and benzaldehyde in ethanol, aqueous potassium hydroxide in water was then added. The precipitate was filtered, washed with water and dried to give chalcone **5** in 90% yield. Lastly, sodium borohydride was added to a stirred mixture of 5,7,8-trimethoxyflav-3-ene **5**. After the removal of ethanol, the resulting solid was treated with 10% aqueous acetic acid and extracted with toluene. The toluene solution was separated and evaporated, followed by silica gel column chromatography to provide 5,7,8-trimethoxyflav-3-ene **6** in 71% yield.



Scheme 2. The synthesis of dependensin natural product.

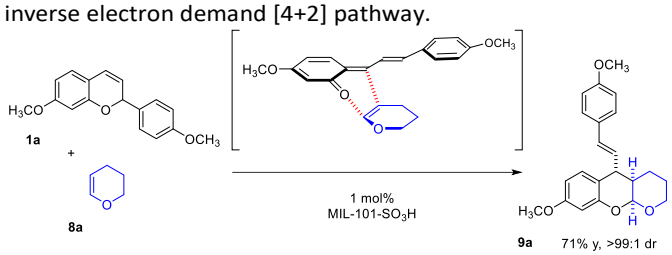
The dimerization reaction strategy was utilized in the synthesis of dependensin (7) via the homodimerization of 5,7,8-trimethoxyflav-3-ene **6**. This new route for the synthesis of

dependensin accounts for a reduction in the number of steps and high stereocontrol (Scheme 2).[20] Subjecting 5,7,8-trimethoxy-3-flavene **6** to reaction in presence of 1 mol% of MIL-101-SO_3H afforded (±)-dependensin (7) as a single diastereomer in 35% overall yield from 1,2,3,5-tetramethoxybenzene.



Scheme 3. Dimerization comparison for mechanism study.

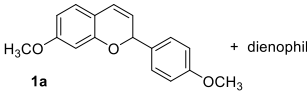
*o*QM **(*E*)-8** was synthesized to investigate the mechanism in detail. **(*E*)-8** and **1b** homodimerize into the same product **2b** in similar yields and equal diastereoselectivities. This observation suggests the equilibrium between chromene **1b** and vinyl *o*QM **(*E*)-8**.The homodimerization reaction proceeds well to give the chromeno[2,3-b]chromene heterodimer **2b** in high yield as a single diastereomer, supporting our mechanistic hypothesis The same product was isolated in comparable yield and equal diastereoselectivity, which provides further evidence for the inverse electron demand [4+2] pathway.

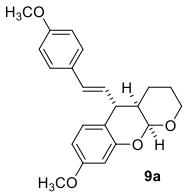
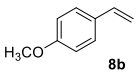
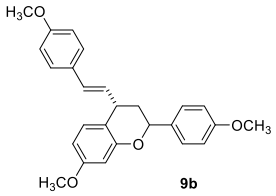
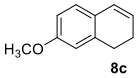
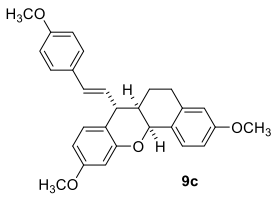
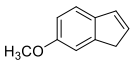
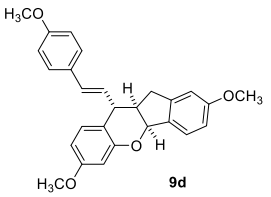
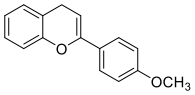
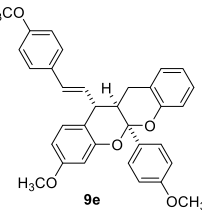


Scheme 4. Model substrate study for reaction mechanism study.

Inspired by natural products such as the mulberrofurans[21] and australisine[22] we first evaluated hetero-Diels-Alder reactions between 2*H*-chromenes **1a** and 3,4-dihydro-2*H*-pyran **8a** under MIL-101-SO_3H catalysis. A hetero-Diels-Alder reaction process involving *o*QM intermediate is proposed as the main step of our reaction mechanism. We then designed further experiments based on our mechanistic hypothesis. We first postulated that a model substrate 2*H*-pyran **8a** would react with the *o*QM generated *in situ* from 2*H*-chromene **1a** under the acid-promoted conditions (Scheme 4). The reaction proceeded well, yielding the corresponding heterodimer **9a** in 71% yield as the only diastereomer. At present, a limited substrate scope motivates us to optimize the dimerization reaction of various dienophiles.

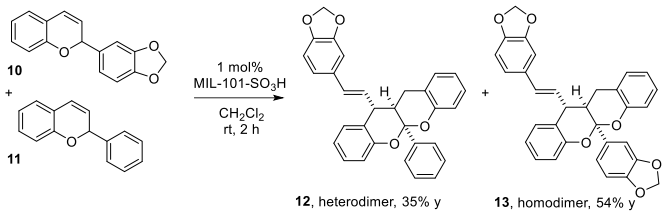
Table 4. Substrate scope for the hetero-Diels-Alder reaction.



Entry	Dienophile	[4+2] Cycloadduct	Yield	D.r.
1	 8a	 9a	71%	>99:1
2	 8b	 9b	81%	2:1
3	 8c	 9c	88%	>99:1
4	 8d	 9d	76%	7:1
5	 8e	 9e	90%	4:1

The hetero-Diels-Alder reaction promoted by MIL-101-SO_3H was carried out by using various dienophiles, which furnished several [4+2] cycloadducts in high diastereoselectivities. We further explored the scope of the cycloaddition reaction pathway using the *in situ* generated *o*QM of chromene **1a** with a variety of dienophiles (Table 4). The hetero-Diels-Alder reaction proceeded smoothly with dihydropyran **8a** to produce the corresponding acetal **9a** (Table 4, entry 1). Under the optimized reaction conditions, *p*-methoxystyrene **8b** successfully afforded chromane **9b** in good yields (Table 4, entry 2). Dihydronaphthalene **8c** yielded the [4 + 2] adduct **9c** as a

single diastereomer (Table 4, entry 3). Furthermore, electron rich indene **8d** was also a suitable dienophile (Table 4, entry 4). Lastly, electron-rich flavene was also tested and the resulting tetrahydrochromeno polycyclic compound was obtained in 90% yield (Table 4, entry 5).



Scheme 5. Mix coupling between two 2H-chromenes.

Mix coupling between two different chromenes **10** and **11** is possible (Scheme 5). The homodimerization reaction occurs faster than the heterodimerization pathway. The hetero-Diels-Alder reaction occurs faster with electron-rich substrate **11**.

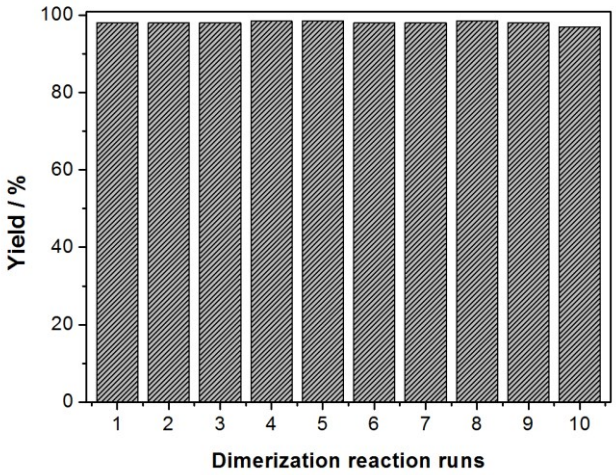


Fig. 6 MIL-101-SO_3H catalyst recycling test for the homodimerization of **1a**.

The acidic MIL-101-SO_3H catalyst can be recycled up to ten times without compromising the yield and selectivity of the reaction. The recyclability of the MIL-101-SO_3H catalyst was evaluated using 7-methoxy-2-(4-methoxyphenyl)-2*H*-chromene **1a** in 2 mL of CH_2Cl_2 at room temperature. As for MIL-101-SO_3H, the yield of desired benzopyranobenzopyran **2a** remained 97% after usage of the same recycled catalyst with 10 batches of fresh reagent (Fig. 6).

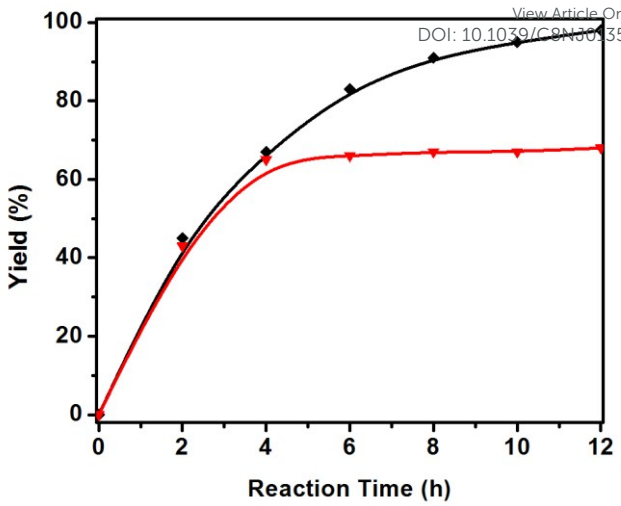


Fig. 7 MIL-101-SO_3H catalyst filtration test.

A hot filtration test was run for the MIL-101-SO_3H catalyzed dimerization reaction of **1a**; the solid catalyst was filtered after 4 h of reaction. The dimerization of 2*H*-chormene **1a** did not further proceed after the MIL-101-SO_3H catalyst was removed from the solution, which further suggests no acid leaches into the solution (Fig. 7). Furthermore, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of the filtrate showed the presence of 1.9 ppm of the Cr ion, which indicates extremely low leaching of the metal ion during the dimerization catalysis. SEM images and X-ray powder diffraction spectrum of the MIL-101-SO_3H catalyst were collected after ten reaction cycles; these data were found to be indistinguishable from those of the fresh catalyst (Fig. S1 and S2). This observation suggests the high chemical stability of the MIL-101-SO_3H catalyst.

4 Conclusions

In conclusion, a heterogeneous MIL-101-SO_3H catalyst bearing an aromatic sulfonic acid group was synthesized and utilized in 2*H*-chromene dimerization reaction. The structural morphology of MIL-101-SO_3H was fully characterized by SEM, XRD, TGA, FTIR and BET. The newly developed MIL-101-SO_3H showed high activity and diastereoselectivity in the dimerization reaction at only 1 mol% catalyst loadings, which provides higher TON and TOF than several other heterogeneous Brønsted acid catalysts. The high chemical stability of the MIL-101-SO_3H catalyst was due to its strong covalent bond, and did not suffer from leaching. Further studies involving new synthetic applications of the MIL-101-SO_3H catalyst are in progress.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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A facile 2*H*-chromene dimerization through an *ortho*-quinone methide intermediate catalyzed by a sulfonyl derived MIL-101 MOF

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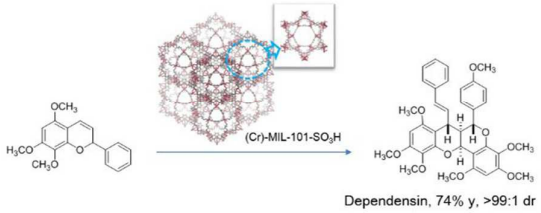

An efficient homo-dimerization of 2*H*-chromenes was achieved in high yield and diastereoselectivity using MIL-101-SO_3H MOF catalyst.