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Synthesis of 3-methyl-4-[(chromon-3-yl)methylene]-1-phenylpyrazolin-5-(4*H*)-ones catalysed by MCM-41-SO_3H

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The condensation of 4-oxo-4*H*-1-benzopyran-3-carbaldehydes with 3-methyl-1-phenylpyrazolin-5-(4*H*)-ones in dioxane to afford 3-methyl-4-[(chromon-3-yl)methylene]-1-phenylpyrazolin-5-(4*H*)-ones was performed using MCM-41-SO_3H as a catalyst.

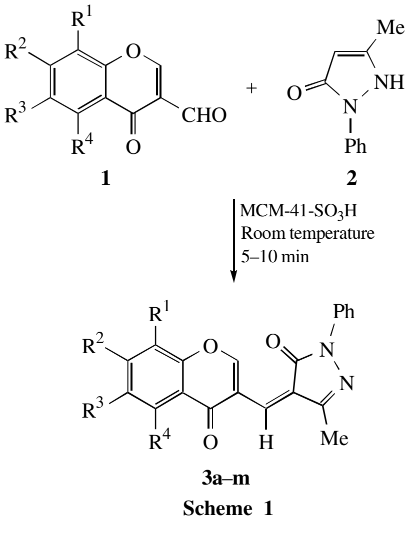
The discovery of mesoporous materials has raised the general expectation that the catalytic efficiency of microporous zeolites can be expanded to mesoporous dimensions.[1,2] It is necessary to introduce functionality into MCM or HMS structures, so surface modification techniques are enjoying a renewed interest, and it is clear that the pore walls of mesoporous materials are easily modified with either purely inorganic or with hybrid semi-organic functional groups.[3–6] Reports on Ti-MCM-41 prove that this oxidation catalyst can indeed handle voluminous substrates such as alkylated phenols.[7,8] The use of guanidine-functionalised MCM-41 in base-catalysed condensations was reported.[9] Progress in acid catalyst is lagging behind, largely because of the low acid strength of Al-substituted mesoporous silica such as Al-MCM-41.[10] As an alternative, the covalent attachment of alkylsulfonic acid groups to the surface of MCM molecular sieves *via* secondary or direct synthesis is now proposed.[11] The resulting MCM-41-SO_3H materials perform well in typical strong acid-catalysed reactions. The hydrophobic nature of the active sites environment can be explained to perform reactions, which are outside the reach of other inorganic solid catalysts.

The catalytic properties of the new material MCM-41-SO_3H were first tested in the synthesis of 2,2-bis(5-methylfuryl)propane (DMP). Bisfuryl alkanes are relevant intermediates for the macromolecular chemistry.[12] Condensation of 2-methylfuran and acetone with a strong acid catalyst (MCM-41-SO_3H) produces DMP.[11]

Sulfonic acid-functionalised MCM materials are new and worthwhile materials for reactions in which zeolites fail.

Herein we report the synthesis of 3-methyl-4-[(chromon-3-yl)-methylene]-1-phenylpyrazolin-5-(4*H*)-ones in quantitative yield by the use of MCM-41-SO_3H as a catalyst.

In continuation of works on 4-oxo-4*H*-1-benzopyran-3-carbaldehyde,[13–16] we have developed a newer route for the synthesis of 3-methyl-4-[(chromon-3-yl)methylene]-1-phenylpyrazolin-5-(4*H*)-ones[13,15,16] by the condensation of 4-oxo-4*H*-benzopyran-3-carbaldehyde with 3-methyl-1-phenylpyrazolin-5-(4*H*)-ones, which was carried out in dioxane at room temperature by using MCM-41-SO_3H. The substrate, 4-oxo-4*H*-1-benzopyran-3-carbaldehyde, has three active sites: the α,β-unsaturated carbonyl group, *i.e.*, a pyrone ring, a carbon–carbon double bond and a formyl group. Of these, the formyl group has the highest reactivity towards active methylene compounds. In this methodology, reactions were completed in a shorter time and with higher yields. The reaction occurred under very mild conditions. The condensed products were easily isolated.†



3a–m

Scheme 1

Table 1 Characterisation of 3-methyl-4-[(chromon-3-yl)methylene]-1-phenylpyrazolin-5-(4*H*)-ones synthesised using the catalyst MCM-41-SO_3H.

Entry	R^1	R^2	R^3	R^4	Elemental analysis C (%) calc. (found)	H (%) calc. (found)	N (%) calc. (found)	mp/°C	Yield (%)
3a	H	H	Cl	H	65.85 (65.84)	3.59 (3.60)	7.68 (7.69)	239	88
3b	H	H	Me	H	73.24 (73.25)	4.68 (4.65)	8.13 (8.15)	239	89
3c	Me	H	Me	H	73.73 (73.73)	5.06 (5.05)	7.82 (7.82)	282	82
3d	H	Me	H	Me	73.73 (73.72)	5.06 (5.05)	7.82 (7.83)	214	86
3e	H	Me	H	H	73.24 (73.25)	4.68 (4.69)	8.13 (8.15)	203	86
3f	H	Me	Me	H	73.73 (73.74)	5.06 (5.05)	7.82 (7.83)	248	82
3g	Cl	H	Cl	H	60.17 (60.17)	3.03 (3.05)	7.02 (7.05)	281	80
3h	H	Me	Cl	H	66.58 (66.60)	3.99 (4.00)	7.40 (7.40)	256	86
3i	Cl	H	H	Cl	60.17 (60.17)	3.03 (3.04)	7.02 (7.00)	291	81
3j	H	Cl	Cl	H	60.17 (60.17)	3.03 (3.03)	7.02 (7.02)	268	84
3k	Cl	H	H	H	65.85 (65.85)	3.59 (3.56)	7.68 (7.68)	218	83
3l	H	H	Br	H	59.31 (59.30)	4.03 (4.01)	6.59 (6.57)	234	86
3m	H	H	H	H	72.82 (72.80)	5.24 (5.25)	8.09 (8.09)	230	80

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† All the melting points were taken in open capillaries and were matched with the authentic.[13] Spectra were recorded on a FTIR spectrophotometer, and ^1H NMR spectra were recorded on a 300 MHz spectrometer.

General procedure. The title compounds (**3a**–**m**) have been synthesised by mixing a solution of 4-oxo-4*H*-1-benzopyran-3-carbaldehyde (10 mmol) and 3-methyl-1-phenylpyrazolin-5-(4*H*)-one (10 mmol) in dioxane with acidic catalyst MCM-41-SO_3H (0.2 g) and stirred for 5–10 min. The solid product obtained was recrystallised from the specified solvent. After recrystallisation the catalyst can be separated and reused in other reactions.

Spectroscopic data. IR Spectrum of **3a** showed characteristic absorption bands at 1654 (C=O, chromone), 1790 (C=O, pyrazolin), 1685 (C=N, pyrazolin), 1461 (γ-pyrone), 1607 (C=C), 3063 (=C–H) and 750 cm^{-1} (C–Cl).

The ^1H NMR spectrum of **3a** exhibited characteristic signals (δ/ppm) at 2.4 (s, Me), 7.1–7.9 (m, 8H, aromatic and olefinic protons), 8.2 (s, 1H), 10.8 (s, 1H, C_2–H of chromone moiety).

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