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Hybrid silica materials derived from Hoveyda–Grubbs ruthenium carbenes. Electronic effects of the nitro group on the activity and recyclability as diene and enyne metathesis catalysts

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ABSTRACT

The preparation of several organic–inorganic hybrid materials by sol–gel process derived from Hoveyda-type monomers is described. One of them presents a nitro group at the *para* position with respect to the alkoxy moiety. These materials were treated with Grubbs catalysts to generate the corresponding Hoveyda–Grubbs carbene ruthenium complexes covalently bonded to the silica matrix, which were tested as recyclable catalysts for diene and enyne RCM. Electronic effects of the nitro group resulted in enhanced activity of the catalyst. Whereas the recyclability decreased in RCM of dienes, the presence of this electron-withdrawing group was highly advantageous for the RCM of enynes, the reusability being greatly improved.

1. Introduction

Olefin metathesis has emerged in the last decade as one of the most powerful carbon–carbon bond forming tools for the preparation of a great variety of compounds.[1] More recently, enyne metathesis has also been used in both intramolecular and intermolecular applications.[2] The enyne bond reorganization is atom economical and is driven by the enthalpic stability of the conjugated 1,3-diene final product. The enormous success of metathesis reactions during the last years can be attributed to the discovery of several well-defined metal carbenes, which have proven to be efficient and selective promoters. The second generation Grubbs ruthenium catalysts[3] **1B**,**C** (Fig. 1) and specially the Hoveyda–Grubbs catalysts[4] **2A**,**B** (Fig. 1) show enhanced reactivity, stability, and recovery profiles compared to the first generation Grubbs catalyst **1A** (Fig. 1), the chelating styrenic ligands playing a crucial role on such improvement. Moreover, Grela and Blechert have described the influence of electronic and steric effects in Hoveyda-type ruthenium carbenes. From the electronic point of view it was found that enhanced reactivity could be achieved with several variants of the catalyst **2B** bearing strong electron-withdrawing groups in the *para* position with respect to the alkoxy group and/or the alkylidene group.[5]

On the other hand, the increased robustness and stability of the Hoveyda–Grubbs carbenes facilitates the preparation of recoverable metathesis catalysts[6] and the number of publications dealing with catalyst recovery has increased very significantly in the last few years. One of the most used recycling strategies consists of the immobilization of the carbene complex on a polymeric insoluble support. Filtration at the end of the reaction permits an easy

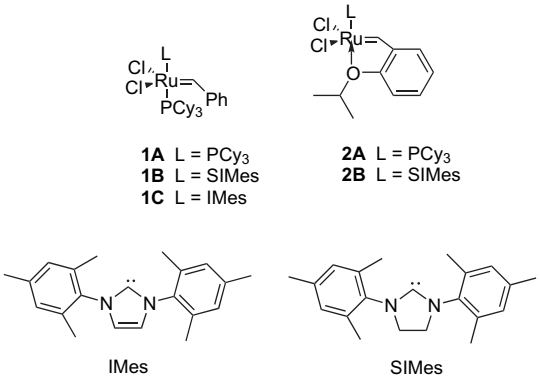

Figure 1. Ruthenium carbene metathesis catalysts.

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separation of the product and recovery of the catalyst, avoiding time-consuming chromatography. Anchoring of ruthenium carbenes of type **1** and **2** to the polymeric support has been performed via phosphine exchange,[7] via the *N*-heterocyclic carbene ligand,[8] through halogen exchange,[9] or via alkylidene exchange (*boomerang*-type catalysts).[10] The efficiency of *boomerang* supported catalysts increases notably when Hoveyda-type chelating ligands are used.[11] Insoluble organic polymers are the most frequently used supports, although anchoring to soluble poly(ethylene glycol)[11a–c] and some recent examples of silica-bound carbene ruthenium complexes have also been described.[7b,8c–e,9b–e,11f,g,j,k,n,p]

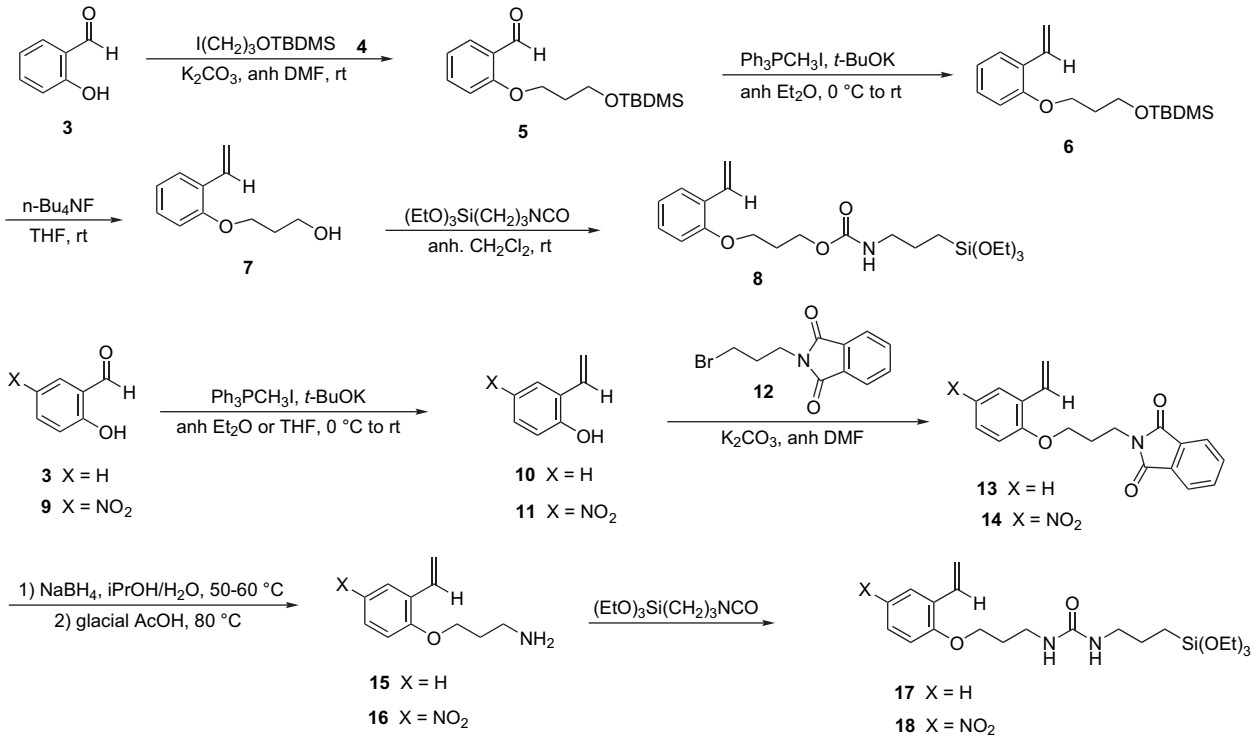
In this context, hybrid organic–inorganic materials formed by catalytic species covalently anchored to silica have chemical, mechanical, and thermal stability superior to that of organic polymers and, sometimes, higher surface areas. Most of the above-mentioned examples about silica-bound catalysts refer to anchoring to porous and non-porous silicas and to non-porous glass monoliths. The sol–gel hydrolytic-condensation[12–14] of suitable organo-alkoxysilanes is a convenient method to prepare solid hybrid materials with targeted properties.[15–17] We have previously reported the preparation and the activity as recyclable metathesis catalysts of bridged silsesquioxanes[11k] synthesized from a bis-silylated Hoveyda-type monomer and of hybrid silicas[11n] from a monosilylated Hoveyda-type isopropoxybenzylidene via the sol–gel process. This was the first example in the literature concerning the use of a bis-silylated ligand in a sol–gel process for the preparation of reusable metathesis catalysts. Some excellent results in enyne metathesis we have obtained recently prompt us to present here our further developments in reusable catalysts, which bear an electron-withdrawing nitro group in *para* position with respect to the chelating alkoxy moiety and their comparison in terms of efficiency and recyclability with materials, which do not present this group. Furthermore, two different linkers, bearing carbamate and urea moieties, have been tested. Both strategies for materials preparation, grafting, and sol–gel co-gelification with tetraethoxysilane (TEOS) were used. Grafting does not allow the control of neither the concentration of organic groups nor their distribution. These parameters depend, rather, on the number of surface silanol groups, on the diffusion of reagents through the pore channels, and on steric factors, with some organic moieties remaining on the surface of the pores. The co-gelification of a silylated monomer with TEOS would allow a higher and controllable loading of the organic moiety throughout the matrix, which results in a supported catalyst different from those prepared by grafting.

2. Results and discussion

2.1. Monomer synthesis

Three monosilylated monomers for the synthesis of hybrid silica materials were prepared (Scheme 1). Salicylaldehyde, **3**, was reacted with iodide **4** in anhydrous DMF at room temperature in the presence of potassium carbonate to afford the aldehyde **5** in 91% yield, which upon Wittig olefination gave the styrene **6** in 55% yield after column chromatography. Subsequent alcohol deprotection with tetrabutylammonium fluoride furnished the alcohol **7** (89% yield), which was treated with commercial 3-(isocyanatopropyl)triethoxysilane in anhydrous dichloromethane at room temperature to afford the desired carbamate **8** in 97% yield.

Two silylated ureas were obtained by an analogous synthetic pathway as summarized in Scheme 1. Wittig olefination of commercial aldehydes **3** and **9** afforded the styrenic compounds **10** and **11** in 65 and 74% isolated yields, which upon alkylation with bromide **12** in anhydrous DMF in the presence of potassium carbonate gave the styrenes **13** and **14** in 75 and 77% yields, respectively. Standard hydrazine deprotection of the phtalimido group was unsuccessful, but amines **15** and **16** could be obtained in 74 and 76% yields after a two-step procedure, which involves partial reduction with sodium borohydride and subsequent acidic hydrolysis of the amide intermediate.[18] Reaction of the corresponding amines with 3-(isocyanatopropyl)triethoxysilane furnished the monosilylated ureas **17** and **18** in 90 and 76%, respectively. It was performed at



Scheme 1. Preparation of monosilylated Hoveyda-type monomers **8**, **17**, and **18**.

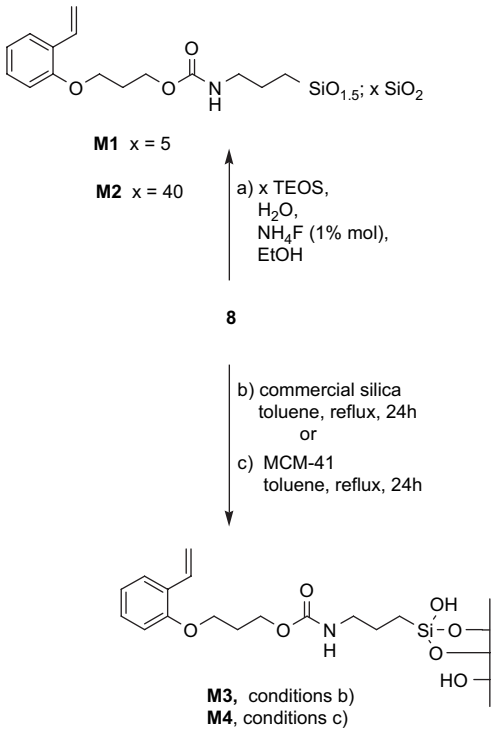
room temperature in anhydrous THF in the case of **15** and without solvent in the case of the nitro-containing amine **16**, as the presence of solvent was deleterious. Compounds **16**–**18** were not very stable and they were used in the next step immediately after their preparation.

2.2. Hybrid materials and catalysts preparation

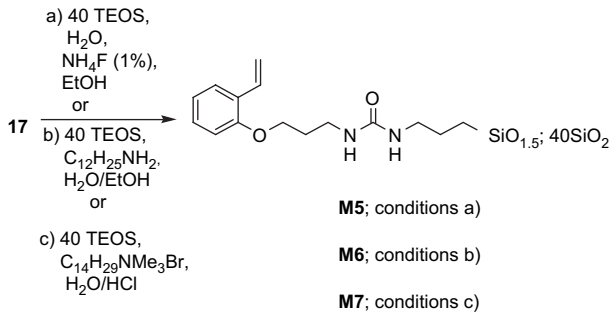
Hybrid silica materials prepared from the silylated monomers **8**, **17**, and **18** are summarized in Schemes 2–4, respectively.

Co-gelification of **8** with different amounts of tetraethoxysilane (5:1 and 40:1 as molar ratio of TEOS/**8**) in ethanol at room temperature under nucleophilic conditions (stoichiometric water, 1 mol % of ammonium fluoride as catalyst) afforded materials **M1** and **M2** (Scheme 2). On the other hand, anchoring of **8** to a commercial silica gel (ref. 36006 ACROS, 500 m^2/g)[19] and to a mesostructured silica MCM-41 (28 Å, 1050 m^2/g)[20] under standard conditions (in refluxing toluene for 24 h) afforded materials **M3** and **M4**, respectively (Scheme 2).

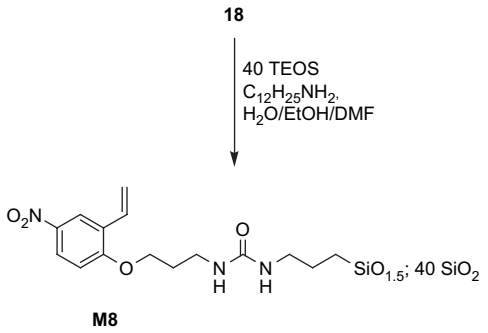
Sol–gel co-gelification of TEOS with urea **17** (molar ratio 40:1 in all cases) was performed in three different conditions (Scheme 3).



Scheme 2. Preparation of hybrid silica materials **M1**–**M4** from **8**.



Scheme 3. Preparation of hybrid silica materials **M5**–**M7**.



Scheme 4. Preparation of hybrid silica material **M8** from **18**.

The standard method under nucleophilic catalysis by fluoride ion gave rise to **M5**. Material **M6** was obtained with dodecylamine acting as both basic catalyst and surfactant.[21,22] Direct synthesis of **M7** was accomplished under acidic conditions using myristyltrimethylammonium bromide as surfactant.[23]

The nitro-containing urea **18** was also co-gelified with TEOS (40:1 ratio for TEOS/**18**) under dodecylamine catalysis to give **M8** (Scheme 4). Use of dimethylformamide as co-solvent was required due to the low solubility of the monomer in ethanol.

The materials were studied by several techniques (^{29}Si CP-MAS NMR, BET surface area measurements, PXRD). The ^{29}Si solid-state NMR data, some textural properties, and the ligand loading of hybrid materials **M1**–**M8** are summarized in Table 1.

^{29}Si CP-MAS NMR of all materials confirmed the covalent bonding of the organic moiety to the matrix by the appearance of T^2 and T^3 signals due to the ligand in addition to the characteristic Q^3 and Q^4 signals due to the condensed TEOS (Fig. 2).

A very low surface area was observed for hybrid material **M1** (5:1). However, increasing the amount of TEOS in the co-gelification process (40:1) led to a highly porous material **M2**, with a corresponding BET surface area of 681 m^2/g. The grafted material **M4** had a much higher BET surface area (773 m^2/g) and narrower pore size distribution (23–26 Å) than **M3** (293 m^2/g, 30–150 Å) as expected. The ordered hexagonal structure characteristic of MCM-41 was maintained in **M4** as confirmed by TEM. With respect to materials derived from urea **17** we observed that the use of dodecylamine and myristyltrimethylammonium bromide as surfactants gave materials **M6** and **M7** with higher porosity (760 and 659 m^2/g) and narrower pore size distribution (18–19 and 18–22 Å) than the material derived from standard sol–gel (529 m^2/g and 37–48 Å for **M5**). Powder X-ray diffraction (PXRD) (Fig. 3) showed an intense diffraction peak at low angle indicative of a worm-like structure for both materials **M6** and **M7**, which were synthesized in the presence of the surfactants. This intense peak was not observed for **M5**, which suggests the lack of organization in this hybrid material. The use of dodecylamine as surfactant in the co-gelification of the nitro-containing urea **18** produced a high specific surface area of the corresponding material (1163 m^2/g for **M8**) and also resulted in a worm-like organization for **M8** (Fig. 3).

The materials **M1**–**M8** were charged with the metal by treatment with the second generation Grubbs catalyst **1B** (0.96–1.2 equiv, except 0.49 equiv for **C1B**) in refluxing anhydrous and degassed dichloromethane for 24 h (Scheme 5) to give the corresponding catalysts **C1B**–**C8B**. Materials **M1** and **M3** were also treated with the first generation Grubbs catalyst **1A** following an analogous procedure (Scheme 5) to give **C1A** and **C3A**, respectively. Ruthenium content in materials **C1A**, **C3A**, and **C1B**–**C8B** was determined by inductively coupled plasma (ICP) analysis, the results being summarized in Table 2.

Table 1
Some analytical and textural data of hybrid materials **M1**–**M8**

	^{29}Si CP-MAS NMR						S_{BET} (m^2/g)	Pore diameter (Å)	mmol/g
	T^1	T^2	T^3	Q^2	Q^3	Q^4			
M1	—	−57.0	−64.8	−90.6	−100.8	−110.2	8	50–300	1.55
M2	—	—	−65.0	−91.4	−100.2	−109.1	681	20–200	0.325
M3	—	−56.6	—	—	−101.0	−109.8	293	30–150	0.407
M4	−51.4	—	—	−92.3	−100.8	−109.5	773	25	0.361
M5	—	—	−64.0	−91.9	−101.2	−109.6	529	43	0.207
M6	—	—	−63.4	—	−101.8	−110.4	760	19	0.221
M7	—	—	−64.2	−91.3	−100.8	−109.5	659	20	0.203
M8	—	—	−64.8	—	−101.5	−109.5	1163	25	0.265

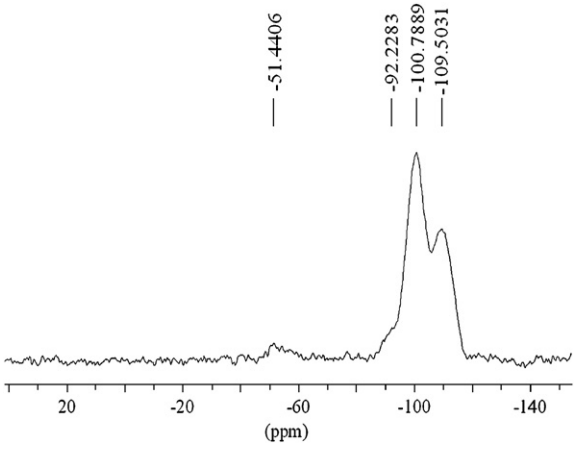


Figure 2. Solid-state ^{29}Si CP-MAS NMR of **M4**.

2.3. Assay of supported catalysts in diene and enyne ring-closing metathesis reactions

Supported catalysts **C1A**, **C3A**, and **C1B**–**C8B** have been tested in the ring-closing metathesis reaction of *N*,*N*-diallyl-4-methylbenzenesulfonamide, **19**,[24] to give 1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole, **20**[24] (Scheme 6, Tables 3 and 4). In all cases the reaction was performed in dichloromethane (0.05 M for **19**) at room temperature under an inert atmosphere, using a 3.5 mol % concentration of catalyst for the times indicated in Tables 3 and 4 (the disappearance of **19** was monitored by GC). Filtration and evaporation of the solvent afforded pure **20**, together with small amounts of **19** in some cases (the molar ratio **20**/**19** was determined by ^{1}H NMR). Heterogeneous catalysts were reused directly in the next run, five cycles being performed for each catalyst. The reaction times were maintained the same in order to follow the efficiency of the catalyst upon recycling.

Table 3 summarizes the results with catalysts prepared from catalytic materials **C1A**, **C3A**, and **C1B**–**C4B** derived from carbamate monomer **8**. It was clearly observed that the activity of catalysts **C1B** and **C3B** was superior to that of catalysts **C1A** and **C3A**. Thus, faster reactions and better recycling were obtained with supported catalysts prepared with the second generation Grubbs complex **1B**. For this reason, treatment of the remaining materials **M2**, **M4**, and **M5**–**M8** with the first generation Grubbs complex **1A** was not performed.

If we compare catalysts **C1B** and **C2B** prepared by sol–gel we notice that higher dilution of the organic ligand in the inorganic matrix improves the activity of the catalysts (**C2B**>**C1B**). In the case of materials derived from grafting, mesostructured **C4B** remains superior to non-organized **C3B**. Diluted sol–gel material **C2B** is preferred to grafting mesostructured material **C4B** in terms of activity and recycling.

We present in Table 4 the results corresponding to catalysts prepared from the urea materials **M5**–**M8**. For catalysts **C5B**–**C7B** the introduction of some ordering in the materials improves the activity (compare **C5B** and **C6B**), probably as a result of a higher BET

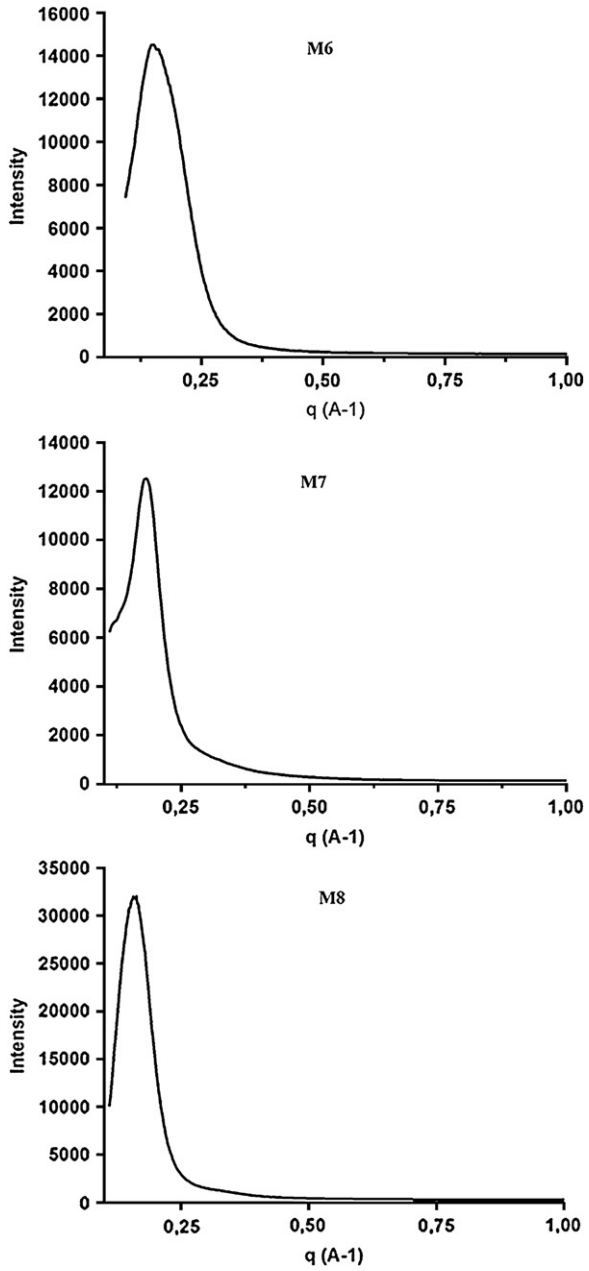
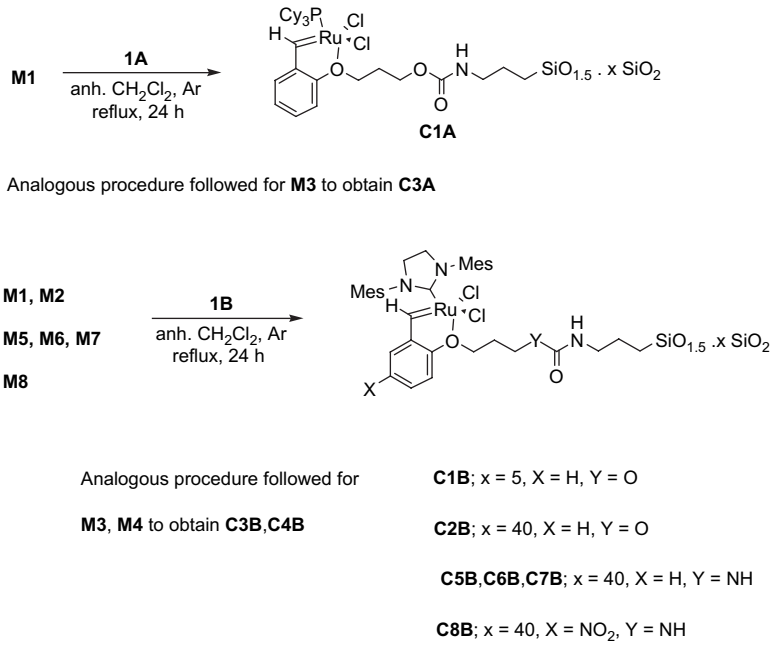


Figure 3. Powder X-ray diffraction of materials **M6**, **M7**, and **M8**.



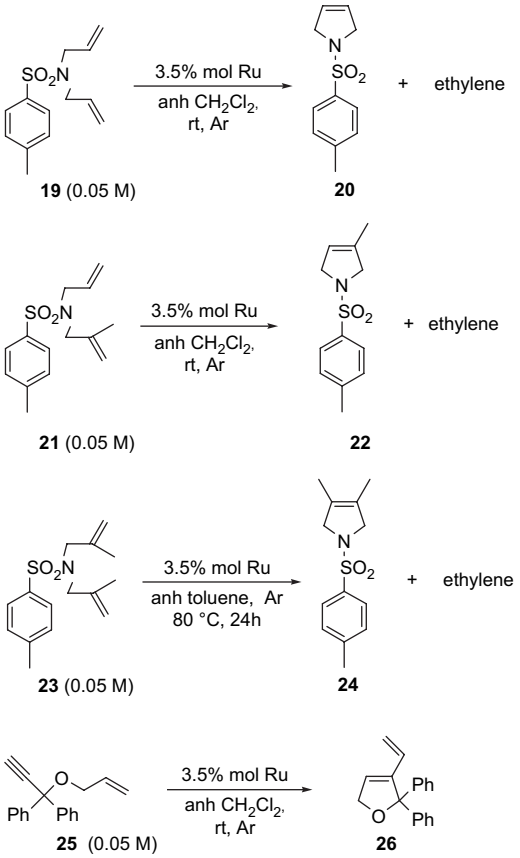
Scheme 5. Preparation of ruthenium heterogeneous catalysts **C1A**, **C3A**, and **C1B–C8B** from the corresponding materials **M1–M8**.

Table 2
Ruthenium content in catalytic materials **C1A**, **C3A**, and **C1B–C8B**

	% Ru	mmol Ru/g
C1A	0.54	0.053
C3A	1.17	0.115
C1B	0.60	0.060
C2B	1.75	0.173
C3B	1.20	0.119
C4B	1.32	0.130
C5B	1.20	0.119
C6B	1.29	0.128
C7B	0.68	0.067
C8B	1.36	0.135

surface area and an easier diffusion. Unexpectedly, **C7B** prepared under acidic conditions with cationic surfactant, presents a marked decrease in activity in the fourth cycle. Contrarily, catalyst **C8B**, containing the nitro group and prepared with dodecylamine, was very efficient in terms of activity (compare the reaction times for full conversion on the first cycle for **C6B** and **C8B**), although this results in a decrease of their reusability from the third run.

The ring-closing metathesis reaction to afford **20** has been performed in the literature with several recyclable immobilized catalyst types under different conditions.[10c,e,11a,h,j–n,p–s,25] Mauduit[25a] and Yao[25b] used imidazolium-tagged Grubbs ruthenium complexes in ionic liquid as immobilizing solvent. Gibson[25c] reported the encapsulation of second generation Grubbs catalyst in polystyrene. Curran[25d] performed the reaction with fluorous versions of first and second generation Hoveyda–Grubbs catalysts. Recently, Lee[25e] has attached a second generation Hoveyda–Grubbs catalyst on gold clusters. Yao[11a] described soluble polymers of first generation Hoveyda–Grubbs catalyst anchored to PEG. Blechert[11h] has used a soluble polymer of second generation Hoveyda–Grubbs catalyst derivative generated by ROMP. Grela and Mauduit[11q] have designed a pyridinium-tagged boomerang ligand toward an optimal compromise between activity and reusability in ionic liquids. Bergbreiter[11r] has prepared a heptane-soluble catalyst to be recycled by liquid/liquid or liquid/solid separations after catalysis. Lee[11s] has synthesized a self-supported oligomeric Ru-carbene, which work homogeneously and may be recovered by precipitation in ethyl acetate. But the simplest method to isolate and recycle the catalyst is by its immobilization in a solid insoluble support. Barrett[10c] has anchored a second generation Grubbs catalyst to polystyrene by the alkylidene moiety and has described five cycles with decreasing conversions (100–42%). Nolan[10e] has reported the same



Scheme 6. RCM reactions tested with recyclable catalysts **C1A**, **C3A**, and **C1B–C8B**.

Table 3
Results for the RCM of **19** to **20** with supported catalysts **C1A**, **C3A**, and **C1B**–**C4B**

Run	**C1A**[a]		**C3A**		**C1B**		**C2B**		**C3B**		**C4B**	
	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)
1	38	87	20	96	8	96	4	>98	8	>98	4.3	>98
2	51	73	20	30	8	98	2	>98	8	98	4	98
3	48	32	20	8	8	51	2	96	8	94	4	92
4	48	13	95	6	8	67	2	88	8	84	4	81
5	—	—	—	—	8	62	2	76	8	60	4	65
6	—	—	—	—	24	27	24	95	18	38	24	92

[a] A 2 mol % Ru was used.

Table 4
Results for the RCM of **19** to **20** with supported catalysts **C5B**–**C8B**

Run	**C5B**		**C6B**		**C7B**		**C8B**	
	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)
1	4	96	3	96	3	>98	0.75	>98
2	4	97	3	98	3	>98	0.75	96
3	4	94	3	94	3	74	0.75	80
4	4	90	3	88	3	31	0.75	51
5	4	87	3	82	3	—	0.75	30
6	24	>98	24	>98	24	—	24	78

type of catalysts anchored to polydivinylbenzene resins, performing three cycles with modest GC yields (30–38%). By anchoring a second generation Hoveyda–Grubbs catalyst to silica gel, Blechert[11j] reported recently four cycles with decreasing conversions (>99% to 68%). Bannwarth[11l] performed the reaction in $scCO_2$ (five cycles) with several solid phase-bound Hoveyda-type catalysts with conversions going from 95 to 84% and 93 to 57% in the best cases. Grela[11m] has very recently achieved a non-covalent immobilization of Hoveyda–Grubbs catalyst to polymeric phases by means of electrostatic binding, performing five cycles of the reaction with gradual loss of activity. We have recently reported several recyclable organic–inorganic hybrid materials prepared from a bis-silylated[11k] and a monosilylated[11n] Hoveyda-type monomers by sol–gel methodologies. Our conditions[11k,n] for the preparation of **20** were milder than those used in most of the preceding works (percentage of catalyst and/or reaction temperature and/or reaction time), achieving a better recycling than in most of the aforementioned solid insoluble supports. Ying[11p] has reported the use of siliceous mesocellular foam-supported catalysts with good activity. Our present results with material **C8B** offer a clear improvement in terms of activity, although in terms of recyclability the catalysts **C1B**, **C2B**, **C5B**, and **C6B** are better. Although some recycling strategies involving the reaction performed under homogeneous conditions[11h,25a,b,d,e] remain superior, the advantage of simplicity in the separation procedure must be taken into account.

Then, we tested the more challenging dienes **21** and **23**, from which the corresponding trisubstituted and tetrasubstituted olefins **22** and **24** should be obtained (Scheme 6, Tables 5 and 6). Complete conversion of **21** to 3-methyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole, **22**, with second generation Grubbs catalyst **1B** under homogeneous conditions (3.5 mol %, 0.05 M of **21**,

Table 5
Results for the RCM of **21** to **22** with catalysts **C2B**, **C6B**, and **C8B**

Run	**C2B**		**C6B**		**C8B**	
	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)
1	3	>98	5	96	1.5	>98
2	3	>98	5	>98	1.5	92
3	3	93	5	96	1.5	78
4	3	86	5	94	1.5	70
5	3	73	5	92	1.5	25
6	24	>98	24	>98	24	>98

Table 6
Results for the RCM of **23** to **24** with catalysts **C2B**, **C6B**, and **C8B**

Run	**C2B**		**C6B**		**C8B**	
	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)
1	24	78	24	8	24	74
2	24	4	—	—	—	—

dichloromethane, rt) required less than 3 h. This transformation was only tested with the supported catalysts C**2B**, **C6B**, and **C8B**, which had shown the best performance for the diene **19**. The good results obtained are outlined in Table 5. Complete conversions were achieved in 3, 5, and 1.5 h, respectively. Again, the faster reaction corresponds to the nitro-containing catalyst **C8B**, although in terms of reusability the analogous catalytic material **C6B** lacking this nitro group is preferred (92% after 5 h in the fifth cycle).

Mauduit[25a,11q] has assayed this reaction with immobilized catalysts using imidazolium- and pyridinium-tagged Hoveyda-type complexes in room temperature ionic liquids as solvents and immobilizing agents. Ying[11p] performed seven cycles with decreasing conversions. Bergbreiter[11r] used a heptane-soluble catalyst and the product was precipitated in this solvent. The reusability of our catalyst **C6B** is superior and the working-up very advantageous. We also improve here our previous results with a supported catalyst.[11n]

In our hands, treatment of *N*,*N*-bis(2-methylallyl)-4-methylbenzenesulfonamide, **23**, with second generation Grubbs catalyst **1B** under homogeneous conditions (3.5% molar Ru, 0.05 M of **23**, toluene, 80 °C, 7 h) gave 90% conversion to 3,4-dimethyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole, **24**. Supported catalysts **C2B**, **C6B**, and **C8B** were also assayed under analogous conditions. Catalyst **C2B** afforded a 78% conversion (^{1}H NMR) after 24 h (Scheme 6 and Table 6). The conversion decreased to 4% after the same reaction time in the second cycle. The catalytic materials **C6B** and **C8B** gave poorer results (8 and 74% conversion after 24 h), the recycling not being attempted.

It is worth to mention that very few reports have appeared about this challenging ring-closing metathesis reaction. Grela[11e] found a 45% conversion in a homogeneous process with a modified Hoveyda–Grubbs second generation catalyst, describing also a failed attempt to obtain **24** with a supported catalyst. Mauduit[25a] described this reaction using imidazolium-tagged ruthenium complexes in room temperature ionic liquids, but no recycling could be achieved. We have also reported this reaction with silica-based hybrid materials derived from a bis-silylated[11k] and a monosilylated[11n] Hoveyda-type monomer, the last type of materials[11n] being superior reusable catalysts for this challenging reaction (three runs), probably due to the presence there of an isopropoxy group that is absent in the materials presented now. Ying[11p] has found a recyclable system for this reaction, which affords a moderate conversion (31%) on the second run. Few reports can be found about the recyclability of ruthenium catalysts in the preparation of other tetrasubstituted alkenes, such as (*Z*)-4,5-dimethyl-1-tosyl-2,3,6,7-tetrahydro-1*H*-azepine[11b,25b] and diethyl

Table 7
Results for the enyne metathesis of **25** to **26** with catalysts **C2B**, **C6B**, and **C8B**

Run	**C2B**		**C6B**		**C8B**	
	t (h)	Conv (%)	t (h)	Conv (%)	t (h)	Conv (%)
1	5	93	2	>98	1.3	>98
2	5	72	2	>98	1	>98
3	5	40	2	94	1	>98
4	—	—	2	90	1	>98
5	—	—	2	90	1	97
6	—	—	—	—	1	94

3,4-dimethylcyclopent-3-ene-1,1-dicarboxylate.[10e] For the first substrate, Yao[11b] described three cycles using a soluble second generation Hoveyda–Grubbs carbene complex immobilized on poly(ethylene glycol) and the same author[25b] performed two cycles with an imidazolium-tagged second generation Hoveyda–Grubbs catalyst. For the second substrate, Nolan[10e] achieved four cycles with modest yields with a second generation Grubbs catalyst anchored to a cross-linked polystyrene through the alkylidene ligand.

The ring-closing enyne metathesis was also successfully performed on 1-allyloxy-1,1-diphenyl-2-propyne, **25**, to give 2,2-diphenyl-3-vinyl-2,5-dihydrofuran, **26**, with our heterogeneous catalysts **C2B**, **C6B**, and **C8B** (Scheme 6 and Table 7). Good conversions were obtained in short reaction times (1–5 h) with 3.5 mol % of catalyst in anhydrous dichloromethane (0.05 M of **25**) at room temperature. The urea-containing organized materials **C6B** and **C8B** were more active and exhibit better recycling properties than the carbamate-type non-organized material **C2B**. The presence of the nitro group in the Hoveyda ligand is very advantageous for this RCM reaction (compare **C6B** and **C8B**), not only promoting faster reactions but also improving the recyclability (five cycles with no decrease of activity), contrarily to what we have found for the RCM of dienes. Under analogous homogeneous conditions with the second generation Grubbs catalyst **1B** we obtained full conversion in 1 h. Thus, the supported catalyst **C8B** competes very well with homogeneous versions. This enyne RCM process has been described in the literature[5a,b,11q,26,27] using several catalysts and homogeneous conditions, but there is no report about recycling and about using polymer supported catalysts for the obtention of **26** except our own recent works[11k,n] and the report of Grela,[11m] which do not mention the recycling with this enyne substrate. Thus, our catalyst **C8B** constitutes the best recyclable catalyst described for this enyne metathesis reaction.

It is worth to mention that an assay was made to introduce the metal before hybrid material formation. Thus, the silylated monomer **8** was reacted with first generation Grubbs catalyst **1A** in refluxing anhydrous dichloromethane and the resulting complex was co-gelified with TEOS (molar ratio 1:5 of complex to TEOS) in ethanol under ammonium fluoride catalysis. The material thus obtained had a very low surface area (4 m^2/g), a ruthenium content lower than expected, and showed no catalytic activity. Further attempts to improve these results were not undertaken. The use of second generation Grubbs catalyst **1B** and a much higher dilution of the organic moiety into the inorganic matrix could be envisaged in order to increase the surface area of the material and to improve its catalytic performance.

3. Conclusion

In summary, we have described the synthesis of three monosilylated Hoveyda-type monomers, **8**, **17**, and **18**, and the preparation of several hybrid organic–inorganic materials **M1**, **M2**, **M5**–**M8** by sol–gel co-gelification with TEOS under different conditions. For monomer **8** also anchorage to commercial and mesostructured MCM-41 has been performed (materials **M3** and **M4**). Then the corresponding Hoveyda–Grubbs type ruthenium complexes **C1A**, **C3A**, and **C1B**–**C8B** have been obtained and they have been evaluated as recyclable catalysts in the ring-closing metathesis reactions of dienes **19**, **21**, and **23** and enyne **25**. As expected, supported catalysts **C1B**–**C8B** prepared from the second generation Grubbs complex **1B** gave much higher reaction rates than catalysts **C1A** and **C3A**, prepared from the first generation Grubbs complex **1A**, in the RCM on *N*,*N*-diallyl-4-methylbenzenesulfonamide, **19**. They offer milder conditions and better recyclability than other catalysts anchored to insoluble solid supports already described in previous works. The RCM on more challenging substrates, *N*-allyl-*N*-(2-methylallyl)-4-methylbenzenesulfonamide, **21**, and *N*,*N*-bis(2-methylallyl)-4-methylbenzenesulfonamide, **23**, gave rise to trisubstituted and tetrasubstituted alkenes **22** and **24**, respectively, good yields and recyclability being achieved for the trisubstituted olefin. Our materials are also good recyclable catalysts for the ring-closing enyne metathesis performed on 1-allyloxy-1,1-diphenyl-2-propyne, **25**. This is the third case described in the literature about recycling in this ring-closing enyne metathesis reaction, the other ones being recently reported by us.[11k,n] In all cases, materials prepared from sol–gel process are superior to those coming from anchorage to commercial silica or mesostructured MCM-41. Worm-like organized materials prepared with dodecylamine as surfactant showed improved activities. The presence of a nitro group in the *para* position with respect to the alkoxy moiety in the Hoveyda-type ligand enhanced the reactivity of the catalysts in RCM of dienes, faster reactions being achieved, but the recyclability decreased significantly. On the contrary, for the RCM of enyne **25**, both enhanced reactivity and recyclability are achieved, catalyst **C8B** constituting the best reusable catalyst described for this reaction (five cycles with no decrease of activity). Further investigations are underway with other structurally modified ligands in order to get improved supported catalysts.

4. Experimental section

4.1. General remarks

When required, experiments were carried out with standard high-vacuum and Schlenk techniques. Solvents were dried and distilled just before use. Chemical shifts (δ, ppm) in NMR were referenced to Me_4Si (^1H and ^{13}C). The abbreviations used are s for singlet, d for doublet, dd for double doublet, t for triplet, q for quartet, quint for quintuplet, sept for septet, and m for multiplet. The ^{29}Si CP-MAS solid-state NMR spectra were recorded with a repetition time of 5 s with contact times of 5 ms. Surface areas were determined by Brunauer–Emmett–Teller (BET) method and the average pore diameter was calculated by the BJH method. ESI mass spectra were acquired in the positive ion mode (ES+) at a probe tip voltage of 3 kV. The content of ruthenium was determined by inductively coupled plasma (ICP).

1-(*tert*-Butyldimethylsiloxy)-3-iodopropane, **4**,[28] was prepared in two steps from 3-chloro-1-propanol as reported.[29] Mesostructured silica MCM-41 was prepared following the standard procedure.[20b] Methyltriphenylphosphonium iodide was synthesized from methyl iodide and triphenylphosphine. The dienes **19** and **23**, and enyne **25** were prepared as previously described by us.[11k] The diene **21**[30] was synthesized from *N*-allyl-*p*-toluenesulfonamide[31] and 3-bromo-2-methyl-1-propene.

4.2. Synthesis of silylated monomers

*4.2.1. Synthesis of 2-(3-tert-butyldimethylsiloxypropoxy)-benzaldehyde (**5**)*

Potassium carbonate (4.30 g, 30 mmol) was added to a stirred solution of salicylaldehyde, **3** (0.754 g, 6.17 mmol) and 1-(*tert*-butyldimethylsiloxy)-3-iodopropane, **4** (1.84 g, 6.12 mmol) in DMF

(50 mL). The mixture was stirred overnight at room temperature under argon. Water was added (50 mL) and the solution was extracted with petroleum ether (3×50 mL). The combined organic layers were washed with water and then with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum, the desired compound **5** being obtained (1.64 g, 91%) as a colorless liquid. ^{1}H NMR (250 MHz, $CDCl_3$) δ=10.52 (s, 1H), 7.84 (dd, 1H, J=8.0, 1.8 Hz), 7.54 (ddd, 1H, J=8.4, 7.5, 1.8 Hz), 7.03 (m, 2H), 4.21 (t, 2H, J=6.2 Hz), 3.84 (t, 2H, J=5.9 Hz), 2.07 (quint, 2H, J=6.1 Hz), 0.90 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=189.4, 161.2, 135.6, 128.0, 124.7, 120.3, 112.2, 64.8, 58.9, 32.0, 25.6, 18.0, −5.7. IR (ATR): ν=2952, 2928, 2855, 1687, 1598, 1457, 1389, 1285, 1242, 1188, 1161, 1100, 1007, 968, 833, 775, 755, 651 cm^{-1}.

4.2.2. Synthesis of 2-(3-tert-butyldimethylsiloxypropoxy)styrene (6)

Potassium *tert*-butoxide 98% (3.13 g, 27.3 mmol) was added over a suspension of Ph_3PCH_3I (11.00 g, 27.2 mmol) in anhydrous diethyl ether (100 mL) at 0 °C. The mixture was stirred for 15 min and then a solution of **5** (4.0 g, 13.6 mmol) in anhydrous diethyl ether (50 mL) was added. After stirring at 0 °C under argon for 1 h, water was added (150 mL) and the organic layer was removed. The aqueous layer was extracted with diethyl ether (2×100 mL). The combined organic layers were filtered, washed with water (100 mL), then with brine (50 mL), and dried over anhydrous Na_2SO_4. After removing of the solvent the residue was chromatographed through silica gel (hexane/CH_2Cl_2 3:1), obtaining **6** as a colorless liquid (2.19 g, 55%). ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.24–6.92 (m, 5H), 5.81 (dd, 1H, J=17.7, 1.4 Hz), 5.31 (dd, 1H, J=11.1, 1.4 Hz), 4.15 (t, 2H, J=6.1 Hz), 3.89 (t, 2H, J=6.1 Hz), 2.08 (quint, 2H, J=6.1 Hz), 0.96 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=156.0, 131.6, 128.6, 126.6, 126.2, 120.2, 113.9, 111.7, 64.5, 59.4, 32.3, 25.7, 18.1, −5.6. IR (ATR): ν=2952, 2928, 2856, 1625, 1598, 1488, 1471, 1453, 1414, 1290, 1241, 1103, 1018, 970, 904, 832, 774, 746, 662 cm^{-1}. MS: m/z=235 (M^+−[C_4H_9]) (25), 177 (M^+−[$C_6H_{15}Si$]) (100), 161 (12), 151 (16), 135 (5), 91 (6), 73 (14), 59 (7), 41 (3). HRMS: m/z=292.1859 (calcd for $C_{17}H_{28}O_2Si$: 292.1864).

4.2.3. Synthesis of 3-(2-vinylphenoxy)propan-1-ol (7)

A solution of tetrabutylammonium fluoride 97% (3.08 g, 9.46 mmol) in anhydrous THF (15 mL) was added over **6** (1.19 g, 4.07 mmol) in anhydrous THF (10 mL) at 0 °C, and the mixture was stirred overnight at room temperature. Water was added (25 mL) and extracted with diethyl ether (3×25 mL). The combined organic layers were washed with water (2×20 mL) and dried over anhydrous Na_2SO_4. After evaporation of the solvent **7** was obtained as an oil (0.64 g, 89%). ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.46 (dd, 1H, J=7.7, 1.8 Hz), 7.21–6.85 (m, 4H), 5.73 (dd, 1H, J=17.7, 1.6 Hz), 5.25 (dd, 1H, J=11.1, 1.6 Hz), 4.11 (t, 2H, J=5.9 Hz), 3.85 (t, 2H, J=5.9 Hz), 2.06 (masked s, 1H), 2.05 (quint, 2H, J=5.9 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=155.7, 131.4, 128.7, 126.7, 126.3, 120.6, 114.3, 111.7, 65.6, 60.0, 31.9. IR (ATR): ν=3314, 2930, 2878, 1624, 1597, 1487, 1452, 1415, 1290, 1239, 1108, 1054, 992, 952, 907, 835, 746 cm^{-1}. MS: m/z=178 (M^+) (36), 163 (6), 145 (12), 133 (8), 120 (M^+−[C_3H_6O]) (100), 91 (93), 77 ([C_6H_5]$^+$) (13), 65 (18), 51 (9), 41 (6). HRMS: m/z=178.0994 (calcd for $C_{11}H_{14}O_2$: 178.1000).

4.2.4. Synthesis of O-(3-(2-vinylphenoxy)propyl)-N-(3-triethoxysilylpropyl)carbamate (8)

Freshly distilled 3-(triethoxysilyl)propyl isocyanate (1.8 mL, 0.99 g/mL, 7.2 mmol) was added dropwise via syringe under argon to **7** (0.805 g, 4.52 mmol) in anhydrous dichloromethane (5 mL). The mixture was stirred under argon at room temperature for 8 days (^{1}H NMR monitoring). The solvent was removed under vacuum and excess isocyanate was distilled off (100 °C, 1.7 mbar). Anhydrous diethyl ether (5 mL) was added to the residue, the solution was filtered under nitrogen atmosphere, and the solvent was evaporated, the desired compound **8** being obtained as a pale yellow oil (1.88 g, 97%). ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.51 (dd, 1H, J=7.7, 1.7 Hz), 7.28–6.87 (m, 4H), 5.76 (dd, 1H, J=17.9, 1.7 Hz), 5.28 (dd, 1H, J=11.2, 1.5 Hz), 4.95 (br s, 1H), 4.30 (t, 2H, J=6.2 Hz), 4.10 (t, 2H, J=6.2 Hz), 3.84 (q, 6H, J=6.9 Hz), 3.20 (apparent q, 2H, J=6.3 Hz), 2.16 (quint, 2H, J=6.2 Hz), 1.65 (quint, 2H, J=7.0 Hz), 1.25 (t, 9H, J=7.0 Hz), 0.65 (t, 2H, J=8.2 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=156.2, 155.7, 131.3, 128.5, 126.7, 126.2, 120.5, 114.0, 111.6, 64.6, 61.3, 58.2, 43.1, 28.9, 23.0, 18.0, 7.4. IR (ATR): ν=3338, 2972, 2926, 2883, 1700 (br), 1525, 1488, 1453, 1389, 1237, 1164, 1100, 1073, 953, 857, 748 cm^{-1}. Anal. Calcd for $C_{21}H_{35}NSiO_6$: C, 59.27; H, 8.29; N, 3.29. Found: C, 59.37; H, 8.65; N, 3.68.

4.2.5. Synthesis of 2-vinylphenol (10)

Potassium *tert*-butoxide 98% (3.86 g, 33.7 mmol) was added over a suspension of Ph_3PCH_3I (6.92 g, 17.1 mmol) in anhydrous diethyl ether (100 mL) at 0 °C. The mixture was stirred for 15 min and then a solution of salicylaldehyde, **3** (2.0 g, 16.4 mmol) in anhydrous diethyl ether (50 mL) was added. After stirring overnight at room temperature under argon, a saturated ammonium chloride solution was added (100 mL) and the organic layer was removed. The aqueous layer was extracted with diethyl ether (2×60 mL). The combined organic layers were filtered, washed with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent the residue was chromatographed through silica gel (hexane/EtOAc 30:1 then 5:1), obtaining **10**[32] (1.28 g, 65%) as a room temperature melting point solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.43 (dd, 1H, J=7.7, 1.6 Hz), 7.18 (dt, 1H, J=7.7, 1.6 Hz), 6.98 (m, 2H), 6.82 (dd, 1H, J=8.0, 1.0 Hz), 5.78 (dd, 1H, J=17.7, 1.4 Hz), 5.39 (dd, 1H, J=11.1, 1.3 Hz), 5.25 (s, 1H). IR (ATR): ν=3383, 3085, 1626, 1604, 1578, 1485, 1453, 1420, 1328, 1292, 1213, 1172, 1093, 994, 910, 839, 746 cm^{-1}.

4.2.6. Synthesis of 2-(3-(2-vinylphenoxy)propyl)isoindoline-1,3-dione (13)

2-Vinylphenol, **10** (1.016 g, 8.37 mmol) was dissolved in DMF (60 mL), and *N*-(3-bromopropyl)phtalimide, **12** (2.273 g, 8.31 mmol) and potassium carbonate (3.492 g, 25.0 mmol) were added. After stirring overnight at 60 °C under argon the solution was cooled and water (150 mL) was added. The white solid was filtered, washed three times with water, and dried under vacuum at 60 °C overnight (1.910 g, 75%). Mp 84–86 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.89–7.72 (m, 4H), 7.47 (dd, 1H, J=7.5, 1.7 Hz), 7.26–6.85 (m, 4H), 5.72 (dd, 1H, J=17.7, 1.5 Hz), 5.19 (dd, 1H, J=11.2, 1.5 Hz), 4.10 (t, 2H, J=6.0 Hz), 3.96 (t, 2H, J=7.0 Hz), 2.26 (quint, 2H, J=6.8 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=168.3, 155.8, 133.9, 132.1, 131.4, 128.7, 126.8, 126.4, 123.2, 120.8, 114.2, 111.9, 66.0, 35.5, 28.5. IR (ATR): ν=3060, 2943, 2871, 1711, 1596, 1393, 1369, 1243, 1144, 943, 710 cm^{-1}. MS: m/z=307 (M^+) (4), 188 (M^+−[C_8H_7O]) (100), 160 (M^+−[$C_8H_5NO_2$]) (86), 130 (19), 91 (19), 77 (15), 41 (13). Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57; N, 4.56. Found: C, 73.96; H, 5.63; N, 4.64.

4.2.7. Synthesis of 3-(2-vinylphenoxy)propan-1-amine (15)

Sodium borohydride 98% (0.305 g, 7.90 mmol) was added to a solution of **13** (0.495 g, 1.61 mmol) in a mixture of isopropanol (14.4 mL) and water (2.5 mL) at 50 °C and stirred overnight. Glacial acetic acid (2.5 mL) was added and the solution was heated to 80 °C for 24 h. After cooling to room temperature 1 M HCl was added until the pH was 1–2. Extractions with diethyl ether were performed (3×50 mL). The aqueous layer was basified until the pH was 9–10 with 2 M NaOH and extracted with diethyl ether (3×50 mL). These organic layers were combined, washed with water (15 mL), dried over anhydrous Na_2SO_4, and concentrated, the desired compound **15** being obtained as a white solid after 2 days under vacuum (0.210 g, 74%). Mp 61–64 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.47 (dd, 1H, J=7.7, 1.8 Hz), 7.25–6.85 (m, 4H), 5.74 (dd, 1H, J=17.9, 1.6 Hz),

5.25 (dd, 1H, J=11.1, 1.4 Hz), 4.07 (t, 2H, J=6.1 Hz), 2.94 (t, 2H, J=6.8 Hz), 1.96 (quint, 2H, J=6.2 Hz), 1.43 (s, 2H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=155.8, 131.4, 128.6, 126.6, 126.2, 120.4, 114.0, 111.6, 65.9, 39.1, 32.9. MS: m/z=177 (M^+) (11), 120 ($M^+-[C_3H_7N]$) (31), 91 (59), 77(15), 70 (10), 65 (21), 58 (86), 56 (100), 51 (11), 41 (25). HRMS: m/z=177.1148 (calcd for $C_{11}H_{15}NO$: 177.1154).

4.2.8. Synthesis of 1-(3-(triethoxysilyl)propyl)-3-(3-(2-vinylphenoxy)propyl)urea (**17**)

Freshly distilled 3-(triethoxysilyl)propyl isocyanate (220 μL, 0.99 g/mL, 0.88 mmol) was added dropwise via syringe under argon to **15** (0.161 g, 0.88 mmol) in anhydrous THF (2 mL). The mixture was stirred under argon at room temperature for 1 h (^{1}H NMR monitoring). It was filtered under N_2 and the solvent was evaporated, the desired compound **17** being obtained as a white solid (0.363 mg, 96%). The compound was not very stable and it was used immediately for the next step. ^{1}H NMR (250 MHz, $CDCl_3$) δ=7.60 (dd, 1H, J=7.7, 1.7 Hz), 7.25–7.18 (m, 1H), 7.10–6.84 (m, 3H), 5.74 (dd, 1H, J=17.7, 1.5 Hz), 5.26 (dd, 1H, J=11.2, 1.7 Hz), 4.77 (t, 1H, J=5.7 Hz), 4.60 (t, 1H, J=5.7 Hz), 4.06 (t, 2H, J=5.7 Hz), 3.80 (q, 6H, J=7.0 Hz), 3.39 (q, 2H, J=6.35 Hz), 3.12 (q, 2H, J=6.8 Hz), 2.01 (quint, 2H, J=6.2 Hz), 1.58 (quint, 2H, J=7.3 Hz), 1.21 (t, 9H, J=6.9 Hz), 0.61 (t, 2H, J=8.4 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=158.0, 155.5, 131.5, 128.7, 126.5, 126.3, 120.6, 114.3, 111.6, 66.1, 58.1, 42.7, 37.8, 29.5, 23.3, 18.0, 7.3. IR (ATR): ν=3321, 2973, 2925, 2879, 1623, 1578, 1487, 1454, 1389, 1242, 1074, 951, 746 cm^{-1}.

4.2.9. Synthesis of 4-nitro-2-vinylphenol (**11**)

Potassium *tert*-butoxide (3.050 g, 26.6 mmol) was added over a suspension of Ph_3PCH_3I (5.204 g, 12.9 mmol) in anhydrous THF (40 mL) at 0 °C. The mixture was stirred for 30 min and then a solution of 2-hydroxy-5-nitrobenzaldehyde, **9** (2.054 g, 12.2 mmol) in anhydrous THF (20 mL) was added. After stirring at room temperature under argon for 4 h a saturated ammonium chloride solution was added (70 mL) and the organic layer was separated and mixed with water (70 mL) and diethyl ether (70 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (2×60 mL). The combined organic layers were washed with water (50 mL), then with brine (50 mL) and dried over anhydrous Na_2SO_4. After removing of the solvent the residue was chromatographed through silica gel (hexane/EtOAc 3:1), obtaining **11**[33] (1.48 g, 74%) as an orange solid. Mp 78–80 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ=8.31 (d, 1H, J=2.7 Hz), 8.06 (dd, 1H, J=8.9, 2.7 Hz), 6.90 (d, 1H, J=8.9 Hz), 6.92 (dd, 1H, J=17.7, 11.2 Hz), 6.08 (s, 1H), 5.88 (dd, 1H, J=17.7, 0.8 Hz), 5.53 (dd, 1H, J=11.2, 0.8 Hz).

4.2.10. Synthesis of 2-(3-(4-nitro-2-vinylphenoxy)propyl)-isoindoline-1,3-dione (**14**)

4-Nitro-2-vinylphenol, **11** (2.000 g, 11.62 mmol) and *N*-(3-bromopropyl)phtalimide, **12** (3.176 g, 11.61 mmol) were dissolved in anhydrous DMF (85 mL), and potassium carbonate (6.729 g, 48.2 mmol) was added. After stirring at room temperature under argon for 4 days water (200 mL) was added. The solid formed was filtered, washed three times with water, and chromatographed through silica gel (hexane/EtOAc 5:1, then 1:1, EtOAc) (1.910 g, 75%), the desired compound **14** being obtained as a pale yellow solid (3.166 g, 77%). Mp 174–175 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ=8.30 (d, 1H, J=2.7 Hz), 8.10 (dd, 1H, J=9.0, 2.8 Hz), 7.81–7.69 (m, 4H), 6.95–6.84 (m, 2H), 5.79 (dd, 1H, J=17.5, 1.0 Hz), 5.28 (dd, 1H, J=11.1, 1.0 Hz), 4.17 (t, 2H, J=5.8 Hz), 3.93 (t, 2H, J=6.7 Hz), 2.27 (quint, 2H, J=6.2 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=168.0, 160.1, 141.3, 133.8, 131.8, 129.2, 127.2, 124.3, 123.0, 121.8, 116.8, 110.8, 66.5, 34.9, 28.0. IR (ATR): ν=3089, 2952, 1706, 1501, 1373, 1329, 1273, 1244, 1137, 1085, 1057, 1026, 937, 831, 717 cm^{-1}. MS: m/z=352 (M^+) (17), 188 (100), 160 (96), 130 (28), 41 (18). Anal. Calcd for $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58; N, 7.95. Found: C, 64.24; H, 4.54; N, 7.84.

4.2.11. Synthesis of 3-(4-nitro-2-vinylphenoxy)propan-1-amine (**16**)

Sodium borohydride (0.152 g, 3.94 mmol) was added to a solution of **14** (0.297 g, 0.84 mmol) in a stirred mixture of isopropanol (7.5 mL) and water (1.2 mL) at 60 °C, the reaction being monitored by TLC (hexane/EtOAc 1:1). After 1 h glacial acetic acid (1 mL) was added and the solution was heated to 80 °C overnight. After cooling to room temperature 1 M HCl was added until the pH was 1–2. Extractions with diethyl ether were performed (2×25 mL). The aqueous layer was basified until the pH was 11–12 with NH_4OH and extracted with diethyl ether (3×50 mL). These organic layers were combined, washed with water, then with brine, dried over anhydrous Na_2SO_4, and concentrated, the desired compound **16** being obtained as an orange oil (0.143 g, 76%). The compound was not very stable and it was used immediately for the next step. ^{1}H NMR (250 MHz, $CDCl_3$) δ=8.35 (d, 1H, J=2.8 Hz), 8.13 (dd, 1H, J=9.0, 2.8 Hz), 6.99 (dd, 1H, J=17.6, 11.0 Hz), 6.93 (d, 1H, J=9.2 Hz), 5.87 (dd, 1H, J=17.8, 1 Hz), 5.41 (dd, 1H, J=11.2, 1 Hz), 4.20 (t, 2H, J=6.2 Hz), 2.95 (t, 2H, 6.7 Hz), 2.01 (quint, 2H, J=6.7 Hz).

4.2.12. Synthesis of 1-(3-(4-nitro-2-vinylphenoxy)propyl)-3-(3-(triethoxysilyl)propyl)urea (**18**)

Freshly distilled 3-(triethoxysilyl)propyl isocyanate (217 μL, 0.99 g/mL, 0.87 mmol) was added dropwise via syringe under argon to **14** (0.193 g, 0.87 mmol) and the mixture was stirred at room temperature under argon. After 4 h the solid formed was dissolved in anhydrous dichloromethane, filtered under N_2, and the solvent was evaporated, the desired compound **18** being obtained as an orange solid (0.229 g, 70%). The compound was not very stable and it was used immediately for the next step. ^{1}H NMR (250 MHz, $CDCl_3$) δ=8.32 (d, 1H, J=2.7 Hz), 8.11 (dd, 1H, J=9.0, 2.7 Hz), 6.98 (dd, 1H, J=18.0, 11.3 Hz), 6.91 (d, 1H, J=9.0 Hz), 5.86 (d, 1H, J=17.7 Hz), 5.42 (d, 1H, J=11.0 Hz), 4.61 (t ample, 1H), 4.54 (t ample, 1H), 4.15 (t, 2H, J=6.0 Hz), 3.80 (q, 6H, J=7.0 Hz), 3.40 (q, 2H, J=6.2 Hz), 3.14 (q, 2H, J=6.3 Hz), 2.07 (quint, 2H, J=6.3 Hz), 1.60 (quint, 2H, J=7.85 Hz), 1.21 (t, 9H, J=6.8 Hz), 0.62 (t, 2H, J=8.3 Hz). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ=160.3, 157.9, 141.2, 129.5, 127.2, 124.4, 121.9, 117.1, 110.9, 66.6, 58.2, 42.6, 37.2, 29.5, 23.3, 18.1, 7.3.

4.3. Preparation of hybrid materials

4.3.1. Preparation of hybrid material ***M1***

A solution of ammonium fluoride (30 μL of a 1 M solution, 0.030 mmol of fluoride, 1.67 mmol of water) and distilled and deionized water (0.212 mL, 11.8 mmol) in anhydrous ethanol (3 mL) was added to a solution of **8** (213.3 mg, 0.501 mmol) and TEOS (523 mg, 2.51 mmol) in anhydrous ethanol (3 mL). The mixture was manually stirred for a minute to get a homogeneous solution and was left at room temperature without stirring. Gelation occurred after few minutes and the gel was allowed to age for 2 days, after which it was powdered and washed successively several times with water and then with ethanol. The solid was dried under vacuum (1 mmHg, rt, overnight), yielding **M1** as a white powder (0.288 g). S_{BET}: 8 m^2/g; ^{29}Si CP-MAS NMR: δ=−57.0 (T^2), −64.8 (T^3), −90.6 (Q^2), −100.8 (Q^3), −110.2 (Q^4). Elemental analysis found: C, 25.73; N, 2.16.

4.3.2. Preparation of hybrid material ***M2***

Ammonium fluoride (0.2 mL of a 1 M solution, 0.2 mmol of fluoride, 11.1 mmol of water) and distilled and deionized water (1.0 mL, 55.6 mmol) were added to a solution of **8** (217.2 mg, 0.510 mmol) and TEOS (4.16 g, 20.0 mmol) in anhydrous ethanol (10 mL). The mixture was manually stirred for a minute to get a homogeneous solution and was left at room temperature without stirring. Gelation occurred after few minutes and the gel was allowed to age for 5 days, after which it was powdered and washed successively several times with water and then with ethanol. The

solid was dried under vacuum (1 mmHg, 70 °C, overnight), yielding **M2** as a white powder (1.54 g). S_{BET}: 682 m^2/g; ^{29}Si CP-MAS NMR: δ=−65.0 (T^3), −91.4 (Q^2), −100.2 (Q^3), −109.1 (Q^4). Elemental analysis found: C, 9.57; N, 0.45.

*4.3.3. Preparation of hybrid material **M3***

Activated silica gel (silica gel ultrapure, 60–200 μm, 60 Å, ref: 36006 ACROS, 2.637 g, 43.9 mmol SiO_2) was added to a solution of **8** (0.654 g, 1.54 mmol) in toluene (30 mL). The mixture was refluxed for 24 h. The solid was filtered and washed successively with toluene (four times), ethyl acetate (four times), and dichloromethane (four times), then it was placed in a Soxhlet and extracted with acetone overnight, filtered, washed with acetone, and dried, yielding **M3** as a white powder (2.772 g). S_{BET}: 293 m^2/g; ^{29}Si CP-MAS NMR: δ=−56.6 (T^2), −101.0 (Q^3), −109.8 (Q^4). Elemental analysis found: C, 7.65; H, 1.36; N, 0.57; Si, 36.4.

*4.3.4. Preparation of hybrid material **M4***

Mesostructured MCM-41 (0.699 g, 11.65 mmol SiO_2) was added to a solution of **8** (0.124 g, 0.291 mmol) in toluene (20 mL). The mixture was refluxed for 24 h with a Dean–Stark apparatus. The solid was filtered and washed successively with toluene (three times), ethanol (once), and acetone (four times), and it was dried under vacuum overnight at 60 °C, yielding **M4** as a white powder (0.711 g). S_{BET}: 773 m^2/g; IR (KBr): ν=3392, 1699, 1072, 953, 796, 457 cm^{-1}; ^{29}Si CP-MAS NMR: δ=−51.4 (T^2), −92.3 (Q^2), −100.8 (Q^3), −109.5 (Q^4). ^{13}C CP-MAS NMR: δ=158.0, 131.9, 129.0, 126.5, 113.9, 59.0, 29.2, 16.0. Elemental analysis found: C, 11.12; N, 0.50.

*4.3.5. Preparation of hybrid material **M5***

Ammonium fluoride (77 μL of a 1 M solution, 77 μmol of fluoride, 4.3 mmol of water) and distilled and deionized water (0.48 mL, 26.7 mmol) were added to a solution of **17** (79.8 mg, 0.188 mmol) and TEOS (1.571 g, 7.54 mmol) in anhydrous ethanol (4.7 mL). The mixture was manually stirred for a minute to get a homogeneous solution and was left at room temperature without stirring. Gelation occurred after few minutes and the gel was allowed to age for 4 days, after which it was powdered and washed successively several times with water and then with ethanol. The solid was dried in air, yielding **M5** as a white powder (549 mg). S_{BET}: 529 m^2/g; ^{29}Si CP-MAS NMR: δ=−64.0 (T^3), −91.9 (Q^2), −101.2 (Q^3), −109.6 (Q^4). Elemental analysis found: N, 0.58.

*4.3.6. Preparation of hybrid material **M6***

A solution of dodecylamine (0.20 g, 1.08 mmol) in ethanol (5 mL) was added to distilled and deionized water (15 mL) and stirred for 30 min. Compound **17** (0.106 g, 0.25 mmol) and TEOS (2.06 g, 9.89 mmol) were added. The mixture was stirred at room temperature for 24 h. The formed solid was filtered and left to dry in air overnight. Then it was powdered and extracted with ethanol in a Soxhlet for 48 h. The solid was washed with ethanol and dried at atmospheric pressure, yielding **M6** as a white powder (0.552 g). S_{BET}: 760 m^2/g; ^{29}Si CP-MAS NMR: δ=−63.4 (T^3), −101.8 (Q^3), −110.4 (Q^4). Elemental analysis found: N, 0.62.

*4.3.7. Preparation of hybrid material **M7***

Miristyltrimethylammonium bromide (0.39 g, 1.15 mmol) was dissolved in ethanol (17 mL), HCl 37% (7.5 mL) was added and the mixture was stirred for 1 h. Compound **17** (0.10 g, 0.24 mmol) and TEOS (1.988 g, 9.54 mmol) in ethanol (2 mL) were added and the mixture was stirred at room temperature for 2 days. The formed solid was filtered and washed with water until neutral pH, then with ethanol. The solid was stirred for 24 h in a solution containing 8 mL concentrated HCl in 150 mL methanol, then it was filtered and washed several times with methanol, and dried in air, yielding **M7** (627 mg) as a white powder. S_{BET}: 659 m^2/g; ^{29}Si CP-MAS NMR: δ=−64.2 (T^3), −91.3 (Q^2), −100.8 (Q^3), −109.5 (Q^4). Elemental analysis found: N, 0.57.

*4.3.8. Preparation of hybrid material **M8***

A solution of dodecylamine (0.402 g, 2.17 mmol) in ethanol (10 mL) was added to distilled and deionized water (30 mL) and stirred for 30 min. Compound **18** (0.116 g, 0.25 mmol) and TEOS (2.064 g, 9.91 mmol) in anhydrous DMF (3.5 mL) were added. The mixture was stirred at room temperature for 24 h. The formed solid was filtered and washed three times with ethanol. Then it was powdered and extracted with ethanol in a Soxhlet for 48 h. The solid was filtered, washed several times with ethanol, and dried under vacuum (1 mmHg, 60 °C, overnight), yielding **M8** as a slightly orange powder (0.690 g). S_{BET}: 1163 m^2/g; ^{29}Si CP-MAS NMR: δ=−64.8 (T^3), −101.5 (Q^3), −109.5 (Q^4). Elemental analysis found: C, 11.82; H, 2.24; N, 1.11.

4.4. Preparation of catalysts from hybrid materials

*4.4.1. Preparation of hybrid catalyst **C1A***

Anhydrous and degassed dichloromethane (20 mL) was added under argon to **M1** (120.9 mg, 1.56 mmol N/g, 0.189 mmol) and **1A** (172.8 mg, 0.210 mmol, 1.1 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 5 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C1A** as a brown powder (94.1 mg). Elemental analysis found: C, 25.35; H, 3.48; N, 2.39; Si, 29.3; Ru (ICP), 0.54.

*4.4.2. Preparation of hybrid catalyst **C3A***

Anhydrous and degassed dichloromethane (20 mL) was added under argon to **M3** (0.760 g, 0.407 mmol N/g, 0.309 mmol) and **1A** (0.309 g, 0.375 mmol, 1.2 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 5 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C3A** as a brown powder (0.818 g). Elemental analysis found: C, 10.86; H, 1.86; N, 0.58; Si, 34.4; Ru (ICP), 1.17.

*4.4.3. Preparation of hybrid catalyst **C1B***

Anhydrous and degassed dichloromethane (14 mL) was added under argon to **M1** (172.4 mg, 1.55 mmol N/g, 0.267 mmol) and **1B** (111.3 mg, 0.131 mmol, 0.49 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C1B** as a green powder (163.4 mg). Elemental analysis found: C, 24.13; H, 2.72; N, 2.11; Ru (ICP), 0.60.

*4.4.4. Preparation of hybrid catalyst **C2B***

Anhydrous and degassed dichloromethane (18 mL) was added under argon to **M2** (502 mg, 0.325 mmol N/g, 0.163 mmol) and **1B** (145 mg, 0.171 mmol, 1.05 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C2B** as a green powder (500.8 mg). Elemental analysis found: C, 14.70; H, 2.06; N, 0.97; Ru (ICP), 1.75.

*4.4.5. Preparation of hybrid catalyst **C3B***

Anhydrous and degassed dichloromethane (10 mL) was added under argon to **M3** (0.351 g, 0.407 mmol N/g, 0.142 mmol) and **1B** (0.122 g, 0.139 mmol, 0.96 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt,

overnight) to obtain **C3B** as a green powder (0.400 g). Elemental analysis found: C, 10.98; H, 1.69; N, 1.02; Si, 33.4; Ru (ICP), 1.20.

*4.4.6. Preparation of hybrid catalyst **C4B***

Anhydrous and degassed dichloromethane (13 mL) was added under argon to **M4** (305.2 mg, 0.361 mmol N/g, 0.1102 mmol) and **1B** (101.7 mg, 0.1212 mmol, 1.1 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C4B** as a green powder (291.8 mg). Elemental analysis found: C, 13.78; H, 2.44; N, 1.02; Ru (ICP), 1.32.

*4.4.7. Preparation of hybrid catalyst **C5B***

Anhydrous and degassed dichloromethane (6.7 mL) was added under argon to **M5** (323.8 mg, 0.414 mmol N/g, 0.067 mmol) and **1B** (62.4 mg, 0.073 mmol, 1.1 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 7 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C5B** as a green powder (283.7 mg). Elemental analysis found: Ru (ICP), 1.20.

*4.4.8. Preparation of hybrid catalyst **C6B***

Anhydrous and degassed dichloromethane (7.3 mL) was added under argon to **M6** (329.8 mg, 0.443 mmol N/g, 0.0729 mmol) and **1B** (65.0 mg, 0.0766 mmol, 1.05 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 7 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C6B** as a green powder (326.8 mg). Elemental analysis found: Ru (ICP), 1.29.

*4.4.9. Preparation of hybrid catalyst **C7B***

Anhydrous and degassed dichloromethane (7.3 mL) was added under argon to **M7** (359.6 mg, 0.407 mmol N/g, 0.0733 mmol) and **1B** (69.9 mg, 0.082 mmol, 1.1 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 7 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C7B** as a green powder (315.9 mg). Elemental analysis found: Ru (ICP), 0.68.

*4.4.10. Preparation of hybrid catalyst **C8B***

Anhydrous and degassed dichloromethane (11 mL) was added under argon to **M8** (349.9 mg, 0.796 mmol N/g, 0.0927 mmol) and **1B** (86.5 mg, 0.102 mmol, 1.1 equiv) and the mixture was refluxed under argon overnight. The solid was filtered, washed several times with portions of 10 mL of anhydrous dichloromethane until the filtrate had no color, and dried under vacuum (1 mmHg, rt, overnight) to obtain **C8B** as a brown powder (355.9 mg). Elemental analysis found: C, 16.30; H, 2.81; N, 1.47; Ru (ICP), 1.36.

4.5. Ring-closing metathesis reactions on *N*,*N*-diallyl-4-methylbenzenesulfonamide, 19, with supported catalysts C1B–C8B. Synthesis of 1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole, 20. Typical experimental procedure

A solution of **19** (0.0754 g, 0.300 mmol) in anhydrous and degassed dichloromethane (6 mL) was added under nitrogen to **C8B** (0.0777 g, 0.135 mmol Ru/g, 0.0105 mmol Ru) and the mixture was stirred under argon at room temperature for 45 min (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed four times with 6 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **20**[24] (0.064 g, the molar ratio **20**/**19** by ^{1}H NMR was 85.7:1, >98% conversion). The solid catalyst **C8B** was dried and reused in the next run. The same conditions were adopted for other catalysts except the reaction times that are summarized in Tables 3 and 4 together with the attained conversions.

4.6. Ring-closing metathesis reactions on *N*-allyl-*N*-2-methylallyl-4-methylbenzenesulfonamide, 21, with supported catalysts C1B–C8B. Synthesis of 3-methyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole, 22. Typical experimental procedure

A solution of **21** (0.0798 g, 0.301 mmol) in anhydrous and degassed dichloromethane (6 mL) was added under nitrogen to **C8B** (0.0779 g, 0.135 mmol Ru/g, 0.0105 mmol Ru) and the mixture was stirred under argon at room temperature for 1.5 h (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed four times with 6 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **22**[34] (0.0709 g, the molar ratio **22**/**21** by ^{1}H NMR was 74.3:1, >98% conversion). The solid catalyst **C8B** was dried and reused in the next run. The same conditions were adopted for other catalysts except the reaction times that are summarized in Table 5 together with the attained conversions.

4.7. Ring-closing metathesis reactions on *N*,*N*-bis-(2-methylallyl)-4-methylbenzenesulfonamide, 23, with supported catalysts C1B–C8B. Synthesis of 3,4-dimethyl-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole, 24. Typical experimental procedure

A solution of **23** (0.0754 g, 0.270 mmol) in anhydrous and degassed toluene (6 mL) was added under nitrogen to **C8B** (0.0699 g, 0.135 mmol Ru/g, 0.00944 mmol Ru) and the mixture was stirred under argon at 80 °C for 24 h (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed four times with 6 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **24** (0.0634 g, the molar ratio **24**/**23** by ^{1}H NMR was 2.86:1, 74% conversion). ^{1}H and ^{13}C NMR of **24** were coincident with that described for this compound in the literature.[35] The same conditions were adopted for other catalysts except the reaction time (see Table 6).

4.8. Ring-closing metathesis reactions on 1-allyloxy-1,1-diphenyl-2-propyne, 25, with supported catalysts C1B–C8B. Synthesis of 2,2-diphenyl-3-vinyl-2,5-dihydrofuran, 26. Typical experimental procedure

A solution of **25** (0.0756 g, 0.304 mmol) in anhydrous and degassed dichloromethane (6 mL) was added under nitrogen to **C8B** (0.0788 g, 0.135 mmol Ru/g, 0.0106 mmol Ru) and the mixture was stirred under argon at room temperature for 1.3 h (GC monitoring). The mixture was filtered under nitrogen atmosphere with a cannula and the solid was washed four times with 6 mL portions of anhydrous dichloromethane. The combined filtrates were evaporated to yield **26** (0.0646 g, the molar ratio **26**/**25** by ^{1}H NMR was 103:1, >98% conversion), whose spectroscopic data were coincident with that reported in the literature.[26] The solid catalyst **C8B** was dried and reused in the next run. The same conditions were adopted for other catalysts except the reaction times (see Table 7).

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