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Sol–gel immobilized aryl iodides for the catalytic oxidative α-tosyloxylation of ketones

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ABSTRACT

New hybrid silica materials **M1–M4**, derived from mono and bis-silylated aryl iodides, have been prepared via sol–gel processes, either by the hydrolytic polycondensation of a bis-silylated monomer or by the co-gelification of a monosilylated precursor with tetraethylorthosilicate. They have been fully characterized by elemental analysis, ^{13}C and ^{29}Si CP-MAS solid state NMR, IR, TGA, and nitrogen-sorption measurements. These organosilicas have been successfully applied as supported catalysts in the α-tosyloxylation of aliphatic ketones in the presence of *m*-chloroperbenzoic acid (*m*-CPBA) as an oxidant, with the corresponding α-tosyloxyketones obtained in moderate to good isolated yields. The recyclability of the supported catalysts by a simple filtration has also been investigated.

1. Introduction

Oxidative C—H functionalization at the α position of carbonyl compounds to form new C—O bonds is an attractive transformation that provides rapid access to α-hydroxycarbonyl building blocks. Among other methods, the use of hypervalent organoiodine(III) reagents such as the Koser reagent, PhI(OH)(OTs), has proven especially effective for introducing the —OTs group at this position [1]. Indeed, the synthetic use of hypervalent organoiodanes has become a hot topic in the last two decades due to their unique reactivity beyond that of a simple oxidant. In addition, the use of a hypervalent iodine reagent may, in a number of cases, obviate the need for a metal additive, a particularly attractive feature in pharmaceutical chemistry.

In processes employing hypervalent iodine, the iodoarene side-product may, in principle, be easily removed at the end of the reaction [2,3] and could, once again, be converted to a hypervalent iodane through a simple oxidation. Interestingly, several recent publications describe a modification of this process, whereby catalytic quantities of the aryl iodides are used in the presence of a cheaper terminal oxidant, which ensures the *in situ* regeneration of the organoiodine(III) reagent [4]. This budding area of research was recently the subject of two minireviews [5,6]. In particular, following a 2005 publication by Ochiai and coworkers on the PhI-catalyzed α-acetoxylation of ketones [7], Yamamoto and Togo recently reported that iodobenzene also catalyzes the oxidative α-tosyloxylation of ketones (as illustrated in Scheme 1) under mild conditions using *m*-CPBA as an oxidant [8–10], with promising results achieved at 10 mol% of iodobenzene [8]. The authors also tested polystyrene-supported iodoarenes [9,10] as potentially recyclable heterogeneous catalysts. It should be noted that polymer-supported iodobenzene had also previously been used in the same laboratory for the preparation of a polymeric Koser reagent [11]. However, in most cases, although recovery and reuse in a second cycle was indeed possible, considerable amounts of the material (>0.5 equiv of ArI) were necessary to achieve moderate yields of the α-tosyloxylated ketones. In addition to polymer-based systems, ionic liquid-supported iodobenzene had also been suggested by the same group in 2007 for use as a homogeneous recyclable catalyst [12].

In search of a more efficient recyclable iodoarene, a hybrid silica gel-based iodoarene was considered. The formation of hybrid silica materials or organosilicas is an attractive strategy for the immobilization of organocatalysts, since such materials combine the advantages of a silica matrix, such as thermal and mechanical stability and chemical inertness, with the reactivity of an embedded organic precursor [13–16]. Bridged silsesquioxanes [17,18] represent an interesting class of organosilicas, obtained by the sol–gel hydrolysis-condensation of monomers containing a variable organic bridging fragment previously decorated with two or more trialkoxysilyl groups. These materials feature inherently high homogeneity and permit high loading of organic units, the

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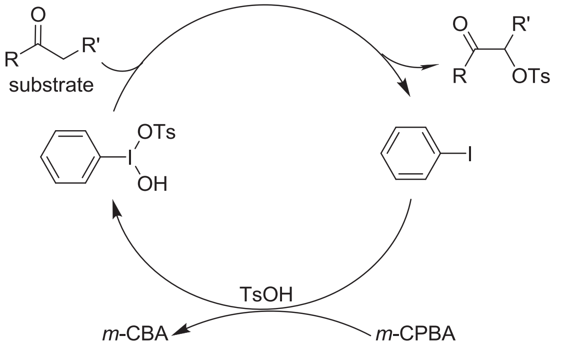


Scheme 1. Catalytic cycle for PhI-catalyzed α-tosyloxylation of ketones.

inorganic network being built directly around the organic moieties. Although the resulting catalytic systems often suffer from low porosity and, thus, low surface areas, some recent reports demonstrate excellent catalytic properties of such catalysts in different organic transformations [19–23]. While two or more pendant $Si(OR)_3$ functional groups may allow for direct condensation, related hybrid silica can also be prepared from singly silylated precursors by their sol–gel co-gelification with tetraethyl orthosilicate (TEOS) [24,25]. Regardless of the strategy employed in the sol–gel formation, when applied as a catalyst, the supported hybrid silica can easily be separated from the reaction mixture by a simple filtration. The recovered material can then be reused, an economically and environmentally relevant factor.

Following our interest in recyclable catalysts based on hybrid silica materials [20–23,26–31], we present herein our results on the synthesis and characterization of silica-immobilized iodoarenes prepared by the sol–gel methodology and their catalytic performance in the oxidative α-tosyloxylation of ketones using *m*-CPBA as a stoichiometric oxidant.

2. Experimental

2.1. Reagents and methods

When required, experiments were carried out using standard high vacuum and Schlenk techniques. Solvents were dried, distilled and degassed shortly before use following standard procedures. Ethanol was distilled from Mg/I_2. Tetraethyl orthosilicate (TEOS) 98%, tetrabutylammonium fluoride (1 M solution in anhydrous THF), *m*-chloroperbenzoic acid (*m*-CPBA) (approximately 65% purity), methanesulfonic acid (99% purity) and camphorsulfonic acid (99% purity) were purchased from Aldrich and used without any further treatment; *p*-toluenesulfonic acid (p-TsOH·H_2O) (98% purity) was purchased from Panreac and used as received. The silica gel for flash chromatography was a Macherey–Nagel GmbH & Co. KG silica gel with a particle size of 230–400 mesh and a pore volume of 0.9 mL/g. The silica gel used for purifying moisture-sensitive organosilanes was dried under a nitrogen flow using a heat gun just before use.

2.2. Physicochemical characterization

IR data were obtained on a Bruker Tensor 27 with an ATR Golden Gate. Liquid ^1H and ^{13}C NMR spectra were recorded on Bruker DRX-250 MHz, DPX-360 MHz and AVANCE III 400 MHz instruments, and CP-MAS ^{29}Si solid state NMR spectra were recorded on a Bruker AV400WB. All NMR experiments were performed at the *Servei de Ressonància Magnètica Nuclear* of the *Universitat Autònoma de Barcelona*. ^1H NMR chemical shifts (δ, ppm) are referenced to the residual *protio* signal of the deuterated solvent, and the ^{13}C shifts are referenced to the ^{13}C resonance of the solvent. N_2-sorption isotherms were obtained on a Micromeritics ASAP2020 analyzer at the *Institut Charles Gerhardt in Montpellier* after degassing the materials at 55 °C for 30 h under high vacuum. The surface areas and pore size distributions were calculated from the desorption branch by the Brunauer-Emmett-Teller (BET) transform and the Barrett–Joyner–Halenda (BJH) method, respectively. High resolution mass spectra were determined at the *Servei d'Anàlisi Química* of the *Universitat Autònoma de Barcelona* using a Bruker Daltonic MicroTOFQ spectrometer (Bremen, Gemany) equipped with an ESI inlet. Elemental analyses were performed at the *Serveis Científico-Tècnics* of the *Universitat de Barcelona*, and the Si content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a multichannel Perkin Elmer model Optima 3200 RL spectrometer under standard conditions. The iodine analysis was performed by combustion of the sample in an oxygen bomb (Calorimeter IKA 5012). The formed gases were absorbed by a 0.25 M sodium hydroxide aqueous solution. The bomb was rinsed twice with deionized water that was collected and added to the sodium hydroxide aqueous solution. The combined solution was diluted to an exact volume in a volumetric flask and analyzed by HPLC (Waters 2690 model equipped with a Waters 996 photodiode array detector, IC-Pak Anion HR column). The corresponding peak was interpreted based on the calibration curve obtained from standard sodium iodide aqueous solutions. TGA analyses were performed under an argon atmosphere at the *Institut de Ciència dels Materials de Barcelona* using a NETZSCH STA 449 F1 instrument (TGA/DSC).

2.3. Synthesis of silylated precursors

2.3.1. Preparation of (3-iodopropyl)triethoxysilane

This compound was prepared following a described procedure [32]. A mixture of NaI (13.48 g, 89.9 mmol), (3-chloropropyl)triethoxysilane (15.0 mL, 1.00 g/mL, 62.3 mmol) and anhydrous acetone (50 mL) was stirred under reflux for 2 days under an argon atmosphere. At this point, the mixture was filtered and the solvent from the filtrate was evaporated under reduced pressure. The residue was triturated with dry hexane (30 mL) and once again filtered. After removal of hexane from the filtrate, the (3-iodopropyl)triethoxysilane was obtained as a pale yellow liquid; yield: 18.63 g (90%). ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 3.82 (q, *J* = 7.0 Hz, 6 H, OCH_2), 3.22 (t, *J* = 7.0 Hz, 2 H, —CH_2I), 1.99–1.87 (m, 2 H, ICH_2CH_2), 1.23 (t, *J* = 7.0 Hz, 9 H, CH_3), 0.79–0.66 (m, 2 H, $SiCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 58.8, 27.8, 18.6, 12.6, 11.1. IR (ATR) ν (cm^{-1}): 2972, 2884, 1073, 784, 629.

2.3.2. Preparation of 1-iodo-3, 5-dimethoxybenzene *1*

This compound was prepared following a described procedure [33]. To a stirred solution of 3,5-dimethoxyaniline (9.15 g, 59.7 mmol) in water (100 mL) maintained at −5 °C, concentrated H_2SO_4 (9 mL) was added dropwise, followed by the addition of a solution of $NaNO_2$ (4.85 g, 70.3 mmol) in water (20 mL). Keeping the temperature below 0 °C, the reaction mixture was stirred for 20 min, then diethyl ether was added (50 mL), followed by a dropwise addition of a solution of potassium iodide (30 g, 180.7 mmol) in water (30 mL). After the mixture was stirred at room temperature for 6 h, the layers were separated and the aqueous phase was extracted with additional diethyl ether (3 × 100 mL). The combined organic fraction was washed successively with 25% (w/v) aqueous $Na_2S_2O_3·5H_2O$ (3 × 50 mL), 1 M HCl (1 × 100 mL) and 2 M NaOH (1 × 100 mL), then dried over anhydrous $MgSO_4$, filtered and concentrated to a brown oil. The crude mixture was purified by silica gel chromatography using hexane/ethyl acetate 95:5 (R_f = 0.56) as the eluent to yield 1-iodo-3,5-dimethoxybenzene, **1**, as a white solid; yield: 11.76 g (75%). ^1H NMR (250 MHz, $CDCl_3$)

δ (ppm): 6.85 (d, *J* = 2.2 Hz, 2 H, *o*-ArH), 6.40 (t, *J* = 2.2 Hz, 1 H, *p*-ArH), 3.76 (s, 6 H, Me). ^{13}C NMR (62.50 MHz, $CDCl_3$) δ (ppm): 164.4, 116.1, 100.9, 94.4, 55.8. IR (ATR) *ν* (cm^{-1}): 3069, 1258, 1026, 1050, 615.

2.3.3. Preparation of 5-iodoresorcinol **2**

This compound was prepared following a described procedure [33]. A mixture of 1-iodo-3,5-dimethoxybenzene (**1**) (6.60 g, 25.0 mmol) and hydroiodic acid (45 wt.%, 60 mL) was heated to reflux for 40 h. The solution was then cooled to room temperature and diluted with water (deionized, 80 mL) and diethyl ether (80 mL). The organic layer was separated and washed successively with 1 M sodium thiosulfate (3 × 60 mL) and distilled water (1 × 50 mL). The solution was dried with anhydrous $MgSO_4$, and the solvent was evaporated to afford an oil that spontaneously solidified at room temperature to give **2** as a white solid; yield: 5.84 g (99%). ^{1}H NMR (360 MHz, DMSO-d_6) δ (ppm): 9.52 (s, 2 H), 6.57 (d, *J* = 1.8 Hz, 2 H), 6.20 (br s, 1 H). ^{13}C NMR (90 MHz, DMSO-d_6) δ (ppm): 159.3, 115.3, 102.4, 94.6. IR (ATR) *ν* (cm^{-1}): 3254, 1383, 1215, 610.

2.3.4. Preparation of the bis-silylated iodoarene **3**

Dry acetone (20 mL) was added to a mixture of compound **2** (2.360 g, 10 mmol), K_2CO_3 (6.90 g, 50 mmol) and (3-iodopropyl)triethoxysilane (10.801 g, 32.5 mmol) under a nitrogen atmosphere. After refluxing for 27 h under nitrogen, the solvent was removed under reduced pressure and the residue was extracted with dry dichloromethane/hexane 1:4 (4 × 10 mL), filtering the resulting solution after each round of extraction. The volatile fraction was removed under vacuum to afford a colorless oily residue, which was purified by silica gel chromatography (hexane/ethyl acetate 25:1 as eluent). R_f = 0.22 (silica gel, hexane/ethyl acetate 95:5). Yield of **3**: 1.93 g, 30%. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 6.83 (d, *J* = 2.1 Hz, 2 H, *o*-ArH), 6.39 (m, 1 H, *p*-ArH), 3.93–3.77 (m, 16 H, —OCH_2), 1.88 (m, 4 H), 1.23 (t, *J* = 7.0 Hz, 18 H, —Me), 0.79 – 0.69 (m, 4 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 160.3, 116.0, 101.4, 93.6, 69.9, 58.1, 22.5, 18.1, 6.3. IR (ATR) *ν* (cm^{-1}): 2972, 2925, 2882, 1293, 1277, 1073, 628. HRMS (ESI): calculated for $[C_{24}H_{45}IO_8Si_2Na]^+$ (M^++Na): 667.1595; found: 667.1600.

2.3.5. Preparation of the monosilylated iodoarene **4**

Dry acetone (20 mL) was added to a mixture of 3-iodophenol (3.30 g, 15.0 mmol), K_2CO_3 (8.29 g, 60 mmol) and (3-iodopropyl)triethoxysilane (4.984 g, 15.0 mmol) under nitrogen atmosphere. The mixture was kept at reflux for 24 h under nitrogen. The organic solvent was evaporated under vacuum and the residue was extracted with dry hexane (4 × 10 mL), filtering the resulting solution after each round of extraction. The solvent was removed under reduced pressure to afford **4** as a colorless oil (2.10 g, 33% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.25–7.12 (m, 2 H), 6.98 (t, *J* = 8.2 Hz, 1 H), 6.85 (d, *J* = 7.1 Hz, 1 H), 3.96–3.71 (m, 8 H), 1.88 (m, 2 H), 1.23 (t, *J* = 7.0 Hz, 9 H), 0.78–0.72 (t, *J* = 7.1 Hz, 2 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 160.0, 131.0, 129.9, 124.0, 114.5, 94.7, 70.4, 58.7, 23.0, 18.6, 6.8. IR (ATR) *ν* (cm^{-1}): 2967, 2883, 1584, 1259, 1075, 1015, 632. HRMS (ESI): calculated for $[C_{15}H_{25}IO_4SiNa]^+$ (M^++Na): 447.0465; found: 447.0467.

2.4. Preparation and characterization of hybrid silica materials

2.4.1. Preparation and characterization of hybrid silica material **M1**

The bis-silylated compound **3** (1.665 g, 2.583 mmol) was dissolved in dry ethanol (1.8 mL). To this solution, a solution of Milli-Q water (0.28 mL, 15.49 mmol) and TBAF (30 μL, commercial 1 M in anhydrous THF) in dry EtOH (0.8 mL) was added. The final mixture was shaken vigorously for 10 s to obtain a homogenous solution and was then kept under static conditions. After 30 min, gelification was observed, and the material was aged at room temperature for 6 days. The resulting gel was pulverized, separated by filtration and washed successively with water (2 × 6 mL), EtOH (2 × 6 mL) and acetone (2 × 6 mL). The final solid was dried overnight at 55 °C under vacuum (2.0 mbar) to afford **M1** as a white solid (1.005 g). ^{13}C CP-MAS NMR (100.62 MHz) δ (ppm): 159.5, 118.2, 113.2, 99.9, 93.7, 68.9, 57.4, 22.2, 17.6, 7.7. ^{29}Si CP-MAS NMR (79.5 MHz) δ (ppm): −47.6 (T^0, 2%), -55.0 (T^1, 8%), −61.0 (T^2, 20%), −68.6 (T^3, 69%). IR (ATR) *ν* (cm^{-1}): 2929, 2880, 1590, 1567, 1433, 1260, 1014 (broad), 797, 676. BET surface area: <5 m^2/g; non-porous material. TGA: (argon, 20–700 °C) residual mass 47.9%. EA calculated for $C_{12}H_{15}ISi_2O_5$ (considering complete condensation): 34.13% C, 3.58% H, 13.30% Si, 30.05% I; found: 34.7% C, 4.5% H, 11.5% Si, 13.5% I.

2.4.2. Preparation and characterization of hybrid silica material **M2**

Bis-silylated compound **3** (0.410 g, 0.636 mmol) and TEOS (0.71 mL, ρ = 0.934 g/mL, 3.18 mmol) were dissolved in dry ethanol (3 mL). A solution of Milli-Q water (0.30 mL, 16.536 mmol) and TBAF (50 μL, commercial solution 1 M in anhydrous THF) in dry EtOH (0.80 mL) was then added to the first solution. The final mixture was shaken vigorously for 10 s to obtain a homogenous solution. After 10 min, a gel formed that was then aged at room temperature for 6 days. The resulting gel was pulverized, filtered and washed successively with water (2 × 6 mL), EtOH (2 × 6 mL) and acetone (2 × 6 mL). The final solid was dried overnight at 55 °C under vacuum (2.0 mbar) to afford **M2** as a white solid (0.410 g). ^{13}C CP-MAS NMR (100.62 MHz) δ (ppm): 160.7, 119.6, 101.7, 94.2, 69.8, 58.6, 22.8, 17.4, 8.5. ^{29}Si CP-MAS NMR (79.5 MHz) δ: −59.3 (T^2), −68.2 (T^3), −93.3 (Q^2), −102.3 (Q^3), −110.8 (Q^4). IR (ATR) *ν* (cm^{-1}): 2944, 1592, 1438, 1050, 800, 679. BET surface area: 255 m^2/g; pore volume: 0.838 cm^3/g. TGA: (argon, 20–700 °C) residual mass 59.8%. EA calculated for $C_{12}H_{15}ISi_2O_5 \cdot 5SiO_2$ (considering complete condensation): 19.94% C, 2.09% H, 27.20% Si, 17.56% I; found: 17.8% C, 2.1% H, 24.2% Si, 8.2% I.

2.4.3. Preparation and characterization of hybrid silica material **M3**

Monosilylated compound **4** (0.800 g, 1.887 mmol) and TEOS (2.10 mL, ρ = 0.934 g/mL, 9.4 mmol) were dissolved in dry ethanol (10 mL). Then, a solution of Milli-Q water (0.78 mL, 43.4 mmol) and TBAF (113 μL, commercial solution 1 M in anhydrous THF) in dry EtOH (1.3 mL) was added to the first solution. The final mixture was shaken vigorously for 10 s to obtain a homogenous solution. After 15 min, a gel formed that was then aged at room temperature for 6 days. The gel obtained was pulverized, filtered off and washed successively with water (2 × 6 mL), EtOH (2 × 6 mL) and acetone (2 × 6 mL). The final solid was dried overnight at 55 °C under vacuum (2.0 mbar) to afford **M3** as a white solid (1.087 g). ^{13}C CP-MAS NMR (100.62 MHz) δ (ppm): 159.8, 130.2, 123.8, 113.5, 94.5, 69.6, 60.2, 58.5, 30.8, 22.9, 19.8, 17.8, 13.7, 8.7. ^{29}Si CP-MAS NMR (79.5 MHz) δ (ppm): −58.3 (T^2), −69.2 (T^3), −104.8 (Q^3), −114.8 (Q^4). IR (ATR) *ν* (cm^{-1}): 2942, 1584, 1050, 801, 680, 654. BET surface area: 109 m^2/g; pore volume: 0.711 cm^3/g. TGA: (argon, 20–700 °C) residual mass 67.1%. EA calculated for $C_9H_{10}ISiO_{2.5} \cdot 5SiO_2$ (considering complete condensation): 17.62% C, 1.64% H, 27.46% Si, 20.68% I; found: 17.3% C, 2.2% H, 27.3% Si, 6.3% I.

2.4.4. Preparation and characterization of hybrid silica material **M4**

Monosilylated compound **4** (0.400 g, 0.943 mmol) and TEOS (4.2 mL, ρ = 0.934 g/mL, 18.9 mmol) were dissolved in dry ethanol (15 mL). Then, a solution of Milli-Q water (1.4 mL, 77.8 mmol) and TBAF (200 μL, commercial solution 1 M in anhydrous THF) in dry EtOH (4.8 mL) was added to the first solution. The final mixture was shaken vigorously for 10 s to obtain a homogenous solution. After 14 min, a gel formed that was then aged at room temperature for 6 days. Then, the gel was pulverized, filtered off and washed successively with water (2 × 6 mL), EtOH (2 × 6 mL) and acetone (2 × 6 mL). The final solid was dried overnight at 55 °C under vacuum (2.0 mbar) to afford **M4** as a white solid (1.302 g). ^{29}Si CP-MAS NMR (79.5 MHz) δ (ppm): −67.8 (T^3), −104.8 (Q^3), −113.0 (Q^4). IR (ATR) ν (cm^{-1}): 2971, 1584, 1050, 800, 681. BET surface area: 124 m^2/g; pore volume: 0.790 cm^3/g. TGA: (argon, 20–700 °C) residual mass 79.5%. EA calculated for $C_9H_{10}ISiO_{2.5}\cdot 20SiO_2$ (considering complete condensation): 7.91% C, 0.74% H, 43.17%Si, 9.29% I; found: 10.1% C, 1.7% H, 44.0% Si, 3.9% I.

2.5. Catalysis

2.5.1. General procedure for the catalytic oxidative α-tosyloxylation of ketones

All catalytic runs were performed in screw-top sealable tubes (10 mL). To a solution of ketone (1 mmol) in CH_3CN (5 mL), *p*-toluenesulfonic acid (247 mg, 1.3 mmol), *m*-CPBA (65% purity, 397 mg, 2.3 mmol) and the supported catalyst (amount calculated to give 0.1 mmol of I, 10 mol% I) were added. The tube was sealed, and the mixture was stirred at 65 °C under a nitrogen atmosphere for the time indicated in Table 3. For the catalyst recycling studies, the reaction mixture was filtered and the recovered catalyst was washed with acetonitrile (2 × 3 mL), further washed with diethyl ether (3 × 3 mL), dried under a vacuum and directly used in the next cycle. The IR spectra of the recovered **M1** and **M2** (see Supporting information) suggested no sign of decomposition. The filtrates were poured into a saturated aq. $NaHCO_3$ solution and extracted with $CHCl_3$ (3 × 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was further purified by flash column chromatography on silica gel.

2.5.2. α-Tosyloxypropiophenone, 5 [9]

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 7.93–7.84 (m, 2H), 7.73 (d, *J* = 8.3 Hz, 2 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 2 H), 7.24 (t, *J* = 8.0 Hz, 2 H), 5.77 (q, *J* = 6.9 Hz, 1 H), 2.36 (s, 3 H), 1.57 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 194.9, 145.2, 134.0, 133.8, 133.5, 129.9, 128.9, 128.8, 128.0, 77.5, 21.7, 18.8; IR (ATR) ν (cm^{-1}): 2936, 1698 (C=O), 1577, 1356.

2.5.3. α-Tosyloxy-p-bromoacetophenone, 6 [34]

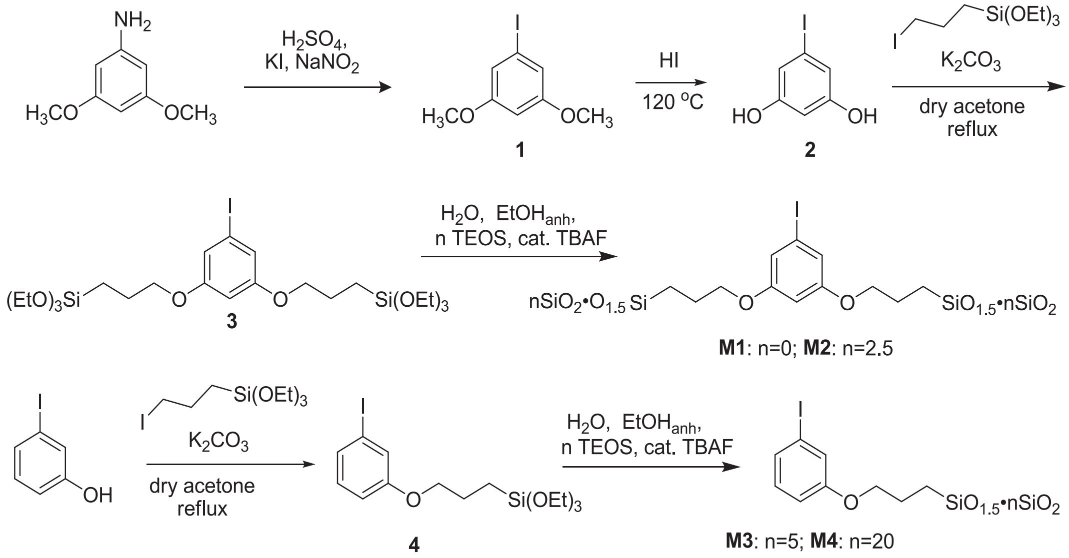
^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 7.83 (d, *J* = 8.2 Hz, 2 H), 7.70 (d, *J* = 8.5 Hz, 2 H), 7.60 (d, *J* = 8.5 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 5.20 (s, 2 H), 2.44 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 189.8, 145.6, 132.6, 132.4, 130.1, 129.7, 128.3, 69.9, 21.8; IR (ATR) ν (cm^{-1}): 2918, 2852, 1699 (C=O), 1586, 1358, 1059.

2.5.4. α-Tosyloxy-p-nitroacetophenone, 7 [9]

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 8.31 (d, *J* = 8.1 Hz, 2 H), 8.02 (d, *J* = 7.7 Hz, 2 H), 7.82 (d, *J* = 7.6 Hz, 2 H), 7.36 (d, *J* = 7.5 Hz, 2 H), 5.24 (s, 2 H), 2.46 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 189.9, 150.9, 145.8, 138.3, 132.4, 130.2, 129.5, 128.3, 124.2, 70.1, 21.8; IR (ATR) ν (cm^{-1}): 2950, 2858, 1708 (C=O), 1598, 1519 (NO_2), 1341 (NO_2), 1320, 848.

2.5.5. α-Tosyloxy-3-pentanone, 8 [9]

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 7.81 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 7.7 Hz, 2 H), 4.85–4.76 (m, 1 H), 2.59 (q, *J* = 7.1 Hz, 2 H), 2.46



Scheme 2. Synthesis of the bis- and monosilylated precursors **3** and **4** and of the hybrid silica materials **M1**–**M4**.

Table 1
Selected physical data for materials **M1**–**M4**.

Mat.	N_2 sorption measurements			TGA[b] (%)	I [c] (mmol/g)	I/Si[d]	
	S_{BET} (m^2/g)	Uptake at saturation[a] cm^3/g STP	Microporous contribution m^2/g			Theor.	Exp.
M1	<5	–	0	48	1.064	0.500	0.260
M2	255	48	47	63	0.646	0.143	0.075
M3	109	42	0	67	0.496	0.166	0.051
M4	124	92	0	79	0.307	0.048	0.020

[a] Amount of gas adsorbed at $p/p° = 0.5$.
[b] Residual mass at 700 °C.
[c] Determined by elemental analysis.
[d] Based on the elemental analysis and ICP-OES results.

(s, 3 H), 1.35 (d, J = 7.0 Hz, 3 H), 1.02 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 207.8, 145.4, 133.3, 130.1, 128.0, 80.8, 31.3, 21.8, 17.7, 7.1; IR (ATR) ν (cm^{-1}): 1724 (C=O), 1407, 1364, 907, 632.

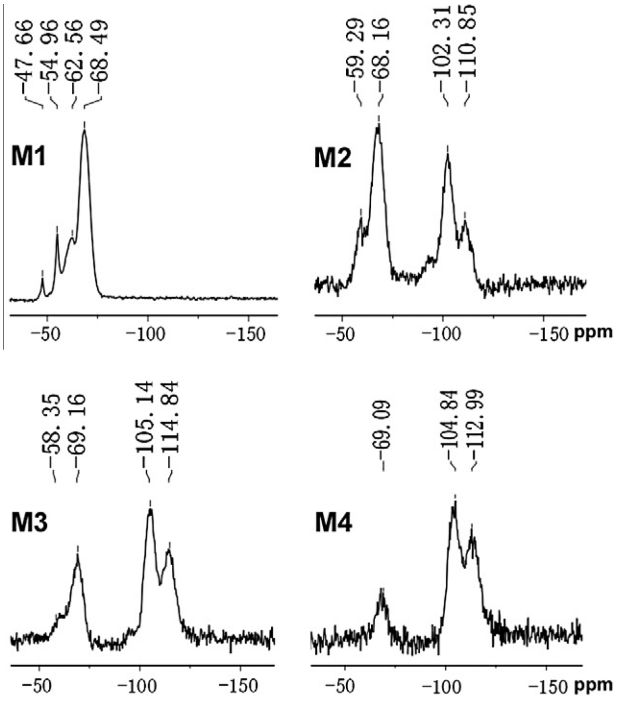


Fig. 1. ^{29}Si CP-MAS solid state NMR spectra of **M1**–**M4**.

2.5.6. α-Tosyloxyacetophenone, **9** [9]

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.87–7.82 (m, 4 H), 7.61 (t, J = 7.3 Hz, 1 H), 7.46 (t, J = 7.6 Hz, 2 H), 7.34 (d, J = 8.0 Hz, 2 H), 5.26 (s, 2 H), 2.44 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 190.4, 145.4, 134.3, 130.0, 129.0, 128.2, 128.1, 70.1, 21.8; IR (ATR) ν (cm^{-1}): 2933, 1712 (C=O), 1596, 1449, 1356.

2.5.7. α-Tosyloxy-p-methylacetophenone, **10** [9]

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 7.84 (d, J = 8.2 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H), 7.34 (d, J = 8.1 Hz, 2 H), 7.25 (d, J = 7.5 Hz, 2 H), 5.23 (s, 2 H), 2.44 (s, 3 H), 2.40 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 190.1, 145.6, 133.0, 131.6, 130.2, 129.9, 128.4, 70.2, 22.1; IR (ATR) ν (cm^{-1}): 1699 (C=O), 1345, 1170.

2.5.8. α-Tosyloxy-p-chloroacetophenone, **11** [9]

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 7.83 (d, J = 8.2 Hz, 2 H), 7.78 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.4 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H), 5.20 (s, 2 H), 2.45 (s, 3 H), 2.40 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 189.6, 145.6, 140.9, 132.6, 132.2, 130.1, 129.6, 129.4, 128.3, 70.0, 21.8; IR (ATR) ν (cm^{-1}): 1699 (C=O), 1359, 1174, 660.

2.5.9. α-Tosyloxy-o-bromoacetophenone, **12** [34]

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 7.80 (d, J = 7.5 Hz, 2 H), 7.60 (d, J = 7.0 Hz, 2 H), 7.38–7.33 (m, 4 H), 5.13 (s, 2 H), 2.45 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 194.8, 145.5, 137.6, 133.9, 133.0, 132.6, 130.0, 129.8, 128.2, 127.7, 119.3, 71.2, 21.8; IR (ATR) ν (cm^{-1}): 1721 (C=O), 1176, 1040, 633.

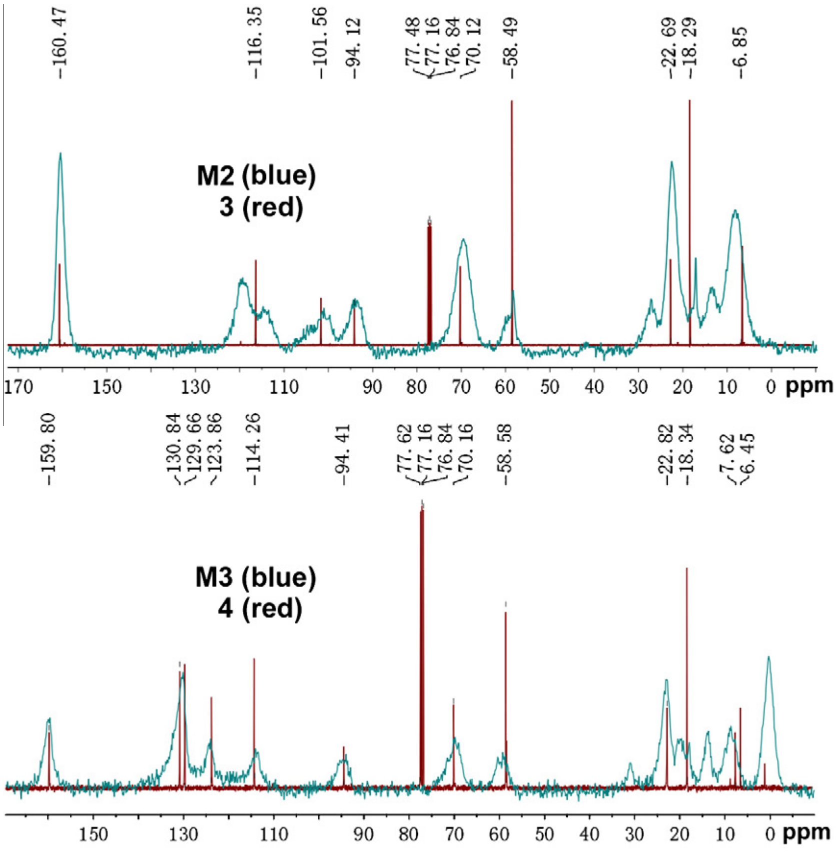


Fig. 2. ^{13}C CP-MAS solid state NMR spectra of **M2** and **M3** and the ^{13}C NMR spectra of the corresponding precursors **3** and **4**.

2.5.10. α-(Camphorsulfonyloxy)acetophenone, **13** [9]

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 7.91 (d, *J* = 7.3 Hz, 2 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 2 H), 5.53 (s, 2 H, CH_2O), 3.80 (d, *J* = 15.1 Hz, 1 H, C*H*HSO_2), 3.34 (d, *J* = 15.1 Hz, 1 H, CH*H*SO_2), 2.48–2.36 (m, 2 H), 2.14–2.06 (m, 2 H), 1.95 (d, *J* = 18.5 Hz, 1 H), 1.82–1.76 (m, 1 H), 1.46 (ddd, *J* = 13.2, 9.4, 4.0 Hz 1 H), 1.12 (s, 3 H, CH_3), 0.90 (s, 3 H, CH_3); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 214.5, 190.9, 134.4, 133.8, 129.2, 128.0, 70.4, 48.6, 48.3, 42.9, 42.7, 27.1, 25.1, 19.9, 19.8; IR (ATR) ν (cm^{-1}): 1744 (C=O), 1707 (C=O), 1171.

2.5.11. α-(Methanesulfonyloxy)acetophenone, **14** [9]

^{1}H NMR (360 MHz, $CDCl_3$) δ (ppm): 7.90 (d, *J* = 7.4 Hz, 2 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.52 (t, *J* = 7.7 Hz, 2 H), 5.52 (s, 2 H), 3.29 (s, 3 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ (ppm): 191.2, 134.6, 133.5, 129.2, 127.9, 70.4, 39.3; IR (ATR) ν (cm^{-1}): 1703 (C=O), 1171, 966.

3. Results and discussion

3.1. Preparation and characterization of hybrid silica materials

In Scheme 2, we summarize the synthesis of bis- and monosilylated iodoarenes **3** and **4** and the materials **M1–M2** and **M3–M4** derived from these precursors. The bis-silylated monomer **3** was prepared from the commercially available 3,5-dimethoxyaniline through a three-step synthetic route involving a diazotization of the aniline to the corresponding iodoarene **1** [33], followed by the deprotection of the methoxy groups to give 5-iodoresorcinol **2** [33] and the subsequent alkylation of the phenolic OH groups with (3-iodopropyl)triethoxysilane. In an analogous manner, the monosilylated precursor **4** was obtained by the alkylation of commercial 3-iodophenol with (3-iodopropyl)triethoxysilane in refluxing acetone in the presence of potassium carbonate. Precursor **3** could either be used directly in the sol–gel reaction to yield the bridged silsesquioxane **M1** or could be co-condensed with five equiv of TEOS to yield **M2**. Similarly, the monosilane **4** was co-condensed with TEOS at molar ratios of 1:5 and 1:20, providing materials **M3** and **M4**, respectively. In all cases, the sol–gel reactions were performed in anhydrous ethanol with a stoichiometric amount of water with respect to the ethoxy groups and under nucleophilic catalysis (TBAF, 1 mol% with respect to Si) [23,31,35]. Materials **M1–M4** were fully characterized by elemental analysis, ^{13}C and ^{29}Si solid state CP-MAS NMR, IR, thermogravimetric analysis (TGA) and nitrogen-sorption measurements. Some physical data of the materials are given in Table 1.

The TGA and DSC curves of **M1**–**M4** (Supporting information) showed a weight decrease of less than 5% below 250 °C, attributed to the loss of the physisorbed water and remaining uncondensed ethoxy groups. For all materials, a more significant weight loss was found in the range of 250–700 °C, assigned to the decomposition of the organic constituent. As expected, **M1** exhibited the highest weight loss (52%) due to the higher content of organic matter in **M1** compared with **M2–M4.** The covalent incorporation of the organosilane in the hybrid silicas was ascertained by ^{29}Si CP-MAS solid state NMR. As shown in Fig. 1, the ^{29}Si CP-MAS NMR spectra of **M1**–**M4** exhibit signals between −50 and −69 ppm corresponding mainly to T^2 and T^3 species (Table 1). For **M1**, despite the presence of low intensity signals around −47 (T^0) and −54 ppm (T^1), the condensation degree of the material is relatively high (85%). Additionally, the spectra of **M2**–**M4** showed signals

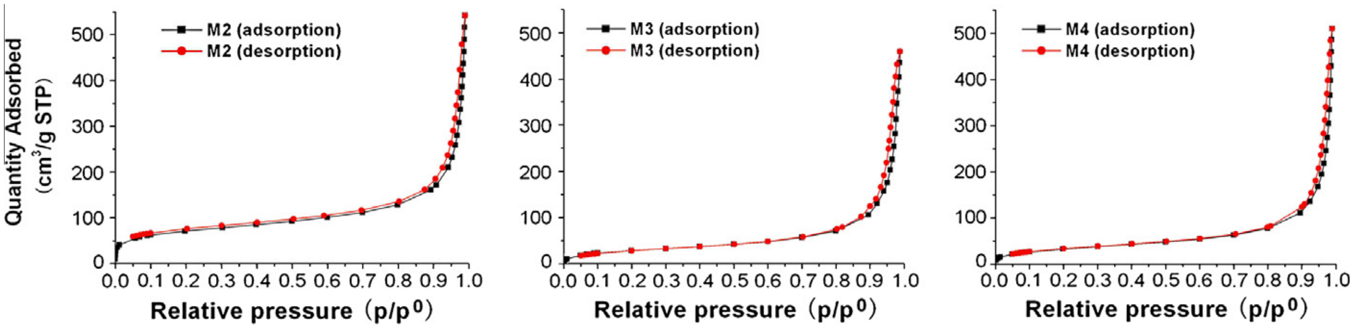
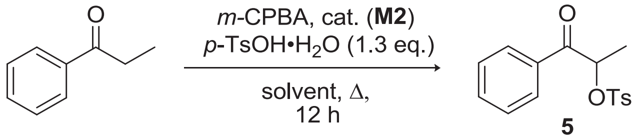


Fig. 3. N_2-sorption isotherms of **M2**–**M4**.

Table 2
Optimization of the reaction conditions with **M2** as the catalyst.



5

Entry[a]	Solvent	*m*-CPBA (equiv)	M2 (mol%)	Temp. (°C)	Yield **5** (%) [b]
1	Acetonitrile	1.1	10	50	25
2	Acetonitrile	1.1	10	65	37
3	Acetonitrile	1.1	10	70	37
4	Acetonitrile	2.3	10	65	69
5	Acetonitrile	3.0	10	65	68
6	Chloroform	2.3	10	65	0
7	Toluene	2.3	10	65	4
8	Acetonitrile	2.3	5	65	15
9	Acetonitrile	2.3	15	65	70

[a] [Substrate] = 0.2 M.

[b] Corrected GC yield (Ph–Ph as int. standard).

typical of silica environments at around −105 and −115 ppm corresponding to Q^3 and Q^4 species, respectively. The incorporation of organic fragments in **M2** and **M3** was further evidenced by the ^{13}C CP-MAS solid state NMR spectra, with a typical signal at around 10 ppm attributed to CH_2—Si. The spectra of these materials and their comparison with the ^{13}C NMR solution spectra of the organic precursors **3** and **4** are shown in Fig. 2. As expected, there is a high degree of correlation between the position of the ^{13}C signals of the precursors and the corresponding hybrid silicas, with the presence of aromatic C—I carbon atoms confirmed by the signal at 94 ppm. However, the observation of additional smaller signals at *ca.* 11, 24, and 59 ppm in the aliphatic C region and the splitting of some aromatic signals (101 and 116 ppm) in the case of **M1** and **M2** led us to believe that the alkyl–aryl ether tethers were partially broken during the sol–gel synthesis. The consequence of this partial cleavage in the case of the mono-ethers **M3** and **M4** would be a lower iodine content than expected, as was indeed observed by elemental analysis. In the case of **M1** and **M2**, the cleavage of both ether functions linking the aromatic fragment to the siloxane network is less probable, so the decrease in iodine content is less pronounced, as observed in Table 1. For the catalytic runs, the catalyst loading was based on the material's % iodine as determined by elemental analysis.

Nitrogen-sorption measurements are important for investigating the texture of materials. Material **M1** displayed non-detectable porosity, as was previously found for other bridged silsesquioxanes prepared in the absence of TEOS under similar conditions [21]. As shown in Fig. 3, materials **M2**–**M4** exhibit type II isotherms (according to IUPAC rules [36]) with a regular increase of nitrogen uptake in the range of $p/p° < 0.7$ and without a sharp increase that would come from a regular porous system. According to the *t*-plot, a slight microporous contribution ($47\ m^2\ g^{-1}$) is detected in the case of **M2**, whereas materials **M3** and **M4**, obtained from the monosilylated precursor **4**, only display porosity arising from mesopores and external surfaces. In particular, the large amount of nitrogen adsorbed at $p/p° > 0.7$ arises from nitrogen that condenses in the voids between particles.

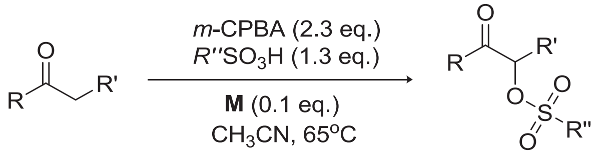
3.2. Catalytic activity of the silica-supported iodoarenes in the α-tosyloxylation of ketones

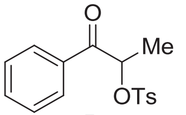
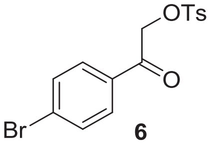
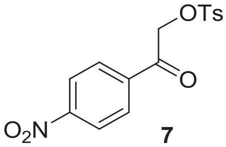
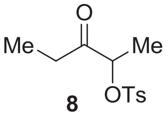
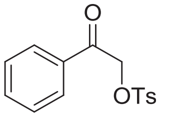
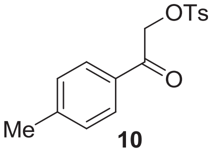
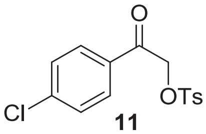
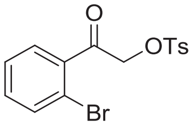
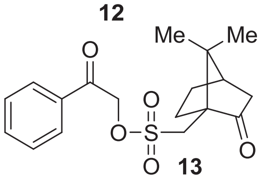
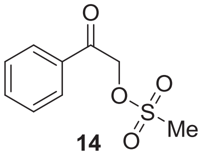
The catalytic activity of materials **M1**–**M4** in the α-tosyloxylation of a range of ketones was then evaluated. As mentioned previously, the precedent for the use of supported ArI in oxidation catalysis has been provided by Togo and coworkers, who used a catalyst loading of 0.5–1.3 equiv of ArI [8–10].

Our initial catalytic tests were performed with propiophenone as the substrate and in the presence of *p*-toluenesulfonic acid (*p*-TsOH, 1.3 equiv), *m*-CPBA as the terminal oxidant and **M2** as the catalyst to afford α-tosyloxypropiophenone (**5**) (Table 2). A screening of different reaction conditions was performed (solvent, catalyst loading, amount of *m*-CPBA, temperature). The reaction using 10 mol% of **M2** in the presence of 1.1 equiv of *m*-CPBA in acetonitrile gave moderate yields (25–37%) of **5** at 50 and 65 °C (Table 2, entries 1–2), and no improvement was achieved by raising the temperature to 70 °C (Table 2, entry 3). In the same solvent, the yield could be improved to 69% by raising the amount of *m*-CPBA to 2.3 equiv, although higher amounts of the oxidant (3.0 equiv) had no beneficial effect (compare entries 4 and 5). Chloroform and toluene were also tested as solvents and proved less effective than acetonitrile (entries 6–7). The effect of catalyst loading was also investigated (entries 8–9). As a result, the optimized reaction conditions were as follows: 65 °C, 10 mol% of catalyst, acetonitrile as solvent, 2.3 equiv of *m*-CPBA and 1.3 equiv of *p*-TsOH.

This protocol was then extended to the oxidative α-tosyloxylation of various ketones with the supported catalysts **M1**–**M4**

Table 3
α-Tosyloxylation of ketones using **M1**–**M4** as catalysts under the optimized conditions specified.



Entry[a]	Product	Cat.	Time (h)	Yield[b] (%)
1	 **5**	**M1**	18	47
2		**M2**	14	67
3		**M3**	27	3
4		**M4**	50	23
5	 **6**	**M1**	21	60
6		**M1**	13	62[c]
7		**M2**	14	55
8		**M3**	19	5
9		**M4**	19	19
10	 **7**	**M1**	21	35
11		**M1**	13	51[c]
12		**M2**	14	25
13	 **8**	**M1**	18	24
14		**M2**	19	26
15	 **9**	**M1**	18	43
16		**M1**	13	36[c]
17		**M2**	19	50
18	 **10**	**M1**	17	21
19		**M2**	18	18
20	 **11**	**M1**	16	54
21	 **12**	**M1**	20	58
22		**M1**	21	47[c]
23	 **13**	**M1**	17	42
24	 **14**	**M1**	18	71
25		**M1**	18	65[c]
26		**M1**	18	42[d]

[a] [Substrate] = 0.2 M.
[b] Isolated yield.
[c] Second cycle.
[d] Third cycle.

(Table 3). The corresponding α-tosyloxyketones **5**–**12** were isolated in yields of up to 67%. As expected, the activities of the new silica-immobilized catalysts were lower than those shown by homogenous iodoarenes for this type of transformation [8,14]. Nevertheless, it is worthwhile to mention a certain improvement with respect to other systems [9], given the possibility of using just 10 mol% of the supported ArI. Materials **M1**–**M4** were tested as catalysts with propiophenone and *p*-bromoacetophenone as substrates (Table 3, entries 1–9). Moderate to good isolated yields of the tosylated ketones **5** and **6** were obtained for materials **M1** and **M2** derived from the bis-silylated monomer **3** (entries 1, 2, 5 and 7), whereas **M4** displayed lower activity (23 and 19% isolated yields of **5** and **6**, respectively) (entries 4 and 9) and material **M3** was essentially inactive under the reaction conditions (entries 3 and 8). The two best catalysts, **M1** and **M2,** were also tested with six other substrates: *p*-nitroacetophenone (entries 10–12), 3-pentanone (entries 13–14), acetophenone (entries 15–17), *p*-methylacetophenone (entries 18–19), *p*-chloroacetophenone (entry 20) and 2-bromoacetophenone (entries 21–22). The corresponding tosyloxyketones **7**–**12** were obtained in moderate isolated yields (from 18% to 58%). To further investigate the generality of the α-oxidative process as suggested by a referee, two other sulfonic acids (camphorsulfonic and methanosulfonic) were also tested with 10 mol% of **M1** as the catalyst, affording the corresponding α-functionalized ketones **13** and **14** in 42% and 71% isolated yields, respectively (entries 23–26). Notably, the material **M1** was successfully separated and reused in a second run in several cases (entries 6, 11, 16, 22 and 25) and even in a third run (entry 26).

4. Conclusions

Organic–inorganic hybrid silica materials **M1**–**M4** containing iodoarene moieties were synthesized by sol–gel methodologies from bis- and monosilylated precursors **3** and **4** under nucleophilic catalysis. The sol–gel process using the bis-silylated iodoarene **3** was performed with and without added TEOS (**M1**, **M2**), whereas the monosilylated monomer **4** was co-gelified with different amounts of TEOS (**M3**, **M4**). The materials were characterized by elemental analysis, ^{13}C and ^{29}Si CP-MAS solid state NMR, IR, TGA, and nitrogen-sorption measurements. The catalytic activity of the materials was tested in the α-tosyloxylation of ketones using *m*-CPBA as an oxidant, affording the corresponding α-tosyloxyketones **5**–**12** in moderate to good isolated yields in the case of catalysts **M1**–**M2**. Camphorsulfonic and methanosulfonic acids have also been successfully used for the oxidative α-functionalization of acetophenone to yield **13** and **14**. The recyclability has been investigated for **M1**, which was recovered by filtration and reused successfully in a second run for several substrates.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2012.10.011.

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