

A Compartmentalized-type Bifunctional Magnetic Catalyst for One-pot Aerobic Oxysulfonylation and Asymmetric Transfer Hydrogenation

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Utilization of the confined cavity of the mesoporous silica, the exploration of the synergetic catalysis process for sequential organic transformations has great significance in asymmetric catalysis. In this study, the yolk-shell-structured magnetic nanoparticles with the chiral Ru/diamine species within the nanochannels of the outer mesoporous silica shell and the FeCl₃ species on the inner magnet core are fabricated. The electron microscopy images and the structural characterizations disclose the uniformly distributed magnetic nanoparticles with the well-defined single-site ruthenium/diamine active centers onto the outer silica shell. As a yolk-shell-structured bifunctional magnet catalyst, the FeCl₃ species enables an efficient aerobic oxy-

sulfonylation between aryl-substituted terminal alkynes and sodium sulfinates to the β -keto sulfones intermediates, and the ruthenium/diamine species sequentially reduces the *in-situ* generated intermediate to the chiral β -hydroxysulfones products. As we envision, this one-pot aerobic oxysulfonylation/ asymmetric transfer hydrogenation process affords various chiral β -hydroxysulfones in high yields with excellent enantiose-lectivities. Furthermore, this magnetic catalyst can also be conveniently recovered *via* an additional outer magnet and repeatedly recycled, showing a potential application in industrial interest.

Introduction

As an environmentally friendly goal in green chemistry, the development of magnetically recyclable catalysts has attracted great concerns due to the salient magnetic separation and recovery.^[1] This specificity not only simplifies the workup procedure via an additional magnet but also enhances the recycling ability of heterogeneous catalysts.^[2] Recently, a variety of well-documented reviews involving in magnet-supported catalysts have appeared in the literature, and many examples have been successfully used in the preparation of various nonchiral organic molecules.^[3] Despite these significant explorations, the application of magnetic catalysts for the preparation of optically pure organic molecules is still a great challenge.^[4] The problems mainly reflect the following issues. A problem is a high demand for the subtle chiral environment in an enantioselective reaction. Generally, the inherent magnetic aggregation often makes a negative effect on the subtle chiral environment

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to diminish enantioselective performance. A further issue is the poor dispersion situation in reaction systems, which often leads to low catalytic performance. Therefore, application them in enantioselective reactions, especially in a multi-step enantioselective organic transformation is still quite lagging when compared with those non-magnetically nanoconfined catalysts.^[5] Therefore, the development of a magnet-coated technology to overcome the magnetic aggregation for maintainable enantioselective performance, and the adjustment of hydrophilicity/hydrophobicity of magnetic catalysts to accelerate catalytic performance, are highly desirable. These improvements not only facilitate the highly efficient enantioselective catalysis but also benefit the multi-step enantioselective organic transformation, greatly widening the applications of magnetically recyclable catalysts.

Optically pure β -hydroxysulfones, as an important chiral motif, are used extensively in the preparations of biologically active γ -butenolides, δ -valerolactone, and so on.^[6] Normally, several single-step enantioselective organic transformations,^[7] such as an asymmetric conjugate boration of $\alpha_{,\beta}$ -unsaturated sulfones,^[7a-b] and enantioselective reductions of β -keto sulfones, are commonly used for the construction of chiral β hydroxysulfones.^[7c-h] Recently, the possibility to accomplish cascade reactions involving non-orthogonal steps has been elegantly demonstrated through site-isolated immobilization of incompatible catalysts.^[8] In this context, a two-step sequential transformation of terminal alkynes and sodium sulfonates to βhydroxysulfones has also been explored. $^{\scriptscriptstyle [8d-e,9]}$ Notably, the development of an atom-economic one-pot synthetic strategy from commercially available starting materials to prepare β hydroxysulfones, together with the benefit of magnetic cata-



lysts for recycling of expensive metals, has great significance both theoretically and practically.

Based on our previous experiences in the magnet-supported catalysts in multi-step sequential organic transformation,^[10] we herein take advantage of a yolk-shellstructured mesoporous silica^[11] to assemble the FeCl₃ and chiral ruthenium/diamine species within the magnetic nanoparticles, designing a compartmentalized-type Fe/Ru bifunctional magnet catalyst. The FeCl₃ species acts as an oxysulfonylation catalyst for the initial aerobic oxysulfonylation of terminal alkynes and sodium sulfinates to β -keto sulfones, whereas chiral ruthenium/ diamine species acts as an asymmetric transfer hydrogenation (ATH) catalyst for the subsequent ATH transformation of the insitu generated β -keto sulfones. As presented in this study, this bifunctional catalyst enables a highly efficient aerobic oxysulfonylation/ATH dual-catalysis process, providing various β hydroxysulfones with enhanced yields and boosted enantioselectivities, which overcomes the intrinsic cross-interaction between the FeCl₃ and chiral ruthenium/diamine dual-species.

Results and Discussion

Synthesis and structural characterization of the heterogeneous catalyst

A four-step procedure for the assembly of the Ru/diamine- and FeCl₃-functionalized Fe₃O₄ nanoparticles to form the yolk-shellstructured magnetic catalyst, abbreviated as [Fe]@Fe₃O₄@[Ru]@ [Si] (5) ([Ru]=MesRuArDPEN:^[12] Mes=Mesitylene, and ArD-PEN=(*S*,*S*)-4-((trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylene-diamine; [Fe]=FeCl₃), was performed as outlined in Scheme 1. In the first step, according to the reported method,^[13] the SiO₂-coated Fe₃O₄ nanoparticles, (Fe₃O₄@SiO₂ (1)), were coated through the condensation of ArDPEN-sioxane and 1,2bis(triethoxysilyl)ethane using the FC-4 (FC-4: [C₃F₇O(CF(CF₃) $CF_2O_2CF(CF_3)CONH(CH_2)_3N^+(C_2H_5)_2CH_3]I^-)$ and CTAB (CTAB: cetyltrimethylammonium bromide) as dual structure-directing templates, forming the chiral diamine-functionalized Fe₃O₄@SiO₂@[Si] (2). In the second step, the selective etching for the removal of the sandwiched SiO₂-coated layer gave the yolk-shell-structured Fe₃O₄@[Si] (3), guaranteeing the chiral diamine–functionality within the nanochannels of the mesoporous silica shell. In the third step, the entrapping the FeCl₃^[14] onto the magnetic core afforded [Fe]@Fe₃O₄@[Si] (4) as a black powder. Finally, the coordination of 4 with (MesRuCl₂)₂ led to the coarse [Fe]@Fe₃O₄@[Ru]@[Si], where a strict Soxhlet extraction provided a pure catalyst 5 as a brownish-red powder. For comparison, a parallel analog 5' without Fe₃O₄ and FeCl₃ in the core, abbreviated as [Ru]@[Si], was also prepared by the reaction of 3' (obtained by the removal of the Fe₃O₄ from 3 under an alkaline condition) and (MesRuCl₂)₂ following a similar procedure (see Figures S1–3 in the ESI).

With the as-made magnetic catalyst in hand, the determination of the well-defined single-site Ru/diamine centers in catalyst 5 is necessary due to the demand for a maintainable homogeneous chiral environment. In this case, we used the 5' as a parallel analog to demonstrate the single-site Ru/diamine active centers within the silica framework of magnetic catalyst 5. As shown in the solid-state ¹³C cross-polarization (CP)/magic angle spinning (MAS) NMR spectra of 3' and 5' (Figure 1), it was found that both presented some similarly general carbon signals. The peaks around $\delta = 9.0$ ppm were responded to the carbon atoms of the ethylene-bridged groups (-SiCH2CH2Si-), whereas those at $\delta = 75.5$ ppm and at $\delta = 122.7 - 162.8$ ascribed the alkyl carbon atoms and the aromatic carbon atoms in the -NCHC₆H₅ moiety. These similar signals suggested that chiral diamine ligands had been immobilized in the silica framework of the magnetic materials. It was notable that 5' exhibited the characteristic carbon signals at $\delta = 24.3$ ppm and $\delta = 109.1$, 106.6 ppm for the methyl carbon atoms bonded to mesitylene and the aromatic carbon atoms in mesitylene, which was absented in its parent material 3'. This comparison disclosed the successful coordination to form the Ru/diamine species in 5'. These observed signals also indicated the well-defined chiral single-site Ru/diamine centers in the magnetic catalyst 5 because 5' had similar chemical shift values to its homogeneous MesRuTsDPEN.^[12a] Some peaks indicated at asterisks were the



Scheme 1. Preparation of catalysts 4-5.

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Figure 1. Solid-state ¹³C CP/MAS NMR spectra of 3' and 5'.

rotational sidebands, and/or the carbon signals of the CTAB and FC-4 moiety remaining in the materials. In addition, the solidstate ²⁹Si MAS NMR spectrum of 5' (See SI in Figure S1) suggested that 5 had a similar organic silica network to 5', where the strongest T³ species (R–Si(OSi)₃: R=ethylene-bridged groups and/or alkyl-linked MesRuArDPEN complexes) was the main silicate components on the silica shell.

In order to demonstrate the magnetic effect after the immobilization of the chiral diamine ligands, and/or the FeCl₃ and Ru/diamine-complexes, a comparison for the wide-angle XRD patterns of Fe₃O₄, Fe₃O₄@[Si] (3), and catalysts 4-5 was performed, as shown in Figure 2. It was found that the Fe₃O₄@ [Si] (3) exhibited the typical diffraction peaks (2θ values at 30.1, 35.4, 43.1, 57.0, and 62.6 degrees), which are similar to those of the Fe₃O₄ nanoparticles. Despite the obvious deceased magnetic intensity of 4-5 relative to those of Fe₃O₄, the corresponding characteristic peaks were still observed clearly. This observation suggested that the coatings and/or immobilizations of chiral diamine ligands and/or FeCl₃ and Ru/diamine-complexes within the magnetic nanoparticles maintained the magnetic nature of the Fe₃O₄ owing to an insitu coating procedure. To further confirm the magnetic ability of catalysts 4-5, their magnetization curves and the magnetic separations



Figure 2. Wide-angle powder XRD patterns of $Fe_3O_4,\,Fe_3O_4@[Si]$ (3), and catalysts 4–5.



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Figure 3. a) Magnetization curves of Fe_3O_{47} , $Fe_3O_4@SiO_2$ (1), $Fe_3O_4@[Si]$ (3), and catalysts **4–5** measured at 300 K. b) Separation-redispersion situation of catalyst **5** using an external magnet.

of catalyst **5** were also investigated, as shown in Figure 3. It was found that the Fe_3O_4 , $Fe_3O_4@SiO_2$ (1), $Fe_3O_4@Si$] (3), and catalysts **4**–**5** had the magnetization saturation values of 60.77, 19.45, 12.26, 10.91, and 10.01 emu g⁻¹, respectively, detected by a superconducting quantum interference device magnetometer (Figure 3a). It was notable that the value of catalyst **5** was enough for the magnetic separation. As shown in Figure 3b, catalyst **5** could steadily be recovered from an aqueous reaction system through the use of an external magnet.

Yolk-shell-structured morphology of the magnetic catalyst 5 with ordered pore arrangements was further characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and nitrogen adsorption-desorption technique. As shown in Figure 4, the SEM images (Figure 4a) revealed that the magnetic nanoparticles in catalyst 5 were uniformly dispersed, where the average size of nanoparticles was around 320 nm. Its TEM image (Figure 4b) was more visual,



Figure 4. a) SEM images of 5, b) TEM images of 5.

where each silica yolk with about 210 nm of the magnetic core in diameter was separated by the ethylene–coated silica with a thin shell of 30 nm in thickness. In addition, the nitrogen adsorption-desorption isotherm of the catalyst **5** exhibited a typical IV character with an H₁ hysteresis loop that was similar to that attained with the general yolk-shell-structured mesoporous silica,^[13a] revealing its mesoporous structure (see Figure S2 in the ESI).

All these investigations, together with the well-defined single-site Ru/diamine centers in its parallel analog 5', demonstrate that catalyst 5 had the uniformly distributed Ru/diamine species within the mesoporous silica shell, which could be readily fabricated following the designed assembled process.

Catalytic property

With the well-established magnet catalyst 5 in hand, we examined the designed aerobic oxysulfonylation/ATH reaction of alkynes and sodium sulfinates for one-pot synthesis of chiral β -hydroxysulfones. Initially, we focused on the two single-step reactions. In the case of aerobic oxysulfonylation, the model reaction of phenylacetylene (6a) and sodium benzenesulfinate (7 a) was carried out through the use of 4 as a catalyst with 20.0 mol% of FeCl₃-loadings determined by TG analysis (see Figure S3 in the ESI) in MeOH/H₂O (v/v = 3/1) under air atmosphere according to the reported reaction conditions.^[9a] The result showed that the reaction of **6a** and **7a** catalyzed by 4 could produce the clear intermediate of 1-phenyl-2-(phenylsulfonyl)ethan-1-one (8a) in a quantitative yield within 16 h. Such a result was comparable to that attained with its homogeneous FeCl₃,^[9a] demonstrating that **4** maintained the original catalytic reactivity after a magnet-immobilization. Due to the consideration of green solvent and compatible secondstep asymmetric reduction, several co-solvents were further optimized (see Table S1 in the ESI). It was found that the model reaction catalyzed by 4 with the EtOH/H₂O (v/v=3/1) as cosolvents could further shorten reaction time from 16 h to 10 for the reaction completion that was similar to those obtained with FeCl₃ (Entry 1 versus entry 2, Table 1), determining that a mixture of EtOH and H_2O (v/v=3/1) was the best co-solvents system. In the case of the single-step ATH transformation, it was found that the ATH of 8a catalyzed by 5 with 2.5 mol% of ruthenium-loadings could provide the target products of (S)-1phenyl-2-(phenylsulfonyl)ethan-1-ol (9a) in 96% yield with 99% ee. Such an ee value was comparable to that attained with its homogeneous counterpart MesRuTsDPEN (Entry 3 versus entry 4, Table 1), indicating the well-defined single-site ruthenium/diamine centers in catalyst 5 verified by the ¹³C CP/MAS NMR spectrum of 5'. Further evidence to support the welldefined single-site ruthenium/diamine centers came from an XPS investigation, as shown in Figure 5. It was found that catalyst 5 had a similar Ru 3d^{5/2} electron binding energy to its corresponding homogeneous MesRuTsDPEN (281.68 eV versus 281.74 eV).

Subsequently, we combined two single-step reactions, the aerobic oxysulfonylation and ATH reduction, into the one-pot

Ph 6a	+ PhSO ₂ Na 7a	Catalyst Air Ph 50 °C	Ba Ba Sa So C Ba		
Entry	Reaction	Catalysts	T [°C]/t [h]	Yield [%] of 8 a ^[b]	Yield [%]/ <i>ee</i> of 9 a ^[b]
1	I	4	50°C/	96	/
2	I	[Fe]	10 h 50°C/	96	/
3	II	5	50°C/	/	96/99
4	II	[Ru]	14 h 50°C/ 14 b	/	98/99
5	cascade	[Fe] → [Bu]	50°C/	83	ND
6	cascade	(Fe] + 5	50°C/	65	35/88
7	cascade	4 +[Ru]	24 II 50°C/	38	62/91
8	cascade	5	24 n 50°C/	trace	91/99
9	cascade	4 +5′	24 h 50°C/ 24 h	trace	90/99
[a] Reaction conditions: For the reaction I, catalyst (20.0 mol% of FeCl ₃ ,					

 Table 1. The optimization of the reaction conditions.^[a]

[a] Reaction conditions: For the reaction I, catalyst (20.0 mol% of FeCl₃, based on TG analysis), **6a** (0.20 mmol), **7a** (0.30 mmol), EtOH/H₂O (v/v=3) 1, 4 mL), under air atmosphere, 50 °C, 10 h. For reaction II, catalyst (2.50 mol% of Ru, based on ICP analysis), **8a** (0.20 mmol), and HCOONa (10 equiv.), EtOH/H₂O (v/v=3:1, 4 mL), under air atmosphere, 50 °C, 14 h. For cascade reaction, catalysts (20.0 mol% of FeCl₃, based on TG analysis, and 2.51 mol% of Ru, based on ICP analysis), **6a** (0.2 mmol), **7a** (0.3 mmol), HCOONa (10 equiv.), EtOH/H₂O (v/v=3:1, 4 mL), under air atmosphere, 50 °C, 24 h. [b] All yields were determined using ¹H NMR spectroscopy and the *ee* values were determined using chiral HPLC analysis. [Ru]= MesRuTsDPEN, and [Fe]=FeCl₃. ND=not detected.

aerobic oxysulfonylation/ATH cascade process. The reaction with the 1: 1.5 of the mole ratio of **6a** to **7a** was carried out at 50 °C for the first 14 h. After completion of the aerobic oxysulfonylation, the HCO₂Na was then added to this solution and further stirred at 50 °C for the second 24 h. In this case, we performed three aspects of comparisons to demonstrate the benefit of the designed bifunctional catalyst. In the first comparison, we integrated the homogeneous FeCl₃ and chiral



Figure 5. XPS spectra of MesRuTsDPEN and catalyst 5.



MesRuTsDPEN (instead of MesRuArDPEN) into a co-catalysts system. It was found that the cascade reaction of **6a** and **7a** mainly produced the intermediate **8a** in 83% yield without the final product (Entry 5, Table 1). As compared with the catalytic result of the single-step aerobic oxysulfonylation, a decreased yield from 96% to 83% yield indicated MesRuTsDPEN species in this homogeneous co-catalyst system affected the catalytic function of the FeCl₃ species. Moreover, no final product also revealed the negative cross-interactions between the FeCl₃ and chiral MesRuTsDPEN species, where the FeCl₃ species destroyed the catalytic and enantioselective performance of the chiral MesRuTsDPEN species.

In the second comparison, we combined the FeCl₃ plus supported **5**', and the supported **4** plus MesRuTsDPEN, into two co-catalyst systems. It was found that the cascade reactions in both co-catalyst systems could produce the final product (**9a**). However, both yields and *ee* values were lower than those attained with the single-step ATH transformations (entries 6–7 versus entries 3 and 1, Table 1). When compared both co-catalyst systems with the corresponding homogeneous co-catalyst system (entries 6–7 versus entry 5, Table 1), the observed final products also indicated that the combination of the supported catalyst and homogeneous one as a co-catalyst system could eliminate the negative cross-interactions to a certain extent.

In the third comparison, we directly used **5** as a bifunctional catalyst. As shown in entry 8, this cascade reaction catalyzed by **5** could produce the target product (**9a**) in 91% yield with 99% *ee.* Such a catalytic performance was not only markedly better than those attained with the other two co-catalyst systems (entry 8 versus entries 5–7, Table 1) but also were compared to those obtained with their corresponding two single-step transformations and the physically mixed supported **4** plus **5'** as dual-catalysts (entry 8 versus entries 2, 4, and 9, Table 1). This observation disclosed that this bifunctional magnetic catalyst eliminated the negative cross-interactions between the FeCl₃ and chiral MesRuTsDPEN species, which could be confirmed by a time course investigation of catalyst **5** in the reaction of phenylacetylene (**6a**) and sodium benzenesulfinate (**7a**) (see Figure S4 in the ESI).

Finally, a series of aryl-substituted alkynes and sodium sulfinates were further tested based on the optimal reaction conditions, as shown in Table 2. It was found that all the tested aerobic oxysulfonylation/ATH one-pot processes could steadily provide various chiral β -hydroxysulfones in good yields and excellent enantioselectivities. It was worth mentioning that the structures and electronic properties of the substituents on the aromatic rings for the aryl-substituted alkynes and sodium sulfinate did not significantly affect their enantioselectivities because the electron-withdrawing (F, Cl, and Br) or -donating substituents (MeO, Me, and Ph) on the aromatic rings were equally efficient. Moreover, thienyl- and pyridyl-substituted terminal alkynes could also be converted into their corresponding final products (9i-9j). In addition, the other sodium aryl sulfinates, such as sodium 4-methylbenzenesulfinate and sodium 4-chlorobenzenesulfinate, could steadily react with



(v/v = 3:1) were added sequentially to a 10.0 mL round – bottom flask. The resulting mixture was then stirred at 50 °C for the first 10–16 h. After completion of the aerobic oxysulfonylation, the HCO₂Na (2.0 mmOl) was added to this solution and the resulting mixture was then stirred at 50 °C for the second 14–24 h. All yields were determined using ¹H NMR spectroscopy and the *ee* values were determined using chiral HPLC analysis (see Figures S5 and S7 in the ESI).

phenylacetylene to produce the corresponding β -hydroxysulfones (9 k-9 l) with excellent *ee* values.

Besides the general substrates tolerability (Table 2), the size selectivity of the nanopores of this magnetic catalyst was also investigated. In this case, the aerobic oxysulfonylation/ATH one-pot process with a mixture of the large-sized 1-ethynylpyrene (**6k**) and small-sized phenylacetylene (**6a**) as competitive substrates was carried out, as shown in Scheme 2. It was found that the main products were **9a** (90% yield and 99% ee) along with a small amount of (*S*)-2-(phenylsulfonyl)-1-(pyren-1-yl) ethan-1-ol (**9m**). As compared the result of **9m** (18% yield and 92% ee) with two homogeneous single-step reactions, the aerobic oxysulfonylation of **6k** (91% yield) and ATH transformation of 2-(phenylsulfonyl)-1-(pyren-1-yl)ethan-1-one (**8k**) (85% yield and 93% ee), a markedly decreased yield of **9m** in Scheme 2 suggested a size selectivity of the nanopores owing to the sterically hindered effect of **6k**.



Scheme 2. Investigation of the substrate selectivity in the supported cocatalytic system.



Catalyst's recyclability

An important consideration for the design of this magnetic catalyst expects efficient recovery and recycling due to its magnetic nature. In this case, it was found that catalyst **5** was easily recovered *via* an outer magnet near the bottle. As shown in Figure 6, in a consecutive aerobic oxysulfonylation/ATH onepot process of phenylacetylene and sodium benzenesulfinate by setting the reaction time to be within 26 h to test catalyst recyclability,^[15] we found that the recycled catalyst **5** could be reused for six times. In the sixth run, the dual catalysis could still produce the chiral final **9a** in 86% yield with 98% *ee* value, where the Ru-loss in catalyst **5** after the sixth run was 7.3% detected by an inductively coupled plasma optical emission spectrometer (ICP–OES) analysis (see Table S2 and Figure S6 in the ESI).

Conclusion

In conclusion, by utilizing a yolk-shell-structured magnetically mesoporous silica as a support, we immobilize chiral Ru/ diamine species into the nanochannels of the outer mesoporous silica shell and the FeCl₃ species on the inner magnet core, constructing a bifunctional magnetic catalyst. As presented in this study, the bifunctional catalyst enables an efficient aerobic oxysulfonylation/ATH one-pot cascade process. The supported FeCl₃/diamine species proceeds an aerobic oxysulfonylation between aryl-substituted alkynes and sodium sulfinates to produce β -keto sulfones intermediate, whereas the supported Ru/diamine- species could sequentially reduce the in-situ generated intermediate, affording various chiral β -hydroxysulfones products with enhanced yields and enantioselectivities. Furthermore, the catalyst can be easily recovered via an outer magnet and repeatedly recycled, presenting a practical advantage in the application. The study here also highlights a compartmentalization-type immobilization method to overcome the negative cross-interactions between FeCl₃ and chiral Ru/diamine-complexes for the realization of feasible sequential enantioselective organic transformation.



Figure 6. Reusability of the aerobic oxysulfonylation/ATH one-pot process of phenylacetylene and sodium benzenesulfinate (the error bars represent the standard deviation).

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Experimental Section

Preparation of catalysts 4-5

In a typical synthesis, (Coating with 1,2-bis(triethoxysilyl)ethane and ArDPEN-siloxane) the obtained solids $Fe_3O_4@SiO_2$ (1) (0.40 g) were suspended in an alkaline solution (0.70 mL of NaOH (2.0 M) in mixed 250.0 mL of water and 50.0 mL of ethanol with ultrasonication for 20 minutes. After that, an aqueous solution (0.08 g (0.088 mmol) of FC-4, 0.16 g (0.44 mmol) of CTAB and 0.40 mL (25 wt%) of NH₃·H₂O in 3.0 mL of water) was added, and the mixture was stirred at 38°C for another 30 minutes. Next, 0.89 g (2.50 mmol) of 1,2-bis(triethoxysilyl)ethane and 0.15 g (0.27 mmol) of ArDPEN-siloxane in 2.0 mL of ethanol (2 minutes later) was added at room temperature, and the mixture was stirred under vigorous stirring for a further 1.5 h. Finally, the temperature was raised to 80 °C and the mixture was stirred at 80 °C for another 3 h. After cooling the above mixture down to room temperature, the solid was collected by filtration to afford the Fe₃O₄@SiO₂@[Si] (2) as a black powder. (Selective etching of SiO₂) To remove the surfactant, the collected 2 were dispersed in 120 mL of solution (80 mg (1.0 mmol) of ammonium nitrate in 120 mL (95%) of ethanol), and the mixture was stirred at 60°C for 10 h. After cooling the above mixture down to room temperature, the solids were filtered and washed with excess water and ethanol, and dried at 60 °C under vacuum overnight to afford the Fe₃O₄@[Si] (3) (0.68 g) as a darkgray powder. (Encapsulation with FeCl₃) An aqueous solution (0.30 g (1.85 mmol) of FeCl₃ in 3.0 mL of water) was added to $\bf 3$ at room temperature under vacuum, and the resulting mixture was filtered and dried at 60 $^\circ\text{C}$ at room temperature. (Coordination with (MesRuCl₂)₂) 50.0 mg (0.086 mmol) of (MesRuCl₂)₂ was added to a suspension of 4 (0.50 g) in 20.0 mL of dry CH₂Cl₂ at room temperature, and the resulting mixture was stirred at 25 °C for 12 h. The solids were filtered and rinsed with excess dry CH₂Cl₂. After Soxhlet extraction for 4.0 h in $CH_2CI_{2'}$ the solids were collected and dried at 60 °C under vacuum overnight to afford the magnetic catalyst 4 as a brownish red powder. The TG analysis showed the FeCl₃-loading was 128.64 mg (0.7941 mmol) per gram of catalyst. An inductively coupled plasma optical emission spectrometer (ICP-OES) analysis showed that the Ru loadings were 50.39 mg (0.4989 mmol of Ru) per gram of catalyst.

General procedure for tandem reaction

In a typical procedure, catalyst 5 (50.37 mg, 20.0 mol% of FeCl₃, based on TG analysis and 2.51 mol% of Ru, based on ICP analysis), alkynes (0.20 mmol), and sodium sulfinates (0.30 mmol), and 4.0 mL of EtOH/H₂O (v/v=3:1) were added sequentially to a 10.0 mL round-bottom flask. The resulting mixture was then stirred at 50 °C for the first 10-16 h. After completion of the aerobic oxysulfonylation, the HCO₂Na (2.0 mmol) was added to this solution and the resulting mixture was then stirred at 50 °C for the second 14-24 h. During this period, the reaction was monitored by TLC. After completion of the reaction, the catalysts were separated by an external magnet for the recycling experiment. The aqueous solution was extracted with ethyl ether $(3 \times 3.0 \text{ mL})$. The combined ethyl ether extracts were washed with aqueous ${\sf Na_2CO_3}$ and then dehydrated with Na2SO4. After evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford the desired product. The ee values were determined using HPLC analysis using a UV-Vis detector and Daicel chiral-cel column (Φ 0.46 \times 25 cm).



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Conflict of Interest

The authors declare no conflict of interest.

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FULL PAPERS



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cascade reaction of aryl-substituted alkynes and sodium sulfinates process to afford various chiral β -hydroxysulfones in good yields and excellent enantioselectivities.

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A Compartmentalized-type Bifunctional Magnetic Catalyst for One-pot Aerobic Oxysulfonylation and Asymmetric Transfer Hydrogenation C