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### Supporting Information for

## Enantioselective 1,2-Reductions of β-Trifluoromethylated-α,β-Unsaturated Ketones to Chiral Allylic Alcohols over Organoruthenium-Functionalized Mesoporous Silica Nanospheres

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### Experimental

### 1. General

All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using the standard Schlenk techniques. (R,R)-1,2-diphenylenediamine, [RuCl<sub>2</sub>(p-Cym)]<sub>2</sub>, triethanolamine (TEAH), surfactant cetyl-trimethylammonium tosylate (CTATos), tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich Company Ltd. Compounds (R,R)-4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylenediamine and the pure MSNs material were synthesized according to the reported literatures [a) *J. Mater. Chem.* **2010**, *20*, 1970. and b) *J. Am. Chem. Soc.* **2013**, 135, 2427.]

# 2. General procedure for the reuse experiments using 4,4,4-trifluoro-1,3-diphenylbut-2-enone as a substrate.

The catalyst **5** (272.50 mg, 0.10 mmol of Ru, based on ICP analysis),  $\beta$ -trifluoromethylated- $\alpha$ , $\beta$ unsaturated ketones (10.0 mmol) and 10.0 mL of HCOOH-NEt<sub>3</sub> (5:2) were added sequentially to a 50.0 mL round-bottom flask. The mixture was then stirred at room temperature (20 °C) for 20 h. After completion of the reaction, the catalyst was separated by centrifugation (10,000 rpm). The collected solids was transfered to a fresh 50.0 mL round-bottom flask and  $\beta$ -trifluoromethylated- $\alpha$ , $\beta$ -unsaturated ketones (10.0 mmol) and 10.0 mL of HCOOH-NEt<sub>3</sub> (5:2) were added sequentially again for next recycle. The aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with NaHCO<sub>3</sub> and brine, and then dehydrated with Na<sub>2</sub>SO<sub>4</sub>. After evaporation of ethyl ether, the residue was purified by silica gel flash column chromatography to afford the desired product, determining its yield and ee value.







**Explanation:** The TG/DTA curves of MSNs materials were treated in the air as shown above. An endothermic peak around 340K with weight loss of (100-93.42) 6.58% could be attributed to the release of physical adsorption water while the comprehensive endothermic peaks between 430K and 1100K with weight loss of (93.42-85.48) 7.94% could be assigned to the release of the residual CTATos surfactant (cetyl-trimethylammonium tosylate) within the extracted samples, which is strongly same as that reported in the literature (V. Cauda, A. Schlossbauer, J. Kecht, A. Zürner, T. Bein, *Am. Chem. Soc.*, 2009, **131**, 11361). Apparently, totally weight loss of the residual CTATos surfactant was 7.94% per 93.42% the extracted samples when eliminated the part of water, meaning the 8.50% weight loss of the residual CTATos surfactant per 100% materials.

For the TsDPEN-functionalized mesoporous silica nanospheres (**3**), it was found easily that a similar endothermic peak around 340 K with weight loss of (100-91.52) 8.48% were strongly similar to that of parent MSNs materials due to the release of physical adsorption water. It was worth mentioning that the all exothermic peaks were combined into one complicated exothermic peak between 430K and 1100K with weight loss of (91.52-56.01) 35.51% could be assigned to the oxidation of organic molecules (including ArDPEN moiety, alkyl fragments and part of the residual CTATos surfactant). Because the totally weight loss of organic molecules was 35.51% per 91.52% the extracted catalyst when eliminated the part of water, meaning the whole weight loss 38.80% of the oxidation of the organic molecules (including CymeneRuArDPEN complexes, ArDPEN moiety, alkyl fragments and part of the residual CTATos surfactant) per 100% materials. In contrast to the weight loss of the residual CTATos

surfactant in MSNs materials, the true weight loss of ArDPEN organic molecules was 30.30% (38.80-8.50) per 100% materials.

For catalyst **5**, an endothermic peak around 348 K with weight loss of (100-93.17) 6.83% could be attributed to the release of physical adsorption water. In addition, the weight loss of (93.17-51.20) 41.97% between 430 and 1100 K could be assigned to the oxidation of the organic moieties (including CymeneRuArDPEN complexes, ArDPEN moiety, alkyl fragments and part of the residual CTATos surfactant). Because the totally weight loss of organic moieties was 41.97% per 93.17% the extracted catalyst when eliminated the part of water, meaning the whole weight loss 45.05% of the oxidation of the organic molecules (including CymeneRuArDPEN complexes, ArDPEN molecules, ArDPEN molecules, ArDPEN molecules (and part of the residual CTATos surfactant) per 100% materials. As compared the weight loss of catalyst **5** with ArDPEN-functionalized MSNs (**3**), the weight loss of the ArRu moieties was 6.25% (45.05-38.80). Thus, the mole ratio of ArDPEN molecules to ArCl moieties was 2.1 [0.0797 (30.30/380) : 0.0372 (6.25/168)], meaning that TsDPEN molecules are excess.

In contrast to TG/DTA curve of ArDPEN-functionalized MSNs (3) and catalyst 5, the true weight loss of ArCl moieties is 6.25% (45.05-38.80), meaning the mole amounts of ArCl is 0.0372 mol% (Mr = 168). The mole amount of Ru (Mr = 101) in the material is 0.372 mmol (37.57 mg) per gram material.

In conclusions, two results could be obtained through above calculations. One is that TsDPEN molecules are excess. Another is that The mole amount of Ru (Mr = 101) is 0.372 mmol (37.57 mg) per gram material.

**Figure S2.** XPS spectra of [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> and [Cp\*RhCl<sub>2</sub>]



Figure S3. SEM and TEM images of ArDPEN-MSN<sub>S</sub> (3). SEM image of ArDPEN-MSN<sub>S</sub> (3).



TEM image of ArDPEN-MSN<sub>S</sub> (3).



Figure S4. SEM image of Ru-SiO<sub>2</sub>.



**Figure 6c.** Enlarged TEM image with a chemical mapping of **5** showing the distribution of Si (white) and Ru (red).



	$\mathbf{R}_1$ C	) Cat	talyst	$\mathbf{R}_1$ OH	
	F <sub>3</sub> C	$R_2$ HCO 20	$\overline{OH-Et_3N}$ $F_3$	C R <sub>2</sub>	
Entry	<b>R</b> <sub>1</sub>	$\mathbf{R}_2$	Time(h)	%Yield <sup>b</sup>	%ee <sup>b</sup>
1	Ph	Ph	20 (15)	98(97)	97 (97) <sup>c</sup>
2	Ph	Ph	30	90	96 <sup>d</sup>
3	Ph	Ph	20	92	96 <sup>e</sup>
4	Ph	Ph	36	95	95 <sup>f</sup>
5	<i>p</i> -FPh	Ph	20	97	97(96)
6	<i>p</i> -ClPh	Ph	20	95	96(97)
7	<i>p</i> -BrPh	Ph	20	93	96(97)
8	<i>p</i> -MePh	Ph	20	96	96(98)
9	<i>p</i> -MeOPh	Ph	20	93	95(97)
10	<i>p</i> -CF <sub>3</sub> Ph	Ph	24	98	94(94)
11	o-MeOPh	Ph	20	99	93(95)
12	Bn	Ph	24	92	89(90)
13	Me	Ph	20	93	92(92)
14	Ph	<i>p</i> -ClPh	20	97	93(93)
15	Ph	<i>p</i> -BrPh	20	94	94(95)
16	Ph	<i>p</i> -MePh	20	93	96(97)
17	Ph	<i>p</i> -MeOPh	20	95	97(98)
18	Ph	<i>m</i> -FPh	20	95	91(91)
19	Ph	<i>m</i> -ClPh	20	94	93(93)
20	Ph	<i>m</i> -BrPh	20	93	92(94)
21	Ph	o-MeOPh	20	92	94(96)
22	Ph	Me	17	96	29 (24)
23	Ph	<i>t</i> -Bu	20	93	10 (11)
24	<i>p</i> -FPh	<i>p</i> -BrPh	24	94	92(93)
25	<i>p</i> -BrPh	<i>p</i> -BrPh	24	92	92(92)

**Table 1.** Enantioselective 1,2-reductions of  $\beta$ -trifluoromethylated- $\alpha$ , $\beta$ -unsaturated ketones.<sup>a</sup>

<sup>a</sup> Reaction conditions: catalyst **5** (27.25 mg, 10.0  $\mu$ mol of Ru based on ICP analysis),  $\beta$ -trifluoromethylated- $\alpha$ , $\beta$ -unsaturated ketones (1.0 mmol), 1.0 mL of HCOOH-NEt<sub>3</sub> (5:2), and reaction time (15-30 h). <sup>b</sup> Yields were determined by <sup>1</sup>H-NMR and ee values were determined chiral HPLC analysis (see SI in Figures S5, S7). <sup>c</sup> Data in bracket were obtained in reported literature.<sup>[6a] d</sup> Data were obtained at substrate-to-catalyst mole ratio of 200. <sup>e</sup> Data were obtained using the mixed **3** and its homogeneous CymeneRuTsDPEN. <sup>f</sup> Data were obtained using a parallel CymeneRuArDPEN-SiO<sub>2</sub> as a catalyst.

**Figure S5.** Enantioselective 1,2-reductions of  $\beta$ -CF<sub>3</sub>-substituted- $\alpha$ , $\beta$ -unsaturated ketones. [The products of ATH were analyzed by a HPLC with a UV-Vis detector using a Daicel OD-H or AD-H chiralcel column ( $\Phi$ 0.46×25 cm)].

Translation of Chinese to English is as follows:

F	ea	ık	RetTim [min]	re Area	Area%	6 Heigl	ı									
	t		t	ŧ	ŧ	ŧ										
	6	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	结构1 名	结构 1 说明	结构 1 分子量	结构 1 公式	结构 1 结构
	1		7.240	29377113	100.00	2033967	8B			未知						C

(*R*,*E*)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C). [Literature (Angew. Chem. Int. Ed. 2012, 51, 6467–6470): HPLC: Chiracel OD-H, flow rate: 1 mL/min, UV = 254 nm, n-hexane/2-propanol = 95/5,  $\tau_{major} = 5.8 \text{ min}, \tau_{minor} = 6.6 \text{ min.}$ ]



Data were obtained at substrate-to-catalyst mole ratio of 200.



Data were obtained using the mixed 3 and its homogeneous CymeneRuArDPEN.



Data were obtained using a parallel CymeneRuArDPEN-SiO<sub>2</sub> as a catalyst





(*R*,*E*)-4,4,4-trifluoro-3-(4-fluorophenyl)-1-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).



(*R*,*E*)-3-(4-chlorophenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).



(*R*,*E*)-3-(4-bromophenyl)-4,4,4-trifluoro-1-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C). [Literature (Angew. Chem. Int. Ed. 2012, 51, 6467–6470): HPLC :Chiracel OD-H, flow rate : 1 mL/min, UV = 254 nm, n-hexane/2-propanol = 95/5,  $\tau_{major}$  = 5.7 min,  $\tau_{minor}$  =7.6 min.]



(*R*,*E*)-4,4,4-trifluoro-1-phenyl-3-(p-tolyl)but-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).





## (R,E)-4,4,4-trifluoro-3-(4-methoxyphenyl)-1-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).

CF<sub>3</sub> \* 0.30-9.873 32 OH 0.20 F<sub>3</sub>C R  $(\pm)$ 0.10 -0.00 1.00 2.00 3.00 4.00 5.00 8.00 9.00 10.00 11.00 6.00 7.00 12.00 13.00 分钟 + • 保留时间 面积 高度 结构1 结构1 结构1 分子量 结构1 结构1 名称 积分类型 单位 峰类型 峰代码 % 面积 含量 (微伏•秒) (微伏) (分钟) 名 说明 公式 结构 未知 C 7.258 VV 7735758 49.86 215805 9.873 未知 C 2 7778535 50.14 218627 VB . CF<sub>3</sub> CF<sub>3</sub> 0.12-0.10-OH QН 0.08 F<sub>3</sub>C F<sub>3</sub>C (*R*) (S)₹ 0.06-0.04 9.954 0.02 4 0.00 • 1.00 3.00 4.00 6.00 2.00 5.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 分钟 4 . 高度 (微伏) 结构1 名 保留时间 面积 结构1 结构1 结构1 结构1 峰代码 名称 积分类型 含量 单位 峰类型 % 面积 分子量 (微伏地) (分钟) 说明 公式 结构 未知 C 1 3752515 97.32 108833 VB 7.113 C 2 9.954 103430 2.68 未知 4154 bb

(*R*,*E*)-4,4,4-trifluoro-1-phenyl-3-(4-(trifluoromethyl)phenyl)but-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, 25 °C).

## (*R*,*E*)-4,4,4-trifluoro-3-(2-methoxyphenyl)-1-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).



(*R*,*E*)-1-(4-chlorophenyl)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).







(*R*,*E*)-1-(4-bromophenyl)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, 25 °C).

(*R*,*E*)-4,4,4-trifluoro-3-phenyl-1-(p-tolyl)but-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).





(*R*,*E*)-4,4,4-trifluoro-1-(4-methoxyphenyl)-3-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).



## 13 (R,E)-4,4,4-trifluoro-1-(3-fluorophenyl)-3-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H,

detected at 254 nm, eluent: n-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, 25 °C).



未知

23.631

59964

4.31

1082 bb

O

(*R*,*E*)-1-(3-chlorophenyl)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol: (HPLC: Chiracel AD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).





(*R*,*E*)-1-(3-bromophenyl)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol: (HPLC: Chiracel AD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).





## (*R*,*E*)-4,4,4-trifluoro-1-(2-methoxyphenyl)-3-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).



## (*R*,*E*)-1-(4-bromophenyl)-4,4,4-trifluoro-3-(4-fluorophenyl)but-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).



6	名称	(分钟)	面积 (微伏*秒)	% 面积	周度 (微伏)	积分类型	含量	单位	峰类型	峰代码	名	说明	分子量	公式	结构
1		6.852	33284704	49.88	1566593	vv			未知						9
2		7.783	33449774	50.12	1464617	VV -			未知						C



(*R*,*E*)-1,3-bis(4-bromophenyl)-4,4,4-trifluorobut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).





(*R*,*E*)-3-benzyl-4,4,4-trifluoro-1-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).





(*R*,*E*)-4,4,4-trifluoro-3-methyl-1-phenylbut-2-en-1-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C).



未知

2

11.716

23254017

96.20

1109835

VV

O

(*R*,*E*)-5,5,5-trifluoro-4-phenylpent-3-en-2-ol: (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C). [Literature (Angew. Chem. Int. Ed. 2012, 51, 6467 –6470): HPLC :Chiracel OD-H, flow rate : 1 mL/min, UV = 254 nm, n-hexane/2-propanol = 97/3,  $\tau_{major} = 6.0 \text{ min}, \tau_{minor} = 6.8 \text{ min.}$ ]



(*R*,*E*)-6,6,6-trifluoro-2,2-dimethyl-5-phenylhex-4-en-3-ol: (HPLC: Chiracel AD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, 25 °C). [Literature (Angew. Chem. Int. Ed. 2012, 51, 6467 –6470): HPLC :Chiracel OD-H, flow rate : 1 mL/min, UV = 254 nm, n-hexane/2-propanol = 95/5,  $\tau_{major}$  = 4.7min,  $\tau_{minor}$  = 5.6 min.]







**Figure S6.** Reusability of the catalyst using 4,4,4-trifluoro-1,3-diphenylbut-2-enone as a substrate. Recycle 2.





Recycle 4



### Recycle 5



#### Recycle 6



### Recycle 7



#### Recycle 8

7.687

283034

2.55

20475 bb



未知

2	2
2	4

0













































