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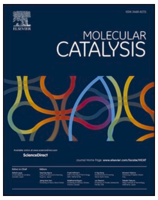

Iridium and copper supported on silicon dioxide as chemoselective catalysts for dehydrogenation and borrowing hydrogen reactions

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ABSTRACT

High active ligand usually plays an important role during catalysis and synthesis chemistry. A new and efficient benzotriazole-pyridinyl-silane ligand (BPS) was designed, and the corresponding iridium and copper catalysts were synthesized and thoroughly characterized by means of EDS, TEM, and XPS. The resulting iridium composite revealed excellent catalytic activity for the reaction of tert-butanesulfinamide with benzyl alcohols, while copper catalyst could realize the synthesis of unsaturated carbonyl compounds through the reaction of benzyl alcohols with ketones. This provided an efficient method for selective synthesis of unsaturated carbonyl compounds from benzyl alcohols and ketones in high yields with good recovery performance.

1. Introduction

Functional sulfinamides and amines have been obtained much attention in medicinal and synthetic chemistry in the past [1] More specifically, sulfinamides are commonly employed in the synthesis of bioactive molecules or intermediates including sulphonamides [2]. Classic methods for N-alkylsulfinamides synthesis include the reaction of amines with active sulfinyl derivatives and N-alkylation of primary sulfinamides [3]. Most methods usually rely on a strong base or acid under harsh conditions, or the stoichiometric generation of undesired byproducts.

The construction of C—C and C—N bonds with alcohols as an alkylation reagent has been considered as a green and efficient method [4], which has gained great attention during the past twenty years [5]. The process of this transformation is usually involved in removing hydrogen to generate ketones (or aldehydes) [6]. After formation of C—C or C—N double bonds, the alkylated products are reduced by using H_2 generated in the upper dehydrogenation step [7]. Water is normal obtained as the sole byproduct and the atom efficiency of this reaction is particularly high [8]. Therefore, the synthesis of sulfinamides and sulphonamides through borrowing hydrogen strategy is highly desirable and reasonable [9]. In 2011, Ramón and Yus reported an inexpensive, versatile, and simple impregnated ruthenium catalytic system for the selective N-monoalkylation of amino derivatives with poor nucleophilic character, such as sulfonamides and sulfinamides used in all cases alcohols with highly selectivity [10]. Xu group described an aldehyde-catalyzed the synthesis of sulfonamides through N-alkylation method with wide substrate adaptability [11]. Dong and Guan found the commercially available ruthenium(II) PNP-type pincer catalyst (Ru-Macho) could promote the synthesis of α-chiral *tert*-butanesulfinylamines from secondary alcohols and Ellman's chiral *tert*butanesulfinamide in good yields [12]. Beller and co-workers discovered the novel rhenium complex bearing a non-innocent PNP pincer could realize the valuable alkylations of ketones and sulfonamides with primary alcohols in high to moderate yields in presence of low concentrations of base [13]. Morrill and co-workers reported an efficient manganese-catalyzed N-alkylation of sulfonamides with a well-defined and bench-stable Mn (I)-PNP pincer precatalyst in excellent isolated yields [14]. Lei, Xiao and Wang reported a practical and convenient method for the synthesis of a-chiral amines by the alkylation of amines with alcohols. Mechanistic explorations including DFT calculations revealed that this hydrogen autotransfer reaction is initiated by a ketone catalyst [15].

Recently, we developed several triazole-based ligands and the corresponding metal catalysts, which could be used for several classical dehydrogenation and borrowing hydrogen reactions with moderate to high yields [16]. However, the high cost and difficulties in recovery of these noble metals have limited the practical applications. Based on the above considerations and our previous research [17], herein, we designed and synthesized a new benzotriazole-pyridinyl-silane skeleton ligand, which could be used to prepare recyclable iridium and copper supported on SiO_2 catalysts (Scheme 1).

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2. Experimental

2.1. The synthesis of BPS-Cu@SiO_2

The unsymmetrical benzotriazole-pyridinyl-silane (BPS) ligand (L) was synthesized in three steps and purified with moderate yield. (Scheme 2) [18]. With BPS in hand, the corresponding iridium and copper catalysts were prepared as follows: To a mixture of ligand **L** (504 mg, 1.1 mmol) and CuI (57 mg, 0.30 mmol) in a dried Schlenk tube with a stirring bar, acetonitrile (15 mL) was added under N_2 atmosphere, the mixture was stirred at room temperature for 12 h until a yellow sediment (BPS-Cu) appeared. After removing the solvent, the sediment was washed with dichloromethane, water and ethanol for three times. Subsequently, SiO_2 (600 mg) was added to the Schlenk tube with BPS-Cu (270 mg), DMSO as a solvent, the resulting mixture was stirred vigorously at 140 °C for 48 h, BPS-Cu@SiO_2 was obtained after filtrating and washing with water and ethanol for four times. Meanwhile, BPS-Ir@SiO_2 was also obtained according to the upper steps (see supporting information for details).

3. Results and discussion

After the synthesis, BPS-Cu@SiO_2 and BPS-Ir@SiO_2 were both carefully characterized through energy dispersive spectrometer (EDS), X-ray photoelectron spectrometry (XPS) and transmission electron microscopy (TEM).

TEM images of Fig. 1b, c showed that copper composite was successful supported on the carrier, and the Fig. 1d demonstrated that iridium was successful supported on the SiO_2 [19]. The structural characteristics and morphologies of the catalysts (BPS-Cu@SiO_2 and BPS-Ir@SiO_2) were observed clearly through the transmission electron microscopy.

In addition, EDS studies were conducted to further examine these composites, and the EDS pattern showed peaks at 2.3, 8.0 and 9.1 keV were characteristic peaks of Cu, and in next EDS image, the peaks at 2.8, 9.3 and 11.3 keV belonged to Ir (Fig. 2a, b). The contents of copper and iridium in the catalysts were obtained 8.56 % and 2.35 % mass fraction from EDS. The chemical composition and surface chemical states of the catalyst composite were shown *via* X-ray photoelectron spectroscopy (XPS). The wide XPS spectra indicated the presence of C, N and Cu elements (Fig. 2c) and it was clear that C, N and Ir elements were detected from Fig. 2d, and the peaks at binding energies of 935 eV and 953 eV belonged to Cu, and the peaks at 60 eV and 63.6 eV came from iridium. All the characterizations provided a direct proof for the successful preparation of BPS-Cu@SiO_2 and BPS-Ir@SiO_2 composites.

Compared to classical borrowing hydrogen reaction of amines with alcohols, the transformation of *tert*-butanesulfinamide with alcohols is much more difficult to realize. Therefore, the reaction of benzyl alcohol and *tert*-butanesulfinamide was selected as a model reaction to test the catalyst activity of BPS-Cu@SiO_2 and BPS-Ir@SiO_2. The results disclosed that BPS-Ir@SiO_2 showed much higher catalytic activity (Table 1). After a series of explorations, it was revealed that base was important for this reaction and sodium hydroxide was best base. Next, the effect of solvents was also explored and it was found that dioxane could produce 84 % yield of desired product. However, CH_2Cl_2 and CH_3OH couldn't promote this reaction. Further screening revealed toluene was the most effective solvent. After a series of condition screenings, we were pleased to find that the best result (95 % yield) was gained with BPS-Ir@SiO_2, while only ligand could not catalyze this transformation (entry 13). It should be noted that the reaction of benzyl alcohol with *tert*-butanesulfinamide couldn't happen in water (Table 1, entry 18). Finally, we tested temperature and reaction time under the condition of BPS-Ir@SiO_2 and optimal solvent. It was disclosed that the combination of 120 °C with 24 h was suitable conditions.

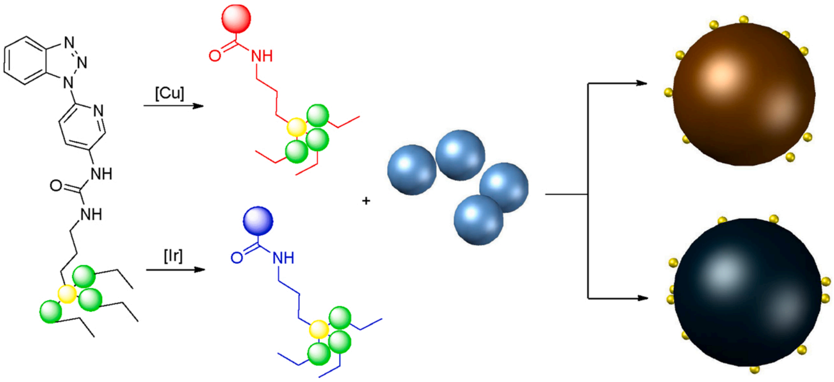
Subsequently, the substrate expansion of this reaction of various benzyl alcohols and *tert*-butanesulfinamides was next examined (Table 2). It was revealed that the substrates with -F, -Br, -Cl on the aryl group moieties could produce the corresponding N-benzyl-2-methylpropane-2-sulfinamides in high yields. Benzyl alcohols with $-OCH_3$ or -X substituents were converted into the desired products in good yields. Interestingly, piperonyl alcohol and 2-naphthalenemethanol could also react with 2-methylpropane-2-sulfinamide smoothly and generate the products in moderate yields (4 l**, 4 m**).

The selective synthesis of substituted ketones and unsaturated carbonyl compounds from benzyl alcohols is a challenging issue, which are both atom-efficient processes, only water (or water with hydrogen gas) produced as byproducts. Considering the success of BPS-Ir@SiO_2 catalyzed reaction of benzyl alcohol and *tert*-butanesulfinamide, we next focused on the reaction of ketones and benzyl alcohols.

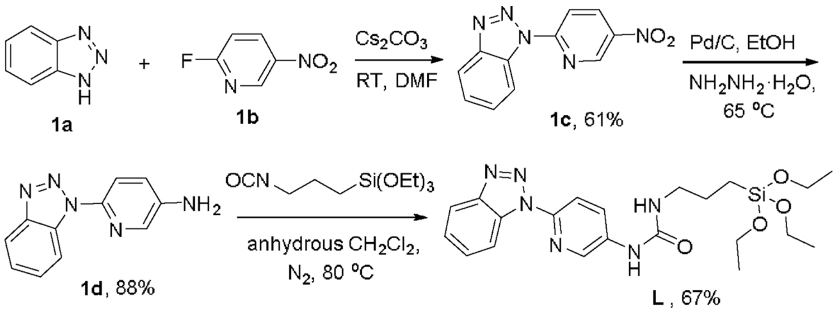
After a series of tests, we found BPS-Cu@SiO_2 could generate **6a** in high yields with high selectivity, while BPS-Ir@SiO_2 only gave a mixture of phenylpropiophenone and chalcone. Therefore, BPS-Cu@SiO_2 was used to explore the reaction of benzyl alcohols and substituted ketones. As shown in Table 3, a wide range of alcohol substrates with functional groups were all tolerated, including -Cl, -F, -Br, $-OCH_3$ and $-CH_3$, the corresponding unsaturated carbonyl compounds were achieved in good to excellent yields. The substrates bearing $-CH_2CH_3$ and -Ph gained the corresponding products in 80 %, 86 % yields, respectively. 2-Naphthalenemethanol was also suitable to this transformation, yielding **6z** in 94 % yield.

3.1. Mechanism exploration

The excellent catalytic activity of BPS-Cu@SiO_2 and BPS-Ir@SiO_2 system in these transformations stimulated us to investigate the possible reason of these two BPS-based copper and iridium catalytic systems. We noticed that BPS-metal was coupled with SiO_2 through silane partner of ligand, which was an important factor for this high catalytic activity. It



Scheme 1. The benzotriazole-pyridinyl-silane based copper and iridium catalysts.



Scheme 2. The synthesis of benzotriazole-pyridinyl-silane.

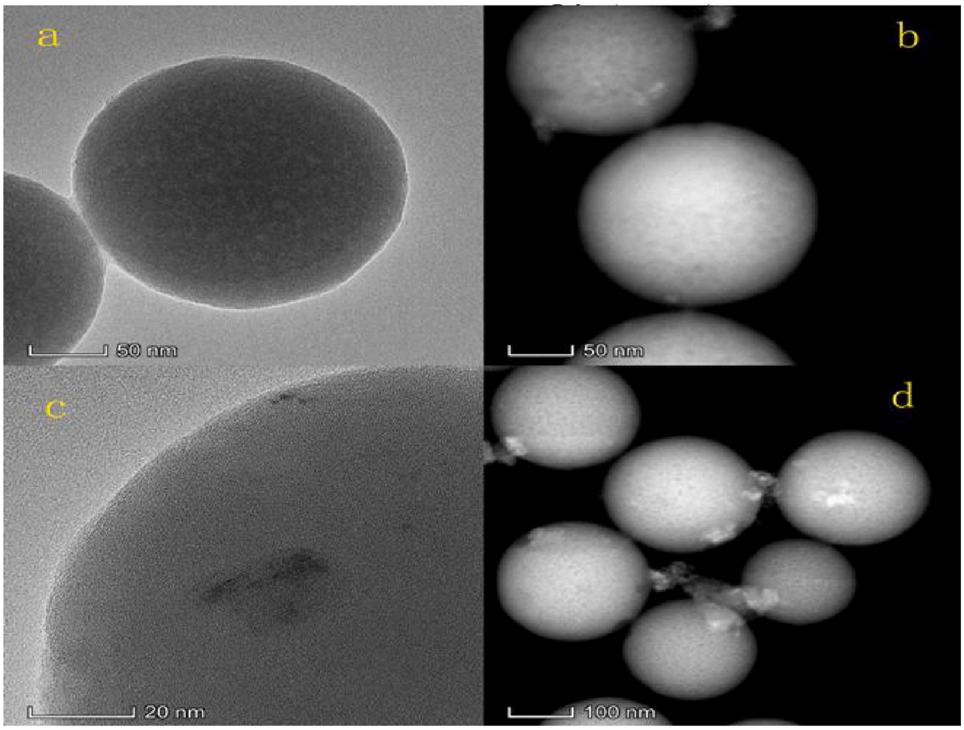


Fig. 1. (a) TEM images of SiO_2, (b)(c): TEM images of BPS-Cu@SiO_2, (d): TEM images of BPS-Ir@SiO_2.

was reported that silane coupling agent is a magical molecule that contained two kinds of isochemical groups (organic functional groups and hydrolyzable groups), the corresponding reagents could be represented by the general formula: $Y(R)_nSiX_{4-n}$ (n = 1, 2) [20]. Y is a non-hydrolyzed organic group, includes -Cl, $-NH_2$, -SH, and hydrocarbon groups of −OCOMe, $-CH = CH_2$, -NCO and other functional groups; X is the group, which can undergo hydrolysis reactions and generate Si−OH bonds, including $-Si(OCH_3)_3$, $-Si(OCH_2CH_3)_3$, which were capable of reacting with inorganic materials in Si-O-Si bonds, or adsorption on the surface of the material. Thereby X and Y are two kinds of reactive groups with different characteristics groups, where X groups were easy to interact with inorganic substances such as SiO_2. At the other end of the silane, Y could be easily coupled with ligand BPS, and different groups in $(R)_n$, which changed the peculiarity of the whole ligand [21].

Meanwhile, we set up a series of experiments to find out the actual role of BPS-Cu@SiO_2 and BPS-Ir@SiO_2 system during the upper two reactions. It was noted that the reaction of *tert*-butanesulfinamide with alcohols is much more difficult to control and BPS-Cu@SiO_2 couldn't catalyze this reaction smoothly, while BPS-Ir@SiO_2 could generate **4a** in high yield with high selectivity. This high catalytic activity was supported and explained by several recent results using unsymmetrical ligand strategy [22]. Moreover, the possible synergistic eff ;ect of benzotriazole-pyridinyl-silane ligand and carrier (silicon dioxide) could not be excluded, which might be another reason for the catalytic activity of BPS-Cu@SiO_2 and BPS-Ir@SiO_2 system. The experiments revealed that homogeneous complex could also catalyze this reaction in only moderate yield. It was found that only ligand or iridium salt could not catalyze this reaction, while high catalytic activity was gained through the assistance of ligand and support (Table 1).

Furthermore, in order to survey the electronic effects of the reaction of substituted benzyl alcohols and *tert*-butanesulfinamides, the Hammett plot equation was applied to this reaction process. Several typical substrates were selected to build the equation and a corresponding plot was summarized in Fig. 3. This slope indicated that the electronic effect of substituted benzyl alcohols had some effect on the initial stage of the conversion, and that the electron withdrawing group of substituted benzyl alcohols was more favorable during this reaction.

Subsequently, kinetic research was also explored by using deuterated benzyl alcohol to find out the reaction rate determining step (Fig. 4). The kinetic isotope effects value of *tert*-butanesulfinamide and benzyl alcohols was obtained by using the first order reaction plot between ln[**3**-*d2*] and ln[**3**], offered an evidence that the dehydrogenation of **3** was the possible rate determining step for the reaction of *tert*-butanesulfinamide

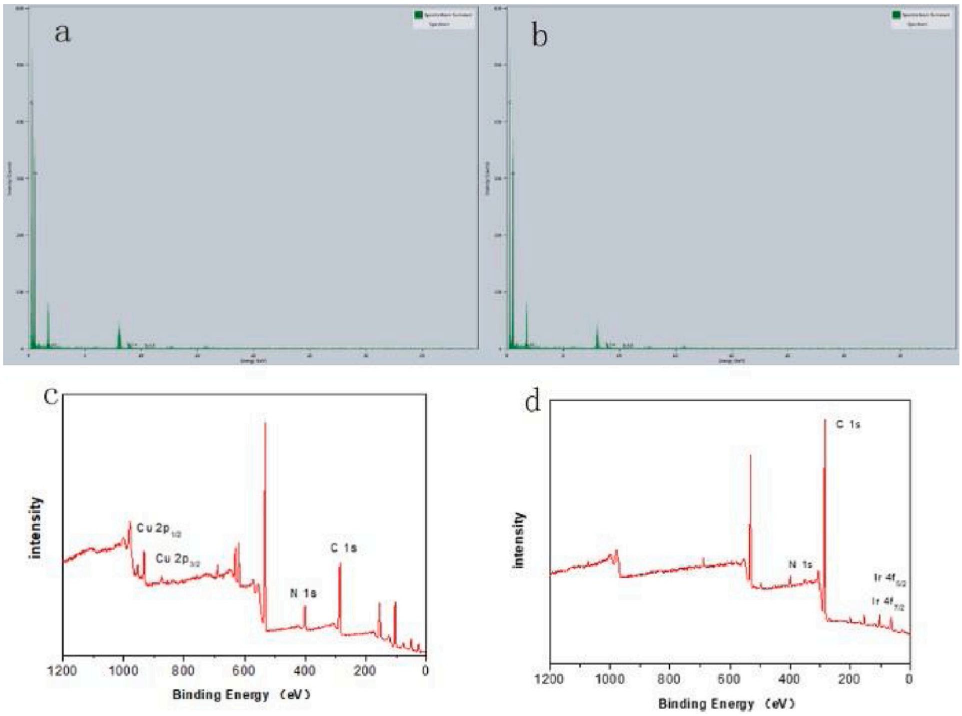
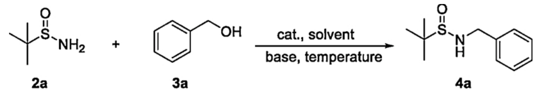


Fig. 2. (a)(b): EDS pattern of BPS-Cu@SiO_2 and BPS-Ir@SiO_2; (c)(d): XPS spectra of BPS-Cu@SiO_2 and BPS-Ir@SiO_2.

Table 1
Optimization of reaction conditions.[a,b]



Entry	Cat.	Base	Sol.	Temp. [°C]	Time [h]	Yield [%]
1	BPS-Ir@SiO_2	NaOH	dioxane	120	24	84 %
2	BPS-Ir@SiO_2	Cs_2CO_3	dioxane	120	24	71%
3	BPS-Cu@SiO	Cs_2CO_3	dioxane	120	24	26%
4	BPS-Ir@SiO_2	*t*-BuOK	dioxane	120	24	79%
5	BPS-Ir@SiO_2	KOH	dioxane	120	24	84 %
6	BPS-Ir@SiO_2	K_2CO_3	dioxane	120	24	79%
7	BPS-Ir@SiO_2	NaOH	toluene	120	24	94 %
8	BPS-Ir@SiO_2	NaOH	MeOH	reflux	24	79%
9	BPS-Ir@SiO_2	NaOH	CH_2Cl_2	reflux	24	80 %
10	BPS-Ir@SiO_2	NaOH	DMF	120	24	63%
11	BPS-Ir	NaOH	toluene	120	24	82%
12	BPS-Ir@SiO_2	NaOH	toluene	120	24	78%
13	BPS	NaOH	toluene	120	24	<5%
15	BPS-Ir@SiO_2	NaOH	toluene	85	24	<5%
16	BPS-Ir@SiO_2	NaOH	toluene	120	12	<50 %
17	BPS-Ir@SiO_2	NaOH	toluene	120	48	92%
18	BPS-Ir@SiO_2	NaOH	water	100	24	<5%
19	$IrCl_3$	NaOH	toluene	120	24	<5%
20	None	NaOH	toluene	120	24	<5%
21	BPS-Ir@SiO_2	NaOH	CH_3CN	reflux	24	58%

[a] Conditions: **2** (1.0 mmol), **3** (1.1 mmol), BPS-Ir@SiO_2 (10 mg), base (0.2 eq.), solvent (3.0 mL), 24 h.

[b] Isolated yields.

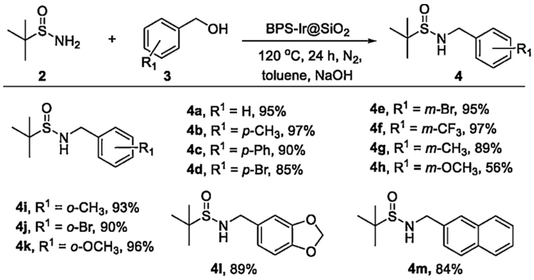
and benzyl alcohols.

In addition, the kinetic investigation of **4a** was further carried out to better explain possible reaction pathway (Fig. 5). The conversion of product (**4a**) was observed to increase with the consuming of starting material. The experiment revealed that aldehyde was the convincing intermediate and suggested the formation and consumption of aldehyde was the key to this reaction.

BPS-Ir@SiO_2 catalyst was recovered and washed with water (10 mL x3), ethanol (10 mL x3), then water (10 mL x3). After drying, the recovered BPS-Ir@SiO_2 was reused to catalyze the reaction of *tert*-butanesulfinamide with benzyl alcohol (**3a**), it was found that yields of the desired product (**4a**) could be nearly maintained when BPS-Ir@SiO_2 composite was recovered for five times (Scheme 3).

Finally, the large scale synthesis of sulfinamide derivatives (**4f**, 4 l, **4 m**) were set up with BPS-Ir@SiO_2 as a catalyst and almost ten grams of desired sulfinamides were isolated smoothly. This further provided an efficient method for the synthesis of sulfinamide derivatives with BPS-Ir@SiO_2 composite in gram scale (Scheme 4).

Table 2
Reaction of benzyl alcohol and *tert*-butanesulfinamide.[a,b]

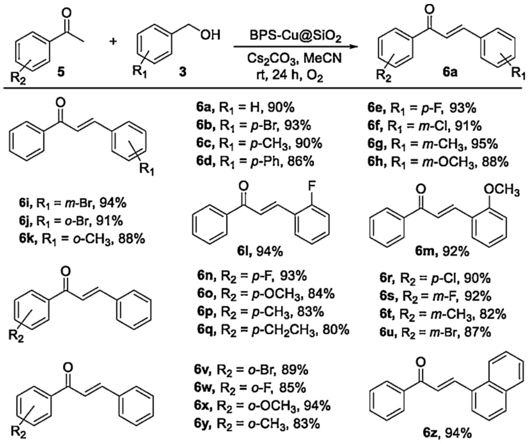


[a] Conditions: **2** (1.0 mmol), **3** (1.1 mmol), BPS-Ir@SiO$_2$ (10 mg), NaOH (1.0 mmol), toluene (3 mL), 24 h. [b] Isolated yields.

[a] Conditions: **2** (1.0 mmol), **3** (1.1 mmol), BPS-Ir@SiO2 (10 mg), NaOH (1.0 mmol), toluene (3 mL), 24 h.

[b] Isolated yields.

Table 3
Substrates expansion of ketones and benzyl alcohols.[a,b].



[a] Conditions: **5** (1.0 mmol), **3** (1.1 mmol), BPS-Cu@SiO$_2$ (10 mg), MeCN (2.0 mL), 24 h, rt, O$_2$. [b] Isolated yields.

[a] Conditions: **5** (1.0 mmol), **3** (1.1 mmol), BPS-Cu@SiO$_2$ (10 mg), MeCN (2.0 mL), 24 h, rt, O$_2$.

[b] Isolated yields.

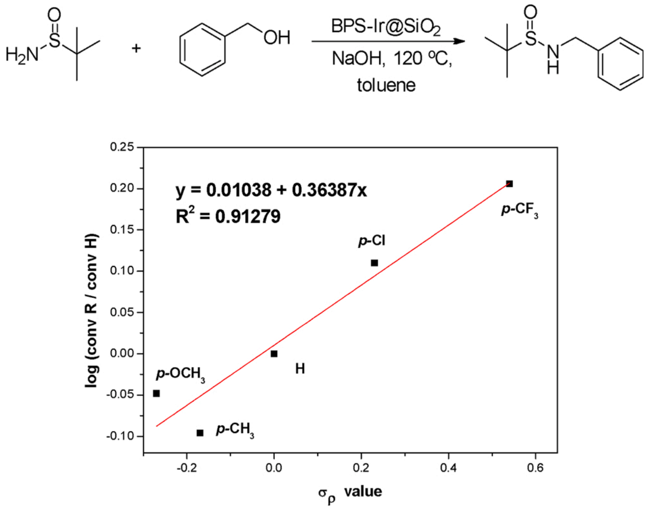


Fig. 3. Hammett plot of *para*-substituted alcohols.

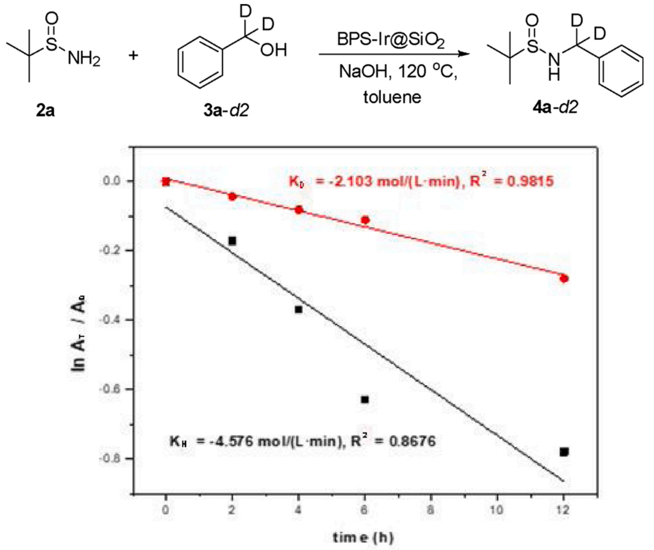


Fig. 4. Kinetic plot of benzyl alcohol and benzyl alcohol-*d2*. A$_0$: original concentration of substrate. A$_t$: Substrate concentration at time t. k: rate constant. K$_H$/K$_D$ = 2.17.

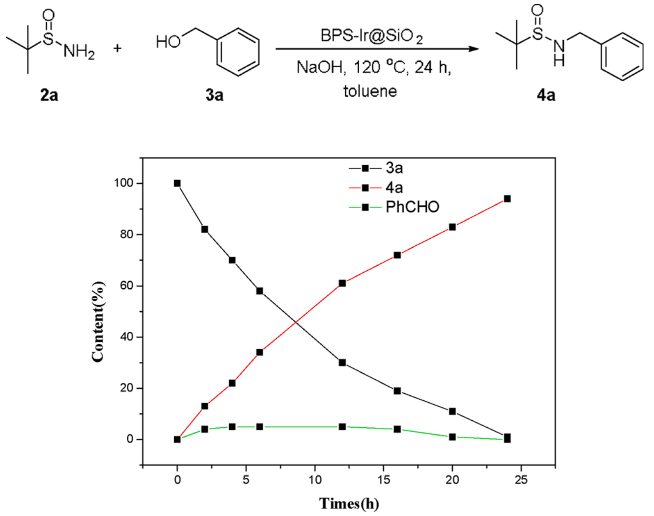
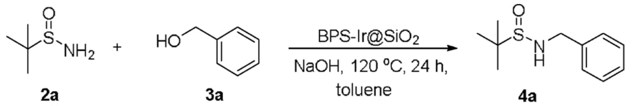


Fig. 5. Kinetic investigations for the synthesis of **4a**.

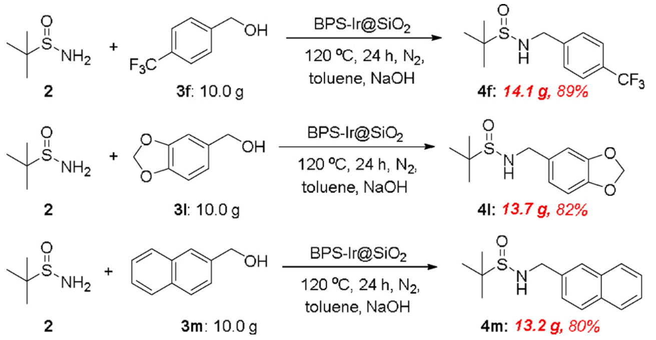


Recycled times	0	1	2	3	4	5
Yields	94%	92%	92%	90%	91%	90%

Scheme 3. Recycled experiments.

4. Conclusions

In conclusion, a new type of ligand was synthesized from benzotriazole-pyridinyl and 3-isocyanatopropyltriethoxy- silane. The corresponding BPS-Cu@SiO$_2$ and BPS-Ir@SiO$_2$ catalysts were prepared and fully characterized through EDS, TEM, and XPS. It was disclosed that BPS-Ir@SiO$_2$ catalyst could promote borrowing hydrogen reaction of *tert*-butanesulfinamide with benzyl alcohols, while BPS-Cu@SiO$_2$



Scheme 4. The synthesis of sulfinamides in gram scale.

catalyst was proved to be effective for synthesis of unsaturated carbonyl compounds. Furthermore, it could be easily recovered and reused for at least five times with good recyclability.

Supplementary material

Detailed experimental procedures, ^{1}H NMR, ^{13}C NMR data. This material is available free of charge *via* the Internet.

CRediT authorship contribution statement

Guanxin Zhu: Methodology, Experiments, Writing. **Zheng-Chao Duan:** Experiments, Investigations. **Haiyan Zhu:** Measurement, Characterizations. **Minghui Qi:** Experiments. **Dawei Wang:** Conceptualization, Writing - Reviewing and Editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111516.

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