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View Article Online
DOI: 10.1039/C9NJ02542A

Journal Name

ARTICLE

The N-alkylation of sulfonamides with alcohols in water catalyzed by a water-soluble metal-ligand bifunctional iridium complex $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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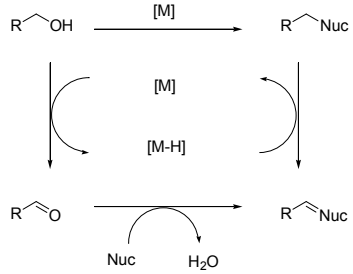
The iridium complex $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ (Cp^* = η^5-pentamethylcyclopentadienyl, $biimH_2$ = 2,2'-biimidazole) was synthesized and developed as a new-type of water-soluble metal-ligand bifunctional catalyst for the *N*-alkylation of poor nucleophilic sulfonamides with alcohols in water. In the presence of catalyst (1 mol %) and Cs_2CO_3 (0.1 equiv), a series of desirable products were obtained in 74-91% yields under microwave irradiation. Mechanistic experiment revealed that the presence of NH units in the imidazole ligand is crucially important for the catalytic activity of iridium complex. Notably, this research would facilitate the process of water-soluble metal-ligand bifunctional catalysts for hydrogen autotransfer process.

Introduction

The N-alkylation of amines presents one of the most fundamental and important C-N bond-forming reactions in organic synthesis.[1] Traditionally, such transformations were performed with alkyl halides as alkylating agents in the presence of stoichiometric bases. In recent years, much attention has been directed to the N-alkylation of amines with alcohols as alkylating agents based on the so-called hydrogen autotransfer process or hydrogen-borrowing strategy,[2] using ruthenium,[3] iridium,[4] palladium,[5] nickel,[6] cobalt,[7] iron[8] and manganese catalysts.[9] In this process, alcohols are first dehydrogenated to form aldehydes, followed by the condensation of the resulting aldehydes with amines afforded imine intermediates, which are hydrogenated by the metal hydride species generated in the step of the dehydrogenation of alcohols to give the final N-alkylated products (Scheme 1). This methodology is attractive because of high atom efficiency and the formation of water as the only by-product. Despite significant advance, most of reactions have to be performed in organic solvents or using several equiv. of alcohols as solvents, which results in the production of a large amount of auxiliary waste and environmental pollution.

Because water is cheap, safe and environmentally benign compared with various organic solvents, the development of catalytic transformations in water has becoming increasingly important.[10] However, the transition metal-catalyzed N-alkylation of amines with alcohols to N-alkylated amines in water remained rarely unexplored and only a few examples have been reported to date (Scheme 2). Fujita, Yamaguchi and co-workers demonstrated the N-alkylation of ammonia, aromatic and aliphatic amines with alcohols in water catalyzed by a water-soluble iridium complex $[Cp^*Ir(NH_3)_3]$[11] Williams and co-workers reported also the N-alkylation of aromatic and aliphatic amines with alcohols in water catalyzed by $[Cp^*IrI_2]_2$.[12] However, when poor nucleophilic sulfonamides were used as substrates, this catalytic system required a stoichiometric amount of base and the products were obtained in only low to moderate yields (25%-74%).[13-14] Recently, we demonstrated the N-alkylation of sulfonamides with alcohols in water catalyzed by a water-soluble Cp*Ir complex bearing a functional 6,6'-dihydroxy-2,2'-bipyridine ligand $[Cp^*Ir(6,6'-(OH)_2bpy)(H_2O)][OTf]_2$.[15,16] A mechanistic investigation revealed that protic hydrogens of OH units in the bpy ligand are crucially important for the catalytic activity.[15] As a part of our continuing interest in the development of iridium-catalyzed environmentally friendly reactions,[15,17] we herein wish to describe our effort towards the synthesis of a



Scheme 1. Transition metal-catalyzed *N*-alkylation of amines with alcohols.

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Electronic Supplementary Information (ESI) available: ^{1}H NMR and ^{13}C NMR spectra of all products. See DOI: 10.1039/x0xx00000x

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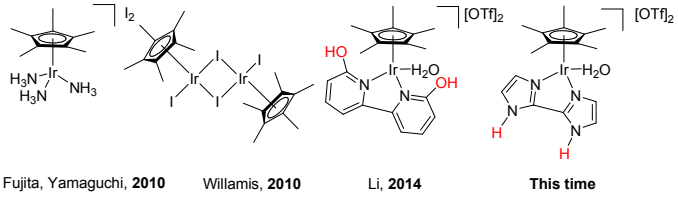
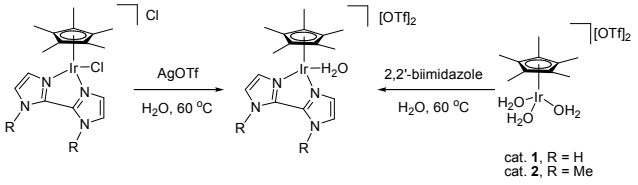


Scheme 2. Organometallic catalysts for the *N*-alkylation of amines with alcohols in water.

water-soluble Cp*Ir complex bearing a functional biimidazole $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ ($biimH_2$ = 2,2'-imidazole) that contains protic hydrogens and a tautomerism structure like hydroxypyridine. Furthermore, such complex was developed as a new-type of water-soluble metal-ligand bifunctional catalyst for the N-alkylation of sulfonamides with alcohols in water.

Results and discussion

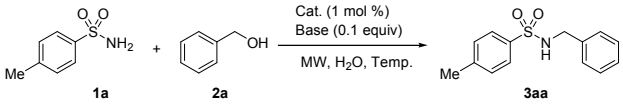
Water-soluble Cp*Ir complexes employed in this work were synthesized outlined in Scheme 3. The reaction of $[Cp^*Ir(biimH_2)Cl]Cl$ and AgOTf (2.2 equiv) carried out at 60 °C in H_2O for 12 h to give the product $[Cp^*Ir(biimH_2)H_2O][OTf]_2$ in 59% yield.[18] This complex could also be prepared in 65% yield through the reaction of $[Cp^*Ir(H_2O)_3][OTf]_2$ with 2,2'-biimidazole (1.2 equiv) in water at 60 °C for 12 h. The analogous complex $[Cp^*Ir(biimMe_2)H_2O][OTf]_2$ was synthesized in 61% yield by the later method. These two complexes are very stable to air and moisture.



Scheme 3. The synthesis of water-soluble iridium complexes $[Cp^*Ir(biimR_2)(H_2O)][OTf]_2$ (R = H, Me).

We next investigated their catalytic activity for the N-alkylation of p-methylbenzenesulfonamide (**1a**) with benzyl alcohol (**2a**) in water. In the presence of $[Cp^*Ir(biimH_2)H_2O][OTf]_2$ (cat. **1**) (1 mol %) and Cs_2CO_3 (0.1 equiv), the reaction was performed at 130 °C for 2 h in a focused, single mode microwave synthesizer (Discover CEM, USA, 300 W) to afford the desired product **3aa** in 97% yield (Table 1, entry 1). Using $[Cp^*Ir(biimMe_2)H_2O][OTf]_2$ (cat. **2**) as an alternative catalyst, only 7% yield was obtained (Table 1, entry 2). Apparently, NH units in the ligand have a significant effect on the catalytic activity of Cp*Ir complex. cat. **1** was chosen as the catalyst for further research. Attempts to use K_2CO_3 and Na_2CO_3 as alternative bases, and decrease the reaction temperature resulted in relatively low yields (Table 1, entries 3-6). When $[Cp^*Ir(biimH_2)Cl]Cl$ was utilized, the

Table 1. *N*-alkylation of *p*-methylbenzenesulfonamide (**1a**) with benzyl alcohol (**2a**) under various conditions.[a]



1a 2a 3aa

Entry	Cat.	Base	Temp. [°C]	Yield [%][b]
1	cat. **1**	Cs_2CO_3	130	97 (91%[c])
2	cat. **2**	Cs_2CO_3	130	7
3	cat. **1**	K_2CO_3	130	47
4	cat. **1**	Na_2CO_3	130	40
5	cat. **1**	Cs_2CO_3	120	71
6	cat. **1**	Cs_2CO_3	110	32
7	$[Cp^*Ir(biimH_2)Cl]Cl$	Cs_2CO_3	110	25
8	-	Cs_2CO_3	100	n.d.

[a] Reactions conditions: **1a** (1 mmol), **2a** (1.2 mmol), $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ (1 mol %), Cs_2CO_3 (0.1 equiv), H_2O (1 mL), MW, 130 °C, 2 h. [b] Isolated yield. [c] **2** (2 mmol), Cs_2CO_3 (0.2 equiv).

product **3aa** was obtained in 25% yield (Table 1, entry 7). No reaction took place in the presence of Cs_2CO_3 alone (Table 1, entry 8).

With the established catalytic system in hand, we investigated the scope of reaction with respect of alcohols and these results are summarized in Table 2. Reactions of benzylic alcohols bearing an electron-donating substituent, such as methyl and *p*-methoxy groups, gave the desired products **3ab-3ad** in 82-84% yields (Table 2, entries 1-3). Similarly, benzylic alcohols bearing an electron-withdrawing group, such as *m*-methoxy or a halide atom (fluorine, chlorine and bromine), were successfully converted to the corresponding products **3ae-3ai** in 81-91% yields (Table 2, entries 4-8). Stronger electron-withdrawing substituents, such as trifluoromethyl and trifluoromethoxy groups, were also tolerated and the corresponding products **3aj** and **3ak** were obtained in 80% and 88%, respectively (Table 2, entries 9-10). Transformations of 1-naphthalenemethanol proceeded smoothly to afford the desired product **3al** in 84% yield (Table 2, entry 11). In the case of aliphatic alcohols, such as 1-butanol, 1-hexanol and cyclic alcohol, the corresponding products **3am-3ao** were obtained in 74-78% yields (Table 2, entries 12-14).

The scope of reaction with respect to sulfonamides was then evaluated (Table 3). The N-alkylation of benzenesulfonamides bearing an electron-donating substituent, such as methyl and methoxy groups, afforded the desired products **3ba** and **3ca** with 80% and 87% yields, respectively (Table 3, entries 1-2). When benzenesulfonamides bearing a halide atom or a more serious electron-withdrawing substituent were served, reactions gave the corresponding products **3da-3ha** in 84-90% yields (Table 3, entries 3-7). Benzenesulfonamide and naphthalenesulfonamide were also proven to be suitable substrates and the desired products **3ia** and **3ja** were obtained with 83% and 85% yields, respectively (Table 3, entries 8-9). Apart from aromatic sulfonamides, aliphatic ones, including phenylmethyl, methyl and cyclopropyl groups, were successfully converted into the desired products

On the basis of experimental results, a plausible mechanism was proposed to account for the present N-alkylation of sulfonamides with alcohols in water catalyzed by

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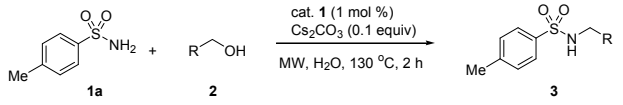
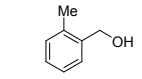
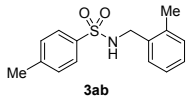
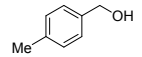
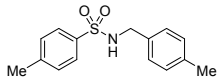
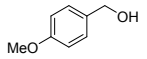
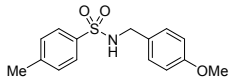
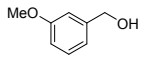
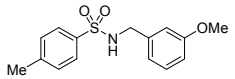
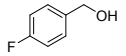
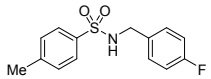
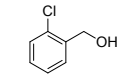
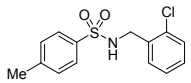
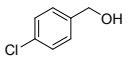
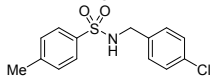
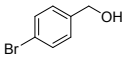
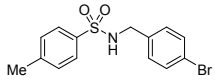
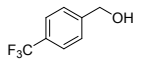
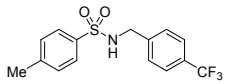
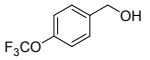
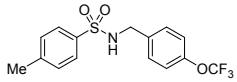
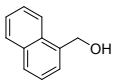
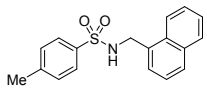
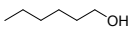
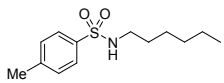
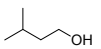
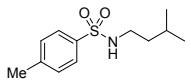
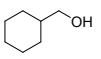
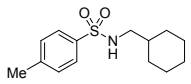
Table 2. *N*-alkylation with respect of alcohols in water[a]

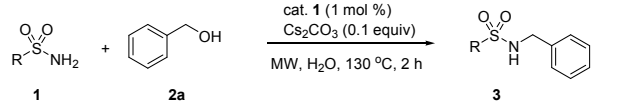


1a 2 3

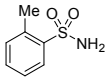
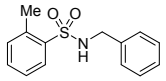
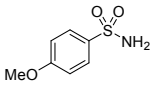
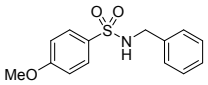
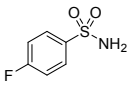
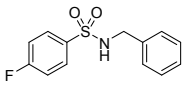
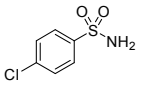
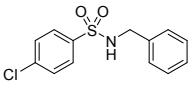
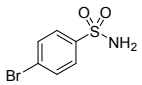
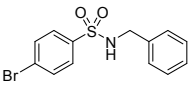
Entry	Alcohol	Product	Yield (%)[b]
1	 2b	 3ab	83
2	 2c	 3ac	82
3	 2d	 3ad	84
4	 2e	 3ae	82
5	 2f	 3af	86
6	 2g	 3ag	81
7	 2h	 3ah	90
8	 2i	 3ai	91
9	 2j	 3aj	80
10	 2k	 3ak	88
11	 2l	 3al	84
12	 2m	 3am	76[c]
13	 2n	 3an	78[c]
14	 2o	 3ao	74[c]

[a] Reactions conditions: **1a** (1 mmol), **2** (1.2 mmol), $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ (1 mol %), Cs_2CO_3 (0.1 equiv), H_2O (1 mL), MW, 130 °C, 2 h. [b] Isolated yield. [c] **2** (2 mmol), Cs_2CO_3 (0.2 equiv).

Table 3. *N*-alkylation with respect of sulfonamides in water[a]



1 2a 3

Entry	Sulfonamide	Product	Yield (%)[b]
1	 1b	 3ba	80
2	 1c	 3ca	87
3	 1d	 3da	84
4	 1e	 3ea	85
5	 1f	 3fa	87
6	1g	3ga	90
7	1h	3ha	88
8	1i	3ia	83
9	1j	3ja	85
10	1k	3ka	78
11	1l	3la	76
12	1m	3ma	83

[a] Reactions conditions: **1** (1 mmol), **2a** (1.2 mmol), $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ (1 mol %), Cs_2CO_3 (0.1 equiv), H_2O (1 mL), MW, 130 °C, 2 h. [b] Isolated yield.

$[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ (Scheme 4). The initial step of the reaction involved the formation of unsaturated species **A** by the deprotonation through the reaction of $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ and Cs_2CO_3, and the dissociation through the elimination of water. Accompanied by the activation of alcohols, the ligand accepted a proton to give

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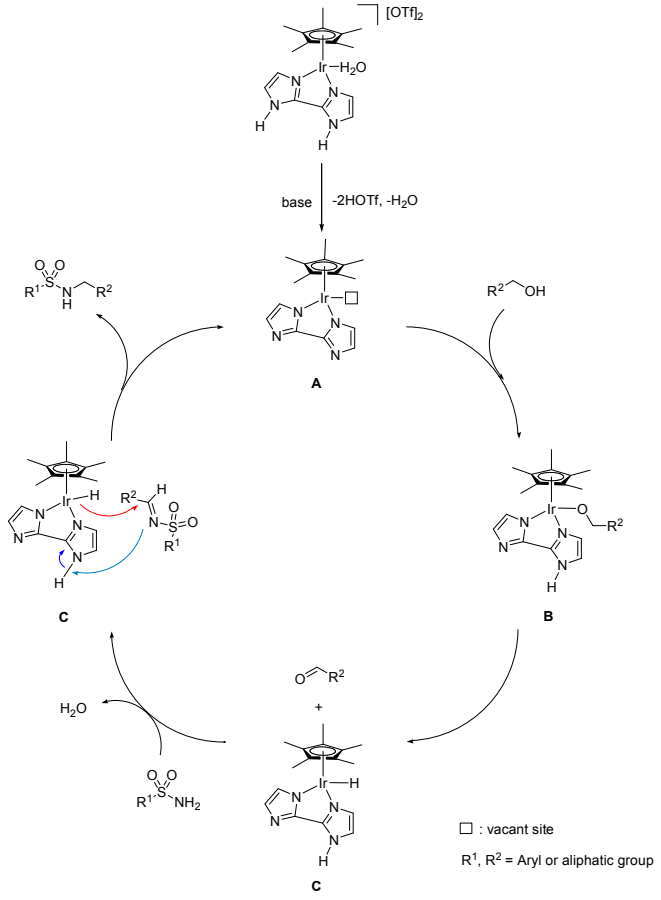
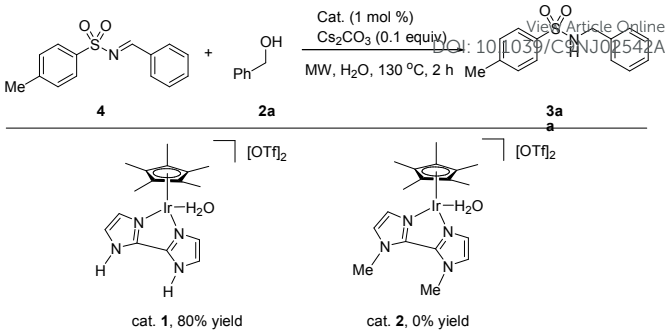
DOI: 10.1039/C9NJ02542A

alkoxy iridium species **B**, which then underwent ß-hydrogen elimination to give iridium hydride species **C** and aldehydes. The condensation between the resulting aldehydes and sulfonamides occurred to give unsaturated sulfonimine intermediates. Furthermore, the simultaneous transfer of the hydride on iridium and the proton on the bisimidazole ligand of species **C** to the C=N bond of sulfonimine intermediates, which resulted in the liberation of N-alkylated products and the regeneration of catalytic active species **A**. Similar mechanism for the simultaneous delivery of hydride and proton to ketones or imines was proposed in metal-ligand bifunctional catalysts, such as Shvo's catalyst,[19] and Noyori-Ikariya catalysts.[20]



Scheme 4. The proposed reaction mechanism.

To support the proposed reaction mechanism, the catalytic hydrogen transfer of a sulfonimine with an alcohol as a hydrogen source in water was investigated (Scheme 5). In the presence of cat. **1** (1 mol %) and Cs_2CO_3 (0.1 equiv), the reaction of (E)-*N*-benzylidene-4-methylbenzenesulfonamide **(4)**, which is synthesized by the condensation between p-methylbenzenesulfonamide and benzaldehyde, with **2a** proceeded for 2 h in water at 130 °C under microwave irradiation to afford the product **3aa** in 80% yield, although the hydration of a part of starting materials occurred. Using cat. **2** as an alternative catalyst, all starting materials were hydrated and none of **3aa** was found under same conditions.



Scheme 5. The hydrogen transfer between a sulfonimine and an alcohol.

Conclusion

We have synthesized a water-soluble iridium complex $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ and developed it as a new-type of metal-ligand bifunctional catalyst for the N-alkylation of poor nucleophilic sulfonamides with alcohols in water. In the presence of catalyst (1 mol %) and Cs_2CO_3 (0.1 equiv), a series of desirable products were obtained in 74-90% yields under microwave irradiation. Mechanistic experiment revealed that the presence of NH units in the imidazole ligand is crucially important for the catalytic activity of iridium complex. Notably, this research would facilitate the process of water-soluble metal-ligand bifunctional catalysts for hydrogen autotransfer process.

Experimental Section

General Experimental Details. High-resolution mass spectra (HRMS) were obtained on Thermo Scientific LTQ Orbitrap XL spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion. Melting points were measured on a X-6 micro-melting apparatus. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$ and 2.50 ppm for DMSO-d_6. Coupling constants J values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 125 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$ and 39.5 ppm for DMSO-d_6. ^{13}C NMR spectra were routinely run with broadband decoupling. All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates.

$[Cp^*Ir(biimH_2)(Cl)]$[18] and $[Cp^*Ir(H_2O)_3][OTf]_2$[21] were synthesized by the according to previous reports.

Procedure for the synthesis of $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$. Method 1: To an oven-dried Schlenk tube were added $[Cp^*Ir(biimH_2)(Cl)]$ (67 mg, 0.126 mmol), AgOTf (71 mg, 0.277 mmol) and H_2O (3 mL), and the mixture was heated at 60 °C for 12 h. The reaction mixture was allowed to cool to ambient temperature. Then, the precipitate was filtered, and the filtrate was concentrated in *vacuo* to afford the product. Yellow solid, 59% yield (58 mg). ^{1}H NMR (500 MHz, D_2O) δ

7.61-7.50 (m, 4 H), 1.76 (s, 15 H); ^{13}C NMR (125 MHz, D_2O) δ 140.6, 126.9, 121.4, 87.3, 8.2; ^{19}F NMR (470 MHz, D_2O) δ -80.7; HRMS (ESI) m/z calcd for $C_{16}H_{20}N_4Ir$ $[M-(OTf)_2-H_2O-H]^+$ 461.13117, found 461.13113

Method 2: To an oven-dried Schlenk tube were added $[Cp^*Ir(H_2O)_3][OTf]_2$ (86 mg, 0.126 mmol), 2,2'-Biimidazole (20 mg, 0.150 mmol) and H_2O (3 mL), and the mixture was heated at 60 °C for 12 h. The reaction mixture was allowed to cool to ambient temperature. Then, the precipitate was filtered, and the filtrate was concentrated in *vacuo* to afford the product in 65% yield (64 mg).

Procedure for the synthesis of $[Cp^*Ir(biimMe_2)(H_2O)][OTf]_2$. To an oven-dried Schlenk tube were added $[Cp^*Ir(H_2O)_3][OTf]_2$ (86 mg, 0.126 mmol), 1-methyl-2-(1-methylimidazol-2-yl)imidazole (24 mg, 0.148 mmol) and H_2O (3 mL), and the mixture was heated at 60 °C for 12 h. The reaction mixture was allowed to cool to ambient temperature. Then, the precipitate was filtered, and the filtrate was concentrated in *vacuo* to afford the product in 61% yield (62 mg). ^{1}H NMR (500 MHz, D_2O) δ 7.59 (s, 2 H), 7.48 (s, 2 H), 4.24 (s, 6 H), 1.76 (s, 15 H); ^{13}C NMR (125 MHz, D_2O) δ 141.5, 127.9, 127.3, 87.5, 37.9, 8.2; ^{19}F NMR (470 MHz, D_2O) δ -80.7; HRMS (ESI) m/z calcd for $C_{18}H_{24}N_4Ir$ $[M-(OTf)_2-H_2O-H]^+$ 489.16247, found 489.16257.

General procedure for the *N*-alkylation of sulfonamides with alcohols in water catalyzed by $Cp^*Ir(biimH_2)(H_2O)][OTf]_2$. sulfonamides (1 mmol), alcohols (1.2 mmol), $[Cp^*Ir(biimH_2)(H_2O)][OTf]_2$ (7.8 mg, 0.01 mmol, 1 mol %), Cs_2CO_3 (33 mg, 0.1 mmol, 0.1 equiv) and water (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 2 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

N-Benzyl-4-methylbenzenesulfonamide (3aa).[14b] White solid, 91% yield (238 mg); mp 113-114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.29-7.24 (m, 5H), 7.19-7.18 (m, 2H), 4.09 (d, *J* = 6.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 136.8, 136.3, 129.7, 128.6, 127.8, 127.8, 127.1, 47.1, 21.4.

N-(2-Methylbenzyl)-4-methylbenzenesulfonamide (3ab).[22] White solid, 83% yield (229 mg); mp 119-120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 7.0 Hz, 1H), 7.11-7.06 (m, 3H), 4.06 (s, 2H), 2.43 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 136.6, 133.9, 130.5, 129.7, 128.8, 128.1,127.1, 126.1, 45.3, 21.4, 18.7.

N-(3-Methoxybenzyl)-4-methylbenzenesulfonamide (3ac).[14b] White solid, 82% yield, (239 mg); mp 83-84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.28-7.16 (m, 3H), 6.76-6.71 (m, 3H), 4.99 (br s, 1H), 4.07 (s, 2H), 3.72 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 143.4, 137.8, 136.8, 129.7, 129.6, 127.1, 120.0, 113.6, 113.0, 55.1, 47.1, 21.4.

N-(4-Methylbenzyl)-4-methylbenzenesulfonamide (3ad).[23] White solid, 82% yield (226 mg); mp 90-91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.06 (s, 4H), 4.85 (br s, 1H), 4.05 (s, 2H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 143.2, 139.5, 136.6, 129.8, 128.5, 127.5, 127.0, 46.4, 44.4, 21.5.

N-(4-Methoxybenzyl)-4-methylbenzenesulfonamide (3ae).[24] White solid, 84% yield (245 mg); mp 120-121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 4.85 (br s, 1H), 4.03 (d, *J* = 5.9 Hz, 2H), 3.76 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 143.3, 136.8, 129.6, 129.2, 128.3, 127.1, 113.9, 55.2, 46.7, 21.5.

N-(4-Fluorobenzyl)-4-methylbenzenesulfonamide (3af).[25] White solid, 86% yield (240 mg); mp 93-94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 2 H), 7.15 (dd, *J* = 8.2 Hz and 5.6 Hz, 2 H), 6.92 (t, *J* = 8.4 Hz, 2 H), 4.91 (br s, 1 H), 4.07 (s, 2 H), 2.42 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, J_{C-F} = 246.7 Hz), 143.5, 136.8, 132.2, 129.7, 129.6 (d, J_{C-F} = 8.2 Hz), 127.1 , 115.4 (d, J_{C-F} = 21.6 Hz), 46.4, 21.5.

N-(2-Chlorobenzyl)-4-methylbenzenesulfonamide (3ag).[26] White solid, 81% yield (239 mg); mp 66-67 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.24-7.31 (m, 4H), 7.14-7.21 (m, 2H), 5.00 (s, 2H), 4.23 (d, *J* = 6.1 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 136.9, 133.9, 133.3, 130.3, 129.6, 129.4,129.2, 127.1, 45.1, 21.5.

N-(4-Chlorobenzyl)-4-methylbenzenesulfonamide (3ah).[14b] White solid, 90% yield (266 mg); mp 103-105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 5.20 (br s, 1 H), 4.07 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 136.8, 134.8, 133.8, 129.8, 129.2, 128.8, 127.1, 46.6, 21.5.

N-(4-Bromobenzyl)-4-methylbenzenesulfonamide (3ai).[27] White solid, 91% yield (310 mg); mp 118-119 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 7.7 Hz, 2H), 5.24 (br s, 1H), 4.05 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 136.7, 135.4, 131.5, 129.6, 129.5, 127.0, 121.6, 46.4, 21.4.

N-[4-(Trifluoromethyl)benzyl]-4-methylbenzenesulfonamide (3aj).[14h] White solid, 80% yield (263 mg); mp 136-137 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 (br s, 1 H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 4.07 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 143.6, 138.8, 130.5, 129.2, 128.7 (q, J_{C-F} = 31.9 Hz), 127.5, 127.2, 126.3, 126.0, 125.2 (q, J_{C-F} = 272.2 Hz), 46.5, 21.8.

N-[4-(Trifluoromethoxy)benzyl]-4-methylbenzenesulfonamide (3ak).[15] White solid, 88% yield (305 mg); mp 85-86 °C; ^{1}H NMR (500 MHz, DMSO) δ 8.15 (br s, 1 H), 7.64 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.2 Hz, 4 H), 7.25 (d, *J* = 8.7 Hz, 2H), 3.99 (ds, 2 H), 2.36 (s, 3 H); ^{13}C NMR (125 MHz, DMSO) δ 148.3, 143.6, 138.8, 138.2, 130.5, 130.4, 127.5, 121.8, 121.2 (q, J_{C-F} = 255.3 Hz), 46.4, 21.8.

4-Methyl-N-(naphthalen-2-ylmethyl)benzenesulfonamide (3al).[14a] White solid, 84% yield (262 mg); mp 145-146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.75 (m, 5H), 7.47 (s, 1H), 7.32-7.27 (m, 4H), 4.52 (s, 2H), 2.43(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 136.5, 133.7, 131.3, 131.1, 129.7, 129.0, 128.7. 127.2, 126.9, 126.7, 126.0, 125.2, 123.2, 45.4, 21.5.

N-Hexyl-4-methylbenzenesulfonamide (3am).[14b] White solid, 76% yield (194 mg); mp 62-63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.54 (br s, 1 H), 2.92 (q, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 1.47-1.41 (m, 2H), 1.26-1.19 (m, 6H), 0.84 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 137.0, 129.6, 127.1, 43.2, 31.2, 29.5, 26.1, 22.4, 21.5, 13.9.

N-isopentyl-4-methylbenzenesulfonamide (3an).[27] Oil, 78% yield (187 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.78 (br s, 1H), 2.92 (q, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.53-1.61 (m, 1H), 1.31-1.35 (m, 2H), 0.81 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 137.0, 129.6, 127.1, 43.2, 31.2, 29.5, 26.1, 22.4, 21.5, 13.9.

N-(Cyclohexylmethyl)-4-methylbenzenesulfonamide (3ao).[14a] White solid, 74% yield (198 mg); mp 80-81 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.91 (br s, 1 H), 2.73 (d, *J* = 5.9 Hz, 2H), 2.42 (s, 3H), 1.67-1.60 (m, 5H), 1.40-1.38 (m, 1 H), 1.17-1.07 (m, 3H), 0.88-0.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 137.0, 129.6, 127.0, 49.3, 37.6, 30.5, 26.2, 25.6, 21.4.

N-Benzyl-2-methylbenzenesulfonamide (3ba).[14h] White solid, 80% yield (209 mg); mp 57-58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.34-7.24 (m, 5H), 7.16-7.15 (m, 2H), 4.79 (br s, 1H), 4.11 (d, *J* = 5.9 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 137.0, 136.2, 132.8, 132.5, 129.6, 128.7, 127.9, 126.2, 47.1, 20.3.

N-Benzyl-4-methoxybenzenesulfonamide (3ca).[28] White solid, 87% yield (241 mg); mp 106-107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.28-7.24 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.49 (br s, 1H), 4.10 (d, *J* = 5.1 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9, 136.3, 131.4, 129.3, 128.6, 127.8, 114.2, 55.6, 47.2.

N-Benzyl-4-fluorobenzenesulfonamide (3da).[14b] White solid, 82% yield (217 mg); mp 95-97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.7 Hz and 5.1 Hz, 2H), 7.25-7.24 (m, 3H), 7.17-7.12 (m, 4H), 4.80 (br s, 1H), 4.13 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0 (d, $J_{C\text{-}F}$ = 254.2 Hz), 136.0, 129.7 (d, $J_{C\text{-}F}$ = 9.3 Hz), 128.6, 127.9, 127.8, 116.2 (d, $J_{C\text{-}F}$ = 22.6 Hz), 47.2.

N-Benzyl-4-chlorobenzenesulfonamide (3ea).[14b] White solid, 85% yield (239 mg); mp 100-101 °C; ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.32-7.25 (m, 5H), 7.28-7.26 (m, 3H), 7.19-7.17 (m, 2H), 4.82 (br s, 1H), 4.15 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 138.5, 135.9, 129.4, 128.8, 128.6, 128.1, 127.9, 47.3.

N-Benzyl-4-bromobenzenesulfonamide (3fa).[14b] White solid, 87% yield (284 mg); mp 119-120 °C; ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.25 (s, 3H), 7.17 (s, 2H), 5.03 (br s, 1H), 4.13 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 135.9, 132.3, 128.7, 128.6, 128.0, 127.8, 127.6, 47.2.

N-Benzyl-4-(trifluoromethyl)benzenesulfonamide (3ga).[29] White solid, 90% yield (284 mg); mp 114-115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.26-7.25 (m, 3H), 7.17-7.17 (m, 2H), 4.19 (s, 2H); ^{13}C NMR (125 MHz, DMSO) δ 145.8, 138.2, 133.0 (q, $J_{C\text{-}F}$ = 31.9 Hz), 129.2, 128.6, 128.4, 128.1, 127.3, 124.5 (q, $J_{C\text{-}F}$ = 272.2 Hz), 47.1.

N-Benzyl-4-(trifluoromethoxy)benzenesulfonamide (3ha).[14b] White solid, 88% yield (292 mg); mp 110-111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.27-7.23 (m, 5H), 7.16-7.15 (m, 2H), 4.47 (br s, 1H), 4.15 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 138.7, 136.0, 129.2, 128.6, 127.9, 127.9, 120.9, 120.2 (q, $J_{C\text{-}F}$ = 259.7 Hz), 47.3.

N-Benzylbenzenesulfonamide (3ia).[14h] White solid, 83% yield;(205 mg); mp 86-87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 6.8 Hz, 3H), 7.18-7.17 (m, 2H), 4.85 (brs, 1H), 4.12 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 136.2, 132.6, 129.1, 128.6, 127.8, 127.0, 47.1.

N-Benzylnaphthalene-2-sulfonamide (3ja).[14b] White solid, 85% yield (253 mg); mp 105-106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1 H), 7.95-7.90 (m, 3H), 7.63 (dd, *J* = 8.7 Hz and 1.8 Hz, 1H), 7.67-7.60 (m, 2H), 7.25-7.17 (m, 5H), 4.16 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.6, 136.1, 134.8, 132.1, 129.5, 129.2, 128.8, 128.7, 128.6, 127.9, 127.9, 127.6, 122.3, 47.4.

N-Benzyl(phenyl)methanesulfonamide (3ka).[30] White solid, 78% yield (204 mg); mp 147-148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.26 (m, 10H), 4.19 (s, 2H), 4.13 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.8, 130.6, 129.1, 128.8, 128.0, 59.3, 47.6.

N-Benzylmethanesulfonamide (3la).[30] White solid, 76% yield (141 mg); mp 58-59 °C; ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.37-7.30 (m, 5H), 4.30 (s, 2H), 2.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 128.8, 128.0, 127.9, 47.1, 40.0.

N-Benzylcyclopropanesulfonamide (3ma).[14b] White solid, 83% yield (176 mg); mp 54-55 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 5 H), 4.87 (br s, 1 H), 4.32 (d, *J* = 5.1 Hz, 2H), 2.34-2.32 (m, 1H), 1.14-1.23 (m, 2H), 0.91 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 128.7, 127.9, 127.8, 47.2, 30.5, 5.4.

Procedure for hydrogen transfer between 4 and 2a catalyzed by Cp*Ir(biimH_2)(H_2O)][OTf]$_2$ (Scheme 5). (*E*)-*N*-benzylidene-4-methylbenzenesulfonamide **4** (1 mmol), benzyl alcohol **2a** (1.2 mmol), cat. **1** (7.8 mg, 1 mol %), Cs_2CO_3 (33 mg, 0.1 mmol, 0.1 equiv) and water (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 2 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product **3aa** in 80% yield (209 mg).

Acknowledgements

Financial support by National Natural Science Foundation of China (21272115), Natural Science Foundation of Jiangsu Province (BK20161494) and the State Key Laboratory of Fine Chemicals (KF1704) is greatly appreciated.

Notes and references

1 M. B. Smith and J. March, in March's Advanced Organic Chemistry, Wiley-Interscience, New York, 2001, pp. 499-501.

2 For selected reviews, see: (*a*) M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv. Synth. Catal.*, 2007, **349**, 1555-1575; (*b*) G. E. Dobereiner and R. H. Grabtree, *Chem. Rev.*, 2010, **110**, 681-703; (*c*) G. Guillena, D. Ramon and M. Yus, *Chem. Rev.,* 2010, **110**, 1611-1641; (*d*) S. Bahn, S. Imm, L. Neubert, M. Zhang, H. Neumann and M. Beller, *ChemCatChem*, 2011, **3**, 1853-1864; (*e*) Q. Yang, Q. Wang and Z. Yu, *Chem. Soc. Rev.*, 2015, **44**, 2305-2329; (*f*) A. Corma, J. Navas and M. J. Sabater, *Chem. Rev.*, 2018, **118**, 1410-1459.

3 For selected examples, see: (*a*) M. H. S. A. Hamid and J. M. J. Williams, *Chem. Commun.*, 2007, 725-727; (*b*) C. Gunanathan and D. Milstein, *Angew. Chem. Int. Ed.*, 2008, **47**, 8661-8664; (*c*) S. Bahn, A. Tillack, S. Imm, K. Mevius, D. Michalik, D. Hollmann, L. Neubert and M. Beller, *ChemSusChem*, 2009, **2**, 551-557; (*d*) D. Pingen, C. Muller and D. Vogt, *Angew. Chem. Int. Ed.*, 2010, **49**, 8130-8133; (*e*) S. Bahn, S. Imm, K. Mevius, L. Neubert, A. Tillack, J. M. J. Williams and M. Beller, *Chem. Eur. J.*, 2010, **16**, 3590-3593; (*f*) S. Imm, S. Bahn, M. Zhang, L. Neubert, H. Neumann, F. Klasovsky, J. Pfeffer, T. Haas and M. Beller, *Angew. Chem. Int. Ed.*, 2011, 50, 7599-7603; (*g*) M. Zhang, S. Imm, S. Bahn, H. Neumann and M. Beller, *Angew. Chem. Int. Ed.*, 2011, **50**, 11197-11201; (*h*) A. J. A. Watson, A. C. Maxwell and J. M. J. Williams, *J. Org. Chem.*, 2011, **76**, 2328-2331; (*i*) D. Weickmann, W. Frey and B. Plietker, *Chem.-Eur. J.*, 2013, **19**, 2741-2748; (*j*) K. O. Marichev and J. M. Takacs, *ACS Catal.*, 2016, **6**, 2205-2210; (*k*) J. J. A. Celaje, X.

Zhang, F. Zhang, L. Kam, J. R. Herron and T. J. Williams, *ACS Catal.*, 2017, **7**, 1136-1142; (*l*) M. Maji, K. Chakrabarti, B. Paul, B. C. Roy and S. Kundu, *Adv. Synth. Catal.*, 2018, **360**, 722-729.

4 For selected examples, see: (*a*) K. Fujita, K. Yamamoto, R. Yamaguchi, *Org. Lett.*, 2002, **4**, 2691-2694; (*b*) K. Fujita, T. Fujii and R. Yamaguchi, *Org. Lett.*, 2004, **6**, 3525-3528; (*c*) S. Whitney, R. Grigg, A. Derrick and A. Keep, *Org. Lett.*, 2007, **9**, 3299-3302; (*d*) A. Prades, R. Corberán, M. Poyatos and E. Peris, *Chem.-Eur. J.*, 2008, **14**, 11474-11479; (*e*) R. Yamaguchi, S. Kawagoe, C. Asai and K. Fujita, *Org. Lett.*, 2008, **10**, 181-184; (*f*) D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito and R. H. Crabtree, *Organometallics*, 2009, **28**, 321-325; (*g*) N. Andrushko, V. Andrushko, P. Roose, K. Moonen, A. Boner, *ChemCatChem*, 2010, **2**, 640-643; (*h*) C. Segarra, E. Mas-Marzá, J. A. Mata and E. Peris, *Adv. Synth. Catal.*, 2011, **353**, 2078-2084; (*i*) M. A. Berliner, S. P. A. Dubant, T. Makowski, K. Ng, B. Sitter, C. Wager and Y. Zhang, *Org. Process Res. Dev.*, 2011, **15**, 1052-1062; (*j*) A. Wetzel. S. Wockel, M. Schelwies, M. K. Brinks, F. Rominger, P. Hofmann and M. Limbach, *Org. Lett.*, 2013, **15**, 266-269; (*k*) Q. Zou, C. Wang, J. Smith, D. Xue and J. Xiao, *Chem.-Eur. J.*, 2015, **21**, 9656-9661; (*l*) Z. Sun, Y. Liu, J. Chen, C. Huang and T. Tu, *ACS Catal.*, 2015, **5**, 6573-6578; (*m*) J. Chen, J. Wu and T. Tu, *ACS Sustainable Chem. Eng.*, 2017, **5**, 11744-11751; (*n*) D. Deng, B. Hu, M. Yang and D. Chen, *Organometallics*, 2018, **37**, 3353-3359; (*o*) M. Huang, Y. Li, J. Liu, X. Lan, Y. Liu, C. Zhaoa and Z. Ke, *Green Chem.*, 2019, **21**, 219-224.

5 T. T. Dang, B. Ramalingam, S. P. Shan and A. M. Seayad, *ACS Catal.*, 2013, **3**, 2536-2540.

6 (*a*) K. Shimizu, N. Imaiida, K. Kon, S. M. A. H. Siddiki and A. Satsuma, *ACS Catal.*, 2013, **3**, 998-1005; (*b*) M. Vellakkaran, K. Singh and D. Banerjee, *ACS Catal.*, 2017, **7**, 8152-8158.

7 (*a*) G. Zhang, Z. Yin and S. Zheng, *Org. Lett.*, 2016, **18**, 300-303; (*b*) M. Mastalir, G. Tomsu, E. Pittenauer, G. Allmaier and K. Kirchner, *Org. Lett.*, 2016, **18**, 3462-3465; (*c*) Z. Liu, Z. Yang, X. Yu, H. Zhang, B. Yu, Y. Zhao and Z. Liu, *Adv. Synth. Catal.*, 2017, **359**, 4278-4283.

8 (*a*) T. Yan, B. L. Feringa and K. Barta, *Nat. Commun.*, 2014, **5**, 5602-5609; (*b*) T. Yan, B. L. Feringa and K. Barta, *ACS Catal.* 2016, **6**, 381-388; (c) B. Emayavaramban, M. Roy and B. Sundararaju, *Chem.-Eur. J.*, 2016, **22**, 3952-3955; (*d*) T. J. Brown, M. Cumbes, L. J. Diorazio, G. J. Clarkson and M. Wills, *J. Org. Chem.*, 2017, **82**, 10489-10503; (*e*) A. Lator, S. Gaillard, A. Poater and J. Renaud, *Org. Lett.*, 2018, **20**, 5985-5990; (*f*) O. S. Nayal, Maheshwar, S. Thakur, M. Kumar, N. Kumar and S. K. Maurya, *Adv. Synth. Catal.*, 2018, **360**, 730-737.

9 (*a*) S. Elangovan, J. Neumann, J.-B. Sortais, K. Junge, C. Darcel and M. Beller, *Nat. Commun.*, 2016, **7**, 12641-12649; (*b*) J. Neumann, S. Elangovan, A. Spannenberg, K. Junge and M. Beller, *Chem.-Eur. J.*, 2017, **23**, 5410-5413; (*c*) R. Fertig, T. Irrgang, F. Freitag, J. Zander and R. Kempe, *ACS Catal.*, 2018, **8**, 8525-8530; (*d*) M. Huang, Y. Li, Y. Li, J. Liu, S. Shu, Y. Liu and Z. Ke, *Chem. Commun.*, 2019, **55**, 6213-6216.

10 For selected reviews, see: (*a*) U. M. Lindström, *Chem. Rev.*, 2002, **102**, 2751-2772; (*b*) C. J. Li, *Chem. Rev.*, 2005, **105**, 3095-3165; (*c*) C. I. Herrerıas, X. Yao, Z. Li and C. J. Li, *Chem. Rev.*, 2007, **107**, 2546-2562; (*d*) A. Chanda and V. V. Fokin, *Chem. Rev.*, 2009, **109**, 725-748; (*e*) R. N. Butler and A. G. Coyne, *Chem. Rev.*, 2010, **110**, 6302-6337; (*f*) M. O. Simon and C. J. Li, *Chem. Soc. Rev.*, 2012, **41**, 1415-1427; (*g*) T. Kitanosono, K. Masuda, P. Xu and S. Kobayashi, *Chem. Rev.*, 2018, **118**, 679-746.

11 (*a*) R. Kawahara, K. Fujita and R. Yamaguchi, *J. Am. Chem. Soc.*, 2010, **132**, 15108-15111; (*b*) R. Kawahara, K. Fujita and R. Yamaguchi, *Adv. Synth. Catal.*, 2011, **353**, 1161-1168.

12 (*a*) O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden and J. M. J. Williams, *Chem. Commun.*, 2010, **46**, 1541-1543; (*b*) O. Saidi, A. J. Blacker, G. W. Lamb, S. P. Marsden, J. E. Taylor and J. M. J. Williams, *Org. Process Res. Dev.*, 2010, **14**, 1046-1049.

13 For selected examples of transition metal-catalyzed the N-alkylaiton of sulfonamides with alcohols in organic solvent, see: (*a*) H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson and J. M. J. Williams, *J. Am. Chem. Soc.*, 2009, **131**, 1766-1774; (*b*) F. Shi, M. K. Tse, S. Zhou, M. M. Pohl, J. Radnik, S. Hubner, K. J. A. Bruckner and M. Beller, *J. Am. Chem. Soc.*, 2009, **131**, 1775-1779; (*c*) R. Cano, D. J. Ramón and M. Yus, *J. Org. Chem.*, 2011, **76**, 5547-5557; (*d*) F. Shi, M. K. Tse, X. Cui, D. Gordes, D. Michalik, K. Thurow, Y. Deng and M. Beller, *Angew. Chem. Int. Ed.*, 2009, **48**, 5912-5915; (*e*) X. Cui, F. Shi, M. K. Tse, D. Gordes, K. Thurow, M. Beller and Y. Deng, *Adv. Synth. Catal.*, 2009, **351**, 2949-2958; (*f*) M. Zhu, K. Fujita and R. Yamaguchi, *Org. Lett.*, 2010, **12**, 1336-1339; (*g*) C. Liu, S. Liao, Q. Li , S. Feng, Q. Sun, X. Yu and Q. Xu, *J. Org. Chem.*, 2011, **76**, 5759-5773; (*h*) X. Yu, C. Liu, L. Jiang and Q. Xu, *Org. Lett.*, 2011, **13**, 6184-6187.

14 For recent examples of N-alkylsulfonamides as biologically active compounds, see: (*a*) M. Tercel, H. H. Lee, S. Y. Mehta, J. Y. Tendoung, S. Y. Bai, H. D. S. Liyanage and F. B. Pruijn, *J. Med. Chem.*, 2017, **60**, 5834-5856; (*b*) M. Bonnet, C. R. Hong, W. W. Wong, L. P. Liew, A. Shome, J. Wang, Y. Gu, R. J. Stevenson, W. Qi, R. F. Anderson, F. B. Pruijn, W. R. Wilson, S. M. F. Jamieson, K. O. Hicks and M. P. Hay, *J. Med. Chem.*, 2018, **61**, 1241-1254; (*c*) A. K. Ghosh, P. R. Nyalapatla, S. Kovela, K. V. Rao, M. Brindisi, H. L. Osswald, M. Amano, M. Aoki, J. Agniswamy, Y. Wang, I. T. Weber and H. Mitsuya, *J. Med. Chem.*, 2018, **61**, 4561-4577; (*d*) W. Amberg, U. E. W. Lange, M. Ochse, F. Pohlki, B. Behl, A. L. Relo, W. Hornberger, C. Hoft, M. Mezler, J. Sydor,Y. Wang, H. Zhao, J. T. Brewer, J. Dietrich, H. Li, I. Akritopoulou-Zanze, Y. Lao, S. Hannick, Y. Ku and A. Vasudevan, *J. Med. Chem.*, 2018, **61**, 7503-7524.

15 P. Qu, C. Sun, J. Ma and F. Li, *Adv. Synth. Catal.*, 2014, **356**, 447-459.

16 This complex was originally synthesized by Fujita, Yamaguchi and co-workers for the acceptorless dehydrogenation of alcohols in water, see: R. Kawahara, K. Fujita and R. Yamaguchi, *J. Am. Chem. Soc.*, 2012, **134**, 3643-3646.

17 (*a*) F. Li, C. Sun and N. Wang, *J. Org. Chem.*, 2014, **79**, 8031-8039; (*b*) P. Qu, C. Sun, J. Ma and F. Li, *Adv. Synth. Catal.*, 2014, **356**, 447-459; (*c*) N. Wang, X. Zou, J. Ma and F. Li, *Chem. Commun.*, 2014, **50**, 8303-8305; (*d*) F. Li, J. Ma and N. Wang, *J. Org. Chem.*, 2014, **79**, 10447-10455; (*e*) R. Wang, J. Ma and F. Li, *J. Org. Chem.,* 2015, **80**, 10769-10776; (*f*) L. Lu, J. Ma, P. Qu and F. Li, *Org. Lett.*, 2015, **17**, 2350-2353; (*g*) W. Zhao, P. Liu and Feng Li, *ChemCatChem*, 2016, **8**, 1523-1530; (*h*) F. Li, L. Lu and P. Liu, *Org. Lett.,* 2016, **18**, 2580-2583; (*i*) R. Wang, H. Fan, W. Zhao and F. Li, *Org. Lett.*, 2016, **18**, 3558-3561; (*j*) R Liang, S. Li, R Wang, L.Lu and F. Li, *Org. Lett.*, 2017, **19**, 5790-5793; (*k*) R. Wang, Y. Tang, M. Xu, C. Meng and F. Li, *J. Org. Chem.*, 2018, **83**, 2274-2281.

18 The synthesis and single crystal structures of $[Cp^*Ir(biimH_2)Cl]Cl$, see: R. Ziessel, M. Youinou, F. Balegroune and D. Grandjean, *J. Organomet. Chem.*, 1992, **441**, 143-154.

19 (*a*) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi and M. Kavana, *J. Am. Chem. Soc.*, 2001, **123**, 1090-1100; (*b*) J. B. Johnson and Jan-E. Backvall, *J. Org. Chem.*, 2003, **68**, 7681-7684; (*c*) B. L. Conley, M. K. Pennington-Boggio, E. Boz and T. J. Williams, *Chem Rev.,* 2010, **110**, 2294-2312.

20 (*a*) K. J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya and R. Noyori, *Angew. Chem. Int. Ed.,* 1997, **36**, 285-287; (*b*) K. Matsumura, S. Hashiguchi, T. Ikariya and R Noyori, *J. Am. Chem. Soc.*, 1997, **119**, 8738-8739; (*c*) R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97-102; (*d*) K. Murata, T. Ikariya and R.

View Article Online
DOI: 10.1039/C9NJ02542A

Noyori, *J. Org. Chem.,* 1999, **64**, 2186-2187; (*e*) T. Ikariya and A. J. Blacker, *Acc. Chem. Res.,* 2007, **40**, 1300-1308.
21 S. Ogo, N. Makihara and Y. Watanabe, *Organometallics*, 1999, **18**, 5470-5474.
22 K. Müther, J. Mohr and M. Oestreich, *Organometallics*, 2013, **32**, 6643-6646.
23 J. D. Wilden, L. Geldeard, C. C. Lee, D. B. Judd and S.Caddick, *Chem. Commun.*, 2007, 1074-1076.
24 G. A. Molander, N. Fleury-Brgeot and M. Hiebel, *Org. Lett.*, 2011, **13**, 1694-1697.
25 B. Sreedhar, P. S. Reddy, M. A. Reddy, B. Neelima and R.Arundhathi, *Tetrahedron Lett.*, 2007, **48**, 8174-8177.
26 A. Martnez-Asencio, D. J. Ramon and M. Yus, *Tetrahedron Lett.*, 2010, **51**, 325-327.
27 X. Liu, Y. Liu and Y. Zhang, *Tetrahedron Lett.*, 2002, **43**, 6787-6789.
28 Z.Sahli, B. Sundararaju, M. Achard and C. Bruneau, *Org. Lett.*, 2011, **13**, 3964-3967.
29 M. Harmata, P. Zheng, C. Huang, M. G. Gomes, W. Ying, K. O. Ranyanil, G. Balan and N. L. Calkins, *J. Org. Chem.*, 2007, **72**, 683-685.
30 M. Harmata, H. Veisi, R. G. Vaghei, S. Hemmati and J. Mahmoodic, *Synlett,* 2011, 2315-2320.