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Amide Iridium Complexes As Catalysts for Transfer Hydrogenation Reduction of *N*-sulfonylimine

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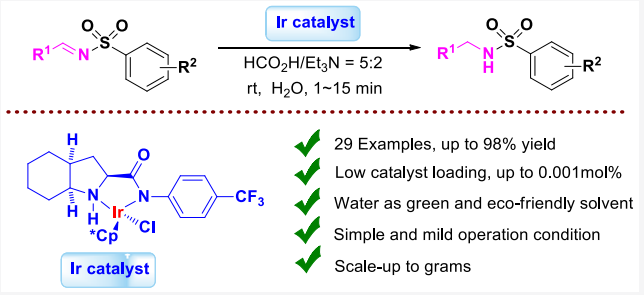
ABSTRACT: Sulfonamide moieties widely exist in natural products, biologically active substance, and pharmaceuticals. Here, an efficient water-soluble amide iridium complexes-catalyzed transfer hydrogenation reduction of *N*-sulfonylimine is developed, which can be carried out under environmentally friendly conditions, affording a series of sulfonamide compounds in excellent yields (96−98%). In comparison with organic solvents, water is shown to be critical for a high catalytic transfer hydrogenation reduction in which the catalyst loading can be as low as 0.001 mol %. These amide iridium complexes are easy to synthesize, one structure of which was determined by single-crystal X-ray diffraction. This protocol gives an operationally simple, practical, and environmentally friendly strategy for synthesis of sulfonamide compounds.



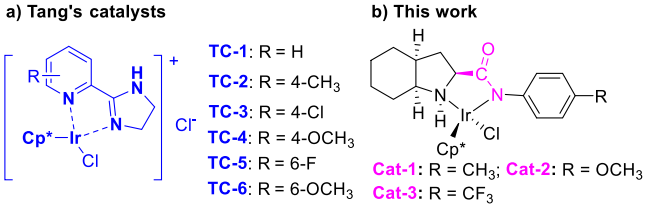
INTRODUCTION

Hydrogenation is the most effective transformation in chemical synthesis.[1] Direct hydrogenation and transfer hydrogenation are two strategies to achieve hydrogenation. Compared with direct hydrogenation, transfer hydrogenation showcases many advantages and becomes a research center in hydrogenation science.[2] So far, great efforts and astonishing achievements have been made in the development of transition-metal-catalyzed symmetric, asymmetric transfer hydrogenation, and a variety of transition metals, ligands, and hydrogen sources are involved in the hydrogen transfer transformation, which has become a central issue in organic synthesis.[2] Since Mestroni's group first reported the iridium-catalyzed hydrogen transfer of ketones,[3] iridium has become one of the most active metals employed in hydrogen transfer transformation.[4] In 1999, Noyori[5a] introduced the Cp*Ir catalysts for this transformation, and a dramatic increase of this kind of catalysts has occurred since then.[5]

Generally, there are two common mechanisms for metal-catalyzed transfer hydrogenation reactions: The hydridic route and direct hydrogen transfer.[6] The commonly accepted mechanism for Cp*Ir-catalyzed hydrogen transfer reactions is the monohydride route (either inner- or outer-sphere),[6a] Usually, Cp*Ir catalysts bearing diamine, triazolyl ligands, NHC fragments, and half-sandwich cyclometalated Ir complexes are employed as TH catalysts.[2] As we all know, ancillary ligands can significantly influence the coordination chemistry and reactivity of transition-metal complexes. Although Cp*Ir catalysts are so important in TH, research on the ligands' effects at the Cp*Ir fragment is still not comprehensive.[7] Compared with the Cp*Ru and Cp*Rh catalysts, the Cp*Ir catalysts have been explored to a lesser degree. In addition, Cp*Ir catalysts containing dinitrogen ligands have shown superior performance, which highlights the great potential of Cp*Ir catalysts containing dinitrogen ligands in catalysis.[7a]

Recently, our group has been devoted to the application of transfer hydrogenation reactions with Cp*Ir catalysts with dinitrogen ligands (Scheme 1a) and developed some efficient catalytic methodologies,[8] but the development of more iridium catalysts which possesses more efficient, broader substrates scope or asymmetric catalysis remains an important goal. Herein, we propose to design and employ half-sandwich iridium complexes of perhydroindolinamide (Scheme 1b) to investigate the catalytic performance.

Scheme 1. Cp*Ir Catalysts



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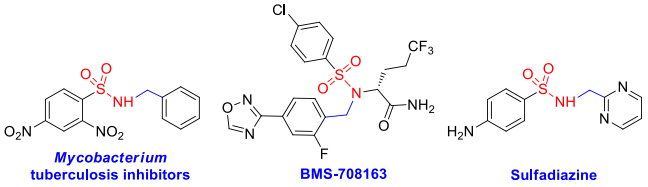
Sulfonamide moieties widely exist in natural products, biologically active substances, and pharmaceuticals, such as potential ETA antagonists,[9] thromboxane receptor antagonists,[10] antimycobacteria agents,[11] matrix metalloproteinase inhibitors,[12] and human EP_3 receptor antagonists[13] (Scheme 2). Therefore, development of methods for the efficient

Scheme 2. Selected Examples of Bioactive Benzylic *N*-Alkylsulfonamide Pharmacores

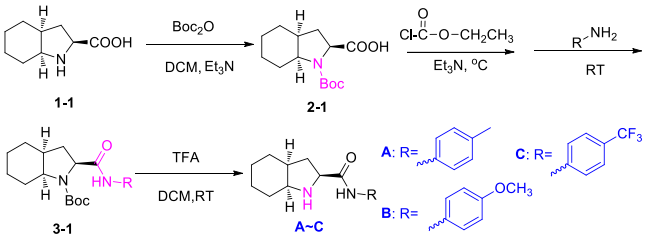


synthesis of sulfonamide moiety is an important facet of organic chemistry. One of the most common synthetic strategies of the *N*-sulfonamide unit is achieved by the reaction of sulfonyl chlorides with alkyl or aryl amine under basic conditions.[14] However, sulfonyl chlorides are often difficult to handle and store due to their instability.[15] Therefore, reduction of *N*-sulfonylimine is among the most typical methods. Generally, there are two main types of strategies, including transition-metal catalysts[16] and metal-free catalysts,[17] to achieve the reduction of *N*-sulfonylimine. Until now, progress in developing homogeneous catalytic systems, including transition-metal catalysts such as Zr,[16a] Ir,[16b] and Al[16c] employed in transformation of *N*-sulfonamide, has been made. However, more improvements are needed in the expansion of the substrate scope and catalytic efficiency. Herein, we describe our efforts on the design and synthesis of amide iridium complexes, which present a highly efficient transfer hydrogenation reduction of *N*-sulfonyl imine. In comparison with organic solvents, water is shown to be critical for a high catalytic transfer hydrogenation reduction.

RESULTS AND DISCUSSION

Synthesis of Amide Ir-Complexes Cat-1−Cat-3. First, the ligands **A**−**C** were prepared according to the reported methods (Scheme 3).[18] With ligands **A**−**C** in hand, the amide Ir-complexes **Cat-1**−**Cat-3** were synthesized according to the literature (Scheme 1b).[19]

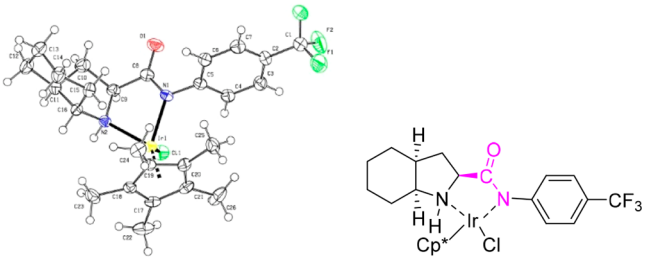
Scheme 3. Procedures for Synthesis of Ligands A−C



At the same time, the absolute configurations of amide Ir-complexes **Cat-3** was determined by single-crystal X-ray diffraction (Scheme 4).

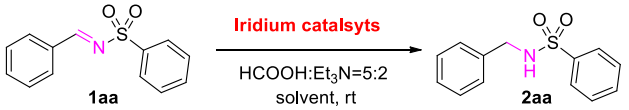
Catalytic Transfer Hydrogenation Reduction of *N*-Sulfonylimine with Amide Ir-Complexes. Initially, we started our investigation by choosing the (*E*)-*N*-benzylidenebenzenesulfonamide (**1a**) as the model substrate, amide Ir-

Scheme 4. X-ray ORTEP Drawing of Cat-3



complexes **Cat-1**−**Cat-3** as precatalysts and HCO_2H/Et_3N as the hydrogen source (Table 1). To our delight, the substrate

Table 1. Catalyst Screening and Optimization of the Reaction Conditions for Transfer Hydrogenation Reduction[a]



entry	catalyst	solvent	time	yield[b] (%)
1	**Cat-1**	H_2O	1 min	>99
2	**Cat-2**	H_2O	1 min	>99
3	**Cat-3**	H_2O	1 min	>99
4	**TC-4**	H_2O	15 min	>99
5	**TC-5**	H_2O	15 min	>99
6	**TC-6**	H_2O	15 min	>99
7[c]	**Cat-3**	H_2O	5 min	>99
8[d]	**Cat-3**	H_2O	10 min	>99
9[e]	**Cat-3**	H_2O	20 min	>99
10[f]	**Cat-3**	H_2O	8 h	>99
11[f]	**Cat-1**	H_2O	60 h	>99
12[f]	**Cat-2**	H_2O	50 h	>99
13[g]	**Cat-3**	H_2O	30 h	>99
14[h]	**Cat-3**	H_2O	96 h	>99
15	**Cat-3**	MeOH	1 min	>99
16	**Cat-3**	toluene	30 min	<5
17	**Cat-3**	hexane	30 min	<5

[a]The reactions of **1a** (1 mmol, 1.0 equiv) and catalyst (1.0 mol %, 0.01 equiv) were carried out under in air and solvents (2.0 mL), $HCOOH/Et_3N$ (5:2) (1.0 mL). [b]Determined by GC−MS. [c]The catalyst loading was 0.75 mol %. [d]The catalyst loading was 0.5 mol %. [e]The catalyst loading was 0.25 mol %. [f]The catalyst loading was 0.1 mol %. [g]The catalyst loading was 0.01 mol %. [h]The catalyst loading was 0.001 mol %.

was quantitativly converted to corresponding amine product within 1 min by employing Ir-complexes **Cat-1**−**Cat-3** as the catalysts (Table 1, entries 1−3). Encouraged by this promising result and intrigued by the curiosity about catalytic activity between our catalysts and Tang's catalysts, the compared experiments were investigated between **Cat-1**−**Cat-3** and TC **4**−**6** under the standard conditions, which demonstrated that **Cat-1**−**Cat-3** showed higher activity than TC **4**−**6** based on the reaction time (Table 1, entries 1−6). Subsequently, **Cat-3** was distinguished from **cat-1** and **cat-2** by decreasing the catalyst loading to 0.1 mol % (Table 1, entries 7−9). As shown in Table 1, **Cat-3** showed the best catalytic activity. In this catalytic system, we speculated the mechanism of this transformation catalyzed by **Cat-3** possibly via inner-sphere monohydride route. The coordinative ability of **Cat-3** with the

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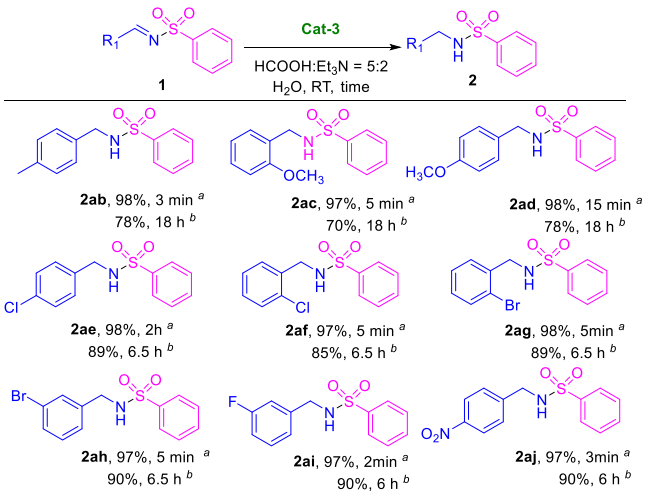
substrates is greatly enhanced due to the strong electron-withdrawing CF_3 group in the ligand, which plays an important role in accelerating this transformation, compared with Tang's catalysts, **cat-1** and **cat-2**.[6] To explore the potential catalytic efficiency, we next evaluated the catalytic performance of **Cat-3** at higher S/C ratios. The results were shown in Table 1 (entries 7−10, entries 13 and 14). As can be seen in Table 1, full conversion was achieved in 20 min even when the catalyst loading was decreased to 0.25 mol % (Table 1, entry 9). But when the catalyst loading was decreased to 0.01 and 0.001 mol %, it took 30 and 96 h to achieve full conversion, respectively. We speculated the actual TOF of the catalyst is very high when active catalyst exists. But when 0.1 mol % or even lower catalyst loading is employed, there is very little real active catalyst, which consumes significantly higher reaction time. Interestingly, we noticed that the reaction under the polar solvents, such as H_2O and MeOH, was faster than the nonpolar solvents toluene and hexane (Table 1, entries 15−17).

With the best optimal conditions in hand, the substrate scope of the aqueous HCO_2H/Et_3N conditions with 1.0 mol % **Cat-3** as the catalyst was initially screened in the reactions of imines which were condensed by phenylsulfonamide with different substituted aldehydes. As can be seen in Scheme 5,

Scheme 5. Transfer Hydrogenation Reduction of Phenylsulfonamide Imines



the electron-donating substituents Me (**1ab**), and OMe (**1ac**, **1ad**) were well tolerated, affording the desire products in yields of 97−98%. Likewise, different halide substituents (Cl, Br, and F) (**1ae**−**1ai**) were also tolerated in different positions of the phenyl ring in nearly quantitative yields. Notably, the nitro substituent that is sensitive to hydrogenation was again tolerated in this catalytic system, providing the corresponding product **2aj** in high yields of 97%. Interestingly, the electron-withdrawing substituted imines (**1ae**−**2ag**) were distinguished from electron-donating substituted imines (**1ab**−**2ad**) by decreasing the catalyst loading to 0.1 mol % in general.

Next, the transfer hydrogenation reduction of various substituted phenylsulfonamide imines was investigated with 1.0 mol % **Cat-3**, which is summarized in Scheme 6. First, chlorine-substituted phenylsulfonamide imines were investigated under standard conditions. Encouragingly, the electronic effects of the substituents are not obvious. For example, the imines with heteroaromatic (**1am**) and naphthalene ring structures (**1ak**, **1al**) all reacted well, affording excellent yields in 96−98%. Meanwhile, the electron-donating, such as methyl (**1an**) and methoxy (**1ao**, **1ap**), or electron-withdrawing, such as bromine (**1aq**) and chlorine (**1ar**), substituted imines were also well tolerated.

Subsequently, methyl-substituted phenylsulfonamide imines were also explored. As can be seen in Scheme 6, all substrates, including electron-donating (**1as**−**1av**) or electron-withdrawing substituents (**1aw**−**1ba**), were well tolerated in this catalytic transfer hydrogenation reduction system, providing various sulfonamide compounds in excellent yields (>96% yield). Likewise, the *N*-(2-hydroxybenzyl)-4-methylbenzenesulfonamide possessing phenolic hydroxyl showed the same activity (**1bb**). Similarly, *N*-benzyl-4-methoxyaniline is also a good substrate (**1bc**).

To explore the potential substrates scope and the asymmetric results of this chiral iridium complexes catalyzed transfer hydrogenation reduction system, *N*-sulfonamideketimine was chosen as the model reaction to investigate this catalytic activity under the same conditions. To our disappointment, the *N*-sulfonamide ketimine (Scheme 6, **1bd**) was immediately decomposed into the corresponding acetophenone under the standard reaction conditions. Therefore, the chiral catalytic performance of this iridium complexed is seriously limited in the *N*-sulfonamide ketimine substrates.

To explore the reactivities of different substrates and the catalytic efficiency of this catalytic system, a lower catalyst loading such as 0.1 mol % was also studied (Scheme 6). In general, lower yields are obtained by using a lower catalyst loading (0.1 mol %), and greatly prolonged reaction times are needed, accompanied by a small amount of substrate decomposition. Compared with 1.0 mol % catalyst, unequal reactivities of different substrates are showcased by employing 0.1 mol % **Cat-3** as catalyst. Generally, the electronegativities of the R^2 substituents have little effects on the activities of the reaction, while they have more obvious effects on the R^1 substituents. For example, when naphthalene (**1al**), heterocyclic (**1am**), and benzene containing electron-donating groups (**1an**−**1ap**) are employed as substrates, the reaction activities are lower and longer reaction times are required. In particular, when thiophene (**1am**) and 2-methoxyphenyl imines (**1ap**) are employed as substrates, only moderate yields are obtained.

Encouraged by the results, we next enforced a scale-up experiment under the established conditions with 0.001 mol % **cat-3** catalyst loading at the scale of **1aa** in 40 mmol, giving **2aa** in a yield of 90% (Scheme 7).

To better understand the reaction mechanism, we conducted deuterated experiments (Scheme 8). Study showed that the hydrogen inserted in the product of this hydrogen transfer reduction came from formic acid. In addition, the hydride iridium **B** (Scheme 9) which was detected by NMR by mixing the iridium catalyst with formic acid and triethylamine, and the distinctive high-field signal appeared at −12.3 ppm (see the Supporting Information).

On the basis of our experimental results and previous reports,[20,6] a plausible mechanism is proposed in Scheme 9. As we know, the formate anion exchanged with the chloride ligand on bis-nitrogen iridium complexes to yield active **A** first.[21] Subsequently, active catalyst **A** gave rise to iridium hydride **B** along with extruding carbon dioxide. Then the imines were trapped by iridium hydride **B** and formed a four-

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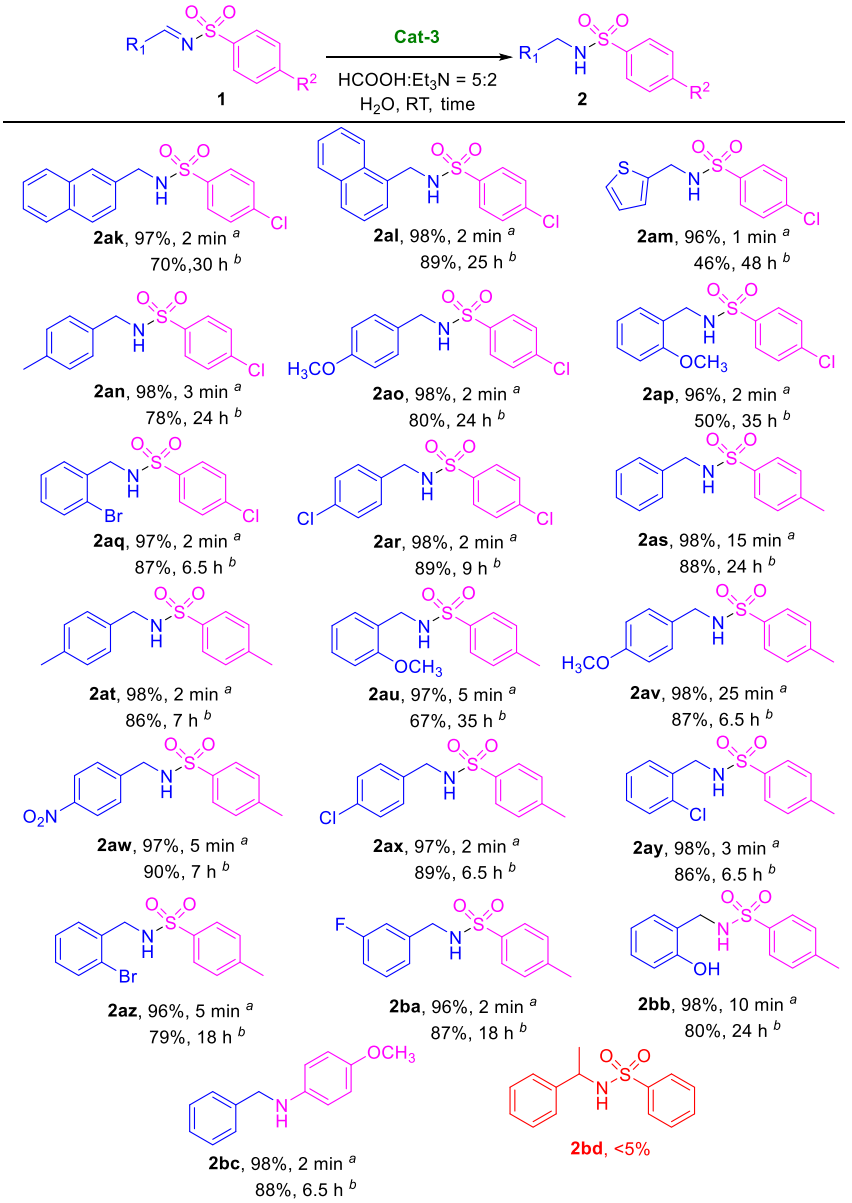
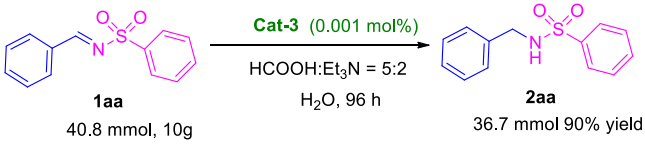
Scheme 6. Transfer Hydrogenation Reduction of Substituted Phenylsulfonamide Imines

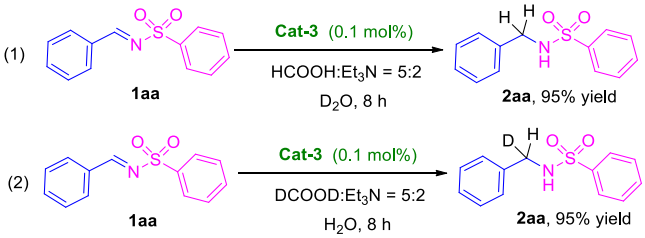


[a]1.0 mol % catalyst was added. [b]0.1 mol % catalyst was added.

Scheme 7. Large-Scale Experiment



Scheme 8. Deuterated Experiments



membered transition intermediate C. Finally, the desired products were achieved via protonation.

CONCLUSIONS

In summary, we have designed and synthesized a type of amide iridium complex as an efficient catalyst for transfer hydrogenation reduction of *N*-sulfonylaldimines by using formic acid as the hydrogen source and water as the solvent in air. This protocol allows for a low catalyst loading as 0.001 mol %, offering an efficient method for synthesis of sulfonamide compounds. The broad substrate scope, simple operation, good functional group tolerance, and excellent yield are the attractive features of this transformation. The application of ketimine substrate and its asymmetric catalysis research is underway.

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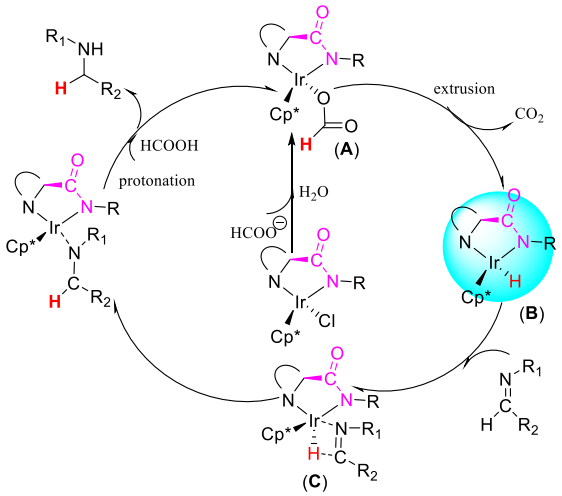
Scheme 9. Proposed Reaction Mechanism



EXPERIMENTAL SECTION

General Information. Reagents were purchased from commercial sources. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AVANCE NEO 400 MHz NMR spectrometers. Chemical shifts (δ) are reported in ppm from internal tetramethylsilane or the central $CDCl_3$ resonance (δ = 7.26 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.16 ppm) for ^{13}C NMR spectroscopy. The melting points were determined on WRR melting point apparatus and are uncorrected. Conversion was monitored by thin-layer chromatography (TLC). Flash column chromatography was performed over silica gel (200−300 mesh). HRMS ESI data were acquired on a Bruker microTOF II spectrometer.

Synthesis of the Ligands A−C.[18] To solution of (2*S*,3a*S*,7a*S*)-octahydro-1*H*-indole-2-carboxylic acid (25.0 g, 147.9 mmol, 1.0 equiv), dichloromethane (250.0 mL), and di-*tert*-butyl dicarbonate (35.5 g, 1.1 equiv) was added TEA (23.0 mL, 1.1 equiv) at room temperature and the mixture stirred overnight until full conversion. The pH of the reaction mixture was adjusted to about 7−8 with citric acid solution. The organic layer was separated, and the inorganic layers were re-extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated to afford **2-1**, which was used in the next step directly.

To a solution of compound **2-1** and Et_3N in dichloromethane was added ethyl carbonochloridate (1.2 equiv) dropwise at 0 °C and the mixture stirred for 1 h. Amines (1.2 equiv) were added, and the reaction was stirred overnight. The reaction was wash sequentially with citric acid solution, saturated Na_2CO_3, and brine. The organic layer was dried over Na_2SO_4 and concentrated to afford compounds **3−1**.

To a solution of compounds **3-1** (1.0 equiv) in CH_2Cl_2 was added TFA (20.0 equiv). The solution was stirred until completion. The reaction was neutralized with saturated Na_2CO_3 until pH ∼9. The aqueous layer was extracted with CH_2Cl_2 (3 × 50.0 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Finally, the crude product was purified by flash column chromatography with petroleum ether/EtOAc (1:1) and concentrated to afford amides **A−C**.

*(2S,3aS,7aS)-N-(p-Tolyl)octahydro-1H-indole-2-carboxamide (**A**).* White solid; mp 129.0−130.0 °C (36.6 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.84 (dd, *J* = 10.7, 4.7 Hz, 1H), 3.36 (q, *J* = 4.7 Hz, 1H), 2.39−2.32 (m, 1H), 2.31 (s, 3H), 2.22−2.08 (m, 1H), 2.04−1.94 (m, 1H), 1.93−1.85 (m, 1H), 1.65−1.54 (m, 3H), 1.53−1.46 (m, 2H), 1.43−1.35 (m, 1H), 1.34−1.28 (m, 1H), 1.27−1.17 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.2, 135.5, 133.5, 129.6, 119.2, 59.4, 57.6, 38.1, 35.7, 29.5, 27.7, 23.8, 22.0, 21.0; HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{16}H_{23}N_2O$ 259.1810; Found 259.1807.

*(2S,3aS,7aS)-N-(4-methoxyphenyl) octahydro-1H-indole-2-carboxamide (**B**).* White solid; mp 130.0−131.0 °C (38.9 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) 9.82 (s, 1H), 7.50 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.84 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.78 (s, 3H), 3.38−3.32 (m, 1H), 2.39−2.28 (m, 1H), 2.08−1.96 (m, 2H), 1.93−1.84 (m, 1H), 1.65−1.43 (m, 5H), 1.42−1.16 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.1, 156.2, 131.4, 120.8, 114.3, 59.4, 57.6, 55.6, 38.2, 35.7, 29.5, 27.7, 23.7, 22.0; HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{16}H_{23}N_2O_2$ 275.1760; Found 275.1756.

*(2S,3aS,7aS)-N-(4-(Trifluoromethyl)phenyl) octahydro-1H-indole-2-carboxamide (**C**).* White solid; mp 83.0−84.0 °C (44.2 g, 96%); ^{1}H NMR (400 MHz, $CDCl_3$) 10.22 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 3.90 (dd, *J* = 10.7, 4.8 Hz, 1H), 3.41 (q, *J* = 5.1 Hz, 1H), 2.48−2.30 (m, 1H), 2.18−1.84 (m, 3H), 1.75−1.39 (m, 6H), 1.37−1.19 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.8, 141.0, 126.4 (q, $^4J_{C-F}$ = 3.8 Hz), 125.7 (q, $^3J_{C-F}$ = 33.3 Hz), 124.3 (q, $^1J_{C-F}$ = 272.7 Hz), 118.8, 59.5, 57.7, 38.2, 35.7, 29.4, 27.7, 23.6, 22.1; ^{19}F{^{1}H} NMR (367 MHz, $CDCl_3$) δ −62.00. HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{16}H_{20}F_3N_2O$ 313.1528; Found 313.1525.

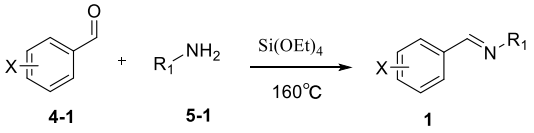
*General Procedure for Preparation of Catalysts **Cat-1−Cat-3**.* Catalysts **Cat-1−Cat-3** were synthesized according to the literature[19] by mixing $[IrCp^*Cl_2]_2$ (1.0 equiv) and the corresponding ligands **A−C** (2.0 equiv) in dry dichloromethane at room temperature. After being stirred overnight, the yellow solutions were evaporated to obtain yellow solids, which were used directly in the reduction of imine. A single crystal of **Cat-3** suitable for X-ray diffraction analysis was obtained in MeOH after many attempts.

Cat-1. Yellow solid; mp 181−182.0 °C (608 mg, 98%); ^{1}H NMR (400 MHz, D_2O) δ 7.32 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 3.86−3.72 (m, 2H), 2.54−2.41 (m, 1H), 2.39 (s, 3H), 2.19−2.06 (m, 1H), 1.99−1.85 (m, 1H), 1.84−1.62 (m, 4H), 1.61−1.53 (m, 2H), 1.52−1.44 (m, 1H), 1.43 (s, 15H), 1.32−1.17 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, D_2O) δ 192.4, 145.3, 137.0, 129.7, 125.3, 90.5, 63.5, 61.2, 38.8, 30.0, 29.4, 24.3, 20.0, 18.7, 8.6; HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{26}H_{37}N_2OClIr$ 621.2224; Found 621.2221.

Cat-2. Yellow solid; mp 181−182.0 °C (624.5 mg, 98%); ^{1}H NMR (400 MHz, D_2O) δ 7.08 (d, *J* = 9.1 Hz, 2H), 7.02 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H), 3.77−3.66 (m, 1H), 2.55−2.38 (m, 1H), 2.17−2.06 (m, 1H), 1.96−1.87 (m, 1H), 1.85−1.61 (m, 6H), 1.42 (s, 15H), 1.31−1.19 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, D_2O) δ 191.4, 157.3, 141.6, 126.6, 114.5, 90.1, 63.3, 61.4, 55.5, 38.7, 29.5, 29.4, 24.4, 24.3, 18.8, 8.6; HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{26}H_{37}N_2O_2ClIr$ 637.2173; Found 637.2148.

Cat-3: Yellow solid; mp 191−192.0 °C (660.5 mg, 98%); ^{1}H NMR (400 MHz, D_2O) δ 7.32 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 3.82 (dd, *J* = 7.6, 10.0 Hz, 1H), 3.78−3.70 (m, 1H), 2.55−2.42 (m, 1H), 2.23−2.08 (m, 1H), 2.01−1.89 (m, 1H), 1.87−1.60 (m, 5H), 1.54−1.44 (m, 1H), 1.42 (s, 15H), 1.33−1.23 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, D_2O) δ 190.6, 151.4, 126.7, 126.6, 126.4, 89.9, 63.3, 61.4, 38.8, 29.3, 24.4, 24.3, 23.0, 18.8, 8.51; HRMS (ESI) *m*/*z* [M + H]$^+$ Calcd for $C_{26}H_{34}N_2OClF_3Ir$ 675.1941; Found 675.1918.

General Procedure for the Synthesis of Imine. A solution of aldehyde (1.0 equiv) and amide derivatives (1.0 equiv) was added



$Si(OEt)_4$ (1.2 equiv) and the mixture stirred in a flask equipped at 160 °C until the reaction were completed. The reaction mixture was suspended in Et_2O or *n*-pentane, filtered, and washed by Et_2O or *n*-pentane. The target product was directly used in the reaction without further purification. Imines **1aa**,[22] **1ab**,[23] **1ad**,[23a] **1ae**,[24] **1af**,[25] **1ai**,[26] **1aj**,[27] **1an**,[28] **1ao**,[29] **1ap**,[30] **1aq**,[30] **1ar**,[28] **1as**,[31] **1at**,[32] **1au**,[31,33] **1av**,[32] **1aw**,[31] **1ax**,[31,32] **1ay**,[25] **1az**,[34] **1ba**,[35] **1bb**,[36] and **1bc**[37] were prepared according to the literature.

*(E)-N-(2-Methoxybenzylidene)benzenesulfonamide (**1ac**).* Light yellow solid; yield 10.2 g, 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57

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(s, 1H), 8.12−7.98 (m, 3H), 7.65−7.48 (m, 4H), 7.02−6.94 (m, 2H), 3.93 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.0, 161.9, 138.8, 137.2, 133.4, 129.5, 129.2 (2C), 128.0 (2C), 126.5, 121.0, 111.6, 55.9; HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{14}H_{14}NO_3S$ 276.0694; Found 276.0691.

*(E)-N-(2-Bromobenzylidene)benzenesulfonamide (**1ag**).* Light yellow solid; yield 8.8 g, 93%; ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.15 (dd, *J* = 7.7, 1.5 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.49−7.34 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.8, 137.8, 136.0, 134.0, 133.9, 131.3, 130.8, 129.4, 129.2, 128.4, 128.1; HRMS (ESI) *m/z:* $[M + H]^+$ Calcd for $C_{13}H_{11}BrNO_2S$ 323.9694; Found: 323.9691.

*(E)-N-(3-Bromobenzylidene)benzenesulfonamide (**1ah**).* Light yellow solid; yield 7.2 g, 91%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.10 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.69−7.62 (m, 1H), 7.60−7.54 (m, 2H), 7.38 (t, *J* = 7.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.1, 137.9, 134.3, 134.0, 133.4, 130.8, 130.4, 129.4, 128.3, 126.5, 123.5; HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{13}H_{11}BrNO_2S$ 323.9694; Found 323.9691.

*(E)-4-Chloro-N-(naphthalen-2-ylmethylene)benzenesulfonamide (**1ak**).* White solid; yield 5.3 g, 92%; ^1H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.34 (s, 1H), 8.05−7.93 (m, 4H), 7.92−7.86 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 140.1, 137.0, 136.8, 136.7, 132.7, 130.0, 129.8, 129.7, 129.6, 129.6, 129.4, 128.2, 127.5, 124.1; HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{17}H_{13}ClNO_2S$ 330.0356; Found 330.0353

*(E)-4-Chloro-N-(naphthalen-1-ylmethylene)benzenesulfonamide (**1al**).* White solid; yield 6.2 g, 93%; ^1H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.97 (d, *J* = 8.6 Hz, 1H), 8.15 (dd, *J* = 7.7, 15.9 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.73−7.66 (m, 1H), 7.63−7.56 (m, 2H), 7.53 (d, *J* = 8.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.0, 140.4, 137.0, 136.8, 136.7, 132.7, 130.0, 129.8, 129.7, 129.6, 129.6, 129.5, 129.4, 128.2, 128.1, 127.5, 124.1; HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{17}H_{13}ClNO_2S$ 330.0356; Found 330.0353.

*(E)-4-Chloro-N-(thiophene-2-ylmethylene)benzenesulfonamide (**1am**).* White solid; yield 4.5 g, 91%; ^1H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 9.90 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 4.3 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.21 (t, *J* = 4.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 163.1, 140.2, 139.8, 138.0, 137.5, 137.1, 129.5, 129.4, 129.2; HRMS (ESI) *m/z* $[M + H]^+$ Calcd for $C_{11}H_9ClNO_2S_2$ 285.9763; Found 285.9760.

General Procedure for Transfer Hydrogenation of *N*-Sulfonylimine. The reaction flask was charged with a mixture of **1** (1.0 mmol), **cat-3** (1 mol %), H_2O (2.0 mL), and hydrogen donor (1 mL, HCO_2H/Et_3N = 5:2) at room temperature. Upon full conversion of imine, as monitored by TLC, the mixture was isolated via a short silica column with petroleum ether/EtOAc (20:1−2:1) to afford the desired product.

*N-Benzylbenzenesulfonamide (**2aa**).*[22] Purified with petroleum ether/EtOAc (5:1). Colorless oil; yield 240.1 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−7.82 (m, 2H), 7.60−7.54 (m, 1H), 7.52−7.44 (m, 2H), 7.31−7.22 (m, 3H), 7.21−7.14 (m, 2H), 5.46 (t, *J* = 6.3 Hz, 1H), 4.13 (d, *J* = 6.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.9, 136.3, 132.6, 129.1, 128.6, 127.9, 127.8, 127.1, 47.1.

*N-(4-Methylbenzyl)benzenesulfonamide (**2ab**).*[23] Purified with petroleum ether/EtOAc (10:1). White solid; yield 253.9 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.06 (m, 4H), 5.22 (t, *J* = 6.0 Hz, 1H), 4.07 (d, *J* = 6.2 Hz, 2H), 2.29 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.9, 137.6, 133.3, 132.6, 129.3, 129.1, 127.9, 127.1, 47.0, 21.1.

*N-(2-Methoxybenzyl)benzenesulfonamide (**2ac**).*[22] Purified with petroleum ether/EtOAc (5:1). White solid; yield 266.8 mg, 97%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.71 (m, 2H), 7.52−7.46 (m, 1H), 7.44−7.36 (m, 2H), 7.23−7.15 (m, 1H), 7.09−7.05 (m, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.72(d, *J* = 8.2 Hz, 1H), 5.41 (t, *J* = 6.2 Hz, 1H), 4.18 (d, *J* = 6.4 Hz, 2H), 3.72 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.2, 140.3, 132.3, 129.8, 129.4, 128.8, 127.0, 124.2, 120.5, 110.1, 55.2, 44.0.

*N-(4-Methoxybenzyl)benzenesulfonamide (**2ad**).*[38] Purified with petroleum ether/EtOAc (10:1). Colorless oil; yield 269.5 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87−7.80 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 5.17 (t, *J* = 5.9 Hz, 1H), 4.04 (d, *J* = 6.1 Hz, 2H), 3.74 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.2, 140.0, 132.7, 129.3, 129.2, 128.3, 127.1, 114.0, 55.3, 46.8.

*N-(4-Chlorobenzyl)benzenesulfonamide (**2ae**).*[38,40] Purified with petroleum ether/EtOAc (5:1). White solid; yield 273.4 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.44 (t, *J* = 6.2 Hz, 1H), 4.10 (d, *J* = 6.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.8, 135.0, 133.7, 132.9, 129.3, 129.2, 128.8, 127.1, 46.5.

*N-(2-Chlorobenzyl)benzenesulfonamide (**2af**).*[39] Purified with petroleum ether/EtOAc (5:1). White solid; yield 270.6 mg, 97%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33−7.26 (m, 1H), 7.25−7.20 (m, 1H), 7.19−7.08 (m, 2H), 5.60 (t, *J* = 6.2 Hz, 1H), 4.25 (d, *J* = 6.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.9, 133.8, 133.2, 132.6, 130.1, 129.4, 129.2, 129.0, 127.0, 126.9, 45.0.

*N-(2-Bromobenzyl)benzenesulfonamide (**2ag**).*[39] Purified with petroleum ether/EtOAc (5:1). Colorless oil; Yield: 316.5 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.57−7.49 (m, 1H), 7.45 (t, *J* = 8.2 Hz, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.09 (td, *J* = 7.8, 1.3 Hz, 1H), 5.40 (t, *J* = 6.4 Hz, 1H), 4.25 (d, *J* = 6.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.0, 135.4, 132.8, 132.7, 130.5, 129.6, 129.1, 127.7, 127.1, 123.5, 47.5.

*N-(3-Bromobenzyl)benzenesulfonamide (**2ah**).* Purified with petroleum ether/EtOAc (5:1). White solid; yield 313.3 mg, 97%; mp 73.9−74.2; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.61−7.54 (m, 1H), 7.52−7.44 (m, 2H), 7.35−7.29 m, 2H), 7.16−7.07 (m, 2H), 5.57 (t, *J* = 6.3 Hz, 1H), 4.10 (d, *J* = 6.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.7, 138.7, 132.9, 130.9, 130.8, 130.2, 129.2, 127.0, 126.5, 122.6, 46.5; HRMS (ESI) *m/z* $[M + Na]^+$ Calcd for $C_{13}H_{12}BrNNaO_2S$ 347.9670; Found 347.9663.

*N-(3-Fluorobenzyl)benzenesulfonamide (**2ai**).* Purified with petroleum ether/EtOAc (5:1). Colorless oil; yield 255.1 mg, 97%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.23−7.14 (m, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.92−6.83 (m, 2H), 5.62 (t, *J* = 6.3 Hz, 1H), 4.10 (d, *J* = 6.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.8 (d, $^1J_{C-F}$ = 246.4 Hz), 139.8, 139.0 (d, $^3J_{C-F}$ = 7.2 Hz), 132.8, 130.1 (d, $^2J_{C-F}$ = 8.1 Hz), 129.2, 127.0, 123.4 (d, $^4J_{C-F}$ = 2.9 Hz), 114.8 (d, $^2J_{C-F}$ = 8.1 Hz), 114.5 (d, $^3J_{C-F}$ = 7.2 Hz), 46.5; $^{19}F\{^1H\}$ NMR (367 MHz, $CDCl_3$) δ −122.66; HRMS (ESI) *m/z* $[M + Na]^+$ Calcd for $C_{13}H_{12}FNNaO_2S$ 288.0470; Found 288.0464.

*N-(4-Nitrobenzyl)benzenesulfonamide (**2aj**):*[38] Purified with petroleum ether/EtOAc (4:1). White solid; yield 281.3 mg, 97%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 5.43 (t, *J* = 6.2 Hz, 1H), 4.25 (d, *J* = 6.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.6, 144.0, 139.7, 133.2, 129.4, 128.5, 127.1, 123.9, 46.5.

*4-Chloro-N-(naphthalen-2-ylmethyl)benzenesulfonamide (**2ak**).* Purified with petroleum ether/EtOAc (5:1). White solid; yield 319.1 mg, 97%; mp 149.8−150.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82−7.77 (m, 1H), 7.76−7.69 (m, 4H), 7.58 (s, 1H), 7.50−7.44 (m, 2H), 7.39−7.34 (m, 2H), 7.29−7.23 (m, 1H), 5.17 (t, *J* = 5.7 Hz, 1H), 4.28 (d, *J* = 6.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.3, 138.6, 133.4, 133.2, 133.0, 129.4, 128.8, 128.7, 127.9, 127.8, 126.9, 126.6, 126.4, 125.7, 47.6; HRMS (ESI) *m/z* $[M + Na]^+$ Calcd for $C_{17}H_{14}ClNNaO_2S$ 354.0331; Found 354.0325.

*4-Chloro-N-(naphthalen-1-ylmethyl)benzenesulfonamide (**2al**).* Purified with petroleum ether/EtOAc (5:1). White solid; yield 322.4 mg, 98%; M.p.128.6−128.8; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89−7.83 (m, 1H), 7.82−7.76 (m, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.69−

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7.63 (m, 2H), 7.50−7.43 (m, 2H), 7.36−7.22 (m, 4H), 5.23 (t, J = 5.7 Hz, 1H), 4.50 (d, J = 5.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.1, 138.2, 133.8, 131.1, 131.1, 129.3, 129.2, 128.9, 128.6, 127.2, 126.8, 126.2, 125.2, 123.2, 45.5; HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{17}H_{14}ClNNaO_2S$ 354.0331; Found 354.0325.

4-Chloro-N-(thiophene-2-ylmethyl) benzenesulfonamide (**2am**). Purified with petroleum ether/EtOAc (5:1). White solid; yield 273.6 mg, 96%; mp 114.5−114.6; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.16 (dd, J = 4.7, 1.5 Hz, 1H), 6.87−6.79 (m, 2H), 5.45 (t, J = 5.9 Hz, 1H), 4.33 (d, J = 6.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.2, 138.8, 138.5, 129.4, 128.6, 126.9, 126.8, 126.0, 42.0; HRMS (ESI) m/z $[M - H]^-$ Calcd for $C_{11}H_9ClNO_2S_2$ 285.9763; Found 285.9769.

4-Chloro-N-(4-methylbenzyl)benzenesulfonamide (**2an**).[41] Purified with petroleum ether/EtOAc (5:1). White solid; yield 287.2 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.07 (s, 4H), 5.32 (t, J = 5.9 Hz, 1H), 4.09 (d, J = 6.1 Hz, 2H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.1, 138.6, 137.8, 133.0, 129.4, 129.4, 128.6, 127.9, 47.1, 21.2.

4-Chloro-N-(4-methoxybenzyl)benzenesulfonamide (**2ao**). Purified with petroleum ether/EtOAc (5:1). White solid; yield 302.8 mg, 98%; mp 98.8−99.0; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.7 Hz, 2H), 5.03 (t, J = 5.9 Hz, 1H), 4.09 (d, J = 6.1 Hz, 2H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.5, 139.2, 138.7, 129.5, 129.4, 128.7, 128.0, 114.2, 55.4, 46.9; HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{14}H_{14}ClNNaO_3S$ 334.0281; Found 334.0274.

4-Chloro-N-(2-methoxybenzyl)benzenesulfonamide (**2ap**). Purified with petroleum ether/EtOAc (5:1). Colorless oil; yield 296.7 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.7 Hz, 2H), 7.29 (dd, J = 8.7 Hz, 2H), 7.16 (td, J = 8.0, 1.7 Hz, 1H), 7.03 (dd, J = 7.4, 1.6 Hz, 1H), 6.77 (td, J = 7.4, 0.9 Hz, 1H), 6.66 (d, J = 8.1 Hz, 1H), 5.67 (t, J = 6.4 Hz, 1H), 4.15 (d, J = 6.4 Hz, 2H), 3.68 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.1, 138.9, 138.5, 129.8, 129.3, 128.9, 128.4, 123.9, 120.4, 110.0, 55.1, 44.0; HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{14}H_{14}ClNNaO_3S$ 334.0281; Found 334.0274.

N-(2-Bromobenzyl)-4-chlorobenzenesulfonamide (**2aq**). Purified with petroleum ether/EtOAc (5:1). White solid; yield 346.2 mg, 97%; mp 88.2−88.4; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.7 Hz, 2H), 7.44 (dd, J = 7.9, 1.1 Hz, 1H), 7.39 (d, J = 8.7 Hz, 2H), 7.29 (dd, J = 7.6, 1.7 Hz, 1H), 7.21 (td, J = 7.5, 1.2 Hz, 1H), 7.12 (td, J = 7.7, 1.8 Hz, 1H), 5.44 (t, J = 6.4 Hz, 1H), 4.26 (d, J = 6.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.1, 138.6, 135.2, 132.9, 130.7, 129.8, 129.3, 128.6, 127.8, 123.6, 47.5; HRMS (ESI) m/z $[M + Na]^+$ Calcd for $C_{13}H_{11}BrClNO_2SNa$ 381.9280; Found 381.9282.

4-Chloro-N-(4-chlorobenzyl)benzenesulfonamide (**2ar**). Purified with petroleum ether/EtOAc (5:1). White solid; yield 306.7 mg, 98%; Mp 114.2−114.4; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 5.48 (t, J = 6.2 Hz, 1H), 4.06 (d, J = 6.3 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.4, 138.3, 134.6, 133.9, 129.5, 129.3, 128.9, 128.6, 46.6; HRMS (ESI) m/z $[M - H]^-$ Calcd for $C_{13}H_{10}C_{l2}NO_2S$ 313.9809; Found 313.9815.

N-Benzyl-4-methylbenzenesulfonamide (**2as**).[38] Purified with petroleum ether/EtOAc (5:1). White solid; yield 253.8 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81−7.69 (m, 2H), 7.36−7.14 (m, 7H), 5.30 (t, J = 6.2 Hz, 1H), 4.10 (d, J = 6.3 Hz, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.4, 136.8, 136.4, 129.7, 128.6, 127.9, 127.7, 127.2, 47.2, 21.5.

4-Methyl-N-(4-methylbenzyl)benzenesulfonamide (**2at**).[42] Purified with petroleum ether/EtOAc (10:1). White solid; yield 260.4 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.08 (q, J = 8.2 Hz, 4H), 5.35 (t, J = 6.1 Hz, 1H), 4.06 (d, J = 6.2 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.3, 137.3, 136.8, 133.4, 129.6, 129.2, 127.8, 127.1, 46.9, 21.5, 21.0.

N-(2-Methoxybenzyl)-4-methylbenzenesulfonamide (**2au**).[41] Purified with petroleum ether/EtOAc (10:1). Colorless oil; yield 280.4 mg, 97%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 2H), 7.20−7.13 (m, 3H), 7.06 (dd, J = 7.4, 1.2 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 6.70(d, J = 8.2 Hz, 1H), 5.42 (t, J = 6.3 Hz, 1H), 4.12 (d, J = 6.4 Hz, 2H), 3.69 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.2, 143.0, 137.2, 129.7, 129.4, 129.1, 127.0, 124.3, 120.4, 110.1, 55.1, 43.8, 21.4.

N-(4-Methoxybenzyl)-4-methylbenzenesulfonamide (**2av**).[41] Purified with petroleum ether/EtOAc (10:1). White solid; yield 283.3 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 5.06 (t, J = 5.9 Hz, 1H), 4.04 (d, J = 6.1 Hz, 2H), 3.77 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.2, 143.5, 136.9, 129.8, 129.3, 128.4, 127.2, 114.0, 55.3, 46.8, 21.6.

4-Methyl-N-(4-nitrobenzyl)benzenesulfonamide (**2aw**).[41] Purified with petroleum ether/EtOAc (4:1). White solid; yield 294.9 mg, 97%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.49 (t, J = 6.5 Hz, 1H), 4.23 (d, J = 6.5 Hz, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.5, 144.2, 144.1, 136.6, 130.0, 128.6, 127.2, 123.8, 46.4, 21.6.

N-(4-Chlorobenzyl)-4-methylbenzenesulfonamide (**2ax**).[40,41] Purified with petroleum ether/EtOAc (5:1). White solid; yield 284.2 mg, 97%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 4.97 (t, J = 6.2 Hz, 1H), 4.10 (d, J = 6.3 Hz, 2H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.8, 136.9, 135.0, 133.8, 129.9, 129.3, 128.9, 127.3, 46.7, 21.7.

N-(2-Chlorobenzyl)-4-methylbenzenesulfonamide (**2ay**).[40] Purified with petroleum ether/EtOAc (5:1). White solid; yield 287.2 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H), 7.35−7.29 (m, 1H), 7.28−7.20 (m, 3H), 7.19−7.11 (m, 2H), 5.44 (t, J = 6.4 Hz, 1H), 4.23 (d, J = 6.5 Hz, 2H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.4, 136.9, 134.0, 133.3, 130.1, 129.6, 129.4, 129.2, 127.1, 127.0, 45.0, 21.5.

N-(2-Bromobenzyl)-4-methylbenzenesulfonamide (**2az**).[41] Purified with petroleum ether/EtOAc (5:1). Colorless oil; yield 323.5 mg, 96%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 8.1 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 5.35 (t, J = 6.5 Hz, 1H), 4.22 (d, J = 6.5 Hz, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.5, 136.9, 135.6, 132.8, 130.4, 129.7, 129.5, 127.7, 127.1, 123.4, 47.4, 21.6.

N-(3-Fluorobenzyl)-4-methylbenzenesulfonamide (**2ba**).[42] Purified with petroleum ether/EtOAc (5:1). White solid; yield 265.9 mg, 96%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.19 (dd, J = 14.4, 7.8 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.93−6.84 (m, 2H), 5.68 (t, J = 6.4 Hz, 1H), 4.08 (d, J = 6.5 Hz, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.7 (d, J = 246.2 Hz), 143.6, 139.2 (d, J = 7.2 Hz), 136.7, 130.1 (d, J = 8.1 Hz), 129.7, 127.1, 123.4 (d, J = 2.9 Hz), 114.7 (d, J = 18.5 Hz), 114.5 (d, J = 17.6 Hz), 46.5 (d, J = 1.7 Hz), 21.5.

N-(2-Hydroxybenzyl)-4-methylbenzenesulfonamide (**2bb**).[43] Purified with petroleum ether/EtOAc (2:1). White solid; yield 269.5 mg, 98%; ^1H NMR (400 MHz, acetone-d_6) δ 8.54 (s, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.25−7.19 (m, 1H), 7.08 (td, J = 7.9, 1.5 Hz, 1H), 6.82 (d, J = 7.9 Hz, 1H), 6.77 (t, J = 7.5 Hz, 1H), 6.63 (t, J = 6.3 Hz, 1H), 4.14 (d, J = 6.4 Hz, 2H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, acetone-d_6) δ 155.4, 143.6, 138.6, 130.2, 129.9, 129.2, 127.6, 124.2, 120.2, 115.6, 42.9, 21.3.

N-Benzyl-4-methoxyaniline (**2bc**):[44] Purified with petroleum ether/EtOAc (20:1). White solid; yield 206.8 mg, 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.38 (m, 4H), 7.37−7.31 (m, 1H), 6.89−6.82 (m, 2H), 6.70−6.63 (m, 2H), 4.35 (s, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.2, 142.5, 139.8, 128.6, 127.6, 127.2, 115.0, 114.2, 55.8, 49.2.

■ ASSOCIATED CONTENT

Supporting Information

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^{1}H and ^{13}C NMR spectra for all compounds prepared (PDF)

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CCDC 2040520 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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