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Rhodium(III)-Catalyzed Intermolecular Amidation with Azides via C(sp^3)−H Functionalization

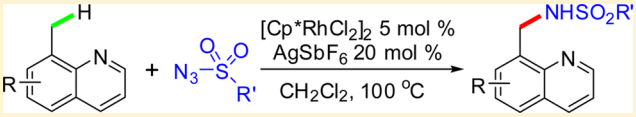
Nuancheng Wang,[†] Renhe Li,[†] Liubo Li,[†] Shansheng Xu,[†] Haibin Song,[†] and Baiquan Wang*[,†,‡]

[†]State Key Laboratory of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), College of Chemistry, Nankai University, Tianjin 300071, China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting Information

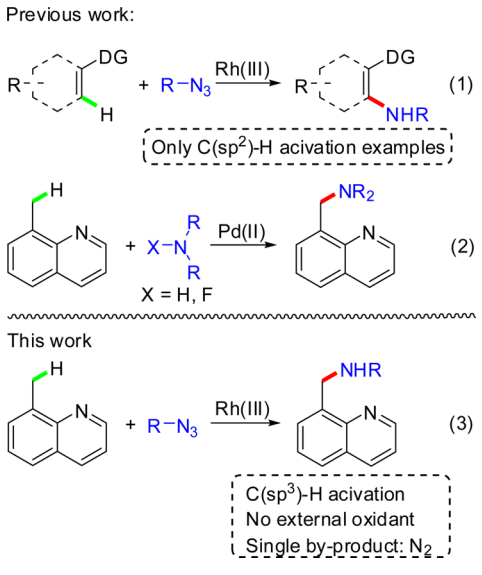
ABSTRACT: The amidation reactions of 8-methylquinolines with azides catalyzed by a cationic rhodium(III) complex proceed efficiently to give quinolin-8-ylmethanamine derivatives in good yields via C(sp^3)−H bond activation under external oxidant-free conditions. A catalytically competent five-membered rhodacycle has been isolated and characterized, revealing a key intermediate in the catalytic cycle.



Nitrogen is a key component of many natural products and drug molecules. It has been estimated that among all natural products, the average number of nitrogen atoms per molecule is 0.7, while for medicinal drugs, this number rises to 3.0.[1] Transition-metal-catalyzed direct C−H amination is currently a "hot topic" in organic synthesis.[2] This approach is highly promising as it alleviates the need for prefunctionalization. Nevertheless, it still generates stoichiometric amounts of byproducts from external oxidants,[3] halide salts, or bases.[4] Using azides as the N atom source would address these limitations because no oxidant would be required and the only byproduct would be the environmentally benign N_2.[5] Recently, many groups such as Chang, Li, Jiao, Sahoo, and Ackermann et al., continuously disclosed Rh-, Ru-, and Ir-catalyzed direct C−H amination protocols using organic azides as the amino source (Scheme 1, eq 1). However, most efforts were made on the C(sp^2)−N formation.[6] There are only limited works focusing on C(sp^3)−N formation.[7,8]

The quinolin-8-ylmethanamine derivatives have been reported as a building block in enormous areas involved in medicinal chemistry, organic synthesis, and analytical chemistry.[9] Meanwhile, the quinolin-8-ylmethanamine derivatives contain two nitrogen atoms, thus enabling this kind of molecular structure to be a potential ligand. 8-Methylquinoline is an ideal substrate that could be used to obtain quinolin-8-ylmethanamine derivatives through C−H functionalization. Before our work, Che and Muñiz, respectively, have realized Pd(II)-catalyzed amination of 8-methylquinoline (Scheme 1, eq 2).[3d,4f] Our group is continuously interested in Cp*Rh-catalyzed C−H bond activation.[10] Herein, we report Cp*Rh-catalyzed intermolecular C(sp^3)−H amidation of 8-methylquinolines (Scheme 1, eq 3). It should be noted that when we prepared this work, similar work was also demonstrated by the research group of Chang using Cp*Ir catalyst system.[8g] However, the Cp*Rh catalyst did not work under their conditions.

Scheme 1. Transition-Metal-Catalyzed Amidation via C−H Bond Activation



At the outset of our study, we searched for optimal C−H amidation conditions of 8-methylquinoline (**1a**) with sulfonyl azides (Table 1). By treating **1a** (0.3 mmol) with 4-(trifluoromethyl)benzenesulfonyl azide (**2a**) (0.6 mmol) in the presence of a cationic Rh(III) catalyst (5.0 mmol %) generated in situ from $[Cp^*RhCl_2]_2$ and $AgSbF_6$ in $ClCH_2CH_2Cl$ (1.5 mL) at 100 °C for 12 h, the desired product **3aa** was obtained in 35% yield (entry 1). CH_2C1_2 was more efficient at improving the yield, while other solvents gave inferior yields (entries 2−4). Neither raising the temperature

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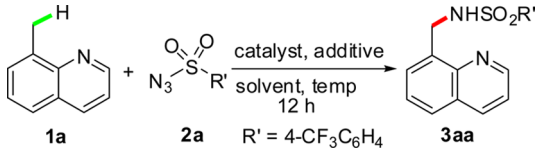
Table 1. Optimization of Reaction Conditions[a]



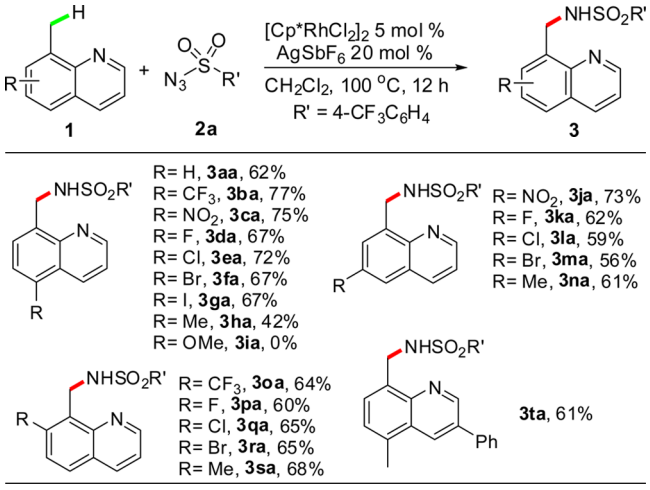
entry	cat (mmol %)	sol	temp (°C)	yield[b] (%)
1	$[Cp^*RhCl_2]_2$ 5/$AgSbF_6$ 20	$ClCH_2CH_2Cl$	100	35
2	$[Cp^*RhCl_2]_2$ 5/$AgSbF_6$ 20	CH_2Cl_2	100	47
3	$[Cp^*RhCl_2]_2$ 5/$AgSbF_6$ 20	toluene	100	trace
4	$[Cp^*RhCl_2]_2$ 5/$AgSbF_6$ 20	*t*-AmOH	90	n.r.
5	$[Cp^*RhCl_2]_2$ 5/$AgSbF_6$ 20	CH_2Cl_2	80	23
6	$[Cp^*RhCl_2]_2$ 5/$AgSbF_6$ 20	CH_2Cl_2	120	42
7	$[Cp^*RhCl_2]_2$ 10/$AgSbF_6$ 40	CH_2Cl_2	100	46
8[c]	**$[Cp^*RhCl_2]_2$ 5/$AgSbF_6$ 20**	CH_2Cl_2	**100**	**62**
9	$[Cp^*RhCl_2]_2$ 5 or $AgSbF_6$ 20	CH_2Cl_2	100	n.r.
10	$[Cp^*RhCl_2]_2$ 5/$AgBF_4$ 20	CH_2Cl_2	100	30
11	$[Cp^*RhCl_2]_2$ 5/KPF_6 20	CH_2Cl_2	100	trace
12	$[Cp^*Rh(MeCN)_3][SbF_6]_2$ 10	CH_2Cl_2	100	37
13	$[(Cymene)RuCl_2]_2$ 5/$AgSbF_6$ 20	CH_2Cl_2	100	n.r.
14	$[Cp^*IrCl_2]_2$ 5/$AgSbF_4$ 20	CH_2Cl_2	100	n.r.
15	$Pd(OAc)_2$	CH_2Cl_2	100	n.r.

[a]Conditions: **1a** (0.3 mmol), **2a** (2.0 equiv), catalyst, additive, solvent (1.5 mL) at the indicated temperature for 12 h, under Ar. [b]Isolated yield. [c]**1a** (2.0 equiv), **2a** (0.3 mmol) in CH_2Cl_2 (6.0 mL).

nor decreasing the temperature is helpful to the improvement of the yield (entries 5 and 6). Then, we attempted to double the catalyst loading, but the yield remained unchanged (entry 7). Silver hexafluoroantimonate proved to be the most effective additive. Alteration of the cationic or anionic part of the additive gave reduced efficiency (entries 10 and 11). We were pleased to observe that higher yield was obtained by changing the ratio of **1a**:**2a** to **2**:**1** in a diluted system (CH_2Cl_2 6 mL) (entry 8). When the reaction was carried out in the absence of $[Cp^*RhCl_2]_2$ or $AgSbF_6$, no product was observed (entry 9). Using a pregenerated cationic rhodium species afforded a slightly lower yield (entry 12). Other transition metals such as ruthenium, iridium, and palladium complexes were ineffective in the present direct amidation reaction (entries 13−15).

With the optimized conditions in hand, we investigated the reaction of various substituted 8-methylquinolines **1** with **2a** (Table 2). The reaction proceeded smoothly to afford C(sp^3)-amidated products in moderate to good yields. The structure of **3na** was confirmed by its ^1H and ^{13}C NMR spectra, mass spectrometry data, and single-crystal X-ray diffraction analysis. Various functional groups commonly encountered in organic synthesis were tolerated well, such as halide (products **3da**−**ga**, **3ka**−**ma**, and **3pa**−**ra**). Higher yields were obtained with 8-methylquinolines bearing electron-withdrawing groups than those bearing electron-donating groups. This is probably due to that the electron-withdrawing groups may increase the acidity of the methyl C−H bond of 8-methylquinolines. Notably, the 5-OMe substrate (**1i**) gave no desired product. In addition, we found that the amidation reaction of 5-substituted substrates worked a little better than that of 6-substituted or 7-substituted substrates. The multisubstituted substrate 5,8-dimethyl-3-phenylquinoline also gave a moderate yield (61%). The effect of steric hindrance was investigated. When 8-methylquinoline was replaced by 8-ethylquinoline, no product was detected.

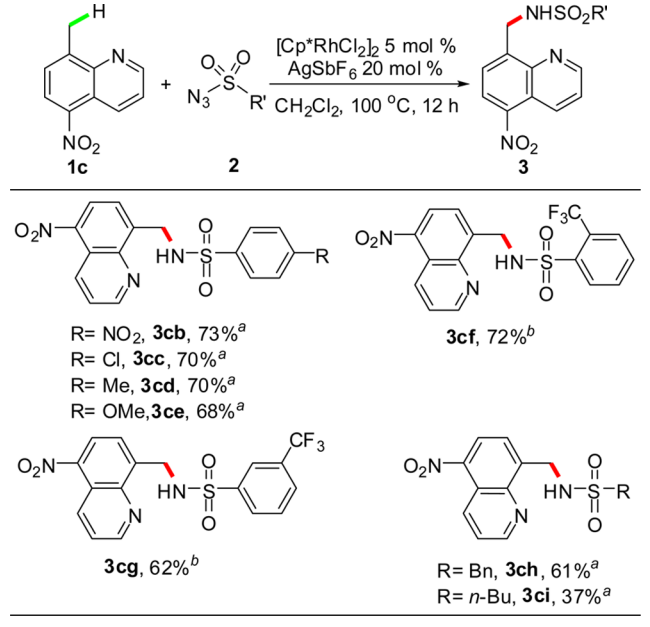
Table 2. Substrate Scope of 8-Methylquinolines[a]



[a]Conditions: **1** (0.6 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), CH_2Cl_2, (6.0 mL), 100 °C, 12 h, under Ar; isolated yields are shown.

In addition to **2a**, different sulfonyl azides were examined in the amidation process (Table 3). Arenesulfonyl azide substrates

Table 3. Sulfonyl Azide Scope[a]



[a]Reaction conditions: **1c** (0.3 mmol), **2** (0.45 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), CH_2Cl_2, (1.5 mL), 100 °C, 12 h, under Ar. [b]Reaction conditions: **1c** (0.6 mmol), **2** (0.3 mmol).

with electron-withdrawing groups and electron-donating groups both provided good yields (62−73%). Compared with azides bearing electron-donating substituents, azides bearing electron-withdrawing substituents afforded the corresponding products in slightly higher yields. Besides, *para*-substituted arenesulfonyl azides displayed higher activity than *ortho*- and *meta*-substituted arenesulfonyl azides. Then, phenylmethanesulfonyl azide and the aliphatic sulfonyl azide were tested to give the corresponding products.

To demonstrate further the synthetic utility of 8-allylquinoline products, two derivatization reactions were done. The

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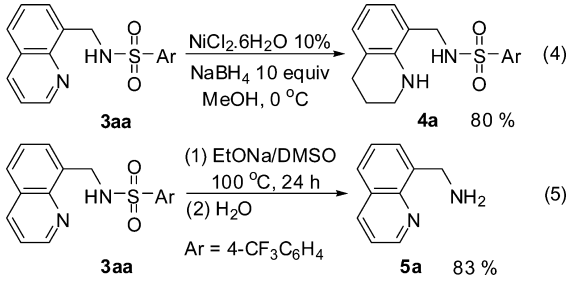
amidation product **3aa** could be reduced selectively by $NaBH_4$/$NiCl_2{\cdot}6H_2O$, giving *N*-((1,2,3,4-tetrahydroquinolin-8-yl)-methyl)-4-(trifluoromethyl)benzenesulfonamide in 80% yield (Scheme 2, eq 4).[11] In addition, when deprotection was

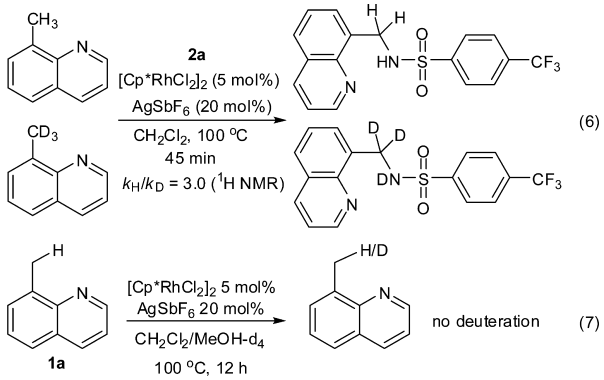
Scheme 2. Derivatization Reactions



conducted under an EtONa/DMSO system, quinolin-8-ylmethanamine derivatives were obtained (Scheme 2, eq 5). Thus, this protocol provides a new and simple route to synthesize these kinds of compounds.

To gain more insight into the mechanism of the present direct C−H amidation, preliminary mechanistic experiments were carried out. A notable primary kinetic isotope effect (KIE, k_H/k_D = 3.0) was observed for two separate competition reactions with **1a** and **1a**-d_3 (Scheme 3, eq 6), suggesting that

Scheme 3. Deuterium Exchange and KIE Reactions

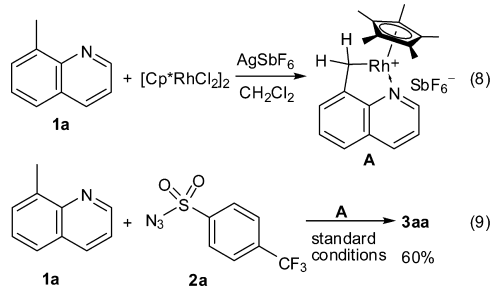


the C−H bond cleavage is likely involved in the rate-determining step.[12] The H/D exchange reactions were also carried out. When the reaction was performed in the absence of sulfonyl azides (Scheme 3, eq 7), no deuteration of the methyl C−H bonds was detected, indicating that the C−H bond activation was irreversible.

Fortunately, a rhodacycle intermediate **A** was isolated by the reaction of 8-methylquinoline with $[Cp^*RhCl_2]_2$ and $AgSbF_6$ (Scheme 4, eq 8). Its structure was fully characterized by ^1H and ^{13}C NMR spectra and high-resolution mass spectrometry data, though we failed to grow a single crystal. Then intermediate **A** was used as the catalyst instead of $[Cp^*RhCl_2]_2$/$AgSbF_6$ in the standard conditions, giving the product in a 60% yield (Scheme 4, eq 9). These results supported the idea that intermediate **A** probably was an active species in this reaction.

Based on the above experimental results and known transition-metal-catalyzed C(sp^2)−H bond amidation reactions,[6] a possible mechanism is proposed for the present catalytic reaction (Figure 1). The first step is likely to be a

Scheme 4. Synthesis of Intermediate A and the Amidation Reaction Using Intermediate A as the Catalyst



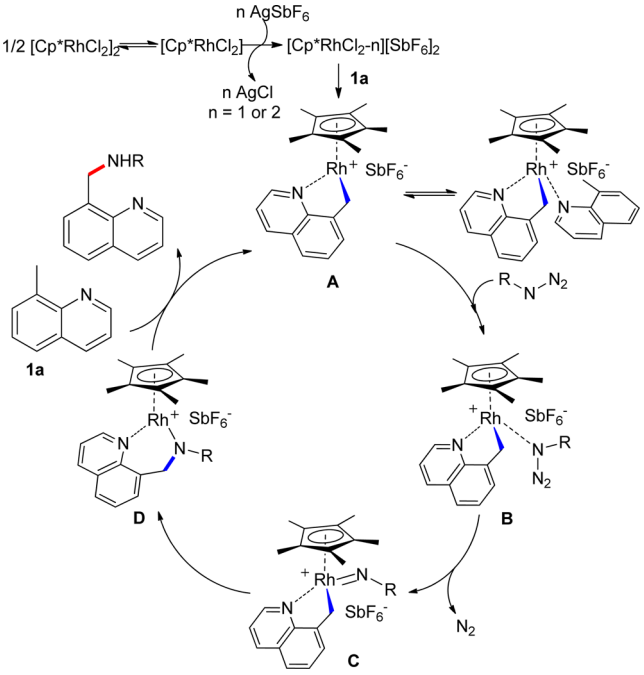


Figure 1. Proposed mechanistic pathway of the amidation reaction.

C(sp^3)−H activation process affording a five-membered rhodacyclic intermediate **A**. Coordination of an azide to **A**, leading to **B**, is assumed to follow before a stepwise pathway which involves a Rh(V)−nitrenoid intermediate, which has been proved in the work of Chang.[6q] The sulfonamido moiety subsequently inserts into the rhodacycle to form intermediate **D**. Finally, protonolysis of **D** delivers the desired product **3**.

In summary, we have developed the Rh(III)-catalyzed direct amidation via C(sp^3)−H activation. Quinolin-8-ylmethanamine derivatives were obtained by using sulfonyl azides as the amine source in a simple way. The reaction proceeds with a broad range of 8-methylquinolines in moderate to good yields and requires no external oxidants or bases. The amidated products could be applied widely to areas such as organic synthesis and pharmaceutical chemistry.

EXPERIMENTAL SECTION

General Information. All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^1H NMR (400 MHz), ^{19}F (376 M), and ^{13}C NMR (100 MHz) were recorded on a NMR spectrometer with $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts of ^1H, ^{19}F, and ^{13}C NMR spectra are reported in parts per million (ppm). High-resolution mass spectrometry (HRMS) was done on a FTICR-mass spectrometer. X-ray structure analysis was

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performed on an X-ray diffractometer. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3 \cdot xH_2O$ following a literature procedure.[13]

General Procedure for the Preparation of Substituted 8-Methylquinolines 1. Glycerin (11.1 g, 0.12 mol) was added dropwise over a period of 0.5 h to a solution of substituted aniline (0.1 mol) and NaI (0.2 g, 1.3 mmol) in 80% aqueous H_2SO_4 (55 g, 0.45 mmol) at 140 °C. The mixture was then heated at 140−145 °C for 3.5 h while distilling the water formed during this period. Upon cooling to room temperature, the dark solution was carefully poured into ice (100 g) and then neutralized with 25% NaOH (109.3 g, 0.69 mol) to basic pH 8−11. The mixture was extracted with benzene (3 × 50 mL). The combined organic solution was washed with water (2 × 50 mL) and brine (50 mL), and then dried with anhydrous sodium sulfate. After benzene was removed, the residue was distilled under vacuum to give the corresponding substituted 8-methylquinoline.[14]

The substrates **1b** and **1o**, **1u**, 8-ethylquinoline, and 8-methylquinoline-d_3 were separately prepared according to the literatures.[15−18]

The structures of 8-methylquinoline substrates were confirmed by ^{1}H NMR spectroscopy, which are consistent with those reported previously.[10d,14−18]

Data for **1o**: pale yellow oil; 1.40 g, 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (dd, J = 4.0, 1.6 Hz, 1H), 8.17 (dd, J = 8.3, 1.7 Hz, 1H), 7.75 (s, 2H), 7.50 (dd, J = 8.3, 4.1 Hz, 1H), 3.00 (d, J = 1.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.2, 147.0, 137.9, 136.1, 129.4, 129.3, 129.3, 129.1, 128.8, 128.7, 128.5, 126.3, 125.9, 125.8, 123.2, 122.4, 122.4, 122.3, 122.3, 77.3, 77.0, 76.7, 13.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ −59.69 (s); HRMS (ESI) calcd for $C_{11}H_9F_3N$ $[M + H]^+$ 212.0682, found 212.0677.

General Procedure for the Preparation of 2. To a solution of sodium azide (1.99 g, 30 mmol) in water (10 mL) was added dropwise over 1 h to a solution of *p*-toluenesulfonyl chloride (3.85 g, 20 mmol) in acetone (20 mL) at 0 °C. The reaction was warmed to room temperature and stirred for 11 h, the acetone was removed under reduced pressure, and the reaction mixture was extracted by EtOAc for three times. The combined organic layers were washed with water and saturated Na_2CO_3 solution and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product can be used without any further purification.

The structures of azides substrates were confirmed by ^{1}H NMR spectroscopy, which are consistent with those reported previously.[19]

General Procedure for Rh(III)-Catalyzed Amidation with Azides. A mixture of the substituted 8-methylquinoline (**1**) (0.6 mmol, 2.0 equiv), the sulfonyl azide (**2**) (if solid) (0.30 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol, 5.0 mol %), and $AgSbF_6$ (20.6 mg, 0.06 mmol, 20.0 mol %) were weighted in a Schlenk tube equipped with a stir bar. Dry DCM (6.0 mL) was added (followed immediately by the sulfonyl azide if it is a liquid), and the mixture was stirred at 100 °C for 12 h under Ar atmosphere. Afterward, it was transferred to a round-bottom flask. Silica was added to the flask, and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:10).

*N-(Quinolin-8-ylmethyl)-4-(trifluoromethyl)benzenesulfonamide (**3aa**):* white solid (68 mg, 62%); mp 110−112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.82 (d, J = 2.6 Hz, 1H), 8.01 (d, J = 7.3 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.1 Hz, 2H), 7.46−7.40 (m, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.28 (s, 1H), 6.70 (br s, 1H), 4.75 (d, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.4, 145.9, 143.8, 136.7, 133.6, 133.3, 133.0, 132.8, 132.7, 129.6, 128.3, 127.0, 126.8, 126.2 (q), 125.9, 124.9 (q, CF_3), 124.4, 121.7, 121.3, 46.6. ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s); HRMS (ESI) calcd for $C_{17}H_{14}F_3N_2O_2S$ $[M + H]^+$ 367.0723, found 367.0721.

*N-((5-(Trifluoromethyl)quinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ba**):* white solid (100 mg, 77%); mp 112−114 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.92 (dd, J = 4.1, 1.2 Hz, 1H), 8.43 (d, J = 8.7 Hz, 1H), 7.72 (d, J = 7.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.57−7.52 (m, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.69 (t, J = 6.9 Hz, 1H), 4.78 (d, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.1, 146.0, 143.8, 138.2, 133.9, 133.6, 133.3, 128.0, 127.0, 126.9, 126.5, 125.3 (q), 124.9, 124.5 (q), 124.3, 124.3, 122.5, 122.2, 121.6, 46.2; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −59.4 (s), −63.41 (s); HRMS (ESI) calcd for $C_{18}H_{13}F_6N_2O_2S$ $[M + H]^+$ 435.0596, found 435.0595.

*N-((5-Nitroquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ca**):* white solid (93 mg, 75%); mp 101−103 °C; ^{1}H NMR (DMSO, 400 MHz) δ 9.00 (dd, J = 4.1, 1.5 Hz, 1H), 8.78 (dd, J = 8.8, 1.5 Hz, 1H), 8.70 (t, J = 6.1 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 7.91−7.87 (m, 3H), 7.81−7.78 (m, 3H), 4.78 (d, J = 6.0 Hz, 2H). ^{13}C NMR (DMSO, 101 MHz) δ 150.9, 144.4, 144.4, 144.3, 142.6, 132.1, 131.7, 131.7, 127.2, 126.7, 126.0 (q), 124.7, 124.2, 124.1, 122.0, 119.7, 42.4; ^{19}F NMR (DMSO, 376 MHz) −63.3 (s); HRMS (ESI) calcd for $C_{17}H_{13}F_3N_3O_4S$ $[M + H]^+$ 412.0573, found 412.0570.

*N-((5-Fluoroquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3da**):* white solid (77 mg, 67%); mp 115−117 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (d, J = 3.9 Hz, 1H), 8.00 (d, J = 8.3 Hz, 1H), 7.62 (d, J = 8.1 Hz, 2H), 7.42 (dd, J = 8.2, 4.2 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.26−7.24 (m, 1H), 7.22 (d, J = 8.5 Hz, 1H), 6.76 (t, J = 5.3 Hz, 1H), 4.72 (d, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 160.6, 158.1, 148.7, 148.7, 143.8, 143.0, 136.2, 136.1, 136.0, 133.9, 133.6, 133.3, 133.0, 129.2, 129.1, 127.0, 125.1 (q), 124.4, 122.1, 121.6, 120.1, 119.8, 110.8, 110.6, 46.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s), −112.9 (s); HRMS (ESI) calcd for $C_{17}H_{13}F_4N_2O_2S$ $[M + H]^+$ 385.0628, found 385.0627.

*N-((5-Chloroquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ea**):* white solid (87 mg, 72%); mp 143−145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.85 (d, J = 4.2, 1H), 8.47 (d, J = 8.5, 1H), 7.58 (d, J = 8.2 Hz, 2H), 7.51 (dd, J = 8.5, 4.1 Hz, 1H), 7.41 (q, J = 11.0, 7.8 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.32 (s, 1H), 6.62 (t, J = 6.3 Hz, 1H), 4.70 (d, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.0, 146.4, 143.8, 133.7, 133.6, 133.2, 132.9, 132.6, 131.8, 129.5, 126.9, 126.8, 126.3, 125.8, 125.1(q), 124.8, 124.7, 124.7, 124.4, 122.1, 121.7, 120.9, 46.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.1 (s); HRMS (ESI) calcd for $C_{17}H_{13}ClF_3N_2O_2S$ $[M + H]^+$ 401.0333, found 401.0330.

*N-((5-Bromoquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3fa**):* white solid (89 mg, 67%); mp 152−154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.83 (dd, J = 4.2, 1.6 Hz, 1H), 8.44 (dd, J = 8.6, 1.5 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.51 (dd, J = 7.6, 4.3 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.32 (s, 1H), 6.63 (t, J = 6.2 Hz, 1H), 4.70 (d, J = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.1, 146.5, 143.9, 136.3, 133.6, 133.4, 133.3, 130.0, 129.6, 127.6, 126.9, 125.1(q), 124.4, 122.4, 122.2, 121.7, 46.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.1 (s); HRMS (ESI) calcd for $C_{17}H_{13}BrF_3N_2O_2S$ $[M + H]^+$ 444.9828, found 444.9820.

*N-((5-Iodoquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ga**):* white solid (99 mg, 67%); mp 147−149 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (dd, J = 4.2, 1.4 Hz, 1H), 8.26 (dd, J = 8.5, 1.3 Hz, 1H), 7.91 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 8.3 Hz, 2H), 7.46 (dd, J = 8.5, 4.2 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 7.5 Hz, 1H), 6.64 (t, J = 6.5 Hz, 1H), 4.69 (d, J = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.2, 146.3, 143.8, 141.2, 137.0, 134.3, 133.6, 133.3, 130.7, 130.1, 126.9, 125.1(q), 124.4, 122.9, 121.7, 98.6, 46.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.9 (s); HRMS (ESI) calcd for $C_{17}H_{13}F_3IN_2O_2S$ $[M + H]^+$ 492.9689, found 492.9685.

*N-((5-Methylquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ha**):* white solid (48 mg, 42%); mp 118−120 °C; ^{1}H NMR (DMSO, 400 MHz) δ 8.83 (d, J = 3.8 Hz, 1H), 8.41 (t, J = 6.0 Hz, 1H), 8.35 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.57−7.52 (m, 2H), 7.31 (d, J = 7.2 Hz, 1H), 4.66 (d, J = 6.1 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (DMSO, 101 MHz) δ 149.1, 145.2, 144.6, 134.1, 132.7, 132.4, 132.1, 131.7, 131.4, 131.1, 128.0, 127.1, 126.7, 126.1, 125.7 (q), 124.7, 122.0, 121.0, 42.4, 17.9; ^{19}F NMR (DMSO, 376 MHz) δ −61.6 (s); HRMS (ESI) calcd for $C_{18}H_{16}F_3N_2O_2S$ $[M + H]^+$ 381.0879, found 381.0880.

*N-((6-Nitroquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ja**):* white solid (90 mg, 75%); mp 172−174 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.03 (d, J = 1.7 Hz, 1H), 8.61 (s, 1H), 8.30 (d, J = 8.2 Hz, 1H), 8.25 (s, 1H), 7.72 (d, J = 7.9 Hz, 2H), 7.63−7.60 (m, 1H), 7.43 (d, J = 7.9 Hz, 1H), 6.54 (br s, 1H), 4.81 (d, J = 5.9 Hz, 2H); ^{13}C NMR (DMSO, 101 MHz) δ 153.3, 146.8, 144.5, 144.3, 138.7, 137.6, 132.1, 131.8, 127.2, 126.7, 126.1, 126.0, 124.6,

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124.1, 123.3, 121.9, 120.6, 41.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.35 (s); HRMS (ESI) calcd for $C_{17}H_{13}F_3N_3O_4S$ $[M + H]^+$ 412.0573, found 412.0575.

*N-((6-Fluoroquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ka**):* white solid (71 mg, 62%); mp 114−117 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.78 (dd, J = 4.2, 1.5 Hz, 1H), 8.00 (dd, J = 8.4, 1.4 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.42 (dd, J = 8.3, 4.2 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.27−7.24 (m, 1H), 7.22 (dd, J = 8.5, 2.7 Hz, 1H), 6.75 (t, J = 6.2 Hz, 1H), 4.72 (d, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 160.6, 158.1, 148.7, 143.9, 143.1, 136.2, 136.2, 136.1, 134.0, 133.7, 133.3, 133.0, 129.2, 129.1, 127.0, 125.2 (q), 124.4, 122.1, 121.7, 120.1, 119.8, 119.0, 110.8, 110.6, 46.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.40 (s), −112.9 (s); HRMS (ESI) calcd for $C_{17}H_{13}F_4N_2O_2S$ $[M + H]^+$ 385.0628, found 385.0634.

*N-((6-Chloroquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3la**):* white solid (71 mg, 59%); mp 135−137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.81 (d, J = 4.1 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.59 (d, J = 8.5 Hz, 3H), 7.43 (dd, J = 8.2, 4.2 Hz, 1H), 7.39 (s, 1H), 7.34 (d, J = 7.9 Hz, 2H), 6.68 (t, J = 6.0 Hz, 1H), 4.71 (d, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.6, 144.2, 143.8, 135.8, 134.9, 133.9, 133.6, 133.3, 132.9, 131.7, 130.4, 128.9, 127.0, 126.5, 125.1(q), 124.3, 122.2, 121.6, 45.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s); HRMS (ESI) calcd for $C_{17}H_{13}ClF_3N_2O_2S$ $[M + H]^+$ 401.0333, found 401.0329.

*N-((6-Bromoquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ma**):* white solid (75 mg, 56%); mp 160−164 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.83 (d, J = 4.2 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.77 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.53 (s, 1H), 7.45 (dd, J = 8.2, 4.3 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 6.69 (br s, 1H), 4.72 (d, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.7, 144.4, 143.8, 135.7, 134.9, 133.6, 133.3, 133.0, 130.0, 129.4, 126.9, 125.1(q), 124.3, 122.2, 121.6, 119.8, 45.8; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s); HRMS (ESI) calcd for $C_{17}H_{13}BrF_3N_2O_2S$ $[M + H]^+$ 444.9828, found 444.9824.

*N-((6-Methylquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3na**):* white solid (70 mg, 61%); mp 130−132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.74 (dd, J = 4.1, 1.2 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.37−7.34 (m, 2H), 7.28 (d, J = 8.3 Hz, 2H), 7.21 (br s, 1H), 7.45 (dd, J = 8.2, 4.3 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 6.88 (br s, 1H), 4.70 (d, J = 6.5 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 148.5, 144.6, 144.0, 136.0, 135.9, 133.7, 133.4, 133.0, 132.7, 132.4, 131.9, 128.4, 127.0, 126.8, 124.9(q), 124.4, 121.7, 121.3, 119.0, 46.5, 21.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s); HRMS (ESI) calcd for $C_{18}H_{16}F_3N_2O_2S$ $[M + H]^+$ 381.0879, found 381.0880.

*N-((7-(Trifluoromethyl)quinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3oa**):* white solid (84 mg, 64%); mp 140−142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.94 (dd, J = 4.1, 1.6 Hz, 1H), 8.15 (dd, J = 8.3, 1.5 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.69−7.66 (m, 3H), 7.55 (dd, J = 8.3, 4.2 Hz, 1H), 7.38 (d, J = 8.3 Hz, 2H), 7.11 (br s, 1H), 4.97 (br s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.6, 146.1, 143.7, 137.0, 129.6, 128.7, 127.1, 125.2(q), 125.0, 124.4, 123.0, 122.5, 122.5, 122.4, 122.4, 77.3, 77.0, 76.7, 41.5, 41.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −57.2 (s), −63.3 (s); HRMS (ESI) calcd for $C_{18}H_{13}F_6N_2O_2S$ $[M + H]^+$ 435.0596, found 435.0591.

*N-((7-Fluoroquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3pa**):* white solid (69 mg, 60%); mp 146−149 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.86 (d, J = 4.2 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.59−7.57 (m, 1H), 7.40 (dd, J = 8.3, 4.3 Hz, 1H), 7.29 (d, J = 8.3 Hz, 2H), 7.15 (t, J = 9.0 Hz, 1H), 6.92 (t, J = 6.1 Hz, 1H), 4.82 (d, J = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 160.8, 158.3, 150.4, 147.0, 146.9, 143.7, 136.7, 133.9, 133.5, 133.2, 132.9, 129.7, 129.6, 125.2, 125.0(q), 124.4, 121.7, 120.6, 120.6, 119.0, 117.4, 117.3, 116.8, 116.5, 37.8, 37.7; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s), −111.6 (s); HRMS (ESI) calcd for $C_{17}H_{13}F_4N_2O_2S$ $[M + H]^+$ 385.0628, found 385.0626.

*N-((7-Chloroquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3qa**):* white solid (78 mg, 65%); mp 166−171 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.85 (dd, J = 4.3, 1.7 Hz, 1H), 8.04 (dd, J = 8.3, 1.5 Hz, 1H), 7.60 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.0 Hz, 1H), 7.43 (dd, J = 8.3, 4.3 Hz, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.26 (d, J = 8.2 Hz, 2H), 6.99 (t, J = 6.3 Hz, 1H), 4.99 (d, J = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.1, 146.4, 143.7, 136.9, 134.8, 133.8, 133.5, 133.1, 132.8, 130.3, 128.7, 128.0, 126.8, 126.8, 125.0(q), 124.4, 121.6, 121.4, 42.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s); HRMS (ESI) calcd for $C_{17}H_{13}ClF_3N_2O_2S$ $[M + H]^+$ 401.0333, found 401.0336.

*N-((7-Bromoquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ra**):* white solid (87 mg, 65%); mp 150−153 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.82 (dd, J = 4.2, 1.7 Hz, 1H), 7.95 (dd, J = 8.3, 1.6 Hz, 1H), 7.75 (d, J = 2.1 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 2.0 Hz, 1H), 7.43 (dd, J = 8.3, 4.3 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 6.65 (t, J = 6.5 Hz, 1H), 4.71 (d, J = 6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.1, 146.4, 143.7, 136.9, 133.8, 133.5, 133.1, 132.8, 132.4, 130.9, 128.8, 127.3, 127.0, 126.8, 126.2(q), 125.5, 124.9(q, CF_3), 124.4, 121.6, 121.6, 45.1; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s); HRMS (ESI) calcd for $C_{17}H_{13}BrF_3N_2O_2S$ $[M + H]^+$ 444.9828, found 444.9822.

*N-((7-Methylquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3sa**):* white solid (78 mg, 68%); mp 126−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.77 (d, J = 3.0 Hz, 1H), 7.98 (d, J = 7.3 Hz, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.4 Hz, 1H), 7.34 (dd, J = 7.1, 3.6 Hz, 1H), 7.27 (d, J = 6.4 Hz, 2H), 7.20 (d, J = 8.0 Hz, 1H), 6.92 (br s, 1H), 4.81 (d, J = 6.5 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.2, 146.2, 143.9, 137.8, 136.5, 133.5, 133.2, 132.9, 132.5, 129.9, 129.6, 127.4, 127.1, 126.6, 126.4, 124.8(q), 124.4, 121.7, 120.4, 41.6, 19.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.4 (s); HRMS (ESI) calcd for $C_{18}H_{16}F_3N_2O_2S$ $[M + H]^+$ 381.0879, found 381.0881.

*N-((5-Methyl-3-phenylquinolin-8-yl)methyl)-4-(trifluoromethyl)-benzenesulfonamide (**3ta**):* white solid (84 mg, 61%); mp 123−126 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.05 (s, 1H), 8.297 (s, 1H), 7.69 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.5 Hz, 2H), 7.53−7.47 (3H, m), 7.32 (d, J = 6.2 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 6.7 Hz, 1H), 6.86 (br s, 1H), 4.74 (d, J = 6.5 Hz, 2H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 148.2, 145.0, 143.9, 137.6, 135.5, 133.8, 133.0, 132.7, 130.8, 130.4, 129.4, 129.3, 128.4, 127.4, 127.3, 126.8, 126.6, 124.7(q), 124.5, 121.8, 46.7, 18.2; ^{19}F NMR (CDCl3, 376 MHz) δ −63.0 (s); HRMS (ESI) calcd for $C_{24}H_{20}F_3N_2O_2S$ $[M + H]^+$ 457.1192, found 457.1193.

*N-((5-Nitroquinolin-8-yl)methyl)-4-nitrobenzenesulfonamide (**3cb**):* white solid (85 mg, 73%); mp 130−134 °C; ^{1}H NMR (DMSO, 400 MHz) δ 9.00 (dd, J = 2.7, 1.4 Hz, 1H), 8.79 (t, J = 6.2 Hz, 1H), 8.75 (dd, J = 7.4, 1.4 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 8.25 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.79 (dd, J = 8.8, 4.7 Hz, 1H), 4.79 (d, J = 6.1 Hz, 2H); ^{13}C NMR (DMSO, 101 MHz) δ 151.0, 149.3, 146.0, 144.4, 144.4, 142.5, 131.7, 127.9, 126.7, 124.3, 124.2, 119.7, 42.5; HRMS (ESI) calcd for $C_{16}H_{13}N_4O_6S$ $[M + H]^+$ 389.0550, found 389.0540.

*N-((5-Nitroquinolin-8-yl)methyl)-4-chlorobenzenesulfonamide (**3cc**):* white solid (79 mg, 70%); mp 134−136 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.00−8.96 (m, 2H), 8.23 (d, J = 7.9 Hz, 1H), 7.71−7.66 (m, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.39 (br s, 1H), 4.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.6, 145.8, 145.3, 141.3, 138.8, 138.6, 132.7, 128.7, 128.1, 127.6, 124.0, 121.1, 45.7; HRMS (ESI) calcd for $C_{16}H_{13}ClN_3O_4S$ $[M + H]^+$ 378.0310, found 378.0308.

*N-((5-Nitroquinolin-8-yl)methyl)-4-methylbenzenesulfonamide (**3cd**):* white solid (75 mg, 70%); mp 118−120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.94 (d, J = 3.9 Hz, 1H), 8.89 (d, J = 8.8 Hz, 1H), 8.14 (d, J = 7.9 Hz, 1H), 7.65−7.61 (m, 2H), 7.44 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.35 (br s, 1H), 4.74 (s, 2H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.5, 145.7, 145.1, 143.2, 141.6, 137.1, 132.6, 129.0, 127.6, 126.6, 124.0, 123.9, 121.0, 45.7, 21.3; HRMS (ESI) calcd for $C_{17}H_{16}N_3O_4S$ $[M + H]^+$ 358.0856, found 358.0851.

*N-((5-Nitroquinolin-8-yl)methyl)-4-methoxybenzenesulfonamide (**3ce**):* white solid (76 mg, 68%); mp 108−110 °C; ^{1}H NMR (DMSO, 400 MHz) δ 8.84 (dd, J = 4.1, 1.6 Hz, 1H), 8.51 (t, J = 6.1 Hz, 1H), 8.37 (dd, J = 8.5, 1.6 Hz, 1H), 8.21 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 7.3 Hz, 1H), 7.54 (dd, J = 8.5, 4.2 Hz, 1H), 7.35

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(d, J = 7.3 Hz, 1H), 4.66 (d, J = 6.0 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (DMSO, 101 MHz) δ 149.2, 149.0, 146.2, 145.2, 134.3, 132.8, 132.4, 128.1, 127.8, 126.7, 126.2, 123.9, 121.1, 42.4, 18.0; HRMS (ESI) calcd for $C_{17}H_{16}N_3O_5S$ $[M + H]^+$ 374.0805, found 374.0801.

*N-((5-Nitroquinolin-8-yl)methyl)-2-(trifluoromethyl)-benzenesulfonamide (**3cf**):* white solid (89 mg, 72%); mp 116−120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.94 (d, J = 8.9 Hz, 1H), 8.89 (d, J = 8.8 Hz, 1H), 8.18 (d, J = 7.9 Hz, 1H), 7.98 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.65−7.63 (m, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.49−7.43 (m, 2H), 6.61 (br s, 1H), 4.82 (d, J = 4.7 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.7, 145.7, 145.3, 141.2, 138.5, 132.5, 132.3, 131.7, 131.0, 127.9, 127.8, 127.8, 127.7, 127.1, 126.8, 126.7, 124.0, 123.8, 121.3, 120.9, 46.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −58.1 (s); HRMS (ESI) calcd for $C_{17}H_{13}F_3N_3O_4S$ $[M + H]^+$ 412.0573, found 412.0569.

*N-((5-Nitroquinolin-8-yl)methyl)-3-(trifluoromethyl)-benzenesulfonamide (**3cg**):* white solid (77 mg, 62%); mp 117−119 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.96 (d, J = 4.0 Hz, 1H), 8.92 (d, J = 8.9 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.79 (s, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.67 (dd, J = 9.4, 4.9 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.32 (t, J = 7.9 Hz, 1H), 6.57 (br s, 1H), 4.81 (d, J = 5.2 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.7, 145.6, 145.3, 141.4, 140.8, 132.7, 131.6, 131.2, 130.9, 130.6, 129.9, 129.7, 129.2, 128.7(q), 127.7, 126.9, 124.2, 124.1, 123.9, 123.6(q, CF_3), 121.5, 121.0, 45.9; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −62.8 (s); HRMS (ESI) calcd for $C_{17}H_{13}F_3N_3O_4S$ $[M + H]^+$ 412.0573, found 412.0572.

*N-((5-Nitroquinolin-8-yl)methyl)-1-phenylmethanesulfonamide (**3ch**):* white solid (65 mg, 61%); mp 60−63 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.07 (d, J = 8.8 Hz, 1H), 8.95 (d, J = 2.9 Hz, 1H), 8.34 (d, J = 7.8 Hz, 1H), 7.79 (s, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.38−7.28 (m, 5H), 5.94 (br s, 1H), 4.73 (s, 2H), 4.28 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.7, 146.1, 145.2, 142.6, 132.6, 130.7, 130.5, 129.0, 128.8, 128.6, 128.6, 127.1, 124.5, 124.0, 121.2, 59.4, 45.5; HRMS (ESI) calcd for $C_{17}H_{16}N_3O_4S$ $[M + H]^+$ 358.0856, found 358.0857.

*N-((5-Nitroquinolin-8-yl)methyl)-butane-1-sulfonamide (**3ci**):* white solid (36 mg, 37%); mp 104−106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.06 (d, J = 8.9 Hz, 1H), 9.02 (d, J = 3.2 Hz, 1H), 8.35 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.72 (dd, J = 8.7, 4.0 Hz, 1H), 5.90 (br s, 1H), 4.87 (s, 2H), 2.95 (t, J = 7.8 Hz, 2H), 1.71−1.63 (m, 2H), 1.36−1.27 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 150.8, 146.1, 145.2, 142.8, 132.8, 127.2, 124.5, 124.1, 121.2, 53.0, 45.1, 25.5, 21.4, 13.5; HRMS (ESI) calcd for $C_{14}H_{18}N_3O_4S$ $[M + H]^+$ 324.1013, found 324.1019.

Selective Reduction (eq 4).[20] Compound **3aa** (0.30 mmol, 110.0 mg) and $NiCl_6{\cdot}H_2O$ (10 mol %, 7.20 mg) were dissolved in MeOH (4 mL), $NaBH_4$ (3.0 mmol, 113.5 mg) was added in portions with stirring under cooling for 1 h, then the stirring was continued for another 1 h. After removal of the solvents, the residue was absorbed to small amounts of silica. After purification by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:5), **4a** was obtained as white solid (89 mg, 80%): mp 128−130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 7.4 Hz, 1H), 6.73 (d, J = 7.3 Hz, 1H), 6.53 (t, J = 7.5 Hz, 1H), 4.93 (br s, 1H), 4.05 (s, 2H), 3.32 (t, J = 5.5 Hz, 2H), 2.72 (t, J = 6.3 Hz, 2H), 1.92−1.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 143.0, 134.6, 134.2, 133.9, 130.2, 128.2, 127.7, 126.2(q), 124.5, 122.4, 121.8, 117.8, 116.2, 45.5, 42.0, 27.2, 21.5; ^{19}F NMR ($CDCl_3$, 376 MHz) δ −63.1 (s); HRMS (ESI) calcd for $C_{17}H_{18}F_3N_2O_2S$ $[M + H]^+$ 371.1036, found 371.1032.

Deprotection of 3aa (eq 5). A mixture of **3aa** (0.3 mmol) and EtONa (0.9 mmol) in DMSO (5 mL) was stirred at 100 °C under Ar atmosphere for 20 h. After being cooled to ambient temperature, the reaction mixture was quenched with H_2O, The aqueous phase was extracted with EtOAc, and the combined organic phase was dried over Na_2SO_4. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:20) to give **5a** as a red solid (40 mg, 83%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.93 (dd, J = 4.1, 1.6 Hz, 1H), 8.16 (dd, J = 8.2, 1.6 Hz, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 6.8 Hz, 1H), 7.49 (t, J = 7.3 Hz, 1H), 7.42 (dd, J = 8.2, 4.2 Hz, 1H), 4.43 (s, 2H), 2.18 (br s, 2H).[4f]

H/D Exchange Reaction (eq 6). A mixture of $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol) and $AgSbF_6$ (20.6 mg, 0.06 mmol) was weighed in a Schlenk tube equipped with a stir bar. CH_2Cl_2/MeOH-d_6 (5/1, 6.0 mL) was added followed immediately by the 8-methylquinoline (86.0 mg, 0.6 mmol), and the mixture was stirred at 100 °C for 12 h under Ar atmosphere. The mixed products were purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:20).

KIE Experiments (eq 7). A mixture of 4-(trifluoromethyl)-benzenesulfonyl azide (0.3 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol, 5.0 mol %), and $AgSbF_6$ (20.6 mg, 20.0 mol %) were weighed in a Schlenk tube equipped with a stir bar. Dry DCM (6.0 mL) was added followed immediately by 8-methylquinoline (0.6 mmol, 2 equiv) or 8-methylquinoline-d_3 (0.6 mmol, 2 equiv), and the mixture was stirred at 100 °C for 45 min under Ar atmosphere. Afterward, the two independent reactions were poured into the same round flask, the solvent was evaporated under reduced pressure, and the residue was absorbed to small amounts of silica. The purification was performed by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:10).

Preparation of Intermediate A (eq 8). A mixture of substituted 8-methylquinoline (286.7 mg, 2.0 mmol), $[Cp^*RhCl_2]_2$ (18.6 mg, 0.2 mmol), and $AgSbF_6$ (274.8 mg, 0.8 mmol) were weighed in a Schlenk tube equipped with a stir bar. Dry CH_2Cl_2 (6 mL) was added. The reaction mixture was stirred at 100 °C overnight and then concentrated under vacuum. After purification by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:1) intermediate **A** was obtained as an orange-red solid (50 mg, 20%): mp 213−215 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.92 (d, J = 4.4 1H), 8.07 (dd, J = 8.3, 1.1 Hz, 1H), 7.61 (dd, J = 6.5, 1.3 Hz, 1H), 7.46−7.40 (m, 2H), 7.35 (dd, J = 8.3, 4.9 Hz, 1H), 3.96 (d, J = 13.3 Hz, 1H), 3.69 (d, J = 13.3 Hz, 1H), 1.61 (s, 15H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 153.5, 151.7, 151.4, 136.6, 123.0, 128.7, 128.0, 123.0, 122.0, 93.9, 93.8, 33.8, 33.5, 9.2; HRMS (ESI) calcd for $C_{20}H_{23}NRh$ $[M - SbF_6^-]^+$ 380.0880, found 380.0881.

Amidation Reaction Catalyzed by Intermediate A (eq 9). A mixture of **1a** (0.6 mmol, 2.0 equiv), **2a** (0.30 mmol, 1.0 equiv), and intermediate A (10.0 mol %) were weighed in a Schlenk tube equipped with a stir bar. Dry DCM (6.0 mL) was added, and the mixture was stirred at 100 °C for 12 h under Ar. Afterward, it was transferred to a round-bottom flask. Silica was added to the flask, and volatiles were evaporated under reduced pressure. After purification by flash column chromatography on silica gel **3aa** was obtained in 60% yield.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full spectroscopic data for all new compounds and CIF files giving X-ray structural information for **3na**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bqwang@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

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