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# Pincer-Nickel-Catalyzed Cross-Coupling of Aryl Sulfamates with Arylzinc Chlorides

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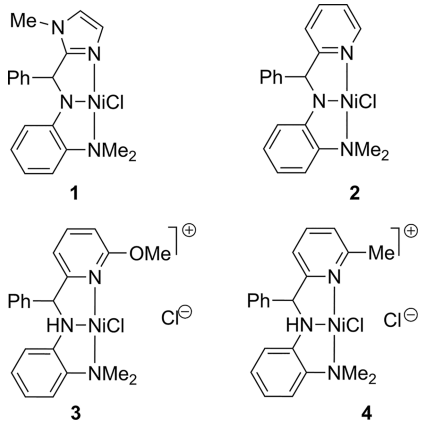
**Keywords:** Homogeneous catalysis / Cross-coupling / Pincer complexes / Nickel / Ligand design / Sulfamates

The nickel *N*,*N*,*N*-pincer complex **2** was demonstrated to effectively catalyze the cross-coupling of aryl sulfamates with arylzinc chlorides under mild conditions. The reaction is suitable for a wide range of substrates, and tolerates various functional groups.

## Introduction

Transition-metal-catalyzed cross-coupling reactions of organometallic reagents with various electrophiles are powerful tools for the synthesis of biaryls, which are an important class of compounds in the areas of natural product chemistry, agrochemicals, liquid crystals, pharmaceuticals, and advanced materials.[1,2] Organic halides are the electrophiles that have been used most often in recent decades.[1] Phenolic derivatives are also attractive electrophiles, reacting through C–O bond cleavage, due to the wide availability of phenols from nature and industry. Aryl triflates are the most widely investigated of the phenol-based electrophiles due to their good reactivity. However, their high cost and instability limit their use. Hence, other phenol-derived electrophiles such as mesylates, tosylates, esters, carbonates, phosphates, carbamates, sulfamates, and ethers have also been studied.[3] Of these, aryl sulfamates have recently received attention. Aryl sulfamates are readily synthesized, and they are more stable and less expensive than aryl triflates. The O-sulfamate moiety is an effective directing group for arene functionalization.[4] Hence sulfamates can be used as an alternative to triflates, even though their C–O bonds are less reactive than those in triflates. Cross-coupling reactions that have been reported using aryl sulfamates as electrophiles include Suzuki reactions,[4a,4b,5] Kumada reactions,[4c,6] amination reactions,[7] and C–H bond functionalizations.[8]

Organozinc reagents are readily prepared nucleophilic species that show higher reactivity than organoboron, -silicon, and -tin reagents and better functional-group compatibility than organomagnesium reagents. Hence, it would be interesting to explore the reactions of aryl sulfamates with arylzinc reagents to construct biaryl compounds. The reactions of arylzinc reagents with various phenol derivatives, including aryl pivalates and aryl methyl ethers, have been reported. However, only reactive electrophiles such as naphthyl pivalates, electron-deficient phenyl pivalates, and electron-deficient aryl methyl ethers can be used in these reactions.[9] This is another reason that we chose to investigate the reactions of aryl sulfamates with arylzinc reagents. In our previous studies on Negishi-type cross-coupling reactions using aryl halides or aromatic ammonium salts as electrophiles, nickel pincer complexes were shown to be effective catalysts.[10] For example, nickel *P*,*N*,*N*-pincer complex [Ni(Cl){N(2-$Ph_2PC_6H_4$)(2′-$Me_2NC_6H_4$)}] catalyzes the cross-coupling of aryltrimethylammonium triflates with aryl- or heteroarylzinc chlorides under mild conditions with extremely low catalyst loadings.[10a] On the basis of the results achieved, we intended to investigate nickel-pincer-complex-catalyzed cross-coupling of aryl sulfamates with arylzinc reagents. We found that phosphorus-free nickel *N*,*N*,*N*-pincer complexes **1**–**4** (Scheme 1) can catalyze the reaction, and we report the results in this paper.




Scheme 1. Nickel pincer complexes **1**–**4**.

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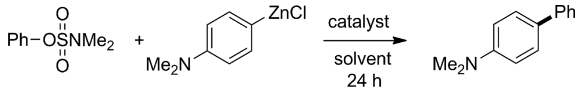
## Results and Discussion

The synthesis and characterization of complexes **1**–**4** are presented in the Supporting Information. Each of these complexes is diamagnetic, and was characterized by elemental analysis and $^1H$ and $^{13}C$ NMR spectroscopy. The structure of complex **2** was also determined by single-crystal X-ray diffraction,[11] which showed the pincer coordination mode. The fact that complexes **3** and **4** are diamagnetic implies that in both of these structures the central Ni atom has a square-planar coordination geometry. Hence, for each of **3** and **4** an ion-pair structure consisting of a tridentate chelate nickel chloride cation and an chloride anion was proposed.

We used the reaction of $PhOSO_2NMe_2$ with *p*-$Me_2NC_6H_4ZnCl$ to evaluate the catalytic properties of complexes **1**–**4** and optimize the reaction conditions. The results are listed in Table 1. Initially, the reaction was run in a 1:1 mixture of THF and NMP (*N*-methylpyrrolidine) at 80 °C for 24 h using a catalyst loading of 5 mol-%. Each of the complexes was found to be catalytically active. Complex **2** resulted in the highest yield of the desired product, and complex **3** led to the lowest product yield (Table 1, entries 1–4). It seems that a strongly electron-donating group on the pyridine ring of the ligand is disadvantageous to the catalytic activity of the complexes. Then the effect of the solvent was examined. A series of solvents or solvent combinations including THF, NMP, THF/DMA (*N*,*N*-dimethylacetamide), THF/toluene, and THF/NMP were tested, and a 2:1 mixture of THF and NMP was found to be the best (Table 1, entries 5–10). Examination of reaction temperature showed that the reaction proceeded most effectively at 50 °C, with higher or lower reaction temperatures leading to lower yields (Table 1, entries 11–14). Testing the salt effect showed that the zinc reagent *p*-$Me_2NC_6H_4ZnCl$, prepared from the corresponding Grignard reagent and $ZnCl_2$ in the presence of LiCl (2 equiv.) gave better results than the reagents prepared from *p*-$Me_2NC_6H_4Li$ and $ZnCl_2$, *p*-$Me_2NC_6H_4MgBr$ and $ZnCl_2$, or *p*-$Me_2NC_6H_4Li$ and $ZnCl_2$ in the presence of $MgBr_2$ (1 equiv.) (Table 1, entries 15–17). That is to say, lithium and magnesium ions both play important roles in the reaction. This may be due to the presence of a multimetallic synergistic effect in the reaction process.[12] In addition, the role of LiCl may also involve (1) breaking the aggregation of ArZnCl with the co-product of $MgCl_2$ through the formation of a trimetallic adduct, and (2) enhancing the reactivity of the zinc reagents by forming more nucleophilic zincates.[9b,12,13] When the reaction time was shortened to 12 h, the reaction still gave a 99% yield of the product (Table 1, entry 18). We also noted that the amount of catalyst could be reduced. A catalyst loading of 1 mol-% resulted in a 95% yield of the product using the optimized reaction solvent, temperature, and time (Table 1, entry 19). It was reported that $(Cy_3P)_2NiCl_2$ can catalyze the cross-coupling of aryl/alkenyl pivalates with arylzinc reagents.[9a] For comparison, we also tested catalysis of $(Cy_3P)_2NiCl_2$ in the cross-coupling of $PhOSO_2NMe_2$ with *p*-$Me_2NC_6H_4ZnCl$. We found that the catalytic efficiency of $(Cy_3P)_2NiCl_2$ is clearly lower than that of complex **2**; when $(Cy_3P)_2NiCl_2$ was used with catalyst loadings of 5 and 1 mol-%, the cross-coupling products were formed in 93 and 84% yields, respectively (Table 1, entries 20 and 21). In addition, in the absence of any metal catalyst, the reaction gave a 25% yield of the product at 50 °C, and 21% yield at 80 °C (Table 1, entries 22 and 23). This means that a direct nucleophilic substitution can take place with a low efficiency.

Table 1. Catalyst evaluation and optimization of reaction conditions.[a]




| Entry | Cat. (mol-%) | Solvent | Temp. [°C] | Yield [%][b] |
|---|---|---|---|---|
| 1 | **1** (5) | THF/NMP (1:1) | 80 | 60 |
| 2 | **2** (5) | THF/NMP (1:1) | 80 | 65 |
| 3 | **3** (5) | THF/NMP (1:1) | 80 | 49 |
| 4 | **4** (5) | THF/NMP (1:1) | 80 | 56 |
| 5 | **2** (5) | THF | 80 | 37 |
| 6 | **2** (5) | NMP | 80 | 55 |
| 7 | **2** (5) | THF/DMA (1:1) | 80 | 48 |
| 8 | **2** (5) | THF/toluene (1:1) | 80 | 25 |
| 9 | **2** (5) | THF/NMP (1:2) | 80 | 68 |
| 10 | **2** (5) | THF/NMP (2:1) | 80 | 74 |
| 11 | **2** (5) | THF/NMP (2:1) | 70 | 75 |
| 12 | **2** (5) | THF/NMP (2:1) | 60 | 85 |
| 13 | **2** (5) | THF/NMP (2:1) | 50 | 99 |
| 14 | **2** (5) | THF/NMP (2:1) | 25 | 60 |
| 15[c] | **2** (5) | THF/NMP (2:1) | 50 | 54 |
| 16[d] | **2** (5) | THF/NMP (2:1) | 50 | 57 |
| 17[e] | **2** (5) | THF/NMP (2:1) | 50 | 69 |
| 18[f] | **2** (5) | THF/NMP (2:1) | 50 | 99 |
| 19[f] | **2** (1) | THF/NMP (2:1) | 50 | 95 |
| 20 | $(Cy_3P)_2NiCl_2$ (5) | THF/NMP (2:1) | 50 | 93 |
| 21 | $(Cy_3P)_2NiCl_2$ (1) | THF/NMP (2:1) | 50 | 84 |
| 22[f] | none | THF/NMP (2:1) | 50 | 25 |
| 23[f] | none | THF/NMP (2:1) | 80 | 21 |

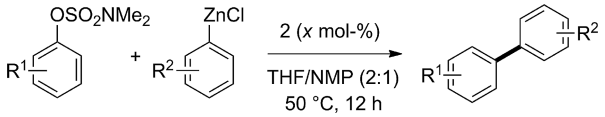
[a] The reactions were carried out on a 0.5 mmol scale, 2.0 equiv. of *p*-$Me_2NC_6H_4ZnCl$ were used. Unless otherwise specified, *p*-$Me_2NC_6H_4ZnCl$ was prepared from *p*-$Me_2NC_6H_4MgBr$ and $ZnCl_2$ in the presence of 2 equiv. of LiCl. [b] Isolated yield. [c] The zinc reagent was prepared from *p*-$Me_2NC_6H_4Li$ and $ZnCl_2$. [d] *p*-$Me_2NC_6H_4ZnCl$ was prepared from *p*-$Me_2NC_6H_4MgBr$ and $ZnCl_2$ (1 equiv.). [e] *p*-$Me_2NC_6H_4ZnCl$ was prepared from *p*-$Me_2NC_6H_4Li$ and $ZnCl_2$ (1 equiv.) in the presence of $MgBr_2$ (1 equiv.). [f] The reaction time was 12 h.

Under the optimized reaction conditions, the scope of the reaction with respect to the arylzinc chloride and aryl sulfamate components was examined (Table 2). As can be seen from Table 2, the reaction of $PhOSO_2NMe_2$ with *p*-$MeOC_6H_4ZnCl$ gave a similar yield to that obtained using *p*-$Me_2NC_6H_4ZnCl$ as the nucleophile (Table 2, entry 1). The deactivated derivatives *p*-$BnC_6H_4OSO_2NMe_2$, *p*-$MeC_6H_4OSO_2NMe_2$, and *m*-$MeC_6H_4OSO_2NMe_2$ showed good reactivity in the coupling reactions with *p*-$Me_2NC_6H_4ZnCl$, *p*-$MeOC_6H_4ZnCl$, and *p*-$MeC_6H_4ZnCl$ in the presence of 1 mol-% of complex **2** (Table 2, entries 2–8). However, the reaction of *o*-$MeC_6H_4OSO_2NMe_2$ was much more difficult than those of *p*-$MeC_6H_4OSO_2NMe_2$

and *m*-$MeC_6H_4OSO_2NMe_2$ due to steric hindrance. It required a higher catalyst loading, and gave lower product yields (Table 2, entries 9 and 10). Strongly deactivated derivatives *p*-$MeOC_6H_4OSO_2NMe_2$, *p*-$Me_2NC_6H_4OSO_2NMe_2$, and *m*-$Me_2NC_6H_4OSO_2NMe_2$ also reacted with arylzinc reagents including *p*-$MeC_6H_4ZnCl$, *p*-$Me_2NC_6H_4ZnCl$, and PhZnCl when 3 mol-% of **2** was used, giving the desired products in good to excellent yields (Table 2, entries 11–18). A series of electron-deficient sulfamates including *p*-$NCC_6H_4OSO_2NMe_2$, *p*-$MeOC(O)C_6H_4OSO_2NMe_2$, *p*-$FC_6H_4OSO_2NMe_2$, *p*-$CF_3C_6H_4OSO_2NMe_2$, and *p*-$PhC(O)C_6H_4OSO_2NMe_2$ were tested, and each of them showed good reactivity and led to the products in excellent yield in the presence of 1 mol-% **2** (Table 2, entries 19–26). *o*-$MeOC(O)C_6H_4OSO_2NMe_2$ was less reactive due to steric hindrance. Its reaction with *p*-$MeC_6H_4ZnCl$ gave a 62% yield of the product, even in the presence of 5 mol-% of complex **2**. The sterically hindered zinc reagent *o*-$MeC_6H_4ZnCl$ also showed a reactivity lower than that of *p*-$MeC_6H_4ZnCl$. The reaction of *o*-$MeC_6H_4ZnCl$ with deactivated sulfamates such as *p*-$MeOC_6H_4OSO_2NMe_2$ and *p*-$Me_2NC_6H_4OSO_2NMe_2$ gave the desired products in quite low yields in the presence of 5 mol-% **2** (Table 2, entries 28–29). In contrast, the reaction of *o*-$MeC_6H_4ZnCl$ with activated sulfamates such as *p*-$MeOC(O)C_6H_4OSO_2NMe_2$ and *p*-$NCC_6H_4OSO_2NMe_2$ resulted in good product yields using 3 mol-% of **2** as catalyst (Table 2, entries 30–31). The electron-poor arylzinc reagent *p*-$CF_3C_6H_4ZnCl$ was also tested. Its reactions with the activated sulfamates *p*-$MeOC(O)C_6H_4OSO_2NMe_2$ and *p*-$NCC_6H_4OSO_2NMe_2$ gave excellent results (Table 2, entries 32–33). However, its reaction with deactivated sulfamates such as *p*-$MeOC_6H_4OSO_2NMe_2$ and *p*-$Me_2NC_6H_4OSO_2NMe_2$ did not give any of the desired products.

Table 2. Cross-coupling of substituted phenyl sulfamates with arylzinc chlorides catalyzed by complex **2**.[a]

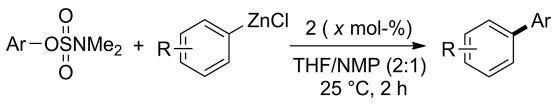



| Entry | $R^1$ | $R^2$ | *x* | Yield [%][b] |
|---|---|---|---|---|
| 1 | H | *p*-OMe | 1 | 98 |
| 2 | *p*-Bn | *p*-$NMe_2$ | 1 | 89 |
| 3 | *p*-Bn | *p*-OMe | 1 | 90 |
| 4 | *p*-Bn | *p*-Me | 1 | 88 |
| 5 | *p*-Me | *p*-$NMe_2$ | 1 | 90 |
| 6 | *p*-Me | *p*-OMe | 1 | 80 |
| 7 | *m*-Me | *p*-$NMe_2$ | 1 | 85 |
| 8 | *m*-Me | *p*-OMe | 1 | 80 |
| 9 | *o*-Me | *p*-$NMe_2$ | 5 | 57 |
| 10 | *o*-Me | *p*-OMe | 5 | 35 |
| 11 | *p*-MeO | *p*-Me | 3 | 94 |
| 12 | *p*-MeO | *p*-$NMe_2$ | 3 | 94 |
| 13 | *p*-MeO | H | 3 | 92 |
| 14 | *p*-$NMe_2$ | *p*-Me | 3 | 80 |
| 15 | *p*-$NMe_2$ | *p*-OMe | 3 | 81 |
| 16 | *p*-$NMe_2$ | H | 3 | 80 |
| 17 | *m*-$NMe_2$ | *p*-Me | 3 | 81 |
| 18 | *m*-$NMe_2$ | *p*-OMe | 3 | 80[c] |
| 19 | *p*-CN | *p*-Me | 1 | 92 |
| 20 | *p*-MeOC(O) | *p*-Me | 1 | 95 |
| 21 | *p*-F | *p*-OMe | 1 | 92 |
| 22 | *p*-F | *p*-$NMe_2$ | 1 | 99 |
| 23 | *p*-$CF_3$ | *p*-$NMe_2$ | 1 | 92 |
| 24 | *p*-$CF_3$ | *p*-OMe | 1 | 90 |
| 25 | *p*-$CF_3$ | *p*-Me | 1 | 90[c] |
| 26 | *p*-PhC(O) | *p*-Me | 1 | 85 |
| 27 | *o*-MeOC(O) | *p*-Me | 5 | 62 |
| 28 | *p*-MeO | *o*-Me | 5 | 20 |
| 29 | *p*-$NMe_2$ | *o*-Me | 5 | 17 |
| 30 | *p*-MeOC(O) | *o*-Me | 3 | 88 |
| 31 | *p*-CN | *o*-Me | 3 | 88 |
| 32 | *p*-CN | *p*-$CF_3$ | 3 | 87 |
| 33 | *p*-MeOC(O) | *p*-$CF_3$ | 3 | 86 |

[a] The reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation; the zinc reagents were prepared from the corresponding Grignard reagents and $ZnCl_2$ in the presence of LiCl (2 equiv.); 2.0 equiv. of zinc reagent was used. [b] Isolated yield. [c] A mixture of cross-coupling product and homocoupling product of the zinc reagent was obtained, and their ratio was calculated using integrals of the $^1H$ NMR spectrum.

Next, we tested the reactivity of naphthyl, pyridyl, and quinolyl sulfamates in cross-coupling reactions with arylzinc chlorides catalyzed by **2** (Table 3). Both 1- and 2-naphthyl sulfamates showed excellent reactivity. Their reactions with *p*-$MeC_6H_4ZnCl$, *p*-$Me_2NC_6H_4ZnCl$, and *p*-$MeOC_6H_4ZnCl$ proceeded smoothly at room temperature in the presence of complex **2** (0.5 mol-%) to give the desired products in excellent yields (Table 3, entries 1–6). The reaction of 2-naphthyl sulfamate with the sterically hindered *o*-$MeC_6H_4ZnCl$ also gave an excellent result under the same conditions. 2-Pyridyl and 8-quinolyl sulfamates both showed lower reactivity than 1- and 2-naphthyl sulfamates. They could react smoothly with *p*-$MeC_6H_4ZnCl$ at 50 °C in the presence of 1 mol-% of complex **2**. Their reaction with the electron-deficient zinc reagent *p*-$CF_3C_6H_4ZnCl$ required

Table 3. Cross-coupling of naphthyl, pyridyl, and quinolyl sulfamates with arylzinc chlorides catalyzed by complex **2**.[a]



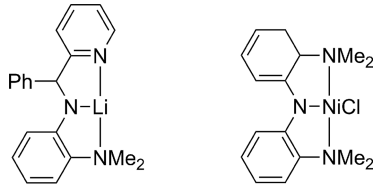

| Entry | Ar | R | *x* | Yield [%][b] |
|---|---|---|---|---|
| 1 | 1-naphthyl | *p*-Me | 0.5 | 97 |
| 2 | 1-naphthyl | *p*-MeO | 0.5 | 95 |
| 3 | 1-naphthyl | *p*-$NMe_2$ | 0.5 | 95 |
| 4 | 2-naphthyl | *p*-Me | 0.5 | 98 |
| 5 | 2-naphthyl | *p*-MeO | 0.5 | 96 |
| 6 | 2-naphthyl | *p*-$NMe_2$ | 0.5 | 98 |
| 7 | 2-naphthyl | *o*-Me | 0.5 | 92 |
| 8[c] | 2-pyridyl | *p*-Me | 1 | 88 |
| 9[c] | 2-pyridyl | *p*-$CF_3$ | 3 | 82 |
| 10[c] | 8-quinolyl | *p*-Me | 1 | 89 |
| 11[c] | 8-quinolyl | *p*-$CF_3$ | 3 | 83 |

[a] Unless otherwise specified, the reactions were carried out on a 0.5 mmol scale according to the conditions indicated by the above equation. The zinc reagents were prepared from corresponding Grignard reagents and $ZnCl_2$ in the presence of LiCl (2 equiv.); 2.0 equiv. of the zinc reagent was used. [b] Isolated yield. [c] The reaction was run at 50 °C for 12 h.

higher catalyst loadings. A catalyst loading of 3 mol-% of complex **2** was necessary to drive the reaction to completion (Table 3, entries 8–11).

A preliminary mechanistic study was carried out using the reaction of $PhOSO_2NMe_2$ with *p*-$Me_2NC_6H_4ZnCl$ catalyzed by **2** under the optimized conditions. When 1,1-diphenylethylene (10 mol-%) was added to the reaction mixture, the cross-coupling product was obtained in 33% yield, which is slightly higher than the yield obtained by direct nucleophilic substitution in the absence of a catalyst (Table 1, entry 22). It seems that the reaction proceeded through a free-radical process. A combination of Ni(COD)$_2$ (1 mol-%; COD = cyclooctadienyl) and complex **5** (1 mol-%, prepared in situ by reaction of the ligand precursor with *n*BuLi) (Scheme 2) led to only a 40% yield of the cross-coupling product. Hence, the active catalyst should not be a $Ni^0$ species. In another experiment, a mixture of complex **2** (0.5 mmol) and *p*-$Me_2NC_6H_4ZnCl$ (0.75 mmol) in THF was stirred at room temperature for 4 h. The resulting mixture was treated with $PhOSO_2NMe_2$ (0.5 mmol) in THF/NMP (2:1) at 50 °C for 12 h. No cross-coupling product was obtained. This observation contrasts with reports of nickel pincer **6** catalyzed cross-coupling reactions of alkyl halides with alkyl Grignard reagents reported by Hu et al.[14] Based on the experimental facts given above and the reported mechanistic studies of nickel-catalyzed cross-coupling reactions,[15] we inferred that the catalytic process may involve a $Ni^I$ species, although we cannot yet give a clear catalytic cycle.




**5** **6**

Scheme 2. Lithium (**5**) and nickel (**6**) pincer complexes.

## Conclusions

We have synthesized nickel *N*,*N*,*N*-pincer complexes **1**–**4** and evaluated their catalytic behavior in the cross-coupling reaction of aryl sulfamates with arylzinc reagents. Complex **2**, a phosphorus-free and air-stable catalyst, can effectively catalyze the cross-coupling of activated, unactivated, and deactivated aryl sulfamates and heteroaryl sulfamates with arylzinc chlorides, forming biaryls in high yields. The reactions required low catalyst loadings and mild reaction conditions in most cases. A range of functional groups including MeO, $Me_2N$, PhC(O), COOMe, CN, $CF_3$, and F groups, and also nitrogen-containing heterocycles were tolerated. The extension to more challenging substrate combinations using these nickel pincer catalysts is currently underway in our laboratory.

## Experimental Section

**General:** All air- or moisture-sensitive manipulations were carried out under nitrogen using standard Schlenk techniques. Toluene was distilled under nitrogen from sodium; THF and DME were distilled under nitrogen from sodium/benzophenone; NMP and DMA were dried with molecular sieves (4 Å), fractionally distilled under reduced pressure, and stored under a nitrogen atmosphere. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. The preparation of aryl sulfamates, ligand precursors, and complexes **1**–**4** is given in the Supporting Information. NMR spectra were recorded with a Bruker Avance III 400 spectrometer at ambient temperature. The chemical shifts of $^1H$ and $^{13}C$ NMR spectra were referenced to tetramethylsilane or to internal solvent resonances.

**General Procedure:** A Schlenk tube was charged with aryl sulfamate (0.5 mmol), complex **2** (2.0 mg, 0.005 mmol), and NMP (1.0 mL). ArZnCl solution (0.5 M solution in THF; 2 mL, 1.0 mmol) was added by syringe to the stirred mixture. The reaction mixture was stirred at 50 °C for 12 h. Water (10 mL) and several drops of glacial acetic acid were then successively added. The mixture was extracted with $Et_2O$ (3× 10 mL). The combined organic phases were dried with anhydrous $Na_2SO_4$, and concentrated by rotary evaporation, and the residue was purified by column chromatography (silica gel).

**4-Benzyl-4′-methylbiphenyl:**[16] $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.38 (s, 3 H), 4.01 (s, 2 H), 7.18–7.26 (m, 7 H), 7.27–7.32 (m, 2 H), 7.46 (d, $J$ = 8 Hz, 2 H), 7.49 (d, $J$ = 8 Hz, 2 H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 21.23, 41.72, 126.26, 126.98, 127.16, 128.65, 129.11, 129.42, 129.59, 136.96, 138.26, 139.11, 140.08, 141.21 ppm.

**4′-Benzyl-*N*,*N*-dimethylbiphenyl-4-amine:**[17] $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.98 (s, 6 H), 4.00 (s, 2 H), 6.79 (d, $J$ = 8.4 Hz, 2 H), 7.18–7.24 (m, 5 H), 7.30 (t, $J$ = 7.6 Hz, 2 H), 7.47 (d, $J$ = 8.4 Hz, 4 H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 40.73, 41.69, 112.94, 126.18, 126.48, 127.70, 128.61, 129.10, 129.26, 129.35, 138.99, 139.19, 141.38, 149.98 ppm.

**4-Benzyl-4′-methoxybiphenyl:**[18] $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.83 (s, 3 H), 4.00 (s, 2 H), 6.95 (d, $J$ = 8.8 Hz, 2 H), 7.19–7.25 (m, 5 H), 7.29 (t, $J$ = 7.2 Hz, 2 H), 7.46 (d, $J$ = 8.4 Hz, 2 H), 7.49 (d, $J$ = 8.8 Hz, 2 H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 41.70, 55.46, 114.31, 126.25, 126.92, 128.14, 128.64, 129.09, 129.43, 133.71, 138.79, 139.74, 141.24, 159.15 ppm.

***N*,*N*-Dimethylbiphenyl-4-amine:**[10c] $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.99 (s, 6 H), 6.81 (d, $J$ = 8.8 Hz, 2 H), 7.23–7.27 (m, 1 H), 7.39 (t, $J$ = 7.8 Hz, 2 H), 7.51 (d, $J$ = 8.8 Hz, 2 H), 7.54–7.57 (m, 2 H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 40.64, 112.88, 126.08, 126.37, 127.79, 128.76, 129.32, 141.32, 150.07 ppm.

**4-Methoxybiphenyl:**[10c] $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.85 (s, 3 H), 6.98 (d, $J$ = 8.8 Hz, 2 H), 7.28–7.32 (m, 1 H), 7.41 (t, $J$ = 7.8 Hz, 2 H), 7.51–7.56 (m, 4 H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 55.49, 114.35, 126.80, 126.88, 128.30, 128.86, 133.93, 140.98, 159.29 ppm.

***N*,*N*,4′-Trimethylbiphenyl-4-amine:**[16] $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.28 (s, 3 H), 2.88 (s, 6 H), 6.68–6.71 (m, 2 H), 7.11 (d, $J$ = 8.0 Hz, 2 H), 7.33–7.42 (m, 4 H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 21.16, 40.74, 112.96, 126.29, 127.64, 129.45, 129.49, 135.71, 138.51, 149.94 ppm.

**4-Methoxy-4′-methylbiphenyl:**[18] $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 2.36 (s, 3 H), 3.80 (s, 3 H), 6.94 (d, $J$ = 8.8 Hz, 2 H), 7.20 (d, $J$ = 8.0 Hz, 2 H), 7.43 (d, $J$ = 8.0 Hz, 2 H), 7.49 (d, $J$ = 8.8 Hz, 2 H) ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$): $\delta$ = 21.15, 55.40, 114.28, 126.68, 128.05, 129.56, 133.84, 136.43, 138.08, 159.06 ppm.

***N*,*N*,3′-Trimethylbiphenyl-4-amine:**[19] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.30 (s, 3 H), 2.86 (s, 6 H), 6.69 (d, $J$ = 8.8 Hz, 2 H), 6.97 (d, $J$ = 7.2 Hz, 1 H), 7.18 (t, $J$ = 7.4 Hz, 1 H), 7.26 (d, $J$ = 9.2 Hz, 2 H), 7.40 (d, $J$ = 9.2 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 20.70, 39.67, 111.87, 122.53, 125.88, 126.21, 126.81, 127.67, 128.50, 137.22, 140.32, 149.03 ppm.

**4′-Methoxy-3-methylbiphenyl:**[20] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.38 (s, 3 H), 3.79 (s, 3 H), 6.94 (d, $J$ = 8.8 Hz, 2 H), 7.10 (d, $J$ = 7.6 Hz, 1 H), 7.28 (t, $J$ = 7.4 Hz, 1 H), 7.33 (d, $J$ = 10.0 Hz, 2 H), 7.50 (d, $J$ = 8.8 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.65, 55.38, 114.25, 123.95, 127.52, 127.65, 128.25, 128.74, 133.98, 138.36, 140.92, 159.20 ppm.

***N*,*N*,2′-Trimethylbiphenyl-4-amine:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.22 (s, 3 H), 2.89 (s, 6 H), 6.70 (d, $J$ = 8.8 Hz, 2 H), 7.09–7.19 (m, 6 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 20.80, 40.72, 112.22, 125.85, 126.64, 130.07, 130.21, 130.40, 135.64, 142.14, 149.52 ppm.

**4′-Methoxy-2-methylbiphenyl:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.27 (s, 3 H), 3.84 (s, 3 H), 6.95 (d, $J$ = 8.8 Hz, 2 H), 7.19–7.28 (m, 6 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 20.68, 55.41, 113.63, 125.89, 127.11, 130.04, 130.38, 130.43, 134.52, 135.62, 141.69, 158.65 ppm.

**Methyl 4′-Methylbiphenyl-2-carboxylate:**[21] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.38 (s, 3 H), 3.65 (s, 3 H), 7.20 (s, 4 H), 7.33–7.39 (m, 2 H), 7.46–7.51 (m, 1 H), 7.77–7.81 (m, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.30, 52.02, 127.02, 128.29, 128.91, 129.80, 130.83, 130.94, 131.30, 137.00, 138.43, 142.54, 169.33 ppm.

**Methyl 4′-Methylbiphenyl-4-carboxylate:**[5g] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.29 (s, 3 H), 3.82 (s, 3 H), 7.15 (d, $J$ = 7.9 Hz, 2 H), 7.41 (d, $J$ = 8.1 Hz, 2 H), 7.52 (d, $J$ = 8.4 Hz, 2 H), 7.98 (d, $J$ = 8.4 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.23, 52.14, 126.85, 127.17, 128.67, 129.73, 130.16, 137.14, 138.17, 145.63, 167.10 ppm.

**Methyl 2′-Methylbiphenyl-4-carboxylate:**[22] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.17 (s, 3 H), 3.84 (s, 3 H), 7.11–7.19 (m, 4 H), 7.30 (d, $J$ = 8.3 Hz, 2 H), 7.99 (d, $J$ = 8.3 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 19.47, 51.20, 125.01, 126.94, 127.71, 128.37, 128.52, 128.62, 129.59, 134.25, 139.96, 145.86, 166.14 ppm.

**4′-Methoxy-*N*,*N*-dimethylbiphenyl-4-amine:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.95 (s, 6 H), 3.81 (s, 3 H), 6.78 (d, $J$ = 8.8 Hz, 2 H), 6.93 (d, $J$ = 8.8 Hz, 2 H), 7.44 (d, $J$ = 8.8 Hz, 2 H), 7.47 (d, $J$ = 8.8 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 39.77, 54.43, 112.04, 113.23, 126.40, 126.42, 128.26, 133.07, 148.72, 157.37 ppm.

***N*,*N*,4′-Trimethylbiphenyl-3-amine:**[23] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.37 (s, 3 H), 2.98 (s, 6 H), 6.80 (d, $J$ = 8.8 Hz, 2 H), 7.20 (d, $J$ = 7.9 Hz, 2 H), 7.45 (d, $J$ = 8.0 Hz, 2 H), 7.48 (d, $J$ = 8.8 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.16, 40.73, 112.97, 126.28, 127.63, 129.45, 129.50, 135.71, 138.50, 149.93 ppm.

**4′-Fluoro-*N*,*N*-dimethylbiphenyl-4-amine:**[24] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.98 (s, 6 H), 6.79 (d, $J$ = 8.8 Hz, 2 H), 7.07 (t, $J$ = 8.8 Hz, 2 H), 7.40–7.52 (m, 4 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 39.68, 111.93, 114.54 (d, $J$ = 21.4 Hz), 126.70, 126.81 (d, $J$ = 7.8 Hz), 127.45, 136.51 (d, $J$ = 3.1 Hz), 149.05, 160.86 (d, $J$ = 245.4 Hz) ppm.

**4-Fluoro-4′-methoxybiphenyl:**[25] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.84 (s, 3 H), 6.96 (d, $J$ = 8.7 Hz, 2 H), 7.09 (t, $J$ = 8.7 Hz, 2 H), 7.43–7.52 (m, 4 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 55.39, 114.36, 115.63 (d, $J$ = 21.4 Hz), 128.12, 128.31 (d, $J$ = 8.0 Hz), 132.90, 137.07 (d, $J$ = 3.2 Hz), 159.24, 162.21 (d, $J$ = 246.3 Hz) ppm.

***N*,*N*-Dimethyl-4′-(trifluoromethyl)biphenyl-4-amine:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.01 (s, 6 H), 6.80 (d, $J$ = 8.8 Hz, 2 H), 7.52 (d, $J$ = 8.8 Hz, 2 H), 7.61–7.66 (m, 4 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 40.56, 112.77, 124.67 ($J$ = 272.7 Hz), 125.73 ($J$ = 4.0 Hz), 126.34, 127.42, 127.97 ($J$ = 32.3 Hz), 128.01, 144.80, 150.64 ppm.

**4-Methoxy-4′-(trifluoromethyl)biphenyl:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.84 (s, 3 H), 6.99 (d, $J$ = 8.8 Hz, 2 H), 7.53 (d, $J$ = 8.8 Hz, 2 H), 7.61–7.66 (m, 4 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 55.48, 114.57, 124.54 ($J$ = 272.7 Hz), 125.81 ($J$ = 3.8 Hz), 126.99, 128.48, 128.82 ($J$ = 32.3 Hz), 132.29, 144.43, 160.00 ppm.

**(4′-Methylbiphenyl-4-yl)(phenyl)methanone:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.41 (s, 3 H), 7.28 (d, $J$ = 7.9 Hz, 2 H), 7.49 (t, $J$ = 7.4 Hz, 2 H), 7.55 (d, $J$ = 8.4 Hz, 2 H), 7.57–7.61 (m, 1 H), 7.68 (d, $J$ = 8.4 Hz, 2 H), 7.81–7.85 (m, 2 H), 7.88 (d, $J$ = 8.4 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.30, 126.83, 127.26, 128.42, 129.83, 130.11, 130.87, 132.45, 136.07, 137.19, 137.97, 138.31, 145.32, 196.49 ppm.

**4′-Methylbiphenyl-4-carbonitrile:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.42 (s, 3 H), 7.29 (d, $J$ = 8.0 Hz, 2 H), 7.49 (d, $J$ = 8.0 Hz, 2 H), 7.67 (d, $J$ = 8.6 Hz, 2 H), 7.71 (d, $J$ = 8.6 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.33, 110.70, 119.19, 127.21, 127.62, 129.98, 132.71, 136.43, 138.90, 145.76 ppm.

**2′-Methylbiphenyl-4-carbonitrile:**[26] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.26 (s, 3 H), 7.19 (d, $J$ = 7.3 Hz, 1 H), 7.25–7.34 (m, 3 H), 7.44 (d, $J$ = 8.4 Hz, 2 H), 7.71 (d, $J$ = 8.4 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 20.45, 110.84, 119.10, 126.23, 128.42, 129.55, 130.12, 130.79, 132.10, 135.17, 140.12, 146.91 ppm.

**4′-(Trifluoromethyl)biphenyl-4-carbonitrile:**[27] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.69–7.71 (m, 4 H), 7.74–7.79 (m, 4 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 112.11, 118.73, 124.13 ($J$ = 273.7 Hz), 126.22 ($J$ = 3.7 Hz), 127.77, 128.10, 130.82 ($J$ = 32.9 Hz), 132.93, 142.79, 144.27 ppm.

**Methyl 4′-(Trifluoromethyl)biphenyl-4-carboxylate:**[28] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.86 (s, 3 H), 7.57 (d, $J$ = 8.4 Hz, 2 H), 7.63 (s, 4 H), 8.05 (d, $J$ = 8.4 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 51.35, 123.28 ($J$ = 272.7 Hz), 125.00 ($J$ = 3.0 Hz), 126.37, 126.74, 128.95, 129.30 ($J$ = 33.3 Hz), 142.65, 143.17, 165.87 ppm.

**1-*p*-Tolylnaphthalene:**[29] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.45 (s, 3 H), 7.29 (d, $J$ = 7.8 Hz, 2 H), 7.37–7.53 (m, 6 H), 7.83 (d, $J$ = 8.1 Hz, 1 H), 7.90 (t, $J$ = 8.1 Hz, 2 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.38, 125.54, 125.84, 126.06, 126.24, 127.02, 127.57, 128.39, 129.11, 130.09, 131.86, 133.96, 137.05, 137.96, 140.39 ppm.

***N*,*N*-Dimethyl-4-(naphthalen-1-yl)aniline:**[29] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.99 (s, 6 H), 6.83 (d, $J$ = 8.4 Hz, 2 H), 7.37–7.49 (m, 6 H), 7.78 (d, $J$ = 8.0 Hz, 1 H), 7.86 (d, $J$ = 8.0 Hz, 1 H), 8.02 (d, $J$ = 8.4 Hz, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 40.72, 112.38, 125.61, 125.70, 125.82, 126.46, 126.87, 126.96, 128.33, 128.87, 130.93, 132.09, 134.06, 140.62, 149.91 ppm.

**1-(4-Methoxyphenyl)naphthalene:**[29] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.86 (s, 3 H), 7.01 (d, $J$ = 8.7 Hz, 2 H), 7.38–7.42 (m, 4 H), 7.44–7.50 (m, 2 H), 7.81 (d, $J$ = 8.2 Hz, 1 H), 7.88 (d, $J$ = 7.6 Hz, 1 H), 7.92 (d, $J$ = 8.4 Hz, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 55.46, 113.86, 125.54, 125.83, 126.05, 126.20, 127.04, 127.46, 128.39, 131.24, 131.98, 133.26, 133.99, 140.05, 159.09 ppm.

**2-*p*-Tolylnaphthalene:**[16] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.43 (s, 3 H), 7.26–7.34 (m, 2 H), 7.46–7.51 (m, 2 H), 7.59–7.67 (m, 2 H), 7.72–7.76 (m, 1 H), 7.82–7.94 (m, 3 H), 8.03 (s, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.28, 125.57, 125.70, 125.91, 126.37, 127.40, 127.77, 128.28, 128.49, 129.74, 132.65, 133.87, 137.30, 138.37, 138.63 ppm.

***N*,*N*-Dimethyl-4-(naphthalen-2-yl)aniline:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.01 (s, 6 H), 6.84 (d, $J$ = 8.8 Hz, 2 H), 7.39–7.49 (m, 2 H), 7.64 (d, $J$ = 8.8 Hz, 2 H), 7.73 (dd, $J$ = 1.8, 8.5 Hz, 1 H), 7.80–7.89 (m, 3 H), 7.97 (s, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 40.73, 113.00, 124.32, 125.38, 125.46, 126.21, 127.73, 128.08, 128.11, 128.33, 129.15, 132.20, 134.04, 138.70, 150.20 ppm.

**2-*o*-Tolylnaphthalene:**[30] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.31 (s, 3 H), 7.24–7.35 (m, 4 H), 7.45–7.53 (m, 3 H), 7.77 (s, 1 H), 7.83–7.90 (m, 3 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 20.68, 125.97, 125.99, 126.30, 127.52, 127.64, 127.82, 127.88, 127.93, 128.15, 130.15, 130.51, 132.42, 133.46, 135.72, 139.69, 142.00 ppm.

**2-(4-Methoxyphenyl)naphthalene:**[10c] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.85 (s, 3 H), 7.01 (d, $J$ = 8.8 Hz, 2 H), 7.42–7.50 (m, 2 H), 7.65 (d, $J$ = 8.8 Hz, 2 H), 7.70 (dd, $J$ = 1.8, 8.6 Hz, 1 H), 7.81–7.90 (m, 3 H), 7.97 (s, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 55.50, 114.46, 125.16, 125.57, 125.78, 126.36, 127.76, 128.19, 128.48, 128.56, 132.46, 133.76, 133.90, 138.29, 159.39 ppm.

**2-*p*-Tolylpyridine:**[16] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 2.38 (s, 3 H), 7.11–7.19 (m, 1 H), 7.26 (d, $J$ = 8.0 Hz, 2 H), 7.64–7.70 (m, 2 H), 7.89 (d, $J$ = 8.1 Hz, 2 H), 8.66 (d, $J$ = 4.8 Hz, 1 H) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 21.16, 120.26, 121.83, 126.84, 129.53, 136.69, 138.97, 149.65, 157.53 ppm.

**2-[4-(Trifluoromethyl)phenyl]pyridine:**[29] $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.27–7.31 (m, 1 H), 7.70–7.81 (m, 4 H), 8.11 (d, $J$ = 8.2 Hz, 2 H), 8.72 (d, $J$ = 4.6 Hz, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 120.96, 123.07, 124.34 ($J$ = 273.2 Hz), 125.79 ($J$ = 3.8 Hz), 127.31, 130.91 ($J$ = 33.3 Hz), 137.09, 142.81, 150.05, 155.98 ppm.

**8-*p*-Tolylquinoline:**[31] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.42 (s, 3 H), 7.30 (d, $J$ = 7.8 Hz, 2 H), 7.34–7.38 (m, 1 H), 7.54–7.60 (m, 3 H), 7.70 (dd, $J$ = 1.5, 7.1 Hz, 1 H), 7.77 (dd, $J$ = 1.4, 8.1 Hz, 1 H), 8.15 (dd, $J$ = 1.8, 8.3 Hz, 1 H), 8.93 (dd, $J$ = 1.8, 4.2 Hz, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 21.38, 121.00, 126.34, 127.36, 128.82, 128.85, 130.16, 130.56, 136.26, 136.72, 137.11, 141.02, 146.26, 150.27 ppm.

**8-[4-(Trifluoromethyl)phenyl]quinoline:**[31] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.43 (dd, $J$ = 4.2, 8.3 Hz, 1 H), 7.59–7.63 (m, 1 H), 7.71–7.82 (m, 5 H), 7.86 (dd, $J$ = 1.4, 8.1 Hz, 1 H), 8.21 (dd, $J$ = 1.8, 8.3 Hz, 1 H), 8.94 (dd, $J$ = 1.8, 4.2 Hz, 1 H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 121.39, 124.57 ($J$ = 272.7 Hz), 125.02 ($J$ = 3.8 Hz), 126.39, 128.49, 128.87, 129.42 ($J$ = 32.3 Hz), 130.51, 131.05, 136.49, 139.50, 143.34, 145.87, 150.60 ppm.

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