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Palladium-catalyzed direct C-H arylation of ferrocenecarboxamides with aryl halides

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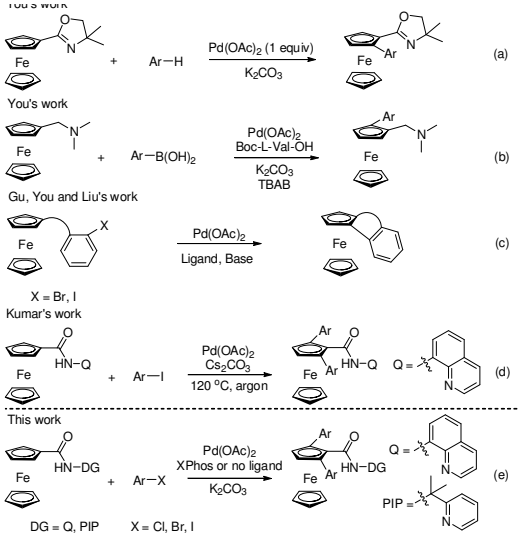
A simple and facile protocol for palladium-catalyzed *ortho*-arylation of ferrocenecarboxamides with aryl halides was developed with the assistance of the bidentate directing group. The substrate scope could be extended to aryl iodides, bromides and even chlorides, as well as heterocyclic halides, affording diarylated products in moderate to good yields.

Introduction

Ferrocenyl derivatives have wide applications in organic synthesis,[1] materials science,[2] medicinal chemistry,[3] and biological science[4] due to their unique structures, chemical and thermal stabilities, and redox properties. Furthermore, some of the *ortho*-difunctionalized ferrocene can also serve as excellent planar chiral ligands in efficient enantioselective catalysis.[5] Therefore, many efforts have been devoted to the development of economical and environment-friendly routes to *ortho*-functionalized ferrocenyl derivatives.[6]

During the past decades, transition metal-catalyzed C-H functionalization has become a robust and facile tool in organic synthesis and a series of transformations from C-H to C-C and C-heteroatom bonds have been demonstrated. [7]- [9] In particular, the pioneering work of C-H arylation of ferrocenes belongs to You and co-workers, who developed a protocol of direct arylation of simple arenes with ferrocenyl oxazolines in 2007 (Scheme 1a), but this reaction employed a stoichiometric loading of the palladium salt (1 equiv).[6b] Subsequently, You's group developed another successful palladium-catalyzed C-H arylation of N,N-dimethylaminomethyl ferrocene with arylboronic acids (Scheme 1b), [6g] albeit some of functionalized arylboronic acids are not very cheap and their preparation needs a multi-step synthesis. After that, palladium-catalyzed intramolecular C-H arylation of ferrocenyl derivatives was reported by Gu, [6i] You[6j] and Liu[6l] respectively (Scheme 1c), although the starting materials needed to be prefunctionalized.



Scheme 1 Transition Metal-Promoted C-H Arylation of Ferrocenyl derivatives.

Just recently, Kumar's group reported palladium-catalyzed C-H arylation of N-(quinolin-8-yl)ferrocenecarboxamide with aryl iodides (Scheme 1d). [6o] Nevertheless, aryl iodides are usually expensive, not very easily available. Aryl bromides and chlorides are much cheaper and commercially available, and therefore, using them as the aryl sources would be the promising choice. However, the relative reports remain rare until now (on the ferrocenyl ring). Our research interest is to demonstrate a simple and easy protocol for *ortho*-arylation on the ferrocenyl ring. And we envisioned developing the catalytic intermolecular C-H arylation of ferrocenecarboxamides with aryl bromides and even some chlorides (Scheme 1e).

Results and discussion

We commenced our investigation by the reaction of ferrocenecarboxamide [DG= quinolin-8-ylamino moiety (Q-

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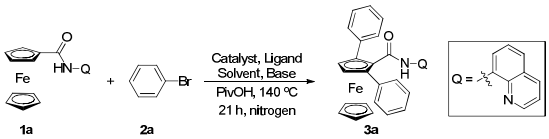
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Table 1 Optimization of the reaction conditions[a]

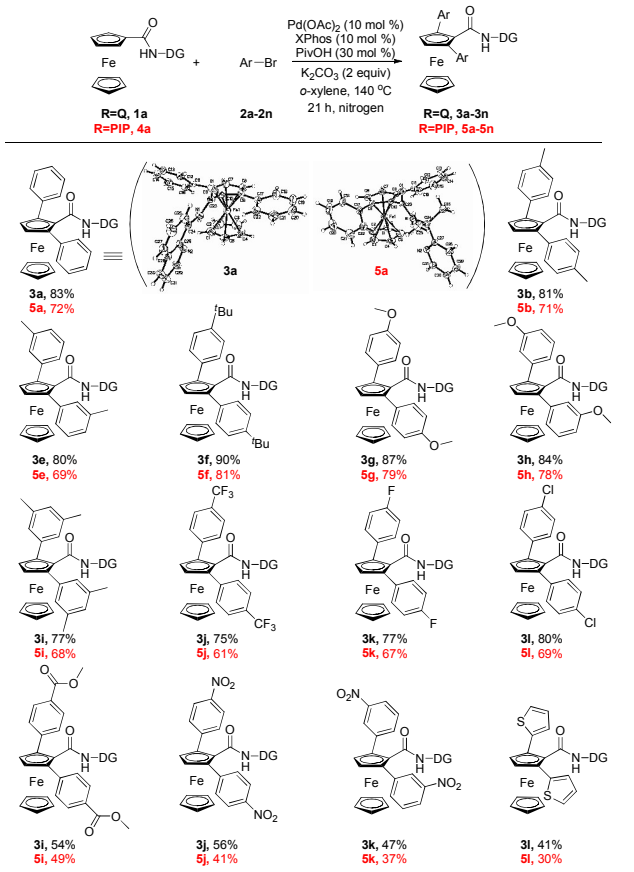


Entry	Solvent	Base	Ligand	Yield(%)[b]
1	toluene	K_2CO_3	PPh_3	8
2	*o*-xylene	K_2CO_3	PPh_3	30
3	*o*-xylene	Na_2CO_3	PPh_3	20
4	*o*-xylene	Cs_2CO_3	PPh_3	Trace
5	*o*-xylene	K_3PO_4	PPh_3	18
6	*o*-xylene	$KHCO_3$	PPh_3	Trace
7	*o*-xylene	K_2CO_3	PPy_3	23
8	*o*-xylene	K_2CO_3	DPPF	49
9	*o*-xylene	K_2CO_3	RuPhos	61
10	*o*-xylene	K_2CO_3	XPhos	83
11	*o*-xylene	K_2CO_3	XantPhos	42
12	*o*-xylene	K_2CO_3	^{t}BuXPhos	60
13[c]	*o*-xylene	K_2CO_3	XPhos	72
14[d]	*o*-xylene	K_2CO_3	XPhos	82
15[e]	*o*-xylene	K_2CO_3	XPhos	51

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Catalyst (0.02 mmol), Ligand (0.02 mmol), PivOH (0.06 mmol), Base (0.4 mmol) and Solvent (1.0 mL) under nitrogen at 140 °C for 21 h unless otherwise noted. [b] Isolated yield based on **1a**. [c] Without PivOH. [d] At 150 °C. [e] At 130 °C.

amino)] [10] (**1a**) with bromobenzene (**2a**) in toluene in the presence of $Pd(OAc)_2$ as the model reaction (Table 1), and the desired product **3a** was obtained in 8% yield (Table 1, entry 1). After extensive solvents were screened, and to our delight, the desired product **3a** was obtained in 30% yield using *o*-xylene as the solvent (Table 1, entry 2); other solvents such as 1,2-dichloroethane, dioxane, acetonitrile and DMF could not facilitate the reaction (see Supporting Information (SI)). A thorough screening of bases revealed that K_2CO_3 was proved to be the most effective base (Table 1, entry 2 *vs.* entries 3-6). When the catalyst was switched to $PdCl_2$, Pd_2dba_3, $Pd(CF_3COO)_2$, $Ni(OAc)_2$ and $[RuCl_2(cymene)]_2$, they could not match the efficacy of $Pd(OAc)_2$ in our reaction, and the reaction could not take place at all without catalyst (see SI). Moreover, the results demonstrated that the choice of a ligand was also crucial, tricyclohexyl phosphine (PPy_3), 1,1'-bis(diphenylphosphino)ferrocene (DPPF), 2-dicyclohexylphosphino-2',6'-diisopropoxy-1,1'-biphenyl (RuPhos), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos), 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (XantPhos) and 2-di-*tert*-butylphosphino-2',4',6'-trisopropyl-1,1'-biphenyl (^{t}BuXPhos) were also tested in this transformation, in which XPhos gave the best result affording the desired product **3a** in 83% yield (Table 1, entries 7-12). PivOH played an important role in the reaction,[10] as the pivalate anion might be a key component in C-H bond cleaving, which could lower the energy of C-H bond cleavage and act as a catalytic proton shuttle[10b]. However, other additives such as AcOH, AcOK, and benzoic acid showed the lower effect (see SI). And the absence of the PivOH resulted in the decrease of the yield of **3a** (Table 1, entry 13). When the reaction temperature

Table 2 Substrate scope of aryl bromides.[a, b]

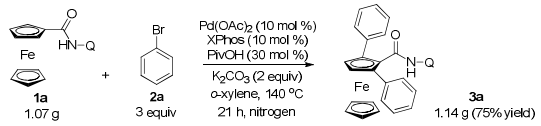


[a] Reaction conditions: **1a** or **4a** (0.2 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (0.02 mmol), XPhos (0.02 mmol), PivOH (0.06 mmol), K_2CO_3 (0.4 mmol) and *o*-xylene (1.0 mL) under nitrogen at 140 °C for 21 h. [b] Isolated yield based on **1a** or **4a**.

was increased to 150 °C or decreased to 130 °C, no much better results were observed and the coupling products were afforded in 82% and 51%, respectively (Table 1, entries 14 and 15). In addition, it is worthwhile to mention that the same type of product **5a** could be obtained in 72% yield when we use the 2-(pyridine-2-yl)isopropylamino (PIP-amino) [12] moiety as a directing group.

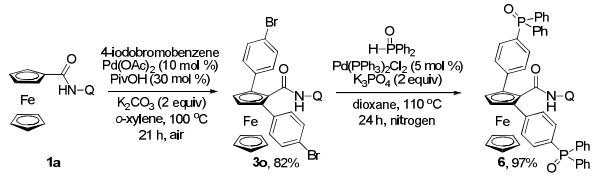
With the optimized reaction conditions in hand, the scope of aryl bromides was examined and the results were summarized in Table 2. Generally, a variety of aryl bromides bearing electron-donating and electron-withdrawing groups are well tolerated, generating the desired products in moderate to high yields. Whether the directing group is Q-amino or PIP-amino, electron-donating substituents (**1b-g**, R = Me, OMe, and ^{t}Bu) resulted in higher yields than those of the electron-withdrawing substituents (**1h-m**, R= CF_3, F, Cl, COOMe, and NO_2). Moreover, a heterocyclic bromide (such as 2-bromothiophene) could also participate in the coupling, producing the target products in moderate yields (**3n** and **5n**). Overall, the two bidentate directing groups Q-amino and PIP-

amino could work well in this reaction and the results of quinolin-8-ylamino moiety as the directing group are a little better than those of 2-(pyridine-2-yl)isopropylamino group. The molecular structures of **3a**[11] and **5a**[12] were unambiguously confirmed by single crystal X-ray diffraction study.



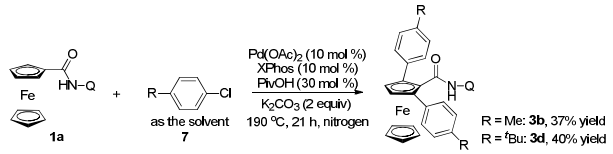
Scheme 2. The gram scale reaction.

To demonstrate the synthetic value of this protocol, a gram-scale reaction of **1a** with **2a** was performed (Scheme 2). This reaction could generate the desired product in an isolated yield of 75%.



Scheme 3. Further functionalization of ferrocenyl derivatives.

Moreover, 4-iodobromobenzene could also participate in the coupling with **1a**, generating the desired product **3o** in 82% yield (Scheme 3). This reaction did not involve the phosphine ligand (XPhos) and high temperature (only at 100 °C). It could also work well in air, which is easier to operate than that of Kumar's protocol for aryl iodides (at 120 °C under argon).[6o] Furthermore, the product **3o** was easily converted into the interesting more complicated compound **6** in 97% yield.



Scheme 4. The arylation of ferrocenecarboxamides with aryl chlorides.

Finally, we also explored the reaction of aryl chlorides shown in Scheme 4. Both 4-chlorotoluene and 1-(*tert*-butyl)-4-chlorobenzene were well tolerated in this reaction, leading to the desired products in moderate yields (**3b** and **3d**).

Conclusions

In conclusion, we have developed a Pd(II)-catalyzed intermolecular *ortho* C-H arylation of ferrocenecarboxamides with aryl halides using the bidentate directing groups, i.e., quinolin-8-ylamino and 2-(pyridine-2-yl)isopropylamino groups. The protocol exhibites excellent functional group tolerance for both electron-rich (e.g., Me, OMe and ^{t}Bu) and electron-poor (e.g., CF_3, F, Cl, COOMe and NO_2) groups. Moreover, gram-scale reaction of this arylation is also successfully realized, which demonstrates its potential applicable value in organic synthesis. In addition, some aryl chlorides could also participate in the coupling, affording the desired products in moderate yields.

Experimental

General Information

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High resolution mass spectra were ensured on a MALDI-FTMS. All solvents were used directly without further purification. Dichloromethane, ethyl acetate, and hexane were used for column chromatography. Chemicals were obtained from commercial sources and used as-received without further purification unless otherwise noted.

Typical Procedure for the Products

a) For aryl bromides: A 25 mL Schlenk tube was equipped with a magnetic stir bar and charged with **1a** or **4a** (0.2 mmol), **2a-2n** (0.6 mmol, 3 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol %), XPhos (9.5 mg, 0.02 mmol, 10 mol %), PivOH (6.2 mg, 0.06 mmol, 30 mol %) in *o*-xylene (1.0 mL). The resulting mixture was heated under nitrogen at 140 °C for 21 h, and cooled to room temperature. Upon completion, CH_2Cl_2 (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane-EtOAc as an eluent to afford the pure product **3** or **5**.

2,5-diphenyl-N-(quinolin-8-yl)ferrocenecarboxamide (3a): Orange solid (84 mg, 83%); mp 184–185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.87 (d, J = 7.5 Hz, 1H), 8.57 (d, J = 3.7 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 7.5 Hz, 4H), 7.56 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.36 (dd, J = 6.3 Hz, J = 2.2 Hz, 1H), 7.22 (t, J = 7.3 Hz, 4H), 7.15 (t, J = 7.2 Hz, 2H), 4.79 (s, 2H), 4.44 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 147.8, 138.5, 136.8, 136.0, 134.7, 128.8, 128.0, 127.8, 127.4, 126.7, 121.4, 116.1, 88.6, 82.2, 72.7, 69.3; HRMS (ESI+) calcd for $C_{32}H_{24}FeN_2O$ $[M+H]^+$: 509.1311, found: 509.1313.

N-(quinolin-8-yl)-2,5-di-*p*-tolylferrocenecarboxamide (3b): Orange solid (87 mg, 81%); mp 149–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.89 (dd, J = 4.2 Hz, J = 3.3 Hz, 1H), 8.59 (dd, J = 2.5 Hz, J = 2.2 Hz, 1H), 8.11 (dd, J = 4.9 Hz, J = 3.5 Hz, 1H), 7.59–7.49 (m, 6H), 7.36 (dd, J = 6.3 Hz, J = 2.1 Hz, 1H), 7.02 (d, J = 8.0 Hz, 4H), 4.78 (s, 2H), 4.42 (s, 5H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 147.7, 138.6, 136.3, 136.0, 134.8, 133.8, 128.7, 128.7, 127.8, 127.4, 121.3, 116.2, 88.5, 82.1, 72.5, 69.0, 21.0; HRMS (ESI+) calcd for $C_{34}H_{28}FeN_2O$ $[M+H]^+$: 537.1624, found: 537.1629.

N-(quinolin-8-yl)-2,5-di-*m*-tolylferrocenecarboxamide (3c): Orange solid (86 mg, 80%); mp 209–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (s, 1H), 8.85 (d, J = 7.5 Hz, 1H), 8.58 (dd, J = 2.8 Hz, J = 1.2 Hz, 1H), 8.11 (dd, J = 5.0 Hz, J = 3.5 Hz, 1H), 7.56 (t, J = 8.1 Hz, 1H), 7.51–7.47 (m, 3H), 7.42 (s, 2H), 7.37 (dd, J = 6.3 Hz, J = 2.1 Hz, 1H), 7.11 (t, J = 7.6 Hz, 2H), 6.95 (d, J = 7.5 Hz, 2H), 4.75 (s, 2H), 4.42 (s, 5H), 2.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 147.7, 138.5, 137.3, 136.7, 136.0, 134.9, 129.6, 127.8, 127.5, 127.4, 126.2, 121.3, 121.3, 116.1, 88.7, 82.4, 72.5, 69.2, 21.3; HRMS (ESI+) calcd for $C_{34}H_{28}FeN_2O$ $[M+H]^+$: 537.1624, found: 537.1628.

2,5-bis(4-(*tert*-butyl)phenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3d): Yellow solid (111 mg, 90%); mp 279–282 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.87 (d, J = 7.4 Hz, 1H), 8.52 (d, J = 4.5 Hz, 1H), 8.06 (dd, J = 8.4 Hz, 1H), 7.59–7.47 (m, 6H), 7.33 (dd, J = 6.3 Hz, J = 2.1 Hz, 1H), 7.21 (d, J = 8.0 Hz, 4H), 4.76 (s, 2H), 4.42 (s, 5H), 1.23 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 149.5, 147.6, 138.5, 135.9, 134.9, 133.7, 128.6, 127.7, 127.4, 121.2, 121.1, 116.0, 88.7, 81.5, 72.6, 69.2, 34.4, 31.2; HRMS (ESI+) calcd for $C_{40}H_{40}FeN_2O$ $[M+H]^+$: 621.2563, found: 621.2569.

2,5-bis(4-methoxyphenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3e): Orange solid (99 mg, 87%); mp 180–181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.88 (dd, J = 4.2 Hz, J = 3.3 Hz, 1H), 8.59 (dd, J = 2.8 Hz, J = 1.2 Hz, 1H), 8.11 (dd, J = 5.0 Hz, J = 3.4 Hz, 1H), 7.58–7.48 (m, 6H), 7.36 (dd, J = 6.3 Hz, J = 2.1 Hz, 1H), 6.76 (d, J = 8.4 Hz, 4H), 4.69 (s, 2H), 4.40 (s, 5H), 3.70 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 158.5, 147.7, 138.5, 136.0, 134.8, 129.9, 128.9, 127.8, 127.3, 121.3, 121.3, 116.1, 113.5, 88.4, 81.5, 72.4, 68.8, 55.1; HRMS (ESI+) calcd for $C_{34}H_{28}FeN_2O_3$ $[M+H]^+$: 569.1522, found: 569.1524.

2,5-bis(3-methoxyphenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3f): Orange solid (95 mg, 84%); mp 111–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.90 (s, 1H), 8.88 (dd, J = 4.3 Hz, J = 3.2 Hz, 1H), 8.60 (dd, J = 2.8 Hz, J = 1.2 Hz, 1H), 8.10 (dd, J = 5.0 Hz, J = 3.4 Hz, 1H), 7.57–7.48 (m, 2H), 7.37 (dd, J = 6.3 Hz, J = 2.0 Hz, 1H), 7.25 (d, J = 6.0 Hz, 2H), 7.21 (m, 2H), 7.13 (t, J = 8.2 Hz, 2H), 6.69 (dd, J = 5.1 Hz, J = 3.1 Hz, 2H), 4.78 (s, 2H), 4.44 (s, 5H), 3.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 159.1, 147.8, 138.5, 138.3, 136.1, 134.8, 128.9, 127.8, 127.3, 121.5, 121.4, 121.4, 116.1, 114.0, 112.7, 88.2, 82.9, 72.7, 69.2, 55.0; HRMS (ESI+) calcd for $C_{34}H_{28}FeN_2O_3$ $[M+H]^+$: 569.1522, found: 569.1518.

2,5-bis(3,5-dimethylphenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3g): Orange solid (87 mg, 77%); mp 189–190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.78 (s, 1H), 8.84 (d, J = 7.5 Hz, 1H), 8.60 (dd, J = 2.8 Hz, J = 1.2 Hz, 1H), 8.12 (dd, J = 4.8 Hz, J = 3.4 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.50 (m, 1H), 7.38 (dd, J = 6.3 Hz, J = 2.1 Hz, 1H), 7.26 (s, 4H), 6.77 (s, 2H), 4.73 (s, 2H), 4.44 (s, 5H), 2.18 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 147.7, 138.6, 137.2, 136.6, 135.9, 135.0, 128.5, 127.8, 127.4, 126.9, 121.3, 121.2, 116.0, 88.8, 82.5, 72.6, 69.1, 21.2; HRMS (ESI+) calcd for $C_{36}H_{32}FeN_2O$ $[M+H]^+$: 565.1937, found: 565.1938.

N-(quinolin-8-yl)-2,5-bis(4-(trifluoromethyl)phenyl)ferrocenecarboxamide (3h): Orange solid (97 mg, 75%); mp 168–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.83 (dd, J = 4.2 Hz, J = 2.9 Hz, 1H), 8.51 (dd, J = 2.9 Hz, J = 1.3 Hz, 1H), 8.14 (dd, J = 4.9 Hz, J = 3.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 4H), 7.61–7.53 (m, 2H), 7.47 (d, J = 8.4 Hz, 4H), 7.38 (dd, J = 6.3 Hz, J = 2.1 Hz, 1H), 4.87 (s, 2H), 4.43 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 147.9, 141.0, 138.4, 136.2, 134.3, 129.0, 128.9 (q, $J_{C\text{-}F}$ = 33.1 Hz), 127.9, 127.3, 125.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.0 (q, $J_{C\text{-}F}$ = 272.5 Hz), 121.9, 121.5, 116.3, 87.3, 82.5, 73.1, 70.0; HRMS (ESI+) calcd for $C_{34}H_{22}F_6FeN_2O$ $[M+H]^+$: 645.1059, found: 645.1057.

2,5-bis(4-fluorophenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3i): Yellow solid (84 mg, 77%); mp 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.84 (dd, J = 4.3 Hz, J = 3.1 Hz, 1H), 8.59 (dd, J = 2.8 Hz, J = 1.4 Hz, 1H), 8.13 (dd, J = 4.8 Hz, J = 3.5 Hz, 1H), 7.62–7.59 (m, 4H), 7.56–7.51 (m, 2H), 7.39 (dd, J = 6.2 Hz, J = 2.1 Hz, 1H), 6.92 (t, J = 8.7 Hz, 4H), 4.72 (s, 2H), 4.40 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 161.9 (d, $J_{C\text{-}F}$ = 247.7 Hz), 147.8, 138.4, 136.1, 134.5, 132.6, 132.6, 130.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 127.9, 127.4, 121.6, 121.5, 116.1, 114.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 87.9, 81.8, 72.7, 69.3; HRMS (ESI+) calcd for $C_{32}H_{22}F_2FeN_2O$ $[M+H]^+$: 545.1122, found: 545.1118.

2,5-bis(4-chlorophenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3j): Orange solid (92 mg, 80%); mp 213–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.84 (dd, J = 4.4 Hz, J = 3.0 Hz, 1H), 8.59 (dd, J = 2.9 Hz, J = 1.3 Hz, 1H), 8.13 (dd, J = 4.9 Hz, J = 3.4 Hz, 1H), 7.59–7.52 (m, 6H), 7.39 (dd, J = 6.2 Hz, J = 2.1 Hz, 1H), 7.18 (d, J = 8.0 Hz, 4H), 4.76 (s, 2H), 4.41 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 147.9, 138.4, 136.1, 135.4, 134.4, 132.6, 130.0, 128.2, 127.9, 127.3, 121.7, 121.5, 116.2, 87.5, 82.1, 72.7, 69.4; HRMS (ESI+) calcd for $C_{32}H_{22}Cl_2FeN_2O$ $[M+H]^+$: 577.0531, found: 577.0531.

dimethyl-4,4'-(2-(quinolin-8-ylcarbamoyl)ferrocene-1,3-diyl)dibenzoate (3k): Orange solid (67 mg, 54%); mp 197–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.84 (dd, J = 4.4 Hz, J = 3.0 Hz, 1H), 8.55 (dd, J = 2.5 Hz, J = 2.2 Hz, 1H), 8.12 (dd, J = 4.9 Hz, J = 3.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 4H), 7.68 (d, J = 8.4 Hz, 4H), 7.59–7.51 (m, 2H), 7.36 (dd, J = 6.2 Hz, J = 2.1 Hz, 1H), 4.88 (s, 2H), 4.42 (s, 5H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 166.8, 147.9, 138.4, 136.2, 134.4, 129.3, 128.5, 128.4, 127.9, 127.4, 121.8, 121.5, 116. 3, 87.2, 83.1, 73.0, 69.9, 51.9; HRMS (ESI+) calcd for $C_{36}H_{28}FeN_2O_5$ $[M+H]^+$: 625.1420, found: 625.1421.

2,5-bis(4-nitrophenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3l): Dark red solid (67 mg, 56%); mp 223–226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 8.83 (dd, J = 4.4 Hz, J = 2.5 Hz, 1H), 8.55 (dd, J = 2.9 Hz, J = 1.3 Hz, 1H), 8.15 (dd, J = 4.9 Hz, J = 3.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 4H), 7.78 (d, J = 8.4 Hz, 4H), 7.62–7.55 (m, 2H), 7.39 (dd, J = 6.2 Hz, J = 2.1 Hz, 1H), 4.97 (s, 2H), 4.46 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 148.0, 146.5, 144.7, 138.3, 136.5, 134.0, 129.2, 128.0, 127.4, 123.4, 122.3, 121.7, 116.4, 86.4, 83.4, 73.4, 70.6; HRMS (ESI+) calcd for $C_{32}H_{22}FeN_4O_5$ $[M+H]^+$: 599.1012, found: 599.1009.

2,5-bis(3-nitrophenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3m): Dark red solid (56 mg, 47%); mp 165–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.68 (s, 1H), 8.79 (dd, J = 4.4 Hz, J = 2.8 Hz, 1H), 8.54 (t, J = 2.0 Hz, 1H), 8.51 (dd, J = 2.9 Hz, J = 1.3 Hz, 1H),

8.13 (dd, *J* = 5.0 Hz, *J* = 3.4 Hz, 1H), 8.02–8.00 (m, 2H), 7.95–7.92 (m, 2H), 7.59–7.51 (m, 2H), 7.39–7.33 (m, 3H), 4.94 (s, 2H), 4.48 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 148.1, 148.0, 138.9, 138.3, 136.3, 134.7, 134.0, 129.0, 127.8, 127.4, 123.6, 122.0, 121.8, 121.6, 116.4, 86.8, 82.2, 73.1, 70.3; HRMS (ESI+) calcd for $C_{32}H_{22}FeN_4O_5$ $[M+H]^+$: 599.1012, found: 599.1013.

N-(quinolin-8-yl)-2,5-di(thiophen-2-yl)ferrocenecarboxamide (3n): Orange solid (43 mg, 41%); mp 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (s, 1H), 8.95 (dd, *J* = 4.3 Hz, *J* = 3.2 Hz, 1H), 8.70 (dd, *J* = 2.8 Hz, *J* = 1.3 Hz, 1H), 8.16 (dd, *J* = 4.8 Hz, *J* = 3.5 Hz, 1H), 7.62–7.53 (m, 2H), 7.42 (dd, *J* = 6.2 Hz, *J* = 2.1 Hz, 1H), 7.22 (d, *J* = 3.5 Hz, 2H), 7.14 (d, *J* = 5.1 Hz, 2H), 6.82 (dd, *J* = 4.4 Hz, *J* = 0.7 Hz, 2H), 4.79 (s, 2H), 4.51 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.0, 139.7, 138.6, 136.2, 134.8, 128.0, 127.5, 127.2, 126.0, 124.5, 121.7, 121.6, 116.4, 82.8, 81.2, 73.3, 69.4; HRMS (ESI+) calcd for $C_{28}H_{20}FeN_2OS_2$ $[M+H]^+$: 521.0439, found: 521.0435.

2,5-bis(4-bromophenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (3o): Orange solid (109 mg, 82%); mp 229–230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 8.82 (dd, *J* = 4.4 Hz, *J* = 2.8 Hz, 1H), 8.59 (dd, *J* = 2.9 Hz, *J* = 1.3 Hz, 1H), 8.14 (dd, *J* = 4.9 Hz, *J* = 3.4 Hz, 1H), 7.59–7.48 (m, 6H), 7.40 (dd, *J* = 6.2 Hz, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 4H), 4.74 (s, 2H), 4.40 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 148.0, 138.5, 136.2, 135.9, 134.5, 131.2, 130.4, 128.0, 127.4, 121.8, 121.6, 120.8, 116.3, 87.6, 82.1, 72.9, 69.5; HRMS (ESI+) calcd for $C_{32}H_{22}Br_2FeN_2O$ $[M+H]^+$: 664.9521, found: 664.9524.

2,5-diphenyl-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5a): Yellow solid (72 mg, 72%); mp 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.36 (d, *J* = 3.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 5H), 7.32–7.11 (m, 8H), 4.66 (s, 2H), 4.29 (s, 5H), 1.77 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 164.4, 147.2, 137.3, 136.9, 128.8, 127.8, 126.6, 121.7, 119.4, 87.6, 85.0, 72.4, 68.1, 57.1, 26.9; HRMS (ESI+) calcd for $C_{31}H_{28}FeN_2O$ $[M+H]^+$: 501.1624, found: 501.1624.

N-(2-(pyridin-2-yl)propan-2-yl)-2,5-di-*p*-tolylferrocenecarboxamide (5b): Yellow solid (74 mg, 70%); mp 179–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.41–8.39 (m, 1H), 7.69–7.64 (m, 1H), 7.55 (d, *J* = 8.2 Hz, 4H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.16–7.13 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 4H), 4.63 (s, 2H), 4.30 (s, 5H), 2.31 (s, 6H), 1.77 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 164.5, 147.2, 136.9, 136.1, 134.2, 128.6, 128.5, 121.6, 119.4, 87.5, 84.7, 72.2, 67.8, 57.1, 26.9, 21.1; HRMS (ESI+) calcd for $C_{33}H_{32}FeN_2O$ $[M+H]^+$: 529.1937, found: 529.1936.

N-(2-(pyridin-2-yl)propan-2-yl)-2,5-di-*m*-tolylferrocenecarboxamide (5c): Orange solid (73 mg, 69%); mp 141–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.41 (d, *J* = 4.6 Hz, 1H), 7.69–7.65 (m, 1H), 7.48 (s, 1H), 7.46 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.18–7.13 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 2H), 4.65 (s, 2H), 4.30 (s, 5H), 2.31 (s, 6H), 1.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 164.5, 147.2, 137.2, 137.1, 137.0, 129.4, 127.7, 127.3, 125.9, 121.7, 119.4, 87.6, 85.1, 72.3, 68.0, 57.2, 26.9, 21.4; HRMS (ESI+) calcd for $C_{33}H_{32}FeN_2O$ $[M+H]^+$: 529.1937, found: 529.1938.

2,5-bis(4-(*tert*-butyl)phenyl)-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5d): Orange solid (87 mg, 71%); mp 151–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.39–8.37 (m, 1H), 7.66–7.62 (m, 1H), 7.58–7.55 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.29–7.27 (m, 4H), 7.14–7.11 (m, 1H), 4.63 (s, 2H), 4.29 (s, 5H), 1.79 (s, 6H), 1.30 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 164.5, 149.3, 147.2, 136.8, 134.1, 128.6, 124.6, 121.5, 119.3, 87.8, 84.0, 72.3, 68.0, 57.1, 34.4, 31.3, 26.9; HRMS (ESI+) calcd for $C_{39}H_{44}FeN_2O$ $[M+H]^+$: 613.2876, found: 613.2880.

2,5-bis(4-methoxyphenyl)-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5e): Orange solid (88 mg, 79%); mp 203–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.40–8.39 (m, 1H), 7.68–7.64 (m, 1H), 7.58–7.54 (m, 4H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.16–7.12 (m, 1H), 6.82–6.78 (m, 4H), 4.58 (s, 2H), 4.37 (s, 5H), 3.78 (s, 6H), 1.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 164.5, 158.4, 147.2, 136.9, 129.8, 121.6, 119.4, 113.3, 87.4, 84.3, 72.1, 67.6, 57.1, 55.2, 27.0; HRMS (ESI+) calcd for $C_{33}H_{32}FeN_2O_3$ $[M+H]^+$: 561.1836, found: 561.1830.

2,5-bis(3-methoxyphenyl)-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5f): Orange solid (87 mg, 78%); mp 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.41 (d, *J* = 4.4 Hz, 1H), 7.68–7.64 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.28 (s, 1H), 7.26 (s, 3H), 7.21–7.13 (m, 3H), 6.79–6.76 (m, 2H), 4.67 (s, 2H), 4.34 (s, 5H), 3.79 (s, 6H), 1.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 164.3, 159.0, 147.1, 138.6, 136.9, 128.7, 121.6, 121.4, 119.3, 114.4, 112.3, 87.5, 85.4, 72.4, 68.1, 57.1, 55.1, 26.9; HRMS (ESI+) calcd for $C_{33}H_{32}FeN_2O_3$ $[M+H]^+$: 561.1836, found: 561.1836.

2,5-bis(3,5-dimethylphenyl)-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5g): Orange solid (76 mg, 68%); mp 162–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.45–7.43 (m, 1H), 7.71–7.66 (m, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.29 (s, 4H), 7.18–7.15 (m, 1H), 6.86 (s, 2H), 4.64 (s, 2H), 4.33 (s, 5H), 2.30 (s, 12H), 1.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 164.6, 147.1, 137.1, 137.0, 137.0, 128.3, 126.6, 121.7, 119.3, 87.5, 85.3, 72.2, 67.8, 57.2, 26.9, 21.2; HRMS (ESI+) calcd for $C_{35}H_{36}FeN_2O$ $[M+H]^+$: 557.2250, found: 557.2251.

N-(2-(pyridin-2-yl)propan-2-yl)-2,5-bis(4-(trifluoromethyl)phenyl)ferrocenecarboxamide (5h): Orange solid (77 mg, 61%); mp 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.34–8.33 (m, 1H), 7.75 (d, *J* = 8.1 Hz, 4H), 7.72–7.68 (m, 1H), 7.51 (d, *J* = 8.2 Hz, 4H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.18–7.15 (m, 1H), 4.76 (s, 2H), 4.32 (s, 5H), 1.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 164.0, 147.1, 141.5, 137.2, 128.8, 128.6 (q, $J_{C\text{-}F}$ = 31.1 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.3 (q, $J_{C\text{-}F}$ = 272.0 Hz), 122.0, 119.4, 86.2, 85.4, 72.7, 68.9, 57.2, 26.9; HRMS (ESI+) calcd for $C_{33}H_{26}F_6FeN_2O$ $[M+H]^+$: 637.1372, found: 637.1372.

2,5-bis(4-fluorophenyl)-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5i): Yellow solid (72 mg, 67%); mp 177–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.38–8.37 (m, 1H), 7.71–7.66 (m, 1H), 7.62–7.57 (m, 4H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.18–7.14 (m, 1H), 6.98–6.92 (m, 4H), 4.61 (s, 2H), 4.29 (s, 5H), 1.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 164.2, 161.7 (d, $J_{C\text{-}F}$ = 246.6 Hz), 147.1, 137.1, 133.1, 133.1, 130.2 (d, $J_{C\text{-}F}$ = 8.0 Hz), 121.8, 119.4, 114.7 (d, $J_{C\text{-}F}$ = 21.3 Hz),

86.9, 84.7, 72.3, 68.1, 57.1, 26.9; HRMS (ESI+) calcd for $C_{31}H_{26}F_2FeN_2O$ $[M+H]^+$: 537.1436, found: 537.1440.

2,5-bis(4-chlorophenyl)-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5j): Orange solid (78 mg, 69%); mp 169–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.38 (d, J = 4.4 Hz, 1H), 7.71–7.68 (m, 1H), 7.55 (d, J = 8.5 Hz, 4H), 7.35 (d, J = 8.2 Hz, 1H), 7.22 (d, J = 8.5 Hz, 4H), 7.17 (dd, J = 6.0 Hz, J = 0.9 Hz, 1H), 4.64 (s, 2H), 4.28 (s, 5H), 1.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 164.1, 147.1, 137.1, 135.9, 132.3, 129.9, 128.0, 121.9, 119.4, 86.4, 85.0, 72.5, 68.2, 57.2, 26.9; HRMS (ESI+) calcd for $C_{31}H_{26}Cl_2FeN_2O$ $[M+H]^+$: 569.0845, found: 569.0850.

dimethyl-4,4'-(2-(2-(pyridin-2-yl)propan-2-ylcarbamoyl)ferrocene-1,3-diyl)dibenzoate (5k): Orange solid (60 mg, 49%); mp 157–159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.35 (d, J = 4.2 Hz, 1H), 7.92 (d, J = 8.5 Hz, 4H), 7.70–7.66 (m, 5H), 7.36 (d, J = 8.1 Hz, 1H), 7.15 (dd, J = 5.9 Hz, J = 1.0 Hz, 1H), 4.77 (s, 2H), 4.29 (s, 5H), 3.88 (s, 6H), 1.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 167.0, 164.1, 147.1, 142.8, 137.2, 129.2, 128.3, 121.9, 119.4, 86.4, 86.0, 72.7, 68.8, 57.3, 52.0, 26.9; HRMS (ESI+) calcd for $C_{35}H_{32}FeN_2O_5$ $[M+H]^+$: 617.1734, found: 617.1738.

2,5-bis(4-nitrophenyl)-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5l): Dark red solid (48 mg, 41%); mp 162–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.32 (d, J = 4.3 Hz, 1H), 8.12 (d, J = 8.8 Hz, 4H), 7.75–7.71 (m, 5H), 7.39 (d, J = 8.4 Hz, 1H), 7.18 (dd, J = 6.3 Hz, J = 0.9 Hz, 1H), 4.87 (s, 2H), 4.34 (s, 5H), 1.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 163.7, 147.0, 146.4, 145.3, 137.5, 128.9, 123.3, 122.2, 119.5, 86.3, 85.3, 73.1, 69.6, 57.3, 26.9; HRMS (ESI+) calcd for $C_{31}H_{26}FeN_4O_5$ $[M+H]^+$: 591.1326, found: 591.1328.

2,5-bis(3-nitrophenyl)-N-(2-(pyridin-2-yl)propan-2-yl)ferrocenecarboxamide (5m): Orange solid (44 mg, 37%); mp 127–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.50 (t, J = 1.9 Hz, 2H), 8.29 (d, J = 4.3 Hz, 1H), 8.07–7.92 (m, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.73–7.69 (m, 1H), 7.42 (t, J = 8.2 Hz, 2H), 7.37 (d, J = 8.4 Hz, 1H), 7.17–7.14 (m, 1H), 4.82 (s, 2H), 4.36 (s, 5H), 1.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.9, 148.1, 146.9, 139.5, 137.4, 134.5, 128.8, 123.4, 122.0, 121.6, 119.5, 85.7, 85.3, 72.8, 69.1, 57.3, 26.9; HRMS (ESI+) calcd for $C_{31}H_{26}FeN_4O_5$ $[M+H]^+$: 591.1326, found: 591.1328.

N-(2-(pyridin-2-yl)propan-2-yl)-2,5-di(thiophen-2-yl)ferrocenecarboxamide (5n): Orange solid (31 mg, 30%); mp 101–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.45–8.43 (m, 1H), 7.72–7.68 (m, 1H), 7.40 (d, J = 8.1 Hz, 1H), 7.22 (dd, J = 2.4 Hz, J = 1.2 Hz, 2H), 7.18–7.15 (m, 3H), 6.88 (dd, J = 4.4 Hz, J = 0.8 Hz, 2H), 4.68 (s, 2H), 4.37 (s, 5H), 1.87 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.5, 147.1, 140.1, 137.1, 127.0, 125.8, 124.2, 121.8, 119.5, 84.9, 80.5, 73.0, 68.6, 57.3, 27.0; HRMS (ESI+) calcd for $C_{27}H_{24}FeN_2OS_2$ $[M+H]^+$: 513.0753, found: 513.0753.

b) For gram reaction: A 100 mL Schlenk tube was equipped with a magnetic stir bar and charged with **1a** (1.07 g, 3.0 mmol), **2a** (0.945 mL, 9.0 mmol, 3 equiv), K_2CO_3 (829.5 mg, 6.0 mmol, 2 equiv), $Pd(OAc)_2$ (67.5 mg, 0.3 mmol, 10 mol %), XPhos (142.5 mg, 0.3 mmol, 10 mol %), PivOH (93.0 mg, 0.9 mmol, 30 mol %) in *o*-xylene (15 mL). The resulting mixture was heated under nitrogen at 140 °C for 21 h, and cooled to room temperature. Upon completion, CH_2Cl_2 (100 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with H_2O (50 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane-EtOAc as an eluent to afford the pure product **3a**.

c) For aryl iodide: A 10 mL round-bottomed flask was equipped with a magnetic stir bar and charged with **1a** (71.2 mg, 0.2 mmol), aryl iodide(0.6 mmol, 3 equiv), K_2CO_3 (55.3 mg, 0.4 mmol, 2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol %), PivOH (6.2 mg, 0.06 mmol, 30 mol %) in *o*-xylene (1.0 mL). The resulting mixture was heated under air at 100 °C for 21 h, and cooled to room temperature. Upon completion, CH_2Cl_2 (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane-EtOAc as an eluent to afford the pure product **3**.

d) For aryl chlorides: A 25 mL Schlenk tube was equipped with a magnetic stir bar and charged with **1a** (71.2 mg, 0.2 mmol), aryl chlorides (1 mL), K_2CO_3 (55.3 mg, 0.4 mmol, 2 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol %), ligand (9.5 mg, 0.02 mmol, 10 mol %) and PivOH (6.2 mg, 0.06 mmol, 30 mol %). The resulting mixture was heated under nitrogen at 190 °C for 21 h, and cooled to room temperature. Upon completion, CH_2Cl_2 (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane-EtOAc as an eluent to afford the pure product **3**.

e) For the product 6: A 25 mL Schlenk tube was equipped with a magnetic stir bar and charged with **3o** (33.2 mg, 0.05 mmol), diphenylphosphine oxide (40.5 mg, 0.2 mmol, 4 equiv), K_3PO_4 (42.5 mg, 0.2 mmol, 4 equiv), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 10 mol %) in dioxane (1.0 mL). The resulting mixture was heated under nitrogen at 110 °C for 24 h, and cooled to room temperature. Upon completion, CH_2Cl_2 (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with H_2O (20 mL), and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane-EtOAc as an eluent to afford the pure product **6**.

2,5-bis(4-(diphenylphosphoryl)phenyl)-N-(quinolin-8-yl)ferrocenecarboxamide (6): Orange solid (44 mg, 97%); mp 139–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 8.80–8.76 (m, 1H), 8.58 (dd, J = 2.9 Hz, J = 1.3 Hz, 1H), 8.15 (dd, J = 4.9 Hz, J = 3.4 Hz, 1H), 7.71 (dd, J = 5.4 Hz, J = 2.9 Hz, 4H), 7.59–7.47 (m, 18H), 7.41–7.33 (m, 9H), 4.87 (s, 2H), 4.39 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 148.1, 141.3, 141.3, 138.4, 136.2, 134.3, 132.9, 132.8, 132.1, 132.0, 132.0, 131.9, 131.9, 131.8, 131.1, 130.0, 128.8, 128.7, 128.5, 128.5, 128.4, 128.4, 127.9, 127.4, 121.8, 121.7, 116.2, 87.3, 82.5, 73.1, 70.2; ^{31}P NMR (163 MHz, $CDCl_3$) δ 29.02; HRMS (ESI+) calcd for $C_{56}H_{42}FeN_2O_3P_2$ $[M+H]^+$: 909.2093, found: 909.2093.

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11 CCDC 1446343 (**3a**).† Crystal data for compound **3a**: $C_{32}H_{24}FeN_2O$, *M* = 508.38, Monoclinic, a = 11.3423(6) Å, α = 90°, b = 14.2822(5) Å, β = 107.980(5)°, c = 16.0589(7) Å, γ = 90°, V = 2474.4(2) Å ^{3}, T = 291.15 K, space group = $P2_1/c$, Z = 4, number of reflections = 9066, Independent reflections = 4408, [R(int) = 0.0267], Final *R* indices [I>2σ (I)] R_1 = 0.0401, wR_2 = 0.0962, *R* indices (all data) R_1 = 0.0531, wR_2 = 0.1034.

12 CCDC 1446344 (**5a**).† Crystal data for compound **5a**: $C_{63}H_{58}Cl_2Fe_2N_4O_2$, *M* = 1085.73, Monoclinic, a = 14.7314(2) Å, α = 90°, b = 10.30632(19) Å, β = 95.6050(17)°, c = 17.8542(4) Å, γ = 90°, V = 2697.78(9) Å ^{3}, T = 291.15 K, space group = $P2_1/c$, Z = 2, number of reflections = 9723, Independent reflections = 4818, [R(int) = 0.0292], Final *R* indices [I>2σ (I)] R_1 = 0.0497, wR_2 = 0.1388, *R* indices (all data) R_1 = 0.0625, wR_2 = 0.1497.

Palladium-Catalyzed Direct C-H Arylation of Ferrocenecarboxamides with Aryl Halides

Huijie Qiao, Suyan Sun, Fan Yang, Yu Zhu, Weiguo Zhu, Yusheng Wu, and Yangjie Wu

A simple and facile protocol for palladium-catalyzed *ortho*-arylation of ferrocenecarboxamides with aryl halides was developed with the assistance of the bidentate directing group.