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Palladium-Catalyzed C–H Functionalization of Ferrocenecarboxylic Acid by using 8-Aminoquinoline as a Removable Directing Group

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Dedicated to Professor Harkesh B. Singh, IIT Bombay on the occasion of his 60th birthday.

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Abstract: A mild and efficient palladium-catalyzed synthetic method for the C–H functionalization of *N*-(quinolin-8-yl)ferrocenecarboxamide has been developed. Various aryl iodides containing I, NO_2, CN, COMe, CO_2Et, and NH functionalities and also alkyl iodides underwent the Pd-catalyzed intermolecular carbon-carbon bond forming reaction with ferrocenecarboxamide successfully which led to a diverse array of bis(aryl/alkyl)ferrocenecarboxamides in 34–92% yields. Cross-coupling of the ferrocenyl C–H bond with aryl iodides can also be achieved utilizing an economical Ni catalyst. Additionally, selective monoalkylation of ferrocenecarboxamide was studied using sodium bicarbonate as base and dibenzylphosphoric acid as additive under Pd-catalyzed reaction conditions. Subsequently, removal of the directing group, 8-aminoquinoline, from bis(aryl)ferrocenecarboxamides led to bis(aryl)ferrocenes bearing versatile methyl ester and carboxaldehyde functional groups.

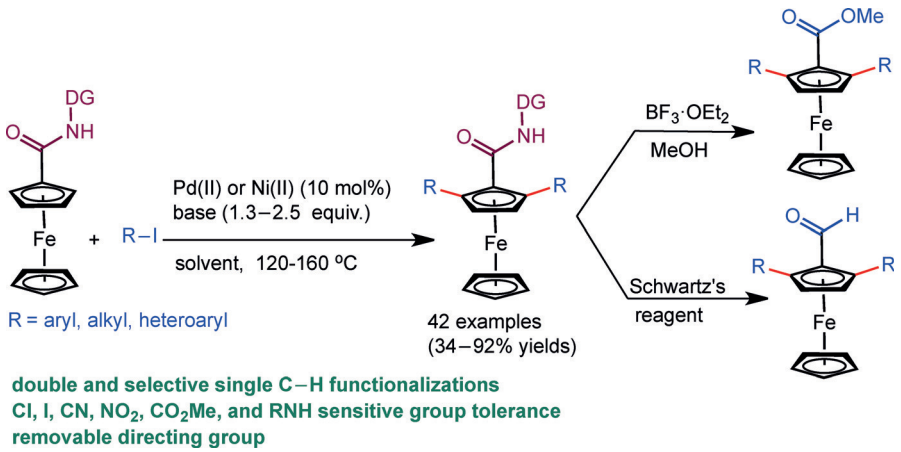
Keywords: biaryls; C–C cross coupling; ferrocenes; ligand-directed C–H functionalization; nickel catalysts; palladium catalysts

Introduction

Functionalized ferrocenes have attracted considerable interest in catalysis, materials science and as components of polymers, molecular switches, drugs, and sensors.[1–6] Most applications involve the use of di-, tri- or even higher substituted ferrocenes such as tetraphenyl-substituted ferrocenes which can be used as molecular switches for complexations,[2a] bis(4-bromophenyl)ferrocene which is used as the precursor for the synthesis of redox-active conjugated polymers,[2b] also aryl ring-containing ferrocenes exhibit potential antitumor activities,[3b,c,d] and 2-silylated/germylated/phosphorylated arylferrocenes are effective precursors for enantioselective C–H functionalization of metallocenes.[7]

Consequently, there is a permanent interest in new strategies for the derivatization of ferrocene. The most common methods of functionalization of ferrocene are Friedel–Crafts reactions and the use of organolithium reagents, which generate potent nucleophiles followed by substitution reactions with various electrophiles. A significant advantage of this approach is the presence of *ortho*-directing groups for the metallation, which allow the precise control of regioselectivity or stereoselectivity for the synthesis of 1,2-disubstituted ferrocenes.[8] On the other hand, organolithium reagents are highly reactive and impose restrictions related to functional group tolerance. Particularly, coupling partners containing functionalities such as NO_2, I, CN, CO_2Et, CHO and NH, which are important for further functionalization in the post-modification strategy, have not been documented. Moreover, *ortho*-lithiation and Friedel–Crafts reactions are not viable routes to construct arylferrocenes due to the poor reactivity of the aryl halides in these reactions.

Transition metal (TM)-catalyzed C–H functionalization of cyclopentadienyl rings is an atom economical alternative approach for structural diversification. Although C–H functionalization of ferrocenes by various transition metals have been presented in the lit-



Scheme 1. C–H functionalization of *N*-(quinolin-8-yl)ferrocenecarboxamide.

erature, limited reports on the catalytic C–H functionalization of ferrocenes are available.[9–13] Shibata et al. have presented an elegant Ir-catalyzed methodology for the alkenylation and alkylation of ferrocenes.[6a,b,11]

Oxazoline ligand-directed C–H arylation of ferrocenes has been studied using Pd(II) complexes, nonetheless, a stoichiometric amount of the expensive Pd-catalyst is required, additionally reactions are poor yielding and showed poor substrate scope.[12] Ferrocenes bearing oxazoline directing groups are either expensive or difficult to synthesize. Also conversion of oxazoline to acid/ester or aldehyde is difficult because of the stability of ferrocene under harsh reaction conditions. On the other hand, functionalities such as ester and CHO are desirable for further transformation at later stages.

The pioneering work of Chatani,[14] Daugulis,[15] and others[16,17] in the area of ligand-directed TM-catalyzed C–H arylation and alkylation, as well as several formidable applications in total synthesis served as our inspiration for this work. The substrate containing bidentate ligand would bind tightly to the catalyst in close proximity of the C–H bond and hence enhances the functionalization of C–H bond under mild reaction conditions. Also bidentate ligand strategies enable economically viable transition metals such as Cu and Ni to act as catalysts for the functionalization of C–H bonds. Additionally, the bidentate directing group can be transformed or removed to obtain various synthetically useful functional groups on ferrocene.

Our group has utilized aryl amide substrates for intramolecular carbon-carbon and carbon-heteroatom (nitrogen, oxygen, sulfur, and selenium) bond forming reactions for the synthesis of various heterocycles *via* functionalization of carbon-halogen or C–H bonds.[18] Nonetheless, C–H functionalization of aryl amides for an intermolecular carbon-carbon coupling reaction has not been achieved.

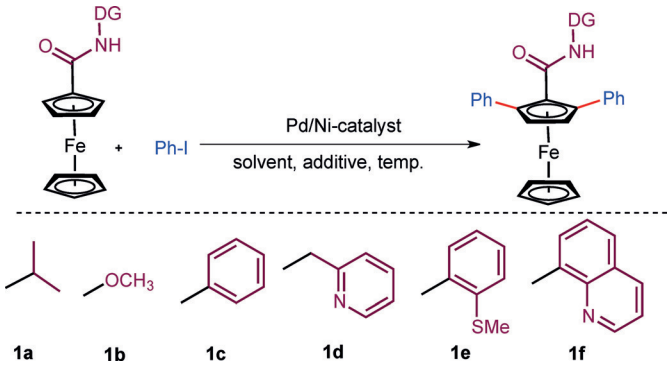
Here we present a Pd- or Ni-catalyzed C–H functionalization of readily accessible *N*-(quinolin-8-yl)ferrocenecarboxamide for the synthesis of diversely substituted bis(arylated), bis(alkylated), and monoalkylated ferrocenecarboxamides (Scheme 1). Additionally, the 8-aminoquinoline directing group has been removed and thereby synthesized bis(aryl)ferrocenecarboxamides were transformed into bis(aryl)ferrocenecarboxaldehydes and esters.

Results and Discussion

For optimization of the reaction conditions, ferrocenes with various amide directing groups (**1a**–**1f**) were synthesized and treated with iodobenzene in the presence of a base, additives, and TM catalysts in various solvents. *N*-Isopropyl-, *N*-methoxy-, and *N*-phenylferrocenecarboxamides **1a**–**1c** failed to give any C–H arylated product with iodobenzene in the presence of $Pd(OAc)_2$ catalyst, Cs_2CO_3 and AgOAc in toluene at 120 °C (entries 1–3, Table 1).

N-2-Pyridylferrocenecarboxamide **1d** bearing a coordinating N-atom provided a 54% yield of the C–H functionalized bis(phenyl)-*N*-2-pyridylferrocenecarboxamide **2a** (entry 4, Table 1). *N*-(2-Methylthiophenyl)ferrocenecarboxamide having a methylthio coordinating group failed to yield C–H arylated ferrocene, unexpectedly (entry 5, Table 1). Next, the ferrocenecarboxamide having an 8-aminoquinoline directing group yielded 83% of arylated ferrocence **3a**. Moreover, a slightly better yield (93%) of **3a** was obtained in the absence of AgOAc (entry 7, Table 1). The use of silver acetate alone offered a comparatively low yield of **3a** (entry 8, Table 1). Next, various bases such as $NaHCO_3$, Na_2CO_3, and K_2CO_3 were screened in the Pd-catalyzed reaction, nonetheless, all proved to be less effective (entries 9–11, Table 1). The reaction can also be carried out in *t*-BuOH and *t*-amylOH solvents, albeit with low yields (45 and 40%, respective-

Table 1. Optimization for arylation of ferrocene carboxamide.[a]



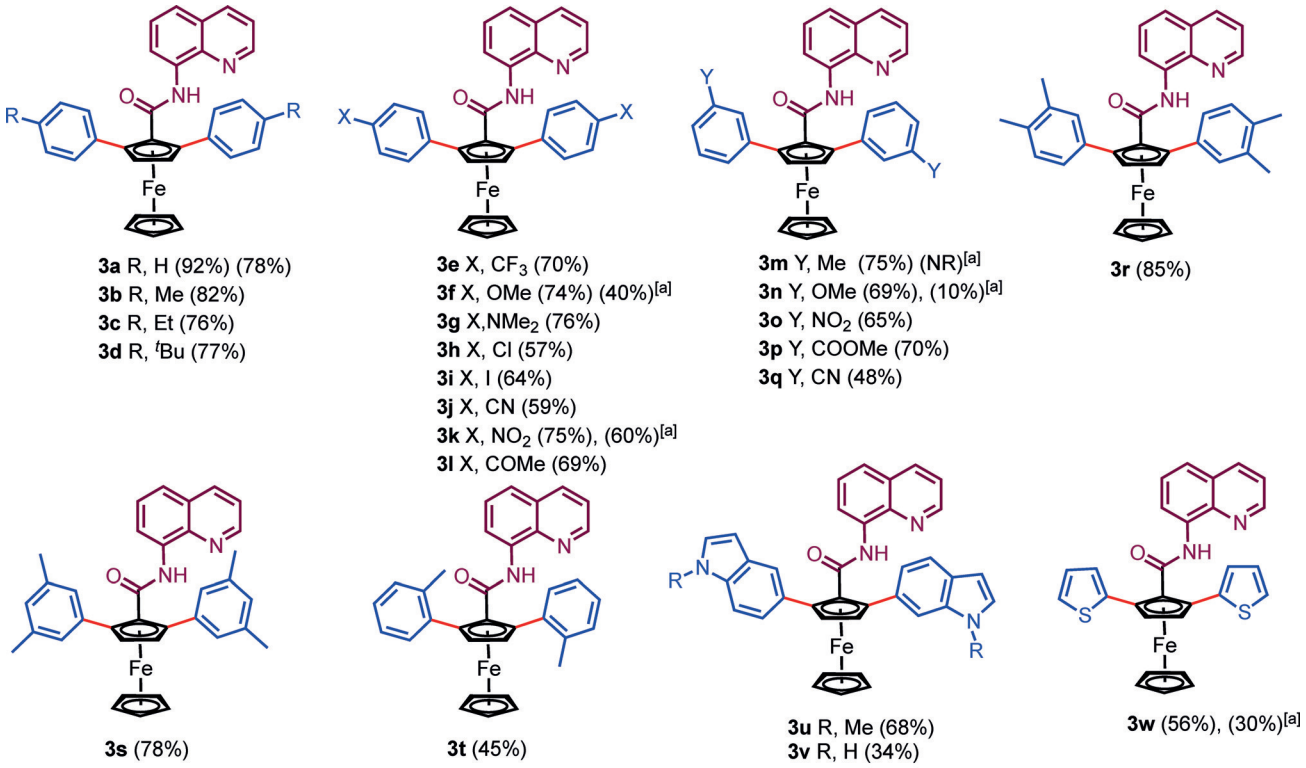
Entry	TM	DG	Base	Solvent	Yield[%][b]
1[c]	$Pd(OAc)_2$	**1a**	Cs_2CO_3	toluene	NR
2[c]	$Pd(OAc)_2$	**1b**	Cs_2CO_3	toluene	NR
3[c]	$Pd(OAc)_2$	**1c**	Cs_2CO_3	toluene	NR
4[c]	$Pd(OAc)_2$	**1d**	Cs_2CO_3	toluene	**2a** [54]
5[c]	$Pd(OAc)_2$	**1e**	Cs_2CO_3	toluene	NR
6[c]	$Pd(OAc)_2$	**1f**	Cs_2CO_3	toluene	**3a** [83]
7	$Pd(OAc)_2$	**1f**	**Cs_2CO_3**	**toluene**	**3a [92]**
8	$Pd(OAc)_2$	**1f**	AgOAc	toluene	**3a** [74]
9	$Pd(OAc)_2$	**1f**	$NaHCO_3$	toluene	**3a** [47]
10	$Pd(OAc)_2$	**1f**	Na_2CO_3	toluene	**3a** [24]
11	$Pd(OAc)_2$	**1f**	K_2CO_3	toluene	**3a** [55]
12	$Pd(OAc)_2$	**1f**	Cs_2CO_3	*t*-BuOH	**3a** [45]
13	$Pd(OAc)_2$	**1f**	Cs_2CO_3	*t*-amyl-OH	**3a** [40]
14	$Pd(OAc)_2$	**1f**	Cs_2CO_3	DCE	**3a** [84]
15	$Pd(PPh_3)_4$	**1f**	Cs_2CO_3	toluene	NR
16	$PdCl_2$	**1f**	Cs_2CO_3	toluene	**3a** [38]
17	$PdCl_2$ $(ACN)_2$	**1f**	Cs_2CO_3	toluene	**3a** [44]
18[d]	$NiCl_2$	**1f**	Cs_2CO_3	toluene	NR
19[d]	$Ni(OTf)_2$	**1f**	Cs_2CO_3	toluene	NR
20[e]	$Ni(OTf)_2$	**1f**	Cs_2CO_3	toluene	**3a** [50]
21[f]	$Ni(OTf)_2$	**1f**	**$NaHCO_3$**	**toluene**	**3a [78]**

[a] Amide **1** (0.1 mmol, 35.6 mg), PhI (0.3 mmol, 33 μL), $Pd(OAc)_2$ (10 mol%, 2 mg) Cs_2CO_3 (0.25 mmol, 86 mg) in toluene (1.5 mL) at 120 °C for 8–16 h unless otherwise noted.
[b] Isolated yields.
[c] 1.1 equiv. of AgOAc and Cs_2CO_3 were used.
[d] Reaction was carried out at 120 °C for 18 h.
[e] Reaction at 140 °C, for 18 h.
[f] Reaction at 160 °C, for 18 h. NR = no reaction.

ly) being obtained (entries 12 and 13, Table 1). 1,2-Dichloroethane provided a comparable yield (84%) of **3a** as obtained from toluene (entry 4 *vs.* 7, Table 1). Among various Pd catalysts screened, $Pd(OAc)_2$ was observed to be effective for C–H functionalization of **1f** (entries 14–17, Table 1).

Next, an economically viable Ni(II) catalyst was explored for C–H functionalization of ferrocenecarboxamide **1f** (entries 18–21, Table 1). Disappointingly, substitution of Pd(II) with Ni(II) failed in the C–H functionalization of **1f** under the optimized reaction conditions. Elevating the temperature to 140 °C provided a moderate yield of **3a** under the optimized reaction conditions (entry 20, Table 1). Furthermore, on switching the base from Cs_2CO_3 to $NaHCO_3$ and elevating temperature from 140 to 160 °C, the yield of the product increased by 28% (entry 21, Table 1).

After screening of various conditions, we chose 10 mol% of $Pd(OAc)_2$, 2.5 equiv. of Cs_2CO_3 in toluene to study the substrate scope of the reaction (Scheme 2). Also $Ni(OTf)_2$ as catalyst in the presence of $NaHCO_3$ in toluene at 160 °C was also employed in selected examples. As evident from the Scheme 2, *p*-methyl-, *p*-ethyl-, *p*-*tert*-butyl- and *p*-trifluoromethylphenyl iodides successfully reacted with *N*-(quinolin-8-yl)ferrocenecarboxamide **1f** to form 2,5-bis(4-alkylbenzene)-1-*N*-(quinolin-5-yl)ferrocenecarboxamides **3b–3e** in 70–80% yields under Pd-catalyzed reaction



[a] Yields were obtained using 10 mol% $Ni(OTf)_2$.

Scheme 2. Substrate scope with regard to aryl/heteroaryl iodides. Unless otherwise stated, isolated yields using 10 mol% of $Pd(OAc)_2$ in toluene are given.

conditions. Next, bis(4-substituted benzene)-1-*N*-(quinolin-5-yl)ferrocenamides **3f–3i** with electron-donating functional groups such as OCH_3, $N(CH_3)_2$, and electron-withdrawing groups NO_2, CN, $C(O)CH_3$, Cl, and even iodo were also obtained in good yields. Similarly, *meta*, di-*meta*, and *para*-substituted-arylferrocenecarboxamides **3l–3q** were obtained under the optimized Pd-catalyzed reaction conditions. On the other hand, *ortho*-substituted aryl iodides reacted sluggishly and only one *ortho*-methylbenzeneferrocenecarboxamide **3p** was obtained in 45% yield under the optimized conditions while *o*-NO_2-, *o*-OMe-, and *o*-CH_2CO_2H-substituted phenyl iodides were observed to be unreactive, presumably due to the steric effect. Next, *N*-methylindolyl iodide and indolyl iodide having acidic N*H* proton showed compatibility to the Pd-catalyzed conditions and yielded the respective indolylferrocenecarboxamides **3u** and **3v** in 68 and 34% yields, respectively. A heteroarene, 2-iodothiophene, also smoothly reacted with ferrocenecarboxamide **1f** to form novel 2,5-bis(thiophenyl)ferrocenecarboxamide **3w** in moderate 56% yield.

Structures of bis(phenyl)-, bis(4-iodophenyl)- and bis(thiophenyl)ferrocenecarboxamides **3a**, **3i** and **3w** are also determined by single crystal X-ray study (Figure 1, for details, see the Supporting Information, pages S152–S159).[19]

Synthesis of selected bis(aryl)ferrocenecarboxamides has also been studied under economical Ni-catalyzed reaction conditions and compared with the yields obtained using Pd-catalyst. Bis(aryl)ferrocenecarboxamides **3f**, **3m**, and **3n** having electron-donating methyl and methoxy substituents were obtained in poor yields under Ni-catalyzed reaction conditions as compared to Pd-catalyst (40, NR, and 10% for Ni catalyst *vs.* 74, 75, and 69% for Pd catalyst). On the other hand bis(4-nitrophenyl)ferrocenecarboxamide **3k** having electron-withdrawing NO_2 groups was obtained in 68% yield which is comparable to the yield (75%) obtained using Pd catalyst.

After synthesizing various bis(aryl)ferrocenecarboxamides, we explored the synthesis of bis(alkyl)ferrocenecarboxamides and monosubstituted aryl- and alkylferrocenecarboxamides. Unfortunately, the synthesis of bis(alkyl)ferrocenecarboxamide and also selective monoarylation of ferrocenecarboxamide **1f** could not be accomplished under the optimized reaction conditions by varying the stoichiometry of alkyl and aryl iodides. Therefore, we searched for reaction conditions which could provide access to bis(alkyl)- and selective monoaryl- or alkyl-substituted ferrocenecarboxamides (Table 2).

The reaction in toluene provided traces or poor yield of bis(ethyl)ferrocenecaboxamide **4a**. The reac-

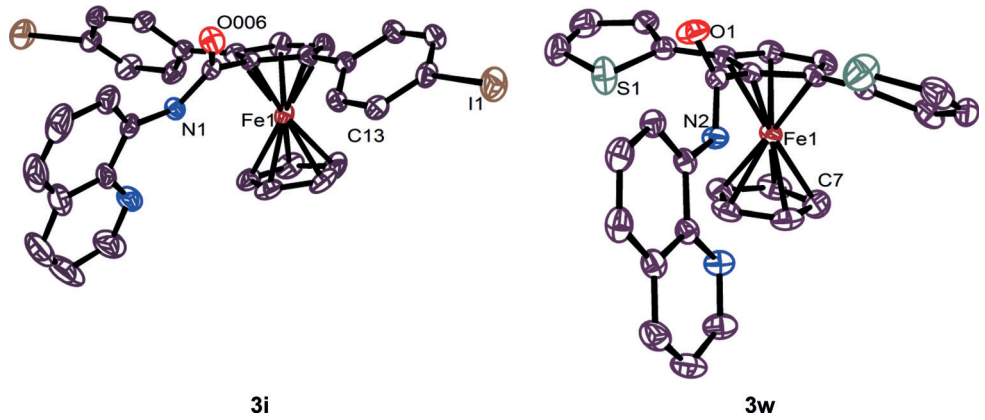


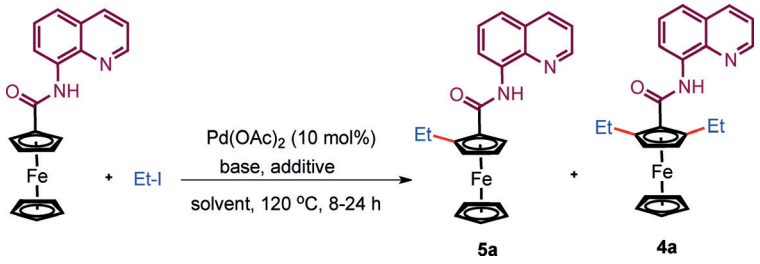
Figure 1. ORTEP views of 4-iodophenyl- and 2-thiophenylferrocenecarboxamides **3i** and **3w**.

tion in *tert*-amyl alcohol and dichoroethane solvents combination (1:1) in the presence of $(BnO)_2POOH$ additive smoothly provided bis(ethyl)ferrocenecarboxamide **4a** in 55% yield (entry 6, Table 2). Interestingly, use of sodium bicarbonate under similar reaction conditions yielded monoethylferrocenecarboxamide **5a** in 45% yield (entry 12, Table 2).

As summarized in Scheme 3, various primary alkyl iodides namely, methyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, isopentyl and even benzyl iodides and iodoethyl acetate reacted smoothly with ferrocenecarboxamide **1f** to form bis(alkyl)ferrocenecarboxamides **4b–4i** in the presence of Cs_2CO_3 in an equimolar mixture of *tert*-amyl alcohol and DCE under Pd-catalyzed reaction conditions.

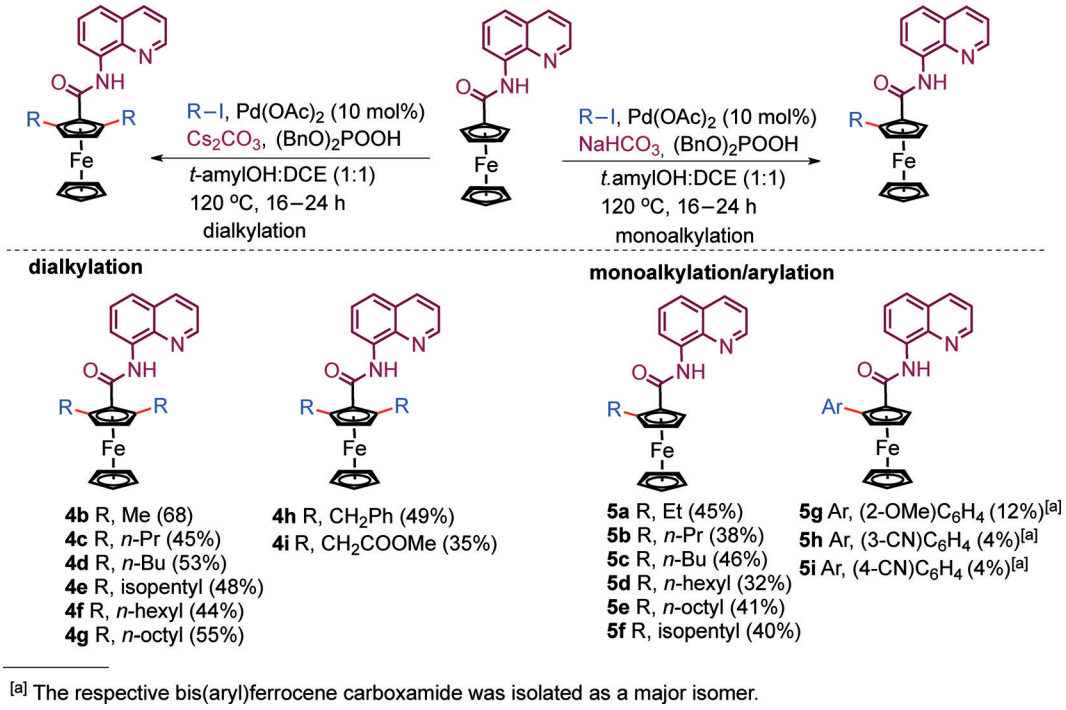
Next, various monoalkyl-substituted ferrocenecarboxamides **5a–5f** were obtained using $NaHCO_3$ in place of Cs_2CO_3 under optimized reaction conditions (entry 12, Table 2). The obtained yields of monoalkyl-substituted ferrocenecarboxamides **5a–5f** were moder-

Table 2. Reaction conditions for the synthesis of bisalkyl- and monoalkylferrocenecarboxamides.[a]



Entry	Base	Additive	Solvent	Yield [%] of monoalkyl/dialkyl product[b]
1	Cs_2CO_3	–	toluene	trace
2	Cs_2CO_3	AgOAc	toluene	0/20
3	Cs_2CO_3	$(BnO)_2POOH$	toluene	0/35
4[b]	K_2CO_3	$(BnO)_2POOH$	*t*-amyl-OH:DCE	0/45
5	Na_2CO_3	$(BnO)_2POOH$	*t*-amyl-OH:DCE	0/35
6	**Cs_2CO_3**	**$(BnO)_2POOH$**	***t*-amyl-OH:DCE**	**0/66**
7	K_2HPO_4	$(BnO)_2POOH$	*t*-amyl-OH:DCE	40/5
8	Na_2HPO_4	$(BnO)_2POOH$	*t*-amyl-OH:DCE	35/15
9[c]	$NaHCO_3$	$(BnO)_2POOH$	*t*-amyl-OH:DCE	15/15
10	$NaHCO_3$	Piv-OH	*t*-amyl-OH:DCE	40/8
11	K_2HPO_4	Piv-OH	*t*-amyl-OH:DCE	15/5
12	**$NaHCO_3$**	**$(BnO)_2POOH$**	***t*-amyl-OH:DCE**	**45/0**

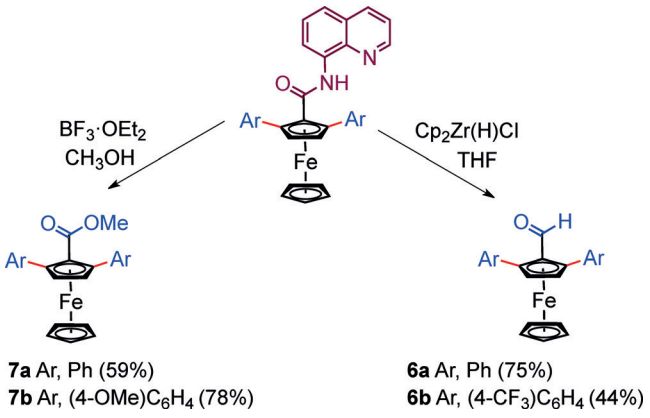
[a] Reaction was carried out on a 0.1 mmol scale using 2.5 equiv. of iodoethane, 2.5 equiv. of base, 0.3 equiv. of additive, and 10 mol% of $Pd(OAc)_2$ under argon, unless otherwise noted.
[b] isolated yield.
[c] *t*-Amyl-OH:DCE in a 1:1 ratio was used.
[d] $PdCl_2(MeCN)_2$ was used.



Scheme 3. Selective monoalkylation and dialkylation. Isolated yields are given.

ate (32–46%) and the rest of the unreactive ferrocenecarboxamide **1f** was recovered from the reaction. We also attempted the synthesis of monoarylated ferrocenecarboxamides under optimized reaction conditions (entry 12, Table 2). Disappointingly, a mixture of bis(arylated) and monoarylated ferrocenecarboxamides (major and minor, respectively) was obtained and selective monoarylated ferrocenecarboxamides **5g–5i** were isolated in poor yields.

Removal of the directing ligand was studied in the end (Scheme 4). The addition of NaOH in CH_3OH to the bis(aryl)ferrocenecarboxamide **3a** under reflux conditions failed to remove the 8-aminoquinoline ligand. Similarly, addition of ceric ammonium nitrate to **3a** in CH_3CN at room temperature was unsuccessful. Treatment of **3a** and **3f** with $BF_3{\cdot}OEt_2$ in CH_3OH led to the smooth removal of 8-aminoquinoline, resulting in bis(aryl)ferrocenoylmethyl acetates **7a** and **7b** in 59 and 78% yields, respectively. Next, reaction of bis(aryl)ferrocenecarboxamide with $Cp_2Zr(H)Cl$ reagent[20] provided bis(aryl)ferrocenecarboxaldehydes, which are useful for late stage transformations.

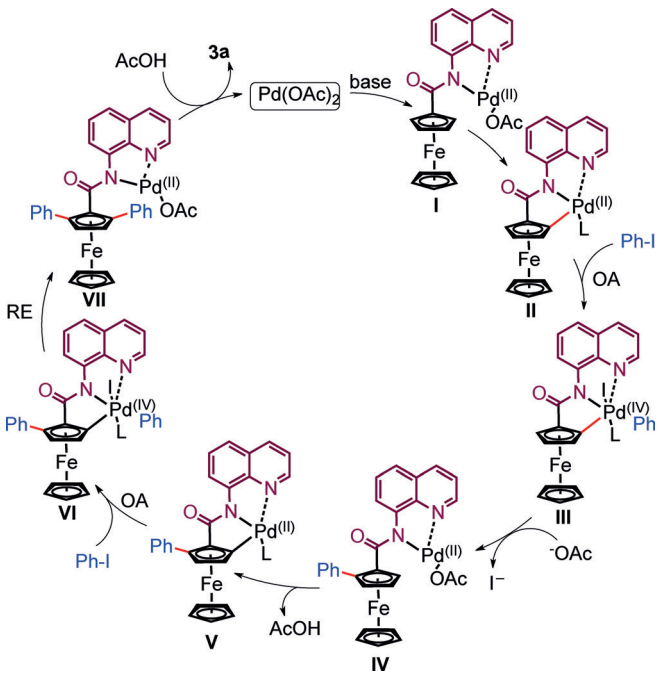


Scheme 4. Removal of the directing 8-aminoquinoline ligand.

Mechanism

The tentative mechanism for bis-arylation of ferrocenecarboxamide is depicted in Scheme 5.

The presence of a nitrogen atom seems important for the coordination of metal with the substrate for C–H functionalization of the Cp ring as the substrates **1a–1c** lacking a coordinating atom failed to yield the arylated product. The coordination of Pd with the nitrogen atom followed by intramolecular OAc substitution with N–H group would form Pd(II) amidate intermediate **I**. Pd(II)-amidate **I** may undergo substitution with the C–H bond, forming Pd-carbon bonded intermediate **II**.[15b,16e] Next, oxidative addition of aryl iodide would furnish Pd(IV) intermediate **III**. Reductive elimination would generate Pd(II) **IV** which further led to substitution of OAc by C–H forming **V**. Oxidative addition of second molecule of aryl iodide would afford Pd(IV) intermediate **VI**. Reductive elimination would give **VII** and subsequent reaction with AcOH would furnish bis(phenyl)ferrocenecar-



Scheme 5. Proposed mechanism for the Pd-catalyzed bis-arylation of ferrocenecarboxamide.

boxamide **3a** and concomitantly regeneration of Pd(II) catalyst. A similar mechanism could be hypothesized in the presence of Ni(II) catalysts.[14f]

Conclusions

Synthesis of bis(aryl)- and alkylferrocenecarboxamides has been established from readily accessible ferrocenecarboxylic acid in two steps using the 8-aminoquinoline directing ligand by Pd-catalyzed C–H functionalization. Aryl iodides containing various functionalities such as NO_2, I, CN, CO_2Et, COMe and NH showed amenability to the Pd-catalyzed reaction conditions. The reaction could also be carried out using a more economical Ni(II) catalyst. Moreover, selective monoalkylation of ferrocenecarboxamide was also achieved by using $(BnO)_2POOH$ and sodium bicarbonate base under Pd-catalyzed reaction conditions. Also bis(aryl)ferrocenecarboxaldehyde and methyl ester, which could be easily manipulated under mild reaction condition for later stage transformation, have been obtained by the removal of the directing ligand 8-aminoquinoline. Because monoalkylation of ferrocenecarboxamide has been demonstrated, it is possible to synthesize monosubstituted ferrocenecarboxamides with planar chirality[8,21] and is under investigation in our laboratory.

Experimental Section

General Information

All NMR experiments were carried out on 400 MHz and 700 MHz spectrometers and NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$, (7.26 ppm for ^1H and 77.16 (±0.06) ppm for ^{13}C, respectively), DMSO-d_6 (3.31 ppm for H_2O, 2.47 ppm for DMSO, 39.9 ppm for carbon). High resolution mass analysis was performed on a quadruple-time of flight (Q-TOF) mass spectrometer equipped with an ESI source (+ve). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Ferrocenecarboxylic acid was prepared by following the reported method.[22] *N*-Aryl-/alkylferrocenecarboxamides were synthesized from the corresponding ferrocenoyl chloride and primary amines (see experimental procedure). Iodoarenes, iodoalkanes, 8-aminoquinoline, $Pd(OAc)_2$, $(BnO)_2POOH$, Cs_2CO_3, and $NaHCO_3$ were purchased from Sigma–Aldrich Company. Silica gel (100–200 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates purchased from Merck.

Synthesis of *N*-Isopropylferrocenecarboxamide (1a);[23] Typical Procedure

Oxalyl chloride (0.76 mL, 10 mmol) was added to stirred ferrocenecarboxylic acid (208 mg, 0.9 mmol) in a 25-mL round-bottom flask at room temperature under nitrogen and after complete addition, the resulting brown coloured suspension was stirred for 30 min. After this, oxalyl chloride was removed by distillation and the resulting ferrocenoyl chloride was dried under high vacuum. The resultant viscous brown solid was taken up in CH_2Cl_2 (5 mL) and added *via* syringe to a stirred solution of isopropylamine (80 μL, 1.0 mmol) and triethyamine (0.14 mL, 1.0 mmol) under nitrogen at 0 °C and stirred for 1 h at this temperature. Water (50 mL) was added to the reaction mixture and extracted with (20 mL × 3) CH_2Cl_2, dried over Na_2SO_4 and concentrated under vacuum. The resulting crude amide was purified by column chromatography on silica gel using hexane/ethyl acetate (7:3) to afford an orange yellow solid; yield: 198 mg (81%); R_f = 0.5 (3:7 EtOAc:hexane). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.48 (s, 1H), 4.63 (s, 2H), 4.30 (s, 2H), 4.18 (s, 5H), 2.15 (s, 1H), 1.22 (d, J = 6.5 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 70.2, 69.7, 68.0, 41.2, 30.9, 23.0; GC-LR-MS: m/z = 271.0, calcd. for $C_{14}H_{17}FeNO$: 271.0.

This procedure was followed for the synthesis of **1c**, **1d**, **1e**, and **1f**.

Synthesis of *N*-Methoxyferrocene-1-carboxamide (1b)

In a 25-mL round-bottom flask, *O*-methylhydroxylamine salt (188 mg, 2.25 mmol) and potassium carbonate (415 mg, 3.0 mmol) were combined in a 2:1 mixture of EtOAc:H_2O (20 mL). The mixture was cooled in an ice bath. The ferrocenoyl chloride (372 mg, 1.5 mmol) was added dropwise and the reaction was stirred at room temperature for 16 h. The reaction mixture was washed with brine and extracted with ethyl acetate. The organic layer was dried over Na_2SO_4. The crude product was purified by column chromatography on neutral alumina using CH_2Cl_2 to give pure amide **1b** as

a dark brown solid; yield: 495 mg (85%), R_f = 0.9 (100% CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.00 (s, 1H), 4.70 (s, 2H), 4.34 (s, 2H), 4.15 (s, 5H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.6, 74.1, 70.58, 69.9, 68.4, 63.7; HR-MS (ESI): m/z = 282.0205, calcd. for $C_{12}H_{13}FeNO_2$ $[M+Na]^+$: 282.0188.

***N*-Phenylferrocene-1-carboxamide (c):**[24] Yellow solid; yield: 205 mg (74%); R_f = 0.6 (100% CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 7.8 Hz, 1H), 7.48 (s, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 4.81 (d, J = 23.4 Hz, 1H), 4.40 (s, 1H), 4.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 138.1, 129.1, 124.0, 119.8, 76.2, 70.9, 69.8, 68.2; GC-LR-MS: m/z = 305.1, calcd. for $C_{17}H_{15}FeNO$ $[M]^+$: 305.1.

***N*-(2-Pyridylmethyl)ferrocene-1-carboxamide (1d):**[25] Blackish-green solid; yield: 243 mg (76%); R_f = 0.4 (5:5, EA:hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, J = 3.7 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.22–7.16 (m, 1H), 7.10 (s, 1H), 4.70 (d, J = 18.6 Hz, 1H), 4.63 (d, J = 4.3 Hz, 1H), 4.39–4.24 (m, 1H), 4.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 156.9, 149.0, 136.8, 122.44, 122.43, 76.0, 70.4, 69.7, 68.2, 44.4; GC-LR-MS: m/z = 320.1, calcd. for $C_{17}H_{16}FeN_2O$ $[M]^+$: 320.1.

***N*-(2-Methylthiophenyl)ferrocene-1-carboxamide (1e):** Yellow solid; yield: 242 mg (69%); R_f = 0.7 (1:9 EA:hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (s, 1H), 8.44 (dd, J = 8.2, 0.9 Hz, 1H), 7.51 (dd, J = 7.8, 1.4 Hz, 1H), 7.38–7.28 (m, 1H), 7.06 (td, J = 7.6, 1.2 Hz, 1H), 4.91–4.76 (m, 2H), 4.50–4.37 (m, 2H), 4.25 (d, J = 8.8 Hz, 5H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 138.8, 133.2, 129.2, 124.4, 123.8, 120.0, 76.3, 71.0, 69.9, 68.3, 19.1; HR-MS (ESI): m/z = 352.0448, calcd. for $C_{18}H_{17}FeNOS$ $[M+H]^+$: 352.0453.

***N*-(Quinolin-8-yl)ferrocene-1-carboxamide (1f):**[26] Orange crystalline solid; yield: 303 mg (85%); R_f = 0.6 (100% CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.28 (s, 1H), 8.87 (dd, J = 4.2, 1.6 Hz, 1H), 8.79 (dd, J = 7.6, 1.2 Hz, 1H), 8.17 (dd, J = 8.3, 1.5 Hz, 1H), 7.56 (t, J = 7.9 Hz, 1H), 7.52–7.43 (m, 2H), 4.95 (s, 2H), 4.45 (s, 2H), 4.27 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 148.2, 138.5, 136.4, 134.8, 128.0, 127.5, 121.6, 121.0, 116.1, 76.9, 70.9, 69.9, 68.5; HR-MS (ESI): m/z = 357.0676, calcd. for $C_{20}H_{16}FeN_2O$ $[M+H]^+$: 357.0685.

General Procedure for Bis-arylation of *N*-(Quinolin-8-yl)ferrocene-1-carboxamide

One equiv. of *N*-(quinolin-8-yl)ferrocene-1-carboxamide (35.6 mg, 0.1 mmol), $Pd(OAc)_2$ (2.24 mg, 10 mol%), Cs_2CO_3 (43 mg, 2.1 equiv.), and aryl iodide (3 equiv.) were added into dry toluene (2 mL) in a dried sealed tube having a magnetic bead purged with argon to evacuate air in dry toluene (2 mL). The reaction mixture was heated at 120 °C for 8–24 h. The reaction mixture was then cooled and filtered through celite and the organic layer was extracted with ethyl acetate (10 mL x 3) and washed with water. The organic layer passed through Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography.

2,5-Bisphenyl(2-pyridylmethylamino)ferrocene-1-carboxamide (2a): Yellow brown solid; yield: 26 mg (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, J = 4.6 Hz, 1H), 7.68–7.52 (m, 6H), 7.29–7.25 (m, 3H), 7.23–7.13 (m, 5H), 4.68 (s, 2H), 4.63 (d, J = 5.3 Hz, 2H), 4.27 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.0, 156.2, 148.8, 137.1, 136.6, 128.6, 128.0, 126.7, 122.20, 122.14, 87.9, 83.0, 72.4, 68.4, 45.0; HR-MS (ESI): m/z = 473.1331, calcd. for $C_{29}H_{24}FeN_2O$ $[M+H]^+$ 473.1311.

2,5-Bisphenyl)-1-(*N*-quinolin-8-yl)ferrocene carboxamide (3a): Orange solid; yield: 46 mg (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.77 (s, 1H), 8.85 (d, J = 7.4 Hz, 1H), 8.56 (dd, J = 4.0, 1.3 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.63 (d, J = 7.3 Hz, 4H), 7.54 (t, J = 7.9 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.34 (dd, J = 8.2, 4.2 Hz, 1H), 7.23–7.15 (m, 4H), 7.13 (t, J = 7.3 Hz, 2H), 4.76 (s, 2H), 4.41 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 147.8, 138.5, 136.8, 136.0, 134.7, 128.9, 128.0, 127.8, 127.4, 126.7, 121.41, 121.39, 116.1, 88.6, 82.2, 72.7, 69.3; HR-MS (ESI): m/z = 508.1225, calcd. for $C_{32}H_{24}FeN_2O$ $[M]^+$: 508.1233.

2,5-Bis(4-methylphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3d): Orange yellow solid; yield: 44 mg (82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.77 (s, 1H), 8.85 (d, J = 7.4 Hz, 1H), 8.57 (d, J = 2.8 Hz, 1H), 8.10 (d, J = 8.1 Hz, 1H), 7.59–7.45 (m, 6H), 7.35 (dd, J = 8.2, 4.1 Hz, 1H), 7.00 (d, J = 7.8 Hz, 4H), 4.71 (s, 2H), 4.39 (s, 5H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.2, 147.8, 138.6, 136.47, 136.11, 134.9, 133.9, 128.84, 128.83, 127.92, 127.48, 121.48, 121.44, 116.2, 88.6, 82.2, 72.7, 69.1, 21.2; HR-MS (ESI): m/z = 537.1625, calcd. for $C_{34}H_{28}FeN_2O$ $[M+H]^+$: 537.1624.

2,5-Bis(4-ethylphenyl)-1-(*N*-quinolin-8-yl)ferrocenecarboxamide (3c): Orange solid; yield: 43 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.73 (s, 1H), 8.84 (dd, J = 7.5, 0.9 Hz, 1H), 8.54 (dd, J = 4.1, 1.5 Hz, 1H), 8.09 (dd, J = 8.3, 1.4 Hz, 1H), 7.54 (m, 5H), 7.48 (dd, J = 8.2, 0.9 Hz, 1H), 7.33 (dd, J = 8.3, 4.2 Hz, 1H), 7.02 (d, J = 8.1 Hz, 4H), 4.71 (s, 2H), 4.39 (s, 5H), 2.52 (q, J = 7.6 Hz, 4H), 1.12 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 147.7, 142.7, 138.5, 136.0, 134.9, 134.0, 128.9, 127.8, 127.5, 127.4, 121.3, 121.3, 116.1, 88.7, 81.9, 72.6, 69.2, 28.5, 15.3; HR-MS (ESI): m/z = 565.1931, calcd. for $C_{36}H_{32}FeN_2O$ $[M+H]^+$: 565.1937.

2,5-Bis(4-*tert*-butylphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3d): Light yellow solid; yield: 48 mg (77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.73 (s, 1H), 8.91–8.86 (m, 1H), 8.55 (dd, J = 4.2, 1.6 Hz, 1H), 8.12 (dd, J = 8.3, 1.6 Hz, 1H), 7.58 (d, J = 8.3 Hz, 5H), 7.51 (dd, J = 8.3, 1.2 Hz, 1H), 7.36 (dd, J = 8.3, 4.2 Hz, 1H), 7.23 (d, J = 8.4 Hz, 4H), 4.76 (s, 2H), 4.43 (s, 5H), 1.24 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 149.5, 147.7, 138.5, 137.1, 135.9, 134.9, 133.7, 128.7, 127.94–127.31 (m), 124.8, 121.2, 121.2, 116.0, 88.7, 81.5, 72.6, 69.3, 34.4, 31.2; HR-MS (ESI): m/z = 621.2590, calcd. for $C_{40}H_{40}FeN_2O$ $[M+H]^+$: 621.2563.

2,5-Bis(4-trifluoromethylphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3e): Light yellow solid; yield: 45 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.71 (s, 1H), 8.84 (dd, J = 7.3, 1.4 Hz, 1H), 8.51 (dd, J = 4.2, 1.5 Hz, 1H), 8.12 (dd, J = 8.3, 1.5 Hz, 1H), 7.74 (d, J = 8.1 Hz, 4H), 7.60–7.50 (m, 2H), 7.47 (d, J = 8.2 Hz, 4H), 7.35 (dt, J = 10.6, 5.3 Hz, 1H), 4.86 (s, 2H), 4.43 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.20, 147.99, 141.05, 141.03, 138.39, 136.26, 134.33, 129.09, 127.95, 127.35, 125.56, 122.86, 121.99, 121.59, 116.30, 87.32, 82.46, 73.12, 70.12; HR-MS (ESI): m/z = 645.1074, calcd. for $C_{34}H_{22}F_6FeN_2O$ $[M+H]^+$: 645.1059.

2,5-Bis(4-methoxyphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3f): Red brown solid; yield: 42 mg (74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.75 (s, 1H), 8.85 (dd, J = 7.5, 1.2 Hz, 1H), 8.58 (dd, J = 4.2, 1.6 Hz, 1H), 8.10 (dd, J = 8.3, 1.5 Hz, 1H), 7.57–7.52 (m, 5H), 7.48 (dd, J = 8.3, 1.2 Hz, 1H), 7.35 (dd, J = 8.3, 4.2 Hz, 1H), 6.74 (d, J = 8.8 Hz, 4H), 4.67 (s, 2H), 4.38 (s, 5H), 3.70 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 158.5, 147.8, 138.5, 136.0, 134.8, 129.9, 128.9, 127.89, 127.43, 121.40, 121.34, 116.1, 113.5, 88.4, 81.5, 77.36, 77.04, 76.7, 72.4, 68.8, 55.1; HR-MS (ESI): m/z = 568.1469, calcd. for $C_{34}H_{28}FeN_2O_3$ $[M]^+$: 568.1444.

2,5-Bis(4-*N*,*N*-dimethylphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3g): Light red solid; yield: 45 mg (76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.82 (s, 1H), 8.88 (d, J = 6.9 Hz, 1H), 8.58 (dd, J = 4.1, 1.4 Hz, 1H), 8.09 (dd, J = 8.2, 1.3 Hz, 1H), 7.60–7.43 (m, 6H), 7.34 (dd, J = 8.2, 4.2 Hz, 1H), 6.57 (d, J = 8.7 Hz, 4H), 4.64 (s, 2H), 4.38 (s, 5H), 2.84 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 149.4, 147.7, 138.7, 135.9, 135.1, 129.5, 127.8, 127.4, 124.6, 121.2, 121.1, 116.1, 112.2, 88.9, 81.3, 72.2, 68.2, 40.5; HR-MS (ESI): m/z = 595.2157, calcd for $C_{36}H_{34}FeN_4O$ $[M+H]^+$: 595.2155.

2,5-Bis(4-chlorophenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3h): Light yellow solid; yield: 33 mg (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.70 (s, 1H), 8.81 (dd, J = 7.2, 1.5 Hz, 1H), 8.57 (dd, J = 4.1, 1.5 Hz, 1H), 8.13 (dd, J = 8.3, 1.5 Hz, 1H), 7.57–7.50 (m, 6H), 7.38 (dd, J = 8.3, 4.2 Hz, 1H), 7.16 (d, J = 8.5 Hz, 4H), 4.74 (s, 2H), 4.38 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 147.9, 138.4, 136.2, 135.4, 134.4, 132.6, 130.0, 128.2, 127.9, 127.3, 121.7, 121.5, 116.2, 87.5, 82.0, 72.8, 69.4; HR-MS (ESI): m/z = 576.0490, calcd. for $C_{32}H_{22}Cl_2FeN_2O$ $[M]^+$: 576.0454.

2,5-Bis(4-iodophenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3i): Yellow solid; yield: 49 mg (64%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.70 (d, J = 16.8 Hz, 1H), 8.79 (dd, J = 7.1, 1.6 Hz, 1H), 8.57 (dd, J = 4.1, 1.4 Hz, 1H), 8.13 (dd, J = 8.3, 1.4 Hz, 1H), 7.57–7.47 (m, 6H), 7.40 (dd, J = 8.2, 4.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 4H), 4.73 (s, 2H), 4.37 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 148.0, 138.4, 137.1, 136.5, 136.2, 134.4, 130.6, 127.9, 127.3, 121.8, 121.6, 116.2, 92.3, 87.6, 82.0, 72.8, 69.4; HR-MS (ESI): m/z = 759.9137, calcd. for $C_{32}H_{22}FeI_2N_2O$ $[M]^+$: 759.9166.

2,5-Bis(4-cyanophenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3j): Yellow brown solid; yield: 33 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.67 (s, 1H), 8.78 (dd, J = 6.6, 2.2 Hz, 1H), 8.54 (dd, J = 4.1, 1.5 Hz, 1H), 8.15 (dd, J = 8.3, 1.5 Hz, 1H), 7.69 (d, J = 8.4 Hz, 4H), 7.61–7.54 (m, 2H), 7.48 (d, J = 8.4 Hz, 4H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H), 4.88 (s, 2H), 4.40 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 148.0, 142.4, 138.3, 136.4, 134.0, 131.8, 129.2, 127.9, 127.4, 122.2, 121.7, 118.8, 116.3, 110.4, 86.8, 82.8, 73.2, 70.3; HR-MS (ESI): m/z = 581.1058, calcd. for $C_{34}H_{22}FeN_4O$ $[M+Na]^+$: 581.1036.

2,5-Bis(4-nitrophenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3k): Dark red solid; yield: 45 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.74 (s, 1H), 8.80 (dd, J = 6.9, 1.9 Hz, 1H), 8.53 (dd, J = 4.2, 1.5 Hz, 1H), 8.13 (dd, J = 8.3, 1.5 Hz, 1H), 8.05 (d, J = 8.8 Hz, 4H), 7.75 (d, J = 8.8 Hz, 4H), 7.56 (q, J = 6.7 Hz, 2H), 7.37 (dd, J = 8.3, 4.2 Hz, 1H), 4.96 (s, 2H), 4.44 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 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, 77.3, 77.0, 76.7, 73.4, 70.6; HR-MS (ESI): m/z = 597.0838, calcd. for $C_{32}H_{22}FeN_4O_5$ $[M-H]^-$: 597.0856.

2,5-Bis(4-acylphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3l): Reddish brown solid; yield: 41 mg (69%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.80 (s, 1H), 8.84 (dd, J = 7.4, 1.3 Hz, 1H), 8.53 (dd, J = 4.2, 1.5 Hz, 1H), 8.11 (dd, J = 8.3, 1.5 Hz, 1H), 7.78 (d, J = 8.4 Hz, 4H), 7.69 (d, J = 8.4 Hz, 4H), 7.61–7.44 (m, 2H), 7.35 (dd, J = 8.3, 4.2 Hz, 1H), 4.89 (s, 2H), 4.41 (s, 5H), 2.48 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.6, 167.3, 147.9, 142.5, 138.4, 136.2, 135.4, 134.4, 128.7, 128.2, 127.9, 127.4, 121.9, 121.5, 116.3, 87.2, 83.1, 73.1, 70.1, 26.5; HR-MS(ESI): m/z = 593.1512, calcd. for $C_{36}H_{28}FeN_2O_3$ $[M+H]^+$: 593.1523.

2,5-Bis(3-methylphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3m): Orange red solid; yield: 53.6 mg (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.77 (s, 1H), 8.84 (dd, J = 7.5, 0.9 Hz, 1H), 8.57 (dd, J = 4.1, 1.5 Hz, 1H), 8.10 (dd, J = 8.3, 1.5 Hz, 1H), 7.55 (t, J = 7.9 Hz, 1H), 7.48 (dd, J = 10.7, 3.9 Hz, 3H), 7.40 (s, 2H), 7.35 (dd, J = 8.3, 4.2 Hz, 1H), 7.09 (t, J = 7.6 Hz, 2H), 6.93 (d, J = 7.5 Hz, 2H), 4.74 (s, 2H), 4.42 (s, 5H), 2.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = ?168.2, 147.8, 138.5, 137.4, 136.84, 136.11, 134.9, 129.6, 127.9, 127.9, 121.6, 127.4, 126.2, 121.4, 116.1, 88.7, 82.4, 72.7, 69.3, 21.4; HR-MS (ESI): m/z = 536.1544, calcd. for $C_{34}H_{28}FeN_2O$ $[M]^+$: 536.1546.

2,5-Bis(3-methoxyphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3n): Red solid; yield: 41 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.90 (s, 1H), 8.88 (d, J = 7.4 Hz, 1H), 8.59 (dd, J = 4.0, 1.3 Hz, 1H), 8.15–8.03 (m, 1H), 7.54 (t, J = 7.9 Hz, 1H), 7.47 (dd, J = 14.9, 7.3 Hz, 1H), 7.35 (dd, J = 8.2, 4.2 Hz, 1H), 7.25 (dd, J = 16.9, 9.2 Hz, 4H), 7.12 (t, J = 7.9 Hz, 2H), 6.69 (dd, J = 8.1, 2.0 Hz, 2H), 4.77 (s, 2H), 4.44 (s, 5H), 3.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 159.1, 147.9, 138.54, 138.40, 136.1, 134.8, 129.0, 127.9, 127.4, 121.57, 121.49, 121.44, 116.1, 114.1, 112.7, 88.3, 82.9, 72.7, 69.2, 55.0; HR-MS (ESI): m/z = 569.1520, calcd. for $C_{34}H_{28}FeN_2O_3$ $[M+H]^+$: 569.1523.

2,5-Bis(3-nitrophenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3o): Red solid; yield: 39 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.67 (s, 1H), 8.77 (dd, J = 7.3, 1.5 Hz, 1H), 8.52 (t, J = 1.8 Hz, 2H), 8.50 (dd, J = 4.2, 1.6 Hz, 1H), 8.12 (dd, J = 8.3, 1.5 Hz, 1H), 8.00 (dd, J = 8.2, 1.3 Hz, 2H), 7.92 (d, J = 7.9 Hz, 2H), 7.53 (dd, J = 8.3, 4.4 Hz, 2H), 7.39–7.31 (m, 3H), 4.93 (s, 2H), 4.46 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 148.1, 148.0, 138.9, 138.3, 136.3, 134.8, 134.0, 129.0, 127.9, 127.4, 123.7, 122.0, 121.8, 121.6, 116.4, 86.8, 82.2, 73.1, 70.3; HR-MS (ESI): m/z = 599.1006, calcd. for $C_{32}H_{22}FeN_4O_5$ $[M+H]^+$: 599.1013.

2,5-Bis(3-methylbenzoate)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3p): Dark brown solid; yield: 44 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.74 (s, 1H), 8.81 (d, J = 7.2 Hz, 1H), 8.51 (d, J = 2.9 Hz, 1H), 8.31 (s, 2H), 8.10 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 3.2 Hz, 4H), 7.58–7.45 (m, 2H), 7.35 (dd, J = 8.2, 4.1 Hz, 1H), 7.24 (t, J = 7.7 Hz, 3H), 4.86 (s, 2H), 4.42 (s, 5H), 3.81 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$): δ = 167.5, 166.9, 147.9, 138.4, 137.3, 136.2, 134.5, 133.2, 129.9, 129.8, 128.2, 128.0, 127.8, 127.4, 121.7, 121.6, 116.3, 87.6, 82.1, 72.9, 69.9, 52.2; HR-MS (ESI): m/z = 647.1269, calcd. for $C_{36}H_{28}FeN_2O_5$ $[M+Na]^+$: 647.1240.

2,5-Bis(3-cyanophenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3q): Yellow brown solid; yield: 27 mg (48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.59 (s, 1H), 8.76 (dd, J = 7.2, 1.5 Hz, 1H), 8.56 (dd, J = 4.1, 1.5 Hz, 1H), 8.13 (dd, J = 8.3, 1.4 Hz, 1H), 7.92 (s, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.60–

7.50 (m, 2H), 7.45–7.36 (m, 3H), 7.27 (t, $J=7.9$ Hz, 2H), 4.82 (s, 2H), 4.42 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 166.6, 148.0, 138.5, 138.3, 136.3, 134.0, 133.3, 132.2, 130.5, 128.9, 127.9, 127.4, 122.0, 121.6, 118.7, 116.3, 112.3, 86.9, 81.9, 73.1, 70.0; HR-MS (ESI): $m/z=581.1026$, calcd. for $C_{34}H_{22}FeN_4O$ $[M+Na]^+$: 581.1036.

2,5-Bis(3,4-dimethylphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3r): Orange yellow solid; yield: 48 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.80$ (s, 1H), 8.86 (dd, $J=$ 7.5, 1.3 Hz, 1H), 8.60 (dd, $J=4.2$, 1.6 Hz, 1H), 8.14 (dd, $J=$ 8.3, 1.6 Hz, 1H), 7.58 (t, $J=7.9$ Hz, 1H), 7.52 (dd, $J=8.2$, 1.2 Hz, 1H), 7.40 (dd, $J=12.0$, 7.9 Hz, 5H), 6.99 (d, $J=$ 7.8 Hz, 2H), 4.74 (s, 2H), 4.44 (d, $J=1.2$ Hz, 5H), 2.15 (d, $J=9.7$ Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.3$, 147.7, 138.6, 136.0, 136.9, 135.0, 135.0, 134.2, 130.1, 129.3, 127.8, 127.4, 126.5, 121.3, 121.2, 116.1, 88.7, 82.2, 72.5, 69.0, 19.7, 19.4; HR-MS (ESI): $m/z=565.1949$, calcd. for $C_{36}H_{32}FeN_2O$ $[M+H]^+$: 565.1937.

2,5-Bis(3,5-dimethyphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3s): Orange solid; yield: 44 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.74$ (s, 1H), 8.80 (dd, $J=$ 7.5, 1.0 Hz, 1H), 8.58 (dd, $J=4.1$, 1.5 Hz, 1H), 8.11 (dd, $J=$ 8.3, 1.5 Hz, 1H), 7.54 (t, $J=7.9$ Hz, 1H), 7.48 (dd, $J=8.2$, 1.0 Hz, 1H), 7.36 (dd, $J=8.3$, 4.2 Hz, 1H), 7.22 (s, 4H), 6.74 (s, 2H), 4.70 (s, 2H), 4.41 (s, 5H), 2.15 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.1$, 147.7, 138.6, 137.2, 136.6, 136.0, 135.0, 128.5, 127.8, 127.4, 126.9, 121.3, 121.2, 116.0, 88.8, 82.4, 72.6, 69.1, 21.2; HR-MS (ESI): $m/z=564.1882$, calcd. for $C_{36}H_{32}FeN_2O$ $[M]^+$: 564.1859.

2,5-Bis(2-methylphenyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3t): Yellow solid; yield: 24 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.10$ (s, 1H), 8.63–8.56 (m, 1H), 8.52 (dd, $J=4.1$, 1.5 Hz, 1H), 8.07–8.00 (m, 3H), 7.38–7.29 (m, 3H), 7.24 (t, $J=7.27$ Hz, 2H), 7.20–7.12 (m, 2H), 7.09 (d, $J=7.4$ Hz, 2H), 4.58 (s, 5H), 4.53 (s, 2H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=167.8$, 147.4, 138.4, 138.3, 135.8, 135.2, 134.9, 132.1, 129.6, 127.7, 127.3, 125.3, 121.1, 120.6, 115.8, 90.9, 78.5, 72.1, 71.5, 20.5; HR-MS (ESI): $m/z=$ 536.1532, calcd. for $C_{34}H_{28}FeN_2O$ $[M]^+$: 536.1546.

2,5-Bis(1-methyl-indol-5-yl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3u): Light yellow solid; yield: 42 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.82$ (s, 1H), 8.87 (dd, $J=$ 7.6, 0.9 Hz, 1H), 8.41–8.31 (m, 1H), 8.00 (dd, $J=8.3$, 1.5 Hz, 1H), 7.93 (t, $J=9.2$ Hz, 2H), 7.55 (dt, $J=5.3$, 2.6 Hz, 2H), 7.51 (t, $J=8.0$ Hz, 1H), 7.41 (dd, $J=8.2$, 0.9 Hz, 1H), 7.21 (dd, $J=12.2$, 8.0 Hz, 1H), 7.11 (d, $J=8.5$ Hz, 2H), 6.94 (d, $J=3.0$ Hz, 2H), 6.39 (d, $J=2.8$ Hz, 2H), 4.77 (s, 2H), 4.46 (s, 5H), 3.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 168.7, 147.6, 138.6, 135.97, 135.81, 135.12, 128.92, 128.34, 127.79, 127.73, 127.39, 123.4, 121.14, 121.10, 121.03, 116.2, 108.6, 101.0, 90.2, 82.4, 72.4, 68.9, 32.7; HR-MS (ESI): $m/z=$ 614.1746, calcd. for $C_{38}H_{30}FeN_4O$ $[M]^+$: 614.1764.

2,5-Bis(1*H*-indol-5-yl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3v): Light yellow solid; yield: 20 mg (34%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.80$ (s, 1H), 8.85 (d, $J=$ 6.8 Hz, 1H), 8.34 (dd, $J=4.1$, 1.5 Hz, 1H), 8.07 (s, 2H), 8.01 (dd, $J=8.2$, 1.4 Hz, 1H), 7.91 (s, 2H), 7.49 (dd, $J=13.0$, 4.8 Hz, 3H), 7.42 (d, $J=7.4$ Hz, 1H), 7.24–7.20 (m, 1H), 7.14 (d, $J=8.5$ Hz, 2H), 7.11–7.05 (m, 2H), 6.44 (s, 2H), 4.75 (s, 2H), 4.43 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 168.8, 147.6, 138.6, 135.8, 135.05, 135.03, 128.1, 127.78, 127.76, 127.3, 124.3, 123.9, 121.1, 121.0, 120.9, 116.1, 110.4, 102.6, 90.2, 82.0, 72.4, 69.1; HR-MS (ESI): $m/z=587.1567$, calcd. for $C_{36}H_{26}FeN_4O$ $[M+H]^+$: 587.1529.

2,5-Bis(2-thiophene)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (3w): Red solid; yield: 29 mg (56%); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=11.16$ (s, 1H), 8.98 (d, $J=7.3$ Hz, 1H), 8.68 (d, $J=2.2$ Hz, 1H), 8.12 (d, $J=8.1$ Hz, 1H), 7.59 (t, $J=7.8$ Hz, 1H), 7.52 (d, $J=8.0$ Hz, 1H), 7.43–7.33 (m, 1H), 7.23 (s, 2H), 7.13 (d, $J=4.7$ Hz, 2H), 6.88–6.73 (m, 2H), 4.79 (s, 2H), 4.51 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=166.9$, 148.0, 139.7, 138.6, 136.2, 134.7, 128.0, 127.52, 127.28, 125.9, 124.6, 121.80, 121.63, 116.4, 82.8, 81.1, 73.3, 69.4; HR.MS (ESI): $m/z=521.0447$, calcd. for $C_{28}H_{20}FeN_2OS_2$ $[M+H]^+$: 521.0440.

General Procedure for Bis-alkylation of *N*-(Quinolin-8-yl)ferrocene-1-carboxamide

N-(Quinolin-8-yl)ferrocene-1-carboxamide (0.1 mmol, 35.6 mg), $Pd(OAc)_2$ (2.24 mg, 10 mol%), Cs_2CO_3 (65.2 mg, 2.0 equiv.), and alkyl iodide (3 equiv.) were added into a mixture of DCE and *tert*-amyl alcohol (0.75 mL + 0.75 mL) in a sealed tube containing a magnetic bead and purged with argon. The reaction mixture was heated at 120 °C for 8–24 h. The reaction mixture was cooled and filtered through celite and the organic layer was extracted with ethyl acetate (10 mL × 3) and washed with water (50 mL). The organic layer passed through Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography.

2,5-Bisethyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (4a): Yellow viscous liquid; yield: 27 mg (66%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.73$ (s, 1H), 8.86 (dd, $J=4.8$, 2.8 Hz, 2H), 8.18 (dd, $J=8.3$, 1.5 Hz, 1H), 7.57 (t, $J=$ 7.9 Hz, 1H), 7.51 (dd, $J=8.2$, 1.3 Hz, 1H), 7.46 (dd, $J=8.3$, 4.2 Hz, 1H), 4.28 (s, 5H), 4.19 (s, 2H), 2.77–2.58 (m, 4H), 1.33–1.14 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.7$, 148.2, 138.6, 136.3, 135.0, 128.1, 127.60, 121.62, 121.10, 116.1, 91.0, 79.2, 70.7, 67.4, 21.8, 15.2; HR-MS (ESI): $m/z=$ 412.1262, calcd. for $C_{24}H_{24}FeN_2O$ $[M]^+$: 412.1233.

2,5-Bismethyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (4b): Light yellow viscous liquid; yield: 26 mg (68%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.67$ (s, 1H), 8.92–8.79 (m, 2H), 8.18 (dd, $J=8.3$, 1.5 Hz, 1H), 7.57 (t, $J=7.9$ Hz, 1H), 7.51 (dd, $J=8.2$, 1.1 Hz, 1H), 7.46 (dd, $J=8.3$, 4.2 Hz, 1H), 4.25 (s, 5H), 4.17 (s, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.8$, 148.2, 138.6, 136.3, 135.0, 128.1, 127.5, 121.61, 121.08, 116.1, 84.2, 79.3, 71.0, 69.7, 14.7 HR-MS (APCI): $m/z=383.0841$, calcd. for $C_{22}H_{20}FeN_2O$ $[M-H]^-$: 383.0842.

2,5-Bis(*n*-propyl)-1-*N*-(quinolin-5-yl)ferrocenamide (4c): Yellow viscous liquid; yield: 20 mg (45.4%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.74$ (s, 1H), 8.91–8.86 (m, 2H), 8.22 (d, $J=8.2$ Hz, 1H), 7.61 (t, $J=7.9$ Hz, 1H), 7.55 (d, $J=$ 8.1 Hz, 1H), 7.50 (dd, $J=8.2$, 4.2 Hz, 1H), 4.30 (s, 5H), 4.22 (s, 2H), 2.83–2.74 (m, 2H), 2.59–2.50 (m, 2H), 1.74–1.61 (m, 4H), 0.96 (t, $J=7.3$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.7$, 148.1, 138.7, 136.3, 135.0, 128.1, 127.6, 121.6, 121.0, 116.1, 89.3, 70.8, 69.7, 68.3, 31.1, 24.4, 14.2; HR-MS (ESI): $m/z=440.1527$, calcd. for $C_{26}H_{28}FeN_2O$ $[M]^+$: 440.1546.

2,5-Bis(*n*-butyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (4d): Yellow orange viscous liquid; yield: 25 mg (53%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.71$ (s, 1H), 8.88–8.80 (m,

2H), 8.18 (dd, $J=8.3$, 1.5 Hz, 1H), 7.57 (t, $J=7.9$ Hz, 1H), 7.53–7.49 (m, 1H), 7.46 (dd, $J=8.3$, 4.2 Hz, 1H), 4.26 (s, 5H), 4.18 (s, 2H), 2.81–2.70 (m, 2H), 2.60–2.49 (m, 2H), 1.67–1.54 (m, 4H), 1.33 (dd, $J=14.8$, 7.4 Hz, 4H), 0.86 (t, $J=7.3$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=164.44$, 142.80, 133.38, 131.04, 129.74, 122.81, 122.30, 116.29, 115.71, 110.80, 84.29, 73.81, 65.49, 62.92, 28.07, 23.34, 17.46, 8.69; HR-MS (ESI): $m/z=468.1888$, calcd. for $C_{28}H_{32}FeN_2O$ $[M]^+$: 468.1859.

2,5-Bis(isopentyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (4e): Yellow viscous liquid; yield: 24 mg (48%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.68$ (s, 1H), 8.85 (dd, $J=6.2$, 2.4 Hz, 2H), 8.18 (dd, $J=8.3$, 1.4 Hz, 1H), 7.57 (t, $J=7.9$ Hz, 1H), 7.53–7.49 (m, 1H), 7.46 (dd, $J=8.3$, 4.2 Hz, 1H), 4.25 (s, 5H), 4.17 (s, 2H), 2.73 (ddd, $J=15.5$, 10.3, 5.4 Hz, 2H), 2.62–2.52 (m, 2H), 1.56–1.42 (m, 6H), 0.86 (t, $J=6.4$ Hz, 12H), ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=169.7$, 148.1, 138.6, 136.3, 135.0, 128.1, 127.6, 121.61, 121.01, 116.0, 89.8, 79.0, 70.8, 67.9, 40.2, 28.1, 26.6, 22.64, 22.52; HR-MS (ESI): $m/z=496.2172$, calcd. for $C_{30}H_{36}FeN_2O$ $[M]^+$: 496.2172.

2,5-Bis(*n*-hexyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (4f): Yellow viscous liquid; yield: 23 mg (44%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.71$ (s, 1H), 8.90–8.82 (m, 2H), 8.21–8.16 (m, 1H), 7.57 (t, $J=7.9$ Hz, 1H), 7.51 (d, $J=7.4$ Hz, 1H), 7.46 (dd, $J=8.2$, 4.2 Hz, 1H), 4.26 (s, 5H), 4.17 (s, 2H), 2.80–2.70 (m, 2H), 2.57–2.48 (m, 2H), 1.61 (dd, $J=20.2$, 7.3 Hz, 4H), 1.37–1.26 (m, 8H), 1.22 (s, 4H), 0.79 (t, $J=6.6$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=169.7$, 148.1, 138.7, 136.3, 135.0, 128.1, 127.6, 121.59, 121.01, 116.1, 89.6, 70.8, 69.7, 68.2, 31.68, 31.13, 29.4, 28.9, 22.6, 14.0; HR-MS (ESI): $m/z=524.2489$, calcd. for $C_{32}H_{40}FeN_2O$ $[M]^+$: 524.2485.

2,5-Bis(*n*-octyl)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (4g): Yellow viscous liquid; yield: 32 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.70$ (s, 1H), 8.92–8.80 (m, 2H), 8.18 (dd, $J=8.3$, 1.4 Hz, 1H), 7.57 (t, $J=7.9$ Hz, 1H), 7.53–7.49 (m, 1H), 7.46 (dd, $J=8.3$, 4.2 Hz, 1H), 4.26 (s, 5H), 4.17 (s, 2H), 2.78–2.71 (m, 2H), 2.58–2.46 (m, 2H), 1.69–1.57 (m, 4H), 1.29 (m, 6H), 1.20 (m, 14H), 0.82 (t, $J=6.9$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.7$, 148.1, 138.6, 136.3, 135.0, 128.1, 127.6, 121.5, 121.0, 116.1, 89.6, 79.1, 70.7, 68.2, 31.8, 31.1, 29.7, 29.4, 29.2, 28.9, 22.6, 14.1; HR-MS (ESI): $m/z=580.3112$, calcd. for $C_{36}H_{48}FeN_2O$ $[M]^+$: 580.3111.

2,5-Bisbenzyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (4h): Yellow viscous liquid; yield: 26 mg (49%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.78$ (s, 1H), 8.85 (dd, $J=7.4$, 1.3 Hz, 1H), 8.81 (dd, $J=4.2$, 1.5 Hz, 1H), 8.19 (dd, $J=8.3$, 1.5 Hz, 1H), 7.58 (t, $J=7.9$ Hz, 1H), 7.53 (dd, $J=8.2$, 1.2 Hz, 1H), 7.47 (dd, $J=8.3$, 4.2 Hz, 1H), 7.29–7.23 (m, 8H), 7.17 (ddd, $J=8.4$, 5.4, 2.6 Hz, 2H), 4.29 (d, $J=7.1$ Hz, 5H), 4.17 (s, 1H), 4.14 (s, 1H), 4.09 (s, 2H), 3.97 (s, 1H), 3.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.1$, 148.2, 140.9, 138.6, 136.4, 134.8, 128.89, 128.30, 128.13, 127.6, 126.0, 121.65, 121.28, 116.3, 88.6, 79.2, 71.2, 69.3, 34.9; HR-MS (ESI): $m/z=536.1563$, calcd. for $C_{34}H_{28}FeN_2O$ $[M]^+$: 536.1546.

2,5-Bis(ethyl acetate)-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (4i): Yellow viscous liquid; yield: 19 mg (36%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.57$ (s, 1H), 8.85–8.72 (m, 2H), 8.19 (dd, $J=8.3$, 1.2 Hz, 1H), 7.59–7.52 (m, 2H), 7.47 (dd, $J=8.2$, 4.2 Hz, 1H), 5.21 (s, 1H), 4.47–4.42 (m, 2H), 4.36 (s, 5H), 4.23 (dtd, $J=10.6$, 7.1, 3.5 Hz, 2H), 4.14–4.07 (m, 2H), 4.00 (d, $J=16.3$ Hz, 1H), 3.68 (d, $J=16.3$ Hz, 1H), 1.26 (d, $J=7.1$ Hz, 3H), 1.18–1.07 (m, 4H); HR-MS (ESI): $m/z=527.1284$, calcd. for $C_{28}H_{28}FeN_2O_5$ $[M]^+$: 527.1264.

General Procedure for Monoalkylation of *N*-(Quinolin-8-yl)ferrocene-1-carboxamide

N-(Quinolin-8-yl)ferrocene-1-carboxamide (0.1 mmol, 35.6 mg), $Pd(OAc)_2$ (2.24 mg, 10 mol%), $NaHCO_3$ (21 mg, 2.5 equiv.), $(BnO)_2POOH$ (8.4 mg, 0.3 equiv.), and alkyl iodide (3 equiv.) were transferred to a sealed tube containing a 1:1 mixture of DCE and *tert*-amyl alcohol (1.5 mL). The reaction mixture was heated at 120 °C for 8–24 h. The reaction mixture was cooled and filtered through celite and the organic layer was extracted with ethyl acetate (10 mL × 3) and the organic layer dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography using silica gel with 5% ethyl acetate and hexane as eluent.

2-Ethyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5a): Yellow orange viscous liquid; yield: 17 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.40$ (s, 1H), 8.86 (dd, $J=4.2$, 1.6 Hz, 1H), 8.79 (dd, $J=7.5$, 1.2 Hz, 1H), 8.17 (dd, $J=8.3$, 1.5 Hz, 1H), 7.56 (t, $J=7.9$ Hz, 1H), 7.51–7.45 (m, 2H), 4.82 (s, 1H), 4.37 (s, 1H), 4.30 (s, 1H), 4.26 (s, 5H), 2.97–2.87 (m, 1H), 2.80–2.71(m, 1H), 1.30–1.25 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=170.0$, 148.2, 138.6, 136.3, 135.0, 128.1, 127.5, 121.6, 120.9, 116.1, 92.4, 75.3, 71.0, 70.3, 68.78, 68.11, 22.0, 15.2; HR-MS (ESI): $m/z=384.0922$, calcd. for $C_{22}H_{20}FeN_2O$ $[M]^+$: 384.0920.

2-*n*-Propyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5b): Yellow viscous liquid; yield: 15 mg (38%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.43$ (s, 1H), 8.90 (dd, $J=4.1$, 1.5 Hz, 1H), 8.84 (d, $J=7.5$ Hz, 1H), 8.21 (dd, $J=8.3$, 1.4 Hz, 1H), 7.59 (t, $J=7.9$ Hz, 1H), 7.55–7.48 (m, 2H), 4.86 (s, 1H), 4.39 (s, 1H), 4.34 (t, $J=2.4$ Hz, 1H), 4.26 (s, 5H), 3.04 (ddd, $J=14.9$, 9.8, 5.4 Hz, 1H), 2.68–2.59 (m, 1H), 1.81–1.73 (m, 1H), 1.70–1.62 (m, 1H), 1.03 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=170.0$, 148.1, 138.6, 136.3, 135.0, 128.1, 127.5, 121.5, 120.8, 116.1, 90.7, 75.3, 71.8, 70.4, 68.7, 68.2, 31.1, 24.5, 14.2; HR-MS (ESI): $m/z=398.1076$, calcd. for $C_{23}H_{22}FeN_2O$ $[M]^+$: 398.1076.

2-*n*-Butyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5c): Yellow orange viscous liquid; yield: 19 mg (46%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.40$ (s, 1H), 8.86 (dd, $J=4.1$, 1.5 Hz, 1H), 8.80 (dd, $J=7.5$, 1.1 Hz, 1H), 8.17 (dd, $J=8.3$, 1.5 Hz, 1H), 7.55 (t, $J=7.9$ Hz, 1H), 7.53–7.43 (m, 2H), 4.82 (s, 1H), 4.35 (s, 1H), 4.29 (t, $J=2.5$ Hz, 1H), 4.25 (s, 5H), 3.03–2.95 (m, 1H), 2.70–2.59 (m, 1H), 1.75–1.64 (m, 1H), 1.42 (dq, $J=14.8$, 7.4 Hz, 2H), 1.27 (dd, $J=13.7$, 5.9 Hz, 1H), 0.99–0.89 (t, $J=7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=170.0$, 148.1, 138.6, 136.3, 135.0, 128.1, 127.5, 121.5, 120.8, 116.1, 90.9, 75.3, 71.7, 70.4, 68.78, 68.19, 33.4, 28.8, 22.8, 14.0; HR-MS (ESI): $m/z=435.1160$, calcd. for $C_{24}H_{24}FeN_2O$ $[M+Na]^+$: 435.1130.

2-*n*-Hexyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5d): Yellow orange viscous liquid; yield: 14 mg (32%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.39$ (s, 1H), 8.86 (d, $J=3.2$ Hz, 1H), 8.79 (d, $J=7.4$ Hz, 1H), 8.17 (d, $J=8.1$ Hz, 1H), 7.55 (t, $J=7.9$ Hz, 1H), 7.51–7.44 (m, 2H), 4.81 (s, 1H), 4.35 (s,

1H), 4.29 (s, 1H), 4.23 (s, 5H), 3.03–2.94 (m, 1H), 2.67–2.59 (m, 1H), 1.73–1.64 (m, 2H), 1.42–1.36 (m, 2H), 1.32–1.27 (m, 4H), 0.86 (t, J=6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=170.0, 148.1, 138.6, 136.3, 135.0, 128.1, 127.5, 121.6, 120.8, 116.1, 90.9, 75.3, 71.7, 70.4, 68.78, 68.19, 31.7, 29.46, 29.07, 22.7, 19.1, 14.1; HR-MS (ESI): m/z=440.1554, calcd. for $C_{26}H_{28}FeN_2O$ $[M]^+$: 440.1546.

2-Octyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5e): Yellow orange viscous liquid; yield: 19 mg (41%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.35 (s, 1H), 8.86 (dd, J=4.1, 1.5 Hz, 1H), 8.79 (dd, J=7.5, 1.1 Hz, 1H), 8.17 (dd, J=8.3, 1.5 Hz, 1H), 7.56 (t, J=7.9 Hz, 1H), 7.51–7.43 (m, 2H), 4.81 (s, 1H), 4.35 (s, 1H), 4.29 (t, J=2.5 Hz, 1H), 4.22 (s, 5H), 3.04–2.92 (m, 1H), 2.68–2.57 (m, 1H), 1.79–1.61 (m, 2H), 1.38 (dd, J=12.8, 5.6 Hz, 2H), 1.28 (m, 8H), 0.84 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=170.0, 148.1, 138.6, 136.3, 135.0, 128.1, 127.5, 121.6, 120.8, 116.1, 90.9, 75.3, 71.7, 70.4, 68.77, 68.19, 31.93, 31.29, 29.80, 29.55, 29.36, 29.07, 22.6, 14.1; HR-MS (ESI): m/z=468.1862, calcd. for $C_{28}H_{32}FeN_2O$ $[M]^+$: 468.1859.

2-Isopentyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5f): Yellow orange viscous liquid; yield: 17 mg (40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.40 (s, 1H), 8.86 (dd, J=4.1, 1.5 Hz, 1H), 8.80 (dd, J=7.5, 1.0 Hz, 1H), 8.17 (dd, J=8.2, 1.4 Hz, 1H), 7.58–7.45 (m, 3H), 4.82 (s, 1H), 4.35 (s, 1H), 4.30 (d, J=2.4 Hz, 1H), 4.23 (s, Hz, 5H), 2.95 (ddd, J=15.4, 10.8, 4.9 Hz, 1H), 2.73–2.64 (m, 1H), 1.69–1.59 (m, 2H), 0.96 (dd, J=10.6, 6.2 Hz, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=170.0, 148.1, 138.6, 136.3, 135.0, 130.9, 127.5, 121.5, 120.8, 116.1, 91.1, 75.3, 71.4, 70.4, 68.8, 68.1, 40.2, 28.1, 27.7, 26.8, 19.1; HR-MS (ESI): m/z=426.1393, calcd. for $C_{25}H_{26}FeN_2O$ $[M]^+$: 426.1389.

2-Methoxyphenyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5g): Yellow orange solid; yield: 10 mg (13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.16 (s, 1H), 8.78 (dd, J=7.6, 1.0 Hz, 1H), 8.43 (dd, J=4.1, 1.6 Hz, 1H), 8.06 (dd, J=8.3, 1.5 Hz, 1H), 7.93 (dd, J=7.5, 1.7 Hz, 1H), 7.50 (t, J=8.1 Hz, 1H), 7.41 (dd, J=8.2, 1.0 Hz, 1H), 7.32 (dd, J=8.3, 4.2 Hz, 1H), 7.21 (td, J=8.2, 1.7 Hz, 1H), 7.06 (td, J=7.5, 0.8 Hz, 1H), 6.61 (t, J=8.2 Hz, 1H), 5.03 (q, J=2.54, 1.6 Hz, 1H), 4.54–4.50 (m, 1H), 4.48 (t, J=2.5 Hz, 1H), 4.32 (s, 5H), 3.47 (s, 3H); HR-MS (ESI): m/z=485.0945, calcd. for $C_{27}H_{22}FeN_2O_2$ $[M+Na]^+$: 485.0923.

3-Cyanophenyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5h): Yellow orange solid; yield: 3.2 mg (4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.29 (s, 1H), 8.75 (dd, J=7.4, 1.3 Hz, 1H), 8.63 (dd, J=4.2, 1.6 Hz, 1H), 8.15 (dd, J=8.3, 1.5 Hz, 1H), 8.00 (s, 1H), 7.87 (d, J=8.0 Hz, 1H), 7.57–7.48 (m, 3H), 7.42 (dd, J=8.3, 4.2 Hz, 1H), 7.34 (t, J=7.8 Hz, 1H), 5.06–5.05 (m, 1H), 4.67–4.62 (m, 1H), 4.56 (t, J=2.6 Hz, 1H), 4.35 (s, 5H); HR-MS (ESI): m/z=487.0785, calcd. for $C_{27}H_{19}FeN_3O$ $[M+Na]^+$: 487.0770.

4-Cyanophenyl-1-*N*-(quinolin-8-yl)ferrocenecarboxamide (5i): Yellow orange solid; yield: 3.2 mg (4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.33 (s, 1H), 8.76 (dd, J=7.4, 1.4 Hz, 1H), 8.62 (dd, J=4.2, 1.5 Hz, 1H), 8.15 (dd, J=8.3, 1.5 Hz, 1H), 7.75 (d, J=8.4 Hz, 2H), 7.58–7.50 (m, 4H), 7.43 (dt, J=6.6, 3.3 Hz, 1H), 5.07–5.06 (m, 1H), 4.72–4.65 (m, 1H), 4.59 (t, J=2.4 Hz, 1H), 4.36 (s, 5H); HR-MS (ESI): m/z=457.0898, calcd. for $C_{27}H_{19}FeN_3O$ $[M]^+$: 457.0872.

General Procedure for the Removal of the 8-Aminoquinoline Directing Ligand

Bis-arylferrocenecarboxamide **3a** (53.6 mg. 0.1 mmol) was dissolved in dry THF (2 mL) under argon. This solution was then added to $Cp_2Zr(H)Cl$ (51.6 mg, 0.2 mmol), at room temperature under argon. After 30 min, the reaction mixture was concentrated under vacuum. The resulting crude solid was purified by column chromatography using silica gel with 5% ethyl acetate in hexane as eluent.

2,5-Bisphenylferrocene-1-carbaldehyde (6a): Yellow viscous liquid; yield: 27 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.30 (d, J=12.2 Hz, 1H), 7.65–7.59 (m, 4H), 7.38–7.27 (m, 6H), 4.92 (s, 2H), 4.23 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=192.75, 135.98, 130.16, 127.96, 127.37, 92.90, 74.27, 72.68; HR-MS (ESI): m/z=389.0628, calcd. for $C_{23}H_{18}FeO$ $[M+Na]^+$: 389.0599..

2,5-Bis(4-trifluoromethylphenyl)ferrocene-1-carbaldehyde (6b): The synthesis of compound **6b** follows the same procedure as **6a** to afford a yellow viscous liquid; yield: 22 mg (44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.26 (s, 1H), 7.72 (d, J=8.1 Hz, 4H), 7.61 (d, J=8.2 Hz, 4H), 5.01 (s, 2H), 4.26 (s, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.76, 139.98, 130.30, 129.68, 125.50, 125.04–124.93(q, CF_3), 91.5, 75.0, 73.2, 72.6; HR-MS (ESI): m/z=525.0335, calcd. for $C_{25}H_{16}F_6FeO$ $[M+Na]^+$: 525.0347.

General Procedure for the Removal of 8-Aminoquinolone Directing Group; Transformation into Ester

A mixture of bis-arylferrocenecarboxamide **3a** (53.6 mg, 0.1 mmol,) and $BF_3{\cdot}OEt_2$ (123 μL, 1.0 mmol) in one mL of MeOH was refluxed for 24 h under a nitrogen atmosphere. After this the reaction mixture was bought to room temperature, then quenched with Et_3N (139 μL, 1.0 mmol) and concentrated under vacuum. The resulting crude solid was purified by column chromatography using silica gel and hexane and ethyl acetate as eluents.

2,5-Bisphenylferrocene-1-methyl carboxylate (7a): Yellow viscous liquid; yield: 23.4 mg (59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.56–7.51 (m, 4H), 7.31 (t, J=7.2 Hz, 4H), 7.29–7.25 (m, 2H), 4.66 (s, 2H), 4.18 (s, 5H), 3.67 (s, 3H); HR-MS (ESI): m/z=396.0827, calcd. for $C_{24}H_{20}FeO_2$ $[M]^+$: 396.0807..

2,5-Bis(4-methoxyphenyl)ferrocene-1-methyl carboxylate (7b): The synthesis of **7b** follows the same procedure as **7a** to afford a yellow solid; yield: 35.6 mg (78%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.46 (d, J=8.7 Hz, 4H), 6.86 (d, J=8.7 Hz, 4H), 4.58 (s, 2H), 4.16 (s, 5H), 3.82 (s, 6H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=171.4, 158.5, 130.2, 129.4, 113.2, 89.5, 74.5, 72.5, 69.5, 55.2, 51.8; HR-MS (ESI): m/z=456.1040, calcd. for $C_{26}H_{24}FeO_4$ $[M]^+$: 456.1019.

Supporting Information

^{1}H, ^{13}C NMR and HR-mass spectra of the synthesized ferrocenecarboxamides **1a–1f** and bisaryl-, alkyl-, monoaryl-, alkylferrocenecarboxamides **2a**, **3a–3w**, **4a–4i**, **5a–5i**, **6a**, **6b**, **7a**, and **7b** and crystal structure data of **3a**, **3i**, **3o**, and **3w**[19] are given in the Supporting Information.

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