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Directed Iron-Catalyzed *ortho*-Alkylation and Arylation: Toward the Stereoselective Catalytic Synthesis of 1,2-Disubstituted Planar-Chiral Ferrocene Derivatives

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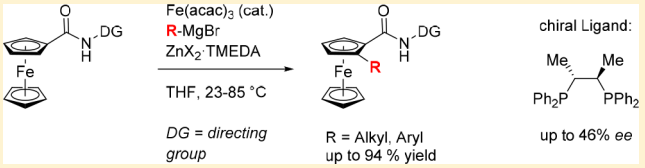
Supporting Information

ABSTRACT: The iron-catalyzed directed *ortho*-functionalization of arenes developed to an important method in the field of C−H activation. On the other hand, the iron-catalyzed *ortho*-functionalization of ferrocenes bearing *ortho*-directing groups (ODGs) has scarcely been investigated. Herein we present the iron-catalyzed *ortho*-alkylation and -arylation of ODG-substituted ferrocenes bearing a bidentate ODG with the formation of racemic 1,2-disubstituted ferrocenes in up to 94% yield. The approach toward an enantioselective iron-catalyzed C−H activation resulted in an *ortho*-phenylation with a promising enantiomeric excess of 46%. The first iron-catalyzed diastereoselective *ortho*-methylation gave an excellent diastereomeric excess of ≥99%.



1. INTRODUCTION

While the electrophilic aromatic substitution has dominated the functionalization of arenes for many years, *ortho*-lithiation in the presence of an *ortho* directing group (ODG) has recently significantly enlarged the toolbox of synthetic methods.[1−3] Application to ferrocene using a chiral ODG afforded planar chiral 1,2-disubstituted ferrocenes with high enantiomeric excess,[4−8] which found widespread use as powerful ligands in asymmetric catalysis.[9] However, this method suffers from the drawback that only a limited range of electrophiles can successfully be used in the functionalization step after the lithiation. Lately, directed catalytic C−H activation at ferrocene derivatives came into play as an alternative for the synthesis of 1,2-disubstituted ferrocene derivatives. The major interest in this context is the development of enantioselective metal-catalyzed C−H activation reactions, and the progress in this field has recently been reviewed.[10−13] For a greater part of the reported catalytic enantioselective C−H functionalizations of ODG-substituted ferrocenes, $Pd(OAc)_2$-catalyzed $C(sp^2)$-$C(sp^2)$ bond-forming reactions were presented, for instance, the highly enantioselective intramolecular *ortho*-alkenylation reported by You et al.[14] A different interesting approach was the enantioselective intramolecular *ortho*-silylation and -germylation without the need of any particular ODG.[15−18]

In addition to palladium, other noble metals were used as metal catalysts (Ir,[19] Rh,[20,21] Au,[22] Pt,[23] Cu[24]). Therefore, the development of enantioselective C−H functionalization reactions of ferrocenes using economically as well as environmentally more benign metal catalysts is desirable. Recently, we reported on the cobalt-catalyzed *ortho*-methylation of ODG-substituted ferrocenes, yielding the 1,2-disubstituted products in racemic form.[25] We note that Yoshikai et al. just provided another example using a cobalt(II) *N*-heterocyclic carbene complex as the catalyst.[26] However, because of the high toxicity of Co(II) salts,[27] the use of iron as metal catalyst is even more preferable.[28−32]

The progress on iron-catalyzed C−H activation reactions of arenes resulting in newly formed C−C bonds was greatly influenced by the work of Nakamura et al. as well as of Ackermann et al. Mainly, the use of Grignard or organozinc reagents enabled the success of these reactions, as they form the catalytically active species by the reaction with the appropriate iron(II)- or iron(III)-salt.[33−42] In addition, Nakamura et al. reported the use of organoborates for the arylation and alkenylation of $C(sp^2)$-H or $C(sp^3)$-H bonds.[43,44] The first example of an iron-catalyzed C−H activation of an ODG-substituted ferrocene was recently presented by Ackermann et al. with the reaction of ferrocenoylamide **5** with allyl chloride to give the allylated 1,2-disubstituted product in 47% yield.[45,46]

Herein, we present an approach toward the unexplored enantioselective iron-catalyzed C−H activation of ODG-substituted ferrocenes bearing a bidentate ODG.[47] Among the investigated substrates was ferrocenoylamide **1** bearing the 8-aminoquinolinyl group, which had been investigated by Daugulis et al. for the first time.[48]

2. RESULTS AND DISCUSSION

In first experiments, the iron-catalyzed *ortho*-benzylation of **1** was investigated by using a catalytic system developed by Nakamura et al.[37] with the difference that the commercially available 2,3-dichlorobutane (DCB, *meso*/*rac* mixture) was used instead of 1,2-dichloro-2-methylpropane (dichloroisobutane, DCIB). With this dichloroalkane acting as a mild oxidant, the transfer of the Grignard substituent to the product is achieved. 1,2-Bis-

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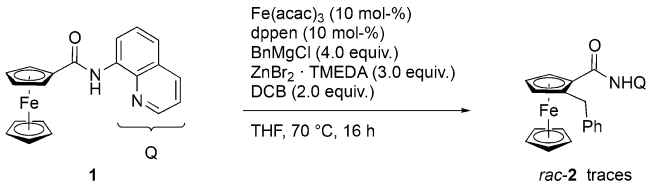
(diphenylphosphino)ethene (dppen) was used as the ligand, and the THF-soluble complex $ZnBr_2$·TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) was used for the in situ formation of the organozinc species together with benzylmagnesium chloride. Unfortunately, only traces of the desired product *rac*-**2** could be observed (Scheme 1).

Scheme 1



After some slight changes [1,2-bis(diphosphino)ethane (dppe) as the ligand, 6.0 equiv instead of 4.0 equiv of the Grignard reagent], *rac*-**2** was isolated but still in a low yield of 11% together with unreacted starting material. Nevertheless, the capability of the adjusted catalytic system was proven even at a slightly lower oil bath temperature of 55 °C (Table 1). The *ortho*-phenylation of **1** delivered the desired 1,2-disubstituted product *rac*-**3** in a very high yield of 85% together with the product of a 2-fold *ortho*-phenylation **4** in 10% yield (Table 1, entry 1).

In contrast to similar known examples of palladium-catalyzed C−H activation reactions at the amide **1**,[49−51] which needed much higher reaction temperatures, the single *ortho*-phenylation product *rac*-**3** prevailed under these conditions as the main product and showed only a low tendency to undergo a second *ortho*-phenylation. This result surpasses the only similar example for a mono *ortho*-arylation of **1**, which gave yields of 4−12%.[49]

The use of dppe and ZnX_2·TMEDA (X = Br, Cl) was crucial as the reaction failed in the absence of either one of them (entries 2−3). $ZnBr_2$·TMEDA gave slightly higher yields for the *ortho*-arylation. Next, the influence of changing the amount of Grignard reagent and $ZnBr_2$·TMEDA was investigated (entries 4−5). Reduction of the amount of $ZnBr_2$·TMEDA to 2.0 equiv gratifyingly increased the yield of the desired product *rac*-**3** to 94%, whereas the formation of the byproduct **4** was limited to 2% yield. A simultaneous decrease of the amount of phenylmagnesium bromide led to a still very high yield of 86% of *rac*-**3**. A ratio of 1:3 between $ZnBr_2$·TMEDA and the Grignard reagent presumably leads to a shift of the respective Schlenk equilibrium to the zincate complex and shows a beneficial effect on the yield in this case. However, this positive outcome was not observed to this extent in the other investigated reactions.

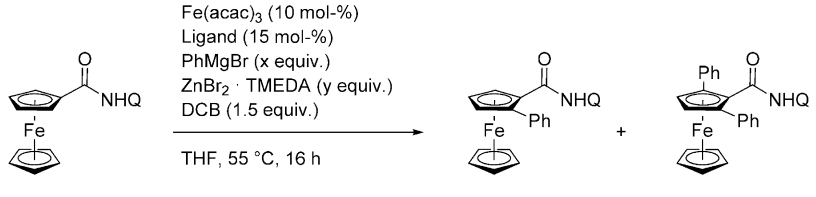
Two further representatives with bidentate ODGs could also successfully be used as the substrate for *ortho*-phenylation (Scheme 2). The triazole-containing TAM-group in **5**, introduced by Ackermann et al.,[45] showed a similar potency as the 8-aminoquinoinyl-group, yielding *rac*-**6** in 84% yield and the byproduct **7** in 14% yield, whereas the PIP-group in **8**, developed by Shi et al.,[52] selectively gave a slightly lower yield of the desired product *rac*-**9** without the observation of the respective diphenylation byproduct. In contrast to this type of iron-catalyzed *ortho*-arylation of arenes, the use of a bidentate ODG substituted ferrocene derivative seemed to be mandatory, as 2-ferrocenylpyridine did not show reactivity under the optimized reaction conditions.

Additional arylmagnesium bromides (ArMgBr) were tested for the *ortho*-arylation of **1** and **5** (Scheme 3). The oil bath temperature was increased to 85 °C in order to ensure a full conversion of the respective starting material, as the product yields were lower at an oil bath temperature of 55 °C. Again, the desired 1,2-disubstituted racemic products were isolated as the main products in yields between 58 and 90%.

After these successful $C(sp^2)$-$C(sp^2)$-bond formation reactions, $C(sp^2)$-$C(sp^3)$-*ortho*-alkylations in addition to the initial *ortho*-benzylation were envisaged. For this purpose, the reactions of **1** with methyl- and with ethylmagnesium bromide were examined (Table 2).

The yield of *rac*-**16** could be improved to 45% by increasing the oil bath temperature from 55 to 85 °C (entries 1−3) At 85 °C reaction temperature, the starting material was completely consumed, and **17** was isolated as the byproduct in low yields. Interestingly, $ZnCl_2$·TMEDA gave a slightly better yield than $ZnBr_2$·TMEDA (entry 4). A further increase of the reaction temperature by using the higher boiling methoxycyclopentane (cyclopentylmethyl ether, CPME)[53] as co-solvent did not improve the yield (entry 5). The use of DCIB instead of DCB lowered the yield by 10% (entry 6). In contrast to the *ortho*-arylation, in spite of a complete consumption of the starting material, the yield of the desired product remained moderate, presumably because of the formation of side products. The *ortho*-methylation of **1** resulted in a moderate yield of *rac*-**18** at 55 °C (entries 7−8) alongside of **19** as the result of a 2-fold *ortho*-methylation. At 70 °C, there was a complete consumption of **1**,

Table 1. Investigations of the *ortho*-Phenylation of 1[a]



entry	ligand (15 mol %)	$ZnBr_2$·TMEDA (equiv)	PhMgBr (equiv)	isolated yield of *rac*-**3** (%)	isolated yield of **4** (%)
1	dppe	3.0	6.0	85	10
2	dppe		6.0		
3		3.0	6.0		
4	dppe	2.0	6.0	94	2
5	dppe	2.0	4.0	86	6

[a]Ferrocenoylamide **1** (0.25 mmol), PhMgBr (3.0 M in Et_2O, 1.5 mmol), $ZnBr_2$·TMEDA (0.75 mmol), $Fe(acac)_3$ (10 mol %), dppe (15 mol %), DCB (0.38 mmol), and THF (2 mL) under inert gas at 55 °C for 16 h.

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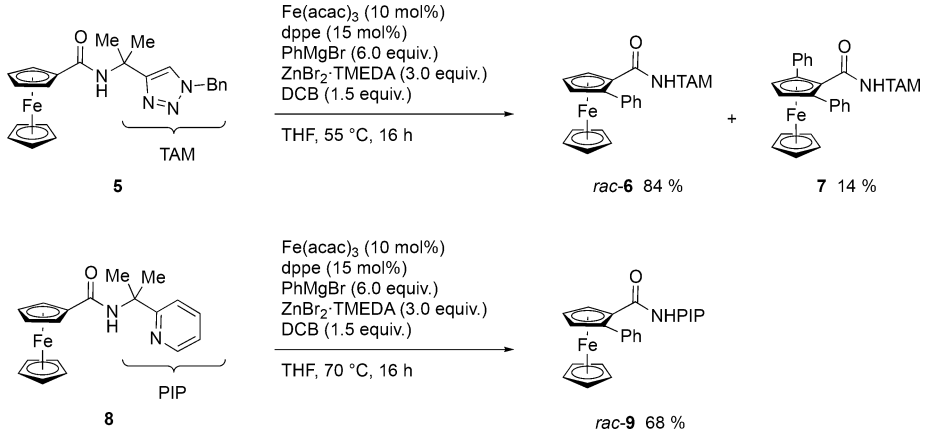
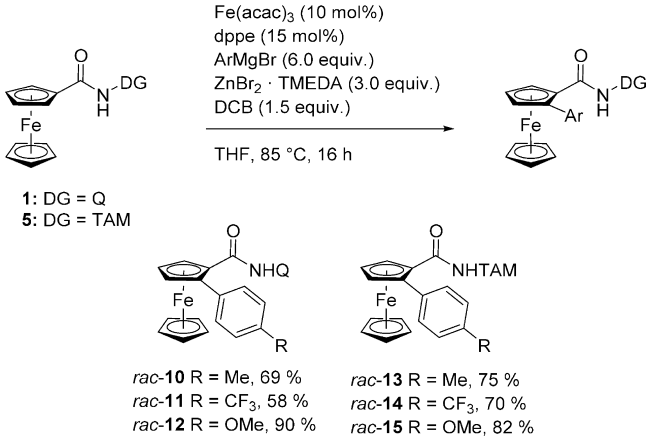
Scheme 2



Scheme 3

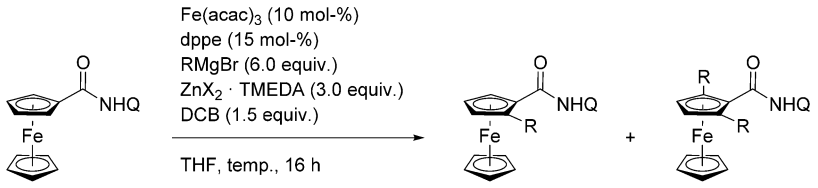


and **19** was obtained as the main product (entry 9), indicating that the catalytic *ortho*-methylation showed a higher reactivity in comparison to the previously tested *ortho*-ethylation. Under the conditions of entry 9, two unexpected side products **20** and *rac*-**21** were isolated and fully characterized (Scheme 4).

These compounds had formed by an unanticipated dehydrogenative dimerization of ferrocene derivative **1**, and in the case of *rac*-**21**, by a subsequent *ortho*-methylation of **20**. The formation of these compounds accounts for the moderate yield of the desired 1,2-disubstituted product *rac*-**18**. Regarding the *ortho*-ethylation under the conditions of entry 3, **20** could also be isolated in 9% yield. It was possible to obtain crystals of **20** suitable for an X-ray crystal structure analysis (Figure 1). Interestingly, **20** exists only in its racemic form. DFT-calculations showed that the *rac*-form is slightly more stable in the ground state than the *meso*-form.[54] The steric hindrance between the 8-aminoquinolinyl and ferrocenyl groups is probably more accentuated in the *meso*-form.

The dehydrogenative dimerization of ODG-substituted arenes, e.g., under cobalt promotion[55] or cobalt,[56] palladium[57,58] or ruthenium catalysis,[59] is well-known but unprecedented in ferrocene chemistry. Jäckle et al. succeeded in the stereoselective Negishi coupling and dimerization of a chiral ferrocenyl sulfoxide.[60] The formation of **20** represents the first example of

Table 2. Optimization of the *ortho*-Ethylation and -Methylation of 1[a]



entry	RMgBr	ZnX_2·TMEDA	oil bath temperature (°C)	product (yield)	product (yield)
1	EtMgBr	X = Br	55	*rac*-**16** (23%)	**17** (0%)
2	EtMgBr	X = Br	70	*rac*-**16** (36%)	**17** (0%)
3	EtMgBr	X = Br	85	*rac*-**16** (45%)	**17** (4%)
4	EtMgBr	X = Cl	85	*rac*-**16** (48%)	**17** (traces)
5[b]	EtMgBr	X = Br	110	*rac*-**16** (39%)	**17** (traces)
6[c]	EtMgBr	X = Cl	85	*rac*-**16** (38%)	**17** (traces)
7	MeMgBr	X = Br	55	*rac*-**18** (38%)	**19** (17%)
8	MeMgBr	X = Cl	55	*rac*-**18** (42%)	**19** (7%)
9	MeMgBr	X = Br	70	*rac*-**18** (22%)	**19** (31%)

[a]Ferrocenoylamide **1** (0.25 mmol), MeMgBr (3.0 M in Et_2O, 1.5 mmol) or EtMgBr (1.0 M in THF, 1.5 mmol), ZnX_2·TMEDA (0.75 mmol), $Fe(acac)_3$ (10 mol %), dppe (15 mol %), DCB (0.38 mmol), and THF (2 mL) under inert gas at 55−85 °C for 16 h. [b]Isolated yields: CPME/THF 1:1 (2 mL) as solvent at 110 °C. [c]Isolated yields: DCIB (0.38 mmol) instead of DCB.

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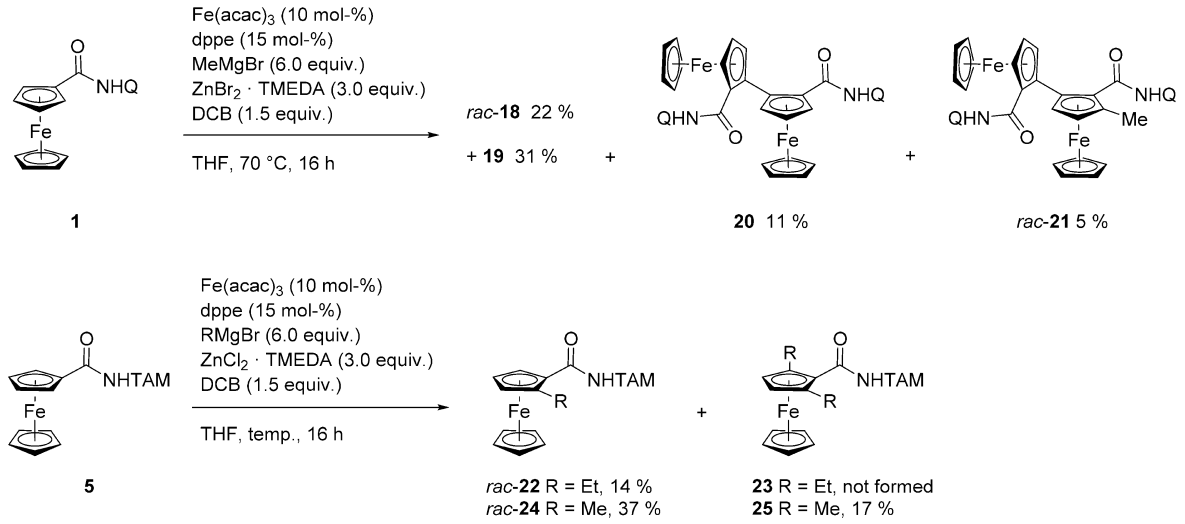
Scheme 4



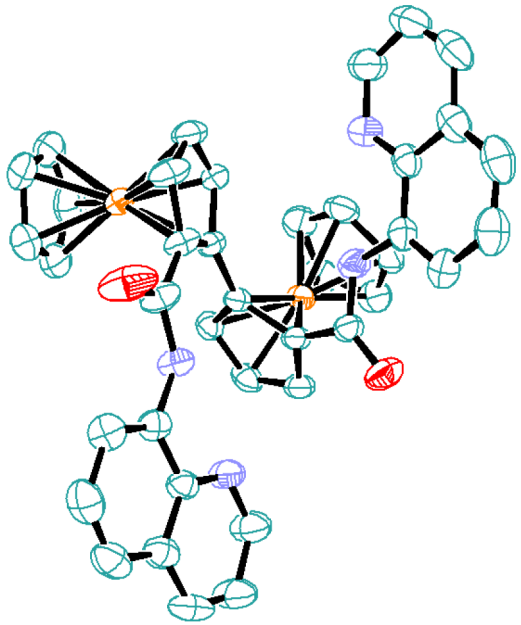


Figure 1. Structure of **20** in the crystal. Hydrogen atoms omitted for clarity; blue (C), orange (Fe), violet (N), red (O) (see Accession Code information).

a dehydrogenative dimerization of an ODG-substituted ferrocene derivative by C−H activation. Further investigations to improve the yield of **20** and to study the mechanistic details are currently underway. With **5** as the starting material, the yields of the desired *ortho* methylation and ethylation products *rac*-**22** and *rac*-**24** were low to moderate, with the difference that products of a dehydrogenative dimerization of **5** could not be identified (Scheme 4).

To improve the yields of the alkylation, a benzylation using the method recently introduced by Cook et al.[61,62] was tested. Treatment of **1** with 10 mol % of $Fe(acac)_3$ in the presence of 15 mol % of dppe, 3.75 equiv of phenylmagnesium bromide, and 3.0 equiv of benzyl chloride afforded 49% of *rac*-**2**. Using the double amount of $Fe(acac)_3$ and of dppe afforded 57% yield, however, the high amount of catalyst makes this less attractive. An attempt toward a methylation resulted in only 22% yield. Thus, the Cook system did not lead to significantly better results for the alkylation.

As the most promising results were obtained with the *ortho*-phenylation of **1** and **5**, respectively, the following attempts toward an enantioselective iron-catalyzed C−H activation were conducted with this reaction (Table 3).

A range of commercially available chiral *P*,*P*-ligands was tested as sources of chirality in the enantioselective C−H activation. It was striking that an alkylchain-backbone was mandatory, as no reaction took place in the presence of (*S*)-BINAP as chiral ligand (entry 1). (*R*,*R*)-Chiraphos has an obvious similarity with dppe and consequently gave the highest yield and enantiomeric excess with either one, **1** and **5**, as starting material. (+)-**3** was obtained in 95% yield and 43% ee, and (+)-**6** was obtained in 89% yield and 46% ee (entries 2−3). Other chiral ligands with an ethylene bridge gave high (entries 6, 10) or low (entry 5) yields, but the measured enantiomeric excesses were not as good as for (*R*,*R*)-Chiraphos. Longer alkyl backbones between the two phosphorus atoms resulted in both poorer yields and enantiomeric excesses. Unfortunately, we had to cope with issues in reproducing the promising results obtained with (*R*,*R*)-Chiraphos as the chiral ligand (entries 2−3). The yields were consistently excellent, but the measured ee fluctuated in a range of 20 to 46%. At 23 °C reaction temperature, the yield was still very good, but the ee did not improve and was 36% ee as the best result of two conducted reactions (entry 4). Besides, different alkyldihalides (DCIB, 1,2-dichloroethane, *trans*-1,2-dichlorocyclohexane) were tested under the conditions of entry 4, all resulting in lower ee than with using DCB. Yet, in an NMR experiment with a slight excess of DCB, we could exclude by integration of the ^{1}H NMR signals of the *meso* and the *rac* diastereoisomers of DCB before and after the reaction that one of them had preferentially been consumed. A deeper understanding of the transfer of chirality into this type of C−H activation is therefore mandatory in order to achieve higher enantioselectivities in a reliable manner. Nevertheless, we could provide an encouraging first example for an enantioselective iron-catalyzed C−H activation of ODG-substituted ferrocenes, and with (*R*,*R*)-Chiraphos as the lead structure, it will presumably be possible to improve the enantioselectivity of this *ortho*-arylation and related *ortho*-functionalization reactions at ferrocenes.

In a second stereoselective approach, we envisaged that a chiral bidentate ODG might lead to a diastereoselective iron-catalyzed

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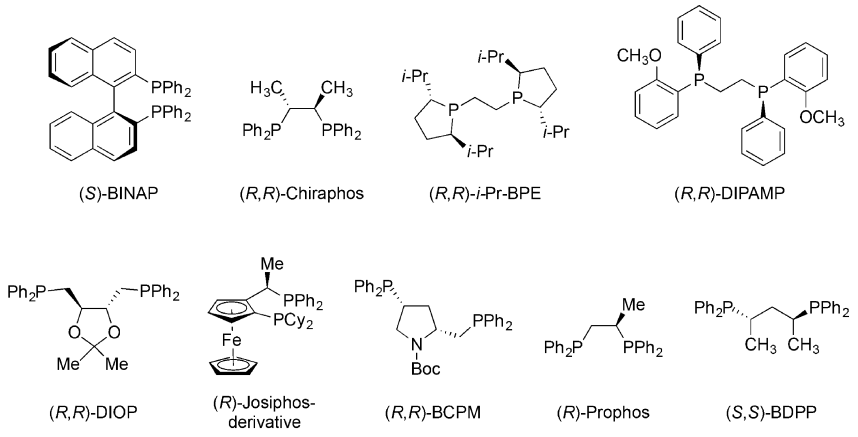
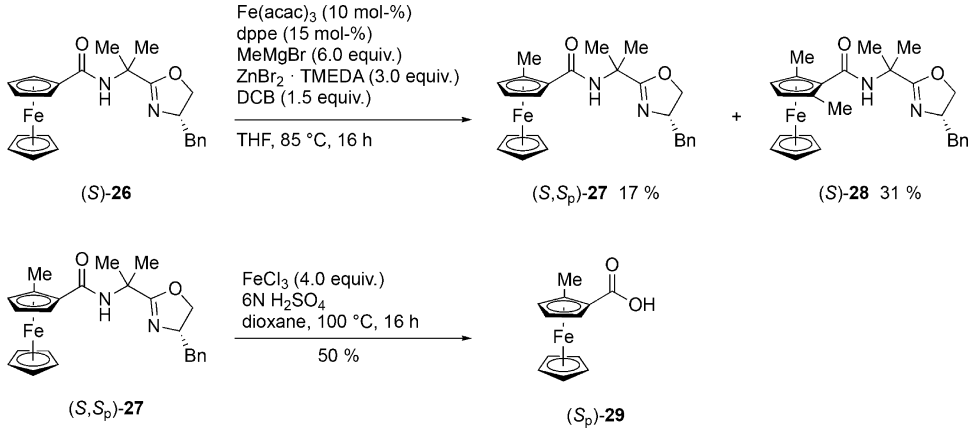
Table 3. Enantioselective *ortho*-Phenylation of 1[a]



entry	ligand	reaction temp (°C)	product (isolated yield)	highest *ee* (%)
1	(*S*)-BINAP	55	no reaction	
2	(*R*,*R*)-Chiraphos	55	**3** (95%)	43
3	(*R*,*R*)-Chiraphos	55	**6** (89%)	46
4	(*R*,*R*)-Chiraphos	23	**6** (89%)	36
5	(*R*,*R*)-*i*-Pr-BPE	55	**6** (13%)	4
6	(*R*,*R*)-DIPAMP	23	**6** (83%)	24
7	(*R*,*R*)-DIOP	55	no reaction	
8	(*R*)-Josiphos derivative	23	**6** (46%)	0
9	(*R*,*R*)-BCPM	55	**6** (traces)	
10	(*R*)-Prophos	23	**6** (81%)	5%
11	(*S*,*S*)-BDPP	55	**6** (traces)	

[a]Ferrocenoylamide **1** (0.2 mmol), PhMgBr (3.0 M in Et_2O, 1.2 mmol), $ZnBr_2$·TMEDA (0.6 mmol), $Fe(acac)_3$ (10 mol %), chiral ligand (15 mol %), DCB (0.3 mmol), and THF (2 mL) under inert gas at 23−55 °C for 16 h. *ee* determined by chiral HPLC.

Scheme 5



ortho-functionalization. The work of Chen et al. inspired us to synthesize the chiral ferrocene derivative (*S*)-**26** in a five-step procedure starting from ferrocenecarboxylic acid and 2-amino-2-methylpropanoic acid[63] and to test this compound as the starting material in the iron-catalyzed C−H activation (Scheme 5). The *ortho*-methylation of (*S*)-**26** at 85 °C with dppe as the ligand

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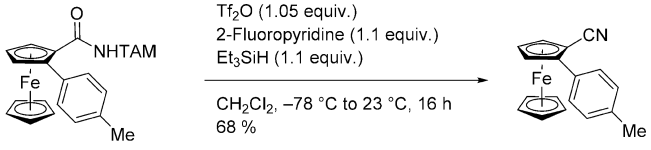
yielded the desired product **27** reproducibly in 17% yield together with dimethylation product (*S*)-**28** in 31% yield and unreacted starting material (45%). Fortunately, the ^{1}H and ^{13}C NMR spectra of **27** showed only one set of signals, respectively. To compare this highly diastereoselective *ortho*-methylation of (*S*)-**26**, a diastereoselective *ortho*-lithiation protocol followed by quenching with methyl iodide was tested. In this case, **27** was obtained in 34% yield in a diastereomeric ratio of 1.7:1 in favor of the diastereomer, which had been formed in the diastereoselective *ortho*-methylation (see Supporting Information). To determine the absolute configuration, **27** was transformed into the literature-known carboxylic acid **29**.[64] The measurement of the specific rotation of the product and the comparison with the reported specific rotation proved that we had (S_p)-**29** in hand. Therefore, (S,S_p)-**27** had been obtained. Unfortunately, the *ortho*-phenylation of (*S*)-**26** under the same conditions as the *ortho*-methylation gave no conversion. This matches our observation in related cobalt catalyzed reactions, which gave only poor yields in attempted phenylations.[25] Yet, (*S*)-**26** is a promising chiral substrate for other diastereoselective metal-catalyzed C−H activation reactions.

The removal of an ODG represents a useful method for subsequent functionalization steps after the desired C−H activation.[65] In this context, we intended to transform the secondary amide *rac*-**13** into an aldehyde by following a protocol developed by Charette et al.[66] (Scheme 6). Remarkably, instead

Scheme 6



rac-**13** rac-**30**

of an aldehyde, the nitrile *rac*-**30** was obtained in 68% yield. The observation of the characteristic IR band for nitriles at 2220 cm^{-1} as well as the ^{1}H and ^{13}C NMR-spectra of *rac*-**30** are fully consistent. Beller et al. reported a similar hydrosilane-mediated dehydration of amides to nitriles.[67]

CONCLUSION

In summary, we were able to achieve the iron-catalyzed *ortho*-functionalization of ODG-substituted ferrocene compounds by directed C−H activation with C(sp^2)-C(sp^2) or C(sp^2)-C(sp^3) coupling. The *ortho*-arylation delivered good to excellent and in general better yields than the conducted *ortho*-alkylation reactions. The moderate yields of the investigated *ortho*-methylation and -ethylation of **1** are explained by the occurrence of an unprecedented dehydrogenative dimerization of the ferrocene derivative and a subsequent *ortho*-alkylation, which lowered the yields of the desired C−H activation. The first enantioselective *ortho*-phenylation of **1** and **5** with (*R*,*R*)-Chiraphos as the chiral ligand gave excellent yields and an enantiomeric excess of up to 46%. Furthermore, the highly diastereoselective *ortho*-methylation of (*S*)-**26** yielded the desired product in ≥99% de, albeit in a low yield. These are the first promising examples for stereoselective iron-catalyzed C−H activation reactions at ferrocenes, and as such the starting point for further studies directed toward enantioselective iron-catalyzed C−H activation, which will include not only phosphane but also *N*-heterocyclic carbene ligands.[26,46]

EXPERIMENTAL SECTION

General Information. All reactions were carried out in an argon atmosphere using the Schlenk technique. Reaction vessels were heated at reduced pressure with a heat gun and flushed with argon prior to use. This procedure was repeated three times. THF was distilled from sodium wire/benzophenone under argon. *N*,*N*,*N*′,*N*′-Tetramethylethane-1,2-diamine (TMEDA) was distilled from CaH_2 and collected in a Schlenk flask over molecular sieves (4 Å) under argon. **1**,[68] **5**,[45] ZnX_2·TMEDA (X = Cl, Br),[69] ferrocenecarboxylic acid,[70] 2-(2-pyridyl)-2-propanamine,[52] and 1,2-dichloro-2-methylpropane (dichloroisobutane, DCIB)[71] were synthesized according to literature procedures. Commercially unavailable Grignard reagents were prepared according to a literature protocol[72] and titrated prior to use.[73] All other chemicals were obtained from commercial sources and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Ultrashield 400 MHz or Ascend 400 MHz (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) instruments. Chemical shifts (δ) are reported in parts per million (ppm) referenced to residual solvent signals as internal standards. ^{19}F NMR spectra were referenced to benzotrifluoride as external standard. IR spectra were measured with a Perkin-Elmer FT 1710 spectrometer; intensities are indicated as br (broad), s (strong), m (medium), and w (weak). High-resolution mass spectra (HRMS) were recorded with a Micromass LCT spectrometer with a lock-spray unit (ESI). Analytical TLC was performed with Merck 60F-254 silica gel thin-layer plates. Column chromatography was performed with J. T. Baker silica gel (60 μm) as the stationary phase. Petroleum ether (bp 40−60 °C) and ethyl acetate as eluents were obtained in analytical reagent grade and used without further purification. Melting points were measured with an Electrothermal IA9000 instrument. Specific rotations were measured with a Perkin-Elmer 341 polarimeter. Chiral HPLC was performed with a Beckmann System Gold (125 Solvent Module, 166 Detector) instrument using a Chiralcel OJ or Chiralcel OD-H column with hexane/2-propanol 9:1 as the eluent and with a flow rate of 0.5 mL/min.

*N-[2-(2-Pyridyl)propan-2-yl]ferrocenoylamide (**8**).* Ferrocenecarboxylic acid (0.96 g, 4.2 mmol) was placed in a Schlenk tube and dissolved in CH_2Cl_2 (40 mL). At 23 °C, oxalyl chloride (0.72 mL, 8.3 mmol) was added dropwise. After the evolution of gas had finished, the reaction mixture was stirred for an additional 30 min. The solvent was removed under reduced pressure. The obtained ferrocenoyl chloride was dissolved in CH_2Cl_2 (15 mL) and subsequently added dropwise at 23 °C to a solution of 2-(2-pyridyl)-2-propaneamine (1.10 g, 8.3 mmol) and pyridine (2.1 mL, 25.8 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 16 h and afterward quenched with satd aq $NaHCO_3$ (15 mL). The aqueous layer was extracted with portions of CH_2Cl_2 (10 mL) until the organic layer was colorless. The combined organic layers were washed with brine (30 mL), dried with $MgSO_4$, filtered, and concentrated at reduced pressure. Column chromatography (30 cm × 5 cm, petroleum ether/ethyl acetate 6:1 to 2:1) afforded **8** (0.87 g, 2.5 mmol, 60%) as a yellow solid (mp 153−155 °C). Spectroscopic data are missing in the literature.[50] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 6H, CH_3), 4.22 (s, 5H, CpH), 4.33 + 4.75 (AA′BB′, 2 × 2H, CpH), 7.23 (dd, J = 7.3, 4.9 Hz, 1H, C_5H_4N), 7.47 (d, J = 8.1 Hz, 1H, C_5H_4N), 7.75 (dt, J = 7.8, 1.7 Hz, 1H, C_5H_4N), 8.24 (br s, 1H, NH), 8.59−8.60 (m, 1H, C_5H_4N) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 27.9 (CH_3), 56.6 [$C(CH_3)_2$], 68.4 ($C_{Cp}H$), 69.9 (C_5H_5), 70.2 ($C_{Cp}H$), 78.2 ($C_{Cp}C$), 119.7 ($C_{Py}H$), 122.0 ($C_{Py}H$), 137.3 ($C_{Py}H$), 147.8 ($C_{Py}H$), 165.0 ($C_{Py}C$), 169.4 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3335 (w), 2970 (w), 1632 (s), 1589 (w), 1570 (w), 1520 (s), 1466 (m), 1431 (m), 1298 (s), 1221 (m), 1105 (m), 1049 (m), 1015 (m), 851 (s), 785 (s), 748 (s), 625 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{19}H_{21}FeN_2O$ [(M + H)$^+$] 349.1003, found 349.1003.

General Procedure (GP) for the Iron-Catalyzed *ortho*-Arylation and -Alkylation. At 23 °C, ferrocenoylamide (0.25 mmol, 1.0 equiv) and $ZnBr_2$·TMEDA (256 mg, 0.75 mmol) or $ZnCl_2$·TMEDA (189 mg, 0.75 mmol) were placed in a Schlenk tube and dissolved in THF (1 mL). The Grignard reagent (1.5 mmol) was added dropwise, and the reaction mixture was stirred for 10 min. A solution of $Fe(acac)_3$ (11 mmol, 0.03 mmol) and dppe (16 mg, 0.04 mmol) in THF (1 mL) was added dropwise with a syringe followed by the addition of

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DCB (40 μL, 0.4 mmol). The reaction mixture was heated for 16 h at 55−85 °C oil bath temperature, then it was cooled to 23 °C. CH_2Cl_2 (5 mL) and satd aq NH_4Cl (5 mL) were added, and the aqueous layer was extracted with portions of CH_2Cl_2 (5 mL) until the organic layer was colorless. The combined organic layers were washed with brine (10 mL), dried with $MgSO_4$, filtered, and concentrated at reduced pressure. The crude product was purified by column chromatography with petroleum ether/ethyl acetate or toluene/ethyl acetate as eluent.

*N-(8-Quinolinyl)-2-benzylferrocenoylamide (rac-**2**).* GP; **1** (90 mg, 0.25 mmol), $ZnCl_2$·TMEDA, and BnMgCl (1.4 M in THF, 1.1 mL, 1.5 mmol) at 70 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 10:1) afforded *rac*-**2** (12 mg, 0.03 mmol, 11%) as an orange oil. ^{1}H NMR (400 MHz, [D_6]acetone): δ = 3.97 (d, J = −14.8 Hz, 1H, CH_2), 4.32 (s, 5H, CpH), 4.41 (ABC, 1H, CpH), 4.44 (ABC, 1H, CpH), 4.48 (d, J = −14.8 Hz, 1H, CH_2), 4.87 (ABC, 1H, CpH), 7.12−7.16 (m, 1H, C_6H_5), 7.22−7.26 (m, 2H, C_6H_5), 7.38 (d, J = 7.4 Hz, 2H, C_6H_5), 7.62−7.66 (m, 3H, C_9H_6N), 8.40 (dd, J = 8.3, 1.6 Hz, 1H, C_9H_6N), 8.81 (dd, J = 7.0 Hz, 1.9 Hz, 1H, C_9H_6N), 8.99 (dd, J = 4.2 Hz, 1.6 Hz, 1H, C_9H_6N), 10.43 (s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, [D_6]acetone): δ = 35.2 (CH_2), 69.2 ($C_{Cp}H$), 69.6 ($C_{Cp}H$), 71.4 (C_5H_5), 73.3 ($C_{Cp}H$), 76.2 ($C_{Cp}C$), 90.9 ($C_{Cp}C$), 116.5 ($C_{Quin}H$), 121.9 ($C_{Quin}H$), 123.0 ($C_{Quin}H$), 126.6 ($C_{Ar}H$), 128.1 ($C_{Quin}H$), 128.9 ($C_{Ar}H$), 129.2 ($C_{Quin}C$), 129.6 ($C_{Ar}H$), 136.0 ($C_{Quin}C$), 137.5 ($C_{Quin}H$), 139.3 ($C_{Quin}C$), 143.1 ($C_{Ar}C$), 149.6 ($C_{Quin}H$), 169.8 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3350 (w), 3026 (w), 2918 (w), 1701 (w), 1665 (s), 1518 (s), 1483 (s), 1423 (s), 1381 (s), 1325 (s), 1244 (m), 1105 (m), 999 (m), 880 (m), 824 (s), 791 (s), 702 (s), 486 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{23}FeN_2O$ [(M + H)$^+$] 447.1160, found 447.1161.

*N-(8-Quinolinyl)-2-phenylferrocenoylamide (rac-**3**) and N-(8-Quinolinyl)-2,5-diphenylferrocenoylamide (**4**).*[54] GP; **1** (90 mg, 0.25 mmol), $ZnBr_2$·TMEDA, and PhMgBr (3 M in Et_2O, 0.5 mL, 1.5 mmol) at 55 °C oil bath temperature; column chromatography (25 × 2.5 cm; toluene/ethyl acetate 20:1).

I: **4** (13 mg, 0.03 mmol, 10%) was isolated as an orange oil, and identified spectroscopically (^{1}H NMR[54]).

II: *rac*-**3** (92 mg, 0.2 mmol, 85%) was isolated as an orange oil.

rac-**3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.34 (s, 5H, CpH), 4.51 (ABC, 1H, CpH), 4.64 (ABC, 1H, CpH), 5.05 (ABC, 1H, CpH), 7.27−7.32 (m, 3H, C_6H_5), 7.36 (dd, J = 8.3, 4.2 Hz, 1H, C_9H_6N), 7.45−7.48 (m, 1H, C_9H_6N), 7.52−7.56 (m, 1H, C_9H_6N), 7.68−7.70 (m, 2H, C_6H_5), 8.10 (dd, J = 8.3, 1.7 Hz, 1H, C_9H_6N), 8.51 (dd, J = 4.2, 1.7 Hz, 1H, C_9H_6N), 8.80−8.82 (m, 1H, C_9H_6N), 10.28 (br s, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 69.2 ($C_{Cp}H$), 70.7 ($C_{Cp}H$), 71.5 (C_5H_5), 73.4 ($C_{Cp}H$), 77.0 ($C_{Cp}C$), 89.5 ($C_{Cp}C$), 116.1 ($C_{Quin}H$), 121.1 ($C_{Quin}H$), 121.5 ($C_{Quin}H$), 127.2 ($C_{Ph}H$), 127.6 ($C_{Quin}H$), 128.0 ($C_{Quin}C$), 128.2 ($C_{Ph}H$), 130.5 ($C_{Ph}H$), 135.0 ($C_{Quin}C$), 136.1 ($C_{Quin}H$), 136.6 ($C_{Ph}C$), 138.6 ($C_{Quin}C$), 147.9 ($C_{Quin}H$), 169.0 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3310 (w), 3051 (w), 1663 (s), 1518 (s), 1481 (s), 1448 (m), 1423 (s), 1383 (m), 1325 (s), 1242 (m), 1123 (m), 1107 (m), 1001 (m), 874 (m), 824 (s), 791 (s), 762 (s), 694 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{26}H_{21}FeN_2O$ [(M + H)$^+$] 433.1003, found 433.1005.

*N-[2-(1-Benzyl-1H-1,2,3-triazol-4-yl)propan-2-yl]-2-phenylferrocenoylamide (rac-**6**) and N-[2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-propan-2-yl]-2,5-diphenylferrocenoyl-amide (**7**).* GP; **5** (120 mg, 0.28 mmol, 1.0 equiv), $ZnBr_2$·TMEDA, and PhMgBr (3 M in Et_2O, 0.57 mL, 1.7 mmol) at 55 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 4:1 to 2:1).

I: 7 (22 mg, 0.04 mmol, 14%) was isolated as an orange oil.

II: *rac*-**6** (118 mg, 0.23 mmol, 84%) was isolated as an orange solid (mp 114.5−115.5 °C).

7: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 (s, 6H, CH_3), 4.18 (s, 5H, CpH), 4.61 (s, 2H, CpH), 5.47 (s, 2H, CH_2), 6.71 (br s, 1H, NH), 7.21−7.25 (m, 8H, C_6H_5), 7.32 (s, 1H, CH), 7.34−7.37 (m, 3H, C_6H_5), 7.51−7.53 (m, 4H, C_6H_5) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.6 (CH_3), 52.0 [$C(CH_3)_2$], 54.2 (CH_2), 68.3 ($C_{Cp}H$), 72.6 (C_5H_5), 83.9 ($C_{Cp}C$), 88.1 ($C_{Cp}C$), 120.9 (CH), 126.9 ($CpC_{Ph}H$), 128.05 ($CpC_{Ph}H$), 128.07 ($CH_2C_{Ph}H$), 128.8 ($CH_2C_{Ph}H$), 129.0 ($CpC_{Ph}H$), 129.2 ($CH_2C_{Ph}H$), 135.0 ($CH_2C_{Ph}C$), 137.1 ($CpC_{Ph}C$), 153.5 (BnNCHC), 167.9 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3397 (w), 2974 (w), 1655 (s), 1601 (m), 1499 (s), 1449 (m), 1362 (m), 1277 (m), 1107 (m), 1049 (m), 1001 (m), 908 (m), 820 (m), 764 (s), 723 (s), 694 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{35}H_{33}FeN_4O$ [(M + H)$^+$] 581.2004, found 581.2000.

rac-**6**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 4.18 (s, 5H, CpH), 4.37 (ABC, 1H, CpH), 4.44 (ABC, 1H, CpH), 4.84 (ABC, 1H, CpH), 5.49 (s, 2H, CH_2), 6.12 (br s, 1H, NH), 7.28−7.37 (m, 8H, C_6H_5), 7.41 (s, 1H, CH), 7.58 (d, J = 7.2 Hz, 2H, Cp-C_6H_5) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.8 (CH_3), 28.2 (CH_3), 51.3 [$C(CH_3)_2$], 54.2 (CH_2), 68.8 ($C_{Cp}H$), 70.6 ($C_{Cp}H$), 71.1 (C_5H_5), 72.9 ($C_{Cp}H$), 76.7 ($C_{Cp}C$), 88.7 ($C_{Cp}C$), 120.8 (CH), 127.5 ($C_{Ph}H$), 128.2 ($C_{Ph}H$), 128.3 ($C_{Ph}H$), 128.7 ($C_{Ph}H$), 129.2 ($C_{Ph}H$), 130.8 ($C_{Ph}H$), 135.0 ($C_{Ph}C$), 136.7 ($C_{Ph}C$), 153.5 (BnNCHC), 169.2 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3374 (w), 3117 (w), 2972 (w), 1638 (s), 1600 (w), 1514 (s), 1503 (s), 1454 (m), 1287 (s), 1217 (m), 1049 (s), 818 (s), 760 (s), 737 (w), 718 (s), 696 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{29}H_{29}FeN_4O$ [(M + H)$^+$] 505.1691, found 505.1685.

*N-[2-(2-Pyridyl)propan-2-yl]-2-phenylferrocenoylamide (rac-**9**).* GP; **8** (90 mg, 0.25 mmol), $ZnBr_2$·TMEDA, and PhMgBr (3 M in Et_2O, 0.5 mL, 1.5 mmol) at 70 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 4:1) afforded *rac*-**9** (75 mg, 0.18 mmol, 68%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.72 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 4.27 (s, 5H, CpH), 4.38 (ABC, 1H, CpH), 4.48 (ABC, 1H, CpH), 4.88 (ABC, 1H, CpH), 7.09−7.11 (m, 1H, C_5H_4N), 7.20−7.30 (m, 3H, C_6H_5), 7.36 (d, J = 8.2 Hz, 1H, C_5H_4N), 7.62−7.68 (m, 3H, C_5H_4N + C_6H_5), 7.84 (br s, 1H, NH), 8.27−8.28 (m, 1H, C_5H_4N) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.5 (CH_3), 27.8 (CH_3), 56.9 [$C(CH_3)_2$], 68.5 ($C_{Cp}H$), 70.5 ($C_{Cp}H$), 71.1 (C_5H_5), 72.6 ($C_{Cp}H$), 78.3 ($C_{Cp}C$), 88.8 ($C_{Cp}C$), 119.4 ($C_{Py}H$), 121.6 ($C_{Py}H$), 127.1 ($C_{Ph}H$), 128.0 ($C_{Ph}H$), 130.6 ($C_{Ph}H$), 136.9 ($C_{Py}H$), 137.0 ($C_{Ph}C$), 147.6 ($C_{Py}H$), 164.6 ($C_{Py}C$), 168.9 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 2930 (w), 2833 (w), 1603 (m), 1557 (w), 1510 (s), 1462 (m), 1439 (m), 1418 (m), 1302 (m), 1246 (s), 1173 (s), 1107 (m), 1032 (s), 957 (m), 816 (s), 779 (m), 750 (m), 441 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{25}FeN_2O$ [(M + H)$^+$] 425.1316, found 425.1316.

*N-(8-Quinolinyl)-2-(4-methylphenyl)ferrocenoylamide (rac-**10**).* GP; **1** (100 mg, 0.28 mmol, 1.0 equiv), $ZnBr_2$·TMEDA, and 4-methylphenylmagnesium bromide (1 M in THF, 1.7 mL, 1.7 mmol) at 85 °C oil bath temperature; column chromatography (25 × 2.5 cm; toluene/ethyl acetate 20:1) afforded *rac*-**10** (86 mg, 0.19 mmol, 69%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 4.34 (s, 5H, CpH), 4.49 (ABC, 1H, CpH), 4.61 (ABC, 1H, CpH), 5.03 (ABC, 1H, CpH), 7.10−7.12 + 7.56−7.58 (AA′BB′, 2 × 2H, C_6H_4), 7.37 (dd, J = 8.2, 4.2 Hz, 1H, C_9H_6N), 7.45−7.48 (m, 1H, C_9H_6N), 7.53 (d, J = 7.9 Hz, 1H, C_9H_6N), 8.11 (dd, J = 8.2, 1.6 Hz, 1H, C_9H_6N), 8.52 (dd, J = 4.2, 1.6 Hz, 1H, C_9H_6N), 8.81 (dd, J = 7.6, 1.3 Hz, 1H, C_9H_6N), 10.30 (br s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 21.3 (CH_3), 69.1 ($C_{Cp}H$), 70.5 ($C_{Cp}H$), 71.4 (C_5H_5), 73.1 ($C_{Cp}H$), 76.9 ($C_{Cp}C$), 89.6 ($C_{Cp}C$), 116.1 ($C_{Quin}H$), 121.0 ($C_{Quin}H$), 121.5 ($C_{Quin}H$), 127.6 ($C_{Quin}H$), 128.0 ($C_{Quin}C$), 128.9 ($C_{Ar}H$), 130.3 ($C_{Ar}H$), 133.4 ($C_{Ar}C$), 135.1 ($C_{Quin}C$), 136.1 ($C_{Quin}H$), 136.9 ($C_{Ar}C$), 138.6 ($C_{Quin}C$), 147.8 ($C_{Quin}H$), 169.2 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3306 (w), 2918 (w), 1661 (s), 1595 (w), 1578 (w), 1516 (s), 1481 (s), 1423 (s), 1381 (s), 1325 (s), 1107 (m), 1101 (m), 874 (m), 816 (s), 789 (s), 486 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{23}FeN_2O$ [(M + H)$^+$] 447.1160, found 447.1161.

*N-(8-Quinolinyl)-2-(4-trifluoromethylphenyl)ferrocenoylamide (rac-**11**).* GP; **1** (100 mg, 0.28 mmol, 1.0 equiv), $ZnBr_2$·TMEDA, and (4-trifluoromethyl-phenyl)magnesium bromide (1 M in THF, 1.7 mL, 1.7 mmol) at 85 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; toluene/ethyl acetate 20:1) afforded *rac*-**11** (81 mg, 0.16 mmol, 58%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.35 (s, 5H, CpH), 4.57 (ABC, 1H, CpH), 4.69 (ABC, 1H, CpH), 5.08 (ABC, 1H, CpH), 7.40 (dd, J = 8.2, 4.2 Hz, 1H, C_9H_6N), 7.48−7.57 (m, 4H, C_6H_4 + C_9H_6N), 7.78−7.80 (AA′BB′, 2H, C_6H_4), 8.14 (dd, J = 8.3, 1.6 Hz, 1H, C_9H_6N), 8.54 (dd, J = 4.2, 1.7 Hz, 1H, C_9H_6N), 8.80 (dd, J = 7.5, 1.4 Hz, 1H, C_9H_6N), 10.30 (br s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 69.8 ($C_{Cp}H$), 71.2 ($C_{Cp}H$), 71.7 (C_5H_5), 73.3 ($C_{Cp}H$), 77.3 ($C_{Cp}C$), 87.4 ($C_{Cp}C$), 116.1 ($C_{Quin}H$), 121.4 ($C_{Quin}H$), 121.7 ($C_{Quin}H$),

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124.5 (q, $J_{C,F}$ = 272 Hz, CF_3), 125.0 (q, $J_{C,F}$ = 3.8 Hz, $C_{Ar}H$), 127.6 ($C_{Quin}H$), 128.1 ($C_{Quin}C$), 129.1 (q, $J_{C,F}$ = 32 Hz, $C_{Ar}CF_3$), 130.5 ($C_{Ar}H$), 134.8 ($C_{Quin}C$), 136.3 ($C_{Quin}H$), 138.5 ($C_{Quin}C$), 141.2 (d, $J_{C,F}$ = 1.5 Hz, $C_{Ar}C$), 148.0 ($C_{Quin}H$), 168.6 (C═O) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −63.39 (s, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 3325 (w), 1736 (w), 1665 (s), 1616 (m), 1518 (s), 1483 (s), 1425 (m), 1321 (s), 1242 (m), 1161 (s), 1119 (s), 1103 (s), 1069 (s), 1001 (m), 843 (s), 791 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{19}FeN_2OF_3Na$ [$(M + Na)^+$] 523.0697, found 523.0697.

*N-(8-Quinolinyl)-2-(4-methoxyphenyl)ferrocenoylamide (rac-**12**).* GP; **1** (90 mg, 0.25 mmol), $ZnBr_2$·TMEDA, and 4-methoxyphenylmagnesium bromide (0.5 M in THF, 3.0 mL, 1.5 mmol) at 85 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 8:1 to 5:1) afforded *rac*-**12** (104 mg, 0.23 mmol, 90%) as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3H, OCH_3), 4.33 (s, 5H, CpH), 4.48 (ABC, 1H, CpH), 4.58 (ABC, 1H, CpH), 5.03 (ABC, 1H, CpH), 6.84−6.86 + 7.60−7.62 (AA′BB′, 2 × 2H, C_6H_4), 7.37 (dd, J = 8.2, 4.2 Hz, 1H, C_9H_6N), 7.45−7.48 (m, 1H, C_9H_6N), 7.52−7.56 (m, 1H, C_9H_6N), 8.11 (dd, J = 8.2, 1.6 Hz, 1H, C_9H_6N), 8.53 (dd, J = 4.2, 1.6 Hz, 1H, C_9H_6N), 8.81 (dd, J = 7.6, 1.2 Hz, 1H, C_9H_6N), 10.29 (br s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 55.4 (OCH_3), 69.0 ($C_{Cp}H$), 70.4 ($C_{Cp}H$), 71.3 (C_5H_5), 73.1 ($C_{Cp}H$), 76.7 ($C_{Cp}C$), 89.5 ($C_{Cp}C$), 113.7 ($C_{Ar}H$) 116.1 ($C_{Quin}H$), 121.0 ($C_{Quin}H$), 121.5 ($C_{Quin}H$), 127.6 ($C_{Quin}H$), 128.0 ($C_{Quin}C$), 128.5 ($C_{Ar}C$), 131.6 ($C_{Ar}H$), 135.1 ($C_{Quin}C$), 136.1 ($C_{Quin}H$), 138.6 ($C_{Quin}C$), 147.8 ($C_{Quin}H$), 159.1 ($C_{Ar}C$), 169.2 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3306 (w), 1734 (w), 1659 (s), 1609 (m), 1516 (s), 1481 (s), 1423 (m), 1381 (m), 1325 (m), 1242 (s), 1175 (m), 1105 (m), 1032 (m), 824 (s), 791 (s), 727 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{27}H_{23}FeN_2O_2$ [$(M + H)^+$] 463.1109, found 463.1110.

*N-[2-(1-Benzyl-1H-1,2,3-triazol-4-yl)propan-2-yl]-2-(4-methylphenyl)ferrocenoyl-amide (rac-**13**).* GP; **5** (120 mg, 0.28 mmol, 1.0 equiv), $ZnBr_2$·TMEDA, and (4-methylphenyl)magnesium bromide (1 M in THF, 1.7 mL, 1.7 mmol) at 85 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 4:1 to 2:1) afforded *rac*-**13** (109 mg, 0.21 mmol, 75%) as a yellow solid (mp 134−136.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 [s, 3H, $C(CH_3)_2$], 1.63 [s, 3H, $C(CH_3)_2$], 2.36 (s, 3H, $ArCH_3$), 4.18 (s, 5H, CpH), 4.36 (ABC, 1H, CpH), 4.42 (ABC, 1H, CpH), 4.83 (ABC, 1H, CpH), 5.49 (s, 2H, CH_2), 6.15 (br s, 1H, NH), 7.13−7.15 + 7.26−7.28 (AA′BB′, 2 × 2H, C_6H_4), 7.33−7.37 (m, 3H, C_6H_5), 7.45−7.47 (m, 3H, C_6H_5 + CH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 21.3 ($ArCH_3$), 27.8 [$C(CH_3)_2$], 28.3 [$C(CH_3)_2$], 51.2 [$C(CH_3)_2$], 54.2 (CH_2), 68.6 ($C_{Cp}H$), 70.5 ($C_{Cp}H$), 71.0 (C_5H_5), 72.8 ($C_{Cp}H$), 76.5 ($C_{Cp}C$), 88.6 ($C_{Cp}C$), 120.9 (CH), 128.1 ($C_{Ph}H$), 128.7 ($C_{Ph}H$), 129.0 ($C_{Ar}H$), 129.2 ($C_{Ph}H$), 130.6 ($C_{Ar}H$), 133.5 ($C_{Ar}C$), 135.0 ($C_{Ph}C$), 137.3 ($C_{Ar}C$), 153.5 (BnNCHC), 169.2 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3404 (w), 2941 (w), 1638 (s), 1506 (s), 1452 (w), 1348 (m), 1267 (m), 1109 (m), 1051 (m), 1001 (m), 814 (s), 766 (m), 718 (s), 498 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{30}H_{31}FeN_4O$ [$(M + H)^+$] 519.1847, found 519.1846.

*N-[2-(1-Benzyl-1H-1,2,3-triazol-4-yl)propan-2-yl]-2-(4-trifluoromethylphenyl)ferrocenoylamide (rac-**14**).* GP; **5** (120 mg, 0.28 mmol, 1.0 equiv), $ZnBr_2$·TMEDA, and (4-trifluoromethylphenyl) magnesium bromide (1 M in THF, 1.7 mL, 1.7 mmol) at 85 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 4:1 to 2:1) afforded *rac*-**14** (112 mg, 0.20 mmol, 70%) as a yellow solid (mp 156−158 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 4.21 (s, 5H, CpH), 4.41 (ABC, 1H, CpH), 4.51 (ABC, 1H, CpH), 4.79 (ABC, 1H, CpH), 5.50 (s, 2H, CH_2), 6.46 (br s, 1H, NH), 7.27−7.29 (m, 2H, C_6H_5), 7.33−7.39 (m, 3H, C_6H_5), 7.41 (s, 1H, CH), 7.52−7.54 + 7.66−7.68 (AA′BB′, 2 × 2H, C_6H_4) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 28.1 (CH_3), 51.6 [$C(CH_3)_2$], 54.3 (CH_2), 69.1 ($C_{Cp}H$), 70.8 ($C_{Cp}H$), 71.4 (C_5H_5), 72.4 ($C_{Cp}H$), 77.9 ($C_{Cp}C$), 86.7 ($C_{Cp}C$), 120.4 (CH), 124.4 (q, $J_{C,F}$ = 272 Hz, CF_3), 124.9 (q, $J_{C,F}$ = 3.8 Hz, $C_{Ar}H$), 128.2 ($C_{Ph}H$), 128.9 ($C_{Ph}H$), 129.0 (q, $J_{C,F}$ = 32 Hz, $C_{Ar}CF_3$), 129.3 ($C_{Ph}H$), 130.4 ($C_{Ar}H$), 134.8 ($C_{Ph}C$), 141.5 (d, $J_{C,F}$ = 1.5 Hz, $C_{Ar}C$), 153.7 (BnNCHC), 168.8 (C═O) ppm. ^{19}F-NMR (376.5 MHz, $CDCl_3$): δ = −63.43 (s, CF_3) ppm. IR (ATR): $\tilde{\nu}$ = 3408 (w), 1643 (s), 1616 (m), 1506 (s), 1325 (s), 1267 (m), 1153 (m), 1121 (s), 1105 (s), 1070 (s), 1049 (s), 841 (s), 824 (s), 775 (m), 719 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{30}H_{28}FeN_4OF_3$ [$(M + H)^+$] 573.1565, found 573.1561.

*N-[2-(1-Benzyl-1H-1,2,3-triazol-4-yl)propan-2-yl]-2-(4-methoxyphenyl)ferrocenoylamide (rac-**15**).* GP; **5** (107 mg, 0.25 mmol), $ZnBr_2$·TMEDA, and 4-methoxyphenylmagnesium bromide (0.5 M in THF, 3.0 mL, 1.5 mmol) at 85 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 4:1 to 2:1) afforded *rac*-**15** (109 mg, 0.20 mmol, 82%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59 [s, 3H, $C(CH_3)_2$], 1.64 [s, 3H, $C(CH_3)_2$], 3.83 (s, 3H, OCH_3), 4.17 (s, 5H, CpH), 4.34 (ABC, 1H, CpH), 4.38 (ABC, 1H, CpH), 4.81 (ABC, 1H, CpH), 5.49 (s, 2H, CH_2), 6.16 (br s, 1H, NH), 6.87−6.89 + 7.50−7.52 (AA′BB′, 2 × 2H, C_6H_4), 7.27−7.28 (m, 2H, C_6H_5), 7.33−7.39 (m, 3H, C_6H_5), 7.43 (s, 1H, CH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 27.8 [$C(CH_3)_2$], 28.3 [$C(CH_3)_2$], 51.2 [$C(CH_3)_2$], 54.2 (CH_2), 55.5 (OCH_3), 68.6 ($C_{Cp}H$), 70.4 ($C_{Cp}H$), 71.0 (C_5H_5), 72.8 ($C_{Cp}H$), 76.3 ($C_{Cp}C$), 88.5 ($C_{Cp}C$), 113.8 ($C_{Ar}H$), 120.9 (CH), 128.2 ($C_{Ph}H$), 128.4 ($C_{Ar}C$), 128.8 ($C_{Ph}H$), 129.2 ($C_{Ph}H$), 131.9 ($C_{Ar}H$), 135.0 ($C_{Ph}C$), 153.5 (BnNCHC), 159.2 ($C_{Ar}C$), 169.3 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3410 (w), 1649 (s), 1609 (w), 1518 (s), 1456 (m), 1244 (s), 1175 (m), 1105 (m), 1047 (m), 1030 (m), 980 (s), 820 (s), 721 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{30}H_{31}FeN_4O_2$ [$(M + H)^+$] 535.1796, found 535.1788.

*N-(8-Quinolinyl)-2-ethylferrocenoylamide (rac-**16**)[54] and N-(8-Quinolinyl)-2,5-diethylferrocenoylamide (**17**).*[51] GP; **1** (135 mg, 0.4 mmol, 1.0 equiv), $ZnBr_2$·TMEDA, and EtMgBr (1 M in THF, 2.4 mL, 2.4 mmol) at 85 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 10:1). Compound **17** (6 mg, 0.01 mmol, 4%) was isolated as an orange oil and identified spectroscopically (^{1}H NMR[55]). Compound *rac*-**16** (65 mg, 0.17 mmol, 45%) was isolated as an orange oil and identified spectroscopically (^{1}H NMR[49]).

*N-(8-Quinolinyl)-2-methylferrocenoylcarbamide (rac-**18**) and N-(8-Quinolinyl)-2,5-dimethylferrocenoylcarbamide (**19**).*[51] GP; **1** (90 mg, 0.25 mmol), $ZnCl_2$·TMEDA, and MeMgBr (3 M in Et_2O, 0.5 mL, 1.5 mmol) at 55 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 10:1).

I: **19** (7 mg, 0.02 mmol, 7%) was isolated as an orange oil and identified spectroscopically (^{1}H NMR[51]).

II: *rac*-**18** (39 mg, 0.11 mmol, 42%) was isolated as an orange oil.

rac-**18**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H, CH_3), 4.25 (s, 5H, C_5H_5), 4.29 (ABC, 1H, CpH), 4.36 (ABC, 1H, CpH), 4.82 (ABC, 1H, CpH), 7.46−7.60 (m, 3H, ArH), 8.19 (dd, J = 8.3 Hz, 1.7 Hz, 1H, ArH), 8.81 (dd, J = 7.2 Hz, 1.9 Hz, 1H, ArH), 8.88 (dd, J = 4.4 Hz, 1.7 Hz, 1H, ArH), 10.43 (bs, 1H, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.9 (CH_3), 68.2 ($C_{Cp}H$), 68.8 ($C_{Cp}H$), 70.7 ($C_{Cp}H$), 73.3 ($C_{Cp}H$), 75.9 ($C_{Cp}C$), 85.7 ($C_{Cp}C$), 116.2 ($C_{Quin}H$), 121.1 ($C_{Quin}H$), 121.7 ($C_{Quin}H$), 127.7 ($C_{Quin}H$), 128.2 ($C_{Quin}C$), 135.1 ($C_{Quin}C$), 136.5 ($C_{Quin}H$), 138.8 ($C_{Quin}C$), 148.4 ($C_{Quin}H$), 170.3 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 3352 (w), 2922 (w), 1665 (s), 1593 (w), 1518 (s), 1483 (s), 1424 (m), 1379 (m), 1325 (m), 1072 (m), 999 (m), 881 (m), 824 (s), 789 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{21}H_{19}FeN_2O$ [$(M + H)^+$] 371.0847, found 371.0848.

*meso-N,N′-Bis(8-quinolinyl)-1,1′-diferrocenoylamide (**20**) and N,N′-Bis(8-quinolinyl)-2-methyl-1,1′-diferrocenoylamide (rac-**21**).* GP; **1** (90 mg, 0.25 mmol), $ZnBr_2$·TMEDA, and MeMgBr (3 M in Et_2O, 0.5 mL, 1.5 mmol) at 70 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 10:1).

I: **19** (29 mg, 0.08 mmol, 31%) was isolated as an orange oil (vide supra).

II: *rac*-**18** (20 mg, 0.06 mmol, 22%) was isolated as an orange oil (vide supra).

III: *rac*-**21** (9 mg, 0.01 mmol, 5%) was isolated as an orange oil.

IV: **20** (20 mg, 0.03 mmol, 11%) was isolated as an orange solid (mp 210 °C, dec.).

20: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.40 (br s, 10H, 2 × C_5H_5), 4.56 (m, 2H, CpH), 5.03 (m, 4H, C_9H_6N), 7.29−7.37 (m, 6H, C_9H_6N), 8.01−8.04 (m, 2H, C_9H_6N), 8.59−8.63 (m, 4H, C_9H_6N), 9.91 (br s, 2H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 69.1 ($C_{Cp}H$), 70.4 ($C_{Cp}H$), 71.2 (C_5H_5), 76.7 ($C_{Cp}H$), 79.7 ($C_{Cp}C$), 83.4 ($C_{Cp}C$), 116.4

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($C_{Quin}H$), 120.7 ($C_{Quin}H$), 121.4 ($C_{Quin}H$), 127.4 ($C_{Quin}H$), 127.9 ($C_{Quin}C$), 134.9 ($C_{Quin}C$), 136.0 ($C_{Quin}H$), 138.6 ($C_{Quin}C$), 147.7 ($C_{Quin}H$), 168.4 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3306 (w), 2918 (w), 1719 (w), 1655 (s), 1518 (s), 1481 (s), 1423 (m), 1383 (m), 1323 (m), 1258 (m), 1143 (m), 1099 (m), 1003 (m), 826 (s), 791 (s), 762 (s), 478 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{40}H_{31}Fe_2N_4O_2$ $[(M + H)^+]$ 711.1146, found 711.1141.

rac-**21**: ^1H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H, CH_3), 4.34 (br s, 10H, 2 × C_5H_5), 4.43 (ABC, 1H, Cp′H), 4.49 (d, J = 2.4 Hz, 1H, CpH), 4.85 (ABC, 1H, Cp′H), 4.90 (d, J = 2.4 Hz, 1H, CpH), 4.99 (ABC, 1H, Cp′H), 7.24−7.25 (m, 2H, C_9H_6N), 7.31−7.39 (m, 4H, C_9H_6N), 8.00 (dd, J = 8.3, 1.7 Hz, 1H, C_9H_6N), 8.06 (dd, J = 8.2, 1.6 Hz, 1H, C_9H_6N), 8.53−8.59 (m, 3H, C_9H_6N), 8.62−8.65 (m, 1H, C_9H_6N), 9.93 (br s, 2H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.1 (CH_3), 68.9 ($C_{Cp}H$), 69.8 ($C_{Cp}H$), 71.0 ($C_{Cp}H$), 71.2 (C_5H_5), 71.9 (C_5H_5), 73.3 ($C_{Cp}H$), 76.5 ($C_{Cp}H$), 79.2 ($C_{Cp}C$), 80.5 ($C_{Cp}C$), 83.2 ($C_{Cp}C$), 84.2 ($C_{Cp}C$), 86.0 ($C_{Cp}C$), 116.0 ($C_{Quin}H$), 116.3 ($C_{Quin}H$), 120.6 ($C_{Quin}H$), 120.7 ($C_{Quin}H$), 121.29 ($C_{Quin}H$), 121.31 ($C_{Quin}H$), 127.3 ($C_{Quin}H$), 127.5 ($C_{Quin}H$), 127.8 ($C_{Quin}C$), 127.9 ($C_{Quin}C$), 134.8 ($C_{Quin}C$), 135.0 ($C_{Quin}C$), 135.9 ($C_{Quin}H$), 136.0 ($C_{Quin}H$), 138.5 ($C_{Quin}C$), 138.6 ($C_{Quin}C$), 147.56 ($C_{Quin}H$), 147.63 ($C_{Quin}H$), 168.4 (C═O), 168.5 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3314 (w), 2922 (w), 1721 (w), 1655 (s), 1518 (s), 1481 (s), 1423 (m), 1381 (m), 1325 (m), 1260 (m), 1107 (m), 1003 (m), 822 (s), 791 (s), 482 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{41}H_{33}Fe_2N_4O_2$ $[(M + H)^+]$ 725.1302, found 725.1304.

Crystal Structure Analysis of ***20****.* Single crystals of **20** were obtained by crystallization from dichloromethane/hexane (1:5). $C_{40}H_{30}Fe_2N_4O_2$, orange plates, M_r = 710.38 g mol^{-1}, crystal system monoclinic, space group $P21/c$, a = 15.3908(9), b = 9.0106(5), c = 22.4692(15) Å, β = 96.489(2)°, V = 3096.1(3) $Å^3$, Z = 4, ρ_{calcd} = 1.524 g cm^{-3}, μ = 0.982 mm^{-1}, crystal size 0.16 × 0.28 × 0.58 mm^3; $F(000)$ = 1464, Bruker Smart X2S diffractometer, T = 199(2) K, Mo Kα radiation (λ = 0.71073 Å), 2.44° ≤ θ ≤ 27.50°, index ranges −19 ≤ h ≤ 19, −11 ≤ k ≤ 11, −26 ≤ l ≤ 29, reflections collected/unique 41150/7102, parameter/restraints 433/0, structure solution, and refinement with SHELXL-2014/7,[74] refinement method full-matrix least-squares, multiscan absorption correction (SADABS), goodness-of-fit on F^2 = 1.037, $R1$ = 0.0426 [$I > 2\sigma(I)$], $wR2$ = 0.0996 (all data), and final difference electron density 0.478 and −0.295 e $Å^{-3}$.

*N-[2-(1-Benzyl-1H-1,2,3-triazol-4-yl)propan-2-yl]-2-ethylferrocenoylamide (rac-****22****).* GP; **5** (120 mg, 0.28 mmol, 1.0 equiv), $ZnCl_2$·TMEDA, and EtMgBr (1 M in THF, 1.7 mL, 1.7 mmol) at 85 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 4:1 to 2:1) afforded *rac*-**22** (18 mg, 0.04 mmol, 14%) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.5 Hz, 3H, CH_2CH_3), 1.82 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.58−2.77 (m, 2H, CH_2CH_3), 4.11 (s, 5H, CpH), 4.14 (ABC, 1H, CpH), 4.23 (ABC, 1H, CpH), 4.46 (ABC, 1H, CpH), 5.52 (br. s, 2H, CH_2), 6.64 (br s, 1H, NH), 7.28−7.40 (m, 5H, C_6H_5), 7.47 (s, 1H, CH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.1 (CH_2CH_3), 22.0 (CH_2CH_3), 28.43 (CH_3), 28.46 (CH_3), 51.7 [$C(CH_3)_2$], 54.4 (CH_2), 67.6 ($C_{Cp}H$), 68.2 ($C_{Cp}H$), 70.3 (C_5H_5), 70.6 ($C_{Cp}H$), 75.6 ($C_{Cp}C$), 92.2 ($C_{Cp}C$), 120.4 (CH), 128.2 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 129.3 ($C_{Ar}H$), 134.9 ($C_{Ar}C$), 154.4 (BnNCHC), 170.6 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 3383 (w), 1636 (s), 1516 (s), 1458 (m), 1045 (m), 1001 (m), 820 (m), 795 (m), 719 (s), 696 (m) cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{29}FeN_4O$ $[(M + H)^+]$ 457.1691, found 457.1688.

*N-[2-(1-Benzyl-1H-1,2,3-triazol-4-yl)propan-2-yl]-2-methylferrocenoylamide (rac-****24****)*[32] *and N-[2-(1-Benzyl-1H-1,2,3-triazol-4-yl)-propan-2-yl]-2,5-dimethylferrocenoylamide (****25****).* GP; **5** (120 mg, 0.28 mmol, 1.0 equiv), $ZnCl_2$·TMEDA, and MeMgBr (3 M in Et_2O, 0.6 mL, 1.7 mmol) at 70 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 4:1 to 2:1).

I: **25** (22 mg, 0.05 mmol, 17%) was isolated as an orange solid (mp 159−161 °C).

II: *rac*-**24** (46 mg, 0.10 mmol, 37%) was isolated as an orange solid, and identified spectroscopically (^1H NMR[25]).

25: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.84 [s, 6H, $C(CH_3)_2$], 2.12 (s, 6H, $CpCH_3$), 4.02 (s, 2H, CpH), 4.05 (s, 5H, CpH), 5.52 (s, 2H, CH_2), 6.96 (br s, 1H, NH), 7.28−7.30 (m, 2H, C_6H_5), 7.35−7.40 (m, 3H, C_6H_5), 7.47 (s, 1H, CH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 14.7 ($CpCH_3$), 28.5 [$C(CH_3)_2$], 51.9 [$C(CH_3)_2$], 54.3 (CH_2), 69.3 ($C_{Cp}H$), 70.9 (C_5H_5), 79.9 ($C_{Cp}C$), 83.8 ($C_{Cp}C$), 120.3 (CH), 128.2 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 129.3 ($C_{Ar}H$), 134.8 ($C_{Ar}C$), 154.3 (BnNCHC), 170.2 (C═O) ppm. IR (ATR): $\tilde{\nu}$ = 1649 (s), 1544 (w), 1499 (s), 1377 (m), 1223 (m), 1192 (m), 1165 (m), 1105 (s), 1049 (s), 1001 (s), 814 (s), 723 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{28}FeN_4ONa$ $[(M + Na)^+]$ 479.1510, found 479.1506.

Enantioselective Phenylation of ***1****.* Table 3, entry 2: GP; **1** (90 mg, 0.25 mmol), $ZnBr_2$·TMEDA (256 mg, 0.75 mmol), (*R*,*R*)-Chiraphos (16 mg, 0.04 mmol), and PhMgBr (3 M in Et_2O, 0.5 mL, 1.5 mmol); column chromatography (25 cm × 2.5 cm, petroleum ether/ethyl acetate 6:1) afforded (+)-**3** (103 mg, 0.24 mmol, 95%) as an orange oil, $[\alpha]_D^{20}$: + 31.6 (c = 1.0, $CHCl_3$ for 43% ee). The enantiomeric excess was determined by HPLC: Daicel Chiralcel OJ, hexane/2-propanol as eluent with a flow rate of 0.5 mL/min, λ = 254 nm, t(minor) = 30.72 min, t(major) = 36.63 min. For details, see Supporting Information. Entry 3: GP; **5** (86 mg, 0.2 mmol), $ZnBr_2$·TMEDA (205 mg, 0.6 mmol), (*R*,*R*)-Chiraphos (13 mg, 0.03 mmol), and PhMgBr (3 M in Et_2O, 0.4 mL, 1.2 mmol); column chromatography (25 cm × 2.5 cm, petroleum ether/ethyl acetate 6:1) afforded (+)-**6** (90 mg, 0.18 mmol, 89%) as an orange solid, $[\alpha]_D^{20}$: + 2.7 (c = 1.0, $CHCl_3$ for 46% ee). Analytical data: see *rac*-**6**. The enantiomeric excess was determined by Daicel Chiralcel OD-H, hexane/2-propanol as eluent with a flow rate of 0.5 mL/min, λ = 254 nm, t(minor) = 48.22 min, t(major) = 54.48 min. For details, see Supporting Information.

*(S)-N-[2-(4-Benzyloxazolin-2-yl)propan-2-yl]ferrocenoylamide [(S)-****26****].* In a Schlenk flask, (*S*)-2-(4-benzyloxazolin-2-yl)-2-propanylisoindoline-1,3-dione (1.22 g, 3.5 mmol) was dissolved in ethanol (25 mL), and NH_2NH_2·H_2O (85%, 0.7 mL, 10.5 mmol) was added. The mixture was heated at 70 °C for 3 h. After cooling to 23 °C, the solvent was evaporated under reduced pressure. The residue was taken up in diethyl ether (20 mL) and filtered. The solvent was evaporated under reduced pressure. The amine was dissolved in CH_2Cl_2 (25 mL), and the solution was cooled to 0 °C. Then, NEt_3 (0.7 mL, 5.3 mmol) was added. In a second Schlenk flask, ferrocenecarboxylic acid (0.81 g, 3.5 mmol) was dissolved in CH_2Cl_2 (25 mL). At 23 °C, oxalyl chloride (0.6 mL, 7.0 mml) was added dropwise. After the evolution of gas had ended, the reaction mixture was stirred for additional 30 min. The solvent was evaporated under reduced pressure. The obtained ferrocenoyl chloride was dissolved in CH_2Cl_2 (20 mL) and subsequently added at 0 °C to the other Schlenk flask. 4-(Dimethylamino)pyridine (DMAP, 20 mg, 0.2 mmol) was added, and the mixture was warmed to 23 °C and stirred for 16 h. The reaction was quenched by addition of water (20 mL). After phase separation, the organic layer was washed with satd aq $NaHCO_3$ (20 mL) and with water (20 mL). The combined aqueous layers were extracted with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine (25 mL), dried with $MgSO_4$, filtered, and concentrated at reduced pressure. Column chromatography (35 cm × 5 cm; petroleum ether/ethyl acetate 4:1 to 1:1) afforded (*S*)-**26** (0.76 g, 1.8 mmol, 51%) as a yellow solid (mp 110−112.5 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.65 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 2.78 (dd, J = −13.7, 7.6 Hz, 1H, CH_2), 3.07 (dd, J = −13.7, 5.4 Hz, 1H, CH_2), 4.10−4.14 (m, 1H, OCH_2), 4.22 (s, 5H, CpH), 4.31−4.35 (m, 3H, OCH_2 and CpH), 4.43−4.50 (m, 1H, NCH), 4.67 (AA′BB′, 2H, CpH), 6.98 (s, 1H, NH), 7.22−7.25 (m, 3H, C_6H_5), 7.30−7.33 (m, 2H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 24.9 (CH_3), 25.1 (CH_3), 41.6 (CH_2), 53.2 [$C(CH_3)_2$], 66.7 (NCH), 68.30 ($C_{Cp}H$), 68.33 ($C_{Cp}H$), 69.9 (C_5H_5), 70.4 ($C_{Cp}H$), 73.1 (OCH_2), 77.0 ($C_{Cp}C$), 126.7 ($C_{Ph}H$), 128.6 ($C_{Ph}H$), 129.6 ($C_{Ph}H$), 137.7 ($C_{Ph}C$), 169.3 (C═O), 171.5 (C═N) ppm. IR (ATR): $\tilde{\nu}$ = 1638 (s), 1521 (s), 1454 (m), 1439 (m), 1383 (m), 1354 (m), 1298 (m), 1217 (m), 1138 (s), 1105 (m), 1024 (m), 1001 (m), 978 (m), 910 (m), 819 (m), 727 (s), 700 (s), 482 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{24}H_{27}FeN_2O_2$ $[(M + H)^+]$ 431.1422 found 431.1419; $[\alpha]_D^{20}$: −12.3 (c = 1.0, $CHCl_3$).

*(S,S$_p$)-N-[2-(4-Benzyl-2-oxazolinyl)propan-2-yl]-2-methylferrocenoylamide [(S,S$_p$)-****27****] and (S)-N-[2-(4-benzyl-2-oxazolinyl)propan-2-yl]-2,5-dimethylferrocenoylamide [(S)-****28****].* GP; (*S*)-**26** (86 mg, 0.20 mmol, 1.0 equiv), $ZnBr_2$·TMEDA, and MeMgBr (3 M in Et_2O, 0.4 mL,

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1.2 mmol) at 85 °C oil bath temperature; column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 3:1 to 1:1).

I: (*S*)-**28** (28 mg, 0.06 mmol, 31%) was isolated as an orange oil.

II: (S,S_p)-**27** (15 mg, 0.03 mmol, 17%, ≥ 99% de) was isolated as an orange oil.

(*S*)-**28**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 [s, 3H, $C(CH_3)_2$], 1.72 [s, 3H, $C(CH_3)_2$], 2.13 (s, 3H, $CpCH_3$), 2.14 (s, 3H, $CpCH_3$), 2.79 (dd, J = −13.8, 7.3 Hz, 1H, CH_2), 3.02 (dd, J = −13.8, 6.0 Hz, 1H, CH_2), 4.03 (s, 2H, CpH), 4.07 (s, 5H, CpH), 4.10−4.14 (m, 1H, OCH_2), 4.33−4.38 (m, 1H, OCH_2), 4.45−4.52 (m, 1H, NCH), 7.22−7.24 (m, 3H, C_6H_5), 7.28−7.32 (m, 2H, C_6H_5), 7.50 (br s, 1H, NH) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 14.63 ($CpCH_3$), 14.67 ($CpCH_3$), 24.7 [$C(CH_3)_2$], 25.0 [$C(CH_3)_2$], 41.7 (CH_2), 53.6 [$C(CH_3)_2$], 66.8 (NCH), 69.19 ($C_{Cp}H$), 69.21 ($C_{Cp}H$), 70.9 (C_5H_5), 73.2 (OCH_2), 80.0 ($C_{Cp}C$), 83.8 ($C_{Cp}C$), 83.9 ($C_{Cp}C$), 126.7 ($C_{Ph}H$), 128.6 ($C_{Ph}H$), 129.5 ($C_{Ph}H$), 137.8 ($C_{Ph}C$), 169.7 (C═O), 171.6 (C═N) ppm. IR (ATR): $\tilde{\nu}$ = 3385 (w), 2922 (w), 1645 (s), 1506 (s), 1450 (s), 1379 (m), 1356 (m), 1146 (s), 1105 (m), 999 (m), 968 (m), 932 (m), 862 (m), 816 (m), 731 (s), 700 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{26}H_{31}FeN_2O_2$ [$(M + H)^+$] 459.1735, found 459.1735; $[\alpha]_D^{20}$: − 3.2 (c = 1.0, $CHCl_3$).

(S,S_p)-**27**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 [s, 3H, $C(CH_3)_2$], 1.68 [s, 3H, $C(CH_3)_2$], 2.26 (s, 3H, $CpCH_3$), 2.80 (dd, J = −13.8, 7.4 Hz, 1H, CH_2), 3.04 (dd, J = −13.8, 5.6 Hz, 1H, CH_2), 4.11−4.14 (m, 2H, OCH_2 and CpH), 4.15 (s, 5H, CpH), 4.22 (ABC, 1H, CpH), 4.32−4.37 (m, 1H, OCH_2), 4.44−4.50 (m, 2H, NCH and CpH), 7.14 (br s, 1H, NH), 7.23−7.25 (m, 3H, C_6H_5), 7.29−7.33 (m, 2H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 14.9 ($CpCH_3$), 24.9 [$C(CH_3)_2$], 25.0 [$C(CH_3)_2$], 41.6 (CH_2), 53.3 [$C(CH_3)_2$], 66.7 (NCH), 67.6 ($C_{Cp}H$), 68.4 ($C_{Cp}H$), 70.4 (C_5H_5), 72.8 ($C_{Cp}H$), 73.1 (OCH_2), 75.9 ($C_{Cp}C$), 85.2 ($C_{Cp}C$), 126.7 ($C_{Ph}H$), 128.6 ($C_{Ph}H$), 129.6 ($C_{Ph}H$), 137.7 ($C_{Ph}C$), 170.2 (C═O), 171.6 (C═N) ppm. IR (ATR): $\tilde{\nu}$ = 2962 (w), 1645 (s), 1510 (s), 1451 (m), 1381 (w), 1356 (m), 1260 (s), 1142 (s), 1103 (s), 1028 (s), 968 (m), 932 (m), 868 (m), 802 (s), 750 (s), 700 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{25}H_{29}FeN_2O_2$ [$(M + H)^+$] 445.1578, found 445.1580. $[\alpha]_D^{20}$: −66.1 (c = 1.0, $CHCl_3$).

*(S_p)-2-Methyl-1-ferrocenecarboxylic Acid [(S_p)-**29**].* (S,S_p)-**27** (40 mg, 0.09 mmol) was dissolved in 1,4-dioxane (1 mL) and 6N H_2SO_4 (1 mL), and $FeCl_3$ (6 mg, 0.36 mmol) was added. The mixture was heated at 100 °C for 16 h. After cooling to 23 °C, ethyl acetate (10 mL) was added. The organic layer was extracted with 2N NaOH (3 × 5 mL). The combined aqueous layers were acidified with conc HCl until pH < 5 and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were washed with brine (5 mL), dried with $MgSO_4$, filtered, and concentrated at reduced pressure. Compound (S_p)-**29** (11 mg, 0.05 mmol, 50%) was obtained as an orange solid and identified spectroscopically (^{1}H NMR[64]); $[\alpha]_D^{20}$: −7.2 (c = 0.1, $CHCl_3$).

*2-(4-Methylphenyl)ferrocene-1-carbonitrile (rac-**30**).* Procedure according to ref 66. *rac*-**13** (190 mg, 0.4 mmol) was dissolved in CH_2Cl_2 (1.5 mL), and 2-fluoropyridine (35 μL, 0.4 mmol) was added. The solution was cooled to −78 °C, then trifluoromethylsulfonic acid anhydride (Tf_2O, 66 μL, 0.4 mmol) was added dropwise and the mixture was stirred for 10 min. The solution was heated to 0 °C and stirred for additional 10 min. Et_3SiH (65 μL, 0.4 mmol) was added dropwise. The solution was stirred at 0 °C for 10 min and after warming to 23 °C for additional 16 h. Then, an aqueous solution of citric acid (0.08 M, 1.5 mL) and THF (1.5 mL) were added. The mixture was heated at 45 °C for 3 h. After cooling to 23 °C, the aqueous layer was extracted with CH_2Cl_2 (3 mL). The combined organic layers were washed with brine (5 mL), dried with $MgSO_4$, filtered, and concentrated at reduced pressure. Column chromatography (25 cm × 2.5 cm; petroleum ether/ethyl acetate 10:1) afforded *rac*-**30** (77 mg, 0.25 mmol, 68%) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H, CH_3), 4.25 (s, 5H, CpH), 4.49 (ABC, 1H, CpH), 4.75 (ABC, 1H, CpH), 4.77 (ABC, 1H, CpH), 7.18−7.20 (m, 2H, C_6H_4), 7.59−7.61 (m, 2H, C_6H_4) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 21.3 (CH_3), 50.8 ($C_{Cp}C$), 70.1 ($C_{Cp}H$), 70.5 ($C_{Cp}H$), 72.2 (C_5H_5), 72.7 ($C_{Cp}H$), 89.8 ($C_{Cp}C$), 120.7 (CN), 127.4 ($C_{Ar}H$), 129.4 ($C_{Ar}H$), 132.5 ($C_{Ar}C$), 137.6 ($C_{Ar}C$) ppm. IR (ATR): $\tilde{\nu}$ = 3096 (w), 2920 (w), 2220 (s), 1524 (m), 1443 (m), 1412 (m), 1107 (m), 1001 (m), 957 (w), 816 (s), 718 (m), 542 (s) cm^{-1}. HRMS (ESI) m/z calcd for $C_{18}H_{16}FeN$ [$(M + H)^+$] 302.0632, found 302.0620.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00799.

Diastereoselective ortho-lithiation of (*S*)-**26**, ^{1}H and ^{13}C NMR spectra of new compounds, enantioselective phenylation of **1** and **5** (PDF)

Accession Codes

CCDC 1566265 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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