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Picolinamide Assisted Oxidation of CH_2 Groups Bound to Organic and Organometallic Compounds Using Ferrocene as a Catalyst

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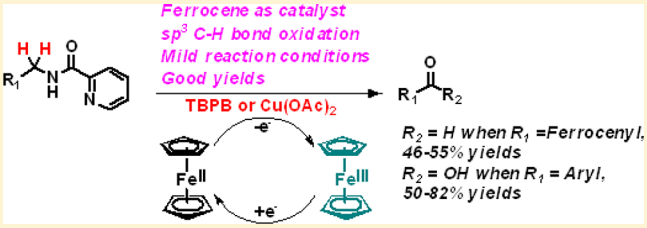
Supporting Information

ABSTRACT: Picolinamide group assisted sp^3 C−H bond oxidation of methylene groups to the corresponding carbonyl compounds has been achieved by using simple bottle ferrocene as catalyst and $Cu(OAc)_2$ or *tert*-butyl peroxybenzoate (TBPB) as oxidant under mild conditions. This method is applicable for picolinamide bound organic as well as organometallic compounds with yields in the range of 46−82%. Control experiments and mechanistic studies indicate that a radical mechanism is responsible for these oxidative transformations in which ferrocene acts as a catalyst.



INTRODUCTION

Oxidation reactions are one of the most important tools for transformation of functional groups in organic synthesis.[1] Among all the oxidized feedstocks, aldehydes and carboxylic acids are needed as bulk chemicals in large amounts in various fields including fine chemicals, polymers, and many commercial products.[2] Direct oxidation of alcohols to the corresponding carbonyl compounds such as ketones, aldehydes, and carboxylic acids have been achieved using various transition metal catalysts as well as metal free catalysts.[3−8] However, direct oxidation of primary amines to carbonyl compounds have rarely been reported.[9] This is due to fact that the direct oxidation of primary amines inherently produces imines during the oxidation process.[10] Recently, Beller and co-workers have reported direct oxidation of benzyl amines to benzamide derivatives using $FeCl_3/ZnCl_2$ as the catalyst and *tert*-butyl hydroperoxide (TBHP) as the oxidant (Scheme 1A) .[9a] The mechanistic studies on this reaction indicated that the free amine or N-protected amine could not be removed from the parent molecules, and as a result the reaction ended up with amide derivatives. Therefore, synthesis of aldehydes and carboxylic acids are not possible using this approach. Recently, we have developed a directing group assisted Ru-catalyzed C−H bond oxidation to the corresponding aldehydes (Scheme 1B).[11] However, this method was found to be applicable only on methylene units bound to sandwich compounds and required the relatively expensive organometallic compound $[(RuCl_2(p\text{-cym})]_2$ as the catalyst.

Ferrocene is one of the most stable, readily available, and inexpensive organometallic compounds. Functionalized ferrocenes have attracted the attention of chemists of various disciplines due to their applications as pharmaceuticals, biosensors, fuel additives, and most importantly as ligands in asymmetric synthesis.[12−14] Recently, use of ferrocene derivatives in the field of electroactive materials such as semiconductors, conducting polymers, and charge storage materials have also been reported.[15,16] However, only a handful of reports exist indicating the use of nonfunctionalized ferrocene as a catalyst for organic transformations.[17−19] Mao and co-workers have reported ferrocene catalyzed decarboxylative cross coupling with toluene.[17] Ferrocene has also been used in catalytic amounts for the borylation of diazonium salts.[18] Baran and co-workers have reported ferrocene catalyzed C−H imidation of arenes.[19] Recently, we have reported oxidation of primary amines to imines using ferrocinium hexafluorophosphate.[20] However, to the best of our knowledge simple ferrocene or functionalized ferrocene has never been used as catalyst for such oxidation reactions.

Herein, we report ferrocene catalyzed oxidation of picolinamide bound CH_2 groups of organic and organometallic compounds using TBPB or $Cu(OAc)_2$ as the oxidant (Scheme 1). To the best of our knowledge, this represents an unprecedented use of a picolinamide directing group as well as ferrocene for the oxidation of sp^3 CH_2 units bound to the phenyl ring or Cp ring of metal sandwich compounds.

RESULTS AND DISCUSSION

Picolinamide is a well-known bidentate directing group for transition metal catalyzed C−H functionalization in organic synthesis.[21a,d,e] The picolinamide group, in the pioneering report by Daugulis in 2005, demonstrated excellent directing abilities that enable various types of functionalization including arylation, alkylation and alkenylation of aromatic and aliphatic substrates. In addition, picolinamide directed C−C, C−Se, C−Ge bond formation has also been reported.[21,22] Recently, we have reported picolinamide directed sp^3 C−H bond oxidation

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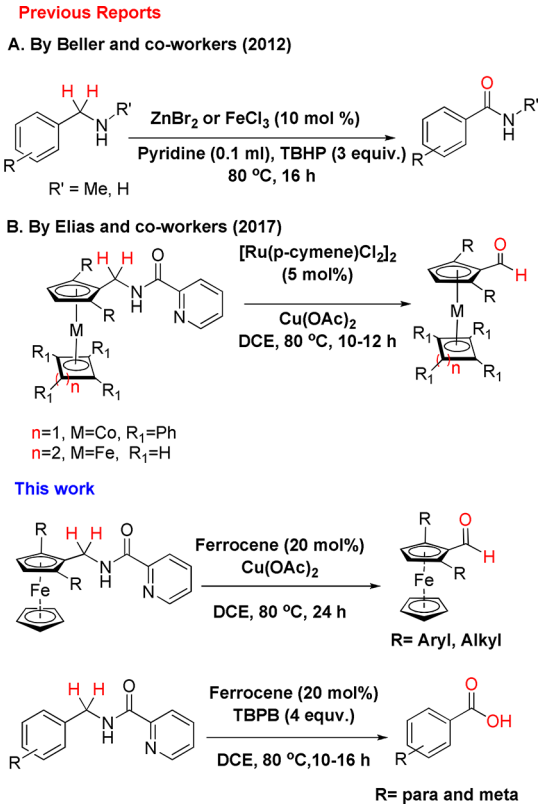
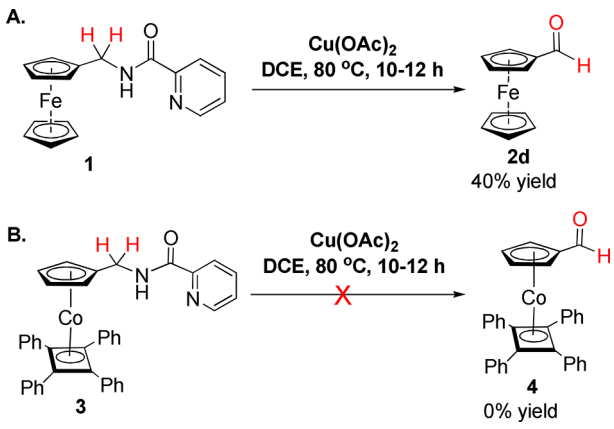
Scheme 1. Comparison of Reported Methods for C−H Bond Oxidation to Carbonyl Compounds of Organic and Organometallic Sandwich Compounds with the Present Study



of metal sandwich compounds using ruthenium *para*-cymene as a catalyst and $Cu(OAc)_2$ as an oxidant.[11]

During these studies, we observed that ferrocene derived picolinamides were undergoing oxidation even in the absence of the Ru-catalyst (Scheme 2A). However, there was no such oxidation when the picolinamide derived cobalt sandwich compound $[\eta^5\text{-}(CH_2R)C_5H_4]Co(\eta^4\text{-}C_4Ph_4)$ (R = Picolinamido) was used along with $Cu(OAc)_2$ (Scheme 2B). This observation indicated that ferrocene unit has some role to play in this oxidation. Therefore, detailed studies were undertaken to find out the possibility of using ferrocene as catalyst for this oxidation.

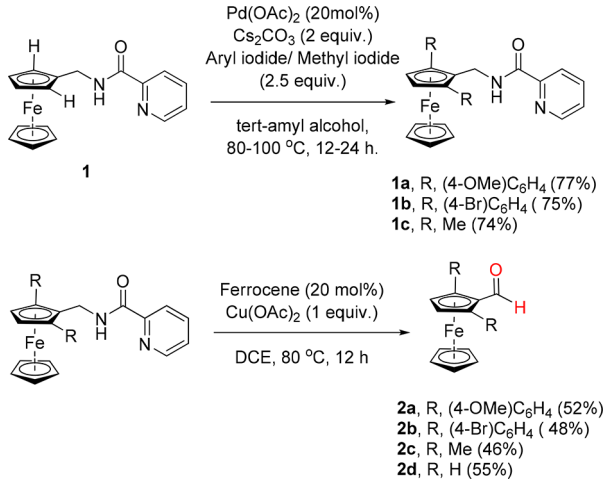
Scheme 2. Differences in the $Cu(OAc)_2$ Oxidation of Picolinamide Derived Iron and Cobalt Sandwich Compound



After detailed studies (Table S1−S2 in the Supporting Information) it was found that 20 mol % ferrocene brings out this sp^3 C−H bond oxidation most effectively.

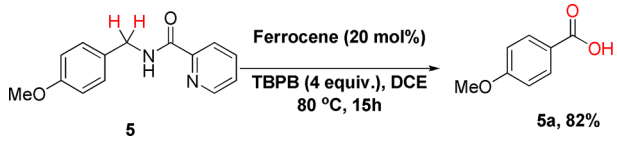
We performed sp^2 C−H bond activation reactions with the ferrocene picolinamides and sp^3 C−H bond oxidation in a stepwise manner and also as a one pot method. This reaction worked well with both α,α-bis-alkyl and α,α-bis-aryl substituted picolinamides (Scheme 3, **2a−2c**).

Scheme 3. Substrate Scope for sp^2 C−H Bond Functionalization and sp^3 C−H Bond Oxidation on Ferrocene



We were keen to explore this method for the oxidation of CH_2-units bound to an organic substrate. First we tried out the oxidation reactions of benzylic picolinamides under identical reaction conditions (Scheme 3). However, this reaction did not yield the target product and we recovered the benzyl picolinamide. We assumed that oxidant may be playing a significant role in this transformation. Therefore, we varied the oxidants to attempt oxidation of the CH_2 unit of the picolinamide. We chose 4-methoxybenzyl picolinamide as the model compound for optimization studies, and after several reactions, it was found that ferrocene (20 mol %) and *tert*-butyl peroxybenzoate (TBPB) work well for this transformation (Scheme 4). However, in this case we obtained 4-methoxy benzoic acid as the final product which may have resulted due to the reactivity of corresponding benzaldehyde under this reaction condition. The effect of reaction parameters were also optimized (Table S3−S7 in the Supporting Information). On the basis of isolated yields, it was observed that DCE was the most appropriate solvent for the reaction with TBPB as oxidant and ferrocene as the catalyst at 80 °C (Scheme 4).

Scheme 4. Optimized Reaction Conditions for Oxidation of 4-Methoxy Benzyl Picolinamide to Its Carboxylic Acid



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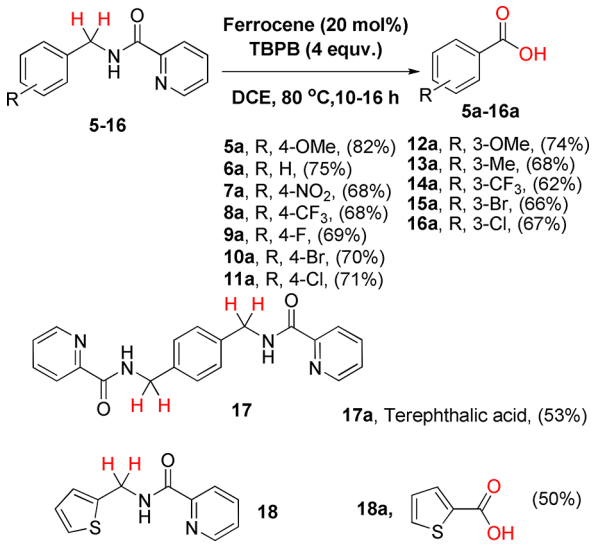
After optimizing the reaction conditions, we were keen to explore the substrate scope for this reaction. The reaction was found to work well with *para* as well as *meta*-substituted benzylamines (Scheme 5).

Scheme 5. Substrate Scope for the Oxidation of Benzyl Picolinamide to Corresponding Carboxylic Acids

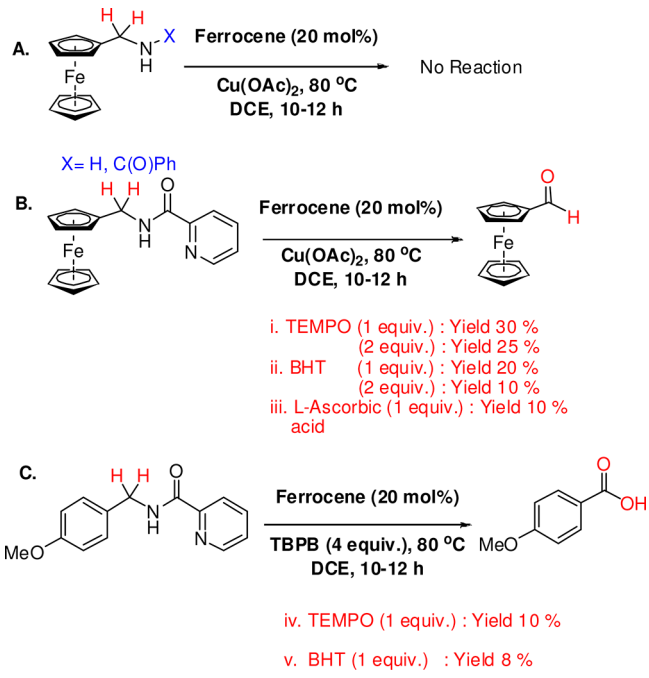


We observed that yields are slightly better for *para* substituted products. Both electron rich and electron poor benzylamines gave good to moderate yields of benzoic acids. The study was extended to a few amines of higher complexity as well. However, *ortho*-substituted benzyl picolinamides were unreactive under this optimized reaction conditions possibly due to steric constraints. Compounds substituted at the benzylic position were also unresponsive under this optimized reaction condition.

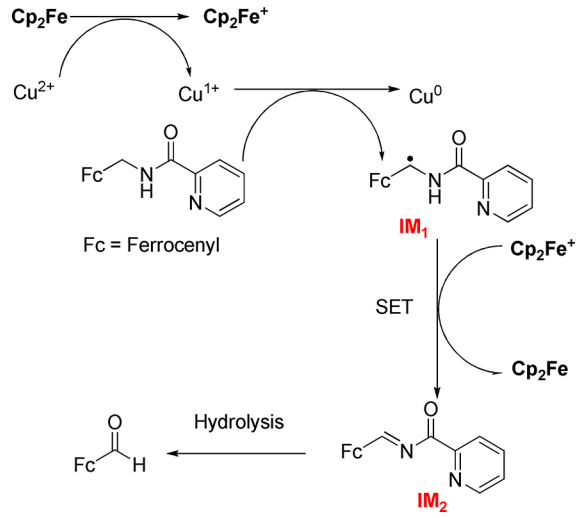
Proposed Mechanism for sp^3 C−H Bond Oxidation. To investigate the possible reaction mechanism for the sp^3 C−H bond oxidation, we have carried out some control experiments (Scheme 6).

Since, single electron transfer (SET) can be a possible mechanistic pathway for the sp^3 C−H bond oxidation reaction, we have carried out this reaction in the presence of radical inhibitors. When performed in the presence of TEMPO ((2,2,6,6-tetramethylpiperidine-1-yl)oxyl) as additive (1−2 equiv), **1** reacted to give aldehyde **2** in 30% and 25% yields, respectively (Scheme 6B). We have also performed the reaction with 1 and 2 equiv of BHT (butylated hydroxytoluene), which gave aldehyde **2** in 20% and 10% yields, respectively. Reaction of **1** with 1 equiv of L-ascorbic acid gave 10% yield of the aldehyde **2**. This study indicates that a free radical process is involved in the oxidation of picolinamide to aldehyde. Picolinamide group does play an important role in this oxidation, as changing the picolinamide directing group with aminomethyl group or the benzamide derivative of metal sandwich compounds, the oxidation reactions are unresponsive (Scheme 6A). On the basis of our observation and related studies, we have proposed a possible catalytic cycle as shown in Scheme 7. At the outset Cu^{2+} oxidizes ferrocene to ferrocinium and itself gets reduced to Cu^{1+} in a redox reaction, which was confirmed by UV studies (Supporting Information Page S7). Then Cu^{1+} abstracts a proton from C−H bond of ferrocene picolinamide to form the radical intermediate **IM1**. Afterward

Scheme 6. Control Experiments for Ferrocene Catalyzed sp^3 C−H Bond Oxidation



Scheme 7. Proposed Reaction Mechanism for Ferrocene Catalyzed sp^3 C−H Bond Oxidation of Metal Sandwich Compounds



IM1 is converted to an iminium intermediate **IM2**, in the presence of $FeCp_2^+$ by a single electron transfer (SET) reaction. Thereafter **IM2** undergoes hydrolysis to form the aldehyde.

Reaction of **5**, an organic substrate with equivalent amount of TEMPO and BHT gave 10% and 8% yields of corresponding acid respectively (Scheme 6C). A sharp decrease in yield indicated that the reaction mechanism goes through a radical process. We have carried out a UV study (Supporting Information Page S7−S8) of the reaction mixture, we observed the presence of the ferrocinium ion from its characteristic peak. On the basis of our observations and control experiments, we have proposed a possible mechanism (Scheme 8).

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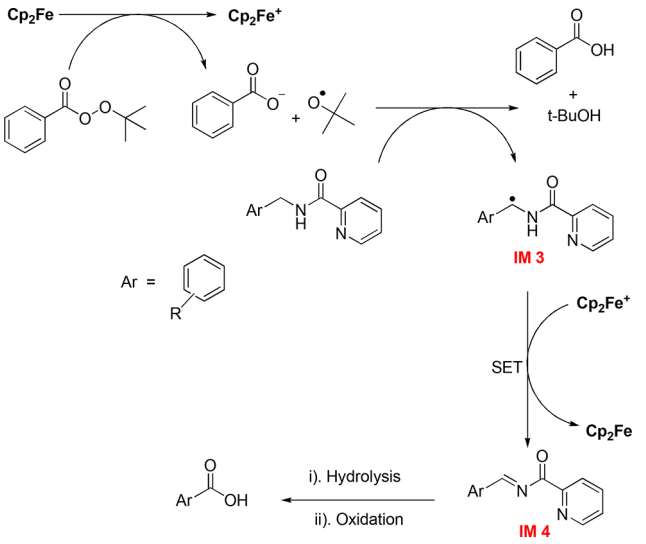
Scheme 8. Proposed Reaction Mechanism for Ferrocene Catalyzed sp^3 C−H Bond Oxidation of Aryl Picolinamide



At first TBPB oxidizes ferrocene to ferrocinium and cleaves itself to form benzoate anion and *tert*-butyl radical. Then the *tert*-butyl radical abstracts a proton from the C−H bond of the organic picolinamide to form the radical intermediate **IM3** and converts itself to *tert*-butanol. Afterward a single electron transfer takes place to generate an iminium ion intermediate **IM4**, which subsequently goes through a hydrolysis followed by oxidation to form the corresponding acid.

CONCLUSIONS

In conclusion, we report for the first time ferrocene catalyzed picolinamide group directed oxidation of sp^3 C−H bond to carbonyl compounds both for organic and metal-sandwich compounds. Both electron-donating and electron-withdrawing groups were found to be suitable for this reaction. Picolinamides having *para* and *meta* substituted aryl groups underwent oxidation effectively under these reaction conditions, but *ortho* substituted substrate groups were unresponsive. We have also demonstrated sp^3 C−H bond oxidation after sp^2 C−H functionalization on the ferrocene backbone. More interestingly, for the first time, we report a novel methodology to convert primary amines to acids by removing the directing group under oxidation conditions. A possible mechanism has been proposed for the C−H oxidation. This novel finding has the potential to convert many aminomethyl derivatives to the corresponding aldehydes or acids.

EXPERIMENTAL SECTION

General Procedure for Bis-Arylation of [η^5-(CH$_2$R)C$_5$H$_4$]Fe-(η^5-C$_5$H$_5$) (R = Picolinamido). A 15 mL screw capped vial was charged with a magnetic bead. One equivalent of ferrocenyl picolinamide (0.03 g, 0.10 mmol), Pd(OAc)$_2$ (20 mol %), Cs$_2$CO$_3$ (2 equiv), and aryl iodide (2.5 equiv) were dissolved in *tert*-amyl alcohol (5 mL). The reaction mixture was heated at 80−110 °C for 16−24 h. The reaction was monitored by TLC, and after completion, the reaction mixture was dried under a vacuum, and the crude product was purified through column chromatography using silica and hexane/ethyl acetate (70/30) as eluent.

[2,5-(4-OMeC$_6$H$_4$)$_2$-η^5-(CH$_2$R)C$_5$H$_2$]Fe(η^5-C$_5$H$_5$) (R = Picolinamido) ***(1a)***. Red semisolid; yield 77%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.41−8.46 (m, 2H), 8.19−8.21 (d, 1H), 7.80−7.85 (m, 1H), 7.50−7.53 (m, 5H), 6.83−6.86 (d, 4H, Ph-*H*), 4.58−4.64 (m, 4H), 4.22 (s, 5H, Cp-*H*), 3.82 (s, 6H, OMe-*H*). ^{13}C NMR (75 MHz, CDCl$_3$) δ 163.44, 158.40, 149.88, 148.04, 137.17, 130.13, 129.51, 125.98, 122.02, 113.66, 89.05, 80.57, 71.46, 68.55, 55.27. HRMS *m*/*z* 555.1342, calcd for C$_{31}$H$_{28}$FeN$_2$NaO$_3$ [M + Na]$^+$ 555.1347.

[2,5-(4-BrC$_6$H$_4$)$_2$-η^5-(CH$_2$R)C$_5$H$_2$]Fe(η^5-C$_5$H$_5$) (R = Picolinamido) ***(1b)***. Red orange semisolid; yield 75%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.43−8.44 (s, 1H), 8.15−8.18 (s, 1H), 7.84−7.85 (m, 2H), 7.41−7.48 (s, 8H), 7.37−7.38 (s, 1H), 4.60−4.62 (s, 4H), 4.24 (s, 5H, Cp-*H*).^{13}C NMR (75 MHz, CDCl$_3$) δ 163.46, 149.57, 148.02, 137.33, 136.46, 131.30, 130.57, 126.18, 122.14, 120.62, 88.25, 80.81, 71.79, 70.21, 36.60. HRMS *m*/*z* 650.9341, calcd for C$_{29}$H$_{22}$FeBr$_2$N$_2$NaO [M + Na]$^+$ 650.9346.

General Procedure for Bis-Alkylation of [η^5-(CH$_2$R)C$_5$H$_4$]Fe-(η^5-C$_5$H$_5$) (R = Picolinamido). A 15 mL screw capped vial was charged with a magnetic bead. One equivalent of ferrocenyl picolinamide (0.03 g, 0.10 mmol), Pd(OAc)$_2$ (20 mol %), Cs$_2$CO$_3$ (2 equiv), and alkyl iodide (2.5 equiv) were dissolved in *tert*-amyl alcohol (5 mL). The reaction mixture was heated at 80−90 °C for 5−10 h. The reaction was monitored by TLC. After completion, the reaction mixture was dried under a vacuum, and the crude product was purified through column chromatography using silica and hexane/ethyl acetate (90/10) as eluent.

[2,5Bis(methyl)η^5(CH$_2$R)C$_5$H$_2$]Fe(η^5C$_5$H$_5$) (R = Picolinamido) ***(1c)***. Yellow-orange semisolid; yield 74%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.51 (s, 1H, N-*H*), 8.21−8.23 (dd, 2H), 7.81−7.85 (m, 1H), 7.37−7.40 (d, 1H), 4.43 (d, 2H, CH$_2$−*H*), 3.99−4.07 (m, 7H, Cp-*H*), 1.99 (s, 6H, CH$_3$-*H*). ^{13}C NMR (75 MHz, CDCl$_3$) δ 163.65, 150.17, 148.21, 137.45, 126.20, 122.40, 83.59, 82.69, 69.94, 67.67, 35.88, 13.38. HRMS *m*/*z* 371.0817, calcd for C$_{19}$H$_{20}$FeN$_2$NaO [M+ Na]$^+$ 371.0823.

General Procedure for Synthesis of α,α-Bis-Substituted Aldehydes of Ferrocene. To a 150 mL flask equipped with stirrer bars, bis-aryl or bis-alkyl picolinamides were dissolved in DCE (10 mL) and stirred at room temperature for 15 min. Afterward ferrocene (20 mol %) and Cu(OAc)$_2$ (1 equiv) were added to the solution, and this mixture was then heated at 80 °C for 10−16 h. The reaction was monitored by TLC, and after completion, the mixture was dried over a vacuum, and the crude product was purified through column chromatography on silica gel using hexane/ethyl acetate (80/20) as eluent.

[2,5-(4-OMeC$_6$H$_4$)$_2$-η^5-(CHO)C$_5$H$_2$]Fe(η^5-C$_5$H$_5$) ***(2a)***. Red solid; yield 52%. Anal. Found: C, 70.41; H, 5.17; N, 0.00. Calcd for C$_{25}$H$_{22}$O$_3$Fe: C, 70.44; H, 5.20, N, 0.00. ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.20 (s, 1H, CHO-*H*), 7.46−7.49 (d, 4H, Ph-*H*), 6.81−6.84 (d, 4H, Ph-*H*), 4.77 (s, 2H, Cp-*H*), 4.20 (s, 5H, Cp-*H*), 3.77 (s, 6H, OMe-*H*). ^{13}C NMR (75 MHz, CDCl$_3$) δ 193.00, 158.96, 131.16, 130.77, 127.97, 113.83, 92.67, 71.01, 69.65, 55.33. HRMS *m*/*z* 449.0796, calcd for C$_{25}$H$_{22}$FeNaO$_3$ [M + Na]$^+$ 449.0811.

[2,5-(4-BrC$_6$H$_4$)$_2$-η^5-(CHO)C$_5$H$_2$]Fe(η^5-C$_5$H$_5$) ***(2b)***. Red orange solid; yield 48%. Anal. Found: C, 52.66; H, 3.18; N, 0.00. Calcd for C$_{23}$H$_{16}$OBr$_2$Fe: C, 52.72; H, 3.08, N, 0.00. . ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.24 (s, 1H, CHO-*H*), 7.48 (s, 8H, Ph-*H*), 4.92 (s, 2H, Cp-*H*), 4.23 (s, 5H, Cp-*H*). ^{13}C NMR (75 MHz, CDCl$_3$) δ 193.44, 158.96, 131.16, 130.77, 127.97, 113.44, 92.09, 79.39, 76.72, 73.22, 69.67. HRMS *m*/*z* 544.8810, calcd for C$_{23}$H$_{16}$FeBr$_2$NaO [M + Na]$^+$ 544.8815.

[2,5-Bis(methyl)-η^5-(CHO)C$_5$H$_2$]Fe(η^5-C$_5$H$_5$) ***(2c)***. Red solid; yield 46%. Anal. Found: C, 64.62; H, 5.75; N, 0.00. Calcd for C$_{13}$H$_{14}$OFe: C, 64.50; H, 5.83, N, 0.00. ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.29 (s, 1H, CHO-*H*), 4.34 (s, 2H, Cp-*H*), 4.12 (s, 5H, Cp-*H*), 2.21 (s, 6H, CH$_3$-*H*). ^{13}C NMR (75 MHz, CDCl$_3$) δ 194.63, 87.03, 72.51, 70.74, 13.69. HRMS *m*/*z* 265.0286, calcd for C$_{13}$H$_{14}$FeNaO [M + Na]$^+$ 265.0292.

[η^5-(CHO)C$_5$H$_4$]Fe(η^5-C$_5$H$_5$) ***(2d)***. Red solid; yield 50%. Anal. Found: C, 61.67; H, 4.65; N, 0.00. Calcd for C$_{11}$H$_{10}$OFe: C, 61.73; H, 4.73, N, 0.00. ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.97 (s, 1H, CHO-*H*), 4.81−4.82 (s, 2H, Cp-*H*), 4.62−4.63 (s, 2H, Cp-*H*), 4.29 (s, 5H, Cp-*H*), ^{13}C NMR (75 MHz, CDCl$_3$) δ 193.47,73.19, 69.65. HRMS *m*/*z* 215.0154, calcd for C$_{11}$H$_{11}$FeO [M + H]$^+$ 215.0159.

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General Procedure for Synthesis of Picolinamide of Benzyl Amines. Picolinamide of benzylamines were prepared according to literature procedure as follows. To a 150 mL flask charged with a magnetic bead, picolinic acid (0.92 g, 7.50 mmol) was dissolved in dry DCM (50 mL). The solution was cooled in an ice bath followed by addition of oxalyl chloride (1.16 g, 9.50 mmol) and two drops of DMF. The solution was then stirred for 5 min in an ice bath and then at room temperature for 1 h. Amine (5 mmol) was dissolved in dry DCM and acid chloride was added dropwise using a syringe. The solution was warmed to room temperature and stirred for 12 h. Afterward the solution was concentrated under a vacuum, and the crude product was purified through column chromatography on neutral alumina using hexane/ethyl acetate (70:30) as eluant. The experimental data matched with reported values.

General Procedure for Picolinamide Group Assisted sp^3 C–H bond Oxidation of Benzyl Amines. A 15 mL screw capped vial was charged with a magnetic bead and organic derived picolinamide (1 mmol) was dissolved in 5 mL of DCE and stirred at room temperature for 10 min. Then ferrocene (0.2 mmol, 20 mol %) was added to it followed by addition of *tert*-butyl peroxybenzoate (TBPB) (4 mmol). The mixture was heated at 80 °C for 12 h. Afterward, the solution was concentrated under a vacuum, and the crude product was purified through column chromatography on silica gel using hexane/ethyl acetate (90:10) as eluent.

4-OMe(C_6H_4-COOH) ***(5a)***. White solid; yield 82%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 12.65 (s, 1H, COOH-*H*), 7.90–7.93 (d, 2H, Ph-*H*), 7.01–7.04 (d, 2H, Ph-*H*), 3.83 (s, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 166.99, 162.78, 131.67, 122.96, 113.66, 55.24.

(C_6H_5-COOH) ***(6a)***. White solid; yield 75%. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 12.71 (s, 1H, COOH-*H*), 8.17–8.20 (m, 2H, Ph-*H*), 7.63–7.78 (t, 1H, Ph-*H*), 7.37–7.49 (t, 2H, Ph-*H*); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 172.72, 133.87, 130.27, 129.96, 128.52.

4-NO_2(C_6H_4-COOH) ***(7a)***. Pale yellow solid; yield 68%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.62 (s, 1H, COOH-*H*), 8.30–8.32 (d, 2H, Ph-*H*), 8.16–8.19 (d, 2H, Ph-*H*); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 166.16, 150.36, 136.81, 131.04, 123.79.

4-CF_3(C_6H_4-COOH) ***(8a)***. Pale yellow solid; yield 68%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.46 (s, 1H, COOH-*H*), 8.12–8.15 (d, 2H, Ph-*H*), 7.86–7.89 (d, 2H, Ph-*H*); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ 166.64, 135.05, 130.52, 125.99, 125.95, 79.60. ^{19}F-NMR (DMSO-d_6, 282 MHz, ppm) −62.55.

4-F(C_6H_4-COOH) ***(9a)***. Pale yellow solid; yield 69%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 12.93 (s, 1H, COOH-*H*), 7.92–8.03 (d, 2H, Ph-*H*), 7.43–7.49 (d, 2H, Ph-*H*); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 167.78, 133.25, 132.61, 131.26, 127.84. ^{19}F-NMR (DMSO-d_6, 282 MHz, ppm) −106.91.

4-Br(C_6H_4-COOH) ***(10a)***. White solid; yield 70%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.20 (s, 1H, COOH-*H*), 7.87–7.90 (d, 2H, Ph-*H*), 7.71–7.74 (d, 2H, Ph-*H*,); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 167.05, 132.14, 131.74, 130.48, 127.32.

4-Cl(C_6H_4-COOH) ***(11a)***. White solid; yield 71%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.20 (s, 1H, COOH-*H*), 7.84–7.87 (d, 2H, Ph-*H*), 7.67–7.71 (d, 2H, Ph-*H*); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 166.06, 132.16, 131.74, 130.48, 127.32.

3-OMe(C_6H_4-COOH) ***(12a)***. White solid, yield 74%, ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) δ 13.07(s, 1H, COOH-*H*), 7.54–7.56 (s, 1H, Ph-*H*), 7.41–7.46 (d, 1H, Ph-*H*), 7.37–7.39 (dt, 1H, Ph-*H*), 7.15–7.16 (t, 1H, Ph-*H*), 3.79 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz, ppm) δ 167.60, 159.67, 132.68, 130.06, 122.00, 119.21, 114.40, 55.60.

3-Me(C_6H_4-COOH) ***(13a)***. White solid, yield 68%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 12.85 (s, 1H, COOH-*H*), 7.74–7.77 (d, 2H, Ph-*H*), 7.32–7.40 (d, 2H, Ph-*H*), 2.33–2.41(s, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 167.39, 137.78, 133.32, 130.71, 129.69, 128.30, 126.40, 20.69.

3-CF_3(C_6H_4) COOH ***(14a)***. White solid, yield 62%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.05 (br, 1H, COOH-*H*), 8.18–8.24 (s, 2H, Ph-*H*), 7.68–7.85 (d, 1H, Ph-*H*), 7.45–7.62 (s, 1H, Ph-*H*), ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 172.60, 133.89, 133.38, 130.25, 129.31, 129.24, 128.52, 127.13. ^{19}F-NMR (DMSO-d_6, 282 MHz, ppm) −61.48.

3-Br(C_6H_4-COOH) ***(15a)***. White solid, yield 66%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.40 (br, 1H, COOH-*H*), 7.92–7.93 (d, 2H,Ph-*H*), 7.70–7.72 (d, 1H, Ph-*H*), 7.53–7.59 (dt, 1H, Ph-*H*); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 166.52, 133.79, 133.35, 131.10, 131.02, 129.30, 128.35.

3-Cl(C_6H_4-COOH) ***(16a)***. White solid, yield 67%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.36 (s, 1H, COOH-*H*), 7.77 (s, 2H, Ph-*H*), 7.70 (d, 1H, Ph-*H*), 7.55–7.57 (dt, 1H, Ph-*H*); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm) δ 171.01, 134.72, 133.94, 130.94, 130.28, 129.86, 128.33.

COOH-C_6H_4-COOH ***(17a)***. White solid, yield 53%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.33 (br, 2H, COOH-*H*), 8.05–8.11 (s, 4H, Ph-*H*); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 167.13, 134.85, 129.84.

C_4H_3S-COOH ***(18a)***. White solid, yield 50%. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm) δ 13.09 (br, 1H, COOH-*H*), 7.88–7.90 (s, 1H), 7.75–7.77 (s, 1H), 7.18–7.22(s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz, ppm) δ 162.88, 134.63, 133.14, 128.14.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00085.

General information; Experimental section; UV–visible spectroscopic studies; ^{1}H NMR and ^{13}C{^{1}H} NMR spectra; References (PDF)

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Notes

The authors declare no competing financial interest.

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