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Iron-Catalyzed Regioselective α-C−H Alkylation of *N*-Methylanilines: Cross-Dehydrogenative Coupling between Unactivated C(sp^3)−H and C(sp^3)−H Bonds via a Radical Process

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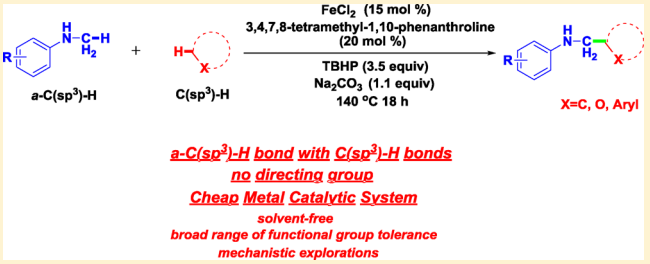
Supporting Information

ABSTRACT: The iron-catalyzed α-C−H alkylation of *N*-methylanilines without any directing group by cross-dehydrogenative coupling between unactivated C(sp^3)−H and C(sp^3)−H bonds has been established for the first time, which provides a good complement to C(sp^3)−H activation reactions and expands the field of Fe-catalyzed C−H functionalizations. Many different C(sp^3)−H bonds in cyclic alkanes, cyclic ethers, and toluene derivatives can be used as coupling partners. Mechanistic investigations including the radical reaction process, the main role of various reagents, and the kinetic isotope effect experiment were also described.



INTRODUCTION

Aniline derivatives have found broad application in organic synthesis and can be easily used for fundamental building blocks of bioactive compounds.[1] In addition, they also play very important roles in numerous natural products, agrochemicals, dyestuff industry, and pharmaceuticals,[2] for example (Figure 1, **1**−**3**), mabuterol **1** (treatment of tracheal

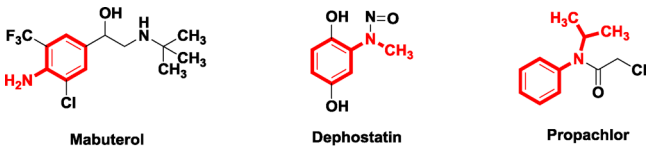


Figure 1. Representative examples of applications of aniline derivatives.

obstructive diseases), dephostatin **2** (potential inhibitor of cysteine-containing enzymes such as protein tyrosine phosphatases, papain, and caspase) and propachlor **3** (highly selective herbicide for rice field).

Due to the significance of this substructure in various fields, the development of efficient synthetic methods that allow for easy access to substituted anilines and their derivatives is of great importance. Over the past decade, a significant number of procedures have been established for the direct N−H bond and *ortho* C−H bond functionalization of anilines.[3,4] For instance, the Cu(II)-catalyzed oxidative N-nitrosation of secondary and tertiary amines with nitromethane under an oxygen atmosphere was provided by Sakai and his co-workers;[3d] this catalytic system could be applied to the N-nitrosation of aromatic amines and enabled the cleavage of the C−N bond of an aromatic tertiary amine. In 2016, Kandasamy's group[3c] developed an efficient synthesis of *N*-nitrosamines using *tert*-butyl nitrite, featuring a broad substrate scope, metal-free conditions, easy operation, and excellent yields. On the other hand, a significant number of methods have been described for the direct *ortho* C−H bond functionalization of anilines.[4] As a representative example, a nickel-catalyzed direct C−H trifluoromethylation of free anilines with Togni's reagent by Wu et al.[4a] provides a concise and efficient alternative protocol to synthesize trifluoromethylated free anilines. Despite the breakthrough in the N−H bond and *ortho* C−H bond functionalization of anilines, the research in the field of α-C(sp^3)−H activation of *N*-methylanilines is still in its primary stage.

In recent years, several transition metal complexes containing Ir,[5a] Sc,[5b] Ti,[5c] Zr,[5d] Ta,[5e] and Nb[5f] have been developed for α-C(sp^3)−H activation of *N*-methylanilines (Scheme 1). Examples include work in the direct C−H alkylation adjacent to nitrogen in unprotected secondary amines by using 2-pyridonate-Ta(NMe_2)$_3$Cl complex, which does not require additives, protecting/directing groups, terminal oxidants, or photoinitiators. In 2015, the first example of a titanium-based catalyst for intermolecular hydroaminoalkylation reactions of alkenes and styrenes with secondary amines was developed by Doye's group,[5c] showing excellent

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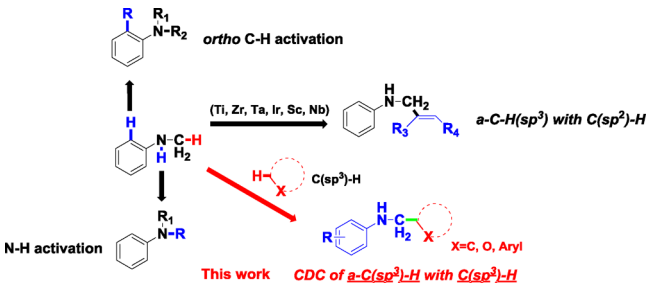
Scheme 1. Representative Examples of Activation of the N−H/C−H Bond in Anilines



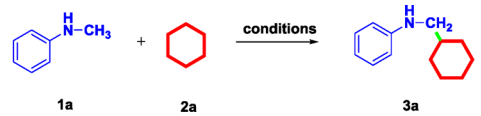
regioselectivity. Furthermore, Nishibayashi and co-workers[5a] demonstrated the addition of α-aminoalkyl radicals to electron-deficient alkenes by visible-light-mediated electron transfer using transition metal polypyridyl complexes as photocatalysts, opening up a novel synthetic route for the direct functionalization of the C(sp^3)−H bond adjacent to the N atom of anilines. However, previous works were all limited to the coupling of C(sp^3)−H with C(sp^2)−H bonds in terminal alkenes or dienes or internal alkenes, and the catalysts are very high-cost. The catalytic cross-dehydrogenative coupling reaction between C(sp^3)−H bonds of *N*-methylaniline and C(sp^3)−H bonds has thus far remained elusive, especially in the area of employing a cheap transition metal.

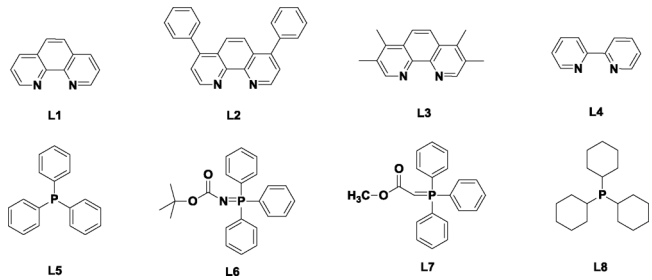
We herein demonstrate the first example of a cheap transition metal iron-catalyzed cross-dehydrogenative coupling of C(sp^3)−H bonds in the *N*-methylanilines with C(sp^3)−H bonds of cyclic alkanes, cyclic ethers, and toluene derivatives without any directing group (DG) via a radical process.

RESULTS AND DISCUSSION

At first, we examined the reaction of *N*-methylaniline **1a** with cyclohexane **2a** under various conditions, and the results are summarized in Table 1. When the reaction of **1a** with **2a** was carried out at 140 °C using $FeCl_2$ as the catalyst, **L1** as the ligand, TBHP (*tert*-butyl hydroperoxide) as the oxidant, and in the presence of Na_2CO_3 under air for 18 h, **3a** was obtained in 35% total yield (entry 1). Next, a survey of different iron catalysts such as $FeSO_4$ and $Fe(OAc)_2$, $Fe(acac)_3$ was investigated. The results showed that $FeCl_2$ was the best catalyst, and the anion bound to iron plays a crucial role in the catalysis (entries 2−4). Other catalysts including $NiCl_2$ and $CuCl_2$ all failed to give the desired product (entries 5−6). Thereafter, we explored various ligands with **L3** furnishing particularly effective catalysis (entries 7−13). In addition, a range of peroxides were also screened (Table 1, entries 14−16), but none of them were found to be effective for the reaction, and this might be due to the different half-life of peroxides under high-temperature reaction conditions (caution: TBHP is unstable above 75 °C, and heating large amounts of TBHP at 140 °C is potentially dangerous[7c]). Among the additives tested, Na_2CO_3 was found to be the best choice (entries 17−20). Moreover, decreasing the reaction temperature reduced the yield (entries 21 and 22). Finally, optimizations in other solvents were made (entries 23 and 24), and cyclohexane was proved as the best for this reaction. One possible reason is that cyclohexane (4 equiv) is transferred from liquid to gas under a high-temperature procedure, thus resulting in a decrease of yield.

Table 1. Optimization of the Reaction Conditions[a]





entry	cat.	ligand	peroxide	base	yield[b] (%) of **3a**
1	$FeCl_2$	**L1**	TBHP	Na_2CO_3	35
2	$FeSO_4$	**L1**	TBHP	Na_2CO_3	11
3	$Fe(OAc)_2$	**L1**	TBHP	Na_2CO_3	13
4	$Fe(acac)_3$	**L1**	TBHP	Na_2CO_3	26
5	$NiCl_2$	**L1**	TBHP	Na_2CO_3	0
6	$CuCl_2$	**L1**	TBHP	Na_2CO_3	0
7	$FeCl_2$	**L2**	TBHP	Na_2CO_3	50
8	$FeCl_2$	**L3**	TBHP	Na_2CO_3	75
9	$FeCl_2$	**L4**	TBHP	Na_2CO_3	39
10	$FeCl_2$	**L5**	TBHP	Na_2CO_3	trace
11	$FeCl_2$	**L6**	TBHP	Na_2CO_3	trace
12	$FeCl_2$	**L7**	TBHP	Na_2CO_3	0
13	$FeCl_2$	**L8**	TBHP	Na_2CO_3	0
14	$FeCl_2$	**L3**	DTBP	Na_2CO_3	41
15	$FeCl_2$	**L3**	TBPB	Na_2CO_3	30
16	$FeCl_2$	**L3**	DCP	Na_2CO_3	46
17	$FeCl_2$	**L3**	TBHP	Cs_2CO_3	63
18	$FeCl_2$	**L3**	TBHP	DMAP	31
19	$FeCl_2$	**L3**	TBHP	^{t}BuOK	27
20	$FeCl_2$	**L3**	TBHP	TFA	0
21[c]	$FeCl_2$	**L3**	TBHP	Na_2CO_3	trace
22[d]	$FeCl_2$	**L3**	TBHP	Na_2CO_3	0
23[e]	$FeCl_2$	**L3**	TBHP	Na_2CO_3	0
24[f]	$FeCl_2$	**L3**	TBHP	Na_2CO_3	0

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (2.0 mL), cat. (0.075 mmol), ligand (0.1 mmol), peroxide (1.75 mmol), (0.55 mmol), 140 °C, 18 h. [b]Isolated yield. [c]125 °C. [d]110 °C. [e]**2a** (4 equiv), DMF (2.0 mL). [f]**2a** (4 equiv), DMSO (2.0 mL).

With the optimized conditions in hand, we next explored the scope of the substrates, and the results are summarized in Scheme 2. In general, a variety of *N*-methylanilines were applicable, and moderate to excellent isolated yields of the products were achieved (**3a**−**3l**). Substrates bearing electron-donating groups at the C-4 position afforded the alkylation products **3b** and **3c** in 70 and 66% yields, respectively. Meanwhile, a series of common electron-withdrawing groups, such as halogen, cyano, trifluoromethyl, and phenyl, were all well-tolerated (**3d**−**3i**). In addition, *meta*-substituted (**3k**−**3l**) and *ortho*-substituted (**3j**) *N*-methylanilines gave the corresponding products in moderate yields, which show the position of substituents on the phenyl ring did not have a significant effect on the reaction yields. When anisole was applied to the reaction under standard conditions (**3m**), however, alkylation

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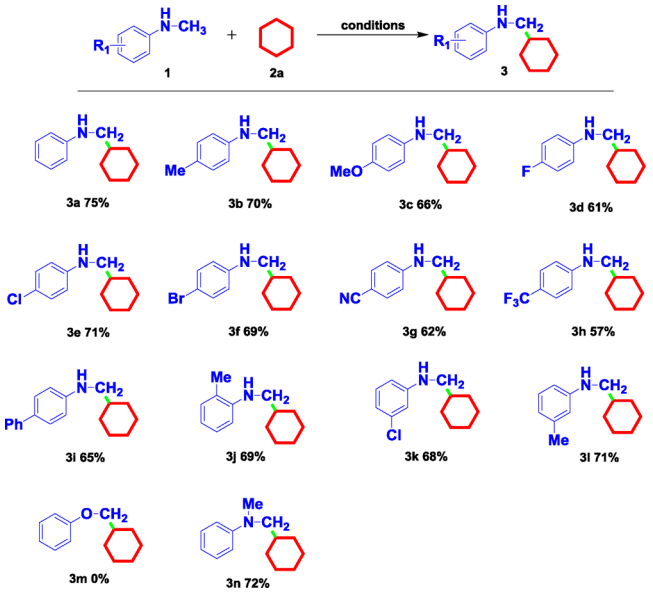
Scheme 2. Substrate Scope of Aniline Derivatives[a]

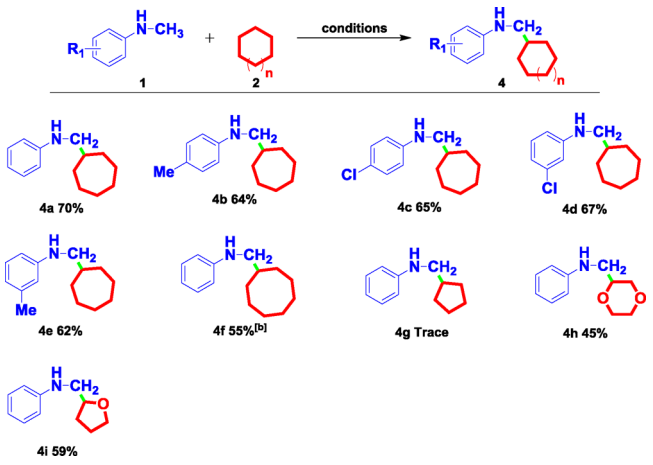


[a]Reaction condition: 1 (0.5 mmol), 2a (2.0 mL), $FeCl_2$ (0.075 mmol), L3 (0.1 mmol), TBHP (1.75 mmol), Na_2CO_3 (0.55 mmol), 140 °C, 18 h.

reaction could not proceed smoothly. It is worth noting that *N*,*N*-dimethylaniline was tolerated in this procedure (**3n**).

Next, we turned our attention to the scope of other cyclic alkanes (Scheme 3). As expected, substrates possessing

Scheme 3. Substrate Scope of Other Cyclic Alkanes and Cyclic Ethers[a]

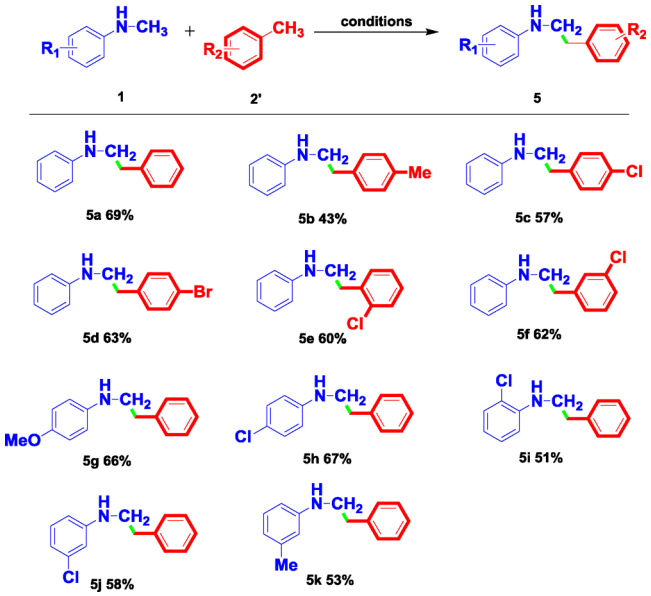


[a]Reaction conditions: **1** (0.5 mmol), **2** (2.0 mL), $FeCl_2$ (0.075 mmol), **L3**L3 (0.1 mmol), TBHP (1.75 mmol), Na_2CO_3 (0.55 mmol), 140 °C, 18 h. [b]150 °C.

electron-donating (**4b**, **4e**) or electron-withdrawing (**4c**, **4d**) substituents at the C-3 and C-2 positions afforded the desired products in satisfactory yields (62−67%). Furthermore, this method was compatible with cyclooctane (**4f**) when we increased the temperature from 140 to 150 °C. Unfortunately, cyclopentane (**4g**) could not be coupled with **1a** under standard conditions (detected by GC−MS). It is worth noting that dioxane (**4h**) and tetrahydrofuran (**4i**) reacted with **1a** to afford corresponding products in good yields too.

With the successful development of methods for the cross-dehydrogenative coupling of C(sp^3)−H bonds in *N*-methylanilines with C(sp^3)−H bonds from cyclic alkanes and cyclic ether, we then sought to investigate the tolerance of C(sp^3)−H bonds in toluene derivatives (Scheme 4). To our delight, this

Scheme 4. Substrate Scope of Toluene Derivatives[a]



[a]Reaction conditions: **1a** (0.5 mmol), **2**′′′ (2.0 mL), $FeCl_2$ (0.075 mmol), **L3**L3 (0.1 mmol), TBHP (1.75 mmol), Na_2CO_3 (0.55 mmol), 140 °C, 18 h.

procedure is compatible with both electron-donating and -withdrawing toluenes (**5b**−**5f**). Remarkably, *N*-methylanilines bearing methyl, methoxy, and chloro groups at different positions were well-tolerated too, and the corresponding products were obtained in good yields (**5g**−**5k**).

To clarify the mechanism of the reaction, several control experiments were carried out (Scheme 5). Upon the addition of radical inhibitors 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, 4.0 equiv), butylated hydroxytoluene (BHT, 4.0 equiv), or 1,1-diphenylethene (4.0 equiv), the cross-dehydrogenative coupling reaction (Scheme 5, **D1**−**D3**) of **1a** with cyclohexane **2a** is completely suppressed (determined by GC−MS and NMR **6a**). On the other hand, when the radical scavenger TEMPO was added to the cross-dehydrogenative coupling reaction of **1a** with toluene **2**′**a**, no product **5a** was formed (determined by GC−MS). These results suggested that the cross-dehydrogenative coupling reaction might involve a radical process.

At the same time, only trace desired product was detected in the absence of the iron catalyst, suggesting that the iron catalyst plays a critical role in electron transfer (Scheme 6, **E1**). In our procedure, the ligand might work as an activating reagent of catalyst to facilitate the reaction (Scheme 6, **E2**). When the reaction was run without TBHP, no product was obtained (Scheme 6, **E3**). It might work as both oxidant and radical initiator. Importantly, less than 20% yield of the product **3a** was observed without Na_2CO_3 (Scheme 6, **E4**), showing that the deprotonation process is very dependent on the base additive. Notably, the procedure under argon resulted in no significant decrease of the yield (Scheme 6, **E5**), indicating that additional oxygen is not required for the

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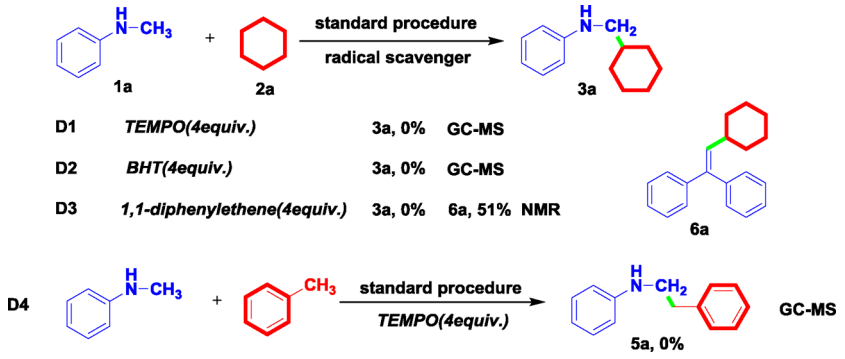
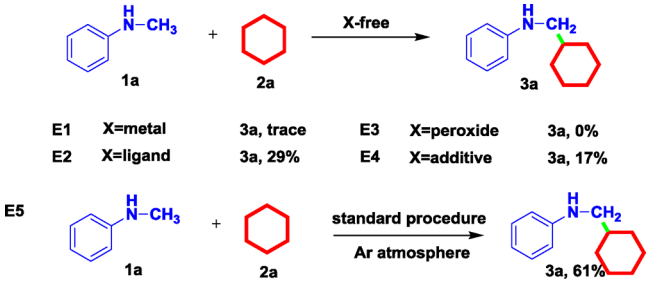
Scheme 5. Control Experiment



Scheme 6. Control Experiment

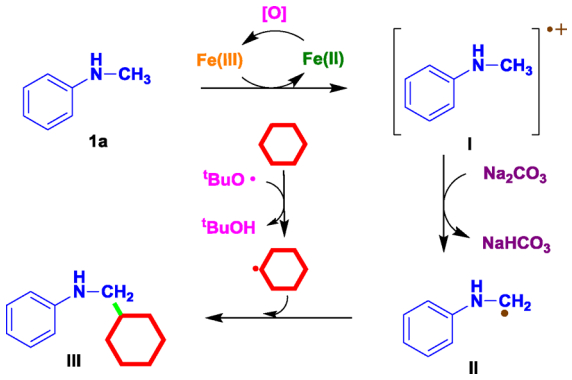


reaction, and TBHP plays a major role in oxidation. It is worth noting that the side product was 1,1′-bi(cyclohexane) from homo-coupling of two cyclohexane radicals, and the yield of the side product was 10% under our reaction conditions (determined by GC−MS).

A primary kinetic isotope effect (KIE) in competing KIE experiments (the KIE was determined by ^{1}H NMR spectroscopy by analyzing the ratio of **3a** vs **3a-D**) was observed (K_H/K_D = 7.69), suggesting that the cleavage of the C(sp^3)−H bond might be involved in the turnover-limiting step (Scheme 7).

On the basis of the above experiments and previous work,[6] a plausible reaction mechanism for this iron-catalyzed cross-dehydrogenative coupling is described in Scheme 8. First, Fe(II) is oxidized into Fe(III) species under aerobic conditions, which then undergoes single-electron transfer (SET) from **1a** to give the radical cation intermediate **I**.[6d] Meanwhile, the radical initiator TBHP undergoes a thermal decomposition to generate the *tert*-butoxyl radical. Subsequently, the abstraction of a hydrogen atom from the intermediate **I** with the help of Na_2CO_3 affords the radical intermediate **II**. Finally, the *tert*-butoxyl radical grabs one of the hydrogen atoms in cyclohexane to generate the respective radical, which reacts with the radical intermediate **II** to generate the corresponding product **III**.

Scheme 8. Proposed Reaction Mechanism



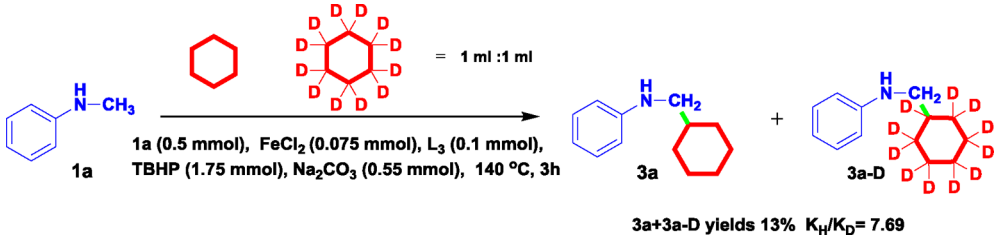
CONCLUSIONS

In summary, we have developed the first example of a cheap transition metal iron-catalyzed highly selective cross-dehydrogenative coupling of C(sp^3)−H bonds in the *N*-methylanilines with C(sp^3)−H bonds of cyclic alkanes, cyclic ethers, and toluene derivatives without any directing group (DG) via a radical process. This procedure provides a good complement to C(sp^3)−H activation reactions and expands the field of Fe-catalyzed C−H functionalizations. Detailed exploration of the mechanism has also been carried out.

EXPERIMENTAL SECTION

General Information. All compounds are characterized by ^{1}H NMR, ^{13}C NMR, and MS. Analytical thin-layer chromatography is performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm. GC analyses are performed on an Agilent 7890A instrument (column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, H, FID

Scheme 7. KIE Experiment



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detection). GC−MS data were recorded on a 5975C mass selective detector, coupled with a 7890A gas chromatograph (Agilent Technologies). High-resolution mass spectral data were acquired on an Agilent Technologies Accurate-Mass Q-TQF LC/MS 6520 operated by China Pharmaceutical University.

General Procedure for the Preparation of *N*-Methylanilines.[7] Sodium metal (5 mmol) was added portionwise to dry MeOH (20 mL) at 0 °C. After complete consumption of the sodium metal were added aniline (1 mmol) and paraformaldehyde (5 mmol) at room temperature (26 °C), and the mixture was stirred for 2 h at reflux to give an imine intermediate. The mixture was then reacted with $NaBH_4$ (1.5 mmol) at 0 °C and then refluxed for an additional 2 h. The reaction mixture was then cooled to room temperature, and the solvent was evaporated on a rotary evaporator to give a residue that was diluted with CH_2Cl_2 (15 mL) then washed with water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on a silica gel column chromatography using hexane as an eluent.

General Procedure for Cross-Dehydrogenative Coupling of α-C(sp^3)−H Bonds in *N*-Methylamides and C(sp^3)−H Bonds from Cyclic Alkanes. To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a sealed reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. The reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine (30 mL × 1), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **3a**.

General Procedure for Cross-Dehydrogenative Coupling of α-C(sp^3)−H Bonds in *N*-Methylamides and C(sp^3)−H Bonds from Toluene Derivatives. To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a sealed reaction was added to the solvent (toluene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. The reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine (30 mL × 1), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **5a**.

*N-(Cyclohexylmethyl)aniline (**3a**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3a** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (70.9 mg, 75%).[8a] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.24−7.15 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.65 (dd, *J* = 8.3, 3.2 Hz, 2H), 3.81 (s, 1H), 3.10−2.86 (m, 2H), 1.89−1.81 (m, 2H), 1.81−1.71 (m, 3H), 1.65−1.56 (m, 1H), 1.33−1.20 (m, 3H), 1.07−0.97 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 147.4, 128.3, 116.1, 111.8, 49.8, 36.6, 30.4, 25.6, 25.0. GC−MS (EI) *m*/*z*: 189.

*N-(Cyclohexylmethyl)-4-methylaniline (**3b**).* To a mixture of *N*,4-dimethylaniline (60.5 mg, 0.5 mmol) **1b**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3b** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (71.1 mg, 70%).[8b] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.02 (d, *J* = 8.1 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 2.97 (d, *J* = 6.7 Hz, 2H), 2.27 (s, 3H), 1.89−1.83 (m, 2H), 1.80−1.77 (m, 1H), 1.74−1.70 (m, 1H), 1.61 (td, *J* = 7.4, 3.8 Hz, 1H), 1.29−1.21 (m, 3H), 1.03−0.99 (m, 1H), 0.91−0.88 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 145.3, 128.7, 125.2, 112.0, 50.1, 36.6, 30.4, 25.7, 25.0, 19.4. GC−MS (EI) *m*/*z*: 203.

*N-(Cyclohexylmethyl)-4-methoxyaniline (**3c**).* To a mixture of 4-methoxy-*N*-methylaniline (68.5 mg, 0.5 mmol) **1c**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3c** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (72.3 mg, 66%).[8c] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 6.81 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 3.78 (s, 3H), 2.95 (d, *J* = 6.6 Hz, 2H), 1.89−1.82 (m, 2H), 1.80−1.77 (m, 1H), 1.74−1.70 (m, 1H), 1.60 (ddd, *J* = 11.1, 7.6, 4.1 Hz, 1H), 1.32−1.21 (m, 3H), 1.00 (td, *J* = 12.1, 3.4 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 150.9, 141.8, 114.0, 113.1, 54.9, 50.8, 36.6, 30.4, 25.6, 25.0. GC−MS (EI) *m*/*z*: 219.

*N-(Cyclohexylmethyl)-4-fluoroaniline (**3d**).* To a mixture of 4-fluoro-*N*-methylaniline (62.5 mg, 0.5 mmol) **1d**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3d** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (63.1 mg, 61%).[8d] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 6.96−6.85 (m, 2H), 6.60−6.52 (m, 2H), 2.94 (d, *J* = 6.7 Hz, 2H), 1.88−1.82 (m, 2H), 1.80−1.77 (m, 1H), 1.74−1.71 (m, 1H), 1.59 (ddd, *J* = 7.8, 5.7, 3.2 Hz, 1H), 1.31−1.20 (m, 3H), 1.07−0.96 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 155.6, 143.9, 114.6 (d, *J* = 22 Hz), 112.5, 50.5, 36.6, 30.3, 25.6, 25.0. GC−MS (EI) *m*/*z*: 207.

*4-Chloro-N-(cyclohexylmethyl)aniline (**3e**).* To a mixture of 4-chloro-*N*-methylaniline (79.2 mg, 0.5 mmol) **1e**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3e** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (63.1 mg, 71%).[8e] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.14 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 2.95 (d, *J* = 6.7 Hz, 2H), 1.87−1.80 (m, 2H), 1.79−1.76 (m, 1H), 1.74−1.70 (m, 1H), 1.63−1.58 (m, 1H), 1.27−1.22 (m, 3H), 1.03−1.00 (m, 1H), 0.92−0.90 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 146.0, 128.0, 129.6, 112.9, 49.8, 36.5, 30.3, 25.6, 25.0. GC−MS (EI) *m*/*z*: 223.

*4-Bromo-N-(cyclohexylmethyl)aniline (**3f**).* To a mixture of 4-bromo-*N*-methylaniline (92.5 mg, 0.5 mmol) **1f**, FeCl2 (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3f** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (92.1 mg, 69%). ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.27 (td, *J* = 10.3, 9.0, 2.7 Hz, 2H), 6.54−6.45 (m, 2H), 2.95 (d, *J* = 6.5 Hz, 2H), 1.87−1.80 (m, 2H), 1.79−1.76 (m, 1H), 1.72 (d, *J* = 9.9 Hz, 1H), 1.63−1.57 (m, 1H), 1.28−1.22 (m, 3H), 1.03−0.99 (m, 1H), 0.92−0.88 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 146.5, 130.9, 113.3, 107.5, 49.7, 36.5, 30.3, 25.6, 25.0. GC−MS (EI) *m*/*z*: 267. HRMS (ESI) *m*/*z*: calcd for $[C_{13}H_{18}BrN + H]^+$, 268.0701; found, 268.0705.

*4-((Cyclohexylmethyl)amino)benzonitrile (**3g**).* To a mixture of 4-(methylamino)benzonitrile (66.0 mg, 0.5 mmol) **1g**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent

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(cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3g** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (66.3 mg, 62%). ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.44 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 3.02 (d, *J* = 6.7 Hz, 2H), 1.85−1.76 (m, 4H), 1.75−1.70 (m, 1H), 1.64−1.58 (m, 1H), 1.32−1.27 (m, 2H), 1.26−1.21 (m, 1H), 1.06−0.98 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 150.6, 132.7, 119.5, 111.1, 99.0, 48.8, 36.5, 30.2, 25.4, 24.9. GC−MS (EI) *m*/*z*: 214. HRMS (ESI) *m*/*z*: calcd for $[C_{14}H_{18}N_2 + H]^+$, 215.1548; found, 215.1552.

*N-(Cyclohexylmethyl)-4-(trifluoromethyl)aniline (**3h**).* To a mixture of *N*-methyl-4-(trifluoromethyl)aniline (87.5 mg, 0.5 mmol) **1h**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na2CO3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3h** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (73.2 mg, 57%). ^{1}H NMR (500 MHz, DMSO-d6, δ): 7.32 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 8.5 Hz, 2H), 2.87 (t, *J* = 6.2 Hz, 2H), 1.79−1.73 (m, 2H), 1.70−1.66 (m, 1H), 1.63−1.59 (m, 1H), 1.55−1.47 (m, 1H), 1.24−1.12 (m, 4H), 0.96−0.88 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d6, δ): 151.5, 125.3 (q, *J* = 94 Hz), 113.9, 110.5, 99.0, 48.3, 36.2, 30.1, 25.6, 24.9. GC−MS (EI) *m*/*z*: 257. HRMS (ESI) *m*/*z*: calcd for $[C_{14}H_{18}F_3N + H]^+$, 258.1470; found, 258.1463.

*N-(Cyclohexylmethyl)-[1,1′-biphenyl]-4-amine (**3i**).* To a mixture of *N*-methyl-[1,1′-biphenyl]-4-amine (91.5 mg, 0.5 mmol) **1i**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3i** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (86.1 mg, 65%).[8f] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.60−7.51 (m, 2H), 7.45 (dt, *J* = 25.4, 7.7 Hz, 4H), 7.27 (dd, *J* = 18.6, 7.8 Hz, 2H), 6.76−6.62 (m, 2H), 4.12 (s, 1H), 3.04 (t, *J* = 6.2 Hz, 2H), 1.92−1.85 (m, 1H), 1.84−1.72 (m, 3H), 1.70−1.58 (m, 2H), 1.35−1.22 (m, 3H), 1.07−0.96 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 140.3, 129.1, 127.7, 127.0, 125.3, 125.0, 118.2, 112.1, 49.9, 36.6, 30.3, 25.6, 25.0. GC−MS (EI) *m*/*z*: 265.

*N-(Cyclohexylmethyl)-2-methylaniline (**3j**).* To a mixture of *N*,2-dimethylaniline (60.5 mg, 0.5 mmol) **1j**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3j** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (70.0 mg, 69%).[8g] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.16 (td, *J* = 7.7, 1.6 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.69 (t, *J* = 7.8 Hz, 2H), 3.04 (d, *J* = 6.7 Hz, 2H), 2.19 (s, 3H), 1.92−1.84 (m, 2H), 1.82−1.76 (m, 2H), 1.74−1.64 (m, 2H), 1.31−1.22 (m, 3H), 1.08−1.01 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6, δ): 146.0, 129.1, 126.2, 120.8, 114.6, 108.3, 49.0, 35.8, 30.3, 25.7, 25.0, 17.1. GC−MS (EI) *m*/*z*: 203.

*3-Chloro-N-(cyclohexylmethyl)aniline (**3k**).* To a mixture of 3-chloro-*N*-methylaniline (70.5 mg, 0.5 mmol) **1k**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3k** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (75.8 mg, 68%).[8h] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.09 (t, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.60 (d, *J* = 2.3 Hz, 1H), 6.49 (dd, *J* = 8.2, 2.3 Hz, 1H), 2.96 (d, *J* = 6.7 Hz, 2H), 2.73 (s, 1H), 1.86−1.83 (m, 1H), 1.80−1.75 (m, 2H), 1.74−1.70 (m, 1H), 1.63−1.57 (m, 2H), 1.27−1.23 (m, 3H), 1.04−1.01 (m, 1H), 0.93−0.90 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 134.0, 129.1, 115.8, 111.2, 110.1, 101.4, 49.5, 36.5, 30.3, 25.6, 24.9. GC−MS (EI) *m*/*z*: 223.

*N(Cyclohexylmethyl)-3-methylaniline (**3l**).* To a mixture of *N*,3-dimethylaniline (60.5 mg, 0.5 mmol) **1l**, FeCl2 (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na2CO3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3l** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (72.1 mg, 71%).[8h] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.09 (td, *J* = 7.5, 3.1 Hz, 1H), 6.60−6.51 (m, 1H), 6.50−6.40 (m, 2H), 3.03−2.94 (m, 2H), 2.31 (s, 3H), 1.85 (d, *J* = 13.1 Hz, 2H), 1.79−1.76 (m, 1H), 1.72 (d, *J* = 10.2 Hz, 1H), 1.65−1.58 (m, 1H), 1.28−1.21 (m, 3H), 1.04−1.00 (m, 1H), 0.91−0.88 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 147.6, 138.0, 128.1, 117.0, 112.5, 108.9, 49.7, 36.6, 30.4, 25.6, 25.0, 20.7. GC−MS (EI) *m*/*z*: 203.

*N-(Cyclohexylmethyl)-N-methylaniline (**3n**).* To a mixture of *N*,*N*-dimethylaniline (60.5 mg, 0.5 mmol) **1n**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3n** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (73.1 mg, 72%).[8i] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.29 (td, *J* = 8.6, 7.2, 2.4 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 3H), 3.19 (d, *J* = 6.7 Hz, 2H), 3.02 (s, 3H), 1.87−1.70 (m, 6H), 1.33−1.22 (m, 3H), 1.06−0.96 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 149.6, 129.1, 115.4, 111.7, 59.8, 39.6, 36.9, 31.4, 26.6, 26.1. GC−MS (EI) *m*/*z*: 203.

*N-(Cycloheptylmethyl)aniline (**4a**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cycloheptane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **4a** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (71.1 mg, 70%).[8j] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.18 (t, *J* = 7.8 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 2H), 3.72 (s, 1H), 2.96 (d, *J* = 6.6 Hz, 2H), 1.89−1.80 (m, 2H), 1.79−1.74 (m, 1H), 1.74−1.67 (m, 2H), 1.64−1.59 (m, 2H), 1.57−1.50 (m, 3H), 1.47−1.42 (m, 1H), 1.31−1.25 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 150.3, 128.2, 115.9, 111.6, 49.8, 38.2, 31.5, 27.6, 25.4. GC−MS (EI) *m*/*z*: 203.

*N-(Cycloheptylmethyl)-4-methylaniline (**4b**).* To a mixture of *N*,4-dimethylaniline (60.5 mg, 0.5 mmol) **1b**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cycloheptane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **4b** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (69.4 mg, 64%).[8h] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.02 (d, *J* = 8.1 Hz, 2H), 6.58 (d, *J* = 8.1 Hz, 2H), 2.97 (d, *J* = 6.6 Hz, 2H), 2.28 (s, 3H), 1.88−1.81 (m, 2H), 1.75−1.69 (m, 2H), 1.64−1.62 (m, 1H), 1.56−1.48 (m, 3H), 1.31−1.25 (m, 3H), 0.95−0.88 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 145.2, 128.7, 125.2, 111.9, 50.3, 38.1, 31.4, 27.6, 25.4, 19.4. GC−MS (EI) *m*/*z*: 217.

*4-Chloro-N-(cycloheptylmethyl)aniline (**4c**).* To a mixture of 4-chloro-*N*-methylaniline (70.5 mg, 0.5 mmol) **1e**, FeCl2 (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na2CO3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cycloheptane = 2.0 mL). The reaction mixture was stirred at 140 °C

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in an oil bath for 18 h in air. Following the general procedure, **4c** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (77.0 mg, 65%).[8h] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.14 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 2.95 (d, *J* = 6.6 Hz, 2H), 1.86−1.79 (m, 2H), 1.73−1.70 (m, 1H), 1.64−1.59 (m, 2H), 1.55−1.48 (m, 3H), 1.28−1.23 (m, 3H), 0.93−0.89 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 145.9, 128.0, 112.9, 99.0, 50.1, 38.1, 31.4, 27.5, 25.4. GC−MS (EI) *m*/*z*: 237.

*3-Chloro-N-(cycloheptylmethyl)aniline (**4d**).* To a mixture of 3-chloro-*N*-methylaniline (70.5 mg, 0.5 mmol) **1k**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cycloheptane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **4d** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (79.4 mg, 67%). ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.09 (t, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.61 (s, 1H), 6.50 (dd, *J* = 8.2, 2.3 Hz, 1H), 2.96 (d, *J* = 6.6 Hz, 2H), 1.85−1.79 (m, 2H), 1.73−1.70 (m, 1H), 1.62 (dt, *J* = 9.2, 3.1 Hz, 2H), 1.55−1.48 (m, 3H), 1.28−1.21 (m, 3H), 0.93−0.88 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 134.1, 129.2, 116.0, 111.4, 110.2, 101.8, 49.8, 38.0, 31.4, 27.6, 25.4. GC−MS (EI) *m*/*z*: 237. HRMS (ESI) *m*/*z*: calcd for $[C_{14}H_{20}ClN + H]^+$, 238.1363; found, 238.1358.

*N-(Cycloheptylmethyl)-3-methylaniline (**4e**).* To a mixture of *N*,3-dimethylaniline (60.5 mg, 0.5 mmol) **1l**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cycloheptane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **4e** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (67.3 mg, 62%). ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.09 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.4 Hz, 1H), 6.46 (s, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 2.97 (d, *J* = 6.5 Hz, 2H), 2.31 (s, 3H), 1.87−1.81 (m, 2H), 1.73−1.70 (m, 1H), 1.66−1.60 (m, 2H), 1.55−1.47 (m, 3H), 1.29−1.21 (m, 3H), 0.95−0.89 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 147.6, 138.0, 128.1, 117.0, 112.5, 108.9, 49.9, 38.2, 31.5, 27.6, 25.4, 20.7. GC−MS (EI) *m*/*z*: 217. HRMS (ESI) *m*/*z*: calcd for $[C_{15}H_{23}N + H]^+$, 218.1909; found, 218.1923.

*N-(Cyclooctylmethyl)aniline (**4f**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclooctane = 2.0 mL). The reaction mixture was stirred at 150 °C in an oil bath for 18 h in air. Following the general procedure, **4f** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (59.7 mg, 55%).[8j] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.18 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 2.95 (d, *J* = 6.9 Hz, 2H), 1.85−1.79 (m, 1H), 1.77−1.68 (m, 5H), 1.63−1.59 (m, 3H), 1.53−1.49 (m, 3H), 1.39−1.34 (m, 2H), 1.30−1.27 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 147.7, 128.2, 115.9, 111.6, 50.2, 36.5, 29.7, 26.1, 25.4, 24.6. GC−MS (EI) *m*/*z*: 217.

*(R)-N-((1,4-Dioxan-2-yl)methyl)aniline (**4h**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (1,4-dioxane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **4h** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (43.4 mg, 45%). ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.23 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.78 (dd, *J* = 7.9, 6.8 Hz, 1H), 6.69−6.65 (m, 2H), 4.05 (s, 1H), 3.89−3.85 (m, 2H), 3.82−3.76 (m, 2H), 3.74−3.65 (m, 2H), 3.51 (dd, *J* = 11.4, 9.7 Hz, 1H), 3.24 (dd, *J* = 12.7, 4.0 Hz, 1H), 3.14 (dd, *J* = 12.7, 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 128.3, 116.9, 112.1, 111.6, 72.9, 68.4, 67.6, 65.6, 44.1. GC−MS (EI) *m*/*z*: 193. HRMS (ESI) *m*/*z*: calcd for $[C_{11}H_{15}NO_2 + H]^+$, 194.1181; found, 194.1183.

*(S)-N-((Tetrahydrofuran-2-yl)methyl)aniline (**4i**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (tetrahydrofuran = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **4i** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (52.2 mg, 59%).[8k] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.23 (q, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.74−6.66 (m, 2H), 4.22−4.15 (m, 1H), 3.94 (t, *J* = 7.4 Hz, 1H), 3.84 (t, *J* = 7.2 Hz, 1H), 3.36−3.26 (m, 1H), 3.19−3.07 (m, 1H), 2.15−2.05 (m, 1H), 2.04−1.91 (m, 2H), 1.78−1.66 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 148.3, 129.2, 117.6, 113.2, 76.8, 68.1, 48.3, 29.2, 25.9. GC−MS (EI) *m*/*z*: 177.

*N-Phenethylaniline (**5a**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (toluene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5a** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (68.0 mg, 69%).[8l] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.38 (t, *J* = 7.4 Hz, 2H), 7.32−7.26 (m, 3H), 7.24 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.80−6.74 (m, 1H), 6.71−6.66 (m, 2H), 3.46 (t, *J* = 7.1 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 146.9, 138.3, 128.3, 127.8, 127.7, 125.5, 116.7, 112.2, 44.2, 34.5. GC−MS (EI) *m*/*z*: 197.

*N-(4-Methylphenethyl)aniline (**5b**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (*p*-xylene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5b** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (45.4 mg, 43%).[8m] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.24 (t, *J* = 7.7 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 3.44 (t, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 147.0, 135.2, 135.0, 128.4, 128.3, 127.7, 116.6, 112.1, 44.3, 34.1, 20.1. GC−MS (EI) *m*/*z*: 211.

*N-(4-Chlorophenethyl)aniline (**5c**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (1-chloro-4-methylbenzene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5c** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (65.8 mg, 57%).[8n] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.36 (t, *J* = 7.5 Hz, 2H), 7.31−7.23 (m, 3H), 7.19−7.14 (m, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.41 (t, *J* = 7.0 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 145.4, 138.0, 128.1, 127.8, 127.7, 125.6, 121.3, 113.3, 44.3, 34.3. GC−MS (EI) *m*/*z*: 231.

*N-(4-Bromophenethyl)aniline (**5d**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (1-bromo-4-methylbenzene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5d** was purified by column chromatography on silica gel (petroleum ether/

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ethyl acetate = 7:3) as a white solid (86.6 mg, 63%).[8o] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.47 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 3.43 (t, *J* = 7.0 Hz, 2H), 2.91 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 146.7, 137.3, 130.7, 129.6, 128.4, 119.3, 116.8, 112.1, 44.0, 33.9. GC−MS (EI) *m*/*z*: 275.

*N-(2-Chlorophenethyl)aniline (**5e**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (1-chloro-2-methylbenzene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5e** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (69.3 mg, 60%).[8p] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.42 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.28−7.20 (m, 5H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.7 Hz, 2H), 3.47 (t, *J* = 7.2 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 146.7, 136.0, 133.2, 130.0, 128.7, 128.4, 127.0, 126.0, 116.7, 112.1, 42.6, 32.5. GC−MS (EI) *m*/*z*: 231.

*N-(3-Chlorophenethyl)aniline (**5f**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (1-chloro-3-methylbenzene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5f** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (71.6 mg, 62%).[8q] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.36 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.30−7.24 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.65 (t, *J* = 2.2 Hz, 1H), 6.53 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.42 (t, *J* = 7.0 Hz, 2H), 2.96 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 138.7, 137.9, 134.1, 129.3, 127.8, 127.7, 125.6, 116.6, 111.8, 110.6, 44.1, 34.3. GC−MS (EI) *m*/*z*: 231.

*4-Methoxy-N-phenethylaniline (**5g**).* To a mixture of 4-methoxy-*N*-methylaniline (68.5 mg, 0.5 mmol) **1c**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (toluene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5g** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (74.9 mg, 66%).[8r] ^{1}H NMR (500 MHz, chloroform-*d*, δ) 7.36 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 8.9 Hz, 3H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.41 (t, *J* = 7.0 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 151.3, 141.1, 138.4, 127.8, 127.6, 125.4, 114.0, 113.6, 54.9, 45.2, 34.6. GC−MS (EI) *m*/*z*: 227.

*4-Chloro-N-phenethylaniline (**5h**).* To a mixture of 4-chloro-*N*-methylaniline (70.5 mg, 0.5 mmol) **1e**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (toluene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5h** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (77.4 mg, 67%).[8s] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.32 (d, *J* = 8.3 Hz, 2H), 7.25−7.16 (m, 4H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 3.43 (t, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 146.6, 136.7, 131.3, 129.1, 128.4, 127.7, 116.9, 112.2, 44.1, 33.8. GC−MS (EI) *m*/*z*: 231.

*2-Chloro-N-phenethylaniline (**5i**).* To a mixture of 2-chloro-*N*-methylaniline (70.5 mg, 0.5 mmol) **1′**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (toluene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5i** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (58.9 mg, 51%).[8t] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.42 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.29−7.20 (m, 5H), 6.77 (d, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 2H), 3.47 (t, *J* = 7.2 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 146.8, 136.0, 130.0, 128.7, 128.4, 127.0, 125.9, 116.6, 112.1, 42.5, 32.5. GC−MS (EI) *m*/*z*: 231.

*3-Chloro-N-phenethylaniline (**5j**).* To a mixture of 3-chloro-*N*-methylaniline (70.5 mg, 0.5 mmol) **1k**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (toluene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5j** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (67.0 mg, 58%).[8u] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.32−7.20 (m, 5H), 7.14 (d, *J* = 7.0 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 2H), 3.45 (t, *J* = 7.0 Hz, 2H), 2.94 (t, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 146.6, 140.4, 133.4, 128.9, 128.4, 127.9, 126.0, 125.7, 116.8, 112.1, 43.9, 34.2. GC−MS (EI) *m*/*z*: 231.

*3-Methyl-N-phenethylaniline (**5k**).* To a mixture of *N*,3-dimethylaniline (60.5 mg, 0.5 mmol) **1l**, $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (toluene = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **5k** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (55.9 mg, 53%).[8v] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.36 (dd, *J* = 8.6, 6.5 Hz, 2H), 7.28 (dd, *J* = 8.2, 6.6 Hz, 3H), 7.12 (dd, *J* = 9.0, 7.3 Hz, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.49 (d, *J* = 6.4 Hz, 2H), 3.44 (t, *J* = 7.0 Hz, 2H), 2.96 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 147.0, 138.1, 128.2, 127.8, 127.6, 125.4, 117.6, 112.9, 109.3, 44.2, 34.6, 20.7. GC−MS (EI) *m*/*z*: 211.

*(2-Cyclohexylethene-1,1-diyl)dibenzene (**6a**).* To a mixture of *N*-methylaniline (53.5 mg, 0.5 mmol) **1a**, ethene-1,1-diyldibenzene (360.0 mg, 2.0 mmol), $FeCl_2$ (9.5 mg, 0.075 mmol, 15 mol %), ligand **L3** (23.6 mg, 0.1 mmol, 20 mol %), TBHP (157.7 mg, 1.75 mmol, 3.5 equiv), and additive Na_2CO_3 (58.3 mg, 0.55 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 2.0 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **6a** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) as a white solid (267.2 mg, 51%).[8w] ^{1}H NMR (500 MHz, chloroform-*d*, δ): 7.38 (t, *J* = 7.2 Hz, 2H), 7.33 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.29−7.23 (m, 3H), 7.22−7.17 (m, 4H), 5.92 (d, *J* = 10.0 Hz, 1H), 2.14 (dd, *J* = 10.3, 3.2 Hz, 1H), 1.71−1.67 (m, 3H), 1.61 (d, *J* = 4.9 Hz, 1H), 1.23−1.13 (m, 5H), 0.91−0.84 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, chloroform-*d*, δ): 143.0, 140.6, 139.6, 136.0, 129.8, 128.2, 128.1, 127.2, 126.8, 126.7, 38.3, 33.4, 26.0, 25.6. GC−MS (EI) *m*/*z*: 262.

Scale-Up Experiment. To a mixture of *N*-methylaniline (535 mg, 5 mmol) **1a**, $FeCl_2$ (95 mg, 0.75 mmol, 15 mol %), ligand **L3** (236 mg, 1 mmol, 20 mol %), TBHP (1.577 g, 17.5 mmol, 3.5 equiv), and additive Na_2CO_3 (583 mg, 5.5 mmol, 1.1 equiv) in a reaction tube was added to the solvent (cyclohexane = 20 mL). The reaction mixture was stirred at 140 °C in an oil bath for 18 h in air. Following the general procedure, **3a** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 7:3) as a white solid (652.1 mg, 69%) (caution: TBHP is unstable above 75 °C, and heating large amounts of TBHP at 140 °C is potentially dangerous[7c]).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00625.

NMR spectra of the obtained compounds (ZIP)

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Notes

The authors declare no competing financial interest.

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