Use of (Cyclopentadienone)iron Tricarbonyl Complexes for C−N Bond Formation Reactions between Amines and Alcohols

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Supporting Information

ABSTRACT: The application of a series of (cyclopentadienone)iron tricarbonyl complexes to “borrowing hydrogen” reactions between amines and alcohols was completed in order to assess their catalytic activity. The electronic variation of the aromatic groups flanking the C=O of the cyclopentadienone influenced the efficiency of the reactions; however, in other cases, the Knöllker catalyst 1, containing trimethylsilyl groups flanking the cyclopentadienone ketone, gave the best results. In some cases, the change of the ratio of amine to alcohol improves the conversion significantly. The application of iron catalysts to the synthesis of a range of amines, including unsaturated amines, was investigated.

INTRODUCTION

“Hydrogen borrowing” is a term commonly used to describe the use of an organometallic catalyst to form a new C−N or C−C bond with the generation of water as the only side product.1 In the case of the C−N bond formation, the key steps are (i) the sequential removal of hydrogen from an alcohol to form an aldehyde or ketone through oxidation, (ii) the formation of an imine via reaction with an amine, and (iii) the reduction of the imine to the corresponding amine by the hydride of the catalyst used in step 1 (Scheme 1).

There are many reports of the use of metal-based organometallic catalysts for this application; however, the majority of examples are based on precious metals such as ruthenium, iridium, etc.2a−f although with some recent work reported on the use of lower cost metals such as manganese.26 Iron-based catalysts for organic transformations represent a desirable alternative due to the low cost and ready availability of this element.3−11 In recent research, (cyclopentadienone)iron tricarbonyl complexes have been extensively applied to the oxidation of alcohols,4 the reduction of imines,5 and the reduction of ketones (including asymmetric examples).6 The use of these complexes in hydrogen borrowing reactions has only been reported recently however.6−9 The first example was in 2014 by Feringa et al.7 using complex 1 as the precatalyst.12 Scheme 2 illustrates the reaction cycle; the active species 2 is generated in situ through loss of a CO from the precatalyst 1 using one of a number of activation methods. A hydride

Scheme 1. Steps of a “Hydrogen Borrowing” Reaction

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intermediate, the Knölker complex 3,13 is generated through the oxidation step, and this provides the hydride for the reduction step.

In our own studies, we previously reported the use of iron catalyst 4 in the synthesis of a range of secondary amines via borrowing hydrogen methodology from aryl amines and primary alcohols, although our best results were obtained from the reactions of benzyl alcohols with aromatic amines (Scheme 3).8

Zhao et al. published a modification to the methodology whereby the addition of a Lewis acid to increase the reactivity of the imine assisted the imine reduction step to form the desired final amine product in reactions with secondary alcohols (Scheme 4).9

We have continued to work on an extended range of iron complexes for hydrogen borrowing applications, and on extending the scope of the catalysts, and our recent detailed results from this study are described below.

## RESULTS AND DISCUSSION

To date, the iron cyclopentadienone complexes used in C–N bond formation include the tetraphenyl-substituted 4 and the complex 1, and close derivatives of these.11–13 Complexes analogous to 1, but containing aromatic rings flanking the central C==O, benefit from the ease of preparation14 and offer an opportunity to investigate the effect of changes to the electron-rich or electron-poor nature of the substituent groups on their reactivity. Hence, iron complexes 5–9 and 16, each based on the cyclohexyl backbone, were targeted for preparation via an intramolecular Fe(CO)5-catalyzed cyclization of dialkyne precursors 10–15.14

The synthesis of iron complexes 5–8 was achieved starting from the respective diaryl dialkyne precursors 10–13, themselves synthesized via a Sonogashira reaction16 (Scheme 5), except for 12, which was more challenging and required an alternative set of conditions to yield intermediate 12, but with a yield of only 12%. The synthesis of iron complexes using the intramolecular cyclization approach was successful for compounds 5–8, giving products in yields of 91–98% (Scheme 5).14 The synthesis of iron complex 9 was unsuccessful, and the
reaction resulted in the complete decomposition of the starting material. However, the electron-deficient iron bis-trifluoromethoxyphenyl complex 16 was prepared in a yield of 97% from the dialkyne precursor 15. Crystals of complex 6 suitable for analysis by X-ray diffraction were grown by slow evaporation from EtOAc (Figure 1, full details in the Supporting Information, Table S1). An interesting aspect of the structure is the twisted nature of the aromatic rings flanking the C=O bond of the cyclopentadienyl group, creating a "propeller-type" arrangement.

Before testing all of the catalysts, we screened a number of solvents in the reaction between aniline 17 and benzyl alcohol 18 to give amine 19 (Scheme 6) using catalyst 5 for the initial tests. Activation of the catalyst was achieved using trimethylamine oxide.14b,16 Of the solvents tested, good results were obtained using xylene, toluene, tetrahydrofuran, and ethyl acetate, which all gave conversions of 85% with the best conversion of 90% being observed with xylene. The use of cyclopentylmethyl ether was also examined as this solvent had been previously used with success by Feringa,7 but only a 70% conversion was observed in our study. A poorer result was obtained with the use of diethyl ether with a conversion of 60%, and the use of dichloromethane resulted in the formation of an insoluble solid with no conversion to the desired product. However, this solid was not characterized.

With a screening of possible solvents complete, xylene was selected for use in further "hydrogen borrowing" reactions with iron complexes 6–8 and 10 to compare their potential for the catalysis of the reaction of amine 17 with a range of primary alcohols to give products 19–24 (Table 1). Conversions were recorded in all cases, and isolated yields were obtained where stated. For the reaction with benzaldehyde, the highest conversions were achieved using the more electron-rich and electron-poor iron complexes analogues, 7 and 10, which gave conversions of 91% and 87%, respectively. Iron complexes 6 and 8 gave lower conversions of 60% and 66%, respectively. This pattern was not consistent throughout the substrates however. Catalyst 7 generally gave lower conversions, while the phenyl catalyst 5 and the bis p-methoxyphenyl catalyst 6 performed well for most substrates. Some combinations were quite specific; for example, catalyst 10 was the best for the reaction with 4-phenylbutanol, while 5 and 6 were significantly better than the other catalysts for the conversion of 2-(4-methoxyphenyl)ethanol.

3-(4-Methoxyphenyl)-1-propanol also reacted in high yield with substituted anilines using the bis(methoxyphenyl)-substituted complex 6 to give products 25 and 26 (Scheme 7). N-Methylaniline gave a tertiary amine product 27 in 50% yield using the same catalyst. Under the conditions used, which required an excess of amine in line with our earlier communication,8 more basic nonaromatic amines such as benzylamine, pyrrolidine, and 4-phenylbutylamine failed to give products, possibly due to catalyst inhibition.17 Diphenylamine also failed to react under the conditions attempted.

A complex pattern of results emerged from the reactions of aniline with cyclic alcohols and diols using the bis(aryl)-substituted catalysts (Figure 2). Aliphatic secondary cyclic alcohols cyclopentanol, cyclohexanol, cycloheptanol, and β-tetralol gave products in good yields, representing a valuable

![Scheme 6. Solvent Screening in C–N Bond Formation](image)

![Figure 1. Single-crystal X-ray structure of 6. Hydrogens were omitted for clarity, and ellipsoids were drawn at 50% probability.](image)

![Table 1. Results of C–N Bond Formation via "Hydrogen Borrowing" Reactions](image)
application of the methodology. However, cyclic or acyclic benzylic/propargylic alcohols including α-tetralol, 1-phenyl-ethanol, and 2-hydroxy-4-phenyl-but-3-yne did not give the products of hydrogen borrowing (Figure 2). It is possible that these alcohols form a stable imine or possibly the enamine upon condensation of the corresponding ketone with aniline, but these intermediates were not isolated from the reactions. The reaction of aniline with diols was also briefly assessed, and

Figure 2. Products formed from the reaction of aniline with cyclic alcohols (2:1 aniline/alcohol), cyclic alcohols, which did not work (10% catalyst, 2:1, 140 °C, 16h), and products of reactions with diols (2 equiv diol employed).

Figure 3. Products of the reaction of aliphatic and unsaturated alcohols to (A) anilines and (B) benzylamine using catalyst 1. For the best results in reaction A, an excess of the aniline is required. For reaction B, an excess of alcohol gives the best results.
products were isolated from the reactions, but in low yields. In the case of 1,5-dihydroxypentane, a product could not be isolated (Figure 2). In the diol reactions, some aminoalcohol was also formed in each case, i.e., from the reaction of only one alcohol in the diol.

The reactions of amines with alcohols containing an unsaturated functionality more distant from the alcohol are capable of forming valuable addition products (Figure 3). Initially, we used our standard conditions, i.e., an excess of amine, which had previously given good results. Unfortunately, for these substrates, the yields were low using the bis(aryl) complexes 5 and 6 as catalysts. In contrast, improved results were achieved using the Knölker catalyst precursor 1 (Figure 3A). At 140 °C, both alkene- and alkyne-containing products 37 and 38 were formed in 95% and 80% isolated yields, respectively, and 37 was also formed in 75% yield at 120 °C. Successful additions of the pentenyl group were also achieved using p-methoxy and p-chloro anilines to give 39 and 40, respectively (Figure 3A). As far as we are aware, these represent the first reported examples of C–N bond formation under hydrogen borrowing conditions of unsaturated alcohols using an iron-based catalyst. Under these conditions, however, the reaction of the corresponding non-TMS-protected alkyne hex-5-yn-1-ol did not yield a product, possibly due to an interaction with the terminal alkyne causing catalyst inhibition.

In an extension of this work, we thought it was possible that more basic (i.e., nonaromatic) amines could be inhibiting the iron catalyst; therefore, we reversed the ratio of reagents so that an excess of alcohol was used. This resulted in the successful formation of the desired amine products from the reaction of benzylamine with pentanol (Figure 3B), and products 41–44 containing alkene, alkyne, and aromatic functionality were successfully added to the amine. To expand upon this improved reactivity, the amine/alcohol 1:2 ratio was applied to the hydrogen borrowing reactions of the cyclic basic amine 4-phenylpiperidine, and in the coupling products, 45–53 were formed in good yields from primary and secondary alcohols (Figure 4). 4-Phenylpiperidine, possibly due to its more hydrophobic nature and better solubility in xylene, was found to be more compatible with this application, under the reaction conditions used, than more hydrophilic amines such as piperidine and morpholine, from which products were not isolated.

The revised reaction conditions, coupled to the use of catalyst 1, permitted further C–N bond formation reactions with a benzylic amine (Figure 5). In these examples, 3-trifluoromethyl benzylamine was selected as a representative
coupled with benzyl alcohol to form the secondary amine, a longer chain amine, 4-phenylbutylamine, was successfully generated and was used in the formation of secondary amine products from cyclic alcohols. An understanding of this reaction and its potential solution are not immediately clear, although it is possible that the substrate or an intermediate in the reaction inhibits the catalyst by chelation. Studies are ongoing in order to establish a better understanding of this reaction and a potential solution.

**CONCLUSION**

A series of novel iron complexes, containing aryl groups flanking the central C≡O in the cyclopentadienyl ring, were prepared and applied to the catalysis of the formation of C–N bond formation of aromatic amines via hydrogen borrowing. For alcohols containing double or triple bonds, the Knöller catalyst 1 was more effective, however, and gave unsaturated products in good yields using anilines as the amine component. For coupling reactions involving basic amines, the reversed 1:2 ratio of amine/alcohol gave improved results, possibly due to reduced inhibition of the catalyst.

**EXPERIMENTAL SECTION**

General Experimental Methods. All solvents and reagents were degassed before use, and all reactions were carried out under a nitrogen atmosphere. Reactions were monitored by TLC using aluminum backed silica gel 60 (F254) plates and were visualized using UV 254 nm and phosphomolybdic acid or potassium permanganate dips as appropriate. Flash column chromatography was carried out routinely on silica gel. Reagents were used as received from commercial sources unless otherwise stated. Dry solvents were purchased and used as received. All syntheses of iron complexes and iron catalytic reactions were carried out in ACE 15 MI 150 psi pressure tested pressure tubes and heated in aluminum heating blocks. 1H NMR spectra were recorded on a Bruker DPX (400 or 500 MHz) spectrometer. Chemical shifts were reported in δ units, parts per million relative to the singlet at 7.26 ppm for chloroform and 0.00 ppm for TMS. Mass spectra for the analysis of synthetic products were recorded on a Bruker Esquire2000 or a Bruker MicroTOF mass spectrometer. Coupling constants (J) were measured in hertz (Hz). IR spectra were recorded on a PerkinElmer Spectrum One FT-IR Golden Gate. Melting points were recorded on a Stuart Scientific SMP 1 instrument and were uncorrected.

Figure 6. Products formed from the reaction of secondary alcohols with primary amines using catalyst 1 and a 1:2 ratio of amine/alcohol. The arrow indicates the position of the newly formed bond.

A class of alcohol substrates, which continue to be challenging in this application, contain oxygen atoms at a nearby position to the alcohol (Figure 7). The reasons for this are not immediately clear, although it is possible that the substrate or an intermediate in the reaction inhibits the catalyst by chelation. Studies are ongoing in order to establish a better understanding of this reaction and a potential solution.

![Image](image_url)

Figure 7. Oxygen-containing alcohols that did not work in this application.
8,14-Methano-1H-inden-2-one (11). 1,8-Bis-(4-methoxyphenyl)octa-1,7-dyne was prepared via the same method as 1,8-diphenyl-1,7-diyne, with 1,8-bis(4-methoxyphenyl)octa-1,7-dyne as the white solid (1.77 g, 5.66 mmol); mp 79-80°C; IR ν max 2954, 2855, 1619 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 7.73, 7.69, 7.18, 4.07, 3.95, 3.84, 1.71, 1.69 ppm; 13C NMR (100 MHz, CDCl₃) δ 141.1, 139.2, 131.9, 102.0, 81.6, 68.9, 59.3, 28.0, 22.3 ppm; MS (ESI) m/z 461 [M + H⁺].

Tricarbonyl(1,3-dimethyl-4,5,6,7-tetrahydro-2H-inden-2-one)iron (7). Tricarbonyl(1,3-dimethyl-4,5,6,7-tetrahydro-2H-inden-2-one)iron was prepared via the same procedure as used for tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2H-inden-2-one)iron, using 1,8-bis(4-methoxyphenyl)octa-1,7-diyne (1.00 g, 3.91 mmol) and Fe(CO)₅ (62 mg, 0.30 mmol). The reaction mixture was stirred at 80°C overnight. Complex 7 was isolated as a brown solid (276 mg, 1.49 mmol, 49.8%); mp 157-158°C; HRMS (ESI-TOF) m/z [M + Na⁺] calc'd for C₂₆H₁₆F₆FeNaO₄ 585.0195, found 585.0196; IR ν max 2941, 2054, 1618 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 7.74 (4H, d, J = 10.0 Hz, ArH), 7.38 (4H, d, J = 8.8 Hz, ArH), 2.37-3.04 (4H, m, CH₂CH₂CH₂CH₂) ppm; 13C NMR (100 MHz, CDCl₃) δ 139.6, 131.6, 130.7, 129.9, 128.7, 103.1, 80.3, 23.8, 22.2 ppm; MS (ESI) m/z 495 [M + H⁺].

1,8-Bis-(4-nitrophenyl)octa-1,7-dyne (14). 1,8-Bis-(4-nitrophenyl)octa-1,7-dyne was synthesized via the same procedure as used for 1,8-bis(4-methoxyphenyl)octa-1,7-dyne, using 1,7-octadiyne (440 mg, 2.33 mmol) and Fe(CO)₅ (62 mg, 0.30 mmol). The reaction mixture was stirred at 80°C overnight. Complex 14 was isolated as a brown solid (257 mg, 0.141 mmol), and Pr₂NH (6.60 mmol, 4.77 g, 47.11 mmol) to give 1,8-bis-(4-nitrophenyl)octa-1,7-dyne as an orange solid (0.339 g, 0.974 mmol, 34%); mp 40-42°C; HRMS (ESI-TOF) m/z [M + Na⁺] calc'd for C₂₆H₂₀N₂O₄ 450.1148, found 450.1147; IR ν max 2941, 2054, 1618 cm⁻¹; 1H NMR (400 MHz, CDCl₃) δ 8.16 (4H, d, J = 8.0 Hz, ArH), 7.52 (4H, d, J = 8.0 Hz, ArH), 2.54 (4H, br s, CH₂CH₂CH₂CH₂) ppm; 13C NMR (100 MHz, CDCl₃) δ 146.7, 132.3, 130.7, 123.5, 95.8, 79.8, 78.6, 19.2 ppm; MS (ESI) m/z 349 [M + H⁺].

1,8-Bis-(4-trifluoromethylphenyl)octa-1,7-dyne (15). 1,8-Bis-(4-trifluoromethylph)enyl)octa-1,7-dyne was synthesized via the same procedure as previously used to synthesize 1,8-diphenyl-1,7-diyne, with 1,7-octadiyne (375 mg, 2.33 mmol) and 4-fluorobenzonitrile (916 mg, 7.623 mmol), PdCl₂(PPh₃)₂ (30.0 mg, 0.0425 mmol), Cu (160 mg, 0.0850 mmol), and Pr₂NH (3.97 ml, 2.86 g, 28.3 mmol). The reaction was performed at room temperature overnight, and the reaction mixture was passed through a Celite silica plug with 20/80 ethyl acetate/pentane. Subsequent column chromatography eluted with 0-20% ethyl acetate in pentane gave the product as a white solid (0.759 g, 2.32 mmol, 82.2%); mp 42-43°C; HRMS (ESI-TOF) m/z [M + Ag⁺] calc'd for C₃₉H₂₅FeAgCl₄ 543.9668, found 543.9655; IR ν max 2941, 2871, 2769, 1624 cm⁻¹; 1H NMR (500 MHz, CDCl₃) δ 7.30 (4H, d, J = 10.0 Hz, ArH), 7.23 (4H, d, J = 10.0 Hz, ArH), 2.46-2.42 (4H, m, CH₂CH₂CH₂CH₂), 1.75 (4H, m, CH₂CH₂CH₂CH₂) ppm; 13C NMR (126 MHz, CDCl₃) δ 134.6, 133.1, 128.6, 122.5, 90.9, 80.0, 27.8, 19.1 ppm; MS (ESI) m/z 435 [M + Ag⁺].
In a dried and degassed 250 ml round-bottom flask, under N₂, Zn(OtBu)₂ (335 mg, 0.922 mmol) and NEt₃ (7.70 mL, 5.59 g, 55.3 mmol) were dissolved in anhydrous DCM (50.0 mL), and the solution was cooled to 0 °C in an ice bath. A solution of 1,7-octadiyne (2.44 mL, 19.6 g, 18.4 mmol) in anhydrous DCM (15.0 mL) was slowly added under N₂ followed by a solution of TMSOTf (10.0 mL, 12.3 g, 55.3 mmol) in anhydrous DCM (15.0 mL), also slowly added under N₂ with the ice bath remaining in place. Heavy white fumes were produced, which dispersed to give a red/brown solution. The reaction was stirred overnight at room temperature, quenched with NH₄Cl and extracted with Et₂O (3 × 50 mL). The organic fraction was dried with anhydrous Na₂SO₄ and filtered, and the solvent was removed via a rotary evaporator to give a brown oil. 1,8-Bis(trimethylsilyl)octa-1,7-diyne was isolated through column chromatography on silica gel eluted with pentane to give the product as a colorless oil (201 μL, 1.46 mmol). 1,8-Bis(trimethylsilyl)octa-1,7-diyne was synthesized via the general procedure previously described for 1,8-bis(trimethylsilyl)octa-1,7-diyne, using 1,8-bis(trimethylsilyl)octa-1,7-diyne (300 mg, 2.00 mmol) and Fe(CO)₅ (792 μL, 1.18 g, 6.00 mmol) in toluene (5 mL). Tricarbonyl(1,3-di(trimethylsilyl))-4,5,6,7-tetrahydro-2Hinden-2-one (1).¹⁻⁻⁵ Tricarbonyl(1,3-di(trimethylsilyl))-4,5,6,7-tetrahydro-2H-inden-2-one was synthesized via the general procedure previously used for tricarbonyl(1,3-diphenyl)-4,5,6,7-tetrahydro-2H-inden-2-one, using 1,3-di(trimethylsilyl)-1,7-octadiyne (500 mg, 2.00 mmol) and Fe(CO)₅ (186 mg, 1.25 mmol) in toluene (5 mL). The Journal of Organic Chemistry N-(4-Phenylbutyl)aniline (2).²⁻⁻⁶ N-(4-Phenylbutyl)aniline was synthesized via the same procedure as previously described method using 3-(4-methoxyphenylethyl)-1-propanol (166 mg, 1.00 mmol), aniline (182 μL, 2.00 mmol), tricarbonyl(1,3-di(4-fluoromethylphenyl))-4,5,6,7-tetrahydro-2H-inden-2-one (56.2 mg, 0.100 mmol), and trimethylamine N-oxide (6.75 mg, 0.09 mmol) in pentane. Column chromatography eluted with 0–5% ethyl acetate in pentane gave the product as a colorless oil (226 μg, 0.938 mmol, 94%). Chromatography column eluted with 0–5% ethyl acetate in pentane afforded the product as a colorless oil (226 μg, 0.938 mmol, 94%). HRMS (ESI-TOF) m/z [M + H]⁺ calculated for C₂₃H₂₃N₂ 212.1590 (26.261589), C₂₃H₂₅ClO 221.1590, C₂₃H₂₅NClO (26.261589)
N-3-(4-Methoxyphenyl)propyl-N-methylamine (27)  
N-3-(4-Methoxyphenyl)propyl-N-methylamine was prepared via the general procedure using N-methylamine (217 μL, 214 mg, 2.00 mmol), 3-(4-methoxyphenyl)-1-propanol (166 mg, 1.00 mmol), tricarbonyl(1,3-dimethyl-4-phenyl)pentadienyliron as a colorless oil (127 mg, 0.498 mmol, 49.8%). HRMS (ESI-TOF) m/z [M + H]+ calcd for C16H19ClNO 276.1150 and 278.1120, found 276.1151 and 278.1142.

N-Cyclohexylamine was synthesized via the general method using aniline (91 μL, 93 mg, 1.00 mmol), 1,6-hexanediol (210 μL, 236 mg, 2.00 mmol), tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.6 mg, 0.100 mmol), and trimethylamine N-oxide (6.75 mg, 0.09 mmol). Flash chromatography with 0–5% ethyl acetate in pentane gave N-phenylcyclohexylamine as a colorless oil (131 mg, 0.587 mmol, 58.7%). HRMS (ESI-TOF) m/z [M + H]+ calcd for C21H22N 304.1661, found 304.1667.

N-(4-Methoxyphenyl)aniline (20)  
N-(4-Methoxyphenyl)aniline was prepared via the general procedure using aniline (182 μL, 186 mg, 2.00 mmol), 1,6-hexanediol (210 μL, 236 mg, 2.00 mmol), tricarbonyl(1,3-dimethyl-4-phenyl)pentadienyliron as a colorless oil (127 mg, 0.498 mmol, 49.8%). HRMS (ESI-TOF) m/z [M + H]+ calcd for C16H19ClNO 276.1150 and 278.1120, found 276.1151 and 278.1142.

N-Cyclohexylamine (29)  
N-Cyclohexylamine was synthesized via the general method from aniline (182 μL, 186 mg, 2.00 mmol), cyclohexane (105 μL, 100 mg, 1.00 mmol), tricarbonyl(1,3-dimethyl-4-phenyl)pentadienyliron as a yellow oil (166 mg, 0.949 mmol, 95.6%). HRMS (ESI-TOF) m/z [M + H]+ calcd for C15H16N 224.1234, found 224.1243.

N-Phenylcyclohexylamine (28)  
N-Phenylcyclohexylamine was prepared via the general procedure using aniline (182 μL, 186 mg, 2.00 mmol), 1,6-hexanediol (210 μL, 236 mg, 2.00 mmol), tricarbonyl(1,3-dimethyl-4-phenyl)pentadienyliron as a colorless oil (127 mg, 0.498 mmol, 49.8%). HRMS (ESI-TOF) m/z [M + H]+ calcd for C16H19ClNO 276.1150 and 278.1120, found 276.1151 and 278.1142.
general procedure using aniline (182 μL, 186 mg, 2.00 mmol), 6-(trimethylsilyl)hex-5-yn-1-yl (166 mg, 1.00 mmol), tricarbonyl(1,3-di( trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.200 mmol). N-(6-(Trimethylsilyl)hex-5-yn-1-yl)amine was isolated via column chromatography (196 mg, 0.799 mmol, 79.9%). HRMS (ESI-TOF) m/z [M + H]+ calc'd for C17H22NO 246.1682, found 246.1988; HRMS (EI) m/z [M + H]+ calc'd for C17H22NO 231.1715, found 231.1707; 1H NMR (500 MHz, CDCl3) δ 7.20 (2H, d, J = 8.5 Hz, ArH), 7.29 (2H, t, J = 8.0 Hz, ArH), 6.95 (2H, t, J = 8.0 Hz, ArH), 6.21 (2H, t, J = 7.0 Hz, NCH2CH2), 6.06 (2H, t, J = 7.0 Hz, NCH2CH2), 3.25 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.57 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.40 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.33 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.19 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)); 13C NMR (126 MHz, CDCl3) δ 140.2, 134.3, 128.9, 128.2, 127.0, 54.0, 49.4, 29.7, 26.6, 21.8 ppm; MS (EI) m/z 117 (M + H), 100%. N-Benzylpent-4-en-1-ylamine was synthesized via the general procedure using benzaline (109 μL, 107 mg, 1.00 mmol), 1-pentanol (217 μL, 172 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.200 mmol). The product was isolated via column chromatography eluted with 0–60% ethyl acetate in pentane to give N-benzylpent-4-en-1-ylamine as a colorless oil (134 mg, 0.698 mmol, 69.8%): HRMS (ESI-TOF) m/z [M + H]+ calcd for C12H18NO, 192.1383, found 192.1389; 1H NMR (500 MHz, CDCl3) δ 7.06 (2H, t, J = 7.6 Hz, ArH), 7.07 (2H, t, J = 7.6 Hz, ArH), 7.06 (2H, t, J = 7.6 Hz, ArH), 6.83 (2H, t, J = 7.6 Hz, ArH), 6.21 (2H, t, J = 7.6 Hz, ArH), 6.06 (2H, t, J = 7.6 Hz, ArH), 3.25 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.57 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.40 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.33 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.19 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)); 13C NMR (126 MHz, CDCl3) δ 140.2, 134.3, 128.9, 128.2, 127.0, 54.0, 49.4, 29.7, 26.6, 21.8 ppm; MS (EI) m/z 117 (M + H), 100%. N-Benzylpent-4-en-1-ylamine was synthesized via the general procedure using benzaline (109 μL, 107 mg, 1.00 mmol), 1-pentanol (217 μL, 172 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.200 mmol). The product was isolated via column chromatography eluted with 0–60% ethyl acetate in pentane to give N-benzylpent-4-en-1-ylamine as a colorless oil (134 mg, 0.698 mmol, 69.8%): HRMS (ESI-TOF) m/z [M + H]+ calcd for C12H18NO, 192.1383, found 192.1389; 1H NMR (500 MHz, CDCl3) δ 7.06 (2H, t, J = 7.6 Hz, ArH), 7.07 (2H, t, J = 7.6 Hz, ArH), 7.06 (2H, t, J = 7.6 Hz, ArH), 6.83 (2H, t, J = 7.6 Hz, ArH), 6.21 (2H, t, J = 7.6 Hz, ArH), 6.06 (2H, t, J = 7.6 Hz, ArH), 3.25 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.57 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.40 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.33 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)), 1.19 (2H, q, J = 7.0 Hz, CH2Cl, C(H2)); 13C NMR (126 MHz, CDCl3) δ 140.2, 134.3, 128.9, 128.2, 127.0, 54.0, 49.4, 29.7, 26.6, 21.8 ppm; MS (EI) m/z 117 (M + H), 100%.
oxides (15.0 mg, 0.2 mmol). The product was isolated using column chromatography eluted with 0–30% ethyl acetate in pentane to give 1-(pent-4-en-1-yl)-4-phenylpiperidine as a colorless oil (218 mg, 0.952 mmol, 95.2%); HRMS (ESI-TOF) m/z [M + H] + calculated for C21H24NO 310.2165, found 310.2167; IR νmax 2935, 2864 cm⁻¹; 1H NMR (500 MHz, CDCl3) δ 7.83–7.34 (2H, m, ArH), 2.74–2.79 (2H, m, ArH), 7.19–6.94 (1H, m, ArH), 5.27 (1H, dd, J = 17.0, 2.6, 6.7 Hz, CH2CH=CH2), 5.07 (1H, dd, J = 17.1, 6.4 Hz, CH=CH), 3.09 (2H, d, J = 11.6 Hz, NCH2), 2.52 (1H, t, J = 10.5, 5.5 Hz, PhCH2), 2.38–2.44 (2H, m, NCH2CH2CH2), 1.22 (2H, q, J = 7.1 Hz, CH2CH=CH2), 2.04–2.10 (2H, m, NCH2CH2), 1.79–1.91 (4H, m, PhCHCH2), 1.68 (2H, quin, J = 7.7 Hz, CH2CH2CH2) ppm; 13C NMR (126 MHz, CDCl3) δ 146.5, 138.6, 128.4, 126.9, 126.1, 114.6, 58.7, 54.5, 42.9, 33.6, 31.9, 26.4 ppm; MS (ESI) m/z 230 ([M + H]+, 100%).

1-Benzyl-4-phenylpiperidine (47). 1-Benzyl-4-phenylpiperidine was synthesized via the general procedure using 4-phenylpiperidine (161 mg, 1.00 mmol), benzylic alcohol (207 μL, 216 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.2 mmol). The product was isolated via column chromatography eluted with 0–30% ethyl acetate in pentane to give 1-benzyl-4-phenylpiperidine as a colorless oil (239 mg, 0.952 mmol, 95.2%); HRMS (ESI) m/z [M + H]+ calculated for C21H24NO 310.2165, found 310.2167; IR νmax 2935, 2795 cm⁻¹; 1H NMR (500 MHz, CDCl3) δ 7.14–7.37 (10H, m, ArH), 3.54 (1H, t, J = 12.0, 3.9 Hz, CH(PhCH2)), 3.01 (2H, d, J = 11.6 Hz, CH2CH2CH2), 2.42–2.55 (1H, m, PhCH(PhCH2)), 2.02–2.13 (2H, m, NCH2CH2), 1.74–1.86 (4H, m, CHCH2CH2) ppm; 13C NMR (126 MHz, CDCl3) δ 146.8, 138.7, 129.5, 128.6, 128.4, 127.2, 127.1, 126.3, 63.8, 54.5, 42.9, 33.7 ppm; MS (ESI) m/z 252 ([M + H]+, 100%).

1-(3-(4-Methoxyphenyl)propyl)-4-phenylpiperidine (48). 1-(3-(4-Methoxyphenyl)propyl)-4-phenylpiperidine was synthesized via the general procedure using 4-phenylpiperidine (161 mg, 1.00 mmol), 3-(4-methoxyphenyl)propanol (332 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.2 mmol). The product was isolated via column chromatography eluted with 0–50% ethyl acetate in pentane to give 1-(3-(4-methoxyphenyl)propyl)-4-phenylpiperidine as a colorless oil (298 mg, 0.964 mmol, 96.4%); HRMS (ESI) m/z [M + H]+ calculated for C21H24NO 310.2165, found 310.2167; IR νmax 2935, 1632 cm⁻¹; 1H NMR (500 MHz, CDCl3) δ 7.15–7.35 (35H, m, ArH), 7.11 (2H, d, J = 8.1 Hz, ArH), 6.83 (2H, d, J = 8.2 Hz, ArH), 3.78 (3H, s, OCH3), 3.04 (2H, d, J = 11.0 Hz, CH2CH2), 2.59 (2H, t, J = 7.6 Hz, NCH2CH2), 1.70–2.09 (4H, m, CH2CH2CH2), 1.72–1.91 (6H, m, CH2CH2CH2) ppm; 13C NMR (126 MHz, CDCl3) δ 157.7, 146.5, 134.3, 129.3, 128.4, 126.9, 126.1, 113.8, 88.5, 55.3, 54.5, 42.8, 33.6, 33.0, 29.1 ppm; MS (ESI) m/z 290 (M + H)+, 100%.

4-Phenyl-1-16-(trimethylsilyl)hex-5-yn-1-yl)piperidine (49). 4-Phe-nyl-1-16-(trimethylsilyl)hex-5-yn-1-yl)piperidine was synthesized via the general method from 4-phenylpiperidine (161 mg, 1.00 mmol), 6-(trimethylsilyl)hex-5-yn-1-ol (332 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.2 mmol). Purification via column chromatography eluted with 0–60% ethyl acetate in pentane gave 4-phenyl-1-16-(trimethylsilyl)hex-5-yn-1-yl)piperidine as a colorless oil (232 mg, 0.741 mmol, 74.1%); HRMS (ESI) m/z [M + H]+ calculated for C21H31NSi 341.2299, found 341.2297; IR νmax 2935, 2864 cm⁻¹; 1H NMR (500 MHz, CDCl3) δ 7.15–7.34 (35H, m, ArH), 3.05 (2H, d, J = 11.6 Hz, NCH2), 2.49 (1H, ddd, J = 22.1, 11.1, 5.8 Hz, PhCH2), 2.35–2.41 (2H, m, CH2), 2.26 (2H, t, J = 7.0 Hz, NCH2), 2.02 (2H, td, J = 11.2, 3.4 Hz, CH2CH(NHCN)), 1.73–1.90 (4H, m, CH2), 1.48–1.71 (4H, m, CH2CH2CH2) ppm; 13C NMR (126 MHz, CDCl3) δ 146.3, 128.2, 126.7, 125.9, 107.2, 84.4, 58.4, 54.2, 42.6, 33.3, 26.6, 26.0, 19.7, 0.0 ppm; MS (ESI) m/z 234 ([M + H]+, 100%).

1-Cyclopentyl-4-phenylpiperidine (50). 1-Cyclopentyl-4-phenylpiperidine was synthesized via the general procedure using 4-phenylpiperidine (161 mg, 1.00 mmol), cyclohexanol (210 μL, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.200 mmol). The product was isolated using column chromatography eluted with 0–20% ethyl acetate in pentane to give N-(3-
(trifluoromethyl)benzyl)pent-4-en-1-amine as a colorless oil (220 mg, 0.898 mmol, 89.8%). 1H NMR (500 MHz, CDCl3) δ 7.60 (1H, s, ArH), 7.47−7.55 (2H, m, ArH), 7.39−7.46 (1H, m, ArH), 3.84 (2H, s, ArCH2N), 2.62 (2H, t, J = 7.2 Hz, NHCH2CH3), 1.63 (1H, br s, NH), 1.52 (2H, quin, J = 7.2 Hz, CH2), 1.26−1.39 (4H, m, CH2CH2), 0.85−0.94 (3H, methyl, CH3 ppm); 13C NMR (126 MHz, CDCl3) δ 141.33, 130.67 (q, J = 32.1 Hz), 128.75, 124.77 (q, J = 4.0 Hz), 123.8 (J = 3.0 Hz), 124.2 (q, J = 272.0 Hz), 122.5, 53.5, 29.7, 29.5, 22.6, 14.0 ppm; MS (ESI) m/z 266 [M + H]+, 100%.

N-(3-(Trifluoromethyl)benzyl)pent-4-en-1-amine (55). N-(3-(Trifluoromethyl)benzyl)pent-4-en-1-amine was synthesized via the general procedure using 3-(trifluoromethyl)benzylamine (143 µL, 175 mg, 1.00 mmol), cyclopentanol (182 µL, 172 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylene N-oxide (15.0 mg, 0.200 mmol). N-(3-(Trifluoromethyl)benzyl)cyclopentanamine was isolated through the use of column chromatography eluted with 0−60% ethyl acetate in pentane to give a colorless oil (233 mg, 0.959 mmol, 95.9%): HRMS (ESI-TOF) m/z [M + H]+ calculated for C18H13F3N1 307.1270, found 307.1270.

N-(3-(Trifluoromethyl)benzyl)cyclohexanamine (59). N-(3-(Trifluoromethyl)benzyl)cyclohexanamine was synthesized via the general procedure using 3-(trifluoromethyl)benzylamine (143 µL, 175 mg, 1.00 mmol), cyclohexanol (210 µL, 200 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylene N-oxide (15.0 mg, 0.200 mmol). N-(3-(Trifluoromethyl)benzyl)cyclohexanamine was isolated through column chromatography eluted with 0−60% ethyl acetate in pentane to give a colorless oil (249 mg, 0.969 mmol, 96.9%): HRMS (ESI-TOF) m/z [M + H]+ calculated for C16H16F3N1 348.1327, found 348.1327.

3-(4-Methoxyphenyl)-N-(3-(trifluoromethyl)benzyl)propan-1-amine (56). 3-(4-Methoxyphenyl)-N-(3-(trifluoromethyl)benzyl)propan-1-amine was synthesized via the general procedure using 3-(trifluoromethyl)benzylamine (147 µL, 175 mg, 1.00 mmol), 3-(4-methoxyphenyl)-1-propanol (332 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylene N-oxide (15.0 mg, 0.200 mmol). The product was isolated using column chromatography eluted with 0−30% ethyl acetate in pentane to give 3-(4-methoxyphenyl)-N-(3-(trifluoromethyl)benzyl)propan-1-amine as a colorless oil 395 mg, 0.913 mmol, 91.3%: HRMS (ESI) m/z [M + H]+ calculated for C23H21F3N1O1 395.1361, found 395.1364.

N-Benzyl-1-(3-(trifluoromethyl)phenyl)methanamine (57). N-Benzyl-1-(3-(trifluoromethyl)phenyl)methanamine was synthesized via the general reaction procedure using 3-(trifluoromethyl)benzylamine (143 µL, 175 mg, 1.00 mmol), benzyl alcohol (310 µL, 324 mg, 3.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylene N-oxide (15.0 mg, 0.200 mmol). N-Benzyl-1-(3-(trifluoromethyl)phenyl)methanamine was isolated through column chromatography eluted with 0−60% ethyl acetate in pentane to give a colorless oil (232 mg, 0.875 mmol, 87.5%): HRMS (ESI) m/z [M + H]+ calculated for C18H15F3N1 291.1151, found 291.1151.

N-(3-(Trifluoromethyl)benzyl)cyclopentanamine (58). N-(3-(Trifluoromethyl)benzyl)cyclopentanamine was synthesized via the general procedure using 3-(trifluoromethyl)benzylamine (143 µL, 175 mg, 1.00 mmol), cyclopentanol (182 µL, 172 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylene N-oxide (15.0 mg, 0.200 mmol). N-(3-(Trifluoromethyl)benzyl)cyclopentanamine was isolated through the use of column chromatography eluted with 0−60% ethyl acetate in pentane to give a colorless oil (233 mg, 0.959 mmol, 95.9%): HRMS (ESI-TOF) m/z [M + H]+ calculated for C18H13F3N1 307.1270, found 307.1270.
The product was isolated via column chromatography eluted with 0–60% ethyl acetate in pentane to give N-Methyl-N-(6-trimethylsilyl)hex-5-syn-1-yl)cyclohexanamine (112 mg, 1.00 mmol), 6-(trimethylsilyl)hex-5-syn-1-ol (332 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.2 mmol). The product was isolated via column chromatography eluted with 0–60% ethyl acetate in pentane to give N-Methyl-N-(6-trimethylsilyl)hex-5-syn-1-yl)cyclohexanamine as a colorless oil (243 mg, 0.931 mmol, 93%): HRMS (EI) m/z [M + H]+ calcd for C14H31NO 258.2146, found 258.2145; 1H NMR (500 MHz, CDCl3) δ 2.28–2.38 (2H, m, CH2), 2.15–2.28 (2H, m, CH2), 2.0–2.08 (4H, m, CH2), 1.79 (4H, d, J = 9.3 Hz, CH2 in ring), 1.43–1.57 (9H, CH2, CH3), 0.96–1.11 (1H, CHCH2), 0.12 (9H, Si(CH3)3) ppm; 13C NMR (126 MHz, CDCl3) δ 107.4, 64.4, 62.4, 53.0, 37.8, 28.5, 26.9, 26.4, 26.0, 19.7, 0.1 ppm; MS (ESI) m/z 262 (M + H)+, 100%.

N-Methyl-N-(pent-4-en-1-yl)cyclohexanamine (67). N-Methyl-N-(pent-4-en-1-yl)cyclohexanamine was synthesized via the general procedure using N-methylcyclohexylamine (130 μL, 113 mg, 1.00 mmol), 4-penten-1-ol (208 μL, 172 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.2 mmol). The purification of the compound was completed via column chromatography eluted with 0–40% ethyl acetate in pentane to give N-methylcyclohexylamine as a colorless oil (163 mg, 0.884 mmol, 88.4%): HRMS (ESI-TOF) m/z [M + H]+ calcd for C13H21NO 246.1852, found 246.1852; IR νm,νmax 2929, 2855, 1639 cm−1; 1H NMR (500 MHz, CDCl3) δ 5.85 (1H, ddt, J = 17.0, 10.3, 6.6 Hz, CH(CH3)2), 5.02 (1H, d, J = 17.1, 19.1 Hz, CH2), 4.95 (1H, d, J = 10.1 Hz, CH3(CH2)2), 2.40–2.46 (2H, m, 2.31–2.39 (1H, m, NCH2), 2.24 (3H, s, NCH3), 2.05 (2H, q, J = 6.9 Hz, CH2CH2CH2CH2), 1.78 (4H, d, J = 9.5 Hz, CH2 in ring), 1.62 (1H, d, J = 12.7 Hz, CH), 1.55 (2H, quin, J = 7.6 Hz, CH2CH2CH2CH2), 1.14–1.28 (4H, m, CH2), 1.09 (1H, td, J = 12.3, 3.4 Hz, PhCH2) ppm; 13C NMR (126 MHz, CDCl3) δ 138.8, 114.4, 62.6, 53.2, 37.9, 31.8, 28.6, 27.2, 26.4, 26.1 ppm; MS (ESI) m/z 182 (M + H)+, 100%.

N-Allyl-N-(3-(4-methoxyphenyl)propyl)prop-2-en-1-amine (68). N-Allyl-N-(3-(4-methoxyphenyl)propyl)prop-2-en-1-amine was synthesized via the general procedure using diallylamine (132 μL, 97 mg, 1.00 mmol), 3-(4-methoxyphenyl)-1-propanol (332 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine N-oxide (15.0 mg, 0.2 mmol). The product was isolated via column chromatography eluted with 0–20% ethyl acetate in pentane to give N-allyl-N-(3-(4-methoxyphenyl)propyl)prop-2-en-1-amine as a colorless oil (228 mg, 0.931 mmol, 93.1%): HRMS (ESI-TOF) m/z [M + H]+ calcd for C23H35NO 395.2652, found 395.2651; 1H NMR (500 MHz, CDCl3) δ 7.09 (2H, d, J = 8.5 Hz, ArH), 6.82 (2H, d, J = 8.5 Hz, ArH), 3.78 (3H, s, NCH3), 2.35–2.58 (1H, m, CH2), 2.35 (1H, t, J = 7.8 Hz, ArCH2), 2.01–2.09 (2H, m, CH2), 1.75 (2H, quin, J = 7.8 Hz, CH2CH2CH2CH2), 1.57 (2H, quin, J = 7.6 Hz, CH2CH2CH2CH2), 1.15 (3H, d, J = 6.9 Hz, CH(CH3)2), 0.59–0.59 (4H, m, CH(CH2)2), 0.38 (3H, s, OMe), 0.38 (2H, d, J = 6.4 Hz, NCH2CH2CH2), 2.46 (2H, t, J = 7.8 Hz, NCH2CH2CH2CH2), 1.75 (2H, quin, J = 7.7 Hz, CH2CH2CH2CH2) ppm; 13C NMR (126 MHz, CDCl3) δ 177.5, 135.8, 134.6, 129.2, 117.3, 113.7, 56.8, 55.3, 52.9, 32.8, 29.0 ppm; MS (ESI) m/z 246 (M + H)+, 100%.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01990.

NMR spectra of products and the X-ray crystallographic structure of 6 (PDF)

Crystal data of 6 (CIF)
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