JOC The Journal of Organic Chemistry

Article

Cite This: J. Org. Chem. 2017, 82, 10489-10503

pubs.acs.org/joc

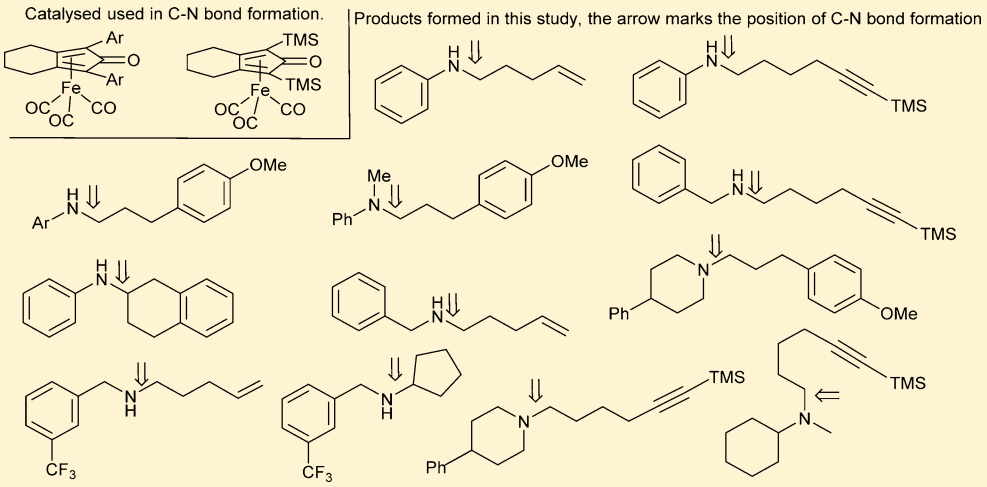
Use of (Cyclopentadienone)iron Tricarbonyl Complexes for C–N Bond Formation Reactions between Amines and Alcohols

Thomas J. Brown,[†] Madeleine Cumbes,[†] Louis J. Diorazio,[‡] Guy J. Clarkson,[†] and Martin Wills*[,†]

[†]Department of Chemistry, The University of Warwick, Coventry CV4 7AL, U.K.

[‡]Pharmaceutical Development, AstraZeneca, Silk Road Business Park, Macclesfield, Cheshire SK10 2NA, U.K.

Supporting Information



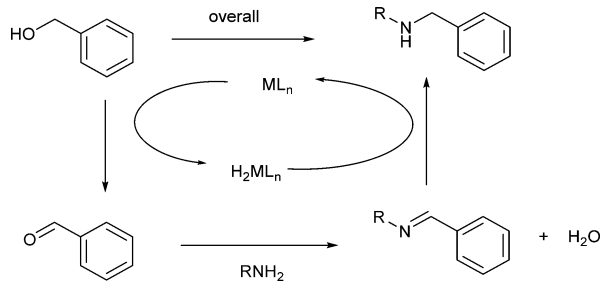
ABSTRACT: The application of a series of (cyclopentadienone)iron tricarbonyl complexes to "borrowing hydrogen" reactions between amines and alcohols was completed in order to assess their catalytic activity. The electronic variation of the aromatic groups flanking the C═O of the cyclopentadienone influenced the efficiency of the reactions; however, in other cases, the Knölker 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.[2g] 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.[5−9] 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

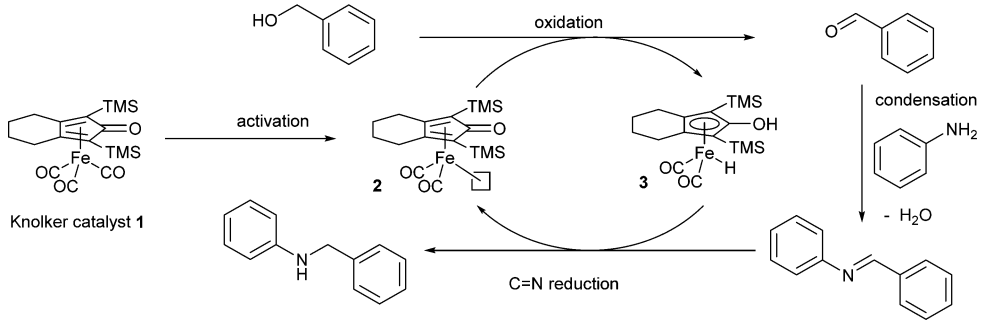
Scheme 1. Steps of a "Hydrogen Borrowing" Reaction



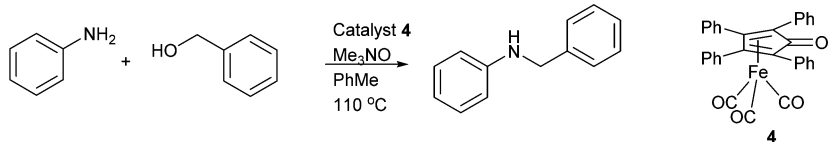
Received: August 7, 2017
Published: September 18, 2017

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

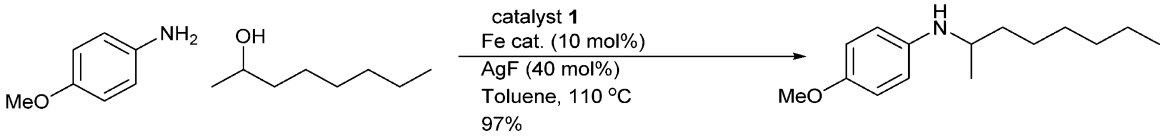
Scheme 2. Steps of a "Hydrogen Borrowing" Reaction Using an Iron Cyclopentadienone Tricarbonyl Catalyst, First Reported by Feringa et al.[7]



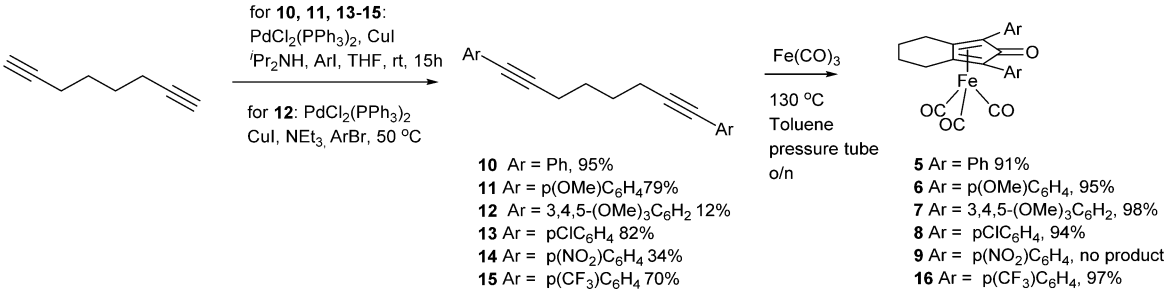
Scheme 3. Use of a Tetraphenyl-Substituted Complex 4 for C−N Bond Formation between a Benzyl Alcohol and Aniline



Scheme 4. Secondary Alcohols as Substrates by Zhao et al.



Scheme 5. Synthesis of Aryl-Substituted Iron(cyclopentadienone) Catalysts



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.[5−10] Complexes analogous to **1**, but containing aromatic rings flanking the central C═O, benefit from the ease of preparation[14] 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 reaction[15] (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

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

reaction resulted in the complete decomposition of the starting material. However, the electron-deficient iron bis-trifluoromethylphenyl 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.[6]

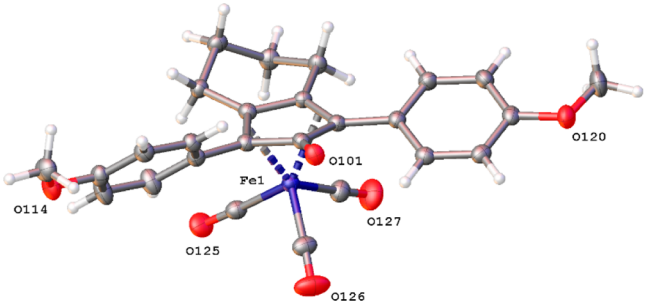
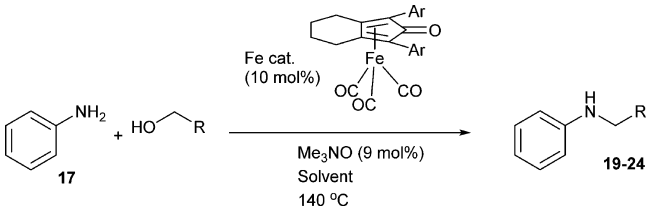


Figure 1. Single-crystal X-ray structure of **6**. Hydrogens were omitted for clarity, and ellipsoids were drawn at 50% probability.

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

Table 1. Results of C–N Bond Formation via "Hydrogen Borrowing" Reactions[a]



Catalyst:	**5** H	**6** OMe	**7** OMe_3	**8** Cl	**16** CF_3
Product	Conv (c) and yield (y) of amine / %				
PhHN **19**	100 (c) 90 (y)	60 (c)	91 (c)	66 (c)	87 (c)
PhHN **20**	90 (c) 65 (y)	95 (c)	>95 (c)	55 (c)	100 (c) 92 (y)
PhHN **21**	100 (c) 96 (y)	>95 (c) 95 (y)	50 (c)	100 (c) 89 (y)	55 (c)
PhHN **22**	>90 (c) 80 (y)	70 (c)	30 (c)	72 (c)	100 (c) 82 (y)
PhHN OMe **23**	40 (c)	100 (c)	100 (c)	nd	100 (c) 94 (y)
PhHN OMe **24**	100 (c) 92 (y)	100 (c) 96 (y)	60 (c)	40 (c)	60 (c)

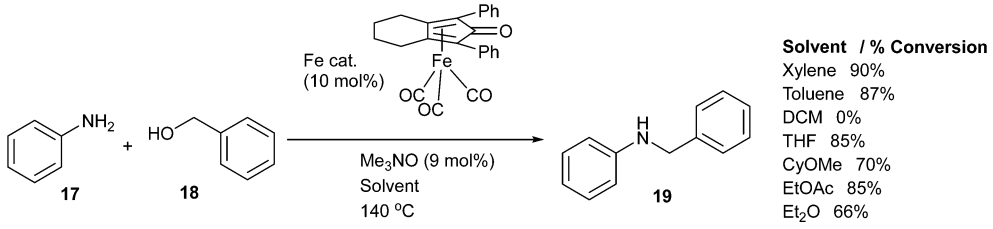
[a]Nd = not determined.

however. Catalyst **7** generally gave lower conversions, while the phenyl catalyst **5** and the bis *p*-methyoxyphenyl 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.

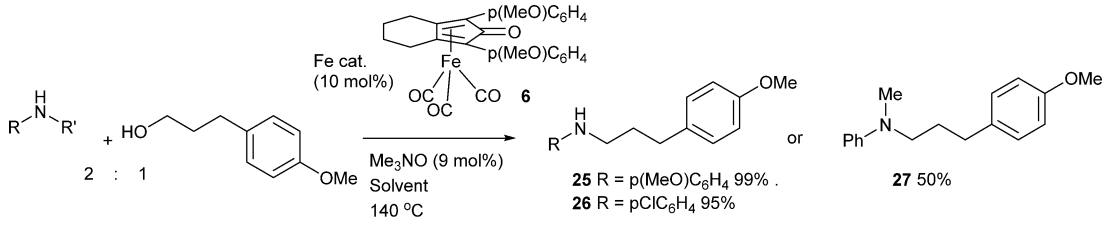
A complex pattern of results emerged from the reactions of aniline with cyclic alcohols and diols using the bis(aryl)-substituted catalysts (Figure 2). Aliphatic secondary cyclic alcohols cyclopentanol, cyclohexanol, cycloheptanol, and *β*-tetralol gave products in good yields, representing a valuable

Scheme 6. Solvent Screening in C–N Bond Formation



DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489–10503

Scheme 7. Variation of the Aniline Derivative in "Hydrogen Borrowing" Reactions Using Bis(methoxyphenyl) Iron Complex 6



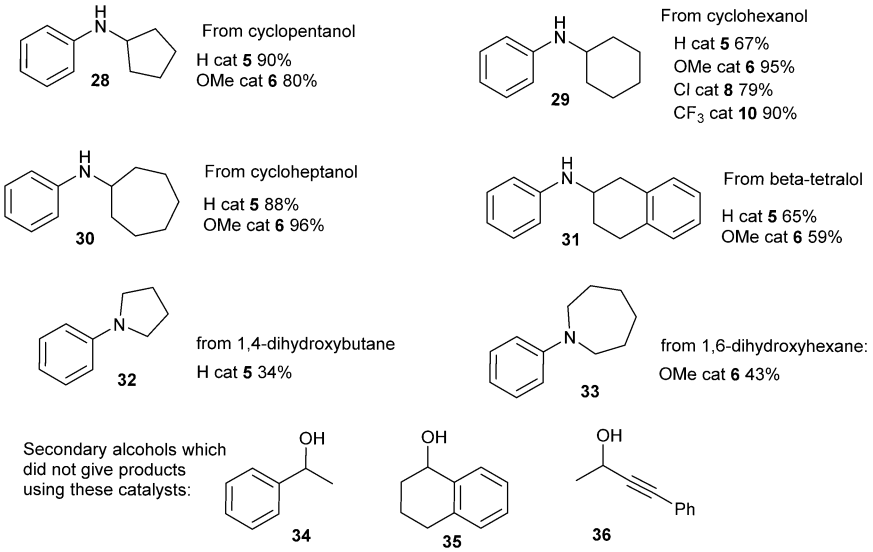


Figure 2. Products formed from the reaction of aniline with cyclic alcohols (2:1 aniline/alcohol), cyclic alcohols, which did not work (10% catalyst, 2:1, 140 °C, 16h), and products of reactions with diols (2 equiv diol employed).

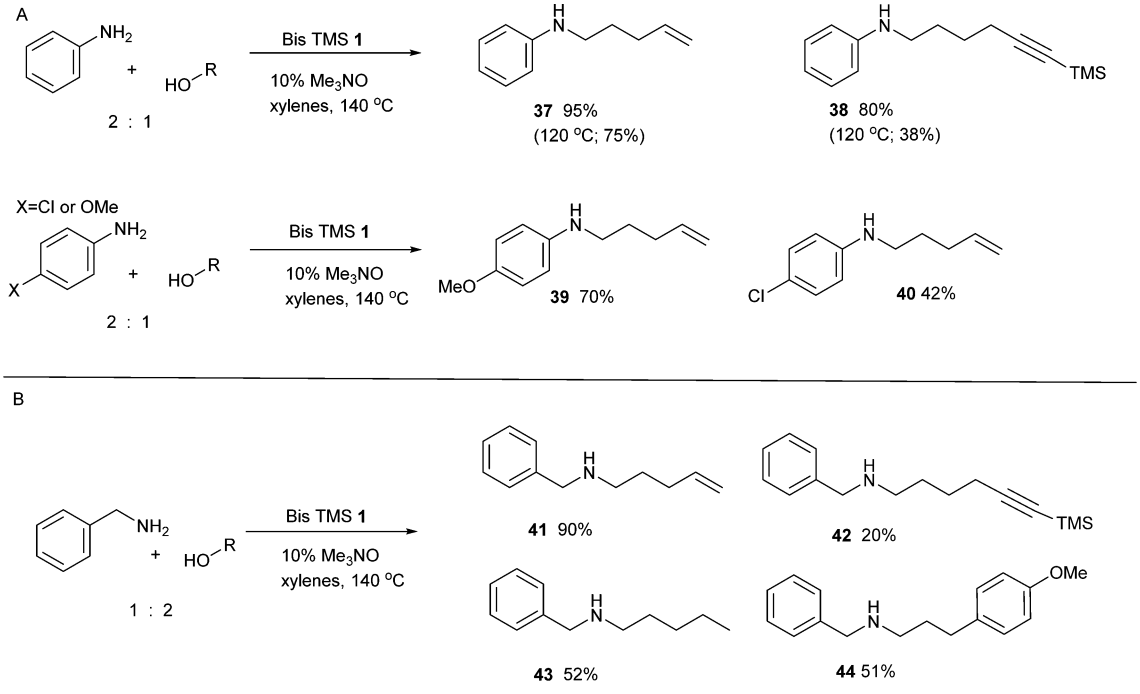


Figure 3. Products of the reaction of aliphatic and unsaturated alcohols to (A) anilines and (B) benzylamine using catalyst **1**. For the best results in reaction A, an excess of the aniline is required. For reaction B, an excess of alcohol gives the best results.

application of the methodology. However, cyclic or acyclic benzylic/propargylic alcohols including α-tetralol, 1-phenylethanol, 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

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

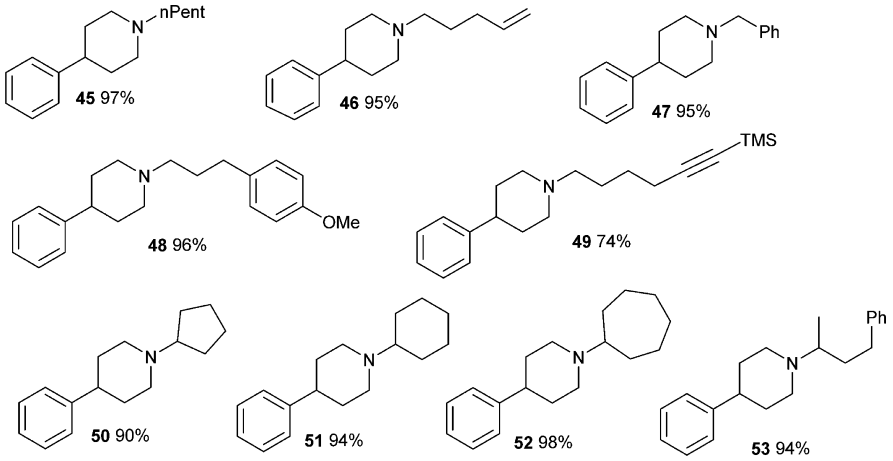


Figure 4. Products formed from the reaction of 4-phenylpiperidine and alcohols using catalyst **1** and a 1:2 ratio of amine/alcohol (140 °C, xylene, 16h).

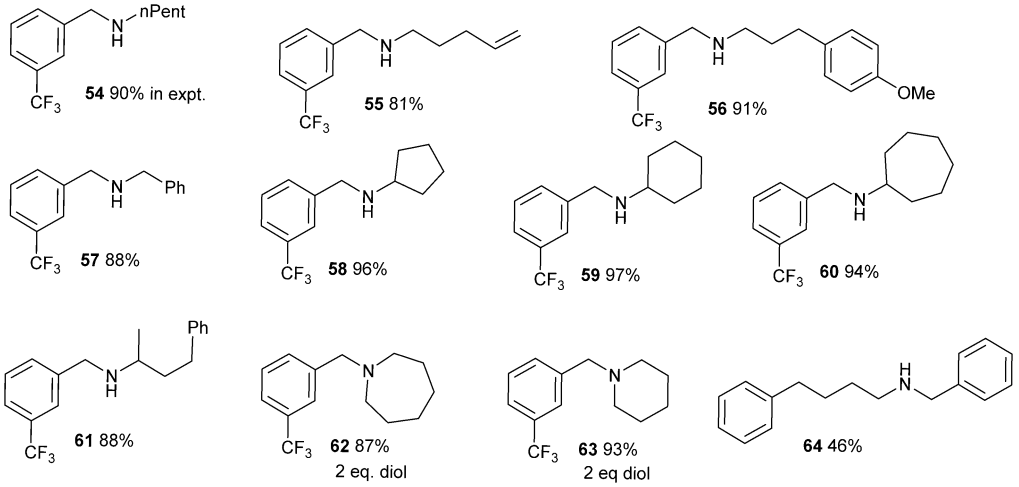


Figure 5. Products of the reaction of 3-trifluoromethylbenzyl alcohol with a range of alcohols and diols, using catalyst **1** and a 1:2 ratio of amine/alcohol.

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-phenylpypiperidine, 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

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

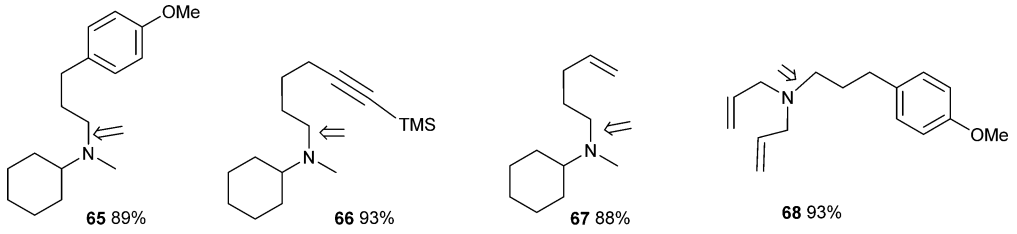


Figure 6. Products formed from the reaction of secondary amines with primary alcohols using catalyst **1** and a 1:2 ratio of amine/alcohol. The arrow indicates the position of the newly formed bond.

substituted benzylic amine as this had been reported to give good results in a previous study.[7] We were able to successfully generate a range of addition products **54**–**63** in good yields, including products from reactions with cyclic alcohols, an acyclic secondary alcohol, and diols. In one further example, a longer chain amine, 4-phenylbutylamine, was successfully coupled with benzyl alcohol to form the secondary amine **64**.

We also found that tertiary amines **65**–**68** could be formed from secondary ones using the modified conditions, including the alkylation of *N*-methyl-*N*-cyclohexylamine, as illustrated in Figure 6.

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

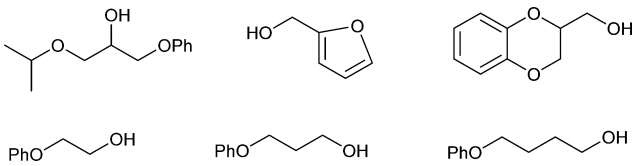


Figure 7. Oxygen-containing alcohols that did not work in this application.

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 Knölker 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 Ml 150 psi pressure tested pressure tubes and heated in aluminum heating blocks. ^{1}H 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.

General Procedure for Aniline-Related "Hydrogen Borrowing" Reactions. Tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (**5**, 43.0 mg, 0.100 mmol, 0.1 equiv) was placed in a thoroughly dried 15 mL pressure tube with a stir bar, and xylene (0.5 mL) was added. Distilled aniline (137 μL, 139 mg, 1.5 equiv) and alcohol (1.00 mmol, 1 equiv) were added with stirring. The pressure tube was sealed with a septum and degassed through a nitrogen bubbler for 15 min. Trimethylamine *N*-oxide (7.00 mg, 0.09 mmol, 0.09 equiv) was then added with stirring, and the solution was further degassed for 5 min before being sealed with a pressure tube lid and stirred at 140 °C for 16 h. The tube was then allowed to cool to room temperature, and its contents were passed through Celite with ethyl acetate. Solvent removal via a rotary evaporator gave the product as a dark brown residue, which was purified as indicated in each case.

General Procedure for Sonogashira Reactions. In a dried and degassed 100 mL round-bottom flask, 1,7-octadiyne (1.00g, 9.42 mmol, 1.0 equiv) and aryl iodide (20.7 mmol, 2.2 equiv) were dissolved in anhydrous THF (34 mL) with stirring. $PdCl_2(PPh_3)_2$ (50.0 mg, 0.0712 mmol, 0.03 equiv) and CuI (27.0 mg, 0.142 mmol, 0.06 equiv) were added to the stirred solution to give a yellow suspension. ^{i}Pr$_2$NH (13.2 mL, 9.53 g, 10 equiv) was added, and a thick precipitate formed. Vigorous stirring overnight was followed by filtration through Celite with ethyl acetate. This served to remove precipitates and metal impurities and gave the product as a brown residue after solvent removal via a rotary evaporator. The products were purified as indicated.

*1,8-Diphenylocta-1,7-diyne (**10**).*[15b] 1,7-Octadiyne (1.00 g, 9.42 mmol) was added to a stirred solution of iodobenzene (4.23 g, 20.7 mmol) in dry THF (34 mL). $PdCl_2(PPh_3)_2$ (50.0 mg, 0.071 mmol), CuI (27.0 mg, 0.141 mmol), and ^{i}Pr$_2$NH (9.53 g, 94.2 mmol) were added, and the reaction was stirred at room temperature overnight. The reaction solidified and was therefore passed through a Celite/silica plug with 20% ethyl acetate/pentane to give a brown oil after solvent removal under reduced pressure. Recrystallization from methanol gave the product as a white solid (2.19 g, 8.49 mmol, 90.1%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (4H, d, J = 4.0 Hz, Ar*H*), 7.25–7.29 (6H, m, Ar*H*), 2.48 (4H, br s, $CH_2CH_2CH_2CH_2$), 1.79 (4H, br s, $CH_2CH_2CH_2CH_2$) ppm.

*Tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2H-inden-2-one)iron (**5**).*[14b] 1,8-Diphenylocta-1,7-diyne (0.500 g, 1.94 mmol) was placed in a dried pressure tube with a stir bar with dry toluene (5.00 mL), and $Fe(CO)_5$ (786 μL, 1.14 g, 5.82 mmol) was added. The reaction solution was degassed thoroughly with N_2 for 15 min. The tube was sealed and heated to 130 °C overnight. The tube was then allowed to cool to room temperature, and tube contents were passed through a silica plug with 50:50 EtOAc/pentane. The solvent was then removed under reduced pressure to give **5** as a brown solid (0.729g, 1.71 mmol, 87.9%): mp 164–165 °C (lit. mp 165–166 °C); IR ν_{max} 3062, 2950,

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489–10503

2864, 1641, 1627 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (4H, d, J = 7.2 Hz, ArH), 7.26−7.47 (6H, m, ArH), 2.64−2.89 (4H, m, CH_2), 1.94 (4H, br s, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.0, 169.5, 22.3, 131.3, 129.7, 128.4, 127.9, 100.4, 81.9, 23.7 ppm; MS (ESI) m/z 427 $[M + H]^+$, 449 $[M + Na]^+$.

*1,8-Bis(4-methoxyphenyl)octa-1,7-diyne (**11**).* 1,8-Bis(4-methoxyphenyl)octa-1,7-diyne was prepared via the same method as 1,8-diphenylocta-1,7-diyne with 1,7-octadiyne (750 mg, 7.07 mmol), 4-iodoanisole (3.31g, 14.1 mmol), $PdCl_2(PPh_3)_2$ (74.0 mg, 0.106 mmol), CuI (40.0 mg, 0.212 mmol), and $^iPr_2NH$ (7.15 g, 70.6 mmol) to give 1,8-bis(4-methoxyphenyl)octa-1,7-diyne as a white solid (1.77g, 5.56 mmol, 78.7%): mp 39−40 °C; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{22}H_{23}O_2$ 319.1693, found 319.1694; IR ν_{max} 2998, 2937, 1605, 1568 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (4H, d, J = 8.8 Hz, Ar*H*), 6.81 (4H, d, J = 8.8 Hz, Ar*H*), 3.79 (6H, s, OCH_3), 2.34−2.37 (4H, m, $CH_2CH_2CH_2CH_2$), 1.73−1.77 (4H, m, $CH_2CH_2CH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 132.9, 116.9, 113.8, 88.2, 80.6, 55.3, 28.0, 19.0 ppm; MS (ESI) m/z 319 $[M + H]^+$.

*Tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (**6**).* Tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron was prepared via the same procedure as was used for tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron. In an oven-dried pressure tube, 1,8-bis(4-methoxyphenyl)-octa-1,7-diyne (500 mg, 1.57 mmol) was placed in dry toluene (5.00 mL) with $Fe(CO)_5$ (637 μL, 4.72 mmol), and the solution was vigorously degassed with a N_2 line for 15 min. The tube was then sealed and heated with stirring to 130 °C overnight. Complex **6** was isolated as a brown solid (726 mg, 1.49 mmol, 94.8%): mp 166−167 °C; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{26}H_{23}FeO_6$ 487.0839, found 487.0842; IR ν_{max} 2941, 2054, 1618 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (4H, d, J = 10.0 Hz, Ar*H*), 6.91 (4H, d, J = 10.0 Hz,Ar*H*), 3.82 (6H, s, OCH_3), 2.84−2.82 (4H, m, CH_2), 1.92 (4H, br s, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.3, 169.3, 159.1, 130.8, 121.9, 113.9, 99.70, 81.9, 55.3, 23.9, 22.3 ppm; MS (ESI) m/z 487 $[M + H]^+$, 509 $[M + Na]^+$.

*1,8-Bis(3,4,5-trimethoxybenzene)octa-1,7-diyne (**12**).* In a dried and degassed (N_2) 100 mL round-bottomed flask equipped with a Findenser, 1,7-octadiyne (1.00 g, 9.42 mmol) and 5-bromo-1,2,3-trimethoxybenzene (5.121 g, 20.7 mmol) were placed in triethylamine (25 mL) with stirring via a magnetic stir bar. $PdCl_2(PPh_3)_2$ (100 mg, 0.142 mmol) and CuI (26 mg, 0.137 mmol) were added, and the reaction was stirred at 50 °C for 2 days. The reaction mixture was purified via column chromatography eluted with 0−50% ethyl acetate in pentane to give the product as a white crystalline solid (0.507 g, 1.16 mmol, 12.3%): mp 51−52 °C; IR ν_{max} 2956, 2918, 1621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.64 (4H, s, Ar*H*), 3.84 (18H, s, ArO*Me*), 2.45−2.49 (4H, m, $CH_2CH_2CH_2CH_2$), 1.77−1.81 (4H, m, $CH_2CH_2CH_2CH_2$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 138.2, 119.0, 108.6, 88.9, 80.9, 60.9, 56.1, 27.9, 19.0 ppm; MS (ESI) m/z 461 $[M + H]^+$.

*Tricarbonyl(1,3-di(3,4,5-trimethoxyphenyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (**7**).* Tricarbonyl(1,3-di(3,4,5-trimethoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron was synthesized via the same procedure as was used for tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron, using 1,8-bis(3,4,5-trimethoxybenzene)octa-1,7-diyne (0.400 g, 0.913 mmol) and $Fe(CO)_5$ (537 μL, 800 mg, 2.74 mmol) in toluene (5 mL) to give **7** as a yellow solid (0.454 mg, 0.897 mmol, 98.2%): mp 167−168 °C; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{30}H_{30}FeNaO_{10}$ 629.1081, found 629.1079; IR ν_{max} 2941, 2837, 1619 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.03 (4H, s, Ar*H*), 3.88 (18H, s, ArO*Me*), 2.82−2.91 (2H, m, CH_2), 2.69−2.79 (2H, m, CH_2), 1.94−1.92 (4H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.2, 169.6, 152.9, 137.9, 126.6, 107.0, 99.9, 82.1, 60.8, 56.1, 23.9, 22.3 ppm; MS (ESI) m/z 629 $[M + Na]^+$.

*1,8-(4-Chlorophenyl)octa-1,7-diyne (**13**).* 1,8-(4-Chlorophenyl)-octa-1,7-diyne was synthesized through the same method as for the synthesis of 1,8-diphenylocta-1,7-diyne, using 1,7-octadiyne (0.300 g, 2.83 mmol), 1-chloro-4-iodobenzene (1.49g, 6.23 mmol), $PdCl_2(PPh_3)_2$ (30.0 mg, 0.0425 mmol), CuI (16.0 mg, 0.0850 mmol), and $^iPr_2NH$ (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 $[M + Ag]^+$ calcd for $C_{20}H_{16}AgCl_2$ 434.9668, found 434.9655; IR ν_{max} 2942, 2871, 2769, 1624 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (4H, d, J = 10.0 Hz, Ar*H*), 7.23 (4H, d, J = 10.0 Hz, Ar*H*), 2.46−2.42 (4H, m, CH_2CH_2CCAr), 1.75 (4H, m, $CH_2CH_2CH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.6, 133.1, 128.6, 122.5, 90.9, 80.0, 27.8, 19.1 ppm; MS (ESI) m/z 435 $[M + Ag]^+$.

*Tricarbonyl(1,3-di(4-chloro)phenyl-4,5,6,7-tetrahydro-2H-inden-2-one)iron (**8**).* Tricarbonyl(1,3-di(4-chloro)phenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron was prepared via the same method used previously to prepare tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron, using 1,8-bis(4-chlorophenyl)octa-1,7-diyne (0.500g, 1.53 mmol) and $Fe(CO)_5$ (620 μL, 4.59 mmol) in dry toluene (5.00 mL) at 130 °C overnight to give **8** as a brown solid (0.708g, 1.43 mmol, 93.8%): mp 152−153 °C; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{17}Cl_2FeO$ 494.9848, found 494.9855; IR ν_{max} 2062, 2013, 1625, 1606 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (4H, d, ArH), 7.38 (4H, d, Ar*H*), 2.37−3.04 (4H, m, $CH_2CH_2CH_2CH_2$), 1.96 (4H, br s, $CH_2CH_2CH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.6, 208.6, 169.0, 133.9, 130.8, 129.9, 128.7, 100.2, 80.3, 23.8, 22.2 ppm; MS (ESI) m/z 495 $[M + H]^+$.

*1,8-Bis(4-nitrophenyl)octa-1,7-diyne (**14**).* 1,8-Bis(4-nitrophenyl)-octa-1,7-diyne was synthesized through the same procedure as used previously for 1,8-diphenylocta-1,7-diyne, using 1,7-octadiyne (300 mg, 2.83 mmol), 1-iodo-4-nitrobenzene (1.551 g, 6.23 mmol), $PdCl_2(PPh_3)_2$ (50.0 mg, 0.0707 mmol), CuI (27.0 mg, 0.141 mmol), and $^iPr_2NH$ (6.60 mL, 4.77 g, 47.1 mmol) to give 1,8-bis(4-nitrophenyl)octa-1,7-diyne as an orange solid (0.339 g, 0.974 mmol, 34.4%): mp 40−42 °C; HRMS (ESI-TOF) m/z [M + Na]+ calcd for $C_{20}H_{16}N_2NaO_4$ 371.1002, found 371.1001; IR ν_{max} 2931, 1590 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (4H, d, J = 8.0 Hz, Ar*H*), 7.52 (4H, d, J = 8.0 Hz, Ar*H*), 2.54 (4H, br s, $CH_2CH_2CH_2CH_2$), 1.82 (4H, br s, $CH_2CH_2CH_2CH_2$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 132.3, 130.7, 123.5, 95.8, 79.8, 27.6, 19.2 ppm; MS (ESI) m/z 349 $[M + H]^+$.

*1,8-Bis(4-(trifluoromethyl)phenyl)octa-1,7-diyne (**15**).* 1,8-Bis(4-(trifluoromethyl)phenyl)octa-1,7-diyne was synthesized through the same procedure as previously used to synthesize 1,8-diphenylocta-1,7-diyne, with 1,7-octadiyne (375 μL, 300 mg, 2.83 mmol), 4-iodobenzotrifluoride (916 μL, 1.70 g 6.23 mmol), $PdCl_2(PPh_3)_2$ (30.0 mg, 0.0425 mmol), CuI (16.0 mg, 0.0850 mmol), and $^iPr_2NH$ (3.97 mL, 2.86 g, 28.3 mmol) to give 1,8-bis(4-(trifluoromethyl)-phenyl)octa-1,7-diyne as a white solid after column chromatography eluted with 0−20% ethyl acetate in hexane (0.780 g, 1.98 mmol, 69.6%): mp 35−36 °C; HRMS (ESI-TOF) m/z $[M + Ag]^+$ calcd for $C_{22}H_{16}AgF_6$ 501.0202, found 501.0212; IR ν_{max} 2073, 2023, 1995 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51−7.59 (4H, d, J = 8.0 Hz, Ar*H*), 7.43−7.51 (4H, d, J = 8.0 Hz, Ar*H*), 2.13−2.80 (4H, m, $CH_2CH_2CH_2CH_2$), 1.59−1.95 (4H, m, $CH_2CH_2CH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.8, 129.4, 127.8 (J = 32 Hz), 125.2, 123.7 (J = 230 Hz), 92.5, 79.9, 27.7, 19.0 ppm; MS (ESI) m/z 501 ([M + Ag], 100%).

*Tricarbonyl(1,3-di(4-trifluoromethylphenyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (**16**).* Tricarbonyl(1,3-di(4-trifluoromethylphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron was synthesized via the procedure previously used to prepare tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron, using 1,8-bis(4-(trifluoromethyl)-phenyl)octa-1,7-diyne (500 mg, 1.27 mmol) and $Fe(CO)_5$ (513 μL, 3.81 mmol) in toluene (5 mL) to give **10** as a brown solid (690 mg, 1.23 mmol, 97%): mp 155−156 °C; HRMS (ESI-TOF) m/z [M + Na]+ calcd for $C_{26}H_{16}F_6FeNaO_4$ 585.0195, found 585.0196; IR ν_{max} 2943, 2070, 1640 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (4H, m, J = 10.0 Hz, Ar*H*), 7.64−7.60 (4H, m, J = 10.0 Hz, Ar*H*), 2.79 (4H, m, CH_2), 1.98 (4H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

207.5, 168.6, 135.9, 129.6, 129.8 (J = 32 Hz), 125.6, 125.2 (J = 230 Hz), 101.7, 79.4, 23.0, 21.6 ppm; MS (ESI) m/z 585 $[M + Na]^+$.

1,8-Bis(trimethylsilyl)octa-1,7-diyne.[12a] In a dried and degassed 250 mL round-bottom flask, under N_2, $Zn(OTf)_2$ (335 mg, 0.922 mmol) and NEt_3 (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, 1.96 g, 18.4 mmol) in anhydrous DCM (15.0 mL) was slowly added under N_2 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 N_2 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 NH_4Cl, and extracted with Et_2O (3 × 50 mL). The organic fraction was dried with anhydrous Na_2SO_4 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 clear solid (3.35 g, 13.3 mmol, 72.7%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20−2.32 (4H, m, $CH_2CH_2CH_2CH_2$), 1.57−1.68 (4H, m, $CH_2CH_2CH_2CH_2$), 0.15 (18H, s, $Si(CH_3)_3$) ppm.

Tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2H-inden-2-one)iron (1).[13,14b] Tricarbonyl(1,8-bis(trimethylsilyl)octa-1,7-diyne was synthesized via the general procedure previously used for tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron, using 1,8-bis(trimethylsilyl)octa-1,7-diyne (500 mg, 2.00 mmol) and $Fe(CO)_5$ (792 μL, 1.18g, 6.00 mmol) in toluene (5 mL). Tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron was isolated through column chromatography eluted with ethyl acetate 0−5% in pentane to give the product as a yellow solid (610 mg, 1.46 mmol, 73.0%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.54−2.58 (4H, m, $CH_2CH_2CH_2CH_2$), 1.80−1.85 (4H, m, $CH_2CH_2CH_2CH_2$), 0.28 (18H, br s, $Si(CH_3)_3$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.0, 181.2, 111.0, 71.7, 24.8, 22.4, −0.3 ppm; MS (ESI) m/z 419 ([M + H], 100%).

N-Benzylaniline (19).[8] *N*-Benzylaniline was synthesized via the same procedure as previously described with benzyl alcohol (110 μL, 108 mg, 1.00 mmol), aniline (182 μL, 186 mg, 2.00 mmol), tricarbonyl(1,3-di(phenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Column chromatography, eluted with 0−5% ethyl acetate in pentane, gave the product as a colorless oil (165 mg, 0.90 mmol, 90.0%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.40 (5H, m, Ar*H*), 7.20−7.10 (2H, m, Ar*H*), 6.70−6.65 (1H, m, Ar*H*), 6.60−6.55 (2H, m, J = 8.0 Hz, Ar*H*), 4.26 (2H, s, CH_2), 3.95 (1H, br s, N*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2 (C), 139.5 (C), 129.3 (CH), 128.7 (CH), 127.6 (CH), 127.3 (CH), 117.6 (CH), 112.5 (CH), 48.4 (CH_2) ppm; MS (ESI) m/z 184.1 ([M^+ + H], 100%), 198.1.

N-Phenethylaniline (20).[18] *N*-Phenethylaniline was synthesized via the same procedure as previously described with 2-phenylethanol (122 μL, 122 mg, 1.00 mmol), aniline (182 μL, 186 mg, 2.00 mmol), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Column chromatography, eluted with 0−5% ethyl acetate in pentane, gave the product as a colorless oil (181 mg, 0.920 mmol, 92.0%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{14}H_{16}N$ 198.1277, found 198.1280; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.40 (2H, m, Ar*H*), 7.09−7.24 (5H, m, Ar*H*), 6.69 (1H, t, J = 8.0 Hz, Ar*H*), 6.58 (2H, d, J = 8.0 Hz, Ar*H*), 3.62 (1H, br s, N*H*), 3.36 (2H, t, J = 7.0 Hz, CH_2), 2.87 (2H, t, J = 7.0 Hz, CH_2) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 139.5, 129.4, 128.9, 128.7, 126.5, 117.6, 113.1, 45.1, 35.6 ppm; MS (ESI) m/z 198 ([M^+ + H], 100%).

N-(3-Phenylpropyl)aniline (21).[18] *N*-(3-Phenylpropyl)aniline was synthesized via the same procedure as previously described with 3-phenyl-1-propanol (136 mg, 1.00 mmol), aniline (182 μL, 186 mg,2.00 mmol), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Column chromatography eluted with 0−5% ethyl acetate in pentane gave the product as a colorless oil (201 mg, 0.952 mmol, 95.2%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{18}N$ 212.1434, found 212.1436; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23−7.33 (2H, m, Ar*H*), 7.10−7.23 (5H, m, Ar*H*), 6.68 (1H, t, J = 7.3 Hz, Ar*H*), 6.57 (2H, d, J = 7.6 Hz, Ar*H*), 3.59 (1H, br s, N*H*), 3.14 (2H, t, J = 6.9 Hz, CH_2), 2.73 (2H, t, J = 7.5 Hz, CH_2), 1.95 (2H, quin, J = 7.3 Hz, CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 141.7, 129.2, 128.4, 126.0, 117.2, 112.8, 43.4, 33.4, 32.0 ppm; MS (ESI) m/z 212 ([M^+ + H], 100%).

N-(4-Phenylbutyl)aniline (22).[19] *N*-(4-Phenylbutyl)aniline was synthesized via the same procedure as previously described with 4-phenyl-1-butanol (152 μL, 150 mg, 1.00 mmol), aniline (182 μL, 186 mg, 2.00 mmol), tricarbonyl(1,3-di(4-trifluoromethylphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (56.2 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Column chromatography eluted with 0−5% ethyl acetate in pentane gave the product as a colorless oil (183 mg, 0.816 mmol, 81.6%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{20}N$ 226.1590, found 226.1589; IR ν_{max} 3399, 2930, 1601 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23−7.38 (2H, m, Ar*H*), 7.03−7.22 (5H, m, Ar*H*), 6.7 (1H, t, J = 7.2 Hz, Ar*H*), 6.57 (2H, d, J = 7.8 Hz, Ar*H*), 3.54 (1H, br s, N*H*), 3.11 (2H, t, J = 6.6 Hz, CH_2), 2.65 (2H, t, J = 7.2 Hz, CH_2), 1.54−1.84 (4H, m, CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 142.3, 129.3, 128.5, 128.4, 125.9, 117.2, 112.7, 43.9, 35.7, 29.2, 29.0 ppm; MS (ESI) m/z 226 ([M^+ + 1], 100%).

N-(3-(4-Methoxyphenyl)propyl)aniline (23).[20] *N*-3-(4-Methoxyphenyl)propyl)aniline was synthesized via the previously described method using 3-(4-methoxyphenyl)-1-propanol (166 mg, 1.00 mmol), aniline (182 μL, 2.00 mmol), tricarbonyl(1,3-di(4-trifluoromethylphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (56.2 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Column chromatography eluted with 0−5% ethyl acetate in pentane afforded the product as a colorless oil (226 mg, 0.938 mmol, 94%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{16}H_{20}NO$ 242.1539, found 242.1536; IR ν_{max} 3399, 2931, 1602 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13−7.20 (2H, m, Ar*H*), 7.11 (2H, d, J = 8.5 Hz, Ar*H*), 6.83 (2H, d, J = 8.5 Hz, Ar*H*), 6.68 (1H, t, J = 7.3 Hz, Ar*H*), 6.57 (2H, d, J = 7.6 Hz, Ar*H*), 3.78 (3H, s, OCH_3), 3.59 (1H, br s, N*H*), 3.12 (2H, t, J = 7.0 Hz, CH_2), 2.67 (2H, t, J = 7.6 Hz, CH_2), 1.91 (2H, quin, J = 7.3 Hz, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 148.4, 133.7, 129.3, 129.2, 117.2, 113.9, 112.8, 55.3, 43.4, 32.5, 31.3 ppm; MS (ESI) m/z 242 ([M^+ + 1], 100%).

N-(4-Methoxyphenethyl)aniline (24).[21] *N*-(4-Methoxyphenethyl)-aniline was prepared via the general procedure using aniline (182 μL, 186 mg, 2.00 mmol), 4-methoxyphenethyl alcohol (152 mg, 1.00 mmol), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Flash chromatography with 0−5% ethyl acetate in pentane gave the product as a colorless oil (216 mg, 0.956 mmol, 95.6%): IR ν_{max} 3418, 2928, 1601 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08−7.23 (4H, m, Ar*H*), 6.86 (2H, d, J = 8.7 Hz, Ar*H*), 6.70 (1H, t, J = 7.3 Hz, H), 6.61 (2H, d, J = 9.3 Hz, Ar*H*), 3.80 (3H, s, OCH_3), 3.65 (1H, br s, N*H*), 3.36 (2H, t, J = 6.9 Hz, CH_2), 2.86 (2H, t, J = 6.9 Hz, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 148.1, 131.3, 129.7, 129.3, 117.4, 114.0, 113.0, 55.3, 45.2, 34.6 ppm; MS (ESI) m/z 227 ([M + H], 100%).

4-Methoxy-N-(3-(4-methoxyphenyl)propyl)aniline (25).[22] 4-Methoxy-*N*-(4-(methoxyphenyl)propyl)aniline was synthesized via the previously described method with 3-(4-methoxyphenyl)-1-propanol (166 mg, 1.00 mmol), anisidine (246 mg, 2.00 mmol), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Column chromatography eluted with 0−5% ethyl acetate in pentane afforded the product as a colorless oil (268 mg, 0.989 mmol, 99%): IR ν_{max} 3401, 2932, 1602 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (2H, d, J = 8.5 Hz, Ar*H*), 6.83 (2H, d, J = 8.5 Hz, Ar*H*), 6.76 (8H, d, J = 8.9 Hz, Ar*H*), 6.55 (2H, d, J = 8.9 Hz, Ar*H*), 3.79 (3H, s, OCH_3), 3.74 (3H, s, OCH_3), 3.08 (2H, t, J = 7.0 Hz, NCH_2), 2.66 (2H, t, J = 7.6 Hz, CH_2), 1.89 (2H, quin, J = 7.3 Hz, $CH_2CH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 152.1, 142.7, 133.8, 129.3, 114.9, 114.1, 113.8, 55.8, 55.3, 44.4, 32.5, 31.4 ppm; MS (ESI) m/z 272 ([M^+ + H], 100%).

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

*4-Chloro-N-(3-(4-methoxyphenyl)propyl)aniline (**26**).*[23] 4-Chloro-*N*-(3-(4-methoxyphenyl)propyl)aniline was synthesized via the previously described method using 3-(4-methoxyphenyl)-1-propanol (166 mg, 1.00 mmol), 4-chloroaniline (255 mg, 2.00 mmol), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Column chromatography eluted with 0−5% ethyl acetate in pentane gave the product as a clear oil (262 mg, 0.953 mmol, 95.3%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{16}H_{19}ClNO$ 276.1150 and 278.1120, found 276.1151 and 278.1121; IR ν_{max} 3402, 2933, 1598 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05−7.07 (4H, m, Ar*H*), 6.83 (2H, d, J = 8.5 Hz, Ar*H*), 6.46 (2H, d, J = 8.9 Hz, Ar*H*), 3.78 (3H, s, OCH_3), 3.60 (1H, br s, N*H*), 3.08 (2H, t, J = 7.0 Hz, NCH_2), 2.65 (2H, t, J = 7.6 Hz, CH_2), 1.89 (2H, quin, J = 7.3 Hz, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 146.9, 133.5, 129.3, 129.0, 121.7, 113.9, 113.8, 55.3, 43.4, 32.4, 31.1 ppm; MS (ESI) m/z 276 ([M$^+$ + H], 100%), 278 ([M$^+$ + H], 40%).

*N-(3-(4-Methoxyphenyl)propyl)-N-methylaniline (**27**).*[20] *N*-(3-(4-Methoxyphenyl)propyl)-*N*-methylaniline was prepared via the general procedure using *N*-methylaniline (217 μL, 214 mg, 2.00 mmol), 3-(4-methoxyphenyl)-1-propanol (166 mg, 1.00 mmol), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 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*-(3-(4-methoxyphenyl)propyl)-*N*-methylaniline as a colorless oil (127 mg, 0.498 mmol, 49.8%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{17}H_{21}NO$ 256.1696, found 256.1698; IR ν_{max} 3412, 2932, 1602 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (2H, t, J = 7.32 Hz, Ar*H*), 7.09 (2H, d, J = 8.0 Hz, Ar*H*), 6.82 (2H, d, J = 7.7 Hz, Ar*H*), 6.57−6.71 (3H, m, Ar*H*), 3.78 (3H, s, OCH_3), 3.31 (2H, t, J = 7.4 Hz, NCH_2), 2.90 (3H, s, NCH_3), 2.58 (2H, t, J = 7.6 Hz, CH_2), 1.87 (2H, quin, J = 7.5 Hz, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 149.4, 133.9, 129.3, 129.2, 116.0, 113.8, 112.3, 55.3, 52.2, 38.3, 32.4, 28.4 ppm; MS (ESI) m/z 256 ([M + H], 100%).

*N-Cyclopentylaniline (**28**).*[24] *N*-Cyclopentylaniline was prepared via the general procedure using aniline (182 μL, 186 mg, 2.00 mmol), cyclopentanol (91 μL, 85 mg, 1.00 mmol), tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-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*-cyclopentylaniline amine as a colorless oil (145 mg, 0.901 mmol, 90.1%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{11}H_{16}N$ 162.1277, found 162.1277; IR ν_{max} 3406, 2955, 160 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (2H, t, J = 7.7 Hz, Ar*H*), 6.67 (1H, t, J = 7.3 Hz, Ar*H*), 6.60 (2H, d, J = 7.7 Hz, Ar*H*), 3.78 (1H, quin, J = 6.1 Hz, NC*H*), 3.631 (1H, br s, N*H*), 2.02 (2H, dd, J = 12.4, 6.2 Hz, CH_2), 1.39−1.83 (6H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 129.2, 116.9, 113.2, 54.7, 33.6, 24.1 ppm; MS (ESI) m/z 162 ([M + H], 100%).

*N-Cyclohexylaniline (**29**).*[19] *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-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Flash chromatography eluted with 0−5% ethyl acetate in pentane gave *N*-cyclohexylaniline as a yellow oil (166 mg, 0.949 mmol, 95%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{18}N$ 176.1434, found 176.1438; IR ν_{max} 3367, 2925, 1600 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07−7.20 (2H, m, Ar*H*), 6.61−6.69 (1H, m, Ar*H*), 6.54−6.68 (2H, m, Ar*H*), 3.47 (1H, br s, N*H*), 3.23 (1H, tt, J = 10.2, 3.7 Hz, NC*H*), 1.94−2.12 (2H, m, CH_2), 1.72−1.76 (2H, m, CH_2), 1.55−1.68 (1H, m, CH_2), 1.28−1.42 (2H, m, CH_2), 1.04−1.27 (3H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 129.4, 116.9, 113.2, 51.8, 33.6, 26.1, 25.1 ppm; MS (ESI) m/z 176 ([M + H], 100%).

*N-Phenylcycloheptanamine (**30**).*[25] *N*-Phenylcycloheptylanimine was prepared via the general procedure using aniline (182 μL, 186 mg, 2.00 mmol), cyclopheptanol (238 mg, 1.00 mmol), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Flash chromatography with 0−2% ethyl acetate in pentane gave *N*-phenylcycloheptylanimine as a colorless oil (182 mg, 0.963 mmol, 96.3%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{20}N$ 190.1590, found 190.1592; IR ν_{max} 3404, 2922, 1600 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (2H, t, J = 7.9 Hz, Ar*H*), 6.75 (1H, t, J = 7.3 Hz, Ar*H*), 6.64 (2H, d, J = 7.8 Hz, Ar*H*), 3.65 (1H, br s, N*H*), 3.55 (1H, m, NC*H*), 2.03−2.21 (2H, m, CH_2), 1.48−1.88 (10H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 129.3, 116.8, 113.3, 53.7, 34.9, 28.5, 24.51 ppm; MS (ESI) m/z 190 ([M + H], 100%).

*N-Phenyl-1,2,3,4-tetrahydronaphthalen-2-amine (**31**).*[26] *N*-Phenyl-1,2,3,4-tetrahydronaphthalen-2-amine was prepared via the general procedure using aniline (182 μL, 186 mg, 2.00 mmol), β-tetralol (148 mg, 1.00 mmol, 1.00), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 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*-phenyl-1,2,3,4-tetrahydronaphthalen-2-amine as a colorless oil (131 mg, 0.587 mmol, 58.7%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{16}H_{18}N$ 224.1434, found 224.1432; IR ν_{max} 3354, 3033, 1600 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03−7.23 (6H, m, Ar*H*), 6.58−6.77 (3H, m, Ar*H*), 3.75−3.92 (1H, m, NC*H*), 3.69 (1H, br s, N*H*), 3.22 (1H, dd, J = 16.2, 4.5 Hz, C*H*H), 2.92 (2H, t, J = 6.5 Hz, ArCH_2), 2.69 (1H, dd, J = 16.2, 8.3 Hz, CH*H*), 2.10−2.29 (1H, m, CH_2), 1.69−1.87 (1H, m, CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 135.9, 134.7, 129.5, 129.4, 128.8, 126.1, 125.9, 117.3, 113.4, 48.5, 36.5, 28.8, 27.5 ppm; MS (ESI) m/z 224 ([M + H], 100%).

*1-Phenylpyrrolidine (**32**).*[19] 1-Phenylpyrrolidine was prepared via the general procedure using aniline (91 μL, 93 mg, 1.00 mmol), 1,4-butanediol (180 mg, 2.00 mmol), tricarbonyl(1,3-diphenyl-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Flash chromatography with 0−2% ethyl acetate in pentane gave 1-phenylpyrrolidine as a colorless oil (50 mg, 0.34 mmol, 34%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17−7.34 (2H, m, Ar*H*), 6.65 (1H, t, J = 7.3 Hz, Ar*H*), 6.57 (2H, d, J = 7.9 Hz, Ar*H*), 3.28 (4H, t, J = 6.6 Hz, NCH_2), 2.00 (4H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 129.1, 115.4, 111.6, 47.6, 25.5 ppm; MS (ESI) m/z 148 ([M + H], 100%).

*1-Phenylazapine (**33**).*[27] 1-Phenylpyrrolidine was prepared via the general procedure using aniline (91. μL, 93 mg, 1.00 mmol) 1,6-hexanediol (210 μL, 236 mg, 2.00 mmol), tricarbonyl(1,3-di(4-methoxyphenyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (48.6 mg, 0.100 mmol), and trimethylamine *N*-oxide (6.75 mg, 0.09 mmol). Flash chromatography with 0−2% ethyl acetate in pentane gave 1-phenylpyrrolidine as a colorless oil (75 mg, 0.43 mmol, 43%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{18}N$ 176.1434, found 176.1436; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (2H, dd, J = 8.8, 7.2 Hz, Ar*H*), 6.69 (2H, d, J = 7.9 Hz, Ar*H*), 6.62 (1H, t, J = 7.3 Hz, Ar*H*), 3.41−3.50 (4H, m, NCH_2), 1.72−1.85 (4H, m, CH_2), 1.51−1.58 (4H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 129.2, 115.1, 111.1, 49.0, 27.8, 27.2 ppm; MS (ESI) m/z 176 ([M + H], 100%).

*N-(Pent-4-en-1-yl)aniline (**37**).*[28] *N*-(Pent-4-en-1-yl)aniline was synthesized through the general procedure using aniline (182 μL, 186 mg, 2.00 mmol), penten-1-ol (105 μL, 86.0 mg, 1.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol) but at 120 °C rather than 140 °C. *N*-(Pent-4-en-1-yl)aniline was isolated through column chromatography eluted with 0−20% ethyl acetate in pentane to give a light brown oil (128 mg, 0.748 mmol, 74.8%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{11}H_{16}N$ 162.1277, found 162.1278; IR ν_{max} 3408 (N—H), 2928, 2858, 1601 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (2H, t, J = 7.9 Hz, Ar*H*), 6.69 (1H, t, J = 7.3 Hz, Ar*H*), 6.60 (2H, d, J = 7.8 Hz, Ar*H*), 5.84 (1H, ddt, J = 17.0, 10.3, 6.6 Hz, CH_2CH═CH_2), 5.06 (1H, dd, J = 17.2, 1.7 Hz, CH═CH*H*), 5.00 (1H, d, J = 10.2 Hz, CH═C*H*H), 3.61 (1H, br s, N*H*), 3.13 (2H, t, J = 7.1 Hz, NHCH_2), 2.17 (2H, q, J = 6.9 Hz, CH_2CH_2CH═CH_2), 1.72 (2H, quin, J = 7.3 Hz, $CH_2CH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 138.0, 129.2, 117.2, 114.7, 112.7, 43.4, 31.3, 28.6 ppm; MS (ESI) m/z 162.1 ([M + H]$^+$).

*N-(6-(Trimethylsilyl)hex-5-yn-1-yl)aniline (**38**).*[29] *N*-(6-(Trimethylsilyl)hex-5-yn-1-yl)aniline was synthesized through the

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

general procedure using aniline (182 μL, 186 mg, 2.00 mmol), 6-(trimethylsilyl)hex-5-yn-1-ol (166 mg, 1.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-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)aniline was isolated via column chromatography (196 mg, 0.799 mmol, 79.9%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{15}H_{24}NS$ 246.1673, found 246.1671; IR ν_{max} 3385 (N—H), 2933, 2169, 1601 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (2H, t, J = 7.6 Hz, Ar*H*), 6.73 (1H, t, J = 7.3 Hz, Ar*H*), 6.64 (2H, d, J = 8.1 Hz, Ar*H*), 3.20 (1H, br s, NH), 3.00 (2H, t, J = 7.0 Hz, NHCH_2), 2.32 (2H, t, J = 7.0 Hz, CH_2CCSi), 1.77 (2H, quin, J = 7.0 Hz, CH_2CH$_2$CH$_2$CC), 1.67 (2H, quin, J = 7.0 Hz, CH_2CH$_2$CC), 0.20 (9H, s, Si(CH_3)$_3$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 129.2, 117.1, 112.6, 106.9, 84.9, 43.3, 28.5, 26.1, 19.6, 0.1 ppm; MS (ESI) m/z 246.2 ($[M + H]^+$). At 120 °C, the yield was 38%.

*4-Methoxy-N-(pent-4-en-1-yl)aniline (**39**).* 4-Methoxy-*N*-(pent-4-en-1-yl)aniline was synthesized via the general procedure using *p*-anisidine (245 mg, 2.00 mmol), 4-penten-1-ol (86 mg, 1.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-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 with 0−40% ethyl acetate in pentane to give 4-methoxy-*N*-(pent-4-en-1-yl)aniline as a colorless oil (134 mg, 0.698 mmol, 69.8%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{18}NO$ 192.1383, found 192.1395; IR ν_{max} 3390, 2931, 1640 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.78 (2H, d, J = 8.9 Hz, Ar*H*), 6.58 (2H, d, J = 8.9 Hz, Ar*H*), 5.70−5.97 (1H, m, C*H*═CH$_2$), 5.05 (1H, d, J = 17.0 Hz, CH═CH*H*), 4.99 (1H, d, J = 10.2 Hz, CH═C*H*H), 3.75 (3H, s, OCH_3), 3.09 (2H, t, J = 8.7 Hz, NHCH_2), 2.17 (2H, q, J = 6.1 Hz, CH_2CH═CH$_2$), 1.70 (2H, quin, J = 7.3 Hz, CH$_2$CH_2CH$_2$), 1.46−1.91 (1H, br s, *NH*) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 142.7, 138.1, 115.0, 114.9, 114.1, 55.9, 44.5, 31.4, 28.8 ppm; MS (ESI) m/z 192 ([M + H], 100%).

*4-Chloro-N-(pent-4-en-1-yl)aniline (**40**).* 4-Chloro-*N*-(pent-4-en-1-yl)aniline was synthesized through the general procedure using 4-chloroaniline (255 mg, 2.00 mmol), penten-1-ol (105 μL, 86.0 mg, 1.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol). 4-Chloro-*N*-(pent-4-en-1-yl)aniline was isolated through column chromatography eluted with 0−20% ethyl acetate in pentane to give a light brown oil (82.0 mg, 0.421 mmol, 42.1%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{11}H_{15}ClN$ 196.0888 and 198.0858, found 196.0886 and 198.0856; ^1H NMR (600 MHz, $CDCl_3$) δ 6.96 (2H, d, J = 8.3 Hz, Ar*H*), 6.36 (2H, d, J = 8.3 Hz, Ar*H*), 5.68 (1H, ddt, J = 17.0, 10.3, 6.6 Hz, C*H*═CH$_2$), 4.91 (1H, d, J = 17.3 Hz, CH═CH*H*), 4.85 (1H, d, J = 10.2 Hz, CH═C*H*H), 3.49 (1H, br s, N*H*), 2.94 (2H, t, J = 7.0 Hz, NHCH_2), 2.01 (2H, q, J = 7.1 Hz, CH$_2$CH_2CH═CH$_2$), 1.55 (2H, quin, J = 7.1 Hz, CH$_2$CH_2CH$_2$) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.8, 137.7, 128.9, 121.5, 115.1, 113.6, 43.3, 31.1, 28.3 ppm; MS (ESI) m/z 196 ([M + H] (^{35}Cl), 100%), 198 ([M + H] (^{37}Cl), 33%).

*N-Benzylpent-4-en-1-amine (**41**).* *N*-Benzylpent-4-en-1-amine was synthesized via the general procedure using benzylamine (109 μL, 107 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-2*H*-inden-2-one) iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). The product was isolated using column chromatography eluted with 0−100% ethyl acetate in pentane to give *N*-benzylpent-4-en-1-amine as a colorless oil (158 mg, 0.903 mmol, 90.3%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{18}N$ 176.1434, found 176.1433; IR ν_{max} 3076, 3064, 1640 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28−7.38 (4H, m, *ArH*), 7.20−7.28 (1H, m, *ArH*), 5.81 (1H, ddt, J = 17.0, 10.2, 6.7 Hz, *C*H═CH$_2$), 4.90−5.05 (2H, m, *CH*$_2$), 3.78 (2H, s, PhCH_2), 2.65 (2H, t, J = 7.2 Hz, NHCH$_2$CH$_2$CH_2), 2.10 (2H, q, J = 7.0 Hz, NHCH_2), 1.61 (2H, quin, J = 7.4 Hz, NHCH$_2$CH_2CH$_2$), 1.47 (1H, br s, *NH*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.49, 138.49, 128.4, 128.1, 126.9, 114.6, 54.0, 48.9, 31.5, 29.2 ppm; MS (ESI) m/z 176 ([M + H], 100%).

*N-Benzyl-6-(trimethylsilyl)hex-5-yn-1-amine (**42**).* *N*-Benzyl-6-(trimethylsilyl)hex-5-yn-1-amine was synthesized via the general procedure using benzylamine (107 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-2*H*-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*-benzyl-6-(trimethylsilyl)hex-5-yn-1-amine as a colorless oil (51.0 mg, 0.197 mmol, 20%): HRMS (EI) m/z $[M + H]^+$ calcd for $C_{16}H_{26}NSi$ 260.1829, found 260.1829; IR ν_{max} 3301, 2955 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.22−7.31 (4H, m, Ar*H*), 7.11−7.22 (1H, m, Ar*H*), 3.72 (2H, s, PhCH_2NH), 2.58 (2H, t, J = 6.9 Hz, NHCH_2CH$_2$), 2.17 (2H, t, J = 6.9 Hz, CH_2CCTMS), 1.45−1.59 (4H, m, CH$_2$CH_2CH_2CH$_2$), 1.41 (1H, br s, *NH*), 0.07 (9H, s, CCSi(CH_3)$_3$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.41, 128.40, 128.1, 126.9, 107.2, 84.6, 54.0, 48.8, 29.2, 26.4, 19.8, 0.1 ppm; MS (ESI) m/z 260 ([M + H], 100%).

*N-Benzylpentan-1-amine (**43**).*[7b] *N*-Benzylpentan-1-amine was synthesized via the general procedure using benzylamine (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-2*H*-inden-2-one) iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). The product was isolated using column chromatography eluted with 0−20% ethyl acetate in pentane to give *N*-benzylpentan-1-amine as a colorless oil (92 mg, 0.518 mmol, 51.8%): HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{12}H_{20}N$ 178.1590, found 178.1590; IR ν_{max} 3310, 2928, 1657 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.06−7.45 (5H, m, Ar*H*), 3.79 (2H, s, PhCH_2), 2.63 (2H, t, J = 7.3 Hz, NCH_2CH$_2$), 1.64 (1H, br s, N*H*), 1.43−1.60 (2H, m, CH_2), 1.31 (4H, m, CH_2), 0.89 (3H, t, J = 6.5 Hz, CH$_2$CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.2, 128.4, 128.2, 127.0, 54.0, 49.4, 29.7, 29.6, 22.6, 14.1 ppm; MS (ESI) m/z 178 ([M + H], 100%).

*N-Benzyl-3-(4-methoxyphenyl)propan-1-amine (**44**).* *N*-Benzyl-3-(4-methoxyphenyl)propan-1-amine was synthesized via the general procedure using benzylamine (107 mg, 1.00 mmol), 3-(4-methoxyphenyl)-1-propanol (332 mg, 2.00 mmol), tricarbonyl(1,3-di-(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-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*-benzyl-3-(4-methoxyphenyl)-propan-1-amine as a colorless oil (129 mg, 0.506 mmol, 51%): HRMS (EI) m/z $[M + H]^+$ calcd for $C_{17}H_{22}NO$ 256.1696, found 256.1701; IR ν_{max} 3061, 3028, 1611 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28−7.35 (4H, m, Ar*H*), 7.22−7.27 (1H, m, Ar*H*), 7.09 (2H, d, J = 8.5 Hz, Ar*H*), 6.82 (2H, d, J = 8.7 Hz, Ar*H*), 3.74−3.82 (5H, m, OCH_3 and PhCH_2), 2.66 (2H, t, J = 7.1 Hz, NHCH_2), 2.60 (2H, t, J = 7.7 Hz, ArCH_2CH$_2$), 1.81 (2H, quin, J = 7.40 Hz, CH$_2$CH_2CH$_2$), 1.49 (1H, br s, *NH*) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 140.5, 134.3, 129.2, 128.4, 128.1, 126.9, 113.7, 55.2, 54.1, 48.9, 32.8, 31.8 ppm; MS (ESI) m/z 256 ([M + H], 100%).

*1-Pentyl-4-phenylpiperidine (**45**).* 1-Pentyl-4-phenylpiperidine was synthesized via the general procedure from 4-phenylpiperidine (161 mg, 1.00 mmol), 1-pentanol (217 μL, 176 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). The compound was purified via column chromatography eluted with 0−40% ethyl acetate in pentane to give the product as a colorless oil (225 mg, 0.974 mmol, 97.4%): HRMS (EI) m/z $[M + H]^+$ calcd for $C_{16}H_{26}N$ 232.2060, found 232.2068; IR ν_{max} 2954, 2871, 1662 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.12−7.41 (5H, m, Ar*H*), 3.06 (2H, d, J = 11.6 Hz, NCH_2), 2.49 (1H, ddd, J = 15.7, 10.5, 5.7 Hz, PhC*H*), 2.27−2.42 (2H, m, NCH_2CH$_2$CH$_2$), 2.02 (2H, td, J = 11.0, 4.2 Hz, NCH_2), 1.72−1.91 (4H, m, CH_2), 1.47−1.62 (2H, m, CH$_2$CH_2CH$_2$), 1.20−1.44 (4H, m, CH_2), 0.91 (3H, t, J = 7.1 Hz, CH$_2$CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 128.4, 126.9, 126.1, 59.3, 54.5, 42.9, 33.5, 30.0, 26.8, 22.7, 14.1 ppm; MS (ESI) m/z 232 ([M + H], 100%).

*1-(Pent-4-en-1-yl)-4-phenylpiperidine (**46**).* 1-(Pent-4-en-1-yl)-4-phenylpiperidine was synthesized via the general method using 4-phenylpiperidine (161 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-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

oxide (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]$^+$ calcd for $C_{16}H_{24}N$ 230.1903, found 230.1901; IR ν_{max} 2933, 2801, 1640 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.34 (2H, m, ArH), 7.24−7.29 (2H, m, ArH), 7.19−7.24 (1H, m, ArH), 5.87 (1H, ddt, J = 17.0, 10.2, 6.7, 6.7 Hz, $CH_2CH{=}CH_2$), 5.07 (1H, dd, J = 17.1, 1.7 Hz, $CH{=}CH_2$), 5.00 (1H, d, J = 10.1 Hz, $CH{=}CH_2$), 3.09 (2H, d, J = 11.6 Hz, NCH_2), 2.52 (1H, tt, J = 10.5, 5.5 Hz, PhCH), 2.38−2.44 (2H, m, $NCH_2CH_2CH_2$), 2.12 (2H, q, J = 7.1 Hz, $CH_2CH_2CH{=}CH_2$), 2.04−2.10 (2H, m, NCH_2CH_2), 1.79−1.91 (4H, m, $PhCHCH_2$), 1.68 (2H, quin, J = 7.7 Hz, $CH_2CH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) 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), benzyl alcohol (207 μL, 216 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-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 (EI) m/z [M + H]$^+$ calcd for $C_{18}H_{22}N$ 252.1747, found 252.1748; IR ν_{max} 2934, 2799 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14−7.37 (10H, m, ArH), 3.54 (2H, s, CH_2Ph), 3.01 (2H, d, J = 11.6 Hz, CH_2NCH_2), 2.42−2.55 (1H, m, $PhCH(CH_2)_2$), 2.02−2.13 (2H, m, CH_2NCH_2), 1.74−1.86 (4H, m, $CHCH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) 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)-1-propanol (332 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). 1-(3-(4-Methoxyphenyl)propyl)-4-phenylpiperidine 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 (EI) m/z [M + H]$^+$ calcd for $C_{21}H_{28}NO$ 310.2165, found 310.2167; IR ν_{max} 2933, 1612 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15−7.35 (5H, m, ArH), 7.11 (2H, d, J = 8.1 Hz, ArH), 6.83 (2H, d, J = 8.2 Hz, ArH), 3.78 (3H, s, OCH_3), 3.04 (2H, d, J = 11.0 Hz, CH_2NCH_2), 2.59 (2H, t, J = 7.6 Hz, $NCH_2CH_2CH_2$), 2.47 (1H, td, J = 10.1, 5.5 Hz, $PhCH(CH_2)_2$), 2.35−2.42 (2H, m, CH_2), 1.97−2.09 (2H, m, CH_2), 1.72−1.91 (6H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 146.5, 134.3, 129.3, 128.4, 126.9, 126.1, 113.8, 58.5, 55.3, 54.5, 42.8, 33.6, 33.0, 29.1 ppm; MS (ESI) m/z 310 ([M + H$^+$], 100%).

*4-Phenyl-1-(6-(trimethylsilyl)hex-5-yn-1-yl)piperidine (**49**).* 4-Phenyl-1-(6-(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-2*H*-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-(6-(trimethylsilyl)hex-5-yn-1-yl)piperidine as a colorless oil (232 mg, 0.741 mmol, 74.1%): HRMS (EI) m/z [M + H]$^+$ calcd for $C_{20}H_{32}NSi$ 314.2299, found 314.2297; IR ν_{max} 2935, 2864 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15−7.34 (5H, m, ArH), 3.05 (2H, d, J = 11.6 Hz, NCH_2), 2.49 (1H, ddd, J = 22.1, 11.1, 5.8 Hz, PhCH), 2.35−2.41 (2H, m, CH_2), 2.26 (2H, t, J = 7.0 Hz, NCH_2), 2.02 (2H, td, J = 11.2, 3.4 Hz, CH_2NCH_2), 1.73−1.90 (4H, m, CH_2), 1.48−1.71 (4H, m, CH_2CH_2 in chain), 0.15 (9H, s, $Si(CH_3)_3$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) 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 314 ([M + H], 100%).

*1-Cyclopentyl-4-phenylpiperidine (**50**).* 1-Cyclopentyl-4-phenylpiperidine was synthesized through the general procedure using 4-phenylpiperidine (161 mg, 1.00 mmol), cyclopentanol (182 μL, 172 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol). 1-Cyclohexyl-4-phenylpiperidine was isolated via column chromatography eluted with 0−60% ethyl acetate in pentane as a colorless oil (207 mg, 0.904 mmol, 90.4%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{16}H_{24}N$ 230.1903, found 230.1905; IR ν_{max} 2954, 2867 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95−7.65 (5H, m, ArH), 3.16 (2H, d, J = 11.8 Hz, CHHNCHH), 2.36−2.60 (2H, m, CHHNCHH), 1.97−2.10 (2H, m, CH_2), 1.76−1.96 (6H, m, CH_2), 1.63−1.76 (2H, m, CH_2), 1.51−1.63 (2H, m, CH_2), 1.36−1.50 (2H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 128.4, 126.9, 126.0, 67.8, 53.4, 42.8, 33.5, 30.6, 24.2 ppm; MS (ESI) m/z 230 ([M + H], 100%).

*1-Cyclohexyl-4-phenylpiperidine (**51**).* 1-Cyclohexyl-4-phenylpiperidine was synthesized via the general procedure using 4-phenylpiperidine (161 mg, 1.00 mmol), cyclohexanol (210 μL, 200 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol). 1-Cyclohexyl-4-phenylpiperidine was isolated via column chromatography eluted with 0−60% ethyl acetate in pentane as a colorless oil (228 mg, 0.938 mmol, 93.8%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{17}H_{26}N$ 244.2060, found 244.2060; IR ν_{max} 2928, 2798 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13−7.38 (5H, m, ArH), 3.03 (2H, d, J = 11.4 Hz, CHHNCHH), 2.47 (1H, tt, J = 12.0, 3.9 Hz, $CH(CH_2)_2$), 2.32 (3H, td, J = 11.5, 2.2 Hz, CH_2), 1.70−2.01 (8H, m, CH_2), 1.64 (1H, d, J = 12.2 Hz, NCH), 1.19−1.33 (4H, m, CH_2), 1.00−1.18 (1H, m, CHH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 128.4, 126.9, 126.0, 64.1, 49.9, 43.3, 34.1, 28.9, 26.5, 26.2 ppm; MS (ESI) m/z 244 ([M + H], 100%).

*1-Cycloheptyl-4-phenylpiperidine (**52**).* 1-Cycloheptyl-4-phenylpiperidine was synthesized via the general procedure using 1-phenylpiperidine (161 mg, 1.00 mmol), cycloheptanol (240 μL, 228 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol). 1-Cycloheptyl-4-phenylpiperidine was isolated via column chromatography eluted with 0−60% ethyl acetate in pentane as a colorless oil (252 mg, 0.981 mmol, 98.1%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{18}H_{28}N$ 258.2216, found 258.2216; IR ν_{max} 2926, 2868 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25−7.33 (2H, m, ArH), 7.20−7.25 (2H, m, ArH), 7.14−7.20 (1H, m, ArH), 2.89 (2H, d, J = 11.4 Hz, CHHNCHH), 2.55−2.66 (1H, m, NCH), 2.45 (1H, tt, J = 11.9, 3.9 Hz, PhCH), 2.37 (2H, td, J = 11.6, 2.4 Hz, CHHNCHH), 1.63−1.95 (8H, m) 1.34−1.63 (8H, m) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.7, 128.4, 126.9, 126.0, 65.4, 49.3, 43.3, 34.1, 29.9, 28.2, 26.0 ppm; MS (ESI) m/z 258 ([M + H], 100%).

*4-Phenyl-1-(4-phenylbutan-2-yl)piperidine (**53**).* 4-Phenyl-1-(4-phenylbutan-2-yl)piperidine was synthesized through the general procedure using 4-phenylpiperidine (161 mg, 1.00 mmol), 4-phenylbutan-2-ol (309 μL, 300 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol). 4-Phenyl-1-(4-phenylbutan-2-yl)piperidine was isolated via column chromatography eluted with 0−60% ethyl acetate in pentane as a colorless oil (275 mg, 0.939 mmol, 93.9%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{21}H_{28}N$ 294.2216, found 294.2217; IR ν_{max} 2975, 2784, 1665 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05−7.50 (10H, m, ArH), 2.88−2.92 (2H, m), 2.57−2.78 (3H, m), 2.45−2.49 (2H, m), 2.26−2.30 (1H, m), 1.66−2.05 (6H, m), 1.53−1.66 (1H, m), 1.06 (3H, d, J = 4.3 Hz, $CHCH_3$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 142.7, 128.5, 128.4, 128.3, 126.9, 126.0, 125.6, 58.6, 51.1, 47.0, 43.2, 35.6, 33.2, 13.9 ppm; MS (ESI) m/z 294 ([M + H], 100%).

*N-(3-(Trifluoromethyl)benzyl)pentan-1-amine (**54**).*[7a] *N*-(3-(Trifluoromethyl)benzyl)pentan-1-amine was synthesized via the general procedure using 3-(trifluoromethyl)benzylamine (147 μL, 175 mg, 1.00 mmol), pentan-1-ol (217 μL, 176 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). The product was isolated using column chromatography eluted with 0−20% ethyl acetate in pentane to give *N*-(3-

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

(trifluoromethyl)benzyl)pent-4-en-1-amine as a colorless oil (220 mg, 0.898 mmol, 89.8%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (1H, s, ArH), 7.47−7.55 (2H, m, ArH), 7.39−7.46 (1H, m, ArH), 3.84 (2H, s, $ArCH_2NH$), 2.62 (2H, t, J = 7.2 Hz, $NHCH_2CH_2$), 1.63 (1H, br s, NH), 1.52 (2H, quin, J = 7.2 Hz, CH_2), 1.26−1.39 (4H, m, CH_2CH_2), 0.85−0.94 (3H, m, CH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.43, 130.67 (q, J = 32.1 Hz), 128.75, 124.77 (q, J = 4.0 Hz), 123.8 (q, J = 3.0 Hz), 124.2 (q, J = 272.0 Hz), 122.5, 53.5, 49.5, 29.7, 29.5, 22.6, 14.0 ppm; MS (ESI) m/z 246 ([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 (147 μL, 175 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-2*H*-inden-2-one) iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 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 (196 mg, 0.807 mmol, 80.7%): HRMS (EI) m/z [M + H]$^+$ calcd for $C_{13}H_{17}F_3N$ 244.1308, found 244.1311; IR ν_{max} 3302, 2930, 2855, 1679 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (1H, s, ArH), 7.48−7.54 (2H, m, ArH), 7.40−7.46 (1H, m, ArH), 5.81 (1H, ddt, J = 17.1, 10.3, 6.7 Hz, $CH{=}CH_2$), 5.02 (1H, dd, J = 17.1, 1.7 Hz, $CH{=}CH_2$), 4.96 (1H, d, J = 10.1 Hz, $CH{=}CH_2$), 3.84 (2H, s, $ArCH_2N$), 2.65 (2H, t, J = 7.2 Hz, NCH_2CH_2), 2.11 (2H, q, J = 6.9 Hz, CH_2CH_2CH), 1.62 (2H, quin, J = 7.3 Hz, $CH_2CH_2CH_2$), 1.44 (1H, br s, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 138.4, 131.4, 130.7 (q, J = 32.1 Hz), 128.8, 124.8 (q, J = 4.0 Hz), 123.7 (q, J = 4.0 Hz), 124.2 (q, J = 272.0 Hz), 114.7, 53.5, 48.9, 31.5, 29.2 ppm; MS (ESI) m/z 244 ([M + H$^+$], 100%).

*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-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 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 (295 mg, 0.913 mmol, 91.3%): HRMS (EI) m/z [M + H]$^+$ calcd for $C_{18}H_{21}F_3NO$ 324.1570, found 324.1575; IR ν_{max} 2932, 2833, 1611 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (1H, s, ArH), 7.46−7.53 (2H, m, ArH), 7.38−7.44 (1H, m, ArH), 7.08 (2H, d, J = 8.7 Hz, ArH), 6.81 (2H, d, J = 8.7 Hz, ArH), 3.81 (2H, s, $ArCH_2NH$), 3.76 (3H, s, OCH_3), 2.64 (2H, t, J = 7.1 Hz, $NHCH_2CH_2$), 2.61 (2H, t, J = 7.7 Hz, $ArCH_2CH_2$), 1.80 (2H, quin, J = 7.36 Hz, $CH_2CH_2CH_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 141.6, 134.1, 131.5, 130.7 (q, J = 32.1 Hz), 129.3, 128.8, 124.8 (q, J = 4.0 Hz), 123.8 (q, J = 4.0 Hz), 124.3 (q, J = 272.0 Hz), 113.8, 55.2, 53.5, 48.9, 32.7, 31.9 ppm; MS (ESI) m/z 324 ([M + H$^+$], 100%).

*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-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). *N*-Benzyl-1-(3-(trifluoromethyl)-phenyl)methanamine was isolated through column chromatography eluted with 0−60% ethyl acetate in pentane to give the product as a colorless oil (232 mg, 0.875 mmol, 87.5%): HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{15}H_{15}F_3N$ 266.1151, found 266.1150; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (1H, s, ArH), 7.52 (2H, m, ArH), 7.40−7.46 (1H, m, ArH), 7.32−7.36 (4H, m, ArH), 7.24−7.29 (1H, m, ArH), 3.86 (2H, s, $NHCH_2$), 3.81 (2H, s, $NHCH_2$), 1.66 (1H, br s, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 140.0, 131.5, 130.7 (q, J = 33.1 Hz), 128.8, 128.5, 128.2, 127.2, 124.8 (q, J = 4.0 Hz), 123.8 (q, J = 4.0 Hz), 124.3 (q, J = 272.0 Hz), 53.3, 52.6 ppm; MS (ESI) m/z 266 ([M + H], 100%).

*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-2*H*-inden-2-one) iron (42.0 mg, 0.100 mmol), and trimethylamine *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 the product as a colorless oil (233 mg, 0.959 mmol, 95.9%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{17}F_3N$ 244.1308, found 244.1305; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (1H, s, ArH), 7.46−7.55 (2H, m, ArH), 7.36−7.45 (1H, m, ArH), 3.82 (2H, s, $ArCH_2$), 3.11 (1H, quin, J = 6.6 Hz, NCH), 1.78−1.95 (2H, m, CH_2), 1.70 (2H, m, CH_2), 1.46−1.62 (2H, m, CH_2), 1.27−1.45 (2H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9, 131.5, 130.6 (q, J = 31.1 Hz), 128.7, 124.8 (q, J = 3.5 Hz), 123.7 (q, J = 3.0 Hz), 124.3 (q, J = 272.1 Hz), 59.4, 52.3, 33.2, 24.0 ppm; MS (ESI) m/z 244 ([M + H], 100%).

*N-(3-(Trifluoromethyl)benzyl)cyclohexanamine (**59**).* *N*-(3-(Trifluoromethyl)benzyl)cyclohexanamine was synthesized through 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-2*H*-inden-2-one) iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol). *N*-(3-(Trifluoromethyl)benzyl)cyclohexanamine was isolated through the use of 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]$^+$ calcd for $C_{14}H_{19}F_3N$ 258.1464, found 258.1463; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (1H, s, ArH), 7.50 (2H, m, ArH), 7.41 (1H, m, ArH), 3.86 (2H, s, $ArCH_2NH$), 2.48 (1H, tt, J = 10.2, 3.7 Hz, NHCH), 1.87−1.99 (2H, m, CH_2), 1.69−1.82 (2H, m, CH_2), 1.56−1.66 (1H, m, CHH), 1.03−1.39 (5H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 132.1, 130.6 (q, J = 32.1 Hz), 128.7, 124.7 (q, J = 3.0 Hz), 123.6 (q, J = 4.0 Hz), 124.2 (q, J = 273.1 Hz), 56.4, 50.6, 33.6, 26.1, 25.0 ppm; MS (ESI) m/z 258 ([M + H], 100%).

*N-(3-(Trifluoromethyl)benzyl)cycloheptanamine (**60**).* *N*-(3-(Trifluoromethyl)benzyl)cycloheptanamine was synthesized following the general procedure using 3-(trifluoromethyl)benzylamine (143 μL, 175 mg, 1.00 mmol), cycloheptanol (240 μL, 228 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one) iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol). *N*-(3-(Trifluoromethyl)benzyl)cycloheptanamine was isolated through column chromatography eluted with 0−60% ethyl acetate in pentane to give a colorless oil (255 mg, 0.941 mmol, 94.1%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{15}H_{21}F_3N$ 272.1621, found 272.1622; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (1H, s, ArH), 7.50 (2H, t, J = 9.0 Hz, ArH), 7.42 (1H, t, J = 7.6 Hz, ArH), 3.83 (1H, s, $ArCH_2$), 2.68 (1H, tt, J = 8.5, 4.1 Hz, CH_2), 1.79−1.93 (2H, m, CHHCHCHH), 1.61−1.75 (2H, m, CHHCHCHH), 1.48−1.61 (4H, m, CH_2 and CH_2), 1.36−1.48 (4H, m, CH_2CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 131.4, 130.6 (q, J = 31.1 Hz), 128.7, 124.7 (q, J = 4.0 Hz), 123.6 (q, J = 4.0 Hz), 124.2 (q, J = 272.1 Hz), 58.5, 51.1, 34.8, 28.3, 24.3 ppm; MS (ESI) m/z 272 ([M + H], 100%).

*4-Phenyl-N-(3-(trifluoromethyl)benzyl)butan-2-amine (**61**).* 4-Phenyl-*N*-(3-(trifluoromethyl)benzyl)butan-2-amine was synthesized following the general procedure using 3-(trifluoromethyl)benzylamine (148 μL, 175 mg, 1.00 mmol), 4-phenylbutan-2-ol (309 μL, 300 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). 4-Phenyl-*N*-(3-(trifluoromethyl)benzyl)butan-2-amine was isolated through column chromatography eluted with 0−60% ethyl acetate in pentane to give a colorless oil (270 mg, 0.879 mmol, 87.9%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{18}H_{21}F_3N$ 308.1621, found 308.1621; IR ν_{max} 2967, 2942, 1599 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (1H, s, ArH), 7.49 (2H, d, J = 7.8 Hz, ArH), 7.36−7.45 (1H, m, ArH), 7.22−7.31 (2H, m, ArH), 7.15−7.20 (3H, m, ArH), 3.87 (1H, AB, J = 13.6 Hz, CHH), 3.78 (1H, AB, J = 13.4 Hz, CHH), 2.59−2.78 (3H, m, CH and CH_2) 1.81 (1H, ddt, J = 13.5, 9.3, 6.6 Hz, CHH) 1.68 (1H, ddt, J = 13.5, 9.3, 6.6 Hz,

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

CHH), 1.28 (1H, br s, NH), 1.15 (3H, d, J = 6.3 Hz, CHCH_3) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 142.0, 131.5, 130.7 (q, J = 32.1 Hz), 128.4, 128.4, 125.8, 124.8 (q, J = 4.0 Hz), 123.7 (q, J = 4.0 Hz), 124.3 (q, J = 272.0 Hz), 52.2, 50.8, 38.7, 32.3, 20.5 ppm; MS (ESI) m/z 308 ([M + H], 100%).

*1-(3-(Trifluoromethyl)benzyl)azepane (**62**).* 1-(3-(Trifluoromethyl)benzyl)azepane was synthesized through the general procedure using 3-(trifluoromethyl)benzylamine (143 μL, 175 mg, 1.00 mmol), 1,6-hexanediol (236 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.200 mmol). 1-(3-(Trifluoromethyl)benzyl)azepane was isolated via column chromatography eluted with 0−60% ethyl acetate in pentane to give the product as a colorless oil (224 mg, 0.872 mmol, 87.2%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{14}H_{19}F_3N$ 258.1464, found 258.1465; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (1H, s, ArH), 7.53 (1H, d, J = 7.6 Hz, ArH), 7.48 (1H, d, J = 7.6 Hz, ArH), 7.40 (1H, t, J = 7.6 Hz, ArH), 3.67 (2H, s, ArCH_2N), 2.59−2.63 (4H, m, CH_2NCH_2 in ring), 1.60−1.64 (8H, m, CH_2CH_2CH_2CH_2 in ring) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 131.9, 130.4 (q, J = 32.1 Hz), 128.5, 125.3 (q, J = 4.0 Hz), 123.5 (q, J = 4.0 Hz), 124.3 (q, J = 272.0 Hz), 62.2, 55.6, 28.3, 27.0 ppm; MS (ESI) m/z 258 ([M + H], 100%).

*1-(3-(Trifluoromethyl)benzyl)piperidine (**63**).*[30] 1-(3-(Trifluoromethyl)benzyl)piperidine was synthesized via the general procedure using 3-(trifluoromethyl)benzylamine (143 μL, 175 mg, 1.00 mmol), 1,5-pentanediol (104 mg, 2.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-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 1-(3-(trifluoromethyl)benzyl)-piperidine as a colorless oil (226 mg, 0.930 mmol, 93%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{17}F_3N$ 244.1308, found 244.1312; IR ν_{max} 2936, 2855, 2798, 1445 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (1H, s, ArH), 7.46−7.54 (2H, m, ArH), 7.35−7.45 (1H, m, ArH), 3.50 (2H, s, PhCH_2N), 2.35−2.39 (4H, m, NCH_2), 1.58 (4H, quin, J = 5.6 Hz, NCH$_2$CH_2), 1.35−1.51 (2H, m, CH_2) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 132.5, 130.5 (q, J = 32.1 Hz), 128.5, 125.8 (q, J = 4.0 Hz), 123.8 (q, J = 4.0 Hz), 124.4 (q, J = 272.0 Hz), 63.3, 54.5, 26.0, 24.3 ppm; MS (ESI) m/z 244 ([M + H], 100%).

*N-Benzyl-4-phenylbutan-1-amine (**64**).* *N*-Benzyl-4-phenylbutan-1-amine was synthesized from 4-phenylbutylamine (149 mg, 1.00 mmol), benzyl alcohol (310 μL, 324 mg, 3.00 mmol), tricarbonyl(1,3-di(trimethylsilyl)-4,5,6,7-tetrahydro-2*H*-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 0−100% ethyl acetate in pentane to give *N*-benzyl-4-phenylbutan-1-amine as a colorless oil (110 mg, 0.460 mmol, 46%): HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{17}H_{22}N$ 240.1747, found 240.1747; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07−7.46 (10H, m, ArH), 3.77 (2H, s, PhCH_2), 2.51−2.83 (4H, m, CH_2CH$_2$CH$_2$CH_2), 1.50−1.74 (4H, m, CH$_2$CH_2CH_2CH$_2$), 1.44 (1H, br s, NH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 140.5, 128.4, 128.4, 128.3, 128.1, 126.9, 125.7, 54.1, 49.3, 35.9, 29.8, 29.2 ppm; MS (ESI) m/z 240 ([M + H], 100%).

*N-(3-(4-Methoxyphenyl)propyl-N-methylcyclohexanamine (**65**).* *N*-(3-(4-Methoxyphenyl)propyl-*N*-methylcyclohexanamine was synthesized via the general procedure using diallylamine (123 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-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). The product was isolated using column chromatography eluted with 0−20% ethyl acetate in pentane to give *N*-(3-(4-methoxyphenyl)propyl-*N*-methylcyclohexanamine as a colorless oil (235 mg, 0.893 mmol, 89.3%): HRMS (EI) m/z [M + H]$^+$ calcd for $C_{17}H_{28}NO$ 262.2165, found 262.2169; IR ν_{max} 2935, 2855 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (2H, d, J = 8.5 Hz, ArH), 6.82 (2H, d, J = 8.5 Hz, ArH), 3.78 (3H, s, OCH_3), 2.55 (2H, t, J = 7.8 Hz, NCH_2), 2.45 (2H, t, J = 7.5 Hz, ArCH_2), 2.30−2.40 (1H, m, NCH), 2.24 (3H, s, NCH_3), 1.69−1.84 (6H, m, CH_2), 1.61 (1H, d, J = 12.5 Hz, CH), 1.13−1.27 (4H, m, CH_2), 1.01−1.12 (1H, m, CH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 134.6, 129.2, 113.7, 62.5, 55.2, 53.2, 37.7, 32.9, 29.9, 28.6, 26.4, 26.1 ppm; MS (ESI) m/z 262 ([M + H$^+$], 100%).

*N-Methyl-N-(6-trimethylsilyl)hex-5-yn-1-yl)cyclohexanamine (**66**).* *N*-Methyl-*N*-(6-trimethylsilyl)hex-5-yn-1-yl)cyclohexanamine was synthesized via the general procedure using *N*-methylcyclohexylamine (112 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-2*H*-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-yn-1-yl)cyclohexanamine as a colorless oil (243 mg, 0.931 mmol, 93%): HRMS (EI) m/z [M + H]$^+$ calcd for $C_{16}H_{32}NSi$ 266.2299, found 266.2305; IR ν_{max} 2929, 2855, 1451 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.42 (2H, t, J = 6.9 Hz, NCH_2), 2.28−2.38 (1H, m, NCH), 2.15−2.28 (5H, m, CH_3 and CH_2), 1.77 (4H, d, J = 9.3 Hz, CH_2 in ring), 1.43−1.67 (5H, m, CH_2), 1.12−1.30 (4H, m, CH_2), 0.96−1.11 (1H, m, CHH), 0.12 (9H, s, Si(CH_3)$_3$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 107.4, 84.4, 62.4, 53.0, 37.8, 28.5, 26.9, 26.5, 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 from *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-2*H*-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 $C_{12}H_{24}N$ 182.1903, found 182.1905; IR ν_{max} 2926, 2853, 2789, 1640 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83 (1H, ddt, J = 17.0, 10.3, 6.6 Hz, CH═CH$_2$), 5.02 (1H, dd, J = 17.1, 1.9 Hz, CH$_2$═CH), 4.95 (1H, d, J = 10.1 Hz, CH$_2$═CH), 2.40−2.46 (2H, m), 2.31−2.39 (1H, m, NCH), 2.24 (3H, s, NCH_3), 2.05 (2H, q, J = 6.9 Hz, CH$_2$CH$_2$CH_2 chain), 1.78 (4H, d, J = 9.5 Hz, CH_2 ring), 1.62 (1H, d, J = 12.7 Hz, CH), 1.55 (2H, quin, J = 7.6 Hz, CH$_2$CH_2CH$_2$ chain), 1.14−1.28 (4H, m, CH_2), 1.09 (1H, td, J = 12.3, 3.4 Hz, PhCH) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) 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 (123 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-2*H*-inden-2-one)iron (42.0 mg, 0.100 mmol), and trimethylamine *N*-oxide (15.0 mg, 0.2 mmol). The product was isolated using 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 $C_{16}H_{24}NO$ 246.1852, found 246.1852; IR ν_{max} 2945, 2866, 1636 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (2H, d, J = 8.5 Hz, ArH), 6.82 (2H, d, J = 8.5 Hz, ArH), 5.85 (2H, ddt, J = 17.0, 10.3, 6.5 Hz, CH$_2$CH═CH$_2$), 5.09−5.19 (4H, m, CH═CH_2), 3.78 (3H, s, OMe), 3.08 (2H, d, J = 6.4 Hz, NCH_2CH═CH$_2$), 2.54 (2H, t, J = 7.8 Hz, NCH_2CH$_2$CH$_2$), 2.46 (2H, t, J = 7.8 Hz, CH_2CH═CH$_2$), 1.75 (2H, quin, J = 7.7 Hz, CH$_2$CH_2CH$_2$) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 135.8, 134.5, 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)

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

AUTHOR INFORMATION

Corresponding Author

*E-mail: m.wills@warwick.ac.uk.

ORCID

Martin Wills: 0000-0002-1646-2379

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank AstraZeneca and EPSRC for the generous funding of T.J.B. through an iCASE studentship. The X-ray diffraction instrument was obtained through the Science City Project with support from the AWM and was partly funded by the ERDF.

REFERENCES

(1) For reviews on hydrogen borrowing, see: (a) Bähn, S.; Imm, S.; Neubert, L.; Zhang, M.; Neumann, H.; Beller, M. *ChemCatChem* **2011**, *3*, 1853−1864. (b) Guillena, G.; Ramon, D. J.; Yus, M. *Chem. Rev.* **2010**, *110*, 1611−1641. (c) Watson, A. J. A.; Williams, J. M. J. *Science* **2010**, *329*, 635−636. (d) Nixon, T. D.; Whittlesey, M. K.; Williams, J. M. *Dalton Trans.* **2009**, 753−762.

(2) For hydrogen borrowing, see: (a) Enyong, A. B.; Moasser, B. *J. Org. Chem.* **2014**, *79*, 7553−7563. (b) Ma, W. M. J.; James, T. D.; Williams, J. M. J. *Org. Lett.* **2013**, *15*, 4850−4853. (c) Berliner, M. A.; Dubant, P. A.; Makowski, T.; Ng, K.; Sitter, B.; Wager, C.; Zhang, Y. *Org. Process Res. Dev.* **2011**, *15*, 1052−1062. (d) Bahn, S.; Imm, S.; Mevius, K.; Neubert, L.; Tillack, A.; Williams, J. M.; Beller, M. *Chem. - Eur. J.* **2010**, *16*, 3590−3593. (e) Yu, X.-J.; He, H.-Y.; Yang, L.; Fu, H.-Y.; Zheng, X.-L.; Chen, H.; Li, R.-X. *Catal. Commun.* **2017**, *95*, 54−57. (f) Feng, C.; Liu, Y.; Peng, S.; Shuai, Q.; Deng, G.; Li, C. *Org. Lett.* **2010**, *12*, 4888−4891. (g) Elangovan, S.; Neumann, J.; Sortais, J.-B.; Junge, K.; Darcel, C.; Beller, M. *Nat. Commun.* **2016**, *7*, 12641.

(3) For reviews on iron catalysis, see: (a) Gopalaiah, K. *Chem. Rev.* **2013**, *113*, 3248−3296. (b) Darwish, M.; Wills, M. *Catal. Sci. Technol.* **2012**, *2*, 243−255. (c) Bauer, I.; Knölker, H.-J. *Chem. Rev.* **2015**, *115*, 3170−3387. (d) Quintard, A.; Rodriguez, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 4044−4055.

(4) For oxidations, see: (a) Coleman, M. G.; Brown, A. N.; Bolton, B. A.; Guan, H. *Adv. Synth. Catal.* **2010**, *352*, 967−970. (b) Moyer, S. A.; Funk, T. W. *Tetrahedron Lett.* **2010**, *51*, 5430−5433. (c) Thorson, M. K.; Klinkel, K. L.; Wang, J.; Williams, T. J. *Eur. J. Inorg. Chem.* **2009**, *2009*, 295−302. (d) Johnson, T. C.; Clarkson, G. J.; Wills, M. *Organometallics* **2011**, *30*, 1859−1868. (e) Coleman, M. G.; Brown, A. N.; Bolton, B. A.; Guan, H. *Adv. Synth. Catal.* **2010**, *352*, 967−970. (f) Zhang, H. H.; Chen, D. Z.; Zhang, Y. H.; Zhang, G. Q.; Liu, J. B. *Dalton Transactions* **2010**, *39*, 1972−1978. (g) Thorson, M. K.; Klinkel, K. L.; Wang, J.; Williams, T. J. *Eur. J. Inorg. Chem.* **2009**, *2009*, 295−302.

(5) For C═N reduction, see: (a) Fleischer, S.; Werkmeister, S.; Zhou, S.; Junge, K.; Beller, M. *Chem. - Eur. J.* **2012**, *18*, 9005−9010. (b) Pagnoux-Ozherelyeva, A.; Pannetier, N.; Mbaye, M. D.; Gaillard, S.; Renaud, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 4976−4980. (c) Moulin, S.; Dentel, H.; Pagnoux-Ozherelyeva, A.; Gaillard, S.; Poater, A.; Cavallo, L.; Lohier, J.; Renaud, J. *Chem. - Eur. J.* **2013**, *19*, 17881−17890. (d) Merel, D. S.; Elie, M.; Lohier, J.; Gaillard, S.; Renaud, J. *ChemCatChem* **2013**, *5*, 2939−2945. (e) Thai, T.-T.; Mérel, D. S.; Poater, A.; Gaillard, S.; Renaud, J.-L. *Chem. - Eur. J.* **2015**, *21*, 7066−7070. (f) Hopmann, K. H. *Chem. - Eur. J.* **2015**, *21*, 10020−10030. (g) Lu, L.-Q.; Li, Y.; Junge, K.; Beller, M. *J. Am. Chem. Soc.* **2015**, *137*, 2763−2768.

(6) For C═O reduction, see: (a) Casey, C. P.; Guan, H. *J. Am. Chem. Soc.* **2009**, *131*, 2499−2507. (b) Berkessel, A.; Reichau, S.; von der Hoh, A.; Leconte, N.; Neudorfl, J. *Organometallics* **2011**, *30*, 3880−3887. (c) Hodgkinson, R. C.; Del Grosso, A.; Clarkson, G. J.; Wills, M. *Dalton Trans.* **2016**, *45*, 3992−4005. (d) Gajewski, P.; Renom-Carrasco, M.; Facchini, S. V.; Pignataro, L.; Lefort, L.; de Vries, J. G.; Ferraccioli, R.; Forni, A.; Piarulli, U.; Gennari, C. *Eur. J. Org. Chem.* **2015**, *2015*, 1887−1893. (e) Lu, X.; Zhang, Y. W.; Turner, N.; Zhang, M. T.; Li, T. L. *Org. Biomol. Chem.* **2014**, *12*, 4361−4371. (f) Natte, K.; Li, W.; Zhou, S.; Neumann, H.; Wu, X.-F. *Tetrahedron Lett.* **2015**, *56*, 1118−1121. (g) Ge, H.; Chen, X.; Yang, X. *Chem. - Eur. J.* **2017**, *23*, 8850−8856. (h) Rosas-Hernández, A.; Junge, H.; Beller, M.; Roemelt, M.; Francke, R. *Catal. Sci. Technol.* **2017**, *7*, 459−465.

(7) (a) Yan, T.; Feringa, B. L.; Barta, K. *Nat. Commun.* **2014**, *5*, 5602. (b) Yan, T.; Feringa, B. L.; Barta, K. *ACS Catal.* **2016**, *6*, 381−388.

(8) Rawlings, A. J.; Diorazio, L. J.; Wills, M. *Org. Lett.* **2015**, *17*, 1086−1089.

(9) Pan, H.; Ng, T. W.; Zhao, Y. *Chem. Commun.* **2015**, *51*, 11907−11910.

(10) (a) Emayavaramban, B.; Sen, M.; Sundararaju, B. *Org. Lett.* **2017**, *19*, 6−9. (b) Elangovan, S.; Quintero-Duque, S.; Dorcet, V.; Roisnel, T.; Norel, L.; Darcel, C.; Sortais, J.-B. *Organometallics* **2015**, *34*, 4521−4528. (c) Elangovan, S.; Sortais, J.-B.; Beller, M.; Darcel, C. *Angew. Chem., Int. Ed.* **2015**, *54*, 14483−14486. (d) Quintard, A.; Constantieux, T.; Rodriguez, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 12883−12887. (e) Yang, Q.; Zhang, N.; Liu, M.; Zhou, S. *Tetrahedron Lett.* **2017**, *58*, 2487−2489. (f) Gustafson, K. P. J.; Guomundsson, A.; Lewis, K.; Bäckvall, J.-E. *Chem. - Eur. J.* **2017**, *23*, 1048−1051. (g) El-Sepelgy, O.; Alandini, N.; Rueping, M. *Angew. Chem., Int. Ed.* **2016**, *55*, 13602−13605.

(11) Mastalir, M.; Stöger, B.; Pittenauer, E.; Puchberger, M.; Allmaier, G.; Kirchner, K. *Adv. Synth. Catal.* **2016**, *358*, 3824−3831.

(12) (a) Schrauzer, G. N. *J. Am. Chem. Soc.* **1959**, *81*, 5307−5310. (b) Knölker, H.-J.; Heber, J.; Mahler, C. H. *Synlett* **1992**, *1992*, 1002−1004. (c) Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 202−203.

(13) Knölker, H.-J.; Baum, E.; Goesmann, H.; Klauss, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 2064−2066.

(14) (a) Pearson, A. J.; Shively, R. J., Jr; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096−4104. (b) Pearson, A. J.; Shively, R. J., Jr *Organometallics* **1994**, *13*, 578−584.

(15) (a) Weymiens, W.; Hartl, F.; Lutz, M.; Slootweg, J. C.; Ehlers, A. W.; Mulder, J. R.; Lammertsma, K. *Eur. J. Org. Chem.* **2012**, *2012*, 6711−6721. (b) Lucht, B.; Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 4354−4365.

(16) (a) Luh, T.-Y. *Coord. Chem. Rev.* **1984**, *60*, 255−276. (b) Dasgupta, B.; Donaldson, W. A. *Tetrahedron Lett.* **1998**, *39*, 343−346. (c) Pearson, A. J.; Kwak, Y. *Tetrahedron Lett.* **2005**, *46*, 5417−5419. (d) Bailey, N. A.; Jassal, V. S.; Vefghi, R.; White, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2815−2822. (e) Knölker, H.-J.; Baum, E.; Heber, J. *Tetrahedron Lett.* **1995**, *36*, 7647−7650.

(17) Hollmann, D.; Jiao, H.; Spannenberg, A.; Bähn, S.; Tillack, A.; Parton, P.; Altink, R.; Beller, M. *Organometallics* **2009**, *28*, 473−479.

(18) Adam, R.; Cabrero-Antonino, J. R.; Junge, K.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2016**, *55*, 11049−11053.

(19) Chen, Z.; Zeng, H.; Girard, S. A.; Wang, F.; Li, C. -J.; Chen, N. *Angew. Chem., Int. Ed.* **2015**, *54*, 14487−14491.

(20) Satoh, T.; Osawa, A.; Ohbayashi, T.; Kondo, A. *Tetrahedron* **2006**, *62*, 7892−7901.

(21) Bartoszewicz, A.; Marcos, R.; Sahoo, S.; Inge, A. K.; Zou, X.; Martin-Matute, B. *Chem. - Eur. J.* **2012**, *18*, 14510−14519.

(22) Garcia, P.; Lau, Y. Y.; Perry, M. R.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2013**, *52*, 9144−9148.

(23) Maytum, H. C.; Francos, J.; Whatrup, D. J.; Williams, J. M. J. *Chem. - Asian J.* **2010**, *5*, 538−542.

(24) Vantourout, J. C.; Law, R. P.; Isidro-Llobet, A.; Atkinson, S. J.; Watson, A. J. B. *J. Org. Chem.* **2016**, *81*, 3942−3950.

(25) Wu, K.; He, W.; Sun, C.; Yu, Z. *Tetrahedron* **2016**, *72*, 8516−8521.

(26) Abdel-Magid, A.; Carson, K.; Harris, B.; Maryanoff, C.; Shah, R. *J. Org. Chem.* **1996**, *61*, 3849−3862.

(27) Joe, C. L.; Doyle, A. G. *Angew. Chem., Int. Ed.* **2016**, *55*, 4040−4043.

(28) Musacchio, A. J.; Nguyen, L. Q.; Beard, G. H.; Knowles, R. R. *J. Am. Chem. Soc.* **2014**, *136*, 12217−12220.

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503

(29) Barluenga, J.; Sanz, R.; Fañanás, F. J. *J. Org. Chem.* **1997**, *62*, 5953−5958.
(30) Tan, P. W.; Haughey, M.; Dixon, D. J. *Chem. Commun.* **2015**, *51*, 4406−4409.

DOI: 10.1021/acs.joc.7b01990
J. Org. Chem. 2017, 82, 10489−10503