4-18-2018

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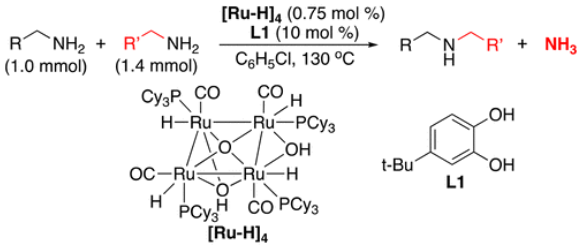
Abstract



The catalytic system generated in situ from the tetranuclear Ru–H complex with a catechol ligand (**1**/**L1**) was found to be effective for the direct deaminative coupling of two primary amines to form secondary amines. The catalyst **1**/**L1** was highly chemoselective for promoting the coupling of two different primary amines to afford unsymmetric secondary amines. The analogous coupling of aniline with primary amines formed aryl-substituted secondary amines. The treatment of aniline-d_7 with 4-methoxybenzylamine led to the coupling product with significant deuterium incorporation on CH_2 (18% D). The most pronounced carbon isotope effect was observed on the α-carbon of the product isolated from the coupling reaction of 4-methoxybenzylamine (C(1) = 1.015(2)). A Hammett plot was constructed from measuring the rates of the coupling reaction of 4-methoxyaniline with a series of *para*-substituted benzylamines 4-X-$C_6H_4CH_2NH_2$ (X = OMe, Me, H, F, CF_3) (ρ = −0.79 ± 0.1). A plausible mechanistic scheme has been proposed for the coupling reaction on the basis of these results. The catalytic coupling method provides an operationally simple and chemoselective synthesis of secondary amine products without using any reactive reagents or forming wasteful byproducts.

Introduction

Designing catalytic C–N bond cleavage methods has attracted considerable research efforts in the field of homogeneous catalysis since such methods are of fundamental importance in a variety of industrial chemical syntheses as well as in biochemical processes of nitrogen compounds.(1) Even though catalytic C–N bond-cleavage methods have been recognized as an essential protocol for harnessing nitrogen compounds from both petroleum and biomass feedstocks, these catalytic methods have long been hampered by a relatively strong C–N bond strength and catalyst poisoning by the nitrogen substrates.(2) In a pioneering report, Fujiwara and co-workers first demonstrated the direct coupling of olefins with arylamines, in which arene sp^2 C–N bond cleavage was promoted by a stoichiometric amount of Pd(II) salts.(3) More recently, Kakiuchi and co-workers devised a ruthenium-catalyzed C–C coupling reaction of arylamines with organoboranes by exploiting a directing group assisted sp^2 C–N bond activation strategy.(4) A few remarkably efficient amide-to-ester conversion methods via amide C–N bond cleavage have been achieved by using Ni catalysts.(5) A number of Pd-catalyzed C–N cleavage methods have also been developed, including intramolecular Heck-type coupling reactions(6) and allylamine coupling reactions.(7) Selective catalytic C–C coupling methods via sp^3 C–N bond activation of allyl- and benzylic amines have been achieved.(8) Other notable examples of catalytic C–N bond cleavage reactions include oxidative C–H coupling reaction of amides with alkynes(9) and the Milstein group's report on the Ru-catalyzed hydrogenolysis of amides.(10) Catalytic C–N cleavage methods have also been successfully utilized for constructing nitrogen heterocycles.(11)

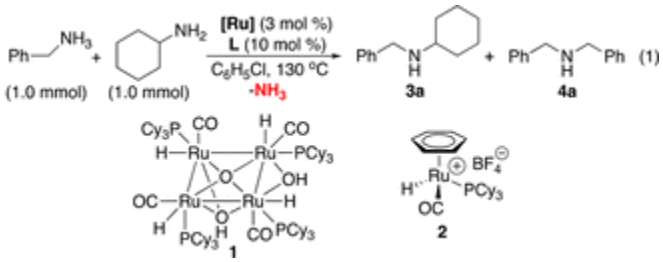
Chemoselective synthesis of amines has long been a pertinent issue in organic synthesis. Much research has been devoted to the development of new catalytic synthesis of amines, and transition-metal-catalyzed dehydrogenative coupling strategies have emerged as highly effective ways to activate amines and alcohols.(12) In particular, late-transition-metal catalysts have been successfully employed to promote amine-to-alcohol coupling reactions via a hydrogen-borrowing strategy to synthesize unsymmetric secondary amines.(13) Traditionally, the reductive amination methods have also been commonly used for the synthesis of secondary amines.(14) Since these methods often require stoichiometric reducing agents and/or additives,

which result in the formation of copious amounts of salt byproducts, catalytic deaminative coupling methods have been recognized as an alternative strategy for the synthesis of secondary amines. Beller and co-workers reported a highly selective dealkylation of amines by using Shvo catalyst.(15) The Zhang group also devised the synthesis of unsymmetric secondary amines from the coupling of aniline with primary amines by using soluble Co catalysts.(16) From both economic and environmental perspectives, the development of chemoselective catalytic coupling methods via C–N bond cleavage of amines and related nitrogen compounds still remains an essential goal in the fields of homogeneous catalysis and organic synthesis.

We previously disclosed the synthesis of unsymmetrical ethers from the dehydrative coupling reactions of alcohols and aldehydes that are catalyzed by a well-defined cationic ruthenium–hydride complex.(17) Since these coupling reactions are driven by the formation of water, we reasoned that the analogous deaminative coupling reactions of amines could be achieved where the formation of ammonia would serve as the driving force for such coupling reactions. Herein, we report the synthesis of symmetric and unsymmetric secondary amines from the catalytic deaminative coupling of primary amines. The catalytic method exhibits high chemoselectivity as well as a broad substrate scope in forming secondary amines, while generating ammonia as the only byproduct.

Results and Discussion

We previously devised a catalytic system composed of the cationic Ru–H complex and a phenol ligand, which was found to exhibit high catalytic activity for the hydrogenolysis of carbonyl compounds to yield the corresponding aliphatic products.(18) By adopting a similar ligand-controlled catalysis strategy, we initially screened soluble Ru catalysts with phenol and related oxygen and nitrogen ligands to promote the C–N bond activation reactions. We have chosen the coupling reaction of benzylamine with cyclohexylamine as a test case to screen both Ru catalysts and the ligands (eq 1).



Among the initially screened Ru catalysts, both the tetranuclear Ru–H complex $[(PCy_3)(CO)RuH]_4(O)(OH)_2$ (**1**) and the cationic complex $[(C_6H_6)(PCy_3)(CO)RuH]^+BF_4^-$ (**2**) with a catechol ligand exhibited the most promising activity for the coupling reaction, as analyzed by both GC and NMR spectroscopic methods (Table1). Among the screened oxygen and nitrogen ligands, 4-(1,1-dimethylethyl)-1,2-benzenediol (**L1**) was found to give the highest activity and selectivity for these Ru catalysts in giving the unsymmetric amine product **3a** over the symmetric one **4a** (entries 9 and 13). After further ligand screening and optimization studies, we have chosen the standard conditions for the 1.0 mmol scale coupling reaction as **1** (0.75 mol %, 3 Ru mol %)/**L1** (10 mol %) in chlorobenzene (2 mL) at 130 °C (Tables S1 and S2, Supporting Information (SI)). A 3:1 ratio of catechol ligand to Ru catalyst was found to be the optimum for the catalytic activity, as a lower ratio (2:1) typically gave a lower product yield. Nonprotic polar solvents such as chlorobenzene and dioxane afforded the highest product yields and selectivity, and the for the sake of consistency, we have chosen chlorobenzene as the solvent for all coupling reactions. The formation of the byproduct ammonia was detected in the crude mixture as analyzed by both NMR and GC–MS methods.

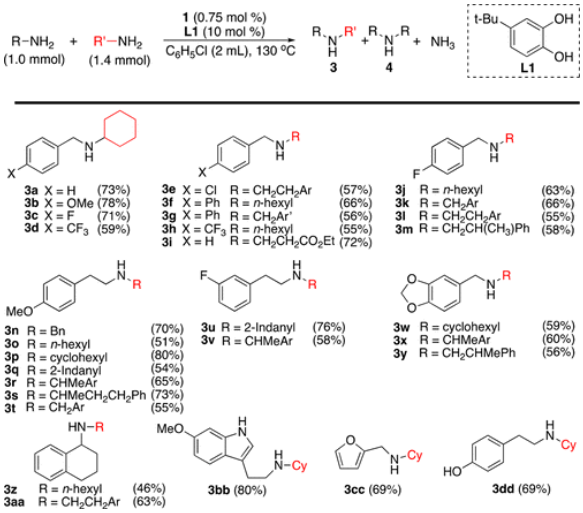
Table 1. Catalyst and Ligand Screening Study[a]

entry	catalyst	ligand[b]	yield (**3a**/**4a**)[c]
1	**1**	**none**	**27:7**
2	**1**	**phenol**	**52:16**
3	**1**	**catechol**	**68:20**
4	**1**	**aniline**	**19:6**
5	**1**	**2-NH_2PhCOMe**	**28:16**
6	**1**	**PhCONH_2**	**trace**
7	**1**	**1,1′-BINOL**	**trace**
8	**1**	**1,2-$C_6H_4(NH_2)_2$**	**27:12**
9	**1**	**L1**	**74:22**
10	**1**	**L2**	**67:6**
11	**1**	**L3**	**62:13**
12	**1**/HBF_4·OEt_2	**L1**	**65:1**
13	**2**	**L1**	**70:16**
14	**2**/HBF_4·OEt_2	**L1**	**60:5**
15	**[Ru(COD)Cl_2]$_x$**	**L1**	**14:7**
16	**$RuCl_3$·3H_2O**	**L1**	**0**
17	**(PPh_3)$_3$(CO)RuH_2**	**L1**	**0**
18	**[(*p*-cymene)$RuCl_2$]$_2$**	**L1**	**<1**
19	**RuHCl(CO)(PCy_3)$_2$**	**L1**	**70:15**
20	**[(PCy_3)$_2$(CO)(CH_3CN)$_2$RuH]BF_4**	**L1**	**0**

[a]Reaction conditions: benzylamine (0.5 mmol), cyclohexylamine (0.7 mmol), catalyst (3 mol %), ligand (10 mol %), chlorobenzene (2 mL), 130 °C, 16 h.
[b]See the Supporting Information for extensive list and structure of ligands.
[c]The product yield was determined by ^{1}H NMR using C_6Me_6 as the internal standard.

We explored the substrate scope of the deaminative coupling reaction by using the optimized catalyst system **1**/**L1** under the standard conditions (Table2). The coupling of benzylic amines with a variety of aliphatic and benzylic primary amines selectively formed the unsymmetric secondary amine products **3a**–**m**. An excess amount (1.4 equiv) of the second amine (usually more electron rich amine) was found to improve the product selectivity for unsymmetric amines **3**. Typically, <20% of the symmetric amine products was formed in the crude mixture in most cases, and analytically pure unsymmetric amine products were readily isolated after silica gel column chromatographic separation. The major byproducts, symmetric amine products **4**, were detected by TLC and GC/MS but were not isolated in these cases. The coupling of phenethyl amines with both benzylic and aliphatic amines also gave the selective formation of **3n**–**v**. Indole-, furanyl-, and phenol-substituted amines with cyclohexylamine selectively yielded the unsymmetric secondary amine products **3bb**–**dd**. For these cases, the coupling of benzylic and other aryl-substituted amines with electron-rich amines tends to favor the formation of unsymmetrical amines over the symmetrical ones. In contrast, the coupling of two different aliphatic amines with a sterically nondemanding group yielded a mixture of symmetric and unsymmetric amines. The coupling reaction with secondary and tertiary amines was found to be very sluggish and unselective, resulting in a complex mixture of products. The catalytic coupling method is operationally simple and exhibits high chemoselectivity toward the formation of unsymmetric secondary amines without resorting to employing any reactive reagents.

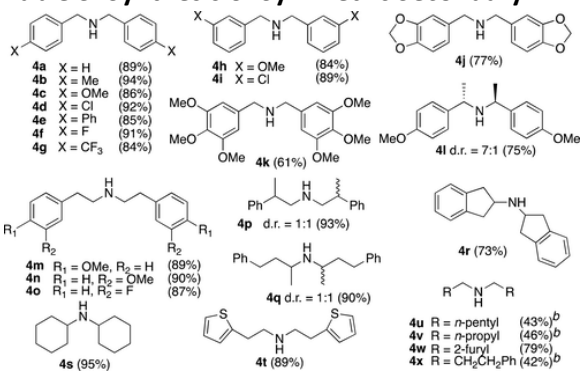
Table 2. Synthesis of Unsymmetric Secondary Amines from the Deaminative Coupling of Primary Amines[a]



[a]Reaction conditions: R-NH_2 (1.0 mmol), R'-NH_2 (1.4 mmol), **1** (0.75 mol %), **L1** (10 mol %), chlorobenzene (2 mL), 130 °C, 16 h. Ar = C_6H_4-4-OMe.

We next explored the substrate scope for the formation of symmetric secondary amines by using the catalyst system **1**/**L1** (Table3). Benzylic primary amines reacted smoothly to afford the secondary amine products **4a**–**k** without the formation of tertiary amines or other side products. The coupling of both phenethyl and indanyl amines formed the corresponding secondary amine products **4m**–**r**. While cyclohexyl- and thiophene-substituted amines predictively yielded the corresponding secondary amine products **4s** and **4t**, respectively, a mixture of secondary and tertiary amines was formed for sterically nondemanding aliphatic amines **4u**–**x**. Generally, the coupling of chiral primary amines led to a 1:1 diastereomeric mixture of products as illustrated by the formation of **4p**-**4q**, but interestingly, a diastereoselective formation of the product **4l** was obtained in the case of (*R*)-4-methoxy-α-methylbenzenemethaneamine (dr = 7:1). The catalytic method delivers a operationally simple synthesis of symmetric secondary amines from readily available primary amines without using any reactive reagents via a deaminative coupling strategy.(14,16)

Table 3. Synthesis of Symmetric Secondary Amines[a]

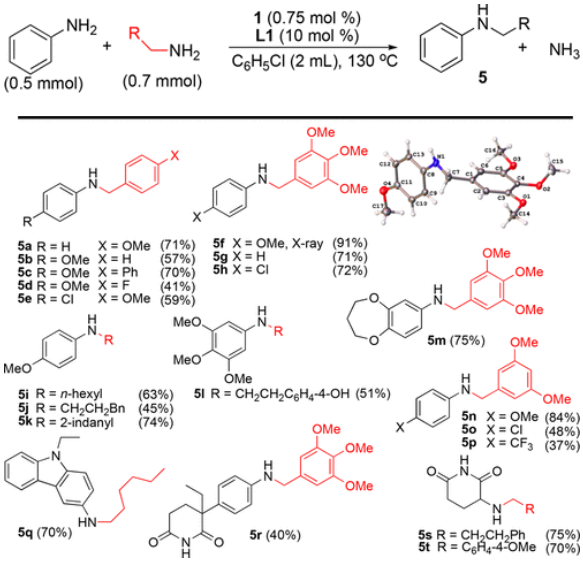


[a]Reaction conditions: amine (1.0 mmol), **1** (0.75 mol %), **L1** (10 mol %), chlorobenzene (2 mL), 130 °C, 16 h.
[b]40–50% of tertiary amines formed.

To further illustrate the synthetic versatility of the catalytic coupling method, we next explored the coupling reaction of aniline derivatives with primary amine substrates of biological relevance (Table4). The coupling of *para*-substituted anilines with benzylic amines led to the selective formation of unsymmetric amine products **5a**–**e** without any significant amount of the symmetric amine products. Similarly, the reaction of *para*-

substituted anilines with 3,4,5-trimethoxybenzylamine afforded the coupling products **5f**–**h** in high yields. Single crystals of **5f** were obtained by slow evaporation in CH_2Cl_2/hexanes, and its structure was determined by X-ray crystallography.

Table 4. Synthesis of Unsymmetric Secondary Amines from the Deaminative Coupling of Anilines with Amines[a]

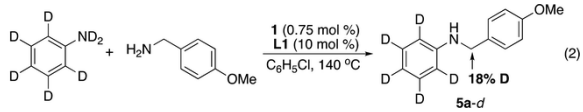


[a]Reaction conditions: aniline (0.5 mmol), R-NH_2 (0.7 mmol), **1** (0.75 mol %), **L1** (10 mol %), chlorobenzene (2 mL), 140 °C, 20 h.

The treatment of 3-amino-9-ethylcarbazole with *n*-hexylamine predictively yielded the product **5q**. The coupling of (*R*)-(+)-aminoglutathimide with 3,4,5-trimethoxybenzylamine led to the optically active coupling product (*R*)-**5r** without any detectable racemization. The coupling of L-glutamine with 3-phenylpropylamine and 4-methoxybenzylamine led to the cyclized amine products **5s** and **5t** in 75% and 70% yields, respectively. The formation of cyclized products **5s** and **5t** can be rationalized by initial dehydrative cyclization of glutamine followed by the deaminative coupling with the primary amine substrates. The optimized standard conditions were used for all of these coupling reactions as described in Tables2–4, with slight modifications on the reaction time and temperature.

We monitored the amine-coupling reaction by NMR spectroscopy to probe the overall reaction profile. In a J-Young NMR tube equipped with Teflon stopcock, 4-methoxybenzylamine (34 mg, 0.25 mmol) and the catalyst system **1** (3 mg, 0.75 mol %)/**L1** (4 mg, 10 mol %) were dissolved in toluene-d_8 (0.5 mL). The tube was immersed in an oil bath at 130 °C, and the reaction progress was monitored by ^{1}H NMR in 20 min intervals.

As shown in Figure 1, the secondary amine product **4c** was formed steadily at the expense of the benzylamine substrate. Initially, the formation of a minor product was also observed (~10%), which gradually disappeared within 200 min of the reaction time. The structure of minor product was subsequently determined to be ArCH═NCH_2Ar (Ar = 4-methoxyphenyl) by both NMR and GC/MS, as obtained from a separate preparatory-scale experiment.



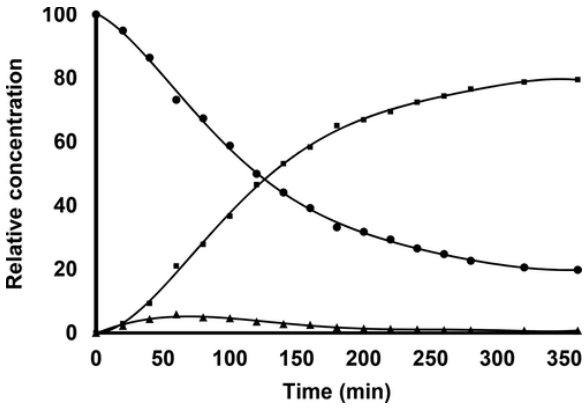
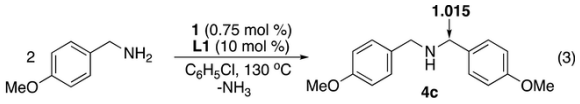


Figure 1. Reaction profile for the coupling of 4-methoxybenzylamine: 4-methoxybenzylamine (●), **4c** (■), and ArCH=NCH$_2$Ar (▲).

Next, we examined the deuterium-labeling pattern on the product from the reaction of aniline-d_7 with 4-methoxybenzylamine (eq 2). A reaction tube consisting of aniline-d_7 (50 mg, 0.5 mmol) with 4-methoxybenzylamine (69 mg, 0.5 mmol) in the presence of **1** (7 mg, 0.75 mol %)/**L1** (8 mg, 10 mol %) in chlorobenzene (1 mL) was heated in an oil bath at 140 °C for 20 h. The product **5a**-*d* was isolated by silica gel column chromatography, and its deuterium content was analyzed by ^{1}H and ^{2}H NMR (Figure S1). A significant amount of deuterium was incorporated into the CH$_2$ position of **5a**-*d* (18% D) without any deuterium exchange on the arene C–H positions. In a control experiment, the treatment of the isolated product **5a** with aniline-d_7 in the presence of **1** (0.75 mol %)/**L1** (10 mol %) did not lead to any significant deuterium exchange into the benzyl position of **5a** under similar reaction conditions after 20 h. A significant amount of the deuterium incorporation suggests that the imine-to-amine hydrogenation–dehydrogenation process might have occurred during the product formation of **5a**.



To discern the rate-limiting step of the catalytic reaction, we employed Singleton's high-precision NMR technique to measure the carbon isotope effect for the coupling reaction (eq 3).(19) The reaction tube of 4-methoxybenzylamine (2 mmol) and **1** (0.75 mol %)/**L1** (10 mol %) in chlorobenzene (4 mL) was heated at 130 °C for 16 h for high conversion and for 2–3 h for low conversion cases. The product **4c** was isolated by column chromatography on silica gel and was analyzed by ^{13}C NMR. The most pronounced carbon isotope effect was observed on the α-carbon of the product **4c** when the ^{13}C ratio of the product at three high conversions (86–89%) was compared with the sample obtained at low conversions (12–15%) [(average of ^{13}C at 87% conversion)/(average of ^{13}C at 13% conversion) at C(1) = 1.015(2)] (Table S2).

The significant carbon isotope effect on the α-CH$_2$ carbon is consistent with the C–N bond cleavage turnover-limiting step. In support of this notion, Singleton and co-workers showed that the observation of the most pronounced carbon isotope effect has been a definitive tool for establishing the rate-limiting step for both C–C and C–O bond-forming reactions.(19c) While C–N bond cleavage has been found to be the turnover-limiting step for a number of chemical and biochemical coupling reactions,(20) very few carbon kinetic isotope effect measurements have been reported for the catalytic coupling reactions of nitrogen compounds. Eubanks and co-workers measured pronounced carbon isotope effects in the Hofmann elimination reaction of *para*-substituted (2-phenylethyl)trimethylammonium bromides, which indicated an E2 mechanism involving C–N bond cleavage step.(21) In a urease-catalyzed hydrolysis of hydroxyurea, Cleland and co-workers observed a significant carbon

isotope effect on the carbonyl carbon but not on the nitrogen atom, which argues for the formation of a common intermediate prior to the C–N bond cleavage step.(22)

The Hammett plot was constructed from measuring the rate of the coupling reaction of a series of *para*-substituted benzylamines 4-X-$C_6H_4CH_2NH_2$ (X = OMe, Me, H, Cl, F, CF_3) in the presence of **1** (0.75 mol %)/**L1** (10 mol %) in toluene-d_8 (Figure 2). The rate of each substrate was obtained by measuring the appearance of the product peaks, which were normalized against an internal standard (C_6Me_6) as analyzed by ^{1}H NMR. The k_{obs} for each catalytic run was determined from a first order plot of ln[(benzylamine)$_t$/(benzylamine)$_0$] vs time. The Hammett plot of log(k_X/k_H) vs σ_p showed a linearly correlated pattern with $\rho = -0.79 \pm 0.1$. A relatively high negative slope suggests a significant cationic character buildup on the amine substrate during the coupling reaction.

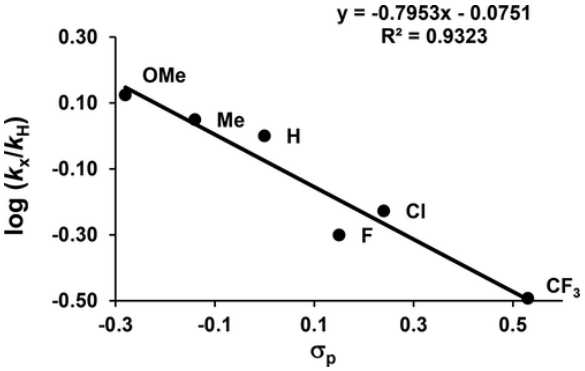
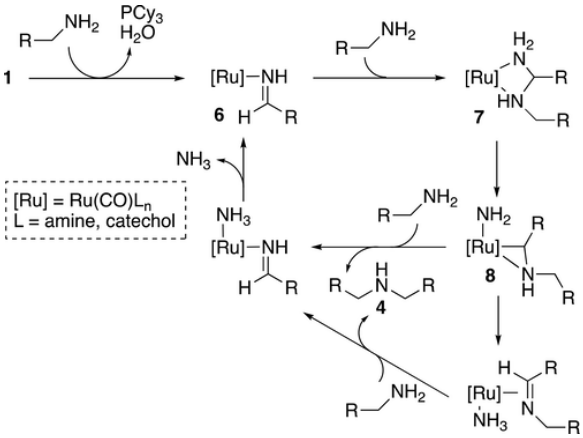


Figure 2. Hammett plot from the coupling of 4-methoxyaniline with 4-X-$C_6H_4CH_2NH_2$ (X = OMe, Me, H, Cl, F, CF_3).

We present a plausible mechanistic hypothesis for the deaminative coupling reaction on the basis of these results (Scheme 1). In light of the observation of imine product ArCH═NCH_2Ar, we propose the formation of a Ru–imine species **6** as a catalytically active species, which would be initially generated from the dehydrogenation of amine substrate.(23) In support of this notion, some oxidative C–N bond cleavage reactions are known to proceed via the formation of an imine intermediate.(24) The coordination of imine substrate to the Ru center would increase the electrophilic nature of the imine carbon, and the nucleophilic addition of the second amine substrate would proceed to form the Ru–1,1-diamine species **7**. Many structurally similar transition metal–urea complexes have been synthesized, and their bonding and reactivity patterns have been well established.(25) The observation of carbon isotope effect provides an experimental support for the rate-limiting C–N cleavage step in forming the Ru-aminoalkyl species **8**. The dehydrogenation of second amine substrate in conjunction with the hydrogen transfer would form the coupling product **4** with the regeneration of imine species **6**. Both the detection of imine product and the selective deuterium incorporation on the α-CH_2 of **5a** suggest that the dehydrogenation and hydrogen transfer steps are likely facile and reversible under the reaction conditions.



Scheme 1. Proposed Mechanism of the Deaminative Coupling of Primary Amines

Conclusion

In conclusion, we successfully devised a highly chemoselective synthesis of secondary amines from the deaminative coupling of primary amines. The catechol ligand promoted ruthenium catalytic system was found to exhibit a uniquely high activity and selectivity in forming both symmetric and unsymmetric secondary amines. The catalytic method has a number of salient features that it is operationally simple, exhibits a broad substrate scope, tolerates common organic functional groups, and forms ammonia as the sole byproduct without employing any reactive reagents. The kinetic and spectroscopic studies thus far indicate that the coupling reaction proceeds via the formation of imine species with the turnover limiting C–N bond cleavage step. At this time, we have not been able to ascertain the exact role of catechol ligand on promoting the Ru catalyst, and we are currently pursuing the detection and/or the isolation of catalytically relevant Ru–catechol species.(26) We are also devoting our efforts to extend synthetic utility of the catalytic method for the synthesis of nitrogen heterocycles of biological importance.

Experimental Section

General Information

All operations were carried out in a nitrogen-filled glovebox or by using standard high vacuum and Schlenk techniques unless otherwise noted. All solvents used were freshly distilled over appropriate drying reagents. Chlorobenzene was distilled from purple solutions of sodium and benzophenone, and hexanes was dried over calcium hydride prior to use. All organic substrates were received from commercial sources and were used without further purification. The ^{1}H, ^{2}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian 400 MHz FT-NMR spectrometer, and the data are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent, coupling constant(s) in Hz, integration. Mass spectra were recorded from an Agilent 6850 GC–MS spectrometer by using a HP-5 (5% phenylmethylpolysiloxane) column (30 m, 0.32 mm, 0.25 μm). High-resolution mass spectra were obtained at the Mass Spectrometry/ICP Lab, Department of Chemistry and Biochemistry, University of Wisconsin—Milwaukee, Milwaukee, WI. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

General Procedure for the Catalytic Synthesis of Secondary Amines

In a glovebox, complex **1** (13 mg, 0.75 mol %) and 4-(1,1-dimethylethyl)-1,2-benzenediol (**L1**), (16 mg, 10 mol %) were dissolved in chlorobenzene (1 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5–10 min until the solution turned to a reddish green color. In an alternative procedure, complex **2** (17 mg, 3 mol %) and **L1** (16 mg, 10 mol %) were dissolved in anhydrous 1,4-dioxane (1 mL). Amine substrate (1.0 and 1.4 mmol) in chlorobenzene (1 mL) was added to the

reaction tube. After the tube was sealed, it was brought out of the glovebox and stirred in an oil bath maintained at 130–140 °C for 16–20 h. The reaction tube was taken out of the oil bath and was cooled to room temperature. After the tube was opened to air, the solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC–MS. Analytically pure product was isolated by a simple column chromatography on silica gel (280–400 mesh, hexanes/EtOAc or hexanes/EtOAc/methanol).

Synthesis of Benzylcyclohexylamine (3a)

In a glovebox, complex **1** (13 mg, 0.75 mol %) and **L1** (16 mg, 10 mol %) were dissolved in chlorobenzene (1 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5–10 min until the solution turned a reddish green color. Benzylamine (1.0 mmol) and cyclohexylamine (1.4 mmol) were dissolved in chlorobenzene (1 mL), and the solution was added to the reaction tube. The tube was brought out of the glovebox and was stirred in an oil bath maintained at 130 °C for 16 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. The resulting solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC–MS. Analytically pure product **3a** was isolated by a simple column chromatography on silica gel (280–400 mesh, *n*-hexane/EtOAc).

Synthesis of Dibenzylamine (4a)

In a glovebox, complex **1** (13 mg, 0.75 mol %) and **L1** (16 mg, 10 mol %) were dissolved in chlorobenzene (1 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5–10 min until the solution turned a reddish green color. Benzylamine (107 mg, 1.0 mmol) in chlorobenzene (1 mL) was added to the reaction mixture. After the tube was sealed, it was brought out of the glovebox and was stirred in an oil bath maintained at 130 °C for 16 h. The reaction tube was taken out of the oil bath and was cooled to room temperature. The resulting solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC–MS. Analytically pure product **4a** was isolated by a simple column chromatography on silica gel (280–400 mesh, *n*-hexane/EtOAc).

Catalyst and Ligand Screening Study

In a glovebox, a Ru catalyst (3 mol % Ru atom) and a ligand (10 mol %) were dissolved in a solvent (1 mL) in a 25 mL Schlenk tube equipped with a Teflon screw cap stopcock and a magnetic stirring bar. After the solution was stirred for 5–10 min, benzylamine (54 mg, 0.5 mmol) and cyclohexylamine (69 mg, 0.7 mmol) were dissolved in chlorobenzene (1 mL), and the solution was added to the reaction tube. The tube was brought out of the glovebox and was stirred in an oil bath at 130 °C for 16 h. The product yield was determined by ^{1}H NMR by using hexamethylbenzene as an internal standard. The results are summarized in Tables S1 and S2.

N-Cyclohexylbenzenemethanamine (3a)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), benzylamine (107 mg, 1.0 mmol) and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3a** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 138 mg, 73%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 4H), 7.28–7.20 (m, 1H), 3.81 (s, 2H), 2.49 (tt, *J* = 10.3, 3.7 Hz, 1H), 1.96–1.88 (m, 2H), 1.78–1.70 (m, 2H), 1.65–1.58 (m, 1H), 1.32–1.07 (m, 5H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.8, 128.3, 128.0, 126.7, 56.1, 51.0, 33.5, 26.1, 25.0 ppm; GC–MS for $C_{13}H_{19}N$, *m*/*z* = 189 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(27)

N-Cyclohexyl-4-methoxybenzenemethanamine (3b)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzylamine (137 mg, 1.0 mmol), and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3b** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 171 mg, 78%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 6.88–6.83

(m, 2H), 3.79 (s, 3H), 3.74 (s, 2H), 2.47 (tt, *J* = 10.4, 3.7 Hz, 1H), 1.96–1.86 (m, 2H), 1.77–1.68 (m, 2H), 1.65–1.56 (m, 1H), 1.31 (br s, 1H), 1.30–1.05 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4, 133.0, 129.2, 113.7, 56.0, 55.2, 50.4, 33.5, 26.1, 25.0 ppm; GC–MS for $C_{14}H_{21}NO$, *m*/*z* = 219 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(28)

N-Cyclohexyl-4-fluorobenzenemethanamine (3c)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol), and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3c** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 147 mg, 71%). TLC: R_f = 0.4 (20% EtOAc in hexanes). Data for **3c**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (m, 2H), 7.02–6.95 (m, 2H), 3.76 (s, 2H), 2.45 (tt, *J* = 10.3, 3.8 Hz, 1H), 1.94–1.85 (m, 2H), 1.77–1.68 (m, 2H), 1.64–1.56 (m, 1H), 1.37 (br s, 1H), 1.32–1.04 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J_{CF} = 244.2 Hz), 136.6 (d, J_{CF} = 3.1 Hz), 129.5 (d, J_{CF} = 7.9 Hz), 115.1 (d, J_{CF} = 21.2 Hz), 56.1, 50.2, 33.5, 26.1, 24.9 ppm; GC–MS for $C_{13}H_{18}FN$, *m*/*z* = 207 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(29)

N-Cyclohexyl-4-(trifluoromethyl)benzenemethanamine (3d)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-(trifluoromethyl)benzylamine (175 mg, 1.0 mmol), and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3d** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 152 mg, 59%). TLC: R_f = 0.4 (20% EtOAc in hexanes). Data for **3d**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.53 (m, 2H), 7.45–7.41 (m, 2H), 3.86 (s, 2H), 2.46 (tt, *J* = 10.3, 3.7 Hz, 1H), 1.95–1.86 (m, 2H), 1.77–1.69 (m, 2H), 1.64–1.56 (m, 1H), 1.30–1.05 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 129.0 (q, J_{CF} = 32.2 Hz), 128.2, 125.2 (q, J_{CF} = 3.8 Hz), 124.3 (q, J_{CF} = 271.9 Hz), 56.2, 50.4, 33.5, 26.0, 24.9 ppm; GC–MS for $C_{14}H_{18}F_3N$, *m*/*z* = 257 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(30)

N-(4-Chlorobenzyl)-2-(4-methoxyphenyl)ethanamine (3e)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-chlorobenzylamine (141 mg, 1.0 mmol), and 4-methoxybenzeneethanamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3e** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 158 mg, 57%). TLC: R_f = 0.4 (20% EtOAc in hexanes). Data for **3e**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.24–7.19 (m, 2H), 7.15–7.09 (m, 2H), 6.87–6.82 (m, 2H), 3.79 (s, 3H), 3.76 (s, 2H), 2.87–2.82 (m, 2H), 2.80–2.74 (m, 2H), 1.73 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 138.6, 132.5, 131.7, 129.5, 129.3, 128.4, 113.8, 55.1, 53.0, 50.5, 35.2 ppm; GC–MS for $C_{16}H_{18}ClNO$, *m*/*z* = 275 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{18}ClNOH$ 276.1150, found 276.1122.

N-(Biphenyl-4-ylmethyl)hexan-1-amine (3f)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-pheylbenzylamine (183 mg, 1.0 mmol), and 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3f** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 176 mg, 66%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3f**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.61–7.54 (m, 4H), 7.46–7.37 (m, 4H), 7.36–7.31 (m, 1H), 3.83 (s, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 1.58–1.50 (m, 2H), 1.36–1.26 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.0, 139.8, 139.6, 128.7, 128.5, 128.4, 127.1, 127.0, 53.7, 49.6, 31.8, 30.1, 27.0, 22.6, 14.1 ppm; GC–MS for $C_{19}H_{25}N$, *m*/*z* = 267 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{25}NH$ 268.2060, found 268.2061.

Benzo[*d*][1,3]dioxol-5-yl-*N*-(biphenyl-4-ylmethyl)methanamine (3g)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-phenylbenzylamine (183 mg, 1.0 mmol), and 1,3-benzodioxol-5-ylmethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3g** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc =

100:1–10:1; 178 mg, 56%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.55 (m, 4H), 7.47–7.39 (m, 4H), 7.37–7.32 (m, 1H), 6.90–6.88 (m, 1H), 6.82–6.76 (m, 2H), 5.95 (s, 2H), 3.84 (s, 2H), 3.75 (s, 2H), 1.67 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.7, 146.5, 140.9, 139.9, 139.3, 134.2, 128.7, 128.6, 127.1, 127.1, 127.0, 121.2, 108.7, 108.0, 100.9, 52.9, 52.6 ppm; GC–MS for $C_{21}H_{19}NO_2$, *m*/*z* = 317 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{19}NO_2H$ 318.1489, found 318.1486.

N-(4-(Trifluoromethyl)benzyl)hexan-1-amine (3h)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-(trifluoromethyl)benzylamine (175 mg, 1.0 mmol), and 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3h** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 142 mg, 55%). TLC: R_f = 0.4 (20% EtOAc in hexanes). Data for **3h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 3.84 (s, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.58 (br s, 1H), 1.55–1.46 (m, 2H), 1.37–1.22 (m, 6H), 0.91–0.84 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.6, 129.1 (q, J_{CF} = 32.3 Hz), 128.3, 125.3 (q, J_{CF} = 3.8 Hz), 124.2 (q, J_{CF} = 272.0 Hz), 53.5, 49.5, 31.7, 30.0, 27.0, 22.6, 14.0; GC–MS for $C_{14}H_{20}F_3N$, *m*/*z* = 259 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{20}F_3NH$ 260.1621, found 260.1627.

Ethyl 3-(Benzylamino)propanoate (3i)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), β-alanine ethyl ester (117 mg, 1.0 mmol), and benzylamine (150 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3i** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 149 mg, 72%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.19 (m, 5H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 2H), 2.87 (t, *J* = 6.5 Hz, 2H), 2.50 (t, *J* = 6.5 Hz, 2H), 1.82 (brs, 1H), 1.23 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.7, 140.0, 128.3, 128.0, 126.8, 60.3, 53.7, 44.4, 34.7, 14.1 ppm; GC–MS for $C_{12}H_{17}NO_2$, *m*/*z* = 207 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(31)

4-Fluoro-*N*-hexylbenzenemethanamine (3j)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol), and 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3j** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 132 mg, 63%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 7.02–6.95 (m, 2H), 3.74 (s, 2H), 2.59 (t, *J* = 7.3, 2H), 1.53–1.44 (m, 2H), 1.35–1.21 (m, 6H), 0.90–0.84 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8 (d, J_{CF} = 244.6 Hz), 136.2 (d, J_{CF} = 3.1 Hz), 129.6 (d, J_{CF} = 7.9 Hz), 115.0 (d, J_{CF} = 21.2 Hz), 53.3, 49.4, 31.7, 30.0, 27.0, 22.6, 14.0 ppm; GC–MS for $C_{13}H_{20}FN$, *m*/*z* = 209 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{20}FNH$ 210.1653, found 210.1654.

N-(4-Fluorobenzyl)-N-(4-methoxybenzyl)amine (3k)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol), and 4-methoxybenzylamine (192 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3k** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 162 mg, 66%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.06–6.99 (m, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 2H), 3.74 (s, 2H), 1.78 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8 (d, J_{CF} = 244.6 Hz), 158.5, 135.9 (d, J_{CF} = 3.1 Hz), 132.1, 129.6 (d, J_{CF} = 7.9 Hz), 129.2, 115.0 (d, J_{CF} = 21.2 Hz), 113.7, 55.1, 52.4, 52.1 ppm; GC–MS for $C_{15}H_{16}FNO$, *m*/*z* = 245 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(32)

N-[(4-fluorophenyl)methyl]-4-methoxybenzeneethanamine (3l)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol), and 4-methoxybenzeneethanamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3l** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 142 mg, 55%).

TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.21 (m, 2H), 7.15–7.10 (m, 2H), 7.03–6.96 (m, 2H), 6.87–6.82 (m, 2H), 3.79 (s, 3H), 3.76 (s, 2H), 2.88–2.83 (m, 2H), 2.80–2.74 (m, 2H), 1.69 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8 (d, J_{CF} = 244.6 Hz), 157.9, 135.8 (d, J_{CF} = 3.1 Hz), 131.8, 129.5, 129.5 (d, J_{CF} = 7.9 Hz), 115.0 (d, J_{CF} = 21.2 Hz), 113.8, 55.1, 53.0, 50.6, 35.2 ppm; GC–MS for $C_{16}H_{18}FNO$, *m*/*z* = 259 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{18}FNOH$ 260.1445, found 260.1439.

N-[(4-Fluorophenyl)methyl]-β-methylbenzeneethanamine (3m)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-fluorobenzylamine (125 mg, 1.0 mmol), and β-methylphenethylamine (189 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3m** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 141 mg, 58%). TLC: R_f = 0.4 (20% EtOAc in hexanes). Data for **3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 2H), 7.26–7.19 (m, 5H), 7.03–6.96 (m, 2H), 3.74 (ABq, *J* = 13.5 Hz, 2H), 2.99 (qt, *J* = 7.1, 7.0 Hz, 1H), 2.84–2.77 (m, 2H), 1.55 (br s, 1H), 1.28 (d, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J_{CF} = 244.2 Hz), 145.1, 135.8 (d, J_{CF} = 3.1 Hz), 129.4 (d, J_{CF} = 7.9 Hz), 128.5, 127.1, 126.3, 115.0 (d, J_{CF} = 21.2 Hz), 56.1, 52.9, 39.9, 20.0 ppm; GC–MS for $C_{16}H_{18}FN$, *m*/*z* = 243 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{18}FNH$ 244.1496, found 244.1500.

4-Methoxy-*N*-(phenylmethyl)benzeneethanamine (3n)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol), and benzylamine (150 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3n** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 169 mg, 70%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **3n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 5H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.3 Hz, 2H), 3.82 (s, 2H), 3.80 (s, 3H), 2.89 (t, *J* = 6.9 Hz, 2H), 2.80 (t, *J* = 6.9 Hz, 2H), 1.66 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 140.1, 131.9, 129.5, 128.3, 128.0, 126.8, 113.8, 55.1, 53.8, 50.6, 35.3 ppm; GC–MS for $C_{16}H_{19}NO$, *m*/*z* = 241 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(33)

N-(4-Methoxyphenethyl)hexan-1-amine (3o)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol), and 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3o** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 119 mg, 51%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **3o**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 2.86–2.81 (m, 2H), 2.78–2.72 (m, 2H), 2.62–2.57 (m, 2H), 1.68 (br s, 1H), 1.50–1.41 (m, 2H), 1.33–1.23 (m, 6H), 0.89–0.84 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 132.0, 129.6, 113.8, 55.2, 51.4, 49.9, 35.3, 31.7, 29.9, 27.0, 22.6, 14.0 ppm; GC–MS for $C_{15}H_{25}NO$, *m*/*z* = 235 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{25}NOH$ 236.2009, found 236.2005.

N-Cyclohexyl-4-methoxybenzeneethanamine (3p)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol), and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3p** was isolated by column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1–10:1; 187 mg, 80%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H), 2.86–2.81 (m, 2H), 2.74–2.68 (m, 2H), 2.39 (tt, *J* = 10.6, 3.8 Hz, 1H), 1.88–1.78 (m, 2H), 1.74–1.64 (m, 2H), 1.62–1.54 (m, 1H), 1.48 (br s, 1H), 1.29–0.95 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.8, 132.0, 129.4, 113.7, 56.6, 55.0, 48.3, 35.5, 33.4, 26.0, 24.9 ppm; GC–MS for $C_{15}H_{23}NO$, *m*/*z* = 233 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{23}NOH$ 234.1852, found 234.1854.

N-(4-Methoxyphenethyl)-2,3-dihydro-1*H*-inden-2-amine (3q)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol), and 2-aminoindane (186 mg, 1.4 mmol) was stirred at 130 °C

for 16 h. The product **3q** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 144 mg, 54%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.12 (m, 6H), 6.89–6.83 (m, 2H), 3.80 (s, 3H), 3.65 (quintet, *J* = 7.0 Hz, 1H), 3.17 (dd, *J* = 15.5, 7.2 Hz, 2H), 2.96–2.90 (m, 2H), 2.82–2.70 (m, 4H), 1.67 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.0, 141.6, 131.9, 129.5, 126.3, 124.6, 113.9, 59.5, 55.2, 49.7, 39.9, 35.5 ppm; GC–MS for $C_{18}H_{21}NO$, *m*/*z* = 267 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{21}NOH$ 268.1696, found 268.1699.

N-(4-Methoxyphenethyl)-1-(4-methoxyphenyl)ethanamine (3r)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol), and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3r** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 186 mg, 65%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.15 (m, 2H), 7.10–7.05 (m, 2H), 6.87–6.79 (m, 4H), 3.79 (s, 3H), 3.78 (s, 3H), 3.73 (q, *J* = 6.6 Hz, 1H), 2.79–2.60 (m, 4H), 1.86 (br s, 1H), 1.32 (d, *J* = 6.6, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 157.8, 137.4, 131.9, 129.4, 127.4, 113.7, 113.6, 57.4, 55.0, 48.9, 35.2, 24.1 ppm (one carbon signal obscured or overlapping); GC–MS for $C_{18}H_{23}NO_2$, *m*/*z* = 285 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{23}NO_2H$ 286.1802, found 286.1798.

N-(4-Methoxyphenethyl)-4-phenylbutan-2-amine (3s)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol), and (±)1-methyl-3-phenyl-1-propanamine (209 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3s** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 208 mg, 73%. TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.21–7.11 (m, 5H), 6.88–6.83 (m, 2H), 3.79 (s, 3H), 2.94–2.84 (m, 1H), 2.82–2.70 (m, 3H), 2.70–2.52 (m, 3H), 1.82–1.72 (m, 1H), 1.66–1.56 (m, 1H), 1.54 (br s, 1H), 1.10 (d, *J* = 6.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 142.2, 132.0, 129.6, 128.3, 128.2, 125.6, 113.8, 55.2, 52.4, 48.5, 38.5, 35.5, 32.2, 20.2 ppm; GC–MS for $C_{19}H_{25}NO$, *m*/*z* = 283 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{25}NOH$ 284.2009, found 284.2010.

4-Methoxy-*N*-[(4-methoxyphenyl)methyl]benzeneethanamine (3t)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-methoxybenzeneethanamine (151 mg, 1.0 mmol), and 4-methoxybenzylamine (192 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3t** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 149 mg, 55%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.90–6.82 (m, 4H), 3.80 (s, 3H), 3.79 (s, 3H), 3.75 (s, 2H), 2.87 (t, *J* = 7.1 Hz, 2H), 2.78 (t, *J* = 7.1 Hz, 2H), 1.71 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.5, 157.9, 132.3, 131.9, 129.5, 129.2, 113.7, 113.6, 55.1, 55.1, 53.2, 50.6, 35.2 ppm; GC–MS for $C_{17}H_{21}NO_2$, *m*/*z* = 271 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(33)

N-(3-Fluorophenethyl)-2,3-dihydro-1*H*-inden-2-amine (3u)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 2-(3-fluorophenyl)ethylamine (139 mg, 1.0 mmol), and 2-aminoindane (186 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3u** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 193 mg, 76%). TLC: R_f = 0.4 (10% EtOAc in hexanes). Data for **3u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 1H), 7.24–7.12 (m, 4H), 7.06–7.00 (m, 1H), 6.99–6.89 (m, 2H), 3.67 (quintet, *J* = 6.9 Hz, 1H), 3.18 (dd, *J* = 15.5, 7.2 Hz, 2H), 3.01–2.92 (m, 2H), 2.89–2.81 (m, 2H), 2.75 (dd, *J* = 15.5, 6.6 Hz, 2H), 1.63 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J_{CF} = 245.5 Hz), 142.5 (d, J_{CF} = 7.2 Hz), 141.5, 129.8 (d, J_{CF} = 8.3 Hz), 126.4, 124.6, 124.3 (d, J_{CF} =

2.7 Hz), 115.4 (d, J_{CF} = 20.8 Hz), 113.0 (d, J_{CF} = 21.0 Hz), 59.4, 49.2, 39.9, 36.2 (d, J_{CF} = 1.6 Hz) ppm; GC–MS for $C_{17}H_{18}FN$, *m*/*z* = 255 (M^+); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{18}FNH$ 256.1496, found 256.1501.

N-(3-Fluorophenethyl)-1-(4-methoxyphenyl)ethanamine (3v)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 2-(3-fluorophenyl)ethylamine (139 mg, 1.0 mmol), and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3v** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 157 mg, 58%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.16 (m, 3H), 6.98–6.80 (m, 5H), 3.80 (s, 3H), 3.73 (q, *J* = 6.6 Hz, 1H), 2.83–2.63 (m, 4H), 1.60 (br s, 1H), 1.32 (d, *J* = 6.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J_{CF} = 245.4 Hz), 158.5, 142.6 (d, J_{CF} = 7.2 Hz), 137.3, 129.7 (d, J_{CF} = 8.3 Hz), 127.5, 124.3 (d, J_{CF} = 2.7 Hz), 115.4 (d, J_{CF} = 20.9 Hz), 113.7, 112.9 (d, J_{CF} = 21.0 Hz), 57.5, 55.2, 48.5, 36.1 (d, J_{CF} = 1.7 Hz), 24.2 ppm; GC–MS for $C_{17}H_{20}FNO$, *m*/*z* = 273 (M^+); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{20}FNOH$ 274.1602, found 274.1604.

N-Cyclohexyl-1,3-benzodioxole-5-methanamine (3w)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1-(1,3-benzodioxol-5-yl)methanamine (151 mg, 1.0 mmol), and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3w** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 138 mg, 59%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3w**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83–6.81 (m, 1H), 6.75–6.73 (m, 2H), 5.92 (s, 2H), 3.70 (s, 2H), 2.45 (tt, *J* = 10.4, 3.8 Hz, 1H), 1.95–1.84 (m, 2H), 1.77–1.67 (m, 2H), 1.64–1.54 (m, 1H), 1.30–1.04 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.6, 146.3, 134.8, 121.1, 108.6, 108.0, 100.8, 55.9, 50.7, 33.4, 26.1, 24.9 ppm; GC–MS for $C_{14}H_{19}NO_2$, *m*/*z* = 233 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(34)

N-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-1-(4-methoxyphenyl)ethanamine (3x)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1-(1,3-benzodioxol-5-yl)methanamine (151 mg, 1.0 mmol), and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3x** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 171 mg, 60%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3x**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 2H), 6.93–6.86 (m, 2H), 6.82–6.78 (m, 1H), 6.77–6.67 (m, 2H), 5.93 (s, 2H), 3.82 (s, 3H), 3.76 (q, *J* = 6.6 Hz, 1H), 3.52 (ABq, *J* = 13.2 Hz, 2H), 1.70 (br s, 1H), 1.34 (d, *J* = 6.6 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.5, 147.6, 146.3, 137.4, 134.5, 127.7, 121.1, 113.8, 108.7, 108.0, 100.8, 56.5, 55.2, 51.3, 24.4 ppm; GC–MS for $C_{17}H_{19}NO_3$, *m*/*z* = 285 (M^+); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}NO_3H$ 286.1438, found 286.1427.

N-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-2-(4-methoxyphenyl)propan-1-amine (3y)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1-(1,3-benzodioxol-5-yl)methanamine (151 mg, 1.0 mmol), and (±)-β-methylphenylethylamine (189 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3y** was isolated by column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1–10:1; 152 mg, 56%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3y**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.28 (m, 2H), 7.24–7.18 (m, 3H), 6.75 (d, *J* = 1.6 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.68 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.93 (s, 2H), 3.66 (ABq, *J* = 13.2 Hz, 2H), 2.96 (sextet, *J* = 7.1 Hz, 1H), 2.77 (d, *J* = 7.2 Hz, 2H), 1.66 (br s, 1H), 1.26 (d, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.6, 146.4, 145.2, 134.1, 128.5, 127.2, 126.4, 121.1, 108.6, 108.0, 100.8, 56.0, 53.5, 39.9, 20.1 ppm; GC–MS for $C_{17}H_{19}NO_2$, *m*/*z* = 269 (M^+); HRMS (ESI-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{19}NO_2H$ 270.1489, found 270.1463.

N-Hexyl-1,2,3,4-tetrahydro-1-naphthalenamine (3z)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1,2,3,4-tetrahydro-1-naphthalenamine (147 mg, 1.0 mmol), and 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3z** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 106 mg, 46%).

TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **3z**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.37–7.30 (m, 1H), 7.21–7.05 (m, 3H), 3.77 (t, *J* = 4.8 Hz, 1H), 2.87–2.61 (m, 1H), 2.03–1.91 (m, 1H), 1.91–1.81 (m, 2H), 1.78–1.68 (m, 1H), 1.56–1.46 (m, 2H), 1.41–1.19 (m, 7H), 0.94–0.85 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.3, 137.3, 129.0, 128.7, 126.5, 125.6, 55.4, 47.3, 31.8, 30.4, 29.3, 28.2, 27.1, 22.6, 18.9, 14.1 ppm; GC–MS for $C_{16}H_{25}N$, *m*/*z* = 231 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{25}NH$ 232.2060, found 232.2053.

N-[2-(4-Methoxyphenyl)ethyl]-1,2,3,4-tetrahydro-1-naphthalenamine (3aa)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 1,2,3,4-tetrahydro-1-naphthalenamine (147 mg, 1.0 mmol), and 4-methoxybenzeneethanamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3aa** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 177 mg, 63%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **3aa**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 1H), 7.21–7.13 (m, 4H), 7.12–7.07 (m, 1H), 6.90–6.85 (m, 2H), 3.82 (s, 3H), 3.81 (t, *J* = 4.7 Hz, 1H), 3.05–2.89 (m, 2H), 2.87–2.69 (m, 4H), 2.01–1.86 (m, 3H), 1.80–1.70 (m, 1H), 1.63 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 139.0, 137.3, 132.1, 129.6, 129.0, 128.5, 126.5, 125.6, 113.7, 55.3, 55.2, 48.6, 35.7, 29.3, 28.2, 19.0 ppm; GC–MS for $C_{19}H_{23}NO$, *m*/*z* = 281 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{23}NOH$ 282.1852, found 282.1843.

N-Cyclohexyl-5-methoxytryptamine (3bb)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 5-methoxytryptamine (190 mg, 1.0 mmol), and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3bb** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 218 mg, 80%). TLC: R_f = 0.2 (30% EtOAc in hexanes). Data for **3bb**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (br s, 1H), 7.26–7.20 (m, 1H), 7.08–7.05 (m, 1H), 7.02–6.99 (m, 1H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.86 (s, 3H), 3.07–2.90 (m, 4H), 2.45 (tt, *J* = 10.5, 3.7 Hz, 1H), 1.91–1.78 (m, 3H), 1.75–1.65 (m, 2H), 1.64–1.55 (m, 1H), 1.29–0.99 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.8, 131.5, 127.8, 122.8, 113.6, 112.1, 111.8, 100.6, 56.8, 55.9, 46.8, 33.5, 26.1, 25.9, 25.0 ppm; GC–MS for $C_{17}H_{24}N_2O$, *m*/*z* = 272 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{24}FN_2OH$ 273.1961, found 273.1960.

N-Cyclohexyl-2-furanmethanamine (3cc)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 2-(2-aminoethyl)furan (97 mg, 1.0 mmol), and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3cc** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 124 mg, 69%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **3cc**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.28 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.14–6.12 (m, 1H), 3.78 (s, 2H), 2.42 (tt, *J* = 10.4, 3.8, Hz, 1H), 1.90–1.81 (m, 2H), 1.74–1.66 (m, 2H), 1.63–1.46 (m, 2H), 1.28–1.02 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.2, 141.5, 110.0, 106.4, 55.7, 43.2, 33.2, 26.0, 24.9 ppm; GC–MS for $C_{11}H_{17}NO$, *m*/*z* = 179 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(35)

4-(2-Cyclohexylaminoethyl)phenol (3dd)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), tyramine (136 mg, 1.0 mmol), and cyclohexylamine (139 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3dd** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 152 mg, 69%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **3dd**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.3 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 4.71 (br s, 1H), 2.93 (t, *J* = 6.9 Hz, 2H), 2.75 (t, *J* = 6.9 Hz, 2H), 2.47 (tt, *J* = 10.6, 3.6 Hz, 1H), 1.92–1.85 (m, 2H), 1.75–1.66 (m, 2H), 1.64–1.55 (m, 1H), 1.28–1.08 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.5, 130.0, 129.7, 115.9, 56.9, 47.6, 34.7, 32.9, 25.9, 25.0 ppm; GC–MS for $C_{14}H_{21}NO$, *m*/*z* = 219 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{21}NOH$ 220.1696, found 220.1698. Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65. Found: C, 76.78; H, 9.35.

Dibenzylamine (4a)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and benzylamine (107 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4a** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 88 mg, 89%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.42–7.24 (m, 10H), 3.84 (s, 4H), 2.08 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.0, 128.4, 128.1, 126.9, 53.0 ppm; GC–MS for $C_{14}H_{15}N$, *m*/*z* = 197 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(36)

Bis(4-methylbenzyl)amine (4b)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 4-methylbenzylamine (121 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4b** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 106 mg, 94%). TLC: R_f = 0.4 (20% EtOAc in hexanes). Data for **4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.9 Hz, 4H), 7.18 (d, *J* = 7.9 Hz, 4H), 3.80 (s, 4H), 2.38 (s, 6H), 1.70 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.2, 136.4, 129.0, 128.1, 52.7, 21.1 ppm; GC–MS for $C_{16}H_{19}N$, *m*/*z* = 225 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(36,37)

Bis(4-methoxylbenzyl)amine (4c)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol), **L1** (16 mg, 10 mol %), and 4-methoxylbenzylamine (137 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4c** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 111 mg, 86%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **4c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.24 (m, 4H), 6.91–6.86 (m, 4H), 3.81 (s, 6H), 3.74 (s, 4H), 1.69 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.5, 132.4, 129.2, 113.6, 55.1, 52.3 ppm; GC–MS for $C_{16}H_{19}NO_2$, *m*/*z* = 257 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(36,37)

N,N-Bis(4-chlorobenzyl)amine (4d)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and 4-chlorobenzylamine (141 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4d** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 122 mg, 92%). TLC: R_f = 0.5 (10% EtOAc in hexanes). Data for **4d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 8H), 3.76 (s, 4H), 1.64 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.5, 132.6, 129.4, 128.5, 52.2 ppm; GC–MS for $C_{14}H_{13}Cl_2N$, *m*/*z* = 265 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(37,38)

N-([1,1′-Biphenyl]-4-ylmethyl)[1,1′-biphenyl]-4-methanamine (4e)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 4-phenylbenzylamine (183 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4e** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 148 mg, 85%). TLC: R_f = 0.5 (20% EtOAc in hexanes). Data for **4e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 8.4 Hz, 8H), 7.49–7.42 (m, 8H), 7.34 (t, *J* = 7.6 Hz, 2H), 3.90 (s, 4H), 1.65 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.9, 139.9, 139.4, 128.7, 128.6, 127.1, 127.0, 52.8 ppm (one carbon signal obscured or overlapping); GC–MS for $C_{26}H_{23}N$, *m*/*z* = 349 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(39)

4-Fluoro-*N*-[(4-fluorophenyl)methyl]benzenemethanamine (4f)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 4-fluorobenzylamine (125 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4f** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 106 mg, 91%). TLC: R_f = 0.4 (20% EtOAc in hexanes). Data for **4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 4H), 7.07–6.99 (m, 4H), 3.78 (s, 4H), 1.67 (br s,

1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.8 (d, J_{CF} = 244.5 Hz), 135.8 (d, J_{CF} = 3.1 Hz), 129.6 (d, J_{CF} = 8.0 Hz), 115.1 (d, J_{CF} = 21.3 Hz), 52.3 ppm; GC–MS for $C_{14}H_{13}F_2N$, *m/z* = 233 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(38)

4-(Trifluoromethyl)-*N*-[[4-(trifluoromethyl)phenyl]methyl]benzenemethanamine (4g)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 4-(trifluoromethyl)benzenemethanamine (175 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4g** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 140 mg, 84%). TLC: R_f = 0.5 (20% EtOAc in hexanes). Data for **4g**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.64–7.57 (m, 4H), 7.51–7.46 (m, 4H), 3.88 (s, 4H), 1.75 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.1, 129.4 (q, J_{CF} = 32.4 Hz), 128.3, 125.3 (q, J_{CF} = 3.8 Hz), 124.2 (q, J_{CF} = 271.8 Hz), 52.6 ppm; GC–MS for $C_{16}H_{13}F_6N$, *m/z* = 333 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(38,40)

Bis(3-methoxylbenzyl)amine (4h)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 3-methoxylbenzylamine (137 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4h** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 108 mg, 84%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **4h** ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 2H), 6.97–6.91 (m, 4H), 6.84–6.78 (m, 2H), 3.82 (s, 6H), 3.80 (s, 4H), 1.71 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 141.9, 129.3, 120.4, 113.5, 112.4, 55.1, 53.0 ppm; GC–MS for $C_{16}H_{19}NO_2$, *m/z* = 257 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(36)

N,N-Bis(3-chlorobenzyl)amine (4i)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 3-chlorobenzylamine (141 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4i** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 118 mg, 89%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **4i**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 2H), 7.29–7.19 (m, 6H), 3.77 (s, 4H), 1.65 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.1, 134.2, 129.6, 128.1, 127.2, 126.2, 52.5 ppm; GC–MS for $C_{14}H_{13}Cl_2N$, *m/z* = 265 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(41)

Bis(3,4-methylenedioxybenzyl)amine (4j)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 1-(1,3-benzodioxol-5-yl)methanamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4j** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 110 mg, 77%). TLC: R_f = 0.4 (40% EtOAc in hexanes). Data for **4j**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 6.77–6.75 (m, 4H), 5.94 (s, 4H), 3.69 (s, 4H), 1.59 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 147.7, 146.5, 134.3, 121.2, 108.7, 108.0, 100.9, 52.7 ppm; GC–MS for $C_{16}H_{15}NO_4$, *m/z* = 285 (M^+); HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{16}H_{15}NO_4H$ 286.1074, found 286.1070.

Bis(3,4,5-trimethoxylbenzyl)amine (4k)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 3,4,5-trimethoxylbenzylamine (197 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4k** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 115 mg, 61%). TLC: R_f = 0.3 (50% EtOAc in hexanes). Data for **4k**: ^1H NMR (400 MHz, $CDCl_3$) 6.56 (s, 4H), 3.84 (s, 12H), 3.81 (s, 6H), 3.74 (s, 4H), 1.80 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 153.1, 136.6, 135.8, 104.7, 60.7, 55.9, 53.3 ppm; GC–MS for $C_{20}H_{27}NO_6$, *m/z* = 377 (M^+); HRMS (ESI-TOF) *m/z* $[M + H]^+$ calcd for $C_{20}H_{27}NO_6H$ 378.1911, found 378.1892.

4-Methoxy-*N*-[(1*R*)-1-(4-methoxyphenyl)ethyl]-α-methyl-(α*R*)-benzenemethanamine (4l)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and (*R*)-(+)-1-(4-methoxyphenyl)ethylamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4l** was isolated by

column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 107 mg, 75%), 7:1 mixture of diastereomers, $[\alpha]_D^{22}$ = −211.1 (*c* = 0.12 in CH_2Cl_2). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **4l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 4H), 6.89–6.84 (m, 4H), 3.82 (s, 6H), 3.45 (q, *J* = 6.7 Hz, 2H), 1.54 (br s, 1H), 1.25 (d, *J* = 6.7 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4, 137.7, 127.6, 113.7, 55.2, 54.2, 24.9 ppm; GC–MS for $C_{18}H_{23}NO_2$, *m*/*z* = 285 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(42)

4-Methoxy-*N*-[2-(4-methoxyphenyl)ethyl]benzeneethanamine (4m)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 4-methoxybenzeneethanamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4m** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 127 mg, 89%). TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **4m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.05 (m, 4H), 6.84–6.79 (m, 4H), 3.79 (s, 6H), 2.88–2.82 (m, 4H), 2.76–2.70 (m, 4H), 1.56 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 131.9, 129.5, 113.8, 55.2, 51.2, 35.3 ppm; GC–MS for $C_{18}H_{23}NO_2$, *m*/*z* = 285 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{23}NO_2H$ 286.1802, found 286.1800.

3-Methoxy-*N*-[2-(3-methoxyphenyl)ethyl]benzeneethanamine (4n)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 3-methoxybenzeneethanamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4n** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1). Isolated yield: 128 mg, 90%. TLC: R_f = 0.3 (10% EtOAc in hexanes). Data for **4n:**^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.16 (m, 2H), 6.80–6.71 (m, 6H), 3.79 (s, 6H), 2.91 (t, *J* = 7.2 Hz, 4H), 2.79 (t, *J* = 7.2 Hz, 4H), 1.91 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 141.4, 129.4, 121.0, 114.3, 111.5, 55.1, 50.9, 36.2 ppm; GC–MS for $C_{18}H_{23}NO_2$, *m*/*z* = 285 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{23}NO_2H$ 286.1802, found 286.1798.

3-Fluoro-*N*-[2-(3-fluorophenyl)ethyl]benzeneethanamine (4o)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 3-fluorobenzeneethanamine (139 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4o** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 114 mg, 87%). TLC: R_f = 0.4 (10% EtOAc in hexanes). Data for **4o:**^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.18 (m, 2H), 6.98–6.83 (m, 6H), 2.93–2.86 (m, 4H), 2.82–2.76 (m, 4H), 1.68 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J_{CF} = 245.7 Hz), 142.3 (d, J_{CF} = 7.1 Hz), 129.9 (d, J_{CF} = 8.3 Hz), 124.3 (d, J_{CF} = 2.8 Hz), 115.4 (d, J_{CF} = 20.9 Hz), 113.1 (d, J_{CF} = 21.0 Hz), 50.6, 35.9 (d, J_{CF} = 1.4 Hz) ppm; GC–MS for $C_{16}H_{17}F_2N$, *m*/*z* = 261 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{17}F_2NH$ 262.1402, found 262.1389.

β-Methyl-*N*-(2-phenylpropyl)benzeneethanamine (4p)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and (*R*)-(+)-β-methylphenethylamine (135 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4p** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 118 mg, 93%), 1.15:1 mixture of diastereomers. TLC: R_f = 0.5 (30% EtOAc in hexanes). Data for **4p**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 4H), 7.20–7.14 (m, 2H), 7.13–7.07 (m, 4H), 2.95–2.84 (m, 2H), 2.84–2.66 (m, 4H), 1.49 (br s, 1H), 1.21–1.17 (2d, *J* = 6.9 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.1, 128.5, 127.0, 126.2, 56.7, 39.5, 19.8 ppm; GC–MS for $C_{18}H_{23}N$, *m*/*z* = 253 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(43)

α-Methyl-*N*-(1-methyl-3-phenylpropyl)benzenepropanamine (4q)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and α-methylbenzenepropanamine (149 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4p** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 126 mg, 90%), 1:1 mixture of diastereomers. TLC: R_f = 0.5 (40% EtOAc in hexanes). Data for **4q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–6.97 (m,

10H), 2.85–2.74 (m, 2H), 2.73–2.58 (m, 4H), 1.84–1.70 (m, 2H), 1.69–1.57 (m, 2H), 1.15–1.04 (m, 6H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.4 (isomers 1 and 2), 128.3 (isomers 1 and 2), 128.2 (isomers 1 and 2), 125.6 (isomers 1 and 2), 49.4 (isomer 1), 49.2 (isomer 2), 39.3 (isomer 1), 38.8 (isomer 2), 32.4 (isomer 1), 32.2 (isomer 2), 21.1 (isomer 1), 20.7 (isomer 2) ppm; GC–MS for $C_{20}H_{27}N$, *m*/*z* = 281 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(44)

Di(2-aminoindane) (4r)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 2-indanamine (133 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4r** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 91 mg, 73%). TLC: R_f = 0.5 (20% EtOAc in hexanes). Data for **4r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (m, 4H), 7.24–7.18 (m, 4H), 3.83 (quintet, *J* = 7.2 Hz, 2H), 3.26 (dd, *J* = 15.4, 7.2 Hz, 4H), 2.85 (dd, *J* = 15.4, 7.2 Hz, 4H), 1.77 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 126.3, 124.5, 58.1, 40.2 ppm; GC–MS for $C_{18}H_{19}N$, *m*/*z* = 249 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{19}NH$ 250.1590, found 250.1598.

Bis(cyclohexyl)amine (4s)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %) and cyclohexylamine (99 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4s** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 86 mg, 95%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **4s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (tt, *J* = 10.6, 3.7 Hz, 2H), 1.82–1.74 (m, 4H), 1.68–1.59 (m, 4H), 1.57–1.49 (m, 2H), 1.24–0.88 (m, 10H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 52.8, 34.1, 26.0, 25.1 ppm; GC–MS for $C_{12}H_{23}N$, *m*/*z* = 181 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(45,46)

N-(2-Thienylethyl)-2-thiopheneethanamine (4t)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 2-thiopheneethanamine (127 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4t** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 106 mg, 89%). TLC: R_f = 0.4 (30% EtOAc in hexanes). Data for **4t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.04 (m, 2H), 6.96–6.87 (m, 2H), 6.85–6.75 (m, 2H), 3.06–2.99 (m, 4H), 2.98–2.90 (m, 4H), 2.45 (br s, 1H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.2, 126.8, 125.0, 123.5, 50.7, 30.2 ppm; GC–MS for $C_{12}H_{15}NS_2$, *m*/*z* = 237 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{15}NS_2H$ 238.0719, found 238.0716.

Di-*n*-hexylamine (4u)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 1-hexamine (101 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4u** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 40 mg, 43%). TLC: R_f = 0.3 (30% EtOAc in hexanes). Data for **4u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (t, *J* = 7.4, 4H), 2.24 (br s, 1H), 1.54–1.44 (m, 4H), 1.35–1.19 (m, 12H), 0.90–0.82 (m, 6H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 50.0, 31.7, 29.8, 27.1, 22.6, 14.0 ppm; GC–MS for $C_{12}H_{27}N$, *m*/*z* = 185 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(46,47)

N,N-Dibutylamine (4v)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and *n*-butylamine (73 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4v** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 30 mg, 46%). TLC: R_f = 0.3 (30% EtOAc in hexanes). Data for **4v**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (t, *J* = 7.2 Hz, 4H), 1.37–1.25 (m, 4H), 1.24–1.11 (m, 4H), 0.86 (br s, 1H), 0.75 (t, *J* = 7.3 Hz, 6H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 49.6, 32.1, 20.2, 13.7 ppm; GC–MS for $C_8H_{19}N$, *m*/*z* = 129 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values change the reference number to 46.(47)

N-(2-Furanylmethyl)-2-furanmethanamine (4w)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and furfurylamine (97 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4w** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 70 mg, 79%). TLC: R_f = 0.3 (30% EtOAc in hexanes). Data for **4w**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.31 (m, 2H), 6.34–6.27 (m, 2H), 6.22–6.13 (m, 2H), 3.78 (s, 4H), 1.89 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 141.9, 110.1, 107.2, 44.9 ppm; GC–MS for $C_{10}H_{11}NO_2$, *m*/*z* = 177 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(48)

N-(3-Phenylpropyl)benzenepropanamine (4x)

A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), and 3-phenyl-1-propanamine (135 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4x** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 100:1–10:1; 53 mg, 42%). TLC: R_f = 0.3 (30% EtOAc in hexanes). Data for **4x**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.14 (m, 10H), 2.65 (t, *J* = 7.4 Hz, 8H), 1.89 (br s, 1H), 1.84 (quintet, *J* = 7.4 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0, 128.3, 128.3, 125.8, 49.4, 33.6, 31.5 ppm; GC–MS for $C_{18}H_{23}N$, *m*/*z* = 253 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values change the ref number to 43.(41)

4-Methoxy-*N*-phenylbenzenemethanamine (5a)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), aniline (47 mg, 0.5 mmol), and 4-methoxybenzylamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5a** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 76 mg, 71%). TLC: R_f = 0.4 (30% EtOAc in hexanes). Data for **5a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.22–7.16 (m, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.77–6.72 (m, 1H), 6.70–6.65 (m, 2H), 4.26 (s, 2H), 3.80 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.9, 147.1, 130.6, 129.3, 129.1, 118.4, 114.0, 113.6, 55.3, 48.4 ppm; GC–MS for $C_{14}H_{15}NO$, *m*/*z* = 213 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(49,50)

N-(4-Methoxyphenyl)phenylmethanamine (5b)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol), and benzylamine (75 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5b** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 61 mg, 57%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **5b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.29 (m, 5H), 6.87–6.81 (m, 2H), 6.69–6.63 (m, 2H), 4.33 (s, 2H), 3.79 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.1, 142.2, 139.5, 128.5, 127.5, 127.1, 114.8, 114.1, 55.7, 49.1 ppm; GC–MS for $C_{14}H_{15}NO$, *m*/*z* = 213 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(51,52)

N-(4-Methoxyphenyl)[1,1′-biphenyl]-4-methanamine (5c)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol), and 4-phenylbenzylamine (128 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5c** was isolated by column chromatography on silica gel (*n*-hexane/ethyl acetate = 150:1–40:1; 101 mg, 70%). TLC: R_f = 0.4 (30% EtOAc in hexanes). Data for **5c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.55 (m, 4H), 7.47–7.42 (m, 4H), 7.35 (tt, *J* = 7.3, 1.3, Hz, 1H), 6.82–6.77 (m, 2H), 6.69–6.65 (m, 2H), 4.34 (s, 2H), 3.75 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.5, 141.7, 140.8, 140.2, 138.3, 128.7, 128.1, 127.3, 127.2, 127.0, 114.9, 114.6, 55.8, 49.2 ppm; GC–MS for $C_{20}H_{19}NO$ *m*/*z* = 289 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(53)

4-Fluoro-*N*-(4-methoxyphenyl)benzenemethanamine (5d)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol), and 4-fluorobenzylamine (88 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5d** was

isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 47 mg, 41%). TLC: R_f = 0.3 (20% EtOAc in hexanes). Data for **5d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 2H), 7.07–6.99 (m, 2H), 6.83–6.76 (m, 2H), 6.66–6.59 (m, 2H), 4.26 (s, 2H), 4.09 (br s, 1H), 3.75 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0 (d, J_{CF} = 245.1 Hz), 152.4, 141.7, 135.0 (d, J_{CF} = 3.1 Hz), 129.1 (d, J_{CF} = 8.0 Hz), 115.3 (d, J_{CF} = 21.4 Hz), 114.8, 114.4, 55.7, 48.6 ppm; GC–MS for $C_{14}H_{14}FNO$ *m*/*z* = 231 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(54,55)

N-(4-Chlorophenyl)-4-methoxybenzenemethanamine (5e)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-chloroaniline (64 mg, 0.5 mmol), and 4-methoxybenzylamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5e** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 73 mg, 59%). TLC: R_f = 0.5 (20% EtOAc in hexanes). Data for **5e**: ^{1}H NMR (400 MHz, $CDCl_3$) 7.30–7.25 (m, 2H), 7.14–7.09 (m, 2H), 6.92–6.87 (m, 2H), 6.59–6.53 (m, 2H), 4.23 (s, 2H), 4.15 (br s, 1H), 3.81 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.9, 146.5, 130.7, 129.0, 128.7, 122.1, 114.0, 114.0, 55.3, 47.9 ppm; GC–MS for $C_{14}H_{14}ClNO$, *m*/*z* = 247 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(56)

3,4,5-Trimethoxy-*N*-(4-methoxyphenyl)benzenemethanamine (5f)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol) and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5f** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 138 mg, 91%). TLC: R_f = 0.5 (50% EtOAc in hexanes). Data for **5f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81–6.76 (m, 2H), 6.65–6.60 (m, 4H), 4.21 (s, 2H), 3.84 (s, 9H), 3.74 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 152.3, 142.1, 136.9, 135.3, 114.8, 114.3, 104.3, 60.8, 56.0, 55.7, 49.7 ppm; GC–MS for $C_{17}H_{21}NO_4$, *m*/*z* = 303 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(57,58)

3,4,5-Trimethoxy-*N*-phenylbenzenemethanamine (5g)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), aniline (47 mg, 0.5 mmol) and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5g** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 97 mg, 71%). TLC: R_f = 0.6 (50% EtOAc in hexanes). Data for **5g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.17 (m, 2H), 6.75 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.69–6.65 (m, 2H), 6.63 (s, 2H), 4.27 (s, 2H), 4.13 (br s, 1H), 3.86 (s, 3H), 3.85 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 148.0, 136.8, 135.1, 129.1, 117.6, 112.8, 104.2, 60.7, 55.9, 48.7 ppm; GC–MS for $C_{16}H_{19}NO_3$, *m*/*z* = 273 (M^+). ^{1}H and ^{13}C NMR spectral data were in good agreement with the literature values.(59,60)

3,4,5-Trimethoxy-*N*-(4-chlorophenyl)benzenemethanamine (5h)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-chloroaniline (64 mg, 0.5 mmol), and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5h** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 111 mg, 72%). TLC: R_f = 0.6 (50% EtOAc in hexanes). Data for **5h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 9.0 Hz, 2H), 6.58 (s, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 4.23 (s, 2H), 3.84 (s, 3H), 3.84 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.4, 146.4, 137.0, 134.5, 129.0, 122.3, 114.0, 104.1, 60.8, 56.0, 48.8 ppm; GC–MS for $C_{16}H_{18}ClNO_3$, *m*/*z* = 307 (M^+). Anal. Calcd for $C_{16}H_{18}ClNO_3$: C, 62.44; H, 5.90. Found: C, 62.88; H, 6.05.

N-Hexyl-4-methoxybenzenamine (5i)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol), and 1-hexamine (71 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5i** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 65 mg, 63%). TLC: R_f = 0.4 (20% EtOAc in hexanes). Data for **5i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82–6.77 (m, 2H), 6.63–6.58 (m, 2H), 3.75 (s, 3H), 3.39 (br s, 1H), 3.06 (t, *J* = 7.2 Hz, 2H), 1.61 (quintet, *J* = 7.4 Hz, 2H), 1.44–1.26 (m, 6H), 0.91 (t, *J* = 6.9 Hz, 3H) ppm; $^{13}C\{^1H\}$

NMR (100 MHz, $CDCl_3$) δ 152.1, 142.5, 114.8, 114.2, 55.8, 45.2, 31.6, 29.5, 26.8, 22.6, 14.0 ppm; GC–MS for $C_{13}H_{21}NO$, *m*/*z* = 207 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values change the ref number to 48.(58)

N-(4-Methoxyphenyl)benzenepropanamine (5j)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol), and 3-phenyl-1-propanamine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5j** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 54 mg, 45%). TLC: R_f = 0.9 (50% EtOAc in hexanes). Data for **5j**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 2H), 7.25–7.18 (m, 3H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.60 (d, *J* = 8.9 Hz, 2H), 3.76 (s, 3H), 3.13 (t, *J* = 7.1 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.96 (quintet, *J* = 7.4 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.2, 142.2, 141.7, 128.4, 128.4, 125.9, 114.8, 114.3, 55.8, 44.6, 33.4, 31.0 ppm; GC–MS for $C_{16}H_{19}NO$, *m*/*z* = 241 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(61,62)

N-(4-Methoxyphenyl)-2,3-dihydro-1*H*-inden-2-amine (5k)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol), and 2-aminoindan (93 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5k** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 88 mg, 74%). TLC: R_f = 0.5 (30% EtOAc in hexanes). Data for **5k**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.17 (m, 4H), 6.86–6.80 (m, 2H), 6.67–6.62 (m, 2H), 4.33 (tt, *J* = 6.8, 4.4 Hz,1H), 3.79 (s, 3H), 3.37 (dd, *J* = 16.0, 6.8 Hz, 2H), 2.90 (dd, *J* = 16.0, 4.4 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.2, 141.4, 141.4, 126.5, 124.9, 114.9, 114.9, 55.7, 54.9, 40.1 ppm; GC–MS for $C_{16}H_{17}NO$, *m*/*z* = 239 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{17}NOH$ 240.1383, found 240.1377.

4-(2-(3,4,5-Trimethoxyphenylamino)ethyl)phenol (5l)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 3,4,5-trimethoxyaniline (91 mg, 0.5 mmol), and 2-(4-hydroxyphenyl)ethanamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5l** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 77 mg, 51%). TLC: R_f = 0.4 (50% EtOAc in hexanes). Data for **5l**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.09–7.05 (m, 2H), 6.81–6.77 (m, 2H), 5.90 (s, 2H), 3.81 (s, 6H), 3.77 (s, 3H), 3.33 (t, *J* = 7.1 Hz, 2H), 2.86 (t, *J* = 7.1 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.4, 153.9, 144.1, 130.7, 130.5, 129.8, 115.5, 91.1, 61.1, 55.9, 46.2, 34.4 ppm; GC–MS for $C_{17}H_{21}NO_4$, *m*/*z* = 303 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{21}NO_4H$ 304.1543, found 304.1516.

N-(3,4,5-Trimethoxybenzyl)-3,4-dihydro-2*H*-benzo[*b*][1,4]dioxepin-7-amine (5m)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 3,4-dihydro-2*H*-1,5-benzodioxepin-7-amine (83 mg, 0.5 mmol), and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5m** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 129 mg, 75%). TLC: R_f = 0.4 (50% EtOAc in hexanes). Data for **5m**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.6 Hz, 1H), 6.59 (s, 2H), 6.38–6.34 (m, 1H), 6.31–6.26 (m, 1H), 4.19 (s, 2H), 4.15 (t, *J* = 5.4 Hz, 2H), 4.09 (t, *J* = 5.5 Hz, 2H), 3.84 (s, 6H), 3.83 (s, 3H), 2.14 (quintet, *J* = 5.5 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.3, 152.1, 143.9, 143.6, 137.0, 134.4, 122.2, 108.7, 106.5, 104.5, 70.9, 70.8, 60.8, 56.1, 49.8, 32.4 ppm; GC–MS for $C_{19}H_{23}NO_5$, *m*/*z* = 345 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{23}NO_5H$ 346.1649, found 346.1618.

N-(3,5-Dimethoxybenzyl)-4-methoxybenzenamine (5n)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-methoxyaniline (62 mg, 0.5 mmol), and 3,5-dimethoxybenzylamine (117 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5n** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 115 mg, 84%). TLC: R_f = 0.7 (50% EtOAc in hexanes). Data for **5n**: δ ^1H NMR (400 MHz, $CDCl_3$) 6.82–6.77 (m, 2H), 6.64–6.59 (m, 2H), 6.57 (d, *J* = 2.3 Hz, 2H), 6.40 (t, *J* = 2.3 Hz, 1H), 4.23 (s, 2H), 3.79 (s, 6H), 3.76 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100

MHz, $CDCl_3$) δ 160.9, 152.0, 142.3, 142.2, 114.7, 114.0, 105.2, 98.9, 55.6, 55.2, 49.2 ppm; GC–MS for $C_{16}H_{19}NO_3$, *m*/*z* = 273 (M^+). ^1H and ^{13}C NMR spectral data were in good agreement with the literature values.(63)

4-Chloro-*N*-(3,5-dimethoxybenzyl)benzenamine (5o)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-chloroaniline (64 mg, 0.5 mmol), and 3,5-dimethoxybenzylamine (117 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5o** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 66 mg, 48%). TLC: R_f = 0.6 (30% EtOAc in hexanes). Data for **5o**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.13–7.08 (m, 2H), 6.58–6.53 (m, 2H), 6.52–6.49 (m, 2H), 6.38 (t, *J* = 2.2 Hz, 1H), 4.24 (s, 2H), 3.78 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.1, 146.3, 141.3, 129.0, 122.3, 114.1, 105.2, 99.1, 55.3, 48.6 ppm; GC–MS for $C_{15}H_{16}ClNO_2$, *m*/*z* = 277 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{16}NO_2ClH$ 278.0942, found 278.0928.

N-(3,5-Dimethoxybenzyl)-4-(trifluoromethyl)benzenamine (5p)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 4-(trifluoromethyl)aniline (81 mg, 0.5 mmol), and 3,5-dimethoxybenzylamine (117 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5p** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 58 mg, 37%). TLC: R_f = 0.4 (30% EtOAc in hexanes). Data for **5p**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.51 (d, *J* = 2.3 Hz, 2H) 6.39 (t, *J* = 2.3 Hz, 1H), 4.55 (br s, 1H), 4.30 (s, 2H), 3.78 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.1, 150.3, 140.9, 126.6 (q, J_{CF} = 3.8 Hz), 124.9 (q, J_{CF} = 270.6 Hz), 119.2 (q, J_{CF} = 32.6 Hz), 112.1 105.2, 99.1, 55.3, 48.0 ppm; GC–MS for $C_{16}H_{16}F_3NO_2$, *m*/*z* = 311 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{16}F_3NO_2H$ 312.1206, found 312.1207.

9-Ethyl-*N*-hexyl-9*H*-carbazol-3-amine (5q)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), 3-amino-9-ethylcarbazole (105 mg, 0.5 mmol), and 1-hexamine (71 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5q** was isolated by column chromatography on silica gel (*n*-hexane/EtOAc = 150:1–40:1; 103 mg, 70%). TLC: R_f = 0.4 (50% EtOAc in hexanes). Data for **5q**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.09–8.04 (m, 1H), 7.48–7.42 (m, 1H), 7.40–7.34 (m, 2H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.19 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.91 (dd, *J* = 8.6, 2.3 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.40 (br s, 1H), 3.25 (t, *J* = 7.2 Hz, 2H), 1.72 (quintet, *J* = 7.4 Hz, 2H), 1.55–1.45 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.41–1.33 (m, 4H), 1.12–0.92 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.9, 140.2, 133.9, 125.2, 123.6, 122.6, 120.3, 117.8, 114.6, 109.0, 108.3, 103.3, 45.7, 37.4, 31.7, 29.7, 27.0, 22.6, 14.0, 13.8 ppm; GC–MS for $C_{20}H_{26}N_2$, *m*/*z* = 294 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{26}N_2H$ 295.2169, found 295.2167.

(*R*)-3-Ethyl-3-(4-(3,4,5-trimethoxybenzylamino)phenyl)piperidine-2,6-dione (5r)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), (*R*)-(+)-aminoglutethimide (116 mg, 0.5 mmol), and 3,4,5-trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5r** was isolated by column chromatography on silica gel (*n*-hexane/ethyl acetate = 100:1–1:1; 82 mg, 40%), $[\alpha]_D^{22}$ = +148.2 (*c* = 0.2 in CH_2Cl_2). TLC: R_f = 0.2 (50% EtOAc in hexanes). Data for **5r**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (br s, 1H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 6.59 (s, 2H), 4.24 (s, 2H), 3.83 (s, 9H), 2.62–2.52 (m, 1H), 2.44 (dd, *J* = 13.2, 4.9 Hz, 1H), 2.31 (ddd, *J* = 14.2, 4.8, 2.7 Hz, 1H), 2.16 (dd, *J* = 13.8, 4.8 Hz, 1H), 1.99 (sext, *J* = 7.4 Hz, 1H), 1.87 (sextet, *J* = 7.4 Hz, 1H), 0.85 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.5, 172.5, 153.4, 147.0, 137.1, 134.5, 127.1, 113.4, 113.4, 104.4, 60.8, 56.1, 50.2, 48.9, 32.9, 29.3, 26.9, 9.0 ppm; GC–MS for $C_{23}H_{28}N_2O_5$, *m*/*z* = 412 (M^+); HRMS (IT-TOF/ESI) calcd for $C_{23}H_{28}N_2O_5$–H ($[M - H]^-$+) 411.1925, found 411.1908.

3-(3-Phenylpropylamino)piperidine-2,6-dione (5s)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), L-glutamine (73 mg, 0.5 mmol), and 3-phenyl-1-propanamine (95 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5s** was

isolated by column chromatography on silica gel (*n*-hexane/ethyl acetate = 50:1–1:1; 92 mg, 75%). TLC: R_f = 0.2 (50% EtOAc in hexanes). Data for **5s**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 7.22–7.12 (m, 3H), 6.73 (br s, 1H), 4.08 (dd, *J* = 9.0, 4.8 Hz, 1H), 3.28 (dd, *J* = 8.9, 4.8 Hz, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.50–2.37 (m, 1H), 2.37–2.19 (m, 2H), 2.16–2.05 (m, 1H), 1.84 (quintet, *J* = 7.4 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 179.5, 172.1, 141.4, 128.4, 128.3, 126.0, 57.1, 39.3, 33.2, 30.8, 29.4, 25.7 ppm; GC–MS for $C_{14}H_{18}N_2O_2$, *m*/*z* = 246 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{14}H_{18}N_2O_2H$ 247.1441, found 247.1408.

3-(4-Methoxybenzylamino)piperidine-2,6-dione (5t)

A chlorobenzene (2.0 mL) solution of complex **1** (7 mg, 0.75 mol %), **L1** (8 mg, 10 mol %), L-glutamine (73 mg, 0.5 mmol), and 4-methoxybenzylamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product **5t** was isolated by column chromatography on silica gel (*n*-hexane/ethyl acetate = 50:1–1:1; 87 mg, 70%). TLC: R_f = 0.2 (50% EtOAc in hexanes). Data for **5t**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.92 (br s, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.40–4.29 (m, 2H), 4.13 (dd, *J* = 9.0, 4.7 Hz, 1H), 3.77 (s, 3H), 2.53–2.41 (m, 1H), 2.34–2.20 (m, 2H), 2.20–2.09 (m, 1H), 1.87 (br s, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 179.5, 172.2, 158.8, 130.1, 128.9, 113.8, 57.0, 55.1, 42.7, 29.2, 25.5 ppm; GC–MS for $C_{13}H_{16}N_2O_3$, *m*/*z* = 248 (M^+); HRMS (ESI-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{16}N_2O_3H$ 249.1234, found 249.1202.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00649.

- Experimental procedures, spectroscopic data, and NMR spectra (PDF)
- X-ray data for compound **5f** (CIF)
- **pdf**
    - jo8b00649_si_001.pdf (4.28 MB)
- **crystallographic information file**
    - jo8b00649_si_002.cif (20.87 kb)

The authors declare no competing financial interest.

Acknowledgments

Financial support from the National Science of Foundation (CHE-1358439, CHE-1664652) and National Institute of Health General Medical Sciences (R15 GM109273) is gratefully acknowledged.

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