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J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.8b00649 • Publication Date (Web): 18 Apr 2018 Downloaded from http://pubs.acs.org on April 18, 2018

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# Synthesis of Symmetric and Unsymmetric Secondary Amines from the Ligand Promoted Ruthenium Catalyzed Deaminative Coupling Reaction of Primary Amines

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**ABSTRACT:** The catalytic system generated *in-sit*u 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<sub>2</sub> (18% D). The most pronounced carbon isotope effect was observed on the  $\alpha$ -carbon of the product isolated from the coupling reaction of 4-methoxybenzylamine (C(1) = 1.015(2)). 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<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NH<sub>2</sub> (X = OMe, Me, H, F, CF<sub>3</sub>). ( $\rho$  = -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.<sup>2</sup> In a pioneering report, Fujiwara and co-workers first demonstrated the direct coupling of olefins with arylamines, in which arene *sp*<sup>2</sup> C–N bond cleavage was promoted by a stoichiometric amount of Pd(II) salts.3 More recently, Kakiuchi and coworkers 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.<sup>4</sup> A few remarkably efficient amide-to-ester conversion methods via amide C–N bond cleavage have been achieved by using Ni catalysts.<sup>5</sup> A number of Pd-catalyzed C–N cleavage methods have also been developed, including intramolecular Heck-type coupling reactions<sup>6</sup> and allylamine coupling reactions.<sup>7</sup> Selective catalytic C–C coupling methods via  $sp^3$  C–N bond activation of allyl- and benzylic amines have been achieved.<sup>8</sup> Other notable examples of catalytic C–N bond cleavage reactions include: oxidative C–H coupling reaction of amides with alkynes,<sup>9</sup> and Milstein group's report on the Ru-catalyzed hydrogenolysis of amides.<sup>10</sup> Catalytic C–N cleavage methods have also been successfully utilized for constructing nitrogen heterocycles.<sup>11</sup>

Chemoselective synthesis of amines has long been a pertinent issue in organic synthesis. Much research efforts 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.<sup>12</sup> In particular, late transition metal catalysts have been successfully employed to promote amine-to-alcohol coupling reactions via 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.<sup>14</sup> 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 Zhang group also devised the synthesis of unsymmetric secondary amines from the coupling of aniline with primary amines by using soluble Co catalysts.<sup>16</sup> 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.

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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.<sup>17</sup> 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 comprised 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.<sup>18</sup> By adopting the 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  $[(C_6H_6)(PCy_3)(CO)RuH]^+BF_4$  (2) with 1,2-

catechol ligand exhibited the most promising activity for the coupling reaction, as analyzed by both GC and NMR spectroscopic methods (Table 1). Among the screened oxygen and nitrogen ligands, 4-(1,1-dimethylethyl)-1,2benzenediol (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 condition 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. Non-protic 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.

en- try	catalyst	ligand <sup>b</sup>	yield ( <b>3a</b> : <b>4a</b> ) <sup>c</sup>	
1	1	none	27:7	
2	1	phenol	52:16	
3	1	1,2-catechol	68:20	
4	1	aniline	19:6	
5	1	2-NH <sub>2</sub> PhCOMe	28:16	
6	1	PhCONH <sub>2</sub>	trace	
7	1	1,1'-BINOL	trace	
8	1	1,2-C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub>	27:12	
9	1	L1	74:22	
10	1	L2	67:6	
11	1	L3	62:13	
12	$1/HBF_4 \cdot OEt_2$	L1	65:1	
13	2	L1	70:16	
14	$2/HBF_4 \cdot OEt_2$	L1	60:5	
15	[Ru(COD)Cl <sub>2</sub> ] <sub>x</sub>	L1	14:7	
16	RuCl <sub>3</sub> ·3H <sub>2</sub> O	L1	0	
17	(PPh <sub>3</sub> ) <sub>3</sub> (CO)RuH <sub>2</sub>	L1	0	
18	[( <i>p</i> -cymene)RuCl <sub>2</sub> ] <sub>2</sub>	L1	<1	
19	RuHCl(CO)(PCy <sub>3</sub> ) <sub>2</sub>	L1	70:15	
20	[(PCy <sub>3</sub> ) <sub>2</sub> (CO)(CH <sub>3</sub> CN) <sub>2</sub> RuH] BF <sub>4</sub>	L1	0	

Table 1. Ca	atalyst and	Ligand So	creening	Study	Va
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<sup>a</sup> Reaction conditions: benzylamine (0.5 mmol), cyclohexylamine (0.7 mmol), catalyst (3 mol %), ligand (10 mol %), chlorobenzene (2 mL), 130 °C, 16 h. <sup>b</sup> See the Supporting Information for extensive list and structure of ligands. <sup>c</sup> The product yield was determined by <sup>1</sup>H NMR using C<sub>6</sub>Me<sub>6</sub> 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 condition (Table 2). The coupling of benzylic amines with a variety of aliphatic and benzylic primary amines selectively formed the unsymmetric secondary amine products **3a-3m**. 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

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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-3v. Indole-, Furanyl- and phenol-substituted amines with cyclohexylamine selectively yielded the unsymmetric secondary amine products 3bb-3dd. For these cases, the coupling of benzylic and other aryl-substituted amines with electron-rich amines tend to favor the formation of unsymmetrical amines over the symmetrical ones. In contrast, the coupling of two different aliphatic amines with sterically non-demanding group yielded in 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<sup>a</sup>



 $^a$  Reaction conditions: R-NH2 (1.0 mmol), R'-NH2 (1.4 mmol), **1** (0.75 mol %), **L1** (10 mol %), chlorobenzene (2 mL), 130 °C, 16 h. Ar = C<sub>6</sub>H<sub>4</sub>-4-OMe.

We next explored the substrate scope for the formation of symmetric secondary amines by using the catalyst system 1/L1 (Table 3). Benzylic primary amines reacted smoothly to afford the secondary amine products **4a-4k** 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-4r**. 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-4x**. 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 case of (*R*)-4-methoxy- $\alpha$ -methylbenzenemethaneamine (d.r. = 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 method.<sup>14,16</sup>

#### Table 3. Synthesis of Symmetric Secondary Amines<sup>a</sup>



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

To further illustrate the synthetic versatility of catalytic coupling method, we next explored the coupling reaction of aniline derivatives with primary amine substrates of biological relevance (Table 4). The coupling of *para*-substituted anilines with benzylic amines led to the selective formation of unsymmetric amine products **5a-5e** 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-5h** in high yields. Single crystals of **5f** were obtained by slow evaporation in CH<sub>2</sub>Cl<sub>2</sub>/hexanes, and its structure was determined by X-ray crystallography.

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 Tables 2-4, 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 <sup>1</sup>H NMR in 20 min intervals.

#### Table 4. Synthesis of Unsymmetric Secondary Amines from the Deaminative Coupling of Anilines with Amines<sup>a</sup>



 $^a$  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.



Figure 1. Reaction Profile for the Coupling of 4-Methoxybenzylamine. 4-Methoxybenzylamine ( $\bullet$ ), 4c ( $\blacksquare$ ) and ArCH=NCH<sub>2</sub>Ar ( $\blacktriangle$ ).

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.



Next, we examined the deuterium labeling pattern on the product from the reaction of aniline- $d_7$  with 4methoxybenzylamine (eq 2). The reaction tube consisted of aniline- $d_7$  (50 mg, 0.5 mmol) with 4methoxybenzylamine (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 <sup>1</sup>H and <sup>2</sup>H NMR (Figure S1, SI). A significant amount of deuterium was incorporated to the CH<sub>2</sub> 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*<sup>7</sup> 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. The significant amount of the deuterium incorporation suggests that the imine-toamine hydrogenation-dehydrogenation process might have occurred during the product formation of **5a**.

$$\begin{array}{c} 1 (0.75 \text{ mol }\%) \\ 1 (0.75 \text{ mol }\%) \\ \underline{L1} (10 \text{ mol }\%) \\ C_6H_5CI, 130 \ ^\circ C \\ -NH_3 \ ^\circ MeO \ 4c \ ^\circ MeO \ ^\circ$$

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).<sup>19</sup> 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 a column chromatography on silica gel, and was analyzed by <sup>13</sup>C NMR. The most pronounced carbon isotope effect was observed on the  $\alpha$ -carbon of the product **4c** when the <sup>13</sup>C ratio of the product at three high conversions (86-89%) was compared with the sample obtained at low conversions (12-15%) [(average of <sup>13</sup>C at 87% conversion)/(average of <sup>13</sup>C at 13% conversion) at C(1) = 1.015(2)] (Table S2, SI).

The significant carbon isotope effect on the  $\alpha$ -CH<sub>2</sub> carbon is consistent with the C-N bond cleavage turnoverlimiting step. In support of this notion, Singleton and coworkers showed that the observation of 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.<sup>19c</sup> While C-N bond cleavage has been found to be the turnover limiting step for a number of chemical and biochemical coupling reactions,<sup>20</sup> 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 Hofmann elimination para-substituted reaction of (2-phenylethyl)trimethylammonium bromides, which indicated an E2 mechanism involving C-N bond cleavage step.<sup>21</sup> In a urease-catalyzed hydrolysis of hydroxyurea, Cleland and coworkers observed the 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.<sup>22</sup>

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<sub>3</sub>) 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<sub>6</sub>Me<sub>6</sub>) as analyzed by <sup>1</sup>H NMR. The  $k_{obs}$  for each catalytic run was determined from а first order plot of  $ln[(benzylamine)_t/(benzylamine)_0]$  vs time. The Hammett

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plot of  $\log(k_X/k_H)$  vs  $\sigma_p$  showed a linearly correlated pattern with  $\rho = -0.79 \pm 0.1$ . A relatively high negative slope suggests a significant cationic character build-up 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<sub>3</sub>).



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

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<sub>2</sub>Ar, 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.<sup>23</sup> In support of this notion, some oxidative C-N bond cleavage reactions are known to proceed via the formation of an imine intermediate.<sup>24</sup> 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.<sup>25</sup> 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  $\alpha$ -CH<sub>2</sub> of **5a** suggest that the dehydrogenation and hydrogen transfer steps are likely facile and reversible under the reaction conditions.

#### 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 Rucatechol species.<sup>26</sup> 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 glove box 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 <sup>1</sup>H, <sup>2</sup>H, <sup>13</sup>C, and <sup>31</sup>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 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 glove box, 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 to 10 minutes until the solution turned to a reddish green color. In an alternative procedure, the 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 mmol 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 glove box, and was 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 open to air, the solution was filtered through a short silica gel column by eluting with CH<sub>2</sub>Cl<sub>2</sub> (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 glove box, complex 1 (13 mg, 0.75 mol %), 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 was turned 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 glove box, 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<sub>2</sub>Cl<sub>2</sub> (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 glove box, 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 to 10 min until the solution was turned 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 glove box, 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<sub>2</sub>Cl<sub>2</sub> (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 glove box, 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 stirring for 5 to 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 glove box, and was stirred in an oil bath at 130 °C for 16 h. The product yield was determined by <sup>1</sup>H NMR by using hexamethylbenzene as an internal standard. The results are summarized in Table 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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 138 mg, 73%). TLC;  $R_f = 0.3$  (10% EtOAc in hexanes). Data for **3a**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.8, 128.3, 128.0, 126.7, 56.1, 51.0, 33.5, 26.1, 25.0 ppm; GC-MS for C<sub>13</sub>H<sub>19</sub>N, m/z = 189 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>27</sup>

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 a column chromatography on silica gel (nhexane/EtOAc = 100:1 to 10:1; 171 mg, 78%). TLC;  $R_f =$ 0.3 (20% EtOAc in hexanes). Data for 3b: 1HNMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.28

N-Cyclohexyl-4-fluorobenzenemethanamine (3c). А 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 a column chromatography on silica gel (nhexane/EtOAc = 100:1 to 10:1; 147 mg, 71%). TLC;  $R_f =$ 0.4 (20% EtOAc in hexanes). Data for 3c: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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;  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 161.7 (d,  $I_{CF} = 244.2$  Hz), 136.6 (d,  $I_{CF} = 3.1$  Hz), 129.5 (d,  $I_{CF} = 7.9 \text{ Hz}$ , 115.1 (d,  $I_{CF} = 21.2 \text{ Hz}$ ), 56.1, 50.2, 33.5, 26.1, 24.9 ppm; GC-MS for  $C_{13}H_{18}FN$ ,  $m/z = 207 (M^+)$ . <sup>1</sup>H and <sup>13</sup>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 %), 4trifluromethylbenzylamine (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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 152 mg, 59%). TLC;  $R_f = 0.4$  (20% EtOAc in hexanes). Data for **3d**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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;  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 145.1, 129.0 (q,  $J_{CF} = 32.2$  Hz), 128.2, 125.2 (q,  $J_{CF} = 3.8$ Hz), 124.3 (q, J<sub>CF</sub> = 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>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

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stirred at 130 °C for 16 h. The product **3e** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 158 mg, 57%). TLC;  $R_f = 0.4$  (20% EtOAc in hexanes). Data for **3e**: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>16</sub>H<sub>18</sub>ClNO, m/z = 275 (M<sup>+</sup>). HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>18</sub>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 a column chromatography on silica gel (n-hexane/EtOAc = 100:1 to 10:1; 176 mg, 66%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for 3f: 1HNMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C19H25NH 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-pheylbenzylamine (183 mg, 1.0 mmol) and 1,3benzodioxol-5-ylmethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product 3g was isolated by a column chromatography on silica gel (n-hexane/EtOAc = 100:1 to 10:1; 178 mg, 56%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for 3g: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>2</sub>H 318.1489, Found 318.1486.

N-(4-(Trifluoromethyl)benzyl)hexan-1-amine (3h). A 42 chlorobenzene (2.0 mL) solution of complex 1 (13 mg, 0.75 43 %), L1 (16 mg, 10 mol %), mol 4-44 trifluromethylbenzylamine (175 mg, 1.0 mmol) and 1-45 hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 46 h. The product **3h** was isolated by a column chromatog-47 raphy on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 14248 mg, 55%). TLC;  $R_f = 0.4$  (20% EtOAc in hexanes). Data for 49 **3h**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (d, J = 8.2 Hz, 2H), 50 7.44 (d, I = 8.2 Hz, 2H), 3.84 (s, 2H), 2.61 (t, I = 7.2 Hz, 51 2H), 1.58 (br s, 1H), 1.55-1.46 (m, 2H), 1.37-1.22 (m, 6H), 52 0.91-0.84 (m, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 144.6, 129.1 (q, J<sub>CF</sub> = 32.3 Hz), 128.3, 125.3 (q, J<sub>CF</sub> = 3.8 53 Hz), 124.2 (q,  $I_{CF} = 272.0$  Hz), 53.5, 49.5, 31.7, 30.0, 27.0, 54 22.6, 14.0; GC-MS for  $C_{14}H_{20}F_3N$ , m/z = 259 (M<sup>+</sup>); HRMS 55 (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>20</sub>F<sub>3</sub>NH 260.1621; 56 Found 260.1627. 57

**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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 149 mg, 72%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for **3i**: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>12</sub>H<sub>17</sub>NO<sub>2</sub>, m/z = 207 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>31</sup>

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-flurobenzylamine (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 a column chromatography on silica gel (n-hexane/EtOAc = 100:1 to 10:1; 132 mg, 63%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for 3j: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 161.8 (d, J<sub>CF</sub> = 244.6 Hz), 136.2 (d,  $J_{CF} = 3.1 \text{ Hz}$ ), 129.6 (d,  $J_{CF} = 7.9 \text{ Hz}$ ), 115.0 (d, J<sub>CF</sub> = 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>20</sub>FNH 210.1653; Found 260.1654.

N-(4-fluorobenzvl)-N-(4-methoxybenzvl)amine (3k). A chlorobenzene (2.0 mL) solution of complex 1 (13 mg, 0.75 mol %), L1 (16 mg, 10 mol %), 4-flurobenzylamine (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 a column chromatography on silica gel (nhexane/EtOAc = 100:1 to 10:1; 162 mg, 66%). TLC;  $R_f =$ 0.3 (20% EtOAc in hexanes). Data for 3k: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.29 (m, 2H), 7.27 (d, J = 8.3 Hz, 2H), 7.06–6.99 (m, 2H), 6.90 (d, I = 8.3 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 2H), 3.74 (s, 2H), 1.78 (br s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.8 (d, *J*<sub>CF</sub> = 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; GC-MS for  $C_{15}H_{16}FNO$ , m/z = 245 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>32</sup>

# *N*-[(4-fluorophenyl)methyl]-4-methoxy-

**benzeneethanamine (31).** A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4-flurobenzylamine (125 mg, 1.0 mmol) and 4-methoxybenzeneethanamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **31** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 142 mg, 55%). TLC; R<sub>f</sub> = 0.3 (20% EtOAc in hexanes). Data for **31**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 161.8 (d, *J*<sub>CF</sub> = 244.6 Hz), 157.9, 135.8 (d, *J*<sub>CF</sub> = 3.1 Hz), 131.8, 129.5, 129.5 (d, *J*<sub>CF</sub> = 7.9 Hz), 115.0 (d, *J*<sub>CF</sub> = 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for  $C_{16}H_{18}FNOH$  260.1445; Found 260.1439.

#### *N*-[(4-Fluorophenyl)methyl]-β-

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methylbenzeneethanamine (3m). A chlorobenzene (2.0 mL) solution of complex 1 (13 mg, 0.75 mol %), L1 (16 mg, 10 mol %), 4-flurobenzylamine (125 mg, 1.0 mmol) and  $\beta$ methylphenethylamine (189 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3m** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 141 mg, 58%). TLC;  $R_f = 0.4$  (20% EtOAc in hexanes). Data for 3m: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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, I = 7.0 Hz, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.7 (d,  $J_{CF}$  = 244.2 Hz), 145.1, 135.8 (d, *J*<sub>CF</sub> = 3.1 Hz), 129.4 (d, *J*<sub>CF</sub> = 7.9 Hz), 128.5, 127.1, 126.3, 115.0 (d,  $J_{CF} = 21.2 \text{ Hz}$ ), 56.1, 52.9, 39.9, 20.0 ppm; GC-MS for  $C_{16}H_{18}FN$ , m/z = 243 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>18</sub>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 %), 4methoxybenzeneethanamine (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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 169mg, 70%). TLC;  $R_f = 0.3$  (10% EtOAc in hexanes). Data for **3n**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37–7.23 (m, 5H), 7.15 (d, *I* = 8.3 Hz, 2H), 6.86 (d, *I* = 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;  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.33

N-(4-Methoxyphenethyl)hexan-1-amine (30). 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 **30** was isolated by a column chromatography on silica gel (nhexane/EtOAc = 100:1 to 10:1; 119 mg, 51%). TLC;  $R_f =$ 0.3 (10% EtOAc in hexanes). Data for 30: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.12 (d, I = 8.7 Hz, 2H), 6.83 (d, I = 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>15</sub>H<sub>25</sub>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 %), 4methoxybenzeneethanamine (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 a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 187 mg, 80%). TLC; R<sub>f</sub> = 0.3 (20% EtOAc in hexanes). Data for **3p**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.10 (d, I = 8.7 Hz, 2H), 6.81 (d, I = 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>15</sub>H<sub>23</sub>NO, m/z = 233 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>23</sub>NOH 234.1852; Found 234.1854.

#### N-(4-Methoxyphenethyl)-2,3-dihydro-1H-inden-2-

**amine (3q).** A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** (16 mg, 10 mol %), 4methoxybenzeneethanamine (151 mg, 1.0 mmol) and 2aminoindane (186 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3q** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 144 mg, 54%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for **3q**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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* = 7.2 Hz, 2H), 2.96–2.90 (m, 2H), 2.82–2.70 (m, 4H), 1.67 (br s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 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<sub>18</sub>H<sub>21</sub>NO, m/z = 267 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>21</sub>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 a column chromatography on silica gel (n-hexane/EtOAc = 100:1 to 10:1; 186 mg, 65%). TLC; R<sub>f</sub> = 0.3 (20% EtOAc in hexanes). Data for 3r: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>23</sub>NO<sub>2</sub>H 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 %), 4methoxybenzeneethanamine (151 mg, 1.0 mmol) and  $(\pm)$ 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 a column chromatography on silica gel (nhexane/EtOAc = 100:1 to 10:1; 208 mg, 73%. TLC;  $R_f = 0.3$ (20% EtOAc in hexanes). Data for 3s: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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, I = 6.3 Hz, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>25</sub>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

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mol %), L1 (16 mg, 10 mol %). methoxybenzeneethanamine (151 mg, 1.0 mmol) and 4methoxybenzylamine (192 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product 3t was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 149 mg, 55%). TLC; R<sub>f</sub> = 0.3 (20% EtOAc in hexanes). Data for **3t**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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  $(t, I = 7.1 \text{ Hz}, 2\text{H}), 1.71 \text{ (br s, 1H) ppm; } {}^{13}\text{C}{}^{1}\text{H} \text{NMR} (100)$ MHz, CDCl<sub>3</sub>) δ 158.5, 157.9, 132.3, 131.9, 129.5, 129.2, 10 113.7, 113.6, 55.1, 55.1, 53.2, 50.6, 35.2 ppm; GC-MS for 11  $C_{17}H_{21}NO_2$ , m/z = 271 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data 12 were in good agreement with the literature values.33 13

N-(3-Fluorophenethyl)-2,3-dihydro-1H-inden-2-amine (3u). A chlorobenzene (2.0 mL) solution of complex 1 (13 mg, 0.75 mol %), L1 (16 mg, 10 mol %), 2-(3fluorophenyl)ethylamine (139 mg, 1.0 mmol) and 2aminoindane (186 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3u** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 193 mg, 76%). TLC;  $R_f = 0.4$  (10% EtOAc in hexanes). Data for **3u**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.3-7.24 (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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.8 (d, *J*<sub>CF</sub> = 245.5 Hz), 142.5 (d, *J*<sub>CF</sub> = 7.2 Hz), 141.5, 129.8 (d, J<sub>CF</sub> = 8.3 Hz), 126.4, 124.6, 124.3 (d, J<sub>CF</sub> = 2.7 Hz), 115.4 (d, J<sub>CF</sub> = 20.8 Hz), 113.0 (d, J<sub>CF</sub> = 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>18</sub>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 a column chromatography on silica gel (n-hexane/EtOAc = 100:1 to 10:1; 157 mg, 58%). TLC; R<sub>f</sub> = 0.3 (20% EtOAc in hexanes). Data for 3v: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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, I = 6.6 Hz, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.8 (d, *J*<sub>CF</sub> = 245.4 Hz), 158.5, 142.6 (d, *J*<sub>CF</sub> = 7.2 Hz), 137.3, 129.7 (d, J<sub>CF</sub> = 8.3 Hz), 127.5, 124.3 (d, J<sub>CF</sub> = 2.7 Hz), 115.4 (d, J<sub>CF</sub> = 20.9 Hz), 113.7, 112.9 (d, J<sub>CF</sub> = 21.0 Hz), 57.5, 55.2, 48.5, 36.1 (d, J<sub>CF</sub> = 1.7 Hz), 24.2 ppm; GC-MS for  $C_{17}H_{20}FNO$ , m/z = 273 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C<sub>17</sub>H<sub>20</sub>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-5yl)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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 138 mg, 59%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for **3w**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl3) & 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<sub>14</sub>H<sub>19</sub>NO<sub>2</sub>, m/z = 233 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>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 1.0 mmol) and (R)-(+)-1-(4mg, methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3x** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 171 mg, 60%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for 3x: 1H NMR (400 MHz, CDCl<sub>3</sub>) 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, I = 13.2 Hz, 2H), 1.70 (br s, 1H), 1.34 (d, I= 6.6 Hz, 3H) ppm;  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>19</sub>NO<sub>3</sub>H 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 and (151)1.0 mmol)  $(\pm)-1-(4$ mg, methoxyphenyl)ethylamine (211 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3y** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 152 mg, 56%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for 3y: 1H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35-7.28 (m, 2H), 7.24–7.18 (m, 3H), 6.75 (d, I = 1.6 Hz, 2H), 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;  $^{13}\text{C}\{^{1}\text{H}\}$  NMR (100 MHz, CDCl3)  $\delta$  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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>19</sub>NO<sub>2</sub>H 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-1naphthalenamine (147 mg, 1.0 mmol) 1-hexamine (141 mg, 1.4 mmol) was stirred at 130 °C for 16 h. The product **3z** was isolated by a column chromatography on silica gel (n-hexane/EtOAc = 100:1 to 10:1; 106 mg, 46%). TLC; R<sub>f</sub> = 0.3 (10% EtOAc in hexanes). Data for 3z: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) & 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>25</sub>NH 232.2060; Found 232.2053.

N-[2-(4-Methoxyphenyl)ethyl]-1,2,3,4-tetrahydro-1naphthalenamine (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 a column chromatography on silica gel (nhexane/EtOAc = 100:1 to 10:1; 177 mg, 63%). TLC; R<sub>f</sub> = 0.3 (10% EtOAc in hexanes). Data for 3aa: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>19</sub>H<sub>23</sub>NO, m/z = 281 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>23</sub>NOH 282.1852; Found 282.1843.

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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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 218 mg, 80%). TLC;  $R_f = 0.2$  (30% EtOAc in hexanes). Data for 3bb: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>24</sub>FN<sub>2</sub>OH 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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 124 mg, 69%). TLC;  $R_f = 0.3$  (10% EtOAc in hexanes). Data for 3cc: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 152 mg, 69%). TLC; R<sub>f</sub> = 0.3 (20% EtOAc in hexanes). Data for **3dd**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>); Anal. Calcd for  $C_{14}H_{21}NO$ : C, 76.67; H, 9.65. Found: C, 76.78; H, 9.35; HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for  $C_{14}H_{21}NOH$  220.1696; Found 220.1698.

**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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 88 mg, 89%). TLC;  $R_f = 0.3$  (10% EtOAc in hexanes). Data for **4a**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.42–7.24 (m, 10H), 3.84 (s, 4H), 2.08 (br s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.0, 128.4, 128.1, 126.9, 53.0 ppm; GC-MS for C<sub>14</sub>H<sub>15</sub>N, m/z = 197 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>36</sup>

**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 a column chromatography on silica gel (*n*-hexane/ethyl acetate = 100:1 to 10:1; 106 mg, 94%). TLC;  $R_f = 0.4$  (20% EtOAc in hexanes). Data for **4b**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.2, 136.4, 129.0, 128.1, 52.7, 21.1 ppm; GC-MS for C<sub>16</sub>H<sub>19</sub>N, m/z = 225 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>36,37</sup>

**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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 111 mg, 86%). TLC; R<sub>f</sub> = 0.3 (10% EtOAc in hexanes). Data for **4c** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.5, 132.4, 129.2, 113.6, 55.1, 52.3 ppm; GC-MS for C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub>, m/z = 257 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>36,37</sup>

*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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 122 mg, 92%). TLC; R<sub>f</sub> = 0.5 (10% EtOAc in hexanes). Data for 4d <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33–7.28 (m, 8H), 3.76 (s, 4H), 1.64 (br s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.5, 132.6, 129.4, 128.5, 52.2 ppm; GC-MS for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>N, m/z = 265 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>37,38</sup>

*N*-([1,1'-Biphenyl]-4-ylmethyl)-[1,1'-biphenyl]-4methanamine (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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 148 mg, 85%). TLC;  $R_f = 0.5$  (20% EtOAc in hexanes). Data for 4e <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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,

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4H), 1.65 (br s, 1H) ppm;  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sup>+</sup>).  ${}^{1}H$  and  ${}^{13}C$  NMR spectral data were in good agreement with the literature values.<sup>39</sup>

# 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-phenylbenzylamine (125 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product 4f was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 106 mg, 91%). TLC; R<sub>f</sub> = 0.4 (20% EtOAc in hexanes). Data for 4f <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36–7.28 (m, 4H), 7.07–6.99 (m, 4H), 3.78 (s, 4H), 1.67 (br s, 1H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.8 (d, *J*<sub>CF</sub> = 244.5 Hz), 135.8 (d, *J*<sub>CF</sub> = 3.1 Hz), 129.6 (d, *J*<sub>CF</sub> = 8.0 Hz), 115.1 (d, *J*<sub>CF</sub> = 21.3 Hz), 52.3 ppm; GC-MS for C<sub>14</sub>H<sub>13</sub>F<sub>2</sub>N, m/z = 233 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>38</sup>

# 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 a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 140 mg, 84%). TLC; R<sub>f</sub> = 0.5 (20% EtOAc in hexanes). Data for 4g <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64–7.57 (m, 4H), 7.51–7.46 (m, 4H), 3.88 (s, 4H), 1.75 (br s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.1, 129.4 (q, *J*<sub>CF</sub> = 32.4 Hz), 128.3, 125.3 (q, *J*<sub>CF</sub> = 3.8 Hz), 124.2 (q, *J*<sub>CF</sub> = 271.8 Hz), 52.6 ppm; GC-MS for C<sub>16</sub>H<sub>13</sub>F<sub>6</sub>N, m/z = 333 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>38,40</sup>

**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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 108 mg, 84%). TLC; R<sub>f</sub> = 0.3 (10% EtOAc in hexanes). Data for **4h** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.6, 141.9, 129.3, 120.4, 113.5, 112.4, 55.1, 53.0 ppm; GC-MS for C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub>, m/z = 257 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>36</sup>

*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 a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 118 mg, 89%). TLC; R<sub>f</sub> = 0.3 (10% EtOAc in hexanes). Data for 4i <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37–7.34 (m, 2H), 7.29–7.19 (m, 6H), 3.77 (s, 4H), 1.65 (br s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 142.1, 134.2, 129.6, 128.1, 127.2, 126.2, 52.5 ppm; GC-MS for C<sub>14</sub>H<sub>13</sub>Cl<sub>2</sub>N, m/z = 265 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>41</sup>

**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-5yl)methanamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4j** was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 110 mg, 77%). TLC;  $R_f = 0.4$  (40% EtOAc in hexanes). Data for **4j** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.85 (s, 2H), 6.77–6.75 (m, 4H), 5.94 (s, 4H), 3.69 (s, 4H), 1.59 (br s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.7, 146.5, 134.3, 121.2, 108.7, 108.0, 100.9, 52.7 ppm; GC-MS for C<sub>16</sub>H<sub>15</sub>NO<sub>4</sub>, m/z = 285 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>4</sub>H 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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 115 mg, 61%). TLC; R<sub>f</sub> = 0.3 (50% EtOAc in hexanes). Data for **4k** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 6.56 (s, 4H), 3.84 (s, 12H), 3.81 (s, 6H), 3.74 (s, 4H), 1.80 (br s, 1H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 153.1, 136.6, 135.8, 104.7, 60.7, 55.9, 53.3 ppm; GC-MS for C<sub>20</sub>H<sub>27</sub>NO<sub>6</sub>, m/z = 377 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>27</sub>NO<sub>6</sub>H 378.1911; Found 378.1892.

4-Methoxy-N-[(1R)-1-(4-methoxyphenyl)ethyl]- $\alpha$ methyl-(*aR*)-benzenemethanamine (4l). A chlorobenzene (2.0 mL) solution of complex **1** (13 mg, 0.75 mol %), **L1** mol %) and (16)mg, 10 (R)-(+)-1-(4methoxyphenyl)ethylamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product 4l was isolated by a column chromatography on silica gel (*n*-hexanes/EtOAc = 100:1 to 10:1; 107 mg, 75%), 7:1 mixture of diastereomers,  $[\alpha]_{D}^{22} = -211.1$  (c = 0.12 in CH<sub>2</sub>Cl<sub>2</sub>); TLC; R<sub>f</sub> = 0.3 (20% EtOAc in hexanes). Data for 41 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>42</sup>

# 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 4methoxybenzeneethanamine (151 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4m** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 127 mg, 89%). TLC;  $R_f = 0.3$  (10% EtOAc in hexanes). Data for 4m <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>23</sub>NO<sub>2</sub>H 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 (139 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4n** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 128 mg, 90%. TLC;  $R_f = 0.3$ 

(10% EtOAc in hexanes). Data for **4n** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.6, 141.4, 129.4, 121.0, 114.3, 111.5, 55.1, 50.9, 36.2 ppm; GC-MS for C<sub>18</sub>H<sub>23</sub>NO<sub>2</sub>, m/z = 285 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>23</sub>NO<sub>2</sub>H 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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 114 mg, 87%). TLC; R<sub>f</sub> = 0.4 (10% EtOAc in hexanes). Data for 4o <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.9 (d, *J*<sub>CF</sub> = 245.7 Hz), 142.3 (d, *J*<sub>CF</sub> = 7.1 Hz), 129.9 (d, *J*<sub>CF</sub> = 8.3 Hz), 124.3 (d, *J*<sub>CF</sub> = 2.8 Hz), 115.4 (d, *J*<sub>CF</sub> = 20.9 Hz), 113.1 (d, *J*<sub>CF</sub> = 21.0 Hz), 50.6, 35.9 (d, *J*<sub>CF</sub> = 1.4 Hz) ppm; GC-MS for C<sub>16</sub>H<sub>17</sub>F<sub>2</sub>NH 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 a column chromatography on silica gel (*n*-hexane/ethyl acetate = 100:1 to 10:1; 118 mg, 93%), 1.15:1 mixture of diastereomers. TLC;  $R_f = 0.5$  (30% EtOAc in hexanes). Data for **4p** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 145.1, 128.5, 127.0, 126.2, 56.7, 39.5, 19.8 ppm; GC-MS for C<sub>18</sub>H<sub>23</sub>N, m/z = 253 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>43</sup>

#### 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  $\alpha$ -methylbenzenepropanamine (149 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4p** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 126 mg, 90%), 1:1 mixture of diastereomers. TLC;  $R_f = 0.5$  (40% EtOAc in hexanes). Data for 4q <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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<sub>3</sub>)  $\delta$  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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 91 mg, 73%). TLC;  $R_f = 0.5$  (20% EtOAc in hexanes).

Data for **4r** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.5, 126.3, 124.5, 58.1, 40.2 ppm; GC-MS for C<sub>18</sub>H<sub>19</sub>N, m/z = 249 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>19</sub>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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 86 mg, 95%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for **4s** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  52.8, 34.1, 26.0, 25.1 ppm; GC-MS for  $C_{12}H_{23}N$ , m/z = 181 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>45,46</sup>

*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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 106 mg, 89%). TLC;  $R_f = 0.4$  (30% EtOAc in hexanes). Data for 4t <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 142.2, 126.8, 125.0, 123.5, 50.7, 30.2 ppm; GC-MS for C<sub>12</sub>H<sub>15</sub>NS<sub>2</sub> m/z = 237 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>15</sub>NS<sub>2</sub>H 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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 40 mg, 43%). TLC;  $R_f = 0.3$  (30% EtOAc in hexanes). Data for **4u**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  50.0, 31.7, 29.8, 27.1, 22.6, 14.0 ppm; GC-MS for C<sub>12</sub>H<sub>27</sub>N, m/z = 185 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>46,47</sup>

*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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 30 mg, 46%). TLC;  $R_f = 0.3$  (30% EtOAc in hexanes). Data for **4v**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  49.6, 32.1, 20.2, 13.7 ppm; GC-MS for C<sub>8</sub>H<sub>19</sub>N, m/z = 129 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>47</sup>

*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 a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 70 mg, 79%). TLC;  $R_f = 0.3$ 

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(30% EtOAc in hexanes). Data for 4w: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>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-1propanamine (135 mg, 1.0 mmol) was stirred at 130 °C for 16 h. The product **4x** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1; 53mg, 42%). TLC;  $R_f = 0.3$  (30% EtOAc in hexanes). Data for **4x**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34–7.14 (m, 10H), 2.65 (t, J = 7.4 Hz, 8H), 1.89 (brs, 1H), 1.84 (quintet, J = 7.4 Hz, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.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 4methoxybenzylamine (96 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product 5a was isolated by a column chromatography on silica gel (n-hexane/EtOAc = 150:1 to 40:1; 76 mg, 71%). TLC;  $R_f = 0.4$  (30% EtOAc in hexanes). Data for **5a**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>49,50</sup>

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 a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 61 mg, 57%). TLC;  $R_f = 0.3$  (20% EtOAc in hexanes). Data for **5b**: <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>51,52</sup>

# N-(4-Methoxyphenyl)[1,1'-biphenyl]-4-methanamine

46 (5c). A chlorobenzene (2.0 mL) solution of complex 1 (7 47 mg, 0.75 mol %), L1 (8 mg, 10 mol %), 4-methoxyaniline 48 (62 mg, 0.5 mmol) and 4-phenylbenzylamine (128 mg, 0.7 49 mmol) was stirred at 140 °C for 20 h. The product 5c was 50 isolated by a column chromatography on silica gel (n-51 hexane/ethyl acetate = 150:1 to 40:1; 101 mg, 70%). TLC; 52  $R_f = 0.4$  (30% EtOAc in hexanes). Data for **5c**: <sup>1</sup>H NMR (400 53 MHz, CDCl<sub>3</sub>) δ 7.61–7.55 (m, 4H), 7.47–7.42 (m, 4H), 7.35 54 (tt, J = 7.3, 1.3, Hz, 1H), 6.82–6.77 (m, 2H), 6.69–6.65 (m, 55 2H), 4.34 (s, 2H), 3.75 (s, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 56 MHz, CDCl<sub>3</sub>) δ 152.5, 141.7, 140.8, 140.2, 138.3, 128.7, 57 128.1, 127.3, 127.2, 127.0, 114.9, 114.6, 55.8, 49.2 ppm; GC-MS for  $C_{20}H_{19}NO m/z = 289 (M^+)$ . <sup>1</sup>H and <sup>13</sup>C NMR 58

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 a column chromatography on silica gel (nhexane/EtOAc = 150:1 to 40:1; 47 mg, 41%). TLC;  $R_f = 0.3$ (20% EtOAc in hexanes). Data for **5d**: <sup>1</sup>H NMR (400 MHz. CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 162.0 (d,  $J_{CF} = 245.1 \text{ Hz}$ ), 152.4, 141.7, 135.0 (d,  $J_{CF} = 3.1 \text{ Hz}$ ), 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>54,55</sup>

#### 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 a column chromatography on silica gel (nhexane/EtOAc = 150:1 to 40:1; 73 mg, 59%). TLC; R<sub>f</sub> = 0.5(20% EtOAc in hexanes). Data for 5e: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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  $C_{14}H_{14}CINO$ , m/z = 247 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>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 a column chromatography on silica gel (*n*-hexane/EtOAc =150:1 to 40:1; 138 mg, 91%). TLC;  $R_f = 0.5$  (50% EtOAc in hexanes). Data for 5f: 1H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>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 a column chromatography on silica gel (nhexane/EtOAc = 150:1 to 40:1; 97 mg, 71%). TLC;  $R_f = 0.6$ (50% EtOAc in hexanes). Data for 5g: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.23–7.17 (m, 2H), 6.75 (tt, I = 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>16</sub>H<sub>19</sub>NO<sub>3</sub>, m/z = 273 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>59,60</sup>

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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 a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 111 mg, 72%). TLC;  $R_f = 0.6$  (50% EtOAc in hexanes). Data for **5h**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>16</sub>H<sub>18</sub>ClNO<sub>3</sub>; m/z = 307 (M<sup>+</sup>). Anal. Calcd for C<sub>16</sub>H<sub>18</sub>ClNO<sub>3</sub>: 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 a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 65 mg, 63%). TLC; R<sub>f</sub> = 0.4 (20% EtOAc in hexanes). Data for 5i: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>13</sub>H<sub>21</sub>NO, m/z = 207 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>58</sup>

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 a column chromatography on silica gel (nhexane/EtOAc = 150:1 to 40:1; 54 mg, 45%). TLC;  $R_f = 0.9$ (50% EtOAc in hexanes). Data for 5i: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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, I = 7.6 Hz, 2H), 1.96 (quintet, I = 7.4Hz, 2H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.61,62

# N-(4-Methoxyphenyl)-2,3-dihydro-1H-inden-2-amine

(5k). A chlorobenzene (2.0 mL) solution of complex 1 (7 mg, 0.75 mol %), L1 (8 mg, 10 mol %), 3,4,5-trimethoxyaniline (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 a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 88 mg, 74%). TLC;  $R_f = 0.5$  (30% EtOAc in hexanes). Data for 5k: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for  $C_{16}H_{17}NOH$  240.1383; Found 240.1377.

**4-(2-(3,4,5-Trimethoxyphenylamino)ethyl)phenol (51).** 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 **51** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 77 mg, 51%). TLC; R<sub>f</sub> = 0.4 (50% EtOAc in hexanes). Data for **51**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>, m/z = 303 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>21</sub>NO<sub>4</sub>H 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-2H-1,5-benzodioxepin-7-(83 0.5 mmol) and 3,4,5amine mg, trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 140 °C for 20 h. The product 5m was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 129 mg, 75%). TLC;  $R_f = 0.4$  (50% EtOAc in hexanes). Data for **5m**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.84 (d, I = 8.6Hz, 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, I = 5.5 Hz, 2H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>23</sub>FNO<sub>5</sub>H 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 a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 115 mg, 84%). TLC; R<sub>f</sub> = 0.7 (50% EtOAc in hexanes). Data for **5n**:  $\delta$  <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>16</sub>H<sub>19</sub>NO<sub>3</sub>, m/z = 273 (M<sup>+</sup>). <sup>1</sup>H and <sup>13</sup>C NMR spectral data were in good agreement with the literature values.<sup>63</sup>

**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 a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 66 mg, 48%). TLC; R<sub>f</sub> = 0.6 (30% EtOAc in hexanes). Data for **5o**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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

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 $C_{15}H_{16}ClNO_2$ , m/z = 277 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> 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-trifluoromethylaniline (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 a column chromatography on silica gel (*n*-hexane/EtOAc =150:1 to 40:1; 58 mg, 37%). TLC;  $R_f = 0.4$  (30% EtOAc in hexanes). Data for **5p**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>CF</sub> = 32.6 Hz), 112.1 105.2, 99.1, 55.3, 48.0 ppm; GC-MS for  $C_{16}H_{16}F_{3}NO_{2}$ , m/z = 311 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H6F<sub>3</sub>NO<sub>2</sub>H 312.1206; Found 312.1207.

9-Ethyl-N-hexyl-9H-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 a column chromatography on silica gel (*n*-hexane/EtOAc = 150:1 to 40:1; 103 mg, 70%). TLC;  $R_f = 0.4$  (50% EtOAc in hexanes). Data for 5q: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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;  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 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<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]+ Calcd for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>H 295.2169; Found 295.2167.

# (R)-3-Ethyl-3-(4-(3,4,5-

38 trimethoxybenzylamino)phenyl)piperidine-2,6-dione (5r). 39 A chlorobenzene (2.0 mL) solution of complex 1 (7 mg, 0.75 mol %), L1 (8 mg, 10 mol %), (R)-(+)-40 aminoglutethimide (116 mg, 0.5 mmol) and 3,4,5-41 trimethoxybenzylamine (138 mg, 0.7 mmol) was stirred at 42 140 °C for 20 h. The product 5r was isolated by a column 43 chromatography on silica gel (n-hexane/ethyl acetate = 44 100:1 to 1:1; 82 mg, 40%),  $[\alpha]_D^{22} = +148.2$  (c = 0.2 in 45 CH<sub>2</sub>Cl<sub>2</sub>); TLC;  $R_f = 0.2$  (50% EtOAc in hexanes). Data for **5r**: 46 δ 7.98 (br s, 1H), 7.07 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 8.7 47 Hz, 2H), 6.59 (s, 2H), 4.24 (s, 2H), 3.83 (s, 9H), 2.62-2.52 48 (m, 1H), 2.44 (dd, J = 13.2, 4.9 Hz, 1H), 2.31 (ddd, J = 14.2, 49 4.8, 2.7 Hz, 1H), 2.16 (dd, *J* = 13.8, 4.8 Hz, 1H), 1.99 (sext, *J* 50 = 7.4 Hz, 1H), 1.87 (sextet, *J* = 7.4 Hz, 1H), 0.85 (t, *J* = 7.4 51 Hz, 3H) ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 175.5, 52 172.5, 153.4, 147.0, 137.1, 134.5, 127.1, 113.4, 113.4, 53 104.4, 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<sup>+</sup>); HRMS (IT-TOF/ESI) 54 Calcd for C<sub>23</sub>H<sub>28</sub>N<sub>2</sub>O<sub>5</sub>-H ([M-H]<sup>-</sup>): 411.1925, Found: 55 411.1908. 56

**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 a column chromatography on silica gel (*n*-hexane/ethyl acetate = 50:1 to 1:1; 92 mg, 75%). TLC;  $R_f = 0.2$  (50% EtOAc in hexanes). Data for **5s**:  $\delta$  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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>, m/z = 246 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>H 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 a column chromatography on silica gel (*n*-hexane/ethyl acetate = 50:1 to 1:1; 87 mg, 70%). TLC;  $R_f = 0.2$  (50% EtOAc in hexanes). Data for **5t** 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; <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) 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<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>, m/z = 248 (M<sup>+</sup>); HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>H 249.1334; Found 249.1202.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, spectroscopic data and NMR spectra (PDF)

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# Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENT

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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