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Bi(OTf)$_3$-Catalyzed Multicomponent α-Amidoalkylation Reactions

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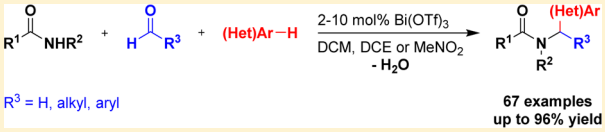
Supporting Information

ABSTRACT: A bismuth(III) triflate catalyzed three-component synthesis of α-substituted amides starting from amides, aldehydes, and (hetero)arenes is reported. The reaction has a broad substrate scope, encompassing formaldehyde as well as aryl and alkyl aldehydes. Low catalyst loadings are required, and water is formed as the only side product. The scope and limitation of this method will be discussed.



INTRODUCTION

Amino- and amidoalkyl moieties are important structural motifs in organic synthesis and pharmaceutical chemistry.[1−3] α-Substituted amides, in particular amidoalkylated arenes and heteroarenes, are found in many important natural products and biological active molecules such as luotonin A,[2] an alkaloid, or the antiretroviral Raltegravir[3] (Figure 1).

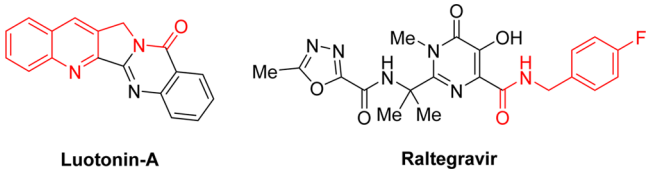


Figure 1. Amidoalkylated moieties in biologically active molecules.

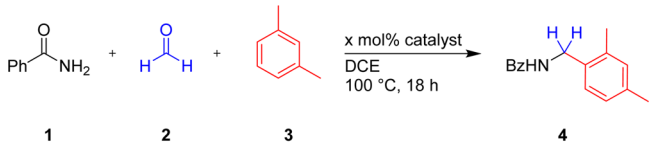
An important approach for the synthesis of this structural motif is the addition of nucleophilic (hetero)arenes to electrophilic carbon−nitrogen double bonds. In particular, three-component aza-Friedel−Crafts-type amidoalkylations with in situ generated acylimines or acyliminium ions provide a useful synthetic tool for the synthesis of α-substituted amides.[4,5] The in situ preparation of these reactive imine compounds from an aldehyde and an amide represents an atom-economical methodology[6] for the synthesis of amidoalkylated (hetero)-arenes. Generating water as the only side product, these reactions could meet the requirements of modern sustainable organic synthesis.[7] However, most common procedures require stoichiometric amounts of Lewis or Brønsted acids[8] or are limited to the reaction of electron-rich aromatics and heteroaromatics, such as indole and naphthol.[9−12]

Our interest in developing novel multicomponent reactions for the rapid synthesis of pharmaceutically active molecules[13−15] has led us to a closer examination of these three-component reactions. In the course of our investigations, we were able to develop a Bi(OTf)$_3$-catalyzed three-component reaction between amides, formaldehyde, and arenes. This reaction provides straightforward access to amidomethylated arenes and heteroarenes.[13] Recently, the group of Jaratjaroonphong reported a similar Bi(OTf)$_3$-catalyzed three-component reaction between carbamates, aldehydes, and arenes.[16] However, this reaction is limited to very electron-rich trimethoxybenzene derivatives or reactive heteroarenes such as furan, thiophene, or indole.[17] Herein, we report the extension of our method to aryl and alkyl aldehydes as well as the scope and limitations of the corresponding reactions and mechanistic investigations.

RESULTS AND DISCUSSION

1. Three-Component Reaction with Formaldehyde. We started our investigations with the identification of a suitable catalyst using the reaction between benzamide (**1**), paraformaldehyde (**2**), and *m*-xylene (**3**), a moderately reactive arene, as a test system (Table 1). From a multitude of tested metal triflates

Table 1. Formaldehyde: Survey of Catalysts[a,b]



1 1.0 equiv. **2** 1.2 equiv. **3** 3.0 equiv. **4**

entry	catalyst (mol %)	yield (%)
1	M(OTf)$_x$ (5.0) M = Cu, Zn, In, Sc, Mg, Yb, etc.	<5
2	$BiBr_3$ (5.0)	<5
3	$BiCl_3$ (5.0)	<5
4	Bi(OTf)$_3$ (1.0)[c,d]	71
5	Bi(OTf)$_3$ (2.5)[c,d]	85
6	Bi(OTf)$_3$ (5.0)[c]	61
7	Bi(OTf)$_3$ (5.0)[c,d]	84
8	Bi(OTf)$_3$ (5.0)[c,d,e]	79
9	TfOH (5.0)	10
10	Bi(OTf)$_3$ (5.0) + dbpy (10.0)[c,d]	75

[a]General reaction conditions: benzamide (1.0 equiv), paraformaldehyde (1.2 equiv), *m*-xylene (3.0 equiv), catalyst (*x* mol %). [b]Isolated yield of analytical pure product. [c]Obtained as a 15:1 mixture of regioisomers. [d]Reaction in $MeNO_2$. [e]Reaction with aqueous formalin.

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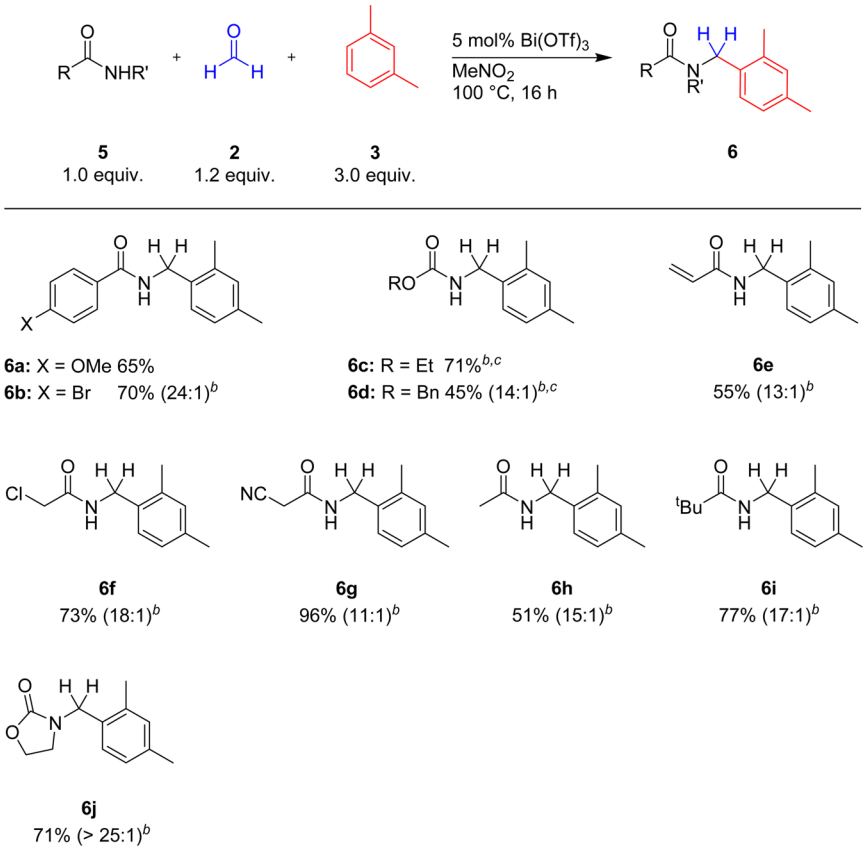
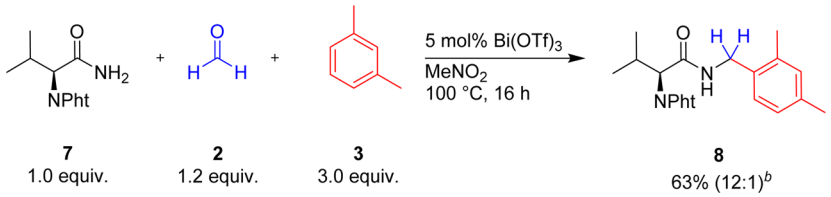
Scheme 1. Formaldehyde: Variation of Amides[a]



[a]Isolated yield of analytical pure product. [b]Obtained as a mixture of regioisomers; ratio of regioisomers given in parentheses. [c]Reaction at 60 °C.

Scheme 2. Reaction of Phthalyl-Protected Valinamide[a]



[a]Isolated yield of analytical pure product. [b]Obtained as a mixture of regioisomers; ratio of regioisomers given in parentheses.

and Bi(III) salts (entries 1–3) only $Bi(OTf)_3$ efficiently catalyzed the transformation even at low catalyst loadings (entries 4–8, 61–85% yield). Since $Bi(OTf)_3$ is commercially available, nontoxic, and air- and moisture-stable, it is a very attractive catalyst.[18−20] Performing the reaction in nitromethane led to an increased yield. Best results could be achieved with 2.5 mol % of $Bi(OTf)_3$ (entry 5, 85% yield). Replacement of paraformaldehyde by aqueous formalin solution as formaldehyde source furnished the product in comparable yield (entries 7 and 8). TfOH, a possible byproduct of the hydrolysis of $Bi(OTf)_3$, displayed reduced catalytic activity (entry 9). To exclude a possible hidden Brønsted acid catalysis, the reaction was performed in the presence of the selective proton scavenger 2,6-di-*tert*-butylpyridine (dbpy) (entry 10).[21] Since no significant decrease in catalytic activity was observed, the Bi(III) species is assumed to be the active catalyst.[22] In all cases, the amidoalkylated product was obtained as a mixture of regioisomers (15:1 *ortho/para*- vs *ortho/ortho*-substitution).

With the optimized conditions established, the scope of the reaction was examined (Scheme 1). Conversion of substituted benzamides led to the products **6a** and **6b** in 65−70% yield. With carbamates as amide component, the corresponding *N*-protected amidomethylarenes **6c** and **6d** were obtained in 45% and 71% yield, respectively. Deprotection of such products would offer a straightforward access to α-aminomethylarenes, which are found in various bioactive substances.[23] Reactions with various alkylamides furnished the corresponding amidoalkylated products in good to excellent yields. Acid-sensitive functionalities, such as an acrylamide, were well tolerated (product **6e**). With the exception of oxazolidin-2-one (product **6j**), secondary amides did not react under the standard conditions. Similar regioselectivities are observed for all different amide components.

In addition, highly functionalized amides are suitable substrates for this three-component reaction, Thus, the reaction of the protected valinamide **7** provided the amino acid derivate **8** in 63% yield (Scheme 2).[24]

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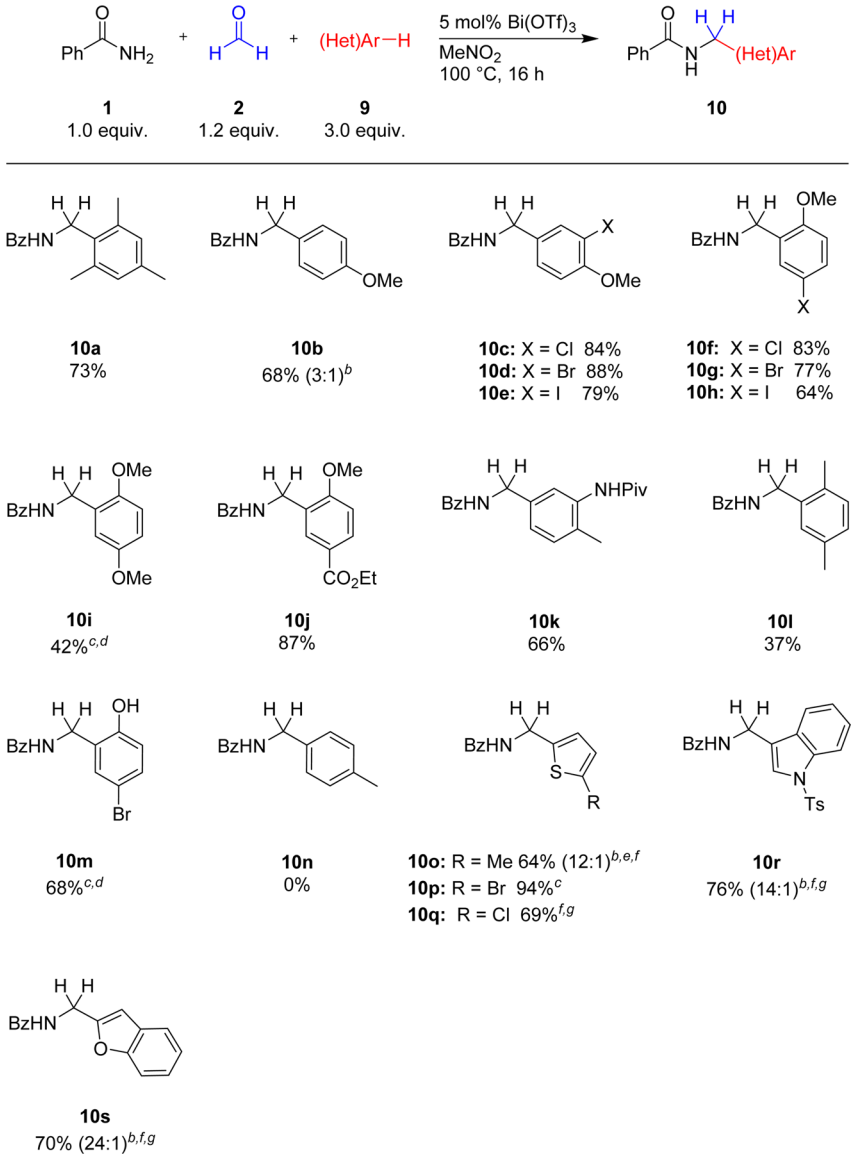
Scheme 3. Formaldehyde: Variation of (Hetero)arenes[a]



[a]Isolated yield of analytical pure product. [b]Obtained as mixture of regioisomers; ratio of regioisomers given in parentheses. [c]Reaction at 80 °C. [d]4.0 equiv of arene. [e]Reaction at rt. [f]Reaction with aqueous formalin. [g]Reaction at 40 °C.

Next, reactions with different aromatic components were examined. Various electron-rich arenes such as mesitylene, anisole, and its halogenated derivatives furnished the desired α-amidoalkylated products in good to excellent yields (**10a**–**h**, 42–88% yield). In general, the α-amidomethylated arenes were obtained with high regioselectivity. Only with anisole as arene was obtained a 1:3 mixture of *ortho*- and *para*-substituted regioisomers, typical for electrophilic aromatic substitutions.[25] Unprotected phenols or acid-labile ester functionalities were well tolerated under the reaction conditions (products **10m** and **10j**). The reaction with sterically hindered pivaloyl amide proceeded in a chemoselective manner, and the amidoalkylated product **10k** was obtained in 66% yield. Less electron-rich arenes, such as toluene or benzene, did not react even under more forcing conditions. In the case of electron-rich heteroarenes, lower reaction temperatures were required to avoid direct addition of the heteroarene to formaldehyde. Several electron-rich heteroaromatics gave the corresponding amidomethylated products in 33–94% yield (Scheme 3, products **10o**–**s**). For some of these reactions considerably higher yields could be obtained with aqueous formalin as aldehyde source (**10o**,**q**,**s**). Regioselective amidoalkylation at the more reactive 2-position over the 3-position was observed for benzofuran and thiophene.

1.1. Mechanistic Considerations. For the development of the three-component reaction, the in situ generation of a reactive acylimine species as electrophilic amidoalkylating agent was assumed to be the first crucial step. Therefore, we investigated the two-component reaction between formaldehyde and benzamide, which should lead to the corresponding acylimine or acyiminium ion. However, we were not able to detect or isolate any acylimine species.[26] The only product we could obtain from the two-component reaction was bisamide **11**, derived from a two-fold addition of benzamide to formaldehyde. This bisamide is formed very rapidly in almost quantitative yield (Scheme 4).

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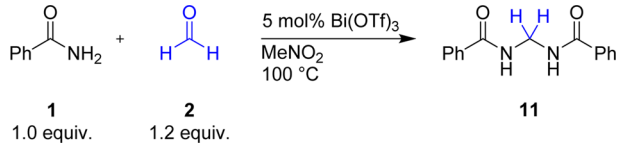
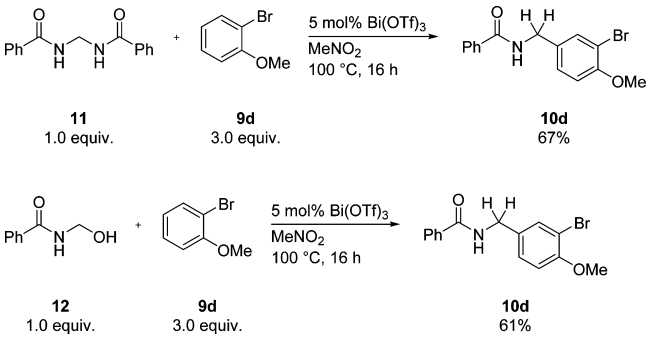
Scheme 4. Formation of Bisamide



In the case of the three-component reactions, we were able to observe the same rapid formation of the bisamide and a slower subsequent conversion of the bisamide to the product during the course of the reaction. It is worth mentioning that we could observe the formation of this bisamide during our initial catalyst screenings with almost every tested Lewis or Brønsted acid.[27] Some Brønsted acids, e.g., TfOH, could catalyze the bisamide formation even more efficiently than $Bi(OTf)_3$. Treatment of the bisamide **11** with 2-bromoanisole as the nucleophilic arene component in the presence of 5 mol % of $Bi(OTf)_3$ furnished the expected amidoalkylated product **10d** in 67% yield (Scheme 5).

Scheme 5. Two-Component Reactions with Preformed Acylimine Precursors



The analogous N,O-aminal **12**, the formal monoaddition product of benzamide to formaldehyde, reacts in a similar manner. Treatment of **12** with bromoanisole in the presence of 5 mol % of $Bi(OTf)_3$ leads to the formation of the amidoalkylation product in 61% yield. No other tested Lewis or Brønsted acid could catalyze those two transformations with comparable efficiency.

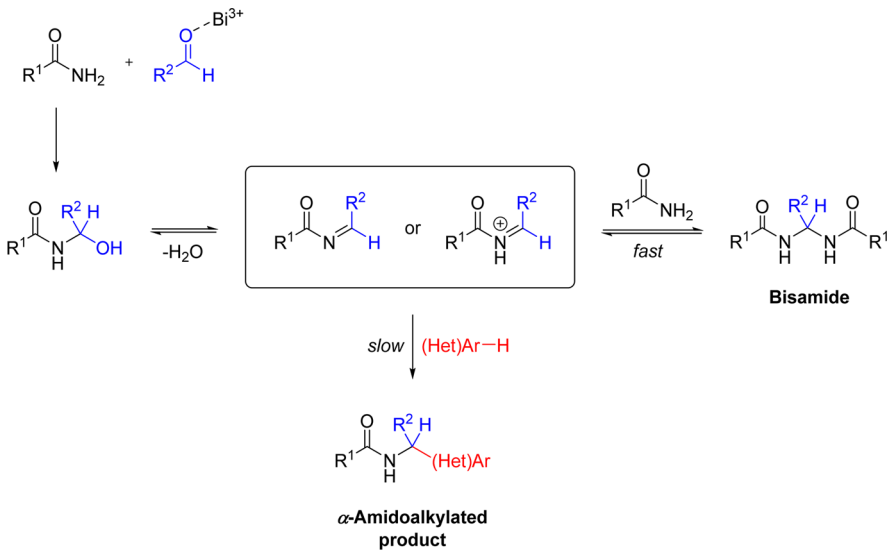
On the basis of those experiments, we assume the following mechanism as shown in Scheme 6. In the first step, the amide adds to the aldehyde to afford an aminal. Elimination of water leads to the formation of a reactive acylimine or acyliminium species.[28] This electrophilic species reacts immediately with a second molecule of the amide in aza-amidoalkylation to furnish the observed and isolated bisamide. Considering the higher nucleophilicity of the amide nitrogen, the fast addition of a second amide to the acylimine is not surprising. Under the reaction conditions, the bisamide, favored under kinetic control, can decompose to form the acylimine. In the presence of a suitable nucleophilic arene, the electrophilic acylimine can react in an aza-Friedel–Crafts reaction to afford the amidoalkylated product containing a thermodynamically stable C–C bond. The unique catalytic activity of $Bi(OTf)_3$ can be explained by two reasons. On the one hand, $Bi(OTf)_3$, although easily hydrolyzed,[20b] does not lose its catalytic activity in the presence of higher amounts of water.[19] On the other hand, $Bi(OTf)_3$ is a strong Lewis acid and could further activate the formed acylimine toward the addition of nucleophiles.[29]

During our studies, we often observed the formation of bis(hetero)arylmethane derivatives, especially for reactions with more reactive (hetero)arenes such as thiophene, furan, or *N*-tosylindole.[30] Since we were never able to isolate the amidoalkylation products of very reactive heteroarenes, such as indole, we cannot rule out that these products decompose under our reaction conditions. Control experiments showed that these side products arise from the direct addition of two (hetero)-arenes to the aldehyde, presumably via in situ formed benzyl cations (Scheme 7).[31]

The amidoalkylated products proved to be stable under our reaction conditions. Prolonged treatment of **4** with excess *m*-xylene in the presence of 5 mol % of $Bi(OTf)_3$ did not lead to the formation of any diarylmethane (Scheme 8).

2. Three-Component Reaction with Alkylaldehydes. Encouraged by the results of the α-amidoalkylation reaction with formaldehyde, we turned our attention to reactions with simple alkylaldehydes. Unfortunately, the reaction of benzamide (**1a**),

Scheme 6. Proposed Mechanism of the Three-Component α-Amidoalkylation Reaction



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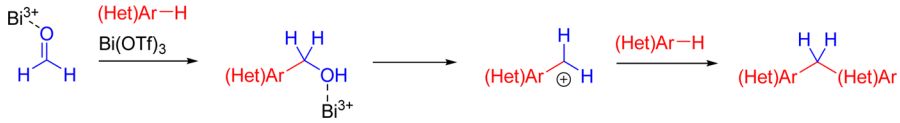
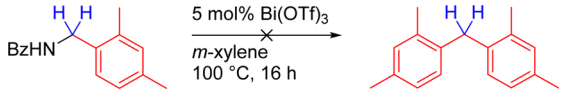
Scheme 7. Side Reaction with Electron-Rich (Hetero)arenes



Scheme 8. Stability of Amidoalkylated Products



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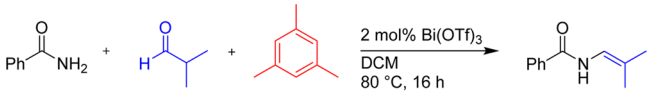
isobutyraldehyde (**13**), and mesitylene (**9a**) led to the selective formation of enamide **14** in 75% yield (Scheme 9).[32]

Scheme 9. Multicomponent Reactions with Alkylaldehydes Fail at Elevated Temperatures



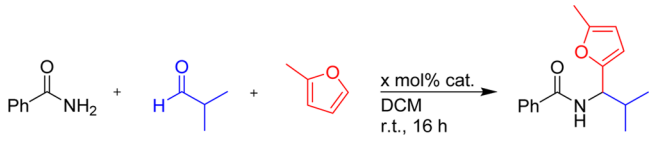
1	**13**	**9a**	**14**
1.2 equiv.	1.0 equiv.	3.0 equiv.	75%

Therefore, the corresponding two-component reaction between benzamide and isobutyraldehyde was investigated in more detail (Scheme 10). These investigations revealed a rapid formation of the corresponding bisamide **15** in the presence of $Bi(OTf)_3$ even at room temperature. However, this bisamide is not stable at elevated temperatures. At temperatures above 35 °C, formation of the enamide occurs, presumably via elimination of one molecule of benzamide.[33] Enamide **14** is stable in the presence of $Bi(OTf)_3$ at temperatures below 100 °C. In the presence of stronger acids or at higher temperatures, dimerization and polymerization of the enamide are observed.

From these results, we can draw two conclusions. One the one hand, alkylaldehydes are not suitable aldehyde components for our amidoalkylation reactions with moderately nucleophilic arenes. On the other hand, the formation of bisamide **15** clearly shows that a reactive acylimine species is formed even at room temperature. Therefore, trapping of the electrophilic acylimine with more reactive, electron-rich (hetero)arenes at temperatures below 35 °C should be possible. With these considerations in mind, we investigated the three-component reaction between benzamide (**1**), isobutyraldehyde (**13**), and 2-methylfuran (**16**) as a more nucleophilic arene component (Table 2).[17] Indeed, $Bi(OTf)_3$ can efficiently catalyze this reaction at 2−5 mol % catalyst loading. The yield of the reaction can be improved by a slight modification of the reaction protocol. Slow addition of the nucleophilic component over 2 h leads to an increased yield and decreased direct addition of the arene to the aldehyde.

With the optimized conditions in hand, we investigated reactions with different alkylaldehydes. In general, the desired amidoalkylated products were obtained in moderate to high

Table 2. Alkylaldehydes: Survey of Catalysts[a,b]



1	**13**	**16**	**17**
1.2 equiv.	1.0 equiv.	3.0 equiv.	

entry	catalyst (mol %)	yield (%)
1	$Bi(OTf)_3$ (0.5)	
2	$Bi(OTf)_3$ (1.0)	
3	$Bi(OTf)_3$ (2.0)	44
4	$Bi(OTf)_3$ (2.0)[c]	61
5	$Bi(OTf)_3$ (5.0)	35
6	$BiCl_3$ (5.0)	
7	$BiNO_3$ (5.0)	

[a]General reaction conditions: benzamide (1.2 equiv), isobutyraldehyde (1.0 equiv), 2-methylfuran (3.0 equiv), $Bi(OTf)_3$ (*x* mol %). [b]Isolated yield of analytical pure product. [c]The arene was added dropwise over a period of 2 h to the reaction mixture.

yields (Scheme 11). In the case of 2-benzyloxyacetaldehyde, the corresponding 1,2-amino alcohol **19d** could be isolated in 77% yield. Reactions of alkylaldehydes bearing a stereocenter in the α-position furnished the amides **19b** and **19f** in good yields and moderate to high diastereoselectivities.

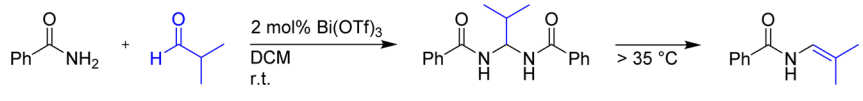
Different amides and carbamates are suitable amide components for this three-component reaction. The reaction with alkyl amides or various carbamates leads to the formation of amidoalkylated furans in 32−76% yield (Scheme 12). *tert*-Butyl carbamate is a suitable substrate for this transformation (product **20e**).

The acid-sensitive Boc functionality is well tolerated under the very mild reaction conditions (Scheme 13). The reaction of Boc-protected valinamide **21** furnished the corresponding product **22** in 62% yield and with a 2:1 diastereoselectivity.

As indicated above, three-component reactions with alkylaldehydes are limited to electron-rich arenes and heteroarenes. Therefore, the reaction of 2-methylthiophene and 1,3-dimethoxybenzene furnished the products **23a** and **23c** in 61 and 58% yield (Scheme 14). Further examination of this three-component reaction revealed a second limitation. Very reactive heteroarenes, such as indole or pyrrole, are not suitable substrates for this transformation. In the case of such highly reactive aromatic components only direct addition to the aldehyde is observed.

3. Three-Component Reaction with Aryl Aldehydes. We next turned our attention to reactions with aryl aldehydes as the aldehyde component. In this case, enamide formation is not

Scheme 10. Two-Component Reaction between Benzamide and Isobutyraldehyde



1 **13** **15** **14**

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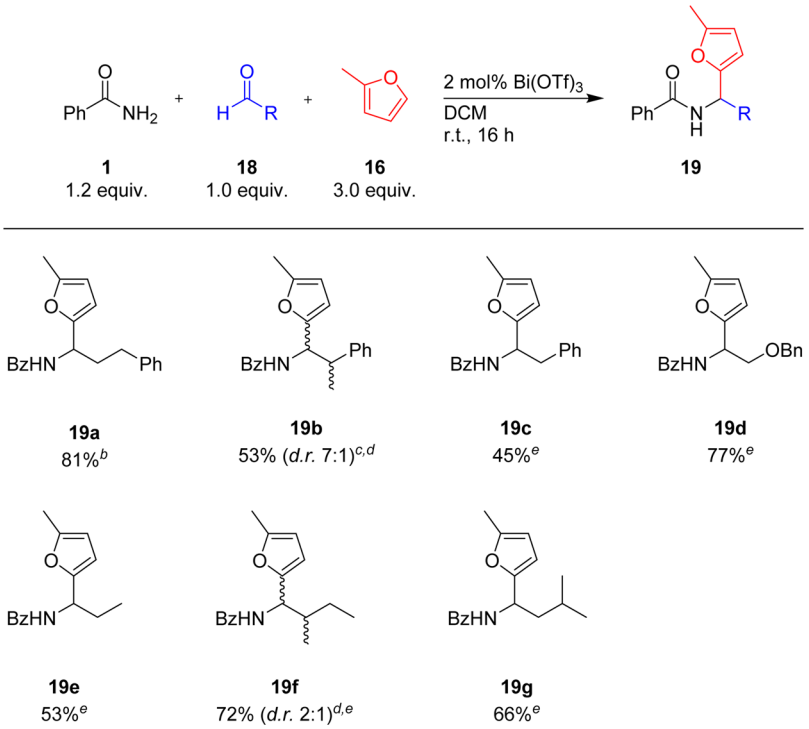
Scheme 11. Alkylaldehydes: Variation of Aldehydes[a]



[a]Isolated yield of analytical pure product. [b]The reaction mixture was cooled to 0 °C, and then the arene was added. [c]The arene was added dropwise over a period of 1 h to the reaction mixture. [d]Obtained as a mixture of diastereomers; ratio of diastereomers given in parentheses. [e]The arene was added dropwise over a period of 2 h to the reaction mixture. Pht = *N*-phthalyl.

possible. During preliminary experiments, rapid formation of the bisamide intermediate was observed at temperatures higher than 50 °C. The reaction between benzamide (**1**), benzaldehyde (**24**), and mesitylene (**9a**) was chosen as a model system to investigate the influence of various reaction parameters (Table 3). Surprisingly, high temperatures of 130 °C were required for efficient product formation. Best yields were obtained using 10 mol % of $Bi(OTf)_3$ (entry 4, 71%). We attribute these forcing reaction conditions with the decreased electrophilicity of *N*-acylimines derived from aryl aldehydes. Comparable results in yields were provided either by lengthening of the reaction time to 48 h or performing the reaction at 150 °C (entries 2 and 3, 63 and 60% yield). Addition of Brønsted acids, such as TfOH, did not affect the yield (entry 5).

The use of TfOH as Brønsted acid additive in the three-component reaction with less reactive *m*-xylene led to considerably higher yield (Table 4, entries 1 and 3). Best yields of **26** were obtained by an additional increase of temperature to 150 °C (entry 4).

With the optimized reaction conditions at hand, we examined reactions with various aryl aldehydes (Scheme 15). Aryl aldehydes bearing halogens in the *meta* or *para* position afforded the products in good yields (**28a−d**, 54−72% yield). Reaction with 2-chloro-5-nitrobenzaldehyde provided the product **28e** in 66% yield. The α-amidoalkylated product **28f** of naphthylaldehyde was isolated in 29% yield.

As shown in Scheme 16, variation of the amide component afforded the desired products **29a−d**; **29f,g** in 33−89% yield. In the case of aryl aldehydes, carbamates are not suitable amide components. Only in the case of urethane was the desired product **29g** formed, albeit in only 33% yield. Most likely, carbamates are not stable under these conditions.

Next, we investigated reactions with various arenes (Scheme 17). Anisole and its halogenated derivatives gave the desired amidoalkylated products **30a−d** in 25−40% yield. Only in the case of 3,5-*di*-methylanisole was the α-substituted amide isolated in a satisfactory yield of 74%. In general, reactions with various electron-rich heterocycles were not successful. The intermediate species is efficiently generated at 50 °C, but the high reactivity of the heteroarenes promotes synthesis of the direct addition products at these temperatures. Best results were achieved with 2-bromothiophene (**30f**, 36% yield). The high reactivity of the heteroarenes leads to a rapid direct addition to the aldehyde temperatures below 50 °C, necessary for the acylimine formation.

CONCLUSIONS

In summary, a general $Bi(OTf)_3$-catalyzed multicomponent between amides, aldehydes and arenes was developed. Formaldehyde, alkylaldehydes and aryl aldehydes were successfully employed as aldehyde compounds. Scope and limitations for all three types of aldehyde components were investigated.

These practical and operational simple multicomponent reactions provide straightforward and versatile access to α-amidoalkylated (hetero)arenes. The use of the nontoxic catalyst and generation of water as only side product constitute a valuable approach toward the concept of sustainable chemistry.

EXPERIMENTAL SECTION

General Considerations. Solvents for reactions and column chromatography were obtained from different commercial suppliers in >97% purity and used as received. Reagents: (*S*)-*N*-(2,4-Dimethylbenzyl)-3-methyl-2-(1,3-dioxoisoindolin-2-yl)butanamide,[34] *N*-benzyl-2-oxoacetamide,[35] ethyl-4-methoxybenzoate,[36] 3,5-dimethylanisole,[37] 2-

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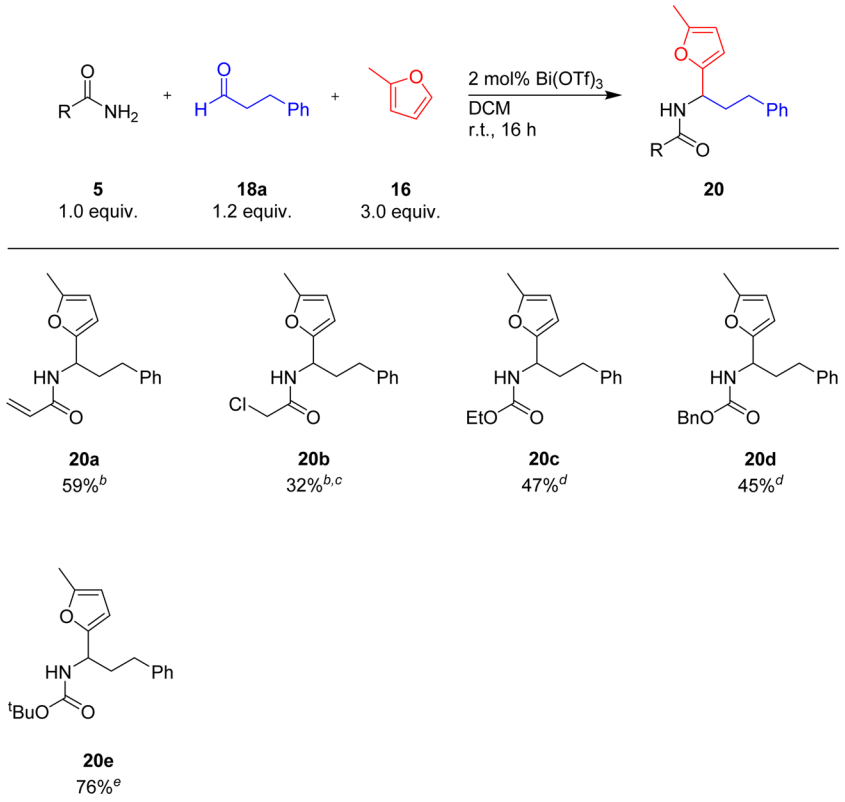
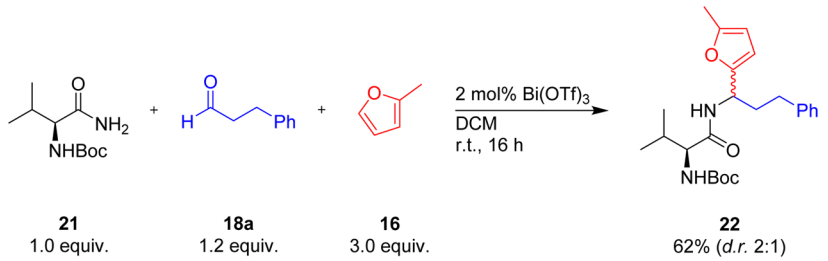
Scheme 12. Alkylaldehydes: Variation of Amides[a]



[a]Isolated yield of analytical pure product. [b]The arene was added dropwise over a period of 2 h to the reaction mixture. [c]The bis(heteroaryl)phenylpropane species was formed as the major product. [d]The reaction mixture was cooled to 0 °C, and then the arene was added. [e]The arene was added dropwise over a period of 1 h to the reaction mixture.

Scheme 13. Alkylaldehydes: Reaction of Boc-Protected Valinamide[a−c]



[a]Isolated yield of analytical pure product. [b]The arene was added dropwise over a period of 2 h to the reaction mixture. [c]Obtained as a mixture of diastereomers; ratio of diastereomers given in parentheses.

methylpivalanilide,[38] 3-ethylpivalanilide,[38] *N*-tosylindole,[39] and *N*-tosylpyrrole[40] were synthesized according to the literature. All other starting materials were purchased from commercial sources and used without further purification. Anhydrous $Bi(OTf)_3$ was obtained from different providers and used directly. No special precautions were taken to avoid exposure of $Bi(OTf)_3$ to moisture. Therefore, we cannot rule out the formation of $Bi(OTf)_3 \cdot xH_2O$ during storage. Indeed, depending on the provider and storage time (or even the time for weighting out a defined amount for elemental analysis), $Bi(OTf)_3$ contained up to six molecules of water. However, no changes in catalytic activity and yield even upon prolonged storage (>1 year) were observed. Therefore, the amount of $Bi(OTf)_3$ used is always calculated on anhydrous $Bi(OTf)_3$. The actual catalyst loading for particular reactions might be slightly lower, depending on the batch quality and storage time. Column chromatography was performed with silica 0.04−0.063 mm/230−400 mesh. Thin-layer chromatography was done using aluminum plates coated with SiO_2. The spots were visualized by ultraviolet light, iodine, or CAM. NMR spectroscopy: ^1H and ^{13}C NMR spectra were recorded at 300 or 400 MHz and 75 or 101 MHz, respectively. Mass spectra (MS) were measured using ESI (electrospray ionization) coupled to a quadrupole mass mass analyzer. High-resolution mass spectra (MALDI-HRMS) were measured using MALDI (matrix-assisted laser desorption/ionization) coupled to an ion-trap mass spectrometer. Melting points are uncorrected. All yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^1H NMR or elementary analysis.

Typical Procedures. All reactions were performed in vials sealed with a screw cap to avoid evaporation of the solvent. For reactions performed at room temperature, the screw cap was replaced with a rubber septum. For reactions performed at temperatures below the boiling point of the solvent culture, tubes with a PTFE-lined screw cap were used. For reactions performed at or above the boiling point of the solvent special thick-walled pressure tubes have to be used.

TP 1: Reactions with Formaldehyde. A 10 mL screw cap vial was charged with $Bi(OTf)_3$ (5 mol %), amide (1.0 equiv), formaldehyde (1.2 equiv), (hetero)arene (3−4 equiv), and nitromethane and closed with a

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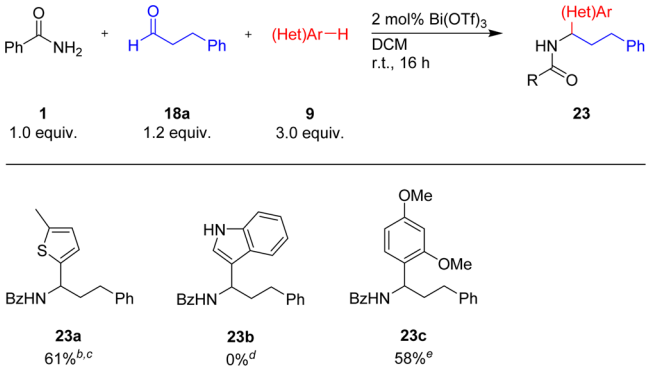
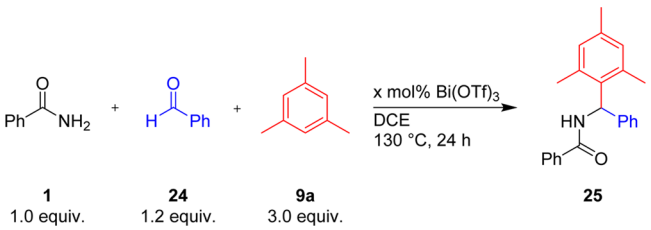
Scheme 14. Alkylaldehydes: Variation of (Hetero)arenes[a]



[a]Isolated yield of analytical pure product. [b]Reaction at 35 °C. [c]5 mol % of $Bi(OTf)_3$. [d]The bis(heteroaryl)phenylpropane species was formed. [e]The reaction mixture was cooled to 0 °C, and then the arene was added.

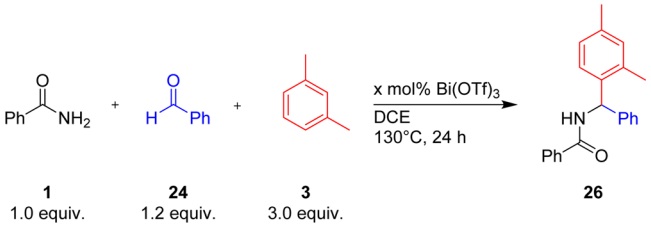
Table 3. Aryl aldehydes: Optimization of Catalysts[a,b]



entry	catalyst (mol %)	yield (%)
1	$Bi(OTf)_3$ (5.0)	23
2	$Bi(OTf)_3$ (5.0)[c]	63
3	$Bi(OTf)_3$ (5.0)[d]	60
4	$Bi(OTf)_3$ (10.0)	71
5	$Bi(OTf)_3$ (5.0) + TfOH (5.0)	25

[a]General reaction conditions: benzamide (1.0 equiv), benzaldehyde (1.2 equiv), mesitylene (3.0 equiv), $Bi(OTf)_3$ (x mol %), 130 °C, 24 h. [b]Isolated yield of analytical pure product. [c]Reaction time: 48 h. [d]Reaction at 150 °C.

Table 4. Aryl aldehydes: Use of TfOH Elevates Yield in the Case of *m*-Xylene[a,b]



entry	catalyst (mol %)	yield (%)
1	$Bi(OTf)_3$ (5.0)[c]	43
2	$Bi(OTf)_3$ (10.0)	35
3	$Bi(OTf)_3$ (5.0) + TfOH (5.0)[d,e]	58
4	$Bi(OTf)_3$ (5.0) + TfOH (5.0)[e,f]	76

[a]General reaction conditions: benzamide (1.0 equiv), benzaldehyde (1.2 equiv), mesitylene (3.0 equiv), $Bi(OTf)_3$ (*x* mol %), 130 °C, 24 h. [b]Isolated yield of analytical pure product. [c]Reaction time: 48 h. [d]Reaction at 100 °C. [e]Benzamide (1.2 equiv), benzaldehyde (1.0 equiv). [f]Reaction at 150 °C.

Teflon lined screw cap. The reaction mixture was stirred at 25−100 °C for the specified time. After being cooled to room temperature, the reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by column chromatography (hexane/EtOAc) afforded the analytically pure product.

TP 2: Reactions with Aryl aldehydes. A 10 mL screw cap vial was charged with $Bi(OTf)_3$ (10 mol %), amide (1.0 equiv), aryl aldehyde (1.2 equiv), (hetero)arene (3−4 equiv), and nitromethane and closed with a Teflon lined screw cap. The reaction mixture was stirred at 50−130 °C for the specified time. After being cooled to room temperature, the reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by column chromatography (hexane/EtOAc) afforded the analytically pure product.

*N-(2,4-Dimethylbenzyl)benzamide (**4**).* Compound **4** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), *m*-xylene (0.74 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 5 mol %) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (403 mg, 84%, ratio of regioisomers 15:1). Mp: 94−95 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for major regioisomer): δ = 7.77 (d, J = 8 Hz, 2H), 7.51−7.47 (m, 1H), 7.44−7.40 (m, 2H), 7.19 (d, J = 8 Hz, 1H), 7.04−7.00 (m, 2H), 6.17 (bs, 1H), 4.61 (d, J = 5 Hz, 2H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) (peaks are listed only for major regioisomer): δ = 167.3, 137.8, 136.7, 134.6, 132.9, 131.6, 129.1, 128.7, 128.7, 127.0, 127.0, 42.3, 21.1, 19.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO$ 240.14, found 240.40. Anal. Calcd: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.13; H, 7.06; N, 5.78. IR (cm^{-1}): 3284 (m), 1626 (s), 1578 (m), 1524 (m), 1487 (w), 1474 (w), 1363 (w), 1308 (m), 1281 (m), 1219 (w), 1182 (w), 1144 (w), 1057 (w), 1055 (w), 1026 (w), 968 (w), 920 (w), 877 (w), 831 (w), 823 (m), 800 (m), 769 (m), 704 (w), 690 (s), 660 (w). R_f (hexane/EtOAc 4:1) = 0.3.

*N-(2,4-Dimethylbenzyl)-4-methoxybenzamide (**6a**).* Compound **6a** was synthesized according to TP 1 from 4-methoxybenzamide (76 mg, 0.5 mmol), paraformaldehyde (19 mg, 0.6 mmol), *m*-xylene (0.24 mL, 2.0 mmol, 4 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol) in nitromethane (2 mL) at 80 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (87 mg, 65%). Mp: 134−135 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 7.6 Hz, 1H), 7.03−6.99 (m, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.07 (bs, 1H), 4.58 (d, J = 5.1 Hz, 2H), 3.84 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 166.8, 162.3, 137.8, 136.7, 133.1, 131.6, 129.1, 128.9, 127.0, 126.8, 113.9, 55.5, 42.3, 21.1, 19.1. MS (ESI) m/z: calcd for $C_{17}H_{19}NO_2Na$ 292.13; found 292.21 $[M + Na]^+$. Anal. Calcd: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.61; H, 6.91; N, 5.10. IR (cm^{-1}): 3284 (m), 1618 (s), 1574 (w), 1531 (m), 1497 (m), 1462 (m), 1408 (w), 1367 (w), 1304 (m), 1281 (m), 1250 (s), 1176 (m), 1111 (w), 1032 (m), 968 (w), 533 (w), 883 (w), 843 (m), 823 (s), 771 (m), 683 (w). R_f (hexane/EtOAc 4:1) = 0.1.

*N-(2,4-Dimethylbenzyl)-4-bromobenzamide (**6b**).* Compound **6b** was synthesized according to TP 1 from 4-bromobenzamide (400 g, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), *m*-xylene (0.74 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (448 mg, 70%, ratio of regioisomers 24:1). Mp: 174−175 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for major regioisomer): δ = 7.63 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.04−7.00 (m, 2H), 6.12 (bs, 1H), 4.59 (d, J = 5.1 Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 166.3, 138.0, 136.7, 133.4, 132.6, 132.0, 131.7, 129.2, 128.7, 127.1, 126.3, 42.4, 21.2, 19.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}BrNO$ 318.04, found 318.00. Anal. Calcd: C, 60.39; H, 5.07; N, 4.40 Found: C, 60.23; H, 5.02; N, 4.21. IR (cm^{-1}): 3286 (w), 2906 (w), 1626 (s), 1589 (w), 1529 (m), 1481 (m), 1358 (w), 1304 (w), 1277 (w), 1180 (w), 1146 (w), 1072 (w), 1009 (m), 972 (w), 881 (w), 843 (m), 823 (m), 771 (w), 756 (w), 677 (w). R_f (hexane/EtOAc 4:1) = 0.4.

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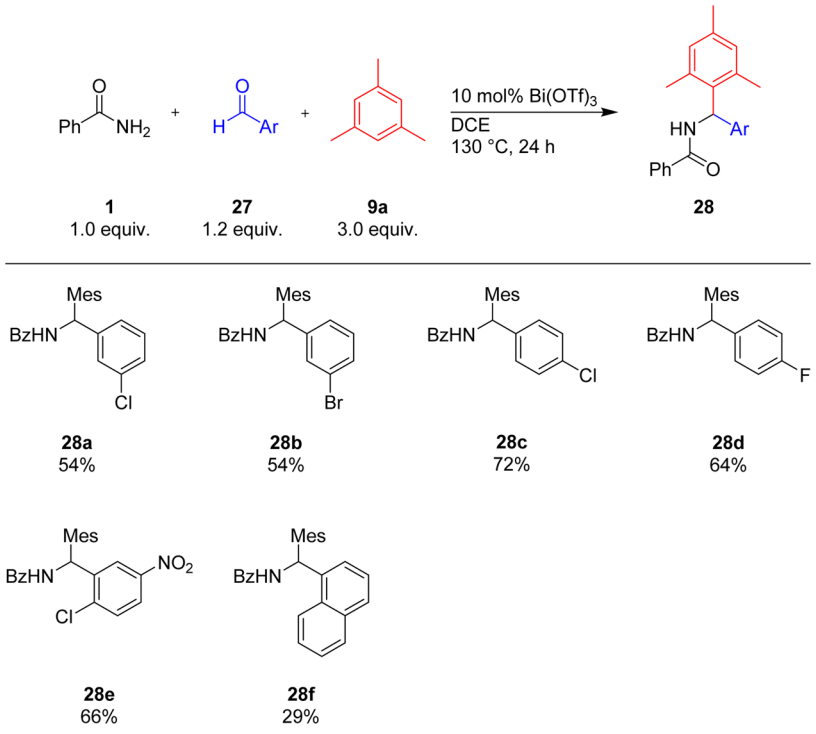
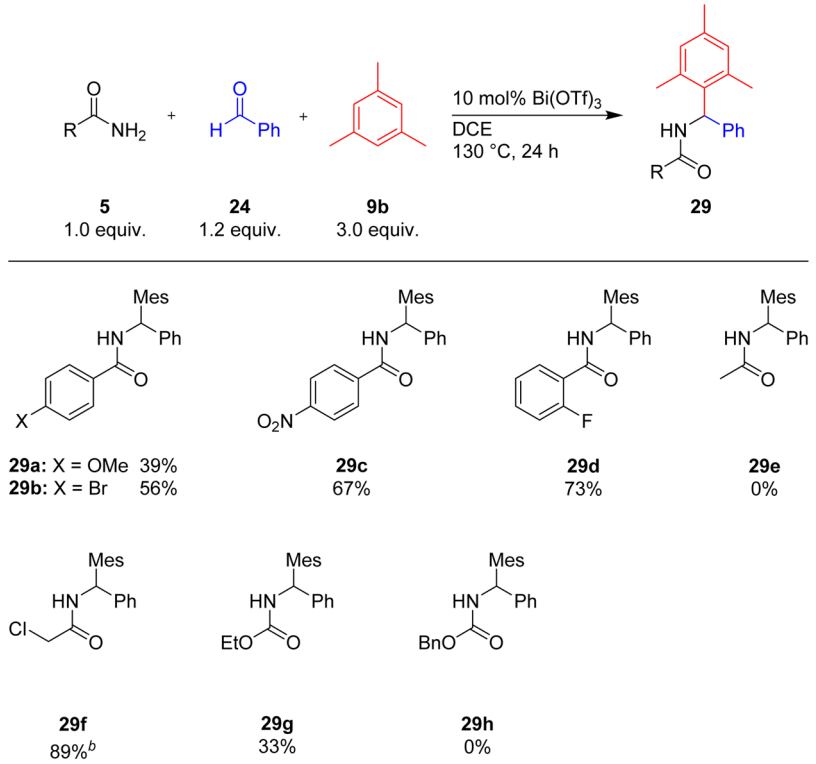
Scheme 15. Aryl aldehydes: Variation of Aldehydes[a]



[a]Isolated yield of analytical pure product. Mes = mesityl (2,4,6-trimethylphenyl).

Scheme 16. Aryl aldehydes: Variation of Amides[a]



[a]Isolated yield of analytical pure product. [b]Reaction at 100 °C. Mes = mesityl (2,4,6-trimethylphenyl).

*Ethyl 2,4-Dimethylbenzylcarbamate (**6c**).* Compound **6c** was synthesized according to TP 1 from urethane (45 mg, 0.5 mmol), paraformaldehyde (19 mg, 0.6 mmol), *m*-xylene (0.18 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol %) in nitromethane (2 mL) at 60 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (73 mg, 71%). Mp: 54−55 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.13 (d, J = 7.4 Hz, 1H), 6.99−6.97 (m, 2H), 4.76 (bs, 1H), 4.32 (d, J = 5.2 Hz, 2H), 4.14 (q, J = 6.9, 6.9

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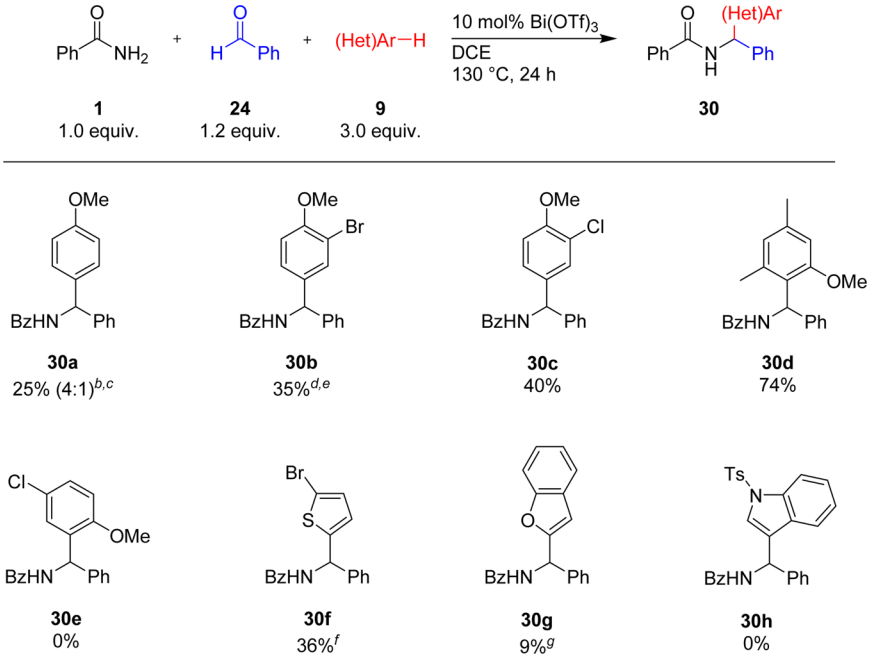
Scheme 17. Aryl aldehydes: Variation of (Hetero)arenes[a]



[a]Isolated yield of analytical pure product. [b]Obtained as a mixture of regioisomers; ratio of regioisomers given in parentheses. [c]Reaction at 100 °C. [d]Reaction with 5 mol % of $Bi(OTf)_3$. [e]Reaction with 5 mol % of TfOH. [f]Reaction at 80 °C. [g]Reaction at 50 °C.

Hz, 2H), 2.31 (s, 6H), 1.25 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 156.6, 137.5, 136.2, 133.3, 131.5, 128.5, 126.9, 61.0, 43.0, 21.1, 19.0, 14.8. MS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{17}NO_2Na$ 230.12, found 230.23. HRMS (MALDI) m/z: $[M + H]^+$ calcd for $C_{12}H_{18}NO_2$ 208.1332, found 208.1333. IR (cm^{-1}): 3321 (m), 2979 (m), 2921 (w), 1686 (s), 1617 (w), 1525 (m), 1479 (m), 1470 (m), 1375 (m), 1356 (m), 1301 (m), 1243 (s), 1160 (m), 1128 (m), 1047 (s), 965 (m), 925 (m), 880 (m), 822 (s), 780 (m), 638 (m), 580 (s), 550 (m), 505 (m). R_f (hexane/EtOAc 4:1) = 0.4.

*Benzyl 2,4-Dimethylbenzylcarbamate (**6d**).* Compound **6d** was synthesized according to TP 1 from benzylcarbamate (76 mg, 0.5 mmol), paraformaldehyde (19 mg, 0.6 mmol), *m*-xylene (0.18 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol %) in nitromethane (2 mL) at 60 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (61 mg, 45%, ratio of regioisomers 14:1). Mp: 74−76 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for major regioisomer): δ = 7.36−7.30 (m, 5H), 7.12 (d, J = 7.5 Hz, 1H), 6.99−6.97 (m, 2H), 5.13 (s, 2H), 4.85 (bs, 1H), 4.35 (d, J = 5.5 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) (compound exists as a mixture of rota- and regioisomers, peaks are not assigned): δ = 156.3, 137.5, 136.7, 136.2, 133.1, 131.5, 128.7, 128.5, 128.3, 128.0, 126.9, 126.8, 66.9, 43.2, 21.1, 19.0. MS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{19}NO_2Na$ 292.13, found 292.21. Anal. Calcd: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.67; H, 7.09; N, 4.97. IR (cm^{-1}): 3318 (w), 2946 (w), 2921 (w), 1683 (s), 1519 (s), 1505 (s), 1463 (m), 1453 (m), 1379 (w), 1356 (m), 1303 (w), 1241 (s), 1159 (w), 1118 (m), 1080 (w), 1047 (s), 1028 (m), 1003 (w), 965 (m), 925 (w), 912 (m), 881 (w), 852 (m), 823 (m), 780 (m), 756 (s), 719 (m), 706 (m), 693 (m), 627 (m), 588 (s), 568 (m), 538 (m), 504 (m), 468 (m). R_f (hexane/EtOAc 4:1) = 0.5.

*N-(2,4-Dimethylbenzyl)-2-acrylamide (**6e**).* Compound **6e** was synthesized according to TP 1 from acrylamide (142 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), *m*-xylene (0.74 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (207 mg, 55%, ratio of regioisomers 13:1). Mp: 122−123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for major regioisomer): δ = 7.14−7.12 (m, 1H), 7.01-6.68 (m, 2H), 6.31 (dd, J = 17.0, 1.5 Hz, 1H), 6.12−6.08 (m, 1H), 5.65 (dd, J = 10.2, 1.5 Hz, 1H), 4.48 (d, J = 5.4 Hz, 2H), 2.31 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) (peaks are listed only for major regioisomer): δ = 165.3, 137.8, 136.6, 132.7, 131.6, 130.8, 129.1, 127.0, 126.7, 41.8, 38.5, 21.1, 19.0. MS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{15}NONa$ 212.11, found 212.17. Anal. Calcd: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.02; H, 7.79; N, 7.32. IR (cm^{-1}): 3286 (m), 2916 (w), 1653 (s), 1620 (s), 1537 (m), 1464 (w), 1404 (w), 1352 (w), 1304 (w), 1234 (s), 1046 (m), 995 (s), 145 (s), 879 (w), 822 (m), 775 (w), 688 (m). R_f (hexane/EtOAc 4:1) = 0.1.

*N-(2,4-Dimethylbenzyl)-2-chloroacetamide (**6f**).* Compound **6f** was synthesized according to TP 1 from 2-chloroacetamide (187 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), *m*-xylene (0.74 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (308 mg, 73%, ratio of regioisomers 18:1). Mp: 120−121 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) (peaks are listed only for major regioisomer): δ = 7.13 (d, J = 7.5 Hz, 1H), 7.02−7.00 (m, 2H), 6.63 (bs, 1H), 4.45 (d, J = 5.4 Hz, 2H), 4.09 (s, 2H), 2.32 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) (peaks are listed only for major regioisomer): δ = 165.7, 138.0, 136.5, 132.0, 131.6, 128.9, 127.1, 42.7, 42.0, 21.1, 19.1. MS (ESI) m/z: $[M]^+$ calcd for $C_{11}H_{14}ClNO$ 211.08, found 211.40. Anal. Calcd: C, 62.41; H, 6.67; N, 6.62. Found: C, 62.33; H, 6.57; N, 6.43. IR (cm^{-1}): 3282 (m), 3003 (w), 1645 (s), 1541 (m), 1466 (w), 1416 (w), 1362 (w), 1319 (w), 1225 (m), 1157 (w), 1061 (w), 1034 (w), 995 (w), 124 (w), 879 (w), 820 (m), 771 (w), 702 (s), 667 (m). R_f (hexane/EtOAc 4:1) = 0.3.

*N-(2,4-Dimethylbenzyl)-2-cyanoacetamide (**6g**).* Compound **6g** was synthesized according to TP 1 from 2-cyanoacetamide (168 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), *m*-xylene (0.74 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (387 mg, 96%, ratio of regioisomers 11:1). Mp: 136−137 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks only for major regioisomer listed): δ = 7.11 (d, J = 7.6 Hz, 1H), 7.03−7.00 (m, 2H), 6.15 (bs, 1H), 4.44 (d, J = 5.3 Hz, 2H), 3.37 (s, 2H), 2.32 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) (peaks not assigned to regioisomers): δ = 160.5, 138.3, 136.5, 131.8, 131.5, 129.1, 128.8, 127.2, 114.7, 52.3, 42.5, 25.9, 21.1, 19.9, 19.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{15}N_2O$ 203.12, found 203.40. Anal. Calcd: C, 71.26;

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H, 6.98; N, 13.85. Found: C, 71.28; H, 7.05; N, 13.66. IR (cm^{-1}): 3275 (m), 1647 (w), 1645 (s), 1571 (m), 1504 (w), 1468 (w), 1367 (m), 1365 (m), 1325 (w), 1232 (m), 1066 (w), 991 (w), 922 (w), 876 (w), 822 (m), 793 (m), 768 (w), 687 (m). R_f (hexane/EtOAc 1:1) = 0.5.

*N-(2,4-Dimethylbenzyl)acetamide (**6h**).* Compound **6h** was synthesized according to TP 1 from acetamide (29 mg, 0.5 mmol), paraformaldehyde (19 mg, 0.6 mmol), *m*-xylene (0.18 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol %) in nitromethane (2 mL) at 100 °C for 8 h. Purification by chromatography (hexane/EtOAc 1:1) yielded the product as a colorless solid (45 mg, 51%, ratio of regioisomers 15:1). Mp: 110−112 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for major regioisomer): δ = 7.11 (d, J = 7.6 Hz, 1H), 7.01-6.98 (m, 2H), 5.54 (bs, 1H), 4.39 (d, J = 5.3 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 3H), 1.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) (peaks are not assigned to regioisomers): δ = 169.8, 137.7, 137.6, 136.5, 134.0, 132.9, 131.5, 129.0, 158.6, 128.1, 127.0, 41.8, 38.6, 23.3, 23.2, 21.1, 19.8, 19.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{16}NO$ 178.12, found 178.21. Anal. Calcd: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.20; H, 8.65; N, 7.75. IR (cm^{-1}): 3289 (w), 3000 (w), 2920 (w), 2871 (w), 1689 (w),1634 (s), 1538 (s), 1463 (s), 1377 (s), 1352 (w), 1300 (w), 1275 (s), 1215 (w), 1159 (w), 1124 (w), 1092 (m), 1037 (w), 998 (m), 951 (w), 886 (w), 816 (s), 770 (w), 713 (s), 617 (m), 598 (s), 573 (s), 552 (w), 508 (w), 467(s). R_f (hexane/EtOAc 1:1) = 0.2.

*N-(2,4-Dimethylbenzyl)-2,2,2-trimethylacetamide (**6i**).* Compound **6i** was synthesized according to TP 1 from 2,2,2-trimethylacetamide (202 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), *m*-xylene (0.74 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (337 mg, 77%, ratio of regioisomers 17:1). Mp: 85−86 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for major regioisomer): δ = 7.10 (d, J = 8 Hz, 1H), 7.01-6.98 (m, 2H), 5.67 (bs, 1H), 4.39 (d, J = 5 Hz, 2H), 2.31 (s, 3H), 2.28 (s, 3H), 1.21 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz) (peaks are listed only for major regioisomer): δ = 178.1, 137.6, 136.6, 133.2, 131.5, 128.9, 126.9, 41.9, 38.9, 27.8, 21.1, 19.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{22}NO$ 220.17, found 220.80. Anal. Calcd: C, 76.67; H, 9.65; N, 6.39; Found: C, 76.42; H, 9.75; N, 6.11. IR (cm^{-1}): 3317 (m), 2954 (w), 1633 (s), 1539 (m), 1504 (w), 1425 (w), 1365 (w), 1296 (w), 1225 (w), 1213 (m), 1005 (m), 931 (w), 866 (w), 814 (m), 787 (m), 702 (w), 677 (m). R_f (hexane/EtOAc 1:1) = 0.4.

*3-(2,4-Dimethylbenzyl)oxazolidin-2-one (**6j**).* Compound **6j** was synthesized according to TP 1 from oxazolidin-2-one (44 mg, 0.5 mmol), paraformaldehyde (19 mg, 0.6 mmol), *m*-xylene (0.18 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol) in nitromethane (2 mL) at 100 °C for 6 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless oil (73 mg, 71%, ratio of regioisomers >25:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.08 (d, J = 7.6 Hz, 1H), 7.02−6.98 (m, 2H), 4.42 (s, 2H), 4.30−4.26 (m, 2H), 3.38−3.34 (m, 2H), 2.31 (s, 3H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 158.3, 138.1, 136.9, 131.7, 130.7, 129.3, 126.9, 61.9, 46.5, 44.1, 21.1, 19.1. MS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{15}NO_2Na$ 228.10, found 227.80. Anal. Calcd: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.94; H, 7.35; N, 6.74. IR (cm^{-1}): 3491 (w), 2919 (w), 1740 (s), 1616 (w), 1484 (m), 1424 (s), 1376 (m), 1355 (m), 1320 (w), 1252 (s), 1204 (m), 1185 (m), 1158 (m), 1119 (m), 1067 (s), 1034 (s), 975 (m), 954 (m), 921 (m), 878 (w), 833 (m), 803 (m), 778 (m), 760 (s), 728 (m), 717 (m), 693 (m), 652 (m), 581 (m), 538 (w), 490 (m). R_f (hexane/EtOAc 4:1) = 0.1.

*N-(2,4-Dimethylbenzyl)-3-methyl-2-(1,3-dioxoisoindolin-2-yl)-butanamide (**8**).* Compound **8** was synthesized according to TP 1 from (*S*)-3-methyl-2-(1,3-dioxoisoindolin-2-yl)butanamide (123 mg, 0.5 mmol), paraformaldehyde (19 mg, 0.6 mmol), *m*-xylene (0.18 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol %) in nitromethane (2 mL) at 100 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless, very viscous foam (115 mg, 63%, mixture of regioisomers as determined by analytical HPLC 12:1). ^{1}H NMR ($CDCl_3$, 400 MHz) (mixture of regioisomer and rotamers, peaks are not assigned): δ = 7.87−7.85 (m, 2H), 7.76−7.74 (m, 2H), 7.09 (d, J = 7.6 Hz, 1H), 7.03−7.02 (m, 1H), 6.98−6.94 (m, 2H), 4.49−4.42 (m, 2H), 4.35−4.31 (m, 1H), 2.85−2.85 (m, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.10 (d, J = 6.7 Hz, 3H), 0.85 (d, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) (mixture of regioisomer and rotamers, peaks are not assigned): δ = 168.6, 168.6, 137.5, 136.3, 134.6, 132.7, 131.5, 131.5, 128.7, 128.6, 128.0, 127.0, 123.8, 63.3, 41.7, 38.6, 27.8, 21.1, 20.0, 19.8, 19.6, 19.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{25}N_2O_3$ 365.19, found 365.90. Anal. Calcd: C, 72.50; H, 6.64; N, 7.69. Found: C, 72.20; H, 6.60; N, 7.58. IR (cm^{-1}): 3329 (w), 2966 (m), 2926 (w), 2874 (w), 1770 (m), 1706 (s), 1660 (m), 1615 (m), 1530 (m), 1467 (m), 1381 (s), 1355 (s), 1332 (s), 1288 (m), 1225 (m), 1192 (m), 1172 (m), 1157 (m), 1123 (w), 1070 (s), 1014 (m), 988 (m), 961 (w), 927 (w), 888 (m), 817 (m), 791 (m), 716 (s), 660 (m), 627 (m), 575 (m), 560 (m), 530 (s). R_f (hexane/EtOAc 4:1) = 0.2.

*N-(2,4,6-Trimethylbenzyl)benzamide (**10a**).* Compound **10a** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), mesitylene (0.83 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 5 mol %) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (371 mg, 73%). Mp: 151-152 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, J = 8.1 Hz, 2H), 7.48 (t, J = 7.1 Hz, 1H), 7.40 (t, J = 7.5 Hz, 2H), 6.91 (s, 2H), 5.89 (bs, 1H), 4.64 (d, J = 4.4 Hz, 2H), 2.37 (s, 6H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.5, 137.9, 137.7, 136.6, 134.5, 131.6, 130.9, 129.7, 129.4, 128.7, 127.0, 38.9, 21.1, 19.8. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO$ 254.15, found 254.40. Anal. Calcd: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.72; H, 7.65; N, 5.13. IR (cm^{-1}): 3296 (m), 1626 (s), 1578 (m), 1516 (s) 1471 (m), 1377 (w), 1269 (w), 1178 (w), 1076 (w), 1022 (w), 906 (w), 854 (m), 802 (m), 771 (w), 692 (s), 660 (w). R_f (hexane/EtOAc 4:1) = 0.3.

*N-(2-Methoxybenzyl)benzamide (**10b**).* Compound **10b** was synthesized according to TP 1 from benzamide (61 mg, 0.5 mmol), formalin (45 μL, 37 wt % solution in H_2O, 0.6 mmol), anisole (0.22 mL, 2.0 mmol, 4 equiv), and $Bi(OTf)_3$ (16 mg, 0.1 mmol, 5 mol %) in nitromethane (2 mL) at 100 °C for 24 h. Purification by chromatography (hexane/EtOAc 9:1 → 4:1) yielded the product as a yellow solid (82 mg, 68%, ratio of regioisomers 3:1). Mp: 110−111 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for *para*-regioisomer): δ = 7.75−7.71 (m, 2H), 7.47−7.30 (m, 3H), 7.24−7.22 (m, 2H), 6.92−6.81 (m, 2H,), 6.33 (bs, 1H), 4.55 (d, J = 5.5 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) (peaks are not assigned to *ortho*- and *para*-isomer): δ = 167.4, 137.2, 136.1, 135.7, 134.6, 131.6, 130.1, 129.9, 129.5, 128.7, 128.7, 127.2, 127.1, 127.1, 125.9, 125.6, 44.1, 43.3, 20.6, 19.9, 19.5, 15.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}NO_2$ 242.12, found 242.40. Anal. Calcd: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.44; H, 6.26; N, 5.63. IR (cm^{-1}): 1300 (w), 3223 (w), 3055 (w), 2924 (w), 2831 (w), 1630 (s), 1546 (w), 1539 (m), 1489 (m), 1460 (c), 1429 (w), 1350 (w), 1296 (m), 1238 (s), 1176 (m), 1109 (m), 1072 (w), 1032 (s), 172 (w), 926 (w), 812 (m), 752 (s), 694 (s), 667 (s). R_f (hexane/EtOAc 4:1) = 0.2.

*N-(3-Chloro-4-methoxybenzyl)benzamide (**10c**).* Compound **10c** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), 2-chloroanisole (0.76 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 5 mol %) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow solid (462 mg, 84%). Mp: 117−118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79−7.77 (m, 2H), 7.51-7.47 (m, 1H), 7.43−7.39 (m, 2H), 7.35 (d, J = 2 Hz, 1H), 7.20 (dd, $J1$ = 2 Hz, $J2$ = 8 Hz, 1H), 6.87 (d, J = 8 Hz, 1H), 6.57 (bs, 1H), 4.54 (d, J = 6 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.5, 154.6, 134.3, 131.8, 131.6, 129.9, 128.7, 127.5, 127.1, 122.7, 112.3, 56.3, 43.2. MS (ESI) m/z: [M + H] calcd for $C_{15}H_{15}ClNO_2$ 276.08, found 276.00. Anal. Calcd: C, 65.34; H, 5.12; N, 5.08. Found: C, 65.05; H, 5.10; N, 4.91. IR (cm^{-1}): 3311 (w), 3242 (w), 3059 (w), 3010 (w), 2943 (w), 2927 (w), 2833 (w), 1626 (m), 1574 (w), 1541 (s), 1504 (m), 1462 (w), 1427 (w), 1354 (w), 1282 (s), 1182 (w), 1147 (w), 1063 (s), 1094 (m), 974 (m), 937 (w), 872 (m), 814 (m), 756 (m), 698 (s), 654 (w). R_f (hexane/EtOAc 4:1) = 0.1.

*N-(3-Bromo-4-methoxybenzyl)benzamide (**10d**).* Compound **10d** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), 2-bromoanisole (0.74 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4

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mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow solid (563 mg, 88%). Mp: 112−113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79−7.77 (m, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.49−7.47 (m, 1H), 7.43−7.39 (m, 2H), 7.27−7.24 (m, 1H), 6.84 (d, J = 6.8 Hz, 1H), 6.58 (bs, 1H), 4.54 (d, J = 4.5 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.5, 155.5, 134.3, 133.0, 132.1, 131.7, 128.7, 128.3, 127.1, 112.2, 111.9, 56.4, 43.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO_2$ 320.03, found 320.00. Anal. Calcd: C, 56.27; H, 4.41; N, 4.37; Found: C, 56.08; H, 4.39; N, 4.25. IR (cm^{-1}): 3307 (w), 3240 (w), 3055 (w), 3008 (w), 2964 (w), 2926 (w), 2831 (w), 1626 (m), 1539 (s), 1493 (s), 1460 (w), 1427 (w), 1402 (w), 1352 (w), 1261 (s), 1259 (s), 1180 (w), 1147 (w), 1061 (w), 1024 (m), 1022 (m), 170 (w), 137 (w), 885 (w), 860 (w), 814 (m), 754 (m), 698 (s), 667 (w). R_f (hexane/EtOAc 4:1) = 0.1.

*N-(3-Iodo-4-methoxybenzyl)benzamide (**10e**).* Compound **10e** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), 2-iodoanisole (0.78 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (578 mg, 79%). Mp: 106−107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79−7.76 (m, 3H), 7.50 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.42 (bs, 1H), 4.54 (d, J = 5.7 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.4, 157.8, 139.1, 134.4, 132.6, 131.8, 129.5, 128.8, 127.1, 111.1, 86.3, 56.6, 43.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}INO_2$ 368.01, found 368.40. Anal. Calcd: C, 49.07; H, 3.84; N, 3.81. Found: C, 49.03; H, 3.88; N, 3.66. IR (cm^{-1}): 3280 (w), 3030 (w), 2927 (w), 2831 (w), 1626 (s), 1578 (w), 1527 (m), 1485 (m), 1460 (m), 1400 (w), 1363 (w), 1288 (m), 1250 (m), 1225 (m), 1178 (w), 1144 (w), 1074 (w), 1047 (m), 1018 (m), 978 (w), 922 (w), 887 (w), 841 (w), 798 (m), 692 (s), 667 (m). R_f (hexanes/EtOAc 4:1) = 0.1.

*N-(5-Chloro-2-methoxybenzyl)benzamide (**10f**).* Compound **10f** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), 4-chloroanisole (0.73 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (459 mg, 83%). Mp: 138−139 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.0 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.31 (bd, J = 2.1 Hz, 1H), 7.22 (dd, J = 8.7, 2.3 Hz, 1H), 6.81 (d, 1H, J = 8.7 Hz), 6.65 (bs, 1H), 4.60 (d, J = 6.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.3, 156.3, 134.7, 131.6, 129.7, 128.7, 128.6, 128.2, 127.1, 125.8, 111.7, 55.9, 39.5. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}ClNO_2$ 276.08, found 275.90. Anal. Calcd: C, 65.34; H, 5.12; N, 5.08. Found: C, 65.19; H, 5.07; N, 4.93. IR (cm^{-1}): 3269 (m), 3055 (w), 1624 (m), 1576 (m), 1543 (m), 1487 (m), 1443 (w), 1423 (w), 1352 (w), 1294 (w), 1254 (w), 1244 (m), 1176 (w), 1174 (w), 1126 (m), 1053 (w), 1049 (w), 1026 (m), 989 (w), 930 (w), 877 (w), 806 (m), 692 (s), 667 (w). R_f (hexane/EtOAc 4:1) = 0.1.

*N-(5-Bromo-2-methoxybenzyl)benzamide (**10g**).* Compound **10g** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), 4-bromoanisole (0.75 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (494 mg, 77%). Mp: 123−124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78−7.75 (m, 2H), 7.53−7.40 (m, 4H), 7.38−7.35 (m, 1H), 6.76 (d, J = 9 Hz, 1H), 6.61 (bs, 1H), 4.61 (d, J = 6 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.3, 156.8, 134.7, 132.6, 131.6, 131.6, 128.7, 128.6, 127.1, 113.1, 112.2, 55.9, 39.5. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}BrNO_2$ 320.03, found 320.00. Anal. Calcd: C, 56.27; H, 4.41; N, 4.37. Found: C, 56.15; H, 4.52; N, 4.27. IR (cm^{-1}): 3265 (w), 3055 (w), 1624 (m), 1576 (m), 1541 (m), 1489 (m), 1443 (w), 1421 (w), 1398 (w), 1350 (w), 1292 (w), 1244 (m), 1176 (w), 1174 (w), 1120 (w), 1055 (w), 1051 (w), 1024 (m), 987 (w), 131 (w), 856 (w), 806 (m), 692 (s), 667 (w). R_f (hexanes/EtOAc 4:1) = 0.2.

*N-(5-Iodo-2-methoxybenzyl)benzamide (**10h**).* Compound **10h** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), 4-iodoanisole (1.40 g, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (465 mg, 64%). Mp: 117−118 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.78−7.74 (m, 2H), 7.63 (d, J = 2.3 Hz, 1H), 7.58−7.40 (m, 4H), 6.66 (d, J = 8.6 Hz, 1H), 6.59 (bs, 1H), 4.58 (d, J = 5.9 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.3, 157.7, 138.4, 137.8, 134.7, 131.6, 129.0, 128.7, 127.1, 112.9, 83.1, 55.8, 39.4. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{15}INO_2$ 368.01, found 368.40. Anal. Calcd: C, 49.07; H, 3.84; N, 3.81; Found: C, 49.18; H, 3.89; N, 3.69. IR (cm^{-1}): 3267 (w), 3061 (w), 3008 (w), 2947 (w), 2835 (w) 2158 (w), 1992 (w), 1633 (s), 1551 (w), 1539 (s), 1495 (f), 458 (m), 1433 (m), 1360 (w), 1309 (m), 1279 (m), 1263 (m), 1242 (w), 1215 (s), 1118 (m), 1151 (w), 1059 (w), 1045 (m), 1020 (m), 993 (w), 924 (w) 906 (w), 879 (m), 825 (m), 795 (s), 710 (s), 665 (w). R_f (hexanes/EtOAc 4:1) = 0.1.

*N-(3,6-Dimethoxybenzyl)benzamide (**10i**).* Compound **10i** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), 1,4-dimethoxybenzene (1.128 g, 8.0 mmol, 4 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 5 mol %) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow solid (0.18 g, 42%). Mp: 101-102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.76 (d, J = 8 Hz, 2H), 7.48 (t, J = 7 Hz, 1H), 7.41 (t, J = 7 Hz, 2H), 6.94 (d, J = 2 Hz, 1H), 6.84−6.78 (m, 2H), 6.68 (bs, 1H), 4.62 (d, J = 6 Hz, 2H), 3.84 (s, 3H), 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.1, 153.6, 151.8, 134.7, 131.3, 128.5, 127.2, 126.9, 115.9, 113.3, 111.4, 55.9, 55.8, 40.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO_3$ 272.1, found 272.4. Anal. Calcd: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.92; H, 6.21; N, 5.11. IR (cm^{-1}): 3267 (m), 3062 (w), 3008 (w), 2949 (w), 2833 (w), 2154 (w), 1996 (w), 1952 (w), 1633 (s), 1579 (w), 1539 (s), 1495 (s), 1458 (m), 1431 (m), 1360 (w), 1309 (s), 1279 (m), 1242 (w), 1215 (s), 1180 (m), 1149 (w), 1115 (m), 1059 (w), 1045 (s), 1020 (s), 993 (m), 924 (w), 874 (w), 879 (m), 825 (m), 795 (s), 710 (s), 667 (w). R_f (Hexane/EtOAc 4:1): 0.1.

*Ethyl 3-((Benzamido)methyl)-4-methoxybenzoate (**10j**).* Compound **10j** was synthesized according to TP 1 from benzamide (61 mg, 0.5 mmol), paraformaldehyde (19 mg, 0.6 mmol), ethyl-4-methoxybenzoate (0.25 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol) in nitromethane (2 mL) at 100 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (135 mg, 87%). Mp: 127−129 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.03−7.99 (m, 2H), 7.78−7.75 (m, 2H), 7.50−7.46 (m, 1H), 7.42−7.40 (m, 2H), 6.92 (d, J = 8.5 Hz, 1H), 6.60 (bs, 1H), 4.67 (d, J = 5.9 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.4, 166.4, 161.4, 134.8, 131.5, 131.4, 131.2, 128.7, 127.1, 126.3, 123.2, 110.1, 60.9, 55.9, 39.9, 14.5. MS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{19}NO_4Na$ 336.12, found 336.25. HRMS (MALDI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}NO_4$ 314.1387, found 314.1389. IR (cm^{-1}): 3279 (w), 2978 (w), 1710 (s), 1626 (s), 1611 (m), 1578 (m), 1549 (m), 1504 (m), 1491 (w), 1462 (w), 1446 (w), 1413 (w), 1361 (m), 1314 (s), 1264 (s), 1174 (m), 1125 (s), 1050 (w), 1022 (s), 993 (w), 931 (w), 909 (w), 875 (w), 832 (m), 768 (s), 695 (s), 672 (m), 628 (m), 607 (w), 539 (w), 510 (w).R_f (hexane/EtOAc 4:1) = 0.1.

*N-(4-Methyl-3-pivalamido)benzamide (**10k**).* Compound **10k** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), *N-o*-tolylpivalamide (1.15 g, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (430 mg, 66%). Mp: 170−171 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78 (d, J = 7.8 Hz, 3H), 7.49 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.23 (bs, 1H), 7.18−7.16 (m, 2H), 6.45 (bs, 1H), 4.56 (d, J = 5.6 Hz, 2H), 2.23 (s, 3H), 1.34 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 176.7, 167.4, 135.4, 134.9, 134.5, 131.7, 130.3, 129.6, 128.7, 127.1, 126.5, 123.5, 43.9, 39.9, 27.9, 17.8. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{25}N_2O_2$ 325.19, found 325.60. HRMS (MALDI) m/z: $[M + H]^+$ calcd for $C_{20}H_{25}N_2O_2$ 325.1916, found 325.1914. IR (cm^{-1}): 3307 (b), 2953 (w), 1643 (s), 1558 (w), 1541 (m), 1506 (s), 1417 (w), 1309 (w), 1221 (w), 1178 (w),

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1051 (w), 1005 (w), 984 (w), 980 (w), 930 (w), 849 (w), 802 (m), 737 (w), 694 (s), 667 (w). R_f (hexane/EtOAc 1:1) = 0.3.

*N-(2,5-Dimethylbenzyl)benzamide (**10l**).* Compound **10l** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), *p*-xylene (0.74 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 5 mol %) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (177 mg, 37%). Mp: 113−114 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79−7.78 (m, 2H), 7.52−7.48 (m, 1H), 7.45−7.40 (m, 2H), 7.12−7.09 (m, 2H), 7.04 (d, J = 8 Hz, 1H), 6.22 (bs, 1H), 4.61 (d, J = 5 Hz, 2H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.1, 135.8, 135.5, 134.4, 133.4, 131.5, 130.6, 129.6, 129.6, 128.6, 126.9, 42.4, 20.9, 18.6. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}NO$ 240.1, found 240.4. Anal. Calcd: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.28; H, 7.05; N, 5.76. IR (cm^{-1}): 2290 (m), 2912 (w), 1626 (s), 1578 (m), 1531 (s), 1460 (w), 1360 (w), 1308 (m), 1298 (w), 1236 (w), 1180 (w), 1147 (w), 1074 (w), 1053 (w), 1028 (w), 1001 (w), 970 (w), 922 (w), 864 (w), 856 (w), 814 (m), 712 (w), 694 (s), 669 (w). R_f (hexane/EtOAc 4:1) = 0.3.

*N-(5-Bromo-2-hydroxybenzyl)benzamide (**10m**).* Compound **10m** was synthesized according to TP 1 from benzamide (61 mg, 0.5 mmol), paraformaldehyde (19 mg, 0.6 mmol), 4-bromophenol (346 mg, 2.0 mmol, 4 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol) in nitromethane (2 mL) at 80 °C for 24 h. Purification by chromatography (hexane/EtOAc 9:1 → 4:1) yielded the product as a colorless solid (104 mg, 68%). Mp: 154−156 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.67 (bs, 1H), 7.78−7.76 (m, 2H), 7.56−7.52 (m, 1H), 7.46−7.42 (m, 2H), 7.31-7.29 (m, 2H), 6.98 (bs, 1H), 6.85 (d, J = 8.6 Hz, 1H), 4.50 (d, J = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 170.0, 155.4, 133.4, 133.0, 132.7, 132.5, 129.0, 127.4, 126.3, 120.2, 111.5, 40.8. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}BrNO_2$ 306.01, found 306.05. Anal. Calcd: C, 54.92; H, 3.95; N, 4.58. Found: C, 54.58; H, 3.93; N, 4.41. IR (cm^{-1}): 3343 (w), 2598 (w), 1682 (w), 1615 (w), 1545 (s), 1481 (s), 1392 (m), 1352 (w), 1310 (m), 1268 (m), 1254 (s), 1222 (m), 1180 (w), 1117 (m), 1081 (w), 1032 (w), 1002 (w), 972 (w), 932 (w), 907 (w), 817 (s), 789 (m), 738 (w), 711 (s), 690 (s), 630 (s), 551 (m), 516 (s), 492 (w). R_f (hexane/EtOAc 4:1) = 0.1.

*N-((5-Methylthiophene-2-yl)methyl)benzamide (**10o**).* Compound **10o** was synthesized according to TP 1 from benzamide (73 mg, 0.6 mmol), formalin (37 μL, 37 wt % solution in H_2O, 0.5 mmol), 2-methylthiophene (0.15 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol %) in nitromethane (2 mL) at 25 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow solid (74 mg, 64%, mixture of regioisomers 12:1). Mp: 105−107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for major regioisomer): δ = 7.81-7.75 (m, 2H), 7.52−7.48 (m, 1H), 7.46−7.41 (m, 2H), 6.82 (bd, J = 3.3 Hz, 1H), 6.61-6.60 (m, 1H), 6.36 (s, 1H), 4.73 (d, J = 5.5 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.2, 140.2, 138.4, 134.4, 131.7, 128.7, 127.1, 126.3, 125.0, 39.3, 15.5. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}NOS$ 232.08, found 232.60. Anal. Calcd: C, 67.50; H, 5.66; N, 6.06; S, 13.86. Found: C, 67.47; H, 5.52; N, 5.91; S, 14.14. IR (cm^{-1}): 3345 (m), 3060 (w), 2917 (w), 2856 (w), 1630 (s), 1602 (m), 1576 (m), 1538 (s), 1490 (s), 1445 (m), 1424 (m), 1350 (m), 1325 (m), 1294 (s), 1260 (m), 1216 (m), 1190 (m), 1153 (m), 1101 (w), 1075 (m), 1049 (m), 1032 (m), 1003 (w), 976 (m), 930 (w), 866 (m), 808 (m), 797 (s), 742 (m), 711 (s), 686 (s), 662 (m), 600 (s), 556 (s), 499 (m). R_f (hexane/EtOAc 4:1) = 0.2.

*N-(5-Bromothiophene-3-yl)benzamide (**10p**).* Compound **10p** was synthesized according to TP 1 from benzamide (242 mg, 2.0 mmol), paraformaldehyde (72 mg, 2.4 mmol), 2-bromothiophene (0.6 mL, 6.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow solid (558 mg, 94%). Mp: 117−118 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79−7.78 (m, 1H), 7.77−7.76 (m, 1H), 7.54−7.48 (m, 1H), 7.45−7.40 (m, 2H), 6.90 (d, J = 4 Hz, 1H), 6.79−6.78 (m, 1H), 6.53 (bs, 1H), 4.71 (d, J = 6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.4, 142.8, 134.0, 131.9, 129.7, 128.8, 127.1, 126.7, 112.0, 39.2. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}BrNOS$ 295.97, found 295.90. HRMS (MALDI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}BrNOS$ 295.9745, found 295.9748. IR (cm^{-1}): 3278 (w), 3055 (w), 2924 (w), 1626 (m), 1601 (w), 1552 (w), 1531 (s), 1489 (m), 1441 (m), 1417 (m), 1354 (w), 1292 (m), 1255 (e), 1205 (m), 1142 (m), 1051 (w), 1047 (m), 182 (m), 157 (m), 330 (w), 783 (m), 739 (m), 688 (s). R_f (hexane/EtOAc 4:1) = 0.3.

*N-((5-Chlorothiophene-2-yl)methyl)benzamide (**10q**).* Compound **10q** was synthesized according to TP 1 from benzamide (61 mg, 0.6 mmol), formalin (45 μL, 37 wt % solution in H_2O, 0.6 mmol), 2-chlorothiophene (0.14 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol %) in nitromethane (2 mL) at 40 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (86 mg, 69%). Mp: 109−110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78−7.76 (m, 2H), 7.53−7.51 (m, 1H), 7.43 (t, J = 7.5 Hz, 2H), 6.80 (d, J = 3.7 Hz, 1H), 6.76 (d, J = 3.7 Hz, 1H), 6.51 (bs, 1H), 4.70 (d, J = 5.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.4, 139.9, 134.1, 131.9, 129.9, 128.8, 127.1, 125.9, 125.7, 39.3. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{11}ClNOS$ 252.02, found 252.50. HRMS (MALDI) m/z: calcd for $C_{12}H_{11}ClNOS$ 252.0244 $[M + H]^+$, found 252.0243. IR (cm^{-1}): 3317 (w), 1683 (w), 1629 (s), 1602 (m), 1577 (m), 1550 (s), 1534 (s), 1490 (s), 1453 (m), 1418 (m), 1356 (w), 1296 (m), 1258 (m), 1207 (m), 1189 (w), 1161 (w), 1146 (w), 1057 (w), 1035 (w), 1026 (w), 996 (m), 967 (m), 929 (w), 792 (m), 739 (w), 689 (s), 664 (m), 641 (m), 616 (m), 565 (m), 533 (w), 482 (w). R_f (hexane/EtOAc 4:1) = 0.2.

*N-((1-Tosyl-1H-indol-3-yl)methyl)benzamide (**10r**).* Compound **10r** was synthesized according to TP 1 from benzamide (61 mg, 0.6 mmol), formalin (45 μL, 37 wt % solution in H_2O, 0.6 mmol), 1-tosyl-1*H*-indole (407 mg, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol) in nitromethane (2 mL) at 40 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (155 mg, 76%, ratio of regioisomers 14:1). Mp: 157−159 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks only for major isomer listed): δ = 7.99 (d, J = 8.3 Hz, 1H), 7.79−7.74 (m, 4H), 7.61−7.56 (m, 2H), 7.51−7.47 (m, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.36−7.32 (m, 1H), 7.23 (d, J = 8.6 Hz, 3H), 6.29 (bs, 1H), 4.77 (d, J = 5.5 Hz, 2H), 2.33 (d, J = 8.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz) (peaks are not assigned to regioisomers): δ = 167.5, 145.3, 135.5, 135.4, 134.3, 131.8, 130.1, 129.7, 128.8, 127.1, 127.0, 125.3, 124.6, 123.6, 119.9, 119.4, 113.9, 35.3, 21.7. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{21}N_2O_3S$ 405.13, found 405.70. Anal. Calcd: C, 68.30; H, 4.98; N, 6.93; S, 7.93. Found: C, 67.90; H, 4.91; N, 6.63; S, 7.75. IR (cm^{-1}): 1639 (m), 1602 (w), 1578 (w), 1537 (m), 1490 (m), 1447 (m), 1424 (w), 1371 (s), 1327 (w), 1295 (m), 1273 (m), 1252 (m), 1207 (m), 1187 (m), 1172 (s), 1119 (s), 1093 (m), 1047 (m), 1016 (m), 987 (m), 963 (m), 805 (m), 788 (m), 757 (s), 749 (m), 711 (m), 695 (m), 665 (s), 622 (m), 589 (s), 582 (s), 568 (s), 543 (s), 533 (s), 494 (m). R_f (hexane/EtOAc 4:1) = 0.1.

*N-(Benzofuran-3-yl)benzamide (**10s**).* Compound **10s** was synthesized according to TP 1 from benzamide (61 mg, 0.5 mmol), formalin (45 μL, 37 wt % solution in H_2O, 0.6 mmol), benzofuran (0.16 mL, 1.5 mmol, 3.0 equiv), and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol %) in nitromethane (2 mL) at 40 °C for 24 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a white solid (88 mg, 70%, ratio of regioisomers: 24:1). Mp: 127−128 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) (peaks are listed only for major regioisomer): δ = 7.81 (d, J = 8 Hz, 2H), 7.52−7.51 (m, 2H), 7.45−7.43 (m, 3H), 7.27−7.21 (m, 2H), 6.67 (s, 1H), 6.63 (bs, 1H), 4.79 (d, J = 6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ = 167.5, 155.1, 154.0, 134.2, 131.9, 128.8, 128.4, 127.2, 124.4, 123.0, 121.2, 111.3, 104.6, 37.6. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}NO_2$ 252.10, found 252.40. HRMS (MALDI) m/z: $[M + H]^+$ calcd for $C_{16}H_{14}NO_2$ 252.1019, found 252.1021. IR (cm^{-1}): 3304 (w), 3049 (w), 1626 (m), 1578 (w), 1525 (m), 1489 (m), 1448 (m), 1361 (w), 1279 (m), 254 (w), 1219 (w), 1178 (m), 1076 (w), 1051 (w), 984 (w), 980 (m), 935 (m), 873 (m), 800 (m), 731 (w), 727 (w), 692 (s). R_f (hexane/EtOAc 4:1) = 0.2.

*N,N′-Methylene-bis-benzamide (**11**).* Benzamide (3.00 g, 25 mmol, 2.0 equiv), paraformaldehyde (0.41 g, 12 mmol, 1.0 equiv), and H_2SO_4 (1 drop) in toluene (25 mL) were refluxed in a Dean−Stark apparatus. After being cooled to 0 °C the mixture was filtrated and the crude residue washed with toluene and dried in high vacuum. The product was obtained as a colorless solid, sufficiently pure for further transformations

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(2.77 g, 91%). ^{1}H NMR (DMSO, 250 MHz): δ = 9.07−9.02 (m, 2H), 7.92−7.89 (m, 4H), 7.53−7.42 (m, 6H), 4.89−4.85 (m, 2H). Analytical data are consistent with the literature.[27]

*N-(Hydroxymethylene)benzamide (**12**).* A 50 mL round-bottom flask was charged with benzamide (7.00 g, 46.0 mmol, 1.2 equiv), K_2CO_3 (0.20 g, 1.5 mmol, 3 mol %), and formalin (4.1 mL, 37 wt % solution in H_2O, 55.0 mmol, 1.0 equiv) in H_2O (7 mL). The reaction was stirred at 50 °C until everything was dissolved. After being cooled to rt, the mixture was filtrated. Purification of the crude residue by recrystallization from ethanol yielded the product as a colorless solid, sufficiently pure for further transformations (1.33 g, 19%). ^{1}H NMR (DMSO, 250 MHz): δ = 9.14−9.10 (m, 1H), 7.88 (d, J = 8 Hz, 2H), 7.54 7.44 (m, 3H), 5.66 (bs, 1H), 4.72−4.70 (m, 2H). Analytical data are consistent with literature.[41]

*N-(2-Methyl-1-propen-1-yl)benzamide (**14**).* Compound **14** was isolated during the attempted preparation of *N*-(2-methyl-1-(2,4,6-trimethylbenzyl)propyl)benzamide. A 10 mL flask was charged with benzamide (72 mg, 0.6 mmol), isobutyraldehyde (42 μL, 0.5 mmol), mesitylene (0.21 mL, 1.5 mmol, 3.0 equiv), and Bi(OTf)$_3$ (7 mg, 0.01 mmol, 2 mol %) in DCE (2 mL). The reaction mixture was stirred at 80 °C for 16 h. After being cooled to room temperature, the reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by column chromatography (hexane/EtOAc 4:1) afforded **14** (66 mg, 75%) as a colorless solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.80−7.77 (m, 2H), 7.54−7.41 (m, 4H), 6.76−6.72 (m, 1H), 1.77 (s, 3H), 1.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.3, 134.4, 131.8, 128.8, 127.1, 117.5, 116.5, 22.7, 16.8. Analytical data are consistent with literature.[42]

*N-(2-Methyl-1-(5-methylfuran-2-yl)propyl)benzamide (**17**).* A 10 mL flask was charged with benzamide (72 mg, 0.6 mmol), isobutyraldehyde (42 μL, 0.5 mmol), and Bi(OTf)$_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (2 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a colorless solid (78 mg, 61%). Mp: 82−84 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.81−7.77 (m, 2H), 7.53−7.41 (m, 3H), 6.42 (bd, J = 8.9 Hz, 1H), 6.08 (d, J = 3.0 Hz, 1H), 5.89−5.87 (m, 1H), 5.09−5.03 (m, 1H), 2.27 (s, 3H), 2.24−2.17 (m, 1H), 1.02 (d, J = 6.8 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.8, 151.9, 151.4, 134.9, 131.6, 128.7, 127.1, 107.8, 106.1, 53.4, 32.6, 19.4, 19.0, 13.7. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{20}NO_2$ 258.2, found 258.5. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{16}H_{19}NO_2K$ 296.1048, found 296.1047. IR (cm^{-1}): 3337 (w), 2966 (m), 2923 (m), 1639 (s), 1603 (w), 1580 (m), 1565 (m), 1533 (s), 1492 (m), 1463 (m), 1383 (w), 1361 (m), 1346 (m), 1311 (m), 1269 (m), 1219 (m), 1149 (m), 1111 (w), 1055 (m), 1033 (s), 1018 (m), 1002 (m), 948 (w), 883 (w), 821 (w), 802 (w), 787 (s), 772 (m), 716 (m), 694 (s), 666 (m), 627 (m), 601 (m), 510 (w), 471 (w). R_f (hexane/EtOAc 4:1): 0.3.

*N-(1-(5-Methylfuran-2-yl)-3-phenylpropyl)benzamide (**19a**).* A 10 mL screw-cap vial was charged with benzamide (73 mg, 0.6 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), Bi(OTf)$_3$ (7 mg, 0.025 mmol, 2 mol %), and DCM (2 mL). The mixture was cooled to 0 °C, and 2-methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) was added. The reaction was stirred at rt for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow oil (130 mg, 81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.75−7.72 (m, 2H), 7.51−7.39 (m, 3H), 7.31−7.26 (m, 2H), 7.21−7.19 (m, 3H), 6.40 (bd, J = 8.5 Hz, 1H), 6.14 (d, J = 3.0 Hz, 1H), 5.92−5.90 (m, 1H), 5.33 (q., J = 7.3 Hz, 1H), 2.75−2.65 (m, 2H), 2.30−2.21 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.6, 152.2, 151.8, 141.5, 134.6, 131.6, 128.6, 128.6, 128.5, 127.1, 126.1, 107.6, 106.2, 47.8, 35.8, 32.5, 13.7. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO_2$ 320.2, found 320.5. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{21}H_{21}NO_2K$ 358.1204, found 358.1207. IR (cm^{-1}): 3322 (w), 1634 (s), 1602 (w), 1577 (m), 1527 (s), 1487 (m), 1454 (m), 1437 (m), 1354 (w), 1327 (m), 1289 (m), 1217 (m), 1200 (w), 1158 (w), 1093 (w), 1074 (m), 1062 (w), 1020 (m), 951 (m), 841 (w), 793 (m), 787 (m), 766 (m), 754 (w), 743 (m), 706 (s), 691 (s), 666 (m), 629 (m), 615 (m), 579 (m), 545 (m), 510 (w), 490 (m), 468 (w). R_f (hexane/EtOAc 4:1): 0.3.

*N-(1-(5-Methylfuran-2-yl)-2-phenylpropyl)benzamide (**19b**).* A 10 mL flask was charged with benzamide (72 mg, 0.6 mmol), 2-phenylpropionaldehyde (68 μL, 0.5 mmol), and Bi(OTf)$_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (2 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 1 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a yellow solid (85 mg, 53%, ratio of diastereomers: 7:1). Mp: 132−134 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) (peaks are listed only for major diasteromer): δ = 7.79−7.75 (m, 2H), 7.51−7.41 (m, 3H), 7.27−7.19 (m, 3H), 7.10−7.07 (m, 2H), 6.47 (bd, J = 9.2 Hz, 1H), 5.85 (d, J = 3.1 Hz, 1H), 5.78−5.77 (m, 1H), 5.45 (q, J = 9.2, 7.7 Hz, 1H), 3.34 (quint., J = 7.2 Hz, 1H), 2.20 (s, 3H), 1.42 (d, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) (peaks are listed only for major diastereomer): δ = 166.6, 151.3, 150.6, 142.7, 134.7, 131.7, 128.7, 128.2, 128.7, 127.1, 126.8, 108.7, 106.1, 53.1, 44.2, 18.2, 13.6. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO_2$ 320.2, found 320.6. HRMS (MALDI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{21}NO_2Na$ 342.1465, found 342.1465. IR (cm^{-1}): 3300 (w), 3061 (w), 3029 (w), 2970 (w), 2923 (w), 1635 (s), 1602 (w), 1579 (w), 1530 (m), 1489 (m), 1453 (m), 1375 (w), 1330 (m), 1288 (w), 1220 (w), 1183 (w), 1144 (w), 1075 (w), 1050 (w), 1020 (m), 1000 (w), 965 (w), 950 (w), 910 (w), 866 (w), 784 (m), 762 (m), 698 (s), 666 (m), 616 (w), 551 (w). R_f (hexane/EtOAc 4:1): 0.4.

*N-(1-(5-Methylfuran-2-yl)-2-phenylethyl)benzamide (**19c**).* A 10 mL flask was charged with benzamide (72 mg, 0.6 mmol), 2-phenylacetaldehyde (59 μL, 0.5 mmol), and Bi(OTf)$_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (2 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a colorless solid (68 mg, 45%). Mp: 130−132 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.73−7.70 (m, 2H), 7.50−7.38 (m, 3H), 7.28−7.18 (m, 3H), 7.14−7.11 (m, 2H), 6.37 (bd, J = 8.3 Hz, 1H), 5.96 (d, J = 3.1 Hz, 1H), 5.86−5.85 (m, 1H), 5.51 (q, J = 7.8 Hz, 1H), 3.31-3.17 (m, 2H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.6, 151.7, 151.5, 137.3, 134.6, 131.7, 129.5, 128.7, 128.5, 127.1, 126.8, 107.9, 106.3, 49.2, 40.4, 13.8. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_2$ 306.15, found 306.00. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{20}H_{19}NO_2K$ 344.1047, found 344.1047. IR (cm^{-1}): 3300 (w), 3062 (w), 1637 (s), 1603 (w), 1579 (m), 1533 (s), 1490 (s), 1454 (w), 1296 (w), 1219 (w), 1081 (w), 1038 (w), 1026 (w), 787 (w), 697 (s). R_f (hexane/EtOAc 4:1): 0.3.

*N-(2-(Benzyloxy)-1-(5-methylfuran-2-yl)ethyl)benzamide (**19d**).* A 10 mL flask was charged with benzamide (72 mg, 0.6 mmol), (benzyloxy)acetaldehyde (72 μL, 0.5 mmol), and Bi(OTf)$_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (4 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a yellow oil (129 mg, 77%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.77−7.74 (m, 2H), 7.46−7.36 (m, 3H), 7.29−7.22 (m, 5H), 6.70 (bd, J = 8.2 Hz, 1H), 6.15 (d, J = 3.1 Hz, 1H), 5.89−5.88 (m, 1H), 5.49−5.43 (m, 1H), 4.53 (d, J = 2.4 Hz, 2H), 3.91-3.86 (m, 1H), 3.81-3.76 (m, 1H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz):

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δ = 166.8, 151.7, 150.6, 138.0, 134.4, 131.7, 128.6, 128.5, 127.8, 127.8, 127.2, 108.0, 106.4, 73.2, 70.6, 47.7, 13.7. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NO_3$ 336.2, found 336.3. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{21}H_{21}NO_3K$ 374.1153, found 374.1156. IR (cm^{-1}): 3321 (w), 3063 (w), 3031 (w), 2923 (w), 2866 (w), 1722 (m), 1642 (s), 1602 (m), 1579 (m), 1521 (s), 1486 (m), 1453 (m), 1362 (m), 1270 (m), 1248 (m), 1208 (m), 1177 (m), 1158 (m), 1098 (s), 1072 (s), 1026 (s), 1001 (m), 929 (m), 800 (m), 737 (m), 711 (s), 695 (s), 609 (m), 571 (m). R_f (hexane/EtOAc 4:1): 0.2.

*N-(1-(5-Methylfuran-2-yl)propyl)benzamide (**19e**).* A 10 mL flask was charged with benzamide (72 mg, 0.6 mmol), propanal (37 μL, 0.5 mmol), and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (4 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 22 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a yellow oil (65 mg, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.80−7.76 (m, 2H), 7.52−7.38 (m, 3H), 6.38 (bd, J = 8.3 Hz, 1H), 6.11 (d, J = 3.0 Hz, 1H), 5.89−5.88 (m, 1H), 5.16 (q, J = 7.4 Hz, 1H), 2.27 (s, 3H), 1.98−1.87 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.7, 152.4, 151.7, 134.8, 131.6, 128.7, 127.1, 107.8, 106.2, 49.3, 27.4, 13.7, 10.6. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{18}NO_2$ 244.13, found 244.00. HRMS (MALDI) m/z: $[M - H]^+$ calcd for $C_{15}H_{16}NO_2$ 242.1181, found 242.1177. IR (cm^{-1}): 3311 (w), 2968 (w), 2935 (w), 2876 (w), 1726 (w), 1635 (s), 1602 (w), 1578 (m), 1531 (s), 1489 (m), 1458 (w), 1447 (w), 1385 (w), 1329 (m), 1297 (m), 1244 (w), 1216 (w), 1186 (w), 1153 (w), 1125 (w), 1103 (w), 1074 (w), 1021 (m), 1000 (w), 949 (w), 931 (w), 855 (w), 785 (m), 768 (w), 710 (m), 691 (s), 662 (m), 615 (m), 571 (w), 550 (w). R_f (hexane/EtOAc 4:1): 0.4.). Analytical data are consistent with literature.[43]

*N-(2-Methyl-1-(5-methylfuran-2-yl)butyl)benzamide (**19f**).* A 10 mL flask was charged with benzamide (72 mg, 0.6 mmol), 2-methylbutyraldehyde (56 μL, 0.5 mmol), and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (4 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a yellow oil (98 mg, 72%, ratio of diastereomers 2:1). ^{1}H NMR ($CDCl_3$, 300 MHz) (peaks are not assigned to diastereomers): δ = 7.80−7.77 (m, 2H), 7.53−7.40 (m, 3H), 6.46−6.37 (m, 1H), 6.07 (t, J = 3.5 Hz, 1H), 5.89−5.87 (m, 1H), 5.23−5.10 (m, 1H), 2.27 (s, 3H), 2.02−1.93 (m, 1H), 1.59−1.40 (m, 1H), 1.22−1.11 (m, 1H), 1.00−0.89 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) (peaks are not assigned to diastereomers): δ = 166.8, 166.7, 152.2, 151.8, 151.4, 134.9, 131.6, 128.7, 128.7, 127.1, 107.9, 107.5, 106.1, 52.3, 52.0, 38.9, 26.3, 25.8, 15.8, 15.3, 13.7, 11.7, 11.6. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}NO_2$ 272.2, found 272.4. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{17}H_{21}NO_2K$ 310.1204, found 310.1204. IR (cm^{-1}): 3300 (w), 3061 (w), 2963 (w), 2925 (w), 2876 (w), 1635 (s), 1603 (w), 1579 (m), 1529 (s), 1488 (m), 1462 (m), 1381 (w), 1328 (m), 1287 (m), 1261 (m), 1220 (m), 1187 (w), 1142 (w), 1075 (w), 1020 (m), 1001 (w), 964 (w), 951 (w), 911 (w), 877 (w), 783 (s), 731 (m), 709 (s), 692 (s), 666 (m), 616 (m), 573 (m), 521 (w). R_f (hexane/EtOAc 4:1): 0.4.

*N-(3-Methyl-1-(5-methylfuran-2-yl)butyl)benzamide (**19g**).* A 10 mL flask was charged with benzamide (72 mg, 0.6 mmol), isovaleraldehyde (55 μL, 0.5 mmol), and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (4 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1 → 4:1) yielded the product as a colorless solid (90 mg, 66%). Mp: 111−113 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.79−7.76 (m, 2H), 7.51−7.38 (m, 3H), 6.31 (bd, J = 8.5 Hz, 1H), 6.11 (d, J = 3.0 Hz, 1H), 5.88−5.87 (m, 1H), 5.34 (q, J = 16.2, 7.8 Hz, 1H), 2.26 (s, 3H), 1.82−1.75 (m, 2H), 1.68−1.54 (m, 1H), 1.00−0.94 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.5, 152.9, 151.6, 134.7, 131.6, 128.7, 127.1, 107.1, 106.2, 46.2, 43.4, 25.2, 22.7, 22.7, 13.7. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{22}NO_2$ 272.2, found 272.8. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{17}H_{21}NO_2K$ 310.1204, found 310.1205. IR (cm^{-1}): 3300 (w), 3062 (w), 2955 (w), 2925 (w), 2869 (w), 1634 (s), 1603 (w), 1579 (m), 1532 (s), 1490 (m), 1469 (m), 1448 (w), 1385 (w), 1367 (w), 1331 (m), 1289 (m), 1220 (m), 1187 (w), 1148 (w), 1076 (w), 1037 (w), 1021 (m), 1001 (w), 953 (w), 937 (w), 869 (w), 782 (s), 693 (s), 666 (m), 647 (m), 616 (m), 555 (w). R_f (hexane/EtOAc 4:1): 0.5.

*N-(1-(5-Methylfuran-2-yl)-3-phenylpropyl)acrylamide (**20a**).* A 10 mL flask was charged with acrylamide (76 mg, 1.0 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (2 mL). 2-Methylfuran (59 μL, 0.6 mmol, 1.2 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (78 mg, 59%). Mp: 76−78 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.29−7.24 (m, 2H), 7.19−7.15 (m, 3H), 6.28 (dd, J = 17.0, 1.5 Hz, 1H), 6.11-6.02 (m, 2H), 5.95 (bd, J = 8.6 Hz, 1H), 5.88−5.87 (m, 1H), 5.63 (dd, J = 10.2, 1.5 Hz, 1H), 5.17 (q, J = 7.4 Hz, 1H), 2.68−2.57 (m, 2H), 2.26 (s, 3H), 2.20−2.10 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.7, 152.0, 151.8, 141.5, 130.9, 128.5, 128.5, 126.9, 126.1, 107.6, 106.2, 47.4, 35.8, 32.4, 13.7. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}NO_2$ 270.2, found 270.5. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{17}H_{19}NO_2K$ 308.1047, found 308.1049. IR (cm^{-1}): 3267 (w), 3062 (w), 3027 (w), 2923 (w), 2861 (w), 1655 (s), 1625 (m), 1535(s), 1496 (m), 1454 (m), 1407 (m), 1384 (w), 1314 (w), 1278 (w), 1239 (m), 1219 (m), 1066 (w), 1020 (m), 984(m), 957 (m), 846 (w), 785 (m), 748 (m), 698 (s), 567 (w), 495 (m). R_f (hexane/EtOAc 7:3): 0.3.

*2-Chloro-N-(1-(5-methylfuran-2-yl)-3-phenylpropyl)acetamide (**20b**).* A 10 mL flask was charged with 2-chloroacetamide (91 mg, 1.0 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (2 mL). 2-Methylfuran (0.05 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a yellow oil (46 mg, 32%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31-7.28 (m, 2H), 7.21-7.16 (m, 3H), 6.76 (bd, J = 8.5 Hz, 1H), 6.10 (d, J = 3.1 Hz, 1H), 5.91-5.90 (m, 1H), 5.09 (quart., J = 7.4 Hz, 1H), 4.04 (s, 2H), 2.66−2.60 (m, 2H), 2.28 (s, 3H), 2.23−2.12 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 165.1, 152.1, 151.4, 141.2, 128.6, 128.5, 126.2, 107.8, 106.2, 47.7, 42.8, 35.5, 32.4, 13.7. MS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}ClNO_2Na$ 314.1, found 314.3. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{16}H_{18}ClNO_2K$ 330.0658, found 330.0658. IR (cm^{-1}): 3280 w), 3062 (w), 3027 (w), 2923 (w), 2863 (w), 2076 (w), 1657 (s), 1603 (w), 1527 (m), 1496 (m), 1454 (m), 1410 (w), 1384 (w), 1334 (w), 1219 (m), 1176 (w), 1154 (w), 1055 (m), 1033 (m), 1020 (m), 938 (w), 783 (s), 749 (m), 698 (s), 564 (m), 485 (m). R_f (hexane/EtOAc 4:1): 0.4.

*Ethyl (1-(5-Methylfuran-2-yl)-3-phenylpropyl)carbamate (**20c**).* A 10 mL screw-cap vial was charged with urethane (45 mg, 0.6 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), $Bi(OTf)_3$ (7 mg, 0.025 mmol, 2 mol %), and DCM (2 mL). The mixture was cooled to 0 °C, and 2-methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) was added. The reaction was stirred at rt for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 12:1 → 9:1 → 4:1) yielded the

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product as a yellow oil (68 mg, 47%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.28−7.24 (m, 2H), 7.18−7.15 (m, 3H), 6.04 (bd, J = 2.8 Hz, 1H), 5.87−5.85 (m, 1H), 5.05−4.81 (m, 1H), 4.81−4.66 (m, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.67−2.56 (m, 2H), 2.24 (s, 3H), 2.12−2.03 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.7, 152.7, 151.7, 141.5, 128.5, 126.1, 107.1, 106.1, 61.1, 49.1, 36.2, 32.3, 14.7, 13.7. MS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{21}NO_3Na$ 310.1, found 310.3. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{17}H_{21}NO_3K$ 326.1153, found 326.1154. IR (cm^{-1}): 3319 (w), 3062 (w), 3027 (w), 2981 (w), 2924 (w), 2863 (w), 1693 (s), 1604 (w), 1514 (m), 1497 (m), 1454 (m), 1376 (w), 1329 (m), 1240 (s), 1219 (s), 1172 (m), 1133 (w), 1047 (s), 1033 (m), 1020 (s), 960 (w), 909 (w), 875 (w), 845 (w), 779 (s), 749 (m), 699 (s), 558 (m), 505 (m). R_f (hexane/EtOAc 4:1): 0.6.

*Benzyl (1-(5-Methylfuran-2-yl)-3-phenylpropyl)carbamate (**20d**).* A 10 mL screw-cap vial was charged with benzyl carbamate (76 mg, 0.6 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), $Bi(OTf)_3$ (7 mg, 0.025 mmol, 2 mol %), and DCM (2 mL). The mixture was cooled to 0 °C, and 2-methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) was added. The reaction was stirred at rt for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 12:1 → 9:1 → 4:1) yielded the product as a colorless solid (79 mg, 45%). Mp: 67−69 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.37−7.15 (m, 10H), 6.06 (d, J = 3.0 Hz, 1H), 5.89−5.87 (m, 1H), 5.16−5.01 (m, 3H), 4.83−4.78 (m, 1H), 2.67−2.60 (m, 2H), 2.26 (s, 3H), 2.17−2.07 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 155.8, 152.4, 151.8, 141.5, 136.6, 128.7, 128.6, 128.5, 128.3, 126.1, 107.2, 106.1, 67.0, 49.3, 36.1, 32.4, 13.7. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{24}NO_3$ 350.18, found 350.00. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{22}H_{23}NO_3K$ 388.1310, found 388.1317. IR (cm^{-1}): 3265 (w), 1683 (s), 1585 (w), 1539 (s), 1497 (m), 1454 (m), 1441 (m), 1386 (w), 1358 (w), 1324 (m), 1289 (s), 1257 (s), 1242 (s), 1218 (s), 1197 (m), 1155 (m), 1138 (m), 1090 (m), 1041 (s), 1019 (s), 995 (m), 967 (m), 943 (m), 931 (m), 911 (m), 779 (s), 746 (s), 724 (m), 697 (s), 621 (m), 589 (m), 578 (m), 512 (m), 485 (m), 459 (s). R_f (hexane/EtOAc 4:1): 0.3.

*tert-Butyl (1-(5-Methylfuran-2-yl)-3-phenylpropyl)carbamate (**20e**).* A 10 mL flask was charged with *tert*-butyl carbamate (70 mg, 0.6 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (2 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 1 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a yellow oil (120 mg, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30−7.16 (m, 5H), 6.04 (d, J = 3.0 Hz, 1H), 5.88−5.87 (m, 1H), 4.76 (d, J = 18.4 Hz, 3H), 2.67−2.61 (m, 2H), 2.26 (s, 3H), 2.14−2.03 (m, 2H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 155.3, 153.0, 151.6, 141.7, 128.6, 128.5, 126.0, 106.9, 106.1, 48.8, 36.4, 32.4, 28.5, 28.5, 13.7. MS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{25}NO_3Na$ 338.2, found 338.4. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{19}H_{25}NO_3K$ 354.1472, found 354,1476. IR (cm^{-1}): 3347 (w), 3028 (w), 2979 (w), 2932 (w), 1697 (s), 1603 (m), 1497 (m), 1454 (m), 1392 (m), 1367 (s), 1248 (s), 1153 (s), 1047 (m), 1024 (s), 856 (m), 749 (s), 699 (s), 546 (m), 493 (m). R_f (hexane/EtOAc 4:1): 0.6.

*tert-Butyl ((2S)-3-Methyl-1-((1-(5-methylfuran-2-yl)-3-phenylpropyl)amino)-1-oxobutan-2-yl)carbamate (**22**).* A 10 mL flask was charged with (S)-*tert*-butyl (1-amino-3-methyl-1-oxobutan-2-yl)carbamate (130 mg, 0.6 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (2 mL). 2-Methylfuran (0.14 mL, 1.5 mmol, 3.0 equiv) in DCM (2 mL) was added over 2 h via syringe pump to the solution. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 9:1) yielded the product as a colorless solid (128 mg, 62%, ratio of diastereomers 2:1). Mp: 85−87 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30−7.15 (m, 5H), 6.23−6.15 (m, 1H), 6.06−6.04 (m, 1H), 5.87−5.86 (m, 1H), 5.10−5.04 (m, 2H), 3.91-3.81 (m, 1H), 2.65−2.58 (m, 2H), 2.26−2.24 (m, 3H), 2.17−2.08 (m, 2H), 1.43 (s, 9H), 0.99−0.89 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) (peaks are not assigned to diastereomers): δ = 170.8, 156.0, 152.0, 151.8, 141.4, 128.6, 128.5, 126.1, 126.1, 107.4, 106.2, 106.1, 80.0, 60.6, 47.3, 47.2, 35.8, 35.6, 32.4, 30.9, 28.4, 19.5, 19.3, 17.9, 13.7, 13.6. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{35}N_2O_4$ 415.26, found 415.15. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{24}H_{34}N_2O_4K$ 453.2150, found 453.2142. IR (cm^{-1}): 3681 (w), 3301 (w), 2966 (m), 2924 (m), 2872 (w), 2845 (w), 2248 (w), 1683 (m), 1649 (s), 1604 (w), 1517 (m), 1497 (m), 1454 (m), 1391 (m), 1366 (m), 1298 (m), 1246 (m), 1167 (s), 1053 (m), 1033 (m), 1018 (m), 878 (w), 850 (w), 784 (m), 731 (s), 698 (s), 647 (m), 566 (w), 517 (m), 493 (m), 462 (m). R_f (hexane/EtOAc 4:1): 0.4.

*N-(1-(5-Methylthiophene-2-yl)-3-phenylpropyl)benzamide (**23a**).* A 10 mL screw-cap vial was charged with benzamide (73 mg, 0.6 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), 2-methylthiophene (0.15 mL, 1.5 mmol, 3.0 equiv), $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol %), and DCM (6 mL). The reaction was stirred at 35 °C for 16 h. After being cooled to room temperature, the reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (102 mg, 61%). Mp: 152−154 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (d, J = 7.7 Hz, 2H), 7.52−7.39 (m, J = 14.7, 7.3 Hz, 3H), 7.31−7.16 (m, 5H), 6.82 (d, J = 3.3 Hz, 1H), 6.62 (d, J = 3.0 Hz, 1H), 6.23 (bd, J = 8.2 Hz, 1H), 5.46 (q, J = 7.4 Hz, 1H), 2.75 (t, J = 7.9 Hz, 2H), 2.46 (s, 3H), 2.40−2.25 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.6, 143.2, 141.5, 139.2, 134.5, 131.7, 128.7, 128.7, 128.6, 127.1, 126.2, 125.1, 124.8, 49.7, 38.3, 32.7, 15.5. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NOS$ 336.1, found 336.4. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{21}H_{21}NOSK$ 374.0975, found 374.0975. IR (cm^{-1}): 3288 (w), 3061 (w), 3027 (w), 2920 (w), 2858 (w), 2244 (w), 1633 (s), 1602 (m), 1579 (m), 1530 (s), 1489 (s), 1453 (m), 1327 (m), 1288 (m), 1229 (m), 1184 (w), 1158 (w), 1075 (m), 1044 (w), 1029 (m), 1001 (w), 908 (m), 869 (w), 844 (w), 798 (m), 730 (s), 694 (s), 647 (m), 616 (m), 531 (m), 492 (m). R_f (hexane/EtOAc 4:1) = 0.5.

*N-(1-(2,4-Dimethoxyphenyl)-3-phenylpropyl)benzamide (**23c**).* A 10 mL screw-cap vial was charged with benzamide (73 mg, 0.6 mmol), 3-phenylpropionaldehyde (69 μL, 0.5 mmol), and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol %) in DCM (2 mL)). The solution was stirred at 25 °C for 5 min and cooled to 0 °C. Then 1,3-dimethoxybenzene (0.20 mL, 1.5 mmol, 3.0 equiv) was added. The mixture was stirred at 25 °C for 16 h. The reaction mixture was diluted with EtOAc and filtered over a short plug of Celite and silica gel. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (109 mg, 58%). Mp: 125−127 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.73−7.69 (m, 2H), 7.45−7.36 (m, 3H), 7.27−7.13 (m, 7H), 6.49−6.42 (m, 2H), 5.30 (q, J = 7.5 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 2.72−2.51 (m, 2H), 2.34−2.10 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.3, 160.4, 158.4, 142.0, 135.2, 131.3, 130.1, 128.6, 128.5, 128.4, 127.0, 125.9, 122.0, 104.3, 99.6, 55.6, 55.5, 52.6, 37.1, 33.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{26}NO_3$ 376.19, found 376.33. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{24}H_{25}NO_3K$ 414.1466, found 414.1462. IR (cm^{-1}): 3315 (w), 2999 (w), 2835 (w), 1634 (s), 1616 (m), 1591 (m), 1578 (w), 1527 (s), 1505 (s), 1448 (m), 1419 (m), 1361 (m), 1299 (m), 1260 (s), 1209 (s), 1175 (m), 1157 (s), 1126 (s), 1080 (m), 1037 (s), 922 (m), 871 (w), 819 (s), 803 (m), 786 (m), 725 (s), 692 (s), 680 (s), 633 (m), 546 (m), 508 (m), 475 (m). R_f (hexane/EtOAc 4:1): 0.2. Analytical data are consistent with literature.[43]

*N-(Mesityl(phenyl)methyl)benzamide (**25**).* Compound **25** was synthesized according to TP 2 from benzamide (121 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), mesitylene (0.38 mL, 2.7 mmol, 2.7 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1

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→ 9:1) yielded the product as a colorless solid (235 mg, 71%). Mp: 75−77 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.84−7.81 (m, 2H), 7.53−7.40 (m, 3H), 7.29−7.19 (m, 3H), 7.17−7.14 (m, 2H), 7.00 (bd, J = 8.6 Hz, 1H), 6.89−6.85 (m, 3H), 2.31 (s, 6H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.8, 141.2, 137.4, 136.9, 134.8, 134.5, 131.8, 130.3, 128.8, 128.7, 127.1, 126.9, 126.1, 52.2, 21.1, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{24}NO$ 330.19, found 330.32. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{23}NOK$ 368.1411, found 368.1410. IR (cm^{-1}): 2918 (w), 1640 (m), 1600 (w), 1579 (w), 1513 (s), 1482 (s), 1376 (w), 1344 (w), 1272 (m), 1192 (w), 1127 (w), 1028 (w), 906 (w), 860 (w), 803 (w), 789 (w), 727 (s), 707 (s), 697 (m), 687 (m), 663 (w), 650 (w), 620 (w), 592 (m), 533 (m). R_f (hexane/EtOAc 4:1): 0.5. Analytical data are consistent with literature.[12]

*N-((2,4-Dimethylphenyl)(phenyl)methyl)benzamide (**26**).* Compound **26** was synthesized according to TP 2 benzamide (145 mg, 1.2 mmol), benzaldehyde (99 μL, 1.2 mmol), *m*-xylene (0.37 mL, 3.0 mmol, 3.0 equiv), $Bi(OTf)_3$ (33 mg, 0.05 mmol, 5 mol %), and TfOH (4 μL, 0.05 mmol, 5 mol %) in DCE (4 mL) at 150 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (239 mg, 76%). Mp: 154−156 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.83−7.80 (m, J = 6.9, 1.6 Hz, 2H), 7.54−7.41 (m, 3H), 7.33−7.25 (m, 5H), 7.06−6.86 (m, 3H), 6.64−6.46 (m, 2H), 2.33 (s, 3H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.4, 141.3, 137.4, 136.7, 136.5, 134.4, 131.9, 131.8, 128.8, 128.8, 127.6, 127.5, 127.2, 127.0, 127.0, 54.4, 21.1, 19.6. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}NO$ 316.17, found 316.32. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{22}H_{21}NOK$ 354.1255, found 354.1251. IR (cm^{-1}): 3344 (w), 2919 (w), 1628 (s), 1576 (m), 1524 (s), 1498 (m), 1486 (s), 1379 (w), 1360 (m), 1303 (m), 1278 (m), 1237 (m), 1211 (w), 1135 (w), 1075 (m), 1053 (w), 1030 (m), 978 (w), 930 (w), 853 (w), 819 (s), 805 (m), 738 (s), 713 (s), 702 (s), 689 (s), 663 (m), 646 (m), 620 (m), 586 (s), 563 (m), 542 (m). R_f (hexane/EtOAc 4:1): 0.5.

*N-((3-Chlorophenyl)(mesityl)methyl)benzamide (**28a**).* Compound **28a** was synthesized according to TP 2 from benzamide (121 mg, 1.0 mmol), 3-chlorobenzaldehyde (0.14 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (196 mg, 54%). Mp: 130−132 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.85−7.82 (m, 2H), 7.54−7.44 (m, 3H), 7.26−7.16 (m, 3H), 7.08−7.02 (m, 1H), 6.97 (bd, J = 8.5 Hz, 1H), 6.91 (s, 2H), 6.82 (bd, J = 8.6 Hz, 1H), 2.31 (s, 9H). ^{13} C NMR ($CDCl_3$, 75 MHz): δ = 167.0, 143.8, 137.8, 136.8, 134.8, 134.3, 134.2, 132.0, 130.5, 130.0, 128.9, 127.2, 127.1, 126.2, 124.3, 51.8, 21.1, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}ClNO$ 364.15, found 364.28. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{22}ClNOK$ 402.1022, found 402.1024. IR (cm^{-1}): 1640 (s), 1600 (w), 1580 (m), 1570 (m), 1512 (s), 1481 (s), 1443 (m), 1423 (m), 1379 (w), 1336 (m), 1272 (m), 1236 (w), 1207 (w), 1190 (m), 1146 (w), 1128 (w), 1099 (w), 1073 (w), 1055 (m), 1033 (m), 1001 (w), 893 (w), 861 (m), 795 (w), 762 (s), 746 (m), 713 (s), 703 (m), 685 (s), 665 (w), 650 (m), 595 (s), 551 (m), 523 (m), 486 (w). R_f (hexane/EtOAc 4:1): 0.6.

*N-((3-Bromophenyl)(mesityl)methyl)benzamide (**28b**).* Compound **28b** was synthesized according to TP 2 from benzamide (121 mg, 1.0 mmol), 3-bromobenzaldehyde (0.14 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (222 mg, 54%). Mp: 139−141 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.88−7.78 (m, 2H), 7.57−7.40 (m, 3H), 7.42−7.33 (m, 1H), 7.32−7.30 (m, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.12−7.05 (m, 1H), 6.99−6.96 (m, 1H), 6.91 (s, 2H), 6.79 (bd, J = 8.6 Hz, 1H), 2.30 (s, 9H). ^{13} C NMR ($CDCl_3$, 75 MHz): δ = 167.0, 144.1, 137.8, 136.8, 134.3, 134.2, 132.0, 130.5, 130.3, 130.2, 129.1, 128.9, 127.2, 124.9, 123.1, 51.8, 21.1, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}BrNO$ 408.10, found 408.68. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{22}BrNOK$ 446.0516, found 446.0504. IR (cm^{-1}): 2967 (w), 1640 (s), 1580 (m), 1512 (s), 1481 (s), 1272 (m), 1055 (m), 1033 (s), 861 (m), 760 (s), 709 (s), 687 (s), 675 (m), 595 (s), 548 (m). R_f (hexane/EtOAc 4:1): 0.5.

*N-((4-Chlorophenyl)(mesityl)methyl)benzamide (**28c**).* Compound **28c** was synthesized according to TP 2 from benzamide (121 mg, 1.0 mmol), 4-chlorobenzaldehyde (172 mg, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (261 mg, 72%). Mp: 62−64 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.83−7.81 (m, 2H), 7.56−7.43 (m, 3H), 7.28−7.26 (m, 1H), 7.25−7.24 (m, 1H), 7.11−7.07 (m, 2H), 6.96−6.90 (m, 3H), 6.79 (bd, J = 8.3 Hz, 1H), 2.29 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.9, 140.0, 137.8, 136.8, 134.4, 132.8, 132.0, 130.5, 128.9, 128.8, 127.6, 127.1, 51.8, 21.1, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}ClNO$ 364.15, found 364.28. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{22}ClNOK$ 402.1022, found 402.1017. IR (cm^{-1}): 3313 (w), 2921 (w), 1638 (m), 1579 (w), 1508 (m), 1483 (s), 1378 (w), 1343 (w), 1311 (m), 1178 (w), 1150 (w), 1091 (m), 1058 (m), 1033 (m), 1013 (m), 909 (w), 850 (m), 824 (m), 799 (m), 768 (m), 709 (s), 691 (s), 658 (m), 601 (m), 577 (m), 562 (m), 532 (m), 499 (m). R_f (hexane/EtOAc 4:1): 0.6.

*N-((4-Fluorophenyl)(mesityl)methyl)benzamide (**28d**).* Compound **28d** was synthesized according to TP 2 from benzamide (121 mg, 1.0 mmol), 4-fluorobenzaldehyde (0.13 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (243 mg, 64%). Mp: 60−62 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.84−7.81 (m, 2H), 7.53−7.43 (m, 3H), 7.14−7.09 (m, 2H), 7.00−6.95 (m, 3H), 6.90 (s, 2H), 6.81 (bd, J = 8.5 Hz, 1H), 2.30 (s, 6H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.9, 163.6, 160.3, 137.6, 137.0 (d, J = 3.1 Hz), 136.8, 134.6, 134.3, 131.9, 130.5, 128.9, 127.8 (d, J = 8.0 Hz), 127.1, 115.7, 115.4, 51.7, 21.1, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}FNO$ 348.18, found 348.32. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{22}FNOK$ 386.1317, found 386.1316. IR (cm^{-1}): 3301 (w), 2921 (w), 1639 (m), 1601 (w), 1580 (w), 1505 (s), 1481 (m), 1378 (w), 1310 (w), 1222 (m), 1157 (m), 1098 (w), 1057 (w), 1033 (m), 1014 (m), 849 (m), 833 (m), 804 (w), 770 (m), 710 (m), 691 (m), 661 (m), 612 (m), 585 (m), 533 (m), 503 (m), 459 (m). R_f (hexane/EtOAc 4:1): 0.6.

*N-((2-Chloro-5-nitrophenyl)(mesityl)methyl)benzamide (**28e**).* Compound **28e** was synthesized according to TP 2 from benzamide (121 mg, 1.0 mmol), 2-chloro-5-nitrobenzaldehyde (190 mg, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (269 mg, 66%). Mp: 220−222 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.34 (dd, J = 2.6, 0.7 Hz, 1H), 8.11-8.07 (m, 1H), 7.85−7.82 (m, 2H), 7.58−7.44 (m, 4H), 6.87 (bs, 2H), 6.80 (d, J = 6.6 Hz, 1H), 6.51 (bd, J = 6.6 Hz, 1H), 2.28 (s, 3H), 2.21 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.1, 146.7, 141.6, 140.2, 138.5, 137.1, 133.5, 132.3, 131.9, 131.4, 131.0, 129.0, 127.3, 124.1, 123.4, 52.8, 21.6, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{22}ClN_2O_3$ 409.13, found 409.30. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{21}ClN_2O_3K$ 447.0872, found 447.0871. IR (cm^{-1}): 2921 (w), 1640 (s), 1595 (w), 1580 (w), 1513 (s), 1481 (s), 1423 (w), 1379 (w), 1342 (m), 1318 (w), 1273 (m), 1238 (w), 1207 (w), 1190 (w), 1147 (w), 1129 (w), 1099 (w), 1073 (w), 1055 (w), 1033 (m), 1001 (w), 909 (w), 889 (w), 861 (m), 795 (w), 762 (m), 742 (m), 713 (s), 685 (s), 650 (w), 595 (m), 552 (m), 523 (m), 486 (w), 458 (w). R_f (hexane/EtOAc 4:1): 0.5.

*N-(Mesityl(naphthalen-2-yl)methyl)benzamide (**28f**).* Compound **28f** was synthesized according to TP 2 from benzamide (121 mg, 1.0 mmol), 1-naphthaldehyde (0.16 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a yellow oil (110 mg, 29%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.07−8.04 (m, 1H), 7.92−7.88 (m, 1H), 7.83−7.75 (m, 3H), 7.51−7.33 (m, 7H), 7.26−7.23 (m, 1H), 6.92 (s, 2H), 6.75 (bd, J = 7.8 Hz, 1H), 2.36 (s, 6H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.0, 137.1, 136.9, 134.8, 134.4, 134.1, 133.8, 131.7, 130.6, 129.0, 129.0, 128.8, 127.1, 126.9, 126.2, 126.0, 125.3, 123.9, 51.9, 21.8, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{27}H_{26}NO$ 380.20, found 380.36. HRMS (MALDI) m/z: $[M + K]^+$

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calcd for $C_{27}H_{25}NOK$ 418.1568, found 418.1556. IR (cm^{-1}): 3300 (w), 2921 (w), 2243 (w), 1638 (s), 1600 (w), 1579 (w), 1508 (s), 1481 (s), 1397 (w), 1373 (w), 1348 (w), 1298 (w), 1262 (w), 1238 (w), 1150 (w), 1074 (w), 1033 (m), 907 (m), 852 (m), 800 (m), 778 (s), 728 (s), 709 (s), 691 (s), 647 (m), 624 (w), 602 (m), 563 (m), 534 (m), 506 (m). R_f (hexane/EtOAc 4:1): 0.5.

*N-(Mesityl(phenyl)methyl)-4-methoxybenzamide (**29a**).* Compound **29a** was synthesized according to TP 2 from 4-methoxybenzamide (154 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (140 mg, 39%). Mp: 184−186 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.88 (bd, J = 8.6 Hz, 1H), 8.30 (dd, J = 7.8, 1.8 Hz, 1H), 7.49−7.43 (m, 1H), 7.31−7.28z (m, 1H), 7.24−7.17 (m, 3H), 7.13−7.05 (m, 2H), 6.99 (d, J = 8.3 Hz, 1H), 6.89 (s, 2H), 3.94 (s, 3H), 2.33 (s, 6H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.8, 157.7, 142.0, 137.1, 136.9, 135.6, 133.0, 132.9, 130.2, 128.6, 126.6, 126.0, 121.6, 121.5, 111.4, 56.1, 51.7, 21.0, 20.8. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{26}NO_2$ 360.20, found 360.36. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{24}H_{25}NO_2K$ 398.1517, found 398.1512. IR (cm^{-1}): 2967 (w), 1632 (m), 1598 (m), 1518 (m), 1345 (m), 1292 (m), 1260 (m), 1186 (m), 1062 (s), 1033 (s), 1016 (s), 867 (m), 850 (m), 807 (m), 781 (w), 698 (s), 623 (m), 584 (m). R_f (hexane/EtOAc 4:1): 0.4.

*4-Bromo-N-(mesityl(phenyl)methyl)benzamide (**29b**).* Compound **29b** was synthesized according to TP 2 from 4-bromobenzamide (206 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (228 mg, 56%). Mp: 163−165 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.72−7.69 (m, 2H), 7.61−7.57 (m, 2H), 7.33−7.24 (m, 3H), 7.16 (d, J = 1.3 Hz, 2H), 6.97 (d, J = 8.5 Hz, 1H), 6.91 (s, 2H), 6.80 (bd, J = 8.4 Hz, 1H), 2.30 (s, 6H), 2.30 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 165.9, 141.0, 137.5, 136.9, 134.6, 133.3, 132.1, 130.4, 128.8, 128.7, 127.1, 126.5, 126.1, 52.3, 21.1, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}BrNO$ 408.10, found 408.22. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{22}BrNOK$ 446.0516, found 446.0507. IR (cm^{-1}): 2922 (w), 1636 (m), 1589 (m), 1568 (w), 1516 (s), 1493 (w), 1477 (s), 1448 (m), 1378 (w), 1343 (m), 1309 (m), 1269 (m), 1146 (w), 1127 (w), 1111 (w), 1074 (w), 1051 (w), 1028 (w), 1011 (m), 891 (w), 856 (w), 843 (m), 792 (w), 754 (s), 733 (s), 698 (s), 650 (w), 594 (m), 535 (m), 524 (m), 497 (w). R_f (hexane/EtOAc 9:1): 0.7.

*N-(Mesityl(phenyl)methyl)-4-nitrobenzamide (**29c**).* Compound **29c** was synthesized according to TP 2 from 4-nitrobenzamide (169 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a yellow solid (251 mg, 67%). Mp: 161-163 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.31 (d, J = 8.9 Hz, 2H), 7.99 (d, J = 8.9 Hz, 2H), 7.35−7.29 (m, 3H), 7.16−7.14 (m, 2H), 6.99 (d, J = 8.5 Hz, 1H), 6.96−6.84 (m, 3H), 2.31 (s, 6H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 164.9, 149.9, 140.5, 140.1, 137.8, 136.9, 134.2, 130.5, 128.9, 128.3, 127.3, 126.1, 124.1, 52.7, 21.1, 21.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}N_2O_3$ 375.17, found 375.32. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{22}N_2O_3K$ 413.1262, found 413.1263. IR (cm^{-1}): 1665 (m), 1639 (m), 1614 (w), 1600 (m), 1516 (s), 1493 (m), 1479 (s), 1448 (m), 1380 (w), 1341 (m), 1325 (w), 1304 (m), 1273 (w), 1206 (w), 1156 (w), 1112 (w), 1095 (w), 1048 (w), 1028 (w), 910 (w), 871 (w), 852 (m), 821 (w), 788 (w), 781 (w), 754 (m), 734 (s), 719 (m), 698 (s), 648 (w), 620 (w), 597 (m), 548 (m), 533 (m), 506 (m). R_f (hexane/EtOAc 4:1): 0.6.

*2-Fluoro-N-(mesityl(phenyl)methyl)benzamide (**29d**).* Compound **29d** was synthesized according to TP 2 from 2-fluorobenzamide (142 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless oil (254 mg, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.19−8.13 (m, 1H), 7.66−7.59 (m, 1H), 7.47−7.39 (m, 1H), 7.29−7.02 (m, 8H), 6.87 (s, 2H), 2.29 (s, 6H), 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 162.8 (d, J = 3.4 Hz), 162.6, 159.3, 141.1, 137.3, 136.9, 134.9, 133.5 (d, J = 9.5 Hz), 132.5 (d, J = 2.1 Hz), 130.3, 128.7, 126.9, 125.9, 125.0 (d, J = 3.2 Hz), 120.9 (d, J = 11.0 Hz), 116.1 (d, J = 25.1 Hz), 52.0, 21.0, 20.8. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}FNO$ 348.18, found 348.32. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{22}FNOK$ 386.1317, found 386.1318. IR (cm^{-1}): 3028 (w), 2967 (w), 2919 (w), 1664 (s), 1614 (m), 1582 (w), 1512 (s), 1494 (s), 1478 (s), 1448 (m), 1378 (w), 1346 (w), 1302 (m), 1285 (m), 1205 (m), 1155 (w), 1135 (w), 1095 (m), 1058 (w), 1030 (m), 958 (w), 908 (w), 846 (m), 821 (m), 779 (m), 754 (s), 726 (s), 697 (s), 641 (m), 598 (s), 577 (w), 547 (m), 532 (m), 504 (s). R_f (hexane/EtOAc 4:1): 0.7.

*2-Chloro-N-(mesityl(phenyl)methyl)acetamide (**29f**).* Compound **29f** was synthesized according to TP 2 from 2-chloroacetamide (94 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 100 °C for 24 h. Purification by chromatography (hexane:EtOAc 12:1 → 9:1) yielded the product as a yellow oil (270 mg, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.45 (bd, J = 9.1 Hz, 1H), 7.29−7.18 (m, 3H), 7.09−7.06 (m, 2H), 6.86 (s, 2H), 6.77 (d, J = 9.1 Hz, 1H), 4.16 (d, J = 15.2 Hz, 1H), 4.03 (d, J = 15.2 Hz, 1H), 2.25 (s, 3H), 2.23 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 165.3, 140.3, 137.4, 136.8, 134.2, 130.2, 128.7, 127.1, 125.8, 51.8, 42.9, 20.9, 20.8. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{21}ClNO$ 302.13, found 302.24. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{18}H_{20}ClNOK$ 340.0865, found 340.0865. IR (cm^{-1}): 3301 (w), 3028 (w), 2958 (w), 2920 (w), 2865 (w), 1654 (s), 1611 (m), 1584 (w), 1517 (s), 1494 (s), 1448 (m), 1409 (m), 1378 (m), 1319 (w), 1259 (m), 1192 (w), 1148 (w), 1085 (w), 1062 (w), 1030 (m), 984 (w), 910 (w), 848 (m), 807 (w), 771 (m), 732 (s), 697 (s), 647 (m), 634 (m), 619 (m), 581 (m), 565 (m), 532 (m), 496 (m), 465 (m). R_f (hexane/EtOAc 4:1): 0.4.

*Ethyl (Mesityl(phenyl)methyl)carbamate (**29g**).* Compound **29g** was synthesized according to TP 2 from urethane (92 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a yellow oil (98 mg, 33%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.31-7.22 (m, 3H), 7.16−7.13 (m, 2H), 6.88 (s, 2H), 6.52 (bd, J = 9.1 Hz, 1H), 5.40 (bd, J = 8.5 Hz, 1H), 4.21-4.11 (m, 2H), 2.29 (s, 3H), 2.22 (s, 6H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 156.7, 141.7, 137.3, 136.8, 135.4, 130.2, 128.6, 126.8, 125.9, 61.2, 53.4, 21.0, 20.9, 14.8. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}NO_2$ 298.18, found 298.05. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{19}H_{23}NO_2K$ 336.1360, found 336.1355. IR (cm^{-1}): 3347 (w), 2977 (w), 2919 (w), 1703 (s), 1611 (w), 1583 (w), 1494 (s), 1448 (m), 1377 (m), 1330 (m), 1297 (m), 1245 (m), 1220 (s), 1172 (m), 1117 (m), 1077 (m), 1046 (s), 1023 (s), 963 (w), 935 (w), 913 (w), 887 (w), 848 (m), 796 (w), 775 (m), 733 (s), 697 (s), 633 (m), 601 (m), 542 (m), 528 (m), 496 (m), 458 (m). R_f (hexane/EtOAc 4:1): 0.4.

*N-((4-Methoxyphenyl)(phenyl)methyl)benzamide (**30a**).* Compound **30a** was synthesized according to TP 2 benzamide (121 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), anisole (0.30 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 100 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (80 mg, 25%, ratio of regioisomers 4:1). Mp: 172−174 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) (peaks are listed only for major regioisomer): δ = 7.84−7.80 (m, 2H), 7.51−7.44 (m, 3H), 7.38−7.29 (m, 5H), 7.23−7.20 (m, 2H), 6.90−6.85 (m, 2H), 6.65−6.60 (m, 1H), 6.41 (d, J = 7.7 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) (peaks are not assigned to regioisomers): δ = 166.6, 159.2, 141.8, 134.4, 133.8, 131.8, 131.6, 129.8, 129.2, 128.9, 128.9, 128.8, 128.7, 128.4, 127.6, 127.5, 127.2, 127.1, 126.8, 121.3, 114.3, 111.8, 57.1, 55.8, 55.5, 55.0. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}NO_2$ 318.15, found 318.28. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{21}H_{19}NO_2K$ 356.1047, found 356.1047. IR (cm^{-1}): 3305 (w), 3061 (w), 2955 (w), 1629 (s), 1600 (w), 1578 (m), 1535 (m), 1509 (m), 1490 (m), 1461 (w), 1360 (w), 1314 (m), 1246 (m), 1203 (w), 1175 (m), 1112 (w), 1081 (w), 1031 (m), 1001 (w), 934 (w), 908 (w), 865 (w), 827 (m), 799 (w), 782 (w), 746 (w), 698 (s), 662 (m), 618

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(w), 573 (m), 509 (w). R_f (hexane/EtOAc 4:1): 0.5. Analytical data are consistent with literature.[12]

*N-((3-Bromo-4-methoxyphenyl)(phenyl)methyl)benzamide (**30b**).* Compound **30b** was synthesized according to TP 2 benzamide (121 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), 2-bromoanisole (0.38 mL, 3.0 mmol, 3.0 equiv), $Bi(OTf)_3$ (33 mg, 0.05 mmol, 5 mol %), and TfOH (4 μL, 0.05 mmol, 5 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (114 mg, 35%). Mp: 146−148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.83−7.80 (m, 2H), 7.52−7.42 (m, 4H), 7.37−7.20 (m, 6H), 6.86 (d, J = 8.5 Hz, 1H), 6.63 (bd, J = 7.7 Hz, 1H), 6.37 (d, J = 7.7 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.6, 155.4, 141.2, 135.3, 134.2, 132.4, 131.9, 129.0, 128.8, 128.0, 127.9, 127.6, 127.2, 112.2, 112.1, 56.7, 56.5. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{19}BrNO_2$ 396.06, found 397.91. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{21}H_{18}BrNO_2K$ 434.0153, found 434.0146. IR (cm^{-1}): 3279 (w), 2981 (w), 1633 (s), 1601 (w), 1578 (m), 1525 (m), 1489 (s), 1457 (m), 1438 (w), 1401 (w), 1356 (w), 1315 (m), 1303 (m), 1278 (m), 1257 (s), 1204 (w), 1184 (m), 1157 (w), 1083 (w), 1053 (m), 1022 (m), 1001 (w), 936 (w), 884 (w), 847 (w), 812 (m), 804 (m), 784 (w), 740 (m), 702 (s), 681 (m), 663 (m), 641 (m), 617 (m), 582 (s). R_f (hexane/EtOAc 4:1): 0.2.

*N-((3-Chloro-4-methoxyphenyl)(phenyl)methyl)benzamide (**30c**).* Compound **30c** was synthesized according to TP 2 benzamide (121 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), 2-chloroanisole (0.38 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (142 mg, 40%). Mp: 144−146 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.83−7.80 (m, 2H), 7.52−7.15 (m, 9H), 7.19−7.15 (m, 1H), 6.89 (d, J = 8.5 Hz, 1H), 6.63 (bd, J = 7.5 Hz, 1H), 6.37 (d, J = 7.7 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.6, 154.5, 141.2, 134.9, 134.2, 131.9, 129.3, 129.0, 128.8, 128.0, 127.6, 127.2, 127.1, 122.9, 112.3, 56.8, 56.4. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{19}ClNO_2$ 352.11, found 352.24. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{21}H_{18}ClNO_2K$ 390.0658, found 390.0651. IR (cm^{-1}): 3297 (w), 3060 (w), 1631 (s), 1601 (w), 1578 (w), 1528 (m), 1500 (s), 1491 (s), 1458 (w), 1404 (w), 1356 (w), 1305 (m), 1279 (m), 1257 (s), 1205 (w), 1186 (w), 1159 (w), 1085 (w), 1063 (m), 1023 (m), 1002 (w), 948 (w), 937 (w), 891 (w), 878 (w), 813 (m), 803 (w), 784 (w), 739 (w), 703 (s), 693 (s), 619 (w), 610 (w), 586 (s), 547 (w). R_f (hexane/EtOAc 4:1): 0.2.

*N-((2-Methoxy-4,6-dimethylphenyl)(phenyl)methyl)benzamide (**30d**).* Compound **30d** was synthesized according to TP 2 benzamide (121 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), 3,5-dimethylanisole (408 mg, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 130 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a yellow oil (255 mg, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.01 (bd, J = 9.5 Hz, 1H), 7.84−7.81 (m, 2H), 7.50−7.41 (m, 3H), 7.28−7.17 (m, 5H), 6.91 (d, J = 9.5 Hz, 1H), 6.73 (s, 1H), 6.64 (s, 1H), 3.70 (s, 3H), 2.50 (s, 3H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.5, 158.1, 142.1, 138.5, 137.8, 135.0, 131.5, 128.7, 128.3, 127.2, 126.7, 126.4, 125.0, 124.6, 111.1, 55.9, 50.7, 21.6, 20.4. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{24}NO_2$ 346.18, found 346.32. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{23}H_{23}NO_2K$ 384.1360, found 384.1356. IR (cm^{-1}): 1657 (s), 1611 (m), 1602 (m), 1580 (m), 1508 (s), 1481 (s), 1464 (s), 1447 (m), 1380 (w), 1346 (m), 1304 (s), 1265 (m), 1234 (m), 1183 (m), 1154 (m), 1134 (m), 1093 (s), 1050 (m), 1029 (m), 1001 (m), 971 (w), 937 (w), 914 (w), 891 (w), 833 (m), 800 (m), 733 (s), 710 (s), 695 (s), 668 (m), 639 (m), 606 (s), 592 (s), 568 (s), 518 (m). R_f (hexane/EtOAc 4:1): 0.4.

*N-((5-Bromothiophene-2-yl)(phenyl)methyl)benzamide (**30f**).* Compound **30f** was synthesized according to TP 2 benzamide (121 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), 2-bromothiophene (0.29 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 80 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (133 mg, 36%). Mp: 159−161 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.82−7.79 (m, 2H), 7.53−7.34 (m, 7H), 6.90 (d, J = 3.8 Hz, 1H), 6.72 (bd, J = 7.7 Hz, 1H), 6.63 (dd, J = 3.8, 1.0 Hz, 1H), 6.55 (d, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.5, 147.4, 140.3, 134.0, 132.1, 129.9, 129.1, 128.9, 128.5, 127.3, 127.2, 126.5, 112.2, 53.7. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{15}BrNOS$ 372.01, found 372.44. HRMS (MALDI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{14}BrNOSNa$ 393.9872, found 393.9887. IR (cm^{-1}): 3282 (w), 3030 (w), 1640 (s), 1602 (w), 1578 (w), 1521 (m), 1488 (m), 1455 (w), 1439 (m), 1359 (m), 1311 (m), 1271 (w), 1248 (w), 1214 (m), 1195 (w), 1155 (w), 1084 (w), 1050 (w), 1029 (w), 966 (m), 925 (w), 902 (w), 820 (w), 801 (m), 784 (m), 721 (m), 700 (s), 691 (s), 666 (m), 645 (m), 615 (m), 568 (m), 551 (w), 500 (w), 478 (m). R_f (hexane/EtOAc 4:1): 0.4.

*N-(Benzofuran-2-yl(phenyl)methyl)benzamide (**30g**).* Compound **30g** was synthesized according to TP 2 benzamide (121 mg, 1.0 mmol), benzaldehyde (0.12 mL, 1.2 mmol), benzofuran (0.32 mL, 3.0 mmol, 3.0 equiv), and $Bi(OTf)_3$ (66 mg, 0.1 mmol, 10 mol %) in DCE (4 mL) at 50 °C for 24 h. Purification by chromatography (hexane/EtOAc 12:1 → 9:1) yielded the product as a colorless solid (30 mg, 9%). Mp: 137−139 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.86−7.83 (m, 2H), 7.53−7.30 (m, 12H), 7.28−7.19 (m, 1H), 6.92 (bd, J = 8.1 Hz, 1H), 6.67−6.64 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 166.7, 156.1, 155.3, 139.0, 134.1, 132.0, 129.0, 128.8, 128.3, 128.2, 127.4, 127.3, 124.5, 123.1, 121.3, 111.5, 105.0, 52.1. MS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{18}NO_2$ 328.13, found 328.26. HRMS (MALDI) m/z: $[M + K]^+$ calcd for $C_{22}H_{17}NO_2K$ 366.0891, found 366.0888. IR (cm^{-1}): 3318 (w), 1630 (s), 1600 (m), 1577 (w), 1537 (s), 1490 (m), 1454 (m), 1329 (m), 1284 (w), 1270 (m), 1254 (s), 1203 (w), 1168 (m), 1142 (m), 1104 (w), 1081 (m), 1029 (w), 1002 (w), 966 (m), 904 (m), 857 (w), 823 (m), 802 (m), 752 (s), 742 (s), 725 (s), 711 (s), 697 (s), 690 (s), 647 (s), 624 (m), 615 (m), 585 (m), 565 (m), 461 (m). R_f (hexane/EtOAc 4:1): 0.3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra of all products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00662.

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Notes

The authors declare no competing financial interest.

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