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Microwave-Assisted Intramolecular Ullmann Diaryl Etherification as the Post-Ugi Annulation for Generation of Dibenz[*b*,*f*][1,4]oxazepine Scaffold

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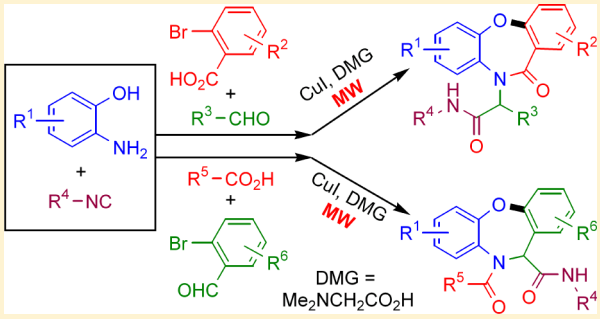
Supporting Information

ABSTRACT: A sequence of the Ugi four-component reaction (U-4CR) and microwave-assisted intramolecular Ullmann etherification has been established for efficient generation of a dibenz[*b*,*f*][1,4]oxazepine scaffold. The U-4CR, using 2-aminophenols and 2-bromobenzoic acids or 2-bromobenzaldehydes as the inputs, was carried out in MeOH at 50−60 °C for 2−3 days to form a collection of 22 linear products in 46−90% yields. A microwave-assisted intramolecular Ullmann etherification was then used to transform these acyclic U-4CR products into the cleft-shaped 6/7/6-fused tricyclic heterocycles. The intramolecular Ullmann diaryl ether formation was catalyzed by 10 mol % of CuI and 30 mol % of *N*,*N*-dimethylglycine hydrochloride (DMG·HCl) in the presence of Cs_2CO_3 with microwave irradiation (150 °C, 30 min) to furnish dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones and dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-carboxamides in 64−100% yields.



INTRODUCTION

The 6/7/6-fused tricyclic core of compounds **6** and **8** (Scheme 1) is an important heterocyclic scaffold. Many derivatives of this class of heterocycle are known to interact with a diverse spectrum of receptors.[1−3] For example, they have been reported as non-nucleoside inhibitors of HIV-1 reverse transcriptase,[1] PGE_2 antagonists,[2] and histone deacetylase inhibitors.[3g] Nucleophilic aromatic substitution (S_NAr) is a classical method for construction of dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones starting from 2-aminophenols and 2-fluoro- or 2-chloro-5-nitrobenzoic acid.[1a,3g,4−6] Similarly, the C11-unsubstituted dibenz[*b*,*f*][1,4]oxazepines are obtained by condensation of 2-aminophenols with 2-fluorobenzaldehyde[7] or salicyladehyde with 1-chloro-2-nitrobenzenes.[3a] Substitution at the C11 position of *N*-Boc-dibenz[*b*,*f*][1,4]oxazepines has been reported by using a benzylic lithiation−alkylation sequence.[8] In recent years, metal-catalyzed C−O and C−N coupling reactions have been advanced significantly and have found applications in the synthesis of dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones.[9−16] Alper and co-workers reported an intramolecular carbonylation of 2-(2-bromo- or 2-iodophenoxy)-anilines for the synthesis of *N*-unsubstituted dibenz[*b*,*f*][1,4]-oxazepin-11(10*H*)-ones by employing recyclable palladium-complexed dendrimers.[9] The aniline precursors were prepared by S_NAr reaction of 2-nitroaryl halides with 2-halophenols followed by reduction of the nitro group. In contrast to Alper's S_NAr−nitro reduction−intramolecular carbonylation sequence, Wu and co-workers established a palladium-catalyzed aminocarbonylation−S_NAr approach to the same 6/7/6-fused tricyclic core starting with 2-aminophenols and 1-bromo-2-fluorobenzens.[10] Moreover, Buchwald and Tsvelikhovsky developed a novel sequence of Ullmann etherification[17] of 2-hydroxyaryl ketones/carboxylates and palladium-catalyzed amination using ammonia solution followed by intramolecular imine/amide formation to afford dibenzooxazepines and dibenzooxazepinones.[11] A palladium-catalyzed intramolecular diaryl etherification was demonstrated by Prasad and co-workers in the construction of the 6/7/6/5/6-fused pentacyclic ring system.[12] Recently, tandem reactions involving Smiles rearrangement for the synthesis of dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones has been reported by the groups of Snieckus,[13,14] Zhang,[15] Ganguly,[16] Li, Shi, and Zhu,[18] Ma,[19] and Ao, Zhang, and Zhang[20] under both copper catalysis (Ullmann−Smiles−S_NAr)[12,13,15,16] and metal-free (S_NAr−Smiles−S_NAr)[14,18−20] conditions. An iodine(III)-mediated intramolecular oxidative C−N bond formation was also applied for the generation of the 6/7/6-fused tricyclic core.[21] In our previous work, we established a microwave-assisted Ugi four-component reaction (U-4CR) followed by an intramolecular S_NAr for one-pot synthesis of dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-carboxamides

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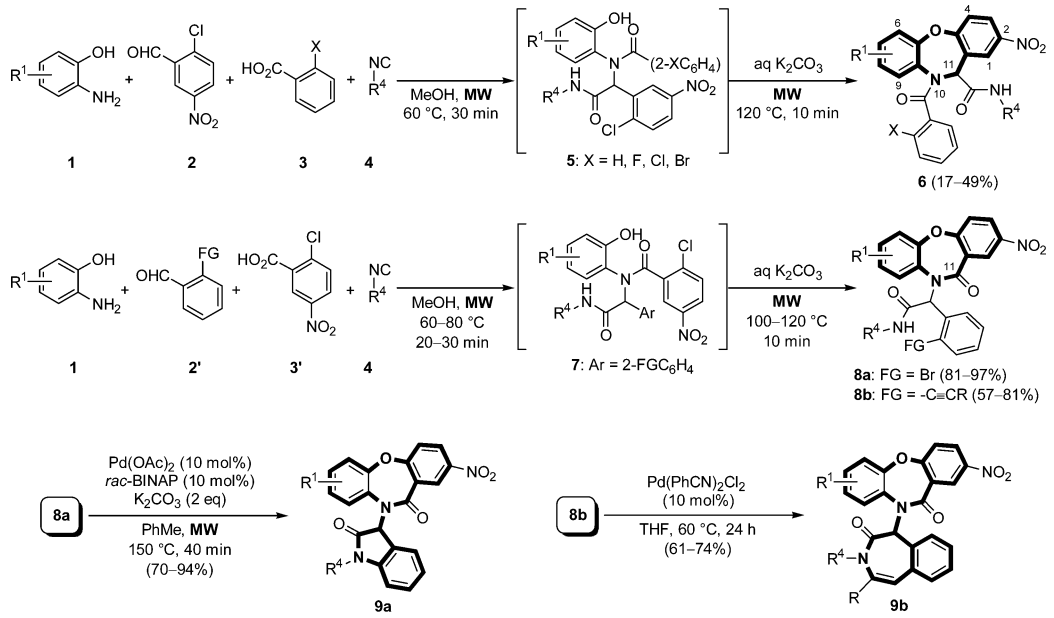
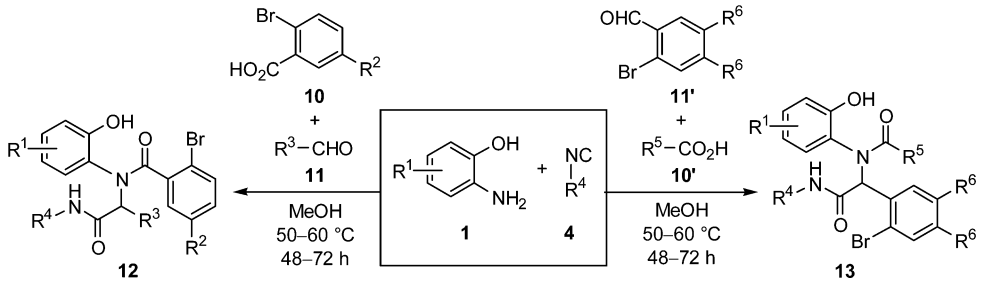
Scheme 1. One-Pot Synthesis of Dibenz[*b*,*f*][1,4]oxazepines via U-4CR–S_NAr and Post-Ugi Transformations



Scheme 2. Synthesis of Acyclic Phenol Derivatives via U-4CR Using 2-Aminophenols 1 as the Amine Input



6[6a] and dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones **8a**,**b** (Scheme 1).[6b,c] By selecting the functionalized benzaldehydes **2**/**2′** and benzoic acids **3**/**3′**, the U-4CR products **5** and **7**, without isolation, were treated with aqueous K_2CO_3 to promote the intramolecular S_NAr, leading to formation of **6** and **8a**,**b**, respectively. Moreover, compounds **8a**,**b** could be transformed into the C–N bond-linked conjugates **9a**,**b** in 61–94% yields by the palladium-catalyzed intramolecular amidation under controlled microwave heating[6a] and the palladium-catalyzed intramolecular hydroamidation of alkynes, respectively.[6b] As compared to our U-4CR–S_N2 and U-4CR–Heck approaches,[22,23] our U-4CR–S_NAr approach enables a rapid access to dibenz[*b*,*f*][1,4]oxazepine scaffold possessing rich points of diversity for further transformations. In the current work, we report on an intramolecular Ullmann diaryl etherification[17] as the post-Ugi annulation[24] for efficient generation of a dibenz[*b*,*f*][1,4]oxazepine scaffold. This new U-4CR–Ullmann sequence[25] toward the 6/7/6-fused tricyclic core does not rely on the chemistry facilitated by the C2-NO_2 group in **6** and **8a**,**b**. Therefore, it offers broader scope of the appendage groups than the U-4CR–S_NAr sequence.[6]

RESULTS AND DISCUSSION

In our previous work, we noted that the efficiency of U-4CR using 2-aminophenols **1** as the amine input is dependent on acidity of the acid input. For the relatively stronger acids such as 2-chloro-5-nitrobenzoic acid **3′** (Scheme 1)[6a] and 2-bromoacetic acid,[22a] the U-4CR could be carried out at 80 °C in only 20–25 min under microwave irradiation. We observed an effect of pK_a of the acids on microwave-assisted U-4CR among **1**–**4** in the formation of **6** (Scheme 1).[6a] For the relatively weaker acids, the U-4CR should be performed at 40–50 °C for 2–4 days to obtain better yields of the products.[6a,23] As given in Scheme 2, the U-4CR of 2-aminophenols **1**, isocyanides **4**, acids **10**/**10′**, and aldehydes **11**/**11′** took place in MeOH at 50–60 °C for 2–3 days to afford the bromophenols **12a–i** and **13a–m**, respectively, in 46–90% yields. The structures and yields are summarized in Tables 1 and 2.

Among the four isocyanides used in the U-4CR involving 2-bromobenzoic acid and benzaldehyde, ethyl isocyanoacetate gave a lower yield of 46% for the product **12c** (Table 1, entry 3 vs entries 1, 2 and 4). The yields for other U-4CR products **12** were generally good (61–84%). In the formation of the U-4CR products **13** using cinnamic and crotonic acids, good yields ranging from 64% to 81% were obtained (Table 2, entries 1, 2, 7, 8, 10, and 11). Aromatic and formic acids furnished **13c**,**d**,**l** in 77–90% yields (Table 2, entries 3, 4, and 12). In contrast, acetic acid afforded **13e**,**i**,**m** in relatively lower yields of 54–65% (Table 2, entries 5, 9, and 13). By using an electron-rich aldehyde, 78% yield of **13f** could be achieved from the U-4CR using acetic acid (Table 2, entry 6). According to the above results, it is concluded that the U-4CR of 2-aminophenols and aromatic aldehydes is sensitive to electronic effects of the acids and aldehydes. Good to excellent yields are obtained for the U-

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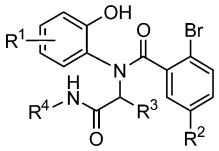
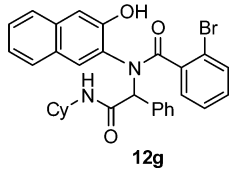
Table 1. Structures and Yields of Bromophenols 12a−i



12a−f,h,i



12g

entry	R^1	R^2	R^3	R^4	U-4CR product	yield[a] (%)
1	H	H	Ph	Bn	**12a**	84
2	H	H	Ph	Cy	**12b**	64
3	H	H	Ph	CH_2CO_2Et	**12c**	46
4	H	H	Ph	*t*-Bu	**12d**	71
5	4-Cl	H	Ph	Cy	**12e**	81
6	4-*t*-Bu	H	Ph	Cy	**12f**	61
7	4,5-benzo	H	Ph	Cy	**12g**	61
8	4-Cl	H	2-thienyl	Cy	**12h**	70
9	4-Cl	MeO	Ph	Cy	**12i**	79

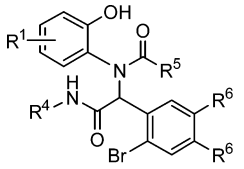
[a]Isolated yields. All compounds are fully characterized.

4CR using the acids having pK_a < 4.76 (acetic acid)[26] and the aldehydes substituted with electron-donating group(s), respectively. An immonium ion formed by protonation of the imine is suggested before isocyanide attack in the reaction pathway of U-4CR.[27] The observed electronic effect seems associated with the easiness of imine protonation. Electron-rich imines and stronger acids both facilitate formation of an immonium ion, therefore resulting in high yields of the U-4CR products.

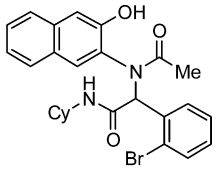
With the U-4CR products **12a−i** and **13a−m** in hand, we next examined the intramolecular Ullmann etherification by using CuI and *N*,*N*-dimethylglycine hydrochloride (DMG·HCl)[28] as the catalyst and Cs_2CO_3 as the base. In order to speed up the reaction, microwave irradiation was used for the annulation performed in closed vessels (Scheme 3).[29] Table 3 summarizes the results obtained during optimization of reaction conditions. The following points can be concluded: (a) no Ullmann etherification took place using K_2CO_3 as the base or DMF as the solvent (Table 3, entries 7, 8, and 15); (b) no reaction was observed at room temperature while good yields of the product were obtained after heating at 90−100 °C for 48 h and at 150 °C for 30 min with microwave irradiation (entries 9−11); (c) at 150 °C in dioxane the product was formed in the absence of a ligand or in the presence of L-proline as the ligand, but higher yields were obtained by using DMG as the ligand (entries 1−5 and 12−14); and (d) for the substrate containing a strong coordinating atom with Cu such as the thienyl moiety in **12h**, no product was isolated in the absence of DMG (entry 6).

Tables 4 and 5 summarize all results of the intramolecular Ullmann etherification of both **12** and **13** under the optimized conditions given in Scheme 3. Dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones **14a−f** and **14i** were obtained in excellent yields of 90−100% (Table 4, entries 1−6 and 9). The 2-naphthol-containing substrate **12g** gave the expected product **14g** in 82% yield (Table 4, entry 7). As mentioned above, the thienyl-containing substrate **12h** afforded the product **14h** in 67% yield (Table 4, entry 8) presumably due to interference of the sulfur atom with the catalyst. We did not observe formation of the 9-membered ring lactones from the phenolic esters **12c** and **13j** (Table 4, entry 3, and Table 5, entry 10). The Ullmann etherification of **13d** is interesting because both dibenz[*b*,*f*]-[1,4]oxazepin-11(10*H*)-one (cyclization with the aryl chloride) and dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-carboxamide (cyclization with the aryl bromide) are the possible products. We only obtained the product **15d** in 96% yield (Table 5, entry 4), indicating an excellent chemoselectivity even under microwave heating at 150 °C. In theory, the substrates **12** and **13** could undergo an intramolecular Goldberg amidation in the presence of the same Cu catalyst to give the 7-membered ring benzodiazepin-2,5-diones **16** from **12**[30] and the 5-membered ring 2-oxindoles **17** from **13**,[22a,b] respectively (Scheme 3). However, our results indicate that the intramolecular Ullmann

Table 2. Structures and Yields of Bromophenols 13a−m



13a−h,j−m



13i

entry	R^1	R^4	R^5	R^6	U-4CR product	yield[a] (%)
1	H	Cy	*trans*-PhCH=CH−	H	**13a**	79
2	H	Cy	*trans*-MeCH=CH−	H	**13b**	81
3	H	Cy	Ph	H	**13c**	90
4	H	Cy	2-ClC_6H_4	H	**13d**	84
5	H	Cy	Me	H	**13e**	54
6	H	Cy	Me	MeO	**13f**	78
7	4-Cl	Cy	*trans*-PhCH=CH−	H	**13g**	64
8	4,6-Me_2	Cy	*trans*-PhCH=CH−	H	**13h**	66
9	4,5-benzo	Cy	Me	H	**13i**	65
10	H	CH_2CO_2Et	*trans*-PhCH=CH−	H	**13j**	64
11	H	Bn	*trans*-PhCH=CH−	H	**13k**	83
12	H	Bn	H	H	**13l**	77
13	H	*t*-Bu	Me	H	**13m**	56

[a]Isolated yields. All compounds are fully characterized.

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Scheme 3. Microwave-Assisted Intramolecular Ullmann Etherification of 12 and 13

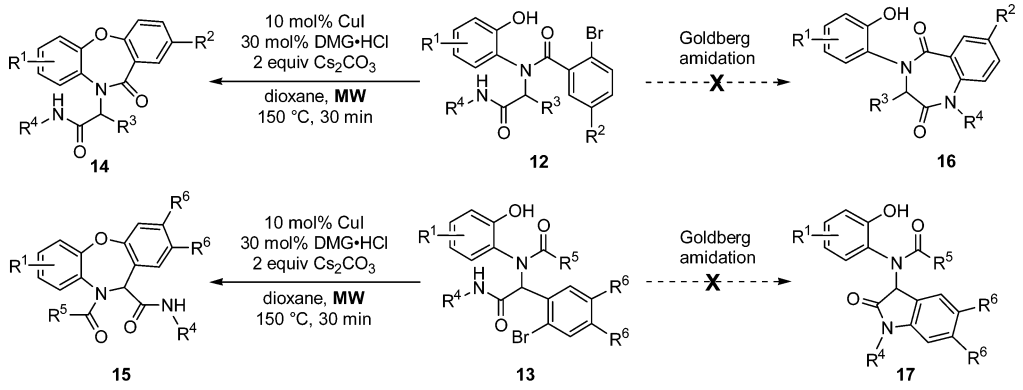
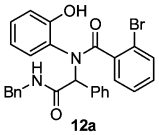
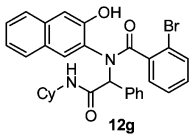
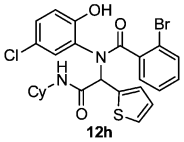
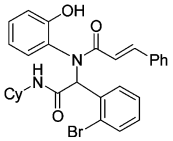
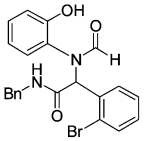


Table 3. Optimization of Reaction Conditions for Intramolecular Ullmann Etherification[a]

entry	substrate	ligand	base	solvent	*T* (°C); *t* (h)	yield (%) [b]
1	 12a	DMG [c]	Cs_2CO_3	dioxane	MW, 150; 0.5	100
2		– [d]	Cs_2CO_3	dioxane	MW, 150; 0.5	64
3	 12g	DMG	Cs_2CO_3	dioxane	MW, 150; 0.5	82
4		–	Cs_2CO_3	dioxane	MW, 150; 0.5	79
5	 12h	DMG	Cs_2CO_3	dioxane	MW, 150; 0.5	67
6		–	Cs_2CO_3	dioxane	MW, 150; 0.5	trace
7	 13a	DMG	K_2CO_3	dioxane	90–100; 48	0 [e]
8		–	K_2CO_3	DMF	90–100; 48	0 [f]
9		DMG	Cs_2CO_3	dioxane	90–100; 48	75
10		DMG	Cs_2CO_3	dioxane	MW, 150; 0.5	64
11	 13l	DMG	Cs_2CO_3	dioxane	25; 12	0
12		DMG	Cs_2CO_3	dioxane	MW, 150; 0.5	82
13		Proline	Cs_2CO_3	dioxane	MW, 150; 0.5	50
14		–	Cs_2CO_3	dioxane	MW, 150; 0.5	66
15		–	Cs_2CO_3	DMF	MW, 150; 0.5	0

[a]10 mol % of CuI, 30 mol % of ligand, and 2 equiv of the base were used. [b]Isolated yields. [c]*N*,*N*-Dimethylglycine hydrochloride (DMG·HCl) was used. [d]No ligand was used. [e]100% of **13a** was recovered. [f]53% of **13a** was recovered.

etherification is far preferred over the intramolecular Goldberg amidation. Conformational preference of the two amide units may also contribute, to some extent, to the observed chemoselectivity under copper catalysis. This argument may be supported by the solvent effect that the bromo phenol **13l** failed to react in a polar solvent, DMF (entry 15 of Table 3). As compared to the facile intramolecular Goldberg amidation of the 1,4-benzoxazine-derived substrates (10 mol % of CuI, 2 equiv of $K_3PO_4·3H_2O$, DMF, 150 °C, 30–35 min, MW),[22a] the failure of formation of 2-oxindoles **17** from the acyclic substrate **13** reinforces the role of conformational preference in dictating reaction pathways.

CONCLUSIONS

In summary, we have established a U-4CR–Ullmann sequence for efficient generation of the dibenz[*b*,*f*][1,4]oxazepine scaffold. The new synthesis tolerates bulky (such as *t*-Bu on 2-aminophenols **1** and isocyanides **4**) and reactive (such as Cl on 2-aminophenols **1** and an ester in isocyanides **4**) groups and various structural motifs such as the thienyl and alkenyl subunits. The intramolecular Ullmann etherification can be performed by using 10 mol % of CuI alone or in combination with 30 mol % of *N*,*N*-dimethylglycine hydrochloride (DMG·HCl) in the presence of Cs_2CO_3 in dioxane with microwave heating at 150 °C for 30 min. The target products, dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones and dibenz[*b*,*f*][1,4]-oxazepin-11(10*H*)-carboxamides, are obtained by the two-step

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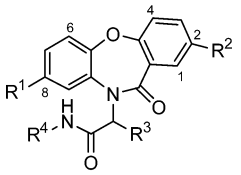
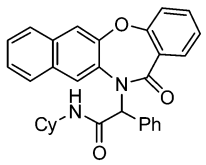
Table 4. Synthesis of Dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones 14a–i from 12a–i via Ullmann Etherification[a]



14a–f,h,i



14g

entry	substrate **12**	Ullmann product **14**	yield[b] (%)
1	**12a**	**14a**: $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = Bn$	100[c]
2	**12b**	**14b**: $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = Cy$	100
3	**12c**	**14c**: $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = CH_2CO_2Et$	100
4	**12d**	**14d**: $R^1 = R^2 = H$, $R^3 = Ph$, $R^4 = t$-Bu	100
5	**12e**	**14e**: $R^1 = Cl$, $R^2 = H$, $R^3 = Ph$, $R^4 = Cy$	92
6	**12f**	**14f**: $R^1 = t$-Bu, $R^2 = H$, $R^3 = Ph$, $R^4 = Cy$	100
7	**12g**	**14g**	82[c]
8	**12h**	**14h**: $R^1 = Cl$, $R^2 = H$, $R^3 = 2$-thienyl, $R^4 = Cy$	67[c]
9	**12i**	**14i**: $R^1 = Cl$, $R^2 = OMe$, $R^3 = Ph$, $R^4 = Cy$	90

[a]Reaction conditions: 10 mol % of CuI, 30 mol % of DMG·HCl, 2 equiv of Cs_2CO_3, dioxane, 150 °C for 30 min with microwave irradiation. [b]Isolated yields. [c]Data taken from Table 3.

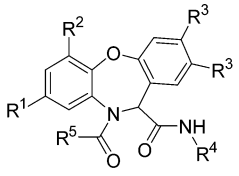
procedure in good overall yields. The advantage of the current synthesis via the U-4CR–Ullmann approach over the previous U-4CR–S_NAr protocol is apparent by incorporating the electron-donating MeO group(s) onto the aromatic ring. More importantly, dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-carboxamides cannot be synthesized using the metal-catalyzed C–O and C–N coupling reactions and the tandem reaction involving Smiles rearrangement under both copper catalysis and metal-free conditions.[9−16,18−21] Moreover, this work expands the scope of post-Ugi transformations[24] which are of current interest in heterocycle library synthesis.

EXPERIMENTAL SECTION

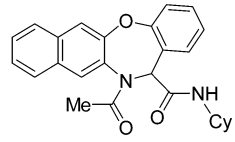
General Methods. All microwave reactions were carried out in closed 10 mL pressurized process vials on a technical microwave reactor (Emrys creator from Personal Chemistry AB, currently Biotage AB, Uppsala, Sweden) with the reaction temperature measured by an IR sensor. The reaction time is the holding time after the set reaction temperature is reached. NMR spectra were recorded at room temperature unless otherwise indicated on a 400 or 500 MHz instrument in $CDCl_3$ and DMSO-d_6 using residual $CHCl_3$ and DMSO, respectively, as the internal reference for ^1H (δ 7.26 or 2.50) and ^{13}C (δ 77.2 or 40.2). Many of the aromatic amide-containing compounds show atropisomers in solution,[31] and for easy assignment of NMR signals and convenience of NMR measurements, some ^1H and ^{13}C NMR spectra are taken in DMSO-d_6 at 80 °C as specified. No attempt was made to study the rotational barriers of these atropisomers at different temperatures. As a result of interconversion among atropisomers, some carbon signals are not observed in the ^{13}C NMR spectra recorded at the specified temperature. IR spectra were taken on a FT-IR spectrophotometer. Mass spectra (MS) were measured by the ESI method. High-resolution mass spectrometry (HRMS) was measured by the CI-TOF method. Elemental analyses were performed for solid samples after recrystallization. Melting points are uncorrected. Silica gel plates 60 F-254 precoated on glass were used for thin-layer chromatography using UV light or 7% ethanolic phosphomolybdic acid and heating as the visualizing methods. Silica gel 60 (particle size 0.040–0.063 mm) was used for flash column chromatography. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials. Reagents were obtained commercially and used as received. Dry dioxane was freshly distilled from sodium and benzophenone under a nitrogen atmosphere. Dry DMF was distilled over CaH_2 under reduced pressure. Petroleum ether (PE, bp 60–90 °C) was used for column chromatographic purification.

General Procedure A for Ugi Four-Component Reactions of 2-Aminophenols. Synthesis of Bromophenols 12a–i and 13a–m. To a 10 mL pressurized process vial were added 2-aminophenol **1** (2.0 mmol), aldehyde **11**/**11′** (2.0 mmol), and methanol (5 mL) followed by stirring for 15 min at room temperature. To the resultant mixture was added the acid **10**/**10′** (2.0 mmol). After the mixture was stirred for 5 min at room temperature, isocyanide **4** (2.0 mmol) was

Table 5. Synthesis of Dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-carboxamides 15a–m from 13a–m via Ullmann Etherification[a]



15a–h, j–m



15i

entry	substrate **13**	Ullmann product **15**	yield[b] (%)
1	**13a**	**15a**: $R^1 = R^2 = R^3 = H$, $R^4 = Cy$, $R^5 = trans$-PhCH=CH–	64[c] (75)[c,d]
2	**13b**	**15b**: $R^1 = R^2 = R^3 = H$, $R^4 = Cy$, $R^5 = trans$-MeCH=CH–	86
3	**13c**	**15c**: $R^1 = R^2 = R^3 = H$, $R^4 = Cy$, $R^5 = Ph$	100
4	**13d**	**15d**: $R^1 = R^2 = R^3 = H$, $R^4 = Cy$, $R^5 = 2$-ClC_6H_4	96
5	**13e**	**15e**: $R^1 = R^2 = R^3 = H$, $R^4 = Cy$, $R^5 = Me$	100
6	**13f**	**15f**: $R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = Cy$, $R^5 = Me$	94
7	**13g**	**15g**: $R^1 = Cl$, $R^2 = R^3 = H$, $R^4 = Cy$, $R^5 = trans$-PhCH=CH–	99
8	**13h**	**15h**: $R^1 = R^2 = Me$, $R^3 = H$, $R^4 = Cy$, $R^5 = trans$-PhCH=CH–	82 (81)[d]
9	**13i**	**15i**	94
10	**13j**	**15j**: $R^1 = R^2 = R^3 = H$, $R^4 = CH_2CO_2Et$, $R^5 = trans$-PhCH=CH–	75
11	**13k**	**15k**: $R^1 = R^2 = R^3 = H$, $R^4 = Bn$, $R^5 = trans$-PhCH=CH–	75 (90)[d]
12	**13l**	**15l**: $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = Bn$	82[c]
13	**13m**	**15m**: $R^1 = R^2 = R^3 = H$, $R^4 = t$-Bu, $R^5 = Me$	100

[a]Reaction conditions: 10 mol % of CuI, 30 mol % of DMG·HCl, 2 equiv of Cs_2CO_3, dioxane, 150 °C for 30 min with microwave irradiation. [b]Isolated yields. [c]Data taken from Table 3. [d]Yields for the reactions conducted under thermal heating at 100 °C for 48 h.

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finally added. The vial was then sealed with a cap containing a silicon septum and was heated at 50−60 °C for 48−72 h. For some entries, the desired products precipitated from the reactions as white solids. The solids were collected by filtration through a piece of filter paper, and the solid was washed with methanol three times. The combined filtrates and washings were concentrated under reduced pressure, and the residue was purified by flash column chromatography over silica gel (eluting with 25−50% EtOAc in PE) to give the product. The latter was combined with the above white solid for calculation of the yield. Tables 1 and 2 list the structures and yields of **12a−i** and **13a−m**.

*N-α-[(Benzylamino)carbonyl]benzyl-N-2-hydroxyphenyl 2-Bromobenzamide (**12a**).* The Ugi reaction was carried out by following procedure A to give **12a** (865.9 mg, 84%) as a white solid; mp 178−180 °C (EtOAc−hexane); R_f = 0.50 (33% EtOAc in hexane); IR (KBr) 3274, 3066, 1667, 1644, 1494, 1358, 1263 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, an 82:18 mixture of two atropisomers) for the major atropisomer δ 11.16 (s, 1 H, O*H*), 7.47−7.00 (m, 13 H), 3.93 (td, *J* = 8.0, 1.2 Hz, 1 H), 6.78 (td, *J* = 8.0, 1.2 Hz, 1 H), 6.63 (td, *J* = 8.0, 1.2 Hz, 1 H), 6.59 (t, *J* = 5.6 Hz, 1 H, N*H*), 6.53 (td, *J* = 8.0, 1.2 Hz, 1 H), 6.33 (s, 1 H), 6.19 (td, *J* = 7.6, 1.6 Hz, 1 H), 4.63 and 4.51 (ABqd, *J* = 15.2, 5.6 Hz, 2 H); for partial signals of the minor atropisomer δ 10.82 (s, 1 H, O*H*), 7.76 (d, *J* = 6.8 Hz, 2 H), 7.54−7.50 (m, 2 H), 6.88 (d, *J* = 7.6 Hz, 1 H), 4.92 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major atropisomer δ 172.9, 170.5, 155.3, 137.7, 136.9, 132.4, 132.0, 130.8, 130.2, 130.1, 130.0, 129.7, 129.4, 129.2, 128.7 (× 3), 127.6, 127.6 (×2), 126.9, 126.7, 125.1, 118.8, 118.6, 117.3, 65.6, 44.2; for the minor atropisomer (four carbon signals are not observed) δ 171.5, 170.1, 153.4, 137.3, 133.5, 132.2, 130.7, 130.3, 130.0, 129.0, 128.8 (×2), 128.5, 128.1, 127.5 (×2), 127.4, 126.9, 126.6, 124.5, 119.3, 117.9, 71.3, 44.3; MS (−ESI) *m*/*z* 515 (M + 2 − H^+, 100), 513 (M − H^+, 85). Anal. Calcd for $C_{28}H_{23}BrN_2O_3$: C, 65.25; H, 4.50; N, 5.44. Found: C, 65.38; H, 4.46; N, 5.45.

*N-α-[(Cyclohexylamino)carbonyl]benzyl-N-2-hydroxyphenyl 2-Bromobenzamide (**12b**).* The Ugi reaction was carried out by following procedure A to give **12b** (649.5 mg, 64%) as a colorless solid: mp 203−206 °C (EtOAc−hexane); R_f = 0.58 (33% EtOAc in hexane); IR (KBr) 3276, 2931, 1633, 1491, 1387, 1251 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C): δ 11.60 (br s, 1 H, O*H*), 8.59 (d, *J* = 7.0 Hz, 1 H, N*H*), 7.41 (d, *J* = 8.0 Hz, 1 H), 7.25 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.21−7.11 (m, 6 H), 7.08 (td, *J* = 8.5, 1.5 Hz, 1 H), 6.75 (td, *J* = 7.0, 1.0 Hz, 1 H), 6.59 (dd, *J* = 7.5, 1.0 Hz, 1 H), 6.50 (d, *J* = 8.0, 1.0 Hz, 1 H), 6.21 (s, 1 H), 6.17 (td, *J* = 7.5, 1.0 Hz, 1 H), 3.78−3.75 (m, 1 H), 1.94−1.85 (m, 1 H), 1.78−1.70 (m, 2 H), 1.68−1.53 (m, 2 H), 1.40−1.25 (m, 3 H), 1.22−1.08 (m, 2 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 171.7, 168.9, 155.5, 138.3, 133.7, 132.0, 131.2, 130.1, 129.8 (×2), 129.7, 128.4, 128.2 (×2), 126.7 (×2), 125.7, 118.5, 117.9, 116.6, 65.1, 48.8, 31.9, 31.8, 25.2, 24.3, 24.2; MS (+ESI) *m*/*z* 531 (M + 2 + Na^+, 100), 529 (M + Na^+, 86), 509 (M + 2 + H^+, 11), 507 (M + H^+, 8). Anal. Calcd for $C_{27}H_{27}BrN_2O_3$: C, 63.91; H, 5.36; N, 5.52. Found: C, 63.94; H, 5.38; N, 5.44.

*N-α-[(((Ethoxycarbonyl)methyl)amino)carbonyl]benzyl-N-2-hydroxyphenyl 2-Bromobenzamide (**12c**).* The Ugi reaction was carried out by following procedure A to give **12c** (470.5 mg, 46%) as a colorless solid: mp 210−212 °C (EtOAc−hexane); R_f = 0.24 (33% EtOAc in hexane); IR (KBr) 3304, 3072, 1724, 1653, 1491, 1355, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, a 78:21 mixture of two atropisomers) for the major atropisomer δ 10.84 (s, 1 H, O*H*), 7.36 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.31 (dd, *J* = 8.0, 0.8 Hz, 1 H), 7.23−7.14 (m, 4 H), 7.10−6.90 (m, 3 H), 6.80−6.75 (m, 2 H), 6.62 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.49 (dd, *J* = 7.6, 1.6 Hz, 1 H), 6.42 (s, 1 H), 6.18 (td, *J* = 8.0, 1.2 Hz, 1 H), 4.20 (dd, *J* = 18.0, 5.6 Hz, 1 H), 4.18 (q, *J* = 7.6 Hz, 2 H), 4.09 (dd, *J* = 18.0, 4.8 Hz, 1 H), 1.25 (t, *J* = 7.6 Hz, 3 H); for partial signals of the minor atropisomer δ 7.80−7.75 (m, 2 H), 7.52−7.44 (m, 3 H), 6.88−6.84 (m, 1 H), 4.92 (s, 1 H), 4.29 (dd, *J* = 18.4, 6.4 Hz, 1 H), 4.18 (q, *J* = 7.6 Hz, 2 H), 3.98 (dd, *J* = 18.4, 4.4 Hz, 1 H), 1.25 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major atropisomer δ 173.2, 170.4, 168.8, 155.2, 137.6, 132.2, 132.0, 130.9, 130.2 (×2), 130.2, 130.1, 129.2, 128.7 (×2), 126.9, 126.7, 125.0, 118.8, 118.6, 117.2, 65.0, 61.7, 42.1, 14.1; for the minor atropisomer δ 171.6, 170.0, 168.9, 153.3, 137.0, 133.2, 132.3, 130.7, 130.3, 129.8, 129.6, 129.4, 129.3 (×2), 128.7 (×2), 126.8, 126.6, 119.3, 119.1, 117.8, 70.8, 61.7, 42.0, 14.1; MS (−ESI) *m*/*z* 511 (M + 2 − H^+, 100), 509 (M − H^+, 72). Anal. Calcd for $C_{25}H_{23}BrN_2O_5$: C, 58.72; H, 4.53; N, 5.48. Found: C, 58.89; H, 4.51; N, 5.50.

*N-α-[(tert-Butylamino)carbonyl]benzyl-N-2-hydroxyphenyl 2-Bromobenzamide (**12d**).* The Ugi reaction was carried out by following procedure A to give **12d** (683.6 mg, 71%) as a colorless solid: mp 208−211 °C (EtOAc−hexane); R_f = 0.52 (33% EtOAc in hexane); IR (KBr) 3308, 2970, 1661, 1566, 1493, 1354, 1257 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, an 82:18 mixture of two atropisomers) for the major atropisomer δ 11.43 (s, 1 H, O*H*), 7.38 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.33 (dd, *J* = 8.0, 0.8 Hz, 1 H), 7.24−7.14 (m, 5 H), 7.11−6.95 (m, 2 H), 6.76 (td, *J* = 8.0, 1.2 Hz, 1 H), 6.60 (dd, *J* = 8.0, 1.2 Hz, 1 H), 6.54 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.18 (td, *J* = 8.0, 0.8 Hz, 1 H), 6.13 (s, 1 H), 5.87 (br s, 1 H, N*H*), 1.40 (s, 9 H); for partial signals of the minor atropisomer δ 11.17 (br s, 1 H, O*H*), 7.73 (d, *J* = 6.8 Hz, 2 H), 7.50−7.42 (m, 2 H), 6.88 (dd, *J* = 8.4, 1.2 Hz, 1 H), 6.48 (td, *J* = 7.6, 1.2 Hz, 1 H), 5.66 (br s, 1 H), 4.81 (s, 1 H), 1.35 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major atropisomer δ 172.0, 170.3, 155.4, 137.7, 132.8, 132.0, 130.8, 130.0 (×2), 129.8 (×2), 129.0, 128.7 (×2), 126.9, 126.7, 125.2, 118.9, 118.4, 117.1, 66.0, 52.7, 28.4 (× 3); MS (−ESI) *m*/*z* 481 (M + 2 − H^+, 100), 479 (M − H^+, 81). Anal. Calcd for $C_{25}H_{25}BrN_2O_3$: C, 62.38; H, 5.23; N, 5.82. Found: C, 62.40; H, 5.25; N, 5.72.

*N-(5-Chloro-2-hydroxy)phenyl-N-α-[(cyclohexylamino)carbonyl]-benzyl 2-Bromobenzamide (**12e**).* The Ugi reaction was carried out by following procedure A to give **12e** (877.8 mg, 81%) as a white solid: mp 258−260 °C (MeOH−$CHCl_3$); R_f = 0.56 (33% EtOAc in hexane); IR (KBr) 3267, 2927, 1635, 1567, 1485, 1373, 1287, 1244 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 11.85 (br s, 1 H, O*H*), 8.67 (d, *J* = 7.0 Hz, 1 H, N*H*), 7.45 (d, *J* = 7.5 Hz, 1 H), 7.27 (d, *J* = 6.5 Hz, 1 H), 7.25−7.15 (m, 6 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 6.78 (dd, *J* = 8.5, 2.5 Hz, 1 H), 6.64 (d, *J* = 3.0 Hz, 1 H), 6.52 (d, *J* = 8.5 Hz, 1 H), 6.22 (s, 1 H), 3.82−3.72 (m, 1 H), 1.93−1.85 (m, 1 H), 1.80−1.50 (m, 4 H), 1.40−1.25 (m, 3 H), 1.25−1.09 (m, 2 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 171.5, 168.6, 154.8, 137.9, 133.5, 132.1, 130.9, 130.5, 129.8 (×2), 129.6, 128.6, 128.3 (×2), 126.9 (×2), 126.6, 121.0, 118.4, 118.0, 65.0, 48.9, 31.8, 31.8, 25.2, 24.3, 24.2; MS (−ESI) *m*/*z* 543 (M + 4 − H^+, 25), 541 (M + 2 − H^+, 100), 539 (M − H^+, 61). Anal. Calcd for $C_{27}H_{26}BrClN_2O_3$: C, 59.85; H, 4.84; N, 5.17. Found: C, 59.83; H, 4.87; N, 5.19.

*N-(5-tert-Butyl-2-hydroxy)phenyl-N-α-[(cyclohexylamino)-carbonyl]benzyl 2-Bromobenzamide (**12f**).* The Ugi reaction was carried out by following procedure A to give **12f** (687.5 mg, 61%) as a colorless solid: mp 202−204 °C (EtOAc−hexane); R_f = 0.62 (33% EtOAc in hexane); IR (KBr) 3329, 2933, 1639, 1509, 1361, 1248 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 11.26 (s, 1 H, O*H*), 8.57 (d, *J* = 7.5 Hz, 1 H, N*H*), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.22 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.18−7.13 (m, 5 H), 7.12 (t, *J* = 7.5 Hz, 1 H), 7.05 (td, *J* = 8.0, 2.0 Hz, 1 H), 6.72 (dd, *J* = 8.5, 2.5 Hz, 1 H), 6.57 (d, *J* = 2.0 Hz, 1 H), 6.41 (d, *J* = 9.0 Hz, 1 H), 6.25 (s, 1 H), 3.81−3.71 (m, 1 H), 1.92−1.85 (m, 1 H), 1.80−1.70 (m, 2 H), 1.69−1.52 (m, 2 H), 1.39−1.25 (m, 3 H), 1.20−1.10 (m, 2 H), 0.88 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 170.4, 152.5, 141.1, 137.9, 133.2, 131.7, 130.0 (×2), 129.8, 128.9, 128.6 (×2), 128.3, 126.9, 126.7, 126.5, 124.4, 118.8, 116.4, 65.0, 49.6, 33.4, 32.4, 32.4, 30.8 (× 3), 25.3, 24.7, 24.5; MS (+ESI) *m*/*z* 587 (M + 2 + Na^+, 91), 585 (M + Na^+, 100), 565 (M + 2 + H^+, 30), 563 (M + H^+, 28). Anal. Calcd for $C_{31}H_{35}BrN_2O_3$: C, 66.07; H, 6.26; N, 4.97. Found: C, 66.06; H, 6.26; N, 4.97.

*N-α-[(Cyclohexylamino)carbonyl]benzyl-N-3-hydroxy-2-naphthyl 2-Bromobenzamide (**12g**).* The Ugi reaction was carried out by following procedure A to give **12g** (680.1 mg, 61%) as a white solid: mp 266−268 °C (MeOH−$CHCl_3$); R_f = 0.57 (33% EtOAc in hexane); IR (KBr) 3261, 2933, 1635, 1570, 1469, 1388 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 11.74 (br s, 1 H, O*H*), 8.65 (d, *J* = 7.0 Hz, 1 H, N*H*), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 8.0, Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 1 H), 7.27−7.23 (m, 3 H), 7.20 (t, *J* = 7.5 Hz, 1 H), 7.17−7.08 (m, 3 H), 7.04 (t, *J* = 7.0 Hz, 2 H), 6.91 (t, *J* = 7.0 Hz, 1 H), 6.93 (s, 1 H), 6.31 (s, 1 H), 3.84−3.70 (m, 1 H), 1.97−

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1.85 (m, 1 H), 1.82−1.70 (m, 2 H), 1.70−1.53 (m, 2 H), 1.42−1.27 (m, 3 H), 1.25−1.10 (m, 2 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 171.6, 168.8, 153.3, 138.3, 134.2, 133.7, 132.0, 130.8, 130.2, 129.8 (×2), 128.4, 128.2 (×2), 127.9, 127.2, 126.9, 126.8, 126.5 (×2), 125.5, 122.9, 118.6, 110.6, 65.2, 48.8, 31.9, 31.8, 25.2, 24.3, 24.2; MS (+ESI) m/z 581 (M + 2 + Na$^+$, 100), 579 (M + Na$^+$, 92), 559 (M + 2 + H$^+$, 6), 557 (M + H$^+$, 4). Anal. Calcd for $C_{31}H_{29}BrN_2O_3$: C, 66.79; H, 5.24; N, 5.03. Found: C, 66.83; H, 5.29; N, 4.89.

*N-(5-Chloro-2-hydroxy)phenyl-N-1-[(cyclohexylamino)carbonyl]-1-(2-thienyl)methyl 2-Bromobenzamide (**12h**).* The Ugi reaction was carried out by following procedure A to give **12h** (767.0 mg, 70%) as a colorless solid; mp 247−250 °C (MeOH−CHCl$_3$); R_f = 0.65 (33% EtOAc in hexane); IR (KBr) 3261, 3100, 2927, 1654, 1635, 1485, 1372, 1284 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 11.67 (br s, 1 H, O*H*), 8.71 (d, J = 6.5 Hz, 1 H, N*H*), 7.46 (d, J = 8.0 Hz, 1 H), 7.40 (d, J = 4.5 Hz, 1 H), 7.26 (d, J = 7.0 Hz, 1 H), 7.19 (t, J = 7.5 Hz, 1 H), 7.14 (t, J = 7.0 Hz, 1 H), 7.01 (d, J = 2.5 Hz, 1 H), 6.90−6.82 (m, 2 H), 6.82 (d, J = 2.5 Hz, 1 H), 6.57 (d, J = 8.5 Hz, 1 H), 6.42 (s, 1 H), 3.80−3.65 (m, 1 H), 1.95−1.82 (m, 1 H), 1.80−1.50 (m, 4 H), 1.40−1.11 (m, 5 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 170.8, 168.5, 154.8, 137.7, 134.7, 132.1, 130.7, 130.5, 129.9, 129.7, 128.3, 126.9, 126.8, 126.8, 126.3, 121.1, 118.4, 118.1, 60.0, 49.0, 31.7, 31.7, 25.1, 24.3, 24.2; MS (−ESI) m/z 549 (M + 4 − H$^+$, 30), 547 (M + 2 − H$^+$, 100), 545 (M − H$^+$, 65). Anal. Calcd for $C_{25}H_{24}BrClN_2O_3S$: C, 54.80; H, 4.42; N, 5.11. Found: C, 54.74; H, 4.45; N, 5.13.

*N-5-Chloro-2-hydroxyphenyl-N-α-[(cyclohexylamino)carbonyl]-benzyl 2-Bromo-5-methoxybenzamide (**12i**).* The Ugi reaction was carried out by following procedure A to give **12i** (903.6 mg, 79%) as a colorless solid: mp 254−256 °C (CH$_3$OH−CHCl$_3$); R_f = 0.66 (33% EtOAc in hexane); IR (KBr) 3321, 2933, 1669, 1626, 1549, 1490, 1288, 1241 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 11.87 (br s, 1 H, O*H*), 8.66 (d, J = 7.0 Hz, 1 H, N*H*), 7.32 (d, J = 9.0 Hz, 1 H), 7.21−7.18 (m, 5 H), 6.85 (d, J = 2.5 Hz, 1 H), 6.80 (dd, J = 8.5, 2.5 Hz, 1 H), 6.71 (dd, J = 8.5, 3.0 Hz, 1 H), 6.64 (d, J = 2.5 Hz, 1 H), 6.54 (d, J = 8.5 Hz, 1 H), 6.21 (s, 1 H), 3.85−3.71 (m, 1 H), 3.66 (s, 3 H), 1.93−1.81 (m, 1 H), 1.79−1.50 (m, 4 H), 1.40−1.09 (m, 5 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 171.4, 168.2, 158.0, 154.8, 138.5, 133.5, 133.0, 131.1, 129.8 (×2), 129.7, 128.7, 128.3 (×2), 126.6, 121.0, 118.0, 117.0, 112.5, 108.8, 64.9, 55.6, 48.9, 31.8, 31.8, 25.1, 24.3, 24.2; MS (+ESI) m/z 597 (M + 4 + Na$^+$, 21), 595 (M + 2 + Na$^+$, 100), 593 (M + Na$^+$, 65). Anal. Calcd for $C_{28}H_{28}BrClN_2O_4$: C, 58.80; H, 4.93; N, 4.90. Found: C, 58.89; H, 4.92; N, 4.95.

*N-α-[(Cyclohexylamino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl (E)-Cinnamamide (**13a**).* The Ugi reaction was carried out by following procedure A to give **13a** (842.9 mg, 79%) as a colorless solid; mp 201−203 °C (EtOAc−hexane); R_f = 0.64 (33% EtOAc in hexane); IR (KBr) 3300, 2931, 1655, 1621, 1493, 1353, 1251, 1226 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, an ca. 50:50 mixture of two atropisomers) δ 11.20 and 11.16 (br s, 1 H, O*H*), 7.67 and 7.62 (d, J = 15.6 Hz, 1 H), 7.51−7.46 (m, 1 H), 7.30−7.20 (m, 5 H), 7.19−7.10 (m, 1 H), 7.10−6.98 (m, 4 H), 6.86 (d, J = 8.4 Hz, 1 H), 6.80 (d, J = 6.4, 1 H, N*H*), 6.63−6.56 (m, 1 H), 6.49 (td, J = 7.6, 1.2 Hz, 1 H), 6.20 and 6.20 (d, J = 15.6 Hz, 1 H), 3.94−3.85 (m, 1 H), 2.10−2.00 (m, 1 H), 1.94−1.85 (m, 1 H), 1.80−1.70 (m, 1 H), 1.70−1.54 (m, 2 H), 1.42−1.00 (m, 5 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.8, 167.4, 155.8, 143.3, 134.8, 133.5, 132.8, 130.8, 130.5, 130.4, 129.6, 128.5 (× 3), 127.9 (×2), 127.7, 126.5, 124.8, 119.0, 117.6, 117.5, 64.7, 49.7, 32.4, 32.3, 25.3, 24.6, 24.6; MS (+ESI) m/z 557 (M + 2 + Na$^+$, 100), 555 (M + Na$^+$, 87), 535 (M + 2 + H$^+$, 6), 533 (M + H$^+$, 6). Anal. Calcd for $C_{29}H_{29}BrN_2O_3$: C, 65.29; H, 5.48; N, 5.25. Found: C, 65.24; H, 5.44; N, 5.30.

*N-α-[(Cyclohexylamino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl (E)-Crotonamide (**13b**).* The Ugi reaction was carried out by following procedure A to give **13b** (763.7 mg, 81%) as a colorless solid: mp 201−203 °C (EtOAc−hexane); R_f = 0.64 (33% EtOAc in hexane); IR (KBr) 3267, 2933, 1655, 1626, 1493, 1371, 1256 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, an ca. 50:50 mixture of two atropisomers) δ 11.11 (s, 1 H, O*H*), 7.51−7.47 (m, 1 H), 7.11−6.86 (m, 5 H), 6.83 (dd, J = 8.0, 1.6 Hz, 1 H), 6.72 (d, J = 7.2 Hz, 1 H), 6.51 (s, 1 H), 6.46 (td, J = 8.0, 1.6 Hz, 1 H), 6.08 (d, J = 7.6 Hz, 1 H, N*H*), 5.61 and 5.61 (d, J = 15.2 Hz, 1 H), 3.90−3.84 (m, 1 H), 2.15−2.00 (m, 1 H), 1.92−1.84 (m, 1 H), 1.78−1.55 (m, 3 H), 1.68 and 1.68 (d, J = 7.2 Hz, 3 H), 1.40−0.92 (m, 5 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.9, 167.2, 155.8, 143.1, 133.6, 132.8, 130.7, 130.4, 130.3, 130.2, 127.7, 126.5, 124.9, 121.6, 118.9, 117.5, 64.4, 49.6, 32.4, 32.3, 25.3, 24.7, 24.6, 18.0; MS (−ESI) m/z 471 (M + 2 − H$^+$, 100), 469 (M − H$^+$, 80). Anal. Calcd for $C_{24}H_{27}BrN_2O_3$: C, 61.15; H, 5.77; N, 5.94. Found: C, 61.13; H, 5.79; N, 6.00.

*N-α-[(Cyclohexylamino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl Benzamide (**13c**).* The Ugi reaction was carried out by following procedure A to give **13c** (913.4 mg, 90%) as a colorless solid: mp 195−197 °C (EtOAc−hexane); R_f = 0.69 (33% EtOAc in hexane); IR (KBr) 3327, 2934, 1636, 1557, 1493, 1369, 1251 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.38 (s, 1 H, O*H*), 7.53−7.47 (m, 1 H), 7.40−7.32 (m, 2 H), 7.26−7.01 (m, 6 H), 6.81 (td, J = 7.6, 1.2 Hz, 1 H), 6.78 (s, 1 H), 6.68−6.60 (m, 2 H), 6.53 (d, J = 7.6 Hz, 1 H, N*H*), 6.24 (td, J = 7.6, 1.2 Hz, 1 H), 3.98−3.83 (m, 1 H), 2.08−1.99 (m, 1 H), 1.96−1.86 (m, 1 H), 1.78−1.69 (m, 1 H), 1.67−1.55 (m, 2 H), 1.42−1.00 (m, 5 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.1, 171.9, 155.4, 135.5, 133.4, 132.8, 131.0, 130.5, 130.4, 129.8, 129.4, 127.7, 127.5 (×2), 127.1 (×2), 126.6, 126.3, 118.6, 117.2, 64.9, 49.8, 32.1, 32.1, 25.3, 24.7, 24.5; MS (−ESI) m/z 507 (M + 2 − H$^+$, 100), 505 (M − H$^+$, 85). Anal. Calcd for $C_{27}H_{27}BrN_2O_3$: C, 63.91; H, 5.36; N, 5.52. Found: C, 63.94; H, 5.52; N, 5.60.

*N-α-[(Cyclohexylamino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl 2-Chlorobenzamide (**13d**).* The Ugi reaction was carried out by following procedure A to give **13d** (910.3 mg, 84%) as a white solid: mp 226−228 °C (EtOAc−hexane); R_f = 0.63 (33% EtOAc in hexane); IR (KBr) 3320, 2934, 1640, 1556, 1493, 1373, 1257 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, an ca. 50:50 mixture of two atropisomers) δ 11.34 (s, 1 H, O*H*), 7.51−7.47 (m, 1 H), 7.34 (dd, J = 7.6, 2.0 Hz, 1 H), 7.20−7.13 (m, 2 H), 7.08−6.97 (m, 4 H), 6.87 (d, J = 6.8 Hz, 1 H), 6.76 (td, J = 7.6, 1.6 Hz, 1 H), 6.60 (s, 1 H), 6.58 (dd, J = 8.4, 1.2 Hz, 1 H), 6.20 (td, J = 8.0, 1.2 Hz, 1 H), 6.07 (d, J = 8.0 Hz, 1 H, N*H*), 4.00−3.89 (m, 1 H), 2.11−2.03 (m, 1 H), 1.94−1.86 (m, 1 H), 1.83−1.55 (m, 3 H), 1.43−1.00 (m, 5 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 171.7, 169.7, 155.1, 135.7, 132.9, 132.9, 130.7, 130.3, 130.2, 130.1, 129.9, 129.7, 129.0, 127.8, 126.8, 126.6, 126.0, 125.1, 118.6, 117.0, 64.7, 49.9, 32.3, 32.3, 25.3, 24.7, 24.6; MS (+ESI) m/z 545 (M + 4 + H$^+$, 21), 543 (M + 2 + H$^+$, 100), 541 (M + H$^+$, 74). Anal. Calcd for $C_{27}H_{26}BrClN_2O_3$: C, 59.85; H, 4.84; N, 5.17. Found: C, 59.84; H, 5.08; N, 5.09.

*N-α-[(Cyclohexylamino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl Acetamide (**13e**).* The Ugi reaction was carried out by following procedure A to give **13e** (481.0 mg, 54%) as a white solid; mp 201−203 °C (EtOAc−hexane); R_f = 0.21 (33% EtOAc in hexane); IR (KBr) 3237, 3069, 2931, 1637, 1493, 1383 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.17 (s, 1 H, O*H*), 7.50 (d, J = 6.8 Hz, 1 H), 7.10−6.95 (m, 4 H), 6.83 (d, J = 8.4 Hz, 1 H), 6.69 (d, J = 7.6 Hz, 1 H), 6.45 (t, J = 7.2 Hz, 1 H), 6.42 (s, 1 H), 6.15 (d, J = 6.0 Hz, 1 H, N*H*), 3.90−3.75 (m, 1 H), 2.05−1.97 (m, 1 H), 1.92−1.80 (m, 1 H), 1.83 (s, 3 H), 1.78−1.68 (m, 1 H), 1.68−1.55 (m, 2 H), 1.40−0.95 (m, 5 H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.4, 171.9, 155.4, 133.7, 132.8, 130.4, 130.3, 130.2, 130.1, 127.7, 126.4, 126.0, 119.2, 117.8, 64.2, 49.7, 32.3, 32.3, 25.3, 24.7, 24.6, 22.3; MS (+ESI) m/z 469 (M + 2 + Na$^+$, 97), 467 (M + Na$^+$, 100). Anal. Calcd for $C_{22}H_{25}BrN_2O_3$: C, 59.33; H, 5.66; N, 6.29. Found: C, 59.38; H, 5.70; N, 6.24.

*N-α-[(Cyclohexylamino)carbonyl]-2-bromo-4,5-dimethoxybenzyl-N-2-hydroxyphenyl Acetamide (**13f**).* The Ugi reaction was carried out by following procedure A to give **13f** (788.4 mg, 78%) as a white solid: mp 148−150 °C (EtOAc−hexane); R_f = 0.35 (33% EtOAc in hexane); IR (KBr) 3339, 3243, 3075, 2932, 1643, 1507, 1492, 1382, 1264 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.23 (s, 1 H, O*H*), 7.14 (d, J = 7.2 Hz, 1 H, N*H*), 6.96 (t, J = 7.2 Hz, 1 H), 6.81 (s, 1 H), 6.77 (d, J = 8.0 Hz, 1 H), 6.62 (d, J = 8.0 Hz, 1 H), 6.52 (s, 1 H), 6.43 (t, J = 7.2 Hz, 1 H), 6.30 (s, 1 H), 380−3.67 (m, 1 H), 3.66 (s, 3 H), 3.48 (s, 3 H), 1.96−1.87 (m, 1 H), 1.84−1.70 (m, 1 H), 1.72 (s, 3 H), 1.72−1.63 (m, 1 H), 1.62−1.48 (m, 2 H), 1.34−0.95 (m, 5 H); ^{13}C NMR (100 MHz, CDCl$_3$, an ca. 50:50 mixture of two atropisomers) δ 172.3, 172.1, 155.4, 149.6 and 149.6, 148.2 and

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148.1, 130.3, 130.1, 126.1, 125.2 and 125.2, 119.3, 117.5, 116.4, 114.7, 112.1, 64.1, 55.8, 55.7, 49.5, 32.2 and 32.1, 32.1 and 32.1, 25.2, 24.6, 24.5, 22.3; MS (+ESI) m/z 529 (M + 2 + Na^+, 100), 527 (M + Na^+, 93). Anal. Calcd for $C_{24}H_{29}BrN_2O_5$: C, 57.04; H, 5.78; N, 5.54. Found: C, 57.07; H, 5.81; N, 5.53.

*N-5-Chloro-2-hydroxyphenyl-N-α-[(cyclohexylamino)carbonyl]-2-bromobenzyl (E)-Cinnamamide (**13g**).* The Ugi reaction was carried out by following procedure A to give **13g** (726.9 mg, 64%) as a white solid: mp 189−191 °C (EtOAc−hexane); R_f = 0.65 (33% EtOAc in hexane); IR (KBr) 3267, 3084, 2933, 1666, 1624, 1489, 1345, 1224 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, an ca. 50:50 mixture of two atropisomers) δ 11.45 and 11.43 (s, 1 H, O*H*), 7.62 and 7.60 (d, J = 15.6 Hz, 1 H), 7.56−7.50 (m, 1 H), 7.35−7.20 (m, 5 H), 7.15−6.99 (m, 4 H), 6.83 (s, 1 H), 6.80 (d, J = 8.8 Hz, 1 H), 6.59 (d, J = 3.2 Hz, 1 H), 6.64−6.57 (m, 0.5 H, N*H*), 6.50 (d, J = 6.4 Hz, 0.5 H, N*H*), 6.18 (d, J = 15.2 Hz, 1 H), 3.95−3.85 (m, 1 H), 2.10−2.00 (m, 1 H), 1.95−1.87 (m, 1 H), 1.80−1.70 (m, 1 H), 1.69−1.55 (m, 2 H), 1.42−1.00 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 167.1, 154.8, 143.9, 134.6, 133.2, 133.0, 130.7, 130.5, 130.3, 130.1, 129.9, 128.5 (×2), 128.0 (×2), 127.8, 126.5, 125.6, 123.0, 118.7, 116.8, 64.7, 49.7, 32.3 (×2), 25.3, 24.7, 24.5; MS (+ESI) m/z 593 (M + 4 + Na^+, 28), 591 (M + 2 + Na^+, 100), 589 (M + Na^+, 72). Anal. Calcd for $C_{29}H_{28}BrClN_2O_3$: C, 61.33; H, 4.97; N, 4.93. Found: C, 61.06; H, 5.14; N, 4.90.

*N-α-[(Cyclohexylamino)carbonyl]-2-bromobenzyl-N-3,5-dimethyl-2-hydroxyphenyl (E)-Cinnamamide (**13h**).* The Ugi reaction was carried out by following procedure A to give **13h** (741.2 mg, 66%) as a colorless solid: mp 161−163 °C (EtOAc−hexane); R_f = 0.63 (33% EtOAc in hexane); IR (KBr) 3289, 2927, 1741, 1644, 1596, 1562, 1371, 1232 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, an 89:11 mixture of two atropisomers) for the major atropisomer δ 10.83 (s, 1 H, O*H*), 7.66 (d, J = 15.2 Hz, 1 H), 7.53−7.48 (m, 1 H), 7.34−7.23 (m, 5 H), 7.14−7.08 (m, 1 H), 7.05−6.98 (m, 2 H), 6.73 (s, 1 H), 6.59 (s, 1 H), 6.39 (s, 1 H), 6.25 (d, J = 16.0 Hz, 1 H), 6.16 (d, J = 7.6 Hz, 1 H, N*H*), 3.99−3.85 (m, 1 H), 2.17 (s, 3 H), 2.10−2.03 (m, 1 H), 1.95 (s, 3 H), 1.95−1.85 (m, 1 H), 1.80−1.70 (m, 1 H), 1.70−1.54 (m, 2 H), 1.42−0.99 (m, 5 H); for partial signals of the minor atropisomer δ 10.39 (s, 1 H, O*H*), 7.92 (d, J = 7.6 Hz, 1 H), 7.74 (d, J = 15.6 Hz, 1 H), 5.45 (d, J = 8.0 Hz, 1 H, N*H*), 5.22 (s, 1 H), 2.16 (s, 3 H), 1.93 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) for the major atropisomer δ 171.8, 167.4, 151.6, 143.0, 135.0, 133.7, 132.6, 132.0, 130.4, 130.3, 129.5, 128.5 (× 2), 128.1, 128.0 (×2), 127.5, 127.2, 126.6, 126.0, 123.8, 117.8, 64.7, 49.6, 32.4, 32.4, 25.3, 24.8, 24.6, 19.9, 16.2; for partial signals of the minor atropisomer δ 168.4, 167.9, 149.7, 143.7, 134.8, 133.7, 133.4, 130.6, 130.4, 129.8, 128.7, 128.6 (×2), 128.5, 128.1 (×2), 127.8, 126.4, 117.2, 70.9, 49.3, 20.2, 16.2; MS (+ESI) m/z 585 (M + 2 + Na^+, 31), 583 (M + Na^+, 29), 563 (M + 2 + H^+, 98), 561 (M + H^+, 100). Anal. Calcd for $C_{31}H_{33}BrN_2O_3$: C, 66.31; H, 5.92; N, 4.99. Found: C, 66.31; H, 5.94; N, 5.00.

*N-α-[(Cyclohexylamino)carbonyl]-2-bromobenzyl-N-3-hydroxy-2-naphthyl Acetamide (**13i**).* The Ugi reaction was carried out by following procedure A to give **13i** (644.0 mg, 65%) as a colorless solid; mp 250−252 °C ($CHCl_3$−hexane); R_f = 0.50 (33% EtOAc in hexane); IR (KBr) 3231, 3065, 2930, 1635, 1507, 1469, 1381 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1 H, O*H*), 7.56 (d, J = 8.0 Hz, 1 H), 7.50−7.43 (m, 2 H), 7.31 (dd, J = 8.4, 1.6 Hz, 1 H), 7.29 (s, 1 H), 7.22 (s, 1 H), 7.16 (t, J = 7.2 Hz, 1 H), 7.07 (t, J = 5.2 Hz, 1 H), 6.90 (d, J = 5.6 Hz, 1 H), 6.89 (d, J = 6.0 Hz, 1 H), 6.52 (s, 1 H), 6.32 (d, J = 7.6 Hz, 1 H, N*H*), 3.95−3.84 (m, 1 H), 2.08−2.00 (m, 1 H), 1.91−1.83 (m, 1 H), 1.83 (s, 3 H), 1.80−1.70 (m, 1 H), 1.68−1.55 (m, 2 H), 1.41−0.99 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.9, 153.1, 134.9, 133.5, 132.8, 130.6, 130.2, 129.6, 128.2, 127.9, 127.5, 127.5, 126.7, 126.4, 126.0, 123.1, 112.2, 64.4, 49.7, 32.3, 32.3, 25.3, 24.7, 24.6, 22.5; MS (+ESI) m/z 519 (M + 2 + Na^+, 20), 517 (M + Na^+, 19), 497 (M + 2 + H^+, 97), 495 (M + H^+, 100). Anal. Calcd for $C_{26}H_{27}BrN_2O_3$: C, 63.03; H, 5.49; N, 5.65. Found: C, 63.03; H, 5.51; N, 5.65.

*N-α-[((((Ethoxycarbonyl)methyl)amino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl (E)-Cinnamamide (**13j**).* The Ugi reaction was carried out by following procedure A to give **13j** (687.9 mg, 64%) as a colorless solid: mp 232−234 °C (EtOAc−hexane); R_f = 0.28 (33% EtOAc in hexane); IR (KBr) 3292, 1741, 1658, 1623, 1493, 1354, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1 H, O*H*), 7.88 (d, J = 15.2 Hz, 1 H), 7.73−7.68 (m, 1 H), 7.50−7.43 (m, 5 H), 7.37−7.22 (m, 4 H), 7.15−7.10 (m, 1 H, N*H*), 7.07 (d, J = 8.0 Hz, 1 H), 7.00 (d, J = 7.6 Hz, 1 H), 6.93 (s, 1 H), 6.71 (t, J = 7.2 Hz, 1 H), 6.39 (d, J = 15.6 Hz, 1 H), 4.49 (dd, J = 18.4, 6.0 Hz, 1 H), 4.39 (q, J = 7.2 Hz, 2 H), 4.24 (dd, J = 18.4, 4.4 Hz, 1 H), 1.46 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 173.7, 169.2, 166.5, 156.0, 142.6, 135.2, 134.3, 133.1, 131.3 (×2), 131.1, 130.9, 130.3, 129.4 (×2), 128.0, 128.0 (×2), 126.9, 125.6, 119.5, 118.7, 117.7, 64.3, 61.1, 42.1, 14.5; MS (−ESI) m/z 537 (M + 2 − H^+, 100), 535 (M − H^+, 86). Anal. Calcd for $C_{27}H_{25}BrN_2O_5$: C, 60.34; H, 4.69; N, 5.21. Found: C, 60.35; H, 4.70; N, 5.21.

*N-α-[(Benzylamino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl (E)-Cinnamamide (**13k**).* The Ugi reaction was carried out by following procedure A to give **13k** (898.8 mg, 83%) as a white solid: mp 253−255 °C ($CHCl_3$−hexane); R_f = 0.54 (33% EtOAc in hexane); IR (KBr) 3294, 1657, 1623, 1493, 1350, 1226 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.04 (s, 1 H, O*H*), 7.62 (d, J = 15.6 Hz, 1 H), 7.52−7.46 (m, 1 H), 7.32−7.20 (m, 10 H), 7.16−6.99 (m, 4 H), 6.88 (d, J = 7.2 Hz, 1 H), 6.82 (d, J = 6.8 Hz, 1 H), 6.75−6.67 (m, 1 H, N*H*), 6.68 (s, 1 H), 6.52 (t, J = 8.0 Hz, 1 H), 6.20 (d, J = 15.6 Hz, 1 H), 4.71 (dd, J = 14.8, 6.4 Hz, 1 H), 4.48 (dd, J = 14.8, 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 167.6, 155.7, 143.7, 136.9, 134.8, 133.0, 132.9, 130.8, 130.7, 130.6, 130.4, 129.8, 128.7 (×2), 128.6 (×2), 128.0 (×2), 127.8 (×2), 127.7, 127.7, 126.5, 124.6, 119.2, 117.6, 117.3, 64.8, 44.3; MS (−ESI) m/z 541 (M + 2 − H^+, 99), 539 (M − H^+, 100). Anal. Calcd for $C_{30}H_{25}BrN_2O_3$: C, 66.55; H, 4.65; N, 5.17. Found: C, 66.58; H, 4.65; N, 4.94.

*N-α-[(Benzylamino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl Formamide (**13l**).* The Ugi reaction was carried out by following procedure A to give **13l** (676.5 mg, 77%) as a white solid: mp 205−207 °C ($CHCl_3$−hexane); R_f = 0.50 (33% EtOAc in hexane); IR (KBr) 3308, 1650, 1495, 1290 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 11.1 (br s, 1 H, O*H*), 9.32 (s, 1 H, C*H*O), 7.57 (dd, J = 7.0, 1.5 Hz, 1 H), 7.38−6.99 (m, 10 H), 6.89 (d, J = 8.0 Hz, 1 H), 6.75 (d, J = 8.0 Hz, 1 H), 6.54 (t, J = 7.5 Hz, 1 H), 6.35 (s, 1 H), 4.44 (d, J = 4.5 Hz, 2 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 171.7, 163.5, 155.7, 138.1, 133.3, 132.8, 130.7, 130.6, 130.3, 130.2, 128.3 (×2), 127.6, 127.5 (×2), 127.1, 126.1, 124.6, 118.7, 117.0, 62.4, 43.3; MS (+ESI) m/z 463 (M + 2 + Na^+, 40), 461 (M + Na^+, 45), 441 (M + 2 + H^+, 100), 439 (M + H^+, 78). Anal. Calcd for $C_{22}H_{19}BrN_2O_3$: C, 60.15; H, 4.36; N, 6.38. Found: C, 60.14; H, 4.39; N, 6.41.

*N-α-[(tert-Butylamino)carbonyl]-2-bromobenzyl-N-2-hydroxyphenyl Acetamide (**13m**).* The Ugi reaction was carried out by following procedure A to give **13m** (469.6 mg, 56%) as a colorless solid: mp 227−229 °C (EtOAc−hexane); R_f = 0.53 (33% EtOAc in hexane); IR (KBr) 3252, 3081, 2969, 2932, 1638, 1569, 1493, 1382 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1 H, O*H*), 7.49 (dd, J = 7.6, 1.6 Hz, 1 H), 7.10−6.95 (m, 4 H), 6.81 (dd, J = 8.0, 1.2 Hz, 1 H), 6.69 (d, J = 7.6 Hz, 1 H), 6.44 (td, J = 8.0, 1.2 Hz, 1 H), 6.31 (s, 1 H), 5.97 (br s, 1 H, N*H*), 1.81 (s, 3 H), 1.36 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 172.1, 155.4, 133.8, 132.8, 130.4, 130.2 (×2), 130.1, 127.8, 126.4, 126.1, 119.1, 117.7, 64.7, 52.6, 28.3 (× 3), 22.3; MS (+ESI) m/z 443 (M + 2 + Na^+, 94), 441 (M + Na^+, 100). Anal. Calcd for $C_{20}H_{23}BrN_2O_3$: C, 57.29; H, 5.53; N, 6.68. Found: C, 57.29; H, 5.57; N, 6.68.

General Procedure B for Microwave-Assisted Intramolecular Ullmann Etherification. Synthesis of Dibenz[*b*,*f*][1,4]oxazepin-11(10*H*)-ones 14a−i and Dibenz[*b*,*f*][1,4]oxazepine-11(10*H*)-carboxamides 15a−m. To a 10 mL pressurized process vial were added the bromophenol **12a−i** or **13a−m** (0.20 mmol), CuI (3.8 mg, 2.0×10^{-2} mmol, 10 mol %), *N*,*N*-dimethylglycine hydrochloride (8.4 mg, 6.0×10^{-2} mmol, 30 mol %), and Cs_2CO_3 (130.3 mg, 4.0×10^{-1} mmol, 2 equiv). The vial was then sealed with a cap containing a silicon septum and was evacuated and backfilled with nitrogen (repeated three times). To the degassed vial was added dry dioxane (5 mL). The loaded vial was then put into the microwave cavity and heated at 150 °C for 30 min (it took ca. 4 min to reach 150 °C from

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room temperature). After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography over silica gel (eluting with 25% PE in EtOAc) to give the Ullmann etherification products. The structures and yields of the products **14a−i** and **15a−m** are found in Tables 3 and 4.

*N-Benzyl 2-[11-Oxodibenz[b,f][1,4]oxazepin-10(11H)-yl]-phenylacetamide (**14a**).* The reaction of **12a** (103.1 mg) was carried out by following procedure B to give **14a** (86.9 mg, 100%) as a colorless solid: mp 172−174 °C (EtOAc−hexane); R_f = 0.45 (33% EtOAc in hexane); IR (KBr) 3356, 3063, 1666, 1632, 1497, 1447, 1353, 1213 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 8.71 (br s, 1 H, N*H*), 7.83 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.63−7.54 (m, 2 H), 7.38−7.13 (m, 13 H), 7.00 (td, *J* = 8.0, 1.5 Hz, 1 H), 6.86 (td, *J* = 8.0, 1.0 Hz, 1 H), 6.44 (s, 1 H), 4.50 (d, *J* = 6.0 Hz, 2 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 169.0, 166.1, 160.9, 155.5, 139.2, 135.3, 133.9, 132.4, 132.1, 129.1 (×2), 128.2 (×2), 128.0 (×2), 127.5, 127.5 (×2), 127.4, 126.9, 126.8, 126.1, 125.3, 124.7, 120.4, 119.9, 66.1, 42.9; MS (−ESI) *m*/*z* 433 (M−H^+, 100). Anal. Calcd for $C_{28}H_{22}N_2O_3$: C, 77.40; H, 5.10; N, 6.45. Found: C, 77.47; H, 5.08; N, 6.48.

*N-Cyclohexyl 2-[11-Oxodibenz[b,f][1,4]oxazepin-10(11H)-yl]-phenylacetamide (**14b**).* The reaction of **12b** (101.5 mg) was carried out by following procedure B to give **14b** (85.3 mg, 100%) as a colorless solid: mp 209−211 °C (EtOAc−hexane); R_f = 0.55 (33% EtOAc in hexane); IR (KBr) 3281, 2932, 1649, 1564, 1491, 1451, 1354 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 8.00 (d, *J* = 7.5 Hz, 1 H, N*H*), 7.80 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.60 (d, *J* = 7.5 Hz, 1 H), 7.56 (td, *J* = 8.5, 2.0 Hz, 1 H), 7.34−7.26 (m, 2 H), 7.25−7.12 (m, 6 H), 6.99 (td, *J* = 8.0, 2.0 Hz, 1 H), 6.85 (td, *J* = 7.5, 1.5 Hz, 1 H), 6.36 (s, 1 H), 3.80−3.75 (m, 1 H), 1.92−1.78 (m, 2 H), 1.77−1.67 (m, 2 H), 1.62−1.54 (m, 1 H), 1.40−1.15 (m, 5 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 167.8, 166.0, 160.9, 155.5, 135.7, 133.8, 132.4, 132.0, 128.9 (×2), 128.0 (×2), 127.4, 127.4, 126.8, 126.1, 125.3, 124.6, 120.3, 119.8, 66.0, 48.2, 32.3, 32.2, 25.3, 24.5 (×2); MS (+ESI) *m*/*z* 449 (M + Na^+, 100), 427 (M + H^+, 59). Anal. Calcd for $C_{27}H_{26}N_2O_3$: C, 76.03; H, 6.14; N, 6.57. Found: C, 76.06; H, 6.15; N, 6.57.

*N-(Ethoxycarbonyl)methyl 2-[11-Oxodibenz[b,f][1,4]oxazepin-10(11H)-yl]phenylacetamide (**14c**).* The reaction of **12c** (102.3 mg) was carried out by following procedure B to give **14c** (86.1 mg, 100%) as a colorless solid: mp 167−169 °C (EtOAc−hexane); R_f = 0.24 (33% EtOAc in hexane); IR (KBr) 3410, 3057, 2973, 1749, 1682, 1635, 1539, 1495, 1459, 1355, 1193 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6, an 84:16 mixture of two atropisomers at 80 °C) for the major atropisomer δ 8.65 (br s, 1 H, N*H*), 7.79 (dd, *J* = 7.5, 1.0 Hz, 1 H), 7.60−7.54 (m, 2 H), 7.37−7.26 (m, 4 H), 7.25−7.13 (m, 4 H), 7.01 (td, *J* = 8.0, 1.0 Hz, 1 H), 6.88 (td, *J* = 8.0, 1.0 Hz, 1 H), 6.46 (s, 1 H), 4.20 (q, *J* = 7.5 Hz, 2 H), 4.14 (dd, *J* = 17.0, 5.5 Hz, 1 H), 3.95 (dd, *J* = 17.0, 5.0 Hz, 1 H), 1.27 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 169.6, 169.4, 166.1, 160.8, 155.4, 135.1, 133.9, 132.4, 132.1, 129.2 (×2), 127.9 (×2), 127.5, 127.2, 126.9, 126.0, 125.3, 124.7, 120.4, 119.8, 65.7, 60.5, 41.5, 14.1; MS (−ESI) *m*/*z* 429 (M − H^+, 100). Anal. Calcd for $C_{25}H_{22}N_2O_5$: C, 69.76; H, 5.15; N, 6.51. Found: C, 69.72; H, 5.16; N, 6.58.

*N-tert-Butyl 2-[11-Oxodibenz[b,f][1,4]oxazepin-10(11H)-yl]-phenylacetamide (**14d**).* The reaction of **12d** (96.3 mg) was carried out by following procedure B to give **14d** (80.1 mg, 100%) as a colorless solid: mp 183−185 °C (EtOAc−hexane); R_f = 0.55 (33% EtOAc in hexane); IR (KBr) 3326, 1660, 1646, 1551, 1496, 1457, 1363 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 7.81 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.73 (br s, 1 H, N*H*), 7.60 (d, *J* = 7.5 Hz, 1 H), 7.55 (td, *J* = 8.0, 1.5 Hz, 1 H), 7.35−7.12 (m, 8 H), 6.99 (td, *J* = 7.5, 1.5 Hz, 1 H), 6.86 (td, *J* = 8.0, 2.0 Hz, 1 H), 6.32 (s, 1 H), 1.33 (s, 9 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 168.2, 166.0, 161.0, 155.5, 135.9, 133.9, 132.6, 132.1, 128.8 (×2), 128.0 (×2), 127.4, 127.3, 126.8, 126.1, 125.3, 124.7, 120.3, 119.9, 66.5, 50.8, 28.6 (× 3); MS (−ESI) *m*/*z* 399 (M − H^+, 100). Anal. Calcd for $C_{25}H_{24}N_2O_3$: C, 74.98; H, 6.04; N, 7.00. Found: C, 75.04; H, 6.04; N, 7.06.

*N-Cyclohexyl 2-[8-Chloro-11-oxodibenz[b,f][1,4]-oxazepin-10-(11H)-yl]phenylacetamide (**14e**).* The reaction of **12e** (108.4 mg) was carried out by following procedure B to give **14e** (84.8 mg, 92%) as a colorless solid: mp 206−208 °C (EtOAc−hexane); R_f = 0.54 (33% EtOAc in hexane); IR (KBr) 3322, 2931, 1655, 1492, 1454, 1347, 1212 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 8.18 (d, *J* = 6.5 Hz, 1 H, N*H*), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.77 (s, 1 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.36−7.15 (m, 8 H), 7.01 (dd, *J* = 8.5, 2.0 Hz, 1 H), 6.42 (s, 1 H), 3.85−3.75 (m, 1 H), 1.96−1.81 (m, 2 H), 1.80−1.67 (m, 2 H), 1.64−1.55 (m, 1 H), 1.41−1.15 (m, 5 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 167.9, 165.7, 160.6, 154.4, 135.2, 134.1, 133.4, 132.1, 128.8 (×2), 128.6, 128.1 (×2), 127.7, 127.6, 126.5, 125.7, 125.6, 121.6, 119.8, 65.7, 48.3, 32.3, 32.2, 25.3, 24.5, 24.5; MS (+ESI) *m*/*z* 485 (M + 2 + Na^+, 42), 483 (M + Na^+, 100). Anal. Calcd for $C_{27}H_{25}ClN_2O_3$: C, 70.35; H, 5.47; N, 6.08. Found; C, 70.37; H, 5.38; N, 6.05.

*N-Cyclohexyl 2-[8-tert-Butyl-11-oxodibenz[b,f][1,4]oxazepin-10-(11H)-yl]phenylacetamide (**14f**).* The reaction of **12f** (112.7 mg) was carried out by following procedure B to give **14f** (96.5 mg, 100%) as a colorless solid: mp 238−240 °C (EtOAc−hexane); R_f = 0.62 (33% EtOAc in hexane); IR (KBr) 3316, 2929, 1675, 1622, 1457, 1356 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 8.05 (d, *J* = 8.0 Hz, 1 H, N*H*), 7.79 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.65 (br s, 1 H), 7.54 (td, *J* = 8.5, 1.0 Hz, 1 H), 7.30−7.26 (m, 2 H), 7.22−7.16 (m, 4 H), 7.16−7.09 (m, 1 H), 7.06 (d, *J* = 8.0 Hz, 1 H), 6.96 (dd, *J* = 8.5, 2.5 Hz, 1 H), 6.38 (s, 1 H), 3.82−3.76 (m, 1 H), 1.93−1.83 (m, 2 H), 1.78−1.68 (m, 2 H), 1.63−1.56 (m, 1 H), 1.40−1.14 (m, 5 H), 1.03 (s, 9 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 168.0, 166.2, 160.9, 153.2, 147.1, 135.7, 133.7, 132.1, 131.3, 128.9 (×2), 127.9 (×2), 127.2, 126.3, 125.1, 124.8, 123.4, 119.8, 119.5, 65.8, 48.2, 34.0, 32.3, 32.2, 30.8 (× 3), 25.3, 24.4 (×2); MS (−ESI) *m*/*z* 481 (M − H^+, 100). Anal. Calcd for $C_{31}H_{34}N_2O_3$: C, 77.15; H, 7.10; N, 5.80. Found: C, 77.15; H, 7.10; N, 5.70.

*N-Cyclohexyl 2-[13-Oxobenzo[f]naphth[2,3-b][1,4]oxazepin-12-(13H)-yl]phenylacetamide (**14g**).* The reaction of **12g** (111.5 mg) was carried out by following procedure B to give **14g** (78.2 mg, 82%) as a colorless solid: mp 256−258 °C (EtOAc−hexane); R_f = 0.57 (33% EtOAc in hexane); IR (KBr) 3306, 2932, 1646, 1456, 1324, 1212 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 8.14 (s, 1 H), 8.07 (d, *J* = 5.5 Hz, 1 H, N*H*), 7.81 (d, *J* = 7.5 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.69 (s, 1 H), 7.60−7.55 (m, 2 H), 7.42−7.20 (m, 6 H), 7.13 (t, *J* = 7.5 Hz, 2 H), 7.01 (t, *J* = 7.0 Hz, 1 H), 6.47 (s, 1 H), 3.81 (br s, 1 H), 1.95−1.85 (m, 2 H), 1.75−1.68 (m, 2 H), 1.61−1.55 (m, 1 H), 1.40−1.13 (m, 5 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 168.0, 166.2, 160.0, 154.4, 135.8, 134.0, 132.0, 131.3, 131.3, 130.1, 128.9 (×2), 128.0 (×2), 127.5, 127.4, 126.8, 126.3 (×2), 126.2, 125.9, 125.5, 120.1, 116.7, 66.5, 48.3, 32.3, 32.2, 25.3, 24.5 (×2); MS (−ESI) *m*/*z* 475 (M − H^+, 100). Anal. Calcd for $C_{31}H_{28}N_2O_3$: C, 78.13; H, 5.92; N, 5.88. Found: C, 78.22; H, 5.95; N, 5.82.

*N-Cyclohexyl 2-[8-Chloro-11-oxodibenz[b,f][1,4]-oxazepin-10-(11H)-yl](2-thienyl)acetamide (**14h**).* The reaction of **12h** (109.6 mg) was carried out by following procedure B to give **14h** (62.6 mg, 67%) as a yellow solid: mp 163−165 °C (EtOAc−hexane); R_f = 0.62 (33% EtOAc in hexane); IR (KBr) 3402, 2933, 1686, 1652, 1509, 1490, 1454, 1329, 1211, 1201 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 8.05 (d, *J* = 7.0 Hz, 1 H, N*H*), 7.80 (s, 1 H), 7.79 (dd, *J* = 7.5, 2.5 Hz, 1 H), 7.59 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.41 (dd, *J* = 5.0, 0.5 Hz, 1 H), 7.35−7.29 (m, 2 H), 7.26 (d, *J* = 8.5 Hz, 1 H), 7.11 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.02 (d, *J* = 3.0 Hz, 1 H), 6.91 (dd, *J* = 5.0, 3.5 Hz, 1 H), 6.54 (s, 1 H), 3.81−3.70 (m, 1 H), 1.92−1.78 (m, 2 H), 1.77−1.67 (m, 2 H), 1.62−1.54 (m, 1 H), 1.40−1.15 (m, 5 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 167.2, 165.5, 160.5, 154.4, 137.6, 134.3, 133.3, 132.2, 128.8, 128.8, 127.6, 126.9, 126.8, 126.4, 125.7, 125.5, 121.9, 119.9, 61.5, 48.5, 32.3, 32.1, 25.3, 24.4 (×2); MS (+ESI) *m*/*z* 491 (M + 2 + Na^+, 37), 489 (M + Na^+, 100). Anal. Calcd for $C_{25}H_{23}ClN_2O_3S$: C, 64.30; H, 4.96; N, 6.00. Found: C, 64.30; H, 5.01; N, 6.00.

*N-Cyclohexyl 2-[8-Chloro-2-methoxy-11-oxodibenz[b,f][1,4]-oxazepin-10(11H)-yl]phenylacetamide (**14i**).* The reaction of **12i** (114.4 mg) was carried out by following procedure B to give **14i** (88.4 mg, 90%) as a colorless solid: mp 232−234 °C (EtOAc−hexane); R_f = 0.63 (33% EtOAc in hexane); IR (KBr) 3339, 2922, 1682, 1636, 1547,

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1480, 1432, 1343, 1198 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6 at 80 °C) δ 8.16 (d, J = 5.5 Hz, 1 H, N*H*), 7.74 (s, 1 H), 7.30−7.09 (m, 9 H), 6.99 (d, J = 7.5 Hz, 1 H), 6.39 (s, 1 H), 3.83−3.73 (m, 1 H), 3.77 (s, 3 H), 1.94−1.81 (m, 2 H), 1.79−1.67 (m, 2 H), 1.63−1.55 (m, 1 H), 1.40−1.13 (m, 5 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 168.0, 165.6, 156.8, 154.9, 154.5, 135.2, 133.4, 128.8 (×2), 128.5, 128.2 (×2), 127.7, 127.7, 126.5, 126.2, 121.5, 121.0, 120.5, 115.7, 65.8, 56.0, 48.4, 32.3, 32.3, 25.3, 24.5, 24.5; MS (+ESI) m/z 515 (M + 2 + Na^+, 36), 513 (M + Na^+, 100). Anal. Calcd for $C_{28}H_{27}ClN_2O_4$: C, 68.50; H, 5.54; N, 5.71. Found: C, 68.14; H, 5.69; N, 5.76.

*N-Cyclohexyl 10-(E)-Cinnamoyldibenz[b,f][1,4]-oxazepine-11-(10H)-carboxamide (**15a**).* The reaction of **13a** (106.7 mg) was carried out by following procedure B to give **15a** (57.9 mg, 64%) as a colorless solid: mp 156−158 °C (EtOAc−hexane); R_f = 0.42 (33% EtOAc in hexane); IR (KBr) 3269, 2931, 1669, 1653, 1494, 1339, 1222 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 15.6 Hz, 1 H), 7.40−7.20 (m, 11 H), 7.17 (t, J = 7.6 Hz, 1 H), 7.10 (t, J = 8.0 Hz, 1 H), 6.75 (s, 1 H), 6.50 (d, J = 15.6 Hz, 1 H), 5.70 (d, J = 8.0 Hz, 1 H, N*H*), 3.65−3.54 (m, 1 H), 1.73−1.65 (m, 1 H), 1.60−1.47 (m, 4 H), 1.30−0.77 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.1, 153.6, 152.8, 143.7, 134.7, 131.3, 130.7, 130.4, 129.9, 129.6, 129.5, 128.7 (×2), 128.0 (×2), 124.6, 123.3, 122.5, 121.6, 121.2, 117.4, 61.0, 48.1, 32.6, 32.5, 25.2, 24.5, 24.4; MS (−ESI) m/z 451 (M − H^+, 100). HRMS (−CI-TOF) m/z [M]$^-$ calcd for $C_{29}H_{28}N_2O_3$ 452.2100, found 452.2079.

*N-Cyclohexyl 10-(E)-Crotonoyldibenz[b,f][1,4]-oxazepine-11-(10H)-carboxamide (**15b**).* The reaction of **13b** (94.3 mg) was carried out by following procedure B to give **15b** (67.2 mg, 86%) as a colorless solid: mp 162−164 °C (EtOAc−hexane); R_f = 0.36 (33% EtOAc in hexane); IR (KBr) 3298, 2935, 1675, 1655, 1530, 1487, 1446, 1229 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, an ca. 50:50 mixture of two atropisomers) δ 7.36−6.99 (m, 9 H), 6.67 (s, 1 H), 5.91 and 5.91 (d, J = 14.8 Hz, 1 H), 5.65 (d, J = 8.0 Hz, 1 H, N*H*), 3.70−3.54 (m, 1 H), 1.79 and 1.79 (d, J = 6.8 Hz, 3 H), 1.76−1.65 (m, 1 H), 1.60−1.41 (m, 4 H), 1.40−0.75 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 165.9, 153.6, 152.9, 143.7, 131.3, 130.8, 130.5, 129.4 (×2), 124.5, 123.2, 122.7, 121.7, 121.5, 121.1, 60.8, 48.1, 32.6, 32.5, 25.2, 24.5, 24.4, 18.1; MS (+ESI) m/z 413 (M + Na^+, 100), 391 (M + H^+, 28). Anal. Calcd for $C_{24}H_{26}N_2O_3$: C, 73.82; H, 6.71; N, 7.17. Found: C, 73.84; H, 6.75; N, 7.15.

*N-Cyclohexyl 10-Benzoyldibenz[b,f][1,4]oxazepine-11(10H)-carboxamide (**15c**).* The reaction of **13c** (101.5 mg) was carried out by following procedure B to give **15c** (85.3 mg, 100%) as a white solid: mp 168−170 °C (EtOAc−hexane); R_f = 0.35 (33% EtOAc in hexane); IR (KBr) 3215, 3066, 2932, 1653, 1497, 1446, 1325, 1267 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.43 (m, 2 H), 7.37−7.10 (m, 9 H), 6.84 (td, J = 8.0, 1.2 Hz, 1 H), 6.77 (s, 1 H), 6.73 (d, J = 6.8 Hz, 1 H), 5.99 (d, J = 8.0 Hz, 1 H, N*H*), 3.70−3.57 (m, 1 H), 1.77−1.68 (m, 1 H), 1.64−1.48 (m, 4 H), 1.35−0.85 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 167.1, 153.9, 152.3, 134.3, 132.7, 131.2, 130.6, 130.5, 129.5, 128.8, 128.6 (×2), 127.9 (×2), 124.6, 123.4, 122.6, 121.3, 121.2, 61.5, 48.1, 32.7, 32.5, 25.3, 24.4, 24.4; MS (−ESI) m/z 425 (M − H^+, 100). Anal. Calcd for $C_{27}H_{26}N_2O_3$: C, 76.03; H, 6.14; N, 6.57. Found: C, 76.02; H, 6.12; N, 6.67.

*N-Cyclohexyl 10-(2-Chlorobenzoyl)dibenz[b,f][1,4]oxazepine-11-(10H)-carboxamide (**15d**).* The reaction of **13d** (108.4 mg) was carried out by following procedure B to give **15d** (88.5 mg, 96%) as a white solid: mp 182−184 °C (EtOAc−hexane); R_f = 0.35 (33% EtOAc in hexane); IR (KBr) 3365, 2931, 1693, 1642, 1499, 1269 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.02 (m, 10 H), 6.99 (d, J = 8.0 Hz, 1 H), 6.81 (d, J = 8.0 Hz, 1 H), 6.79 (s, 1 H), 5.96 (d, J = 6.4 Hz, 1 H, N*H*), 3.67−3.57 (m, 1 H), 1.80−1.72 (m, 1 H), 1.65−1.47 (m, 4 H), 1.34−0.80 (m, 5 H); ^{13}C NMR (125 MHz, DMSO-d_6 at 80 °C) δ 166.8, 166.0, 154.0, 152.6, 135.7, 130.9, 130.7 (×2), 129.9, 129.7, 129.3, 129.2, 129.2, 128.7, 126.9, 124.3, 123.2, 122.9, 120.7, 120.6, 60.8, 48.4, 32.2 (×2), 25.3, 24.7, 24.6; MS (+ESI) m/z 485 (M + 2 + Na^+, 41), 483 (M + Na^+, 100). Anal. Calcd for $C_{27}H_{25}ClN_2O_3$: C, 70.35; H, 5.47; N, 6.08. Found: C, 70.37; H, 5.43; N, 6.07.

*N-Cyclohexyl 10-Acetyldibenz[b,f][1,4]oxazepine-11(10H)-carboxamide (**15e**).* The reaction of **13e** (89.1 mg) was carried out by following procedure B to give **15e** (72.8 mg, 100%) as a white solid: mp 180−182 °C (EtOAc−hexane); R_f = 0.15 (33% EtOAc in hexane); IR (KBr) 3300, 2928, 1679, 1651, 1534, 1380, 1304, 1267 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.14 (m, 7 H), 7.09 (t, J = 7.6 Hz, 1 H), 6.60 (s, 1 H), 5.47 (d, J = 7.6 Hz, 1 H, N*H*), 3.60−3.50 (m, 1 H), 2.03 (s, 3 H), 1.72−1.63 (m, 1 H), 1.57−1.36 (m, 4 H), 1.30−1.10 (m, 2 H), 1.10−0.86 (m, 2 H), 0.73−0.65 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 167.0, 153.6, 153.1, 131.3, 131.3, 130.5, 129.7, 129.6, 124.8, 123.4, 122.6, 121.5, 121.3, 60.8, 48.1, 32.4, 32.4, 25.2, 24.4, 24.4, 22.0; MS (+ESI) m/z 387 (M + Na^+, 100), 365 (M + H^+, 5). Anal. Calcd for $C_{22}H_{24}N_2O_3$: C, 72.50; H, 6.64; N, 7.69. Found: C, 72.50; H, 6.63; N, 7.70.

*N-Cyclohexyl 10-Acetyl-2,3-dimethoxydibenz[b,f][1,4]oxazepine-11(10H)-carboxamide (**15f**).* The reaction of **13f** (101.1 mg) was carried out by following procedure B to give **15f** (79.8 mg, 94%) as a colorless solid: mp 188−190 °C (EtOAc−hexane); R_f = 0.24 (50% EtOAc in hexane); IR (KBr) 3354, 2925, 1661, 1520, 1497, 1381, 1311, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.18 (m, 3 H), 7.12 (t, J = 7.6 Hz, 1 H), 6.71 (s, 1 H), 6.53 (s, 1 H), 6.47 (s, 1 H), 5.48 (d, J = 8.0 Hz, 1 H, N*H*), 3.87 (s, 3 H), 3.78 (s, 3 H), 3.55−3.45 (m, 1 H), 1.96 (s, 3 H), 1.65−1.58 (m, 1 H), 1.53−0.83 (m, 8 H), 0.67−0.55 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 167.2, 153.4, 149.4, 147.4, 144.9, 131.4, 130.5, 129.6, 124.7, 121.2, 113.0, 112.3, 104.7, 60.2, 56.1, 55.9, 48.0, 32.3 (×2), 25.1, 24.4, 24.3, 21.9; MS (+ESI) m/z 447 (M + Na^+, 100), 425 (M + H^+, 96). Anal. Calcd for $C_{24}H_{28}N_2O_5$: C, 67.91; H, 6.65; N, 6.60. Found: C, 67.90; H, 6.64; N, 6.60.

*N-Cyclohexyl 8-Chloro-10-(E)-cinnamoyldibenz[b,f][1,4]-oxazepine-11(10H)-carboxamide (**15g**).* The reaction of **13g** (113.6 mg) was carried out by following procedure B to give **15g** (96.4 mg, 99%) as a colorless solid: mp 157−159 °C (EtOAc−hexane); R_f = 0.41 (33% EtOAc in hexane); IR (KBr) 3282, 2932, 1672, 1650, 1485, 1224 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 14.8 Hz, 1 H), 7.41−7.18 (m, 11 H), 7.10 (t, J = 7.2 Hz, 1 H), 6.71 (s, 1 H), 6.48 (d, J = 15.6 Hz, 1 H), 5.81 (d, J = 8.4 Hz, 1 H, N*H*), 3.65−3.60 (m, 1 H), 1.80−1.47 (m, 5 H), 1.34−0.82 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 165.9, 153.3, 151.6, 144.7, 134.5, 131.3, 131.3, 130.3, 130.2, 129.7, 129.7, 129.2, 128.8 (×2), 128.1 (×2), 123.5, 122.8, 122.5, 121.1, 116.8, 60.9, 48.3, 32.7, 32.6, 25.3, 24.6, 24.5; MS (+ESI) m/z 511 (M + 2 + Na^+, 37), 509 (M + Na^+, 100). Anal. Calcd for $C_{29}H_{27}ClN_2O_3$: C, 71.52; H, 5.59; N, 5.75. Found: C, 71.44; H, 5.82; N, 5.78.

*N-Cyclohexyl 10-(E)-Cinnamoyl-6,8-dimethyldibenz[b,f][1,4]-oxazepine-11(10H)-carboxamide (**15h**).* The reaction of **13h** (112.3 mg) was carried out by following procedure B to give **15h** (78.8 mg, 82%) as a colorless solid: mp 208−210 °C (EtOAc−hexane); R_f = 0.46 (25% EtOAc in hexane); IR (KBr) 3354, 3288, 2930, 1684, 1652, 1615, 1484, 1347, 1232 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 15.6 Hz, 1 H), 7.40−7.23 (m, 7 H), 7.17 (d, J = 7.2 Hz, 1 H), 7.12−7.05 (m, 1 H), 7.02 (s, 1 H), 6.82 (s, 1 H), 6.75 (s, 1 H), 6.51 (d, J = 16.0 Hz, 1 H), 5.91 (d, J = 8.0 Hz, 1 H, N*H*), 3.68−3.62 (m, 1 H), 2.41 (s, 3 H), 2.25 (s, 3 H), 1.76−1.47 (m, 5 H), 1.33−0.85 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.3, 153.6, 149.7, 143.4, 134.7, 133.7, 131.7, 131.2, 130.7, 130.4, 129.7, 128.9, 128.5 (×2), 128.0, 127.9 (×2), 123.1, 123.0, 121.0, 117.6, 60.3, 48.0, 32.6, 32.5, 25.2, 24.4 (×2), 20.5, 16.1; MS (−ESI) m/z 479 (M − H^+, 100). Anal. Calcd for $C_{31}H_{32}N_2O_3$: C, 77.47; H, 6.71; N, 5.83. Found: C, 77.40; H, 6.70; N, 6.09.

*N-Cyclohexyl 12-Acetylbenzo[f]naphth[2,3-b][1,4]oxazepine-13-(12H)-carboxamide (**15i**).* The reaction of **13i** (99.1 mg) was carried out by following procedure B to give **15i** (77.9 mg, 94%) as a colorless solid: mp 161−163 °C (EtOAc−hexane); R_f = 0.18 (33% EtOAc in hexane); IR (KBr) 3298, 2931, 1676, 1653, 1445, 1385, 1291 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, J = 6.8 Hz, 2 H), 7.76 (s, 1 H), 7.72 (s, 1 H), 7.49, (t, J = 7.2 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 1 H), 7.30 (d, J = 4.0 Hz, 2 H), 7.17 (d, J = 7.6 Hz, 1 H), 7.12−7.06 (m, 1 H), 6.70 (s, 1 H), 5.62 (d, J = 7.6 Hz, 1 H, N*H*), 3.55−3.48 (m, 1 H), 2.06 (s, 3 H), 1.67−1.57 (m, 1 H), 1.50−1.34 (m, 2 H), 1.29−1.05 (m, 3 H), 1.04−0.88 (m, 3 H), 0.54−0.52 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 167.2, 154.3, 151.7, 133.6, 131.2, 131.2, 130.6, 129.6,

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129.3, 127.7, 127.3, 127.1, 125.9, 123.6, 122.8, 121.5, 118.3, 60.8, 48.0, 32.4, 32.2, 25.1, 24.3, 24.1, 22.1; MS (−ESI) m/z 413 (M − H$^+$, 100); HRMS (−CI-TOF) m/z [M]$^-$ calcd for $C_{26}H_{26}N_2O_3$ 414.1943, found 414.1939.

*N-(Ethoxycarbonyl)methyl 10(E)-Cinnamoyldibenz[b,f][1,4]-oxazepine-11(10H)-carboxamide (**15j**).* The reaction of **13j** (107.5 mg) was carried out by following procedure B to give **15j** (68.5 mg, 75%) as a colorless solid: mp 170−172 °C (EtOAc−hexane); R_f = 0.20 (33% EtOAc in hexane); IR (KBr) 3248, 3070, 1740, 1661, 1626, 1490, 1378, 1338, 1214 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 15.6 Hz, 1 H), 7.37−7.22 (m, 10 H), 7.20−7.08 (m, 3 H), 6.88 (s, 1 H), 6.60 (br t, J = 4.8 Hz, 1 H), 6.47 (d, J = 16.0 Hz, 1 H), 4.14 (q, J = 7.2 Hz, 2 H), 4.04 (dd, J = 18.4, 6.0 Hz, 1 H), 3.77 (dd, J = 18.0, 4.4 Hz, 1 H), 1.23 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 168.6, 166.5, 153.8, 153.1, 143.9, 134.7, 131.2, 130.7, 130.5, 129.9, 129.6, 129.5, 128.6 (×2), 128.0 (×2), 124.8, 123.4, 122.1, 121.7, 121.3, 117.4, 61.4, 60.3, 41.3, 14.0; MS (−ESI) m/z 455 (M − H$^+$, 100). Anal. Calcd for $C_{27}H_{24}N_2O_5$: C, 71.04; H, 5.30; N, 6.14. Found: C, 71.10; H, 5.29; N, 5.96.

*N-Benzyl 10(E)-Cinnamoyldibenz[b,f][1,4]oxazepine-11(10H)-carboxamide (**15k**).* The reaction of **13k** (108.3 mg) was carried out by following procedure B to give **15k** (69.1 mg, 75%) as a colorless solid: mp 200−202 °C (EtOAc−hexane); R_f = 0.24 (33% EtOAc in hexane); IR (KBr) 3269, 1659, 1627, 1495, 1342, 1213 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 15.2 Hz, 1 H), 7.41−7.07 (m, 16 H), 6.91−6.85 (m, 3 H), 6.48 (d, J = 15.6 Hz, 1 H), 6.29 (br t, J = 5.6 Hz, 1 H, N*H*), 4.42 (dd, J = 14.8, 6.8 Hz, 1 H), 4.19 (dd, J = 15.2, 5.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 166.1, 153.6, 152.7, 143.8, 137.7, 134.6, 131.3, 130.8, 130.3, 129.9, 129.6, 129.5, 128.6 (×2), 128.4 (×2), 127.9 (×2), 127.3 (×2), 127.2, 124.6, 123.3, 122.2, 121.7, 121.3, 117.3, 60.9, 43.4; MS (−ESI) m/z 459 (M − H$^+$, 100). Anal. Calcd for $C_{30}H_{24}N_2O_3$: C, 78.24; H, 5.25; N, 6.08. Found: C, 78.27; H, 5.23; N, 6.03.

*N-Benzyl 10-Formyldibenz[b,f][1,4]oxazepine-11(10H)-carboxamide (**15l**).* The reaction of **13l** (87.9 mg) was carried out by following procedure B to give **15l** (58.8 mg, 82%) as a colorless solid: mp 137−140 °C (EtOAc−hexane); R_f = 0.18 (33% EtOAc in hexane); IR (KBr) 3325, 1684, 1671, 1502, 1319, 1270 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1 H, C*H*O), 7.33−7.05 (m, 11 H), 6.87−6.82 (m, 2 H), 6.39 (s, 1 H), 6.00 (br t, J = 5.2 Hz, 1 H), 4.35 (dd, J = 15.2, 6.8 Hz, 1 H), 4.18 (dd, J = 14.8, 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 161.9, 154.4, 150.6, 137.5, 130.9, 130.3, 128.9, 128.7, 128.5 (×2), 127.3, 127.1 (×2), 126.4, 124.6, 124.0, 123.4, 121.6, 121.5, 59.2, 43.5; MS (−ESI) m/z 357 (M − H$^+$, 100). Anal. Calcd for $C_{22}H_{18}N_2O_3$: C, 73.73; H, 5.06; N, 7.82. Found: C, 73.74; H, 5.09; N, 7.86.

*N-tert-Butyl 10-Acetyldibenz[b,f][1,4]oxazepine-11(10H)-carboxamide (**15m**).* The reaction of **13m** (83.9 mg) was carried out by following procedure B to give **15m** (67.6 mg, 100%) as a colorless solid: mp 166−168 °C (EtOAc−hexane); R_f = 0.25 (33% EtOAc in hexane); IR (KBr) 3329, 2970, 1692, 1658, 1535, 1495, 1391, 1316, 1263 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.21 (m, 7 H), 7.16 (td, J = 7.6, 1.2 Hz, 1 H), 6.62 (s, 1 H), 5.58 (br s, 1 H, N*H*), 2.11 (s, 3 H), 1.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 166.9, 153.3, 152.9, 131.1, 131.1, 130.4, 129.4, 129.3, 124.4, 123.1, 122.7, 121.4, 121.0, 61.1, 51.2, 28.1 (× 3), 21.9; MS (+ESI) m/z 361 (M + Na$^+$, 24), 339 (M + H$^+$, 100). Anal. Calcd for $C_{20}H_{22}N_2O_3$: C, 70.99; H, 6.55; N, 8.28. Found: C, 70.89; H, 6.60; N, 8.35.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01398.

^{1}H and ^{13}C NMR spectra of **12a−i**, **13a−m**, **14a−i**, and **15a−m**; HRMS data (with ^{1}H and ^{13}C NMR spectra) of resynthesized **15a** and **15i** (PDF)

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Notes

The authors declare no competing financial interest.

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