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Chemoselective Intramolecular Wittig Reactions for the Synthesis of Oxazoles and Benzofurans

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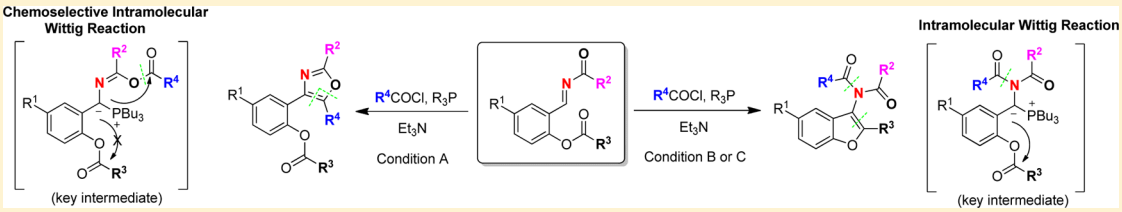
Supporting Information



ABSTRACT: A chemoselective approach was developed for the synthesis of highly functionalized oxazoles and benzofurans using an intramolecular Wittig reaction as the key step. By choosing proper trapping reagent or method of addition of reagents, chemoselectivity can be controlled toward either oxazole or benzofuran derivatives.

INTRODUCTION

Oxazole units can be found in a large number of natural products and bioactive molecules.[1,2] As a result, a lot of attention has been paid to the synthesis of highly functionalized oxazoles, and several efficient methods are known. One of the methods available for the synthesis of this five-membered heteroaromatic ring is direct oxidation of oxazolines.[3] Alternative routes to oxazole synthesis rely on the transition metal- or organocatalyst-mediated[4] cyclization of acyclic precursors, functionalization of oxazoles,[5] and others.[6]

Recently, we have demonstrated an efficient and metal-free method for the synthesis of trisubstituted oxazoles via intramolecular Wittig reactions starting from acyl imines.[7] Although significant progress has been done, the rich chemistry of fully substituted oxazole compounds (as a pharmacologically important moiety[1,2]) are of huge interest in diversity-oriented synthesis.[8] Employing this strategy, a library of functionalized oxazoles were prepared in a one-pot operation.[7] This reaction mode aroused our interest to explore a chemoselective intramolecular Wittig reaction[9] for the synthesis of oxazoles **3** starting from Michael acceptors **1**, Bu_3P and acyl chlorides **2** (Scheme 1). Chemoselective reactions are highly desirable as an atom- and step-economic process.[10] Inspired by our previous report on chemoselective synthesis of benzofurans starting from **1′** (Scheme 1),[9f] we became curious in using analogous compounds **1** as the electrophilic components to investigate the reaction outcome. It is worth mentioning that benzofuran constitutes an important class of privileged structural unit and can be found in many natural products.[11]

RESULTS AND DISCUSSION

Initially, we employed Michael acceptor **1a** and benzoyl chloride (**2a**) as the model reaction partners in the presence of phosphine and base. Chemoselective formation of oxazole **3a** (56%) was observed as the major product in just 1.5 h. The best result was obtained by treating **1a** (1.2 equiv) and **2a** (1 equiv) in the presence of Bu_3P (1.1 equiv) and Et_3N (1.3 equiv) in anhydrous dichloromethane at room temperature (entry 1, Table 1, see Supporting Information (SI) for details).[12] However, formation of benzofuran **4a** (8%) was also noticed. During this study it was observed that by alteration of reaction condition, benzofuran **4** was the major product instead of oxazole **3** (condition B; Table 2). It is also revealed that proper choice of the trapping reagent (acyl chloride or anhydride) can alter the course of the reaction toward chemoselective formation of oxazole (condition A; entry 15, Table 1 and see Scheme 4) or benzofuran (condition C; entry 16, Table 1 and Table 3).

Under the optimal condition, various Michael acceptors (**1a**−**c**) and acyl chlorides (**2a**−**g**) were examined for the generality of the methodology (entries 1−14; Table 1). Michael acceptors **1b** and **1c** were also employed successfully with **2a** in our optimized condition to provide the oxazole products **3b** (68%) and **3c** (59%) along with minor benzofuran products (entries 2 and 3). Next we have tested various acyl chlorides (**2b**−**g**) with **1a** and **1c** (entries 4−14). In most of the cases, chemoselective formation of oxazoles was observed in preference to benzofurans. However, when **1a** was treated with acyl chlorides **2d**−**f**, rearranged oxazole products **3f′**−**h′** (28−34%) were obtained as the major products along with normal oxazoles **3f**−**h** (21−23%) and benzofurans **4f**−**h** (1−14%; entries 6−8). Eventually, we observed that trifluoroacetic anhydride (TFAA, **2h**) was very reactive toward Michael acceptor **1a**, and the reaction proceeded very efficiently to furnish the product **3o** with complete chemoselectivity in just 30 min with 77% yield (entry 15). Although the reaction presented in Table 1 showed inclination toward chemoselective formation of oxazole (or isomeric oxazole), we found a complete reversal of chemoselectivity by using pivaloyl chloride (**2i**) as the

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Scheme 1. Chemoselective Intramolecular Wittig Reaction of 1 or 1′

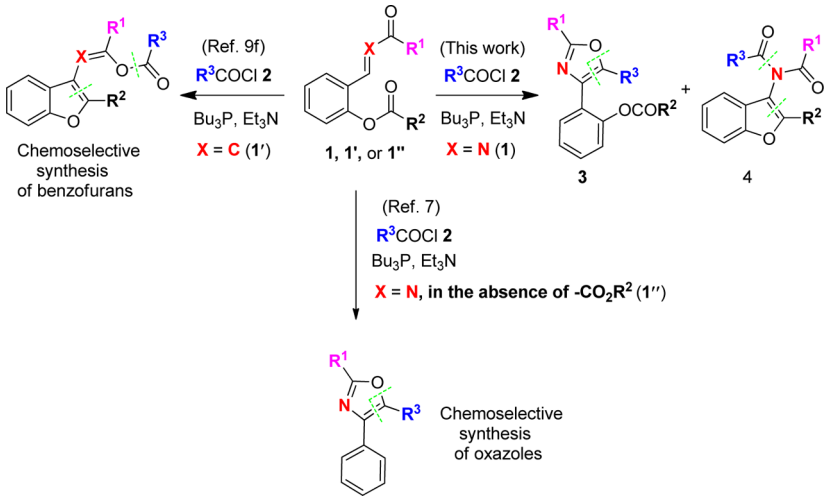
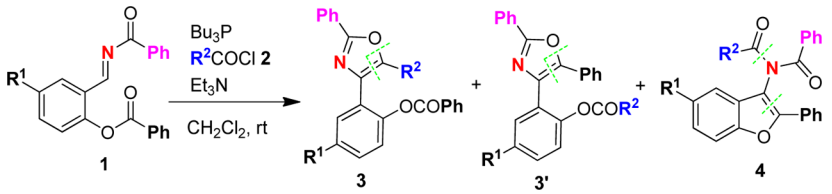
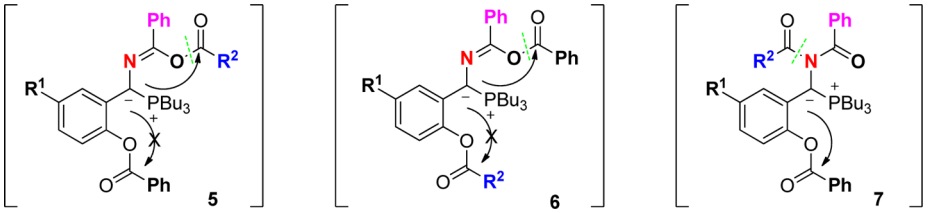


Table 1. Synthesis of Oxazole and Benzofuran Derivatives via Intramolecular Wittig Reaction[a]



entry	R^1	1	R^2 (2)	t (h)	product 3/3′/4	yield (%)[b]
1	Br	**1a**	Ph, **2a**	1.5	**3a**/**4a**[13]	56/8
2	Cl	**1b**	Ph, **2a**	1.0	**3b**/**4b**	68/14
3	OMe	**1c**	Ph, **2a**	0.5	**3c**/**4c**	59/7
4	Br	**1a**	4-$NO_2C_6H_4$, **2b**	1.0	**3d**	45
5	Br	**1a**	4-BrC_6H_4, **2c**	1.0	**3e**[13]/**4e**	43/1
6	Br	**1a**	4-$OMeC_6H_4$, **2d**	1.0	**3f**/**3f′**[13]/**4f**	23/28/14
7	Br	**1a**	2-furyl, **2e**	1.0	**3g**[13]/**3g′**[13]/**4g**[13]	21/31/3
8	Br	**1a**	2-thienyl, **2f**	2.0	**3h**[13]/**3h′**[13]/**4h**	21/34/1
9	OMe	**1c**	4-$NO_2C_6H_4$, **2b**	1.0	**3i**	59
10	OMe	**1c**	4-BrC_6H_4, **2c**	1.0	**3j**	65
11	OMe	**1c**	4-$OMeC_6H_4$, **2d**	1.0	**3k**/**4k**	46/22
12	OMe	**1c**	2-furyl, **2e**	1.0	**3l**[13]/**3l′**	57/4
13	OMe	**1c**	2-thienyl, **2f**	1.0	**3m**[13]/**4m**	60/5
14	OMe	**1c**	2-BrC_6H_4, **2g**	2.0	**3n**/**4n**	49/6
15[c]	Br	**1a**	TFAA, **2h**	0.5	**3o**[13]	77
16[d]	Br	**1a**	*t*-Bu, **2i**	0.5	**4o**[13]	77

[a]Compound **1** (1.2 equiv) was treated with **2** (0.3 mmol) in the presence of Bu_3P (1.1 equiv) and Et_3N (1.1 equiv) in anhydrous CH_2Cl_2 (1.5 mL) at rt under inert atmosphere. [b]Isolated yields. [c]Compound **1a** (0.3 mmol) was treated with Ph_3P (1.1 equiv) and TFAA (1.1 equiv) followed by Et_3N (1.3 equiv) in toluene at rt under inert atmosphere. [d]In 0.6 mL of anhydrous CH_2Cl_2.



trapping reagent. Thus, treatment of **1a** with **2i** at room temperature led to benzofuran product (**4o**) with complete chemoselectivity within 30 min in 77% yield (entry 16). These results suggest that chemoselective formation of phosphorus ylides is possible, which would be a useful route for the synthesis of either oxazoles or benzofurans. The key ylide intermediates (**5**–**7**) that furnished intramolecular Wittig reaction leading to products **3**, **3′** and **4** are shown in Table 1.

We were also pleased to find that the chemoselective outcome of this transformation is dependent on how the reagents are added. For example, when **1a** was treated with Bu_3P in dichloromethane for 30 min followed by addition of **2a** and

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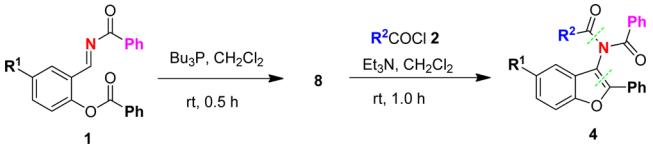
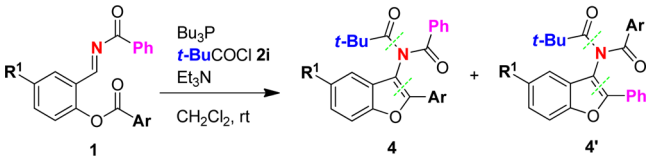
Table 2. Chemoselective Formation of Benzofuran (4) via Intramolecular Wittig Reaction[a]



entry	R^1	1	R^2 (2)	t (h)	product 3/4	yield (%)[b]
1	Br	**1a**	Ph, **2a**	1.5	**4a**	49
2	Cl	**1c**	Ph, **2a**	1.5	**3b**/**4b**	4/60
3	Br	**1a**	4-BrC_6H_4, **2c**	1.5	**4e**	57
4	Br	**1a**	4-$OMeC_6H_4$, **2d**	1.5	**4f**	57
5	Br	**1a**	2-furyl, **2e**	1.5	**4g**	57

[a]**1** (1.2 equiv) was treated with Bu_3P (1.1 equiv) in anhydrous CH_2Cl_2 (1.5 mL) for 0.5 h followed by addition of **2** (0.3 mmol) and Et_3N (1.1 equiv) under inert atmosphere (Condition B). [b]Isolated yields.

Table 3. Chemoselective Synthesis of Benzofuran (4o–s) Starting from *N*-Acyl Imines[a]



entry	R^1	Ar	1	t (h)	product 4/4′	yield[b] (%)
1	Br	Ph	**1a**	0.5	**4o**	77
2	Cl	Ph	**1b**	0.5	**4p**[12]	69
3	OMe	Ph	**1c**	2.0	**4q**	79
4	H	4-BrC_6H_4	**1d**	0.5	**4r**	93
6	OMe	4-BrC_6H_4	**1e**	0.5	**4s**[12]/**4s′**[12]	67/10
7	Br	2-thienyl	**1f**	1.0	**4t′**[12]	73
8[c]	Br	Ph	**1a**	1.5	**4o**/**8a**	40/3

[a]Reactions were performed with **2i** (0.3 mmol), **1** (1.2 equiv), Bu_3P (1.1 equiv) and Et_3N (1.1 equiv) in anhydrous CH_2Cl_2 (0.6 mL) under inert atmosphere (Condition C). [b]Isolated yields. [c]Condition B.

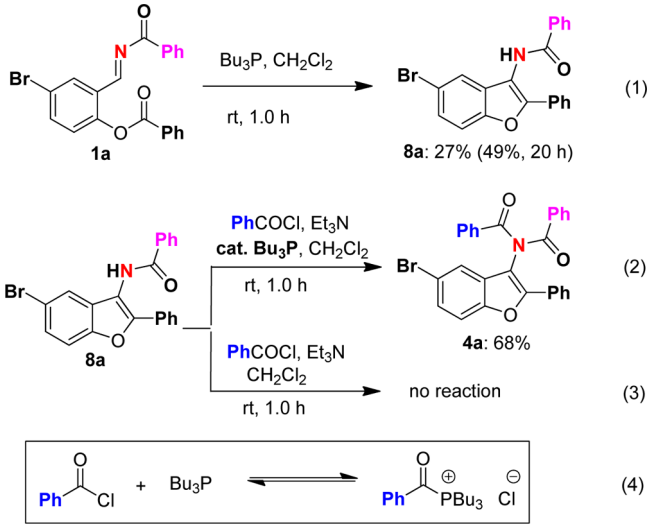
Et_3N, exclusive formation of benzofuran **4a** (49%) was observed (entry 1, Table 2). As shown in Table 2, this protocol was also applicable to Michael acceptor **1c** (entry 2) and acyl chlorides **2c–e** (entries 3–5) and chemoselective formation of benzofuran products **4** was obtained in good yields (57–60%) within 1.5 h.

To understand the actual nature of the intermediate species **8**, some controlled experiments were performed (Scheme 2). When the compound **1a** was treated with Bu_3P in dichloromethane at room temperature, **8a** was obtained in 27% yield after 1 h (eq 1). The compound **4a** (68%) was obtained after treatment of **8a** with **2a** in the presence of catalytic amount of Bu_3P (10 mol %), but no conversion of **8a** was observed without the activation of Bu_3P (eq 2–3). This result indicates that Bu_3P activates **2a**, which performs *N*-acylation of **8a** leading to the formation of **4a** (eq 4).

On the basis of the results obtained from Scheme 2, formation of the compound **4** can be explained by the mechanism as presented in Scheme 3. We believe that the zwitterionic species **9a** (which is generated from Michael addition of Bu_3P to **1a**) provided the ylide **9a′** when the reaction was stirred for long time via proton exchange, which was followed by an intramolecular Wittig reaction to furnish the compound **8a**.

The synthetic utility of chemoselective synthesis of functionalized oxazoles containing a trifluoromethyl substituent starting

Scheme 2. Controlled Experiments to Identify the Intermediates 8



from *N*-acyl imines are further demonstrated by in-corporating various Michael acceptors containing aromatic or aliphatic substituents (entry 15 in Table 1 and Scheme 4). Thus, upon treatment of compound **1** was treated with Ph_3P, trifluoroacetic anhydride, and Et_3N in toluene at room temperature, functionalized oxazoles **3o–y** were obtained in very good yields within 1 h.

The substrate scope for chemoselective synthesis of benzofuran derivatives (**4**) using pivaloyl chloride (**2i**) via intramolecular Wittig reaction starting from *N*-acyl imines (**1**) was further exemplified in Table 3. Under the optimized reaction condition (for optimization data, see SI),[12] various Michael acceptors (**1a–e**) containing an electron-donating or electron-withdrawing group were employed along with **2i** for the synthesis of benzofuran products (**4o–s**). As presented in Table 3, corresponding products were obtained in good yields (entries 1–6). A high degree of chemoselectivity was observed in all the cases; however, formation of rearranged benzofuran product as minor isomer (**4s′**) was also detected (entry 6). Remarkably, in case of using 2-thienyl substituted Michael acceptor **1f**, rearranged benzofuran **4t′** was the only product (entry 7). Furthermore, condition B was also found to proceed with chemoselective formation of benzofuran (**4o**; entry 8).

The synthetic utility of the present protocol is further illustrated by converting some selected products into potentially useful new compounds. For example, benzamide-substituted benzofuran (such as **8a**), which was obtained by treating **1a** with Bu_3P (Scheme 2, eq 1), was prepared by treatment of **4** in the presence of HCl solution in dioxane. Compounds **8a–c** was obtained in quantitative yield and was further converted to the corresponding *N*-protected derivatives **10a–d**. For the protection of an amide group, relatively few methods are available[14] but in the present case, the products were obtained in good chemical yields (Scheme 5; eq 1). Again benzoate-protected oxazoles (**3a**, **3o–q**) were successfully deprotected by treatment with sodium methoxide in THF/MeOH solvent mixture. The corresponding oxazoles bearing the phenol moiety (**11a–d**) were obtained in high chemical yields (76–90%). These oxazoles (**11a–d**) were then converted to the corresponding phenoxy ether-substituted oxazoles (**12a–c**) after treatment with benzyne generated from *o*-(trimethylsilyl)phenyl triflate (Scheme 5; eq 2).[15]

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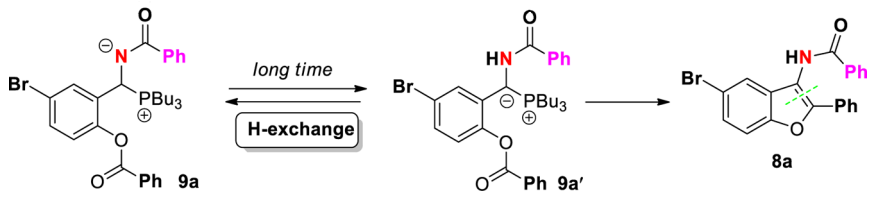
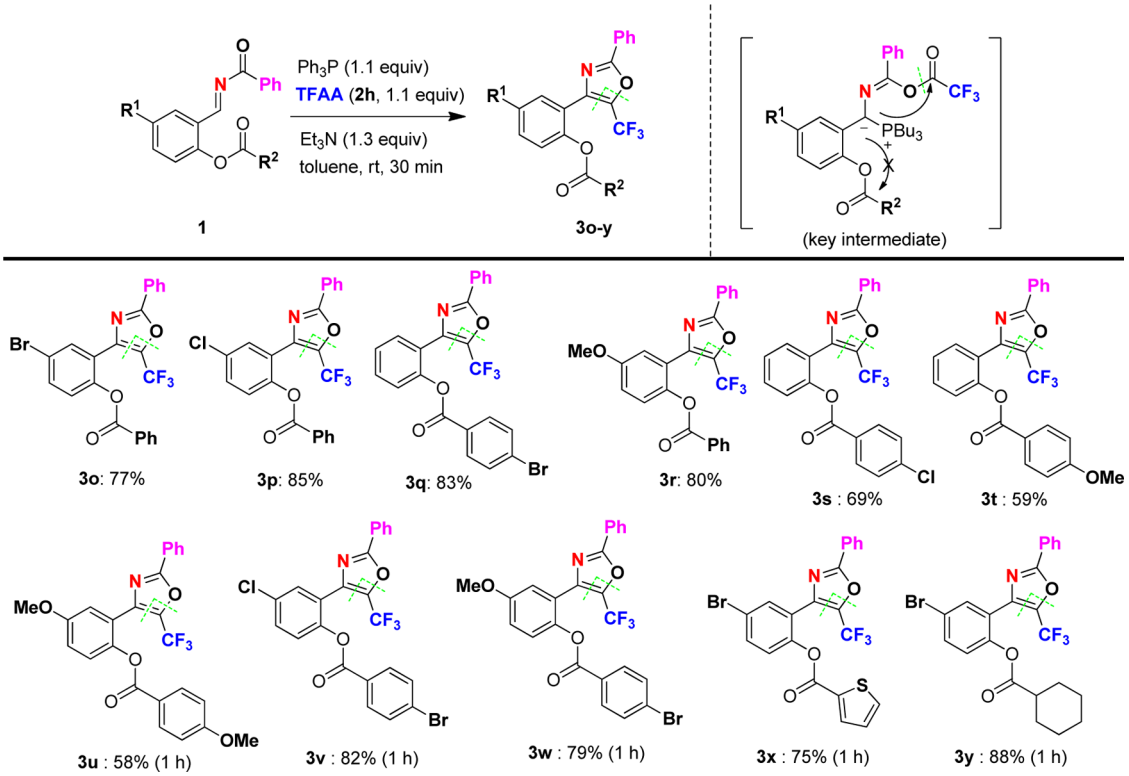
Scheme 3. Plausible Reaction Mechanism for the Intermediate 8a

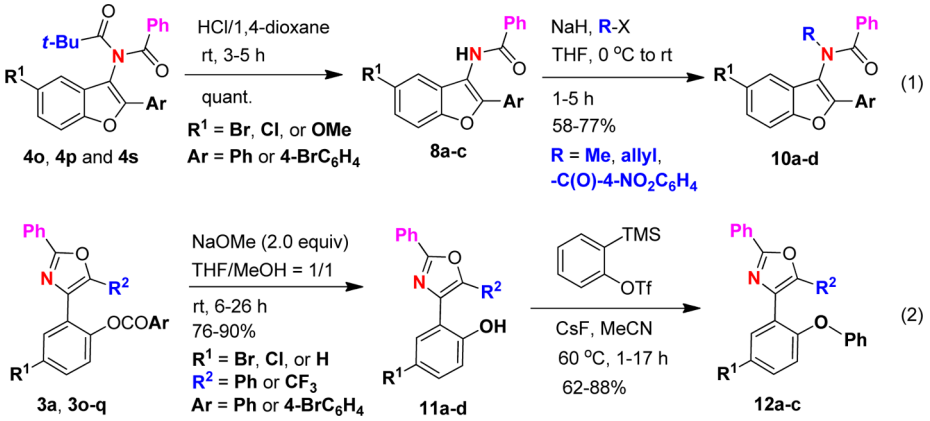


Scheme 4. Chemoselective Synthesis of Trifluoromethyl-Substituted Oxazoles 3o−y from *N*-Acyl Imines 1[a,b]



[a]Reactions were performed with **1** (0.3 mmol) in anhydrous toluene (1.5 mL) under inert atmosphere (Condition A). [b]Isolated yields.

Scheme 5. Transformation of the Products



On the basis of the experimental results (Tables 1−3 and Schemes 2−4), a plausible reaction mechanism is presented in Scheme 6 to explain the formation of products **3** (**3′**) and **4** (**4′**). The reaction initiates via nucleophilic addition of Bu_3P to **1** giving rise to the corresponding zwitterionic species **9**. Chemoselective *O*-acylation of **9** by acyl chloride leads to the formation of **13**. The ylide **5**, which is generated via deprotonation of **13** with Et_3N, undergoes an intramolecular Wittig reaction to furnish oxazole **3** (path a). Formation of benzofuran **4** can be explained by path b which starts via *N*-acylation of zwitterionic species **9** to give **18**, deprotonated **18** of by Et_3N, and then intramolecular Wittig reaction of ylide **7**.

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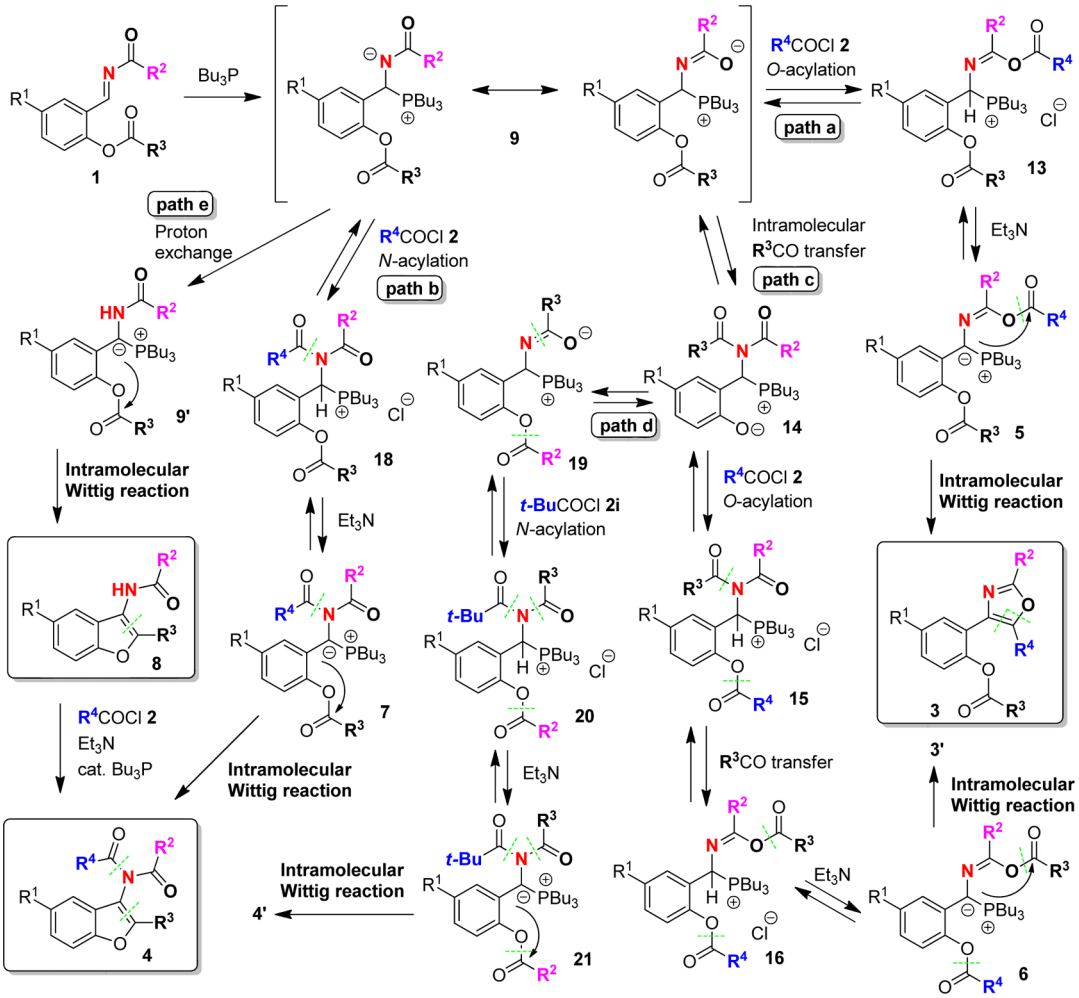
Scheme 6. Proposed Mechanism for Synthesis of 3, 3′ and 4



Intramolecular acyl group (R^3CO) transfer from **9** provides species **14**, which furnished **15** after *O*-acylation by acyl chloride **2**. The second R^3CO group (**15**) transferring and then deprotonation of **16** with Et_3N gives the ylide **6**, which performs intramolecular Wittig reaction to afford oxazole **3′** (path c). Again intramolecular acyl group (R^2CO) transfer from species **14** (path d) generates species **19**, which was then *N*-acylated with pivaloyl chloride (**2i**). Deprotonation by Et_3N and intramolecular Wittig reaction (of **21**) provides benzofuran **4′**

SUMMARY AND CONCLUSIONS

In summary, we have presented a general method for the synthesis of highly functionalized oxazoles and benzofurans. The reaction conditions are very mild with a broad substrate scope. By choosing proper reaction condition, the course of the reaction can be altered for chemoselective formation of either oxazole or benzofuran. We have also proposed a mechanism to explain the product formation. In general, intramolecular Wittig reaction of the presumable phosphorus ylide is the key step. We have also demonstrated some useful synthetic utility of the products. Further synthetic application of this concept for the preparation of useful heterocycles and studies for the detailed mechanism is underway in our laboratory.

EXPERIMENTAL SECTION

Aldehyde precursors, *α*-amido sulfone precursors and *N*-acyl imines **1** were prepared according to the reported literature.[16] All the reactions were carried out in anhydrous solvent under a nitrogen atmosphere in dried glassware. The starting materials purchased from commercial sources were used without further purification. Chemical shifts are reported in *δ* ppm referenced to an internal TMS standard for ^{1}H NMR and chloroform-*d* (*δ* 77.0 ppm) for ^{13}C NMR. The X-ray diffraction measurements were carried out at 298 K on a CCD area detector system equipped with a graphite monochromator and a Mo K*α* fine-focus sealed tube (*k* = 0.71073 Å). High resolution mass spectra (HRMS) were recorded using MALDI (TOF analyzer), ESI (TOF analyzer), fast atom bombardment (FAB^+) (Magnetic Sector Analyzer), and EI (Magnetic Sector Analyzer). Analytical thin layer chromatography (TLC) was performed using precoated silica gel plate (0.2 mm thickness). Compounds were purified by flash-chromatography

Typical Procedure for the Preparation of Oxazoles 3, Oxazoles 3′ and Benzofurans 4 (Table 1). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1** (1.2 equiv) in anhydrous dichloromethane (1.5 mL). To this stirred reaction mixture, Bu_3P (82 *μ*L, 1.1 equiv), acyl chloride **2** (0.3 mmol) and Et_3N (46 *μ*L, 1.1 equiv) were added in sequence. The reaction mixture was further stirred for the indicated time at room temperature and was monitored by ^{1}H NMR data analysis. The solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished the desired adducts **3**, **3′** and **4**.

*4-Bromo-2-(2,5-diphenyloxazol-4-yl)phenyl benzoate (**3a**).* White solid (83.2 mg, 56% yield): R_f 0.26 (ethyl acetate/hexanes 1/20); mp

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125.9−126.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.01 (dd, 2H, J = 7.6 Hz, 2.1 Hz), 7.91 (d, 1H, J = 2.5 Hz), 7.64 (d, 2H, J = 7.8 Hz), 7.57 (dd, 1H, J = 8.7 Hz, 2.5 Hz), 7.51−7.48 (m, 2H), 7.45−7.38 (m, 4H), 7.29−7.27 (m, 3H), 7.25−7.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.1, 160.2, 147.5, 147.1, 133.9, 133.2, 132.4, 131.0, 130.4, 129.9, 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 126.9, 126.3, 125.9, 125.0, 119.1; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3084 (w), 1686 (s), 1458 (m), 1377 (m), 1259 (s), 698 (s); MS (70 eV, EI) m/z (%) 497 $[M+2]^+$ (13), 495 $[M]^+$ (17), 180 (2), 152 (6), 105 (100), 77 (80); HRMS (ESI) for $C_{28}H_{19}BrNO_3$, $[M + H]^+$ (496.0548), found 496.0543.

*N-Benzoyl-N-(5-bromo-2-phenylbenzofuran-3-yl)benzamide (**4a**).* White solid (11.9 mg, 8% yield; in Table 1, entry 1) (72.8 mg, 49% yield; in Table 2, entry 1): R_f 0.17 (ethyl acetate/hexanes 1/20); mp 203.9−205.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.60 (d, 3H, J = 3.2 Hz), 7.58 (d, 2H, J = 3.2 Hz), 7.55−7.53 (m, 2H), 7.46−7.42 (m, 3H), 7.40−7.36 (m, 4H), 7.28 (t, 5H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.6, 153.0, 152.0, 133.8, 132.6, 129.9, 128.9, 128.5, 128.43, 128.41, 127.9, 126.9, 120.9, 117.0, 116.8, 113.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3084 (w), 2924 (w), 1699 (s), 1600 (w), 1455 (m), 1257 (s), 697 (m); MS (70 eV, EI) m/z (%) 497 $[M+2]^+$ (17), 495 $[M]^+$ (17), 105 (100), 77 (83); HRMS (EI) for $C_{28}H_{18}BrNO_3$, $[M]^+$ (495.0470), found 495.0459.

*4-Chloro-2-(2,5-diphenyloxazol-4-yl)phenyl benzoate (**3b**).* White solid (92.0 mg, 68% yield; in Table 1, entry 2) (5.4 mg, 4% yield; in Table 2, entry 2): R_f 0.21 (ethyl acetate/hexanes 1/20); mp 131.8−132.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.03−8.01 (m, 2H), 7.76 (d, 1H, J = 2.6 Hz), 7.66 (dd, 2H, J = 8.3 Hz, 1.2 Hz), 7.53−7.50 (m, 2H), 7.48−7.41 (m, 5H), 7.32−7.30 (m, 4H), 7.25 (t, 2H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.3, 160.3, 147.2, 147.0, 131.5, 131.2, 131.0, 130.4, 130.0, 129.5, 128.8, 128.72, 128.68, 128.6, 128.3, 128.1, 127.6, 127.0, 126.4, 126.0, 124.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3056 (s), 1738 (s), 1601 (m), 1476 (s), 1246 (s), 1052 (s), 698 (s); HRMS (MALDI) for $C_{28}H_{19}ClNO_3$, $[M + H]^+$ (452.1048), found 452.1055.

*N-Benzoyl-N-(5-chloro-2-phenylbenzofuran-3-yl)benzamide (**4b**).* White solid (18.9 mg, 14% yield; in Table 1, entry 2) (81.2 mg, 60% yield; in Table 2, entry 2): R_f 0.13 (ethyl acetate/hexanes 1/20); mp 195.8−196.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.59 (dd, 4H, J = 8.4 Hz, 1.2 Hz), 7.56−7.53 (m, 2H), 7.46−7.37 (m, 7H), 7.30−7.24 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.5, 153.1, 151.5, 133.7, 132.6, 129.8, 129.5, 128.8, 128.5, 128.4, 127.9, 127.3, 126.8, 125.7, 117.8, 116.9, 113.1; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3081 (w), 1694 (s), 1597 (w), 1456 (m), 1258 (s), 694 (m); HRMS (MALDI) for $C_{28}H_{19}ClNO_3$, $[M + H]^+$ (452.1048), found 452.1051.

*2-(2,5-Diphenyloxazol-4-yl)-4-methoxyphenyl benzoate (**3c**).* Yellow solid (79.1 mg, 59% yield): R_f 0.31 (ethyl acetate/hexanes 1/6); mp 108.0−108.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.03−8.00 (m, 2H), 7.69 (dd, 2H, J = 8.4 Hz, 1.2 Hz), 7.56−7.54 (m, 2H), 7.45−7.39 (m, 4H), 7.32−7.21 (m, 7H), 7.02 (dd, 1H, J = 8.9 Hz, 3.0 Hz), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.8, 160.0, 157.3, 146.7, 142.0, 133.0, 132.3, 130.3, 129.9, 129.2, 128.6, 128.51, 128.47, 128.4, 128.0, 127.1, 126.5, 126.3, 126.0, 124.2, 55.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 2924 (m), 1726 (s), 1581 (m), 1490 (s), 1261 (s), 1192 (s), 701 (s), 690 (s); MS (70 eV, EI) m/z (%) 447 $[M]^+$ (51), 342 (7), 314 (3), 168 (5), 139 (3), 105 (100), 77 (48); HRMS (EI) for $C_{29}H_{21}NO_4$, $[M]^+$ (447.1471), found 447.1476.

*N-Benzoyl-N-(5-methoxy-2-phenylbenzofuran-3-yl)benzamide (**4c**).* White solid (9.4 mg, 7% yield): R_f 0.28 (ethyl acetate/hexanes 1/6); mp 132.9−133.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.62 (dd, 4H, J = 8.3 Hz, 1.0 Hz), 7.57−7.55 (m, 2H), 7.44−7.36 (m, 6H), 7.26 (t, 4H, J = 7.8 Hz), 6.94−6.90 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.7, 156.7, 152.3, 148.1, 134.0, 132.4, 129.4, 128.8, 128.5, 128.3, 126.6, 117.5, 113.7, 112.6, 100.9, 56.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3008 (w), 2931 (m), 1707 (s), 1688 (s), 1600 (m), 1482 (m), 1257 (s), 1131 (s), 846 (m), 693 (s); MS (70 eV, EI) m/z (%) 447 $[M]^+$ (13), 105 (100), 77 (33); HRMS (EI) for $C_{29}H_{21}NO_4$, $[M]^+$ (447.1471), found 447.1467.

*4-Bromo-2-(5-(4-nitrophenyl)-2-phenyloxazol-4-yl)phenyl benzoate (**3d**).* Yellow solid (72.9 mg, 45% yield): R_f 0.28 (ethyl acetate/hexanes 1/20); mp 139.5−140.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.11 (d, 2H, J = 8.9 Hz), 8.06 (dd, 2H, J = 7.8 Hz, 1.7 Hz), 7.91 (d, 1H, J = 2.4 Hz), 7.67−7.61 (m, 5H), 7.51−7.43 (m, 4H), 7.30 (d, 1H, J = 8.7 Hz), 7.25 (t, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 163.9, 161.6, 147.5, 147.2, 144.9, 134.4, 134.1, 133.9, 133.6, 133.3, 131.2, 129.8, 128.8, 128.5, 128.2, 127.1, 126.7, 126.4, 126.2, 125.2, 123.9, 119.4; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3063 (w), 1748 (s), 1600 (m), 1550 (w), 1517 (s), 1340 (s), 1199 (s), 702 (s); MS (70 eV, EI) m/z (%) 542 $[M+2]^+$ (28), 540 $[M]^+$ (33), 150 (5), 105 (100), 77 (34); HRMS (ESI) for $C_{28}H_{18}BrN_2O_5$, $[M + H]^+$ (541.0399), found 541.0396.

*4-Bromo-2-(5-(4-bromophenyl)-2-phenyloxazol-4-yl)phenyl benzoate (**3e**).* White solid (73.9 mg, 43% yield): R_f 0.24 (dichloromethane/hexanes 1/3); mp 164.6−164.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.03−8.01 (m, 2H), 7.92 (d, 1H, J = 2.4 Hz), 7.67 (d, 2H, J = 8.0 Hz), 7.61 (dd, 1H, J = 8.7 Hz, 2.5 Hz), 7.50−7.47 (m, 1H), 7.44−7.39 (m, 5H), 7.33−7.21 (m, 3H), 7.27−7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.1, 160.6, 147.4, 146.2, 133.9, 133.4, 132.7, 131.8, 131.6, 130.6, 130.0, 128.7, 128.6, 128.2, 127.6, 127.4, 127.2, 126.8, 126.4, 125.1, 122.8, 119.3; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3063 (w), 1741 (s), 1613 (w), 1491 (m), 1258 (s), 1202 (s), 704 (s); MS (70 eV, EI) m/z (%) 575 $[M+2]^+$ (89), 573 $[M]^+$ (100), 105 (14), 77 (2); HRMS (ESI) for $C_{28}H_{18}Br_2NO_3$, $[M + H]^+$ (573.9653), found 573.9667.

*N-Benzoyl-4-bromo-N-(5-bromo-2-phenylbenzofuran-3-yl)-benzamide (**4e**).* White solid (1.9 mg, 1% yield; in Table 1, entry 5) (98.0 mg, 57% yield; in Table 2, entry 3): R_f 0.29 (dichloromethane/hexanes 1/3); mp 173.3−174.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.58 (d, 3H, J = 8.3 Hz), 7.54−7.51 (m, 2H), 7.47−7.36 (m, 10H), 7.29 (t, 2H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.4, 171.7, 153.0, 151.9, 133.5, 132.8, 132.6, 131.8, 130.0, 129.9, 128.9, 128.53, 128.51, 128.50, 127.71, 127.66, 127.5, 126.9, 120.7, 117.1, 116.5, 113.6; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 2924 (m), 1695 (s), 1589 (m), 1257 (s), 1131 (m), 693 (m); MS (70 eV, EI) m/z (%) 575 $[M+2]^+$ (43), 573 $[M]^+$ (15), 183 (22), 105 (100), 77 (20); HRMS (EI) for $C_{28}H_{17}Br_2NO_3$, $[M]^+$ (572.9575), found 572.9570.

*4-Bromo-2-(5-(4-methoxyphenyl)-2-phenyloxazol-4-yl)phenyl benzoate (**3f**).* White solid (36.2 mg, 23% yield): R_f 0.18 (ethyl acetate/hexanes 1/20); mp 76.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.01−7.99 (m, 2H), 7.90 (d, 1H, J = 2.3 Hz), 7.71 (d, 2H, J = 8.1 Hz), 7.58 (dd, 1H, J = 8.7 Hz, 2.4 Hz), 7.47 (t, 1H, J = 7.5 Hz), 7.43−7.41 (m, 5H), 7.29−7.24 (m, 3H), 6.82 (d, 2H, J = 8.8 Hz), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.2, 160.1, 159.8, 147.5, 147.4, 134.0, 133.3, 132.2, 130.3, 130.1, 129.8, 128.9, 128.7, 128.1, 127.6, 127.1, 126.3, 125.0, 121.0, 119.1, 114.1, 55.3; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (w), 2923 (w), 1742 (m), 1613 (m), 1511 (m), 1255 (s), 1203 (s), 704 (s); MS (70 eV, EI) m/z (%) 528 $[M+2]^+$ (74), 526 $[M]^+$ (100), 135 (5), 105 (17), 77 (3); HRMS (ESI) for $C_{29}H_{21}BrNO_4$, $[M + H]^+$ (526.0654), found 526.0645.

*4-Bromo-2-(2,5-diphenyloxazol-4-yl)phenyl 4-methoxybenzoate (**3f′**).* White solid (44.1 mg, 28% yield): R_f 0.10 (ethyl acetate/hexanes 1/20); mp 168.8−169.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.05−8.03 (m, 2H), 7.90 (d, 1H, J = 2.4 Hz), 7.60−7.57 (m, 3H), 7.52−7.50 (m, 2H), 7.44−7.43 (m, 3H), 7.33−7.31 (m, 3H), 7.24 (d, 1H, J = 8.2 Hz), 6.71 (d, 2H, J = 8.8 Hz), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 163.8, 163.7, 160.3, 147.7, 147.2, 133.9, 132.5, 132.2, 131.1, 130.5, 128.7, 128.6, 128.3, 127.9, 127.0, 126.4, 126.0, 125.1, 121.1, 119.0, 113.4, 55.4; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 1733 (s), 1604 (s), 1512 (m), 1257 (s), 1166 (s), 693 (m); MS (70 eV, EI) m/z (%) 527 $[M+2]^+$ (6), 525 $[M]^+$ (6), 135 (100), 105 (12), 77 (8); HRMS (EI) for $C_{29}H_{20}BrNO_4$, $[M]^+$ (525.0576), found 525.0574.

*N-Benzoyl-N-(5-bromo-2-phenylbenzofuran-3-yl)-4-methoxy-benzamide (**4f**).* White solid (22.1 mg, 14% yield; in Table 2, entry 6) (89.8 mg, 57% yield; in Table 2, entry 4): R_f 0.08 (ethyl acetate/hexanes 1/20); mp 135.0−135.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.61−7.56 (m, 7H), 7.42 (td, 2H, J = 8.7 Hz, 1.9 Hz), 7.39−7.35 (m, 4H), 7.27 (t, 2H, J = 7.7 Hz), 6.76 (d, 2H, J = 8.8 Hz), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.7, 171.8, 163.3, 152.8, 151.9, 134.1, 132.4, 131.1, 129.8, 128.8, 128.5, 128.4, 128.3, 128.1, 128.0, 126.9, 125.8, 120.9, 117.1, 116.9, 113.8, 113.5, 55.4; IR (KBr) $\tilde{\nu}$(cm^{-1}) 1692 (s), 1603 (s), 1512 (m), 1319 (m); MS (70 eV, EI) m/z (%) 527

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[M+2]$^+$ (29), 525 [M]$^+$ (28), 135 (100), 105 (13), 77 (4); HRMS (MALDI) for $C_{29}H_{20}BrNO_4Na$, [M + Na]$^+$ (548.0468), found 548.0469.

*4-Bromo-2-(5-(furan-2-yl)-2-phenyloxazol-4-yl)phenyl benzoate (**3g**).* Brown solid (30.6 mg, 21% yield): R_f 0.29 (ethyl acetate/hexanes 1/20); mp 121.3−122.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.94−7.92 (m, 3H), 7.89 (d, 2H, J = 7.9 Hz), 7.59 (dd, 1H, J = 8.6 Hz, 2.4 Hz), 7.50 (t, 1H, J = 7.4 Hz), 7.43−7.29 (m, 7H), 6.60 (d, 1H, J = 3.3 Hz), 6.42 (dd, 1H, J = 3.3 Hz, 1.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.5, 160.1, 147.7, 143.3, 143.2, 139.7, 133.8, 133.4, 132.4, 131.1, 130.6, 130.1, 129.1, 128.6, 128.2, 126.8, 126.7, 126.4, 124.9, 118.8, 111.6, 109.3; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3137 (w), 1730 (s), 1628 (m), 1507 (w), 1260 (s), 1205 (s), 708 (s); MS (70 eV, EI) m/z (%) 488 [M +2]$^+$ (88), 486 [M]$^+$ (100), 353 (5), 105 (8), 77 (2); HRMS (ESI) for $C_{26}H_{17}BrNO_4$, [M + H]$^+$ (486.0341), found 486.0337.

*4-Bromo-2-(2,5-diphenyloxazol-4-yl)phenyl furan-2-carboxylate (**3g′**).* Yellow solid (45.1 mg, 31% yield): R_f 0.12 (ethyl acetate/hexanes 1/20); mp 175.4−176.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.07−8.04 (m, 2H), 7.91 (d, 1H, J = 2.4 Hz), 7.59 (dd, 1H, J = 8.7 Hz, 2.4 Hz), 7.53−7.50 (m, 2H), 7.46−7.44 (m, 4H), 7.35−7.30 (m, 3H), 7.26 (d, 1H, J = 8.7 Hz), 6.68 (d, 1H, J = 3.5 Hz), 6.35 (dd, 1H, J = 3.5 Hz, 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 160.3, 155.8, 147.3, 147.0, 146.7, 143.3, 134.0, 132.5, 130.9, 130.5, 128.8, 128.7, 128.6, 128.3, 127.8, 126.9, 126.4, 126.0, 124.9, 119.4, 119.3, 111.8; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 1749 (s), 1604 (w), 1550 (m), 1467 (m), 1288 (m), 1200 (s), 1070 (s), 701 (m); MS (70 eV, EI) m/z (%) 487 [M +2]$^+$ (25), 485 [M]$^+$ (25), 105 (38), 95 (100), 77 (9); HRMS (EI) for $C_{26}H_{16}BrNO_4$, [M]$^+$ (485.0263), found 485.0263.

*N-Benzoyl-N-(5-bromo-2-phenylbenzofuran-3-yl)furan-2-carboxamide (**4g**).* Brown solid (4.4 mg, 3% yield; in Table 1, entry 7) (82.9 mg, 57% yield; in Table 2, entry 5): R_f 0.07 (ethyl acetate/hexanes 1/20); mp 176.3−176.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.70−7.67 (m, 2H), 7.58 (d, 1H, J = 1.8 Hz), 7.51 (dd, 2H, J = 7.3 Hz, 1.0 Hz), 7.44−7.36 (m, 7H), 7.23 (td, 2H, J = 7.8 Hz, 1.1 Hz), 7.16 (d, 1H, J = 3.6 Hz), 6.45 (dd, 1H, J = 3.6 Hz, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 171.8, 161.3, 152.9, 151.9, 147.0, 146.4, 133.8, 132.5, 129.9, 128.8, 128.4, 128.30, 128.26, 127.9, 126.7, 121.0, 119.7, 116.9, 115.9, 113.4, 112.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3113 (w), 1681 (s), 1593 (m), 1468 (m), 1262 (s), 694 (m); MS (70 eV, EI) m/z (%) 487 [M +2]$^+$ (22), 485 [M]$^+$ (29), 105 (100), 77 (15); HRMS (ESI) for $C_{26}H_{16}BrNO_4Na$, [M + Na]$^+$ (508.0160), found 508.0164.

*4-Bromo-2-(2-phenyl-5-(thiophen-2-yl)oxazol-4-yl)phenyl benzoate (**3h**).* White solid (31.6 mg, 21% yield): R_f 0.23 (ethyl acetate/hexanes 1/20); mp 140.2−141.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.97−7.95 (m, 2H), 7.90 (d, 1H, J = 2.4 Hz), 7.83 (dd, 2H, J = 8.2 Hz, 1.3 Hz), 7.62 (dd, 1H, J = 8.8 Hz, 2.5 Hz), 7.49 (tt, 1H, J = 7.4 Hz, 1.1 Hz), 7.43−7.38 (m, 3H), 7.33−7.29 (m, 4H), 7.23 (dd, 1H, J = 3.8 Hz, 1.1 Hz), 7.04 (dd, 1H, J = 8.8 Hz, 5.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.4, 159.9, 147.8, 143.2, 133.9, 133.4, 132.8, 130.6, 130.1, 129.5, 129.0, 128.8, 128.7, 128.3, 127.7, 127.2, 126.7, 126.5, 126.4, 126.0, 125.1, 119.1; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 1737 (s), 1604 (w), 1478 (m), 1257 (s), 1200 (s), 1059 (m), 705 (s); MS (70 eV, EI) m/z (%) 503 [M+2]$^+$ (50), 501 [M]$^+$ (50), 158 (11), 105 (100), 77 (81); HRMS (EI) for $C_{26}H_{16}BrNO_3S$, [M]$^+$ (501.0034), found 501.0030.

*4-Bromo-2-(2,5-diphenyloxazol-4-yl)phenyl thiophene-2-carboxylate (**3h′**).* White solid (51.1 mg, 34% yield): R_f 0.18 (ethyl acetate/hexanes 1/20); mp 164.6−165.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.04 (dd, 2H, J = 9.7 Hz, 6.1 Hz), 7.89 (d, 1H, J = 2.4 Hz), 7.59 (dd, 1H, J = 8.7 Hz, 2.5 Hz), 7.53−7.50 (m, 2H), 7.47 (dd, 1H, J = 4.9 Hz, 1.2 Hz), 7.45−7.43 (m, 3H), 7.41 (dd, 1H, J = 3.5 Hz, 1.1 Hz), 7.33−7.27 (m, 4H), 6.94 (dd, 1H, J = 8.7 Hz, 4.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 160.3, 159.6, 147.3, 147.2, 134.6, 133.9, 133.5, 132.5, 132.2, 131.0, 130.5, 128.8, 128.7, 128.6, 128.2, 127.9, 127.5, 127.0, 126.4, 125.9, 125.0, 119.3; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (w), 1730 (s), 1604 (w), 1478 (m), 1200 (s), 701 (m); MS (70 eV, EI) m/z (%) 503 [M+2]$^+$ (42), 501 [M]$^+$ (42), 111 (100), 77 (27); HRMS (EI) for $C_{26}H_{16}BrNO_3S$, [M]$^+$ (501.0034), found 501.0037.

*N-Benzoyl-N-(5-bromo-2-phenylbenzofuran-3-yl)thiophene-2-carboxamide (**4h**).* White solid (1.5 mg, 1% yield): R_f 0.10 (ethyl acetate/hexanes 1/20); mp 168.8−170.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.71−7.66 (m, 4H), 7.59 (d, 1H, J = 1.8 Hz), 7.54 (dd, 1H, J = 3.9 Hz, 1.2 Hz), 7.50−7.44 (m, 3H), 7.42−7.39 (m, 4H), 7.35 (t, 2H, J = 7.8 Hz), 6.94 (dd, 1H, J = 8.9 Hz, 4.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.5, 165.2, 153.1, 151.9, 136.2, 134.1, 133.8, 132.6, 130.0, 128.9, 128.53, 128.49, 128.45, 127.9, 127.6, 126.8, 121.0, 117.1, 116.5, 113.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3084 (w), 1684 (s), 1600 (w), 1455 (w), 1253 (s), 697 (w); MS (70 eV, EI) m/z (%) 503 [M +2]$^+$ (44), 501 [M]$^+$ (53), 284 (8), 224 (27), 135 (53), 105 (100), 77 (34); HRMS (ESI) for $C_{26}H_{16}BrNO_3SNa$, [M + Na]$^+$ (523.9932), found 523.9941.

*4-Methoxy-2-(5-(4-nitrophenyl)-2-phenyloxazol-4-yl)phenyl benzoate (**3i**).* Yellow solid (87.1 mg, 59% yield): R_f 0.25 (ethyl acetate/hexanes 1/6); mp 158.8−159.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.13 (d, 2H, J = 8.9 Hz), 8.08−8.05 (m, 2H), 7.70 (dd, 2H, J = 8.2 Hz, 1.4 Hz), 7.67 (d, 2H, J = 9.0 Hz), 7.48−7.43 (m, 4H), 7.32 (d, 1H, J = 9.0 Hz), 7.25 (dd, 3H, J = 11.6 Hz, 4.2 Hz), 7.09 (dd, 1H, J = 8.9 Hz, 3.1 Hz), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.7, 161.4, 157.6, 147.0, 144.6, 142.0, 135.8, 134.4, 133.3, 131.0, 129.8, 129.0, 128.8, 128.2, 126.7, 126.6, 126.2, 125.8, 124.5, 123.9, 116.2, 115.7, 55.8; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (w), 2931 (w), 1730 (s), 1600 (s), 1512 (s), 1341 (s), 1200 (s), 701 (s); MS (70 eV, EI) m/z (%) 492 [M]$^+$ (21), 105 (100), 77 (61); HRMS (EI) for $C_{29}H_{20}N_2O_6$, [M]$^+$ (492.1321), found 492.1316.

*2-(5-(4-Bromophenyl)-2-phenyloxazol-4-yl)-4-methoxyphenyl benzoate (**3j**).* Yellow solid (102.4 mg, 65% yield): R_f 0.29 (ethyl acetate/hexanes 1/6); mp 168.9−169.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.02 (dd, 2H, J = 7.6 Hz, 4.0 Hz), 7.70 (dd, 2H, J = 8.4 Hz, 1.2 Hz), 7.46 (t, 1H, J = 7.4 Hz), 7.41−7.36 (m, 7H), 7.29−7.24 (m, 4H), 7.03 (dd, 1H, J = 8.9 Hz, 3.1 Hz), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.8, 160.3, 157.5, 145.8, 141.9, 133.2, 132.8, 131.7, 130.6, 129.9, 129.1, 128.7, 128.1, 127.5, 127.4, 126.8, 126.5, 126.0, 124.3, 122.6, 115.8, 115.5, 55.8; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3015 (m), 2931 (m), 1737 (s), 1604 (s), 1482 (s), 1261 (s), 1192 (s), 712 (s), 690 (s); MS (70 eV, EI) m/z (%) 527 [M+2]$^+$ (31), 525 [M]$^+$ (31), 420 (4), 139 (6), 105 (100), 77 (70); HRMS (EI) for $C_{29}H_{20}BrNO_4$, [M]$^+$ (525.0576), found 525.0574.

*4-Methoxy-2-(5-(4-methoxyphenyl)-2-phenyloxazol-4-yl)phenyl benzoate (**3k**).* White solid (65.8 mg, 46% yield): R_f 0.15 (ethyl acetate/hexanes 1/10); mp 155.7−156.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.01−7.99 (m, 2H), 7.75 (dd, 2H, J = 7.2 Hz, 1.1 Hz), 7.48−7.45 (m, 3H), 7.40−7.38 (m, 3H), 7.28−7.24 (m, 4H), 7.00 (dd, 1H, J = 8.9 Hz, 3.1 Hz), 6.82 (d, 2H, J = 8.8 Hz), 3.82 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.9, 159.9, 159.5, 157.3, 146.9, 142.1, 133.0, 131.0, 130.1, 130.0, 129.4, 128.6, 128.0, 127.6, 127.2, 126.6, 126.2, 124.2, 121.2, 115.5, 115.4, 114.0, 55.7, 55.3; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (w), 2939 (m), 2840 (m), 1737 (s), 1604 (s), 1486 (s), 1253 (s), 1029 (s), 693 (s); MS (70 eV, EI) m/z (%) 477 [M]$^+$ (14), 372 (4), 226 (1), 198 (1), 135 (3), 105 (100), 77 (14); HRMS (EI) for $C_{30}H_{23}NO_5$, [M]$^+$ (477.1576), found 477.1585.

*N-Benzoyl-4-methoxy-N-(5-methoxy-2-phenylbenzofuran-3-yl)-benzamide (**4k**).* White solid (31.5 mg, 22% yield): R_f 0.10 (ethyl acetate/hexanes 1/10); mp 73.1−73.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.64−7.58 (m, 6H), 7.42−7.36 (m, 5H), 7.27 (t, 2H, J = 7.8 Hz), 6.93 (dd, 1H, J = 8.9 Hz, 2.5 Hz), 6.89 (d, 1H, J = 2.5 Hz), 6.75 (d, 2H, J = 8.8 Hz), 3.82 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.9, 172.1, 163.2, 156.7, 152.1, 148.2, 134.3, 132.3, 131.1, 129.3, 128.7, 128.6, 128.4, 128.3, 126.8, 126.6, 126.0, 117.8, 113.7, 112.5, 100.9, 56.0, 55.4; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (w), 2931 (w), 1691 (s), 1604 (m), 1482 (m), 1250 (s), 1170 (m), 697 (m); MS (70 eV, EI) m/z (%) 477 [M]$^+$ (37), 343 (10), 135 (100), 105 (40), 77 (17); HRMS (MALDI) for $C_{30}H_{24}NO_5$, [M + H]$^+$ (478.1654), found 478.1667.

*2-(5-(Furan-2-yl)-2-phenyloxazol-4-yl)-4-methoxyphenyl benzoate (**3l**).* Brown solid (74.7 mg, 57% yield): R_f 0.29 (ethyl acetate/hexanes 1/20); mp 130.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.92 (td, 4H, J = 7.6 Hz, 1.3 Hz), 7.48 (t, 1H, J = 7.5 Hz), 7.41−7.30 (m, 8H), 7.02 (dd, 1H, J = 8.9 Hz, 3.1 Hz), 6.60 (d, 1H, J = 3.1 Hz), 6.42 (dd, 1H, J = 3.4 Hz, 1.8 Hz), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 165.1, 159.8, 157.0, 143.5, 143.0, 142.2, 139.3, 133.1,

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132.4, 130.4, 130.0, 129.5, 128.6, 128.1, 126.8, 126.4, 125.3, 124.0, 115.5, 115.4, 111.5, 109.2, 55.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3145 (w), 1730 (s), 1601 (m), 1500 (m), 1262 (s), 1194 (s); MS (70 eV, EI) *m*/*z* (%) 437 $[M]^+$ (30), 332 (12), 105 (100), 77 (36); HRMS (EI) for $C_{27}H_{19}NO_5$, $[M]^+$ (437.1263), found 437.1258.

*2-(2,5-Diphenyloxazol-4-yl)-4-methoxyphenyl furan-2-carboxylate (**3l′**).* White solid (5.2 mg, 4% yield): R_f 0.12 (ethyl acetate/hexanes 1/20); mp 176.0−176.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.06 (dd, 2H, *J* = 6.4 Hz, 2.8 Hz), 7.56 (dd, 2H, *J* = 7.9 Hz, 1.8 Hz), 7.46−7.43 (m, 4H), 7.35−7.24 (m, 5H), 7.01 (dd, 1H, *J* = 8.9 Hz, 3.0 Hz), 6.70 (d, 1H, *J* = 3.4 Hz), 6.35 (dd, 1H, *J* = 3.5 Hz, 1.7 Hz), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 160.1, 157.5, 156.6, 146.9, 146.7, 143.8, 141.2, 130.5, 128.7, 128.6, 128.50, 128.46, 126.5, 126.1, 124.2, 118.8, 115.8, 115.5, 111.7, 55.8; MS (70 eV, EI) *m*/*z* (%) 437 $[M]^+$ (100), 358 (8), 342 (17), 314 (7), 237 (11), 168 (8), 150 (37), 121 (5), 105 (50), 95 (44), 77 (13); HRMS (MALDI) for $C_{27}H_{20}NO_5$, $[M + H]^+$ (438.1336), found 438.1336.

*4-Methoxy-2-(2-phenyl-5-(thiophen-2-yl)oxazol-4-yl)phenyl benzoate (**3m**).* Yellow solid (81.6 mg, 60% yield): R_f 0.31 (ethyl acetate/hexanes 1/20); mp 107.2−108.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.97−7.94 (m, 2H), 7.86 (d, 2H, *J* = 7.4 Hz), 7.46 (t, 1H, *J* = 7.4 Hz), 7.40−7.36 (m, 3H), 7.32−7.24 (m, 6H), 7.05−7.00 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 165.0, 159.6, 157.2, 142.8, 142.2, 133.1, 131.8, 130.3, 130.0, 129.7, 129.4, 128.6, 128.1, 127.6, 126.8, 126.3, 126.1, 125.7, 125.6, 124.2, 115.8, 115.4, 55.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3065 (m), 2944 (m), 1738 (s), 1581 (m), 1492 (s), 1246 (s); MS (70 eV, EI) *m*/*z* (%) 453 $[M]^+$ (41), 348 (8), 111 (18), 105 (100), 77 (48); HRMS (EI) for $C_{27}H_{19}NO_4S$, $[M]^+$ (453.1035), found 453.1026.

*N-Benzoyl-N-(5-methoxy-2-phenylbenzofuran-3-yl)thiophene-2-carboxamide (**4m**).* Yellow solid (6.8 mg, 5% yield): R_f 0.13 (ethyl acetate/hexanes 1/20); mp 168.7−169.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.71 (td, 4H, *J* = 7.9 Hz, 1.6 Hz), 7.56 (dd, 1H, *J* = 3.9 Hz, 1.3 Hz), 7.47−7.45 (m, 2H), 7.43−7.32 (m, 6H), 6.95−6.89 (m, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.7, 165.4, 156.8, 152.4, 148.1, 136.4, 134.4, 134.0, 133.6, 132.4, 129.5, 128.8, 128.51, 128.48, 128.45, 127.5, 127.2, 126.5, 117.2, 114.1, 112.6, 100.7, 56.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (w), 2924 (s), 1691 (s), 1600 (m), 1482 (s), 1246 (s), 1109 (m), 693 (m); MS (70 eV, EI) *m*/*z* (%) 453 $[M]^+$ (42), 167 (9), 149 (17), 111 (42), 105 (100), 77 (17); HRMS (MALDI) for $C_{27}H_{20}NO_4S$, $[M + H]^+$ (454.1113), found 454.1123.

*2-(5-(2-Bromophenyl)-2-phenyloxazol-4-yl)-4-methoxyphenyl benzoate (**3n**).* Colorless oil (77.2 mg, 49% yield): R_f 0.36 (ethyl acetate/hexanes 1/6); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.94−7.89 (m, 4H), 7.56−7.52 (m, 2H), 7.41−7.32 (m, 6H), 7.24−7.15 (m, 3H), 7.07 (d, 1H, *J* = 3.0 Hz), 6.94 (dd, 1H, *J* = 8.9 Hz, 3.1 Hz), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 165.2, 160.7, 157.1, 145.6, 141.9, 134.9, 133.6, 133.1, 131.8, 130.5, 130.3, 130.2, 130.1, 129.5, 128.6, 128.1, 127.4, 127.1, 126.4, 125.7, 124.1, 123.1, 115.3, 114.8, 55.5; MS (70 eV, EI) *m*/*z* (%) 527 $[M+2]^+$ (46), 525 $[M]^+$ (54), 341 (17), 298 (13), 185 (5), 139 (9), 125 (19), 105 (100), 77 (6); HRMS (MALDI) for $C_{29}H_{21}BrNO_4$, $[M + H]^+$ (526.0648), found 526.0637.

*N-Benzoyl-2-bromo-N-(5-methoxy-2-phenylbenzofuran-3-yl)-benzamide (**4n**).* White solid (9.5 mg, 6% yield): R_f 0.31 (ethyl acetate/hexanes 1/6); mp 162.8−163.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.60 (dd, 1H, *J* = 7.7 Hz, 1.6 Hz), 7.57 (dd, 1H, *J* = 8.0 Hz, 0.9 Hz), 7.50−7.47 (m, 2H), 7.42−7.36 (m, 5H), 7.31 (dd, 1H, *J* = 7.8 Hz, 1.8 Hz), 7.26 (dt, 3H, *J* = 8.8 Hz, 1.6 Hz), 7.22 (d, 1H, *J* = 2.5 Hz), 7.05 (t, 2H, *J* = 7.9 Hz), 6.96 (dd, 1H, *J* = 8.9 Hz, 2.6 Hz), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 171.2, 170.2, 156.6, 152.1, 148.2, 137.7, 133.2, 133.1, 132.2, 131.4, 129.6, 129.4, 128.8, 128.5, 128.4, 127.7, 127.6, 126.7, 126.4, 118.7, 117.0, 114.2, 112.6, 102.0, 56.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3048 (w), 2919 (m), 1694 (s), 1597 (w), 1480 (m), 1266 (s), 1250 (s), 690 (m); MS (70 eV, EI) *m*/*z* (%) 527 $[M+2]^+$ (30), 525 $[M]^+$ (30), 421 (10), 342 (12), 238 (14), 183 (98), 149 (10), 105 (100), 77 (8); HRMS (EI) for $C_{29}H_{20}BrNO_4$, $[M]^+$ (525.0576), found 525.0574.

*4-Bromo-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl benzoate (**3o**).* White solid (112.5 mg, 77% yield; in Table 1, entry 15) (112.5 mg, 77% yield; in Scheme 4): R_f 0.25 (ethyl acetate/hexanes 1/20); mp 104.5−105.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.10 (dd, 2H, *J* = 8.5 Hz, 1.3 Hz), 7.89 (dd, 2H, *J* = 8.8 Hz, 1.3 Hz), 7.75 (d, 1H, *J* = 2.4 Hz), 7.65 (dd, 1H, *J* = 8.7 Hz, 2.4 Hz), 7.56 (t, 1H, *J* = 7.4 Hz), 7.47 (t, 1H, *J* = 7.4 Hz), 7.43−7.36 (m, 4H), 7.28 (d, 1H, *J* = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.5, 162.2, 148.0, 137.3 (quart, *J* = 2.1 Hz), 135.3 (quart, *J* = 42.7 Hz), 133.80, 133.76, 133.7, 131.7, 130.3, 128.8, 128.5, 127.0, 125.5, 125.1, 124.7, 119.2 (quart, *J* = 268.4 Hz), 118.9; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3053 (w), 1737 (s), 1608 (m), 1486 (m), 1417 (s), 1368 (s), 1124 (s), 697 (s); MS (70 eV, EI) *m*/*z* (%) 489 $[M+2]^+$ (24), 487 $[M]^+$ (29), 105 (100), 77 (13); HRMS (FAB) for $C_{23}H_{14}BrF_3NO_3$, $[M + H]^+$ (488.0109), found 488.0102.

*N-(5-Bromo-2-phenylbenzofuran-3-yl)-N-pivaloylbenzamide (**4o**).* White solid (109.7 mg, 77% yield; in Table 1, entry 16) (109.7 mg, 77% yield; in Table 3, entry 1) (57.0 mg, 40% yield; in Table 3, entry 8): R_f 0.38 (ethyl acetate/hexanes 1/20); mp 149.5−150.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.61−7.58 (m, 2H), 7.55 (d, 1H, *J* = 1.8 Hz), 7.43−7.40 (m, 4H), 7.35−7.32 (m, 4H), 7.17 (t, 2H, *J* = 7.8 Hz), 1.39 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ/ppm 185.9, 173.0, 153.3, 151.8, 133.9, 132.2, 129.9, 128.8, 128.5, 128.2, 128.1, 128.0, 127.9, 126.9, 120.8, 116.9, 116.5, 113.5, 43.5, 28.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (w), 2961 (m), 1678 (s), 1600 (m), 1508 (w), 1451 (m), 1258 (s), 698 (s); MS (70 eV, EI) *m*/*z* (%) 477 $[M+2]^+$ (72), 476 $[M]^+$ (72), 393 (76), 105 (100), 77 (20), 57 (21); HRMS (ESI) for $C_{26}H_{23}BrNO_3$, $[M + H]^+$ (476.0861), found 476.0862.

Typical Procedure for the Preparation of Benzofurans 4 (Table 2). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1** (0.3 mmol) in anhydrous dichloromethane (1.5 mL). To this reaction mixture, Bu_3P (82 μL, 1.1 equiv) was added and stirred for 30 min. Acyl chloride **2** (0.3 mmol) and Et_3N (46 μL, 1.1 equiv) were added in sequence, and the resulting reaction mixture was further stirred for 1 h at room temperature (monitored by ^{1}H NMR data analysis). The solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished the desired adduct **4**.

Typical Procedure for the Preparation of Benzofuran 8a Using PBu_3 (Scheme 2). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1a** (0.2 mmol) in anhydrous dichloromethane (1.0 mL). To this stirred reaction mixture, Bu_3P (55 μL, 1.1 equiv) was added for 20 h at 40 °C. At this point, the solvent was removed under reduced pressure and to the resulting white solid. This resulted in a suspension that was filtered and washed with hexanes (3 × 10 mL) and dichloromethane (3 × 5 mL). The benzofuran product **8a** was dried in vacuo and used without further purification.

Typical Procedure for the Preparation of Benzofuran 4a (Scheme 2). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **8a** (0.1 mmol) in anhydrous dichloromethane (0.2 mL). To this stirred reaction mixture, Bu_3P (2.5 μL, 0.1 equiv), benzoyl chloride **2a** (13 μL, 1.1 equiv) and Et_3N (15 μL, 1.1 equiv) were added in sequence. The reaction mixture was further stirred for 1 h at room temperature and was monitored by ^{1}H NMR data analysis. The solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished the desired adduct **4a**.

Typical Procedure for the Preparation of Trifluoromethyl-Substituted Oxazoles (3o−y) (Scheme 4). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1** (0.3 mmol) and PPh_3 (87.4 mg, 1.1 equiv) in anhydrous toluene (1.5 mL). To this stirred reaction mixture, TFAA **2h** (46 μL, 1.1 equiv) and Et_3N (54 μL, 1.3 equiv) were added in sequence. The reaction mixture was further stirred for the indicated time at room temperature (monitored by ^{1}H NMR data analysis). The solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished the desired adduct **3**.

*4-Chloro-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl benzoate (**3p**).* White solid (113.0 mg, 85% yield): R_f 0.48 (ethyl acetate/hexanes 1/10); mp 76.1−77.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.10 (dd, 2H, *J* = 8.5 Hz, 1.3 Hz), 7.88 (dd, 2H, *J* = 8.6 Hz, 1.4 Hz), 7.60 (d, 1H, *J* = 2.4 Hz), 7.55 (t, 1H, *J* = 7.5 Hz), 7.50 (dd, 1H, *J* =

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8.8 Hz, 2.6 Hz), 7.48−7.35 (m, 5H), 7.33 (d, 1H, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.6, 162.2, 147.5, 137.5 (quart, J = 2.1 Hz), 135.2 (quart, J = 42.7 Hz), 133.6, 131.7, 131.4, 130.8, 130.3, 128.9, 128.8, 128.5, 127.0, 125.5, 124.8, 124.3, 119.2 (quart, J = 268.4 Hz); IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (m), 1741 (s), 1600 (m), 1558 (m), 1421 (s), 1124 (s), 693 (s); MS (70 eV, EI) m/z (%) 445 [M+2]$^+$ (15), 443 [M]$^+$ (45), 338 (11), 243 (17), 213 (12), 110 (87), 105 (99), 77 (100); HRMS (EI) for $C_{23}H_{13}ClF_3NO_3$, [M]$^+$ (443.0536), found 443.0544.

*2-(2-Phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl 4-bromobenzoate (**3q**).* White solid (121.3 mg, 83% yield): R_f 0.25 (ethyl acetate/hexanes 1/20); mp 105.4−105.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.97 (d, 2H, J = 8.5 Hz), 7.83 (d, 2H, J = 7.3 Hz), 7.60 (d, 1H, J = 7.5 Hz), 7.52−7.50 (m, 3H), 7.42 (t, 1H, J = 7.3 Hz), 7.38−7.33 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.1, 161.8, 148.7, 138.7 (quart, J = 2.1 Hz), 134.8 (quart, J = 42.5 Hz), 131.7, 131.63, 131.55, 131.0 (quart, J = 1.4 Hz), 130.9, 128.7, 128.6, 128.2, 126.8, 126.1, 125.5, 123.3, 122.4, 119.3 (quart, J = 268.3 Hz); IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 1741 (s), 1589 (m), 1486 (m), 1387 (s), 1261 (s), 1070 (s), 709 (m); MS (70 eV, EI) m/z (%) 489 [M+2]$^+$ (13), 487 [M]$^+$ (13), 207 (31), 183 (100), 157 (48), 105 (37), 77 (24); HRMS (EI) for $C_{23}H_{13}BrF_3NO_3$, [M]$^+$ (487.0031), found 487.0035.

*4-Methoxy-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl benzoate (**3r**).* White solid (105.4 mg, 80% yield): R_f 0.15 (ethyl acetate/hexanes 1/20); mp 93.8−94.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.12 (dd, 2H, J = 8.0 Hz, 1.4 Hz), 7.86 (dd, 2H, J = 8.7 Hz, 1.4 Hz), 7.52 (t, 1H, J = 7.4 Hz), 7.45−7.33 (m, 5H), 7.28 (d, 1H, J = 8.9 Hz), 7.12 (d, 1H, J = 3.0 Hz), 7.06 (dd, 1H, J = 8.9 Hz, 3.0 Hz), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 165.2, 161.9, 157.1, 142.4, 138.7 (quart, J = 2.3 Hz), 134.9 (quart, J = 42.5 Hz), 133.3, 131.5, 130.2, 129.5, 128.7, 128.3, 126.9, 125.7, 124.2, 123.2, 119.4 (quart, J = 268.2 Hz), 116.4, 115.7, 55.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 1749 (s), 1608 (m), 1497 (m), 1379 (s), 1200 (s), 701 (m); MS (70 eV, EI) m/z (%) 439 [M]$^+$ (17), 105 (99), 77 (100); HRMS (EI) for $C_{24}H_{16}F_3NO_4$, [M]$^+$ (439.1031), found 439.1030.

*2-(2-Phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl 4-chlorobenzoate (**3s**).* White solid (91.7 mg, 69% yield): R_f 0.26 (ethyl acetate/hexanes 1/20); mp 91.0−92.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.06 (d, 2H, J = 8.6 Hz), 7.85 (dd, 2H, J = 8.7 Hz, 1.4 Hz), 7.61 (d, 1H, J = 7.6 Hz), 7.54 (td, 1H, J = 7.8 Hz, 1.7 Hz), 7.46 (t, 1H, J = 7.4 Hz), 7.40−7.36 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.0, 161.9, 148.7, 140.0, 138.7 (quart, J = 2.2 Hz), 134.9 (quart, J = 42.5 Hz), 131.63, 131.60, 131.1 (quart, J = 1.2 Hz), 131.0. 128.8, 127.8, 126.9, 126.1, 125.6, 123.4, 122.5, 119.3 (quart, J = 268.1 Hz); IR (KBr) $\tilde{\nu}$(cm^{-1}) 3065 (w), 1746 (s), 1593 (m), 1484 (m), 1387 (s), 1165 (s), 746 (m); MS (70 eV, EI) m/z (%) 445 [M+2]$^+$ (15), 443 [M]$^+$ (48), 304 (11), 256 (7), 207 (18), 183 (12), 152 (7), 139 (100), 111 (11); HRMS (MADLI) for $C_{23}H_{14}ClF_3NO_3$, [M + H]$^+$ (444.0609), found 444.0604.

*2-(2-Phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl 4-methoxybenzoate (**3t**).* Yellow oil (77.7 mg, 59% yield): R_f 0.12 (ethyl acetate/hexanes 1/20); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.07 (d, 2H, J = 8.8 Hz), 7.90 (dd, 2H, J = 8.7 Hz, 1.4 Hz), 7.60 (d, 1H, J = 7.6 Hz), 7.54 (td, 1H, J = 7.9 Hz, 1.6 Hz), 7.46 (t, 1H, J = 7.5 Hz), 7.40−7.35 (m, 4H), 6.88 (d, 2H, J = 8.9 Hz), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.5, 163.8, 161.9, 149.1, 138.8 (quart, J = 2.2 Hz), 134.9 (quart, J = 42.5 Hz), 132.4, 131.5, 131.0, 130.9, 128.7, 127.0, 125.8, 123.5, 122.7, 121.7, 119.4 (quart, J = 268.2 Hz), 113.7, 55.4; MS (70 eV, EI) m/z (%) 439 [M]$^+$ (12), 135 (100), 107 (17), 77 (23); HRMS (EI) for $C_{24}H_{16}F_3NO_4$, [M]$^+$ (439.1031), found 439.1024.

*4-Methoxy-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl 4-methoxybenzoate (**3u**).* White solid (81.6 mg, 58% yield): R_f 0.38 (ethyl acetate/hexanes 1/4); mp 106.1−106.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.06 (d, 2H, J = 8.8 Hz), 7.91 (dd, 2H, J = 8.6 Hz, 1.4 Hz), 7.47 (t, 1H, J = 7.4 Hz), 7.39 (t, 2H, J = 7.8 Hz), 7.27 (d, 1H, J = 8.9 Hz), 7.11 (d, 1H, J = 3.0 Hz), 7.06 (dd, 1H, J = 8.9 Hz, 3.1 Hz), 6.88 (d, 2H, J = 9.0 Hz), 3.86 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.9, 163.7, 161.9, 157.0, 142.5, 138.7 (quart, J = 2.3 Hz), 134.9 (quart, J = 42.5 Hz), 132.3, 131.5, 128.7, 127.0, 125.8, 124.3, 123.3, 121.7, 119.3 (quart, J = 268.2 Hz), 116.5, 115.58, 115.57, 113.6, 55.7, 55.4; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3008 (w), 2927 (m), 1734 (s), 1601 (s), 1512 (s), 1375 (s); MS (70 eV, EI) m/z (%) 469 [M]$^+$ (32), 135 (100), 77 (2); HRMS (MALDI) for $C_{25}H_{19}F_3NO_5$, [M + H]$^+$ (470.1215), found 470.1226.

*4-Chloro-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl 4-bromobenzoate (**3v**).* White solid (85.4 mg, 82% yield): R_f 0.51 (ethyl acetate/hexanes 1/20); mp 161.5−161.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.95 (d, 2H, J = 8.5 Hz), 7.88 (dd, 2H, J = 8.6 Hz, 1.4 Hz), 7.60 (d, 1H, J = 2.5 Hz), 7.56 (d, 2H, J = 8.6 Hz), 7.52−7.48 (m, 2H), 7.41 (t, 2H, J = 7.7 Hz), 7.32 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.0, 162.2, 147.2, 137.3 (quart, J = 2.2 Hz), 135.2 (quart, J = 42.8 Hz), 131.9, 131.7, 131.6, 130.9, 129.0, 128.9, 127.8, 127.0, 125.4, 124.7, 124.1, 119.1 (quart, J = 268.4 Hz); IR (KBr) $\tilde{\nu}$(cm^{-1}) 3065 (w), 1738 (s), 1589 (m), 1484 (m), 1419 (m), 1367 (m), 1125 (s), 835 (m), 714 (m); MS (70 eV, EI) m/z (%) 523 [M+2]$^+$ (36), 521 [M]$^+$ (28), 310 (5), 241 (10), 186 (8), 185 (100), 157 (19), 105 (5); HRMS (MALDI) for $C_{23}H_{12}BrClF_3NO_3Na$, [M + Na]$^+$ (543.9539), found 543.9552.

*4-Methoxy-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl 4-bromobenzoate (**3w**).* Yellow solid (122.5 mg, 79% yield): R_f 0.13 (ethyl acetate/hexanes 1/25); mp 102.0−102.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.96 (d, 2H, J = 8.5 Hz), 7.86 (dd, 2H, J = 8.5 Hz, 1.2 Hz), 7.54 (d, 2H, J = 8.6 Hz), 7.47 (t, 1H, J = 7.3 Hz), 7.39 (t, 2H, J = 7.8 Hz), 7.27 (d, 1H, J = 8.9 Hz), 7.12 (d, 1H, J = 2.9 Hz), 7.07 (dd, 1H, J = 8.9 Hz, 3.0 Hz), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 164.6, 161.9, 157.2, 142.1, 138.6 (quart, J = 2.2 Hz), 134.9 (quart, J = 42.6 Hz), 131.8, 131.70, 131.68, 128.8, 128.6, 128.4, 126.9, 125.6, 124.2, 123.1, 119.3 (quart, J = 268.3 Hz), 116.5, 115.7 (quart, J = 1.3 Hz), 55.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3073 (w), 2927 (w), 1742 (s), 1605 (m), 1492 (s), 1198 (s), 685 (m); MS (70 eV, EI) m/z (%) 519 [M+2]$^+$ (35), 517 [M]$^+$ (35), 334 (6), 306 (7), 183 (100), 157 (35), 105 (23), 76 (14); HRMS (ESI) for $C_{24}H_{16}BrF_3NO_4$, [M + H]$^+$ (518.0215), found 518.0220.

*4-Bromo-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl thiophene-2-carboxylate (**3x**).* Yellow solid (110.9 mg, 75% yield): R_f 0.35 (ethyl acetate/hexanes 1/10); mp 108.2−109.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.92−7.88 (m, 3H), 7.73 (d, 1H, J = 2.4 Hz), 7.63 (dd, 1H, J = 8.5 Hz, 2.4 Hz), 7.56 (dd, 1H, J = 4.9 Hz, 1.0 Hz), 7.46 (t, 1H, J = 7.3 Hz), 7.39 (t, 2H, J = 7.8 Hz), 7.28 (d, 1H, J = 8.7 Hz), 7.07 (dd, 1H, J = 8.7 Hz, 4.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 162.2, 159.8, 147.6, 137.2 (quart, J = 2.2 Hz), 135.2 (quart, J = 42.6 Hz), 135.0, 133.9, 133.73, 133.66, 132.1, 131.7, 128.8, 127.9, 127.0, 125.5, 125.0, 124.6, 119.1 (quart, J = 268.4 Hz), 119.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3089 (w), 1730 (s), 1609 (s), 1556 (s), 1415 (s), 1367 (s), 710 (s); HRMS (MALDI) for $C_{21}H_{11}BrF_3NO_3SNa$, [M + Na]$^+$ (515.9493), found 515.9504.

*4-Bromo-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenyl cyclohexanecarboxylate (**3y**).* Colorless oil (130.2 mg, 88% yield): R_f 0.39 (ethyl acetate/hexanes 1/20); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.11 (dd, 2H, J = 8.4 Hz, 1.6 Hz), 7.66 (d, 1H, J = 2.3 Hz), 7.59 (dd, 1H, J = 8.8 Hz, 2.5 Hz), 7.57−7.48 (m, 3H), 7.11 (d, 1H, J = 8.7 Hz), 2.44 (tt, 1H, J = 11.1 Hz, 3.6 Hz), 1.90−1.87 (m, 2H), 1.70−1.65 (m, 2H), 1.60−1.56 (m, 1H), 1.43 (qd, 2H, J = 11.4 Hz, 3.1 Hz), 1.28−1.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 173.5, 162.2, 148.0, 137.3 (quart, J = 1.9 Hz), 135.4 (quart, J = 42.7 Hz), 133.7, 131.9, 129.0, 127.1, 125.6, 124.8, 124.6, 119.1 (quart, J = 268.3 Hz), 118.5; HRMS (ESI) for $C_{23}H_{19}BrF_3NO_3Na$, [M + Na]$^+$ (516.0393), found 516.0378.

Typical Procedure for the Preparation of Benzofurans (4o−t') (Table 3). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **1** (1.2 equiv) in anhydrous dichloromethane (0.6 mL). To this stirred reaction mixture, Bu_3P (82 μL, 1.1 equiv), pivaloyl chloride **2i** (37 μL, 0.3 mmol) and Et_3N (46 μL, 1.1 equiv) were added in sequence. The reaction mixture was further stirred for the indicated time at room temperature and was monitored by ^{1}H NMR data analysis. The solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished the desired adduct **4**.

*N-(5-Chloro-2-phenylbenzofuran-3-yl)-N-pivaloylbenzamide (**4p**).* White solid (89.2 mg, 69% yield): R_f 0.3 (ethyl acetate/hexanes 1/

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20); mp 148.5−149.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.61−7.58 (m, 2H), 7.43−7.40 (m, 4H), 7.37−7.33 (m, 4H), 7.28 (dd, 1H, J = 8.8 Hz, 2.1 Hz), 7.17 (t, 2H, J = 7.8 Hz), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 185.9, 173.0, 153.5, 151.4, 134.0, 132.2, 129.9, 129.5, 128.8, 128.1, 128.0, 127.9, 126.9, 125.5, 117.7, 116.7, 113.0, 43.5, 28.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 2960 (m), 1681 (s), 1597 (w), 1440 (m), 1262 (s), 1133 (s), 685 (m); MS (70 eV, EI) m/z (%) 433 [M+2]$^+$ (24), 431 [M]$^+$ (47), 349 (5), 347 (14), 105 (100), 77 (36), 57 (37); HRMS (EI) for $C_{26}H_{22}ClNO_3$, [M]$^+$ (431.1288), found 431.1291.

N-(5-Methoxy-2-phenylbenzofuran-3-yl)-N-pivaloylbenzamide (***4q***). White solid (101.2 mg, 79% yield): R_f 0.55 (ethyl acetate/hexanes 1/20); mp 135.0−135.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.59 (dd, 2H, J = 8.1 Hz, 1.5 Hz), 7.42−7.30 (m, 7H), 7.14 (t, 2H, J = 7.6 Hz), 6.92−6.88 (m, 2H), 3.84 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.1, 173.1, 156.7, 152.8, 148.0, 134.1, 132.0, 129.4, 128.7, 128.5, 128.0, 127.9, 127.1, 126.6, 117.3, 113.6, 112.5, 100.8, 55.9, 43.5, 28.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3053 (w), 2962 (s), 2924 (s), 1707 (s), 1680 (s), 1604 (m), 1482 (s), 1288 (s), 693 (s); MS (70 eV, EI) m/z (%) 427 [M]$^+$ (27), 343 (47), 238 (18), 105 (100), 77 (47), 57 (96); HRMS (EI) for $C_{27}H_{25}NO_4$, [M]$^+$ (427.1784), found 427.1782.

N-(2-(4-Bromophenyl)benzofuran-3-yl)-N-pivaloylbenzamide (***4r***). Yellow solid (132.5 mg, 93% yield): R_f 0.33 (ethyl acetate/hexanes 1/20); mp 148.8−150.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.60 (dd, 2H, J = 8.2 Hz, 1.6 Hz), 7.50−7.38 (m, 5H), 7.34−7.31 (m, 2H), 7.26 (d, 2H, J = 8.5 Hz), 7.14 (d, 2H, J = 8.4 Hz), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.0, 172.1, 153.1, 152.2, 133.0, 131.3, 129.6, 129.4, 128.8, 128.3, 126.8, 126.7, 126.3, 125.4, 123.9, 117.9, 117.0, 112.1, 43.5, 28.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3061 (w), 2962 (w), 1695 (s), 1589 (m), 1478 (m), 1257 (s), 750 (s); MS (70 eV, EI) m/z (%) 477 [M+2]$^+$ (52), 475 [M]$^+$ (53), 393 (18), 298 (20), 262 (3), 240 (47), 185 (21), 105 (100), 77 (15), 57 (61); HRMS (EI) for $C_{26}H_{22}BrNO_3$, [M]$^+$ (475.0783), found 475.0782.

N-(2-(4-Bromophenyl)-5-methoxybenzofuran-3-yl)-N-pivaloylbenzamide (***4s***). White solid (101.5 mg, 67% yield): R_f 0.33 (ethyl acetate/hexanes 1/20); mp 129.4−130.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.55 (d, 2H, J = 8.6 Hz), 7.46 (d, 2H, J = 8.6 Hz), 7.38−7.34 (m, 4H), 7.18 (t, 2H, J = 7.6 Hz), 6.94 (dd, 1H, J = 8.9 Hz, 2.5 Hz), 6.88 (d, 1H, J = 2.4 Hz), 3.87 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.1, 173.0, 156.8, 151.8, 148.1, 133.9, 132.2, 132.0, 128.2, 128.02, 127.96, 127.5, 127.0, 123.7, 117.7, 114.0, 112.6, 100.8, 55.9, 43.5, 28.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3056 (w), 2960 (m), 1690 (s), 1613 (m), 1480 (s), 1278 (s), 694 (m); MS (70 eV, EI) m/z (%) 507 [M+2]$^+$ (28), 505 [M]$^+$ (28), 423 (10), 237 (5), 183 (3), 105 (100), 77 (25), 57 (60); HRMS (ESI) for $C_{27}H_{24}BrNO_4Na$, [M + Na]$^+$ (528.0786), found 528.0788.

4-Bromo-N-(5-methoxy-2-phenylbenzofuran-3-yl)-N-pivaloylbenzamide (***4s′***). White solid (15.2 mg, 10% yield): R_f 0.38 (ethyl acetate/hexanes 1/20); mp 125.4−126.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.58 (dd, 2H, J = 7.9 Hz, 1.4 Hz), 7.43−7.36 (m, 4H), 7.28 (d, 2H, J = 8.5 Hz), 7.17 (d, 2H, J = 8.5 Hz), 6.94 (dd, 1H, J = 8.9 Hz, 2.5 Hz), 6.85 (d, 1H, J = 2.5 Hz), 3.86 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.1, 172.1, 156.7, 152.9, 148.1, 133.0, 131.3, 129.5, 129.4, 128.8, 128.4, 126.9, 126.8, 126.6, 117.0, 113.6, 112.7, 100.7, 55.9, 43.5, 28.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3065 (w), 2919 (m), 1710 (s), 1673 (s), 1585 (m), 1480 (s), 1254 (s), 698 (m); MS (70 eV, EI) m/z (%) 507 [M+2]$^+$ (27), 505 [M]$^+$ (23), 423 (33), 238 (22), 185 (60), 155 (9), 105 (13), 57 (100); HRMS (ESI) for $C_{27}H_{24}BrNO_4Na$, [M + Na]$^+$ (528.0786), found 528.0788.

N-(5-Bromo-2-phenylbenzofuran-3-yl)-N-pivaloylthiophene-2-carboxamide (***4t′***). Yellow solid (105.3 mg, 73% yield): R_f 0.4 (ethyl acetate/hexanes 1/10); mp 120.8−121.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.77 (dd, 2H, J = 8.2 Hz, 1.8 Hz), 7.54 (d, 1H, J = 1.7 Hz), 7.49−7.40 (m, 7H), 6.89 (dd, 1H, J = 8.8 Hz, 4.8 Hz), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.1, 165.7, 153.1, 151.8, 136.2, 133.5, 133.2, 130.0, 129.1, 128.9, 128.3, 127.9, 127.5, 126.8, 121.1, 117.0, 116.5, 113.4, 43.7, 28.6; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3105 (w), 2960 (m), 1681 (s), 1516 (m), 1258 (s), 1129 (s), 726 (s); HRMS (EI) for $C_{24}H_{20}BrNO_3S$, [M]$^+$ (481.0347), found 481.0352.

N-(5-Bromo-2-phenylbenzofuran-3-yl)benzamide (***8a***). White solid (39.1 mg, 3% yield): mp 256.4−257.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ/ppm 10.44 (s, 1H), 8.01 (d, 2H, J = 7.4 Hz), 7.91 (d, 2H, J = 7.6 Hz), 7.68−7.64 (m, 3H), 7.59 (t, 2H, J = 7.6 Hz), 7.55−7.51 (m, 3H), 7.44 (t, 1H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ/ppm 166.6, 151.6, 149.6, 134.0, 132.5, 129.8, 129.7, 129.5, 129.4, 129.1, 128.4, 128.2, 126.3, 123.0, 115.9, 115.4, 114.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3252 (s), 3023 (m), 2954 (m), 1688 (m), 1650 (s), 1528 (s), 1444 (s), 1208 (m), 804 (m), 709 (s), 690 (s); MS (70 eV, EI) m/z (%) 393 [M+2]$^+$ (57), 391 [M]$^+$ (83), 288 (7), 208 (3), 207 (11), 179 (18), 152 (11), 105 (100), 77 (80); HRMS (EI) for $C_{21}H_{14}BrNO_2$, [M]$^+$ (391.0208), found 391.0202.

Typical Procedure for the Preparation of Benzamide 8 (Scheme 5). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **4** (0.1 mmol) in HCl/1,4-dioxane (0.5 mL). The reaction mixture was stirred for indicated time at room temperature. The solvent was removed by evaporation in vacuo to afford **8**.

N-(5-Bromo-2-phenylbenzofuran-3-yl)benzamide (***8a***). Reaction condition, 5 h; white solid (39.1 mg, quantitative yield): mp 256.4−257.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ/ppm 10.44 (s, 1H), 8.01 (d, 2H, J = 7.4 Hz), 7.91 (d, 2H, J = 7.6 Hz), 7.68−7.64 (m, 3H), 7.59 (t, 2H, J = 7.6 Hz), 7.55−7.51 (m, 3H), 7.44 (t, 1H, J = 7.3 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ/ppm 166.6, 151.6, 149.6, 134.0, 132.5, 129.8, 129.7, 129.5, 129.4, 129.1, 128.4, 128.2, 126.3, 123.0, 115.9, 115.4, 114.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3252 (s), 3023 (m), 2954 (m), 1688 (m), 1650 (s), 1528 (s), 1444 (s), 1208 (m), 804 (m), 709 (s), 690 (s); MS (70 eV, EI) m/z (%) 393 [M+2]$^+$ (57), 391 [M]$^+$ (83), 288 (7), 208 (3), 207 (11), 179 (18), 152 (11), 105 (100), 77 (80); HRMS (EI) for $C_{21}H_{14}BrNO_2$, [M]$^+$ (391.0208), found 391.0202.

N-(5-Chloro-2-phenylbenzofuran-3-yl)benzamide (***8b***). Reaction condition, 5 h; white solid (34.7 mg, quantitative yield): mp 239.2−239.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ/ppm 10.46 (s, 1H), 8.10 (d, 2H, J = 7.2 Hz), 7.92 (d, 2H, J = 7.3 Hz), 7.71 (d, 1H, J = 8.8 Hz), 7.66 (t, 1H, J = 8.8 Hz), 7.60 (t, 2H, J = 7.7 Hz), 7.55−7.51 (m, 3H), 7.45 (d, 1H, J = 7.3 Hz), 7.41 (dd, 2H, J = 8.6 Hz, 2.0 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ/ppm 166.6, 151.3, 149.8, 134.0, 132.5, 129.7, 129.5, 129.4, 129.3, 129.1, 128.4, 128.1, 126.3, 125.5, 120.0, 115.6, 113.6; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 2969 (m), 1707 (s), 1695 (s), 1272 (s), 1112 (m), 693 (m); MS (70 eV, EI) m/z (%) 349 [M+2]$^+$ (33), 347 [M]$^+$ (88), 242 (15), 207 (24), 179 (24), 151 (17), 105 (100), 77 (73); HRMS (EI) for $C_{21}H_{14}ClNO_2$, [M]$^+$ (347.0713), found 347.0714.

N-(2-(4-Bromophenyl)-5-methoxybenzofuran-3-yl)benzamide (***8c***). Reaction condition, 3 h; white solid (42.1 mg, quantitative yield): mp 259.5−260.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ/ppm 10.56 (s, 1H), 8.09 (d, 2H, J = 7.3 Hz), 7.80 (d, 1H, J = 8.6 Hz), 7.70 (d, 2H, J = 8.6 Hz), 7.65 (t, 1H, J = 7.2 Hz), 7.58 (t, 3H, J = 8.2 Hz), 7.00−6.96 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ/ppm 166.4, 156.3, 148.0, 147.8, 134.1, 132.5, 132.4, 129.2, 129.1, 128.4, 128.3, 127.9, 122.4, 116.7, 114.8, 112.6, 102.6, 56.2; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3234 (s), 3032 (w), 2815 (w), 1645 (s), 1613 (m), 1528 (s), 1476 (s), 1218 (s), 827 (m), 690 (m); MS (70 eV, EI) m/z (%) 422 [M+2]$^+$ (95), 421 [M]$^+$ (100), 318 (5), 237 (25), 219 (6), 194 (21), 139 (6), 105 (99), 77 (20); HRMS (MALDI) for $C_{22}H_{17}BrNO_3$, [M + H]$^+$ (422.0386), found 422.0384.

Typical Procedure for the Preparation of Benzamide 10 (Scheme 5). A solution of benzamide **8** (0.2 mmol) in anhydrous THF (1.5 mL) was treated with NaH (1.54 equiv) at 0 °C, and the resulting mixture was stirred at room temperature. To this mixture was added iodomethane (1.54 equiv) for **10a** and **10b**; allyl bromide (3.08 equiv) for **10c**; and 4-nitrobenzoyl chloride **2b** (1.54 equiv) for **10d** at room temperature. The resulting mixture was stirred at room temperature for indicated time, and quenched with water. The product was extracted into ethyl acetate. The organic layer was washed with water and brine, dried ($MgSO_4$), filtered, and concentrated.

N-(5-Bromo-2-phenylbenzofuran-3-yl)-N-methylbenzamide (***10a***). Reaction condition, 2 h; white solid (58.3 mg, 72% yield): R_f 0.39 (ethyl acetate/hexanes 1/5); mp 156.6−157.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.65 (d, 1H, J = 1.3 Hz), 7.64 (d, 2H, J = 1.8 Hz),

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7.44 (t, 2H, J = 7.6 Hz), 7.41−7.38 (m, 2H), 7.29 (d, 1H, J = 8.7 Hz), 7.13−7.09 (m, 3H), 6.96 (t, 2H, J = 7.7 Hz), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 171.7, 151.4, 150.3, 135.0, 130.0, 129.5, 129.0, 128.4, 128.3, 128.2, 127.5, 126.9, 125.7, 121.2, 120.9, 116.7, 113.2, 36.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3056 (m), 2927 (m), 1641 (s), 1492 (m), 1351 (s), 690 (s); MS (70 eV, EI) m/z (%) 407 $[M+2]^+$ (33), 405 $[M]^+$ (25), 300 (15), 252 (5), 239 (14), 220 (37), 192 (30), 163 (17), 139 (8), 118 (19), 105 (100), 77 (53); HRMS (MADLI) for $C_{22}H_{17}BrNO_2$, $[M + H]^+$ (406.0437), found 406.0424.

*N-(5-Chloro-2-phenylbenzofuran-3-yl)-N-methylbenzamide (**10b**).* Reaction condition, 2 h; white solid (52.7 mg, 73% yield): R_f 0.43 (ethyl acetate/hexanes 1/5); mp 138.5−139.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.65 (dd, 2H, J = 7.0 Hz, 1.4 Hz), 7.79−7.38 (m, 4H), 7.34 (d, 1H, J = 8.8 Hz), 7.25 (dd, 1H, J = 8.7 Hz, 2.0 Hz), 7.13−7.09 (m, 3H), 6.96 (t, 2H, J = 7.3 Hz), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 171.7, 151.0, 150.5, 135.0, 130.0, 129.5, 129.3, 129.0, 128.3, 127.8, 127.5, 126.9, 125.6, 125.5, 121.4, 117.9, 112.8, 36.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3056 (w), 2919 (w), 1641 (s), 1492 (m), 1351 (s), 1254 (m), 1069 (m), 690 (s); MS (70 eV, EI) m/z (%) 363 $[M+2]^+$ (17), 361 $[M]^+$ (55), 256 (22), 221 (44), 165 (14), 118 (28), 105 (100), 77 (23); HRMS (MALDI) for $C_{22}H_{17}ClNO_2$, $[M + H]^+$ (362.0948), found 362.0958.

*N-Allyl-N-(5-bromo-2-phenylbenzofuran-3-yl)benzamide (**10c**).* Reaction condition, 5 h; white solid (66.4 mg, 77% yield): R_f 0.5 (ethyl acetate/hexanes 1/5); mp 141.8−142.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 7.73 (d, 2H, J = 7.2 Hz), 7.60 (d, 1H, J = 1.9 Hz), 7.46−7.35 (m, 4H), 7.27 (d, 1H, J = 8.7 Hz), 7.17 (d, 2H, J = 7.5 Hz), 7.11 (t, 1H, J = 7.4 Hz), 6.96 (t, 2H, J = 7.7 Hz), 6.10 (ddt, 1H, J = 16.8 Hz, 10.0 Hz, 6.8 Hz), 5.22−5.15 (m, 2H), 4.84 (dd, 1H, J = 14.2 Hz, 6.3 Hz), 4.25 (dd, 1H, J = 14.2 Hz, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 171.1, 151.4, 150.6, 135.2, 132.3, 130.1, 129.5, 129.1, 128.9, 128.4, 128.1, 127.5, 127.0, 125.8, 121.6, 120.0, 119.8, 116.6, 113.1, 51.8; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3056 (m), 2927 (m), 1653 (s), 1492 (m), 1254 (s), 1117 (s), 690 (s); HRMS (EI) for $C_{24}H_{18}BrNO_2$, $[M]^+$ (431.0521), found 431.0510.

*N-Benzoyl-N-(5-bromo-2-phenylbenzofuran-3-yl)-4-nitrobenzamide (**10d**).* Reaction condition, 1 h; yellow solid (62.6 mg, 58% yield): R_f 0.28 (ethyl acetate/hexanes 1/10); mp 197.6−198.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.13 (d, 2H, J = 8.7 Hz), 7.69 (d, 2H, J = 8.8 Hz), 7.57 (dd, 3H, J = 10.2 Hz, 1.9 Hz), 7.51−7.46 (m, 4H), 7.43−7.38 (m, 4H), 7.30 (t, 2H, J = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 172.1, 170.7, 153.2, 151.9, 149.6, 139.5, 133.2, 132.9, 130.2, 129.1, 129.0, 128.8, 128.6, 128.5, 127.5, 127.3, 126.8, 123.6, 120.6, 117.3, 116.0, 113.8; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3089 (w), 1685 (s), 1601 (m), 1528 (s), 1347 (s), 1238 (s), 1081 (m), 685 (m); HRMS (EI) for $C_{28}H_{17}BrN_2O_5$, $[M]^+$ (540.0321), found 540.0322.

Typical Procedure for the Preparation of Oxazoles 11 (Scheme 5). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of **3** (0.1 mmol) in THF (0.15 mL) and methanol (0.15 mL). To this stirred reaction mixture, sodium methoxide (10.8 mg, 2.0 equiv) was added. The reaction mixture was further stirred for indicated time at room temperature. Thereafter the resulting mixture was extracted with CH_2Cl_2 followed by washing with 1 N $HCl_{(aq)}$. The organic layer was dried over anhydrous $MgSO_4$ and then the solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished the desired adduct **11**.

*4-Bromo-2-(2,5-diphenyloxazol-4-yl)phenol (**11a**).* Reaction condition, 26 h; white solid (31.7 mg, 81% yield): R_f 0.64 (ethyl acetate/hexanes 1/10); mp 147.7−148.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.66 (s, 1H), 8.08 (dd, 2H, J = 9.7 Hz, 3.7 Hz), 7.72 (dd, 2H, J = 7.9 Hz, 1.5 Hz), 7.60 (d, 1H, J = 2.4 Hz), 7.52−7.46 (m, 6H), 7.29 (dd, 1H, J = 8.8 Hz, 2.4 Hz), 6.92 (d, 1H, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 159.5, 155.2, 146.2, 132.8, 132.7, 131.2, 129.8, 129.1, 128.99, 128.97, 128.2, 127.7, 126.6, 125.9, 119.6, 117.2, 111.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3718 (w), 3056 (m), 1605 (w), 1556 (m), 1472 (s), 1282 (s), 1238 (s), 681 (s); MS (70 eV, EI) m/z (%) 393 $[M+2]^+$ (39), 391 $[M]^+$ (31), 288 (24), 259 (6), 207 (5), 181 (5), 152 (15), 126 (3), 105 (100), 77 (57); HRMS (EI) for $C_{21}H_{14}BrNO_2$, $[M]^+$ (391.0208), found 391.0200.

*4-Bromo-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenol (**11b**).* Reaction condition, 16 h; white solid (30.0 mg, 78% yield): R_f 0.18 (dichloromethane/hexanes 1/6); mp 124.1−124.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.36 (s, 1H), 8.09 (d, 2H, J = 7.0 Hz), 7.65 (d, 1H, J = 2.1 Hz), 7.62−7.52 (m, 3H), 7.42 (dd, 1H, J = 8.8 Hz, 2.4 Hz), 6.94 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 161.1, 155.8, 139.2 (quart, J = 2.7 Hz), 134.5, 133.6 (quart, J = 43.6 Hz), 132.6, 130.8 (quart, J = 4.3 Hz), 129.3, 127.3, 124.6, 119.9, 119.4 (quart, J = 268.4 Hz), 114.1, 111.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (m), 3015 (m), 1600 (m), 1558 (m), 1421 (m), 1131 (s), 712 (m); MS (70 eV, EI) m/z (%) 385 $[M+2]^+$ (45), 383 $[M]^+$ (62), 365 (7), 288 (23), 211 (10), 185 (14), 105 (100), 76 (53); HRMS (EI) for $C_{16}H_9BrF_3NO_2$, $[M]^+$ (382.9769), found 382.9762.

*4-Chloro-2-(2-phenyl-5-(trifluoromethyl)oxazol-4-yl)phenol (**11c**).* Reaction condition, 24 h; white solid (30.5 mg, 90% yield): R_f 0.45 (ethyl acetate/hexanes 1/10); mp 119.9−120.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.34 (s, 1H), 8.09 (d, 2H, J = 7.5 Hz), 7.61−7.51 (m, 4H), 7.28 (dd, 1H, J = 8.8 Hz, 2.1 Hz), 6.99 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 161.0, 155.3, 139.3 (quart, J = 2.8 Hz), 133.6 (quart, J = 43.6 Hz), 132.6, 131.6, 129.2, 127.8 (quart, J = 4.2 Hz), 127.2, 124.7, 124.5, 119.44, 119.40 (quart, J = 268.4 Hz), 113.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3084 (m), 3023 (m), 1600 (m), 1474 (s), 1417 (s), 1131 (s), 712 (s); MS (70 eV, EI) m/z (%) 341 $[M+2]^+$ (27), 339 $[M]^+$ (100), 319 (11), 242 (34), 241 (20), 169 (5), 167 (14), 111 (20), 105 (64), 75 (15); HRMS (EI) for $C_{16}H_9ClF_3NO_2$, $[M]^+$ (339.0274), found 339.0277.

*2-(2-Phenyl-5-(trifluoromethyl)oxazol-4-yl)phenol (**11d**).* Reaction condition, 6 h; white solid (23.2 mg, 76% yield): R_f 0.49 (ethyl acetate/hexanes 1/10); mp 127.2−128.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.34 (s, 1H), 8.11 (dd, 2H, J = 6.8 Hz, 1.5 Hz), 7.60−7.52 (m, 4H), 7.35 (td, 1H, J = 8.5 Hz, 1.4 Hz), 7.06 (dd, 1H, J = 8.3 Hz, 0.6 Hz), 6.96 (td, 1H, J = 8.1 Hz, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 160.8, 156.7, 140.6 (quart, J = 2.6 Hz), 133.2 (quart, J = 43.4 Hz), 132.4, 131.8, 129.2, 128.5 (quart, J = 3.8 Hz), 127.3, 124.9, 119.9, 119.7 (quart, J = 268.1 Hz), 118.0, 112.4; MS (70 eV, EI) m/z (%) 305 $[M]^+$ (36), 208 (10), 202 (34), 200 (100), 182 (35), 152 (42), 119 (5), 103 (36), 77 (5); HRMS (EI) for $C_{16}H_{10}F_3NO_2$, $[M]^+$ (305.0664), found 305.0668.

Typical Procedure for the Preparation of Trisubstituted Oxazoles 12a−c from Aryne (Scheme 5). A flame-dried and nitrogen-flushed 10 mL Schlenk tube, equipped with a magnetic stirring bar and a septum, was charged with a solution of oxazoles **11** (0.1 mmol) and CsF (45.6 mg, 3.0 equiv) in anhydrous MeCN (1.0 mL). To this stirred reaction mixture, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (30 μL, 1.2 equiv) was added slowly at 60 °C. The reaction mixture was further stirred for indicated time at 60 °C (monitored by ^{1}H NMR data analysis). Thereafter the resulting mixture was extracted with ethyl acetate followed by washing with sat. $NaHCO_{3(aq)}$. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed by evaporation in vacuo. Purification by flash chromatography furnished the desired adduct **12**.

*4-(5-Bromo-2-phenoxyphenyl)-2,5-diphenyloxazole (**12a**).* Reaction condition, 17 h; white solid (29.0 mg, 62% yield): R_f 0.44 (ethyl acetate/hexanes 1/20); mp 140.1−141.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.13−8.10 (m, 2H), 7.89 (d, 1H, J = 2.6 Hz), 7.57 (dd, 2H, J = 8.3 Hz, 1.5 Hz), 7.49−7.44 (m, 4H), 7.41−7.34 (m, 3H), 7.16 (t, 2H, J = 8.0 Hz), 6.97 (t, 1H, J = 7.3 Hz), 6.81 (d, 1H, J = 8.8 Hz), 6.63 (dd, 1H, J = 8.7 Hz, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 160.1, 156.0, 153.9, 147.6, 134.4, 132.7, 131.2, 130.5, 129.5, 128.9, 128.8, 128.5, 128.4, 127.2, 126.5, 126.2, 125.9, 123.5, 120.0, 118.7, 115.9; MS (70 eV, EI) m/z (%) 469 $[M+2]^+$ (21), 467 $[M]^+$ (21), 364 (7), 283 (11), 255 (17), 226 (11), 180 (69), 152 (39), 126 (13), 105 (100), 77 (55); HRMS (EI) for $C_{27}H_{18}BrNO_2$, $[M]^+$ (467.0521), found 467.0529.

*4-(5-Bromo-2-phenoxyphenyl)-2-phenyl-5-(trifluoromethyl)-oxazole (**12b**).* Reaction condition, 1 h; colorless oil (40.4 mg, 88% yield): R_f 0.38 (dichloromethane/hexanes 1/3.5); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.10 (dd, 2H, J = 7.8 Hz, 1.6 Hz), 7.78 (d, 1H, J = 2.6 Hz), 7.53−7.43 (m, 4H), 7.32 (t, 2H, J = 8.0 Hz), 7.11 (t, 1H, J = 7.4 Hz), 6.99 (dd, 2H, J = 8.7 Hz, 1.0 Hz), 6.78 (d, 1H, J = 8.8 Hz); ^{13}C

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NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 162.2, 155.7, 154.4, 136.7 (quart, J = 2.2 Hz), 135.8 (quart, J = 42.6 Hz), 133.83, 133.75, 131.7, 129.9, 128.9, 127.1, 125.9, 124.2, 122.9, 119.5, 119.3 (quart, J = 268.0 Hz), 119.0, 115.2; MS (70 eV, EI) m/z (%) 461 $[M+2]^+$ (93), 459 $[M]^+$ (100), 369 (4), 366 (11), 327 (9), 279 (10), 249 (15), 190 (8), 180 (32), 152 (28), 105 (89), 77 (63); HRMS (EI) for $C_{22}H_{13}BrF_3NO_2$, $[M]^+$ (459.0082), found 459.0090.

*4-(5-Chloro-2-phenoxyphenyl)-2-phenyl-5-(trifluoromethyl)-oxazole (**12c**).* Reaction condition, 1 h; colorless oil (32.8 mg, 79% yield): R_f 0.33 (ethyl acetate/hexanes 1/20); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.10 (dd, 2H, J = 7.6 Hz, 1.2 Hz), 7.64 (d, 1H, J = 2.5 Hz), 7.54−7.47 (m, 3H), 7.34−7.30 (m, 3H), 7.11 (t, 1H, J = 7.5 Hz), 7.0 (d, 2H, J = 8.4 Hz), 6.85 (d, 1H, J = 8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 162.2, 155.9, 153.8, 136.9 (quart, J = 2.3 Hz), 135.8 (quart, J = 42.6 Hz), 131.7, 131.0, 130.8, 129.9, 129.0, 128.1, 127.1, 125.9, 124.1, 122.5, 119.37, 119.36 (quart, J = 268.0 Hz), 118.8; MS (70 eV, EI) m/z (%) 417 $[M+2]^+$ (5), 415 $[M]^+$ (14), 249 (4), 4 (6), 180 (5), 152 (16), 105 (100), 84 (40), 77 (30); HRMS (EI) for $C_{22}H_{13}ClF_3NO_2$, $[M]^+$ (415.0587), found 415.0580.

Typical Procedure for the Preparation of Imines 1. To a 50 mL round-bottom flask equipped with a magnetic stirring bar was added Cs_2CO_3 (1.6 g, 5.0 equiv) and Na_2SO_4 (717.4 mg, 5.0 equiv). The solids were flame-dried under a high vacuum and allowed to cool. To the solids were added CH_2Cl_2 (20 mL). The resulting slurry was vigorously stirred under N_2 and the requisite α-amido sulfone (1 mmol) was added in one portion. After stirring room temperature for 1 h, hexanes (~20 mL) was added and the mixture was filtered through Celite. The Celite was rinsed with hexanes (2 × 20 mL) and the resulting filtrate was concentrated under reduced pressure. This resulted in a concentrated material that was filtered and washed with hexanes (2 × 20 mL). The imine **1** was dried in vacuo and used without further purification.

*(E)-2-((Benzoylimino)methyl)-4-bromophenyl benzoate (**1a**).* Reaction condition, 1 h; white solid (219.8 mg, 54% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.88 (s, 1H), 8.41 (d, 1H, J = 2.5 Hz), 8.19 (d, 2H, J = 7.5 Hz), 8.07 (d, 2H, J = 7.5 Hz), 7.75 (dd, 1H, J = 8.7 Hz, 2.5 Hz), 7.66 (t, 1H, J = 7.5 Hz), 7.58 (t, 1H, J = 7.5 Hz), 7.51 (t, 2H, J = 7.7 Hz), 7.45 (t, 2H, J = 7.7 Hz), 7.24 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ/ppm 180.6, 164.6, 158.1, 151.1, 136.9, 134.3, 133.8, 132.7, 131.8, 130.4, 130.2, 128.8, 128.6, 128.5, 128.3, 125.2, 119.8; MS (70 eV, EI) m/z (%) 409 $[M+2]^+$ (17), 407 $[M]^+$ (8), 306 (20), 304 (33), 288 (5), 208 (8), 105 (100), 77 (95); HRMS (FAB) for $C_{21}H_{15}BrNO_3$, $[M+H]^+$ (408.0235), found 408.0239.

*(E)-2-((Benzoylimino)methyl)-4-chlorophenyl benzoate (**1b**).* Reaction condition, 1 h; white solid (167.0 mg, 46% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.88 (s, 1H), 8.25 (d, 1H, J = 1.9 Hz), 8.18 (d, 2H, J = 7.6 Hz), 8.07 (d, 2H, J = 7.6 Hz), 7.65 (t, 1H, J = 7.4 Hz), 7.61−7.56 (m, 2H), 7.51 (t, 2H, J = 7.6 Hz), 7.44 (t, 2H, J = 7.5 Hz), 7.30 (d, 1H, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.6, 164.6, 158.2, 150.6, 134.3, 133.9, 133.8, 132.7, 132.3, 130.4, 130.2, 128.8, 128.7, 128.5, 128.3, 128.2, 124.9; MS (70 eV, EI) m/z (%) 365 $[M+2]^+$ (8), 363 $[M]^+$ (28), 127 (1), 121 (14), 105 (100), 77 (42); HRMS (EI) for $C_{21}H_{14}ClNO_3$, $[M]^+$ (363.0662), found 363.0662.

*(E)-2-((Benzoylimino)methyl)-4-methoxyphenyl benzoate (**1c**).* Reaction condition, 1 h; white solid (251.4 mg, 70% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.88 (s, 1H), 8.19 (d, 2H, J = 7.5 Hz), 8.06 (d, 2H, J = 7.5 Hz), 7.73 (d, 1H, J = 2.0 Hz), 7.62 (t, 1H, J = 7.2 Hz), 7.55(t, 1H, J = 7.3 Hz), 7.50 (t, 2H, J = 7.5 Hz), 7.43 (t, 2H, J = 7.5 Hz), 7.25−7.17 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.9, 165.2, 159.1, 157.6, 146.0, 134.0, 133.5, 133.0, 130.3, 130.1, 128.7, 128.4, 127.4, 124.4, 121.2, 111.8, 55.8; MS (70 eV, EI) m/z (%) 359 $[M]^+$ (31), 256 (60), 238 (7), 181 (1), 151 (19), 121(73), 105 (100), 77 (64), 51 (70); HRMS (EI) for $C_{22}H_{17}NO_4$, $[M]^+$ (359.1158), found 359.1152.

*(E)-2-((Benzoylimino)methyl)phenyl 4-bromobenzoate (**1d**).* Reaction condition, 1 h; white solid (305.3 mg, 75% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.90 (s, 1H), 8.22 (dd, 1H, J = 7.8 Hz, 1.2 Hz), 8.06−8.03 (m, 4H), 7.67−7.62 (m, 3H), 7.55 (t, 1H, J = 7.4 Hz), 7.46−7.39 (m, 3H), 7.32 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.7, 164.2, 159.5, 151.7, 134.2, 133.5, 133.0, 132.1, 131.8, 130.12, 130.09, 129.3, 128.4, 127.7, 126.9, 126.6, 123.4; MS (70 eV, EI) m/z (%) 409 $[M+2]^+$ (17), 407 $[M]^+$ (17), 304 (5), 224 (7), 185 (41), 183 (53), 157 (26), 155 (28), 121 (2), 105 (100), 77 (59); HRMS (EI) for $C_{21}H_{14}BrNO_3$, $[M]^+$ (407.0157), found 407.0157.

*(E)-2-((Benzoylimino)methyl)-4-methoxyphenyl 4-bromobenzoate (**1e**).* Reaction condition, 1 h; white solid (297.2 mg, 68% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.84 (s, 1H), 8.06−8.03 (m, 4H), 7.71 (d, 1H, J = 2.8 Hz), 7.64 (d, 2H, J = 8.5 Hz), 7.57 (tt, 1H, J = 7.4 Hz, 1.1 Hz), 7.43 (t, 2H, J = 7.6 Hz), 7.25 (d, 1H, J = 7.8 Hz), 7.20−7.17 (m, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.8, 164.6, 159.1, 157.7, 145.7, 133.6, 132.9, 132.1, 131.8, 130.1, 129.3, 128.5, 127.7, 127.4, 124.3, 121.1, 112.3, 55.9; MS (70 eV, EI) m/z (%) 439 $[M+2]^+$ (13), 437 $[M]^+$ (13), 336 (9), 334 (12), 256 (12), 185 (20), 183 (20), 105 (100), 84 (2); HRMS (EI) for $C_{22}H_{16}BrNO_4$, $[M]^+$ (437.0263), found 437.0254.

*(E)-2-((Benzoylimino)methyl)-4-bromophenyl thiophene-2-carboxylate (**1f**).* Reaction condition, 1 h; white solid (251.9 mg, 61% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.90 (s, 1H), 8.39 (s, 1H), 8.08 (d, 2H, J = 7.7 Hz), 7.99 (d, 1H, J = 3.2 Hz), 7.73 (d, 1H, J = 8.6 Hz), 7.69 (d, 1H, J = 4.8 Hz), 7.59 (t, 1H, J = 7.4 Hz), 7.46 (t, 2H, J = 7.5 Hz), 7.27 (d, 1H, J = 8.5 Hz), 7.18 (t, 1H, J = 4.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.5, 159.8, 158.1, 150.6, 136.8, 135.6, 134.6, 133.8, 132.8, 131.7, 131.3, 130.2, 128.6, 128.3, 125.1, 119.9; HRMS (MALDI) for $C_{19}H_{12}BrNO_3SNa$, $[M + Na]^+$ (435.9619), found 435.9593.

*(E)-2-((Benzoylimino)methyl)phenyl 4-chlorobenzoate (**1g**).* Reaction condition, 1 h; white solid (192.4 mg, 53% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.90 (s, 1H), 8.22 (d, 1H, J = 6.9 Hz), 8.13 (d, 2H, J = 8.5 Hz), 8.04 (d, 2H, J = 7.5 Hz), 7.65 (t, 1H, J = 7.8 Hz), 7.54 (t, 1H, J = 7.4 Hz), 7.47−7.44 (m, 3H), 7.43−7.39 (m, 2H), 7.32 (d, 1H, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.8, 164.1, 159.5, 151.7, 140.6, 134.2, 133.6, 132.9, 131.7, 130.1, 129.1, 128.4, 127.1, 126.8, 126.6, 123.4; MS (70 eV, EI) m/z (%) 365 $[M+2]^+$ (8), 363 $[M]^+$ (14), 224 (5), 139 (100), 105 (54), 77 (25); HRMS (EI) for $C_{21}H_{14}ClNO_3$, $[M]^+$ (363.0662), found 363.0671.

*(E)-2-((Benzoylimino)methyl)phenyl 4-methoxybenzoate (**1h**).* Reaction condition, 40 min; white solid (4.5 mg, 60% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.94 (s, 1H), 8.25 (dd, 1H, J = 7.8 Hz, 1.4 Hz), 8.15 (d, 2H, J = 8.9 Hz), 8.07 (d, 2H, J = 7.6 Hz), 7.63 (td, 1H, J = 7.9 Hz, 1.6 Hz), 7.55 (td, 1H, J = 7.4 Hz, 1.4 Hz), 7.42 (td, 3H, J = 7.7 Hz, 1.6 Hz), 7.32 (d, 1H, J = 8.2 Hz), 6.96 (d, 2H, J = 8.9 Hz), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.9, 164.5, 164.2, 159.5, 152.3, 134.1, 133.5, 133.0, 132.5, 130.1, 129.4, 128.4, 127.0, 126.3, 123.5, 120.8, 114.0, 55.5; MS (70 eV, EI) m/z (%) 360 $[M]^+$ (27), 238 (13), 208 (27), 135 (100), 105 (7), 77 (5); HRMS (EI) for $C_{22}H_{17}NO_4$, $[M]^+$ (359.1158), found 359.1158.

*(E)-2-((Benzoylimino)methyl)-4-methoxyphenyl 4-methoxybenzoate (**1i**).* Reaction condition, 40 min; white solid (245.1 mg, 63% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.87 (s, 1H), 8.14 (d, 2H, J = 8.8 Hz), 8.07 (d, 2H, J = 7.3 Hz), 7.74 (d, 1H, J = 2.9 Hz), 7.57 (t, 1H, J = 7.4 Hz), 7.44 (t, 2H, J = 7.8 Hz), 7.26−7.17 (m, 2H), 6.96 (d, 2H, J = 8.8 Hz), 3.91 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 181.0, 164.9, 164.2, 159.1, 157.5, 146.3, 133.5, 133.0, 132.5, 130.1, 128.5, 127.5, 124.5, 121.3, 120.9, 114.0, 111.5, 55.9, 55.5; MS (70 eV, EI) m/z (%) 389 $[M]^+$ (34), 332 (1), 268 (2), 256 (7), 185 (5), 149 (2), 135 (100), 77 (7); HRMS (ESI) for $C_{23}H_{20}NO_5$, $[M+H]^+$ (390.1341), found 390.1342.

*(E)-2-((Benzoylimino)methyl)-4-chlorophenyl 4-bromobenzoate (**1j**).* Reaction condition, 12 min; white solid (48.5 mg, 22% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.84 (s, 1H), 8.24 (d, 1H, J = 2.6 Hz), 8.05 (t, 4H, J = 6.8 Hz), 7.65 (d, 2H, J = 8.5 Hz), 7.62−7.57 (m, 2H), 7.45 (t, 2H, J = 7.6 Hz), 7.29 (d, 1H, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.5, 164.0, 158.2, 150.3, 134.0, 133.8, 132.7, 132.5, 132.3, 131.8, 130.2, 129.7, 129.1, 128.6, 128.2, 127.2, 124.9; MS (70 eV, EI) m/z (%) 443 $[M+2]^+$ (36), 441 $[M]^+$ (37), 191 (6), 185 (95), 183 (100), 157 (21), 155 (26), 105 (79), 77 (18); HRMS (MALDI) for $C_{21}H_{14}BrClNO_3$, $[M + H]^+$ (441.9846), found 441.9858.

*(E)-2-((Benzoylimino)methyl)-4-bromophenyl cyclohexanecarboxylate (**1k**).* Reaction condition, 1 h; white solid (227.2 mg, 55% yield): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.81 (s, 1H), 8.35 (d, 1H, J = 2.2 Hz), 8.13 (d, 2H, J = 7.6 Hz), 7.67 (dd, 1H, J = 8.9 Hz, 2.3

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Hz), 7.61 (t, 1H, J = 7.4 Hz), 7.49 (t, 2H, J = 7.6 Hz), 7.08 (d, 1H, J = 8.6 Hz), 2.61 (tt, 1H, J = 11.2 Hz, 3.4 Hz), 2.06−2.04 (m, 2H), 1.82−1.78 (m, 2H), 1.69−1.66 (m, 1H), 1.58 (qd, 2H, J = 11.5 Hz, 2.7 Hz), 1.38−1.23 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 180.5, 173.7, 158.1, 151.2, 136.7, 133.8, 132.8, 131.3, 130.2, 128.6, 128.3, 125.0, 119.5, 43.1, 28.8, 25.5, 25.2; HRMS (ESI) for $C_{21}H_{21}BrNO_3$, $[M + H]^+$ (414.0699), found 414.0692.

Typical Procedure for the Preparation of α-Amido Sulfone Precursors.[16] To a flame-dried and nitrogen-flushed 500 mL flask equipped with a magnetic stirring bar was added benzamide (917.7 mg, 1.5 equiv), *p*-toluene sulfinic acid sodium salt monohydrate (1.4 g, 1.5 equiv), anhydrous MeCN (100 mL), and aldehyde precursors (5.0 mmol), sequentially. The resulting slurry was then cooled to 0 °C (ice bath), and TMSCl (1.3 mL, 2.0 equiv) was added over 15 min. The reaction was allowed to warm to room temperature and stir for indicated time. At this point, the solvent was removed under reduced pressure and to the resulting white solid was added Et_2O (∼25 mL). This resulted in a suspension that was filtered and washed with Et_2O (2 × 25 mL). The crude α-amido sulfone was dried in vacuo and used without further purification.

*2-(Benzamido(tosyl)methyl)-4-bromophenyl benzoate (**23a**).* Reaction condition, 24 h; white solid (2.4 g, 85% yield): mp 161.0−162.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.25 (d, 2H, J = 7.6 Hz), 7.82 (s, 1H), 7.73−7.57 (m, 9H), 7.49 (t, 1H, J = 7.2 Hz), 7.36 (t, 2H, J = 7.5 Hz), 7.30 (t, 1H, J = 8.7 Hz), 7.13 (d, 2H, J = 7.8 Hz), 6.90 (d, 1H, J = 10.3 Hz), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 166.3, 163.4, 148.5, 145.6, 134.1, 133.6, 133.4, 132.52, 132.45, 132.4, 130.3, 129.8, 129.0, 128.9, 128.8, 128.6, 127.2, 125.1, 125.0, 119.1, 67.3, 21.6; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3374 (m), 3061 (m), 2962 (m), 1749 (s), 1680 (s), 1592 (m), 1509 (s), 1322 (s), 1219 (s), 701 (s); HRMS (FAB) for $C_{28}H_{23}BrNO_5S$, $[M + H]^+$ (564.0480), found 564.0480.

*2-(Benzamido(tosyl)methyl)-4-chlorophenyl benzoate (**23b**).* Reaction condition, 48 h; white solid (2.0 g, 77% yield): mp 173.1−173.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.25 (d, 2H, J = 7.6 Hz), 7.73−7.65 (m, 4H), 7.60−7.55 (m, 5H), 7.49 (t, 1H, J = 7.4 Hz), 7.44 (dd, 1H, J = 8.8 Hz, 2.2 Hz), 7.38−7.35 (m, 3H), 7.14 (d, 2H, J = 8.0 Hz), 6.90 (d, 1H, J = 10.3 Hz), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 166.2, 163.5, 147.9, 145.6, 134.1, 133.4, 132.5, 132.4, 131.6, 130.7, 130.3, 129.9, 129.5, 129.0, 128.88, 128.86, 128.7, 127.2, 124.7, 124.6, 67.4, 21.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3382 (m), 3069 (w), 2969 (w), 1749 (s), 1684 (s), 1596 (s), 1486 (s), 1326 (s), 1227 (s), 1139 (s), 705 (s); HRMS (ESI) for $C_{28}H_{22}ClNO_5SNa$, $[M + Na]^+$ (542.0805), found 542.0812.

*2-(Benzamido(tosyl)methyl)-4-methoxyphenyl benzoate (**23c**).* Reaction condition, 48 h; white solid (1.9 g, 74% yield): mp 174.5−175.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.25 (d, 2H, J = 7.6 Hz), 7.70 (t, 1H, J = 7.3 Hz), 7.63 (d, 2H, J = 7.6 Hz), 7.59−7.55 (m, 5H), 7.47 (t, 1H, J = 7.2 Hz), 7.36−7.30 (m, 3H), 7.17 (s, 1H), 7.13 (d, 2H, J = 7.8 Hz), 7.00 (dd, 1H, J = 8.8 Hz, 2.0 Hz), 6.85 (d, 1H, J = 10.4 Hz), 3.76 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 166.2, 164.2, 157.2, 145.3, 142.9, 133.8, 133.7, 132.9, 132.2, 130.2, 129.7, 129.3, 129.1, 128.8, 128.6, 127.2, 124.3, 123.6, 116.1, 114.8, 68.2, 55.7, 21.6; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (s), 1749 (m), 1680 (m), 1592 (m), 1505 (m), 1333 (m), 1059 (m); HRMS (ESI) for $C_{29}H_{25}NO_6SNa$, $[M + Na]^+$ (538.1300), found 538.1288.

*2-(Benzamido(tosyl)methyl)phenyl 4-bromobenzoate (**23d**).* Reaction condition, 24 h; white solid (4.4 g, 79% yield): mp 167.8−168.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.11 (d, 2H, J = 8.5 Hz), 7.75 (d, 1H, J = 7.8 Hz), 7.71 (d, 2H, J = 8.4 Hz), 7.63 (d, 3H, J = 7.2 Hz), 7.56 (d, 2H, J = 8.2 Hz), 7.48 (quart, 2H, J = 7.1 Hz), 7.49−7.29 (m, 4H), 7.14 (d, 2H, J = 8.1 Hz), 6.91 (d, 1H, J = 10.4 Hz), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 166.3, 163.1, 149.2, 145.4, 133.6, 132.7, 132.24, 132.18, 131.7, 130.7, 129.8, 129.2, 129.0, 128.6, 128.1, 127.1, 126.3, 123.2, 122.9, 67.5, 21.6; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3397 (m), 3061 (w), 1749 (s), 1684 (s), 1589 (s), 1520 (s), 1486 (s), 1257 (s), 1219 (s), 1074 (s), 579 (s); HRMS (ESI) for $C_{28}H_{22}BrNO_5SNa$, $[M + Na]^+$ (586.0300), found 586.0298.

*2-(Benzamido(tosyl)methyl)-4-methoxyphenyl 4-bromobenzoate (**23e**).* Reaction condition, 24 h; white solid (2.8 g, 95% yield): mp 174.8−175.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ/ppm 9.84 (d, 1H, J = 10.3 Hz), 8.03 (d, 2H, J = 8.4 Hz), 7.92 (d, 2H, J = 8.4 Hz), 7.78 (d, 1H, J = 2.6 Hz), 7.70 (d, 2H, J = 7.5 Hz), 7.55 (t, 3H, J = 7.8 Hz), 7.45 (t, 2H, J = 7.5 Hz), 7.34 (dd, 3H, J = 10.3 Hz, 2.7 Hz), 7.11 (dd, 1H, J = 8.9 Hz, 2.7 Hz), 6.88 (d, 1H, J = 10.2 Hz), 3.82 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ/ppm 167.2, 163.6, 157.5, 145.5, 142.5, 134.3, 133.4, 132.7, 132.3, 132.0, 130.2, 129.1, 128.8, 128.6, 128.5, 128.3, 124.5, 124.1, 116.5, 115.9, 66.8, 56.4, 21.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3389 (m), 3084 (m), 2962 (m), 1745 (s), 1688 (s), 1592 (s), 1501 (s), 1326 (s), 1257 (s), 1139 (s), 712 (m); HRMS (ESI) for $C_{29}H_{24}BrNO_6SNa$, $[M + Na]^+$ (616.0405), found 616.0399.

*2-(Benzamido(tosyl)methyl)-4-bromophenyl thiophene-2-carboxylate (**23f**).* Reaction condition, 120 h; white solid (1.1 g, 79% yield): mp 196.2−197.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ/ppm 9.83 (d, 1H, J = 10.3 Hz), 8.44 (d, 1H, J = 2.2 Hz), 8.20 (d, 1H, J = 4.2 Hz), 8.04 (d, 1H, J = 2.8 Hz), 7.75 (dd, 1H, J = 8.7 Hz, 2.4 Hz), 7.70 (d, 2H, J = 7.4 Hz), 7.56 (d, 3H, J = 8.2 Hz), 7.48−7.43 (m, 3H), 7.40 (t, 1H, J = 4.4 Hz), 7.32 (d, 2H, J = 8.1 Hz), 6.99 (d, 1H, J = 10.3 Hz), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ/ppm 167.3, 159.1, 148.2, 145.9, 136.5, 136.0, 134.0, 133.9, 133.6, 133.2, 132.6, 131.7, 130.4, 129.5, 129.2, 128.8, 128.4, 126.0, 125.7, 119.1, 66.2, 21.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3363 (w), 3105 (w), 2952 (w), 1742 (s), 1685 (s), 1593 (w), 1512 (m), 1214 (s), 702 (m); HRMS (MALDI) for $C_{26}H_{20}BrNO_5S_2Na$, $[M + Na]^+$ (591.9864), found 591.9877.

*2-(Benzamido(tosyl)methyl)phenyl 4-chlorobenzoate (**23g**).* Reaction condition, 72 h; white solid (1.3 g, 98% yield): mp 174.7−175.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ/ppm 9.84 (d, 1H, J = 10.3 Hz), 8.20 (dd, 1H, J = 7.6 Hz, 0.9 Hz), 8.12 (d, 2H, J = 8.5 Hz), 7.79 (d, 2H, J = 8.5 Hz), 7.68 (d, 2H, J = 7.3 Hz), 7.56−7.52 (m, 4H), 7.46−7.40 (m, 4H), 7.32 (d, 2H, J = 8.1 Hz), 6.93 (d, 1H, J = 10.3 Hz), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ/ppm 167.4, 163.3, 149.3, 145.7, 139.9, 134.3, 133.4, 132.6, 132.1, 131.3, 131.2, 130.4, 130.0, 129.2, 128.8, 128.4, 128.1, 126.9, 123.8, 123.5, 66.6, 21.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3379 (m), 3040 (w), 2960 (w), 1754 (s), 1673 (s), 1593 (m), 1516 (s), 1488 (s), 1315 (s), 1218 (s), 1060 (s), 714 (m); HRMS (ESI) for $C_{28}H_{22}ClNO_5SNa$, $[M + Na]^+$ (542.0805), found 542.0802.

*2-(Benzamido(tosyl)methyl)phenyl 4-methoxybenzoate (**23h**).* Reaction condition, 48 h; white solid (2.3 g, 89% yield): mp 156.6−157.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.21 (d, 2H, J = 8.8 Hz), 7.64−7.62 (m, 3H), 7.59 (d, 2H, J = 8.1 Hz), 7.51−7.46 (m, 3H), 7.40−7.35 (m, 3H), 7.31 (t, 1H, J = 7.4 Hz), 7.16 (d, 2H, J = 8.0 Hz), 7.04 (d, 2H, J = 8.8 Hz), 6.88 (d, 1H, J = 10.4 Hz), 3.94 (s, 1H), 2.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 166.3, 164.2, 163.4, 149.5, 145.3, 133.7, 132.8, 132.4, 132.1, 130.6, 129.9, 129.7, 129.0, 128.6, 127.1, 125.9, 123.4, 122.8, 121.3, 114.1, 68.0, 55.6, 21.6; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3382 (m), 3046 (w), 2977 (w), 1752 (s), 1676 (s), 1608 (s), 1512 (s), 1257 (s), 1219 (s), 1170 (s), 709 (m), 568 (s); HRMS (ESI) for $C_{29}H_{25}NO_6SNa$, $[M + Na]^+$ (538.1300), found 538.1297.

*2-(Benzamido(tosyl)methyl)-4-methoxyphenyl 4-methoxybenzoate (**23i**).* Reaction condition, 48 h; white solid (1.2 g, 90% yield): mp 164.6−165.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.20 (d, 2H, J = 8.8 Hz), 7.62 (t, 4H, J = 9.6 Hz), 7.55 (d, 1H, J = 10.3 Hz), 7.47 (t, 1H, J = 7.4 Hz), 7.34 (t, 2H, J = 7.8 Hz), 7.29 (d, 1H, J = 9.0 Hz), 7.17−7.13 (m, 3H), 7.03 (d, 2H, J = 8.9 Hz), 6.99 (dd, 1H, J = 9.0 Hz, 3.0 Hz), 6.84 (d, 1H, J = 10.4 Hz), 3.93 (s, 3H), 3.77 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 166.3, 164.1, 163.9, 157.1, 145.3, 143.1, 133.9, 132.9, 132.4, 132.2, 129.7, 129.1, 128.6, 127.2, 124.4, 123.6, 121.5, 116.1, 114.8, 114.1, 68.3, 55.8, 55.6, 21.6; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3387 (m), 3065 (w), 2968 (w), 1742 (s), 1681 (s), 1605 (s), 1512 (s), 1258 (s), 1165 (s); HRMS (MALDI) for $C_{30}H_{27}NO_7SNa$, $[M + Na]^+$ (568.1406), found 568.1421.

*2-(Benzamido(tosyl)methyl)-4-chlorophenyl 4-bromobenzoate (**23j**).* Reaction condition, 36 h; white solid (2.5 g, 85% yield): mp 183.3−184.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 8.10 (d, 2H, J = 8.5 Hz), 7.72 (d, 2H, J = 8.5 Hz), 7.67−7.63 (m, 3H), 7.58 (d, 2H, J = 8.2 Hz), 7.53 (t, 1H, J = 7.2 Hz), 7.46 (dd, 1H, J = 8.7 Hz, 2.4 Hz), 7.42−7.34 (m, 4H), 7.18 (d, 2H, J = 8.1 Hz), 6.82 (d, 1H, J = 10.4 Hz), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 166.1, 163.0, 147.8, 145.8, 133.4, 132.6, 132.5, 132.3, 131.9, 131.7, 130.8, 129.9, 129.5, 129.0, 128.8, 127.8, 127.1, 124.8, 124.6, 67.1, 21.7; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3403 (w), 3056 (m), 2960 (m), 1746 (s), 1685 (s), 1585 (s),

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1516 (s), 1484 (s), 1222 (s), 1073 (s), 710 (s), 577 (s); HRMS (ESI) for $C_{28}H_{21}BrClNO_5SNa$, $[M + Na]^+$ (619.9910), found 619.9913.

*2-(Benzamido(tosyl)methyl)-4-bromophenyl cyclohexanecarboxylate (**23k**).* Reaction condition, 144 h; white solid (839.4 mg, 59% yield): mp 142.0−142.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ/ppm 9.75 (d, 1H, J = 10.3 Hz), 8.36 (d, 1H, J = 2.4 Hz), 7.70−7.65 (m, 5H), 7.55 (t, 1H, J = 7.4 Hz), 7.46 (t, 2H, J = 7.8 Hz), 7.40 (d, 2H, J = 8.2 Hz), 7.19 (d, 1H, J = 8.7 Hz), 6.78 (d, 1H, J = 10.2 Hz), 2.61 (tt, 1H, J = 11.1 Hz, 3.6 Hz), 2.35 (s, 3H), 2.06−1.99 (m, 2H), 1.79−1.75 (m, 1H), 1.67−1.62 (m, 1H), 1.52 (qd, 2H, J = 12.1 Hz, 3.2 Hz), 1.38−1.35 (m, 2H), 1.29−1.22 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ/ppm 173.5, 167.6, 149.0, 146.2, 134.2, 134.1, 133.9, 133.5, 132.9, 130.7, 129.6, 129.1, 128.6, 126.2, 125.9, 119.0, 66.4, 29.2, 29.1, 26.1, 25.53, 25.47, 21.9; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3206 (s), 3061 (s), 2931 (s), 2863 (s), 1752 (s), 1653 (s), 1615 (s), 1528 (s), 1330 (s), 1147 (s), 1109 (s), 697 (s); HRMS (ESI) for $C_{28}H_{28}BrNO_5SNa$, $[M + Na]^+$ (592.0764), found 592.0767.

Typical Procedure for the Preparation of Aldehyde Precursors.[9f] A dry and nitrogen-flushed 50 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with a solution of salicylaldehyde (10.0 mmol) in dry THF (20 mL). Acyl chloride **2** (1.05 equiv) and NEt_3 (1.5 mL, 1.1 equiv) was added, and the reaction mixture was stirred for indicated time at room temperature. Thereafter the resulting mixture was extracted with CH_2Cl_2 followed by washed with sat. $NaHCO_{3(aq)}$. The organic layer was dried over anhydrous $MgSO_4$ and then evaporated to afford aldehyde precursors.

*4-Bromo-2-formylphenyl benzoate (**22a**).* Reaction condition, 30 min; white solid (3 g, 99% yield): mp 117.0−118.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.16 (s, 1H), 8.22 (dd, 2H, J = 7.2 Hz, 1.2 Hz), 8.07 (d, 1H, J = 2.4 Hz), 7.79 (dd, 1H, J = 8.6 Hz, 2.5 Hz), 7.70 (t, 1H, J = 7.4 Hz), 7.55 (t, 2H, J = 7.7 Hz), 7.25 (d, 2H, J = 8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.8, 164.5, 151.3, 137.9, 134.2, 132.4, 130.3, 130.1, 129.5, 128.8, 128.4, 128.2, 125.3, 119.8; MS (70 eV, EI) m/z (%) 306 $[M+2]^+$ (30), 304 $[M]^+$ (28), 105 (100), 77 (58); HRMS (EI) for $C_{14}H_9BrO_3$, $[M]^+$ (303.9735), found 303.9739.

*4-Chloro-2-formylphenyl benzoate (**22b**).* Reaction condition, 1 h; white solid (2.5 g, 97% yield): mp 108.7−109.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.16 (s, 1H), 8.20 (dd, 2H, J = 7.3 Hz, 1.3 Hz), 7.89 (d, 1H, J = 2.6 Hz), 7.67 (t, 1H, J = 7.6 Hz), 7.61 (dd, 1H, J = 8.6 Hz, 2.8 Hz), 7.53 (t, 2H, J = 7.7 Hz), 7.29 (d, 1H, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.8, 164.6, 150.7, 135.0, 134.2, 132.3, 130.3, 129.3, 129.2, 128.8, 128.2, 125.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3092 (w), 2893 (w), 1745 (s), 1688 (s), 1592 (m), 1265 (s), 697 (s); MS (70 eV, EI) m/z (%) 262 $[M+2]^+$ (6), 260 $[M]^+$ (15), 181 (11), 157 (9), 155 (32), 139 (13), 127 (43), 105 (100), 97 (4), 75 (77), 63 (97); HRMS (EI) for $C_{14}H_9ClO_3$, $[M]^+$ (260.0240), found 260.0237.

*2-Formyl-4-methoxyphenyl benzoate (**22c**).* Reaction condition, 1 h; white solid (2.5 g, 99% yield): mp 75.7−76.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.19 (s, 1H), 8.23 (dd, 2H, J = 8.4 Hz, 1.4 Hz), 7.67 (tt, 1H, J = 7.5 Hz, 1.3 Hz), 7.54 (tt, 2H, J = 7.8 Hz, 1.3 Hz), 7.42 (d, 1H, J = 2.5 Hz), 7.26−7.20 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 188.0, 165.3, 157.7, 146.4, 134.0, 130.3, 128.8, 124.6, 122.4, 111.9, 55.9; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3000 (w), 2954 (w), 1730 (s), 1695 (s), 1600 (m), 1497 (s), 1269 (s), 693 (s); MS (70 eV, EI) m/z (%) 256 $[M]^+$ (17), 151 (8), 123 (3), 105 (100), 77 (77), 51 (26); HRMS (EI) for $C_{15}H_{12}O_4$, $[M]^+$ (256.0736), found 256.0730.

*2-Formylphenyl 4-bromobenzoate (**22d**).* Reaction condition, 30 min; white solid (3.0 g, 99% yield): mp 98.6−99.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.16 (s, 1H), 8.08 (d, 2H, J = 8.5 Hz), 7.93 (dd, 1H, J = 7.7 Hz, 1.5 Hz), 7.70−7.66 (m, 3H), 7.44 (t, 1H, J = 7.5 Hz), 7.31 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 188.4, 164.2, 151.7, 135.3, 132.1, 131.7, 130.9, 129.3, 128.2, 127.7, 126.6, 123.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 2840 (m), 1733 (m), 1684 (s), 1265 (s), 1067 (m), 758 (s); MS (70 eV, EI) m/z (%) 306 $[M+2]^+$ (20), 304 $[M]^+$ (20), 202 (58), 185 (100), 155 (52), 121 (38), 104 (8), 76 (39); HRMS (EI) for $C_{14}H_9BrO_3$, $[M]^+$ (303.9735), found 303.9729.

*2-Formyl-4-methoxyphenyl 4-bromobenzoate (**22e**).* Reaction condition, 1 h; white solid (3.3 g, 99% yield): mp 123.3−123.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.13 (s, 1H), 8.07 (d, 2H, J = 8.6 Hz), 7.68 (d, 2H, J = 8.5 Hz), 7.41 (dd, 1H, J = 2.0 Hz, 1.2 Hz), 7.22−7.21 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 188.0, 164.7, 157.8, 145.8, 132.1, 131.7, 129.3, 128.6, 127.6, 124.5, 122.2, 112.6, 55.9; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3092 (w), 2969 (m), 2870 (m), 1726 (s), 1691 (s), 1589 (s), 1493 (s), 1265 (s), 1070 (s), 750 (s); MS (70 eV, EI) m/z (%) 336 $[M+2]^+$ (14), 334 $[M]^+$ (14), 185 (97), 183 (100), 155 (26), 108 (8), 95 (16), 76 (30); HRMS (EI) for $C_{15}H_{11}BrO_4$, $[M]^+$ (333.9841), found 333.9846.

*4-Bromo-2-formylphenyl thiophene-2-carboxylate (**22f**).* Reaction condition, 1.5 h; white solid (1.5 g, 97% yield): mp 100.1−100.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.17 (s, 1H), 8.03 (d, 1H, J = 2.5 Hz), 8.02 (dd, 1H, J = 3.7 Hz, 1.1 Hz), 7.76−7.72 (m, 2H), 7.26 (d, 1H, J = 8.7 Hz), 7.21 (dd, 1H, J = 4.8 Hz, 3.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.7, 159.7, 150.8, 137.9, 135.5, 134.6, 132.2, 131.1, 129.4, 128.3, 125.2, 119.8; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3097 (m), 2871 (m), 1742 (s), 1685 (s), 1589 (m), 1468 (s), 1250 (s), 1048 (s), 718 (s); HRMS (MALDI) for $C_{12}H_7BrO_3SNa$, $[M + Na]^+$ (332.9197), found 332.9213.

*2-Formylphenyl 4-chlorobenzoate (**22g**).* Reaction condition, 1 h; white solid (2.5 g, 96% yield): mp 99.1−99.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.16 (s, 1H), 8.16 (d, 2H, J = 8.6 Hz), 7.94 (dd, 1H, J = 7.7 Hz, 1.7 Hz), 7.68 (td, 1H, J = 7.9 Hz, 1.7 Hz), 7.51 (d, 2H, J = 8.6 Hz), 7.44 (t, 1H, J = 7.5 Hz), 7.31 (dd, 1H, J = 8.3 Hz, 0.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 188.3, 164.1, 151.7, 140.6, 135.3, 131.7, 130.9, 129.1, 128.2, 127.2, 126.6, 123.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 2839 (m), 2750 (m), 1738 (s), 1694 (s), 1601 (s), 1480 (s), 1395 (s), 1292 (s), 746 (s); MS (70 eV, EI) m/z (%) 262 $[M+2]^+$ (8), 260 $[M]^+$ (24), 141 (34), 139 (100), 113 (6), 111 (17); HRMS (MALDI) for $C_{14}H_9ClO_3Na$, $[M + Na]^+$ (283.0132), found 283.0132.

*2-Formylphenyl 4-methoxybenzoate (**22h**).* Reaction condition, 1 h; white solid (2.5 g, 99% yield): mp 81.3−81.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.23 (s, 1H), 8.18 (d, 2H, J = 9.0 Hz), 7.95 (dd, 1H, J = 7.7 Hz, 1.6 Hz), 7.67 (td, 1H, J = 7.9 Hz, 1.6 Hz), 7.41 (t, 1H, J = 7.5 Hz), 7.32 (d, 1H, J = 8.1 Hz), 7.01 (d, 2H, J = 8.9 Hz), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 188.4, 164.6, 164.3, 152.6, 135.3, 132.5, 129.8, 128.4, 126.3, 123.6, 120.8, 114.0, 55.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3069 (w), 2847 (m), 1726 (s), 1695 (s), 1604 (s), 1509 (s), 1272 (s); MS (70 eV, EI) m/z (%) 256 $[M]^+$ (17), 135 (100), 121 (4), 107 (8), 92 (12), 77 (13); HRMS (EI) for $C_{15}H_{12}O_4$, $[M]^+$ (256.0736), found 256.0732.

*2-Formyl-4-methoxyphenyl 4-methoxybenzoate (**22i**).* Reaction condition, 1 h; yellow solid (2.8 g, 99% yield): mp 113.5−114.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.18 (s, 1H), 8.17 (d, 2H, J = 8.8 Hz), 7.41 (d, 1H, J = 2.5 Hz), 7.21−7.20 (m, 2H), 7.00 (d, 2H, J = 8.9 Hz), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 188.1, 165.0, 164.2, 157.5, 146.7, 132.4, 128.7, 124.6, 122.4, 120.8, 114.0, 111.4, 55.8, 55.5; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3073 (w), 2968 (m), 2879 (m), 1726 (s), 1694 (s), 1601 (s), 1492 (s); MS (70 eV, EI) m/z (%) 286 $[M]^+$ (27), 185 (3), 152 (2), 135 (100), 107 (5), 86 (8), 57 (2); HRMS (EI) for $C_{16}H_{14}O_5$, $[M]^+$ (286.0841), found 286.0847.

*4-Chloro-2-formylphenyl 4-bromobenzoate (**22j**).* Reaction condition, 1 h; white solid (3.3 g, 99% yield): mp 153.7−154.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.11 (s, 1H), 8.07 (d, 2H, J = 8.5 Hz), 7.90 (d, 1H, J = 2.6 Hz), 7.69 (d, 2H, J = 8.6 Hz), 7.64 (dd, 1H, J = 8.7 Hz, 2.7 Hz), 7.29 (d, 1H, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.9, 164.1, 150.3, 135.1, 132.6, 132.3, 131.8, 130.1, 129.7, 129.2, 127.3, 125.0; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3089 (w), 2871 (w), 1734 (s), 1690 (s), 1585 (s), 1391 (s), 746 (s), 625 (m); MS (70 eV, EI) m/z (%) 340 $[M+2]^+$ (17), 338 $[M]^+$ (16), 185 (100), 183 (98), 155 (18), 99 (2), 75 (8); HRMS (EI) for $C_{14}H_8BrClO_3$, $[M]^+$ (337.9345), found 337.9338.

*4-Bromo-2-formylphenyl cyclohexanecarboxylate (**22k**).* Reaction condition, 50 min; white solid (1.5 g, 97% yield): mp 62.8−63.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ/ppm 10.06 (s, 1H), 7.99 (d, 1H, J = 2.5 Hz), 7.71 (dd, 1H, J = 8.8 Hz, 2.4 Hz), 7.07 (d, 1H, J = 8.6 Hz), 2.66 (tt, 1H, J = 11.3 Hz, 3.6 Hz), 2.13−2.09 (m, 2H), 1.87−1.81 (m, 2H), 1.73−1.69 (m, 1H), 1.61 (qd, 2H, J = 12.0 Hz, 3.2 Hz), 1.43−1.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ/ppm 186.9, 173.8, 151.2, 137.8, 132.5, 129.4, 125.3, 119.5, 43.1, 28.8, 25.6, 25.2; IR (KBr) $\tilde{\nu}$(cm^{-1}) 3076 (m), 2924 (s), 2855 (s), 1756 (s), 1695 (s), 1592 (m),

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1470 (m), 1116 (s), 613 (w); HRMS (ESI) for $C_{14}H_{15}BrO_3Na$, $[M + Na]^+$ (333.0097), found 333.0096.

■ ASSOCIATED CONTENT

Supporting Information

^1H NMR and ^{13}C NMR spectra. X-ray crystallographic data (CIF files) have been deposited (CCDC 940039, 997351, 997355−997356, 997359−997369, and 997377). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) For all the detailed information, please see the Supporting Information.

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