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SYNTHESIS OF FURAN-OXAZOLE CONJUGATED FLUORESCENT MATERIALS FROM BIOMASS-DERIVED FURFURAL THROUGH CROSS-COUPLING REACTIONS

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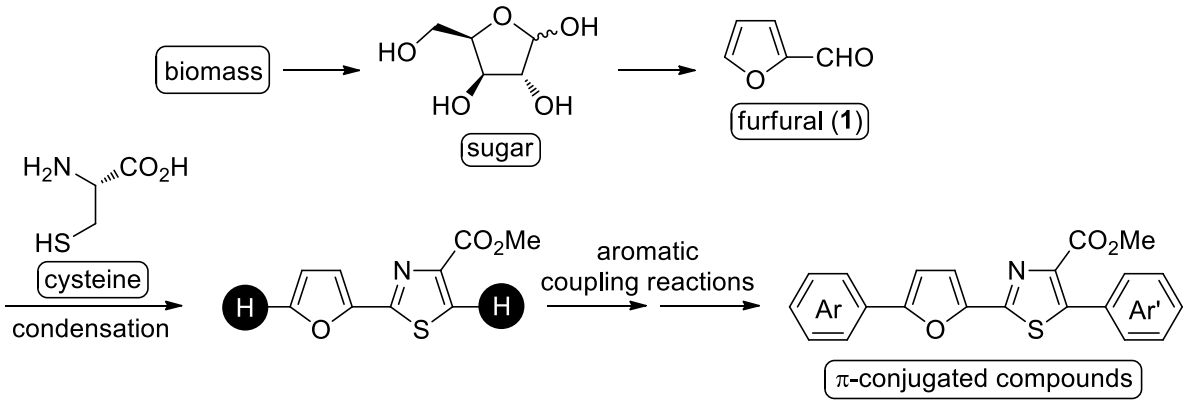
‡This paper is dedicated to Professor Dr. Lutz F. Tietze on celebration of his 75th birthday.

Abstract – Synthesis of furyloxazole was performed from biomass-derived furfural and serine methyl ester through dehydrative condensation and oxidation in one pot. Bromination and subsequent palladium-catalyzed arylation with arylboronates proceeded smoothly at the furan ring to provide arylated furylthiazoles. Arylation of C–H bond at the 5 position of the oxazole ring under Fagnou's conditions led to formation of diarylated furyloxazoles, which exhibit higher quantum yields over those of the related furylthiazole derivatives.

INTRODUCTION

The transition metal-catalyzed aromatic coupling reactions have been utilized as a reliable method for the construction of π-conjugated system in material sciences.[1] Most of the aromatic compounds for the cross-coupling reactions have been obtained by fossil oil. Recent serious decrease of fossil oil prompted us to explore its alternative such as biomass, biological material mainly derived from plants.[2] Among these plant-derived resources, furfural (**1**), which is readily prepared from xylose, has an aromatic furan ring, thus attracting a great deal of attention as a "non-edible" biomass.[3] Several research groups have employed furfural as a starting material to synthesize resins,[4] pesticides,[5] and fuels.[6] In addition to the furan ring, we converted the formyl group of furfural to a thiazole ring through condensation with cysteine and accomplished the construction of novel furan-thiazole conjugated framework (Scheme 1),[7]

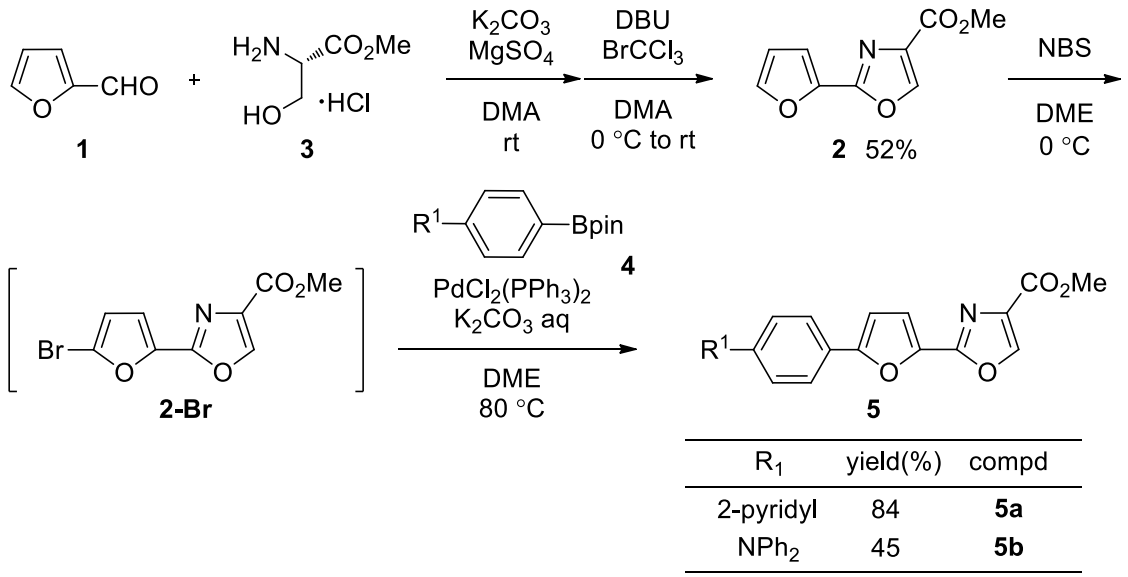
which was expected to show photoluminescent property.[8] Herein, we report the synthesis of furan-oxazole conjugated compounds from serine methyl ester and higher quantum yields over those of the furan-thiazole conjugated compounds.



Scheme 1. Extended π-conjugated heteroaromatic compounds from furfural and cysteine

RESULTS AND DISCUSSION

First, we prepared 2-furyloxazole-4-carboxylic acid methyl ester (**2**) through dehydrative condensation of furfural and L-serine methyl ester hydrochloride (**3**) followed by oxidation of the resultant oxazoline according to Graham's procedure (Scheme 2).[9] With the obtained furyloxazole **2** in hand, we then introduced an aryl group into the 5 position of the furan ring in a two-step sequence, namely, bromination and palladium-catalyzed cross-coupling reaction. Treatment of 2-furyloxazole **2** with *N*-bromosuccinimide (NBS) in DMA at 0 °C exclusively gave the desired brominated product. Since column chromatographic separation led to the formation of a deteriorated mixture, the crude bromide **2-Br** was readily subjected to the palladium-catalyzed Suzuki-Miyaura cross-coupling conditions to afford the arylated product.[10] We chose 2-pyridyl and Ph_2N- groups as electron-withdrawing/donating substituents to investigate the electronic effects on UV-vis absorption and photoluminescent properties. Thus, the reaction with **4a** (R^1 = 2-pyridyl) was found to proceed successfully to give the corresponding product **5a** in 84% yield. The one-pot reaction of **2** with boronate ester **4b** ($R^1 = Ph_2N$-) also took place to provide arylated product **5b** in 45% yield.

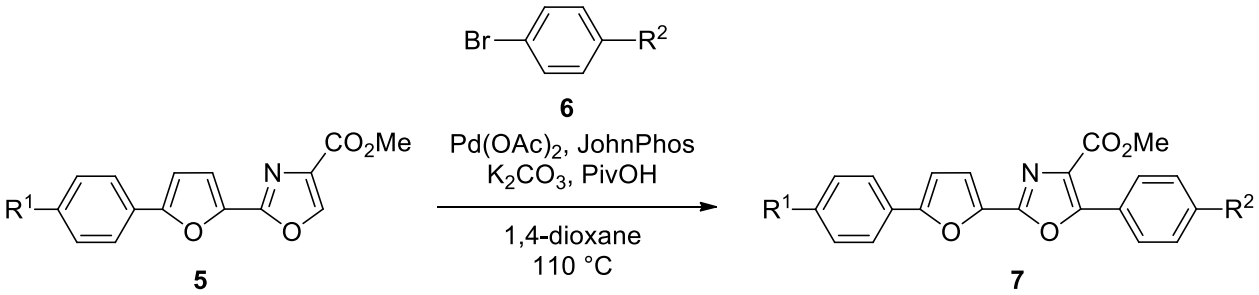


R_1	yield(%)	compd
2-pyridyl	84	**5a**
NPh_2	45	**5b**

Scheme 2. Extension of π-conjugation of furfural through oxazole formation and subsequent Suzuki-Miyaura cross-coupling reaction

Having extended π-conjugation at the 5 position of the furan ring, we then attempted the palladium-catalyzed direct C–H arylation of **5b** at the 5 position of oxazole with ethyl 4-iodobenzoate according to our reported conditions for thiazole derivatives.[7] But, disappointingly, the desired product **7** was not obtained at all with concomitant generation of unidentified compounds. Finally, Fagnou's conditions[11] with aryl bromides were found to be effective for the smooth C–H arylation to provide the corresponding products in moderate to good yields (Table 1).

Table 1. Palladium-catalyzed direct C–H arylation of **5** at the 5 position of oxazole



R^1	R^2	yield (%)	compd
2-pyridyl	SF_5	78	**7aa**
2-pyridyl	NMe_2	41	**7ab**
2-pyridyl	2-pyridyl	89	**7ac**
2-pyridyl	OMe	59	**7ad**
2-pyridyl	CO_2Et	75	**7ae**

NPh_2	SF_5	68	**7ba**
NPh_2	NMe_2	88	**7bb**
NPh_2	2-pyridyl	66	**7bc**
NPh_2	OMe	54	**7bd**
NPh_2	CO_2Et	69	**7be**

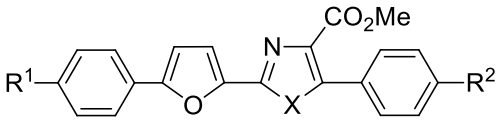
Table 2 describes UV-vis absorption and photoluminescent properties of the obtained furyloxazole derivatives. Absorption and emission maxima of furyloxazole **5a** exhibited 375 nm and 399 nm, respectively, with quantum yield (Φ = 0.33). It was found that monoarylated products **7aa**–**7ae** showed emission at higher wavelengths than those of **5a**. The quantum yields have remarkably increased up to 0.95 (**7ac**). While furyloxazole **5b** shows excellent quantum yield (Φ = 0.98), monoarylated derivatives **7ba**–**7be** have lower quantum yields. Accordingly, introduction of electron-withdrawing pyridyl group into the 5-position of the furan ring effectively improve photoluminescent performance whereas little shifts of absorption and emission maxima to higher wavelengths. By contrast, substantial shifts of both absorption and emission maxima to longer wavelengths were observed in the compounds bearing electron-donating 4-(*N*,*N*-diphenylamino)phenyl group, **7ba** and **7be**, which showed yellow fluorescence.

Table 2. UV-vis absorption and photoluminescent properties of furyloxazole derivatives

compd	λ_{max} (nm)	Em (nm)	Φ
5a	375	399	0.33
7aa	362	435	0.88
7ab	384	461	0.70
7ac	367	440	0.95
7ad	361	430	0.86
7ae	368	446	0.78
5b	345	435	0.98
7ba	396	521	0.26
7bb	397	449	0.60
7bc	392	507	0.29
7bd	379	451	0.67
7be	397	529	0.18

Compared with the furylthiazole derivatives,[7] furyloxazoles thus synthesized exhibited slightly shorter shifts except **5a** and **7ba** (Table 3), which would be the difference of bond lengths of C-S and C-O bonds in the heteroaromatic ring. The longer bond length of C-S bond expands angles of substituents at the 2- and 5-positions of the furan ring to result in a more extended π-conjugation. Worthy of note is that quantum yields of furyloxazoles were generally higher than those of furylthiazoles.

Table 3. Comparison of UV-Vis absorption and photoluminescent properties between furyloxazoles and furylthiazoles



compd	R_1	R_2	X	λ_{max} (nm)	Em (nm)	Φ
5a'	2-pyridyl	H	S	356	418	0.32
5a	2-pyridyl	H	O	375	399	0.33
7ae'	2-pyridyl	CO_2Et	S	373	462	0.40
7ae	2-pyridyl	CO_2Et	O	368	446	0.78
7aa'	2-pyridyl	SF_5	S	373	460	0.43
7aa	2-pyridyl	SF_5	O	362	435	0.88
5b'	NPh_2	H	S	391	472	0.61
5b	NPh_2	H	O	345	435	0.98
7be'	NPh_2	CO_2Et	S	408	539	0.18
7be	NPh_2	CO_2Et	O	397	529	0.18
7ba'	NPh_2	SF_5	S	391	537	0.20
7ba	NPh_2	SF_5	O	396	521	0.26

CONCLUSION

In summary, we have synthesized furan-oxazole conjugated heteroaromatic compounds from furfural (**1**) and serine methyl ester hydrochloride (**3**). The desired 2-furyloxazole-4-carboxylic acid methyl ester (**2**) was readily prepared in one pot, which was further converted to arylated furyloxazole **5** through one-pot bromination/Suzuki–Miyaura coupling sequence. Palladium-catalyzed direct C–H arylation of **5** furnished to provide 5-aryl-2-furyloxazole **7**, which exhibit higher quantum yields over those of the related furylthiazoles. The facile method for the synthesis of π-conjugated furyloxazole would extend utilities of biomass-based organic electronic materials.

EXPERIMENTAL

General. All the reactions were carried out under nitrogen atmosphere. ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Varian Gemini 300 and JEOL ECZ400 as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77.0 ppm for ^{13}C) as internal standards. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254) were used. Purification by HPLC with preparative SEC column (JAI-GEL-2H) was performed by JAI LC-9201. UV–vis spectra were

measured by ALS SEC-2000 UV/VIS spectrometer with SEC-2000 DH as a light source. Photoluminescent spectra were measured with JASCO FP-6200. Other chemicals were purchased and used without further purification.

Synthesis of 2-furyloxazole-4-carboxylic acid methyl ester 2:[9] To a 200-mL Schlenk tube equipped with a magnetic stirring bar were added magnesium sulfate (3.61 g, 30 mmol), L-serine methyl ester hydrochloride (4.67 g, 30 mmol), potassium carbonate (8.29 g, 60 mmol) and *N,N*-dimethylacetamide (80 mL). To the solution was added furfural (2.45 mL, 30 mmol) and stirring was continued under rt for 12 h. The resulting mixture was cooled to 0 °C and treated with bromotrichloromethane (8.9 mL, 90 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (13.3 mL, 90 mmol). After stirring at 0 °C for 2 h and then at rt for 10 h, the mixture was treated by water and the solution was poured into the mixture of diethyl ether/water to result in separation into two phases. Aqueous layer was extracted with diethyl ether repeatedly and the combined organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, which was purified by column chromatography on silica gel (hexane/diethyl ether = 3/2) to afford 3.02 g of **2** (52%), whose ^{1}H NMR spectra were corresponding to those reported in the literature.[9]

General procedure for the one-pot bromination and Suzuki-Miyaura coupling: To a 20-mL Schlenk tube equipped with a magnetic stirring bar were added **2** (386.3 mg, 2.0 mmol) and 1,2-dimethoxyethane (7 mL) under nitrogen atmosphere. After cooling to 0 °C, *N*-bromosuccinimide (NBS, 195.8 mg, 1.1 mmol) was added and the resulting mixture was stirred at 0 °C for 1 h. NBS (117.5 mg, 0.66 mmol) was further added to the reaction mixture and the solution was stirred at 0 °C for 1 h. Another NBS (117.5 mg, 0.66 mmol) was added again and further stirring was continued for 2 h. The reaction mixture warmed to room temperature. To the solution were added 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylpyridine (674.8 mg, 2.4 mmol), aqueous potassium carbonate (2 M, 6 mmol), and $PdCl_2(PPh_3)_2$ (70.2 mg, 0.10 mmol), successively. The mixture was allowed to stir under reflux for 24 h. After cooling to room temperature, the mixture was poured into the mixture of CH_2Cl_2/water and the two phases were separated. Aqueous layer was extracted with CH_2Cl_2 three times and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, which was purified by recrystallization ($CHCl_3$/MeOH) to afford 582 mg of methyl 2-(5-(4-(pyridin-2-yl)phenyl)furan-2-yl)oxazole-4-carboxylate (**5a**, orange solid, 84%): ^{1}H NMR δ 3.97 (s, 3H), 6.88 (d, *J* = 3.6 Hz, 1H), 7.28 (d, *J* = 3.9 Hz, 2H), 7.80 (d, *J* = 3.6 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 8.09 (d, *J* = 8.3 Hz, 2H), 8.28 (s, 1H), 8.73 (d, *J* = 3.9 Hz, 1H); ^{13}C NMR δ 52.3, 107.8, 115.5, 120.5, 122.4, 124.9, 127.3, 129.9, 134.4, 137.0, 139.0, 141.2, 143.2, 149.5, 154.9, 156.2, 156.3, 161.5; IR (ATR)

1725, 1583, 1465, 1437, 1316, 1265, 1149, 1110, 782, 725 cm^{-1}; HRMS (ESI+) Calcd for $C_{20}H_{14}N_2O_4Na$ $[M+Na]^+$: 369.0851; found: *m/z* 369.0842.

Methyl 2-(5-(4-(diphenylamino)phenyl)furan-2-yl)oxazole-4-carboxylate (**5b**, orange solid, 45%): ^1H NMR δ 3.95 (s, 3H), 6.65 (d, *J* = 3.6 Hz, 1H), 7.04-7.11 (m, 4H), 7.13 (d, *J* = 8.5 Hz, 4H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.25-7.31 (m, 4H), 7.64 (d, *J* = 8.8 Hz, 2H), 8.24 (s, 1H); ^{13}C NMR δ 52.1, 105.8, 115.5, 122.6, 123.0, 123.4, 124.7, 125.4, 129.3, 134.2, 140.3, 142.9, 147.1, 148.1, 155.0, 156.7, 161.4; IR (ATR) 1744, 1592, 1487, 1319, 1280, 1148, 1113, 791, 753, 725, 697 cm^{-1}; HRMS (ESI+) Calcd for $C_{27}H_{20}N_2O_4Na$ $[M+Na]^+$: 459.1321; found: *m/z* 459.1323.

General procedure for the palladium-catalyzed C-H coupling of 5 with aryl bromide: To a 20-mL Schlenk tube equipped with a magnetic stirring bar were added **5a** (97.4 mg, 0.28 mmol) at room temperature. 4-Bromophenylsulfur-pentafluoride (79.3 mg, 0.28 mmol), palladium acetate (3.1 mg, 0.014 mmol), JohnPhos (8.4 mg, 0.028 mmol), potassium carbonate (77.4 mg, 0.56 mmol), pivalic acid (8.6 mg, 0.084 mmol), 1,4-dioxane (1.5 mL) were added successively. The mixture was allowed to stir at 110 °C for 21 h. After cooling to room temperature, the mixture was poured into the mixture of Et_2O ether/water and two phases were separated. Aqueous layer was extracted with Et_2O three times and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude solid, which was purified by column chromatography on silica gel (hexane/*i*-PrOAc = 3/1) to afford 120.5 mg of methyl 5-(4-(pentafluoro-λ^6-sulfanyl)phenyl)-2-(5-(4-(pyridin-2-yl)phenyl)furan-2-yl) oxazole-4-carboxylate (**7aa**, orange solid, 78%): ^1H NMR δ 4.02 (s, 3H), 6.92 (d, *J* = 3.6 Hz, 1H), 7.23-7.32 (m, 1H), 7.36 (d, *J* = 3.6 Hz, 1H), 7.80 (d, *J* = 3.6 Hz, 2H), 7.85-7.97 (m, 4H), 8.11 (d, *J* = 8.7 Hz, 2H), 8.32 (d, *J* = 8.7 Hz, 2H), 8.73 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR δ 52.7, 108.0, 116.1, 120.5, 122.4, 124.9, 126.2 (m), 127.3, 128.6, 129.6 (×2), 129.7, 137.0, 139.3, 140.8, 149.6, 152.2, 153.1, 154.5 (m), 156.3, 156.6, 162.2; IR (ATR) 1723, 1587, 1465, 1436, 1219, 1092, 835, 811, 781, 756, 664, 598, 580 cm^{-1}; HRMS (ESI+) Calcd for $C_{26}H_{17}F_5N_2O_4SNa$ $[M+Na]^+$: 571.0727; found: *m/z* 571.0711.

Methyl 5-(4-(dimethylamino)phenyl)-2-(5-(4-(pyridin-2-yl)phenyl)furan-2-yl)oxazole-4-carboxylate (**7ab**, orange solid, 41%): ^1H NMR δ 3.06 (s, 6H), 3.98 (s, 3H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 4.0 Hz, 1H), 7.23-7.29 (m, 2H), 7.79 (d, *J* = 4.0 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 8.09 (d, *J* = 7.8 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 2H), 8.72 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR δ 40.1, 52.2, 107.9, 111.3, 113.9, 114.6, 120.6, 122.3, 124.8, 125.0, 127.3, 129.8, 130.2, 137.2, 138.6, 141.7, 149.4, 151.0, 151.6, 155.7, 156.3, 156.4, 162.9; IR (ATR) 1714, 1608, 1512, 1464, 1435, 1360, 1196, 1086, 781, 754 cm^{-1}; HRMS (ESI+) Calcd for $C_{28}H_{23}N_3O_4Na$ $[M+Na]^+$: 488.1586; found: *m/z* 488.1583.

Methyl 5-(4-(pyridin-2-yl)phenyl)-2-(5-(4-(pyridin-2-yl)phenyl)furan-2-yl)oxazole-4-carboxylate (**7ac**, orange solid, 89%: further purified by recrystallization from $CHCl_3$/MeOH): ^{1}H NMR δ 4.02 (s, 3H), 6.91 (d, *J* = 3.6 Hz, 1H), 7.21-7.32 (m, 2H), 7.34 (d, *J* = 3.6 Hz, 1H), 7.75-7.84 (m, 4H), 7.94 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 8.31 (d, *J* = 8.4 Hz, 2H), 8.71-8.78 (m, 2H); ^{13}C NMR δ 52.5, 107.9, 115.6, 120.5, 120.8, 122.4, 122.7, 124.9, 126.9, 127.0, 127.3, 128.2, 128.8, 129.9, 136.8, 136.9, 139.3, 141.1, 141.2, 149.8, 149.9, 152.6, 154.4, 156.3, 156.4, 156.5, 162.5; IR (ATR) 1721, 1633, 1586, 1568, 1504, 1465, 1435, 1354, 1318, 1215, 1128, 1091, 1025, 1011, 852, 780, 729 cm^{-1}; HRMS (ESI+) Calcd for $C_{31}H_{21}N_3NaO_4$ $[M+Na]^+$:522.1430; found: *m/z* 522.1428.

Methyl 5-(4-methoxyphenyl)-2-(5-(4-(pyridin-2-yl)phenyl)furan-2-yl)oxazole-4-carboxylate (**7ad**, orange solid, 59%): ^{1}H NMR δ 3.89 (s, 3H), 4.00 (s, 3H), 6.88 (d, *J* = 3.6 Hz, 1H), 7.04 (d, *J* = 9.2 Hz, 2H), 7.22-7.29 (m, 2H), 7.75-7.79 (m, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 9.2 Hz, 2H), 8.72 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR δ 52.3, 55.3, 107.8, 113.9, 115.0, 119.1, 120.4, 122.3, 124.8, 126.4, 127.2, 129.9, 130.2, 136.7, 139.1, 141.3, 149.7, 151.7, 155.0, 156.0, 156.4, 161.3, 162.6; IR (ATR) 1717, 1609, 1585, 1505, 1464, 1436, 1259, 1216, 1180, 1091, 835, 780, 720 cm^{-1}; HRMS (ESI+) Calcd for $C_{27}H_{20}N_2O_5Na$ $[M+Na]^+$: 475.1270; found: *m/z* 475.1263.

Methyl 5-(4-(ethoxycarbonyl)phenyl)-2-(5-(4-(pyridin-2-yl)phenyl)furan-2-yl)oxazole-4-carboxylate (**7ae**, orange solid, 75%): ^{1}H NMR δ 1.37 (t, *J* = 7.2 Hz, 3H), 3.94 (s, 3H), 4.35 (q, *J* = 7.2 Hz, 2H), 6.77 (d, *J* = 3.6 Hz, 1H), 7.14-7.19 (m, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.64-7.72 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.4 Hz, 2H), 8.64 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR δ 14.1, 52.4, 61.1, 107.8, 115.7, 120.3, 122.2, 124.7, 127.1, 128.0, 129.0, 129.4, 129.6, 130.3, 131.5, 136.8, 138.9, 140.7, 149.4, 152.6, 153.0, 156.1, 156.2, 162.1, 165.7; IR (ATR) 1715, 1585, 1465, 1435, 1352, 1282, 1231, 1215, 1101, 1014, 771, 722 cm^{-1}; HRMS (ESI+) Calcd for $C_{29}H_{22}N_2O_6Na$ $[M+Na]^+$: 517.1376; found: *m/z* 517.1361.

Methyl 2-(5-(4-(diphenylamino)phenyl)furan-2-yl)-5-(4-(pentafluoro-λ^6-sulfanyl)phenyl)oxazole-4-carboxylate (**7ba**, orange solid, 68%): ^{1}H NMR δ 4.00 (s, 3H), 6.70 (d, *J* = 3.6 Hz, 1H), 7.03-7.17 (m, 9H), 7.27-7.34 (m, 4H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 8.30 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR δ 52.7, 106.1, 116.3, 122.6, 122.9, 123.6 , 125.0, 125.7, 126.2 (m), 128.5, 129.4, 129.5, 129.5, 129.8, 139.9, 147.1, 148.5, 151.9, 153.4, 154.5 (m), 157.3, 162.2; IR (ATR) 1722, 1592, 1486, 1322 ,1282, 1222, 1091, 1026, 835, 754, 697, 664, 598 cm^{-1}; HRMS (ESI+) Calcd for $C_{33}H_{23}F_5N_2O_4SNa$ $[M+Na]^+$: 661.1196; found: *m/z* 661.1204.

Methyl 5-(4-(dimethylamino)phenyl)-2-(5-(4-(diphenylamino)phenyl)furan-2-yl)oxazole-4-carboxylate (**7bb**, orange solid, 88%): ^{1}H NMR δ 3.04 (s, 6H), 3.97 (s, 3H), 6.66 (d, *J* = 3.6 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 2H), 7.03-7.17 (m, 8H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 4H), 7.66 (d, *J* = 8.4 Hz, 2H), 8.12 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR δ 39.9, 52.1, 105.8, 111.2, 113.9, 114.6, 122.7, 123.3, 123.4, 124.7, 124.8, 125.4, 129.3, 129.6, 140.7, 147.2, 147.9, 151.1, 151.4, 156.0, 156.2, 162.9; IR (ATR) 1715, 1608, 1512, 1487, 1280, 1196, 1085, 820, 786, 753, 697 cm^{-1}; HRMS (ESI+) Calcd for $C_{35}H_{29}N_3O_4Na$ $[M+Na]^+$: 578.2056; found: *m/z* 578.2074.

Methyl 2-(5-(4-(diphenylamino)phenyl)furan-2-yl)-5-(4-(pyridin-2-yl)phenyl)oxazole-4-carboxylate (**7bc**, orange solid, 66%): ^{1}H NMR δ 4.00 (s, 3H), 6.70 (d, *J* = 3.6 Hz, 1H), 7.04-7.17 (m, 9H), 7.26-7.31 (m, 5H), 7.68 (d, *J* = 9.2 Hz, 2H), 7.79-7.83 (m, 2H), 8.15 (d, *J* = 8.6 Hz, 2H), 8.30 (d, *J* = 8.6 Hz, 2H), 8.72-8.76 (m, 1H); ^{13}C NMR δ 52.4, 106.0, 115.7, 120.7, 122.6, 122.7, 123.1, 123.4, 124.8, 125.6, 126.8, 127.0, 128.1, 128.7, 129.3, 136.9, 140.3, 140.8, 147.1, 148.2, 149.7, 152.6, 154.0, 156.2, 156.8, 162.5; IR (ATR) 1722, 1588, 1487, 1280, 1216, 1089, 753, 697 cm^{-1}; HRMS (ESI+) Calcd for $C_{38}H_{27}N_3O_4Na$ $[M+Na]^+$: 612.1899; found: *m/z* 612.1898.

Methyl 2-(5-(4-(diphenylamino)phenyl)furan-2-yl)-5-(4-methoxyphenyl)oxazole-4-carboxylate (**7bd**, orange solid, 54%): ^{1}H NMR δ 3.83 (s, 3H), 3.87 (s, 3H), 6.66 (d, *J* = 3.4 Hz, 1H), 6.99-7.16 (m, 10H), 7.22 (d, *J* = 3.4 Hz, 1H), 7.24-7.32 (m, 4H), 7.44-7.51 (m, 1H), 7.56 (dd, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 2H); ^{13}C NMR δ 52.0, 55.6, 105.9, 111.2, 115.1, 116.2, 120.3, 122.8, 123.4, 124.8, 125.5, 129.3, 129.8, 131.2, 131.9, 140.7, 147.2, 148.0, 151.6, 153.3, 156.5, 157.5, 162.3; IR (ATR) 1730, 1591, 1487, 1282, 1078, 1025, 791, 752, 697, 524 cm^{-1}; HRMS (ESI+) Calcd for $C_{34}H_{26}N_2O_5Na$ $[M+Na]^+$: 565.1739; found: *m/z* 565.1721.

Methyl 2-(5-(4-(diphenylamino)phenyl)furan-2-yl)-5-(4-(ethoxycarbonyl)phenyl)oxazole-4-carboxylate (**7be**, orange solid, 69%): ^{1}H NMR δ 1.42 (t, *J* = 7.2 Hz, 3H), 3.98 (s, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 6.68 (d, *J* = 4.0 Hz, 1H), 7.02-7.20 (m, 9H), 7.26-7.34 (m, 4H), 7.66 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.2 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR δ 14.2, 52.5, 61.2, 106.0, 116.0, 122.6, 122.9, 123.5, 124.9, 125.6, 128.0, 129.0, 129.3, 129.5, 130.5, 131.5, 140.1, 147.1, 148.3, 153.0, 157.0, 162.3, 165.8; IR (ATR) 1719, 1591, 1487, 1316, 1275, 1229, 1124, 1108, 1026, 1013, 754, 725, 698, 518 cm^{-1}; HRMS (ESI+) Calcd for $C_{36}H_{28}N_2O_6Na$ $[M+Na]^+$: 607.1845; found: *m/z* 607.1871.

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12. Suporting Information is available: Copies of ^{1}H and ^{13}C NMR spectra of the isolated products.