Supporting Information

Iridium-catalyzed oxidative Ar–H/Ar–H cross-coupling of primary benzamides with thiophenes

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I. General remarks

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The $^1$H NMR (400 MHz) chemical shifts were measured relative to CDCl$_3$ or DMSO-$d_6$ as the internal reference (CDCl$_3$: $\delta = 7.26$; DMSO-$d_6$: $\delta = 2.50$). The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ or DMSO-$d_6$ as the internal standard (CDCl$_3$: $\delta = 77.16$; DMSO-$d_6$: $\delta = 39.52$). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. IrCl$_3$·H$_2$O were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. Various primary benzoamides and thiophenes were purchased from Adamas-beta Ltd.

II. General procedure for the heteroarylation of primary benzoamides

A Schlenk tube with a magnetic stir bar was charged with $[\text{IrCp}^*\text{Cl}_2]_2$ (8.0 mg, 10 μmol), Ag$_2$O (139.0 mg, 0.6 mmol), primary benzoamide 1 (0.2 mmol, 1.0 equiv), and thiophenes 2 (0.6 mmol, 3.0 equiv) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 °C for 6 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product 3 or 4.

III. Procedure for the synthesis of 3a on 4 mmol scale

A Schlenk tube with a magnetic stir bar was charged with $[\text{IrCp}^*\text{Cl}_2]_2$ (160 mg, 0.2 mmol), Ag$_2$O (2780 mg, 12 mmol), benzamide 1a (484 mg, 4.0 mmol, 1.0 equiv), and benzothiophene 2a (1608 mg, 12.0 mmol, 3.0 equiv) in HFIP (5.0 mL) under an air atmosphere. The resulting mixture was stirred at 120 °C for 10 h and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed...
with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product 3a (627 mg, 62% yield).

**IV. Intramolecular annulation of 3a**

A Schlenk tube with a magnetic stir bar was charged with CuI (7.6 mg, 20 mol %), PPh₃ (21.0, 40 mol %), KO'Bu (44.9, 2.0 equiv), and 2-(benzo[b]thiophen-2-yl)benzamide 3a (50.6 mg, 0.2 mmol) in o-xylene (1.0 mL) under an O₂ atmosphere (1 atm). The resulting mixture was stirred at 120 °C for 30 h and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product 5 (23 mg, 47% yield) as a yellow solid. M.p.: > 250 °C.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 7.49-7.55\) (m, 2H), 7.60-7.64 (m, 1H), 7.82-7.88 (m, 2H), 8.06-8.10 (m, 1H), 8.35 (d, \(J = 7.6\) Hz, 1H), 8.43-8.47 (m, 1H), 12.62 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta = 114.1, 121.8, 123.4, 123.7, 124.9, 125.1, 126.8, 127.4, 128.3, 130.1, 132.6, 133.1, 133.5, 137.4, 161.9\) ppm. HRMS (ESI): calcd for C\(_{15}\)H\(_{10}\)NOS [M+H] \(^+\) 252.0483, found 252.0490.

**V. Mechanistic study**

(i) H/D exchange experiments

A Schlenk tube with a magnetic stir bar was charged with [IrCp*Cl\(_2\)]\(_2\) (8.0 mg, 10 \(\mu\)mol), Ag\(_2\)O (139.0 mg, 0.6 mmol), benzamide 1a (24.2 mg, 0.2 mmol), and D\(_2\)O (72 \(\mu\)L, 4.0 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was
stirred at 120 °C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10/1, v/v) to provide [D₆]-1a. The deuterated ratio was calculated from ¹H NMR analysis.

A Schlenk tube with a magnetic stir bar was charged with [IrCp*Cl₂]₂ (8.0 mg, 10 μmol), Ag₂O (139.0 mg, 0.6 mmol), benzothiophene 2a (26.8 mg, 0.2 mmol), and D₂O (72 μL, 4.0 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 °C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10/1, v/v) to provide [D]-2a. The deuterated ratio was calculated from ¹H NMR analysis.
A Schlenk tube with a magnetic stir bar was charged with [IrCp*Cl₂]₂ (8.0 mg, 10 μmol), Ag₂O (139.0 mg, 0.6 mmol), benzamide 1a (24.2 mg), benzothiophene 2a (80.4 mg, 0.6 mmol), and D₂O (72 μL, 4.0 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 °C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10/1, v/v) to provide [D₆]-1a, [D]-2a and 3a. The conversion of 1a and 2a were 47% and 23%, respectively and the yield of 3a was 34%. The deuterated ratio was calculated from ¹H NMR analysis.
(ii) Kinetic isotope experiments

\[
\begin{align*}
&\text{D}_3\text{H}_5\text{NH}_2 + \text{H-S-} \xrightarrow{\text{[IrCp*Cl}_2\text{]}_2 (5.0 \text{ mol }\%)} \text{HFIP, air, 120 }^\circ\text{C, 1h}} \\
&\text{K}_H/K_D = 1.12
\end{align*}
\]

A Schlenk tube with a magnetic stir bar was charged with [IrCp*Cl\(_2\)]\(_2\) (8.0 mg, 10 \(\mu\)mol), Ag\(_2\)O (139.0 mg, 0.6 mmol), benzamide 1a (24.2 mg) or deuterated benzamide [D\(_5\)-1a (25.2 mg), and benzo thiophene 2a (80.4 mg, 0.6 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 \(^\circ\)C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The deuterated ratio was calculated from \(^1\)H NMR analysis. The yield of 3a was determined by \(^1\)H NMR analysis of the crude product using dibromomethane (0.2 mmol, 14 \(\mu\)L) as internal standard. A kinetic isotope effect (KIE) value \((k_H/k_D = 1.12)\) was obtained.
A Schlenk tube with a magnetic stir bar was charged with \([\text{IrCp}^*\text{Cl}_2]_2\) (8.0 mg, 10 μmol), \(\text{Ag}_2\text{O}\) (139.0 mg, 0.6 mmol), benzamide \(1\text{a}\) (24.2 mg), and benzothiophene \(2\text{a}\) (80.4 mg, 0.6 mmol) or deuterated benzothiophene \([\text{D}]\)-\(2\text{a}\) (81.0 mg, 0.6 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 °C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The deuterated ratio was calculated from \(^1\text{H}\) NMR analysis. The yield of \(3\text{a}\) was determined by \(^1\text{H}\) NMR analysis of the crude product using dibromomethane (0.2 mmol, 14 μL) as internal standard. A kinetic isotope effect (KIE) value \((k_H/k_D = 1.24)\) was obtained.
VI. Experimental data for the described substances

2-(Benzo[b]thiophen-2-yl)benzamide (3a)
Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3a as a yellow solid (35 mg, 70% yield). M.p.: 138-139 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.71 (d, $J = 48.4$ Hz, 2H), 7.33-7.40 (m, 2H), 7.42-7.52 (m, 3H), 7.54-7.57 (m, 1H), 7.70 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.78-7.80 (m, 1H), 7.84 (d, $J = 7.2$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 122.3, 124.0, 124.1, 124.82, 124.83, 128.8, 128.9, 130.5, 131.0, 132.0, 135.5, 140.3, 140.4, 141.2, 171.3 ppm. HRMS (ESI): calcd for C$_{15}$H$_{12}$NOS [M+H]$^+$ 254.0640, found 254.0643.

2-(Benzo[b]thiophen-2-yl)-5-methylbenzamide (3b)
Following the general procedure. 3-Methylbenzamide 1b (27.0 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3b as a yellow solid (36 mg, 68% yield). M.p.: 223-224 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.43 (s, 3H), 5.62 (d, $J = 5.2$ Hz, 2H), 7.30-7.29 (m, 2H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.54 (s, 1H), 7.77-7.79 (m, 1H), 7.83 (d, $J = 7.6$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 21.4, 122.3, 123.9, 124.0, 124.7, 124.8, 129.2, 129.5, 131.7, 132.0, 132.6, 140.2, 140.4, 140.9, 141.4, 171.2 ppm. HRMS (ESI): calcd for C$_{16}$H$_{14}$NOS [M+H]$^+$ 268.0796, found 268.0798.
2-(Benzo[b]thiophen-2-yl)-4-methylbenzamide (3c)

Following the general procedure. 4-Methylbenzamide 1c (27.0 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3c as a yellow solid (35 mg, 65% yield). M.p.: 185-186 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 2.42 (s, 3H), 5.67 (d, $J$ = 40 Hz, 2H), 7.25-7.27 (m, 1H), 7.33-7.39 (m, 4H), 7.63 (d, $J$ = 8.0 Hz, 1H), 7.77 (d, $J$ = 7.2 Hz, 1H), 7.83 (d, $J$ = 7.6 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 21.4, 122.3, 123.9, 124.0, 124.7, 124.8, 129.2, 129.5, 131.7, 132.0, 132.6, 140.2, 140.4, 140.9, 141.4, 171.2 ppm. HRMS (ESI): calcd for C$_{16}$H$_{14}$NOS [M+H]$^+$ 268.0796, found 268.0798.

2-(Benzo[b]thiophen-2-yl)-4-methoxybenzamide (3d)

Following the general procedure. 4-Methoxybenzamide 1d (30.2 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3d as a yellow solid (41 mg, 72% yield). M.p.: 187-188 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 3.87 (s, 3H), 5.63 (d, $J$ = 21.2 Hz, 2H), 6.97 (dd, $J$ = 6.0 Hz, 2.4 Hz, 1H), 7.02 (d, $J$ = 2.8 Hz, 1H), 7.34-7.41 (m, 3H), 7.75 (d, $J$ = 8.4 Hz, 1H), 7.79 (dd, $J$ = 7.2 Hz, 2.0 Hz, 1H), 7.83-7.85 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 55.7, 114.2, 116.4, 122.3, 124.1, 124.2, 124.90, 124.92, 127.6, 131.3, 134.0, 140.1, 140.4, 141.3, 161.0, 170.6 ppm. HRMS (ESI): calcd for C$_{16}$H$_{14}$NO$_2$S [M+H]$^+$ 284.0745, found 284.0743.
2-(Benzo[b]thiophen-2-yl)-4,5-dimethylbenzamide (3e)

Following the general procedure. 3,4-Dimethylbenzamide 1e (29.8 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3e as a yellow oil (42 mg, 74% yield). M.p.: 198-199 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.33 (m, 6H), 5.65 (d, $J$ = 38.8 Hz, 2H), 7.30 (s, 1H), 7.32-7.39 (m, 3H), 7.53 (s, 1H), 7.77 (dd, $J$ = 6.8 Hz, 1.6 Hz, 1H), 7.82-7.84 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 19.6, 19.8, 122.2, 123.7, 123.9, 124.6, 124.8, 129.4, 130.3, 132.2, 132.6, 137.8, 139.6, 140.3, 140.4, 141.6, 171.3 ppm. HRMS (ESI): calcd for C$_{17}$H$_{16}$NOS [M+H]$^+$ 282.0953, found 282.0958.

2-(Benzo[b]thiophen-2-yl)-4-ethylbenzamide (3f)

Following the general procedure. 4-Ethylbenzamide 1f (29.8 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3f as a yellow oil (39 mg, 70% yield). M.p.: 152-153 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.28 (t, $J$ = 7.6 Hz, 3H), 2.69-2.75 (m, 2H), 5.67 (d, $J$ = 41.2 Hz, 2H), 7.29 (dd, $J$ = 8.0 Hz, 1.2 Hz, 1H), 7.33-7.40 (m, 4H), 7.66 (d, $J$ = 8.0 Hz, 1H), 7.77-7.79 (m, 1H), 7.84 (d, $J$ = 7.6 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 15.4, 28.8, 122.3, 123.9, 124.0, 124.7, 124.8, 128.4, 129.2, 130.6, 132.1, 132.8, 140.3, 140.4, 141.6, 147.1, 171.2 ppm. HRMS (ESI): calcd for C$_{17}$H$_{16}$NOS [M+H]$^+$ 282.0953, found 282.0949.
2-(Benzo[b]thiophen-2-yl)-4-(tert-butyl)benzamide (3g)

Following the general procedure. 4-(tert-Butyl)benzamide 1g (35.4 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3g as a yellow oil (48 mg, 78% yield). M.p.: 162-163 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.35 (s, 9H), 5.71 (d, $J = 59.6$ Hz, 2H), 7.33-7.41 (m, 3H), 7.48 (dd, $J = 8.4$ Hz, 2.0 Hz, 1H), 7.53 (d, $J = 1.6$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.79 (dd, $J = 7.2$ Hz, 1.6 Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 31.2, 35.0, 122.3, 123.9, 124.0, 124.7, 124.8, 126.0, 128.2, 129.0, 131.8, 132.6, 140.3, 140.4, 141.9, 154.0, 171.2 ppm. HRMS (ESI): calcd for C$_{19}$H$_{20}$NOS [M+H]$^+$ 310.1266, found 310.1263.

2-(Benzo[b]thiophen-2-yl)-4-butylbenzamide (3h)

Following the general procedure. 4-Butylbenzamide 1h (35.4 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3h as a yellow oil (46 mg, 74% yield). M.p.: 145-146 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.94 (t, $J = 7.2$ Hz, 3H), 1.33-1.42 (m, 2H), 1.59-1.67 (m, 2H), 2.67 (t, $J = 7.6$ Hz, 2H), 5.66 (d, $J = 30.4$ Hz, 2H), 7.27 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.33-7.40 (m, 4H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.78 (dd, $J = 6.8$ Hz, 1.6 Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.0, 22.4, 33.4, 35.5, 122.3, 123.9, 124.0, 124.7, 124.8, 128.9, 129.1, 131.1, 132.0, 132.7, 140.3, 140.4, 141.6, 145.8, 171.3 ppm. HRMS (ESI): calcd for C$_{19}$H$_{20}$NOS [M+H]$^+$ 310.1266, found 310.1267.
2-(Benzo[b]thiophen-2-yl)-5-ethoxybenzamide (3i)

Following the general procedure. 3-Ethoxybenzamide 1i (33.0 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3i as a yellow solid (40 mg, 68% yield). M.p.: 195-196 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 1.44 (t, $J = 7.2$ Hz, 3H), 4.08-4.13 (m, 2H), 5.68 (d, $J = 27.6$ Hz, 2H), 7.01 (dd, $J = 8.4$ Hz, 2.8 Hz, 1H), 7.23 (d, $J = 2.8$ Hz, 1H), 7.31-7.39 (m, 3H), 7.45 (d, $J = 8.8$ Hz, 1H), 7.75-7.77 (m, 1H), 7.82 (d, $J = 7.6$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 14.9, 64.0, 114.2, 117.3, 122.2, 123.5, 123.9, 124.1, 124.6, 124.8, 132.4, 136.5, 140.3, 140.4, 141.3, 159.3, 170.1 ppm. HRMS (ESI): calcd for C$_{17}$H$_{16}$NO$_2$S [M+H]$^+$ 298.0902, found 298.0904.

2-(Benzo[b]thiophen-2-yl)-6-fluorobenzamide (3j)

Following the general procedure. 2-Fluorobenzamide 1j (27.8 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3j as a yellow solid (34 mg, 63% yield). M.p.: 122-123 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 5.89 (d, $J = 90$ Hz, 2H), 7.12-7.16 (m, 1H), 7.32-7.46 (m, 4H), 7.54 (s, 1H), 7.77-7.83 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 115.7 (d, $J = 22$ Hz), 122.2, 124.0 (d, $J = 18$ Hz), 124.1, 124.3, 124.8, 125.0, 126.2 (d, $J = 3$ Hz), 131.1 (d, $J = 9$ Hz), 134.0 (d, $J = 3$ Hz), 139.6 (d, $J = 2$ Hz), 140.2, 140.3, 159.4 (d, $J = 248$ Hz), 166.9 ppm. HRMS (ESI): calcd for C$_{13}$H$_{11}$FNO$_2$S [M+H]$^+$ 272.0545, found 272.0544.
2-(Benzo[b]thiophen-2-yl)-4-chlorobenzamide (3k)

Following the general procedure. 4-Chlorobenzamide 1k (31.0 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3k as a yellow solid (37 mg, 65% yield). M.p.: 179-180 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.65 (d, J = 34.8 \text{ Hz}, 2\text{H}), 7.36-7.44 (m, 4\text{H}), 7.54 (d, J = 2.0 \text{ Hz}, 1\text{H}), 7.67 (d, J = 7.6 \text{ Hz}, 1\text{H}), 7.80 (dd, J = 6.8 \text{ Hz}, 2.8 \text{ Hz}, 1\text{H}), 7.84-7.86 (m, 1\text{H}) \text{ ppm.} \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 122.4, 124.3, 124.7, 125.0, 125.2, 128.9, 130.5, 130.9, 133.7, 133.8, 136.5, 139.6, 140.1, 140.5, 170.1 \text{ ppm.} \)

HRMS (ESI): calcd for C\(_{15}\)H\(_{11}\)ClNOS \([\text{M+H}]^+\) 288.0250, found 288.0242.

Methyl 3-(benzo[b]thiophen-2-yl)-4-carbamoylbenzoate (3l)

Following the general procedure. Methyl 4-carbamoylbenzoate 1l (35.8 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3l as a yellow solid (45 mg, 73% yield). M.p.: 173-174 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 3.95 (s, 3\text{H}), 5.81 (d, J = 54.8 \text{ Hz}, 2\text{H}), 7.34-7.38 (m, 2\text{H}), 7.46 (s, 1\text{H}), 7.72 (d, J = 8.0 \text{ Hz}, 1\text{H}), 7.78-7.81 (m, 1\text{H}), 7.83-7.85 (m, 1\text{H}), 8.07 (dd, J = 8.0 \text{ Hz}, 1.6 \text{ Hz}, 1\text{H}), 8.22 (d, J = 1.6 \text{ Hz}, 1\text{H}) \text{ ppm.} \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 52.7, 122.3, 124.2, 124.5, 124.9, 125.1, 129.0, 129.6, 131.9, 132.0, 132.3, 139.3, 140.0, 140.2, 140.5, 166.0, 170.5 \text{ ppm.} \)

HRMS (ESI): calcd for C\(_{17}\)H\(_{14}\)NO\(_3\)S \([\text{M+H}]^+\) 312.0694, found 312.0692.
2-(Benzo[b]thiophen-2-yl)-1-naphthamide (3m)

Following the general procedure. 1-Naphthamide 1m (34.2 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3m as a yellow soild (40 mg, 66% yield). M.p.: 216-217 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.82 (d, $J$ = 65.2 Hz, 2H), 7.34-7.42 (m, 2H), 7.54-7.62 (m, 2H), 7.65-7.69 (m, 2H), 7.82-7.90 (m, 3H), 7.94 (d, $J$ = 8.8 Hz, 1H), 8.10 (d, $J$ = 8.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 110.2, 122.2, 124.2, 124.3, 124.8, 125.8, 127.1, 127.4, 127.9, 128.2, 128.8, 129.8, 130.1, 133.0, 133.2, 140.5, 141.3, 171.4 ppm. HRMS (ESI): calcd for C$_{19}$H$_{14}$NOS [M+H]$^+$ 304.0796, found 304.0793.

3-(Benzo[b]thiophen-2-yl)-2-naphthamide (3n)

Following the general procedure. 2-Naphthamide 1n (34.2 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3n as a yellow soild (44 mg, 72% yield). M.p.: > 250 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.36-7.43 (m, 2H), 7.60-7.63 (m, 4H), 7.86-7.88 (m, 1H), 8.00-8.09 (m, 5H), 8.17 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 132.2, 132.7, 133.8, 134.5, 134.7, 137.1, 137.4, 137.5, 137.9, 138.0, 139.0, 139.2, 141.8, 142.7, 145.5, 149.4, 150.1, 152.0, 180.8 ppm. HRMS (ESI): calcd for C$_{19}$H$_{14}$NOS [M+H]$^+$ 304.0796, found 304.0796.
3-(Benzo[b]thiophen-2-yl)thiophene-2-carboxamide (3o)

Following the general procedure. Thiophene-2-carboxamide 1o (25.4 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 3o as a yellow solid (30 mg, 59% yield). M.p.: 157-158 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 6.18 (s, 2H), 7.15 (dd, $J =$ 5.2 Hz, 0.8 Hz, 1H), 7.38-7.44 (m, 2H), 7.46 (s, 1H), 7.52 (d, $J =$ 5.2 Hz, 1H), 7.80-7.87 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 122.4, 124.2, 125.0, 125.1, 125.3, 129.6, 131.8, 134.8, 135.7, 136.3, 139.7, 140.6, 163.8 ppm. HRMS (ESI): calcd for C$_{13}$H$_{10}$NOS$_2$ [M+H]$^+$ 260.0204, found 260.0193.

2-(Benzo[b]thiophen-2-yl)thiophene-3-carboxamide (3p)

Following the general procedure. Thiophene-3-carboxamide 1p (25.4 mg, 0.2 mmol) and benzothiophene 2a (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded 3p as a yellow solid (23 mg, 44% yield). M.p.: 177-178 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 5.82 (d, $J =$ 54.0 Hz, 2H), 7.34 (d, $J =$ 5.2 Hz, 1H), 7.36-7.43 (m, 2H), 7.48 (d, $J =$ 5.6 Hz, 1H), 7.55 (s, 1H), 7.80-7.84 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 122.3, 124.3, 125.1, 125.5, 125.9, 126.2, 130.0, 133.6, 140.0, 137.0, 139.7, 140.9, 165.4 ppm. HRMS (ESI): calcd for C$_{13}$H$_{10}$NOS$_2$ [M+H]$^+$ 260.0204, found 260.0200.
**2-(Thiophen-2-yl)benzamide (4a)**

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and thiophene 2a (50.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4a as a yellow solid (27 mg, 67% yield). M.p.: 131-132 °C. ¹H NMR (400 MHz, CDCl₃): δ = 5.65 (d, J = 76.0 Hz, 2H), 7.07-7.09 (m, 1H), 7.20 (d, J = 2.8 Hz, 1H), 7.37-7.44 (m, 2H), 7.47 (d, J = 4.0 Hz, 2H), 7.69 (d, J = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 126.7, 127.3, 128.0, 128.3, 128.9, 130.5, 131.0, 132.1, 135.1, 141.1, 171.4 ppm. HRMS (ESI): calcd for C₁₁H₁₀NOS [M+H]⁺ 204.0483, found 204.0479.

**2-(5-Methylthiophen-2-yl)benzamide (4b)**

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 2-methylthiophene 2b (58.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4b as a yellow solid (31 mg, 71% yield). M.p.: 116-117 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.51 (s, 3H), 5.71 (d, J = 64.4 Hz, 2H), 6.73 (d, J = 2.8 Hz, 1H), 6.98 (d, J = 3.6 Hz, 1H), 7.35-7.46 (m, 3H), 7.67 (d, J = 7.2 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 15.5, 126.2, 127.3, 127.9, 128.9, 130.4, 130.7, 132.4, 134.8, 138.6, 141.5, 171.6 ppm. HRMS (ESI): calcd for C₁₂H₁₂NOS [M+H]⁺ 218.0640, found 218.0638.

**2-(5-Phenylthiophen-2-yl)benzamide (4c)**

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 2-phenylthiophene 2c (96.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4c as a yellow solid (34 mg, 61% yield). M.p.: 147-148 °C. ¹H NMR (400 MHz, CDCl₃): δ =
5.76 (d, J = 62.8 Hz, 2H), 7.18 (d, J = 3.6 Hz, 1H), 7.28-7.32 (m, 2H), 7.37-7.43 (m, 3H), 7.44-7.53 (m, 2H), 7.61-7.62 (m, 2H), 7.67-7.69 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 123.9, 125.8, 127.9, 128.2, 128.3, 128.9, 129.1, 130.5, 130.6, 131.9, 134.0, 135.0, 140.3, 145.6, 171.6$ ppm. HRMS (ESI): calcd for C$_{17}$H$_{14}$NOS [M+H]$^+$ 280.0796, found 280.0798.

2-(5-Chlorothiophen-2-yl)benzamide (4d)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 2-chlorothiophene 2d (70.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4d as a yellow solid (27 mg, 58% yield). M.p.: 126-127 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.74$ (d, $J = 85.2$ Hz, 2H), 6.89 (d, $J = 4.0$ Hz, 1H), 6.98 (d, $J = 4.0$ Hz, 1H), 7.39-7.48 (m, 3H), 7.62-7.64 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 126.6, 127.0, 128.6, 128.7, 130.6, 130.7, 131.0, 131.2, 135.2, 139.6, 171.2$ ppm. HRMS (ESI): calcd for C$_{11}$H$_9$ClNOS [M+H]$^+$ 238.0093, found 238.0095.

2-(5-Hexylthiophen-2-yl)benzamide (4e)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 2-hexylthiophene 2e (100.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4e as a yellow solid (42 mg, 73% yield). M.p.: 67-68 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 0.89$ (t, $J = 7.2$ Hz, 3H), 1.25-1.39 (m, 6H), 1.65-1.73 (m, 2H), 2.81 (t, $J = 7.6$ Hz, 2H), 5.72 (d, $J = 71.2$ Hz, 2H), 6.74 (d, $J = 3.2$ Hz, 1H), 6.99 (d, $J = 3.2$ Hz, 1H), 7.34-7.38 (m, 1H), 7.43 (d, $J = 4.0$ Hz, 1H), 7.67 (d, $J = 3.6$ Hz, 1H) ppm. $^{13}$C NMR
(100 MHz, CDCl$_3$): $\delta = 14.2, 22.7, 29.0, 30.3, 31.68, 31.71, 124.9, 127.0, 127.9, 128.9, 130.4, 130.7, 132.5, 134.8, 138.2, 147.7, 171.6$ ppm. HRMS (ESI): calcd for C$_{17}$H$_{22}$NOS [M+H]$^+$ 288.1422, found 288.1413.

2-(3-Methoxythiophen-2-yl)benzamide (4f)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 3-methoxythiophene 2f (68.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded 4f as yellow oil (35 mg, 76% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 3.81$ (s, 3H), 5.90 (d, J = 33.2 Hz, 2H), 6.89 (d, J = 5.6 Hz, 1H), 7.28 (d, J = 5.2 Hz, 1H), 7.36-7.41 (m, 2H), 7.44-7.48 (m, 1H), 7.78-7.80 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 58.6, 116.6, 117.3, 124.5, 128.1, 129.4, 129.9, 130.6, 132.0, 135.7, 154.1$ ppm. HRMS (ESI): calcd for C$_{12}$H$_{12}$NO$_2$S [M+H]$^+$ 234.0589, found 234.0596.

2-(3-Bromothiophen-2-yl)benzamide (4g)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 3-bromothiophene 2g (68.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4g as a yellow solid (35 mg, 63% yield). M.p.: 111-112 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.68$ (d, J = 104.8 Hz, 2H), 7.06 (d, J = 5.2 Hz, 1H), 7.38-7.42 (m, 2H), 7.47-7.54 (m, 2H), 7.83-7.85 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 110.9, 126.9, 129.3, 129.5, 130.4, 130.67, 130.68, 132.2, 136.1, 136.4, 170.1$ ppm. HRMS (ESI): calcd for C$_{11}$H$_9$BrNOS [M+H]$^+$ 281.9588, found 281.9582.
2-(4,5-Dibromothiophen-2-yl)benzamide (4h)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 2,3-dibromothiophene 2h (144.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4h as a yellow solid (36 mg, 51% yield). M.p.: 172-173 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.73\) (d, \(J = 64.4\) Hz, 2H), 7.04 (s, 1H), 7.39-7.48 (m, 3H), 7.61 (dd, \(J = 7.6\) Hz, 1.6 Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 112.0, 114.5, 128.5, 129.1, 129.5, 130.4, 130.5, 130.7, 135.3, 142.4, 170.8\) ppm. HRMS (ESI): calcd for C\(_{11}\)H\(_8\)Br\(_2\)NOS [M+H]\(^+\) 359.8693, found 359.8696.

2-(3,4-Dibromothiophen-2-yl)benzamide (4i)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 3,4-dibromothiophene 2i (144.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4i as yellow oil (37 mg, 52% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 5.68\) (d, \(J = 91.2\) Hz, 2H), 7.36-7.39 (m, 1H), 7.45 (s, 1H), 7.50-7.56 (m, 2H), 7.78-7.82 (m, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 114.0, 114.4, 123.9, 129.0, 129.9, 130.6, 130.8, 132.1, 136.2, 137.6, 170.0\) ppm. HRMS (ESI): calcd for C\(_{11}\)H\(_8\)Br\(_2\)NOS [M+H]\(^+\) 359.8693, found 359.8697.
2-(5-Chlorobenzo[b]thiophen-2-yl)benzamide (4j)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 5-chlorobenzo[b]thiophene 2j (100.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4j as a yellow solid (35 mg, 61% yield). M.p.: 124-125 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 5.71 (d, $J$ = 58.8 Hz, 2H), 7.31 (dd, $J$ = 8.4 Hz, 2.0 Hz, 1H), 7.36 (s, 1H), 7.41-7.60 (m, 4H), 7.67-7.69 (m, 1H), 7.73-7.81 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 123.1, 123.3, 123.5, 125.2, 127.5, 128.8, 129.0, 130.6, 131.0, 131.6, 135.6, 138.5, 141.3, 143.3, 171.2 ppm. HRMS (ESI): calcd for C$_{15}$H$_{11}$ClNOS [M+H]$^+$ 288.0250, found 288.0255.

2-(3-Methylbenzo[b]thiophen-2-yl)benzamide (4k)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and 3-methylbenzo[b]thiophene 2k (88.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4k as a yellow solid (36 mg, 67% yield). M.p.: 143-144 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 2.27 (s, 3H), 5.57 (d, $J$ = 24.4 Hz, 2H), 7.38-7.47 (m, 3H), 7.50-7.58 (m, 2H), 7.73 (d, $J$ = 8.0 Hz, 1H), 7.85 (d, $J$ = 8.0 Hz, 1H), 7.96-7.98 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 12.4, 122.4, 122.6, 124.8, 125.1, 129.1, 130.0, 130.8, 130.9, 131.9, 132.1, 135.0, 135.6, 139.5, 140.4, 170.0 ppm. HRMS (ESI): calcd for C$_{16}$H$_{14}$NOS [M+H]$^+$ 268.0796, found 268.0805.
2-(Thieno[3,2-b]thiophen-2-yl)benzamide (4l)

Following the general procedure. Benzamide 1a (24.2 mg, 0.2 mmol) and thieno[3,2-b]thiophene 2l (84.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded 4l as a yellow solid (29 mg, 56% yield). M.p.: 147-148 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.73$ (d, $J = 61.6$ Hz, 2H), 7.26-7.28 (m, 1H), 7.39-7.42 (m, 2H), 7.43-7.53 (m, 3H), 7.68 (dd, $J = 8.0$ Hz, 1.2 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 119.5$, 119.6, 127.6, 128.5, 128.8, 130.5, 130.9, 132.2, 135.3, 139.8, 142.7, 171.4 ppm. HRMS (ESI): calcd for C$_{13}$H$_{10}$NOS$_2$ [M+H]$^+$ 260.0204, found 260.0191.

**VII. References**

VIII. Copies of $^1$H and $^{13}$C NMR spectra