Supporting Information

Direct C–H/C–H Cross-Coupling of Benzimidates with

Heteroarenes to Access Biheteroaryl-2-carbonitriles

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I. General remarks

Unless otherwise noted, all solvents and reagents were used as purchased without further purification. All reactions were carried out under air. Benzimidates **1a-1m** were prepared according to the reference.¹ Benzonitrile and acetyl chloride were purchased from Chengdu Best-reagent (China) Co., Ltd. Substituted benzonitriles, thiophenes and furans were purchased from Shanghai Energy Chemical Co., Ltd and used without further purification. [Cp*Rh(MeCN)₃](SbF₆)₂ was prepared according to the reference.² AgF was purchased from Adamas Reagent, Ltd. AgSbF₆ was purchased from TCI (China) Development Co., Ltd. Other Ag salts (Ag₂O, AgOAc, and Ag₂CO₃) were purchased from Beijing Ou He Chemical Engineering (China) Co., Ltd. 1,1,1,3,3,3-Hexafluoro-2-propanol was purchased from Shanghai Energy Chemical Co., Ltd.

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ¹H and ¹³C NMR (400 MHz) chemical shifts were recorded relative to CDCl₃ as the internal reference (CDCl₃: δ = 7.26 ppm for ¹H NMR and δ = 77.16 ppm for ¹³C NMR). High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). GC-MS analysis was conducted on a Shimadzu GCMS-QP2010 SE.

II. Optimization of the reaction conditions

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with ethyl benzimidate **1a** (0.2 mmol, 1.0 equiv, 30 μ L), 2-methylthiophene **2a** (0.4 mmol, 2.0 equiv, 39 μ L), a catalyst (5 mol%), an oxidant, an additive and a solvent under an air atmosphere. The mixture was stirred at room temperature for 2 min, and then heated

at the indicated temperature for 24 h. After cooled to room temperature, the reaction mixture was diluted with 25 mL of DCM, filtered through a celite pad, and washed with 25 mL of DCM. The combined filtrate was concentrated under vacuum, and the resulting residue was directly analyzed by means of ¹H NMR by using CH₂Br₂ as the internal standard or purified via column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v).

	NH OEt +	$H \xrightarrow{s} \frac{cat}{ada}$	alyst, oxidant			
Entry	Catalyst	Oxidant (equiv)	Additive (equiv)	Solvent	T (°C)	Yield ^b (%)
1	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	DCE	120	14
2	[Cp*IrCl ₂] ₂ /AgSbF ₆	AgF/2.0	NaOAc/0.2	DCE	120	n. d.
3	[Ru(p-Cymene)Cl ₂] ₂ /AgSbF ₆	AgF/2.0	NaOAc/0.2	DCE	120	n. d.
4	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	toluene	120	20
5	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	o-DCB	120	26
6	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	THF	120	16
7	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	1,4-dioxane	120	15
8	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	DME	120	25
9	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	MTBE	120	20
10	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	MeCN	120	<10
11	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	DMSO	120	0
12	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	^t BuOH	120	43
13	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	^t AmylOH	120	30
14	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	TFE	120	12
15 ^c	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/2.0	NaOAc/0.2	tBuOH	120	38
16	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	Ag ₂ O/1.0	NaOAc/0.2	^t BuOH	120	26
17	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	Ag ₂ CO ₃ /1.0	NaOAc/0.2	^t BuOH	120	15
18	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgOAc/1.0	NaOAc/0.2	^t BuOH	120	18
19	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgTFA/1.0	NaOAc/0.2	^t BuOH	120	0
20	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	CuO/1.0	NaOAc/0.2	^t BuOH	120	0
21	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	$Cu(OAc)_2 \cdot H_2O/1.0$	NaOAc/0.2	^t BuOH	120	0

Table S1.	Optimization	of the Reaction	Conditions ^{<i>a,b</i>}
	opumization	or the reaction	Conditions

22	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	NaOAc/0.2	^t BuOH	120	50
23	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	KOAc/0.2	^t BuOH	120	53
24	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	NaOPiv \cdot H ₂ O/0.2	^t BuOH	120	46
25	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	Na ₂ CO ₃ /0.2	^t BuOH	120	39
26	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	PivOH/0.2	^t BuOH	120	38
27	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	KOAc/0.4	^t BuOH	120	55
28	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	KOAc/0.6	^t BuOH	120	54
29 ^d	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	KOAc/0.6	^t BuOH	120	44
30^e	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	KOAc/0.4	^t BuOH	120	72
31 ^e	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	KOAc/0.4	^t BuOH	100	80 (75 ^f)
32^e	[Cp*Rh(MeCN) ₃ (SbF ₆) ₂]	AgF/3.0	KOAc/0.4	^t BuOH	80	60

^{*a*}Reaction conditions: ethyl benzimidate **1a** (30.0 mg, 0.2 mmol, 1.0 equiv), 2-methylthiophene **2a** (39.4 mg, 0.4 mmol, 2.0 equiv), catalysis (5 mol %), oxidant (x equiv), additive (20 mol%) and solvent (1.0 mL) at 120 °C for 12 h under air. ^{*b*}Yield was calculated from ¹H NMR analysis using CH₂Br₂ as internal standard. ^{*c*}0.5 mL *t*BuOH was used. ^{*d*}ethyl benzimidate **1a** (0.4 mmol, 2.0 equiv), 2-methylthiophene **2a** (19.6 mg, 0.2 mmol, 1.0 equiv) and ^{*t*}BuOH (0.5 mL) were used. ^{*e*}3.0 equiv **2a** was used. ^{*f*}Isolated yield. 1-AdCOOH = 1-adamantane carboxylic acid; DCE = 1,2-dichloroethane; DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide; MTBE = methyl *tert*-butyl ether; TFE = 2,2,2-trifluoroethanol; n. d. = not detected.

III. General procedure for the C–H/C–H Cross-Coupling of Benzimidates with Heteroarenes



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1** (1.0 equiv), **2** (3.0 equiv), $[Cp*Rh(MeCN)_3](SbF_6)_2$ (5.0 mol%), AgF (3.0 equiv), KOAc (0.4 equiv) in 'BuOH (0.2 M) under an air atmosphere. The reaction mixture was stirred at room temperature for 2 min, and then heated at 100 °C for 24 hours. The reaction mixture was cooled to room temperature, diluted with DCM, filtered through a celite pad, and washed with DCM. The combined filtrate was concentrated under

vacuum, and the residue was purified by column chromatography on silica gel to provide the desired product **3**.

For the synthesis of **3ml**: An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **2l** (80.1 mg, 0.6 mmol, 3.0 equiv), $[Cp*Rh(MeCN)_3](SbF_6)_2$ (5.0 mol%), AgF (0.6 mmol, 3.0 equiv), KOAc (0.4 equiv) in 'BuOH (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 100 °C. The imidate **1m** (0.2 mmol, 1.0 equiv) in 'BuOH (0.5 mL) was added into the reaction mixture over 2 h via a syringe pump. Afterward, the reaction was further stirred at 100 °C for 22 h. The reaction mixture was then cooled to ambient temperature, diluted with DCM, filtered through a celite pad, and washed with DCM. The combined filtrate was concentrated under vacuum, and the resulting residue was purified by column chromatography on silica gel to provide the desired product **3ml**.

IV. Mechanistic study

(i) Control experiment



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with benzonitrile (0.2 mmol, 21 μ L), **2a** (0.6 mmol, 3.0 equiv, 58 μ L), [Cp*Rh(MeCN)₃](SbF₆)₂ (5 mol%, 8.3 mg), AgF (0.6 mmol, 3.0 equiv, 75 mg), KOAc (40 mol%, 7.9 mg) and 'BuOH (1.0 mL) under an air atmosphere. The reaction was heated at 100 °C for 24 h. The reaction mixture is cooled to ambient temperature. The

TLC analysis showed that no **3aa** was generated in the catalytic system.

(ii) Parallel competitive reactions for kinetic isotope effect determination



Two separated oven-dried Schlenk tubes charged with **2n** (0.6 mmol, 80.4 mg), $[Cp*Rh(MeCN)_3](SbF_6)_2$ (5 mol%, 8.3 mg), AgF (3.0 equiv, 75.0 mg), KOAc (0.4 equiv, 7.9 mg) and 'BuOH (1.0 mL) were added **1a** (0.2 mmol, 29.8 mg) and **1a**-*d*₅ (0.2 mmol, 30.8 mg) under an air atmosphere, respectively. The reactions were stirred at room temperature for 1 minute and then heated at 100 °C for 1 h. After cooled to ambient temperature in water bath, the reaction mixtures were diluted with DCM, filtered through a celite pad and washed with 10-20 mL of DCM, respectively. The organic filtrates were concentrated under vacuum and the residues were purified by chromatography on silica gel to provide **3an** (9.3 mg, 20%) and **3an**-*d*₄ (6.3 mg, 13%), respectively, giving a KIE value of 1.54.



Two separated oven-dried Schlenk tubes charged with **1a** (0.2 mmol, 29.8 mg), [Cp*Rh(MeCN)₃](SbF₆)₂ (5 mol%, 8.3 mg), AgF (3.0 equiv, 75.0 mg), KOAc (0.4 equiv, 7.9 mg) and 'BuOH (1.0 mL) were added **2n** (0.6 mmol, 80.4 mg) and **2n**-*d* (0.6 mmol, 81.2 mg) under an air atmosphere, respectively. The reactions were stirred at room temperature for 1 minute and then heated at 100 °C for 1 h. After cooled to room temperature in water bath, the reaction mixtures were diluted with DCM, filtered through a celite pad and washed with 10-20 mL of DCM, respectively. The organic filtrates were concentrated under vacuum and the residues were analyzed by NMR without further purification, respectively. The yields were calculated by ¹H NMR using CH₂Br₂ as the internal standard (24% for **2n**, 15% for **2n**-*d*). A KIE value of 1.60 was obtained for the α -C–H bond of **2n**.





(iii) Detection of the intermediate 4aa

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 2-methylthiophene **2a** (58.0 μ L, 0.6 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (5 mol%, 8.3 mg), AgF (0.6 mmol, 3.0 equiv, 75 mg), KOAc (40 mol%, 7.9 mg) and 'BuOH (1.0 mL) under an air atmosphere. The reaction was heated at 100 °C for 0.5 h. Then the reaction mixture was cooled to room temperature in water bath and analyzed by HRMS without purification. The mass spectrum was obtained as below. HRMS (ESI⁺): calculated for **4aa** (C₁₄H₁₆NOS): 246.0953, found: 246.0950.



(iv)Stoichiometric reaction without the oxidant



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with ethyl benzimidates **1a** (15.0 mg, 0.1 mmol), 2-methylthiophene **2a** (29.0 μ L, 0.6 mmol), [Cp*Rh(MeCN)₃](SbF₆)₂ (1.0 equiv, 83 mg), KOAc (1.0 equiv, 9.8 mg) and 'BuOH (0.5 mL) under an air atmosphere. The reaction mixture was heated at 100 °C for 24 h. Then the reaction was cooled to room temperature and analyzed by GC-MS without purification. The result showed that **3aa** was not generated in the reaction system.

V. Experimental data for the described substances



2-(5-methylthiophen-2-yl)benzonitrile (3aa)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 2methylthiophene **2a** (58.0 μ L, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3aa** as a colorless liquid (30.0 mg, 75 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.54 (d, *J* = 1.0 Hz, 3H), 6.81 (dq, *J* = 3.4, 1.0 Hz, 1H), 7.31-7.36 (m, 1H), 7.45 (d, *J* = 3.6 Hz, 1H), 7.56-7.57 (m, 2H), 7.71(dt, *J* = 7.8, 1.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 15.6, 109.6, 119.2, 126.7, 127.2, 127.8, 129.4, 133.0, 134.5, 137.1, 138.0, 142.5 ppm. HRMS (ESI⁺): calculated for C₁₂H₁₀NS [M+H]⁺:200.0534, found: 200.0538.



2-(5-hexylthiophen-2-yl)benzonitrile (3ab)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 2hexylthiophene **2b** (108.0 µL, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 25/1, v/v) provided **3ab** as a colorless liquid (41.0 mg, 76 %). ¹H NMR (400 MHz, CDCl₃): δ = 0.90 (t, *J* = 7.0 Hz, 3H), 1.29-1.44 (m, 6H), 1.71 (quint, *J* = 7.6 Hz, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 6.82 (d, *J* = 3.7 Hz, 1H), 7.33 (ddd, *J* = 7.8, 6.6, 2.1 Hz, 1H), 7.48 (d, *J* = 3.7 Hz, 1H), 7.53-7.60 (m, 2H), 7.69-7.72 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.2, 22.7, 28.9, 30.3, 31.70, 109.5, 119.3, 125.5, 127.1, 127.6, 129.4, 130.0, 134.5, 136.8, 138.1, 148.7 ppm. HRMS (ESI⁺): calculated for C₁₇H₁₉NNaS [M+Na]⁺: 292.1136, found: 292.1134.



2-(5-(2-hydroxyethyl)thiophen-2-yl)benzonitrile (3ac)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 2-(thiophen-2-yl)ethanol **2c** (67.3 µL, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) provided **3ac** as an off-white solid (24.2 mg, 53 %). ¹H NMR (400 MHz, CDCl₃): δ = 1.66 (t, *J* = 5.7 Hz, 1H), 3.12 (td, *J* = 6.2, 0.7 Hz, 2H), 3.92 (q, *J* = 6.0 Hz, 2H), 6.93 (dt, *J* = 3.7, 0.9 Hz, 1H), 7.36 (ddd, *J* = 7.8, 5.0, 3.7 Hz, 1H), 7.51 (d, *J* = 3.7 Hz, 1H), 7.57-7.59 (m, 2H), 7.71-7.74 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 33.7, 63.4, 109.7, 119.1, 127.1, 127.4, 127.8, 129.5, 133.1, 134.5, 137.7, 138.1, 143.5 ppm. HRMS (ESI⁺): calculated for C₁₃H₁₁NNaOS [M+Na]⁺: 252.0459, found: 252.0461.



2-(5-methoxythiophen-2-yl)benzonitrile (3ad)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 2methoxythiophene **2d** (60.0 μ L, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3ad** as a white solid (18.1 mg, 43 %). ¹H NMR (400 MHz, CDCl₃): δ = 3.95 (s, 3H), 6.26 (d, *J* = 4.1 Hz, 1H), 7.30 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (d, *J* = 4.1 Hz, 1H), 7.47-7.57 (m, 2H), 7.69 (dd, *J* = 7.8, 1.1 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 60.4, 105.1, 109.1, 119.4, 125.3, 126.1, 126.7, 128.8, 133.1, 134.6, 137.9, 168.2 ppm. HRMS (ESI⁺): calculated for C₁₂H₉NNaOS [M+Na]⁺: 238.0303, found: 238.0298.



2-(5-chlorothiophen-2-yl)benzonitrile (3ae)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 2chlorothiophene **2e** (56.0 µL, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3ae** as a white solid (26.2 mg, 59 %). ¹H NMR (400 MHz, CDCl₃): δ = 6.98 (d, *J* = 4.0 Hz, 1H), 7.43-7.38 (m, 2H), 7.53 (ddd, *J* = 8.0, 1.3, 0.5 Hz, 1H), 7.60(ddd, *J* = 7.9, 7.5, 1.4 Hz, 1H), 7.74 (ddd, *J* = 7.8, 1.4, 0.5 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 110.0, 118.7, 127.2, 127.5, 128.1, 129.5, 132.2, 133.3, 134.6, 136.7, 137.9 ppm. HRMS (ESI⁺): calculated for C₁₁H₆ClNNaS [M+Na]⁺: 241.9802 (³⁵Cl), 243.9778 (³⁷Cl), found: 241.9802, 243.9882.



5-(2-cyanophenyl)thiophene-2-carbonitrile (3af)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), thiophene-2-carbonitrile **2f** (56.1 μ L, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3af**

as an off-white solid (26.0 mg, 62 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.53 (td, *J* = 7.6, 1.3 Hz, 1H), 7.59 (d, *J* = 4.0 Hz, 1H), 7.60-7.64 (m, 1H), 7.66-7.71 (m, 2H), 7.79-7.83 (m, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ = 110.9, 111.1, 113.8, 118.1, 127.8, 129.6, 130.1, 133.6, 134.7, 135.2, 138.3, 146.4 ppm. HRMS (ESI⁺): calculated for C12H7N2S [M+H]⁺: 211.0330, found: 211.0329.



2-(5-benzoylthiophen-2-yl)benzonitrile (3ag)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), phenyl(thiophen-2-yl)methanone **2g** (124.2 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3ag** as a white solid (38.0 mg, 66 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.48-7.56 (m, 3H), 7.60-7.65 (m, 1H), 7.65-7.73 (m, 4H), 7.80 (dd, *J* = 7.8, 0.7 Hz, 1H), 7.89-7.93 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 110.5, 118.5, 128.3, 128.7, 129.1, 129.4, 130.2, 132.7, 133.4, 134.6, 135.6, 136.6, 137.7, 144.8, 147.6, 188.1 ppm. HRMS (ESI⁺): calculated for C₂₇H₁₉NONa [M+Na]⁺: 396.1359, found: 396.1362.



2-(4-methylthiophen-2-yl)benzonitrile (3ah)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 3methylthiophene **2h** (58.2 μ L, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3ah** as a colorless liquid (28.1 mg, 70 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.32 (d, *J* = 1.0 Hz, 3H), 7.00-7.04, (m, 1H), 7.37 (ddd, *J* = 7.8, 6.9, 1.9 Hz, 1H), 7.47 (d, *J* = 1.4 Hz, 1H), 7.55-7.63 (m, 2H), 7.72 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.0, 109.8, 119.1, 122.9, 127.5, 129.6, 129.9, 133.1, 134.5, 137.9, 139.1, 139.2 ppm. HRMS (ESI⁺): calculated for C₁₃H₉NS [M+H]⁺: 200.0534, found: 200.0542.



2-(4-hexylthiophen-2-yl)benzonitrile (3ai)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 3hexylthiophene **2i** (108 µL, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 25/1, v/v) provided **3ai** as a colorless liquid (38.9 mg, 72 %). ¹H NMR (400 MHz, CDCl₃): δ = 0.89 (t, *J* = 7.0 Hz, 3H), 1.27-1.40 (m, 6H), 1.65 (quint, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 7.03 (dd, *J* = 2.2, 0.9 Hz, 1H), 7.36 (ddd, *J* = 7.7, 7.2, 1.6 Hz, 1H), 7.49 (d, *J* = 1.4 Hz, 1H), 7.55-7.63 (m, 2H), 7.72 (ddd, *J* = 7.8, 1.3, 0.5 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.3, 22.8, 29.1, 30.6, 30.7, 31.8, 109.8, 119.1, 122.2, 127.5, 129.1, 129.6, 133.1, 134.5, 138.0, 139.1, 144.8 ppm. HRMS (ESI⁺): calculated for C₁₇H₁₉NNaS [M+Na]⁺: 292.1136, found: 292.1140.



2-(4,5-dibromothiophen-2-yl)benzonitrile (3aj)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 2,3dibromothiophene **2j** (69.3 µL, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3aj** as a white solid (38.1 mg, 55 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.40 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, c CDCl₃): δ = 110.1, 113.1, 115.1, 118.2, 128.8, 129.4, 130.0, 133.4, 134.6, 135.7, 140.5 ppm. HRMS (ESI⁺): calculated for C₁₁H₅Br₂NNaS [M+Na]⁺: 365.8387(⁷⁹Br⁸¹Br), 363.8407(2⁷⁹Br), 367.8366(2⁸¹Br), found: 365.8390, 363.8402, 367.8372.



2-(5-acetyl-4-bromothiophen-2-yl)benzonitrile (3ak)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 1-(3bromothiophen-2-yl)ethanone **2k** (123.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) provided **3ak** as a white solid (25.0 mg, 41 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.74 (s, 3H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.59 (s, 1H), 7.61-7.70 (m, 2H), 7.79 (d, *J* = 7.7 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 29.9, 110.6, 114.7, 118.0, 129.6, 129.8, 133.2, 133.5, 134.7, 140.5, 145.4, 190.3 ppm. HRMS (ESI⁺): calculated for C₁₃H₉BrNOS [M+H]⁺: 305.9588(⁷⁹Br), 307.9568(⁸¹Br), found: 305.9589, 307.9568.



methyl 5-(2-cyanophenyl)-3-methylthiophene-2-carboxylate (3al)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **2l** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3al** as a white solid (34.1 mg, 66 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.59$ (s, 3H), 3.88 (s, 3H), 7.41 (d, J = 0.4 Hz, 1H), 7.45 (ddd, J = 7.8, 5.0, 3.8 Hz, 1H), 7.61-7.64 (m, 2H), 7.76 (dt, J = 7.8, 1.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.3$, 52.1, 110.4, 118.5, 127.9, 128.7, 129.8, 131.9, 133.3, 134.6, 136.7, 143.1, 147.1, 163.0 ppm. HRMS (ESI⁺): calculated for C₁₄H₁₁NNaO₂S [M+Na]⁺: 280.0408, found: 280.0404.



2-(5-formyl-4-methylthiophen-2-yl)benzonitrile (3am)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 3methylthiophene-2-carbaldehyde **2m** (65.0 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) provided **3am** as a yellow solid (21.1 mg, 46 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.63 (s, 3H), 7.47-7.53 (m, 2H), 7.64-7.68 (m, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 10.07 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.5, 110.4, 118.4, 129.2, 130.0, 131.8, 133.5, 134.7, 136.3, 138.7, 147.5, 148.1, 182.3 ppm. HRMS (ESI⁺): calculated for C₁₃H₁₀NOS [M+H]⁺: 228.0483, found: 228.0485.



2-(benzo[b]thiophen-2-yl)benzonitrile (3an)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), benzo[*b*]thiophene **2n** (80.4 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3an** as an off-white solid (36.0 mg, 76 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.38-7.41 (m, 2H), 7.42-7.47 (m, 1H), 7.65 (td, *J* = 7.8, 1.4 Hz, 1H), 7.70-7.73 (m, 1H), 7.78-7.81 (m, 1H), 7.85-7.90 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 110.6, 118.8, 123.3, 124.5, 124.6, 125.0, 125.4, 128.3, 130.4, 133.2, 134.6, 137.6, 139.2, 140.2, 140.3 ppm. HRMS (ESI⁺): calculated for C₁₅H₉NNaS [M+Na]⁺: 258.0353, found: 258.0340.



2-(benzofuran-2-yl)benzonitrile (3ao)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), benzofurane **2o** (70.8 mg, 0.6 mmol) were used. Purification by column

chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3ao** as an off-white solid (30.0 mg, 68 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.26-7.30 (m, 1H), 7.37 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.55 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.66-7.73 (m, 3H), 7.78 (dd, *J* = 7.8, 0.9 Hz, 1H), 8.12 (dd, *J* = 8.1, 0.7 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 106.9, 108.2, 111.4, 119.0, 122.1, 123.5, 125.8, 127.2, 128.3, 128.9, 133.1, 133.2, 134.6, 151.3, 154.8 ppm. HRMS (ESI⁺): calculated for C₁₅H₉NNaO [M+Na]⁺: 242.0582, found: 242.0586.



2-(thieno[3,2-*b*]thiophen-2-yl)benzonitrile (3ap)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), thieno[3,2-*b*]thiophene **2p** (85.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3ap** as a white solid (30.1 mg, 62 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.29(d, *J* = 5.3 Hz, 1H), 7.39-7.43 (m, 1H), 7.46 (dd, *J* = 5.0, 0.6 Hz, 1H), 7.60-7.68 (m, 2H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.86 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 110.0, 119.0, 119.5, 120.1, 127.9, 128.7, 129.7, 133.3, 134.6, 137.9, 140.1, 140.2, 140.9 ppm. HRMS (ESI⁺): calculated for C₁₃H₈NS₂ [M+H]⁺: 242.0098, found: 242.1003.



2-(3-bromobenzo[b]thiophen-2-yl)benzonitrile (3aq)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 3bromobenzo[*b*]thiophene **2q** (127.9 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3aq** as a white solid (24.0 mg, 38 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.43-7.66 (m, 4H), 7.68-7.74 (m, 1H), 7.76-7.88 (m, 2H), 7.92 (t, *J* = 7.3 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 109.3, 109.9, 114.1, 115.6, 115.9, 117.6, 122.48, 122.51, 124.2, 124.3, 125.70, 125.75, 126.4, 126.5, 129.5, 132.1, 132.2, 132.4, 132.7, 133.65, 136.8, 137.2, 138.18, 138.22, 138.7, 138.8 ppm. HRMS (ESI⁺): calculated for C₁₅H₈BrNNaS 335.9459 (⁷⁹Br), 337.9438 (⁸¹Br), found: 335.9451, 337.9429.



2-(4-bromobenzo[b]thiophen-2-yl)benzonitrile (3ar)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 4bromobenzo[*b*]thiophene **2r** (127.9 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3aq** as a white solid (23.0 mg, 37 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.21-7.26 (m, 1H), 7.48 (td, *J* = 7.6, 1.3 Hz, 1H), 7.55-7.59 (m, 1H), 7.66 (td, *J* = 7.7, 1.2 Hz, 1H), 7.69-7.73 (m, 1H), 7.77-7.83 (m, 2H), 7.96 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 111.0, 118.2, 118.5, 121.4, 124.9, 126.2, 128.3, 128.8, 130.4, 133.2, 134.6, 137.2, 140.1, 140.2, 140.9 ppm. HRMS (ESI⁺): calculated for C₁₅H₈BrNNaS 335.9459 (⁷⁹Br), 337.9438 (⁸¹Br), found: 335.9453, 337.9436.



2-(6-bromobenzo[b]thiophen-2-yl)benzonitrile (3as)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), 6bromobenzo[*b*]thiophene **2s** (127.9 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3at** as a white solid (39.0 mg, 62 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.46 (td, *J* = 7.7, 1.4 Hz, 1H), 7.50 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.65 (td, *J* = 7.6, 1.2 Hz, 1H), 7.68-7.73 (m, 2H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.84 (s, 1H), 8.00 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 110.6, 118.7, 119.4, 124.1, 124.8, 125.7, 128.5, 128.6, 130.3, 133.3, 134.7, 137.1, 139.0, 139.9, 141.6 ppm. HRMS (ESI⁺): calculated for C₁₅H₈BrNNaS 335.9459 (⁷⁹Br), 337.9438 (⁸¹Br), found: 335.9451, 337.9446.



2-(naphtho[2,1-b]thiophen-2-yl)benzonitrile (3at)

Following the general procedure, ethyl benzimidates **1a** (30.0 mg, 0.2 mmol), naphtho[2,1-*b*]thiophene **2t** (110.6 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3as** as a white solid (34.0 mg, 60 %). ¹H NMR (400 MHz, CDCl₃): δ = 7.45 (td, *J* = 7.7, 1.2 Hz, 1H), 7.56 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.61-7.68 (m, 2H), 7.75-7.83 (m, 3H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 8.55 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 110.4, 119.0, 120.2, 122.6, 123.9, 125.8, 126.4, 127.0, 128.1, 128.8, 129.6, 130.2, 131.2, 133.2, 134.7, 136.7, 137.7,



4-methyl-2-(5-methylthiophen-2-yl)benzonitrile (3ba)

Following the general procedure, ethyl 4-methylbenzimidates **1b** (36.2 mg, 0.2 mmol), 2-methylthiophene **2a** (58.0 µL, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3ba** as an almost colorless liquid (34.1 mg, 80 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.42 (s, 3H), 2.53 (d, *J* = 1.0 Hz, 3H), 6.80 (dt, *J* = 3.6, 1.1 Hz, 1H), 7.14 (ddd, *J* = 7.9, 1.6, 0.7 Hz, 1H), 7.37-7.35 (m, 1H), 7.43 (d, *J* = 3.6 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 15.5, 21.9, 106.6, 119.5, 126.6, 127.6, 128.1, 130.0, 134.3, 137.2, 137.8, 142.2, 143.9 ppm. HRMS (ESI⁺): calculated for C₁₃H₁₁NNaS [M+Na]⁺: 236.0510, found: 236.0510.



methyl 5-(2-cyano-4-methylphenyl)-3-methylthiophene-2-carboxylate (3cl)

Following the general procedure, ethyl 3-methylbenzimidate 1c (32.7 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate 2l (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided 3cl as a white solid (32.0 mg, 56 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.41 (s, 3H), 2.58 (s, 3H), 3.88 (s, 3H), 7.38 (s, 1H), 7.42 (ddd, *J* = 8.1, 1.8, 0.6 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.55 (dd, *J* = 1.2, 0.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.3, 21.0, 52.1, 110.1, 118.7, 127.4, 129.7, 131.5, 133.8, 134.2, 134.8, 139.2, 143.3, 147.1, 163.0 ppm. HRMS (ESI⁺): calculated for C₁₅H₁₃NNaO₂S [M+H]⁺: 294.0565, found: 294.0967.



methyl 5-(5-methoxy-2-cyanophenyl)-3-methylthiophene-2-carboxylate (3dl)

Following the general procedure, ethyl 4-methoxybenzimidate **1d** (35.9 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **2l** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3dl** as a white solid (32.0 mg, 56 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.58$ (s, 3H), 3.88 (s, 3H), 3.89 (s, 3H), 6.94 (dd, J = 8.7, 2.5 Hz, 1H), 7.08 (d, J = 2.5 Hz, 1H), 7.41 (s, 1H), 7.67 (d, J = 8.7 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.3, 52.1, 55.9, 102.2, 114.6, 115.2, 118.9, 127.8, 131.9, 136.3, 138.5, 143.1, 147.1, 162.9, 163.0 ppm. HRMS (ESI⁺): calculated for C₁₅H₁₃NNaO₃S [M+Na]⁺: 310.0514, found: 310.0518.$





Following the general procedure, ethyl biphenyl-3-carbimidate **1e** (45.1 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **2l** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3el** as a white solid (30.0 mg, 45 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.61$ (s, 3H), 3.89 (s, 3H), 7.44-7.53 (m, 4H), 7.59-7.68 (m, 3H), 7.80-7.84 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.3$, 52.1, 108.8, 118.6, 127.2, 127.4, 127.9, 128.5, 129.1, 129.3, 132.0, 135.0, 137.1, 138.7, 143.2, 146.3, 147.2, 163.0 ppm. HRMS (ESI⁺): calculated for C₂₀H₁₅NNaO₂S [M+Na]⁺: 365.0721, found: 365.0726.



methyl 5-(5-chloro-2-cyanophenyl)-3-methylthiophene-2-carboxylate (3fl)

Following the general procedure, ethyl 4-chlorobenzimidate **1f** (36.7 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **2l** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3fl** as a white solid (29.1 mg, 50 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.59$ (s, 3H), 3.89 (s, 3H), 7.41-7.44 (m, 2H), 7.61-7.63 (m, 1H), 7.68-7.71 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.3$, 52.2, 108.7, 117.8, 128.6, 128.9, 129.9, 132.4, 135.6, 138.3, 139.9, 141.4, 147.2, 162.8 ppm. HRMS (ESI⁺): calculated for C₁₄H₁₀ClNNaO₂S [M+Na]⁺: 314.0018 (³⁵Cl), 315.9989 (³⁷Cl), found: 314.0020, 315.9993.



methyl 5-(5-bromo-2-cyanophenyl)-3-methylthiophene-2-carboxylate (3gl)

Following the general procedure, ethyl 4-bromobenzimidate **1g** (45.6 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **2l** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3gl** as a white solid (29.0 mg, 43 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.59$ (s, 3H), 3.89 (s, 3H), 7.42 (s, 1H), 7.57-7.62 (m, 2H), 7.78 (dd, J = 1.7, 0.5 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.3, 52.2, 109.1, 117.9, 128.3, 128.6, 131.8, 132.4, 132.8, 135.5, 138.2, 141.3, 147.1, 162.8 ppm. HRMS (ESI⁺): calculated for C₁₄H₁₀BrNNaO₂S [M+Na]⁺: 357.9513 (⁷⁹Br), 359.9493 (⁸¹Br), found: 357.9512, 359.9496.$



methyl 5-(5-iodo-2-cyanophenyl)-3-methylthiophene-2-carboxylate (3hl)

Following the general procedure, ethyl 4-iodobenzimidate **1h** (55.0 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **2l** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3hl** as a white solid (36.0 mg, 47 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.59$ (s, 3H), 3.89 (s, 3H), 7.40 (s, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.79 (ddd, J = 8.2, 1.7, 0.4 Hz, 1H), 7.99 (d, J = 1.7 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.3$, 52.2, 100.7, 109.7, 118.1, 128.6, 132.3, 135.2, 137.7, 137.8, 138.7, 141.2, 147.1, 162.8 ppm. HRMS (ESI⁺): calculated for C₁₄H₁₀INNaO₂S [M+Na]⁺: 405.9375, found: 405.9376.



methyl 5-(5-bromo-2-cyano-4-methylphenyl)-3-methylthiophene-2-carboxylate (3il)

Following the general procedure, ethyl 4-bromo-3-methylbenzimidate **1i** (48.5 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **2l** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3il** as a white solid (32.0 mg, 46 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.45$ (s, 3H), 2.58 (s, 3H), 3.88 (s, 3H), 7.38 (s, 1H), 7.59 (s, 1H), 7.81 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.3$, 22.7, 52.1, 109.1, 118.0, 128.1, 130.8, 132.0, 133.4, 135.4, 135.8, 139.3, 141.5, 147.2, 162.9 ppm. HRMS (ESI⁺): calculated for C₁₅H₁₂BrNNaO₂S [M+Na]⁺: 371.9670 (⁷⁹Br), 373.9649 (⁸¹Br), found: 371.9672, 373.9653.



2-fluoro-6-(5-methylthiophen-2-yl)benzonitrile (3ja)

Following the general procedure, ethyl 2-fluorobenzimidate 1j (45.1 mg, 0.2 mmol), 2-methylthiophene 2a (58.0 μ L, 0.6 mmol) were used. Purification by column

chromatography on silica gel (petroleum ether/ethyl acetate = 25/1, v/v) provided **3ja** as a white solid (20.0 mg, 46 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.54$ (d, J = 1.0 Hz, 3H), 6.81-6.83 (m, 1H), 7.09 (td, J = 8.5, 0.9 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.49-7.57 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 15.6$, 98.9 (d, $J_{C-F} = 16.4$ Hz), 114.0 (d, $J_{C-F} = 20.2$ Hz), 114.1 (d, $J_{C-F} = 0.9$ Hz), 124.7 (d, $J_{C-F} = 3.2$ Hz), 126.9, 128.4, 134.5 (d, $J_{C-F} = 9.5$ Hz), 135.9 (d, $J_{C-F} = 2.7$ Hz), 139.7, 143.3, 164.6 (d, $J_{C-F} = 258.5$) ppm. HRMS (ESI⁺): calculated for C₁₂H₈FNNaS [M+Na]⁺: 240.0259, found: 240.0265.



methyl 5-(2-cyano-3-fluoro-5-methylphenyl)-3-methylthiophene-2-carboxylate (3kl)

Following the general procedure, ethyl 2-fluoro-4-methylbenzimidate **1k** (48.5 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **2m** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **3kl** as a white solid (22.0 mg, 38 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 2.45$ (s, 3H), 2.58 (s, 3H), 3.89 (s, 3H), 7.02 (ddd, J = 9.4, 1.4, 0.7 Hz, 1H), 7.22-7.24 (m, 1H), 7.43-7.44 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.3$, 22.1 (d, $J_{C-F} = 1.8$ Hz), 52.2, 96.8 (d, $J_{C-F} = 16.8$ Hz), 113.7, 116.4 (d, $J_{C-F} = 19.9$ Hz), 126.1 (d, $J_{C-F} = 2.7$ Hz), 128.2, 132.2, 137.8 (d, $J_{C-F} = 1.2$ Hz), 142.0 (d, $J_{C-F} = 3.0$ Hz), 146.7 (d, $J_{C-F} = 9.3$ Hz), 147.1, 162.9, 164.6 (d, $J_{C-F} = 258.8$ Hz) ppm. HRMS

(ESI⁺): calculated for C₁₅H₁₂FNNaO₂S [M+Na]⁺: 312.0470, found: 312.0470.



methyl 5-(3-cyanonaphthalen-2-yl)-3-methylthiophene-2-carboxylate (3ll)

Following the general procedure, ethyl 2-naphthimidate **11** (48.5 mg, 0.2 mmol), methyl 3-methylthiophene-2-carboxylate **21** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, v/v) provided **311** as a white solid (28.0 mg, 46 %), meanwhile, 2-naphthonitrile was obtained in 36% yield (11.0 mg). ¹H NMR (400 MHz, CDCl₃): δ = 2.62 (s, 3H), 3.90 (s, 3H), 7.45 (s, 1H), 7.59-7.70 (m, 2H), 7.87-7.92 (m, 2H), 8.05 (s, 1H), 8.34 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 16.4, 52.1, 108.4, 118.7, 127.5, 128.3, 128.37, 128.42, 129.4, 130.0, 130.9, 131.7, 131.8, 134.7, 136.9, 143.5, 147.2, 163.1 ppm. HRMS (ESI⁺): calculated for C₁₈H₁₃NNaO₂S [M+Na]⁺: 330.0565, found: 330.0570.



methyl 5-(3-cyanobenzo[b]thiophen-2-yl)-3-methylthiophene-2-carboxylate (3ml)

Ethyl benzo[*b*]thiophene-3-carbimidate **1m** (41.4 mg, 0.2 mmol), methyl 3methylthiophene-2-carboxylate **2l** (80.1 mg, 0.6 mmol) were used. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) provided **3ml** as an off-white solid (16.0 mg, 26 %). ¹H NMR (400 MHz, CDCl₃): δ = 2.60 (s, 3H), 3.90 (s, 3H), 7.44-7.49 (m, 1H), 7.50-7.56 (m, 2H), 7.81 (d, J = 7.9 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.1, 52.3, 102.4,$ 114.8, 122.5, 122.9, 126.7, 127.0, 128.9, 132.2, 136.7, 137.1, 138.9, 146.3, 147.2, 162.6 ppm. HRMS (ESI⁺): calculated for C₁₆H₁₁NNaO₂S₂ [M+Na]⁺: 336.0129, found: 336.0132.

VI. Reference

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