

Supporting Information

Rh(III)-Catalyzed Decarboxylative ortho-Heteroarylation of Aromatic Carboxylic Acids by Using the Carboxylic Acid as a Traceless Directing Group

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I. General Remarks

NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer. The ^1H NMR (400 MHz) chemical shifts were measured relative to CDCl_3 , TMS or $\text{DMSO}-d_6$ as the internal reference (CDCl_3 : $\delta = 7.26$ ppm; TMS: $\delta = 0.00$ ppm; $\text{DMSO}-d_6$: $\delta = 2.50$ ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using CDCl_3 or $\text{DMSO}-d_6$ as the internal standard (CDCl_3 : $\delta = 77.16$ ppm; $\text{DMSO}-d_6$: $\delta = 39.52$ ppm). High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (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. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ were purchased from Shaanxi Kaida Chemical Engineering (China) CO., Ltd. AgSbF_6 was purchased from Alfa Aesar. Ag_2CO_3 was purchased from Tianjin Yin Li Da Chemical Engineering (China) CO., Ltd. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ was purchased from Shanghai Kefeng Chemical Reagent (China) CO., Ltd. $[\text{Cp}^*\text{RhCl}_2]_2$,¹ and indole derivatives,² indolizine derivatives,³ were prepared according to the literature procedures. All solvents were purified and dried according to standard methods prior to use.

II. Optimization of the Decarboxylative *ortho*-Heteroarylation of Aromatic Carboxylic Acids

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with the catalyst (2.5-5.0 mol %), oxidant (2.0 equiv), base (2.0 equiv), 2-methoxybenzoic acid (**1a**, 0.25 mmol), benzothiophene (**2a**, 3.0 equiv), and solvent (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under a N_2 atmosphere, and then heated at 130-150 $^\circ\text{C}$ in a pre-heated oil bath for the indicated time. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2 , filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2 . The combined organic extracts were concentrated, and the resulting residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 50/1 v/v) to provide the desired product **3a**.

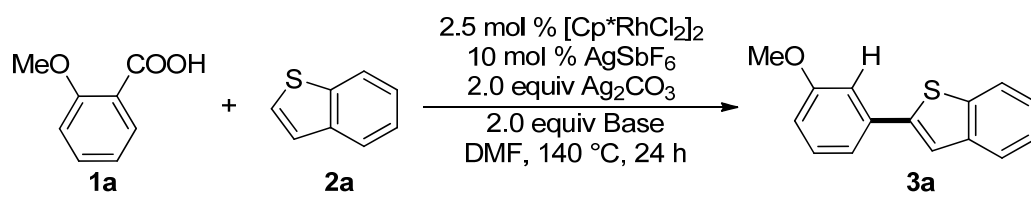
(1) Table S1. Optimization of the Reaction Conditions by Screening Catalyst^{a,b}

COc1ccccc1C(=O)O (1a) + c1ccc2c(c1)sc3ccccc32 (2a) $\xrightarrow[\text{Solvent, 140 } ^\circ\text{C, 24 h}]{\text{Cat., Oxidant, Base}}$ COc1ccccc1C(=O)O-c1ccc2c(c1)sc3ccccc32 (3a)

Entry	Catalyst	Oxidant	Base	Solvent	Yield (%)
1	Pd(OAc) ₂	Ag ₂ CO ₃	KOAc	1,4-dioxane	n.d.
2	Pd(OAc) ₂	Ag ₂ CO ₃	NaOAc	1,4-dioxane	n.d.
3	Pd(OAc) ₂	Ag ₂ CO ₃	K ₂ HPO ₄	1,4-dioxane	n.d.
4	Pd(OAc) ₂	Ag ₂ CO ₃	K ₂ HPO ₄	<i>t</i> -BuOH	n.d.
5	Pd(OAc) ₂	Ag ₂ CO ₃	K ₂ HPO ₄	DMF	n.d.
6	Pd(OAc) ₂	Ag ₂ CO ₃	-	diglyme	n.d.
7	Pd(OAc) ₂	Cu(OAc) ₂	-	DMF	n.d.
8 ^c	[Cp*RhCl ₂] ₂	Ag ₂ CO ₃	-	DMF	35

^aReactions were carried out using Pd(OAc)₂ (5.0 mol %), oxidant (2.0 equiv), base (2.0 equiv), 2-methoxybenzoic acid (0.25 mmol), benzothiophene (3.0 equiv), and solvent (1.0 mL) at 140 °C for 24 h under a N₂ atmosphere. ^bYield of isolated product. ^c[Cp*RhCl₂]₂ (2.5 mol %), AgSbF₆ (10 mol %), 4 Å MS (100 mg). DMF = dimethyl formamide.

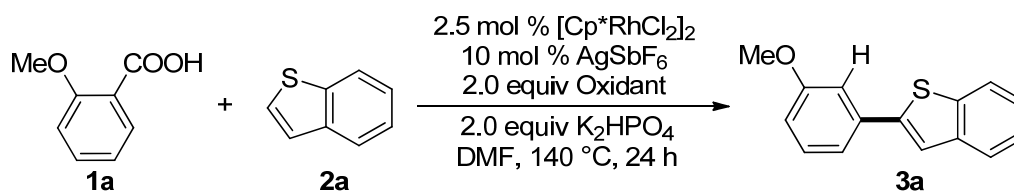
(2) Table S2. Screening Base^{a,b}



Entry	Base	Yield (%)
1	LiCl	27
2	LiOAc	28
3	NaOAc	24
4	KOAc	38
5	Bu ₄ NOAc	35
6	Bu ₄ NBr	trace
7	Cs ₂ CO ₃	n.d.
8	K ₂ CO ₃	trace
9	KHCO ₃	34
10	KH ₂ PO ₄	50
11	K ₃ PO ₄	38
12	KF	trace
13	KHF ₂	14
14	K ₂ HPO ₄	54

^aReactions were carried out using [Cp*RhCl₂]₂ (2.5 mol %), AgSbF₆ (10 mol %), Ag₂CO₃ (2.0 equiv), base (2.0 equiv), 2-methoxybenzoic acid (0.25 mmol), benzothiophene (3.0 equiv), 4 Å MS (100 mg), and DMF (1.0 mL) at 140 °C for 24 h under a N₂ atmosphere. ^bYield of isolated product. DMF = dimethyl formamide.

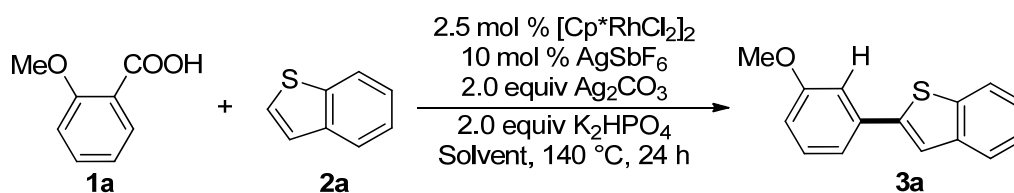
(3) **Table S3. Screening Oxidant**^{a,b}



Entry	Oxidant	Yield (%)
1	Ag ₂ CO ₃	54
2	Ag ₂ O	27
3	AgOAc	41
4	Cu(OAc) ₂	34
5	CuCl ₂	trace
6	K ₂ S ₂ O ₈	n.d.
7	BQ	n.d.
8	-	trace

^aReactions were carried out using [Cp*RhCl₂]₂ (2.5 mol %), AgSbF₆ (10 mol %), oxidant (2.0 equiv), K₂HPO₄ (2.0 equiv), 2-methoxybenzoic acid (0.25 mmol), benzothiophene (3.0 equiv), 4 Å MS (100 mg), and DMF (1.0 mL) at 140 °C for 24 h under a N₂ atmosphere. ^bYield of isolated product. DMF = dimethyl formamide.

(4) **Table S4. Screening Solvent**^{a,b}

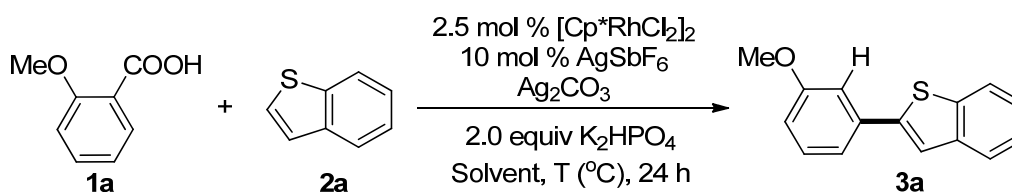


Entry	Solvent	Yield (%)
1	DCE	n.d.
2	1,4-dioxane	35
3	diglyme	14
4	<i>t</i> -AmylOH	trace
5	<i>t</i> -BuOH	trace
6	DMA	52
7	DMSO	n.d.
8	PhCF ₃	33

9	PhCl	40
10	xylene	n.d.
11	AcOH	trace
12	NMP	65
13	NMP/PhCl (v/v = 4/1)	45
14	DMF/DMSO (v/v = 20/1)	33

^aReactions were carried out using [Cp*RhCl₂]₂ (2.5 mol %), AgSbF₆ (10 mol %), Ag₂CO₃ (2.0 equiv), K₂HPO₄ (2.0 equiv), 2-methoxybenzoic acid (0.25 mmol), benzothiophene (3.0 equiv), 4 Å MS (100 mg), and solvent (1.0 mL) at 140 °C for 24 h under a N₂ atmosphere. ^bYield of isolated product. DCE = 1,2-dichloroethane, DMF = dimethyl formamide, DMA = dimethyl acetamide, DMSO = dimethyl sulfoxide, NMP = 1-methylpyrrolidin-2-one.

(5) **Table S5. Screening Temperature, the Amount of Ag₂CO₃, and without AgSbF₆^{a,b}**



Entry	Solvent	T (°C)	Yield (%)
1	DMF	130	41
2	DMF	150	70
3	NMP	150	75
4 ^c	NMP	150	83
5 ^d	NMP	150	65

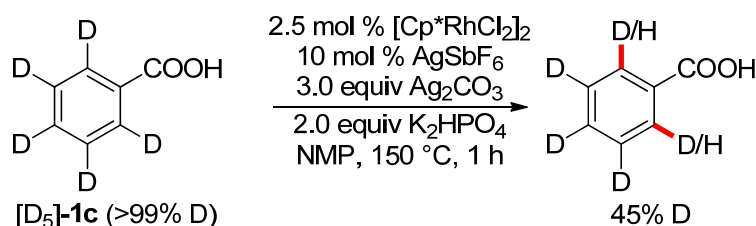
^aReactions were carried out using [Cp*RhCl₂]₂ (2.5 mol %), AgSbF₆ (10 mol %), Ag₂CO₃ (2.0 equiv), K₂HPO₄ (2.0 equiv), 2-methoxybenzoic acid (0.25 mmol), benzothiophene (3.0 equiv), 4 Å MS (100 mg), and solvent (1.0 mL) under a N₂ atmosphere. ^bYield of isolated product. ^cAg₂CO₃ (3.0 equiv). DMF = dimethyl formamide. NMP = 1-methylpyrrolidin-2-one. ^dWithout AgSbF₆.

III. General Procedure for the Decarboxylative *ortho*-Heteroarylation of Aromatic Carboxylic Acids

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with [Cp*RhCl₂]₂ (2.5 mol %), AgSbF₆ (10 mol %), Ag₂CO₃ (0.75 mmol, 3.0 equiv), K₂HPO₄ (0.5 mmol, 2.0 equiv), benzoic acid (0.25 mmol), heteroarene (0.75 mmol, 3.0 equiv), 4 Å MS (100 mg), and NMP (1.0 mL) under a N₂ atmosphere. The reaction mixture was stirred for 10 min at room temperature under an N₂ atmosphere, and then

heated at 150~160 °C in a pre-heated oil bath. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of CH₂Cl₂, filtered through a celite pad, and washed with 10-20 mL of CH₂Cl₂. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

IV. The H/D Exchange Experiments for Each Coupling Partner (1c and 2a)



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with [Cp*RhCl₂]₂ (3.9 mg, 6.25 μmol, 2.5 mol %), AgSbF₆ (8.6 mg, 25.0 μmol, 10 mol %), 2,3,4,5,6-pentadeuteriobenzoic acid⁴ (0.25 mmol), Ag₂CO₃ (0.75 mmol, 3.0 equiv), K₂HPO₄ (0.50 mmol, 2.0 equiv), and 4 Å MS (100 mg) in NMP (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under a N₂ atmosphere, and then heated at 150 °C in a pre-heated oil bath for 1 h. After the mixture was cooled, iodomethane (1.5 mmol, 6.0 equiv), and K₂CO₃ (0.75 mmol, 3.0 equiv) were added, and the resulting mixture was stirred under air at room temperature for 3 h. The reaction mixture was diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH₄Cl solution, and dried over anhydrous Na₂SO₄. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculated from ¹H NMR analysis.

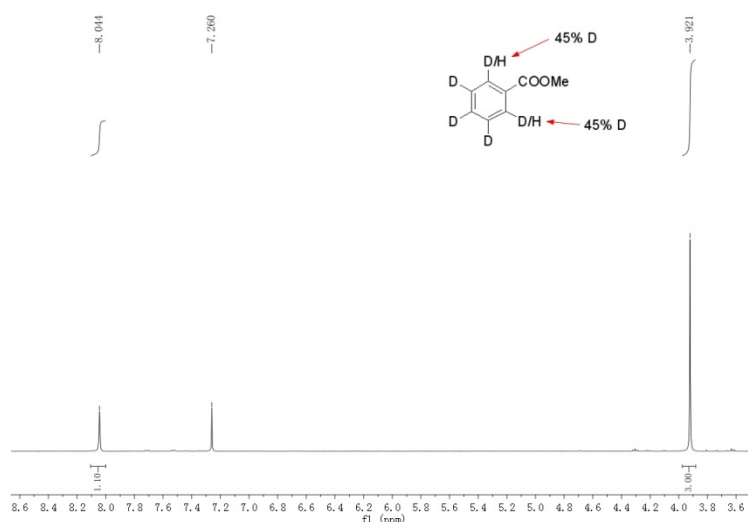
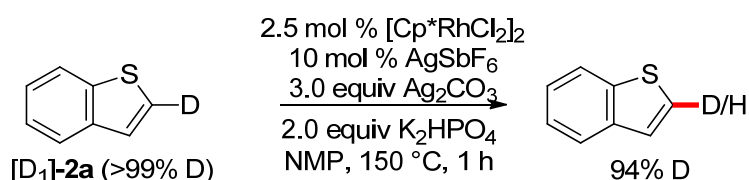


Figure. S1. Copy of ^1H NMR Spectra of H/D Exchange Experiment of 2,3,4,5,6-Pentadeuteriobenzoic Acid.



A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $[\text{Cp}^*\text{RhCl}_2]_2$ (3.9 mg, 6.25 μmol , 2.5 mol %), AgSbF_6 (8.6 mg, 25.0 μmol , 10 mol %), 2-deuterio-benzothiophene⁵ (0.25 mmol), Ag_2CO_3 (0.75 mmol, 3.0 equiv), K_2HPO_4 (0.50 mmol, 2.0 equiv), and 4 Å MS (100 mg) in NMP (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under a N_2 atmosphere, and then heated at 150 $^\circ\text{C}$ in a pre-heated oil bath for 1 h. After the mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH_4Cl solution, and dried over anhydrous Na_2SO_4 . The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculated from ^1H NMR analysis.

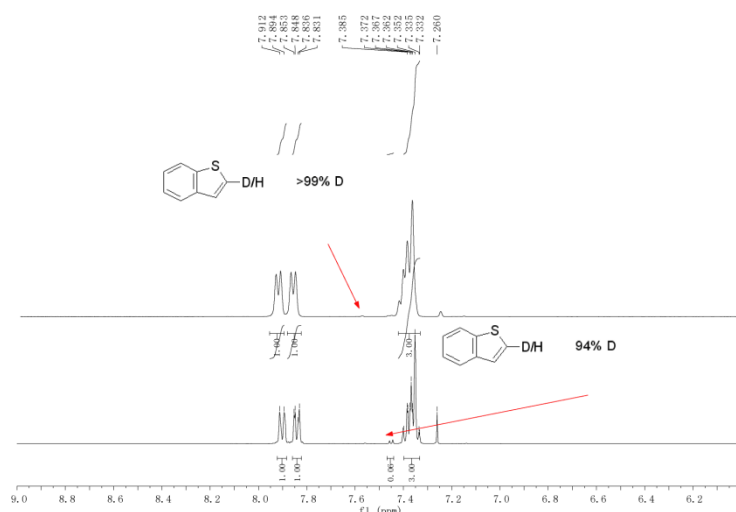
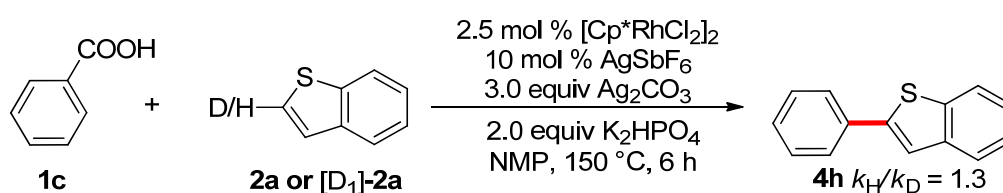
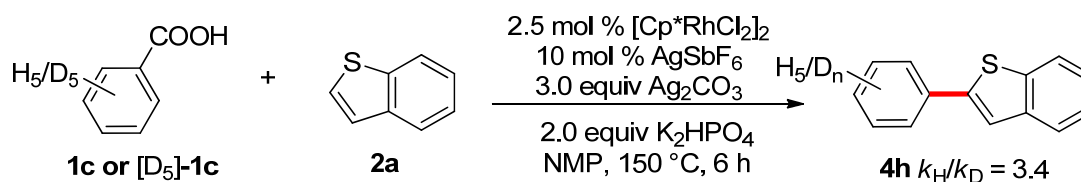


Figure. S2 Copy of ^1H NMR Spectra of H/D Exchange Experiment of 2-Deuterio-benzothiophene.

V. Kinetic Isotope Experiments



Two sets of reactions were carried out in a parallel manner. In each case benzoic acid was allowed to react with benzothiophene and 2-deuterio-benzothiophene, respectively. The sealed tubes were screw capped and heated to 150 $^\circ\text{C}$ (oil bath). After being stirred for 6 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH_4Cl solution, and dried over anhydrous Na_2SO_4 . The yield of **4h** was determined by ^1H NMR of the crude product using 1,3,5-trimethoxybenzene as internal standard.

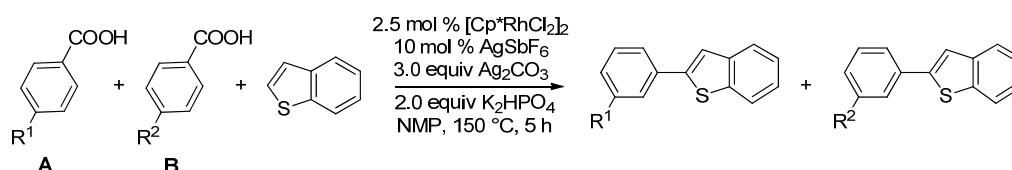


Two sets of reactions were carried out in a parallel manner. In each case benzothiophene was allowed to react with 2,3,4,5,6-pentadeuteriobenzoic acid and benzoic acid, respectively. The sealed tubes were screw capped and heated to 150 $^\circ\text{C}$

(oil bath). After being stirred for 6 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH₄Cl solution, and dried over anhydrous Na₂SO₄. The yield of **4h** was determined by ¹H NMR of the crude product using 1,3,5-trimethoxybenzene as internal standard.

VI. Competition Experiments

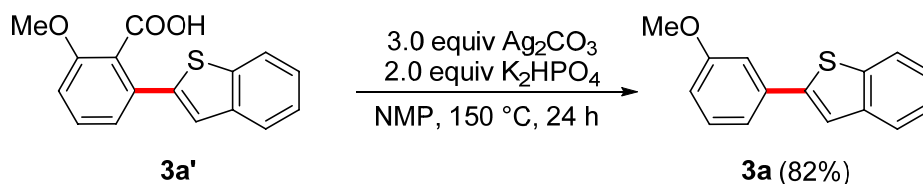
Table S6. Intermolecular Competition Experiments of Benzoic Acids



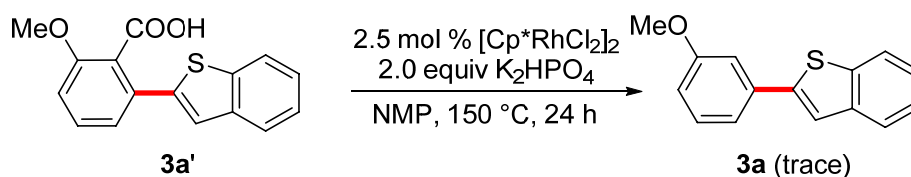
Entry	R ¹	R ²	Ratio of products
1	CN	OMe	4b/3a = 1 : 2.5
2	CN	Br	4b/4a = 1 : 1.3
3	Br	OMe	4a/3a = 1 : 1.8

A flame-dried Schlenk test tube with a magnetic stirring bar was charged with [Cp^{*}RhCl₂]₂ (3.9 mg, 6.25 μmol, 2.5 mol %), AgSbF₆ (8.6 mg, 25.0 μmol, 10 mol %), benzoic acid **A** (0.125 mmol), benzoic acid **B** (0.125 mmol), benzothiophene (0.75 mmol, 3.0 equiv), Ag₂CO₃ (207 mg, 0.75 mmol), K₂HPO₄ (87 mg, 0.50 mmol), 4 Å MS (100 mg), and NMP (1.0 mL). The reaction mixture was stirred for 10 min at room temperature under a N₂ atmosphere, and then heated at 150 °C in a pre-heated oil bath for 5 h. The reaction mixture was cooled to room temperature, diluted with 20 mL of EtOAc, filtered through a celite pad, washed with sat. NH₄Cl solution, and dried over anhydrous Na₂SO₄. The solvent was then removed under reduced pressure. The ratio was determined by ¹H NMR of the crude product.

VII. Decarboxylation of 2-(Benzothiophen-2-yl)-6-methoxybenzoic Acid

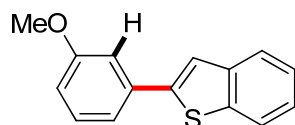


A flame-dried Schlenk test tube with a magnetic stirring bar was charged with Ag_2CO_3 (0.75 mmol, 3.0 equiv), K_2HPO_4 (0.5 mmol, 2.0 equiv), 2-(benzothiophen-2-yl)-6-methoxybenzoic acid (0.25 mmol), 4 Å MS (100 mg), and NMP (1.0 mL) under a N_2 atmosphere. The reaction mixture was stirred for 10 min at room temperature under a N_2 atmosphere, and then heated at 150 °C in a pre-heated oil bath. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2 , filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2 . The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.



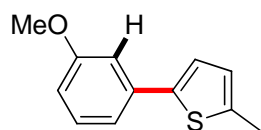
A flame-dried Schlenk test tube with a magnetic stirring bar was charged with $[\text{Cp}^*\text{RhCl}_2]_2$ (6.25 μmol , 2.5 mol %), K_2HPO_4 (0.5 mmol, 2.0 equiv), 2-(benzothiophen-2-yl)-6-methoxybenzoic acid (0.25 mmol), 4 Å MS (100 mg), and NMP (1.0 mL) under a N_2 atmosphere. The reaction mixture was stirred for 10 min at room temperature under a N_2 atmosphere, and then heated at 150 °C in a pre-heated oil bath. The reaction mixture was then cooled to ambient temperature, diluted with 20 mL of CH_2Cl_2 , filtered through a celite pad, and washed with 10-20 mL of CH_2Cl_2 . The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

VIII. Experimental Data for the Described Substances



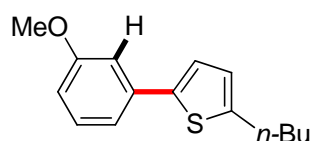
2-(3-Methoxyphenyl)benzothiophene (3a)⁶

Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1 v/v) afforded the desired product as a yellow solid (49.5 mg, 83%). M.p.: 94-96 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.80 (s, 3H), 6.81 (d, J = 7.6 Hz, 1H), 7.17 (s, 1H), 7.21-7.29 (m, 4H), 7.46 (s, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 112.3, 113.9, 119.2, 119.8, 122.4, 123.7, 124.5, 124.7, 130.1, 135.8, 139.6, 140.7, 144.2, 160.1 ppm. HRMS (ESI⁺): calcd for C₁₅H₁₃OS [M+H]⁺ 241.0687, found 241.0681.



2-(3-Methoxyphenyl)-5-methylthiophene (3b)

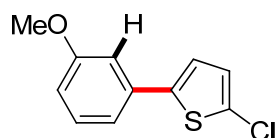
Purification via silica gel column chromatography (petroleum ether/EtOAc = 100/1 v/v) afforded the desired product as yellow oil (29.5 mg, 58%). ¹H NMR (400 MHz, CDCl₃): δ = 2.50 (s, 3H), 3.84 (s, 3H), 6.72-6.73 (m, 1H), 6.78 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.08-7.09 (m, 1H), 7.10 (d, J = 3.6 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 15.6, 55.4, 111.3, 112.6, 118.3, 123.3, 126.3, 129.9, 136.2, 139.8, 141.9, 160.0 ppm. HRMS (ESI⁺): calcd for C₁₂H₁₃OS [M+H]⁺ 205.0687, found 205.0682.



2-Butyl-5-(3-methoxyphenyl)thiophene (3c)

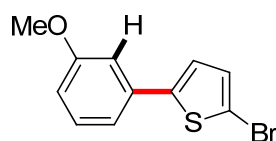
Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1 v/v)

afforded the desired product as yellow oil (42.0 mg, 68%). ^1H NMR (400 MHz, CDCl_3): δ = 0.93 (t, J = 7.4 Hz, 3H), 1.37-1.47 (m, 2H), 1.65-1.72 (m, 2H), 2.80 (t, J = 7.6 Hz, 2H), 3.84 (s, 3H), 6.73 (d, J = 3.6 Hz, 1H), 6.78 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.09 (s, 1H), 7.11 (d, J = 3.6 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.24-7.28 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 14.0, 22.3, 30.1, 33.9, 55.4, 111.2, 112.6, 118.3, 123.0, 125.1, 129.9, 136.2, 141.6, 145.9, 160.0 ppm. HRMS (ESI^+): calcd for $\text{C}_{15}\text{H}_{19}\text{OS}$ $[\text{M}+\text{H}]^+$ 247.1157, found 247.1162.



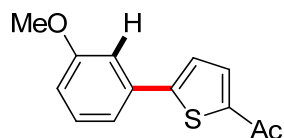
2-Chloro-5-(3-methoxyphenyl)thiophene (3d)

Purification via silica gel column chromatography (petroleum ether/EtOAc = 100/1 v/v) afforded the desired product as yellow oil (37.3 mg, 67%). ^1H NMR (400 MHz, CDCl_3): δ = 3.88 (s, 3H), 6.87 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 6.92 (d, J = 4.0 Hz, 1H), 7.07 (s, 1H), 7.10 (d, J = 3.6 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 55.5, 111.4, 113.4, 118.3, 122.6, 127.2, 129.3, 130.2, 135.1, 142.9, 160.1 ppm. HRMS (ESI^+): calcd for $\text{C}_{11}\text{H}_{10}\text{ClOS}$ $[\text{M}+\text{H}]^+$ 225.0141, found 225.0140.



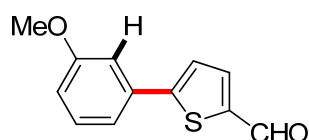
2-Bromo-5-(3-methoxyphenyl)thiophene (3e)

Purification via silica gel column chromatography (petroleum ether/EtOAc = 100/1 v/v) afforded the desired product as a yellow oil (38.5 mg, 57%). ^1H NMR (400 MHz, CDCl_3): δ = 3.87 (s, 3H), 6.86 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.04-7.07 (m, 3H), 7.12-7.14 (m, 1H), 7.29 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 55.5, 111.5, 111.6, 113.4, 118.3, 123.6, 130.2, 130.9, 135.1, 145.8, 160.1 ppm. HRMS (ESI^+): calcd for $\text{C}_{11}\text{H}_{10}\text{BrOS}$ $[\text{M}+\text{H}]^+$ 268.9636, found 268.9636.



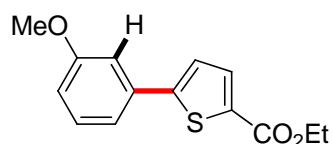
1-(5-(3-Methoxyphenyl)thiophen-2-yl)ethanone (3f)

Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as a yellow solid (37.0 mg, 64%). M.p.: 76-78 °C. ^1H NMR (400 MHz, CDCl_3): δ = 2.57 (s, 3H), 3.86 (s, 3H), 6.91 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.17 (s, 1H), 7.23-7.26 (m, 1H), 7.31-7.35 (m, 2H), 7.65 (d, J = 4.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 26.7, 55.5, 112.0, 114.7, 118.9, 124.2, 130.3, 133.5, 134.7, 143.3, 152.7, 160.2, 190.8 ppm. HRMS (ESI^+): calcd for $\text{C}_{13}\text{H}_{12}\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 255.0456, found 255.0450.



5-(3-Methoxyphenyl)thiophene-2-carbaldehyde (3g)

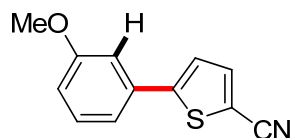
Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as yellow oil (30.0 mg, 55%). ^1H NMR (400 MHz, CDCl_3): δ = 3.79 (s, 3H), 6.86 (dd, J = 8.0 Hz, 2.8 Hz, 1H), 7.11 (t, J = 2.0 Hz, 1H), 7.18-7.20 (m, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 4.0 Hz, 1H), 7.66 (d, J = 4.0 Hz, 1H), 9.82 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 55.6, 112.2, 115.1, 119.1, 124.4, 130.4, 134.5, 137.4, 142.7, 154.3, 160.3, 182.9 ppm. HRMS (ESI^+): calcd for $\text{C}_{12}\text{H}_{10}\text{NaO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 241.0299, found 241.0302.



Ethyl 5-(3-methoxyphenyl)thiophene-2-carboxylate (3h)

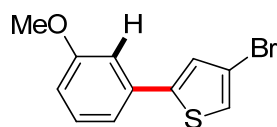
Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as yellow oil (49.3 mg, 75%). ^1H NMR (400 MHz,

CDCl₃): δ = 1.37 (t, J = 7.2 Hz, 3H), 3.86 (s, 3H), 4.34 (q, J = 7.2 Hz, 2H), 6.89 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.16 (s, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.27 (d, J = 3.6 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.75 (d, J = 4.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.5, 55.5, 61.3, 111.9, 114.4, 118.9, 123.9, 130.3, 132.7, 134.3, 134.9, 151.0, 160.2, 162.4 ppm. HRMS (ESI⁺): calcd for C₁₄H₁₄NaO₃S [M+Na]⁺ 285.0561, found 285.0561.



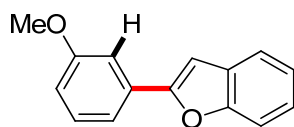
5-(3-Methoxyphenyl)thiophene-2-carbonitrile (3i)

Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as a yellow solid (44.1 mg, 82%). M.p.: 55-57 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.86 (s, 3H), 6.93 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 7.11 (s, 1H), 7.17 (dd, J = 7.6 Hz, 0.4 Hz, 1H), 7.26-7.27 (m, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.58 (d, J = 4.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 108.4, 112.3, 114.5, 114.9, 119.1, 123.6, 130.5, 133.6, 138.4, 151.8, 160.3 ppm. HRMS (ESI⁺): calcd for C₁₂H₉NNaOS [M+Na]⁺ 238.0303, found 238.0302.



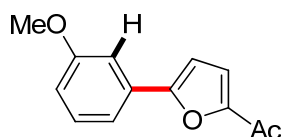
4-Bromo-2-(3-methoxyphenyl)thiophene (3j)

Purification via silica gel column chromatography (petroleum ether/EtOAc = 100/1 v/v) afforded the desired product as yellow oil (43.8 mg, 65%). ¹H NMR (400 MHz, CDCl₃): δ = 3.84 (s, 3H), 6.85 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.07 (s, 1H), 7.13-7.17 (m, 2H), 7.20 (s, 1H), 7.28 (t, J = 7.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 110.6, 111.5, 113.9, 118.4, 122.1, 126.0, 130.2, 134.6, 145.4, 160.1 ppm. HRMS (ESI⁺): calcd for C₁₁H₁₀BrOS [M+H]⁺ 268.9636, found 268.9636.



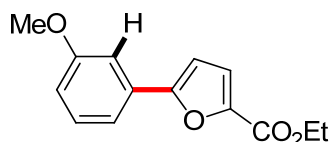
2-(3-Methoxyphenyl)benzofuran (3k)

Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1 v/v) afforded the desired product as yellow oil (31.3 mg, 56%). ^1H NMR (400 MHz, CDCl_3): δ = 3.89 (s, 3H), 6.89 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.02 (s, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.26-7.30 (m, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.41 (s, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 55.5, 101.8, 110.3, 111.3, 114.6, 117.7, 121.1, 123.1, 124.5, 129.3, 130.0, 131.9, 155.0, 155.9, 160.1 ppm. HRMS (ESI^+): calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]^+$ 225.0916, found 225.0916.



1-(5-(3-Methoxyphenyl)furan-2-yl)ethanone (3l)

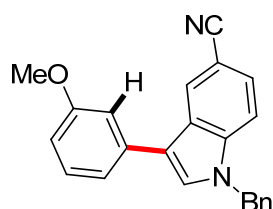
Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1 v/v) afforded the desired product as yellow oil (30.8 mg, 57%). ^1H NMR (400 MHz, CDCl_3): δ = 2.52 (s, 3H), 3.87 (s, 3H), 6.76 (d, J = 3.6 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 7.25-7.26 (m, 1H), 7.32 (s, 1H), 7.34-7.39 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 26.1, 55.6, 107.9, 110.5, 115.1, 117.7, 119.5, 130.2, 130.8, 152.1, 157.6, 160.2, 186.6 ppm. HRMS (ESI^+): calcd for $\text{C}_{13}\text{H}_{12}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$ 239.0684, found 239.0685.



Ethyl 5-(3-methoxyphenyl)furan-2-carboxylate (3m)

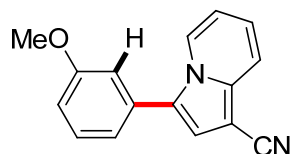
Purification via silica gel column chromatography (petroleum ether/EtOAc = 25/1 v/v) afforded the desired product as yellow oil (46.1 mg, 75%). ^1H NMR (400 MHz,

CDCl₃): δ = 1.38 (t, J = 7.0 Hz, 3H), 3.87 (s, 3H), 4.36 (q, J = 7.0 Hz, 2H), 6.72 (d, J = 3.6 Hz, 1H), 6.88 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.22 (d, J = 3.6 Hz, 1H), 7.30-7.32 (m, 2H), 7.34 (t, J = 7.2 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.5, 55.6, 61.0, 107.3, 110.2, 115.0, 117.6, 119.9, 130.0, 131.0, 144.1, 157.5, 159.0, 160.1 ppm. HRMS (ESI⁺): calcd for C₁₄H₁₄NaO₄ [M+Na]⁺ 269.0790, found 269.0792.



1-Benzyl-3-(3-methoxyphenyl)-1H-indole-5-carbonitrile (3n)

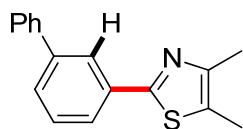
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 160 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 15/1 v/v) afforded the desired product as a yellow solid (38.0 mg, 45%). M.p.: 54-56 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.88 (s, 3H), 5.38 (s, 2H), 6.87 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.12 (s, 1H), 7.13-7.20 (m, 3H), 7.31-7.41 (m, 6H), 7.44 (dd, J = 8.8 Hz, 1.2 Hz, 1H), 8.28 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 50.6, 55.5, 103.5, 111.1, 112.2, 113.5, 118.6, 120.2, 120.8, 125.3, 126.0, 126.5, 127.0, 128.1, 128.4, 129.2, 130.2, 135.4, 136.2, 138.6, 160.3 ppm. HRMS (ESI⁺): calcd for C₂₃H₁₉N₂O [M+H]⁺ 339.1497, found 339.1494.



3-(3-Methoxyphenyl)indolizine-1-carbonitrile (3o)

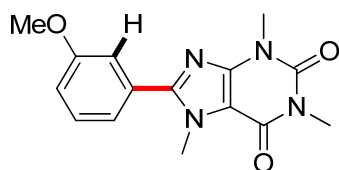
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 160 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 10/1 v/v) afforded the desired product as yellow oil (32.2 mg, 52%). ¹H NMR (400 MHz,

CDCl₃): δ = 3.87 (s, 3H), 6.73 (t, J = 6.8 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 7.04-7.06 (m, 2H), 7.10-7.12 (m, 2H), 7.41 (t, J = 8.0 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 8.31 (d, J = 7.2 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.6, 82.4, 113.3, 114.1, 114.6, 116.5, 117.1, 118.4, 121.0, 122.5, 124.1, 127.0, 130.5, 131.6, 138.6, 160.3 ppm. HRMS (ESI⁺): calcd for C₁₆H₁₂N₂NaO [M+Na]⁺ 271.0847, found 271.0846.



2-([1,1'-Biphenyl]-3-yl)-4,5-dimethylthiazole (3p)

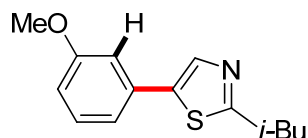
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 160 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1 v/v) afforded the desired product as yellow oil (35.1 mg, 53%). ¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 3H), 2.41 (s, 3H), 7.35-7.39 (m, 1H), 7.44-7.49 (m, 3H), 7.59 (d, J = 8.0 Hz, 1H), 7.63-7.66 (m, 2H), 7.83 (d, J = 7.6 Hz, 1H), 8.09 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 11.7, 15.0, 125.0, 125.2, 126.8, 127.4, 127.7, 128.3, 128.9, 129.4, 134.6, 140.8, 142.1, 149.6, 163.4 ppm. HRMS (ESI⁺): calcd for C₁₇H₁₆NS [M+H]⁺ 266.1003, found 266.0999.



8-(3-Methoxyphenyl)-1,3,7-trimethyl-1H-purine-2,6(3H,7H)-dione (3q)

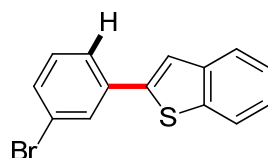
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 160 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 3/1 v/v) afforded the desired product as a yellow solid (41.9 mg, 56%). M.p.: 136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.44 (s, 3H), 3.63 (s, 3H), 3.88 (s, 3H), 4.06 (s, 3H), 7.05 (d, J = 8.0 Hz, 1H), 7.22-7.27 (m, 2H), 7.42 (t, J = 7.6 Hz, 1H) ppm. ¹³C NMR

(100 MHz, CDCl₃): δ = 28.1, 29.9, 34.0, 55.6, 108.7, 115.0, 116.3, 121.5, 129.7, 130.1, 148.4, 151.9, 152.1, 155.7, 160.0 ppm. HRMS (ESI⁺): calcd for C₁₅H₁₆N₄NaO₃ [M+Na]⁺ 323.1120, found 323.1117.



2-*iso*-Butyl-5-(3-methoxyphenyl)thiazole (3r)

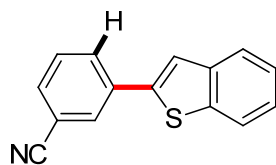
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 160 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 20/1 v/v) afforded the desired product as yellow oil (35.2 mg, 57%). ¹H NMR (400 MHz, CDCl₃): δ = 1.04 (d, *J* = 6.8 Hz, 6H), 2.13-2.20 (m, 1H), 2.89 (d, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 6.87 (d, *J* = 8.4 Hz, 1H), 7.08 (s, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.84 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 22.4, 30.0, 42.7, 55.5, 112.4, 113.6, 119.3, 130.2, 133.1, 137.9, 138.5, 160.1, 169.9 ppm. HRMS (ESI⁺): calcd for C₁₄H₁₈NOS [M+H]⁺ 248.1109, found 248.1108.



2-(3-Bromophenyl)benzothiophene (4a)

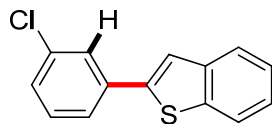
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1 v/v) afforded the desired product as a white solid (45.5 mg, 63%). M.p.: 86-88 °C ¹H NMR (400 MHz, CDCl₃): δ = 7.27-7.39 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.55 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.87 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 120.6, 122.5, 123.2, 124.0, 124.85, 124.89, 125.3, 129.1, 129.5, 130.6, 131.2, 136.5, 140.6, 142.5 ppm. HRMS (ESI⁺):

calcd for C₁₄H₁₀BrS [M+H]⁺ 288.9687, found 288.9684.



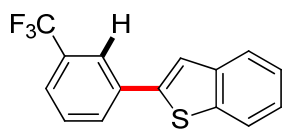
3-(Benzothiophen-2-yl)benzonitrile (4b)

Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as a yellow solid (32.1 mg, 55%). M.p.: 150-152 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.35-7.42 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.61-7.63 (m, 2H), 7.81 (dd, *J* = 6.4 Hz, 2.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 113.4, 118.6, 121.2, 122.5, 124.2, 125.1, 125.3, 129.9, 123.0, 130.7, 131.5, 135.8, 139.8, 140.5, 141.4 ppm. HRMS (ESI⁺): calcd for C₁₅H₉NNaS [M+Na]⁺ 258.0353, found 258.0353.



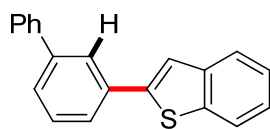
2-(3-Chlorophenyl)benzothiophene (4c)

Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1 v/v) afforded the desired product as a white solid (37.1 mg, 61%). M.p.: 116-118 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.22-7.32 (m, 4H), 7.48 (s, 1H), 7.50 (td, *J* = 7.2 Hz, 1.6 Hz, 1H), 7.63-7.64 (m, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 120.5, 122.5, 123.9, 124.78, 124.85, 124.88, 126.6, 128.3, 130.3, 135.1, 136.3, 139.8, 140.6, 142.6 ppm. HRMS (ESI⁺): calcd for C₁₄H₁₀ClS [M+H]⁺ 245.0192, found 245.0195.



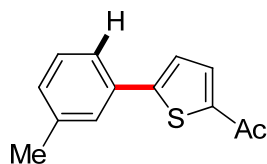
2-(3-(Trifluoromethyl)phenyl)benzothiophene (4d)

Following the general procedure, $[\text{Cp}^*\text{RhCl}_2]_2$ (7.8 mg, 5.0 mol %) and AgSbF_6 (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 100/1 v/v) afforded the desired product as a white solid (47.5 mg, 68%). M.p.: 102-104 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.25-7.32 (m, 2H), 7.44-7.52 (m, 2H), 7.53 (s, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.76 (t, J = 7.6 Hz, 2H), 7.87 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 120.8, 122.5, 122.8, 123.2, 123.3, 124.0, 124.86, 124.89, 124.94, 125.0, 125.5, 129.6, 129.8, 131.4, 131.8, 135.3, 139.8, 140.6, 142.5 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{S}$ $[\text{M}+\text{H}]^+$ 279.0455, found 279.0451.



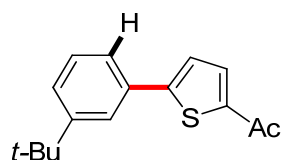
2-([1,1'-Biphenyl]-3-yl)benzothiophene (4e)

Following the general procedure, $[\text{Cp}^*\text{RhCl}_2]_2$ (7.8 mg, 5.0 mol %) and AgSbF_6 (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 100/1 v/v) afforded the desired product as a white solid (37.5 mg, 52%). M.p.: 116-118 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.30-7.41 (m, 3H), 7.46-7.51 (m, 3H), 7.55 (d, J = 7.6 Hz, 1H), 7.61 (s, 1H), 7.64 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.92 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 119.9, 122.4, 123.8, 124.6, 124.7, 125.6, 127.3, 127.4, 127.8, 129.0, 129.5, 135.0, 139.7, 140.8, 140.9, 142.2, 144.3 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{20}\text{H}_{15}\text{S}$ $[\text{M}+\text{H}]^+$ 287.0894, found 287.0895.



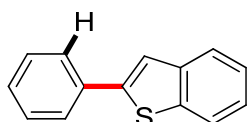
1-(5-(*m*-Tolyl)thiophen-2-yl)ethanone (4f)

Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as a yellow solid (29.6 mg, 55%). M.p.: 90-92 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 3H), 2.57 (s, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.29-7.33 (m, 2H), 7.45-7.47 (m, 2H), 7.65 (d, *J* = 4.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 26.7, 123.6, 123.9, 127.1, 129.2, 130.0, 133.4, 133.6, 139.0, 143.1, 153.2, 190.8 ppm. HRMS (ESI⁺): calcd for C₁₃H₁₂NaOS [M+Na]⁺ 239.0507, found 239.0506.



1-(5-(3-(*tert*-Butyl)phenyl)thiophen-2-yl)ethanone (4g)

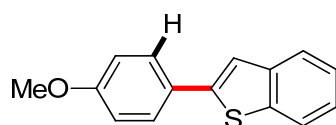
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as a yellow solid (32.9 mg, 51%). M.p.: 100-102 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.29 (s, 9H), 2.50 (s, 3H), 7.24-7.26 (m, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.59-7.60 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 26.7, 31.4, 34.9, 123.6, 123.7, 123.9, 126.4, 129.0, 133.2, 133.6, 143.0, 152.3, 153.7, 190.8 ppm. HRMS (ESI⁺): calcd for C₁₈H₁₉NaOS [M+Na]⁺ 281.0976, found 281.0978.



2-Phenylbenzothiophene (4h)

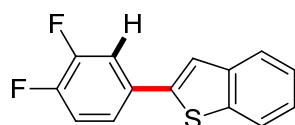
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h.

Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1 v/v) afforded the desired product as a yellow solid (35.8 mg, 68%). M.p.: 166-168 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.29-7.35 (m, 3H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.55 (s, 1H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 119.6, 122.4, 123.7, 124.5, 124.7, 126.7, 128.4, 129.1, 134.5, 139.7, 140.9, 144.4 ppm. HRMS (ESI⁺): calcd for C₁₄H₁₀NaS [M+Na]⁺ 233.0401, found 233.0404.



2-(4-Methoxyphenyl)benzothiophene (4i)

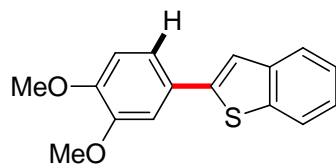
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 50/1 v/v) afforded the desired product as a yellow solid (38.0 mg, 63%). M.p.: 112-114 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.85 (s, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.25-7.35 (m, 2H), 7.42 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 114.5, 118.4, 122.3, 123.4, 124.1, 124.6, 127.2, 127.9, 139.3, 141.0, 144.3, 160.0 ppm. HRMS (ESI⁺): calcd for C₁₅H₁₃OS [M+H]⁺ 241.0687, found 241.0681.



2-(3,4-Difluorophenyl)benzothiophene (4j)

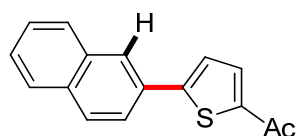
Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 100/1 v/v) afforded the desired product as a white solid (44.2 mg, 72%). M.p.: 136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.18-7.23 (m, 1H), 7.32-7.43 (m, 3H), 7.48-7.53 (m, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz,

CDCl₃): δ = 115.5, 115.7, 117.9, 118.1, 120.4, 122.4, 122.69, 122.73, 122.79, 123.9, 124.90, 124.92, 131.63, 131.67, 131.69, 131.74, 139.7, 140.6, 141.9 ppm. HRMS (ESI⁺): calcd for C₁₄H₈F₂NaS [M+Na]⁺ 269.0212, found 269.0213.



2-(3,4-Dimethoxyphenyl)benzothiophene (4k)

Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as a yellow solid (47.9 mg, 71%). M.p.: 132-134 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.93 (s, 3H), 3.98 (s, 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 7.27-7.36 (m, 3H), 7.44 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 56.1, 109.8, 111.6, 118.6, 119.4, 122.3, 123.4, 124.2, 124.6, 127.5, 139.3, 140.9, 144.4, 149.3, 149.5 ppm. HRMS (ESI⁺): calcd for C₁₆H₁₅O₂S [M+H]⁺ 271.0793, found 271.0793.



1-(5-(Naphthalen-2-yl)thiophen-2-yl)ethanone (4l)

Following the general procedure, [Cp*RhCl₂]₂ (7.8 mg, 5.0 mol %) and AgSbF₆ (17.2 mg, 20 mol %) was added, and the reaction mixture was heated at 150 °C for 48 h. Purification via silica gel column chromatography (petroleum ether/EtOAc = 30/1 v/v) afforded the desired product as a yellow solid (38.8 mg, 62%). M.p.: 146-148 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.60 (s, 3H), 7.45 (d, *J* = 4.0 Hz, 1H), 7.49-7.55 (m, 2H), 7.70 (d, *J* = 3.6 Hz, 1H), 7.75 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.83-7.90 (m, 3H), 8.14 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 26.8, 124.2, 124.3, 125.5, 127.0, 127.1, 127.9, 128.5, 129.1, 130.8, 133.6, 133.7, 143.4, 149.8, 153.0, 190.7 ppm.

HRMS (ESI⁺): calcd for C₁₆H₁₂NaOS [M+Na]⁺ 275.0507, found 275.0508.

IX. References

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X. Copies of ^1H , ^{13}C and ^1H - ^1H NOESY NMR Spectra

