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CONSTRUCTION OF PINPOINT-FLUORINATED BENZOTHIOPHENE FRAMEWORKS USING PALLADIUM-CATALYZED CYCLIZATION OF *o*-(FLUOROVINYL)PHENYL-SUBSTITUTED THIOPHENES

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Dedicated to Professor Tohru Fukuyama in celebration of his 70th birthday

Abstract – *o*-(2,2-Difluorovinyl)phenyl- or *o*-(1,2,2-trifluorovinyl)phenyl-substituted thiophenes underwent palladium(II)-catalyzed Friedel–Crafts-type cyclization on the fluorovinyl moieties to construct regioselectively monofluorinated or difluorinated benzothiophene frameworks (pinpoint-fluorinated naphtho[*b*]thiophenes). The cyclization of less nucleophilic 2-substituted thiophenes was effectively promoted by the addition of a CuOTf complex. Cyclization was also conducted in a tandem process, which facilitated the rapid synthesis of higher-order pinpoint-fluorinated PAHs (polycyclic aromatic hydrocarbons) bearing thiophene rings. Furthermore, cyclization was applied to the corresponding furan systems, which led to pinpoint-fluorinated naphtho[*b*]furans.

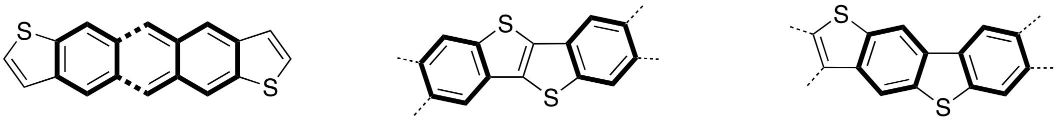
INTRODUCTION

Sulfur-containing π-extended molecules have attracted an increasing amount of attention as organic electronic materials.[1] In particular, oligo- and polythiophenes, where every two thiophene rings are connected to each other by a single bond, have been studied from the very early stage of this chemistry (Figure 1).[2] Semiconducting behavior of thienoacenes (TAcs), in which every two thiophene rings share a C–C double bond, have also been investigated over the past few decades.[3] In addition to these molecules that consist only of thiophene rings, acenedithiophenes (AcDTs),[4] diacene-fused thienothiophenes (DAcTTs),[5] and alternately fused benzothiophenes,[6] which consist of both thiophene and benzene rings have emerged more recently (Figure 2).[7,8]

Oligo/Polythiophenes

Thienoacenes (TAcs)

Figure 1. Typical structures of thiophene-based semiconducting materials consisting solely of thiophene rings



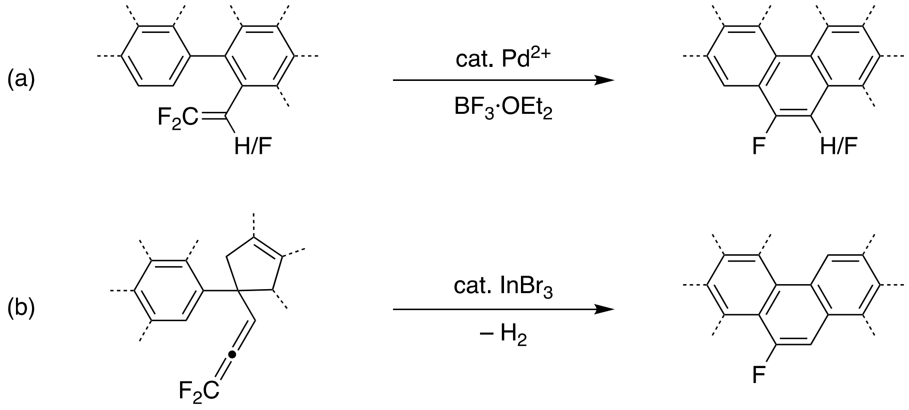
Acenedithiophenes (AcDTs)

Diacene-Fused Thienothiophenes (DAcTTs)

Alternately Fused Benzothiophenes

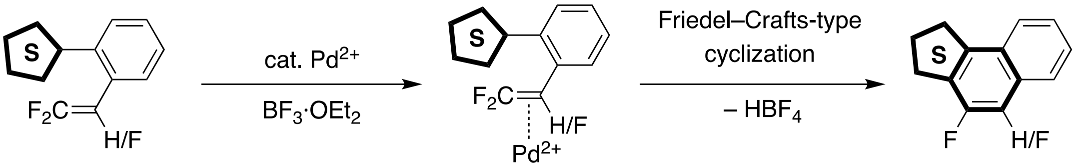
Figure 2. Typical structures of thiophene-based semiconducting materials consisting of thiophene and benzene rings

Over the last few years, we have developed methods of synthesizing regioselectively mono- or difluorinated polycyclic aromatic hydrocarbons (PAHs) (pinpoint-fluorinated PAHs, comprising solely carbocycles) by using the cyclization of fluorinated alkenes (Scheme 1). Palladium(II)[9] and indium(III)[10] catalysts have been used to facilitate the Friedel–Crafts-type cyclization of 1,1-difluoroalkenes, 1,1,2-trifluoroalkenes, and 1,1-difluoroallenes, which provide fluorine-containing π-conjugated compounds in a regioselective manner.[11,12] These molecules represented substantially enhanced solubility in organic solvents because of the fluorine substituent, leading to printable electronics.[13] In fact, some of the fluoropicenes bearing five benzene rings have displayed p-type semiconducting behavior. The pinpoint-fluorinated PAHs also displayed low-lying HOMOs, suggesting an increased resistance to aerial oxidation. Thus, the construction of thiophene ring-containing pinpoint-fluorinated PAHs have remained an objective, as well as a challenge because of the potential coordination of a thiophene moiety with metal catalysts.



Scheme 1. Our Pd(II)- and In(III)-catalyzed syntheses of pinpoint-fluorinated phenacenes

Notably, fluorine has been introduced to electronic materials for OFETs and OPVs.[14] In spite of the advantages of fluorine substitution, the regioselective synthesis of fluorinated benzothiophene derivatives has been achieved by several fluorination methods,[15] which require the task-demanding pre-installation of a functional group or a directing group to govern the regioselectivity. This paper describes the regioselective synthesis of pinpoint-fluorinated naphtho[*b*]thiophenes by constructing fluorinated benzene rings using palladium(II) catalysis (Scheme 2)[16] via C–F bond activation based on β-fluorine elimination.[17]

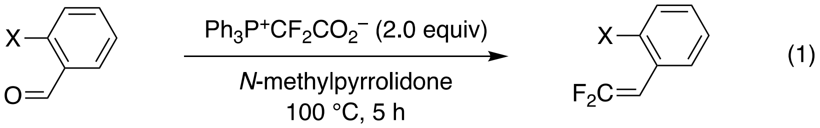


Scheme 2. Strategy for the Pd(II)-catalyzed synthesis of pinpoint-fluorinated naphtho[*b*]thiophenes (the S-centered pentagons represent 2- and -3-thienyl groups)

RESULTS AND DISCUSSION

PREPARATION OF CYCLIZATION PRECURSORS

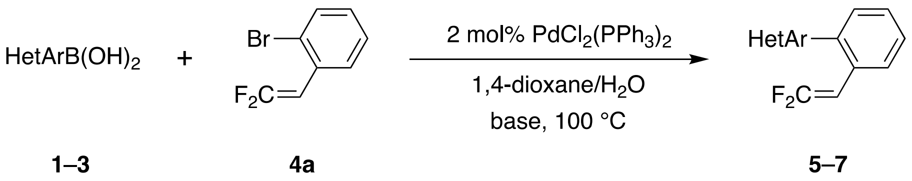
Cyclization precursors (Scheme 2) consist of three parts: a fluoroalkene moiety, a benzene moiety, and a thiophene moiety. Preparation of the precursors was achieved by palladium-catalyzed cross-coupling reaction of two aryl components. The Suzuki–Miyaura coupling of 3-thienylboronic acids **1**, 2-thienylboronic acids **2**, and 2-furylboronic acids **3** was conducted with bromide **4a**, prepared by the difluoromethylidenation of commercially available 2-bromobenzaldehyde with $Ph_3P^+CF_2CO_2^-$ in a 70% yield (Eq. 1).[18] The desired precursors **5a**, **6a**–**c**, and **7a** were obtained in 60–83% yields (Table 1).



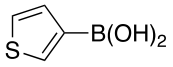
4a (X = Br) 70%
4b (X = I) 68%

1,1-Difluoroalkenes **5b** and **5c** were prepared by the Suzuki–Miyaura coupling of 4-bromo-2-methylthiophene (**8a**) and 3-bromobenzothiophene (**8b**) with 2-formylphenylboronic acid (**9**) in 70% and 74% yields, respectively, followed by difluoromethylidenation of the resulting aldehyde **10a** and **10b** in yields of 63% and 51%, respectively (Scheme 3).[19] 1,1,2-Trifluoroalkenes **6d** and **7b** were prepared via the Suzuki–Miyaura coupling of boronic acids **2c** and **3a** with bromophenyl triflate **11** (82% yield of **12a** and 59% yield of **12b**), followed by the Negishi coupling of the resulting triflate **12a** and **12b** with 1,2,2-trifluorovinylzinc chloride–TMEDA complex [Scheme 4, 89% yield of **6d** and 65% yield of **7b**, TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine, dppp = 1,3-bis(diphenylphosphino)propane].[20]

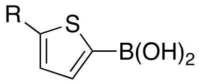
Table 1. Preparation of cyclization precursors (1)



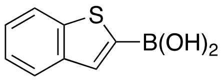
Entry	HetArB(OH)$_2$ equiv	**4a** equiv	Base equiv	Dioxane/H_2O Ratio	Time, h	Difluoroalkene Yield, %a)
1	**1a**, 1.1	1.0	Na_2CO_3, 2.0	2:1	overnight	**5a**, 76
2	**2a**, 1.1	1.0	K_3PO_4, 2.0	9:1	9	**6a**, 60
3b)	**2b**, 1.0	1.1	Na_2CO_3, 3.0	2:1	3	**6b**, 69
4	**2c**, 1.1	1.0	Na_2CO_3, 3.0	2:1	5	**6c**, 68
5	**3a**, 1.1	1.0	K_3PO_4, 2.0	2:1	5	**7a**, 83



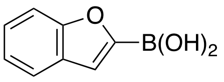
1a



2a (R = H)
2b (R = Me)

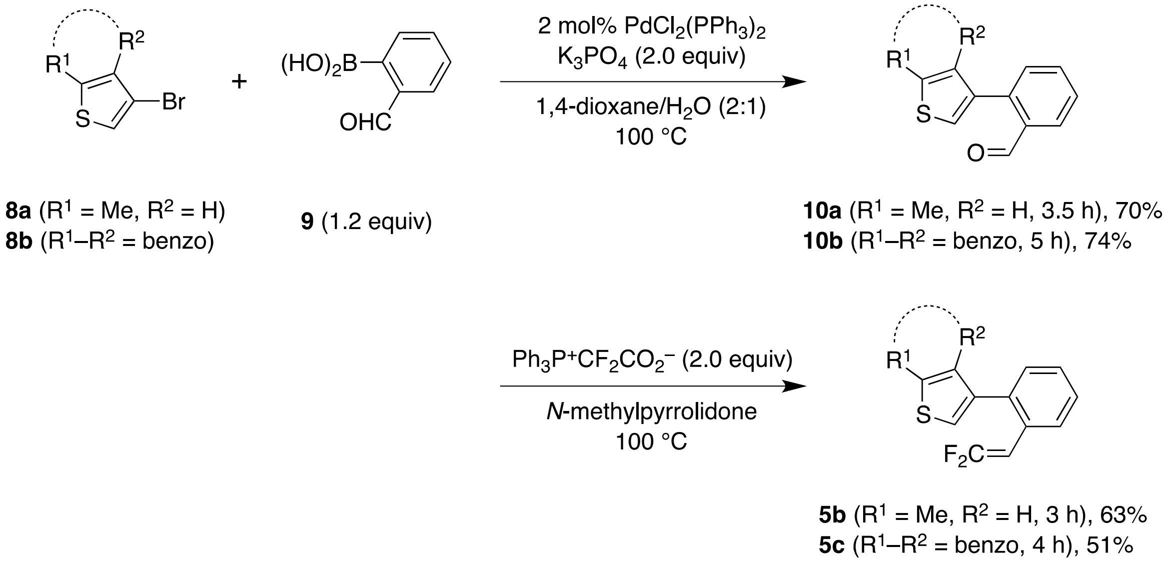


2c

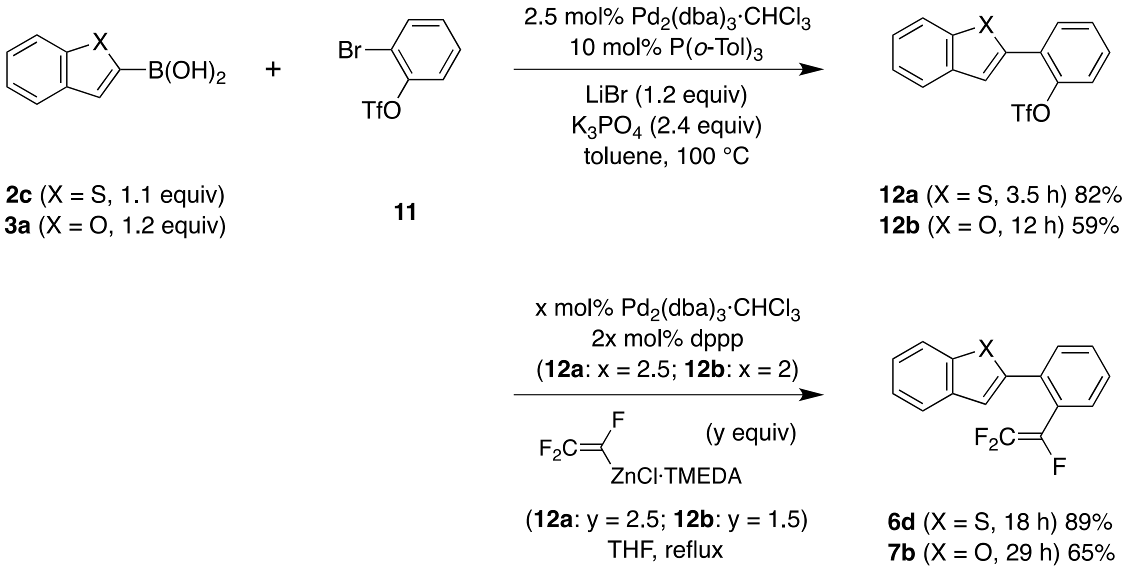


3a

a) Isolated yield. b) 3 mol% $PdCl_2(PPh_3)_2$.

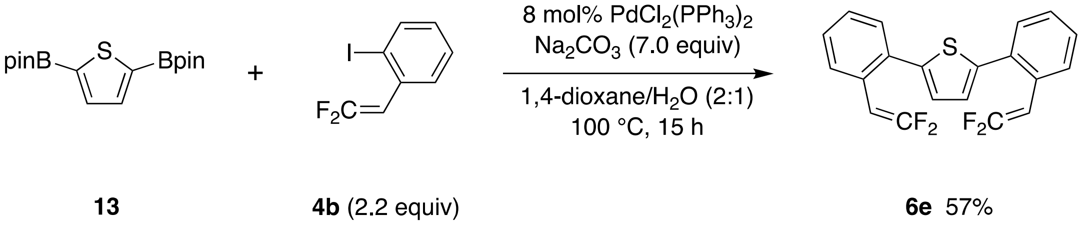


Scheme 3. Preparation of cyclization precursors (2)



Scheme 4. Preparation of cyclization precursors (3)

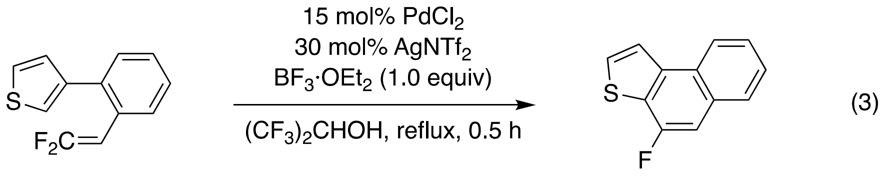
A substrate for tandem cyclization, bis(difluoroalkene) **6e** was prepared in a similar manner. Bis(pinacolate) **13**, which was prepared from thiophene using double Miyaura C–H borylation with an iridium(I) catalyst,[21] underwent tandem coupling with iodide **4b** (Eq. 1) to afford **6e** in a 57% yield (Eq. 2, pin = pinacolate).



(2)

CYCLIZATION OF 2,2-DIFLUOROVINYL- OR 1,2,2-TRIFLUOROVINYL-BEARING THIOPHENES AND MECHANISTIC CONSIDERATION

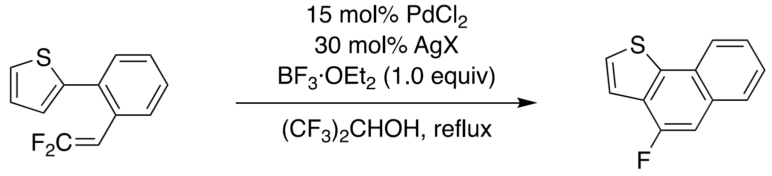
Cyclization of the benchmark compound, 3-substituted thiophene **5a** was examined under the conditions described in our previous paper on pinpoint-fluorinated phenacene synthesis.[9a] Difluoroalkene **5a** was treated with 15 mol% of palladium dichloride and 30 mol% of silver bis(trifluoromethane)sulfonimide in the presence an equimolar amount of boron trifluoride etherate in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP).[22] After heating at reflux for 30 min, the reaction was completed to produce the fluorinated naphtho[2,1-*b*]thiophene **14a** in a 92% yield (^{19}F NMR yield based on $PhCF_3$, Eq. 3).



5a **14a** (92%, ^{19}F NMR)

By contrast, cyclization of less nucleophilic 2-substituted thiophene **6a** (*vide infra*) slightly proceeded under identical conditions, producing the corresponding fluoronaphtho[1,2-*b*]thiophene **14d** only in an 11% yield (Table 2, Entry 1). The optimization of silver salts was performed and the yields of **14d** ranged from trace amounts to 21% (Entries 2–4). Use of a cationic Pd(II) complex, $[Pd(MeCN)_4](BF_4)_2$ did not afford **14d** in spite of the consumption of **6a** (Entry 5).[9b,23,24]

Table 2. Optimization of catalysts



6a **14d**

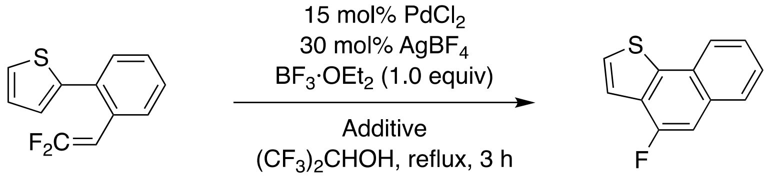
Entry	Pd(II) Catalyst	AgX	Time, h	Yield, %[a)	
				14d	**6a** (Recovery)
1	$PdCl_2$	$AgNTf_2$	15	11	50
2	$PdCl_2$	AgOTf	2.5	Trace	73
3	$PdCl_2$	$AgSbF_6$	2.5	11	61
4	$PdCl_2$	$AgBF_4$	3	21	52
5	$[Pd(MeCN)_4](BF_4)_2$	none	2.5	–	35

Tf = trifluoromethanesulfonyl. a) ^{19}F NMR yield based on an internal standard $PhCF_3$.

The effect of metal-salt additives was examined considering the coordination with a thiophene moiety (the sulfur atom and/or the π system), which could deactivate a key cationic palladium(II) species (Table 3). The use of magnesium, iron(III), or copper(II) salts showed a negative effect and resulted in producing the desired **14d** in a yield of less than 13% (Entries 1–3), whereas copper(I) chloride had a positive effect and improved the yield of **14d** to 35% (Entry 4). Copper(I) acetate and trifluoromethanesulfonate (triflate) further increased the yield up to 71% (Entries 7–9). To replace copper(I) triflate–benzene complex with less expensive copper(I) salts, the combined use of copper(I) iodide and benzene was evaluated (Entry

10), though this effort was not successful. The use of triphenylphosphine or dimethyl sulfide instead of benzene completely deactivated the catalyst (Entries 11 and 12), and the use of copper(I) triflate–benzene complex as a catalyst had no effect (Entry 13). When the reaction was attempted in the presence of copper(I) triflate without a palladium(II), the cyclization product **14d** was not obtained and **6a** was fully recovered, indicating that the cyclization was promoted by a palladium(II) catalyst (Entry 14).

Table 3. Effect of additives



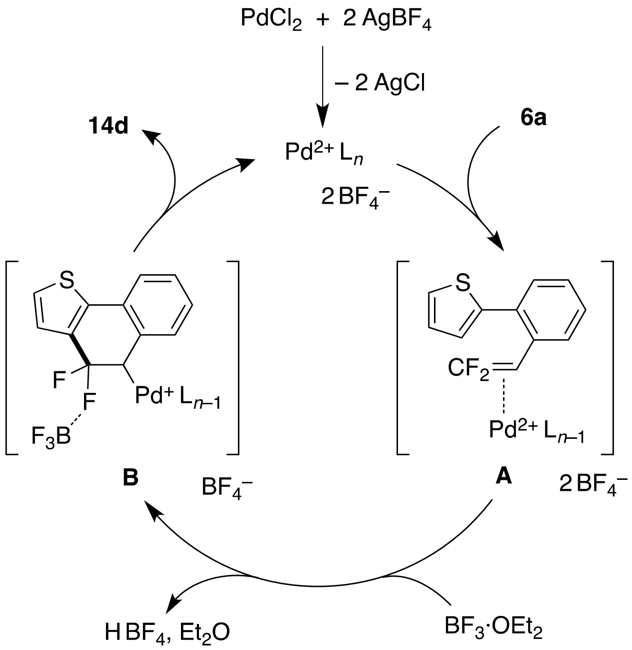
6a **14d**

Entry	Additive	equiv	Yield, %[a)	
			14d	**6a** (Recovery)
1	$Mg(OTf)_2$	1.0	5	40
2	$Fe(OTf)_3$	1.0	–	10
3	$Cu(OTf)_2$	1.0	13	30
4	CuCl	1.0	35	34
5	CuBr	1.0	10	59
6	CuI	1.0	21	73
7	CuOAc	1.0	47	11
8	$CuOTf \cdot 0.5C_6H_6$	1.0	59	19
9[b)	$CuOTf \cdot 0.5C_6H_6$	1.0	71	–
10	CuI, C_6H_6	1.0, 1.0	20	57
11	CuI, PPh_3	1.0, 1.0	–	Quant.
12	CuI, SMe_2	1.0, 1.0	–	97
13	$CuOTf \cdot 0.5C_6H_6$	0.15	23	54
14[c)	$CuOTf \cdot 0.5C_6H_6$	1.0	–	Quant.

a) ^{19}F NMR yield based on an internal standard $PhCF_3$. b) 20 mol% $PdCl_2$, 40 mol% $AgBF_4$.

c) $PdCl_2$ and $AgBF_4$ were not used.

The aforementioned results can be rationalized by our Friedel–Crafts-type mechanism (Scheme 5). Difluoroalkene **6a** coordinated to the cationic palladium(II) species to form π-complex **A**, where the electron density of the fluoroalkene moiety was lowered. This electrophilic activation promoted a Friedel–Crafts-type ring closure to provide cyclic alkylpalladium(II) intermediate **B**, which in turn underwent β-fluorine elimination with the assistance of BF_3 to yield pinpoint-fluorinated naphthothiophene **14d**. The formation of BF_4^- ion regenerated the active cationic palladium(II) species. The Friedel–Crafts reaction of thiophene derivatives preferentially proceeds at the α position rather than the β position, which explains the low reactivity of the substrate **6a** compared with **5a** (Table 2, Entry 1 vs. Eq. 3). The coordination of a thiophene moiety (the sulfur atom and/or the π system) to the palladium(II) center possibly retards Friedel–Crafts-type cyclization. The added copper(I) salt may reactivate the deactivated palladium(II) complexes by removing the thiophene moiety ligated to the palladium (Table 3, Entries 7–9). Lewis bases, such as phosphine and sulfide, deactivate the cationic palladium(II) species by coordination, resulting in the complete recovery of the starting difluoroalkene **6a** (Table 3, Entries 11 and 12).

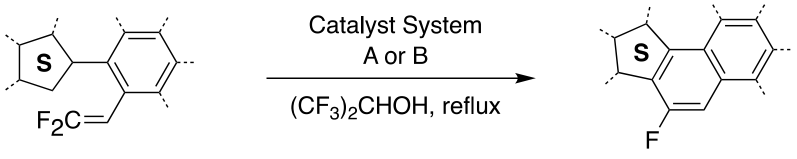


Scheme 5. Plausible catalytic cycle

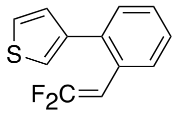
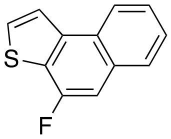
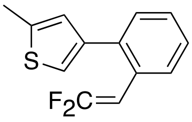
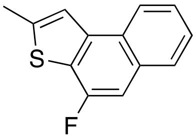
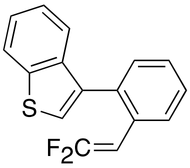
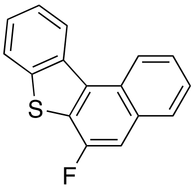
SYNTHESIS OF PINPOINT-FLUORINATED NAPHTHO[*b*]THIOPHENES

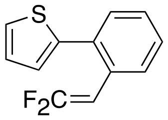
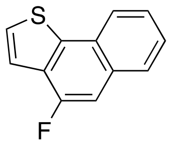
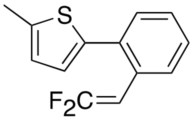
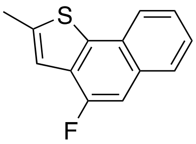
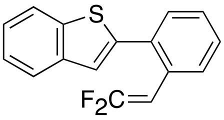
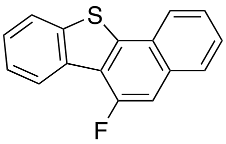
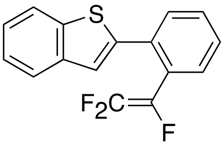
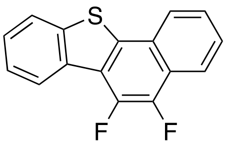
Under optimal conditions, various 1,1-di- or 1,1,2-trifluoroalkenes **5** and **6** underwent the cyclization on the thiophene ring, leading to the desired angular naphtho[*b*]thiophenes **14** (Table 4). Cyclization precursors **5a** and **5b**, which react at the position α to the sulfur atom in the thiophene ring, were sufficiently reactive to produce the corresponding products **14a** and **14b** in 87% and 54%[25] yields, respectively, using catalyst system A [15 mol% $PdCl_2$, 30 mol% $AgNTf_2$, $BF_3 \cdot OEt_2$ (1.0 equiv)] (Entries 1 and 2). Fluorinated thienohelicene **14c** was successfully synthesized from benzothiophene **5c** in a 93% yield (Entry 3). On the other hand, precursors **6a** and **6b**, which react at the position β to the sulfur atom of the thiophene ring, were less reactive and afforded the corresponding products **14d** and **14e** in 70% and 59% yields, respectively, using catalyst system B [20 mol% $PdCl_2$, 40 mol% $AgBF_4$, $CuOTf \cdot 0.5C_6H_6$ (1.0 equiv), $BF_3 \cdot OEt_2$ (1.0 equiv)] (Entries 4 and 5). Benzothiophene **6c** readily reacted on its β position to afford the corresponding pinpoint-fluorinated thienophenacene **14f** in a 91% yield using catalyst system A (Entry 6). In addition to 1,1-difluoroalkenes, 1,1,2-trifluoroalkene **6d** underwent the cyclization to produce the corresponding difluorinated thienophenacene **14g** in a 90% yield (Entry 7). The cyclization proceeded with catalyst system A (Entries 3, 6, and 7), probably because benzothiophene nuclei are more reactive than thiophene nuclei.

Table 4. Synthesis of fluoronaphtho[*b*]thiophenes



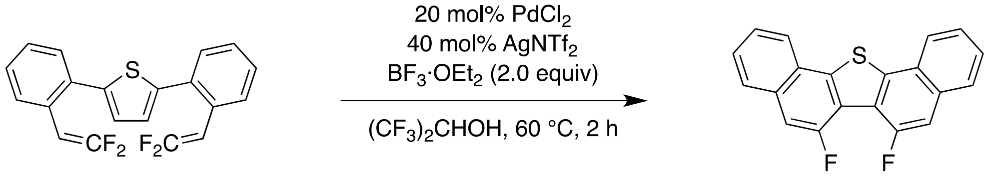
5,6 **14**

Entry	Fluoroalkene		Catalyst System[a]	Time, h	Fluoronaphtho[*b*]thiophene		Yield, %[b]
1[c]		**5a**	A	0.5		**14a**	87 (92)
2		**5b**	A	0.5		**14b**	54[d]
3		**5c**	A	0.5		**14c**	93

4[e)]		**6a**	B	3		**14d**	70 (71)
5		**6b**	B	3		**14e**	59
6		**6c**	A	0.5		**14f**	91 (93)
7		**6d**	A	2		**14g**	90

a) Catalyst system A: 15 mol% $PdCl_2$, 30 mol% $AgNTf_2$, $BF_3{\cdot}OEt_2$ (1.0 equiv); Catalyst system B: 20 mol% $PdCl_2$, 40 mol% $AgBF_4$, $CuOTf{\cdot}0.5C_6H_6$ (1.0 equiv), $BF_3{\cdot}OEt_2$ (1.0 equiv). b) Isolated yield (^{19}F NMR yield based on an internal standard $PhCF_3$ in parentheses). c) Eq. 3. d) 55 °C. e) Table 3, Entry 9.

Cyclization was also performed in a tandem fashion. When thiophene **6e** bearing two difluoroalkene moieties was treated with the palladium(II) catalyst, the reaction proceeded smoothly to provide the corresponding difluorinated thienophenacene **14h** in a 69% yield (Eq. 4).[26]



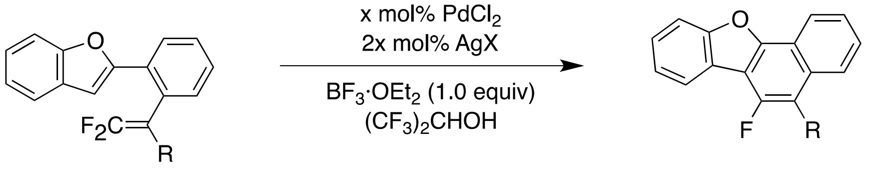
(4)

6e

14h 45% (69%, ^{19}F NMR)[26]

APPLICATION TO FURAN SYSTEMS

The cyclization was then applied to the corresponding furan systems (Eq. 5). 1,1-Difluoroalkene and 1,1,2-trifluoroalkene **7a** and **7b** bearing a benzofuran moiety were treated with the palladium(II) catalyst. Although difluoroalkene **7a** afforded the corresponding monofluorinated naphtho[*b*]furan **15a** in 30% yield without recovery of the starting difluoroalkene under conventional oil bath heating (not shown), **7a** afforded the desired **15a** in 82% yield under microwave (MW) irradiation.[27] Trifluoroalkene **7b** afforded the corresponding difluorinated naphtho[*b*]benzofuran **15b** in 62% yield.



7a (R = H)
7b (R = F)

15a (R = H) 82%
(80 °C, 20 min, MW; x = 30; X = BF_4)
15b (R = F) 62%
(60 °C, 2 h; x = 15; X = NTf_2)

CONCLUSION

The Friedel–Crafts-type cyclizations of *o*-(2,2-difluorovinyl)phenyl- and *o*-(1,2,2-trifluorovinyl)phenyl-substituted thiophenes were promoted by cationic palladium(II) catalysts to construct regioselectively monofluorinated and difluorinated benzothiophene frameworks (pinpoint-fluorinated naphtho[*b*]thiophenes). The cyclization of less nucleophilic 2-substituted thiophenes was successfully effected by the addition of copper(I) triflate–benzene complex. The cyclization was applied to tandem systems, which facilitated the rapid synthesis of fluorinated higher-order PAHs bearing thiophene rings. The cyclization was also applied to the furan systems, which led to pinpoint-fluorinated naphtho[*b*]furans.

EXPERIMENTAL

GENERAL

1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) was distilled from activated molecular sieves 4A and stored over activated molecular sieves 4A. Toluene and THF were dried by passing through a column of activated alumina followed by a column of Q-5 scavenger (Engelhard). 1,4-Dioxane was distilled from sodium and stored over activated molecular sieves 4A. *N*-Methylpyrrolidone (NMP) was purchased from Kishida Chemical Co., Ltd. and used as received.

$PdCl_2$ was purchased from Kojima Chemicals Co., Ltd. and used as received. $AgNTf_2$ was prepared by the reported method.[28] AgOTf was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. $AgBF_4$ and $AgSbF_6$ were purchased from Merck KGaA and used as received. $BF_3 \cdot OEt_2$ was purchased from Tokyo Chemical Industry Co., Ltd. and distilled from CaH_2. 1,2,2-Trifluorovinylzinc chloride–TMEDA complex was prepared by the procedure in our previous publication.[9c] $CuOTf \cdot 0.5C_6H_6$ was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. $PhCF_3$ was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. $Ph_3P^+CF_2CO_2^-$ was prepared by the reported procedure.[18a]

4-Bromo-2-methylthiophene (**8a**) was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. 3-Bromobenzothiophene (**8b**) was prepared by the reported method.[29] Bis(pinacolate) **13** were prepared by the reported procedure.[21]

Column chromatography and preparative thin layer chromatography (PTLC) were conducted on silica gel (Silica Gel 60 N, Kanto Chemical Co., Inc. for column chromatography and Wakogel B-5F, Wako Pure Chemical Industries, Ltd. for PTLC). Purification was also performed by preparative HPLC (GPC), using a Japan Analytical Inductry JAI LC-908 instrument (Jaigel-2H, $CHCl_3$).

IR spectra were recorded on a Horiba FT-300S spectrometer by the attenuated total reflectance (ATR method). NMR spectra were recorded on Bruker Avance 500 or Jeol JNM ECS-400 spectrometers in $CDCl_3$ at 500 or 400 MHz (^{1}H NMR), at 126 or 101 MHz (^{13}C NMR), and at 470 or 376 MHz (^{19}F NMR). Chemical shifts were given in ppm relative to internal Me_4Si (for ^{1}H NMR: $\delta = 0.00$), $CDCl_3$ (for ^{13}C NMR: $\delta = 77.0$), and C_6F_6 (for ^{19}F NMR: $\delta = 0.0$).[30] High-resolution mass spectroscopy (HRMS) was conducted with a Jeol JMS-T100GCV spectrometer (EI, TOF) or a Jeol JMS-T100CS spectrometer (ESI$^+$, TOF). Elemental analysis was performed with a Yanako MT-3 CHN Corder apparatus.

Microwave irradiation was performed using a CEM Discover apparatus in a sealed vessel.

PREPARATION OF *o*-(2,2-DIFLUOROVINYL)PHENYL- AND *o*-(1,2,2-TRIFLUOROVINYL)PHENYL-SUBSTITUTED THIOPHENES AND FURANS

Preparation of **5a** is described as a typical procedure. To a 1,4-dioxane solution (34 mL) of bromide **4a** (1.11 g, 5.07 mmol) and $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol) were added 3-thienylboronic acid **1a** (702 mg, 5.48 mmol), Na_2CO_3 (1.06 g, 10.0 mmol), and distilled water (17 mL). The reaction mixture was freeze-dried and refluxed overnight. Saturated aqueous NH_4Cl (50 mL) was added to quench the reaction at room temperature. Organic materials were extracted with Et_2O (15 mL) three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give difluoroalkene **5a** (871 mg, 76% yield) as a colorless liquid.

SPECTRAL DATA

3-[2-(2,2-Difluorovinyl)phenyl]thiophene 5a

^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.34$ (dd, $J_{HF} = 26.0, 4.0$ Hz, 1H), 7.14 (dd, $J = 5.0, 1.0$ Hz, 1H), 7.24 (dd, $J = 3.0, 1.0$ Hz, 1H), 7.28 (ddd, 7.5, 7.5, 1.0 Hz, 1H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.36 (d, $J = 7.5$ Hz, 1H), 7.38 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.57 (d, $J = 7.5$ Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 80.8$ (dd, $J_{CF} = 30, 13$ Hz), 123.6, 125.6, 127.3, 127.7, 128.3 (dd, $J_{CF} = 6, 6$ Hz), 128.5 (d, $J_{CF} = 9$ Hz), 129.2, 130.1, 136.0 (d, $J = 9$ Hz), 141.2, 156.5 (dd, $J_{CF} = 299, 287$ Hz). ^{19}F NMR (471 MHz, $CDCl_3$): $\delta = 77.8$ (dd, $J =$

32 Hz, J_{FH} = 26 Hz, 1F), 79.7 (dd, J = 32 Hz, J_{FH} = 4 Hz, 1F). IR (neat): $\tilde{\nu}$ 1722, 1234, 1169, 935, 750 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{12}H_8F_2S$ ([M]$^+$): 222.0315; found: 222.0313.

4-[2-(2,2-Difluorovinyl)phenyl]-2-methylthiophene 5b

A colorless liquid, 299 g, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.52 (d, J = 1.1 Hz, 3H), 5.39 (dd, J_{HF} = 26.0, 4.0 Hz, 1H), 6.78–6.80 (m, 1H), 6.97 (d, J = 1.0 Hz, 1H), 7.26 (dd, J = 7.5, 1.5 Hz, 1H), 7.28–7.34 (m, 2H), 7.56 (d, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.3, 80.7 (dd, J_{CF} = 30, 12 Hz), 121.3, 127.1, 127.2, 127.4, 128.0 (dd, J_{CF} = 6, 6 Hz), 128.2 (d, J_{CF} = 9 Hz), 129.8, 136.3 (d, J_{CF} = 5 Hz), 139.8, 140.8, 156.3 (dd, J_{CF} = 298, 287 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ = 76.6 (dd, J = 33 Hz, J_{FH} = 26 Hz, 1F), 78.4 (dd, J = 33 Hz, J_{FH} = 4 Hz, 1F). IR (neat): $\tilde{\nu}$ 3064, 1722, 1227, 1169, 937, 750 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{13}H_{10}F_2S$ ([M]$^+$): 236.0471; found: 236.0465.

3-[2-(2,2-Difluorovinyl)phenyl]benzothiophene 5c

A colorless liquid, 204 mg, 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.10 (dd, J_{HF} = 26.0, 4.0 Hz, 1H), 7.32 (s, 1H), 7.33–7.46 (m, 6H), 7.69 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 80.3 (dd, J_{CF} = 31, 12 Hz), 122.7, 123.1, 124.4, 124.5, 124.9, 127.1, 128.0 (d, J_{CF} = 10 Hz), 128.2, 129.5 (dd, J_{CF} = 6, 6 Hz), 130.8, 134.7 (d, J_{CF} = 4 Hz), 136.2, 138.8, 139.9, 156.3 (dd, J_{CF} = 298, 288 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ = 78.2 (dd, J = 30 Hz, J_{FH} = 26 Hz, 1F), 79.2 (dd, J = 30 Hz, J_{FH} = 4 Hz, 1F). IR (neat): $\tilde{\nu}$ 1724, 1348, 1238, 931, 762 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_{10}F_2S$ ([M]$^+$): 272.0471; found: 272.0466.

2-[2-(2,2-Difluorovinyl)phenyl]thiophene 6a

A colorless liquid, 2.66 g, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.47 (dd, J_{HF} = 26.0, 4.0 Hz, 1H), 7.05–7.07 (m, 1H), 7.07–7.10 (m, 1 H), 7.27 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.31–7.36 (m, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 80.7 (dd, J_{CF} = 31, 13 Hz), 126.0, 127.2, 127.28, 127.32, 128.0, 128.5 (d, J_{CF} = 6 Hz), 128.6 (d, J_{CF} = 9 Hz), 130.7, 133.5 (d, J_{CF} = 5 Hz), 141.8, 156.5 (dd, J_{CF} = 298, 288 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ = 76.6 (dd, J = 31 Hz, J_{FH} = 26 Hz, 1F), 78.8 (dd, J = 31 Hz, J_{FH} = 4 Hz, 1F). IR (neat): $\tilde{\nu}$ 1722, 1234, 1171, 933, 756, 692 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{12}H_8F_2S$ ([M]$^+$): 222.0315; found: 222.0311.

2-[2-(2,2-Difluorovinyl)phenyl]-5-methylthiophene 6b

A colorless liquid, 171 mg, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.52 (d, J = 1.0 Hz, 3H), 5.52 (dd, J_{HF} = 26.0, 4.0 Hz, 1H), 6.74 (dd, J = 3.5, 1.5 Hz, 1H), 6.85 (d, J = 3.5 Hz, 1H), 7.26 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.31 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.41 (dd, J =7.5, 1.5 Hz, 1H), 7.53–7.56 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.2, 80.8 (dd, J_{CF} = 31, 13 Hz), 125.5, 127.1, 127.3, 127.7, 128.3 (dd, J_{CF} = 7, 6 Hz), 128.6 (d, J_{CF} = 9 Hz), 130.5, 133.9, (d, J_{CF} = 5 Hz), 139.5, 140.6, 156.5 (dd, J_{CF} = 297, 288 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ = 76.2 (ddd, J = 30 Hz, J_{FH} = 26, 1 Hz), 78.6 (dd, J = 30 Hz, J_{FH} = 4 Hz). IR (neat): $\tilde{\nu}$ 1722, 1234, 1171, 931, 800, 756 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{13}H_{10}F_2S$

([M]$^+$): 236.0471; found: 236.0468.

2-[2-(2,2-Difluorovinyl)phenyl]benzothiophene 6c

A colorless liquid, 370 mg, 68% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.54 (dd, J_{HF} = 25.5, 4.0 Hz, 1H), 7.27 (s, 1H), 7.31 (dd, J = 7.6, 7.6 Hz, 1H), 7.35 (dd, J = 7.6, 7.6 Hz, 1H), 7.39 (dd, J = 7.6, 7.6 Hz, 2H), 7.52 (dd, J = 7.6, 0.8 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.85 (dd, J = 7.6, 0.8 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 80.6 (dd, J_{CF} = 31, 13 Hz), 122.1, 123.7, 124.0, 124.4, 124.5, 127.2, 128.6, 128.7 (d, J_{CF} = 10 Hz), 128.8 (dd, J_{CF} = 6, 6 Hz), 130.9, 133.5 (d, J_{CF} = 5 Hz), 140.0, 140.3, 142.1, 156.6 (dd, J_{CF} = 298, 288 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 77.2 (dd, J = 26 Hz, J_{FH} = 26 Hz, 1F), 79.4 (dd, J = 26 Hz, J_{FH} = 4 Hz, 1F). IR (neat): $\tilde{\nu}$ 1720, 1344, 1236, 931, 742 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_{10}F_2S$ ([M]$^+$): 272.0471; found: 272.0476.

2-[2-(1,2,2-Trifluorovinyl)phenyl]benzothiophene 6d

A pale yellow liquid, 0.69 g, 89% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.30–7.39 (m, 3H), 7.41 (dd, J = 7.5, 7.5 Hz, 1H), 7.45–7.53 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 122.1, 123.0, 123.9, 124.5, 124.6, 125.2 (dd, J_{CF} = 20, 4 Hz), 127.1 (ddd, J_{CF} = 233, 52, 20 Hz), 128.3, 130.97 (d, J_{CF} = 2 Hz), 131.04, 131.3, 135.3, 140.1, 140.3, 141.1, 153.1 (ddd, J_{CF} = 291, 278, 50 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 4.95 (dd, J = 117, 29 Hz, 1F), 46.2 (dd, J = 117, 73 Hz, 1F), 62.2 (dd, J = 73, 29 Hz, 1F). IR (neat): $\tilde{\nu}$ 1778, 1429, 1286, 1136, 982, 721 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_9F_3S$ ([M]$^+$): 290.0377; found: 290.0369.

2,5-Bis[2-(2,2-difluorovinyl)phenyl]thiophene 6e

A pale yellow liquid, 409 mg, 57% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.58 (dd, J_{HF} = 25.0, 4.0 Hz, 2H), 7.07 (s, 2H), 7.31 (ddd, J = 7.5, 7.5, 1.5 Hz, 2H), 7.36 (ddd, J = 7.5, 7.5, 1.5 Hz, 2H), 7.49 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 80.8 (dd, J_{CF} = 31, 13Hz), 127.4, 127.6, 128.2, 128.4 (dd, J_{CF} = 7, 5 Hz), 128.9 (d, J_{CF} = 8 Hz), 130.6, 133.2 (d, J_{CF} = 5 Hz), 142.5, 156.7 (dd, J_{CF} = 298, 288 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 76.6 (dd, J = 30 Hz, J_{FH} = 25 Hz, 2F), 79.0 (dd, J = 30 Hz, J_{FH} = 4 Hz, 2F). IR (neat): $\tilde{\nu}$ 1724, 1236, 1173, 935, 756 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{20}H_{12}F_4S$ ([M]$^+$): 360.0596; found: 360.0597.

2-[2-(2,2-Difluorovinyl)phenyl]benzofuran 7a

A colorless liquid, 333 mg, 83% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.71 (dd, J_{HF} = 25.5, 4.0 Hz, 1H), 6.91 (d, J = 2.5 Hz, 1H), 7.26 (ddd, J = 7.8, 7.5, 0.8 Hz, 1H), 7.32 (ddd, J = 9.5, 8.3, 1.4 Hz, 1H), 7.35–7.42 (m, 1H) 7.38 (s, 1H), 7.54 (dd, J = 8.3, 0.8 Hz, 1H), 7.56–7.60 (m, 1H), 7.63 (ddd, J = 7.8, 1.4, 0.7 Hz, 1H), 7.82 (dd, J = 7.8, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 80.8 (dd, J_{CF} = 31, 14 Hz), 106.1, 111.2, 121.1, 123.0, 124.6, 127.5, 127.9 (dd, J_{CF} = 7, 6 Hz), 128.7, 128.8, 128.9, 129.3 (d, J_{CF} = 9 Hz), 129.5 (d, J_{CF} = 5 Hz), 154.5, 154.7, 156.8 (dd, J_{CF} = 297, 288 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 76.3–76.5 (m, 1F), 78.5 (dd, J = 31 Hz, J_{FH} = 4 Hz, 1F). IR (neat): $\tilde{\nu}$ 1728, 1348, 1238, 931, 761 cm^{-1}.

HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_{10}F_2O$ ($[M]^+$): 256.0700; found: 256.0701.

2-[2-(1,2,2-Trifluorovinyl)phenyl]benzofuran 7b

A pale yellow liquid, 0.62 g, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.04 (s, 1H), 7.25 (ddd, *J* = 8.2, 7.4, 1.1 Hz, 1H), 7.32 (ddd, *J* = 8.2, 7.4, 1.1 Hz, 1H), 7.43 (dddd, *J* = 8.2, 8.2, 1.3, 1.3, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.53 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.57 (dddd, *J* = 8.2, 8.2, 1.3, 1.3 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 105.0 (d, J_{CF} = 4 Hz), 111.2, 121.3, 123.0, 123.3 (dd, J_{CF} = 21, 4 Hz), 124.9, 127.5 (ddd, J_{CF} = 234, 52, 20 Hz), 128.3, 128.4, 128.9, 130.9 (d, J_{CF} = 3 Hz), 131.0 (d, J_{CF} = 2 Hz), 131.7 (d, J_{CF} = 2 Hz), 153.2, 153.3 (ddd, J_{CF} = 328, 278, 50 Hz), 154.8. ^{19}F NMR (471 MHz, $CDCl_3$): δ = 3.05 (dd, *J* = 117, 29 Hz, 1F), 46.1 (dd, *J* = 117, 74 Hz, 1F), 61.4 (dd, *J* = 74, 29 Hz, 1F). IR (neat): $\tilde{\nu}$ 1780, 1448, 1282, 1132, 982, 744, 613 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_9F_3O$ ($[M]^+$): 274.0606; found: 274.0608.

SYNTHESIS OF PINPOINT-FLUORINATED NAPHTHO[*b*]THIOPHENES AND NAPHTHO[*b*]FURANS, AND THEIR SPECTRAL DATA

Synthesis of pinpoint-fluorinated thiophenes (catalyst system A)

Synthesis of **14a** is described as a typical procedure. To an HFIP solution (20 mL) of difluoroalkene **5a** (89 mg, 0.40 mmol) were added $BF_3 \cdot OEt_2$ (49 μL, 0.40 mmol), $PdCl_2$ (11 mg, 0.06 mmol), and $AgNTf_2$ (47 mg, 0.12 mmol). After the reaction mixture was refluxed for 30 min, phosphate buffer (pH 7, 20 mL) was added to quench the reaction at room temperature. Organic materials were extracted with CH_2Cl_2 (8 mL) three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give pinpoint-fluorinated naphtho[2,1-*b*]thiophene **14a** (70 mg, 87% yield) as colorless crystals.

Synthesis of pinpoint-fluorinated thiophenes (catalyst system B)

Synthesis of **14d** is described as a typical procedure. To an HFIP solution (20 mL) of difluoroalkene **6a** (88 mg, 0.40 mmol) were added $BF_3 \cdot OEt_2$ (50 μL, 0.40 mmol), $CuOTf \cdot 0.5C_6H_6$ (100 mg, 0.40 mmol), $PdCl_2$ (15 mg, 0.08 mmol), and $AgBF_4$ (31 mg, 0.16 mmol). After the reaction mixture was refluxed for 3 h, phosphate buffer (pH 7, 20 mL) was added to quench the reaction at room temperature. Organic materials were extracted with CH_2Cl_2 (8 mL) three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give pinpoint-fluorinated naphtho[1,2-*b*]thiophene **14d** (57 mg, 70% yield) as colorless crystals.

SPECTRAL DATA

4-Fluoronaphtho[2,1-*b*]thiophene 14a

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.39 (d, J_{HF} = 10.8 Hz, 1H), 7.52–7.59 (m, 2H), 7.66 (d, J = 5.3 Hz, 1H), 7.87–7.91 (m, 1H), 8.00 (dd, J = 5.3, 4.0 Hz, 1H), 8.28–8.32 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 106.8 (d, J_{CF} = 18 Hz), 122.4 (d, J_{CF} = 2 Hz), 123.7, 125.5 (d, J_{CF} = 2 Hz), 126.1, 126.5, 126.9, 127.9, 128.0, 132.3 (d, J_{CF} = 8 Hz), 139.4 (d, J_{CF} = 6 Hz), 155.8 (d, J_{CF} = 248 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 44.3 (dd, J_{FH} =11, 4 Hz, 1F). IR (neat): $\tilde{\nu}$ 3103, 1514, 1232, 1058, 837, 721 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{12}H_7FS$ ([M]$^+$): 202.0252; found: 202.0247.

4-Fluoro-2-methylnaphtho[2,1-*b*]thiophene 14b

A colorless liquid, 21 mg, 67% yield by ^{19}F NMR based on PhCF$_3$. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.69 (s, 3H), 7.29 (d, J_{HF} = 10.5 Hz, 1H), 7.45–7.53 (m, 1H), 7.49 (s, 1H), 7.60 (br s, 1H), 7.83 (dd, J = 7.5, 2.0 Hz, 1H), 8.17 (d, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 16.2, 105.9 (d, J_{CF} = 18 Hz), 120.5 (d, J_{CF} = 3 Hz), 123.7, 125.2 (d, J_{CF} = 2 Hz), 125.8, 125.9 (d, J_{CF} = 21 Hz), 126.1, 127.9 (d, J_{CF} = 5 Hz), 132.3 (d, J_{CF} = 8 Hz), 139.9 (d, J_{CF} = 6 Hz), 142.0, 155.5 (d, J_{CF} = 247 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 44.3 (dd, J_{FH} = 11, 3 Hz, 1F). IR (neat): $\tilde{\nu}$ 1529, 1371, 1068, 827, 681 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{13}H_9FS$ ([M]$^+$): 216.0409; found: 216.0403.

6-Fluorobenzo[*b*]naphtho[1,2-*d*]thiophene 14c

Colorless crystals, 94 mg, 93% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.52–7.57 (m, 2H), 7.58 (dd, J = 7.5, 7.5 Hz, 1H), 7.62 (dd, J = 7.5, 7.5 Hz, 1H), 7.68 (dd, J = 8.0, 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 7.5 Hz, 1H), 8.85 (d, J = 7.5 Hz, 1H), 8.97 (d, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 109.4 (d, J_{CF} = 18 Hz), 123.2, 123.5, 124.8, 125.1, 125.7, 125.9, 126.2 (d, J_{CF} = 2 Hz), 127.8, 128.4 (d, J_{CF} = 21 Hz), 128.9 (d, J_{CF} = 5 Hz), 132.6 (d, J_{CF} = 5 Hz), 132.9 (d, J_{CF} = 8 Hz), 136.5 (d, J_{CF} = 2 Hz), 139.9, 155.5(d, J_{CF} = 247 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 45.2 (d, J_{FH} = 10 Hz). IR (neat): $\tilde{\nu}$ 1552, 1518, 1259, 779, 715, 673 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_9FS$ ([M]$^+$): 252.0409; found: 252.0404.

4-Fluoronaphtho[1,2-*b*]thiophene 14d

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.32 (d, J_{HF} = 11.0 Hz, 1H), 7.49–7.53 (m, 2H), 7.51 (d, J = 5.3 Hz, 1H), 7.57 (d, J = 5.3 Hz, 1H), 7.82–7.86 (m, 1H), 8.06–8.11 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 107.1 (d, J_{CF} = 19 Hz), 120.4, 123.5, 125.7, 126.28, 126.36, 127.3 (d, J_{CF} = 10 Hz), 128.2 (d, J_{CF} = 5 Hz), 128.8 (d, J_{CF} = 23 Hz), 131.5 (d, J_{CF} = 9 Hz), 140.2, 156.2 (d, J_{CF} = 252 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 41.2 (d, J_{FH} = 11 Hz, 1F). IR (neat): $\tilde{\nu}$ 1558, 1437, 1315, 922, 771 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{12}H_7FS$ ([M]$^+$): 202.0253; found: 202.0248.

4-Fluoro-2-methylnaphtho[1,2-*b*]thiophene 14e

Colorless crystals, 51 mg, 59% yield ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.67 (d, J = 1.1 Hz, 3H), 7.22 (d,

J_{HF} = 11.5 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 7.44–7.51 (m, 2H), 7.79–7.83 (m, 1H), 7.96–8.00 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 16.0, 106.8 (d, J_{CF} = 19 Hz), 118.0, 123.2, 125.4 (d, J_{CF} = 2 Hz), 125.7, 126.0, 128.1 (d, J_{CF} = 5 Hz), 129.0 (d, J_{CF} = 23 Hz), 130.9 (d, J_{CF} = 9 Hz), 139.1 (d, J_{CF} = 8 Hz), 140.6, 155.5 (d, J_{CF} = 251 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 41.1 (d, J_{FH} = 12 Hz, 1F). IR (neat): $\tilde{\nu}$ 2919, 1508, 1444, 1101, 744 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{13}H_9FS$ ([M]$^+$): 216.0409; found: 216.0414.

5-Fluorobenzo[*b*]naphtho[2,1-*d*]thiophene 14f

Colorless crystals, 84 mg, 91% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.47 (d, J_{HF} = 11.5 Hz, 1H), 7.50–7.54 (m, 2H), 7.54–7.59 (m, 2H), 7.88–7.92 (m, 1H), 7.96 (dd, J = 6.5 Hz, 1.7 Hz, 1H), 8.08–8.13 (m, 1H), 8.49 (d, J = 7.2 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 108.1 (d, J_{CF} = 20 Hz), 122.6, 124.2, 125.0, 125.05, 125.10, 125.7, 125.8, 126.0, 126.3, 127.0, 128.1 (d, J_{CF} = 5 Hz), 132.3 (d, J_{CF} = 10 Hz), 134.3, 138.6, 157.7(d, J_{CF} = 252 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 41.6 (d, J_{FH} = 12 Hz). IR (neat): $\tilde{\nu}$ 1516, 1431, 1213, 951, 750 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_9FS$ ([M]$^+$): 252.0409; found: 252.0412.

5,6-Difluorobenzo[*b*]naphtho[2,1-*d*]thiophene 14g

Colorless crystals, 74 mg, 90% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.47–7.56 (m, 2H), 7.57–7.68 (m, 2H), 7.88–7.97 (m, 1H), 8.06 (d, J = 7.6 Hz, 1H), 8.18 (d, J = 7.9 Hz, 1H), 8.40–8.49 (m, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 121.4 (dd, J_{CF} = 6, 6 Hz), 122.7, 123.4 (d, J_{CF} = 16 Hz), 123.6 (d, J_{CF} = 15 Hz), 124.2, 124.9, 125.0, 125.2, 125.3 (d, J_{CF} = 4 Hz), 126.7, 127.1, 133.6, 134.4 (dd, J_{CF} = 4, 4 Hz), 138.9, 143.0 (dd, J_{CF} = 236, 12 Hz), 144.3 (dd, J_{CF} = 253, 14 Hz). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 6.81 (d, J = 18 Hz, 1F), 13.8 (d, J = 18 Hz, 1F). IR (neat): $\tilde{\nu}$ 2927, 1612, 1437, 1213, 746, 727 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_8F_2S$ ([M]$^+$): 270.0315; found: 270.0324.

6,7-Difluorodinaphtho[1,2-*b*, 2,1-*d*]thiophene 14h

Colorless crystals, 15 mg, 45% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.55 (dd, J = 5.5, 5.5 Hz, 2H), 7.57–7.63 (m, 4H), 7.90 (dd, J = 5.5, 3.0 Hz, 2H), 8.20 (dd, J = 5.5, 3.5 Hz, 2H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 109.3 (dd, J_{CF} = 13, 11 Hz), 122.2 (dd, J_{CF} = 9, 9 Hz), 124.0, 125.6, 125.9, 127.3, 127.8 (d, J_{CF} = 3 Hz), 132.2 (dd, J_{CF} = 5, 5 Hz), 139.4 (d, J_{CF} = 4 Hz), 154.2–157.1 (m). ^{19}F NMR (471 MHz, CDCl$_3$): δ = 52.4 (dd, J = 6.1 Hz, 2F). IR (neat): $\tilde{\nu}$ 1518, 1304, 1169, 839, 737 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{20}H_{10}F_2S$ ([M]$^+$): 320.0471; found: 320.0467.

5-Fluorobenzo[*b*]naphtho[2,1-*d*]furan 15a

Colorless crystals, 29 mg, 30% yield. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.38 (d, J_{HF} = 10.4 Hz, 1H), 7.41(dd, J = 7.5, 7.5 Hz, 1H), 7.50 (ddd, J = 8.1, 8.1, 0.9 Hz, 1H), 7.53–7.60 (m, 2H), 7.70 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.5 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 8.39 (d, J = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, CDCl$_3$): δ = 105.9 (d, J_{CF} = 19 Hz), 110.9 (d, J_{CF} = 25 Hz), 111.7, 118.7, 121.1, 122.3 (d, J_{CF} = 2 Hz), 122.5 (d, J_{CF} = 2 Hz), 123.5, 125.5 (d, J_{CF} = 2 Hz), 126.6, 127.0, 127.8 (d, J_{CF} = 5 Hz), 133.0 (d, J_{CF} = 9 Hz), 153.5 (d, J_{CF} = 11 Hz), 155.6, 155.8 (d, J_{CF} = 250 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ = 40.9 (d, J_{FH} = 10 Hz, 1F). IR (neat): $\tilde{\nu}$ 1531, 1367, 1219, 1074, 877 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_9FO$ ($[M]^+$): 236.0637; found: 236.0642.

5,6-Difluorobenzo[*b*]naphtho[2,1-*d*]furan 15b

Colorless crystals, 47 mg, 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (dd, *J* = 6.4, 6.4 Hz, 1H), 7.53 (ddd, *J* = 7.8, 7.8, 1.0 Hz, 1H), 7.64 (d, *J* = 6.4 Hz, 1H), 7.65 (d, *J* = 6.4 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 8.15–8.21 (m, 1H), 8.33–8.40 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 110.8 (d, J_{CF} = 20 Hz), 111.8, 118.0, 120.9, 121.1 (dd, J_{CF} = 6, 6 Hz), 122.2, 122.8, 123.4, 123.5, 126.4 (d, J_{CF} = 2 Hz), 126.99, 127.04, 141.1 (dd, J_{CF} = 245, 11 Hz), 141.8 (dd, J_{CF} = 251, 14 Hz), 148.0 (d, J_{CF} = 9 Hz), 155.8. ^{19}F NMR (471 MHz, $CDCl_3$): δ = 6.18 (d, *J* = 19 Hz, 1F), 15.5 (d, *J* = 19 Hz, 1F). IR (neat): $\tilde{\nu}$ 1448, 1367, 1228, 1063, 993, 876, 739 cm^{-1}. HRMS (70 eV, EI): *m/z* calcd. for $C_{16}H_8F_2O$ ($[M]^+$): 254.0543; found: 254.05344.

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