SHORT COMMUNICATION

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Decarboxylative Julia–Kocienski *gem*-Difluoro-Olefination of 2-Pyridinyl Sulfonyldifluoroacetate

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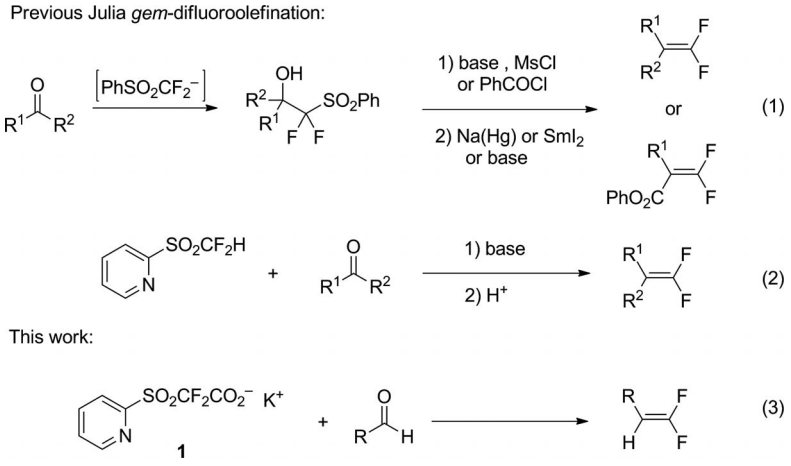
The decarboxylation of potassium 2-pyridinyl sulfonyldifluoroacetate and its subsequent reaction with aldehydes was found to be an efficient approach for the Julia–Kocienski reaction under mild conditions to give *gem*-difluoro olefins in moderate to excellent yields. Owing to its high stability in the pure state and its easy decarboxylation in polar solvents, potassium 2-pyridinyl sulfonyldifluoroacetate is expected to be an efficient *gem*-difluoro-olefination reagent.

Introduction

The installation of fluorine or fluorine-containing functional groups into organic molecules usually has a profound effect on the physical, chemical, and biological properties of the target molecules.[1] As an important class of fluorinated compounds, *gem*-difluoro olefins have the potential to be used in a wide range of research areas, such as medical and agricultural chemistry and material sciences.[2] Owing to their versatility, considerable effort has been directed towards the search for efficient and general methods for the construction of the *gem*-difluorovinylidene moiety (CF_2=C).[3] Traditional methods, including organometallic[3c,4] and elimination[5] approaches and Julia,[6] Horner–Wadsworth–Emmons,[7] and Wittig reactions,[8] require the tedious multistep synthesis of the fluorinated precursors, the presence of base, careful handling of the reagents owing to their sensitivity to moisture, and the use of environmentally unfriendly reagents. We previously found that the decarboxylative Wittig reaction was an efficient approach for the synthesis of *gem*-difluoro olefins.[9] As an extension of our studies on this chemistry,[9,10] we describe the decarboxylative Julia–Kocienski reaction of aldehydes with 2-pyridinyl sulfonyldifluoroacetate to afford *gem*-difluoro olefins.



Scheme 1. Julia *gem*-difluoro-olefination.

The classic Julia *gem*-difluoro-olefination reaction employs $PhSO_2CF_2^-$ as the nucleophile, which is generated in situ from $PhSO_2CF_2H$[6a–6c] or $PhSO_2CF_2Br$[6d] by deprotonation or single-electron transfer, respectively. In these approaches, desulfonylation is problematic because it needs multistep treatment or the use of the toxic reagent Na(Hg) [Scheme 1, Eq. (1)]. Recently, Hu and co-workers found that difluoromethyl 2-pyridinyl sulfone could act as a

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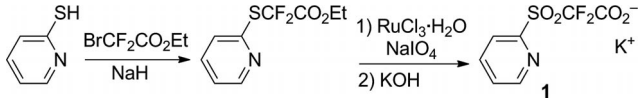
powerful *gem*-difluoro-olefination reagent. This approach is quite promising because the transformation is applicable to both aldehydes and ketones, but strong base was required to generate 2-$PySO_2CF_2^-$ at low temperature [Scheme 1, Eq. (2)].[6e] In this communication, we report the decarboxylation of potassium 2-pyridinyl sulfonyldifluoroacetate and its subsequent reaction with aldehydes to give *gem*-difluoro olefins under mild conditions [Scheme 1, Eq. (3)]. No base is needed in this simple and convenient conversion.

Results and Discussion

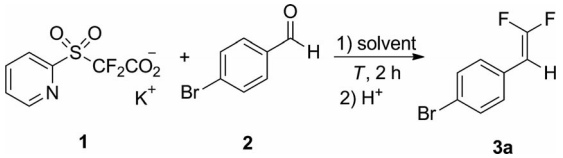
Potassium 2-pyridinyl sulfonyl-difluoroacetate (**1**) could be easily synthesized from the reaction of 2-pyridinethiol and ethyl bromodifluoroacetate, followed by oxidation and hydrolysis (Scheme 2). The salt is stable under air atmosphere. Thermal analysis (DSC-TGA) showed no decomposition below 100 °C (see the ESI), demonstrating relatively good thermal stability. However, as shown by ^{19}F NMR, slow decomposition via decarboxylation commenced in the presence of polar solvent such as DMF even at room temperature, which means decarboxylation of salt **1** in solvent could happen under mild conditions. The high stability in pure state and easy decarboxylation in polar solvent suggested this salt could be stored for a long time and *gem*-difluoro-olefination could be achieved under mild conditions, which is indeed the case.



Scheme 2. The synthesis of potassium 2-pyridinyl sulfonyl-difluoroacetate.

With stable salt **1** in hand, we then attempted the *gem*-difluoro-olefination with aldehydes. The reaction mixture of salt **1** with 4-bromobenzaldehyde in DMF was stirred at 60 °C for 2 h and then quenched with 3 N HCl. With (trifluoromethyl)(benzene) as an internal standard, analysis of the organic phase by ^{19}F NMR spectroscopy showed that the product was obtained in 63% yield (Table 1, entry 1). The transformation in DMSO gave the same result (Table 1, entry 2). With the use of a less polar solvent, the yield decreased dramatically (Table 1, entries 3–5), and no desired product was detected in 1,4-dioxane (Table 1, entry 5). We next screened other conditions in DMF. The examination of the reaction temperature (Table 1, entries 6–8) showed that slight heating (40 °C) was necessary (Table 1, entry 7). If the temperature was lowered to room temperature, the conversion was suppressed greatly (Table 1, entry 8). Prolonging the reaction time to 6 h gave the same yield as that obtained after 2 h (Table 1, entry 9 vs. 1). The amount of salt **1** had a strong effect on the reaction. By increasing the amount to 1.5 equiv., the yield improved significantly (Table 1, entry 10 vs. 1), but any further increase in the amount of **1** gave the same results (Table 1, entries 11 and 12). In contrast, an excess amount of aldehyde resulted in poor results (Table 1, entry 13).

Table 1. Optimization of the reaction conditions for the *gem*-difluoro-olefination.[a]



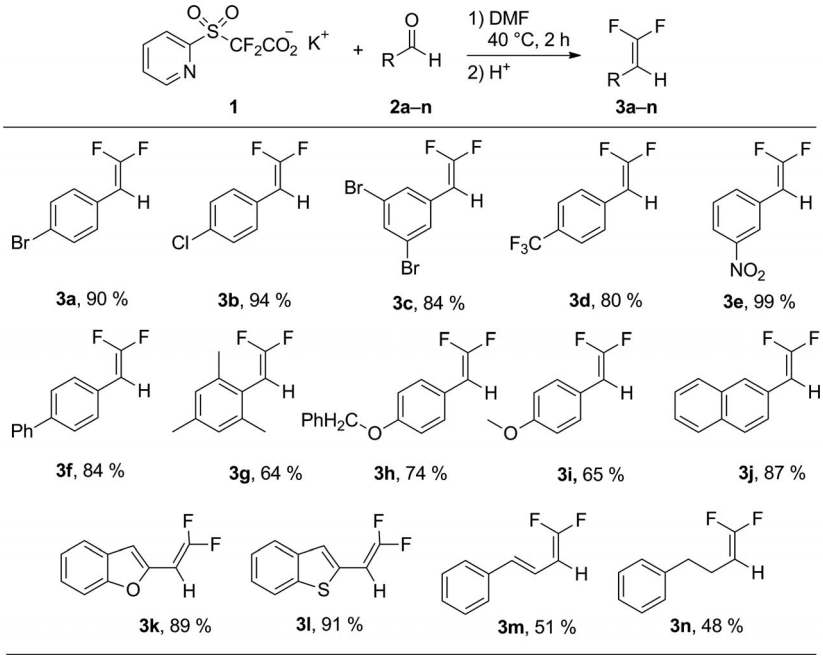
1 **2** **3a**

Entry	**1**/**2**[b]	*T* [°C]	Solvent	Yield[c] [%]
1	1:1	60	DMF	63
2	1:1	60	DMSO	63
3	1:1	60	CH_3CN	15
4	1:1	60	THF	trace
5	1:1	60	1,4-dioxane	0
6	1:1	80	DMF	63
7	1:1	40	DMF	63
8	1:1	r.t.	DMF	15
9[d]	1:1	40	DMF	63
10	1.5:1	40	DMF	93
11	2:1	40	DMF	93
12	3:1	40	DMF	93
13	1:2	40	DMF	75

[a] Reaction conditions: salt **1** and aldehyde in solvent (2 mL) at 40 °C for 2 h, followed by 3 N HCl (1.2 mL) for 2 h. [b] Molar ratio. [c] Determined by ^{19}F NMR spectroscopy with trifluoromethylbenzene as an internal standard;. [d] The reaction was run for 6 h.

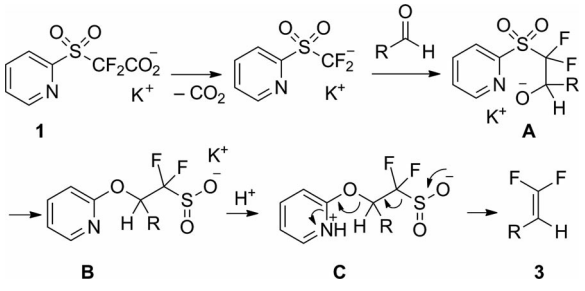
The substrates scope of the *gem*-difluoro-olefination reaction of salt **1** with aldehydes was then explored under the optimized reaction conditions (Table 1, entry 10). As shown in Scheme 3, the reaction tolerated various functional groups and gave the corresponding *gem*-difluoro olefins in moderate to excellent yields. Examination of electronic substituent effects (see **3a**–**i**) showed that electron-withdrawing groups on the phenyl ring (as in **3a**–**e**) in the substrates led to better results, presumably as a result of the stronger electrophilic ability of these substrates. The reaction is not quite sensitive to steric hindrance. With two methyl groups in the *ortho* position of the phenyl ring, a moderate yield of **3g** was still obtained. In the cases of 2-naphthyl or heteroaromatic substrates **3j**–**l**, the conversion gave the desired products in good yields. The transformation proceeded smoothly for an α,β-unsaturated aldehyde, even though the yield of **3m** was lower. The reaction was also applicable to enolizable aliphatic aldehydes. The low yield of **3n** is probably due to enolization of the aldehyde in the presence of salt **1**, which could be considered as a weak base. *gem*-Difluoro-olefination of ketones proceeded sluggishly, and only trace amounts of the products were detected by GC–MS.

As for the reaction mechanism, it is reasonable to conceive a pathway involving the condensation of the aldehyde with 2-$PySO_2CF_2^-$, which is generated in situ by decarboxylation of salt **1** (Scheme 4). The condensation gives intermediate **A**, followed by rearrangement to afford more stable salt **B**. If the conversion into salt **B** is completed, the reaction is quenched by acid. Protonation of salt **B** leads to intermediate **C**, which results in enhanced leaving ability of the 2-pyridyloxyl group. Decomposition of intermediate **C** gives the final product. The mechanism is supported by the experimental observation of the formation of salt **B** by ^{19}F



Scheme 3. *gem*-Difluoro-olefination of aldehydes with $PySO_2CF_2CO_2^-K^+$. Reaction conditions: Salt **1** (0.9 mmol) and aldehyde (0.6 mmol) in DMF (2 mL) at 40 °C for 2 h, followed by 3 N HCl (1.2 mL) for 2 h, yields of the isolated products are given.

NMR spectroscopy {δ = –128.7 ppm [(ABq)d, δ_{AB} = 157.3 ppm, J_d = 11.8 Hz, 2 F]} and ESIMS {*m*/*z* = 375.5, 377.5 $[M - K]^-$; calcd. 375.9, 377.9} before the reaction system of salt **1** with 4-bromobenzaldehyde was quenched with acid, which is consistent with the results obtained by Hu and co-workers.[6e]



Scheme 4. Proposed mechanism for the *gem*-difluoro-olefination of aldehydes.

Conclusions

In summary, we found that the generation of 2-$PySO_2CF_2^-$ through the decarboxylation of potassium 2-pyridinyl sulfonyldifluoroacetate was an efficient method for the Julia–Kocienski *gem*-difluoro-olefination of aldehydes. Potassium 2-pyridinyl sulfonyldifluoroacetate exhibits good stability in the pure state and readily undergoes decarboxylation in polar solvents under mild conditions, which suggests that this salt might be expected to be a convenient *gem*-difluoro-olefination reagent. Investigation into the application of potassium 2-pyridinyl sulfonyldifluoroacetate in other reactions is currently underway.

Experimental Section

General Information: ^1H NMR and ^{13}C NMR spectra were recorded at 400 or 300 and 100 MHz, respectively, with tetramethylsilane as the internal standard. ^{19}F NMR spectra were recorded at 376 MHz with $CFCl_3$ (positive for downfield shifts) as the external standard. All solvents were purified by standard methods. Flash column chromatography was performed by using 300–400 mesh silica gel.

Preparation of Potassium 2-Pyridinyl Sulfonyl-difluoroacetate (1): A solution of pyridine-2-thiol (16 g, 0.14 mol, 1.0 equiv.) in DMF (70 mL) was added dropwise over a period of 5 h at 0 °C under an atmosphere of N_2 to a suspension of NaH (60 wt.-%, 6.04 g, 0.15 mol, 1.07 equiv.) in DMF (100 mL). Upon completion of the addition, the reaction mixture was warmed up to room temperature and stirred for another 0.5 h. $BrCF_2CO_2C_2H_5$ (28 g, 0.14 mol, 1.0 equiv.) was added. The resulting mixture was stirred overnight. Upon completion of the conversion, the reaction was quenched by water (100 mL), followed by extraction with Et_2O (100 mL × 3). The organic phase was washed with brine and then dried with anhydrous Na_2SO_4. After the solution was filtered, the solvent was evaporated under vacuum to give a yellow oil. CCl_4 (120 mL), H_2O (300 mL), $NaIO_4$ (100 g, 0.47 mol), and ruthenium trichloride hydrate (20 mg) were added to a solution of this oil in CH_3CN (120 mL). The mixture was stirred over a period of 36 h at room temperature. Upon completion of the oxidation, H_2O (300 mL) was added to quench the reaction. The mixture was extracted with diethyl ether (200 mL × 3). The combined organic phase was washed successively with saturated $NaHCO_3$ and NaCl solution and then dried with anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was subjected to silica gel column chromatography (petroleum ether/ethyl acetate, 4:1 v/v) to give a colorless liquid (10 g). KOH (2 g, 0.035 mol) was added to a solution of this colorless liquid (10 g) in MeOH (20 mL). The mixture was stirred at room temperature for 6 h. After filtration and concentration, the pure product was ob-

tained as a white solid (9.8 g, 0.035 mol, 25% yield over 3 steps), m.p. 142 °C. ^{1}H NMR (300 MHz, D_2O): δ = 8.77 (s, 1 H), 8.29–8.14 (m, 2 H), 7.94–7.77 (m, 1 H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 161.2 (t, J = 22.9 Hz), 150.9, 150.2, 133.9, 130.3, 127.2, 115.3 (t, J = 301.6 Hz) ppm. ^{19}F NMR (282 MHz, D_2O): δ = –106.02 (s, 2 F) ppm. IR (KBr): $\tilde{\nu}$ = 3097, 3063, 1682, 1582, 1456, 1371, 1339, 1145, 1111, 995, 806, 789, 737, 602, 546 cm^{-1}. MS (ESI): m/z = 236 $[M – K]^-$. $C_7H_4F_2KNO_4S$ (275.27): calcd. C 30.54, N 5.09, H 1.46; found C 30.48, N 5.09, H 1.56.

General Procedure for the *gem*-Difluoro-Olefination of Aldehydes: Potassium 2-pyridinyl sulfonyldifluoroacetate (**1**; 248 mg, 0.9 mmol) was added to a solution of 4-bromobenzaldehyde (110 mg, 0.6 mmol) in DMF (2 mL). The mixture was stirred at 40 °C for 2 h. The reaction was quenched with aqueous saturated ammonium chloride (1.2 mL), followed by 3 N HCl (1.2 mL). The resulting mixture was stirred at 40 °C for another 2 h. After cooling to room temperature, the mixture was diluted with diethyl ether (10 mL), washed with H_2O (5 mL × 3), dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane) to afford pure product **3a**.

1-Bromo-4-(2,2-difluorovinyl)benzene (3a):[9] Colorless oil, 117 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.5 Hz, 2 H), 7.19 (d, J = 8.5 Hz, 2 H), 5.23 (dd, J = 25.9, 3.6 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.35 (dd, J = 29.2, 25.9 Hz, 1 F), –83.16 (dd, J = 29.2, 3.6 Hz, 1 F) ppm.

1-Chloro-4-(2,2-difluorovinyl)benzene (3b):[11] Colorless oil, 98 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.7 Hz, 2 H), 7.24 (d, J = 8.7 Hz, 2 H), 5.22 (dd, J = 25.9, 3.6 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.71 (dd, J = 29.9, 25.9 Hz, 1 F), –83.50 (dd, J = 29.9, 3.6 Hz, 1 F) ppm.

1,3-Dibromo-5-(2,2-difluorovinyl)benzene (3c): Colorless oil, 150 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (t, J = 1.6 Hz, 1 H), 7.39 (d, J = 1.6 Hz, 2 H), 5.18 (dd, J = 25.3, 3.3 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7 (dd, J = 300.3, 291.3 Hz), 135.3, 133.9 (dd, J = 7.6, 6.2 Hz), 132.5 (t, J = 1.9 Hz), 129.1 (dd, J = 7.0, 3.6 Hz), 128.6 (d, J = 1.3 Hz), 123.2, 80.6 (dd, J = 30.9, 13.2 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –78.68 (dd, J = 25.5, 25.3 Hz, 1 F), –80.64 (dd, J = 25.4, 3.3 Hz, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 1724, 1586, 1549, 1415, 1348, 1243, 1177, 1108, 969, 854, 746 cm^{-1}. GC–MS (EI): m/z = 298 $[M]^+$. HRMS (EI): calcd. for $C_8H_4Br_2F_2$ 295.8648; found 295.8651.

1-(2,2-Difluorovinyl)-4-(trifluoromethyl)benzene (3d):[4b] Colorless oil, 100 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 8.2 Hz, 2 H), 5.33 (dd, J = 25.7, 3.5 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.83 (s, 3 F), –79.82 (t, J = 25.7 Hz, 1 F), –81.47 (dd, J = 25.7, 3.5 Hz, 1 F) ppm.

1-(2,2-Difluorovinyl)-3-nitrobenzene (3e):[9] White solid, 110 mg, 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1 H), 8.09 (d, J = 8.0 Hz, 1 H), 7.65 (d, J = 8.0 Hz, 1 H), 7.52 (t, J = 8.0 Hz, 1 H), 5.39 (dd, J = 25.2, 3.0 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –79.02 (t, J = 25.2 Hz, 1 F), –80.74 (dd, J = 25.2, 3.0 Hz, 1 F) ppm.

4-(2,2-Difluorovinyl)-1,1′-biphenyl (3f):[9] White solid, 108 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.57 (m, 4 H), 7.53–7.31 (m, 5 H), 5.34 (dd, J = 26.2, 2.7 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.91 (t, J = 26.2 Hz, 1 F), –83.84 (d, J = 26.2 Hz, 1 F) ppm.

2-(2,2-difluorovinyl)-1,3,5-trimethylbenzene (3g):[9] Colorless oil, 70 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94, (s, 2 H), 5.23 (dd, J = 27.4, 2.0 Hz, 1 H), 2.33 (s, 3 H), 2.29 (s, 6 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –83.86 (dd, J = 34.0, 27.4 Hz, 1 F), –87.52 (dd, J = 34.0, 2.0 Hz, 1 F) ppm.

1-(Benzyloxy)-4-(2,2-difluorovinyl)benzene (3h):[8e] Colorless oil, 109 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.28 (m, 5 H), 7.24 (d, J = 8.7 Hz, 2 H), 6.93 (d, J = 8.7 Hz, 2 H), 5.19 (dd, J = 26.4, 3.7 Hz, 1 H), 5.04 (s, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –84.49 (dd, J = 36.4, 26.4 Hz, 1 F), –86.29 (dd, J = 36.4, 3.7 Hz, 1 F) ppm.

1-(2,2-Difluorovinyl)-4-methoxybenzene (3i):[9] Colorless oil, 66 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (d, J = 8.8 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 5.20 (dd, J = 26.4, 3.8 Hz, 1 H), 3.79 (s, 3 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –84.75 (dd, J = 36.9, 26.4 Hz, 1 F), –86.54 (dd, J = 36.9, 3.8 Hz, 1 F) ppm.

2-(2,2-Difluorovinyl)naphthalene (3j):[6e] White solid, 100 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.73 (m, 4 H), 7.54–7.42 (m, 3 H), 5.44 (dd, J = 26.2, 3.8 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –81.94 (dd, J = 30.7, 26.2 Hz, 1 F), –83.66 (dd, J = 30.7, 3.8 Hz, 1 F) ppm.

2-(2,2-Difluorovinyl)benzofuran (3k):[9] Colorless oil, 96 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.33 (m, 2 H), 7.31–7.10 (m, 2 H), 6.62 (s, 1 H), 5.40 (d, J = 25.1 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –76.05 (dd, J = 25.1, 16.4 Hz, 1 F), –82.30 (d, J = 16.4 Hz, 1 F) ppm.

2-(2,2-Difluorovinyl)benzo[*b*]thiophene (3l): White solid, 107 mg, 91% yield, m.p. 79–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, J = 7.7, 0.9 Hz, 1 H), 7.72 (dd, J = 7.7, 0.9 Hz, 1 H), 7.40–7.29 (m, 2 H), 7.20 (s, 1 H), 5.63 (dd, J = 25.6, 1.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5 (dd, J = 299.3, 291.0 Hz), 139.5 (t, J = 2.5 Hz), 139.5, 132.4 (dd, J = 7.7, 6.6 Hz), 124.5, 124.4, 123.2, 122.6 (dd, J = 7.2, 4.7 Hz), 122.0, 78.3 (dd, J = 33.4, 16.5 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –78.90 (dd, J = 25.6, 23.1 Hz, 1 F), –84.80 (dd, J = 23.1, 1.8 Hz, 1 F) ppm. IR (KBr): $\tilde{\nu}$ = 3073, 2650, 1951, 1916, 1727, 1520, 1456, 1343, 1303, 1159, 931, 874, 844, 747, 727, 673, 520 cm^{-1}. GC–MS (EI): m/z = 196 $[M]^+$. HRMS (EI): calcd. for $C_{10}H_6F_2S$ 196.0158; found 196.0159.

(*E*)-(4,4-difluorobuta-1,3-dien-1-yl)benzene (3m):[9] Yellow oil, 49 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.11 (m, 5 H), 6.65 (dd, J = 15.9, 10.9 Hz, 1 H), 6.46 (d, J = 15.9 Hz, 1 H), 5.11 (ddd, J = 24.1, 10.9, 1.0 Hz, 1 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –85.37 (dd, J = 26.2, 24.1 Hz, 1 F), –87.09 (dd, J = 26.2, 1.0 Hz, 1 F) ppm.

(4,4-Difluorobut-3-en-1-yl)benzene (3n):[9] Colorless oil, 52 mg, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–6.90 (m, 5 H), 4.14 (dt, J = 25.4, 7.7 Hz, 1 H), 2.67 (t, J = 7.7 Hz, 2 H), 2.30 (q, J = 7.7 Hz, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –89.04 (d, J = 47.4 Hz, 1 F), –91.08 (dd, J = 47.4, 25.4 Hz, 1 F) ppm.

Supporting Information (see footnote on the first page of this article): Copies of the differential scanning calorimetry/thermogravimetric analysis of potassium 2-pyridinyl sulfonyldifluoroacetate; copies of the ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra of the final compounds.

Acknowledgments

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