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# Gram-Scale Synthesis of 2,5-Difluoro-7,7,8,8-tetracyanoquinodimethane ($F_2$-TCNQ)

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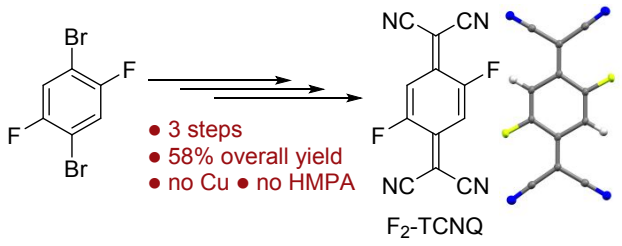
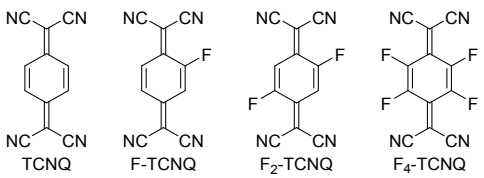
*Supporting Information Placeholder*




**ABSTRACT:** The molecule 2,5-difluoro-7,7,8,8-tetracyanoquinodimethane ($F_2$-TCNQ) is an organic semiconductor with many promising properties, including high charge mobility ($\mu$). However, an efficient gram-scale synthesis of $F_2$-TCNQ has not been fully documented. Herein, we report a synthesis of $F_2$-TCNQ via a three-step sequence that afforded $F_2$-TCNQ in 58% cumulative yield. This synthesis was used to prepare over one gram of $F_2$-TCNQ.

Organic semiconductors (OSCs) can be lightweight, flexible, and cost effective components, which are used in many devices. Because of these properties, there is an increasing interest in synthesizing new OSCs and optimizing the synthesis of known OSCs.[1–3] High charge mobility ($\mu$) is essential for many OSCs and some privileged arenes and heteroarenes have been described with exceptionally high charge mobility.[3–6] Often, a single crystal of these organic compounds is required, which complicates utilizing some promising OSC candidates.[3] One interesting OSC is 7,7,8,8-tetracyanoquinodimethane (TCNQ), which was first reported in the 1960s.[7–9] TCNQ has become a promising OSC because it functions as an excellent electron acceptor with a notably high conductivity relative to other organic electron acceptors.[10–12] Calculations proposed that adding substituents to the TCNQ core could enhance these properties.[13]

**Figure 1.** $F_n$-TCNQ Organic Semiconductor Family




This effort led to the development of a family of fluorinated TCNQ analogues (Figure 1). It was reported that the stability of $F_n$-TCNQ increases with an increasing number of fluorine substituents.[14] The room temperature single crystal electron transport properties of TCNQ, $F_2$-TCNQ, and $F_4$-TCNQ were investigated.[15] Relative to TCNQ and $F_4$-TCNQ, $F_2$-TCNQ exhibits an unusually high electron mobility ($\mu$ = 0.1, 0.2, and 6-7 $cm^2\ V^{-1}\ s^{-1}$, respectively).[15] By conducting the mobility measurement under vacuum at 150 K, the electron mobility of $F_2$-TCNQ could be further enhanced to 25 $cm^2\ V^{-1}\ s^{-1}$.[15] Computational studies revealed that the family of $F_n$-TCNQ molecules have comparable LUMO energies, electron affinities (EA), and electron reorganization energies, which makes the higher experimental electron mobility for $F_2$-TCNQ an apparent anomaly.[16] Among the $F_n$-TCNQ family, $F_2$-TCNQ has a unique stacking in a single crystal structure.[15–18] The unique face-to-face crystal stacking of $F_2$-TCNQ is thought to account for the phenomenal electron mobility relative to TCNQ and $F_4$-TCNQ. Furthermore, the properties of the $F_n$-TCNQ family have been investigated as complexes,[19–21] co-crystals,[22–27] and adducts with various metal ions and other materials.[28–30]

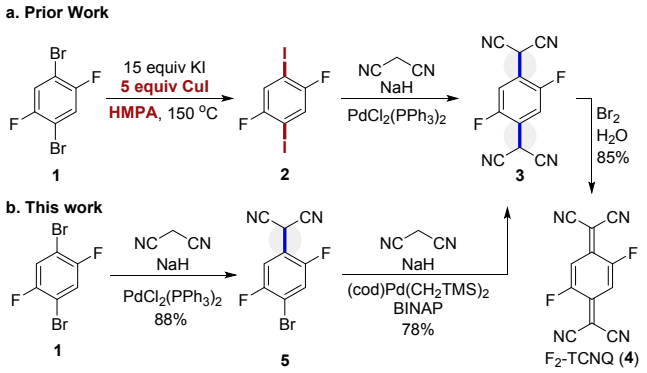
Multiple syntheses of TCNQ and $F_4$-TCNQ have been reported. The first synthesis of TCNQ was via a Knoevenagel condensation followed by oxidation using elemental bromine.[7] Yamaguchi and co-workers improved the synthesis of TCNQ by starting with terephthaloyl dichloride.[31,32] The synthesis of $F_4$-TCNQ has been reported using a similar Knoevenagel condensation pathway.[33,34] A patent also described synthesizing $F_4$-TCNQ from *tetra*-fluoro-terephthalic acid.[35,36] Even though syntheses of TCNQ, $F_4$-TCNQ, and other analogues[37] are well documented, an efficient, scalable, peer reviewed synthesis of $F_2$-TCNQ has not, to the best of our knowledge, been published.

A patent disclosed that $F_2$-TCNQ could be obtained from 1,4-dibromo-2,5-difluorobenzene **1** (Scheme 1a).[38,39] Iodination of compound **1** afforded compound **2**.[38,39] A double Pd-catalyzed cross-coupling of compound **2** with malononitrile was reported to afford *tetra*-nitrile **3**, which could be readily oxidized to $F_2$-TCNQ (**4**) using elemental bromine.[10]

We needed a relatively large quantity of $F_2$-TCNQ and several aspects of the halogen exchange reaction were unappealing. The reported iodination required a large excess of

potassium iodide, super stoichiometric quantities of copper(I) iodide, and the use of HMPA, which is carcinogenic, as the solvent. Reported herein is an alternative synthesis of $F_2$-TCNQ from dibromide **1** that proceeds in 58% overall yield and avoids the iodination described above (Scheme 1b). This synthesis was used to prepare over 1 gram of $F_2$-TCNQ.

**Scheme 1.** Synthesis of $F_2$-TCNQ

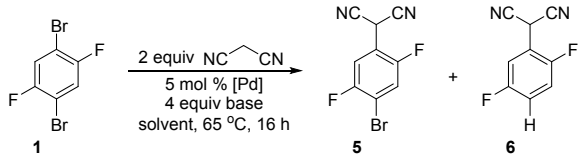



An optimization screen was conducted for the first cross-coupling (Table 1). We hypothesized that two different palladium-catalyzed cross-coupling reactions might be more efficient because the ligand could be independently optimized for each reaction.[40] The reaction was performed in various solvents with sodium *tert*-butoxide as the base (entries 1-3).[41,42] Compound **1** was completely consumed in THF (entry 3), whereas using acetonitrile and toluene resulted in poor conversion (entries 1-2). The use of $Pd_2dba_3$ or $PdCl_2(PPh_3)_2$ as a precatalyst with sodium *tert*-butoxide in THF provided improved but unexceptional results (entries 4-6). Using NaH over other bases was beneficial (entries 6-10). With NaH, $PdCl_2(PPh_3)_2$ was the optimal precatalyst (entries 8-10). This is convenient because it is a commercially available, inexpensive, and bench stable precatalyst. The optimal conditions (entry 10) were then scaled and product **5** was isolated in 85% and 90% yield in duplicate trials affording 1.10 g and 1.73 g of material respectively (88% average yield).

With a gram-scale synthesis of compound **5** in hand, a second cross-coupling was investigated. A complicating factor for the second cross-coupling is that starting material **5** is quite acidic and is likely deprotonated prior to oxidative addition. Oxidative addition with an anionic species is likely more difficult because of the increased electron density and potential ligation of the anion to the metal center. Therefore, several precatalysts and ligands were investigated (Table 2). It should be noted that no reaction was observed in THF at 65 °C (not shown), which was optimal for the first cross-coupling. Also, none of the desired product **3** was observed when the reaction was conducted in toluene, nonane, or nitrobenzene. With sodium hydride as the base, other potential solvents resulted in a complicated reaction mixture (not shown). Thus, optimization was conducted using dioxane as a higher boiling THF surrogate (reactions conducted at 100 °C).

Even under the more forcing conditions, minimal conversion was observed with $Pd_2dba_3$ as the precatalyst (Table 2, entries 1-3). The ligand BINAP was the most promising in the initial screen (entry 4). The common catalyst $Pd(PPh_3)_4$ provided ample reactivity; however, debromination was observed as a significant byproduct (entry 5). The use of $[PdCl(allyl)]_2$ with

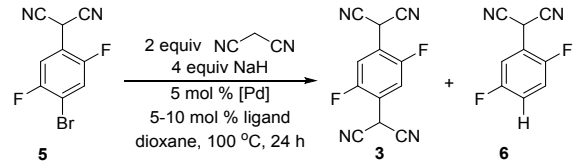
**Table 1.** Optimization for the First Cross-Coupling[a]




| entry | [Pd] | base | solvent | % **1** | % **5** | % **6** |
|---|---|---|---|---|---|---|
| 1 | $Pd(PPh_3)_4$ | NaO$^t$Bu | PhMe | 61 | 9 | n.d. |
| 2 | $Pd(PPh_3)_4$ | NaO$^t$Bu | MeCN | 57 | 15 | 17 |
| 3 | $Pd(PPh_3)_4$ | NaO$^t$Bu | THF | n.d. | 39 | n.d. |
| 4[b] | $Pd_2dba_3$, $PCy_3$ | NaO$^t$Bu | THF | n.d. | 40 | 20 |
| 5[b] | $Pd_2dba_3$, $PPh_3$ | NaO$^t$Bu | THF | n.d. | 54 | n.d. |
| 6 | $PdCl_2(PPh_3)_2$ | NaO$^t$Bu | THF | n.d. | 69 | n.d. |
| 7 | $Pd(PPh_3)_4$ | NaHMDS | THF | n.d. | 3 | 9 |
| 8 | $Pd(PPh_3)_4$ | NaH | THF | n.d. | 48 | 10 |
| 9 | $PdCl_2$(dppf) | NaH | THF | n.d. | 9 | 7 |
| **10** | **$PdCl_2(PPh_3)_2$** | **NaH** | **THF** | **n.d.** | **86** | **4** |

[a]Reaction conducted with compound **1** (0.05 mmol), malononitrile (0.10 mmol), base (0.20 mmol), in various solvents with 5 mol % [Pd]. Yields were determined by calibrated GC-FID using biphenyl as an internal standard. All yields reflect the average of duplicate trials. [b]10 mol % ligand. Not detected = n.d.

**Table 2.** Optimization for the Second Cross-Coupling[a]




| entry | [Pd] | L (mol %) | % **5** | % **3** | % **6** |
|---|---|---|---|---|---|
| 1 | $Pd_2dba_3$ | $PPh_3$ (10) | 98 | n.d. | 6 |
| 2 | $Pd_2dba_3$ | $PCy_3$ (10) | 93 | 3 | 4 |
| 3 | $Pd_2dba_3$ | Xantphos (5) | 89 | n.d. | 5 |
| 4 | $Pd_2dba_3$ | BINAP (5) | 27 | 62 | 8 |
| 5 | $Pd(PPh_3)_4$ | none added | 6 | 71 | 20 |
| 6 | $[PdCl(allyl)]_2$ | $PPh_3$ (10) | 93 | n.d. | 8 |
| 7 | $[PdCl(allyl)]_2$ | $PCy_3$ (10) | 23 | 56 | 15 |
| 8 | $[PdCl(allyl)]_2$ | Xantphos (5) | 70 | 12 | 6 |
| 9 | $[PdCl(allyl)]_2$ | BINAP (5) | 9 | 75 | 7 |
| **10** | **Pd1** | **BINAP (5)** | **7** | **82** | **7** |

[a]Reaction conducted with compound **5** (0.10 mmol), malononitrile (0.20 mmol), NaH (0.40 mmol), in dioxane with 5 mol % [Pd] and 5 or 10 mol % ligand. Yields were determined by $^{19}$F NMR using the crude reaction mixture, with 1-fluoronaphthalene as an internal standard. All yields reflect the average of duplicate trials. Pd1 = $(cod)Pd(CH_2TMS)_2$, Not detected = n.d.

various ligands provided an enhanced yield relative to $Pd_2dba_3$ (entries 6-9). Lastly, the precatalyst (cod)Pd($CH_2TMS$)$_2$[43,44] was identified as being optimal (entry 10). Using these conditions, the reaction of bromide **5** was scaled to produce *tetra*-nitrile **3** in an 78% average isolated yield (1.22 g, 84%; 1.03 g, 71%).

The oxidation of *tetra*-nitrile **3** was executed upon exposure to elemental bromine as reported (Scheme 1).[35,36] This reaction afforded $F_2$-TCNQ (**4**) in 73% and 97% yield in duplicate trials affording 0.81 g and 0.79 g of material respectively (85% average yield, total of 1.6 g of material). Samples of $F_2$-TCNQ could be crystallized from acetonitrile, which provided samples suitable for diffraction analysis. The crystals obtained by this synthesis demonstrated a similar crystal packing arrangement as reported for $F_2$-TCNQ (see SI).[15]

In conclusion, this report describes a three step synthesis of $F_2$-TCNQ that proceeds in 58% cumulative yield. This sequence provided samples of $F_2$-TCNQ that demonstrate similar crystal packing and structures relative to prior work. This synthesis was used to generate over one gram of $F_2$-TCNQ.

## EXPERIMENTAL SECTION

**General:** All reactions sensitive to air or moisture were carried out in oven-dried glassware using standard Schlenk line techniques or in a nitrogen filled glovebox. All reactions conducted at elevated temperature used aluminum heating blocks with magnetic stirring (500 rpm). Reported temperatures were based on an external thermal couple. Dry THF was obtained from a commercial solvent purification system using activated alumina columns and stored under a positive pressure of argon. Dry dioxane was purchased in anhydrous form and stored in a glove box. All other solvents and all reagents were purchased from commercial suppliers and used as received. Reactions were monitored by GC-FID, crude $^{19}$F NMR or thin layer chromatography (TLC) using pre-coated plastic plates impregnated with a fluorescent indicator (254 nm). Visualization was carried out with UV light (254 nm). Column chromatography was performed using a Teledyne Isco CombiFlash Rf purification system utilizing normal phase pre-column load cartridges and gold high performance columns.

**Instrumentation:** All proton ($^1$H) NMR spectra were recorded at 400 MHz or 500 MHz on a Bruker spectrometer. All carbon ($^{13}$C) NMR spectra were recorded at 126 MHz on a Bruker spectrometer and were proton decoupled. All fluorine ($^{19}$F) NMR spectra were recorded at 376 MHz on a Bruker spectrometer. Chemical shifts are expressed in ppm and are referenced to residual solvent as an internal standard ($^1$H: $CHCl_3$, 7.26 ppm; $^{13}$C: $CDCl_3$, 77.2 ppm). Infrared (IR) spectra were performed as a film on NaCl plates on a Nexus 670 FT-IR and are reported in cm$^{-1}$. Mass spectra were taken on Bruker BioTOF II or an Agilent 7890B GC/Agilent 7200 Accurate Mass GQ-TOF. Gas chromatography (GC) was performed on a Shimadzu GC-2010 Plus using an SH-Rxi-5ms 15 m column and a flame ionization detector.

**Optimization for the first Pd-catalyzed cross-coupling: (**Example given for Table 1, entry 1) In a nitrogen filled glovebox, a 4 mL vial was charged with sodium *tert*-butoxide (19 mg, 0.20 mmol). The vial was sealed with a septa cap and removed from glovebox. In a separate 20 mL vial, a stock solution of malononitrile (26 mg, 0.39 mmol) was prepared in toluene (0.8 mL). In a separate 20 mL vial, a stock solution of compound **1** (55 mg, 0.20 mmol) and biphenyl (9.8 mg, 64 µmol, internal standard) was prepared in toluene (0.8 mL). To each vial containing sodium tert-butoxide, an aliquot of malononitrile stock solution (0.2 mL, described above) was added under argon using a Schlenk line. An aliquot of compound **1** was then added to each vial. The vials were brought into a glovebox and $Pd(PPh_3)_4$ (2.9 mg, 2.5 µmol) was added. The vials were sealed with a Teflon lined cap and removed from glovebox. The reaction was heated to 65 ˚C. After 16 h, the reaction was cooled. The reaction was quenched by the addition of 1M HCl solution (0.5 mL). Ethyl acetate (0.5 mL) was added to the vial and the resulting mixture was shaken thoroughly. After two clear phases formed, the organic layer was analyzed by GC-FID to determine the yield.

**Optimization for the second Pd-catalyzed cross-coupling:** (Example given for Table 2, entry 5) In a nitrogen filled glovebox, a 4 mL vial was charged with sodium hydride (11 mg, 0.42 mmol, 90% dry). To a separate 20 mL vial, a stock solution of malononitrile (211 mg, 3.19 mmol) was prepared in dioxane (1.6 mL). To a separate 20 mL vial, a stock solution of compound **5** (411 mg, 1.60 mmol) and 1-fluoronaphthalene (92 mg, 0.63 mmol, internal standard) was prepared in dioxane (3.2 mL). To a separate 4 mL vial, a stock solution of $Pd_2dba_3$ (9.1 mg, 9.9 µmol) and (±)-BINAP (12.7 mg, 20.4 mmol) was prepared in dioxane (0.8 mL). An aliquot of malononitrile stock solution (0.1 mL, described above) was added to each 4 mL vial containing sodium hydride followed by an aliquot of compound **5** stock solution (0.2 mL, described above). After 5 min, an aliquot of palladium complex (0.2 mL, described above) was added. The vial was sealed with a Teflon lined cap and removed from glovebox. The reaction was heated to 100 ˚C. After 24 h, the reaction was cooled to rt. The reaction was quenched by the addition of trifluoroacetic acid (61 µL, 0.8 mmol) and diluted with acetone-$d_6$ (ca. 0.6 mL). The resulting solution was analyzed by $^{19}$F NMR to determine the yield.

***2,2'-(2,5-difluoro-1,4-phenylene)dimalononitrile*** **(3). Safety Note:** This reaction has the potential to generate gas at elivated temperature in a sealed vessel. To mitigate the risk of vessel rupture, this reaction was conducted in separate vials, each with only a few hundered milligams of material. Six 20 mL vials were charged with compound **5** (256-259 mg, 0.995-1.08 mmol) and malononitrile (131-133 mg, 1.98-2.01 mmol). The vials were brought into a glovebox. In the glovebox, dioxane (3 mL) was added to the vial. After the mixture became homogeneous, solid NaH (107-110 mg, 4.01-4.13 mmol, 90% dry) was added at rt. A separate 20 mL vial was charged with (cod)Pd($CH_2TMS$)$_2$ (137 mg, 0.352 mmol), (±)-BINAP (219 mg, 0.352 mmol) and dioxane (14 mL) to prepare the stock solution of palladium. An aliquot of palladium stock solution (2.0 mL) was added to the vials containing compound **5** and NaH. The vials were sealed with a teflon lined cap, removed from the glovebox, and heated to 100 ˚C. After 24 h, the reaction was allowed to cool to rt. The reaction was quenched by slowly transferring the reaction mixture to cold HCl (100 mL, 1 M aq), combining the material from all 6 vials. The resulting mixture was extracted with ethyl acetate (3 x 100 mL). The combined organic phase was dried ($Na_2SO_4$), filtered through a Celite pad, and concentrated under reduced pressure. To the residue, $CHCl_3$ (100 mL) was added and the mixture was agitated for 5 min. The mixture was filtered. The solid was washed with $CHCl_3$ until the filtrate was colorless. The solid was then collected and dried, which afforded compound **3** (1.22 g, 84%) as a red-brown solid. A duplicate experiment afforded compound **3** (1.03 g, 71%). The average yield of 78% is reported. **Note:** This product displayed broad NMR signals under a wide variety of conditions (solvent and temperature). The use of TFA as an NMR co-solvent provided more consistent NMR spectra presumably by ensuring the compound **3** was protonated. $^1$H NMR (500 MHz, acetone-$d_6$ with ca. 5% TFA): δ 7.81 (br, 2H), 6.50 (br, 2H).$^{13}$C{$^1$H} NMR (126 MHz, acetone-$d_6$ with ca. 5% TFA): δ 156.1 (dd, $J_{C\text{-}F}$ = 251.2, 4.4 Hz), 119.8 (t, $J_{C\text{-}F}$ = 12.4 Hz), 118.5 – 117.9 (m), 111.1, 22.8.$^{19}$F{$^1$H} NMR (376 MHz, acetone-$d_6$ with ca. 5% TFA): δ -118.3. IR (NaCl, thin film, cm$^{-1}$): 2931, 2191, 1054, 1427. HRMS (EI-TOF) *m/z*: $[M–H]^–$ Calculated for $C_{12}H_3F_2N_4^–$: 241.0331, Observed: 241.0303.

***2,5-Difluoro-7,7,8,8-tetracyanoquinodimethane*** **(4).** A round bottom flask was charged with compound **3** (1.11 g, 4.54

mmol) and water (200 mL). Bromine (0.94 mL, 18.8 mmol) was added dropwise by syringe. The reaction was conducted with vigorous stirring at rt. After 48 h, the resulting solid was collected by filtration and washed with diethyl ether (ca. 20 mL) until the filtrate was colorless. This afforded compound **4** (807 mg, 73%). In a duplicate experiment 793 mg (97%) of compound **4** was isolated. The average yield of 85% is reported. **Note:** Do not wash compound **4** with a basic solution (pyridine, sodium hydroxide, sodium bicarbonate, etc.). Residual HBr and $Br_2$ should be removed via excessive washing ($Et_2O$) not with a basic quench because this decomposes compound **4**. $^1$H NMR (500 MHz, $CD_3CN$): δ 7.23 (dd, $J$ = 9.4, 7.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_3CN$): δ 157.2 (d, $J_{C\text{-}F}$ = 273.6 Hz), 144.7 (dd, $J_{C\text{-}F}$ = 16.0, 12.5 Hz), 113.1 (dd, $J_{C\text{-}F}$ = 28.3, 7.6 Hz), 112.1, 112.0, 87.5 – 87.2 (m). $^{19}F\{^1H\}$ NMR (376 MHz, $CD_3CN$): δ -108.0. HRMS (EI-TOF) *m/z*: $[M]^-$ Calculated for $C_{12}H_2F_2N_4^-$: 240.0253, Observed: 240.0263.

***2-(4-bromo-2,5-difluorophenyl)malononitrile* (5).** In a glovebox, a two-necked round bottom flask was charged with sodium hydride (536 mg, 20.1 mmol, 90% dry) and sealed with septa. The flask was removed from the glovebox and equipped with a condenser under argon. THF (40 mL) was added to the flask via syringe. A separate vessel was charged with malononitrile (660 mg, 9.99 mmol) and THF (20 mL). At rt, the solution of malononitrile was added dropwise via syringe to the flask containing NaH. A separate vial was charged with 1,4-dibromo-2,5-difluorobenzene (**1**, 1.36 g, 5.00 mmol) and THF (20 mL). At rt, the solution of compound **1** was added dropwise via syringe to the flask containing NaH. The vial containing compound **1** was rinsed with THF (5 mL). After 10 min, solid $PdCl_2(PPh_3)_2$ (177 mg, 252 µmmol, 5 mol %) was added. The reaction was heated to reflux. After 16 h, the reaction was allowed to cool to rt. The reaction was slowly quenched by the addition of HCl (40 mL, 1 M aq) and diluted with ethyl acetate (20 mL). The resulting mixture was extracted with ethyl acetate (3 x 80 mL). The combined organic phase was dried ($Na_2SO_4$), filtered, and concentrated under reduced pressure. Purification by column chromatography (ethyl acetate/hexane gradient from 0-40%) afforded compound **5** as a pale yellow solid (1.10 g, 85%). In a duplicate experiment 1.73 g (90%) of compound **5** was obtained. The average yield of 88% is reported. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, $J$ = 8.6, 5.4 Hz, 1H), 7.44 (t, $J$ = 6.8 Hz, 1H), 5.21 (s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 156.1 (dd, $J_{C\text{-}F}$ = 249.5, 3.2 Hz), 155.0 (dd, $J_{C\text{-}F}$ = 253.4, 3.5 Hz), 121.9 (d, $J_{C\text{-}F}$ = 25.2 Hz), 116.3 (dd, $J_{C\text{-}F}$ = 27.2, 2.4 Hz), 114.7 (dd, $J_{C\text{-}F}$ = 16.3, 6.7 Hz), 113.1 (dd, $J_{C\text{-}F}$ = 23.4, 9.9 Hz), 109.9, 22.4 (d, $J_{C\text{-}F}$ = 4.3 Hz). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -108.7 (d, $J$ = 15.5 Hz, 1F), -118.7 (d, $J$ = 15.6 Hz, 1F). IR (NaCl, thin film, $cm^{-1}$): 3057, 2914, 2260, 1614, 1489, 1404, 1183, 1008, 894, 787. HRMS (EI-TOF) *m/z*: $[M–H]^-$ Calculated for $C_9H_2BrF_2N_2^-$: 254.9375, Observed: 254.9369.

***2-(2,5-difluorophenyl)malononitrile* (6).** A two-necked round bottom flask was charged with compound **5** (98 mg, 0.38 mmol) and THF (5 mL) under argon. The flask was cooled in an acetone/dry ice bath. Dropwise addition of *n*-BuLi (0.34 mL, 2.5 M solution in hexanes, 0.85 mmol) was conducted over 5 min. After 1 h, the reaction was quenched by dropwise addition of HCl (1.0 mL, 1.0 M aq). The resulting solution was diluted with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic solution was washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude material was filtered through a short plug of silica gel. The procedure afforded compound **6** (97%, 66 mg) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.33 (m, 1H), 7.28 – 7.21 (m, 2H), 5.25 (s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.9 (dd, $J_{C\text{-}F}$ = 248.6, 2.7 Hz), 155.6 (dd, $J_{C\text{-}F}$ = 248.9, 3.1 Hz), 119.6 (dd, $J_{C\text{-}F}$ = 23.9, 8.5 Hz), 118.1 (dd, $J_{C\text{-}F}$ = 23.1, 8.5 Hz), 116.0 (dd, $J_{C\text{-}F}$ = 26.9, 2.1 Hz), 115.5 (dd, $J_{C\text{-}F}$ = 16.7, 8.2 Hz), 110.3, 22.5, 22.4. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -114.3 (d, $J$ = 17.1 Hz, 1F), -121.1 (d, $J$ = 17.5 Hz, 1F). IR (NaCl, thin film, $cm^{-1}$): 3082, 2945, 2268, 1502, 1228. HRMS (EI-TOF) *m/z*: $[M–H]^-$ Calculated for $C_9H_3F_2N_2^-$: 177.0270, Observed: 177.0269.

## ASSOCIATED CONTENT

**Supporting Information**.
The Supporting Information is available free of charge on the ACS Publications website.

Crystallographic and spectral data (cif and PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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