Rhodium-Catalyzed Merging of 2-Arylquinazolinone and 2,2-Difluorovinyl Tosylate: Diverse Synthesis of Monofluoroolefin Quinazolinone Derivatives

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ABSTRACT: An efficient method for the synthesis of 2-(o-monofluoroalkenylaryl)quinazolinone derivatives was developed. In this context, the quinazolinone ring served as the inherent directing group, 2,2-diﬂuorovinyl tosylate was used as the monofluorooleﬁn synthon, and Rh(III)-catalyzed C−H bond diﬂuorovinylation of 2-arylquinazolins was performed to give the corresponding monofluoroalkene-containing quinazolins in yields of 65−92%. The method is characterized by broad synthetic utility, mild conditions, and high efﬁciency.

INTRODUCTION

In recent decades, organoﬂuorine chemistry has been widely developed in the fields of medicine and pesticides.1 The combination of a ﬂuorine atom or a ﬂuorine-containing compound with a small organic molecule increases the organic molecule’s polarity and lipophilicity and alters its biological activity and physicochemical properties.2 Among ﬂuorine-containing compounds, monofluoroolefins play an important role in organic synthesis, medicinal chemistry, and peptide chemistry.3 Consequently, a growing number of efﬁcient methodologies for the synthesis of monofluoroalkenes have been reported.4

In recent years, transition-metal-catalyzed C−H bond activations have been implemented in order to introduce a monofluoroolefin moiety into small organic molecules.5 Various ﬂuorine-containing reagents, such as gem-diﬂuoroalkenes,5a−i α-ﬂuoracrylic acids,5j and gem-bromofluoroalkenes,5k have been employed as monofluoroolefin synths. Among these reagents, 2,2-diﬂuorovinyl tosylate has seen broad use in recent years (Scheme 1).6a For example, Li and Wang reported the use of 2,2-diﬂuorovinyl tosylate as a coupling reagent in the Rh(III)-catalyzed C−H activation of the N−X bond of benzamides. This allowed for the assembly of a monofluorinated alkene intermediate with retention of the tosylate functionality, allowing for the preparation of the corresponding ﬂuorinated heterocycles under various conditions (Scheme 1a,b).6a,b Li described the Rh(III)-catalyzed α-ﬂuoralkenylation of N-nitrosoanilines with 2,2-diﬂuorovinyl tosylates via C−H bond activation and subsequent β-F elimination to form the desired monofluoroalkene-containing compounds (Scheme 1c).6c
Table 1. Optimization of the Reaction Conditions

| entry | catalyst (5 mol %) | solvent | additive | T (°C) | yield (%) |
|-------|---------------------|---------|----------|--------|-----------|
| 1     | RhCp*(MeCN)2(SbF6)2 | CF3CH2OH| CsOPiv   | 60     | 39        |
| 2     | RhCp*(MeCN)2(SbF6)2 | MeOH    | CsOPiv   | 60     | 22        |
| 3     | RhCp*(MeCN)2(SbF6)2 | EtOH    | CsOPiv   | 60     | 19        |
| 4     | RhCp*(MeCN)2(SbF6)2 | 1,4-dioxane | CsOPiv | 60 | trace |
| 5     | RhCp*(MeCN)2(SbF6)2 | DMF     | CsOPiv   | 60     | NR        |
| 6     | RhCp*(MeCN)2(SbF6)2 | DMSO    | CsOPiv   | 60     | NR        |
| 7     | RhCp*(MeCN)2(SbF6)2 | THF     | CsOPiv   | 60     | trace     |
| 8     | RhCp*(MeCN)2(SbF6)2 | toluene | CsOPiv   | 60     | NR        |
| 9     | RhCp*(MeCN)2(SbF6)2 | benzotrifluoride | CsOPiv | 60 | NR |
| 10    | RhCp*(MeCN)2(SbF6)2 | t-BuOH  | CsOPiv   | 60     | NR        |
| 11    | RhCp*(MeCN)2(SbF6)2 | HFIP    | CsOPiv   | 60     | 86        |
| 12    | RhCp*(MeCN)2(SbF6)2 | HFIP    | CsOPiv   | 60     | 76        |
| 13    | RhCp*(MeCN)2(SbF6)2 | HFIP    | Cs2CO3   | 60     | 80        |
| 14    | RhCp*(MeCN)2(SbF6)2 | HFIP    | CsF      | 60     | 41        |
| 15    | IrCp*Cl2/AgSbF6     | HFIP    | CsOPiv   | 60     | 22        |
| 16    | RhCp*Cl2/AgSbF6     | HFIP    | CsOPiv   | 60     | 70        |
| 17†   | RhCp*(MeCN)2(SbF6)2 | HFIP    | CsOPiv   | 60     | 92        |
| 18‡   | RhCp*(MeCN)2(SbF6)2 | HFIP    | CsOPiv   | 80     | 82        |
| 19‡   | RhCp*(MeCN)2(SbF6)2 | HFIP    | CsOPiv   | 40     | 72        |
| 20‡   | RhCp*(MeCN)2(SbF6)2 | HFIP    | CsOPiv   | 60     | 77        |
| 21‡   | RhCp*(MeCN)2(SbF6)2 | HFIP    | CsOPiv   | 60     | 74        |
| 22‡   | HFIP                |         | CsOPiv   | 60     | NR        |

*Yields based on isolated. †Time was 6 h. ‡CsOPiv was added 0.5 equiv.

The quinazolinone skeleton is present in numerous natural products and has a wide range of applications in medicine and biology. So far, tremendous efforts have been devoted to the development of new synthetic methods for the construction of diverse quinazolinone architectures and the evaluation of their bioactivities. In the past few years, our group has focused extensively on the development of methods for the synthesis of quinazolinone cores and the late-stage functionalization of 2-arylquinazolinones with a desire to construct a quinazolinone-based molecular library for bioactivity assays. Despite progress, there is room for improvement with regard to efficiency and selectivity, especially for the introduction of a fluorovinyl moiety into the quinazolinone skeleton to form novel fluorinated quinazolinone derivatives. Monofluoroolefins and the quinazolinone core are important structural motifs in pharmaceuticals and biologically active molecules. Monofluoroolefin-containing quinazolinones may exhibit a wide range of potent applications in the pharmaceutical, agrochemical, and material sciences. Thus, the development of efficient and straightforward protocols to access monofluoroolefin-containing quinazolinones is highly desirable. Thus, we have focused on the preparation of a diverse range of monofluoroolefin-containing quinazolinones (Scheme 1d).

Results and Discussion

We initiated our investigation by screening the coupling reaction conditions between 2-(p-methylphenyl)quinazolinone 1a (0.2 mmol) with 2,2-difluorovinyl tosylate 2a (1.1 equiv) in the presence of RhCp*(MeCN)2(SbF6)2 (4.0 mol %) and CsOPiv (1.0 equiv). Fortunately, the corresponding monofluoroolefin-quinazolinone compound 3a was isolated in a yield of 39% when the reaction was conducted in CF3CH2OH at 60°C (entry 1). The structure of 3a was confirmed unambiguously by X-ray crystal diffraction (see the Supporting Information). The results of solvent screening indicated that carrying out the reaction in HFIP gave the corresponding product in a high yield of 86% (entries 2–11). The fluorinated solvent HFIP not only have acidic properties but also have H-bonding with the substrate, which can enhance the reaction. Next, the additives, such as Cs2CO3, CsOAc, CsF, and so forth were examined, and no better result was obtained (entries 12–14). Lower yields were obtained when other catalysts such as IrCp*Cl2/AgSbF6 or RhCp*Cl2/AgSbF6 were used (entries 15–16). The desired product was obtained in 92% yield when the reaction time was reduced to 6 h (entry 17). Increasing or decreasing the reaction temperature resulted in slightly diminished yields (entries 18–19). Decreasing the loading of CsOPiv gave lower product yields (entries 20–21). Control experiments showed that none of the desired product was obtained in the absence of the RhCp*(MeCN)2(SbF6)2 catalyst (entry 22) (Table 1).

After establishing the optimized conditions, we investigated the generality and the substrate scope of the reaction. The results are presented in Table 2. As shown in Table 2, a number of substrates bearing different substituents were amenable to the reaction conditions, giving the corresponding products in good to excellent yields under the optimal conditions. First, the effects of R1 on the reaction were explored. The results revealed that the electronic nature and...
the position of the R₁ substituent have a significant influence on the reaction. When the substituent R₁ is at the para position of the 2-arylquinazoline and is an electron-donating group, such as methyl, ethyl, i-propyl, methoxy, ethoxy, or an N,N-dimethylamino substituent, the desired products are obtained in excellent yields of 83−92% (entries 3a−3f). When R₁ is at the para position or ortho position of the 2-aryl group and is electron-withdrawing in character (F, Cl, Br, CN, or NO₂), no reaction occurs (3h−3i). When the substituent R₁ is at the ortho position and is an electron-donating group, such as a methyl, methoxy, or ethoxy substituent, the expected products are prepared in good to excellent yields (3j−3l). Substrates with an electron-donating R₁ group at the meta position of the 2-aryl functionality (methyl, methoxy, and ethoxy) were not amenable to the reaction conditions (3m−3n). However, the desired products were obtained in good yields when an electron-withdrawing R₁ group is present at this position (3o−3p).

Subsequently, the effects of the R₂ group on the quinazolinone ring were explored. Surprisingly, electron-withdrawing and electron-donating groups are tolerated, providing the desired products in excellent yields, no matter what the position of the R₂ substituent is (entries 3q−3za).

Table 2. Scope Investigation for the Reaction of 2-Arylquinazolinones 1 and 2,2-Difluorovinyl Tosylate 2

| R₁  | R₂  | Yield (%) |
|-----|-----|-----------|
| H   | Cl  | 85%       |
| H   | NO₂ | 83%       |
| H   | CN  | 85%       |
| H   | F   | 87%       |

Yields based on isolated. Reaction conditions: 1 (0.2 mol), 2 (0.22 mol), RhCp*(MeCN)₃(SbF₆)₂ (5.0 mol %), CsOPiv (1.0 equiv), HFIP (1.5 mL), 60 °C, 6 h, under air. NR = no reaction.
To demonstrate the potential synthetic utility of this reaction, we performed a gram-scale reaction with 2-p-methylphenyl-quinazolinone. As shown in Scheme 2, the product (3a) was isolated in a yield of 84%.

On the basis of previous reports, a plausible mechanism is described in Scheme 3. First, an active cation Rh(III) reacts with 2-arylquinazolinone via a key C−H activation to generate the five-membered rhodacycle intermediate A, which coordinates with the difluorolefin to give intermediate B. Next, insertion of the difluorolefin into the C−Rh bond produces a seven-membered Rh(III) complex C, which undergoes selective β-F elimination via the syn-coplanar state to form the product 3a and Rh(III).

**CONCLUSIONS**

In summary, we have developed an efficient method for the synthesis of 2-(α-monofluoroalkenyl)quinazolinone derivatives. The reaction of 2-arylquinazolinones and 2,2-difluorovinyl tosylate in the presence of a Rh catalyst produces the corresponding products via C−H bond activation and C−F bond cleavage. The methodology is available to a wide range of substrates, and the presence of a double bond provides the possibility for subsequent research.

**EXPERIMENTAL SECTION**

Unless otherwise noted, all reactions were carried out under air atmosphere unless otherwise stated. Commercial reagents were purchased from Aldrich, Alfa, or other commercial suppliers. Commercial reagents were used without further purification. Reactions were conducted using standard techniques on the vacuum line. Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with 0.25 mm 230−400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Flash column chromatography was performed using silica gel (60 °A pore size, 32−63 μm, standard grade). Organic solutions were concentrated on rotary evaporators at 20 Torr (house vacuum) at 25−35 °C. The 1H NMR spectra were recorded on a 400 MHz NMR spectrometer. The 13C NMR spectra were recorded at 100 MHz. The 19F NMR spectra were recorded at 375 MHz. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million (ppm) from internal standard tetramethylsilane (TMS) on the δ scale.

**General Procedures for Synthesis of Compound 3.** A mixture of 2-arylquinazolinone 1 (0.2 mmol), 2,2-difluorovinyl tosylate 2 (56.16 mg, 0.24 mmol), RhCp*(MeCN)3(SbF6)2 (8.33 mg, 5 mol%), and CsOPiv (46.80 mg, 0.2 mmol) in HFIP (1.5 mL) was stirred at 60 °C until 1a was completed consumed (detected by TLC). Evaporation of the solvent followed purification by column chromatograph over silica gel (normal ratio: petroleum ether/ethyl acetate = 3/1) provided the corresponding product 3.

2-[2-(1-Fluoro-2-p-methylbenzenesulfonyloxyl-vinyl)-p-methylphenyl]-3H-quinazolin-4-one (3a). The product is obtained as a white solid in 92% yield, 83 mg, mp 205−208 °C,
2-(1-Fluoro-2-p-methylbenzenesulfonyloxyl-vinyl)-p-ethylphenyl-3H-quinazolin-4-one (3b). The product is obtained as a white solid in 88% yield, 82 mg, mp 166–168 °C, R_f = 0.46 (petroleum ether/ethyl acetate = 2/1). 1H NMR (400 MHz, DMSO-d_6): δ 12.56 (s, 1H), 8.17 (d, J = 7.2 Hz, 1H), 7.83 (ddd J = 8.4, 7.2, 1.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.59–7.53 (m, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.46–7.38 (m, 4H), 6.91 (d, J = 29.6 Hz, 1H), 2.40 (s, 6H). 13C NMR (100 MHz, DMSO-d_6): δ 162.1, 153.6, 151.1 (d, J_C-F = 25.30 Hz), 148.9, 146.5, 140.8, 134.9, 131.7, 131.3, 130.8, 130.5, 129.6 (d, J_C-C = 4.0 Hz), 128.2, 127.8, 127.4 (d, J_C-C = 22.0 Hz), 127.3, 126.3, 121.5, 121.2 (d, J_C-C = 13.0 Hz), 121.1, 21.7, 21.1. 19F NMR (376 MHz, DMSO-d_6): δ --117.80. HRMS (ESI) m/z: [M + H]^+ calc for C_{24}H_{20}FN_{2}O_{5}S+ [M + H]^+, 465.1122; found, 465.1117.

2-(1-Fluoro-2-p-methylbenzenesulfonyloxyl-vinyl)-p-N,N-dimethylaminophenyl-3H-quinazolin-4-one (3f). The product is obtained as a white solid in 83% yield, 80 mg, mp 199–201 °C, R_f = 0.44 (petroleum ether/ethyl acetate = 2/1). 1H NMR (400 MHz, DMSO-d_6): δ 12.56 (s, 1H), 8.17 (d, J = 7.2 Hz, 1H), 7.83 (t, J = 7.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.59–7.53 (m, 2H), 7.49–7.45 (m, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 20.0 Hz, 2H), 2.70 (q, J = 7.6 Hz, 2H), 2.40 (s, 3H), 1.22 (t, J = 7.6 Hz, 3H). 13C NMR (100 MHz, DMSO-d_6): δ 162.1, 153.6, 151.2 (d, J_C-C = 253.1 Hz), 148.9, 146.9, 146.4, 134.9, 131.7, 130.8, 130.7, 130.6, 130.2, 128.6 (d, J_C-C = 4.2 Hz), 128.2, 127.8, 127.6 (d, J_C-C = 21.5 Hz), 127.3, 126.3, 121.5, 121.2 (d, J_C-C = 12.5 Hz), 28.3, 21.6, 15.73. 19F NMR (376 MHz, DMSO-d_6): δ --117.59. HRMS (ESI) m/z: [M + H]^+ calc for C_{25}H_{22}FN_{2}O_{5}S+ [M + H]^+, 468.1228; found, 481.1223.

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2-[1-(1-Fluoro-2-p-methylbenzenesulfonyloxyl-vinyl)-6-ethyloxylphenyl]-3H-quinazolin-4-one (3I). The product is obtained as a white solid in 86% yield, 83 mg, mp 151–153 °C, Rf = 0.48 (petroleum ether/ethyl acetate = 2/1). 1H NMR (400 MHz, DMSO-d6): δ 12.45 (s, 1H), 8.21 (d, J = 6.7 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.62–7.49 (m, 3H), 7.35 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 20.0 Hz, 1H), 4.07 (q, J = 7.0 Hz, 2H), 3.28 (s, 3H), 1.16 (t, J = 7.0 Hz, 3H). 13C NMR (101 MHz, DMSO-d6): δ 161.1, 157.4, 151.5, 150.4 (d, 3J 2.4 Hz), 149.2, 146.4, 134.8, 131.8, 131.5, 130.7, 128.6 (d, 3J 2.2 Hz), 128.1, 127.8, 127.3, 126.3, 122.7, 121.7, 121.7 (d, 3J 13.0 Hz), 120.2 (d, 13C 5.0 Hz), 115.4, 64.9, 21.6, 14.8. 19F NMR (376 MHz, DMSO-d6): δ −118.71. HRMS (ESI) m/z: [M + H]+ calc for C23H25FN6O8S6 [M + H]+, 481.1228; found, 481.1230.

2-[1-(1-Fluoro-2-p-methylbenzenesulfonyloxyl-vinyl)-5-methylphenyl]-3H-quinazolin-4-one (3m). The product is obtained as a white solid in 30% yield, 27 mg, mp 169–170 °C, Rf = 0.53 (petroleum ether/ethyl acetate = 2/1). 1H NMR (400 MHz, DMSO-d6): δ 12.53 (s, 1H), 8.18 (d, J = 8.0, 1.2 Hz, 1H), 7.85 (d, J = 8.4, 6.8, 1.6 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.0, 6.8, 1.2 Hz, 1H), 7.53–7.48 (m, 3H), 7.34 (s, 1H), 7.39 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 20.0 Hz, 1H), 2.40 (s, 6H). 13C NMR (101 MHz, DMSO-d6): δ 162.0, 153.7, 151.0 (d, 3J 2.2 Hz), 148.9, 146.4, 140.9, 1350.0, 133.2, 131.7, 131.2, 131.1, 130.7, 129.1 (d, 3J 3.0 Hz), 128.2, 127.8, 127.3, 126.3, 124.6 (d, 3J 2.2 Hz), 121.5, 120.9 (d, 3J 13.0 Hz), 21.7, 21.2. 19F NMR (376 MHz, DMSO-d6): δ −117.45. HRMS (ESI) m/z: [M + H]+ calc for C22H23FN6O8S6 [M + H]+, 451.1122; found, 451.1120.

2-[1-(1-Fluoro-2-p-methylbenzenesulfonyloxyl-vinyl)-4-chlorophenyl]-3H-quinazolin-4-one (3o). The product is obtained as a pale yellow solid in 65% yield, 59 mg, mp 191–192 °C, Rf = 0.54 (petroleum ether/ethyl acetate = 2/1). 1H NMR (400 MHz, DMSO-d6): δ 12.65 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.66–7.51 (m, 5H), 7.34 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 20.0 Hz, 1H), 3.78 (s, 3H), 2.38 (s, 3H). 13C NMR (101 MHz, DMSO-d6): δ 161.8, 158.0, 151.4, 150.3 (d, 3J 5.0 Hz), 149.1, 146.5, 134.9, 131.8, 131.5, 130.7, 128.6 (d, 3J = 22.0 Hz), 128.0, 127.8, 127.4, 126.3, 122.4, 121.7, 121.6 (d, 3J = 13.0 Hz), 120.2 (d, 3J = 5.0 Hz), 114.3, 56.6, 21.6. 19F NMR (376 MHz, DMSO-d6): δ −118.87. HRMS (ESI) m/z: [M + H]+ calc for C20H17F2N2O5S6 [M + H]+, 476.1072; found, 476.1077.

2-[1-(1-Fluoro-2-p-methylbenzenesulfonyloxyl-vinyl)-5-methylphenyl]-3H-quinazolin-4-one (3n). The product is obtained as a white solid, 82 mg, 88% yield, mp 209–210 °C, Rf = 0.40 (petroleum ether/ethyl acetate = 2/1). 1H NMR (400 MHz, DMSO-d6): δ 12.54 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.68–7.55 (m, 5H), 7.50–7.36 (m, 4H), 6.88 (d, J = 19.6 Hz, 1H), 3.91 (s, 3H), 2.39 (s, 3H). 13C NMR (101 MHz, DMSO-d6): δ 161.8, 158.5, 151.2, 152.0 (d, 3J = 254.0 Hz), 146.4, 143.4, 133.4, 131.6, 130.8, 130.7, 130.6 (d, 3J = 5.0 Hz), 129.5, 129.2 (d, 3J = 5.0 Hz), 128.2, 127.5 (d, 3J = 22.0 Hz), 124.3, 122.4, 121.3 (d, 3J = 12.0 Hz), 106.4, 56.2, 21.6. 19F NMR (376 MHz, DMSO-d6): δ −117.94. HRMS (ESI) m/z: [M + H]+ calc for C22H23FN6O8S6 [M + H]+, 455.0872; found, 455.0879.
The product is obtained as a white solid, 83 mg, 83% yield, mp 204–206 °C. 

{\text{1H NMR (400 MHz, DMSO-\text{d}_6):} \delta 12.70 (s, 1H), 8.08 (d, J = 2.0 Hz, 1H), 7.83 (dd, J = 8.4, 2.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.51 (dd, J = 8.4 Hz, 1H), 7.47 (s, 2H), 7.31 (s, 1H), 6.98 (d, J = 19.6 Hz, 1H), 3.87 (s, 3H), 2.46 (s, 3H), 2.17 (d, J = 8.4, 2.0 Hz, 1H), 3.12 (s, 3H), 2.12 (d, J = 12 Hz, 2H).} 

{\text{13C NMR (101 MHz, DMSO-\text{d}_6):} \delta 161.3, 160.9, 153.9, 150.7 (d, J_{\text{CF}} = 253.0 Hz), 147.5, 146.5, 135.0, 132.3, 131.6, 131.5, 130.7, 128.2, 128.2, 128.1, 122.5, 121.5 (d, J_{\text{CF}} = 12.0 Hz), 116.1, 114.8 (d, J_{\text{CF}} = 6.0 Hz), 56.2, 21.6.} 

{\text{19F NMR (376 MHz, DMSO-\text{d}_6):} \delta −117.45.} 

{\text{HRMS (ESI) m/z:} [M + H]^{+} \text{ calc for C}_{24}\text{H}_{17}\text{ClF}_{2}\text{N}_{2}\text{O}_{3}\text{S}^{+} \left[ \text{M + H}^{+}\right], 456.1279; \text{found, 456.1286.}} 

The product is obtained as a white solid, 83 mg, 83% yield, mp 204–206 °C, R_f = 0.39 (petroleum ether/ethyl acetate = 2/1). 

{\text{1H NMR (400 MHz, DMSO-\text{d}_6):} \delta 12.46 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.45–7.35 (m, 6H), 6.89 (d, J = 19.6 Hz, 1H), 2.46 (s, 3H), 2.39 (d, J = 6.8 Hz, 6H), 1.3C NMR (101 MHz, DMSO-\text{d}_6):} \delta 162.0, 153.7, 151.1 (d, J_{\text{CF}} = 254.0 Hz), 149.0, 146.4, 145.5, 140.7, 131.7, 131.3, 130.7, 130.6, 129.5 (d, J_{\text{CF}} = 5.0 Hz), 128.7, 128.2, 127.4 (d, J = 21.0 Hz), 127.3, 126.2, 121.2 (d, J_{\text{CF}} = 13.0 Hz), 119.1, 21.8, 21.6, 21.1.} 

{\text{19F NMR (376 MHz, DMSO-\text{d}_6):} \delta −117.83.} 

{\text{HRMS (ESI) m/z:} [M + H]^{+} \text{ calc for C}_{23}\text{H}_{18}\text{F}_{2}\text{N}_{2}\text{O}_{3}\text{S}^{+} \left[ \text{M + H}^{+}\right], 465.1279; \text{found, 465.1286.}}
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