

## Article

# Synthesis of Novel $\alpha$ -Trifluorothioanisole Derivatives Containing Phenylpyridine Moieties with Herbicidal Activity

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**Abstract:** To discover novel herbicidal compounds with favorable activity, a range of phenylpyridine-moiety-containing  $\alpha$ -trifluorothioanisole derivatives were designed, synthesized, and identified via NMR and HRMS. Preliminary screening of greenhouse-based herbicidal activity revealed that compound **5a** exhibited >85% inhibitory activity against broadleaf weeds *Amaranthus retroflexus*, *Abutilon theophrasti*, and *Eclipta prostrate* at 37.5 g a.i./hm<sup>2</sup>, which was slightly superior to that of fomesafen. The current study suggests that compound **5a** could be further optimized as an herbicide candidate to control various broadleaf weeds.

**Keywords:** synthesis;  $\alpha$ -trifluorothioanisole derivatives; phenylpyridine; herbicidal activity



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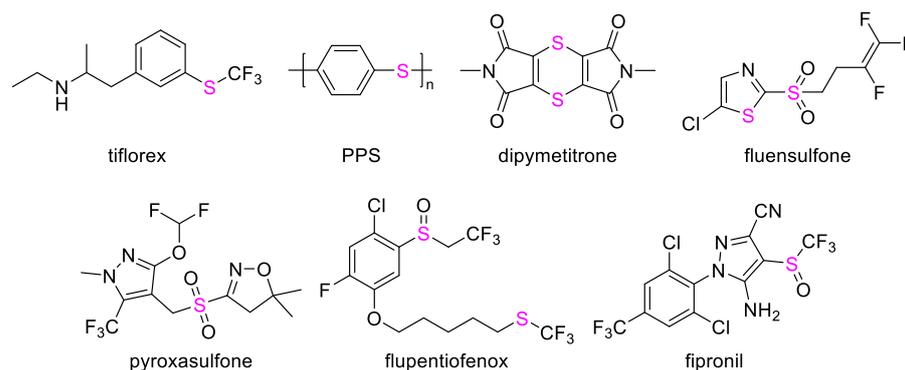
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## 1. Introduction

Organosulfur compounds are widely present in animals and plants due to their physiological activities, such as diallyl disulfide compounds in garlic, isothiocyanate compounds in cruciferous vegetables and some fruits, and sulfur-containing amino acids and vitamins. These molecules play a vital role in maintaining the metabolism of organisms and various life activities. Therefore, many researchers have conducted in-depth research on these compounds and found that some molecules containing thioheterocycles, thioureas, sulfonamides, thioethers, sulfoxides, sulfones, and other structures show biological activity [1–8]. For instance, Wang et al. [9] reported a class of sulfonylurea compounds with high herbicidal activities against *Echinochloa crusgalli* and *Digitaria sanguinalis* for pre- and post-emergence treatment and noted that they were safe for peanut as post-emergence treatment. A range of 5-substituted sulfonylurea derivatives discovered by Li et al. [10] showed good herbicidal activities against *Amaranthus retroflexus* and *Brassica campestris* for pre-emergence treatment. It is worth noting that compounds containing sulfide, sulfoxide, and sulfone structures have been widely used in materials [11,12], medicine [13–15], and pesticides [16–22] in the past few decades (Figure 1). The pre-emergence herbicide pyroxasulfone, discovered by Todoroki et al. [23], exhibited excellent herbicidal activity and crop safety, and it is currently used in the field.

Substituted 2-phenylpyridines discovered by Schaefer et al. exhibited good inhibition activity against weeds [24,25]. Substituted 3-(pyridin-2-yl)benzenesulfonamide derivatives disclosed by Liu et al. showed excellent inhibitory activity against a variety of weeds [26–28]. Du et al. also reported that a range of kresoxim-methyl derivatives containing phenylpyridine moieties exhibited higher inhibitory activities against broadleaf weeds than mesotrione [29,30].

Herein, 18 novel  $\alpha$ -trifluorothioanisole derivatives were synthesized through introducing phenylpyridine moieties into  $\alpha$ -trifluorothioanisole. The inhibitory activities of the resultant compounds against broadleaf and grass weeds were determined.

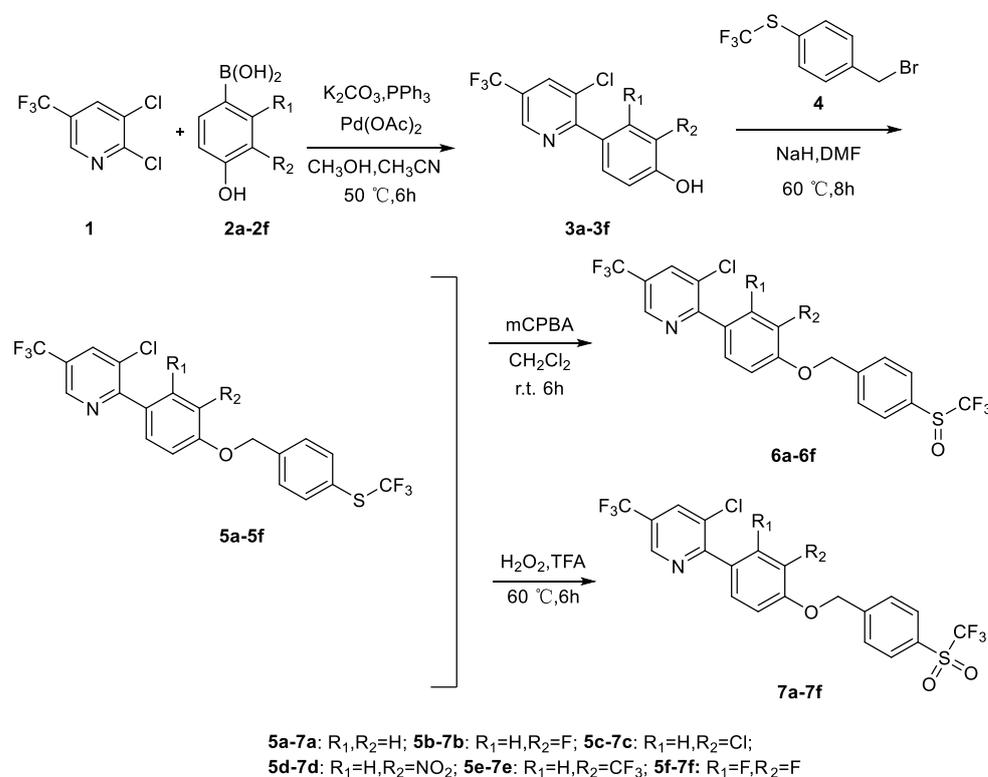


**Figure 1.** Structures of reported sulfur-containing compounds.

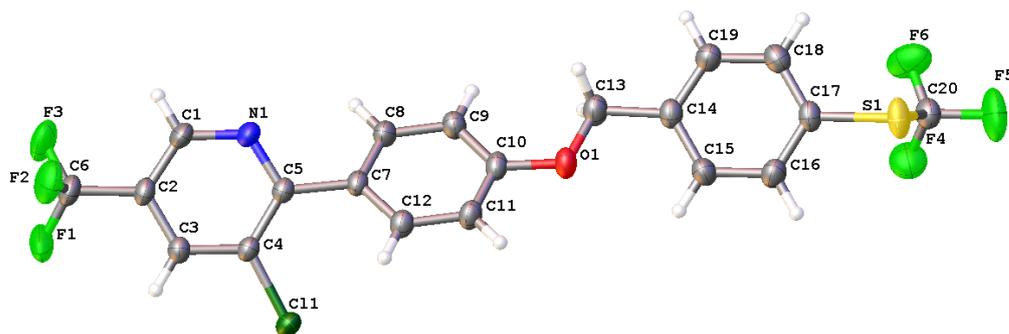
## 2. Results and Discussions

### 2.1. Chemistry

The synthesis procedures for the target compounds used in this work are outlined in Scheme 1. Intermediates **3a–3f** were obtained according to the literature [31]. The target compounds **5a–5f** were prepared via nucleophilic substitution reaction from intermediates **3a–3f** and compound **4**. In addition, compounds **5a–5f** were oxidized to yield compounds **6a–6f** and **7a–7f** using 3-chloroperbenzoic acid or hydrogen peroxide as oxidants according to previously disclosed methods [32,33]. After synthesis, all target compounds were characterized via HRMS and NMR. X-ray diffraction crystallography was further used to confirm the structure of compound **5a** (Figure 2). The crystal data of compound **5a** and the NMR spectrum of all target compounds are shown in the Supplementary Materials.



**Scheme 1.** Overview synthesis methods of  $\alpha$ -trifluorothioanisole derivatives.



**Figure 2.** The X-ray crystal structure of compound 5a.

## 2.2. Greenhouse Herbicidal Activity Assays

As can be seen from Table 1, some target compounds exhibited excellent inhibitory activity against the tested dicotyledonous weeds but proved ineffective against monocotyledonous weeds. Of these, at 150 g a.i./hm<sup>2</sup>, compounds **5a**, **5f**, **6b**, and **7a** exhibited >80% inhibitory activity when used for the post-emergence treatment of the broadleaf weeds *AT*, *AR*, and *EP*, while compounds **6f** and **7f** exhibited >80% activity against *AT* and *AR*. Furthermore, compound **5a** also effectively suppressed the growth of *DS* and *SV*, which was slightly better than the positive control fomesafen. Other compounds exhibited varying levels of general herbicidal activity. Further analysis revealed that compound **5a** exhibited >85% inhibition against *AT*, *AR*, and *EP* for post-emergence treatment at 37.5 g a.i./hm<sup>2</sup>, which was slightly superior to the inhibition ability of fomesafen, whereas compound **5f** also exhibited >70% inhibition against these three weeds.

**Table 1.** The structures and herbicidal activities of  $\alpha$ -trifluoroanisole derivatives for post-emergence treatment in a greenhouse assay setting.

| Compound  | Chemical Structure |                 | Dosage/<br>(g a.i./hm <sup>2</sup> ) | Weed <sup>a</sup> |        |        |         |         |         |
|-----------|--------------------|-----------------|--------------------------------------|-------------------|--------|--------|---------|---------|---------|
|           | R <sub>1</sub>     | R <sub>2</sub>  |                                      | EC                | DS     | SV     | AT      | AR      | EP      |
| 5a        | H                  | H               | 150                                  | 10 ± 2            | 90 ± 5 | 80 ± 3 | 100 ± 0 | 100 ± 0 | 90 ± 2  |
|           |                    |                 | 75                                   | 0 ± 0             | 20 ± 3 | 0 ± 0  | 95 ± 1  | 100 ± 0 | 90 ± 5  |
|           |                    |                 | 37.5                                 | 0 ± 0             | 0 ± 0  | 0 ± 0  | 90 ± 3  | 100 ± 0 | 85 ± 4  |
| 5b        | H                  | F               | 150                                  | 0 ± 0             | 50 ± 4 | 30 ± 5 | 60 ± 2  | 70 ± 5  | 85 ± 1  |
| 5c        | H                  | Cl              | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 0 ± 0   | 100 ± 0 | 40 ± 5  |
| 5d        | H                  | NO <sub>2</sub> | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 20 ± 4  | 20 ± 2  | 100 ± 0 |
| 5e        | H                  | CF <sub>3</sub> | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 0 ± 0   | 20 ± 3  | 100 ± 0 |
|           |                    |                 | 150                                  | 20 ± 4            | 75 ± 2 | 60 ± 5 | 100 ± 0 | 95 ± 1  | 100 ± 0 |
| 5f        | F                  | F               | 75                                   | 0 ± 0             | 0 ± 0  | 0 ± 0  | 100 ± 0 | 100 ± 0 | 95 ± 1  |
|           |                    |                 | 37.5                                 | 0 ± 0             | 0 ± 0  | 0 ± 0  | 70 ± 5  | 90 ± 2  | 80 ± 4  |
| 6a        | H                  | H               | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 30 ± 1  | 90 ± 4  | 30 ± 3  |
| 6b        | H                  | F               | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 100 ± 0 | 100 ± 0 | 80 ± 5  |
| 6c        | H                  | Cl              | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 0 ± 0   | 0 ± 0   | 0 ± 0   |
| 6d        | H                  | NO <sub>2</sub> | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 0 ± 0   | 80 ± 5  | 0 ± 0   |
| 6e        | H                  | CF <sub>3</sub> | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 0 ± 0   | 80 ± 2  | 0 ± 0   |
| 6f        | F                  | F               | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 90 ± 3  | 80 ± 4  | 30 ± 3  |
| 7a        | H                  | H               | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 90 ± 4  | 85 ± 3  | 80 ± 1  |
| 7b        | H                  | F               | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 20 ± 2  | 95 ± 1  | 70 ± 5  |
| 7c        | H                  | Cl              | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 0 ± 0   | 30 ± 3  | 0 ± 0   |
| 7d        | H                  | NO <sub>2</sub> | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 0 ± 0   | 80 ± 4  | 0 ± 0   |
| 7e        | H                  | CF <sub>3</sub> | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 0 ± 0   | 60 ± 2  | 0 ± 0   |
| 7f        | F                  | F               | 150                                  | 0 ± 0             | 0 ± 0  | 0 ± 0  | 100 ± 0 | 90 ± 5  | 70 ± 2  |
|           |                    |                 | 150                                  | 68 ± 4            | 76 ± 3 | 78 ± 5 | 98 ± 2  | 100 ± 0 | 76 ± 5  |
|           |                    |                 | 75                                   | 63 ± 1            | 69 ± 5 | 67 ± 3 | 92 ± 2  | 95 ± 3  | 67 ± 4  |
| fomesafen | /                  | /               | 37.5                                 | 47 ± 3            | 44 ± 2 | 56 ± 4 | 90 ± 1  | 87 ± 5  | 55 ± 2  |

<sup>a</sup> EC, *Echinochloa crusgalli*; DS, *Digitaria sanguinalis*; SV, *Setaria viridis*; AT, *Abutilon theophrasti*; AR, *Amaranthus retroflexus*; EP, *Eclipta prostrate*.

From Table 1, we can see that the herbicidal activities of compound 5 were slightly better than those of compounds 6 and 7. According to the SAR of compound 5 in the field of herbicidal activity, when R<sub>1</sub> and R<sub>2</sub> were both substituted by hydrogen atoms (5a), the activities of compound 5 against three broadleaf weeds were better than those of other compounds. For compound 6, when R<sub>1</sub> was substituted by a hydrogen atom and R<sub>2</sub> was substituted by a fluorine atom (6b), the herbicidal activities of compound 6 were optimal. For compound 7, the optimal herbicidal activities were observed when R<sub>1</sub> and R<sub>2</sub> were substituted by either hydrogen atoms or fluorine atoms (7a, 7f).

### 3. Materials and Methods

#### 3.1. Instrumentation

All reagents and other materials were purchased from commercial sources and used without additional purification unless otherwise noted. A B-545 melting point instrument was used to determine melting point without calibration. A Bruker AV-400 or AV-500 MHz spectrometer was used to generate NMR spectra with DMSO-d<sub>6</sub> or CDCl<sub>3</sub> serving as solvents. An Agilent 6545 Q-TOF LCMS spectrometer was used for mass spectrometry. A Bruker D8 Venture diffractometer was utilized to collect crystallographic data.

#### 3.2. Synthesis

The synthesis methods of the title compounds are outlined in Scheme 1.

##### 3.2.1. General Approach to the Synthesis of Compounds 3a–3f

2,3-Dichloro-5-(trifluoromethyl)pyridine 1 (5 mmol), triphenylphosphorus (0.5 mmol), K<sub>2</sub>CO<sub>3</sub> (10 mmol), substituted p-hydroxybenzeneboronic acid 2a–2f (5.5 mmol), and palladium(II) acetate (0.25 mmol) were mixed and stirred for 6 h with CH<sub>3</sub>CN (10 mL) and CH<sub>3</sub>OH (5 mL) at 50 °C under N<sub>2</sub>. Thereafter, the mixture was extracted using ethyl acetate (30 mL × 3), rinsed using brine, and concentrated. The remaining residue was then recrystallized using ethanol and water as solvents at 70 °C to obtain compounds 3a–3f [31].

##### 3.2.2. General Approach to the Synthesis of Compounds 5a–5f

Substituted phenylpyridines 3a–3f (2 mmol), *N,N*-dimethylformamide (10 mL), and NaH (3 mmol, 0.12 g) were mixed and stirred at 20 °C for 30 min under N<sub>2</sub>. Next, 4-trifluoromethylthiobenzyl bromide (2.4 mmol) was added and stirred for 8 h at 60 °C. The mixture was extracted thrice using ethyl acetate (30 mL × 3), rinsed using brine, and concentrated. Residues were then purified via silica gel column chromatography using ethyl acetate (EA) and petroleum ether (PE) (V<sub>EA</sub>:V<sub>PE</sub>=1:15) to obtain compounds 5a–5f [31].

##### 3.2.3. General Approach to the Synthesis of Compounds 6a–6f

Compounds 5a–5f (0.5 mmol), 85% 3-chloroperbenzoic acid (0.5 mmol), and dichloromethane (10 mL) were mixed and stirred at 20 °C for 6 h. The mixture was evaporated to remove the solvent. Residues were then purified via silica gel column chromatography using ethyl acetate (EA) and petroleum ether (PE) (V<sub>EA</sub>:V<sub>PE</sub>=1:7) to obtain compounds 6a–6f [32].

##### 3.2.4. General Approach to the Synthesis of Compounds 7a–7f

Compounds 5a–5f (0.4 mmol), 30% hydrogen peroxide (1.6 mmol), and trifluoroacetic acid (2 mL) were mixed and stirred at 60 °C for 6 h. Thereafter, the mixture was made alkaline using a sodium hydroxide solution, extracted thrice using ethyl acetate (30 mL × 3), rinsed using Na<sub>2</sub>SO<sub>3</sub>, and concentrated. Residues were then purified via silica gel column chromatography using ethyl acetate (EA) and petroleum ether (PE) (V<sub>EA</sub>:V<sub>PE</sub>=1:10) to obtain compounds 7a–7f [33].

*3-chloro-5-(trifluoromethyl)-2-(4-((4-((trifluoromethyl)thio)benzyl)oxy)phenyl)pyridine (5a)*: White solid, yield 78.8%, m.p. 93.2–95.4 °C. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ: 8.99 (s, 1H), 8.51 (s, 1H), 7.76 (dd, J = 8.4, 3.4 Hz, 4H), 7.64 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H), 5.29 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ: 159.17, 158.79, 144.27 (q, J = 4.0 Hz), 140.63,

136.27, 135.71 (q, J = 3.1 Hz), 131.02, 129.57 (q, J = 308.4 Hz), 129.37, 129.17, 128.82, 124.39 (q, J = 33.0 Hz), 122.86 (q, J = 273.4 Hz), 122.29 (q, J = 2.0 Hz), 114.37, 68.43. HRMS (ESI): calculated for C<sub>20</sub>H<sub>13</sub>ClF<sub>6</sub>NOS [M+H]<sup>+</sup> 464.0305, 466.0276, found 464.0308, 466.0277.

*3-chloro-2-(3-fluoro-4-((4-(trifluoromethyl)thio)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (5b)*: White solid, yield 85.9%, m.p. 63.5–65.0 °C. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ: 9.01 (d, J = 0.9 Hz, 1H), 8.55 (s, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.70–7.64 (m, 3H), 7.61 (d, J = 8.6 Hz, 1H), 7.41 (t, J = 8.7 Hz, 1H), 5.38 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ: 157.57, 150.96 (d, J = 244.7 Hz), 147.15 (d, J = 10.6 Hz), 144.33 (q, J = 3.9 Hz), 140.06, 136.34, 135.89 (q, J = 3.3 Hz), 129.79 (d, J = 6.7 Hz), 129.58 (q, J = 308.3 Hz), 129.42, 128.92, 126.27 (d, J = 3.2 Hz), 124.85 (q, J = 33.1 Hz), 122.80 (q, J = 273.4 Hz), 122.59 (q, J = 1.9 Hz), 117.22 (d, J = 20.0 Hz), 114.71, 69.36. HRMS (ESI): calculated for C<sub>20</sub>H<sub>10</sub>ClF<sub>7</sub>NOS [M–H]<sup>−</sup> 480.0065, 482.0036, found 480.0064, 482.0043.

*3-chloro-2-(3-chloro-4-((4-(trifluoromethyl)thio)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (5c)*: White solid, yield 94.0%, m.p. 82.0–83.5 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.02 (s, 1H), 8.57 (s, 1H), 7.88 (s, 1H), 7.78 (t, J = 10.5 Hz, 3H), 7.67 (d, J = 7.2 Hz, 2H), 7.40 (d, J = 8.3 Hz, 1H), 5.41 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 157.49, 154.37, 144.38 (q, J = 3.9 Hz), 140.14, 136.38, 135.89 (q, J = 3.1 Hz), 130.94, 130.25, 129.68, 129.60 (q, J = 309.1 Hz), 129.45, 128.62, 124.87 (q, J = 33.4 Hz), 122.81 (q, J = 274.1 Hz), 122.48, 121.21, 113.62, 69.28. HRMS (ESI): calculated for C<sub>20</sub>H<sub>10</sub>Cl<sub>2</sub>F<sub>6</sub>NOS [M–H]<sup>−</sup> 495.9770, 497.9740, found 495.9767, 497.9740.

*3-chloro-2-(3-nitro-4-((4-(trifluoromethyl)thio)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (5d)*: White solid, yield 86.5%, m.p. 114.5–116.5 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.06 (s, 1H), 8.63 (s, 1H), 8.35 (d, J = 2.2 Hz, 1H), 8.11 (dd, J = 8.8, 2.2 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 7.61 (d, J = 8.9 Hz, 1H), 5.51 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 156.76, 151.71, 144.63 (q, J = 3.6 Hz), 139.64, 138.99, 136.51, 136.12 (q, J = 3.5 Hz), 135.49, 129.74, 129.66 (q, J = 308.8 Hz), 129.27, 128.63, 126.42, 125.33 (q, J = 33.3 Hz), 122.83 (q, J = 274.1 Hz), 122.66 (q, J = 1.9 Hz), 115.28, 69.85. HRMS (ESI): calculated for C<sub>20</sub>H<sub>10</sub>ClF<sub>6</sub>N<sub>2</sub>O<sub>3</sub>S [M–H]<sup>−</sup> 507.0010, 508.9981, found 507.0010, 508.9983.

*3-chloro-5-(trifluoromethyl)-2-(3-(trifluoromethyl)-4-((4-(trifluoromethyl)thio)benzyl)oxy)phenyl)pyridine (5e)*: White solid, yield 93.4%, m.p. 111.6–113.5 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.07 (s, 1H), 8.62 (s, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.10 (s, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.7 Hz, 1H), 5.52 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 157.42, 156.64, 144.47 (q, J = 3.6 Hz), 139.94, 136.39, 135.93 (q, J = 3.5 Hz), 135.35, 129.60 (q, J = 308.7 Hz), 129.51, 129.06, 128.33, 128.15 (q, J = 5.1 Hz), 125.02 (q, J = 33.3 Hz), 123.45 (q, J = 273.6 Hz), 122.80 (q, J = 274.1 Hz), 122.48 (q, J = 1.8 Hz), 117.04 (q, J = 30.7 Hz), 113.76, 69.21. HRMS (ESI): calculated for C<sub>21</sub>H<sub>10</sub>ClF<sub>9</sub>NOS [M–H]<sup>−</sup> 530.0033, 532.0004, found 530.0031, 532.0010.

*3-chloro-2-(2,3-difluoro-4-((4-(trifluoromethyl)thio)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (5f)*: White solid, yield 80.2%, m.p. 79.5–82.0 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.84 (d, J = 1.1 Hz, 1H), 8.06 (d, J = 1.5 Hz, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.19–7.15 (m, 1H), 6.92–6.89 (m, 1H), 5.26 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 155.42, 149.29 (dd, J = 252.8, 11.0 Hz), 149.28 (dd, J = 8.2, 2.8 Hz), 144.45 (q, J = 3.6 Hz), 141.76 (dd, J = 249.8, 14.4 Hz), 139.03, 136.78, 134.93 (q, J = 3.2 Hz), 132.36, 129.68 (q, J = 308.6 Hz), 128.26, 127.20 (q, J = 33.9 Hz), 124.84 (t, J = 3.6 Hz), 124.65, 122.74 (q, J = 273.6 Hz), 120.22 (d, J = 12.2 Hz), 110.36 (q, J = 2.6 Hz), 70.97. HRMS (ESI): calculated for C<sub>20</sub>H<sub>9</sub>ClF<sub>8</sub>NOS [M–H]<sup>−</sup> 497.9971, 499.9942, found 497.9969, 499.9949.

*3-chloro-5-(trifluoromethyl)-2-(4-((4-(trifluoromethyl)sulfinyl)benzyl)oxy)phenyl)pyridine (6a)*: White solid, yield 41.7%, m.p. 123.3–124.7 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.00 (s, 1H), 8.53 (s, 1H), 7.94 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 5.35 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 159.17, 158.87, 144.40 (q, J = 3.7 Hz), 143.20, 135.85 (q, J = 3.4 Hz), 134.70 (q, J = 1.4 Hz), 131.14, 129.50, 129.28, 128.67, 126.26, 124.83 (q, J = 337.5 Hz), 124.47 (q, J = 32.9 Hz), 122.96 (q, J = 273.7 Hz), 114.45, 68.47. HRMS (ESI): calculated for C<sub>20</sub>H<sub>13</sub>ClF<sub>6</sub>NO<sub>2</sub>S [M+H]<sup>+</sup> 480.0254, 482.0225, found 480.0254, 482.0227.

*3-chloro-2-(3-fluoro-4-((4-((trifluoromethyl)sulfinyl)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (6b)*: White solid, yield 80.3%, m.p. 113.0–115.0 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.02 (s, 1H), 8.57 (s, 1H), 7.97 (d, J = 7.8 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.69 (dd, J = 12.2, 1.5 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.43 (t, J = 8.6 Hz, 1H), 5.45 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 157.59, 150.96 (d, J = 245.2 Hz), 147.10 (d, J = 10.4 Hz), 144.36 (q, J = 3.7 Hz), 142.56, 135.91 (q, J = 3.2 Hz), 134.94 (q, J = 1.0 Hz), 129.88 (d, J = 6.6 Hz), 129.44, 128.68, 126.31, 126.25, 124.86 (q, J = 33.1 Hz), 124.77 (q, J = 337.7 Hz), 122.81 (q, J = 273.9 Hz), 117.26 (d, J = 19.9 Hz), 114.75, 69.38. HRMS (ESI): calculated for C<sub>20</sub>H<sub>10</sub>ClF<sub>7</sub>NO<sub>2</sub>S [M–H]<sup>−</sup> 496.0014, 497.9985, found 496.0015, 497.9993.

*3-chloro-2-(3-chloro-4-((4-((trifluoromethyl)sulfinyl)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (6c)*: White solid, yield 50.1%, m.p. 119.3–120.3 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.01 (s, 1H), 8.58 (s, 1H), 7.96 (d, J = 8.1 Hz, 2H), 7.87–7.83 (m, 3H), 7.76 (dd, J = 8.6, 1.9 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 5.46 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 157.55, 154.35, 144.47 (q, J = 3.9 Hz), 142.68, 135.98 (q, J = 3.3 Hz), 134.86 (q, J = 1.0 Hz), 131.02, 130.37, 129.78, 129.53, 128.44, 126.33, 124.93 (q, J = 33.2 Hz), 124.83 (q, J = 337.6 Hz), 122.88 (q, J = 274.1 Hz), 121.23, 113.67, 69.30. HRMS (ESI): calculated for C<sub>20</sub>H<sub>10</sub>Cl<sub>2</sub>F<sub>6</sub>NO<sub>2</sub>S [M–H]<sup>−</sup> 511.9719, 513.9689, found 511.9718, 513.9692.

*3-chloro-2-(3-nitro-4-((4-((trifluoromethyl)sulfinyl)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (6d)*: Yellow solid, yield 96.2%, m.p. 116.0–118.0 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.09 (s, 1H), 8.66 (s, 1H), 8.41 (d, J = 2.1 Hz, 1H), 8.17 (dd, J = 8.8, 2.1 Hz, 1H), 8.01 (d, J = 8.1 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.9 Hz, 1H), 5.61 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 156.67, 151.67, 144.54 (q, J = 3.6 Hz), 142.05, 138.94, 136.03 (q, J = 3.5 Hz), 135.44, 134.97, 129.67, 129.31, 128.30, 126.38, 126.28, 125.30 (q, J = 33.3 Hz), 124.77 (q, J = 337.8 Hz), 122.76 (q, J = 274.1 Hz), 115.28, 69.86. HRMS (ESI): calculated for C<sub>20</sub>H<sub>10</sub>ClF<sub>6</sub>N<sub>2</sub>O<sub>4</sub>S [M–H]<sup>−</sup> 522.9959, 524.9930, found 522.9961, 524.9921.

*3-chloro-5-(trifluoromethyl)-2-(3-(trifluoromethyl)-4-((4-((trifluoromethyl)sulfinyl)benzyl)oxy)phenyl)pyridine (6e)*: White solid, yield 51.1%, m.p. 117.9–120.1 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.05 (s, 1H), 8.60 (s, 1H), 8.09 (d, J = 9.8 Hz, 2H), 7.98 (s, 2H), 7.82 (d, J = 5.1 Hz, 2H), 7.54 (d, J = 6.4 Hz, 1H), 5.55 (s, 2H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ: 157.40, 156.58, 144.48 (q, J = 2.7 Hz), 142.44, 135.95, 135.37, 134.86 (q, J = 1.5 Hz), 129.53, 129.15, 128.20, 128.09, 126.29, 125.04 (q, J = 33.2 Hz), 124.77 (q, J = 339.3 Hz), 123.44 (q, J = 273.4 Hz), 122.80 (q, J = 274.3 Hz), 117.06 (q, J = 30.8 Hz), 113.78, 69.23. HRMS (ESI): calculated for C<sub>21</sub>H<sub>10</sub>ClF<sub>9</sub>NO<sub>2</sub>S [M–H]<sup>−</sup> 545.9983, 547.9953, found 545.9985, 547.9960.

*3-chloro-2-(2,3-difluoro-4-((4-((trifluoromethyl)sulfinyl)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (6f)*: White solid, yield 48.4%, m.p. 122.4–24.4 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 8.79–8.75 (m, 1H), 7.99 (d, J = 1.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.5 Hz, 2H), 7.13–7.10 (m, 1H), 6.86–6.83 (m, 1H), 5.25 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 154.15, 148.13 (dd, J = 253.0, 11.6 Hz), 147.93 (dd, J = 8.1, 3.1 Hz), 143.30 (q, J = 3.9 Hz), 140.90, 140.59 (dd, J = 250.4, 14.4 Hz), 134.73 (q, J = 1.5 Hz), 133.79 (q, J = 3.5 Hz), 131.19, 127.08, 126.08 (q, J = 33.9 Hz), 125.42, 123.76 (t, J = 4.0 Hz), 123.66 (q, J = 335.8 Hz), 121.56 (q, J = 273.6 Hz), 119.28 (d, J = 12.4 Hz), 109.16 (d, J = 3.1 Hz), 69.60. HRMS (ESI): calculated for C<sub>20</sub>H<sub>9</sub>ClF<sub>8</sub>NO<sub>2</sub>S [M–H]<sup>−</sup> 513.9920, 515.9891, found 513.9916, 515.9887.

*3-chloro-5-(trifluoromethyl)-2-(4-((4-((trifluoromethyl)sulfonyl)benzyl)oxy)phenyl)pyridine (7a)*: White solid, yield 40.1%, m.p. 132.7–134.8 °C. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ: 9.02–8.97 (m, 1H), 8.53 (d, J = 1.5 Hz, 1H), 8.19 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.78–7.75 (m, 2H), 7.21–7.18 (m, 2H), 5.45 (s, 2H). <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ: 158.92, 158.78, 147.74, 144.32 (q, J = 3.8 Hz), 135.76 (q, J = 3.5 Hz), 131.12, 131.03, 129.65, 129.23, 128.92, 128.58, 124.46 (q, J = 32.9 Hz), 122.88 (q, J = 273.3 Hz), 119.41 (q, J = 326.7 Hz), 114.42, 68.10. HRMS (ESI): calculated for C<sub>20</sub>H<sub>11</sub>ClF<sub>6</sub>NO<sub>3</sub>S [M–H]<sup>−</sup> 494.0058, 496.0028, found 494.0061, 496.0035.

*3-chloro-2-(3-fluoro-4-((4-((trifluoromethyl)sulfonyl)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (7b)*: White solid, yield 48.4%, m.p. 111.8–114.0 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.02 (s, 1H), 8.58 (s, 1H), 8.23 (d, J = 8.2 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.71 (dd, J = 12.3, 1.9 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 7.41 (t, J = 8.7 Hz, 1H), 5.54 (s, 2H). <sup>13</sup>C NMR (101 MHz,

DMSO- $d_6$ )  $\delta$ : 157.57, 150.93 (d,  $J = 245.4$  Hz), 147.12, 146.91 (d,  $J = 10.5$  Hz), 144.37 (q,  $J = 3.9$  Hz), 135.92 (q,  $J = 3.4$  Hz), 131.11, 130.09 (d,  $J = 6.8$  Hz), 129.47, 128.96, 128.79, 126.34 (d,  $J = 3.2$  Hz), 124.90 (q,  $J = 33.3$  Hz), 122.81 (q,  $J = 274.0$  Hz), 119.41 (q,  $J = 327.6$  Hz), 117.33 (d,  $J = 19.8$  Hz), 114.76, 68.99. HRMS (ESI): calculated for  $C_{20}H_{10}ClF_7NO_3S [M-H]^-$  511.9964, 513.9934, found 511.9968, 513.9937.

*3-chloro-2-(3-chloro-4-((4-((trifluoromethyl)sulfonyl)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (7c)*: White solid, yield 68.9%, m.p. 142.6–144.8 °C.  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$ : 9.04–9.00 (m, 1H), 8.57 (d,  $J = 1.5$  Hz, 1H), 8.24 (d,  $J = 8.4$  Hz, 2H), 7.97 (d,  $J = 8.5$  Hz, 2H), 7.90 (d,  $J = 2.2$  Hz, 1H), 7.78 (dd,  $J = 8.6, 2.2$  Hz, 1H), 7.40 (d,  $J = 8.7$  Hz, 1H), 5.57 (s, 2H).  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$ : 157.43, 154.12, 147.14, 144.36 (d,  $J = 3.7$  Hz), 135.86 (d,  $J = 3.3$  Hz), 131.07, 130.97, 130.50, 129.71, 129.45, 128.74, 128.66, 124.91 (q,  $J = 33.3$  Hz), 122.78 (q,  $J = 273.4$  Hz), 121.23, 119.39 (q,  $J = 326.9$  Hz), 113.64, 68.94. HRMS (ESI): calculated for  $C_{20}H_{10}Cl_2F_6NO_3S [M-H]^-$  527.9668, 529.9639, found 527.9664, 529.9640.

*3-chloro-2-(3-nitro-4-((4-((trifluoromethyl)sulfonyl)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (7d)*: Yellow solid, yield 24.8%, m.p. 129.1–131.6 °C.  $^1H$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$ : 9.06 (d,  $J = 0.9$  Hz, 1H), 8.62 (d,  $J = 1.4$  Hz, 1H), 8.40 (d,  $J = 2.3$  Hz, 1H), 8.25 (d,  $J = 8.4$  Hz, 2H), 8.15 (dd,  $J = 8.8, 2.3$  Hz, 1H), 7.95 (d,  $J = 8.4$  Hz, 2H), 7.63 (d,  $J = 8.9$  Hz, 1H), 5.67 (s, 2H).  $^{13}C$  NMR (126 MHz, DMSO- $d_6$ )  $\delta$ : 156.61, 151.50, 146.52, 144.51 (q,  $J = 3.8$  Hz), 138.85, 136.00 (q,  $J = 3.6$  Hz), 135.50, 131.09, 129.65, 129.47, 128.86, 128.61, 126.43, 125.30 (q,  $J = 33.3$  Hz), 122.72 (q,  $J = 273.5$  Hz), 119.38 (q,  $J = 326.8$  Hz), 115.26, 69.51. HRMS (ESI): calculated for  $C_{20}H_{10}ClF_6N_2O_5S [M-H]^-$  538.9909, 540.9879, found 538.9905, 540.9882.

*3-chloro-5-(trifluoromethyl)-2-(3-(trifluoromethyl)-4-((4-((trifluoromethyl)sulfonyl)benzyl)oxy)phenyl)pyridine (7e)*: White solid, yield 35.2%, m.p. 111.2–113.4 °C.  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.05 (s, 1H), 8.61 (s, 1H), 8.26 (d,  $J = 8.1$  Hz, 2H), 8.13 (d,  $J = 9.0$  Hz, 1H), 8.09 (s, 1H), 7.93 (d,  $J = 8.2$  Hz, 2H), 7.53 (d,  $J = 8.7$  Hz, 1H), 5.65 (s, 2H).  $^{13}C$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 157.39, 156.37, 146.94, 144.49 (q,  $J = 3.6$  Hz), 135.95 (q,  $J = 3.4$  Hz), 135.44, 131.17, 129.55, 129.34, 128.77, 128.46, 128.22 (q,  $J = 5.3$  Hz), 125.07 (q,  $J = 33.0$  Hz), 123.44 (q,  $J = 273.5$  Hz), 122.80 (q,  $J = 274.1$  Hz), 119.41 (q,  $J = 327.3$  Hz), 117.04 (q,  $J = 30.7$  Hz), 113.77, 68.90. HRMS (ESI): calculated for  $C_{21}H_{10}ClF_9NO_3S [M-H]^-$  561.9932, 563.9902, found 561.9935, 563.9913.

*3-chloro-2-(2,3-difluoro-4-((4-((trifluoromethyl)sulfonyl)benzyl)oxy)phenyl)-5-(trifluoromethyl)pyridine (7f)*: White solid, yield 37.7%, m.p. 102.8–104.8 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 8.77 (d,  $J = 1.1$  Hz, 1H), 8.02 (d,  $J = 8.3$  Hz, 2H), 7.99 (d,  $J = 1.6$  Hz, 1H), 7.72 (d,  $J = 8.4$  Hz, 2H), 7.15–7.11 (m, 1H), 6.87–6.82 (m, 1H), 5.29 (s, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$ : 155.22, 149.30 (dd,  $J = 253.0, 11.3$  Hz), 148.83 (dd,  $J = 8.2, 3.1$  Hz), 145.53, 144.47 (q,  $J = 3.8$  Hz), 141.75 (dd,  $J = 250.2, 14.3$  Hz), 134.96 (q,  $J = 3.5$  Hz), 132.35, 131.42, 131.27, 128.14, 127.29 (q,  $J = 33.9$  Hz), 124.99 (t,  $J = 3.9$  Hz), 122.70 (q,  $J = 273.6$  Hz), 119.92 (q,  $J = 326.4$  Hz), 120.71 (d,  $J = 12.5$  Hz), 110.29 (d,  $J = 3.1$  Hz), 70.38. HRMS (ESI): calculated for  $C_{20}H_9ClF_8NO_3S [M-H]^-$  529.9869, 531.9840, found 529.9869, 531.9824.

### 3.3. Herbicidal Activity Test

Levels of herbicidal activity for compounds **5a–5f**, **6a–6f**, and **7a–7f** against the monocotyledonous weeds *Digitaria sanguinalis* (DS), *Echinochloa crusgalli* (EC), and *Setaria viridis* (SV), and the dicotyledonous weeds *Abutilon theophrasti* (AT), *Amaranthus retroflexus* (AR), and *Eclipta prostrata* (EP) were determined using previously disclosed methods [29–31,34].

All target compounds were dissolved in *N,N*-dimethylformamide, diluted to an appropriate dose with distilled water containing 0.1% Tween-80 emulsifier, and used for seedlings at the three-leaf stage with three replicates. Seedlings treated with *N,N*-dimethylformamide and distilled water containing 0.1% Tween-80 emulsifier served as blank controls, with fomesafen-treated seedlings serving as positive controls. The application rates were 150, 75, and 37.5 g a.i./ha. Herbicidal activity was assessed visually after a 20-day period, with the results being listed in Table 1.

#### 4. Conclusions

In conclusion, 18 novel  $\alpha$ -trifluorothioanisole derivatives containing phenylpyridine moieties were prepared as candidate herbicides. The preliminary herbicidal activity assay results show that some target compounds exhibited good herbicidal activities against broadleaf weeds at 150 g a.i./hm<sup>2</sup>. Among these, compound **5a** possessed excellent activity (>85%) against AT, AR, and EP at 37.5 g a.i./hm<sup>2</sup>, which was slightly superior to fomesafen. Furthermore, compound **5f** possessed good activity (>70%) against AT, AR, and EP at 37.5 g a.i./hm<sup>2</sup>, which was equivalent to that of fomesafen. Thus, compound **5a** may be a lead compound for further structural optimization.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules27185879/s1>, Table S1: Crystal data and structure refinement parameters of compound **5a**; Table S2: Bond angles of compound **5a**; Table S3: Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) of the nonhydrogen atoms; Table S4: Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ); Table S5: Bond lengths of compound **5a**; Figure S1–S36: <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of target compounds **5a–5f**, **6a–6f**, and **7a–7f**.

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