

# A new synthetic route of 4,4'-hexafluoroisopropylidene-2,2-bis-(phthalic acid anhydride) and characterization of 4,4'-hexafluoroisopropylidene-2,2-bis-(phthalic acid anhydride)-containing polyimides

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## Abstract

The title product 4,4'-hexafluoroisopropylidene-2,2-bis-(phthalic acid anhydride) was prepared from hexafluoroacetone and *o*-xylene as the starting materials by condensation, oxidation and dehydration three-step reaction sequence. It reacted with diamines in DMF or xylene to give polyimides by condensation polymerization. Thermal and viscosity analyses show that these polyimides have lower molecular weight but excellent thermal stability.

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**Keywords:** 4,4'-Hexafluoroisopropylidene-2,2-bis-(phthalic acid anhydride); Diamines; Condensation; Polyimides oligomers

## 1. Introduction

There is a growing demand for high strength high dielectric constant and thermal stability polymeric materials in civil and military applications. Polyimide oligomers offer considerable promise as planarizing coatings in the electronic industry. An acetylene-terminated polyimide resin has been investigated for this purpose [1]. However, most commercially available polymers lack structural integrity and thermal stability. The incorporation of 4,4'-hexafluoroisopropylidenediphthalimide group (6-FDA) into polymer precursors is known [2,3] to provide marked improvements in flexibility and roughness of their polymers along with a lowering of the glass transition temperature ( $T_g$ ). Furthermore, these 6-FDA groups prohibit extensive conjugation of the aromatic moieties, thereby providing good electric insulation and resistance to photochemical degradation.

Low moisture absorption and good chemical resistance are also anticipated [4]. Herein, we report the synthesis and characterization of the polyimide which was obtained by condensation polymerization of 4,4'-hexafluoroisopro-

pylidene-2,2-bis-(phthalic acid anhydride) (6-FDA) with diamines.

## 2. Results and discussion

### 2.1. Preparation of 6-FDA

The title product 6-FDA was prepared in a three-step synthetic sequence using hexafluoroacetone and *o*-xylene as the starting materials (Scheme 1).

Try to simplify the reaction process, in stead of *o*-xylene, phthalic anhydride was used to react with hexafluoroacetone. However, under various reaction conditions, all failed to obtain the condensed product **5**. When hexafluoropropene oxide was treated with *o*-xylene under the same reaction conditions no reactions occurred, while in the presence of  $AlCl_3$  a mixture of **3**, **3a**, and **3b** was obtained in the 25% total yield (Scheme 2).

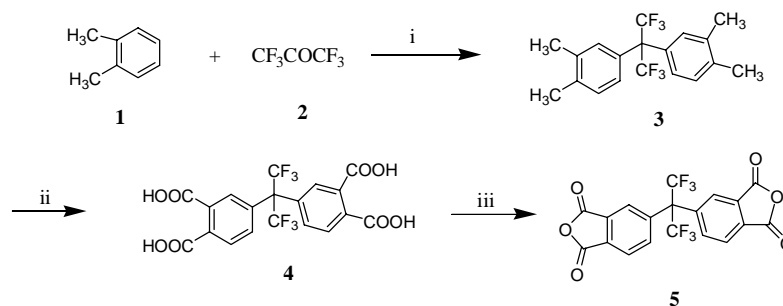
To establish the optimal reaction conditions for preparation of the condensation product **3**, several reaction conditions were tried, and the results are summarized in Table 1.

Due to substitute effect of hexafluoroisopropyl group, general oxidizer such as  $HNO_3$ ,  $CrO_3/H_2SO_4$ ,  $KCrO_3/HOAc$ , etc., failed to transform **3** into the bis-(phthalic acid) **4**. The oxidation of **3** was accomplished by using  $KMnO_4$

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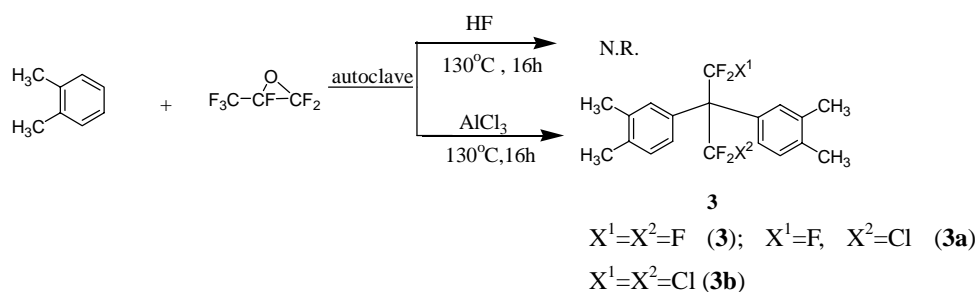
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Reagents, conditions and yields: i. HF, 130°C, 16h, autoclave, 68%; ii. KMnO<sub>4</sub>, NaOH, PY., H<sub>2</sub>O, reflux 12h, 66%; iii. xylene, 170°C, 4h, 78%.

Scheme 1.



Scheme 2.

Table 1  
Preparation of compound **3**

Entry	Reactants (g)			Conditions		Pressure (kg/cm <sup>2</sup> )	Yield (%)
	<b>1</b>	<b>2</b>	HF	T (°C)	t (h)		
1 <sup>a</sup>	10.6	10	22	100	24	17.5	48
2 <sup>a</sup>	10.6	10	22	110	20	20	67
3 <sup>a</sup>	10.6	10	10	110	16	18.5	51
4 <sup>a</sup>	10.6	10	30	130	16	28	68
5 <sup>b</sup>	70	70	130	110	16	21	65
6 <sup>b</sup>	70	70	130	130	18	30	69

<sup>a</sup> Reaction carried out in 100 ml autoclave.

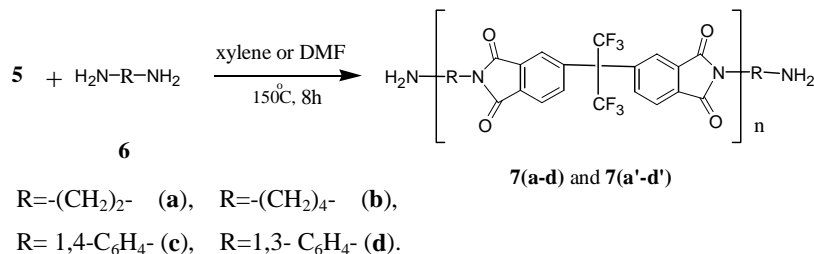
<sup>b</sup> Reaction carried out in 1000 ml autoclave.

under the basic reaction conditions (NaOH and pyridine), the optimum yield of **4** is 66%. Reflux of **4** with xylene for 3 h gave the dehydrated product **5** [5].

## 2.2. Preparation of the polyimide with end group of amine

The reactions of **5** with diamine were carried out in xylene or DMF at 150 °C with the diamines in little excess, after heating and stirring for 8 h, the solvent was evaporated under vacuum, the remained solid was dried in a drying box at 60 °C for 24 h to give the imide oligomer **7** (Scheme 3).

Comparing the NMR spectra data of the starting acid anhydride **5** [ $\delta_F = -64.0$ ,  $\delta_H = 8.53$ – $8.16$  (ppm)] with the oligomer **7a'** prepared in DMF [ $\delta_F = -65.0$  (CF<sub>3</sub>),  $\delta_H = 8.05$ – $8.43$  (Ar-H), 4.60 (NH<sub>2</sub>), 3.30 (CH<sub>3</sub>), (ppm)], it is clear that both of the chemical shift  $\delta_F$  and  $\delta_H$  (Ar-H) in **7a'** are shift to higher field. The IR spectra of **7** shows a very strong –NH<sub>2</sub> group absorption at 3250–3300 cm<sup>-1</sup> and the amido-carbonyl group at 1660 and 1680 cm<sup>-1</sup>. The carbonyl absorption in **5** is at 1770 and 1840 cm<sup>-1</sup>. It was noticed that in the IR spectra of **7a** and **7b** which were prepared in



Scheme 3.

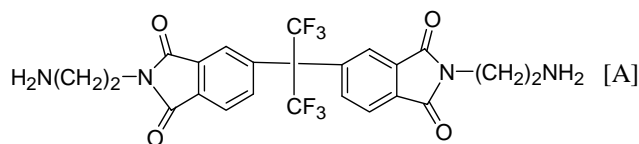
Table 2  
The relative viscosity of **7**

Entry	Oligomer <b>7</b> <sup>a</sup>	$\eta$ (ml/g) <sup>b</sup>
1	<b>7a</b>	13.44
2	<b>7a'</b>	17.30
3	<b>7b</b>	8.38
4	<b>7b'</b>	8.99
5	<b>7c</b>	14.02
6	<b>7c'</b>	21.85
7	<b>7d</b>	4.70
8	<b>7d'</b>	5.66

<sup>a</sup> **7a–d** are prepared in xylene. **7a'–d'** are prepared in DMF.

<sup>b</sup>  $\eta = [2(\eta_{sp} - \ln \eta_t)]^{1/2} / C_0$ .

xylene, there are weak absorptions at 1770 and 1840  $\text{cm}^{-1}$ , indicating the remainder of the acid anhydride group. The MS spectrum of **7a'** has the largest fragment peak 529 ( $\text{A}^+\text{H}$ ).



Other fragments are: 512 ( $\text{A}^+\text{-NH}_2$  or  $\text{A}^+\text{-O}$ ), 499 ( $\text{A}^+\text{-CH}_2\text{NH}_2$ ), 469 ( $\text{A}^+\text{-NH}_2(\text{CH}_2)_2\text{NH}_2$ ) and the base peak 91 ( $\text{NH}_2\text{CH}_2\text{NHCO}^+$ ). All above spectral data shown that the end group in the oligomer is  $\text{-NH}_2$ , and the condensation reaction in DMF is more completely.

Table 3  
DSC analysis results of **7**

Entry	Oligomer <b>7</b>	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$	
			Onset temperature ( $^{\circ}\text{C}$ )	Maximum temperature ( $^{\circ}\text{C}$ )
1	<b>7a</b>	– <sup>a</sup>	109.2	139.6
1	<b>7a'</b>	– <sup>a</sup>	103.2	110.1
2	<b>7c</b>	110.93	193.04	219.65
3	<b>7c'</b>	197.87	–	–
4	<b>7d</b>	97.23	187.87	213.30
5	<b>7d'</b>	163.80	–	–

<sup>a</sup> Show no  $T_g$ .

Table 4  
TG analysis results of **7**

Entry	Oligomer <b>7</b>	Temperature of the weight lost 50% ( $^{\circ}\text{C}$ )
1	<b>7a'</b>	544
2	<b>7b</b>	502
3	<b>7b'</b>	501
4	<b>7c</b>	610
5	<b>7c'</b>	658
6	<b>7d'</b>	584

### 2.3. Viscosity and thermal analysis

The relative viscosity [ $\eta$ ] of the oligomer **7** are taken on an Ubbelodhe viscosimeter using a  $r = 0.49$  mm capillary tube at 30  $^{\circ}\text{C}$  in DMF. The results are summarized in Table 2.

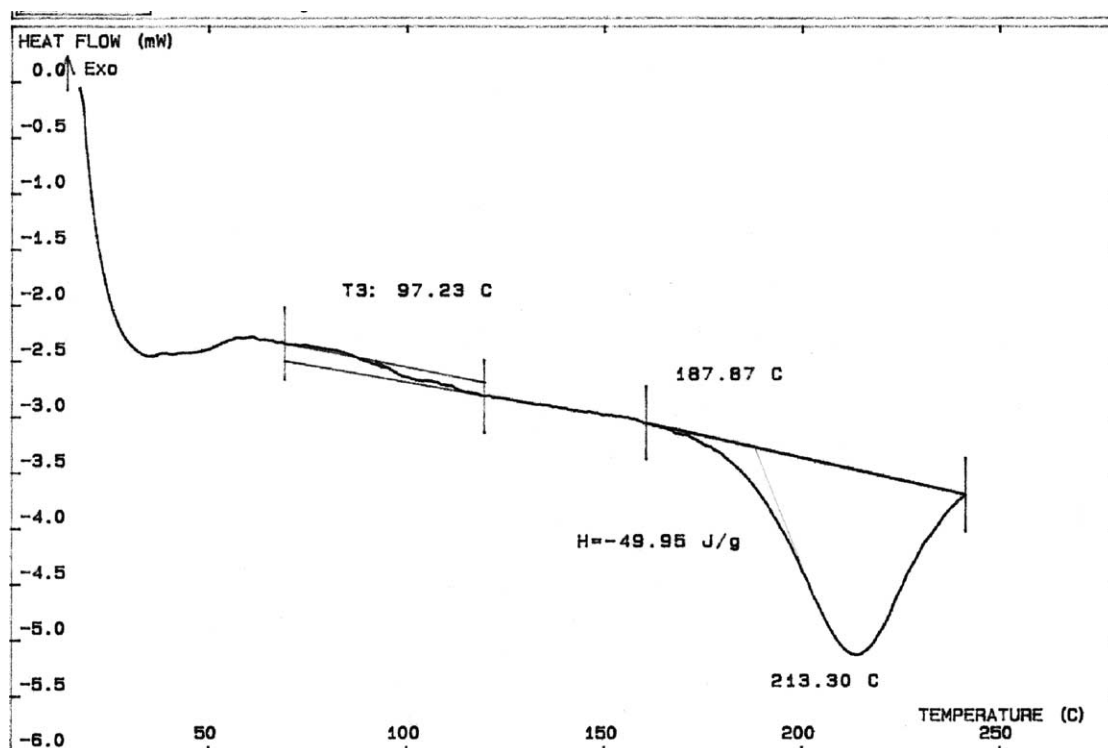


Fig. 1. The DSC analysis of **7d**.

From the relative viscosity data, we could conclude that the polyimides **7a'–d'** prepared in DMF have higher molecular weight than that of **7a–d** prepared in xylene. The extent of polymerization of 6-FDA with 1,2-diaminoethane is better than the extent of polymerization of 6-FDA with 1,2-diaminohexane, while 1,4-phenylenediamine is better than that of 1,3-phenylenediamine. Comparing to the data of  $[\eta]$ , it means that the raw of polyimide **7c'** which prepared from 6-FDA with 1,4-phenylenediamine in DMF was highest.

The thermal behavior of the polyimide **7** were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Measurements were carried out in nitrogen atmosphere at a flow rate of 100 ml/min and at a heating rate of 10 °C/min. The results are summarized in Tables 3 and 4.

The DSC analyses (shown in Fig. 1) show that the polyimide **7d** and **7d'** obtained from the reaction of 6-FDA with 1,3-phenylenediamine have lower  $T_g$  comparing with **7c** and **7c'** [6]. While the  $T_g$  of **7d** is lower than that of **7d'** which was prepared in DMF. Also the results of  $T_m$  which were listed in Table 3 shown the substitute groups of amines effect the  $T_m$  of polyimide was higher  $T_g$  using aromatic amine in stead of alkyl amine.

From Table 4, it is clear that all these polyimide **7** show good thermal stability and rigidity. Among those, **7c** is the best one. It should be contributed to the rigidity of the aromatic ring and molecular symmetry.

### 3. Conclusion

We have successfully prepared the polyimide **7** as the condensation polymerization of 6-FDA with diamines in different solvents. The spectral, thermal and viscosity analyses of these polyimide demonstrated that they have high thermal stability with lower glass transition temperature. The polyimide **7c'**, prepared from 6-FDA with 1,4-phenylenediamine in DMF has the best thermal stability and higher molecular weight. The electric properties of **7** are under further investigation.

### 4. Experimental

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker DRX-300 spectrometer operating at 282 MHz for  $^{19}\text{F}$  NMR (internal standard  $\text{CFCl}_3$ ) and 300 MHz for  $^1\text{H}$  NMR (internal standard TMS). Highfield shifts from TMS and  $\text{CCl}_3\text{F}$  are negative. IR spectra were obtained with a Perkin-Elmer 983G spectrophotometer using KBr disks. Lower resolution mass spectra was obtained on a Finnigan GC-MS 4021. Elemental analyses were undertaken by the analysis department of Shanghai Institute of Organic Chemistry. Thermal analyses were performed on a SETARAM DSC-92 instrument. Intrinsic viscosity was measured on an Ubbelodhe viscosimeter. Melting points were measured in a melting point apparatus and reported uncorrected.

#### 4.1. Preparation of 4,4'-(hexafluoroisopropylidene)-bis-(*o*-xylene) (**3**)

##### 4.1.1. Preparation of 4,4'-(hexafluoroisopropylidene)-bis-(*o*-xylene) (**3**) from hexafluoroacetone (**2**)

An autoclave (100 ml) was charged with *o*-xylene (10.6 g, 0.1 mol), hexafluoroacetone (10 g, 0.06 mol), and HF (22 g, 1 mol). The mixture was heated to 110 °C for 20 h, and the pressure was about 20 kg/cm<sup>2</sup>. After cooling, the reaction mixture was poured into ice-water, and the oil layer was separated, while the aqueous layer was extracted with toluene (3 ml × 50 ml). The solvent was evaporated, and the residue was distilled under vacuum giving crude product 15 g (bp: 110–115 °C/1 mmHg), Recrystallization from acetone and benzene gave pure **3** (14.5 g, yield 67%). Melting point was 78–80 °C.

FT-IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3020 (w, Ar-H), 2950 (m, C-H), 1497 (s, Ar-H), 1180 (vs, C-F), 1120 (vs, C-F), 960 (s);  $^1\text{H}$  NMR  $\delta$ : 3.3 (s, 12H, 4CH<sub>3</sub>), 8.0 (s, 6H, 6Ar-H);  $^{19}\text{F}$  NMR  $\delta$ : -64.0 (s, 6F, 2CF<sub>3</sub>); MS  $m/z$  (ion, %): 360 ( $M^+$ , 100), 345 ( $M^+ - \text{CH}_3$ , 10), 341 ( $M^+ - \text{F}$ , 9), 291 ( $M^+ - \text{CF}_3$ , 98), 276 ( $M^+ - \text{CF}_3 - \text{CH}_3$ , 56), 207 ( $M^+ - 2\text{CF}_3 - \text{CH}_3$ , 27).

##### 4.1.2. Preparation of 4,4'-(hexafluoroisopropylidene)-bis-(*o*-xylene) (**3**) from hexafluoropropene oxide

Hexafluoropropene oxide (HFPO) (17 g, 0.1 mol), *o*-xylene (17 g, 0.16 mol) and  $\text{AlCl}_3$  (4 g, 0.03 mol) were charged into a 100 ml autoclave. The mixture was heated to 110 °C for 16 h. After cooling, HFPO (8 g) was recovered. A mixture of  $\text{Ar}_2\text{CCF}_3(\text{CF}_2\text{Cl})$ ,  $\text{Ar}_2\text{C}(\text{CF}_3)_2$  and  $\text{Ar}_2\text{C}(\text{CF}_2\text{Cl})_2$  was obtained, and the overall yield was 25%. The ratio of  $\text{CF}_3$  and  $\text{CF}_2\text{Cl}$  was 2:5 (according to the  $^{19}\text{F}$  NMR).

#### 4.2. Preparation of 4,4'-(hexafluoroisopropylidene)-bis-(*phthalic acid*) (**4**)

In a 250 ml flask, 4,4'-(hexafluoroisopropylidene)-bis-(*o*-xylene) (**3**) (7.2 g, 0.02 mol) was dissolved in a mixture of pyridine (100 g) and water (50 ml) at 100 °C. The solution was stirred and refluxed gently for 4 h. During this time potassium permanganate (15 g) was added carefully. The hot solution was filtered and the cake of manganese oxide was washed with a hot solution of pyridine (32 g) and water (8 ml). The filtrate was evaporated to 40 ml, and then added to sodium hydroxide (10 g, 0.25 mol) in 110 ml water. The solution was boiled in a 200 ml flask, potassium permanganate (20 g) was added over 1 h. After refluxing another 1 h, the solution was cooled somewhat and the excess potassium permanganate was destroyed by cautious addition of ethyl alcohol (2 ml). The mixture was filtered, and the cake washed with hot water (40 ml). The filtrate was evaporated until no residue pyridine can be detected and then acidified to pH = 1 with hydrochloric acid. The solution was evaporated to dryness and extracted with acetone (3 ml × 50 ml). The acetone solution was evaporated giving 6.3 g crude product (**4**), yield 66%.

FT-IR ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3400 (m, OH), 1705 (vs, C=O), 1250 (vs, C–O), 1200 (vs, C–F), 1105 (s, C–F);  $^1\text{H NMR } \delta$ : 8.05–8.42 (m, 6H, 6Ar-H);  $^{19}\text{F NMR } \delta$ : –65.0 (s, 6F, 2CF<sub>3</sub>); MS  $m/z$  (ion, %): 480 ( $M^+$ , 7), 463 ( $M^+ - \text{OH}$ , 13), 434 ( $M^+ - \text{CO}_2\text{H}-\text{H}$ , 21), 417 ( $M^+ - \text{CO}_2-\text{OH}-\text{H}$ , 100), 165 (HOCC<sub>6</sub>H<sub>3</sub>COOH<sup>+</sup>, 8). Anal. Calcd. for C<sub>17</sub>H<sub>10</sub>F<sub>6</sub>O<sub>8</sub>: C, 42.50%; H, 2.08%; F, 23.75. Found: C, 42.89%; H, 2.16%; F, 23.88%.

#### 4.3. Preparation of 4,4'-(hexafluoroisopropylidene)-bis-(phthalic anhydride) (5)

4,4'-(Hexafluoroisopropylidene)-bis-(phthalic acid) (4) (4.8 g, 0.01 mol) was dissolved in 50 ml *o*-xylene in a 100 ml flask, then heated at 180 °C for 3 h. After solvent and the forming water were gone, the crude anhydride was purified by vacuum sublimation giving 3.5 g of **5** (yield 78%). Melting point was 249–253 °C.

FT-IR ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 1840 (vs, C=O), 1770 (vs, C=O), 1240 (vs, C–O–C), 1150 (vs, C–F);  $^1\text{H NMR } \delta$ : 8.15–8.48 (m, 6H, 6Ar-H);  $^{19}\text{F NMR } \delta$ : –64.0 (s, 6F, 2CF<sub>3</sub>); MS  $m/z$  (ion, %): 445 ( $M^+\text{H}$ , 7), 444 ( $M^+$ , 13), 401 ( $M^+\text{H}-\text{CO}_2$ , 21), 400 ( $M^+ - \text{CO}_2$ , 100), 328 ( $M^+ - 2\text{CO}_2-\text{CO}$ , 11), 300 ( $M^+ - 2\text{CO}_2-2\text{CO}$ , 3), 231 ( $M^+ - 2\text{CO}_2-2\text{CO}-\text{CF}_3$ , 8). Anal. Calcd. for C<sub>17</sub>H<sub>6</sub>F<sub>6</sub>O<sub>6</sub>: C, 51.35%; H, 1.32%; F, 25.67. Found: C, 51.51%; H, 1.17%; F, 25.52%.

#### 4.4. Preparation of the oligomer (7) of the 4,4'-(hexafluoroisopropylidene)-bis-(phthalic anhydride) (5) with the diaminoethane

In a 50 ml flask **5** (0.55 g, 1.2 mmol) was dissolved in 20 ml xylene, and the solution was heated at 150 °C. At this

temperature, diaminoethane (1 g, 1.67 mmol) and xylene were dropped into the flask slowly and constantly in order to remain 20 ml liquid in the flask. After stirring for 8 h, the mixture of the reaction was cooled at room temperature and the solvent and excess diaminoethane were evaporated. The residue was dried and gave 0.46 g oligomer (**7a**). Similarly, other polyimide oligomers **7b–d** are prepared.

FT-IR ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 1660 (vs, C=O), 1850 (vs, C=O), 1780 (vs, C=O), 1622 (s, C–N);  $^1\text{H NMR } \delta$ : 3.3 (s, 12H, 2NCH<sub>2</sub>), 4.6 (s, 4H, 2NH<sub>2</sub>) 8.0–8.8 (s, 6H, 6Ar-H);  $^{19}\text{F NMR } \delta$ : –63.0 (s, 6F, 2CF<sub>3</sub>); MS  $m/z$  (%): 529 (10), 512 (30), 499 (9), 469 (28), 91 (100). Anal. Calcd. Found: C, 47.04%; N, 11.93%; H, 4.12%.

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