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Article

CuCl/Zn-promoted Mukaiyama Aldol Reaction of Phenyl α-fluoro silyl enol ether with Aldehydes†

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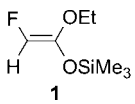
2-Fluoro-1-phenyl-1-trimethylsiloxyethene reacted efficiently with aldehydes to give α-fluoro β-hydroxy ketones in HMPA in the presence of Zn powder and CuCl.

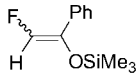
Keywords 2-fluoro-1-phenyl-1-trimethylsiloxyethene, α-fluoro β-hydroxy ketone, Mukaiyama Aldol reaction

Organic molecules containing one or more fluorine atoms play an important role in organic synthesis, because they are used widely in the syntheses of biologically active fluoro-containing compounds.[1] Mukaiyama Aldol reaction is one of the most important methods for carbon-chain extension, and chiral catalyzed Mukaiyama Aldol reactions of α,α-difluoro silyl enol ether and carbonyl compounds have also been reported.[2,3] But for α-fluoro silyl enol ether, Welch's method has disadvantages because ethyl fluoroacetate used is extremely poisonous and the formed silyl enol ether decomposes above 50 ℃. Lately, we have stereoselectively synthesized ethyl α-fluoro silyl enol ether (**1**) from ethyl chlorofluoroacetate, and found that the Lewis acid can promote the aldol reactions of this enol ether with aldehydes and ketones. When BF_3•OEt_2 or TMS-OTf was employed as a catalyst, ethyl α-fluoro silyl enol ether (**1**) only reacted with electron-deficient aromatic aldehydes, but using CuCl/HMPA system, the enol ether reacted well with aromatic and aliphatic aldehydes.[4] Almost at the same time Dolbier *et al*.[5] reported the similar results of $CeCl_3$ catalyzed the Reformatsky reaction of ethyl bromofluoroacetate. Compared with α-fluoro β-hydroxy ester, α-fluoro β-hydroxy ketones were studied much less, although they can be obtained from silyl enol ethers or metal enolates, yet both methods have their disadvantages, *e.g.* very low reaction temperature or poisonous fluoroacetate was used.[6] Encouraged by the Mukaiyama Aldol reactions of silyl enol ether **1** with aldehydes in the presence of CuCl/HMPA, we envisioned that the silyl enol ether **2** could be applied for the syntheses of α-fluoro β-hydroxy ketones.



1

2-Fluoro-1-ethoxy-1-trimethylsiloxyethene



2

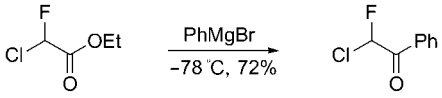
2-Fluoro-1-phenyl-1-trimethylsiloxyethene

Results and discussion

Preparation of 2-fluoro-1-phenyl-1-trimethylsiloxyethene (2)

In order to study the reactivity of 2-fluoro-1-phenyl-1-trimethylsiloxyethene (**2**), PhCOCHFCl (**3**) is required. There were three reported methods to prepare it, but either the reaction time is too long or the yield of relative intermediate is too low.[7-10] After some efforts, it was found that **3** could be prepared from the reaction of ethyl chlorofluoroacetate with phenyl Grignard reagent (Scheme 1).

Scheme 1 Preparation of compound **3**



3

However, **3** was unstable and the reaction mixture should be worked up as soon as possible, otherwise the yield would decrease from 72% (worked up immediately) to 50% (worked up when warming up to room temperature), and even to 20% if it was kept at room temperature for more than 2 h.

Starting from compound **3**, 2-fluoro-1-phenyl-1-trimethylsiloxyethene (**2**) was prepared as shown in Scheme 2.[11]

After the usual treatment, the crude product was failed to be purified by distillation or column chromatography

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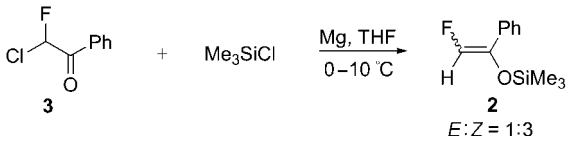
Scheme 2 Preparation of silyl enol ether **2**



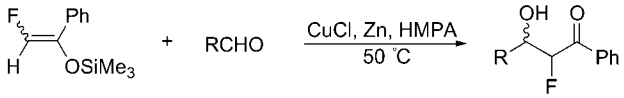
because the silyl enol ether **2** was not stable enough under these conditions. But GC-Mass spectrum showed that the main fraction of the crude product was enol ether **2**. Furthermore, GC and ^{19}F NMR spectra indicated that enol ether **2** was a mixture of *E/Z* isomers (1∶3) and a purity of 90%. Thus, **2** was freshly prepared and used directly for the following reactions.

Mukaiyama Aldol Reaction of 2-fluoro-1-phenyl-1-trimethylsiloxyethene (2) and aldehydes

Smiliar to the reaction of **1**, the CuCl/HMPA system was also adopted for the reaction of **2**, but the reaction did not take place at all. When the reaction of **1** and aldehyde was repeated, the reaction was successful only occasionally. For all the failed reactions there was a common phenomenon: the color of the reaction mixture was changed from pale-green to dark-green, which indicated that CuCl was oxidated, so Zn powder should be added as a reducing agent in order to make the reaction take place as we wanted. After a few attempts, it was found that using HMPA as the solvent, Zn/CuCl (1∶1 Molar ratio) could efficiently promote the aldol reactions of **2** with aromatic aldehydes, α,β-unsaturated aldehydes and aliphatic aldehydes at 50 ℃, to give the corresponding α-fluoro β-hydroxy ketones (**5**) in good yields with various syn/anti ratios. The results are listed in Table 1.

Table 1 showed that the reaction posesses some extent of selectivity: a) in the reaction of silyl enol ether with α,β-unsaturated carbonyl compound, 3, 4 and 1, 4 addition products were obtained in previous reports,[12] in our case, only the 3, 4 addition product was yielded

Table 1 CuCl/Zn catalyzed Mukaiyama Aldol reaction of ether **2** and aldehydes[a]



R=Ph (**4a**); 4-Cl-C_6H_4 (**4b**); 3-CF_3-C_6H_4 (**4c**); 4-NO_2-C_6H_4 (**4d**); 4-F-C_6H_4 (**4e**);  (**4f**); $C_6H_5(CH_3)CH$— (**4g**); $C_6H_5CH_2CH_2$ (**4h**); 4-Br-C_6H_4 (**4i**); *n*-C_4H_9 (**4j**); *i*-C_4H_9 (**4k**); 4-CH_3O-C_6H_4 (**4l**); 4-CF_3-C_6H_4 (**4m**); 4-CH_3-C_6H_4 (**4n**); $PhCH=CH_2$ (**4o**)

Entry	RCHO	*T*/h	Conv.[b] /%	Product **5**	Yield of **5**[c]/%	*syn/anti* of **5**[d]
1[e]	**4a**	10	100	**5a**	50	60∶40
2	**4a**	10	100	**5a**	92	60∶40
3	**4b**	11	100	**5b**	93	50∶50
4	**4c**	12	100	**5c**	85	65∶35
5	**4d**	12	100	**5d**	80	67∶33
6	**4e**	12	100	**5e**	85	69∶31
7[f]	**4f**	10	100	**5f**	86	66∶34
8[g]	**4f**	10	100	**5f**	96	66∶34
9[f]	**4g**	11	100	**5g**	67	26∶74
10[g]	**4g**	11	100	**5g**	60	26∶74
11[f]	**4h**	12	100	**5h**	81	41∶59
12[g]	**4h**	11	100	**5h**	90	41∶59
13[f]	**4i**	12	100	**5i**	92	57∶43
14[g]	**4i**	12	100	**5i**	98	57∶43
15[f]	**4j**	10	100	**5j**	90	72∶28
16[g]	**4j**	10	100	**5j**	80	72∶28
17	**4k**	10	100	**5k**	80	58∶42
18	**4l**	10	100	**5l**	92	51∶49
19	**4m**	10	100	**5m**	95	68∶32
20	**4n**	11	100	**5n**	96	46∶54
21	**4o**	10	100	**5o**	87	48∶52

[a] **4**∶CuCl=1∶1.1. [b] Conversion of **2** (based on ^{19}F NMR). [c] Isolated yield of **5**. [d] *Syn/anti* ratio determined by ^{19}F NMR spctra. [e] In the absence of CuCl, Zn. [f] **2**∶**4**=2∶1. [g] **2**∶**4**=1∶1.

(Entry 21); b) the α-bulky group of carbonyl compound has a great effect on the selectivity, if with bulkier group, the syn/anti selectivity reverses, and anti isomer becomes main product (Entry 9). The hindrance of ortho group of the carbonyl compound is unfavorable to the reaction, *e.g.* the yield of compound **5g** is just 67%, while those of the others are all above 80% .

The conformations of the product α-fluoro-β-hydroxyketone (**5**) were determined by ^{19}F NMR spectra, and syn isomer showed a higher field signal than anti isomer as reported in literature.[13] An example is shown in Scheme 3.

Scheme 3

5a (*Syn*) δ_F = −189.66, −189.83

5b (*Anti*) δ_F = −198.43, −198.60

Experimental

Material and measurement

The melting points were determined on a METTLER FP62 melting point apparatus and uncorrected. The IR spectra were recorded on a Shimadzu IR-440 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM-300 (300 MHz) spectrometer with TMS as an internal standard. ^{19}F NMR spectra were recorded on a Bruker AM-300 (282 MHz) spectrometer using $CFCl_3$ as an external standard. The solvent for NMR measurement was $CDCl_3$. GC-MS were performed on a Finnigan MD800 instrument. THF was distilled under a nitrogen atmosphere over sodium/benzophenone ketyl prior to use. Column chromatography was carried out using silica gel (300—400 mesh).

Preparation of 3

To a 250 mL three-necked flask fitted with a dropping funnel, a thermometer and a stirrer, $CHFClCO_2Et$ (40 mmol) in 50 mL of dry ether was added. The solution was cooled to −78 ℃ and PhMgBr (equivalent) was added dropwise during a period of 45 min. After 3 h the reaction was quenched with a saturated NH_4Cl solution, and the aqueous phase was extracted with ether several times. The combined ether phase was further washed with brine successively for three times. The organic phase was dried over anhydrous Na_2SO_4. After removal of the solvent, the product was purified by silica gel column chromatography (petroleum ether/ether =5∶1) to give 5 g of **3** as a pale yellow solid, yield 72%.

3[14]: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.48—8.07 (m, 5H), 6.85 (d, J=51 Hz, 1H); ^{19}F NMR ($CDCl_3$) δ: −146.736 (d, J=54 Hz).

Preparation of 2

Under a nitrogen atmosphere, to a mixture of 154 mg (6 mmol) of magnesium turnings and 1.7 mL (12 mmol) of TMSCl in 13 mL of dry THF at 0 ℃, was added 505 mg (3 mmol) of **3** in 2 mL of dry THF. The mixture was stirred at 5—10 ℃ for 4 h, then THF and excess TMSCl were removed under vacuum. To the residue was added 40 mL of hexane. The solid was removed by suction filtration, and the filtrate was evaporated to give 457 mg of crude product, yield 73%. GC showed the purity is 90%.

2[7]: *Z*-isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.25 (s, 9H), 6.99 (d, J=78.3 Hz, 1H), 7.33—7.92 (m, 5H); ^{19}F NMR ($CDCl_3$) δ: 158.68 (d, J=77.3 Hz). *E*-isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.19 (s, 9H), 6.93 (d, J= 79.2 Hz, 1H), 7.33—7.92 (m, 5H); ^{19}F NMR ($CDCl_3$) δ: 164.15 (d, J=80.4 Hz); GC: percent (time): 26.66 (7.683 min), 66.78 (7.911 min).

Mukaiyama Aldol reaction of 2 and aldehydes

To a flask containing Zn powder (72 mg, 1.1 mmol) and CuCl (110 mg, 1.1 mmol), anhydrous HMPA (1 mL), **2** and **4a** (1 mmol) were added successively under a nitrogen atmosphere. Then the mixture was stirred at 50 ℃ for 10 h. ^{19}F NMR spetra showed the conversion of **2** was 100%. The reaction was quenched with 5% HCl solution and extracted with ether (20 mL×3). The combined organic phase was washed with water, brine, dried over anhydrous Na_2SO_4, then filtered and concentrated. Purification by silica gel column chromatography afforded **5a** in 90% yield.

5a: White solid, m.p. 102 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.26—5.33 (m, 1H), 5.51—5.65 (m, 1H), 7.32—7.92 (m, 10H); ^{19}F NMR ($CDCl_3$) δ: −189.74—−189.99 (m, 0.6F), −198.52——198.71 (m, 0.4F); IR (KBr) ν: 3380, 3032, 1709, 1598, 1580, 1496, 1450 cm^{-1}; MS (70 eV) *m*/*z* (%): 244 (M^+, 0.18), 224 (22.66), 138 (42.43), 105 (68.58), 77 (100), 51 (38.90). Anal. calcd for $C_{15}H_{13}FO_2$: C 73.96, H 5.20, F 7.39; found C 74.06, H 4.97, F 7.81.

5b: White solid, m.p. 92 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.20—5.27 (m, 1H), 5.41—5.60 (m, 1H), 7.30—7.90 (m , 9H); ^{19}F NMR ($CDCl_3$) δ: −189.72—−189.91 (m, 0.5F), −198.08——198.33 (m, 0.5F); IR (KBr) ν: 3374, 3060, 2977, 1701, 1599, 1580, 1492, 1449 cm^{-1} ; MS (70 eV) *m*/*z* (%): 258 (M^+−20, 16.33), 141 (26.22), 138 (58.70), 105 (65.60), 77 (100), 51 (24.77). Anal. calcd for $C_{15}H_{12}ClFO_2$: C 65.05, H 4.16, F 7.25; found C 64.88, H 3.99, F 6.84.

5c: White solid, m.p. 90 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.96 (s, 1H), 5.34—5.41 (m, 1H), 5.52—5.68 (m, 1H), 7.43—7.93 (m, 9H); ^{19}F NMR ($CDCl_3$) δ: −63.23 (s, 3F), −189.28——189.44 (m, 0.65F), −199.13——199.38 (m, 0.35F); IR (KBr) ν: 3462,

3070, 2933, 1693, 1599, 1581, 1495, 1451 cm^{-1}; MS (70 eV) *m/z* (%): 292 (M^+−20, 13.35), 175 (12.33), 145 (31.17), 138 (47.45), 105 (100), 77 (78.47), 51 (26.94). Anal. calcd for $C_{16}H_{12}F_4O_2$: C 61.84, H 3.63, F 24.23; found C 61.74, H 3.56, F 24.42.

5d: Yellow solid, m.p. 112 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.35—5.45 (m, 1H), 5.50—5.69 (m, 1H), 7.44—8.22 (m, 9H); ^{19}F NMR ($CDCl_3$) δ: −188.50——188.69 (m, 0.67), −198.53——198.78 (m, 0.33F); IR (KBr) *v*: 3492, 3359, 1685, 1597, 1579, 1525, 1450 cm^{-1}; MS (70 eV) *m/z* (%): 268 (M^+−20, 1.54), 151 (31.51), 138 (8.99), 105 (99.04), 77 (100), 51 (51.34). Anal. calcd for $C_{15}H_{12}FNO_4$: C 62.11, H 4.01, F 6.16, N 4.60; found C 62.50, H 3.85, F 6.59, N 4.86.

5e: Yellow solid, m.p. 92 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.21—5.33 (m, 1H), 5.65—5.43 (m, 1H), 7.91—7.36 (m, 9H); ^{19}F NMR ($CDCl_3$) δ: −113.38 (s, 1F), −190.11——190.40 (m, 0.69F), −197.95——198.21 (m, 0.31F); IR (KBr) *v*: 3367, 3071, 2929, 1705, 1599, 1580, 1511, 1450 cm^{-1} ; MS (70 eV) *m/z* (%): 262 (M^+, 0.89), 242 (46.66), 138 (83.45), 125 (46.10), 105 (90.05), 77 (100). Anal. calcd for $C_{15}H_{12}F_2O_2$: C 68.72, H 4.76, F 14.55; found C 68.96, H 4.24, F 14.54.

5f: White solid, m.p. 92 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.27—5.29 (m, 1H), 5.73—5.91 (m, 1H), 6.33—6.38 (m, 2H), 7.26—7.95 (m, 6H); ^{19}F NMR ($CDCl_3$) δ: −192.02——192.34 (m, 0.66F), −199.55——199.80 (m, 0.34F); IR (KBr) *v*: 3446, 1692, 1598, 1580, 1505, 1450 cm^{-1}; MS (70 eV) *m/z* (%): 233 (M^+−1, 0.62), 214 (1.73), 138 (4.35), 97 (4.52), 105 (100.00), 77 (63.89). Anal. calcd for $C_{13}H_{11}FO_3$: C 66.58, H 4.93, F 7.98; found C 66.66, H 4.73, F 8.11.

5g: Pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.43—1.46 (m, 3H), 3.07—3.33 (m, 1H), 4.07—4.34(m, 2H), 5.18—5.47 (m, 1H), 7.25—7.92 (m, 10H); ^{19}F NMR ($CDCl_3$) δ: −191.28——191.48 (m, 0.26F), −211.80——212.07 (m, 0.74F); IR (neat) *v*: 3458, 3030, 2934, 2879, 1695, 1599, 158, 1495, 1450 cm^{-1} ; MS (70 eV) *m/z* (%): 271 (M^+−1, 2.69), 138 (0.98), 134 (10.00), 105 (100.00), 77 (63.89). Anal. calcd for $C_{17}H_{17}FO_2$: C 74.51, H 6.54, F 6.86; found C 74.98, H 6.29, F 6.98.

5h: White solid, m.p. 90 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.90—2.11 (m, 2H), 2.79—2.90 (m, 2H), 4.21—4.13 (m, 1H), 5.36—5.53 (m, 1H), 7.18—7.62 (m, 8H), 7.90—7.93 (m, 2H); ^{19}F NMR ($CDCl_3$) δ: −193.77——193.98 (m, 0.41F), −203.55——203.82 (m, 0.59F); IR (KBr) *v*: 3454, 3029, 2928, 2860, 1683, 1598, 1580, 1495, 1450 cm^{-1}; MS (70 eV) *m/z* (%): 272 (M^+, 0.80), 254 (3.07), 234 (7.40), 138 (6.56), 105 (100.00), 77 (48.43). Anal. calcd for $C_{17}H_{17}FO_2$: C 75.07, H 6.33, F 6.86; found C 74.98, H 6.29, F 6.98.

5i: Pale yellow solid, m.p. 92 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.19—5.32 (m, 1H), 5.43—5.64 (m, 1H), 7.28—7.93 (m, 9H); ^{19}F NMR ($CDCl_3$) δ: −189.78——189.98 (m, 0.57F), −198.60——198.85 (m, 0.43F); IR (KBr) *v*: 3373, 3059, 1700, 1599 1581, 1488, 1449 cm^{-1}; MS (70 eV) *m/z* (%): 302 (M^+−20, 13.58), 303 (14.36), 183 (28.47), 185 (31.61), 157 (13.41), 138 (46.47), 105 (75.77), 77 (100.00). Anal. calcd for $C_{15}H_{12}BrFO_2$: C 56.22, H 3.92, F 6.18; found C 55.93, H 3.44, F 5.90.

5j: Pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.93—0.85 (q, 3H), 1.29—1.59 (m, 6H), 4.13—4.16 (m, 1H), 5.38—5.55 (m, 1H), 7.45—8.00 (m, 5H); ^{19}F NMR ($CDCl_3$) δ: −195.15——195.39 (m, 0.72F), −203.68——203.94 (m, 0.28F); IR (neat) *v*: 3446, 3065, 2959, 2872, 1694, 1599, 1581, 1450, 1380 cm^{-1}; MS (70 eV) *m/z* (%): 225 (M^++1, 0.77), 204 (0.53), 138 (17.08), 105 (100.00), 85 (10.14), 77 (39.97). Anal. calcd for $C_{13}H_{17}FO_2$: C 69.15, H 7.72, F 8.59; found C 69.62, H 7.64, F 8.47.

5k: Pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.86—0.99 (m, 6H), 1.38—1.57 (m, 3H), 4.18—4.30 (m, 1H), 5.33—5.52 (m, 1H), 7.47—8.00 (m, 5H); ^{19}F NMR ($CDCl_3$) δ: −194.92——195.15 (m, 0.58F), −202.97——203.23 (m, 0.42F); IR (neat) *v*: 3442, 3065, 2959, 2872, 1693, 1599, 1581, 1450, 1387, 1369 cm^{-1}; MS (70 eV) *m/z* (%): 225 (M^++1, 0.77), 204 (0.43), 138 (16.33), 105 (100.00), 77 (45.10). Anal. calcd for $C_{13}H_{17}FO_2$: C 69.78, H 7.54, F 8.59; found C 69.62, H 7.64, F 8.47.

5l: White solid, m.p. 90 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.78 (s, 3H), 5.15—5.26 (m, 1H), 5.47—5.65 (m, 1H), 6.83—6.88 (m, 2H), 7.30—7.89 (m, 7H); ^{19}F NMR ($CDCl_3$) δ: −190.54——190.75 (m, 0.51F), −197.21——197.45 (m, 0.49F); IR (KBr) *v*: 3464, 3065, 2639, 1689, 1598, 1515, 1450 cm^{-1}; MS (70 eV) *m/z* (%): 274 (M^+, 0.43), 254 (18.28), 137 (96.27), 105 (93.42), 77 (100.00). Anal. calcd for $C_{16}H_{15}FO_3$: C 69.58, H 5.68, F 6.83; found C 70.06, H 5.51, F 6.93.

5m: White solid, m.p. 92 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 5.31—5.48 (m, 1H), 5.50—5.69 (m, 1H), 7.46—7.98 (m, 9H); ^{19}F NMR ($CDCl_3$) δ: −63.28 (s, 3F), −188.88——189.09 (m, 0.68F), −198.58——198.83 (m, 0.32F); IR (KBr) *v*: 3462 3070, 1695, 1600, 1581, 1495, 1450 cm^{-1}; MS (70 eV) *m/z* (%): 292 (M^+−20, 14.58), 175 (11.19), 145 (39.41), 138 (35.30), 105 (100.00), 77 (73.41). Anal. calcd for $C_{16}H_{12}F_4O_2$: C 62.01, H 4.01, F 24.17; found C 61.74, H 3.56, F 24.42.

5n: White solid, m.p. 90 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.33 (s, 3H), 5.18—5.24 (m, 1H), 5.50—5.66 (m, 1H), 7.17—7.91 (m, 9H); ^{19}F NMR ($CDCl_3$) δ: −198.72——198.98 (m, 0.46F), −203.63——203.91 (m, 0.54F); IR (KBr) *v*: 3380, 2864, 1707, 1599, 1581, 1515, 1450 cm^{-1}; MS (70 eV) *m/z* (%): 238 (M^+−20, 36.94), 138 (55.81), 121 (80.67), 105 (79.66), 93 (56.44), 77 (100.00). Anal. calcd for $C_{16}H_{15}FO_2$: C 74.39, H 5.93, F 6.93; found C 74.40, H 5.85, F 7.36.

5o: White solid, m.p. 94 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.65 (d, J=6 Hz, 0.57H), 2.79 (d, J=5.1 Hz, 0.43H), 4.84—4.91 (m, 1H), 5.47—5.67 (m, 1H), 6.24—6.33 (m, 1H), 6.73 (t, J=18.3 Hz, 1H), 7.25—7.64 (m, 7H), 7.98—8.00 (m, 2H); ^{19}F NMR ($CDCl3$) δ: −193.85——194.11 (m, 0.48F), −198.92——199.21 (m, 0.52F); IR (KBr) *v*: 3435, 3026, 2894, 1706, 1686, 1597, 1578, 1493, 1448 cm^{-1}; MS (70 eV) *m/z* (%): 250 (M^+−20, 7.31), 232 (13.39), 138 (25.54), 133 (82.23),

105 (94.56), 77 (100.00). Anal. calcd for $C_{17}H_{15}FO_2$: C 75.53, H 5.62, F 7.09; found C 75.54, H 5.59, F 7.03.

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