

**Mg-promoted Double Silylation of Trifluoroacetimidoyl Chlorides. A New Entry to the Fluorinated Dianion Equivalents**

Takeshi Kobayashi, Takashi Nakagawa, Hideki Amii\* and Kenji Uneyama\*

*Department of Applied Chemistry, Faculty of Engineering,*

*Okayama University*

*3-1-1 Tsushimanaka, Okayama 700-8530, Japan*

*uneyamak@cc.okayama-u.ac.jp*

**General.**  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded at 200 and 188 MHz respectively, using  $\text{CDCl}_3$  as a solvent. The chemical shifts are reported in  $\delta$  (ppm) values relative to  $\text{CHCl}_3$  ( $\delta$  7.26 ppm for  $^1\text{H}$  NMR) and  $\text{C}_6\text{F}_6$  ( $\delta$  0 ppm for  $^{19}\text{F}$  NMR). Coupling constants are reported in hertz (Hz).

All air and/or moisture sensitive reactions were carried out under argon atmosphere with dry, freshly distilled solvents using standard syringe-cannula/septa techniques. THF was distilled from sodium/benzophenone ketyl.  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{P}_2\text{O}_5$ . DMF and pyridine were distilled from  $\text{CaH}_2$ . All other reagents and solvents were

employed without further purification.

**A typical procedure for the synthesis of bis-silylated difluoroenamines**

**(3).** To the suspension of Mg (7.78 g, 320 mmol) in freshly distilled THF (140 mL) were added chlorotrimethylsilane (20.4 mL, 160 mmol) and **4a** (9.47 g, 40 mmol) at 0 °C under an argon atmosphere. And then the reaction mixture was stirred for additional 30 min at 0 °C. After evaporation of the most of THF and chlorotrimethylsilane, hexane (100 mL) was added to the residue, and the resulting salts were removed by filtration through Celite<sup>®</sup>. Evaporation of the filtrate and bulb-to-bulb distillation (0.8 mmHg, 105 °C) provided **3a** as a pale yellow oil (11.6 g, 85%).

**1,N-Bis(trimethylsilyl)-2,2-difluoro-1-(N-phenyl)aminoethene (3a).**

IR (neat) 1682, 1598 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 0.11 (s, 9H), 0.33 (s, 9H), 6.77-6.82 (m, 1H), 6.85-6.88 (m, 2H), 7.16-7.21 (m, 2H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>, C<sub>6</sub>F<sub>6</sub> as an internal standard) δ 71.1 (d, *J* = 32.5 Hz, 1F), 86.2 (d, *J* = 32.5 Hz, 1F); GC/MS *m/z* (%) 299 (M<sup>+</sup>, 2), 172 (32), 73 (100); Anal. Calcd for C<sub>14</sub>H<sub>23</sub>F<sub>2</sub>NSi<sub>2</sub>: C, 56.14; H, 7.74; N, 4.68. Found: C, 56.40; H, 7.47; N, 4.49.

**1,N-Bis(trimethylsilyl)-2,2-difluoro-1-[N-(*p*-methoxyphenyl)]aminoethene (3b).**

A pale yellow oil; 84% yield; bp 120 °C/ 0.6 mmHg; IR (neat) 1682, 1598  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.07 (s, 9H), 0.27 (s, 9H), 3.76 (s, 3H), 6.77 (d,  $J$  = 8.5 Hz, 2H), 6.85 (d,  $J$  = 8.5 Hz, 2H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  70.5 (d,  $J$  = 34.2 Hz, 1F), 86.2 (d,  $J$  = 34.2 Hz, 1F); GC/MS  $m/z$  (%) 329 ( $\text{M}^+$ , 2), 172 (22), 73 (100); Anal. Calcd for  $\text{C}_{15}\text{H}_{25}\text{F}_2\text{NOSi}_2$ : C, 54.67; H, 7.65; N, 4.25. Found: C, 54.27; H, 7.88; N, 4.65.

**1,*N*-Bis(trimethylsilyl)-2,2-difluoro-1-[*N*-(*p*-methylphenyl)]aminoethene (3c).**

A yellow oil; 82% yield; bp 125 °C/ 0.8 mmHg; IR (neat) 1682, 1616, 1512  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.09 (s, 9H), 0.29 (s, 9H), 2.25 (s, 3H), 6.77 (d,  $J$  = 8.5 Hz, 2H), 6.99 (d,  $J$  = 8.5 Hz, 2H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  71.1 (d,  $J$  = 33.1 Hz, 1F), 86.3 (d,  $J$  = 33.1 Hz, 1F); GC/MS  $m/z$  (%) 313 ( $\text{M}^+$ , 2), 172 (54), 73 (100); Anal. Calcd for  $\text{C}_{15}\text{H}_{25}\text{F}_2\text{NSi}_2$ : C, 57.46; H, 8.04; N, 4.47. Found: C, 57.70; H, 7.92; N, 4.78.

**1,*N*-Bis(trimethylsilyl)-1-[*N*-(*m*-chlorophenyl)]amino-2,2-difluoroethene (3d).**

A pale yellow oil; 80% yield; bp 120 °C/ 0.8 mmHg; IR (neat) 1682, 1596  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.11 (s, 9H), 0.32 (s, 9H), 6.74-6.82 (m, 3H), 7.09 (t,  $J$  = 8.2 Hz, 1H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  72.2 (d,  $J$  = 33.2 Hz, 1F), 87.4 (d,  $J$  = 33.2 Hz, 1F); GC/MS  $m/z$  (%) 335 ( $\text{M}^+$ , 2), 333 ( $\text{M}^+$ , 7), 172 (51), 73 (100); Anal. Calcd for  $\text{C}_{14}\text{H}_{22}\text{ClF}_2\text{NSi}_2$ : C, 50.35; H,

6.64; N, 4.19. Found: C, 50.60; H, 6.70; N, 4.58.

**1,*N*-Bis(trimethylsilyl)-1-[*N*-(*p*-chlorophenyl)]amino-2,2-difluoroethene (3e).**

A pale yellow oil; 85% yield; bp 120 °C/ 0.8 mmHg; IR (neat) 1682, 1596  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.10 (s, 9H), 0.30 (s, 9H), 6.79 (d,  $J = 6.8$  Hz, 2H), 7.14 (d,  $J = 6.8$  Hz, 2H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  71.9 (d,  $J = 31.4$  Hz, 1F), 87.1 (d,  $J = 31.4$  Hz, 1F); GC/MS  $m/z$  (%) 335 ( $\text{M}^+$ , 16), 333 ( $\text{M}^+$ , 49), 172 (56), 73 (100); Anal. Calcd for  $\text{C}_{14}\text{H}_{22}\text{ClF}_2\text{NSi}_2$ : C, 50.35; H, 6.64; N, 4.19. Found: C, 50.10; H, 6.78; N, 4.47.

**Lewis acid-catalyzed aldol reactions of bis(silyl)enamine 3b with aldehydes.**

To a mixture of **3b** (1.65 g, 5.0 mmol) and benzaldehyde (636.7 mg, 6.0 mmol) in dichloromethane (15 mL) which was cooled down to -78 °C under an argon atmosphere,  $\text{BF}_3 \cdot \text{OEt}_2$  (851 mg, 6.0 mmol) was added dropwise and the reaction mixture was allowed to warm up to 0 °C and then stirred for additional 1.5 h. After evaporation of the solvents, ethyl acetate was added to the residue. The residue was filtered through a short pad of activated neutral  $\text{Al}_2\text{O}_3$  with ethyl acetate. After removal of the solvent, purification of the crude product by chromatography on silica gel (hexane:ethyl acetate = 15:1), which was pretreated with triethylamine,

afforded **8a** (1.60g, 88%) as a yellow solid.

**2,2-Difluoro-3-[N-(*p*-methoxypheny)]imino-1-phenyl-3-(trimethylsilyl)propan-1-ol (8a).**

A yellow solid; mp 89-90 °C; IR (KBr) 3404, 1608, 1506  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.03 (s, 9H), 3.83 (s, 3H), 4.83 (d,  $J = 4.1$  Hz, 1H), 5.28 (ddd,  $J = 3.8, 4.1, 18.9$  Hz, 1H), 6.72 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 7.36-7.49 (m, 5H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  50.0 (dd,  $J_{\text{HF}} = 18.9$  Hz,  $J_{\text{FF}} = 302.0$  Hz, 1F), 61.2 (dd,  $J_{\text{HF}} = 3.8$  Hz,  $J_{\text{FF}} = 302.0$  Hz, 1F); Anal. Calcd. for  $\text{C}_{19}\text{H}_{23}\text{F}_2\text{NO}_2\text{Si}$ : C, 62.78; H, 6.38; N, 3.85. Found: C, 62.66; H, 6.46; N, 3.84.

**1,N-Bis(*p*-methoxypheny)-2,2-difluoro-3-imino-3-(trimethylsilyl)propan-1-ol (8b).**

A yellow solid; 84% yield; mp 94-95 °C; IR (KBr) 3492, 1618, 1518  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.02 (s, 9H), 3.82 (s, 3H), 3.83 (s, 3H), 4.76 (d,  $J = 3.6$  Hz, 1H), 5.22 (ddd,  $J = 3.6, 3.6, 19.7$  Hz, 1H), 6.72 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 6.93 (d,  $J = 8.4$  Hz, 2H), 7.43 (d,  $J = 8.4$  Hz, 2H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  49.5 (dd,  $J_{\text{HF}} = 19.7$  Hz,  $J_{\text{FF}} = 301.8$  Hz, 1F), 61.1 (dd,  $J_{\text{HF}} = 3.6$  Hz,  $J_{\text{FF}} = 301.8$  Hz, 1F); Anal. Calcd. for  $\text{C}_{20}\text{H}_{25}\text{F}_2\text{NO}_3\text{Si}$ : C, 61.05; H, 6.40; N, 3.56. Found: C, 61.04; H, 6.23; N, 3.51.

**2,2-Difluoro-3-[N-(*p*-methoxypheny)]imino-1-(*p*-chlorophenyl)-3-**

**(trimethylsilyl)propan-1-ol (8c).**

A pale yellow solid; 86% yield; mp 105-106 °C; IR (KBr) 3392, 2976, 1606, 1504  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.01 (s, 9H), 3.83 (s, 3H), 4.87 (d,  $J = 4.0$  Hz, 1H), 5.25 (ddd,  $J = 3.4, 4.0, 19.6$  Hz, 1H), 6.72 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 7.36 (d,  $J = 8.8$  Hz, 2H), 7.44 (d,  $J = 8.8$  Hz, 2H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  49.4 (dd,  $J_{\text{HF}} = 19.6$  Hz,  $J_{\text{FF}} = 304.7$  Hz, 1F), 61.2 (dd,  $J_{\text{HF}} = 3.4$  Hz,  $J_{\text{FF}} = 304.7$  Hz, 1F); Anal. Calcd. for  $\text{C}_{19}\text{H}_{22}\text{ClF}_2\text{NO}_2\text{Si}$ : C, 57.35; H, 5.57; N, 3.52. Found: C, 57.11; H, 5.76; N, 3.72.

**2,2-Difluoro-1-(2-furyl)-3-[*N*-(*p*-methoxypheny)]imino-3-(trimethylsilyl)propan-1-ol (8d).**

A yellow oil; 87% yield; IR (neat) 3444, 1608, 1504  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.01 (s, 9H), 3.82 (s, 3H), 4.76 (d,  $J = 6.2$  Hz, 1H), 5.29 (ddd,  $J = 5.6, 6.2, 15.6$  Hz, 1H), 6.41 (dd,  $J = 1.8, 3.2$  Hz, 1H), 6.45 (dd,  $J = 0.8, 3.2$  Hz, 1H), 6.70 (d,  $J = 9.0$  Hz, 2H), 6.88 (d,  $J = 9.0$  Hz, 2H), 7.45 (dd,  $J = 0.8, 1.8$  Hz, 1H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  52.6 (dd,  $J_{\text{HF}} = 15.6$  Hz,  $J_{\text{FF}} = 299.5$  Hz, 1F), 61.0 (dd,  $J_{\text{HF}} = 5.6$  Hz,  $J_{\text{FF}} = 299.5$  Hz, 1F); Anal. Calcd. for  $\text{C}_{17}\text{H}_{21}\text{F}_2\text{NO}_3\text{Si}$ : C, 57.78; H, 5.99; N, 3.96. Found: C, 58.04; H, 5.98; N, 4.01.

**2,2-Difluoro-3-[*N*-(*p*-methoxypheny)]imino-1-(2-thienyl)-3-(trimethylsilyl)propan-1-ol (8e).**

A yellow oil; 85% yield; IR (neat) 3432, 1582, 1506  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.00 (s, 9H), 3.82 (s, 3H), 5.03 (d,  $J = 5.5$  Hz, 1H), 5.51 (ddd,  $J = 5.0, 5.5, 16.4$  Hz, 1H), 6.71 (d,  $J = 8.5$  Hz, 2H), 6.88 (d,  $J = 8.5$  Hz, 2H), 7.03 (dd,  $J = 3.5, 5.2$  Hz, 1H), 7.14 (dd,  $J = 1.5, 3.5$  Hz, 1H), 7.34 (dd,  $J = 1.5, 5.2$  Hz, 1H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  51.5 (dd,  $J_{\text{HF}} = 16.4$  Hz,  $J_{\text{FF}} = 298.1$  Hz, 1F), 61.0 (dd,  $J_{\text{HF}} = 5.0$  Hz,  $J_{\text{FF}} = 298.1$  Hz, 1F); Anal. Calcd. for  $\text{C}_{17}\text{H}_{21}\text{F}_2\text{NO}_2\text{SSi}$ : C, 55.26; H, 5.73; N, 3.79. Found: C, 55.1; H, 5.88; N, 4.08.

**(*E*)-4,4-Difluoro-5-[*N*-(*p*-methoxyphenyl)]imino-1-phenyl-5-(trimethylsilyl)pent-1-en-3-ol (8f).**

A pale yellow solid; 59% yield; mp 64-65  $^{\circ}\text{C}$ ; IR (KBr) 3462, 1610, 1506  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  0.05 (s, 9H), 3.82 (s, 3H), 4.49 (d,  $J = 4.8$  Hz, 1H), 4.87 (dddd,  $J = 4.5, 4.8, 5.6, 16.1$  Hz, 1H), 6.36 (dd,  $J = 5.6, 15.2$  Hz, 1H), 6.70 (d,  $J = 8.5$  Hz, 2H), 6.78 (d,  $J = 15.2$  Hz, 1H), 6.87 (d,  $J = 8.5$  Hz, 2H), 7.26-7.35 (m, 3H), 7.40-7.45 (m, 2H);  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ )  $\delta$  50.6 (dd,  $J_{\text{HF}} = 16.1$  Hz,  $J_{\text{FF}} = 299.3$  Hz, 1F), 60.0 (dd,  $J_{\text{HF}} = 4.5$  Hz,  $J_{\text{FF}} = 299.3$  Hz, 1F); Anal. Calcd. for  $\text{C}_{21}\text{H}_{25}\text{F}_2\text{NO}_2\text{Si}$ : C, 64.75; H, 6.47; N, 3.60. Found: C, 64.97; H, 6.31; N, 3.43.

**2,2-Difluoro-1-[*N*-(*p*-methoxyphenyl)]imino-4-methyl-1-(trimethylsilyl)pentan-3-ol (8g).**

A colorless oil; 87% yield; IR (neat) 3472, 1582, 1506  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300

MHz, CDCl<sub>3</sub>)  $\delta$  0.05 (s, 9H), 1.08 (d,  $J$  = 6.9 Hz, 3H), 1.09 (d,  $J$  = 6.9 Hz, 3H), 2.14-2.24 (m, 1H), 3.82 (s, 3H), 3.93-4.08 (m, 2H), 6.69 (d,  $J$  = 8.5 Hz, 2H), 6.86 (d,  $J$  = 8.5 Hz, 2H); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  50.2 (dd,  $J_{\text{HF}}$  = 23.9 Hz,  $J_{\text{FF}}$  = 302.7 Hz, 1F), 61.2 (dd,  $J_{\text{HF}}$  = 3.4 Hz,  $J_{\text{FF}}$  = 302.7 Hz, 1F); Anal. Calcd. for C<sub>16</sub>H<sub>25</sub>F<sub>2</sub>NO<sub>2</sub>Si: C, 58.33; H, 7.65; N, 4.25. Found: C, 58.67; H, 7.98; N, 3.99.

**3,3-Difluoro-4-[N-(*p*-methoxyphenyl)]imino-2-methyl-4-(trimethylsilyl)butan-2-ol (8h).**

A yellow solid; 40% yield; mp 52-53 °C; IR (KBr) 3396, 1608, 1506 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.05 (s, 9H), 1.40 (s, 6H), 3.82 (s, 3H), 5.35 (s, 1H), 6.71 (d,  $J$  = 8.7 Hz, 2H), 6.87 (d,  $J$  = 8.7 Hz, 2H); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>)  $\delta$  54.3 (s, 2F); Anal. Calcd. for C<sub>15</sub>H<sub>23</sub>F<sub>2</sub>NO<sub>2</sub>Si: C, 57.12; H, 7.35; N, 4.44. Found: C, 56.94; H, 7.08; N, 4.37.

**Lewis acid-catalyzed aldol reactions of bis(silyl)enamine 3b with aldimines.**

To a mixture of **3b** (329.5 mg, 1.0 mmol) and *N*-benzylideneaniline (217.5 mg, 1.2 mmol) in dichloromethane (5 mL) which was cooled down to 0 °C under an argon atmosphere, BF<sub>3</sub>•OEt<sub>2</sub> (170.3 mg, 1.2 mmol) was added dropwise and the reaction mixture was allowed to warm up to reflux temperature and then stirred for additional 12 h. After evaporation of the



solvents, ethyl acetate was added to the residue. The residue was filtered through a short pad of activated neutral  $\text{Al}_2\text{O}_3$  with ethyl acetate. After removal of the solvent, purification of the crude product by chromatography on silica gel (hexane:ethyl acetate = 20:1), which was pretreated with triethylamine, afforded **8i** (337.1 mg, 79% ) as a yellow oil.

**2,2-Difluoro-1,*N*-diphenyl-3-[*N'*-(*p*-methoxyphenyl)]imino-3-(trimethylsilyl)propanamine (8i).**

IR (neat) 3416, 1608, 1508  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.13 (s, 9H), 3.80 (s, 3H), 4.99 (d,  $J$  = 6.6 Hz, 1H), 5.26-5.32 (m, 1H), 6.52 (d,  $J$  = 9.0 Hz, 2H), 6.62 (d,  $J$  = 7.5 Hz, 2H), 6.67 (t,  $J$  = 7.5 Hz, 1H), 6.82 (d,  $J$  = 9.0 Hz, 2H), 7.09 (t,  $J$  = 7.5 Hz, 2H), 7.27-7.35 (m, 3H), 7.46 (t,  $J$  = 7.5 Hz, 2H);  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  58.2 (dd,  $J_{\text{HF}}$  = 14.1 Hz,  $J_{\text{FF}}$  = 269.0 Hz, 1F), 61.7 (dd,  $J_{\text{HF}}$  = 9.3 Hz,  $J_{\text{FF}}$  = 269.0 Hz, 1F); Anal. Calcd. for  $\text{C}_{25}\text{H}_{28}\text{F}_2\text{N}_2\text{OSi}$ : C, 68.46; H, 6.43; N, 6.39. Found: C, 68.67; H, 6.47; N, 6.47.

**Ethyl 2-Amino-*N,N'*-bis(*p*-methoxyphenyl)-3,3-difluoro-4-imino-4-(trimethylsilyl)butanoate (8j).**

An orange oil; 60% yield; IR (neat) 3400, 1744, 1608, 1516  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.02 (s, 9H), 1.25 (t,  $J$  = 7.2 Hz, 3H), 3.73 (s, 3H), 3.80 (s, 3H), 4.21 (q,  $J$  = 7.0 Hz, 1H), 4.24 (q,  $J$  = 7.0 Hz, 1H), 4.25-4.28 (brs, 1H), 4.90 (ddd,  $J$  = 7.0, 8.5, 16.4 Hz, 1H), 6.61 (d,  $J$  = 8.8 Hz, 2H),

6.75 (m, 4H), 6.83 (d,  $J = 8.8$  Hz, 2H);  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  58.1 (dd,  $J_{\text{HF}} = 16.4$  Hz,  $J_{\text{FF}} = 282.3$  Hz, 1F), 63.1 (dd,  $J_{\text{HF}} = 7.0$  Hz,  $J_{\text{FF}} = 282.3$  Hz, 1F); Anal. Calcd. for  $\text{C}_{23}\text{H}_{30}\text{F}_2\text{N}_2\text{O}_4\text{Si}$ : C, 59.46; H, 6.51; N, 6.03. Found: C, 59.20; H, 6.27; N, 6.11.

### **Iododesilylation of *O*-protected imidoysilane **8a'**.**

To a suspension of KF (1.1 mmol) and iodine (248 mg, 1.2 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (3 mL) which was cooled down to 0 °C, was added dropwise the solution of **8a'** in dry  $\text{CH}_2\text{Cl}_2$  (2 mL) and the reaction mixture was stirred for additional 6 h. After evaporation of the solvents, ethyl acetate was added to the residue. The residue was filtered through a short pad of activated neutral  $\text{Al}_2\text{O}_3$  with ethyl acetate. After removal of the solvent, purification of the crude product by chromatography on silica gel (hexane:ethyl acetate = 20:1), which was pretreated with triethylamine, afforded **9** (500 mg, 96%) as a pale yellow solid.

### **2,2-Difluoro-3-iodo-3-[*N*-(*p*-methoxyphenyl)]imino-1-phenylpropyl Benzoate (**9**).**

A pale yellow solid; mp 113-114 °C; IR (KBr) 1732, 1694, 1604, 1582, 1506  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82 (s, 3H), 6.76 (d,  $J = 8.5$  Hz, 2H), 6.81 (dd,  $J = 9.3, 16.4$  Hz, 1H), 6.88 (d,  $J = 8.5$  Hz, 2H), 7.38-7.51 (m, 5H), 7.58-7.63 (m, 3H), 8.10-8.14 (m, 2H);  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  57.7 (dd,  $J_{\text{HF}} = 16.4$  Hz,  $J_{\text{FF}} = 260.2$  Hz, 1F), 60.9 (dd,  $J_{\text{HF}} = 9.3$  Hz,  $J_{\text{FF}} =$

260.2 Hz, 1F); Anal. Calcd for C<sub>23</sub>H<sub>18</sub>F<sub>2</sub>INO<sub>3</sub>: C, 52.99; H, 3.48; N, 2.69. Found: C, 52.93; H, 3.62; N, 2.52.

**Pd(0)-catalyzed carboalkoxylation of imidoyl iodide 9.**

A two-necked flask with a CO (1 atm) ballon attached was charged Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (15.9 mg, 0.015 mmol) and K<sub>2</sub>CO<sub>3</sub> (55 mg, 0.4 mmol). Then 104.3 mg (0.2 mmol) of imidoyl iodide **9** in 2.5 mL of toluene was added to the catalyst mixture. After reaction mixture was stirred for 10 min. at rt, 20.3 mg (0.44 ml) of ethyl alcohol was added to the reaction mixture. The reaction vessel was wrapped in aluminum foil to minimize exposure to the light and the mixture was stirred for 20 h at room temperature. The resulted suspension was filtered through a short Florisil column (CH<sub>2</sub>Cl<sub>2</sub>). After removal of solvent, the residue was purified by silica gel column chromatography (hexane : ether (15:1) elute) to afford **10a** as a yellow oil (91.6 mg, 98%).

**Ethyl 4-Benzoyloxy-3,3-difluoro-2-[N-(*p*-methoxyphenyl)]imino-4-phenylbutanoate (10a).**

IR (neat) 1736, 1658, 1582, 1504 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.08 (t, *J* = 7.2 Hz, 3H), 3.78 (s, 3H), 4.15 (q, *J* = 7.2 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 1H), 6.73-6.85 (m, 5H), 7.37-7.49 (m, 5H), 7.56-7.63 (m, 3H), 8.12~8.15 (m, 2H); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 47.4 (dd, *J*<sub>HF</sub> = 16.1 Hz, *J*<sub>FF</sub> = 268.0 Hz, 1F), 56.1 (dd, *J*<sub>HF</sub> = 9.3 Hz, *J*<sub>FF</sub> = 268.0 Hz, 1F); Anal.

Calcd for C<sub>26</sub>H<sub>23</sub>F<sub>2</sub>NO<sub>5</sub>: C, 66.80; H, 4.96; N, 3.00. Found: C, 67.00; H, 5.19; N, 3.20.

**Benzyl 4-Benzoyloxy-3,3-difluoro-2-[N-(*p*-methoxyphenyl)]imino-4-phenylbutanoate (10b).**

A yellow solid; 97% yield; mp 101-102 °C; IR (KBr) 1732, 1606, 1526, cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.75 (s, 3H), 5.08 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 2H), 6.76 (dd, *J* = 9.3, 16.4 Hz, 1H), 7.04-7.06 (m, 2H), 7.23-7.30 (m, 3H), 7.38-7.43 (m, 5H), 7.53-7.60 (m, 3H), 8.01-8.11 (m, 2H); <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>) δ 47.5 (dd, *J*<sub>HF</sub> = 16.4 Hz, *J*<sub>FF</sub> = 268.2 Hz, 1F), 56.4 (dd, *J*<sub>HF</sub> = 9.3 Hz, *J*<sub>FF</sub> = 268.2 Hz, 1F); Anal. Calcd for C<sub>31</sub>H<sub>25</sub>F<sub>2</sub>NO<sub>5</sub>: C, 70.31; H, 4.76; N, 2.65. Found: C, 70.31; H, 4.93; N, 2.65.