

## Supporting Information

### Lithium Triethylborohydride-Promoted Generation of $\alpha,\alpha$ -Difluoroenolates From 2-Iodo-2,2-Difluoroacetophenones: An Unprecedented Utilization of Lithium Triethylborohydride

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#### Table of Contents

1 General procedures .....	S2
2 The procedure for preparation of <b>Compounds 2</b> .....	S2
3 The reduction reactions with LiEt <sub>3</sub> BH and $\alpha$ -halogen acetophenones.....	S4
4 Typical reduction reactions of 2-iodo-2,2-difluoroacetophenone.....	S5
5 The aldol reactions of 2-iodo-2,2-difluoroacetophenones.....	S5
6 LiEt <sub>3</sub> BH-promoted reaction of 2,2-difluoro-3-hydroxy-1,3-diphenylpropan-1-one with benzaldehyde.....	S6
7 References.....	S6
8 Spectral data of Products.....	S7-S21

## 1 General procedures.

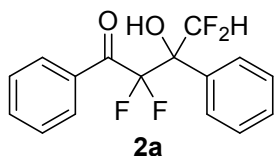
All reactions were carried out under argon atmosphere. Tetrahydrofuran (THF) were distilled over sodium. All reagents were commercially available and used without further purification unless indicated otherwise. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on GF254 plates (0.25 mm layer thickness) using UV light as visualizing agent. Flash chromatography was performed with 400-500 mesh silica gels.

All NMR spectra were recorded on a Bruker Avance 500 (resonance frequencies 500 MHz for  $^1\text{H}$  and 125 MHz for  $^{13}\text{C}$ ) equipped with a 5 mm inverse broadband probe head with z-gradients at 295.8 K with standard Bruker pulse programs. The samples were dissolved in 0.6 ml  $\text{CDCl}_3$  (99.8% D.TMS). Chemical shifts were given in values of  $\delta^{\text{H}}$  and  $\delta^{\text{C}}$  referenced to residual solvent signals ( $\delta_{\text{H}}$  7.26 for  $^1\text{H}$ ,  $\delta_{\text{C}}$  77.0 for  $^{13}\text{C}$  in  $\text{CDCl}_3$ ). The  $^{19}\text{F}$  NMR spectra were obtained using a 500 spectrometer (470 MHz) using trifluorotoluene as external standard. High resolution mass spectra (HRMS) were recorded on a Bruker solan X 70 FT-MS (samples was dissolved in  $\text{CH}_3\text{OH}$  and the ion source was ESI), and the energy was 22.5eV at MS/MS. Melting points are uncorrected.

## 2 The procedure for preparation of Compound 2.

To a solution of 2-iodo-2,2-difluoroacetophenones **1** (1 mmol, 1.0 equiv.) in THF(dry, 10mL) was dropwise added Lithium triethylborohydride ( $\text{LiEt}_3\text{BH}$ , a superhydride, 1M in THF) (1.2 mmol, 1.2 equiv.) at  $-78^\circ\text{C}$ . The mixture was stirred at that temperature under  $\text{N}_2$  protection for 4h. The reaction was quenched with water (10mL), and extracted with ethyl acetate (3 x 20mL), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo to give the crude product, which was purified carefully by column chromatography, eluting Petroleum ether /Ethyl acetate to afford the product **2** as yellow oil (70-87%).

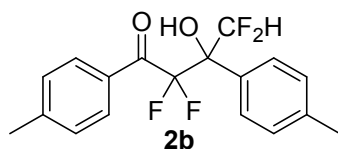
### 2,2,4,4-tetrafluoro-3-hydroxy-1,3-diphenylbutan-1-one (**2a**)



Yellow liquid, 86% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.94 (d,  $J$  = 5.0Hz, 2H), 7.62 (m, 3H), 7.41 (m, 5H), 6.39 (t,  $J$  = 15.0 Hz 1H), 4.24 (s, 1H).

$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -105.5 (dt,  $J$  = 296.1, 9.4Hz, 1F), -106.6 (dt,  $J$  = 296.1, 9.4Hz, 1F), -128.7 (dt,  $J$  = 286.7, 9.4Hz, 1F), -130.3 (m, 1F). Spectral data matched those previously reported.<sup>1</sup>

### 2,2,4,4-tetrafluoro-3-hydroxy-1,3-di-p-tolylbutan-1-one (**2b**)



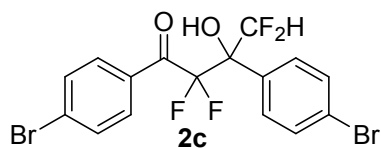
Yellow liquid, 83% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.87 (d,  $J$  = 10.0Hz, 2H), 7.52 (d,  $J$  = 10.0Hz, 2H), 7.22(dd,  $J$  = 20.0, 5.0Hz, 4H), 6.35 (t,  $J$  = 55.0 Hz 1H), 4.26 (s, 1H), 2.38(d,  $J$  = 35.0Hz, 6H).

$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -105.2 (m, 1F), -106.5 (dt,  $J$  = 296.1, 9.4Hz, 1F), -128.7 dt,  $J$  = 286.7, 9.4Hz, 1F), -130.5 (m, 1F).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  190.0 (t,  $J$  = 28.8 Hz), 146.2, 139.2, 130.5, 129.3 (d,  $J$  = 20.0 Hz), 115.0(t,  $J$  = 124.4 Hz), 114.0 (t,  $J$  = 250.0 Hz), 78.0 (t,  $J$  = 22.5 Hz), 21.4, 21.1.

ESI-HRMS (m/z): calculated for  $\text{C}_{18}\text{H}_{16}\text{F}_4\text{O}_2$  ( $\text{M}+\text{Na}$ )<sup>+</sup> : 363.0978, found: 363.0977.

1,3-bis(4-bromophenyl)-2,2,4,4-tetrafluoro-3-hydroxybutan-1-one (**2c**)



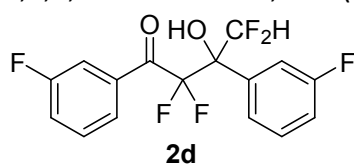
Yellow liquid, 85% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.86 (d,  $J$  = 10.0 Hz, 2H), 7.59 (m, 6H), 6.36 (t,  $J$  = 55.0 Hz, 1H), 4.19 (s, 1H).

$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -105.3 (m, 1F), -106.8 (dt,  $J$  = 296.1, 9.4 Hz, 1F), -128.1 (dt,  $J$  = 291.4, 9.4 Hz, 1F), -130.2 (m, 1F).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  189.2 (t,  $J$  = 30.0 Hz), 132.2, 131.7, 131.6, 131.3, 131.0, 130.8, 129.5, 124.1, 115.6 (t,  $J$  = 137.5 Hz), 113.6 (t,  $J$  = 250.0 Hz), 77.9 (t,  $J$  = 12.5 Hz).

ESI-HRMS ( $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{10}\text{Br}_2\text{F}_4\text{O}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 490.8875, found: 490.8866.

2,2,4,4-tetrafluoro-1,3-bis(3-fluorophenyl)-3-hydroxybutan-1-one (**2d**)



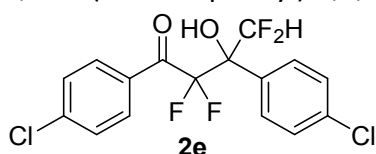
Yellow liquid, 72% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.78 (d,  $J$  = 5.0 Hz, 1H), 7.65 (d,  $J$  = 5.0 Hz, 1H), 7.40 (m, 4H), 7.26 (t,  $J$  = 5.0 Hz, 1H), 7.106 (t,  $J$  = 5.0 Hz, 1H), 6.35 (t,  $J$  = 55.0 Hz, 1H), 4.15 (s, 1H).

$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -105.6 (dt,  $J$  = 296.1, 9.4 Hz, 1F), -106.9 (dt,  $J$  = 296.1, 9.4 Hz, 1F), -110.9, -111.6, -128.4 (dt,  $J$  = 286.7, 9.4 Hz, 1F), -130.2 (m, 1F).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  188.8 (t,  $J$  = 32.5 Hz), 163.7, 163.4, 161.8, 161.4, 134.7 (d,  $J$  = 7.5 Hz), 134.3, 130.4 (d,  $J$  = 8.8 Hz), 130.0 (d,  $J$  = 7.5 Hz), 126.1, 122.5, 122.0 (d,  $J$  = 21.3 Hz), 117.0 (d,  $J$  = 23.8 Hz), 116.5 (d,  $J$  = 20.0 Hz), 115.6, 115.1, 114.9, 114.7, 114.5, 112.8 (t,  $J$  = 121.9 Hz), 77.8 (t,  $J$  = 11.3 Hz).

ESI-HRMS ( $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{F}_4\text{O}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 371.0477, found: 371.0474.

1,3-bis(4-chlorophenyl)-2,2,4,4-tetrafluoro-3-hydroxybutan-1-one (**2e**)



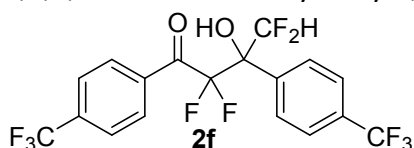
Yellow liquid, 87% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.92 (d,  $J$  = 5.0 Hz, 2H), 7.57 (d,  $J$  = 10.0 Hz, 2H), 7.41 (dd,  $J$  = 30.0, 10.0 Hz, 4H), 6.34 (t,  $J$  = 55.0 Hz, 1H), 4.23 (s, 1H).

$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -105.3 (m, 1F), -106.8 (dt,  $J$  = 291.4, 9.4 Hz, 1F), -128.0 (dt,  $J$  = 291.4, 9.4 Hz, 1F), -130.2 (m, 1F).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  189.0 (t,  $J$  = 30.0 Hz), 141.9, 135.7, 131.3, 130.7 (d,  $J$  = 13.8 Hz), 129.1, 128.7, 128.4, 115.7 (t,  $J$  = 132.5 Hz), 113.7 (t,  $J$  = 250.0 Hz), 77.8 (t,  $J$  = 21.3 Hz).

ESI-HRMS ( $m/z$ ): calculated for  $\text{C}_{16}\text{H}_{10}\text{Cl}_2\text{F}_4\text{O}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 402.9886, found: 402.9879.

2,2,4,4-tetrafluoro-3-hydroxy-1,3-bis(4-(trifluoromethyl)phenyl)butan-1-one (**2f**)



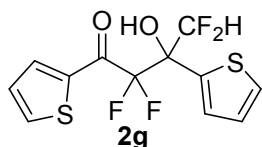
Yellow liquid, 71% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.08 (d,  $J$  = 10.0 Hz, 2H), 7.79 (d,  $J$  = 5.0 Hz, 2H), 7.73 (d,  $J$  = 10.0 Hz, 2H), 7.68 (d,  $J$  = 10.0 Hz, 2H), 6.40 (t,  $J$  = 55.0 Hz, 1H), 4.17 (s, 1H).

$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -63.0(s, 3F), -63.6(s, 3F), -105.5 (dt,  $J$  = 296.1, 9.4Hz, 1F) , -107.2 (dt,  $J$  = 296.1, 9.4Hz, 1F), -127.9 (dt,  $J$  = 291.4, 9.4Hz, 1F), -130.0 (m, 1F).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  189.1 (t,  $J$  = 30.0 Hz), 136.0, 135.6, 128.3(d,  $J$  = 6.3Hz), 127.5, 125.4, 125.3, 122.6, 122.1, 115.6(t,  $J$  = 131.9Hz), 113.6 (t,  $J$  = 250.0Hz), 77.9 (t,  $J$  = 20.0Hz).

ESI-HRMS (m/z): calculated for  $\text{C}_{18}\text{H}_{10}\text{F}_{10}\text{O}_2$  (M+Na) $^+$  : 471.0413 , found:471.0447.

### 2,2,4,4-tetrafluoro-3-hydroxy-1,3-di(thiophen-2-yl)butan-1-one (**2g**)



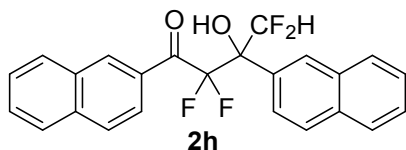
Yellow liquid, 70% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.04 (s, 1H), 7.88 (d,  $J$  = 5.0 Hz, 1H), 7.43 (d,  $J$  = 5.0 Hz, 1H), 7.31 (s, 1H), 7.21 (t,  $J$  = 5.0 Hz, 1H), 7.08 (t,  $J$  = 5.0 Hz, 1H), 6.26 (t,  $J$  = 55.0 Hz, 1H), 4.78 (s, 1H).

$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -108.3 (ddd,  $J$  = 286.7, 14.1, 4.7Hz, 1F) , -109.5 (dt,  $J$  = 282.0, 9.4Hz, 1F), -128.0 (m, 1F), -130.6 (m, 1F).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  183.0 (t,  $J$  = 62.5 Hz), 138.1(d,  $J$  = 11.3 Hz), 137.2 (t,  $J$  = 6.3 Hz), 135.3, 129.1, 127.3(d,  $J$  = 16.3Hz), 113.6 (t,  $J$  = 245.0Hz), 113.1 (t,  $J$  = 250.0Hz), 77.9 (t,  $J$  = 22.5 Hz).

ESI-HRMS (m/z): calculated for  $\text{C}_{12}\text{H}_8\text{F}_4\text{O}_2\text{S}_2$  (M+Na) $^+$  : 346.9794, found: 346.9789.

### 2,2,4,4-tetrafluoro-3-hydroxy-1,3-di(naphthalen-2-yl)butan-1-one (**2h**)



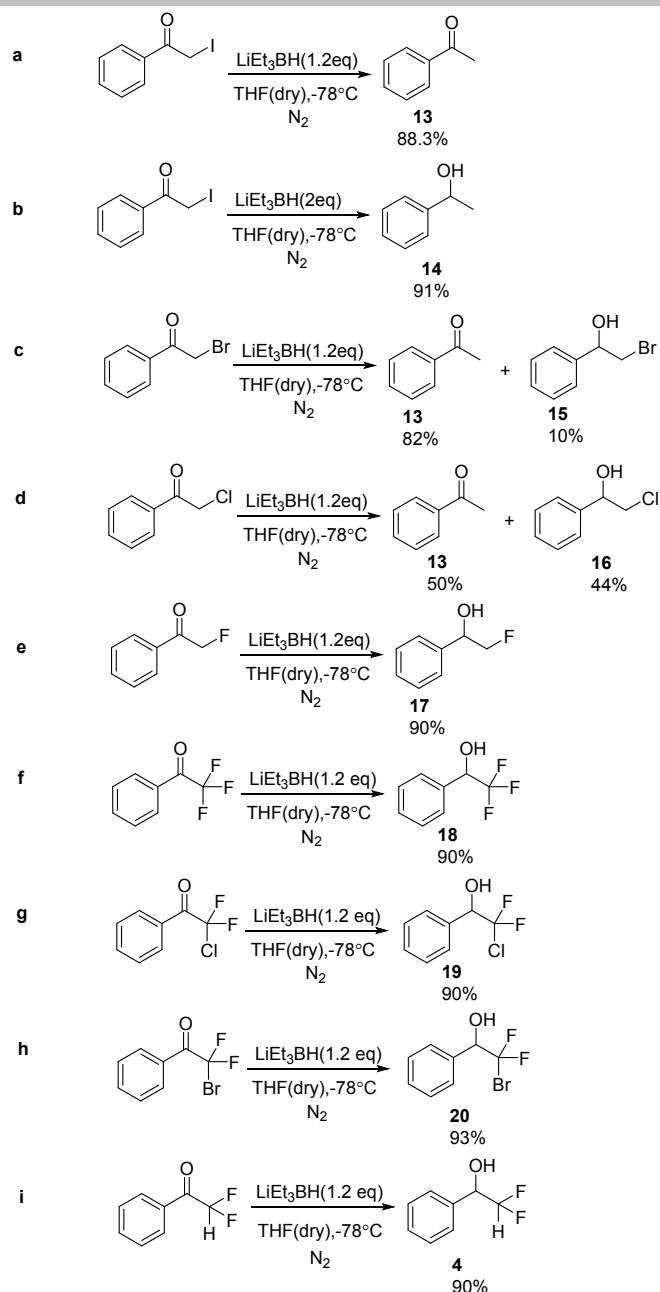
Colourless liquid, 84% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.53 (s, 1H), 8.18 (s, 1H), 7.83 (m, 8H), 7.60 (t,  $J$  = 5.0 Hz, 1H), 7.50 (m, 3H), 6.52 (t,  $J$  = 55.0 Hz, 1H), 4.49 (s, 1H).

$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -104.3 (dt,  $J$  = 296.1, 9.4Hz, 1F) , -105.6 (dt,  $J$  = 291.4, 9.4Hz, 1F), -128.1 (dt,  $J$  = 291.4, 9.4Hz, 1F), -130.0 (dt,  $J$  = 286.7, 9.4Hz, 1F) . Spectral data matched those previously reported.<sup>2</sup>

### 3 The reduction reactions with $\text{LiEt}_3\text{BH}$ and $\alpha$ -halogen acetophenones.

To a solution of 2-iodo-1-phenylethanone (1 mmol, 1.0 equiv.) in THF(dry, 10mL) was dropwise added Lithium triethylborohydride ( $\text{LiEt}_3\text{BH}$ , a superhydride, 1M in THF) (1.2mmol, 1.2 equiv.) at  $-78^\circ\text{C}$ . The mixture was stirred at that temperature under  $\text{N}_2$  protection for 4h. The reaction was quenched with water (10mL), and extracted with ethyl acetate (3 x 20mL), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo to give the crude product, then analysed by GC.

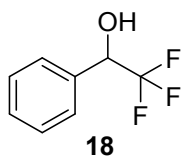
The result was shown in scheme 1.



<sup>a</sup> Yield based on GC.

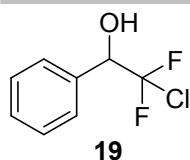
**Scheme 1** The reduction reactions of 2-iodo-2,2-difluoroacetophenone **1a**.<sup>a</sup>

2,2,2-trifluoro-1-phenylethan-1-ol (**18**)



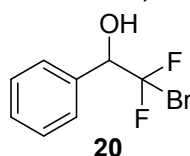
Yellow liquid, 90% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.42 (m, 5H), 4.98 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.91 (s, 1H). Spectral data matched those previously reported.<sup>3</sup>

2-chloro-2,2-difluoro-1-phenylethan-1-ol (**19**)



Yellow liquid, 90% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta = 7.43$  (m, 5H), 4.97 (t,  $J = 10.0$  Hz, 1H), 3.10 (s, 1H). Spectral data matched those previously reported.<sup>4</sup>

#### 2-bromo-2,2-difluoro-1-phenylethan-1-ol (**20**)



Yellow liquid, 93% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta = 7.48$  (t,  $J = 5.0$  Hz, 2H), 7.40 (t,  $J = 5.0$  Hz, 3H), 5.00 (t,  $J = 5.0$  Hz, 1H), 3.00 (s, 1H) ppm. Spectral data matched those previously reported.<sup>5</sup>

#### 4 Typical reduction reactions of 2-iodo-2,2-difluoroacetophenone.

The reduction of **1a** with  $\text{NaBH}_4$ : To a solution of **1a** (1.0 mmol, 1.0 equiv.) in MeOH was added  $\text{NaBH}_4$  (1.0 mmol, 1.0 equiv.) at  $0^\circ\text{C}$ . The mixture was stirred at that temperature for 5 min. Then, remove the solvent under reduced pressure, extracted with DCM (10 mL). Analysed by GC.

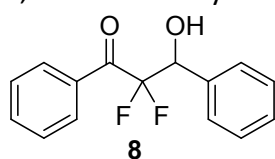
The reduction of **1a** with DIBAL-H: To a solution of **1a** (1.0 mmol, 1.0 equiv.) in Toluene was dropwise added DIBAL-H (2.0 mmol, 2.0 equiv.) at  $0^\circ\text{C}$ . The mixture was stirred at room temperature under  $\text{N}_2$  protection overnight. Then, the reaction was quenched with water (10 mL), and extracted with ethyl acetate (10 mL). Analysed by GC.

The reduction of **1a** with Zn powder: To a solution of **1a** (1.0 mmol, 1.0 equiv.) in EtOH was added Zn powder (1.0 mmol, 1.0 equiv.) and  $\text{CaCl}_2$  (1.0 mmol, 1.0 equiv.) at room temperature. The mixture was stirred at rt for 5 min. Then, the mixture was refluxed for 1 h. Moved out the solid. Analysed by GC.

#### 5 The aldol reactions of 2-iodo-2,2-difluoroacetophenone with $\text{LiEt}_3\text{BH}$ .

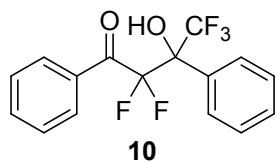
To a solution of **1a** (1 mmol, 1.0 equiv.) and **7** (1 mmol, 1.0 equiv.) in THF (dry, 10 mL) was dropwise added Lithium triethylborohydride ( $\text{LiEt}_3\text{BH}$ , a superhydride, 1M in THF) (1.2 mmol, 1.2 equiv.) at  $-78^\circ\text{C}$ . The mixture was stirred at that temperature under  $\text{N}_2$  protection for 4 h. The reaction was quenched with water (10 mL), and extracted with ethyl acetate (3 x 20 mL), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo to give the crude product, which was purified carefully by column chromatography, eluting Petroleum ether / Ethyl acetate to afford the product **8** as yellow oil (93%).

#### 2,2-difluoro-3-hydroxy-1,3-diphenylpropan-1-one (**8**)



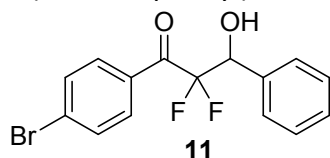
Yellow liquid, 93% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta = 7.94$  (d,  $J = 5.0$  Hz, 2H), 7.62 (m, 3H), 7.42 (m, 5H), 6.39 (dt,  $J = 55.0$  Hz, 1H), 4.24 (s, 1H). Spectral data matched those previously reported.<sup>6</sup>

## 2,2,4,4,4-pentafluoro-3-hydroxy-1,3-diphenylbutan-1-one (**10**)



Yellow liquid, 86% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.91 (d,  $J$  = 5.0 Hz, 2H), 7.73 (d,  $J$  = 5.0 Hz, 2H), 7.62 (t,  $J$  = 5.0 Hz, 1H), 7.41 (m, 5H), 4.87 (s, 1H) ppm. Spectral data matched those previously reported.<sup>7</sup>

## 1-(4-bromophenyl)-2,2-difluoro-3-hydroxy-3-phenylpropan-1-one (**11**)



Yellow liquid, 89% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.89 (d,  $J$  = 10.0 Hz, 2H), 7.61 (d,  $J$  = 10.0 Hz, 2H), 7.48 (d,  $J$  = 5.0 Hz, 2H), 7.39 (t,  $J$  = 5.0 Hz, 3H), 5.34 (dt,  $J$  = 20.0, 5.0 Hz, 1H), 3.10 (dd,  $J$  = 5.0 Hz, 1H).

$^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )  $\delta$  = -104.9 (d,  $J$  = 291.4 Hz, 1F), -116.4 (d,  $J$  = 286.7 Hz, 1F).

$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  190.2 (t,  $J$  = 30.0 Hz), 134.6, 132.1, 131.6, 130.2, 129.2, 128.4, 128.1, 115.8 (t,  $J$  = 250.0 Hz), 73.3 (t,  $J$  = 25.0 Hz).

ESI-HRMS ( $m/z$ ): calculated for  $\text{C}_{15}\text{H}_{11}\text{F}_2\text{O}_2\text{Br}$  ( $\text{M}+\text{Na}$ )<sup>+</sup> : 362.9802, found: 362.9840.

## 6 $\text{LiEt}_3\text{BH}$ -promoted reaction of 2,2-difluoro-3-hydroxy-1,3-diphenylpropan-1-one with benzaldehyde.

To a solution of 2,2-difluoro-3-hydroxy-1,3-diphenylpropan-1-one (1 mmol, 1.0 equiv.) and **7** (1 mmol, 1.0 equiv.) in THF (dry, 10 mL) was dropwise added Lithium triethylborohydride ( $\text{LiEt}_3\text{BH}$ , a superhydride, 1 M in THF) (1.2 mmol, 1.2 equiv.) at  $-78^\circ\text{C}$ . The mixture was stirred at that temperature under  $\text{N}_2$  protection for 4 h. The reaction was quenched with water (10 mL), and extracted with ethyl acetate (3 x 20 mL), the combined organic layers were dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo to give the crude product, which was purified carefully by column chromatography, eluting Petroleum ether / Ethyl acetate to afford the product **8** as yellow oil (76%) and **2a** (19%).

## 7 References

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## 8 Spectral data of Products

