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Rational and practical synthesis of α,α-difluoro-γ-lactams

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ABSTRACT

Treatment of *N*-phenyl-iododifluoroacetamide (**1**) with terminal alkenes (**2**) in the presence of $Na_2S_2O_4$ and $NaHCO_3$ in CH_3CN/H_2O gave good yields of *N*-phenyl-2,2-difluoro-4-iodoalkanamide (**3**), which cyclized under strong basic conditions to afford *N*-phenyl-α,α-difluoro-γ-lactams (**4**). Or simply, these lactams **4** can be directly prepared in one-pot from **1** and **2** in the presence of $Na_2S_2O_4$ and NaOH.

1. Introduction

Lactams and their benzo-/hetero-fused analogues represent an important class of organic azaheterocycles for their presence in numerous natural products and synthetic organic compounds along with diverse bio-, physio- and pharmacological activities [1]. Introduction of a difluoromethylene group into lactams is of great interest due to the fact that difluoromethylenation of natural products and drugs has demonstrated significant improvements of their activities and properties [2]. Extensive work has generated several synthetic approaches to α,α-difluoro-γ-lactams [3], including intramolecular cyclization of *N*-allylhalodifluoroacetamides [3a] or difluoropropargyl amides [3b], the reaction of ethyl 2,2-difluoro-4-iodo-4-(trimethylsilyl)butanolate with primary amines [3c], and the transformation of the α-carbonyl group of cyclic α-keto amide to difluoromethylene group by utilization of Deoxofluor [3d]. Each of these approaches represents an important advance toward the objective of a general method for the synthesis of α,α-difluoro-γ-lactams. However, they are still more or less limited in their use by their lack of generality, poor yields, or the difficulties in obtaining the starting materials. In light of this, development of efficient synthetic approaches from easily available starting materials for such fluorine-containing heterocycles is still in demand.

In connection with our ongoing interest in fluoroalkylation of organic compounds [4], we envisioned that $Na_2S_2O_4$ induced addition of *N*-phenyl-iododifluoroacetamide to alkenes could give *N*-phenyl-2,2-difluoro-4-iodoalkanamide, which might undergo cyclization under basic conditions to afford *N*-phenyl-α,α-difluoro-γ-lactams. Herein we present the results.

2. Results and discussion

The starting material, *N*-phenyl-iododifluoroacetamide (**1**) was easily prepared from *N*-phenyl-α-fluorosulfonyldifluoroacetamide in 66% yield according to the literature method [5] (Scheme 1).

Then, **1** was subjected to the typical sulfinatodehalogenation [6] conditions, i.e., **1** was treated with 1-hexene (**2a**) in the presence of $Na_2S_2O_4$ and $NaHCO_3$ in a mixture solvent of CH_3CN/H_2O at 10–15 °C. TLC analysis revealed that the reaction was completed within 20 min. After work-up and purification by chromatography, a pale yellow solid was obtained. To our delight, the solid was characterized to be the desired *N*-phenyl-2,2-difluoro-4-iodo-octanamide (**3a**) by its NMR, MS, IR and HRMS. Under similar conditions, the reaction of **1** with other terminal alkenes also proceeded smoothly to give the addition products **3b**–**3e** in good yields (Table 1).

With these *N*-phenyl-2,2-difluoro-4-iodo-alkanamide in hands, we next examined their reactions under basic conditions expecting to prepare *N*-phenyl-α,α-difluoro-γ-lactams *via* intramolecular substitution reaction. As illustrated in Table 2, when 1.0 equiv. of $NaHCO_3$ was used, no reaction occurred (entry 1, Table 2). Even when 6.0 equiv. of $NaHCO_3$ was used, only a trace amount of cyclization product **4a** was observed (entry 2, Table 2). Then, stronger bases were examined. The addition of 3.0 equiv. of K_2CO_3 instead of $NaHCO_3$ led to a significant increase in the yield of **4a** to 47% (entry 3, Table 2). The best result was obtained by using 1.0 equiv. NaOH in aqueous acetonitrile solution (entry 4, Table 2).

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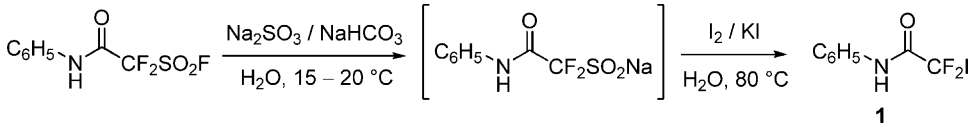
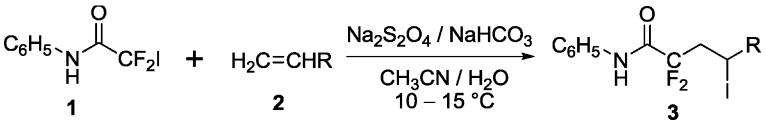


Scheme 1. Preparation of iododifluoroacetamide **1**.

Table 1
The reaction of *N*-phenyl-iododifluoroacetamide with terminal alkenes.[a] .



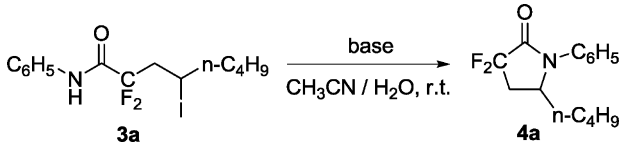
Entry	R	Product	Yield (%)[b]
1	1-Butyl	**3a**	83
2	Trimethylsilyl	**3b**	84
3	CH_2OH–	**3c**	78
4	$C_6H_5CH_2$–	**3d**	75
5	$CH_3(O)COCH_2$–	**3e**	76

[a] Reaction conditions: 2.0 equiv. alkene, 1.2 equiv. $Na_2S_2O_4$, 1.2 equiv. $NaHCO_3$, CH_3CN (5 mL), H_2O (3 mL), under nitrogen, 10–15 °C, 20 min, at 2.0 mmol scale.
[b] Isolated yields.

Having established a two-step procedure for **4a**, and considering that the two steps were both performed under basic conditions, we turned our attention to achieve a one-pot method for the synthesis of *N*-phenyl-α,α-difluoro-γ-lactams. Thus, **1** was treated with 1-hexene (**2a**) in the presence of $Na_2S_2O_4$ and NaOH in CH_3CN/H_2O at 10–15 °C, and *N*-phenyl-α,α-difluoro-γ-lactam **4a** was indeed formed in 72% yield (entry 1, Table 3). When other terminal alkenes were used (entry 2–5, Table 3), the corresponding *N*-phenyl-α,α-difluoro-γ-lactams **4** can also be obtained in good yields except the one bearing a hydroxymethyl group (entry 3, Table 3). The low yield of **4c** might be attributed to the involvement of the hydroxymethyl group in the reaction under strong basic conditions. It should be noted that in the case of **4d**, the addition of another portion of NaOH was needed, otherwise **4d** could only be produced in 36% yield, and **3d** was obtained in 40% yield in the meantime (entry 4, Table 3). The structures of these cyclization products were fully characterized. Among them, the structure of **4e** was unambiguously determined by the X-ray crystallography (Fig. 1).

On the basis of the above experimental results together with the related reports [7], a possible mechanism for the formation of **3** and **4** is proposed and depicted in Scheme 2. Initially, R_fI **1** accepted one electron from the radical anion of sulfur dioxide, which was produced by decomposition of $Na_2S_2O_4$, and dissociated to give $R_f^{\bullet}$ and I^- [8]. The $R_f^{\bullet}$ added to terminal alkenes to form intermediate **A**.

Table 2
Optimization of conditions for the cyclization of *N*-phenyl-2,2-difluoro-4-iodo-alkanamide. .



Entry	Base	Equivalent	Time (h)	Yield (%)[a]
1	$NaHCO_3$	1.0	10	0[b]
2	$NaHCO_3$	6.0	10	Trace[b]
3	K_2CO_3	3.0	6	47[c]
4	NaOH	1.0	0.5	92

[a] Isolated yields.
[b] Recovery of starting material was 99%.
[c] Recovery of starting material was 50%.

The intermediate **A** abstracted iodine from R_fI to afford 4-iodo-alkanamide **3**. The amide **3** could form anions **B** by deprotonation of the nitrogen in the presence of strong base. Finally, the intramolecular *N*-alkylation of intermediate **B** led to the formation of lactams **4**.

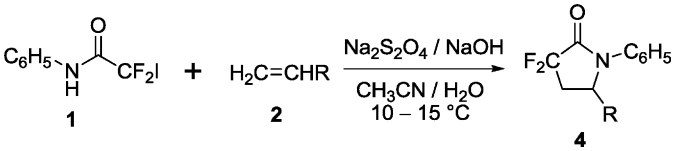
In conclusion, a rational and practical synthetic method for *N*-phenyl-α,α-difluoro-γ-lactams had been developed. A possible mechanism for the formation of *N*-phenyl-2,2-difluoro-4-iodo-alkanamides and *N*-phenyl-α,α-difluoro-γ-lactams is proposed.

3. Experimental

3.1. General experimental procedures

Unless otherwise mentioned, solvents and regents were commercially available and used as received. *N*-phenyl-α-fluorosulfonyldifluoroacetamide was prepared according to the literature method. All melting points were uncorrected. IR spectra were taken on Nicolet AV-360 spectrophotometer. ^{1}H NMR spectra were recorded on Bruker 300 or Mercury 300 spectrometers with Me_4Si as internal standard. ^{19}F NMR spectra were recorded on Bruker 300 or Mercury 300 spectrometers with $CFCl_3$ as external standard. Mass spectra were obtained on a HP5989A spectrometer.

Table 3
One-pot synthesis of *N*-phenyl-α,α-difluoro-γ-lactam derivatives.[a] .



Entry	R	Product	Yield (%)[b]
1	1-Butyl	**4a**	72
2	Trimethylsilyl	**4b**	79
3	CH_2OH–	**4c**	40
4[c]	$C_6H_5CH_2$–	**4d**	66
5	$CH_3(O)COCH_2$–	**4e**	64

[a] Reaction conditions: 2.0 equiv. alkene, 1.5 equiv. $Na_2S_2O_4$, 1.5 equiv. NaOH, CH_3CN (5 mL), H_2O (3 mL), under nitrogen, 10–15 °C, 30 min, at 1.0 mmol scale.
[b] Isolated yields.
[c] After being stirred for 30 min, another portion of NaOH (1.5 equiv.) was added to the reaction mixture, and the stirring was continued for 30 min.

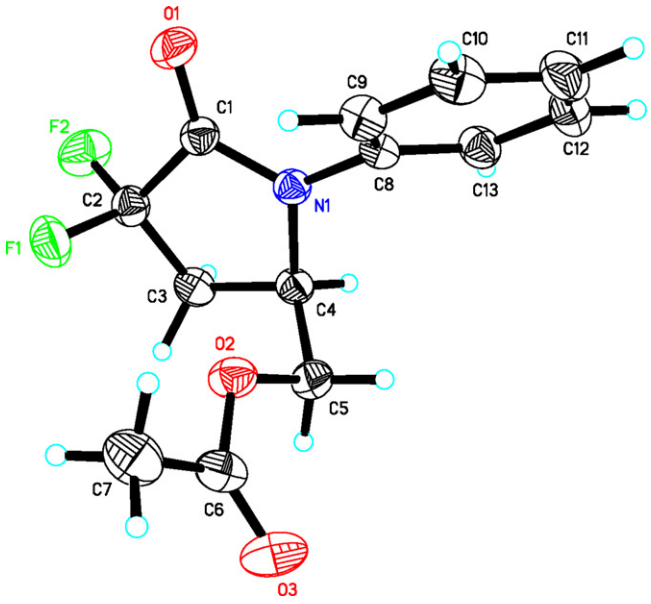


Fig. 1. Top view of the X-ray crystal structure of **4e**.

3.2. Preparation of N-phenyl-iododifluoroacetamide (1)

Under a nitrogen atmosphere, Na_2SO_3 (1.51 g, 12 mmol, 1.2 equiv.) and $NaHCO_3$ (2.02 g, 24 mmol, 2.4 equiv.) were added in several portions to the mixture of *N*-phenyl-α-fluorosulfonyldifluoroacetamide (2.53 g, 10 mmol) and water (40 mL) at 15–20 °C with stirring. And the stirring was continued for 1 h at the same temperature. Then, I_2 (5.08 g, 20 mmol, 2.0 equiv.) and KI (2.49 g, 15 mmol, 1.5 equiv.) were added. The reaction mixture was heated at 80 °C for 1 h. After being cooled to room temperature, the resulted mixture was extracted with ether (3 × 40 mL). The combined organic extracts were washed with 10% Na_2SO_3 (30 mL), water (3 × 30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to yield the crude product, which was purified by column chromatography to give pure *N*-phenyl-iododifluoroacetamide **1** as a white solid (2.25 g, 76%).

3.2.1. N-phenyl-iododifluoroacetamide (1)

White solid, mp: 112.0–113.6 °C. IR (KBr): ν_{max}: 3330, 1695, 1608, 1552, 1448, 1134, 1119, 933 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 8.00 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −57.3 (s, 2F). EI-MS *m*/*z* (%): 297 (98.57), 170 (55.10), 120 (100.00), 77 (60.31). HRMS calcd. for $C_8H_6F_2INO$: 296.9462, found: 296.9464.

3.3. General procedure for the preparation of compounds 3

Under a nitrogen atmosphere, to a mixture of *N*-phenyl-iododifluoroacetamide **1** (594 mg, 2.0 mmol), alkenes (4.0 mmol, 2.0 equiv.), H_2O (3 mL), and CH_3CN (5 mL) stirred magnetically at 10–15 °C was added a mixture of $Na_2S_2O_4$ (418 mg, 2.4 mmol, 1.2 equiv.) and $NaHCO_3$ (202 mg, 2.4 mmol, 1.2 equiv.). The mixture was stirred at the same temperature for ca. 20 min until the reaction had finished (monitored by TLC). The mixture was poured into H_2O (20 mL) and extracted with ether (3 × 20 mL). The combined organic layer was washed with saturated brine and dried over anhydrous sodium sulfate. After the evaporation of ether, the residue was purified by column chromatography to give **3**.

3.3.1. N-Phenyl-2,2-difluoro-4-iodo-octanamide (3a)

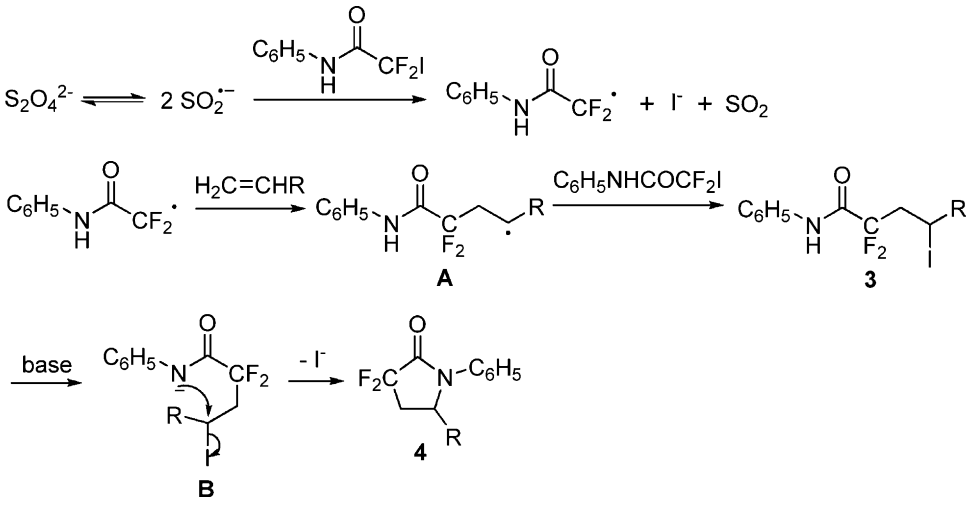
Pale yellow solid, mp: 39.2–40.8 °C. IR (KBr): ν_{max}: 3310, 2957, 2930, 1690, 1603, 1542, 1450, 1448 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 8.11 (s, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.25 (q, *J* = 6.6 Hz, 1H), 2.79–3.09 (m, 2H), 1.72–1.86 (m, 2H), 1.26–1.50 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −102.6 (dt, *J* = 258.3, 16.6 Hz, 1F), −105.6 (dt, *J* = 258.6, 15.9 Hz, 1F). EI-MS *m*/*z* (%): 381 (3.47), 254 (100.00), 120 (31.20), 77 (26.26). HRMS calcd. for $C_{14}H_{18}F_2INO$: 381.0401, found: 381.0396.

3.3.2. N-Phenyl-2,2-difluoro-4-iodo-4-(trimethylsilyl)butanamide (3b)

Pale yellow oil. IR (KBr): ν_{max}: 3320, 2955, 1695, 1602, 1541, 1448, 1252, 842 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 8.24 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 3H), 3.11 (d, *J* = 11.4 Hz, 1H), 2.59–2.90 (m, 2H), 0.19 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −103.3 (dt, *J* = 267.3, 17.2 Hz, 1F), −105.2 (dt, *J* = 254.6, 15.2 Hz, 1F). EI-MS *m*/*z* (%): 397 (11.05), 270 (35.68), 178 (35.62), 77 (54.15), 73 (100.00). HRMS calcd. for $C_{13}H_{18}F_2INOSi$: 397.0171, found: 397.0174.

3.3.3. N-Phenyl-2,2-difluoro-5-hydroxyl-4-iodo-pentanamide (3c)

White solid, mp: 60.4–61.9 °C. IR (KBr): ν_{max}: 3323, 1686, 1600, 1536, 1449, 751 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 8.15 (s, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 4.37 (q, *J* = 6.1 Hz, 1H), 3.80 (d, *J* = 5.4 Hz, 2H), 2.81–3.16 (m, 2H), 2.50 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −103.3 (dt, *J* = 256.6,



Scheme 2. Proposed mechanisms for the formation of **3** and **4**.

17.3 Hz, 1F), −104.7 (dt, *J* = 257.7, 16.8 Hz, 1F). EI-MS *m*/*z* (%): 355 (11.97), 228 (100.00), 210 (62.49), 120 (63.91), 77 (44.71). HRMS calcd. for $C_{11}H_{12}F_2INO_2$: 354.9881, found: 354.9879.

*3.3.4. N-Phenyl-2,2-difluoro-4-iodo-5-phenyl-pentanamide (**3d**)*

White solid, mp: 83.1–84.5 °C. IR (KBr): ν_{max}: 3318, 1687, 1601, 1539, 1448, 1180 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 8.04 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.30–7.42 (m, 5H), 7.20–7.25 (m, 3H), 4.40–4.45 (m, 1H), 3.19–3.34 (m, 2H), 2.85–3.11 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −101.4 (dt, *J* = 256.3, 16.6 Hz, 1F), −104.7 (dt, *J* = 256.3, 16.1 Hz, 1F). EI-MS *m*/*z* (%): 415 (3.28), 288 (100), 77 (22.59). HRMS calcd. for $C_{17}H_{16}F_2INO$: 415.0245, found: 415.0247.

*3.3.5. N-Phenyl-5-acetyloxy-2,2-difluoro-4-iodo-pentanamide (**3e**)*

Pale yellow oil. IR (KBr): ν_{max}: 3331, 1734, 1702, 1603, 1546, 1448, 1236 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 8.28 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 4.23–4.41 (m, 3H). 2.80–3.10 (m, 2H), 2.11 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −103.1 (dt, *J* = 260.0, 15.4 Hz, 1F), −105.4 (dt, *J* = 260.3, 15.6 Hz, 1F). EI-MS *m*/*z* (%): 397 (14.12), 270 (100.00), 210 (85.98), 120 (70.43), 77 (32.83). HRMS calcd. for $C_{13}H_{14}F_2INO_3$: 396.9987, found: 396.9985.

3.4. Preparation of N-phenyl-α,α-difluoro-γ-lactam derivatives

Under a nitrogen atmosphere, to a mixture of *N*-phenyliododifluoroacetamide **1** (297 mg, 1.0 mmol), alkenes (2.0 mmol, 2.0 equiv.), H_2O (3 mL), and CH_3CN (5 mL) stirred magnetically at 10–15 °C was added a mixture of $Na_2S_2O_4$ (261 mg, 1.5 mmol, 1.5 equiv.) and NaOH (60 mg, 1.5 mmol, 1.5 equiv.). The mixture was stirred at the same temperature for ca. 30 min until the reaction had finished (monitored by TLC). The mixture was poured into H_2O (20 mL) and extracted with ether (3 × 20 mL). The combined organic layer was washed with saturated brine and dried over anhydrous sodium sulfate. After the evaporation of ether, the residue was purified by column chromatography to give **4**. The results are given in Table 3.

*3.4.1. N-Phenyl-α,α-difluoro-γ-(n-butyl)-γ-lactam (**4a**)*

White solid, mp: 46.0–47.5 °C. IR (KBr): ν_{max}: 2970, 2950, 2930, 2861, 1714, 1679, 1599, 1500, 1340 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.39–7.48 (m, 4H), 7.28–7.33 (m, 1H), 4.19–4.24 (m, 1H), 2.70–2.87 (m, 1H), 2.26–2.42 (m, 1H), 1.67–1.79 (m, 1H), 1.22–1.45 (m, 5H), 0.85 (t, *J* = 6.6 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −101.5 (dtd, *J* = 266.8, 16.4, 5.6 Hz, 1F), −104.7 (ddd, *J* = 268.1, 18.6, 14.4 Hz, 1F). EI-MS *m*/*z* (%): 253 (35.36), 196 (100.00), 104 (41.48), 77 (20.76). Anal. calcd. for $C_{14}H_{17}F_2NO$: C, 66.39; H, 6.77; N, 5.53. Found: C, 66.34; H, 6.94; N, 5.47.

*3.4.2. N-Phenyl-α,α-difluoro-γ-trimethylsilyl-γ-lactam (**4b**)*

White solid, mp: 107.6–108.3 °C. IR (KBr): ν_{max}: 3060, 2990, 2961, 1714, 1673, 1597, 1495, 1253, 1052 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.28–7.45 (m, 5H), 3.81–3.87 (m, 1H), 2.68–2.85 (m, 1H), 2.32–2.51 (m, 1H), −0.12 (s, 9H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −103.5 (ddd, *J* = 267.3, 16.1, 12.7 Hz, 1F), −105.2 (dt, *J* = 266.8, 17.8 Hz, 1F). EI-MS *m*/*z* (%): 269 (68.53), 149 (89.84), 104 (58.98), 77 (59.19), 73 (100.00). Anal. calcd. for $C_{13}H_{17}F_2NOSi$: C, 57.97; H, 6.36; N, 5.20. Found: C, 57.96; H, 6.95; N, 5.19.

*3.4.3. N-Phenyl-α,α-difluoro-γ-hydroxymethyl-γ-lactam (**4c**)*

White solid, mp: 78.6–79.2 °C. IR (KBr): ν_{max}: 3298, 3068, 2972, 1708, 1675, 1599, 1496, 1426, 1018 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.38–7.47 (m, 4H), 7.32 (t, *J* = 6.8 Hz, 1H), 4.31 (d, *J* = 2.7 Hz, 1H), 3.57–3.68 (m, 2H), 2.71 (dt, *J* = 15.5, 6.3 Hz, 2H), 2.17 (t, *J* = 5.1 Hz, 1H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −101.8 (dt, *J* = 270.8, 12.1 Hz, 1F), −103.0 (dt, *J* = 271.2, 12.6 Hz, 1F). EI-MS *m*/*z* (%): 227 (38.42), 196 (100.00), 104 (78.04), 77 (36.11). Anal. calcd. for $C_{11}H_{11}F_2NO_2$: C, 58.15; H, 4.88; N, 6.16. Found: C, 58.09; H, 4.94; N, 5.97.

*3.4.4. N-Phenyl-γ-benzyl-α,α-difluoro-γ-lactam (**4d**)*

White solid, mp: 90.5–91.0 °C. IR (KBr): ν_{max}: 2888, 1732, 1598, 1494, 1315, 1138 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.47–7.55 (m, 4H), 7.29–7.36 (m, 4H), 7.12 (d, *J* = 7.2 Hz, 2H), 4.43–4.53 (m, 1H), 3.15 (d, *J* = 13.2 Hz, 1H), 2.58 (d, *J* = 13.2 Hz, 1H), 2.33–2.64 (m, 2H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −100.8 (dt, *J* = 270.4, 16.4 Hz, 1F), −105.5 (dt, *J* = 270.1, 14.2 Hz, 1F). EI-MS *m*/*z* (%): 287 (19.39), 196 (100.00), 104 (45.35), 77 (21.26). Anal. calcd. for $C_{17}H_{15}F_2NO$: C, 71.07; H, 5.26; N, 4.88. Found: C, 71.44; H, 5.49; N, 4.73.

*3.4.5. N-Phenyl-γ-acetyloxymethyl-α,α-difluoro-γ-lactam (**4e**)*

White solid, mp: 124.3–125.0 °C. IR (KBr): ν_{max}: 3065, 2966, 1738, 1716, 1594, 1496, 1431, 1340, 1249 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.40–7.49 (m, 4H), 7.33 (t, *J* = 6.6 Hz, 1H), 4.48–4.52 (m, 1H), 4.27 (dd, *J* = 12, 3.3 Hz, 1H), 4.01 (dd, *J* = 12, 4.5 Hz, 1H), 2.72–2.91 (m, 1H), 2.49–2.64 (m, 1H), 2.00 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −100.6 (dtd, *J* = 271.0, 17.2, 4.2 Hz, 1F), −104.0 (ddd, *J* = 271.5, 15.8, 9.0 Hz, 1F). EI-MS *m*/*z* (%): 269 (18.89), 196 (100.00), 104 (88.73), 77 (39.47), 43 (18.99). Anal. calcd. for $C_{13}H_{13}F_2NO_3$: C, 57.99; H, 4.87; N, 5.20. Found: C, 57.85; H, 4.92; N, 5.07.

$C_{13}H_{13}F_2NO_3$ (**4e**) crystallized by diffusion of petroleum ether into a dichloromethane solution. Crystal data. *M* = 269.24, monoclinic, space group *C*2/*c*, *a* = 31.900(4), *b* = 6.0408(8), *c* = 12.9384(16) Å, α = 90.00, β = 97.099(2), γ = 90.00°, *V* = 2474.1(5) $Å^3$, *T* = 293(2) K, *Z* = 8, *Dc* = 1.446 g cm^{-3}, μ(mo Kα) = 0.122 mm^{-1}, 6473 reflections measured, 2425 unique which were used in all calculations. R_1 (all data) = 0.0593. R_1 = 0.0511. CCDC 822545.

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