Preparation of Novel Fluorous Alkylating Agents and Pyrrolidines from Fluorous γ-Lactone Precursors

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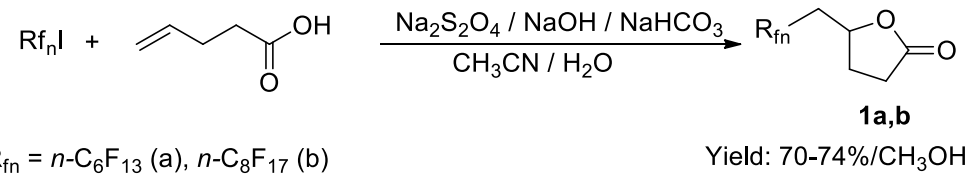
Abstract: *5-Perfluoroalkyl-pentane-1,4-diols obtained by the reduction of fluorinated γ-lactone precursors can easily be converted to 5- perfluoroalkyl-pentane-1,4-diiodides or 5-perfluoroalkyl-pentane-1,4-dimesylates. These novel bis-alkylating reagents were reacted with primary amines to afford fluorous N-substituted-pyrrolidines.*

Keywords*:* fluorous (=perfluoroalkyl substituted) γ-valerolactones, fluorous alkylating agents and pyrrolidines

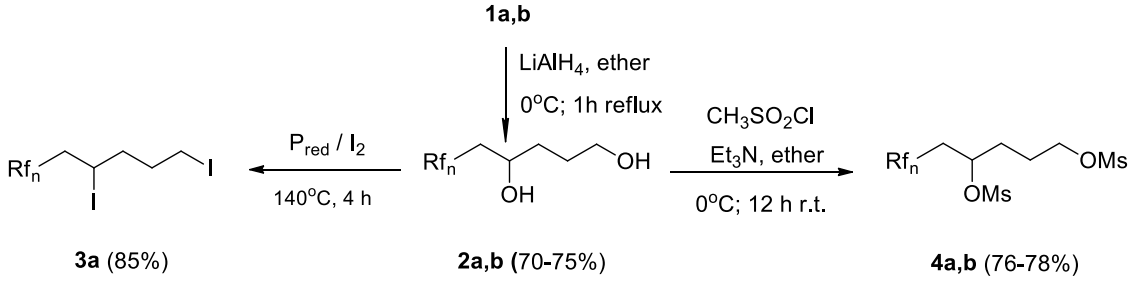
γ-Valerolactone (GVL) has been suggested by Horváth to consider it as an ideal sustainable liquid which could be used for the production of both energy and carbon-based consumer products [1]. On the other hand, *fluorous chemistry* makes use of the unique physical-chemical properties of fluorocarbons and that of structural elements derived from them allowing easy phase separation of fluorous catalyst and/or reagents from organic liquid phases [2].

We tested two 4-(perfluoroalkylmethyl)-γ-butyrolactones (**1a,b**) if they were suitable precursors for the synthesis of novel fluorous reagents. These lactones were prepared with the radical chain addition of perfluoroalkyl iodides to 4-pentenoic acid, followed by base assisted lactonization of the formed 4-iodo-5-perfluoroalkyl-pentanoate intermediates according to reported procedures of Wu and coworkers (Scheme 1) [3].



Scheme 1. Polyfluoroalkyl-lactonization of 4-pentenoic acids (Cf. Ref. [3]).

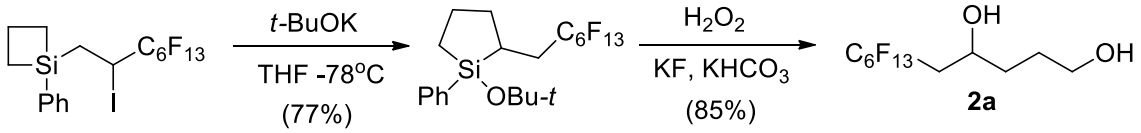
Fluorous GVLs (**1a,b**) were reduced with $LiAlH_4$ in boiling ether to affrod 5-(*F*-alkyl)-1,4-pentanediols (**2a,b**) in 70-75% yield after recrystallization of the crude diols from THF solvent (Scheme 2). They can be used for the synthesis of fluorous bis-alkylating reagents, such as 5-perfluorohexyl-1,4-diiodopentane (**3a**) and 5-perfluorohexyl- or 5-perfluorooctyl-1,4-pentanediyl-bis(methanesulfonate) (**4a,b**), respectively (Scheme 3).



Scheme 2. Synthesis of novel fluorous difunctional alkylating reagents (**3** and **4**).

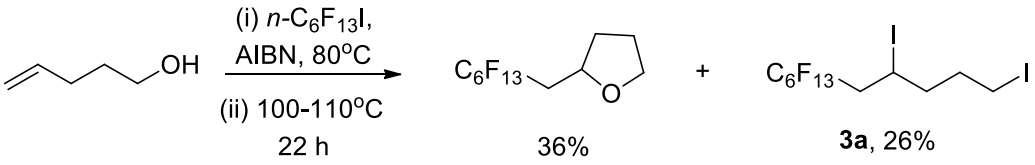
Fluorous-diiodide (**3a**) was prepared by heating the precursor diol (**2a**) with a mixture of red phosphorus and iodine according to a simple procedure elaborated for the synthesis of primary fluorous alkyl iodides [4], while dimesylates **4a,b** were prepared by the reaction of fluorous diols **2a,b** with a slight excess of both methanesulfonyl chloride and triethylamine in an ether solution at ice temperature in analogy to reported methods (Scheme 2) [5].

According to the literature fluorous 1,4-diol with the shorter perfluoroalkyl chain (R_{fn} = C_6F_{13}, **2a)** has been prepared in a multistep reaction involving the ring expansion of a silacyclobutane derivative, which then followed by the oxidative cleavage of the formed 2-fluoroalkyl silacyclopentane as decribed by Matsumoto *et al.* [6] (Scheme 3).



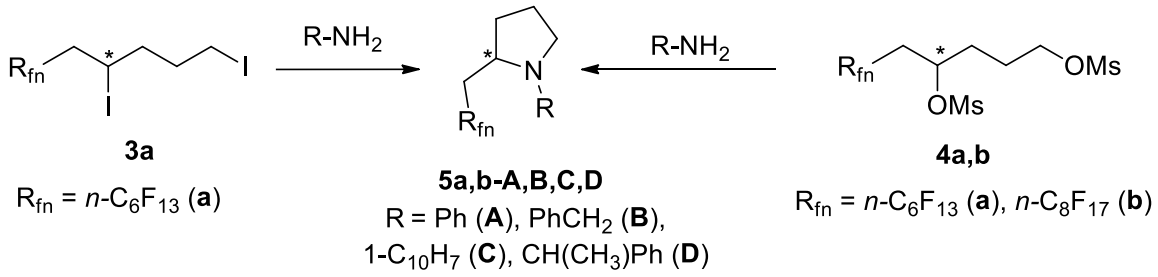
Scheme 3. Silacycloalkane based synthesis of fluorous diol **2a** (Ref. [6]).

Fluorous diiodide **3a** can also be obtained as the side product of the AIBN initiated radical addition reaction of 4-pentenol with n-$C_6F_{13}I$ which gives 2-perfluorohexylmethyl-THF as the main product using distillation and chromatography for their separation and purification according to Greiner *et al.* [7] (Scheme 4).



Scheme 4. Literature access to 5-perfluorohexyl-1,4-diiodopentane **3a** (Ref. [7]).

Finally we prepared a series of *N*-substituted-pyrrolidines (**5**) by heating a mixture of the alkylating reagents and an excess of aniline, benzylamine, 1-naphthylamine or (R/S)-1-phenylethylamine, respectively, without solvents at 100°C temperature for 3h. Following 10% aq-NaOH/hexane extraction the pyrrolidines were isolated and then purified by chromatography (SiO_2/hexane). Pyrrolidines **5** were obtained in 45-89% yields as pale yellow oils or white crystals (Scheme 5). New compounds were characterized by IR; ^{1}H-,^{13}C- and ^{19}F-NMR spectra (Experimental).



Scheme 5. Synthesis of 2-(perfluoroalkylmethyl)-pyrrolidines by double alkylation of primary amines.

Although pyrrolidines **5** were obtained as racemates (**5a,b-A,B,C**) or diastereomeric mixtures (**5a,b-D**) we are planning their optical resolution [8] for testing them as chiral organocatalysts in some base induced reactions [9].

Experimental

^{1}H-, ^{13}C- and ^{19}F-NMR spectra were recorded on Bruker Avance 250 instrument using a 5 mm inverse $^{1}H/^{13}C/^{31}P/^{19}F$ probe head at room temperature. Chemical shifts (δ) are given in parts per million (ppm) units relatively to the internal standard TMS (δ=0.00 for ^{1}H, δ=0.00 for ^{13}C) and to $CFCl_3$ as external standard (δ=0.00 for ^{19}F). Melting points were determined on a Böetius micro-melting point apparatus and are uncorrected.

General Procedure for the Synthesis of 5-Perfluoralkyl-1,4-pentanediols (GP-1)

Under an argon atmosphere $LiAlH_4$ (181 mg, 4.78 mmol) was suspended in absolute ether (6 mL) and a solution of *F*-GVL (**1a,b;** 4.78 mmol) in absolute ether (15 mL) was added with external cooling and stirring to keep the reaction temparature at 0°C. Then the mixture was stirred at room temperature and consecutively refluxed for 1 h. The mixture then was cooled to 0°C and carefully treated with water (20 mL), then the ether layer was separated. The aqueous layer was extracted with ether and the combined extracts were dried (Na_2SO_4), filtered and evaporated to obtain the crude diols as solids. They were further purified by recrystallization from THF.

6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoroundecane-1,4-diol (2a)

According to GP-1 the reduction of lactone **1a** (2.00 g, 4.78 mmol) gave 1.51 g (75%) of the title diol as a white solid; mp = 59-60°C. (Lit. mp = 59.5-60.5°C, [6]). ^{1}H NMR ($CDCl_3$) δ: 1.43-1.92 (4H, m), 2.02-2.47 (2H, m), 2.58-3.49 (2H, br.), 3.58-3.79 (2H, m), 4.06-4.25 (1H, m), ^{13}C NMR ($CDCl_3$) δ: 28.8, 35.4, 38.4 (t, J = 21.6 Hz), 63.0, 65.5, 100-120 (R_{f6}-chain), ^{19}F NMR ($CDCl_3$) δ: -81.3 (3F), -113.6 (2F), -122.3 (2F), -123.4 (2F), -124.2 (2F), -126.6 (2F).

6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heptadecafluorotridecane-1,4-diol (2b)

According to GP-1 the reduction of the lactone **1b** (2.48 g, 4.78 mmol) gave 1.75 g (70%) of the title diol as a white solid; mp = 73-74°C. IR (KBr, v, cm^{-1}): 3317, 3210, 2946, 1246, 1197, 1143, 1114, 1037, 961, 655, 639, 608.
^{1}H NMR ($CDCl_3$) δ: 1.38-1.88 (4H, m), 1.94-2.55 (2H, m), 1.31-2.88 (2H, br.), 3.58-3.85 (2H, m), 4.11-4.31 (1H, m). ^{13}C NMR (DMSO-d6) δ: 28.8, 34.6, 37.6 (t, J = 20.8 Hz), 61.1, 63.9, 100-120 (R_{f8}-chain). ^{19}F NMR ($CDCl_3$) δ: -81.3 (3F), -113.6 (2F), -121.6 (2F), -122.3 (2F), -123.4 (4F), -124.2 (2F), -126.6 (2F).

Typical Procedure (TP): 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8,11-diiodoundecane (3a)

A 25 mL volume Pyrex tube having a Teflon-valve was charged with diol **2a** (1.00 g, 2.37 mmol), iodine (750 mg, 2.95 mmol), dry red phosphorus (63 mg, 2.03 mmol) and a magnetic stirrer bar, then it was flushed with Argon and the valve closed. The mixture was stirred in a 140°C oil-bath for 4 h. Then it was cooled to room temperature and opened. After drop-by-drop addition of saturated aq-Na_2CO_3 the product was isolated with extraction using pentane (2x10 mL). The combined pentane extracts were washed with aq-Na_2CO_3 until the violet colour of iodine ceased. Then the pentane phases were dried (Na_2SO_4) and the filtrate was concentrated and the residual oil short-path distilled at 16 mmHg pressure using an oil-bath set to 130°C external temperature. Yield: 1.29 g (85%) colourless oil. (Lit. bp = 97°C/0.04 mmHg, [7]) ^{1}H NMR ($CDCl_3$) δ: 1.75-2.31 (5H, m), 2.57-3.12 (2H, m), 3.15-3.31 (2H, m), 4.22-4.42 (1H, m). ^{13}C NMR ($CDCl_3$) δ: 4.4, 18.7, 33.6, 41.2, 42.1 (t, J = 20.7 Hz), 100-120 (R_{f6}-chain). ^{19}F NMR ($CDCl_3$) δ: -81.5 (3F), -113.7 (2F), -122.4 (2F), -123.5 (2F), -124.2 (2F), -126.8 (2F).

General Procedure for the Preparation of Dimesylates (GP-2)

To a stirred solution of the diol **2a** or **2b** (4.74 mmol) and triethylamine (1.12 g, 11.8 mmol) in ether (20 mL) was added drop-by-drop methanesulfonyl chloride (1.20 g, 10.4 mmol) dissolved in ether (10 mL) at 0°C. Then the mixture was stirred overnight at room temperature during which white precipitate formed. The mixture was diluted with ethyl acetate (30 mL) and treated with water (20 mL). The two liquid phase was separated and the aqueous layer extracted with ethyl acetate (2 x 20 mL). The organic layer was dried (Na_2SO_4), filtered and the solvent evaporated. The crude solids obtained were recrystallized from ethyl acetate.

6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoroundecane-1,4-diyl dimethanesulfonate (4a)

According to GP-2 the reaction of diol **2a** (2.00 g, 4.74 mmol) gave 2.14 g (78%) **4a** as white crystals; mp =79-80°C/ EtOAc. IR (KBr, v, cm^{-1}): 1346, 1233, 1171, 1142, 1089, 1067, 975, 926, 864, 842, 697, 647, 574 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.83-2.10 (4H, m), 2.23-2.80 (2H, m), 3.02 (3H, s), 3.05 (3H, s), 4.16-4.37 (2H, m), 5.06-5.23 (1H, m), ^{13}C NMR ($CDCl_3$) δ: 24.7, 31.8, 35.4 (t, J = 21.4 Hz), 37.3, 38.8, 68.8, 74.0, 100-120 (R_{f6}-chain), ^{19}F NMR ($CDCl_3$) δ: -126.2 (2F), -123.6 (2F), -122.9 (2F), -121.8 (2F), -113.1 (2F), -80.8 (3F).

6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heptadecafluorotridecane-1,4-diyl dimethanesulfonate (4b)

According to GP-2 the reaction of diol **2b** (3.00 g, 5.75 mmol) gave 2.96 g (76 %) **4b** as white crystals; mp =96-97°C/ EtOAc. IR 1346, 1198, 1170, 1145, 1117, 1067, 974, 925, 863, 830, 776, 705, 658, 609 cm^{-1} ^1H NMR ($CDCl_3$) δ: 1.80-2.07 (4H, m), 2.27-2.76 (2H, m), 3.01 (3H, s), 3.04 (3H, s), 4.15-4.36 (2H, m), 5.05-5.22 (1H, m), ^{13}C NMR ($CDCl_3$) δ: 24.4, 31.8, 35.4 (t, J = 21.4 Hz), 37.4, 38.9, 68.8, 74.0, 100-120 (R_{f8}-chain). ^{19}F NMR ($CDCl_3$) δ: -126.2 (2F), -123.5 (2F), -122.8 (2F), -121.9 (4F), -121.6 (2F), -113.0 (2F), -80.9 (3F)

General Procedure for the Synthesis of Pyrrolidines (GP-3)

The *F*-alkylating reagent **3a** and/or **4a** and 4**b** (1.0 mmol) was mixed with an excess of aniline (**A,** 1.0 mL, 11 mmol), benzyl amine (**B,** 1.0 mL, 9.2 mmol), 1-naphthylamine (**C,** 1.0 g, 7.0 mmol) or (±)-1-phenylethylamine (**D**, 1.0 mL, 7.8 mmol), respectively, and stirred for 3 h at 100 °C using oil bath. The progress of the reaction was indicated by the formation of a second liquid phase. Then the mixture was cooled to room temperature and the lower layer was separated, while the upper one treated with 1M NaOH (1 mL) and extracted with hexane (3 x 1mL). The hexane extracts and the lower layer separated earlier were combined and dried (Na_2SO_4). After filtration the solvent was evaporated in vacuum and the crude product obtained was purified with chromatography (SiO_2/hexane).

1-Phenyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)pyrrolidine (5aA)

Yield: 390 mg (82%, pale yellow oil, IR (KBr, v, cm^{-1}): 2955, 1599, 1504, 1231, 1184, 1141, 1120, 1035, 809, 746, 691, 647 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.92-2.24 (5H, m), 2.37-2.67 (1H, m), 3.14-3.29 (1H, m), 3.42-3.55 (1H, m), 4.16-4.31 (1H, m), 6.57-6.68 (2H, d), 6.71-6.82 (1H, t), 7.23-7.37 (2H, t) ^{13}C NMR ($CDCl_3$) δ: 23.4, 32.2, 33.7 (t, J = 20.7 Hz), 48.1, 52.6, 112.2, 116.7, 129.9, 146.5, 100-120 (R_{f6}-chain).

1-Benzyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)pyrrolidine (**5aB**)

Yield: 380 mg (77 %), pale yellow oil), IR (KBr, v, cm^{-1}): 2972, 2795, 1454, 1365, 1319, 1233, 1190, 1142, 1048, 811, 729, 698, 655 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.55-1.90 (3H, m), 1.93-2.28 (3H, m), 2.28-2.62 (1H, m), 2.75-3.08 (2H, m), 3.33 (1H, d), 3.96 (1H, d), 7.02-7.43 (5H, m), ^{13}C NMR ($CDCl_3$) δ: 22.4, 32.0, 36.1 (t, J = 20.2 Hz), 53.5, 57.3, 58.6, 127.0, 128.3, 128.7, 139.0, 100-120 (R_{f6}-chain)

1-(Naphthalen-1-yl)-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)pyrrolidine *(5aC)*

Yield: 455 mg (86 %), pale yellow oil, IR (KBr, v, cm^{-1}): 2927, 2853, 1576, 1366, 1238, 1194, 1142, 1046, 1017, 800, 792, 773, 694, 652, 566 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.76-2.23 (4H, m), 2.35-2.73 (2H, m), 2.77-3.00 (1H, m), 3.82-3.96 (1H, m), 3.99-4.16 (1H, m), 7.10 (1H, d), 7.39-7.63 (4H, m), 7.80-7.91 (1H, m), 8.16-8.28 (1H, m) ^{13}C NMR ($CDCl_3$) δ: 23.9, 32.6, 34.9 (t, J = 20.2 Hz), 53.5, 55.7, 114.0, 123.3, 124.4, 125.1, 125.9, 128.2, 130.3, 134.9, 145.7, 100-120 (R_{f6}-chain)

1-(1-Phenylethyl)-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)pyrrolidine *(5aD)*

Yield: 230 mg (45 %), mixture of diastereomers, pale yellow oil, IR (KBr, v, cm^{-1}): 2975, 1453, 1360, 1233, 1191, 1142, 1119, 1047, 842, 810, 700, 645, 565 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.42 (3H, d), 1.48 (3H, m), 1.56-1.86 (6H, m), 1.86-2.16 (4H, m), 2.25-2.58 (4H, m), 2.72-3.03 (2H, m), 3.06-3.35 (2H, m), 3.69 (1H, q), 3.80 (1H, q) 7.13-7.47 (10H, m), ^{13}C NMR ($CDCl_3$) δ: 18.6, 21.6, 23.0, 23.3, 31.7, 32.0, 36.0 (t, J = 20.2 Hz), 36.8 (t, J = 20.2 Hz) 49.8, 50.0, 53.1, 54.8, 61.0, 61.6, 127.0, 127.1, 127.5, 127.8, 128.2, 128.3, 142.5, 144.5, 100-120 (R_{f6}-chain)

2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-1-phenylpyrrolidine *(5bA)*

Yield: 476 mg (82 %), white solid (mp: 70-71 °C), IR (KBr, v, cm^{-1}): 1600, 1506, 1369, 1197, 1146, 1115, 1046, 992, 745, 692, 649, 560 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.84-2.30 (5H, m), 2.31-2.69 (1H, m), 3.06-3.33 (1H, m), 3.35-3.58 (1H, m), 4.12-4.32 (1H, m), 6.56-6.70 (2H, d), 6.70-6.82 (1H, t), 7.20-7.38 (2H, t) ^{13}C NMR ($CDCl_3$) δ: 23.0, 31.8, 33.3 (t, J = 21.1 Hz), 47.7, 51.7, 111.8, 116.4, 129.5, 146.1, 100-120 (R_{f8}-chain).

1-Benzyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-heptadecafluorononyl)pyrrolidine *(5bB)*

Yield: 460 mg (78 %), white solid, IR (KBr, v, cm^{-1}): 2959, 2802, 1495, 1369, 1329, 1193, 1145, 1134, 1116, 1029, 963,749, 700, 652, 557 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.55-1.87 (3H, m), 1.95-2.27 (3H, m), 2.29-2.62 (1H, m), 2.74-3.02 (2H, m), 3.34 (1H, d), 3.96 (1H, d), 7.18-7.41 (5H, m), ^{13}C NMR ($CDCl_3$) δ: 22.4, 32.0, 36.1 (t, J = 20.2 Hz), 53.5, 57.3, 58.6, 127.0, 128.3, 128.7, 139.0, 100-120 (R_{f8}-chain).

2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-1-(naphthalen-1-yl)pyrrolidine *(5bC)*

Yield: 560 mg (89 %), white solid (mp: 68-69 °C), IR (KBr, v, cm^{-1}): IR 1574, 1398, 1329, 1240, 1197, 1146, 1115, 1047, 964, 798, 775, 703, 656, 560 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.80-2.24 (4H, m), 2.35-2.70 (2H, m), 2.79-3.00 (1H, m), 3.77-3.97 (1H, m), 3.99-4.19 (1H, m), 7.11 (1H, d), 7.36-7.66 (4H, m), 7.78-7.93 (1H, m), 8.16-8.31 (1H, m) ^{13}C NMR ($CDCl_3$) δ: 23.8, 32.5, 35.0 (t, J = 20.2 Hz), 53.5, 55.6, 114.1, 123.3, 124.3, 125.1, 125.9, 128.2, 130.4, 134.9, 145.7, 100-120 (R_{f8}-chain).

2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl)-1-(1-phenylethyl)pyrrolidine *(5bD)*

Yield: 460 mg (76 %), diastereomeric mixture, pale yellow oil, IR (KBr, v, cm^{-1}): 2975, 1453, 1237, 1199, 1144, 1113, 970, 872, 765, 718, 700, 655, 559 cm^{-1}, ^1H NMR ($CDCl_3$) δ: 1.42 (3H, d), 1.47 (3H, d), 1.61-1.86 (6H, m), 1.86-2.24 (4H, m), 2.29-2.61 (4H, m), 2.76-3.03 (2H, m), 3.07-3.35 (2H, m), 3.69 (1H, q), 3.79 (1H, q) 7.12-7.49 (10H, m), ^{13}C NMR ($CDCl_3$) δ: 18.6, 21.6, 23.0, 23.3, 31.7, 32.0, 36.0 (t, J = 20.2 Hz), 36.8 (t, J = 20.2 Hz) 49.8, 49.9, 53.1, 54.8, 61.0, 61.5, 127.0, 127.1, 127.6, 127.8, 128.2, 128.3, 142.6, 144.6, 100-120 (R_{f8}-chain).

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References

[1] Horváth, I.T.; Mehdi, H.; Fábos, V.; Boda, L.; Mika, L.T. "γ-Valerolactone—a sustainable liquid for energy and carbon-based chemicals". *Green Chemistry* 2008, 10 (2) 238-242. **DOI:** 10.1039/B712863K

[2] (a) Horváth, I.T., Rábai, J. Facile Catalyst Separation without Water: Fluorous Biphase Hydroformylation of Olefins. *Science* **1994**, *266,* 72-75; DOI:10.1126/science.266.5182.72

(b) *Handbook of Fluorous Chemistry,* Gladysz, J.A.; Curran, D.P.; Horváth, I.T., Eds.; Wiley/VCH: Weinheim, **2004**; DOI: 10.1002/3527603905

(c) *Fluorous Chemistry,* Volume Editor: Horváth, I.T.; Topics in Currant Chemistry, Springer, Vol. 308, 2012; Heidelberg. DOI 10.1007/978-3-642-25234-1.

[3] (a) Zou, X.; Wu, F.; Shen, Y.; Xu, S.; Huang, W. Synthesis of polyfluoroalkyl-γ-lactones from polyfluoroalkyl halides and 4-pentenoic acids, *Tetrahedron* **2003,** *59,* 2555–2560; http://dx.doi.org/10.1016/S0040-4020(03)00250-3

(b) Wu, F.; Yang, X.; Wang, Z.; Huang, W. Studies on sulfinatodehalogenation: The addition of polyfluoroalkyl iodides to olefins promoted by sodium bisulfite and sodium sulfite. *J. Fluorine Chem.* **2007**, *128,* 84–86. http://dx.doi.org/10.1016/j.jfluchem.2006.10.001

(c) Zhu, Y.; Yang, X.; Fang, X.; Yang, X.; Ye,L.L.; Cai, W.; Zhang, Y.; Wu, F. Sodium dithionite initiated reaction of pent-4-en-1-amines with fluoroalkyl iodides for the synthesis of 2-fluoroalkyl pyrrolidine derivatives, *Tetrahedron* **2011**, *67,* 1251-1257. doi:10.1016/j.tet.2010.11.090

[4] (a) Menczinger, B.; Jakab, G.; Szabó, D.; Rábai, J.; Synthesis of 1-Iodo-3-perfluoroalkyl propanes and 1-Iodo-4-perfluoroalkylbutanes, *Fluorine Notes*, No 3(94) 2014 (May-June); http://notes.fluorine1.ru/public/2014/3_2014/letters/letter3.html (accessed 04.02.17).

(b) Menczinger, B.; Jakab, G.; Szabó, D.; Rábai, J.; СИНТЕЗ 1-ЙОД-3-ПЕРФТОРАЛКИЛПРОПАН ОВ И 1-ЙОД-4-ПЕРФТОРАЛКИЛБУТАНОВ; *Фторные заметки*, No 3(94) 2014 (Май — Июнь); http://notes.fluorine1.ru/public/2014/3_2014/letters/rusletter3.html (accessed 04.02.17).

[5] Nemes, A.; Tölgyesi, L.; Bodor, A.; József Rábai, Szabó, D.; Greener fluorous chemistry: Convenient preparation of new types of 'CF_3-rich' secondary alkyl mesylates and their use for the synthesis of azides, amines, imidazoles and imidazolium salts. *J. Fluorine Chem.* **2010,** *131*, 1368-1376. http://dx.doi.org/10.1016/j.jfluchem.2010.10.001

[6] (a) Matsumoto, K.; Miura, K.; Oshima, K.; Utimoto, K. Potassium t-butoxide or silver acetate induced ring enlargement of silacyclobutane into silacyclopentane. Application to the Synthesis of 1,4-Diol. *Tetrahedron Letters*, **1991** , *32*, 6383 – 6386; http://dx.doi.org/10.1016/0040-4039(91)80175-6

(b) Matsumoto, K.; Takeyama, Y.; Miura, K.; Oshima, K.; Utimoto, K. Nucleophile-Induced Ring Enlargement of 1-(1-Iodoalkyl)silacyclobutane and 1-(1,2-Epoxyalkyl)silacyclobutane into Silacyclopentane. Application to the Syntheses of 1,4-Diol, 4-Alken-1-ol, and 1,4,5-Triol *Bull. Chem. Soc.Jpn.,* **1995**, *68*, 250 – 261; DOI: http://dx.doi.org/10.1246/bcsj.68.250

[7] Greiner, J.; Milius, A.; Riess, J. G. Addition of perfluoroalkyl iodides to 4-pentenol and its derivatives: one-pot preparation of 2-[(F-alkyl)methyl]-tetrahydrofurans**,** *J. Fluorine Chem.,* **1992,** *56*, 285-293. http://dx.doi.org/10.1016/S0022-1139(00)81175-6

[8] Rábai, J., Nemes, A., Farkas, V., Szabó, D. Unusual optical resolution processes for racemic carboxylic acids; *ICOS-20 - 20th International Conference on Organic Synthesis - 29 June - 4 July 2014* – MKE/HCS/, Budapest, Hungary, http://www.icos20.hu/images/stories/abstracts/Oral/L-25_abstract231.pdf (accessed 04.02.17)

[9] Mukherjee, S.; Yang, J. W.; Hoffmann, S.; List, B., Asymmetric Enamine Catalysis, *Chem. Rev.* **2007**, *107,* 5471−5569. **DOI:** 10.1021/cr0684016