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Phosgene-free synthesis of symmetric bis(polyfluoroalkyl) carbonates

Anna M. Semenova, Marina A. Ezhikova, Mikhail I. Kodess, Aleksandr Ya. Zapevalov and Aleksandr V. Pestov

^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 and DRX-500 spectrometers. The ^{1}H and ^{19}F chemical shifts were measured from the internal standards of tetramethylsilane and hexafluorobenzene, respectively, the ^{13}C shifts were measured from the solvent (DMSO-d_6) signal δ_C = 39.5 ppm. IR spectra were obtained on a Nicolet 6700 FTIR spectrometer using an ATR attachment with a diamond crystal in the range 400–4000 cm^{-1}. Elemental analysis was performed on a Perkin Elmer CHN PE 2400 automatic analyzer. Chromatographic analysis was performed using a Shimadzu GC2010 gas chromatograph with a flame ionization detector and a ZB-5 quartz capillary column (length 30 m, diameter 0.25 mm, film thickness 0.25 μm). Carrier gas was nitrogen, split flow 1:30. The initial column temperature was 40 °C (isotherm 3 min), followed by a temperature increase of 10 K min^{-1} to a final temperature of 280 °C (isotherm 15 min). Injector temperature 250 °C, detector 300 °C.

Compounds **3a-c** *(general procedure).* A mixture of trihydroperfluoroalkyl alcohol **1a-c** (0.439 mol of alcohol **1a**, 0.270 mol of alcohol **1b**, or 0.175 mol of alcohol **1c**) and titanium alkoxide (0.044 mol) was heated to boiling, and the alkanol that formed was distilled off in a mixture with excess **1a-c**. After that, diphenyl carbonate (0.075 mol) was added to the mixed titanium alkoxide **A** formed *in situ*, and the mixture was distilled to collect the mixture of carbonates **2-4**. Individual products were isolated by rectification.

Bis(2,2,3,3-tetrafluoropropyl) carbonate **3a**. Yield 51%. Colourless liquid, b.p. 181–182 °C, n_D^{20} 1.335. IR (ν, cm^{-1}): 2983 (C–H), 1778 (C=O), 1279 (C–F), 1108 (C–O). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 4.77 (t, 2 H, *J* 14.2 Hz, OCH_2), 6.63 (tt, 1 H, *J* 51.8, 5.2 Hz, CF_2H). ^{19}F NMR (376 MHz, DMSO-d_6), δ: 23.95 (dt, 2 F, *J* 51.8, 5.2 Hz, CF_2H), 37.55 (tq, 2 F, *J* = 14.2, 5.2 Hz, OCH_2CF_2). ^{13}C NMR (126 MHz, DMSO-d_6), δ: 63.41 (t, $^{2}J_{CF}$ 26.7 Hz, OCH_2), 109.23 (tt, $^{1}J_{CF}$ 248.1 Hz, $^{2}J_{CF}$ 33.2 Hz, CF_2H), 114.14 (tt, $^{1}J_{CF}$ 249.7 Hz, $^{2}J_{CF}$ 26.9 Hz, $OCH_2\underline{C}F_2$), 152.97 (CO). Found %: C 28.95; H 2.07; F 52.21. $C_7H_6F_8O_3$. Calculated %: C 28.98; H 2.08; F 52.39.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) carbonate **3b**. Yield 64%. Colourless liquid, b.p. 234–235 °C, n_D^{20} 1.324. IR (ν, cm^{-1}): 2986 (C–H), 1780 (C=O), 1274 (C–F), 1124 (C–O). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 5.00 (t, 2 H, *J* 14.2 Hz, OCH_2), 7.07 (tt, 1 H, *J* 50.2, 5.6 Hz, CF_2H). ^{19}F NMR (376 MHz, DMSO-d_6), δ: 24.30 (dm, 2 F, *J* 50.2 Hz, CF_2H), 33.23 (m, 2 F, CF_2), 38.03 (m, 2 F, CF_2), 43.22 (m, 2 F, OCH_2CF_2). ^{13}C NMR (126 MHz, DMSO-d_6), δ: 63.07 (t, $^{2}J_{CF}$ 26.2 Hz, OCH_2), 109.22 (tt, $^{1}J_{CF}$ 251.4 Hz, $^{2}J_{CF}$ 30.7 Hz, CF_2H), 107.8-113.0 (m, 2 CF_2), 114.27 (tt, $^{1}J_{CF}$ 257.1 Hz, $^{2}J_{CF}$ 31.0 Hz, $CH_2\underline{C}F_2$), 152.61 (CO). Found %: C 26.71; H 1.14; F 62.03. $C_7H_6F_8O_3$. Calculated %: C 26.96; H 1.23; F 62.02.

Bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) carbonate **3c**. Yield 71%. Colourless liquid, b.p. 300–301 °C, n_D^{20} 1.325. IR (ν, cm^{-1}): 2987 (C–H), 1781 (C=O), 1279 (C–F), 1140 (C–O). ^{1}H NMR (400 MHz, DMSO-d_6), δ: 5.03 (t, 2 H, *J* 13.8 Hz, OCH_2), 7.14 (tt, 1 H, *J* 50.2, 5.3 Hz, CF_2H). ^{19}F NMR (376 MHz, DMSO-d_6), δ: 24.23 (dm, 2 F, *J* 50.2 Hz, CF_2H), 33.64 (m, 2 F, CF_2), 39.57 (m, 2 F, CF_2), 40.55 (m, 2 F, CF_2), 43.49 (qm, *J* 13.8 Hz, 2 F, OCH_2CF_2). ^{13}C NMR (126 MHz, DMSO-d_6), δ: 63.06 (t, $^{2}J_{CF}$ 26.8 Hz, OCH_2), 107.88 (tt, $^{1}J_{CF}$ 252.0 Hz, $^{2}J_{CF}$ 31.1 Hz, CF_2H), 108.0-116.6 (m, 5 CF_2), 152.50 (CO). Found %: C 26.11; H 0.80; F 65.98. $C_{15}H_6F_{24}O_3$. Calculated %: C 26.10; H 0.88; F 66.06.

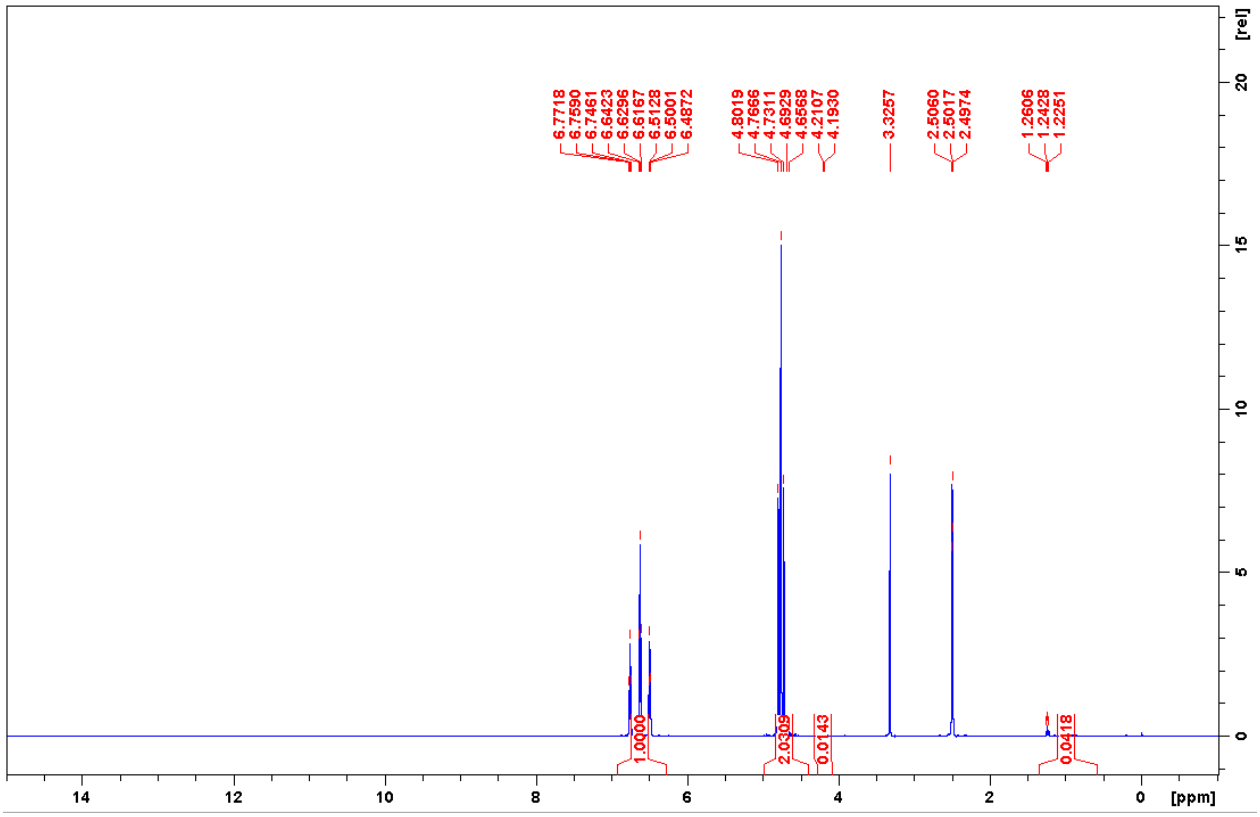


Figure S1 ^{1}H NMR (DMSO-d_6) of bis(2,2,3,3-tetrafluoropropyl) carbonate **3a**

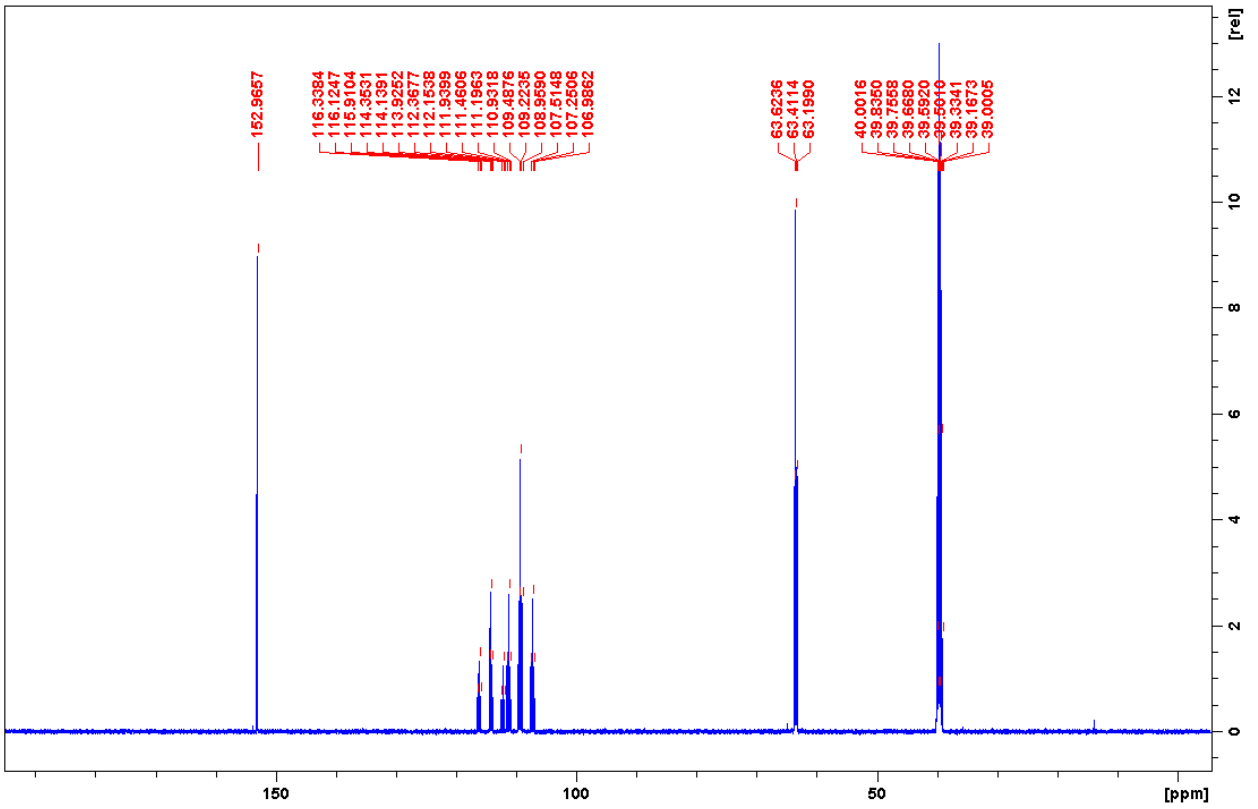


Figure S2 ^{13}C NMR (DMSO-d_6) of bis(2,2,3,3-tetrafluoropropyl)carbonate **3a**

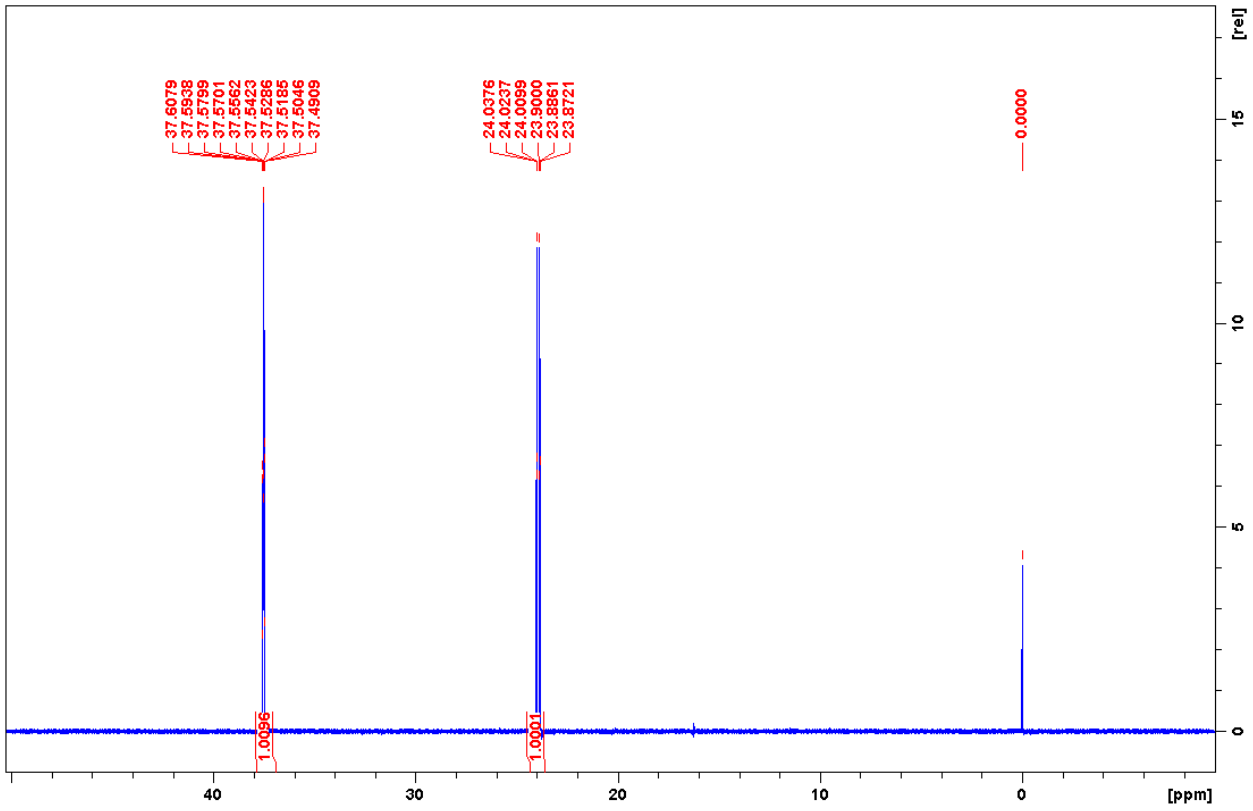


Figure S3 ^{19}F NMR (DMSO-d_6) of bis(2,2,3,3-tetrafluoropropyl) carbonate **3a**

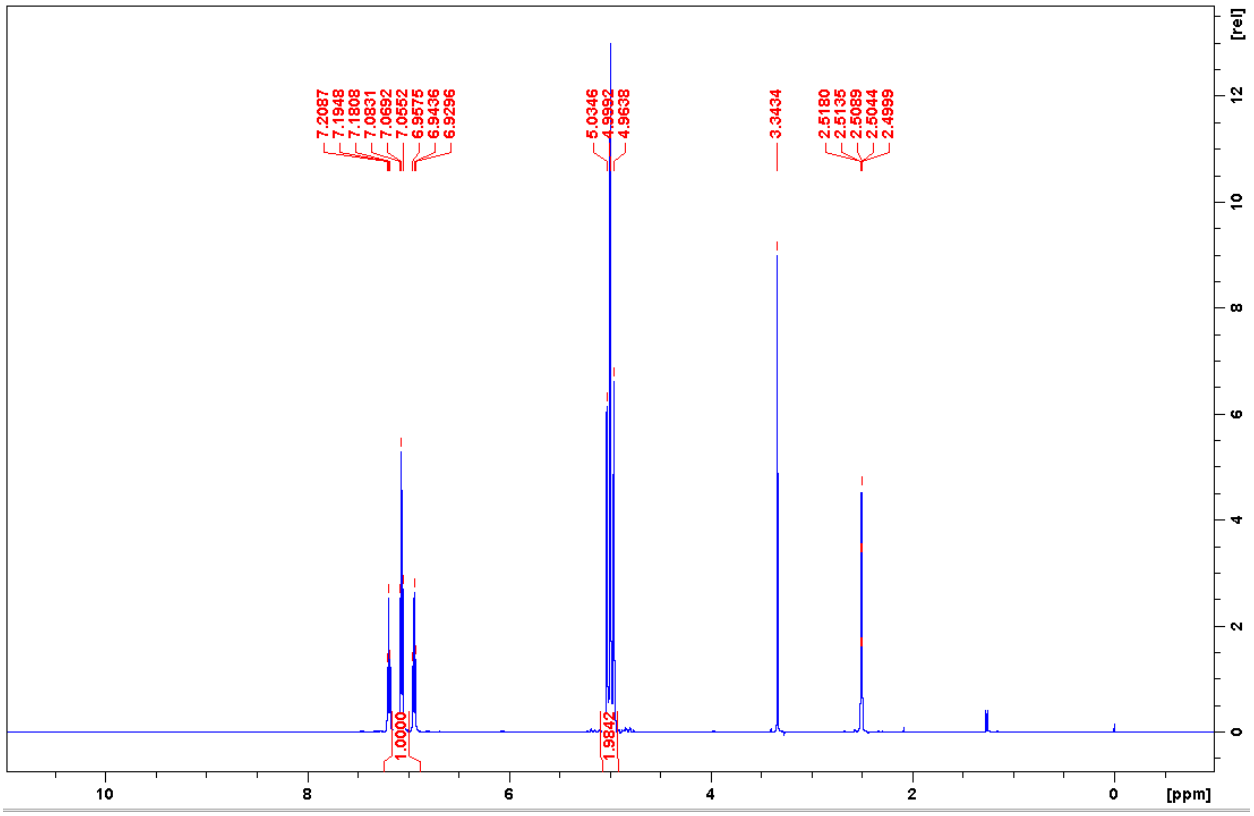


Figure S4 ^{1}H NMR (DMSO-d_6) of bis(2,2,3,3,4,4,5,5-octafluoropentyl) carbonate **3b**

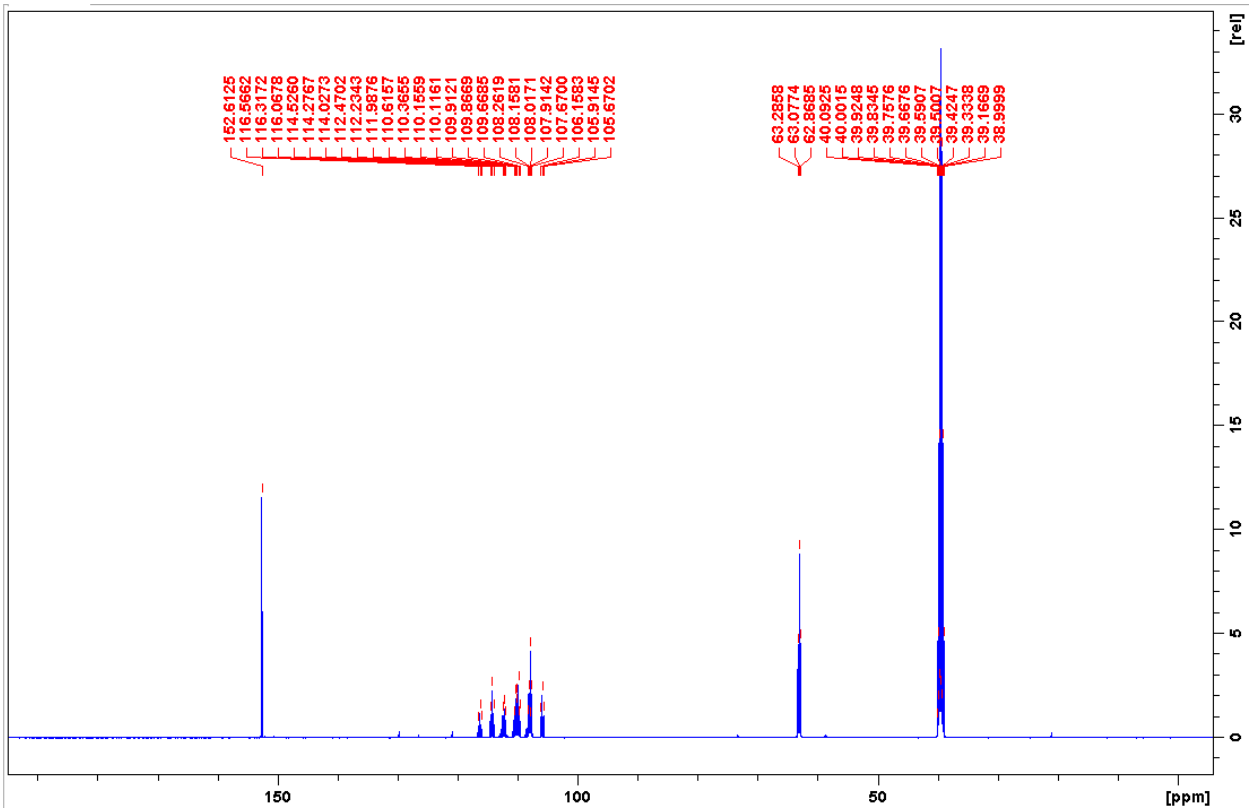


Figure S5 ^{13}C NMR (DMSO-d_6) of bis(2,2,3,3,4,4,5,5-octafluoropentyl) carbonate **3b**

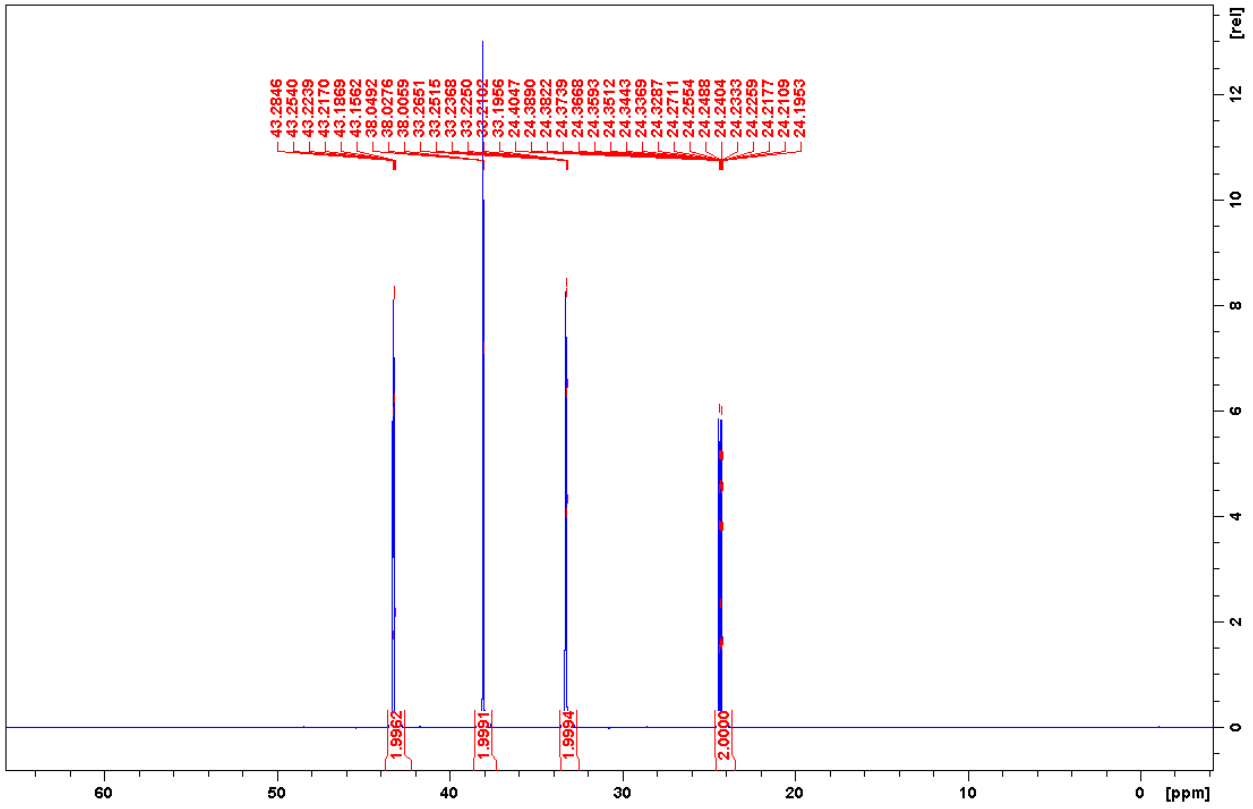


Figure S6 ^{19}F NMR (DMSO-d_6) of bis(2,2,3,3,4,4,5,5-octafluoropentyl) carbonate **3b**

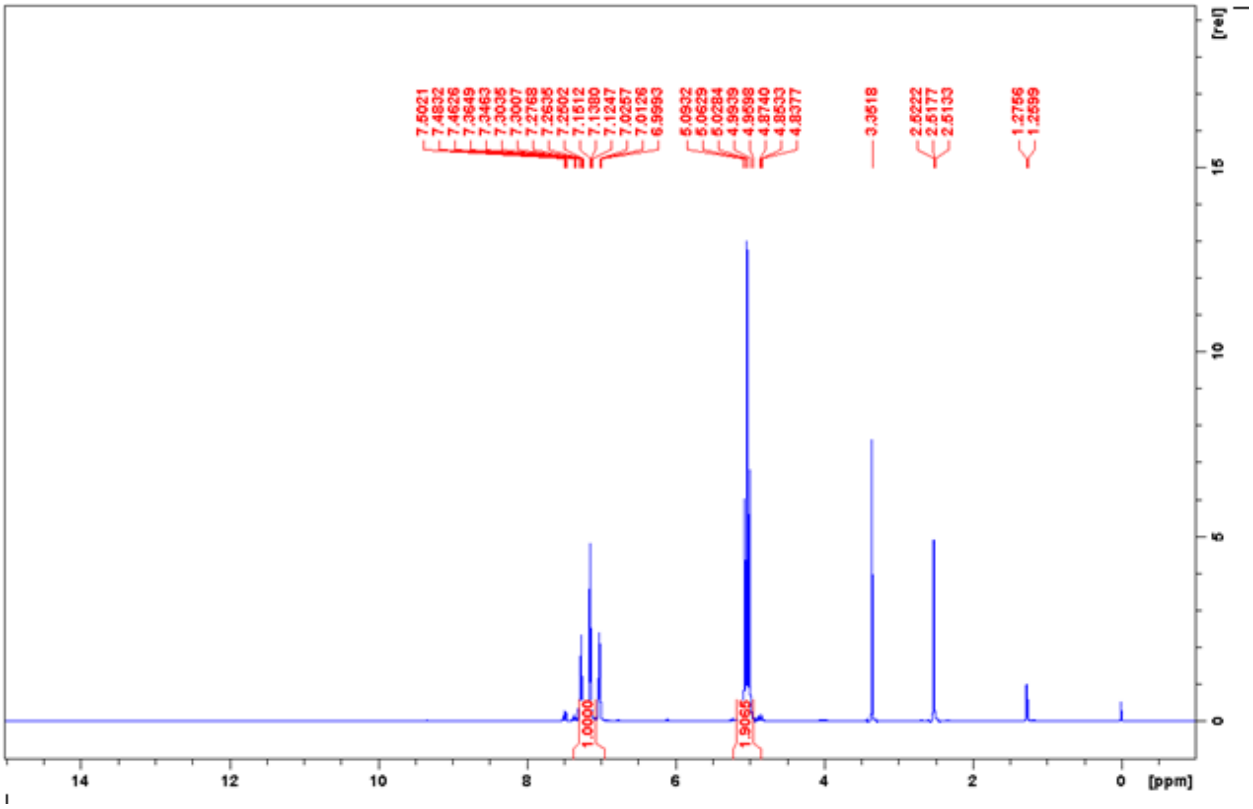


Figure S7 ^{1}H NMR (DMSO-d_6) of bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) carbonate **3c**

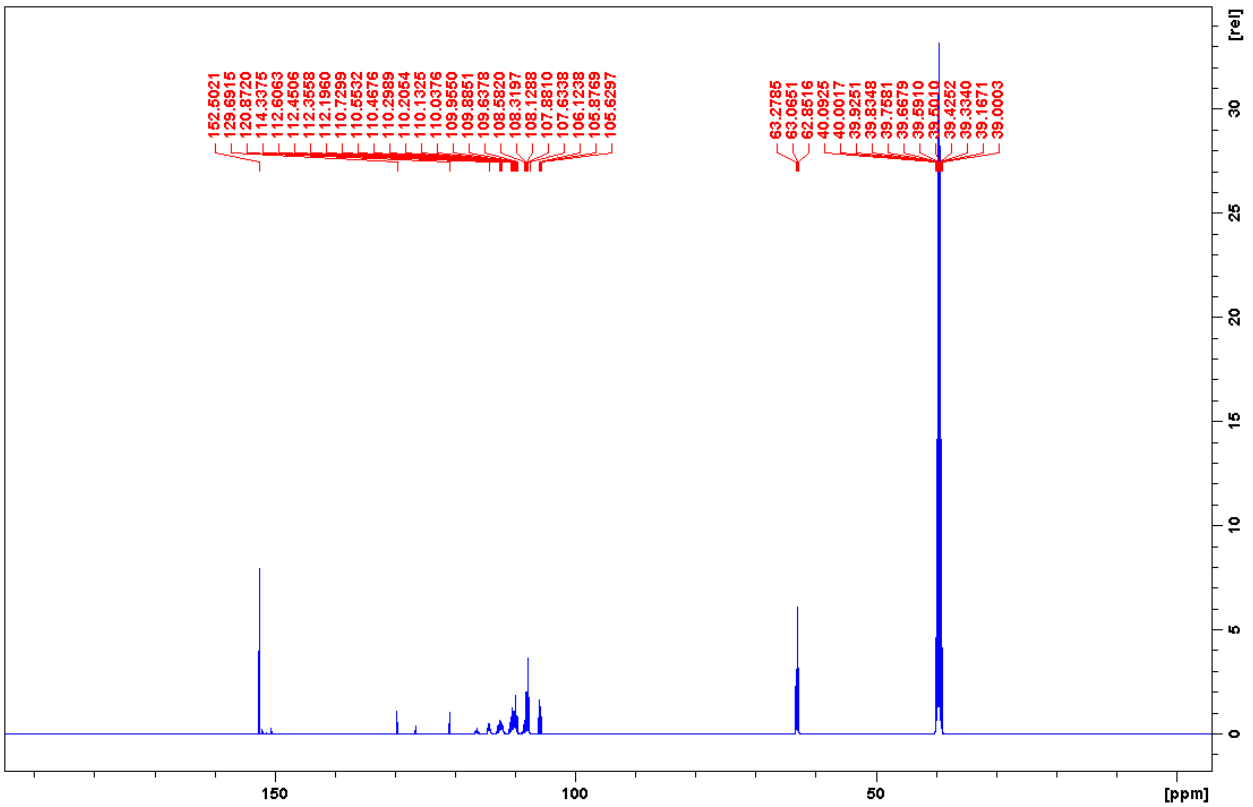


Figure S8 ^{13}C NMR (DMSO-d_6) of bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) carbonate **3c**

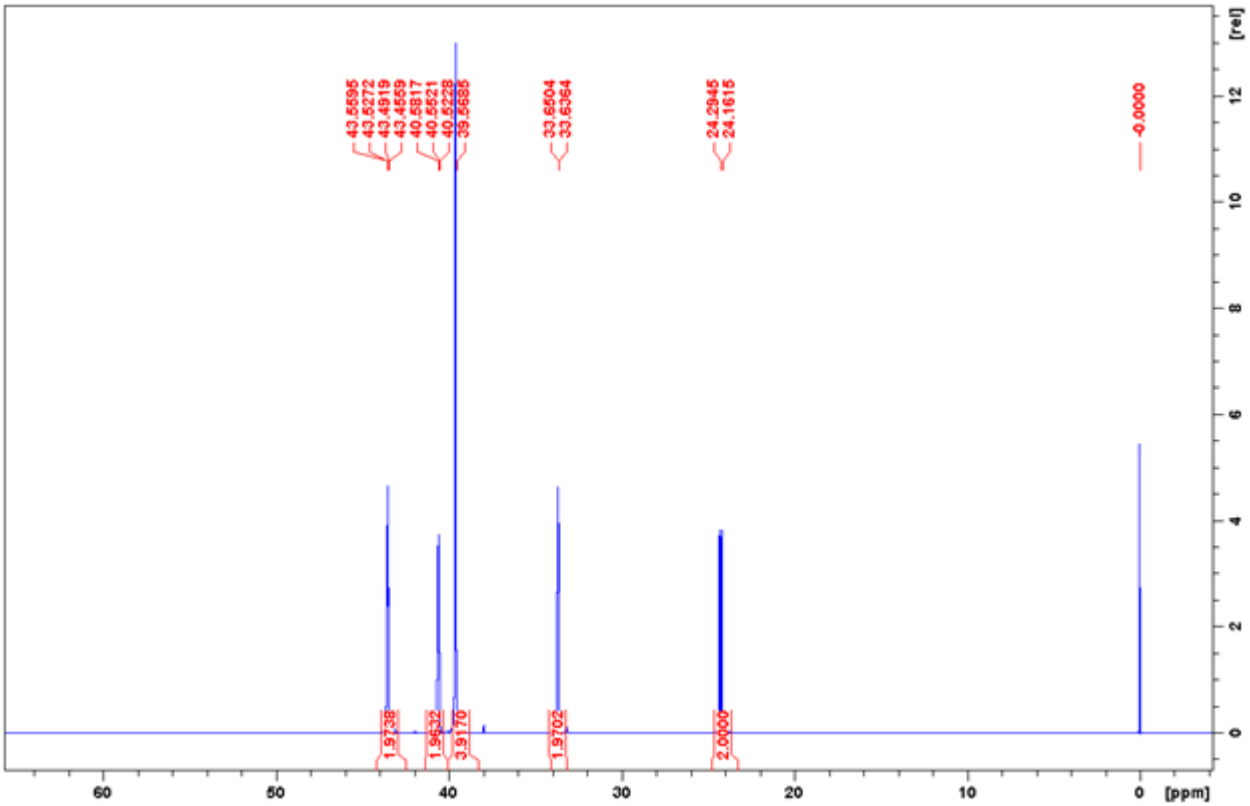
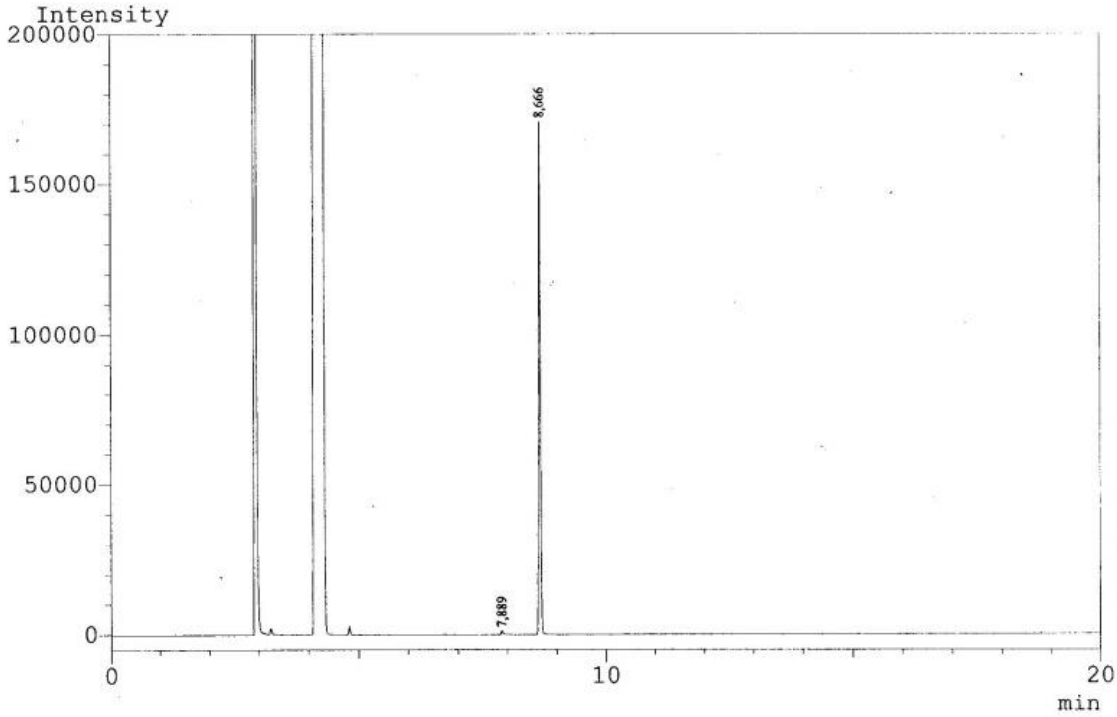


Figure S9 ^{19}F NMR (DMSO-d_6) of bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl) carbonate **3c**

Shimadzu GC-2010 solv-cont-AOC
GsBP-5MS 30*0.25*0.25, T кол 40/3/10/280/50 (77 мин), азот, 74.3 кПа, 1.0 мл/мин,
T исп 250 0C,- 1:30, 34/25,6 , purge 3.0,
T дип 300 0C (N2 30 мл/мин, H2 40 мл/мин, воздух 400 мл/мин)
скорость выборки 40 мсек, время задержки 0.0 мин

Analysis Date & Time : 01.02.2018 12:49:56
User Name : Admin
Vial# : 2
Sample Name : SAM-191-63
Sample ID :
Sample Type : Неизвестный
Injection Volume : 1,00
ISTD Amount :

Data Name : C:\GCsolution\Data\Project1\FID\Лаб. ОМ\Семенова\SAM-191-63_1.gcd
Method Name : C:\GCsolution\Data\Project1\FID\Тест-1-AOC.gcm
[Description]
Образец SAM-191-63
конц. 3.75 мг/мл в хлороформе
ввод 1.0 мкл AOC



Peak#	Ret.Time	Area	Height	Площадь%	Высота%	Conc.
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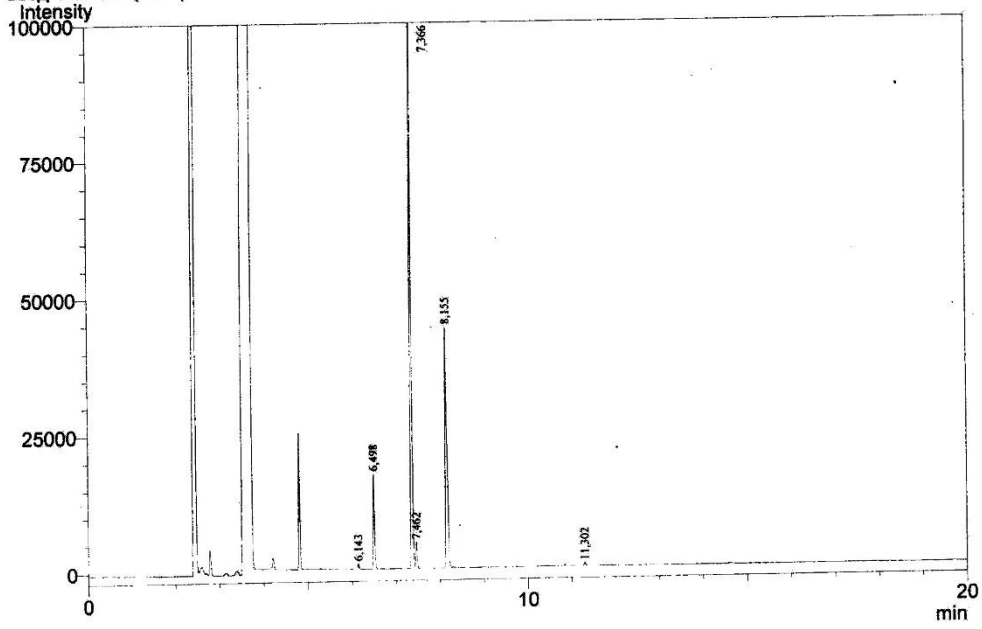
2	8,666	411610	168434	99,2344	99,2658	99,234
Сумма		414786	169680	100,0000	100,0000	100,000

Figure S10 Chromatogram of bis(2,2,3,3-tetrafluoropropyl) carbonate **3a**

Shimadzu GC-2010Plus method: solvent-AOC-40
ZB-5 30*0.25*0.25, T кол 40/3/10/280/50 (77 мин), азот, 74,3 кПа, 1.0 мл/мин
T исп 250 0C. 1:30, 34/25,6, purge 3.0
T дип 300 0C, (N2 30 мл/мин, H2 40 мл/мин, воздух 400 мл/мин)
скорость выборки 40 мсек, время задержки 0.0 мин

Analysis Date & Time : 16.11.2020 12:15:43
User Name : Admin
Vial# : 2
Sample Name : SAM-324-3
Sample ID :
Sample Type : Проба
Injection Volume : 1,00
ISTD Amount :

Data Name : C:\GCsolution\Data\Project1\LabOM\Семёнова\SAM-324-3_1.gcd
Method Name : C:\GCsolution\Data\Project1\Solvent-AOC-40-ПИД.gcm
[Description]
Раствор образца SAM-324-3 в ХЛФ,
c= 2.86 мг/мл
ввод 1.0 мкл (AOC)



Peak#	Ret.Time	Area	Площадь%	Высота	Высота%	Конц.
1	6,143	2013	0,4802	965	0,5271	0,480
2	6,498	35137	8,3817	17157	9,3674	8,382
3	7,366	247049	58,9323	116080	63,3774	58,932
4	7,462	10049	2,3970	4781	2,6104	2,397
5	8,155	123798	29,5313	43667	23,8412	29,531
6	11,302	1163	0,2775	507	0,2765	0,278
Общий		419209	100,0000	183157	100,0000	100,000

Figure S11 Chromatogram of a mixture of diethyl carbonate **4a**, ethyl 2,2,3,3-tetrafluoropropyl carbonate **2a** and bis(2,2,3,3-tetrafluoropropyl) carbonate **3a**

Ret. time	Carbonate
6.498	diethyl carbonate **4a**
7.366	ethyl 2,2,3,4-tetrafluoropropyl carbonate **2a**
8.155	bis(2,2,3,3-tetrafluoropropyl) carbonate **3a**

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Shimadzu GC-2010  solv-cont-AOC
GsBP-5MS 30*0.25*0.25, T кол 40/3/10/280/50 (77 мин), азот, 74.3 кПа, 1.0 мл/мин,
T исп 250 0C,  1:30, 34/25,6 , purge 3.0,
T дип 300 0C (N2 30 мл/мин, H2 40 мл/мин, воздух 400 мл/мин)
скорость выборки 40 мсек, время задержки 0.0 мин

Analysis Date & Time      : 19.12.2017 15:27:53
User Name     : Admin
Vial#         : 6
Sample Name   : SAM-140-3-3
Sample ID     :
Sample Type   : Неизвестный
Injection Volume          : 1,00
ISTD Amount   :

Data Name     : C:\GCsolution\Data\Project1\FID\Лаб. ОМ\Семенова\SAM-140-3-3_1.gcd
Method Name   : C:\GCsolution\Data\Project1\FID\Тест-1-AOC.gcm
[Description]
Образец SAM-140-3-3
конц. 4.1 мг/мл в хлороформе
ввод 1.0 мкл AOC
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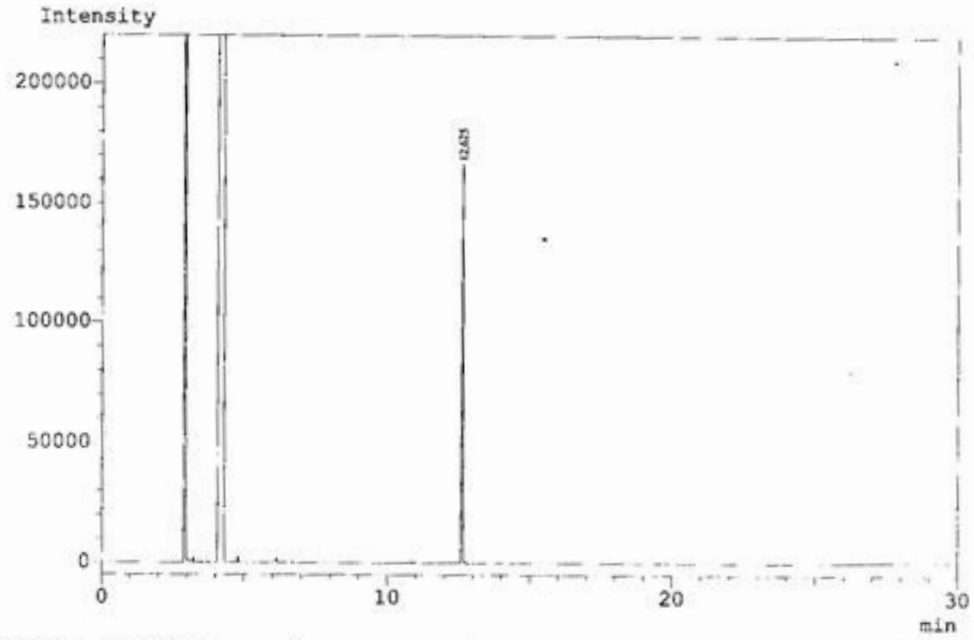

Peak#	Ret.Time	Area	Height	Площадь%	Высота%	Conc.
1	12,625	398817	165938	100,0000	100,0000	100,000
Сумма		398817	165938	100,0000	100,0000	100,000

Figure S12 Chromatogram of bis(2,2,3,3,4,4,5,5-octafluoropentyl) carbonate **3b**

Shimadzu GC-2010 solv-cont-AOC
GsBP-5MS 30*0.25*0.25, T кол 40/3/10/280/50 (77 мин), азот, 74.3 кПа, 1.0 мл/мин,
T исп 250 0C, 1:30, 34/25,6 , purge 3.0,
T дип 300 0C (N2 30 мл/мин, H2 40 мл/мин, воздух 400 мл/мин)
скорость выборки 40 мсек, время задержки 0.0 мин

Analysis Date & Time : 19.12.2017 17:15:41
User Name : Admin
Vial# : 3
Sample Name : SAM-171-6
Sample ID :
Sample Type : Неизвестный
Injection Volume : 1,00
ISTD Amount :

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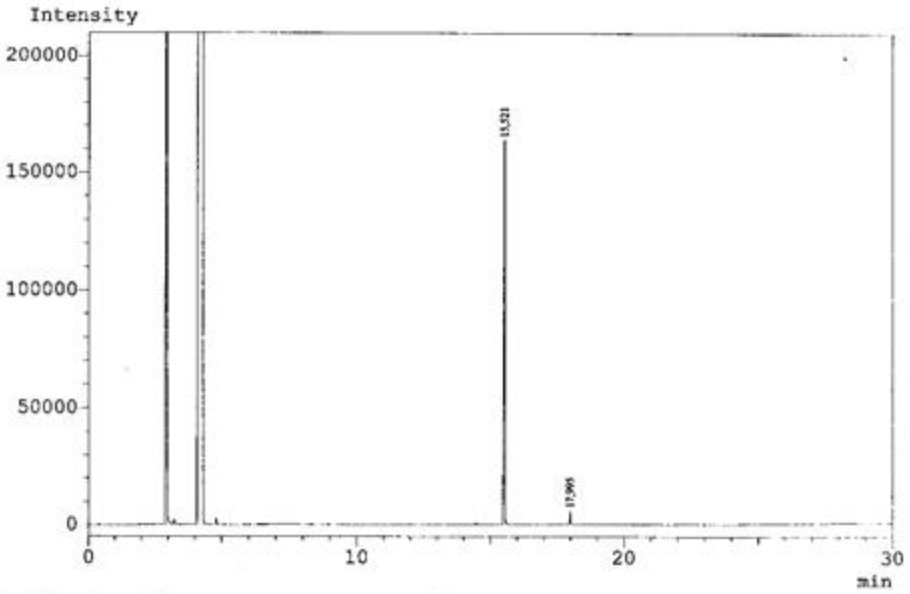
[Description]
Образец SAM-171-6
конц. 4.50мг/мл в хлороформе
ввод 1.0 мкл AOC



Peak#	Ret.Time	Area	Height	Площадь%	Высота%	Conc.
1	15,521	419237	162496	96,9685	96,5546	96,968
2	17,995	13107	5798	3,0315	3,4454	3,032
Сумма		432344	168294	100,0000	100,0000	100,000

Figure S13 Chromatogram of bis(2,2,3,3,4,4,5,5,5,6,6,7,7-dodecafluoroheptyl) carbonate **3c**