

Anhang

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4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[14,14,15,15,16,16,17,17,18,18,-19,19,19-tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorheptadecyl)-nonadecyloxy]biphenyl 45.26	A-63
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4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[14,14,15,15,16,16,17,17,18,18,19,19,-20,20,21,21,22,22,23,23,23-henicosafuor-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,-19,19,20,20,21,21,21-henicosafuorhenicosyl)tricosyloxy]biphenyl 45.28	A-65
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[(2R)-2-(12,12,13,13,14,14,15,15,-16,16,17,17,18,18,19,19,19-heptadecafluoronadecyloxy)propyloxy]biphenyl 45.29	A-65
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[2-(12,12,13,13,14,14,15,15,16,16,-17,17,18,18,19,19,19-heptadecafluoronadecyloxy)propyloxy]biphenyl 45.30	A-66
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[6-(cholesteryloxy)hexyloxy]biphenyl 45.31	A-67
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[11-(cholesteryloxy)undecyloxy]-biphenyl 45.32	A-67
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[(12-menthyloxy)dodecyloxy]biphenyl 45.33	A-68
A.46 Synthese der in 2-Position substituierten Biphenylderivate 46.X	A-68
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,-14,14,15,15,16,16,16-henicosafuorhexadecyloxy)biphenyl 46.1	A-68
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluor-2-nonylundecyloxy)biphenyl 46.2	A-69
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2-[(2R)-2-(12,12,13,13,14,14,15,15,-16,16,17,17,18,18,19,19,19-heptadecafluoronadecyloxy)propyloxy]biphenyl 46.3	A-70
A.47 Synthese der Biphenylderivate 47.X	A-70
4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,13,13,14,14,15,15,16,16,17,17,-18,18,19,19,19-heptadecafluoronadecyloxy)-2'-methylbiphenyl 47.1	A-70

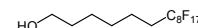
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,13,13,14,14,15,15,16,16,17,17,-18,18,19,19,19-heptadecafluorononadecyloxy)-3'-methylbiphenyl 47.2	A-71
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methyl-3-(6,6,7,7,8,8,9,9,9-nonafluor-2-heptyltridecyloxy)biphenyl 47.3	A-72
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methyl-3-(6,6,7,7,8,8,9,9,9-nonafluor-2-heptyltridecyloxy)biphenyl 47.4	A-72
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methyl-3-[14,14,15,15,16,16,17,17,-18,18,19,19,19-tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorheptadecyl)nonadecyloxy]biphenyl 47.5	A-73
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methyl-3-[14,14,15,15,16,16,17,17,-18,18,19,19,19-tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorheptadecyl)nonadecyloxy]biphenyl 47.6	A-73
A.48	Synthese von 3-(Allkenyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl 48.X	A-74
	3-(Allyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl 48.1	A-74
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(undec-10-en-1-yloxy)biphenyl 48.2	A-75
A.49	Synthese der Biphenylderivate mit Carbosilansubstituenten 49.X	A-75
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8-tetramethyl-4,8-disilanonyloxy)biphenyl 49.1	A-75
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8,12,12-hexamethyl-4,8,12-trisilatridecyloxy)biphenyl 49.2	A-76
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8,12,12,16,16-octamethyl-4,8,12,16-tetrasilahaheptadecyloxy)biphenyl 49.3	A-76
	4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,16,16,20,20,24,24-octamethyl-12,16,20,24-tetrasilapentacosyloxy)biphenyl 49.4	A-77
A.50	Synthese von 2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluorundecyl)-pent-4-en-1-ol 50	A-78
A.51	Synthese von 3-(2-Allyl-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluor-tridecyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl 51	A-78
A.52	Synthese von 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[2-(4,4,5,5,6,6,7,7,8,8,-9,9,10,10,11,11,11-heptadecafluorundecyl)-12,12,16,16,20,20,24,24-octamethyl-12,16,20,24-tetrasilapentacosyloxy]biphenyl 52	A-79
A.53	Synthese der lateral substituierten Terphenylderivate 53.X	A-79
	4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(14,14,15,15,16,16,17,17,18,18,-19,19,20,20,21,21,21-heptadecafluor-2-methylhenicosyloxy)-1,1':4',1''-terphenyl 53.1	A-79
	4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(6,6,7,7,8,8,9,9,9-nonafluor-2-heptylnonyloxy)-1,1':4',1''-terphenyl 53.2	A-80
	4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluor-2-nonylundecyloxy)-1,1':4',1''-terphenyl 53.3	A-81
	4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(6,6,7,7,8,8,9,9,10,10,11,11,-12,12,13,13,13-heptadecafluor-2-undecyltridecyloxy)-1,1':4',1''-terphenyl 53.4	A-81
	4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis[14,14,15,15,16,16,17,17,17-nonafluor-2-(12,12,13,13,14,14,15,15,15-nonafluorpentadecyl)heptadecyloxy]-1,1':4',1''-terphenyl 53.5	A-82
	4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis[14,14,15,15,16,16,17,17,-18,18,19,19,19-tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorheptadecyl)nonadecyloxy]-1,1':4',1''-terphenyl 53.6	A-83

	4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis[14,14,15,15,16,16,17,17,18,18,- 19,19,20,20,21,21,22,22,23,23,23-henicosafuor-2-(12,12,13,13,14,14,15,15,16,16,17,17,- 18,18,19,19,20,20,21,21,21-henicosafuorhenicosyl)]tricosyloxy]-1,1':4',1''-terphenyl 53.7	A-83
A.54	Synthese der lateral substituierten Tolanderivate 54.X	A-84
	1,1'-Ethin-1,2-diylbis[4-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(7,7,8,8,9,9,10,10,10- nonafluordecyloxy)]benzol 54.1	A-84
	1,1'-Ethin-1,2-diylbis[4-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3- (7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptadecafluortetradecyloxy)]benzol 54.2	A-85
	1,1'-Ethin-1,2-diylbis[4-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(14,14,15,15,16,16,- 17,17,18,18,19,19,20,20,21,21,21-heptadecafluor-2-methylhenicosyloxy)]benzol 54.3	A-85
B	Liste der verwendeten Volumeninkremente nach IMMIRZI	A-87
C	Verwendete Gleichungen zur Berechnung der Gitterparameter aus den ermittelten Beugungswinkeln	A-87

A.1 Synthese der semiperfluorierten Alkohole 1.X

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluortetradecan-1-ol **1.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 5.00 g (9.16 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,-Heptadecafluor-8-iodoctan
 0.92 g (9.16 mmol) 5-Hexen-1-ol (Hex-5-en-1-ol)
 0.42 g (0.37 mmol) Pd(PPh₃)₄
 100 ml Hexan
 0.35 g (9.16 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: zweimalige Umkristallisation aus Hexan

Ausbeute: 2.83 g (59 % d. Th.), farbloser Feststoff

Analytik: C₁₄H₁₃F₁₇O M = 520.23 g/mol

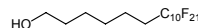
Fp.: 48-52 °C

¹H-NMR (CDCl₃, J/Hz, 500 MHz): δ = 3.64 (t, ³J(H,H) = 6.5, 2H, CH₂OH), 2.09-1.99 (m, 2H, CH₂CF₂), 1.63-1.54 (m, 4H, CH₂CH₂CF₂, CH₂CH₂OH), 1.40 (t, ³J(H,H) = 3.7, 4H, CH₂CH₂CH₂OH, CH₂CH₂CH₂CF₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.16 (t, ⁴J(F,F) = 9.8, 3F, CF₃), -114.81 (s, 2F, CH₂CF₂), -122.15 (s, 2F, CF₂), -122.34 (s, 4F, CF₂), -123.12 (s, 2F, CF₂), -123.93 (s, 2F, CF₂), 126.51 (s, 2F, CF₂CF₃).

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Henicosaf fluorhexadecan-1-ol **1.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 5.00 g (7.74 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Henicosaf fluor-10-ioddecan
 0.85 g (7.74 mmol) Hex-5-en-1-ol
 0.36 g (0.31 mmol) Pd(PPh₃)₄
 50 ml Hexan
 0.29 g (7.74 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: zweimalige Umkristallisation aus Hexan/Essigsäureethylester (5:1, V/V)

Ausbeute: 3.70 g (77 % d. Th.), farbloser Feststoff

Analytik: C₁₆H₁₃F₂₁O M = 620.24 g/mol

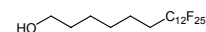
Fp.: 88-90 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.64 (t, ³J(H,H) = 6.5, 2H, CH₂OH), 2.11-1.97 (m, 2H, CH₂CF₂), 1.65-1.54 (m, 4H, CH₂), 1.42-1.39 (m, 4H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.35 (t, ⁴J(F,F) = 9.2, 3F, CF₃), -114.76 (s, 2F, CH₂CF₂), -122.12 (s, 10F, CF₂), -123.04 (s, 2F, CF₂CF₂CF₂CF₃), -123.89 (s, 2F, CF₂CF₂CF₃), -126.44 (s, 2F, CF₂CF₃).

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-Pentacosafluorooctadecan-1-ol **1.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 5.00 g (6.70 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-Pentacosafluor-12-iodododecan
 0.67 g (6.70 mmol) Hex-5-en-1-ol
 0.31 g (0.27 mmol) Pd(PPh₃)₄
 50 ml Hexan
 0.25 g (6.70 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: zweimalige Umkristallisation aus Hexan

Ausbeute: 3.33 g (69 % d. Th.), farbloser Feststoff

Analytik: C₁₈H₁₃F₂₅O M = 720.26 g/mol

Fp.: 115-117 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.64 (t, ³J(H,H) = 6.4, 2H, CH₂OH), 2.11-1.98 (m, 2H, CH₂CF₂), 1.63-1.55 (m, 4H, CH₂), 1.44-1.39 (m, 4H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.33 (t, ⁴J(F,F) = 9.2, 3F, CF₃), -114.70 (s, 2F, CH₂CF₂), -122.06 (s, 14F, CF₂), -123.00 (s, 2F, CF₂), -123.88 (s, 2F, CF₂), -126.44 (s, 2F, CF₂CF₃).

12,12,13,13,14,14,15,15,15-Nonafluorpentadecan-1-ol **1.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 5.00 g (14.5 mmol) 1,1,1,2,2,3,3,4,4-Nonafluor-4-iodobutan
 2.46 g (14.5 mmol) Undec-10-en-1-ol
 0.68 g (0.58 mmol) Pd(PPh₃)₄
 100 ml Hexan
 0.55 g (14.5 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: zweimalige Umkristallisation aus Hexan

Ausbeute: 3.20 g (57 % d. Th.), farbloser Feststoff

Analytik: C₁₅H₂₃F₉O M = 390.33 g/mol

Fp.: 33-35 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.62 (t, ³J(H,H) = 6.6, 2H, CH₂OH), 2.09-1.96 (m, 2H, CH₂CF₂), 1.61-1.51 (m, 4H, CH₂CH₂CF₂, CH₂CH₂OH), 1.38-1.25 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.66 (t, ⁴J(F,F) = 9.7, 3F, CF₃), -114.84-(-115.18) (m, 2F, CH₂CF₂), -124.79-(-124.94) (m, 2F, CF₂), -126.30-(-126.52) (m, 2F, CF₂CF₃).

12,12,13,13,14,14,15,15,16,16,17,17,17-Tridecafluorheptadecan-1-ol **1.5**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.13.



Ansatz: 15.0 g (33.6 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluor-6-iodhexan
5.73 g (33.6 mmol) Undec-10-en-1-ol
1.55 g (1.34 mmol) Pd(PPh₃)₄
100 ml Hexan
1.27 g (33.6 mmol) LiAlH₄
150 ml Diethylether

Reinigung: zweimalige Umkristallisation aus Hexan

Ausbeute: 9.15 g (56 % d. Th.), farbloser Feststoff

Analytik: C₁₇H₂₃F₁₃O M = 490.34 g/mol

Fp.: 52-53 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.64 (t, ³J(H,H) = 6.4, 2H, CH₂OH), 2.11-1.98 (m, 2H, CH₂CF₂), 1.63-1.55 (m, 4H, CH₂), 1.44-1.39 (m, 4H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.33 (t, ⁴J(F,F) = 9.2, 3F, CF₃), -114.70 (s, 2F, CH₂CF₂), -122.06 (s, 14F, CF₂), -123.00 (s, 2F, CF₂) -123.88 (s, 2F, CF₂), -126.44 (s, 2F, CF₂CF₃).

12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19-Heptadecafluormonadecan-1-ol **1.6**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.13.



Ansatz: 5.00 g (9.16 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan
1.56 g (9.16 mmol) Undec-10-en-1-ol
0.42 g (0.37 mmol) Pd(PPh₃)₄
100 ml Hexan
0.35 g (9.16 mmol) LiAlH₄
100 ml Diethylether

Reinigung: zweimalige Umkristallisation aus Hexan

Ausbeute: 4.80 g (89 % d. Th.), farbloser Feststoff

Analytik: C₁₉H₂₃F₁₇O M = 590.36 g/mol

Fp.: 76-78 °C

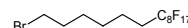
¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.62 (t, ³J(H,H) = 6.6, 2H, OCH₂), 2.10-1.96 (m, 2H, CH₂CF₂), 1.62-1.52 (m, 4H, CH₂CH₂OH, CH₂CH₂CF₂), 1.40-1.24 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.34 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.73 (s, 2F, CH₂CF₂), -122.22 (s, 6F, CF₂), -123.05 (s, 2F, CF₂) -123.88 (s, 2F, CF₂), 126.42 (s, 2F, CF₂CF₃).

A.2 Synthese der semiperfluorierten ω -Bromalkane 2.X

14-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluortetradecan 2.1

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 2.80 g (5.38 mmol) 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluortetradecan-1-ol **1.1**

50 ml HBr (48%-ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Umkristallisation aus Methanol

Ausbeute: 1.92 g (61% d. Th.), farbloser Feststoff

Analytik: C₁₄H₁₂BrF₁₇ M = 583.12 g/mol

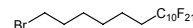
Fp.: 30-32 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.40 (t, ³J(H,H) = 6.7, 2H, CH₂Br), 2.12-1.98 (m, 2H, CH₂CF₂), 1.86 (quint, ³J(H,H) = 7.0, 2H, CH₂CH₂Br), 1.61 (quint, ³J(H,H) = 7.7, 2H, CH₂CH₂CF₂), 1.50-1.38 (m, 4H, CH₂CH₂CH₂OH, CH₂CH₂CH₂CF₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.16 (t, ⁴J(F,F) = 9.8, 3F, CF₃), -114.71 (s, 2F, CH₂CF₂), -122.10 (s, 2F, CF₂), -122.29 (s, 4F, CF₂), -123.08 (s, 2F, CF₂), -123.88 (s, 2F, CF₂), 126.48 (s, 2F, CF₂CF₃).

16-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosaf fluorhexadecan 2.2

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 2.60 g (4.19 mmol)

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Henicosaf fluorhexadecan-1-ol **1.2**

50 ml HBr (48%ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Umkristallisation aus Methanol

Ausbeute: 2.30 g (82 % d. Th.), farbloser Feststoff

Analytik: C₁₆H₁₂BrF₂₁ M = 683.14 g/mol

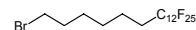
Fp.: 64-65 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.40 (t, ³J(H,H) = 6.7, 2H, CH₂Br), 2.12-1.98 (m, 2H, CH₂CF₂), 1.86 (quint, ³J(H,H) = 6.8, 2H, CH₂CH₂Br), 1.61 (quint, ³J(H,H) = 7.7, 2H, CH₂CH₂CF₂), 1.50-1.38 (m, 4H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.35 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.76 (s, 2F, CH₂CF₂), -122.12 (s, 10F, CH₂CF₂(CF₂)₅), -123.04 (s, 2F, CF₂CF₂CF₂CF₃), -123.87 (s, 2F, CF₂CF₂CF₃), -126.44 (s, 2F, CF₂CF₃).

18-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-pentacosafiuoroctadecan **2.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 0.70 g (0.97 mmol)
 7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-Pentacosafiuoroctadecan-1-ol **1.3**
 50 ml HBr (48%-ig)
 2 ml H₂SO₄
 0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Umkristallisation aus Methanol

Ausbeute: 2.30 g (66 % d. Th.), farbloser Feststoff

Analytik: C₁₈H₁₂BrF₂₅ M = 783.15 g/mol

Fp.: 102-103 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.40 (t, ³J(H,H) = 6.7, 2H, CH₂Br), 2.12-1.98 (m, 2H, CH₂CF₂), 1.87 (quint, ³J(H,H) = 6.8, 2H, CH₂CH₂Br), 1.62 (quint, ³J(H,H) = 7.7, 2H, CH₂CH₂CF₂), 1.53-1.38 (m, 6H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.15 (t, ⁴J(F,F) = 9.3, 3F, CF₃), -114.72 (s, 2F, CH₂CF₂), -122.06 (s, 10F, CH₂CF₂(CF₂)₅), -122.23 (s, 4F, CH₂CF₂(CF₂)₂), -122.06 (s, 2F, CF₂CF₂CF₂CF₃), -123.88 (s, 2F, CF₂CF₂CF₃), -126.47 (s, 2F, CF₂CF₃).

15-Brom-1,1,1,2,2,3,3,4,4-nonafluorpentadecan **2.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 3.20 g (8.20 mmol) 12,12,13,13,14,14,15,15,15-Nonafluorpentadecan-1-ol **1.4**
 50 ml HBr (48%ig)
 2 ml H₂SO₄
 0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 3.00 g (81 % d. Th.), farblose Flüssigkeit

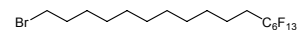
Analytik: C₁₅H₂₂BrF₉ M = 453.22 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.39 (t, ³J(H,H) = 6.8, 2H, BrCH₂), 2.10-1.96 (m, 2H, CH₂CF₂), 1.84 (quint, ³J(H,H) = 7.1, 2H, CH₂CH₂Br), 1.58 (quint, ³J(H,H) = 7.7, 2H, CH₂CH₂CF₂), 1.43-1.24 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.66 (t, ⁴J(F,F) = 9.5, 3F, CF₃), -114.84-(-115.17) (m, 2F, CH₂CF₂), -124.86 (s, 2F, CF₂), -126.31-(-126.53) (m, 2F, CF₂CF₃).

17-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorheptadecan **2.5**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 3.00 g (6.12 mmol)
 12,12,13,13,14,14,15,15,16,16,17,17,17-Tridecafluorheptadecan-1-ol **1.5**
 50 ml HBr (48%-ig)
 2 ml H₂SO₄
 0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 2.39 g (71 % d. Th.), farblose Flüssigkeit

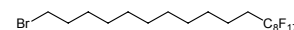
Analytik: C₁₇H₂₂BrF₁₃ M = 553.24 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.39 (t, ³J(H,H) = 6.9, 2H, BrCH₂), 2.10-1.96 (m, 2H, CH₂CF₂), 1.84 (quint, ³J(H,H) = 7.1, 2H, CH₂CH₂Br), 1.58 (quint, ³J(H,H) = 7.7, 2H, CH₂CH₂CF₂), 1.44-1.24 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz):) δ = -81.37 (s, 3F, CF₃), -114.76 (s, 2F, CH₂CF₂), -122.31 (s, 2F, CF₂), -123.25 (s, 2F, CF₂) -123.92 (s, 2F, CF₂), 126.47 (s, 2F, CF₂CF₃).

19-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoronadecan **2.6**

Die Darstellung erfolgte nach der allgemeinen
 Arbeitsvorschrift 5.3.14.



Ansatz: 4.80 g (8.13 mmol) 12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluoronadecan-1-ol **1.6**
 50 ml HBr (48%-ig)
 2 ml H₂SO₄
 0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 3.40 g (64% d. Th.), farbloser Feststoff

Analytik: C₁₉H₂₂BrF₁₇ M = 553.24 g/mol

Fp.: 36-37 °C

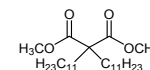
¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.39 (t, ³J(H,H) = 6.8, 2H, BrCH₂), 2.10-1.96 (m, 2H, CH₂CF₂), 1.84 (quint, ³J(H,H) = 7.1, 2H, CH₂CH₂Br), 1.58 (quint, ³J(H,H) = 7.7, 2H, CH₂CH₂CF₂), 1.43-1.24 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.35 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.73 (s, 2F, CH₂CF₂), -122.22 (s, 6F, CF₂), -123.06 (s, 2F, CF₂) -123.88 (s, 2F, CF₂), 126.43 (s, 2F, CF₂CF₃).

A.3 Synthese der Dialkylmalonsäuredimethylester 3.X

Diundecylmalonsäuredimethylester **3.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 15.0 g (52.3 mmol) Undecylmalonsäuredimethylester
 13.9 g (54.9 mmol) 1-Bromundecan

1.20 g (52.3 mmol) Na

100 ml Methanol

Reinigung: Hochvakuumdestillation und Säulenchromatographie des Sumpfes
(Eluent: CHCl₃)

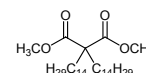
Ausbeute: 15.0 g (65 % d. Th.), farblose Flüssigkeit

Analytik: C₂₇H₅₂O₄ M = 440.70 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.68 (s, 6H, OCH₃), 1.88-1.82 (m, 4H, CCH₂), 1.30-1.08 (m, 36H, CH₂), 0.86 (t, ³J(H,H) = 6.8, 6H, CH₃).

Ditetradecylmalonsäuredimethylester **3.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 20.0 g (38.1 mmol) Tetradeacylmalonsäuredimethylester

12.7 g (45.7 mmol) 1-Bromtetradecan

0.88 g (38.1 mmol) Na

100 ml Methanol

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 13.0 g (67% d. Th.), farblose Flüssigkeit

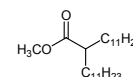
Analytik: C₃₃H₆₄O₄ M = 524.86 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.71 (s, 6H, OCH₃), 1.89-1.84 (m, 4H, CCH₂), 1.27-1.18 (m, 48H, CH₂), 0.85 (t, ³J(H,H) = 6.7, 6H, CH₃).

A.4 Synthese der 2-Alkylalkansäuremethylester **4.X**

2-Undecyltridecansäuremethylester **4.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 15.0 g (34.0 mmol) Diundecylmalonsäuredimethylester **3.2**

2.88 g (68.0 mmol) LiCl

0.61 g (34.0 mmol) Wasser

100 ml DMSO

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

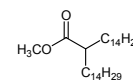
Ausbeute: 4.60 g (35 % d. Th.), farblose Flüssigkeit

Analytik: C₂₅H₅₀O₂ M = 382.66 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.65 (s, 3H, OCH₃), 2.34-2.25 (m, 1H, CH), 1.61-1.52 (m, 2H, CH₂), 1.45-1.37 (m, 2H, CH₂), 1.30-1.18 (m, 36H, CH₂), 0.86 (t, ³J(H,H) = 6.8, 6H, CH₃).

2-Tetradecylhexadecansäuremethylester **4.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 13.0 g (25.0 mmol) Ditetradecylmalonsäuredimethylester **3.3**
 2.10 g (50.0 mmol) LiCl
 0.45 g (25.0 mmol) Wasser
 100 ml DMSO

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

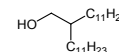
Ausbeute: 4.78 g (41 % d. Th.), farblose Flüssigkeit

Analytik: C₂₅H₅₀O₂ M = 382.66 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.65 (s, 3H, OCH₃), 2.33-2.27 (m, 1H, CH), 1.59-1.54 (m, 4H, CH₂), 1.43-1.38 (m, 4H, CH₂), 1.23 (bs, 44H, CH₂), 0.86 (t, ³J(H,H) = 6.7, 6H, CH₃).

A.5 Synthese der 2-Alkylalkan-1-ole 5.X2-Undecyltridecan-1-ol **5.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.12.



Ansatz: 3.60 g (9.41 mmol) 2-Undecyltridecansäuremethylester **4.2**
 1.07 g (28.2 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 2.80 g (84 % d. Th.), farbloser Feststoff

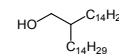
Analytik: C₂₄H₅₀O M = 354.65 g/mol

Fp.: 25-27 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.52 (d, ³J(H,H) = 5.5, 2H, CH₂OH), 1.45-1.42 (m, 1H, CH), 1.33-1.19 (m, 40H, CH₂), 0.86 (t, ³J(H,H) = 6.9, 6H, CH₃).

2-Tetradecylhexadecan-1-ol **5.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.12.



Ansatz: 4.78 g (12.5 mmol) 2-Tetradecylhexadecansäuremethylester **4.3**
 1.42 g (37.5 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 4.33 g (79 % d. Th.), farbloser Feststoff

Analytik: C₃₀H₆₂O M = 438.81 g/mol

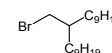
Fp.: 43-45 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.52 (d, ³J(H,H) = 5.5, 2H, CH₂OH), 1.46-1.42 (m, 1H, CH), 1.33-1.19 (m, 52H, CH₂), 0.86 (t, ³J(H,H) = 7.0, 6H, CH₃).

A.6 Synthese der (Brommethyl)alkane 6.X

10-(Brommethyl)nonadecan 6.1

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 5.00 g (16.7 mmol) 2-Nonylundecan-1-ol
50 ml HBr (48%-ig)
2 ml H₂SO₄
0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

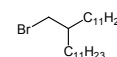
Ausbeute: 4.80 g (80 % d. Th.), farblose Flüssigkeit

Analytik: C₂₀H₄₁Br M = 361.44 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.43 (d, ³J(H,H) = 4.8, 2H, BrCH₂), 1.60-1.55 (m, 1H, CH), 1.45-1.20 (m, 32H, CH₂), 0.87 (t, ³J(H,H) = 6.9, 6H, CH₃).

12-(Brommethyl)tricosan 6.2

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 2.60 g (7.33 mmol) 2-Undecyltridecan-1-ol **5.2**
50 ml HBr (48%ig)
2 ml H₂SO₄
0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

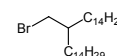
Ausbeute: 2.30 g (75 % d. Th.), farblose Flüssigkeit

Analytik: C₂₄H₄₉Br M = 417.55 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.42 (d, ³J(H,H) = 4.8, 2H, CH₂Br), 1.60-1.55 (m, 1H, CH), 1.37-1.20 (m, 40H, CH₂), 0.86 (t, ³J(H,H) = 6.9, 6H, CH₃).

15-(Brommethyl)nonacosan 6.3

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 4.30 g (9.80 mmol) 2-Tetradecylhexadecan-1-ol **5.3**
50 ml HBr (48%-ig)
2 ml H₂SO₄
0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 3.78 g (77 % d. Th.), farblose Flüssigkeit

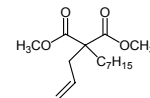
Analytik: C₃₀H₆₁Br M = 501.71 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.43 (d, ³J(H,H) = 4.8, 2H, BrCH₂), 1.60-1.55 (m, 1H, CH), 1.40-1.20 (m, 52H, CH₂), 0.87 (t, ³J(H,H) = 6.8, 6H, CH₃).

A.7 Synthese der Alkyl(alkenyl)malonsäuredimethylester 7.X

Allyl(heptyl)malonsäuredimethylester 7.1

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 25.0 g (109 mmol) Heptylmalonsäuredimethylester
 15.8 g (130 mmol) Allylbromid
 3.00 g (130 mmol) Na
 200 ml Methanol

Reinigung: Hochvakuumdestillation

Ausbeute: 16.1 g (55 % d. Th.), farblose Flüssigkeit

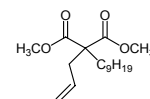
Analytik: $C_{15}H_{26}O_4$ $M = 270.36$ g/mol

Kp.: 79-80 °C ($1.3 \cdot 10^{-2}$ mbar)

1H -NMR ($CDCl_3$, J/Hz , 500 MHz): $\delta = 5.65$ - 5.57 (m, 1H, $CH=CH_2$), 5.08 - 5.04 (m, 2H, $CH_2=CH$), 3.68 (s, 6H, OCH_3), 2.62 (d, $^3J(H,H) = 7.4$, 2H, $CH_2CH=CH_2$), 1.85 - 1.81 (m, 2H, CCH_2), 1.28 - 1.22 (m, 8H, CH_2), 1.16 - 1.11 (m, 2H, CH_2), 0.85 (t, $^3J(H,H) = 7.1$, 3H, CH_3).

Allyl(nonyl)malonsäuredimethylester 7.2

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 30.0 g (116 mmol) Nonylmalonäuredimethylester
 14.7 g (122 mmol) Allylbromid
 2.70 g (116 mmol) Na
 200 ml Methanol

Reinigung: Hochvakuumdestillation

Ausbeute: 12.2 g (35 % d. Th.), farblose Flüssigkeit

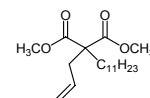
Analytik: $C_{17}H_{30}O_4$ $M = 298.42$ g/mol

Kp.: 115-116 °C ($5.1 \cdot 10^{-2}$ mbar)

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 5.66$ - 5.56 (m, 1H, $CH=CH_2$), 5.09 - 5.04 (m, 2H, $CH_2=CH$), 3.69 (s, 6H, OCH_3), 2.62 (d, $^3J(H,H) = 7.4$, 2H, $CH_2CH=$), 1.86 - 1.81 (m, 2H, CCH_2), 1.30 - 1.21 (m, 14H, CH_2), 0.85 (t, $^3J(H,H) = 6.9$, 3H, CH_3).

Allyl(undecyl)malonsäuredimethylester 7.3

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 30.0 g (116 mmol) Undecylmalonäuredimethylester
 12.7 g (105 mmol) Allylbromid
 2.40 g (105 mmol) Na

200 ml Methanol

Reinigung: Hochvakuumdestillation

Ausbeute: 15.0 g (53 % d. Th.), farblose Flüssigkeit

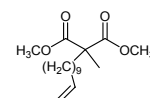
Analytik: $C_{19}H_{34}O_4$ $M = 326.47$ g/mol

Kp.: 103-106 °C ($0.5 \cdot 10^{-2}$ mbar)

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 5.67$ - 5.56 (m, 1H, $CH=CH_2$), 5.09 - 5.04 (m, 2H, $CH_2=CH$), 3.69 (s, 6H, OCH_3), 2.62 (d, $^3J(H,H) = 7.4$, 2H, $CH_2CH=CH_2$), 1.90 - 1.81 (m, 2H, CCH_2), 1.28 - 1.21 (m, 16H, CH_2), 1.19 - 1.10 (m, 2H, CH_2), 0.86 (t, $^3J(H,H) = 6.9$, 3H, CH_3).

Methyl(undec-10-en-1-yl)malonsäuredimethylester 7.4

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 30.0 g (205 mmol) Methylmalonsäuredimethylester

57.3 g (246 mmol) 11-Bromundec-1-en

5.66 g (246 mmol) Na

200 ml Methanol

Reinigung: Hochvakuumdestillation und Säulenchromatographie des Sumpfes
(Eluent: $CHCl_3$)

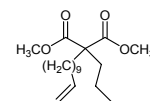
Ausbeute: 45.1 g (74 % d. Th.), farblose Flüssigkeit

Analytik: $C_{17}H_{30}O_4$ $M = 298.42$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 5.83$ - 5.73 (m, 1H, $CH=CH_2$), 4.99 - 4.88 (m, 2H, $CH_2=CH$), 3.68 (s, 6H, OCH_3), 2.01 (q, $^3J(H,H) = 7.1$, 2H, $CH_2CH=$), 1.84 - 1.80 (m, 2H, CCH_2), 1.38 (s, 3H, CH_3), 1.37 - 1.20 (m, 14H, CH_2).

Propyl(undec-10-en-1-yl)malonsäuredimethylester 7.5

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 10.0 g (49.4 mmol) Propylmalonsäuredimethylester

11.5 g (49.4 mmol) 11-Bromundec-1-en

1.14 g (49.4 mmol) Na

200 ml Methanol

Reinigung: Säulenchromatographie (Eluent: PE/ $CHCl_3$, 1:1, V/V)

Ausbeute: 7.40 g (46 % d. Th.), farblose Flüssigkeit

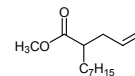
Analytik: $C_{19}H_{34}O_4$ $M = 326.47$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 5.83$ - 5.73 (m, 1H, $CH=CH_2$), 4.99 - 4.88 (m, 2H, $CH_2=CH$), 3.71 (s, 6H, OCH_3), 2.01 (q, $^3J(H,H) = 7.1$, 2H, $CH_2CH=$), 1.87 - 1.80 (m, 4H, CCH_2), 1.37 - 1.20 (m, 16H, CH_2), 0.91 (q, $^3J(H,H) = 7.1$, 3H, CH_3).

A.8 Synthese der 2-Alkylalkensäuremethylester 8.X

2-Allylnonansäuremethylester 8.1

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 16.1 g (59.6 mmol) Allyl(heptyl)malonsäuredimethylester **7.1**
 5.05 g (119 mmol) LiCl
 1.0 ml (59.6 mmol) Wasser
 100 ml DMSO

Reinigung: Hochvakuumdestillation

Ausbeute: 6.20 g (49 % d. Th.), farblose Flüssigkeit

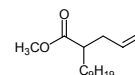
Analytik: C₁₃H₂₄O₂ M = 212.33 g/mol

Kp.: 50-53 °C (1.2·10⁻² mbar)

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 5.76-5.66 (m, 1H, CH=CH₂), 5.05-4.96 (m, 2H, CH₂=CH), 3.64 (s, 3H, OCH₃), 2.45-2.38 (m, 1H, CH), 2.36-2.17 (m, 2H, CH₂CH=CH₂), 1.63-1.41 (m, 2H, CHCH₂), 1.29-1.21 (m, 10H, CH₂), 0.86 (t, ³J(H,H) = 6.9, 3H, CH₃).

2-Allylundecansäuremethylester 8.2

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 12.0 g (40.2 mmol) Allyl(nonyl)malonsäuredimethylester **7.2**
 3.40 g (80.4 mmol) LiCl
 7.2 ml (40.2 mmol) Wasser
 100 ml DMSO

Reinigung: Hochvakuumdestillation

Ausbeute: 3.40 g (34 % d. Th.), farblose Flüssigkeit

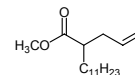
Analytik: C₁₅H₂₈O₂ M = 240.38 g/mol

Kp.: 80-83 °C (3.1·10⁻² mbar)

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 5.76-5.66 (m, 1H, CH=CH₂), 5.05-4.96 (m, 2H, CH₂=CH), 3.64 (s, 3H, OCH₃), 2.45-2.38 (m, 1H, CH), 2.36-2.16 (m, 2H, CH₂CH=CH₂), 1.63-1.41 (m, 2H, CHCH₂), 1.29-1.21 (m, 14H, CHCH₂), 0.86 (t, ³J(H,H) = 6.8, 3H, CH₃).

2-Allyltridecansäuremethylester 8.3

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 15.0 g (45.9 mmol) Allyl(undecyl)malonsäuredimethylester **7.3**
 3.89 g (91.8 mmol) LiCl
 0.8 ml (45.9 mmol) Wasser
 100 ml DMSO

Reinigung: Hochvakuumdestillation

Ausbeute: 3.00 g (24 % d. Th.), farblose Flüssigkeit

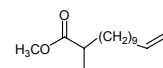
Analytik: $C_{17}H_{32}O_2$ $M = 268.43$ g/mol

Kp.: $85-89$ °C ($0.6 \cdot 10^{-2}$ mbar)

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 5.77-5.66$ (m, 1H, $CH=CH_2$), $5.05-4.97$ (m, 2H, $CH_2=CH$), 3.64 (s, 3H, OCH_3), $2.45-2.38$ (m, 1H, CH), $2.36-2.17$ (m, 2H, $CH_2CH=CH_2$), $1.63-1.42$ (m, 2H, $CHCH_2$), $1.30-1.18$ (m, 18H, CH_2), 0.86 (t, $^3J(H,H) = 6.9$, 3H, CH_3).

2-Methyltridec-12-ensäuremethylester 8.4

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 45.0 g (151 mmol) Methyl(undec-10-en-1-yl)malonsäuredimethylester **7.4**

2.88 g (302 mmol) LiCl

2.71 g (151 mmol) Wasser

100 ml DMSO

Reinigung: Säulenchromatographie (Eluent: $CHCl_3/MeOH$ 10:0.2, V/V)

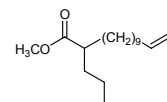
Ausbeute: 15.5 g (43 % d. Th.), farblose Flüssigkeit

Analytik: $C_{15}H_{28}O_2$ $M = 240.38$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 200 MHz): $\delta = 5.88-5.68$ (m, 1H, $CH=CH_2$), $5.01-4.86$ (m, 2H, $CH_2=CH$), 3.63 (s, 3H, OCH_3), 2.38 (q, $^3J(H,H) = 6.8$, 1H, CH), 2.01 (q, $^3J(H,H) = 6.8$, 2H, $CH_2CH=$), $1.68-1.54$ (m, 2H, $CHCH_2$), $1.41-1.19$ (m, 14H, CH_2), 1.11 (d, $^3J(H,H) = 7.0$, 3H, CH_3).

2-Propyltridec-12-ensäuremethylester 8.5

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 7.40 g (22.7 mmol) Propyl(undec-10-en-1-yl)malonsäuredimethylester **7.5**

1.92 g (45.3 mmol) LiCl

0.41 g (22.7 mmol) Wasser

100 ml DMSO

Reinigung: Säulenchromatographie (Eluent: $CHCl_3/MeOH$ 10:0.2, V/V)

Ausbeute: 3.17 g (52 % d. Th.), farblose Flüssigkeit

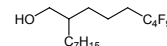
Analytik: $C_{17}H_{32}O_2$ $M = 268.43$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 400 MHz) $\delta = 5.83-5.73$ (m, 1H, $CH=CH_2$), $4.99-4.88$ (m, 2H, $CH_2=CH$), 3.68 (s, 3H, OCH_3), 2.38 (m, 1H, CH), 2.01 (q, $^3J(H,H) = 7.1$, 2H, $CH_2CH=$), $1.87-1.80$ (m, 4H, CCH_2), $1.36-1.22$ (m, 16H, CH_2), 0.91 (q, $^3J(H,H) = 7.2$, 3H, CH_3).

A.9 Synthese der semiperfluorierten 2-Alkylalkohole 9.X

6,6,7,7,8,8,9,9,9-Nonafluor-2-heptylnonan-1-ol 9.1

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 6.00 g (28.3 mmol) 2-Allylnonansäuremethylester **8.1**

9.79 g (28.3 mmol) 1,1,1,2,2,3,3,4,4-Nonafluor-4-iodbutan
 1.31 g (1.13 mmol) Pd(PPh₃)₄
 100 ml Hexan
 3.21 g (84.9 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: Hochvakuumdestillation

Ausbeute: 3.80 g (33 % d. Th.), farblose Flüssigkeit

Analytik: C₁₆H₂₅F₉O M = 404.35 g/mol

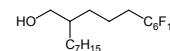
Kp.: 100-102 °C (1.0·10⁻² mbar)

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.60-3.50 (m, 2H, CH₂OH), 2.12-1.98 (m, 2H, CH₂CF₂), 1.62 (quint, ³J(H,H) = 7.9, 2H, CH₂CH₂CF₂), 1.50-1.41 (m, 2H, CH₂), 1.37-1.20 (m, 15H, CH, CH₂), 0.87 (t, ³J(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.46 (t, ⁴J(F,F) = 9.8, 3F, CF₃), -114.96 (s, 2F, CH₂CF₂), -124.93 (s, 2F, CH₂CF₂CF₂), -126.48 (s, 2F, CF₂CF₃).

6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluor-2-heptylundecan-1-ol **9.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 2.27 g (10.7 mmol) 2-Allylnonansäuremethylester **8.1**
 4.77 g (10.7 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluor-6-iodhexan
 0.49 g (1.13 mmol) Pd(PPh₃)₄
 50 ml Hexan
 1.22 g 32.1 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 3.20 g (59 % d. Th.), farblose Flüssigkeit

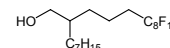
Analytik: C₁₈H₂₅F₁₃O M = 504.37 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.60-3.50 (m, 2H, CH₂OH), 2.11-1.98 (m, 2H, CH₂CF₂), 1.62 (quint, ³J(H,H) = 8.0, 2H, CH₂CH₂CF₂), 1.52-1.41 (m, 3H, CH, CH₂), 1.37-1.22 (m, 12H, CH₂), 0.87 (t, ³J(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.40 (t, ⁴J(F,F) = 9.2, 3F, CF₃), -114.50-(-114.88) (m, 2F, CH₂CF₂), -122.29 (s, 2F, CF₂), -123.26 (s, 2F, CF₂), -123.94 (s, 2F, CH₂), -126.39-(-126.56) (m, 2F, CF₂CF₃).

6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heptadecafluor-2-heptyltridecan-1-ol **9.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 2.20 g (10.4 mmol) 2-Allylnonansäuremethylester **8.1**
 5.68 g (10.4 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan
 0.48 g (0.42 mmol) Pd(PPh₃)₄
 150 ml Hexan

1.18 g (31.2 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Umkristallisation aus Hexan

Ausbeute: 2.50 g (40 % d. Th.), farbloser Feststoff

Analytik: C₂₀H₂₅F₁₇O M = 604.38 g/mol

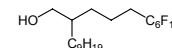
Fp.: 40-41 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.60-3.50 (m, 2H, CH₂OH), 2.11-1.98 (m, 2H, CH₂CF₂), 1.62 (quint, ³J(H,H) = 8.0, 2H, CH₂CH₂CF₂), 1.50-1.42 (m, 3H, CH, CH₂), 1.37-1.20 (m, 12H, CH₂), 0.87 (t, ³J(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.35 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.63 (s, 2F, CH₂CF₂), 122.20 (s, 6F, CF₂), -123.05 (s, 2F, CF₂), 123.89 (s, 2F, CH₂), -126.42 (s, 2F, CF₂CF₃).

6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluor-2-nonylundecan-1-ol **9.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 1.60 g (6.66 mmol) 2-Allylundecansäuremethylester **8.2**

2.97 g (6.66 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluor-6-iodhexan

0.38 g (3.33 mmol) Pd(PPh₃)₄

50 ml Hexan

0.76 g (19.9 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Hochvakuumdestillation

Ausbeute: 2.00 g (56 % d. Th.), farblose Flüssigkeit

Analytik: C₂₀H₂₉F₁₃O M = 532.42 g/mol

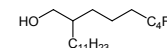
Kp.: 99-102 °C (0.5·10⁻² mbar)

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.60-3.50 (m, 2H, CH₂OH), 2.12-1.97 (m, 2H, CH₂CF₂), 1.66-1.58 (m, 2H, CH₂CH₂CF₂), 1.50-1.45 (m, 1H, CH), 1.31-1.24 (m, 18H, CH₂), 0.86 (t, ³J(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.30 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.47-(-114.64) (m, 2F, CH₂CF₂), 122.25 (s, 2F, CF₂), -123.11 (s, 2F, CF₂), -123.89 (s, 2F, CF₂), -126.49 (s, 2F, CF₂CF₃).

2-(4,4,5,5,6,6,7,7,7-Nonafluorheptyl)tridecan-1-ol **9.5**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 3.50 g (13.0 mmol) 2-Allyltridecansäuremethylester **8.3**

4.51 g (13.0 mmol) 1,1,1,2,2,3,3,4,4-Nonafluor-4-iodbutan

0.60 g (0.52 mmol) Pd(PPh₃)₄

50 ml Hexan

1.48 g (39.0 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 4.40 g (74 % d. Th.), farblose Flüssigkeit

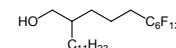
Analytik: C₂₀H₃₃F₉O M = 460.46 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.60-3.50 (m, 2H, CH₂OH), 2.11-1.97 (m, 2H, CH₂CF₂), 1.62 (quint, ³J(H,H) = 8.0, 2H, CH₂CH₂CF₂), 1.50-1.33 (m, 3H, CH, CH₂), 1.31-1.20 (m, 20H, CH₂), 0.86 (t, ³J(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.65 (t, ⁴J(F,F) = 9.7, 3F, CF₃), -114.75-(-115.08) (m, 2F, CH₂CF₂), -124.86 (s, 2F, CF₂), -126.30-(-126.51) (m, 2F, CF₂CF₃).

6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluor-2-undecylundecan-1-ol **9.6**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 1.50 g (5.59 mmol) 2-Allyltridecansäuremethylester **8.3**

4.51 g (5.59 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluor-6-iodhexan

0.26 g (0.22 mmol) Pd(PPh₃)₄

50 ml Hexan

0.64 g (16.8 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 2.10 g (67 % d. Th.), farblose Flüssigkeit

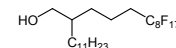
Analytik: C₂₂H₃₃F₁₃O M = 560.48 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.60-3.50 (m, 2H, CH₂OH), 2.11-1.98 (m, 2H, CH₂CF₂), 1.62 (quint, ³J(H,H) = 8.0, 2H, CH₂CH₂CF₂), 1.50-1.42 (m, 2H, CH₂), 1.37-1.19 (m, 20H, CH₂), 0.86 (t, ³J(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.41 (t, ⁴J(F,F) = 9.7, 3F, CF₃), -114.52-(-114.86) (m, 2F, CH₂CF₂), 122.30 (s, 2F, CF₂), -123.26 (s, 2F, CF₂), 123.95 (s, 2F, CH₂), -126.39-(-126.62) (m, 2F, CF₂CF₃).

6,6,7,7,8,8,9,9,10,10,12,12,13,13,14,14,14-Heptadecafluor-2-undecyltridecan-1-ol **9.7**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 3.00 g (11.2 mmol) 2-Allyltridecansäuremethylester **8.3**

9.79 g (11.2 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan

0.52 g (0.45 mmol) Pd(PPh₃)₄

50 ml Hexan

1.27 g (33.6 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Umkristallisation aus Hexan/Essigsäureethylester (5:1, V/V)

Ausbeute: 2.11 g (28 % d. Th.), farbloser Feststoff

Analytik: C₂₄H₃₃F₁₇O M = 660.49 g/mol

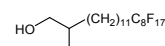
Fp.: 52-53 °C

¹H-NMR (CDCl₃, *J*/Hz, 500 MHz): δ = 3.59-3.50 (m, 2H, CH₂OH), 2.09-1.99 (m, 2H, CH₂CF₂), 1.61 (quint, ³*J*(H,H) = 8.0, 2H, CH₂CH₂CF₂), 1.57-1.52 (m, 2H, CH₂), 1.50-1.44 (m, 1H, CH), 1.36-1.21 (m, 20H, CH₂), 0.86 (t, ³*J*(H,H) = 7.0, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 470 MHz) δ = -81.15 (t, ⁴*J*(F,F) = 9.8, 3F, CF₃), -114.70 (s, 2F, CH₂CF₂), -122.12 (s, 2F, CF₂), -122.33 (s, 4F, CF₂), -123.12 (s, 2F, CF₂), -123.93 (s, 2F, CF₂), -126.50 (s, 2F, CF₂CF₃).

14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,21-Heptadecafluor-2-methylhenicosan-1-ol **9.8**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 2.00 g (8.32 mmol) 2-Methyltridec-12-ensäuremethylester **8.4**
 5.68 g (8.32 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan
 0.38 g (0.33 mmol) Pd(PPh₃)₄
 50 ml Hexan
 0.95 g (25.0 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: Umkristallisation aus Hexan

Ausbeute: 4.40 g (84 % d. Th.), farbloser Feststoff

Analytik: C₂₂H₂₉F₁₇O M = 632.44 g/mol

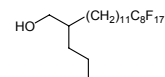
Fp.: 73-74 °C

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 3.51-3.38 (m, 2H, CH₂OH), 2.10-1.96 (m, 2H, CH₂CF₂), 1.62-1.54 (m, 3H, CH₂CH₂CF₂, CHCH₃), 1.39-1.22 (m, 18H, CH₂), 0.90 (d, ³*J*(H,H) = 6.7, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.36 (t, ⁴*J*(F,F) = 9.9, 3F, CF₃), -114.74 (s, 2F, CH₂CF₂), -122.20 (s, 6F, CF₂), -123.06 (s, 2F, CF₂), -123.88 (s, 2F, CF₂), -126.43 (s, 2F, CF₂CF₃).

14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,21-Heptadecafluor-2-propylhenicosan-1-ol **9.9**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 3.10 g (11.5 mmol) 2-Propyltridec-12-ensäuremethylester **8.5**
 5.68 g (11.5 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan
 0.53 g (0.46 mmol) Pd(PPh₃)₄
 50 ml Hexan
 1.31 g (34.5 mmol) LiAlH₄
 100 ml Diethylether

Reinigung: Umkristallisation aus Hexan

Ausbeute: 5.62 g (74 % d. Th.), farbloser Feststoff

Analytik: $C_{24}H_{33}F_{17}O$ $M = 660.49$ g/mol

Fp.: 42-44 °C

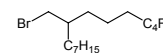
1H -NMR ($CDCl_3$, J /Hz, 200 MHz): $\delta = 3.52$ (d, $^3J(H,H) = 5.2$, 2H, CH_2OH), 2.16-1.90 (m, 2H, CH_2CF_2), 1.61-1.51 (m, 2H, $CH_2CH_2CF_2$), 1.33-1.26 (m, 23H, CH, CH_2), 0.89 (t, $^3J(H,H) = 6.5$, 3H, CH_3).

^{19}F -NMR ($CDCl_3$, J /Hz, 470 MHz): $\delta = -81.16$ (t, $^4J(F,F) = 9.8$, 3F, CF_3), -114.70-(-114.83) (m, 2F, CH_2CF_2), -122.16 (s, 2F, CF_2), -122.35 (s, 4F, CF_2), -123.14 (s, 2F, CF_2), -123.95 (s, 2F, CF_2), -126.53 (s, 2F, CF_2CF_3).

A.10 Synthese der alkylsubstituierten semiperfluorierten ω -Bromalkane 10.X

8-(Brommethyl)-1,1,1,2,2,3,3,4,4-nonafluorpentadecan 10.1

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 3.80 g (9.40 mmol) 6,6,7,7,8,8,9,9,9-Nonafluor-2-heptylnonan-1-ol **9.1**
 50 ml HBr (48%-ig)
 2 ml H_2SO_4
 0.05 g (0.15 mmol) Bu_4NHSO_3

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 2.50 g (57 % d. Th.), farblose Flüssigkeit

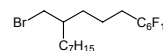
Analytik: $C_{16}H_{24}BrF_9$ $M = 467.25$ g/mol

1H -NMR ($CDCl_3$, J /Hz, 500 MHz): $\delta = 3.47$ -3.40 (m, 2H, CH_2Br), 2.10-2.00 (m, 2H, CH_2CF_2), 1.66-1.54 (m, 3H, CH_2 , CH), 1.50-1.23 (m, 14H, CH_2), 0.87 (t, $^3J(H,H) = 7.1$, 3H, CH_3).

^{19}F -NMR ($CDCl_3$, J /Hz, 470 MHz) $\delta = -81.46$ (t, $^4J(F,F) = 9.8$, 3F, CF_3), -114.99 (s, 2F, CH_2CF_2), -124.91 (s, 2F, $CH_2CF_2CF_2$), -126.47 (s, 2F, CF_2CF_3).

10-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorundecan 10.2

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 3.20 g (6.34 mmol) 6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluor-2-heptylundecan-1-ol **9.2**
 50 ml HBr (48%ig)
 2 ml H_2SO_4
 0.05 g (0.15 mmol) Bu_4NHSO_3

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 2.20 g (61 % d. Th.), farblose Flüssigkeit

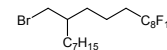
Analytik: $C_{18}H_{24}BrF_{13}$ $M = 567.27$ g/mol

1H -NMR ($CDCl_3$, J /Hz, 500 MHz) $\delta = 3.47$ -3.40 (m, 2H, CH_2Br), 2.11-2.00 (m, 2H, CH_2CF_2), 1.66-1.53 (m, 3H, $CH_2CH_2CF_2$, CH), 1.51-1.34 (m, 4H, CH_2), 1.31-1.27 (m, 10H, CH_2), 0.87 (t, $^3J(H,H) = 7.0$, 3H, CH_3).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): $\delta = -81.30$ (t, $^4J(\text{F},\text{F}) = 9.9$, 3F, CF₃), -114.66-(-114.82) (m, 2F, CH₂CF₂), -122.26 (s, 2F, CF₂), -123.16 (s, 2F, CF₂), -123.97 (s, 2F, CH₂), -126.54-(-126.62) (m, 2F, CF₂CF₃).

13-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluortridecan **10.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 2.50 g (4.14 mmol) 6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Heptadecafluor-2-heptyltridecan-1-ol **9.3**

50 ml HBr (48%ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 1.20 g (43 % d. Th.), farblose Flüssigkeit

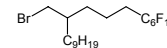
Analytik: C₂₀H₂₄BrF₁₇ M = 667.28 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 500 MHz): $\delta = 3.46$ -3.40 (m, 2H, CH₂Br), 2.10-2.00 (m, 2H, CH₂CF₂), 1.65-1.55 (m, 3H, CH₂CH₂CF₂, CH), 1.49-1.32 (m, 4H, CH₂), 1.30-1.24 (m, 10H, CH₂), 0.87 (t, $^3J(\text{H},\text{H}) = 7.0$, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): $\delta = -81.35$ (t, $^4J(\text{F},\text{F}) = 9.9$, 3F, CF₃), -114.63 (s, 2F, CH₂CF₂), 122.20 (s, 6F, CF₂), -123.05 (s, 2F, CF₂), 123.89 (s, 2F, CH₂), -126.42 (s, 2F, CF₂CF₃).

10-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluornonadecan **10.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 2.00 g (3.76 mmol) 6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluor-2-nonylundecan-1-ol **9.4**

50 ml HBr (48%ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 1.20 g (43 % d. Th.), farblose Flüssigkeit

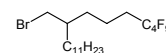
Analytik: C₂₀H₂₈BrF₁₃ M = 595.32 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz) $\delta = 3.47$ -3.39 (m, 2H, CH₂Br), 2.12-1.99 (m, 2H, CH₂CF₂), 1.66-1.57 (m, 2H, CH₂CH₂CF₂), 1.51-1.23 (m, 19H, CH), 0.87 (t, $^3J(\text{H},\text{H}) = 6.8$, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): $\delta = -81.30$ (t, $^4J(\text{F},\text{F}) = 9.9$, 3F, CF₃), -114.47-(-114.64) (m, 2F, CH₂CF₂), 122.25 (s, 2F, CF₂), -123.11 (s, 2F, CF₂), -123.89 (s, 2F, CF₂), -126.49 (s, 2F, CF₂CF₃).

8-(Brommethyl)-1,1,1,2,2,3,3,4,4-nonafluoronadecan **10.5**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 4.40 g (9.56 mmol) 2-(4,4,5,5,6,6,7,7,7-Nonafluorheptyl)tridecan-1-ol **9.5**

50 ml HBr (48%ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 3.80 g (76 % d. Th.), farblose Flüssigkeit

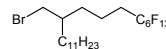
Analytik: C₂₀H₃₂BrF₉ M = 523.36 g/mol

¹H-NMR (CDCl₃, J/Hz, 500 MHz): δ = 3.74-3.40 (m, 2H, CH₂Br), 2.11-2.00 (m, 2H, CH₂CF₂), 1.65-1.56 (m, 3H, CH₂CH₂CF₂, CH), 1.51-1.34 (m, 2H, CH₂), 1.30-1.25 (m, 20H, CH₂), 0.87 (t, ³J(H,H) = 7.0, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.54 (t, ⁴J(F,F) = 9.7, 3F, CF₃), -114.80-(-115.13) (m, 2F, CH₂CF₂), -124.90 (s, 2F, CF₂), -126.39-(-126.58) (m, 2F, CF₂CF₃).

10-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorhenicosan **10.6**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 2.10 g (3.75 mmol) 6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluor-2-undecylundecan-1-ol **9.6**

50 ml HBr (48%ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 1.70 g (73 % d. Th.), farblose Flüssigkeit

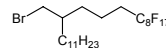
Analytik: C₂₂H₃₂BrF₁₃ M = 623.37 g/mol

¹H-NMR (CDCl₃, J/Hz, 500 MHz): δ = 3.47-3.40 (m, 2H, CH₂Br), 2.11-2.00 (m, 2H, CH₂CF₂), 1.65-1.56 (m, 3H, CH₂CH₂CF₂, CH), 1.51-1.34 (m, 4H, CH₂), 1.30-1.25 (m, 18H, CH₂), 0.87 (t, ³J(H,H) = 7.0, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.41 (t, ⁴J(F,F) = 9.8, 3F, CF₃), -114.55-(-114.88) (m, 2F, CH₂CF₂), 122.31 (s, 2F, CF₂), -123.28 (s, 2F, CF₂), 123.97 (s, 2F, CH₂), -126.44-(-126.63) (m, 2F, CF₂CF₃).

12-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluortricosan **10.7**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 2.10 g (3.18 mmol) 6,6,7,7,8,8,9,9,10,10,12,12,13,13,14,14,14-Heptadecafluor-2-undecyltridecan-1-ol **9.7**

50 ml HBr (48%ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 1.30 g (57 % d. Th.), farblose Flüssigkeit

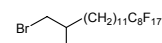
Analytik: $C_{24}H_{32}BrF_{17}$ $M = 723.39$ g/mol

1H -NMR (CDCl₃, J /Hz, 400 MHz): $\delta = 3.47$ -3.39 (m, 2H, CH₂Br), 2.12-1.99 (m, 2H, CH₂CF₂), 1.84 (quint, $^3J(H,H) = 7.1$, 1H, CH), 1.66-1.55 (m, 2H, CH₂), 1.43-1.20 (m, 22H, CH₂), 0.87 (t, $^3J(H,H) = 6.8$, 3H, CH₃).

^{19}F -NMR (CDCl₃, J /Hz, 470 MHz): $\delta = -81.15$ (t, $^4J(F,F) = 9.8$, 3F, CF₃), -114.66 (s, 2F, CH₂CF₂), -122.07 (s, 2F, CF₂), -122.28 (s, 4F, CF₂), -123.07 (s, 2F, CF₂), -123.87 (s, 2F, CF₂), -126.46 (s, 2F, CF₂CF₃).

21-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluor-20-methylhenicosan **10.8**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 4.30 g (6.80 mmol) 14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,21-Heptadecafluor-2-methylhenicosan-1-ol **9.8**

50 ml HBr (48%ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 1.20 g (43 % d. Th.), farbloser Feststoff

Analytik: $C_{22}H_{28}BrF_{17}$ $M = 695.33$ g/mol

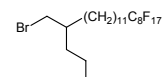
Fp.: 37-38 °C

1H -NMR (CDCl₃, J /Hz, 400 MHz): $\delta = 3.40$ -3.28 (m, 2H, CH₂Br), 2.10-1.97 (m, 2H, CH₂CF₂), 1.78-1.68 (m, 1H, CHCH₃), 1.58 (quint, $^3J(H,H) = 7.7$, 2H, CH₂CH₂CF₂), 1.45-1.21 (m, 18H, CH₂), 0.99 (d, $^3J(H,H) = 6.6$, 3H, CH₃).

^{19}F -NMR (CDCl₃, J /Hz, 188 MHz): $\delta = -81.35$ (t, $^4J(F,F) = 9.9$, 3F, CF₃), -114.72 (s, 2F, CH₂CF₂), -122.19 (s, 6F, CF₂), -123.03 (s, 2F, CF₂), -123.89 (s, 2F, CF₂), -126.42 (s, 2F, CF₂CF₃).

20-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluortricosan **10.9**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 5.60 g (8.48 mmol) 14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,21-Heptadecafluor-2-propylhenicosan-1-ol **9.9**

50 ml HBr (48%ig)

2 ml H₂SO₄

0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 3.19 g (52 % d. Th.), farbloser Feststoff

Analytik: $C_{24}H_{32}BrF_{17}$ $M = 723.39$ g/mol

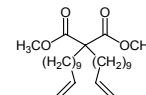
Fp.: 27-29 °C

$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 3.42$ (d, $^3J(\text{H,H}) = 4.8$, 2H, CH_2Br), 2.09-1.96 (m, 2H, CH_2CF_2), 1.60-1.54 (m, 3H, CH, $\text{CH}_2\text{CH}_2\text{CF}_2$), 1.37-1.26 (m, 22H, CH_2), 0.89 (t, $^3J(\text{H,H}) = 6.9$, 3H, CH_3).

$^{19}\text{F-NMR}$ (CDCl_3 , J/Hz , 470 MHz): $\delta = -81.23$ (t, $^4J(\text{F,F}) = 9.8$, 3F, CF_3), -114.78-(-114.85) (m, 2F, CH_2CF_2), -122.20 (s, 2F, CF_2), -122.38 (s, 4F, CF_2), -123.18 (s, 2F, CF_2), -123.99 (s, 2F, CF_2), -126.58 (s, 2F, CF_2CF_3).

A.11 Synthese von Bis(undec-10-en-1-yl)malonsäuredimethylester 11

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 25.0 g (189 mmol) Malonsäuredimethylester
95.6 g (397 mmol) 11-Bromundec-1-en
11.7 g (510 mmol) Na
200 ml Methanol

Reinigung: Hochvakuumdestillation und Säulenchromatographie des Sumpfes
(Eluent: CHCl_3)

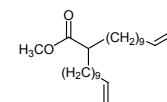
Ausbeute: 57.1 g (69 % d. Th.), farblose Flüssigkeit

Analytik: $\text{C}_{27}\text{H}_{48}\text{O}_4$ $M = 436.67$ g/mol

$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 5.84$ -5.74 (m, 2H, $\text{CH}=\text{CH}_2$), 5.00-4.89 (m, 4H, $\text{CH}_2=\text{CH}$), 3.68 (s, 6H, OCH_3), 2.02 (q, $^3J(\text{H,H}) = 7.1$, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.86-1.82 (m, 4H, CCH_2), 1.38-1.31 (m, 4H, CH_2), 1.28-1.22 (m, 20H, CH_2), 1.14-1.06 (m, 4H, CH_2).

A.12 Synthese von 2-(Undec-10-en-1-yl)tridec-12-ensäuremethylester 12

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 28.6 g (65.5 mmol) Bis(undec-10-en-1-yl)malonsäuredimethylester **11**
5.55 g (131 mmol) LiCl
2.36 g (65.5 mmol) Wasser
100 ml DMSO

Reinigung: Säulenchromatographie (Eluent: CHCl_3)

Ausbeute: 8.10 g (33 % d. Th.), farblose Flüssigkeit

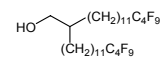
Analytik: $\text{C}_{25}\text{H}_{46}\text{O}_2$ $M = 378.63$ g/mol

$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 5.84$ -5.74 (m, 2H, $\text{CH}=\text{CH}_2$), 5.00-4.89 (m, 4H, $\text{CH}_2=\text{CH}$), 3.65 (s, 3H, OCH_3), 2.34-2.27 (m, 1H, CH), 2.02 (q, $^3J(\text{H,H}) = 7.1$, 4H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.61-1.52 (m, 2H, CH_2), 1.45-1.19 (m, 30H, CH_2).

A.13 Synthese der verzweigten semiperfluorierten Alkohole 13.X

14,14,15,15,16,16,17,17,17-Nonafluor-2-(12,12,13,13,14,14,15,15,15-nonafluorpentadecyl)heptadecan-1-ol **13.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 2.00 g (5.23 mmol) Synthese von 2-(Undec-10-en-1-yl)tridec-12-ensäuremethylester **12**

3.65 g (10.6 mmol) 1,1,1,2,2,3,3,4,4-Nonafluor-4-iodbutan

0.48 g (0.42 mmol) Pd(PPh₃)₄

50 ml Hexan

0.59 g (15.7 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 2.70 g (65 % d. Th.), farbloser Feststoff

Analytik: C₃₂H₄₈F₁₈O M = 790.69 g/mol

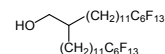
Fp.: <30 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.52 (d, ³J(H,H) = 5.5, 2H, CH₂OH), 2.09-1.96 (m, 4H, CH₂CF₂), 1.58 (quint, ³J(H,H) = 7.7, 4H, CH₂CH₂CF₂), 1.45-1.40 (m, 1H, CH), 1.37-1.23 (m, 36H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.66 (t, ⁴J(F,F) = 9.7, 6F, CF₃), -115.00 (s, 4F, CH₂CF₂), -124.90 (s, 4F, CF₂), -126.34-(-126.53) (m, 4F, CF₂CF₃).

14,14,15,15,16,16,17,17,18,18,19,19,19-Tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorpentadecyl)nonadecan-1-ol **13.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 2.00 g (5.23 mmol) Synthese von 2-(Undec-10-en-1-yl)tridec-12-ensäuremethylester **12**

4.73 g (10.6 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluor-6-iodhexan

0.48 g (0.42 mmol) Pd(PPh₃)₄

50 ml Hexan

0.59 g (15.7 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃) und Umkristallisation aus MeOH

Ausbeute: 3.10 g (60 % d. Th.), farbloser Feststoff

Analytik: C₃₆H₄₈F₂₆O M = 990.72 g/mol

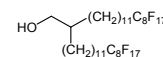
Fp.: 44-45 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.52 (d, ³J(H,H) = 5.5, 2H, CH₂OH), 2.10-1.96 (m, 4H, CH₂CF₂), 1.58 (quint, ³J(H,H) = 7.7, 4H, CH₂CH₂CF₂), 1.46-1.42 (m, 1H, CH), 1.37-1.21 (m, 36H, CH₂).

$^{19}\text{F-NMR}$ (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.41$ (t, $^4J(\text{F},\text{F}) = 9.7$, 6F, CF_3), -114.62 - (-114.97) (m, 4F, CH_2CF_2), -122.33 (s, 4F, CF_2), -123.26 (s, 4F, CF_2), -123.95 (s, 4F, CF_2), -126.40 - (-126.60) (m, 4F, CF_2CF_3).

14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,21-Heptadecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecyl)henicosan-1-ol **13.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 2.00 g (5.23 mmol) Synthese von 2-(Undec-10-en-1-yl)tridec-12-ensäuremethylester **12**

5.79 g (10.6 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan

0.48 g (0.42 mmol) $\text{Pd}(\text{PPh}_3)_4$

50 ml Hexan

0.59 g (15.7 mmol) LiAlH_4

100 ml Diethylether

Reinigung: Umkristallisation aus MeOH

Ausbeute: 3.30 g (53 % d. Th.), farbloser Feststoff

Analytik: $\text{C}_{40}\text{H}_{48}\text{F}_{34}\text{O}$ $M = 1190.75$ g/mol

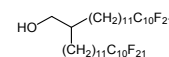
Fp.: 65-67 °C

$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 3.52$ (d, $^3J(\text{H},\text{H}) = 5.4$, 2H, CH_2OH), 2.10-1.96 (m, 4H, CH_2CF_2), 1.58 (quint, $^3J(\text{H},\text{H}) = 7.7$, 4H, $\text{CH}_2\text{CH}_2\text{CF}_2$), 1.37-1.21 (m, 37H, CH, CH_2).

$^{19}\text{F-NMR}$ (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.35$ (t, $^4J(\text{F},\text{F}) = 9.1$, 6F, CF_3), -114.75 (s, 4F, CH_2CF_2), -122.26 (s, 12F, CF_2), -123.12 (s, 4F, CF_2), -123.90 (s, 4F, CF_2), -126.49 (m, 4F, CF_2CF_3).

14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,22,22,23,23,23-Henicosacafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,21-henicosafafluorhenicosyl)tricosan-1-ol **13.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 1.25 g (3.30 mmol) Synthese von 2-(Undec-10-en-1-yl)tricos-21-ensäuremethylester **12**

4.27 g (6.60 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Henicosafafluor-10-ioddecan

0.23 g (0.24 mmol) $\text{Pd}(\text{PPh}_3)_4$

50 ml Hexan

0.38 g (9.90 mmol) LiAlH_4

100 ml Diethylether

Reinigung: Umkristallisation aus Hexan

Ausbeute: 3.30 g (72 % d. Th.), farbloser Feststoff

Analytik: $C_{44}H_{48}F_{42}O$ $M = 1390.78$ g/mol

Fp.: 95-97 °C

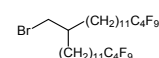
1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 3.52$ (d, $^3J(H,H) = 5.5$, 2H, CH_2OH), 2.09-1.96 (m, 4H, CH_2CF_2), 1.57 (quint, $^3J(H,H) = 7.7$, 4H, $CH_2CH_2CF_2$), 1.45-1.21 (m, 37H, CH, CH_2).

^{19}F -NMR ($CDCl_3$, J/Hz , 188 MHz): $\delta = -81.38$ (t, $^4J(F,F) = 9.7$, 6F, CF_3), -114.79 (s, 4F, CH_2CF_2), -122.15 (s, 12F, CF_2), -123.07 (s, 4F, CF_2), -123.90 (s, 4F, CF_2), -126.47 (m, 4F, CF_2CF_3).

A.14 Synthese der verzweigten semiperfluorierten Bromalkane 14.X

16-(Brommethyl)-1,1,1,2,2,3,3,4,4,28,28,29,29,30,30,31,31,31-octadecafluorhentriacontan 14.1

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 2.70 g (3.41 mmol) 14,14,15,15,16,16,17,17,17-Nonafluor-2-(12,12,13,13,14,14,15,15,15-nonafluorpentadecyl)heptadecan-1-ol **13.1**
50 ml HBr (48%ig)
2 ml H_2SO_4
0.05 g (0.15 mmol) Bu_4NHSO_3

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 1.40 g (48 % d. Th.), farblose Flüssigkeit

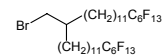
Analytik: $C_{32}H_{47}BrF_{18}$ $M = 853.59$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 3.43$ (d, $^3J(H,H) = 4.8$, 2H, CH_2Br), 2.09-1.96 (m, 5H, CH_2CF_2 , CH), 1.58 (quint, $^3J(H,H) = 7.7$, 4H, $CH_2CH_2CF_2$), 1.40-1.21 (m, 36H, CH_2).

^{19}F -NMR ($CDCl_3$, J/Hz , 188 MHz): $\delta = -81.66$ (t, $^4J(F,F) = 9.7$, 6F, CF_3), -114.84-(-115.17) (m, 4F, CH_2CF_2), -124.87 (s, 4F, CF_2), -126.31-(-126.53) (m, 4F, CF_2CF_3).

18-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,30,30,31,31,32,32,33,33,34,34,35,35,35-hexacosafuorpentatriacontan 14.2

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 3.00 g (3.03 mmol) 14,14,15,15,16,16,17,17,18,18,19,19,19-Tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorpentadecyl)nonadecan-1-ol **13.2**
50 ml HBr (48%ig)
2 ml H_2SO_4
0.05 g (0.15 mmol) Bu_4NHSO_3

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 2.20 g (69 % d. Th.), farbloser Feststoff

Analytik: $C_{36}H_{47}BrF_{26}$ $M = 1053.62$ g/mol

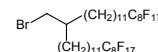
Fp.: 39-40 °C

$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 3.42$ (d, $^3J(\text{H,H}) = 4.8$, 2H, CH_2Br), 2.09-1.96 (m, 5H, CH_2CF_2 , CH), 1.61-1.52 (m, 4H, $\text{CH}_2\text{CH}_2\text{CF}_2$), 1.37-1.22 (m, 36H, CH_2).

$^{19}\text{F-NMR}$ (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.40$ (t, $^4J(\text{F,F}) = 9.7$, 6F, CF_3), -114.60-(-114.95) (m, 4F, CH_2CF_2), -122.31 (s, 4F, CF_2), -123.27 (s, 4F, CF_2), -123.95 (s, 4F, CF_2), -126.40-(-126.60) (m, 4F, CF_2CF_3).

20-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,32,32,33,33,34,34,35,35,36,36,37,37,-38,38,39,39-tetratriacontafluormonatriacontan **14.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 1.30 g (1.09 mmol) 14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,21-Heptadecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluormonadecyl)henicosan-1-ol **13.3**

50 ml HBr (48%ig)

2 ml H_2SO_4

0.05 g (0.15 mmol) Bu_4NHSO_3

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 0.58 g (42 % d. Th.), farbloser Feststoff

Analytik: $\text{C}_{40}\text{H}_{47}\text{BrF}_{34}$ $M = 1253.65$ g/mol

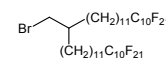
Fp.: 70-72 °C

$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 3.42$ (d, $^3J(\text{H,H}) = 4.8$, 2H, CH_2Br), 2.10-1.96 (m, 4H, CH_2CF_2), 1.58 (quint, $^3J(\text{H,H}) = 7.5$, 4H, $\text{CH}_2\text{CH}_2\text{CF}_2$), 1.37-1.24 (m, 37H, CH, CH_2).

$^{19}\text{F-NMR}$ (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.36$ (t, $^4J(\text{F,F}) = 9.7$, 6F, CF_3), -114.75 (s, 4F, CH_2CF_2), -122.22 (s, 12F, CF_2), -123.07 (s, 4F, CF_2), -123.87 (s, 4F, CF_2), -126.47 (m, 4F, CF_2CF_3).

22-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,34,34,35,35,36,36,37,37,-38,38,39,39,40,40,41,41,42,42,43,43,43-dotetracontafluortritetracontan **14.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 3.20 g (2.30 mmol) 14,14,15,15,16,16,17,17,18,18,19,19,20,20,-21,21,22,22,23,23,23-Henicosacafluor-2-(12,12,13,13,14,14,15,15,16,16,-17,17,18,18,19,19,20,20,21,21,21-henicosafuorhenicosyl)tricosan-1-ol **13.4**

50 ml HBr (48%ig)

2 ml H_2SO_4

0.05 g (0.15 mmol) Bu_4NHSO_3

Reinigung: Säulenchromatographie (Eluent: CHCl_3) und Umkristallisation aus PE

Ausbeute: 2.04 g (61 % d. Th.), farbloser Feststoff

Analytik: $\text{C}_{44}\text{H}_{47}\text{BrF}_{42}$ $M = 1453.68$ g/mol

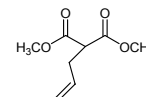
Fp.: 91-94 °C

$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 3.43$ (d, $^3J(\text{H,H}) = 4.8$, 2H, CH_2Br), 2.10-1.96 (m, 4H, CH_2CF_2), 1.58 (quint, $^3J(\text{H,H}) = 7.7$, 4H, $\text{CH}_2\text{CH}_2\text{CF}_2$), 1.38-1.22 (m, 37H, CH, CH_2).

^{19}F -NMR (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.36$ (t, $^4J(\text{F},\text{F}) = 9.9$, 6F, CF_3), -114.76 (s, 4F, CH_2CF_2), -122.13 (s, 12F, CF_2), -123.04 (s, 4F, CF_2), -123.89 (s, 4F, CF_2), -126.44 (m, 4F, CF_2CF_3).

A.15 Synthese von Allylmalonsäuredimethylester 15

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 20.0 g (151 mmol) Malonsäuredimethylester
18.3 g (151 mmol) Allylbromid
3.47 g (151 mmol) Na
200 ml Methanol

Reinigung: Säulenchromatographie (Eluent: PE/ CHCl_3 1:2, V/V)

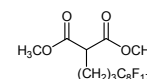
Ausbeute: 10.7 g (41 % d. Th.), farblose Flüssigkeit

Analytik: $\text{C}_8\text{H}_{12}\text{O}_4$ M = 172.18 g/mol

^1H -NMR (CDCl_3 , J/Hz , 400 MHz): $\delta = 5.78$ - 5.69 (m, 1H, $\text{CH}=\text{CH}_2$), 5.11 - 5.01 (m, 2H, $\text{CH}_2=\text{CH}$), 3.70 (s, 6H, OCH_3), 3.43 (t, $^3J(\text{H},\text{H}) = 7.6$, 1H, CH), 2.62 (t, $^3J(\text{H},\text{H}) = 7.2$, 2H, $\text{CH}_2\text{CH}=\text{}$).

A.16 Synthese von (4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluorundecyl)-malonäuredimethylester 16

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13; anstelle der Reduktion mit LiAlH_4 wurde die Iodgruppe durch Hydrogenolyse an Palladium/Aktivkohle mit NaHCO_3 in Methanol entfernt.



Ansatz: 10.0 g (18.3 mmol) 1,1,1,2,2,3,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan
3.15 g (18.3 mmol) Allylmalonsäuredimethylester 15
0.85 g (0.73 mmol) $\text{Pd}(\text{PPh}_3)_4$
50 ml Hexan
0.02 g Pd/C
1.54 g (18.3 mmol) NaHCO_3
100 ml MeOH

Reinigung: Säulenchromatographie (Eluent: CHCl_3)

Ausbeute: 5.10 g (47 % d. Th.), farblose Flüssigkeit

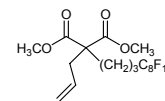
Analytik: $\text{C}_{16}\text{H}_{13}\text{F}_{17}\text{O}_4$ M = 592.24 g/mol

^1H -NMR (CDCl_3 , J/Hz , 400 MHz): $\delta = 3.73$ (s, 6H, OCH_3), 3.37 (t, $^3J(\text{H},\text{H}) = 7.4$, 1H, CH), 2.15 - 2.02 (m, 2H, CH_2CF_2), 1.98 (q, $^3J(\text{H},\text{H}) = 7.9$, 2H, CHCH_2), 1.67 - 1.59 (m, 2H, CH_2).

^{19}F -NMR (CDCl_3 , J/Hz , 470 MHz): $\delta = -81.21$ (t, $^4J(\text{F},\text{F}) = 9.8$, 3F, CF_3), -114.89 - (-114.96) (m, 2F, CH_2CF_2), -122.16 (s, 2F, CF_2), -122.37 (s, 4F, CF_2) -123.16 (s, 2F, CF_2), -123.87 (s, 2F, CF_2), 126.56 (s, 2F, CF_2CF_3).

A.17 Synthese von Allyl(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluorundecyl)malonäuredimethylester **17**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.10.



Ansatz: 5.10 g (8.61 mmol) Allyl(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluorundecyl)malonäuredimethylester **16**
 1.25 g (10.3 mmol) Allylbromid
 0.24 g (10.3 mmol) Na
 100 ml Methanol

Reinigung: Säulenchromatographie (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 3.60 g (66 % d. Th.), farblose Flüssigkeit

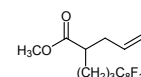
Analytik: C₁₉H₁₇F₁₇O₄ M = 632.31 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 5.65-5.55 (m, 1H, CH=CH₂), 5.12-5.08 (m, 2H, CH=CH₂), 3.71 (s, 6H, OCH₃), 2.66 (d, ³J(H,H) = 7.4, 2H, CH₂CH=), 2.17-1.97 (m, 4H, CH₂CF₂, CCH₂), 1.67-1.60 (m, 2H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.27 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.25-(-114.82) (m, 2F, CH₂CF₂), -122.30 (s, 4F, CF₂), -123.15 (s, 2F, CF₂), -123.74 (s, 2F, CF₂), -123.96 (s, 2F, CF₂), 126.56 (s, 2F, CF₂CF₃).

A.18 Synthese von 2-Allyl-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluor-tridecansäuremethylester **18**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.11.



Ansatz: 4.80 g (7.59 mmol) (4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11,11-Heptadecafluor-undecyl)malonäuredimethylester **17**
 2.10 g (15.2 mmol) LiCl
 0.14 g (7.59 mmol) Wasser
 100 ml DMSO

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 2.50 g (57 % d. Th.), farblose Flüssigkeit

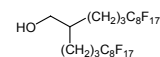
Analytik: C₁₇H₁₅F₁₇O₂ M = 574.27 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 5.76-5.65 (m, 1H, CH=CH₂), 5.08-5.00 (m, 2H, CH=CH₂), 3.67 (s, 3H, OCH₃), 2.50-2.43 (m, 1H, CH), 2.41-2.33 (m, 2H, CH₂CH=), 2.14-2.00 (m, 2H, CH₂CF₂), 1.74-1.55 (m, 4H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.24 (t, ⁴J(F,F) = 9.2, 3F, CF₃), -114.76-(-114.83) (m, 2F, CH₂CF₂), -122.29 (s, 6F, CF₂), -123.13 (s, 2F, CF₂), -123.95 (s, 2F, CF₂), 126.51 (s, 2F, CF₂CF₃).

A.19 Synthese von 2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluorundecyl)-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluortridecan-1-ol **19**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 0.95 g (1.74 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan
 1.00 g (1.74 mmol) 2-Allyl-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluortridecansäuremethylester **18**
 0.08 g (0.07 mmol) Pd(PPh₃)₄
 50 ml Hexan
 0.20 g (5.22 mmol) LiAlH₄
 50 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃/MeOH 10:1, V/V)

Ausbeute: 0.70 g (42 % d. Th.), farbloser Feststoff

Analytik: C₂₄H₁₆F₃₄O M = 966.33 g/mol

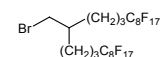
Fp.: 53-54 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.58 (d, ³J(H,H) = 5.1, 2H, CH₂OH), 2.12-1.99 (m, 4H, CH₂CF₂), 1.67-1.58 (m, 4H, CH₂CH₂CF₂), 1.56-1.34 (m, 5H, CH, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.23 (t, ⁴J(F,F) = 9.9, 6F, CF₃), -114.61-(-114.69) (m, 4F, CH₂CF₂), -122.29 (s, 12F, CF₂), -123.13 (s, 4F, CF₂), -123.95 (s, 4F, CF₂), -126.52 (m, 4F, CF₂CF₃).

A.20 Synthese von 12-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,16,16,17,17,-18,18,19,19,20,20,21,21,22,22,23,23,23-tetratriacontafluortricosan **20**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.14.



Ansatz: 700 mg (0.72 mmol) 2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluorundecyl)-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluortridecan-1-ol **19**
 50 ml HBr (48%ig)
 2 ml H₂SO₄
 0.05 g (0.15 mmol) Bu₄NHSO₃

Reinigung: Säulenchromatographie (Eluent: PE)

Ausbeute: 650 mg (88 % d. Th.), farbloser Feststoff

Analytik: C₂₄H₁₅BrF₃₄ M = 1029.23 g/mol

Fp.: 49-51 °C

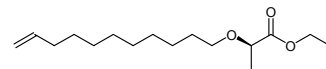
¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.44 (d, ³J(H,H) = 3.9, 2H, CH₂Br), 2.13-2.00 (m, 4H, CH₂CF₂), 1.92-1.85 (m, 1H, CH), 1.70-1.40 (m, 8H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.26 (t, ⁴J(F,F) = 9.9, 6F, CF₃), -114.65-(-114.75) (m, 4F, CH₂CF₂), -122.30 (s, 12F, CF₂), -123.15 (s, 4F, CF₂), -123.94 (s, 4F, CF₂), -126.54 (m, 4F, CF₂CF₃).

A.21 Synthese von (2R)-2-(Undec-10-en-1-yloxy)propansäureester **21** und *rac*-**21**

(2R)-2-(Undec-10-en-1-yloxy)propansäureethylester **21**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.16.



Ansatz: 15.0 g (0.13 mol) (*S*)-2-Hydroxypropansäureethylester
81.8 g (0.29 mol) 11-Iodundec-1-en
51.2 g (0.22 mol) Ag₂O

Reinigung: Hochvakuumdestillation und Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 5.70 g (16 % d. Th.), farblose Flüssigkeit

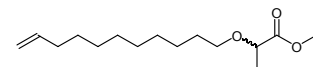
Analytik: C₁₆H₃₀O₃ M = 270.41 g/mol

Kp.: 103-105 °C (3.3·10⁻² mbar)

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 5.84-5.73 (m, 1H, CH=CH₂), 4.99-4.88 (m, 2H, CH₂=CH), 4.24-4.12 (m, 2H, OCH₂CH₃), 3.91 (q, ³*J*(H,H) = 6.8, 1H, OCH), 3.55-3.30 (m, 2H, OCH₂), 2.01 (q, ³*J*(H,H) = 7.1, 2H, CH₂=CHCH₂), 1.57 (quint, ³*J*(H,H) = 7.3, 2H, OCH₂CH₂), 1.37 (d, ³*J*(H,H) = 6.8, 3H, CHCH₃), 1.35-1.24 (m, 12H, CH₂), 1.26 (t, ³*J*(H,H) = 7.1, 3H, CH₂CH₃).

2-(Undec-10-en-1-yloxy)propansäuremethylester *rac*-**21**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.16.



Ansatz: 9.00 g (86.4 mmol) 2-Hydroxypropansäuremethylester
55.7 g (199 mmol) 11-Iodundec-1-en
34.1 g (147 mmol) Ag₂O

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 5.70 g (26 % d. Th.), farblose Flüssigkeit

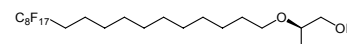
Analytik: C₁₅H₂₈O₃ M = 256.38 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 5.84-5.74 (m, 1H, CH=CH₂), 4.99-4.88 (m, 2H, CH₂=CH), 3.94 (q, ³*J*(H,H) = 6.8, 1H, CHCH₃), 3.72 (s, 3H, CH₃), 3.55-3.30 (m, 2H, OCH₂), 2.01 (q, ³*J*(H,H) = 7.1, 2H, CH₂=CHCH₂), 1.58 (quint, ³*J*(H,H) = 7.1, 2H, OCH₂CH₂), 1.38 (d, ³*J*(H,H) = 6.8, 3H, CHCH₃), 1.35-1.24 (m, 12H, CH₂).

A.22 Synthese von (2R)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptafluorundecyloxy)propan-1-ol **22** und *rac*-**22**

(2R)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptafluorundecyloxy)propan-1-ol **22**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.13.



Ansatz: 3.00 g (11.1 mmol) (2R)-2-(Undec-10-en-1-yloxy)propansäureethylester **21**
6.06 g (11.1 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptafluor-8-

iodoctan

0.51 g (0.04 mmol) Pd(PPh₃)₄

100 ml Hexan

1.26 g (33.3 mmol) LiAlH₄

200 ml Diethylether

Reinigung: Umkristallisation aus Hexan

Ausbeute: 3.50 g (49 % d. Th.), farbloser Feststoff

Analytik: C₂₂H₂₉F₁₇O₂ M = 648.44 g/mol

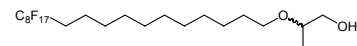
Fp.: 54-56 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.58-3.37 (m, 3H, CH₂OH, OCH), 3.43-3.33 (m, 2H, OCH₂), 2.10-1.96 (m, 2H, CH₂CF₂), 1.61-1.52 (m, 4H, CH₂CH₂CF₂, OCH₂CH₂), 1.39-1.24 (m, 14H, CH₂), 1.09 (d, ³J(H,H) = 6.1, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.23 (t, ⁴J(F,F) = 9.5, 3F, CF₃), -114.75 (s, 2F, CH₂CF₂), -122.25 (s, 6F, CF₂), -123.11 (s, 2F, CF₂), -123.95 (s, 2F, CF₂), -126.50 (s, 2F, CF₂CF₃).

2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19)-Heptadecafluor-nonadecyloxy)propan-1-ol **rac-22**

Die Darstellung erfolgte nach der allgemeinen



Arbeitsvorschrift 5.3.13.

Ansatz: 2.50 g (9.75 mmol) 2-(Undec-10-en-1-yloxy)propansäuremethylester **rac-21**

5.32 g (9.75 mmol) 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-Heptadecafluor-8-iodoctan

0.51 g (0.04 mmol) Pd(PPh₃)₄

100 ml Hexan

0.37 g (9.75 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 4.50 g (71 % d. Th.), farbloser Feststoff

Analytik: C₂₂H₂₉F₁₇O₂ M = 648.44 g/mol

Fp.: 50-51 °C

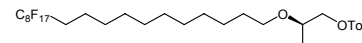
¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.58-3.47 (m, 3H, CH₂OH, OCH), 3.44-3.33 (m, 2H, OCH₂), 2.10-1.96 (m, 2H, CH₂CF₂), 1.62-1.49 (m, 4H, CH₂CH₂CF₂, OCH₂CH₂), 1.37-1.24 (m, 14H, CH₂), 1.09 (d, ³J(H,H) = 6.2, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.21 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.74 (s, 2F, CH₂CF₂), -122.24 (s, 6F, CF₂), -123.09 (s, 2F, CF₂), -123.93 (s, 2F, CF₂), -126.48 (s, 2F, CF₂CF₃).

A.23 Synthese von (2*R*)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluoronadecyloxy)propyl-1-tosylat **23** und *rac*-**23**

(2*R*)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluoronadecyloxy)propyl-1-tosylat **23**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.15.



Ansatz: 3.50 g (5.40 mmol) (2*R*)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluoronadecyloxy)propan-1-ol **22**
2.06 g (10.8 mmol) 4-Methylbenzolsulfonylchlorid
25 ml Pyridin

Reinigung: Säulenchromatographie (Eluent: CHCl₃/MeOH 10:0.1)

Ausbeute: 3.78 g (70 % d. Th.), farbloses Öl

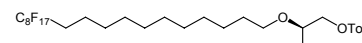
Analytik: C₂₉H₃₅F₁₇O₄S M = 802.62 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.79 (d, ³*J*(H,H) = 8.4, 2H, Ar-H), 7.31 (d, ³*J*(H,H) = 8.0, 2H, Ar-H), 4.15-4.03 (m, 3H, CH₂OTos, OCH), 3.45-3.33 (m, 2H, OCH₂), 2.42 (s, 3H, PhCH₃), 2.10-1.96 (m, 2H, CH₂CF₂), 1.61-1.52 (m, 4H, CH₂CH₂CF₂, OCH₂CH₂), 1.39-1.24 (m, 14H, CH₂), 1.09 (d, ³*J*(H,H) = 6.1, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.23 (t, ⁴*J*(F,F) = 9.5, 3F, CF₃), -114.75 (s, 2F, CH₂CF₂), -122.25 (s, 6F, CF₂), -123.11 (s, 2F, CF₂), -123.95 (s, 2F, CF₂), -126.50 (s, 2F, CF₂CF₃).

2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluoronadecyloxy)-propyl-1-tosylat *rac*-**23**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.15.



Ansatz: 4.50 g (6.94 mmol) 2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Heptadecafluoronadecyloxy)propan-1-ol *rac*-**22**
2.66 g (13.9 mmol) 4-Methylbenzolsulfonylchlorid
25 ml Pyridin

Reinigung: Säulenchromatographie (Eluent: CHCl₃/MeOH 10:0.1)

Ausbeute: 3.51 g (63 % d. Th.), farbloses Öl

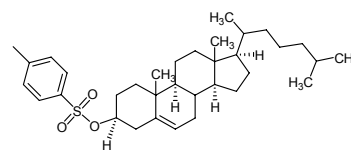
Analytik: C₂₉H₃₅F₁₇O₄S M = 802.62 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.77 (d, ³*J*(H,H) = 8.4, 2H, Ar-H), 7.30 (d, ³*J*(H,H) = 8.0, 2H, Ar-H), 4.15-4.03 (m, 3H, CH₂OTos, OCH), 3.43-3.33 (m, 2H, OCH₂), 2.42 (s, 3H, PhCH₃), 2.10-1.96 (m, 2H, CH₂CF₂), 1.61-1.52 (m, 4H, CH₂CH₂CF₂, OCH₂CH₂), 1.39-1.24 (m, 14H, CH₂), 1.09 (d, ³*J*(H,H) = 6.1, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.21 (t, ⁴*J*(F,F) = 9.5, 3F, CF₃), -114.75 (s, 2F, CH₂CF₂), -122.23 (s, 6F, CF₂), -123.11 (s, 2F, CF₂), -123.96 (s, 2F, CF₂), -126.50 (s, 2F, CF₂CF₃).

A.24 Synthese von Cholest-5-en-3 β -tosylat **24**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.15.



Ansatz: 5.00 g (12.9 mmol) Cholest-5-en-3 β -ol
4.93 g (25.8 mmol) 4-Methylbenzolsulfonylchlorid
30 ml Pyridin

Reinigung: Säulenchromatographie (Eluent: CHCl₃/MeOH 10:0.1, V/V) und Umkristallisation aus Aceton

Ausbeute: 4.50 g (65 % d. Th.), farbloser Feststoff

Analytik: C₃₄H₅₂O₃S M = 540.84 g/mol

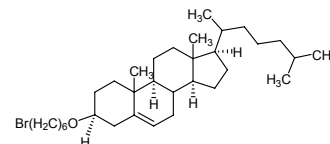
Fp.: 130-132 °C

¹H-NMR (CDCl₃, J/Hz, 200 MHz) δ = 7.77 (d, ³J(H,H) = 8.4, 2H, Ar-H), 7.30 (d, ³J(H,H) = 8.0, 2H, Ar-H), 5.29-5.26 (m, 1H, CH=C), 4.30 (quint, ³J(H,H) = 5.6, 1H, OCH), 2.42 (s, 3H, PhCH₃), 2.29-2.19 (m, 2H, CH₂), 2.02-1.69 (m., 6H, CH₂), 1.53-0.82 (m, 33H, CH, CH₂, CH₃), 0.63 (s, 3H, CH₃).

A.25 Synthese der ω -Brom-1-(cholest-5-en-3 β -oxy)alkane **25.X**

6-Brom-1-(cholest-5-en-3 β -oxy)hexan **25.1**

Zu einer Lösung von 2.50 g (4.62 mmol) Cholest-5-en-3 β -tosylat **24** in 30 ml trockenem Dioxan gibt man 2.32 g (23.1 mmol) 6-Bromhexan-1-ol und rührt 4 h unter Rückfluss. Anschließend wird das Lösungsmittel am Rotationsverdampfer entfernt, der Rückstand in 100 ml Diethylether aufgenommen und mit je 50 ml Wasser, ges. NaHCO₃-Lösung und NaCl-Lösung gewaschen. Nach dem Trocknen über Na₂SO₄ destilliert man das Lösungsmittel unter vermindertem Druck ab.



Reinigung: Säulenchromatographie (Eluent: CHCl₃) und Umkristallisation aus EE

Ausbeute: 0.43 g (17 % d. Th.), farbloser Feststoff

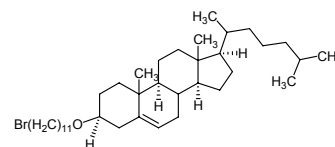
Analytik: C₃₃H₅₇BrO M = 549.71 g/mol

Fp.: 96-98 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 5.33-5.32 (m, 1H, CH=C), 3.43 (t, ³J(H,H) = 6.7, 2H, OCH₂), 3.39 (t, ³J(H,H) = 6.8, 2H, BrCH₂), 3.14-3.06 (m, 1H, OCH), 2.35-2.13 (m, 2H, CH₂), 2.03-1.76 (m., 7H, CH₂), 1.59-1.20 (m, 18H, CH,CH₂), 1.17-0.83 (m, 22H, CH, CH₂, CH₃), 0.66 (s, 3H, CH₃).

11-Brom-1-(cholest-5-en-3 β -oxy)undecan **25.2**

Zu einer Lösung von 1.00 g (1.85 mmol) Cholest-5-en-3 β -tosylat **24** in 30 ml trockenem Dioxan gibt man 2.32 g (9.25 mmol) 11-Bromundecan-1-ol und rührt 4 h unter



Rückfluss. Anschließend wird das Lösungsmittel am Rotationsverdampfer entfernt, der Rückstand in 100 ml Diethylether aufgenommen und mit je 50 ml Wasser, ges. NaHCO₃-Lösung und NaCl-Lösung gewaschen. Nach dem Trocknen über Na₂SO₄ destilliert man das Lösungsmittel unter vermindertem Druck ab.

Reinigung: Säulenchromatographie (Eluent: CHCl₃) und Umkristallisation aus Methanol

Ausbeute: 0.55 g (48 % d. Th.), farbloser Feststoff

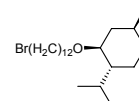
Analytik: C₃₈H₆₇BrO M = 619.84 g/mol

Fp.: 73-75 °C

¹H-NMR (CDCl₃, J/Hz, 200 MHz): δ = 5.33-5.32 (m, 1H, CH=C), 3.43 (t, ³J(H,H) = 6.8, 2H, OCH₂), 3.39 (t, ³J(H,H) = 6.9, 2H, BrCH₂), 3.13-3.07 (m, 1H, OCH), 2.36-2.13 (m, 2H, CH₂), 2.02-1.79 (m., 8H, CH₂), 1.55-1.24 (m, 20H, CH,CH₂), 1.17-0.84 (m, 22H, CH, CH₂, CH₃), 0.66 (s, 3H, CH₃).

A.26 Synthese von (1*R*,2*S*,4*S*)-2-(12-Bromdodecyloxy)-1-isopropyl-4-methylcyclohexan 26

Eine Suspension von 1.00 g (6.40 mmol) (1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexanol, 4.20 g (12.8 mmol) 1,12-Dibromdodecan und 0.18 g (7.68 mmol) NaH in 50 ml Dioxan wird 4 Tage unter Rückfluss gerührt.



Anschließend lässt man auf RT abkühlen und fügt tropfenweise 20 ml Wasser zu. Nach der zweimaligen Extraktion mit 50 ml Diethylether werden die vereinigten organischen Phasen mit je 50 ml Wasser, ges. NaHCO₃-Lösung und NaCl-Lösung gewaschen, über Na₂SO₄ getrocknet und das Lösungsmittel unter vermindertem Druck abdestilliert.

Reinigung: Fließkraftvermittelte präparative Dünnschichtchromatographie (Eluent: PE/CHCl₃ 1:2, V/V)

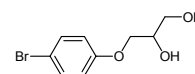
Ausbeute: 1.30 g (74% d. Th.), farblose Flüssigkeit

Analytik: C₂₂H₄₃BrO M = 403.48 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 3.61-3.55 (m, 1H, OCH₂), 3.38 (t, ³J(H,H) = 6.8, 2H, CH₂Br), 3.25-3.20 (m, 1H, OCH₂), 2.97 (dt, 1H, ³J(H,H) = 10.5, ⁴J(H,H) = 4.1, OCH), 2.24-2.16 (m, 1H, CH), 2.09-2.04 (m, 1H, CH), 1.83 (quint, ³J(H,H) = 7.1, 2H, CH₂CH₂O), 1.65-1.46 (m, 5H, CH, CH₂), 1.42-1.22 (m, 18H, CH, CH₂), 0.89 (d, ³J(H,H) = 6.5, 3H, CH₃), 0.87 (d, ³J(H,H) = 7.1, 3H, CH₃), 0.75 (d, ³J(H,H) = 7.0, 3H, CH₃).

A.27 Synthese von 3-(4-Bromphenoxy)propan-1,2-diol 27

Zu einer Lösung von 0.23 g (0.01 mol) Natrium in 250 ml abs. Methanol gibt man 50.0 g (0.28 mol) 4-Bromphenol, rührt 15 Minuten bei Raumtemperatur, fügt anschließend 22.2 g (0.30 mol) 2,3-Epoxypropan-1-ol hinzu und erhitzt 6 h unter Rückfluss. Nach dem Abdestillieren des Lösungsmittels unter vermindertem Druck wird der Rückstand in 200 ml Essigsäureethylester aufgenommen, mit je 100 ml ges. NaHCO₃-Lösung, Wasser und ges. NaCl-Lösung gewaschen, über Na₂SO₄ getrocknet und das Lösungsmittel im Vakuum entfernt.



Reinigung: Umkristallisation aus Essigsäureethylester

Ausbeute: 43.1 g (69 % d. Th.), farbloser Feststoff

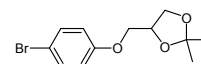
Analytik: $C_9H_{11}O_3$ $M = 247.09$ g/mol

Fp.: 80-81 °C

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.36$ (d, $^3J(H,H) = 9.0$, 2H, Ar-H), 6.78 (d, $^3J(H,H) = 9.2$, 2H, Ar-H), 4.11-4.06 (m, 1H, CHOH), 4.00 (s, 1H, CH_2OH), 3.99 (d, $^4J(H,H) = 2.3$, 1H, CH_2OH), 3.82 (dd, $^2J(H,H) = 11.3$, $^3J(H,H) = 3.9$, 1H, OCH_2), 3.72 (dd, $^2J(H,H) = 11.5$, $^3J(H,H) = 5.5$, 1H, OCH_2).

A.28 Synthese von 4-[(4-Bromphenoxy)methyl]-2,2-dimethyl-1,3-dioxolan 28

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.8.



Anstz: 43.1 g (0.17 mol) 3-(4-Bromphenoxy)propan-1,2-diol **27**

0.05 g Pyridinium-4-methylbenzolsulfonat

100 ml 2,2-Dimethoxypropan

Reinigung: Umkristallisation aus Essigsäureethylester

Ausbeute: 49.0 g (98 % d. Th.), farbloser Feststoff

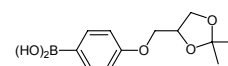
Analytik: $C_{12}H_{15}BrO_3$ $M = 287.15$ g/mol

Fp.: 37-39 °C

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.35$ (d, $^3J(H,H) = 9.2$, 2H, Ar-H), 6.77 (d, $^3J(H,H) = 9.0$, 2H, Ar-H), 4.44 (quint, $^3J(H,H) = 5.9$, 1H, OCH), 4.14 (dd, $^2J(H,H) = 8.6$, $^3J(H,H) = 6.4$, 1H, OCH_2), 4.00 (dd, $^2J(H,H) = 9.4$, $^3J(H,H) = 5.5$, 1H, OCH_2), 3.91-3.85 (m, 2H, OCH_2), 1.44 (s, 3H, CH_3), 1.38 (s, 3H, CH_3).

A.29 Synthese von 4-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)benzoboronsäure 29.1

Zu einer auf -100 °C gekühlten Lösung von 48.5 g (0.17 mol) 4-[(4-Bromphenoxy)methyl]-2,2-dimethyl-1,3-dioxolan **28** in 500 ml wasserfreiem THF wird unter einer Argonatmosphäre langsam 163 ml (0.26 mol) *n*-Butyllithium (1.6M Lösung in Hexan) zugetropft. Nach zweistündigem Rühren bei dieser Temperatur tropft man 53.2 g (0.51 mol) Borsäuretrimethylester zu, rührt weitere 2 h bei -100 °C und lässt die Reaktionsmischung anschließend über Nacht auf Raumtemperatur erwärmen. Nach Hydrolyse mit 300 ml Phosphatpuffer-Lösung (pH=5) wird dreimal mit je 100 ml Ether extrahiert. Die vereinigten organischen Phasen werden mit je 100 ml Wasser und ges. NaCl-Lösung gewaschen, über Na_2SO_4 getrocknet und das Lösungsmittel unter vermindertem Druck abdestilliert.



Reinigung: Umkristallisation aus Toluol

Ausbeute: 18.0 g (42 % d. Th.), farbloser Feststoff

Analytik: $C_{12}H_{17}BO_5$ $M = 252.07$ g/mol

Fp.: 147-149 °C

1H -NMR (Aceton- d_6 , J/Hz , 400 MHz): $\delta = 7.81$ (d, $^3J(H,H) = 8.8$, 2H, Ar-H), 6.92 (d, $^3J(H,H) = 8.6$, 2H, Ar-H), 4.45 (quint, $^3J(H,H) = 5.5$, 1H, OCH), 4.14 (dd, $^2J(H,H) = 8.2$,

$^3J(\text{H,H}) = 6.4$, 1H, OCH₂), 4.09-4.01 (m, 2H, OCH₂), 3.85 (dd, $^2J(\text{H,H}) = 8.4$, $^3J(\text{H,H}) = 6.1$, 1H, OCH₂), 1.37 (s, 3H, CH₃), 1.32 (s, 3H, CH₃).

A.30 Synthese der (Benzyloxy)phenole 30.X

2-(Benzyloxy)phenol 30.1

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.2.



Ansatz: 50.0 g (0.45 mol) 1,2-Dihydroxybenzol
 25.2 g (0.45 mol) Kaliumhydroxid
 52 ml (0.45 mol) Benzylchlorid
 500 ml Methanol

Reinigung: Hochvakuumdestillation

Ausbeute: 40.2 g (44 % d. Th.), farblose Flüssigkeit

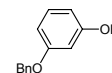
Analytik: C₁₃H₁₂O₂ M = 200.23 g/mol

Kp.: 115-117 °C (1.5·10⁻² mbar)

$^1\text{H-NMR}$ (CDCl₃, J/Hz, 400 MHz) $\delta = 7.43-7.34$ (m, 5H, Ar-H), 6.97-6.81 (m, 4H, Ar-H), 5.68 (bs, 1H, OH), 5.10 (s, 2H, OCH₂Ph).

3-(Benzyloxy)phenol 30.2

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.2.



Ansatz: 30.0 g (0.27 mol) 1,3-Hydroxybenzol
 15.2 g (0.27 mol) Kaliumhydroxid
 34.2 g (0.27 mol) Benzylchlorid
 200 ml MeOH

Reinigung: Umkristallisation aus PE

Ausbeute: 21.60 g (40 % d. Th.), farbloser Feststoff

Analytik: C₁₃H₁₂O₂ M = 200.23 g/mol

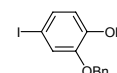
Fp.: 51-53 °C

$^1\text{H-NMR}$ (CDCl₃, J/Hz, 400 MHz): $\delta = 7.42-7.29$ (m, 5H, Ar-H), 7.12 (t, $^3J(\text{H,H}) = 8.1$, 1H, Ar-H), 6.56 (dd, $^3J(\text{H,H}) = 8.3$, $^4J(\text{H,H}) = 2.4$, 1H, Ar-H), 6.47 (t, $^4J(\text{H,H}) = 2.3$, 1H, Ar-H), 6.42 (dd, $^3J(\text{H,H}) = 8.0$, $^4J(\text{H,H}) = 2.3$, 1H, Ar-H), 5.02 (s, 2H, OCH₂), 4.85 (bs, 1H, OH).

A.31 Synthese der (Benzyloxy)-4-halogenphenole 31.X

2-(Benzyloxy)-4-iodphenol 31.1a

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.5.



Ansatz: 16.5 g (82.4 mmol) 2-(Benzyloxy)phenol 30.1

12.4 g (82.4 mmol) NaI
 3.30 g (82.4 mmol) NaOH
 6.13 g (82.4 mmol) NaOCl (4%ige Lösung in Wasser)
 200 ml Methanol

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 9.94 g (37 % d. Th.), farbloser Feststoff

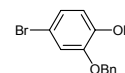
Analytik: C₁₃H₁₁IO₂ M = 326.13 g/mol

Fp.: 61-63 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.43-7.33 (m, 5H, Ar-H), 7.20-7.17 (m, 2H, Ar-H), 6.69 (d, ³J(H,H) = 8.4, 1H, Ar-H), 5.59 (s, 1H, OH), 5.05 (s, 2H, OCH₂Ph).

2-(Benzyloxy)-4-bromphenol **31.1b**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.4.



Ansatz: 27.8 g (0.14 mol) 2-(Benzyloxy)phenol **30.1**

22.4 g (0.14 mol) Brom

140 ml Methylenchlorid

140 ml Eisessig

Reinigung: Säulenchromatographie (Eluent: CHCl₃) und
 Umkristallisation aus Diethylether/PE (1:1, V/V)

Ausbeute: 30.0 g (77 % d. Th.), farbloser Feststoff

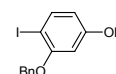
Analytik: C₁₃H₁₁BrO₂ M = 279.13 g/mol

Fp.: 66-68 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.41-7.34 (m, 5H, Ar-H), 7.05 (d, ⁴J(H,H) = 2.2, 1H, Ar-H), 7.00 (dd, ³J(H,H) = 8.4, ⁴J(H,H) = 2.2, 1H, Ar-H), 6.81 (d, ³J(H,H) = 8.5, 1H, Ar-H), 5.58 (s, 1H, OH), 5.06 (s, 2H, OCH₂Ph).

3-(Benzyloxy)-4-iodphenol **31.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.5.



Ansatz: 7.00 g (35.0 mmol) 3-(Benzyloxy)phenol **30.2**

5.23 g (35.0 mmol) NaI

1.40 g (35.0 mmol) NaOH

2.59 g (35.0 mmol) NaOCl als 4%-ige Lösung in Wasser

200 ml Methanol

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

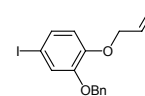
Ausbeute: 5.50 g (48 % d. Th.), farbloser Feststoff

Analytik: C₁₃H₁₁IO₂ M = 326.13 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.56 (d, ³J(H,H) = 8.4, 1H, Ar-H), 7.48-7.35 (m, 5H, Ar-H), 6.41 (d, ³J(H,H) = 2.6, 1H, Ar-H), 6.25 (dd, ³J(H,H) = 8.4, ⁴J(H,H) = 2.6, 1H, Ar-H), 5.09 (s, 2H, OCH₂), 4.98 (bs, 1H, OH).

A.32 Synthese der (Allyloxy)(benzyloxy)halogenbenzole 32.X**1-(Allyloxy)-2-(benzyloxy)-4-iodbenzol 32.1a**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 7.70 g (23.6 mmol) 2-(Benzyloxy)-4-iodphenol **31.1a**
 3.14 g (25.9 mmol) Allylbromid
 16.3 g (118 mmol) K₂CO₃
 250 ml CH₃CN

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 6.20 g (72 % d. Th.), farbloser Feststoff

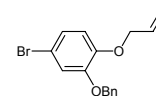
Analytik: C₁₆H₁₅IO₂ M = 366.19 g/mol

Fp.: 63-65 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.43-7.28 (m, 5H, Ar-H), 7.21-7.18 (m, 2H, Ar-H), 6.64 (d, ³J(H,H) = 8.9, 1H, Ar-H), 6.07-5.98 (m, 1H, CH=CH₂), 5.38 (dd, ²J(H,H) = 17.2, ³J(H,H) = 1.4, 1H, CH₂=CH), 5.25 (dd, ²J(H,H) = 10.6, ³J(H,H) = 1.5, 1H, CH₂=CH), 5.08 (s, 2H, OCH₂Ph), 4.56 (d, ³J(H,H) = 5.2, 2H, OCH₂).

1-(Allyloxy)-2-(benzyloxy)-4-brombenzol 32.1b

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 38.9 g (0.14 mol) 2-(Benzyloxy)-4-bromphenol **31.1b**
 18.5 g (0.15 mol) Allylbromid
 96.3 g (0.70 mol) K₂CO₃
 500 ml CH₃CN

Reinigung: Umkristallisation aus MeOH

Ausbeute: 40.1 g (90 % d. Th.), farbloser Feststoff

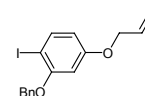
Analytik: C₁₆H₁₅BrO₂ M = 319.19 g/mol

Fp.: 50-52 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.42 (d, ³J(H,H) = 6.8, 2H, Ar-H), 7.36 (t, ³J(H,H) = 7.3, 2H, Ar-H), 7.30 (d, ³J(H,H) = 7.1, 1H, Ar-H), 7.04 (d, ⁴J(H,H) = 2.3, 1H, Ar-H), 7.00 (dd, ³J(H,H) = 8.6, ⁴J(H,H) = 2.3, 1H, Ar-H), 6.76 (d, ³J(H,H) = 8.6, 1H, Ar-H), 6.08-5.99 (m, 1H, CH=CH₂), 5.38 (dd, ³J(H,H) = 17.3, ²J(H,H) = 1.6, 1H, CH=CH₂), 5.26 (dd, ³J(H,H) = 10.5, ²J(H,H) = 1.4, 1H, CH=CH₂), 5.09 (s, 2H, OCH₂Ph), 4.57 (dt, ³J(H,H) = 5.2, ⁴J(H,H) = 1.6, 2H, OCH₂).

4-(Allyloxy)-2-(benzyloxy)-1-iodbenzol 32.2

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 5.41 g (16.6 mmol) 3-(Benzyloxy)-4-iodphenol **31.2**

2.21 g (18.3 mmol) Allylbromid
 11.5 g (83.0 mmol) K₂CO₃
 250 ml CH₃CN

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 5.60 g (92 % d. Th.), farbloser Feststoff

Analytik: C₁₆H₁₅IO₂ M = 366.19 g/mol

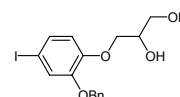
Fp.: 44-46 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.62 (d, ³J(H,H) = 8.6, 1H, Ar-H), 7.49-7.29 (m, 5H, Ar-H), 6.59-6.49 (m, 2H, Ar-H), 6.08-5.95 (m, 1H, CH=CH₂), 5.41-5.25 (m, 2H, CH=CH₂), 5.03 (s, 2H, OCH₂), 4.51-4.46 (m, 2H, CH₂CH=CH₂).

A.33 Synthese der 3-[(Benzyloxy)-4-halogenphenoxy]propan-1,2-diole 33.X

3-[2-(Benzyloxy)-4-iodphenoxy]propan-1,2-diol 33.1a

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.6.



Ansatz: 3.70 g (10.1 mmol) 1-(Allyloxy)-2-(benzyloxy)-4-iodbenzol **32.1a**
 1.42 g (12.1 mmol) *N*-Methylmorpholin-*N*-oxid (50%ige Lösung in Wasser)
 2 ml einer 4mM Lösung von Osmiumtetroxid in *tert*-Butanol
 50 ml Aceton
 20 ml ges. Natriumsulfit-Lösung

Reinigung: Umkristallisation aus Hexan/Essigsäureethylester (3:1, V/V)

Ausbeute: 3.50 g (87 % d. Th.), farbloser Feststoff

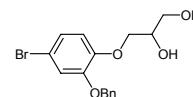
Analytik: C₁₆H₁₇IO₄ M = 400.21 g/mol

Fp.: 115-117 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.41-7.30 (m, 5H, Ar-H), 7.23-7.21 (m, 2H, Ar-H), 6.66 (d, ³J(H,H) = 8.8, 1H, Ar-H), 5.03 (s, 2H, OCH₂Ph), 4.12-4.07 (m, 1H, CHOH), 4.03-3.97 (m, 2H, CH₂OH), 3.77-3.68 (m, 2H, OCH₂).

3-[2-(Benzyloxy)-4-bromphenoxy]propan-1,2-diol 33.1b

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.6.



Ansatz: 20.0 g (62.7 mmol) 1-(Allyloxy)-2-(benzyloxy)-4-brombenzol **32.1b**
 8.07 g (68.9 mmol) *N*-Methylmorpholin-*N*-oxid (50%ige Lösung in Wasser)
 5 ml einer 4mM Lösung von Osmiumtetroxid in *tert*-Butanol
 150 ml Aceton
 50 ml ges. Natriumsulfit-Lösung

Reinigung: Umkristallisation aus Hexan/Essigsäureethylester (3:1, V/V)

Ausbeute: 20.7 g (93 % d. Th.), farbloser Feststoff

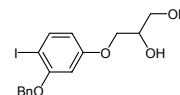
Analytik: C₁₆H₁₇BrO₄ M = 353.21 g/mol

Fp.: 112-114 °C

¹H-NMR (Aceton-d₆, *J*/Hz, 400 MHz): δ = 7.50 (d, ³*J*(H,H) = 6.8, 2H, Ar-H), 7.38 (t, ³*J*(H,H) = 7.3, 2H, Ar-H), 7.31 (d, ³*J*(H,H) = 7.3, 1H, Ar-H), 7.17 (d, ⁴*J*(H,H) = 2.3, 1H, Ar-H), 7.06 (dd, ³*J*(H,H) = 8.6, ⁴*J*(H,H) = 2.3, 1H, Ar-H), 6.97 (d, ³*J*(H,H) = 8.6, 1H, Ar-H), 5.16 (s, 2H, OCH₂Ph), 4.12-4.08 (m, 1H, CHOH), 4.04-3.96 (m, 2H, CH₂OH), 3.74-3.59 (m, 2H, OCH₂).

3-[3-(Benzyloxy)-4-iodphenoxy]propan-1,2-diol **33.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.6.



Ansatz: 5.60 g (15.3 mmol) 4-(Allyloxy)-2-(benzyloxy)-1-iodbenzol **32.2**
 1.42 g (18.4 mmol) *N*-Methylmorpholin-*N*-oxid (50%ige Lösung in Wasser)
 2 ml einer 4mM Lösung von Osmiumtetroxid in *tert*-Butanol
 50 ml Aceton
 20 ml ges. Natriumsulfit-Lösung

Reinigung: Umkristallisation aus Hexan/Essigsäureethylester (3:1, V/V)

Ausbeute: 4.30 g (70 % d. Th.), farbloser Feststoff

Analytik: C₁₆H₁₇IO₄ M = 400.21 g/mol

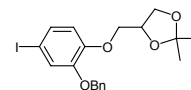
Fp.: 62-64 °C

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.62 (d, ³*J*(H,H) = 8.6, 1H, Ar-H), 7.41-7.28 (m, 5H, Ar-H), 6.60-6.57 (m, 1H, Ar-H), 6.31 (dd, ³*J*(H,H) = 8.6, ⁴*J*(H,H) = 2.7, 1H, Ar-H), 5.08 (s, 2H, OCH₂Ph), 4.12-4.07 (m, 1H, CHOH), 4.00-3.96 (m, 2H, CH₂OH), 3.82-3.77 (m, 2H, OCH₂).

A.34 Synthese der 4-[(Benzyloxy)-4-halogenphoxymethyl]-2,2-dimethyl-1,3-dioxolane **34.X**

4-[2-(Benzyloxy)-4-iodphoxymethyl]-2,2-dimethyl-1,3-dioxolan **34.1a**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.8.



Ansatz: 5.50 g (13.7 mmol) 3-[2-(Benzyloxy)-4-iodphenoxy]propan-1,2-diol **33.1a**
 0.01 g (0.04 mmol) Pyridinium-4-methylbenzolsulfonat
 50 ml 2,2-Dimethoxypropan

Reinigung: Umkristallisation aus Essigsäureethylester

Ausbeute: 5.80 g (96 % d. Th.), farbloser Feststoff

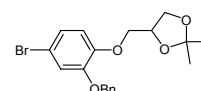
Analytik: C₁₉H₂₁IO₄ M = 440.27 g/mol

Fp.: 85-87 °C

¹H-NMR (CDCl₃, *J*/Hz, 500 MHz): δ = 7.41-7.29 (m, 5H, Ar-H), 7.22-7.19 (m, 2H, Ar-H), 6.67 (d, ³*J*(H,H) = 8.9, 1H, Ar-H), 5.04 (s, 2H, OCH₂Bn), 4.43 (quint, ³*J*(H,H) = 6.1, 1H, OCH), 4.10-4.04 (m, 2H, CH₂OH), 3.96-3.89 (m, 2H, OCH₂), 1.39 (s, 3H, CH₃), 1.36 (s, 3H, CH₃).

4-[2-(Benzyloxy)-4-bromphenoxy]methyl]-2,2-dimethyl-1,3-dioxolan **34.1b**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.8.

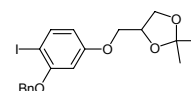


Ansatz: 20.7 g (58.6 mmol) 3-[2-(Benzyloxy)-4-bromphenoxy]propan-1,2-diol **33.1b**
 0.05 g (0.20 mmol) Pyridinium-4-methylbenzolsulfonat
 400 ml 2,2-Dimethoxypropan
 Reinigung: Säulenchromatographie (Eluent: CHCl₃/MeOH, 10:0.2, V/V)
 Ausbeute: 22.3 g (97 % d. Th.), farbloser Feststoff
 Analytik: C₁₉H₂₁BrO₄ M = 393.27 g/mol
 Fp.: 66-68 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.41 (d, ³J(H,H) = 6.7, 2H, Ar-H), 7.36 (t, ³J(H,H) = 7.2, 2H, Ar-H), 7.31 (d, ³J(H,H) = 7.0, 1H, Ar-H), 7.05 (d, ⁴J(H,H) = 2.3, 1H, Ar-H), 7.01 (dd, ³J(H,H) = 8.5, ⁴J(H,H) = 2.3, 1H, Ar-H), 6.80 (d, ³J(H,H) = 8.5, 1H, Ar-H), 5.05 (s, 2H, OCH₂Ph), 4.46-4.40 (m, 1H, OCH), 4.11-4.05 (m, 2H, OCH₂), 3.97-3.90 (m, 2H, OCH₂), 1.40 (m, 3H, CH₃), 1.37 (s, 3H, CH₃).

4-[3-(Benzyloxy)-4-iodphenoxy]methyl]-2,2-dimethyl-1,3-dioxolan **34.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.8.

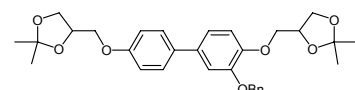


Ansatz: 4.30 g (13.7 mmol) 3-[3-(Benzyloxy)-4-iodphenoxy]propan-1,2-diol **33.2**
 0.01 g (0.04 mmol) Pyridinium-4-methylbenzolsulfonat
 50 ml 2,2-Dimethoxypropan
 Reinigung: Säulenchromatographie (Eluent: CHCl₃/MeOH, 10:0.2, V/V)
 Ausbeute: 3.60 g (60% d. Th.), farbloser Feststoff
 Analytik: C₁₉H₂₁IO₄ M = 440.27 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.62 (d, ³J(H,H) = 8.6, 1H, Ar-H), 7.41-7.28 (m, 5H, Ar-H), 6.60-6.57 (m, 1H, Ar-H), 6.31 (dd, ³J(H,H) = 8.6, ⁴J(H,H) = 2.7, 1H, Ar-H), 5.05 (s, 2H, OCH₂Ph), 4.46-4.40 (m, 1H, OCH), 4.11-4.05 (m, 2H, OCH₂), 3.97-3.90 (m, 2H, OCH₂), 1.40 (m, 3H, CH₃), 1.37 (s, 3H, CH₃).

A.35 Synthese der Biphenylderivate 35.X3-(Benzyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **35.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.1.



Ansatz: 11.0 g (28.0 mmol) 4-[2-(Benzyloxy)-4-bromphenoxy]methyl]-2,2-dimethyl-1,3-dioxolan **34.1b**
 8.46 g (33.6 mmol) 4-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)benzoboronsäure **29**
 1.62 g (1.40 mmol) Pd(PPh₃)₄

100 ml 1,2-Dimethoxyethan

75 ml ges. NaHCO₃-Lösung

Reinigung: Umkristallisation aus CHCl₃/PE (1:1, V/V)

Ausbeute: 8.40 g (58 % d. Th.), farbloser Feststoff

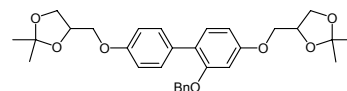
Analytik: C₃₁H₃₆O₇ M = 520.61 g/mol

Fp.: 93-95 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.45-7.28 (m, 5H, Ar-H), 7.11 (d, ⁴J(H,H) = 1.9, 1H, Ar-H), 7.07 (dd, ³J(H,H) = 8.2, ⁴J(H,H) = 2.1, 1H, Ar-H), 5.14 (s, 2H, OCH₂Ph), 4.48 (quint, ³J(H,H) = 6.1, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 4.03-3.88 (m, 4H, OCH₂), 1.46 (s, 3H, CH₃), 1.42 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃).

2-(Benzyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **35.2**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.1.



Ansatz: 3.60 g (8.18 mmol) 4-[3-(Benzyloxy)-4-iodphenoxyethyl]-2,2-dimethyl-1,3-dioxolan **34.2**

1.62 g (9.81 mmol) 4-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)benzolboronsäure **29**

0.47 g (0.41 mmol) Pd(PPh₃)₄

100 ml 1,2-Dimethoxyethan

75 ml ges. NaHCO₃-Lösung

Reinigung: Umkristallisation aus CHCl₃/PE (1:1, V/V)

Ausbeute: 1.05 g (25 % d. Th.), farbloser Feststoff

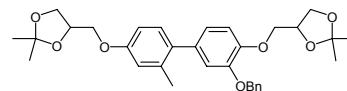
Analytik: C₃₁H₃₆O₇ M = 520.61 g/mol

Fp.: 45-47 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.45 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 2.1, 2H, Ar-H), 7.34-7.26 (m, 5H, Ar-H), 7.21 (d, ³J(H,H) = 8.4, 1H, Ar-H), 6.91 (d, ³J(H,H) = 8.9, 2H, Ar-H), 6.61 (d, ⁴J(H,H) = 2.4, 1H, Ar-H), 6.56 (dd, ³J(H,H) = 8.4, ⁴J(H,H) = 2.4, 1H, Ar-H), 5.03 (s, 2H, OCH₂Ar), 4.52-4.44 (m, 2H, OCH), 4.19-4.14 (m, 2H, OCH₂), 4.10-4.03 (m, 2H, OCH₂), 3.97-3.86 (m, 4H, OCH₂), 1.46 (s, 6H, CH₃), 1.40 (s, 6H, CH₃).

2-(Benzyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methylbiphenyl **35.3**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.1.



Ansatz: 2.00 g (6.13 mmol) 4-[2-(Benzyloxy)-4-iodphenoxyethyl]-2,2-dimethyl-1,3-dioxolan **34.1a**

3.78 g (7.36 mmol) 4-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)-2-methylbenzolboronsäure

0.35 g (0.31 mmol) Pd(PPh₃)₄

40 ml 1,2-Dimethoxyethan

30 ml ges. NaHCO₃-Lösung

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

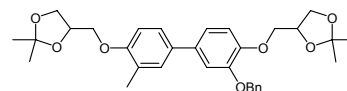
Ausbeute: 1.20 g (37 % d. Th.), farbloses Öl

Analytik: C₃₂H₃₈O₇ M = 534.64 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.41 (d, ³J(H,H) = 6.8, 2H, Ar-H), 7.34 (t, ³J(H,H) = 7.2, 2H, Ar-H), 7.29 (d, ³J(H,H) = 6.9, 1H, Ar-H), 7.04 (d, ³J(H,H) = 8.4, 1H, Ar-H), 6.95 (d, ³J(H,H) = 8.1, 1H, Ar-H), 6.82 (dd, ³J(H,H) = 8.0, ⁴J(H,H) = 2.0, 2H, Ar-H), 6.79-6.73 (m, 2H, Ar-H), 5.09 (s, 2H, OCH₂Ph), 4.52-4.44 (m, 2H, OCH), 4.18-4.12 (m, 4H, OCH₂), 4.08-3.88 (m, 4H, OCH₂), 2.12 (s, 3H, PhCH₃), 1.46 (s, 3H, CH₃), 1.43 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.38 (s, 3H, CH₃).

2-(Benzyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methylbiphenyl **35.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.1.



Ansatz: 2.00 g (6.13 mmol) 4-[2-(Benzyloxy)-4-iodphenoxyethyl]-2,2-dimethyl-1,3-dioxolan **34.1a**

3.78 g (7.36 mmol) 4-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)-3-methylbenzylboronsäure

0.35 g (0.31 mmol) Pd(PPh₃)₄

40 ml 1,2-Dimethoxyethan

30 ml ges. NaHCO₃-Lösung

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 1.60 g (49 % d. Th.), farbloses Öl

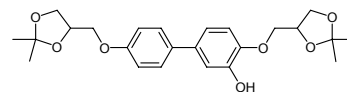
Analytik: C₃₂H₃₈O₇ M = 534.64 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.45 (d, ³J(H,H) = 6.8, 2H, Ar-H), 7.36 (t, ³J(H,H) = 7.3, 2H, Ar-H), 7.31 (d, ³J(H,H) = 7.0, 1H, Ar-H), 7.26-7.24 (m, 2H, Ar-H, überlagert von CDCl₃), 7.10 (d, ⁴J(H,H) = 2.1, 1H, Ar-H), 7.06 (dd, ³J(H,H) = 8.2, ⁴J(H,H) = 2.1, 1H, Ar-H), 6.97 (d, ³J(H,H) = 8.3, 1H, Ar-H), 6.83 (d, ³J(H,H) = 9.2, 1H, Ar-H), 5.14 (s, 2H, OCH₂Ph), 4.51-4.45 (m, 2H, OCH), 4.19-4.08 (m, 4H, OCH₂), 4.03-3.93 (m, 4H, OCH₂), 2.25 (s, 3H, PhCH₃), 1.46 (s, 3H, CH₃), 1.42 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃).

A.36 Synthese der Biphenylolderivate **36.X**

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl-3-ol **36.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.3.



Ansatz: 1.50 g (2.88 mmol) 3-(Benzyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **35.1**

0.03 g Pd 10 % auf Aktivkohle

50 ml Essigsäureethylester

Reinigung: Umkristallisation aus Essigsäureethylester/Petrolether (1:1, V/V)

Ausbeute: 1.10 g (89 % d. Th.), farbloser Feststoff

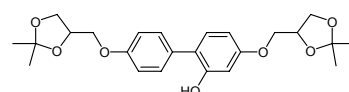
Analytik: $C_{24}H_{30}O_7$ $M = 430.49$ g/mol

Fp.: 135-137 °C

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.44$ (d, $^3J(H,H) = 8.9$, 2H, Ar-H), 7.13 (d, $^4J(H,H) = 2.2$, 1H, Ar-H), 6.98 (dd, $^3J(H,H) = 8.3$, $^4J(H,H) = 2.2$, 1H, Ar-H), 6.94 (d, $^3J(H,H) = 8.8$, 2H, Ar-H), 6.92 (d, $^3J(H,H) = 8.4$, 2H, Ar-H), 6.24 (bs, 1H, OH), 4.48 (quint, $^3J(H,H) = 5.8$, 2H, OCH), 4.18-4.03 (m, 4H, OCH_2), 3.97-3.88 (m, 4H, OCH_2), 1.49 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.40 (s, 3H, CH_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl-2-ol **36.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.3.



Ansatz: 1.05 g (2.02 mmol) 2-(Benzyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **35.2**

0.02 g Pd 10% auf Aktivkohle

50 ml Essigsäureethylester

Reinigung: Umkristallisation aus Essigsäureethylester/Petrolether (1:1, V/V)

Ausbeute: 0.70 g (80 % d. Th.), farbloser Feststoff

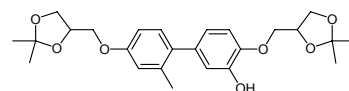
Analytik: $C_{24}H_{30}O_7$ $M = 430.49$ g/mol

Fp.: 118-120 °C

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.31$ (d, $^3J(H,H) = 8.7$, 2H, Ar-H), 7.08 (d, $^3J(H,H) = 8.9$, 1H, Ar-H), 6.99 (d, $^3J(H,H) = 8.7$, 2H, Ar-H), 6.55-6.53 (m, 3H, Ar-H), 5.22 (s, 1H, OH), 4.48 (quint, $^3J(H,H) = 6.0$, 2H, OCH), 4.33-4.13 (m, 2H, OCH_2), 4.10-4.03 (m, 2H, OCH_2), 3.98-3.87 (m, 4H, OCH_2), 1.46 (d, $^4J(H,H) = 1.7$, 6H, CH_3), 1.39 (d, $^4J(H,H) = 2.3$, 6H, CH_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methylbiphenyl-3-ol **36.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.3.



Ansatz: 1.20 g (2.24 mmol) 2-(Benzyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methylbiphenyl **35.3**

0.02 g Pd 10% auf Aktivkohle

50 ml Essigsäureethylester

Reinigung: Fliedkraftvermittelte präparative Chromatographie (Eluent: $CHCl_3$)

Ausbeute: 0.60 g (60 % d. Th.), farbloser Feststoff

Analytik: $C_{25}H_{32}O_7$ $M = 444.52$ g/mol

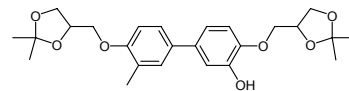
Fp.: 83-85 °C

1H -NMR ($CDCl_3$, J/Hz , 500 MHz): $\delta = 7.10$ (d, $^3J(H,H) = 8.4$, 1H, Ar-H), 6.89 (d, $^3J(H,H) = 8.2$, 1H, Ar-H), 6.87 (d, $^4J(H,H) = 2.1$, 1H, Ar-H), 6.79 (d, $^4J(H,H) = 2.6$, 1H, Ar-H),

6.75 (dd, $^3J(\text{H,H}) = 8.3$, $^4J(\text{H,H}) = 2.5$, 1H, Ar-H), 6.71 (dd, $^3J(\text{H,H}) = 8.2$, $^4J(\text{H,H}) = 2.1$, 1H, Ar-H), 4.51-4.45 (m, 2H, OCH), 4.17-4.13 (m, 2H, OCH₂), 4.12-4.04 (m, 3H, OCH₂), 3.95-3.88 (m, 3H, OCH₂), 2.23 (s, 3H, PhCH₃), 1.49 (s, 3H, CH₃), 1.46 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methylbiphenyl-3-ol **36.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.3.



Ansatz: 1.20 g (2.24 mmol) 2-(Benzyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methylbiphenyl **35.4**
0.02 g Pd 10% auf Aktivkohle
50 ml Essigsäureethylester

Reinigung: Fließkraftvermittelte präparative Chromatographie (Eluent: CHCl₃)

Ausbeute: 0.68 g (68 % d. Th.), farbloser Feststoff

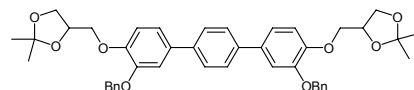
Analytik: C₂₅H₃₂O₇ M = 444.52 g/mol

Fp.: 94-96 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.31-7.28 (m, 2H, Ar-H), 7.13 (d, $^4J(\text{H,H}) = 2.1$, 1H, Ar-H), 6.98 (dd, $^3J(\text{H,H}) = 8.3$, $^4J(\text{H,H}) = 2.2$, 1H, Ar-H), 6.91 (d, $^3J(\text{H,H}) = 8.4$, 1H, Ar-H), 6.84 (d, $^3J(\text{H,H}) = 8.1$, 1H, Ar-H), 4.51-4.45 (m, 2H, OCH), 4.18-4.03 (m, 5H, OCH₂), 3.98-3.87 (m, 3H, OCH₂), 2.25 (s, 3H, PhCH₃), 1.49 (s, 3H, CH₃), 1.46 (s, 3H, CH₃), 1.41 (s, 3H, CH₃), 1.40 (s, 3H, CH₃).

A.37 Synthese von 3,3''-Benzyloxy-4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-1,1':4',1''-terphenyl **37**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.1.



Ansatz: 9.18 g (23.3 mmol) 4-[2-(Benzyloxy)-4-bromphenoxyethyl]-2,2-dimethyl-1,3-dioxolan **34.1b**
2.32 g (14.0 mmol) 1,4-Benzoldiboronsäure
0.73 g (0.64 mmol) Pd(PPh₃)₄
100 ml 1,2-Dimethoxyethan
75 ml ges. NaHCO₃-Lösung

Reinigung: Umkristallisation aus CHCl₃/Petrolether (1:1, V/V)

Ausbeute: 5.30 g (60 % d. Th.), farbloser Feststoff

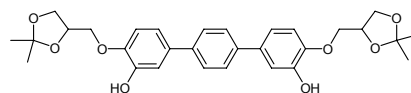
Analytik: C₄₄H₄₆O₈ M = 702.83 g/mol

Fp.: 140-142 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.52 (s, 4H, Ar-H), 7.46 (d, $^3J(\text{H,H}) = 7.0$, 4H, Ar-H), 7.37 (t, $^3J(\text{H,H}) = 7.3$, 4H, Ar-H), 7.31 (d, $^3J(\text{H,H}) = 7.2$, 2H, Ar-H), 7.19-7.15 (m, 4H, Ar-H), 7.01 (d, $^3J(\text{H,H}) = 8.3$, 2H, Ar-H), 5.16 (s, 4H, OCH₂Ar), 4.52-4.46 (m, 2H, OCH), 4.18-4.11 (m, 4H, OCH₂), 4.05-3.95 (m, 4H, OCH₂), 1.43 (s, 6H, CH₃), 1.38 (s, 6H, CH₃).

A.38 Synthese von 4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-1,1':4',1''-terphenyl-3,3''-diol **38**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.3.



Ansatz: 3.80 g (5.41 mmol) 3,3''-Benzyloxy-4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-1,1':4',1''-terphenyl **37**
0.05 g Pd 10% auf Aktivkohle
50 ml Essigsäureethylester

Reinigung: Umkristallisation aus Essigsäure/Petrolether (1:2, V/V)

Ausbeute: 2.30 g (81 % d. Th.), farbloser Feststoff

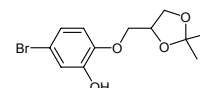
Analytik: C₃₀H₃₄O₈ M = 522.59 g/mol

Fp.: 190-192 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.57 (s, 4H, Ar-H), 7.22 (d, ⁴J(H,H) = 2.2, 2H, Ar-H), 7.08 (dd, ³J(H,H) = 8.3, ⁴J(H,H) = 2.2, 2H, Ar-H), 6.95 (d, ³J(H,H) = 8.4, 2H, Ar-H), 6.28 (bs, 2H, OH), 4.52-4.47 (m, 2H, OCH), 4.18-4.05 (m, 6H, OCH₂), 3.92-3.89 (m, 2H, OCH₂), 1.49 (s, 6H, CH₃), 1.41 (s, 6H, CH₃).

A.39 Synthese von 5-Brom-2-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenol **39**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.3.



Ansatz: 5.00 g (12.7 mmol) 4-{[2-(Benzyloxy)-4-bromphenoxy]methyl}-2,2-dimethyl-1,3-dioxolan **34.1b**
0.13 g Pd 10% auf Aktivkohle
50 ml Essigsäureethylester

Reinigung: Umkristallisation aus Essigsäure/Petrolether (1:2, V/V)

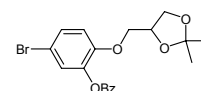
Ausbeute: 3.08 g (80 % d. Th.), farbloser Feststoff

Analytik: C₁₂H₁₅BrO₄ M = 303.15 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.08 (dd, ³J(H,H) = 8.3, ⁴J(H,H) = 2.2, 1H, Ar-H), 6.98 (d, ⁴J(H,H) = 2.4, 1H, Ar-H), 6.98 (d, ³J(H,H) = 8.4, 1H, Ar-H), 6.22 (bs, 1H, OH), 4.52-4.47 (m, 1H, OCH), 4.13-4.05 (m, 2H, OCH₂), 3.92-3.87 (m, 2H, OCH₂), 1.48 (s, 3H, CH₃), 1.41 (s, 3H, CH₃).

A.40 Synthese von 5-Brom-2-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenylbenzoat **40**

Eine Lösung von 3.00 g (9.90 mmol) 5-Brom-2-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenol **39**, 1.40 g (9.90 mmol) frisch destilliertes Benzoylchlorid und 1.50 g (14.8 mmol) Triethylamin in 50 ml trockenem Methylenchlorid wird 12 h bei Raumtemperatur gerührt. Anschließend werden 50 ml ges. NH₄HCO₃-Lösung zugegeben und dreimal mit je 100 ml Diethylether extrahiert. Die vereinigten organischen Phasen werden mit je 50 ml Wasser und ges. NaCl-Lösung gewaschen, über Na₂SO₄ getrocknet und das Lösungsmittel unter vermindertem Druck abdestilliert.



Reinigung: Säulenchromatographie (Eluent: CHCl₃/MeOH 10:1, V/V)

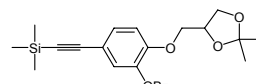
Ausbeute: 4.03 g (85 % d. Th.), farbloses Öl

Analytik: C₁₉H₁₉BrO₅ M = 407.26 g/mol

¹H-NMR (Aceton-d₆, J/Hz, 400 MHz): δ = 8.16 (d, ³J(H,H) = 8.4, 2H, Ar-H), 7.62 (t, ³J(H,H) = 7.4, 1H, Ar-H), 7.49 (t, ³J(H,H) = 7.8, 2H, Ar-H), 7.16-7.14 (m, 1H, Ar-H), 7.12 (d, ⁴J(H,H) = 2.2, 1H, Ar-H), 7.02 (d, ³J(H,H) = 8.3, 1H, Ar-H), 4.30-4.24 (m, 1H, OCH), 4.10-4.06 (m, 1H, OCH₂), 3.95-3.89 (m, 2H, OCH₂), 3.78 (dd, ³J(H,H) = 8.6, ⁴J(H,H) = 5.9, 1H, OCH₂), 1.28 (s, 3H, CH₃), 1.27 (s, 3H, CH₃).

A.41 Synthese von 2-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)-5-(trimethylsilylethynyl)phenylbenzoat 41

Eine Suspension von 1.00 g (2.46 mmol) 5-Brom-2-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenylbenzoate **40**, 253 mg (2.58 mmol) Trimethylsilylethin, 142 mg (0.12 mmol) Pd(PPh₃)₄ und 23.0 mg (0.12 mmol) CuI in 50 ml trockenem Triethylamin wird unter einer Argonatmosphäre 24 h unter Rückfluss erhitzt. Anschließend werden zur abgekühlten Reaktionsmischung 100 ml Wasser zugeben und dreimal mit je 50 ml Diethylether extrahiert. Die organische Phase wird mit je 50 ml Wasser und ges. NaCl-Lösung gewaschen, über Na₂SO₄ getrocknet und das Lösungsmittel unter vermindertem Druck abdestilliert.



Reinigung: Säulenchromatographie (Eluent: CHCl₃/PE 1:1, V/V)

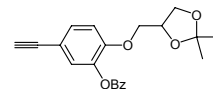
Ausbeute: 0.80 g (77% d. Th.), farbloses Öl

Analytik: C₂₄H₂₈O₅Si M = 424.56 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 8.16 (d, ³J(H,H) = 8.5, 2H, Ar-H), 7.61 (t, ³J(H,H) = 7.4, 1H, Ar-H), 7.48 (t, ³J(H,H) = 7.7, 2H, Ar-H), 7.13-7.09 (m, 2H, Ar-H), 7.07 (d, ³J(H,H) = 8.1, 1H, Ar-H), 4.30-4.24 (m, 1H, OCH), 4.12-4.09 (m, 1H, OCH₂), 3.95-3.89 (m, 2H, OCH₂), 3.80-3.76 (m, 1H, OCH₂), 1.29 (s, 3H, CH₃), 1.27 (s, 3H, CH₃), 0.24 (s, 9H, SiCH₃).

A.42 Synthese von 2-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)-5-ethynylphenylbenzoat 42

Zu einer Lösung von 800 mg (1.88 mmol) 2-(2,2-Dimethyl-1,3-dioxolan-4-ylmethoxy)-5-(trimethylsilylethynyl)phenylbenzoat **41** in 50 ml THF und 5 ml Wasser werden 2 ml einer 1M Lösung von Tetra-*n*-butylammoniumfluorid in THF gegeben und 1h bei 0 °C gerührt. Anschließend wird das Lösungsmittel am Rotationsverdampfer entfernt und der Rückstand mit 50 ml Wasser versetzt. Nach dreimaliger Extraktion mit je 20 ml Hexan wäscht man die vereinigten organischen Phasen mit je 20 ml Wasser und ges. NaCl-Lösung, trocknet über Na₂SO₄ und entfernt das Lösungsmittel unter vermindertem Druck.



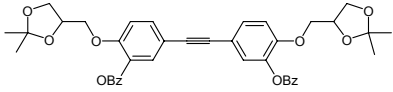
Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 600 mg (91 % d. Th.), farbloses Öl

Analytik: C₂₁H₂₀O₅ M = 352.38 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 8.16 (d, ³*J*(H,H) = 8.5, 2H, Ar-H), 7.61 (t, ³*J*(H,H) = 7.4, 1H, Ar-H), 7.48 (t, ³*J*(H,H) = 7.8, 2H, Ar-H), 7.16-7.13 (m, 2H, Ar-H), 7.09 (d, ³*J*(H,H) = 8.0, 1H, Ar-H), 4.30-4.24 (m, 1H, OCH), 4.09 (dd, ²*J*(H,H) = 9.5, ³*J*(H,H) = 4.3, 1H, OCH₂), 3.95-3.88 (m, 2H, OCH₂), 3.78 (dd, ²*J*(H,H) = 8.6, ³*J*(H,H) = 5.9, 1H, OCH₂), 1.47 (s, 6H, CH₃), 1.39 (s, 6H, CH₃).

A.43 Synthese von 3,3'-Ethin-1,2-diylbis[6-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenylbenzoat] 43

Eine Suspension von 770 mg (1.89 mmol) 5-Brom-2-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenylbenzoate **40**,  700 mg (1.99 mmol) 2-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-5-ethynylphenylbenzoat **42**, 109 mg (0.09 mmol) Pd(PPh₃)₄ und 18.0 mg (0.09 mmol) CuI in 50 ml trockenem Triethylamin wird unter einer Argonatmosphäre 24 h unter Rückfluss erhitzt. Anschließend werden zur abgekühlten Reaktionsmischung 100 ml Wasser zugeben und dreimal mit je 50 ml Diethylether extrahiert. Die organische Phase wird mit je 50 ml Wasser und ges. NaCl-Lösung gewaschen, über Na₂SO₄ getrocknet und das Lösungsmittel unter vermindertem Druck abdestilliert.

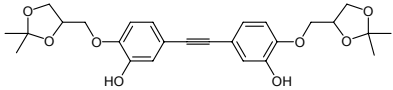
Reinigung: Säulenchromatographie (Eluent: CHCl₃/PE 1:1, V/V)

Ausbeute: 0.80 g (62% d. Th.), gelbes Öl

Analytik: C₄₀H₃₈O₁₀ M = 678.72 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 8.18 (d, ³*J*(H,H) = 8.4, 4H, Ar-H), 7.63 (t, ³*J*(H,H) = 7.4, 2H, Ar-H), 7.50 (t, ³*J*(H,H) = 7.7, 4H, Ar-H), 7.21-7.19 (m, 4H, Ar-H), 7.14 (d, ³*J*(H,H) = 7.9, 2H, Ar-H), 4.33-4.27 (m, 2H, OCH), 4.15 (dd, ²*J*(H,H) = 9.4, ³*J*(H,H) = 4.3, 2H, OCH₂), 3.98 (dd, ²*J*(H,H) = 9.4, ³*J*(H,H) = 6.8, 2H, OCH₂), 3.93 (dd, ²*J*(H,H) = 8.6, ³*J*(H,H) = 6.3, 2H, OCH₂), 3.81 (dd, ³*J*(H,H) = 8.5, ⁴*J*(H,H) = 5.8, 2H, OCH₂), 1.30 (s, 6H, CH₃), 1.29 (s, 6H, CH₃).

A.44 Synthese von 3,3'-Ethin-1,2-diylbis[6-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenol] 44

Eine Mischung von 600 mg (0.88 mmol) 3,3'-Ethin-1,2-diylbis[6-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenylbenzoat] **43**,  5 ml einer 1M Lösung von KOH in Wasser und 50 ml Methanol wird 1 h bei Raumtemperatur gerührt. Anschließend werden 50 ml Wasser zugegeben und dreimal mit je 20 ml Diethylether extrahiert. Die vereinigten organischen Phasen werden mit 50 ml ges. NaCl-Lösung gewaschen, über Na₂SO₄ getrocknet und das Lösungsmittel am Rotationsverdampfer entfernt.

Reinigung: Säulenchromatographie (Eluent: CHCl₃)

Ausbeute: 300 mg (72 % d. Th.), rötlicher Feststoff

Analytik: C₂₆H₃₀O₈ M = 470.51 g/mol

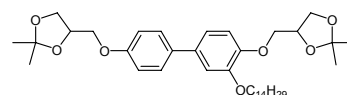
¹H-NMR (CDCl₃, *J*/Hz, 400 MHz) δ = 7.08 (dd, ³*J*(H,H) = 8.2, ⁴*J*(H,H) = 1.8, 2H, Ar-H), 7.03 (d, ⁴*J*(H,H) = 1.8, 2H, Ar-H), 6.87 (d, ³*J*(H,H) = 8.2, 2H, Ar-H), 6.33 (bs, 2H, OH),

4.47 (quint, $^3J(\text{H,H}) = 5.5$, 2H, OCH), 4.14 (dd, $^2J(\text{H,H}) = 8.6$, $^3J(\text{H,H}) = 6.5$, 2H, OCH₂), 4.10-4.01 (m, 4H, OCH₂), 3.88 (dd, $^2J(\text{H,H}) = 8.6$, $^3J(\text{H,H}) = 5.6$, 2H, OCH₂), 1.30 (s, 6H, CH₃), 1.29 (s, 6H, CH₃).

A.45 Synthese der lateral substituierten Biphenylderivate 45.X

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(tetradecyloxy)biphenyl **45.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 155 mg (0.57 mmol) 1-Bromtetradecan
 321 mg (2.32 mmol) K₂CO₃
 50 ml DMF
 50 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

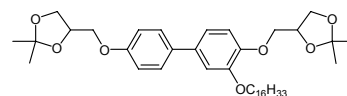
Ausbeute: 280 mg (97 % d. Th.), farblose Flüssigkeit

Analytik: C₃₈H₅₈O₇ M = 626.86 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 500 MHz): $\delta = 7.44$ (d, $^3J(\text{H,H}) = 8.9$, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.95 (d, $^3J(\text{H,H}) = 8.9$, 3H, Ar-H), 4.48 (quint, $^3J(\text{H,H}) = 6.2$, 2H, OCH), 4.18-4.07 (m, 4H, OCH₂), 4.03-3.89 (m, 6H, OCH₂), 1.81 (quint, $^3J(\text{H,H}) = 7.1$, 2H, OCH₂CH₂), 1.48-1.45 (m, 2H, CH₂), 1.46 (m, 3H, CH₃), 1.46 (m, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.36-1.25 (m, 20H, CH₂), 0.87 (t, $^3J(\text{H,H}) = 7.0$, 3H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(hexadecyloxy)biphenyl **45.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 320 mg (0.37 mmol) 1-Bromhexadecan
 242 mg (1.75 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 183 mg (82 % d. Th.), farblose Flüssigkeit

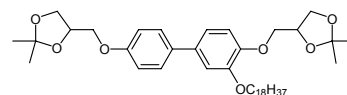
Analytik: C₄₀H₆₂O₇ M = 654.92 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz) $\delta = 7.43$ (dd, $^3J(\text{H,H}) = 8.8$, $^4J(\text{H,H}) = 2.1$, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 6.94 (d, $^3J(\text{H,H}) = 8.9$, 3H, Ar-H), 4.48 (q, $^3J(\text{H,H}) = 6.0$, 2H, OCH), 4.18-3.88 (m, 8H, OCH₂), 3.62 (t, $^3J(\text{H,H}) = 6.6$, 2H, OCH₂), 1.81 (quint, $^3J(\text{H,H}) =$

7.0, 2H, OCH₂CH₂), 1.55 (quint, ³J(H,H) = 7.0, 4H, CH₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.35-1.21 (m, 24H, CH₂), 0.86 (t, ³J(H,H) = 6.7, 3H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(octadecyloxy)biphenyl **45.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

134 mg (0.37 mmol) 1-Bromooctadecan

242 mg (1.75 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fließkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 160 mg (67 % d. Th.), farbloser Feststoff

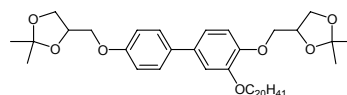
Analytik: C₄₂H₆₆O₇ M = 682.97 g/mol

Fp.: 37-39 °C

¹H-NMR (CDCl₃, J/Hz, 200 MHz): δ = 7.44 (d, ³J(H,H) = 8.9, 2H, Ar-H), 7.04-7.00 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.8, 3H, Ar-H), 4.48 (quint, ³J(H,H) = 5.9, 2H, OCH), 4.20-3.86 (m, 10H, OCH₂), 1.81 (quint, ³J(H,H) = 6.9, 2H, OCH₂CH₂), 1.46 (m, 6H, CH₃), 1.39 (s, 6H, CH₃), 1.33-1.22 (m, 30H, CH₂), 0.86 (t, ³J(H,H) = 6.4, 3H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(icosyloxy)biphenyl **45.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

134 mg (0.37 mmol) 1-Bromicosan

242 mg (1.75 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fließkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 160 mg (64 % d. Th.), farbloser Feststoff

Analytik: C₄₄H₇₀O₇ M = 711.02 g/mol

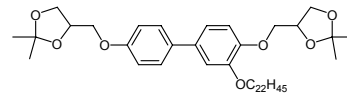
Fp.: 43-45 °C

¹H-NMR (CDCl₃, J/Hz, 200 MHz): δ = 7.44 (d, ³J(H,H) = 8.7, 2H, Ar-H), 7.04-7.00 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.8, 3H, Ar-H), 4.48 (quint, ³J(H,H) = 5.9, 2H, OCH), 4.20-

3.86 (m, 10H, OCH₂), 1.81 (quint, ³J(H,H) = 6.9, 2H, OCH₂CH₂), 1.46-1.44 (m, 8H, CH₂, CH₃), 1.39 (s, 6H, CH₃), 1.33-1.22 (m, 35H, CH₂), 0.86 (t, ³J(H,H) = 6.5, 3H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(docosyloxy)biphenyl **45.5**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

144 mg (0.37 mmol) 1-Bromdocosan

242 mg (1.75 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fließkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 150 mg (58 % d. Th.), farbloser Feststoff

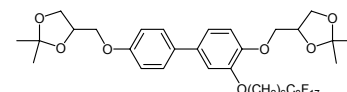
Analytik: C₄₆H₇₄O₇ M = 739.08 g/mol

Fp.: 47-49 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.7, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.95 (d, ³J(H,H) = 8.7, 3H, Ar-H), 4.48 (quint, ³J(H,H) = 5.8, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 4.04-3.89 (m, 6H, OCH₂), 1.81 (quint, ³J(H,H) = 7.4, 2H, OCH₂CH₂), 1.46-1.44 (m, 8H, CH₂, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.31-1.25 (m, 36H, CH₂), 0.87 (t, ³J(H,H) = 6.8, 3H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-heptafluortetradecyloxy)biphenyl **45.6**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

284 mg (0.49 mmol) 14-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptafluortetradecan **2.1**

318 mg (2.30 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fließkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 302 mg (70 % d. Th.), farbloser Feststoff

Analytik: C₃₈H₄₁F₁₇O₇ M = 932.70 g/mol

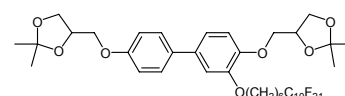
Fp.: 72-73 °C

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.43 (dd, ³*J*(H,H) = 8.9, ⁴*J*(H,H) = 2.2, 2H, Ar-H), 7.05-7.02 (m, 2H, Ar-H), 6.94 (d, ³*J*(H,H) = 8.9, 3H, Ar-H), 4.51-4.45 (m, 2H, OCH), 4.19-3.88 (m, 10H, OCH₂), 2.13-2.00 (m, 2H, CH₂CF₂), 1.83 (quint, ³*J*(H,H) = 6.9, 2H, OCH₂CH₂), 1.64 (quint, ³*J*(H,H) = 7.9, 2H, CH₂CH₂CF₂), 1.57-1.47 (m, 4H, CH₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.33 (t, ⁴*J*(F,F) = 9.7, 3F, CF₃), -114.70 (s, 2F, CH₂CF₂), -122.21 (s, 8F, CF₂), -123.04 (s, 2F, CF₂), -123.84 (s, 2F, CF₂), -126.41 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,-14,14,15,15,16,16,16-henicosafuorhexadecyloxy)biphenyl **45.7**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 275 mg (0.64 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

481 mg (0.70 mmol) 16-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafuorhexadecan **2.2**

442 mg (3.20 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 610 mg (92 % d. Th.), farbloser Feststoff

Analytik: C₄₀H₄₁F₂₁O₇ M = 1032.72 g/mol

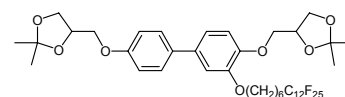
Fp.: 85-87 °C

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.43 (d, ³*J*(H,H) = 8.8, 2H, Ar-H), 7.05-7.02 (m, 2H, Ar-H), 6.94 (dd, ³*J*(H,H) = 8.8, 3H, Ar-H), 4.51-4.45 (m, 2H, OCH), 4.19-3.88 (m, 10H, OCH₂), 2.13-1.99 (m, 2H, CH₂CF₂), 1.84 (quint, ³*J*(H,H) = 6.6, 2H, OCH₂CH₂), 1.64 (quint, ³*J*(H,H) = 7.7, 2H, CH₂CH₂CF₂), 1.56-1.48 (m, 4H, CH₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.32 (t, ⁴*J*(F,F) = 9.7, 3F, CF₃), -114.69 (s, 2F, CH₂CF₂), -122.08 (s, 10F, CH₂CF₂(CF₂)₅), -122.99 (s, 2F, CF₂CF₂CF₂CF₃), -123.78 (s, 2F, CF₂CF₂CF₃), -126.39 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,-14,14,15,15,16,16,17,17,18,18,18-pentacosafuoroctadecyloxy)biphenyl **45.8**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 122 mg (0.28 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

244 mg (0.31 mmol) 18-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,-
11,12,12-pentacosafuorooctadecan **2.3**

193 mg (1.40 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fließkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 270 mg (85 % d. Th.), farbloser Feststoff

Analytik: C₄₂H₄₁F₂₅O₇ M = 1132.73 g/mol

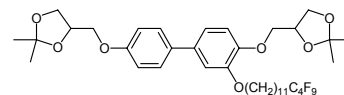
Fp.: 57-61 °C

¹H-NMR (CDCl₃, J/Hz, 500 MHz): δ = 7.43 (d, ³J(H,H) = 8.8, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.95 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 1.8, 3H, Ar-H), 4.50-4.45 (m, 2H, OCH), 4.18-3.89 (m, 10H, OCH₂), 2.11-2.01 (m, 2H, CH₂CF₂), 1.83 (quint, ³J(H,H) = 6.6, 2H, OCH₂CH₂), 1.63 (quint, ³J(H,H) = 7.7, 2H, CH₂CH₂CF₂), 1.56-1.47 (m, 4H, CH₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.38 (s, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.14 (t, ⁴J(F,F) = 9.8, 3F, CF₃), -114.69 (s, 2F, CH₂CF₂), -122.04 (s, 10F, CH₂CF₂(CF₂)₅), -122.21 (s, 4F, CH₂CF₂(CF₂)₂), -123.04 (s, 2F, CF₂CF₂CF₂CF₃), -123.84 (s, 2F, CF₂CF₂CF₃), -126.45 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,13,13,14,14,15,15,15-nonafluorpentadecyloxy)biphenyl **45.9**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-
biphenyl-3-ol **36.1**

168 mg (0.37 mmol) 15-Brom-1,1,1,2,2,3,3,4,4-nonafluorpentadecan **2.4**

242 mg (1.75 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fließkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 150 mg (53% d. Th.), farbloses Öl

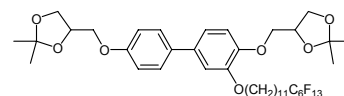
Analytik: C₃₉H₅₁F₉O₇ M = 802.80 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.43 (dd, ³J(H,H) = 8.7, ⁴J(H,H) = 2.0, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.7, 3H, Ar-H), 4.51-4.45 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 4.03-3.88 (m, 6H, OCH₂), 2.10-1.96 (m, 2H, CH₂CF₂), 1.81 (quint, ³J(H,H) = 7.1, 2H, OCH₂CH₂), 1.62-1.53 (m, 6H, CH₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.36-1.27 (m, 10H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.64 (t, ⁴J(F,F) = 9.7, 3F, CF₃), -114.81(-115.15) (m, 2F, CH₂CF₂), -124.84 (s, 2F, CF₂), -126.29(-126.51) (m, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,13,13,14,14,15,15,16,16,-
17,17,17-tridecafluorheptadecyloxy)biphenyl **45.10**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-
biphenyl-3-ol **36.1**

271 mg (0.49 mmol) 17-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluor-
heptadecan **2.5**

318 mg (2.30 mmol) K_2CO_3

50 ml DMF

5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/ $CHCl_3$ 1:2, V/V)

Ausbeute: 390 mg (94 % d. Th.), farbloser Feststoff

Analytik: $C_{41}H_{51}F_{13}O_7$ M = 902.82 g/mol

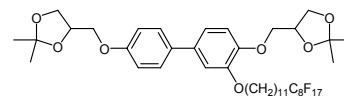
Fp.: 59-61 °C

1H -NMR ($CDCl_3$, J/Hz, 400 MHz): δ = 7.44 (dd, $^3J(H,H) = 8.9$, $^4J(H,H) = 2.1$, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.94 (d, $^3J(H,H) = 8.9$, 3H, Ar-H), 4.51-4.45 (m, 2H, OCH), 4.19-4.16 (m, 4H, OCH_2), 4.03-3.88 (m, 6H, OCH_2), 2.10-1.96 (m, 2H, CH_2CF_2), 1.81 (quint, $^3J(H,H) = 7.0$, 2H, OCH_2CH_2), 1.58 (quint, $^3J(H,H) = 7.5$, 2H, $CH_2CH_2CF_2$), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.37-1.27 (m, 14H, CH_2).

^{19}F -NMR ($CDCl_3$, J/Hz, 188 MHz) δ = -81.37 (t, $^4J(F,F) = 9.9$, 3F, CF_3), -114.64-(-114.86) (m, 2F, CH_2CF_2), -122.30 (s, 8F, CF_2), -123.24 (s, 2F, CF_2), -123.91 (s, 2F, CF_2), -126.47 (s, 2F, CF_2CF_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,13,13,14,14,15,15,16,16,17,17,-
18,18,19,19,19-heptadecafluornonadecyloxy)biphenyl **45.11**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-
biphenyl-3-ol **36.1**

320 mg (0.49 mmol) 19-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadeca-
fluornonadecan **2.6**

318 mg (2.30 mmol) K_2CO_3

50 ml DMF

5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/ $CHCl_3$ 1:2, V/V)

Ausbeute: 450 mg (98 % d. Th.), farbloser Feststoff

Analytik: $C_{43}H_{51}F_{17}O_7$ M = 1002.83 g/mol

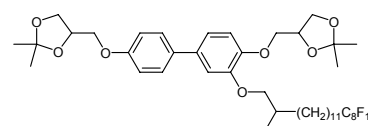
Fp.: 47-49 °C

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.44 (dd, ³*J*(H,H) = 8.8, ⁴*J*(H,H) = 2.1, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.94 (d, ³*J*(H,H) = 8.8, 3H, Ar-H), 4.51-4.45 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 4.03-3.88 (m, 6H, OCH₂), 2.10-1.96 (m, 2H, CH₂CF₂), 1.81 (quint, ³*J*(H,H) = 7.0, 2H, OCH₂CH₂), 1.62-1.53 (m, 2H, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃) 1.36-1.27 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.32 (t, ⁴*J*(F,F) = 9.9, 3F, CF₃), -114.73 (s, 2F, CH₂CF₂), -122.21 (s, 6F, CF₂), -123.04 (s, 2F, CF₂) -123.86 (s, 2F, CF₂), -126.41 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(14,14,15,15,16,16,17,17,18,18,19,19,-20,20,21,21,21-hepta-decafluor-2-methylhenicosyloxy)biphenyl **45.12**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 254 mg (0.37 mmol) 21-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hepta-decafluor-20-methylhenicosan **10.8**
 242 mg (1.75 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fließkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 200 mg (55 % d. Th.), farbloser Feststoff

Analytik: C₄₆H₅₇F₁₇O₇ M = 1044.91 g/mol

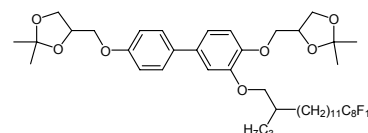
Fp.: 57-61 °C

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.44 (d, ³*J*(H,H) = 8.9, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.95 (dd, ³*J*(H,H) = 8.8, 3H, Ar-H), 4.51-4.44 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 4.98-3.76 (m, 6H, OCH₂), 2.10-1.93 (m, 2H, CH₂CF₂), 1.62-1.48 (m, 3H, CH, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.35-1.25 (m, 18H, CH₂), 1.04 (t, ³*J*(H,H) = 6.7, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.38 (t, ⁴*J*(F,F) = 9.7, 3F, CF₃), -114.75-(-114.82) (m, 2F, CH₂CF₂), -122.23 (s, 6F, CF₂), -123.08 (s, 2F, CF₂), -123.89 (s, 2F, CF₂), -126.44 (m, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(14,14,15,15,16,16,17,17,18,18,19,19,-20,20,21,21,21-hepta-decafluor-2-propylhenicosyloxy)biphenyl **45.13**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 268 mg (0.37 mmol) 20-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluortricosan **10.9**
 242 mg (1.75 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 250 mg (67 % d. Th.), farbloser Feststoff

Analytik: C₄₈H₆₁F₁₇O₇ M = 1072.97 g/mol

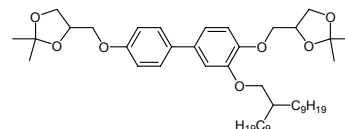
Fp.: 43-45 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.5, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 6.94 (dd, ³J(H,H) = 8.6, ⁴J(H,H) = 2.3, 3H, Ar-H), 4.47 (sext, ³J(H,H) = 5.9, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 4.00-3.89 (m, 6H, OCH₂), 2.09-1.96 (m, 2H, CH₂CF₂), 1.86-1.81 (m, 3H, CH), 1.61-1.54 (m, 2H, CF₂CH₂CH₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.37-1.26 (m, 22H, CH₂), 0.91 (t, ³J(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.18 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.70 (-114.76) (m, 2F, CH₂CF₂), -122.12 (s, 2F, CF₂), -122.30 (s, 4F, CF₂), -123.09 (s, 2F, CF₂), -123.90 (s, 2F, CF₂), -126.49 (m, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(2-nonylundecyloxy)biphenyl **45.14**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 176 mg (0.49 mmol) 10-(Brommethyl)nonadecan **6.1**
 318 mg (2.30 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

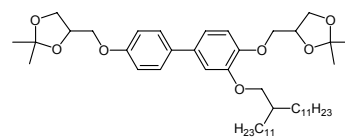
Ausbeute: 307 mg (92 % d. Th.), farbloses Öl

Analytik: C₄₄H₇₀O₇ M = 711.02 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 2.1, 2H, Ar-H), 7.03-7.00 (m, 2H, Ar-H), 6.94 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 2.1, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 3.99-3.88 (m, 6H, OCH₂), 1.84-1.78 (m, 1H, CH), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.34-1.22 (m, 32H, CH₂), 0.86 (t, ³J(H,H) = 6.9, 6H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(2-undecyltridecyloxy)biphenyl **45.15**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.23 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 100 mg (0.24 mmol) 12-(Brommethyl)tricosan **6.2**
 160 mg (1.16 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

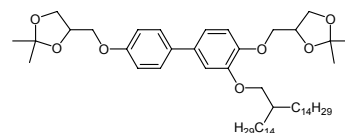
Ausbeute: 160 mg (91 % d. Th.), farbloses Öl

Analytik: C₄₈H₇₈O₇ M = 767.13 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 2.1, 2H, Ar-H), 7.03-7.00 (m, 2H, Ar-H), 6.94 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 2.1, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 3.99-3.88 (m, 6H, OCH₂), 1.84-1.77 (m, 1H, CH), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.33-1.21 (m, 40H, CH₂), 0.86 (t, ³J(H,H) = 6.9, 6H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(2-tetradecylhexadecyloxy)biphenyl **45.16**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 186 mg (0.37 mmol) 15-(Brommethyl)nonacosan **6.3**
 241 mg (1.75 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

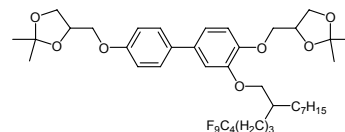
Ausbeute: 280 mg (94 % d. Th.), farbloses Öl

Analytik: C₄₈H₇₈O₇ M = 767.13 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.45 (d, ³J(H,H) = 8.7, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.96-6.94 (m, 3H, Ar-H), 4.48 (sext, ³J(H,H) = 6.0, 2H, OCH), 4.19-4.07 (m, 4H, OCH₂), 4.00-3.89 (m, 6H, OCH₂), 1.84-1.79 (m, 1H, CH), 1.47 (s, 3H, CH₃), 1.46 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.35-1.21 (m, 52H, CH₂), 0.87 (t, ³J(H,H) = 6.8, 6H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(6,6,7,7,8,8,9,9,9-nonafluor-2-heptylnonyloxy)biphenyl **45.17**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 226 mg (0.49 mmol) 8-(Brommethyl)-1,1,1,2,2,3,3,4,4-nonafluorpentadecan **10.1**
 318 mg (2.30 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 240 mg (64 % d. Th.), farblose Flüssigkeit

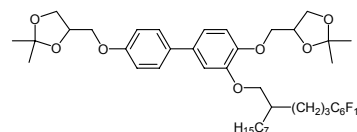
Analytik: C₄₀H₅₃F₉O₇ M = 816.83 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (dd, ³J(H,H) = 8.7, ⁴J(H,H) = 2.0, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.94 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 2.0, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 3.98-3.85 (m, 6H, OCH₂), 2.14-2.00 (m, 2H, CH₂CF₂), 1.88-1.82 (m, 1H, CH), 1.73-1.65 (m, 4H, CH₂, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.37 (s, 3H, CH₃), 1.31-1.24 (m, 12H, CH₂), 0.86 (t, ³J(H,H) = 7.3, 3H, CH₃).

¹⁹F-NMR (CD₃OD, J/Hz, 188 MHz): δ = -82.98 (t, ³J(F,F) = 9.9, 3F, CF₃), -115.72-(-115.87) (m, 2F, CH₂CF₂), -125.81 (s, 2F, CF₂), -127.50-(-127.61) (m, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluor-2-heptylundecyloxy)biphenyl **45.18**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.23 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 136 mg (0.24 mmol) 10-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorundecan **10.2**
 159 mg (1.15 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 190 mg (90 % d. Th.), farblose Flüssigkeit

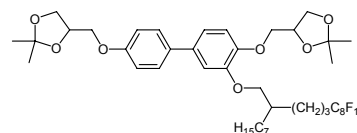
Analytik: $C_{42}H_{53}F_{13}O_7$ $M = 916.85$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.44$ (dd, $^3J(H,H) = 8.7$, $^4J(H,H) = 2.0$, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.94 (dd, $^3J(H,H) = 8.8$, $^4J(H,H) = 2.0$, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH_2), 3.98-3.85 (m, 6H, OCH_2), 2.14-2.00 (m, 2H, CH_2CF_2), 1.88-1.82 (m, 1H, CH), 1.73-1.65 (m, 4H, CH_2 , $CH_2CH_2CF_2$), 1.46 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.31-1.24 (m, 12H, CH_2), 0.86 (t, $^3J(H,H) = 7.3$, 3H, CH_3).

^{19}F -NMR ($CDCl_3$, J/Hz , 188 MHz): $\delta = -81.36$ (t, $^4J(F,F) = 9.7$, 3F, CF_3), -114.46-(-114.81) (m, 2F, CH_2CF_2), -122.25 (s, 2F, CF_2), -123.22 (s, 2F, CF_2), -123.89 (s, 2F, CF_2), -126.45 (m, 2F, CF_2CF_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,-13,13,13-heptafluor-2-heptyltridecyloxy)biphenyl **45.19**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.23 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

160 mg (0.24 mmol) 13-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptafluor-2-tridecan **10.3**

159 mg (1.15 mmol) K_2CO_3

50 ml DMF

5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie (Eluent: PE/ $CHCl_3$ 1:2, V/V)

Ausbeute: 190 mg (98 % d. Th.), farblose Flüssigkeit

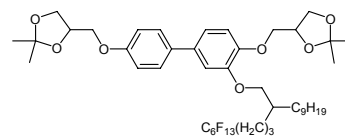
Analytik: $C_{44}H_{53}F_{17}O_7$ $M = 1016.86$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.44$ (dd, $^3J(H,H) = 8.9$, $^4J(H,H) = 2.1$, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.94 (dd, $^3J(H,H) = 8.8$, $^4J(H,H) = 2.1$, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH_2), 3.98-3.85 (m, 6H, OCH_2), 2.12-2.00 (m, 2H, CH_2CF_2), 1.88-1.82 (m, 1H, CH), 1.73-1.58 (m, 4H, CH_2 , $CH_2CH_2CF_2$), 1.46 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.30-1.24 (m, 12H, CH_2), 0.86 (t, $^3J(H,H) = 7.0$, 3H, CH_3).

^{19}F -NMR ($CDCl_3$, J/Hz , 188 MHz): $\delta = -81.31$ (t, $^4J(F,F) = 9.9$, 3F, CF_3), -114.59 (s, 2F, CH_2CF_2), -122.20 (s, 6F, CF_2), -123.03 (s, 2F, CF_2), -123.85 (s, 2F, CF_2), -126.40 (m, 2F, CF_2CF_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluor-2-nonylundecyloxy)biphenyl **45.20**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 160 mg (0.37 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 242 mg (0.41 mmol) 10-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluor-nonadecan **10.4**
 257 mg (1.86 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 283 mg (80 % d. Th.), farblose Flüssigkeit

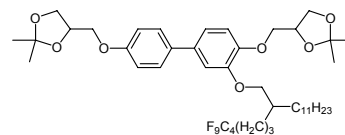
Analytik: C₄₄H₅₇F₁₃O₇ M = 944.90 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.7, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.8, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 3.98-3.85 (m, 6H, OCH₂), 2.14-2.00 (m, 2H, CH₂CF₂), 1.88-1.82 (m, 1H, CH), 1.73-1.58 (m, 4H, CH₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.37 (s, 3H, CH₃), 0.86 (t, ³J(H,H) = 6.8, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.30 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.47-(-114.64) (m, 2F, CH₂CF₂), 122.25 (s, 2F, CF₂), -123.11 (s, 2F, CF₂), -123.89 (s, 2F, CF₂), -126.49 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(6,6,7,7,8,8,9,9,9-nonafluor-2-undecylnonyloxy)biphenyl **45.21**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 300 mg (0.70 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 383 mg (0.73 mmol) 8-(Brommethyl)-1,1,1,2,2,3,3,4,4-nonafluoronadecan **10.5**
 483 mg (3.50 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 210 mg (35 % d. Th.), farblose Flüssigkeit

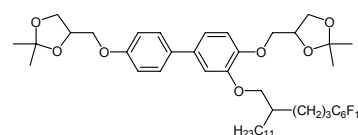
Analytik: C₄₄H₆₁F₉O₇ M = 872.94 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.44 (dd, ³*J*(H,H) = 8.8, ⁴*J*(H,H) = 2.1, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.94 (dd, ³*J*(H,H) = 8.8, ⁴*J*(H,H) = 2.1, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 3.98-3.85 (m, 6H, OCH₂), 2.13-2.00 (m, 2H, CH₂CF₂), 1.88-1.83 (m, 1H, CH), 1.72-1.58 (m, 2H, CH₂CH₂CF₂), 1.50-1.22 (m, 22H, CH₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 0.86 (t, ³*J*(H,H) = 6.8, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.62 (t, ⁴*J*(F,F) = 9.7, 3F, CF₃), -114.70-(-115.04) (m, 2F, CH₂CF₂), -124.83 (s, 2F, CF₂), -126.26-(-126.48) (m, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(6,6,7,7,8,8,9,9,10,10,11,11,11,11-tridecafluor-2-undecylundecyloxy)biphenyl **45.22**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.23 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 152 mg (0.24 mmol) 10-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorhenicosan **10.6**
 159 mg (1.15 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 150 mg (67 % d. Th.), farblose Flüssigkeit

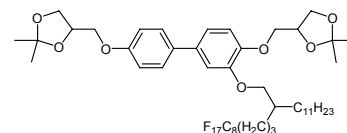
Analytik: C₄₆H₆₁F₁₃O₇ M = 972.95 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.44 (dd, ³*J*(H,H) = 8.6, ⁴*J*(H,H) = 2.1, 2H, Ar-H), 7.05-7.02 (m, 2H, Ar-H), 6.94 (dd, ³*J*(H,H) = 8.8, ⁴*J*(H,H) = 2.2, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 3.98-3.85 (m, 6H, OCH₂), 2.11-2.00 (m, 2H, CH₂CF₂), 1.87-1.84 (m, 1H, CH), 1.72-1.65 (m, 2H, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.37 (s, 3H, CH₃), 1.29-1.22 (m, 22H, CH₂), 0.86 (t, ³*J*(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.36 (t, ⁴*J*(F,F) = 9.9, 3F, CF₃), -114.63 (m, 2F, CH₂CF₂), -122.25 (s, 2F, CF₂), -123.22 (s, 2F, CF₂), -123.89 (s, 2F, CF₂), -126.43 (m, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(6,6,7,7,8,8,9,9,10,10,11,11,12,12,-13,13,13-heptadecafluor-2-undecyltridecyloxy)biphenyl **45.23**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 354 mg (0.49 mmol) 12-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluortricosan **10.7**
 318 mg (2.30 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 270 mg (55 % d. Th.), farblose Flüssigkeit

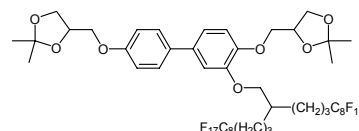
Analytik: C₄₈H₆₁F₁₇O₇ M = 1072.97 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.7, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.94 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 1.9, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 3.98-3.86 (m, 6H, OCH₂), 2.14-2.00 (m, 2H, CH₂CF₂), 1.88-1.83 (m, 1H, CH), 1.72-1.63 (m, 2H, CH₂CH₂CF₂), 1.51-1.19 (m, 22H, CH₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 0.86 (t, ³J(H,H) = 6.8, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.32 (t, ⁴J(F,F) = 9.8, 3F, CF₃), -114.70 (s, 2F, CH₂CF₂), -122.26 (s, 2F, CF₂), -123.10 (s, 6F, CF₂), -123.90 (s, 2F, CF₂), 126.48 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluor-2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorundecyl)tridecyloxy]-biphenyl **45.24**

Die Darstellung erfolgte nach der allgemeinen
 Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.23 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 247 mg (0.24 mmol) 12-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,-16,16,17,17,18,18,19,19,20,20,21,21,22,22,23,23-tetratriacontafluortricosan **20**
 160 mg (1.16 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 100 mg (32 % d. Th.), farbloser Feststoff

Analytik: C₄₈H₄₄F₃₄O₇ M = 1378.80 g/mol

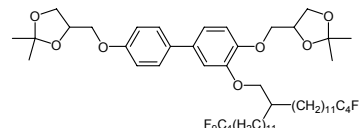
Fp.: 69-71 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.3, 2H, Ar-H), 7.09-7.03 (m, 2H, Ar-H), 6.95 (d, ³J(H,H) = 8.2, 3H, Ar-H), 4.47 (sext, ³J(H,H) = 5.7, 2H, OCH), 4.20-

4.05 (m, 4H, OCH₂), 4.01-3.86 (m, 6H, OCH₂), 2.19-1.88 (m, 5H, CH, CH₂CF₂), 1.77-1.54 (m, 8H, CH₂), 1.46 (s, 3H, CH₃), 1.43 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.37 (s, 3H, CH₃).
¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.23 (t, ⁴J(F,F) = 9.9, 6F, CF₃), -114.56-(-114.65) (m, 4F, CH₂CF₂), -122.28 (s, 12F, CF₂), -123.13 (s, 4F, CF₂), -123.91 (s, 4F, CF₂), -126.51 (s, 4F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[14,14,15,15,16,16,17,17,17-nonafluor-2-(12,12,13,13,14,14,15,15,15-nonafluorpentadecyl)heptadecyloxy]biphenyl **45.25**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 316 mg 16-(Brommethyl)-1,1,1,2,2,3,3,4,4,28,28,29,29,30,30,31,31,31-octadecafluorhentriacontan **14.1**
 241 mg (1.74 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 270 mg (64% d. Th.), farbloser Feststoff

Analytik: C₅₆H₇₆F₁₈O₇ M = 1203.17 g/mol

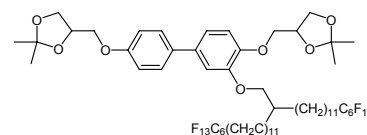
Fp.: 36-37 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 2.1, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.8, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 3.99-3.88 (m, 6H, OCH₂), 2.09-1.95 (m, 4H, CH₂CF₂), 1.83-1.78 (m, 1H, CH), 1.57 (quint., ³J(H,H) = 7.7, 4H, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.36-1.24 (m, 36H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.65 (t, ⁴J(F,F) = 9.7, 6F, CF₃), -114.93-(-115.09) (m, 4F, CH₂CF₂), -122.86 (s, 4F, CF₂), 126.30-(-126.51) (m, 4F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[14,14,15,15,16,16,17,17,18,18,-19,19,19-tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorheptadecyl)-nonadecyloxy]biphenyl **45.26**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 390 mg (0.37 mmol) 18-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,30,30,31,31,-

32,32,33,33,34,34,35,35,35-hexacosafuorpentatriacontan **14.2**241 mg (1.74 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 310 mg (63 % d. Th.), farbloser Feststoff

Analytik: C₆₀H₇₆F₂₆O₇ M = 1403.20 g/mol

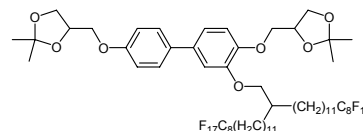
Fp.: 48-50 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.7, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.8, 3H, Ar-H), 4.49-4.44 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 3.99-3.88 (m, 6H, OCH₂), 2.09-1.95 (m, 4H, CH₂CF₂), 1.83-1.79 (m, 1H, CH), 1.59-1.51 (m, 4H, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.34-1.23 (m, 36H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.38 (t, ⁴J(F,F) = 9.7, 6F, CF₃), -114.77 (s, 4F, CH₂CF₂), -122.30 (s, 4F, CF₂), -123.22 (s, 4F, CF₂), -123.93 (s, 4F, CF₂), -126.47 (s, 4F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[14,14,15,15,16,16,17,17,18,18,19,19,20,20,21,21,21-heptadecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluorononadecyl)henicosyloxy]biphenyl **45.27**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.23 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

306 mg (0.24 mmol) 20-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,-32,32,33,33,34,34,35,35,36,36,37,37,38,38,39,39,39-tetraatriacontafuor-nonatriacontan **14.3**

160 mg (1.16 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 290 mg (79 % d. Th.), farbloser Feststoff

Analytik: C₆₄H₇₆F₃₄O₇ M = 1603.23 g/mol

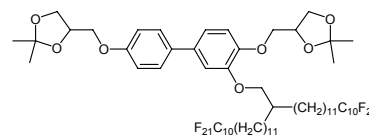
Fp.: 60-62 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (dd, ³J(H,H) = 8.9, ⁴J(H,H) = 2.1, 2H, Ar-H), 7.03-7.00 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.8, 3H, Ar-H), 4.51-4.44 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 3.99-3.88 (m, 6H, OCH₂), 2.09-1.95 (m, 4H, CH₂CF₂), 1.82-1.79 (m, 1H, CH), 1.61-1.51 (m, 4H, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.34-1.24 (m, 36H, CH₂).

^{19}F -NMR (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.35$ (t, $^4J(\text{F},\text{F}) = 9.9$, 6F, CF_3), -114.74 (s, 4F, CH_2CF_2), -122.23 (s, 12F, CF_2), -123.08 (s, 4F, CF_2), -123.88 (s, 4F, CF_2), -126.43 (s, 4F, CF_2CF_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[14,14,15,15,16,16,17,17,18,18,19,19,-20,20,21,21,22,22,23,23-henicosafuor-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,-19,19,20,20,21,21,21-henicosafuorhenicosyl)tricosyloxy]biphenyl **45.28**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.23 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 349 mg (0.24 mmol) 22-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,-9,9,10,10,34,34,35,35,36,36,37,37,38,38,39,39,40,40,41,41,42,42,43,43,43-dotetracontafluortritetracontan **14.4**
 160 mg (1.16 mmol) K_2CO_3
 50 ml DMF
 5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie (Eluent: PE/ CHCl_3 1:2, V/V)

Ausbeute: 230 mg (55 % d. Th.), farbloser Feststoff

Analytik: $\text{C}_{68}\text{H}_{76}\text{F}_{42}\text{O}_7$ M = 1803.26 g/mol

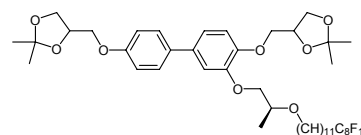
Fp.: 88-90 °C

^1H -NMR (CDCl_3 , J/Hz , 400 MHz): $\delta = 7.44$ (dd, $^3J(\text{H},\text{H}) = 8.8$, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 6.95 (d, $^3J(\text{H},\text{H}) = 8.8$, 3H, Ar-H), 4.51-4.44 (m, 2H, OCH), 4.19-4.06 (m, 4H, OCH_2), 4.00-3.89 (m, 6H, OCH_2), 2.09-1.96 (m, 4H, CH_2CF_2), 1.85-1.79 (m, 1H, CH), 1.57 (quint, $^3J(\text{H},\text{H}) = 7.7$, 4H, $\text{CH}_2\text{CH}_2\text{CF}_2$), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.35-1.24 (m, 36H, CH_2).

^{19}F -NMR (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.43$ (t, $^4J(\text{F},\text{F}) = 9.7$, 6F, CF_3), -114.82 (s, 4F, CH_2CF_2), -122.18 (s, 20F, CF_2), -123.10 (s, 4F, CF_2), -123.94 (s, 4F, CF_2), -126.51 (s, 4F, CF_2CF_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[(2R)-2-(12,12,13,13,14,14,15,15,-16,16,17,17,18,18,19,19,19-hepta-decafluoronadecyloxy)propyloxy]biphenyl **45.29**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 393 mg (0.49 mmol) (2R)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,-

19,19,19-Heptadecafluoronadecyloxy)propyl-1-tosylat **23**318 mg (2.30 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 350 mg (72 % d. Th.), farbloser Feststoff

Analytik: C₄₆H₅₇F₁₇O₈ M = 1060.91 g/mol

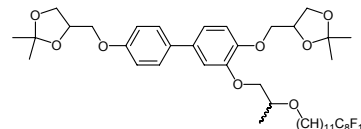
Fp.: 67-69 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.43 (dd, ³J(H,H) = 8.9, ⁴J(H,H) = 2.2, 2H, Ar-H), 7.06-7.03 (m, 2H, Ar-H), 6.94 (dd, ³J(H,H) = 8.8, ⁴J(H,H) = 2.1, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.18-4.04 (m, 5H, OCH₂), 3.99-3.87 (m, 5H, OCH₂), 3.81 (t, ³J(H,H) = 6.0, 1H, CHCH₃), 3.55 (q, ³J(H,H) = 6.7, 2H, OCH₂), 2.09-1.95 (m, 2H, CH₂CF₂), 1.60-1.52 (m, 4H, OCH₂CH₂, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.38 (s, 3H, CH₃) 1.36-1.24 (m, 17H, CH₂, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.32 (t, ⁴J(F,F) = 9.7, 3F, CF₃), -114.72 (s, 2F, CH₂CF₂), -122.20 (s, 6F, CF₂), -123.04 (s, 2F, CF₂), -123.85 (s, 2F, CF₂), -126.41 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluoronadecyloxy)propyloxy]biphenyl **45.30**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.23 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-
biphenyl-3-ol **36.1**

197 mg (0.24 mmol) (2R)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,-
19,19,19-Heptadecafluor-nonadecyloxy)propyl-1-tosylat **rac-23**

159 mg (1.15 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 230 mg (94 % d. Th.), farbloser Feststoff

Analytik: C₄₆H₅₇F₁₇O₈ M = 1060.91 g/mol

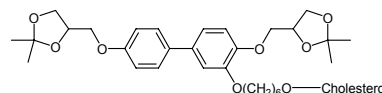
Fp.: 53-55 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.43 (dd, ³J(H,H) = 8.9, ⁴J(H,H) = 2.1, 2H, Ar-H), 7.07-7.03 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.6, 3H, Ar-H), 4.51-4.43 (m, 2H, OCH), 4.18-4.04 (m, 5H, OCH₂), 4.00-3.79 (m, 5H, OCH₂), 3.58-3.51 (m, 3H, OCH₂, CHCH₃), 2.07-1.96 (m, 2H, CH₂CF₂), 1.59-1.54 (m, 4H, OCH₂CH₂, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃) 1.36-1.23 (m, 14H, CH₂), 1.09 (d, ³J(H,H) = 6.1, 3H, CH₃).

^{19}F -NMR (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.32$ (t, $^4J(\text{F},\text{F}) = 9.9$, 3F, CF_3), -114.71 (s, 2F, CH_2CF_2), -122.18 (s, 6F, CF_2), -123.04 (s, 2F, CF_2) -123.85 (s, 2F, CF_2), -126.40 (s, 2F, CF_2CF_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[6-(cholesteryloxy)hexyloxy]biphenyl **45.31**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 170 mg (0.39 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 228 mg (0.41 mmol) 6-Brom-1-(cholest-5-en-3 β -oxy)hexan **25.1**
 272 mg (1.97 mmol) K_2CO_3
 50 ml DMF
 5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/ CHCl_3 1:2, V/V)

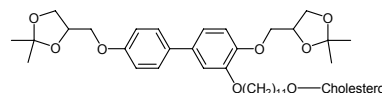
Ausbeute: 320 mg (91% d. Th.), farbloses Öl

Analytik: $\text{C}_{57}\text{H}_{86}\text{O}_8$ $M = 899.29$ g/mol

^1H -NMR (CDCl_3 , J/Hz , 400 MHz): $\delta = 7.43$ (d, $^3J(\text{H},\text{H}) = 8.9$, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 6.94 (d, $^3J(\text{H},\text{H}) = 8.8$, 3H, Ar-H), 5.32-5.31 (m, 1H, CH=C), 4.51-4.44 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH_2), 4.03-3.88 (m, 6H, OCH_2), 3.44 (t, $^3J(\text{H},\text{H}) = 6.6$, 2H, OCH_2), 3.14-3.06 (m, 1H, OCH), 2.36-2.31 (m, 1H, CH), 2.20-2.13 (m, 1H, CH), 2.01-1.91 (m, 2H, CH_2), 1.89-1.76 (m, 5H, CH, CH_2), 1.61-0.98 (m, 41H, CH, CH_2 , CH_3), 0.90 (d, $^3J(\text{H},\text{H}) = 6.5$, 4H, CH, CH_3), 0.85 (dd, $^3J(\text{H},\text{H}) = 6.6$, $^4J(\text{H},\text{H}) = 1.7$, 6H, CH_3), 0.66 (s, 3H, CH_3).

4,4'-Bis-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[11-(cholesteryloxy)undecyloxy]-biphenyl **45.32**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 186 mg (0.43 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 281 mg (0.45 mmol) 11-Brom-1-(cholest-5-en-3 β -oxy)undecan **25.2**
 300 mg (2.15 mmol) K_2CO_3
 50 ml DMF
 5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/ CHCl_3 1:2, V/V)

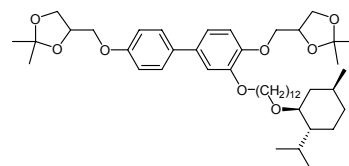
Ausbeute: 260 mg (62 % d. Th.), farblose Flüssigkeit

Analytik: $\text{C}_{62}\text{H}_{96}\text{O}_8$ $M = 969.42$ g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.43 (d, ³*J*(H,H) = 8.9, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 6.94 (d, ³*J*(H,H) = 8.9, 3H, Ar-H), 5.33-5.31 (m, 1H, CH=C), 4.51-4.44 (m, 2H, OCH), 4.18-3.88 (m, 10H, OCH₂), 3.42 (t, ³*J*(H,H) = 6.8, 2H, OCH₂), 3.14-3.06 (m, 1H, OCH), 2.36-2.31 (m, 2H, CH₂), 2.01-1.77 (m., 8H, CH₂), 1.55-1.22 (m, 42H, CH,CH₂), 1.14-0.98 (m, 14H, CH, CH₂, CH₃), 0.90 (d, ³*J*(H,H) = 6.5, 4H, CH), 0.85 (dd, ³*J*(H,H) = 6.5, ⁴*J*(H,H) = 1.7, 6H, CH), 0.66 (s, 3H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[(12-menthyloxy)dodecyloxy]biphenyl **45.33**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 197 mg (0.49 mmol) (1*R*,2*S*,4*S*)-2-(4-Bromdodecyloxy)-1-isopropyl-4-methylcyclohexan **26**
 318 mg (2.30 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 260 mg (75 % d. Th.), farblose Flüssigkeit

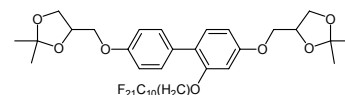
Analytik: C₄₆H₇₂O₈ M = 753.06 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.43 (d, ³*J*(H,H) = 8.7, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 6.94 (d, ³*J*(H,H) = 8.6, 3H, Ar-H), 4.47 (quint, ³*J*(H,H) = 5.9, 2H, OCH), 4.18-4.05 (m, 4H, OCH₂), 4.03-3.88 (m, 6H, OCH₂), 3.61-3.20 (m, 1H, OCH₂), 2.96 (dt, 1H, ³*J*(H,H) = 10.5, ⁴*J*(H,H) = 4.1, OCH), 2.24-2.16 (m, 1H, CH), 2.09-2.04 (m, 1H, CH), 1.80 (quint, ³*J*(H,H) = 7.1, 2H, CH₂CH₂O), 1.69-1.50 (m, 5H, CH, CH₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.35-1.25 (m, 15H, CH, CH₂), 0.89 (d, ³*J*(H,H) = 6.6, 3H, CH₃), 0.87 (d, ³*J*(H,H) = 7.1, 3H, CH₃), 0.74 (d, ³*J*(H,H) = 7.0, 3H, CH₃).

A.46 Synthese der in 2-Position substituierten Biphenylderivate **46.X**

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-henicosafuorhexadecyloxy)biphenyl **46.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 200 mg (0.46 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-2-ol **36.2**

335 mg (0.49 mmol) 16-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosfluorhexadecan **2.2**

320 mg (2.32 mmol) K_2CO_3

50 ml DMF

5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/ $CHCl_3$ 1:2, V/V)

Ausbeute: 400 mg (84 % d. Th.), farbloser Feststoff

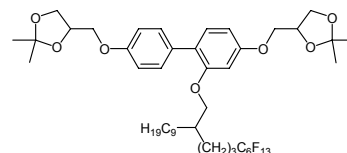
Analytik: $C_{40}H_{41}F_{21}O_7$ $M = 1032.72$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.39$ (d, $^3J(H,H) = 8.9$, 2H, Ar-H), 7.18 (d, $^3J(H,H) = 8.2$, 1H, Ar-H), 6.90 (d, $^3J(H,H) = 8.9$, 2H, Ar-H), 6.54-6.51 (m, 3H, Ar-H), 4.51-4.44 (m, 2H, OCH), 4.18-4.14 (m, 2H, OCH_2), 4.09-4.05 (m, 2H, OCH_2), 3.97-3.87 (m, 6H, OCH_2), 2.07-1.94 (m, 2H, CH_2CF_2), 1.71 (quint, $^3J(H,H) = 6.8$, 2H, OCH_2CH_2), 1.60-1.52 (m, 2H, $CH_2CH_2CF_2$), 1.56-1.48 (m, 4H, CH_2), 1.46 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.39 (s, 3H, CH_3).

^{19}F -NMR ($CDCl_3$, J/Hz , 188 MHz): $\delta = -81.32$ (t, $^4J(F,F) = 9.7$, 3F, CF_3), -114.69 (s, 2F, CH_2CF_2), -122.08 (s, 10F, $CH_2CF_2(CF_2)_5$), -122.99 (s, 2F, $CF_2CF_2CF_2CF_3$), -123.78 (s, 2F, $CF_2CF_2CF_3$), -126.39 (s, 2F, CF_2CF_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2-(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluor-2-nonylundecyloxy)biphenyl **46.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-2-ol **36.2**

218 mg (0.37 mmol) 10-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluor-nonadecan **10.4**

242 mg (1.75 mmol) K_2CO_3

50 ml DMF

5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/ $CHCl_3$ 1:2, V/V)

Ausbeute: 260 mg (79 % d. Th.), farblose Flüssigkeit

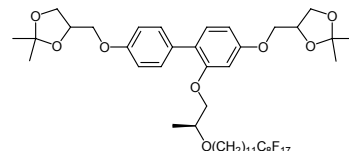
Analytik: $C_{44}H_{57}F_{13}O_7$ $M = 944.90$ g/mol

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.36$ (d, $^3J(H,H) = 8.8$, 2H, Ar-H), 7.18 (d, $^3J(H,H) = 8.2$, 1H, Ar-H), 6.89 (d, $^3J(H,H) = 8.9$, 2H, Ar-H), 6.55-6.51 (m, 2H, Ar-H), 4.51-4.44 (m, 2H, OCH), 4.19-4.14 (m, 2H, OCH_2), 4.09-4.05 (m, 2H, OCH_2), 3.97-3.88 (m, 4H, OCH_2), 3.85-3.75 (m, 2H, OCH_2), 2.00-1.86 (m, 2H, CH_2CF_2), 1.74-1.68 (m., 1H, OCH), 1.52 (quint, $^3J(H,H) = 7.9$, 2H, $CH_2CH_2CF_2$), 1.47 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.40 (s, 6H, CH_3), 1.34-1.21 (m, 18H, CH_2), 0.87 (t, $^3J(H,H) = 6.9$, 3H, CH_3).

$^{19}\text{F-NMR}$ (CDCl_3 , J/Hz , 188 MHz) $\delta = -81.39$ (t, $^4J(\text{F},\text{F}) = 9.5$, 3F, CF_3), -114.57 - (-114.83) (m, 2F, CH_2CF_2), -122.27 (s, 2F, CF_2), -123.23 (s, 2F, CF_2) -123.88 (s, 2F, CF_2), -126.40 - (-126.52) (m, 2F, CF_2CF_3).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2-[(2*R*)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-hepta-decafluoronadecyloxy)propyloxy]biphenyl **46.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.35 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-2-ol **36.2**
 297 mg (0.37 mmol) (2*R*)-2-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-Hepta-decafluoronadecyloxy)propyl-1-tosylat **23**
 242 mg (1.75 mmol) K_2CO_3
 50 ml DMF
 5 mg Bu_4NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/ CHCl_3 1:2, V/V)

Ausbeute: 230 mg (62 % d. Th.), farblose Flüssigkeit

Analytik: $\text{C}_{46}\text{H}_{57}\text{F}_{17}\text{O}_8$ $M = 1060.91$ g/mol

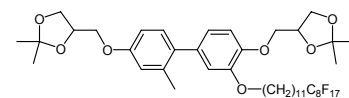
$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 7.42$ (d, $^3J(\text{H},\text{H}) = 8.8$, 2H, Ar-H), 7.18 (d, $^3J(\text{H},\text{H}) = 8.2$, 1H, Ar-H), 6.89 (d, $^3J(\text{H},\text{H}) = 8.9$, 2H, Ar-H), 6.54-6.51 (m, 2H, Ar-H), 4.48 (quint, $^3J(\text{H},\text{H}) = 6.0$, 2H, OCH), 4.17 (d, $^3J(\text{H},\text{H}) = 6.4$, 1H, OCH₂), 4.15 (d, $^3J(\text{H},\text{H}) = 6.4$, 1H, OCH₂), 4.09-4.04 (m, 2H, OCH₂), 3.96-3.87 (m, 5H, OCH₂), 3.78-3.66 (m, 2H, OCH₂), 3.47-3.37 (m, 2H, OCH₂), 2.09-1.96 (m, 2H, CH_2CF_2), 1.61-1.48 (m., 4H, $\text{CH}_2\text{CH}_2\text{CF}_2$, OCH₂ CH_2), 1.46 (s, 6H, CH_3), 1.40 (s, 6H, CH_3), 1.37-1.24 (m, 14H, CH_2), 1.16 (t, $^3J(\text{H},\text{H}) = 6.3$, 3H, CH_3).

$^{19}\text{F-NMR}$ (CDCl_3 , J/Hz , 188 MHz): $\delta = -81.36$ (t, $^4J(\text{F},\text{F}) = 9.9$, 3F, CF_3), -114.72 (s, 2F, CH_2CF_2), -122.22 (s, 6F, CF_2), -123.05 (s, 2F, CF_2) -123.87 (s, 2F, CF_2), -126.43 (s, 2F, CF_2CF_3).

A.47 Synthese der Biphenylderivate 47.X

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-hepta-decafluoronadecyloxy)-2'-methylbiphenyl **47.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.34 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methylbiphenyl-3-ol **36.3**

233 mg (0.36 mmol) 19-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoronadecan **2.6**

235 mg (1.70 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 280 mg (81 % d. Th.), farbloses Öl

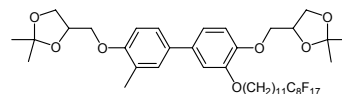
Analytik: C₄₄H₅₃F₁₇O₇ M = 1016.86 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.11 (d, ³J(H,H) = 8.4, 1H, Ar-H), 6.92 (d, ³J(H,H) = 8.0, 1H, Ar-H), 6.80-6.74 (m, 4H, Ar-H), 4.52-4.44 (m, 2H, OCH), 4.18-4.05 (m, 4H, OCH₂), 4.02-3.88 (m, 6H, OCH₂), 2.22 (s, 3H, PhCH₃), 2.10-1.96 (m, 2H, CH₂CF₂), 1.78 (quint, ³J(H,H) = 7.1, 2H, OCH₂CH₂), 1.62-1.54 (m, 2H, CH₂CH₂CF₂), 1.46 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 1.36-1.26 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.14 (t, ⁴J(F,F) = 9.8, 3F, CF₃), -114.72-(114.79) (m, 2F, CH₂CF₂), -122.15 (s, 2F, CF₂), -122.33 (s, 4F, CF₂), -123.12 (s, 2F, CF₂), -123.93 (s, 2F, CF₂), -126.51 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,19-heptadecafluoronadecyloxy)-3'-methylbiphenyl **47.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.34 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methylbiphenyl-3-ol **36.4**

233 mg (0.36 mmol) 19-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoronadecan **2.6**

235 mg (1.70 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 320 mg (93 % d. Th.), farbloser Feststoff

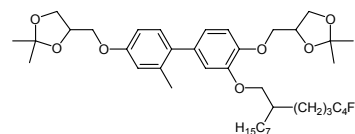
Analytik: C₄₄H₅₃F₁₇O₇ M = 1016.86 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.30-7.28 (m, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.7, 1H, Ar-H), 6.85 (d, ³J(H,H) = 8.9, 1H, Ar-H), 4.51-4.45 (m, 2H, OCH), 4.19-4.09 (m, 4H, OCH₂), 4.04-3.95 (m, 6H, OCH₂), 2.27 (s, 3H, PhCH₃), 2.10-1.97 (m, 2H, CH₂CF₂), 1.81 (quint, ³J(H,H) = 7.0, 2H, OCH₂CH₂), 1.62-1.53 (m, 2H, CH₂CH₂CF₂), 1.47 (s, 3H, CH₃), 1.46 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.35-1.29 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.39 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.75 (s, 2F, CH₂CF₂), -122.23 (s, 6F, CF₂), -123.08 (s, 2F, CF₂), -123.89 (s, 2F, CF₂), -126.45 (s, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methyl-3-(6,6,7,7,8,8,9,9,9-nonafluor-2-heptyltri-decyloxy)biphenyl **47.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.34 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methylbiphenyl-3-ol **36.3**
167 mg (0.36 mmol) 8-(Brommethyl)-1,1,1,2,2,3,3,4,4-nonafluor-pentadecan **10.1**

235 mg (1.70 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 160 mg (57 % d. Th.), farbloses Öl

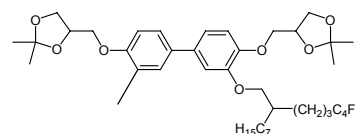
Analytik: C₄₁H₅₅F₉O₇ M = 830.86 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.11 (d, ³J(H,H) = 8.3, 1H, Ar-H), 6.91 (d, ³J(H,H) = 8.7, 1H, Ar-H), 6.81-6.74 (m, 4H, Ar-H), 4.50-4.44 (m, 2H, OCH), 4.18-4.05 (m, 4H, OCH₂), 4.00-3.78 (m, 6H, OCH₂), 2.22 (s, 3H, PhCH₃), 2.12-1.99 (m, 2H, CH₂CF₂), 1.86-1.80 (m, 1H, CH), 1.71-1.63 (m, 2H, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.35-1.24 (m, 14H, CH₂), 0.86 (t, ³J(H,H) = 6.8, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.44 (t, ⁴J(F,F) = 9.4, 3F, CF₃), -114.87-(-114.93) (m, 2F, CH₂CF₂), -124.93 (s, 2F, CF₂), -126.45-(-126.49) (m, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methyl-3-(6,6,7,7,8,8,9,9,9-nonafluor-2-heptyltri-decyloxy)biphenyl **47.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.34 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methylbiphenyl-3-ol **36.4**
167 mg (0.36 mmol) 8-(Brommethyl)-1,1,1,2,2,3,3,4,4-nonafluor-pentadecan **10.1**

235 mg (1.70 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 230 mg (81 % d. Th.), farblose Flüssigkeit

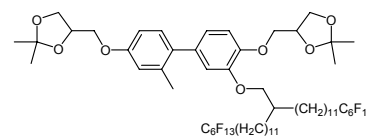
Analytik: C₄₁H₅₅F₉O₇ M = 830.86 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.31-7.28 (m, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.94 (d, ³*J*(H,H) = 8.0, 1H, Ar-H), 6.85 (d, ³*J*(H,H) = 9.1, 1H, Ar-H), 4.52-4.43 (m, 2H, OCH), 4.19-4.09 (m, 4H, OCH₂), 3.99-3.87 (m, 6H, OCH₂), 2.27 (s, 3H, PhCH₃), 2.14-2.01 (m, 2H, CH₂CF₂), 1.86 (quint, ³*J*(H,H) = 5.8, 2H, CH), 1.73-1.66 (m, 2H, CH₂CH₂CF₂), 1.47 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.41 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.37-1.26 (m, 14H, CH₂). 0.87 (t, ³*J*(H,H) = 6.9, 3H, CH₃).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.46 (t, ⁴*J*(F,F) = 9.4, 3F, CF₃), -114.86-(-114.92) (m, 2F, CH₂CF₂), -124.91 (s, 2F, CF₂), -126.91-(-126.50) (m, 2F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methyl-3-[14,14,15,15,16,16,17,17,-18,18,19,19,19-tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorheptadecyl)nonadecyloxy]biphenyl **47.5**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.22 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-2'-methylbiphenyl-3-ol **36.3**

249 mg 18-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,30,30,31,31,32,32,33,33,-34,34,35,35,35-hexacosafuorpentatriacontan **14.2**

155 mg (1.12 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 190 mg (61 % d. Th.), farbloses Öl

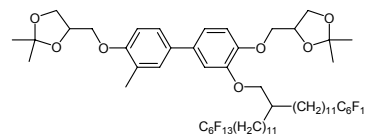
Analytik: C₆₁H₇₈F₂₆O₇ M = 1417.23 g/mol

¹H-NMR (CDCl₃, *J*/Hz, 400 MHz): δ = 7.12 (d, ³*J*(H,H) = 8.3, 1H, Ar-H), 6.91 (d, ³*J*(H,H) = 8.1, 1H, Ar-H), 6.81-6.75 (m, 4H, Ar-H), 4.48 (quint, ³*J*(H,H) = 5.9, 2H, OCH), 4.18-4.09 (m, 4H, OCH₂), 4.02-3.88 (m, 4H, OCH₂), 3.82 (d, ³*J*(H,H) = 5.6, 2H, OCH₂), 2.31 (s, 3H, PhCH₃), 2.10-1.96 (m, 4H, CH₂CF₂), 1.82-1.78 (m, 2H, CH), 1.58 (quint, ³*J*(H,H) = 7.7, 4H, CH₂CH₂CF₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.37-1.26 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, *J*/Hz, 188 MHz): δ = -81.27 (t, ⁴*J*(F,F) = 9.2, 6F, CF₃), -114.72-(-114.87) (m, 4F, CH₂CF₂), -122.37 (s, 4F, CF₂), -123.33 (s, 4F, CF₂), -124.00 (s, 4F, CF₂), -126.57 (s, 4F, CF₂CF₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methyl-3-[14,14,15,15,16,16,17,17,-18,18,19,19,19-tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluorheptadecyl)nonadecyloxy]biphenyl **47.6**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.22 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3'-methylbiphenyl-3-ol **36.4**
 249 mg 18-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,30,30,31,31,32,32,33,33,-34,34,35,35,35-hexacosafuorpentatriacontan **14.2**
 155 mg (1.12 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 180 mg (58 % d. Th.), farbloses Öl

Analytik: C₆₁H₇₈F₂₆O₇ M = 1417.23 g/mol

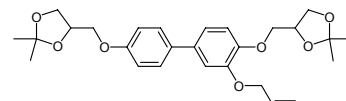
¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.31-7.28 (m, 2H, Ar-H), 7.03-7.00 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.9, 1H, Ar-H), 6.85 (d, ³J(H,H) = 9.1, 1H, Ar-H), 4.51-4.54 (m, 2H, OCH), 4.19-4.09 (m, 4H, OCH₂), 4.00-3.94 (m, 4H, OCH₂), 3.89 (d, ³J(H,H) = 5.8, 2H, OCH₂), 2.27 (s, 3H, PhCH₃), 2.15-1.96 (m, 4H, CH₂CF₂), 1.81-1.80 (m, 2H, CH), 1.57 (quint, ³J(H,H) = 7.6, 4H, CH₂CH₂CF₂), 1.47 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.35-1.26 (m, 14H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.27 (t, ⁴J(F,F) = 9.2, 6F, CF₃), -114.63-(-114.96) (m, 4F, CH₂CF₂), -122.37 (s, 4F, CF₂), -123.29-(-123.32) (m, 4F, CF₂), -124.00 (s, 4F, CF₂), -126.47-(-126.62) (m, 4F, CF₂CF₃).

A.48 Synthese von 3-(Allkenyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl **48.X**

3-(Allyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **48.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 300 mg (0.70 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**
 88.3 mg (0.73 mmol) Allylbromid
 482 mg (3.48 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: PE/CHCl₃ 1:2, V/V)

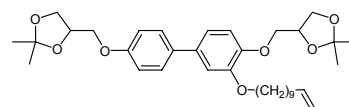
Ausbeute: 220 mg (67 % d. Th.), farbloses Öl

Analytik: C₂₇H₃₄O₇ M = 470.55 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.43 (d, ³J(H,H) = 8.8, 2H, Ar-H), 7.06-7.04 (m, 2H, Ar-H), 6.95 (d, ³J(H,H) = 8.8, 1H, Ar-H), 6.94 (d, ³J(H,H) = 8.8, 2H, Ar-H), 6.12-6.02 (m, 1H CH=CH₂) 5.44-5.39 (m, 1H, CH₂=CH), 5.29-5.25 (m, 1H, CH₂=CH), 4.48 (td, ³J(H,H) = 5.3, ⁴J(H,H) = 1.5, 2H, CH₂CH=CH₂), 4.48 (quint, ³J(H,H) = 7.5, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 4.01-3.88 (m, 4H, OCH₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃).

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(undec-10-en-1-yloxy)biphenyl **48.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 300 mg (0.70 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**

172 mg (0.73 mmol) 11-Bromundec-1-en

482 mg (3.48 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie (Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 220 mg (54 % d. Th.), farblose Flüssigkeit

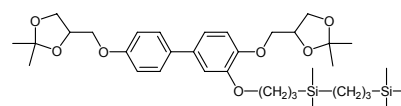
Analytik: C₃₅H₅₀O₇ M = 582.77 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.44 (d, ³J(H,H) = 8.8, 2H, Ar-H), 7.04-7.01 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.5, 3H, Ar-H), 5.85-5.74 (m, 1H CH=CH₂) 5.00-4.89 (m, 2H, CH₂=CH), 4.48 (quint, ³J(H,H) = 5.9, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 4.03-3.88 (m, 6H, OCH₂), 2.03 (q, ³J(H,H) = 7.1, 2H, CH₂CH=CH₂), 1.81 (quint, ³J(H,H) = 7.1, 2H, OCH₂CH₂), 1.48-1.44 (m, 8H, CH₃, CH₂), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.38-1.27 (m, 10H, CH₂).

A.49 Synthese der Biphenylderivate mit Carbosilansubstituenten **49.X**

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8-tetramethyl-4,8-disilanonyloxy)biphenyl **49.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.17.



Ansatz: 350 mg (0.74 mmol) 3-(Allyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **48.1**

259 mg (1.49 mmol) 1,1,5,5-Tetramethyl-1,5-disilahexan

20 ml Toluol

1 Tropfen Karstedt's-Katalysator in Xylol

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 400 mg (84 % d. Th.), farblose Flüssigkeit

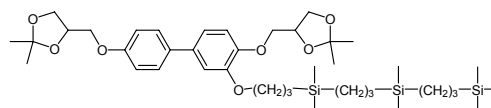
Analytik: C₃₅H₅₆O₇Si₂ M = 644.99 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz) δ = 7.44 (d, ³J(H,H) = 8.8, 2H, Ar-H), 7.05-7.02 (m, 2H, Ar-H), 6.95 (d, ³J(H,H) = 8.9, 3H, Ar-H), 4.51-4.55 (m, 2H, OCH), 4.17-4.06 (m, 4H, OCH₂), 4.00-3.88 (m, 6H, OCH₂), 1.85-1.78 (m, 2H, OCH₂CH₂), 1.46 (s, 6H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.37-1.31 (m, 2H, CH₂), 0.62-0.54 (m, 6H, SiCH₂), 0.00 (s, 6H, SiCH₃), -0.03 (s, 9H, SiCH₃).

²⁹Si-NMR (CDCl₃, J/Hz, 100 MHz): δ = 2.29, 0.57.

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8,12,12-hexamethyl-4,8,12-trisilatrityloxy)biphenyl **49.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.17.



Ansatz: 350 mg (0.74 mmol) 3-(Allyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **48.1**

409 mg (1.49 mmol) 1,1,5,5,9,9-Hexamethyl-1,5,9-trisiladecan

20 ml Toluol

1 Tropfen Karstedt's-Katalysator in Xylol

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 420 mg (76 % d. Th.), farblose Flüssigkeit

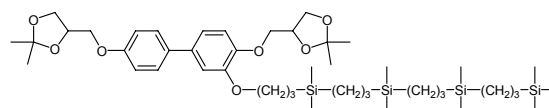
Analytik: C₄₀H₆₈O₇Si₃ M = 745.22 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.6, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.95 (d, ³J(H,H) = 8.7, 3H, Ar-H), 4.52-4.55 (m, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 4.01-3.89 (m, 6H, OCH₂), 1.85-1.77 (m, 2H, OCH₂CH₂), 1.46 (s, 6H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.36-1.28 (m, 4H, CH₂), 0.62-0.52 (m, 10H, SiCH₂), -0.01 (s, 6H, SiCH₃), -0.04 (s, 9H, SiCH₃), -0.06 (s, 6H, SiCH₃).

²⁹Si-NMR (CDCl₃, J/Hz, 100 MHz): δ = 2.29, 0.99, 0.57.

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(4,4,8,8,12,12,16,16-octamethyl-4,8,12,16-tetrasilheptadecyloxy)biphenyl **49.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.17.



Ansatz: 220 mg (0.47 mmol) 3-(Allyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **48.1**

351 mg (0.94 mmol) 1,1,5,5,9,9,13,13-Octamethyl-1,5,9,13-tetrasilatetradecan

20 ml Toluol

1 Tropfen Karstedt's-Katalysator in Xylol

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 240 mg (60 % d. Th.), farblose Flüssigkeit

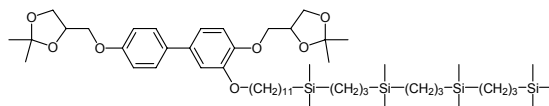
Analytik: C₄₅H₈₀O₇Si₄ M = 845.45 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.8, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.8, 3H, Ar-H), 4.48 (quint, ³J(H,H) = 5.8, 2H, OCH), 4.18-4.06 (m, 4H, OCH₂), 4.00-3.88 (m, 6H, OCH₂), 1.85-1.77 (m, 2H, OCH₂CH₂), 1.46 (s, 6H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.37-1.27 (m, 6H, CH₂), 0.62-0.51 (m, 14H, SiCH₂), 0.00-(-0.01) (m, 6H, SiCH₃), -0.04 (s, 9H, SiCH₃), -0.06-(-0.07) (m, 12H, SiCH₃).

²⁹Si-NMR (CDCl₃, J/Hz, 100 MHz): δ = 2.29, 0.98, 0.57.

4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(12,12,16,16,20,20,24,24-octamethyl-12,16,20,24-tetrasilapentacosyloxy)biphenyl **49.4**

Die Darstellung erfolgte nach der
allgemeinen Arbeitsvorschrift 5.3.17.



Ansatz: 230 mg (0.39 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(undec-10-en-1-yloxy)biphenyl **48.2**

296 mg (0.79 mmol) 1,1,5,5,9,9,13,13-Octamethyl-1,5,9,13-tetrasilatetradecan

20 ml Toluol

1 Tropfen Karstedt's-Katalysator in Xylol

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 230 mg (62 % d. Th.), farblose Flüssigkeit

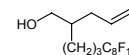
Analytik: C₅₃H₉₆O₇Si₄ M = 957.67 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.9, 2H, Ar-H), 7.04-7.02 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.9, 3H, Ar-H), 4.48 (quint, ³J(H,H) = 6.0, 2H, OCH), 4.18-4.07 (m, 4H, OCH₂), 4.03-3.89 (m, 6H, OCH₂), 1.81 (quint, ³J(H,H) = 7.1, 2H, OCH₂CH₂), 1.46 (s, 3H, CH₃), 1.45 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.39 (s, 3H, CH₃), 1.35-1.26 (m, 16H, CH₂), 0.55-0.52 (m, 12H, SiCH₂), 0.47-0.44 (m, 2H, SiCH₂), -0.04 (s, 9H, Si(CH₃)₃), -0.07 (s, 18H, Si(CH₃)₂).

²⁹Si-NMR (CDCl₃, J/Hz, 100 MHz): δ = 2.29, 0.98, 0.57.

A.50 Synthese von 2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluorundecyl)-pent-4-en-1-ol **50**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.12.



Ansatz: 1.50 g (2.61 mmol) 2-Allyl-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluorotridecansäuremethylester **18**

0.30 g (7.84 mmol) LiAlH₄

100 ml Diethylether

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 0.55 g (39 % d. Th.), farbloses Öl

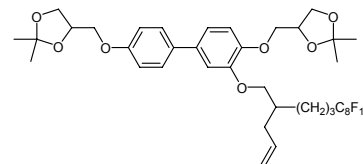
Analytik: C₁₆H₁₅F₁₇O M = 546.26 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 5.83-5.72 (m, 1H, CH=CH₂), 5.08-5.01 (m, 2H, CH=CH₂), 3.56 (dd, ³J(H,H) = 5.5, ⁴J(H,H) = 1.2, 2H, CH₂OH), 2.14-1.97 (m, 4H, CH₂CH=, CH₂CF₂), 1.67-1.58 (m, 3H, CH, CH₂), 1.47-1.31 (m, 2H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.24 (t, ⁴J(F,F) = 9.2, 3F, CF₃), -114.76 (-114.83) (m, 2F, CH₂CF₂), -122.29 (s, 6F, CF₂), -123.13 (s, 2F, CF₂), -123.95 (s, 2F, CF₂), 126.51 (s, 2F, CF₂CF₃).

A.51 Synthese von 3-(2-Allyl-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluorotridecyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **51**

Eine Lösung von 328 mg (0.76 mmol) 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-biphenyl-3-ol **36.1**, 499 mg (0.91 mmol) 2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluorundecyl)pent-4-en-1-ol **50**, 517 mg (2.29 mmol)



Triphenylphosphan und 319 mg (2.29 mmol) DEAD in 50 ml THF wird 6 h bei Raumtemperatur gerührt. Anschließend wird das Lösungsmittel unter vermindertem Druck abdestilliert und das Rohprodukt chromatographisch gereinigt.

Reinigung: Fliehkraftvermittelte präparative Chromatographie

(Eluent: PE/CHCl₃ 1:2, V/V) und Umkristallisation aus MeOH

Ausbeute: 110 mg (15 % d. Th.), farbloser Feststoff

Analytik: C₄₀H₄₃F₁₇O₇ M = 985.74 g/mol

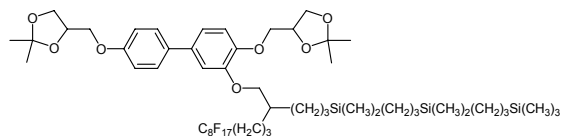
Fp.: 88-90 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.43 (d, ³J(H,H) = 8.7, 2H, Ar-H), 7.06-7.02 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.7, 3H, Ar-H), 5.85-5.75 (m, 1H, CH=CH₂), 5.08-5.03 (m, 2H, CH=CH₂), 4.47 (sext, ³J(H,H) = 6.1, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 3.99-3.88 (m, 6H, OCH₂), 2.28 (m, 2H, CH₂CH=), 2.09-1.96 (m, 4H, CH₂, CH₂CF₂), 1.72-1.60 (m, 3H, CH, CH₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.20 (t, ⁴J(F,F) = 9.9, 3F, CF₃), -114.68 (m, 2F, CH₂CF₂), -122.27 (s, 6F, CF₂), -123.10 (s, 2F, CF₂), -123.93 (s, 2F, CF₂), -126.49 (m, 2F, CF₂CF₃).

A.52 Synthese von 4,4'-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-[2-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluorundecyl)-12,12,16,16,20,20,24,24-octamethyl-12,16,20,24-tetrasilapentacosyloxy]biphenyl 52

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.17.



Ansatz: 110 mg (0.11 mmol) 3-(2-Allyl-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadeca-fluortridecyloxy)-4,4'-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)biphenyl **51**

63 mg (0.23 mmol) 1,1,5,5,9,9-Hexamethyl-1,5,9-trisiladecan

20 ml Toluol

1 Tropfen Karstedt's-Katalysator in Xylol

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 60 mg (44 % d. Th.), farbloses Öl

Analytik: C₅₃H₇₈F₁₇O₇Si₃ M = 1234.41 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.44 (d, ³J(H,H) = 8.7, 2H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.94 (d, ³J(H,H) = 8.9, 3H, Ar-H), 4.47 (quint, ³J(H,H) = 5.3, 2H, OCH), 4.19-4.06 (m, 4H, OCH₂), 3.97-3.84 (m, 6H, OCH₂), 2.09-2.03 (m, 2H, CH₂CF₂), 1.89-1.86 (m, 1H, CH), 1.71-1.60 (m, 2H, CF₂CH₂CH₂), 1.46 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.38 (s, 3H, CH₃), 1.35-1.25 (m, 6H, CH₂), 0.56-0.49 (m, 10H, SiCH₂), -0.05(-0.09) (m, 21H, SiCH₃).

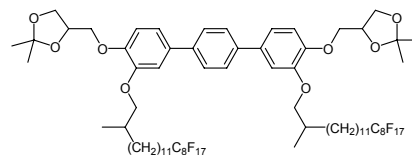
¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.19 (t, ⁴J(F,F) = 9.2, 3F, CF₃), -114.61(-114.69) (m, 2F, CH₂CF₂), -122.26 (s, 6F, CF₂), -123.09 (s, 2F, CF₂), -123.90 (s, 2F, CF₂), -126.47 (m, 2F, CF₂CF₃).

²⁹Si-NMR (CDCl₃, J/Hz, 500 MHz): δ = 1.61, 0.98, 0.57.

A.53 Synthese der lateral substituierten Terphenylderivate 53.x

4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(14,14,15,15,16,16,17,17,18,18,-19,19,20,20,21,21,21-heptadecafluor-2-methylhenicosyloxy)-1,1':4',1''-terphenyl **53.1**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 120 mg (0.23 mmol) 4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-1,1':4',1''-terphenyl-3,3''-diol **38**

335 mg (0.48 mmol) 21-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluor-20-methylhenicosan **10.8**

159 mg (1.15 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 160 mg (40 % d. Th.), farbloser Feststoff

Analytik: C₇₄H₈₈F₃₄O₈ M = 1751.43 g/mol

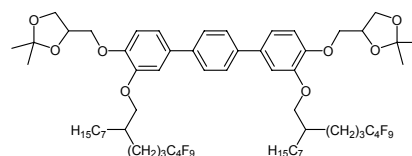
Fp.: 130-135 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.57 (s, 4H, Ar-H), 7.13-7.11 (m, 4H, Ar-H), 6.98 (d, ³J(H,H) = 8.9, 2H, Ar-H), 4.48 (quint, ³J(H,H) = 5.8, 2H, OCH), 4.18-4.13 (m, 4H, OCH₂), 4.02-3.98 (m, 4H, OCH₂), 3.92-3.88 (m, 2H, OCH₂), 3.82-3.78 (m, 2H, OCH₂), 2.09-1.96 (m, 6H, CHCH₃, CH₂CF₂), 1.61-1.53 (m, 4H, CH₂CH₂CF₂), 1.46 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 1.37-1.25 (m, 36H, CH₂), 1.04 (d, ³J(H,H) = 6.7, 6H, CHCH₃).

¹⁹F-NMR (Pyridin-d₅, J/Hz, 188 MHz): δ = -80.94 (t, ³J(F,F) = 9.2, 6F, CF₃), -113.80 (s, 4F, CH₂CF₂), -121.83 (s, 12F, CF₂), -122.70 (s, 4F, CF₂), -123.27 (s, 4F, CF₂), -126.10 (s, 4F, CF₂CF₃).

4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(6,6,7,7,8,8,9,9,9-nonafluor-2-heptylnonyloxy)-1,1':4',1''-terphenyl **53.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.29 mmol) 4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-1,1':4',1''-terphenyl-3,3''-diol **38**

187 mg (0.60 mmol) 8-(Brommethyl)-1,1,1,2,2,3,3,4,4-nonafluorpentadecan **10.1**

367 mg (2.87 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: CHCl₃/MeOH 10:0.5, V/V)

Ausbeute: 240 mg (64 % d. Th.), farbloser Feststoff

Analytik: C₆₂H₈₀F₁₈O₈ M = 1295.27 g/mol

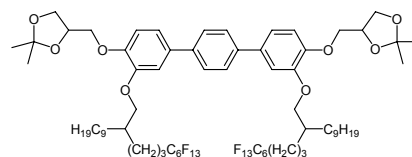
Fp.: 56-59 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.59 (s, 4H, Ar-H), 7.16-7.12 (m, 4H, Ar-H), 6.99 (d, ³J(H,H) = 8.1, 2H, Ar-H), 4.48 (quint, ³J(H,H) = 5.8, 2H, OCH), 4.17-4.12 (m, 4H, OCH₂), 4.02-3.97 (m, 6H, OCH₂), 3.93-3.89 (m, 2H, OCH₂), 2.14-2.02 (m, 4H, CH₂CF₂), 1.91-1.85 (m, 2H, CH), 1.75-1.61 (m, 4H, CH₂CH₂CF₂), 1.46 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 1.55-1.25 (m, 28H, CH₂), 0.86 (t, ³J(H,H) = 6.7, 6H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz) δ = -81.44 (s, 6F, CF₃), -114.90 (s, 4F, CH₂CF₂), -124.92 (s, 4F, CF₂), -126.46 (s, 4F, CF₂CF₃).

4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluor-2-nonylundecyloxy)-1,1':4',1''-terphenyl **53.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.29 mmol) 4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-1,1':4',1''-terphenyl-3,3''-diol **38**
 357 mg (0.60 mmol) 10-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluor-nonadecan **10.4**
 367 mg (2.87 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: CHCl₃/MeOH 10:0.5, V/V)

Ausbeute: 150 mg (33 % d. Th.), farbloses Öl

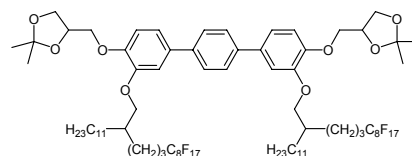
Analytik: C₇₀H₈₈F₂₆O₈ M = 1551.40 g/mol

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.58 (s, 4H, Ar-H), 7.16-7.12 (m, 4H, Ar-H), 6.98 (d, ³J(H,H) = 8.1, 2H, Ar-H), 4.48 (quint, ³J(H,H) = 5.8, 2H, OCH), 4.17-4.11 (m, 4H, OCH₂), 4.01-3.96 (m, 6H, OCH₂), 3.92-3.88 (m, 2H, OCH₂), 2.13-2.02 (m, 4H, CH₂CF₂), 1.91-1.85 (m, 2H, OCH₂CH), 1.74-1.59 (m, 6H, CH₂CH₂CF₂, CH₂), 1.52-1.53 (m, 50H, CH₃, CH₂), 0.86 (t, ³J(H,H) = 6.9, 6H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.40 (t, ⁴J(F,F) = 9.9, 6F, CF₃), -114.56 (-114.73) (m, 4F, CH₂CF₂), -122.28 (s, 4F, CF₂), -123.25 (s, 4F, CF₂) -123.92 (s, 4F, CF₂), -126.38 (-126.54) (m, 4F, CF₂CF₃).

4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis(6,6,7,7,8,8,9,9,10,10,11,11,-12,12,13,13,13-hepta-decafluor-2-undecyltridecyloxy)-1,1':4',1''-terphenyl **53.4**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.19 mmol) 4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-1,1':4',1''-terphenyl-3,3''-diol **38**
 289 mg (0.40 mmol) 12-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hepta-decafluortricosan **10.7**
 262 mg (1.90 mmol) K₂CO₃
 50 ml DMF
 5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
 (Eluent: CHCl₃/MeOH 10:0.5, V/V)

Ausbeute: 190 mg (55 % d. Th.), farbloser Feststoff

Analytik: $C_{78}H_{96}F_{34}O_8$ $M = 1807.54$ g/mol

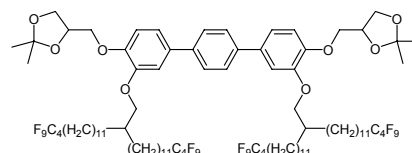
Fp.: 59-62 °C

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.58$ (s, 4H, Ar-H), 7.15-7.11 (m, 4H, Ar-H), 6.98 (d, $^3J(H,H) = 8.2$, 2H, Ar-H), 4.47 (quint, $^3J(H,H) = 5.8$, 2H, OCH), 4.17-4.11 (m, 4H, OCH₂), 4.01-3.96 (m, 6H, OCH₂), 3.92-3.88 (m, 2H, OCH₂), 2.15-2.01 (m, 4H, CH₂CF₂), 1.90-1.84 (m, 2H, CH), 1.74-1.60 (m, 4H, CH₂CH₂CF₂), 1.45 (s, 6H, CH₃), 1.38 (s, 6H, CH₃), 1.50-1.21 (m, 44H, CH₂), 0.86 (t, $^3J(H,H) = 6.7$, 6H, CH₃).

^{19}F -NMR ($CDCl_3$, J/Hz , 470 MHz): $\delta = -81.15$ (t, $^4J(F,F) = 9.9$, 6F, CF₃), -114.70-(114.81) (m, 4F, CH₂CF₂), -122.25 (s, 4F, CF₂), -122.33 (s, 8F, CF₂), -123.02 (s, 4F, CF₂), -123.91 (s, 4F, CF₂), -126.41 (s, 4F, CF₂CF₃).

4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis[14,14,15,15,16,16,17,17,17-nonafluor-2-(12,12,13,13,14,14,15,15,15-nonafluorpentadecyl)heptadecyloxy]-1,1':4',1''-terphenyl **53.5**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.19 mmol) 4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-1,1':4',1''-terphenyl-3,3''-diol **38**

343 mg (0.40 mmol) 16-(Brommethyl)-1,1,1,2,2,3,3,4,4,28,28,29,29,30,30,-31,31,31-octadecafluorhentriacontan **14.1**

262 mg (1.90 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fließkraftvermittelte präparative Chromatographie
(Eluent: CHCl₃/MeOH 10:0.5, V/V)

Ausbeute: 320 mg (81 % d. Th.), farbloser Feststoff

Analytik: $C_{94}H_{126}F_{36}O_8$ $M = 2067.94$ g/mol

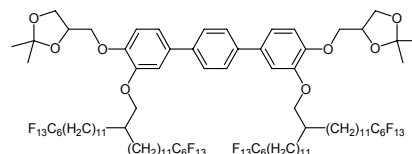
Fp.: 55-60 °C

1H -NMR ($CDCl_3$, J/Hz , 400 MHz): $\delta = 7.57$ (s, 4H, Ar-H), 7.13-7.11 (m, 4H, Ar-H), 6.98 (d, $^3J(H,H) = 8.7$, 2H, Ar-H), 4.47 (quint, $^3J(H,H) = 5.8$, 2H, OCH), 4.17-4.14 (m, 4H, OCH₂), 4.02-3.97 (m, 4H, OCH₂), 3.92 (d, $^3J(H,H) = 5.4$, 4H, OCH₂), 2.10-1.96 (m, 8H, CH₂CF₂), 1.86-1.80 (m, 2H, CH), 1.58 (quint, 8H, $^3J(H,H) = 7.5$, CH₂CH₂CF₂), 1.46 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 1.37-1.26 (m, 72H, CH₂).

^{19}F -NMR ($CDCl_3$, J/Hz , 470 MHz): $\delta = -81.48$ (t, $^4J(F,F) = 9.8$, 12F, CF₃), -115.00-(-115.06) (m, 8F, CH₂CF₂), -124.95 (s, 8F, CF₂), 126.49-(-126.53) (m, 8F, CF₂CF₃).

4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis[14,14,15,15,16,16,17,17,-
18,18,19,19,19-tridecafluor-2-(12,12,13,13,14,14,15,15,16,16,17,17,17-
tridecafluorheptadecyl)nonadecyloxy]-1,1':4',1''-terphenyl **53.6**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.7.



Ansatz: 150 mg (0.29 mmol) 4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-
1,1':4',1''-terphenyl-3,3''-diol **38**
632 mg (0.60 mmol) 18-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,30,30,-
31,31,32,32,33,33,34,34,35,35,35-hexacosafuorpentatriacontan **14.2**
401 mg (2.90 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: CHCl₃/MeOH 10:0.5, V/V)

Ausbeute: 170 mg (24 % d. Th.), farbloser Feststoff

Analytik: C₁₀₁H₁₂₄F₅₂O₈ M = 2453.98 g/mol

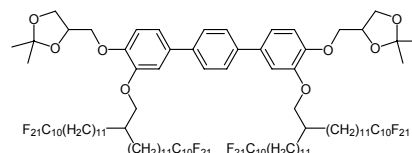
Fp.: 70-73 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.58 (s, 4H, Ar-H), 7.14-7.11 (m, 4H, Ar-H), 6.98 (d, ³J(H,H) = 8.8, 2H, Ar-H), 4.48 (quint, ³J(H,H) = 5.9, 2H, OCH), 4.18-4.13 (m, 4H, OCH₂), 4.01-3.97 (m, 4H, OCH₂), 3.92 (d, ³J(H,H) = 5.9, 4H, OCH₂), 2.09-1.96 (m, 8H, CH₂CF₂), 1.86-1.80 (m, 2H, OCH₂CH), 1.57 (quint, ³J(H,H) = 7.7, 8H, CH₂CH₂CF₂), 1.48-1.22 (m, 84H, CH₃, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.46 (t, ⁴J(F,F) = 9.7, 12F, CF₃), -114.73-(-114.90) (m, 8F, CH₂CF₂), -122.35 (s, 8F, CF₂), -123.29 (s, 8F, CF₂) -123.97 (s, 8F, CF₂), -126.51 (m, 8F, CF₂CF₃).

4,4''-Bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3,3''-bis[14,14,15,15,16,16,17,17,18,18,-
19,19,20,20,21,21,22,22,23,23,23-henicosafuor-2-(12,12,13,13,14,14,15,15,16,16,17,17,-
18,18,19,19,20,20,21,21,21-henicosafuorhenicosyl)]tricosyloxy]-1,1':4',1''-terphenyl **53.7**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.19 mmol) 4,4''-bis(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-
1,1':4',1''-terphenyl-3,3''-diol **38**
580 mg (0.40 mmol) 22-(Brommethyl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,-
10,10,34,34,35,35,36,36,37,37,-38,38,39,39,40,40,41,41,42,42,43,43,43-
dotetracontafluortritetracontan **14.4**

262 mg (1.90 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: CHCl₃/MeOH 10:0.5, V/V)

Ausbeute: 180 mg (29 % d. Th.), farbloser Feststoff

Analytik: C₁₁₈H₁₂₆F₈₄O₈ M = 3268.12 g/mol

Fp.: 114-115 °C

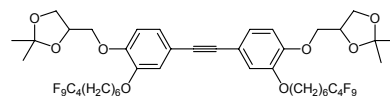
¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.57 (s, 4H, Ar-H), 7.12-7.10 (m, 4H, Ar-H), 6.97 (d, ³J(H,H) = 8.9, 2H, Ar-H), 4.47 (quint, ³J(H,H) = 6.0, 2H, OCH), 4.17-4.12 (m, 4H, OCH₂), 4.00-3.96 (m, 4H, OCH₂), 3.91 (d, ³J(H,H) = 5.8, 4H, OCH₂), 2.08-1.95 (m, 8H, CH₂CF₂), 1.84-1.81 (m, 2H, CH), 1.60-1.54 (m, 8H, CH₂CH₂CF₂), 1.45 (s, 6H, CH₃), 1.39 (s, 6H, CH₃), 1.35-1.24 (m, 72H, CH₂).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.18 (t, ⁴J(F,F) = 9.8, 12F, CF₃), -114.80 (s, 8F, CH₂CF₂), -122.16 (s, 24F, CF₂), -122.31 (s, 16F, CF₂), -123.13 (s, 8F, CF₂), -123.96 (s, 8F, CF₂), -126.55 (s, 8F, CF₂CF₃).

A.54 Synthese der lateral substituierten Tolanderivate 54.X

1,1'-Ethin-1,2-diylbis[4-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(7,7,8,8,9,9,10,10,10-nonafluordecyloxy)]benzol **54.1**

Die Darstellung erfolgte nach der allgemeinen
Arbeitsvorschrift 5.3.7.



Ansatz: 100 mg (0.21 mmol) 3,3'-Ethin-1,2-diylbis[6-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenol] **44**

171 mg (0.45 mmol) 10-Brom-1,1,1,2,2,3,3,4,4,4-nonafluordecan

294 mg (2.13 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 200 mg (89 % d. Th.), farbloser Feststoff

Analytik: C₄₆H₅₂F₁₈O₈ M = 1074.87 g/mol

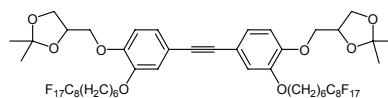
Fp.: 82-84 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.09 (dd, ³J(H,H) = 8.3, ⁴J(H,H) = 1.9, 2H, Ar-H), 7.04 (d, ⁴J(H,H) = 1.9, 2H, Ar-H), 6.80 (d, ³J(H,H) = 8.4, 2H, Ar-H), 4.47 (quint, ³J(H,H) = 5.8, 2H, OCH), 4.16-4.07 (m, 4H, OCH₂), 4.00-3.94 (m, 8H, OCH₂), 2.13-1.99 (m, 4H, CH₂CF₂), 1.82 (quint, ³J(H,H) = 6.9, 4H, OCH₂CH₂), 1.67-1.61 (m, 4H, CH₂CH₂CF₂), 1.55-1.47 (m, 8H, CH₂), 1.45 (s, 6H, CH₃), 1.38 (s, 6H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 188 MHz): δ = -81.51 (t, ⁴J(F,F) = 9.4, 3F, CF₃), -114.90-(-115.05) (m, 2F, CH₂CF₂), -124.90 (s, 2F, CF₂), -126.45-(-126.52) (m, 2F, CF₂CF₃).

1,1'-Ethin-1,2-diylbis[4-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-heptafluortetradecyloxy)]benzol **54.2**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 80 mg (0.17 mmol) 3,3'-Ethin-1,2-diylbis[6-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenol] **44**
194 mg (0.36 mmol) 14-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptafluortetradecan **2.1**

235 mg (1.70 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 150 mg (60 % d. Th.), farbloser Feststoff

Analytik: C₅₄H₅₂F₃₄O₈ M = 1474.93 g/mol

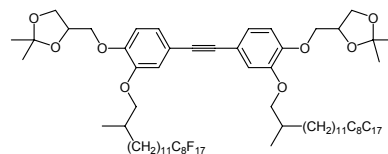
Fp.: 97-99 °C

¹H-NMR (CDCl₃, J/Hz, 400 MHz): δ = 7.08 (dd, ³J(H,H) = 8.9, ⁴J(H,H) = 1.9, 2H, Ar-H), 7.04 (d, ⁴J(H,H) = 1.9, 2H, Ar-H), 6.79 (d, ³J(H,H) = 8.4, 2H, Ar-H), 4.46 (quint, ³J(H,H) = 5.8, 2H, OCH), 4.15-4.07 (m, 4H, OCH₂), 3.99-3.94 (m, 8H, OCH₂), 2.13-1.99 (m, 4H, CH₂CF₂), 1.81 (quint, ³J(H,H) = 6.8, 4H, OCH₂CH₂), 1.67-1.59 (m, 4H, CH₂CH₂CF₂), 1.57-1.46 (m, 8H, CH₂), 1.45 (s, 6H, CH₃), 1.38 (s, 6H, CH₃).

¹⁹F-NMR (CDCl₃, J/Hz, 470 MHz): δ = -81.21 (t, ⁴J(F,F) = 9.9, 6F, CF₃), -114.72 (s, 4F, CH₂CF₂), -122.27 (s, 12F, CF₂), -123.11 (s, 4F, CF₂), -123.90 (s, 4F, CF₂), -126.49 (s, 4F, CF₂CF₃).

1,1'-Ethin-1,2-diylbis[4-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)-3-(14,14,15,15,16,16,-17,17,18,18,19,19,20,20,21,21,21-heptafluor-2-methylhenicosyloxy)]benzol **54.3**

Die Darstellung erfolgte nach der allgemeinen Arbeitsvorschrift 5.3.7.



Ansatz: 80 mg (0.17 mmol) 3,3'-Ethin-1,2-diylbis[6-(2,2-dimethyl-1,3-dioxolan-4-ylmethoxy)phenol] **44**

248 mg (0.36 mmol) 21-Brom-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptafluor-20-methylhenicosan **10.8**

235 mg (1.70 mmol) K₂CO₃

50 ml DMF

5 mg Bu₄NI

Reinigung: Fliehkraftvermittelte präparative Chromatographie
(Eluent: PE/CHCl₃ 1:2, V/V)

Ausbeute: 180 mg (62 % d. Th.), farbloser Feststoff

Analytik: $C_{70}H_{84}F_{34}O_8$ $M = 1699.36$ g/mol

Fp.: 88-92 °C

$^1\text{H-NMR}$ (CDCl_3 , J/Hz , 400 MHz): $\delta = 7.08$ (dd, $^3J(\text{H,H}) = 8.2$, $^4J(\text{H,H}) = 2.0$, 2H, Ar-H), 7.04 (d, $^4J(\text{H,H}) = 1.9$, 2H, Ar-H), 6.79 (d, $^3J(\text{H,H}) = 8.3$, 2H, Ar-H), 4.46 (quint, $^3J(\text{H,H}) = 5.9$, 2H, OCH), 4.16-4.09 (m, 4H, OCH_2), 4.00-3.94 (m, 4H, OCH_2), 3.85-3.81 (m, 2H, OCH_2), 3.75-3.70 (m, 2H, OCH_2), 2.08-1.92 (m, 6H, CHCH_3 , CH_2CF_2), 1.62-1.54 (m, 4H, $\text{CH}_2\text{CH}_2\text{CF}_2$), 1.45 (s, 6H, CH_3), 1.39 (s, 6H, CH_3), 1.36-1.23 (m, 36H, CH_2), 1.01 (d, $^3J(\text{H,H}) = 6.6$, 6H, CHCH_3).

$^{19}\text{F-NMR}$ (CDCl_3 , J/Hz , 470 MHz): $\delta = -81.21$ (t, $^4J(\text{F,F}) = 9.9$, 6F, CF_3), -114.75-(114.83) (m, 4F, CH_2CF_2), -122.27 (s, 12F, CF_2), -123.11 (s, 4F, CF_2), -123.93 (s, 4F, CF_2), -126.49 (s, 4F, CF_2CF_3).

B Liste der verwendeten Volumeninkremente nach IMMIRZI^[49]

Atomgruppe	Volumeninkrement [\AA^3]
-H	6.9
-C \equiv	15.3
>C<	11.0
>CH-	17.9
>CH ₂	24.8
-CH ₃	31.7
-O-	9.2
-OH	16.1
-F	12.8
>CF ₂	36.6
-CF ₃	49.4
Benzolring (nur C-Atome)	75.2
O-H \cdots O (H-Brücke)	-2.6

C Verwendete Gleichungen zur Berechnung der Gitterparameter aus den ermittelten Beugungswinkeln

lamellare Phasen: $n \cdot \lambda = 2d \cdot \sin\theta$

rechtwinklig kolumnare Phasen: $\sin^2\theta = \frac{\lambda^2}{4} \cdot \left[\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 \right]$

schiefwinklig kolumnare Phasen: $\sin^2\theta = \frac{\lambda^2}{4 \cdot \sin^2\gamma} \cdot \left[\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 - \frac{2hk \cdot \cos\gamma}{ab} \right]$

hexagonal kolumnare Phasen: $\sin^2\theta = \frac{\lambda^2}{4} \cdot \left[\frac{4}{3a^2} \cdot (h^2 + hk + k^2) \right]$

kubische Phasen: $\sin^2\theta = \frac{\lambda^2}{4 \cdot a} \cdot (h^2 + k^2 + l^2)$