Journal of Fluorine Chemistry 132 (2011) 898–906

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Towards functional fluorous surfactants. Synthesis of hydrophilic fluorous 1,2,3-triazolylmethyl ethers and di(1,2,3-triazolylmethyl) ethers

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ARTICLE INFO

Article history:
Received 1 April 2011
Received in revised form 30 June 2011
Accepted 4 July 2011
Available online 12 July 2011

Keywords:
Fluorous chemistry
Microwave acceleration
Dipolar cycloaddition
Fluorous 1,2,3-triazoles
Triazolylmethyl ethers
Fluorous surfactants

ABSTRACT

Copper(I)-accelerated Huisgen–Meldal dipolar cycloaddition reactions between polyfluoroalkyl azides and propargyl ethers of *n*-octanol and of triethyleneglycol monomethyl ether exhibited variation in yield of 1,2,3-triazol-4-ylmethyl ethers. Microwave acceleration, and *in situ* generation of the azides, provided improvements in yield and efficiency. In contrast, very good yields of equivalent fluorous triazoles were obtained from a range of *n*-alkyl azides with propargyl ethers of perfluorohexylethanol and of perfluoroheptylmethanol through conventional copper(I)-promoted reactions. Together, the resulting substances with systematic variations in polyfluoroalkyl and alkyl substituent length and position of substitution, and degree of oxygen content, make up small libraries of hybrid fluorous 1,2,3-triazol-4-ylmethyl ethers as candidates for study as hydrophilic fluorous surfactants. In addition, a pilot sample of di(1,2,3-triazol-4-ylmethyl) ethers with 1′-octyl-1-polyfluoroalkyl-substituents and 1′-nonyl-1-perfluorooctylethyl substituents were synthesised for the first time in an effort to develop more functional, fluorous surfactants.

1. Introduction

There has been widespread interest in polymeric and other, hybrid fluorous compounds because of the unique surface activity and physical and biological properties of materials derived from them [1–10]. Implicit in many reports has also been the potential of the compounds for the carriage of added functionality [11]. Fluorous modifications of small molecules derived from heterocycles have received less systematic attention as surfactants [11–19], although many innovative applications of fluorous tagged molecules have appeared [20], especially in terms of separation strategies [21] and recyclable catalysts [22,23]. We have recently outlined the potential of small fluorous heterocycles as surfactants and participants in self-assembly [24], and have described the synthesis of 1,2,3-triazoles [24,25] and tetrazoles [25] with one perfluoroalkyl substituent and one *n*-alkyl substituent, as examples of such compounds. A study of the influence of members of this library of heterocycles at various concentrations on the surface tension of *m*-xylene, in the accompanying paper [26], revealed considerable surface activity, but indicated some anomalies in the expected behaviour [24,25]. Similar anomalies of unpredictable behaviour had been reported by others for solutions of polyfluorocarbon–hydrocarbon hybrid molecules in vaseline oil [27]. In this case, it was suggested that the discrepancies were possibly attributable to issues of viscosity. We have chosen to examine the possibility that the unpredictable surface tension behaviour was due to the combination of fluorophilic and lipophilic components of the two quite different sets of heterocyclic and non-heterocyclic compounds. For example, relatively simple and non-polymeric, 1H-1,2,3-triazole derivatives in which there was a perfluorobutylethyl, perfluorohexylethyl, or perfluorooctylethyl substituent at position 1 on the ring, and an *n*-alkyl chain located at position 4 on the ring, showed consistent behaviour when the *n*-alkyl chain was 4 or 6 carbons in length, but very different behaviour when the chain was 8 carbons in length. This was irrespective of the fluorous chain length. Our interest therefore turned to analogues of the fluorous heterocyclic molecules in which the partner group was more hydrophilic.

This paper describes the synthesis of fluorous 1,2,3-triazole analogues in which the 1-polyfluoroalkyl group is retained and: (a) the 4-*n*-alkyl chain is replaced by an *n*-alkoxymethyl substituent, **1**–**3**, or (b) the 4-*n*-alkyl chain is replaced by a methoxytriethyleneglycolmethyl group, **4**–**6**, and (c) there is a 1-*n*-alkyl substituent in combination with a 4-perfluorohexylethoxymethyl group, **7**–**11**, or 4-perfluoroheptylmethoxymethyl group, **12**–**16**, respectively. In addition, a preliminary study towards a new class of ether linked bis-1,2,3-triazoles [14] is described.

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doi:10.1016/j.jfluchem.2011.07.002

2. Results and discussion

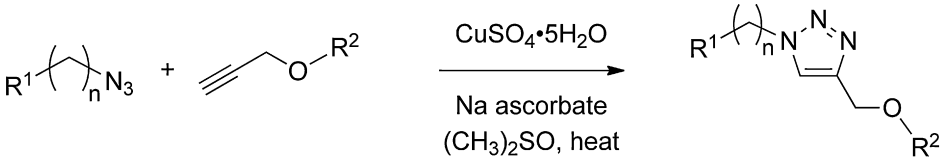
Two synthetic pathways were taken to substances **1**–**16**, and the methods used reflect our modular approach to such fluorous surfactants that are based on relatively simple heterocyclic core molecules [24].

In the first approach, the heterocyclic portion was constructed from fully substituted precursors. Known building blocks, fluorous azides **17**–**19** [28,29], were made to react with each of propargyl ethers **20** [30] and **21**, under Cu(I)-catalysed Huisgen–Meldal 1,3-dipolar cycloaddition conditions [31]. A number of different protocols were tested. In our earlier studies [24], aqueous dimethyl sulfoxide [31(d)], was adopted as solvent with good success. It was recognised that dimethyl sulfoxide itself, in the absence of water, was a useful dipolar aprotic solvent for the displacement of iodide in the preparation of perfluoroalkylethyl azides. This prompted a two-step, but one-pot procedure, to be examined in which the azides **17**–**19** were prepared *in situ*. Such *in situ* generation of non-fluorous azides followed by dipolar cycloaddition with copper-ligated alkynes to generate 1,4-disubstituted triazoles has been reported in various aqueous organic solvent combinations [32–34], but in our case, to respect the hydrophobicity of the fluorous substrates, neat dimethyl sulfoxide was used as solvent in both steps, with no added water. In addition, each step in the overall process using propargyl ether **20** was carried out under microwave irradiation [35], while each step using propargyl ether **21** was carried out under 'conventional' conditions, by regular heating. The former reactions were complete within a total of 3 h while those under conventional conditions required reaction times of 36 h. The reactions all proceeded with excellent regioselectivity to afford the desired 1,4-disubstituted derivatives **1**–**6** in acceptable to good yields, with the highest derived from the microwave accelerated protocol (Scheme 1). The fluorous azides **17**–**19** were also prepared separately, purified and reacted directly with propargyl ether **21** under conventional conditions, by way of comparison, but the expected triazoles **4**–**6** were isolated in only 52–58% yield. When the last of these, reaction between fluorous azide **19** and propargyl ether **21**, was carried out under microwave irradiation conditions, the product was obtained in much higher yield (80%) (Scheme 1). This confirmed the benefits of microwave acceleration, which are well-known, and demonstrated that they applied to this fluorous setting.

The simpler ether derivatives **1**–**3** were higher melting than the triethyleneglycol-substituted derivatives **4**–**6**, while the latter were noticeably more difficult to handle and purify.

Next, a series of *n*-alkyl azides, including benzyl azide, **22**–**26**, were made to react under the same 1,3-dipolar cycloaddition conditions with each of fluorous propargyl ethers, **27** and **28**. Compounds **27** and **28** were readily prepared under phase transfer conditions from the corresponding alcohol and propargyl bromide [36]. In this series, the 1,3-dipolar cycloaddition reactions were carried out under conventional conditions, and because the azides **22**–**26** were prepared from a variety of alkyl halides, they were pre-prepared separately. Again, the reactions proceeded with virtually perfect regioselectivity to yield the 1,2,3-triazoles **7**–**16** in good to excellent yields. The compounds were isolated in some cases as oils and waxes and in others crystalline materials. As expected, the more highly fluorinated derivatives, **12**–**16**, were higher melting than their less fluorinated analogues (see Tables in Supplementary Data).

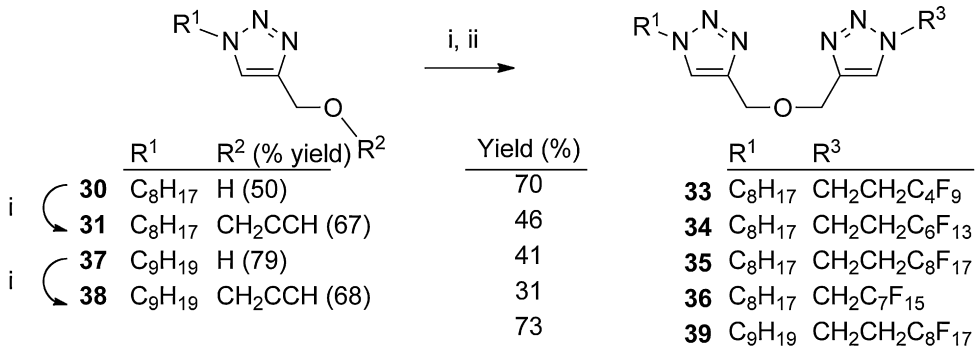
The influence of the compounds on surface tension of *m*-xylene has been described in the accompanying paper [26], but, by and large, these materials behaved consistently in reducing the surface tension, although again, the 1-*n*-octyl derivatives showed some deviation from the expected behaviour. Very significantly, it was noted that the hydrophilic derivatives showed higher and more consistent surface activity than the lipophilic analogues. This difference in behaviour was consistent with similar findings for perfluoroalkyl ether-substituted *versus* perfluoroalkyl-substituted



	R^1	n		R^2	Yield[a] (%)		R^1	n	R^2
17	C_4F_9	2	**20**	C_8H_{17}	87[b,c]	**1**	C_4F_9	2	C_8H_{17}
18	C_6F_{13}	2	**21**	$(CH_2CH_2O)_3CH_3$	81[b,c]	**2**	C_6F_{13}	2	C_8H_{17}
19	C_8F_{17}	2	**27**	$CH_2CH_2C_6F_{13}$	83[b,c]	**3**	C_8F_{17}	2	C_8H_{17}
22	C_4H_9	0	**28**	$CH_2C_7F_{15}$	52(66[b])	**4**	C_4F_9	2	$(CH_2CH_2O)_3CH_3$
23	C_6H_{13}	0	**29**	H	58(71[b])	**5**	C_6F_{13}	2	$(CH_2CH_2O)_3CH_3$
24	C_8H_{17}	0			58(80[c])(74[b])	**6**	C_8F_{17}	2	$(CH_2CH_2O)_3CH_3$
25	C_9H_{19}	0			64	**7**	C_4H_9	0	$CH_2CH_2C_6F_{13}$
26	CH_2Ph	0			97	**8**	C_6H_{13}	0	$CH_2CH_2C_6F_{13}$
					90	**9**	C_8H_{17}	0	$CH_2CH_2C_6F_{13}$
					82	**10**	C_9H_{19}	0	$CH_2CH_2C_6F_{13}$
					88	**11**	CH_2Ph	0	$CH_2CH_2C_6F_{13}$
					84	**12**	C_4H_9	0	$CH_2C_7F_{15}$
					88	**13**	C_6H_{13}	0	$CH_2C_7F_{15}$
					82	**14**	C_8H_{17}	0	$CH_2C_7F_{15}$
					81	**15**	C_9H_{19}	0	$CH_2C_7F_{15}$
					74	**16**	CH_2Ph	0	$CH_2C_7F_{15}$
					50[d]	**30**	C_8H_{17}	0	H

NOTES
[a] Conventional reaction conditions (see Experimental for details).
[b] *In situ* preparation of azide.
[c] Microwave accelerated conditions.
[d] Reaction performed in aqueous *tert*-BuOH instead of $(CH_3)_2SO$.

Scheme 1. Preparation of triazolyl ethers **1**–**16** and hydroxymethyltriazole **30** through Cu(I)-catalysed azide–alkyne dipolar cycloaddition.



Scheme 2. Preparation of hydroxymethyltriazoles **30** and **37**, triazolyl propargyl ethers **31** and **38**, and di(triazolylmethyl) ethers **33**–**36** and **39**.

benzenes [37]. An alternative approach to ether-substituted triazoles involving functionalisation of preformed heterocycles was therefore investigated and access to more elaborate fluorous 1,2,3-triazole derivatives was also explored.

There has been some interest in gemini fluorous surfactants, such as bis-tetraalkylammonium salts [19], because they have enhanced bioactivity and can form unique self assembled clusters. The fluorous, ether-substituted triazoles have similar potential to be fashioned into interesting gemini heterocycles through synthesis of ether linked di-heterocycles. We wished to demonstrate this concept in principle and have synthesised two pseudo symmetrical and three unsymmetrical examples. Huisgen–Meldal dipolar cycloaddition [32] between *n*-octyl azide **25** and propargyl alcohol **29** proceeded well in aqueous *tert*-butanol (Scheme 1) and the intermediate 4-hydroxymethyl-1-*n*-octyl-1,2,3-triazole **30** [35] was treated with propargyl bromide under phase transfer conditions with sodium hydroxide as base (Scheme 2). Subsequent reaction of the propargyl ether **31** with perfluorobutylethyl azide **17**, perfluorohexylethyl azide **18**, perfluorooctylethyl azide **19**, and perfluoroheptylmethyl azide **32**, again under copper(I)-promoted click conditions [31], gave the desired, new bis-1,2,3-triazoles **33**–**36**. Similarly, dipolar cycloaddition of *n*-nonyl azide **25** with propargyl alcohol **29** yielded new 4-hydroxymethyl-1-*n*-nonyl-1,2,3-triazole **37**, which was subsequently transformed into its propargyl ether **38**. Treatment of propargyl ether **38** with perfluorooctylethyl azide **19** under copper(I)-promoted conditions proceeded without incident to bis-1,2,3-triazole **39**.

The structures of triazoles **33**–**36** contain the same *n*-octyl substituent in one triazole ring but (a) increasing fluorous substituents of increasing chain length (**33**–**35**), and (b) fluorous chains of equal length and increasing fluorine content (**34** and **36**), in the second ring. Meanwhile, bis-triazoles **35** and **39** bear identical N-perfluorooctylethyl substituents in one heterocyclic ring but non-fluorous *n*-alkyl substituents of increasing chain length in the other. Together, this collection of new compounds comprises a valuable small library with highly systematic structural variations for further study.

The scope of these functionalised fluorous molecules for self-assembly, drug transport, and additional functionalisation, will be investigated in future.

3. Experimental

3.1. General

Melting points were determined using a Köfler hotstage melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet Avatar 320 FT-IR spectrophotometer as thin films of neat liquid and in KBr disks for solids; measurements are reported as wavenumbers in cm^{-1}. Routine ^1H, ^{13}C and ^{19}F NMR spectra were obtained on a Bruker DPX300F spectrometer. Chemical shifts were recorded in parts per million (ppm) relative to solvent nuclei as an internal reference. Mass spectra were measured using the electrospray ionization (ESI) technique, at low resolution on a Waters Micromass ZQ2000 LC–MS instrument by direct injection and at high resolution using a Thermo LTQ Orbitrap XL instrument. Samples were dissolved in MeOH. Microanalyses were carried out at the Microanalytical Laboratory, Australian National University. All chemicals were commercial reagent grade unless otherwise specified.

3.2. General method for preparation of alkynyl ethers 20 and 21

A dry flask was charged with THF (15 mL), NaOH pellets (2.40 g, 60 mmol), and *n*-octanol or triethyleneglycol monomethyl ether (15 mmol). The flask was immersed in an ice-bath and the contents stirred for 10 min. before propargyl bromide (2.51 mL, 22.5 mmol) was added dropwise. The reaction mixture was then allowed to stir for 24 h, gradually warming to r.t. The reaction mixture was poured into Et_2O (20 mL) and water (50 mL) and the layers were separated. The aqueous layer was further extracted with Et_2O (2 × 20 mL), and the combined organic extracts were washed with 10% aq. HCl, followed by sat. $NaHCO_3$ solution and brine, and then dried over $MgSO_4$. Column chromatography (silica gel, Et_2O/light petroleum, 10:90) followed by Kulgelrohr distillation gave the desired products.

3.2.1. 1-(Prop-2-ynyloxy)octane 20

n-Octanol (1.95 g) gave 1-(prop-2-ynyloxy)octane **20** as a colourless oil (2.39 g, 95%) bp 79–81 °C/0.1 mmHg (lit. [30]: bp 80 °C (oven)/0.13 mmHg). IR (neat): 3583, 3312, 2927, 2856, 2117, 1467, 1443, 1378, 1357, 1269, 1104, 1026, 945, 917, 722, 665, 622, 422 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, *J* 6.6 Hz, 3H, CH_3CH_2), 1.26 (m, 8H, $(CH_2)_4CH_3$), 1.33 (m, 2H, $CH_2CH_2CH_2O$), 1.58 (m, 2H, CH_2CH_2O), 2.40 (t, *J* 2.4 Hz, 1H, OCH_2CCH), 3.49 (t, *J* 6.7 Hz, 2H, CH_2CH_2O), 4.12 (d, *J* 2.4 Hz, 2H, OCH_2CCH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0 (CH_3), 22.5 (CH_2CH_3), 26.0 (CH_2), 29.1 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 31.7 (CH_2CH_2O), 57.9 (OCH_2CCH), 70.2 (CH_2OCH_2CCH), 73.9 (OCH_2CCH), 80.0 (OCH_2CCH). HR-MS (ESI) Calcd. for $[C_{11}H_{20}O+H]^+$: *m*/*z* 169.1587. Found: *m*/*z* 169.1582. Anal. Calcd. for $C_{11}H_{20}O{\cdot}0.33H_2O$: C, 75.83; H, 11.96%. Found: C, 75.73; H, 12.11%.

3.2.2. 3-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)prop-1-yne 21

Triethyleneglycol monomethyl ether (2.46 g) gave *3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)prop-1-yne* **21** as a colourless oil

(2.48 g, 82%) bp 130–133 °C (oven)/0.1 mmHg. IR (neat): 3582, 3428, 3278, 2880, 2114, 1724, 1650, 1454, 1352, 1287, 1247, 1197, 1104, 1032, 935, 887, 850, 666 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.41 (t, *J* 2.4 Hz, 1H, OCH_2CCH), 3.36 (s, 3H, OCH_3), 3.54 (m, 2H, $CH_2CH_2OCH_3$), 3.62 (m, 2H, $OCH_2CH_2OCH_3$), 3.65 (m, 4H, 2 × OCH_2CH_2), 3.66 (m, 2H, CH_2OCH_2CCH), 3.67 (m, 2H, $OCH_2CH_2OCH_2CCH$), 4.18 (d, *J* 2.4 Hz, 2H, OCH_2CCH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 58.3 (OCH_2CCH), 58.9 (OCH_3), 69.0 (CH_2OCH_2CCH), 70.3 (OCH_2CH_2), 70.4 (OCH_2CH_2), 70.5 (2 × OCH_2CH_2), 71.8 (CH_2OCH_3), 74.4 (OCH_2CCH), 79.5 (OCH_2CCH). MS (ESI) *m*/*z*: 226.17 ($[M+H+Na]^+$, 10%), 225.16 ($[M+Na]^+$, 100). Anal. Calcd. for $C_{10}H_{18}O_4$ requires C, 59.39; H, 8.97%. Found: C, 59.24; H, 9.28%.

3.3. General method for the microwave accelerated reactions of propargyl ether 20 with in situ prepared perfluoroalkylethyl azides 17–19

Perfluoroalkylethyl iodide (1.0 mol equiv.) (3–4 mmol) and NaN_3 (1.2 mol equiv.) were added to dry DMSO (2 mL) in a 10 mL CEM microwave glass reactor tube, a magnetic stirring bead added and the system sealed. The tube was subjected to stirring and microwave irradiation at 250 W and 65 °C for 1 h then immediately cooled to r.t. The tube was opened and *n*-octyl propargyl ether **41** (1.0 mol equiv.) added, followed by sodium ascorbate (0.1 mol equiv.) and $CuSO_4{\cdot}5H_2O$ (0.05 mol equiv.) and additional DMSO (1 mL). The tube was again sealed and again subjected to stirring and microwave irradiation at elevated temperature. At the conclusion of the reaction, the tube was cooled, opened, and the contents diluted with water (25 mL). The product was then extracted into Et_2O (3 × 20 mL), and the combined extracts washed in turn with brine (2 × 10 mL), H_2O (2 × 10 mL) and again brine (10 mL), and then dried and evaporated. The residue was chromatographed on silica gel and the product eluted with a gradient of Et_2O/light petroleum.

3.3.1. 4-((Octyloxy)methyl)-1-(2-(perfluorobutyl)ethyl)-1H-1,2,3-triazole 1

Perfluorobutylethyl iodide (1.496 g, 4.0 mmol) was converted to its azide **17** at 75 °C for 1 h and then treated with propargyl ether **20** (0.673 g, 4.0 mmol) at 95 °C for 2 h to afford *4-((octyloxy)-methyl)-1-(2-(perfluorobutyl)ethyl)-1H-1,2,3-triazole* **1** as white needles (1.59 g, 87%) mp 40–42 °C (Et_2O-light petroleum). IR (KBr): 3500, 2924, 1467, 1359, 1225, 1134, 1053, 1018, 988, 881, 859, 771, 738, 700, 668, 646, 596, 531 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, *J* 7.0 Hz, 3H, CH_3), 1.28 (m, 8H, $(CH_2)_4CH_3$), 1.31 (m, 2H, $OCH_2CH_2CH_2$), 1.58 (tt, *J* 7.4, 6.7 Hz, 2H, OCH_2CH_2), 2.81 (tt, $^3J_{H-F}$ 18.0, $^3J_{H-H}$ 7.4 Hz, 2H, CH_2CF_2), 3.50 (t, *J* 6.7 Hz, 2H, OCH_2CH_2), 4.61 (s, 2H, 4-CH_2O), 4.66 (dd, *J* 7.6, 7.3 Hz, 2H, $N1CH_2CH_2CF_2$), 7.58 (s, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2 (CH_3), 22.8 (CH_2CH_3), 26.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.8 (CH_2), 31.90 (t, $^2J_{C-F}$ 21.7 Hz, $N1CH_2CH_2CF_2$), 31.93 (OCH_2CH_2), 42.4 (br t, $^3J_{C-F}$ 5.2 Hz, $N1CH_2CH_2CF_2$), 64.4 (4-CH_2O), 71.2 (OCH_2CH_2), 122.9 (C5), 146.2 (C4). MS (ESI) *m*/*z*: 481.07 ($[M+H+Na]^+$, 31%), 480.13 ($[M+Na]^+$, 100). Anal. Calcd. for $C_{17}H_{24}F_9N_3O$ requires: C, 44.64; H, 5.29; N, 9.19%. Found: C, 44.76; H, 5.02; N, 9.33%.

3.3.2. 4-((Octyloxy)methyl)-1-(2-(perfluorohexyl)ethyl)-1H-1,2,3-triazole 2

Perfluorohexylethyl iodide (1.422 g, 3.0 mmol) was converted to its azide **18** through treatment at 75 °C for 1 h, then treated with propargyl ether **20** (0.505 g, 3.0 mmol) at 95 °C for 2 h to afford *4-((octyloxy)methyl)-1-(2-(perfluorohexyl)ethyl)-1H-1,2,3-triazole* **2** as white needles (1.35 g, 81%) mp 52–54 °C (Et_2O-light petroleum). IR (KBr): 3521, 3101, 2935, 1468, 1240, 1196, 1138, 1118, 1095, 1078, 1054, 998, 982, 845, 786, 768 725, 712, 680, 642, 565 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.85 (t, *J* 6.8 Hz, 3H, CH_3), 1.24 (m, 8H, $(CH_2)_4CH_3$), 1.31 (m, 2H, $OCH_2CH_2CH_2$), 1.58 (tt, *J* 7.0, 6.6 Hz, 2H, OCH_2CH_2), 2.80 (tt, $^3J_{H-F}$ 18.0, $^3J_{H-H}$ 7.4 Hz, 2H, CH_2CF_2), 3.50 (t, *J* 6.6 Hz, 2H, OCH_2CH_2), 4.62 (s, 2H, 4-CH_2O), 4.67 (dd, *J* 7.5, 7.4 Hz, 2H, $N1CH_2CH_2CF_2$), 7.61 (s, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2 (CH_3), 22.8 (CH_2CH_3), 26.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 31.8 (t, $^2J_{C-F}$ 21.7 Hz, $N1CH_2CH_2CF_2$), 31.9 (OCH_2CH_2), 42.2 (br t, $^3J_{C-F}$ 4.9 Hz, $N1CH_2CH_2CF_2$), 64.3 (4-CH_2O), 71.1 (OCH_2CH_2), 123.1 (C5-H), 146.0 (C4). MS (ESI) *m*/*z*: 596.00 ($[M+K]^+$, 3%), 581.03 ($[M+H+Na]^+$, 25), 580.03 ($[M+Na]^+$, 100), 558.04 ($[M+H]^+$, 14). Anal. Calcd. for $C_{19}H_{24}F_{13}N_3O$ requires: C, 40.94; H, 4.34; N, 7.54%. Found: C, 40.71; H, 4.46; N, 7.77%.

3.3.3. 4-((Octyloxy)methyl)-1-(2-(perfluorooctyl)ethyl)-1H-1,2,3-triazole 3

Perfluorooctylethyl iodide (1.722 g, 3.0 mmol) was converted to its azide **19** through microwave irradiation at 85 °C for 1 h, then treated with propargyl ether **20** (0.505 g, 3.0 mmol) at 98 °C for 2.5 h to afford *4-((octyloxy)methyl)-1-(2-(perfluorooctyl)ethyl)-1H-1,2,3-triazole* **3** as white needles (1.63 g, 83%) mp 80–82 °C (Et_2O-light petroleum). IR (KBr): 3646, 3410, 2933, 1443, 1359, 1204, 1148, 1116, 1063, 1032, 983, 957, 921, 746, 706, 660, 585, 557, 518 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, *J* 6.8 Hz, 3H, CH_3), 1.24 (m, 8H, $(CH_2)_4CH_3$), 1.31 (m, 2H, $OCH_2CH_2CH_2$), 1.58 (tt, *J* 7.1, 6.8 Hz, 2H, OCH_2CH_2), 2.81 (tt, $^3J_{H-F}$ 18.0, $^3J_{H-H}$ 7.5 Hz, 2H, CH_2CF_2), 3.50 (t, *J* 6.7 Hz, 2H, OCH_2CH_2), 4.62 (s, 2H, 4-CH_2O), 4.68 (dd, *J* 7.5, 7.3 Hz, 2H, $N1CH_2CH_2CF_2$), 7.61 (s, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.2 (CH_3), 22.8 (CH_2CH_3), 26.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 31.86 (t, $^2J_{C-F}$ 21.8 Hz, $N1CH_2CH_2CF_2$), 31.93 (OCH_2CH_2), 42.4 (br t, $^3J_{C-F}$ 4.6 Hz, $N1CH_2CH_2CF_2$), 64.3 (4-CH_2O), 71.1 (OCH_2CH_2), 123.1 (C5-H), 146.1 (C4). MS (ESI) *m*/*z*: 680.93 ($[M+Na]^+$, 23%), 679.93 ($[M-H+Na]^+$, 100). Anal. Calcd. for $C_{21}H_{24}F_{17}N_3O$ requires: C, 38.37; H, 3.68; N, 6.39%. Found: C, 38.44; H, 3.76; N, 6.46%.

3.4. General method for the preparation of 4-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl)-1-(2-perfluoroalkylethyl)-1H-1,2,3-triazoles 4–6 by conventional, thermal reactions of propargyl ether 21 with in situ prepared perfluoroalkylethyl azides 17–19

Perfluoroalkylethyl iodide (1.0 mol equiv.) (3–5 mmol) and NaN_3 (1.0–1.5 mol equiv.) were added to dry DMSO (4 mL), a magnetic stirring bead added, and the mixture stirred under argon in a bath at 65 °C for 24 h then cooled to r.t. The methoxytriethylenoxy propargyl ether **21** (1.0 mol equiv.) added, followed by sodium ascorbate (0.1 mol equiv.) and $CuSO_4{\cdot}5H_2O$ (0.05 mol equiv.), and additional DMSO (2 mL). The mixture was again stirred under argon at elevated temperature for 48 h. The contents were cooled and diluted with water (50 mL). The product was then extracted into Et_2O (3 × 20 mL), and the combined extracts washed in turn with brine (2 × 10 mL), H_2O (2 × 10 mL) and again brine (10 mL), then dried and evaporated. The residue was chromatographed on silica gel and the product eluted with a gradient of Et_2O/light petroleum and distilled or characterized directly as an oil.

3.4.1. 4-((2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)methyl)-1-(2-perfluorobutylethyl)-1H-1,2,3-triazole 4

Perfluorobutylethyl iodide (1.87 g, 5.0 mmol) was treated with NaN_3 (0.49 g, 7.5 mmol) at 65 °C for 24 h to generate azide **17**, which was then treated with propargyl ether **21** (1.02 g, 5.0 mmol) at 90 °C for 48 h to give *4-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl)-1-(2-perfluorobutylethyl)-1H-1,2,3-triazole* **4** as pale yellow wax (1.62 g, 66%) bp 223–228 °C (oven)/0.1 mmHg. IR (neat): 3139, 2882, 2357, 2248, 1714, 1664, 1646, 1455, 1403, 1352, 1223, 1135, 1049, 990, 928, 881, 858, 832, 748, 710, 666 cm^{-1}. ^1H NMR

(300 MHz, $CDCl_3$) δ: 2.78 (tt, $^3J_{H-F}$ 18.1, $^3J_{H-H}$ 7.2 Hz, 2H, CH_2CF_2), 3.32 (s, 3H, OCH_3), 3.50 (t, *J* 4.4 Hz, 2H, CH_2OCH_3), 3.55–3.67 (m, 10H, 5 × OCH_2CH_2), 4.64 (partially obscured dd, *J* 7.2, *ca.* 6.4 Hz, 2H, $N1CH_2CH_2CF_2$), 4.65 (s, 2H, 4-CH_2O), 7.65 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.6 (t, $^2J_{C-F}$ 21.7 Hz, $N1CH_2CH_2CF_2$), 42.1 (t, $^3J_{C-F}$ *ca.* 4 Hz, $N1CH_2CH_2CF_2$), 58.8 (OCH_3), 64.5 (4-CH_2O), 69.7 (4-CH_2OCH_2), 70.35 (OCH_2CH_2), 70.40 (OCH_2CH_2), 70.42 (OCH_2CH_2), 70.47 (OCH_2CH_2), 71.8 (CH_2OCH_3), 123.0 (C5-H), 145.6 (C4). MS (ESI) *m*/*z*: 515.29 ($[M+H+Na]^+$, 23%), 514.22 ($[M+Na]^+$, 100), 492.10 ($[M+H]^+$, 20). HR-MS (ESI) Anal. Calcd. for $[C_{16}H_{22}N_3O_4F_9+Na+H]^+$ *m*/*z*: 515.1443. Found: *m*/*z* 515.1390 (19%); Anal. Calcd. for $[C_{16}H_{22}N_3O_4F_9+Na]^+$ *m*/*z* 514.1365. Found: *m*/*z* 514.1361 (100); Anal. Calcd. for $[C_{16}H_{22}N_3O_4F_9+H]^+$ *m*/*z* 492.1545. Found: *m*/*z* 492.1549 (15).

3.4.2. 4-((2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)methyl)-1-(2-perfluorohexylethyl)-1H-1,2,3-triazole 5

Perfluorohexylethyl iodide (2.37 g, 5.0 mmol) was treated with NaN_3 (0.48 g, 7.5 mmol) at 65 °C for 24 h to generate azide **18**, which was then treated with propargyl ether **21** (1.03 g, 5.1 mmol) in a bath at 100 °C for 48 h to give *4-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl)-1-(2-perfluorohexylethyl)-1H-1,2,3-triazole* **5** as a pale yellow wax (2.09 g, 71%). IR (neat): 3138, 2879, 1731, 1646, 1456, 1402, 1366, 1351, 1319, 1240, 1206, 1145, 1122, 1050, 989, 949, 850, 810, 746, 736, 708, 699, 666 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.82 (tt, $^3J_{H-F}$ 18.5, $^3J_{H-H}$ 7.2 Hz, 2H, CH_2CF_2), 3.37 (s, 3H, OCH_3), 3.55 (t, *J* 4.7 Hz, 2H, CH_2OCH_3), 3.60–3.80 (m, 10H, 5 × OCH_2CH_2), 4.68 (dd, *J* 7.5, 7.5 Hz, 2H, $N1CH_2CH_2CF_2$), 4.71 (s, 2H, 4-CH_2O), 7.71 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.7 (t, $^2J_{C-F}$ 21.7 Hz, $N1CH_2CH_2CF_2$), 42.1 (br, $N1CH_2CH_2CF_2$), 58.8 (OCH_3), 64.5 (4-CH_2O), 69.7 (4-CH_2OCH_2), 70.35 (OCH_2CH_2), 70.40 (OCH_2CH_2), 70.42 (OCH_2CH_2), 70.48 (OCH_2CH_2), 71.8 (CH_2OCH_3), 123.1 (C5-H), 145.7 (C4). MS (ESI) *m*/*z*: 615.36 ($[M+H+Na]^+$, 8%), 614.30 ($[M+Na]^+$, 100). HR-MS (ESI) Anal. Calcd. for $[C_{18}H_{22}N_3O_4F_{13}+Na+H]^+$ *m*/*z*: 615.1379. Found: *m*/*z* 615.1337 (21%); Anal. Calcd. for $[C_{18}H_{22}N_3O_4F_{13}+Na]^+$ requires *m*/*z* 614.1301. Found: *m*/*z* 614.1309 (100). Anal. Calcd. for $[C_{18}H_{22}N_3O_4F_{13}+H]^+$ requires *m*/*z* 592.1481. Found: *m*/*z* 592.1500 (22).

3.4.3. 4-((2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)methyl)-1-(2-perfluorooctylethyl)-1H-1,2,3-triazole 6

Perfluorooctylethyl iodide (1.72 g, 3.0 mmol) was treated with NaN_3 (0.23 g, 3.0 mmol) in a bath at 70 °C for 24 h to generate azide **19**, which was then treated with propargyl ether **21** (0.61 g, 3.0 mmol) in a bath at 110 °C for 48 h to give *4-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl)-1-(2-perfluorooctylethyl)-1H-1,2,3-triazole* **6** as a white powder (1.53 g, 79%) mp 47–49 °C (Et_2O/light petroleum). IR (KBr): 3126, 2875, 2368, 1715, 1557, 1539, 1455, 1401, 1372, 1338, 1201, 1151, 1115, 1053, 989, 958, 851, 706, 660 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.82 (tt, $^3J_{H-F}$ 18.5, $^3J_{H-H}$ 7.5 Hz, 2H, CH_2CF_2), 3.36 (s, 3H, OCH_3), 3.55 (t, *J* 4.2 Hz, 2H, CH_2OCH_3), 3.60–3.75 (m, 10H, 5 × OCH_2CH_2), 4.68 (dd, *J* 7.5, 7.5 Hz, 2H, $N1CH_2CH_2CF_2$), 4.71 (s, 2H, 4-CH_2O), 7.70 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.6 (t, $^2J_{C-F}$ 21.7 Hz, $N1CH_2CH_2CF_2$), 42.1 (br, $N1CH_2CH_2CF_2$), 58.7 (OCH_3), 64.4 (4-CH_2O), 69.6 (4-CH_2OCH_2), 70.30 (OCH_2CH_2), 70.36 (OCH_2CH_2), 70.38 (OCH_2CH_2), 70.43 (OCH_2CH_2), 71.7 (CH_2OCH_3), 123.2 (C5-H), 145.5 (C4). MS (ESI) *m*/*z*: 715.36 ($[M+H+Na]^+$, 14%), 714.23 ($[M+Na]^+$, 100). Anal. Calcd. for $C_{20}H_{22}F_{17}N_3O_4$ requires: C, 34.74; H, 3.21; N, 6.08%. Found: C, 34.63; H, 2.97; N, 5.90%.

3.5. General method for the preparation of alkynyl ethers 27 and 28

A dry flask was charged with THF (9 mL), NaOH pellets (0.48 g, 12 mmol), and perfluorohexylethanol or perfluoroheptylmethanol (3 mmol). The flask was immersed in an ice-bath and the contents stirred for 10 min. Propargyl bromide (0.54 g, 4.5 mmol) was added dropwise and the reaction mixture stirred and gradually allowed to warm to r.t. over 24 h. The reaction mixture was poured into Et_2O (20 mL) and water (50 mL), the layers separated and the aqueous layer extracted with more Et_2O (3 × 20 mL). The combined organic extracts were washed with 10% HCl soln. followed by sat. aq. $NaHCO_3$ and brine, and then dried over Na_2SO_4. Column chromatography (silica gel, Et_2O/LP, 10:90) followed by Kulgelrohr distillation gave the desired products.

3.5.1. 3-((2-Perfluorohexyl)ethoxy)prop-1-yne 27

Perfluorohexylethanol (1.09 g) gave *3-((2-perfluorohexyl)ethoxy)prop-1-yne* **27** as a colourless oil (0.96 g, 80%) bp 125–128 °C (oven)/0.1 mmHg. IR (neat): 3850, 3608, 3683, 3317, 2960, 2898, 2859, 2360, 2342, 2122, 1362, 1240, 1146, 1010, 913, 811, 708, 698, 653 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.43 (ttt, $^3J_{H-F}$ 18.6, $^3J_{H-H}$ 6.8, $^4J_{H-F}$ 1.4 Hz, 2H, $OCH_2CH_2CF_2$), 2.46 (t, *J* 2.4 Hz, 1H, OCH_2CCH), 3.82 (t, *J* 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 4.18 (d, *J* 2.4 Hz, 2H, OCH_2CCH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.3 (t, $^2J_{C-F}$ 21.5 Hz, $OCH_2CH_2CF_2$), 58.3 (OCH_2CCH), 61.6 (t, $^3J_{C-F}$ *ca.* 5 Hz, $OCH_2CH_2CF_2$), 74.9 (OCH_2CCH), 78.8 (OCH_2CCH). MS (ESI) *m*/*z*: 425.14 ($[M+Na]^+$). Anal. Calcd. for $C_{11}H_7F_{13}O$ requires C, 32.85; H, 1.75%. Found: C, 32.53; H, 1.68%.

3.5.2. 3-((2-Perfluoroheptyl)methoxy)prop-1-yne 28

Perfluoroheptylmethanol (1.20 g) gave *3-(perfluoroheptylmethoxy)prop-1-yne* **28** as a colourless oil (1.12 g, 85%) b.p. 130–132 °C (oven)/0.1 mmHg. IR (neat): 3850, 3583, 3317, 2924, 2360, 2342, 2126, 1690, 1464, 1448, 1362, 1328, 1213, 1150, 1090, 1023, 963, 884, 808, 722, 702, 660 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.54 (t, *J* 2.4 Hz, 1H, OCH_2CCH), 4.05 (tt, $^3J_{H-F}$ 13.8, $^4J_{H-F}$ 1.5 Hz, 2H, OCH_2CF_2), 4.32 (d, *J* 2.4 Hz, 2H, OCH_2CCH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 59.3 (OCH_2CCH), 65.7 (t, *J* 25.5 Hz, OCH_2CF_2), 76.2 (OCH_2CCH), 77.4 (OCH_2CCH). MS (ESI) *m*/*z*: 439.21($[M+1]^+$). Anal. Calcd. for $C_{11}H_5F_{15}O$ requires C, 30.16; H, 1.15%. Found: C, 30.32; H, 1.08%.

3.6. General procedure for the preparation of triazoles 7–16

Propargyl ether (alkyne) (1 mmol) and alkyl azide (2 mmol) were added to a suspension of sodium ascorbate (0.0198 g, 0.10 mmol) and $CuSO_4 \cdot 5H_2O$ (0.0125 g, 0.05 mmol) in $(CH_3)_2SO$ (4 mL). The mixture was stirred and heated in a bath to 60 °C for 48 h. The reaction mixture was diluted with water (20 mL), extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with brine (2 × 10 mL), dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, Et_2O/LP 10:90 to 20:80) and the main fraction recrystallized from light petroleum where appropriate.

3.6.1. Preparations involving 3-(2-perfluorohexylethoxy)propyne 27

Propargyl ether **27** (0.40 g, 1.00 mmol) was made to react with the following sections.

3.6.1.1. 1-n-Butyl-4-(2-perfluorohexylethoxy)methyl-1H-1,2,3-triazole 7.

n-Butyl azide (0.20 g, 2.02 mmol) to give *1-n-butyl-4-(2-perfluorohexylethoxy)methyl-1H-1,2,3-triazole* **7** as a pale yellow oil (0.32 g, 64%). IR (neat): 3850, 3583, 3444, 3137, 2965, 2939, 2879, 2359, 2342, 1643, 1468, 1441, 1366, 1318, 1240, 1206, 1146, 1124, 1049, 1023, 951, 810, 708, 698, 652 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.95 (t, *J* 7.5 Hz, 3H, CH_3), 1.36 (qt, *J* 7.5, 7.2 Hz, 2H, CH_2CH_3), 1.89 (tt, *J* 7.5, 7.2 Hz, 2H, $N1CH_2CH_2$), 2.42 (tt, $^3J_{H-F}$ 18.5, $^3J_{H-H}$ 6.4 Hz, 2H, $OCH_2CH_2CF_2$), 3.82 (t, *J* 6.4 Hz, 2H, $OCH_2CH_2CF_2$), 4.36 (t, *J* 7.5 Hz, 2H, $N1CH_2CH_2$), 4.68 (s, 2H, 4-CH_2O), 7.52 (s, 1H,

H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.2 (CH_3), 19.6 (CH_2CH_3), 31.4 (t, $^2J_{C-F}$ 22.4 Hz, $OCH_2CH_2CF_2$), 32.1 ($N1CH_2CH_2$), 50.0 ($N1CH_2CH_2$), 62.1 (br, $OCH_2CH_2CF_2$), 64.5 (4-CH_2O), 122.2 (C5-H), 144.4 (C4). MS (ESI) m/z: 540.33 ([M+K]$^+$), 524.31 ([M+Na]$^+$). Anal. Calcd. for $C_{15}H_{16}F_{13}N_3O$ requires: C, 35.94; H, 3.22; N, 8.38%. Found: C, 35.95; H, 3.33; N, 8.12%.

3.6.1.2. 1-n-Hexyl-4-(2-perfluorohexylethoxy)methyl-1H-1,2,3-triazole **8**. *n*-Hexyl azide (0.25 g, 1.97 mmol) to give *1-n-hexyl-4-(2-perfluorohexylethoxy)methyl-1H-1,2,3-triazole* **8** as pale yellow wax (0.51 g, 97%) mp 31–32 °C. IR (KBr): 3130, 2960, 2935, 2862, 2362, 1466, 1445, 1368, 1320, 1238, 1208, 1192, 1145, 1124, 1107, 1091, 1057, 1008, 951, 844, 708, 700, 653 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, *J* 6.8 Hz, 3H, CH_3), 1.27 (m, 2H, CH_2CH_3), 1.31 (m, 4H, $N1CH_2CH_2(CH_2)_2$), 1.90 (tt, *J* 6.8, 6.8 Hz, 2H, $N1CH_2CH_2$), 2.42 (tt, $^3J_{H-F}$ 18.8, $^3J_{H-H}$ 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 3.82 (t, *J* 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 4.34 (t, *J* 7.5 Hz, 2H, $N1CH_2CH_2$), 4.67 (s, 2H, 4-CH_2O), 7.51 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.7 (CH_3), 22.3 (CH_2CH_3), 26.0 (CH_2), 30.1 (CH_2), 31.0 ($N1CH_2CH_2$), 31.4 (t, $^2J_{C-F}$ 21.7 Hz, $OCH_2CH_2CF_2$), 50.3 ($N1CH_2CH_2$), 62.1 (br, $OCH_2CH_2CF_2$), 64.5 (4-CH_2O), 122.2 (C5-H), 144.4 (C4). MS (ESI), m/z: 553.48 ([M+H+Na]$^+$, 30%), 552.53 ([M+Na]$^+$, 100). Anal. Calcd. for $C_{17}H_{20}F_{13}N_3O$ requires: C, 38.57; H, 3.81; N, 7.94%. Found: C, 38.95; H, 3.83; N, 7.72%.

3.6.1.3. 1-n-Octyl-4-(2-perfluorohexylethoxy)methyl-1H-1,2,3-triazole **9**. *n*-Octyl azide (0.31 g, 2.00 mmol) to give *1-n-octyl-4-(2-perfluorohexylethoxy)methyl)-1H-1,2,3-triazole* **9** as white powder (0.50 g, 90%) mp 34–35 °C. IR (KBr): 3132, 2958, 2928, 2856, 2360, 1542, 1466, 1368, 1322, 1237, 1192, 1144, 1124, 1109, 1092, 1057, 1006, 951, 835, 789, 731, 702, 654 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, *J* 6.8 Hz, 3H, CH_3), 1.26 (m, 6H, $(CH_2)_3CH_3$), 1.32 (m, 4H, $N1CH_2CH_2(CH_2)_2$), 1.90 (tt, *J* 7.2, 6.8 Hz, 2H, $N1CH_2CH_2$), 2.42 (tt, $^3J_{H-F}$ 18.8, $^3J_{H-H}$ 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 3.82 (t, *J* 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 4.34 (t, *J* 7.5 Hz, 2H, $N1CH_2CH_2$), 4.67 (s, 2H, 4-CH_2O), 7.51 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.8 (CH_3), 22.4 (CH_2CH_3), 26.3 (CH_2), 28.8 (CH_2), 30.2 (CH_2), 31.4 (t, $^2J_{C-F}$ 21.3 Hz, $OCH_2CH_2CF_2$), 31.7 ($N1CH_2CH_2$), 50.3 ($N1CH_2CH_2$), 62.1 (t, *J* 4.3 Hz, $OCH_2CH_2CF_2$), 64.5 (4-CH_2O), 122.2 (C5-H), 144.4 (C4). MS (ESI) m/z: 580.59 ([M+Na]$^+$, 100%). Anal. Calcd. for $C_{19}H_{24}F_{13}N_3O$ requires: C, 40.94; H, 4.59; N, 7.54%. Found: C, 41.25; H, 4.53; N, 7.29%.

3.6.1.4. 1-n-Nonyl-4-(2-perfluorohexylethoxy)methyl-1H-1,2,3-triazole **10**. *n*-Nonyl azide (0.58 g, 3.43 mmol) to give *1-n-nonyl-4-(2-perfluorohexylethoxy)methyl)-1H-1,2,3-triazole* **10** as white powder (0.47 g, 82%) mp 41–43 °C. IR (KBr): 3842, 3133, 2957, 2925, 2851, 2360, 2341, 1547, 1467, 1368, 1322, 1236, 1207, 1191, 1144, 1124, 1109, 1056, 1028, 843, 790, 732, 702, 654 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, *J* 6.4 Hz, 3H, CH_3), 1.25 (m, 8H, $(CH_2)_4CH_3$), 1.32 (m, 4H, $N1CH_2CH_2(CH_2)_2$), 1.90 (tt, *J* 7.2, 6.8 Hz, 2H, $N1CH_2CH_2$), 2.42 (tt, $^3J_{H-F}$ 18.8, $^3J_{H-H}$ 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 3.82 (t, *J* 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 4.34 (t, *J* 7.2 Hz, 2H, $N1CH_2CH_2$), 4.67 (s, 2H, 4-CH_2O), 7.51 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.9 (CH_3), 22.5 (CH_2CH_3), 26.4 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 30.2 (CH_2), 31.4 (t, $^2J_{C-F}$ 20.9 Hz, $OCH_2CH_2CF_2$), 31.7 ($N1CH_2CH_2$), 50.4 ($N1CH_2CH_2$), 62.1 (t, *J* 4.3 Hz, $OCH_2CH_2CF_2$), 64.5 (4-CH_2O), 122.2 (C5-H), 144.4 (C4). MS (ESI) m/z: 594.40 ([M+Na]$^+$). Anal. Calcd. for $C_{20}H_{26}F_{13}N_3O$ requires: C, 42.04; H, 4.59; N, 7.35%. Found: C, 42.28; H, 4.65; N, 7.34%.

3.6.1.5. 1-n-Benzyl-4-(2-perfluorohexylethoxy)methyl-1H-1,2,3-triazole **11**. Benzyl azide (0.27 g, 2.03 mmol) to give *1-benzyl-4-(2-perfluorohexylethoxy)methyl)-1H-1,2,3-triazole* **11** as white flakes (0.47 g, 88%) mp 53–55 °C. IR (KBr): 3566, 3128, 3090, 2909, 2362, 1717, 1559, 1458, 1367, 1235, 1209, 1189, 1142, 1091, 1060, 1012, 913, 860, 722, 699, 653 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (tt, $^3J_{H-F}$ 18.5, $^3J_{H-H}$ 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 3.80 (t, *J* 6.8 Hz, 2H, $OCH_2CH_2CF_2$), 4.64 (s, 2H, 4-CH_2O), 5.53 (s, 2H, $N1CH_2C_6H_5$), 7.28 (m, 2H, $N1CH_2C_6H_5$-*ortho*), 7.36 (m, 1H, $N1CH_2C_6H_5$-*para*), 7.37 (m, 2H, $N1CH_2C_6H_5$-*meta*), 7.44 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.4 (t, $^2J_{C-F}$ 20.9 Hz, $OCH_2CH_2CF_2$), 54.2 ($N1CH_2C_6H_5$), 62.2 (t, *J* 4.3 Hz, $OCH_2CH_2CF_2$), 64.5 (4-CH_2O), 122.3 (C5-H), 128.0 ($N1CH_2C_6H_5$-*ortho*), 128.7 ($N1CH_2C_6H_5$-*para*), 129.0 ($N1CH_2C_6H_5$-*meta*), 134.3 ($N1CH_2C_6H_5$-*ipso*), 144.9 (C4). MS (ESI) m/z: 558.33 ([M+Na]$^+$, 100%). Anal. Calcd. for $C_{18}H_{14}F_{13}N_3O$ requires: C, 40.39; H, 2.64; N, 7.85%. Found: C, 40.21; H, 2.68; N, 7.76%.

3.6.2. Preparations involving 3-(perfluoroheptylmethoxy)propyne **28**

Propargyl ether **28** (0.44 g, 1.00 mmol) was made to react with the following sections.

3.6.2.1. 1-n-Butyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole **12**. *n*-Butyl azide (0.20 g, 2.02 mmol) to give *1-n-butyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole* **12** as pale yellow oil (0.45 g, 84%). IR (neat): 3850, 3685, 3583, 3138, 2965, 2940, 2880, 1642, 1552, 1468, 1366, 1327, 1241, 1210, 1150, 1051, 1030, 992, 953, 808, 711, 698, 658 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.96 (t, *J* 7.5 Hz, 3H, CH_3), 1.36 (qt, *J* 7.5, 7.2 Hz, 2H, CH_2CH_3), 1.89 (tt, *J* 7.3, 7.2 Hz, 2H, $N1CH_2CH_2$), 4.03 (t, $^3J_{H-F}$ 13.9 Hz, 2H, OCH_2CF_2), 4.37 (t, *J* 7.3 Hz, 2H, $N1CH_2CH_2$), 4.80 (s, 2H, 4-CH_2O), 7.56 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.1 (CH_3), 19.5 (CH_2CH_3), 32.1 ($N1CH_2CH_2$), 50.0 ($N1CH_2CH_2$), 65.6 (4-CH_2O), 66.7 (t, $^2J_{C-F}$ 25.3 Hz, OCH_2CF_2), 122.5 (C5-H), 143.4 (C4). MS (ESI) m/z: 560.45 ([M+Na]$^+$, 100%). Anal. Calcd. for $C_{15}H_{14}F_{15}N_3O$ requires: C, 33.53; H, 2.63; N, 7.82%. Found: C, 33.82; H, 2.66; N, 7.53%.

3.6.2.2. 1-n-Hexyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole **13**. *n*-Hexyl azide (0.25 g, 1.97 mmol) to give *1-n-hexyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole* **13** as a pale yellow wax (0.50 g, 88%) mp 29–31 °C. IR (neat): 3616, 3132, 2958, 2932, 2862, 2360, 1563, 1468, 1369, 1329, 1207, 1147, 1058, 1028, 992, 956, 808, 701, 659 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.88 (t, *J* 6.8 Hz, 3H, CH_3), 1.20–1.40 (m, 6H, $(CH_2)_3CH_3$), 1.91 (tt, *J* 7.2, 7.2 Hz, 2H, $N1CH_2CH_2$), 4.02 (t, $^3J_{H-F}$ 13.6 Hz, 2H, OCH_2CF_2), 4.36 (t, *J* 7.2 Hz, 2H, $N1CH_2CH_2$), 4.80 (s, 2H, 4-CH_2O), 7.55 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.6 (CH_3), 22.2 (CH_2CH_3), 26.0 (CH_2), 30.1 (CH_2), 30.9 ($N1CH_2CH_2$), 50.4 ($N1CH_2CH_2$), 65.6 (4-CH_2O), 66.7 (t, $^2J_{C-F}$ 25.3 Hz, OCH_2CF_2), 122.4 (C5-H), 143.5 (C4). MS (ESI) m/z: 589.52 ([M+H+Na]$^+$, 4%), 588.58 ([M+Na]$^+$, 100). Anal. Calcd. for $C_{17}H_{18}F_{15}N_3O$ requires: C, 36.12; H, 3.21; N, 7.43%. Found: C, 36.35; H, 3.36; N, 7.37%.

3.6.2.3. 1-n-Octyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole **14**. *n*-Octyl azide (0.31 g, 2.00 mmol) to give *1-n-octyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole* **14** as white powder (0.49 g, 82%) mp 39–40 °C. IR (neat): 3648, 3093, 2956, 2926, 2852, 2360, 1716, 1684, 1558, 1466, 1371, 1329, 1204, 1146, 1058, 1027, 991, 957, 886, 807, 703, 660 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, *J* 6.8 Hz, 3H, CH_3), 1.26 (m, 6H, $(CH_2)_3CH_3$), 1.32 (m, 4H, $N1CH_2CH_2(CH_2)_2$), 1.91 (tt, *J* 7.2, 6.8 Hz, 2H, $N1CH_2CH_2$), 4.03 (t, $^3J_{H-F}$ 13.6 Hz, 2H, OCH_2CF_2), 4.36 (t, *J* 7.2 Hz, 2H, $N1CH_2CH_2$), 4.81 (s, 2H, 4-CH_2O), 7.55 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.9 (CH_3), 22.5 (CH_2CH_3), 26.3 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 30.1 (CH_2), 31.7 ($N1CH_2CH_2$), 50.4 ($N1CH_2CH_2$), 65.6 (4-CH_2O), 66.7 (t, $^2J_{C-F}$ 25.3 Hz, OCH_2CF_2), 122.6 (C5-H), 143.5 (C4). HR-MS (ESI): Calcd. for $2 \times C_{19}H_{22}F_{15}N_3O$–2H+Na: m/z 1207.2790. Found: m/z 1207.2738 ($2 \times$ M–2H+Na]+, 9%); Calcd. for $C_{19}H_{22}F_{15}N_3O$+Na: m/z 616.1422. Found: m/z 616.1422 ([M+Na]$^+$, 100).

3.6.2.4. 1-n-Nonyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole **15**. *n*-Nonyl azide (0.58 g, 3.43 mmol) to give *1-n-nonyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole* **15** as a white

powder (0.49 g, 81%) mp 55–56 °C. IR (neat): 3134, 2954, 2921, 2849, 1560, 1467, 1371, 1329, 1206, 1147, 1132, 1105, 1026, 990, 886, 808, 703, 661 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.87 (t, J 6.8 Hz, 3H, CH_3), 1.26 (m, 8H, $(CH_2)_4CH_3$), 1.32 (m, 4H, $N1CH_2CH_2(CH_2)_2$), 1.91 (tt, J 7.2, 6.8 Hz, 2H, $N1CH_2CH_2$), 4.03 (t, $^3J_{H-F}$ 13.6 Hz, 2H, OCH_2CF_2), 4.36 (t, J 7.2 Hz, 2H, $N1CH_2CH_2$), 4.80 (s, 2H, 4-CH_2O), 7.55 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.9 (CH_3), 22.5 (CH_2CH_3), 26.3 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 30.1 (CH_2), 31.7 ($N1CH_2CH_2$), 50.4 ($N1CH_2CH_2$), 65.6 (4-CH_2O), 66.7 (t, $^2J_{C-F}$ 25.3 Hz, OCH_2CF_2), 122.6 (C5-H), 143.5 (C4). MS (ESI) m/z: 1237.3211 ([2M+Na]$^+$, 100%; 2 × $C_{20}H_{24}F_{15}N_3O$+Na requires m/z: 1237.3260), 630.1592 ([M+Na]$^+$, 57; $C_{20}H_{24}F_{15}N_3O$+Na requires m/z 630.1579). Anal. Calcd. for $C_{20}H_{24}F_{15}N_3O$ requires: C, 39.55; H, 3.98; N, 6.92%. Found: C, 39.56; H, 3.94; N, 6.75%.

3.6.2.5. 1-n-Benzyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole **16**. Benzyl azide (0.27 g, 2.03 mmol) to give *1-benzyl-4-(perfluoroheptylmethoxy)methyl-1H-1,2,3-triazole* **16** as white needles (0.42 g, 74%) mp 70–71 °C. IR (KBr): 3648, 3126, 3089, 1716, 1684, 1647, 1558, 1473, 1458, 1370, 1326, 1250, 1202, 1142, 1129, 1111, 1065, 1018, 990, 867, 723, 698, 659 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 4.02 (t, $^3J_{H-F}$ 13.9 Hz, 2H, OCH_2CF_2), 4.78 (s, 2H, 4-CH_2O), 5.54 (s, 2H, $N1CH_2C_6H_5$), 7.28 (m, 5H, $N1CH_2C_6H_5$-*ortho*), 7.37 (m, 5H, $N1CH_2C_6H_5$-*para*), 7.44 (m, 5H, $N1CH_2C_6H_5$-*meta*), 7.50 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 54.2 ($N1CH_2C_6H_5$), 65.6 (4-CH_2O), 66.8 (t, $^2J_{C-F}$ 26.0 Hz, OCH_2CF_2), 122.7 (C5-H), 128.0 ($N1CH_2C_6H_5$-*ortho*), 128.8 ($N1CH_2C_6H_5$-*para*), 129.1 ($N1CH_2C_6H_5$-*meta*), 134.2 ($N1CH_2C_6H_5$-*ipso*), 144.1 (C4). HR-MS (ESI) Calcd. for 2 × $C_{18}H_{12}F_{15}N_3O$+Na: m/z 1165.1380. Found: m/z 1165.1246 ([2M+Na]$^+$, 100%); Calcd. for $C_{18}H_{12}F_{15}N_3O$+Na: m/z 594.0639. Found: m/z 594.0632 ([M+Na]$^+$, 40); Anal. Calcd. for $C_{18}H_{12}F_{15}N_3O$ requires: C, 37.84; H, 2.12; N, 7.36%. Found: C, 37.91; H, 2.32; N, 7.19%.

3.7. Preparation of bis-triazolyl ethers 33–36

3.7.1. 4-Hydroxymethyl-1-n-octyl-1H-1,2,3-triazole **30**

Following a modification of the method of Rostovtsev et al. [31(a)], $CuSO_4{\cdot}5H_2O$ (0.13 g, 2 mmol) and Na ascorbate (0.20 g, 1 mmol) were added to $(CH_3)_2SO$ (20 mL) and the mixture stirred for 5 min at r.t. Propargyl alcohol (1.24 mL, 1.20 g, 22 mmol) was added dropwise with continued stirring, followed after 2 min by dropwise addition of a solution of azide **24** (3.10 g, 20 mmol) in $(CH_3)_2SO$ (80 mL). The reaction mixture was heated in an oil bath at 65 °C for 24 h then quenched with H_2O (50 mL) and extracted with Et_2O (3 × 50 mL). The organic phases were combined and washed sequentially with brine (2 × 50 mL), H_2O (50 mL), and more brine (50 mL), then dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The resulting brown liquid crystallized at r.t. and was flash chromatographed on silica gel using an Et_2O/light petroleum gradient (10:90 to 20:80). The major product (2.70 g) was recrystallized from pentane to give *4-hydroxymethyl-1-n-octyl-1H-1,2,3-triazole* **30** as white plates (2.12 g, 50%) mp 40–42 °C (lit. [35]: mp 46–49 °C). IR (Nujol) ν_{max} 3310, 3208, 3132, 1336, 1297, 1257, 1220, 1212, 1147, 1055, 1043, 1017, 843, 784, 726, 675, 657 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.86 (t, J 6.5 Hz, 3H, CH_2CH_3), 1.24 (m, 6H, $(CH_2)_3CH_3$), 1.30 (m, 4H, $N1CH_2CH_2(CH_2)_2$), 1.88 (tt, J 7.2, 6.9 Hz, 2H, $N1CH_2CH_2CH_2$), 4.02 (s, 1H, OH), 4.33 (t, J 7.2 Hz, 2H, $N1CH_2CH_2CH_2$), 4.77 (s, 2H, 4-CH_2OH), 7.57 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.2 (CH_3), 22.7 (CH_2CH_3), 26.6 (CH_2), 29.05 (CH_2), 29.14 (CH_2), 30.3 (CH_2), 31.8 ($N1CH_2CH_2$), 50.8 ($N1CH_2CH_2$), 56.2 (4-CH_2OH), 122.0 (C5-H), 147.6 (C4). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ: 14.0 (CH_3), 22.2 (CH_2CH_3), 25.9 (CH_2), 28.5 (CH_2), 28.6 (CH_2), 29.9 (CH_2), 31.3 ($N1CH_2CH_2$), 49.3 ($N1CH_2CH_2$), 55.2 (4-CH_2OH), 122.7 (C5-H), 148.0 (C4). MS (ESI) m/z: 235.15 ([M+H+Na]$^+$, 12%); 234.20 ([M+Na]$^+$, 100); 212.16 ([M+H]$^+$, 7). Anal. Calcd. for $C_{11}H_{21}N_3O$ requires: C, 62.51; H, 10.04; N, 19.89%. Found: C, 62.89; H, 10.30; N, 19.98%.

3.7.2. 1-n-Octyl-4-((prop-2-ynyloxy)methyl)-1H-1,2,3-triazole **31**

Following a method reported by Jones et al. [36(a)], triazolyl alcohol **30** (0.35 g, 1.7 mmol) was dissolved in dry DMF (10 mL) and crushed NaOH pellets (0.25 g, 6.3 mmol) were added. The mixture was stirred vigorously for 15 min in an ice bath under Ar, then propargyl bromide (0.20 mL of 80% solution in toluene, 0.214 g, 1.8 mmol) was added dropwise and the heterogeneous reaction mixture was stirred vigorously for 48 h, slowly warming to r.t. H_2O (30 mL) was added and the product was extracted with EtOAc (4 × 50 mL). The organic phases were combined and washed sequentially with 3% HCl (2 × 30 mL) and H_2O (30 mL). The organic phase was dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The resulting dark orange liquid (0.31 g) was flash chromatographed over silica gel (Et_2O/hexane, 50:50) to generate *(1-n-octyl-4-((prop-2-ynyloxy)methyl)-1H-1,2,3-triazole* **31** as a pale orange oil (0.27 g, 67%), which decomposed upon attempted vacuum distillation. IR (neat) ν_{max}: 3290, 3138, 2926, 2856, 2114, 1466, 1338, 1359, 1263, 1222, 1142, 1084, 1051, 1024, 942, 908, 891, 820, 784, 723, 665, 570 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.84 (t, J 6.4 Hz, 3H, CH_3), 1.27 (m, 10H, $(CH_2)_5CH_3$), 1.87 (m, 2H, $N1CH_2CH_2$), 2.45 (t, J 2.4 Hz, 1H, OCH_2CCH), 4.20 (d, J 2.4 Hz, 2H, OCH_2CCH), 4.32 (t, J 7.2 Hz, 2H, $N1CH_2CH_2$), 4.71 (s, 2H, 4-CH_2O), 7.54 (s, 1H, H5). ^{13}C NMR (75 MHz) δ: 14.0 (CH_3), 22.5 (CH_2CH_3), 26.4 (CH_3), 28.9 (CH_2), 29.0 (CH_2), 30.2 (CH_2), 31.6 ($N1CH_2CH_2$), 50.4 ($N1CH_2CH_2$), 57.4 (4-CH_2O), 63.0 (OCH_2CCH), 74.9 (OCH_2CCH), 79.3 (OCH_2CCH), 122.6 (C5-H), 144.2 (C4). MS (ESI) m/z: 521.22 ([2M+Na]$^+$, 15%), 273.03 ([M+H+Na]$^+$, 17), 272.12 ([M+Na]$^+$, 100), 250.27 ([M+H]$^+$, 15). Anal. Calcd. for $C_{14}H_{23}N_3O$ requires: C, 67.43; H, 9.30; N, 16.86%. Found: C, 67.46; H, 9.61; N, 17.00%.

3.7.3. General method for the reaction of propargyl ether **31** *with perfluoroalkylethyl azides* **17**, **18** *and* **19** *and perfluoroheptylmethyl azide* **32**

Propargyl ether **31** (0.18 g, 0.72 mmol) and perfluorobutylethyl azide **17** [13] (0.20 g, 0.69 mmol), perfluorohexylethyl azide **18** (0.28 g, 0.72 mmol), perfluorooctylethyl azide **19** [13] (0.34 g, 0.70 mmol) or perfluoroheptylmethyl azide **32** (0.31 g, 0.73 mmol) were added to a stirred suspension of sodium ascorbate (0.022 g, 0.09 mmol) and $CuSO_4{\cdot}5H_2O$ (0.012 g, 0.045 mmol) in $(CH_3)_2SO$ (8 mL). The mixture was stirred with heating in a bath at 65 °C for 48 h. The reaction mixture was diluted with H_2O (20 mL) and the solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with H_2O (2 × 10 mL), dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was rapidly column chromatographed on silica gel and the major fraction recrystallized.

3.7.3.1. 4-(((1-n-Octyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluorobutyl)ethyl)-1H-1,2,3-triazole **33**. Perfluorobutylethyl azide **17** afforded the crude product as a low melting yellow solid. The solid was chromatographed on silica gel and the major fraction (0.21 g), eluted with 33:67 EtOAc/Et_2O and recrystallized from pentane, yielded *4-(((1-n-octyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluorobutyl)ethyl)-1H-1,2,3-triazole* **33** as a white crystalline powder (0.26 g, 70%) mp 68–70 °C. IR (Nujol): ν_{max} 2724, 2359, 1306, 1228, 1214, 1171, 1131, 1097, 1051, 1018, 989, 859, 815, 746, 724, 708 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.85 (t, J 6.6 Hz, 3H, CH_3CH_2), 1.24 (m, 6H, $(CH_2)_3CH_3$), 1.29 (m, 4H, $N1'CH_2CH_2(CH_2)_2$), 1.88 (tt, J 7.2, 6.9 Hz, 2H, $N1'CH_2CH_2CH_2$), 2.88 (tt, $^3J_{H-F}$ 18.0, $^3J_{H-H}$ 7.4 Hz, 2H, $N1CH_2CH_2CF_2$), 4.32 (t, J 7.2 Hz, 2H, $N1'CH_2CH_2CH_2$), 4.66 (dd, J 7.5, 7.4 Hz, 2H, $N1CH_2CH_2CF_2$), 4.69 (s, 2H, 4′-CH_2O), 4.70 (s, 2H, 4-CH_2O), 7.57 (s, 1H, H5′ from N-alkyl

ring), 7.68 (s, 1H, H5 from N-perfluorobutylethyl ring). ^{13}C NMR (100.1 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.7 (CH_2CH_3), 26.6 ($CH_2CH_2CH_3$), 29.0 (CH_2), 29.1 (CH_2), 30.3 (CH_2), 31.78 (N1′$CH_2CH_2CH_2$), 31.82 (t, $^2J_{C-F}$ 21.8 Hz, N1$CH_2CH_2CF_2$), 42.4 (t, $^3J_{C-F}$ 5 Hz, N1$CH_2CH_2CF_2$), 50.7 (N1′$CH_2CH_2CH_2$), 63.48 (4′-CH_2O),[a] 63.53 (4-CH_2O),[a] 123.0 (br, C5′-H), 123.6 (C5-H) 144.3 (br, C4′), 145.1 (C4). MS (ESI) *m/z*: 561.11 ([M+Na]$^+$, 9%), 540.07 ([M+2H]$^+$, 26), 539.15 ([M+H]$^+$, 100), 538.53 ([M]$^+$, 94). [aNote: assignments of ^{13}C NMR signals at δ 63.48 and 63.53 are likely, but might be interchanged and could not be confirmed spectroscopically.] Anal. Calcd. for $C_{20}H_{27}F_9N_6O$ requires C, 44.61; H, 5.05; N, 15.61%. Found: C, 44.79; H, 4.99; N, 15.64%.

3.7.3.2. 4-(((1-n-Octyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluorohexyl)ethyl)-1H-1,2,3-triazole **34**. Perfluorohexylethyl azide **18** afforded the crude product as a pale yellow solid, which when eluted from the silica gel column with 33:67 EtOAc/Et_2O afforded the major fraction that crystallized from pentane to yield *4-(((1-n-octyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluorohexyl)ethyl)-1H-1,2,3-triazole* **34** as white crystalline powder (0.21 g, 46%) mp 88–90 °C. IR (Nujol): ν_{max} 3132, 3086, 1398, 1324, 1236, 1140, 1123, 1098, 1081, 1054, 1031, 1003, 989, 918, 850, 815, 728, 714, 703, 660, 635, 567 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, *J* 6.6 Hz, 3H, CH_3CH_2), 1.22 (m, 6H, (CH_2)$_3CH_3$), 1.28 (m, 4H, N1′CH_2CH_2(CH_2)$_2$), 1.86 (tt, *J* 7.3, 6.9 Hz, 2H, N1′$CH_2CH_2CH_2$), 2.79 (tt, $^3J_{H-F}$ 18.0, $^3J_{H-H}$ 7.5 Hz, 2H, N1$CH_2CH_2CF_2$), 4.31 (t, *J* 7.3 Hz, 2H, N1′$CH_2CH_2CH_2$), 4.65 (dd, *J ca.* 7.5, *ca.* 7.4 Hz, 2H, N1$CH_2CH_2CF_2$), 4.67 (s, 2H, 4′-CH_2O), 4.68 (s, 2H, 4-CH_2O), 7.58 (s, 1H, H5′ from N-alkyl ring), 7.70 (s, 1H, H5 from N-perfluorohexyl ring). ^{13}C NMR (100.1 MHz, $CDCl_3$): δ 14.0 (CH_3), 22.6 (CH_2CH_3), 26.5 ($CH_2CH_2CH_3$), 29.0 (CH_2), 29.1 (CH_2), 30.3 (CH_2), 31.7 (N1′$CH_2CH_2CH_2$), 31.9 (t, $^2J_{C-F}$ 21.7 Hz, N1$CH_2CH_2CF_2$), 42.4 (t, $^3J_{C-F}$ 5.1 Hz, N1$CH_2CH_2CF_2$), 50.6 (N1′$CH_2CH_2CH_2$), 63.46 (4-CH_2O), 63.50 (4′-CH_2O), 122.9 (C5′-H), 123.6 (C5-H), 144.3 (C4′), 145.1 (C4). MS (ESI) *m/z*: 561.11 ([M+Na]$^+$, 10%), 540.07 ([M+2H]$^+$, 25), 539.11 ([M+H]$^+$, 100), 538.86 ([M]$^+$, 95). Anal. Calcd. for $C_{22}H_{27}F_{13}N_6O$ requires C, 41.38; H, 4.26; N, 13.16%. Found: C, 41.58; H, 4.01; N, 13.04%.

3.7.3.3. 4-(((1-n-Octyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluorooctyl)ethyl)-1H-1,2,3-triazole **35**. Perfluorooctylethyl azide **19** afforded the crude product as a pale yellow solid, which when eluted from the silica gel column with 33:67 EtOAc/Et_2O yielded *4-(((1-n-octyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluorooctyl)ethyl)-1H-1,2,3-triazole* **35** as white crystalline powder (0.21 g, 41%) mp 104–106 °C. IR (Nujol): ν_{max} 3131, 3083, 2426, 2252, 1905, 1694, 1562, 1418, 1375, 1336, 1200, 1146, 1099, 1056, 1003, 989, 958, 907, 852, 824, 774, 736, 690, 654, 560 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.85 (t, *J* 6.8 Hz, 3H, CH_3CH_2), 1.25 (m, 6H, (CH_2)$_3CH_3$), 1.30 (m, 4H, N1′CH_2CH_2(CH_2)$_2$), 1.88 (tt, *J* 7.2, 6.4 Hz, 2H, N1′$CH_2CH_2CH_2$), 2.81 (tt, $^3J_{H-F}$ 17.9, $^3J_{H-H}$ 7.5 Hz, 2H, N1$CH_2CH_2CF_2$), 4.33 (t, *J* 7.2 Hz, 2H, N1′$CH_2CH_2CH_2$), 4.66 (dd, *J* 7.7, 7.4 Hz, 2H, N1$CH_2CH_2CF_2$), 4.70 (s, 4H, 4-CH_2O and 4′-CH_2O), 7.58 (s, 1H, H5′ from N-alkyl ring), 7.69 (s, 1H, H5 from N-perfluorooctyl ring). ^{13}C NMR (100.1 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.7 (CH_2CH_3), 26.6 ($CH_2CH_2CH_3$), 29.0 (CH_2), 29.1 (CH_2), 30.4 (CH_2), 31.8 (N1′$CH_2CH_2CH_2$), 31.9 (t, $^2J_{C-F}$ 22.0 Hz, N1$CH_2CH_2CF_2$), 42.4 (t, $^3J_{C-F}$ 4.1 Hz, N1$CH_2CH_2CF_2$), 50.7 (N1′$CH_2CH_2CH_2$), 63.51 (4-CH_2O) 63.54 (4′-CH_2O), 123.0 (C5′-H), 123.7 (C5-H) 144.4 (C4′), 145.2 (C4). MS (ESI) *m/z*: 561.11 ([M+Na]$^+$, 10%), 540.07 ([M+2H]$^+$, 25), 539.11 ([M+H]$^+$, 100), 538.86 (M$^+$, 95). Anal. Calcd. for $C_{24}H_{27}F_{17}N_6O_2$ requires C, 39.03; H, 3.69; N, 11.38%. Found: C, 38.88; H, 3.60; N, 11.20%.

3.7.3.4. 4-(((1-n-Octyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-((perfluoroheptyl)methyl)-1H-1,2,3-triazole **36**. Perfluoroheptylmethyl azide **32** afforded the crude product as pale yellow solid, which when eluted from the silica gel column with 33:67 EtOAc/Et_2O yielded *4-(((1-n-octyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluoroheptyl)methyl)-1H-1,2,3-triazole* **36** as white crystalline powder (0.15 g, 31%) mp 114–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, *J* 6.5 Hz, 3H, CH_3CH_2), 1.25 (m, 6H, (CH_2)$_3CH_3$), 1.30 (m, 4H, N1′CH_2CH_2(CH_2)$_2$), 1.89 (tt, *J* 6.7, 6.7 Hz, 2H, N1′$CH_2CH_2CH_2$), 4.33 (t, *J* 7.2 Hz, 2H, N1′$CH_2CH_2CH_2$), 4.71 (s, 2H, 4′-CH_2O), 4.73 (s, 2H, 4-CH_2O), 5.05 (t, $^3J_{H-F}$ 14.8 Hz, NCH_2CF_2), 7.58 (br s, 1H, H5′ from N-alkyl ring), 7.78 (s, 1H, H5 from N-perfluoroheptylmethyl ring). ^{13}C NMR (100.1 MHz, $CDCl_3$) δ: 14.1 (CH_3), 22.7 (CH_2CH_3), 26.6 ($CH_2CH_2CH_3$), 29.0 (CH_2), 29.1 (CH_2), 30.3 (CH_2), 31.8 (N1′$CH_2CH_2CH_2$), 49.4 (t, $^2J_{C-F}$ 23 Hz, NCH_2CF_2), 50.8 (N1′$CH_2CH_2CH_2$), 63.5 (2C, 4-CH_2O and 4′-CH_2O), 123.1 (br, C5′-H), 124.7 (C5-H) 144.4 (br, C4′), 145.8 (C4). HR-MS (ESI) (Found *m/z*: 1371.3598 ([2M+Na]$^+$, 100%), 697.1727 ([M+Na]$^+$, 28). $C_{22}H_{27}N_6OF_{13}$ requires *m/z*: 1371.3598 ([2M+Na]$^+$), 697.1748 ([M+Na]$^+$). Anal. Calcd. for $C_{22}H_{25}F_{15}N_6O_2$ requires C, 39.18; H, 3.74; N, 12.46%. Found: C, 39.18; H, 3.58; N, 12.25%.

3.8. Preparation of 4-(((1-n-nonyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluorooctyl)ethyl)-1H-1,2,3-triazole 38

3.8.1. 4-Hydroxymethyl-1-n-nonyl-1H-1,2,3-triazole 37

Propargyl alcohol **29** (0.58 mL, 10 mmol) was added dropwise to a solution of sodium ascorbate (0.178 g, 0.90 mmol) and $CuSO_4{\cdot}5H_2O$ (0.112 g, 0.45 mmol) in $(CH_3)_2SO$ (25 mL). The bright yellow-green solution was stirred for 1 min before nonyl azide **25** (1.70 g, 10 mmol) was added dropwise, then stirring was continued in a bath at 70 °C for 36 h. The reaction mixture was diluted with water (75 mL), extracted with EtOAc (3 × 50 mL), the combined organic layers were washed with brine (2 × 25 mL), dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, Et_2O/EtOAc 1:1) to give *4-hydroxymethyl-1-n-nonyl-1H-1,2,3-triazole* **37** [38] (1.87 g, 79%) mp 55–57 °C (Et_2O/light petroleum). IR (Nujol): 3301, 3195, 3131, 2922, 2853, 1463, 1376, 1218, 1144, 1055, 1046, 1018, 724 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.84 (t, *J* 6.6 Hz, 3H, CH_2CH_3), 1.22 (m, 8H, (CH_2)$_4CH_3$), 1.27 (m, 4H, N1CH_2CH_2(CH_2)$_2$), 1.85 (tt, *J* 7.2, 6.9 Hz, 2H, N1$CH_2CH_2CH_2$), 4.25 (s, 1H, OH), 4.29 (t, *J* 7.2 Hz, 2H, N1$CH_2CH_2CH_2$), 4.74 (s, 2H, 4-CH_2OH), 7.55 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0 (CH_3), 22.5 (CH_2CH_3), 26.4 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 30.1 (CH_2), 31.7 (N1CH_2CH_2), 50.4 (N1CH_2CH_2), 55.9 (4-CH_2OH), 121.7 (C5-H), 147.7 (C4). MS (ESI) *m/z*: 473.11 ([2M+Na]$^+$, 22%), 263.99 ([M+K]$^+$, 7), 249.22 ([M+H+Na]$^+$, 16), 248.14 ([M+Na]$^+$, 100), 226.18 ([M+H]$^+$, 13). Anal. Calcd. for $C_{12}H_{23}N_3O$ requires C, 63.99; H, 10.29; N, 18.65%. Found: C, 63.59, H, 10.37; N, 18.29%.

3.8.2. 1-n-Nonyl-4-((prop-2-ynyloxy)methyl)-1H-1,2,3-triazole 38

Alcohol **37** (0.53 g, 2.35 mmol) was dissolved in DMF (10 mL) and powdered NaOH pellets (0.32 g, 8.0 mmol) were added. The contents were stirred in a salt-ice bath for 10 min then propargyl bromide (0.25 mL, 2.82 mmol) was added dropwise. The reaction mixture allowed to stir for 24 h, gradually warming to r.t. The reaction mixture was partitioned between Et_2O (30 mL) and water (50 mL) and the aqueous layer extracted with more Et_2O (3 × 30 mL). The combined organic extracts were dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, Et_2O/light petroleum 1:1) to give *1-n-nonyl-4-((prop-2-ynyloxy)methyl)-1H-1,2,3-triazole* **38** as needles (0.42 g, 68%) mp 77–79 °C (Et_2O/light petroleum). IR (Nujol): 3278, 3089, 2922, 2853, 2108, 1460, 1376, 1224, 1153, 1103, 1059, 1027, 935, 730 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86 (t, *J* 6.9 Hz, 3H, CH_2CH_3), 1.24 (m, 8H, (CH_2)$_4$), 1.30 (m, 4H, (CH_2)$_2$), 1.89 (tt, *J* 7.2, 7.0 Hz, 2H, CH_2CH_2N), 2.46 (t, *J* 2.4 Hz, 1H, OCH$_2$CC*H*), 4.22 (d, *J* 2.4 Hz, 2H, OCH_2CCH), 4.34 (t, *J* 7.2 Hz, 2H,

CH_2N), 4.74 (d, *J* 0.5 Hz, 2H, 4-CH_2O), 7.56 (s, 1H, H5). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0 (CH_3), 22.6 (CH_2CH_3), 26.4 (CH_3), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 30.2 (CH_2), 31.7 (N1CH_2CH_2), 50.5 (N1CH_2CH_2), 57.5 (4-CH_2O), 62.9 (OCH_2CCH), 74.9 (OCH_2CCH), 79.2 (OCH_2CCH), 122.6 (C5-H), 144.1 (C4). MS (ESI) *m*/*z*: 286.08 ([M+Na]$^+$, 39%), 264.24 ([M+H]$^+$, 46). Anal. Calcd. for $C_{15}H_{25}N_3O$ requires C, 68.40; H, 9.57; N, 15.95%. Found: C, 68.70; H, 9.84; N, 15.86%.

3.8.3. 4-(((1-n-Nonyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)-1-(2-(perfluorooctyl)ethyl)-1H-1,2,3-triazole ***39***

Propargyl ether **38** (0.263 g, 1.0 mmol) and perfluorooctylethyl azide **19** (0.49 g, 2.0 mmol) were added to a stirred suspension of sodium ascorbate (0.018 g, 0.09 mmol) and $CuSO_4{\cdot}5H_2O$ (0.012 g, 0.048 mmol) in $(CH_3)_2SO$ (15 mL). The mixture was stirred with heating in a bath at 85 °C for 48 h. The reaction mixture was diluted with H_2O (30 mL), extracted with EtOAc (3 × 30 mL), and the combined organic layers were washed with brine (2 × 20 mL), dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, Et_2O/EtOAc 1:1) to yield *4-(((1-n-nonyl-1H-1,2,3-triazol-4-yl)methoxy)-methyl)-1-(2-(perfluorooctyl)ethyl)-1H-1,2,3–triazole* **39** as white prisms (0.55 g, 73%) mp 117–119 °C (pentane). IR (Nujol): 3131, 3081, 2924, 2724, 1563, 1459, 1376, 1336, 1220, 1200, 1146, 1116, 1099, 1055, 1041, 1031, 1003, 988, 956, 850, 723 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86 (t, *J* 6.9 Hz, 3H, CH_3CH$_2$), 1.25 (m, 8H, (CH_2)$_4$CH$_3$), 1.31 (m, 4H, N1′CH$_2$CH$_2$(CH_2)$_2$), 1.90 (tt, *J* 7.3, 6.9 Hz, 2H, N1′CH$_2$CH_2CH$_2$), 2.82 (m, 2H, N1CH$_2$CH_2CF$_2$), 4.34 (t, *J* 7.3 Hz, 2H, N1′CH_2CH$_2$CH$_2$), 4.68 (dd, *J* 7.5, 7.4 Hz, 2H, N1CH_2CH$_2$CF$_2$), 4.72 (br s, 4H, 4-CH_2O and 4′-CH_2O), 7.61 (br s, 1H, H5′ from N-alkyl ring), 7.71 (br s, 1H, H5 from N-perfluorooctyl ring). ^{19}F NMR (282 MHz, $CDCl_3$) δ: −81.2 (t, 3F), −114.5 (t, 2F), −122.2 (m, 6F), −123.1 (s, 2F), −123.8 (s, 2F), −126.4 (m, 2F). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.0 (CH_3), 22.6 (CH_2CH$_3$), 26.4 (CH_2CH$_2$CH$_3$), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 30.2 (CH_2), 31.75 (N1′CH$_2$CH_2CH$_2$), 31.80 (t, $^2J_{C-F}$ 22.1 Hz, N1CH$_2$CH_2CF$_2$), 42.3 (br, N1CH_2CH$_2$CF$_2$), 50.6 (N1′CH_2CH$_2$CH$_2$), 63.3 (4′-CH_2O) 63.4 (4-CH_2O), 122.9 (C5′-H), 123.5 (C5-H) 144.2 (C4′), 145.0 (C4). MS (ESI) *m*/*z*: 791.43 ([M+K]$^+$, 22%), 776.06 ([M+H+Na]$^+$, 23), 774.98 ([M+H]$^+$, 100), 752.87 (M$^+$, 16). Anal. Calcd. for $C_{25}H_{29}F_{17}N_6O$ requires C, 39.90; H, 3.88; N, 11.17%. Found: C, 39.95; H, 3.67; N, 11.09%.

Acknowledgements

This work was financially supported by Australian Research Council Discovery Project Grant DP0346614 and the University of New South Wales. High resolution mass spectrometric analysis for this work was carried out at the Bioanalytical Mass Spectrometry Facility, UNSW, and was supported in part by infrastructure funding from the New South Wales Government as part of its co-investment in the National Collaborative Research Infrastructure Strategy. A.I.M. was generously supported through an Australian Research Council Endeavour Postdoctoral Research Fellowship Award. Ms. Berta Litvak is thanked for her English language translation of Ref. [38].

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.07.002.

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