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ACCESSORY PUBLICATION

Efficient Alkylation Methods for the Synthesis of Hybrid Fluorocarbon-Hydrocarbon Tetrazoles as Potential Fluorinated Surfactants

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Full Experimental Conditions and Compound Spectroscopic Data
(reference numbers refer to those in the main body of the paper)

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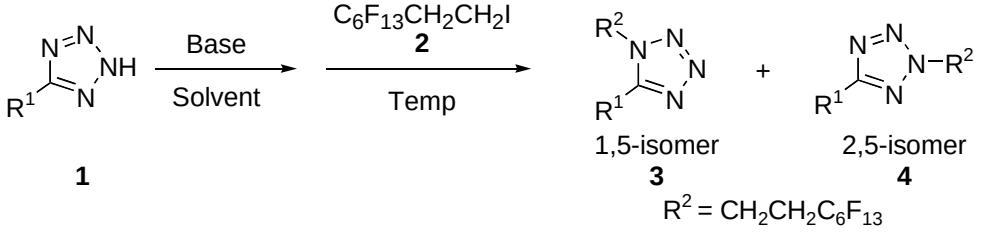
Experimental

General. Melting points were measured in open capillaries and are uncorrected. Microanalyses were performed by the Microanalytical Unit, Research School of Chemistry, Australian National University. The ^{1}H, ^{19}F and ^{13}C n.m.r. spectra were recorded on a Bruker DPX-300 spectrometer operating at 300.17, 282.5 and 75.5 MHz, respectively, using solutions in deuteriochloroform. Infrared spectra were measured on thin films for liquids or low melting solids and as KBr disks for solids. Mass spectra were acquired by electrospray ionization on a Waters Micromass ZQ2000 instrument by direct probe insertion of solutions in methanol.

Tetrazoles **1a-d** were known compounds and were prepared according to the literature methods.[30] Tetrazole **7** was synthesized in 89% yield from 3-perfluorooctylpropanonitrile by similar treatment.

1. Alkylation of tetrazoles using perfluoroalkylethyl halides

Table 1. Alkylation of 5-alkyl-1*H*-tetrazoles with perfluorohexylethyl iodide **2** under basic conditions.[a]



Entry	R^1	Base	Solvent	Temp (°C)	Product (Yield, %)[b]		**3**/**4** Yield (%), (Ratio)
1	*n*-C_6H_{13}	K_2CO_3	1,4-dioxane	80	–[c]	–[c]	–
2	*n*-C_6H_{13}	Et_3N	THF	40	**3a** (trace)	**4a** (trace)	trace
3	*n*-C_6H_{13}	Et_3N	CH_3CN	reflux	**3a** (24)	**4a** (30)	54 (44:56)
4	*n*-C_6H_{13}	Et_3N	CH_2Cl_2	reflux	**3a** (33)	**4a** (32)	65 (51:49)
5[d]	*n*-C_6H_{13}	Et_3N	toluene	90	**3a** (16)	**4a** (22)	38 (42:58)
6	*n*-C_4H_9	KH	DMSO	90	**3b** (17)	**4b** (36)	53 (32:68)
7	*n*-C_4H_9	Et_3N	CH_2Cl_2	reflux	**3b** (25)	**4b** (28)	53 (47:53)
8	*n*-C_8H_{17}	Et_3N	CH_2Cl_2	reflux	**3c** (24)	**4c** (27)	51 (47:53)
9	EtO_2CCH_2	Et_3N	CH_2Cl_2	reflux	**3d** (22)	**4d** (24)	46 (48:52)

[a] 5-Alkyl-1*H*-tetrazole **1** (1.1 eq), base (1.2 eq) and perfluorohexylethyl iodide **2** (1.0 eq) in solvent. [b]Isolated yield. [c] No products were detected. [d] 'One-pot' process: heptanonitrile (1.0 mmol), NaN_3 (1.5 mmol), Et_3N•HCl (1.5 mmol), dry toluene (4 mL), followed by addition of **2** (1.0 mmol).

1.1 *General procedure* (Table 1, Entry 4): Triethylamine (56 mg, 0.55 mmol) was added to a solution of 5-*n*-hexyltetrazole **1a** (77 mg, 0.50 mmol) in dry CH_2Cl_2 (5 mL). After 30 min at room temperature, perfluorohexylethyl iodide **2** (284 mg, 0.6 mmol) was added and the mixture was heated to reflux for 36 h. The reaction mixture was diluted with water (15 mL), extracted with Et_2O (3x15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (diethyl ether : light petroleum, 5:95 to 20:80) to afford in order of elution, 5-hexyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2*H*-tetrazole **4a** as a colourless liquid (79 mg, 32%) and 5-hexyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1*H*-tetrazole **3a** as a white solid (82 mg, 33%) mp 48-51°C.

This general procedure was adopted successfully in the alkylation of tetrazoles **1b-d** (see Table 1, Entries 7-9).

1.2 *Variations*

1.2.1 *Solvent and temperature*

The general procedure was repeated using 5-hexyltetrazole **1a** and perfluorohexylethyl iodide **2** and triethylamine but in tetrahydrofuran at 40°C and in acetonitrile at reflux, with mixed results (see Table 1, Entries 2 and 3).

1.2.2 *One-pot procedure*

Heptanonitrile (111 mg, 1.0 mmol), sodium azide (98 mg, 1.5 mmol), triethylammonium iodide (207 mg, 1.5 mmol) and dry toluene (4 mL) were combined under argon and heated under reflux for 2 d. The mixture was cooled to 80°C and perfluorohexylethyl iodide (474 mg, 1.0 mmol) added. Heating and stirring were continued for 4 d then the mixture was cooled. Aqueous workup and diethyl ether extraction, followed by flash chromatography of the reside on silica gel (diethyl ether : light petroleum, 20:80 to 50:50) gave, in order of elution, tetrazole **4a** as a colourless oil (107 mg, 22%) and tetrazole **3a** as a pale yellow solid (82 mg, 16%).

1.2.3 *Potassium carbonate in dioxane* (Table 1, Entry 1)

Solid potassium carbonate (69 mg, 0.5 mmol) was added to a solution of tetrazole **1a** (77 mg, 0.5 mmol) and perfluorohexylethyl iodide (284 mg, 0.6 mmol) in dioxane (3 mL) at room temperature and the mixture warmed to 80°C. Reaction seemed to take place and a salt appeared to form, but addition of dilute hydrochloric acid and extractive workup with diethyl ether gave only recovery of the original tetrazole **1a** (64 mg, 83% recovery).

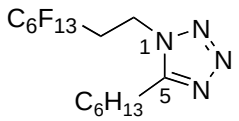
1.2.4 *Potassium hydride in DMSO* (Table 1, Entry 6)

(i) A flask was charged with potassium hydride (69 mg of 35% in oil, 0.6 mmol) and the oil removed under argon with dry diethyl ether. Dry dimethyl sulfoxide 1.2 mL) was added cautiously and the mixture heated at 75°C for 2 h. The dark solution was cooled to

room temperature and tetrazole **1b** (63 mg, 0.5 mmol) and commercial copper(I) iodide (19 mg, 0.1 mmol) were added. The mixture was stirred at ambient temperature for 30 min the perfluorohexylethyl iodide (285 mg, 0.6 mmol) was added and the mixture stirred and warmed to 75°C in a bath overnight. The mixture was then cooled, poured into brine (20 mL), extracted with diethyl ether and the organic layer washed with brine and dried over sodium sulfate. Evaporation of solvent and chromatography of the residue afforded in order of elution, tetrazole **4a** as a colourless oil (84 mg, 36%) and tetrazole **3a** as a white solid (40 mg, 17%) mp 40.5-42°C.

(ii) The reaction in 1.2.4(i) was repeated under identical conditions, using potassium hydride 114 mg of 35% in oil, 1.0 mmol), tetrazole **1b** (100 mg, 0.8 mmol) and perfluorohexylethyl iodide (474 mg, 1.0 mmol), but without the addition of copper(I) iodide, to give tetrazole **4a** (127 mg, 34%) and tetrazole **3a** (73 mg, 18%).

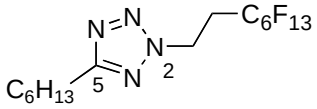
5-Hexyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1*H*-tetrazole 3a



3a

mp 48-51°C. υ_{max} (KBr)/cm^{-1} 2957, 2933, 2859, 1515, 1470, 1237, 1210, 1143, 1078, 707. δ_H ($CDCl_3$) 4.54 (t, *J* 7.4 Hz, 2H, NC*H*$_2$CH$_2$), 2.85 (m, 2H, NCH$_2$C*H*$_2$CF$_2$), 2.84 (t, *J* 7.9 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.81 (tt, *J* 7.9, 7.5 Hz, 2H, 5-CH$_2$C*H*$_2$), 1.42 (m, 2H, C*H*$_2$), 1.35 (m, 4H, (C*H*$_2$)$_2$), 0.88 (t, *J* 7.0 Hz, 3H, CH$_2$C*H*$_3$). δ_C ($CDCl_3$) 13.8 (*C*H$_3$), 22.3 (*C*H$_2$), 22.9 (*C*H$_2$), 26.9 (*C*H$_2$), 28.6 (*C*H$_2$), 31.0 (t, *J* 21.6 Hz, NCH$_2$*C*H$_2$CF$_2$), 31.1 (*C*H$_2$), 38.9 (t, *J* < 2 Hz, NCH$_2$CH$_2$CF$_2$), 118.9 (m, NCH$_2$CH$_2$*C*F$_2$), 155.0 (C5). δ_F ($CDCl_3$) -81.2 (3F), -114.6 (2F), -122.2 (2F), -123.2 (2F), -123.8 (2F), -126.5 (2F). *m*/*z* (ESI) 539.48 (M+K$^+$), 523.52 (M+Na$^+$), 501.46 (M+1$^+$). Anal. Calc. for $C_{15}H_{17}F_{13}N_4$ (FW 500.30): C 36.01, H 3.42, N 11.20. Found: C 36.32, H 3.51, N 11.03%.

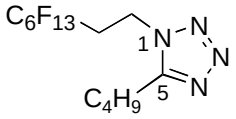
5-Hexyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2*H*-tetrazole 4a



4a

colourless liquid. υ_{max} (film)/cm^{-1} 2961, 2933, 2863, 1498, 1459, 1240, 1146, 1021, 810. δ_H ($CDCl_3$) 4.89 (t, *J* 7.5 Hz, 2H, NC*H*$_2$CH$_2$), 2.88 (m, 2H, NCH$_2$C*H*$_2$CF$_2$), 2.88 (t, *J* 7.7 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.78 (m, 2H, 5-CH$_2$C*H*$_2$), 1.20-1.39 (m, 6H, (C*H*$_2$)$_3$), 0.88 (t, *J* 6.8 Hz, 3H, CH$_2$C*H*$_3$). δ_C ($CDCl_3$) 13.8 (*C*H$_3$), 22.3 (*C*H$_2$), 25.2 (*C*H$_2$), 27.8 (*C*H$_2$), 28.3 (*C*H$_2$), 30.8 (t, *J ca.* 25 Hz, NCH$_2$*C*H$_2$CF$_2$), 31.2 (*C*H$_2$), 44.7 (t, *J* < 2 Hz, N*C*H$_2$CH$_2$CF$_2$), 117.0 (m, NCH$_2$CH$_2$*C*F$_2$), 167.4 (C5). δ_F ($CDCl_3$) -81.2 (3F), -114.6 (2F), -122.2 (2F), -123.2 (2F), -123.8 (2F), -126.5 (2F). *m*/*z* (ESI) 539.48 (M+K$^+$), 523.46 (M+Na$^+$), 501.46 (M+1$^+$). Anal. Calc. for $C_{15}H_{17}F_{13}N_4$ (FW 500.30): C 36.01, H 3.42, N 11.20. Found: C 36.38, H 3.73, N 10.99%.

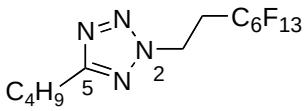
5-Butyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1*H*-tetrazole 3b



3b

mp 40.5-42.0°C. υ_{max} (KBr)/cm^{-1} 2965, 2850, 1515, 1473, 1236, 1210, 1143, 1078, 707. δ_H ($CDCl_3$) 4.55 (t, *J* 7.5 Hz, 2H, NC*H*$_2$CH$_2$), 2.85 (m, 2H, NCH$_2$C*H*$_2$CF$_2$), 2.84 (t, *J* 7.5 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.82 (tt, *J*, 7.5, 7.5 Hz, 2H, 5-CH$_2$C*H*$_2$), 1.44 (tq, *J* 7.5, 7.2 Hz, 2H, C*H*$_2$CH$_3$), 0.98 (t, *J* 7.1 Hz, 3H, CH$_2$C*H*$_3$). δ_C ($CDCl_3$) 13.4 (*C*H$_3$), 22.1 (*C*H$_2$), 22.6 (*C*H$_2$), 28.9 (*C*H$_2$), 31.0 (t, *J* 21.8 Hz, NCH$_2$*C*H$_2$CF$_2$), 38.8 (t, *J* < 2 Hz, N*C*H$_2$CH$_2$CF$_2$), 116.6 (m, NCH$_2$CH$_2$*C*F$_2$), 155.0 (C5). δ_F ($CDCl_3$) -81.1 (3F), -114.6 (2F), -122.1 (2F), -123.2 (2F), -123.8 (2F), -126.5 (2F). *m*/*z* (ESI) 511.33 (M+K$^+$), 495.30 (M+Na$^+$), 473.24 (M+1$^+$). Anal. Calc. For $C_{13}H_{13}F_{13}N_4$ (FW 472.25): C 33.06, H 2.77, N 11.86. Found: C 33.69, H 2.81, N 11.45%.

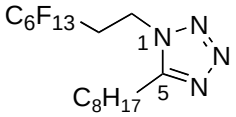
5-Butyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2*H*-tetrazole 4b



4b

colourless liquid. υ_{max} (film)/cm^{-1} 2964, 2938, 2877, 1498, 1459, 1240, 1146, 1078, 810. δ_H ($CDCl_3$) 4.89 (t, *J* 7.5 Hz, 2H, NC*H*$_2$CH$_2$), 2.88 (m, 2H, NCH$_2$C*H*$_2$CF$_2$), 2.89 (t, *J* 7.5 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.76 (tt, *J* 7.5, 7.5 Hz, 2H, 5-CH$_2$C*H*$_2$), 1.39 (tq, *J* 7.5, 7.1 Hz, 2H, C*H*$_2$CH$_3$), 0.95 (t, *J* 7.1 Hz, 3H, CH$_2$C*H*$_3$). δ_C ($CDCl_3$) 13.5 (*C*H$_3$), 22.0 (*C*H$_2$), 25.0 (*C*H$_2$), 29.9 (*C*H$_2$), 30.8 (t, *J* 21.8 Hz, NCH$_2$*C*H$_2$CF$_2$), 38.9 (t, *J* < 2 Hz, N*C*H$_2$CH$_2$CF$_2$), 117 (m, NCH$_2$CH$_2$*C*F$_2$), 167.4 (C5). δ_F ($CDCl_3$) -81.1 (3F), -114.6 (2F), -122.2 (2F), -123.2 (2F), -123.8 (2F), -126.5 (2F). *m*/*z* (ESI) 495.31 (M+Na$^+$), 473.30 (M+H$^+$). Anal. Calc. for $C_{13}H_{13}F_{13}N_4$ (FW 472.25): C 33.06, H 2.77, N 11.86. Found: C 33.15, H 2.77, N 12.04%.

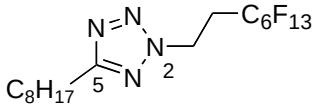
5-Octyl-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1*H*-tetrazole 3c



3c

mp 65-67°C. υ_{max} (KBr)/cm^{-1} 2958, 2925, 2855, 1515, 1470, 1237, 1143, 1078, 707. δ_H ($CDCl_3$) 4.54 (t, *J* 7.5 Hz, 2H, NC*H*$_2$CH$_2$), 2.85 (m, 2H, NCH$_2$C*H*$_2$CF$_2$), 2.84 (t, *J* 7.2 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.84 (tt, *J* 7.5, 7.2 Hz, 2H, 5-CH$_2$C*H*$_2$), 1.40 (m, 2H, C*H*$_2$), 1.25-1.35 (m, 8H, (C*H*$_2$)$_4$), 0.88 (t, *J* 6.6 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -114.6 (2F), -122.1 (2F), -123.2 (2F), -123.7 (2F), -126.4 (2F). *m*/*z* (ESI) 567.22 (M+K$^+$), 551.26 (M+Na$^+$), 529.27 (M+1$^+$). Anal. Calc. for $C_{17}H_{21}F_{13}N_4$ (FW 528.35): C 38.64, H 4.01, N 10.60. Found: C 38.49, H 3.94, N 10.35%.

5-Octyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2*H*-tetrazole 4c

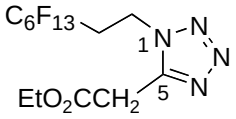


4c

colourless liquid. υ_{max} (film)/cm^{-1} 2930, 2859, 1498, 1459, 1240, 1146, 1078, 810. δ_H ($CDCl_3$) 4.89 (t, *J* 7.5 Hz, 2H, NC*H*$_2$CH$_2$), 2.89 (m, 2H, NCH$_2$C*H*$_2$CF$_2$), 2.88 (t, *J* 7.5 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.78 (tt, *J* 7.5, 7.5 Hz, 2H, 5-CH$_2$C*H*$_2$), 1.27-1.33 (m, 10H, (C*H*$_2$)$_5$), 0.87 (t, *J* 6.4 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -114.6 (2F), -122.2 (2F), -123.2 (2F), -123.8 (2F), -126.4 (2F). *m*/*z* (ESI) 567.35 (M+K$^+$), 551.39 (M+Na$^+$), 529.40 (M+1$^+$).

Anal. Calc. for $C_{17}H_{21}F_{13}N_4$ (FW 528.35): C 38.64, H 4.01, N 10.60. Found: C 38.92, H 3.94, N 10.92%.

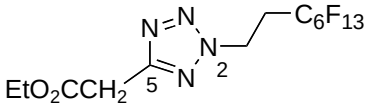
[1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-1*H*-tetrazol-5-yl]-acetic acid ethyl ester 3d



3d

mp 64-67°C. υ_{max} (KBr)/cm^{-1} 2993, 2935, 1739, 1473, 1237, 1192, 1147, 1081, 704. δ_H ($CDCl_3$) 4.61 (t, *J* 7.5 Hz, 2H, NC*H*$_2$CH$_2$), 4.23 (q, *J* 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 4.07 (s, 2H, 5-C*H*$_2$CO$_2$CH$_2$CH$_3$), 2.95 (m, 2H, NCH$_2$C*H*$_2$CF$_2$), 1.30 (t, *J* 7.2 Hz, 3H, OCH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -114.5 (2F), -122.2 (2F), -123.2 (2F), -123.8 (2F), -126.5 (2F). *m*/*z* (ESI) 541.08 (M+K$^+$), 525.12 (M+Na$^+$). Anal. Calc. for $C_{13}H_{11}F_{13}N_4O_2$ (FW 502.23): C, 31.09; H, 2.21; N, 11.16. Found: C 30.83, H 2.10, N 10.97%.

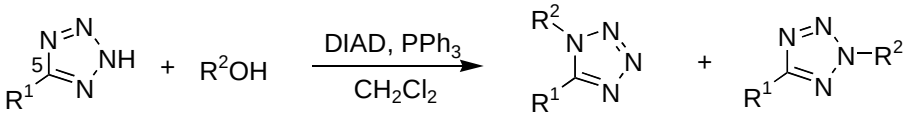
[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-2*H*-tetrazol-5-yl]acetic acid ethyl ester 4d



4d

colourless oil. υ_{max} (film)/cm^{-1} 3473, 2988, 1745, 1508, 1240, 1146, 1030. δ_H ($CDCl_3$) 4.94 (t, *J* 7.5 Hz, 2H, NC*H*$_2$CH$_2$), 4.21 (q, *J* 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 3.98 (s, 2H, 5-C*H*$_2$CO$_2$CH$_2$CH$_3$), 2.91 (m, 2H, NCH$_2$C*H*$_2$CF$_2$), 1.27 (t, *J* 7.0 Hz, 3H, OCH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -114.6 (2F), -122.2 (2F), -123.2 (2F), -123.8 (2F), -126.5 (2F). *m*/*z* (ESI) 541.15 (M+K$^+$), 525.12 (M+Na$^+$). Anal. Calc. for $C_{13}H_{11}F_{13}N_4O_2$ (FW 502.23): C 31.09, H 2.21, N, 11.16. Found: C 31.24, H 2.29, N 11.13%.

Table 2. Alkylation of 5-alkyltetrazoles with fluorous alcohols using Mitsunobu approach.[a]



1 + R^2OH (**5**: $CH_2CH_2C_6F_{13}$; **6**: $CH_2C_7F_{15}$)

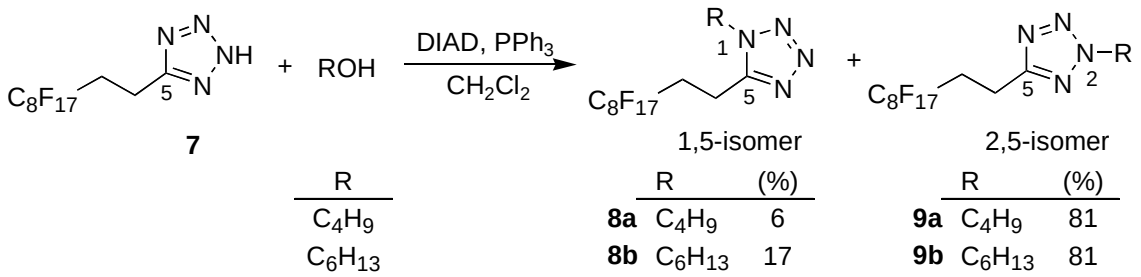
Entry	R^2OH	R^1	Products (Yields, %)[b]		**3**/**4** Yield (%), (Ratio)
1	**5**	**1a** *n*-C_6H_{13}	**3a** (21)	**4a** (68)	89 (24:76)
2	**5**	**1b** *n*-C_4H_9	**3b** (28)	**4b** (71)	99 (28:72)
3	**5**	**1c** *n*-C_8H_{17}	**3c** (27)	**4c** (63)	90 (30:70)
4	**5**	**1d** EtO_2CCH_2	**3d** (20)	**4d**(79)	99 (20:80)
5	**6**	**1a** *n*-C_6H_{13}	–[c]	–[c]	–

[a] 5-Alkyl-1*H*-tetrazoles **1** (0.8 mmol), DIAD (diisopropyl azodicarboxylate) (1.0 mmol), PPh_3 (1.0 mmol) and alcohols **5** or **6** (1.0 mmol) in dry CH_2Cl_2; [b]Isolated yield; [c] No products were detected and most of **6** was recovered.

Alkylation of tetrazoles using perfluoroalkylethyl alcohols and the Mitsunobu reaction

General procedure (Table 2, Entry 5): Triphenylphosphine (262 mg, 1.0 mmol) was added in one portion to a stirred mixture of tetrazole **1d** (125 mg, 0.8 mmol) and 2-perfluorohexylethanol **5** (364 mg, 1.0 mmol) in dry CH_2Cl_2 (8 mL) at 5°C under argon followed by the dropwise addition of neat diisopropyl azodicarboxylate (202 mg, 1.0 mmol) over 10 min. The reaction mixture was stirred at 5°C for 30 min, and then allowed to warm to room temperature overnight. After removing the solvent, the residue was diluted with hexane (10 mL) and filtered. The filtrate was concentrated under reduced pressure and the residue was flash chromatographed on silica gel (diethyl ether : light petroleum, 5:95 to 20:80) to afford [1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1*H*-tetrazol-5-yl]-acetic acid ethyl ester **3d** as a white solid (82 mg, 20%) mp 64-67°C and -(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2*H*-tetrazol-5-yl]acetic acid ethyl ester **4d** as a colourless liquid (316 mg, 79%).

This method was applied to the alkylation of tetrazoles **1a-d** (see Table 2).



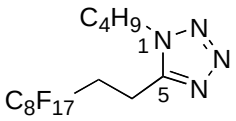
	R		R	(%)
	C_4H_9	**8a**	C_4H_9	6
	C_6H_{13}	**8b**	C_6H_{13}	17

	R	(%)
9a	C_4H_9	81
9b	C_6H_{13}	81

Scheme 1

The general procedure was also used to alkylate tetrazole **7** (258 mg, 0.5 mmol) with *n*-butanol (45 mg, 0.6 mmol) and, separately, with *n*-hexanol (102 mg, 1.0 mmol) (Scheme 1). The reactions yielded, after flash chromatography on silica gel (diethyl ether : light petroleum, 30:70 to 50:50), 1-butyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-2*H*-tetrazole **8a** as a white solid (17 mg, 6%) mp 79-81°C and 2-butyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-2*H*-tetrazole **9a** as a colourless oil (231 mg, 81%), and 5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-1-hexyl-2*H*-tetrazole **8b** as a white solid (50 mg, 17%) mp 79.5-82.5°C and 5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-2-hexyl-2*H*-tetrazole **9b** as a colourless liquid (244 mg, 81%), respectively.

1-Butyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-2*H*-tetrazole 8a

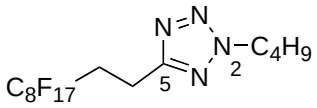


8a

white solid, mp 79-81°C. υ_{max} (KBr)/cm^{-1} 3418, 2965, 2880, 1520, 1336, 1240, 1201, 1146, 1114, 984. δ_H ($CDCl_3$) 4.28 (t, *J* 7.3 Hz, 2H, NC*H*$_2$CH$_2$), 3.09 (m, 2H, 5-C*H*$_2$CH$_2$), 2.82 (m, 2H, 5-CH$_2$C*H*$_2$CF$_2$), 1.91 (tt, *J* 7.5, 7.3 Hz, 2H, NCH$_2$C*H*$_2$), 1.36 (tq, *J* 7.5, 7.4 Hz, 2H, C*H*$_2$CH$_3$), 0.99 (t, *J* 7.4 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.2 (3F), -115.2 (2F), -122.0 (2F), -122.2 (4F), -123.0 (2F), -123.7 (2F), -126.4 (2F). *m*/*z* (ESI) 611.42 (M+K$^+$),

595.40 ($M+Na^+$), 573.41 ($M+H^+$). Anal. Calc. for $C_{15}H_{13}F_{17}N_4$ (FW 572.26): C 31.48, H 2.29, N 9.79. Found: C 31.48, H 2.43, N 9.75%.

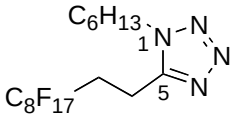
2-Butyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-2*H*-tetrazole 9a



9a

colourless liquid. υ_{max} (KBr)/cm^{-1} 3447, 2967, 2880, 1503, 1370, 1208, 1151, 1114, 1029, 704. δ_H ($CDCl_3$) 4.57 (t, *J* 7.2 Hz, 2H, NC*H*$_2$CH$_2$), 3.21 (m, 2H, 5-C*H*$_2$CH$_2$), 2.65 (m, 2H, 5-CH$_2$C*H*$_2$CF$_2$), 1.98 (tt, *J* 7.5, 7.2 Hz, 2H, NCH$_2$C*H*$_2$), 1.36 (tq, *J* 7.5, 7.4 Hz, 2H, C*H*$_2$CH$_3$), 0.96 (t, *J* 7.4 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.2 (3F), -115.3 (2F), -122.1 (2F), -122.3 (4F), -123.1 (2F), -123.8 (2F), -126.5 (2F). *m*/*z* (ESI) 611.30 ($M+K^+$), 595.28 ($M+Na^+$), 573.29 ($M+H^+$). Anal. Calc. for $C_{15}H_{13}F_{17}N_4$ (FW 572.26): C 31.48, H 2.29, N 9.79. Found: C 31.40, H 2.32, N 9.69%.

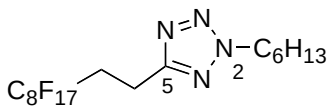
5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-1-hexyl-2*H*-tetrazole 8b



8b

white solid. mp 79.5-82.5°C. υ_{max} (KBr)/cm^{-1} 3416, 2961, 2862, 1520, 1336, 1240, 1201, 1114, 984. δ_H ($CDCl_3$) 4.28 (t, *J* 7.4 Hz, 2H, NC*H*$_2$CH$_2$), 3.09 (m, 2H, 5-C*H*$_2$CH$_2$), 2.81 (m, 2H, 5-CH$_2$C*H*$_2$CF$_2$), 1.92 (m, 2H, NCH$_2$C*H*$_2$), 1.27-1.37 (m, 6H, (C*H*$_2$)$_3$), 0.89 (t, *J* 7.0 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.2 (3F), -115.3 (2F), -122.0 (2F), -122.2 (4F), -123.1 (2F), -123.7 (2F), -126.4 (2F). *m*/*z* (ESI) 639.44 ($M+K^+$), 623.49 ($M+Na^+$), 601.50 ($M+H^+$). Anal. Calc. for $C_{17}H_{17}F_{17}N_4$ (FW 600.32): C 34.01, H 2.85, N 9.33. Found: C 34.25, H 2.99, N 9.36%.

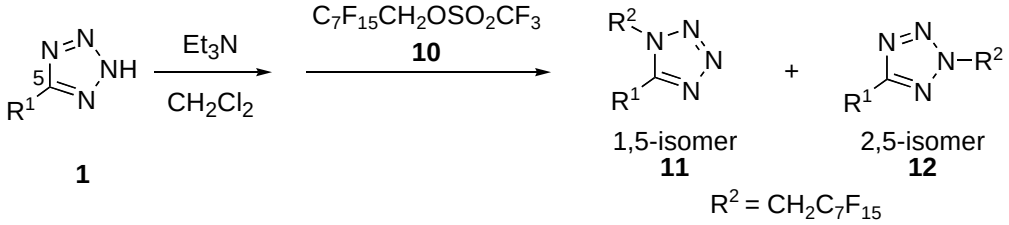
5-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-2-hexyl-2*H*-tetrazole 9b



9b

colourless liquid. υ_{max} (KBr)/cm^{-1} 3436, 2962, 2936, 2864, 1501, 1369, 1240, 1210, 1152, 1115, 1029, 705. δ_H ($CDCl_3$) 4.56 (t, *J* 7.2 Hz, 2H, NC*H*$_2$CH$_2$), 3.21 (m, 2H, 5-C*H*$_2$CH$_2$), 2.65 (m, 2H, 5-CH$_2$C*H*$_2$CF$_2$), 1.99 (m, 2H, NCH$_2$C*H*$_2$), 1.27-1.32 (m, 6H, (C*H*$_2$)$_3$), 0.87 (t, *J* 7.0 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.2 (3F), -115.3 (2F), -122.0 (2F), -122.3 (4F), -123.1 (2F), -123.8 (2F), -126.5 (2F). *m*/*z* (ESI) 639.32 ($M+K^+$), 623.36 ($M+Na^+$), 601.37 ($M+H^+$). Anal. Calc. for $C_{17}H_{17}F_{17}N_4$ (FW 600.32): C 34.01, H 2.85, N 9.33. Found: C 33.05, H 3.00, N 9.00%.

Table 3. Alkylation of 5-alkyltetrazoles with fluorous triflate **10** under basic conditions.[a]



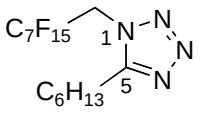
Entry	R^1	Products (Yields, %)[b]		**11**/**12** Yields (%), (Ratio)
1	*n*-C_6H_{13} **1a**	**11a** (21)	**12a** (29)	50 (42:58)
2	*n*-C_4H_9 **1b**	**11b** (19)	**12b** (19)	38 (50:50)
3[c]	*n*-C_4H_9 **1b**	**11b** (40)	**12b** (47)	87 (46:54)
4	*n*-C_8H_{17} **1c**	**11c** (30)	**12c** (32)	62 (48:52)
5	EtO_2CCH_2 **1d**	**11d** (27)	**12d** (29)	56 (48:52)

[a] 5-Alkyl-1*H*-tetrazoles (1.1 eq), Et_3N (1.2 eq) and perfluoroheptylmethyl triflate **10** (1.0 eq) in dry CH_2Cl_2, reflux, 36 h. [b]Isolated yield. [c] 5-Alkyl-1H-tetrazole (1.7 eq), Et_3N (2.0 eq) and perfluoroheptylmethyl triflate **10** (1.0 eq) were used and the yield calculated on the amount of triflate **10**.

General procedure: Triethylamine (0.28 mL, 202 mg, 2.0 mmol) was added by syringe to a solution of 5-*n*-butyltetrazole **1b** (126 mg, 1.0 mmol) in dry dichloromethane (5 mL) at ambient temperature. The mixture was stirred for 30 min then a solution of triflate **10** (320 mg, 0.61 mmol) in dichloromethane (2 mL) was added dropwise. The stirred mixture was then heated to reflux overnight (16 h) when t.l.c. showed complete consumption of the triflate. The mixture was evaporated to dryness under reduced pressure and flash chromatographed on sílica gel (ethyl acetate : light petroleum, 3:7) to give 5-butyl-1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-1*H*-tetrazole **11b** as a white solid (139 mg, 40%) mp 59-60°C and 5-butyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-1*H*-tetrazole **12b** as a white solid (163 mg, 47%) mp 35-36°C.

The same general procedure with minor modifications was adopted in the alkylation of tetrazoles **1a-d** with triflate **10**.

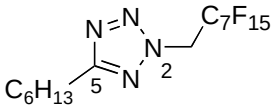
5-Hexyl-1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-1*H*-tetrazole 11a



11a

mp 75-77°C. υ_{max} (KBr)/cm^{-1} 3448, 2970, 1720, 1518, 1206, 1149, 1022. δ_H ($CDCl_3$) 4.96 (t, *J* 14.5 Hz, 2H, NC*H*$_2$CF$_2$), 2.83 (t, *J* 7.7 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.89 (m, 2H, 5-CH$_2$C*H*$_2$), 1.43 (m, 2H, C*H*$_2$), 1.30-1.34 (m, 4H, (C*H*$_2$)$_2$), 0.90 (t, *J* 7.0 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -116.2 (2F), -121.8 (2F), -122.2 (2F), -123.0 (2F), -123.1 (2F), -126.4 (2F). *m*/*z* (ESI) 575.14 (M+K$^+$), 559.24 (M+Na$^+$). Anal. Calc. for $C_{15}H_{15}F_{15}N_4$ (FW 536.28): C 33.59, H 2.82, N 10.45. Found: C 33.44, H 2.65, N 10.44%.

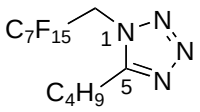
5-Hexyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-2*H*-tetrazole 12a



12a

mp 34-35°C. υ_{max} (KBr)/cm^{-1} 3434, 2932, 1738, 1506, 1242, 1206, 1148, 1023. δ_H ($CDCl_3$) 5.24 (t, *J* 13.9 Hz, 2H, NC*H*$_2$CF$_2$), 2.93 (t, *J* 7.5 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.80 (m, 2H, 5-CH$_2$C*H*$_2$), 1.32-1.40 (m, 6H, (C*H*$_2$)$_3$), 0.88 (t, *J* 7.0 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -116.5 (2F), -122.0 (2F), -122.3 (2F), -123.0 (2F), -123.3 (2F), -126.4 (2F). *m*/*z* (ESI) 575.14 (M+K$^+$), 559.18 (M+Na$^+$). Anal. Calc. for $C_{15}H_{15}F_{15}N_4$ (FW 536.28): C 33.59, H 2.82, N 10.45. Found: C 33.90, H 2.99, N 10.40%.

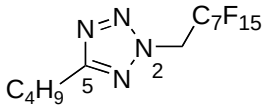
5-Butyl-1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-1*H*-tetrazole 11b



11b

mp 59-60°C. υ_{max} (KBr)/cm^{-1} 3440, 2972, 2880, 1522, 1243, 1205, 1148, 1021, 644. δ_H ($CDCl_3$) 4.96 (t, *J* 14.5 Hz, 2H, NC*H*$_2$CF$_2$), 2.84 (t, *J* 7.5 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.88 (tt, *J* 7.5, 7.5 Hz, 2H, 5-CH$_2$C*H*$_2$), 1.46 (tq, *J* 7.5, 7.4 Hz, 2H, C*H*$_2$CH$_3$), 0.98 (t, *J* 7.4 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -116.2 (2F), -121.8 (2F), -122.3 (2F), -123.1 (4F), -126.5 (2F). *m*/*z* (ESI) 509.24 (M+1$^+$). Anal. Calc. for $C_{13}H_{11}F_{15}N_4$ (FW 508.23): C 30.72, H 2.18, N 11.02. Found: C 31.10, H 2.35, N 11.27%.

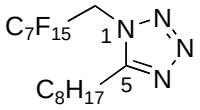
5-Butyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-2*H*-tetrazole 12b



12b

mp 35-36°C. υ_{max} (KBr)/cm^{-1} 3439, 2975, 2877, 1505, 1243, 1206, 1148, 1022. δ_H ($CDCl_3$) 5.24 (t, *J* 13.9 Hz, 2H, NC*H*$_2$CF$_2$), 2.94 (t, *J* 7.5 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.79 (tt, *J* 7.5, 7.5 Hz, 2H, 5-CH$_2$C*H*$_2$), 1.40 (tq, *J* 7.5, 7.4 Hz, 2H, C*H*$_2$CH$_3$), 0.94 (t, *J* 7.4 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -116.5 (2F), -122.0 (2F), -122.3 (2F), -123.0 (2F), -123.3 (2F), -126.4 (2F). *m*/*z* (ESI) 509.24 (M+1$^+$). Anal. Calc. for $C_{13}H_{11}F_{15}N_4$ (FW 508.23): C 30.72, H 2.18, N 11.02. Found: C 31.19, H 2.27, N 11.18%.

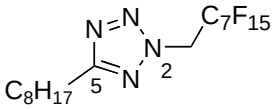
5-Octyl-1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-1*H*-tetrazole 11c



11c

mp 64.0-67.5°C. υ_{max} (KBr)/cm^{-1} 3438, 2958, 2925, 2856, 1744, 1520, 1451, 1207, 1148, 1068, 814. δ_H ($CDCl_3$) 4.96 (t, *J* 14.5 Hz, 2H, NC*H*$_2$CF$_2$), 2.83 (t, *J* 7.7 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.89 (m, 2H, 5-CH$_2$C*H*$_2$), 1.40 (m, 2H, C*H*$_2$), 1.27-1.35 (m, 8H, (C*H*$_2$)$_4$), 0.87 (t, *J* 6.8 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -116.3 (2F), -122.9 (2F), -122.3 (2F), -123.1 (4F), -126.5 (2F). *m*/*z* (ESI) 587.33 (M+Na$^+$). Anal. Calc. for $C_{17}H_{19}F_{15}N_4$ (FW 564.34): C 36.18, H 3.39, N 9.93. Found: C 36.31, H 3.32, N 9.80%.

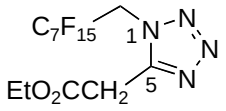
5-Octyl-2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl)-2*H*-tetrazole 12c



12c

mp 31-32°C. υ_{max} (KBr)/cm^{-1} 3440, 2958, 2924, 2853, 1500, 1469, 1208, 1146, 1024, 648. δ_H ($CDCl_3$) 5.24 (t, *J* 13.6 Hz, 2H, NC*H*$_2$CF$_2$), 2.92 (t, *J* 7.5 Hz, 2H, 5-C*H*$_2$CH$_2$), 1.79 (tt, *J* 7.5, 7.5 Hz, 2H, 5-CH$_2$C*H*$_2$), 1.20-1.35 (m, 10H, (C*H*$_2$)$_5$), 0.87 (t, *J* 6.4 Hz, 3H, CH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -116.6 (2F), -122.0 (2F), -122.4 (2F), -123.1 (2F), -123.3 (2F), -126.5 (2F). *m*/*z* (ESI) 587.33 (M+Na$^+$). Anal. Calc. for $C_{17}H_{19}F_{15}N_4$ (FW 564.34): C 36.18, H 3.39, N 9.93. Found: C 36.33, H 3.27, N 9.87%.

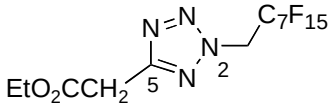
[1-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyl)-1*H*-tetrazol-5-yl]acetic acid ethyl ester 11d



11d

mp 80-83°C. υ_{max} (KBr)/cm^{-1} 3435, 3029, 2989, 1724, 1539, 1249, 1206, 1149, 1022, 641. δ_H ($CDCl_3$) 5.27 (t, *J* 15.1 Hz, 2H, NC*H*$_2$CF$_2$), 4.24 (q, *J* 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 4.14 (s, 2H, C*H*$_2$CO$_2$Et), 1.23 (t, *J* 7.0 Hz, 3H, OCH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -115.9 (2F), -121.9 (2F), -122.3 (2F), -123.0 (2F), -123.2 (2F), -126.4 (2F). *m*/*z* (ESI) 539.32 (M+1$^+$). Anal. Calc. for $C_{13}H_9F_{15}N_4O_2$ (FW 538.21): C 29.01, H 1.69, N 10.41. Found: C 29.16, H 1.52, N 10.40%.

[2-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctyl)-2*H*-tetrazol-5-yl]acetic acid ethyl ester 12d



12d

mp 52-53°C. υ_{max} (KBr)/cm^{-1} 3445, 3026, 2979, 1732, 1521, 1240, 1203, 1143, 1022. δ_H ($CDCl_3$) 5.29 (t, *J* 13.8 Hz, 2H, NC*H*$_2$CF$_2$), 4.21 (q, *J* 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 4.02 (s, 2H, C*H*$_2$CO$_2$Et), 1.26 (t, *J* 7.0 Hz, 3H, OCH$_2$C*H*$_3$). δ_F ($CDCl_3$) -81.1 (3F), -116.4 (2F), -121.9 (2F), -122.3 (2F), -123.0 (2F), -123.2 (2F), -126.4 (2F). *m*/*z* (ESI) 577.34 (M+K$^+$), 561.32 (M+Na$^+$). Anal. Calc. for $C_{13}H_9F_{15}N_4O_2$ (FW 538.21): C 29.01, H 1.69, N 10.41. Found: C 29.10, H 1.56, N 10.55%.