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-perfluoroctylpropanonitrile by similar treatment.
1. Alkylation of tetrazoles using perfluoroalkylethyl halides

Table 1. Alkylation of 5-alkyl-1H-tetrazoles with perfluorohexylethyl iodide 2 under basic conditions.\textsuperscript{a}

\[ \text{N}^3\text{N} \quad \text{R}^1 \quad \text{N} = \text{N} \quad \text{NH} \rightarrow \text{Base} \quad \text{Solvent} \rightarrow \text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{I} \quad 2 \rightarrow \text{Temp} \quad \text{R}^2 \quad \text{N}^3\text{N} \quad \text{N} = \text{N} \quad \text{R}^1 \quad \text{N} \quad \text{N} \quad \text{R}^2 \]

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<th>Temp (°C)</th>
<th>Product (Yield, %)\textsuperscript{b}</th>
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<td>Et\textsubscript{3}N</td>
<td>CH\textsubscript{2}Cl\textsubscript{2} reflux</td>
<td>90</td>
<td>3a (16) 4a (22)</td>
<td>38 (42:58)</td>
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<td>3b (25) 4b (28)</td>
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<td>3d (22) 4d (24)</td>
<td>46 (48:52)</td>
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\textsuperscript{a}5-Alkyl-1H-tetrazole 1 (1.1 eq), base (1.2 eq) and perfluorohexylethyl iodide 2 (1.0 eq) in solvent.
\textsuperscript{b}Isolated yield. \textsuperscript{c}No products were detected. \textsuperscript{d}‘One-pot’ process: heptanonitrile (1.0 mmol), NaN\textsubscript{3} (1.5 mmol), Et\textsubscript{3}N•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\textsubscript{2}Cl\textsubscript{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\textsubscript{2}O (3x15 mL). The combined organic layers were dried over Na\textsubscript{2}SO\textsubscript{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)-2H-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)-1H-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 residue 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-tridecafluoroctyl)-1H-tetrazole 3a

\[
\begin{align*}
\text{C}_6\text{H}_{13} \quad \text{N} & \quad \text{N} \\
\text{C}_6\text{F}_{13} & \quad \text{C}_5 \\
\end{align*}
\]

mp 48-51°C. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 2957, 2933, 2859, 1515, 1470, 1237, 1210, 1143, 1078, 707. \(\delta_H\) (CDCl\(_3\)) 4.54 (t, \(J 7.4\) Hz, 2H, NCH\(_2\)CH\(_2\)), 2.85 (m, 2H, NCH\(_2\)CH\(_2\)CF\(_2\)), 2.84 (t, \(J 7.9\) Hz, 2H, 5-CH\(_2\)CH\(_2\)), 1.81 (tt, \(J 7.9, 7.5\) Hz, 2H, 5-CH\(_2\)CH\(_2\)), 1.42 (m, 2H, CH\(_2\)), 1.35 (m, 4H, (CH\(_2\))\(_2\)), 0.88 (t, \(J 7.0\) Hz, 3H, CH\(_2\)CH\(_3\)). \(\delta_C\) (CDCl\(_3\)) 13.8 (CH\(_3\)), 22.3 (CH\(_2\)), 22.9 (CH\(_2\)), 26.9 (CH\(_2\)), 28.6 (CH\(_2\)), 31.0 (t, \(J 21.6\) Hz, NCH\(_2\)CH\(_2\)CF\(_2\)), 31.1 (CH\(_2\)), 38.9 (t, \(J < 2\) Hz, NCH\(_2\)CH\(_2\)CF\(_2\)), 118.9 (m, NCH\(_2\)CH\(_2\)CF\(_2\)), 155.0 (C5). \(\delta_F\) (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-tridecafluoroctyl)-2H-tetrazole 4a
colourless liquid. $\nu_{\text{max}}$ (film)/cm$^{-1}$ 2961, 2933, 2863, 1498, 1459, 1240, 1146, 1021, 810.

$\delta$H (CDCl$_3$) 4.89 (t, $J$ 7.5 Hz, 2H, NCH$_2$CH$_2$), 2.88 (m, 2H, NCH$_2$CH$_2$CF$_2$), 2.88 (t, $J$ 7.7 Hz, 2H, 5-CH$_2$CH$_2$), 1.78 (m, 2H, 5-CH$_2$CH$_2$), 1.20-1.39 (m, 6H, (CH$_2$)$_3$), 0.88 (t, $J$ 6.8 Hz, 3H, CH$_2$CH$_3$). $\delta$C (CDCl$_3$) 13.8 (CH$_3$), 22.3 (CH$_2$), 25.2 (CH$_2$), 27.8 (CH$_2$), 28.3 (CH$_2$), 30.8 (t, $J$ ca. 25 Hz, NCH$_2$CH$_2$CF$_2$), 31.2 (CH$_2$), 44.7 (t, $J$ < 2 Hz, NCH$_2$CH$_2$CF$_2$), 117.0 (m, NCH$_2$CH$_2$CF$_2$), 167.4 (C5). $\delta$F (CDCl$_3$) -81.2 (3F), -114.6 (2F), -122.2 (2F), -123.2 (2F), -123.8 (2F), -126.6 (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)-1H-tetrazole 3b

mp 40.5-42.0°C. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2965, 2850, 1515, 1473, 1236, 1210, 1143, 1078, 707.

$\delta$H (CDCl$_3$) 4.55 (t, $J$ 7.5 Hz, 2H, NCH$_2$CH$_2$), 2.85 (m, 2H, NCH$_2$CH$_2$CF$_2$), 2.84 (t, $J$ 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.82 (tt, $J$, 7.5, 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.44 (tt, $J$ 7.5, 7.2 Hz, 2H, CH$_2$CH$_3$), 0.98 (t, $J$ 7.1 Hz, 3H, CH$_2$CH$_3$). $\delta$C (CDCl$_3$) 13.4 (CH$_3$), 22.1 (CH$_2$), 22.6 (CH$_2$), 28.9 (CH$_2$), 31.0 (t, $J$ 21.8 Hz, NCH$_2$CH$_2$CF$_2$), 38.8 (t, $J$ < 2 Hz, NCH$_2$CH$_2$CF$_2$), 116.6 (m, NCH$_2$CH$_2$CF$_2$), 155.0 (C5). $\delta$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)-2H-tetrazole 4b
colourless liquid. $\nu_{\text{max}}$ (film)/cm$^{-1}$ 2964, 2938, 2877, 1498, 1459, 1240, 1146, 1078, 810.

$\delta_H$ (CDCl$_3$) 4.89 (t, $J$ 7.5 Hz, 2H, NCH$_2$CH$_2$), 2.88 (m, 2H, NCH$_2$CH$_2$CF$_2$), 2.89 (t, $J$ 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.76 (tt, $J$ 7.5, 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.39 (tq, $J$ 7.5, 7.1 Hz, 2H, CH$_2$CH$_3$), 0.95 (t, $J$ 7.1 Hz, 3H, CH$_2$CH$_3$). $\delta_C$ (CDCl$_3$) 13.5 (CH$_3$), 22.0 (CH$_2$), 25.0 (CH$_2$), 29.9 (CH$_2$), 30.8 (t, $J$ 21.8 Hz, NCH$_2$CH$_2$CF$_2$), 38.9 (t, $J$ < 2 Hz, NCH$_2$CH$_2$CF$_2$), 117 (m, NCH$_2$CH$_2$CF$_2$), 167.4 (C5). $\delta_F$ (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)-1H-tetrazole 3c

![3c](image)

mp 65-67°C. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2958, 2925, 2855, 1515, 1470, 1237, 1143, 1078, 707. $\delta_H$ (CDCl$_3$) 4.54 (t, $J$ 7.5 Hz, 2H, NCH$_2$CH$_2$), 2.85 (m, 2H, NCH$_2$CH$_2$CF$_2$), 2.84 (t, $J$ 7.2 Hz, 2H, 5-CH$_2$CH$_2$), 1.84 (tt, $J$ 7.5, 7.2 Hz, 2H, 5-CH$_2$CH$_2$), 1.40 (m, 2H, CH$_2$), 1.25-1.35 (m, 8H, (CH$_2$)$_4$), 0.88 (t, $J$ 6.6 Hz, 3H, CH$_2$CH$_3$). $\delta_F$ (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)-2H-tetrazole 4c

![4c](image)

colourless liquid. $\nu_{\text{max}}$ (film)/cm$^{-1}$ 2930, 2859, 1498, 1459, 1240, 1146, 1078, 810. $\delta_H$ (CDCl$_3$) 4.89 (t, $J$ 7.5 Hz, 2H, NCH$_2$CH$_2$), 2.89 (m, 2H, NCH$_2$CH$_2$CF$_2$), 2.88 (t, $J$ 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.78 (tt, $J$ 7.5, 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.27-1.33 (m, 10H, (CH$_2$)$_5$), 0.87 (t, $J$ 6.4 Hz, 3H, CH$_2$CH$_3$). $\delta_F$ (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)-1H-tetrazol-5-yl]acetic acid ethyl ester 3d

![3d]

mp 64-67°C. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2993, 2935, 1739, 1473, 1237, 1192, 1147, 1081, 704. $\delta_H$ (CDCl$_3$) 4.61 (t, $J$ 7.5 Hz, 2H, NCH$_2$CH$_2$), 4.23 (q, $J$ 7.2 Hz, 2H, OCH$_2$CH$_3$), 4.07 (s, 2H, 5-CH$_2$CO$_2$CH$_2$CH$_3$), 2.95 (m, 2H, NCH$_2$CH$_2$CF$_2$), 1.30 (t, $J$ 7.2 Hz, 3H, OCH$_2$CH$_3$). $\delta_F$ (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$_4$O$_2$ (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)-2H-tetrazol-5-yl]acetic acid ethyl ester 4d

![4d]

colourless oil. $\nu_{\text{max}}$ (film)/cm$^{-1}$ 3473, 2988, 1745, 1508, 1240, 1146, 1030. $\delta_H$ (CDCl$_3$) 4.94 (t, $J$ 7.5 Hz, 2H, NCH$_2$CH$_2$), 4.21 (q, $J$ 7.1 Hz, 2H, OCH$_2$CH$_3$), 3.98 (s, 2H, 5-CH$_2$CO$_2$CH$_2$CH$_3$), 2.91 (m, 2H, NCH$_2$CH$_2$CF$_2$), 1.27 (t, $J$ 7.0 Hz, 3H, OCH$_2$CH$_3$). $\delta_F$ (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$_4$O$_2$ (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.\(^a\)

\[
\begin{array}{cccc}
\text{Entry} & R^2\text{OH} & R^1 & \text{Products (Yields, \%)}^b \\
1 & 5 & \text{1a } n\text{-C}_6\text{H}_{13} & 3a (21) \ 4a (68) \ 89 (24:76) \\
2 & 5 & \text{1b } n\text{-C}_4\text{H}_9 & 3b (28) \ 4b (71) \ 99 (28:72) \\
3 & 5 & \text{1c } n\text{-C}_8\text{H}_{17} & 3c (27) \ 4c (63) \ 90 (30:70) \\
4 & 5 & \text{1d } \text{EtO}_2\text{CCH}_2 & 3d (20) \ 4d (79) \ 99 (20:80) \\
5 & 6 & \text{1a } n\text{-C}_6\text{H}_{13} & -^c -^c -^c \\
\end{array}
\]

\(^a\)5-Alkyl-1H-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\(_2\)Cl\(_2\); \(^b\)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\(_2\)Cl\(_2\) (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-tridecafluoroctyl)-1H-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-tridecafluoroctyl)-2H-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).

\[
\begin{align*}
\text{ROH} + \text{DIAD, PPh}_3 & \xrightarrow{\text{CH}_2\text{Cl}_2} \begin{array}{c}
\text{1,5-isomer} \\
\text{2,5-isomer}
\end{array} \\
\end{align*}
\]

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<th>R</th>
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<th>9a (%)</th>
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<td>C_6H_{13}</td>
<td>17</td>
<td>C_6H_{13}</td>
<td>81</td>
</tr>
</tbody>
</table>

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 \(8a\)

White solid, mp 79-81°C. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3418, 2965, 2880, 1520, 1336, 1240, 1201, 1146, 1114, 984. \(\delta_{\text{H}}\) (CDCl\(_3\)) 4.28 (t, \(J\) 7.3 Hz, 2H, NCH\(_2\)CH\(_2\)), 3.09 (m, 2H, NCH\(_2\)CH\(_2\)), 2.82 (m, 2H, 5-CH\(_2\)CH\(_2\)CF\(_2\)), 1.91 (tt, \(J\) 7.5, 7.3 Hz, 2H, NCH\(_2\)CH\(_2\)), 1.36 (tq, \(J\) 7.5, 7.4 Hz, 2H, CH\(_2\)CH\(_3\)), 0.99 (t, \(J\) 7.4 Hz, 3H, CH\(_2\)CH\(_3\)). \(\delta_{\text{F}}\) (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\(^+\)).

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

![Structure 9a]

colourless liquid. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3447, 2967, 2880, 1503, 1370, 1208, 1151, 1114, 1029, 704. \(\delta_H\) (CDCl\(_3\)) 4.57 (t, \(J\) 7.2 Hz, 2H, NCH\(_2\)CH\(_2\)), 3.21 (m, 2H, 5-C\(_3\)H\(_2\)CH\(_2\)), 2.65 (m, 2H, 5-CH\(_2\)CH\(_2\)CF\(_2\)), 1.98 (tt, \(J\) 7.5, 7.2 Hz, 2H, NCH\(_2\)CH\(_2\)), 1.36 (tq, \(J\) 7.5, 7.4 Hz, 2H, CH\(_3\)CH\(_2\)), 0.96 (t, \(J\) 7.4 Hz, 3H, CH\(_2\)CH\(_3\)). \(\delta_F\) (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

![Structure 8b]

white solid. mp 79.5-82.5\(^\circ\)C. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3416, 2961, 2862, 1520, 1336, 1240, 1201, 1114, 984. \(\delta_H\) (CDCl\(_3\)) 4.28 (t, \(J\) 7.4 Hz, 2H, NCH\(_2\)CH\(_2\)), 3.09 (m, 2H, 5-CH\(_2\)CH\(_2\)), 2.81 (m, 2H, 5-CH\(_2\)CH\(_2\)CF\(_2\)), 1.92 (m, 2H, NCH\(_2\)CH\(_2\)), 1.27-1.37 (m, 6H, (C\(_3\)H\(_2\))\(_3\)), 0.89 (t, \(J\) 7.0 Hz, 3H, CH\(_3\)CH\(_2\)). \(\delta_F\) (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-Heptadecafluorodecyl)-2-hexyl-2\(H\)-tetrazole 9b

![Structure 9b]
colourless liquid. $\nu_{\text{max}} \text{(KBr)/cm}^{-1} 3436, 2962, 2936, 2864, 1501, 1369, 1240, 1210, 1152, 1115, 1029, 705. \ \delta_H \text{(CDCl}_3\text{)} 4.56 \text{ (t, } J 7.2 \text{ Hz, 2H, NCH}_2\text{CH}_2\text{)}, 3.21 \text{ (m, 2H, 5-CH}_2\text{CH}_2\text{)}, 2.65 \text{ (m, 2H, 5-CH}_2\text{CH}_2\text{CF}_2\text{)}, 1.99 \text{ (m, 2H, NCH}_2\text{CH}_2\text{)}, 1.27-1.32 \text{ (m, 6H, (CH}_2\text{)_3)}, 0.87 \text{ (t, } J 7.0 \text{ Hz, 3H, CH}_2\text{CH}_3\text{). } \delta_F \text{(CDCl}_3\text{)} -81.2 \text{ (3F), -115.3 (2F), -122.0 (2F), -122.3 (4F), -123.1 (2F), -123.8 (2F), -126.5 (2F). } m/z \text{ (ESI) 639.32 (M+K$^+$), 623.36 (M+Na$^+$), 601.37 (M+H$^+$). Anal. Calc. for C}_{17}\text{H}_{17}\text{F}_{17}\text{N}_4\text{(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.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R¹</th>
<th>Products (Yields, %)</th>
<th>11/12 Yields (%)</th>
<th>(Ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-C₆H₁₃ 1a</td>
<td>11a (21)</td>
<td>12a (29)</td>
<td>50 (42:58)</td>
</tr>
<tr>
<td>2</td>
<td>n-C₄H₉ 1b</td>
<td>11b (19)</td>
<td>12b (19)</td>
<td>38 (50:50)</td>
</tr>
<tr>
<td>3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>n-C₄H₉ 1b</td>
<td>11b (40)</td>
<td>12b (47)</td>
<td>87 (46:54)</td>
</tr>
<tr>
<td>4</td>
<td>n-C₈H₁₇ 1c</td>
<td>11c (30)</td>
<td>12c (32)</td>
<td>62 (48:52)</td>
</tr>
<tr>
<td>5</td>
<td>EtO₂CH₂</td>
<td>1d</td>
<td>11d (27)</td>
<td>12d (29)</td>
</tr>
</tbody>
</table>

<sup>a</sup> 5-Alkyl-1H-tetrazoles (1.1 eq), Et₃N (1.2 eq) and perfluoroheptylmethyl triflate 10 (1.0 eq) in dry CH₂Cl₂, reflux, 36 h. <sup>b</sup> Isolated yield. <sup>c</sup> 5-Alkyl-1H-tetrazole (1.7 eq), Et₃N (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 silica 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)-1H-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)-1H-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)-1H-tetrazole 11a
mp 75-77°C. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3448, 2970, 1720, 1518, 1206, 1149, 1022. $\delta_H$ (CDCl$_3$) 4.96 (t, $J$ 14.5 Hz, 2H, NCH$_2$CF$_2$), 2.83 (t, $J$ 7.7 Hz, 2H, 5-CH$_2$CH$_2$), 1.89 (m, 2H, 5-CH$_2$CH$_2$), 1.43 (m, 2H, CH$_2$), 1.30-1.34 (m, 4H, (CH$_2$)$_2$), 0.90 (t, $J$ 7.0 Hz, 3H, CH$_2$CH$_3$). $\delta_F$ (CDCl$_3$) -81.1 (3F), -116.2 (2F), -121.8 (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-pentadecafluoroctyl)-2H-tetrazole 12a

mp 34-35°C. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3434, 2932, 1738, 1506, 1242, 1206, 1148, 1023. $\delta_H$ (CDCl$_3$) 5.24 (t, $J$ 13.9 Hz, 2H, NCH$_2$CF$_2$), 2.93 (t, $J$ 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.80 (m, 2H, 5-CH$_2$CH$_2$), 1.32-1.40 (m, 6H, (CH$_2$)$_3$), 0.88 (t, $J$ 7.0 Hz, 3H, CH$_2$CH$_3$). $\delta_F$ (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-pentadecafluoroctyl)-1H-tetrazole 11b

mp 59-60°C. $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3440, 2972, 2880, 1522, 1243, 1205, 1148, 1021, 644. $\delta_H$ (CDCl$_3$) 4.96 (t, $J$ 14.5 Hz, 2H, NCH$_2$CF$_2$), 2.84 (t, $J$ 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.88 (tt, $J$ 7.5, 7.5 Hz, 2H, 5-CH$_2$CH$_2$), 1.46 (tq, $J$ 7.5, 7.4 Hz, 2H, CH$_2$CH$_3$), 0.98 (t, $J$ 7.4 Hz, 3H, CH$_2$CH$_3$). $\delta_F$ (CDCl$_3$) -81.1 (3F), -116.2 (2F), -121.8 (2F), -122.3 (2F), -123.1 (2F), -126.5 (2F). m/z (ESI) 509.24 (M+H$^+$). 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-(2,2,3,3,4,4,5,6,7,7,8,8,8-pentadecafluoroctyl)-2H-tetrazole 12b

\[
\begin{align*}
\text{C}_4\text{H}_9 & - \text{N} = \text{N} - \text{C}_7\text{F}_{15} \\
\text{12b}
\end{align*}
\]

mp 35-36°C. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3439, 2975, 2877, 1505, 1243, 1206, 1148, 1022. \(\delta_H\) (CDCl\(_3\)) 5.24 (t, \(J 13.9\) Hz, 2H, NCH\(_2\)CF\(_2\)), 2.94 (t, \(J 7.5\) Hz, 2H, 5-CH\(_2\)CH\(_2\)), 1.79 (tt, \(J 7.5, 7.5\) Hz, 2H, 5-CH\(_2\)CH\(_2\)), 1.40 (tq, \(J 7.5, 7.4\) Hz, 2H, CH\(_3\)CH\(_2\)), 0.94 (t, \(J 7.4\) Hz, 3H, CH\(_3\)CH\(_3\)). \(\delta_F\) (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-(2,2,3,3,4,4,5,6,7,7,8,8,8-pentadecafluoroctyl)-1H-tetrazole 11c

\[
\begin{align*}
\text{C}_8\text{H}_{17} & - \text{N} = \text{N} - \text{C}_7\text{F}_{15} \\
\text{11c}
\end{align*}
\]

mp 64.0-67.5°C. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3439, 2958, 2925, 2856, 1744, 1520, 1451, 1207, 1148, 1068, 814. \(\delta_H\) (CDCl\(_3\)) 4.96 (t, \(J 14.5\) Hz, 2H, NCH\(_2\)CF\(_2\)), 2.83 (t, \(J 7.7\) Hz, 2H, 5-CH\(_2\)CH\(_2\)), 1.89 (m, 2H, 5-CH\(_2\)CH\(_2\)), 1.27-1.35 (m, 8H, (CH\(_2\))\(_5\)), 0.87 (t, \(J 6.8\) Hz, 3H, CH\(_2\)CH\(_2\)). \(\delta_F\) (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-(2,2,3,3,4,4,5,6,7,7,8,8,8-pentadecafluoroctyl)-2H-tetrazole 12c

\[
\begin{align*}
\text{C}_8\text{H}_{17} & - \text{N} = \text{N} - \text{C}_7\text{F}_{15} \\
\text{12c}
\end{align*}
\]

mp 31-32°C. \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 3440, 2958, 2924, 2853, 1500, 1469, 1208, 1146, 1024, 648. \(\delta_H\) (CDCl\(_3\)) 5.24 (t, \(J 13.6\) Hz, 2H, NCH\(_2\)CF\(_2\)), 2.92 (t, \(J 7.5\) Hz, 2H, 5-CH\(_2\)CH\(_2\)), 1.79 (tt, \(J 7.5, 7.5\) Hz, 2H, 5-CH\(_2\)CH\(_2\)), 1.20-1.35 (m, 10H, (CH\(_2\))\(_5\)), 0.87 (t, \(J 6.4\) Hz, 3H, CH\(_2\)CH\(_2\)). \(\delta_F\) (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-(2,2,3,3,4,5,6,6,7,7,8,8,8-Pentadecafluoroctyl)-1H-tetrazol-5-yl]acetic acid ethyl ester 11d

\[
\begin{align*}
\text{C}_2\text{F}_{15} & \begin{array}{c}
\text{N}
\end{array} \begin{array}{c}
\text{N}
\end{array} \begin{array}{c}
\text{N}
\end{array} \\
\text{EtO}_2\text{CCH}_2 & \begin{array}{c}
5
\end{array} \\
\end{align*}
\]

11d

mp 80-83°C. \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 3435, 3029, 2989, 1724, 1539, 1249, 1206, 1149, 1022, 641. \( \delta \)\(_H\) (CDCl\(_3\)) 5.27 (t, \( J \) 15.1 Hz, 2H, NCH\(_2\)CF\(_2\)), 4.24 (q, \( J \) 7.0 Hz, 2H, OCH\(_2\)CH\(_3\)), 4.14 (s, 2H, CH\(_2\)CO\(_2\)Et), 1.23 (t, \( J \) 7.0 Hz, 3H, OCH\(_2\)CH\(_3\)). \( \delta \)\(_F\) (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\(_9\)F\(_{15}\)N\(_4\)O\(_2\) (FW 538.21): C 29.01, H 1.69, N 10.41. Found: C 29.16, H 1.52, N 10.40%.

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

\[
\begin{align*}
\text{EtO}_2\text{CCH}_2 & \begin{array}{c}
\text{N}
\end{array} \begin{array}{c}
\text{N}
\end{array} \begin{array}{c}
\text{C}_7\text{F}_{15}
\end{array} \\
\end{align*}
\]

12d

mp 52-53°C. \( \nu_{\text{max}} \) (KBr)/cm\(^{-1} \) 3445, 3026, 2979, 1732, 1521, 1240, 1203, 1143, 1022. \( \delta \)\(_H\) (CDCl\(_3\)) 5.29 (t, \( J \) 13.8 Hz, 2H, NCH\(_2\)CF\(_2\)), 4.21 (q, \( J \) 7.0 Hz, 2H, OCH\(_2\)CH\(_3\)), 4.02 (s, 2H, CH\(_2\)CO\(_2\)Et), 1.26 (t, \( J \) 7.0 Hz, 3H, OCH\(_2\)CH\(_3\)). \( \delta \)\(_F\) (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\(_9\)F\(_{15}\)N\(_4\)O\(_2\) (FW 538.21): C 29.01, H 1.69, N 10.41. Found: C 29.10, H 1.56, N 10.55%.