Supporting Information

Direct regioselective synthesis of tetrazolium salts by activation of secondary amides under mild conditions

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General information

All glassware was oven dried at 100 °C before use. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Triflic anhydride was freshly distilled over P$_2$O$_5$ before use. Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers ($\tilde{\nu} = 1/\lambda$) are reported in cm$^{-1}$. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI) All $^1$H-NMR and $^{13}$C-NMR experiments were recorded using Bruker AV-400, spectrometers at 300 K. Chemical shifts (δ) are quoted in ppm and coupling constants (J) are quoted in Hz. The 7.27 ppm resonance of residual CHCl$_3$ for proton spectra and 77.16 ppm resonance for carbon spectra were used as internal references. $^1$H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q) or combinations thereof, splitting patterns that could not be interpreted were designated as multiplet (m). Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminum plates coated with kieselgel F254 with 0.2 mm thickness. Visualization was achieved by a combination of ultraviolet light (254 nm) and acidic potassium permanganate. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.) or aluminium oxide 90 active neutral (70-230 mesh, ASTM).

General procedure for the synthesis of the starting materials

Amides synthesis

Amides were synthetized from the corresponding chloride or acid according to the procedure A or B. Spectroscopic data of known compounds are according to the literature.$^{[1]}$

General procedure A:

To a solution of Et$_3$N (3 eq.) and amine (1.5 eq.) in dichloromethane (0.2 M) at 0°C was slowly added the corresponding acyl chloride (1 eq.) and the reaction was allowed to warm to r.t. overnight. The reaction was quenched by addition of NH$_4$Cl, extracted with dichloromethane, dried over Na$_2$SO$_4$ and evaporated. The crude product was purified by column chromatography (0 to 50% heptane/ethyl acetate) to afford the pure amide.

General procedure B:

To a solution of Et$_3$N (2.4 eq.), amine (1.2 eq.) and carboxylic acid (1 eq.) in DMF (0.2 M) was added HATU (1.2 eq.) and the reaction was stirred at r.t. overnight. The reaction was quenched with NaOH 1M, extracted with dichloromethane, dried over Na$_2$SO$_4$ and evaporated. The crude product was purified by column chromatography (0 to 50% heptane/ethyl acetate) to afford the pure amide.
Azides synthesis

**General Procedure for the synthesis of 6 a-t**

A solution of bromide (1 eq.) and NaN₃ (1.5 eq.) in DMF (0.2M) was heated at 80°C overnight. The reaction mixture was cooled, diluted with EtOAc, washed with H₂O and brine, dried over Na₂SO₄ and concentrated under vacuum, to afford the corresponding azide which was used without further purification. Spectroscopic data are according to the literature.⁡[^2]

2-((3r,5r,7r)-adamantan-1-yl)-N-butyricamide 8j

![Structure of 2-((3r,5r,7r)-adamantan-1-yl)-N-butyricamide 8j](image)

To a solution of Et₃N (2.4 mmol, 2.4 eq., 243 mg), amine (1.2 mmol, 1.2 eq., 87.4 mg) and carboxylic acid (1 mmol, 1 eq., 194 mg) in DMF (0.2 M) was added HATU (1.2 mmol, 1.2 eq., 456 mg) and the reaction was stirred at r.t. overnight. The reaction was quenched with NaOH 1M, extracted with DCM, dried over Na₂SO₄ and evaporated. The crude product was purified by column chromatography (0 to 50% heptane/ethyl acetate) to afford 230 mg of the pure amide as a white solid 92% yield. **¹H NMR (400 MHz, CDCl₃)** δ = 5.40 (bs, 1H), 3.22 (dd, J = 13.3, 6.7 Hz, 2H), 1.95 (bs, 3H), 1.89 (s, 2H), 1.70 – 1.60 (m, 12H), 1.50 – 1.43 (m, 2H), 1.34 (dd, J = 15.1, 7.3 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H) ppm. **¹³C NMR (100MHz, CDCl₃)**: δ = 170.9, 52.1, 42.8, 39.3, 36.9, 32.8, 32.0, 28.8, 20.3, 13.9. **HRMS (ESI) m/z** calculated for [M+H]⁺ 250.2165, found 250.2162. **ATR-FTIR (cm⁻¹)**: 3298, 2957, 2920, 2850, 1641, 1551, 1454.
General procedure for the synthesis of tetrazolium salts

To a mixture of amide (0.2 mmol) and 2-fluoropyridine (0.4 mmol, 2 equiv., 38.8 mg, 34.4 µl) in dichloromethane (0.6 mL) triflic anhydride was added dropwise (0.2 mmol, 1 equiv., 56.4 mg, 33.6 µl) at 0 °C under Ar. The mixture was stirred for 15 minutes at this temperature. Then a solution of azide (0.4 mmol, 2 equiv.) in 0.5 ml of dichloromethane was added and the mixture was brought to room temperature ad heated to 40°C. After 16 hours, the solvent was removed under reduced pressure. Purification through column chromatography on Al₂O₃ with 0 to 100% dichloromethane /DMA (DMA = dichloromethane/methanol/NH₄OH mixture 9:1:0.75) afforded the desired products.

1,4-diphenethyl-5-propyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9a

Yellow solid, 46 mg, 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.26 (m, 3H), 7.12 – 7.09 (m, 2H), 4.68 (t, J = 7.0 Hz, 4H), 3.37 (t, J = 7.0 Hz, 4H), 2.93 – 2.89 (m, 2H), 0.91 – 0.85 (m, 2H), 0.73 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ = 154.5, 135.5 (2C), 129.3 (4C), 128.9 (4C), 127.8 (2C), 52.4, 34.3, 24.0, 19.7, 13.8 ppm. HRMS (ESI) m/z calculated for [M]+ 321.2074, found 321.2073. ATR-FTIR (cm⁻¹): 2935, 1555, 1499, 1455, 1224, 1152, 1029, 753, 700, 636.

4-butyl-1-phenethyl-5-propyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9b

Yellow oil, 76 mg, 90% yield (0.2 mmol scale); 2.589 g, 88% yield (7 mmol scale). ¹H NMR (400 MHz, CDCl₃) δ = 7.30-7.26 (m, 3H), 7.14-7.12 (m, 2H), 4.77 (t, J = 6.9 Hz, 2H), 4.44 (t, J = 7.6, 2H), 3.43 (t, J = 6.9 Hz, 2H), 3.15 – 3.10 (m, 2H), 2.05 – 2.01 (m, 2H), 1.43 (dt, J = 14.8, 7.4 Hz, 2H), 1.18 (m, 2H, C14), 1.00 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) 154.0, 135.6, 129.3, 129.0, 127.9, 52.3, 50.7, 34.4, 30.3, 24.2, 19.9, 19.6, 13.9, 13.4 ppm. HRMS (ESI) m/z calculated for [M]+ 273.2074, found 273.2070. ATR-FTIR (cm⁻¹): 2963, 2925, 2877, 1657, 1501, 1458, 1256, 1224, 1154, 637.

4-butyl-5-isobutyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9c
White solid, 60.5 mg, 70 % yield. $^1$H NMR (400 MHz, CDCl$_3$): 7.33–7.26 (m, 3H), 7.19–7.17 (m, 2H), 4.73 (t, $J$ = 7.2 Hz, 2H), 4.46 – 4.42 (m, 2H), 3.49 (t, $J$ = 7.2 Hz, 2H), 3.16 (d, $J$ = 7.9 Hz, 2H), 2.08 (t, $J$ = 7.6 Hz, 2H), 1.62 – 1.60 (m, 2H), 1.53 – 1.43 (m, 2H), 1.01 (t, $J$ = 7.4 Hz, 3H), 0.84 (d, $J$ = 6.6 Hz, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 153.8, 135.6, 129.3, 129.1, 127.9, 52.7, 51.0, 34.10, 31.1, 30.1, 28.2, 22.3, 19.8, 13.5 ppm. HRMS (ESI) $m/z$ calculated for [M]$^+$ 287.2230, found 287.2232. ATR-FTIR (cm$^{-1}$): 2963, 2927, 2876, 1658, 1501, 1466, 1374, 1260, 1224, 1155, 1031.

4-buty-5-neopentyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9d

Brown oil, 76 mg, 84% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.34 – 7.28 (m, 5H), 4.71 – 4.69 (m, 2H), 4.49 – 4.46 (m, 2H), 3.54 (dd, $J$ = 8.7, 7.1 Hz, 2H), 3.30 (s, 2H), 2.19 – 2.14 (m, 2H), 1.54 – 1.50 (m, 2H), 1.04 – 1.01 (m, 1H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 152.9, 135.4, 129.3, 129.2, 127.9, 53.0, 51.7, 35.9, 35.2, 33.9, 30.0, 29.9 (C'Bu), 19.9, 13.6. HRMS (ESI) $m/z$ calculated for [M]$^+$ 301.2387, found 301.2388. ATR-FTIR (cm$^{-1}$): 2962, 2924, 2876, 2853, 1256, 1224, 1152, 1030, 636.

4-buty-5-octyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9e

Yellow sticky oil, 41 mg, 41% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.30 – 7.26 (m, 3H), 7.12 – 7.10 (m, 2H), 4.75 (t, $J$ = 6.9 Hz, 2H), 4.45 – 4.41 (m, 2H), 3.43 (t, $J$ = 6.9 Hz, 2H), 3.14 – 3.10 (m, 2H), 2.06 – 1.98 (m, 2H), 1.46 – 1.38 (m, 2H), 1.31 – 1.21 (m, 10H), 1.07 – 0.98 (m, 5H), 0.88 (m, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 154.5, 135.7, 129.4, 129.0, 128.0, 52.6, 50.8, 34.5, 31.8, 30.3, 29.5, 29.0, 28.9, 26.3, 22.9, 22.7, 19.7, 14.2, 13.5 ppm. HRMS-(ESI) $m/z$ calculated for [M]$^+$ 343.2856 found 343.2850. ATR-FTIR (cm$^{-1}$): 2960, 2929, 2859, 1659, 1588, 1501, 1458, 1264, 1224, 1157, 1032, 753, 702, 638.

4-buty-5-ethyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9f

Orange solid, 59 mg, 72% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.33 – 7.24 (m, 3H), 7.11 (dd, $J$ = 7.7, 1.6 Hz, 2H), 4.79 (t, $J$ = 6.9 Hz, 2H), 4.61 – 4.34 (m, 2H), 3.41 (t, $J$ = 6.9 Hz, 2H), 3.16 (q, $J$ = 7.8 Hz, 2H), 2.09 – 1.89 (m, 2H), 1.41 (dq, $J$ = 14.8, 7.4 Hz, 2H), 0.99 (t, $J$ = 7.4 Hz, 2H), 0.91 (t, $J$ = 7.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.1, 135.5, 129.3, 128.8, 127.9, 52.3, 50.6, 34.5, 30.2, 19.5, 16.3, 13.3, 10.0 ppm. HRMS (ESI) $m/z$ calculated for [M]$^+$ 259.1917, found 259.1919. ATR-FTIR (cm$^{-1}$): 2961, 2922, 2852, 1508, 1459, 1261, 1225, 1156, 1031.

4-buty-1-phenethyl-5-(2,4,4-trimethylpentyl)-1H-tetrazol-4-ium trifluoromethanesulfonate 9g
White solid, 61 mg, 62% $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.33 – 7.28 (m, 3H), 7.21 (d, $J$ = 7.5 Hz, 2H), 4.80 – 4.76 (m, 1H), 4.72 – 4.66 (m, 1H), 4.49 – 4.45 (m, 2H), 3.53 – 3.47 (m, 2H), 3.32 (dd, $J$ = 15.5, 5.4 Hz, 1H), 3.06 – 3.00 (m, 1H), 2.12 – 2.08 (m, 2H), 1.73 – 1.69 (m, 1H), 1.50 (dq, $J$ = 14.7, 7.3 Hz, 2H), 1.29 – 1.26 (m, 2H), 1.05 – 1.01 (m, 3H), 0.89 (s, 9H), 0.70 (d, $J$ = 6.6 Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 153.6, 135.5, 129.3, 129.0, 127.9, 52.6, 51.0, 50.9, 34.0, 31.6, 31.1, 30.1, 29.9, 29.5, 21.7, 19.8, 13.5. HRMS (ESI) m/z calculated for [M]$^+$ 343.2856 found 343.2844. ATR-FTIR (cm$^{-1}$): 2960, 2874, 1501, 1466, 1366, 1260, 1224, 1031

5-benzyl-4-butyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9h

Brown oil, 57 mg, 61% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.36 – 7.28 (m, 5H), 7.10 – 7.09 (m, 2H), 6.73 (d, $J$ = 7.5 Hz, 2H), 4.78 (t, $J$ = 7.1 Hz, 2H), 4.65 (s, 2H), 4.32 – 4.29 (m, 2H), 3.32 (t, $J$ = 7.1 Hz, 2H), 1.71 (dd, $J$ = 14.5, 6.9 Hz, 2H), 1.23 (dd, $J$ = 14.9, 7.5 Hz, 2H), 0.84 (t, $J$ = 7.4 Hz, 3H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 152.7, 153.5, 130.1, 129.4, 129.4, 129.2, 129.0, 128.7, 127.9, 52.6, 51.1, 34.2, 29.9, 29.1, 19.5, 13.3 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 321.2074, found 321.2073. ATR-FTIR (cm$^{-1}$): 2961, 2927, 2876, 1253, 1224, 1152, 1079, 1030, 753, 700, 636.

4-butyl-5-(cyclopentylmethyl)-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9i

Orange oil, 79 mg, 85% yield. $^1$H NMR (500 MHz, d$_6$-DMSO, 373K) 7.36 – 7.27 (m, 5H), 4.89 (t, $J$ = 7.3 Hz, 2H), 4.61 (t, $J$ = 7.3 Hz, 2H), 3.37 (t, $J$ = 7.3 Hz, 2H), 3.32 (d, $J$ = 7.6 Hz, 2H), 2.04 (m, 1H), 1.99 – 1.93 (m, 2H), 1.72 – 1.66 (m, 4H), 1.51 – 1.43 (m, 2H), 1.43 (dt, $J$ = 14.8, 7.4 Hz, 2H), 1.24 (m, 2H), 0.97 (t, $J$ = 7.4 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, d$_6$-DMSO, 373K) $\delta$ = 153.0, 135.7, 128.8, 128.2, 126.7, 50.5, 49.5, 37.2, 33.2, 32.3, 29.4, 25.6, 23.6, 18.4, 12.6 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 313.2387, found 313.2388. ATR-FTIR (cm$^{-1}$): 2961, 2875, 1257, 1224, 1153, 1030, 756, 702, 637, 573.

5-(((3r,5r,7r)-adamantan-1-yl)methyl)-4-butyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9j

Brownish semi-solid, 84 mg, 99% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.36 – 7.26 (m, 5H), 4.69 (dd, $J$ = 8.6, 6.9 Hz, 2H), 4.46 – 4.44 (m, 2H), 3.57 – 3.55 (m, 2H), 3.16 (s, 2H), 2.18 (ddd, $J$ = 15.5, 11.2, 8.0 Hz, 2H), 1.98 (bs, 2H), 1.70 – 1.68 (bs, 3H), 1.55 – 1.45 (m, 11H), 1.04 (t, $J$ = 7.4 Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 152.4, 135.7, 129.3, 127.8, 126.9, 53.1, 51.7, 42.8, 37.4, 37.0, 35.9, 33.8, 30.0, 28.3, 20.0, 13.6 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 379.2856, found 379.2866. ATR-FTIR (cm$^{-1}$): 2908, 2852, 1258, 1223, 1152, 1113, 1095, 1030, 637.
5-(but-3-en-1-yl)-4-butyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9k

Orange oil, 70 mg, 81 % yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.34 – 7.26 (m, 3H), 7.17 – 7.15 (m, 2H), 5.59 (ddt, $J$ = 17.0, 10.2, 6.9 Hz, 1H), 5.01 (dd, $J$ = 10.2, 0.8 Hz, 1H), 4.84 – 4.79 (m, 1H), 4.77 (t, $J$ = 7.0 Hz, 2H), 4.45 – 4.41 (m, 2H), 3.45 (t, $J$ = 7.0 Hz, 2H), 3.32 (t, $J$ = 7.6 Hz, 2H), 2.07 – 1.97 (m, 4H), 1.44 (dq, $J$ = 14.8, 7.4 Hz, 2H), 1.00 (t, $J$ = 7.4 Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 154.0, 135.7, 133.3, 129.4, 129.1, 128.0, 119.2, 52.7, 50.9, 34.3, 30.2, 30.2, 22.6, 19.7, 13.5 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 285.2074, found 285.2063. ATR-FTIR (cm$^{-1}$): 2963, 2931, 2877, 1255, 1152, 1030, 929, 845, 754, 702, 636.

4-butyl-1-phenethyl-5-phenyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9l

Yellow oil, 74 mg, 81% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.73 (t, $J$ = 7.6 Hz, 2H), 7.57 (t, $J$ = 7.8 Hz, 2H), 7.29 – 7.23 (m, 5H), 6.93 (d, $J$ = 7.4 Hz, 2H), 4.72 (t, $J$ = 6.6 Hz, 2H), 4.38 (t, $J$ = 7.4 Hz, 2H), 3.36 (t, $J$ = 6.8 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.31 – 1.26 (m, 2H), 0.88 (t, $J$ = 7.4 Hz, 3H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 151.8, 135.6, 134.4, 130.3, 129.9, 129.4, 128.9, 127.9, 115.4, 52.6, 51.0, 34.7, 30.4, 19.5, 13.3. HRMS (ESI) m/z calculated for [M]$^+$ 307.1917, found 307.1921. ATR-FTIR (cm$^{-1}$): 2962, 2923, 2853, 1605, 1567, 1262, 1224, 1155, 1031, 784, 699, 637.

4-butyl-5-(5-methoxy-5-oxopentyl)-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9m

Yellow oil, 76 mg, 77% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.30 – 7.26 (m, 3H), 7.12 (d, $J$ = 6.1 Hz, 2H), 4.80 (t, $J$ = 6.8 Hz, 2H), 4.47 (t, $J$ = 7.5 Hz, 2H), 3.66 (s, 3H), 3.43 (t, $J$ = 6.8 Hz, 2H), 3.18 – 3.14 (m, 2H), 2.26 (t, $J$ = 6.8 Hz, 2H), 2.02 (dt, $J$ = 15.2, 7.6 Hz, 2H), 1.59 – 1.55 (m, 2H), 1.42 (dt, $J$ = 14.8, 7.4 Hz, 2H), 1.18 – 1.16 (m, 2H), 1.01 (t, $J$ = 7.4 Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 173.2, 154.1, 135.7, 129.4, 129.1, 127.9, 52.6, 51.9, 50.8, 34.6, 32.5, 30.3, 25.3, 24.1, 22.4, 19.7, 13.5 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 345.2285, found 345.2286. ATR-FTIR (cm$^{-1}$): 2958, 2922, 2851, 1729, 1440, 1256, 1224, 1154, 1071, 1030, 637.

1-phenethyl-1,5,6,7,8,9,10,11,12,13,14,15-dodecahydrotetrazolo[1,5-a][1]azacyclotridecin-4-ium trifluoromethanesulfonate 9n
White oil, 71 mg, 75% yield $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 7.30 – 7.26 (m, 3H), 7.14 – 7.13 (m, 2H), 4.77 (t, $J = 6.9$ Hz, 2H), 4.51 (t, $J = 7.0$ Hz, 2H), 3.45 (t, $J = 6.9$ Hz, 2H), 3.22 (t, $J = 7.7$ Hz, 2H), 2.20 – 2.17 (m, 2H), 1.38 – 1.35 (m, 2H), 1.32 – 1.27 (m, 4H), 1.26 – 1.24 (m, 2H), 1.10 – 1.09 (m, 2H), 1.08 – 0.93 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.0, 135.7, 129.4, 129.1, 128.0, 52.6, 50.0, 34.4, 26.3, 26.2, 25.7, 25.3, 24.7, 24.6, 24.1, 23.9, 22.9, 22.4 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 327.2543, found 327.2538. ATR-FTIR (cm$^{-1}$): 2931, 2862, 1501, 1457, 1260, 1224, 1153, 1031.

4-allyl-1-phenethyl-5-propyl-1H-tetrazol-4-iium trifluoromethanesulfonate 9o

Yellow oil, 34 mg, 42% $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.31 - 7.25 (m, 3H), 7.15 – 7.14 (m, 2H), 6.04 (dq, $J = 10.7$, 6.1 Hz, 1H), 5.44 (dd, $J = 40.3$, 13.6 Hz, 2H), 5.22 (d, $J = 6.1$ Hz, 2H), 4.82 (t, $J = 7.0$ Hz, 2H), 3.43 (t, $J = 6.9$ Hz, 2H), 3.26 – 3.23 (m, 2H), 1.19 – 1.15 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 154.9, 135.6, 129.4, 129.0, 127.9, 127.9, 123.0, 53.2, 52.6, 34.5, 24.8, 20.1, 13.9 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 257.1761, found 257.1753. ATR-FTIR (cm$^{-1}$): 2925, 2854, 1737, 1464, 1373, 1236, 1159, 1097, 1044, 938.

4-cyclohexyl-1-phenethyl-5-propyl-1H-tetrazol-4-iium trifluoromethanesulfonate 9p

Yellow oil, 65 mg, 73% $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.31 – 7.25 (m, 3H), 7.12 (dd, $J = 7.7$, 1.4 Hz, 2H), 4.78 (t, $J = 6.9$ Hz, 2H), 4.46 – 4.40 (m, 1H), 3.42 (t, $J = 6.9$ Hz, 2H), 3.18 – 3.14 (m, 2H), 2.17 – 2.14 (m, 2H), 2.04 – 1.96 (m, 2H), 1.79 (d, $J = 12.5$ Hz, 2H), 1.50 – 1.43 (m, 1H), 1.33 – 1.30 (m, 2H), 1.17 – 1.16 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 153.5, 135.7, 129.3, 129.0, 127.9, 51.9, 52.5, 34.5, 32.5, 25.0, 24.6, 24.5, 20.4, 14.0 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 299.2230, found 299.2221. ATR-FTIR (cm$^{-1}$): 2940, 1497, 1455, 1262, 1224, 1153, 1031.

1-benzyl-4-butyl-5-propyl-1H-tetrazol-4-iium trifluoromethanesulfonate 9q

Yellow solid, 62 mg, 76% yield $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.43 – 7.39 (m, 5H), 5.80 (s, 2H), 4.48 – 4.45 (m, 2H), 3.27 – 3.25 (m, 2H), 2.06 – 2.01 (m, 2H), 1.49 – 1.42 (m, 2H), 1.34 – 1.29 (m, 2H), 0.98 (t, $J = 7.4$ Hz, 3H), 0.90 (t, $J = 7.3$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 154.2, 130.7, 130.1, 129.7, 128.9, 54.7, 50.8, 30.2, 24.7, 20.0, 19.7, 13.9, 13.4 ppm. HRMS (ESI) m/z calculated for [M]$^+$ 259.1905. ATR-FTIR (cm$^{-1}$): 2965, 2933, 2879, 1659, 1504, 1460, 1266, 1225, 1156, 1031.

1-(4-bromobenzyl)-4-butyl-5-propyl-1H-tetrazol-4-iium trifluoromethanesulfonate 9r

Yellow solid, 62 mg, 81% $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.56 (d, $J = 8.4$, 2H), 7.33 (d, $J = 8.4$, 2H), 5.76 (s, 2H), 4.48 – 4.45 (m, 2H), 3.33 – 3.30 (m, 2H), 2.05 – 2.00 (m, 2H),
1.47 – 1.45 (m, 4H), 1.00 – 0.96 (m, 6H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 154.3, 132.8, 130.9, 129.6, 124.5, 53.9, 50.8, 30.3, 24.6, 20.2, 19.7, 13.9, 13.5 ppm. HRMS (ESI) m/z calculated for [M$^+$] $^{337.1022}$, found 337.1028. ATR-FTIR (cm$^{-1}$): 2966, 2937, 2877, 1659, 1593, 1556, 1492, 1466, 1411, 1383, 1255, 1224, 1152, 1093, 1071, 1029, 913, 857, 878.

5-((3r,5r,7r)-adamantan-1-yl)methyl)-4-butyl-1-(naphthalen-2-ylmethyl)-1H-tetrazol-4-ium trifluoromethanesulfonate 9s

Yellow semi-solid, 51 mg, 45% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.03 (s, 1H), 7.89 – 7.83 (m, 3H), 7.61 (dd, $J$ = 8.5, 1.6 Hz, 1H), 7.54 (ddd, $J$ = 9.1, 7.8, 2.5 Hz, 2H), 5.94 (s, 2H), 4.53 – 4.50 (m, 2H), 3.48 (s, 2H), 2.16 – 2.14 (m, 2H), 1.97 (bs, 3H), 1.68 – 1.66 (m, 3H), 1.60 – 1.49 (m, 10H), 0.99 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ = 152.7, 133.6, 133.2, 129.9, 129.4, 128.4, 127.9, 127.5, 127.4, 127.0, 126.3, 55.7, 51.8, 42.8, 37.5, 35.9, 30.0, 28.3, 19.9, 13.6. HRMS (ESI) m/z calculated for [M$^+$] 415.2856, found 415.2858. ATR-FTIR (cm$^{-1}$): 2910, 2852, 1672, 1456, 1286, 1268, 1249, 1224, 1156.7, 1031.

4-butyl-1-(5-cyanopentyl)-5-(2,4,4-trimethylpentyl)-1H-tetrazol-4-ium trifluoromethanesulfonate 9t

Yellow oil, 85 mg, 88% $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 4.55 – 4.45 (m, 4H), 3.38 (dd, $J$ = 15.6, 6.2 Hz, 1H), 3.19 (dd, $J$ = 15.6, 10 Hz, 1H), 2.41 (t, $J$ = 6.8 Hz, 2H), 2.20 – 2.18 (m, 2H), 2.10 – 2.08 (m, 2H), 1.99, 1.96 (m, 2H), 1.78 – 1.73 (m, 1H), 1.67 – 1.63 (m, 4H), 1.52 – 1.47 (m, 2H), 1.38 (dd, $J$ = 14.2, 6.8 Hz, 1H), 1.26 (dd, $J$ = 14.2, 3.7 Hz, 1H), 1.03 – 1.98 (m, 6H), 0.93 (s, 9H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 153.5, 119.7, 51.0, 50.8, 50.5, 31.6, 31.2, 30.1, 29.9, 29.5, 27.3, 25.4, 24.7, 22.2, 19.8, 16.9, 13.5. HRMS (ESI) m/z calculated for [M$^+$] 334.2965, found 334.2974. ATR-FTIR (cm$^{-1}$): 2958, 2873, 1506, 1467, 1366, 1255, 1223, 1151, 1067, 1030.

4-butyl-5-(cyclopentylmethyl)-1-heptyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9u

Transparent liquid, 84 mg, 90% $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ = 4.49 (dd, $J$ = 15.4, 7.6 Hz, 4H), 3.39 (d, $J$ = 7.9 Hz, 2H), 2.14 – 2.06 (m, 5H), 1.81 – 1.75 (m, 4H), 1.63 – 1.59 (m, 2H), 1.53 – 1.40 (m, 4H), 1.38 – 1.34 (m, 2H), 1.33 – 1.25 (m, 6H), 1.01 (t, $J$ = 7.4 Hz, 3H), 0.88 (t, $J$ = 6.9 Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 153.7, 51.1, 50.9, 38.5, 32.8, 32.5, 30.2, 28.7, 28.3, 28.2, 26.4, 24.5, 22.6, 19.8, 14.1, 13.5 ppm. HRMS (ESI) m/z calculated for [M$^+$] 307.2856, found 307.2858. ATR-FTIR (cm$^{-1}$): 2957, 2931, 2873, 1506, 1463, 1255, 1223, 1151, 1030.
Gram scale experiment

To a mixture of amide (7 mmol, 1.003 g) and 2-fluoropyridine (14 mmol, 2 equiv., 1.359 g, 1.21 ml) in DCM (20 mL) triflic anhydride was added dropwise (7 mmol, 1 equiv., 1.975 g, 1.18 mL) at 0 °C under Ar. The mixture was stirred for 15 minutes at this temperature. Then a solution of azide (14 mmol, 2 equiv., 2.061 g) in 14 ml of dichloromethane was added and the mixture was brought to room temperature ad heated to 40°C. After 16 hours, the solvent was removed under reduced pressure. Purification through column chromatography on Al₂O₃ with dichloromethane/DMA 0 to 100% (DMA = dichloromethane/methanol/NH₄OH mixture 9:1:0.75) afforded 2.569 g (88% yield) of the desired product 9b as a yellow oil.
Computational details

All geometries were optimized at the B3LYP-D3/6-31+G(d,p) level of theory. The nature of all stationary points (minima and transition states) was verified through computation of the vibrational frequencies. The thermal corrections to the Gibbs free energy were combined with single point energies calculated at the RI-MP2/def2-TZVP//B3LYP-D3/6-31+G(d,p) level to yield Gibbs free energies (G_{298}) at 298.15 K (all energies are reported in kcal mol\(^{-1}\)). The density-based solvation model SMD (for geometry optimization) and Conductor-like screening model COSMO (for RI-MP2 single-point calculations) were applied to consider solvent effects. The DFT calculations have been performed with the Gaussian09 program package, while for the RI-MP2 single point calculations the Turbomole V7.0 program package was used. Computed structures were visualized using the Chemcraft software.

Cartesian coordinates (the most stable (\Delta G_{298}) conformations) as computed at the RI-MP2-COSMO/def2-TZVP//B3LYP-D3-SMD/6-31+G(d,p) level of theory
|   |      |      |      |
|---|------|------|------|
| N | 1.8339600 | 1.4068000 | 1.3191900 |
| N | 0.9509700 | -1.6525400 | 1.9150400 |
| N | 1.0127000 | -2.2942000 | 0.9696900 |
| N | 1.2329700 | -3.0042300 | -0.0085700 |
| C | 2.4099600 | 0.9121400 | 0.4587900 |
| C | 0.0710500 | -3.3407000 | -0.8647000 |
| H | -0.7339000 | -3.7899100 | 0.2731700 |
| H | -0.2930200 | -2.4451900 | 1.3744300 |
| H | 0.4294200 | -4.0649500 | 1.5958700 |
| C | 3.1805200 | 0.3212200 | -0.6186600 |
| H | 4.2171500 | 0.2578800 | 0.2670600 |
| H | 2.7996500 | 0.4587900 | 1.9150400 |
| C | 3.0704200 | 1.1290800 | -0.7503700 |
| H | 5.5333300 | 0.2857800 | 1.5958700 |
| H | 5.2168800 | 0.7848700 | -0.1297800 |
| C | 0.7955700 | 2.2516800 | 0.7285100 |

|   |      |      |
|---|------|------|
| N | 1.8615700 | 1.8766900 | -0.1671100 |
| N | 1.8794800 | -0.4794800 | 2.7240500 |
| N | 1.8168300 | -0.6364300 | 1.6012400 |
| N | 1.9814400 | -0.6904900 | 0.3645800 |
| C | 2.4546100 | 0.8982900 | -0.5224900 |
| C | 1.7651000 | -2.0018200 | -0.2927700 |
| H | 1.3804600 | -1.7899500 | -1.2886100 |
| H | 2.7133200 | -2.5423300 | -0.3517500 |
| H | 1.0252600 | -2.5742600 | 0.2682700 |
| C | 3.5159700 | 0.4655000 | -1.4586200 |
| H | 3.1083700 | -0.3221700 | -2.1006300 |
| H | 3.7148400 | 1.3356400 | -2.0924500 |
| C | 4.7946200 | -0.0091300 | -0.7525900 |
| H | 4.6050200 | -0.8836600 | -0.1242500 |
| H | 5.5333300 | -0.2857000 | -1.5096700 |
| H | 5.2168800 | 0.7848700 | -0.1298900 |
| C | 0.7955700 | 2.2516800 | 0.7285100 |
|     |  X         |  Y         |  Z         |
|-----|------------|------------|------------|
| H   | 0.1542300  | 2.9714400  | 0.2173500  |
| H   | 0.2119900  | 1.3792500  | 1.0282600  |
| H   | 1.2384700  | 2.7380800  | 1.6026600  |
| S   | -1.4798800 | -0.6828100 | -0.2903900 |
| O   | -0.6417600 | 0.1037100  | -1.2280500 |
| O   | -0.9422200 | -0.7677500 | 1.0928500  |
| O   | -2.0317300 | -1.9455100 | -0.8322600 |
| C   | -3.0040800 | 0.4013700  | -0.0076900 |
| F   | -2.5776100 | 3.5735700  | -0.8322600 |
| F   | -3.1222500 | -0.5211700 | 0.4461800  |
| B   | -2.6736100 | 1.6031600  | 0.4461800  |
| N   | 1.9012500  | 1.3774600  | 0.6251600  |
| N   | 0.5432300  | -0.3693700 | 2.8286100  |
| N   | 1.0156700  | -0.6556800 | 1.8534300  |
| N   | 1.5940100  | -0.9016000 | 0.7508300  |
| C   | 2.0356100  | 0.3005500  | -0.0076900 |
| C   | 1.6377000  | -2.3196400 | 0.2982600  |
| H   | 0.9208400  | -2.4430900 | -0.5112600 |
| H   | 2.6586300  | -2.5290100 | -0.0191200 |
| H   | 1.3745600  | -2.9529600 | 1.1441300  |
| C   | 2.5926700  | -0.0178800 | -1.3671000 |
| H   | 2.0933600  | -0.8935800 | -1.7829000 |
| H   | 2.3297700  | 0.8198000  | -2.0180300 |
| C   | 4.1192500  | -0.2114200 | -1.3374000 |
| H   | 4.4037000  | -1.0549900 | -0.7000700 |
| H   | 4.4815600  | -0.4125400 | -2.3500100 |
| H   | 4.6222900  | 0.6851600  | -0.9625300 |
| C   | 2.2711200  | 2.6642000  | 0.0628700  |
| H   | 2.6382800  | 2.6304300  | -0.9684100 |
| H   | 1.3961000  | 3.3202500  | 0.1105900  |
| H   | 3.0438700  | 3.1060700  | 0.7007600  |
| S   | -1.6965800 | -0.8360000 | -0.5477000 |
| O   | -0.5179100 | -0.5946700 | -1.4185700 |
| O   | -1.3659100 | -1.4810900 | 0.7505400  |
| O   | -2.9044000 | -1.3486400 | -1.2289000 |
| C   | -2.1953000 | 0.9016600  | -0.0218300 |
| F   | -2.4631900 | 1.6788300  | -1.0914500 |
| F   | -3.2949800 | 0.8769900  | 0.7584900  |
| F   | -1.2037700 | 1.4925300  | 0.6799000  |

**TS_{B-C}**

|     |  X         |  Y         |  Z         |
|-----|------------|------------|------------|
| N   | 1.8253300  | 1.3951100  | 0.5475600  |
| N   | 0.8794500  | 0.1248600  | 2.6941800  |
| N   | 1.1977900  | -0.6120600 | 1.8974400  |
| N   | 1.7109400  | -0.9048600 | 0.7691000  |
| C   | 2.0176700  | 0.3084500  | -0.0432000 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| O       | -2.5203600| -1.9211200| -0.8707700|
| C       | -2.4452700| 0.5163700 | 0.1706700 |
| F       | -3.3630000| 0.2094400 | 1.1106400 |
| F       | -1.6203900| 1.4525400 | 0.6892200 |
| F       | -3.0925600| 1.0710400 | -0.8745000|
X-ray Analysis

The X-ray intensity data was measured on Bruker X8 APEX2 or D8 Venture diffractometer equipped with multilayer monochromators, Mo K/α INCOATEC micro focus sealed tube, Photon or APEX2 detector and Kryoflex cooling device. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted at calculated positions and refined with a riding model. The following software was used: APEX2 (v2011.2-0 or v2013.6-2)\[^{12}\] for data collection, cell refinement, data reduction. SADABS\[^{13}\] for absorption correction, OLEX2\[^{14}\] for structure solution, refinement, molecular diagrams and graphical user-interface, Shelxle\[^{15}\] for refinement and graphical user-interface SHELXS-2013\[^{16}\] for structure solution, SHELXL-2013\[^{17}\] for refinement, Platon\[^{18}\] for symmetry check. Experimental data and CCDC-code can be found in Table 1. Crystal data, data collection parameters, and structure refinement details are given in Tables 2 to 5. Molecular structure in “Ortep View” is displayed in Figures 1 and 2.

Table 1. Experimental parameter and CCDC-Code.

| Manuscript No. | Machine | Source | Temp. | Detector Distance | Time/Frame | #Frames | Frame width | CCDC   |
|---------------|---------|--------|-------|-------------------|------------|---------|-------------|--------|
| 9g            | D8      | Mo     | 100   | 37                | 60         | 1380    | 0.5         | 1541876 |
| 9a            | X8      | Mo     | 130   | 35                | 10         | 1069    | 0.5         | 1541875 |
4-butyl-1-phenethyl-5-(2,4,4-trimethylpentyl)-1H-tetrazol-4-ium trifluoromethanesulfonate [9g] for Organic Letters.

Figure 1 Asymmetric Unit of [9g], drawn with 50% displacement ellipsoids.

Table 2 Sample and crystal data of [9g].

| Chemical formula | C22H35F3N4O3S | Crystal system | monochromatic |
|------------------|----------------|---------------|---------------|
| Formula weight [g/mol] | 492.6 | Space group | P21/n |
| Temperature [K] | 100 | Z | 4 |
| Measurement method | μf and μw scans | Volume [Å³] | 2567.0(4) |
| Radiation (Wavelength [Å]) | MoKα (λ = 0.71073) | Unit cell dimensions [Å] and [°] | 8.4504(7) | 90 |
| Crystal size [mm³] | 0.25 × 0.2 × 0.01 | 22.707(2) | 92.561(4) |
| Crystal habit | clear colourless plate | 13.3915(11) | 90 |
| Density (calculated) / [g/cm³] | 1.275 | Absorption coefficient / [mm⁻¹] | 0.177 |
| Abs. correction Tmin | 0.6672 | Abs. correction Tmax | 0.746 |
Table 3 Data collection and structure refinement of [9g].

| Index ranges      | -11 ≤ h ≤ 11, -32 ≤ k ≤ 31, -18 ≤ l ≤ 18 | Theta range for data collection [°] | 4.706 to 60.42 |
|-------------------|--------------------------------------------|-------------------------------------|----------------|
| Reflections number| 66236                                      | Data / restraints / parameters       | 7492/0/303     |
| Refinement method | Least squares                              | Final R indices                      | R1 = 0.0795, wR2 = 0.1005 |
| Function minimized| Σ w(Fo^2 - Fc^2)^2                          |                                     | I>2σ(I) R1 = 0.0411, wR2 = 0.0897 |
| Goodness-of-fit on F^2 | 1.018                                   | Weighting scheme                    | w=1/[σ^2(Fo^2)+(0.0464P)^2+0.6277P] |
| Largest diff. peak and hole [e Å^3] | 0.26/-0.52            |                                     |                |

1,4-diphenethyl-5-propyl-1H-tetrazol-4-ium trifluoromethanesulfonate [9a] for Organic Letters.

Figure 2 Asymmetric Unit of [9a], drawn with 50% displacement ellipsoids.
Table 4 Sample and crystal data of [9a].

| Chemical formula | C21H25F3N4O3S | Crystal system | triclinic |
|-------------------|----------------|----------------|-----------|
| Formula weight [g/mol] | 470.51 | Space group | P-1 |
| Temperature [K] | 130 | Z | 2 |
| Measurement method | θf and θw scans | Volume [Å³] | 1125.14(18) |
| Radiation (Wavelength [Å]) | MoKα (λ = 0.71073) | Unit cell dimensions [Å] and [°] | 9.3964(9) | 71.424(3) |
| Crystal size [mm³] | 0.3 × 0.2 × 0.07 | 9.5657(8) | 86.759(3) |
| Crystal habit | clear colourless block | Absorption coefficient / [mm⁻¹] | 0.199 |
| Density (calculated) / [g/cm³] | 1.389 | Abs. correction Tmax | 0.7452 |
| Abs. correction Tmin | 0.5063 | F(000) [e⁻] | 492 |

Table 5 Data collection and structure refinement of [9a].

| Index ranges | -11 ≤ h ≤ 11, -11 ≤ k ≤ 8, -16 ≤ l ≤ 15 | Theta range for data collection [°] | 4.358 to 50.922 |
|----------------|-----------------------------------------------|-----------------------------------|------------------|
| Reflections number | 12289 | Data / restraints / parameters | 4125/0/290 |
| Refinement method | Least squares | Final R indices | all data | R1 = 0.0485, wR2 = 0.1003 |
| Function minimized | Σ w(Fo² - Fc²)² | I>2σ(I) | R1 = 0.0388, wR2 = 0.0936 |
| Goodness-of-fit on F² | 1.05 | Weighting scheme | w=1/[σ²(Fo²)+0.0328P²+0.3958P] |
| Largest diff. peak and hole [e Å⁻³] | 0.31/-0.37 | where P=(Fo²+2Fc²)/3 |
Spectra

8j

8j
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