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 ºC 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_2O_5 before use. Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers ($\tilde{\upsilon} = 1/\lambda$) 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_3N (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_4Cl, extracted with dichloromethane, dried over Na_2SO_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:

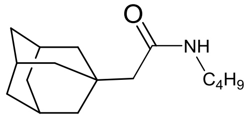
To a solution of Et_3N (2.4 eq.), amine (1.2 eq.) and carboxylic acid (1 eq.) in DMF (0.2 M) was added HATU (1.2 eq.) and the reaction was stirred at r.t. overnight. The reaction was quenched with NaOH 1M, extracted with dichloromethane, dried over Na_2SO_4 and evaporated. The crude product was purified 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

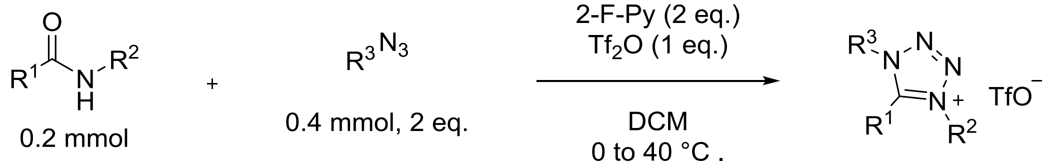
A solution of bromide (1 eq.) and NaN_3 (1.5 eq.) in DMF (0.2M) was heated at 80°C overnight. The reaction mixture was cooled, diluted with EtOAc, washed with H_2O and brine, dried over Na_2SO_4 and concentrated under vacuum, to afford the corresponding azide which was used without further purification. Spectroscopic data are according to the literature. [2]

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



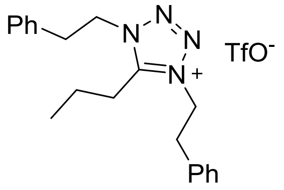
To a solution of Et_3N (2.4 mmol, 2.4 eq., 243 mg), amine (1.2 mmol, 1.2 eq., 87.4 mg) and carboxylic acid (1 mmol, 1 eq., 194 mg) in DMF (0.2 M) was added HATU (1.2 mmol, 1.2 eq., 456 mg) and the reaction was stirred at r.t. overnight. The reaction was quenched with NaOH 1M, extracted with DCM, dried over Na_2SO_4 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. **^{1}H NMR (400 MHz, $CDCl_3$)** 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. **^{13}C NMR (100MHz, $CDCl_3$):** 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



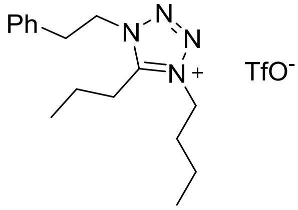
To a mixture of amide (0.2 mmol) and 2-fluoropyridine (0.4 mmol, 2 equiv., 38.8 mg, 34.4 μl) in dichloromethane (0.6 mL) triflic anhydride was added dropwise (0.2 mmol, 1 equiv., 56.4 mg, 33.6 μL.) at 0 °C under Ar. The mixture was stirred for 15 minutes at this temperature. Then a solution of azide (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 Al$_2$O$_3$ with 0 to 100% dichloromethane /DMA (DMA = dichloromethane/methanol/NH$_4$OH mixture 9:1:0.75) afforded the desired products.

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



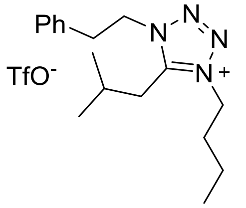
Yellow solid, 46 mg, 50% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.28 – 7.26 (m, 3H), 7.12 – 7.09 (m, 2H), 4.68 (t, *J* = 7.0 Hz, 4H), 3.37 (t, *J* = 7.0 Hz, 4H), 2.93 – 2.89 (m, 2H), 0.91 – 0.85 (m, 2H), 0.73 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$)** δ = 154.5, 135.5 (2C), 129.3 (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



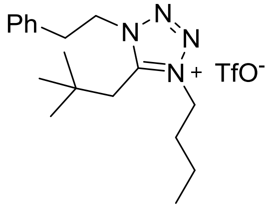
Yellow oil, 76 mg, 90% yield (0.2 mmol scale); 2.589 g, 88% yield (7 mmol scale). **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.30-7.26 (m, 3H), 7.14-7.12 (m, 2H), 4.77 (t, *J* = 6.9 Hz, 2H), 4.44 (t, *J* = 7.6, 2H), 3.43 (t, *J* = 6.9 Hz, 2H,), 3.15 – 3.10 (m, 2H), 2.05 – 2.01 (m, 2H), 1.43 (dt, *J* = 14.8, 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) ppm. **^{13}C NMR (100 MHz, CDCl$_3$)** 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



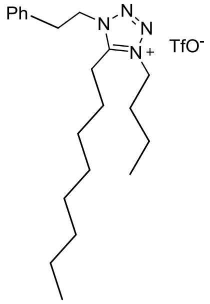
White solid, 60.5 mg, 70 % yield. **^{1}H NMR (400 MHz, CDCl$_3$)** 7.33 – 7.26 (m, 3H), 7.19 – 7.17 (m, 2H), 4.73 (t, *J* = 7.2, 2H), 4.46 – 4.42 (m, 2H), 3.49 (t, *J* = 7.2 Hz, 2H), 3.16 (d, *J* = 7.9 Hz, 2H), 2.08 (t, *J* = 7.6 Hz, 2H), 1.62 - 1.60 (m, 1H), 1.53 – 43 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 6H) ppm.**^{13}C NMR (100 MHz, CDCl$_3$)** δ = 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-butyl-5-neopentyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9d



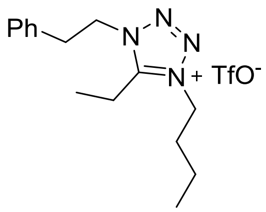
Brown oil, 76 mg, 84% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ= 7.34 – 7.28 (m, 5H), 4.71 – 4.69 (m, 2H), 4.49 – 4.46 (m, 2H), 3.54 (dd, *J* = 8.7, 7.1 Hz, 2H), 3.30 (s, 2H), 2.19 – 2.14 (m, 2H), 1.54 – 1.50 (m, 2H), 1.04 – 1.01 (m, 12H) ppm. **^{13}C NMR (150 MHz, CDCl$_3$)** δ = 152.9, 135.4, 129.3, 129.2, 127.9, 53.0, 51.7, 35.9, 35.2, 33.9, 30.0, 29.9 (C^{t}Bu), 19.9, 13.6. **HRMS** (ESI) m/z calculated for [M]$^+$ 301.23878, found 301.2388. **ATR-FTIR (cm^{-1})**: 2962, 2924, 2876, 2853, 1256, 1224, 1152, 1030, 636.

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



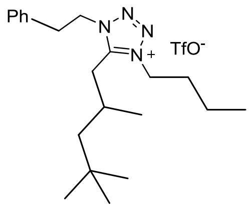
Yellow sticky oil, 41 mg, 41% yield. **^{1}H NMR (400 MHz, CDCl$_3$) δ =** 7.30 – 7.26 (m, 3H), 7.12– 7.10 (m, 2H), 4.75 (t, *J* = 6.9 Hz, 2H), 4.45 – 4.41 (m, 2H), 3.43 (t, *J* = 6.9 Hz, 2H), 3.14 – 3.10 (m, 2H), 2.06 – 1.98 (m, 2H), 1.46 – 1.38 (m, 2H), 1.31 – 1.21 (m, 10H), 1.07 – 0.98 (m, 5H), 0.88 (m, 3H) ppm. **^{13}C NMR (101 MHz, CDCl$_3$) δ** = 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-butyl-5-ethyl-1-phenethyl-1H-tetrazol-4-ium trifluoromethanesulfonate 9f



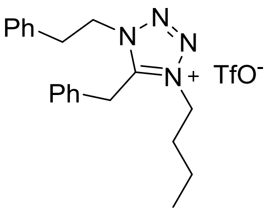
Orange solid, 59 mg, 72% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ= 7.33 – 7.24 (m, 3H), 7.11 (dd, *J* = 7.7, 1.6 Hz, 2H), 4.79 (t, *J* = 6.9 Hz, 2H), 4.61 – 4.34 (m, 2H), 3.41 (t, *J* = 6.9 Hz, 2H), 3.16 (q, *J* = 7.8 Hz, 2H), 2.09 – 1.89 (m, 2H), 1.41 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.8 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ = 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-butyl-1-phenethyl-5-(2,4,4-trimethylpentyl)-1H-tetrazol-4-ium trifluoromethanesulfonate 9g



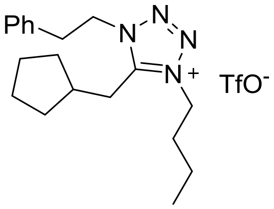
White solid, 61 mg, 62% **^{1}H NMR (400 MHz, CDCl$_3$) δ =** 7.33 – 7.28 (m, 3H), 7.21 (d, *J* = 7.5 Hz, 2H), 4.80 – 4.76 (m, 1H), 4.72 – 4.66 (m, 1H), 4.49 – 4.45 (m, 2H), 3.53 – 3.47 (m, 2H), 3.32 (dd, *J* = 15.5, 5.4 Hz, 1H), 3.06 – 3.00 (m, 1H), 2.12 – 2.08 (m, 2H), 1.73 – 1.69 (m, 1H), 1.50 (dq, *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$_3$) δ =** 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



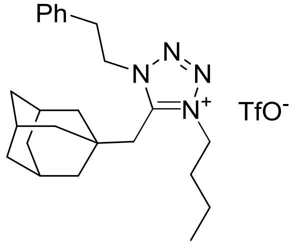
Brown oil, 57 mg, 61% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ = 7.36 – 7.28 (m, 5H), 7.10 - 7.09 (m, 2H), 6.73 (d, *J* = 7.5 Hz, 2H), 4.78 (t, *J* = 7.1 Hz, 2H), 4.65 (s, 2H), 4.32 – 4.29 (m, 2H), 3.32 (t, *J* = 7.1 Hz, 2H), 1.71 (dd, *J* = 14.5, 6.9 Hz, 2H), 1.23 (dd, *J* = 14.9, 7.5 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (150 MHz, CDCl$_3$)** δ = 152.7, 135.3, 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, 1255, 1224, 1152, 1079, 1030, 753, 700, 636.

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



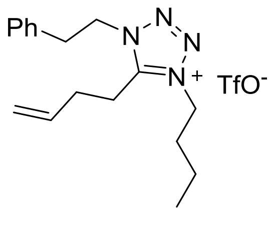
Orange oil, 79 mg, 85% yield. **^{1}H NMR (500 MHz, d6-DMSO, 373K)** 7.36 - 7.27 (m, 5H), 4.89 (t, *J* = 7.3 Hz, 2H), 4.61 (t, *J* = 7.3 Hz, 2H), 3.37 (t, *J* = 7.3 Hz, 2H), 3.32 (d, *J* = 7.6 Hz, 2H), 2.04 (m, 1H), 1.99 – 1.93 (m, 2H), 1.72 – 1.66 (m, 4H), 1.51 – 1.43 (m, 2H), 1.43 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.24 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (125 MHz, d6-DMSO, 373K)** δ = 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



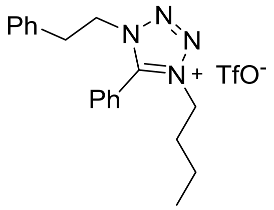
Brownish semi-solid, 84 mg, 99% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.36 – 7.26 (m, 5H), 4.69 (dd, *J* = 8.6, 6.9 Hz, 2H), 4.46 – 4.44 (m, 2H), 3.57 – 3.55 (m, 2H), 3.16 (s, 2H), 2.18 (ddd, *J* = 15.5, 11.2, 8.0 Hz, 2H), 1.98 (bs, 2H), 1.70 – 1.68 (bs, 3H), 1.55 – 1.45 (m, 11H), 1.04 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$)** δ = 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



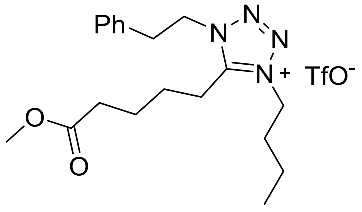
Orange oil, 70 mg, 81 % yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.34 – 7.26 (m, 3H), 7.17 – 7.15 (m, 2H), 5.59 (ddt, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.01 (dd, *J* = 10.2, 0.8 Hz, 1H), 4.84 – 4.79 (m, 1H), 4.77 (t, *J* = 7.0 Hz, 2H), 4.45 – 4.41 (m, 2H), 3.45 (t, *J* = 7.0 Hz, 2H), 3.32 (t, *J* = 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$_3$)** δ = 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, 1224, 1152, 1030, 929, 845, 754, 702, 636.

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



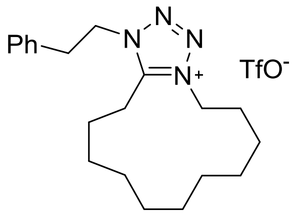
Yellow oil, 74 mg, 81% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ= 7.73 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.23 (m, 5H), 6.93 (d, *J* = 7.4 Hz, 2H), 4.72 (t, *J* = 6.6 Hz, 2H), 4.38 (t, *J* = 7.4 Hz, 2H), 3.36 (t, *J* = 6.8 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.31 – 1.26 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (150 MHz, CDCl$_3$)** δ = 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



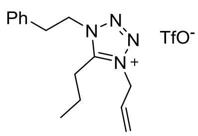
Yellow oil, 76 mg, 77% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ = 7.30 – 7.26 (m, 3H), 7.12 (d, *J* = 6.1 Hz, 2H), 4.80 (t, *J* = 6.8 Hz, 2H), 4.47 (t, *J* = 7.5 Hz, 2H), 3.66 (s, 3H), 3.43 (t, *J* = 6.8 Hz, 2H), 3.18 – 3.14 (m, 2H), 2.26 (t, *J* = 6.8 Hz, 2H), 2.02 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.59 – 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$_3$)** δ = 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



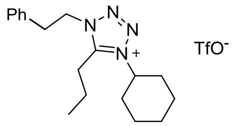
White oil, 71 mg, 75% yield **^{1}H NMR (600 MHz, CDCl$_3$) δ** = 7.30 – 7.26 (m, 3H), 7.14 – 7.13 (m, 2H), 4.77 (t, *J* = 6.9 Hz, 2H), 4.51 (t, *J* = 7.0 Hz, 2H), 3.45 (t, *J* = 6.9 Hz, 2H), 3.22 (t, *J* = 7.7 Hz, 2H), 2.20 – 2.17 (m, 2H), 1.38 – 1.35 (m, 2H), 1.32 – 1.27 (m, 4H), 1.26 – 1.24 (m, 2H), 1.10 – 1.09 (m, 2H), 1.08 – 0.93 (m, 2H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 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-ium trifluoromethanesulfonate 9o



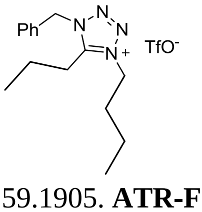
Yellow oil, 34 mg, 42% **^{1}H NMR (400 MHz, CDCl3) δ** = 7.31 - 7.25 (m, 3H), 7.15 – 7.14 (m, 2H), 6.04 (dq, *J* = 10.7, 6.1 Hz, 1H), 5.44 (dd, *J* = 40.3, 13.6 Hz, 2H), 5.22 (d, *J* = 6.1 Hz, 2H), 4.82 (t, *J* = 7.0 Hz, 2H), 3.43 (t, *J* = 6.9 Hz, 2H), 3.26 – 3.23 (m, 2H), 1.19 – 1.15 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 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-ium trifluoromethanesulfonate 9p



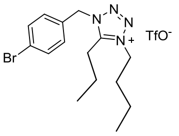
Yellow oil, 65 mg, 73% **^{1}H NMR (400 MHz, CDCl$_3$) δ =** 7.31 – 7.25 (m, 3H), 7.12 (dd, *J* = 7.7, 1.4 Hz, 2H), 4.78 (t, *J* = 6.9 Hz, 2H), 4.46 – 4.40 (m, 1H), 3.42 (t, *J* = 6.9 Hz, 2H), 3.18 – 3.14 (m, 2H), 2.17 – 2.14 (m, 2H), 2.04 – 1.96 (m, 2H), 1.79 (d, *J* = 12.5 Hz, 2H), 1.50 – 1.43 (m, 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$_3$) δ** = 153.5, 135.7, 129.3, 129.0, 127.9, 61.9, 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-ium trifluoromethanesulfonate 9q



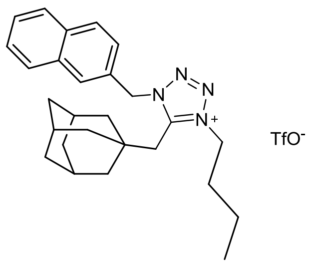
Yellow solid, 62 mg, 76% yield **^{1}H NMR (400 MHz, CDCl$_3$) δ =** 7.43 – 7.39 (m, 5H), 5.80 (s, 2H), 4.48 – 4.45 (m, 2H), 3.27 – 3.25 (m, 2H), 2.06 – 2.01 (m, 2H), 1.49 – 1.42 (m, 2H), 1.34 – 1.29 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 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$^+$] 259.1917, found 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-ium trifluoromethanesulfonate 9r



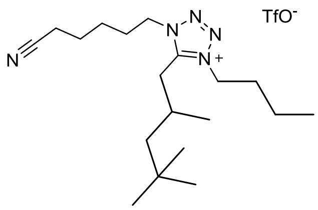
Yellow solid, 62 mg, 81% **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 7.56 (d, *J* = 8.4, 2H), 7.33 (d, *J* = 8.4, 2H), 5.76 (s, 2H), 4.48 – 4.45 (m, 2H), 3.33 – 3.30 (m, 2H), 2.05 – 2.00 (m, 2H), 1.47 – 1.45 (m, 4H,), 1.00 – 0.96 (m, 6H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$) δ** = 154.3, 132.8, 130.9, 129.6, 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, 1013, 935, 878.

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



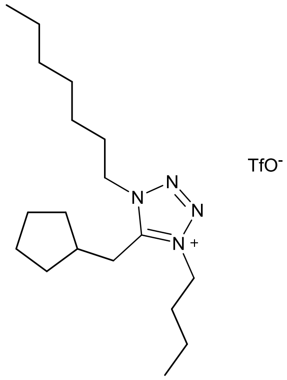
Yellow semi-solid, 51 mg, 45% yield. **^{1}H NMR (400 MHz, CDCl$_3$) δ =** 8.03 (s, 1H), 7.89 – 7.83 (m, 3H), 7.61 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.54 (ddd, *J* = 9.1, 7.8, 2.5 Hz, 2H), 5.94 (s, 2H), 4.53 – 4.50 (m, 2H), 3.48 (s, 2H), 2.16 – 2.14 (m, 2H), 1.97 (bs, 3H), 1.68 – 1.66 (m, 3H), 1.60 – 1.49 (m, 10H), 0.99 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (150 MHz, CDCl$_3$) δ** = 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



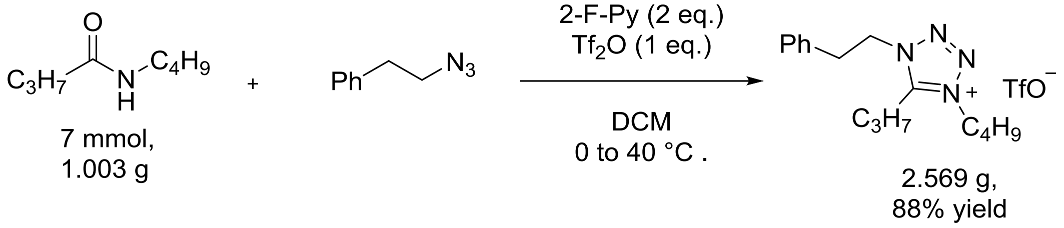
Yellow oil, 85 mg, 88% **^{1}H NMR (400 MHz, CDCl$_3$) δ** = 4.55 – 4.45 (m, 4H), 3.38 (dd, *J* = 15.6, 6.2 Hz, 1H), 3.19 (dd, *J* = 15.6, 10 Hz, 1H), 2.41 (t, *J* = 6.8 Hz, 2H), 2.20 – 2.18 (m, 2H), 2.10 – 2.08 (m, 2H), 1.99 - 1.96 (m, 2H), 1.78 – 1.73 (m, 1H), 1.67 – 1.63 (m, 4H), 1.52 – 1.47 (m, 2H), 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$_3$) δ** = 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$_3$) δ** = 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$_3$) δ** = 153.7, 51.1, 50.9, 38.5, 32.8, 31.5, 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 Al_2O_3 with dichloromethane/DMA 0 to 100% (DMA = dichloromethane/methanol/NH_4OH 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. [3-5] 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[6] 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[7] (for geometry optimization) and Conductor-like screening model COSMO[8] (for RI-MP2 single-point calculations) were applied to consider solvent effects. The DFT calculations have been performed with the Gaussian09 program package,[9] while for the RI-MP2 single point calculations the Turbomole V7.0 program package[10] was used. Computed structures were visualized using the Chemcraft software.[11]

Cartesian coordinates (the most stable (ΔG_{298}) conformations) as computed at the RI-MP2-COSMO/def2-TZVP//B3LYP-D3-SMD/6-31+G(d,p) level of theory

A

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	-0.6973200	-0.7503700
C	3.0704200	1.1290800	-1.9257600
H	3.4419900	2.1484800	-1.7937500
H	3.6792600	0.6296700	-2.6836400
H	2.0347500	1.1602000	-2.2674600
C	1.0408400	1.9740700	2.3565100
H	1.6356300	2.7237700	2.8818000
H	0.1630700	2.4242000	1.8894200
H	0.7462400	1.1717600	3.0360800
S	-0.9637900	0.8215700	-0.9368300
O	-0.6742400	2.1640000	-0.3748700
O	0.1872300	-0.1170700	-0.9098200
O	-1.7632200	0.8007400	-2.1814700
C	-2.1338200	0.0780700	0.3394900
F	-1.5970300	0.1238800	1.5773700
F	-3.3044700	0.7479800	0.3741100
F	-2.4035800	-1.2139800	0.0569200

TS$_{A\text{-}B}$

N	1.8615700	1.8766900	-0.1671100
N	1.8794800	-0.4794800	2.7240500
N	1.9168300	-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

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	-0.0759200
F	-2.6736100	1.6031600	0.4461800
F	-3.6145700	0.6211700	-1.2591200
F	-3.9011900	-0.1728900	0.7518800

B

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	-1.2283900
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$_{\text{B-C}}$

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

C	1.7502100	-2.3157700	0.3231600
H	0.9981400	-2.4596800	-0.4509000
H	2.7539600	-2.5257500	-0.0441200
H	1.5333200	-2.9430200	1.1861600
C	2.5563000	-0.0119300	-1.4125700
H	2.0717200	-0.9062300	-1.8048900
H	2.2554100	0.8142600	-2.0620300
C	4.0865900	-0.1612800	-1.4068300
H	4.4068300	-0.9906000	-0.7679500
H	4.4346400	-0.3618800	-2.4245900
H	4.5698100	0.7536700	-1.0508100
C	2.0680100	2.7039200	-0.0264700
H	2.3842700	2.6811200	-1.0750000
H	1.1506300	3.2929100	0.0627000
H	2.8397600	3.2022000	0.5689200
S	-1.6519500	-0.9027600	-0.4027100
O	-0.5054700	-0.6699400	-1.3178900
O	-1.2584200	-1.3550800	0.9574700
O	-2.8132300	-1.5996900	-0.9961100
C	-2.3033300	0.8369500	-0.0903600
F	-3.3816400	0.8121700	0.7196800
F	-1.3635700	1.6084900	0.4957700
F	-2.6656500	1.4350600	-1.2445800

C

N	1.9706600	0.9519500	-0.9424100
N	1.5855200	2.1302100	-0.4014200
N	1.3529900	1.9354700	0.8412900
N	1.5743000	0.6264900	1.1053700
C	1.9592400	-0.0066400	-0.0092100
C	1.4165500	0.1046300	2.4629100
H	2.3491000	0.2489200	3.0115100
H	0.6036000	0.6534500	2.9358900
H	1.1578800	-0.9495800	2.3987900
C	2.3111100	-1.4409600	-0.1629000
H	1.5326200	-2.0160400	0.3457700
H	2.2556900	-1.6911500	-1.2239800
C	3.7029900	-1.7674400	0.4090000
H	3.7543700	-1.5481200	1.4797000
H	3.9028500	-2.8332300	0.2683100
H	4.4869100	-1.1991700	-0.1007900
C	2.2297600	0.8316300	-2.3767400
H	3.1609800	0.2846500	-2.5256900
H	1.3916200	0.3079300	-2.8388200
H	2.3182800	1.8413500	-2.7750300
S	-1.4756200	-1.0086500	-0.3580800
O	-0.5445100	-0.4627600	-1.3789900
O	-0.8165000	-1.4276500	0.9051500

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**
	Bruker		[K]	[mm]	[s]		[°]	
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.

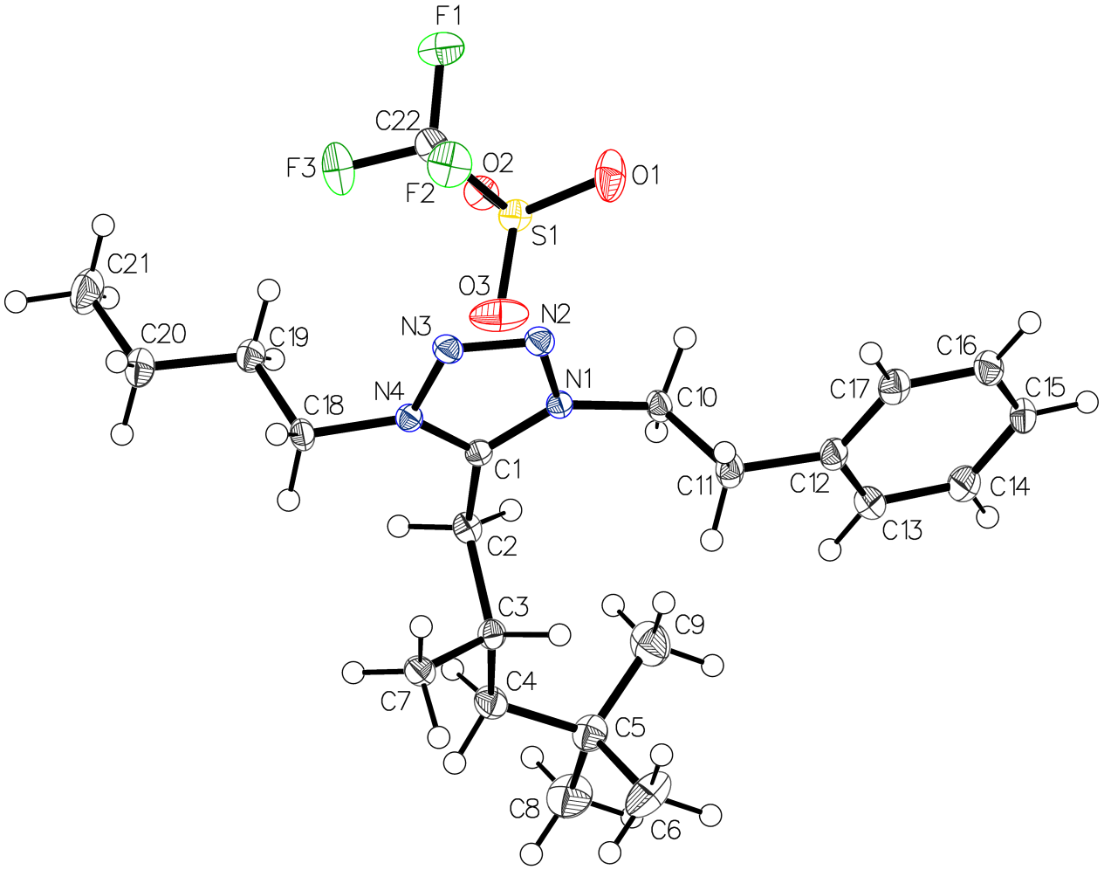


Figure 1 Asymmetric Unit of [**9g**], drawn with 50% displacement ellipsoids.

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

Chemical formula	C22H35F3N4O3S	**Crystal system**	monoclinic	
Formula weight [g/mol]	492.6	**Space group**	*P21/n*	
Temperature [K]	100	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å^3]**	2567.0(4)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	8.4504(7)	90
Crystal size / [mm^3]	0.25 × 0.2 × 0.01		22.707(2)	92.561(4)
Crystal habit	clear colourless plate		13.3915(11)	90
Density (calculated) / [g/cm^3]	1.275	**Absorption coefficient / [mm^{-1}]**	0.177	
Abs. correction Tmin	0.6672	**Abs. correction Tmax**	0.746	

Abs. correction type	multi-scan	**F(000) [e$^-$]**	1048

Table 3 Data collection and structure refinement of [**9g**].

Index ranges	$-11 \leq h \leq 11$, $-32 \leq k \leq 31$, $-18 \leq l \leq 18$	**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**	all data	R1 = 0.0795, wR2 = 0.1005
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		I>2σ(I)	R1 = 0.0411, wR2 = 0.0897
Goodness-of-fit on F^2	1.018	**Weighting scheme**	$w=1/[\sigma^2(F_o^2)+(0.0464P)^2+0.6277P]$	
Largest diff. peak and hole [e Å^{-3}]	0.26/-0.52		where $P=(F_o^2+2F_c^2)/3$	

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

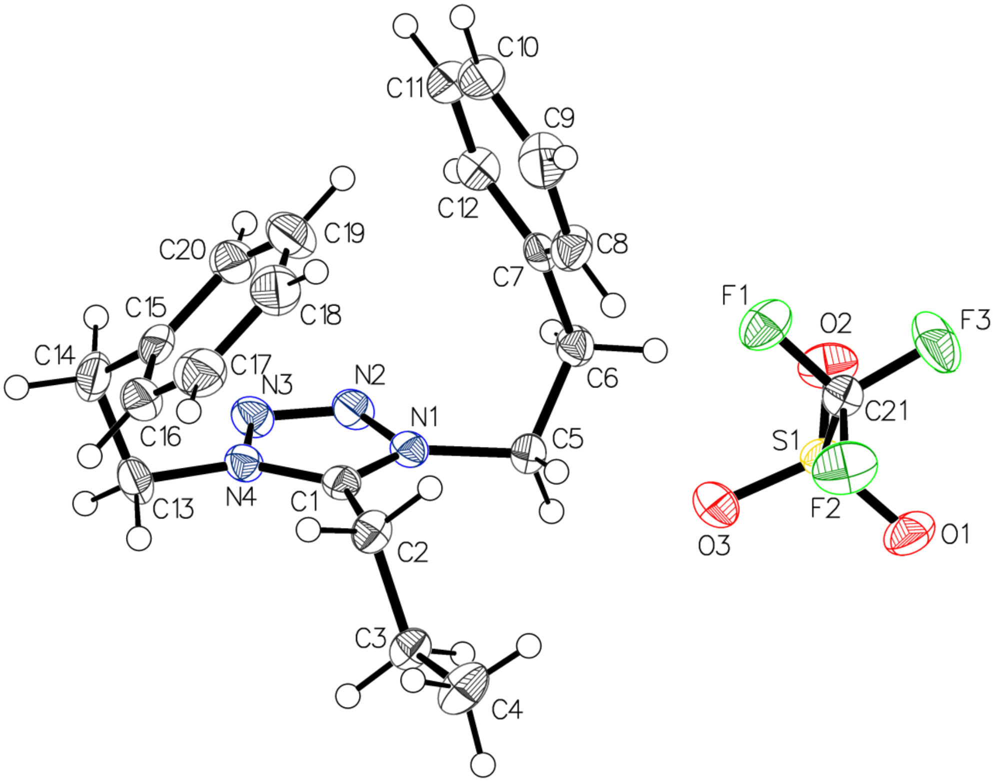


Figure 2 Asymmetric Unit of [**9a**], drawn with 50% displacement ellipsoids.

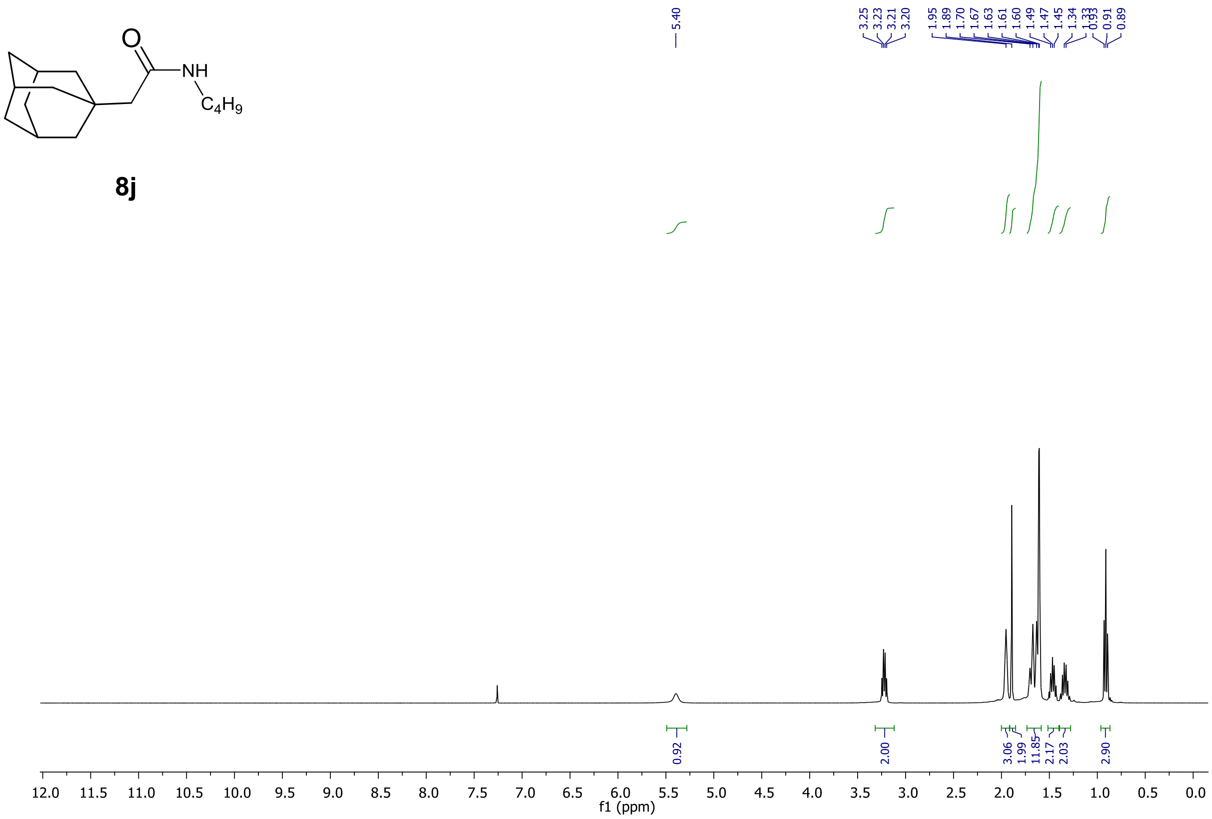
Table 4 Sample and crystal data of [**9a**].

Chemical formula	C21H25F3N4O3S	**Crystal system**	triclinic	
Formula weight [g/mol]	470.51	**Space group**	*P-1*	
Temperature [K]	130	**Z**	2	
Measurement method	\f and \w scans	**Volume [Å^3]**	1125.14(18)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	9.3964(9)	71.424(3)
Crystal size / [mm^3]	0.3 × 0.2 × 0.07		9.5657(8)	86.759(3)
Crystal habit	clear colourless block		13.2782(12)	84.197(3)
Density (calculated) / [g/cm^3]	1.389	**Absorption coefficient / [mm^{-1}]**	0.199	
Abs. correction Tmin	0.5063	**Abs. correction Tmax**	0.7452	
Abs. correction type	multi-scan	**F(000) [e$^-$]**	492	

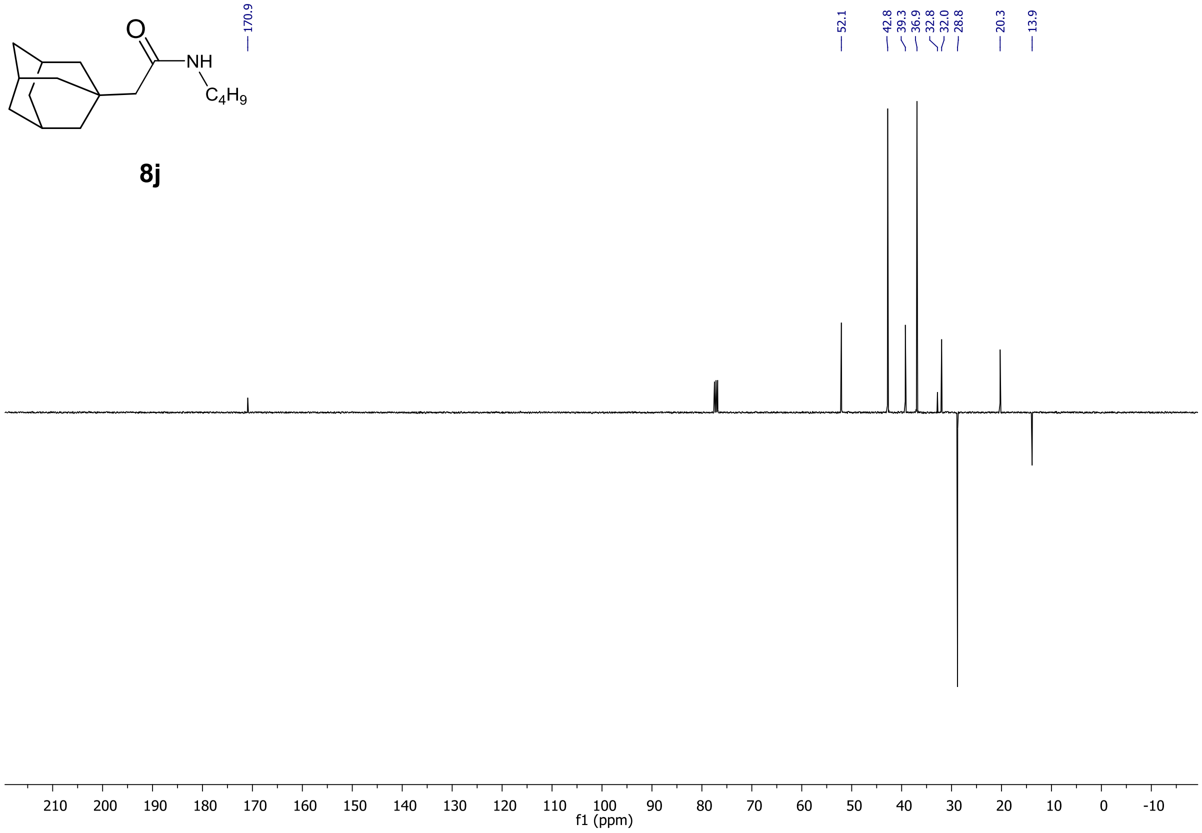
Table 5 Data collection and structure refinement of [**9a**].

Index ranges	$-11 \le h \le 11$, $-11 \le k \le 8$, $-16 \le l \le 15$	**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	$\Sigma\, w(F_o^2 - F_c^2)^2$		$I>2\sigma(I)$	R1 = 0.0388, wR2 = 0.0936
Goodness-of-fit on F^2	1.05	**Weighting scheme**	$w=1/[\sigma^2(F_o^2)+(0.0328P)^2+0.3958P]$	
Largest diff. peak and hole [e Å^{-3}]	0.31/-0.37		where $P=(F_o^2+2F_c^2)/3$	

Spectra



8j



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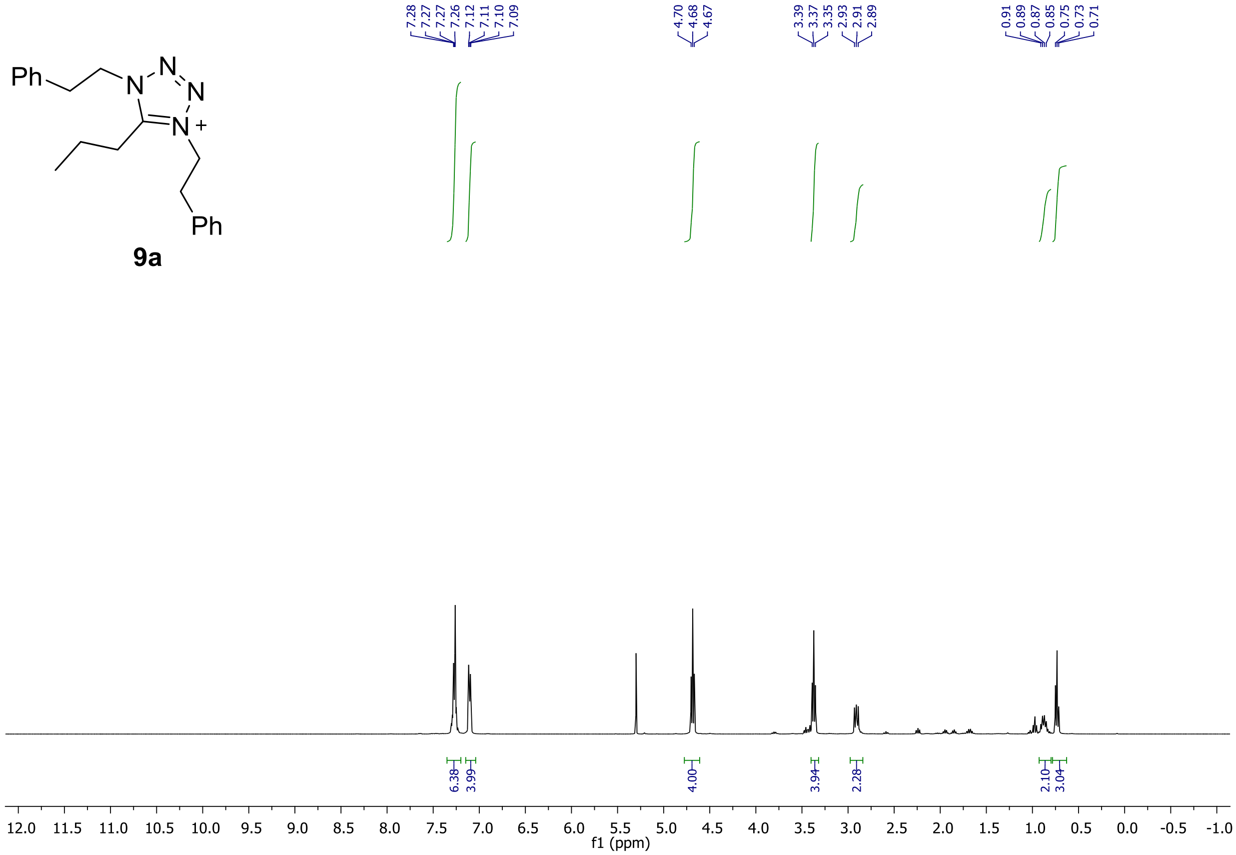
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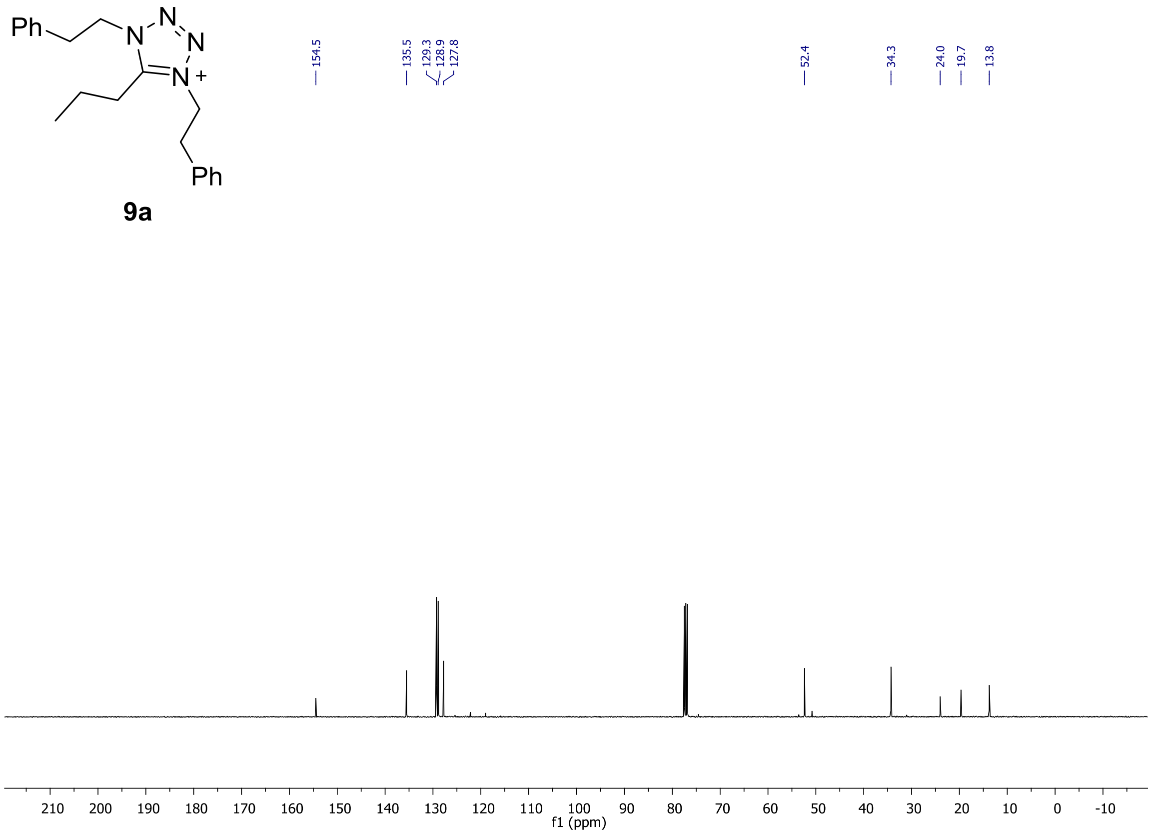
3.35
2.93
2.91
2.89
0.91
0.89
0.87
0.85
0.75
0.73
0.71
Ph
N
N
N
N+
Ph
6.38
3.99
4.00
3.94
2.28
2.10
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

9a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N
N
N+
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127.8
52.4
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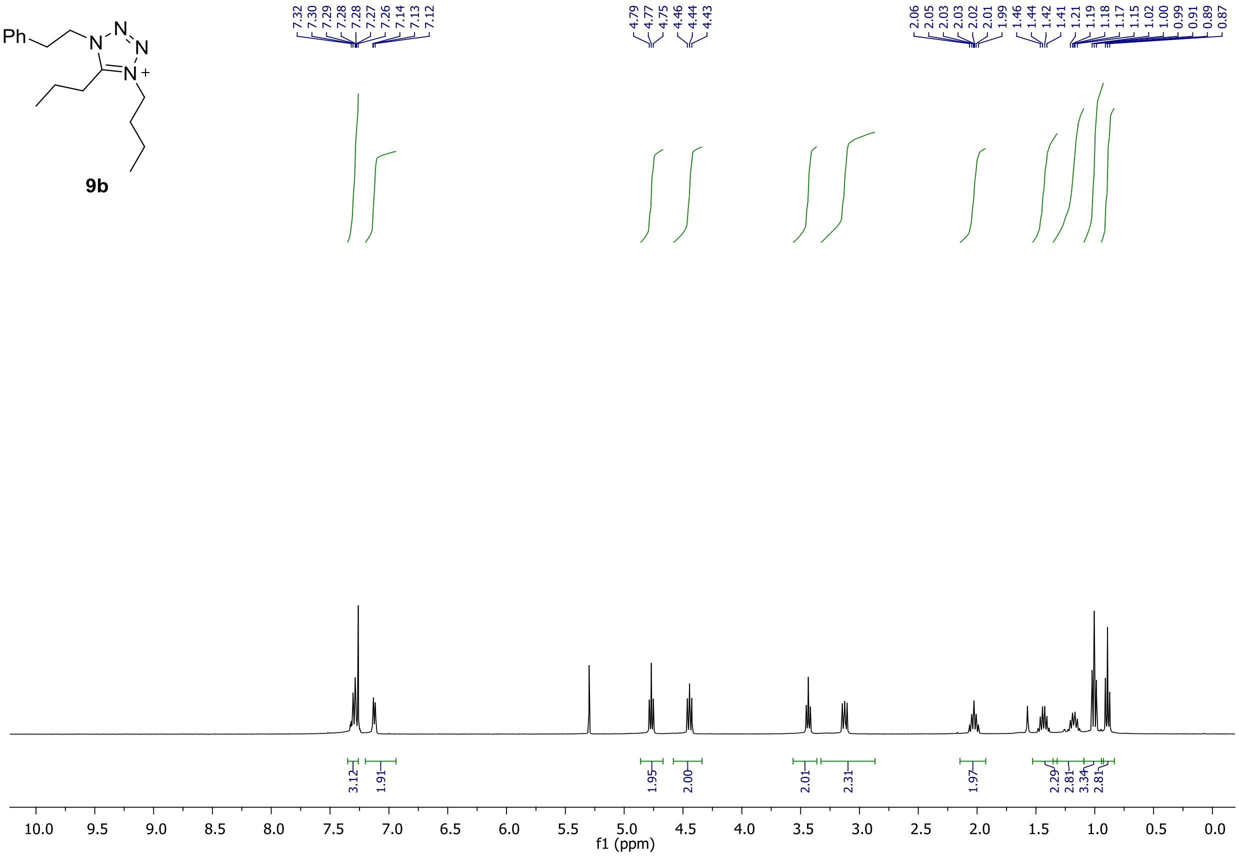
19.7
13.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

9a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N
N+
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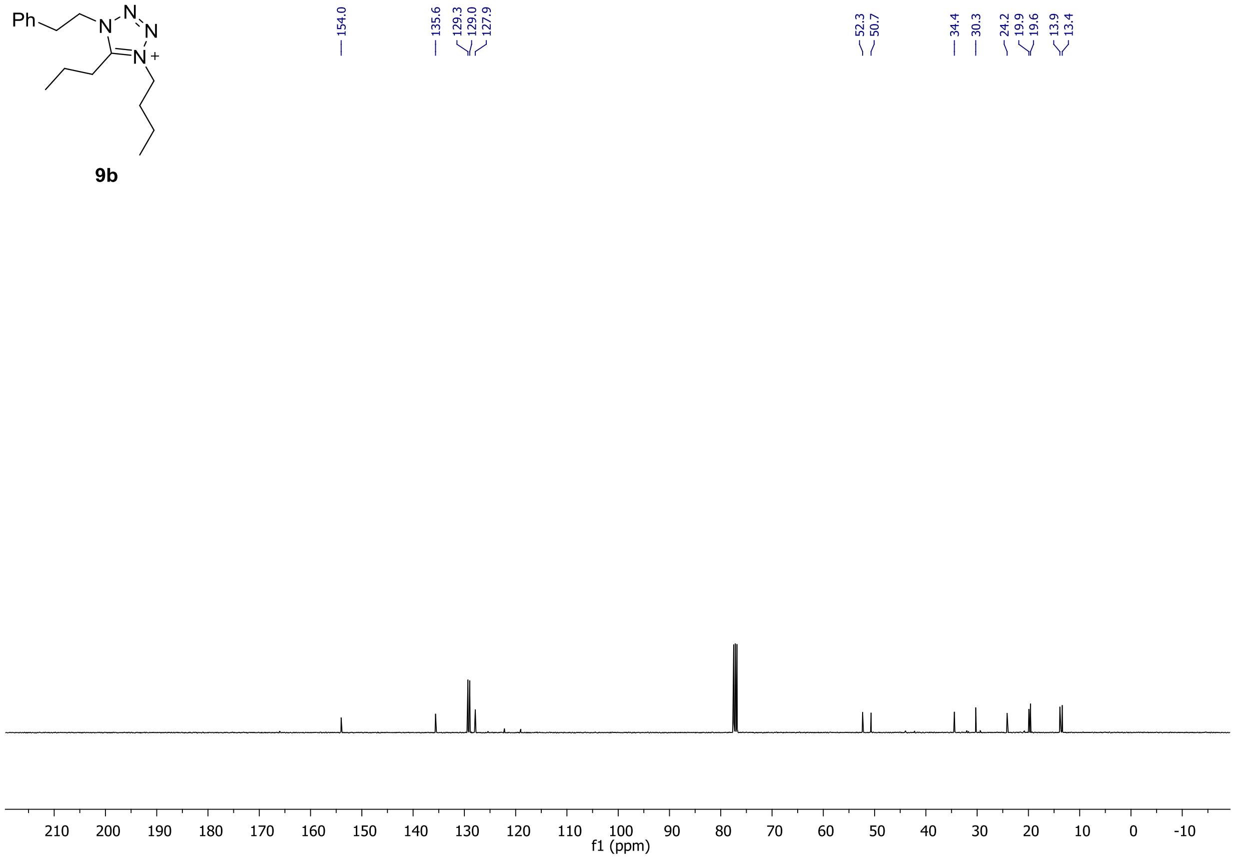
2.06 2.05 2.03 2.03 2.02 2.01 1.99 1.46 1.44 1.42 1.41 1.21 1.19 1.18 1.17 1.15 1.02 1.00 0.99 0.91 0.89 0.87
3.12
1.91
1.95
2.00
2.01
2.31
1.97
2.29
2.81
3.34
2.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

9b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30.3
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13.9
13.4
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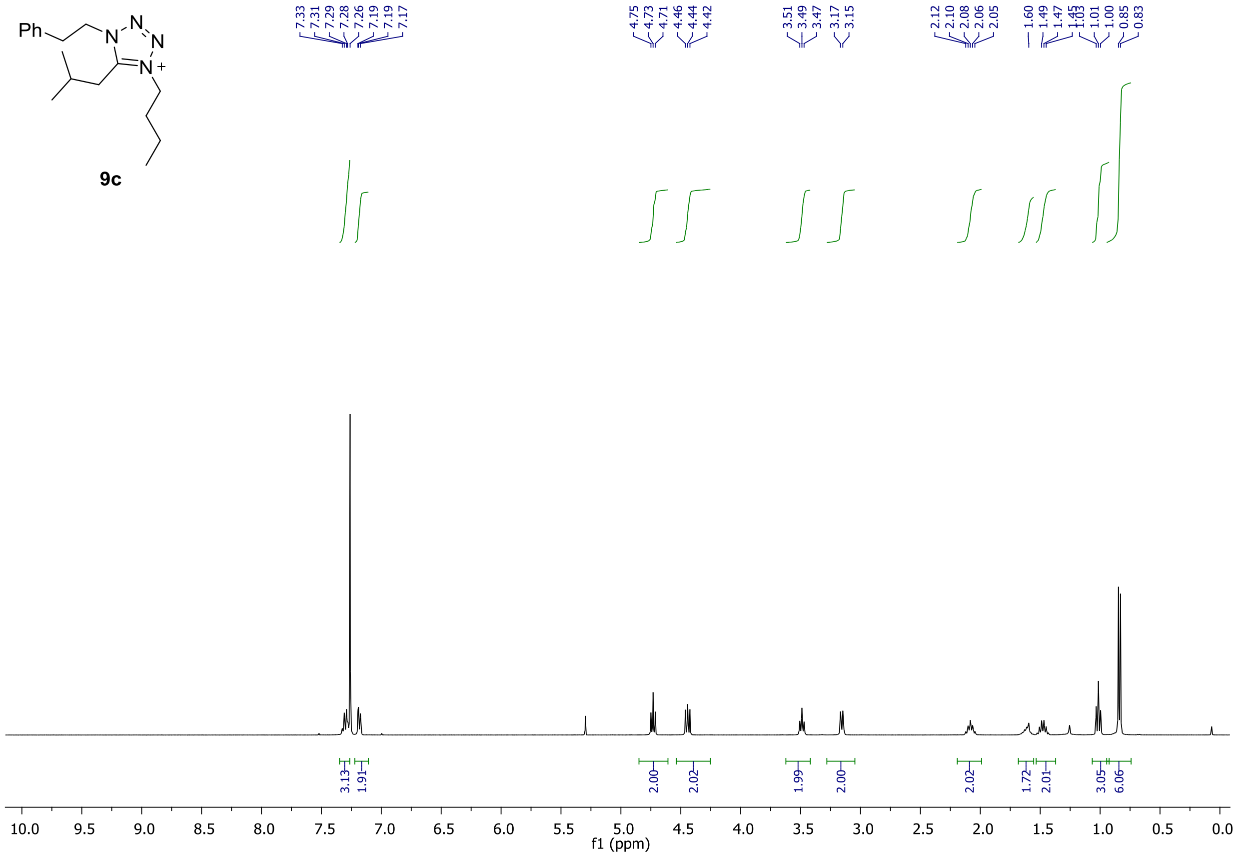
f1 (ppm)

9b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4.46
4.44
4.42
3.51
3.49
3.47
3.17
3.15
2.12
2.10
2.08
2.06
2.05
1.60
1.49
1.47
1.45
1.03
1.01
1.00
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2.00
2.02
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2.00
2.02
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2.01
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6.06
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9.0
8.5
8.0
7.5
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6.5
6.0
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5.0
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4.0
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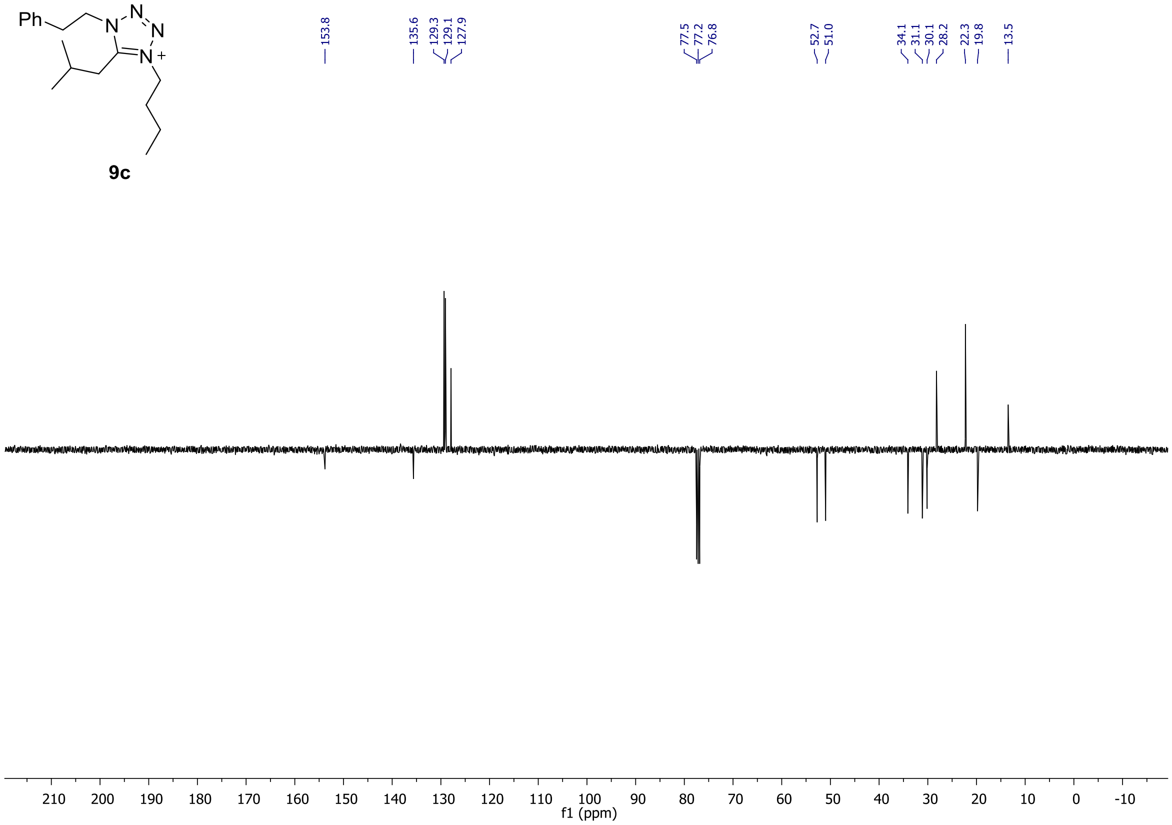
f1 (ppm)

9c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200
190
180
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20
10
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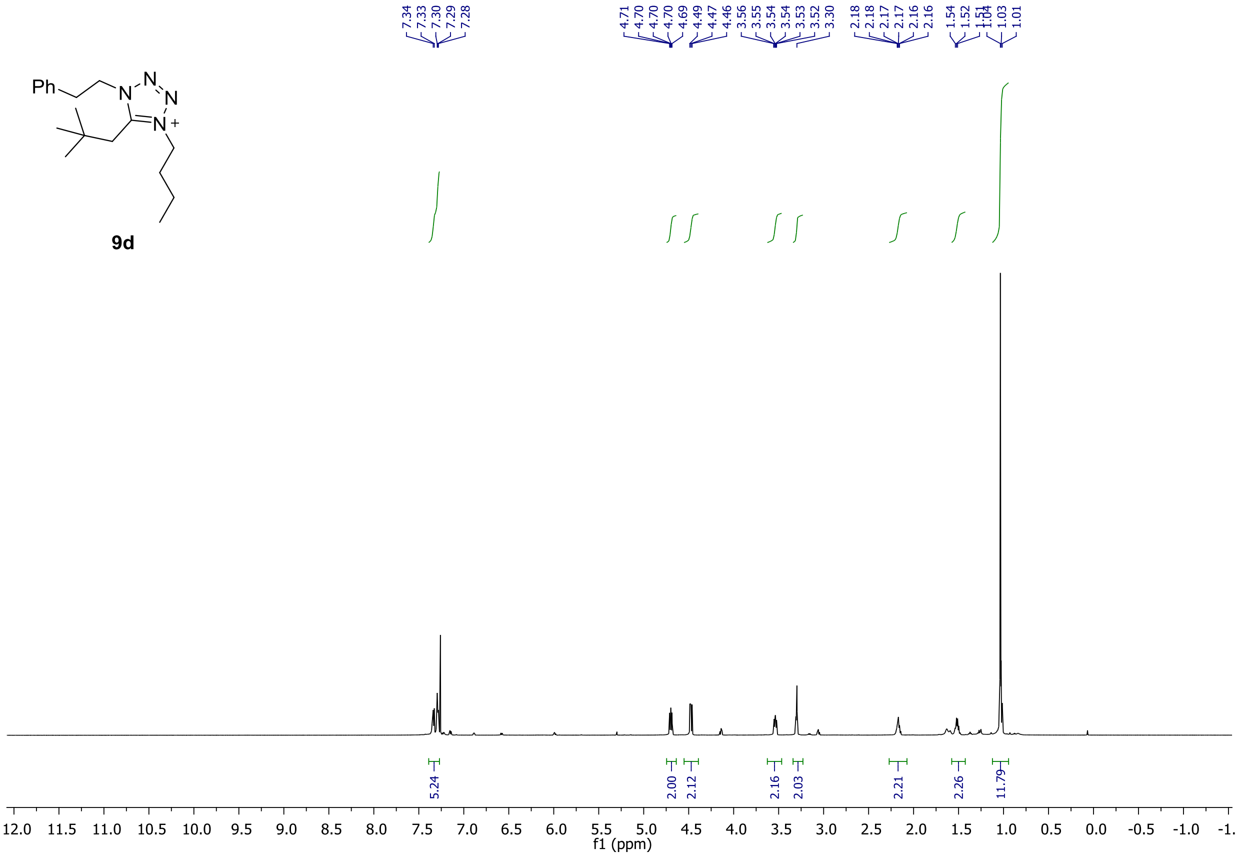
f1 (ppm)

9c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4.47
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3.30
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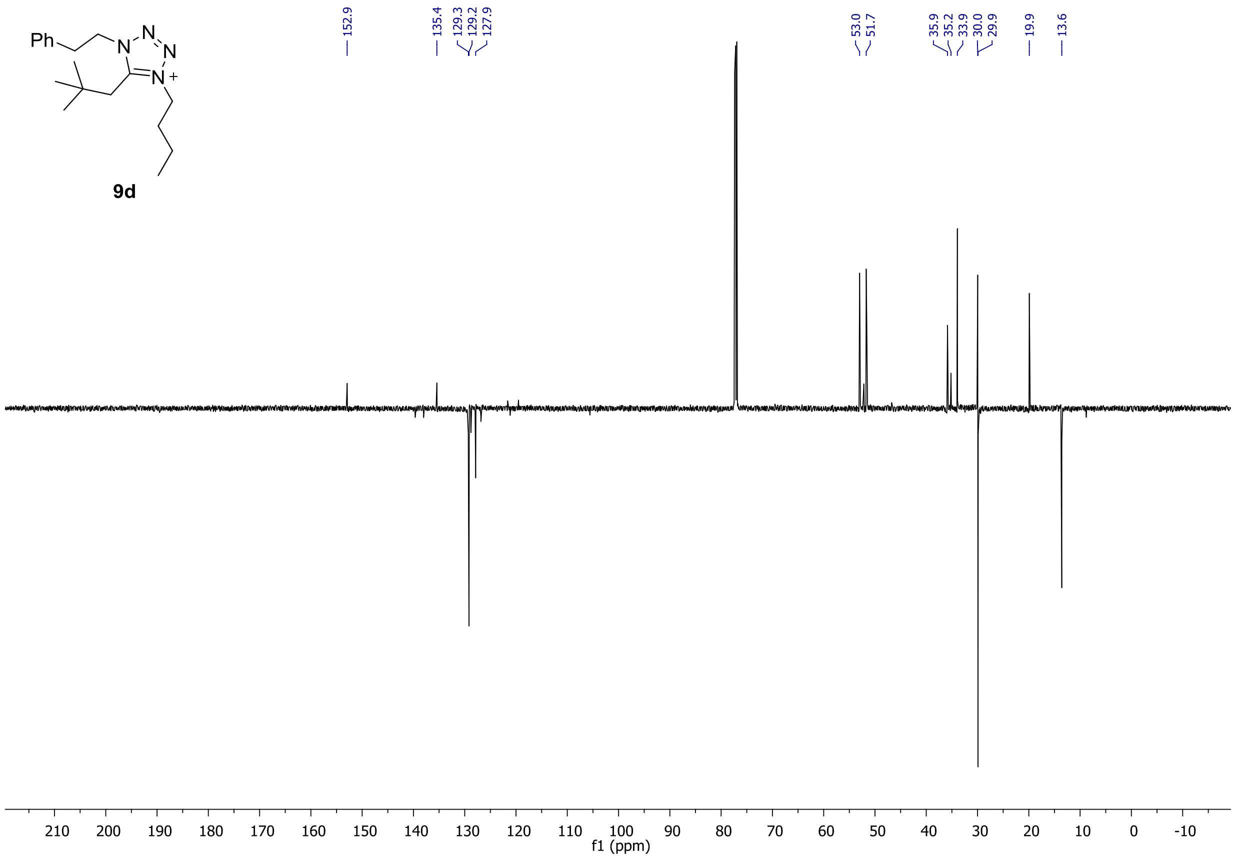
2.18
2.17
2.17
2.16
2.16
1.54
1.52
1.51
1.04
1.03
1.01
5.24
2.00
2.12
2.16
2.03
2.21
2.26
11.79
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

9d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19.9
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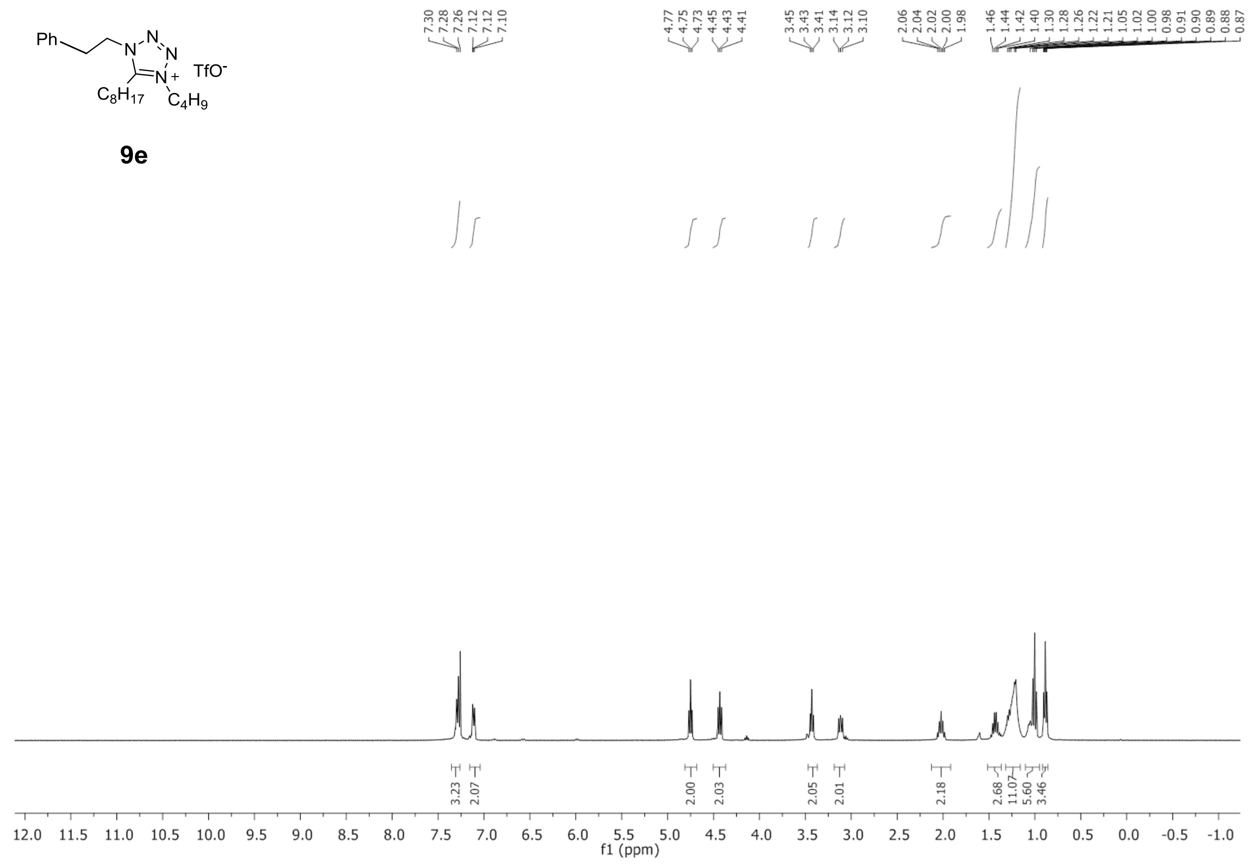
f1 (ppm)

9d


9e

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N
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7.10
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4.73
4.45
4.43
4.41
3.45
3.43
3.41
3.14
3.12
3.10
2.06
2.04
2.02
2.00
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1.42
1.40
1.30
1.28
1.26
1.22
1.21
1.05
1.02
1.00
0.98
0.91
0.90
0.89
0.88
0.87
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2.00
2.03
2.05
2.01
2.18
2.68
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5.60
3.46
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11.5
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9.0
8.5
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6.5
6.0
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5.0
4.5
4.0
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0.0
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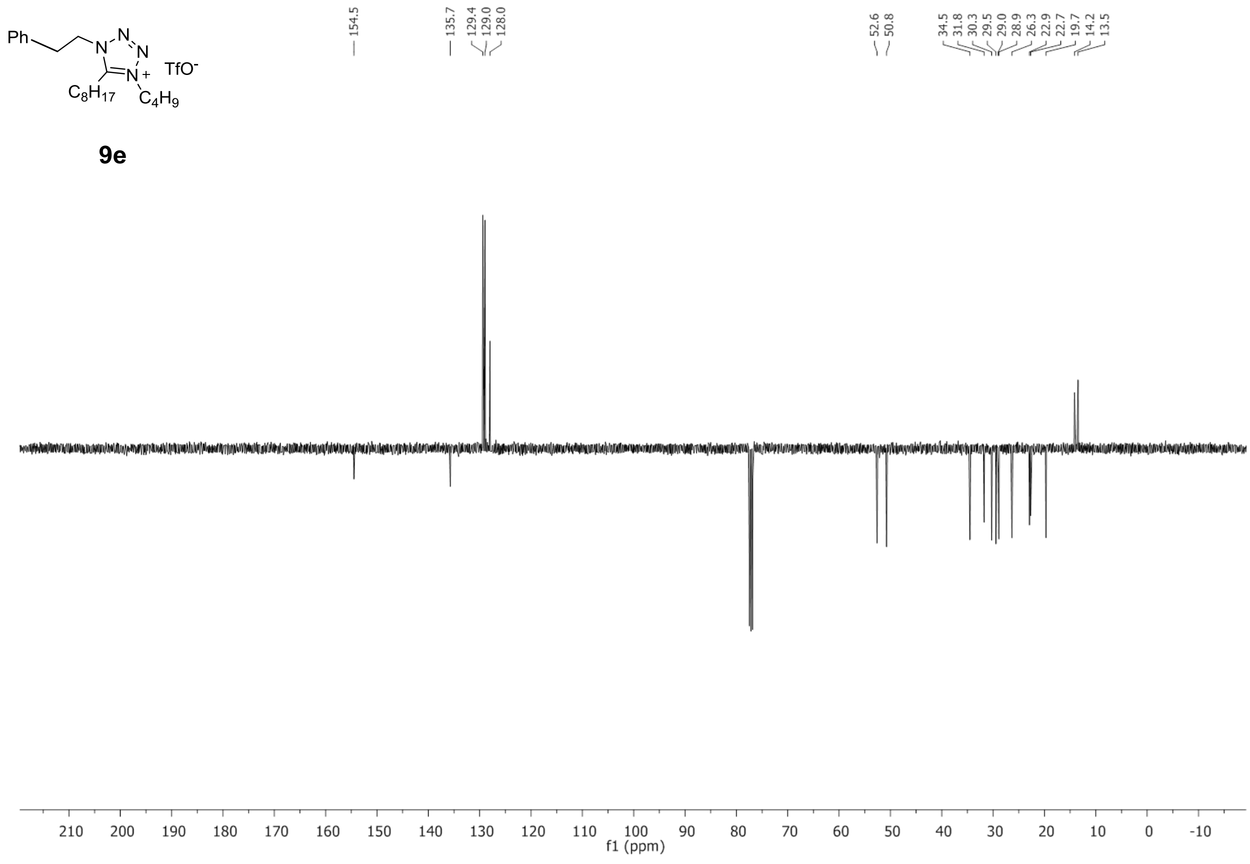
-1.0
f1 (ppm)


9e

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N+
TfO-
C8H17
C4H9
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128.0
52.6
50.8
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31.8
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29.5
29.0
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22.9
22.7
19.7
14.2
13.5
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180
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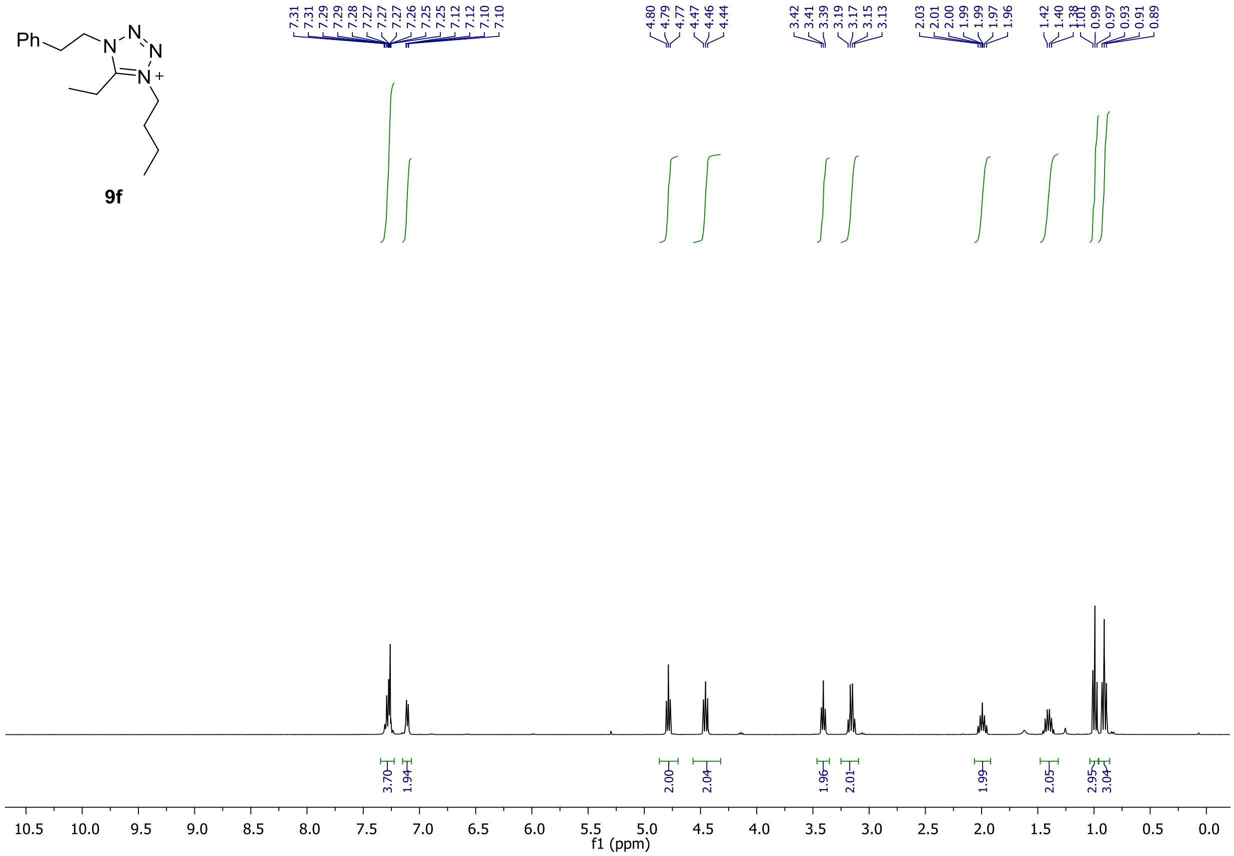
f1 (ppm)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2.00
1.99
1.99
1.97
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1.38
1.01
0.99
0.97
0.93
0.91
0.89
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2.04
1.96
2.01
1.99
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6.0
5.5
5.0
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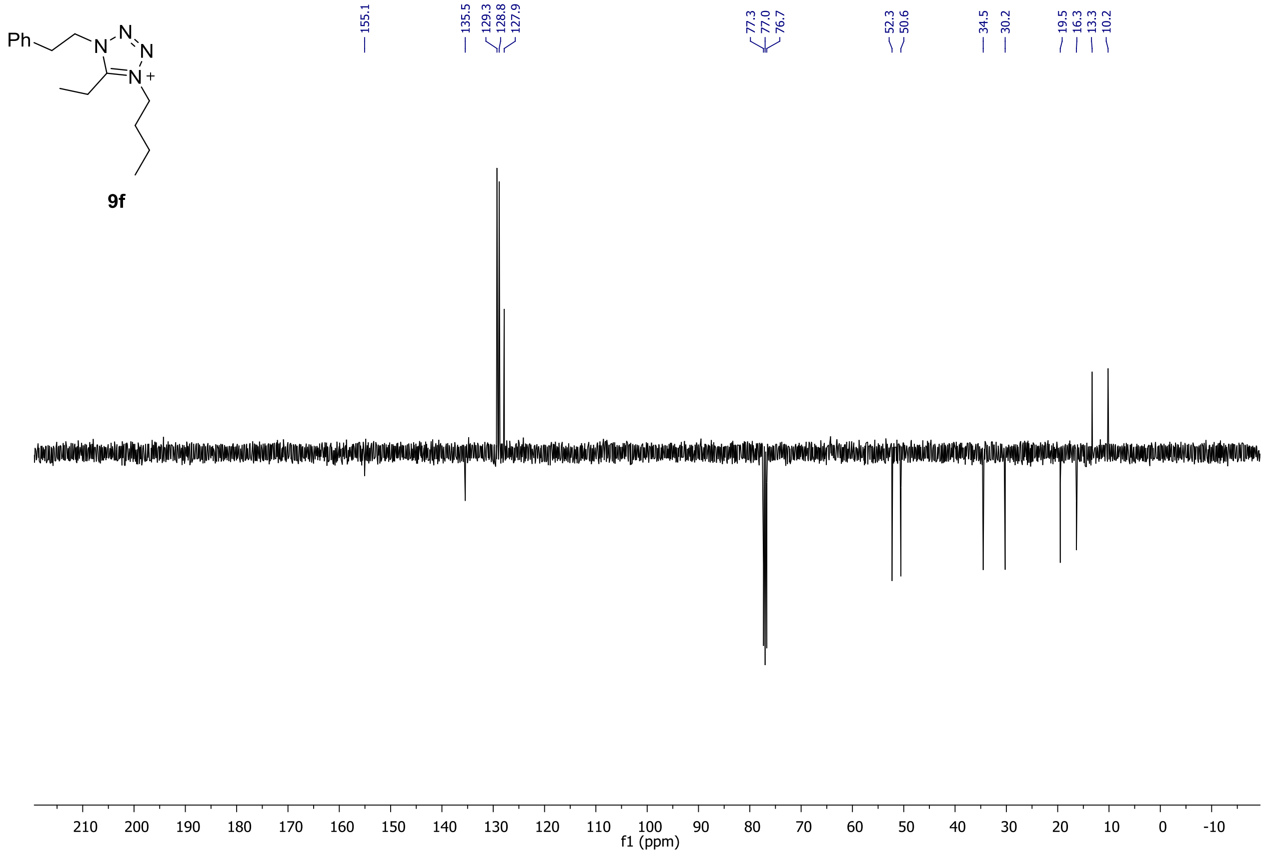
f1 (ppm)

9f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50.6
34.5
30.2
19.5
16.3
13.3
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200
190
180
170
160
150
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10
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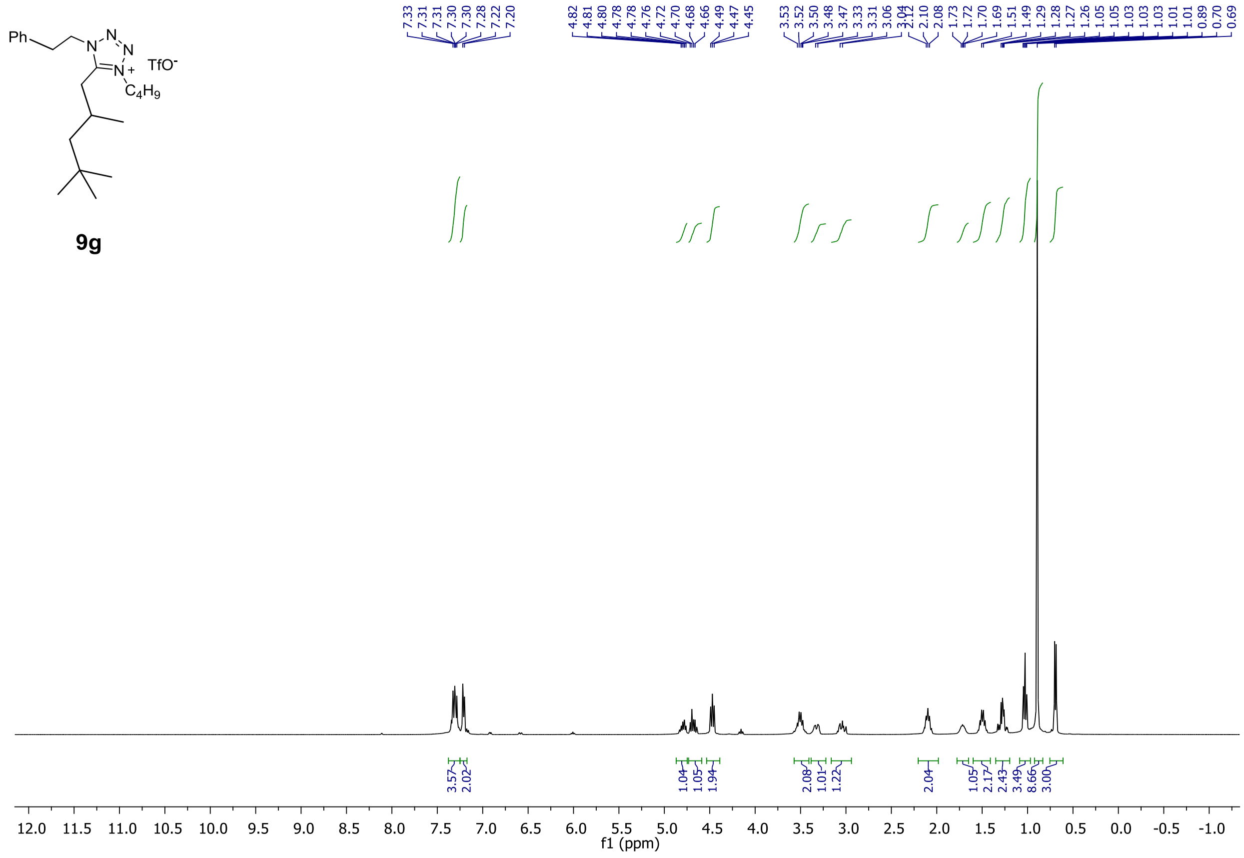
f1 (ppm)

9f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N
N+
TfO-
C4H9
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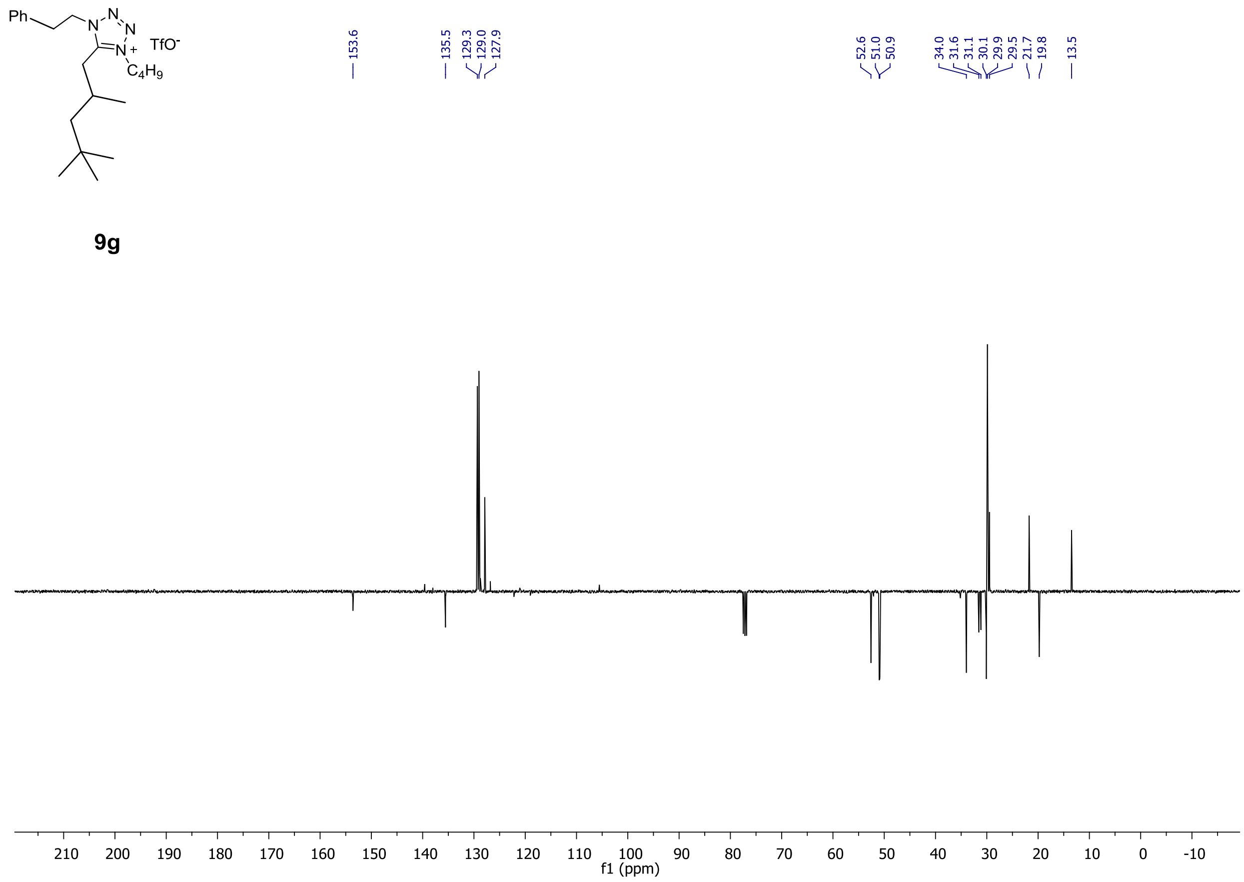
1.73 1.72 1.70 1.69 1.51 1.49 1.29 1.28 1.27 1.26 1.05 1.05 1.03 1.03 1.03 1.01 0.89 0.70 0.69
3.57 2.02 1.04 1.05 1.94 2.08 1.01 1.22 2.04 1.05 2.17 2.43 3.49 8.66 3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

9g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C4H9
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135.5 129.3 129.0 127.9
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34.0 31.6 31.1 30.1 29.9 29.5 21.7 19.8
13.5
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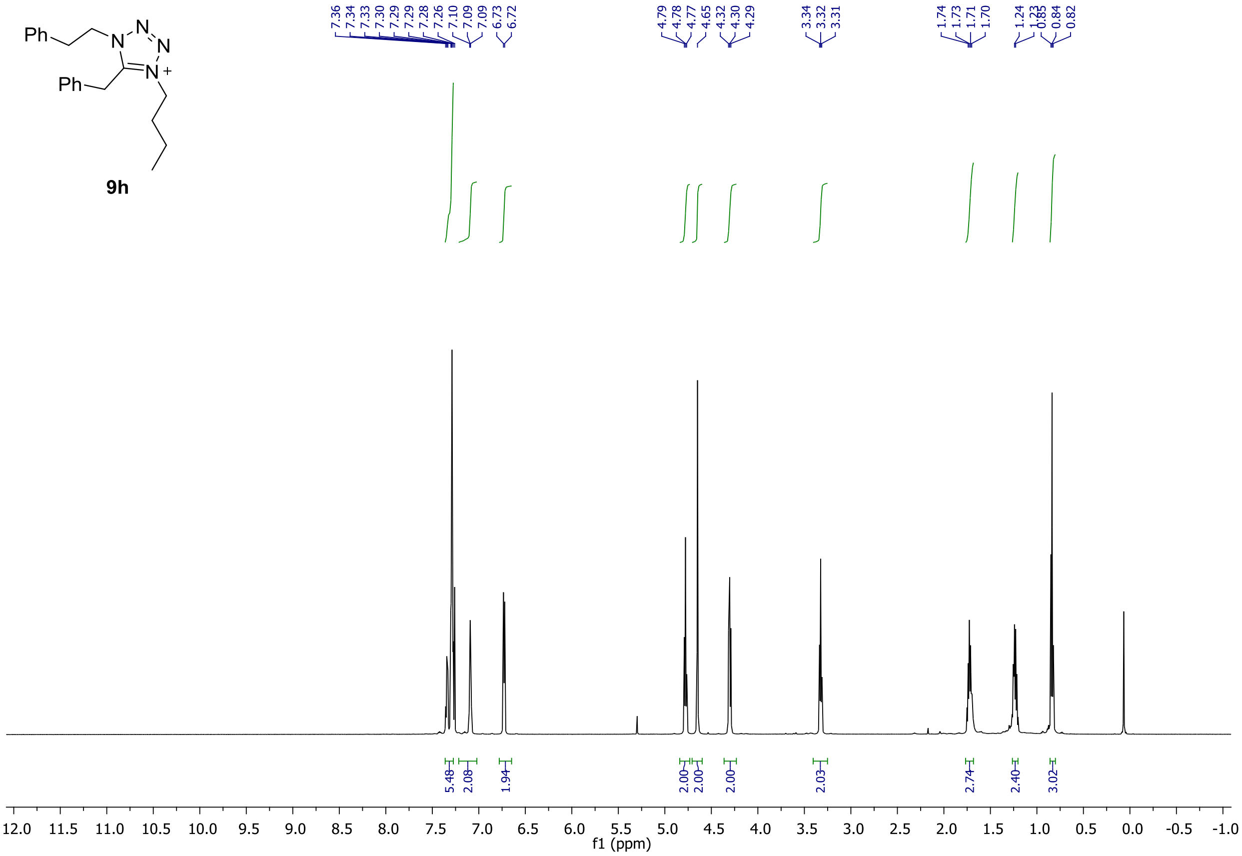
f1 (ppm)

9g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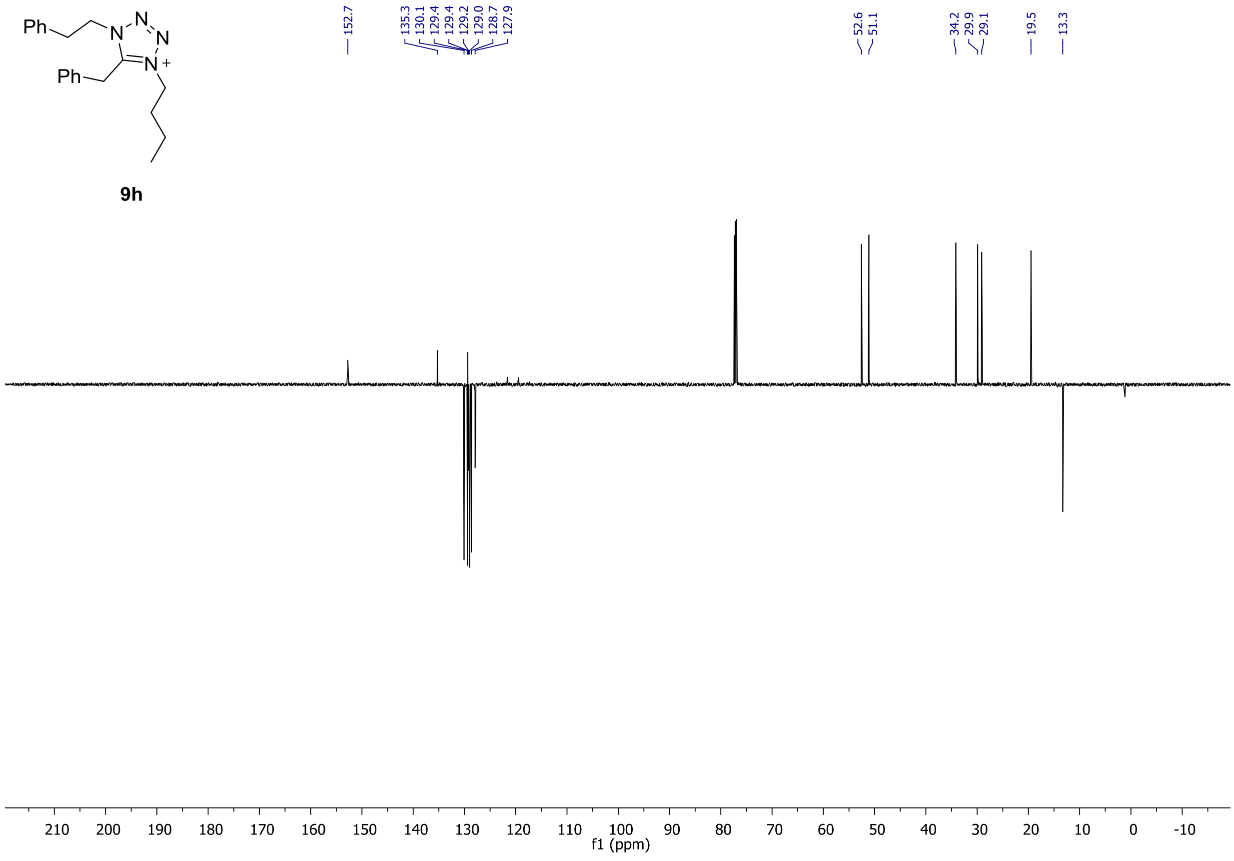
4.32
4.30
4.29
3.34
3.32
3.31
1.74
1.73
1.71
1.70
1.24
1.23
0.85
0.84
0.82
5.48
2.08
1.94
2.00
2.00
2.00
2.03
2.74
2.40
3.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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N+
Ph
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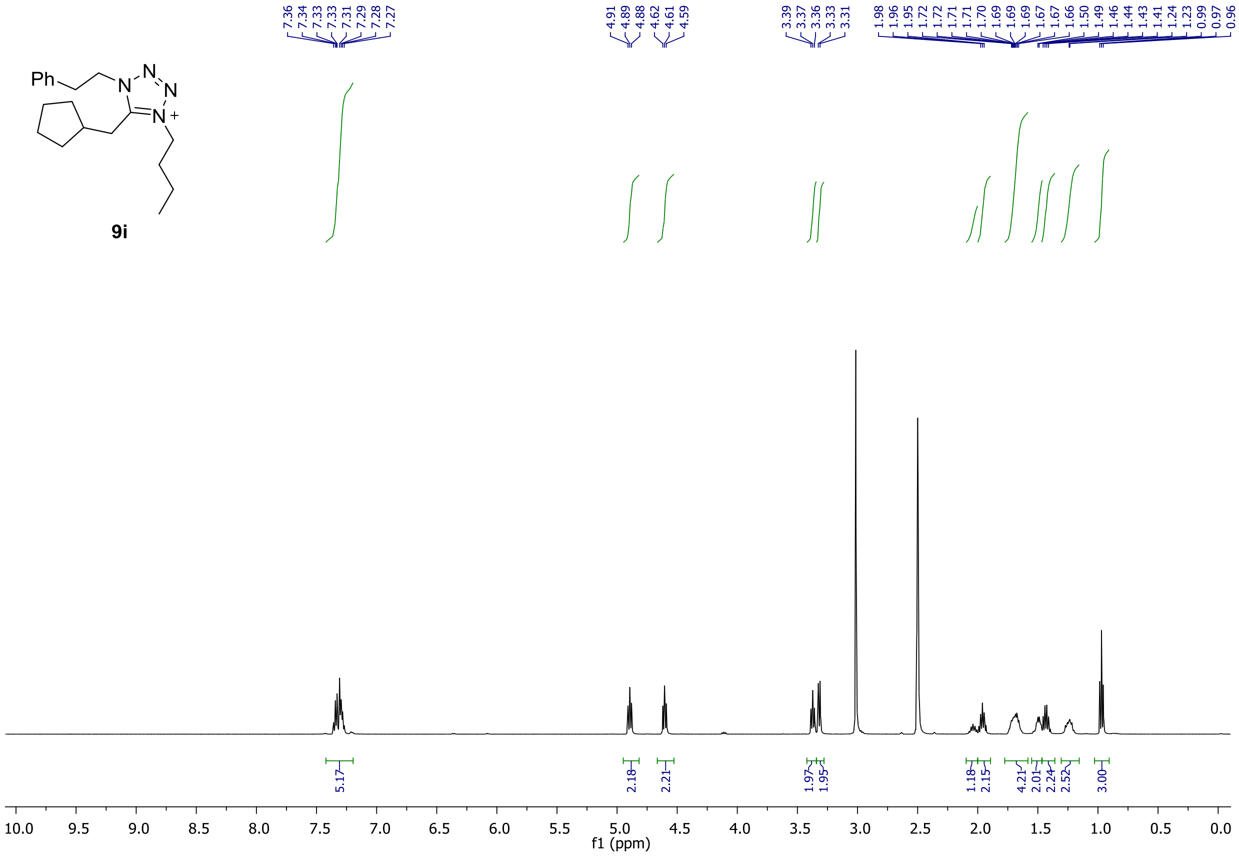
129.4
129.4
129.2
129.0
128.7
127.9
52.6
51.1
34.2
29.9
29.1
19.5
13.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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4.61
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3.31
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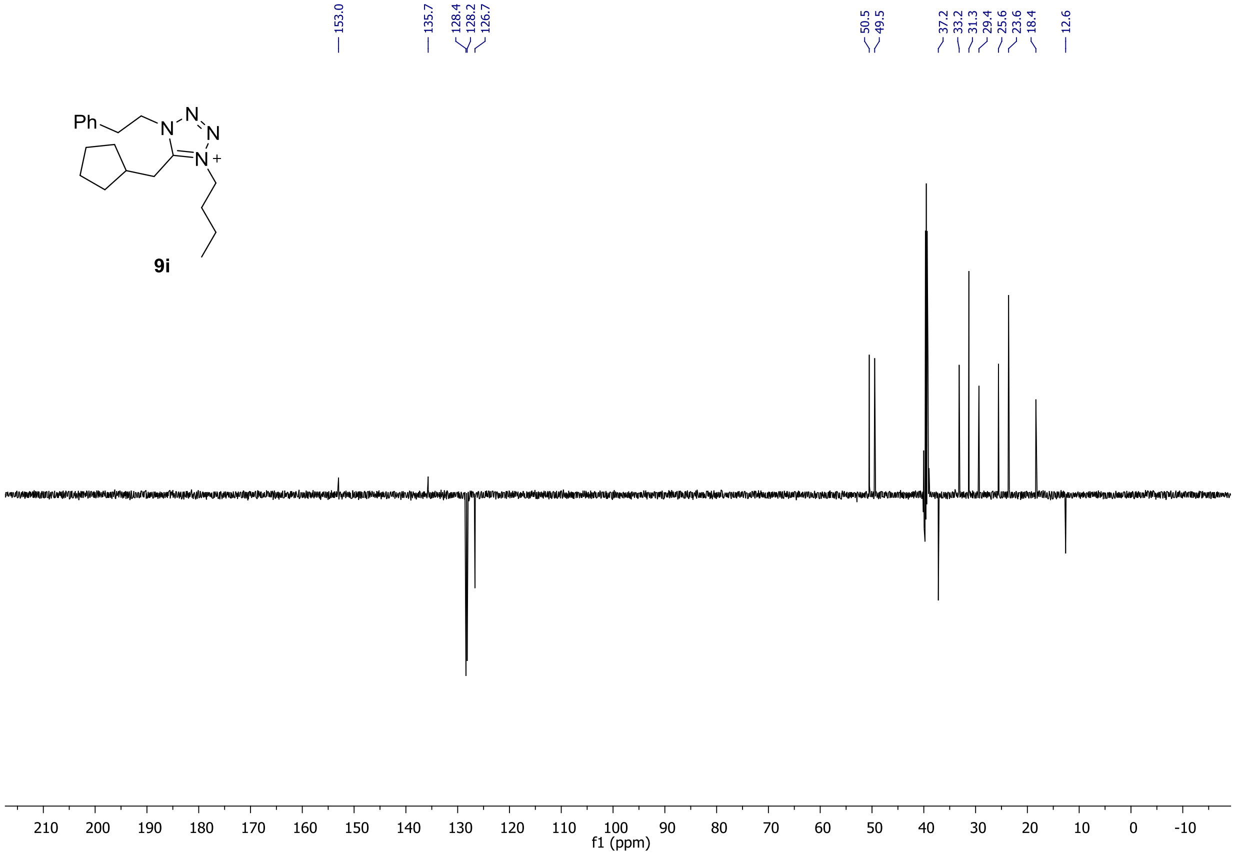
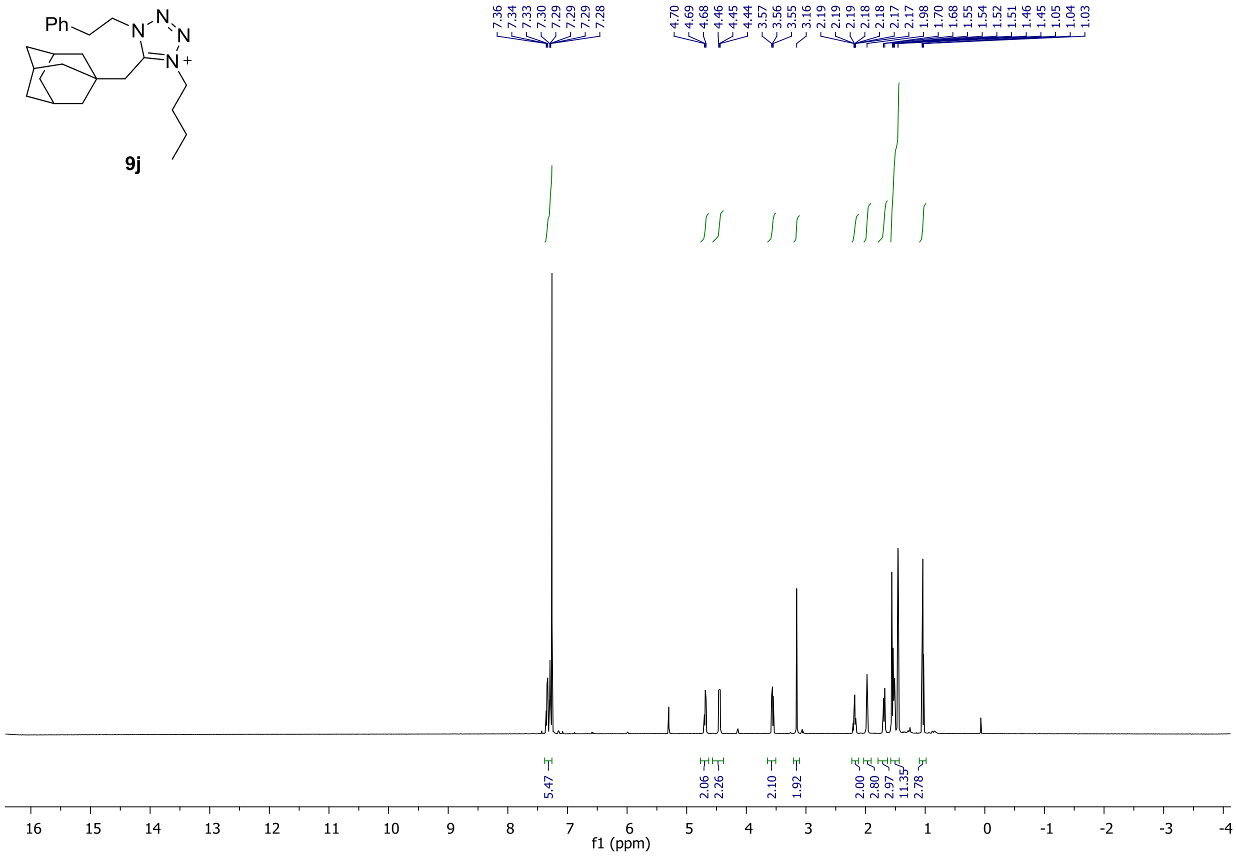
1.95
1.72
1.72
1.71
1.71
1.70
1.69
1.69
1.69
1.67
1.67
1.66
1.50
1.49
1.46
1.44
1.43
1.41
1.24
1.23
0.99
0.97
0.96
5.17
2.18
2.21
1.97
1.95
1.18
2.15
4.21
2.01
2.24
2.52
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

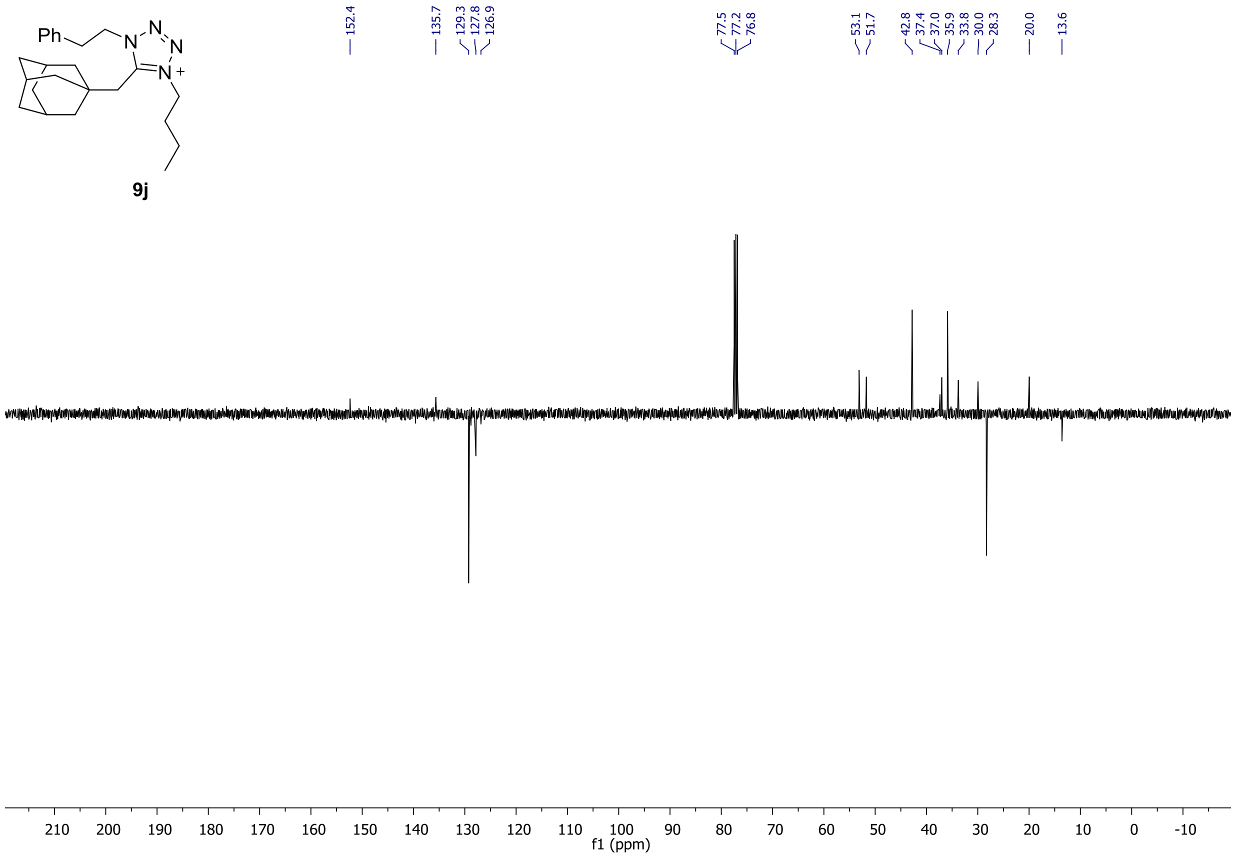
9i


Ph
N
N
N
N
+
153.0
135.7
128.4
128.2
126.7
50.5
49.5
37.2
33.2
31.3
29.4
25.6
23.6
18.4
12.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

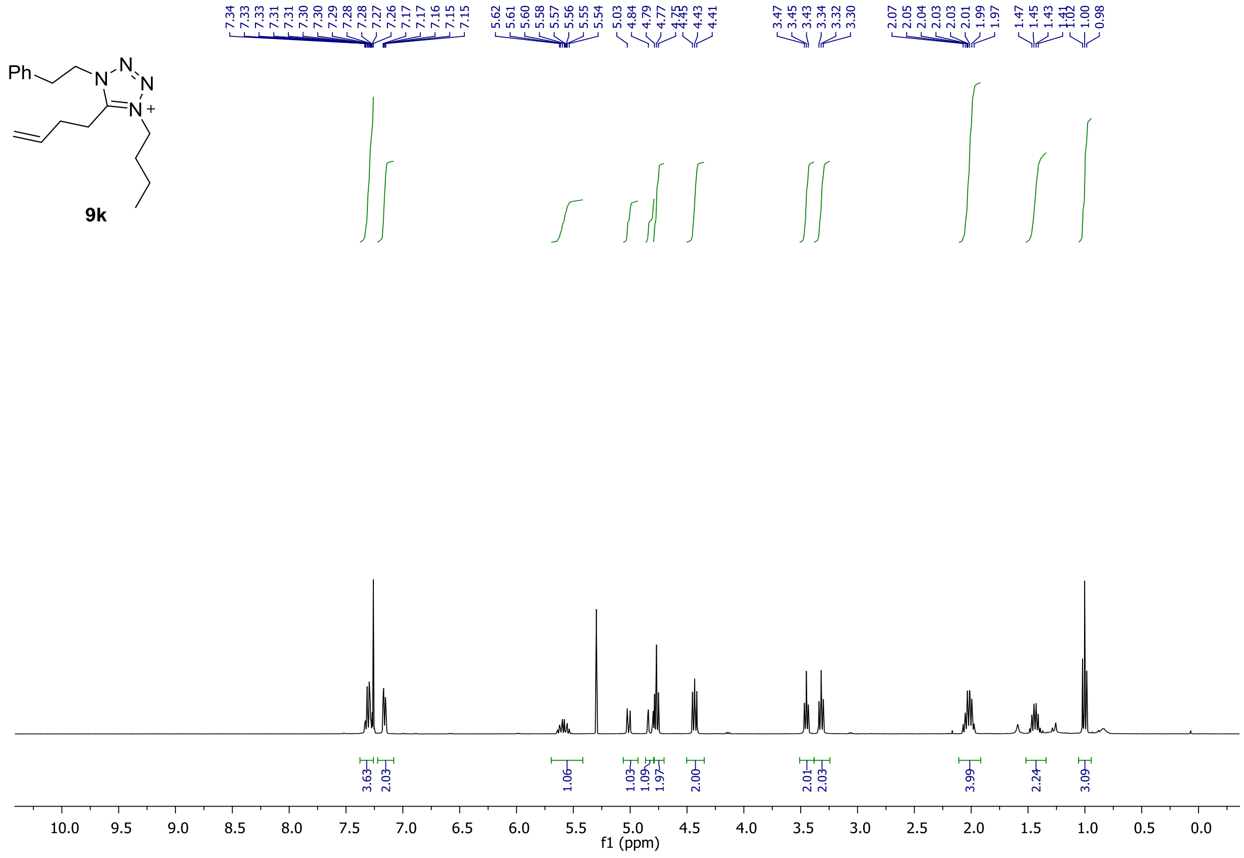
9i


Ph
N
N
N
N+
7.36
7.34
7.33
7.30
7.29
7.29
7.29
7.28
4.70
4.69
4.68
4.46
4.45
4.44
3.57
3.56
3.55
3.16
2.19
2.19
2.19
2.18
2.18
2.17
2.17
1.98
1.70
1.68
1.55
1.54
1.52
1.51
1.46
1.45
1.05
1.04
1.03
5.47
2.06
2.26
2.10
1.92
2.00
2.80
2.97
11.35
2.78
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

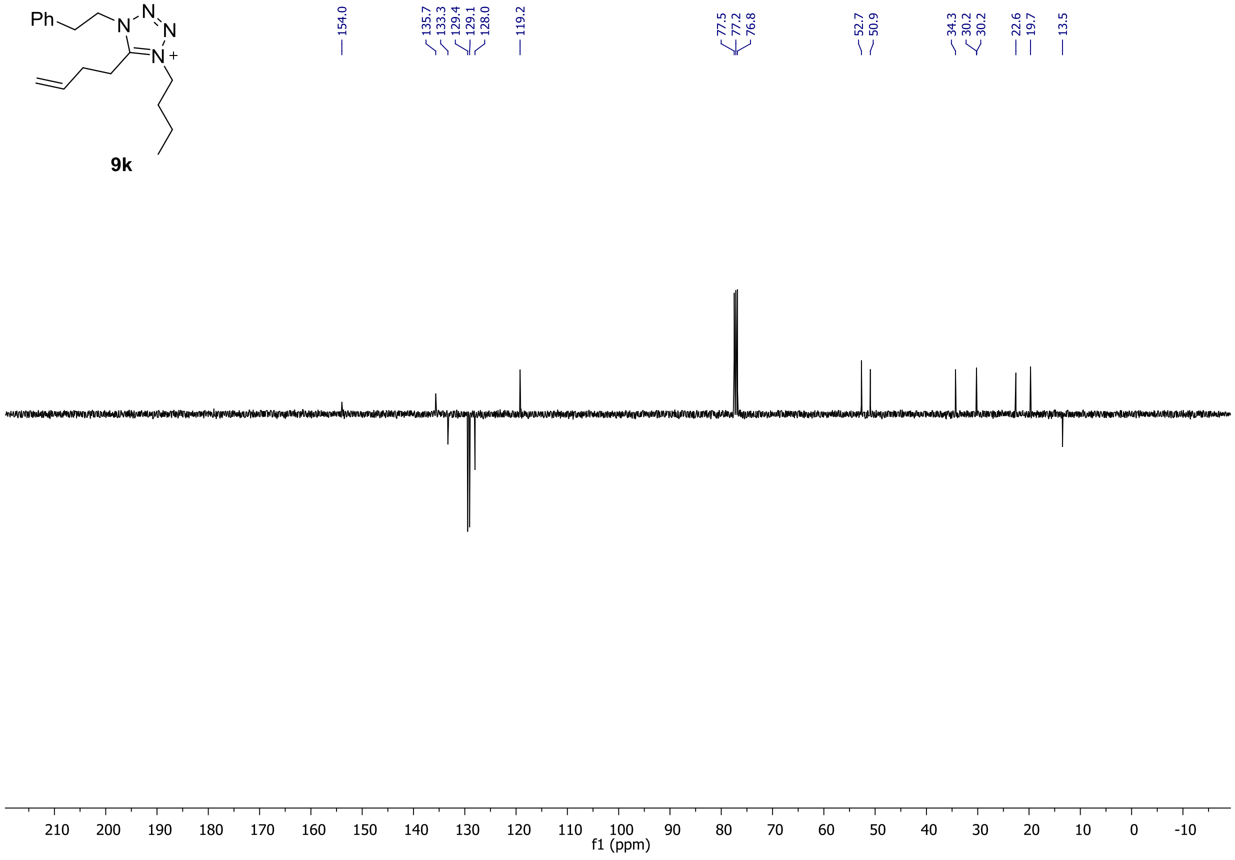
9j


Ph
N
N
N
N+
152.4
135.7
129.3
127.8
126.9
77.5
77.2
76.8
53.1
51.7
42.8
37.4
37.0
35.9
33.8
30.0
28.3
20.0
13.6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

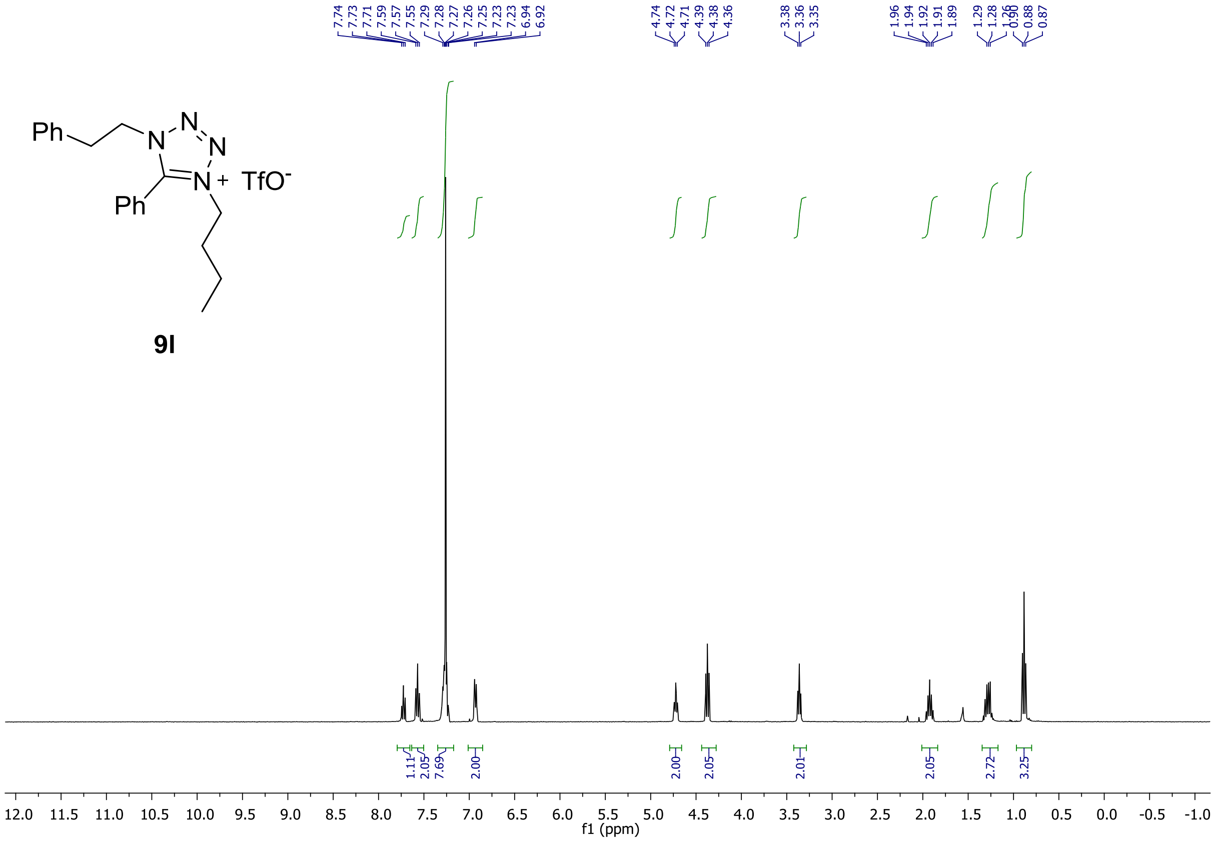
9j


Ph
N
N
N
N+
7.34
7.33
7.33
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.17
7.17
7.16
7.15
7.15
5.62
5.61
5.60
5.58
5.57
5.56
5.55
5.54
5.03
4.84
4.79
4.77
4.75
4.45
4.43
4.41
3.47
3.45
3.43
3.34
3.32
3.30
2.07
2.05
2.04
2.03
2.03
2.01
1.99
1.97
1.47
1.45
1.43
1.41
1.02
1.00
0.98
3.63
2.03
1.06
1.03
1.09
1.97
2.00
2.01
2.03
3.99
2.24
3.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

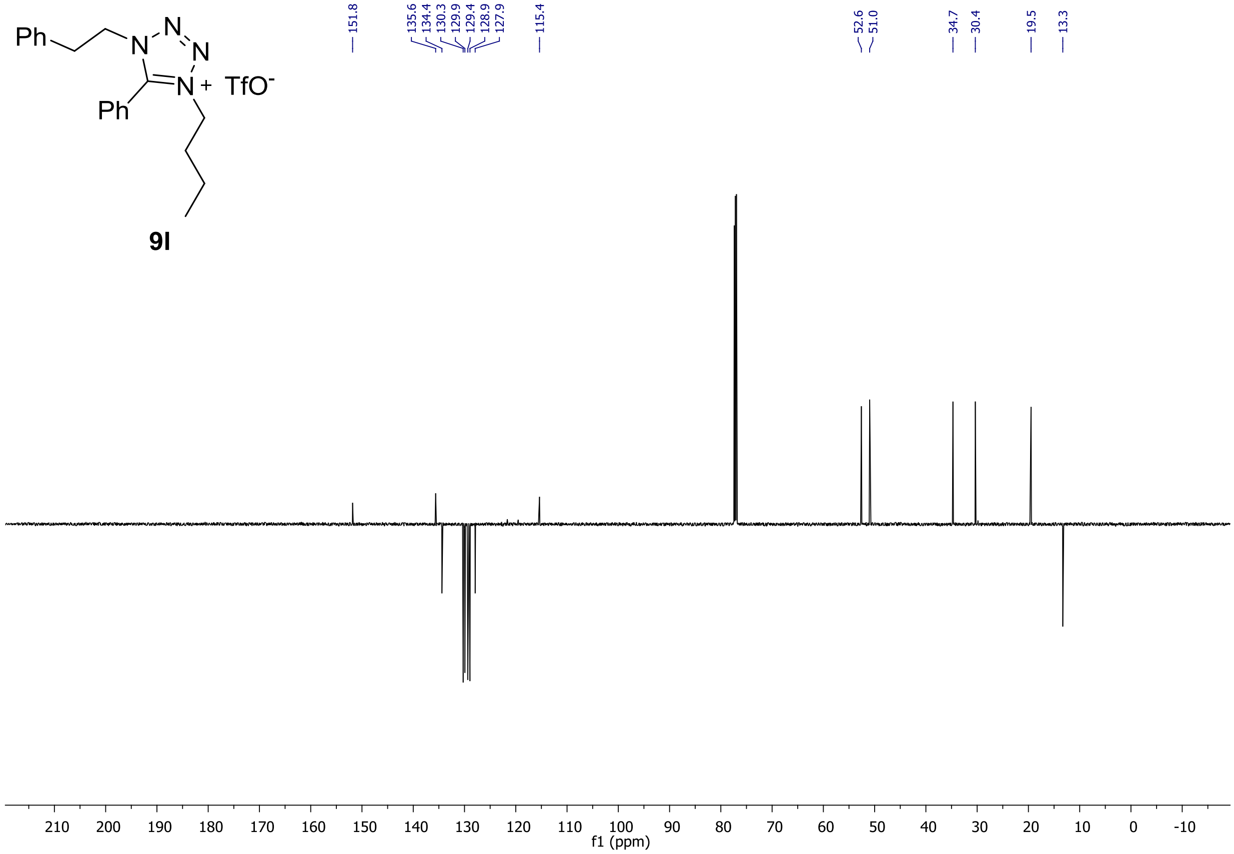
9k


Ph
N
N
N
N+
154.0
135.7
133.3
129.4
129.1
128.0
119.2
77.5
77.2
76.8
52.7
50.9
34.3
30.2
30.2
22.6
19.7
13.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

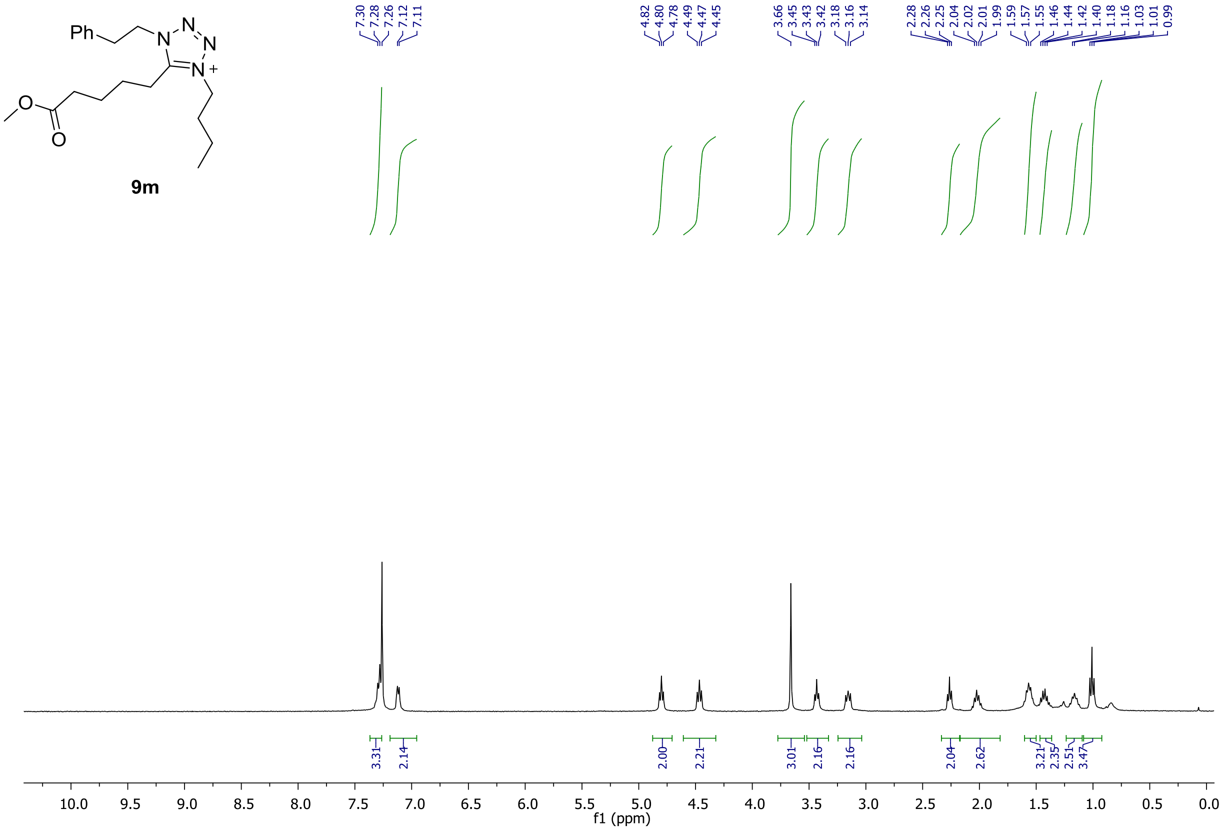
9k


Ph
N
N
N
N+
TfO-
Ph
7.74
7.73
7.71
7.59
7.57
7.55
7.29
7.28
7.27
7.26
7.25
7.23
7.23
6.94
6.92
4.74
4.72
4.71
4.39
4.38
4.36
3.38
3.36
3.35
1.96
1.94
1.92
1.91
1.89
1.29
1.28
1.26
0.90
0.88
0.87
1.11
2.05
7.69
2.00
2.00
2.05
2.01
2.05
2.72
3.25
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

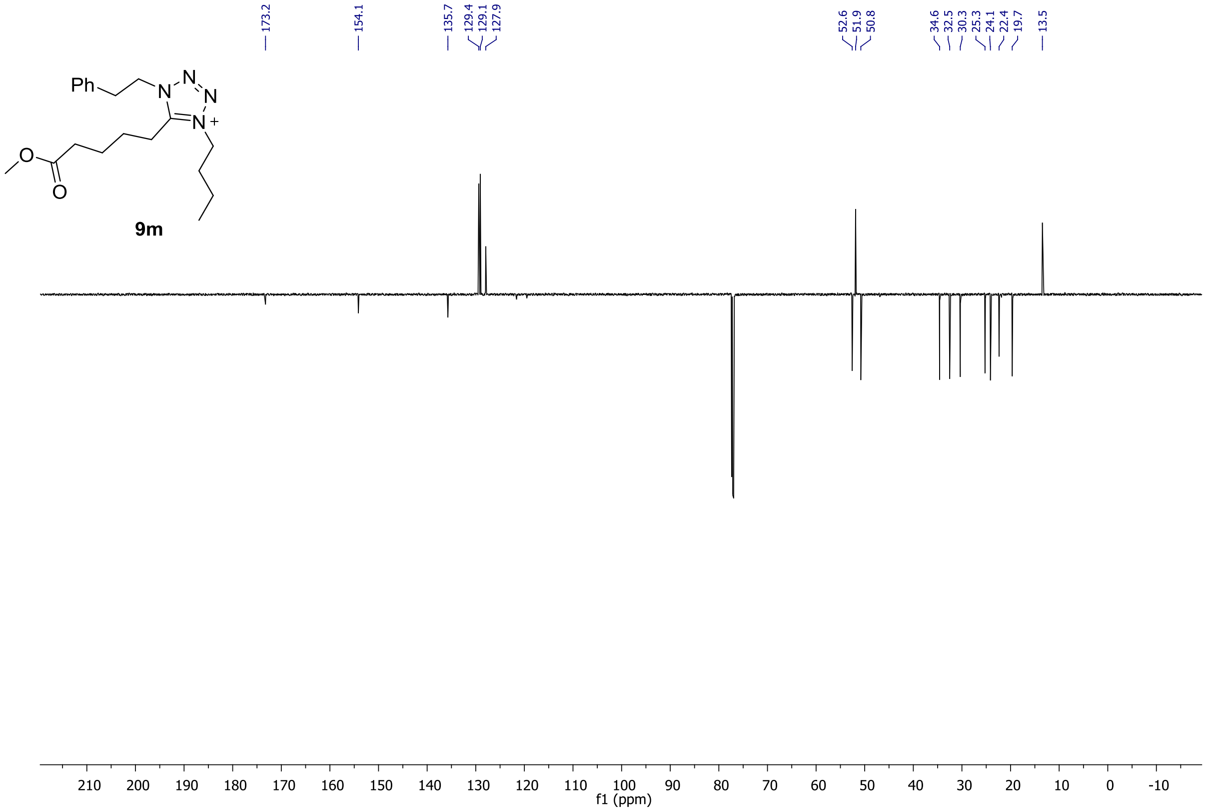
9l


Ph
N
N
N
N+
TfO-
Ph
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
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

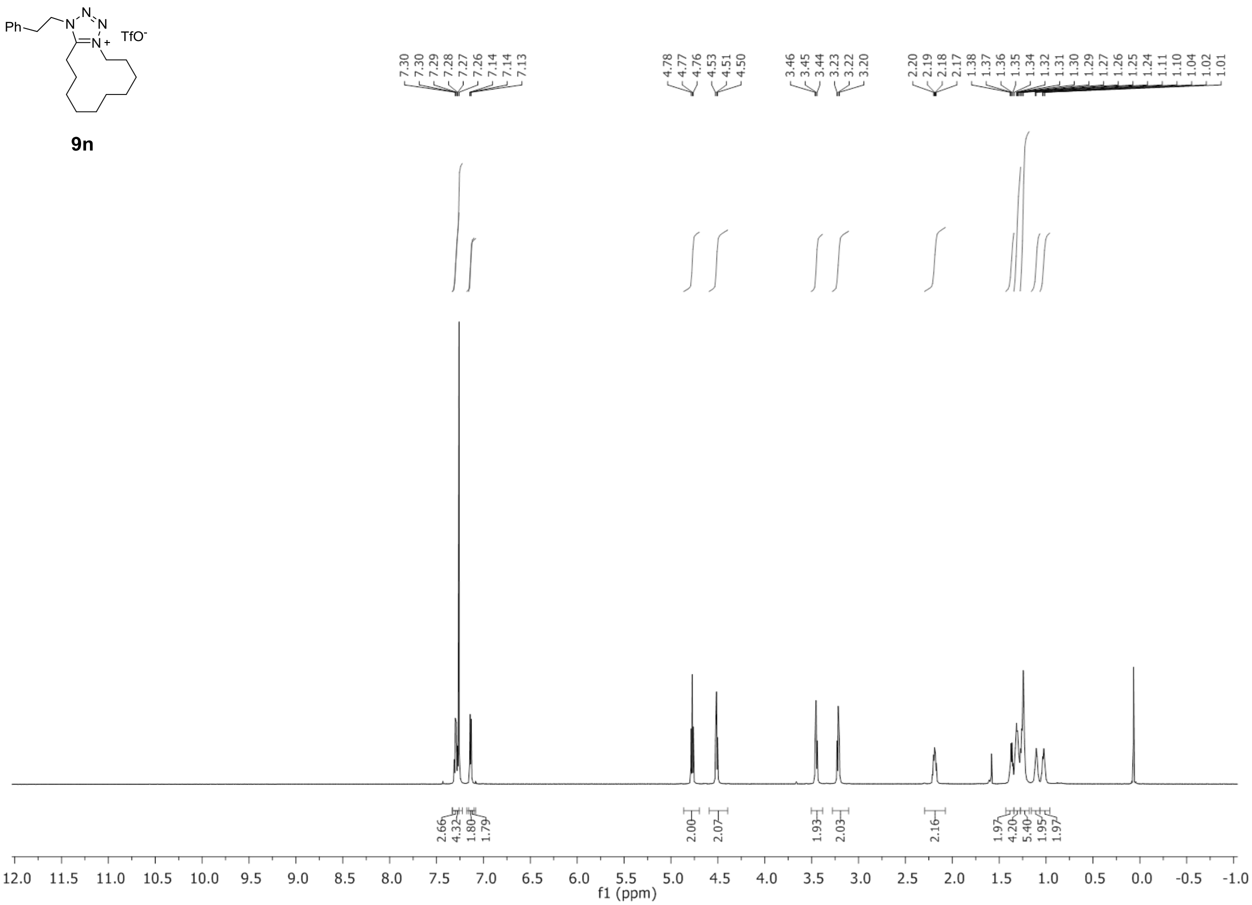
9l


9m

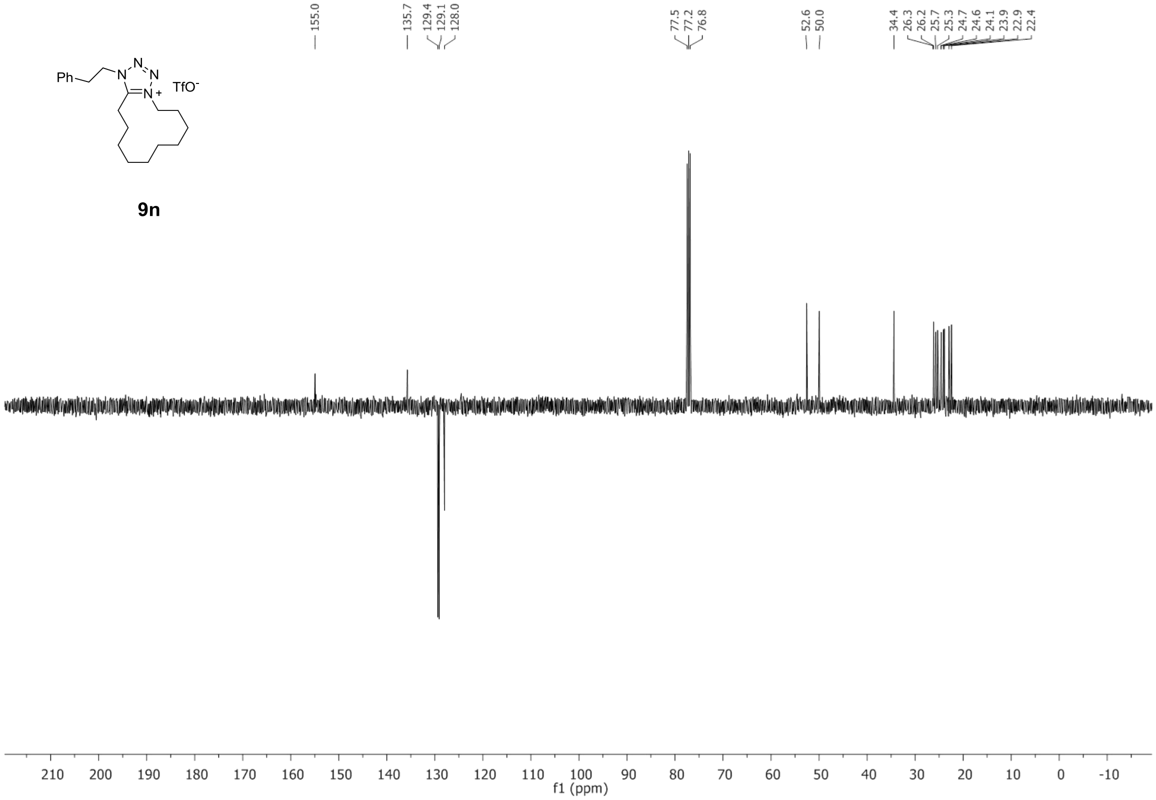
7.30
7.28
7.26
7.12
7.11
4.82
4.80
4.78
4.49
4.47
4.45
3.66
3.45
3.43
3.42
3.18
3.16
3.14
2.28
2.26
2.25
2.04
2.02
2.01
1.99
1.59
1.57
1.55
1.46
1.44
1.42
1.40
1.18
1.16
1.03
1.01
0.99
3.31
2.14
2.00
2.21
3.01
2.16
2.16
2.04
2.62
3.21
2.35
2.51
3.47
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
Ph
N
N
N
N+
O
O


9m

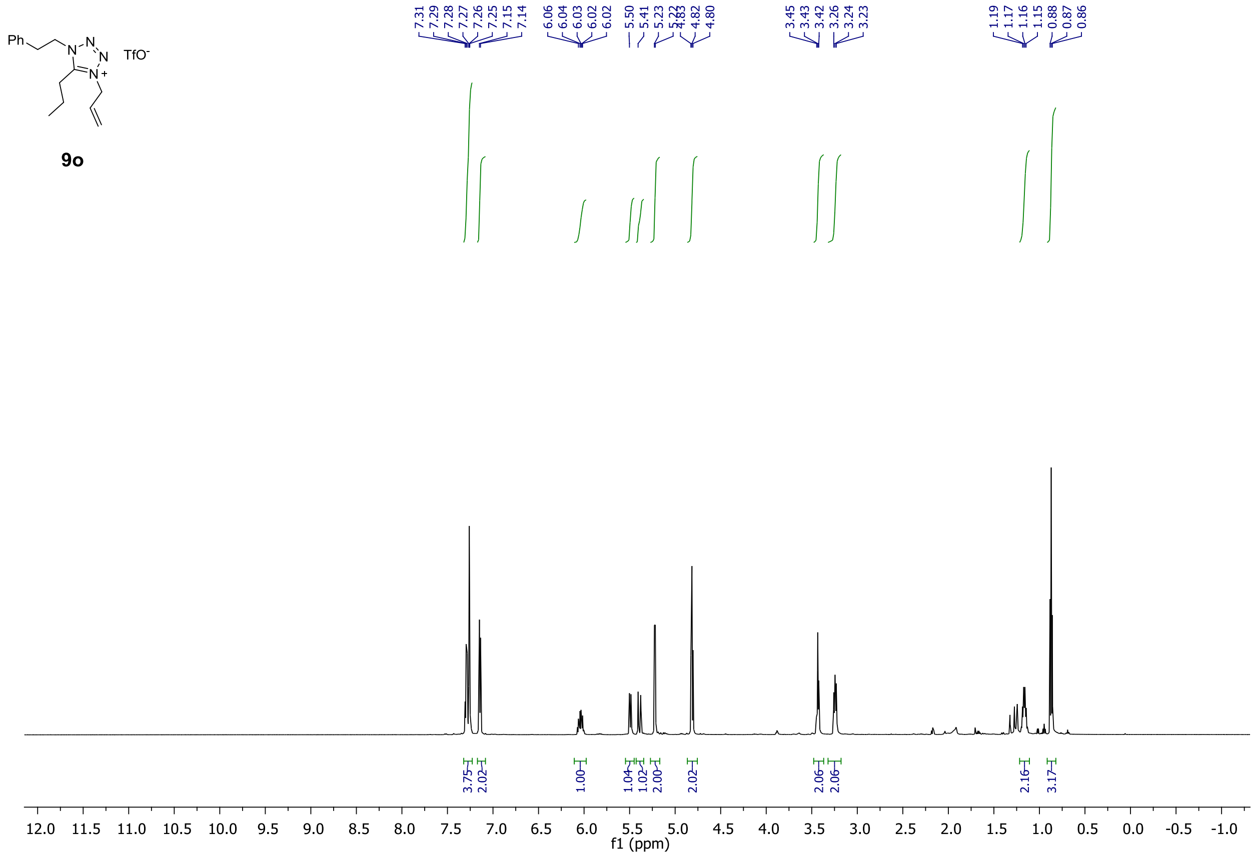
173.2
154.1
135.7
129.4
129.1
127.9
52.6
51.9
50.8
34.6
32.5
30.3
25.3
24.1
22.4
19.7
13.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
Ph
N
N
N
N+
O
O

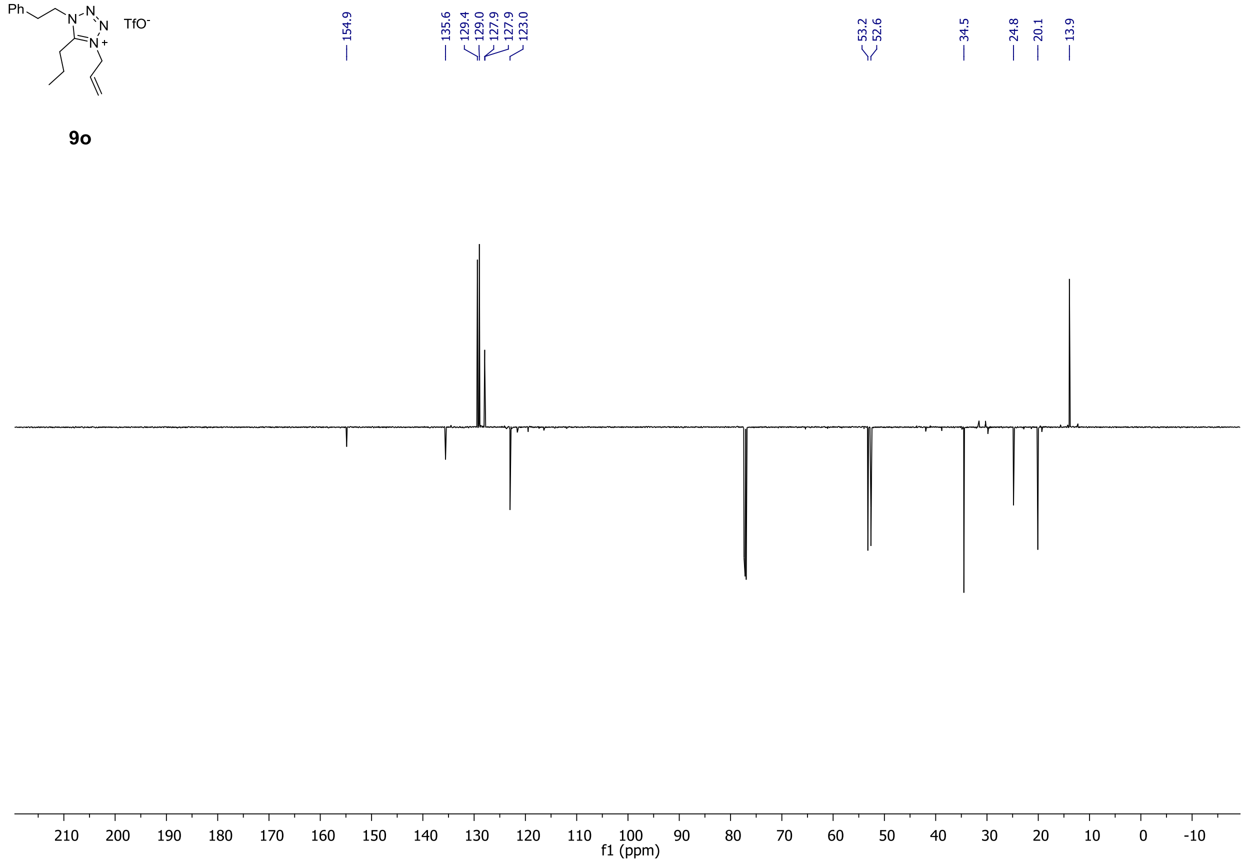

9n

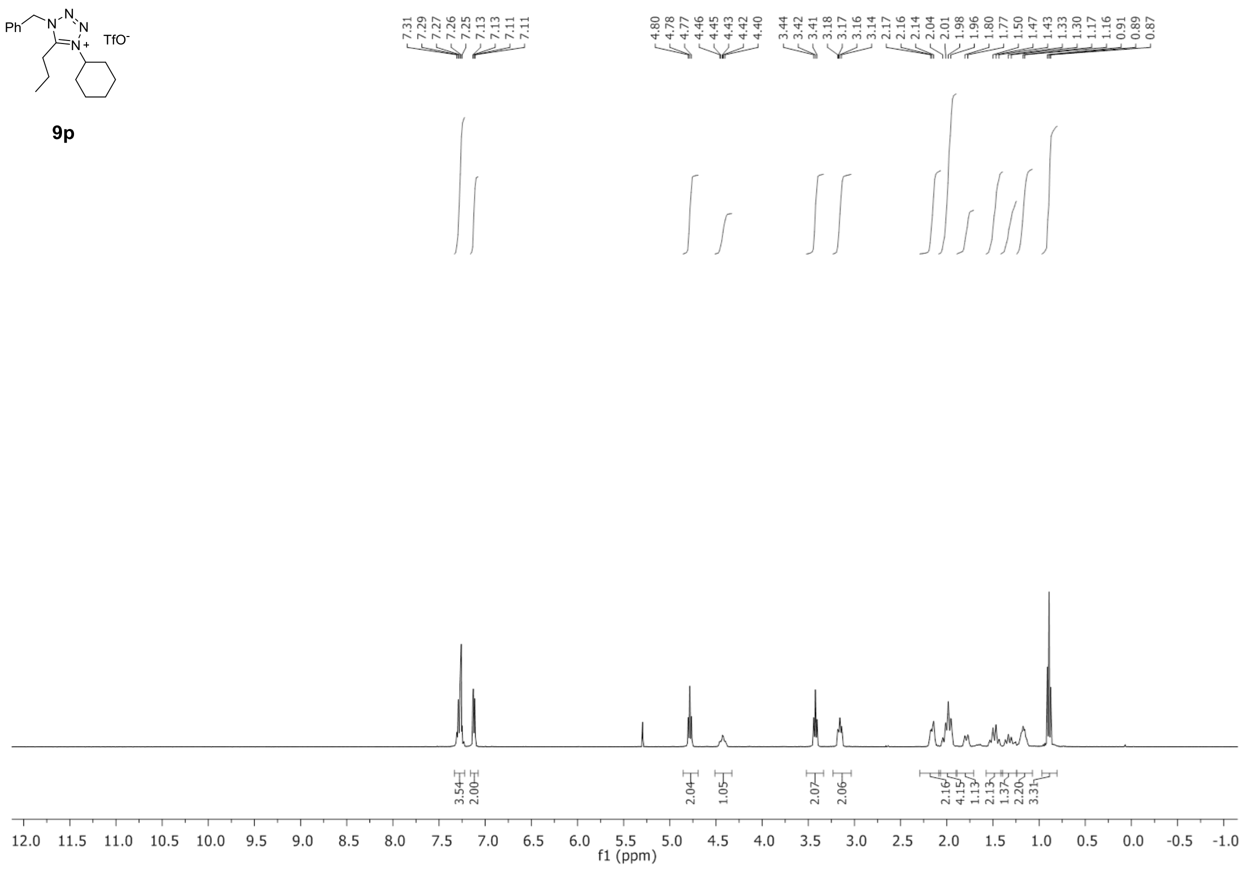
Ph
N
N
N
N+
TfO-
7.30
7.30
7.29
7.28
7.27
7.26
7.14
7.14
7.13
4.78
4.77
4.76
4.53
4.51
4.50
3.46
3.45
3.44
3.23
3.22
3.20
2.20
2.19
2.18
2.17
1.38
1.37
1.36
1.35
1.34
1.32
1.31
1.30
1.29
1.27
1.26
1.25
1.24
1.11
1.10
1.04
1.02
1.01
2.66
4.32
1.80
1.79
2.00
2.07
1.93
2.03
2.16
1.97
4.20
5.40
1.95
1.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


9n

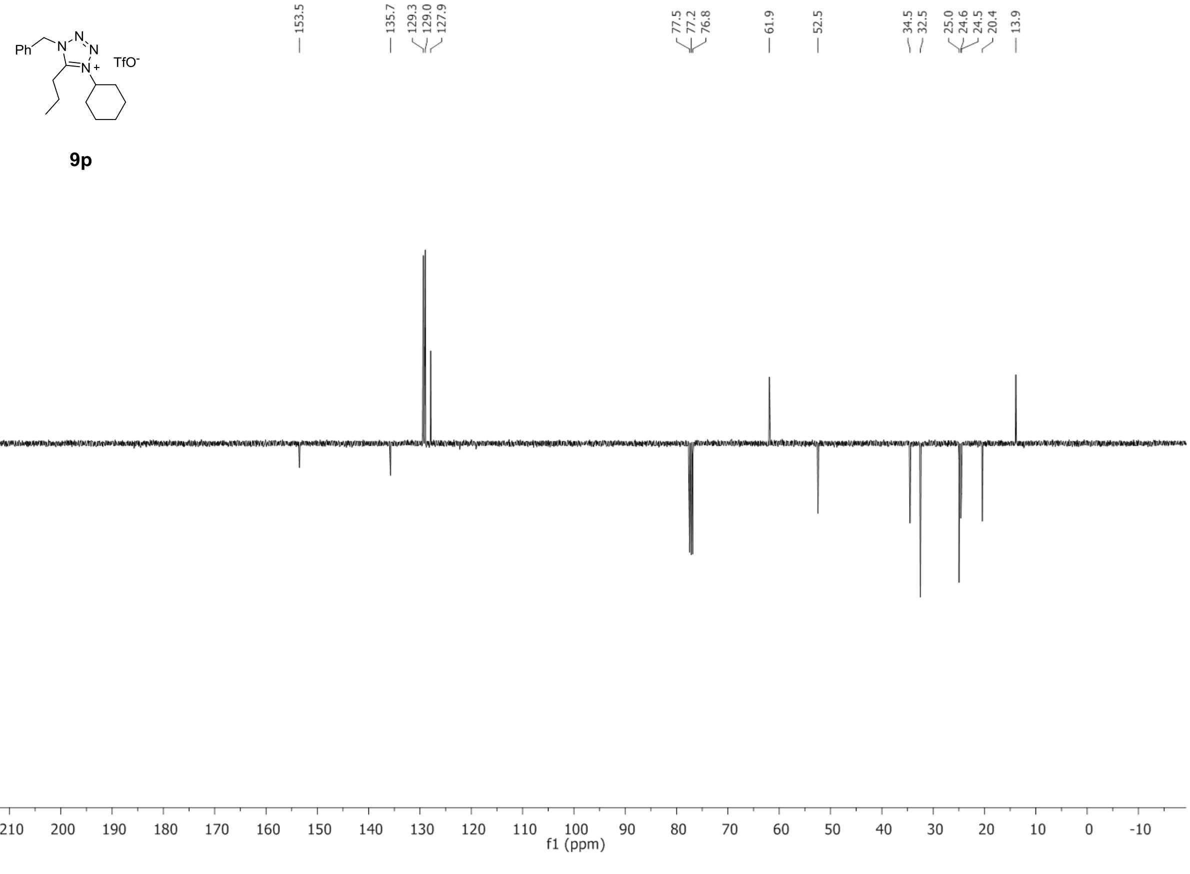
Ph
N
N
N
N+
TfO-
155.0
135.7
129.4
129.1
128.0
77.5
77.2
76.8
52.6
50.0
34.4
26.3
26.2
25.7
25.3
24.7
24.6
24.1
23.9
22.9
22.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
N
N
N
N+
TfO-
9o
7.31
7.29
7.28
7.27
7.26
7.25
7.15
7.14
6.06
6.04
6.03
6.02
6.02
5.50
5.41
5.23
5.22
4.83
4.82
4.80
3.45
3.43
3.42
3.26
3.24
3.23
1.19
1.17
1.16
1.15
0.88
0.87
0.86
3.75
2.02
1.00
1.04
1.02
2.00
2.02
2.06
2.06
2.16
3.17
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

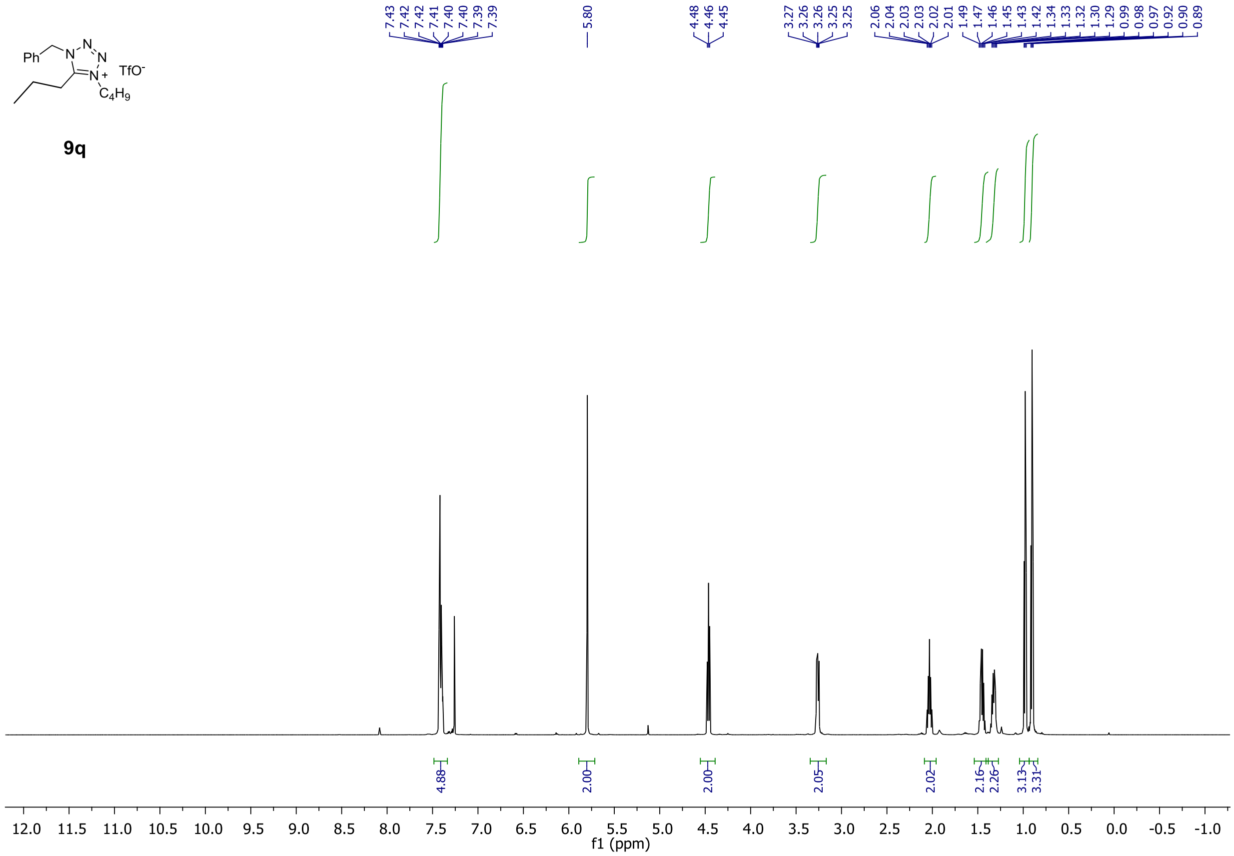

Ph
N
N
N
N+
TfO-
9o
154.9
135.6
129.4
129.0
127.9
127.9
123.0
53.2
52.6
34.5
24.8
20.1
13.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9p

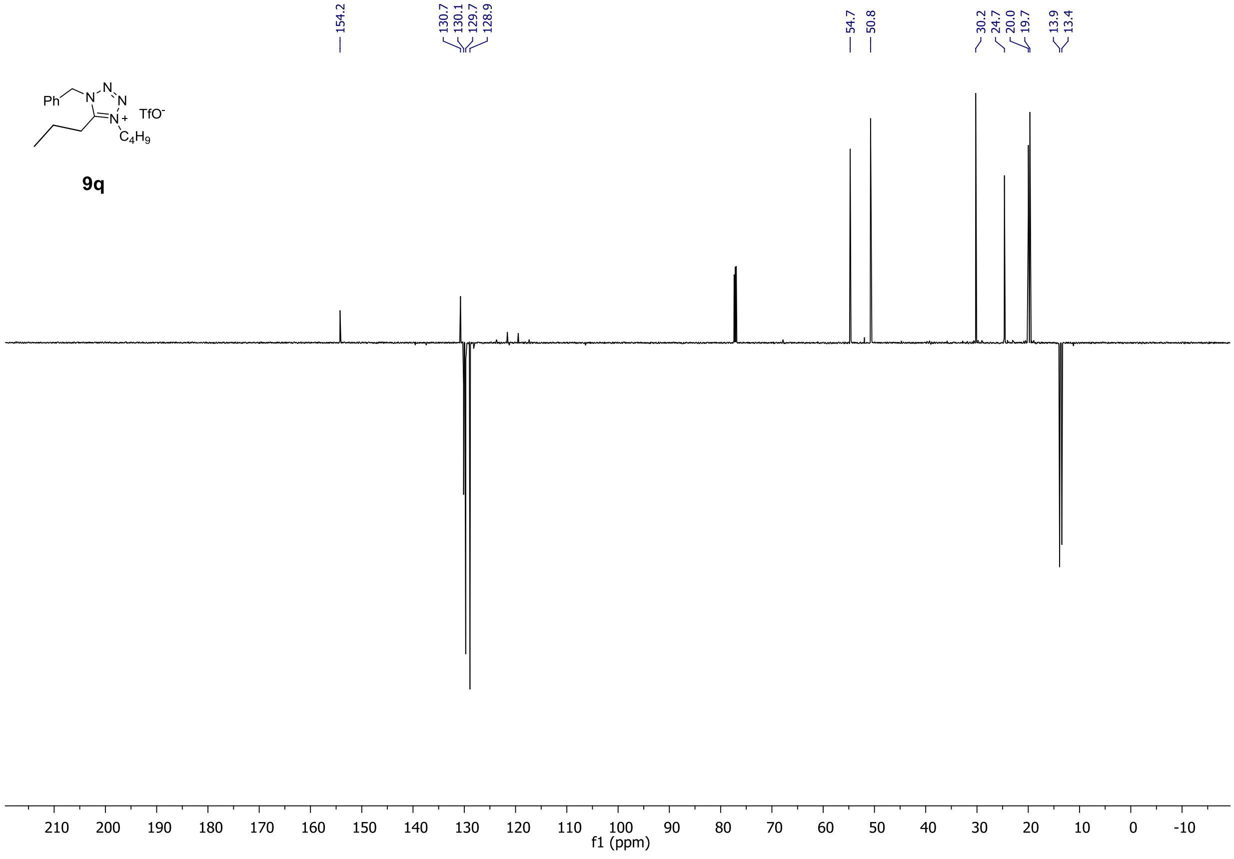
TfO⁻
7.31
7.29
7.27
7.26
7.25
7.13
7.13
7.11
7.11
4.80
4.78
4.77
4.46
4.45
4.43
4.42
4.40
3.44
3.42
3.41
3.18
3.17
3.16
3.14
2.17
2.16
2.14
2.04
2.01
1.98
1.96
1.80
1.77
1.50
1.47
1.43
1.33
1.30
1.17
1.16
0.91
0.89
0.87
3.54
2.00
2.04
1.05
2.07
2.06
2.16
4.15
1.13
2.13
1.37
2.20
3.31
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


9p

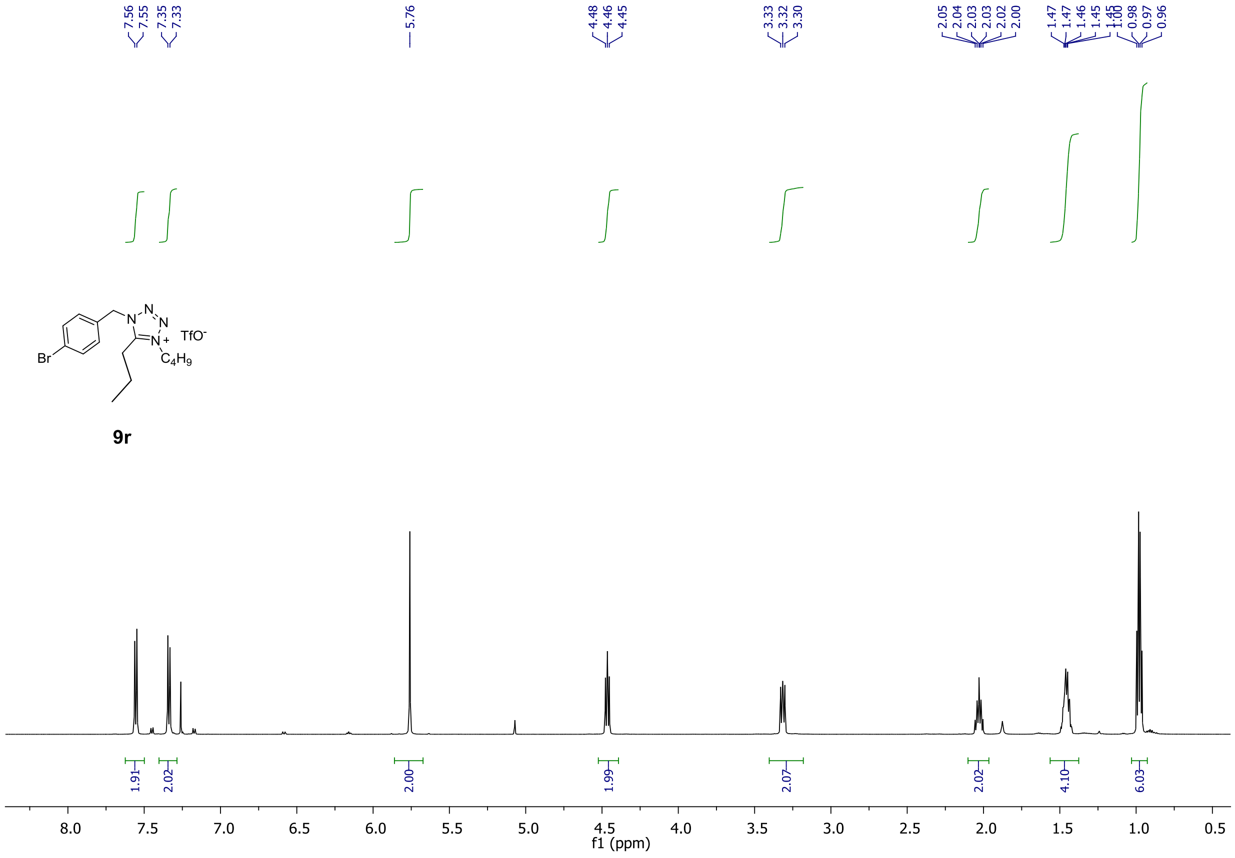
TfO⁻
153.5
135.7
129.3
129.0
127.9
77.5
77.2
76.8
61.9
52.5
34.5
32.5
25.0
24.6
24.5
20.4
13.9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
N
N
N
N+
TfO-
C4H9
7.43
7.42
7.42
7.41
7.40
7.40
7.39
7.39
5.80
4.48
4.46
4.45
3.27
3.26
3.26
3.25
3.25
2.06
2.04
2.03
2.03
2.02
2.01
1.49
1.47
1.46
1.45
1.43
1.42
1.34
1.33
1.32
1.30
1.29
0.99
0.98
0.97
0.92
0.90
0.89
4.88
2.00
2.00
2.05
2.02
2.16
2.26
3.13
3.31
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

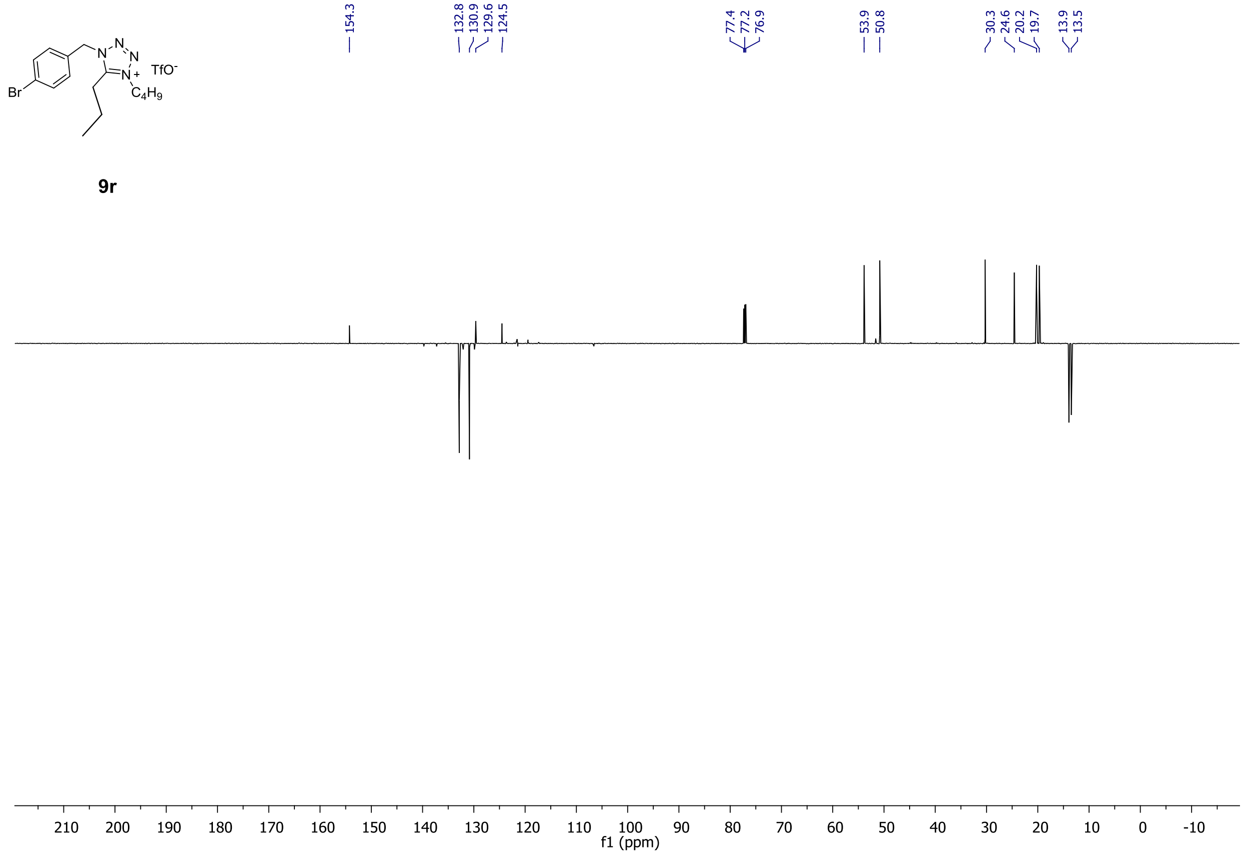
9q


Ph
N
N
N
N+
TfO-
C4H9
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
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

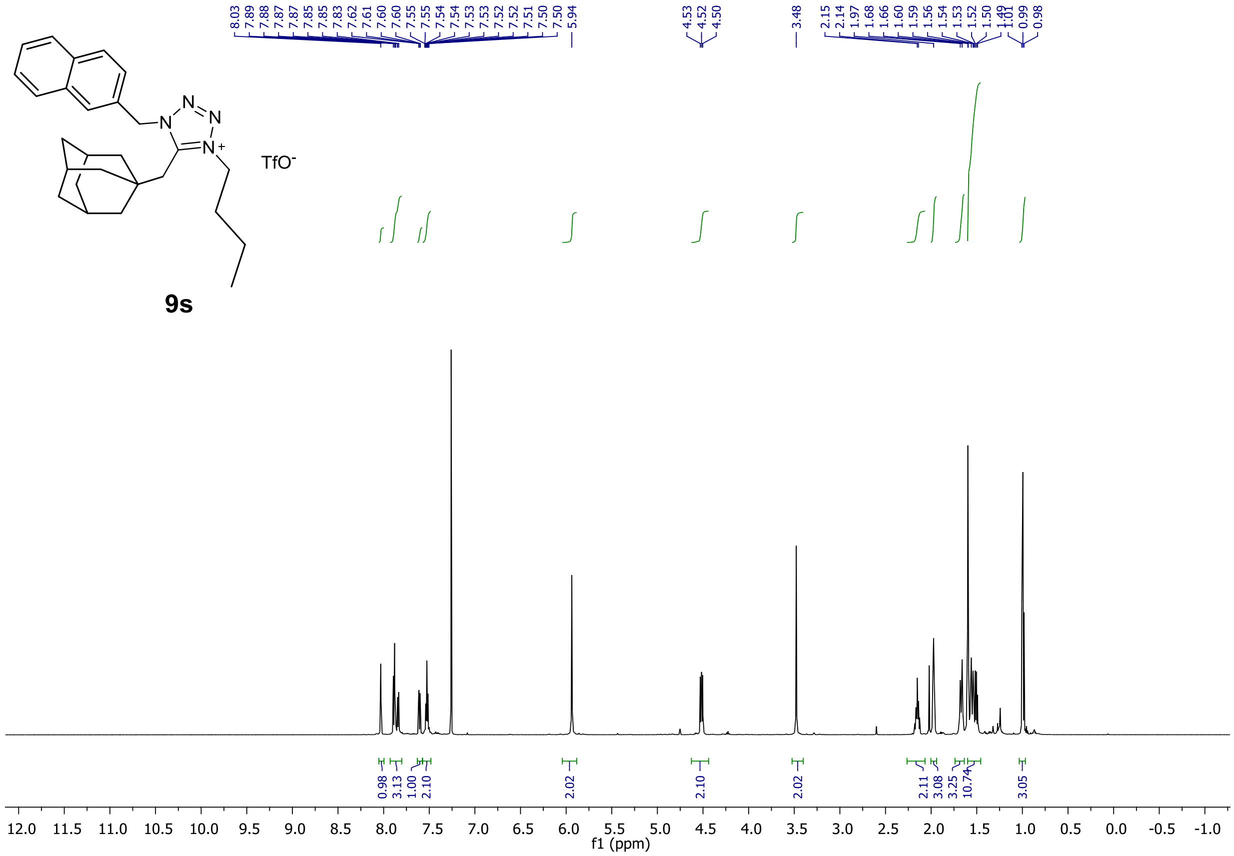
9q

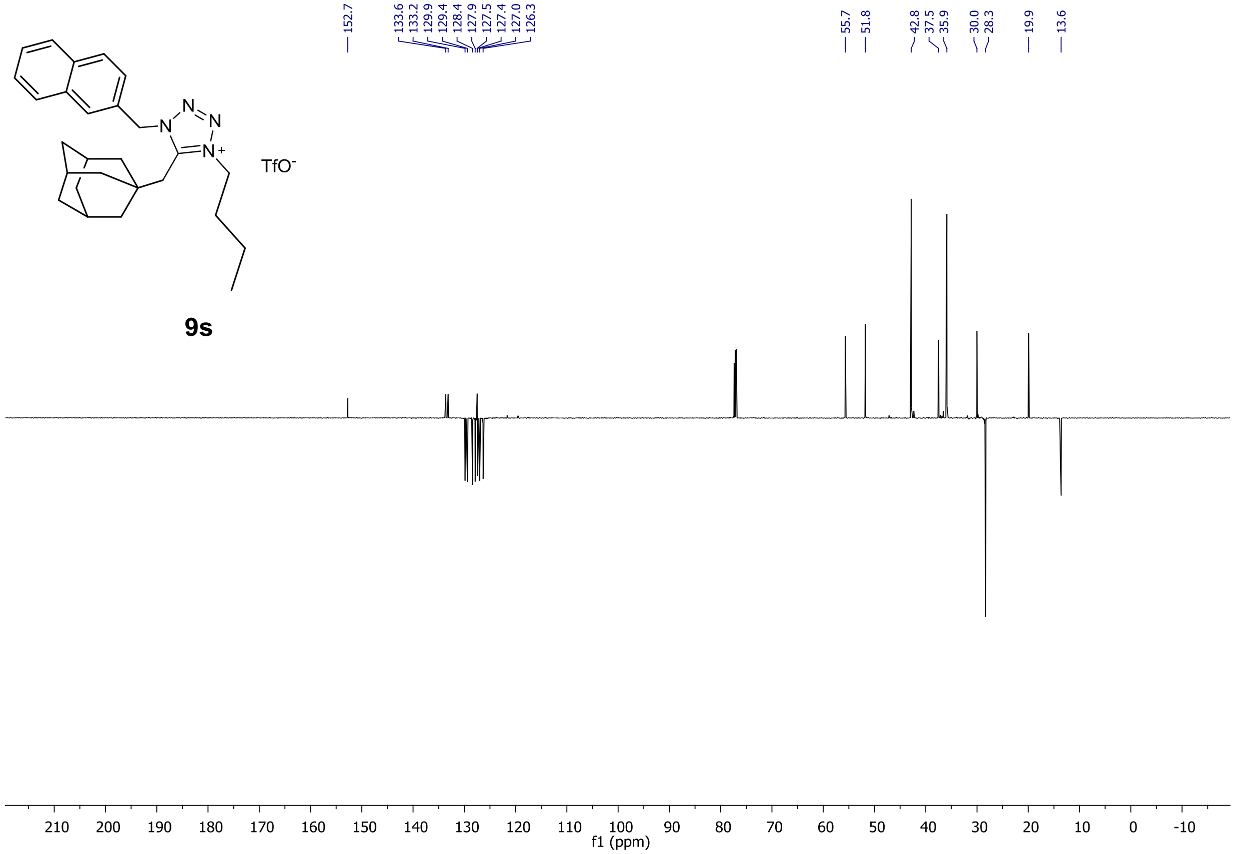

7.56
7.55
7.35
7.33
5.76
4.48
4.46
4.45
3.33
3.32
3.30
2.05
2.04
2.03
2.03
2.02
2.00
1.47
1.47
1.46
1.45
1.45
1.00
0.98
0.97
0.96
N
N
N
N+
TfO⁻
Br
C4H9
1.91
2.02
2.00
1.99
2.07
2.02
4.10
6.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

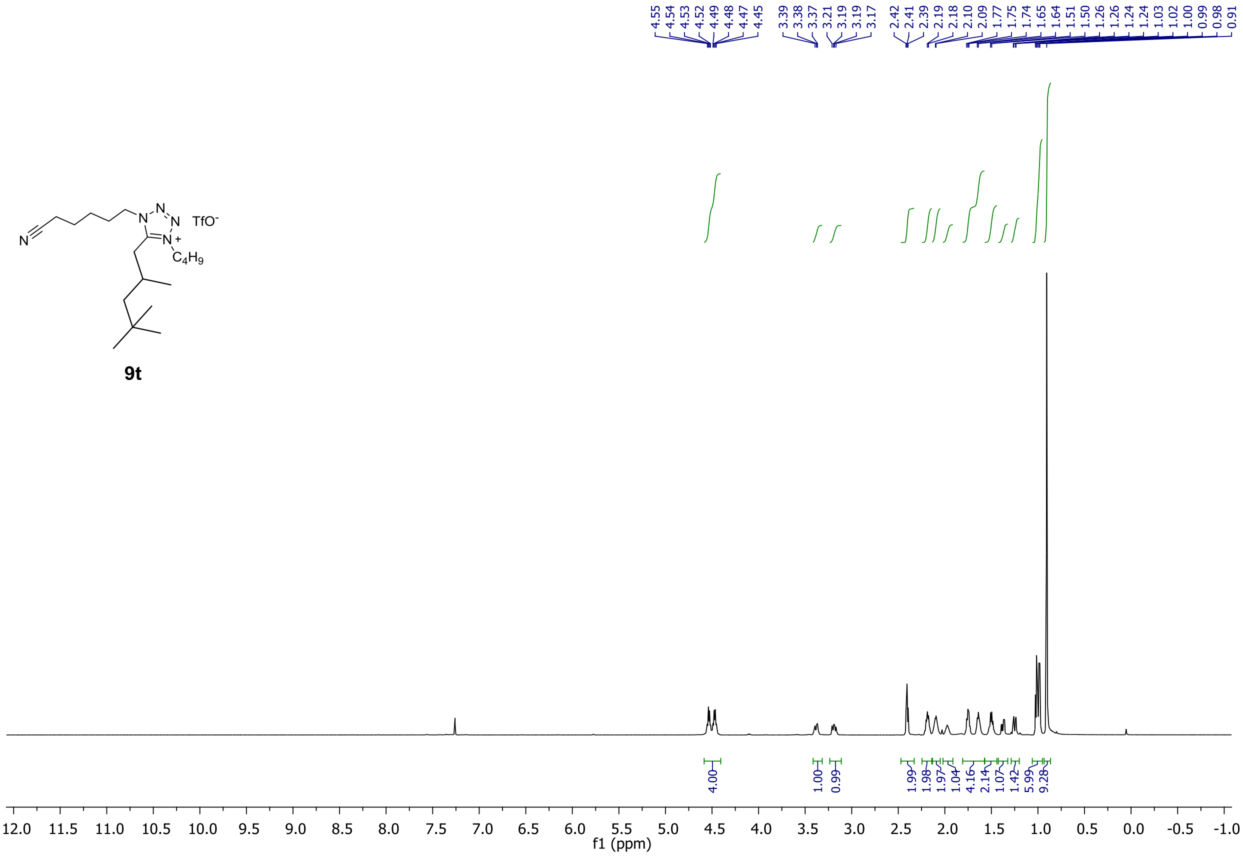
9r


154.3
132.8
130.9
129.6
124.5
77.4
77.2
76.9
53.9
50.8
30.3
24.6
20.2
19.7
13.9
13.5
N
N
N
N+
TfO⁻
Br
C4H9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

9r


8.03
7.89
7.88
7.87
7.87
7.85
7.85
7.83
7.62
7.61
7.60
7.60
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.50
5.94
4.53
4.52
4.50
3.48
2.15
2.14
1.97
1.68
1.66
1.60
1.59
1.56
1.54
1.53
1.52
1.50
1.49
1.01
0.99
0.98
N
N
N
N+
TfO-
9s
0.98
3.13
1.00
2.10
2.02
2.10
2.02
2.11
3.08
3.25
10.74
3.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


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
N
N
N
N+
TfO-
9s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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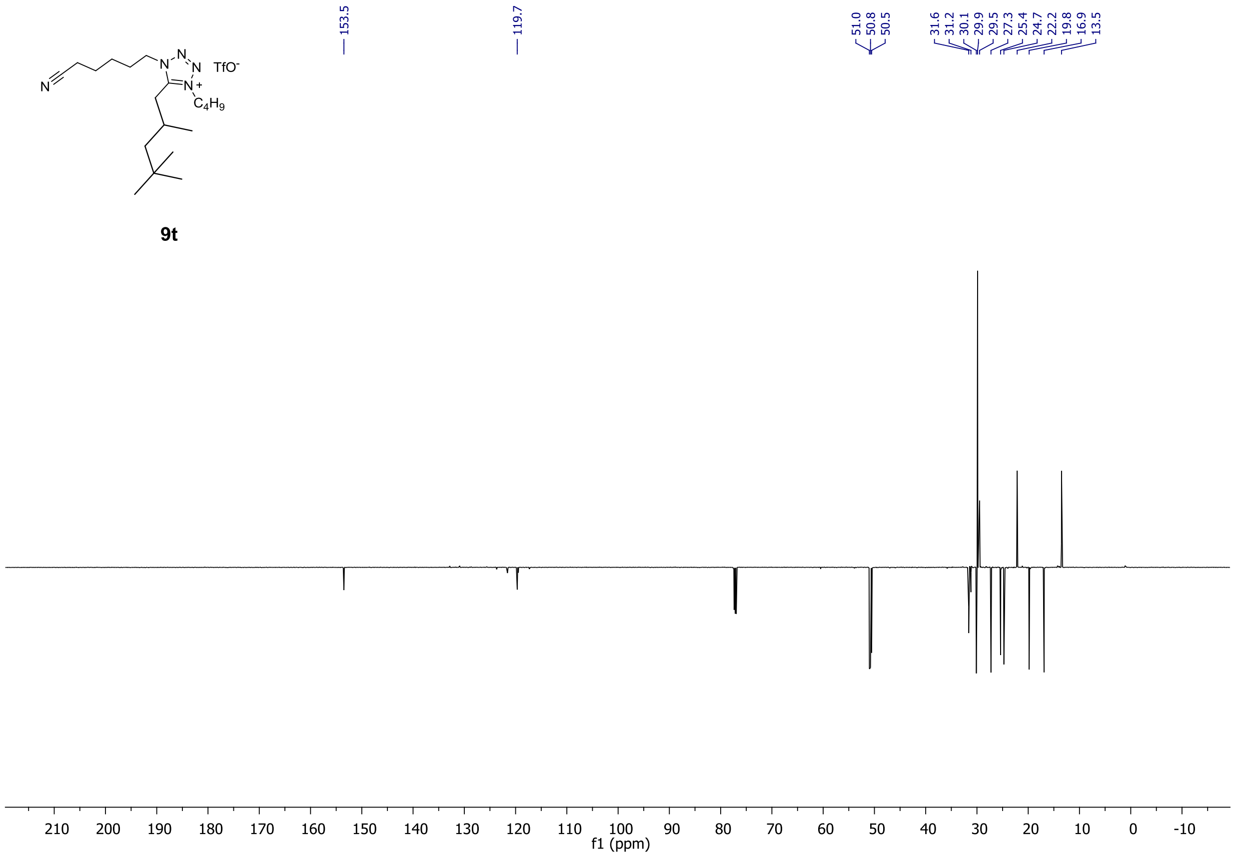
4.53
4.52
4.49
4.48
4.47
4.45
3.39
3.38
3.37
3.21
3.19
3.19
3.17
2.42
2.41
2.39
2.19
2.18
2.10
2.09
1.77
1.75
1.74
1.65
1.64
1.51
1.50
1.26
1.26
1.24
1.24
1.03
1.02
1.00
0.99
0.98
0.91
TfO⁻
N
N
N
N+
C_4H_9
4.00
1.00
0.99
1.99
1.98
1.97
1.04
4.16
2.14
1.07
1.42
5.99
9.28
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

9t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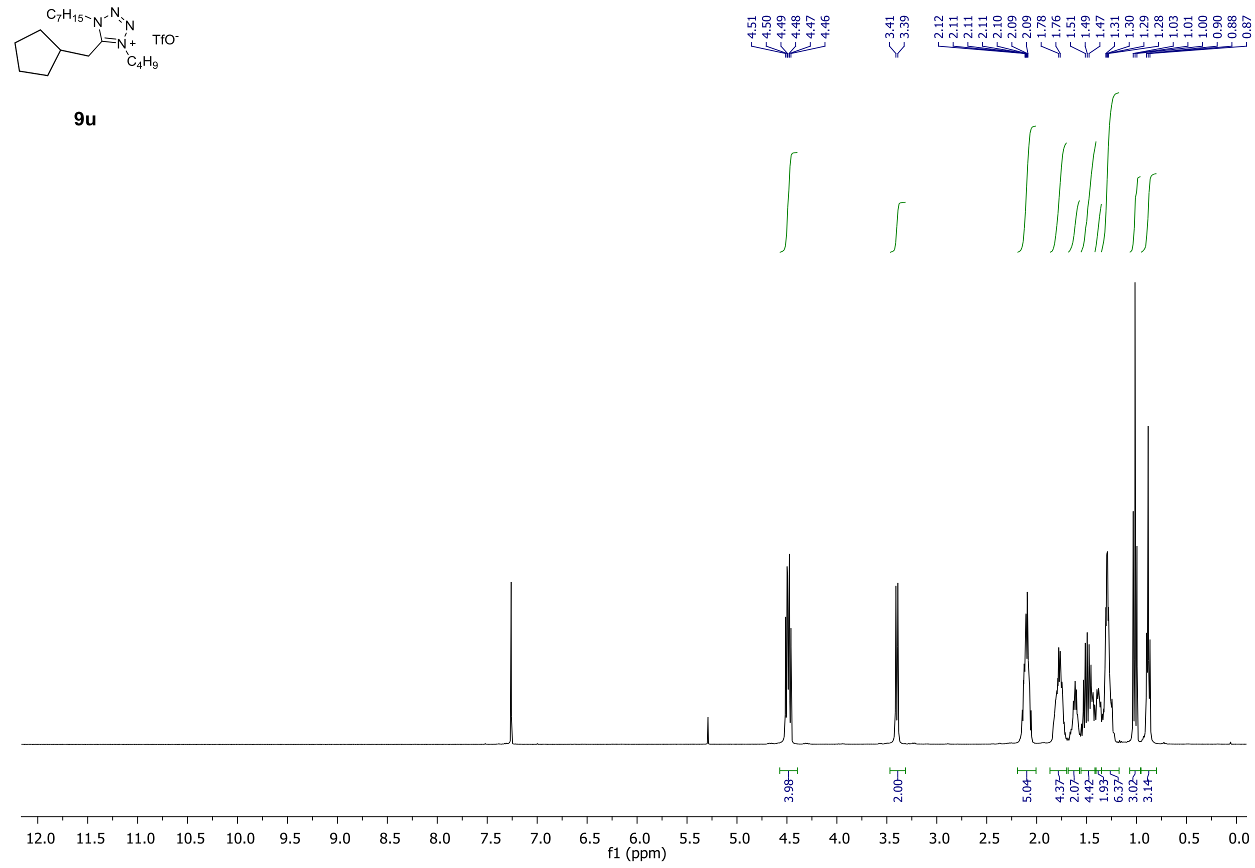
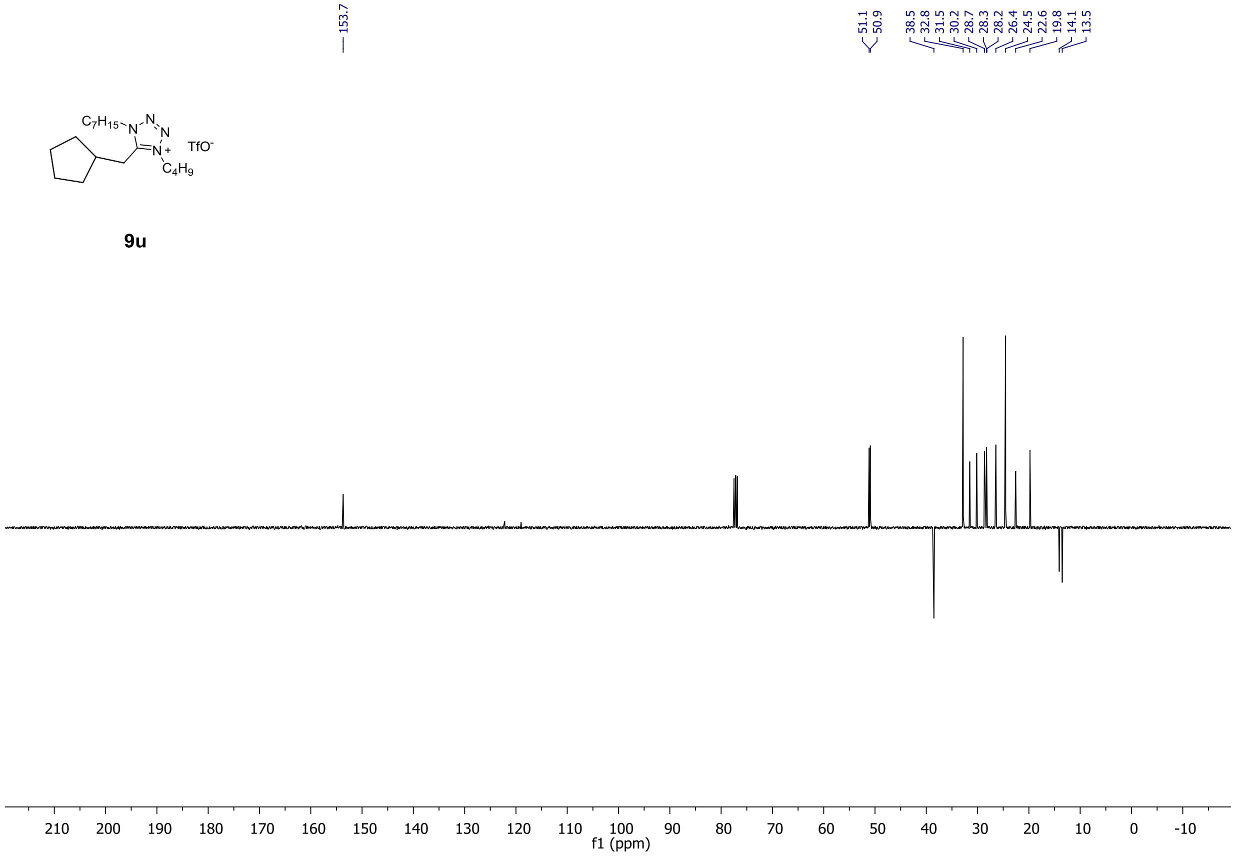
119.7
51.0
50.8
50.5
31.6
31.2
30.1
29.9
29.5
27.3
25.4
24.7
22.2
19.8
16.9
13.5
TfO⁻
N
N
N
N+
C_4H_9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

9t



9u

C7H15
N
N
N
N+
TfO-
C4H9
4.51
4.50
4.49
4.48
4.47
4.46
3.41
3.39
2.12
2.11
2.11
2.11
2.10
2.09
1.78
1.76
1.51
1.49
1.47
1.31
1.30
1.29
1.28
1.03
1.01
1.00
0.90
0.88
0.87
3.98
2.00
5.04
4.37
2.07
4.42
1.93
6.37
3.02
3.14
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



9u

153.7
51.1
50.9
38.5
32.8
31.5
30.2
28.7
28.3
28.2
26.4
24.5
22.6
19.8
14.1
13.5
C7H15
N
N
N
N+
TfO-
C4H9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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