Supporting Information for:

Effects of Biradical Deuteration on the Performance of DNP: Towards Better Performing Polarizing Agents

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DNP CPMAS NMR:

The ^{13}C CPMAS NMR measurements were performed on a Bruker AVANCE III 400 MHz DNP NMR system equipped with a 263 GHz gyrotron and a triple-resonance LTMAS probe. All samples were pipetted (20 μL) into 3.2-mm sapphire rotors that were sealed with silicon rubber plugs and zirconia caps. The bTbK samples were dissolved in tetrachloroethane at a concentration of 16 mM whereas the TOTAPol samples were dissolved at a concentration of 10 mM in protonated and 90% deuterated DNP juice (60:40 mixture of glycerol and water). The bTbK samples were additionally degassed within the NMR probe by repeatedly inserting and ejecting the sample until the enhancement converged to a maximum value (typically 3-5 times). The ^{1}H excitation pulse lasted 2.75 μs and a 3 ms ramped cross-polarization contact time was used. In all cases the relaxation delay was set to 5 times the DNP build-up time (T_{DNP}) and 16 scans were accumulated. The T_{DNP} values were determined using a saturation recovery experiment observing either the ^{1}H signal, in the case of bTbK, or the CPMAS signal, in the case of TOTAPol. All the DNP measurements were performed while spinning at 6 kHz at a temperature of 109 K.

3-(3-phenylureido)propyl-functionalized mesoporous silica nanoparticles (PUP-MSNs) were synthesized as has been previously described in the literature.[1,2,3] The PUP-MSN samples were impregnated with a 16mM TCE solution of the btbk-d0 and –d40 biradicals. These were then degassed by repeated freezing and thawing within the probe, as was done for the liquid samples. ^{13}C and ^{29}Si CPMAS experiments were then performed to evaluate the enhancement factor. The ^{1}H-^{29}Si contact time lasted 3 ms. Shorter T_{DNP} values were measured for the sample than was measured for the solvent (3.1 and 5.4 s for btbk-d0 and –d40, respectively). For both ^{29}Si and ^{13}C the enhancement factors were of 22 and 29 when using btbk-d0 and –d40, respectively, see Figure S1. As may also be observed in Figure S1, the resolution is not compromised when using the deuterated biradical.

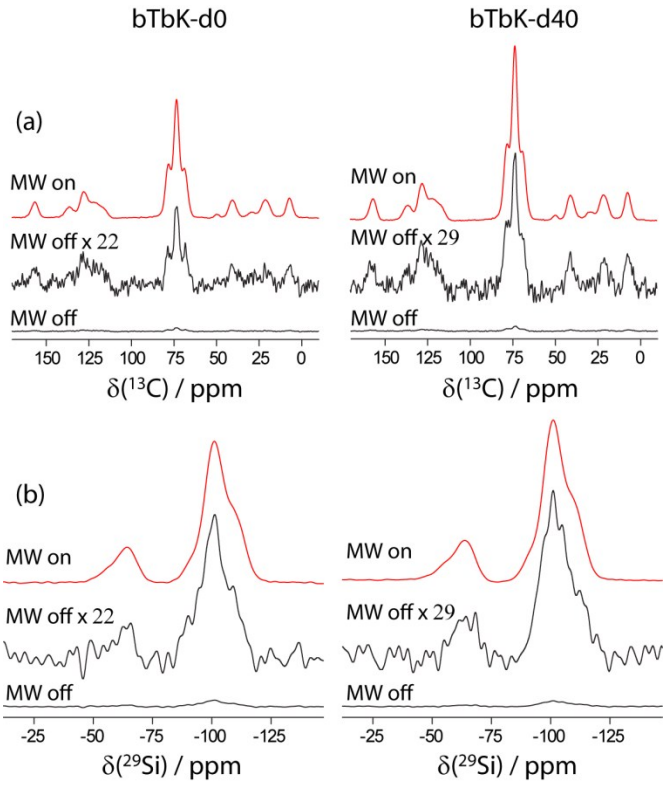

Figure S1. ^{13}C (a) and ^{29}Si (b) DNP-enhanced CPMAS NMR spectra acquired on PUP-MSN using btbk-d0 (left) and btbk-d40 (right). As was measured in solutions, a larger enhancement is obtained by using a deuterated polarizing agent.

EPR Spectroscopy:

The T_{1e} measurements were performed on an X-band Elexsys 580 FT- EPR spectrometer by using an inversion recovery method at a temperature of 100 K. The π/2 and π pulse durations used for the relaxation measurements were 16 ns and 32 ns, respectively. As had been previously described,[4] the relaxation process in these samples is not monoexponential and is better represented by a stretched exponential function:

$$I(t) = I_0 + I_1 e^{-\left(\frac{t}{T_{1e}^*}\right)^{\beta}}.$$

In the expression above, I_0 is the initial intensity, I_1 is a proportionality constant, T_{1e}^* is a decay constant, and β is the stretching parameter. The T_{1e} values mentioned in the text are in fact the mean T_{1e} values, which correspond to the first moment of the stretched exponential decay. These are calculated as:

$$\langle T_{1e} \rangle = \frac{T_{1e}^*}{\beta} \Gamma\left(\frac{1}{\beta}\right).$$

The T_{1e}^* and β fitting parameters are listed in Table S1 below.

Table S1. Fitting parameters for the T_{1e} measurements of the radicals described in the text.

polarizing agent	solvent	T_{1e}^* / μs	β	$\langle T_{1e} \rangle$ / μs
bTbK	96:4	26.8	0.76	35
bTbK-d8	TCE : CD_3OD	40.8	0.66	62
bTbK-d32		46.8	0.54	87
bTbK-d40		69.4	0.57	121
TOTAPol-d0	60:30:10	71.8	0.60	120
TOTAPol-d17	glycerol-d8 :	90.7	0.69	131
TOTAPol-d40	D_2O : H_2O	111.3	0.73	153
TOTAPol-d0	60:40 glycerol	76.50	0.62	124
TOTAPol-d17	: H_2O	86.5	0.67	128
TOTAPol-d40		103.3	0.68	153

Materials and Methods:

All deuterated chemicals were purchased from C/D/N Isotopes Inc. with the exception of pentaerythritol-d12, which was purchased from Cambridge Isotope Laboratories, Inc. Acetonitrile was dried by heating to reflux over calcium hydride followed by distillation. All other chemicals were used as received from suppliers. ^{1}H and ^{13}C{^{1}H} NMR spectra were collected on a Bruker AVII 600 spectrometer. Infrared spectra were measured on a Bruker Vertex 80 FTIR spectrometer. Accurate mass measurements were achieved using an Agilent QTOF 6540 mass spectrometer.

Experimental Procedures:

Preparation of the diamine 2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^9.2^6]henicosane followed a combination of the methods previously reported by Matsuki and Griffin and later by Thankamony, Lafon, and Polshettiwar.[5,6] Synthesis of the bTbK series followed the method reported by Matsuki and Griffin.[1] Synthesis of the epoxide precursor to TOTAPOL followed the procedure reported by Zhang whereas the synthesis of TOTAPOL from the epoxide followed the procedure reported by Song and Griffin.[7,8] All of the syntheses were performed on a significantly smaller scale than what was previously reported. While the reactions proved to be scalable, the yields of the diamines were variable and this is attributed to the low scale of these reactions.

Synthesis of 2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15-diazatrispiro-[5.2.2.5^{12}.2^9.2^6]henicosane.
Pentaerythritol (0.237 g, 1.60 mmol), 2,2,6,6-tetramethyl-4-piperidone (0.500 g, 3.22 mmol) and *p*-toluenesulfonic acid (0.730 g, 3.84 mmol) were mixed together in toluene (15 mL) and heated to reflux for 12 hours in a Dean-Stark trap. The solution was cooled

to room temperature and then washed with 2.0 M NaOH solution (2 × 10 mL) and brine (1 × 10 mL). The organic layer was dried over Na_2SO_4 and filtered, and the solvent was removed under vacuum. Recrystallization from diethyl ether afforded white crystals (0.418 g, 1.02 mmol, 64%). The ^1H and $^{13}C\{^1H\}$ NMR spectra match the reported literature values.[6] ^1H NMR (600 MHz, $CDCl_3$): δ 3.76 (s, 8 H), 1.68 (s, 8 H), 1.21 (s, 24 H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 99.65, 63.56, 51.18, 43.08, 32.64, 32.24. IR (KBr, cm^{-1}): ν 3337, 2954, 2919, 2856, 1487, 1461, 1445, 1420, 1377, 1356, 1311, 1245, 1193, 1164, 1113, 1079, 1036, 1021, 979. Mp. 134-135 °C. ESI-MS: m/z Calcd. for $C_{23}H_{42}N_2O_4$ $[M+H]^+$: 411.32; Found: 411.3224.

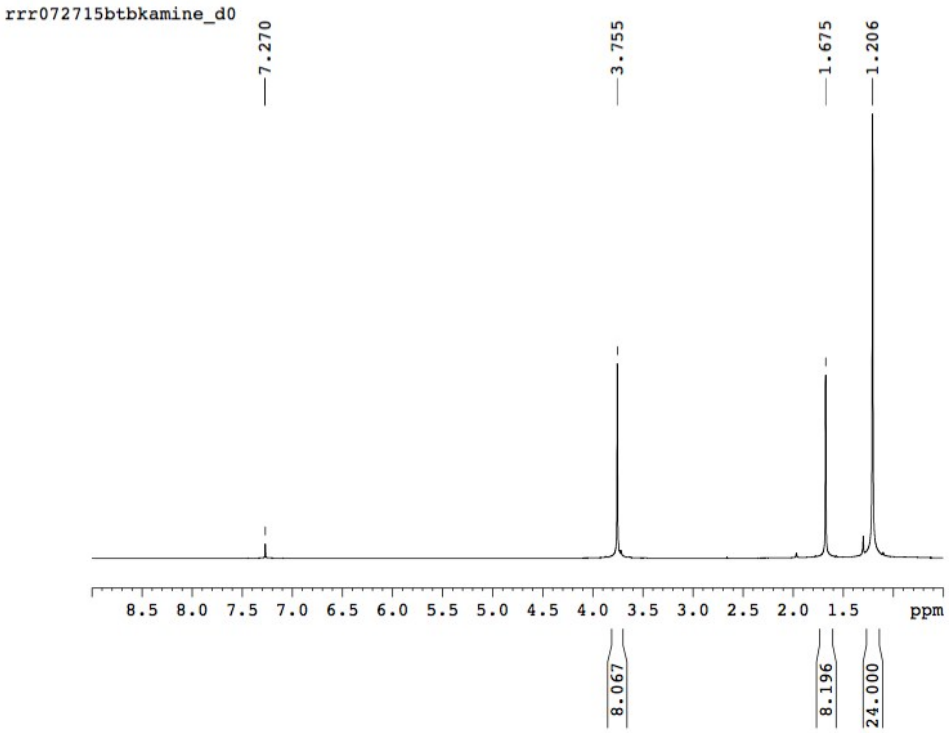

Figure S2. ^1H NMR spectrum of dimino bTbK precursor 2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^9.2^6]henicosane acquired in chloroform-d1.

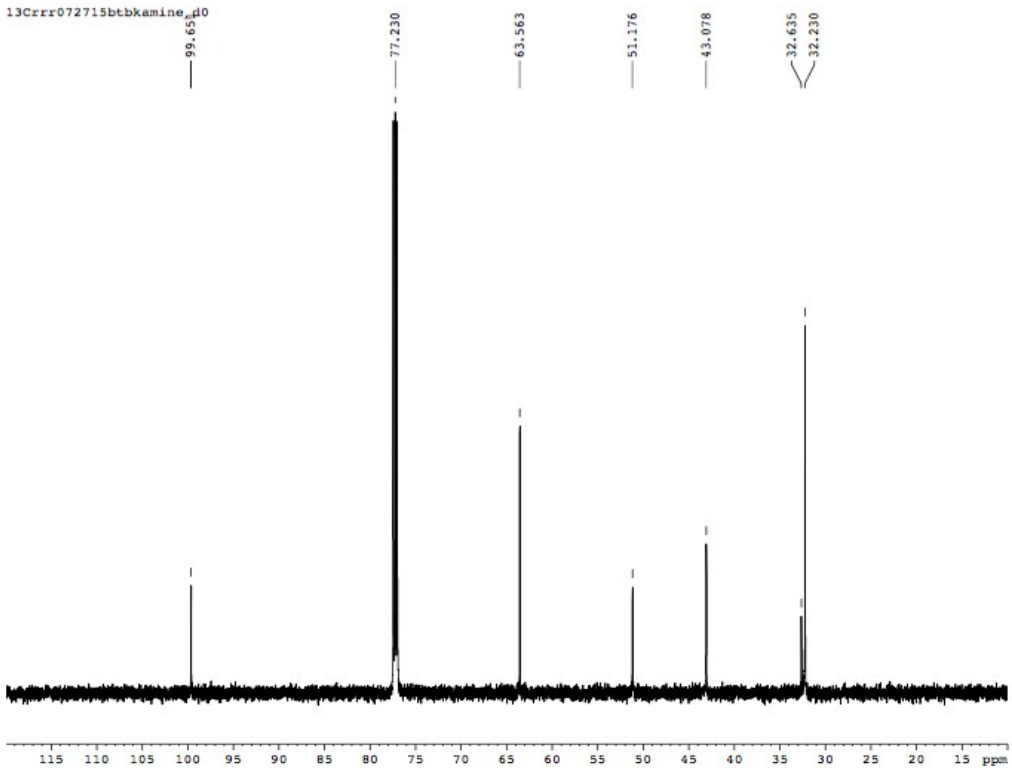

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of bTbK precursor 2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^{9}.2^{6}]henicosane (diamine) acquired in chloroform-d1.

Synthesis of 2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15-diazatrispiro-[5.2.2.5^{12}.2^{9}.2^{6}]henicosane-8,8,10,10,19,19,20,20-d8 (diamine-d8).
Pentaerythritol-d12 (0.237 g, 1.60 mmol), 2,2,6,6-tetramethyl-4-piperidone (0.500 g, 3.22 mmol) and *p*-toluenesulfonic acid (0.730 g, 3.84 mmol) were mixed together in toluene (15 mL) and heated to reflux for 12 hours in a Dean-Stark apparatus with azeotropic removal of water. The solution was cooled to room temperature and then washed with 2.0 M NaOH solution (2 × 10mL) and brine (1 × 10 mL). The organic layer was dried over Na_2SO_4 and filtered, and the solvent was removed under vacuum. Recrystallization from diethyl ether afforded white crystals (0.105 g, 0.25 mmol, 16%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.67 (s, 8 H), 1.21 (s, 24 H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 99.56, 62.76 (br), 51.14, 43.11, 32.25, 31.95. IR (KBr, cm^{-1}): ν 3553, 3499, 3021, 2927, 2864, 2229, 2095, 1652, 1488, 1448, 1424, 1375, 1362, 1314, 1240, 1200, 1155, 1086, 1034, 1018, 1001, 955. Mp. 131-133 °C. ESI-MS: m/z Calcd. for $C_{23}H_{34}D_8N_2O_4$ $[M+H]^+$: 419.37; Found: 420.3782.

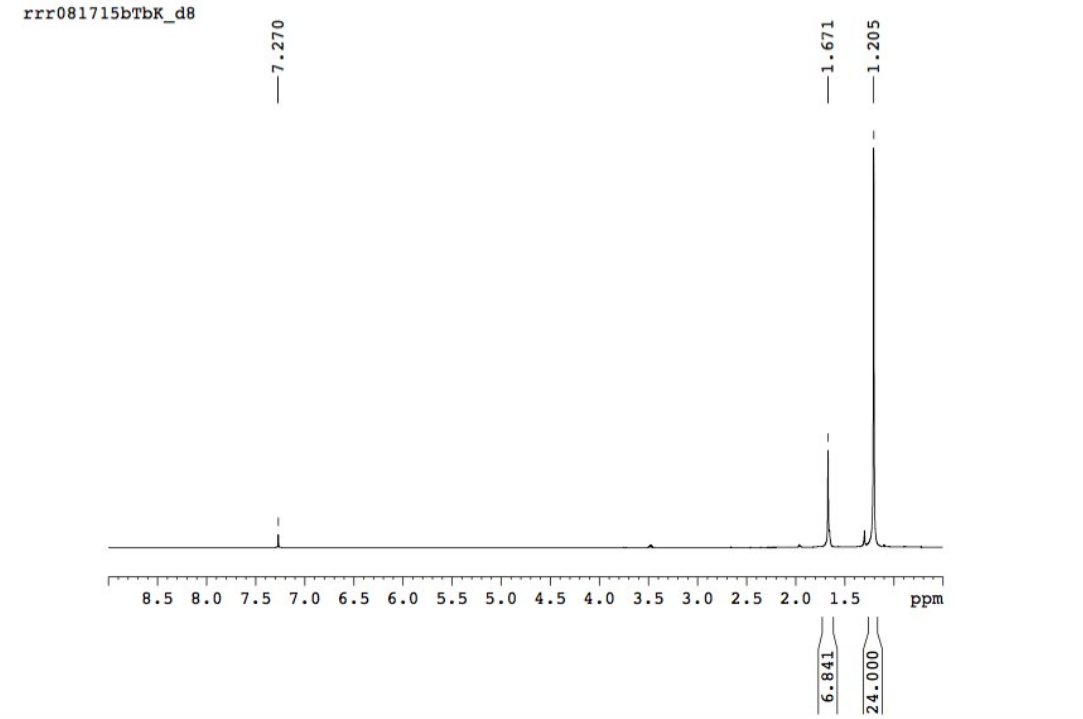

Figure S4. ^{1}H NMR spectrum of 2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^{9}.2^{6}]henicosane-8,8,10,10,19,19,20,20-d8 (diamine-d8) acquired in chloroform-d1.

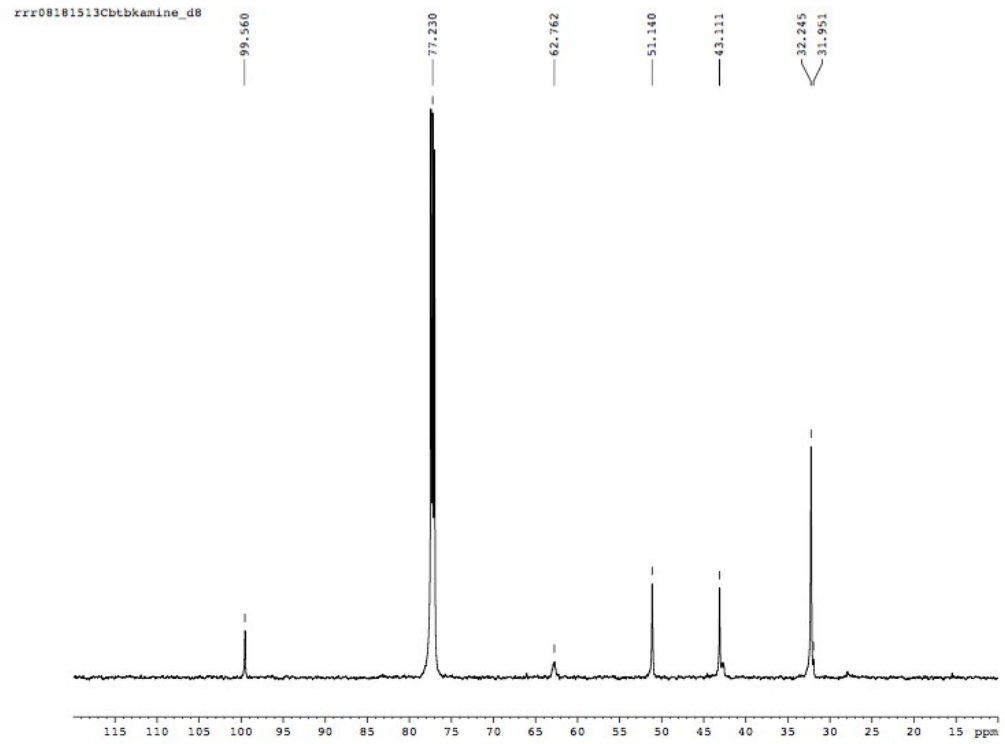

Figure S5. $^{13}C\{^{1}H\}$ NMR NMR spectrum of 2,2,4,4,14,14,16,16-octamethyl-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^{9}.2^{6}]henicosane-8,8,10,10,19,19,20,20-d8 (diamine-d8) acquired in chloroform-d1. Note the broad signal at 62.76 resulting from CD_2 groups.

Synthesis of 2,2,4,4,14,14,16,16-octakis(methyl-d3)-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^{9}.2^{6}]henicosane-1,1,5,5,13,13,17,17-d8 (diamine-d32).
Pentaerythritol (0.197 g, 1.45 mmol), 4-oxo-2,2,6,6-tetramethylpiperidine-d17 (0.500 g, 2.90 mmol) and *p*-toluenesulfonic acid (0.662 g, 3.48 mmol) were mixed together in toluene (15 mL) following the procedure described for the unlabeled or partially labeled diamine described above to afford 0.489 g (1.10 mmol, 76%) of diamine-d32. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.76 (s, 8 H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 99.62, 63.57, 50.62, 43.00, 42.60, 32.62, 31.15 (br). IR (KBr, cm^{-1}): ν 3553, 3499, 2949, 2870, 2253, 2214, 2123, 2061, 1652, 1473, 1381, 1351, 1261, 1194, 1166, 1086, 1067, 907. Mp. 114-116 °C. ESI-MS: m/z Calcd. for $C_{23}H_{10}D_{32}N_2O_4$ $[M+H]^+$: 442.79; Found: 439.4974. The experimentally measured molecular mass distribution (see MS in Figure S9 below) indicates there is a small amount of proton exchange occurring and a fraction of the diamine-d32 contains a decreased level of deuteration. This proton exchange occurs at the acidic methylene position of the TEMPO moiety via the enolization of 4-oxo-2,2,6,6-tetramethylpiperidine-d17, and this position provides a small signal in the ^{1}H NMR spectrum.

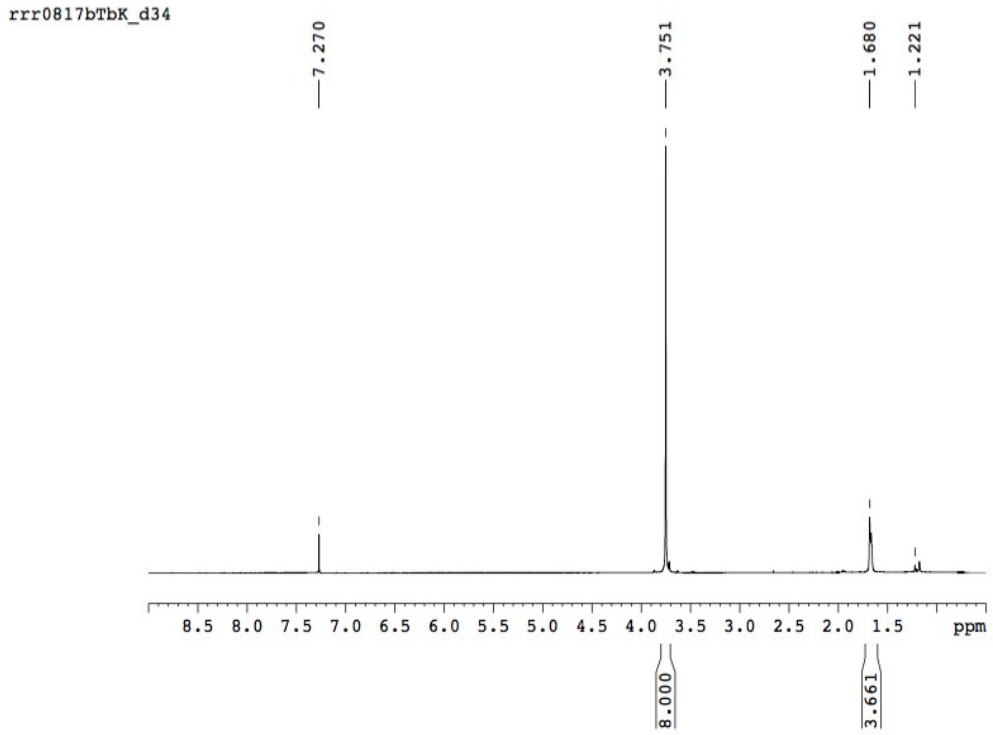

Figure S6. ^{1}H NMR spectrum of 2,2,4,4,14,14,16,16-octakis(methyl-d3)-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^{9}.2^{6}]henicosane-1,1,5,5,13,13,17,17-d8 (diamine-d32) acquired in chloroform-d1. The signal at 1.680 ppm is further evidence for the exchange of protons occurring at the methylene position of the TEMPO group.

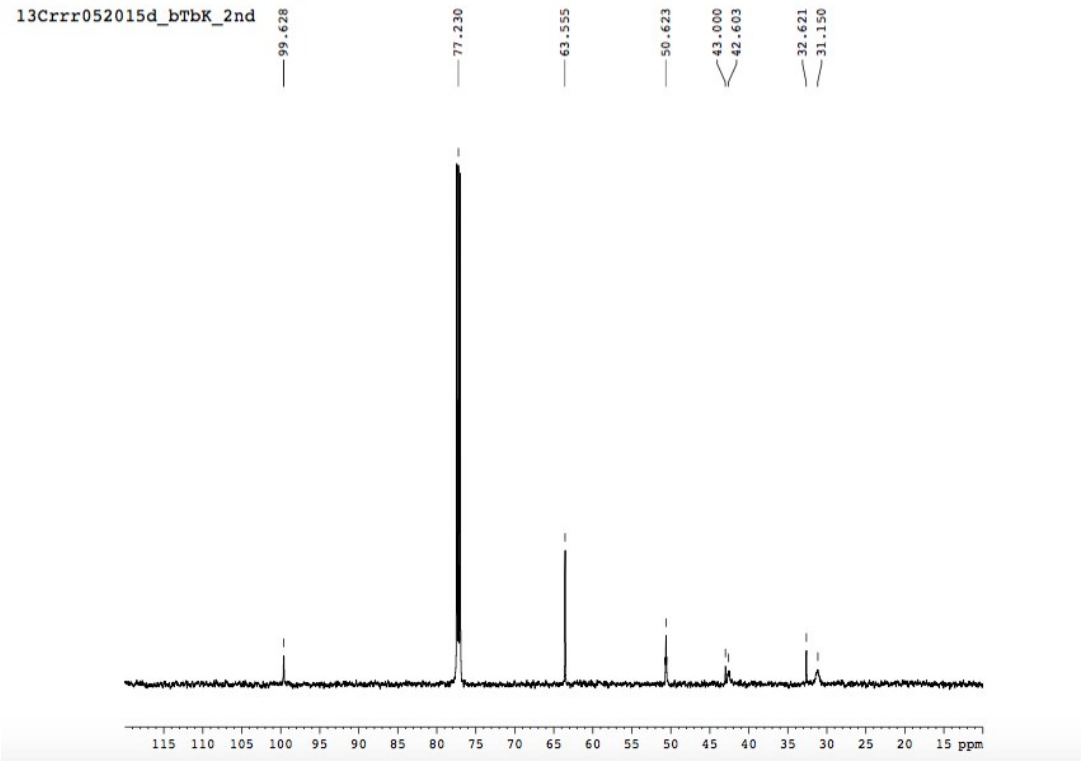

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of 2,2,4,4,14,14,16,16-octakis(methyl-d3)-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^{9}.2^{6}]henicosane-1,1,5,5,13,13,17,17-d8 (diamine-d32) acquired in chloroform-d1. Note the broadened and lower intensity of signals at 31.15 (CD_3) and 42.60 (CD_2) in comparison to their unlabeled isotopomers.

Synthesis of 2,2,4,4,14,14,16,16-octakis(methyl-d3)-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^{9}.2^{6}]henicosane-1,1,5,5,8,8,10,10,13,13,17,17,19,19,20,20-d16 (diamine-d40).

Pentaerythritol-d12 (0.107 g, 0.72 mmol), 4-oxo-2,2,6,6-tetramethylpiperidine-d17 (0.250 g, 1.45 mmol), and *p*-toluenesulfonic acid (0.360 g, 1.89 mmol) were allowed to react following the procedure described above to provide tan colored crystals of diamine-d40 (0.127 g, 0.28 mmol, 39%). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 99.48, 62.69 (br), 50.59, 42.98, 42.58 (br), 31.89, 31.16 (br). IR (KBr, cm^{-1}): ν 3551, 3497, 2961, 2927, 2850, 2214, 2096, 2070, 1654, 1472, 1454, 1349, 1316, 1286, 1263, 1238, 1196, 1175, 1154, 1103, 1071, 1040, 1024, 950. Mp. 112-115 °C. ESI-MS: m/z Calcd. for $C_{23}H_2D_{40}N_2O_4$ $[M+H]^+$: 450.84; Found: 448.5544. As observed for diamine-d32, the experimentally measured molecular mass indicates there is proton exchange occurring resulting in a decreased level of deuteration.

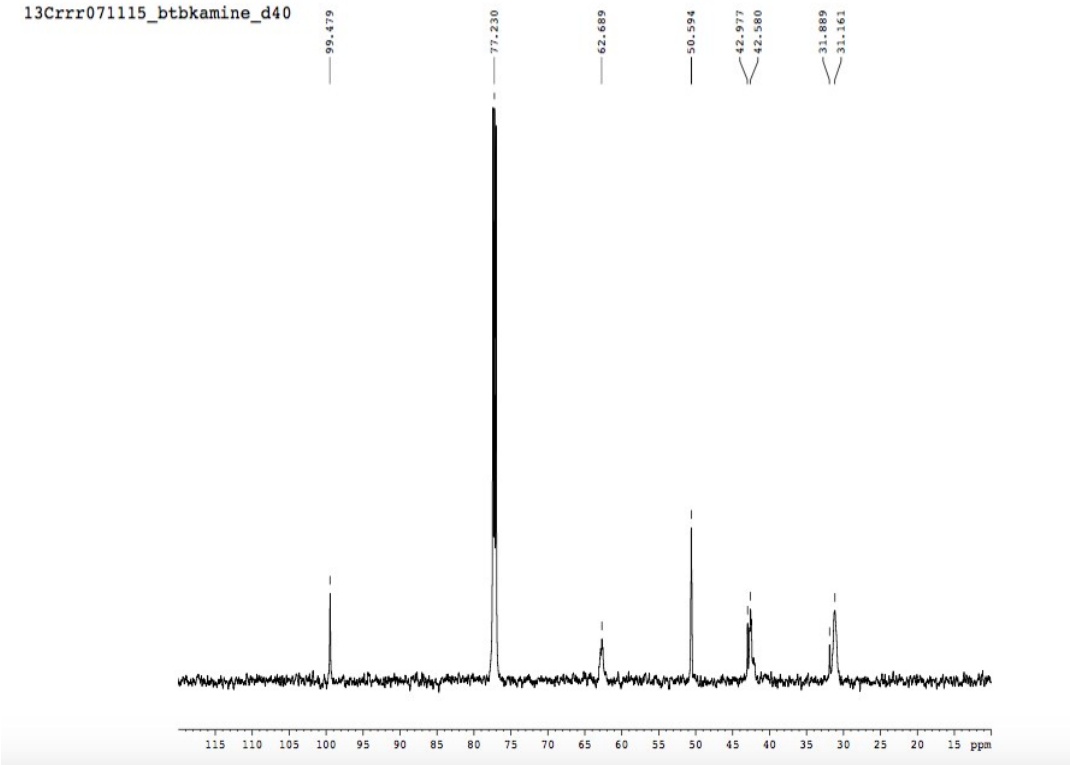

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of 2,2,4,4,14,14,16,16-octakis(methyl-d3)-7,11,18,21-tetraoxa-3,15-diazatrispiro[5.2.2.5^{12}.2^{9}.2^{6}]henicosane-1,1,5,5,8,8,10,10,13,13,17,17,19,19,20,20-d16 (diamine-d40) acquired in chloroform-d1.

Synthesis of bTbK-d0.
A mixture of the diamine-d0 (0.107 g, 0.261 mmol), sodium tungstate dehydrate (0.010 g, 0.030 mmol), and methanol (10 mL) was cooled to 0 °C. Hydrogen peroxide solution (30% in water, 128 μL, 1.28 mmol) was added in a dropwise fashion. The reaction mixture was allowed to warm to room temperature and was stirred for 20 hours. Potassium carbonate (~0.3 g) was added, and the mixture was filtered. The filtrate was dried over magnesium sulfate, the volatiles were evaporated, and the product was purified by silica gel chromatography (hexanes:ethyl acetate = 4:5) to afford bTbK as an orange colored solid (0.076 g, 0.172 mmol, 66%). IR (KBr, cm^{-1}): ν 2976, 2935, 2864, 1471, 1453, 1377, 1344, 1243, 1191, 1167, 1110, 1085, 1024, 1008. Mp. 167-169 °C. ESI-MS: m/z Calcd. for $C_{23}H_{40}N_2O_6^{2\bullet}$ $[M+H]^+$: 441.58; Found: 441.2953.

Synthesis of bTbK-d8.
The procedure described for bTbK-d0 was used with a mixture of the diamine-d8 (0.058 g, 0.138 mmol), sodium tungstate dihydrate (0.023 mg, 0.070 mmol), and methanol (0.9 mL) to afford bTbK-d8 as an orange colored solid (0.031 g, 0.068 mmol, 57%). IR (KBr, cm^{-1}): ν 3566, 3318, 2935, 2870, 2235, 2099, 1728, 1633, 1476, 1363, 1346, 1239, 1195, 1094, 1034, 999. Mp. 174-176 °C. ESI-MS: m/z Calcd. for $C_{23}H_{32}D_8N_2O_6^{2\bullet}$ $[M+H]^+$: 449.63; Found: 450.3528.

Synthesis of bTbK-d32.
The procedure described for bTbK-d0 was used with a mixture of the diamine-d32 (0.100 g, 0.225 mmol), sodium tungstate dihydrate (0.009 mg, 0.027 mmol), and methanol (10 mL) to afford bTbK-d32 as an orange colored solid (0.039 g, 0.082 mmol, 36%). IR (KBr, cm^{-1}): ν 2982, 2933, 2865, 2228, 1462, 1386, 1355, 1252, 1199, 1181, 1168, 1067, 1054. Mp. 163-165 °C. ESI-MS: m/z Calcd. for $C_{23}H_8D_{32}N_2O_6^{2\bullet}$ $[M+H]^+$: 473.78; Found: 469.4709.

Synthesis of bTbK-d40.
The procedure described for bTbK-d0 was used with a mixture of the diamine-d40 (0.050 g, 0.110 mmol), sodium tungstate dihydrate (0.018 mg, 0.055 mmol), and methanol (0.75 mL) to afford bTbK-d40 as an orange colored solid (0.031 g, 0.065 mmol, 59%). IR (KBr, cm^{-1}): ν 3564, 3488, 3317, 2963, 2935, 2241, 2228, 1743, 1353, 1329, 1299, 1261, 1236, 1186, 1139, 1094, 1076, 1042, 1021. Mp. 158-161 °C. ESI-MS: m/z Calcd. for $C_{23}D_{40}N_2O_6^{2\bullet}$ $[M+H]^+$: 481.83; Found: 478.5280.

Synthesis of 4-(2,3-Epoxypropoxy)-2,2,6,6-tetramethyl-1-piperidin-1-oxyl (epoxide-d0).
Epichlorohydrin (2.25 mL, 28.7 mmol), 4-hydroxy-TEMPO (0.250 g, 1.45 mmol) and tetrabutylammonium hydrogen sulfate (0.029 g, 0.085 mmol) were added to a 90% w/w aqueous NaOH solution (0.232 g NaOH/0.263 mL H_2O). The mixture was stirred at 30 °C for 4 hours, at which point the mixture was poured into ice water and the product was extracted with diethyl ether (3 × 10 mL). The organic layer was washed with brine solution, dried over Na_2SO_4, and concentrated in vacuo. The product was purified by silica gel chromatography (hexanes:ethyl acetate = 4:5) to obtain a red oil (0.119 g, 0.521 mmol, 36%). The infrared spectrum of the product matched the literature report.[7] IR (KBr, cm^{-1}): ν 2976, 2938, 2869, 1635, 1465, 1378, 1363, 1245, 1179, 1096. ESI-MS: m/z Calcd. for $C_{12}H_{22}NO_3^{\bullet}$ $[M+H]^+$: 229.16; Found: 229.1676.

Synthesis of 1-(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)oxy-3-(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amino-propan-2-ol (TOTAPol-d0).
Under an inert atmosphere of nitrogen, the epoxide-d0 (0.100 g, 0.438 mmol) and $LiClO_4$ (0.047 g, 0.442 mmol) were dissolved in acetonitrile (0.8 mL). A solution of 4-amino-TEMPO (0.074 g, 0.432 mmol) dissolved in acetonitrile (0.2 mL) was added in a dropwise fashion. The solution was stirred overnight, concentrated, and purified by silica gel chromatography (hexanes:ethyl acetate = 4:5) to obtain a red solid (0.084 g, 0.210 mmol, 49%). The infrared spectrum of the product matched the literature report.[7] IR (KBr, cm^{-1}): ν 3424, 2976, 2938, 2867, 1635, 1466, 1364, 1244, 1179, 1112, 1089. ESI-MS: m/z Calcd. for $C_{21}H_{41}N_3O_4^{2\bullet}$ $[M+H]^+$: 400.32; Found: 400.3169.

Synthesis of 4-(2,3-Epoxypropoxy)-2,2,6,6-tetramethyl-1-piperidin-1-oxyl (epoxide-d22).
Epichlorohydrin-d_5 (1.0 g, 10.3 mmol), 4-hydroxy-TEMPO-d_{17} (0.122 g, 0.644 mmol) and tetrabutylammonium hydrogen sulfate (0.013 g, 0.038 mmol) were added to a 90% w/w aqueous NaOH solution (0.101 g NaOH/0.117 mL H_2O). The mixture was stirred at 30°C for 4 hours, at which point the mixture was poured into ice water and the product

was extracted with diethyl ether (3 × 10 mL). The organic layer was washed with brine solution, dried over Na_2SO_4, and concentrated in vacuo. The product was purified by silica gel chromatography (hexanes:ethyl acetate = 4:5) to obtain a red oil (0.086 g, 0.343 mmol, 53%). ESI-MS: m/z Calcd. for $C_{12}D_{22}NO_3^{\bullet}$ $[M+H]^+$: 251.30; Found: 251.3057.

Synthesis of 1-(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)oxy-3-(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amino-propan-2-ol (TOTAPol-d17).

Under an inert atmosphere of nitrogen, the epoxide-d0 (0.045 g, 0.197 mmol) and $LiClO_4$ (0.021 g, 0.197 mmol) were dissolved in acetonitrile (0.3 mL). A solution of 4-amino-TEMPO-d_{17} (0.038 g, 0.202 mmol) dissolved in acetonitrile (0.1 mL) was added in a dropwise fashion. The solution was stirred overnight, concentrated, and purified by silica gel chromatography (hexanes:ethyl acetate = 4:5) to obtain a red solid (0.018 g, 0.043 mmol, 22%). IR (KBr, cm^{-1}): ν 3435, 2975, 2922, 2851, 2235, 1632, 1467, 1383, 1367, 1261, 1178, 1099, 1054. ESI-MS: m/z Calcd. for $C_{21}H_{24}D_{17}N_3O_4^{2\bullet}$ $[M+H]^+$: 417.42; Found: 417.4241.

Synthesis of 1-(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)oxy-3-(2,2,6,6-tetramethyl-1-oxy-4-piperidinyl)amino-propan-2-ol (TOTAPol-d40).

Under an inert atmosphere of nitrogen, the epoxide-d22 (0.047 g, 0.188 mmol) and $LiClO_4$ (0.020 g, 0.188 mmol) were dissolved in acetonitrile (0.3 mL). A solution of 4-amino-TEMPO-d_{17} (0.035 g, 0.186 mmol) dissolved in acetonitrile (0.5 mL) was added in a dropwise fashion. The solution was stirred overnight, concentrated, and purified by silica gel chromatography (hexanes:ethyl acetate = 4:5) to obtain a red solid (0.042 g, 0.095 mmol, 51%). IR (KBr, cm^{-1}): ν 3437, 2962, 2929, 2768, 2232, 2107, 1735, 1630, 1436, 1368, 1257, 1180, 1109, 1054. ESI-MS: m/z Calcd. for $C_{21}HD_{40}N_3O_4^{2\bullet}$ $[M+H]^+$: 440.82; Found: 439.5619.

Mass Spectrometry:

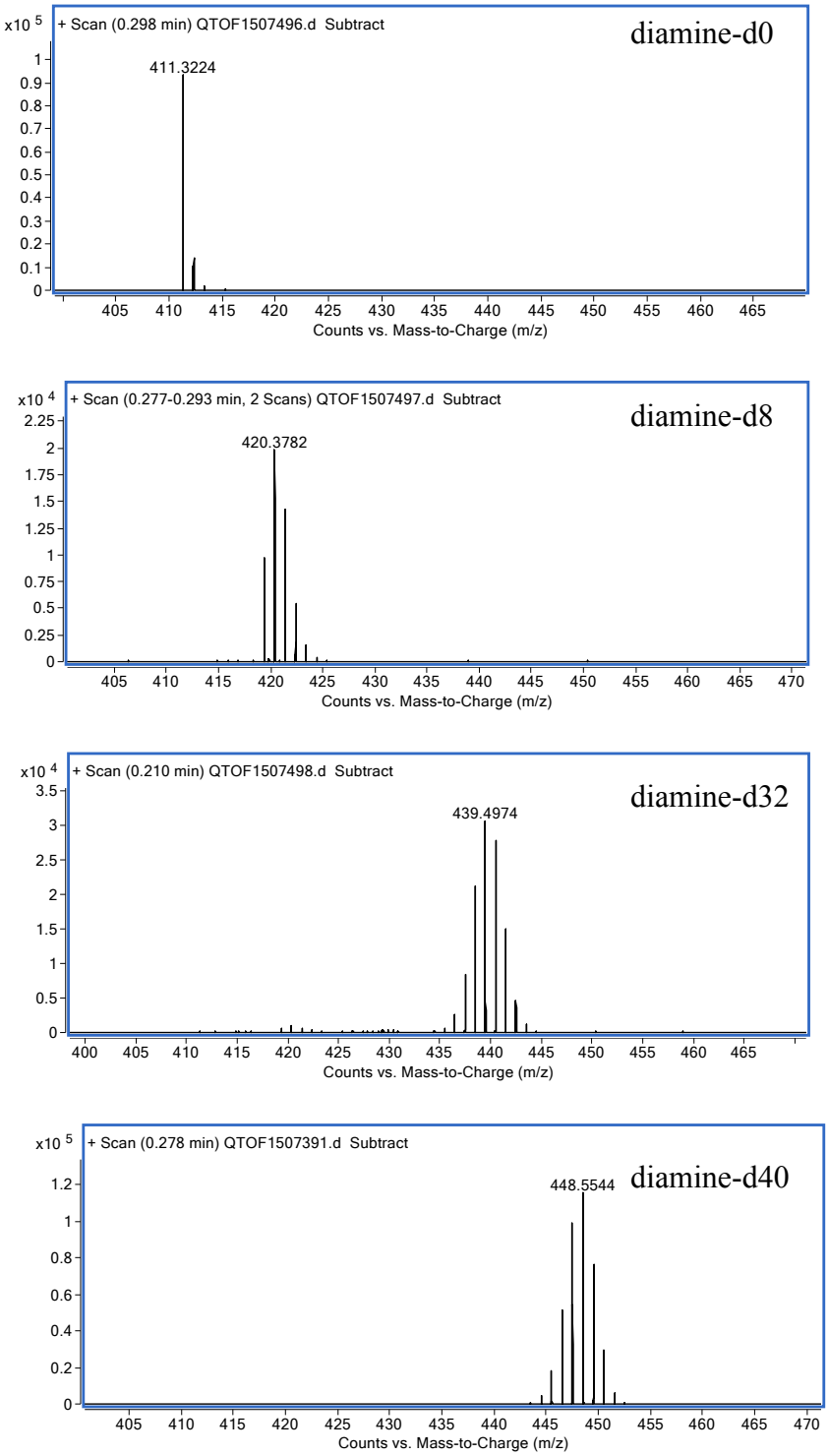

Figure S9. Molecular mass region of the mass spectra for the various diamines.

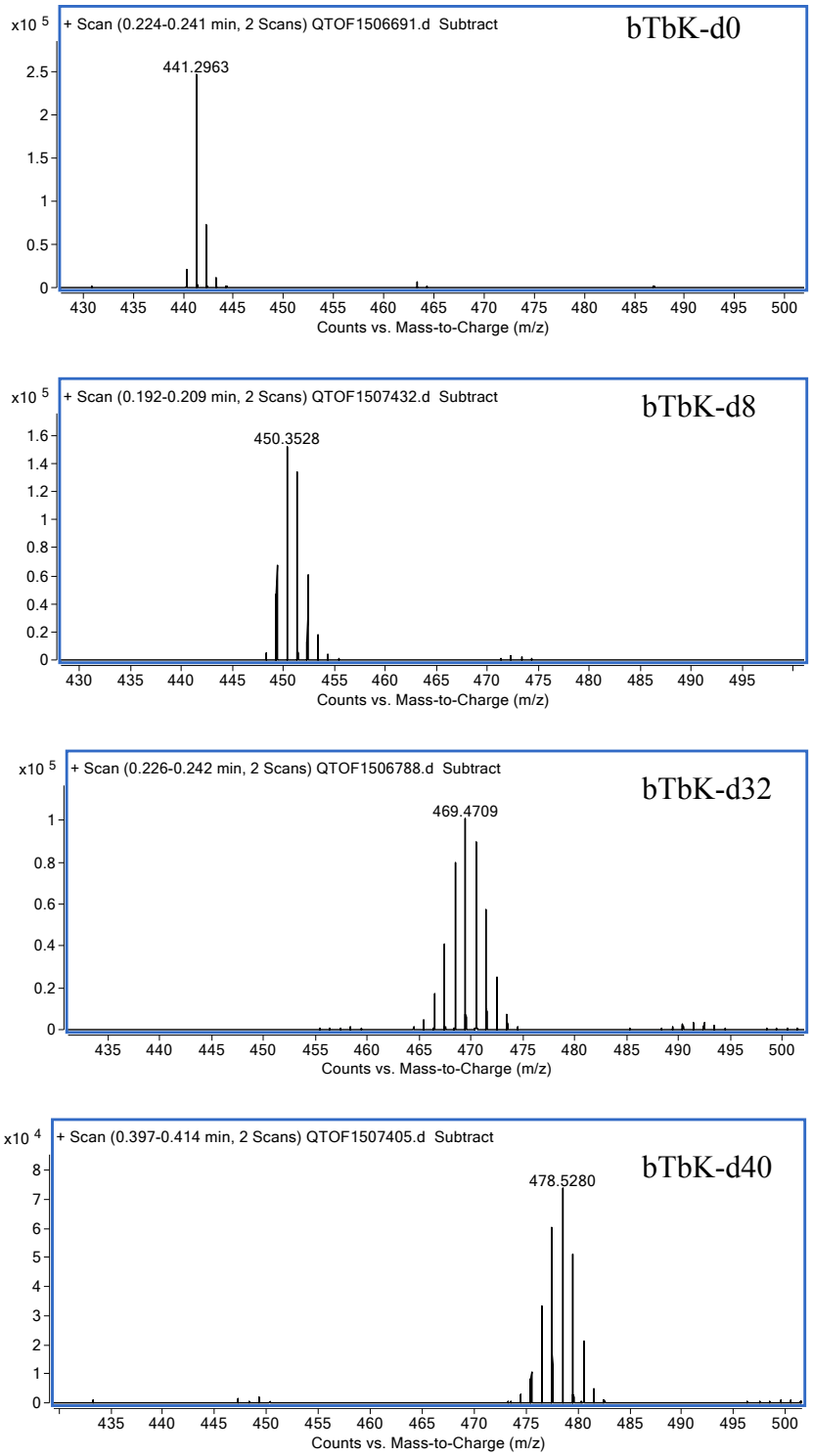

Figure S10. Molecular mass region of the mass spectra for the various bTbK samples.

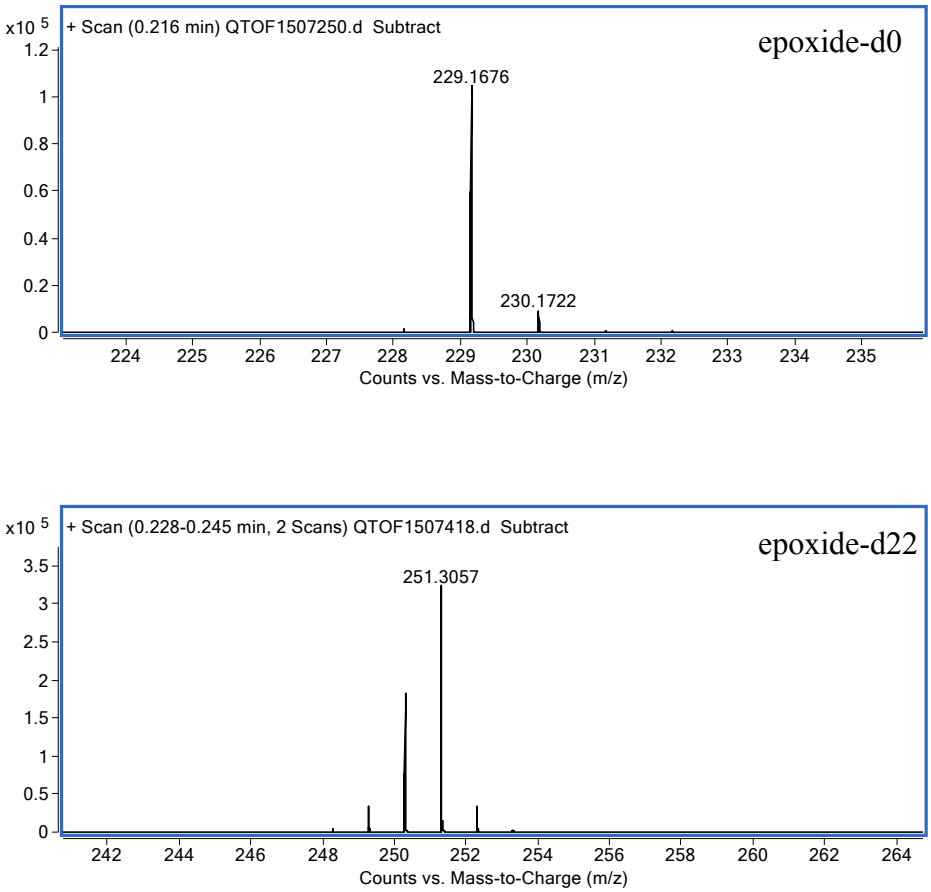

Figure S11. Molecular mass region of the mass spectra for the various epoxides.

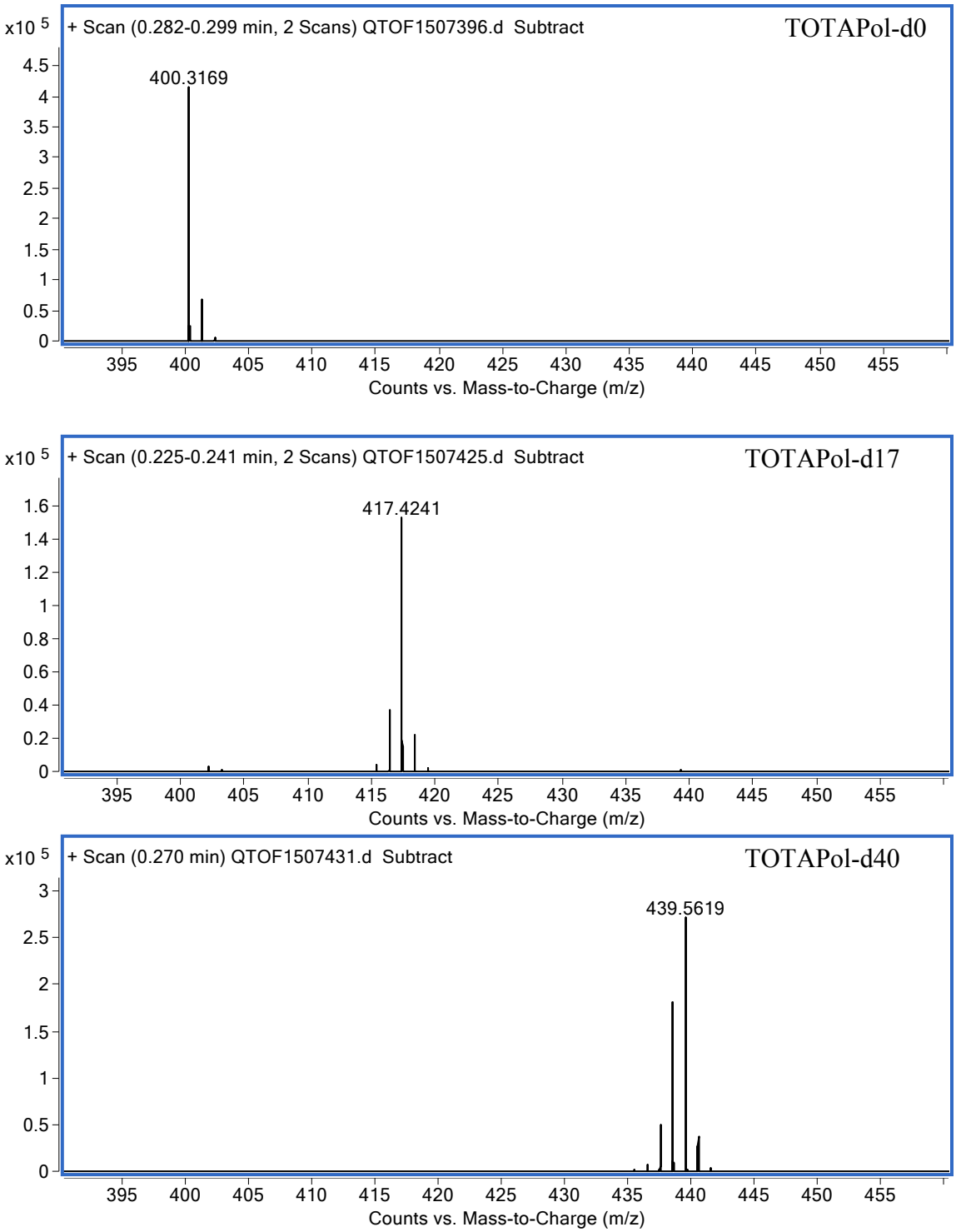

Figure S12. Molecular mass region of the mass spectra for the various TOTAPol samples.

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