

Supplementary Information

Solid-phase synthesis of selectively mono-fluorobenz(o)ylated polyamines towards the development of radiotracers for tumor imaging

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Figure S1: ESI(+) mass spectrum after reduction of N^1 -Boc-3-oxospermidine

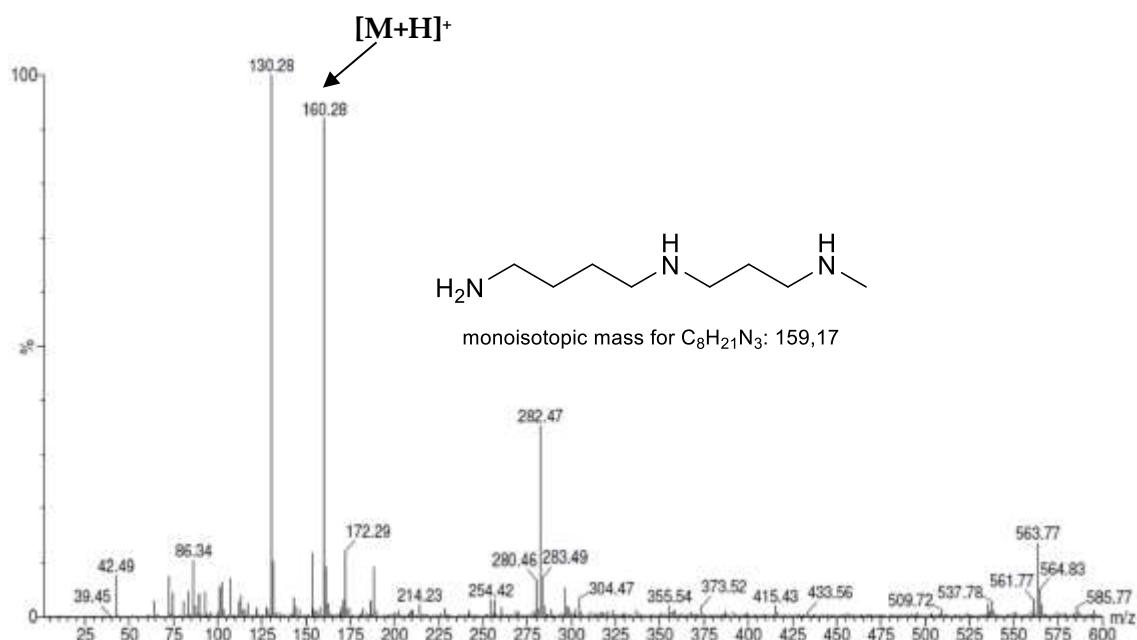


Figure S2: ESI(+) mass spectrum after fluorobenzoylation to N^1 -Dde- N^4 -FBz-spermidine

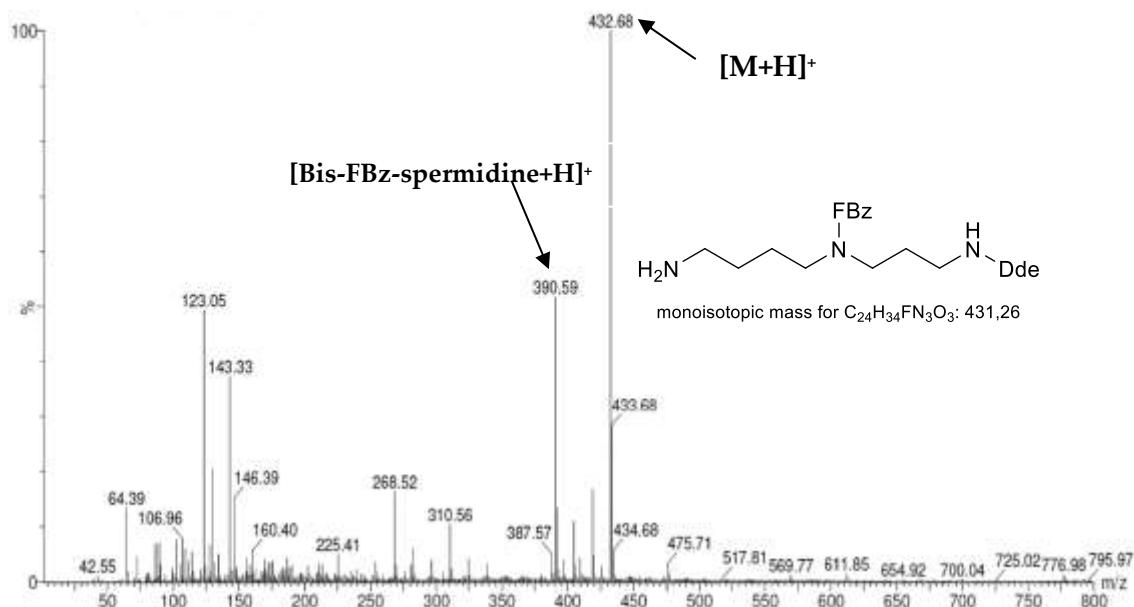
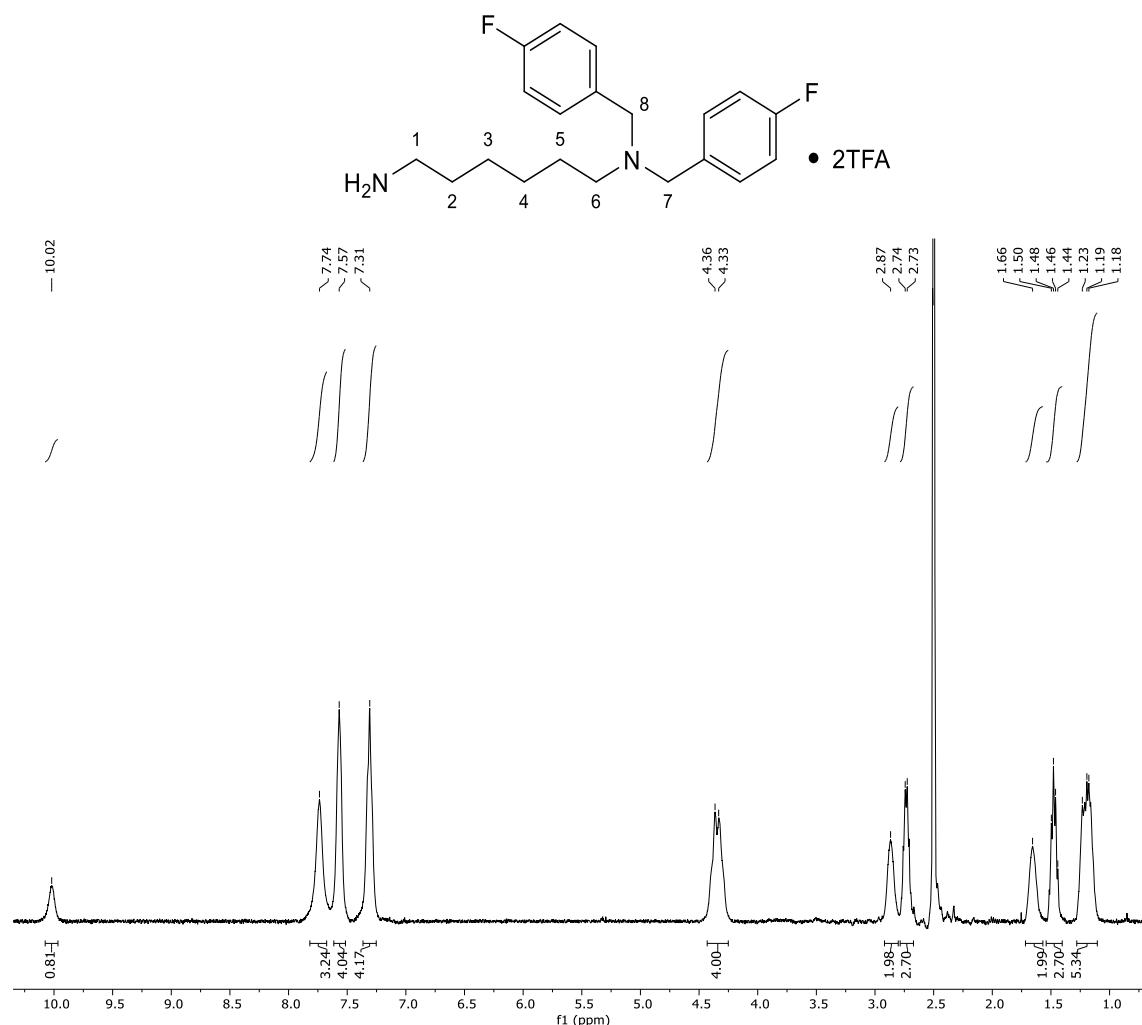


Figure S3: ^1H NMR spectrum of N^1,N^1 -di(4-fluorobenzoyl)-1,6-diaminohexane \times TFA (side product formed during reductive fluorobenzylation)



yield: 19 mg colorless oil

MS (ESI+): m/z=332.97 ($[\text{M}+\text{H}]^+$)

M (monoisotopic) calculated for $\text{C}_{20}\text{H}_{26}\text{F}_2\text{N}_2$: 332.20

^1H NMR (400 MHz, DMSO- d_6) δ =10.02 (s, 1H, NH^+), 7.74 (s, 3H, NH_3^+), 7.57 (s, 4H, H-2,6, FBn), 7.31 (s, 4H, H-3,5 FBn), 4.35 ($^3J = 12.3$ Hz, 4H, H-7/8), 2.87 (s, 2H), 2.73 (d, $^3J = 6.9$ Hz, 2H), 1.66 (s, 2H), 1.53 – 1.42 (m, 2H), 1.28 – 1.10 (m, 4H).

Figure S4: ^1H NMR spectrum of *N*-(4-fluorobenzoyl)-putrescine×TFA (**1**)

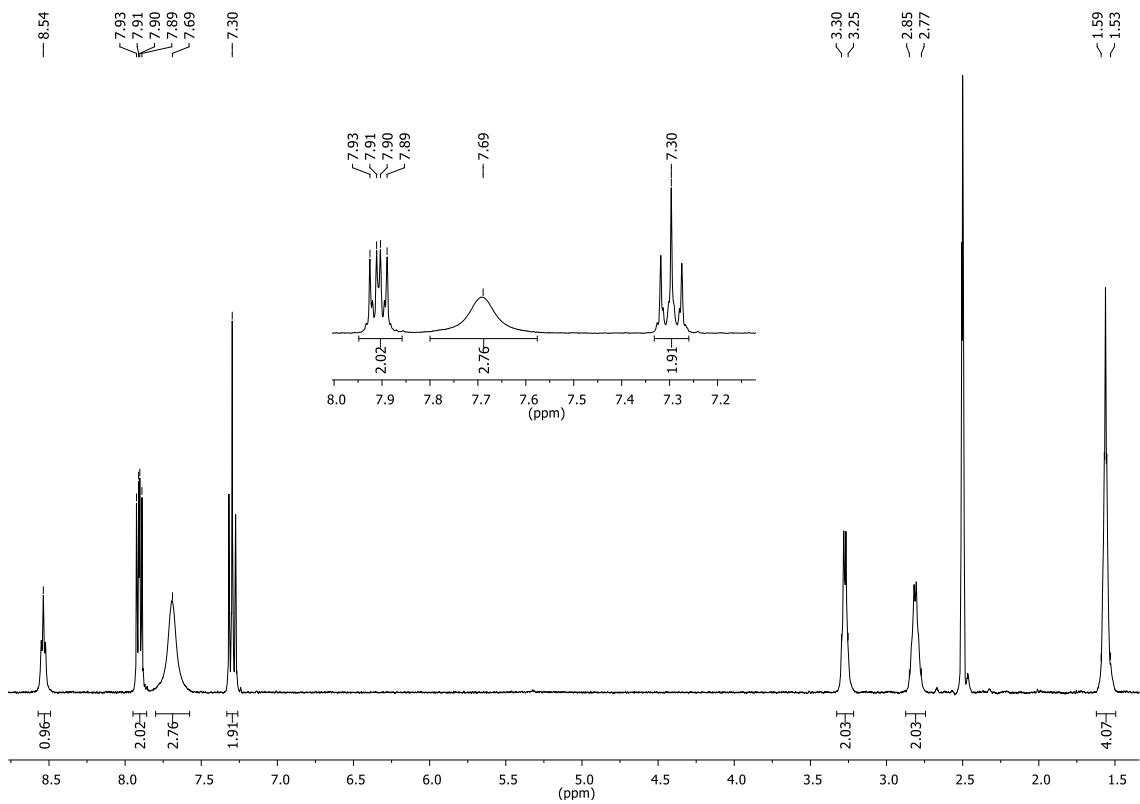


Figure S5: ^{13}C NMR spectrum of *N*-(4-fluorobenzoyl)-putrescine \times TFA (**1**)

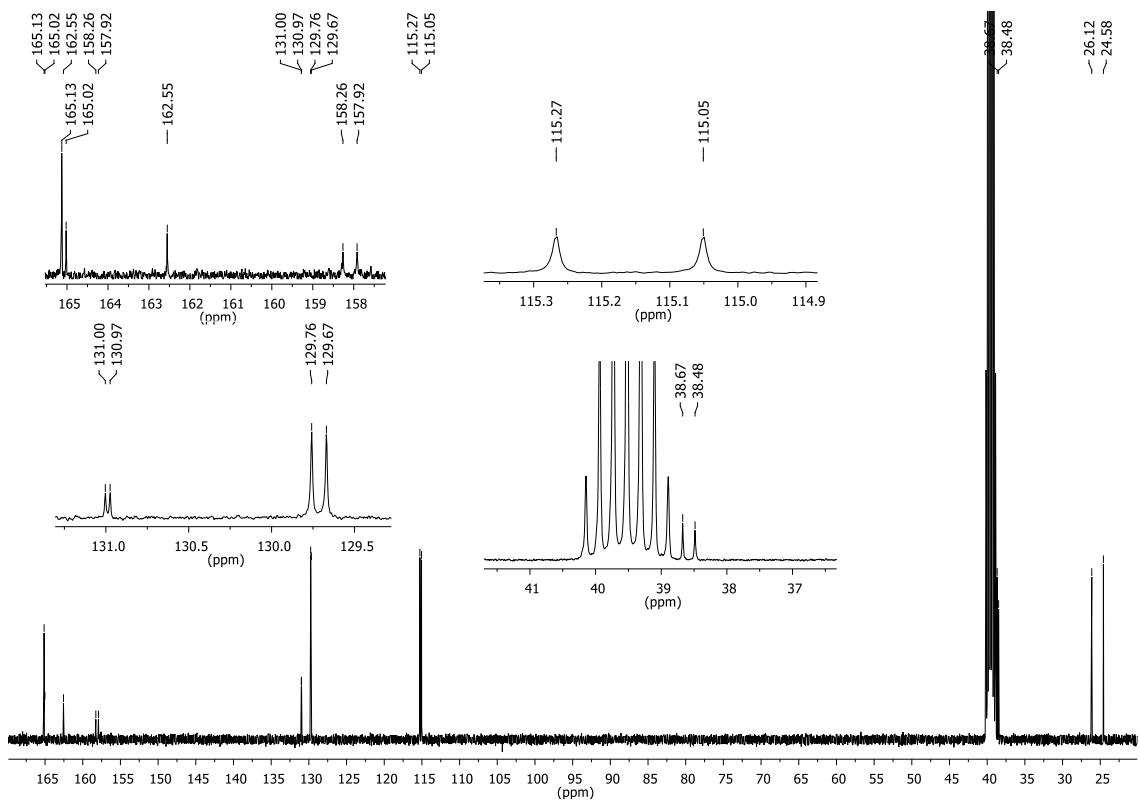


Figure S6: ^1H NMR spectrum of N-(4-fluorobenzoyl)-cadaverine×TFA (2)

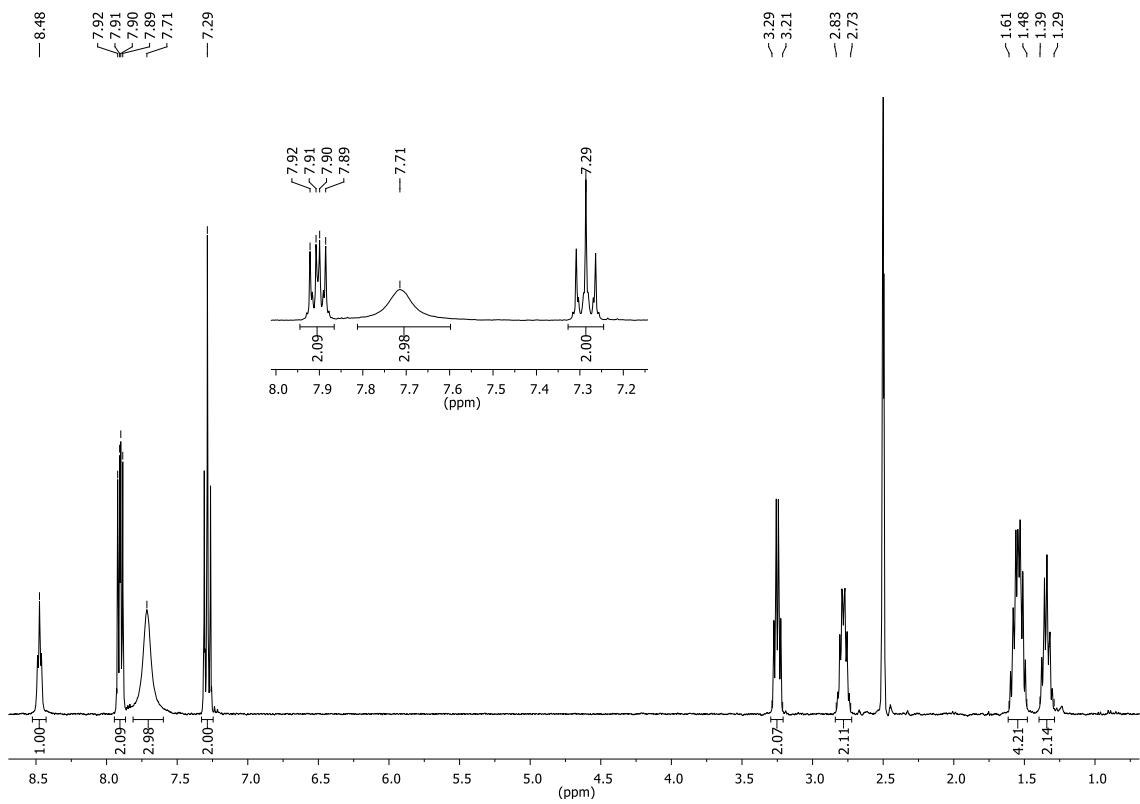


Figure S7: ^{13}C NMR spectrum of *N*-(4-fluorobenzoyl)-cadaverine×TFA (**2**)

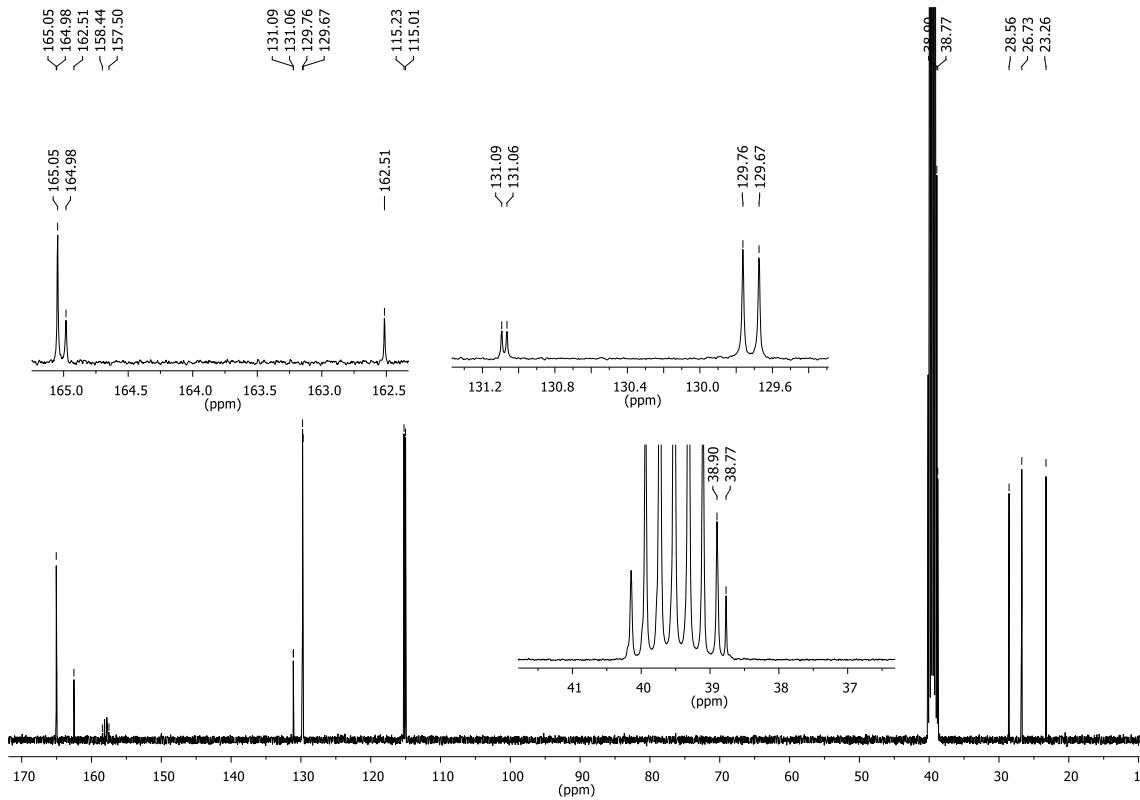


Figure S8: ^1H NMR spectrum of N^1 -(4-fluorobenzoyl)-1,6-diaminohexane×TFA (**3**)

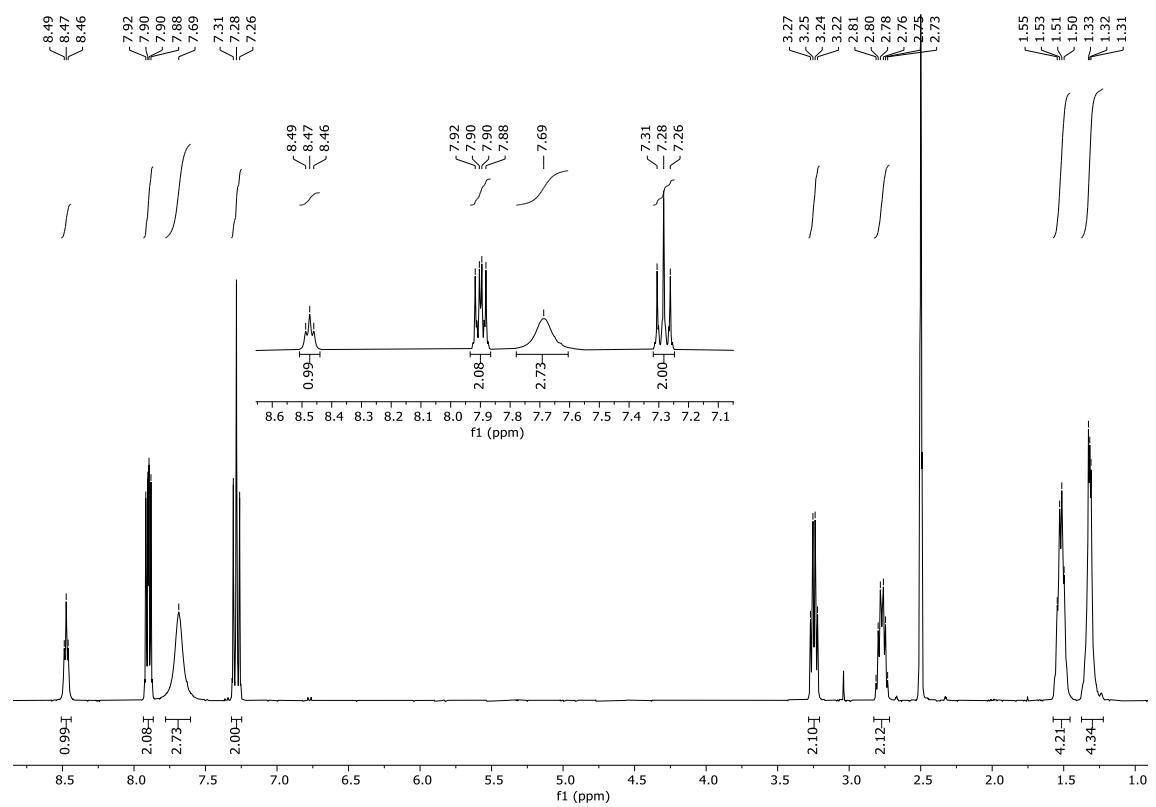


Figure S9: ^{13}C NMR spectrum of N^1 -(4-fluorobenzoyl)-1,6-diaminohexane×TFA (**3**)

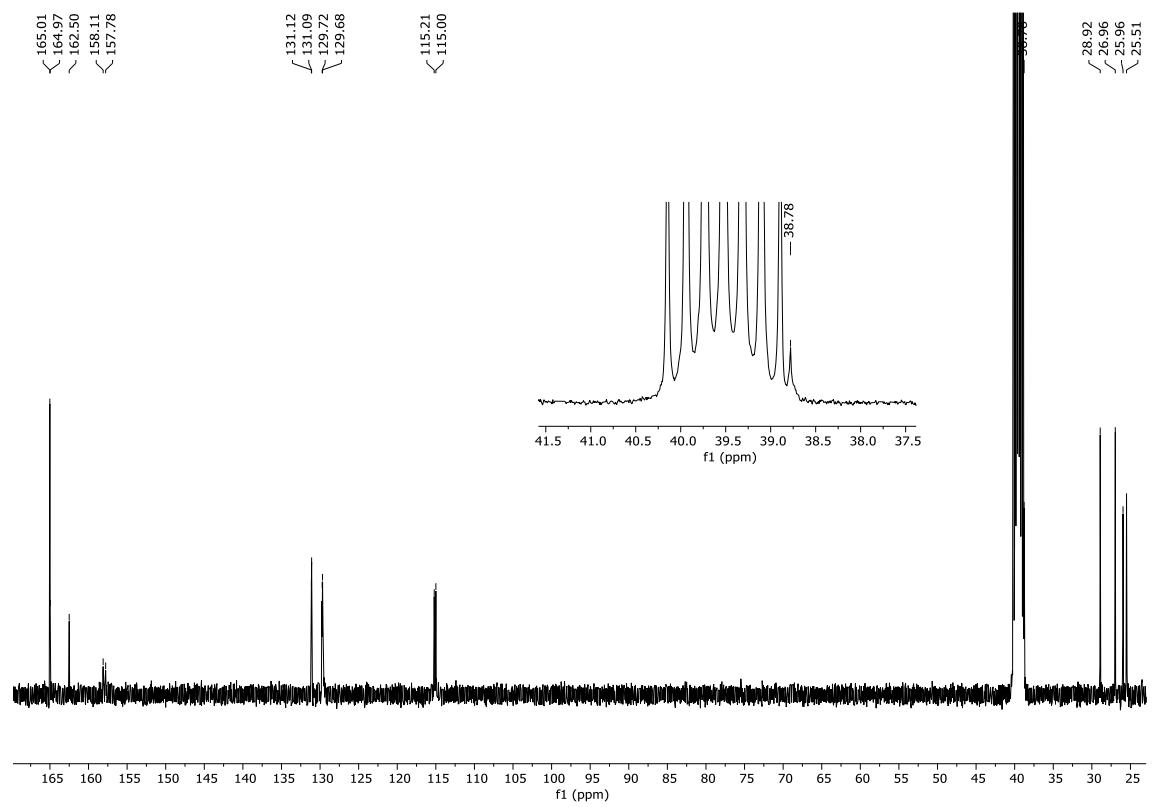


Figure S10: ^1H NMR spectrum of N^1 -(4-fluorobenzoyl)-1,7-diaminoheptane×TFA (**4**)

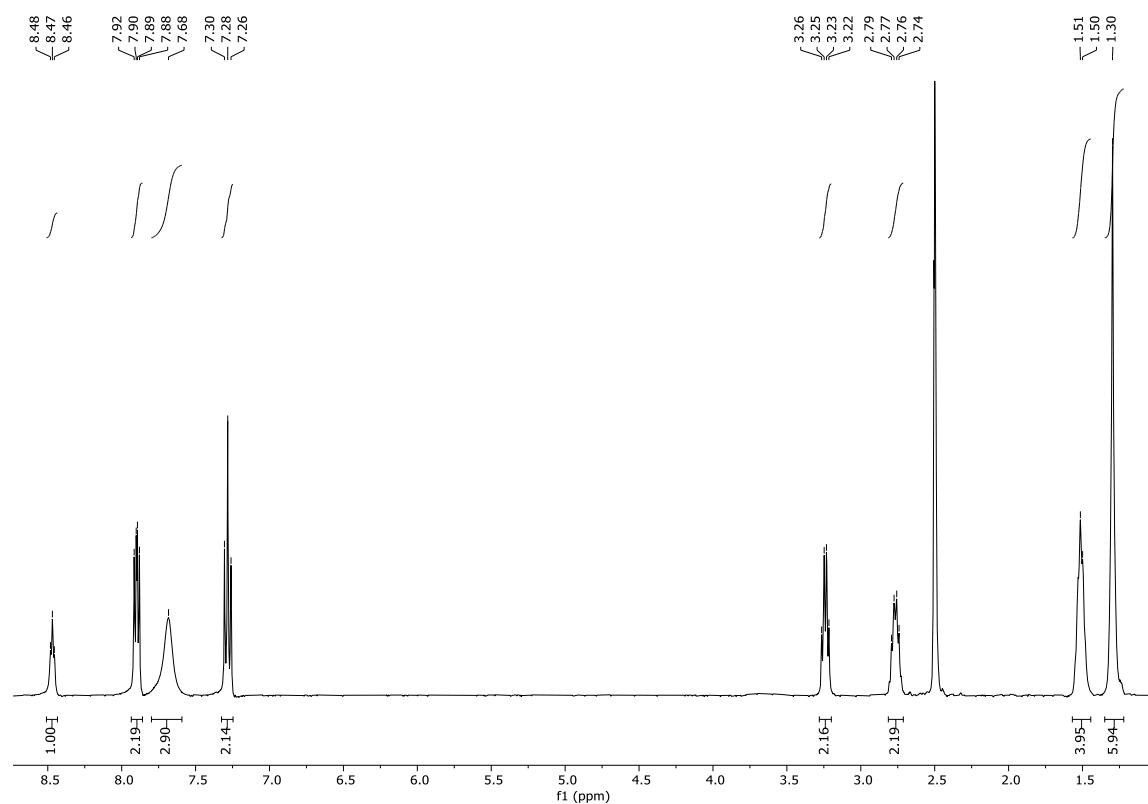


Figure S11: ^{13}C NMR spectrum of N^1 -(4-fluorobenzoyl)-1,7-diaminoheptane×TFA (**4**)

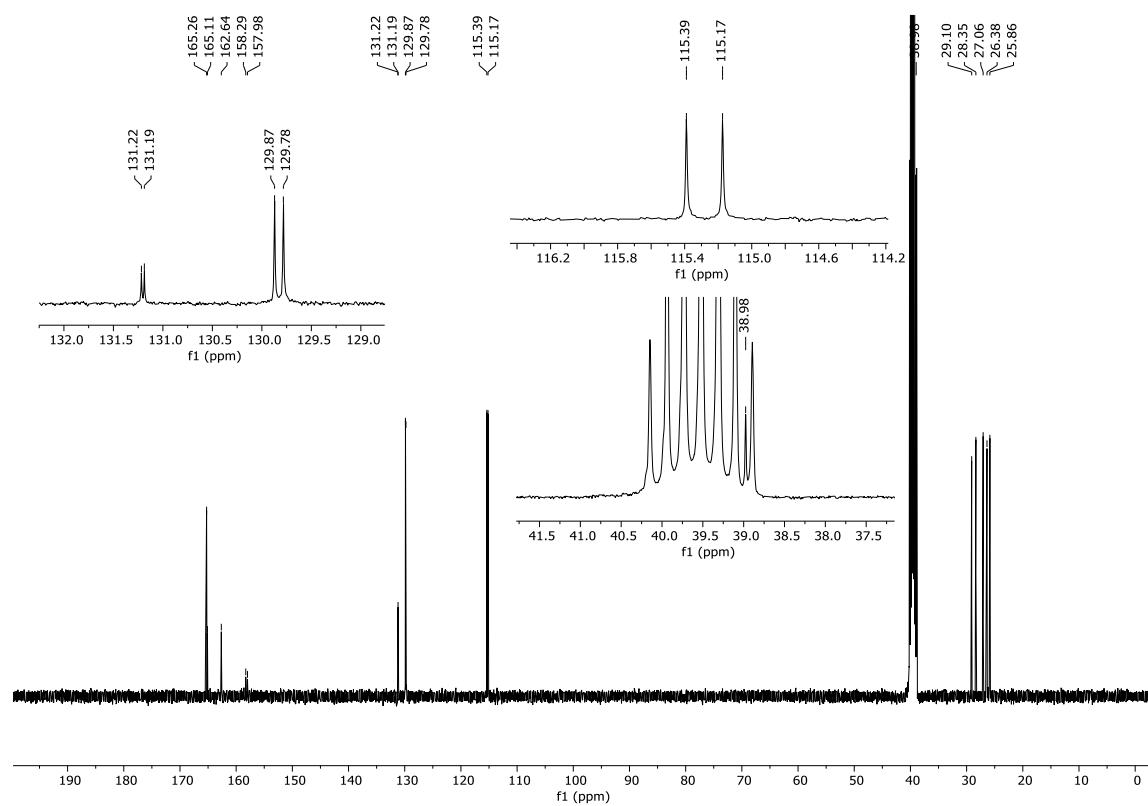


Figure S12: ^1H NMR spectrum of N^1 -(4-fluorobenzoyl)-1,8-diaminoctane×TFA (**5**)

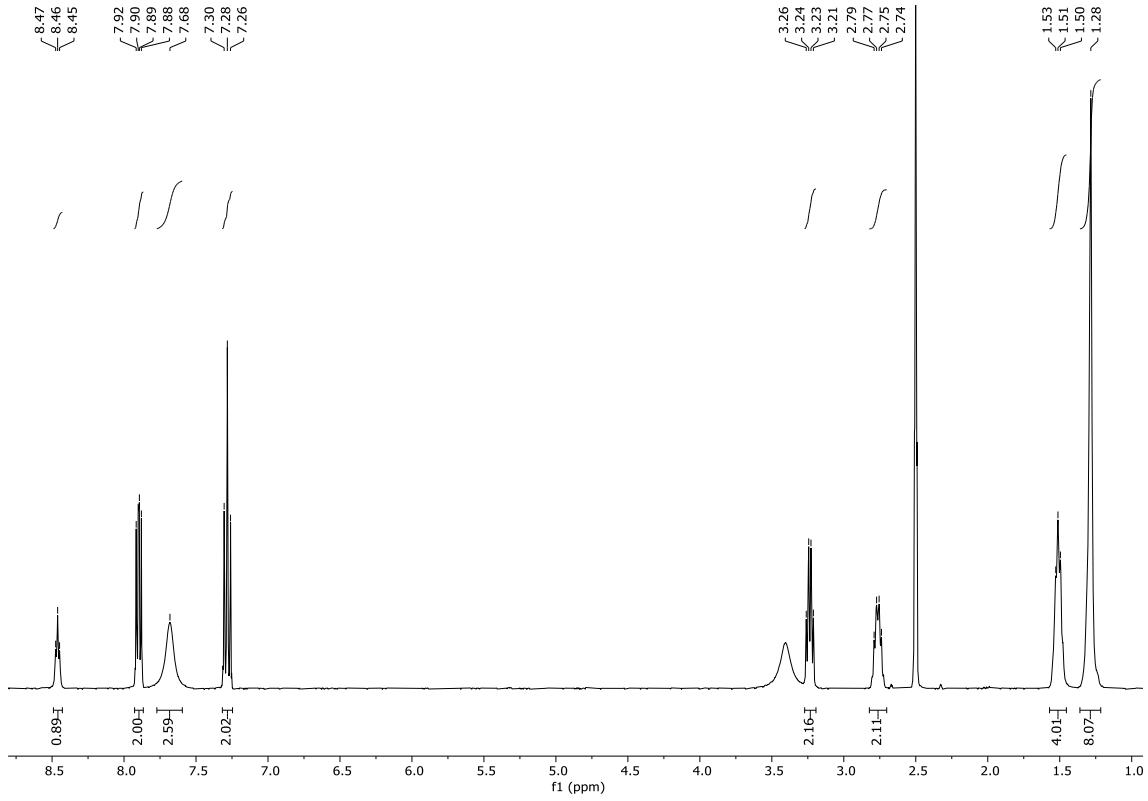


Figure S13: ^{13}C NMR spectrum of N^1 -(4-fluorobenzoyl)-1,8-diaminoctane×TFA (5)

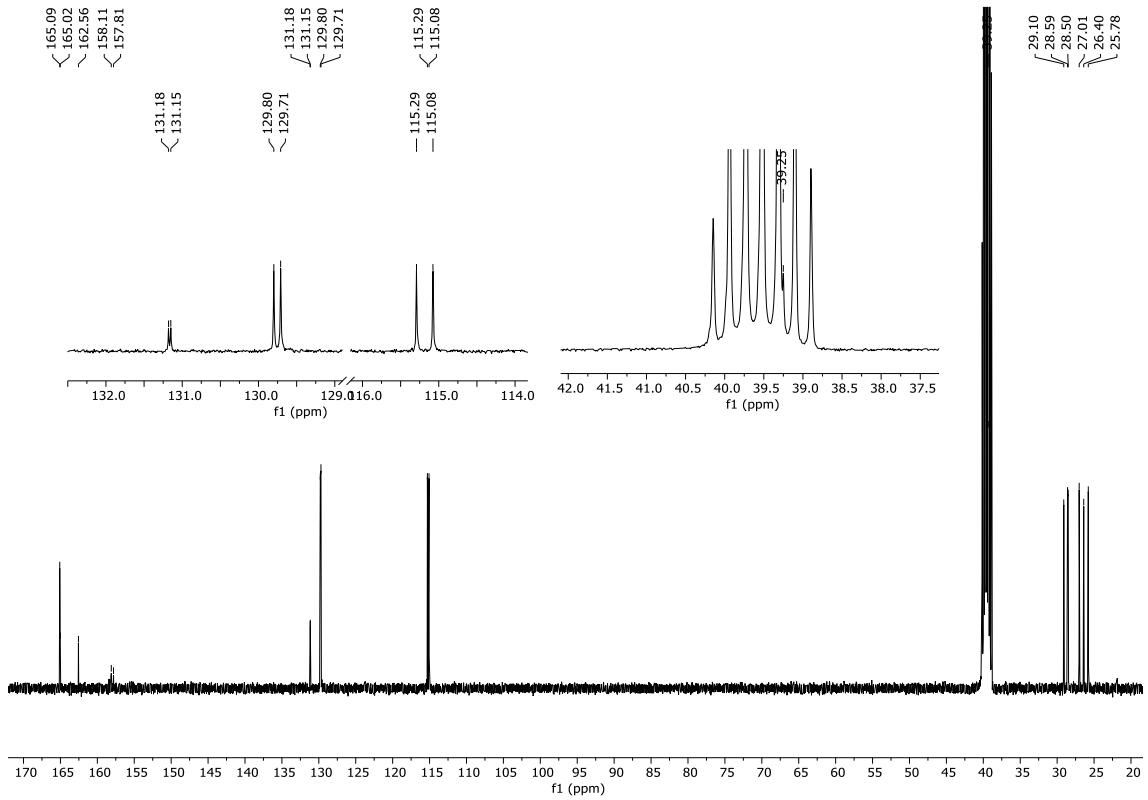


Figure S14: ^1H NMR spectrum of N^1 -(4-fluorobenzoyl)-3-oxospermidine×TFA (**6**)

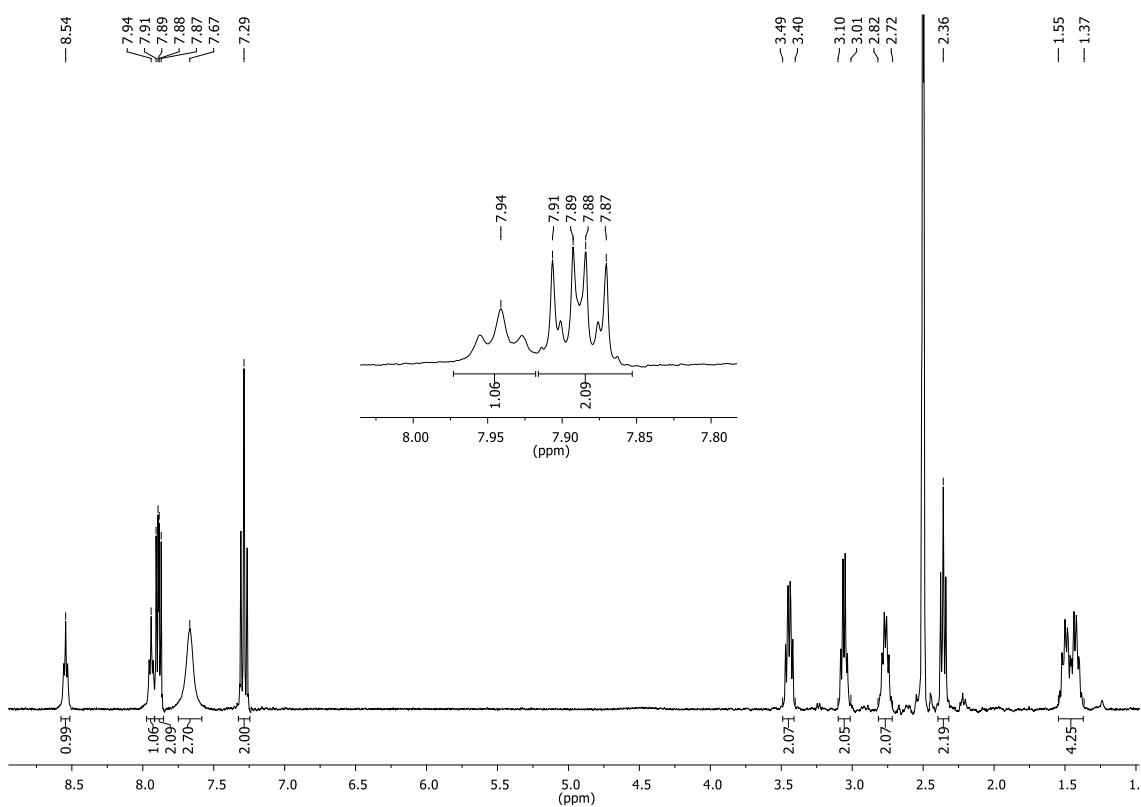


Figure S15: ^{13}C NMR spectrum of N^1 -(4-fluorobenzoyl)-3-oxospermidine×TFA (**6**)

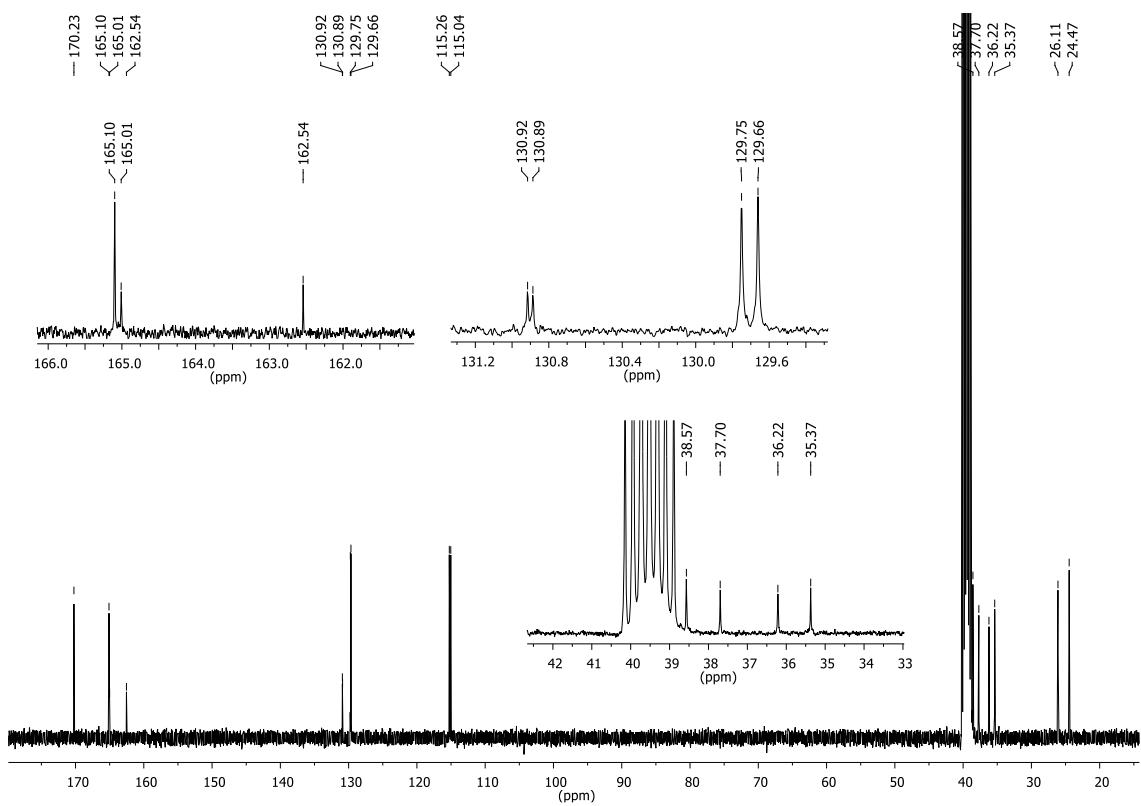


Figure S16: ^1H NMR spectrum of N^8 -(4-fluorobenzoyl)-5-oxospermidine×TFA (7)

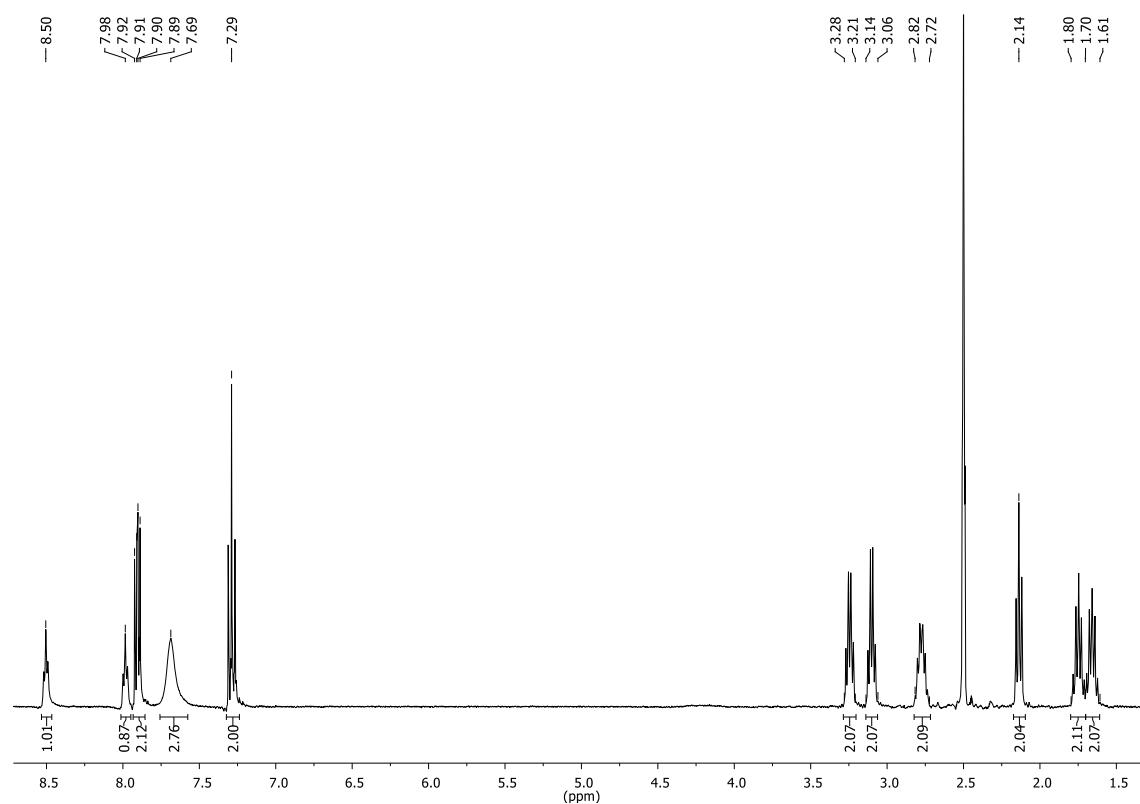


Figure S17: ^{13}C NMR spectrum of N^8 -(4-fluorobenzoyl)-5-oxospermidine×TFA (7)

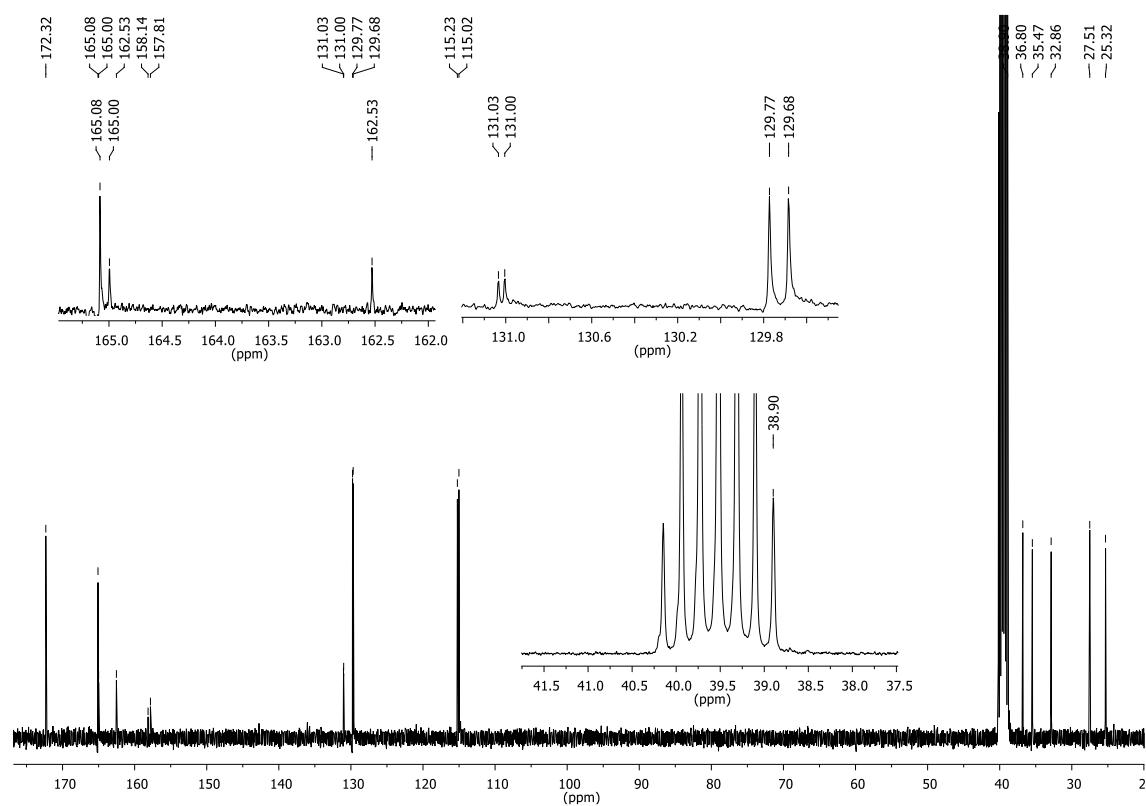


Figure S18: ^1H NMR spectrum of N^1 -(4-fluorobenzoyl)-3,8-dioxospermidine \times TFA (8)

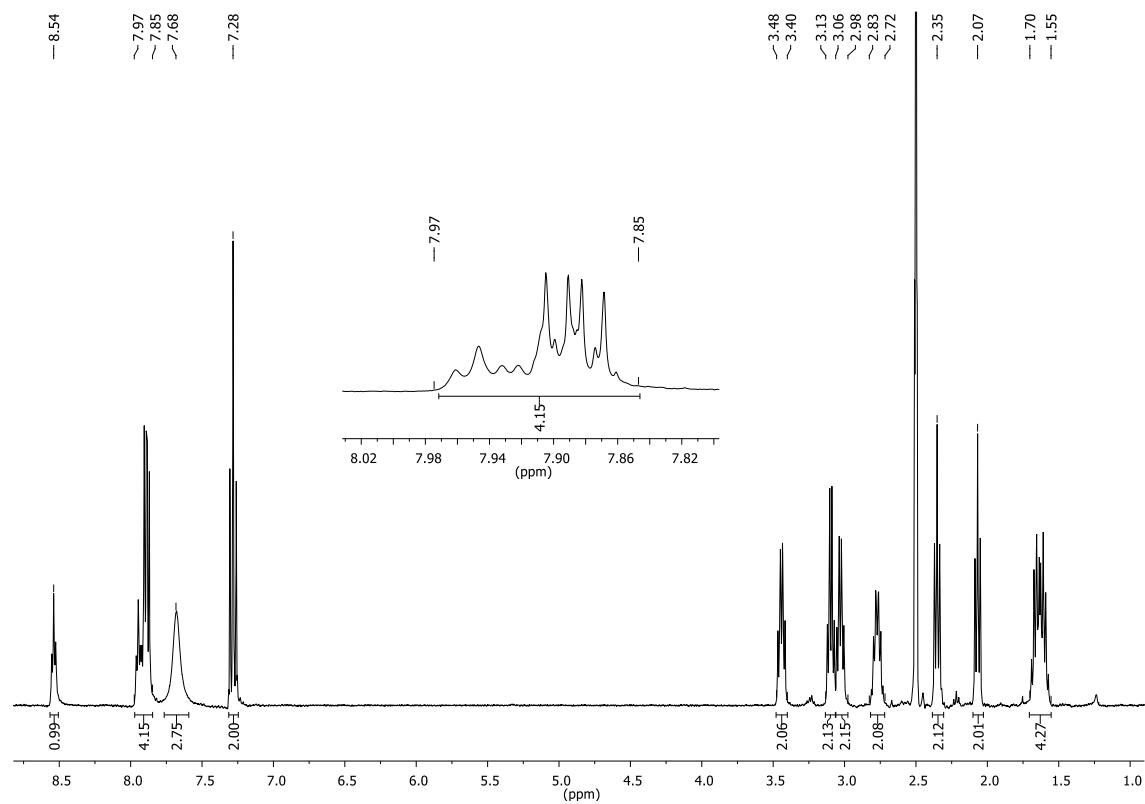


Figure S19: ^{13}C NMR spectrum of N^1 -(4-fluorobenzoyl)-3,8-dioxospermidine \times TFA (8)

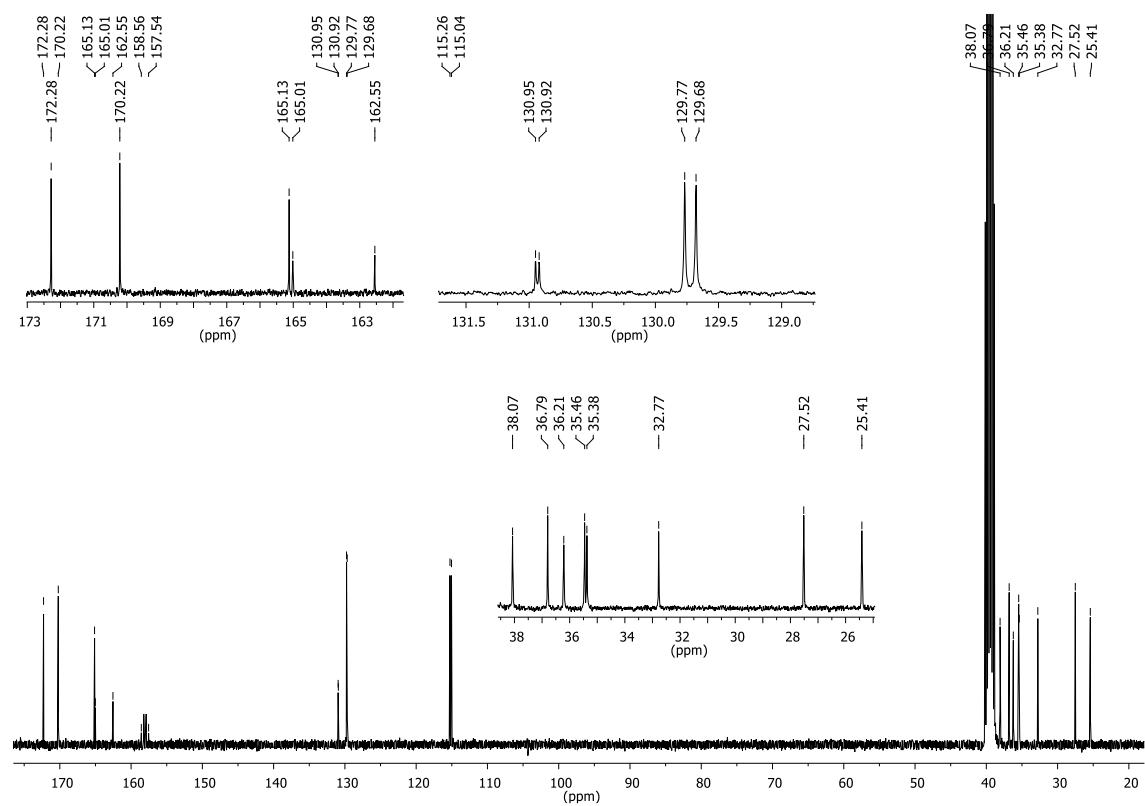


Figure S20: ^1H NMR spectrum of N^1 -(4-fluorobenzoyl)-spermidine \times 2TFA (**9**)

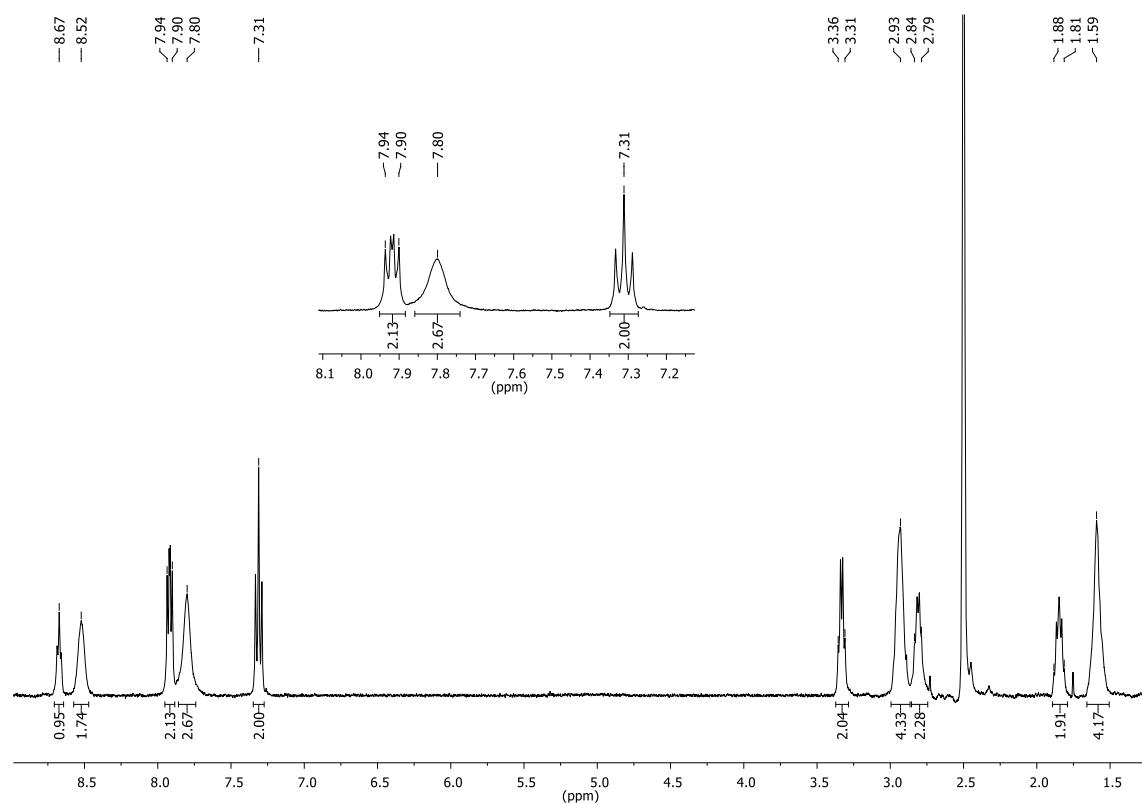


Figure S21: ^{13}C NMR spectrum of N^1 -(4-fluorobenzoyl)-spermidine \times 2TFA (**9**)

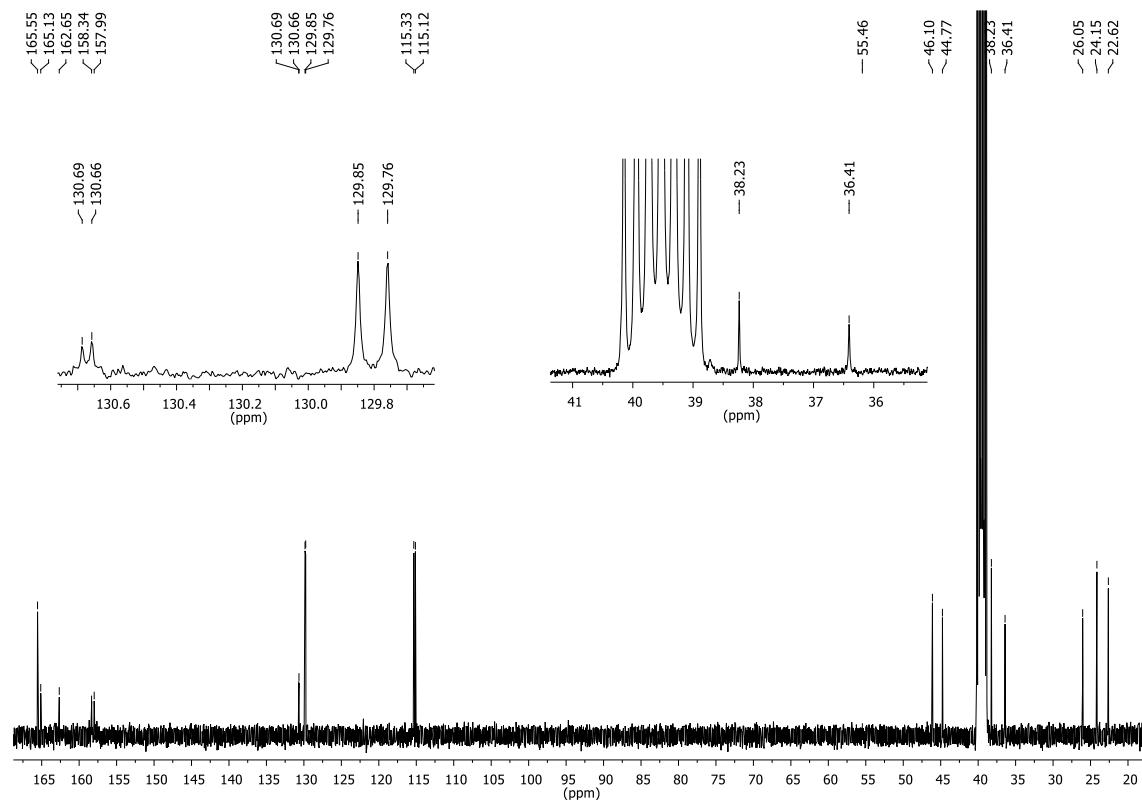


Figure S22: ^1H NMR spectrum of N^4 -(4-fluorobenzoyl)-spermidine \times 2TFA (**10**)

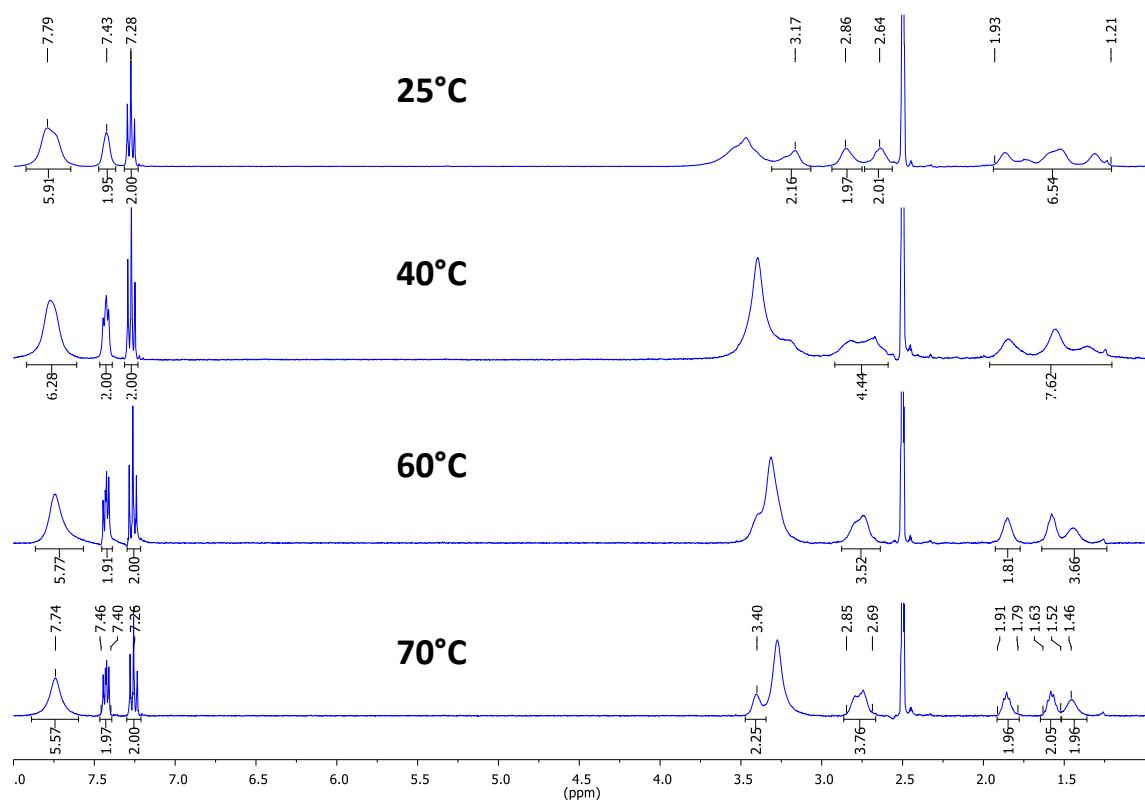


Figure S23: ^{13}C NMR spectrum of N^4 -(4-fluorobenzoyl)-spermidine \times 2TFA (**10**)

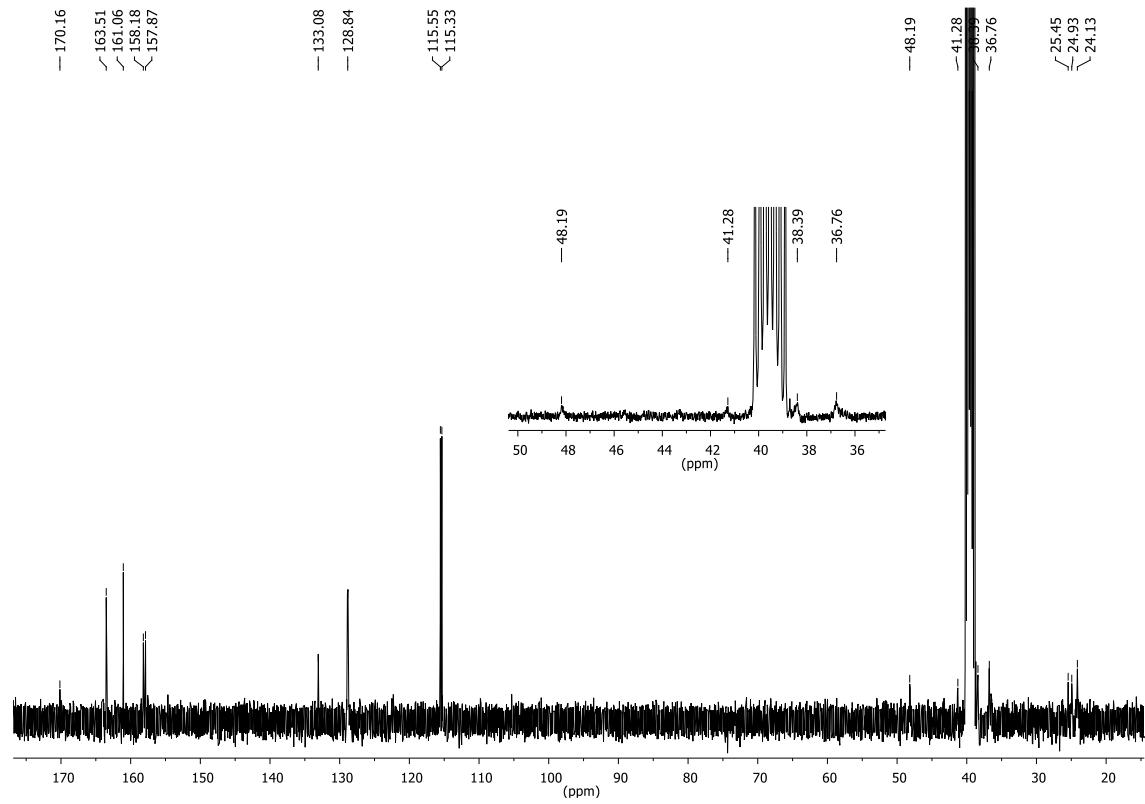


Figure S24: ^1H NMR spectrum of N^8 -(4-fluorobenzoyl)-spermidine \times 2TFA (**11**)

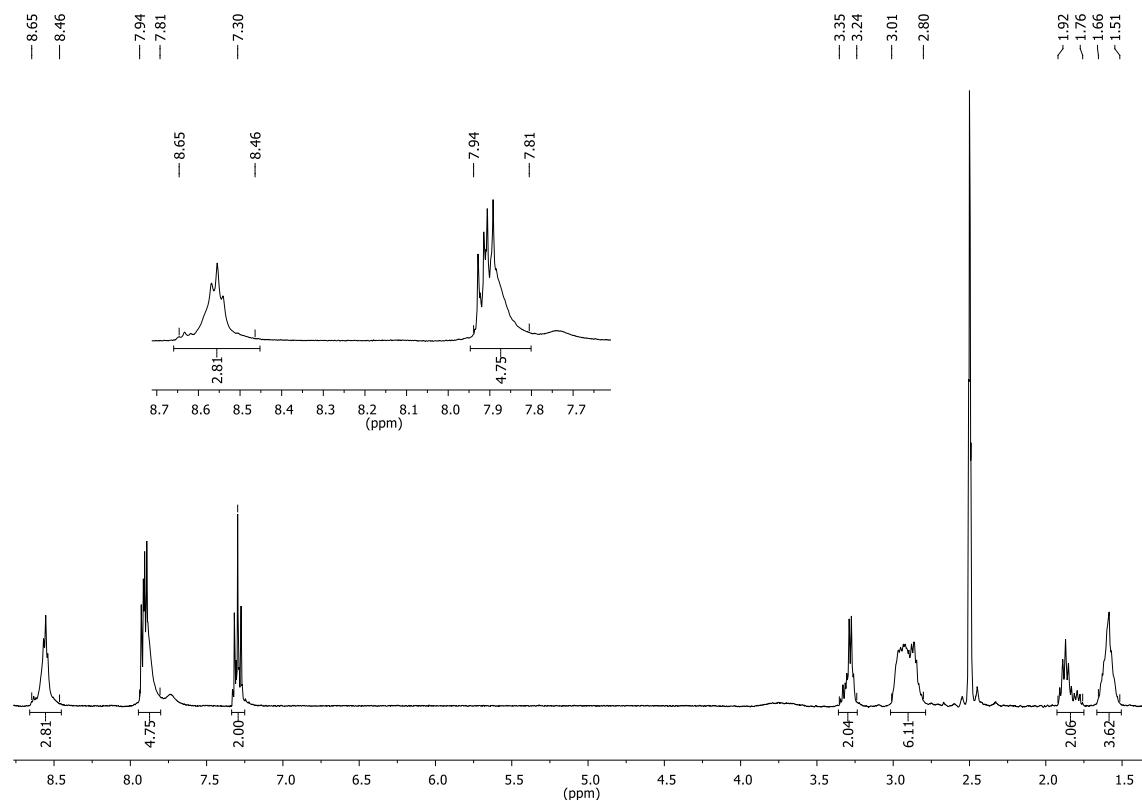


Figure S25: ^{13}C NMR spectrum of N^8 -(4-fluorobenzoyl)-spermidine \times 2TFA (**11**)

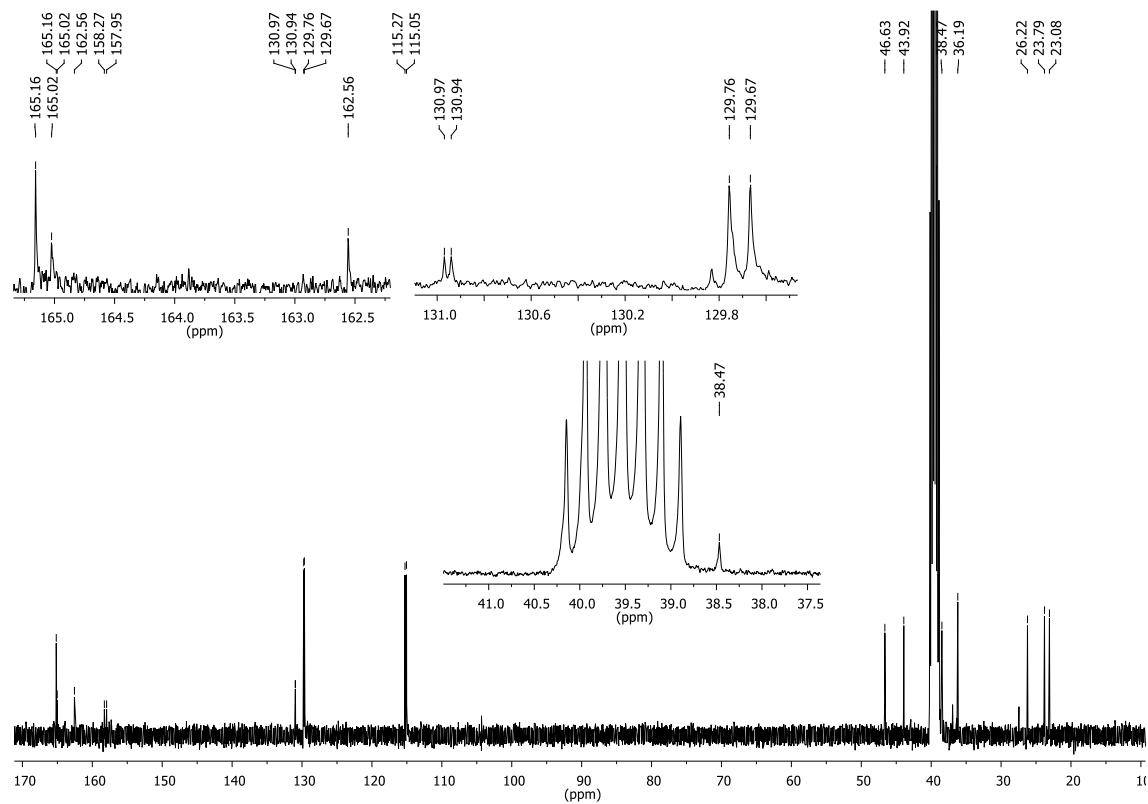


Figure S26: ^1H NMR spectrum of N^1 -(4-fluorobenzoyl)-spermine \times 3TFA (**12**)

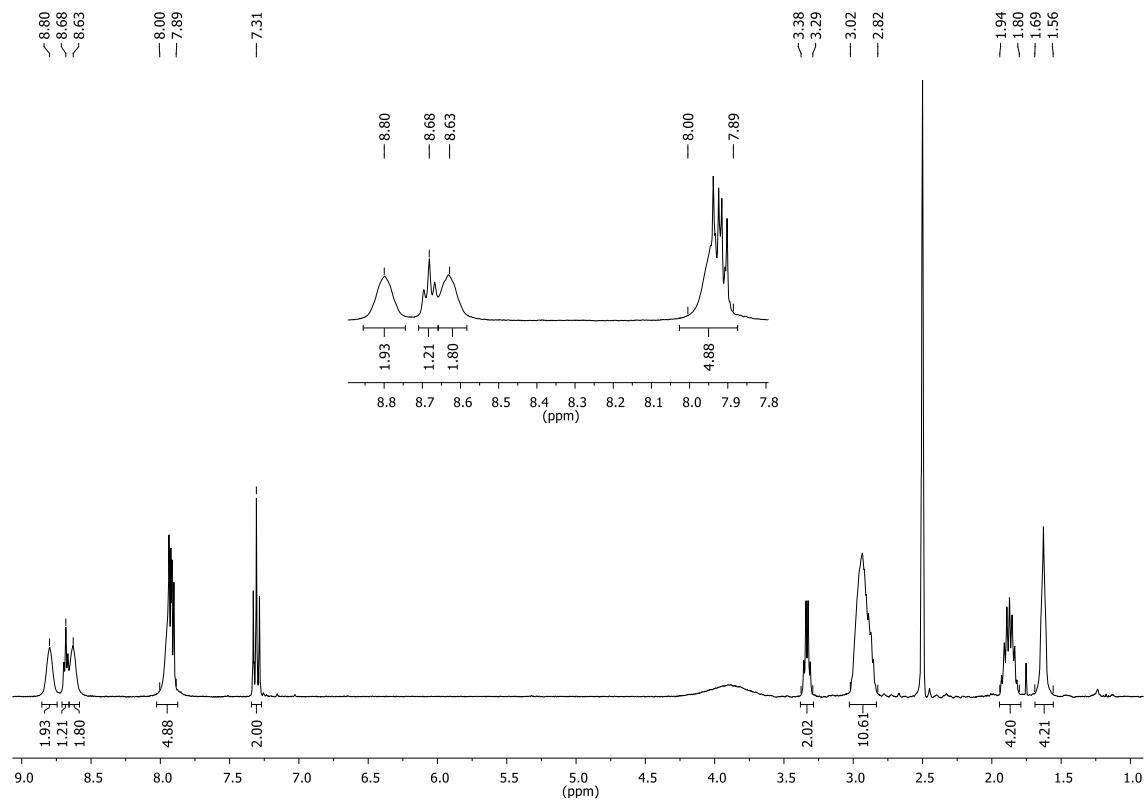


Figure S27: ^{13}C NMR spectrum of N^1 -(4-fluorobenzoyl)-spermine \times 3TFA (**12**)

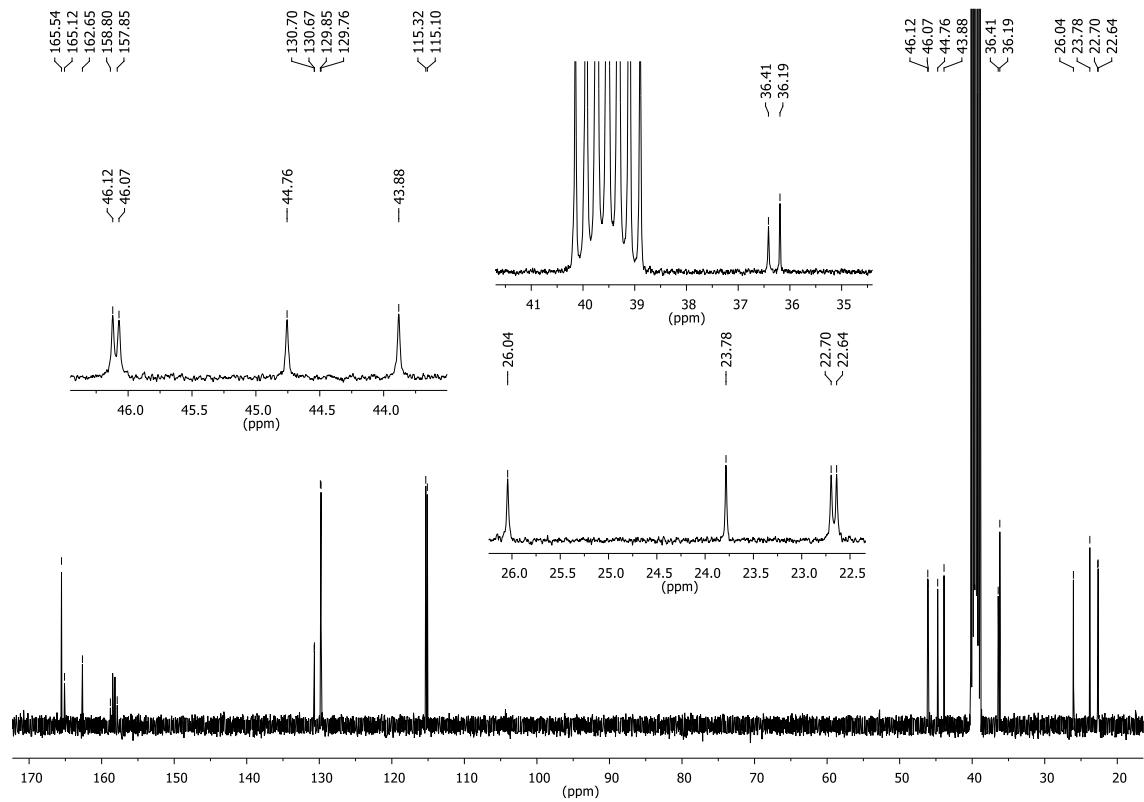


Figure S28: ^1H NMR spectrum of N^1 -(4-fluorobenzyl)-putrescine \times 2TFA (13)

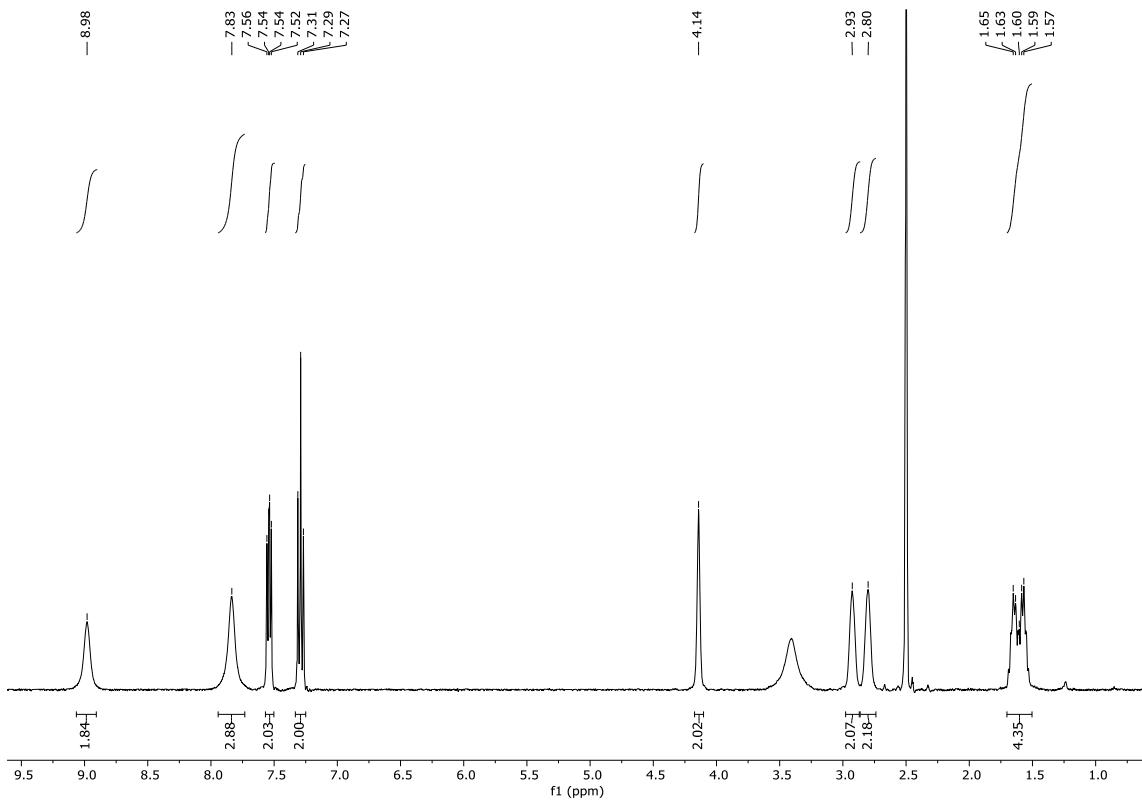


Figure S29: ^{13}C NMR spectrum of N^1 -(4-fluorobenzyl)-putrescine \times 2TFA (13)

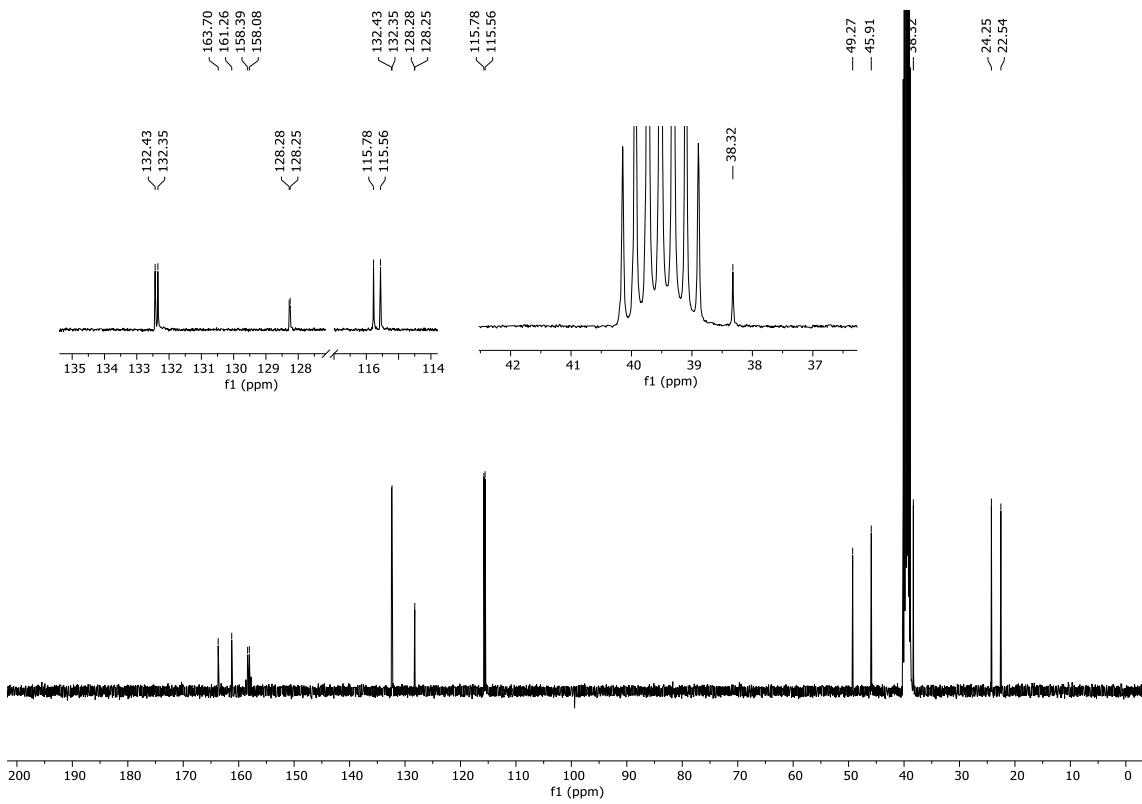


Figure S30: ^1H NMR spectrum of N^1 -(4-fluorobenzyl)-cadaverine \times 2TFA (**14**)

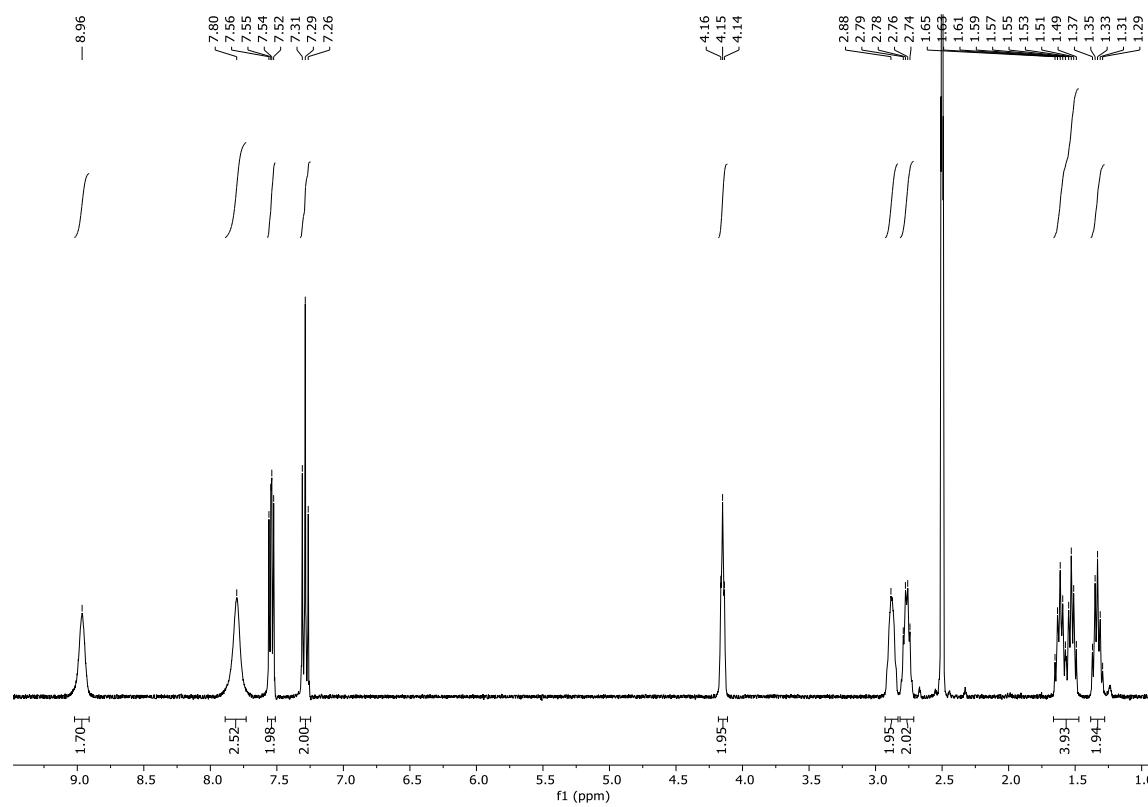


Figure S31: ^{13}C NMR spectrum of N^1 -(4-fluorobenzyl)-cadaverine \times 2TFA (**14**)

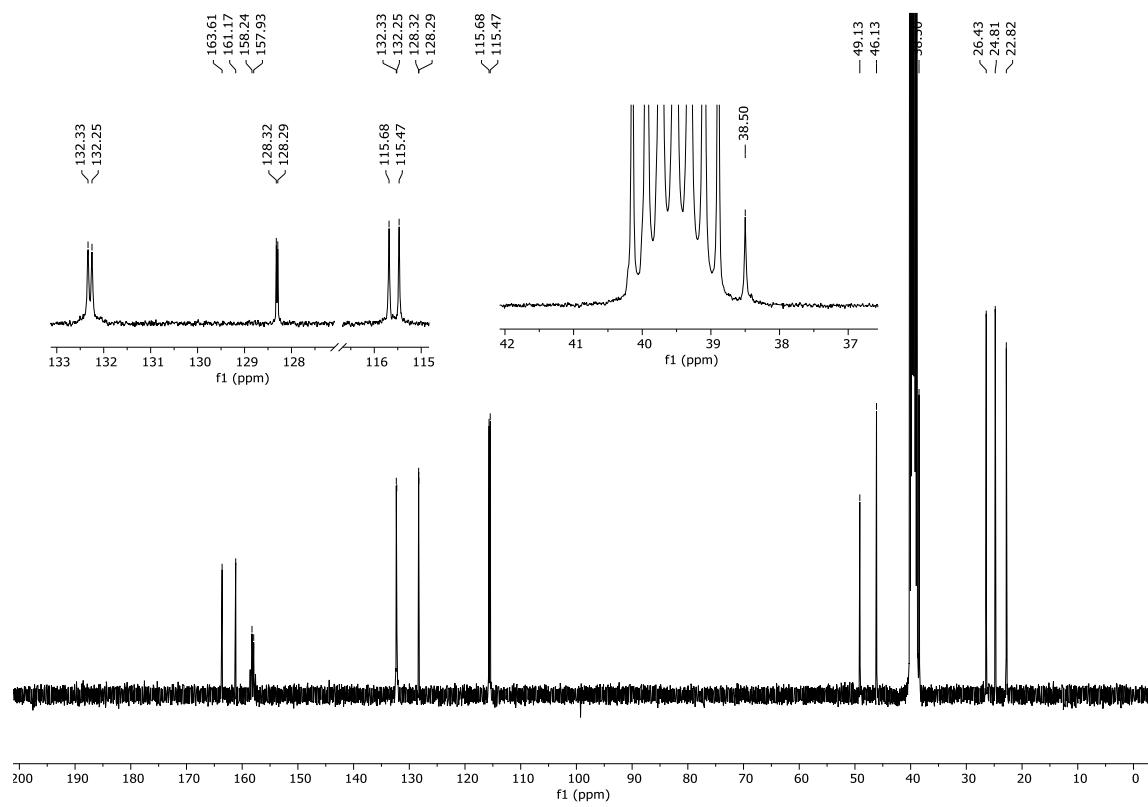


Figure S32: ^1H NMR spectrum of N^1 -(4-fluorobenzyl)-1,6-diaminohexane \times 2TFA (**15**)

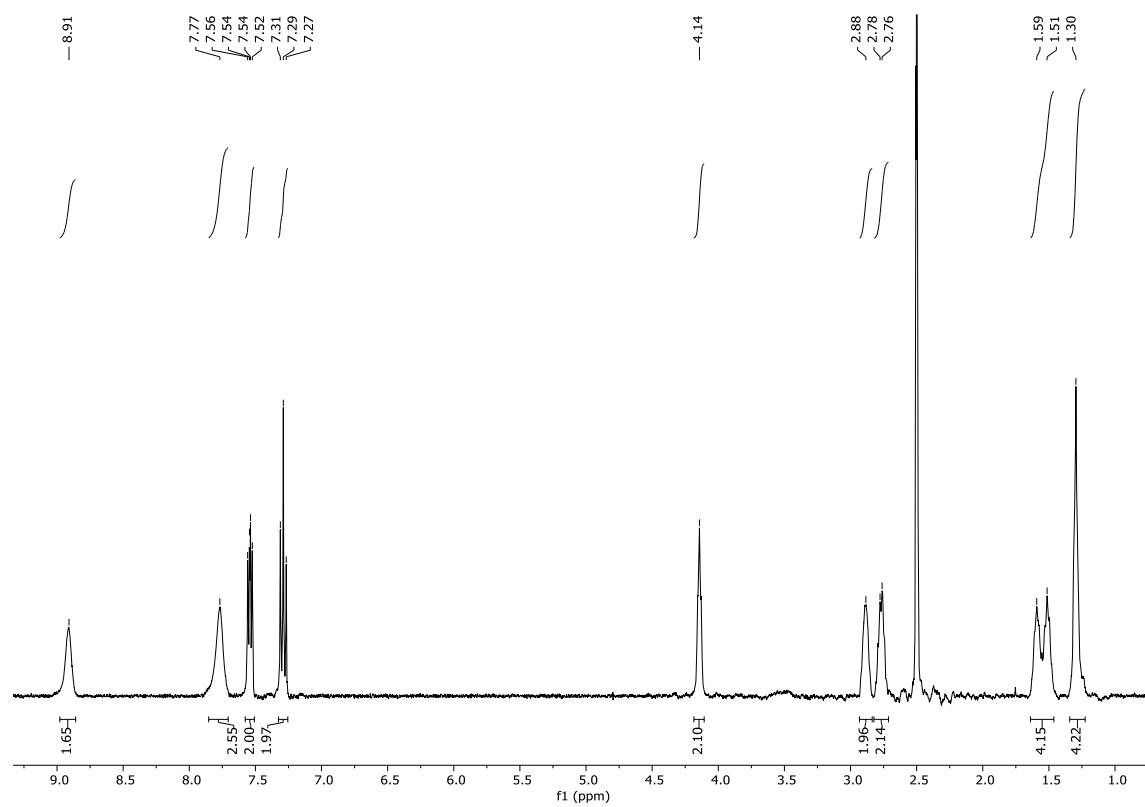


Figure S33: ^{13}C NMR spectrum of N^1 -(4-fluorobenzyl)-1,6-diaminohexane \times 2TFA (**15**)

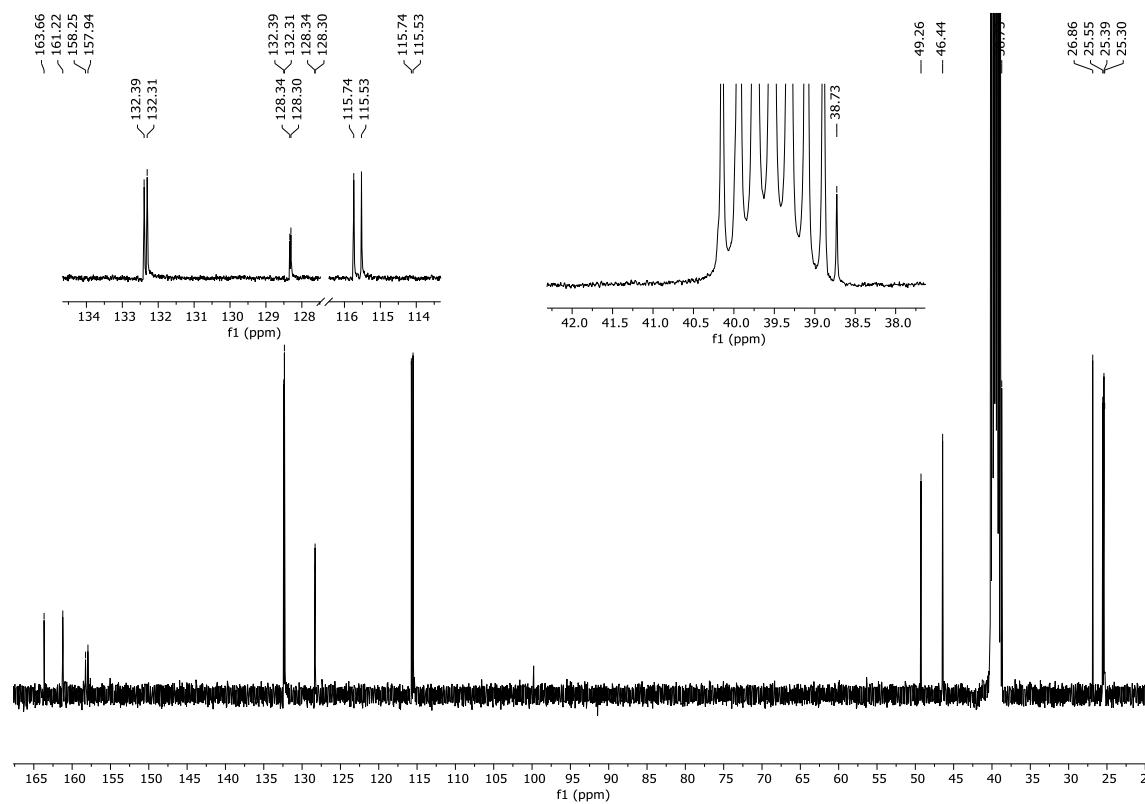


Figure S34: ^1H NMR spectrum of N^1 -(4-fluorobenzyl)-1,7-diaminoheptane \times 2TFA (**16**)

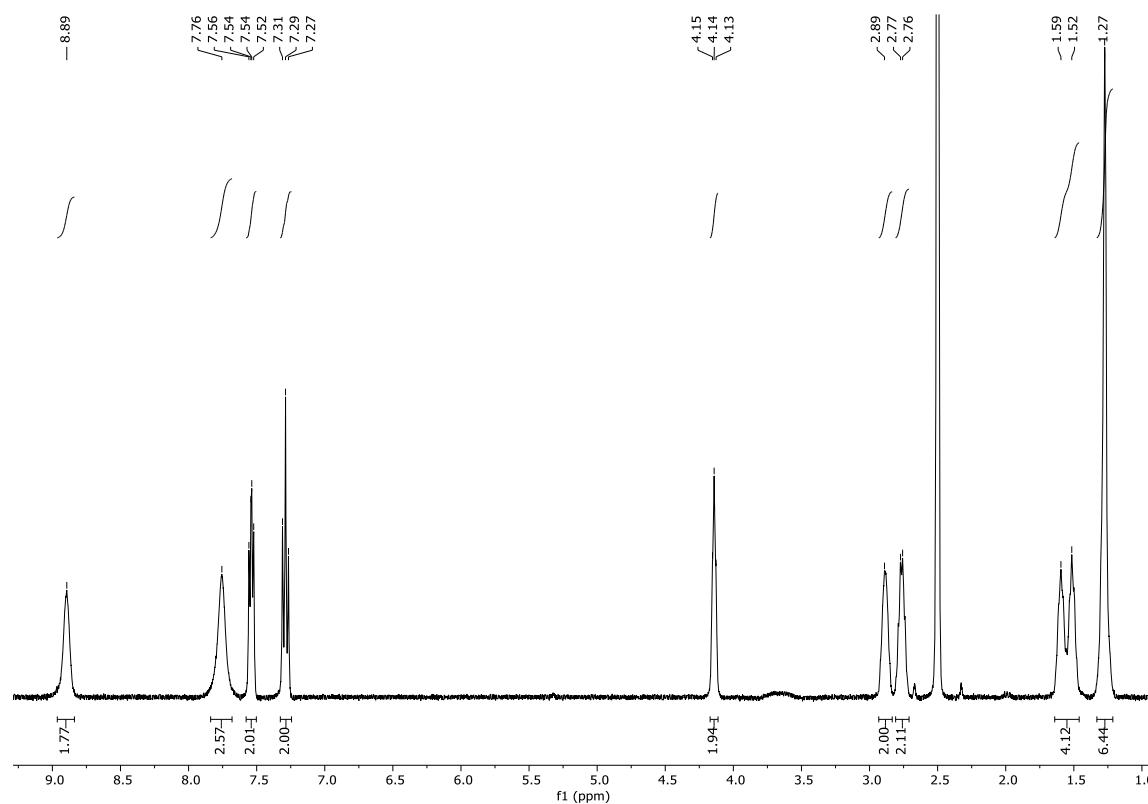


Figure S35: ^{13}C NMR spectrum of N^1 -(4-fluorobenzyl)-1,7-diaminoheptane \times 2TFA (**16**)

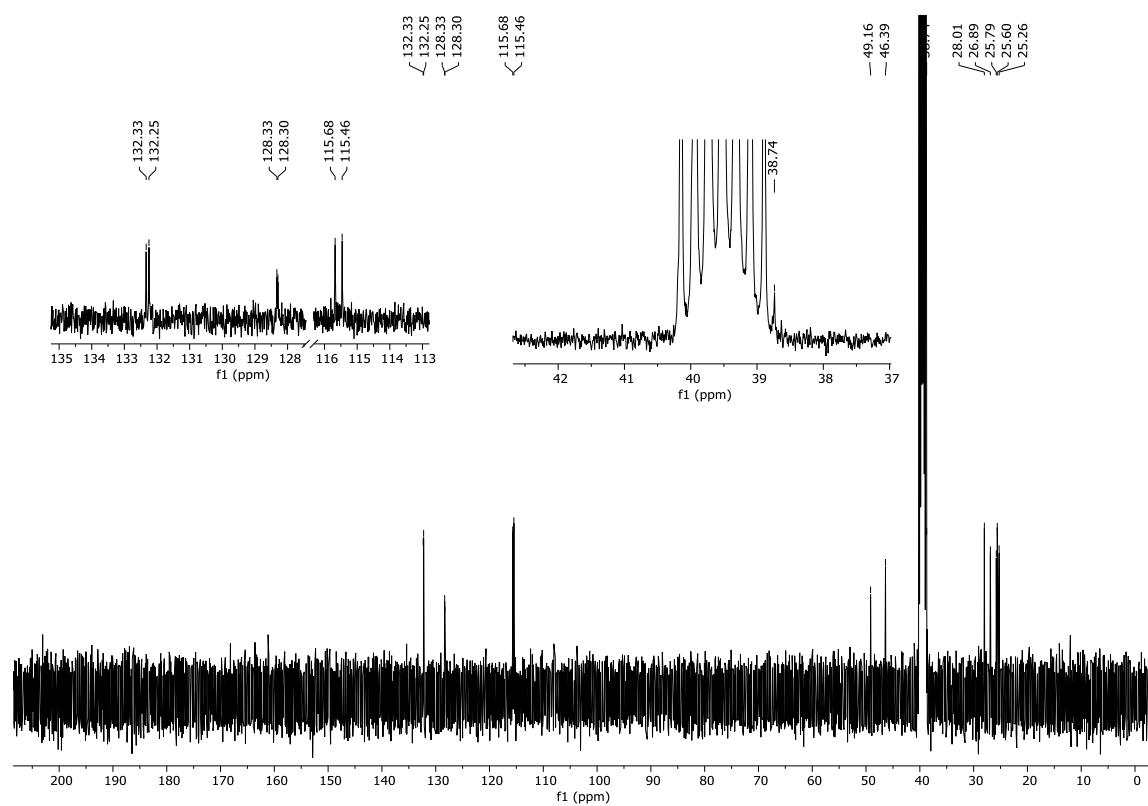


Figure S36: ^1H NMR spectrum of N^1 -(4-fluorobenzyl)-1,8-diaminoctane \times 2TFA (17)

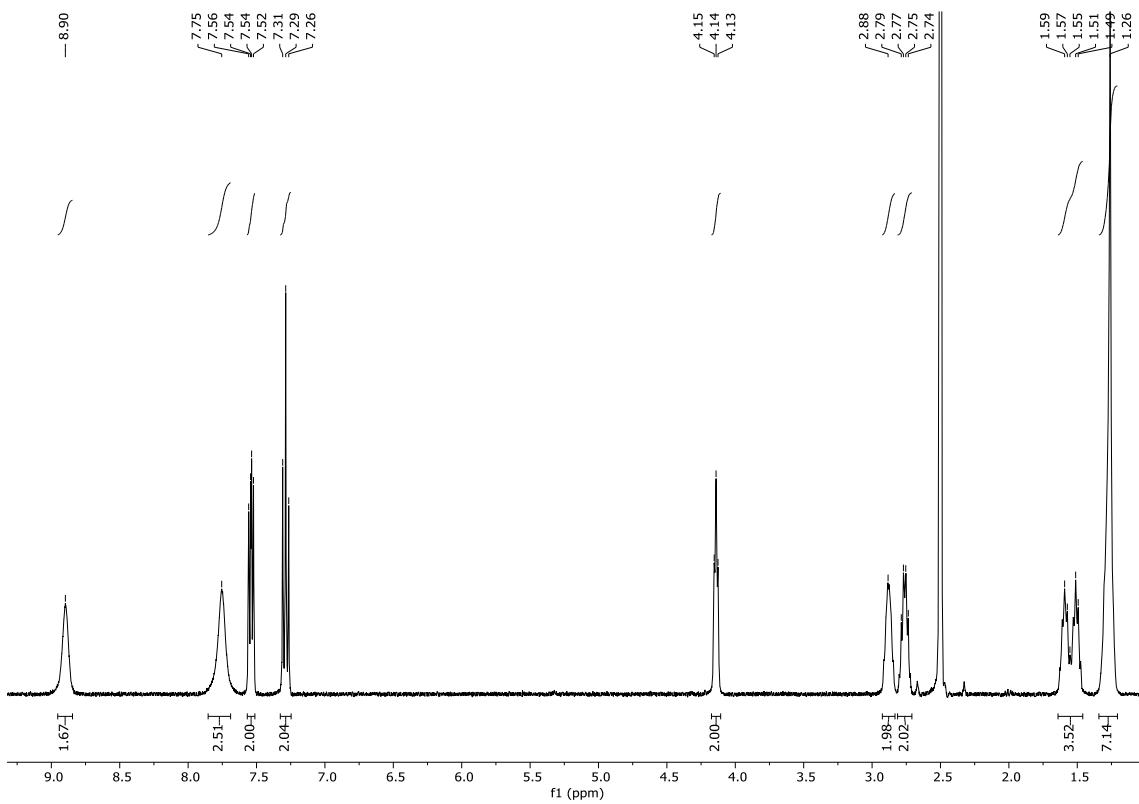


Figure S37: ^{13}C NMR spectrum of N^1 -(4-fluorobenzyl)-1,8-diaminoctane \times 2TFA (17)

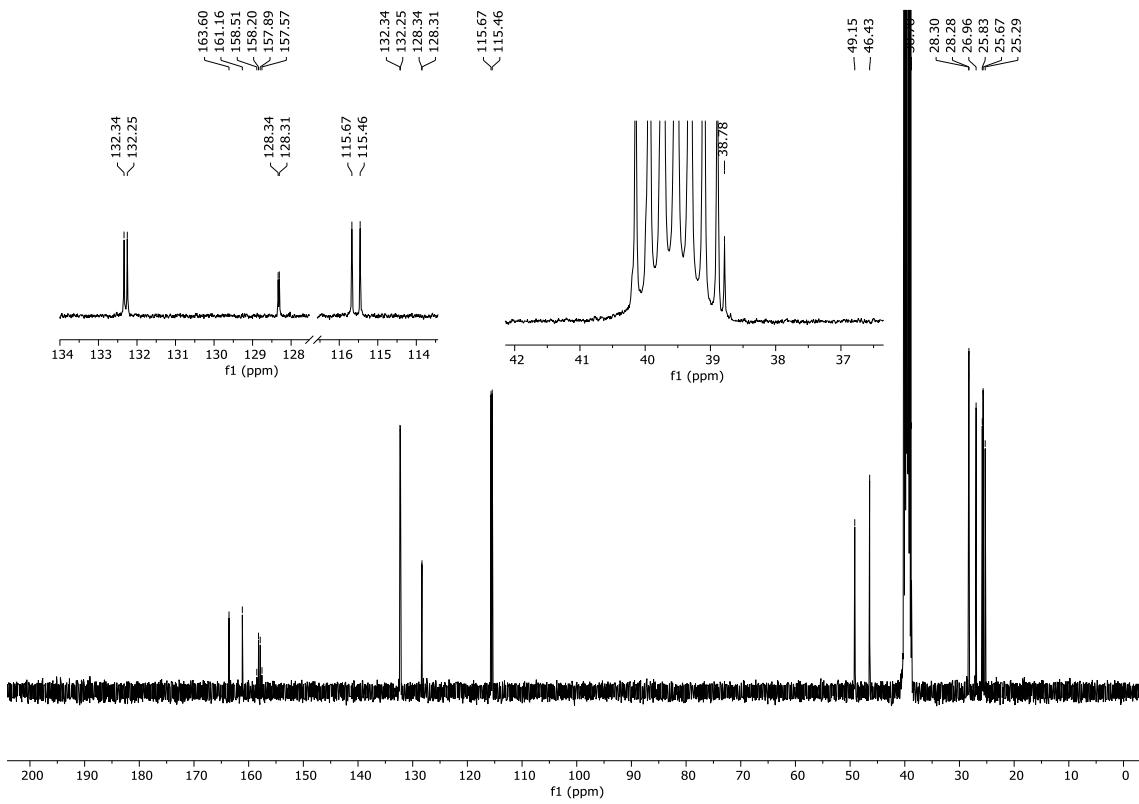


Figure S38: ^1H NMR spectrum of N^1 -(4-fluorobenzyl)-spermine \times 4TFA (**18**)

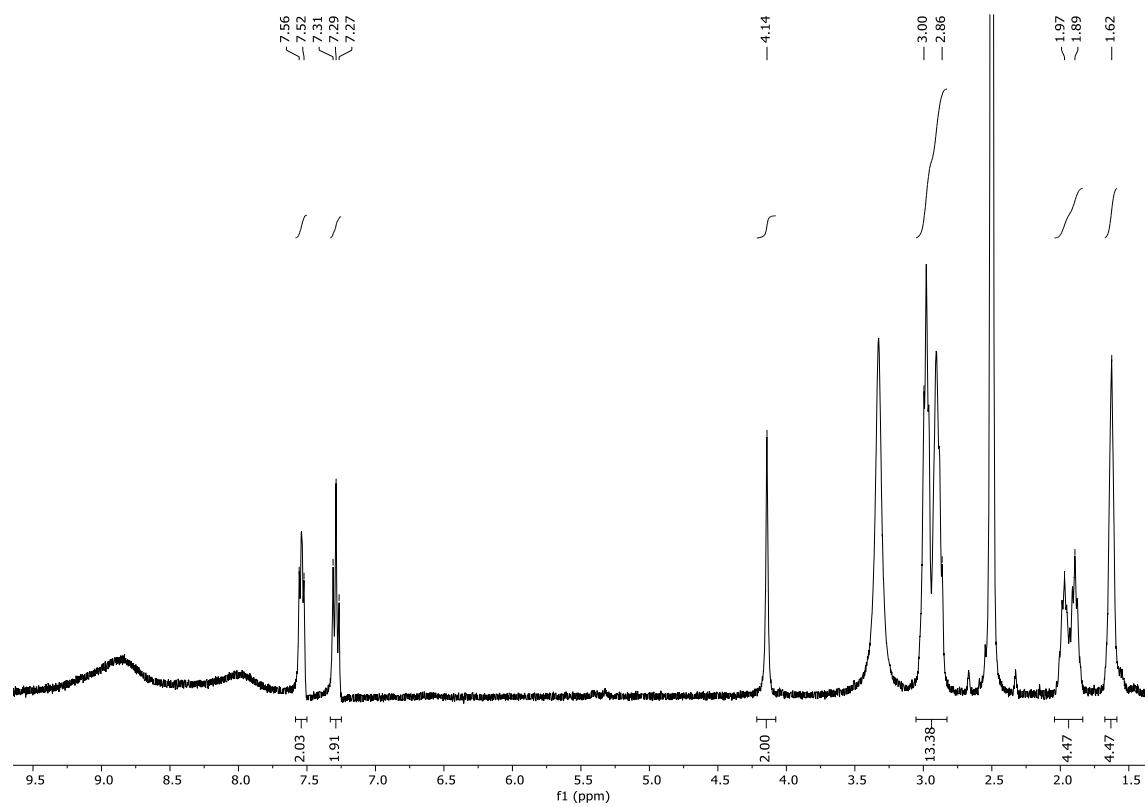


Figure S39: ^{13}C NMR spectrum of N^1 -(4-fluorobenzyl)-spermine \times 4TFA (**18**)

