Electronic supplementary information for New Journal of Chemistry

New highly electrodeficient cationic fluorescent tetrazines: A step toward the strongest purely organic photooxidants.

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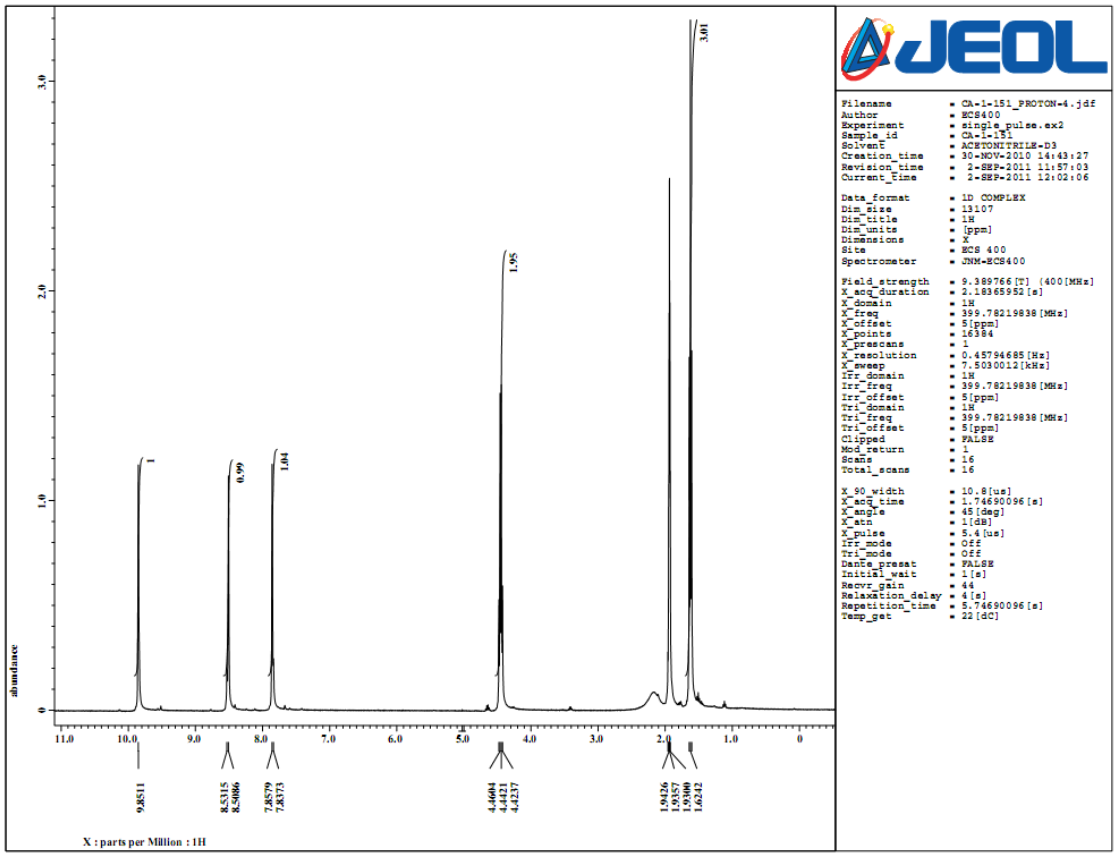


Figure 2: ^{13}C NMR of *3,6-bis(1-N-ethyl-imidazolium)-s-tetrazine tetrafluoroborate* **1**

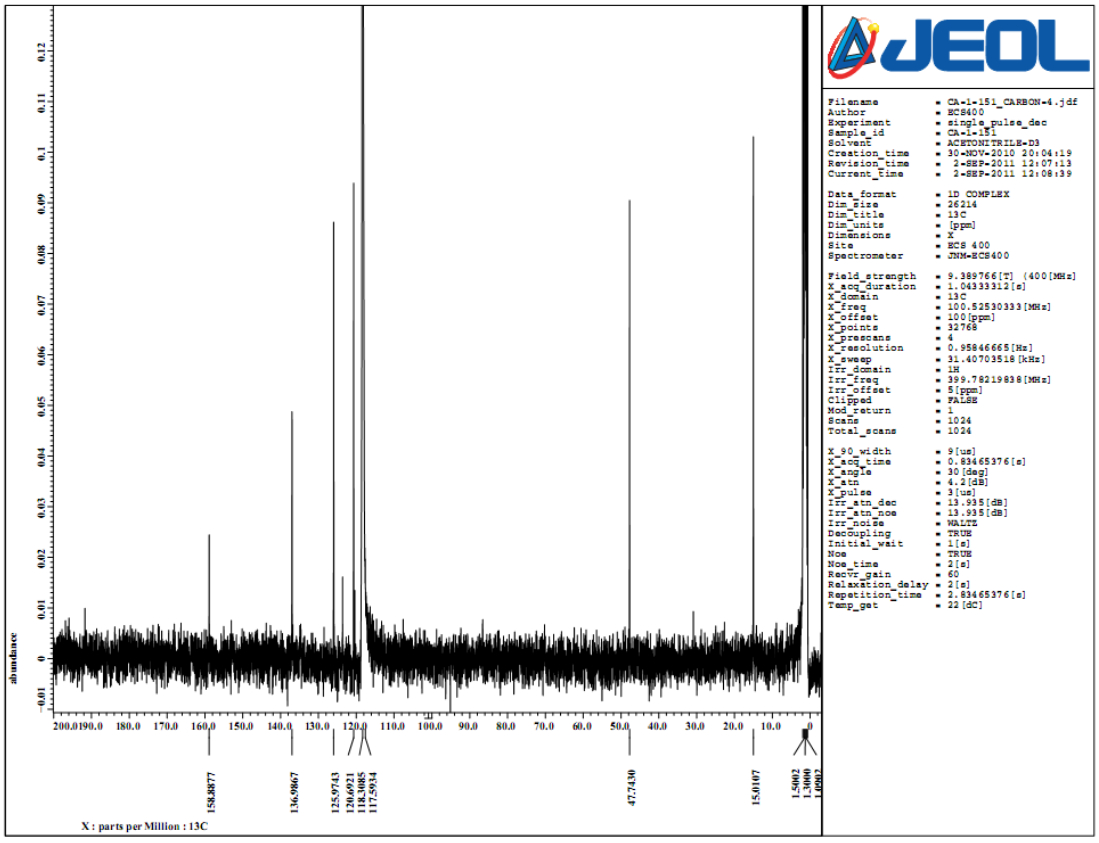


Figure 3: ^{1}H NMR of *3,6-bis(1-N-methyl-benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **2**

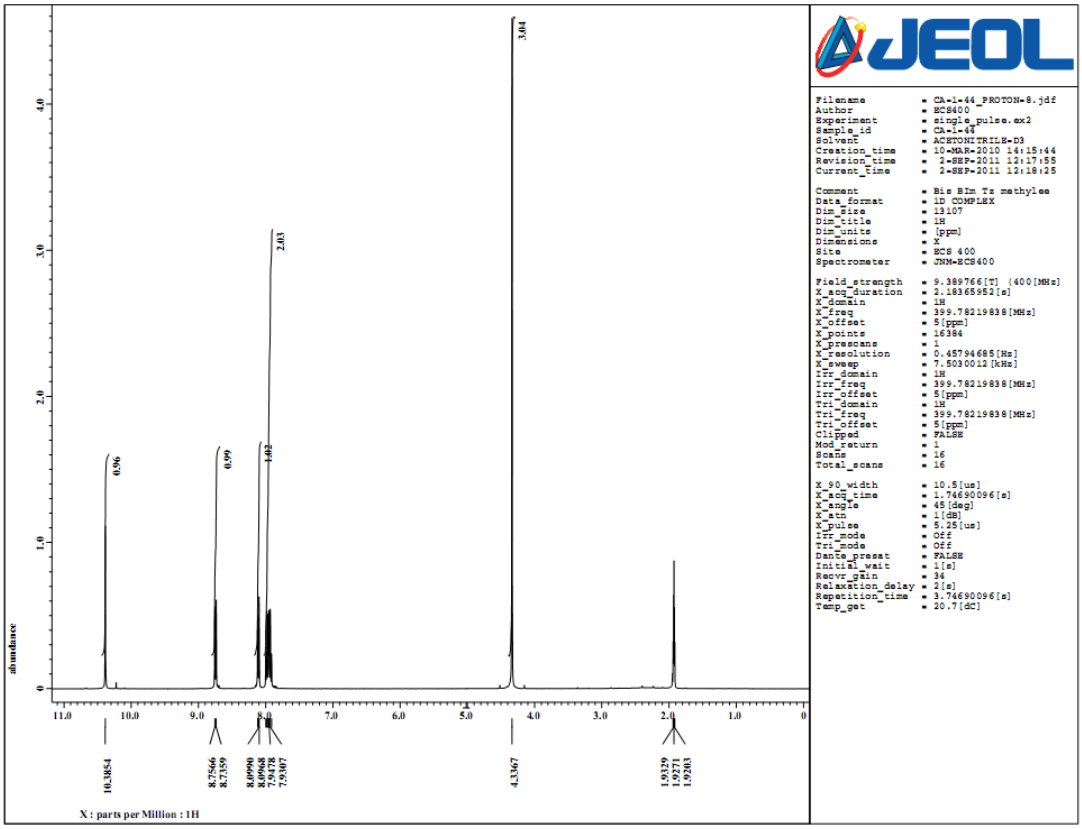


Figure 4: ^{13}C NMR of *3,6-bis(1-N-methyl-benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **2**

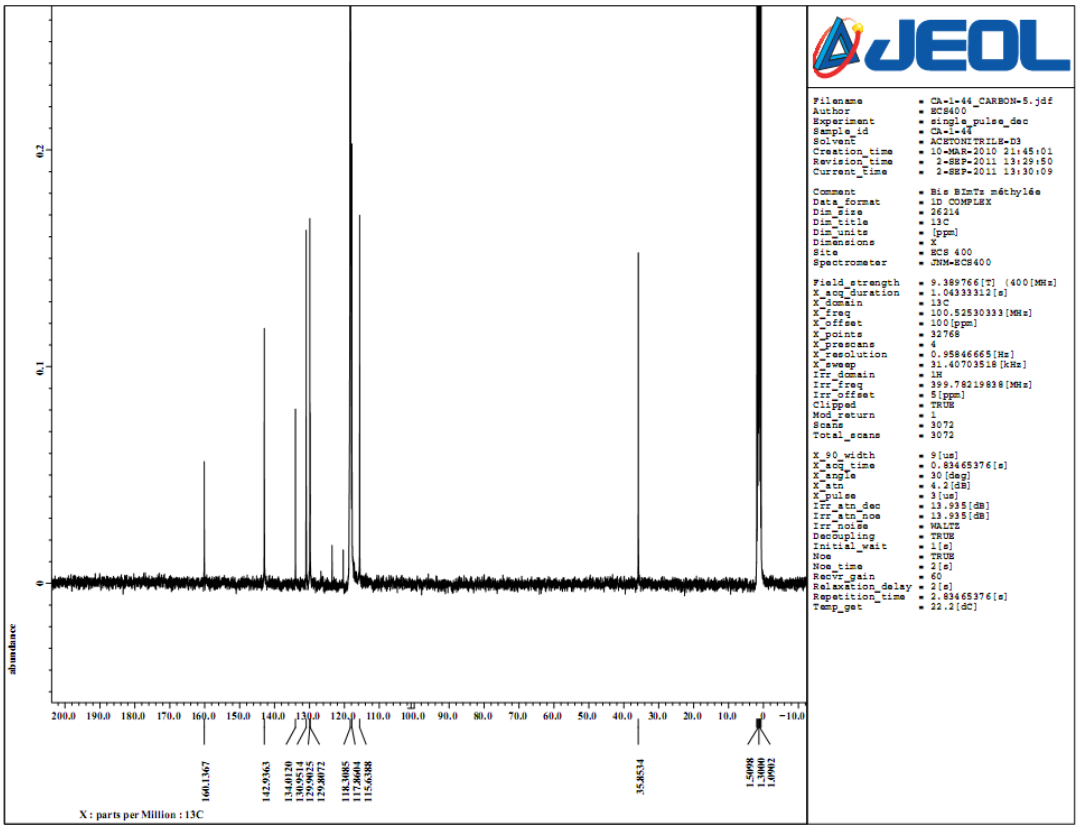


Figure 5: ^{1}H NMR of *6-(methoxyadamantan-1-yl)-3-(1-imidazolyl)-s-tetrazine* **3n**

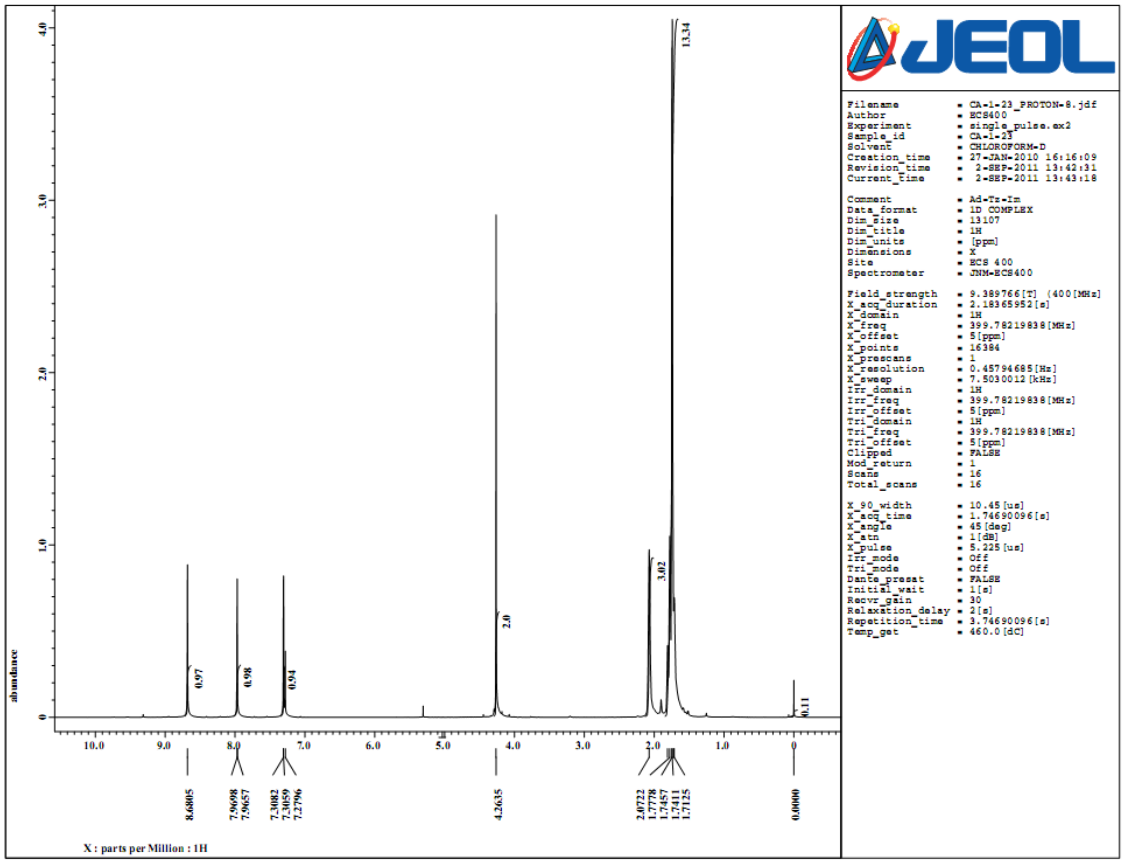


Figure 6: ^{13}C NMR of *6-(methoxyadamantan-1-yl)-3-(1-imidazolyl)-s-tetrazine* **3n**

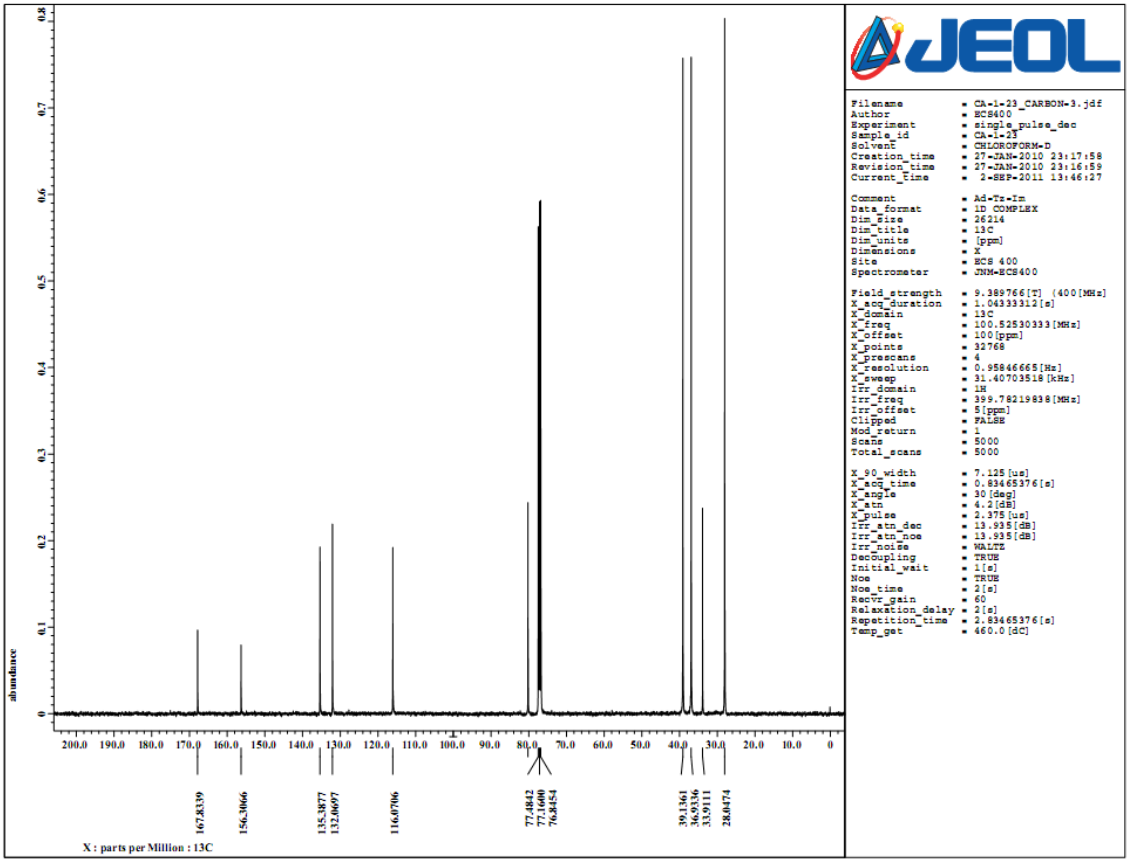


Figure 7: ^{1}H NMR of *6-(methoxyadamantan-1-yl)-3-(1-N-methyl-imidazolium)-s-tetrazine trifluoromethanesulfonate* **3**

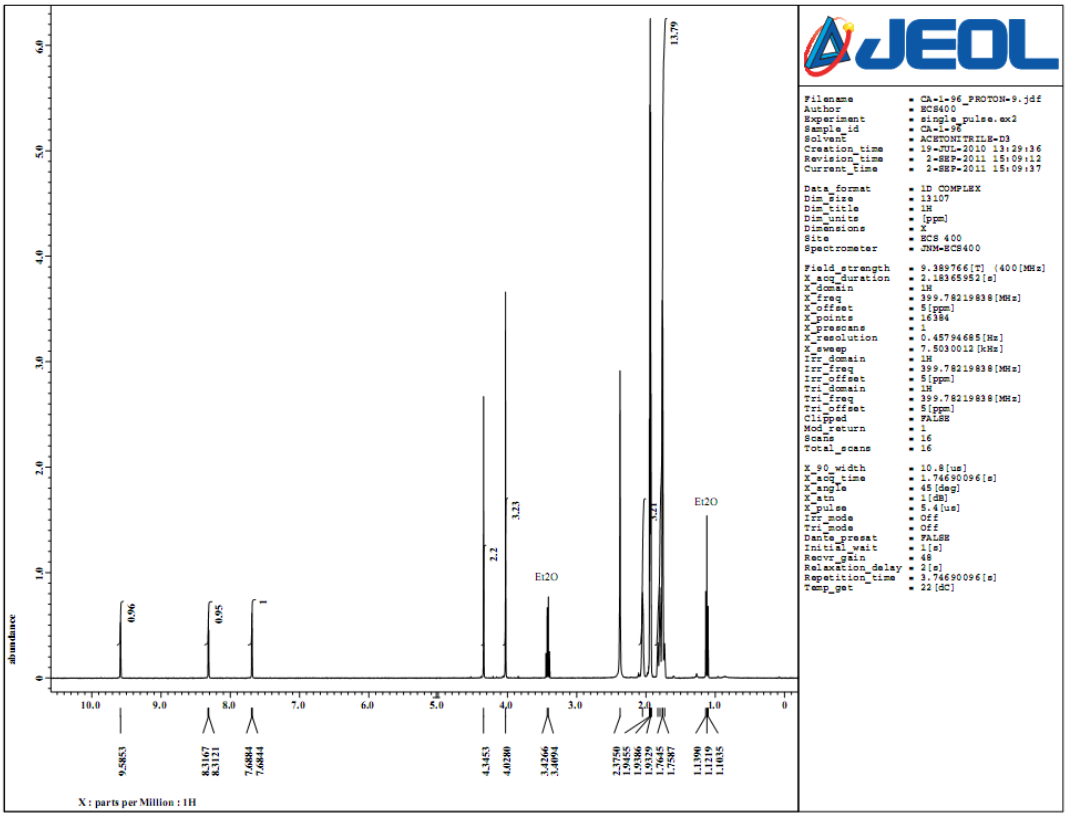


Figure 8: ^{13}C NMR of *6-(methoxyadamantan-1-yl)-3-(1-N-methyl-imidazolium)-s-tetrazine trifluoromethanesulfonate* **3**

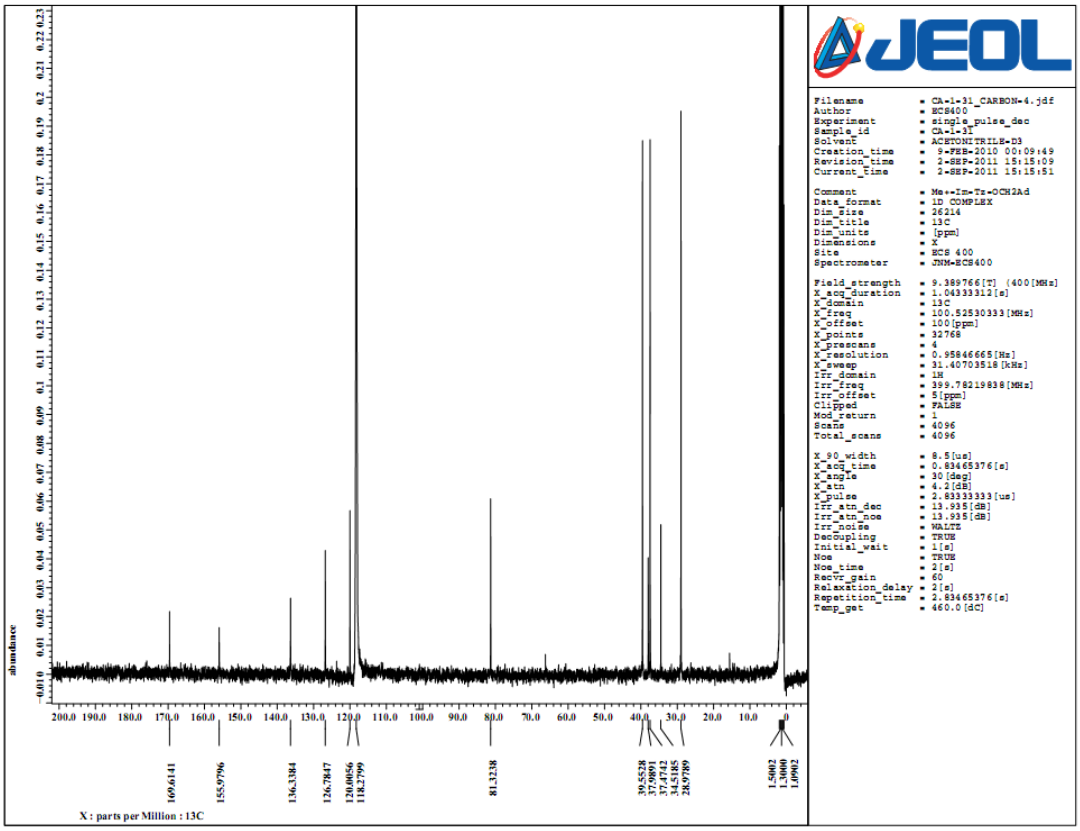


Figure 9: ^{1}H NMR of *6-(methoxyadamantan-1-yl)-3-(1-benzimidazolyl)-s-tetrazine* **4n**

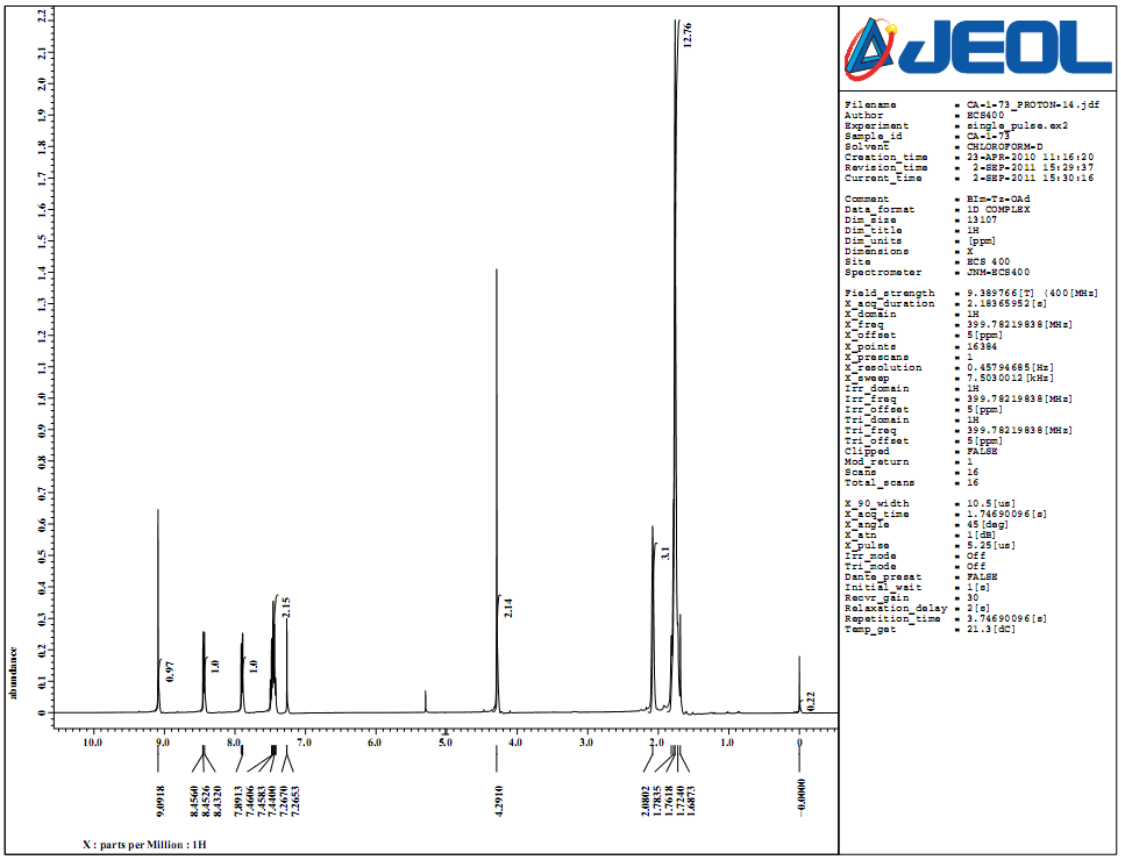


Figure 10: ^{13}C NMR of *6-(methoxyadamantan-1-yl)-3-(1-benzimidazolyl)-s-tetrazine* **4n**

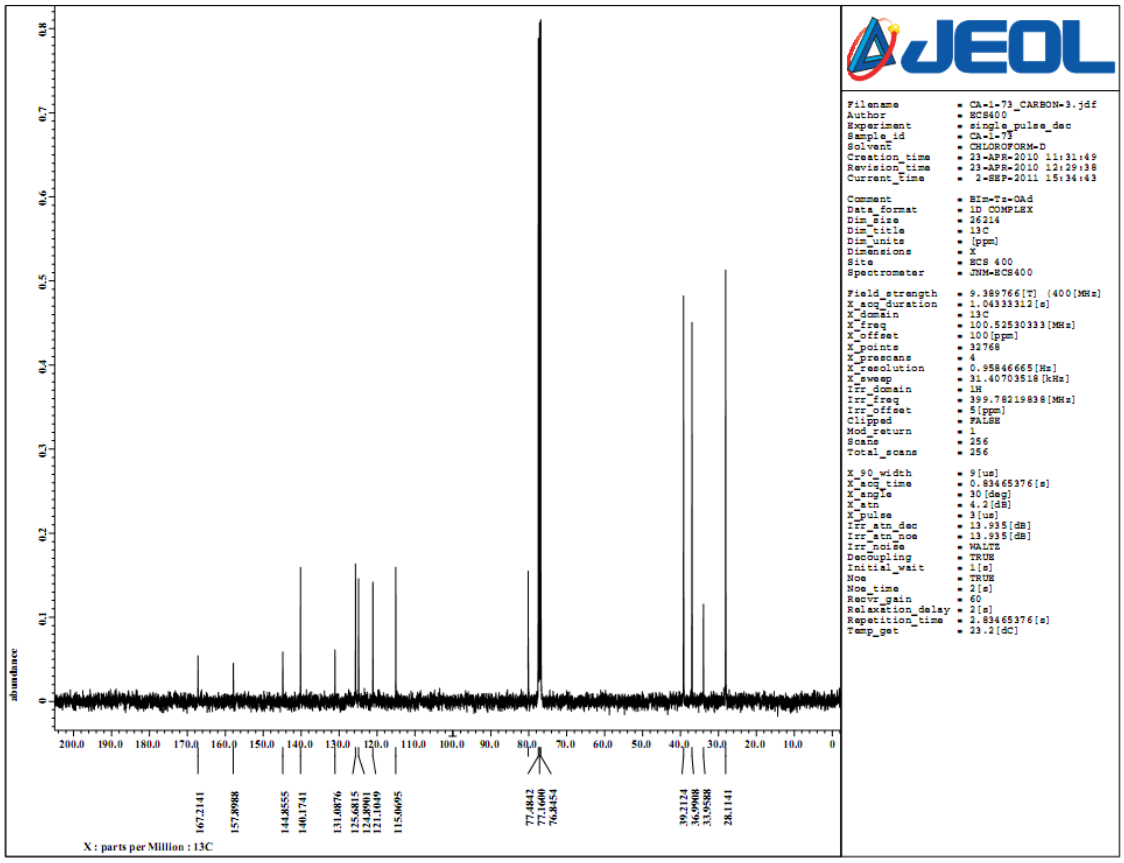


Figure 11: [1]H NMR of *6-(methoxyadamantan-1-yl)-3-(1-N-methyl-benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **4**

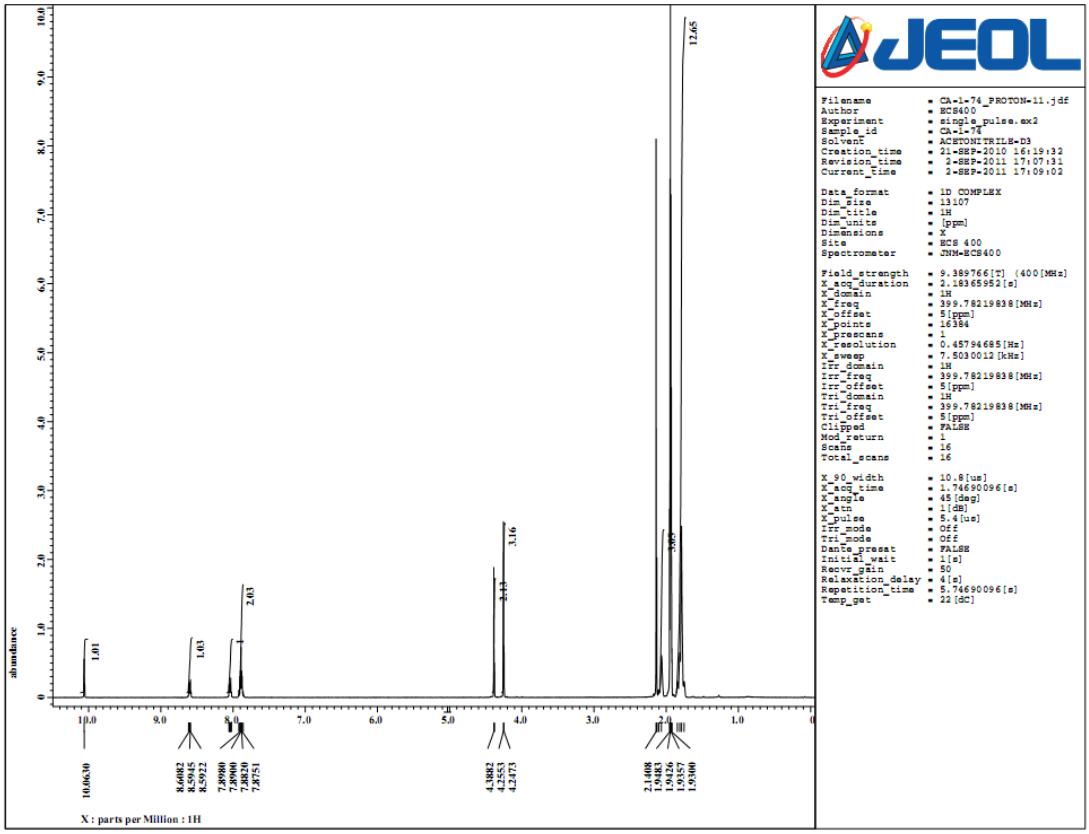


Figure 12: [13]C NMR of *6-(methoxyadamantan-1-yl)-3-(1-N-methyl-benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **4**

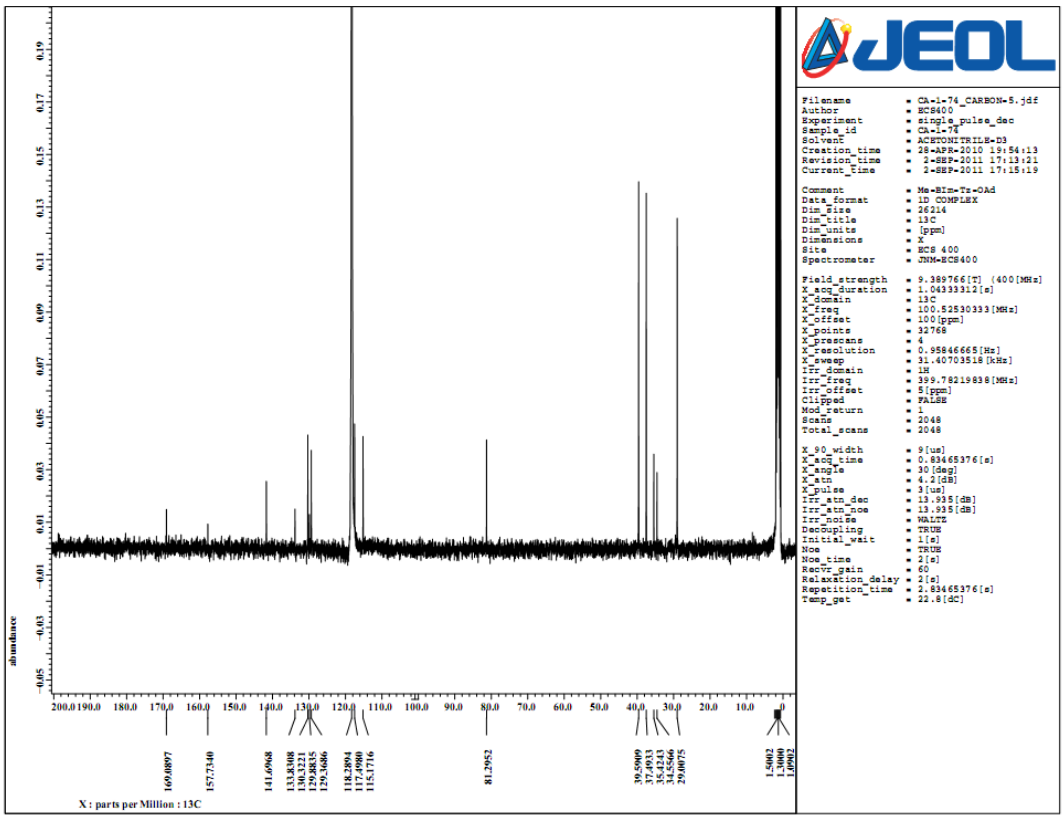


Figure 13: ^{1}H NMR of *6-(methoxyadamantan-1-yl)-3-(1-(2-nonyl)benzimidazolyl)-s-tetrazine* **5n**

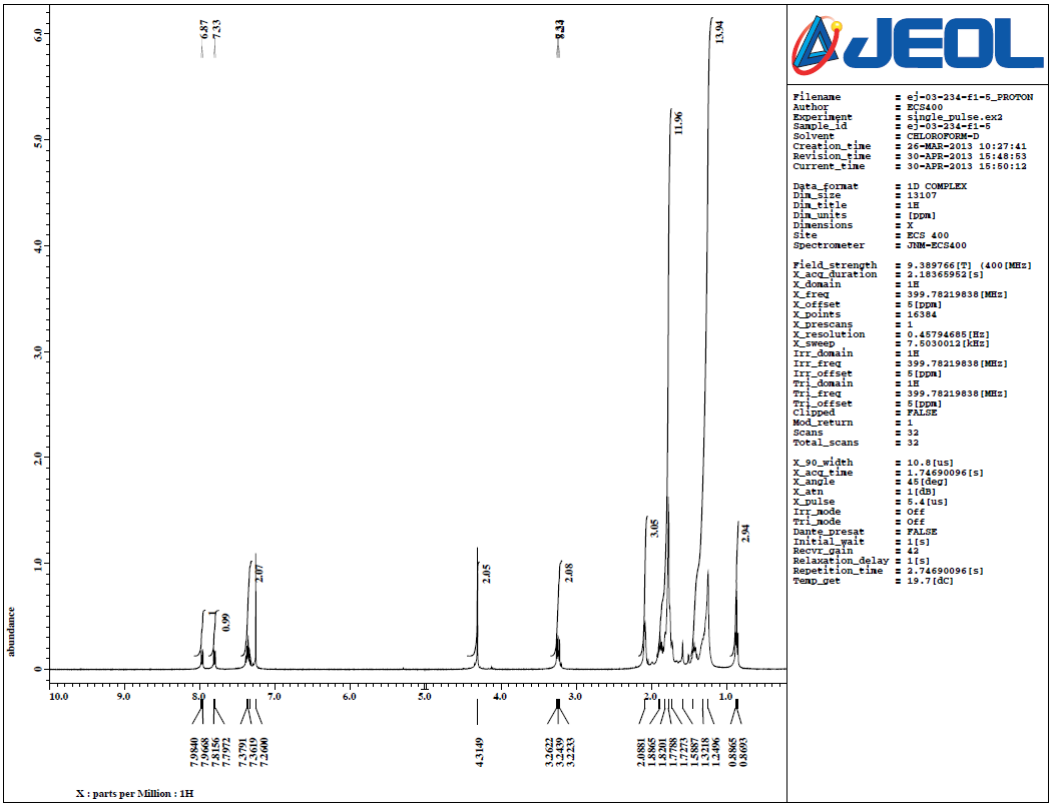


Figure 14: ^{13}C NMR of *6-(methoxyadamantan-1-yl)-3-(1-(2-nonyl)benzimidazolyl)-s-tetrazine* **5n**

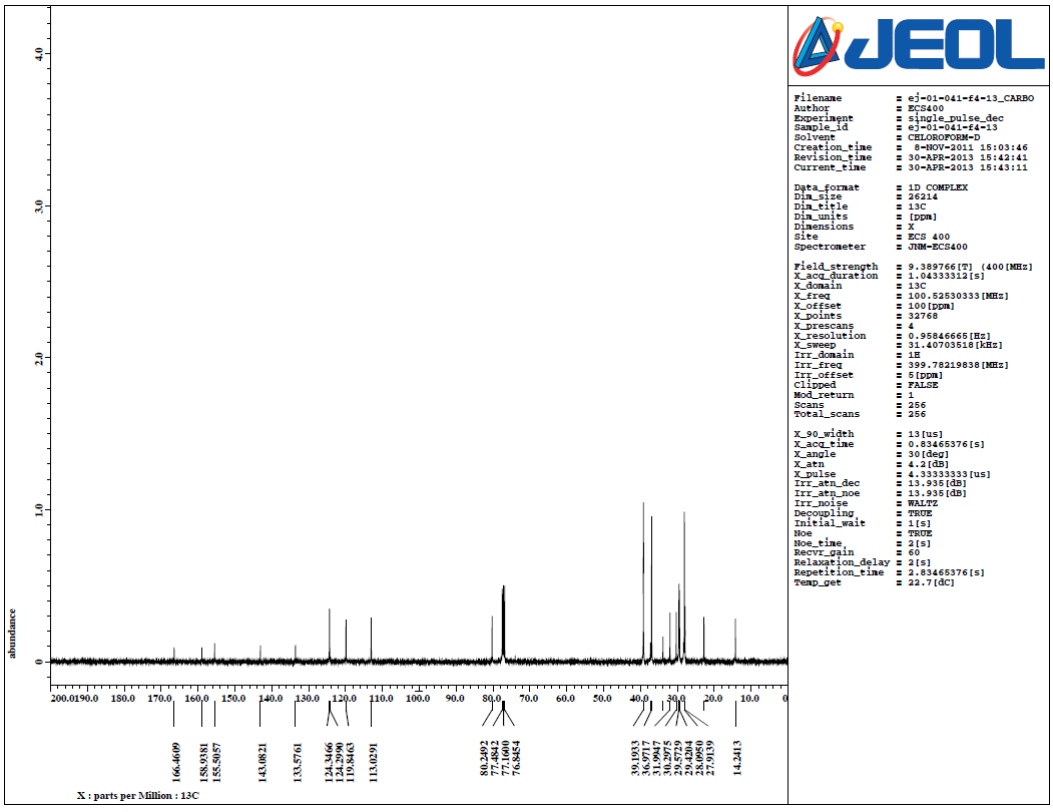
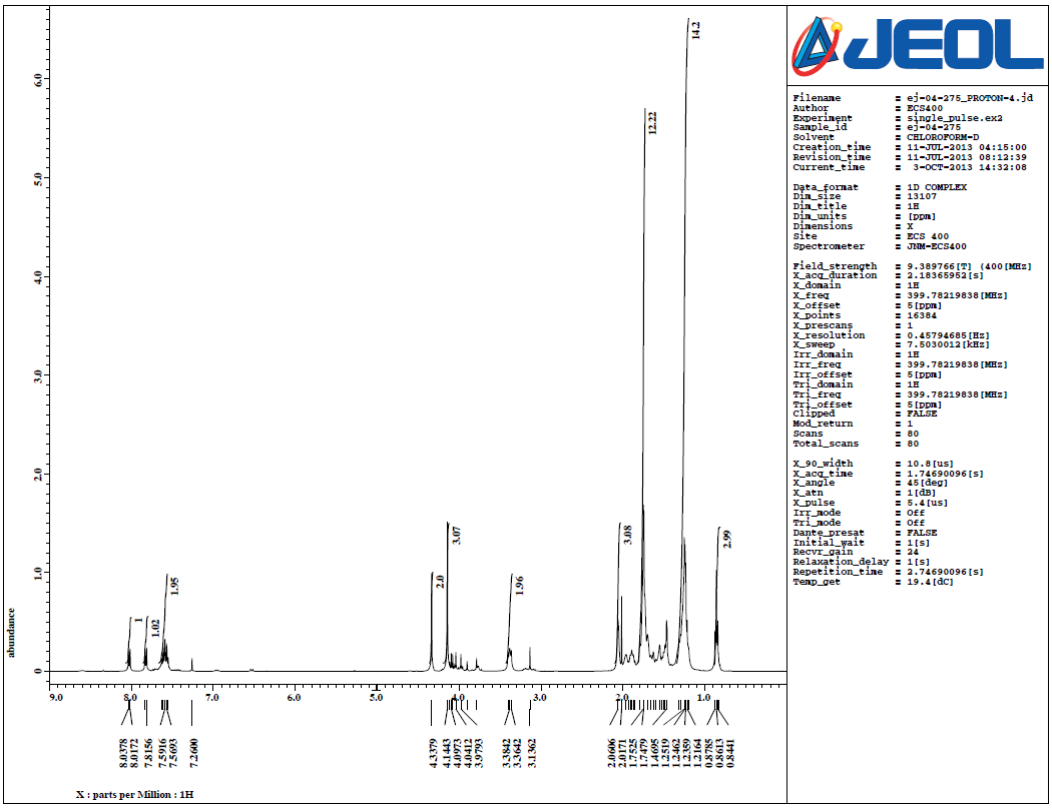


Figure 15: ^{1}H NMR of *6-(methoxyadamantan-1-yl)-3-(1-(2-nonyl)-N-methyl-benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **5**



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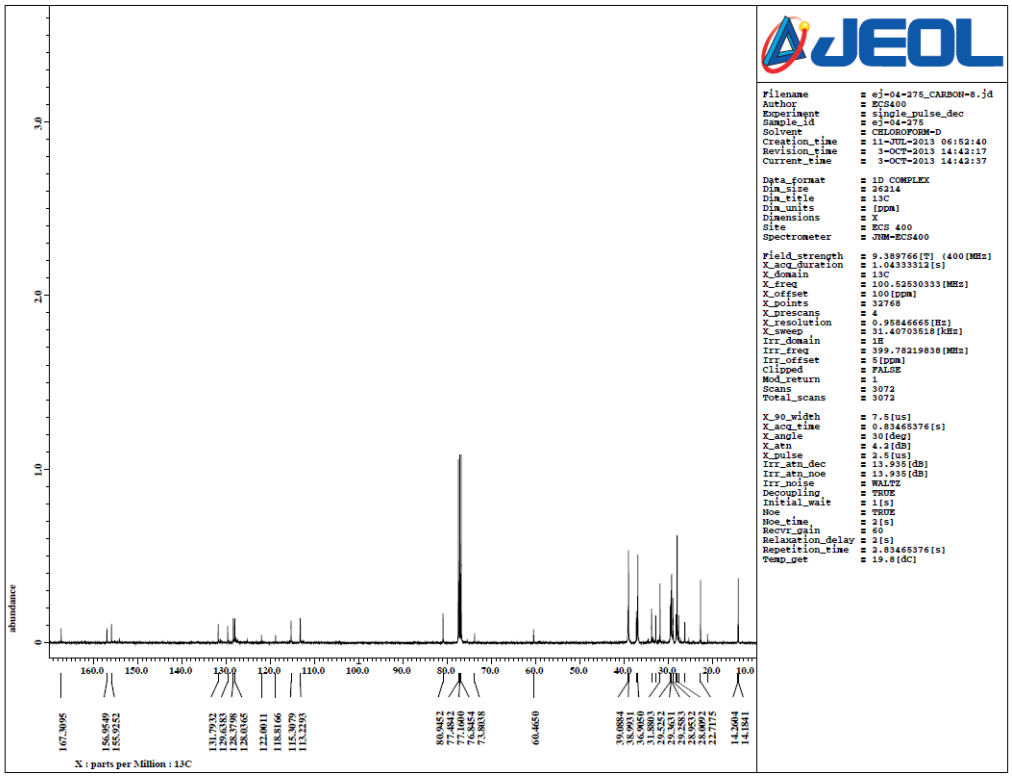


Figure 17 ^{1}H NMR of *6-(methoxyadamantan-1-yl)-3-(1-(5-chloro)benzimidazolyl)-s-tetrazine* **6n**

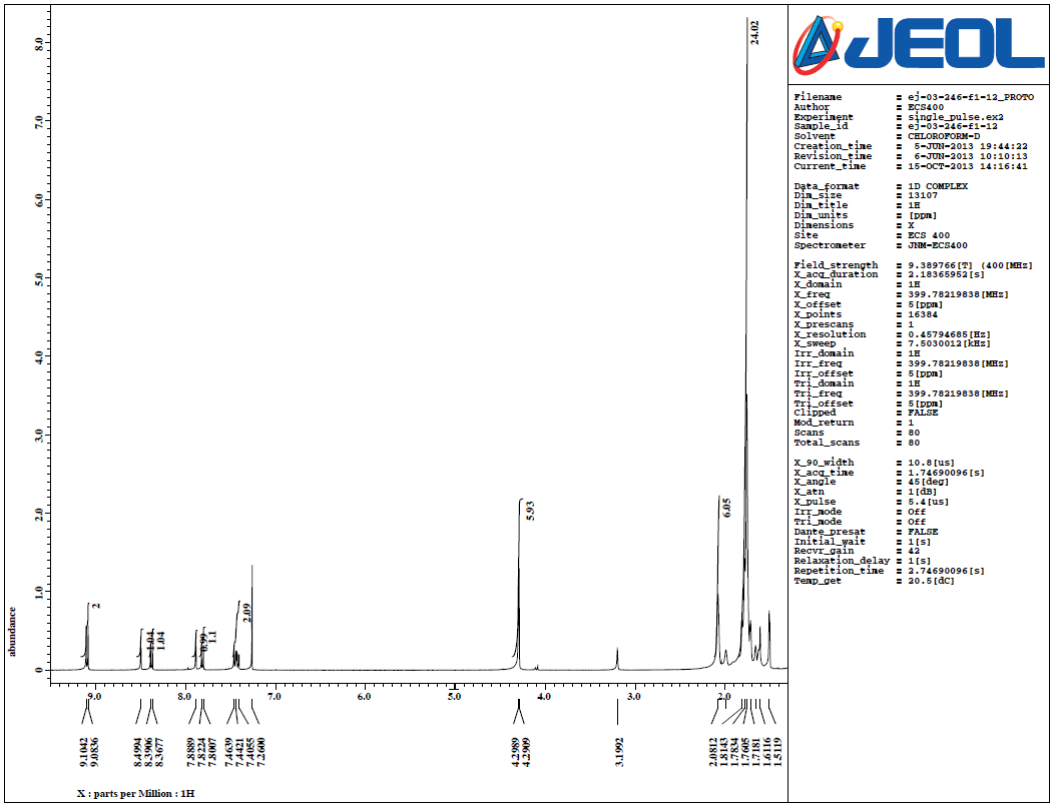


Figure 18 ^{13}C NMR of *6-(methoxyadamantan-1-yl)-3-(1-(5-chloro)benzimidazolyl)-s-tetrazine* **6n**

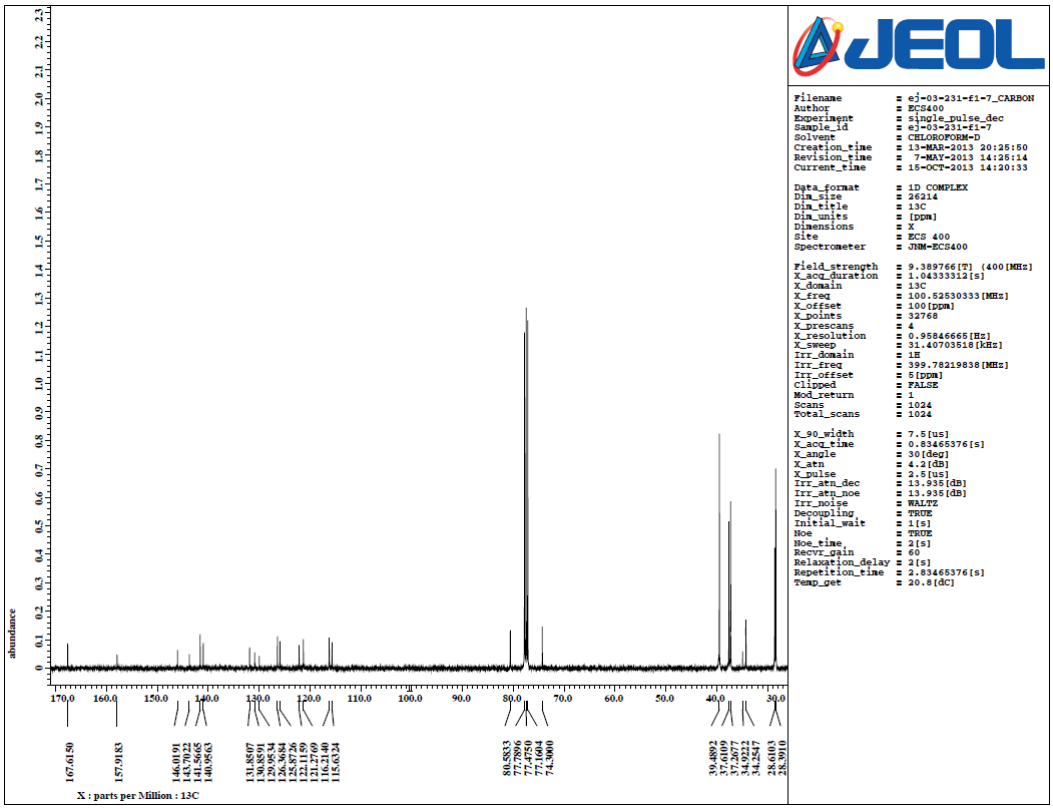


Figure 19: ^{1}H NMR of *6-(methoxyadamantan-1-yl)-3-(1-(5-chloro)benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **6**

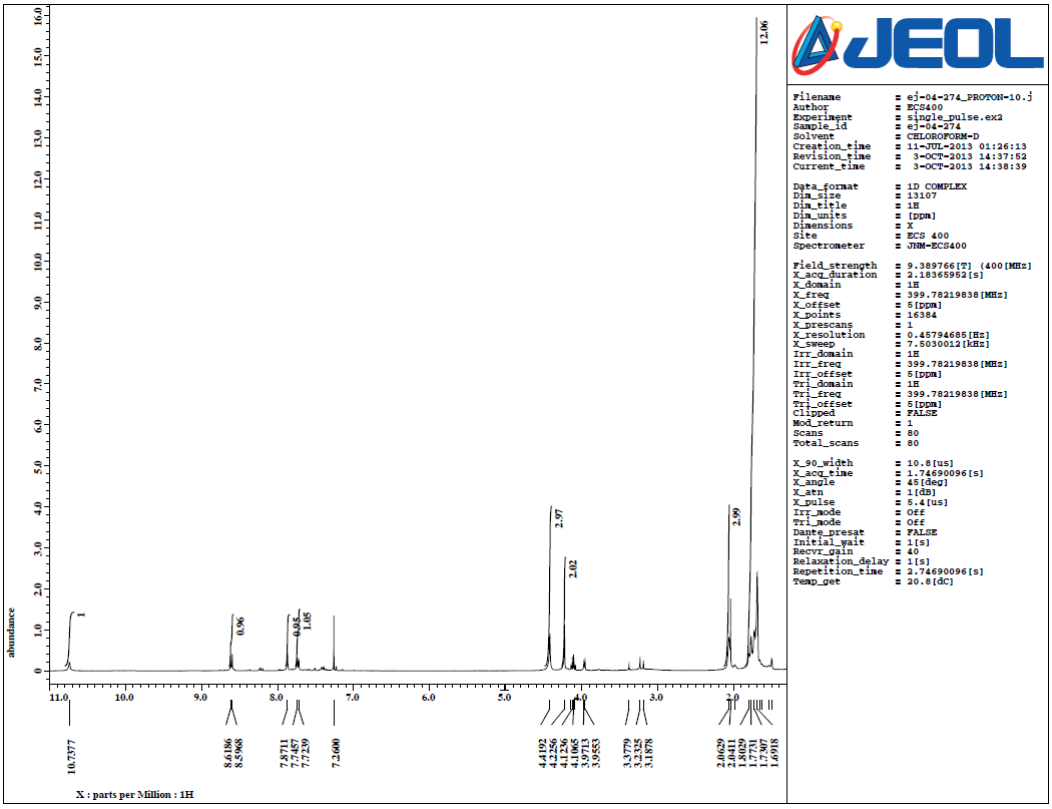
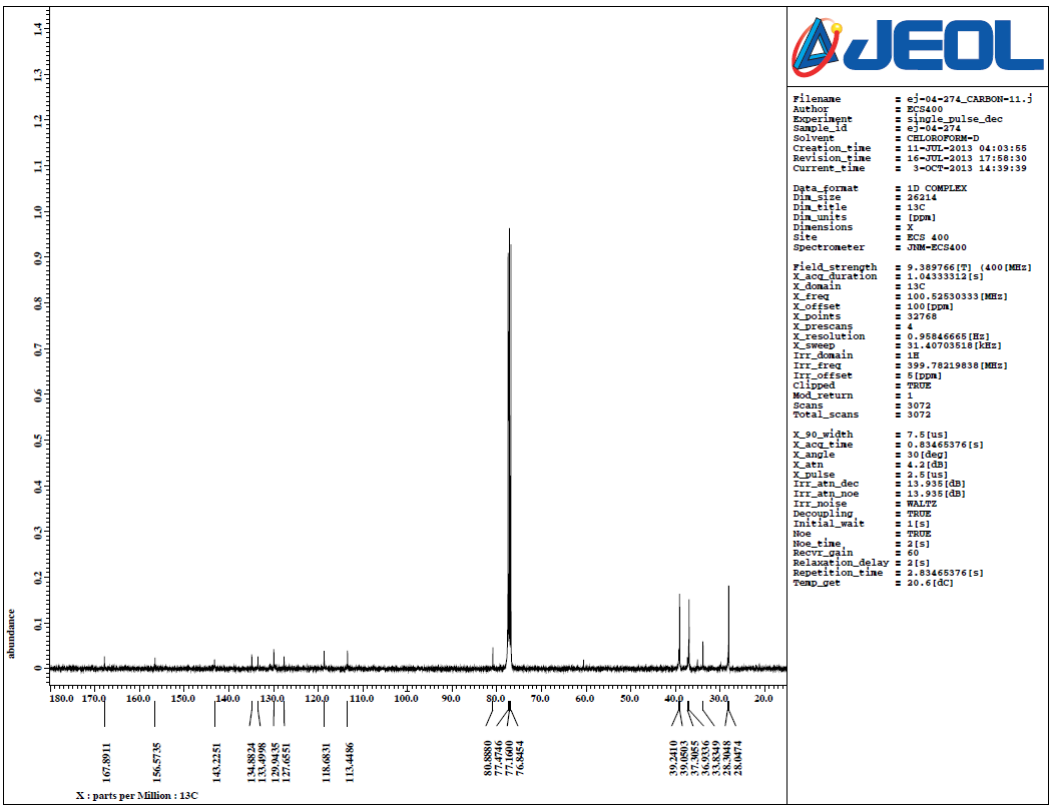
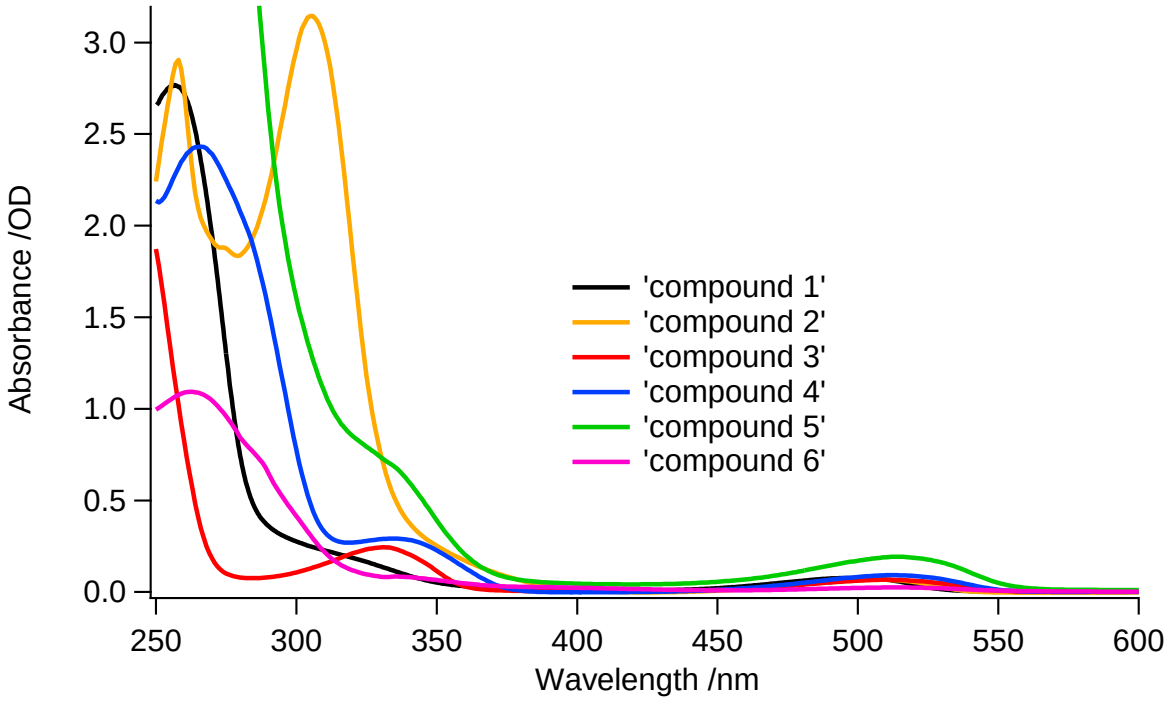


Figure 20: ^{13}C NMR of *6-(methoxyadamantan-1-yl)-3-(1-(5-chloro)benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **6**



UV-Vis absorption and fluorescence emission spectra

Figure 21: UV-Vis absorption spectra of tetrazines **1 -6** in acetonitrile.



Expanded plot of the absorbance between 400 and 600nm (n-π* transition):

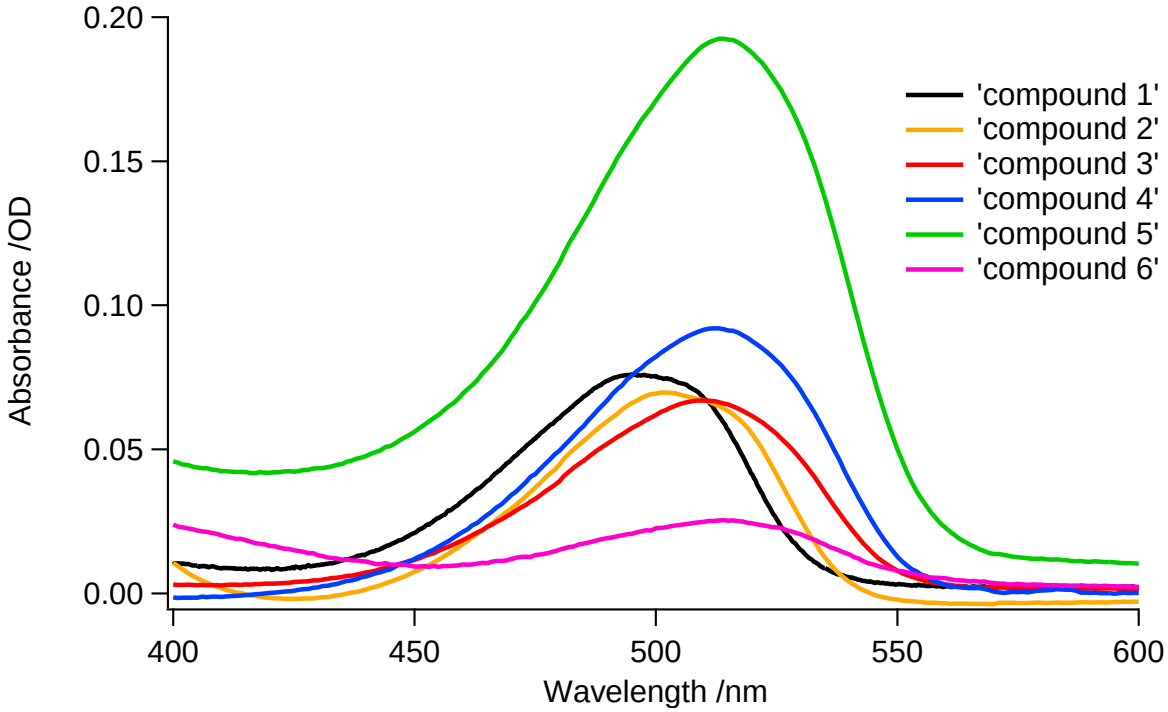
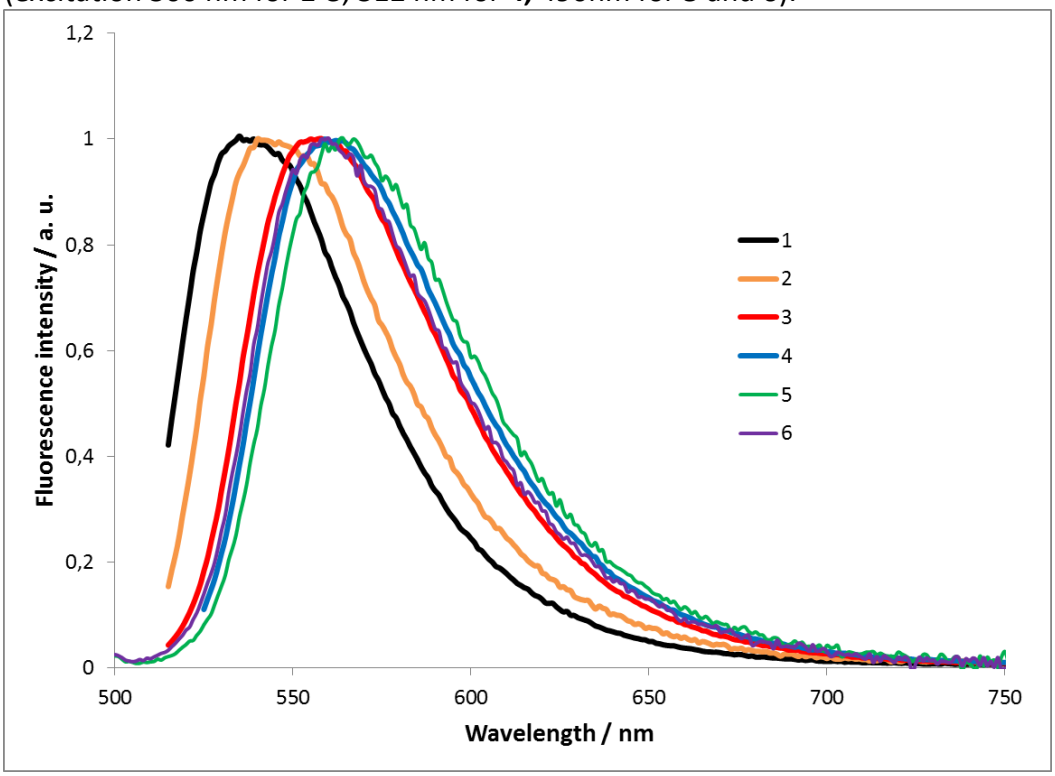
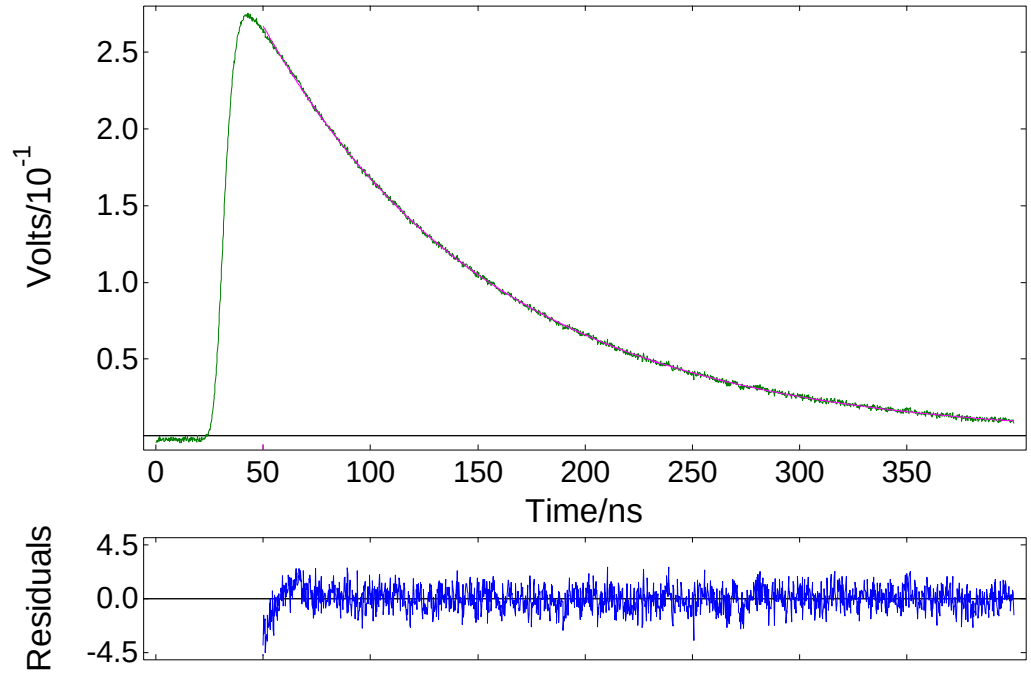


Figure 22: Normalized fluorescence emission spectra of tetrazine **1-4** in acetonitrile (excitation 500 nm for **1**-**3**, 512 nm for **4,** 490nm for **5** and **6**).



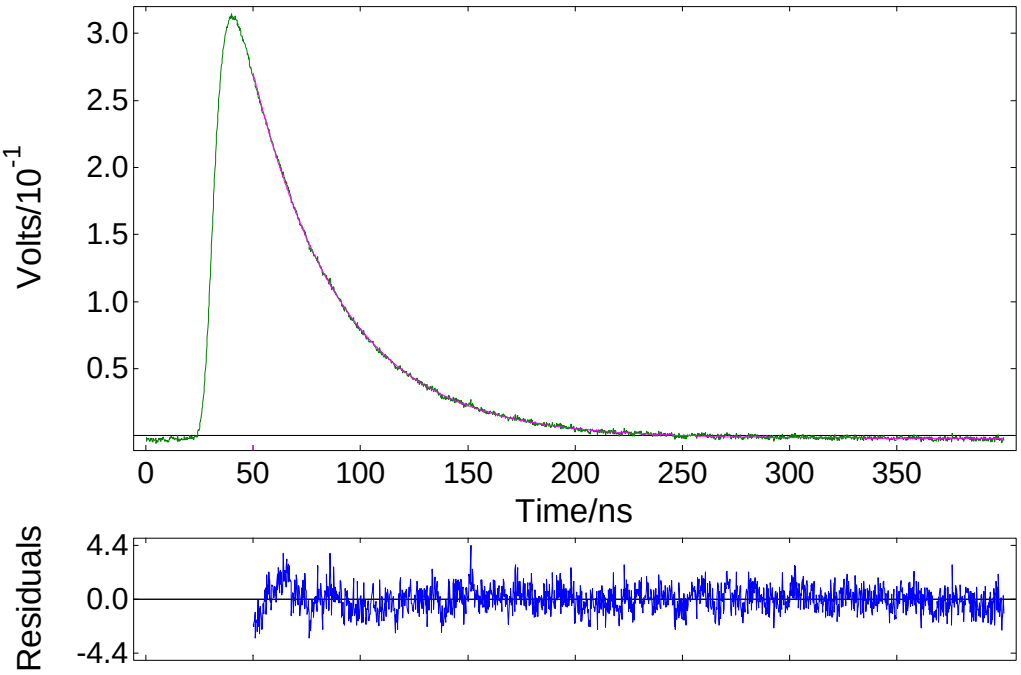
Fluorescence decays

Figure 23: Fluorescence decay of *3,6-bis(1-N-ethyl-imidazolium)-s-tetrazine tetrafluoroborate* **1** in acetonitrile (excitation 355 nm, emission 515 nm)



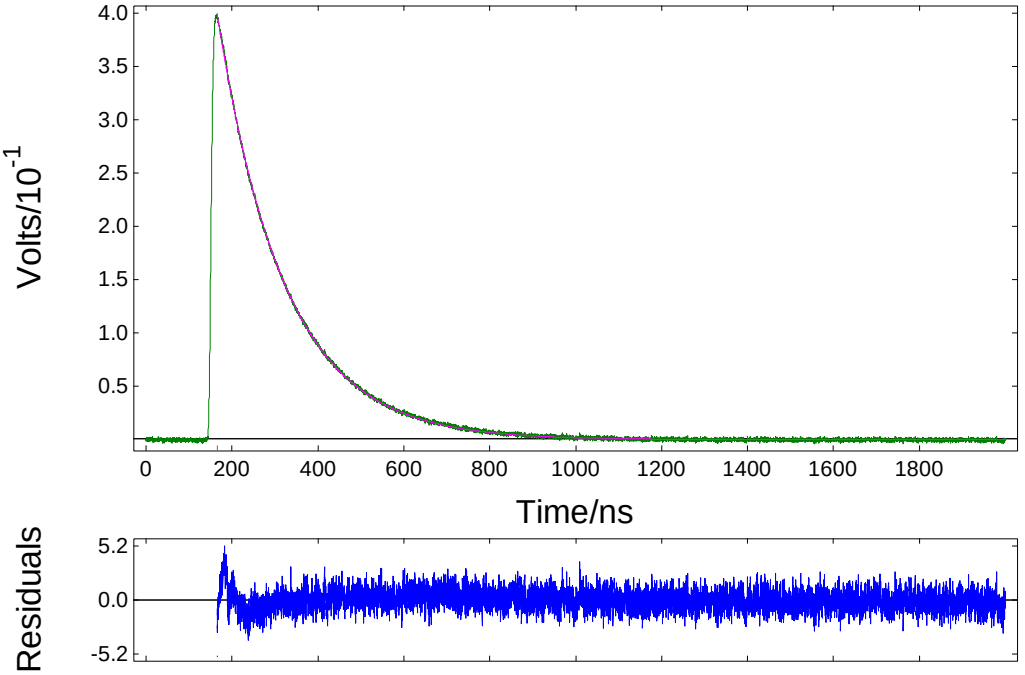
τ=108 ns χ^2=0.956

Figure 24: Fluorescence decay of *3,6-bis(1-N-methyl-benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **2** in acetonitrile (excitation 355 nm, emission 541 nm)



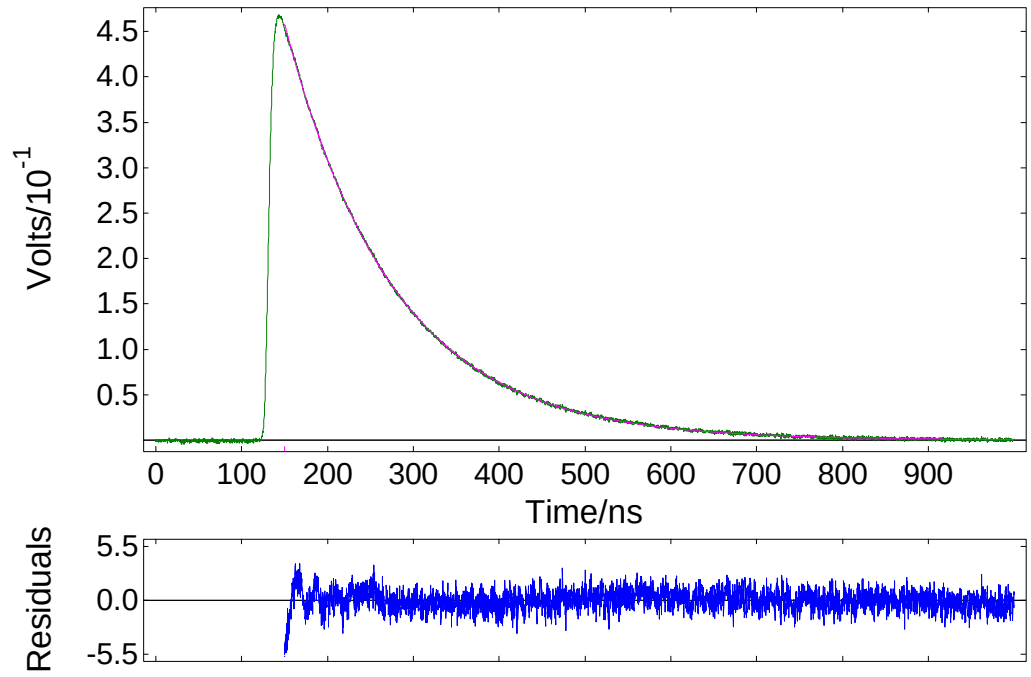
τ=41 ns χ^2=1.03

Figure 25: Fluorescence decay of of *6-(methoxyadamantan-1-yl)-3-(1-N-methyl-imidazolium)-s-tetrazine trifluoromethanesulfonate* **3** in acetonitrile (excitation 355 nm, emission 565 nm)



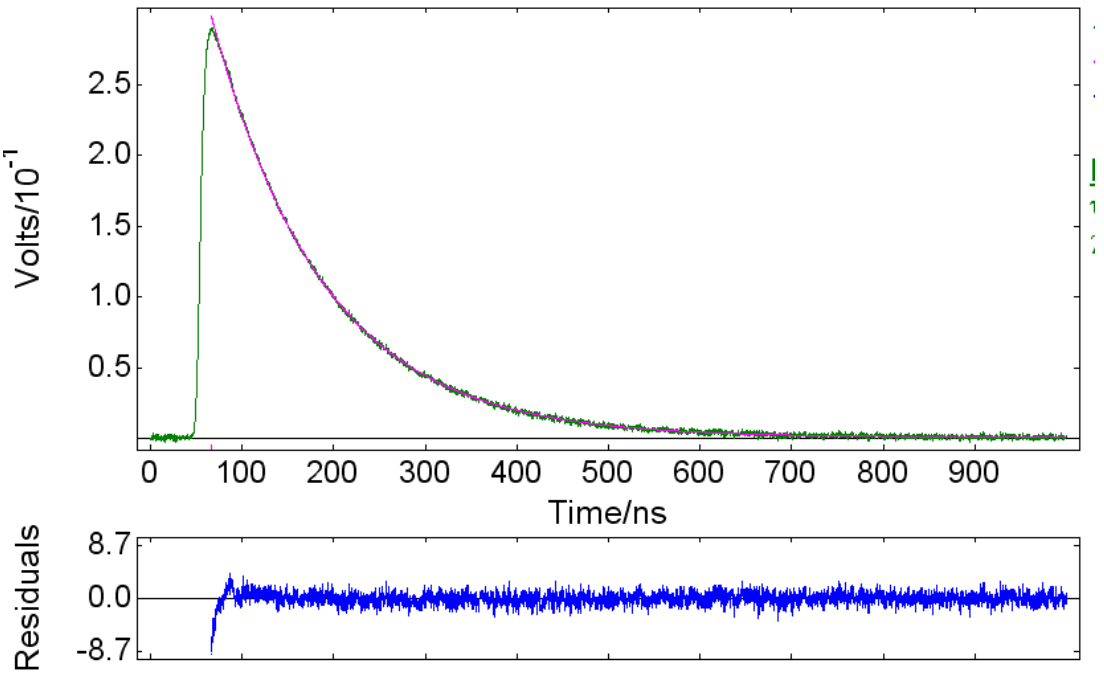
τ=156 ns χ^2=0.97

Figure 26: fluorescence decay of *6-(methoxyadamantan-1-yl)-3-(1-N-methyl-benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **4** in acetonitrile (excitation 355 nm, emission 555 nm)



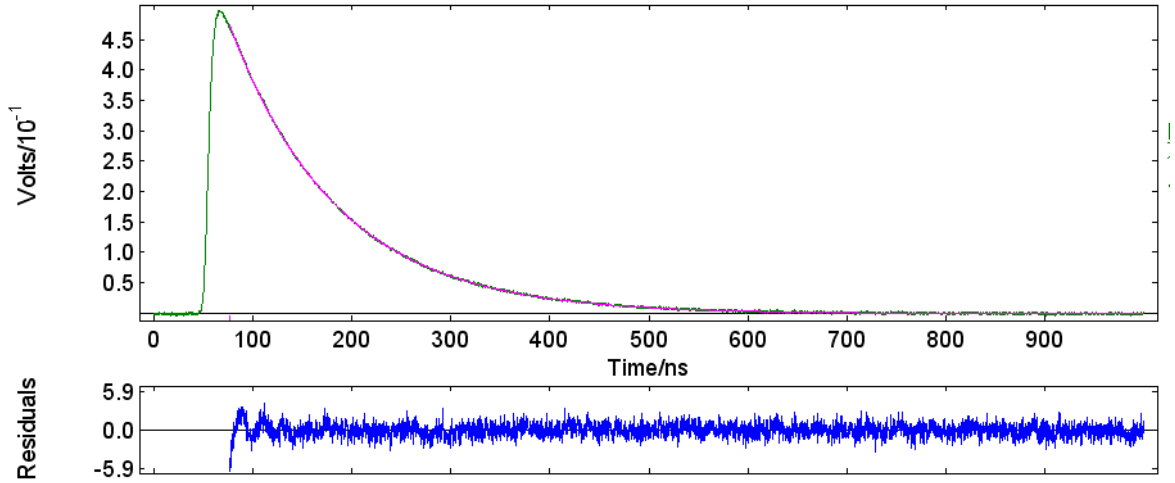
τ=125 ns χ^2=1.05

Figure 27: fluorescence decay of *6-(methoxyadamantan-1-yl)-3-(1-(2-nonyl)-N-methyl-benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **5** in dichloromethane (excitation 355 nm, emission 575 nm)



τ=122 ns χ^2=1.08

Figure 28: fluorescence decay of *6-(methoxyadamantan-1-yl)-3-(1-(5-chloro)benzimidazolium)-s-tetrazine trifluoromethanesulfonate* **6** in dichloromethane (excitation 355 nm, emission 565 nm)



τ=110 ns χ^2=1.08

Time-resolved quenching experiments

Figure 29: Fluorescence decays of tetrazine **1** ($4.0.10^{-4}$ M in acetonitrile) in the presence of increasing amounts of benzene (excitation 532 nm, emission 560 nm)

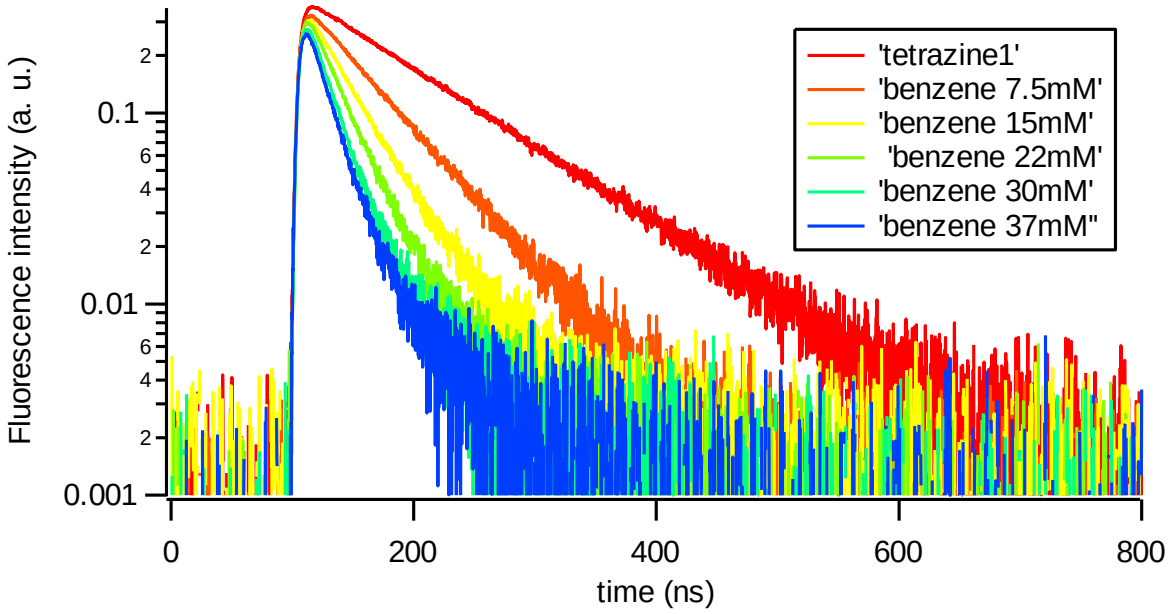


Figure 30: Fluorescence decays of tetrazine **2** ($2.7.10^{-4}$ M in acetonitrile) in the presence of increasing amounts of benzene (excitation 532 nm, emission 560 nm)

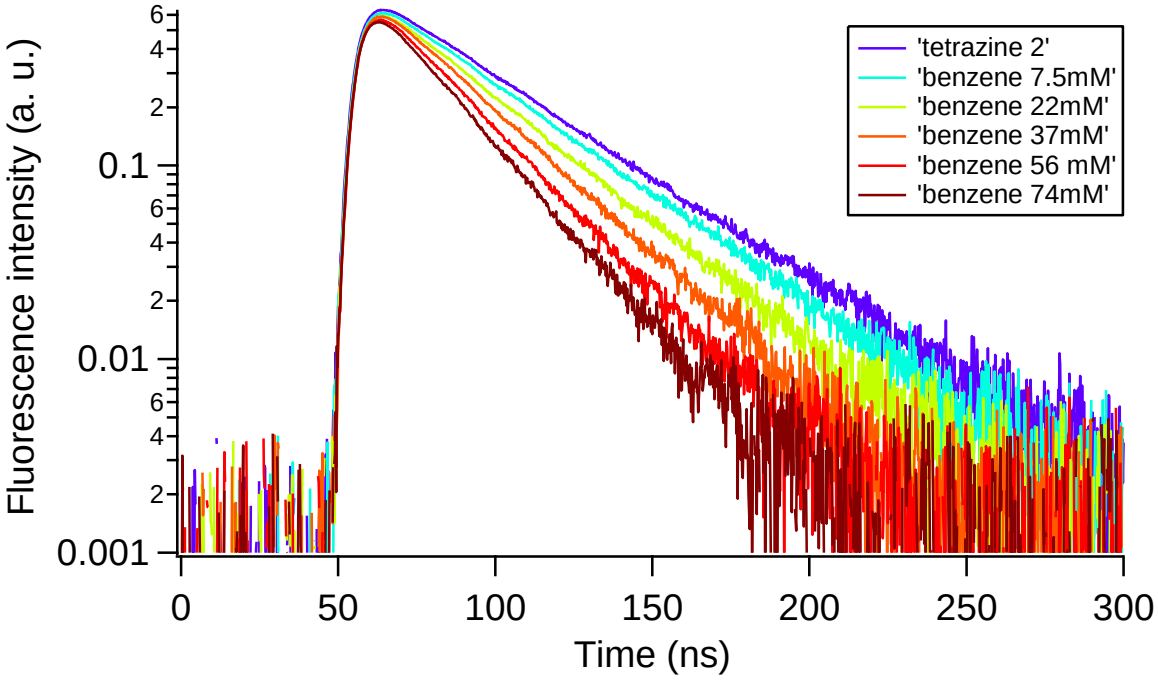


Figure 31: Fluorescence decays of tetrazine **3** ($2.0.10^{-4}$ M in acetonitrile) in the presence of increasing amounts of benzene (excitation 532 nm, emission 560 nm)

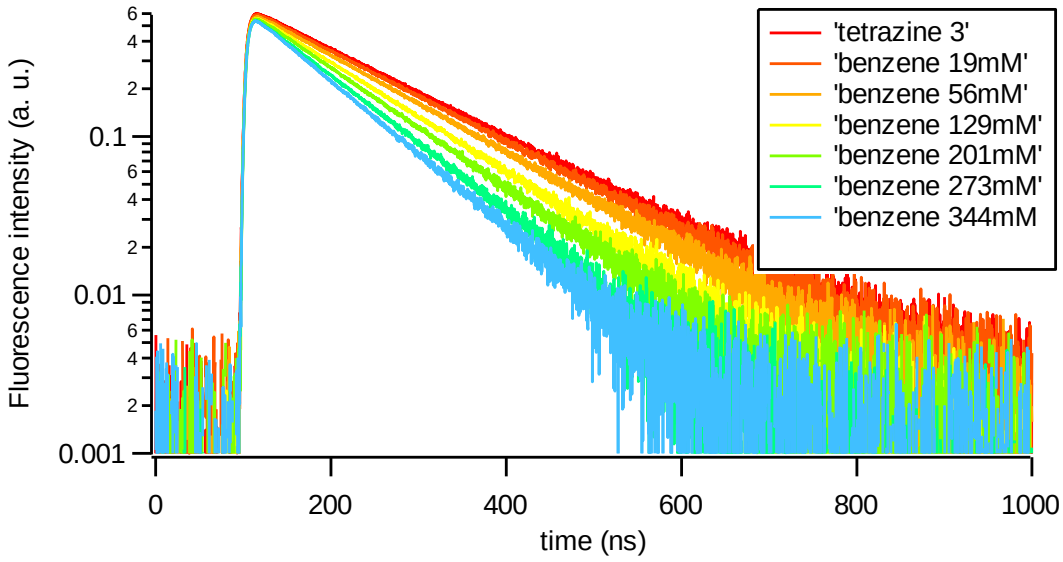


Figure 32: Fluorescence decays of tetrazine **4** ($1.5.10^{-4}$ M in acetonitrile in the presence of increasing amounts of benzene (excitation 532 nm, emission 560 nm)

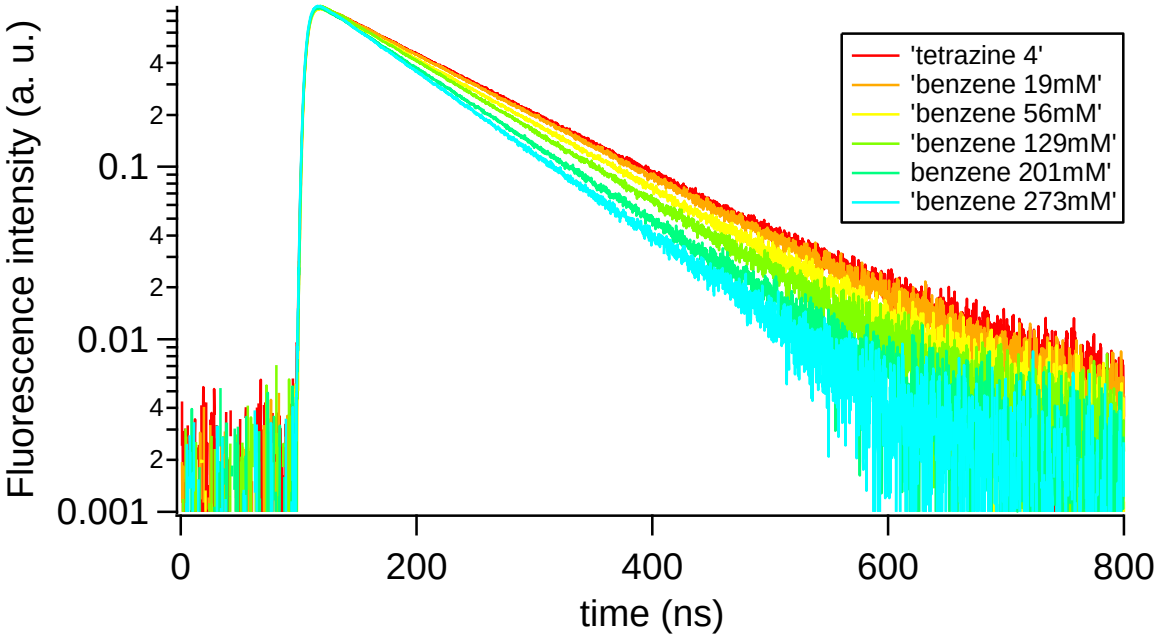


Figure 33: Scheme of the home-made perfusion chamber used for the quenching experiments by benzene vapors. A concentration of 1mmol benzene/L air is obtained upon a 5% v/v benzene solution in squalane at 293K.