

Supplementary Material

1,3,4-Thiadiazol-2-ylphenyl-1,2,4,5-tetrazines: efficient synthesis via Pinner reaction and their luminescent properties

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Table of Contents

1. ¹ H and ¹³ C NMR Spectra of synthesized compounds 6a-d	S2
2. ¹ H and ¹³ C NMR Spectra of synthesized compounds 8a-j	S6
3. UV-Vis spectra 8a-j	S16
4. 3D fluorescence spectra 8a-j	S17
5. 2D fluorescence spectra 8a-j	S21
6. The scatter plots representing relationships between absorption-emission properties	S22

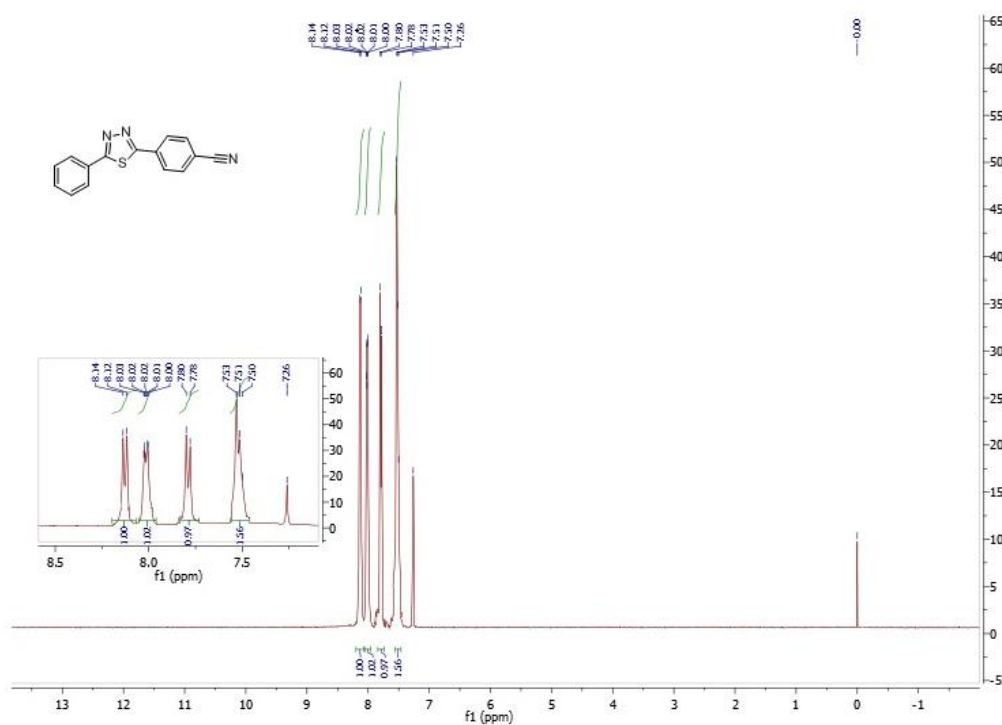
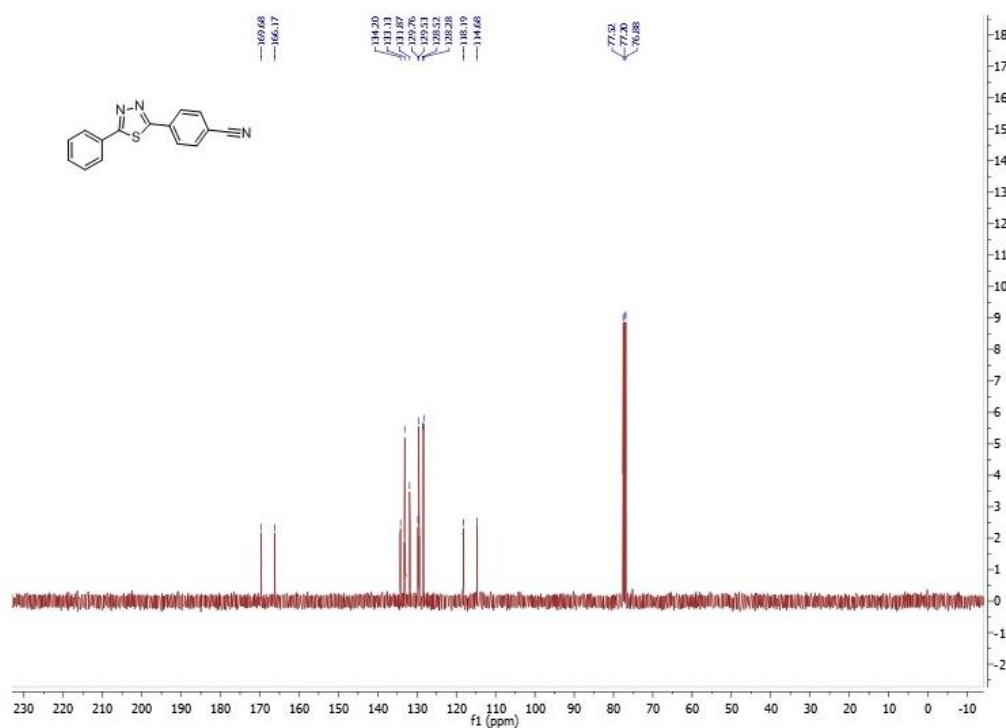
^1H and ^{13}C NMR Spectra of synthesized compounds 6a-d**Figure S1: ^1H NMR 4-(5-Phenyl-1,3,4-thiadiazol-2-yl)benzonitrile (6a)****Figure S2: ^{13}C NMR 4-(5-Phenyl-1,3,4-thiadiazol-2-yl)benzonitrile (6a)**

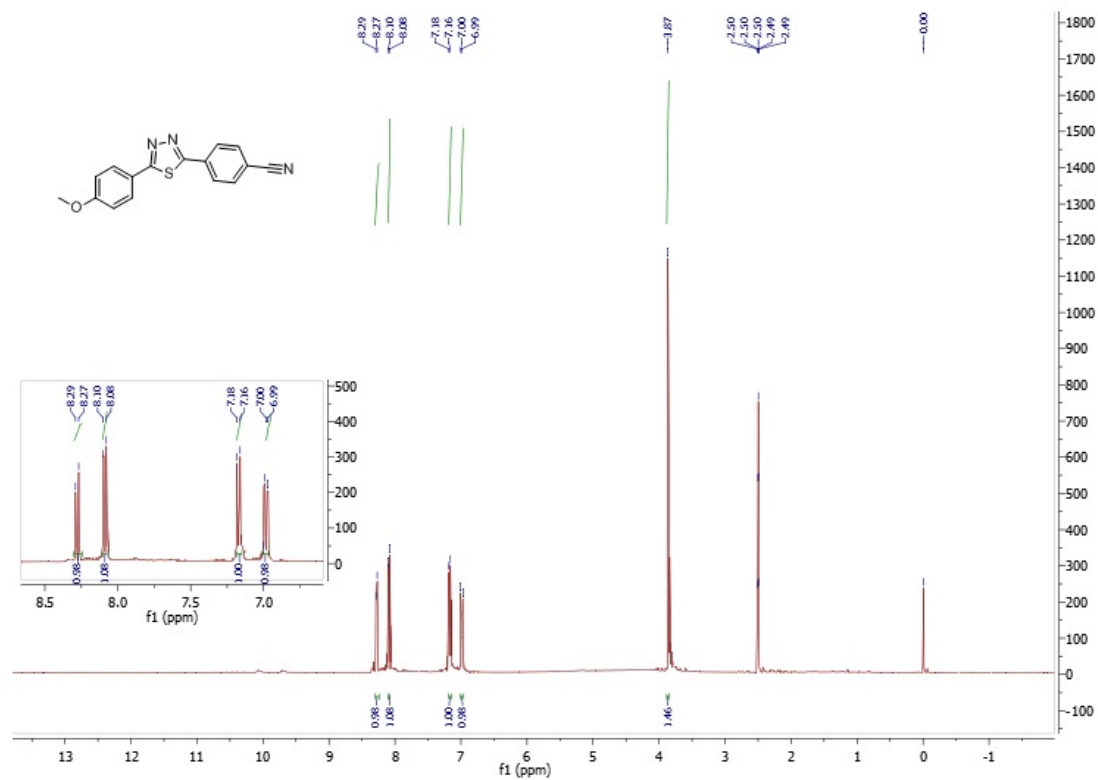
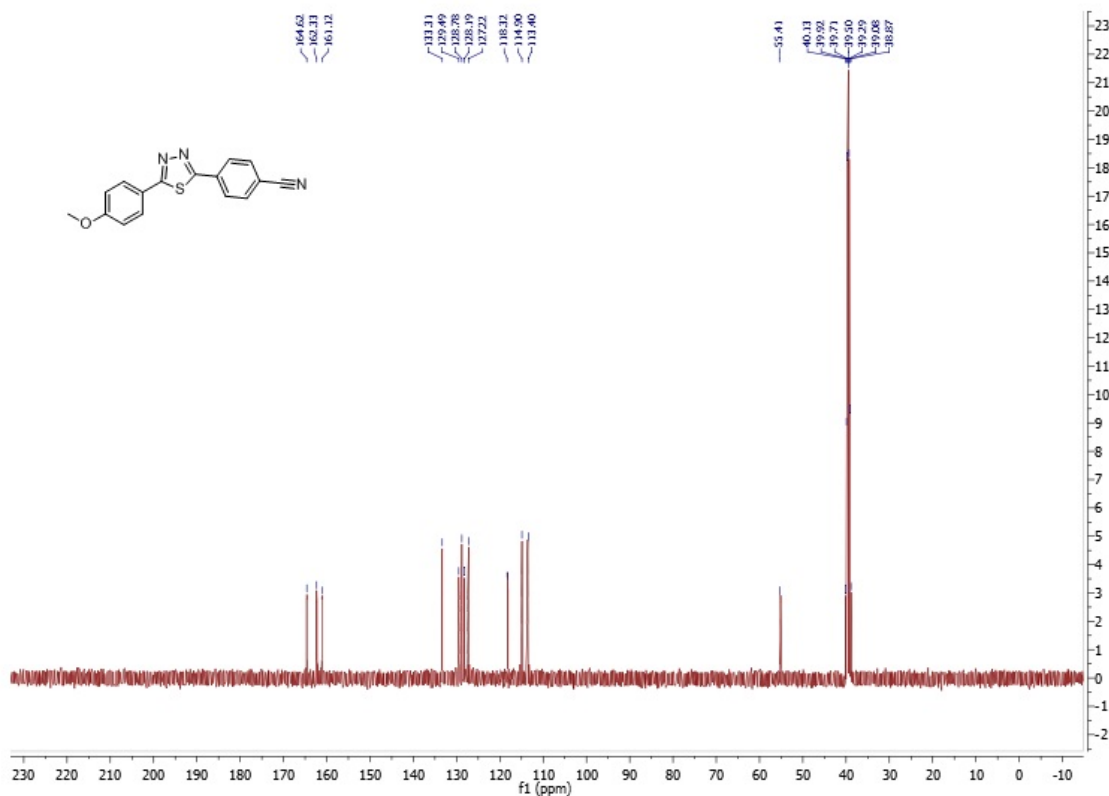
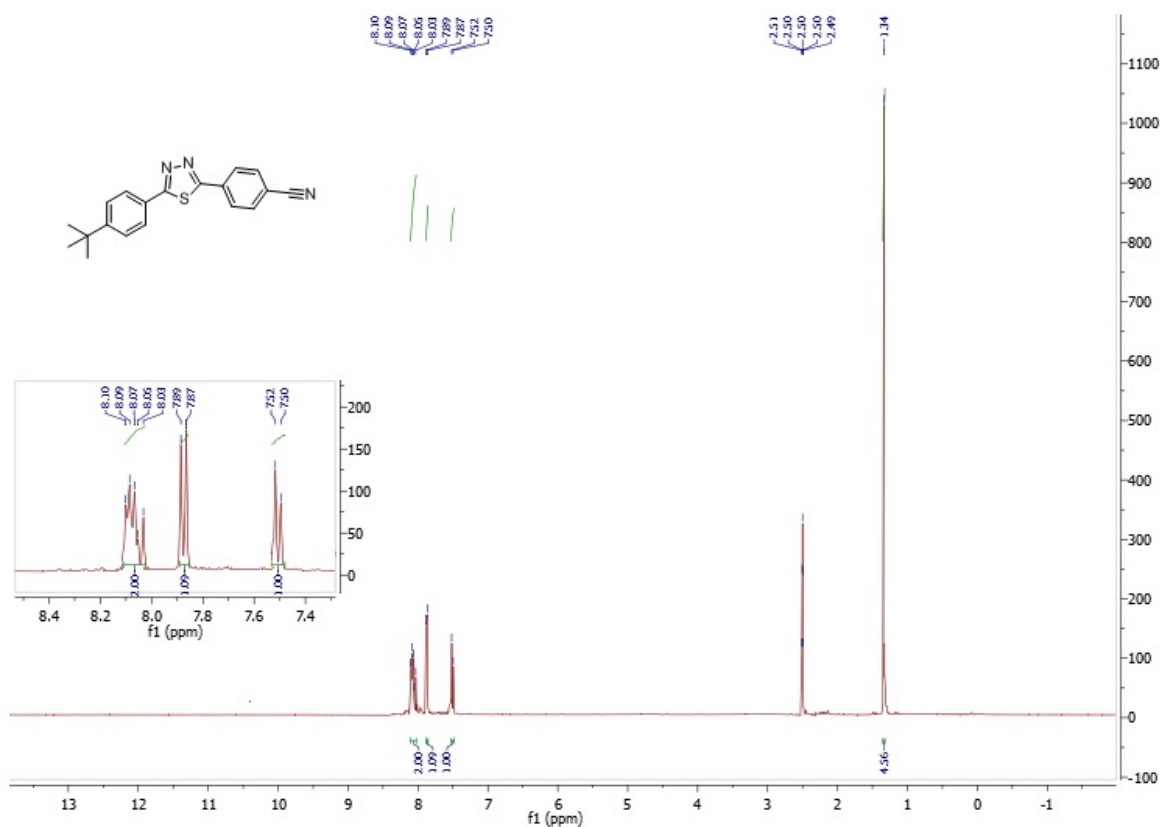
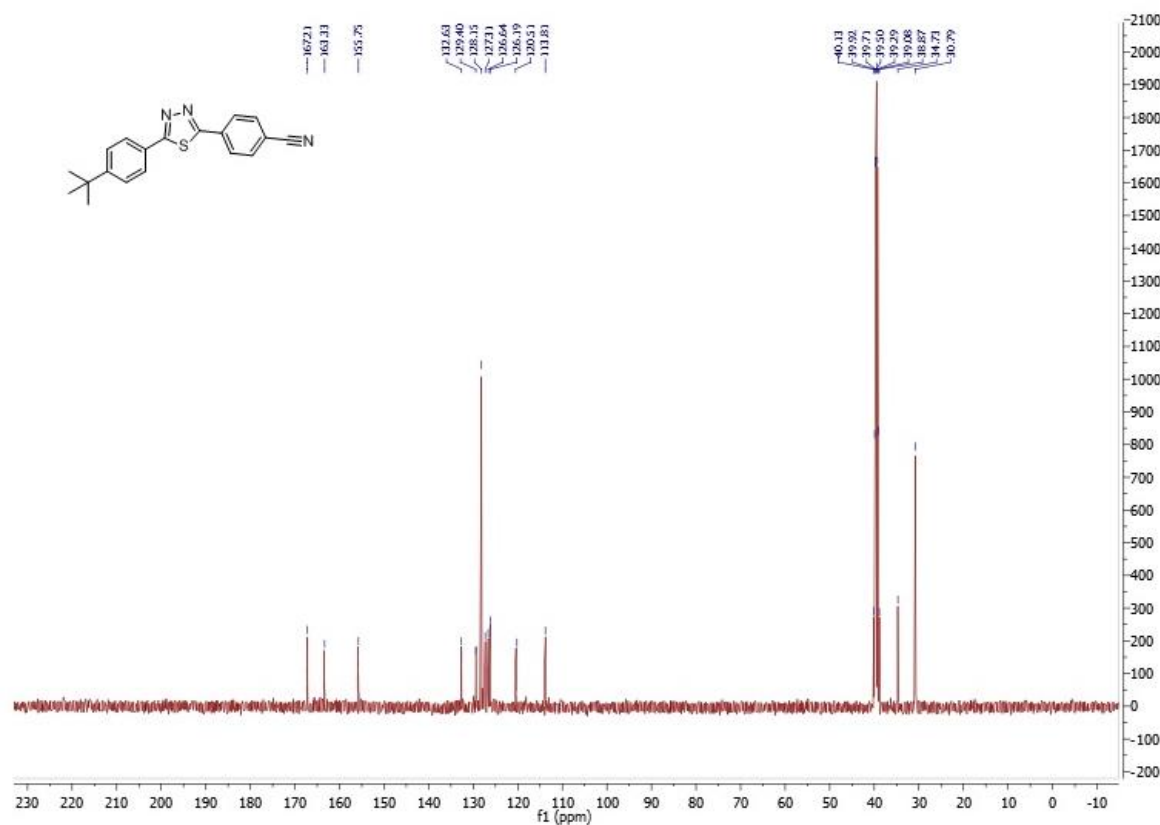
Figure S3: ^1H NMR 4-(5-(4-Methoxyphenyl)-1,3,4-thiadiazol-2-yl)benzonitrile (6b)Figure S4: ^{13}C NMR 4-(5-(4-Methoxyphenyl)-1,3,4-thiadiazol-2-yl)benzonitrile (6b)

Figure S5: ^1H NMR 4-(5-(4-(*tert*-Butyl)phenyl)-1,3,4-thiadiazol-2-yl)benzonitrile (6c)Figure S6: ^{13}C NMR 4-(5-(4-(*tert*-Butyl)phenyl)-1,3,4-thiadiazol-2-yl)benzonitrile (6c)

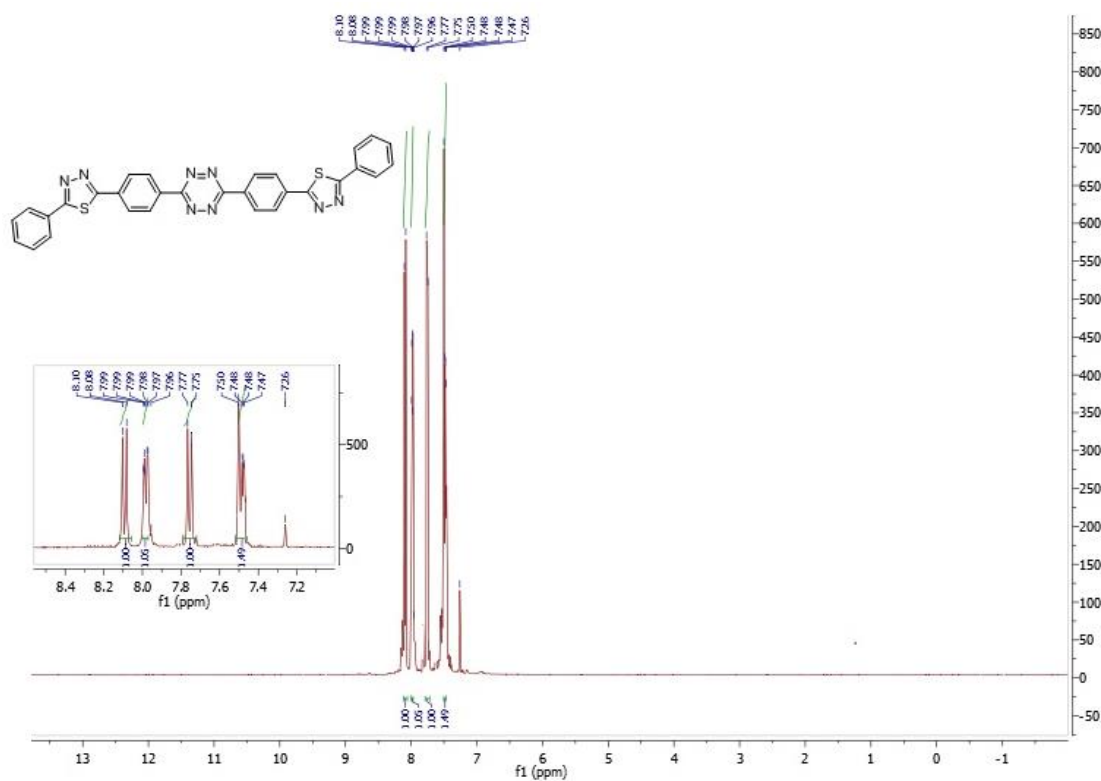
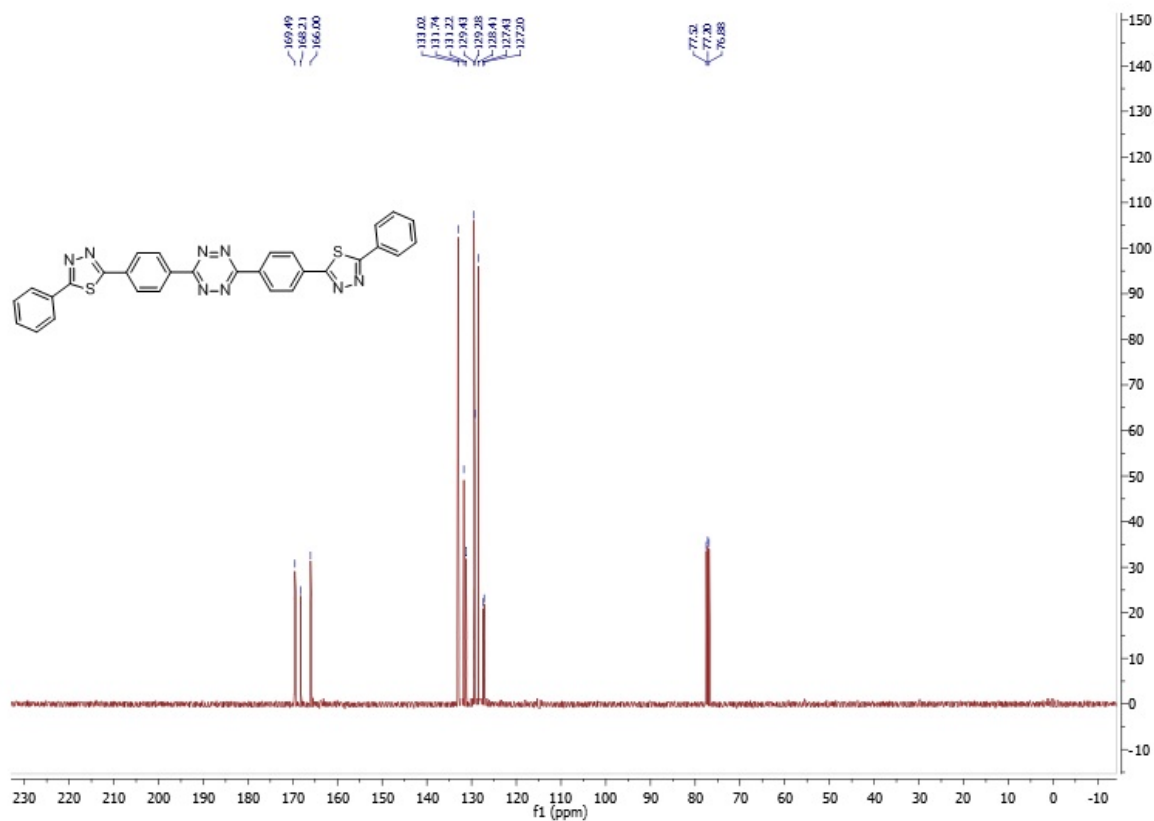
^1H and ^{13}C NMR Spectra of synthesized compounds 8a-jFigure S9: ^1H NMR 3,6-Bis(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8a)Figure S10: ^{13}C NMR 3,6-Bis(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8a)

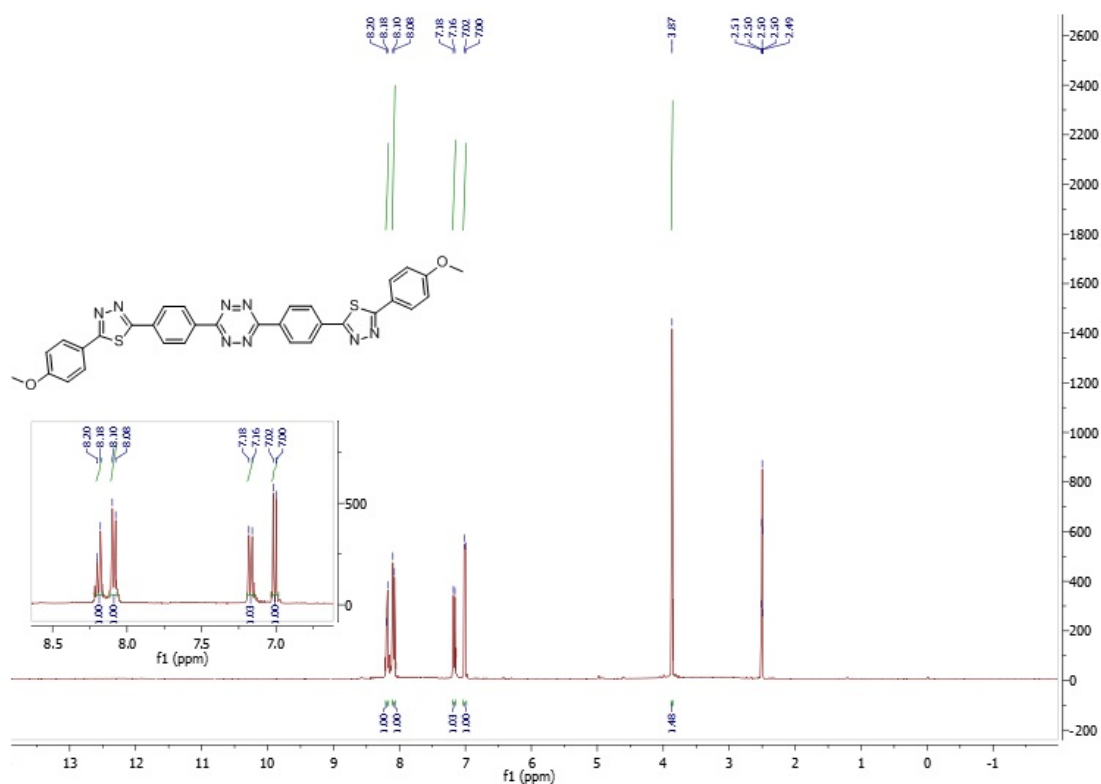
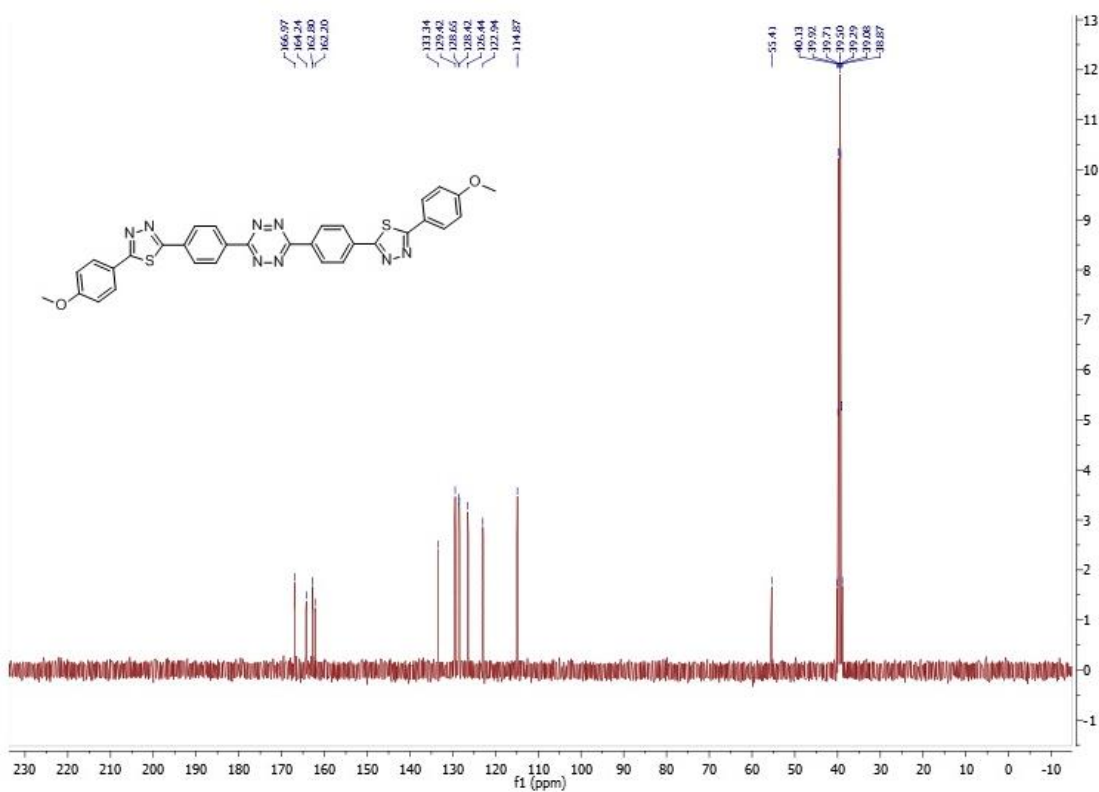
Figure S11: ^1H NMR 3,6-Bis(4-(5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8b)Figure S12: ^{13}C NMR 3,6-Bis(4-(5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8b)

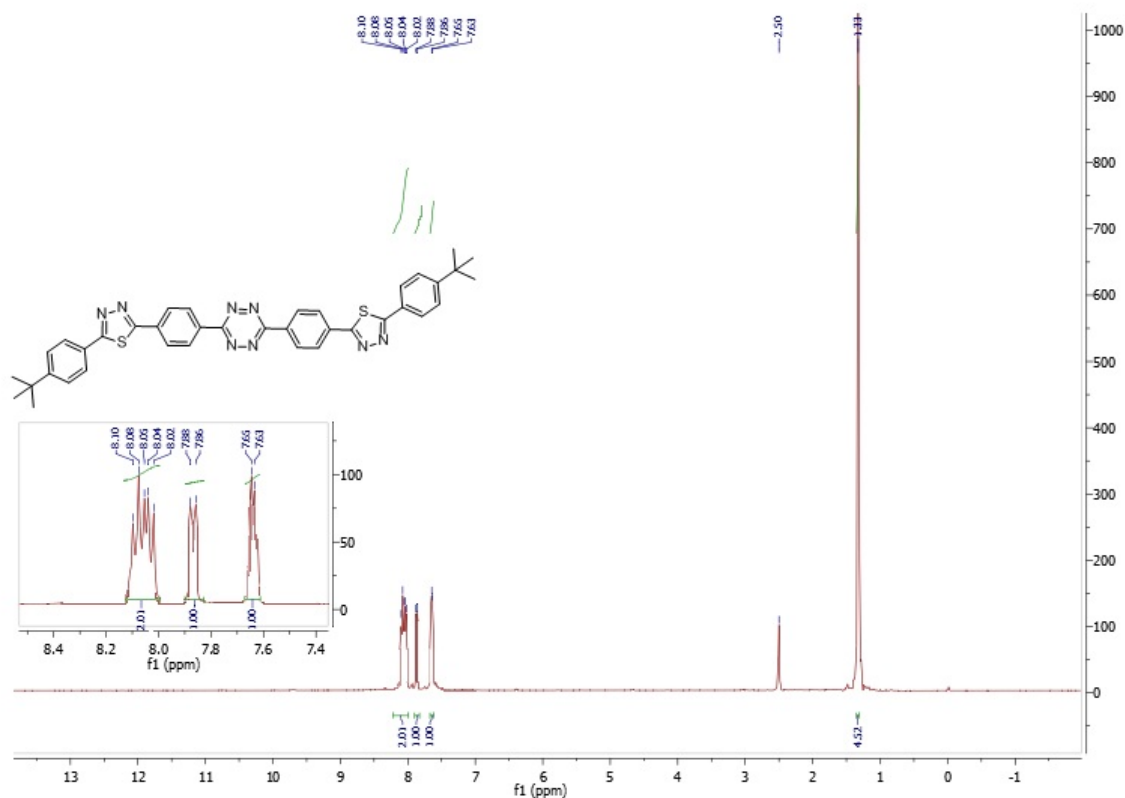
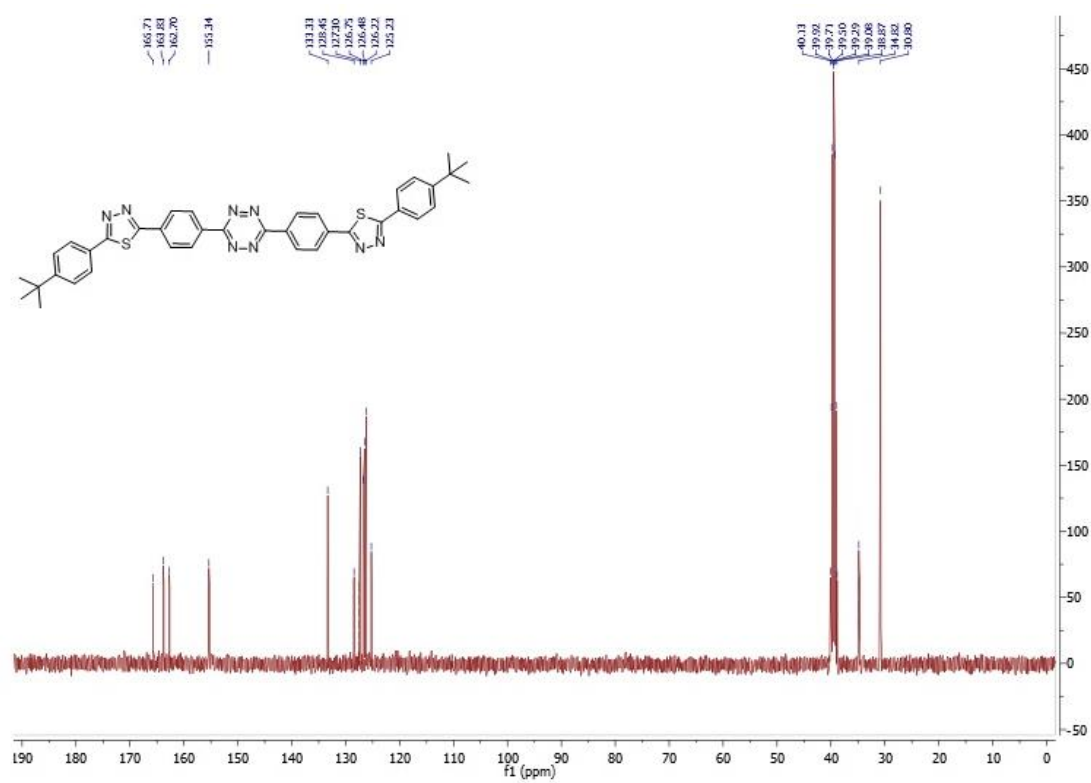
Figure S13: ^1H NMR 3,6-Bis(4-(5-(4-(*tert*-butyl)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8c)Figure S14: ^{13}C NMR 3,6-Bis(4-(5-(4-(*tert*-butyl)phenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8c)

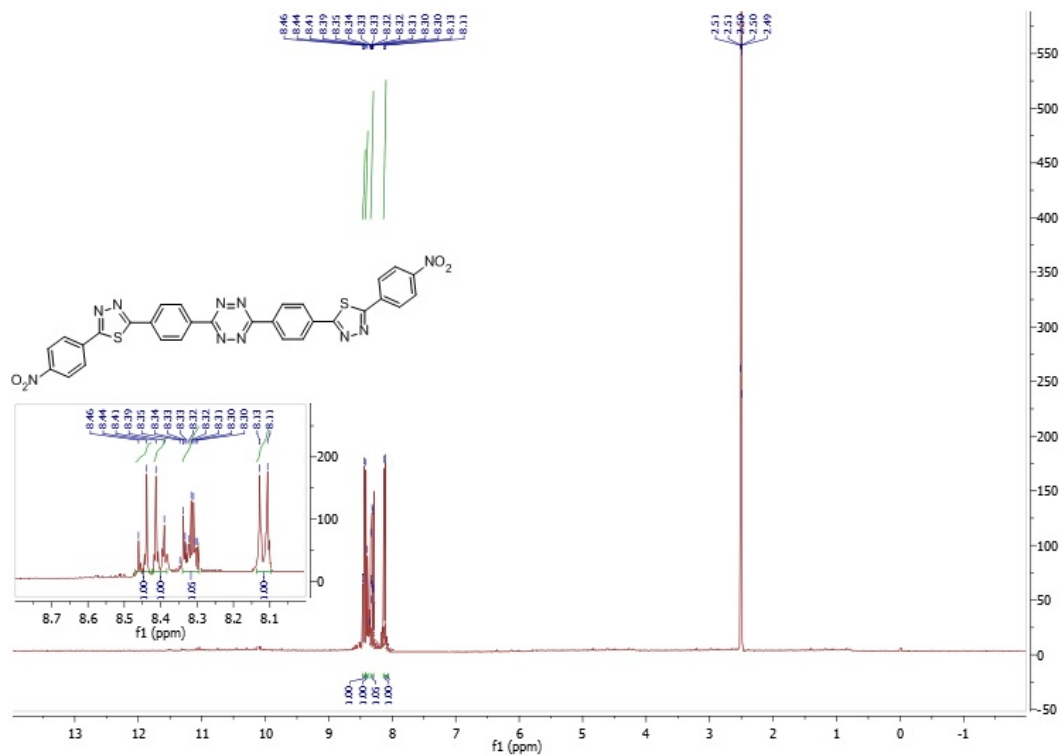
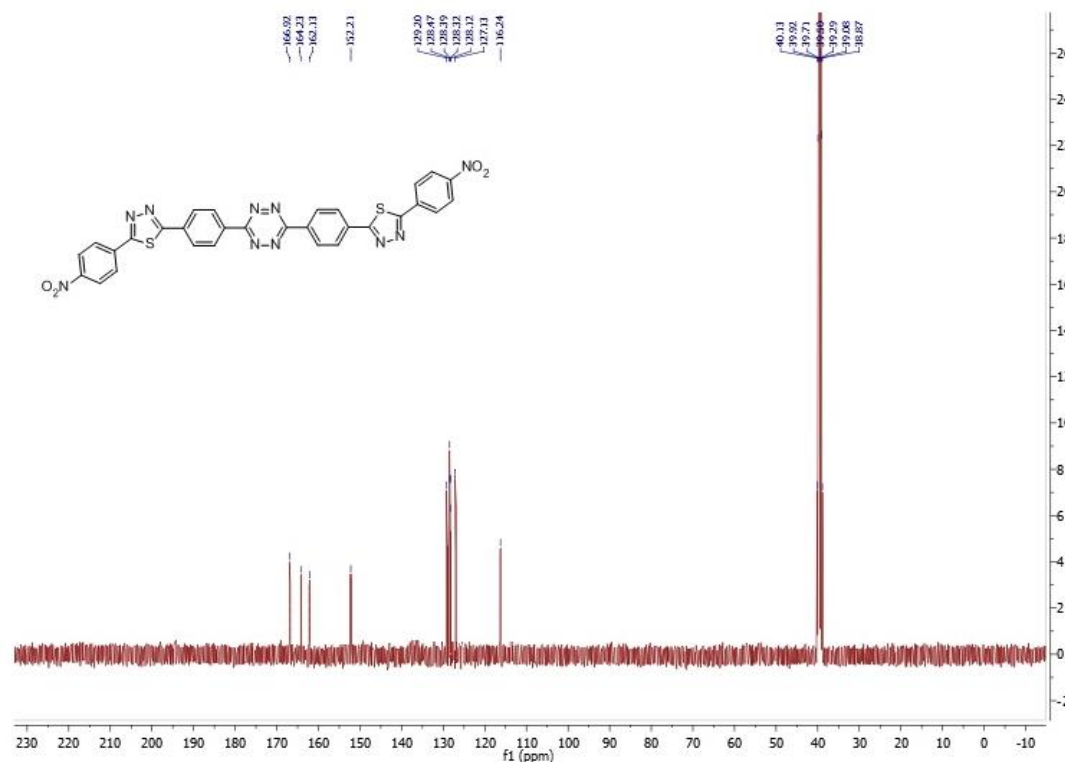
Figure S15: ^1H NMR 3,6-Bis(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8d)Figure S16: ^{13}C NMR 3,6-Bis(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazine (8d)

Figure S17: ^1H NMR 2-(4-Methoxyphenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8e)

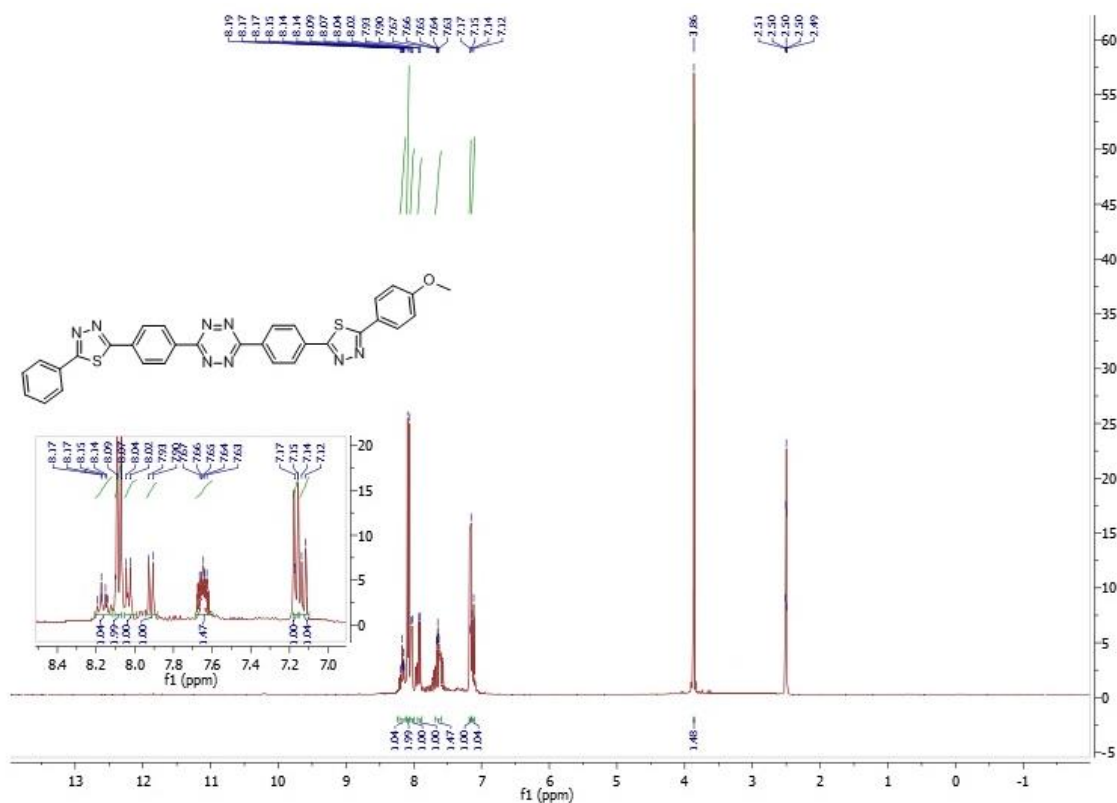


Figure S18: ^{13}C NMR 2-(4-Methoxyphenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8e)

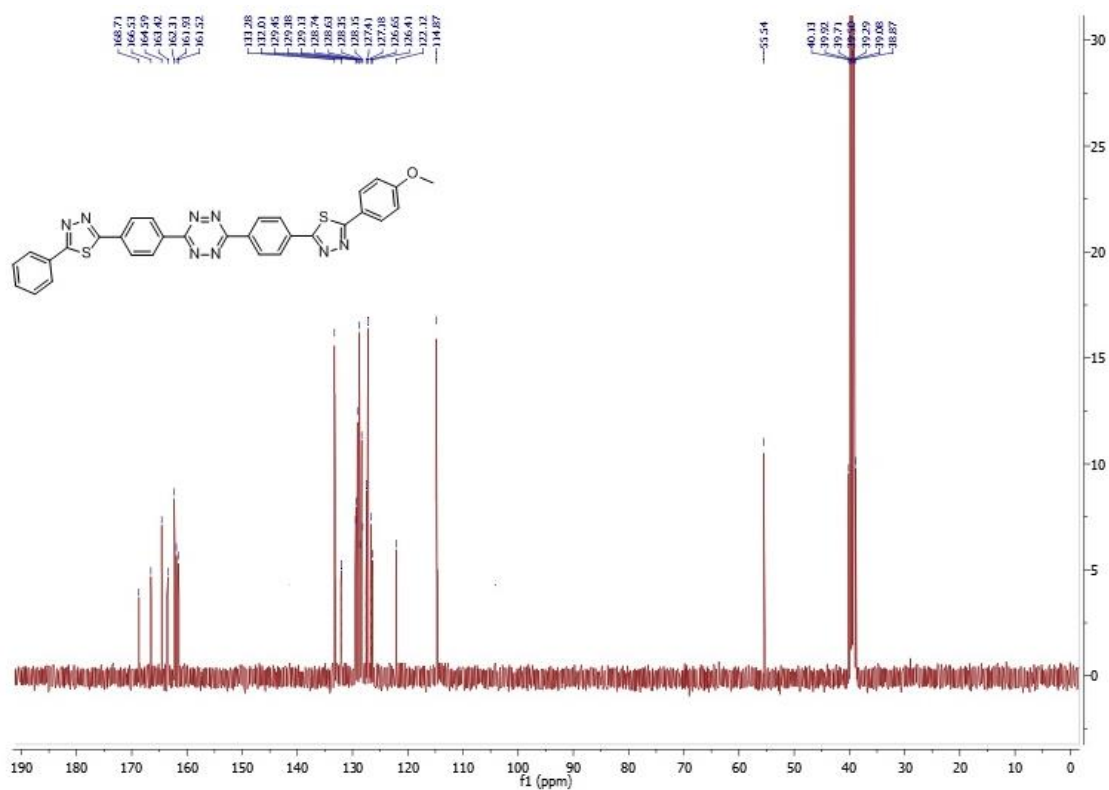


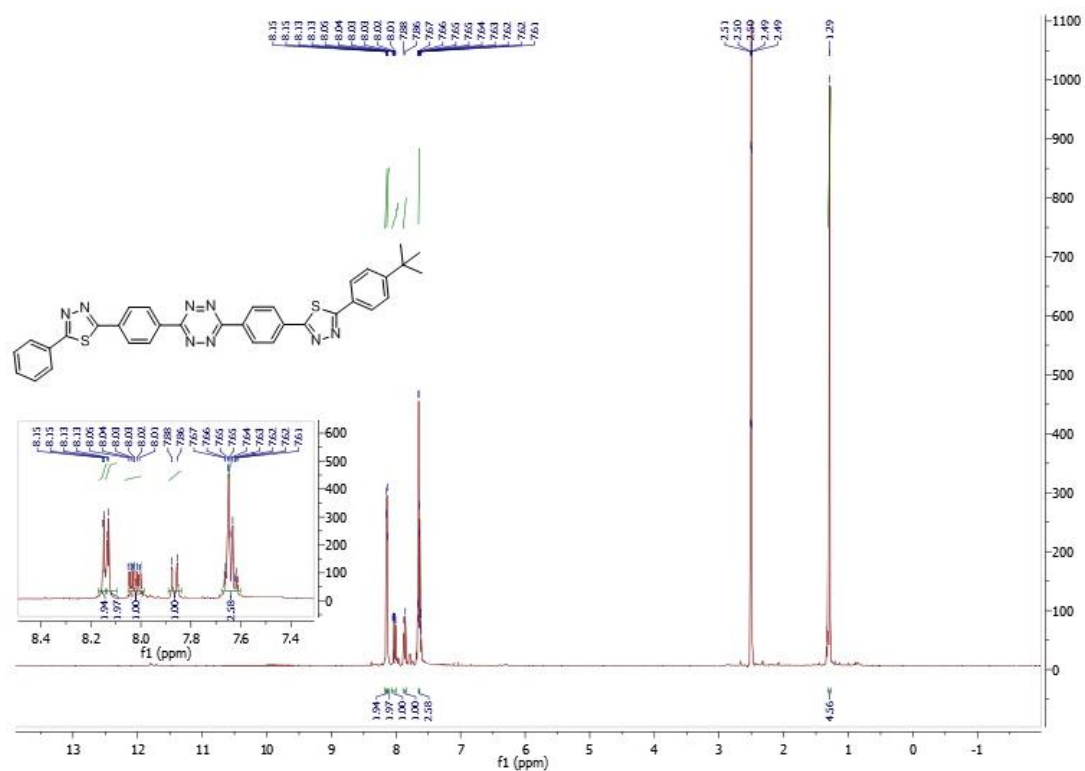
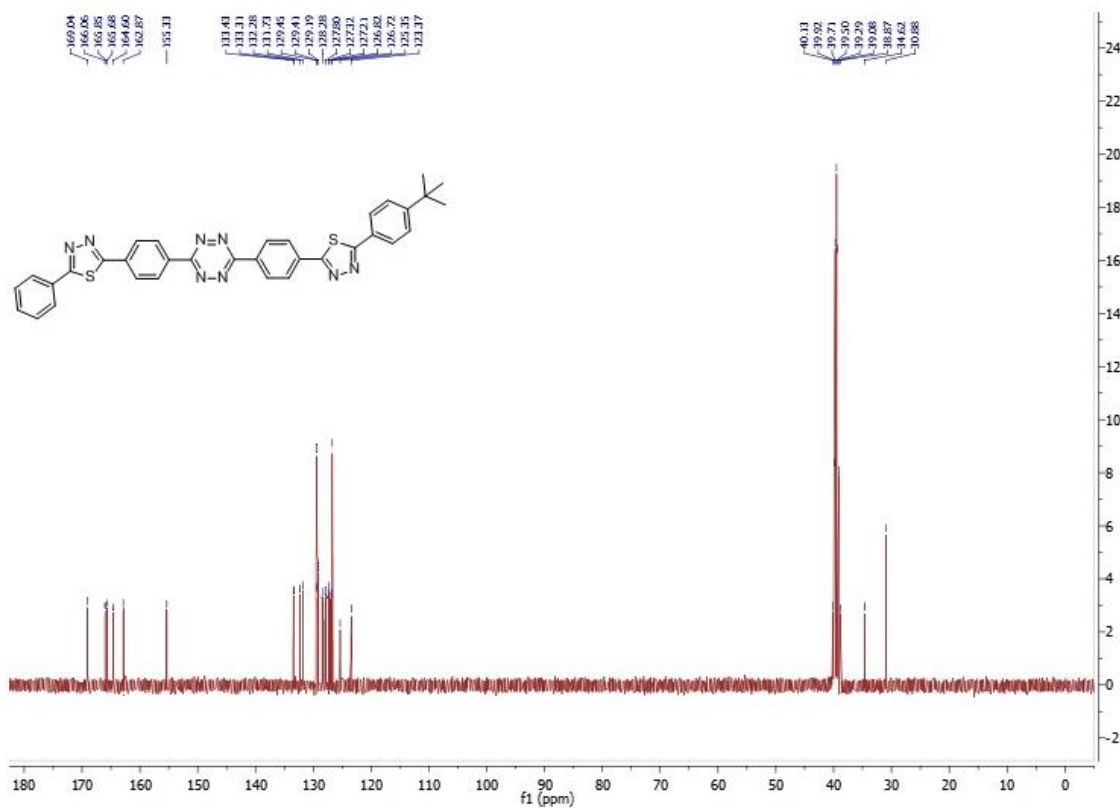
Figure S19: ^1H NMR 2-(4-(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8f)**Figure S20: ^{13}C NMR 2-(4-(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8f)**

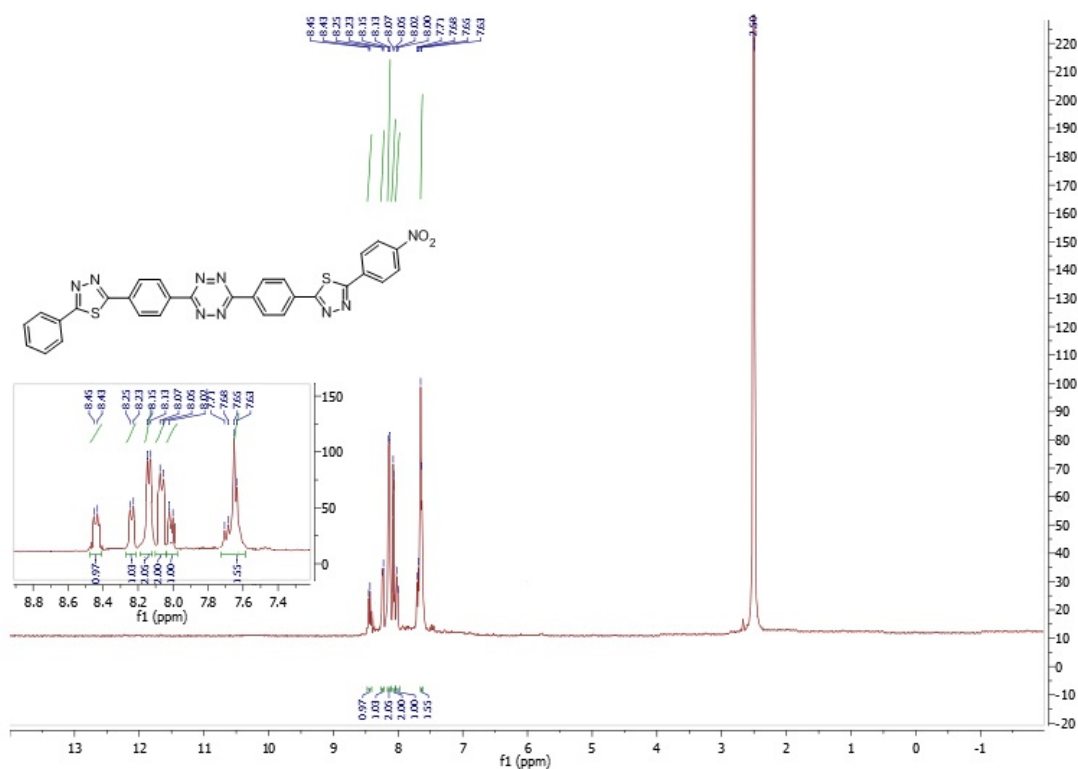
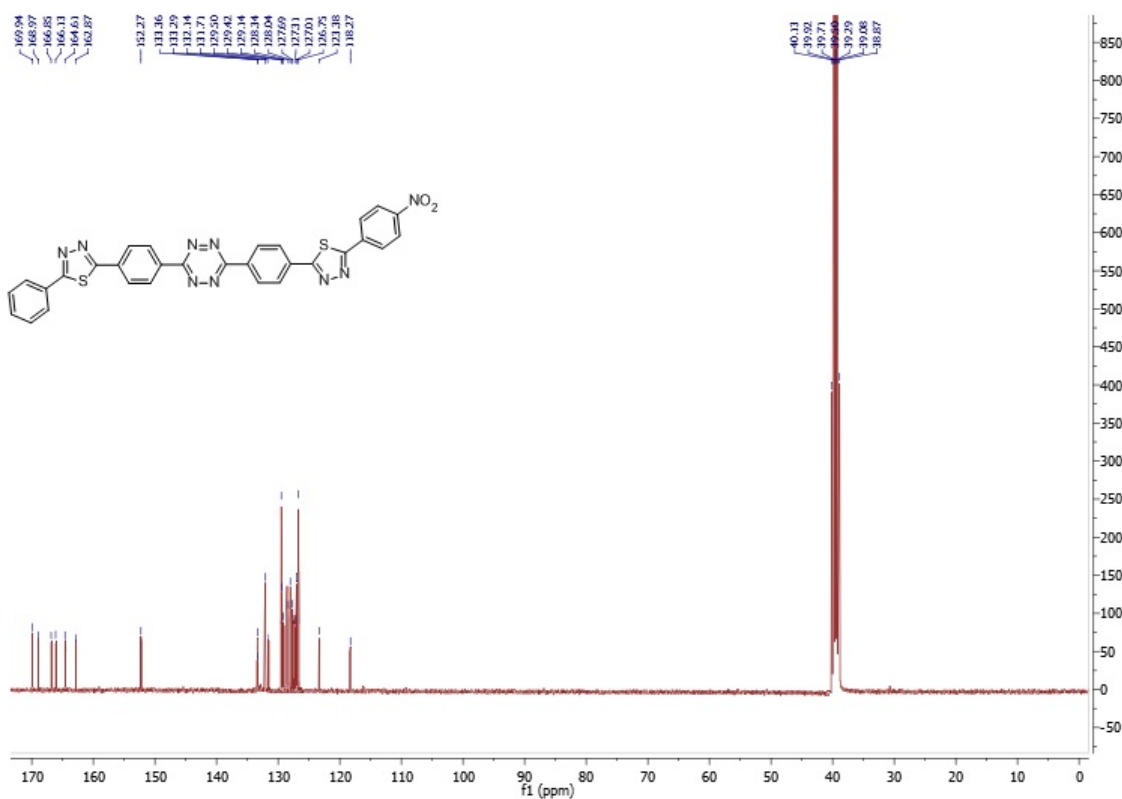
Figure S21: ^1H NMR 2-(4-Nitrophenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8g)**Figure S22: ^{13}C NMR 2-(4-Nitrophenyl)-5-(4-(6-(4-(5-phenyl-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8g)**

Figure S23: ^1H NMR 2-(4(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8h)

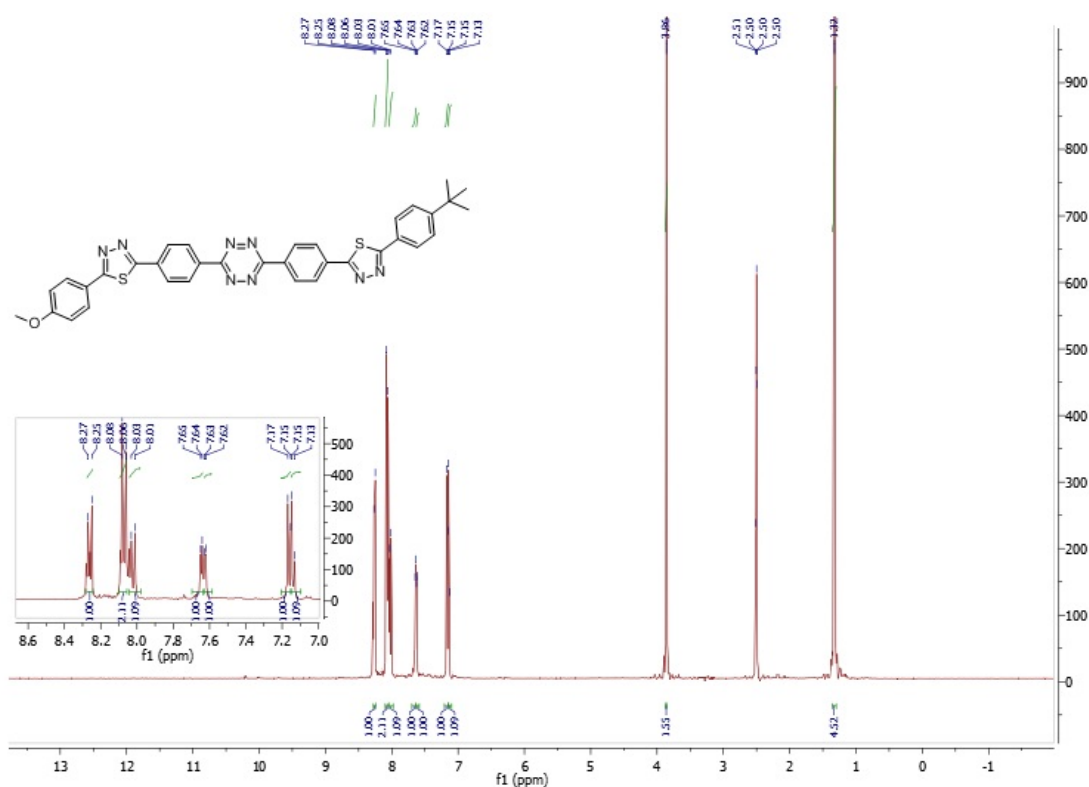


Figure S24: ^{13}C NMR 2-(4(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8h)

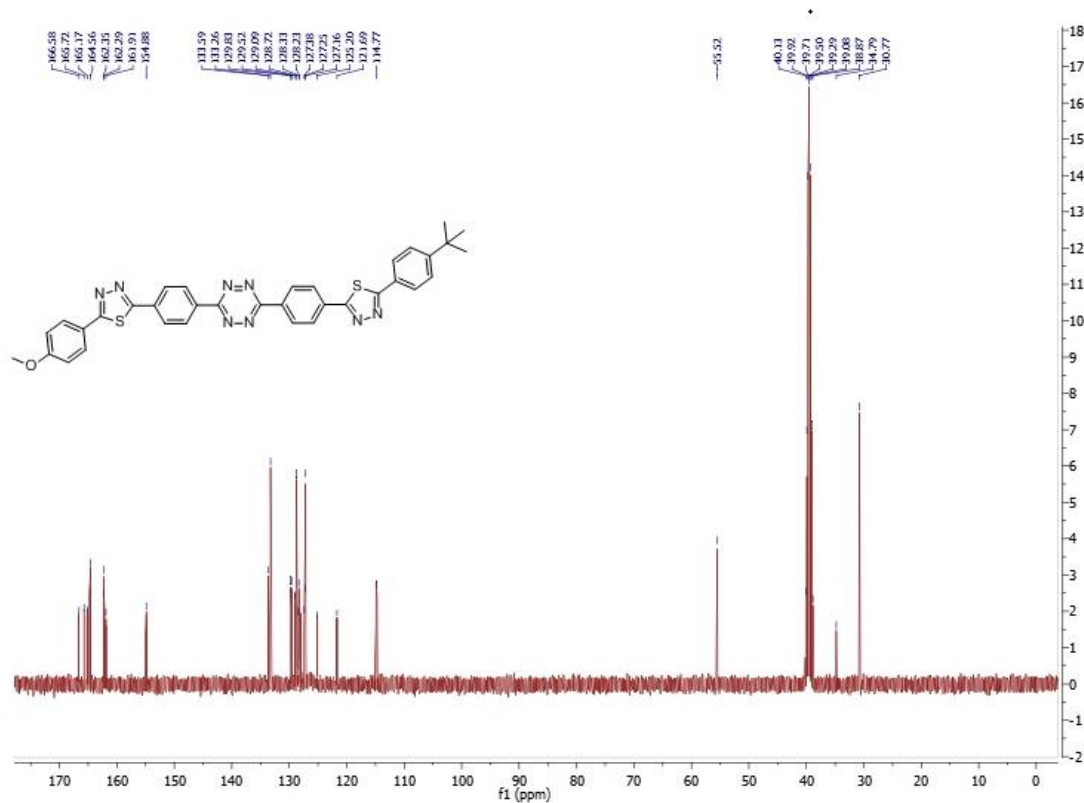


Figure S25: ^1H NMR 2-(4-Methoxyphenyl)-5-(4-(6-(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8i)

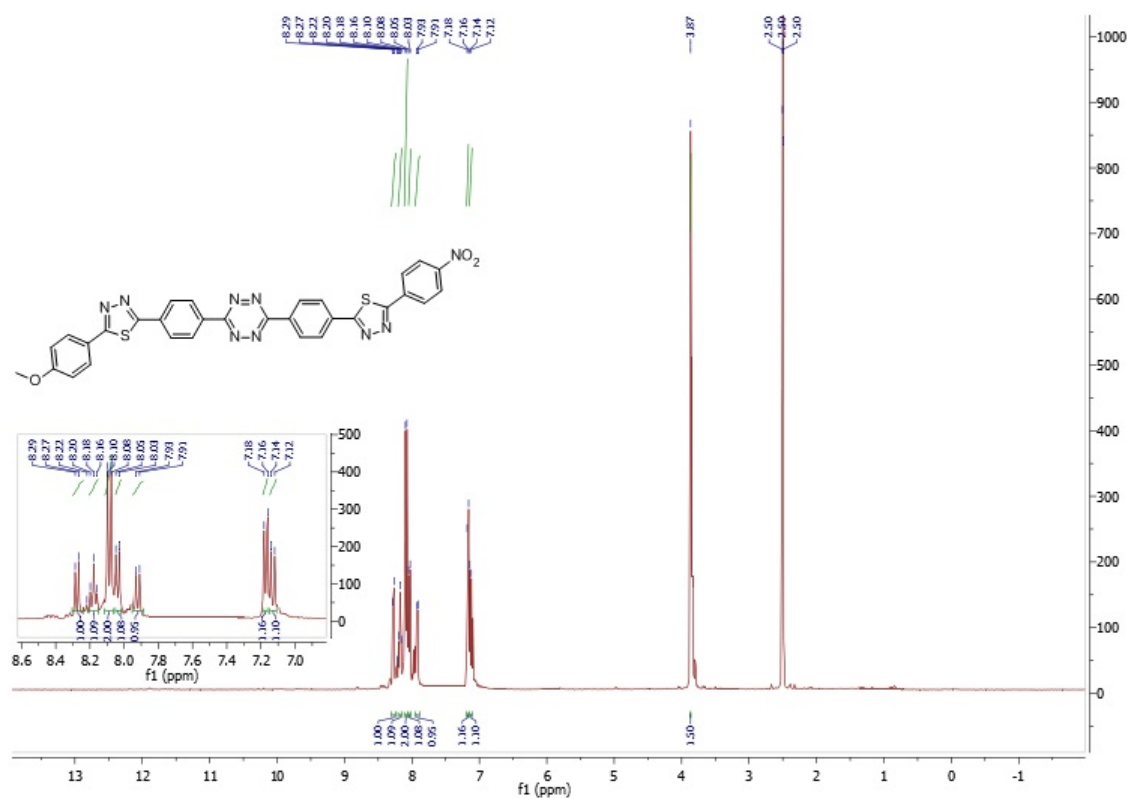


Figure S26: ^{13}C NMR 2-(4-Methoxyphenyl)-5-(4-(6-(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8i)

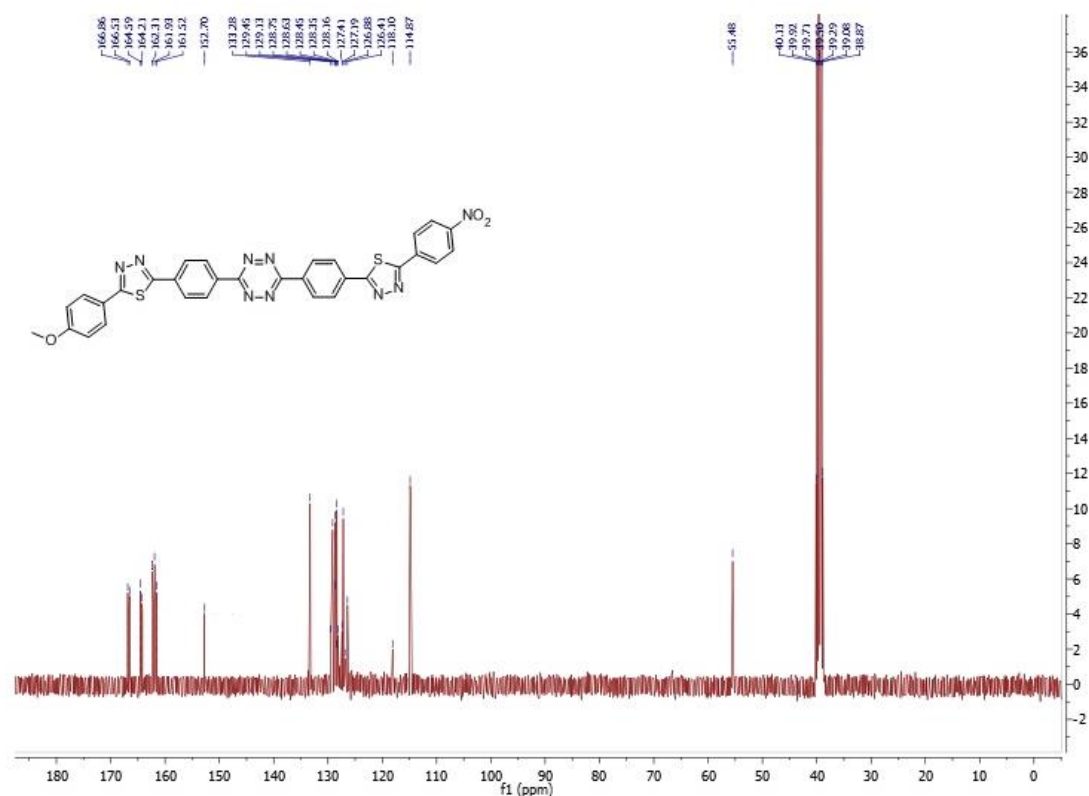


Figure S27: ^1H NMR 2-(4-(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8j)

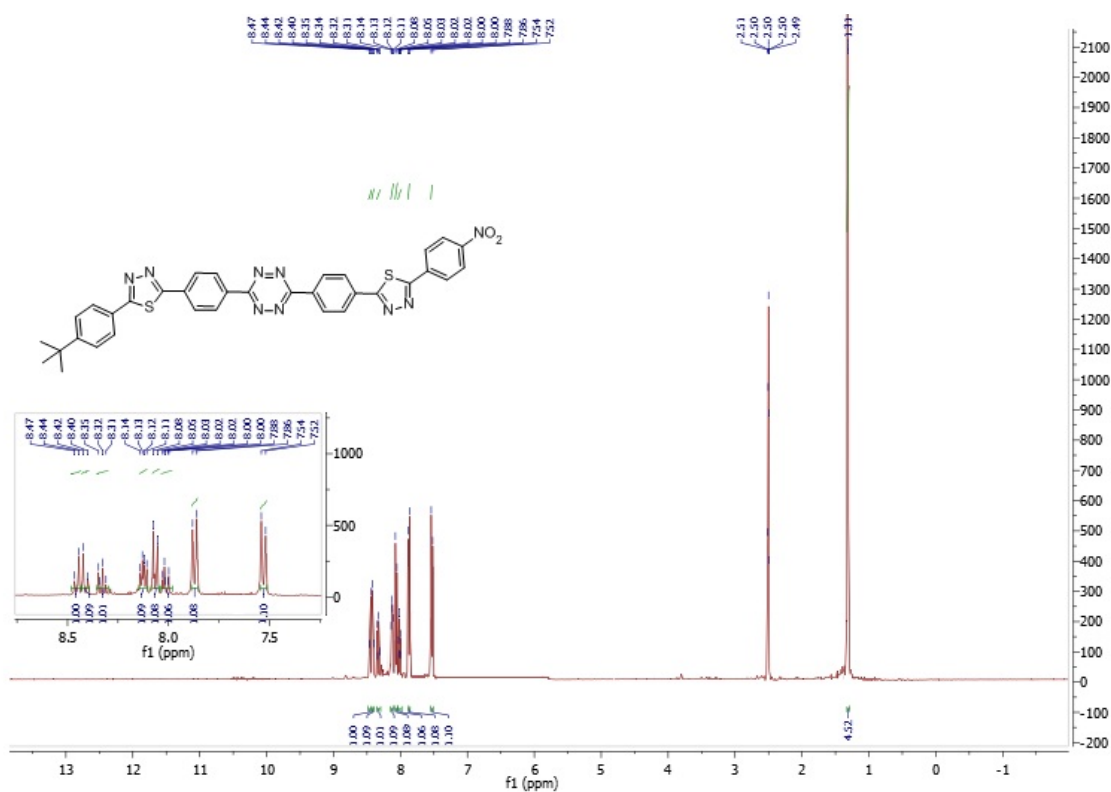
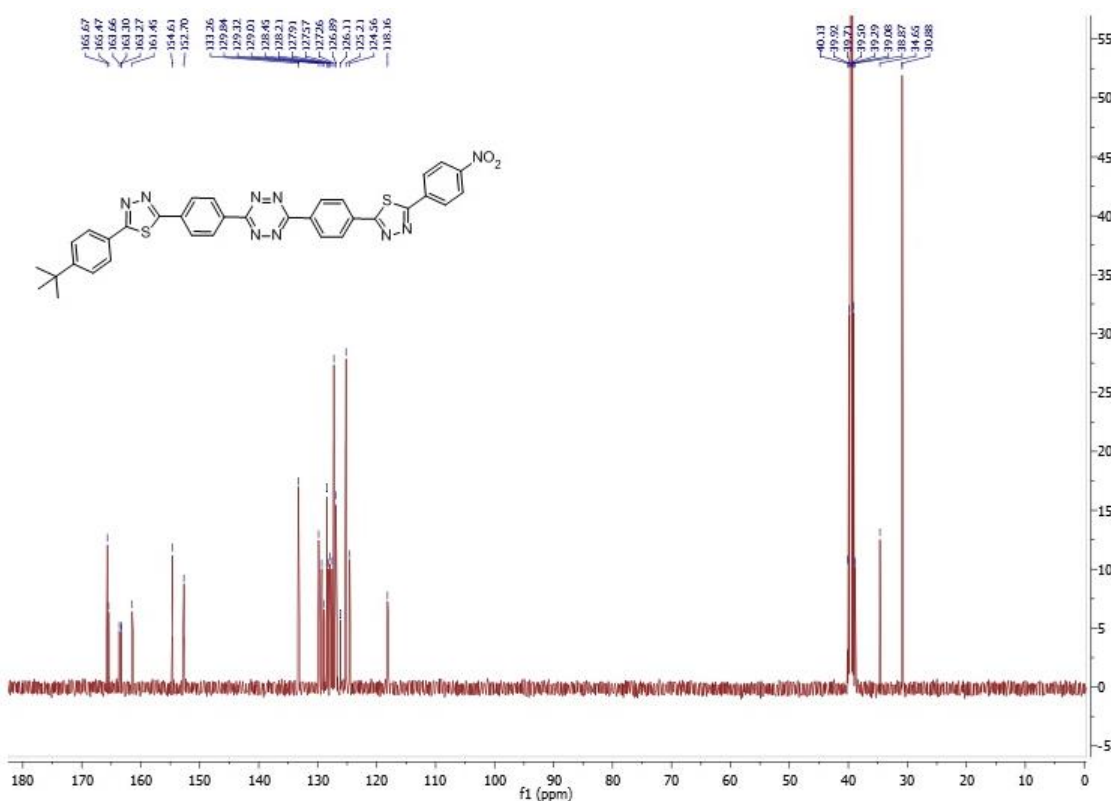
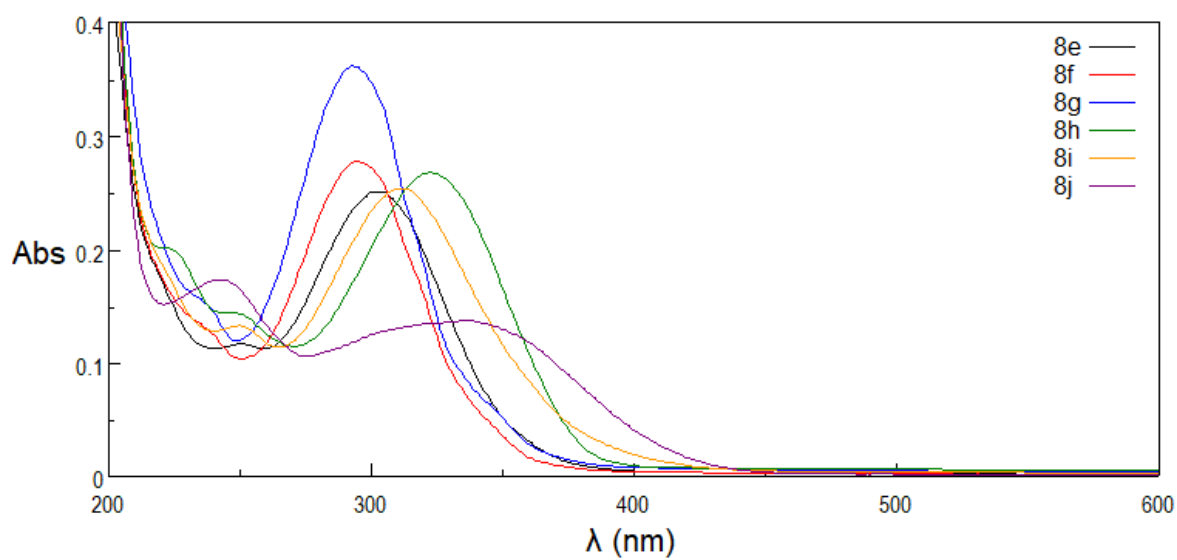
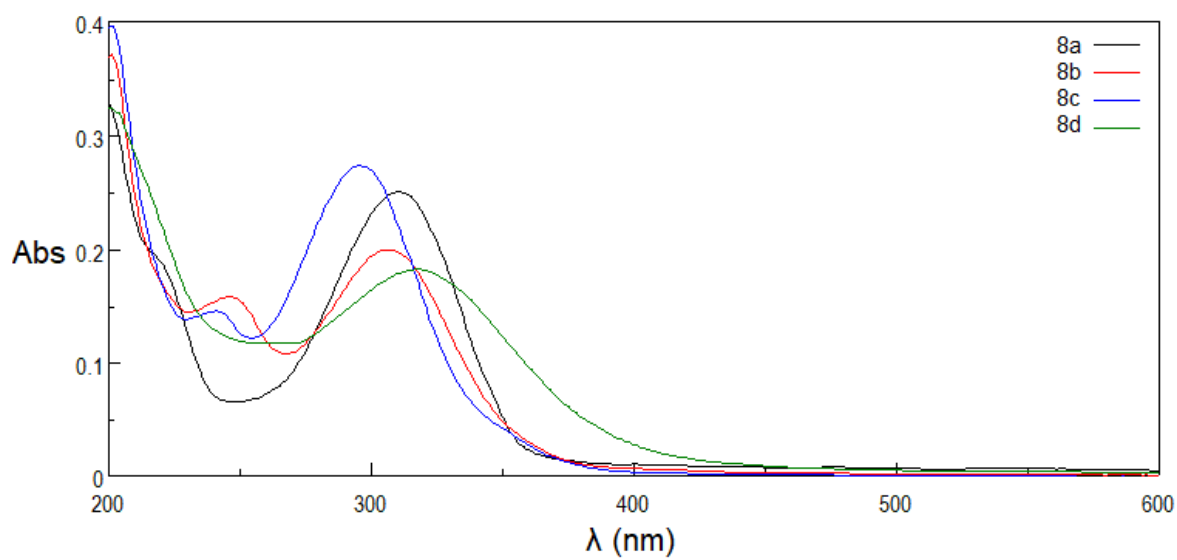


Figure S28: ^{13}C NMR 2-(4-(*tert*-Butyl)phenyl)-5-(4-(6-(4-(5-(4-nitrophenyl)-1,3,4-thiadiazol-2-yl)phenyl)-1,2,4,5-tetrazin-3-yl)phenyl)-1,3,4-thiadiazole (8j)



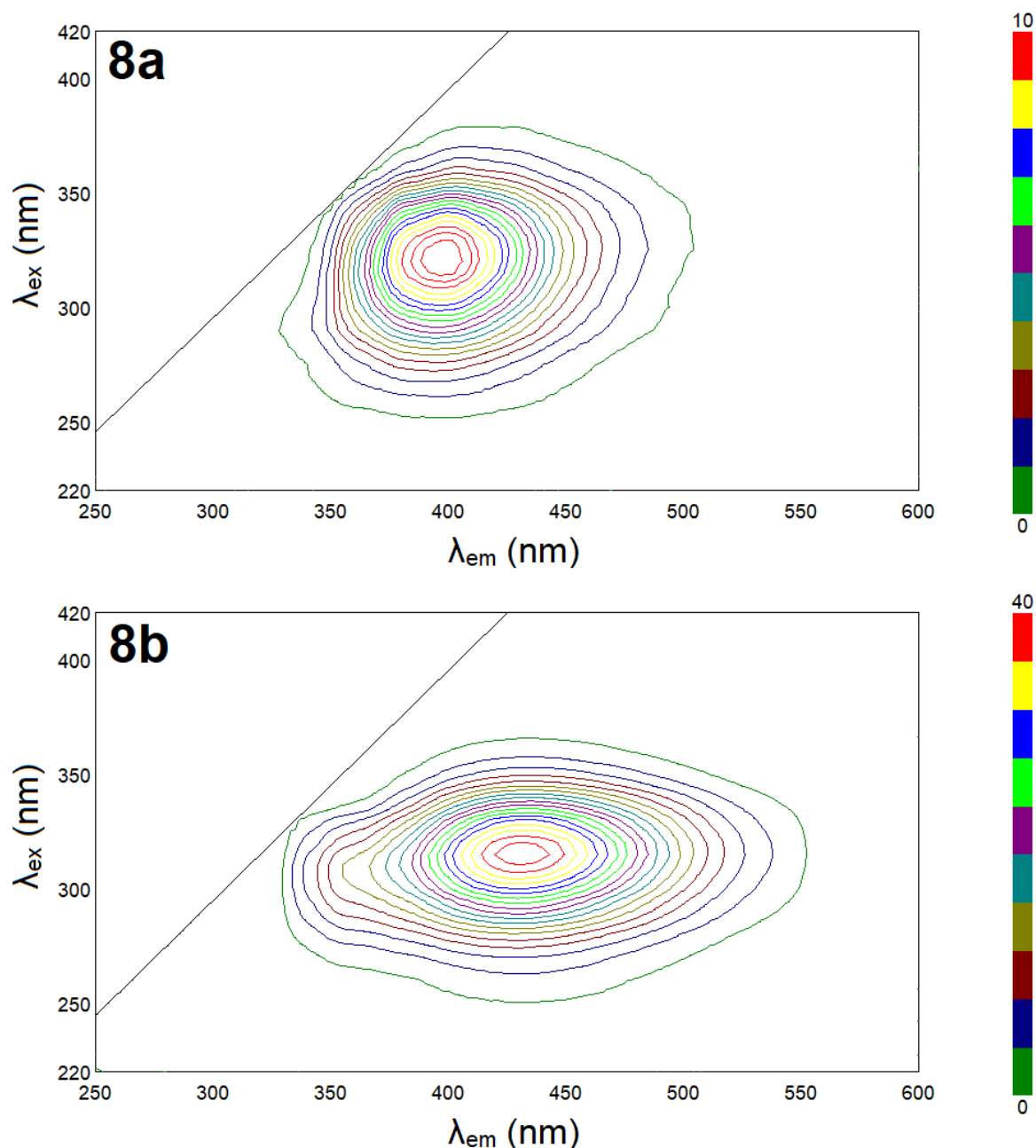
UV-Vis spectra

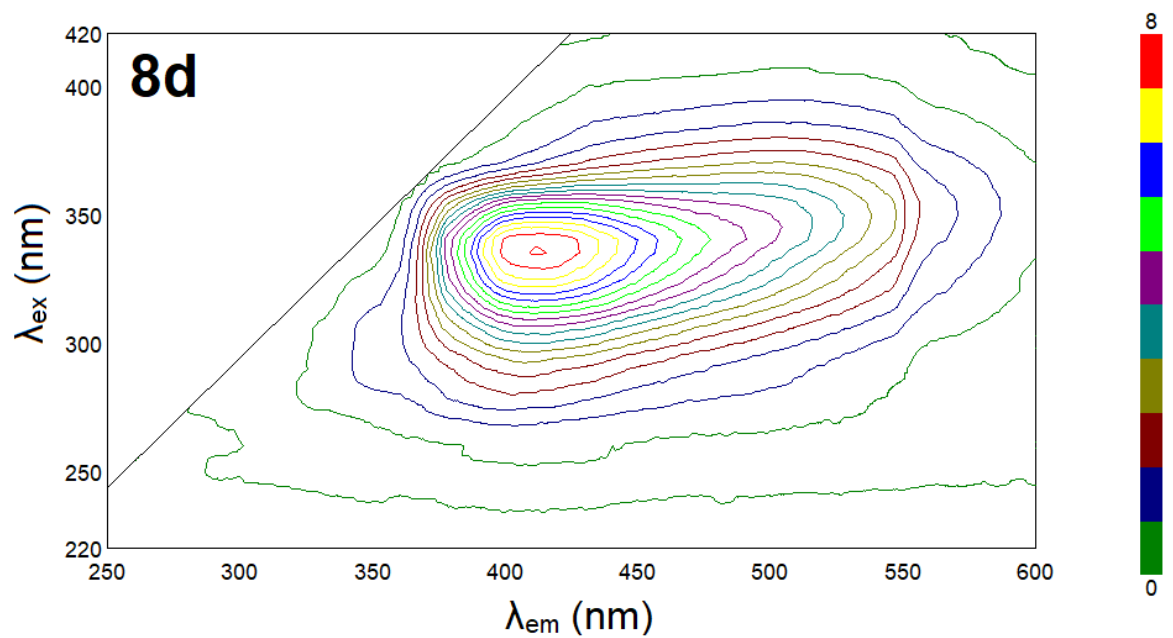
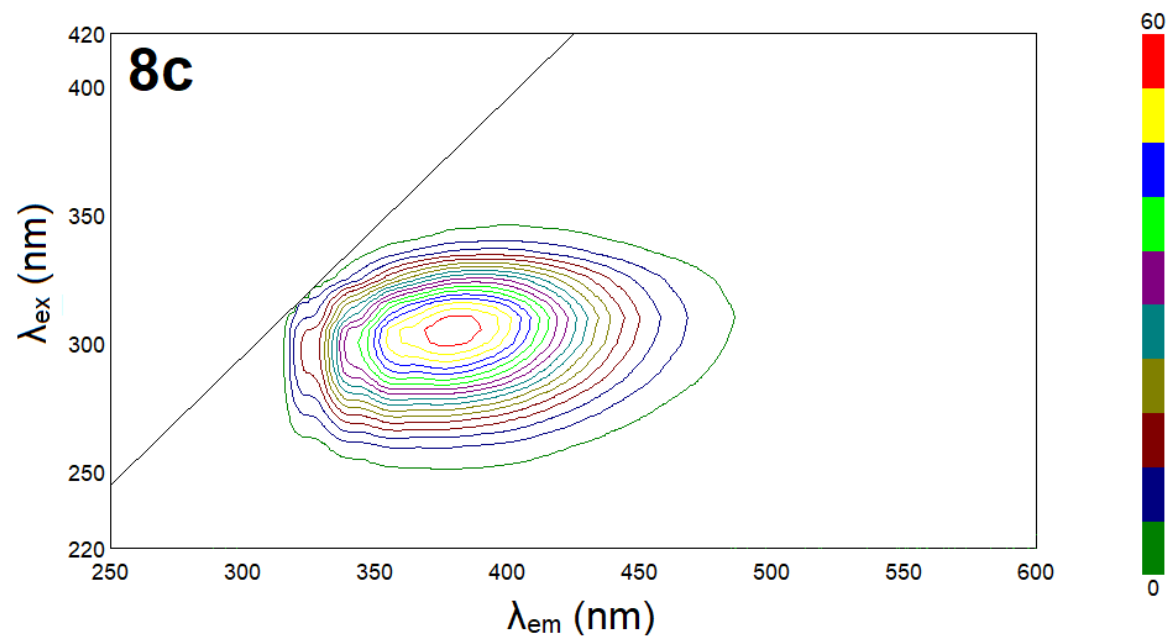
Figure S29: UV-Vis spectra of 8a-j

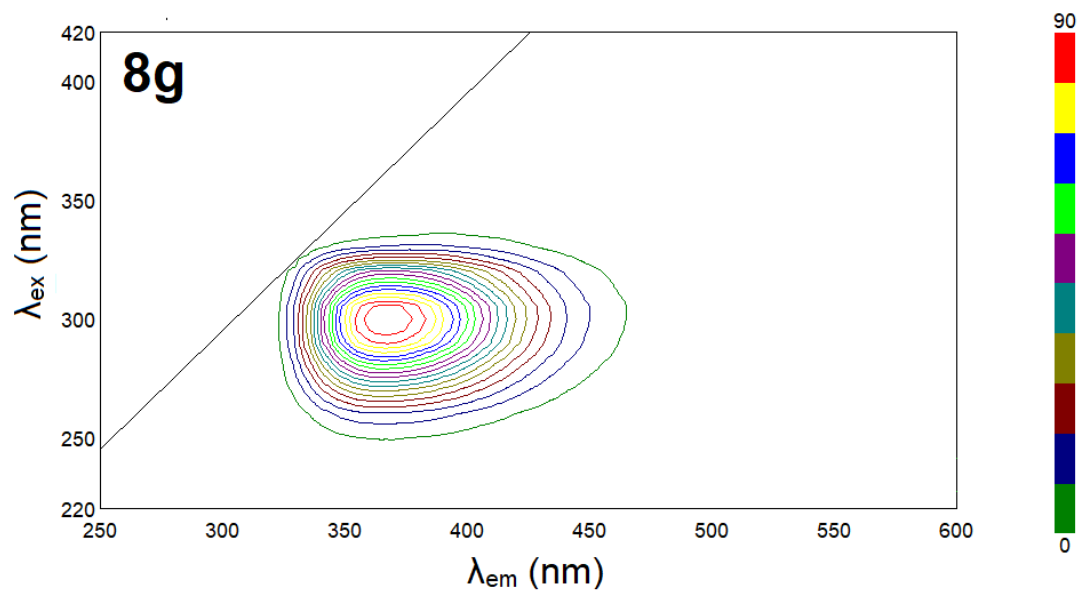
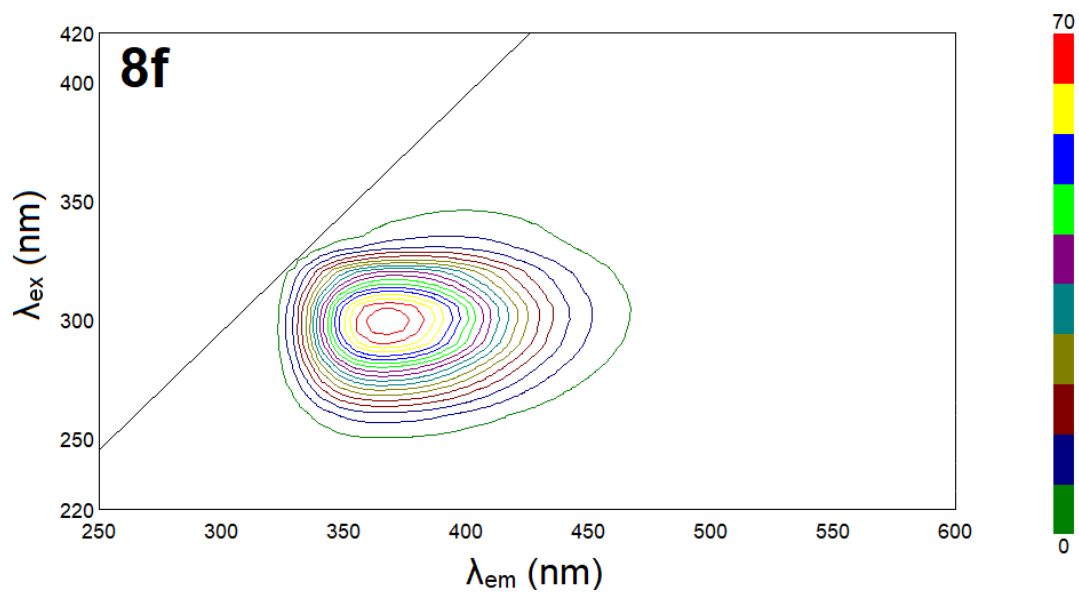
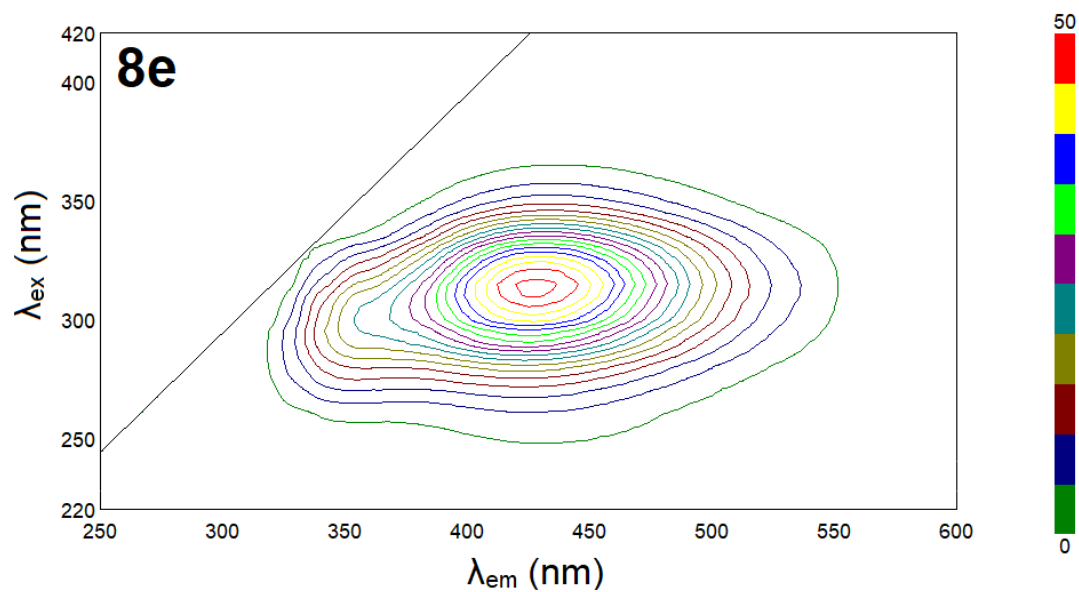


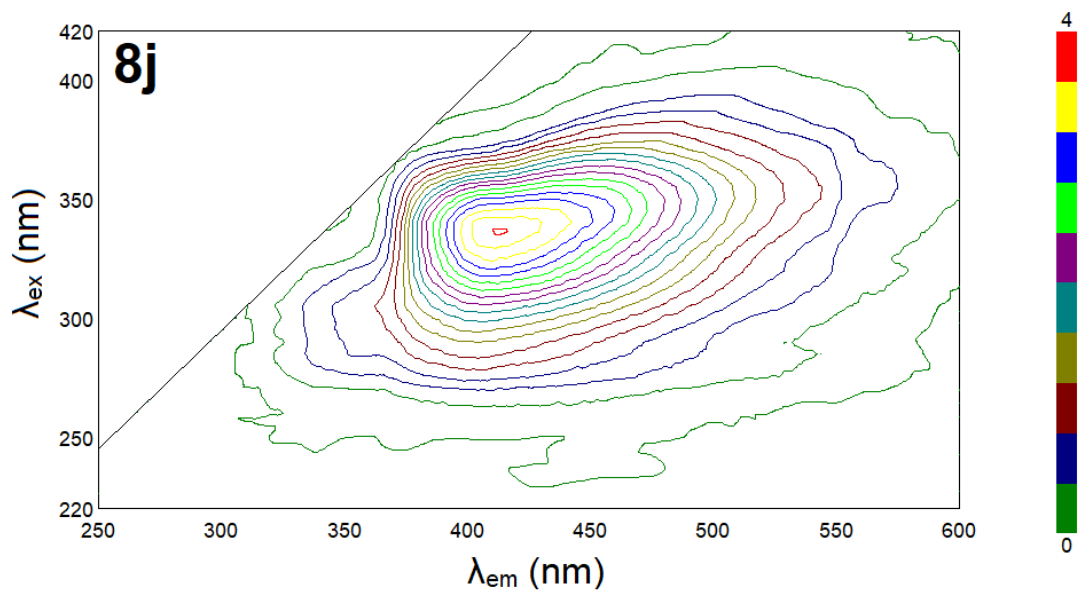
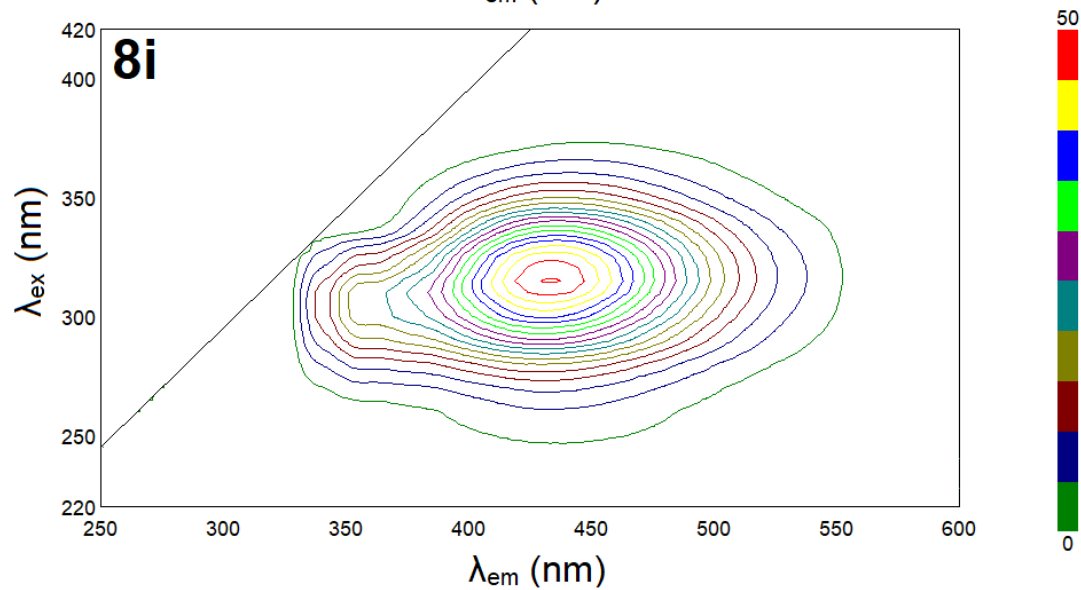
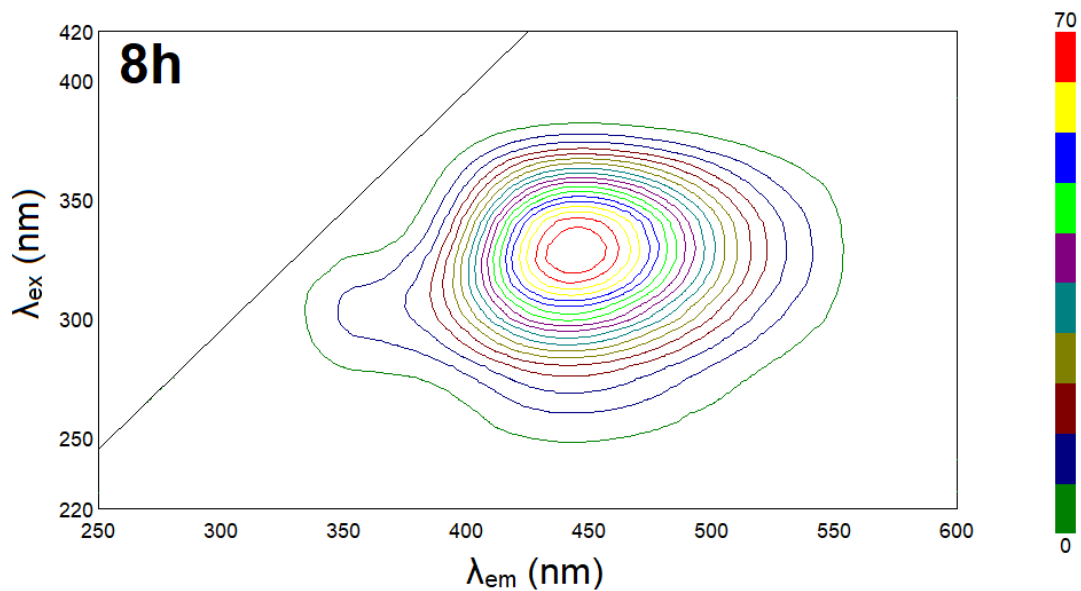
3D fluorescence spectra

Figure S30: 3D fluorescence spectra of compounds 8a-j. The color scale represents a flux of emitted photons. The number above color scales indicates the maximum relative value of emission intensity represented by color scale (and indicated in a respective figure). The unit of measurement in each spectrum represents the same number of emitted photons per second, i.e. fluorescence intensity values in all spectra can be directly compared.



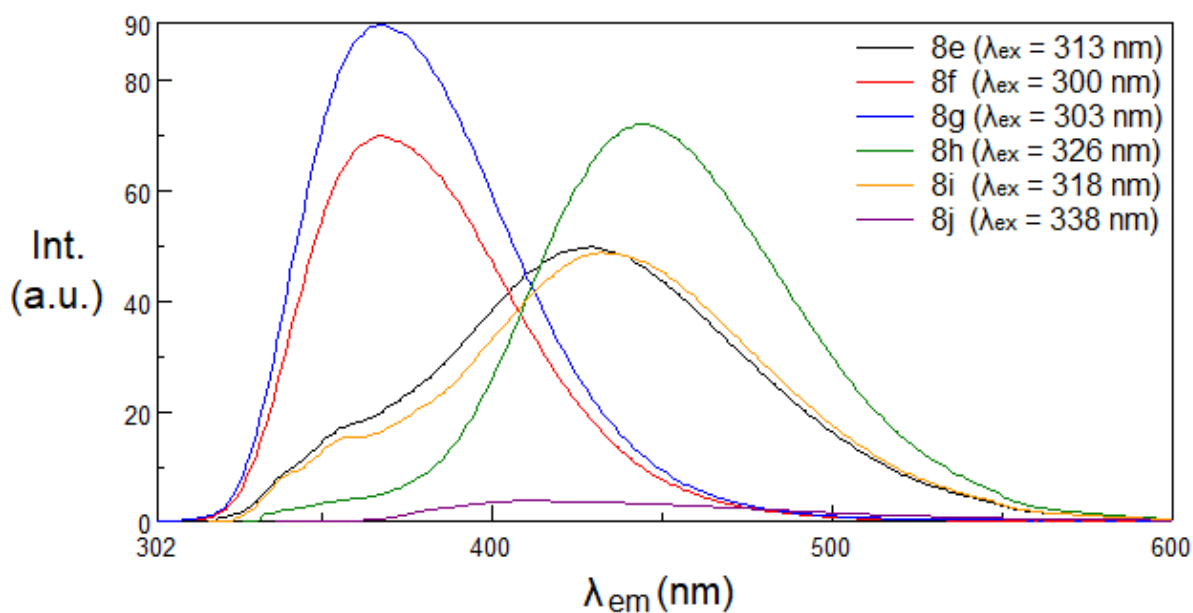
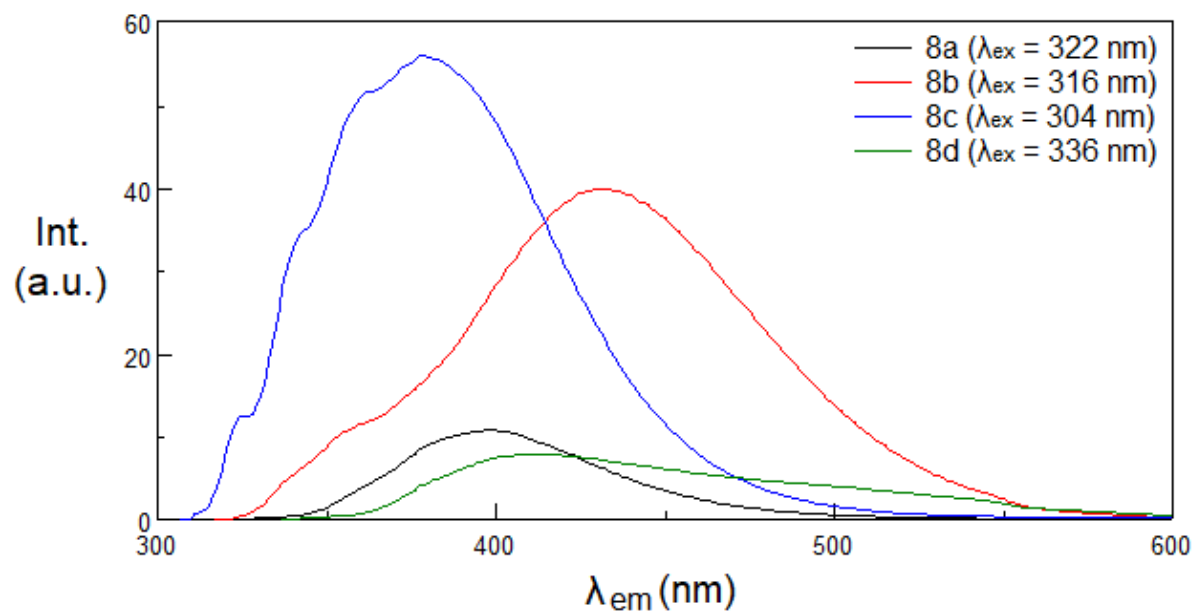






2D fluorescence spectra

Figure S31: 2D fluorescence spectra (extracted from 3D fluorescence spectra) presenting the global emission maximum for each compound. The unit of measurement in each spectrum represents the same number of emitted photons per second, i.e. fluorescence intensity values in all spectra can be directly compared.



The scatter plots presenting relationships between absorption-emission properties

Figure S32: Quantum yields of studied compounds as a function of fluorescence intensity at global maximum

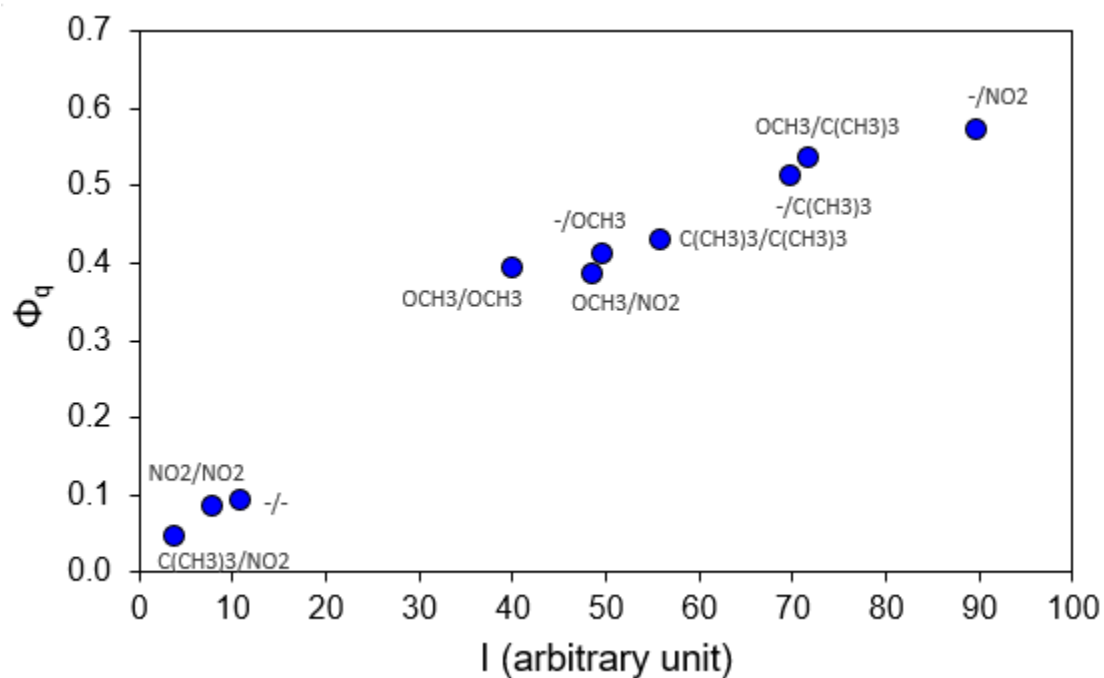


Figure S33: Quantum yields of studied compounds in relation to absorption wavelength at global maximum of fluorescence

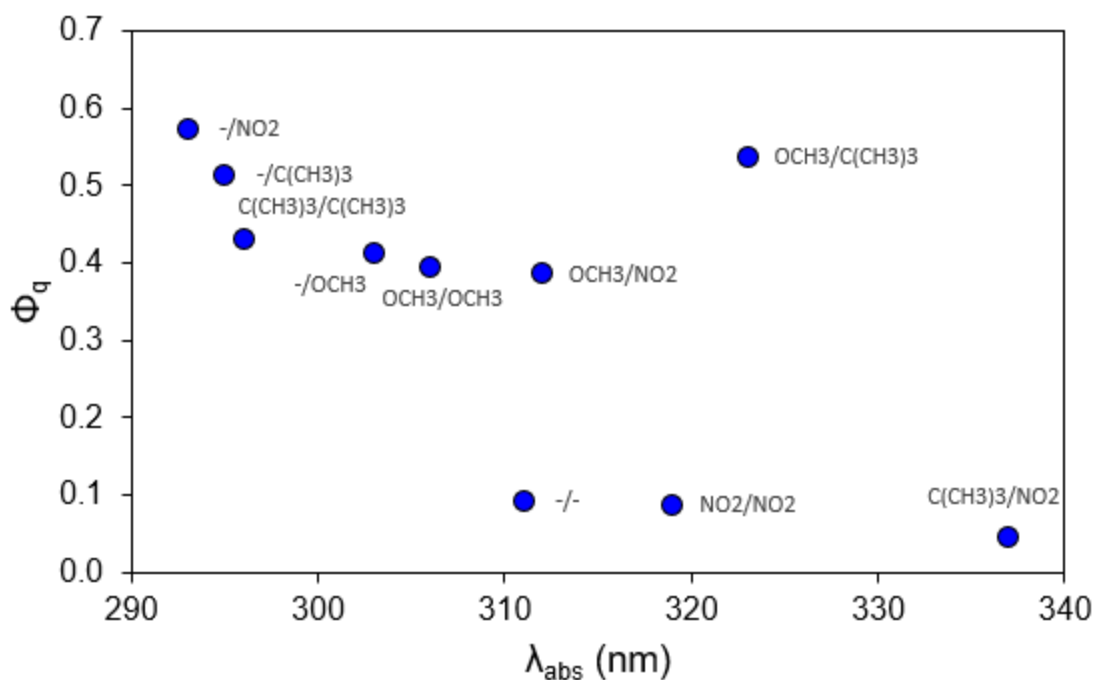
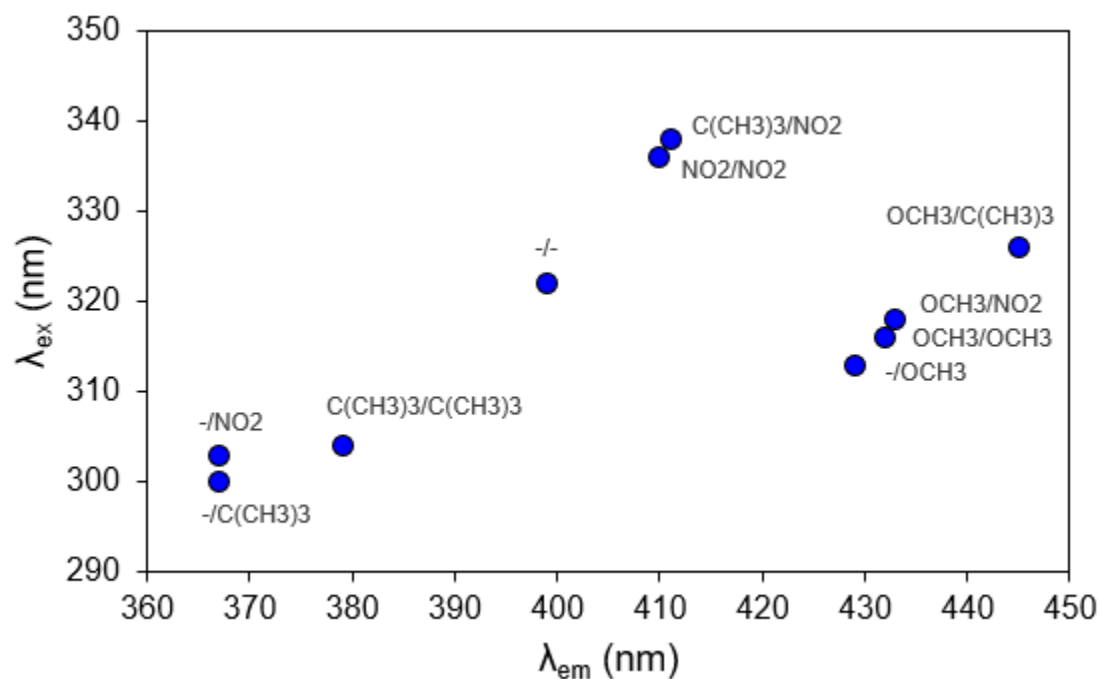


Figure S34: Positions of global maxima for studied compounds.



References

- (1) Barros T.G., Williamson J.S., Antunes O.A.C., Muri E.M.F.; *Letters in Drug Design & Discovery*, **2009**, *6*, 186-192
- (2) Fischer L.J., Ecanow B.; *Journal of Pharmaceutical Sciences*, **1962**, *51*, 287-288
- (3) Tsuchihashi G., Miyajima S., Otsu T., Simamura O.; *Tetrahedron Letters*, **1965**, *21*, 1039-1048
- (4) Kędzia A., Kudelko A., Świątkowski M., Kruszyński R.; *Dyes and Pigments*, **2020**, *183*, 108715