Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

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1. General information

NMR Spectroscopy. ^{1}H NMR spectra were recorded on a high-field spectrometer (^{1}H 600.15 MHz and 500 MHz, ^{13}C 150 MHz and 125.75 MHz), equipped with a broadband inverse gradient probehead. Spectra were referenced to the residual solvent signal (chloroform-d, 7.26 ppm). Two dimensional NMR spectra were recorded with 2048 data points in the t2 domain and up to 1024 points in the t1 domain, with a 1s recovery delay.

Mass Spectrometry. High resolution and Accurate Mass spectra were recorded on a Bruker apex ultra FTMS and a Bruker microTOF-Q spectrometers using the electrospray technique.

UV-Vis Spectroscopy. Electronic spectra were recorded on a Varian Carry-50 Bio spectrophotometer.

Fluorescence. Steady state fluorescence spectra were recorded with a JASCO FP-8600 Spectrofluorometer apparatus.

X-Ray Analysis. X-Ray quality crystals were prepared by diffusion of DCM/hexane (**3a, 5**), precipitation DCM/hexane (**4a**) and diffusion DCM/acetonitryle (**6**). Data were collected at 100K on an Xcalibur PX-κ geometry diffractometer, with Mo (λ=0.7103) (**3a**, **6**) or Cu (λ=1.5406) (**4a**, **5**) Kα radiation. Data were corrected for Lorentz and polarization effect. The structures were solved by direct methods with SHELXT (2015 release) and refined by full matrix least-squares method by using an iteration approach with SHELXL softwarewith anisotropic thermal parameters for the non-H atoms. Hydrogen atoms have been Scattering factors were those incorporated in SHELXT.

Theoretical calculations. Geometry optimizations for **3a**, **4**-*x*, **5**-*x*, **6** and **6***(-)* were carried out with the Gaussian 09[1] software package within unconstrained C1 symmetry, with starting coordinates derived from X-ray analysis. Becke's three-parameter exchange functional with the gradient-corrected correlation formula of Lee, Yang and Parr (DFT-B3LYP)[2] were used with the 6- 31G(d,p) basis set. The polarizable continuum model of solvation was used (PCM, standard dichloromethane/chloroform/ acetone parametrization) for all optimisations. Further analysis for tautomers of **4**-*x* and **5**-*x* has been done after re-optimization of geometries with the same functional and the 6-311++G(d,p) basis set. Harmonic vibrational frequencies were calculated using analytical second derivatives as a verification of local minimum achievement with no negative frequencies observed. The structures were found to have converged to a minimum on the potential energy. The tautomers energies of **4** and **5** have been also checked with a single-point calculation with the 6-311++G(2d,2p) basis set showing values similar to previously obtained for all structures. Proton chemical shifts were

[1] Gaussian 09, Revision E.01; M. J. Frisch et al., Gaussian, Inc.: Wallingford CT, **2009**.

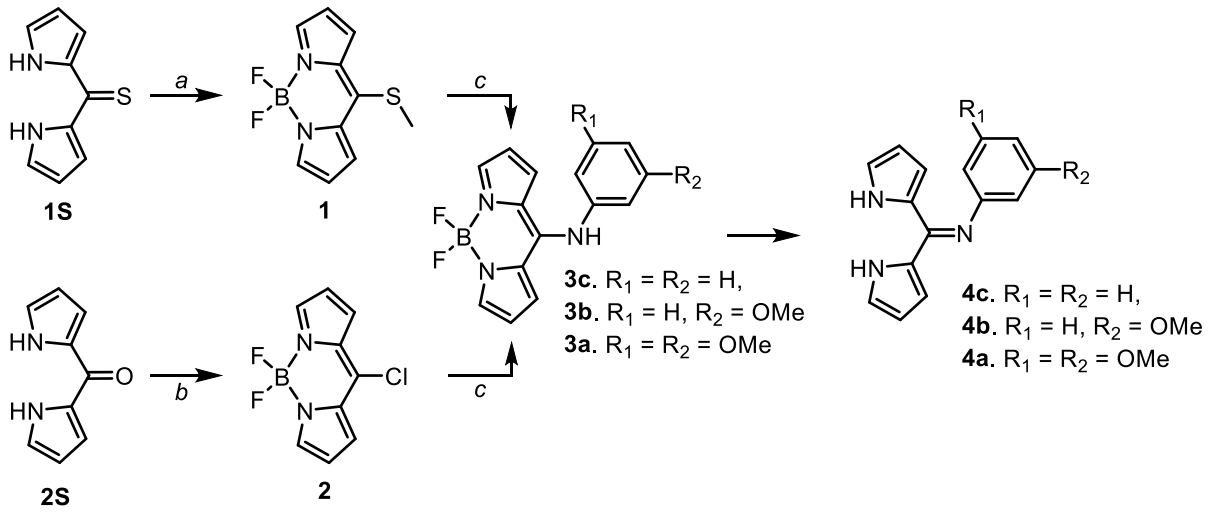
[2] a) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B*, **1988**, 37, 785-789. b) A. D. Becke, *Phys. Rev. A*, **1988**, 38, 3098-3100.

calculated using the GIAO method (6-31G(d,p) for all analysed compounds) and referenced to the absolute shielding of tetramethylsilane calculated at the same level of theory. The electronic spectra were simulated by means of time-dependent density functional theory (TD-DFT) using the Tamm-Dancoff approximation for 25 states and 6-31G(d,p) basis set for **3a**, **6** and **6**(-) and 6-311++G(d,p) for **4**-*x* and **5**-*x*. The electronic transitions and UV/Vis were analysed by means of the GaussSum program. The transitions were convoluted by Gaussian curves with 3000 cm–1 half line width for **4** and **5** and 2000 cm-1 and for **3a**, **6** and **6***(-)*.

2. Experimental section.

All solvents (MeOH, Ethyl Acetate, $CHCl_3$, n-hexane, toluene, acetone, water) if not indicated differently were used without purification. CH_2Cl_2 was distilled over CaH_2. Chloroform-d was prepared directly before using by passing through a basic alumina column. All reactions were performed under inert atmosphere.

2.1 Experimental procedures.



Scheme S1.

Thioketopyrrole 1S and meso-methylthioBODIPY 1 were prepared according to Biellmann et Al. procedure[3].

Ketopyrrole 2S was prepared with Bourhill et Al. procedure[4].

[3] *Tetrahedron*, **2006**, 62, 5084-5091.

[4] *Tetrahedron*, **2002**, 58, 2405-2413.

meso-chloroBODIPY 2 and anilineBODIPY 3c were prepared according to Dehaen et Al. procedure[5].

meso-ANISIDINE BODIPY 3b. In a two-necked round bottom flask SMeBODIPY **1** (476.14 mg, 2.0 mmol) and anisidine (450 µL, 2.0 mmol) were dissolved in dry dichloromethane (20 mL). The solution was stirred overnight under Ar at room temperature. After reaction completion, the mixture was evaporated under reduced pressure. The residue was purified with silica gel (100% DCM) to give an orange solid as the desired compound (yield 70%, 436 mg). ^{1}H NMR (600 MHz, 300K, $CDCl_3$) δ = 7.78 (bs, 1H), 7.61 (bs, 2H), 7.44 (t, J = 8.26 Hz, 2H), 7.05 (dd, J^{12} = 2.57 Hz, J^{13} = 8.38 Hz, 1H), 7.00 (m, 1H), 6.94 (t, J = 2.20 Hz, 2H), 6.58 (d, J = 3.78 Hz, 2H), 6.35 (dd, J^{12} = 2.12 Hz, J^{13} = 4.11 Hz, 2H), 3.83 (s, 3H), ^{13}C NMR (150 MHz, 300K, $CDCl_3$) δ = 161.3, 147.6, 138.6, 135.8, 131.4, 124.0, 120.6, 118.9, 115.6, 114.8, 112.3, 55.8, HRMS (m/z): 336.1087 $[M\text{-}Na]^+$ (theor. calc. for $C_{16}H_{14}BF_2N_3O$ 336.1090), UV-Vis: 264, 324, 333, 420 nm.

DIMETHOXYANILINE BODIPY 3a. In a two necked round bottom flask m-chloroBODIPY (1.47 g, 6.5 mmol) and 3,5-dimethoxyaniline (2.00 g, 13.0 mmol) were dissolved in dry dichloromethane (60 mL). The solution was stirred for 5 hours under Ar at room temperature. After reaction completion, the mixture was poured in 100 mL of diethyl ether and was washed with basic Na_2CO_3 solution. The organic layer was separated and washed with water (3x100 mL), brine (100 mL), it was dried over Na_2SO_4, filtered and the solvent was evaporated. The residue was purified with silica gel (ethyl acetate/dichloromethane, 1:5) to give an orange solid as the desired compound (yield 81%, 1.80 g).

^{1}H NMR (600 MHz, 300K, $CDCl_3$) δ = 7.75 (bs, 1H), 7.60 (bs, 2H), 6.66 (d, J = 3.98 Hz, 2H), 6.57 (m, 1H), 6.55 (m, 2H), 6.36 (dd, J^{12} = 2.22 Hz, J^{13} = 4.23 Hz, 2H), 3.80 (s, 3H), ^{13}C NMR (125.75 MHz, 300K, $CDCl_3$) δ = 162.2, 147.4, 139.1, 135.8, 124.0, 120. 7, 114.9, 104.8, 101.8, 55.9, HRMS (m/z): 366.1183 $[M\text{-}Na]^+$ (theor. calc. for $C_{17}H_{16}BF_2N_3O_2$ 366.1195), UV-Vis: 326, 420 nm.

General procedure for boron decomplexation[6].

In a round bottom flask, BODIPY (1.0 mmol) was dissolved in acetonitrile (30 mL). A solution of $ZrCl_4$ (5.0 eq.) in methanol (5 mL) was added and the mixture was refluxed under nitrogen for two hours. After reaction completion, the solvent was removed under reduced pressure and the solid residue dissolved in dichloromethane, washed with basic Na_2CO_3 solution, water and brine. The organic phase was dried over Na_2SO_4, filtered and the solvent was evaporated. The solid was then precipitated (dichloromethane/n-Hexane) to afford the desired product (quant.).

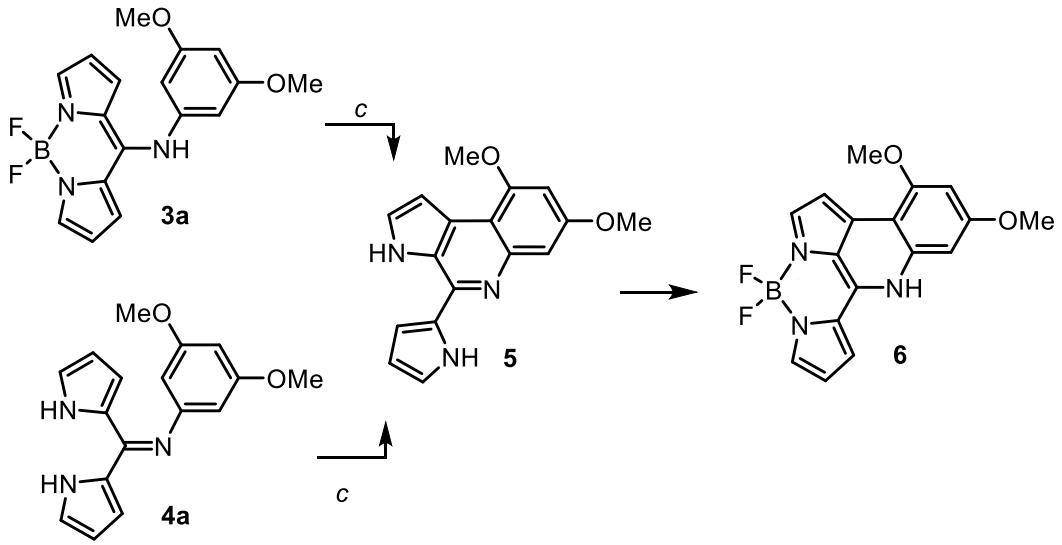
[5] *Org. Lett.*, **2012**, 14 (24), 6150-6153.

[6] *Eur. J. Org. Chem.*, **2014**, 10, 2105-2110.

ANILINE DIPY, 4c. ^{1}H NMR (600 MHz, 300K, $CDCl_3$) δ = 9.51 (bs, 1H), 7.99 (bs, 1H), 7.30 (m, 2H), 7.06 (tt, J^{12} = 1.20 Hz, J^{13} = 7.40 Hz, 1H), 7.01 (bs, 1H), 6.85 (m, 2H), 6.75 (dd, J^{12} = 1.00 Hz, J^{13} = 1.90 Hz, 1H), 6.69 (bs, 1H), 6.61 (bs, 1H), 6,32 (t, J = 3.05 Hz, 1H), 6.16 (bs, 1H), ^{13}C NMR (125.75 MHz, 300K, $CDCl_3$) δ = 151.5, 149.5, 131.7, 129.5, 125.6, 123.4, 122.0, 121.2, 120.6, 116.2, 114.7, 110.2, 109.0, HRMS (m/z): 236.1160 $[M+H]^+$ (theor. calc. for $C_{15}H_{13}N_3$ 236.1182), UV-Vis: 228, 305 nm.

ANISIDINE DIPY, 4b. ^{1}H NMR (600 MHz, 300K, $CDCl_3$) δ = 9.53 (bs, 1H), 8.09 (bs, 1H), 7.20(t, J = 8.00 Hz, 1H), 7.00 (bs, 1H), 6.76 (d, J = 2.88 Hz, 1H), 6.71 (bs, 1H), 6,65 (bs, 1H), 6,63 (dd, J^{12} = 1.15 Hz, J^{13} = 2.30 Hz, 1H), 6,62 (dd, J^{12} = 1.00 Hz, J^{13} = 2.52 Hz, 1H), 6.43 (m, 2H), 6,32 (bs, 1H), 6,17 (bs, 1H), 3,75 (s, 3H), ^{13}C NMR (125.75 MHz, 300K, $CDCl_3$) δ = 160.7, 152.8, 149.6, 131.5, 130.3, 125.5, 122.2, 121.5, 116.3, 115.0, 112.9, 110.2, 109.4, 109.0, 106.0, 55.3, HRMS (m/z): 266.1287 $[M+H]^+$ (theor. calc. for $C_{16}H_{15}N_3O$ 266.1279), UV-Vis: 227, 304 nm.

DIMETHOXYANILINE DIPY, 4a. ^{1}H NMR (600 MHz, 300K, $CDCl_3$) δ = 9.50 (bs, 1H), 8.22 (bs, 1H), 7.00 (bs, 1H), 6.76 (m, 1H), 6.73 (bs, 1H), 6.69 (bs, 1H), 6.31 (t, J = 3.10 Hz, 1H), 6.20 (t, J = 2.30 Hz, 1H), 6,17 (bs, 1H), 6.03 (d, J = 2.30 Hz, 2H), 3.72 (s, 3H), ^{13}C NMR (125.75 MHz, 300K, $CDCl_3$) δ = 161.7, 153.6, 149.4, 131.5, 125.6, 122.0, 121.6, 116.3, 114.9, 110.2, 109.0, 98.5, 96.0, 55.46, HRMS (m/z): 296.1376 $[M+H]^+$ (theor. calc. for $C_{17}H_{17}N_3O_2$ 296.1393), UV-Vis: 305, 227 nm.



Scheme S2. oxydation process

DIPY FUSED SYSTEM, 5. ***Path a:*** To a solution of meso-dimethoxyanilineBODIPY (3a) (190 mg, 0.553 mmol) in dry dichloromethane (10 mL), 360 µL of methanesulfonic acid (10 eq.) and a solution of DDQ (126 mg, 1.0 eq.) in nitromethane (2 mL) were added and the mixture was stirred under Ar at room temperature. After one hour, the reaction mixture was poured in diethyl ether (10 mL) and extracted with Na_2CO_3 (3x20 mL), washed with brine (20 mL) and dried over Na_2SO_4. The solution was filtered and the solvent removed under reduced pressure.

The residue was purified with silica gel (ethyl acetate/dichloromethane, 1:5) to give a green solid as the desired compound (yield 25%, 40 mg).

Path b: To a solution of **4a** (1.0 eq.) in dry dichloromethane, methanesulfonic acid (10 eq.) and a solution of DDQ (1.0 eq.) in nitromethane were added and the mixture was stirred under Ar at room temperature. After one hour, the reaction mixture was poured in diethyl ether (10 mL) and extracted with Na_2CO_3 (3x20 mL), washed with brine (20 mL) and dried over Na_2SO_4. The solution was filtered and the solvent removed under reduced pressure. The residue was purified with silica gel (ethyl acetate/dichloromethane, 1:5) to give a green solid as the desired compound (yield 27%).

^{1}H NMR (600 MHz, 300K, $CDCl_3$) δ = 10.29 (s, 1H), 9.18 (s, 1H), 7.45 (d, J = 3.00 Hz, 1H), 7.33 (d, J = 2.93 Hz, 1H), 7.17 (m, 1H), 7.04 (m, 1H), 6.89 (m, 1H), 6.60 (d, J = 2.25 Hz, 1H), 6.41 (t, J = 3.13 Hz, 1H), 4.06 (s, 3H), 3.95 (s, 3H), ^{13}C NMR (125.75 MHz, 300K, $CDCl_3$) δ = 158.6, 157.2, 144.9, 138.4, 129.6, 127.9, 126.1, 125.3, 120.5, 110.6, 109.7, 108.8, 106.0, 100.5, 97.3, 55.8, 55.6, HRMS (m/z): 294.1223 $[M+H]^+$ (theor. calc. for $C_{17}H_{15}N_3O_2$ 294.1237), UV-Vis: 415, 375, 357, 337, 300, 270, 245.

BODIPY FUSED SYSTEM, 6. To a solution of fused-dipy (36 mg, 0.12 mmol) in dry dichloromethane (10 mL) at 0°C, trimethylamine (171 µL, 10 eq.) was added, followed by, after 30 minutes, boron trifluoride diethyl etherate (151 µL, 10 eq.). The reaction was allowed to reach room temperature and further stirred for 2 hours under Ar and, after this time, it was poured in diethyl ether (10 mL), washed with water (3x20 mL), brine (20 mL), and dried over Na_2SO_4. The solution was filtered and the solvent removed under reduced pressure. The residue was purified with silica gel (ethyl acetate/dichloromethane, 1:10) to give a yellow solid as the desired compound (yield 36%, 14.9 mg).

^{1}H NMR (600 MHz, 300K, $(CD_3)_2CO$) δ = 12.47 (s, 1H), 7.99 (bs, 1H), 7.49 (bs, 1H), 7.35 (m, 1H), 7.24 (m, 1H), 6.98 (d, J = 2.25 Hz, 1H), 6.75 (d, J = 2.30 Hz, 1H), 6.45 (m, 1H), 4.13 (s, 3H), 3,93 (s, 3H), ^{1}H NMR (500 MHz, 300K, ($CDCl_3$) δ = 9.72 (s, 1H), 7.96 (d, J = 2.30 Hz, 1H), 7.50 (bs, 1H), 7.07 (d, J = 2.36 Hz, 1H), 6,94 (d, J = 3.70 Hz, 1H), 6.65 (d, J = 2.10 Hz, 1H), 6.57 (d, J = 2.11 Hz, 1H), 6.30 (dd, J^{12} = 2.30 Hz, J^{13} = 3.82 Hz, 1H), 4.05 (s, 3H), 3.94 (s, 3H), ^{13}C NMR (125.75 MHz, 300K, $(CD_3)_2CO$) δ = 161.6, 158.9, 138.6, 135.8, 134.1, 132.2, 129.9, 125.7, 123.5, 114.7, 113.7, 108.4, 97.9, 93.4, 56.6, 56.1, HRMS (m/z): 364.1040 $[M-Na]^+$ (theor. calc. for $C_{17}H_{13}BF_2N_3O_2$ 364.1039), UV-Vis: 428, 407, 364, 283.

BODIPY FUSED SYSTEM, 6*(-)*. The deprotonated form was prepared by titration in NMR tube. To 2.4 mg of **6** dissolved in $(CD_3)_2CO$, 0.2/0.4/0.6/0.8 and 1.0 eq. of TBAF in $CDCl_3$ were added stepwise.

^{1}H NMR (600 MHz, 300K, $(CD_3)_2CO$) δ = 7.57 (d, J = 2.18 Hz, 1H), 7.30 (bs, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 7.05 (d, J = 2.50 Hz, 1H), 6.51 (d, J = 2.18 Hz, 1H), 6.24 (t, J = 2.90 Hz, 1H), 4.03 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (150 MHz, 300K, $(CD_3)_2CO$), partial signals obtained by correlation

experiments HMBC, HSQC, δ = 129.5, 125.0, 109.8, 105.2, 99.8, 95.4, 55.0, UV-Vis: 267, 339, 345, 363, 382.

3. NMR spectra

3.1. NMR spectra of 3b.

Figure S1. ^{1}H NMR spectrum of **3b** ($CDCl_3$, 300K, 600 MHz).

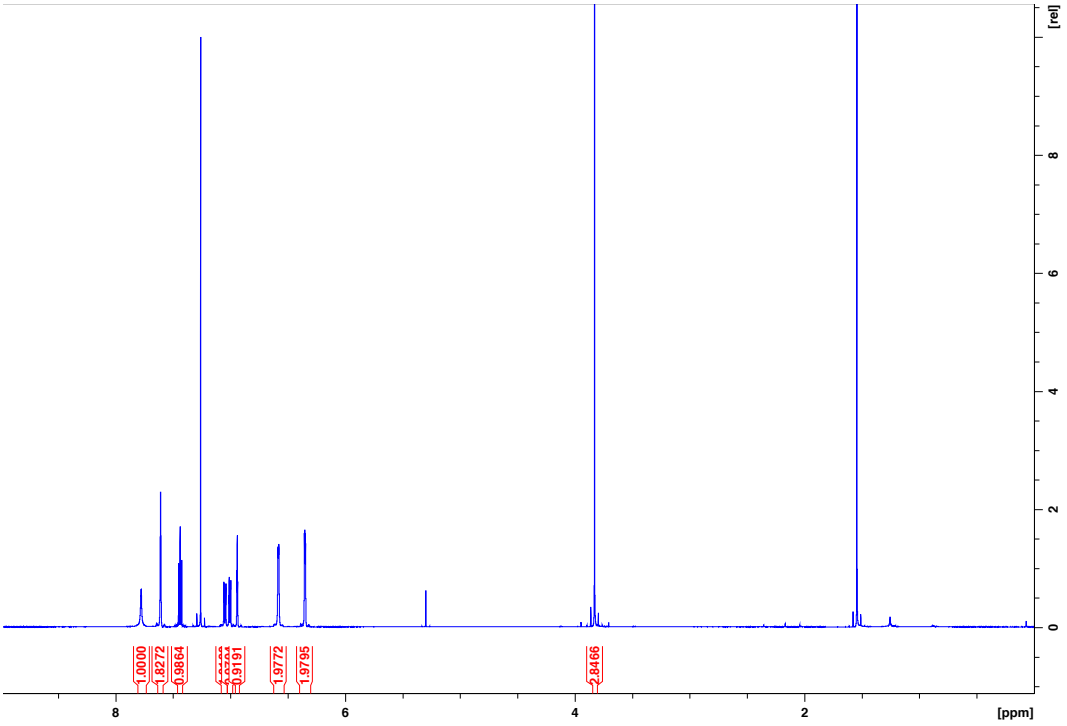


Figure S2. ^{1}H NMR spectrum (zoom, aromatic region) of **3b** ($CDCl_3$, 300K, 600 MHz).

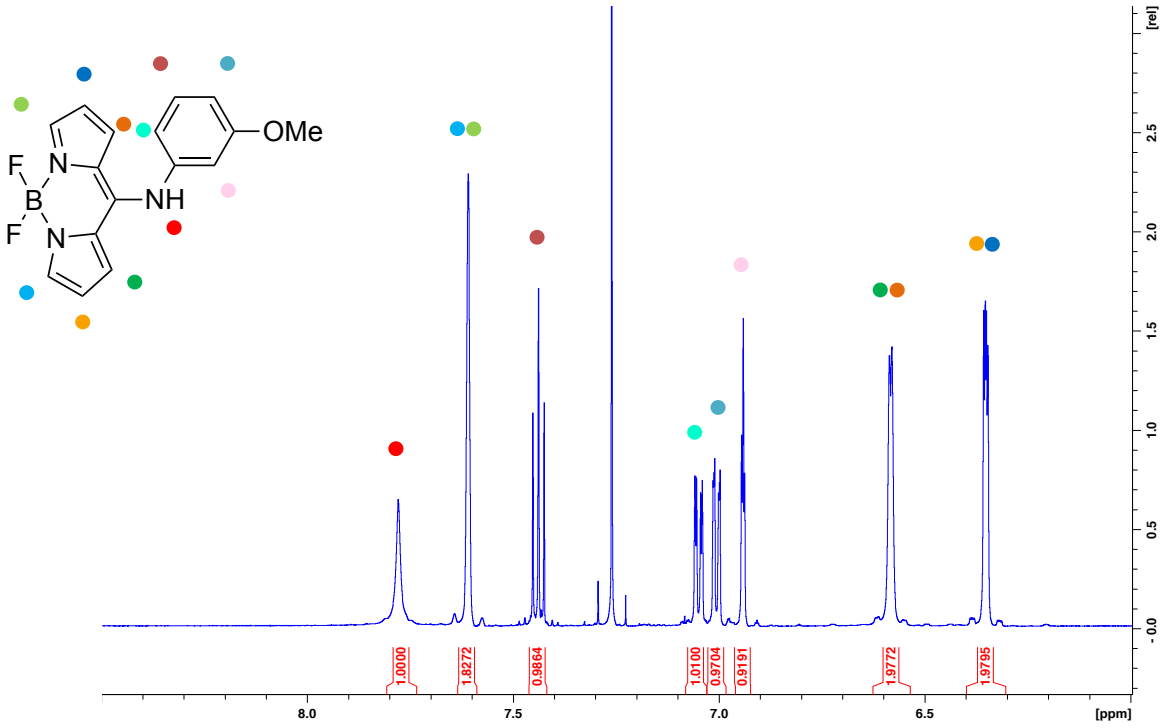


Figure S3. ^{13}C NMR spectrum of **3b** ($CDCl_3$, 300K, 150 MHz).

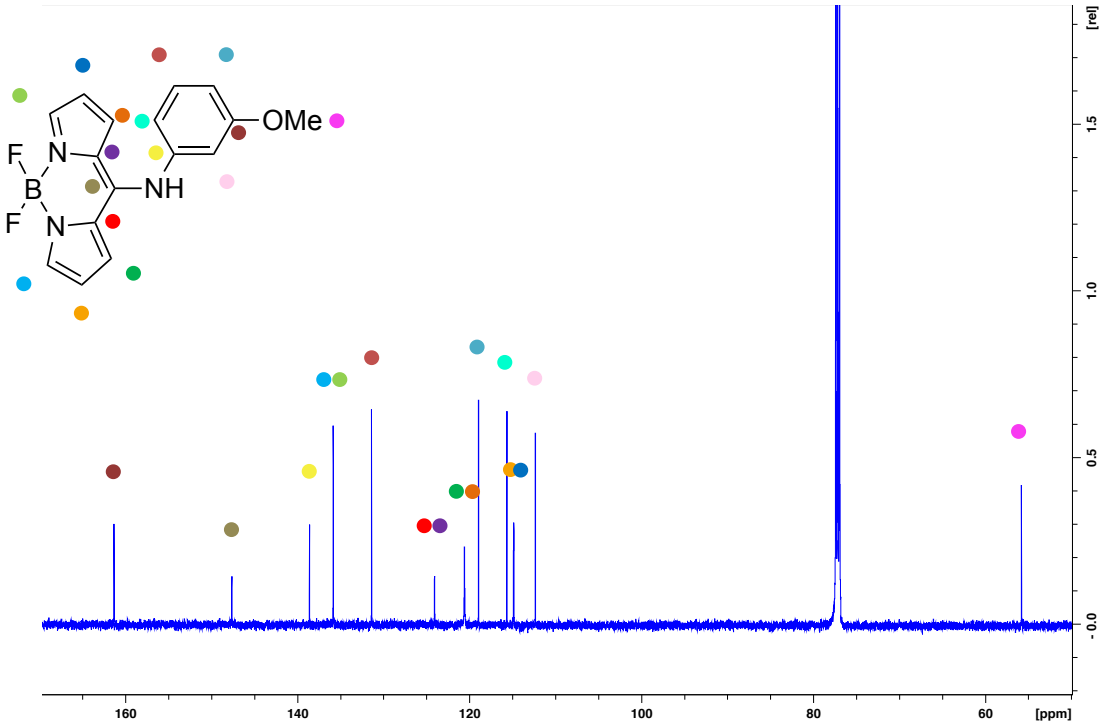


Figure S4. COSY NMR spectrum of **3b** ($CDCl_3$, 300K, 600 MHz).

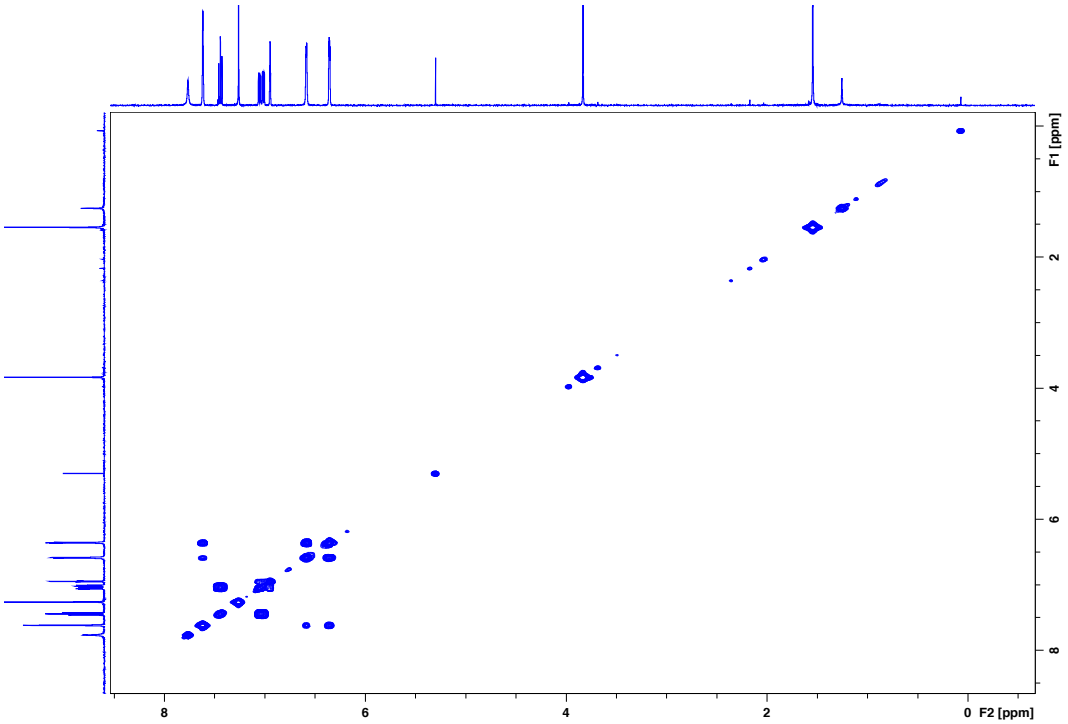


Figure S5. COSY NMR spectrum (zoom, aromatic region) of **3b** ($CDCl_3$, 300K, 600 MHz).

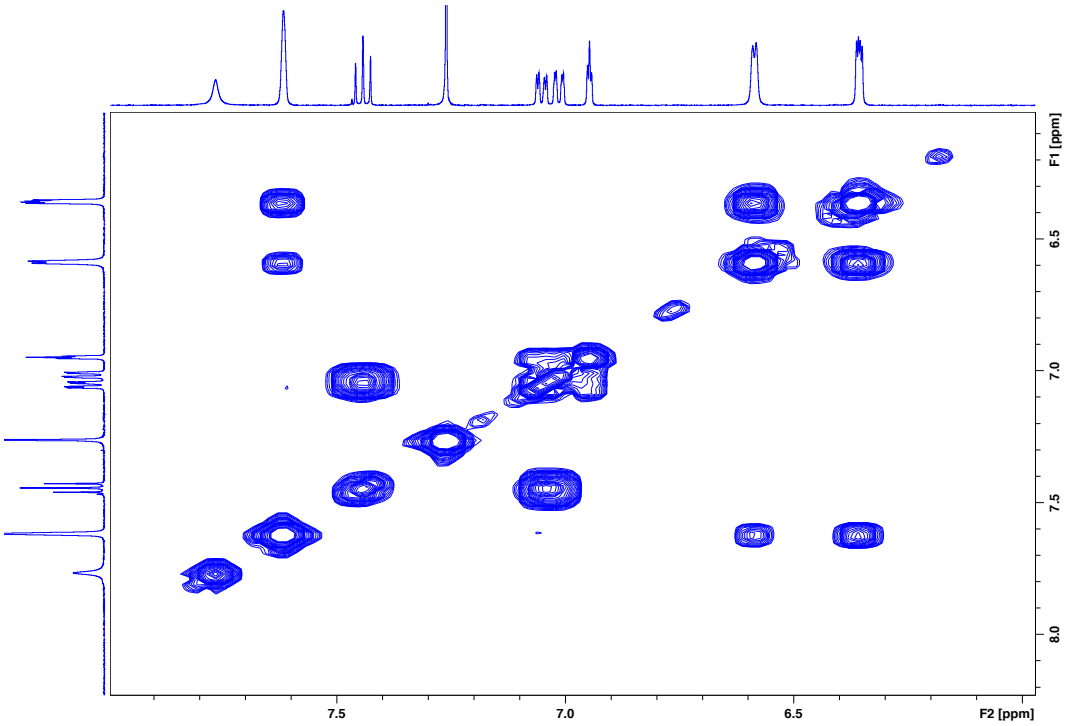


Figure S6. NOESY NMR spectrum of **3b** ($CDCl_3$, 300K, 600 MHz).

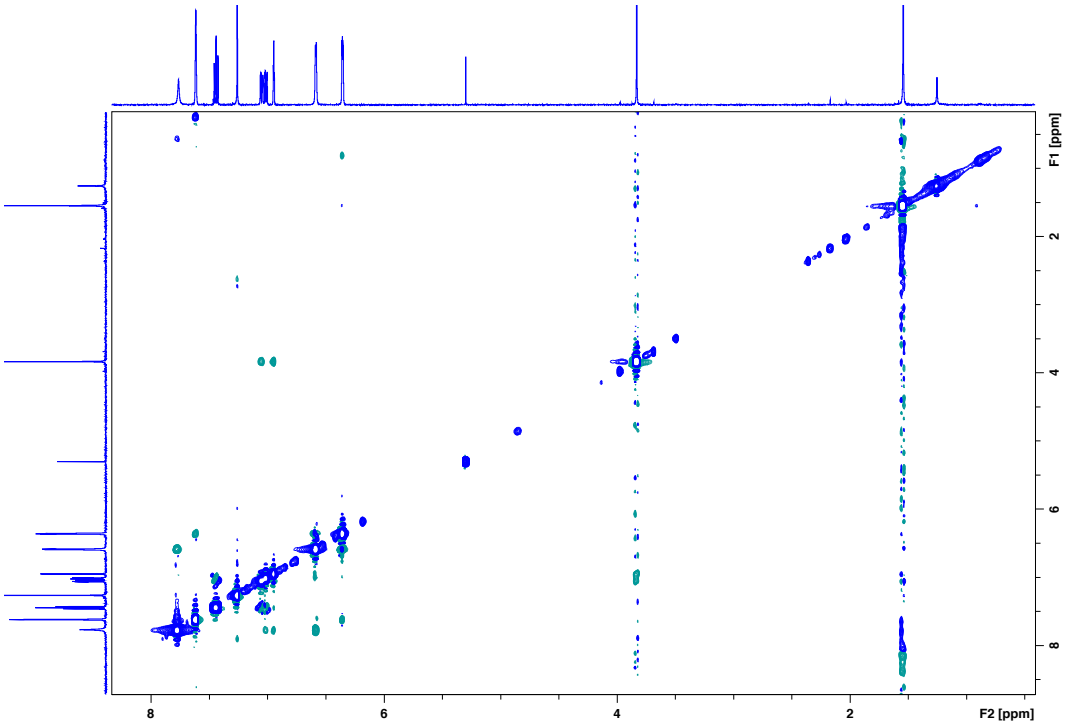


Figure S7. NOESY NMR spectrum (zoom, aromatic region) of **3b** ($CDCl_3$, 300K, 600 MHz).

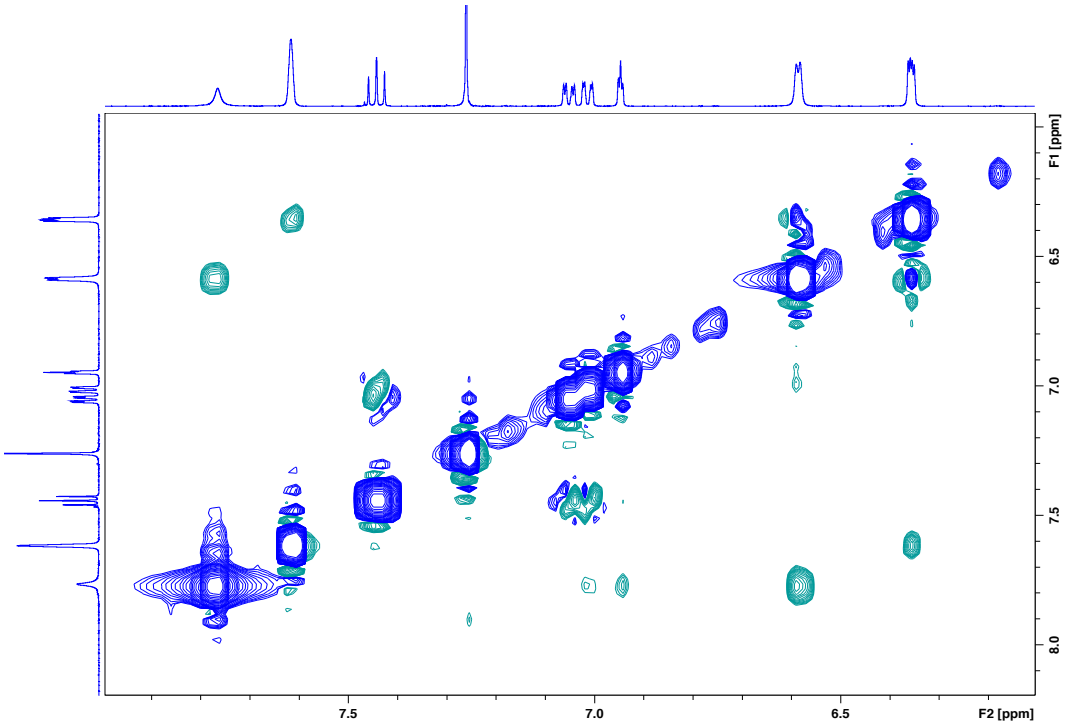


Figure S8. HMBC NMR spectrum of **3b** ($CDCl_3$, 300K, 500 MHz).

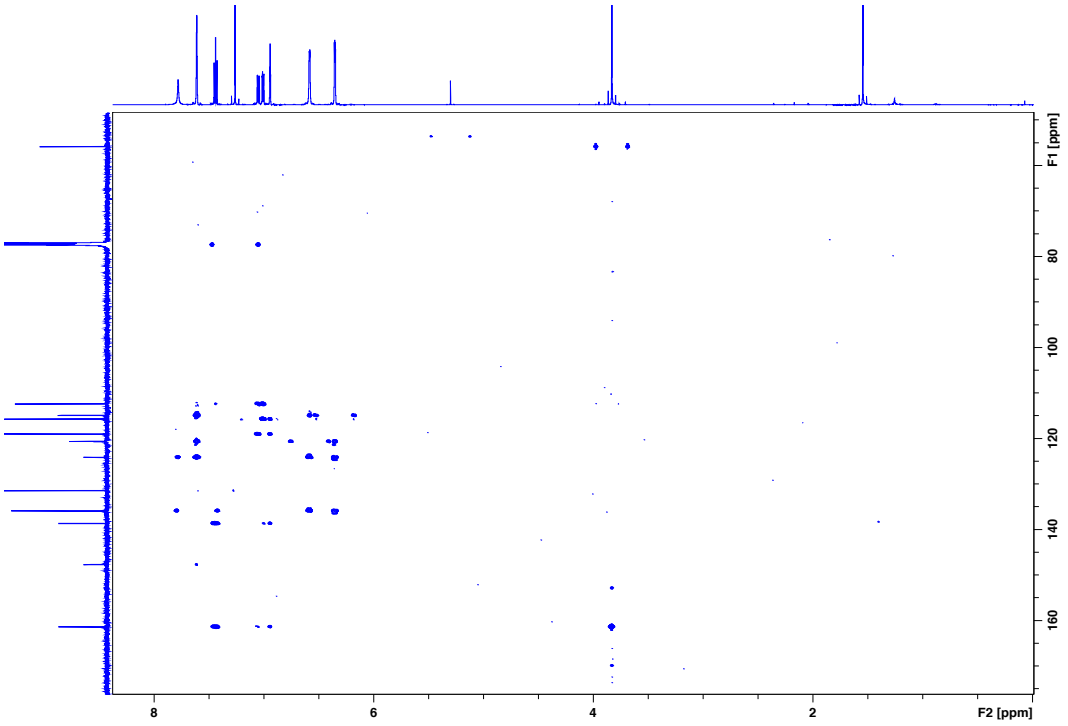


Figure S9. HMBC NMR spectrum (zoom, aromatic region) of **3b** ($CDCl_3$, 300K, 500 MHz).

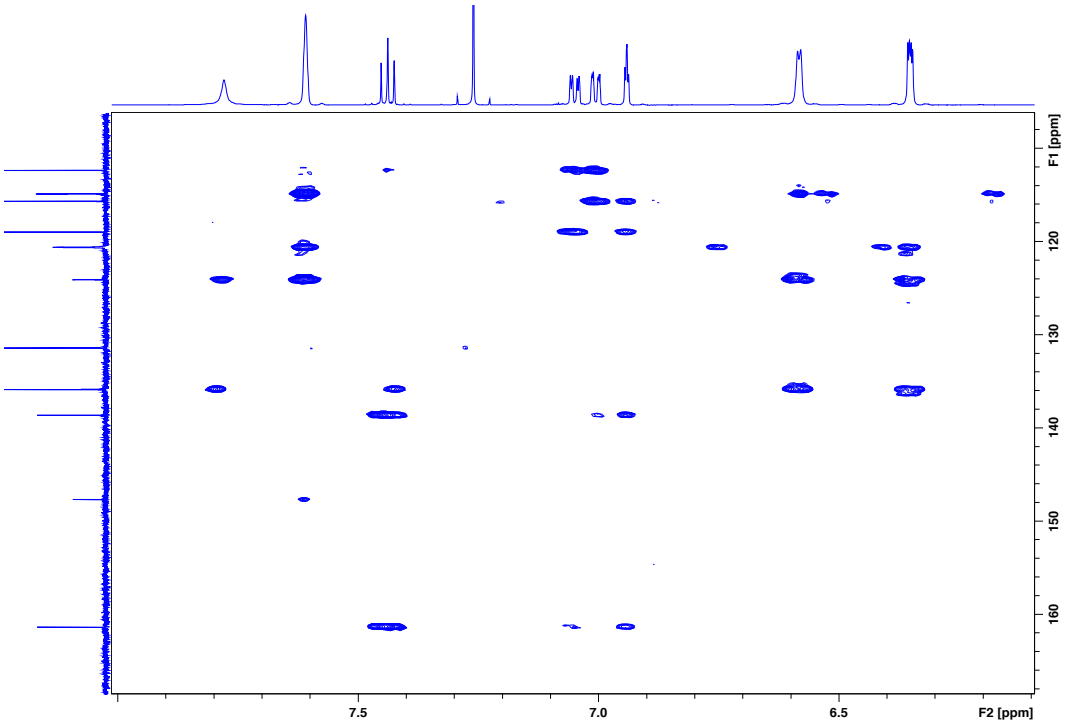


Figure S10. HMQC NMR spectrum of **3b** ($CDCl_3$, 300K, 500 MHz).

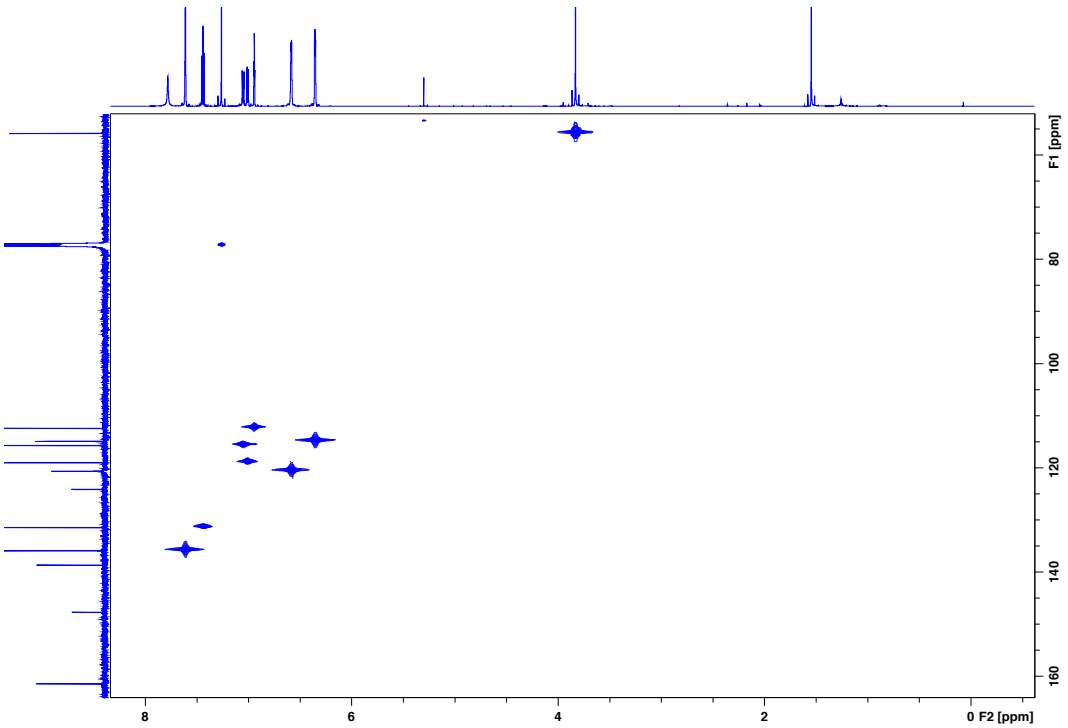
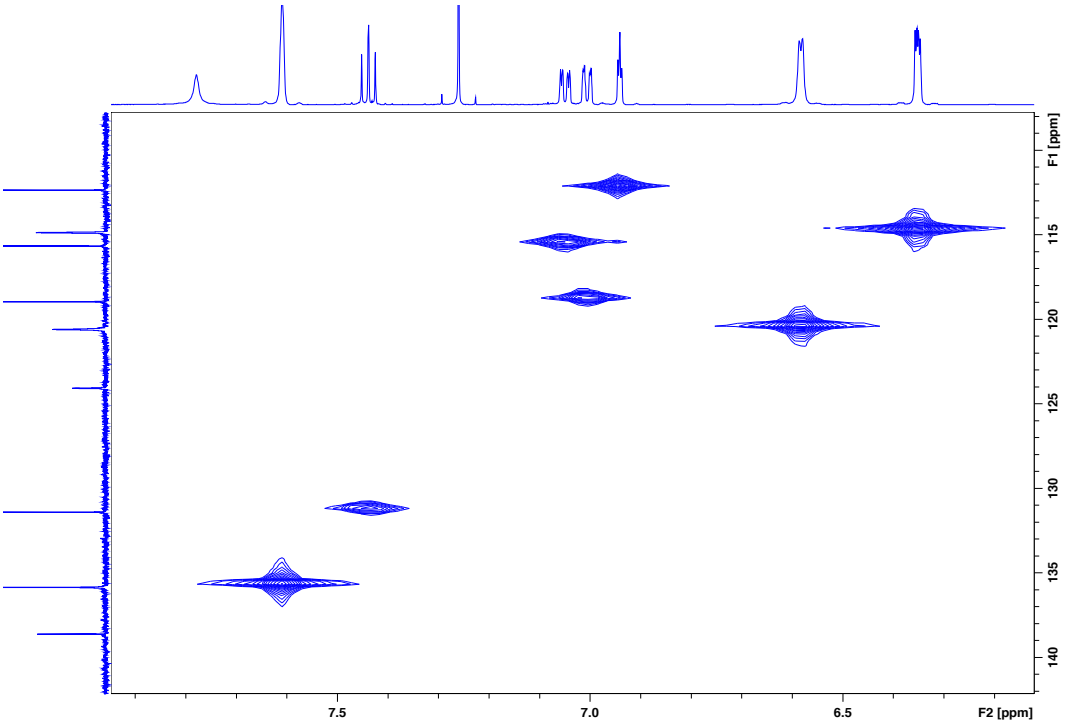


Figure S11. HMQC NMR spectrum (zoom, aromatic region) of **3b** ($CDCl_3$, 300K, 500 MHz).



3.2. NMR spectra of 3a.

Figure S12. ^{1}H NMR spectrum of **3a** ($CDCl_3$, 300K, 600 MHz).

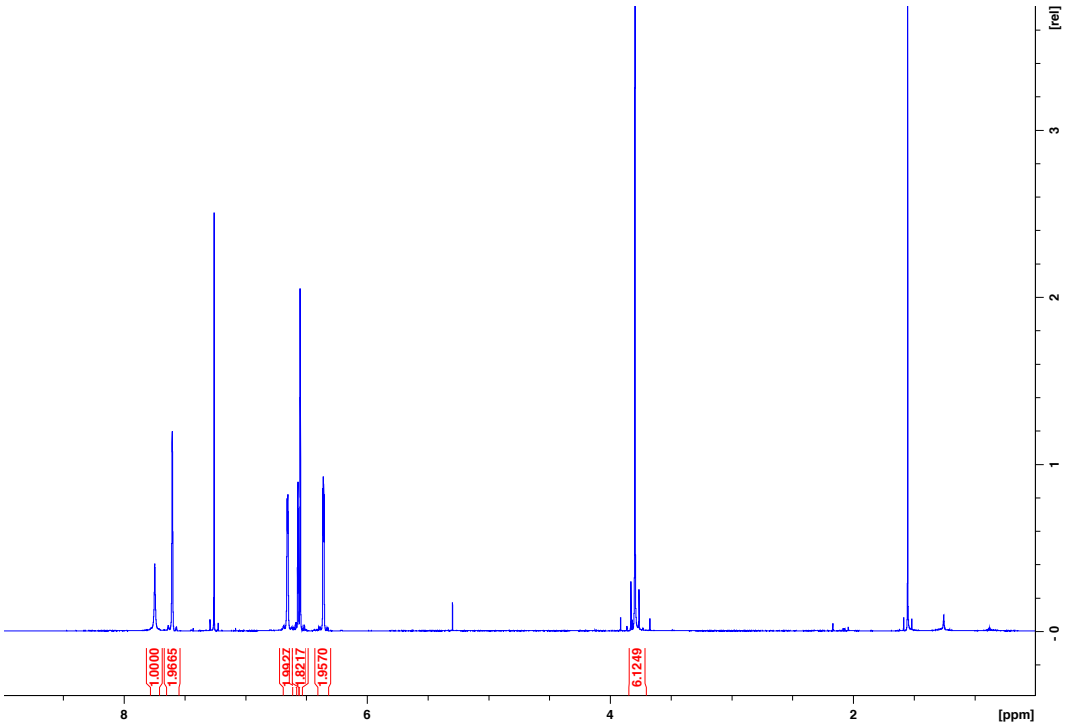


Figure S13. ^{1}H NMR spectrum (zoom, aromatic region) of **3a** ($CDCl_3$, 300K, 600 MHz).

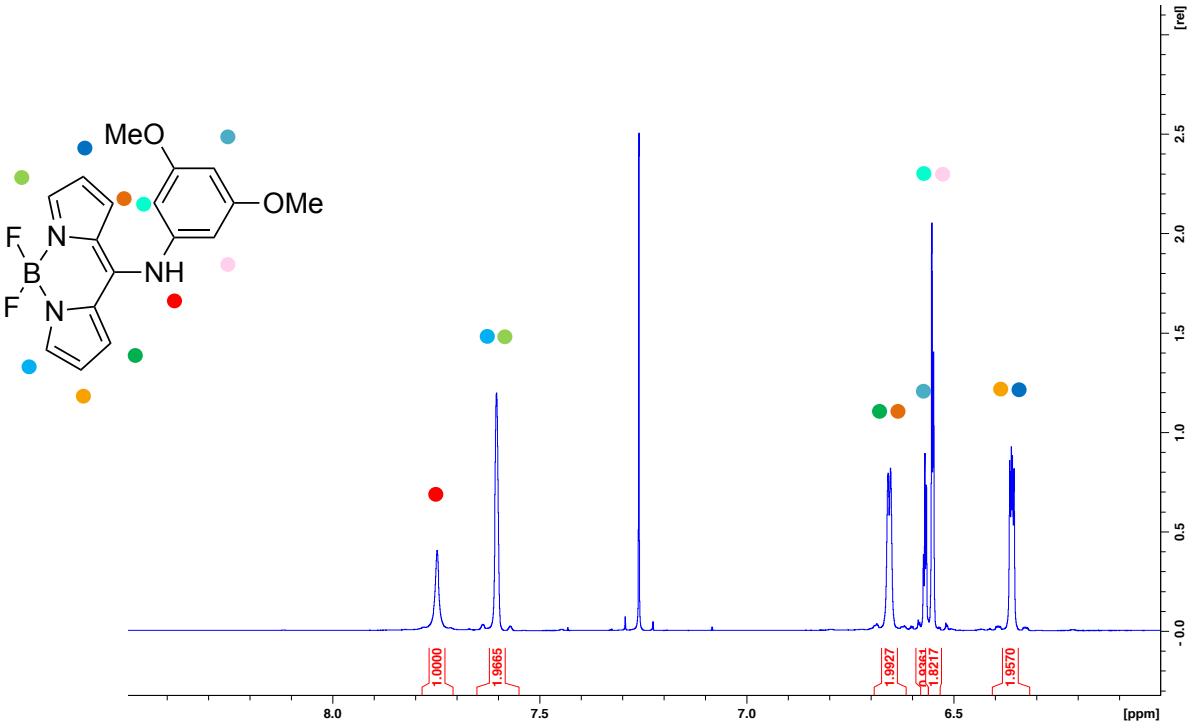


Figure S14. ^{13}C NMR spectrum of **3a** ($CDCl_3$, 300K, 125 MHz).

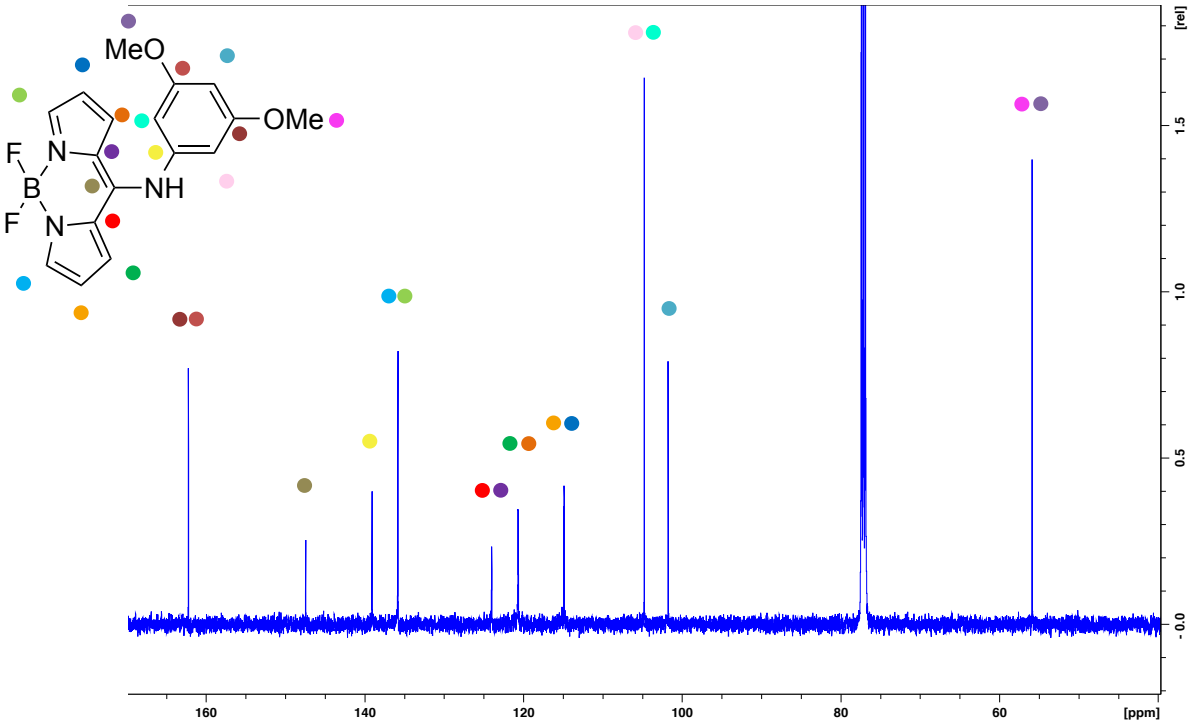


Figure S15. COSY NMR spectrum of **3a** ($CDCl_3$, 300K, 600 MHz).

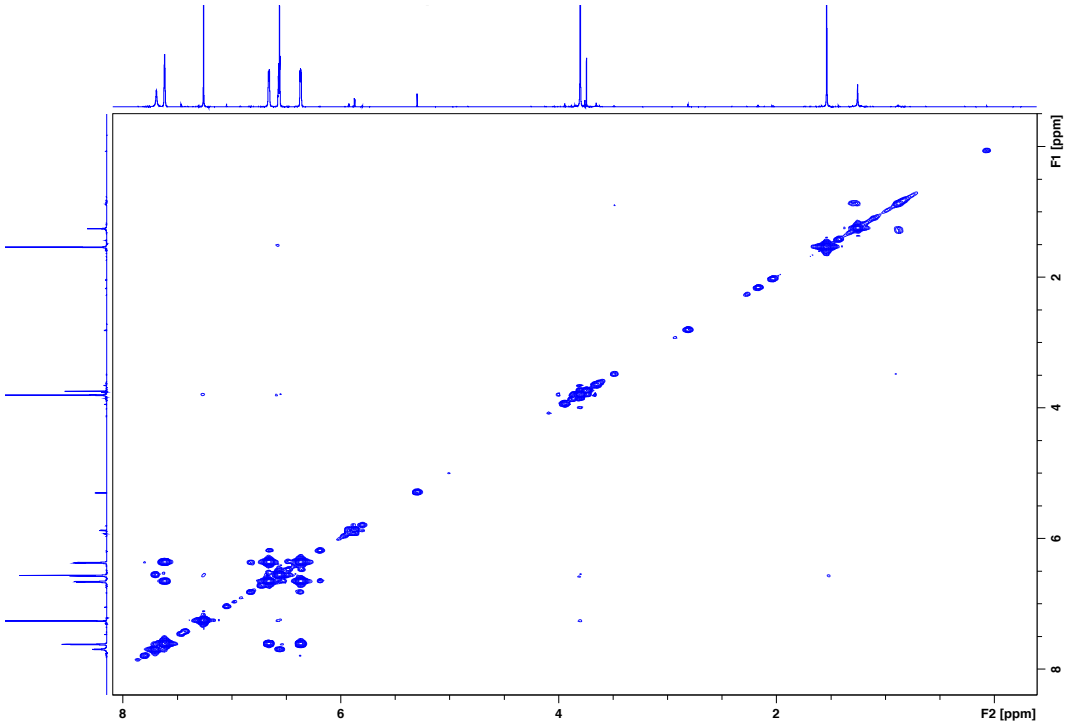


Figure S16. COSY NMR spectrum (zoom, aromatic region) of **3a** ($CDCl_3$, 300K, 600 MHz).

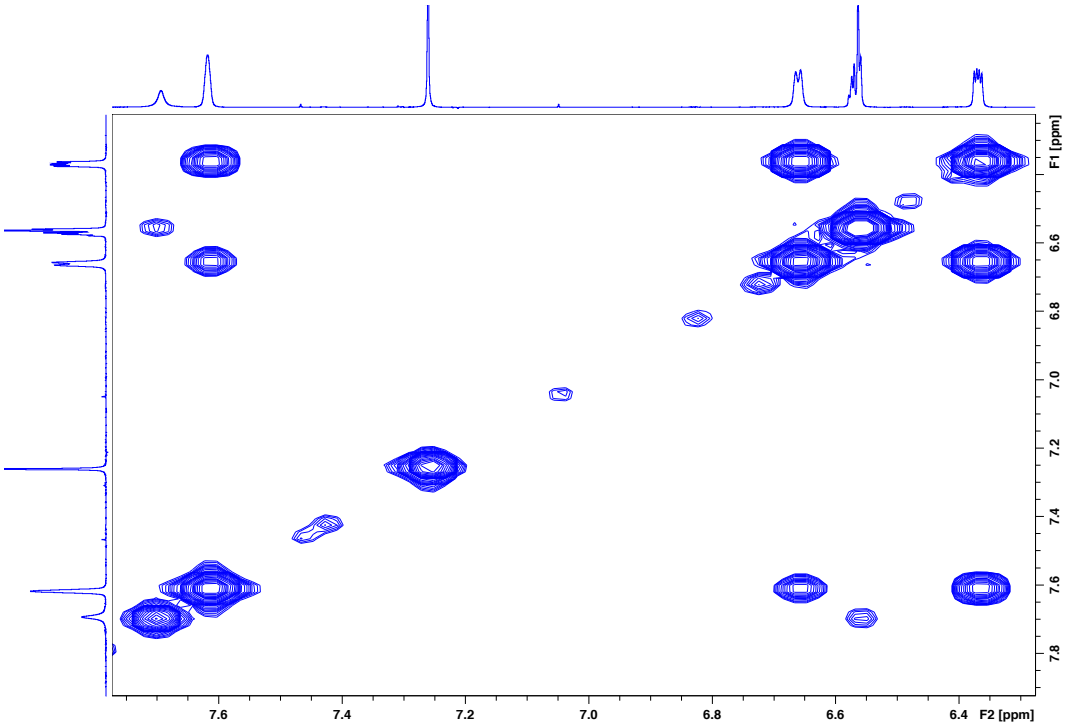


Figure S17. NOESY NMR spectrum of **3a** ($CDCl_3$, 300K, 600 MHz).

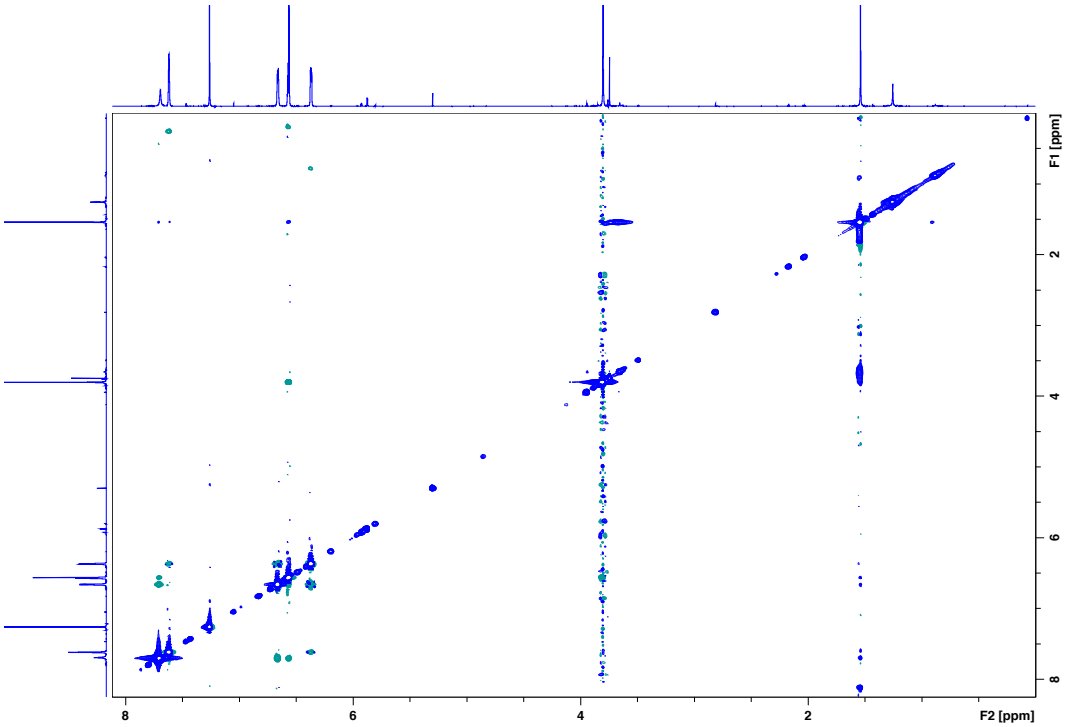


Figure S18. NOESY NMR spectrum (zoom, aromatic region) of **3a** ($CDCl_3$, 300K, 600 MHz).

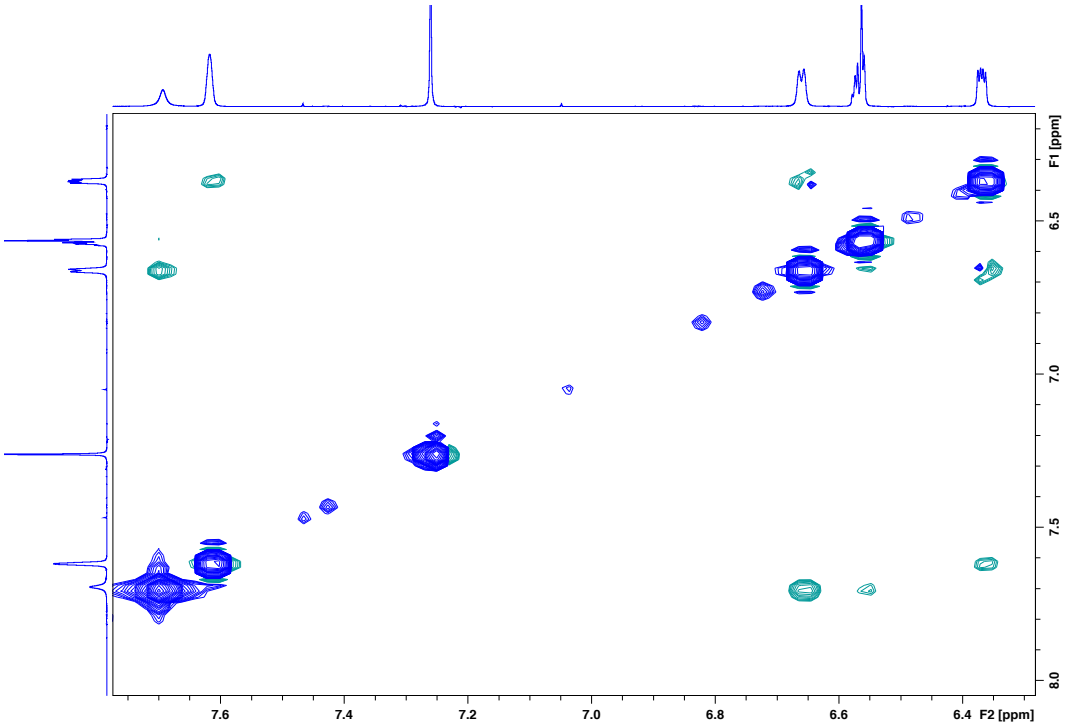


Figure S19. HMBC NMR spectrum of **3a** ($CDCl_3$, 300K, 500 MHz).

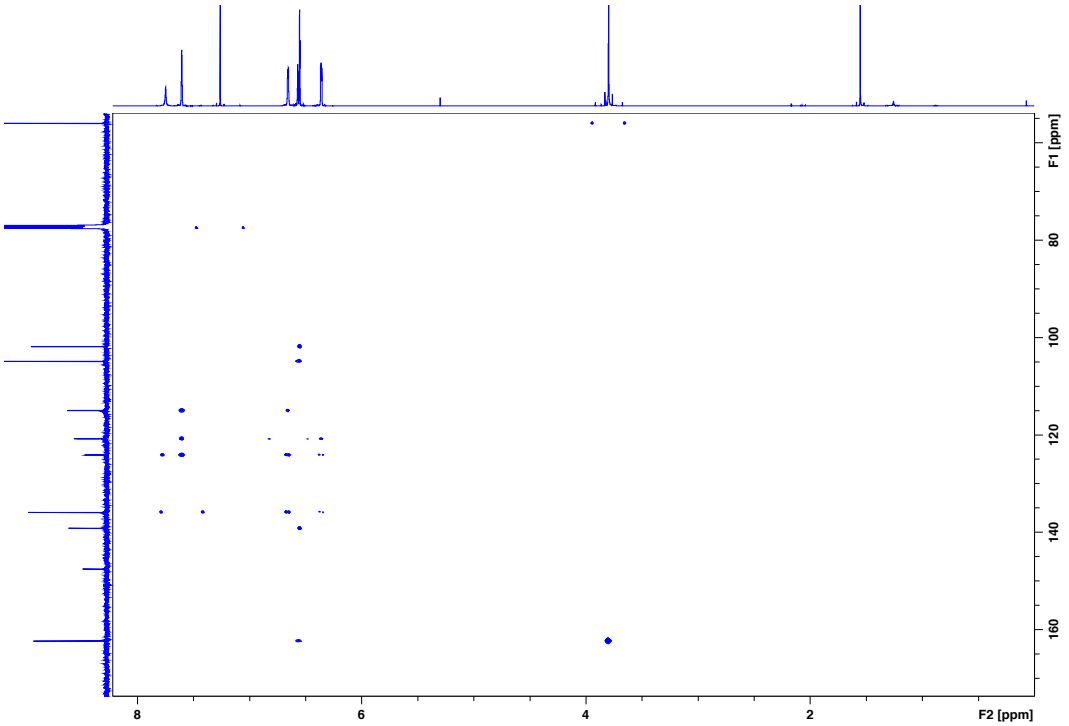


Figure S20. HMBC NMR spectrum (zoom, aromatic region) of **3a** ($CDCl_3$, 300K, 500 MHz).

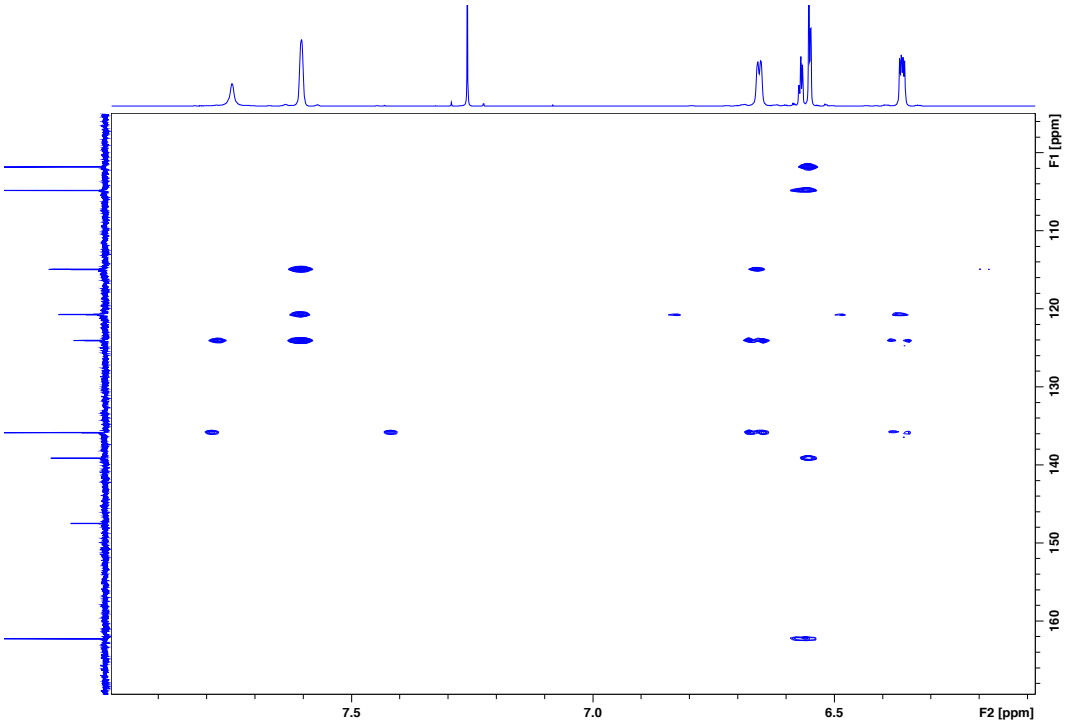
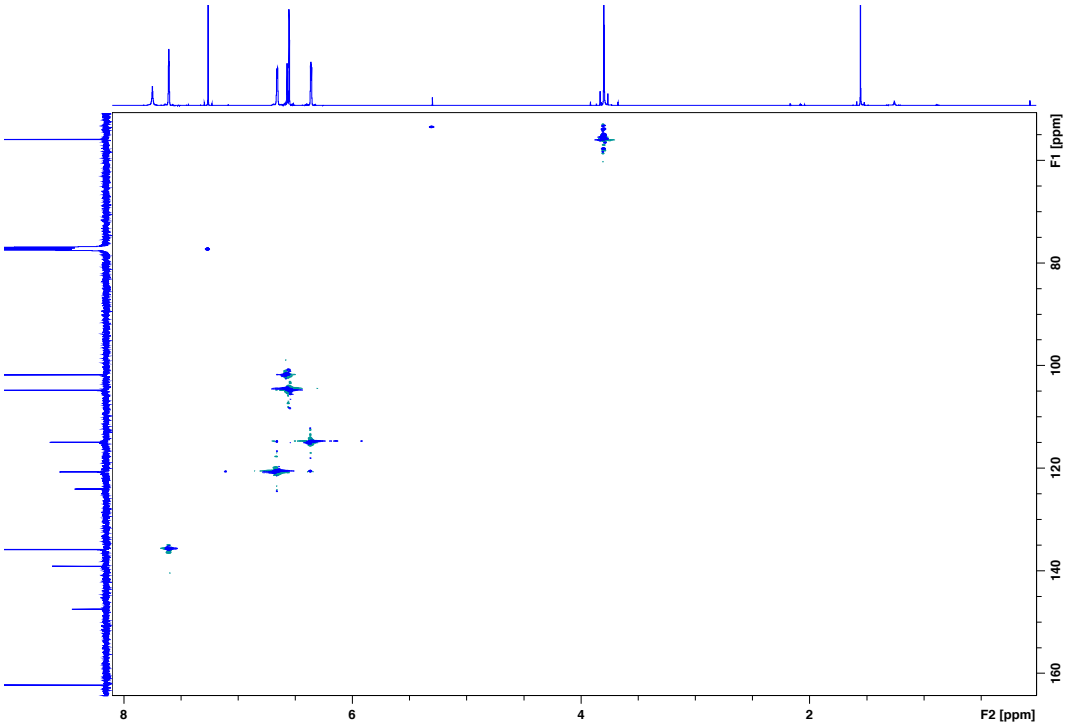


Figure S21. HSQC NMR spectrum of **3a** ($CDCl_3$, 300K, 500 MHz).



3.3. NMR Spectra of 4c.

Figure S22. ^{1}H NMR spectrum of **4c** ($CDCl_3$, 300K, 600 MHz).

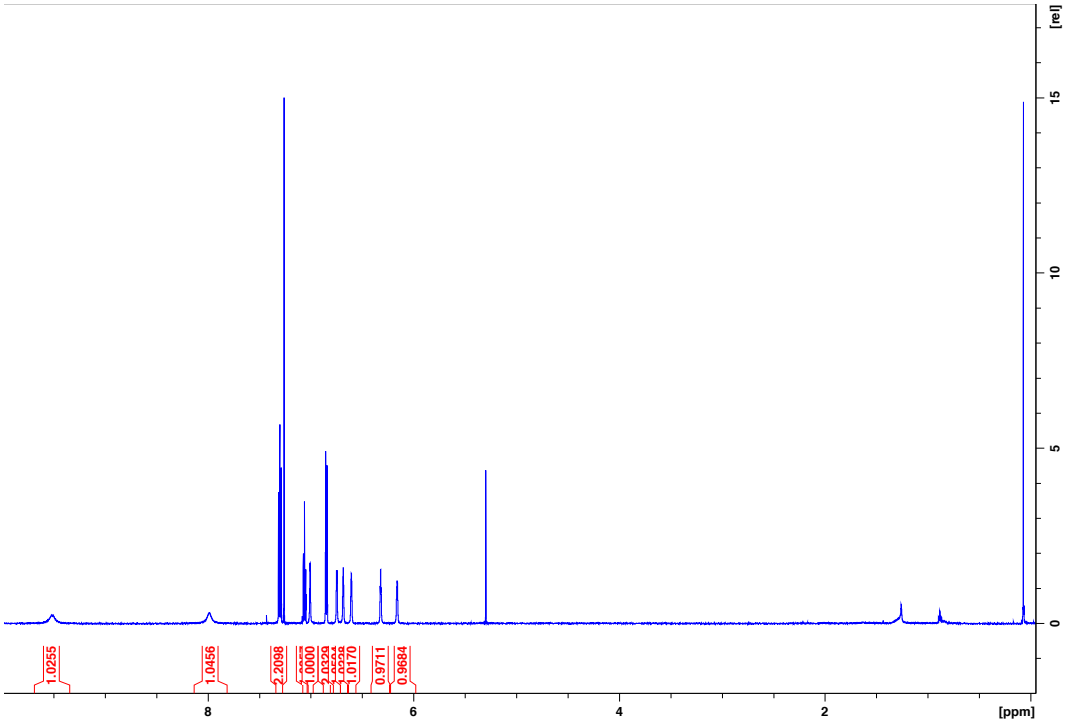


Figure S23. ^{1}H NMR spectrum (zoom, aromatic region) of **4c** ($CDCl_3$, 300K, 600 MHz).

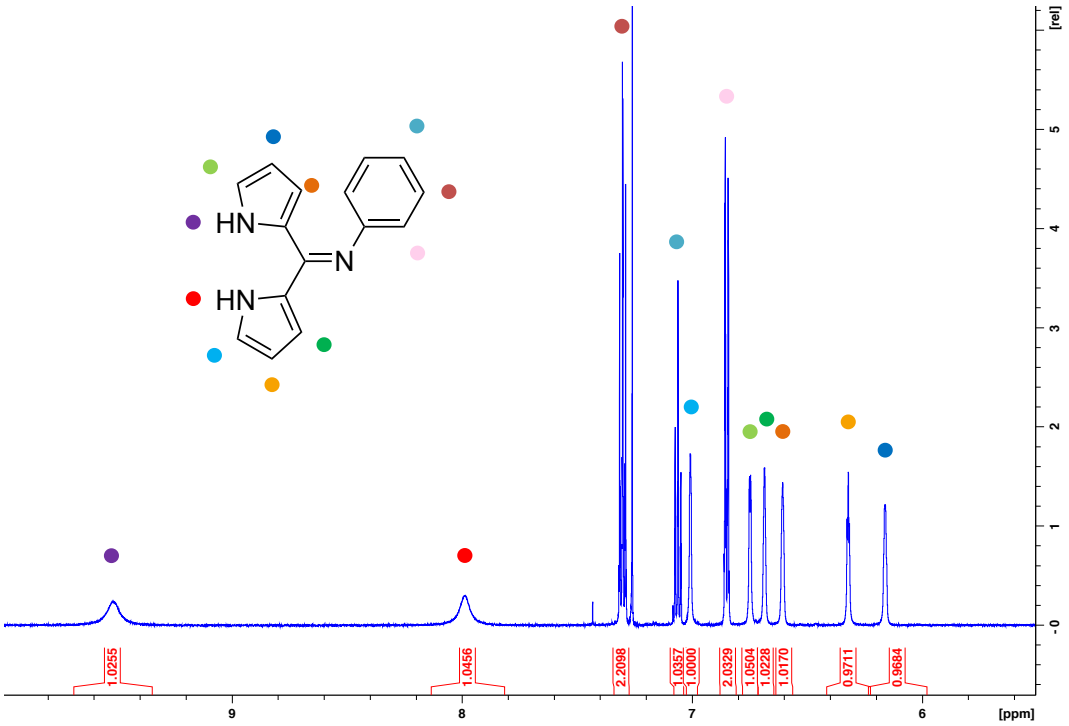


Figure S24. ^{13}C NMR spectrum of **4c** ($CDCl_3$, 300K, 125 MHz).

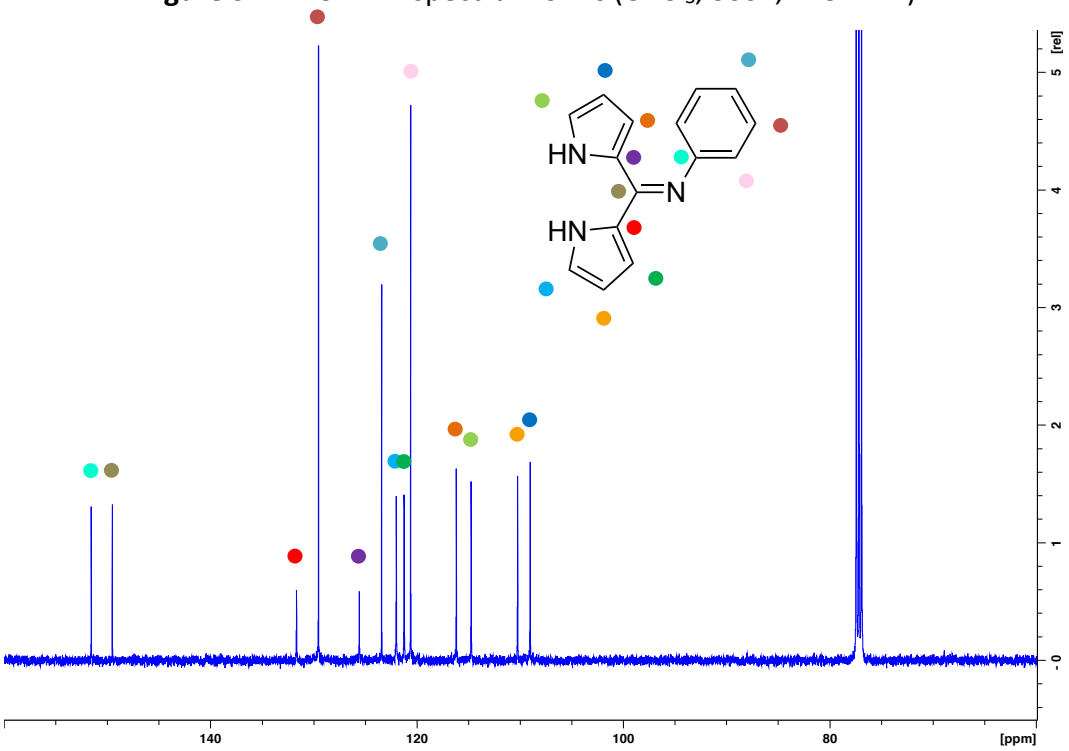


Figure S25. COSY NMR spectrum of **4c** ($CDCl_3$, 300K, 600 MHz).

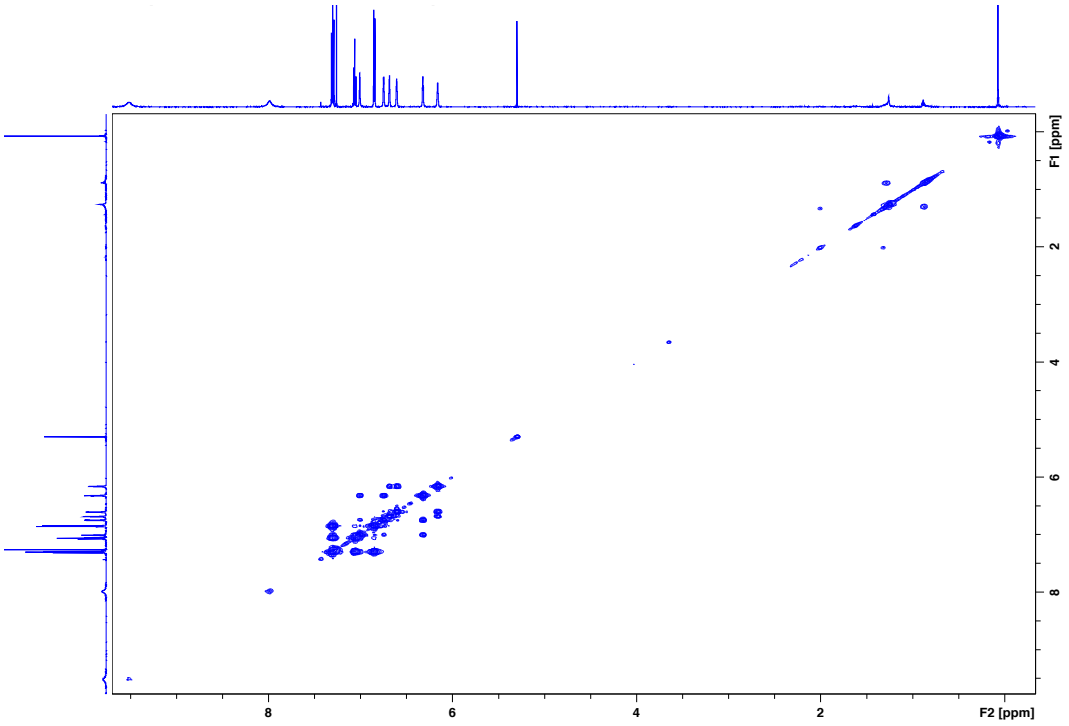


Figure S26. COSY NMR spectrum (zoom, aromatic region) of **4c** ($CDCl_3$, 300K, 600 MHz).

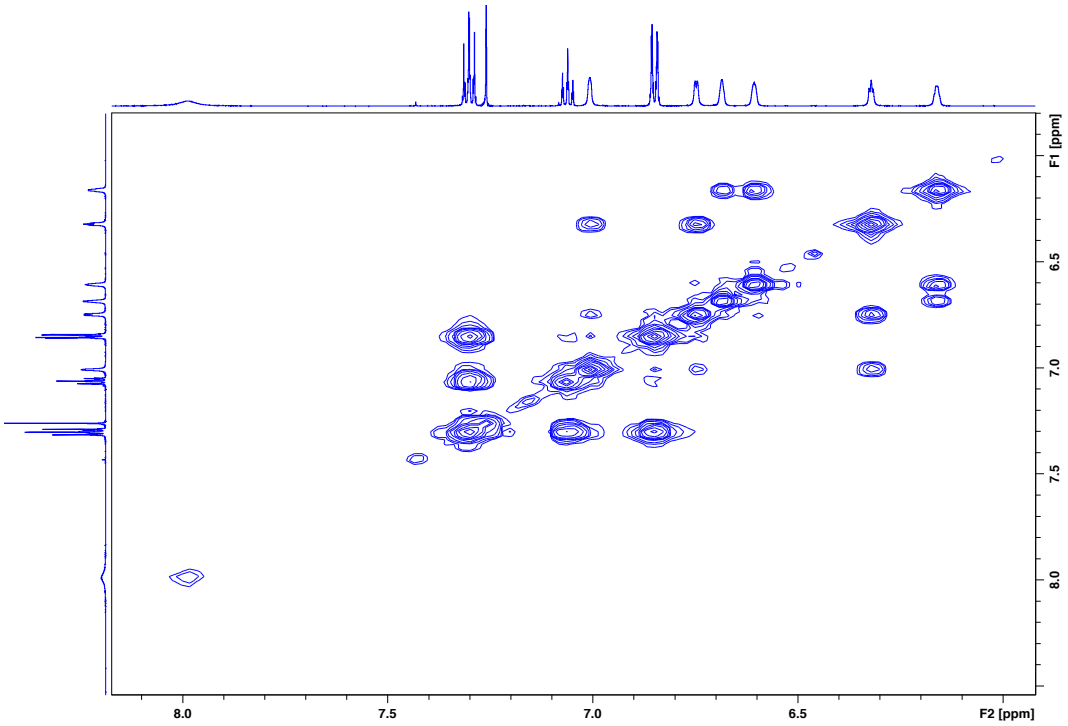


Figure S27. NOESY NMR spectrum of **4c** ($CDCl_3$, 300K, 600 MHz).

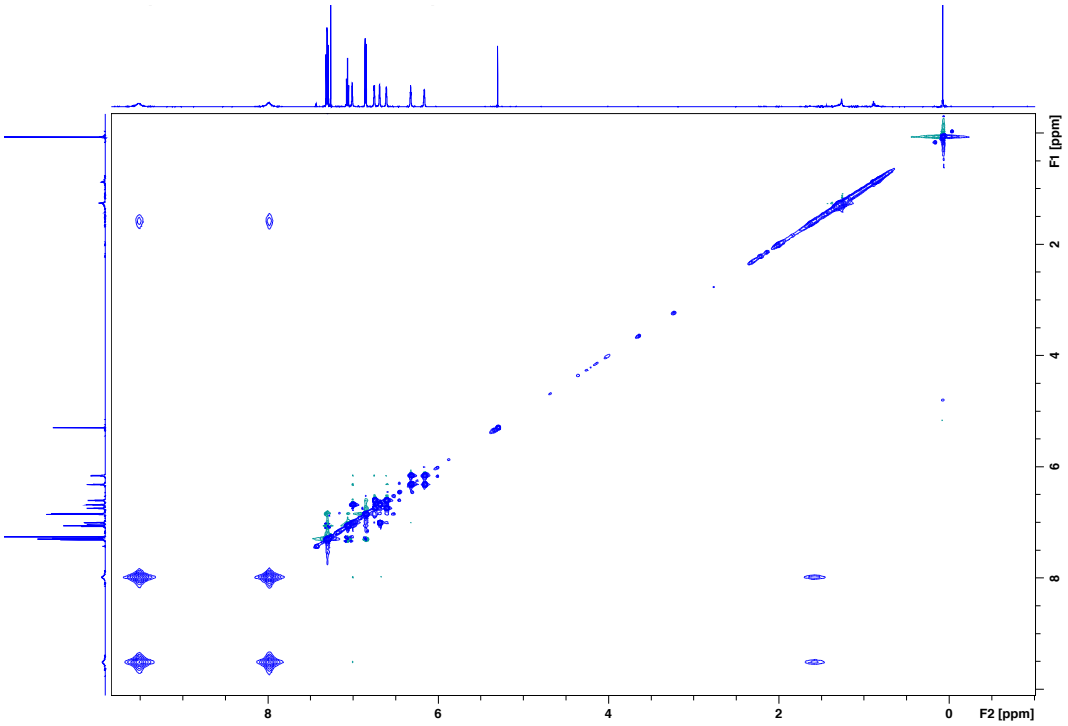


Figure S28. NOESY NMR spectrum (zoom, aromatic region) of **4c** ($CDCl_3$, 300K, 600 MHz).

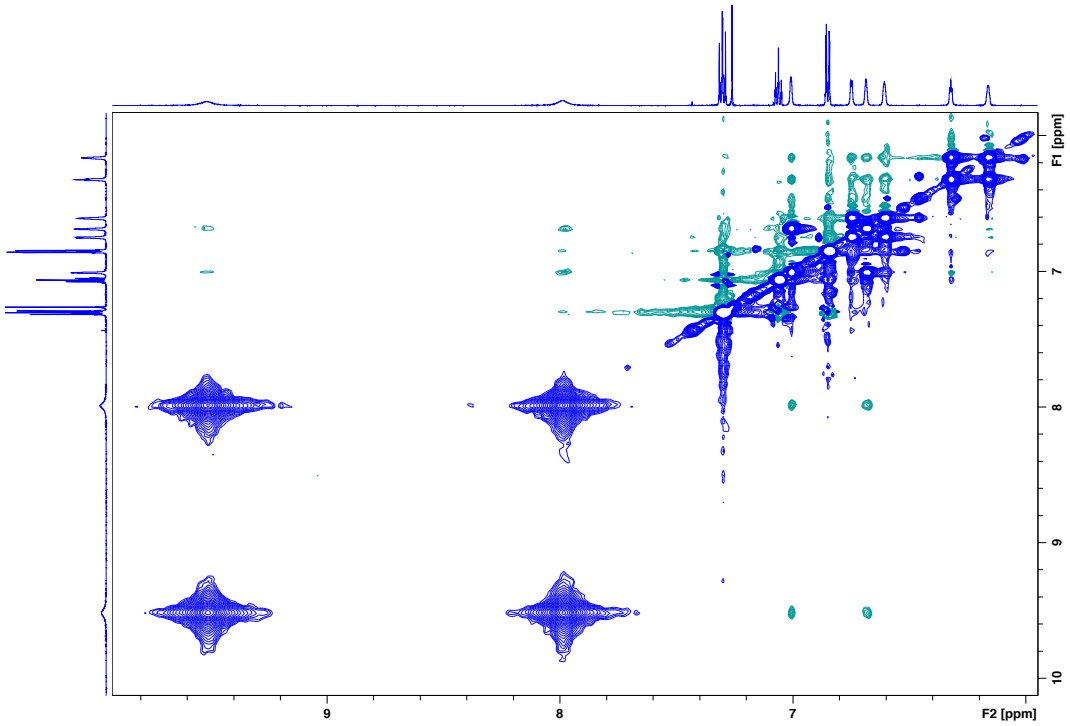


Figure S29. HMBC NMR spectrum of **4c** ($CDCl_3$, 300K, 500 MHz).

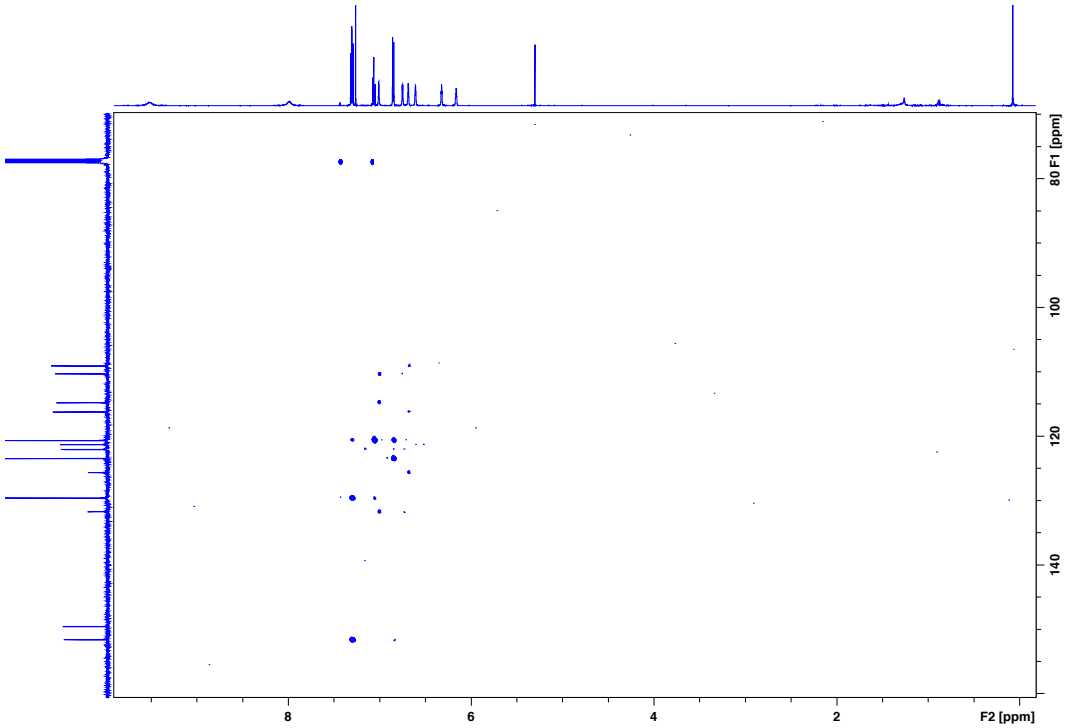


Figure S30. HMBC NMR spectrum (zoom, aromatic region) of **4c** ($CDCl_3$, 300K, 500 MHz).

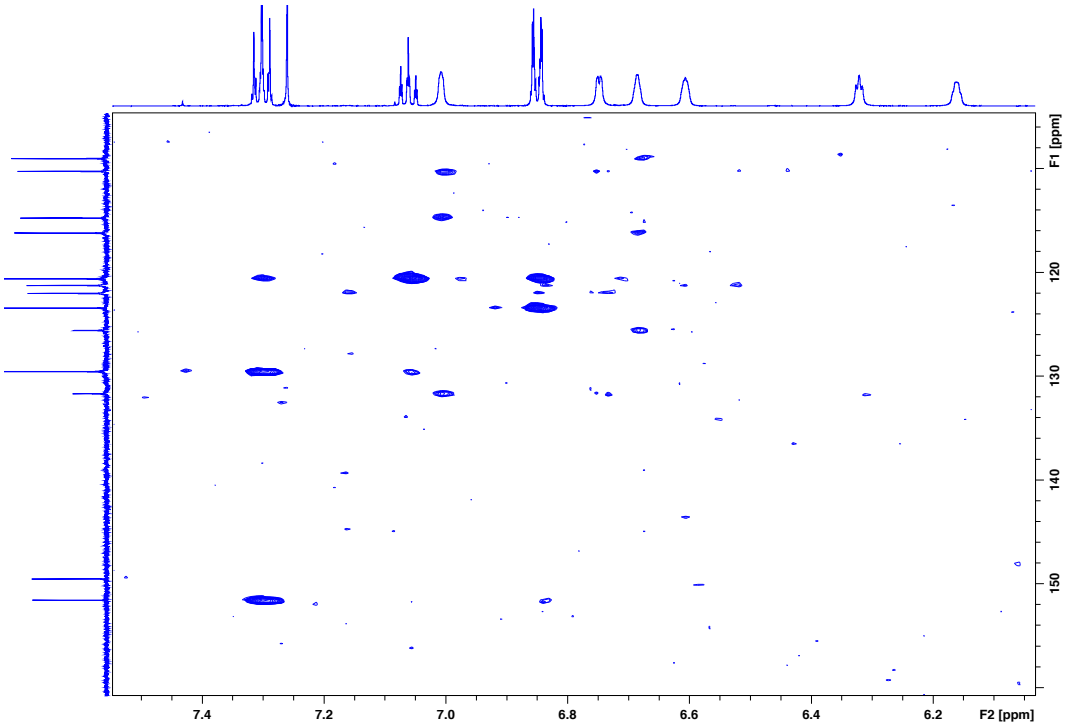


Figure S31. HSQC NMR spectrum of **4c** ($CDCl_3$, 300K, 500 MHz).

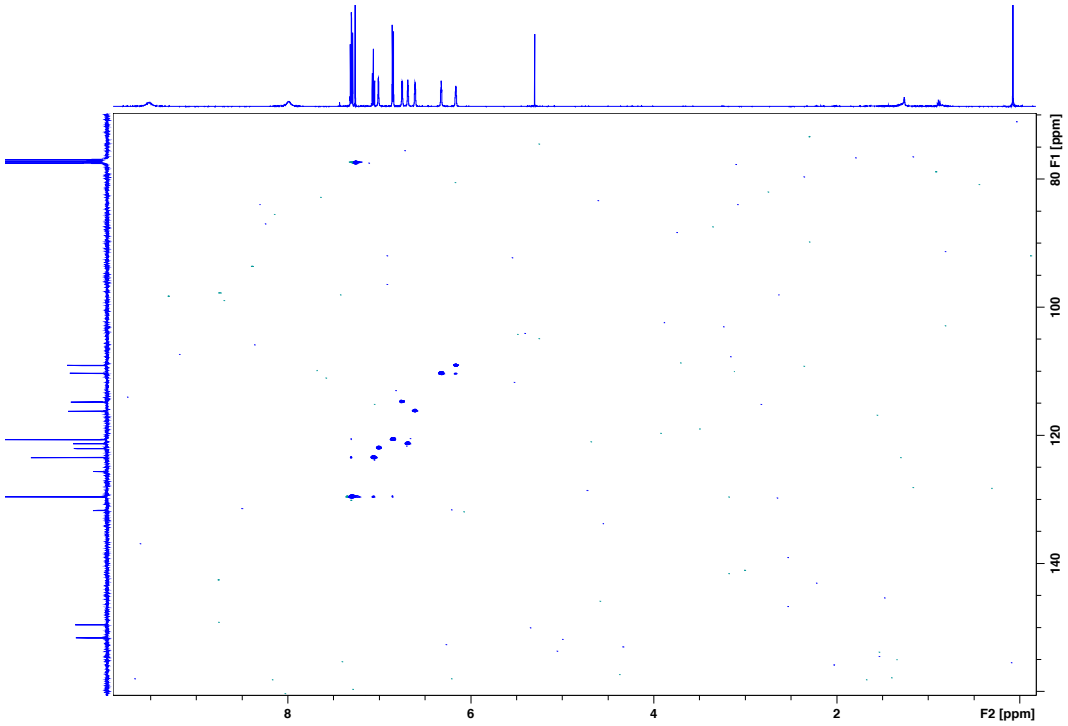
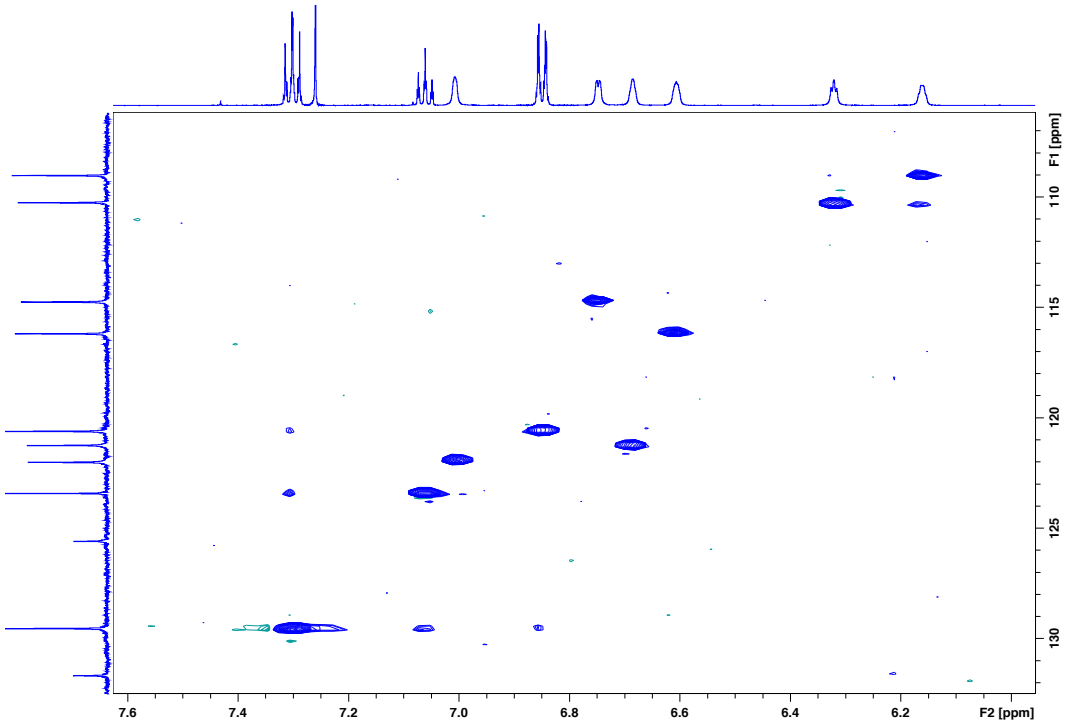


Figure S32. HSQC NMR spectrum (zoom, aromatic region) of **4c** ($CDCl_3$, 300K, 500 MHz).



3.4. NMR Spectra of 4b.

Figure S33. ^{1}H NMR spectrum of **4b** ($CDCl_3$, 300K, 600 MHz).

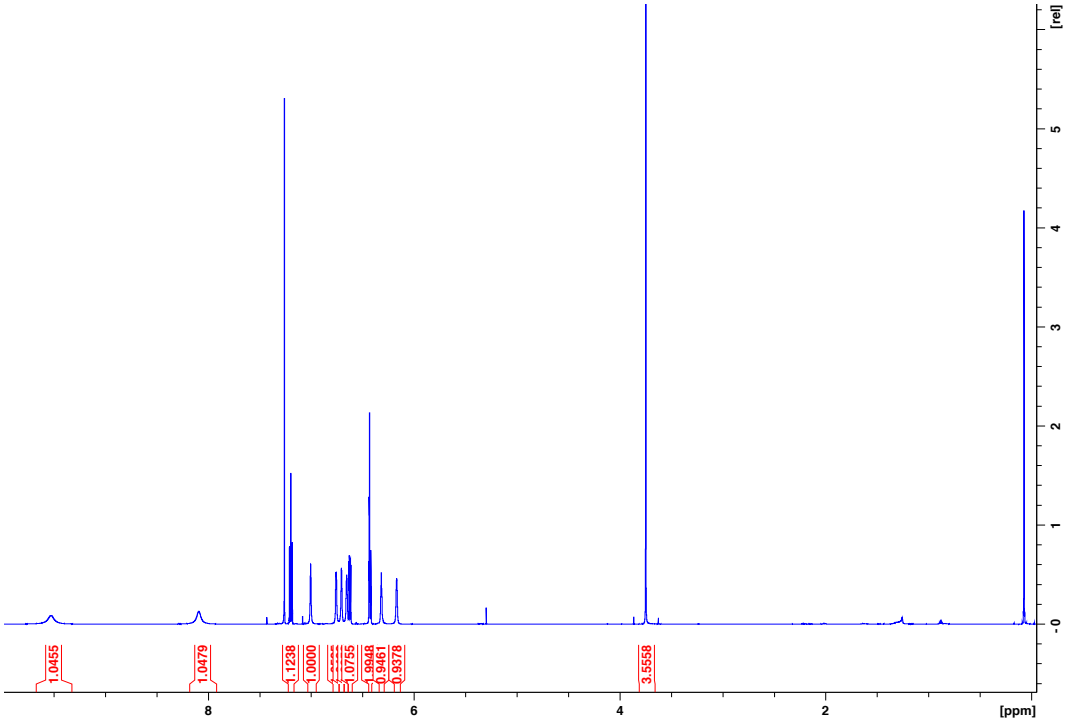


Figure S34. ^{1}H NMR spectrum (zoom, aromatic region) of **4b** ($CDCl_3$, 300K, 600 MHz).

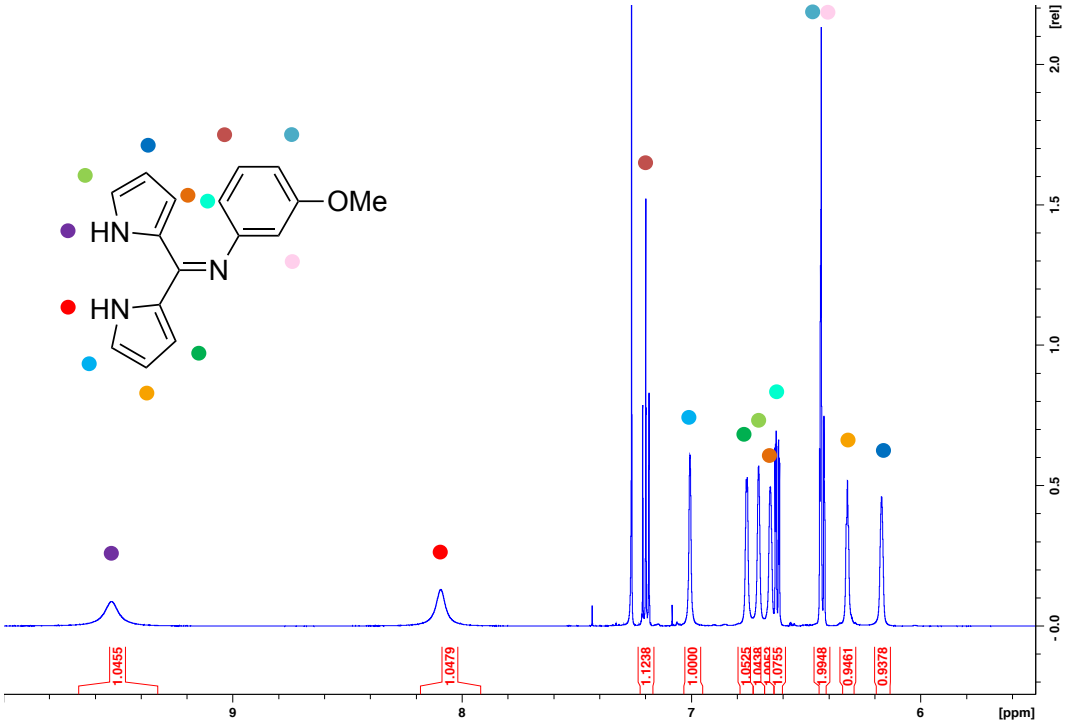


Figure S35. ^{13}C NMR spectrum of **4b** ($CDCl_3$, 300K, 125 MHz).

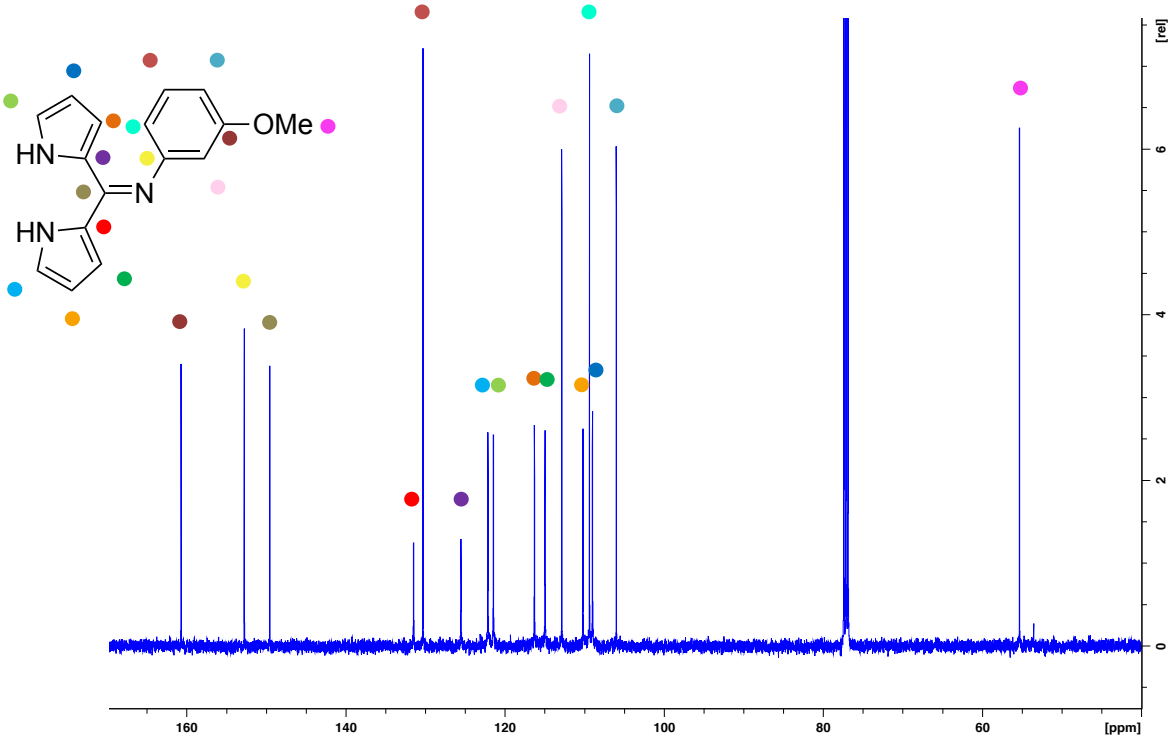


Figure S36. COSY NMR spectrum of **4b** ($CDCl_3$, 300K, 600 MHz).

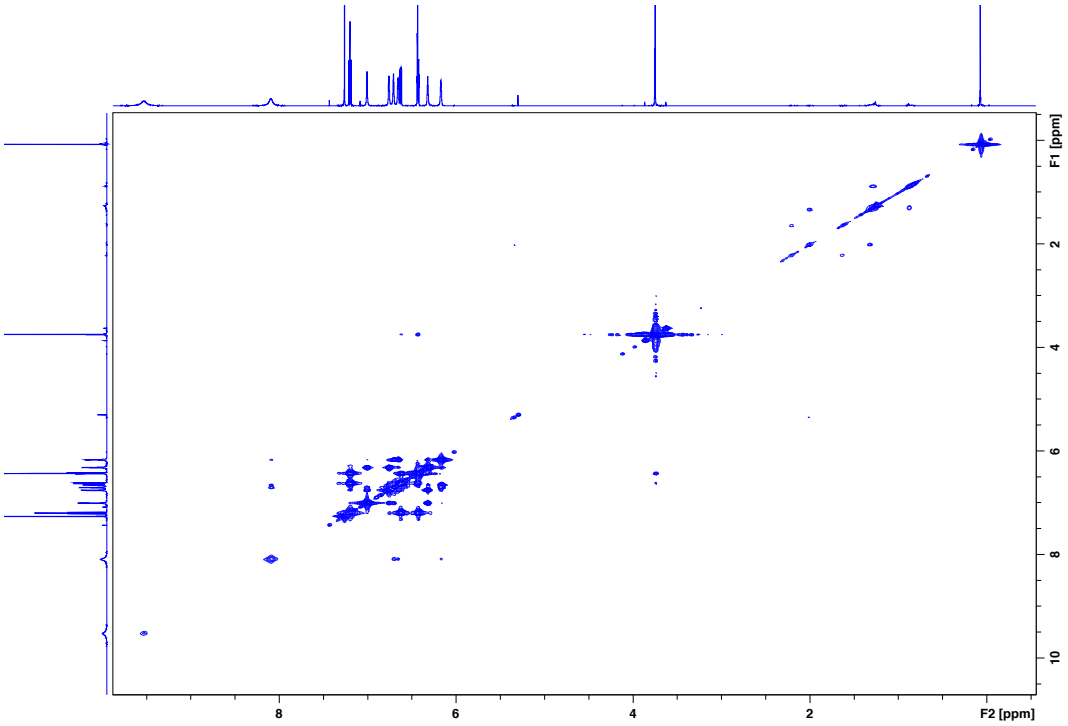


Figure S37. COSY NMR spectrum (zoom, aromatic region) of **4b** ($CDCl_3$, 300K, 600 MHz).

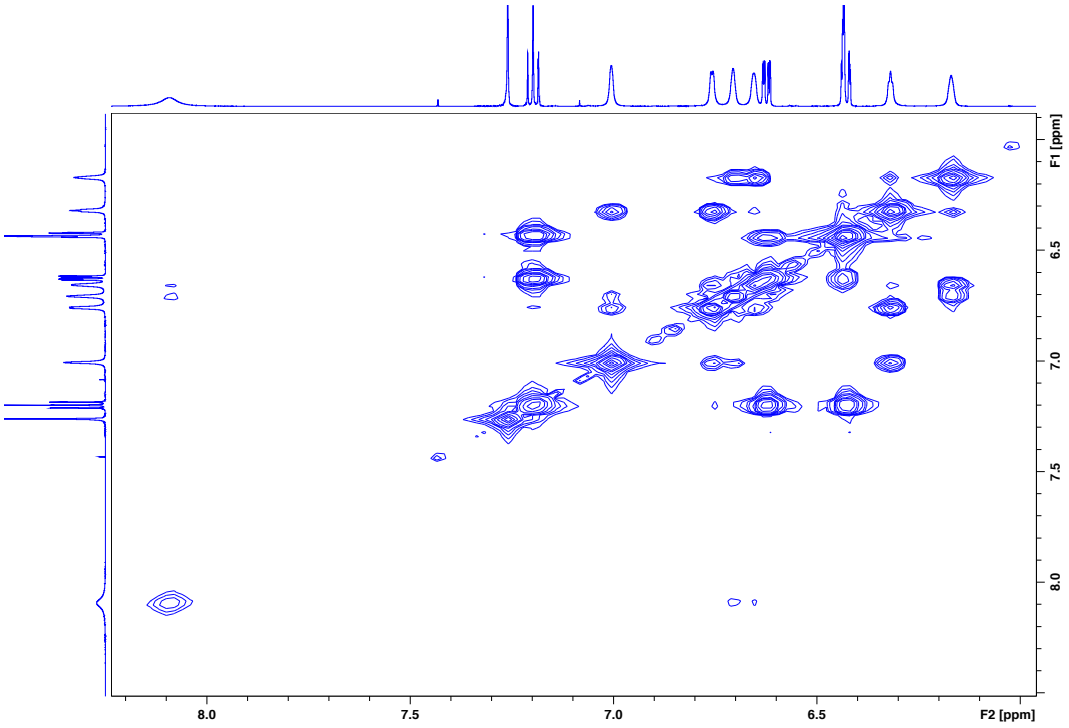


Figure S38. NOESY NMR spectrum of **4b** ($CDCl_3$, 300K, 600 MHz).

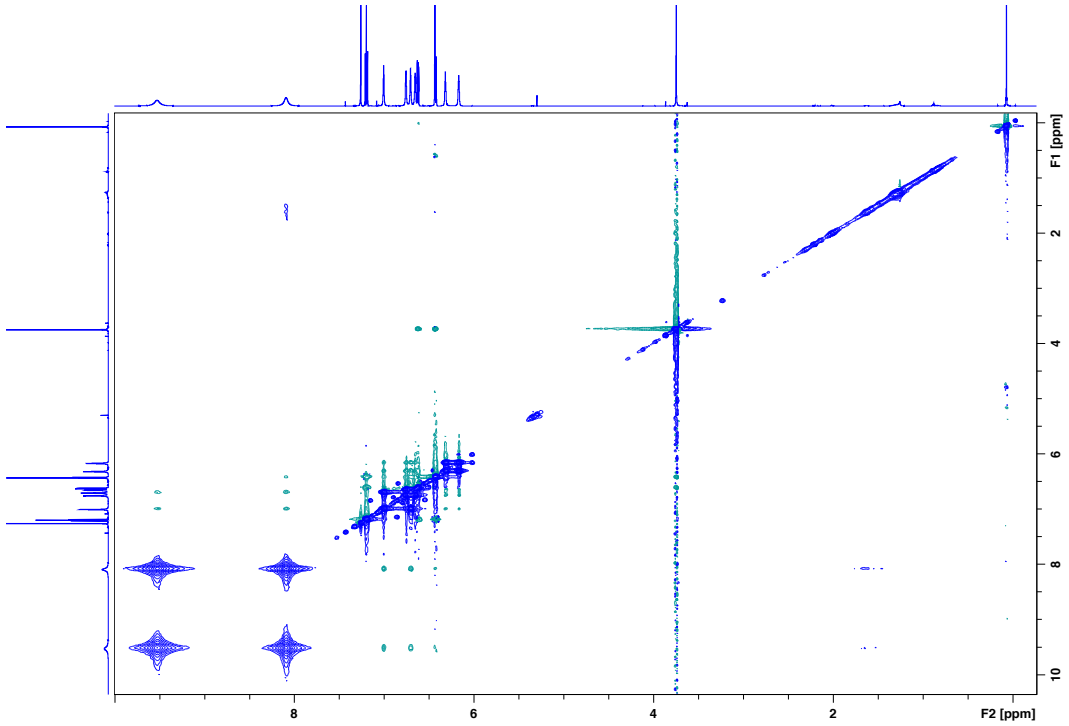


Figure S39. NOESY NMR spectrum (zoom, aromatic region) of **4b** ($CDCl_3$, 300K, 600 MHz).

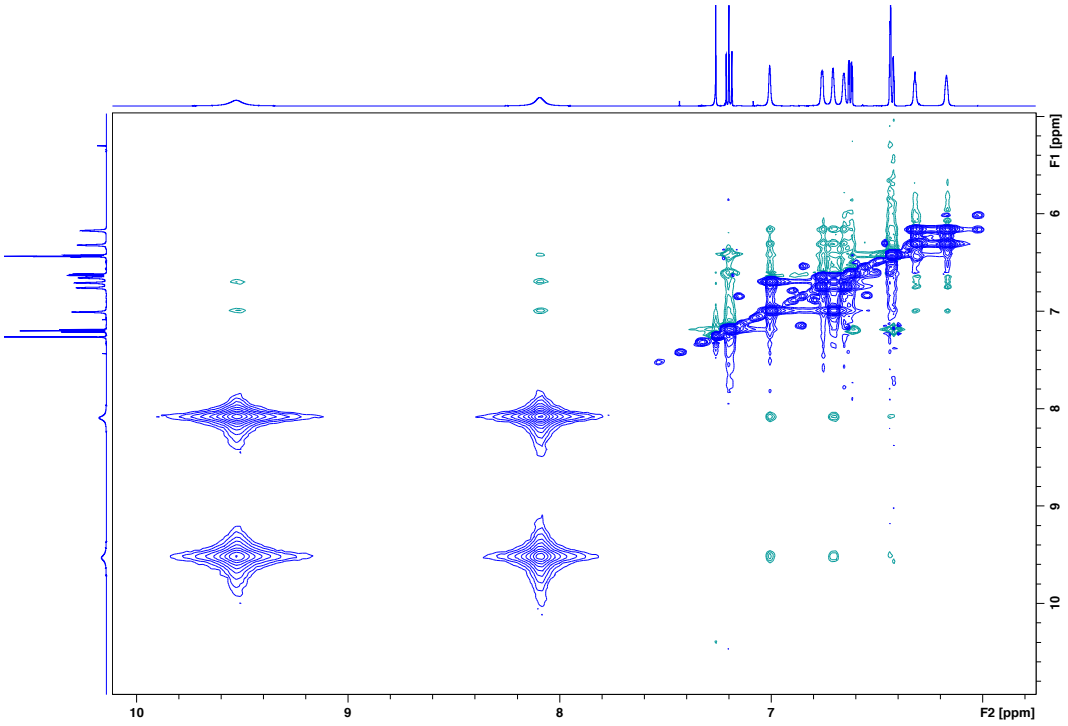


Figure S40. HMBC NMR spectrum of **4b** ($CDCl_3$, 300K, 500 MHz).

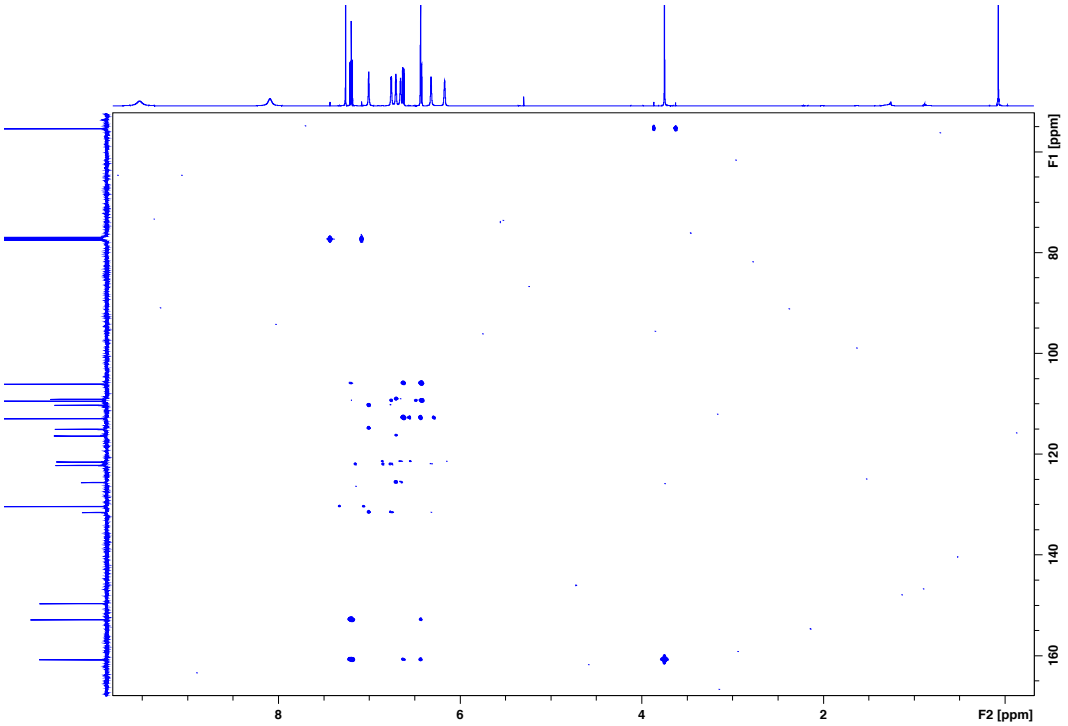


Figure S41. HMBC NMR spectrum (zoom, aromatic region) of **4b** ($CDCl_3$, 300K, 500 MHz).

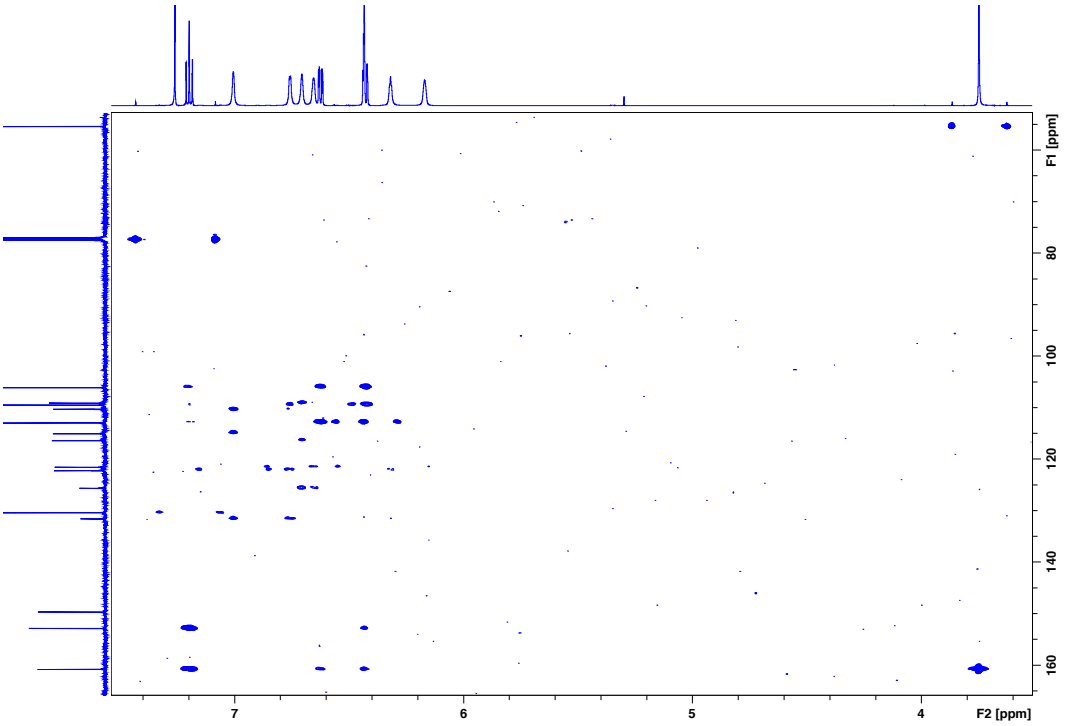


Figure S42. HSQC NMR spectrum of **4b** ($CDCl_3$, 300K, 500 MHz).

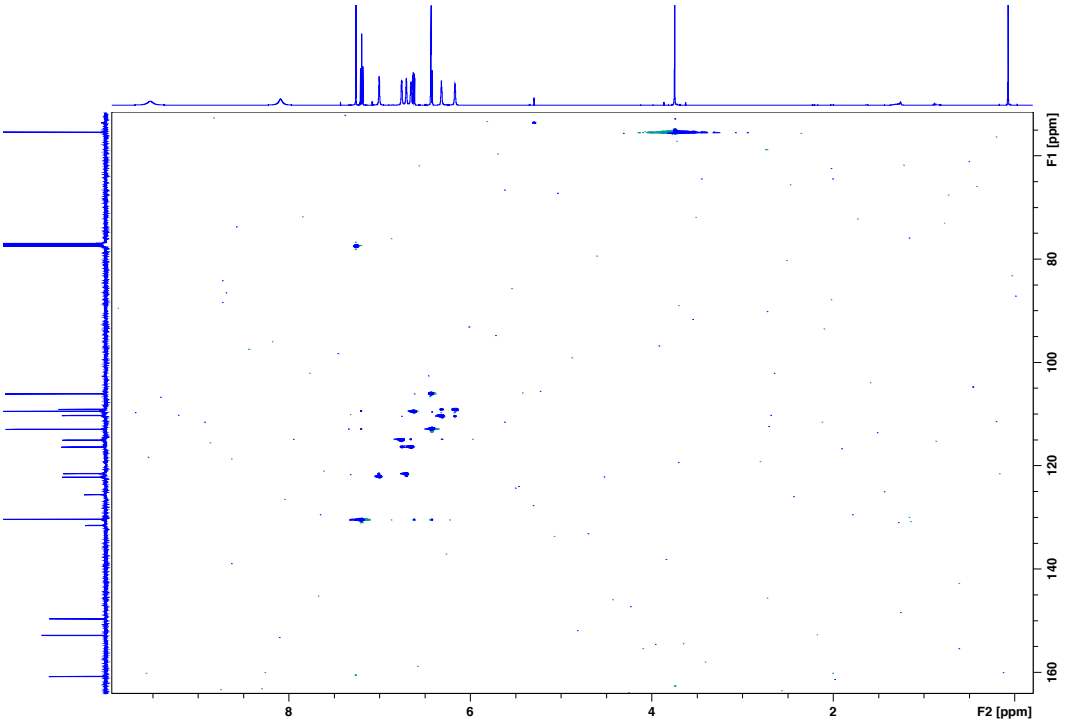
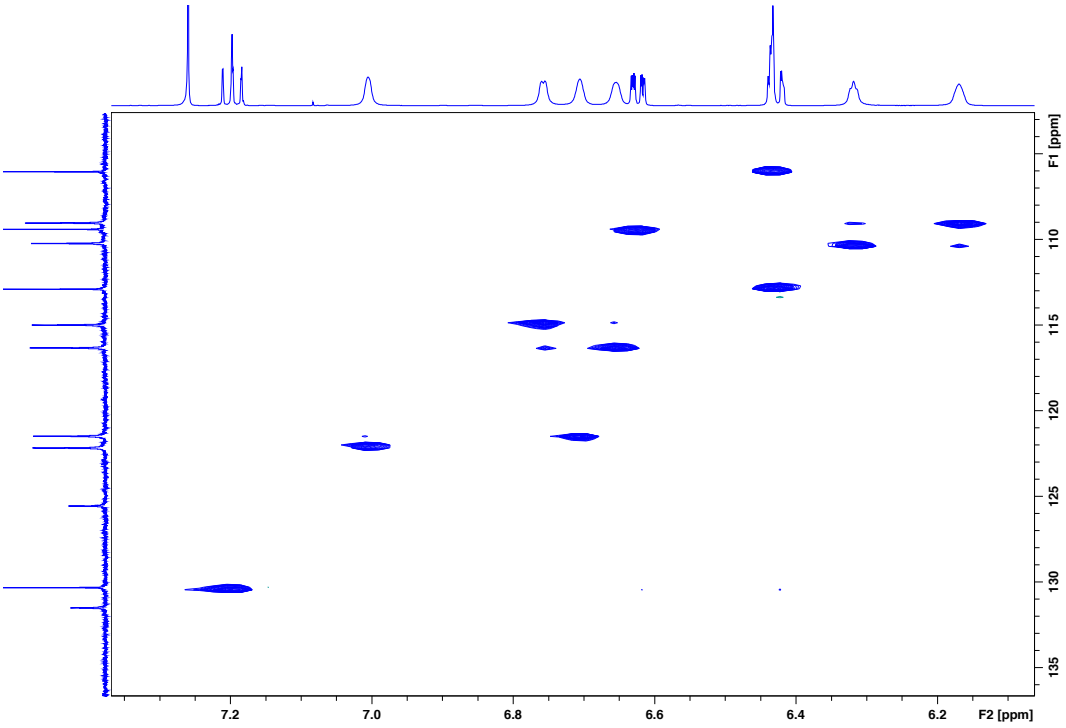


Figure S43. HSQC NMR spectrum (zoom, aromatic region) of **4b** ($CDCl_3$, 300K, 500 MHz).



3.5. NMR Spectra of 4a.

Figure S44. ^{1}H NMR spectrum of **4a** ($CDCl_3$, 300K, 600 MHz).

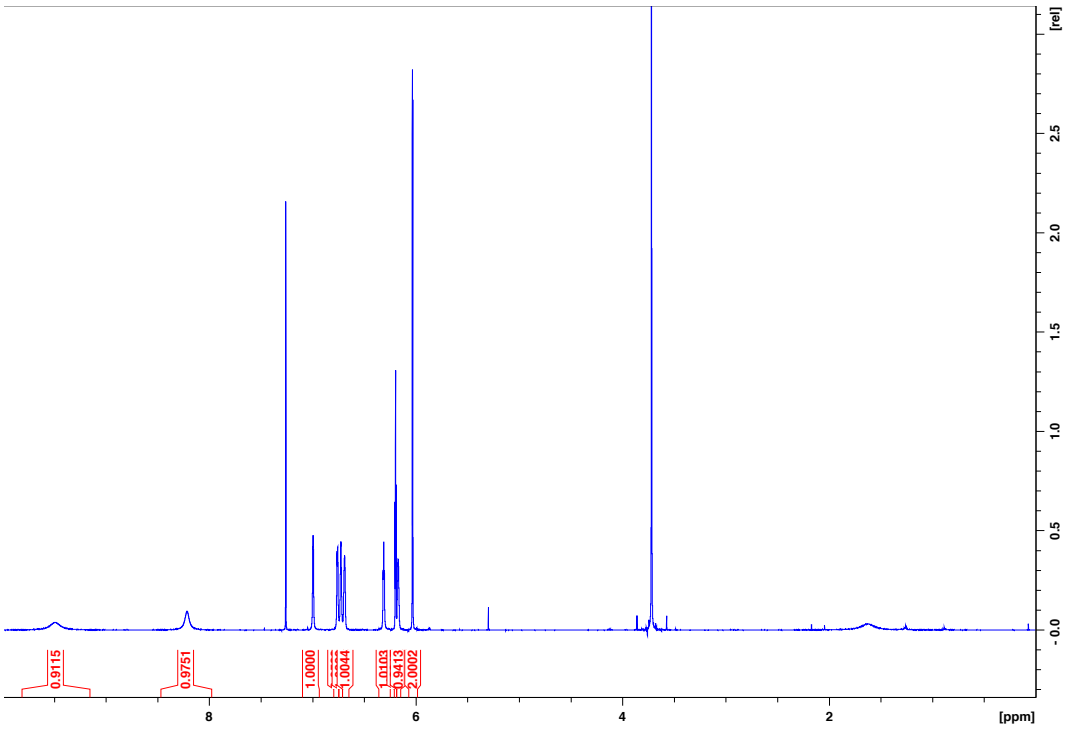


Figure S45. ^{1}H NMR spectrum (zoom, aromatic region) of **4a** ($CDCl_3$, 300K, 600 MHz).

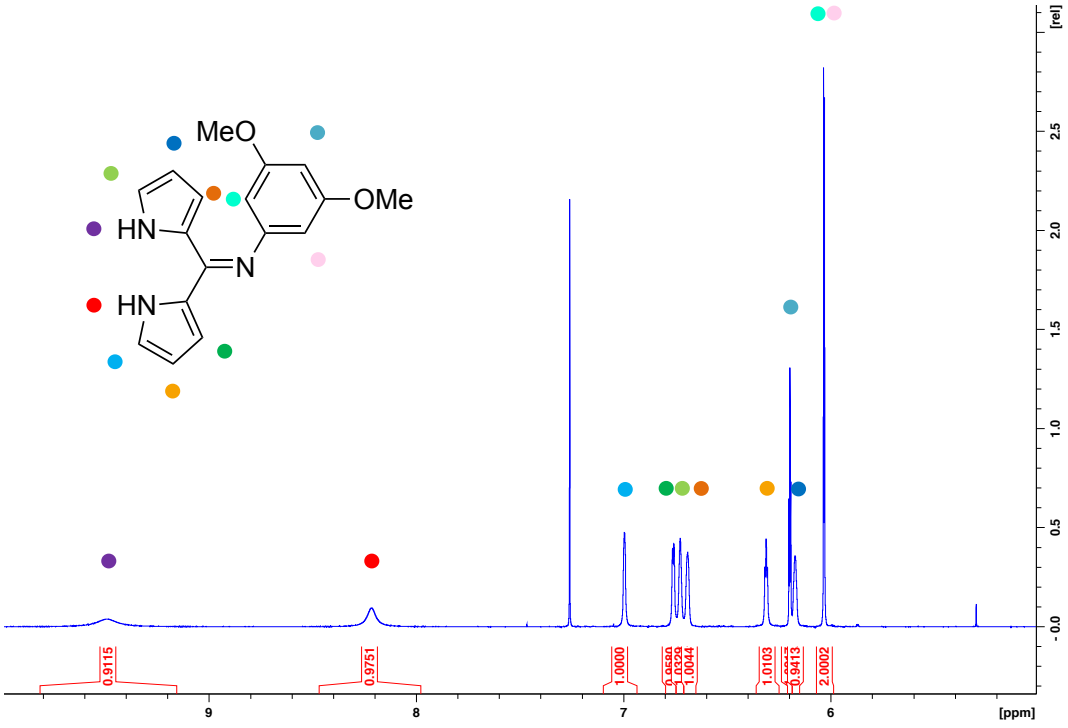


Figure S46. ^{13}C NMR spectrum of **4a** ($CDCl_3$, 300K, 125 MHz).

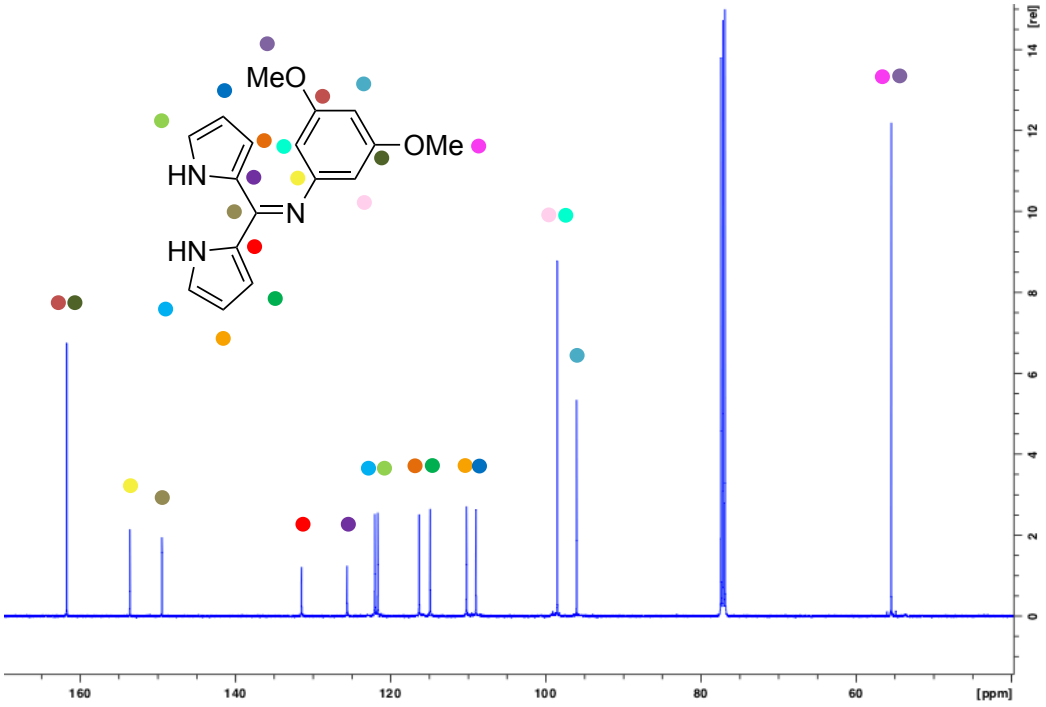


Figure S47. COSY NMR spectrum of **4a** ($CDCl_3$, 300K, 600 MHz).

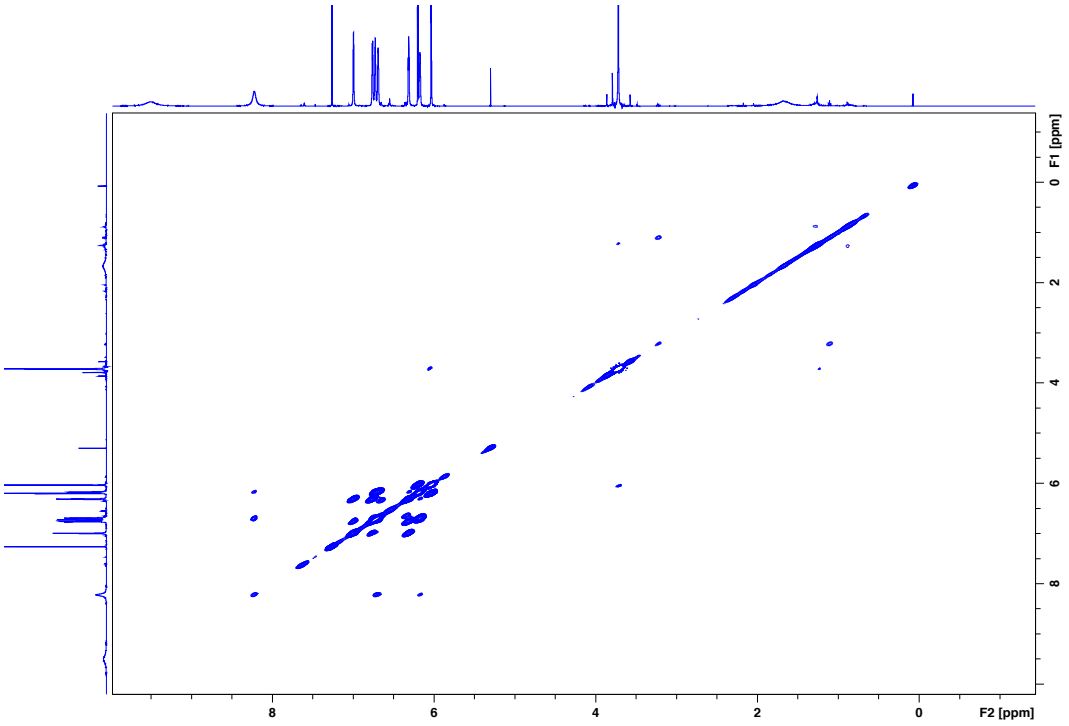


Figure S48. COSY NMR spectrum (zoom, aromatic region) of **4a** ($CDCl_3$, 300K, 600 MHz).

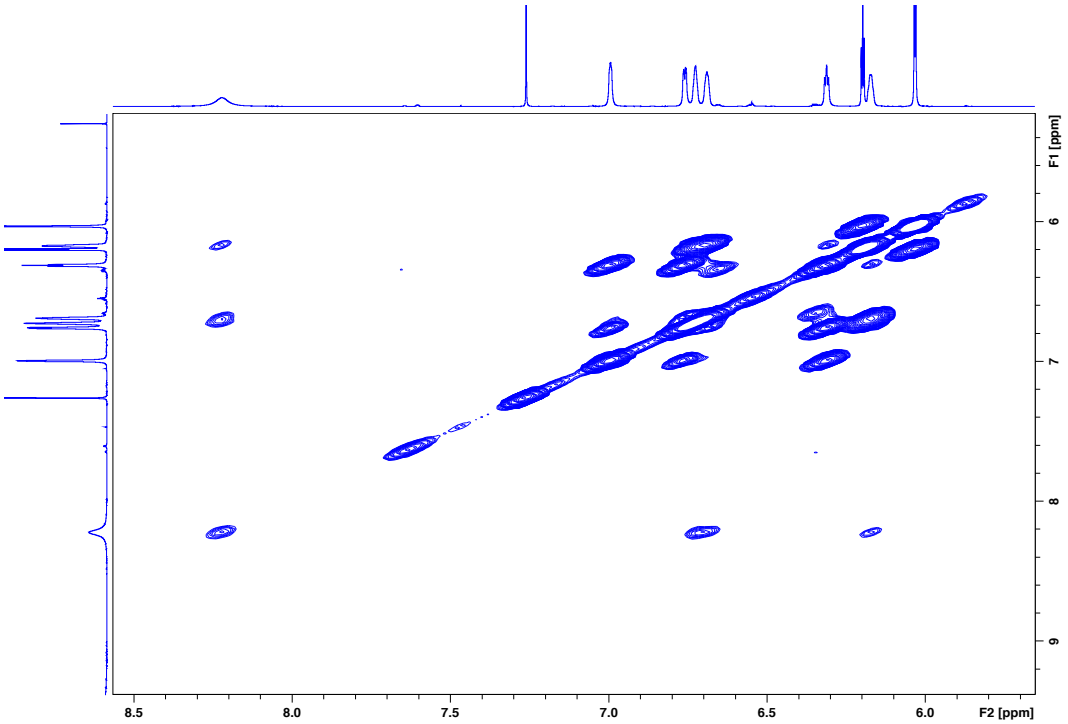


Figure S49. NOESY NMR spectrum of **4a** ($CDCl_3$, 300K, 600 MHz).

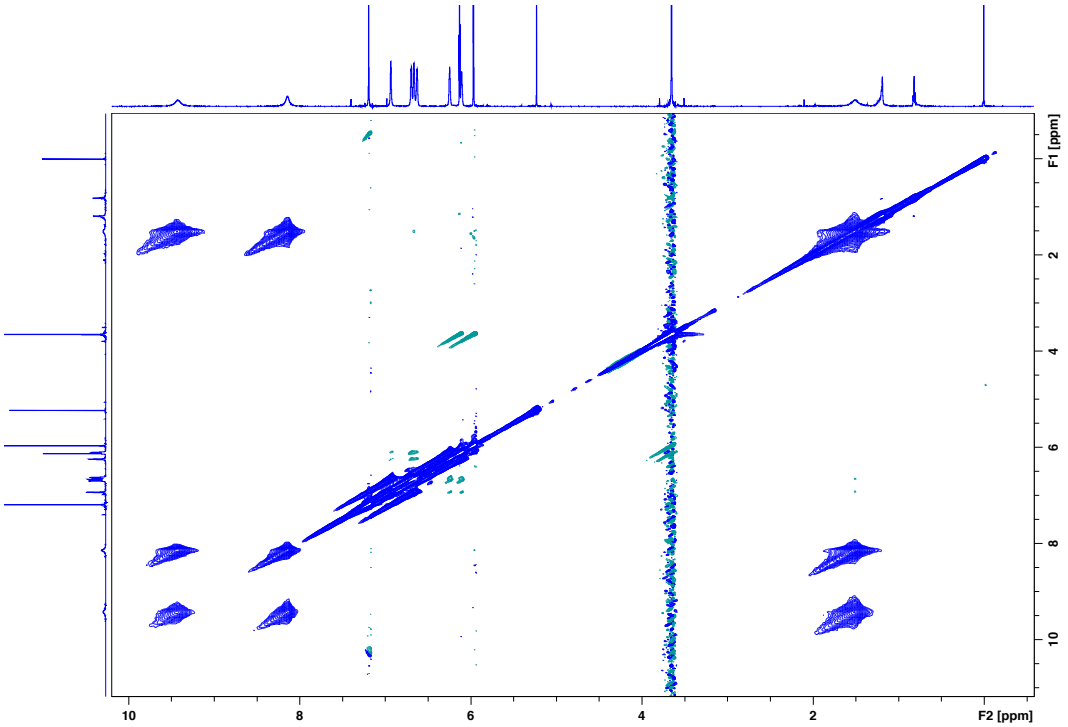


Figure S50. HMBC NMR spectrum of **4a** ($CDCl_3$, 300K, 500 MHz).

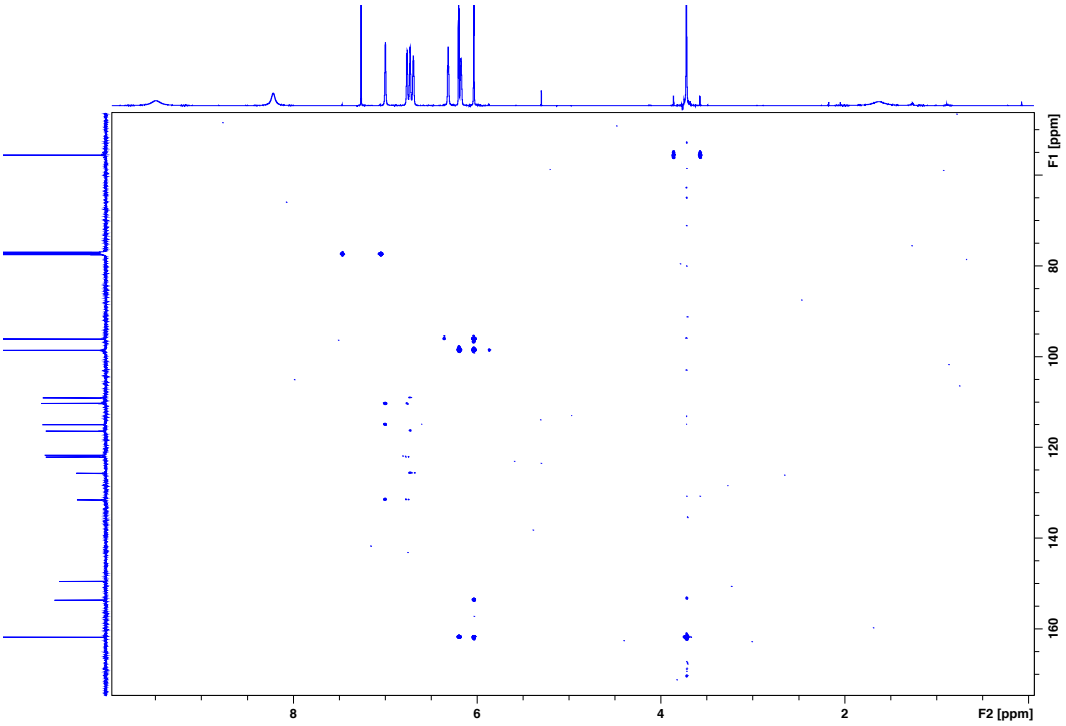


Figure S51. HSQC NMR spectrum of **4a** ($CDCl_3$, 300K, 500 MHz).

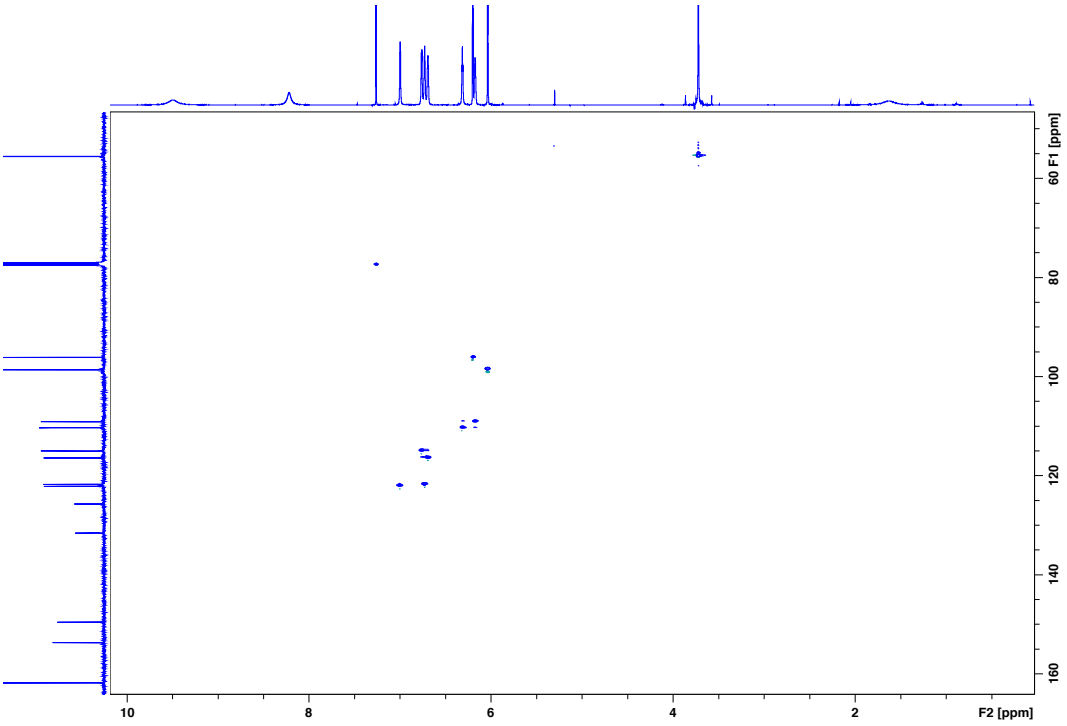
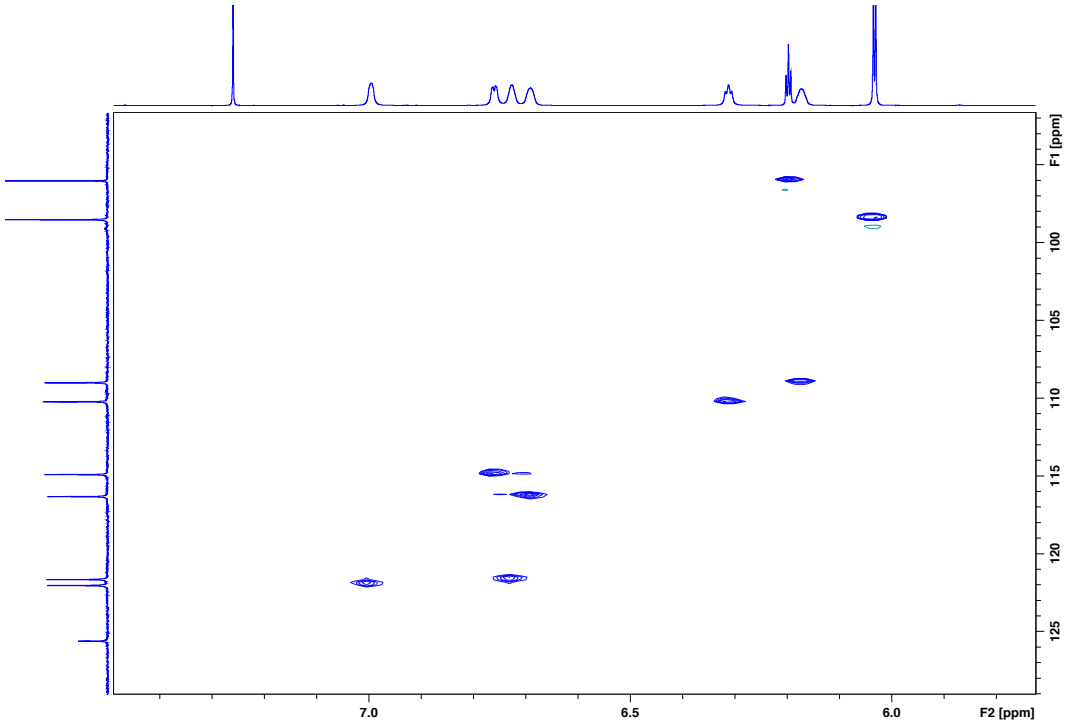


Figure S52. HSQC NMR spectrum (zoom, aromatic region) of **4a** ($CDCl_3$, 300K, 500 MHz).



3.6. NMR Spectra of 5.

Figure S53. ^{1}H NMR spectrum of **5** ($CDCl_3$, 300K, 600 MHz).

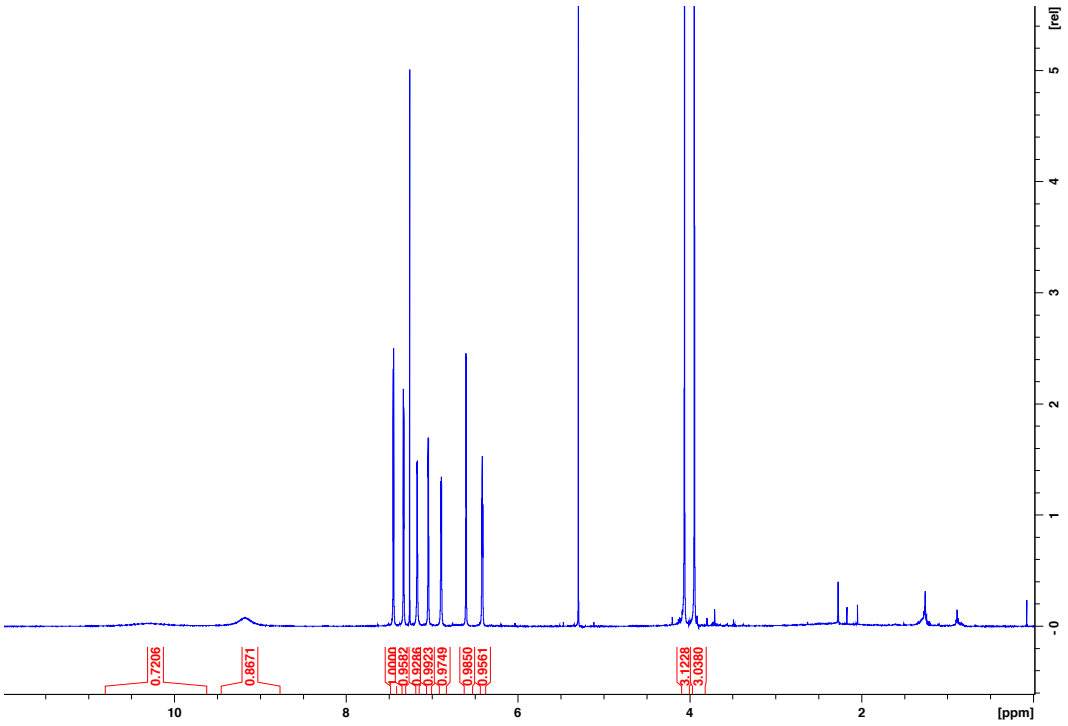


Figure S54. ^{1}H NMR spectrum (zoom, aromatic region) of **5** ($CDCl_3$, 300K, 600 MHz).

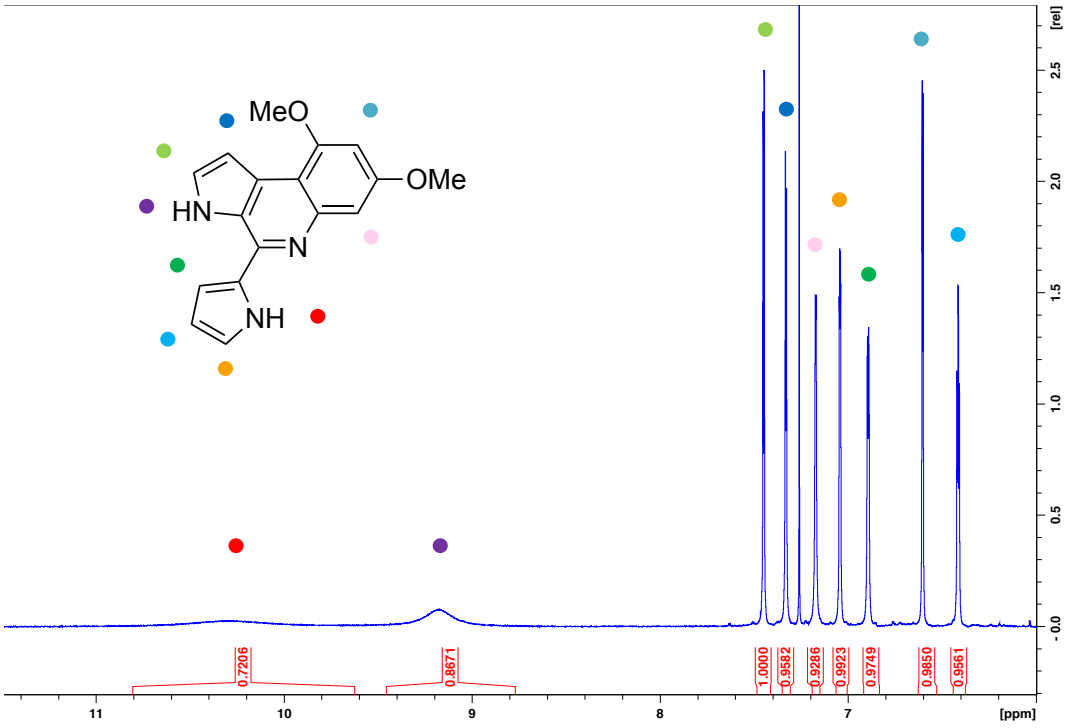


Figure S55. ^{13}C NMR spectrum of **5** ($CDCl_3$, 300K, 125 MHz).

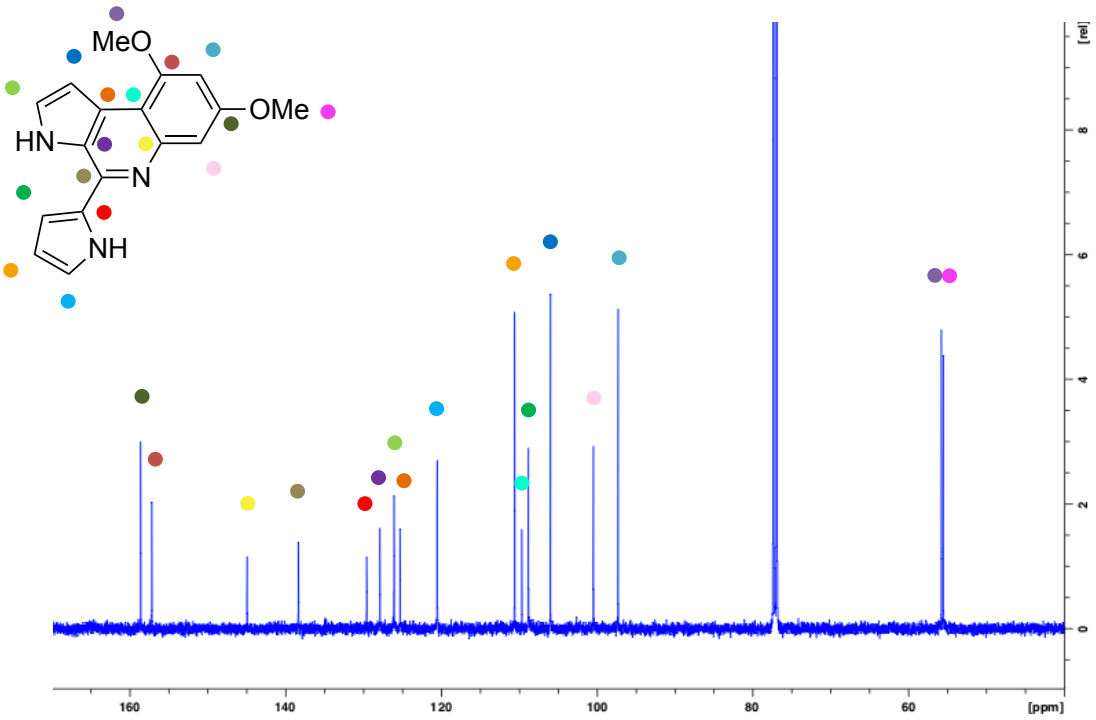


Figure S56. COSY NMR spectrum of **5** ($CDCl_3$, 300K, 600 MHz).

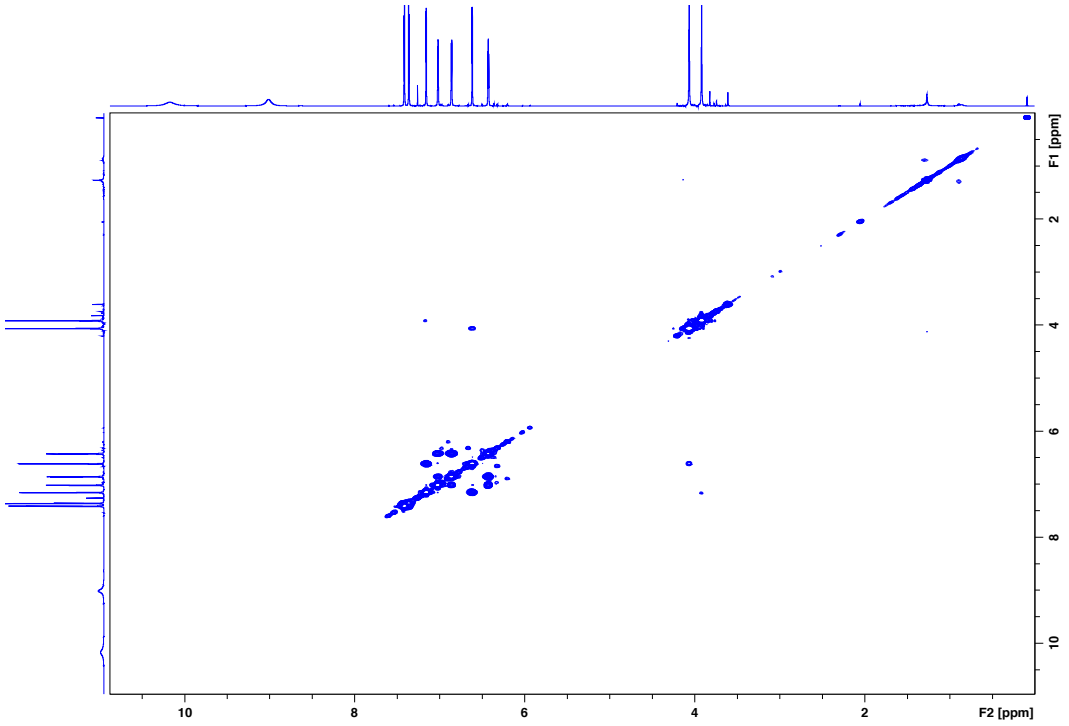


Figure S57. COSY NMR spectrum (zoom) of **5** ($CDCl_3$, 300K, 600 MHz).

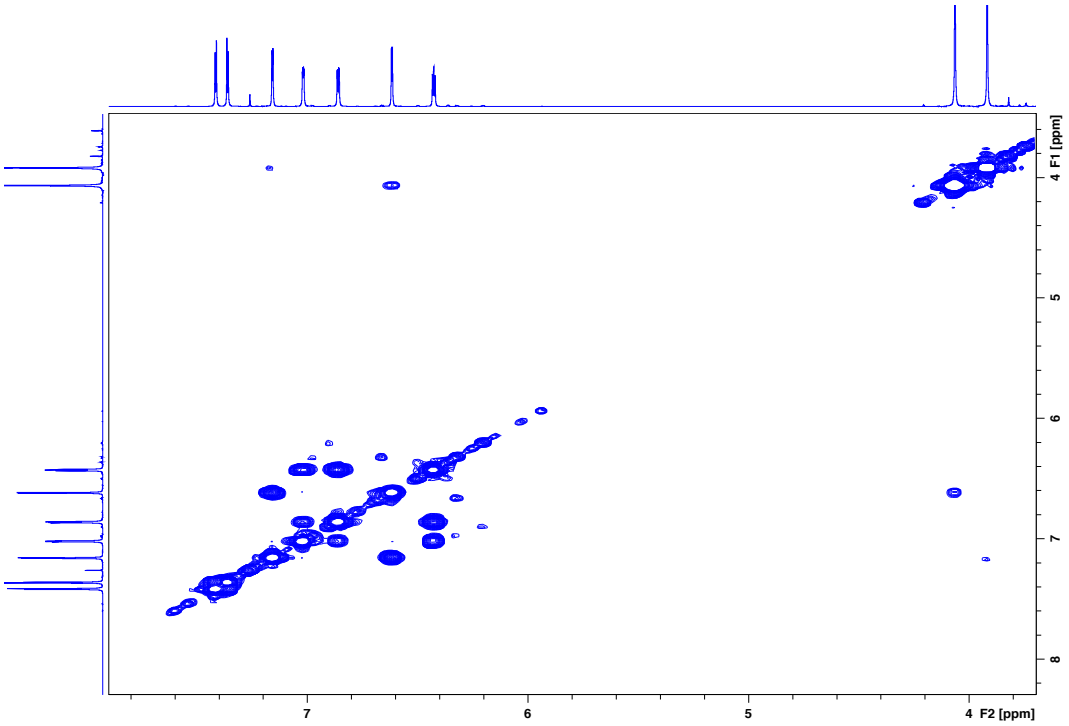


Figure S58. NOESY NMR spectrum of **5** ($CDCl_3$, 300K, 600 MHz).

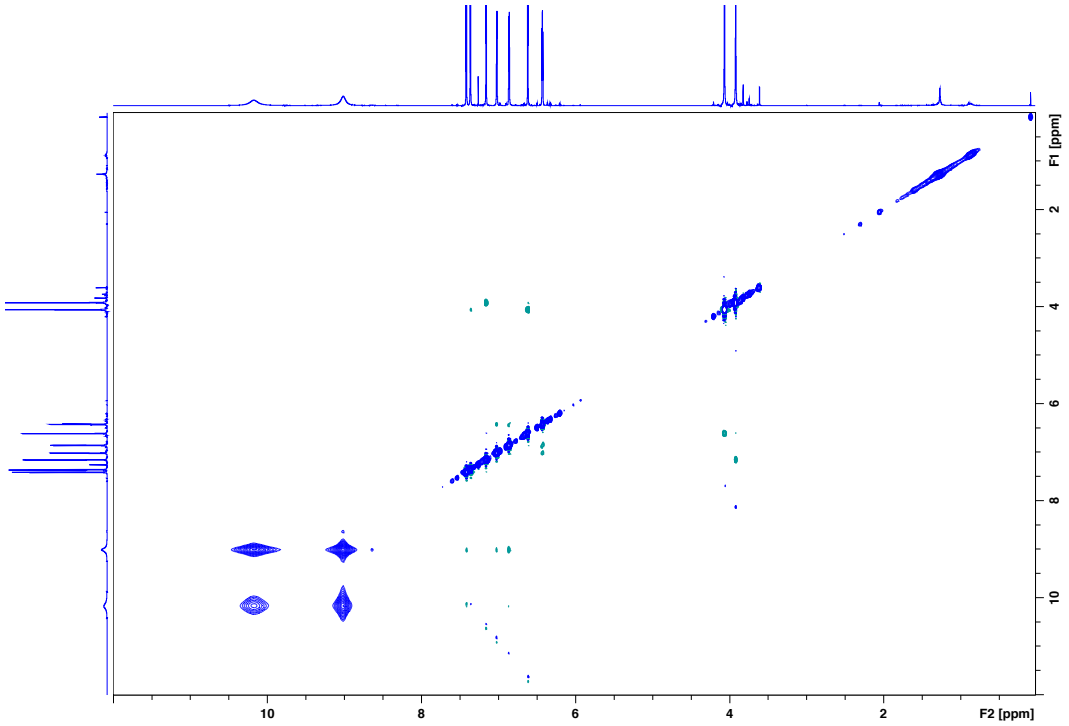


Figure S59. NOESY NMR spectrum (zoom) of **5** ($CDCl_3$, 300K, 600 MHz).

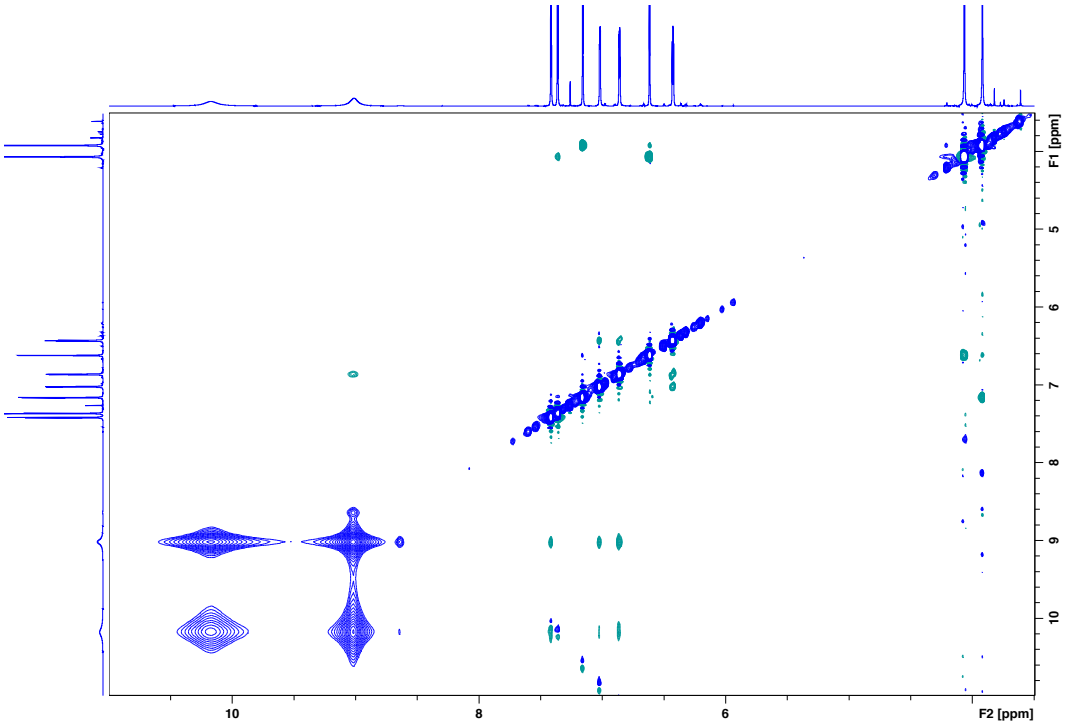


Figure S60. HMBC NMR spectrum of **5** ($CDCl_3$, 300K, 500 MHz).

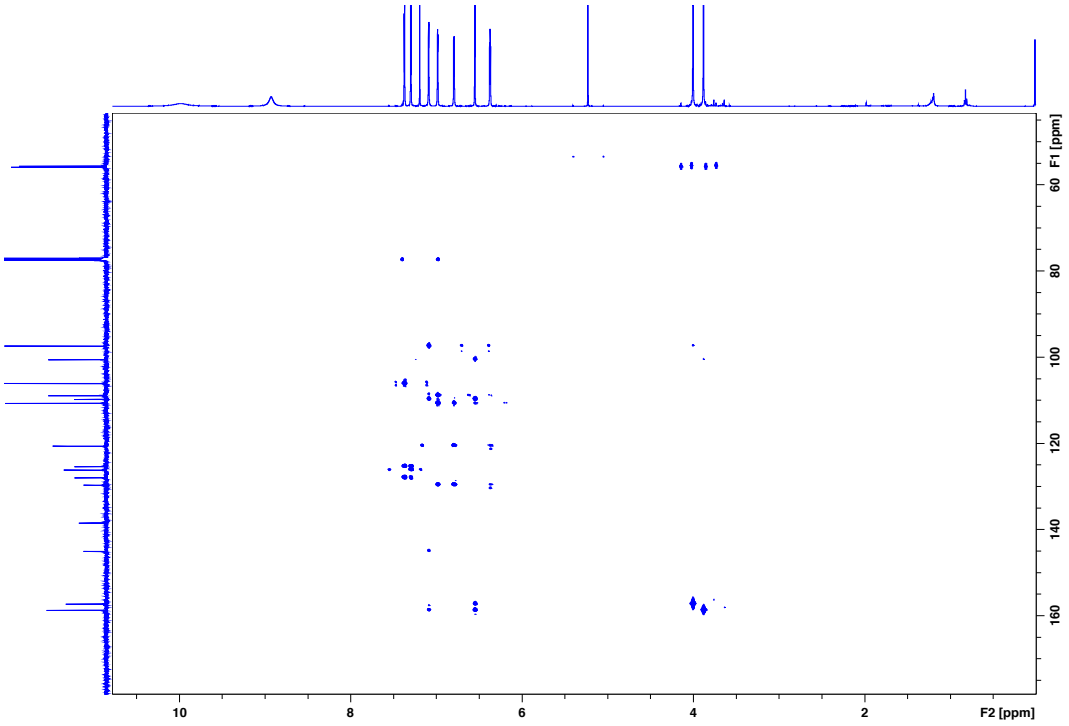


Figure S61. HMBC NMR spectrum (zoom, aromatic region) of **5** ($CDCl_3$, 300K, 500 MHz).

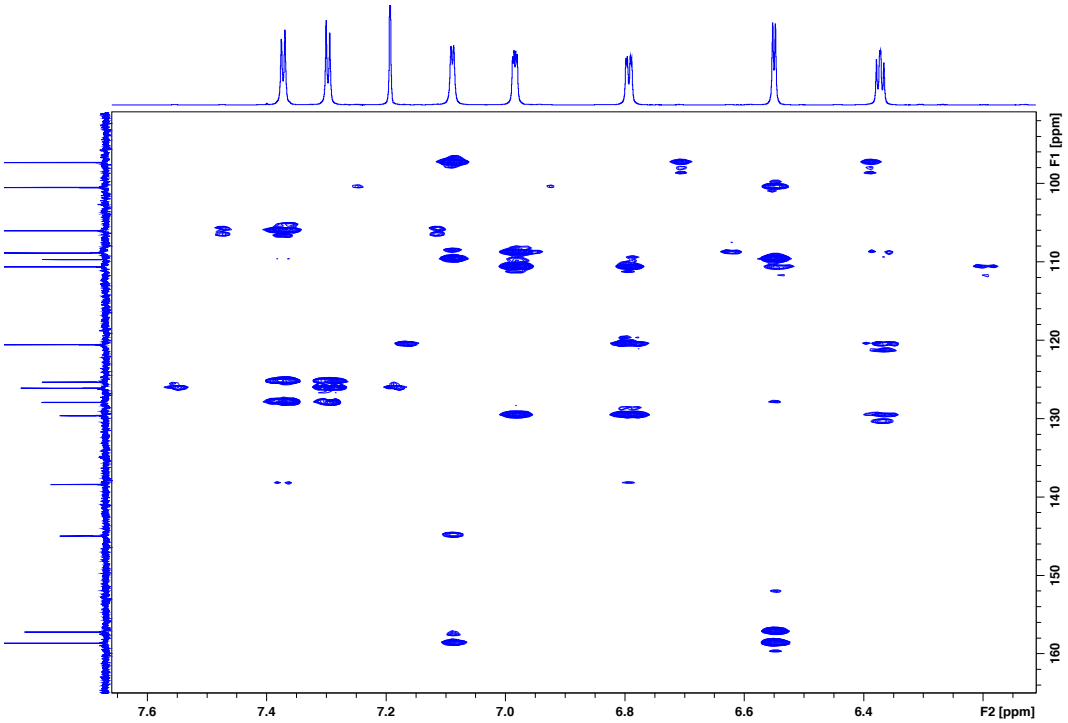
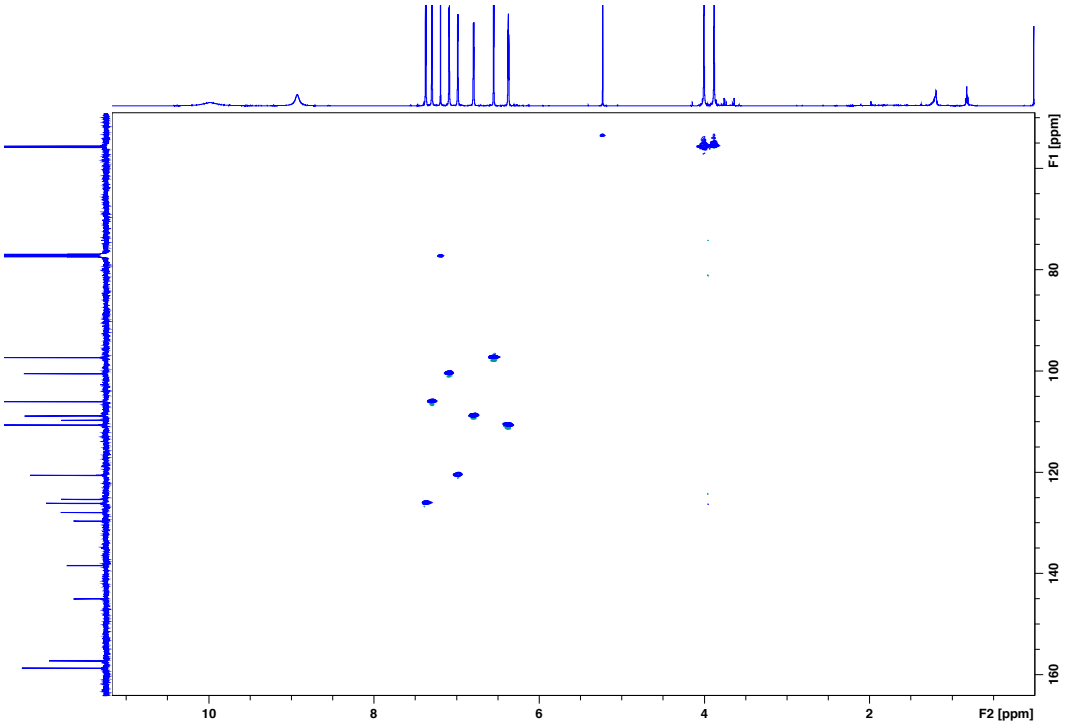


Figure S62. HSQC NMR spectrum of **5** ($CDCl_3$, 300K, 500 MHz).



3.7. NMR Spectra of 6/6(-).

Figure S63. ^{1}H NMR spectrum of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

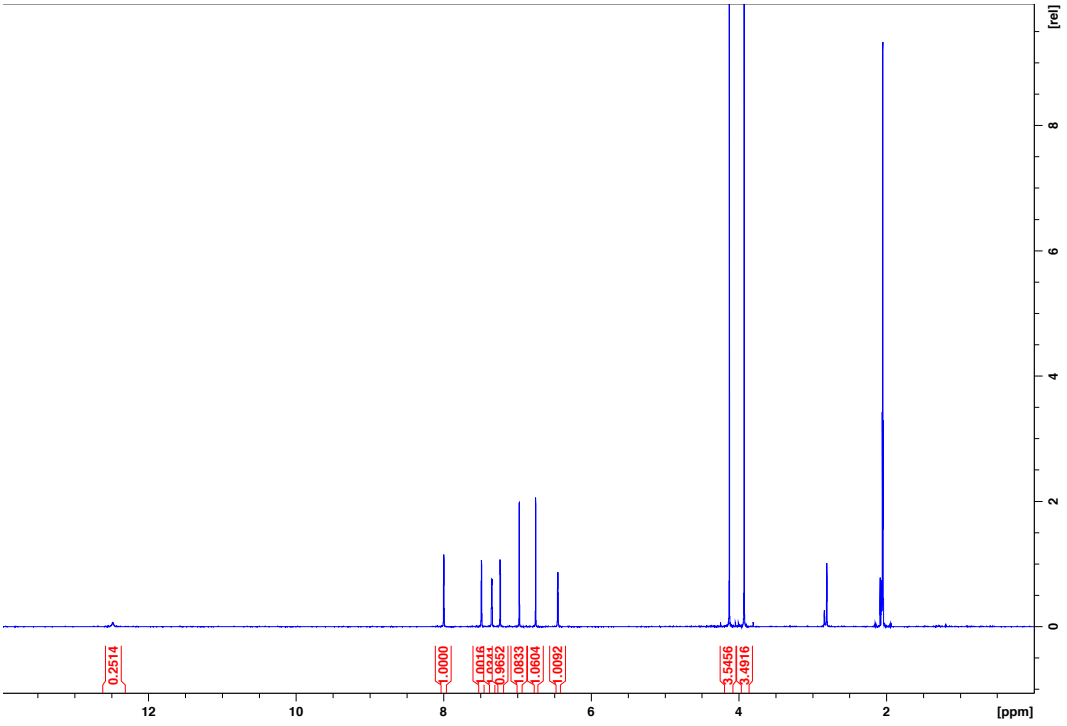


Figure S64. ^{1}H NMR spectrum (zoom, aromatic region) of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

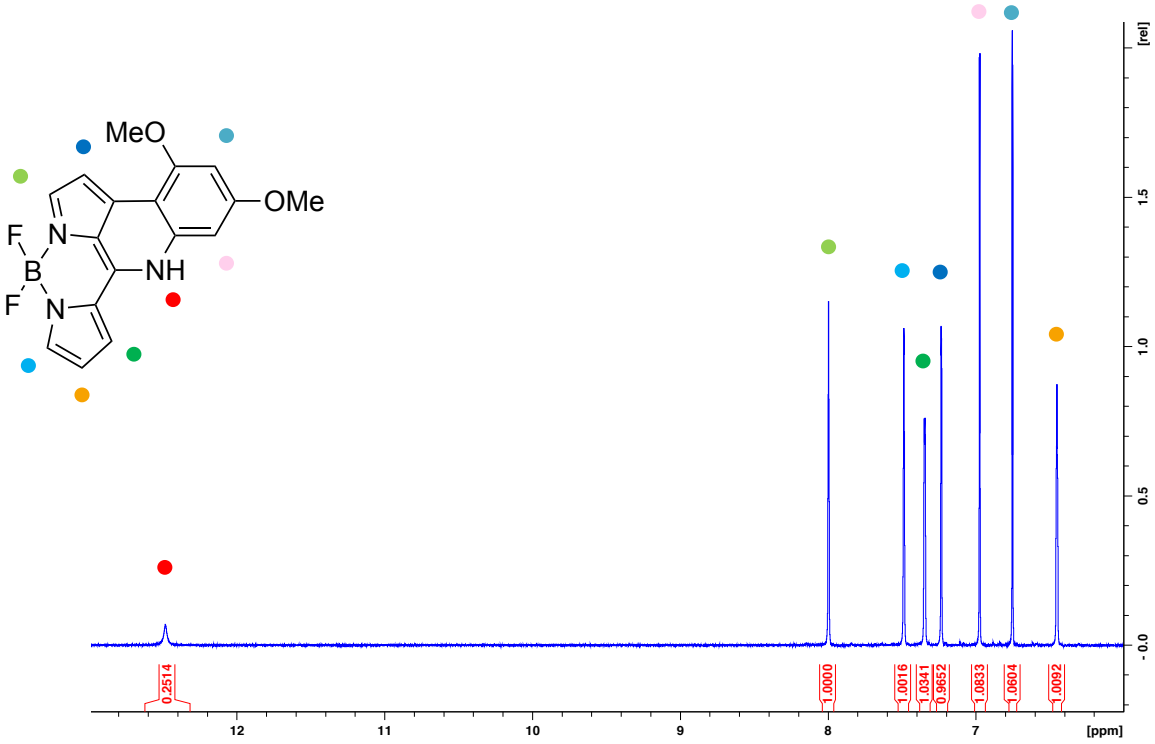


Figure S65. ^{13}C NMR spectrum of **6** ($(CD_3)_2CO$, 300K, 150 MHz).

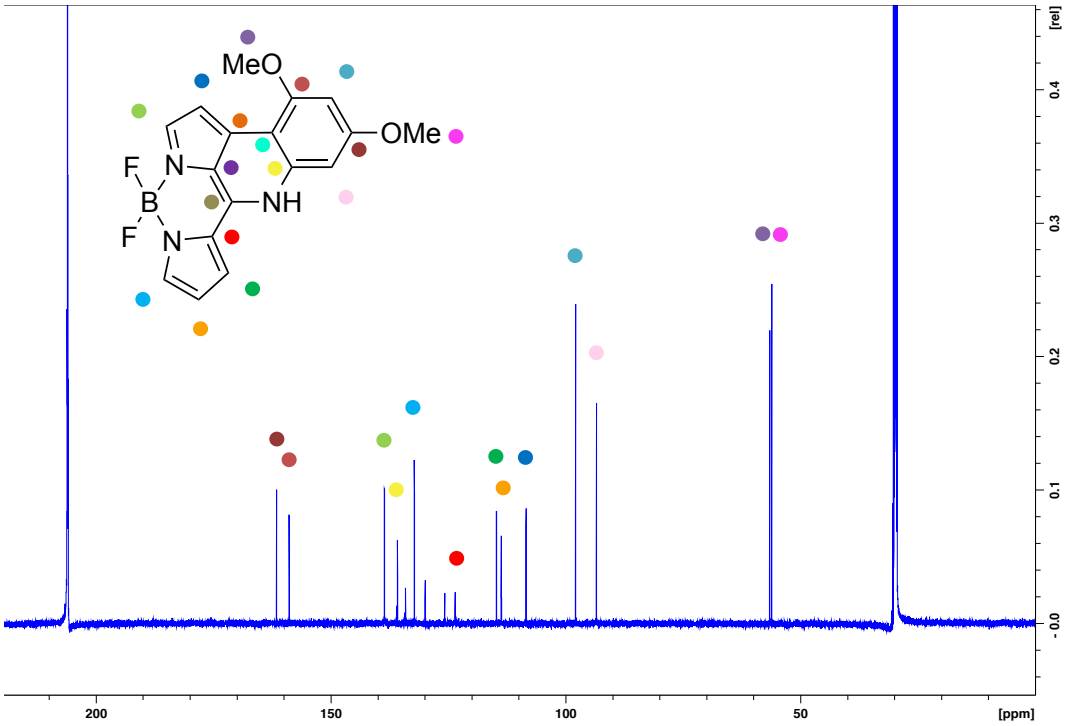


Figure S66. COSY NMR spectrum of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

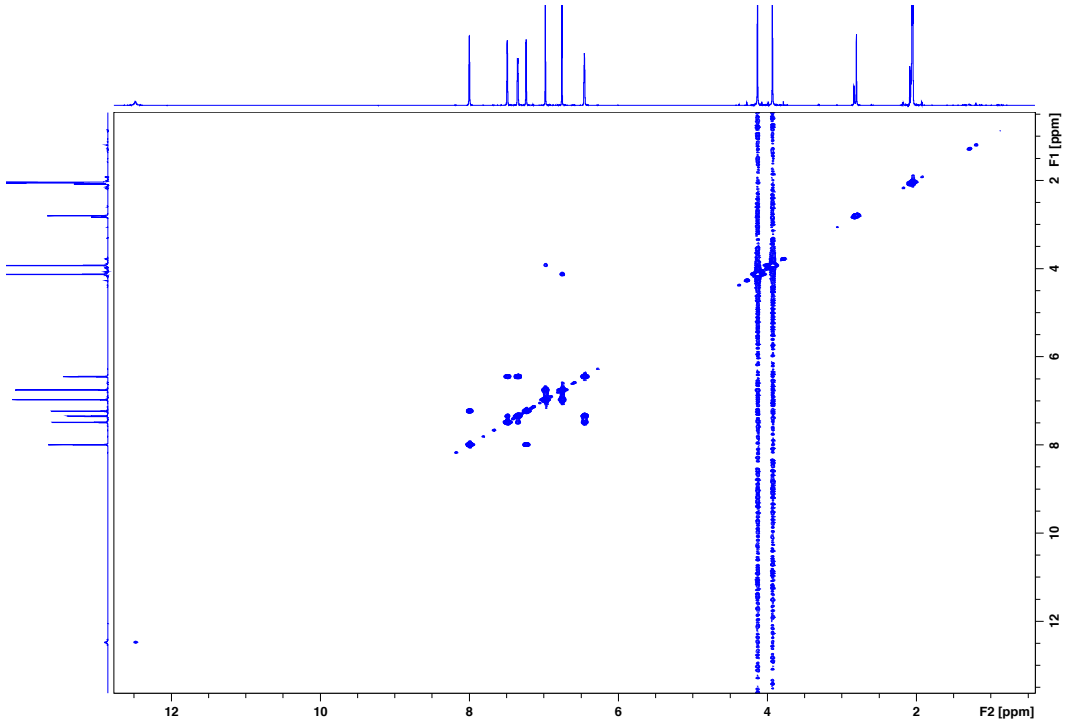


Figure S67. COSY NMR spectrum (zoom, aromatic region) of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

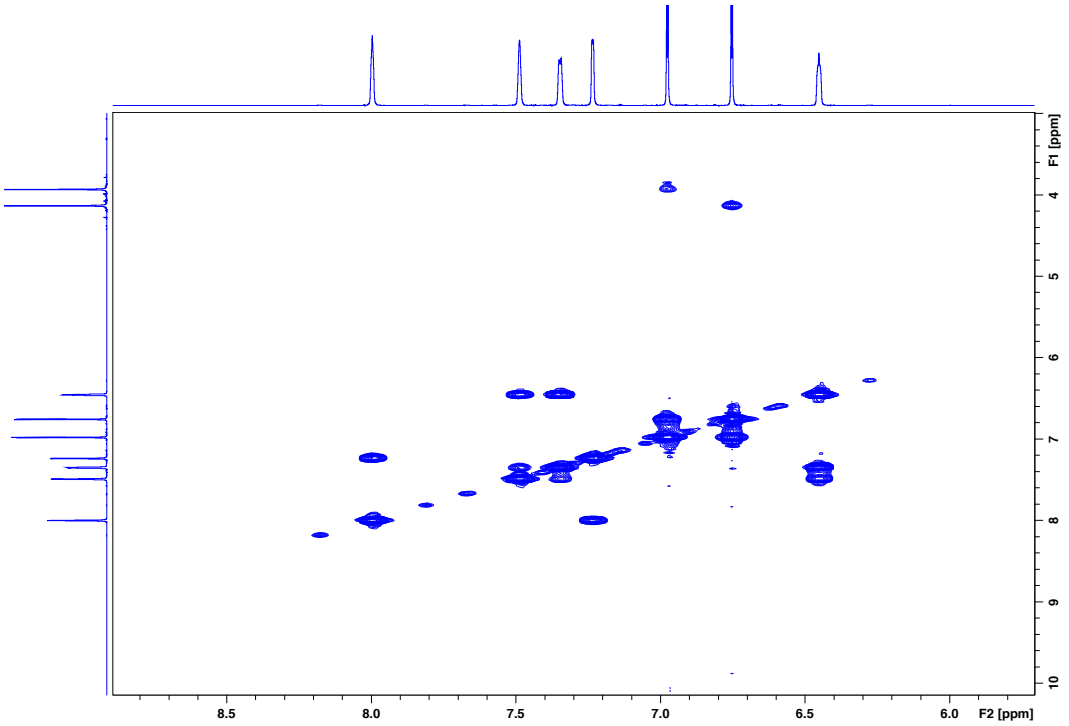


Figure S68. NOESY NMR spectrum of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

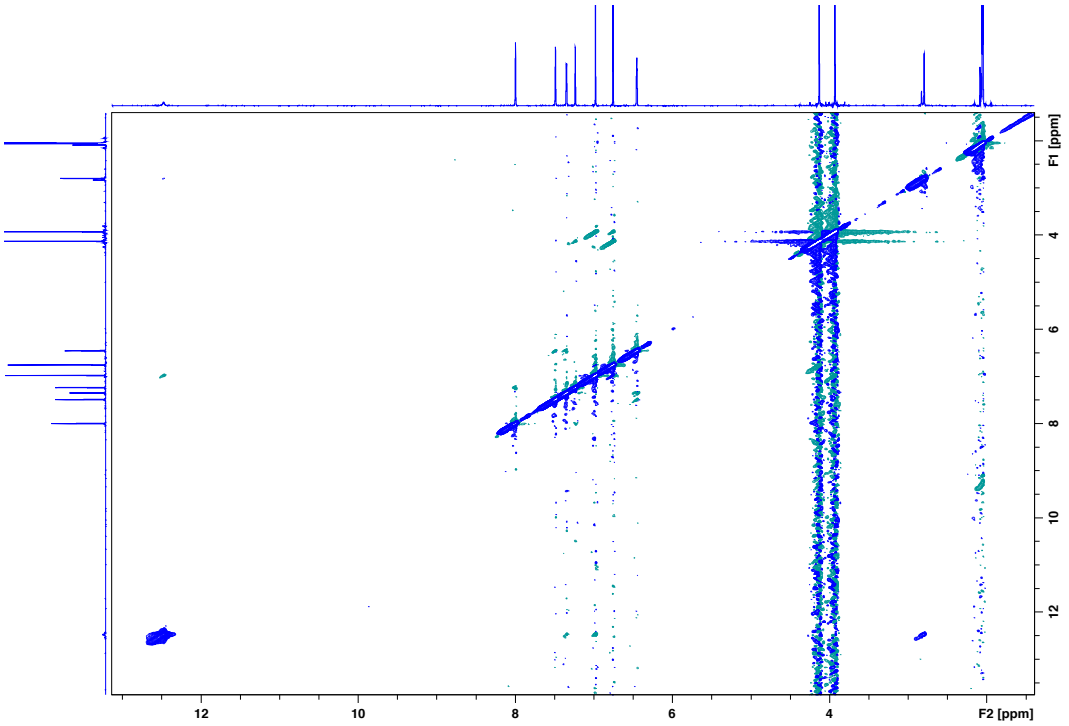


Figure S69. NOESY NMR spectrum (zoom on relevant area) of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

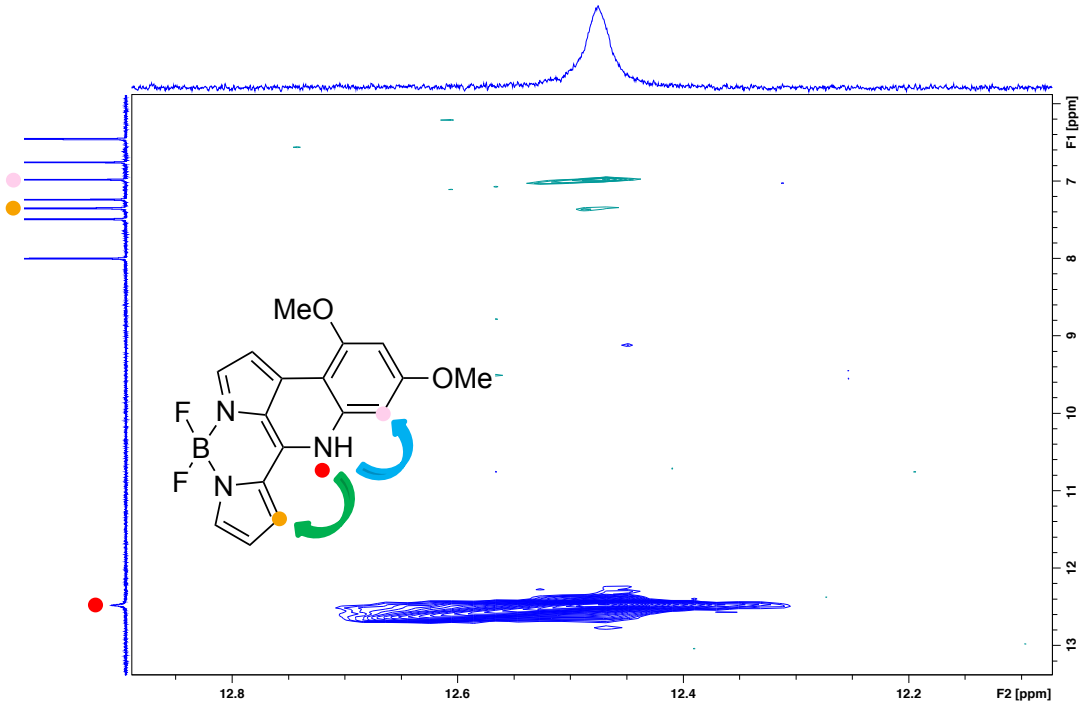


Figure S70. HMBC NMR spectrum of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

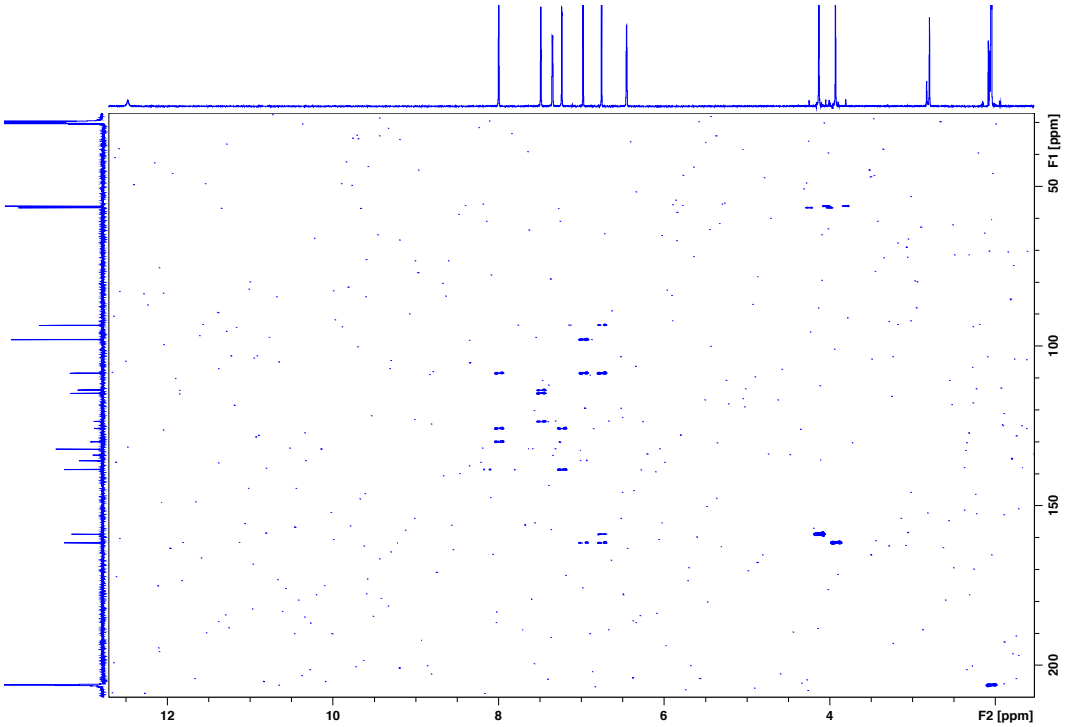


Figure S71. HMBC NMR spectrum (zoom) of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

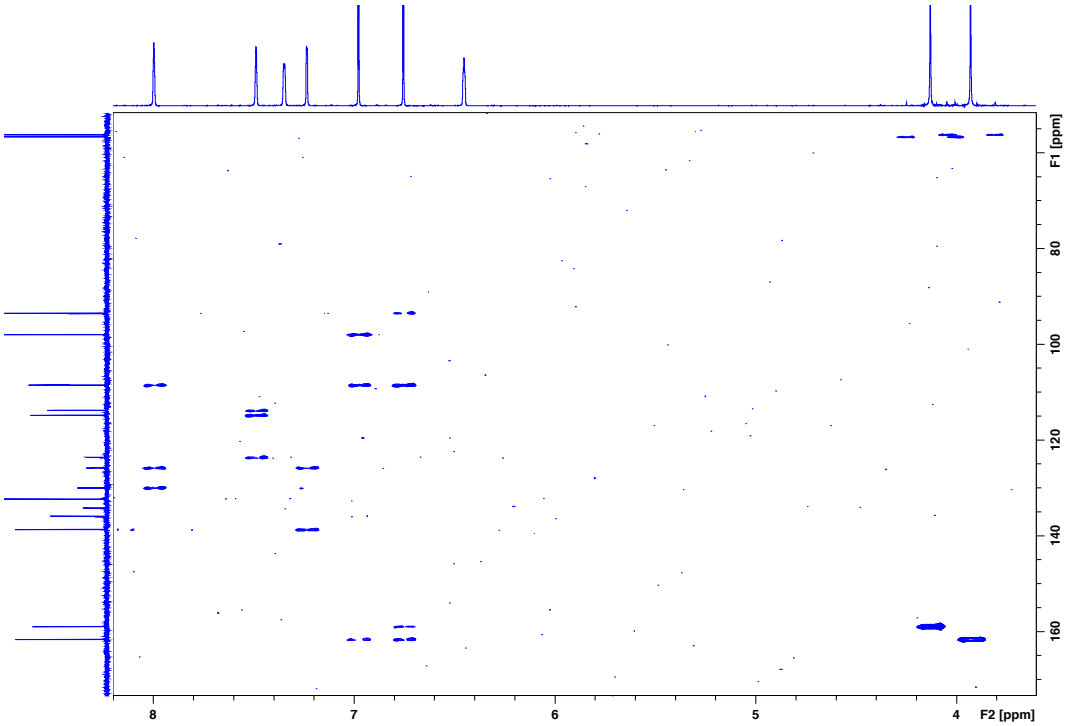


Figure S72. HSQC NMR spectrum of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

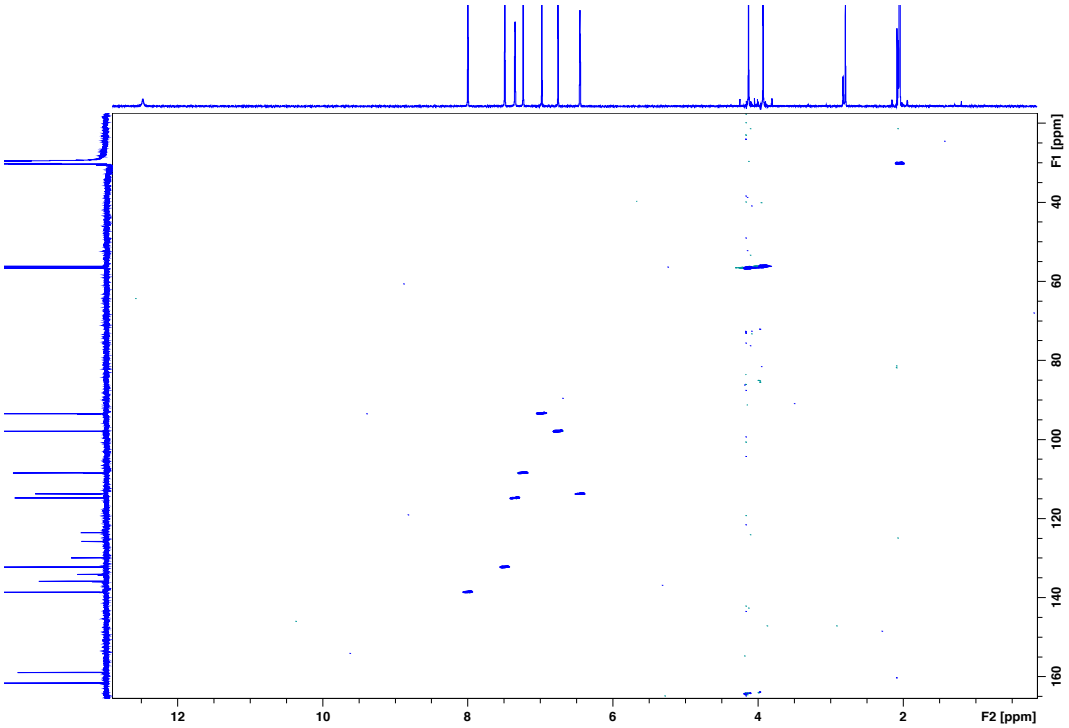


Figure S73. HSQC NMR spectrum (zoom) of **6** ($(CD_3)_2CO$, 300K, 600 MHz).

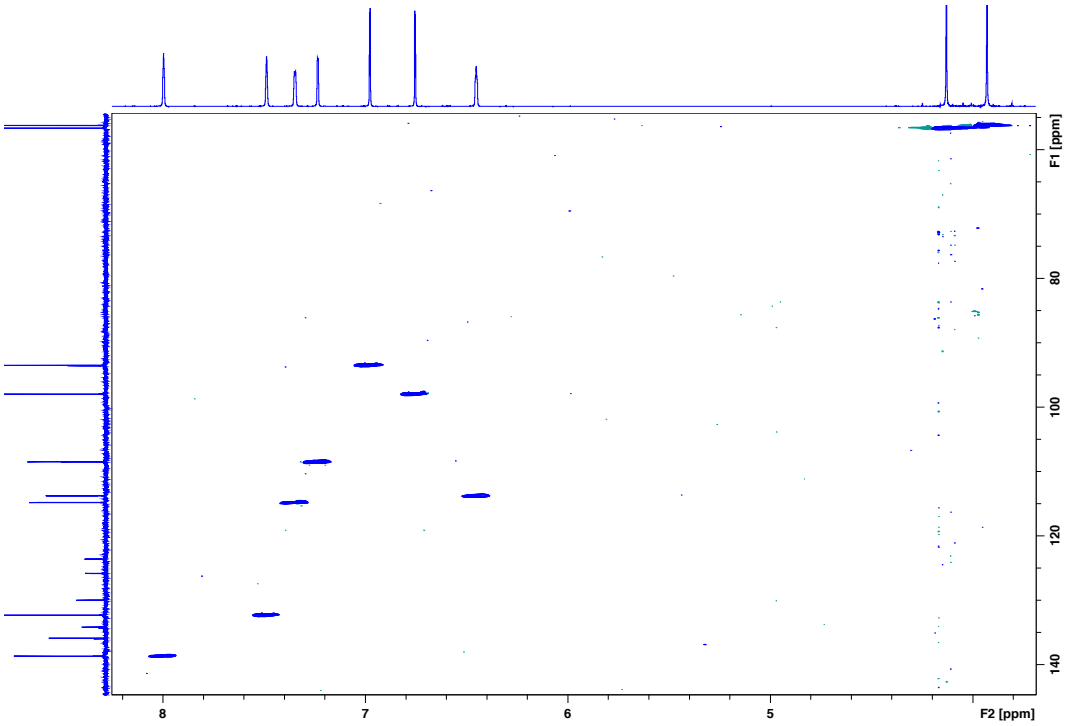


Figure S74. ^1H NMR spectrum of **6**, TBAF titration ($(CD_3)_2CO$, 300K, 600 MHz). red: 0.2 eq., green: 0.4 eq., violet: 0.6 eq., yellow: 0.8 eq., orange: 1.0 eq. **6***(-)*.

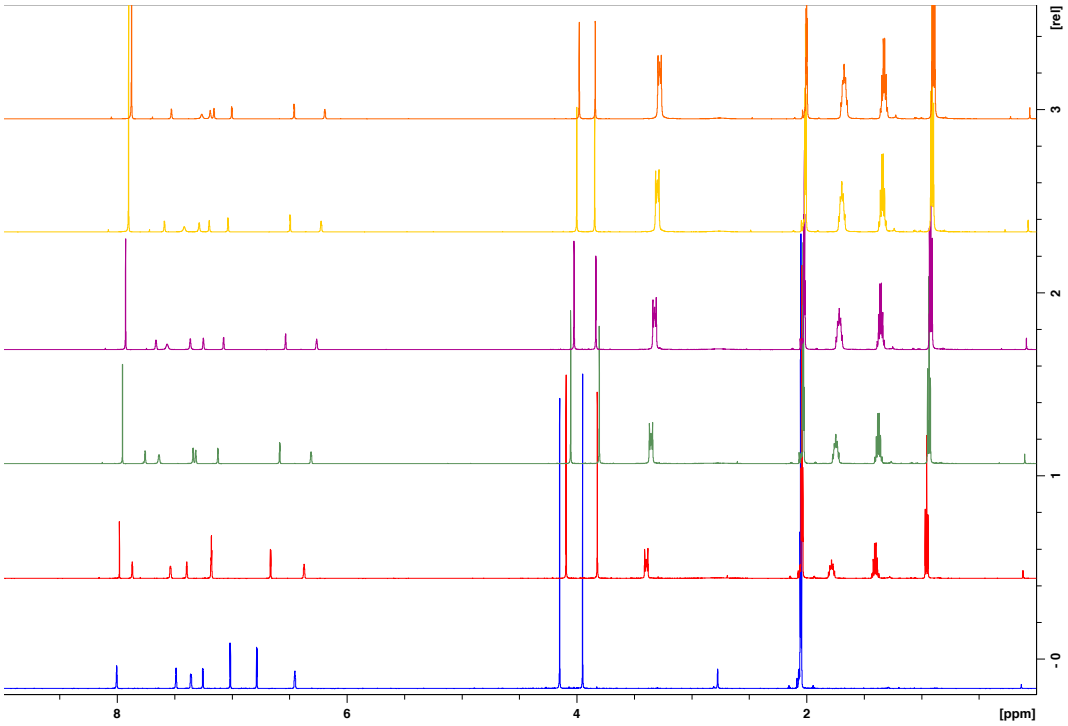


Figure S75. ^{1}H NMR spectrum (zoom, aromatic region) of **6**, TBAF titration ($(CD_3)_2CO$, 300K, 600 MHz). red: 0.2 eq., green: 0.4 eq., violet: 0.6 eq., yellow: 0.8 eq., orange: 1.0 eq. **6***(-)*.

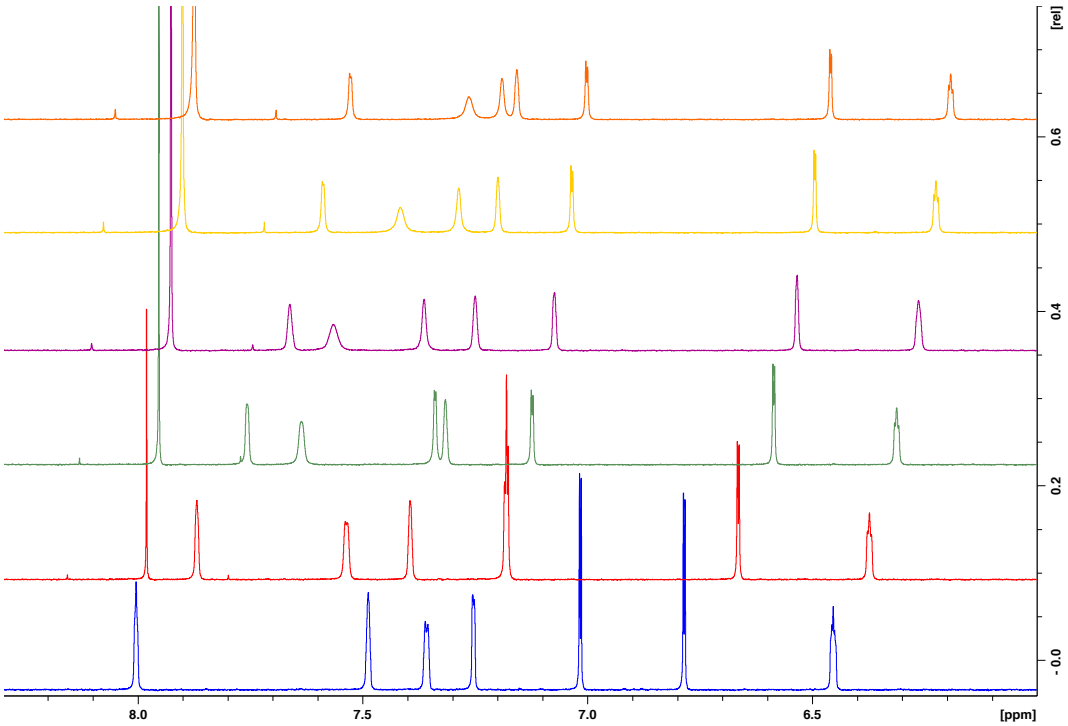


Figure S76. ^{1}H NMR spectrum of **6***(-)* ($(CD_3)_2CO$, 300K, 600 MHz).

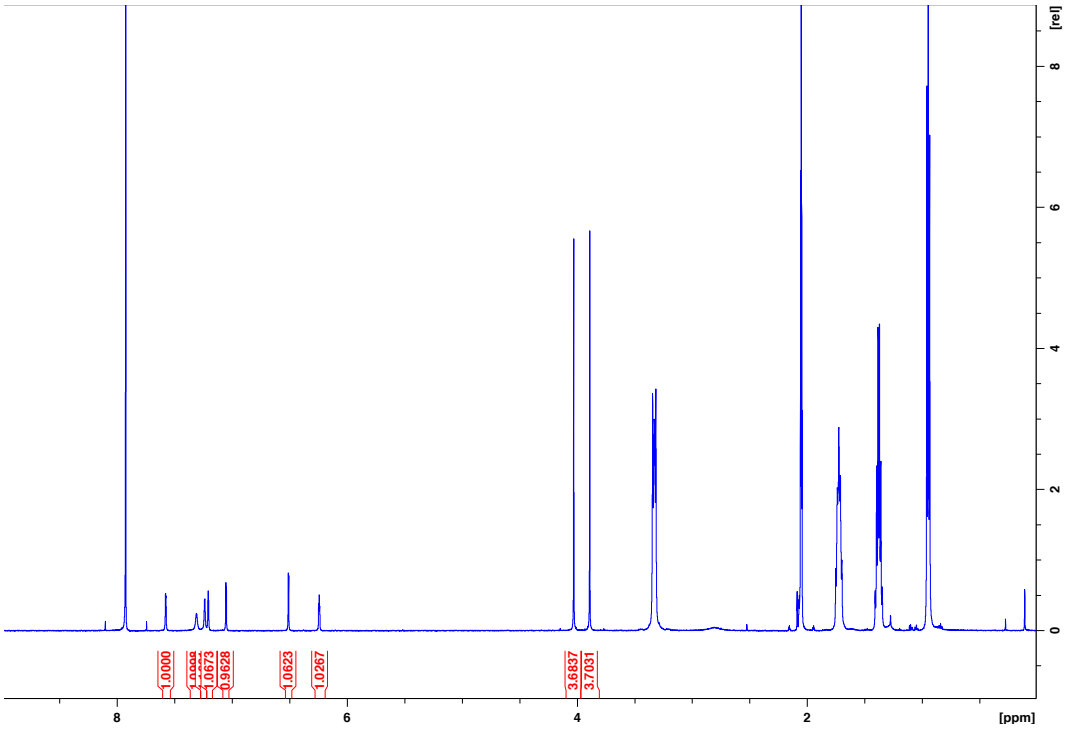


Figure S77. ^{1}H NMR spectrum (zoom, aromatic region) of **6***(-)* ($(CD_3)_2CO$, 300K, 600 MHz).

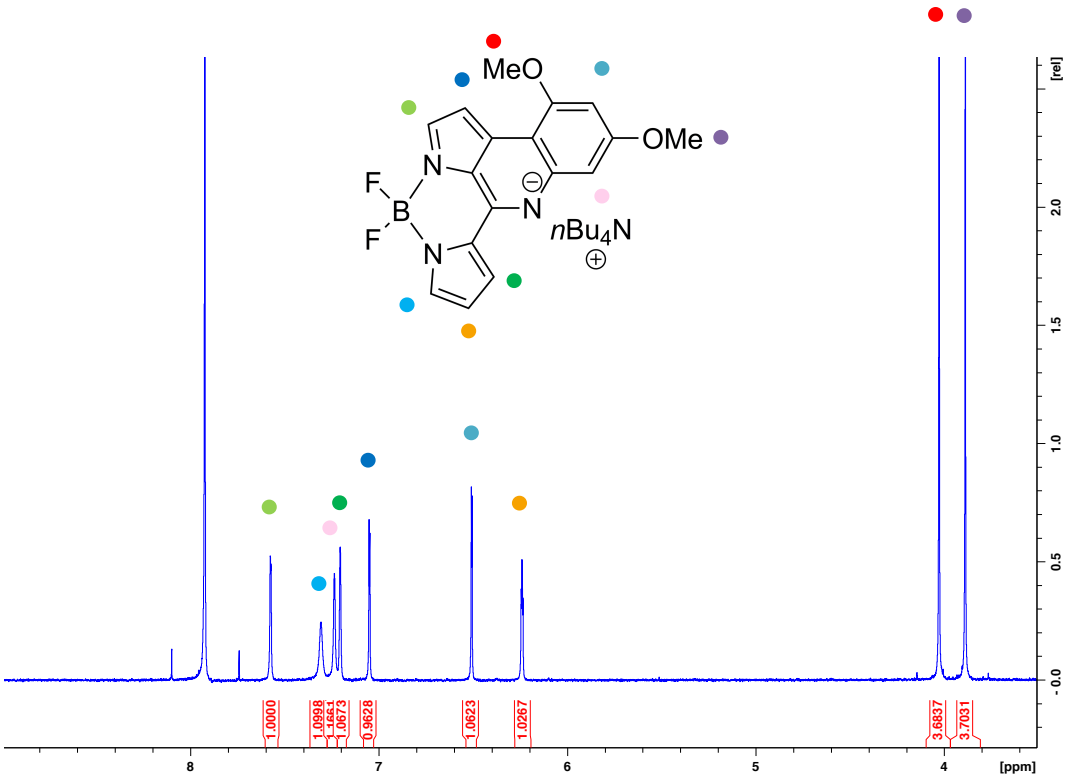


Figure S78. COSY NMR spectrum of **6***(-)* ($(CD_3)_2CO$, 300K, 600 MHz).

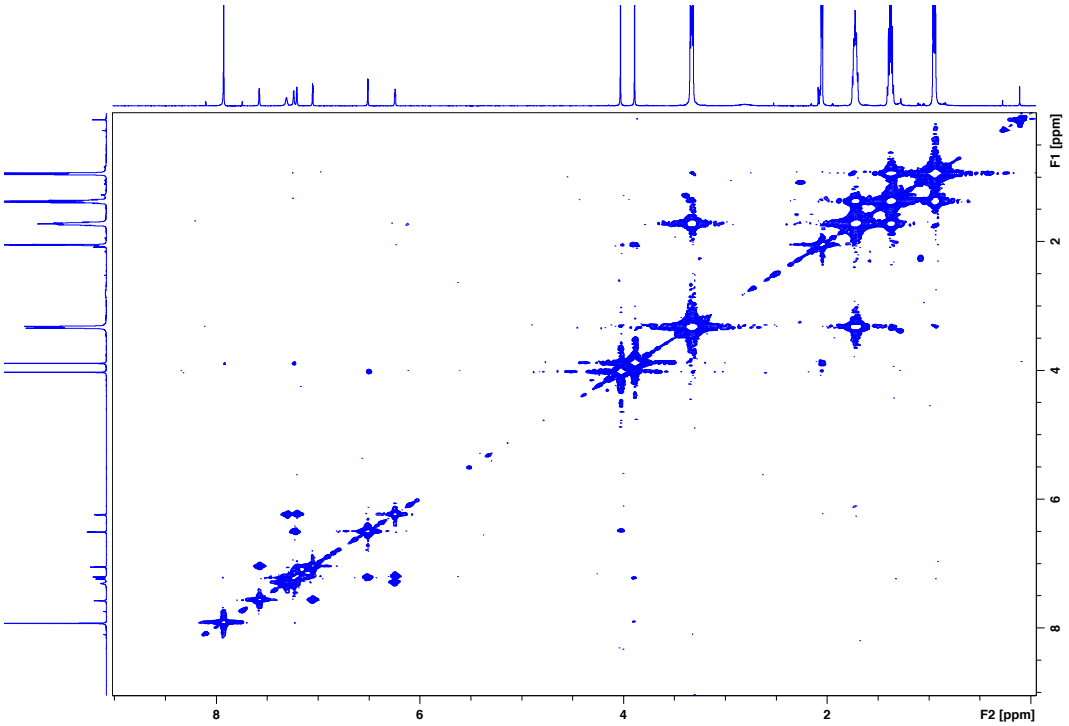


Figure S79. COSY NMR spectrum (zoom, aromatic region) of **6***(-)* ($(CD_3)_2CO$, 300K, 600 MHz).

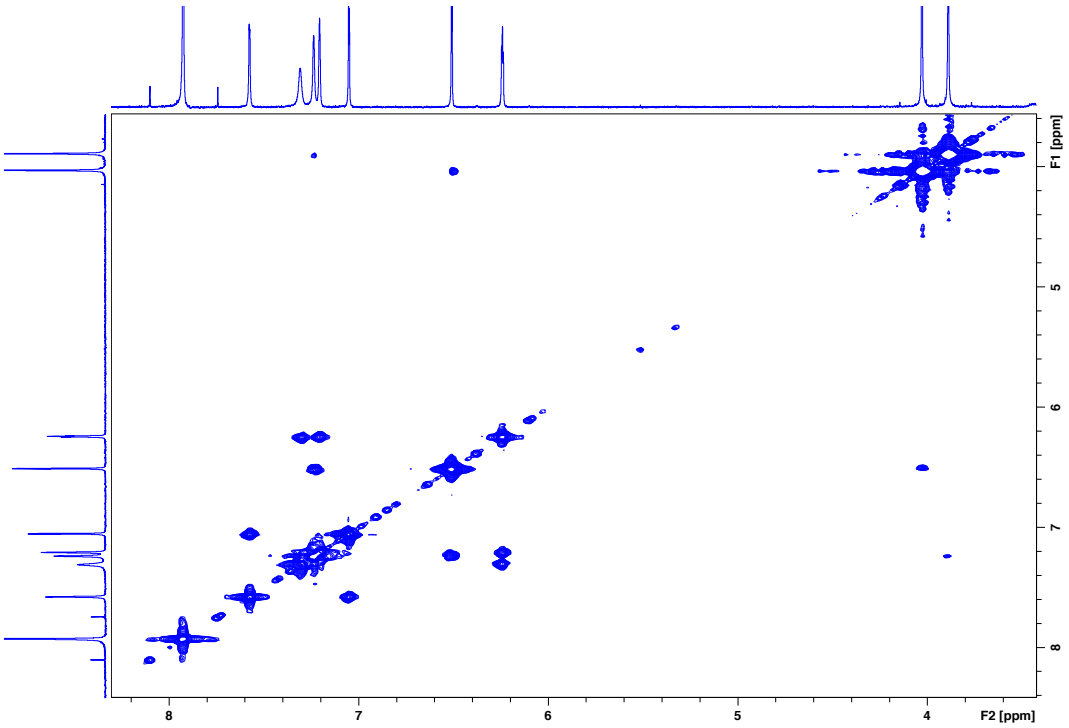


Figure S80. NOESY NMR spectrum of **6***(-)* ($(CD_3)_2CO$, 300K, 600 MHz).

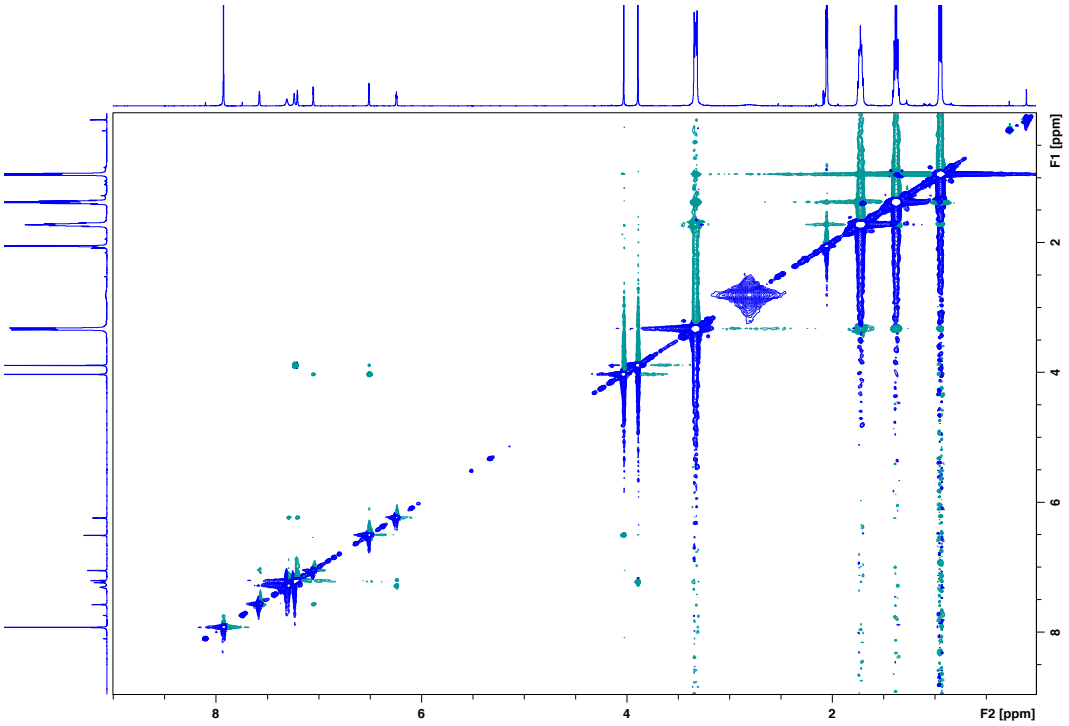
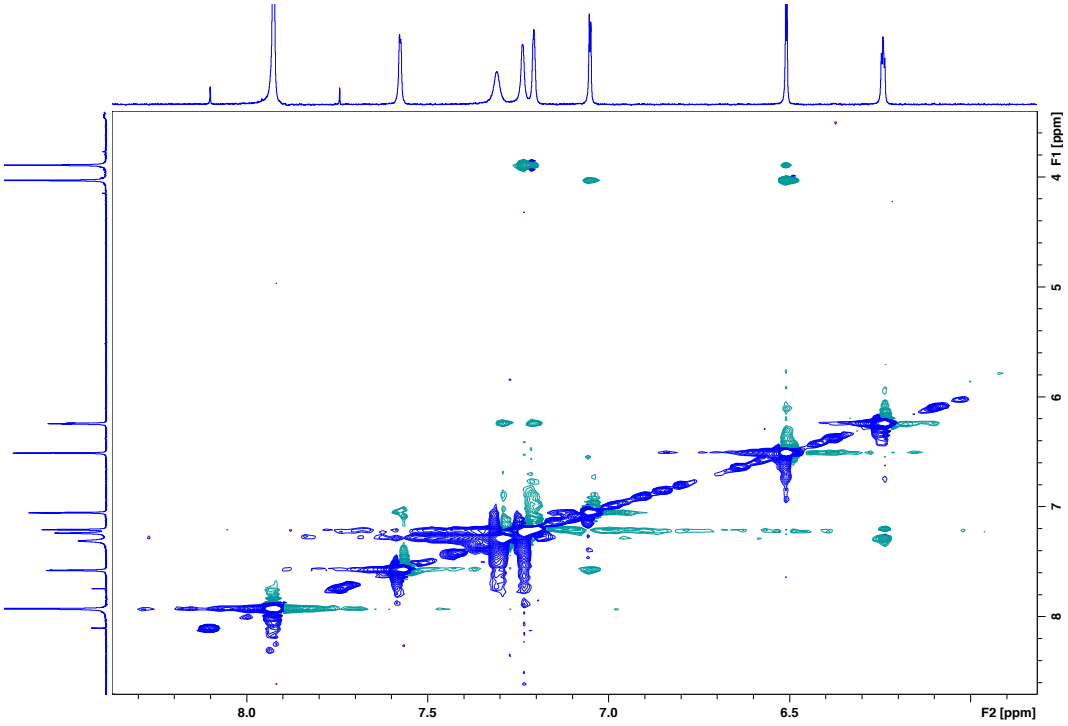


Figure S81. NOESY NMR spectrum (zoom, aromatic region) of **6***(-)* ($(CD_3)_2CO$, 300K, 600 MHz).



4. Mass spectra.

4.1. 3b.

Figure S82. HRMS spectrum of **3b**.

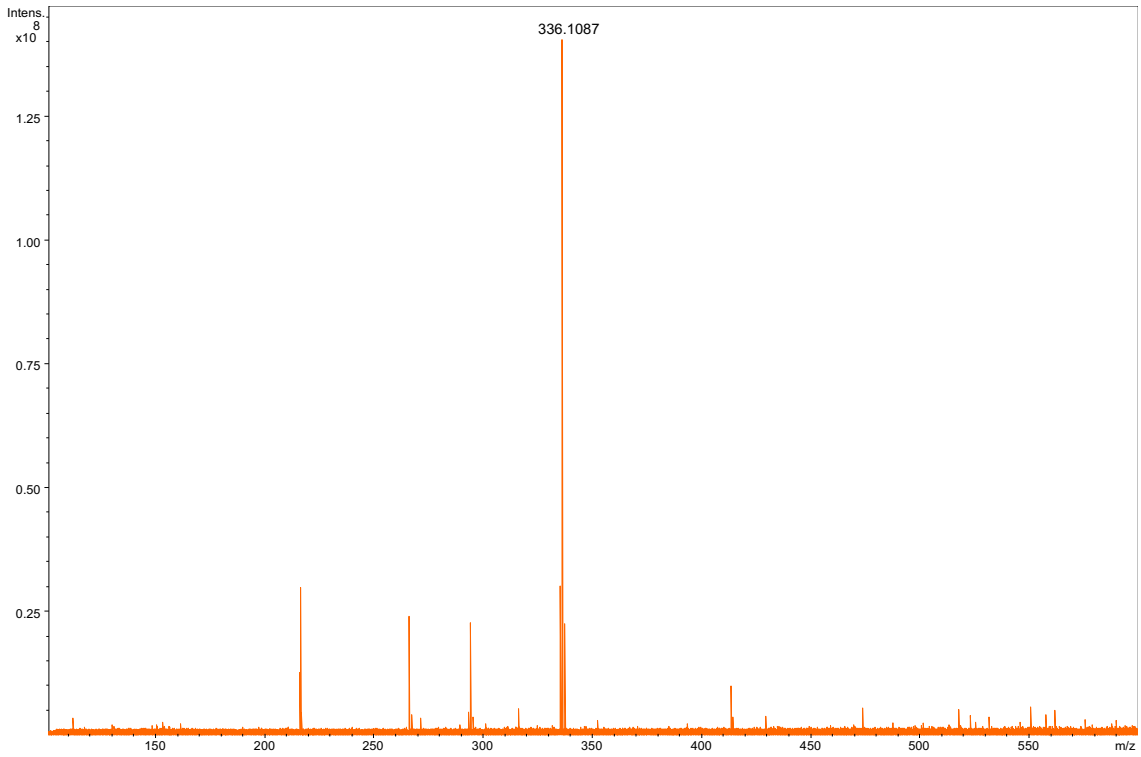
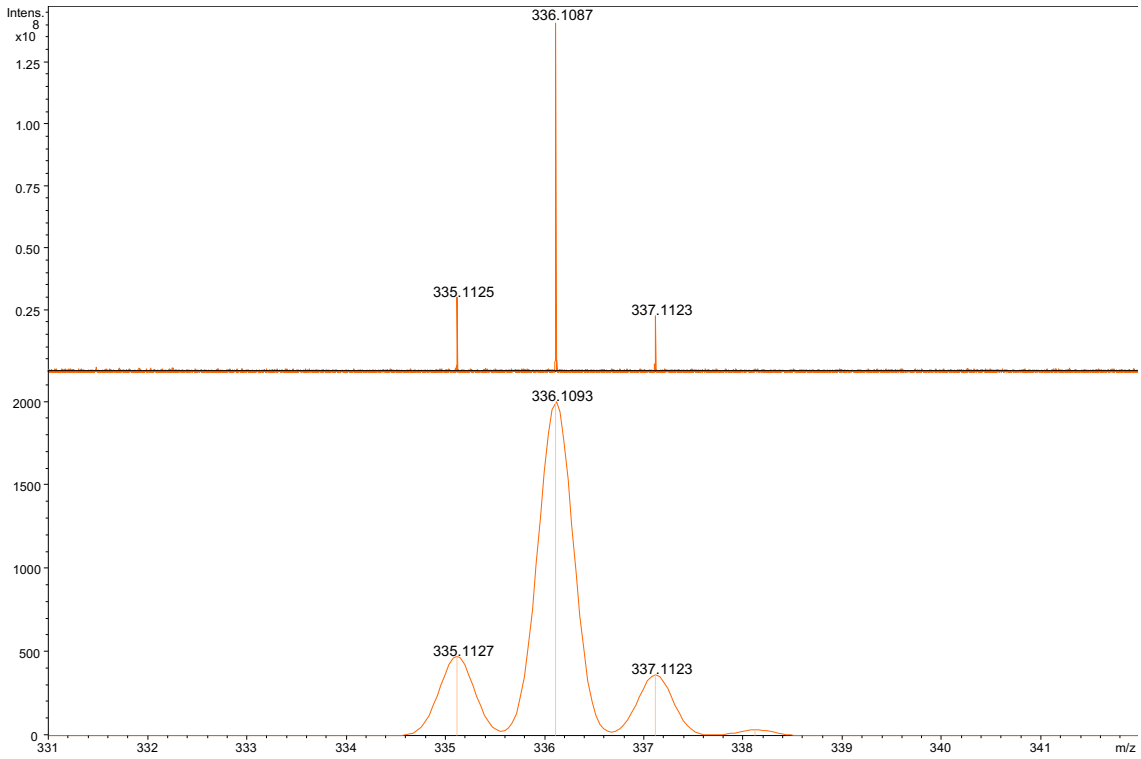


Figure S83. HRMS spectrum (zoom) of **3b** with simulated spectrum.



4.2. 3a.

Figure S84. HRMS spectrum of **3a**.

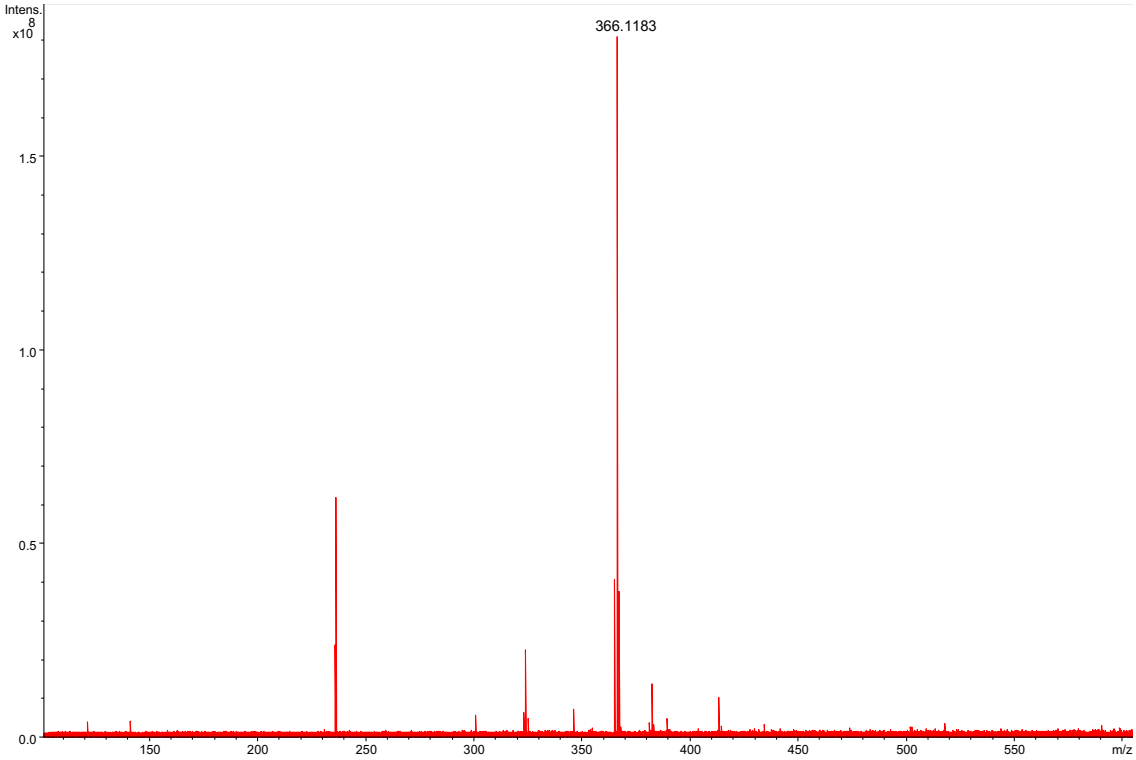
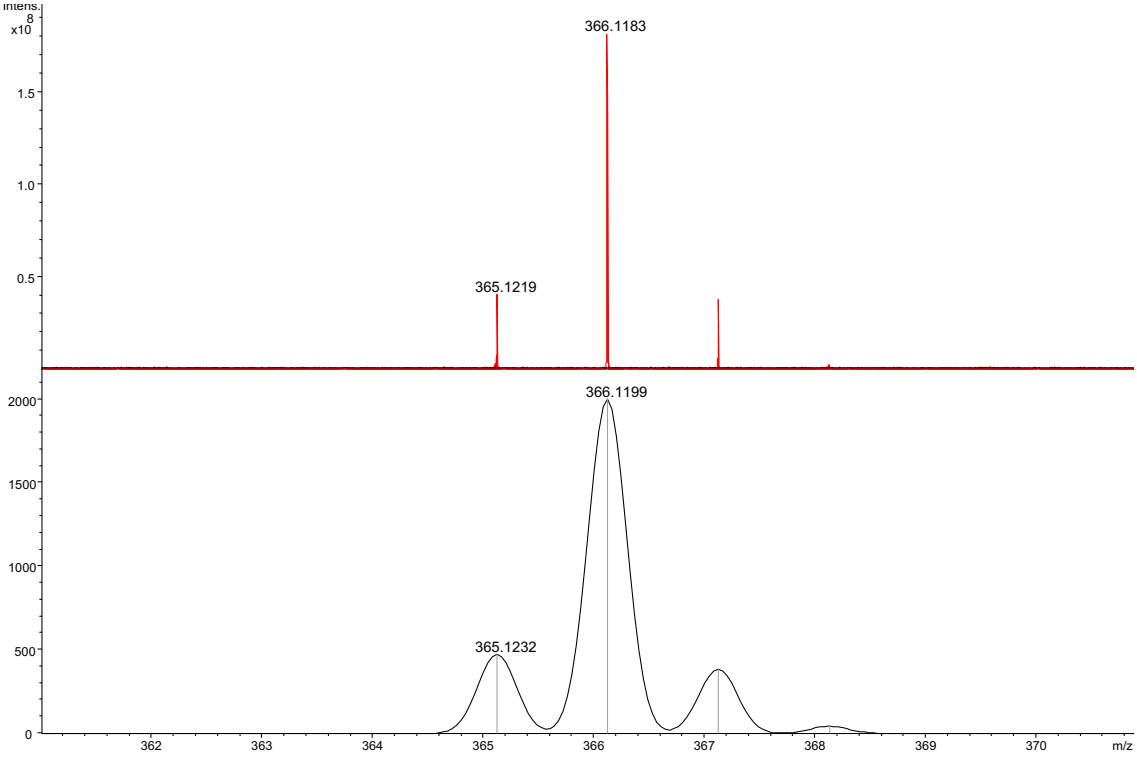


Figure S85. HRMS spectrum (zoom) of **3a** with simulated spectrum.



4.3. 4a

Figure S86. HRMS spectrum of **4a**.

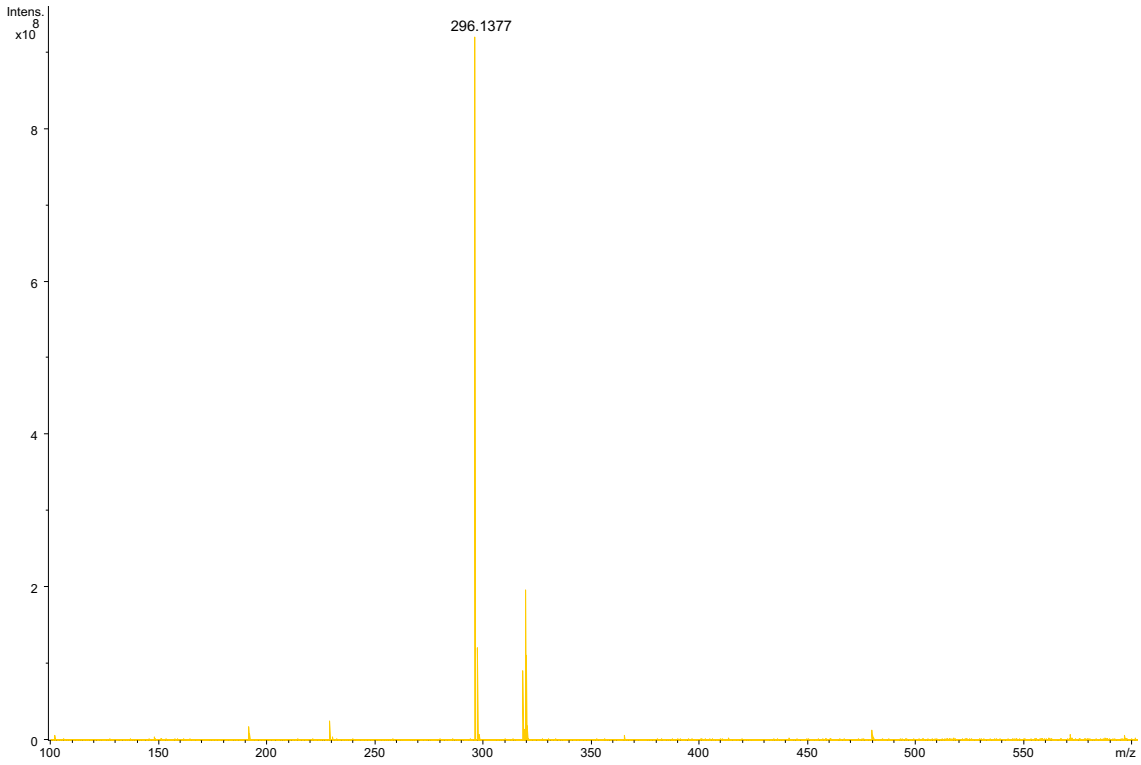
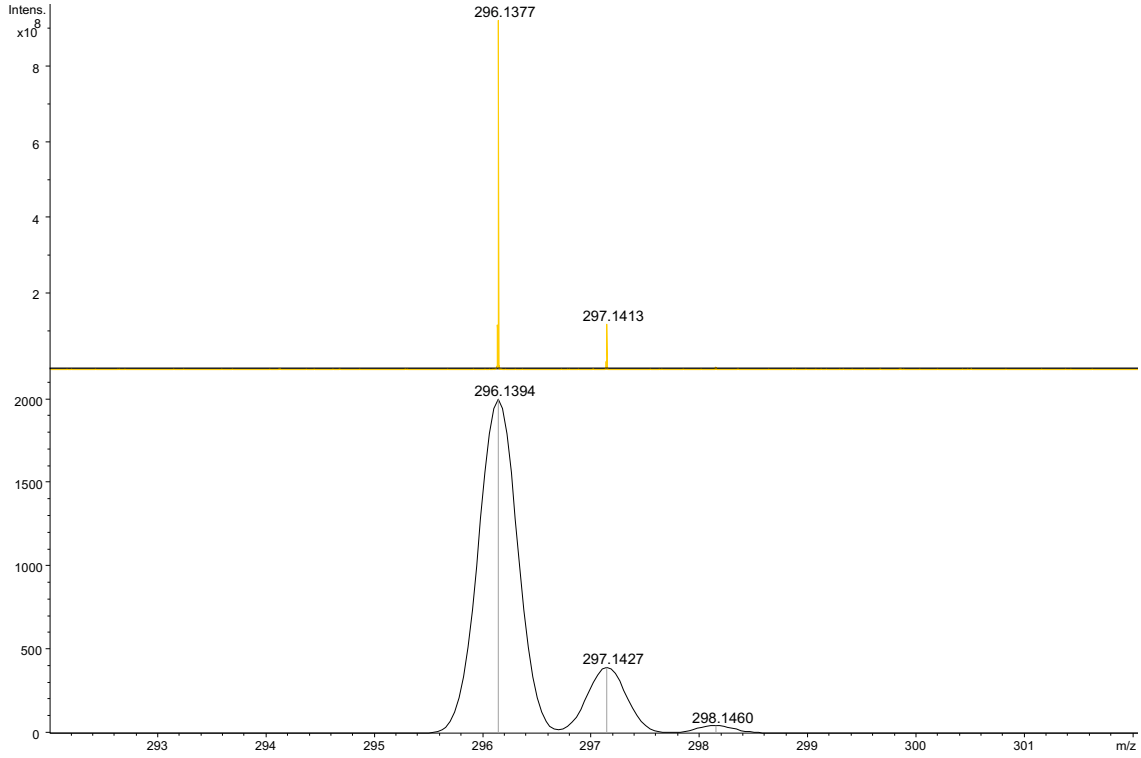


Figure S87. HRMS spectrum (zoom) of **4a** with simulated spectrum.



4.4. 4b

Figure S88. HRMS spectrum of **4b**.

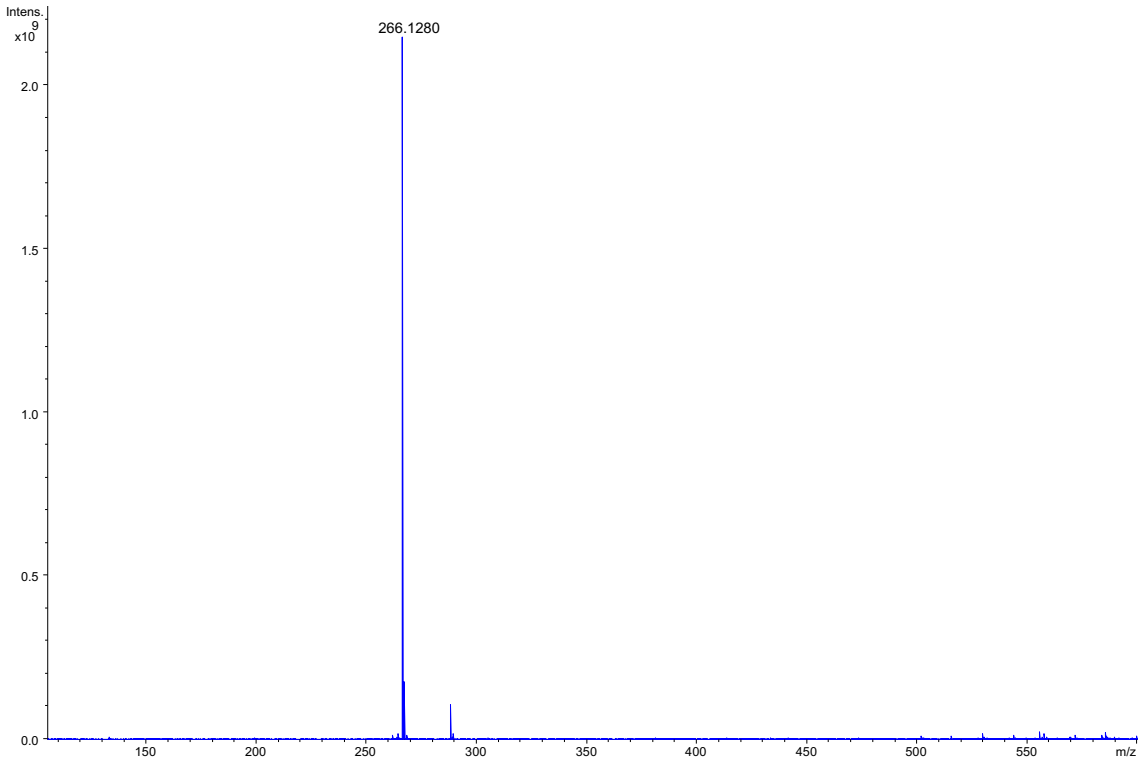
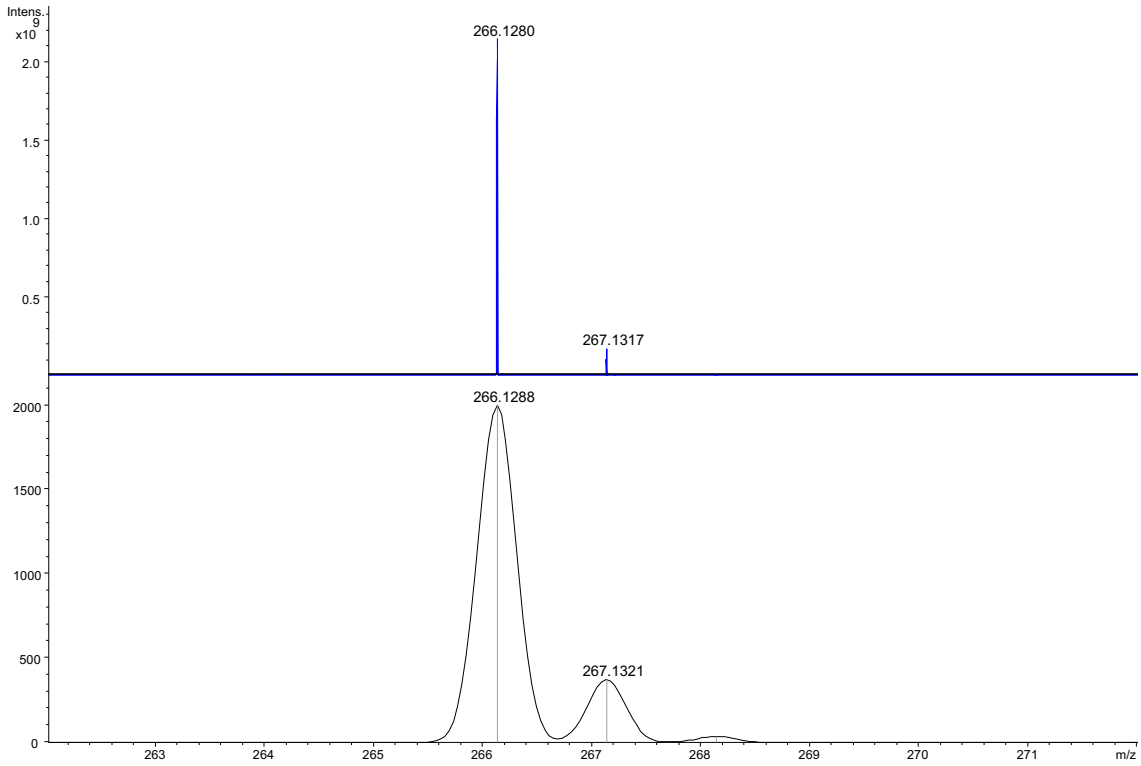


Figure S89. HRMS spectrum (zoom) of **4b** with simulated spectrum.



4.5. 4c

Figure S90. HRMS spectrum of **4c**.

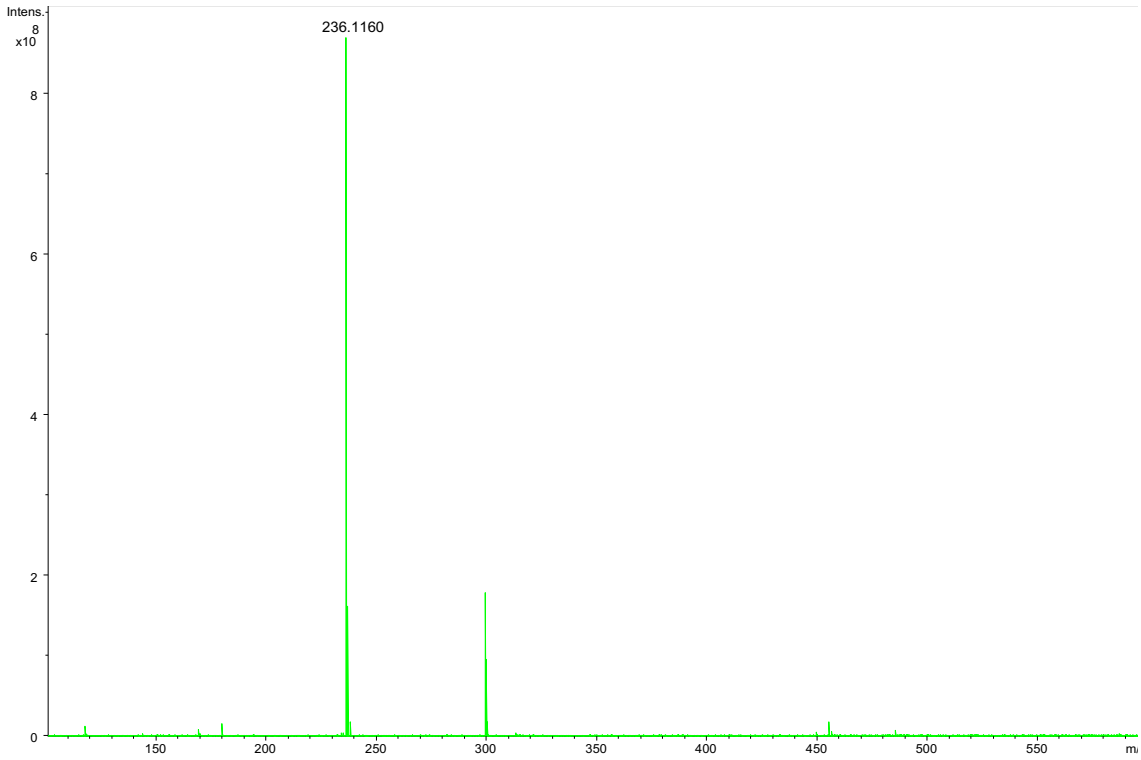
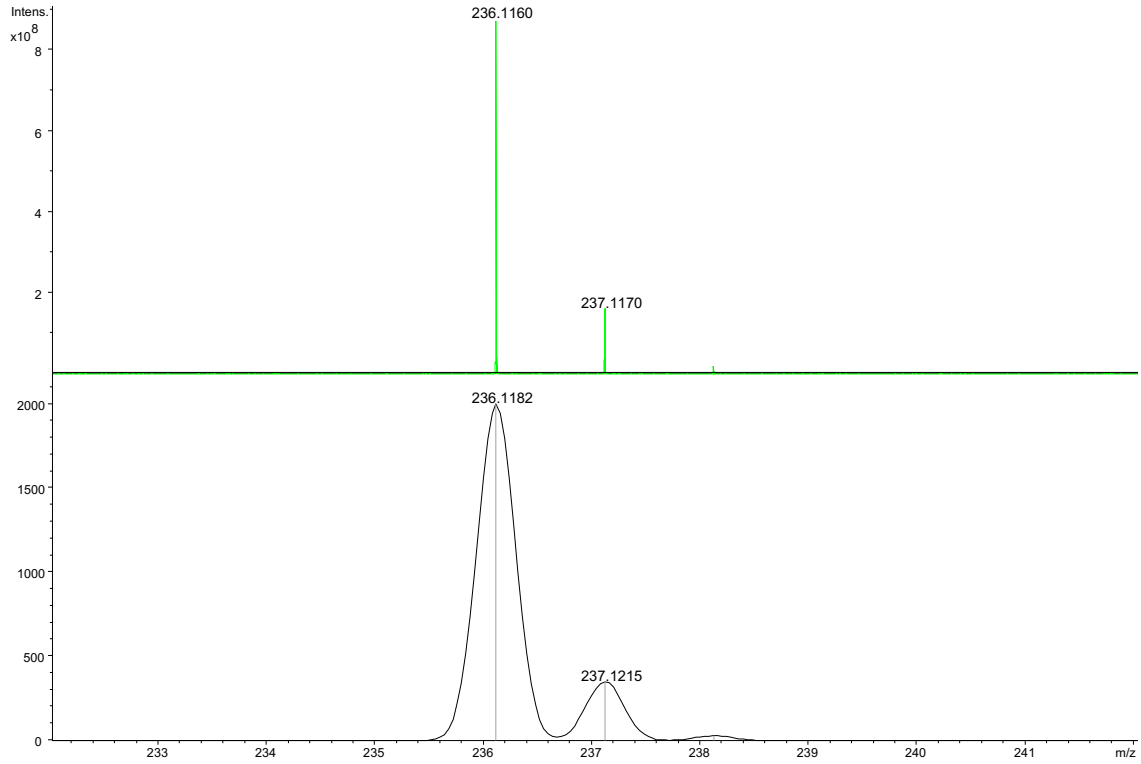


Figure S91. HRMS spectrum (zoom) of **4c** with simulated spectrum.



4.6. 5

Figure S92. HRMS spectrum of **5**.

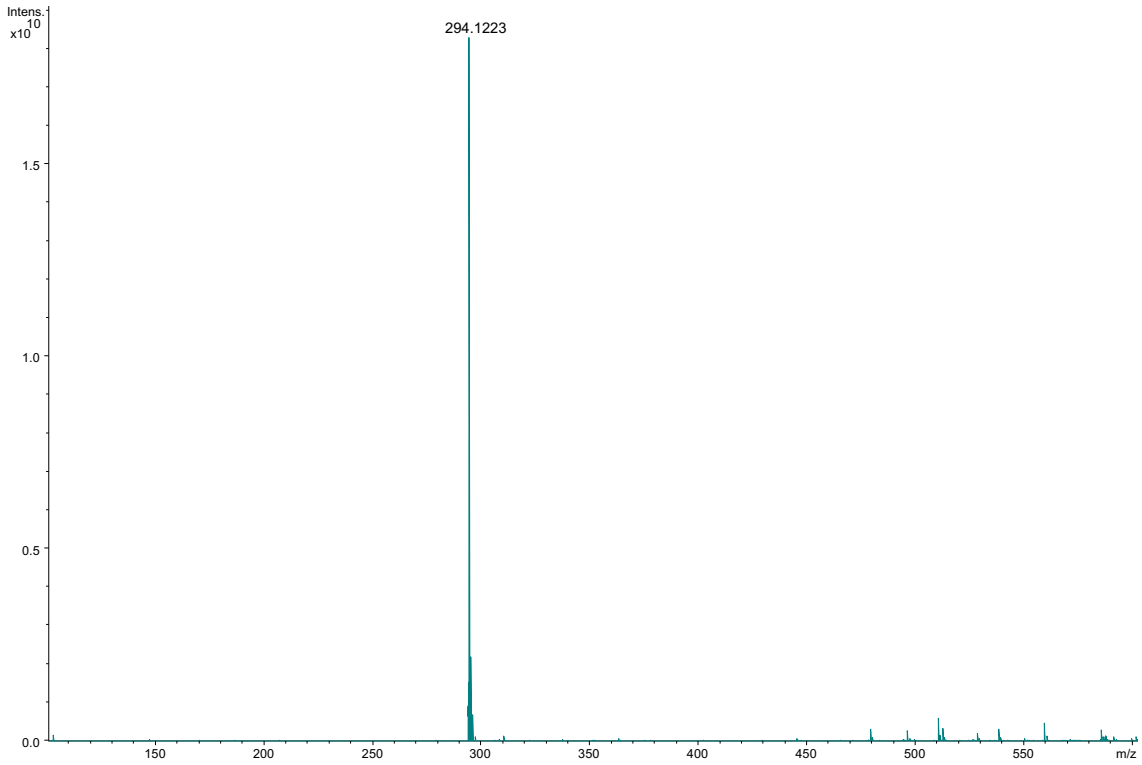
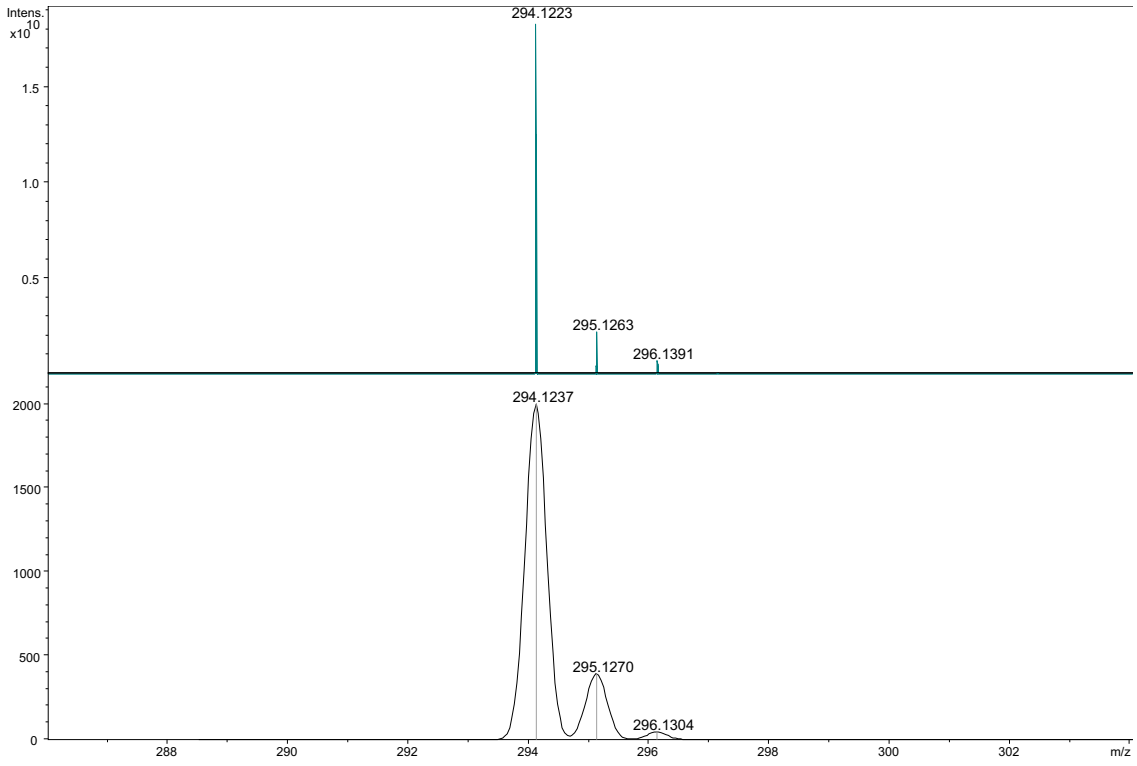
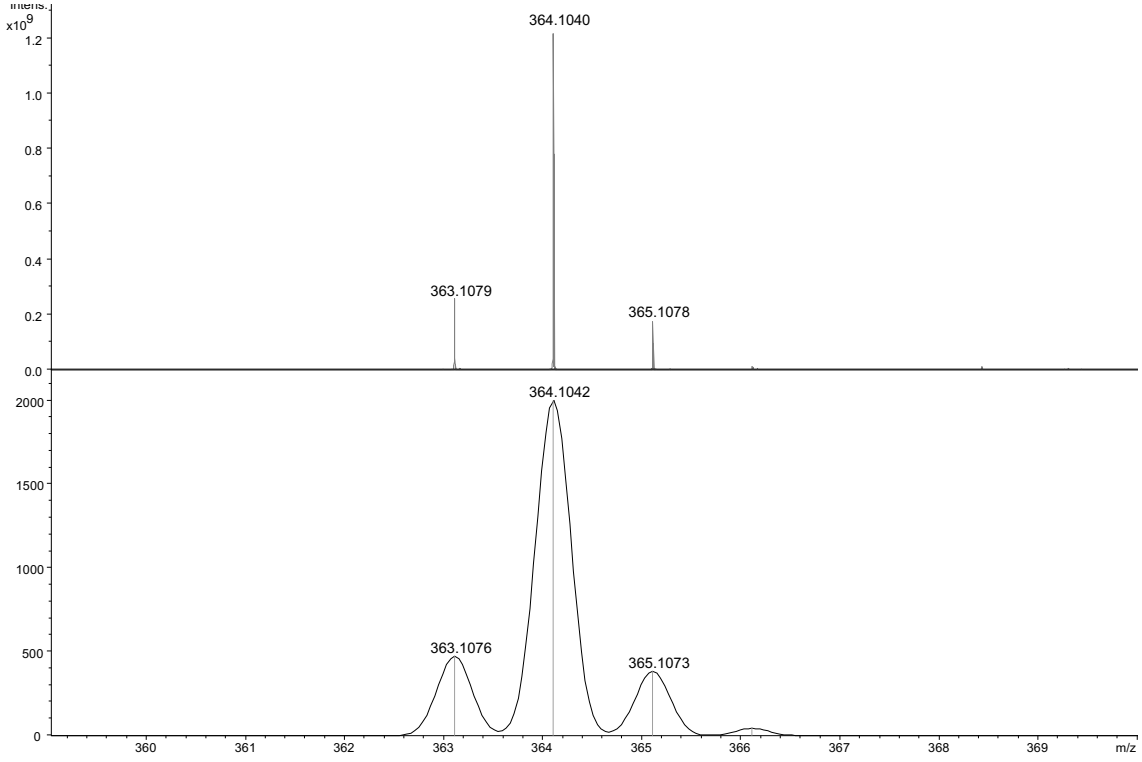


Figure S93. HRMS spectrum (zoom) of **5** with simulated spectrum.



4.7. 6.

Figure S94. HRMS spectrum (zoom) of **6** with simulated spectrum.



5. UV-VIS spectra.

Figure S95. UV-VIS spectrum for all derivatives.

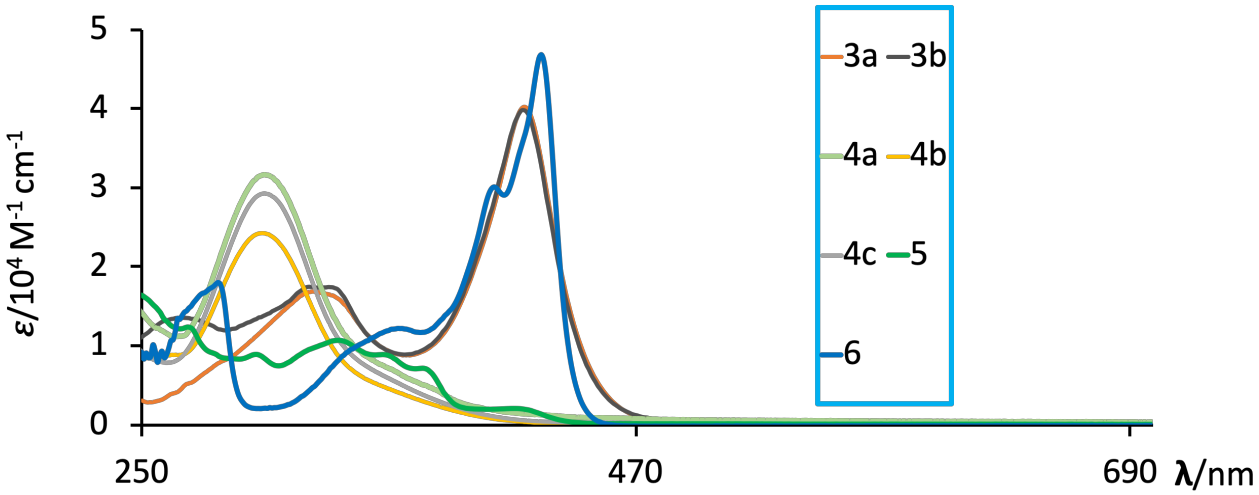


Figure S96. UV-VIS spectrum (DBU titration) for **3a**.

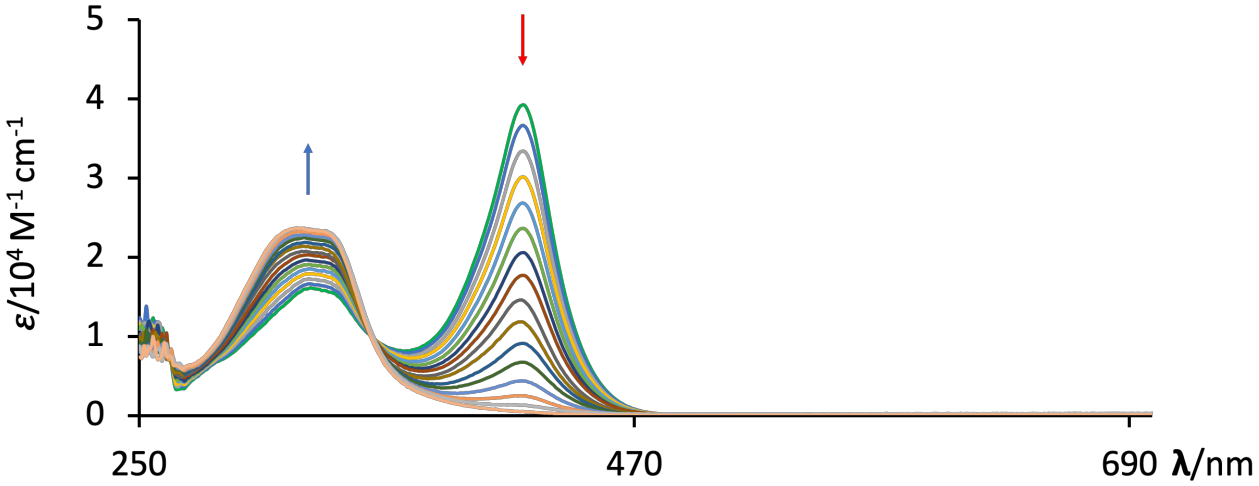
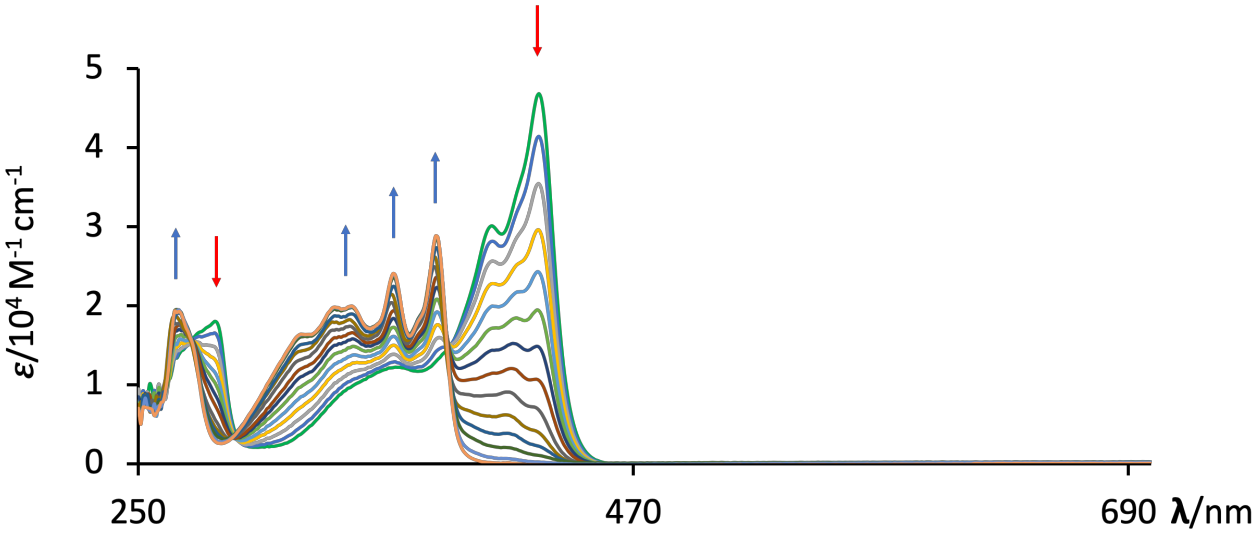


Figure S97. UV-VIS spectrum (DBU titration) for **6**.



6. Emission spectra.

Figure S98. Normalized emission spectrum for fused systems (**5, 6, 6***(-)*) and unfused (**3a**).

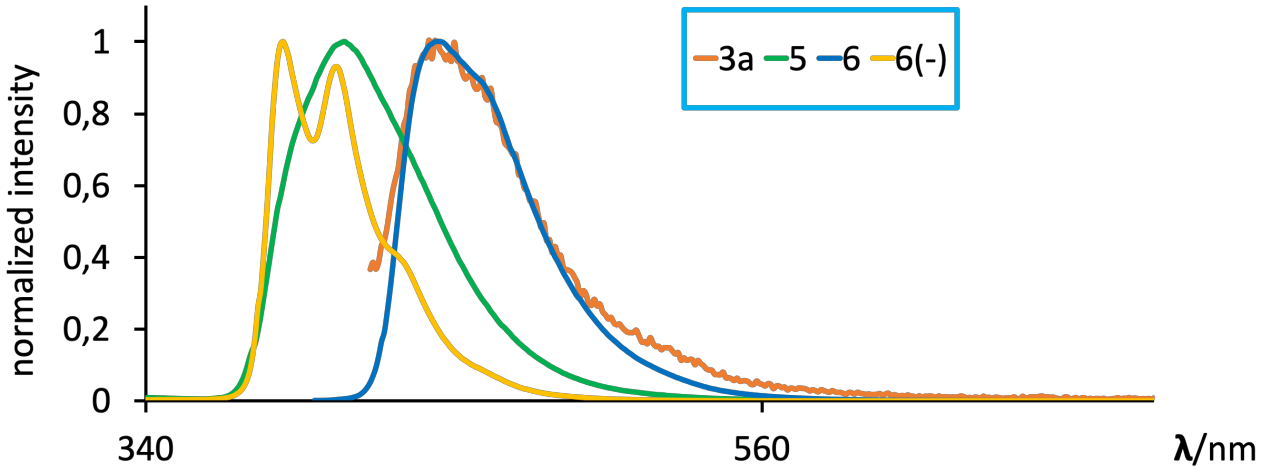


Figure S99. Normalized excitation spectrum displayed with absorbance for fused system **(5)**.

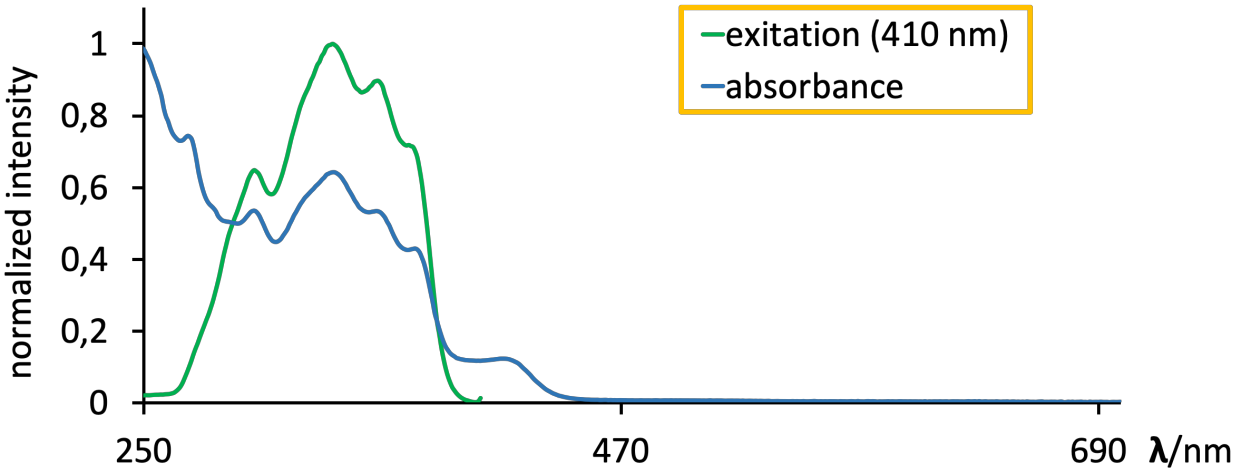


Figure S100. Normalized excitation spectrum displayed with absorbance for fused system **(6)**.

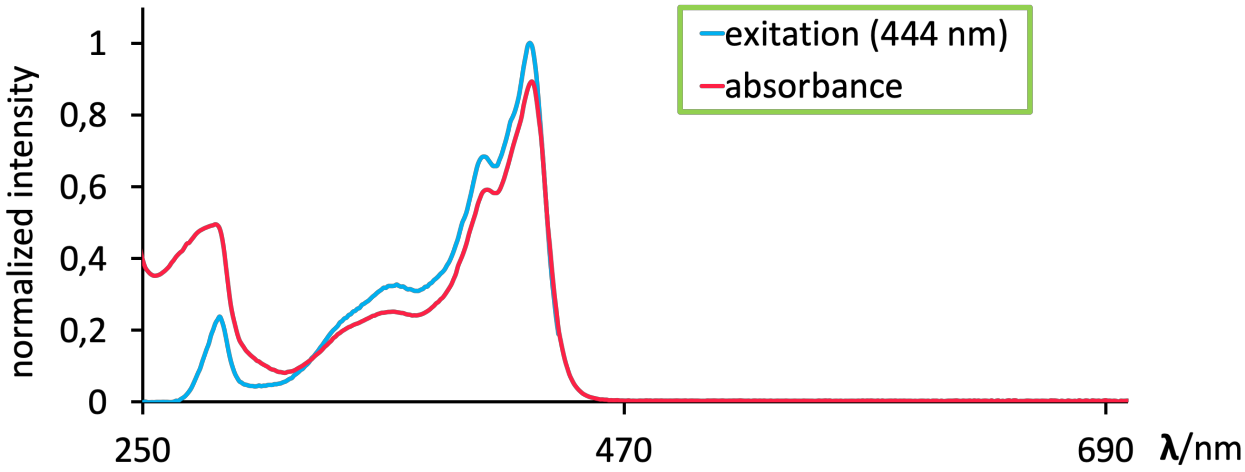
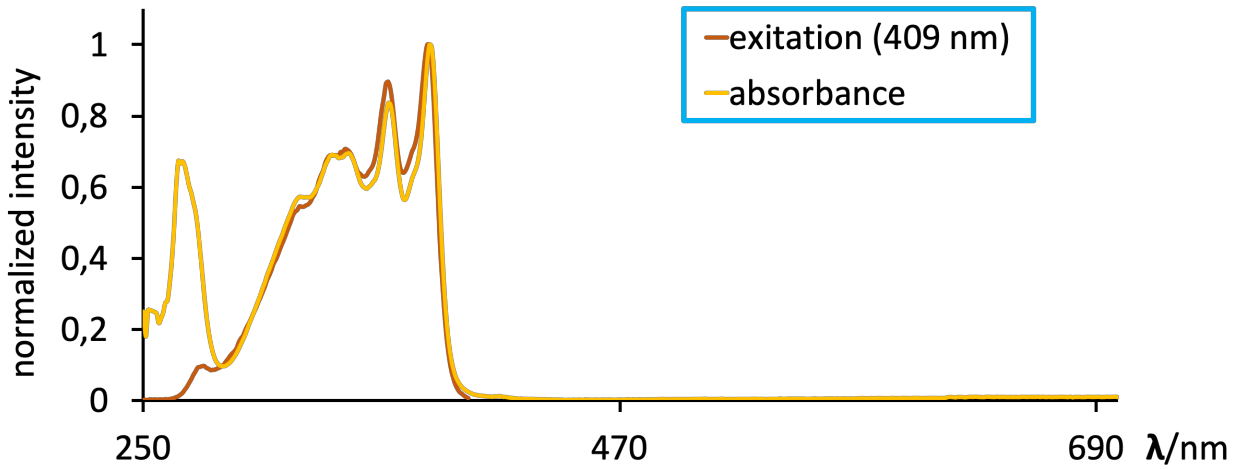


Figure S101. Normalized excitation spectrum displayed with absorbance for fused system **6***(-)*.



7. Lifetime measurements.

Figure S102. Normalized decay traces displayed for **3a** (green), **5** (yellow), **6** (cyan) and **6+DBU** (violet).

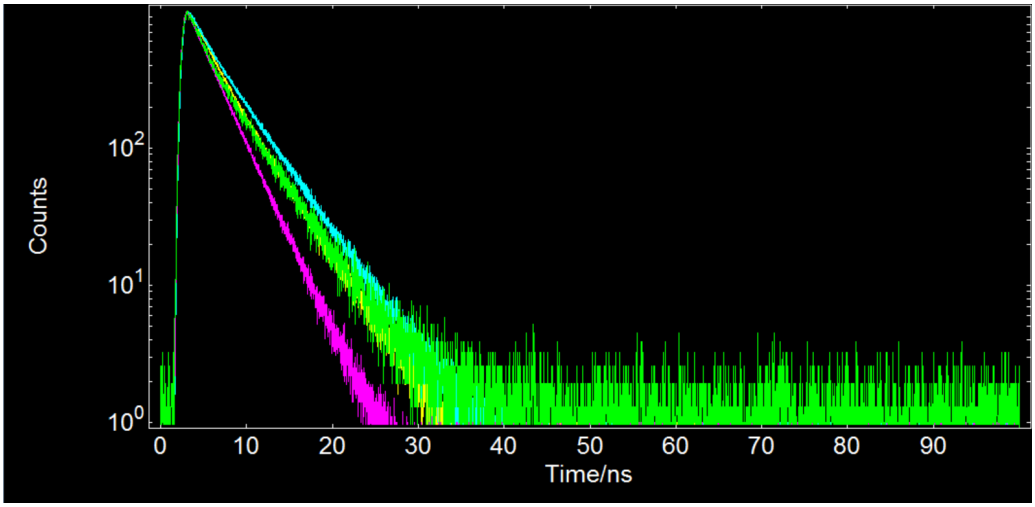


Figure S103. Linear fitting for **3a**.

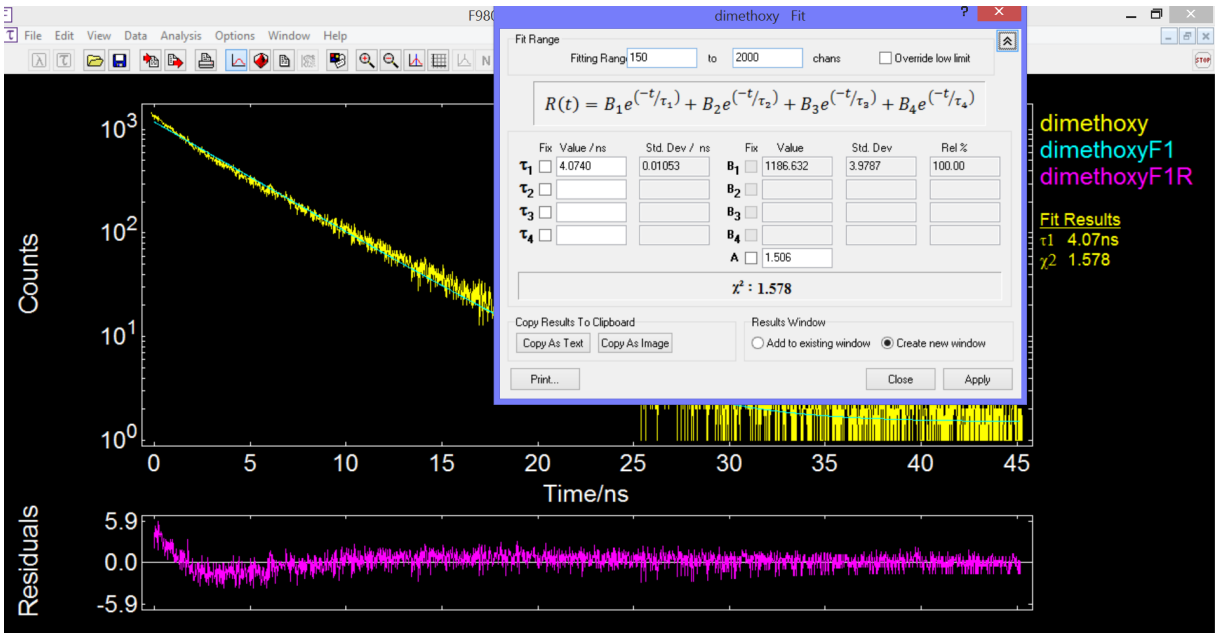


Figure S104. Linear fitting for **5**.

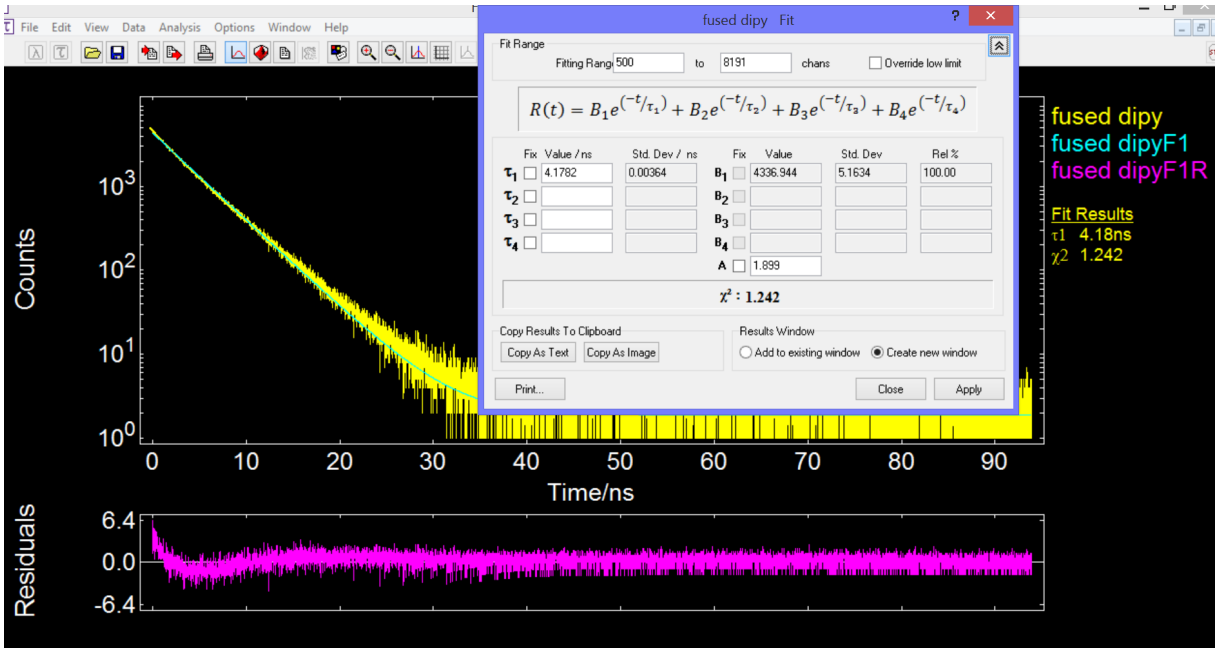


Figure S105. Linear fitting for **6**.

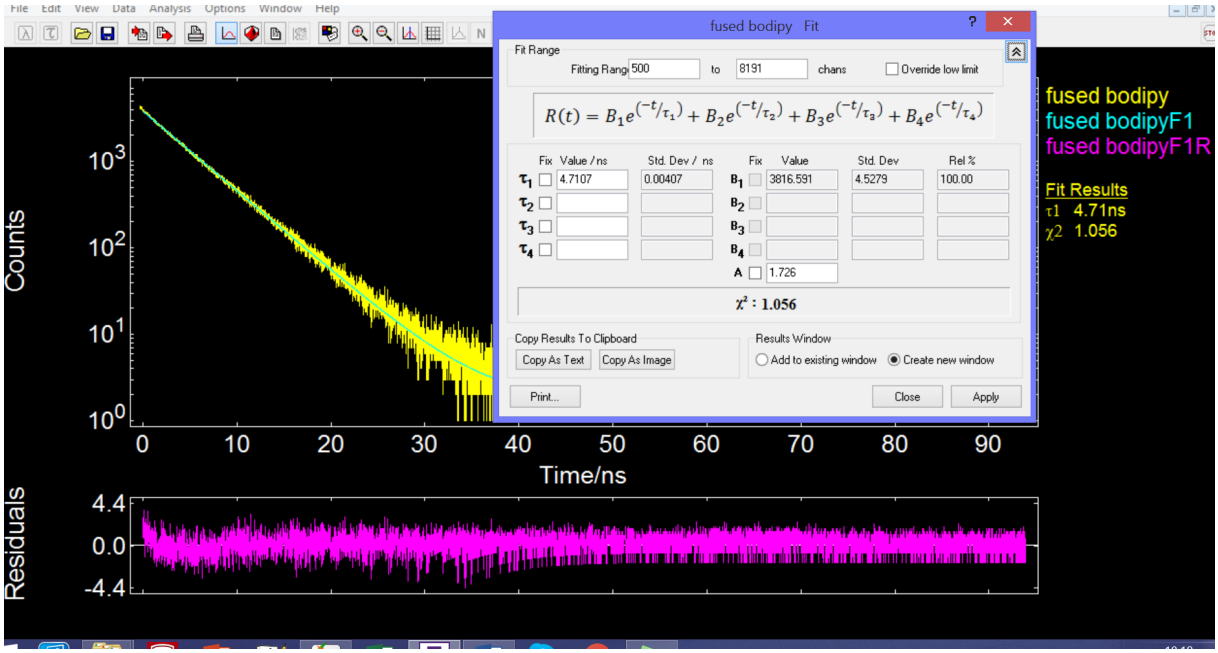
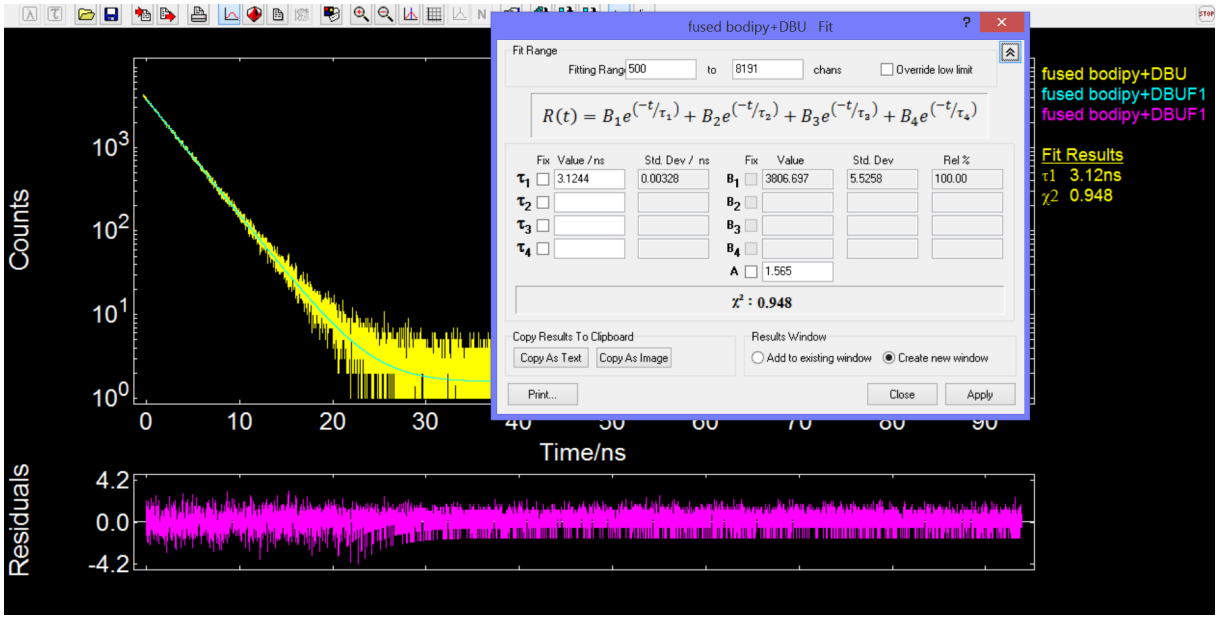


Figure S106. Linear fitting for **6***(-)*.



8. Theoretical calculations.

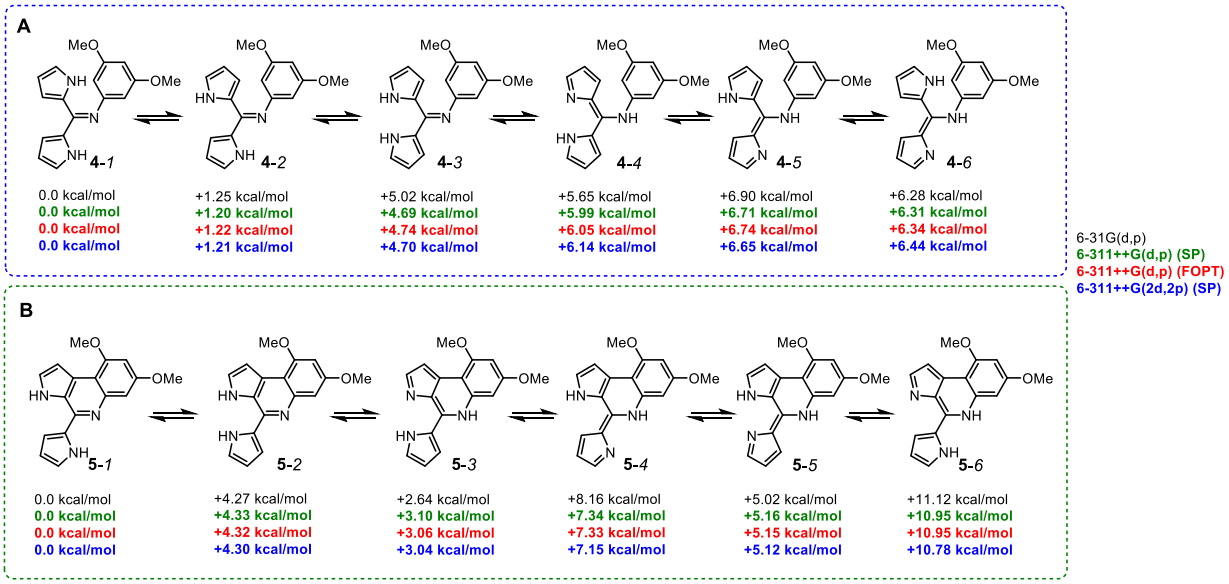
8.1. Optimisation details.

Table 1. optimization details for **3a**, **4**-*x*, **5**-*x*, **6** and **6***(-)*.

Structure	Code[a]	SCF E[b]	ZPV[c]	lowest freq. [d]	G[e]
		a.u.	a.u.	cm^{-1}	a.u.
3a	3_a	-1196.86906034	0.315253	8.37	-1196.553807
6	6	-1195.70057096	0.294967	22.40	-1195.405604
6*(-)*	6_m	-1195.21816424	0.280799	27.47	-1194.937365
4-***1***	4_1	-972.97563642	0.311969	22.11	-972.663667
4-***2***	4_2	-972.97368438	0.311837	23.54	-972.661848
4-***3***	4_3	-972.96808961	0.311328	19.64	-972.656762
4-***4***	4_4	-972.96598651	0.311676	19.57	-972.654311
4-***5***	4_5	-972.96490184	0.311880	18.16	-972.653022
4-***6***	4_6	-972.96549663	0.311963	18.97	-972.653534
5-***1***	5_1	-971.80115212	0.291286	39.26	-971.509866
5-***2***	5_2	-971.79426344	0.291233	39.85	-971.503030
5-***3***	5_3	-971.79619599	0.291670	41.44	-971.504526
5-***4***	5_4	-971.78947529	0.291343	37.67	-971.498132
5-***5***	5_5	-971.79293836	0.291504	43.15	-971.501434
5-***6***	5_6	-971.78369584	0.291417	39.56	-971.492279

[a] Optimized geometry available as <code>.pdb file. [b] Electronic energy. [c] Zero-point vibrational energy. [d] Lowest vibrational frequency. [e] Gibbs free energy.

Figure S107. Energies of all tautomers obtained with different basis sets.



8.2. GIAO ^{1}H NMR chemical shifts of all analysed compounds.

Table 2. Predicted chemical shifts for all tautomeric forms in **5**.

	5-*1*	**5**-*2*	**5**-*3*	**5**-*4*	**5**-*5*	**5**-*6*	
	Theor.	Theor.	Theor.	Theor.	Theor.	Theor.	**Exp**
1	8.04	7.32	7.36	7.40	7.42	8.13	7.45
2	7.20	7.43	7.39	7.25	7.06	7.27	7.33
3^{3}	6.44	6.54	6.52	6.29	6.32	6.44	6.60
5^{3}	6.52	7.11	7.05	6.49	6.38	6.47	7.17
5^{1}	8.06	---	---	10.57	7.82	7.53	---
7	7.01	7.14	6.83	7.05	7.26	8.20	6.89
8	6.44	6.51	6.46	6.49	6.48	6.58	6.41
9	7.19	7.03	7.02	7.41	7.46	7.11	7.04
10	13.48	8.12	9.69	---	12.69	---	10.29
11	---	8.28	8.54	8.77	---	7.98	9.18

Table 3. Predicted chemical shifts for all tautomeric forms in **4**.

	4-*1*	**4**-*2*	**4**-*3*	**4**-*4*	**4**-*5*	**4**-*6*	
	Theor.	Theor.	Theor.	Theor.	Theor.	Theor.	**Exp**
1	7.47	6.90	6.99	7.09	7.59	6.97	7.00
2	6.28	6.41	6.36	6.42	6.53	6.33	6.31
3	7.22	7.12	6.59	6.63	6.94	6.80	6.76
5^{1}	6.05	---	---	8.67	8.68	---	---
5^{4}	5.99	5.88	5.92	5.99	5.94	5.93	6.20
5^{3},**5**^{7}	6.56 6.14	6.17 5.38	6.16 5.46	6.32 5.94	6.28 5.63	6.15 5.59	6.03
7	6.84	6.29	6.24	6.94	7.15	6.85	6.69
8	6.32	6.21	6.19	6.58	6.47	6.17	6.17
9	7.19	6.78	6.78	7.56	6.99	6.69	6.73
10	13.40	7.90	9.13	8.30	7.84	9.07	9.50
11	---	7.85	8.29	---	---	8.18	8.22

Table 4. Predicted chemical shifts for **3a**, **6** and **6***(-)*.

	3a[a]		**6**[a]		**6**[b]		**6***(-)*[b]	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
1	7.61 7.57	7.60	7.96	7.96	7.96	7.99	7.52	7.57
2	6.48 6.26	6.36	7.19	7.07	7.23	7.35	7.03	7.05
3	7.04 6.72	6.66	---	---	---	---	---	---
3^3	6.24	6.55	6.49	6.57	6.61	6.75	6.45	6.51
5^3	6.56 6.39	6.57	6.56	6.65	6.64	6.98	6.87	7.24
5^1	6.73	7.75	8.20	9.72	8.47	12.47	---	---
7	---	---	7.10	6.94	7.22	7.24	7.01	7.21
8	---	---	6.55	6.30	6.60	6.45	6.31	6.24
9	---	---	7.70	7.50	7.68	7.49	7.28	7.31
10	---	---	---	---	---		---	---
11	---	---	---	---	---		---	---

[a] chloroform. [b] acetone.

8.3. TD-DFT predicted UV Vis transitions.

Table 5. TD-DFT predicted absorption spectra for **4**-*x*

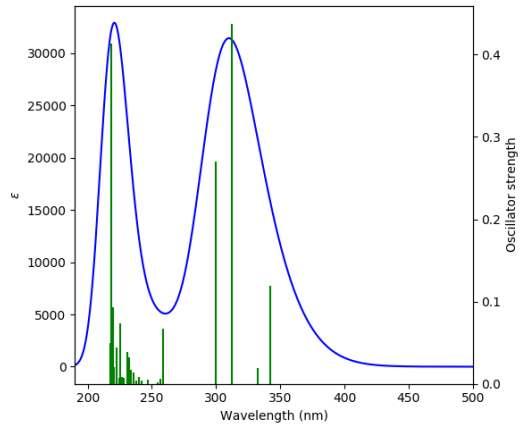
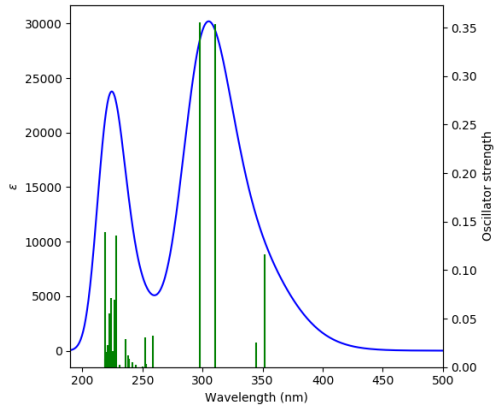
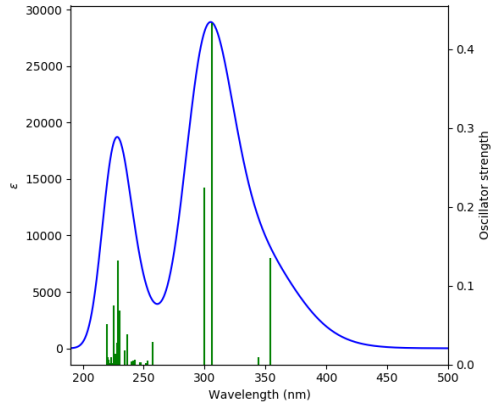
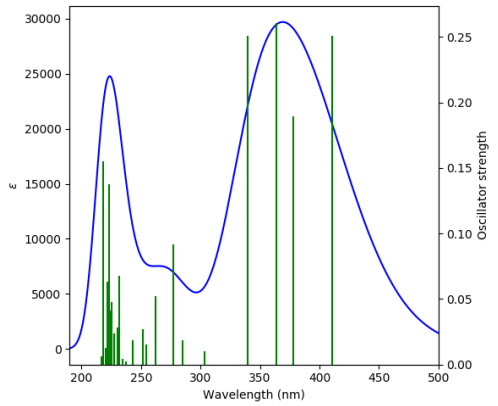
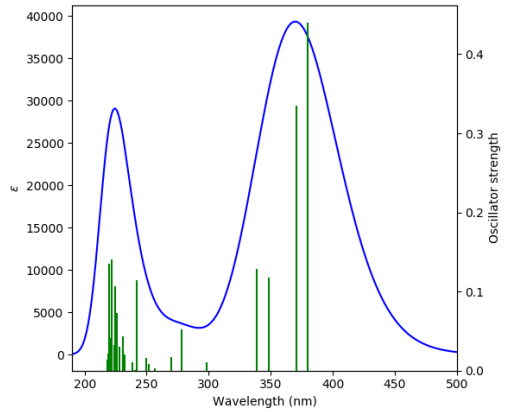
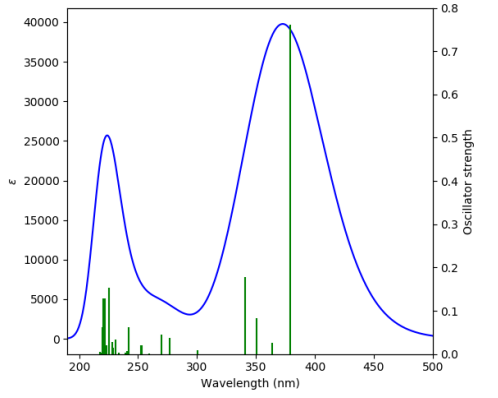
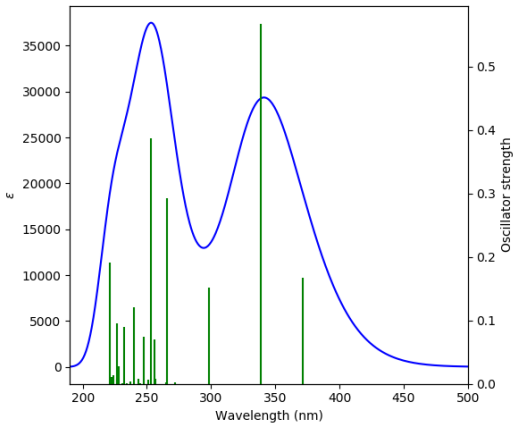
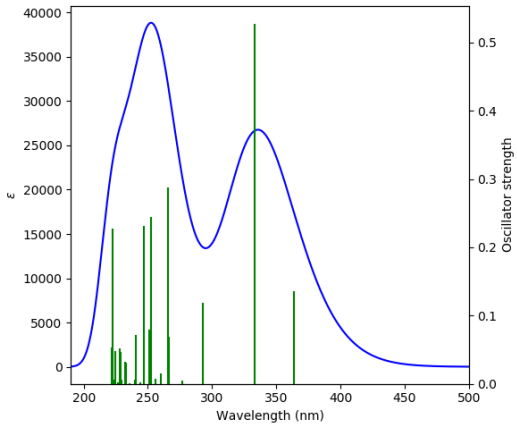
4-*1*	**4**-*2*
	
4-*3*	**4**-*4*
	
4-*5*	**4**-*6*
	

Table 6. TD-DFT predicted absorption spectra for **5**-*x*

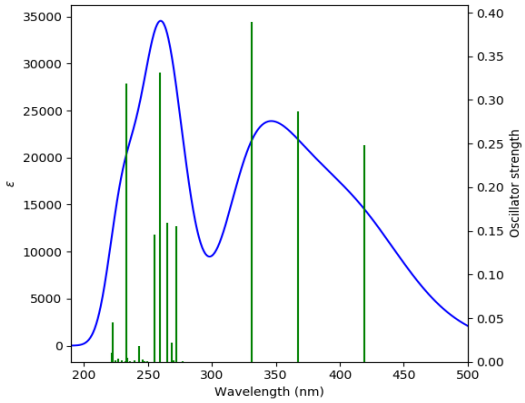
5-*1*



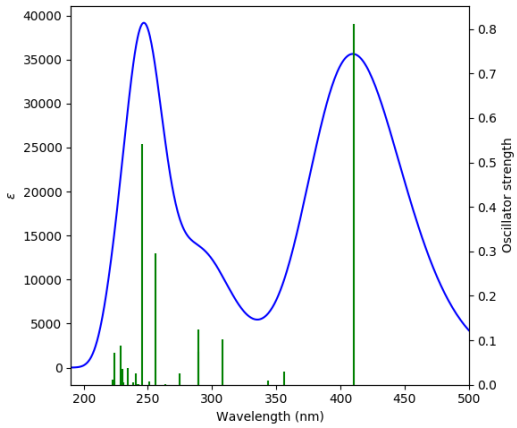
5-*2*



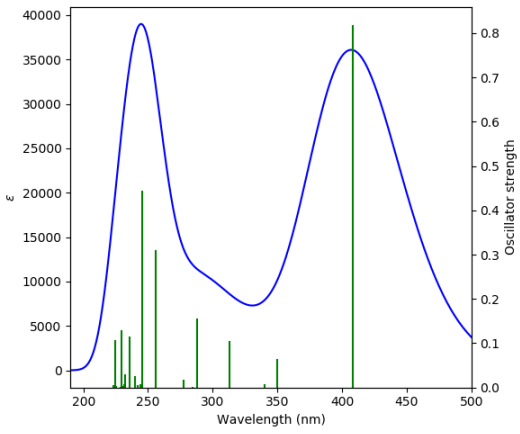
5-*3*



5-*4*



5-*5*



5-*6*

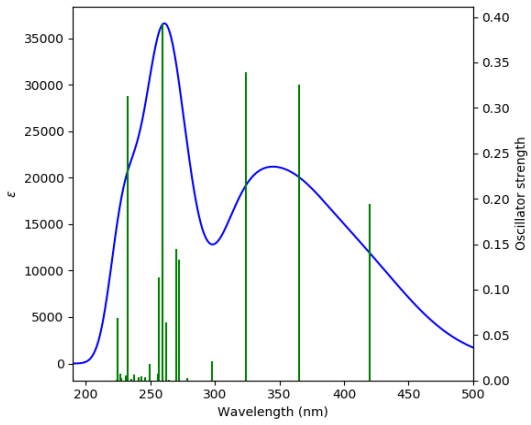
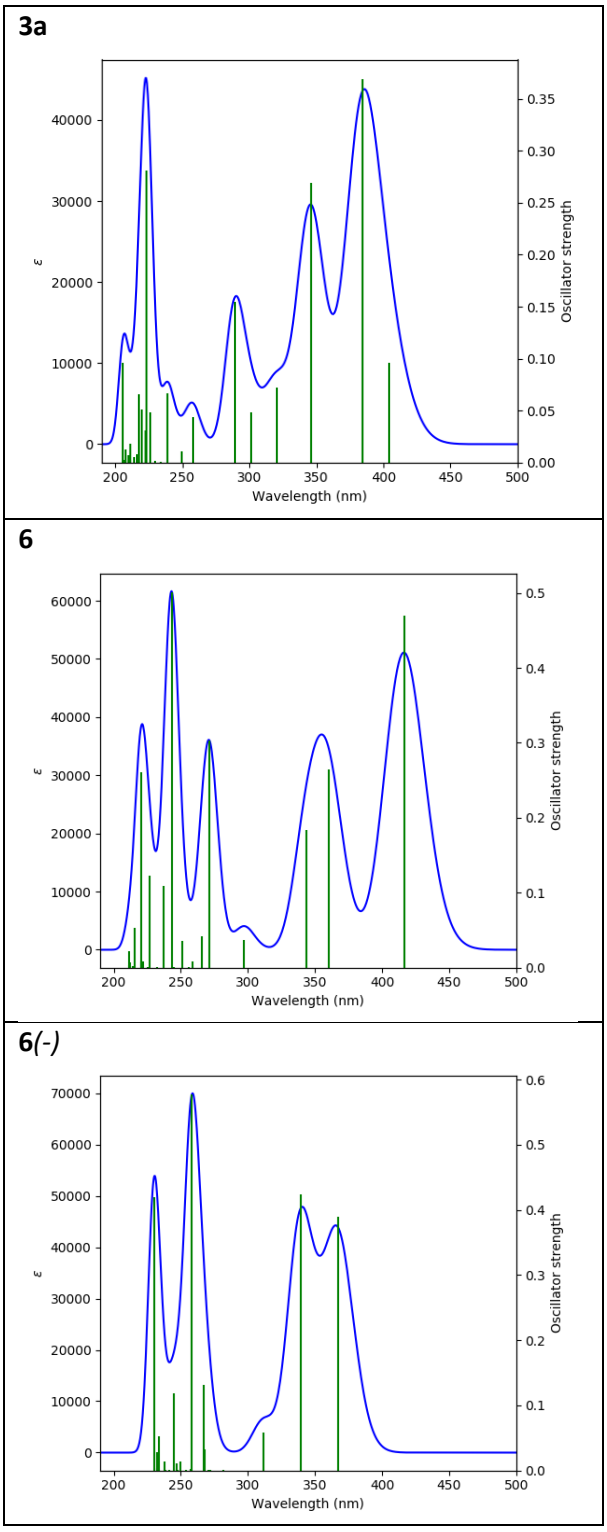


Table 7. TD-DFT predicted absorption spectra for **3a**, **6** and **6***(-)*.



9. Packings for crystal structures.

Figure S108. Molecular packing in crystals of compound **3a** (zoom).

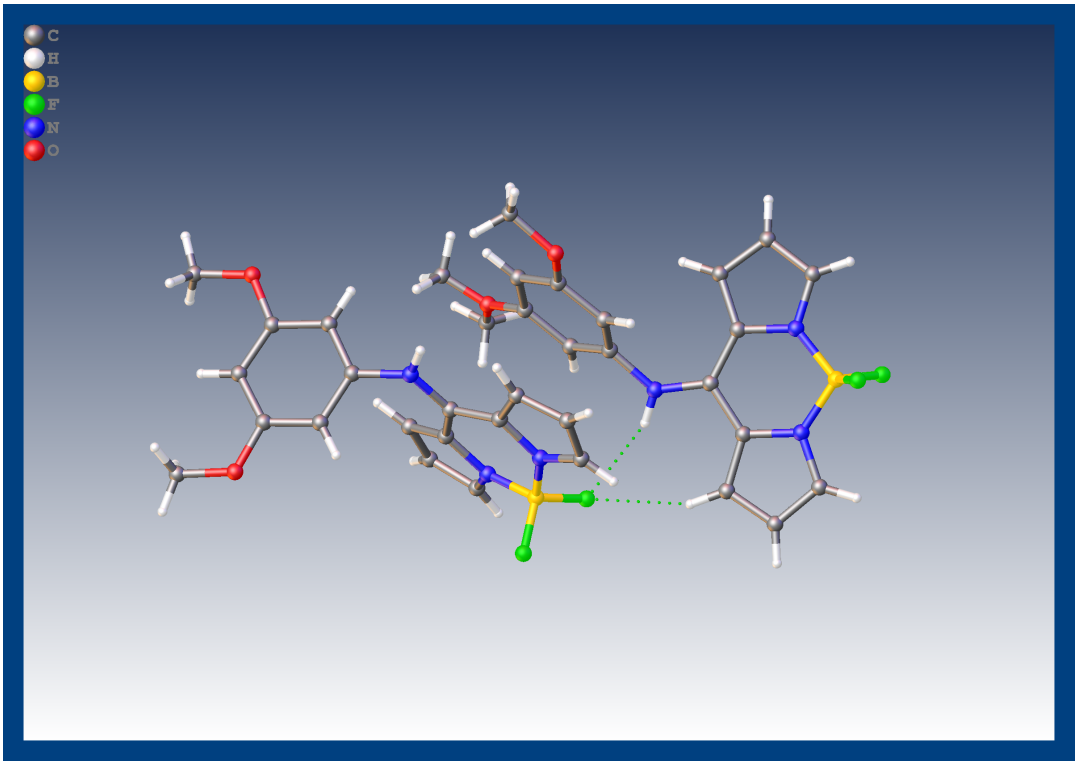


Figure S109. Molecular packing in crystals of compound **3a**.

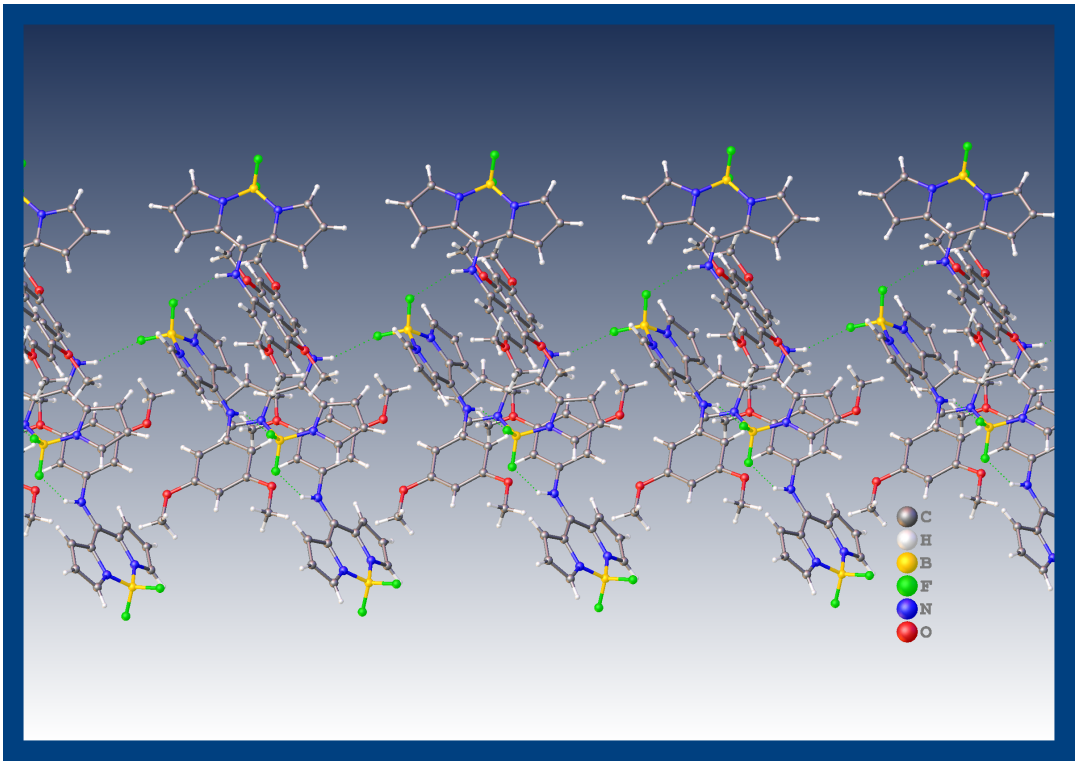


Figure S110. Molecular packing in crystals of compound **4a** (zoom).

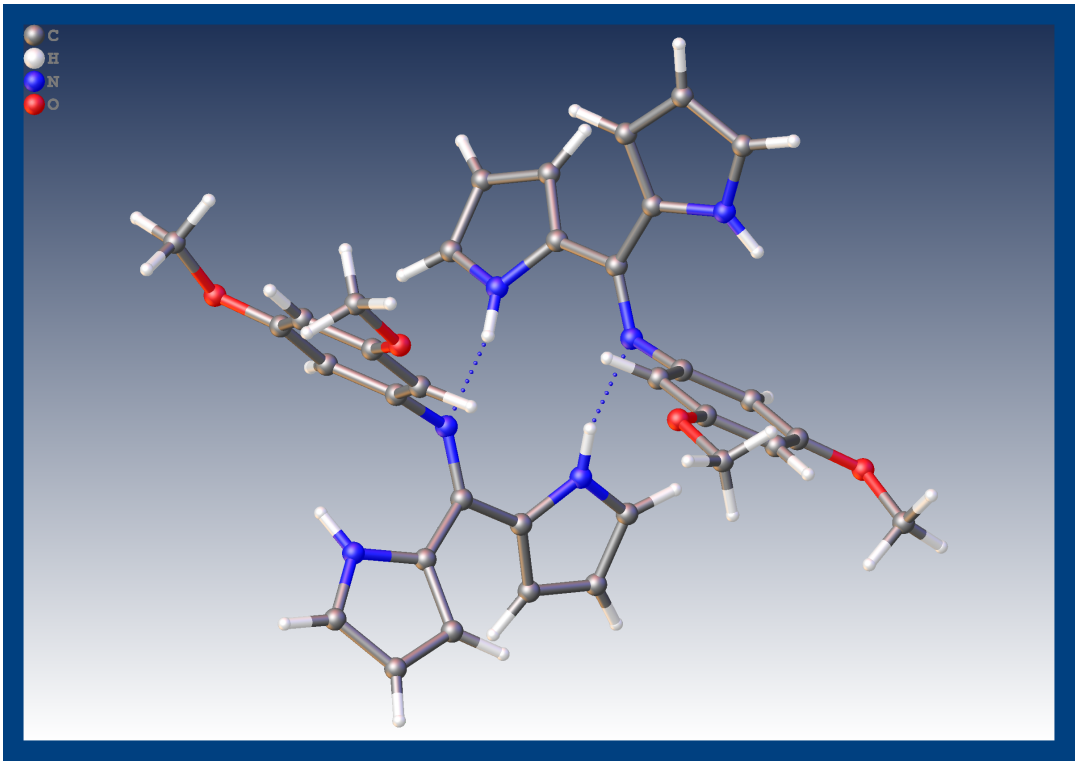


Figure S111. Molecular packing in crystals of compound **4a**.

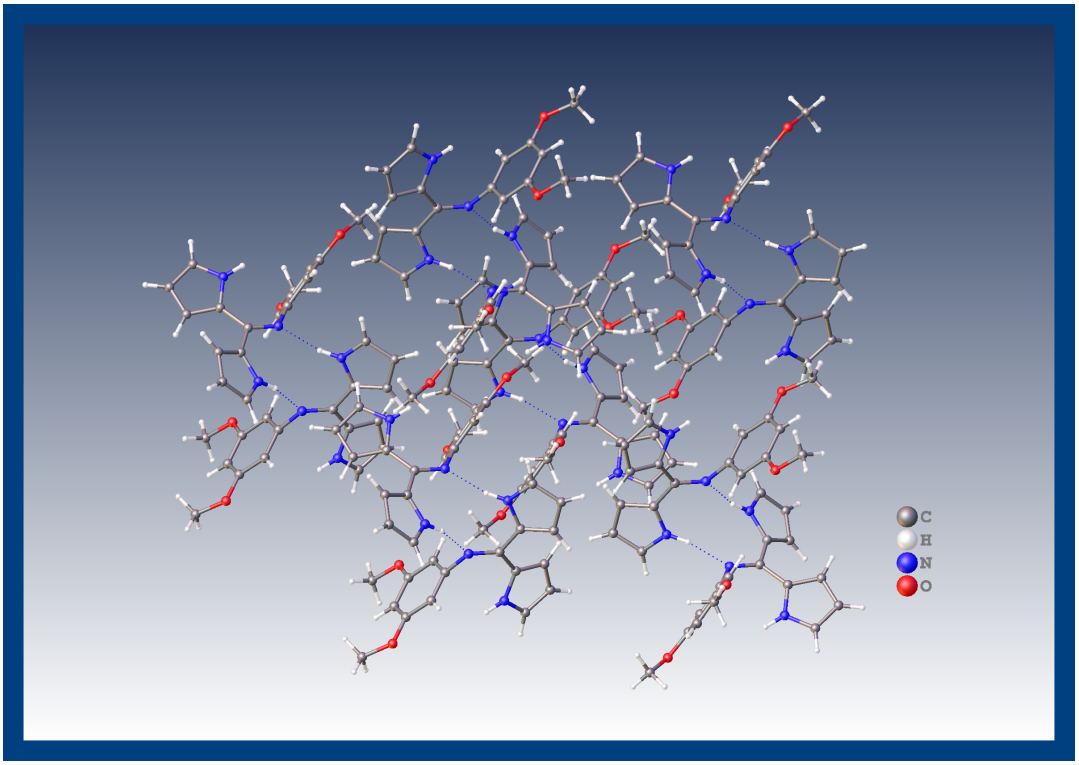


Figure S112. Molecular packing in crystals of compound **5** (zoom).

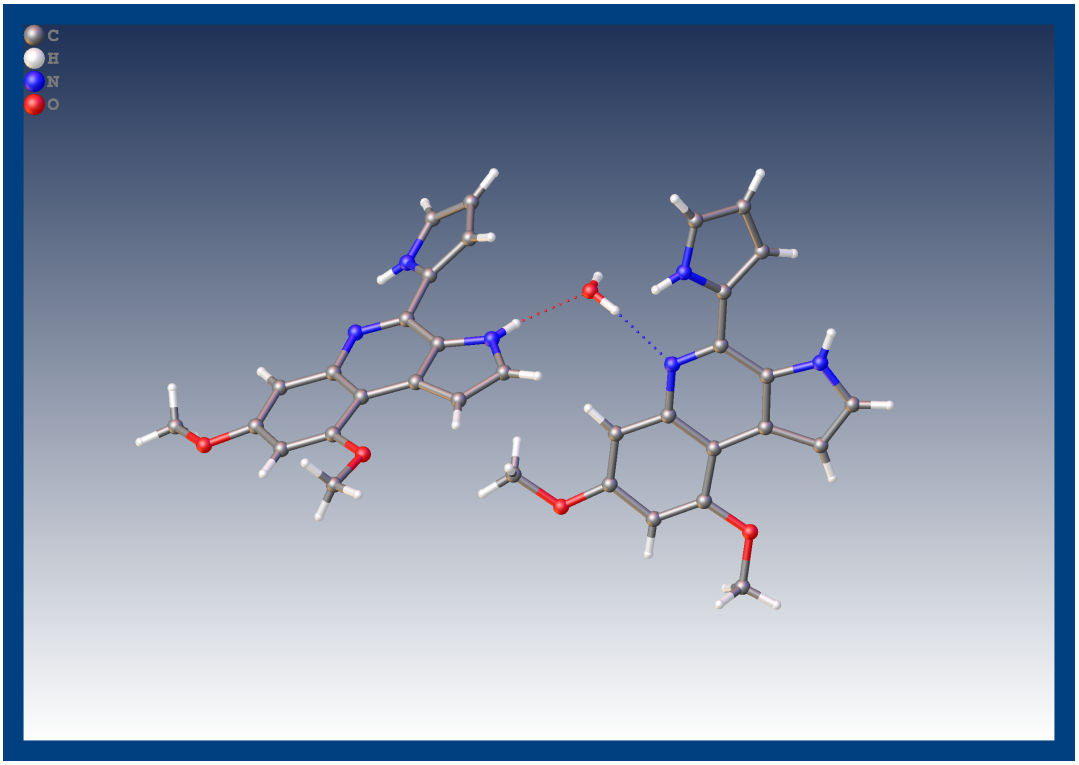


Figure S113. Molecular packing in crystals of compound **5**.

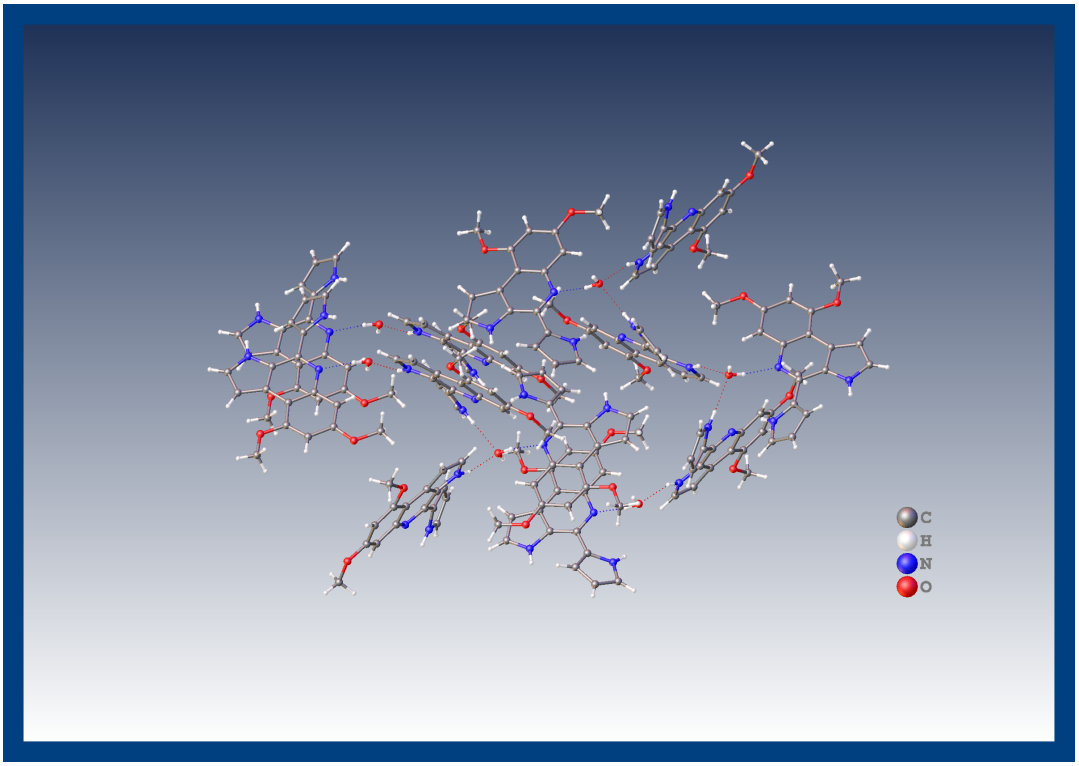


Figure S114. Molecular packing in crystals of compound **6** (zoom).

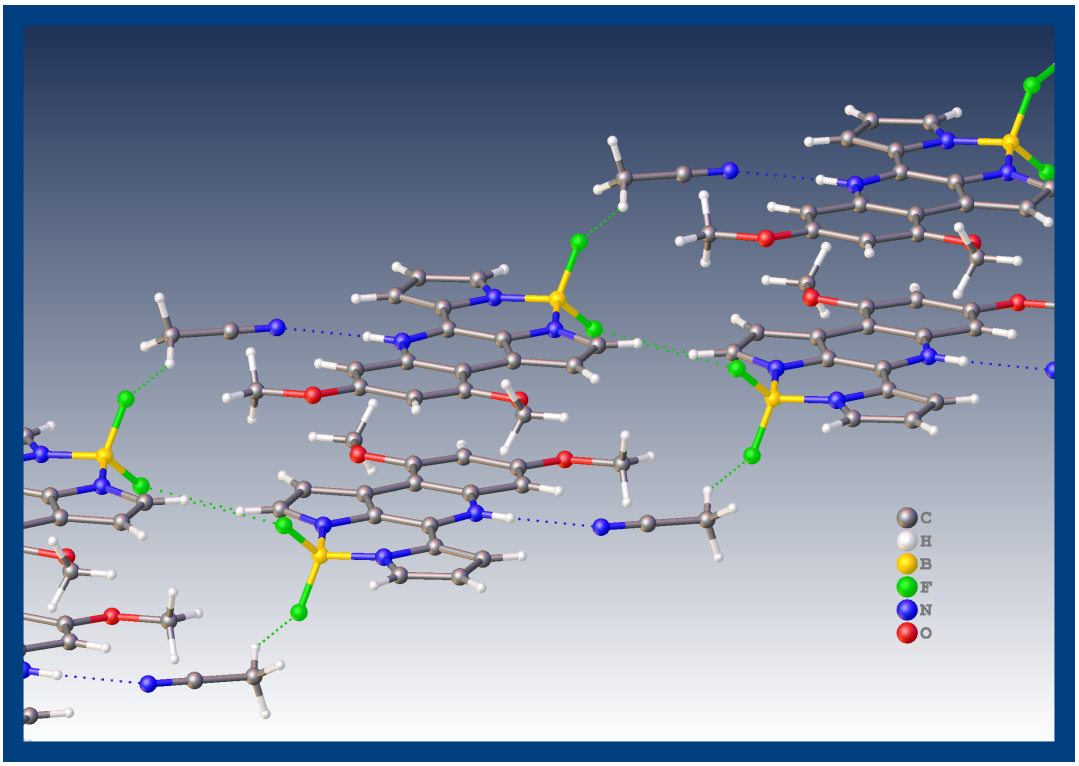


Figure S115. Molecular packing in crystals of compound **6**.