Supporting information

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1 GENERAL EXPERIMENTAL CONDITIONS

All solvents were dried and purified by known procedures and freshly distilled under nitrogen from appropriate drying agents prior to use. All manipulations and reactions involving air and/or moisture-sensitive organometallic compounds were performed under an atmosphere of dry nitrogen using standard Schlenk techniques.

The commercial reagents were purchased from Sigma MERK (Sigma-Aldrich), TCI (Tokio Chemical Industry CO), abcr Gmbh and STREM and were used without further purification.

Characterization

NMR spectra were recorded on a Bruker Avance DPX 300 MHz and 400 MHz (University of the Basque Country, UPV-EHU).

Electrospray ionization Mass Spectrometry (ESI-MS) experiments were carried out with an ESI Agilent Jet Stream ionization source, on a ultra high performance liquid chromatograph (UPLC) coupled to a high resolution quadrupole-time of flight mass spectrometer (QTOF)

Chromatography

Flash column chromatographies were carried out with silica gel 60 (0.040- 0.063 mm). Centrifugal thin-layer chromatographies were performed on a Chromatotron (model 7294T) by Harrison Research. Silica rotors were prepared by deposition of a slurry mixture of 75 g of silicagel 60 Å with fluorescence indicator (Sigma Aldrich ref. 28856), 30 g of calcium sulfate hemihydrate (Sigma Aldrich ref. 12090) and 187 mL of cold distilled water (8 °C) on a glass rotor. After air-drying for 48 h, the rotor with the sorbent bound was scrapped to polish its surface and remove unwanted sorbent at the edge and center of the rotor.

Absorption and emission

UV/Vis and Fluorescence Spectroscopy. UV-Vis spectra were acquired on a Shimatzu UV-2600 Spectrophotometer, utilizing 10 mm cell-path cuvettes (110 QS). Emission spectra in solid state and in solution were acquired on an Agilent Cary Eclipse Fluorescence

Spectrophotometer and Edinburgh FLS-1000. Excitation and emission monochromator bandwidth was fixed at 5 nm.

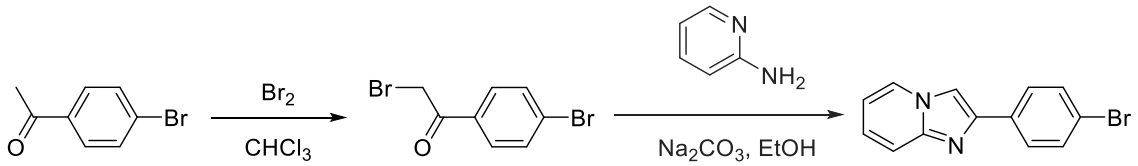
Computational details?

2 CHAPTER 2

2.1 SYNTHESIS AND CHARACTERIZATION

2.1.1 Compound 1 and 2, 2-bromo-1-(4-bromophenyl)ethan-1-one and 2-(4-bromophenyl)imidazo[1,2-a]pyridine

Compound **1** and **2** were synthesized according to the procedure described by Gómez-Cadenas et al.[1]



1 **2**

Bromine (0.94 mL, 18.17 mmol) was added to a solution of 4'-bromoacetophenone (3.62 g, 18.17 mmol) in 100 mL $CHCl_3$, stirred at room temperature for 1 h. The solvent was evaporated *in vacuo* to give a crude oil. The mixture was used without purification in the next step. A mixture of 2-aminopyridine (2.05 g, 21.8 mmol), $NaHCO_3$ (2.30 g, 27.25 mmol) and compound **1** in EtOH was refluxed at 80°C for 16 h. The reaction mixture was cooled to room temperature and filtered to obtain a white solid, which was washed with H_2O and dried *in vacuo*. The product was isolated as a white solid. Yield: 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ δ 8.08 (dt, J = 6.7, 1.3 Hz, 1H), 7.82 (s, 1H), 7.81 (d, J = 6.3 Hz, 2H), 7.61 (d, J = 9.2 Hz, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.16 (ddd, J = 9.1, 6.7, 1.3 Hz, 1H), 6.77 (td, J = 6.8, 1.2 Hz, 1H).

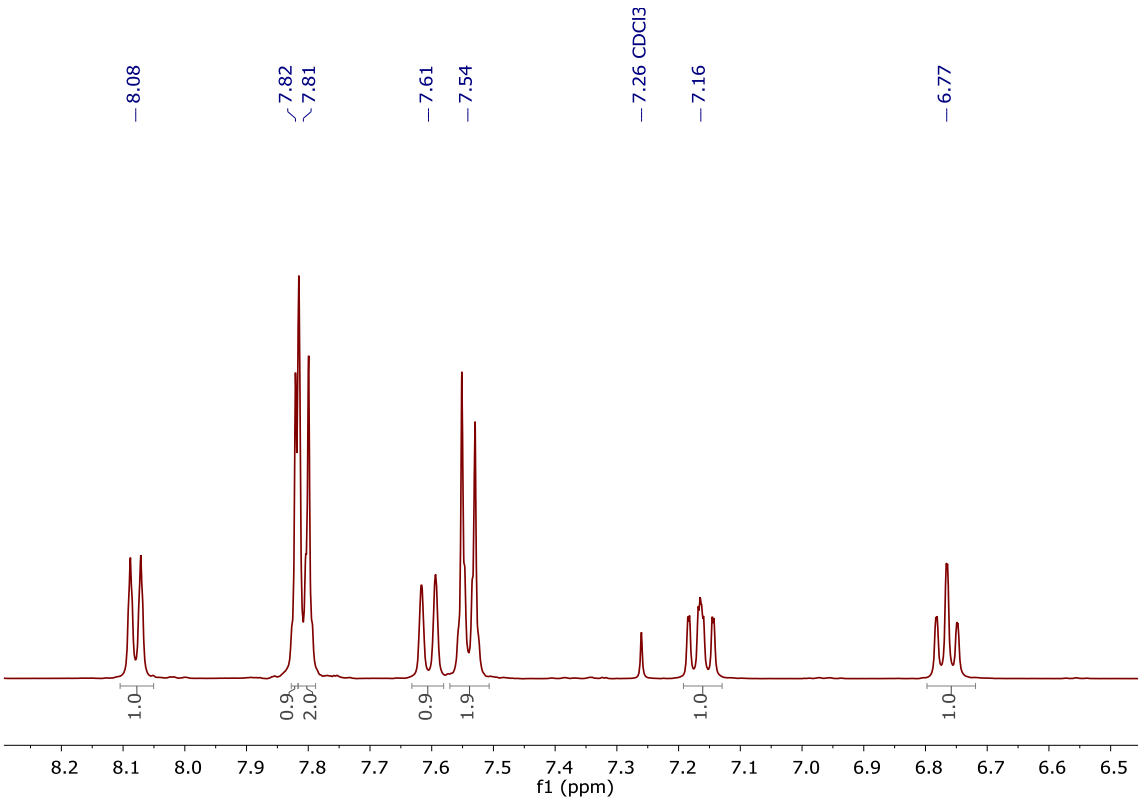
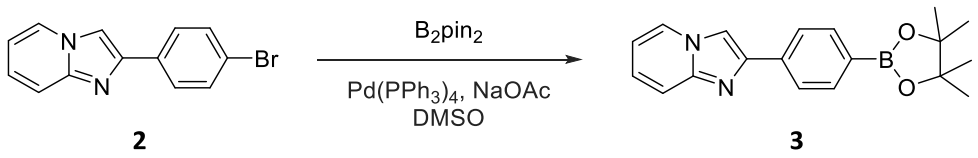


Figure S1. *^{1}H NMR spectrum of compound **2** ($CDCl_3$, 300 MHz).*

2.1.2 Compound 3, 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)imidazo[1,2-a]pyridine

Compound **3** was synthesized by following a modified procedure described by Claffey et al. in a patent.[2]



2 **3**

A mixture of $Pd(PPh_3)_4$ (500 mg, 0.58 mmol), NaOAc (4.76 g, 58 mmol), compound **2** (3.17 g, 11.6 mmol) and bis(pinacolato)diboron (4.42 g, 17.4 mmol) was introduced in a Schlenk tube and dissolved in DMSO (100 mL), under N_2. The mixture was stirred at 80°C for 16 h. The reaction was cooled to room temperature and water, 400 mL, was added to mixture. The precipitate formed was filtered and washed with more water. The precipitate was dissolved in MeOH and filtered again. The filtrate is concentrated *in vacuo* to obtain a garnet solid. The product was used in the next step without further purification. Yield 90%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (dt, J = 6.7, 1.2 Hz, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.91 (s, 1H), 7.87 (d, J = 8.2 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.16 (ddd, J = 9.1, 6.7, 1.3 Hz, 1H), 6.77 (td, J = 6.8, 1.2 Hz, 1H), 1.35 (s, 12H).

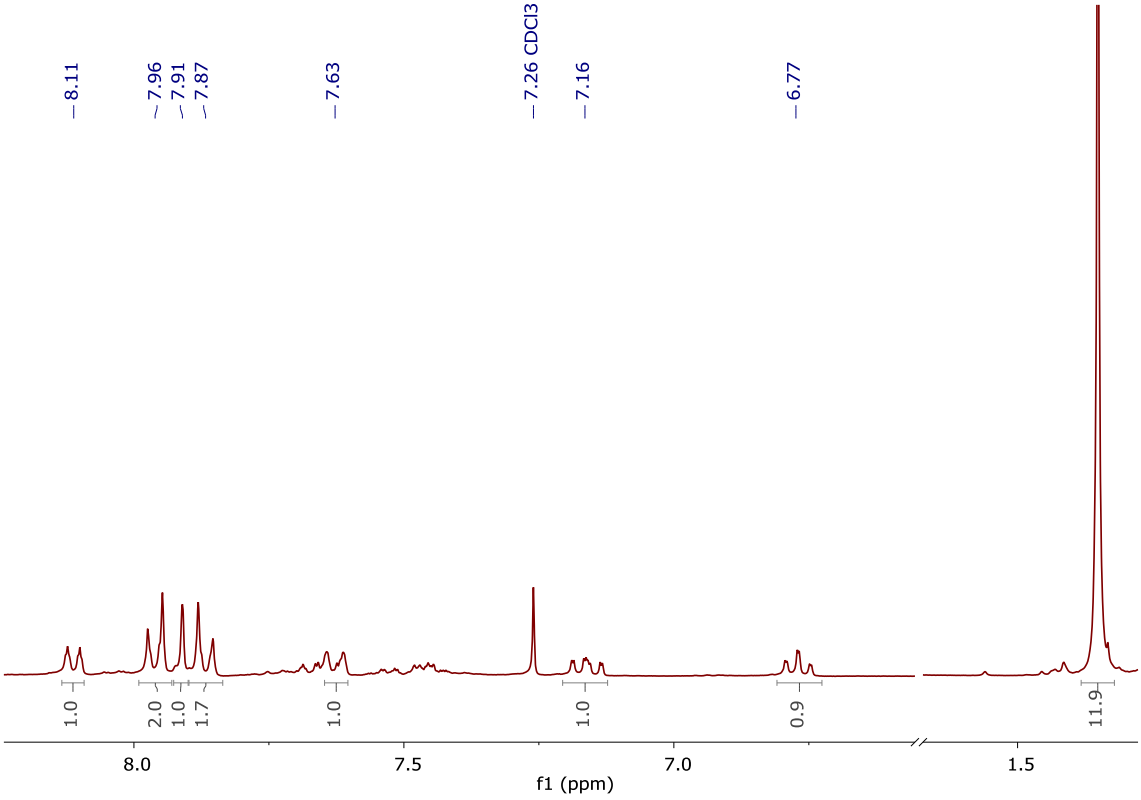
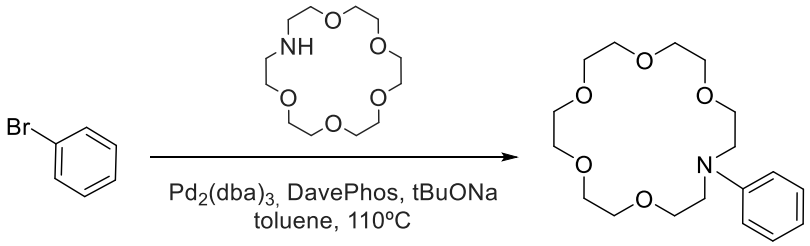


Figure S2. *^{1}H NMR spectrum of compound **3** ($CDCl_3$, 300 MHz).*

2.1.3 Compound 4, 16-phenyl-1,4,7,10,13-pentaoxa-16-azacyclooctadecane

Compound **4** was synthesized according to the procedure described by Aparicio.REF



3 **4**

A mixture of $Pd_2(dba)_3$ (233 mg, 0.25 mmol), DavePhos (300 mg, 0.76 mmol), ^{t}BuONa (1.84 g, 19.11 mmol) and 1-aza-18-crown-6 (3.35 g, 12.74 mmol) was introduced in a Schlenk tube and dissolved in distilled toluene under N_2. To this mixture, bromobenzene

(1.33 ml, 12.74 mmol) was added to the mixture. The Schlenk was sealed and kept under N_2 atmosphere in a preheated oil bath at 110°C for 16 h. The mixture, still hot, was filtered through a celite pad, and concentrated *in vacuo*. The crude brown oil was used in the next step without further purification. Quantitative yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 (d, J = 7.2 Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 6.73 – 6.64 (m, 3H), 3.76 – 3.59 (m, 24H).

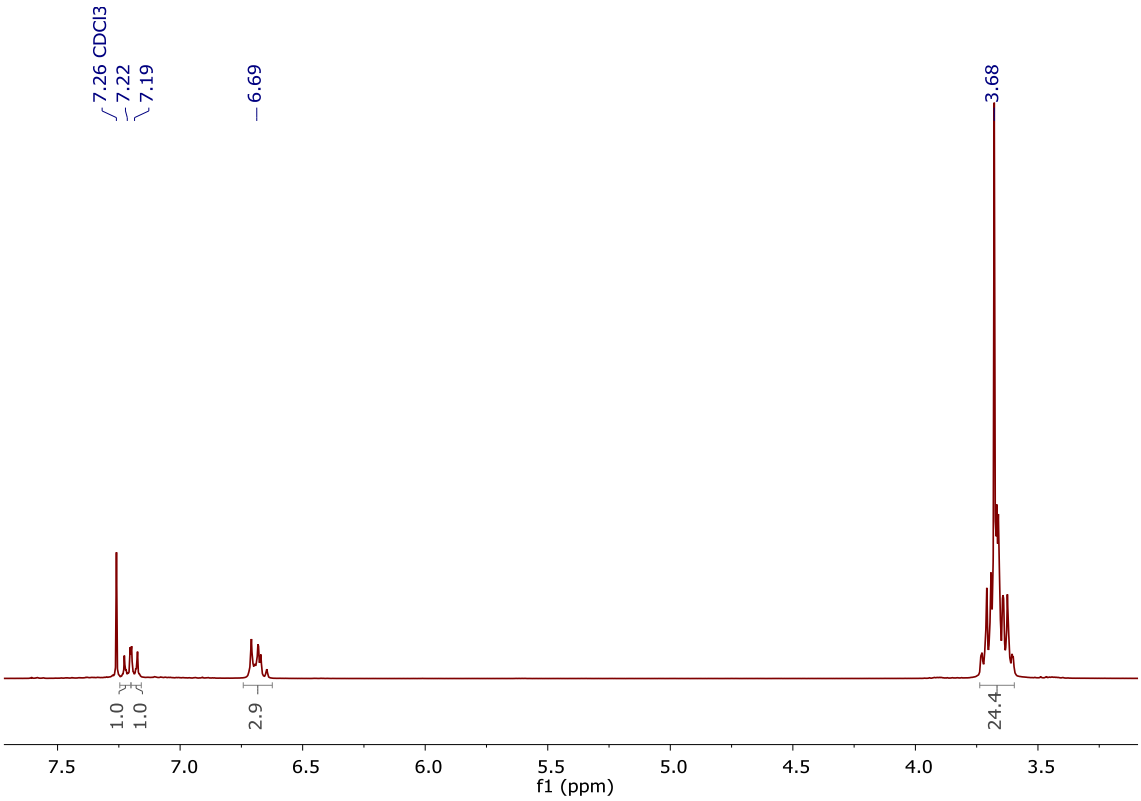
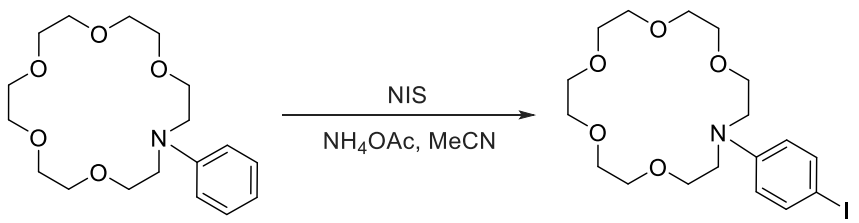


Figure S3. *^{1}H NMR spectrum of compound **4** ($CDCl_3$, 300 MHz).*

2.1.4 Compound 5, 16-(4-iodophenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane

Compound **5** was synthesized according to the procedure described by Aparicio.REF



4 **5**

Compound **4** (4.32 g, 12.74 mmol) was added to a round bottom flask with ammonium acetate (98.21 mg, 1.27 mmol) and dissolved in MeCN. N-Iodosuccinimide (3.01 g, 13.38 mmol) was added to the mixture. The mixture was stirred at room temperature for 5 minutes. The solvent was removed under vacuum. The crude was dissolved in EtOAc and washed three times with aq. K_2CO_3 and brine. The organic phase was dried over $MgSO_4$ and evaporated to yield a brown oil. Yield: 92%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, J = 9.1 Hz, 2H), 6.49 (d, J = 9.1 Hz, 2H), 3.74 – 3.65 (m, 24H).

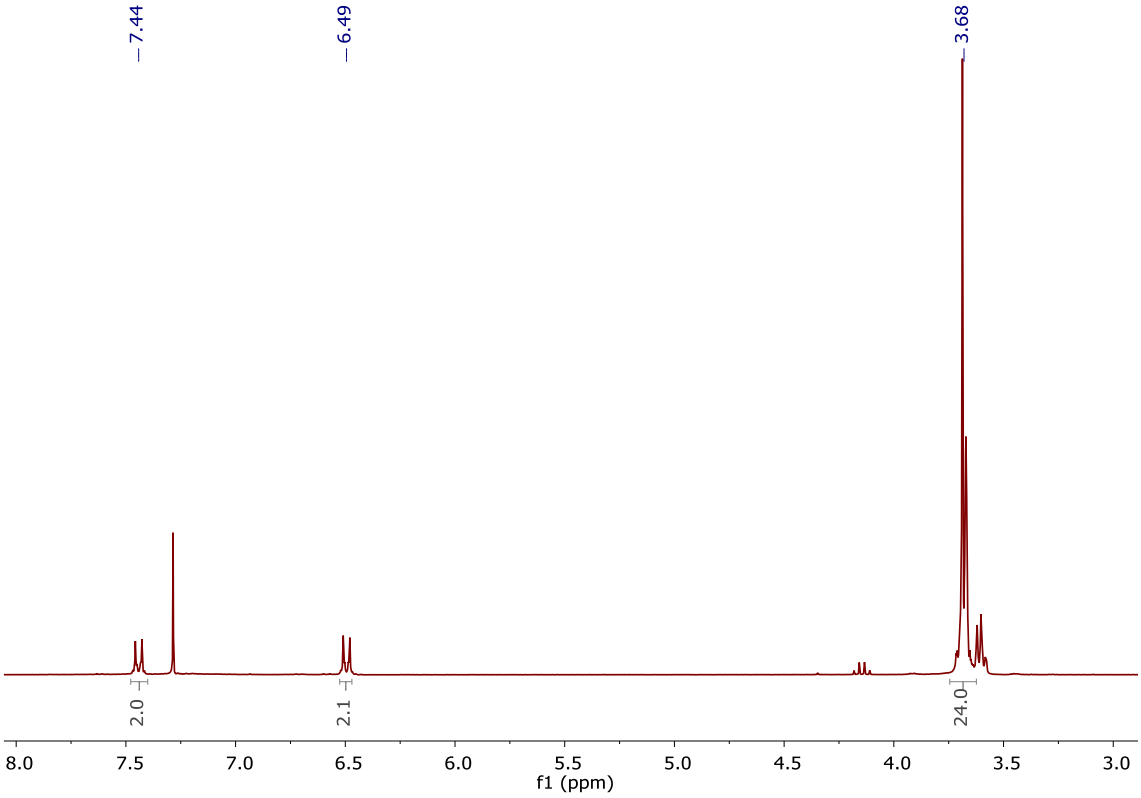
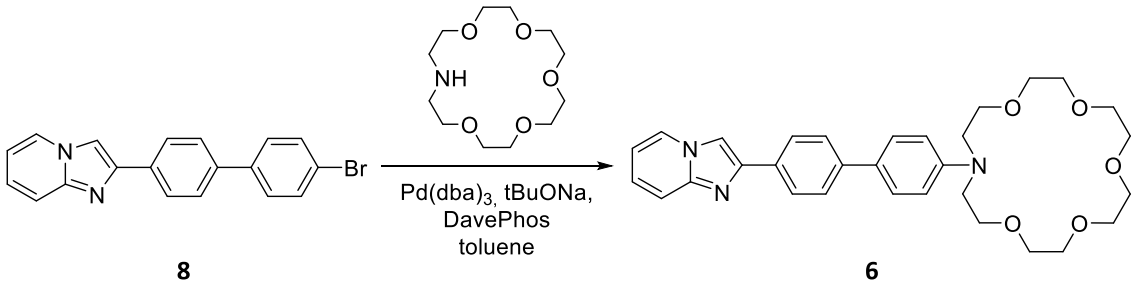


Figure S4. *^{1}H NMR spectrum of compound **5** ($CDCl_3$, 300 MHz).*

2.1.5 Compound 6, 16-(4'-(imidazo[1,2-a]pyridin-2-yl)-[1,1'-biphenyl]-4-yl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



8 **6**

A mixture of $Pd_2(dba)_3$ (160 mg, 0.17 mmol), DavePhos (202 mg, 0.52 mmol), ^tBuONa (619 mg, 6.4 mmol), compound **8** (1.5 g, 4.3 mmol) and 1-aza-18-crown-6 (1.13g, 4.3 mmol) was introduced in a Schlenk tube and dissolved in 50 mL of anhydrous toluene, under N_2. The tube was sealed and kept in a preheated oil bath at and stirred at 110°C for 16 h. After this time, the reaction mixture was cooled to room temperature, filtered through a celite pad and the filtrate was concentrated *in vacuo*. The residue is triturated with diethyl ether and the title compound was obtained as a brown solid. Yield 62%.

Exact mass: ESI-MS [$C_{31}H_{37}N_3O_5$]: calculated: m/z= 531.2733, found: m/z= 531.2738.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (dt, J = 6.8, 1.2 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 0.7 Hz, 1H), 7.66–7.60 (m, 3H), 7.53 (d, J = 8.8 Hz, 2H), 7.16 (ddd, J = 9.1, 6.8, 1.3 Hz, 1H), 6.80–6.72 (m, 3H), 3.79–3.56 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.36 (1C, C_{quat}), 145.84 (1C, C_{quat}), 145.73 (1C, C_{quat}), 140.61 (1C, C_{quat}), 131.35 (1C, C_{quat}), 128.13 (1C, C_{quat}), 127.73 (2C, CH, C_6H_4), 126.36 (2C, CH, C_6H_4), 126.27 (2C, CH, C_6H_4), 125.52(1C, CH), 124.50(1C, CH), 117.50(1C, CH), 112.33(1C, CH), 111.95 (2C, CH, C_6H_4), 107.90 (1C, CH), 70.76 (8C, CH_2, crown), 68.81 (2C, CH_2, crown), 51.39 (2C, CH_2, crown).

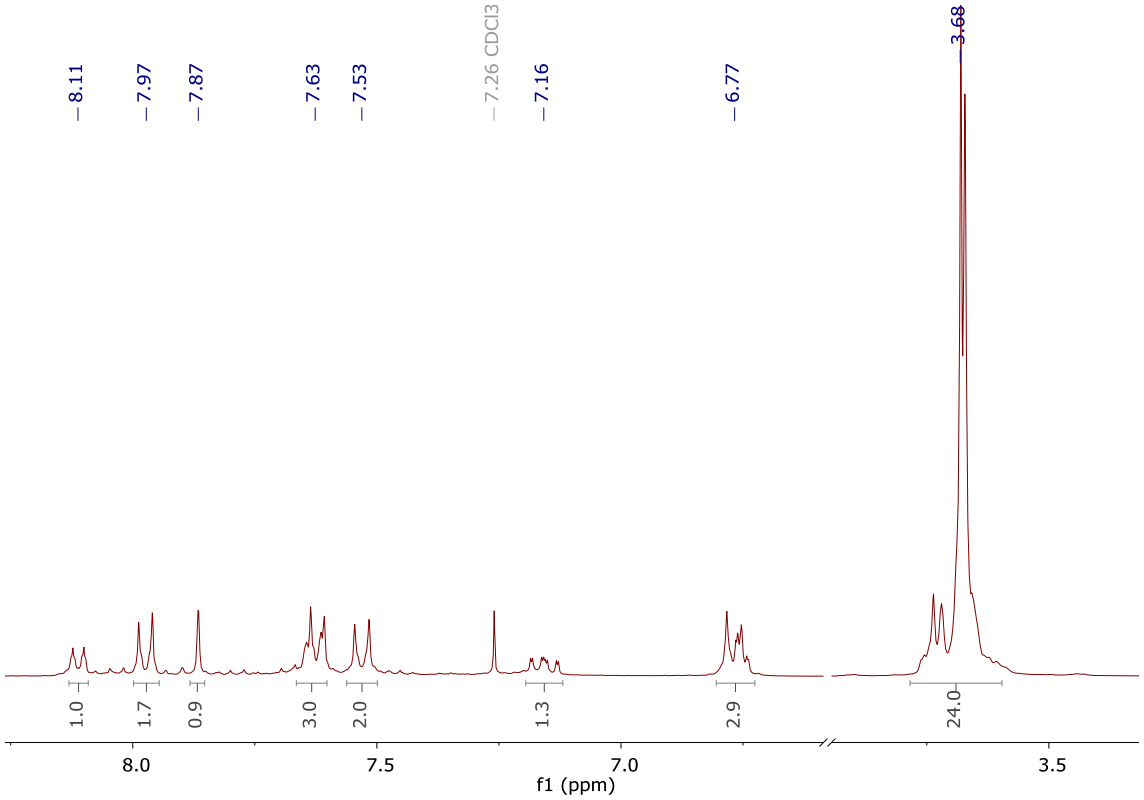


Figure S5. *^{1}H NMR spectrum of compound **6** ($CDCl_3$, 300 MHz).*

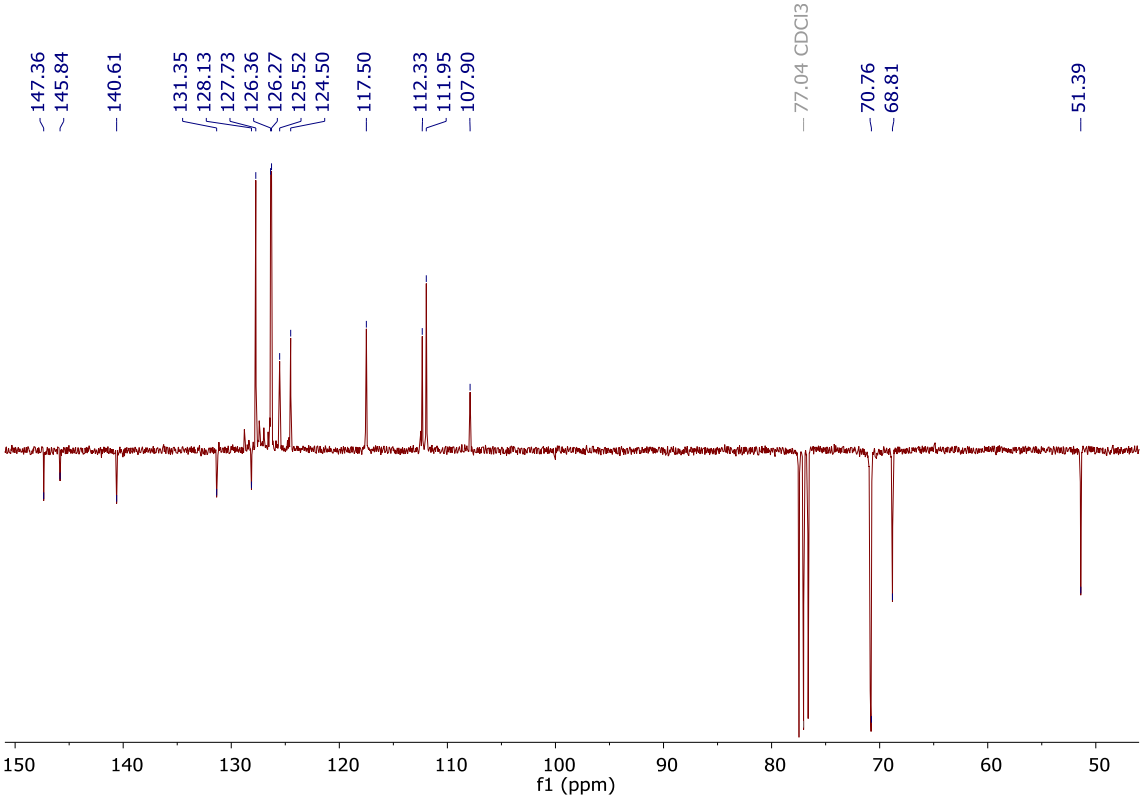


Figure S6. *^{13}C APT NMR spectrum of compound **6** ($CDCl_3$, 300 MHz).*

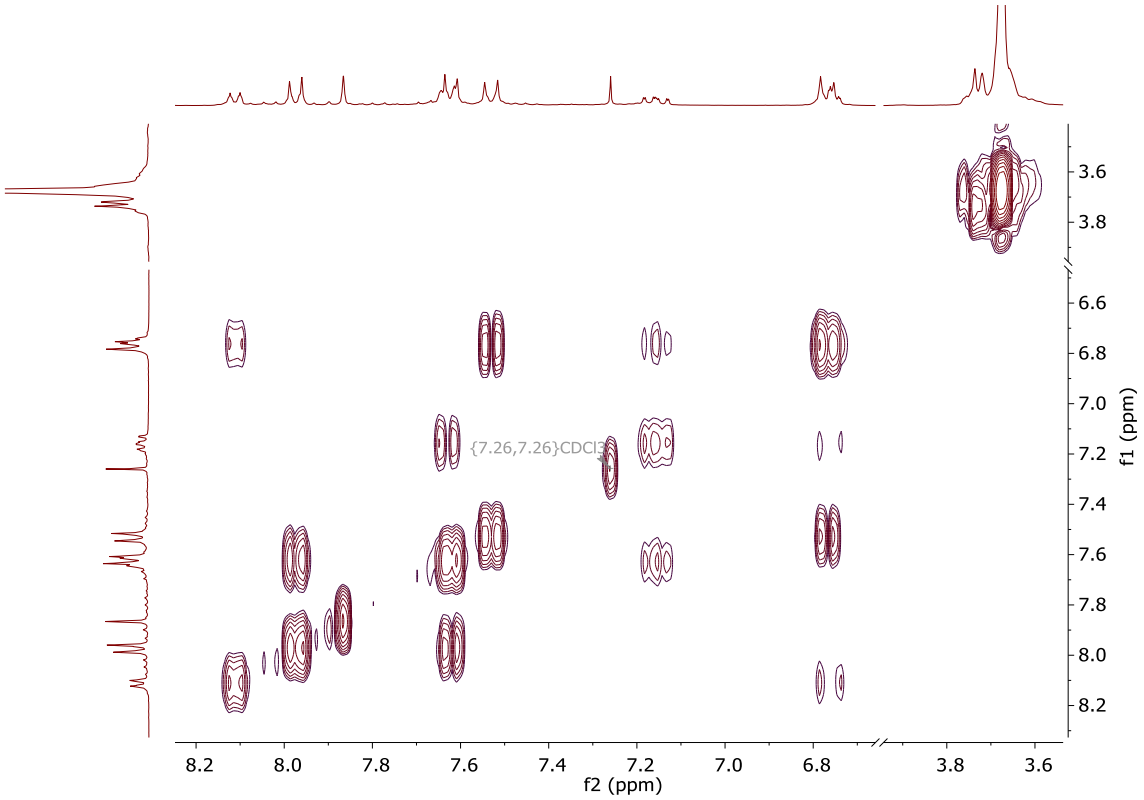


Figure S7. *COSY NMR spectrum of compound* ***6*** *($CDCl_3$, 300 MHz).*

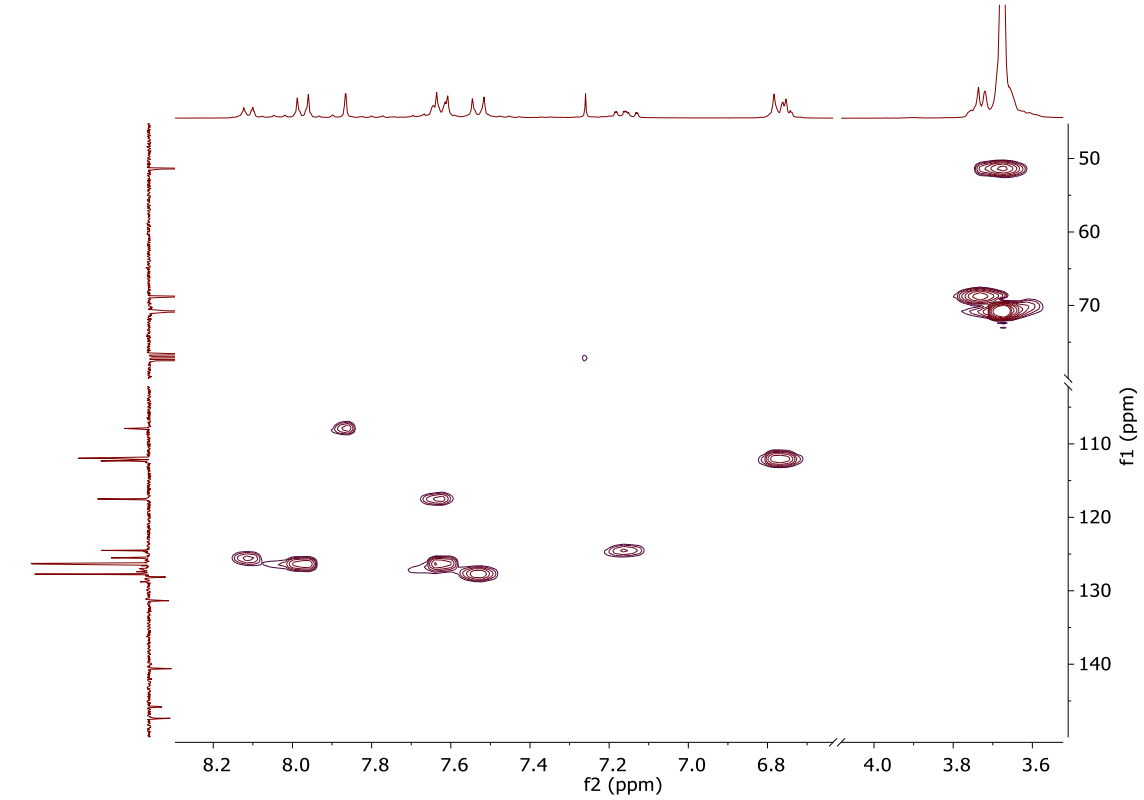


Figure S8. *HSQC NMR spectrum of compound* ***6*** *($CDCl_3$, 300 MHz).*

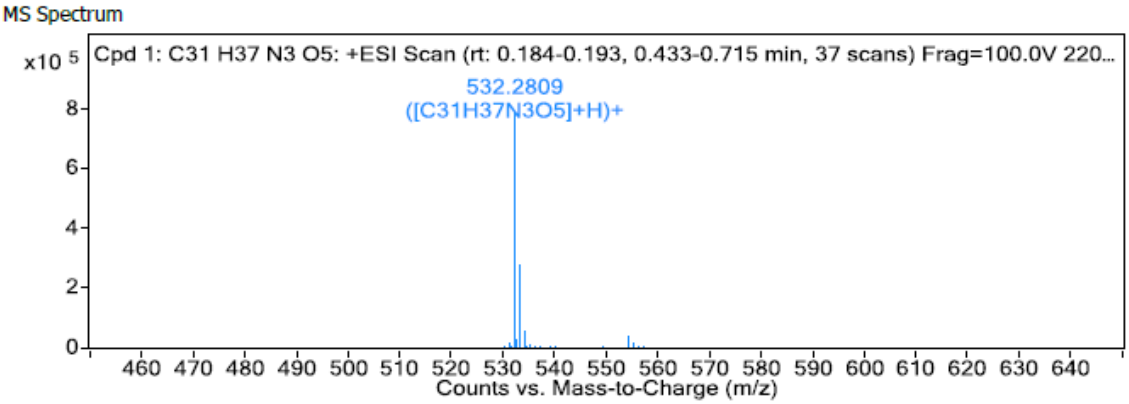
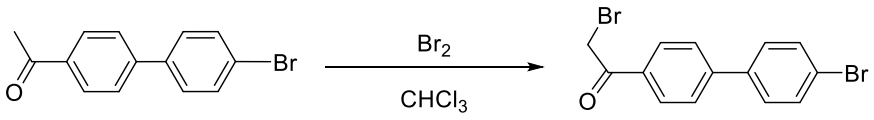


Figure S9. *Mass spectrum of compound* ***6****.*

2.1.6 Compound 7, 2-bromo-1-(4'-bromo-[1,1'-biphenyl]-4-yl)ethan-1-one

Compound **7** was synthesized by following a slightly modified procedure described by Kourounakis et al.[3]



7

Bromine (0.94 mL, 18.17 mmol) was added to a solution of 4-(4'-bromophenyl)acetophenone (5.00 g, 18.17 mmol) in CH_3Cl (100 mL) and the mixture was stirred at room temperature for 40 min. The dissolution was washed with water, and the organic phase was dried over $MgSO_4$ and evaporated *in vacuo* to give a white solid. Yield 98%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 4.47 (s, 2H).

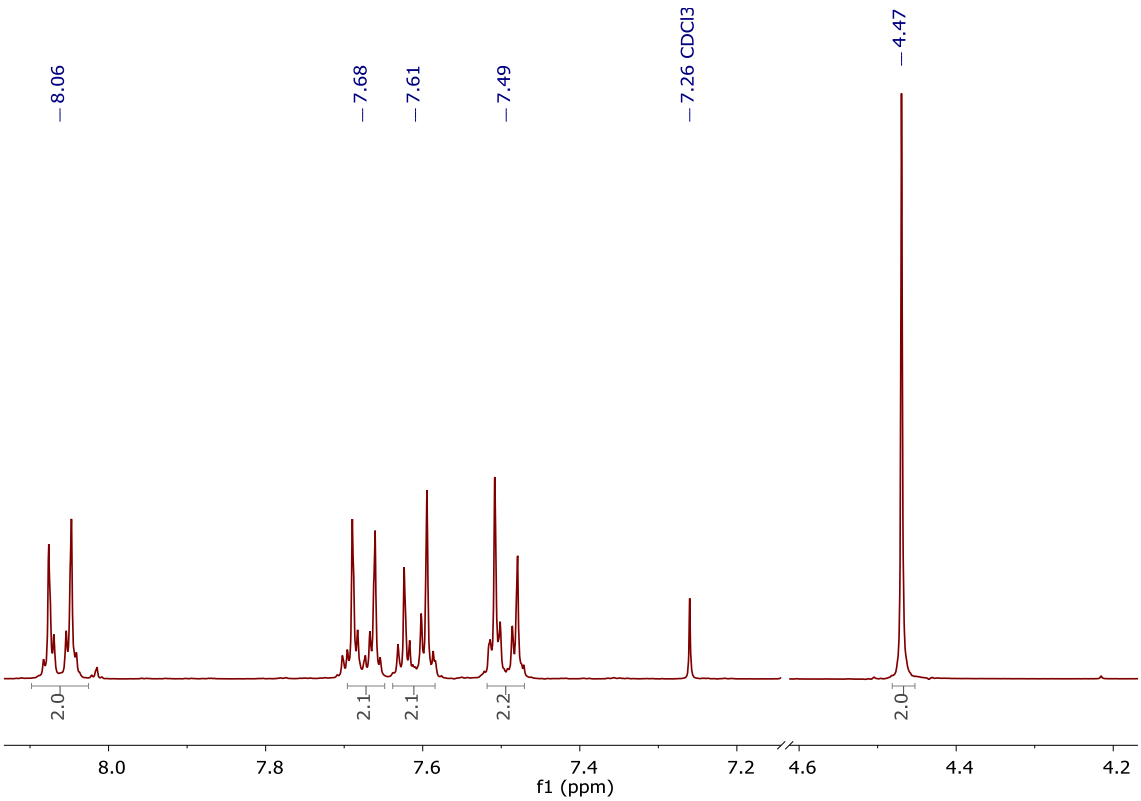
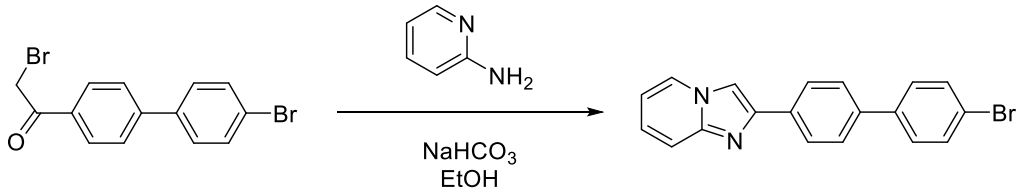


Figure S10. *^{1}H NMR spectrum of compound **7** ($CDCl_3$, 300 MHz).*

2.1.7 Compound 8, 2-(4'-bromo-[1,1'-biphenyl]-4-yl)imidazo[1,2-a]pyridine



7 **8**

A mixture of compound **7** (12.2 g, 34.5 mmol), 2-aminopyridine (3.57 g, 37.9 mmol) and $NaHCO_3$ (4.34 g, 51.7 mmol) in EtOH (200 mL) was refluxed at 85°C for 72 h. The reaction mixture was cooled to room temperature and filtered to obtain a white solid, which was washed with H_2O and dried *in vacuo*. The product was isolated as a white solid. Yield: 80%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (dt, J = 6.8, 1.2 Hz, 1H), 8.03 (d, J = 8.6 Hz, 2H), 7.91 (d, J = 0.7 Hz, 1H), 7.67 – 7.62 (m, 3H), 7.58 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.19 (ddd, J = 9.1, 6.8, 1.3 Hz, 1H), 6.80 (td, J = 6.8, 1.2 Hz, 1H).

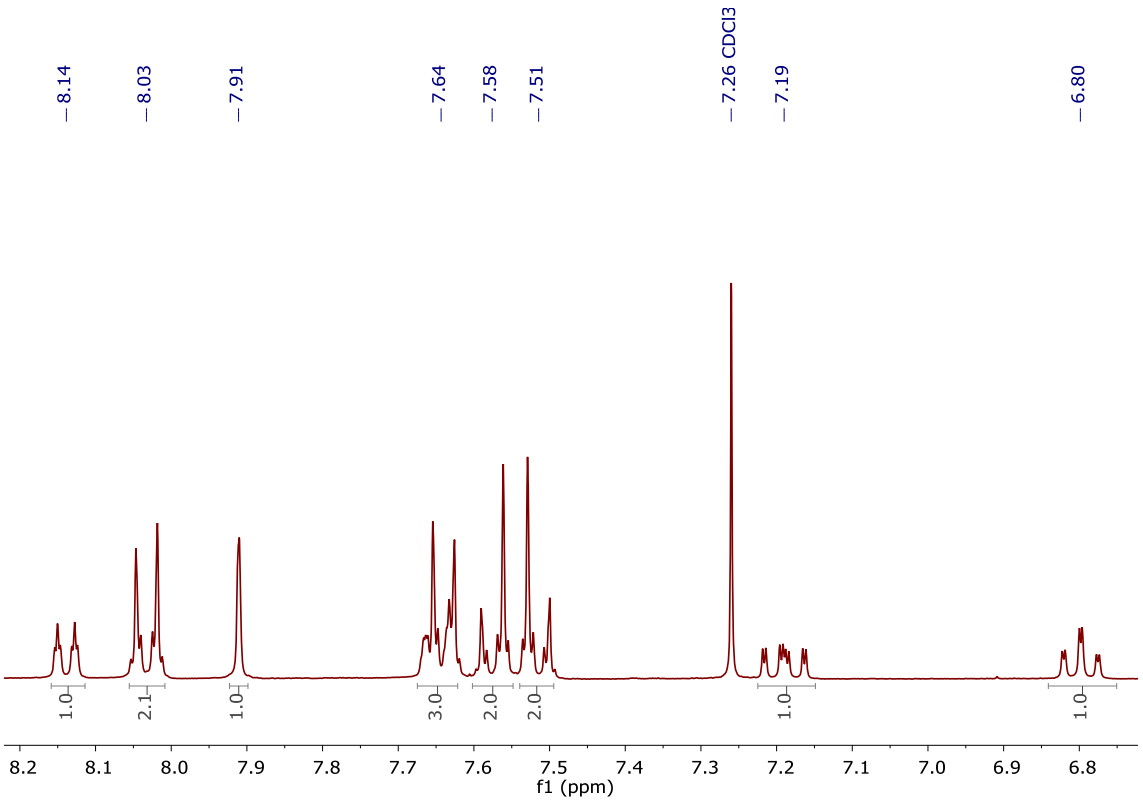
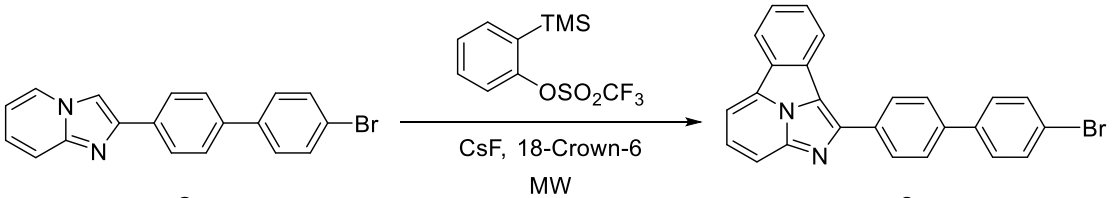


Figure S11. *^{1}H NMR spectrum of compound **8** ($CDCl_3$, 300 MHz).*

2.1.8 Compound 9, 1-(4'-bromo-[1,1'-biphenyl]-4-yl)benzo[a]imidazo[5,1,2-cd]indolizine



8 **9**

A microwave vial equipped with a magnetic stirrer, was charged with compound **8** (500 mg, 1.43 mmol), CsF (217 mg, 1.43 mmol), 18-crown-6-ether (378 mg, 1.43 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (366 µL, 1.43 mmol). The mixture was irradiated with MW during 30 min at 220°C, 100 psi and 200 W. The reaction crude was purified by flash column chromatography on silica gel (1:4 EtOAc/Hex), obtaining a brown solid. Yield 22%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 – 8.46 (m, 3H), 8.43 (dt, J = 8.0, 1.0 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 7.2 Hz, 1H), 7.98 (dd, J = 8.3, 7.3 Hz, 0H), 7.87 – 7.81 (m, 3H), 7.68 – 7.62 (m, 1H), 7.61 (m, 4H).

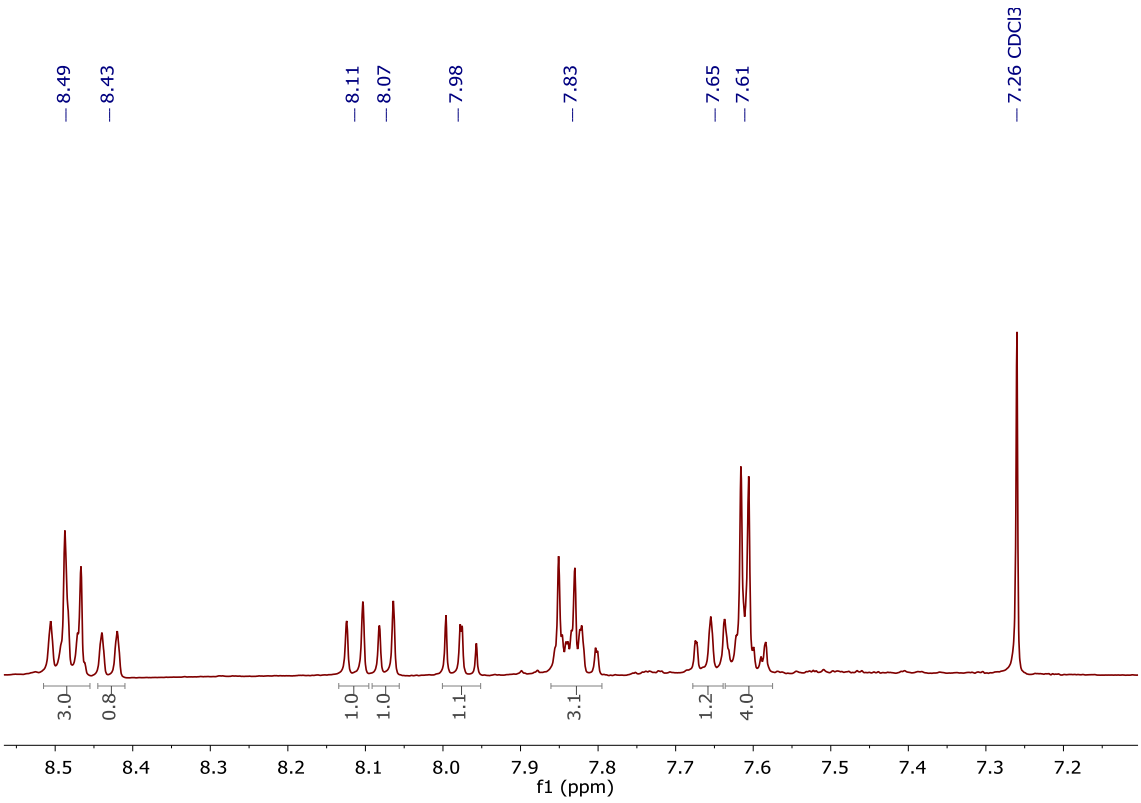
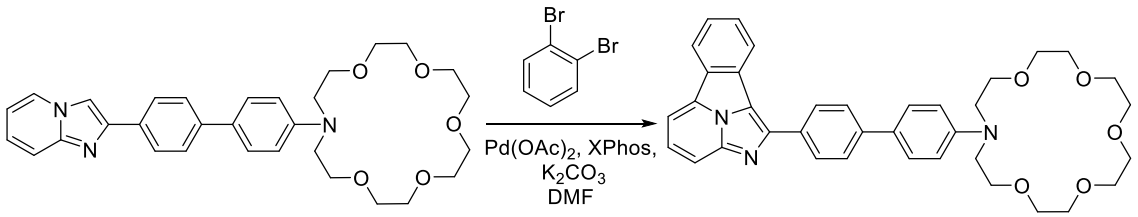


Figure S12. *^{1}H NMR spectrum of compound **9** ($CDCl_3$, 300 MHz).*

2.1.9 Compound G3a, 16-(4'-(benzo[a]imidazo[5,1,2-cd]indolizin-1-yl)-[1,1'-biphenyl]-4-yl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



6 **G3a**

A mixture of $Pd(OAc)_2$ (9.86 mg, 0.044 mmol, 4 mol%), Xphos (36.63 mg, 0.077 mmol, 7 mol%), K_2CO_3 (455.1 mg, 3.29 mmol, 3.0 equiv.) and compound **6** (1.1 mmol, 1.0 equiv.) was introduced in a Schlenk tube and dissolved in 30 mL of DMF, under N_2. To this solution 1,2-dibrobenzene (1.32 mmol, 1.2 equiv.) was added. The tube was sealed and kept in a preheated oil bath and stirred overnight at 160°C. After this time, the reaction mixture was cooled to room temperature, filtered through a celite pad and the filtrate was concentrated *in vacuo*. The residue was purified initially by column chromatography (eluent: hexane to hexane:EtOAc:MeOH (1:4:0.1, v/v/v) and then by centrifugal thin-layer chromatography on silica (eluent: from CH_2Cl_2 to 5% MeOH in CH_2Cl_2). The title compound was obtained as a brown solid. Yield 5%.

Exact mass: ESI-MS [$C_{37}H_{39}N_3O_5$]: calculated: m/z= 605.2890, found: m/z= 605.2887.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (dt, J = 8.2, 1.0 Hz, 1H), 8.47–8.37 (m, 3H), 8.07 (dd, J = 8.3, 0.7 Hz, 1H), 8.03 (d, J = 6.8 Hz, 1H), 7.94 (dd, J = 8.3, 7.3 Hz, 1H), 7.85–7.77 (m, 3H), 7.66–7.59 (m, 3H), 6.82 (d, J = 8.9 Hz, 2H), 3.80–3.65 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.60 (1C, C_{quat}), 146.64 (1C, C_{quat}), 141.71 (1C, C_{quat}), 139.72 (1C, C_{quat}), 132.02 (1C, C_{quat}), 131.26 (1C, C_{quat}), 130.30 (1C, C_{quat}), 129.12 (1C, CH), 129.02 (1C, C_{quat}), 128.72 (2C, CH, C_6H_4), 127.89 (2C, CH, C_6H_4), 126.53 (2C, CH, C_6H_4), 126.39 (1C, CH), 124.71 (1C, CH), 123.15 (1C, CH), 120.96 (1C, CH), 112.96 (1C, CH), 112.00 (2C, CH, C_6H_4), 108.59 (1C, CH), 99.99 (1C, C_{quat}), 70.89 (8C, CH_2, crown), 68.77 (2C, CH_2, crown), 51.39 (2C, CH_2, crown).

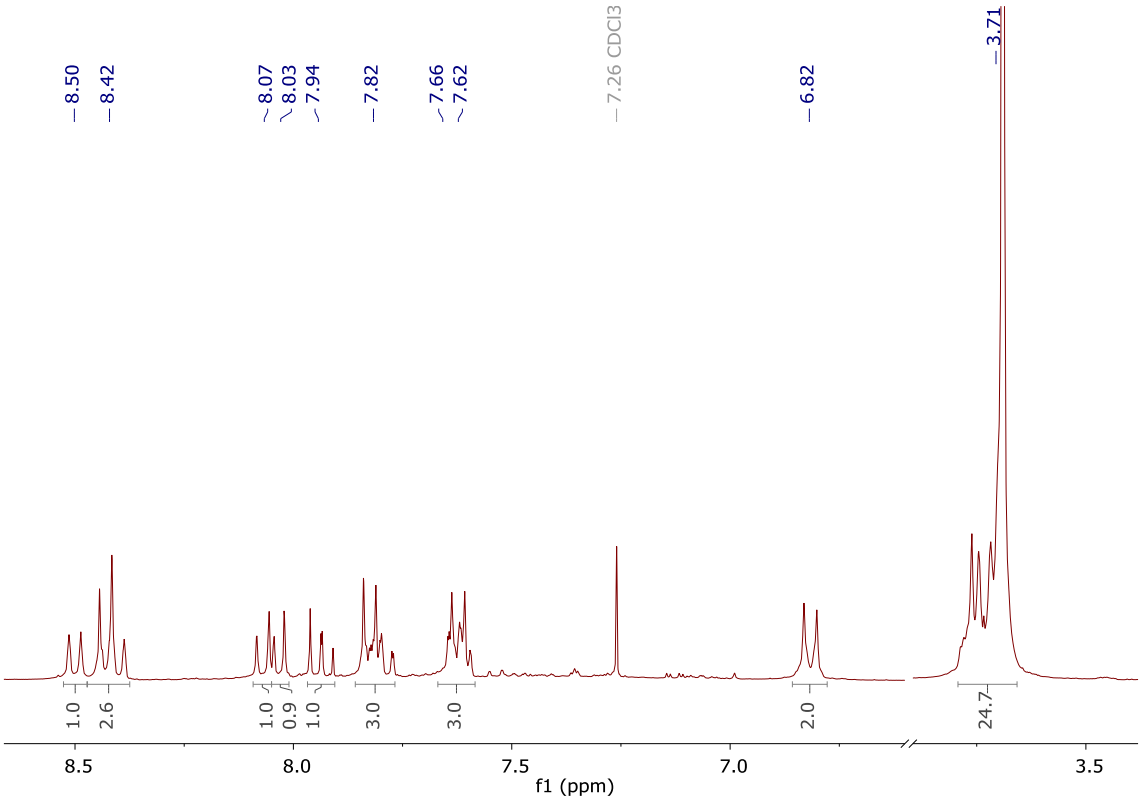


Figure S13. *^{1}H NMR spectrum of compound **G3a** ($CDCl_3$, 300 MHz).*

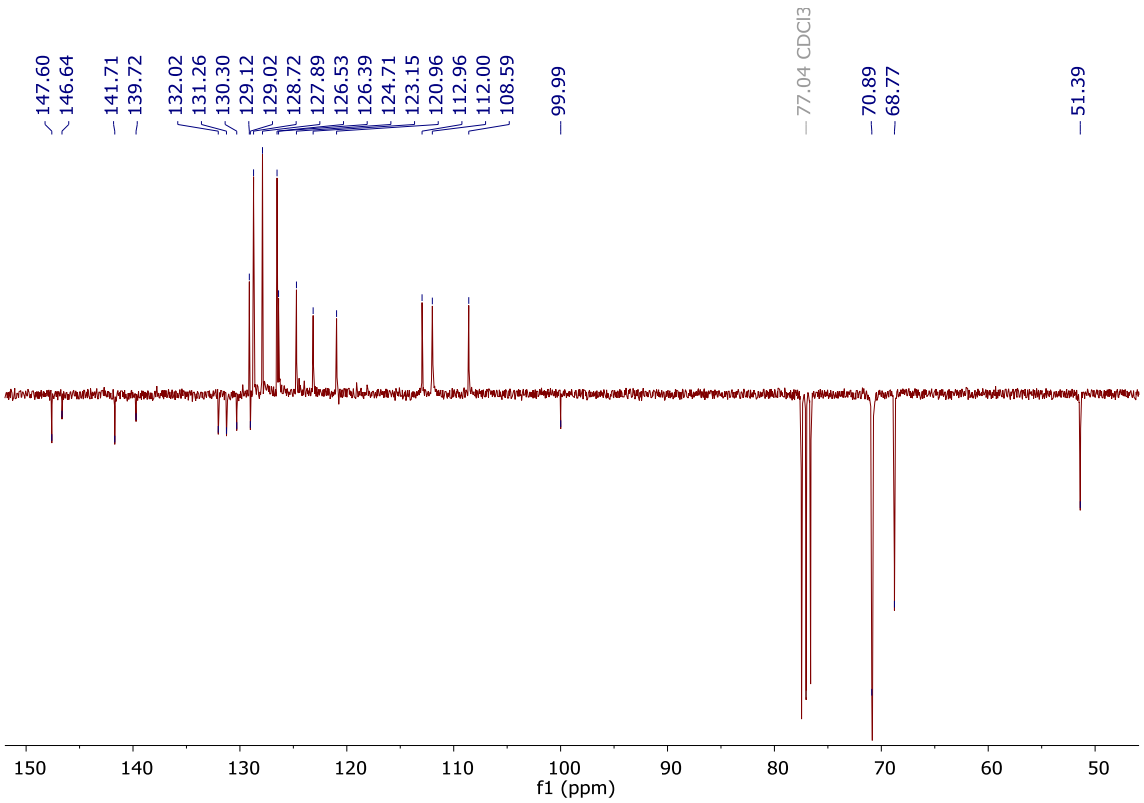


Figure S14. *^{13}C APT NMR spectrum of compound **G3a** ($CDCl_3$, 75 MHz).*

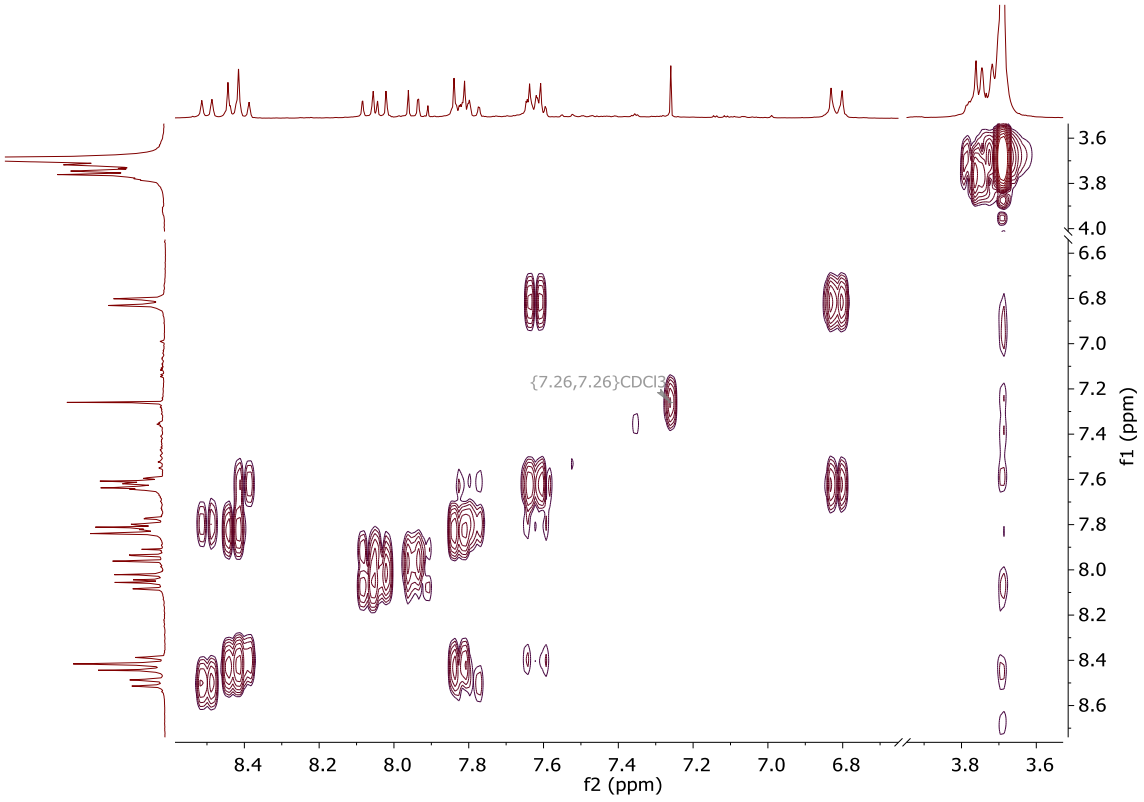


Figure S15. *COSY NMR spectrum of compound **G3a** ($CDCl_3$, 300 MHz).*

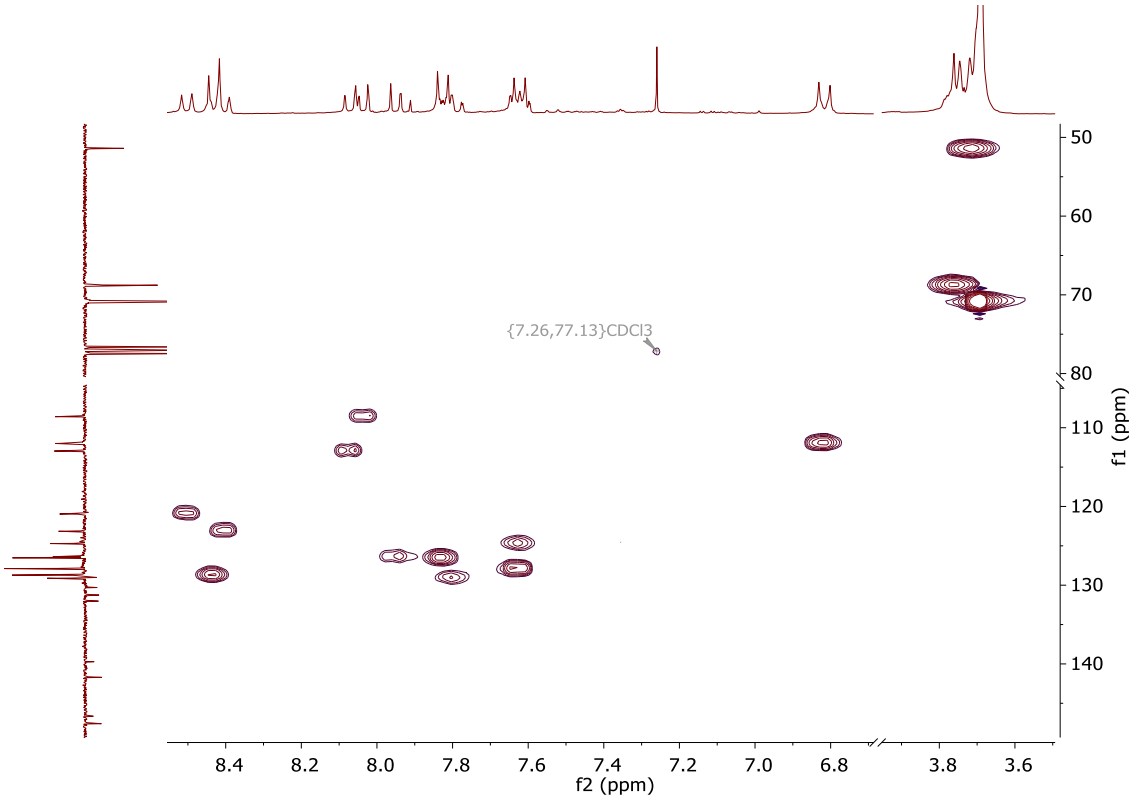


Figure S16. *HSQC NMR spectrum of compound* ***G3a*** *(CDCl₃, 300 MHz).*

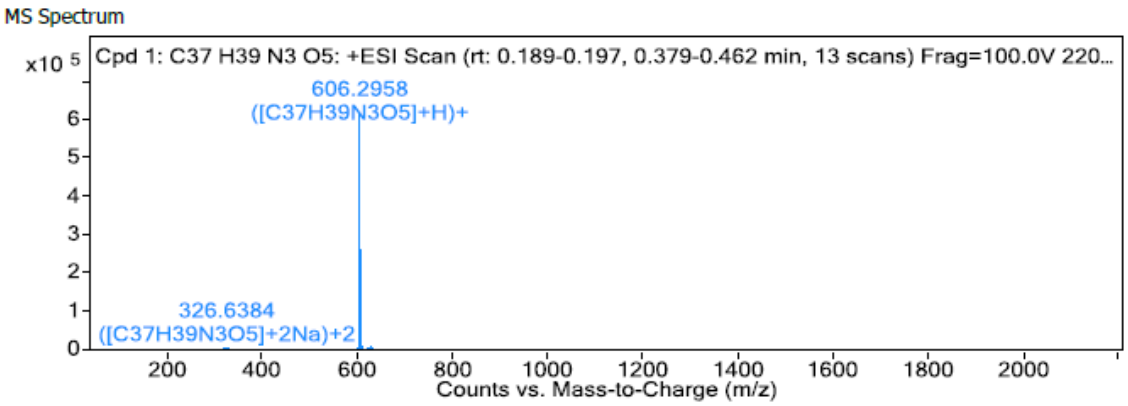
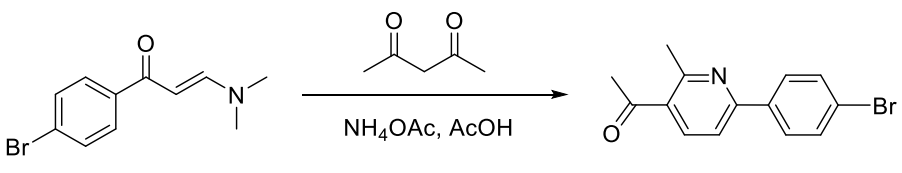


Figure S17. *Mass spectrum of compound* ***G3a****.*

2.1.10 Compound 10, 1-(6-(4-bromophenyl)-2-methylpyridin-3-yl)ethan-1-one

Compound **10** was synthesized by following a slightly modified procedure described by Kumar et al.[4]



10

Acetyl acetone (2.22 mL, 21.6 mmol) and ammonium acetate (9.10 g, 118 mmol) were added to the solution of 1-(4-bromophenyl)-3-(dimethylamino)prop-2-en-1-one (5.00 g, 19.7 mmol) in glacial acetic acid (6.76 mL, 118 mmol). The reaction mixture was heated at 120°C for 4 h. Upon cooling, the solution was poured into ice-cold water (150 mL). The precipitate formed was filtered and washed with hexane followed by water. The product was used in the next step without further purification. Yield 72%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 8.6 Hz, 2H), 7.65 – 7.58 (m, 3H), 2.83 (s, 3H), 2.62 (s, 3H).

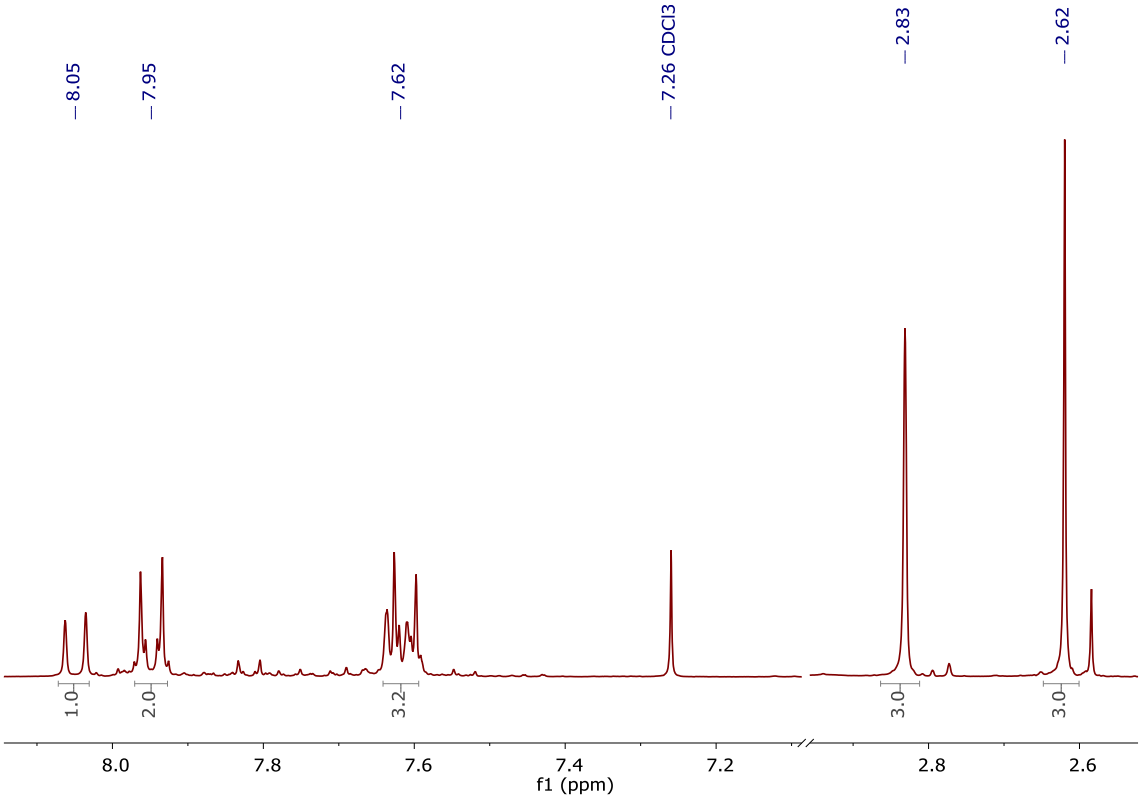
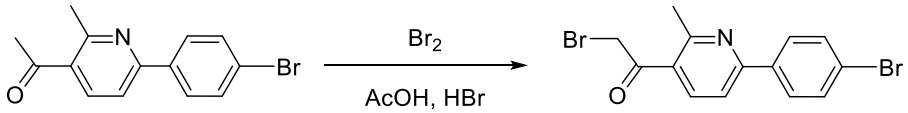


Figure S18. *^{1}H NMR spectrum of compound **10** ($CDCl_3$, 300 MHz).*

2.1.11 Compound 11, 2-bromo-1-(6-(4-bromophenyl)-2-methylpyridin-3-yl)ethan-1-one



10 **11**

To a “paste like” mixture of compound **10** (1.27 g, 4.38 mmol), acetic acid (12.5 mL, 4.38 mmol), and 48% aqueous HBr (0.5 mL, 4.38 mmol) cooled in an ice-bath, bromine (0.25 mL, 4.38 mmol) was added dropwise. The ice-bath was removed, and stirring was

continued at room temperature for 1 h under N_2, then at 75°C for 1.5 h under argon. The reaction mixture was cooled to room temperature, diluted with THF (6 mL), and stirred at room temperature overnight at room temperature. The residue was diluted with EtOAc and to this solution a saturated $NaHCO_3$ solution was carefully added. The two layers were separated, and the organic layer was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated *in vacuo*. The product is isolated as a pale orange solid. Yield 90%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.68 – 7.59 (m, 3H), 4.40 (s, 2H), 2.84 (s, 3H).

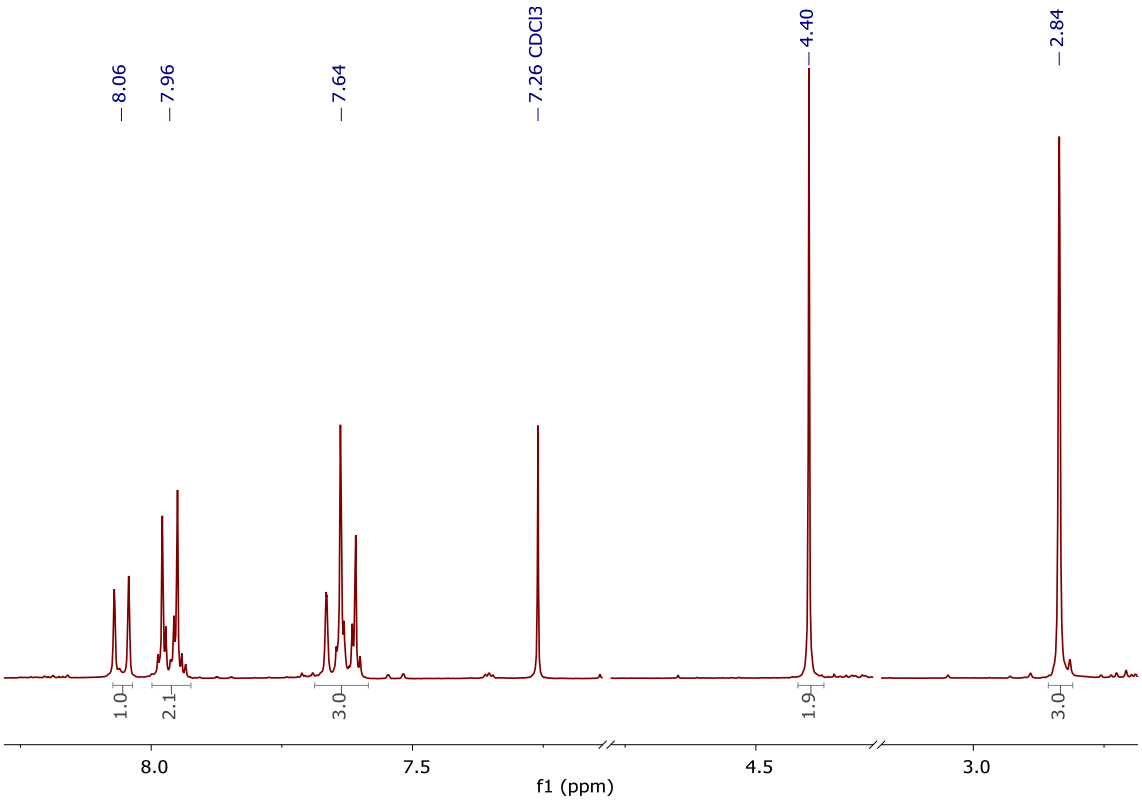
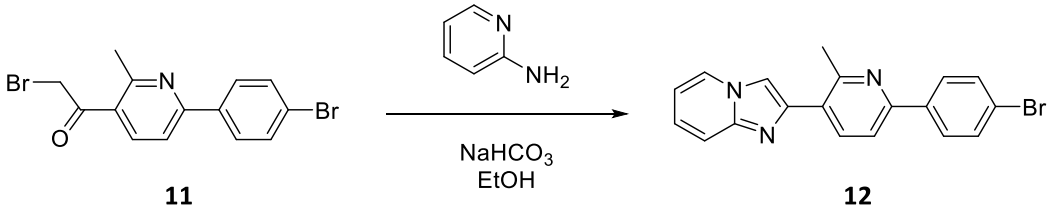


Figure S19. *^{1}H NMR spectrum of compound **11** ($CDCl_3$, 300 MHz).*

2.1.12 Compound 12, 2-(6-(4-bromophenyl)-2-methylpyridin-3-yl)imidazo[1,2-a]pyridine



A mixture of compound **11** (2.7 g, 7.3 mmol), 2-aminopyridine (900 mg, 9.5 mmol) and $NaHCO_3$ (920 mg, 11 mmol) in EtOH (100 mL) was refluxed at 85°C for 72 h. The reaction mixture was cooled to room temperature and filtered to obtain a white solid, which was washed with H_2O and a bit of Et_2O, and dried *in vacuo*. The product was isolated as a white solid. Yield: 80%.

Exact mass: ESI-MS [$C_{19}H_{14}BrN_3$]: calculated: m/z= 363.0371, found: m/z= 363.03668.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (d, J = 8.2 Hz, 1H), 8.18 (dt, J = 6.8, 1.2 Hz, 1H), 7.96 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 0.7 Hz, 1H), 7.66 (ddd, J = 9.1, 1.8, 0.8 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.83 (td, J = 6.8, 1.2 Hz, 1H), 2.88 (s, 3H).

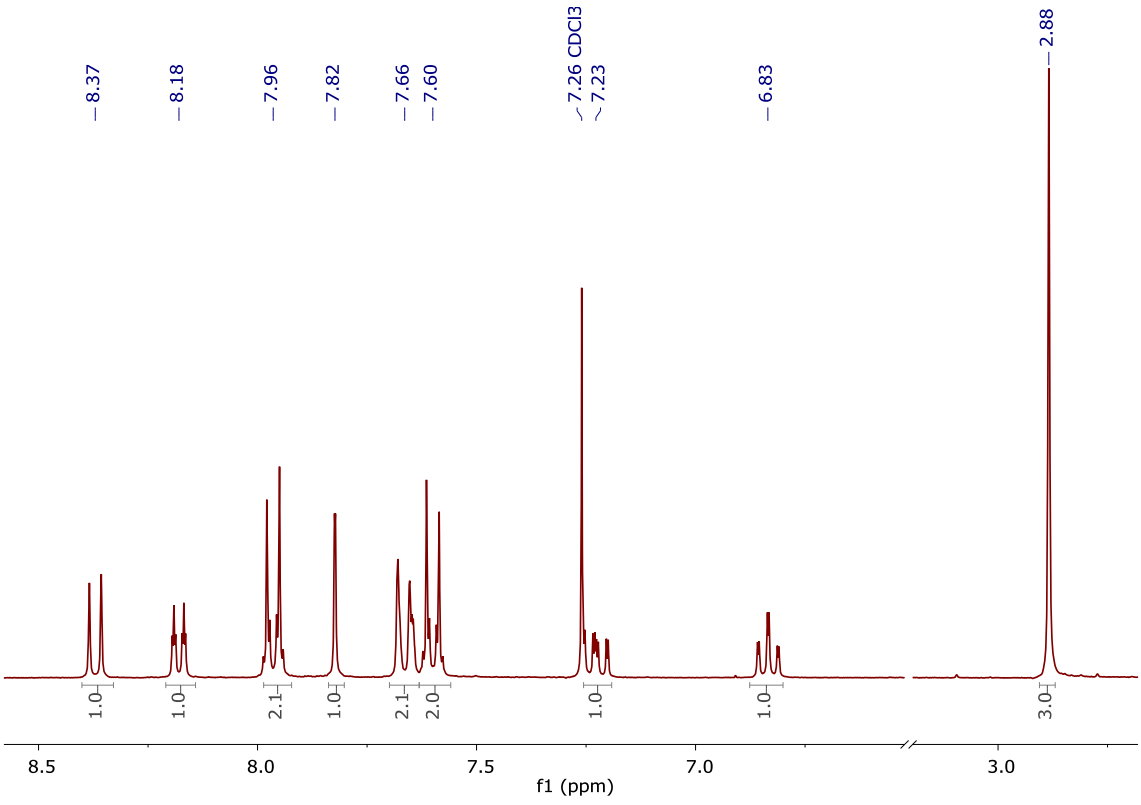


Figure S20. *^{1}H NMR spectrum of compound **12** ($CDCl_3$, 300 MHz).*

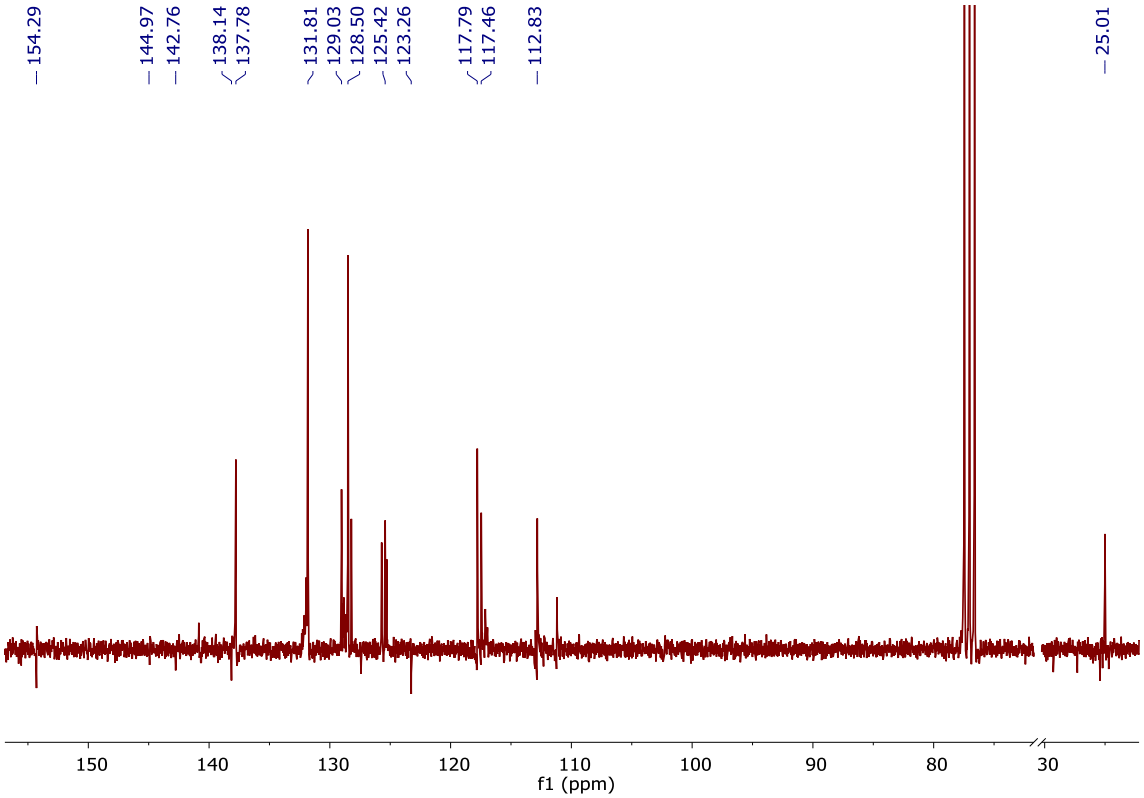


Figure S21. *^{13}C APT NMR spectrum of compound **12** ($CDCl_3$, 75 MHz).*

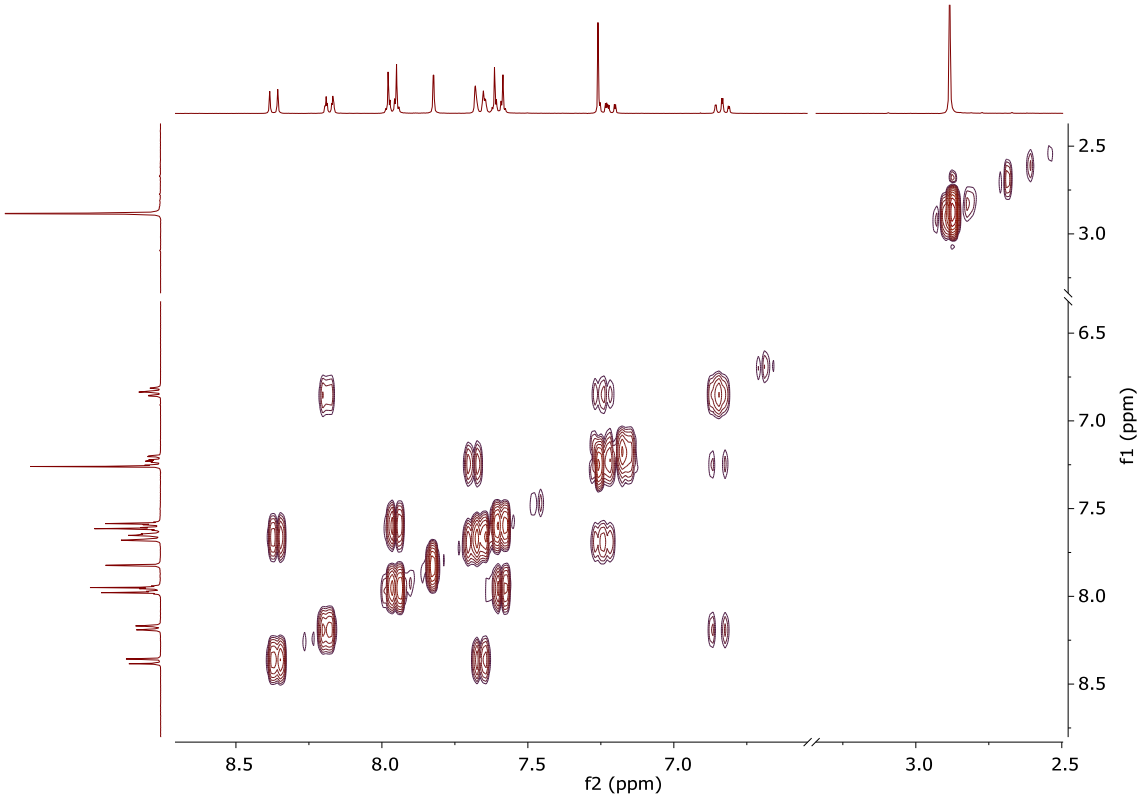


Figure S22. *COSY NMR spectrum of compound **12** ($CDCl_3$, 300 MHz).*

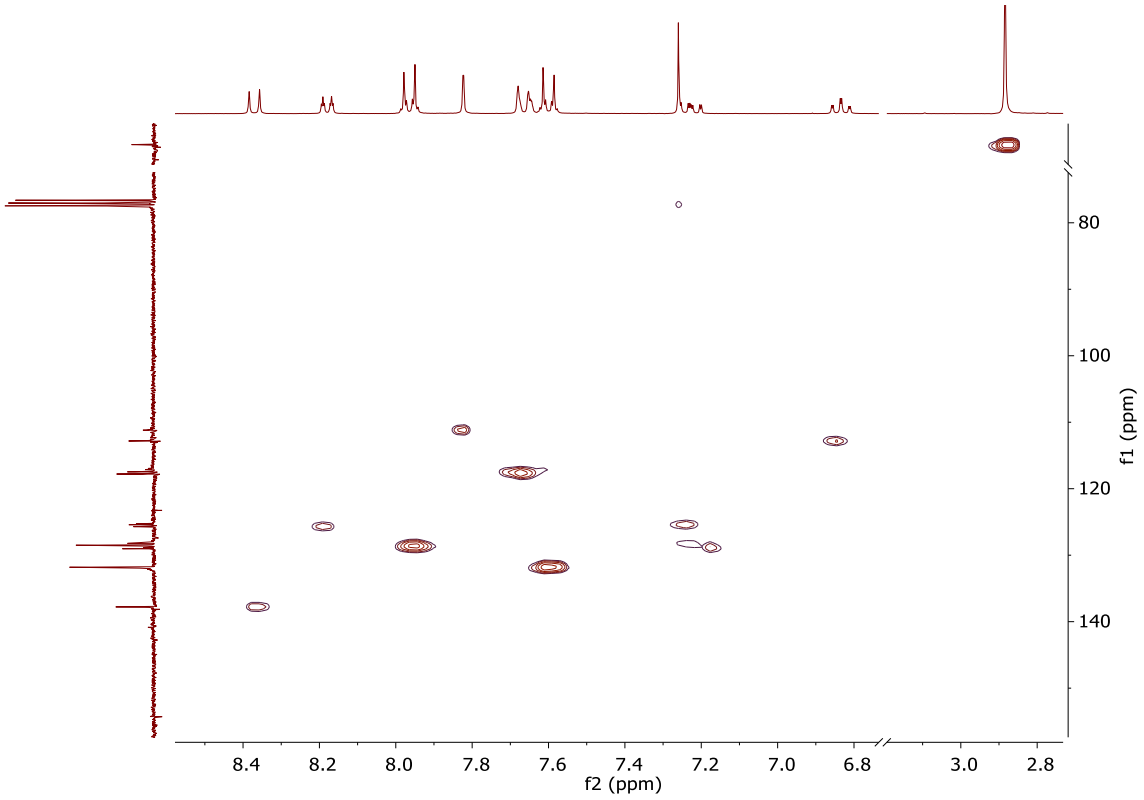


Figure S23. *HSQC NMR spectrum of compound* ***12*** *($CDCl_3$, 300 MHz).*

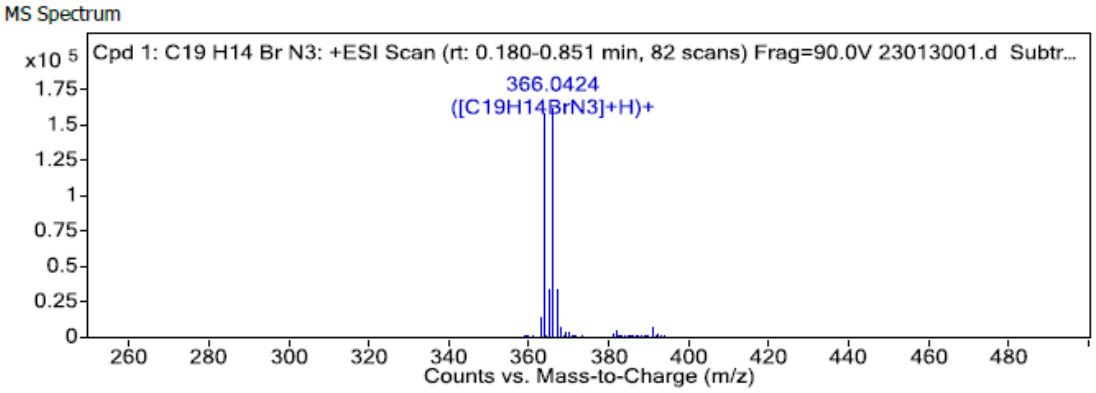
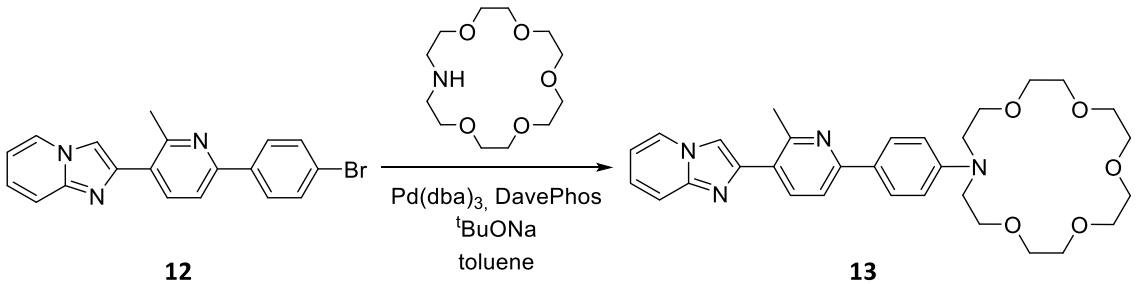


Figure S24. *Mass spectrum of compound* ***12****.*

2.1.13 Compound 13, 16-(4-(5-(imidazo[1,2-a]pyridin-2-yl)-6-methylpyridin-2-yl)phenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



12 **13**

A mixture of $Pd_2(dba)_3$ (173 mg, 0.19 mmol), DavePhos (223 mg, 0.56 mmol), ^tBuONa (681 mg, 7.0 mmol), compound **12** (1.72 g, 4.7 mmol) and 1-aza-18-crown-6 (1.37 g, 5.2 mmol) was introduced in a Schlenk tube and dissolved in 50 mL of anhydrous toluene, under N_2. The tube was sealed and kept in a preheated oil bath at and stirred overnight at 120°C. After this time, the reaction mixture was cooled to room temperature, filtered through a celite pad and the filtrate was concentrated *in vacuo*. The residue was triturated with diethyl ether and the title compound was obtained as a brown solid. Yield 74%.

Exact mass: ESI-MS [$C_{31}H_{38}N_4O_5$]: calculated: m/z= 546.2842, found: m/z= 546.2847.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.2 Hz, 1H), 8.15 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.77 (d, *J* = 0.7 Hz, 1H), 7.64 (dd, *J* = 9.1, 1.0 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.19 (ddd, *J* = 9.1, 6.7, 1.3 Hz, 1H), 6.84–6.73 (m, 3H), 3.78–3.58 (m, 24H), 2.85 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 155.63 (1C, C_{quat}), 154.99 (1C, C_{quat}), 148.43 (1C, C_{quat}), 144.99 (1C, C_{quat}), 143.77 (1C, C_{quat}), 137.37 (1C, CH), 127.98 (2C, CH, C_6H_4), 126.94 (1C, C_{quat}), 125.69 (1C, C_{quat}), 125.56 (1C, CH), 124.78 (1C, CH), 117.52 (1C, CH), 116.49 (1C, CH), 112.39 (1C, CH), 111.69 (2C, CH, C_6H_4), 110.83 (1C, CH), 70.79 (8C, CH_2, crown), 68.71 (2C, CH_2, crown), 51.39 (2C, CH_2, crown), 25.10 (1C, CH_3).

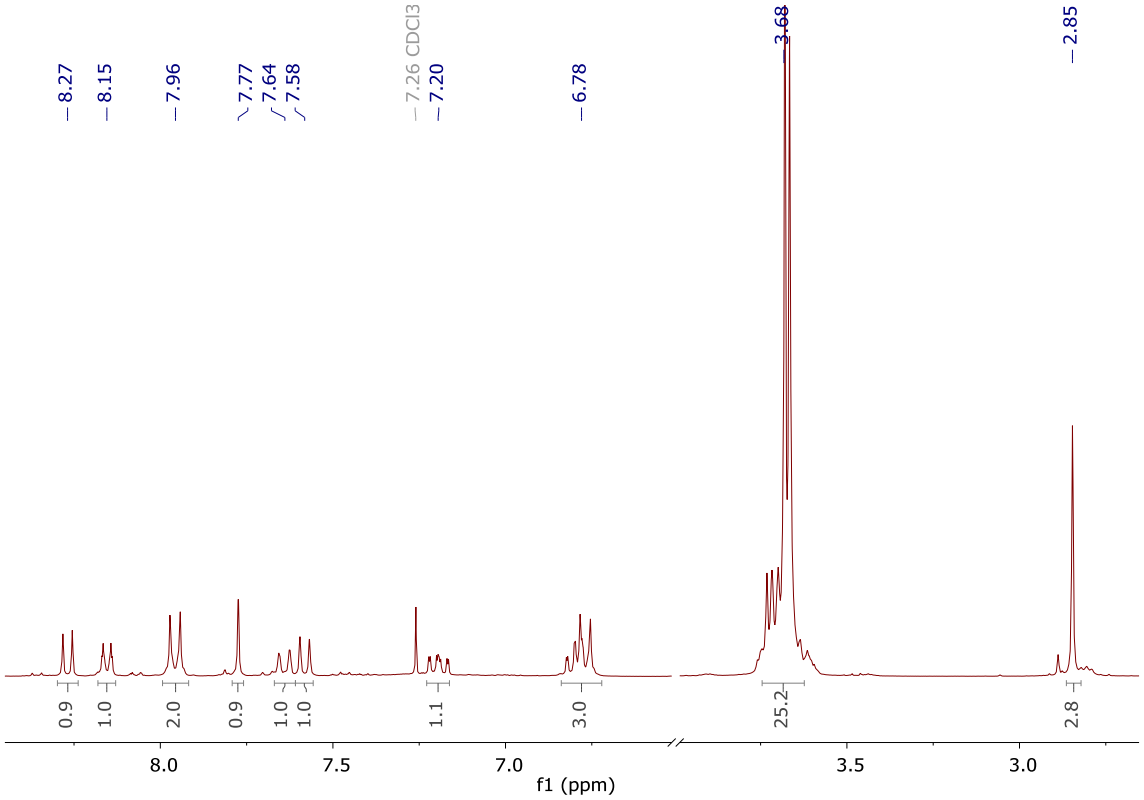


Figure S25. *^{1}H NMR spectrum of compound **13** ($CDCl_3$, 300 MHz).*

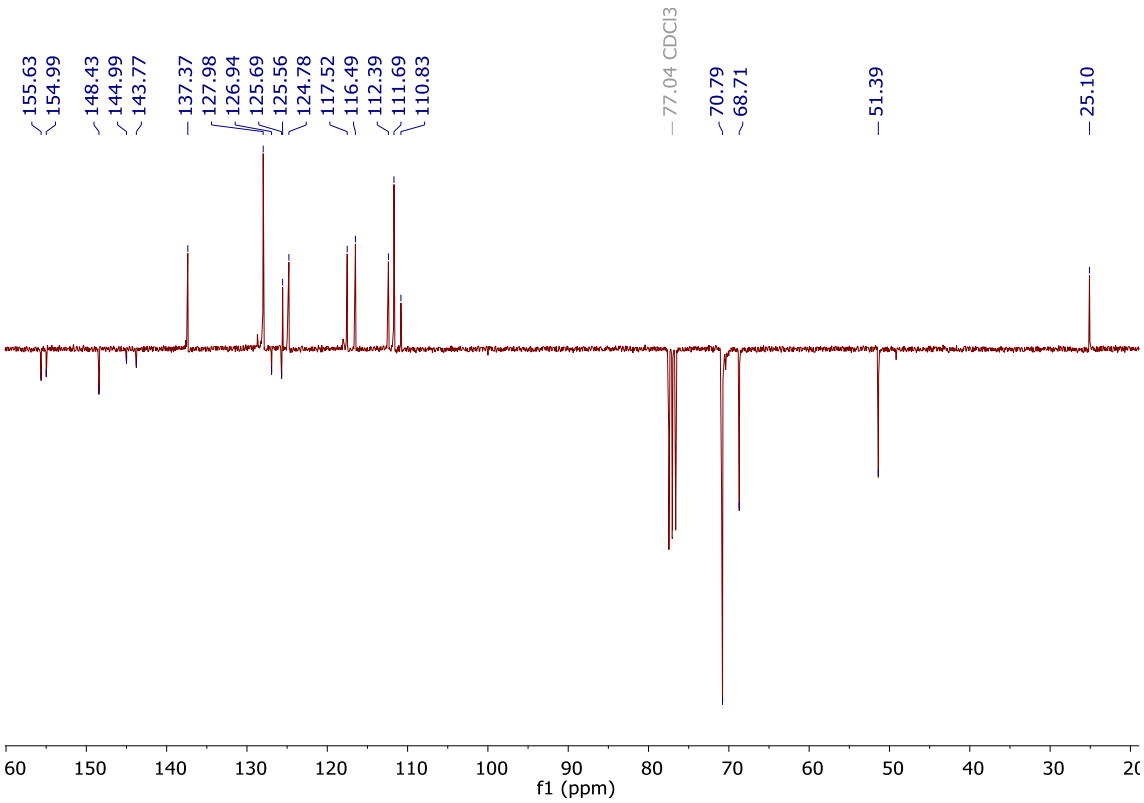


Figure S26. *^{13}C APT NMR spectrum of compound **13** ($CDCl_3$, 300 MHz).*

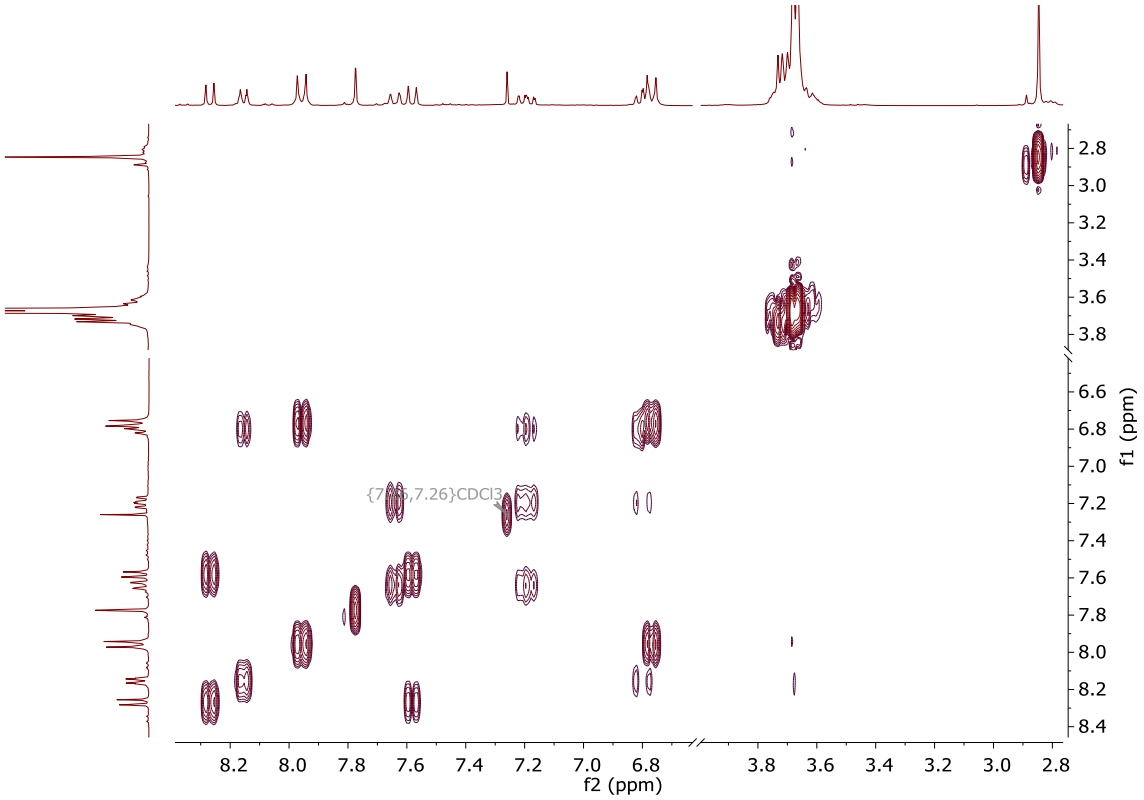


Figure S27. *COSY NMR spectrum of compound* ***13*** *($CDCl_3$, 300 MHz).*

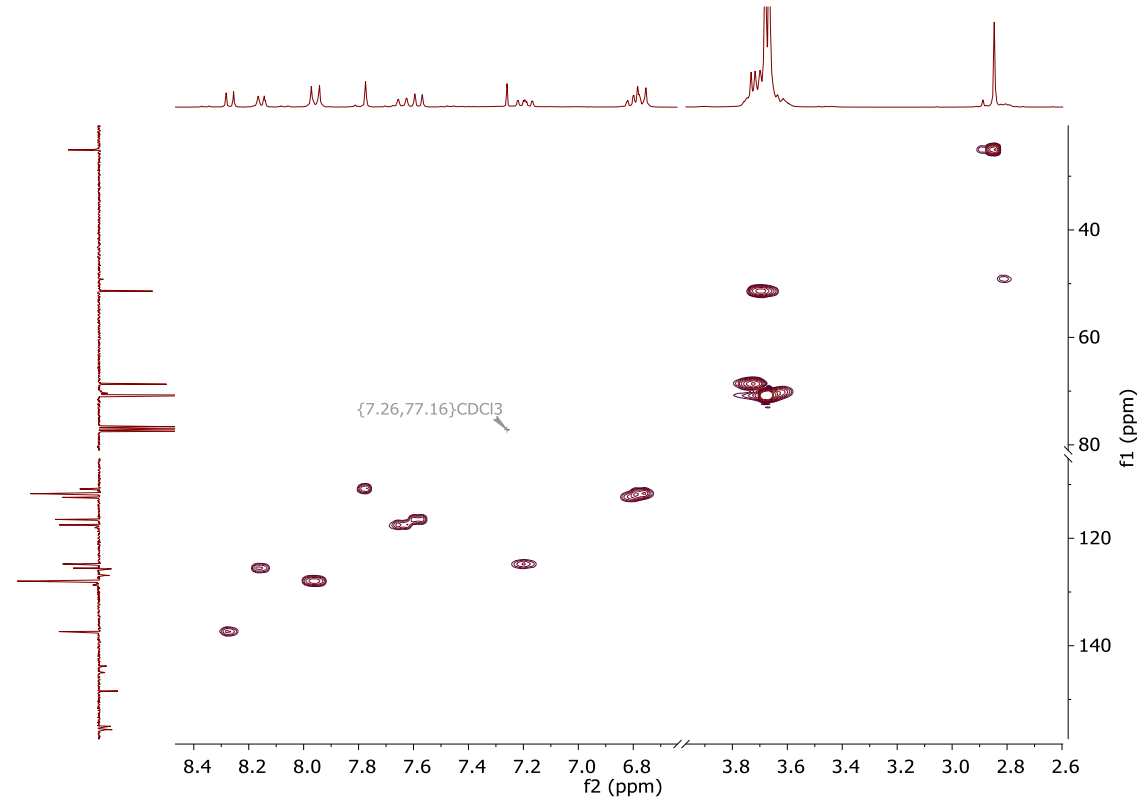


Figure S28. *HSQC NMR spectrum of compound* ***13*** *($CDCl_3$, 300 MHz).*

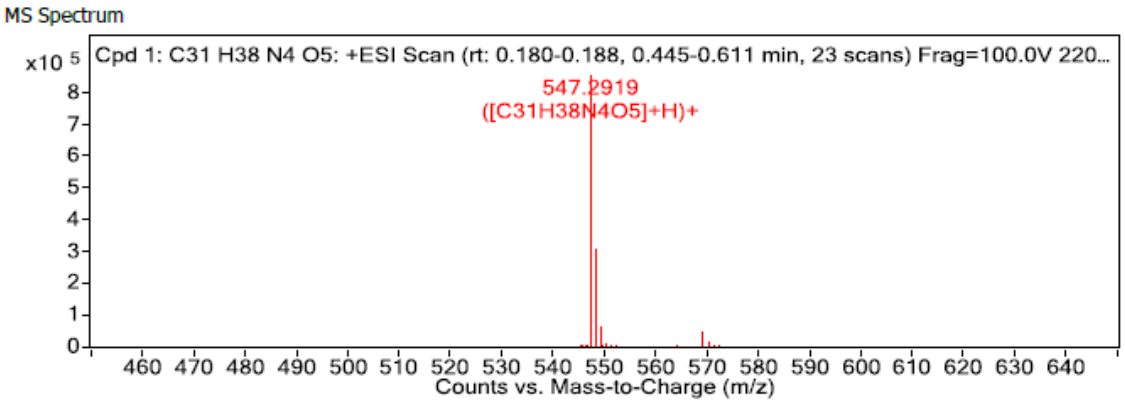
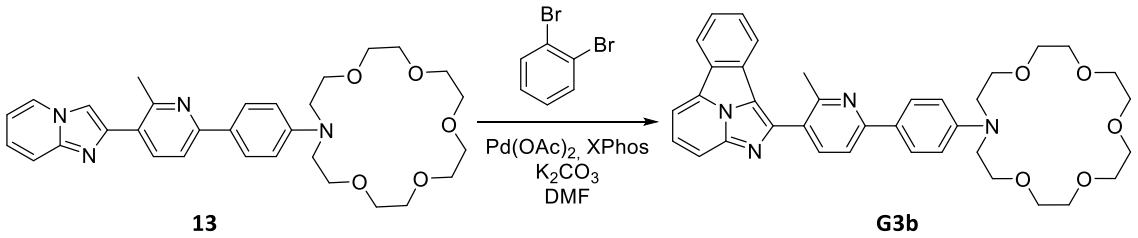


Figure S29. *Mass spectrum of compound* ***13****.*

2.1.14 Compound G3b, 16-(4-(5-(benzo[a]imidazo[5,1,2-cd]indolizin-1-yl)-6-methylpyridin-2-yl)phenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



13 **G3b**

A mixture of $Pd(OAc)_2$ (9.86 mg, 0.044 mmol, 6 mol%), Xphos (34.9 mg, 0.073 mmol, 10 mol%), K_2CO_3 (303 mg, 2.2 mmol, 3.0 equiv.) and compound **13** (400 mg, 0.73 mmol, 1.0 equiv.) was introduced in a Schlenk tube and dissolved in 8 mL of DMF, under N_2. To this solution 1,2-dibrobenzene (106 µL, 0.88 mmol, 1.2 equiv.) was added. The tube was sealed and kept in a preheated oil bath and stirred overnight at 160°C. After this time, the reaction mixture was cooled to room temperature, filtered through a celite pad and the filtrate was concentrated *in vacuo*. The residue was purified with two centrifugal thin-layer chromatography on silica: first one with eluent: CH_2Cl_2 to 10% MeOH in CH_2Cl_2; and, second one eluent: from CH_2Cl_2 to 1% MeOH in CH_2Cl_2. The title compound was obtained as a brown solid. Yield 3%.

Exact mass: ESI-MS [$C_{37}H_{40}N_4O_5$]: calculated: m/z= 620.2999, found: m/z= 620.3003.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (d, J = 7.8 Hz, 1H), 8.28 (d, J = 8.2 Hz, 2H), 8.21 (d, J = 8.0 Hz, 1H), 8.15 – 8.06 (m, 4H), 7.84 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.1 Hz, 1H), 6.87 (d, J = 9.0 Hz, 2H), 3.77 – 3.57 (m, 24H), 2.93 (s, 3H).

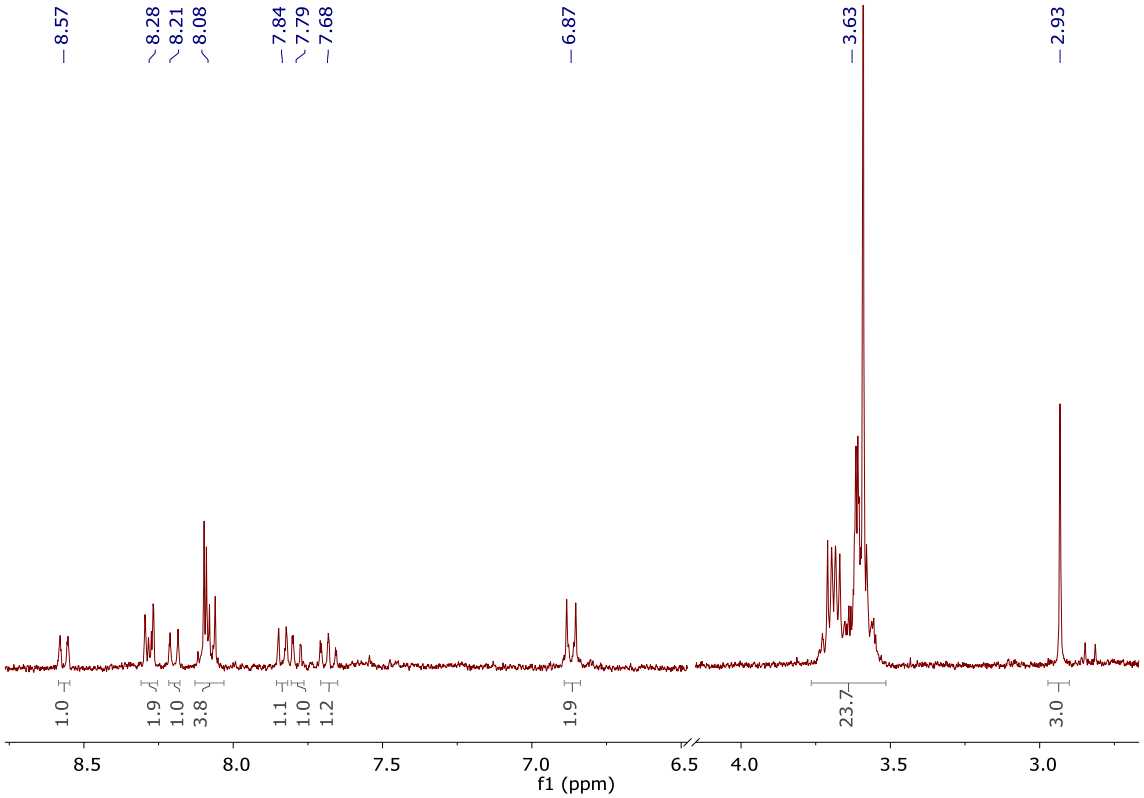


Figure S30. *^{1}H NMR spectrum of compound **G3b** ($CDCl_3$, 300 MHz).*

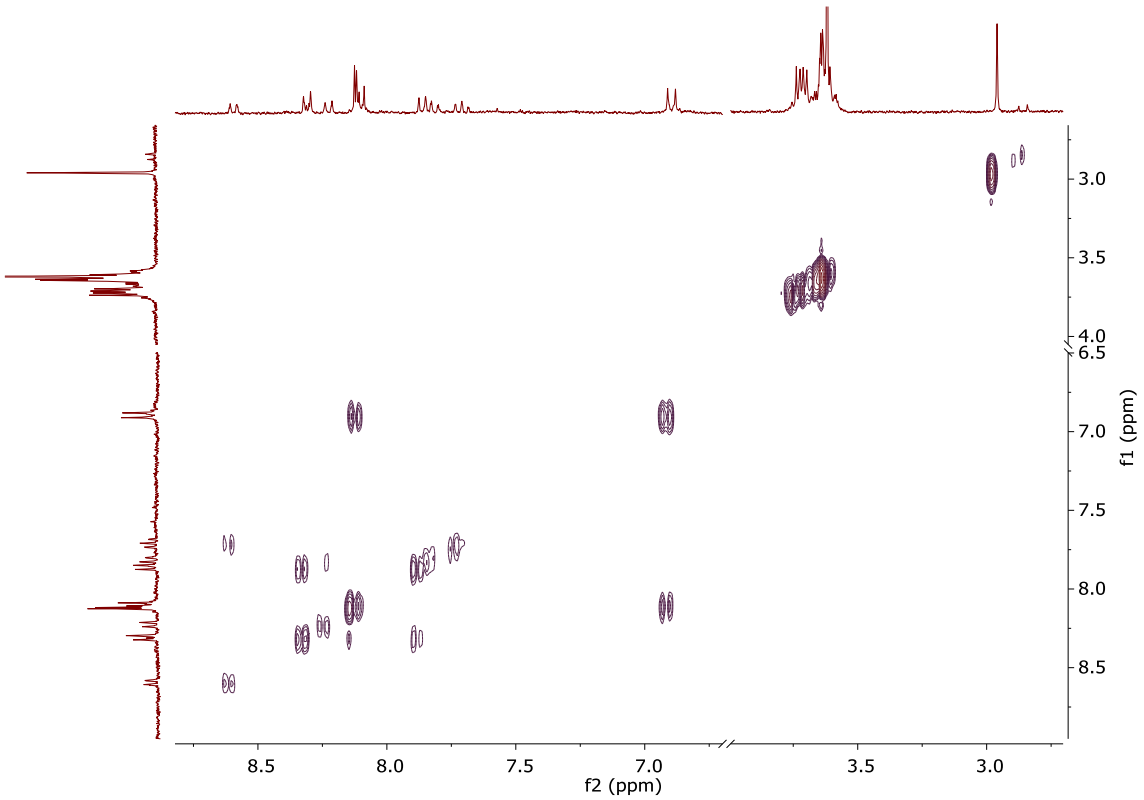


Figure S31. *COSY NMR spectrum of compound **G3b** ($CDCl_3$, 300 MHz).*

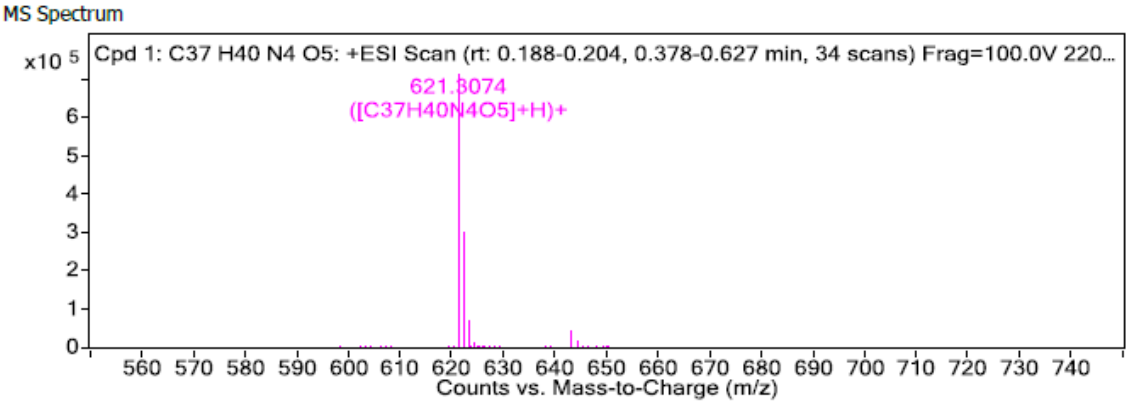
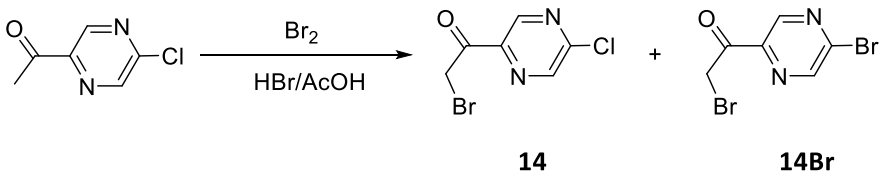


Figure S32. *Mass spectrum of compound* ***G3b****.*

2.1.15 Compound 14/14Br, 2-bromo-1-(5-chloropyrazin-2-yl)ethan-1-one and 2-bromo-1-(5-bromopyrazin-2-yl)ethan-1-one

Compounds **14** and **14Br** were synthesized by following a modified procedure described by Shishido et al. in a patent,[5] and by Lopes et al.[6] The compounds could not be isolated in both cases.



14 **14Br**

Shishido: Bromine (0.52 mL, 10 mmol) was added over a solution of 1-(5-chloropyrazin-2-yl)ethan-1-one (1.50 g, 9.6 mmol) in 12.5 mL of a mixture aqueous 48% HBr and AcOH (1:4, v/v) and the reaction was stirred at 60°C for 2 h. The resulting mixture was neutralized a saturated $NaHCO_3$ solution and extracted with EtOAc. The organic phase was dried over $MgSO_4$ and evaporated to yield a white/orange solid, as a mixture of the two compounds **14** and **14Br**.

Lopes: A solution of bromine (327 µl, 6.39 mmol) in glacial acetic acid (2 mL) was added dropwise to a solution of 1-(5-chloropyrazin-2-yl)ethan-1-one (1.00 g, 6.39 mmol) in glacial acetic acid (2 mL). The mixture was placed in a bath at 40°C for 24 h. After this time, the mixture was allowed to cool to room temperature. The white precipitate was filtered and washed with EtOH and dried under vacuum. The product was obtained as a mixture of the two compounds **14** and **14Br**.

^{1}H NMR of the mixture 1:1 ratio of 14 and 14Br (300 MHz, $CDCl_3$): a) δ 9.05 (d, J = 1.4 Hz, 1H), 8.65 (d, J = 1.4 Hz, 1H), 4.68 (s, 2H); **b)** δ 9.02 (d, J = 1.4 Hz, 1H), 8.75 (d, J = 1.4 Hz, 1H), 4.67 (s, 2H).

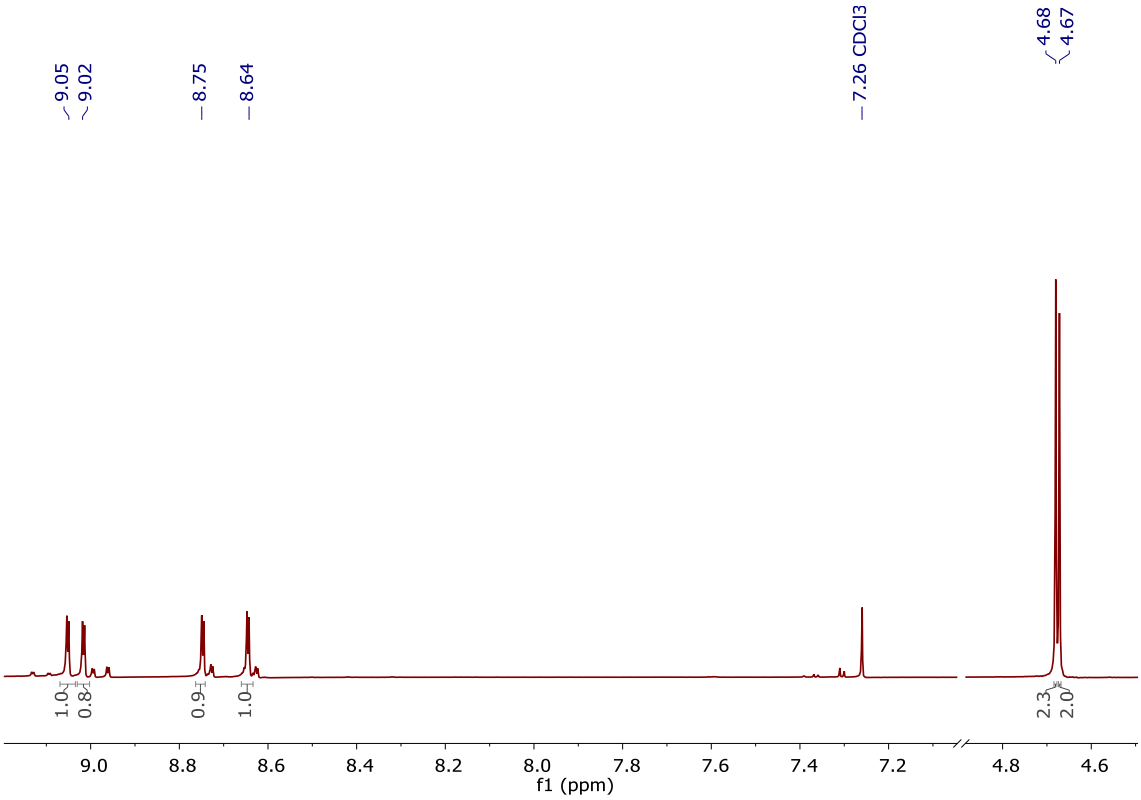
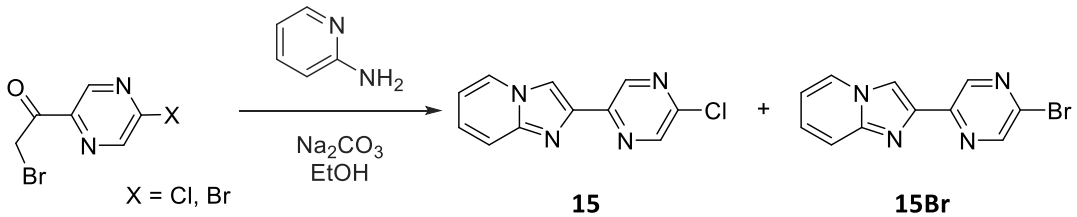


Figure S33. *^{1}H NMR spectrum of the mixture of compounds **14** and **14Br** ($CDCl_3$, 300 MHz).*

2.1.16 Compound 15/15Br, 2-(5-chloropyrazin-2-yl)imidazo[1,2-a]pyridine (15) and 2-(5-bromopyrazin-2-yl)imidazo[1,2-a]pyridine



A mixture of compound **14**/**14Br** (6.39 mmol), 2-aminopyridine (0.72 g, 7.67 mmol) and Na_2CO_3 (2.03 g, 19.2 mmol) in EtOH (40 mL) was refluxed at 85°C for 72 h. The reaction mixture was cooled to room temperature and filtered to obtain a white solid, which was washed with H_2O and dried *in vacuo*. The product was isolated as a white solid. Yield: 80%.

^{1}H NMR of the mixed species 15 and 15Br (300 MHz, $CDCl_3$): a) δ 9.20 (d, J = 1.4 Hz, 1H), 8.55 (d, J = 1.4 Hz, 1H), 8.23 (s, 1H), 8.16 (d, J = 6.9 Hz, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.25

(t, 1H), 6.86 (td, J = 6.8, 1.1 Hz, 1H); **b)** δ 9.18 (d, J = 1.4 Hz, 1H), 8.64 (d, J = 1.4 Hz, 1H), 8.24 (s, 1H), 8.16 (d, J = 6.9 Hz, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.25 (t, 1H), 6.86 (td, J = 6.8, 1.1 Hz, 1H).

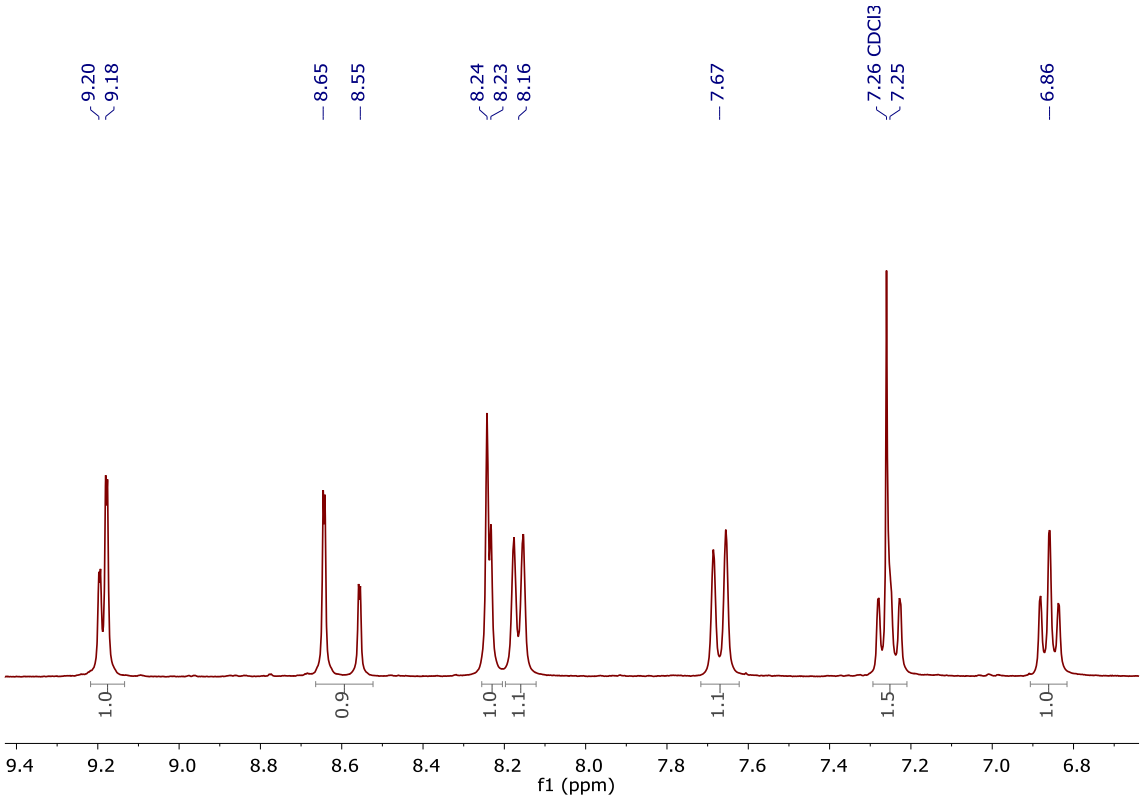


Figure S34. *^{1}H NMR spectrum of the mixture of compounds **15** and **15Br** ($CDCl_3$, 300 MHz).*

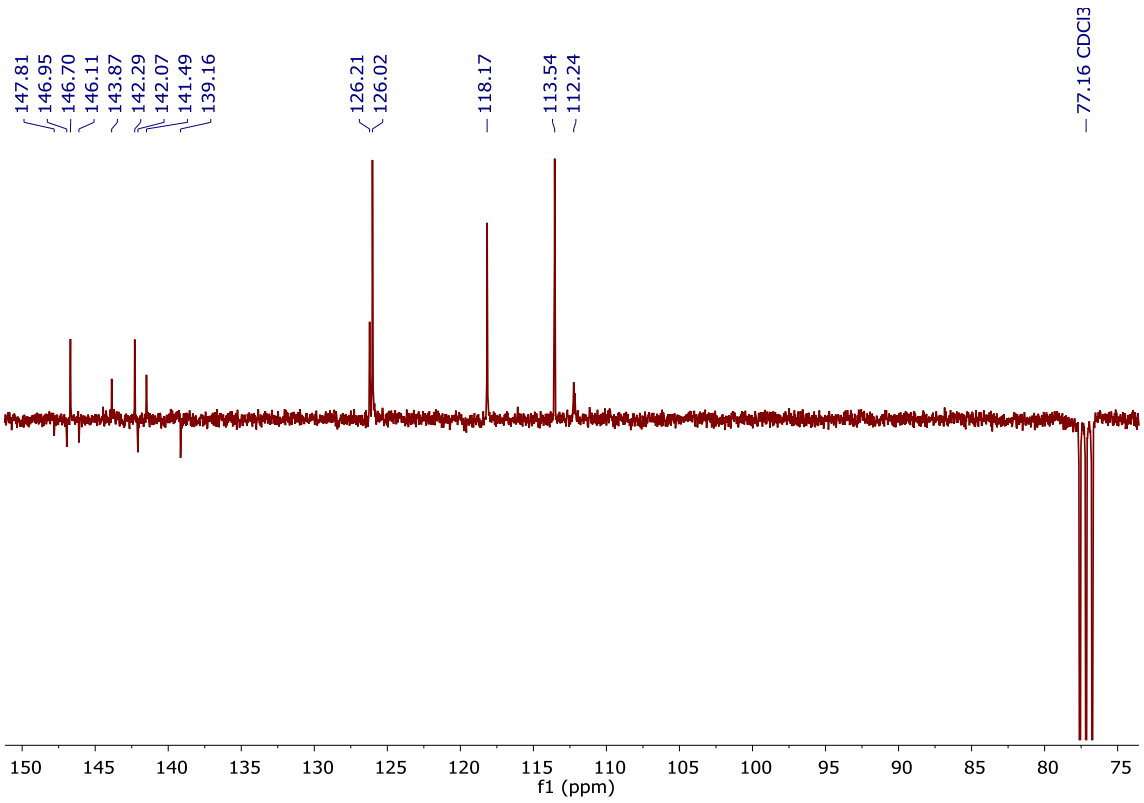


Figure S35. *^{13}C APT NMR spectrum of the mixture of compounds **15** and **15Br** ($CDCl_3$, 300 MHz).*

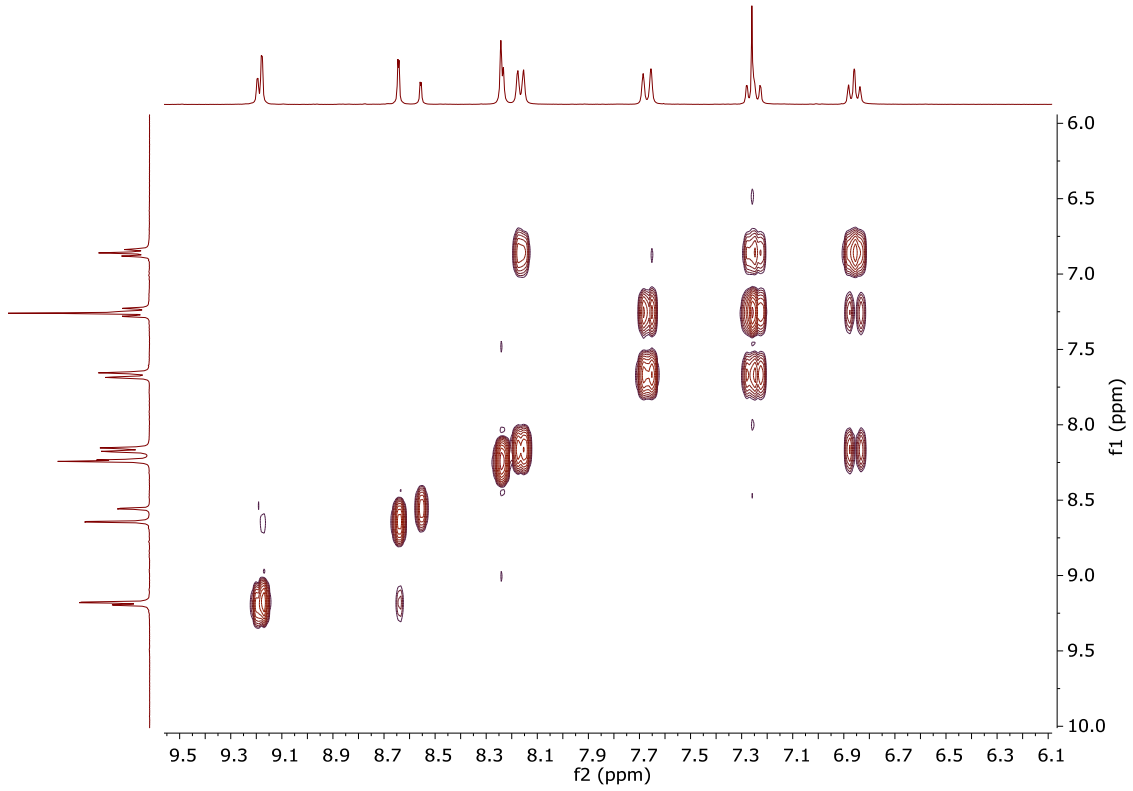


Figure S36. *COSY NMR spectrum of the mixture of compounds **15** and **15Br** ($CDCl_3$, 300 MHz).*

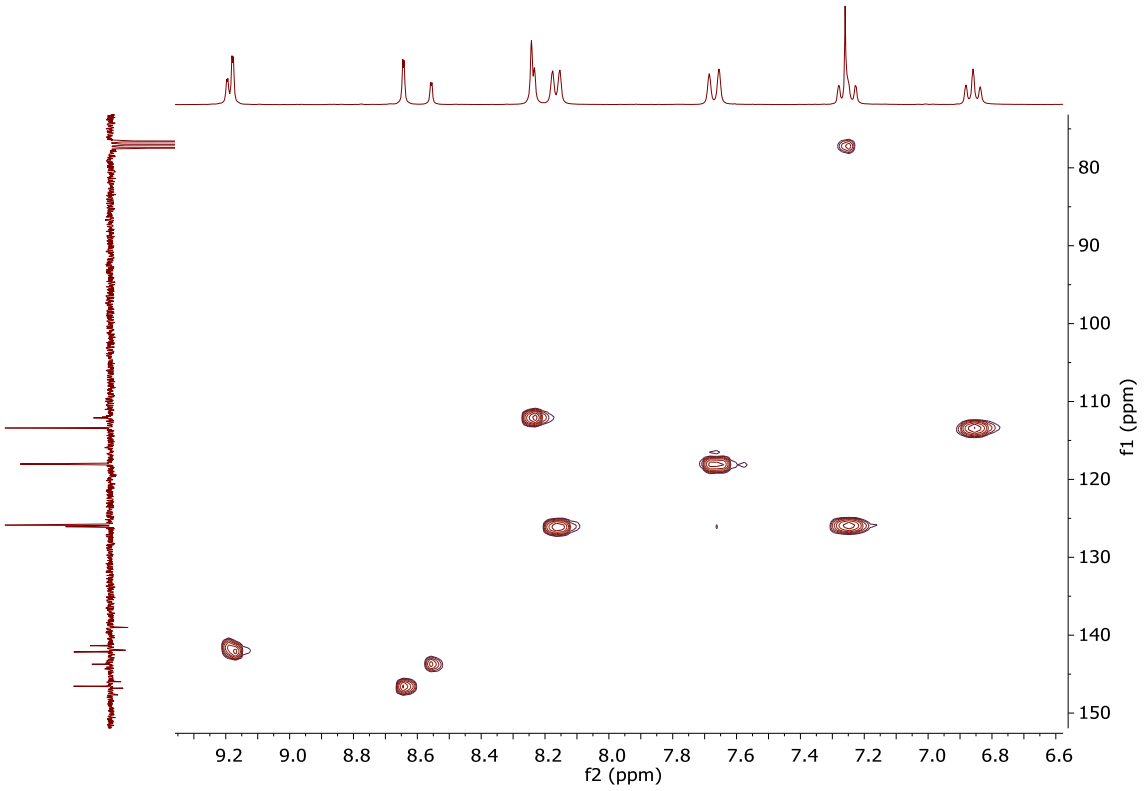


Figure S37. *NMR spectrum of the mixture of compounds* ***15*** *and* ***15Br*** *($CDCl_3$, 300 MHz).*

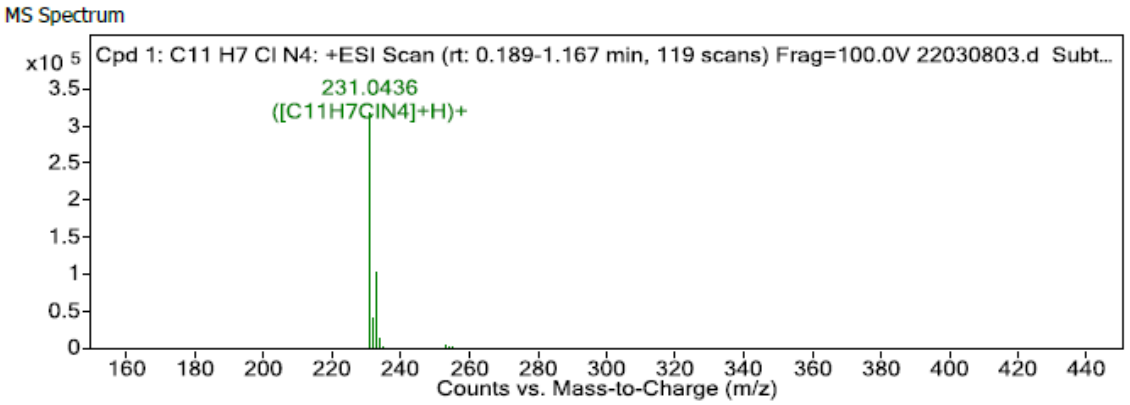
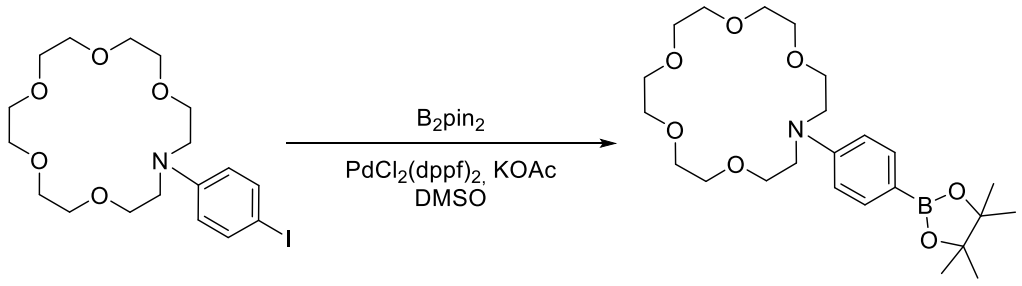


Figure S38. *Mass spectrum of compounds* ***15*** *and* ***15Br****.*

2.1.17 Compound 16, 16-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane

Compound **16** was synthesized according to the procedure described by Aparicio.REF



5 **16**

Compound **5** (1.00 g, 2.15 mmol), anhydrous KOAc (633 mg, 6.45 mmol), $PdCl_2(PPh_3)_2$ (47.17 mg, 0.065 mmol) and bis(pinacolato)diboron (600.29 mg, 2.36 mmol) with DMSO (8.0 mL) were added into a Schlenk tube, under N_2. The Schlenk was sealed and stirred at 80°C for 16 h. The mixture was cooled to room temperature, diluted CH_2Cl_2 and washed with brine. The organic layers were dried over $MgSO_4$ and evaporated to give a brown oil. The crude was used in the next step without further purification. Quantitative yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, J = 8.7 Hz, 2H), 6.65 (d, J = 8.6 Hz, 2H), 3.72 – 3.64 (m, 24H), 1.31 (s, 12H).

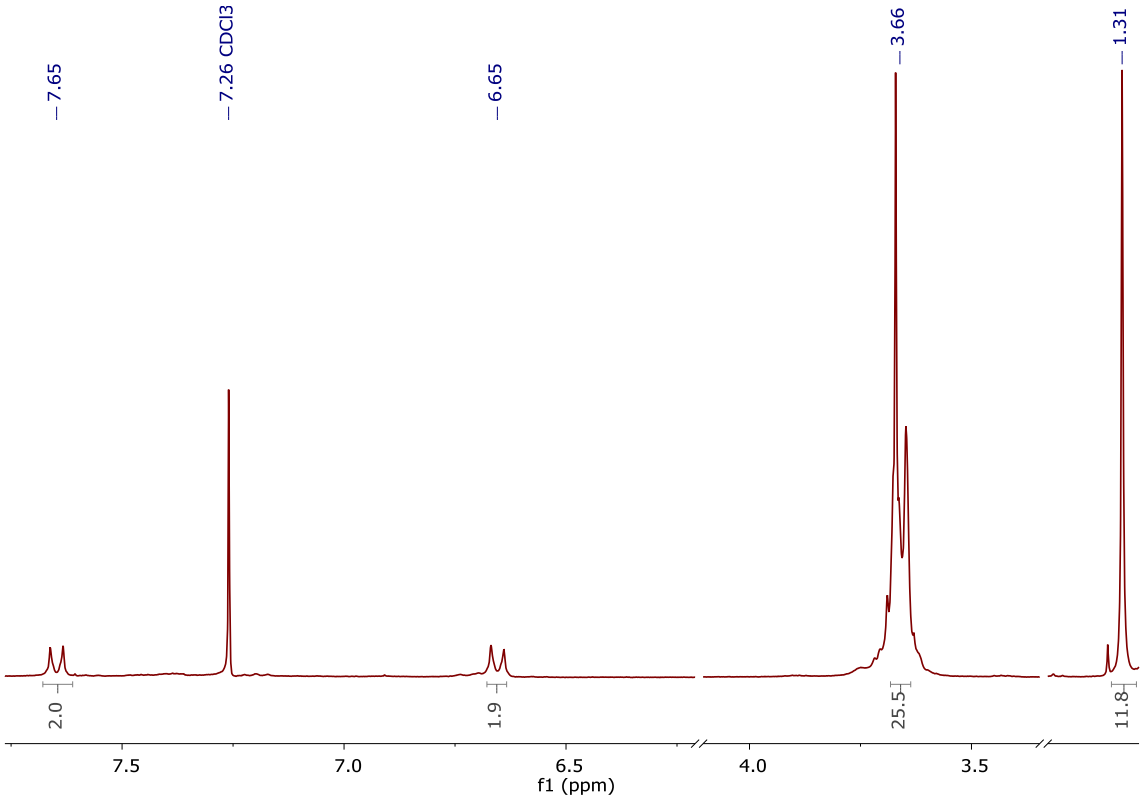
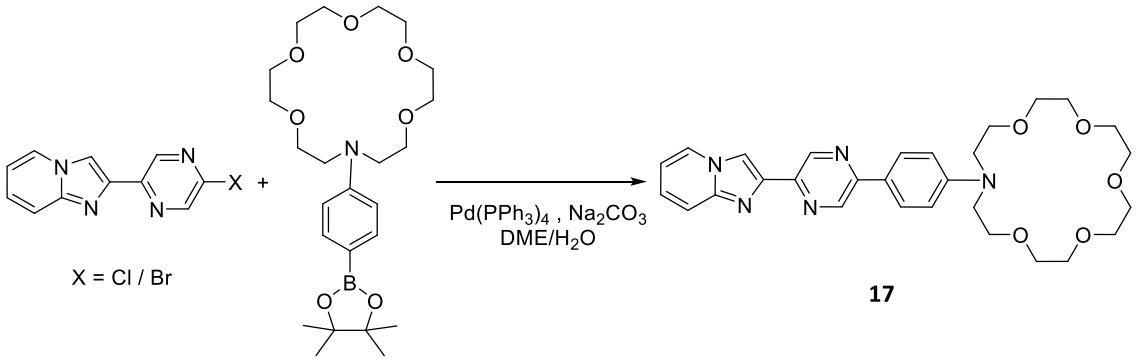


Figure S39. *^{1}H NMR spectrum of compound **16** ($CDCl_3$, 300 MHz).*

2.1.18 Compound 17, 16-(4-(5-(imidazo[1,2-a]pyridin-2-yl)pyrazin-2-yl)phenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



15/15Br **16** **17**

A mixture of $Pd(PPh_3)_4$ (186.2 mg, 0.16 mmol, 5 mol%), Na_2CO_3 (1.71 g, 16.12 mmol, 5 equiv.), **15**/**15Br** (743 mg, 3.22 mmol, 1 equiv.) and **16** (1.50 g, 3.22 mmol, 1 equiv.) was introduced in a Schlenk tube and dissolved in 50 mL of degassed DME/H_2O mixture (3:1, v/v), under N_2. The reaction was refluxed at 85 °C overnight. After this time, the mixture was concentrated *in vacuo* and the residue was purified by column chromatography (eluent: from CH_2Cl_2 to 5% MeOH in CH_2Cl_2). The title compound was obtained as a yellow solid. Yield 30%.

Exact mass: ESI-MS [$C_{29}H_{35}N_5O_5$]: calculated: m/z= 533.2638, found: m/z= 533.2642.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.29 (d, J = 1.5 Hz, 1H), 8.87 (d, J = 1.5 Hz, 1H), 8.17 (s, 1H), 8.10 (dt, J = 6.8, 1.2 Hz, 1H), 7.92 (d, J = 8.9 Hz, 2H), 7.62 (dd, J = 9.1, 1.1 Hz, 1H), 7.16 (ddd, J = 9.2, 6.7, 1.2 Hz, 1H), 6.81–6.71 (m, 3H), 3.76–3.57 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 151.35 (1C, C_{quat}), 149.10 (1C, C_{quat}), 145.89 (1C, C_{quat}), 144.42 (1C, C_{quat}), 143.59 (1C, C_{quat}), 141.26 (1C, CH), 139.90 (1C, CH), 127.93 (2C, CH), 125.93 (1C, CH), 125.17 (1C, CH), 123.70 (1C, C_{quat}), 117.83 (1C, CH), 112.86 (1C, CH), 111.78 (2C, CH), 111.08 (1C, CH), 70.78 (8C, CH_2, crown), 68.58 (2C, CH_2, crown), 51.29 (2C, CH_2, crown).

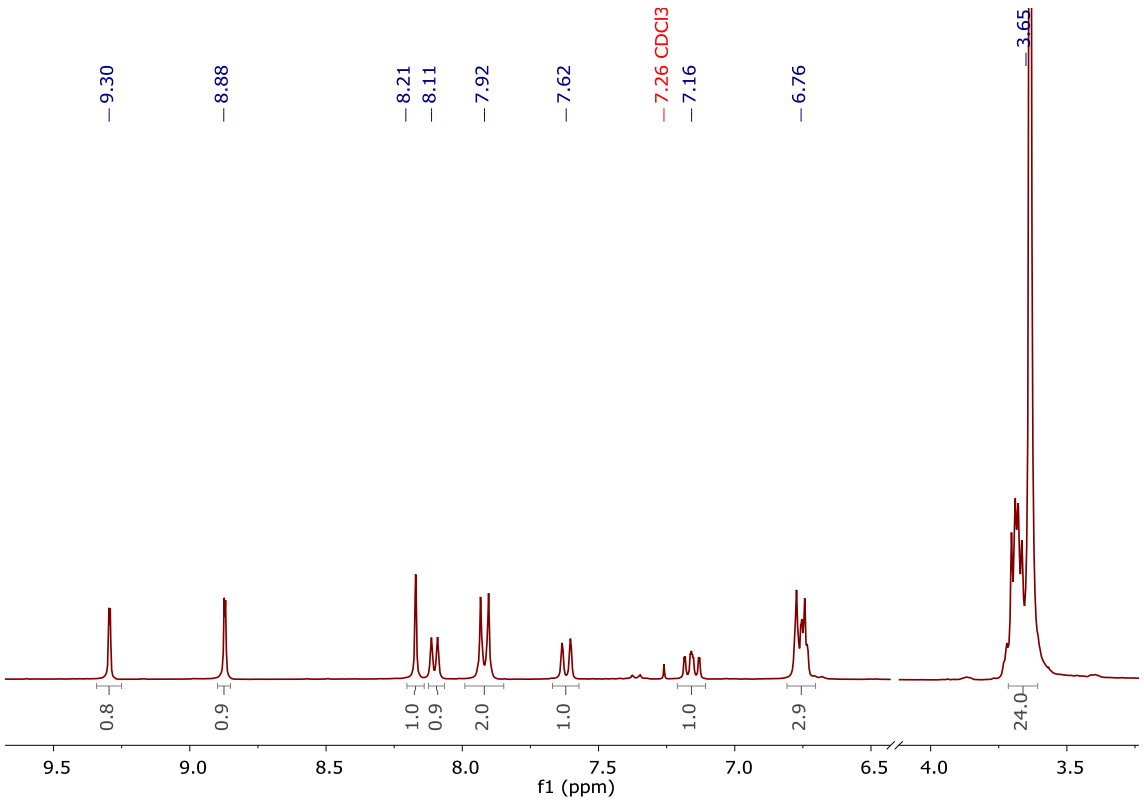


Figure S40. *^{1}H NMR spectrum of compound **17** ($CDCl_3$, 300 MHz).*

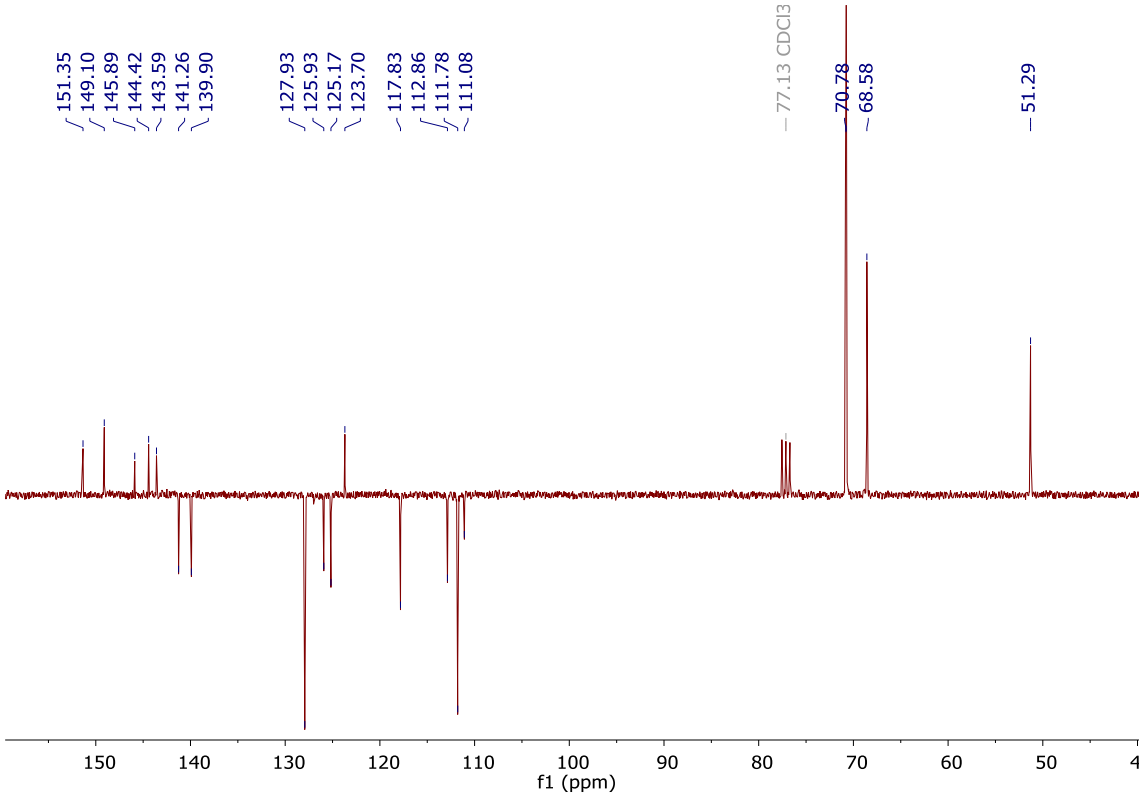


Figure S41. *^{13}C APT NMR spectrum of compound **17** ($CDCl_3$, 300 MHz).*

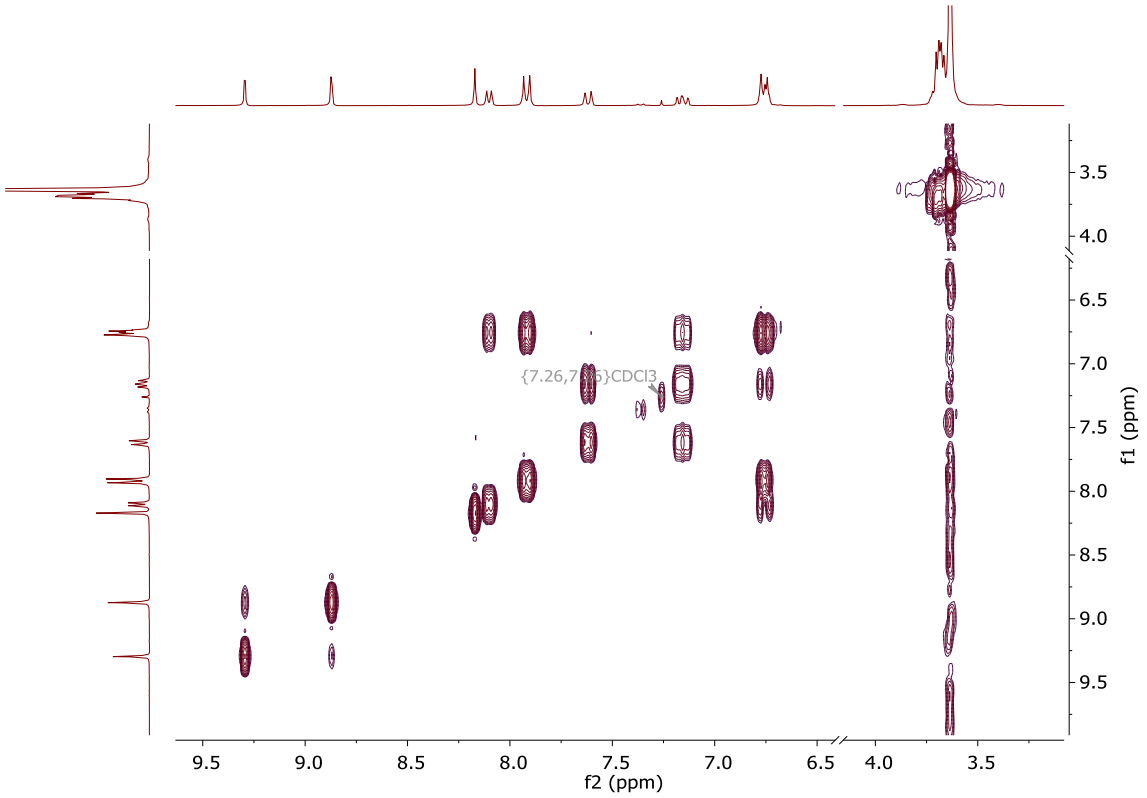


Figure S42. *COSY NMR spectrum of compound* ***17*** *($CDCl_3$, 300 MHz).*

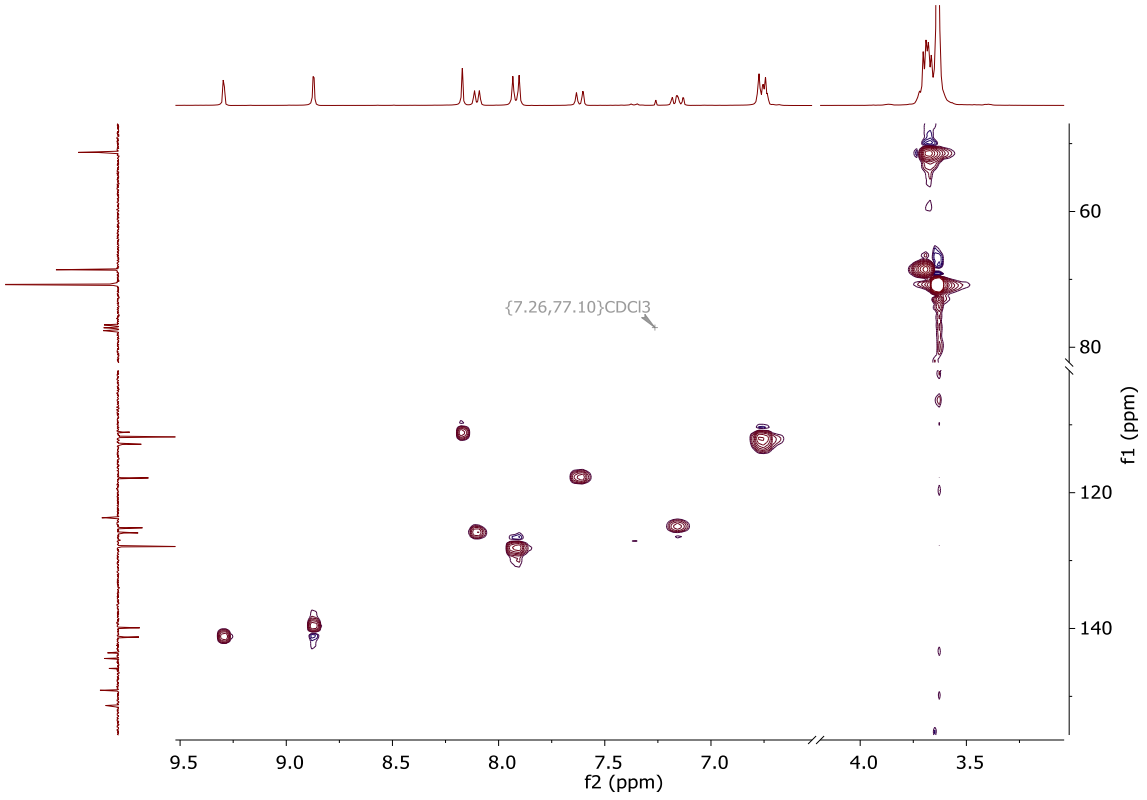


Figure S43. *HSQC NMR spectrum of compound* ***17*** *($CDCl_3$, 300 MHz).*

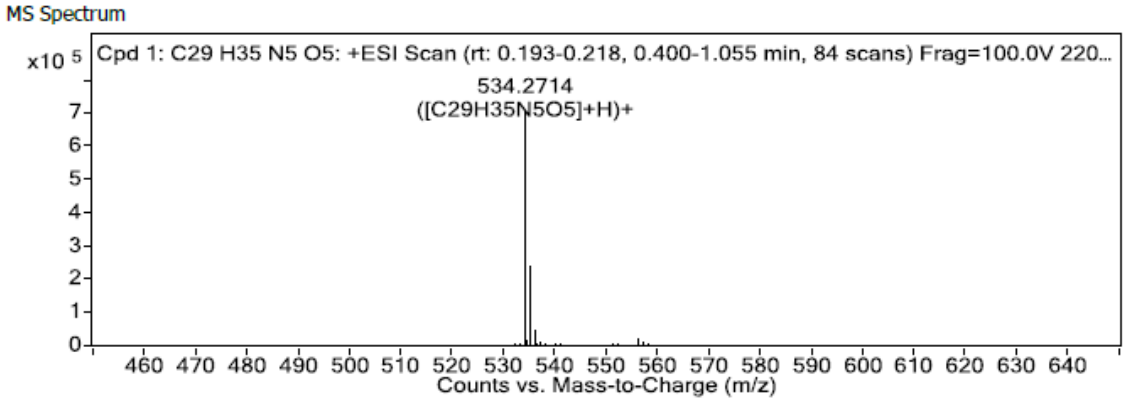
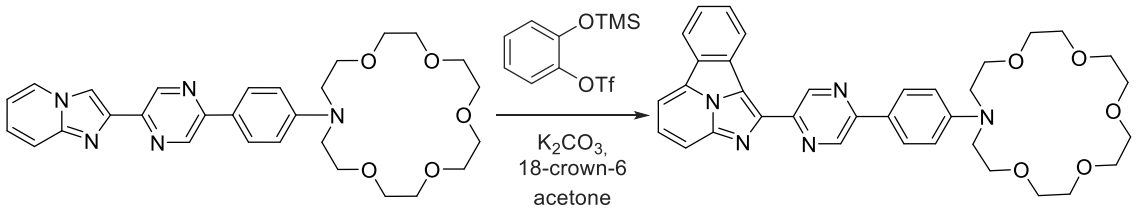


Figure S44. *Mass spectrum of compound* ***17****.*

2.1.19 Compound G3c, 16-(4-(5-(benzo[a]imidazo[5,1,2-cd]indolizin-1-yl)pyrazin-2-yl)phenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



17 **G3c**

A mixture of K_2CO_3 (155 mg, 1.12 mmol, 2 equiv.), 18-crown-6 (297 mg, 1.12 mmol, 2 equiv.), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (455.1 mg, 3.29 mmol, 3.0 equiv.) and compound **17** (300 mg, 0.56 mmol, 1.0 equiv.) was introduced in pressure vial and acetone (2 mL) was added. To this mixture 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (340 µL, 2.2 mmol, 4 equiv.) was added. The reactor was sealed and stirred in a preheated oil bath for 72 h at 75°C. After this time, the reaction mixture was cooled to room temperature and was concentrated *in vacuo*. The residue was purified by column chromatography (eluent: from CH_2Cl_2 to 5% MeOH in CH_2Cl_2). The title compound was obtained as an orange solid. Yield 10%.

Exact mass: ESI-MS [$C_{35}H_{37}N_5O_5$]: calculated: m/z= 607.2795, found: m/z= 607.2799.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.74 (s, 1H), 9.23 (d, J = 1.5 Hz, 1H), 9.01 (d, J = 8.0 Hz, 1H), 8.38 (d, J = 7.9 Hz, 1H), 8.14–8.04 (m, 4H), 8.03–7.95 (m, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 3.88–3.52 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 151.45 (1C, C_{quat}), 149.30 (1C, C_{quat}), 144.95 (1C, C_{quat}), 143.48 (1C, C_{quat}), 142.51 (1C, CH), 140.30 (1C, CH), 139.57 (1C, C_{quat}), 131.48 (1C, C_{quat}), 131.02 (1C, C_{quat}), 129.68 (1C, C_{quat}), 129.26 (1C, CH), 128.15 (2C, CH), 127.01 (1C, CH),

125.42 (1C, CH), 123.72 (1C, C_{quat}), 123.62 (1C, CH), 122.65 (1C, CH), 113.67 (1C, CH), 111.90 (2C, CH), 109.15 (1C, CH), 99.97 (1C, C_{quat}), 70.80 (8C, CH_2, crown), 68.63 (2C, CH_2, crown), 51.36 (2C, CH_2, crown).

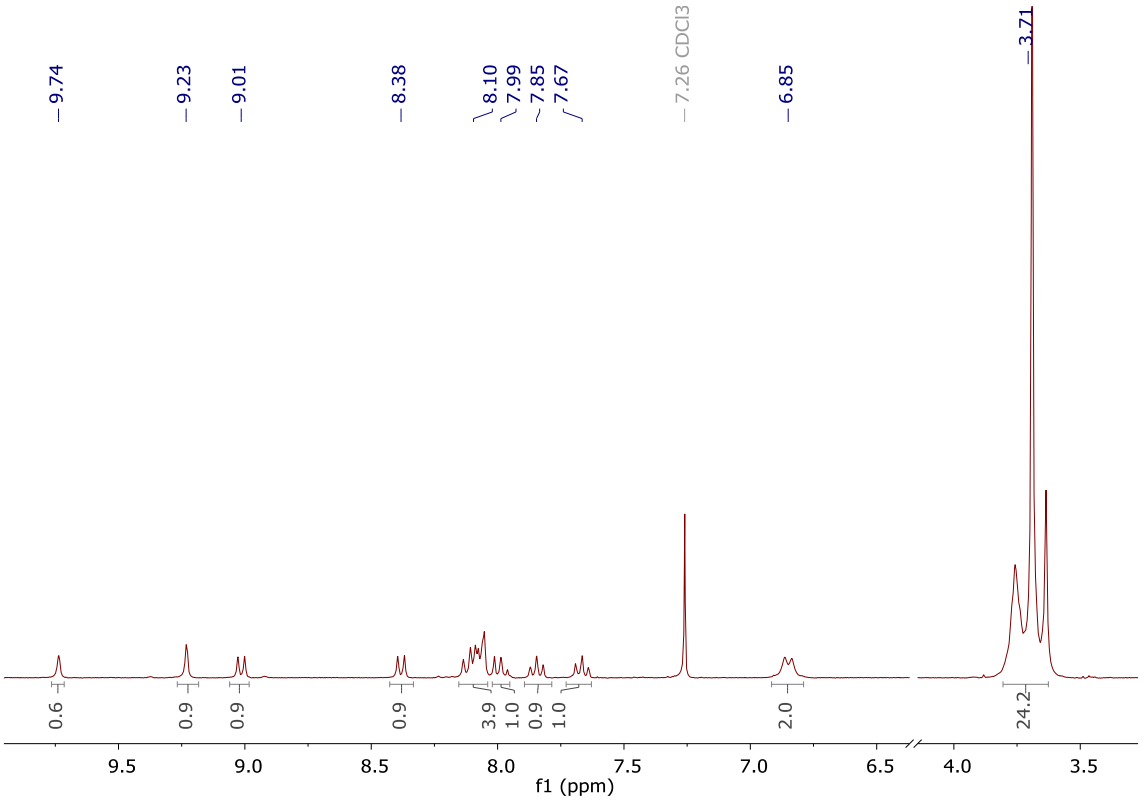


Figure S45. *^{1}H NMR spectrum of compound **G3c** ($CDCl_3$, 300 MHz).*

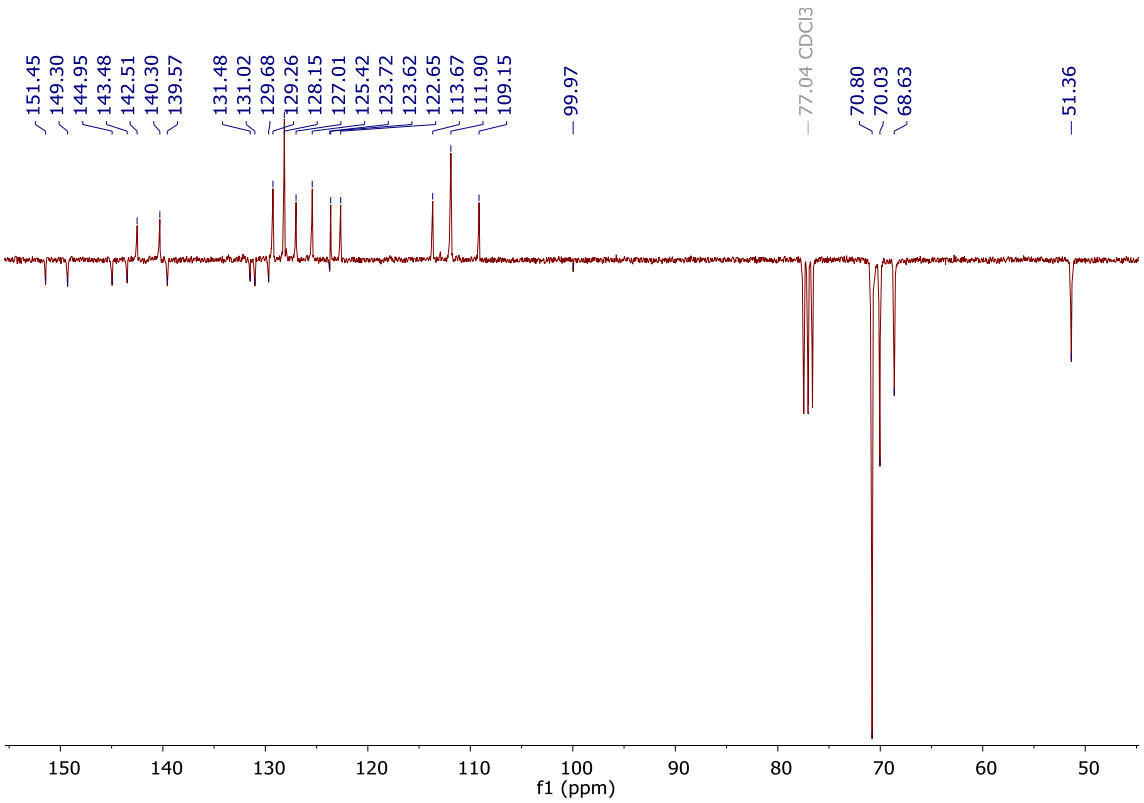


Figure S46. *^{13}C APT NMR spectrum of compound **G3c** ($CDCl_3$, 300 MHz).*

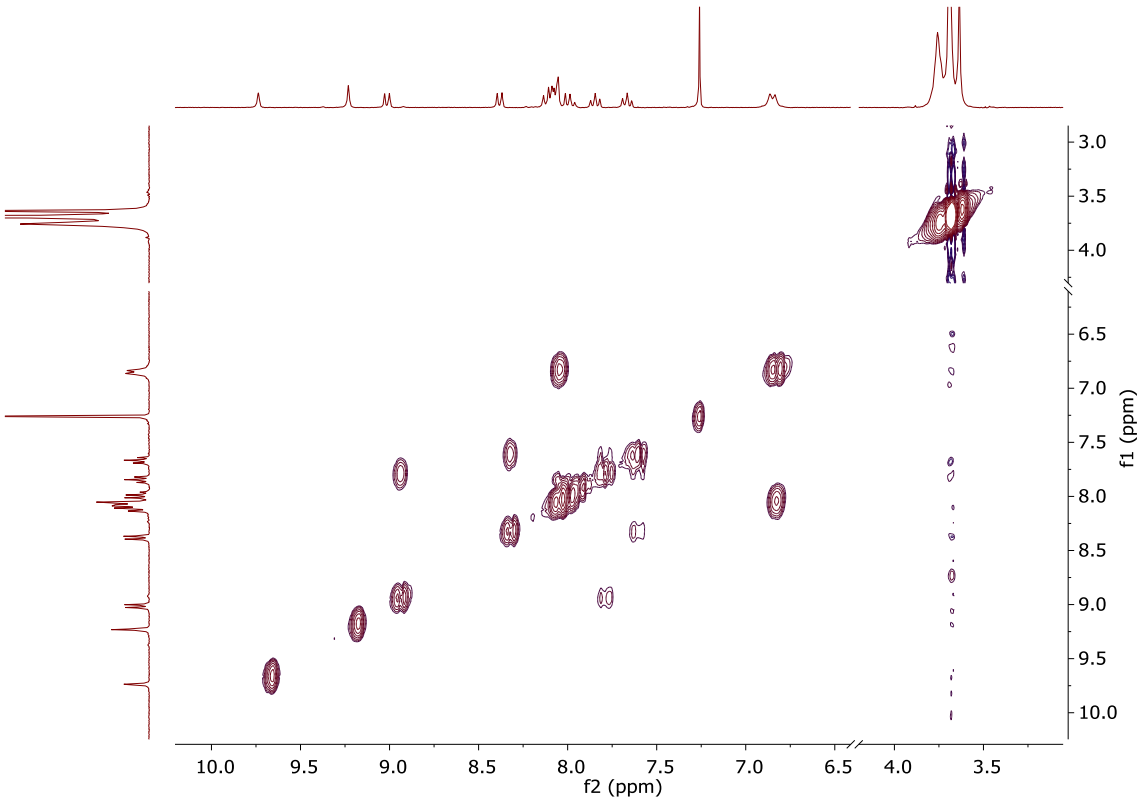


Figure S47. *COSY NMR spectrum of compound **G3c** ($CDCl_3$, 300 MHz).*

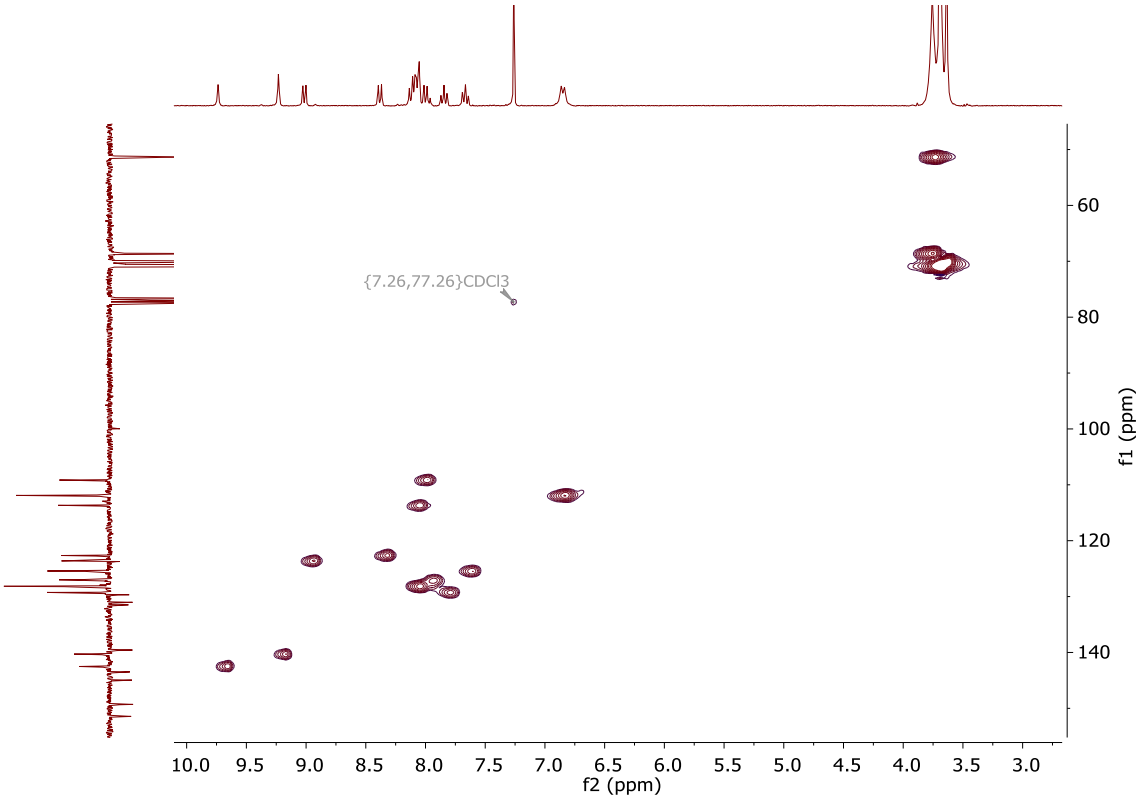


Figure S48. *HSQC NMR spectrum of compound* ***G3c*** *($CDCl_3$, 300 MHz).*

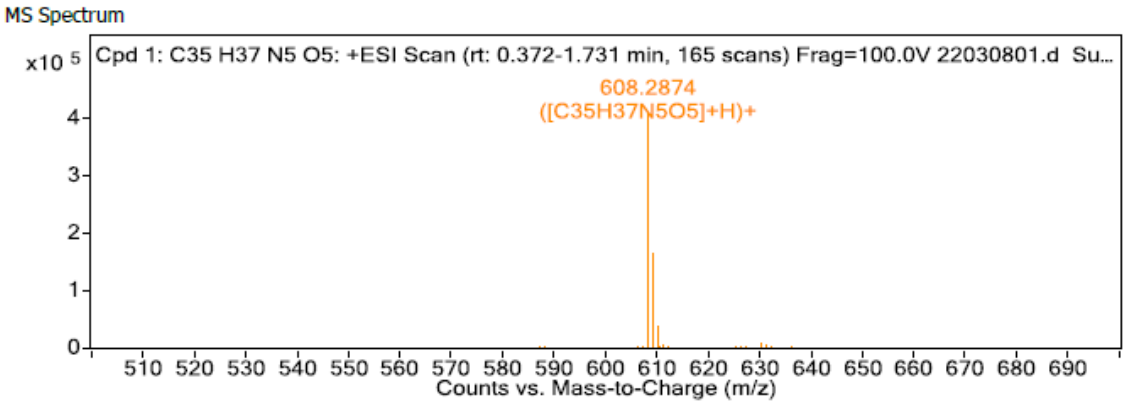
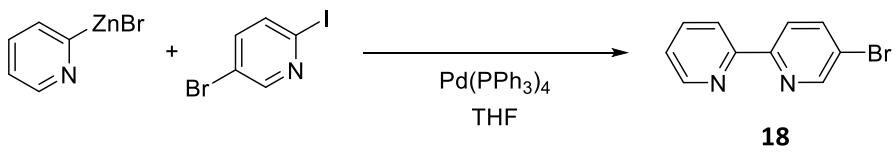


Figure S49. *Mass spectrum of compound* ***G3c****.*

2.1.20 Compound 18, 5-bromo-2,2'-bipyridine

Compound **18** was synthesized by following a slightly modified procedure described by Rieke et al.[7]



18

To 5-bromo-2-iodopyridine (5.00 g, 17.6 mmol) and $Pd(PPh_3)_4$ (204 mg, 0.18 mmol) in a Schlenk under N_2 atmosphere, the commercial 0.5 M 2-pyridylzinc bromide solution in THF (42.3 mL, 21.1 mmol) was added slowly via syringe. The reaction mixture was stirred at 70°C for 72 h. After cooling down, aqueous EDTA/Na_2CO_3 solution was added until the precipitate dissolved and the mixture was extracted with Et_2O. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The beige product was used in the next step without further purification. Quantitative yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 (dd, J = 2.4, 0.7 Hz, 1H), 8.66 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.37 (dt, J = 8.0, 1.1 Hz, 1H), 8.31 (dd, J = 8.5, 0.7 Hz, 1H), 7.93 (dd, J = 8.5, 2.4 Hz, 1H), 7.81 (ddd, J = 8.0, 7.5, 1.8 Hz, 1H), 7.32 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H).

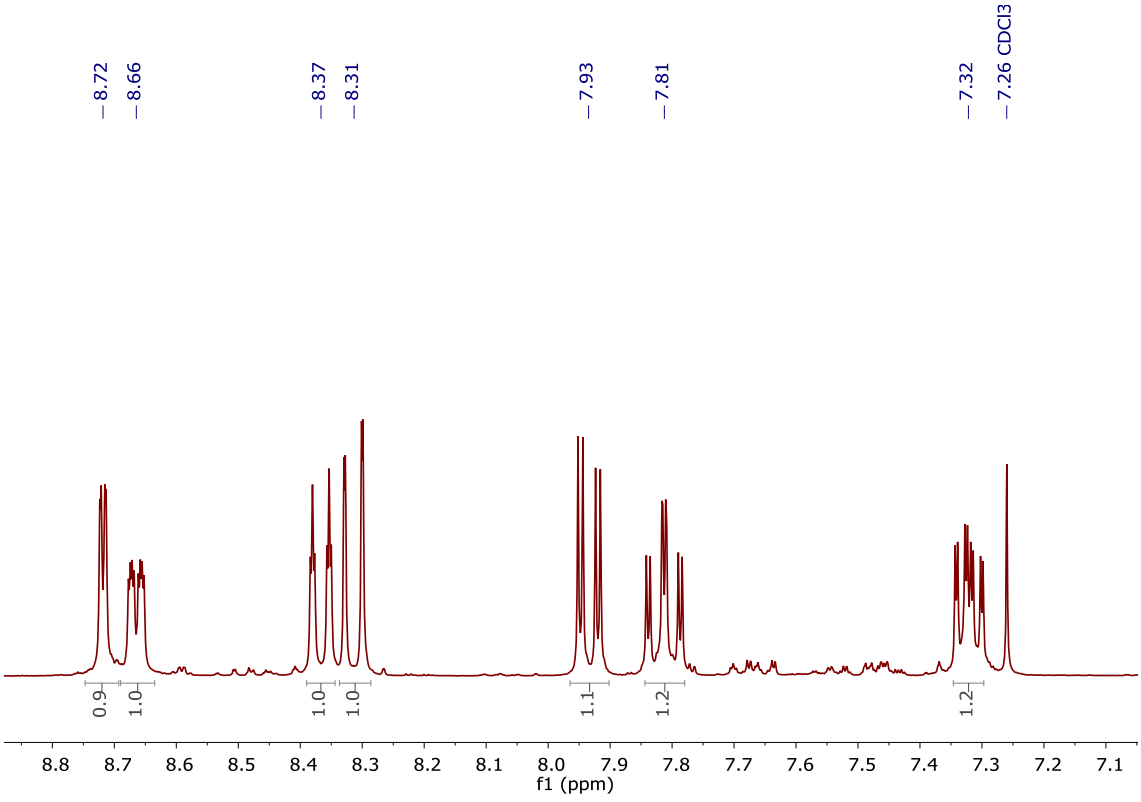
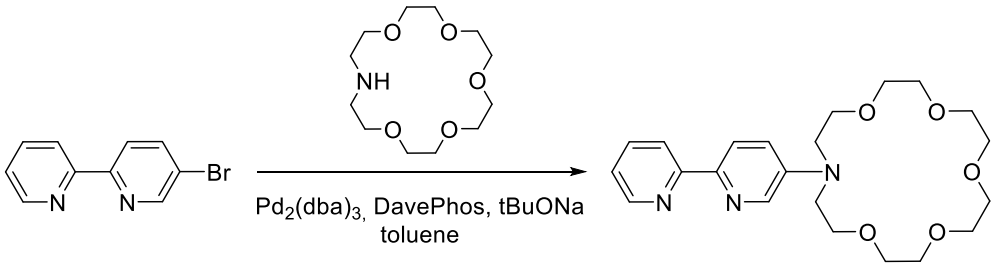


Figure S50. *^{1}H NMR spectrum of compound **18** ($CDCl_3$, 300 MHz).*

2.1.21 Compound L1, 16-([2,2'-bipyridin]-5-yl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



18 **L1**

A mixture of $Pd_2(dba)_3$ (20.2 mg, 22 µmol, 2 mol%), DavePhos (26.1 mg, 66.4 µmol, 6 mol%), ^tBuONa (159 mg, 1.66 mmol, 1.5 equiv.), **18** (260 mg, 1.11 mol, 1 equiv.) and 1-aza-18-crown-6 (291.2 mg, 1.11 mmol, 1 equiv.) was introduced in a Schlenk tube and dissolved in 6 mL of anhydrous toluene, under N_2. The tube was sealed and kept in a preheated oil bath at and stirred overnight at 110°C. After this time, the reaction mixture was cooled to room temperature and was concentrated *in vacuo*. The residue was purified by column chromatography (CH_2Cl_2 as eluent). The title compound was obtained as a brown oil. Yield 50%.

Exact mass: ESI-MS [$C_{22}H_{31}N_3O_5$]: calculated: m/z= 417.2264, found: m/z= 417.2269.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 8.24–8.14 (m, 3H), 7.71 (dt, J = 7.7, 1.7 Hz, 1H), 7.15 (ddd, J = 7.4, 4.9, 1.2 Hz, 1H), 7.08 (dd, J = 8.9, 3.2 Hz, 1H), 3.76–3.59 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.59 (1C, C_{quat}), 148.86 (1C, CH), 143.98 (1C, C_{quat}), 143.93 (1C, C_{quat}), 136.58 (1C, CH), 133.28 (1C, CH), 121.95 (1C, CH), 121.36 (1C, CH), 119.52 (1C, CH), 118.51 (1C, CH), 70.80 (8C, CH_2, crown), 68.46 (2C, CH_2, crown), 51.05 (2C, CH_2, crown).

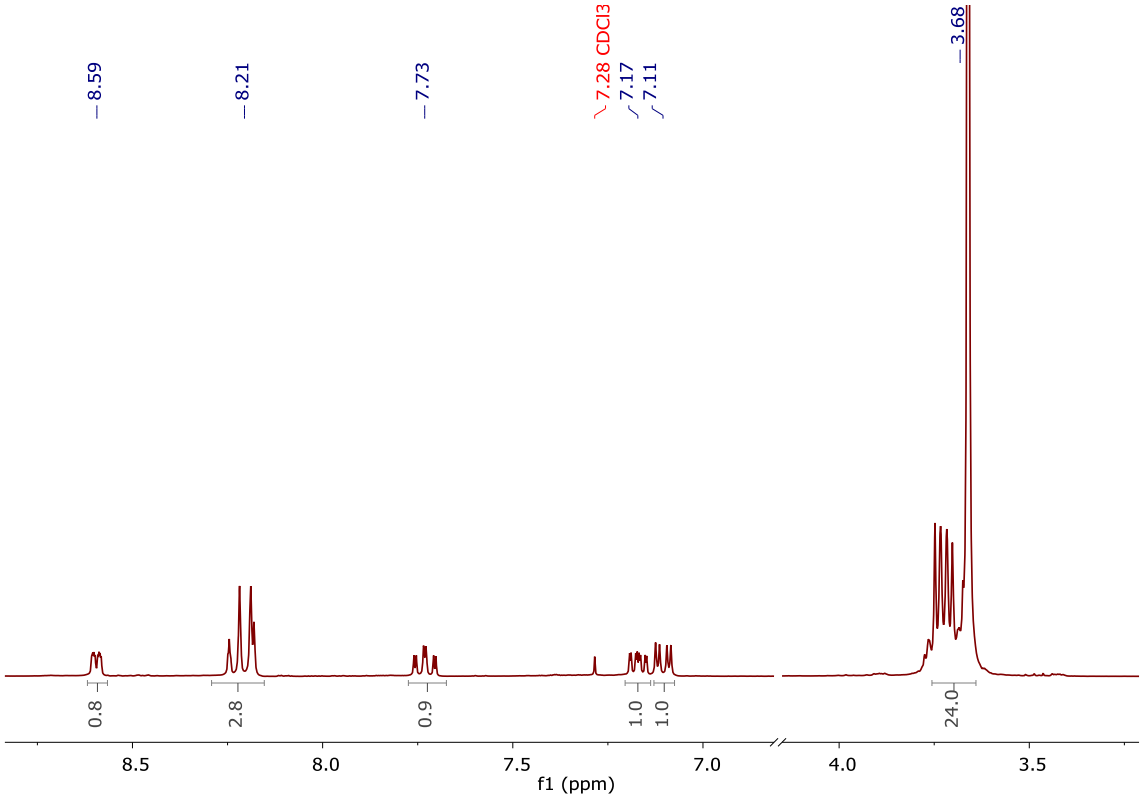


Figure S51. *^{1}H NMR spectrum of compound **L1** ($CDCl_3$, 300 MHz).*

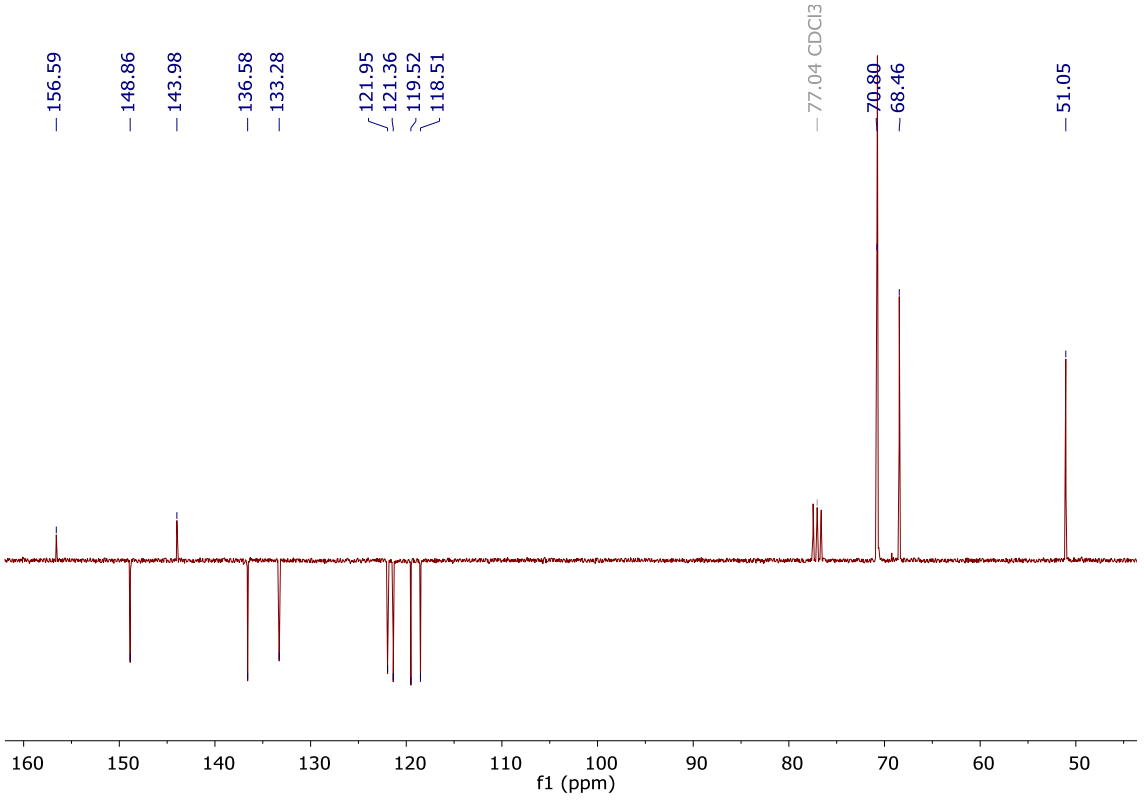


Figure S52. *^{13}C APT NMR spectrum of compound **L1** ($CDCl_3$, 300 MHz).*

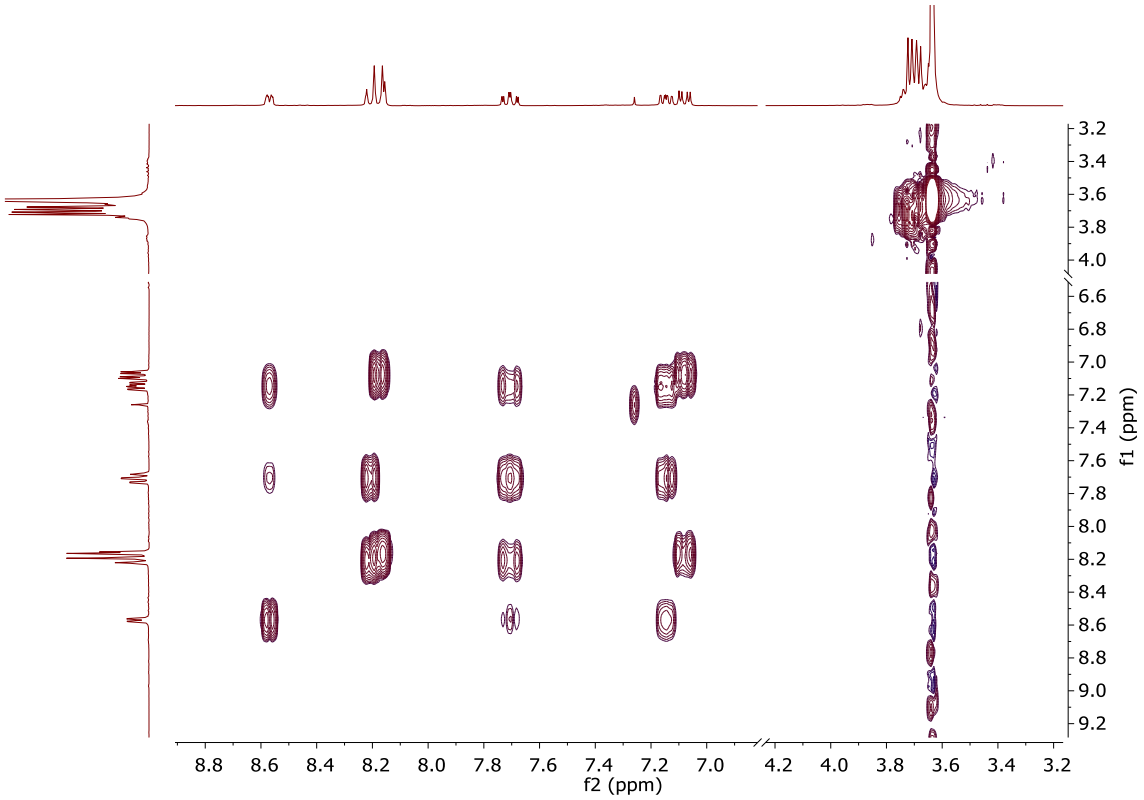


Figure S53. *COSY NMR spectrum of compound* ***L1*** *($CDCl_3$, 300 MHz).*

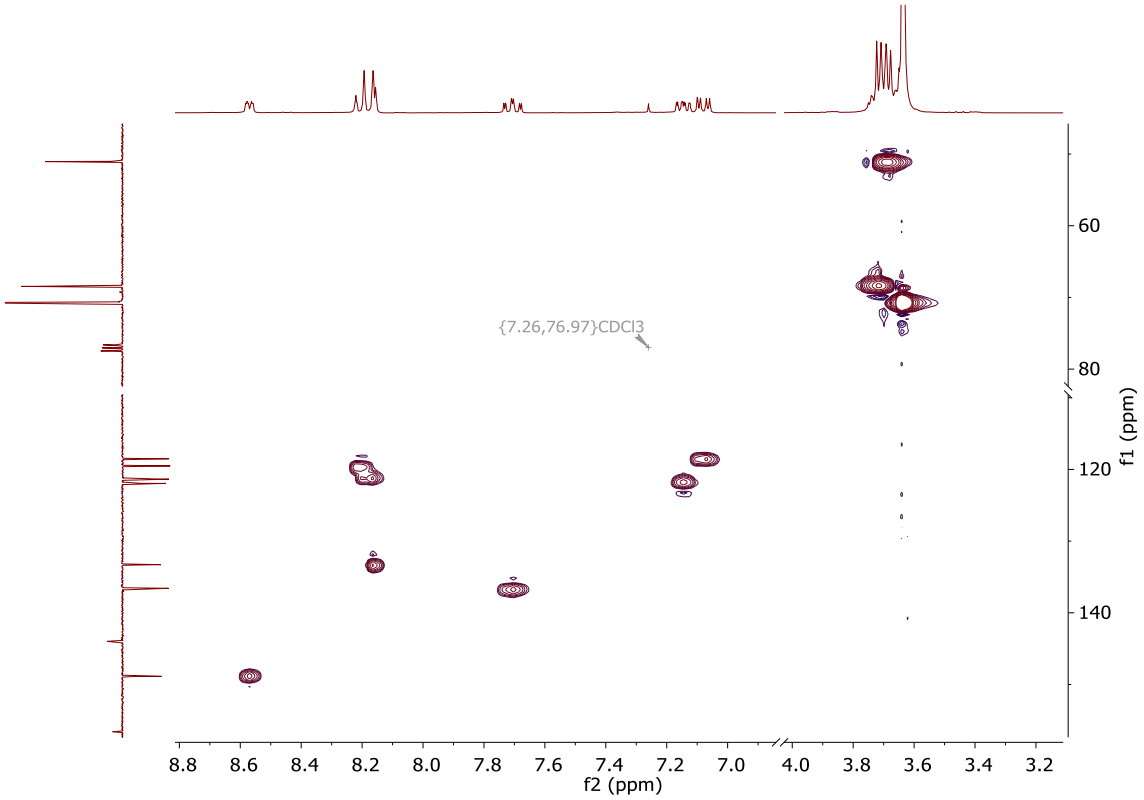


Figure S54. *HSQC NMR spectrum of compound* ***L1*** *($CDCl_3$, 300 MHz).*

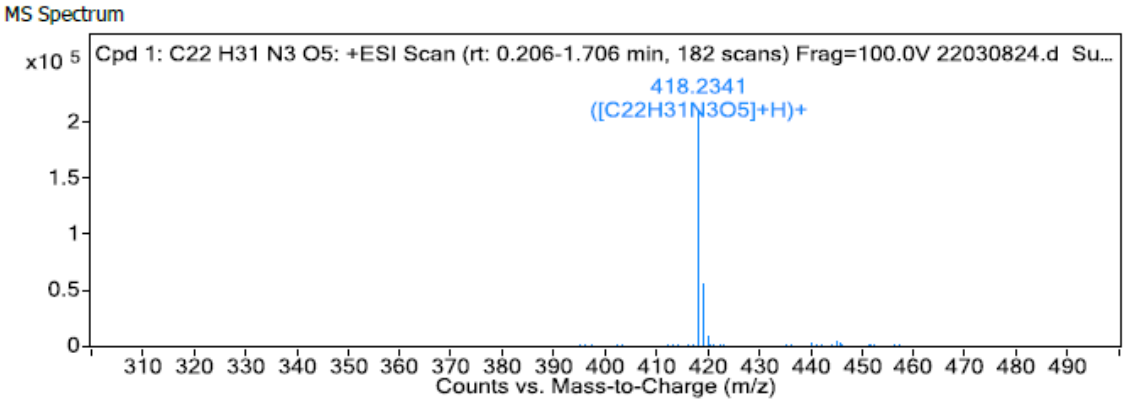
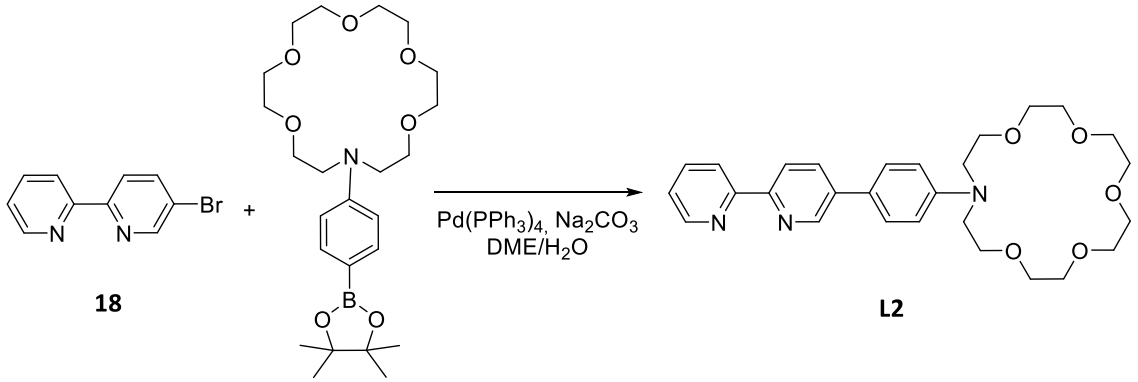


Figure S55. *Mass spectrum of compound* ***L1****.*

2.1.22 Compound L2, 16-(4-([2,2'-bipyridin]-5-yl)phenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



18 **16** **L2**

A mixture of $Pd(PPh_3)_4$ (205 mg, 0.18 mmol), Na_2CO_3 (1.88 g, 17.73 mmol), compound **18** (833 mg, 3.54 mmol) and compound **16** (1.65 g, 3.54 mmol) was introduced in a Schlenk tube and dissolved in 55 mL of degassed DME/H_2O mixture (3:1 v/v), under N_2. The reaction was refluxed at 85 °C overnight. After this time, the solvent was removed and the residue was purified by column chromatography (eluent: from CH_2Cl_2 to 5% MeOH in CH_2Cl_2). The title compound was obtained as a pink solid. Yield 56%.

Exact mass: ESI-MS [$C_{28}H_{35}N_3O_5$]: calculated: m/z= 493.2577, found: m/z= 493.2575.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.89 (dd, J = 2.4, 0.8 Hz, 1H), 8.68 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.37–8.34 (m, 2H), 7.96 (dd, J = 8.3, 2.4 Hz, 1H), 7.81 (td, J = 7.9, 1.8 Hz, 1H), 7.54 (d, J = 8.9 Hz, 2H), 7.29 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 6.81 (d, J = 8.9 Hz, 2H), 3.81–3.61 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.22 (1C, C_{quat}), 153.49 (1C, C_{quat}), 149.20 (1C, CH), 147.98 (1C, C_{quat}), 146.74 (1C, CH), 136.87 (1C, CH), 136.40 (1C, C_{quat}), 133.84 (1C, CH), 127.87 (2C, CH, C_6H_4), 124.60 (1C, C_{quat}), 123.36 (1C, CH), 120.95 (1C, CH), 120.83 (1C, CH), 112.13 (2C, CH, C_6H_4), 70.93 (8C, CH_2, crown), 68.70 (2C, CH_2, crown), 51.43 (2C, CH_2, crown).

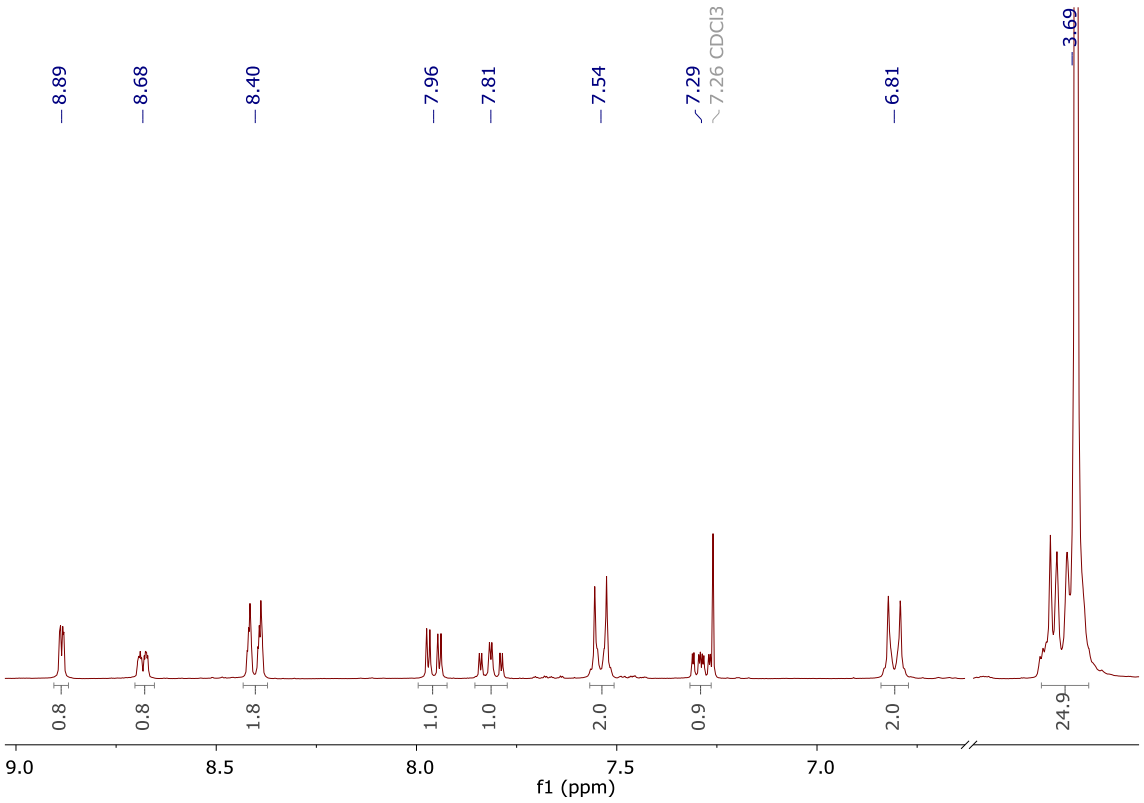


Figure S56. *^{1}H NMR spectrum of compound **L2** ($CDCl_3$, 300 MHz).*

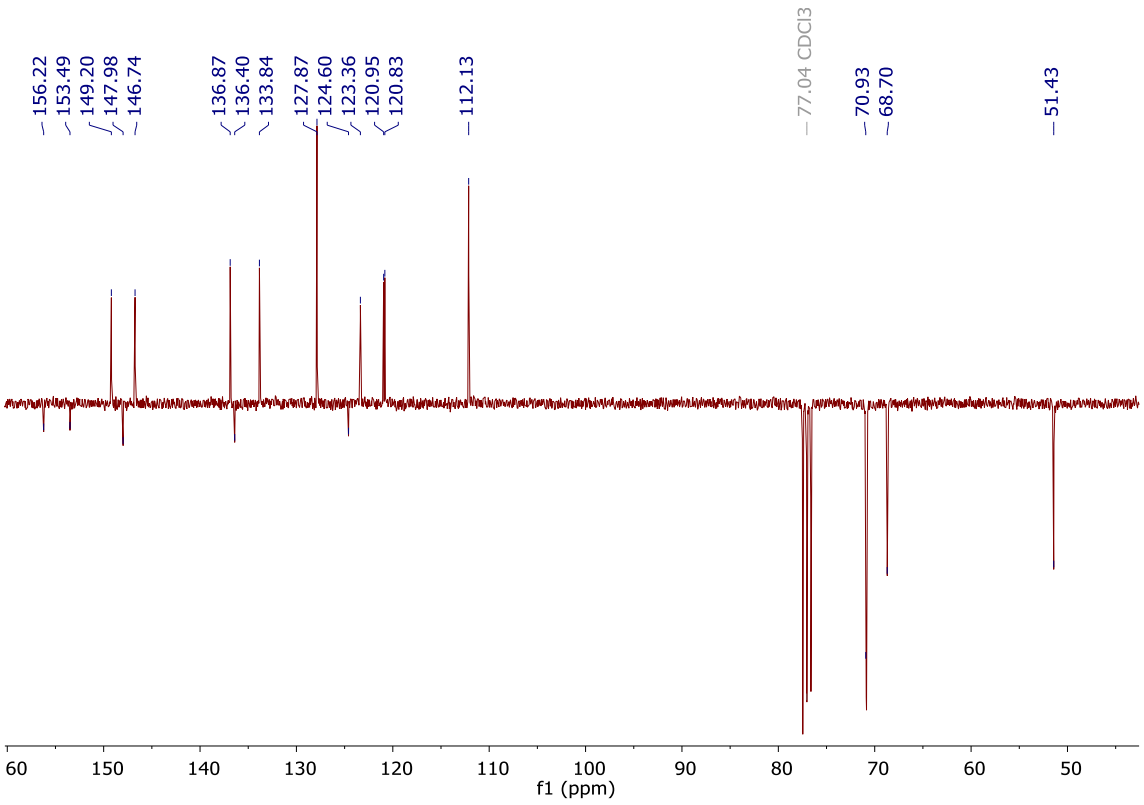


Figure S57. *^{13}C APT NMR spectrum of compound **L2** ($CDCl_3$, 300 MHz).*

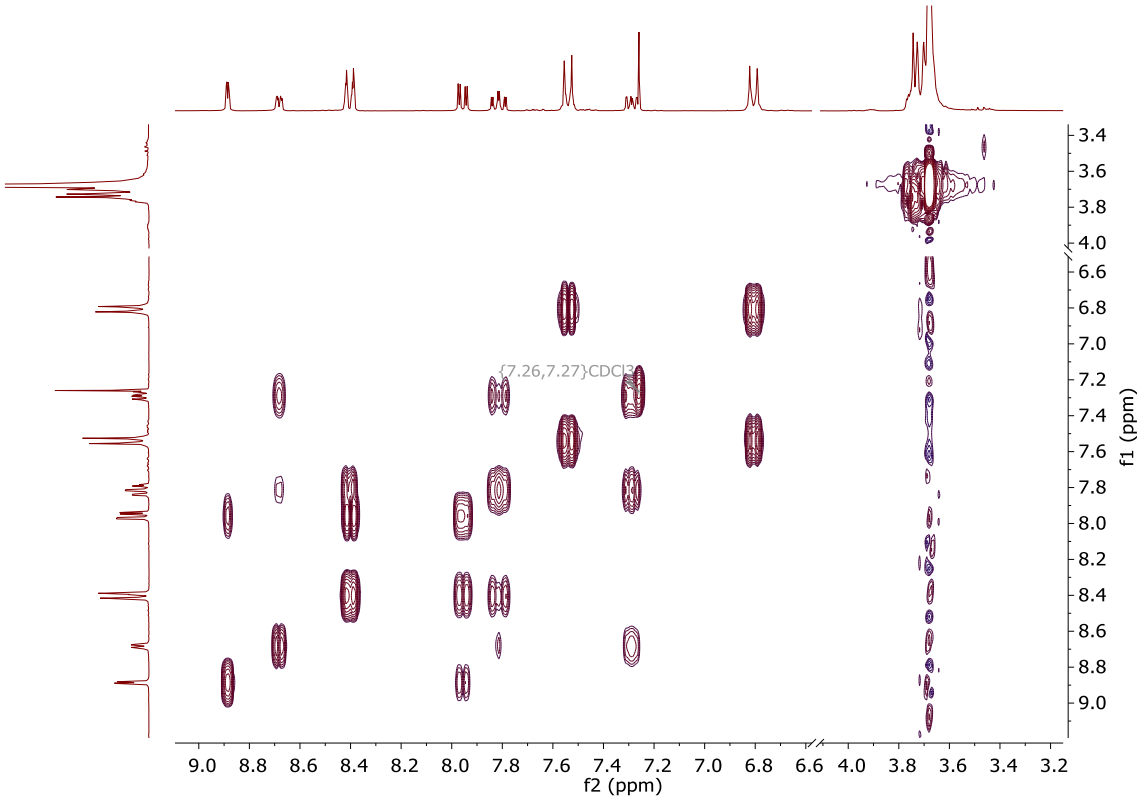


Figure S58. *COSY NMR spectrum of compound **L2** ($CDCl_3$, 300 MHz).*

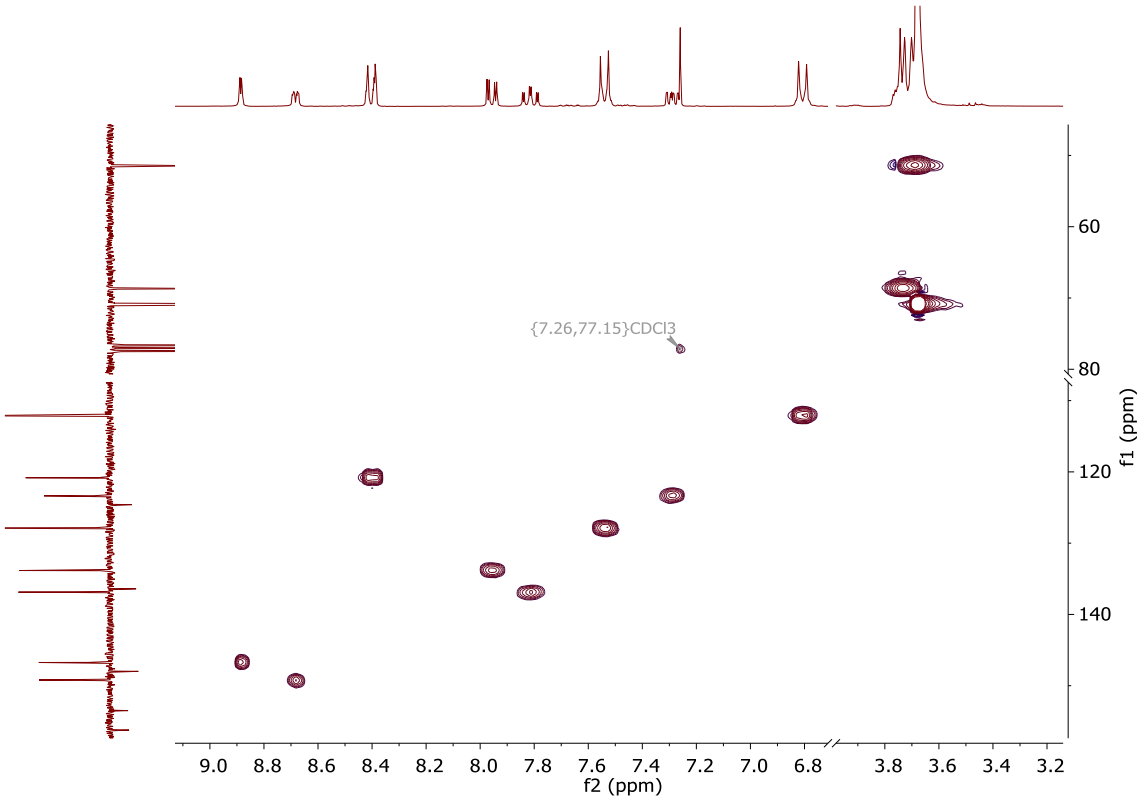


Figure S59. *HSQC NMR spectrum of compound* ***L2*** *($CDCl_3$, 300 MHz).*

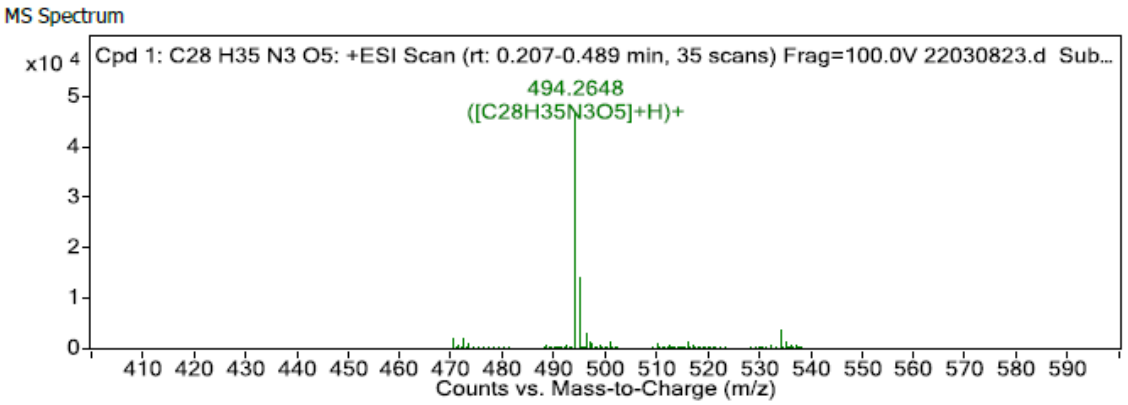
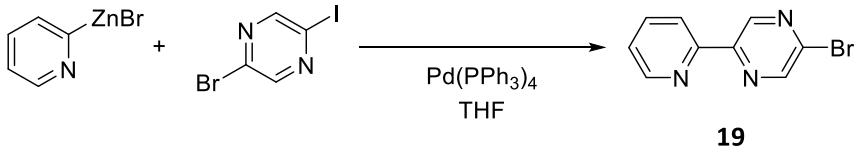


Figure S60. *Mass spectrum of compound* ***L2****.*

2.1.23 Compound 19, 2-bromo-5-(pyridin-2-yl)pyrazine



19

To 2-bromo-5-iodopyrazine (5.00 g, 17.6 mmol) and $Pd(PPh_3)_4$ (204 mg, 0.18 mmol) in a Schlenk under N_2 atmosphere, the commercial 0.5 M 2-pyridylzinc bromide solution in

THF (42.3 mL, 21.1 mmol) was added slowly via syringe. The reaction mixture was stirred at 70°C for 72 h. After cooling down, aqueous EDTA/Na_2CO_3 solution was added until the precipitate dissolved and the mixture was extracted with Et_2O. The organic phase was dried over anhydrous $MgSO_4$ and evaporated. The beige product was used in the next step without further purification. Quantitative yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.40 (d, J = 1.4 Hz, 1H), 8.71 (m, 3H), 8.33 (dt, J = 8.0, 1.1 Hz, 1H), 7.85 (td, J = 7.8, 1.8 Hz, 1H), 7.38 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.36 (1C, C_{quat}), 149.70 (1C, CH), 146.25 (1C, CH), 143.40 (1C, CH), 140.85 (1C, C_{quat}), 137.30 (1C, CH), 124.81 (1C, CH), 121.53 (1C, CH), 100.11 (1C, C_{quat}).

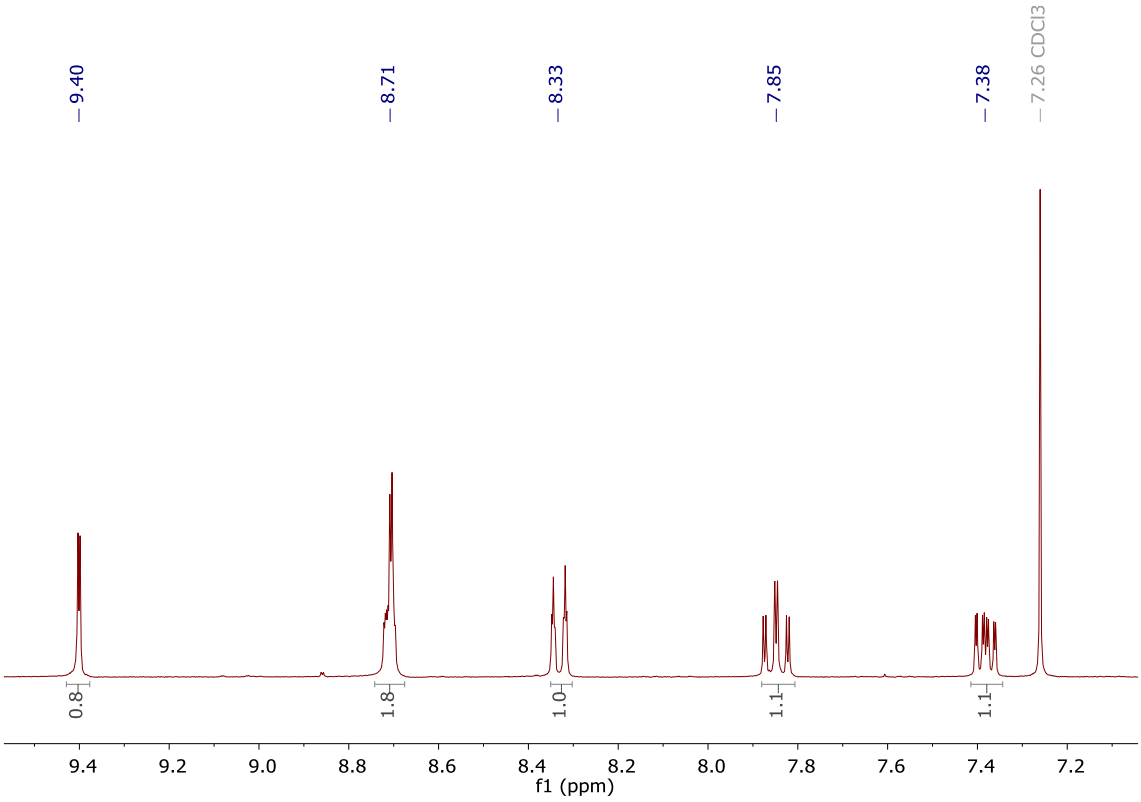


Figure S61. *^{1}H NMR spectrum of compound **19** ($CDCl_3$, 300 MHz).*

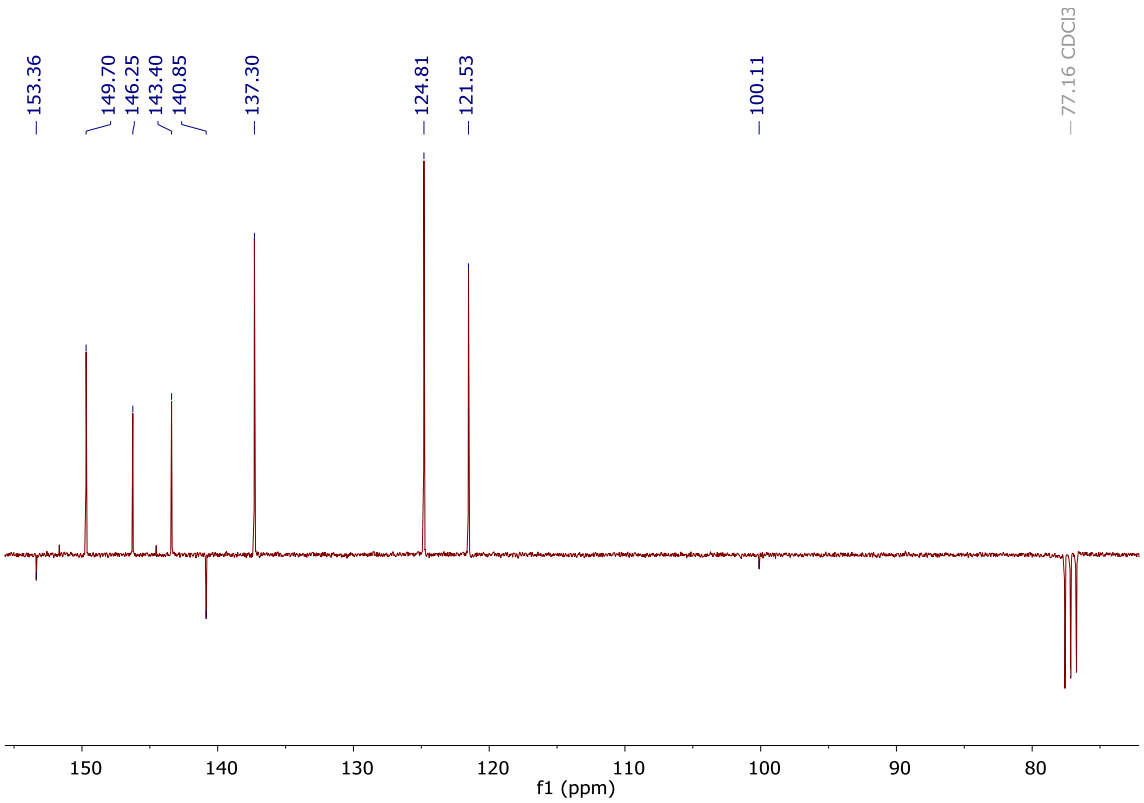


Figure S62. *13C APT NMR spectrum of compound* ***19*** *($CDCl_3$, 300 MHz).*

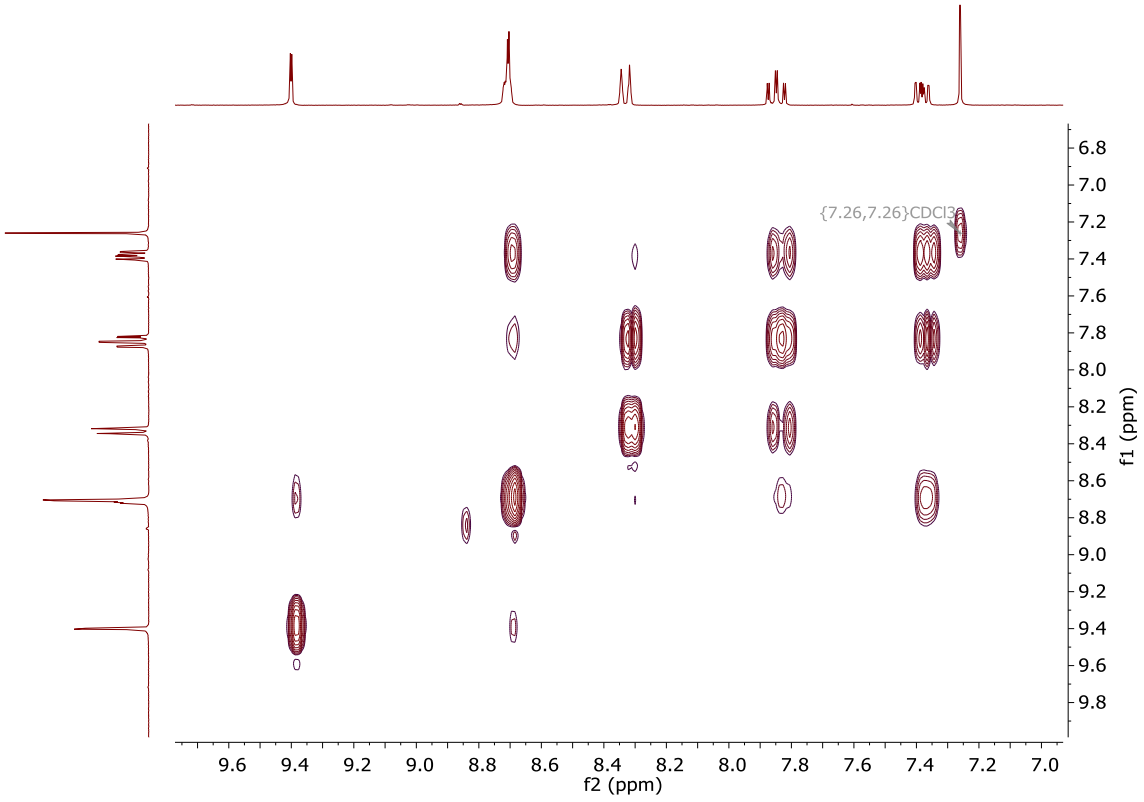


Figure S63. *COSY NMR spectrum of compound* ***19*** *($CDCl_3$, 300 MHz).*

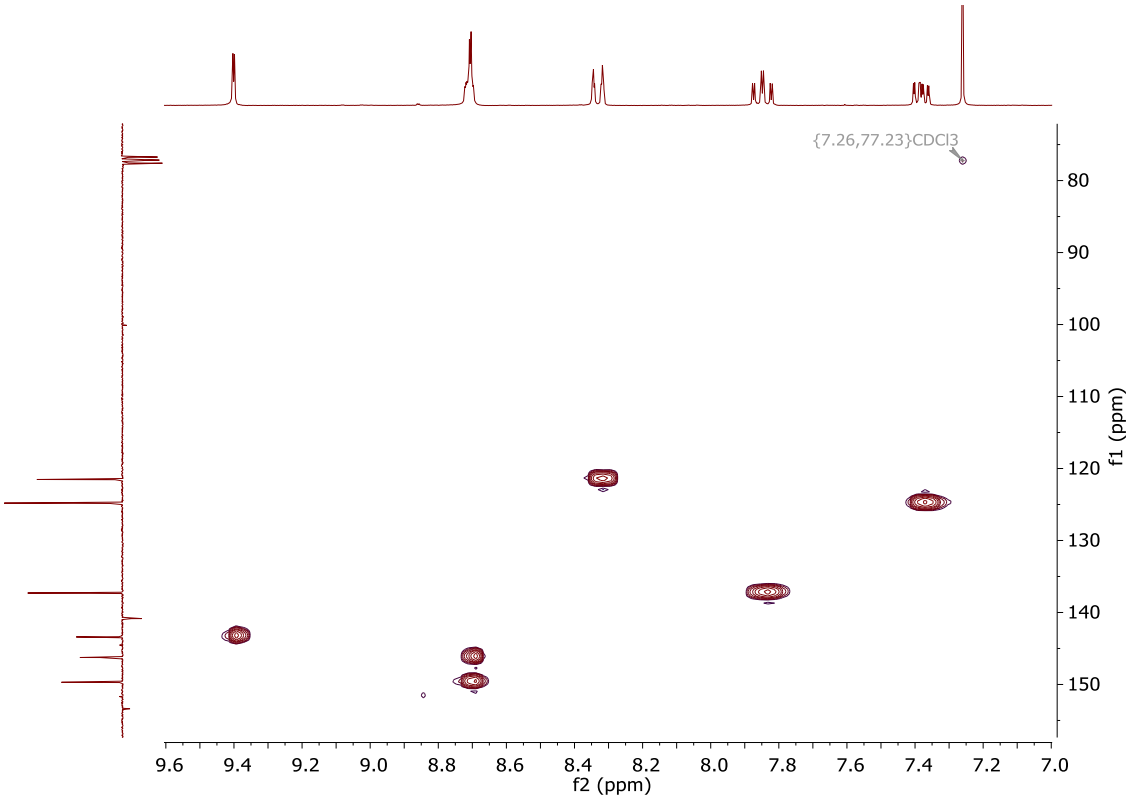
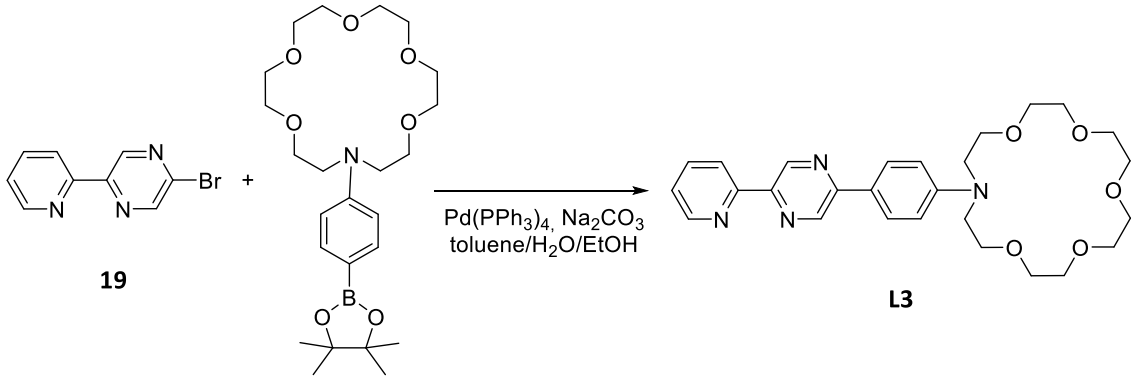


Figure S64. *HSQC NMR spectrum of compound **19** ($CDCl_3$, 300 MHz).*

2.1.24 Compound L3, 16-(4-(5-(pyridin-2-yl)pyrazin-2-yl)phenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane



19 **16** **L3**

A mixture of $Pd(PPh_3)_4$ (122 mg, 0.11 mmol, 5 mol%), Na_2CO_3 (1.12 g, 10.6 mmol, 5 equiv.), compound **19** (500 mg, 2.12 mmol, 1 equiv.) and compound **16** (0.98 g, 2.12 mmol, 1 equiv.) was introduced in a Schlenk tube and a toluene/H_2O/EtOH mixture of solvents was added (5:5:1 v/v/v), under N_2. The reaction was refluxed at 85°C overnight. After this time, the solvent was removed and the residue was purified by column chromatography (eluent: from CH_2Cl_2 to 1% MeOH in CH_2Cl_2). The title compound was obtained as an orange solid. Yield 50%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.52 (d, J = 1.5 Hz, 1H), 8.93 (d, J = 1.5 Hz, 1H), 8.68 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 8.30 (dt, J = 8.0, 1.1 Hz, 1H), 7.96 (d, J = 9.0 Hz, 2H), 7.79 (td, J = 7.8, 1.8 Hz, 1H), 7.28 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H), 6.78 (d, J = 9.1 Hz, 2H), 3.76–3.60 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 154.73 (1C, C_{quat}), 152.30 (1C, C_{quat}), 149.46 (1C, CH), 149.37 (1C, C_{quat}), 147.23 (1C, C_{quat}), 142.25 (1C, CH), 139.50 (1C, CH), 136.95 (1C, CH), 128.20 (2C, CH, C_6H_4), 123.74 (1C, CH), 123.51 (1C, C_{quat}), 120.92 (1C, CH), 111.90 (2C, CH, C_6H_4), 70.91 (8C, CH_2, crown), 68.64 (2C, CH_2, crown), 51.40 (2C, CH_2, crown).

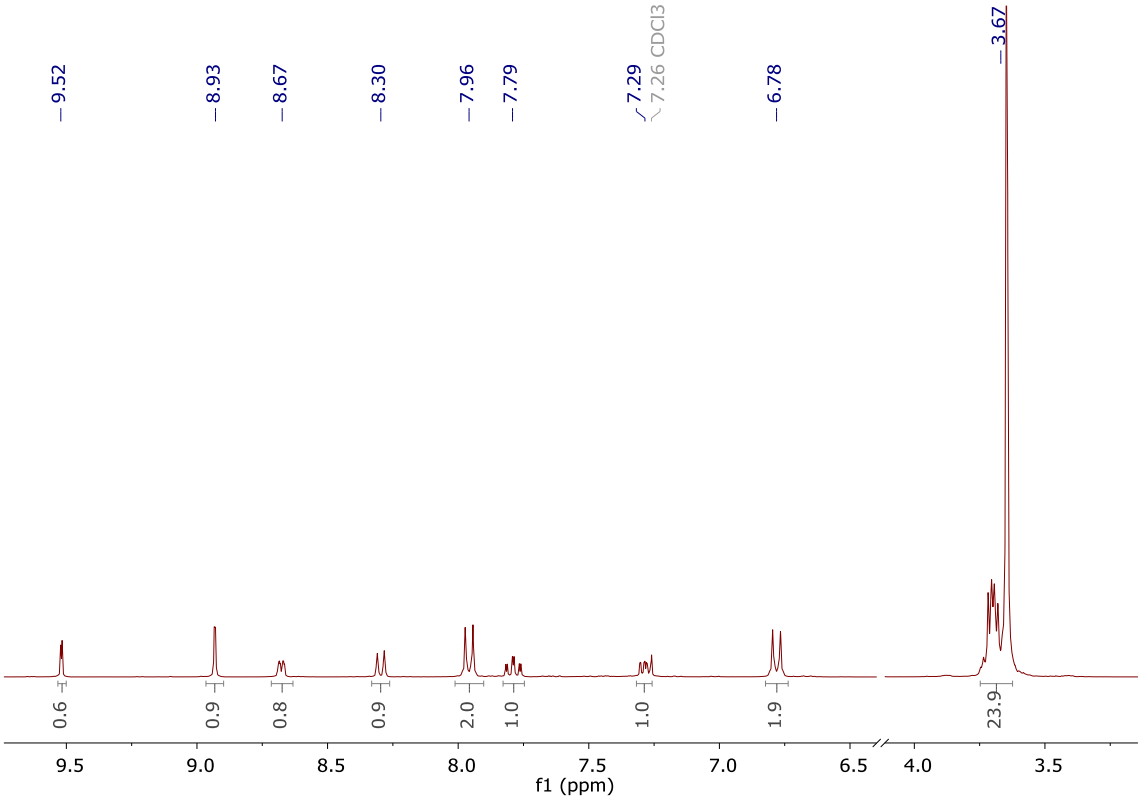


Figure S65. *^{1}H NMR spectrum of compound **L3** ($CDCl_3$, 300 MHz).*

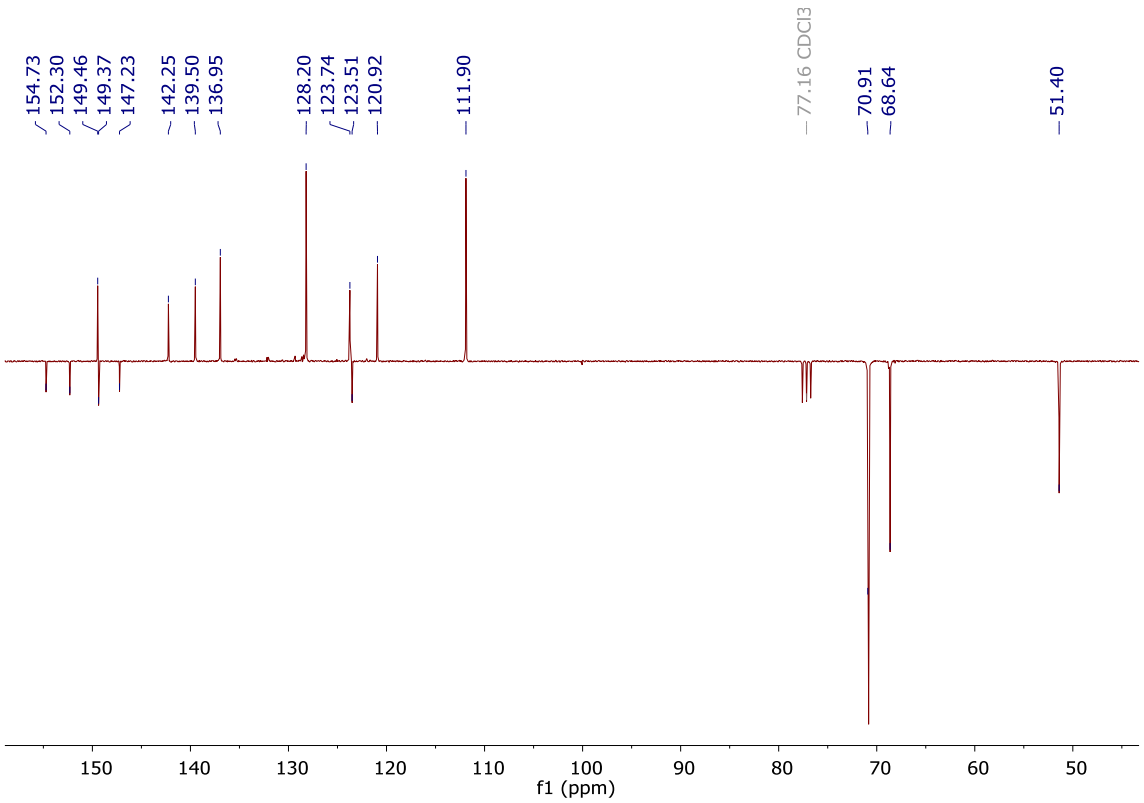


Figure S66. *^{13}C APT NMR spectrum of compound **L3** ($CDCl_3$, 300 MHz).*

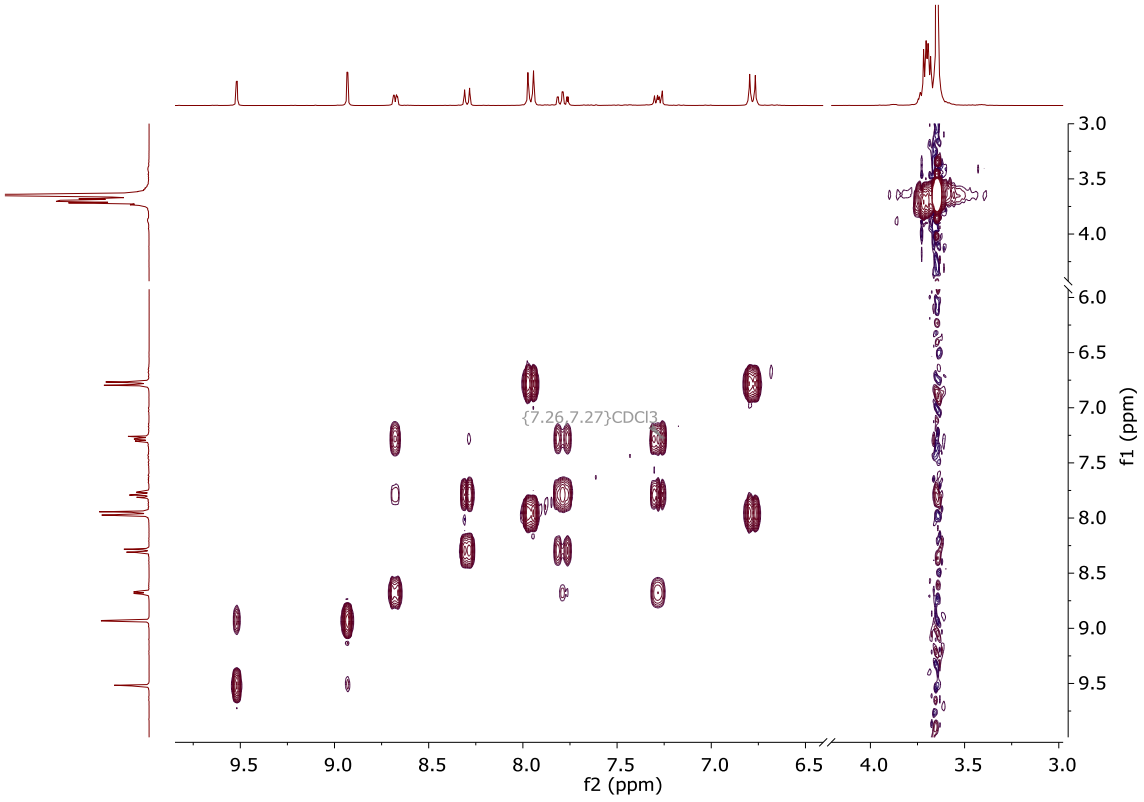


Figure S67. *COSY NMR spectrum of compound **L3** ($CDCl_3$, 300 MHz).*

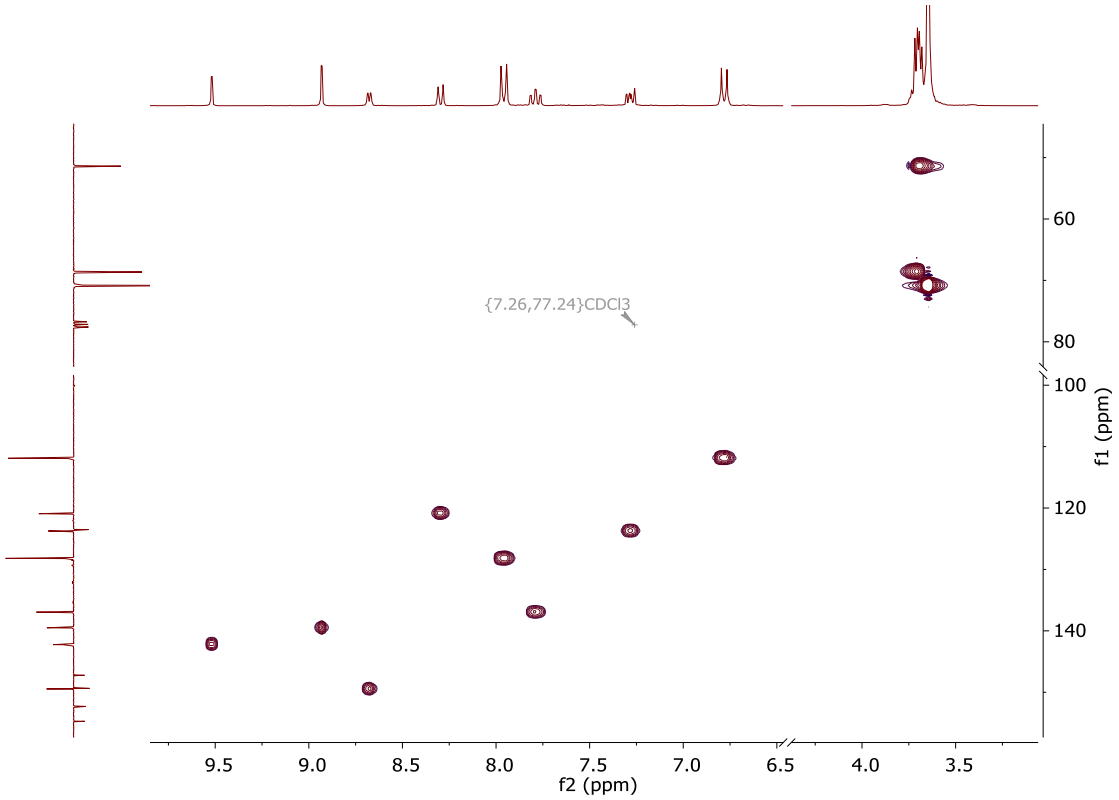


Figure S68. *HSQC NMR spectrum of compound* ***L3*** *($CDCl_3$, 300 MHz).*

2.2 PHOTOPHYSICAL CHARACTERIZATION

2.2.1 G3a

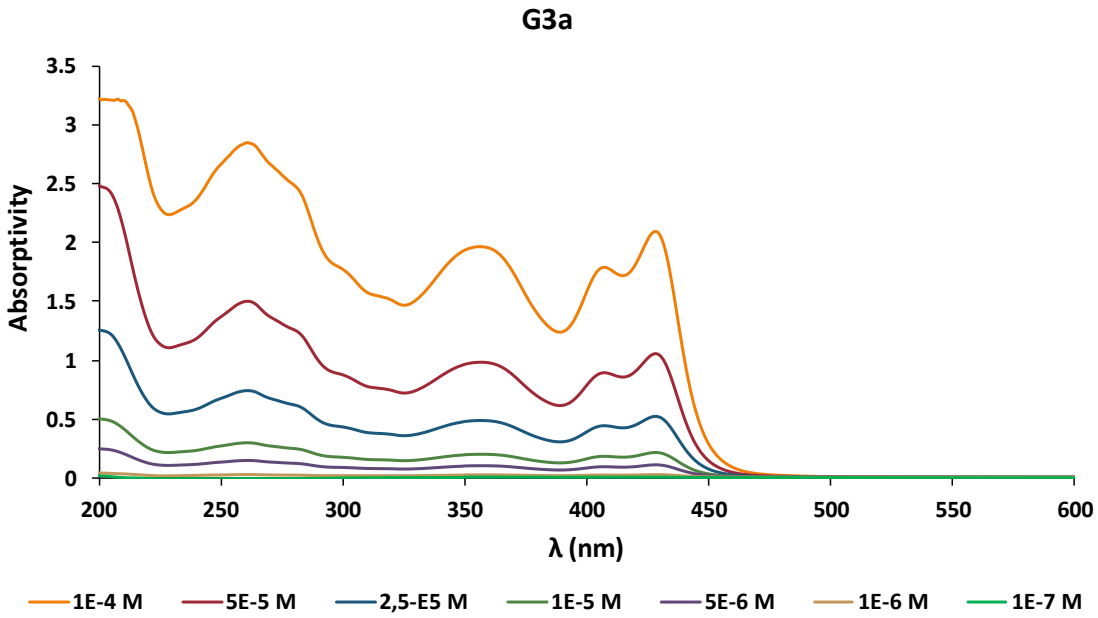
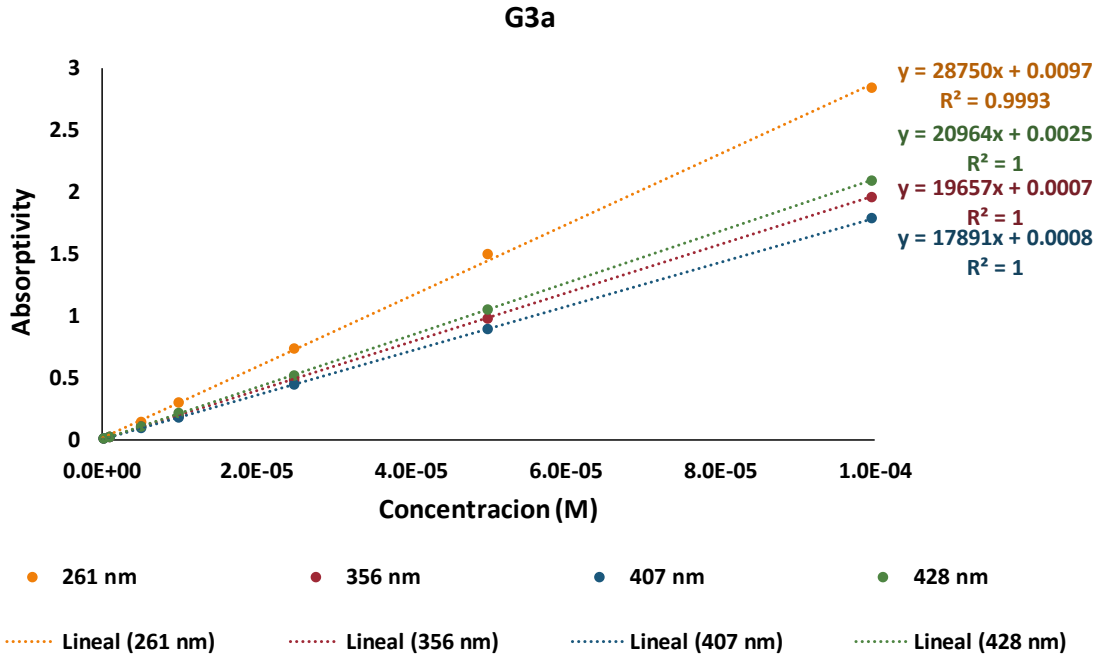


Figure S69. *UV-vis absorption spectra of free* ***G3a*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
261	28750
356	19657
407	17891
428	20964

Figure S70. *Calculated molar extinction coefficients of* ***G3a*** *at selected absorption maxima.*

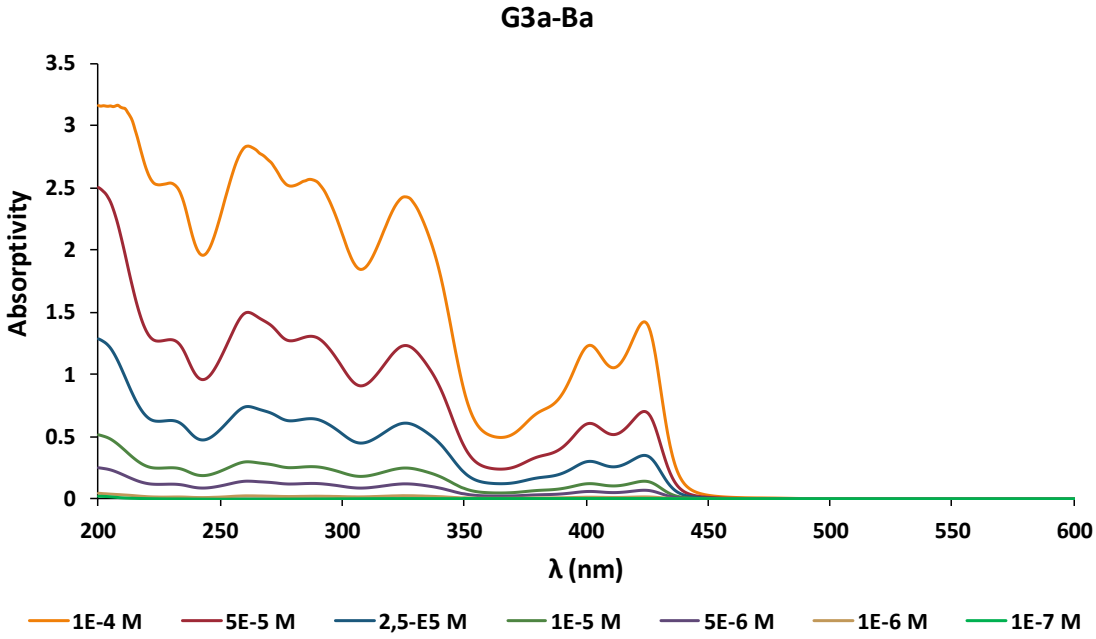
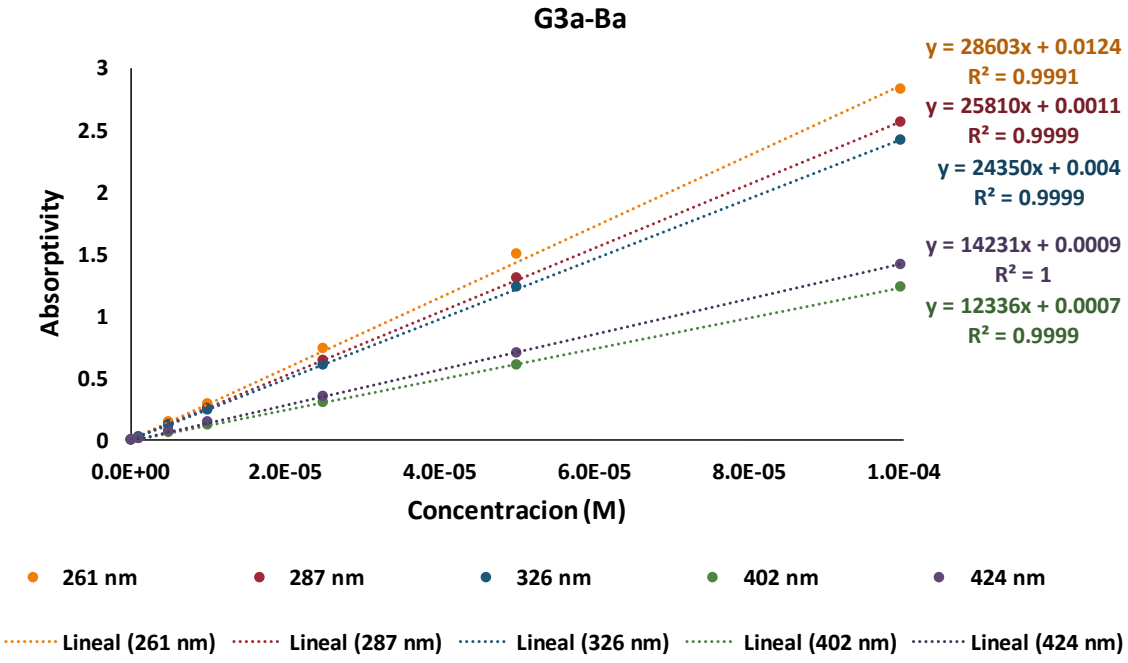


Figure S71. *UV-vis absorption spectra of free* ***G3a-Ba*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
261	28603
287	25810
326	24350
402	12336
424	14321

Figure S72. *Calculated molar extinction coefficients of* ***G3a-Ba*** *at selected absorption maxima.*

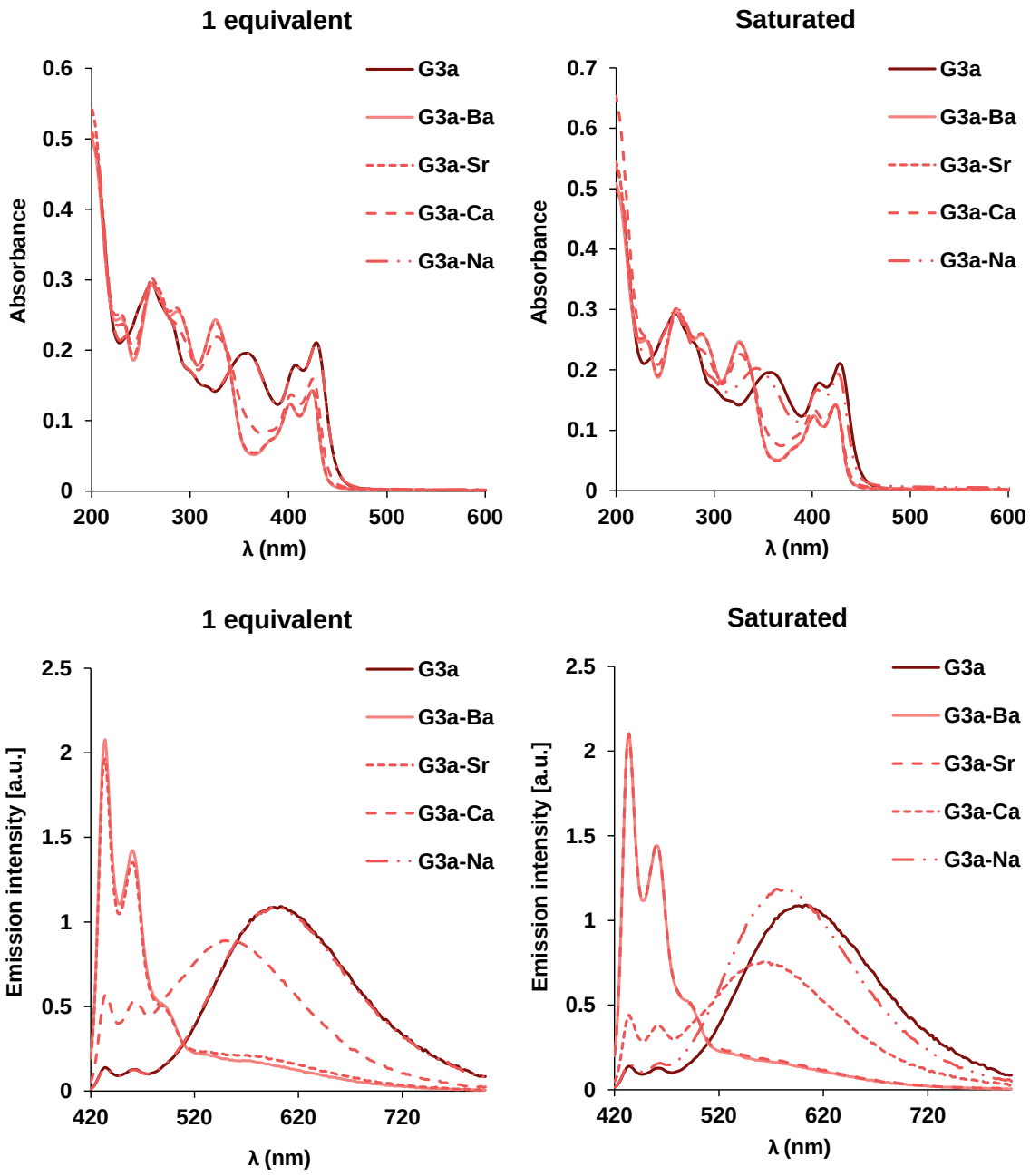


Figure S73. *Absorption and emission spectra of* ***G3a*** *with 1 equivalent and saturated solutions of* Ba^{2+}*,* Sr^{2+}*,* Ca^{2+} *and* Na^{+} *perchlorate salts.*

2.2.2 G3b

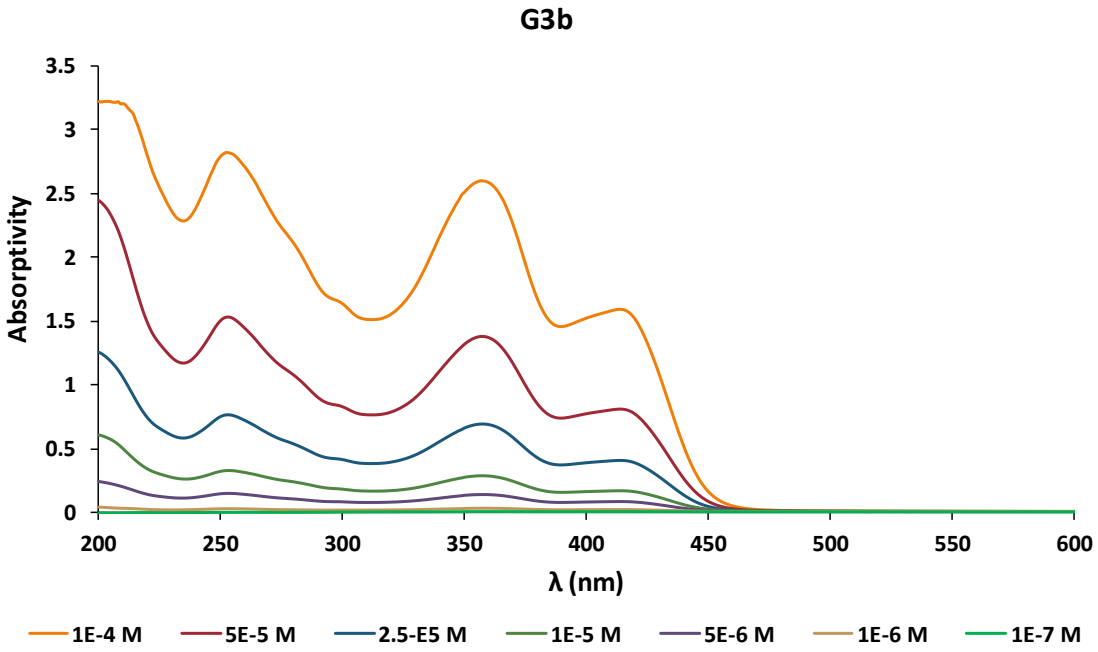
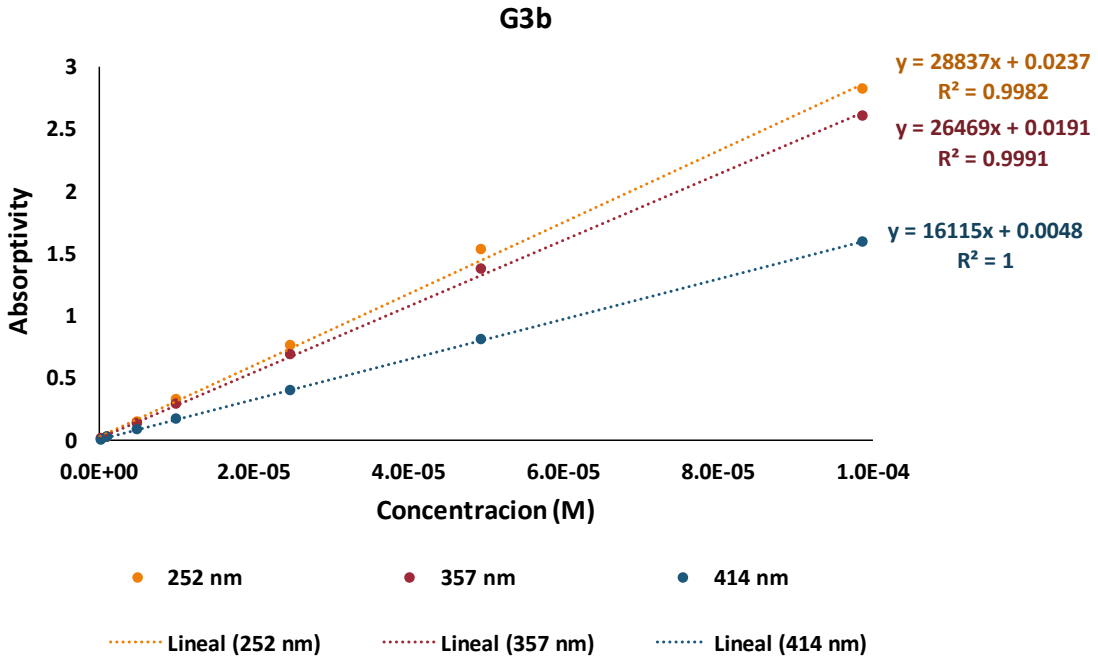


Figure S74. *UV-vis absorption spectra of free* ***G3b*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
252	28837
357	26469
424	16115

Figure S75. *Calculated molar extinction coefficients of* ***G3b*** *at selected absorption maxima.*

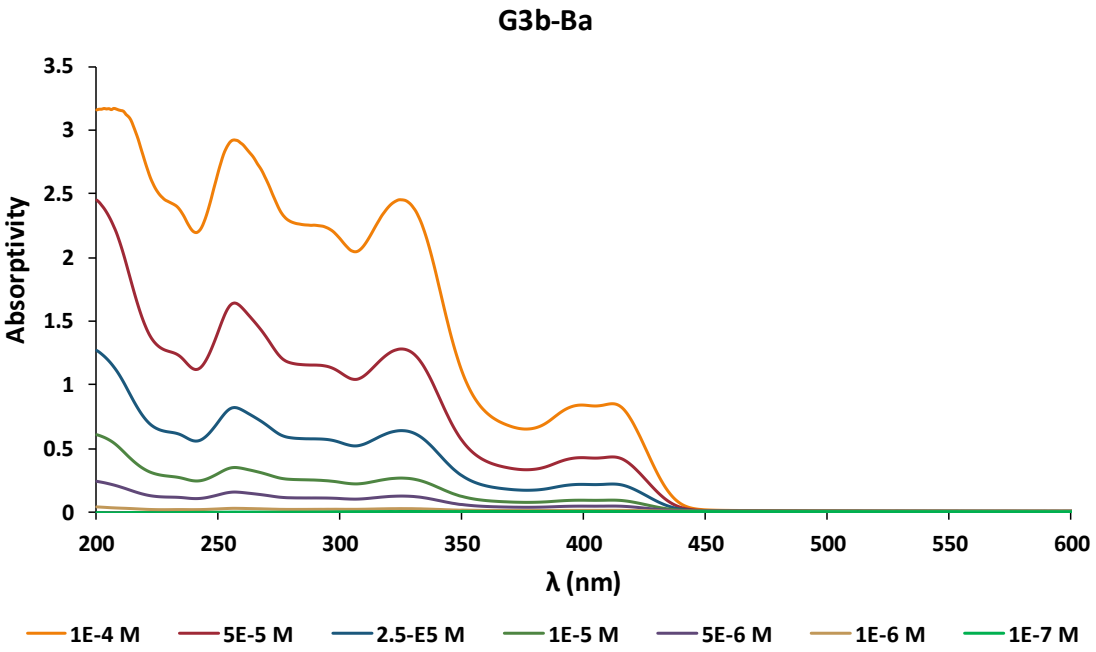
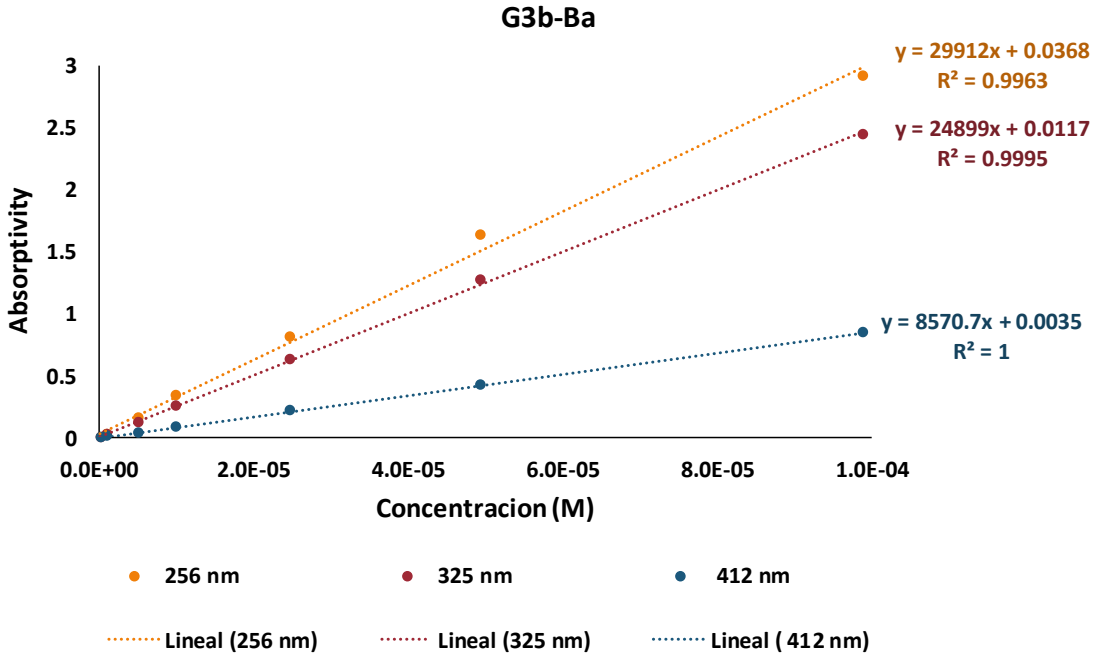


Figure S76. *UV-vis absorption spectra of free* ***G3b-Ba*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
256	29912
325	24899
412	8570.7

Figure S77. *Calculated molar extinction coefficients of* ***G3b-Ba*** *at selected absorption maxima.*

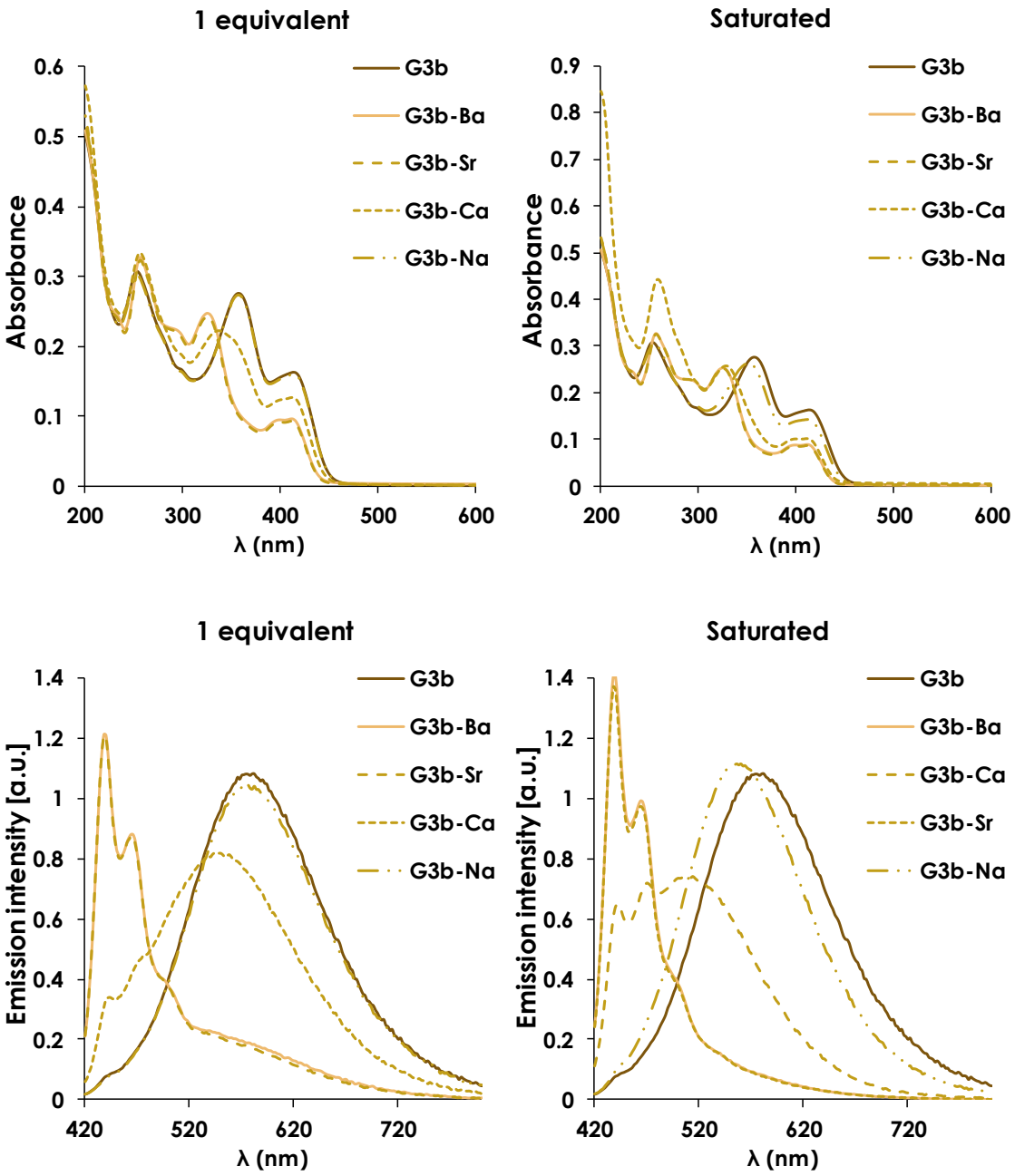


Figure S78. *Absorption and emission spectra of* ***G3b*** *with 1 equivalent and saturated solutions of* Ba^{2+}*,* Sr^{2+}*,* Ca^{2+} *and* Na^{+} *perchlorate salts.*

2.2.3 G3c

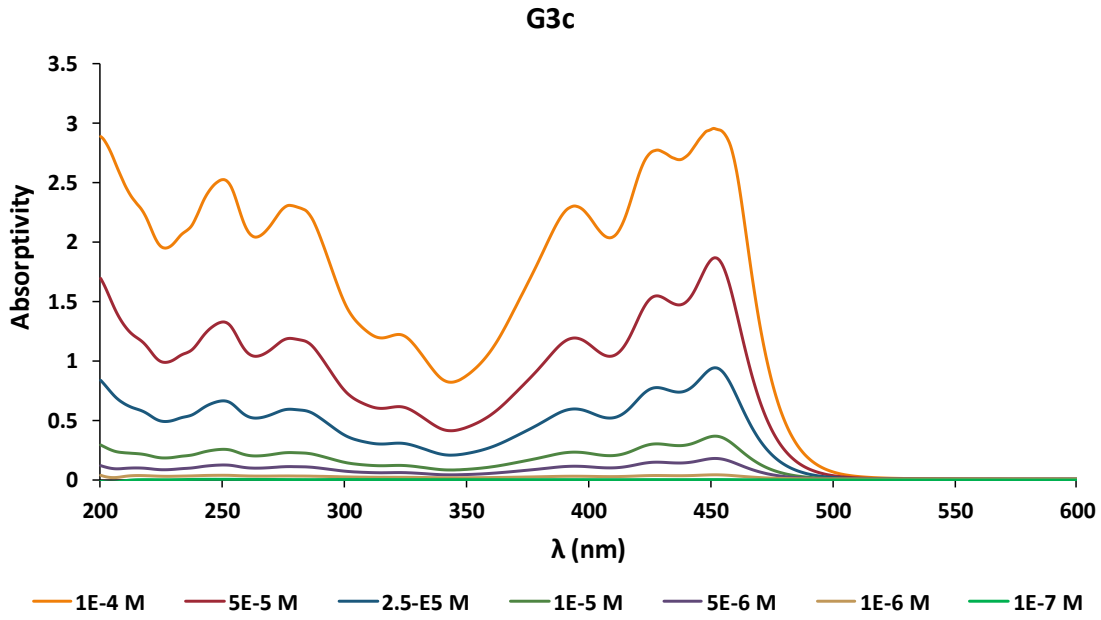
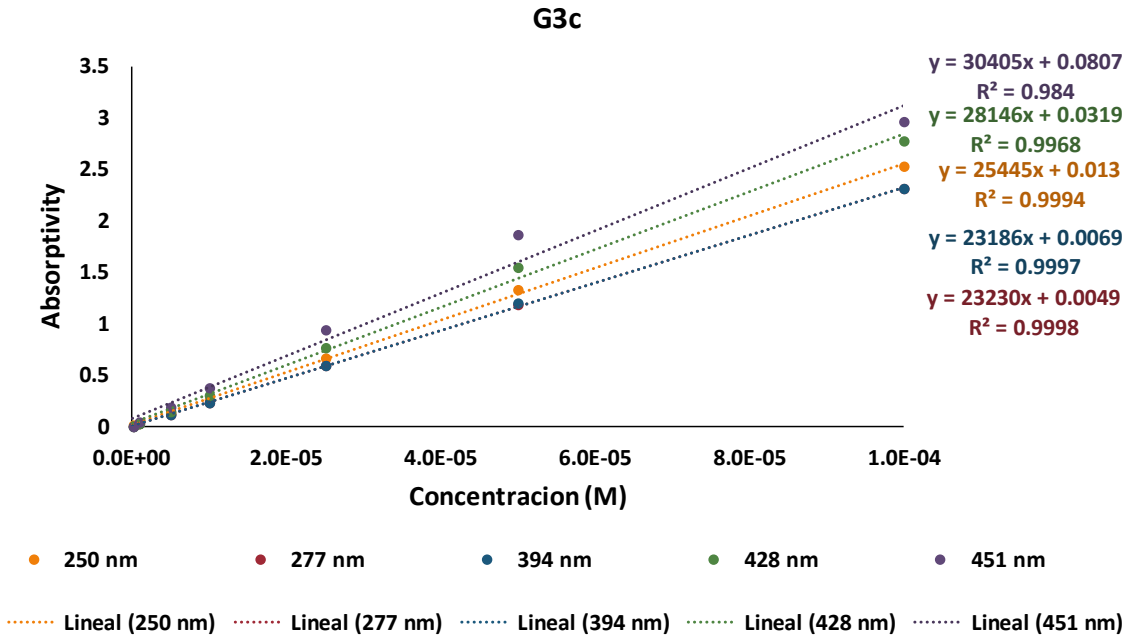


Figure S79. *UV-vis absorption spectra of free* ***G3c*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
250	25445
277	23230
394	23186
428	28146
451	30405

Figure S80. *Calculated molar extinction coefficients of* ***G3c*** *at selected absorption maxima.*

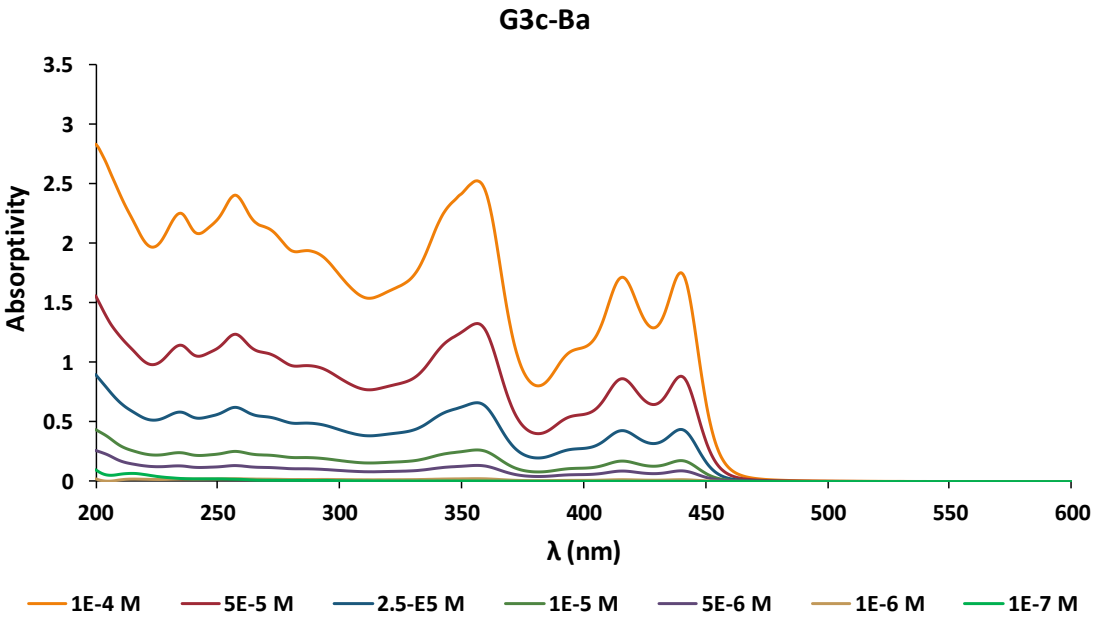
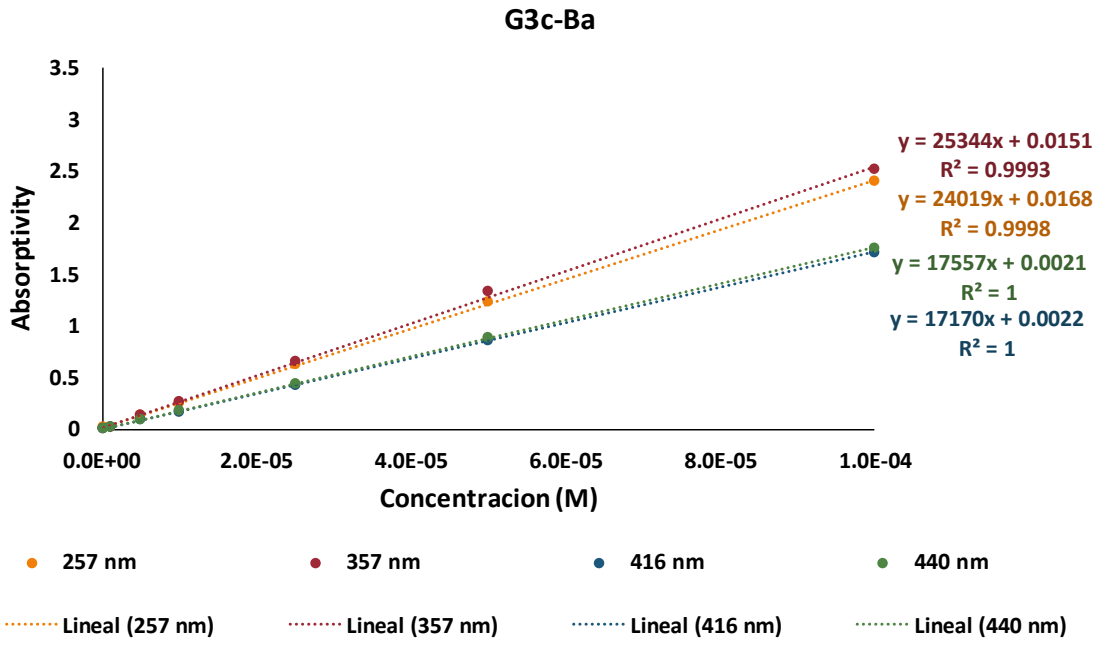


Figure S81. *UV-vis **a**bsorption spectra of free **G3c-Ba** in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
257	24019
357	25344
416	17170
440	17557

Figure S82. *Calculated molar extinction coefficients of **G3c-Ba** at selected absorption maxima.*

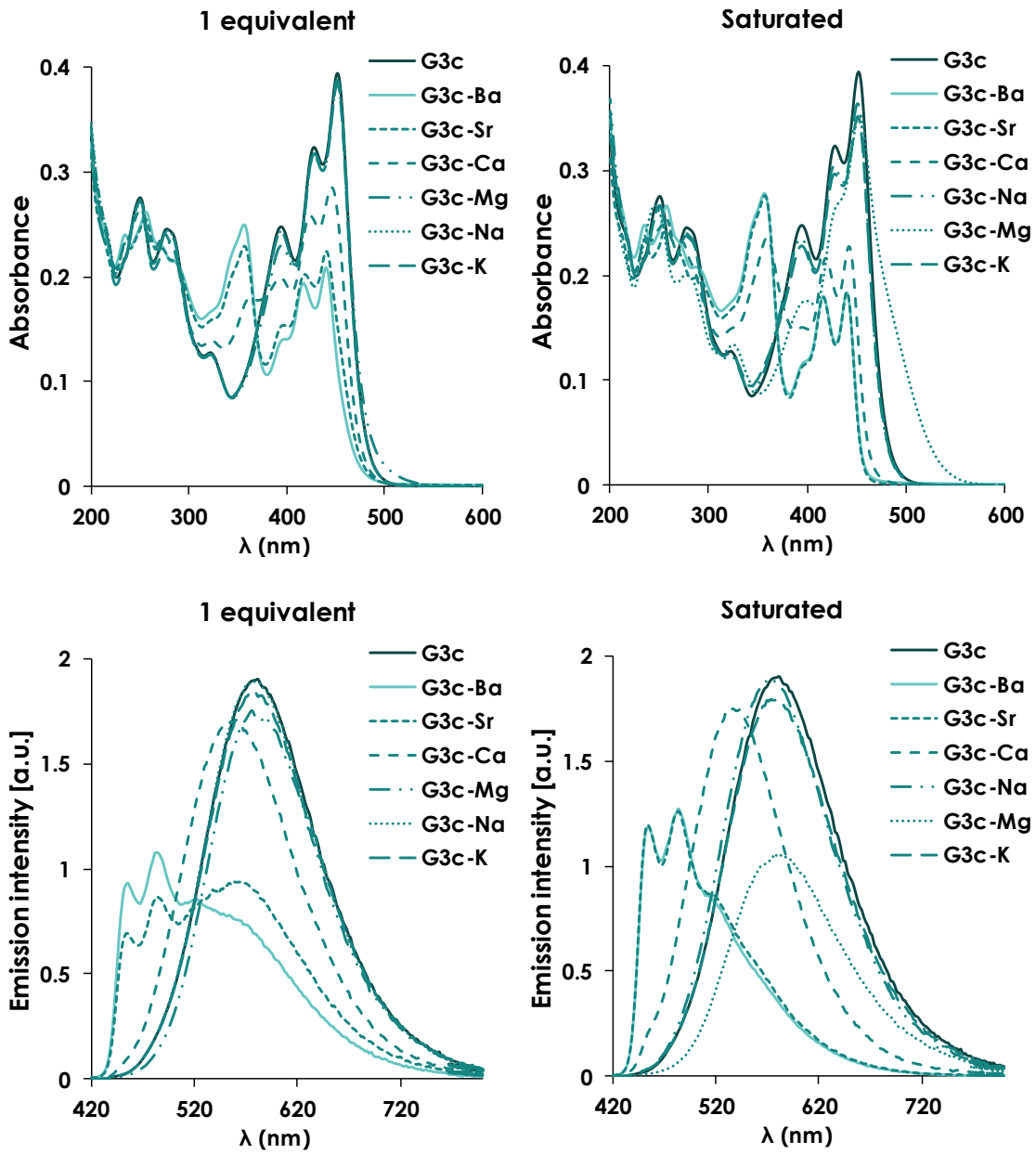


Figure S83. *Absorption and emission spectra of* ***G3c*** *with 1 equivalent and saturated solutions of* Ba^{2+}*,* Sr^{2+}*,* Ca^{2+} *and* Na^{+} *perchlorate salts.*

2.2.4 L1

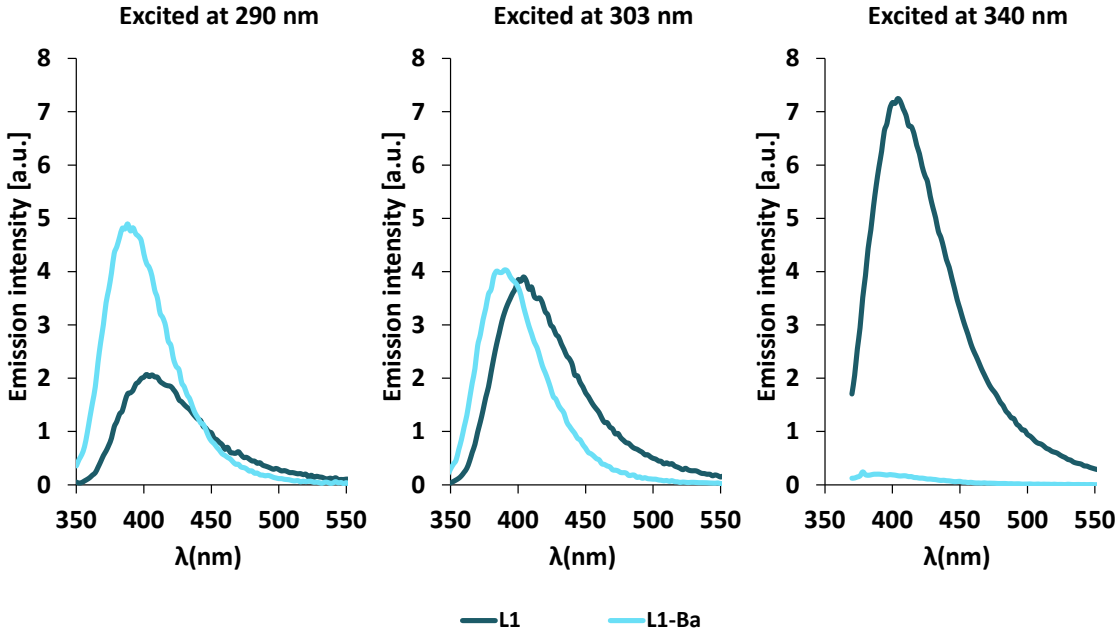
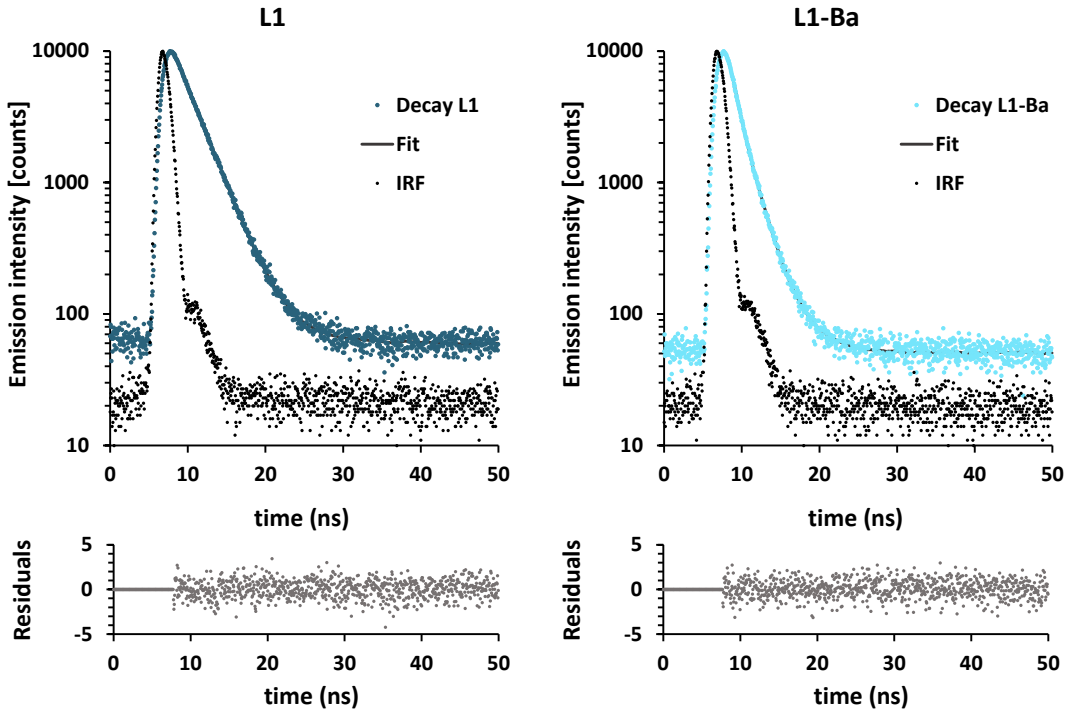


Figure S84. *Emission spectra of **L1** and **L1-Ba** excited at different wavelength.*



Emission at 404 nm EPLED340 TCSPC 20MHz Slit 10, 1024 chanels, 10000 counts	
Result	
τ	χ^2
2.7 ns	1.07

Emission at 388 nm EPLED340 TCSPC 20MHz Slit 13, 1024 chanels, 10000 counts	
Result	
τ	χ^2
1.23 ns (76%) 2.68 ns (24%)	1.1

Figure S85. *Lifetime decay and results of **L1** and **L1-Ba**, excited at emission maxima.*

2.2.5 L2

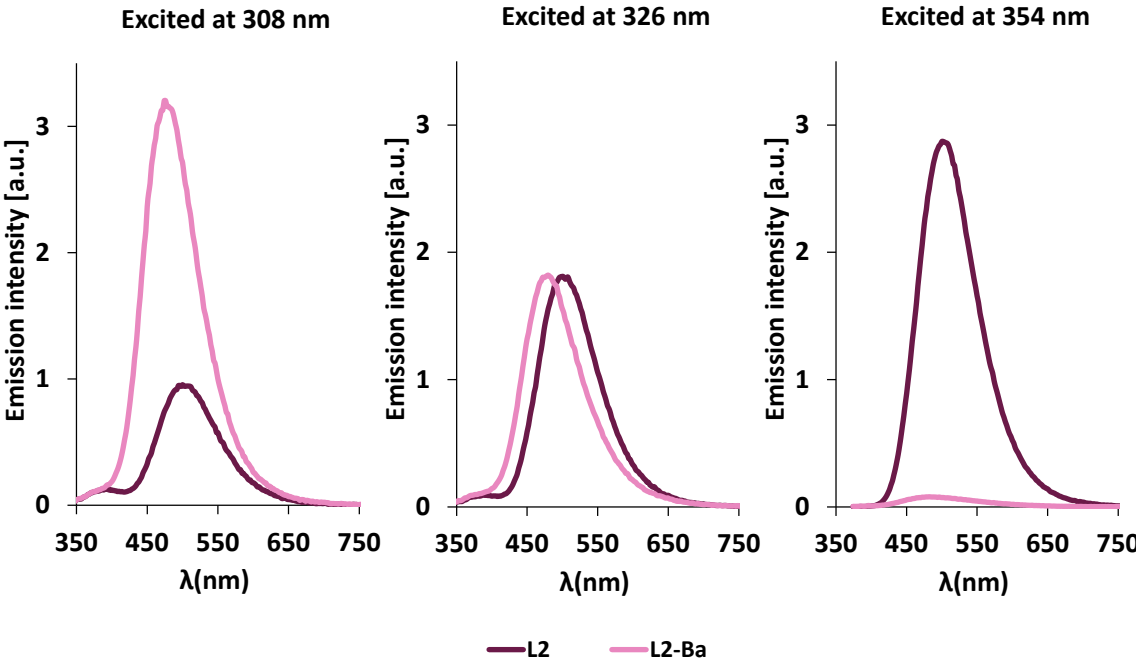
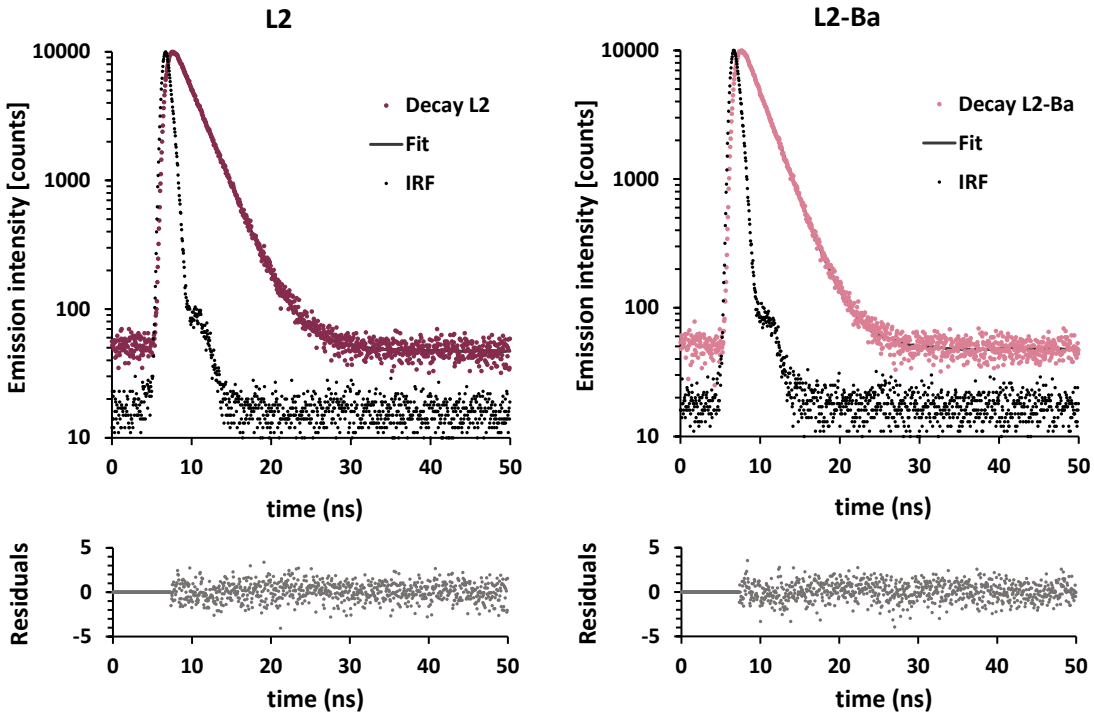


Figure S86. *Emission spectra of **L2** and **L2-Ba** excited at different wavelength.*



Emission at 500 nm EPLED340 TCSPC 20MHz Slit 10, 1024 chanels, 10000 counts	
Result	
τ	χ^2
2.8 ns	1.1

Emission at 474 nm EPLED340 TCSPC 20MHz Slit 10, 1024 chanels, 10000 counts	
Result	
τ	χ^2
2.46 ns	1.1

Figure S87. *Lifetime decay and results of **L2** and **L2-Ba**, excited at emission maxima.*

2.2.6 L3

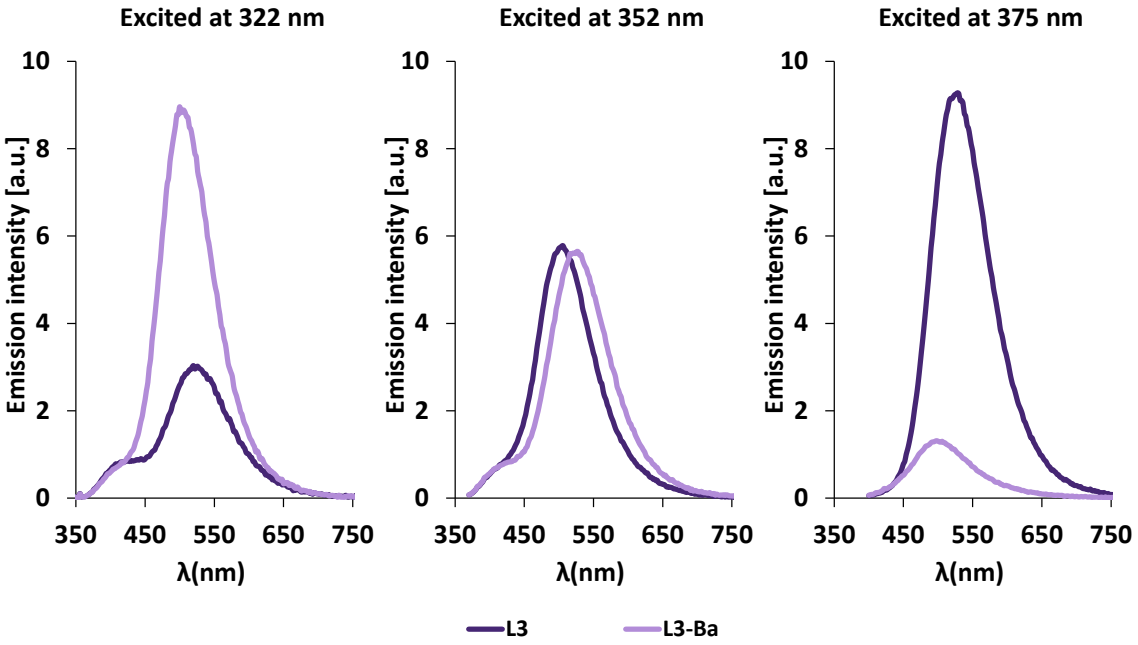
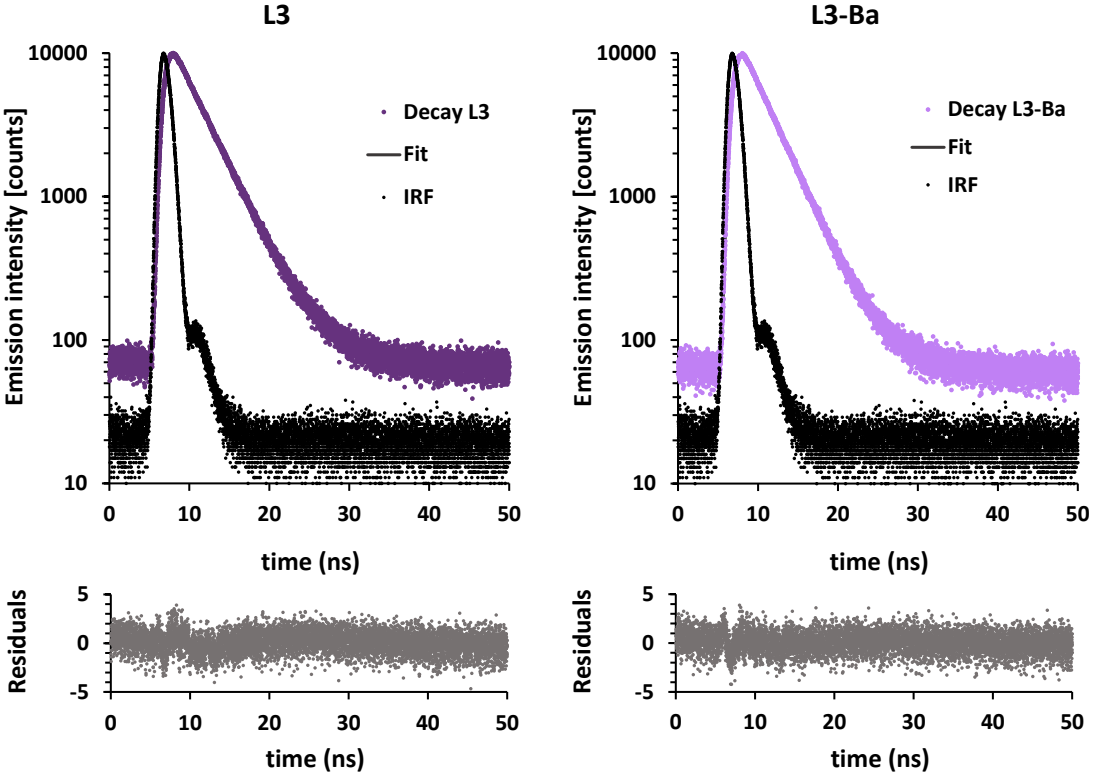


Figure S88. *Emission spectra of **L3** and **L3-Ba** excited at different wavelength.*



Emission at 522 nm EPLED340 TCSPC 20MHz Slit 10, 8192 chanels, 10000 counts	
Result	
τ	χ^2
3.5 ns	1.2

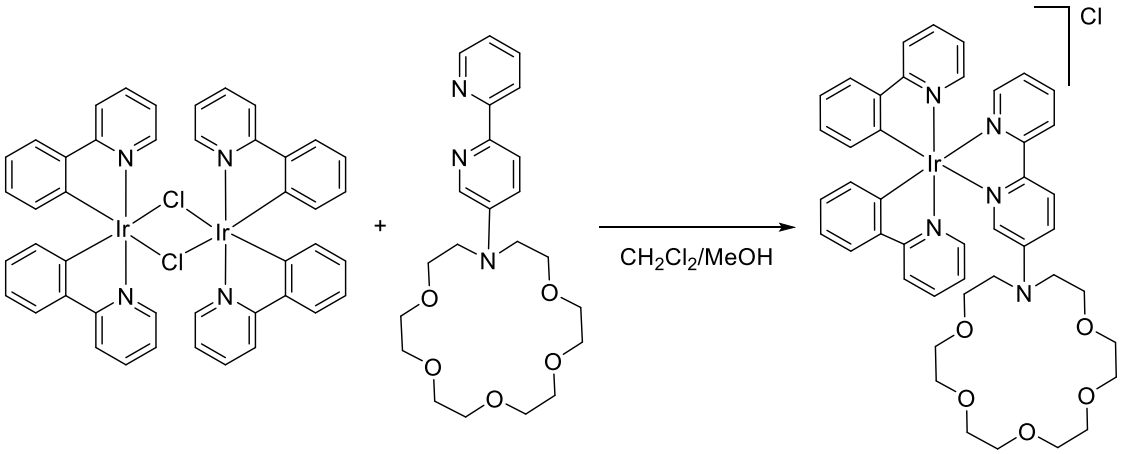
Emission at 505 nm EPLED340 TCSPC 20MHz Slit 10, 8192 chanels, 10000 counts	
Result	
τ	χ^2
3.3 ns	1.1

Figure S89. *Lifetime decay and results of **L3** and **L3-Ba**, excited at emission maxima.*

3 CHAPTER 3

3.1 SYNTHESIS AND CHARACTERIZATION

3.1.1 Complex C5, $[Ir(ppy)_2(L1)]Cl$



C5

Under a N_2 atmosphere, to $[Ir(ppy)_2Cl]_2$ (33.4 mg, 31.1 µmol) and compound **L1** (26 mg, 62.5 µmol) 8 mL of CH_2Cl_2/MeOH (2:1, v/v) was added. The reaction mixture was refluxed overnight at 35°C. The solvents were evaporated to obtain the desired product. A bright yellow solid with quantitative yield.

Exact mass: ESI-MS $[C_{44}H_{47}IrN_5O_5]$: calculated: m/z= 916.3183, found: m/z= 916.3172.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.14 (d, J = 9.6 Hz, 1H), 9.10 (d, J = 8.7 Hz, 1H), 8.09 (td, J = 7.9, 1.7 Hz, 1H), 7.91 (d, J = 8.1 Hz, 2H), 7.77 (tdd, J = 8.2, 4.0, 1.5 Hz, 3H), 7.67 (td, J = 7.9, 1.3 Hz, 2H), 7.56 (t, J = 5.0 Hz, 2H), 7.50 (dd, J = 9.3, 3.0 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.09 – 6.96 (m, 4H), 6.90 (dtd, J = 8.9, 7.4, 1.3 Hz, 2H), 6.33 (ddd, J = 7.6, 4.2, 1.2 Hz, 2H), 3.70 – 3.49 (m, 16H), 3.43 (s, 8H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.98 (1C, C_{quat}), 167.85 (1C, C_{quat}), 157.15 (1C, C_{quat}), 151.98 (1C, C_{quat}), 151.12 (1C, C_{quat}), 149.31 (1C, CH), 148.72 (1C, CH), 148.48 (1C, CH), 147.11 (1C, C_{quat}), 143.74 (1C, C_{quat}), 143.64 (1C, C_{quat}), 142.00 (1C, C_{quat}), 139.49 (1C, CH), 138.12 (1C, CH), 138.02 (1C, CH), 133.83 (1C, CH), 131.94 (1C, CH), 131.82 (1C, CH), 130.73 (1C, CH), 130.62 (1C, CH), 126.99 (1C, CH), 125.24 (1C, CH), 124.82 (1C, CH), 124.54 (1C, CH), 123.82 (1C, CH), 123.37 (1C, CH), 123.30 (1C, CH), 122.45 (2C, CH),

120.09 (1C, CH), 119.53 (2C, CH), 70.82 (2C, CH_2, crown), 70.62 (6C, CH_2, crown), 68.03 (2C, CH_2, crown), 51.03 (2C, CH_2, crown).

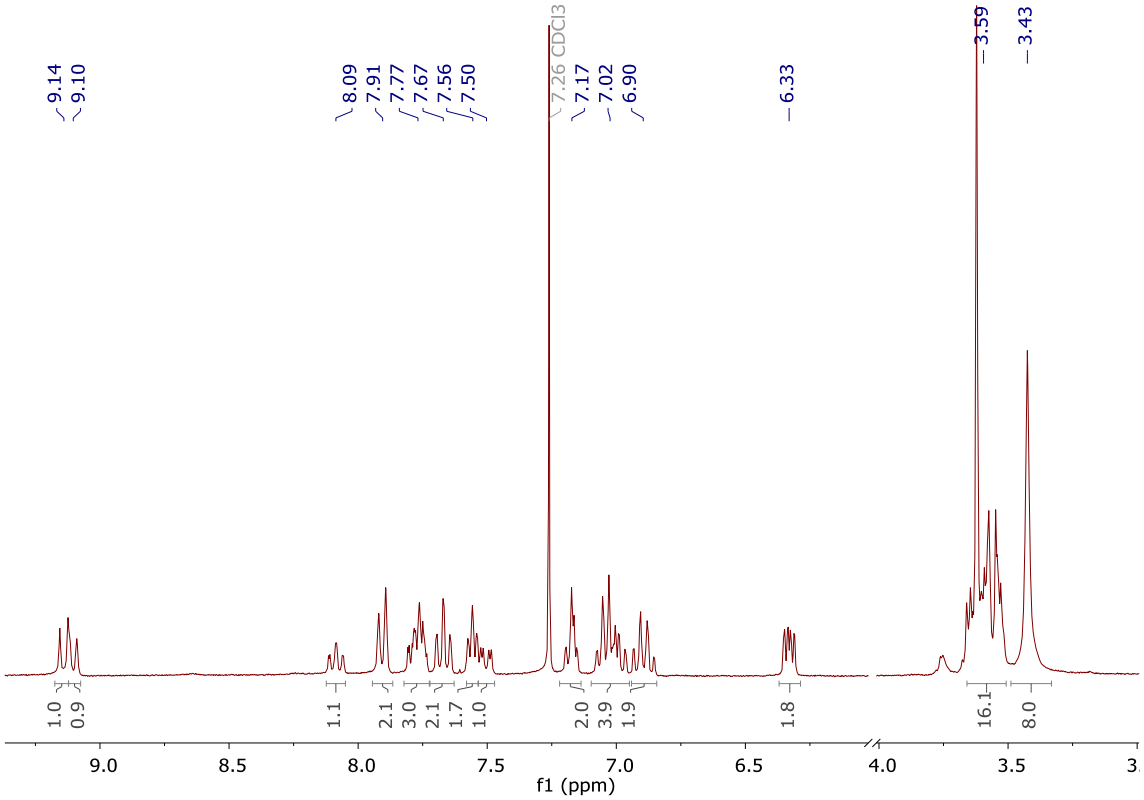


Figure S90. *^{1}H NMR spectrum of compound **C5** ($CDCl_3$, 300 MHz).*

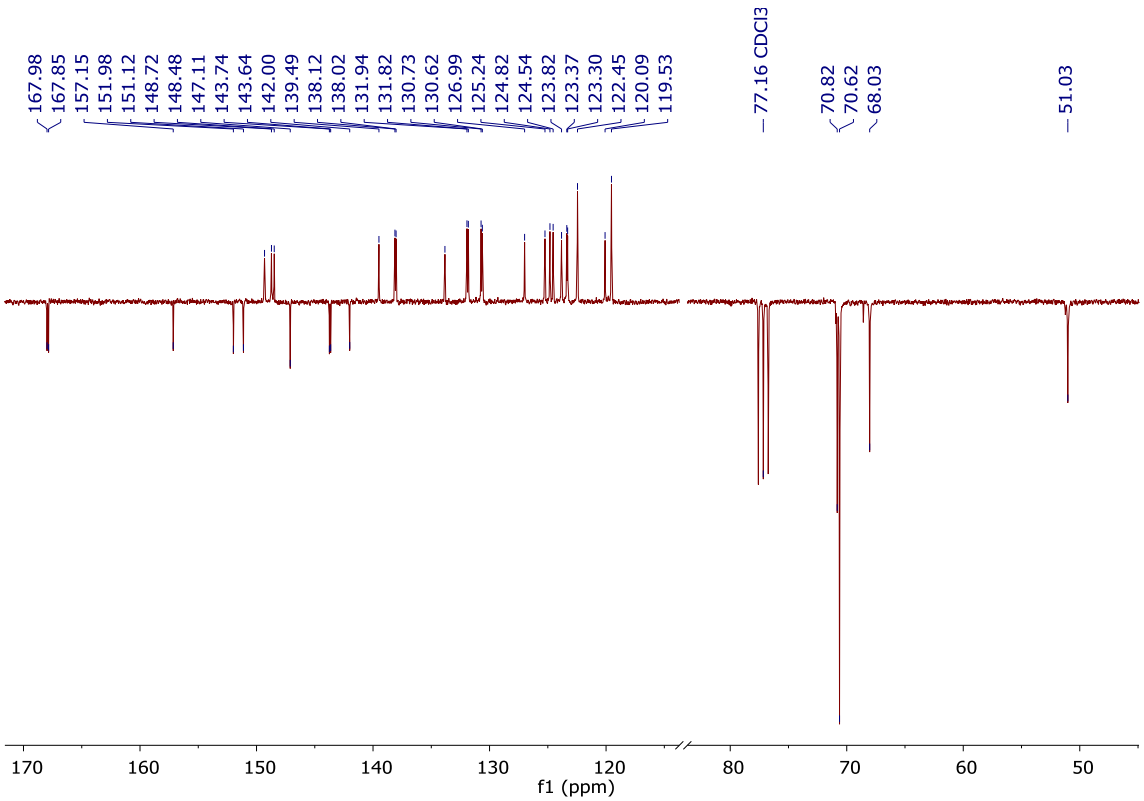


Figure S91. *^{13}C APT NMR spectrum of compound **C5** ($CDCl_3$, 300 MHz).*

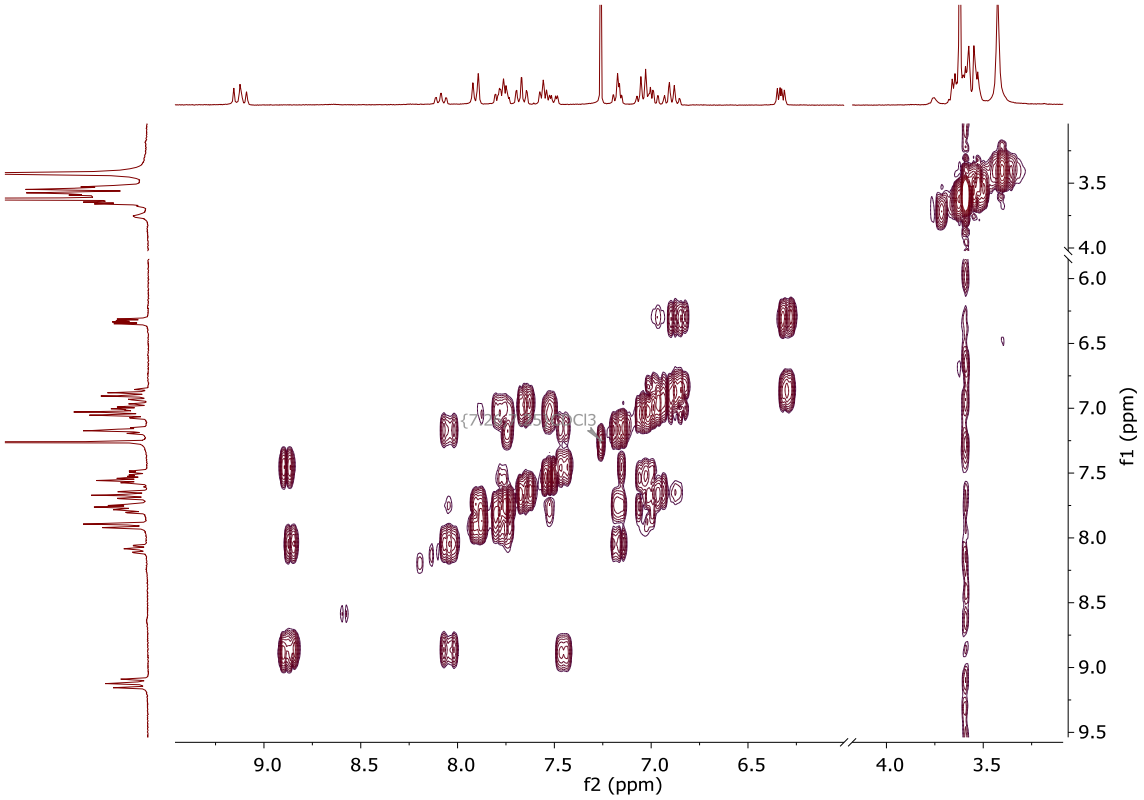


Figure S92. *COSY NMR spectrum of compound **C5** ($CDCl_3$, 300 MHz).*

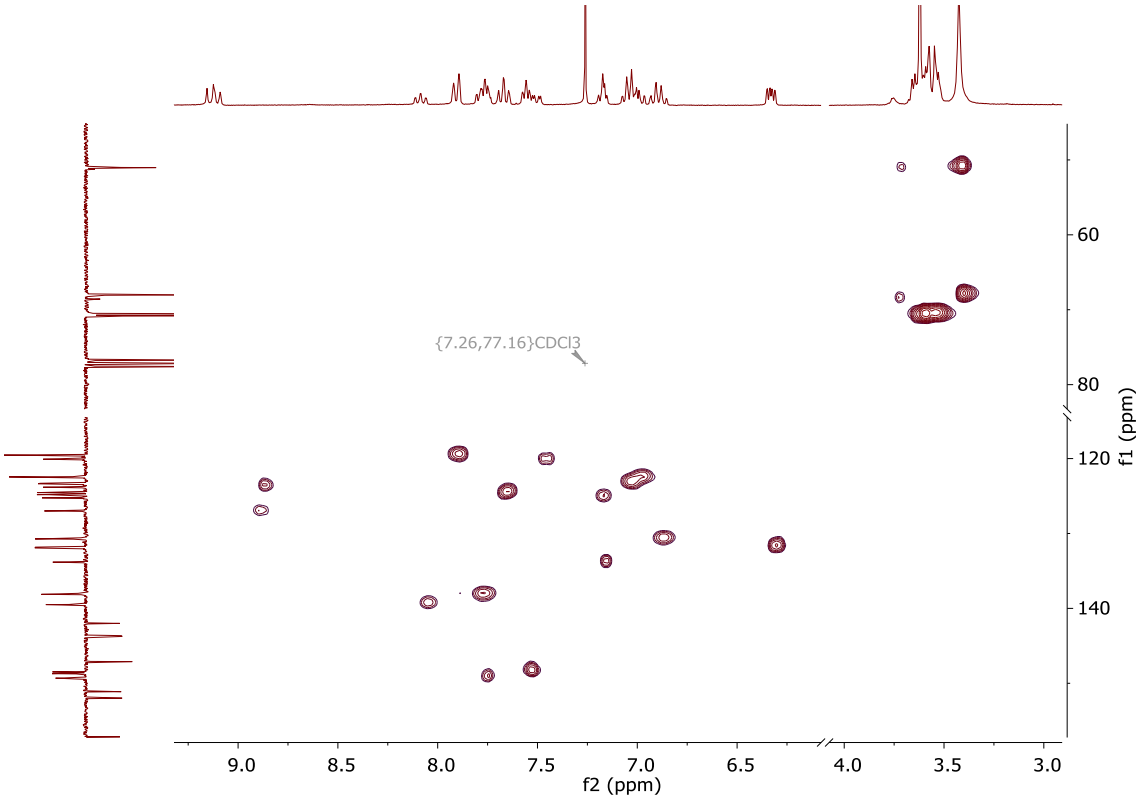


Figure S93. *HSQC NMR spectrum of compound* ***C5*** *($CDCl_3$, 300 MHz).*

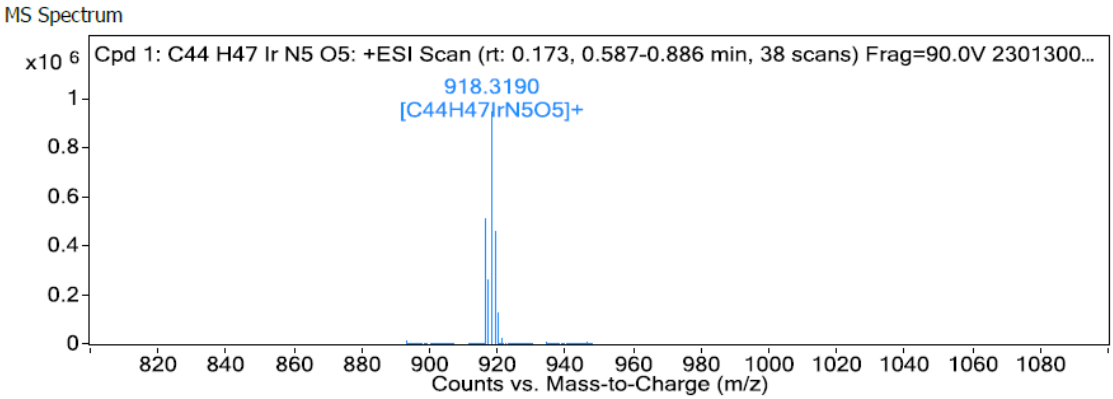


Figure S94. *Mass spectrum of compound* ***C5****.*

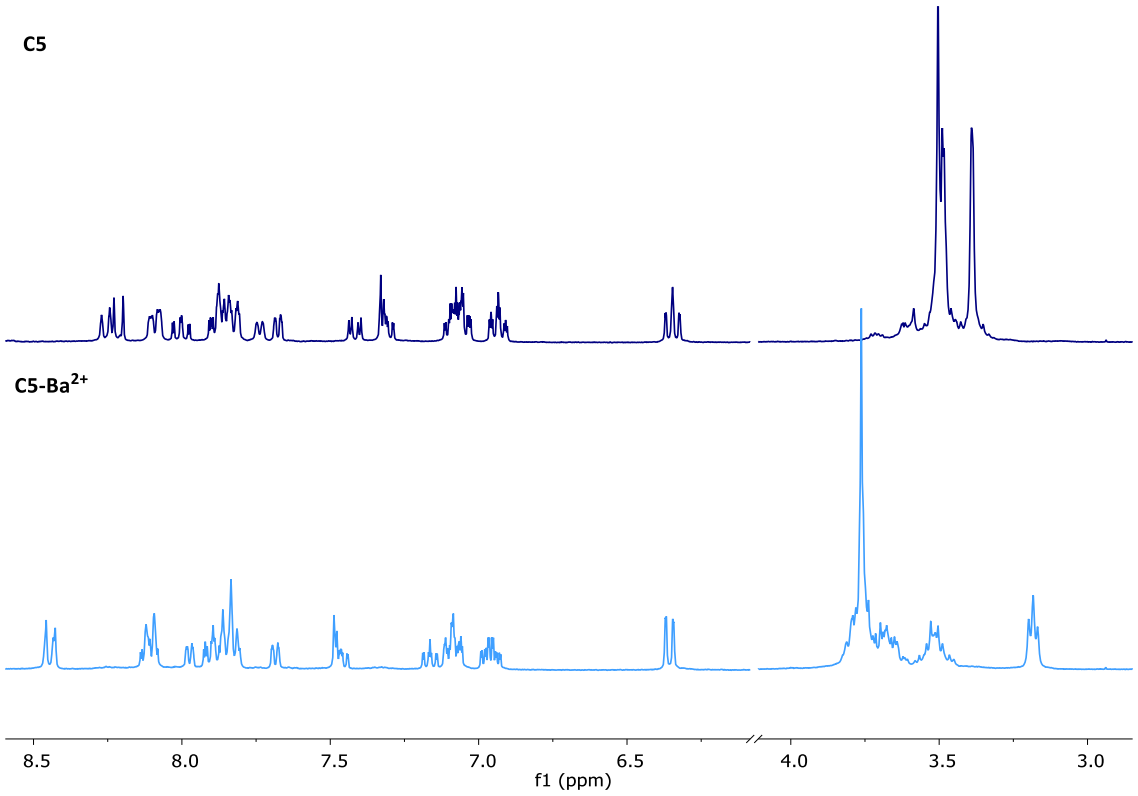
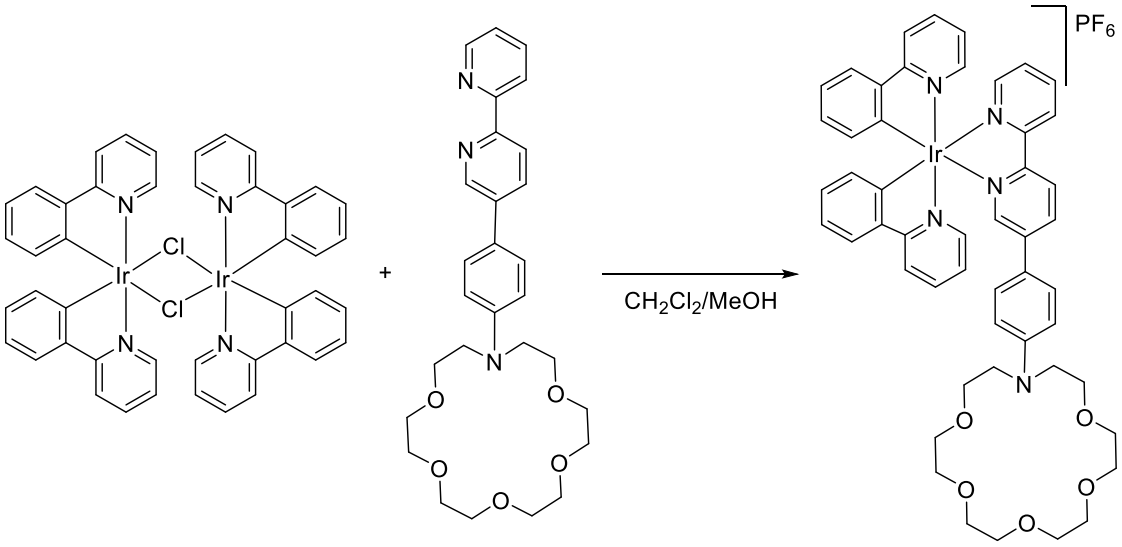


Figure S95. *^{1}H NMR of compound **C5** and **C5-Ba^{2+}**.*

3.1.2 Complex C6, $[Ir(ppy)_2(L2)]PF_6$



C6

Under a N_2 atmosphere, to $[Ir(ppy)_2Cl]_2$ (-) and AAN_160 (-) 8 mL of CH_2Cl_2/MeOH (2:1, v/v) was added. The reaction mixture was refluxed overnight at 35°C. The solvents were evaporated and the title compound was precipitated by adding NH_4PF_6 in MeOH. Yield 85%.

Exact mass: ESI-MS [$C_{57}H_{53}IrN_7O_5$]: calculated: m/z= 1106.3714, found: m/z= 1106.3738.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.60 (t, J = 9.0 Hz, 2H), 8.37–8.28 (m, 1H), 8.17–8.07 (m, 2H), 8.04–7.91 (m, 3H), 7.83–7.76 (m, 3H), 7.73 (d, J = 5.7 Hz, 1H), 7.63 (d, J = 5.7 Hz, 1H), 7.55 (d, J = 5.8 Hz, 1H), 7.41 (t, J = 6.6 Hz, 1H), 7.31 (d, J = 9.0 Hz, 2H), 7.20–7.03 (m, 4H), 7.02–6.91 (m, 4H), 6.40 (d, J = 7.5 Hz, 1H), 6.35 (d, J = 7.5 Hz, 1H), 3.76–3.34 (m, 24H).

^{13}C NMR (75 MHz, CD_2Cl_2): *δ* 168.22 (2C, C_{quat}), 156.20 (1C, C_{quat}), 154.00 (1C, C_{quat}), 151.21 (1C, CH), 150.71 (1C, C_{quat}), 150.44 (1C, C_{quat}), 150.37 (1C, C_{quat}), 149.23 (1C, CH), 149.07 (1C, CH), 148.58 (1C, CH), 144.30 (2C, C_{quat}), 140.64 (1C, C_{quat}), 139.82 (1C, CH), 138.86 (1C, CH), 138.78 (1C, CH), 136.97 (1C, CH), 132.23 (2C, CH), 131.28 (1C, CH), 131.18 (1C, CH), 130.45 (1C, C_{quat}), 128.62 (2C, CH), 128.48 (1C, CH), 125.49 (1C, CH), 125.43 (1C, CH), 125.08 (1C, CH), 124.82 (1C, CH), 123.94 (4C, CH), 123.33 (1C, CH), 123.21 (1C, CH), 120.55 (1C, CH), 120.36 (1C, CH), 70.37 (8C, CH_2, crown), 68.54 (2C, CH_2, crown), 56.23 (2C, CH_2, crown).

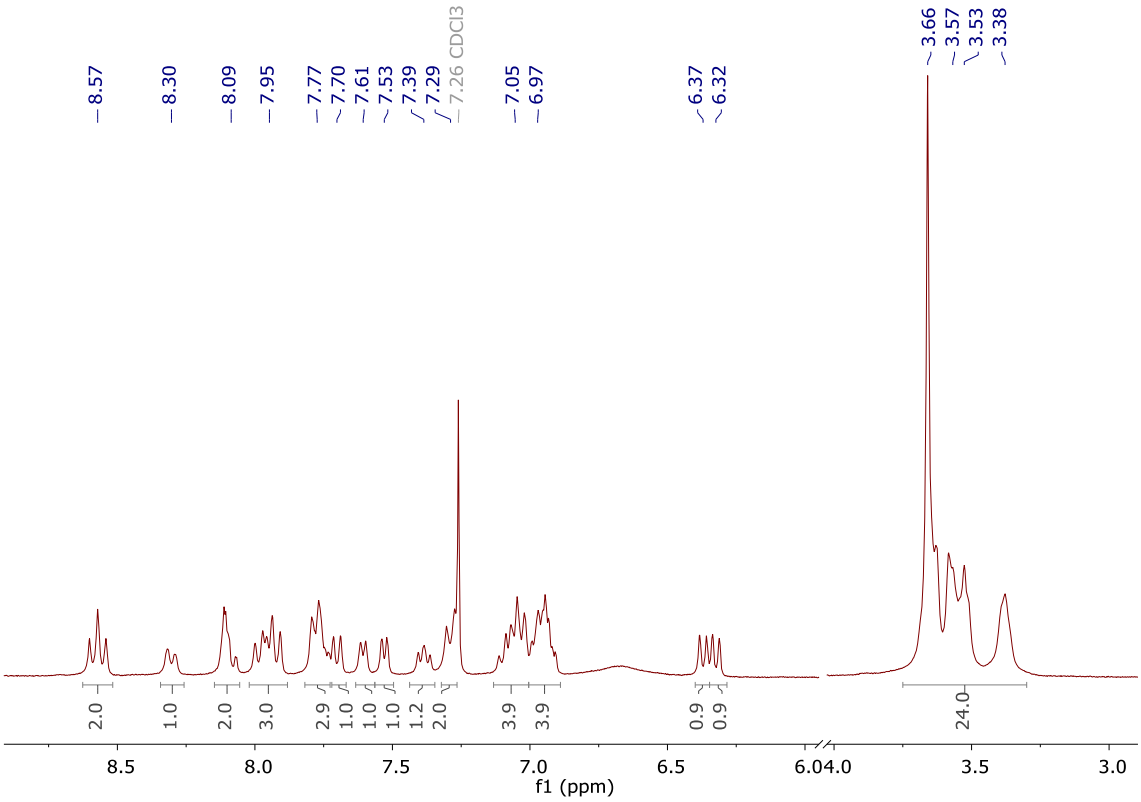


Figure S96. *^{1}H NMR spectrum of compound **C6** ($CDCl_3$, 300 MHz).*

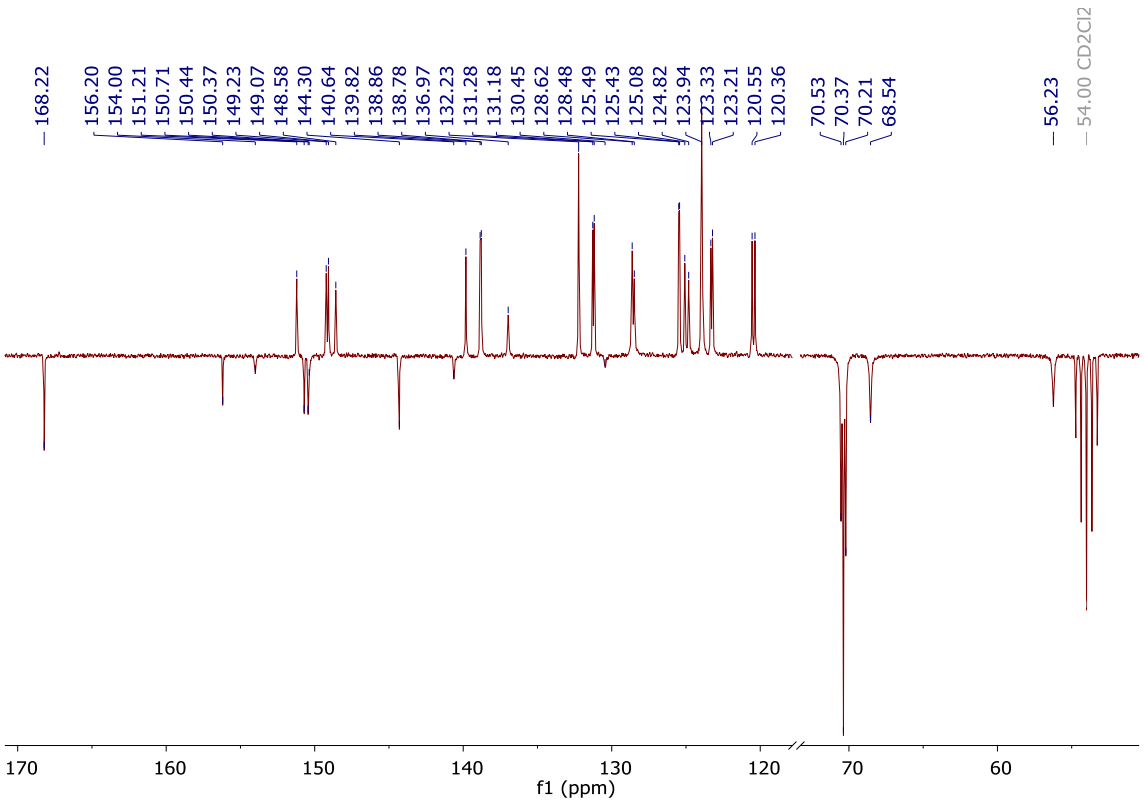


Figure S97. *^{13}C NMR spectrum of compound **C6** (CD_2Cl_2, 300 MHz).*

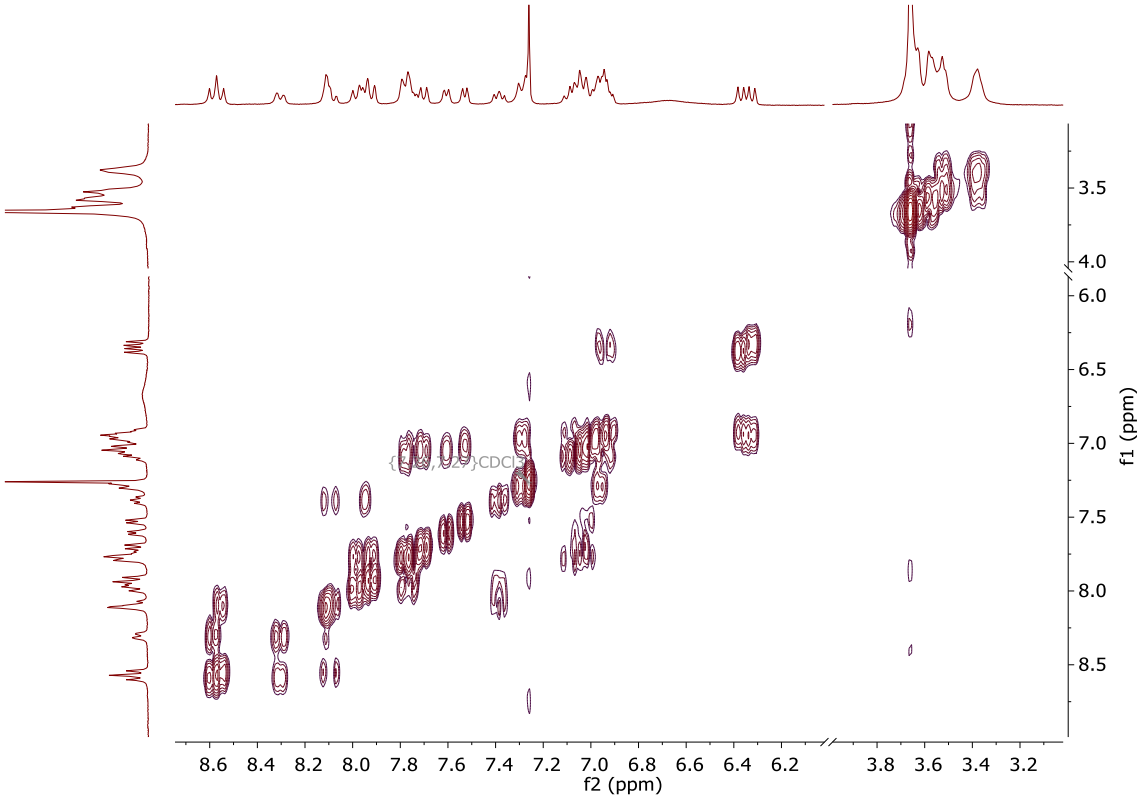


Figure S98. *COSY NMR spectrum of compound **C6** ($CDCl_3$, 300 MHz).*

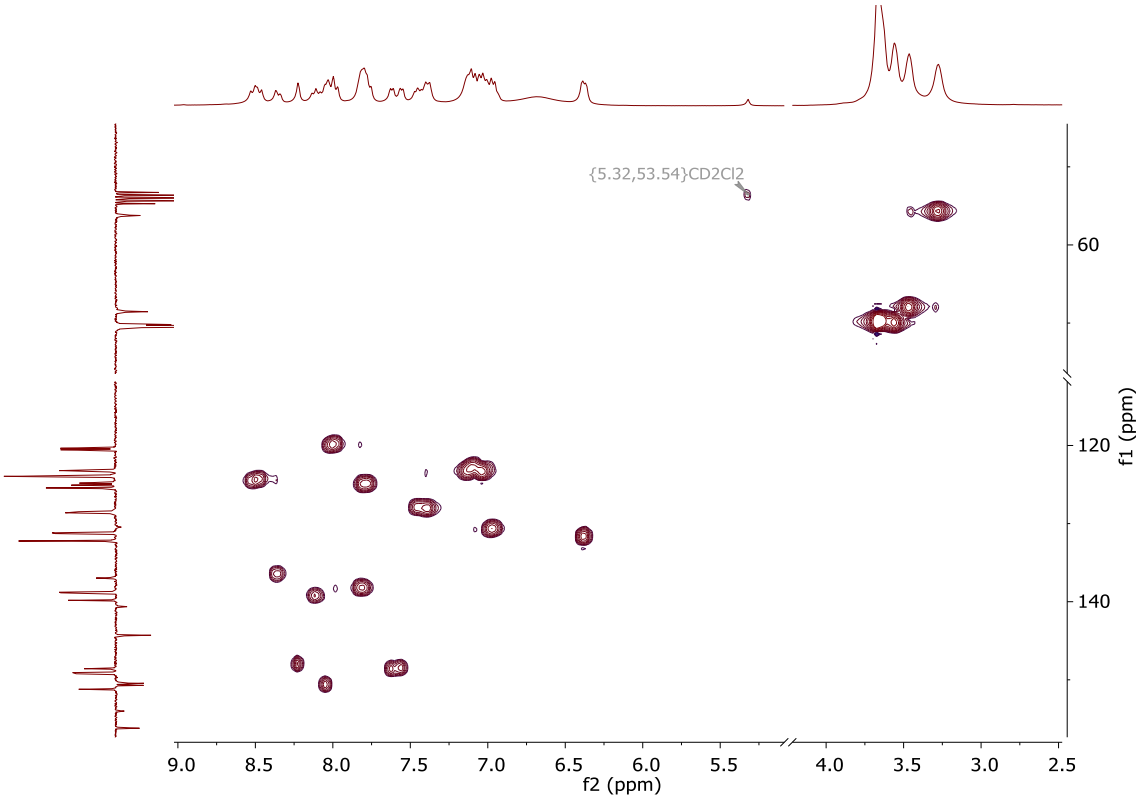


Figure S99. *HSQC NMR spectrum of compound* ***C6*** *(CD_2Cl_2, 300 MHz).*

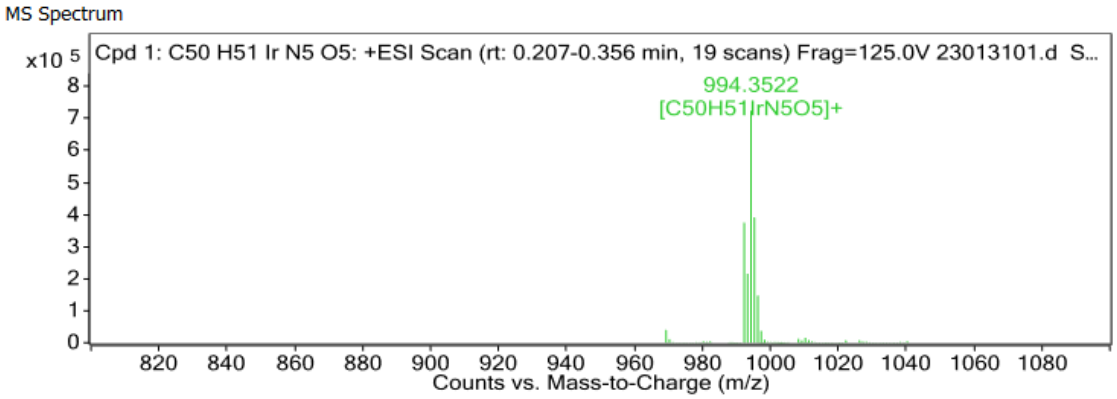


Figure S100. *Mass spectrum of compound* ***C6****.*

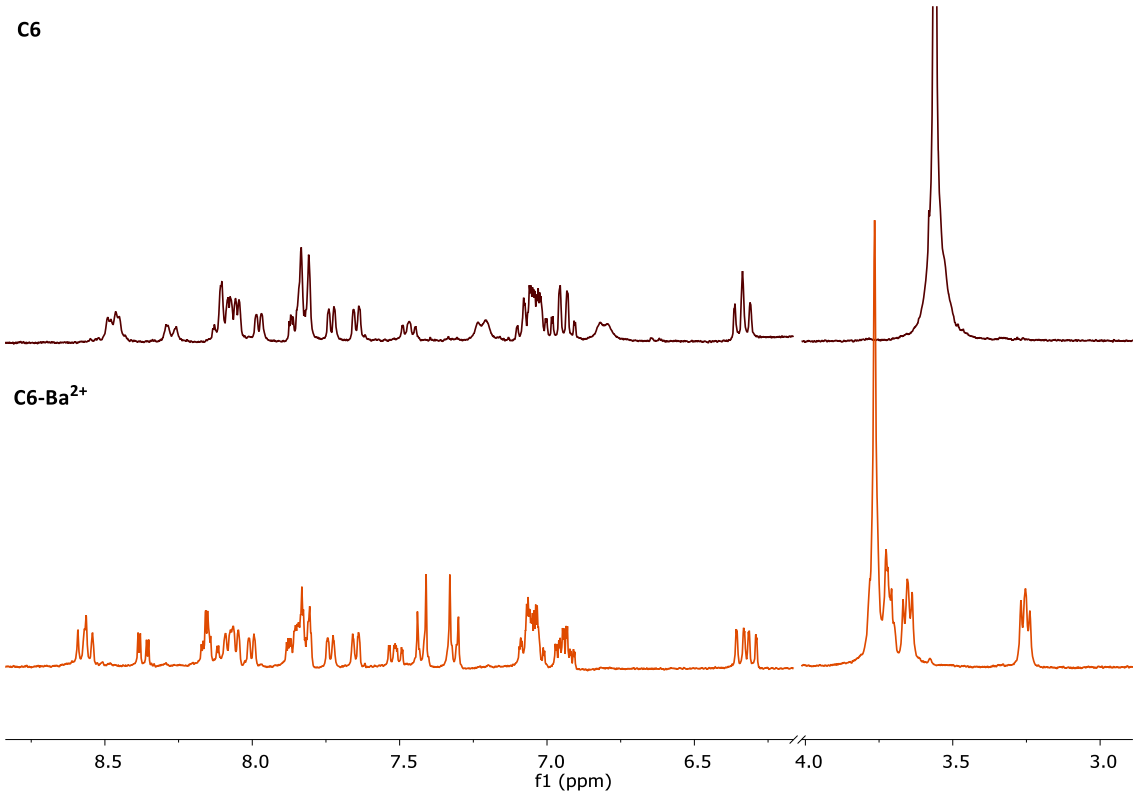
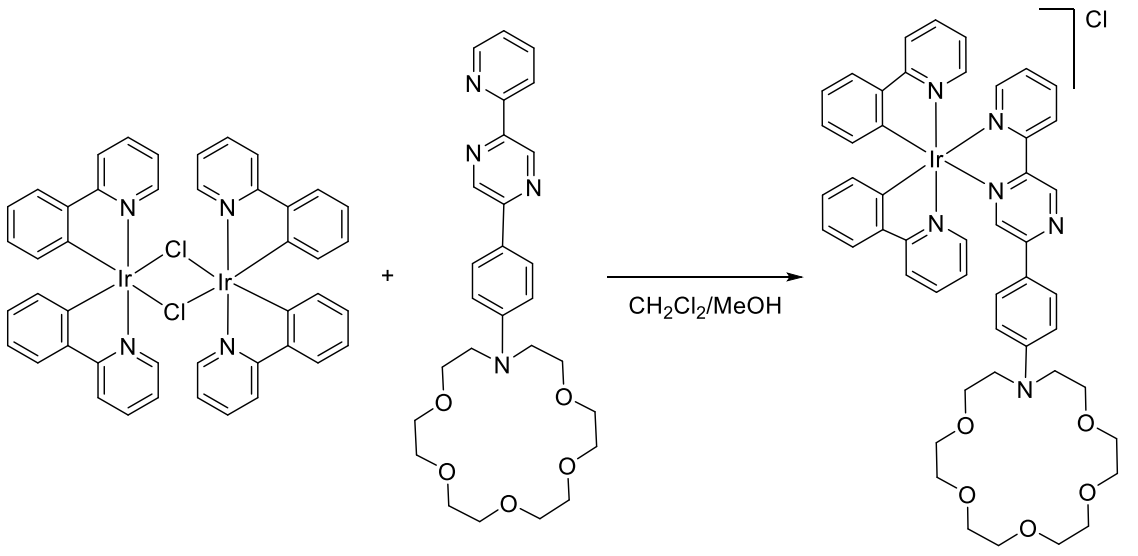


Figure S101. *^{1}H NMR of compound **C6** and **C6-Ba^{2+}**.*

3.1.3 Complex C7, $[Ir(ppy)_2(L3)]Cl$



C7

Under a N_2 atmosphere, to $[Ir(COOH\text{-}ppy)_2Cl]_2$ (-) and AAN_160 (-) 8 mL of CH_2Cl_2/MeOH (2:1, v/v) was added. The reaction mixture was refluxed overnight at 35°C. The solvents were evaporated to obtain the desired product. An orange solid with quantitative yield.

Exact mass: ESI-MS $[C_{49}H_{50}N_6O_5]$: calculated: m/z= 993.3449, found: m/z= 993.3422.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 10.11 (s, 1H), 9.24 (d, J = 4.9 Hz, 1H), 8.23 (s, 1H), 8.13 (s, 1H), 7.98 (dd, J = 8.8, 3.3 Hz, 3H), 7.87 – 7.71 (m, 4H), 7.70 – 7.59 (m, 3H), 7.55 (d, J = 5.3 Hz, 1H), 7.45 (d, J = 6.8 Hz, 1H), 7.21 – 6.88 (m, 6H), 6.72 (d, J = 8.7 Hz, 2H), 6.35 (dd, J = 11.5, 7.5 Hz, 2H), 3.75 – 3.48 (m, 24H).

^{13}C NMR (75 MHz, CD_2Cl_2): δ 168.14 (1C, C_{quat}), 168.10 (1C, C_{quat}), 156.78 (1C, C_{quat}), 155.09 (1C, C_{quat}), 151.68 (1C, C_{quat}), 150.96 (1C, CH), 150.46 (1C, C_{quat}), 149.93 (1C, C_{quat}), 149.29 (1C, CH), 149.20 (1C, CH), 146.97 (1C, CH), 146.03 (1C, C_{quat}), 144.37 (1C, C_{quat}), 144.07 (1C, C_{quat}), 140.42 (1C, CH), 139.23 (1C, CH), 139.02 (1C, CH), 138.91 (1C, CH), 132.30 (1C, CH), 132.13 (1C, CH), 131.38 (1C, CH), 131.27 (1C, CH), 129.16 (2C, CH), 128.14 (1C, CH), 125.66 (1C, CH), 125.50 (2C, CH), 124.15 (1C, CH), 123.99 (1C, CH), 123.61 (1C, CH), 123.38 (1C, CH), 120.86 (1C, C_{quat}), 120.61 (1C, CH), 120.47 (1C, CH), 112.47 (2C, CH), 71.27 (4C, CH_2, crown), 71.16 (2C, CH_2, crown), 71.08 (2C, CH_2, crown), 68.86 (2C, CH_2, crown), 51.74 (2C, CH_2, crown).

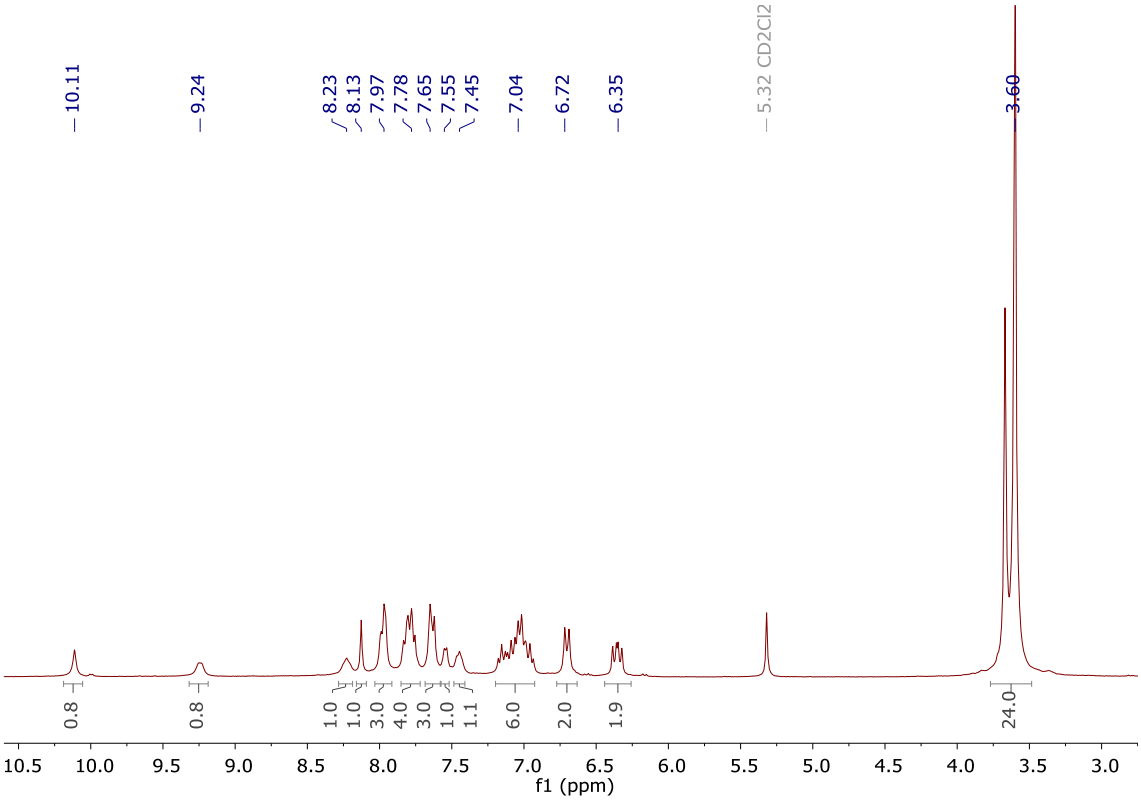


Figure S102. *^{1}H NMR spectrum of compound **C7** (CD_2Cl_2, 300 MHz).*

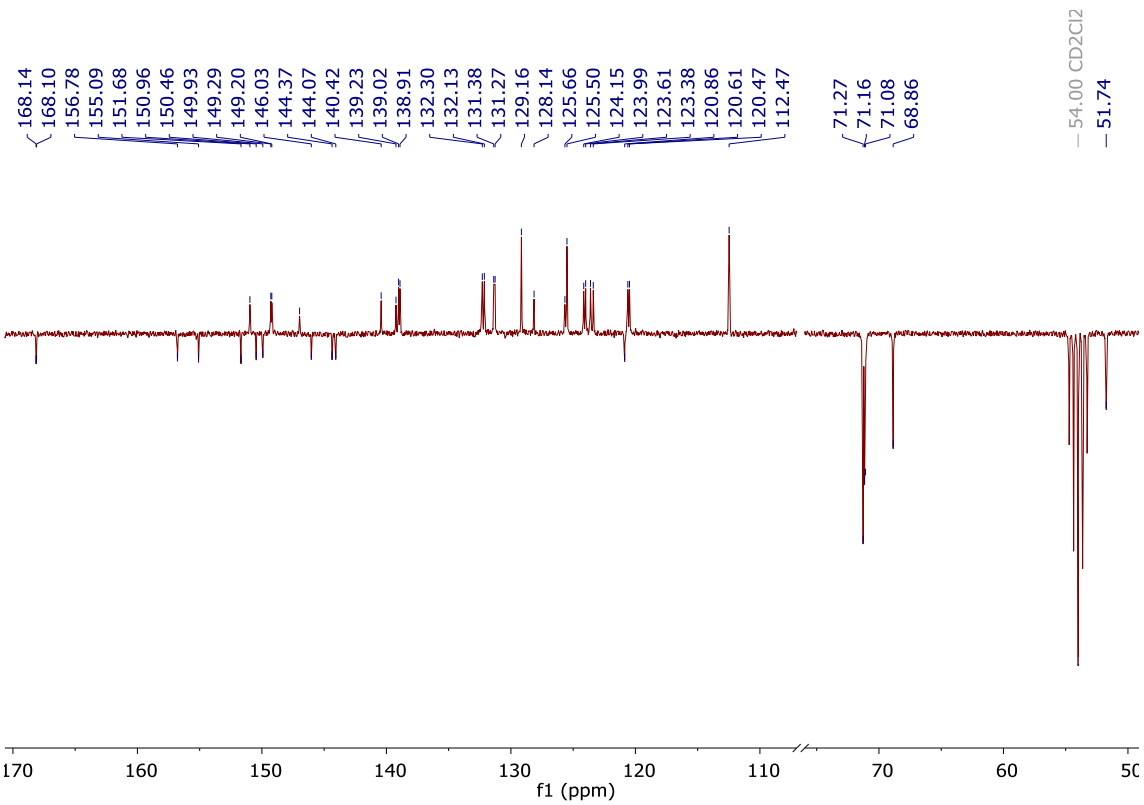


Figure S103. *^{13}C APT NMR spectrum of compound **C7** (CD_2Cl_2, 300 MHz).*

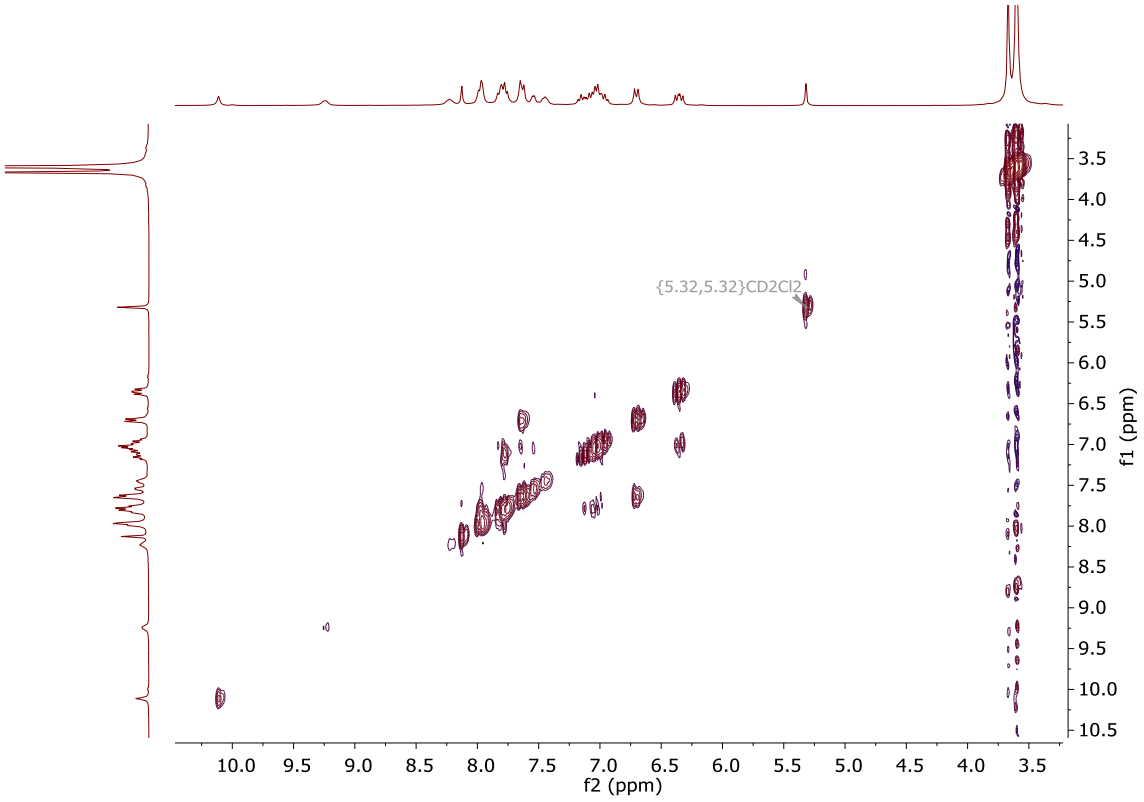


Figure S104. *COSY NMR spectrum of compound **C7** (CD_2Cl_2, 300 MHz).*

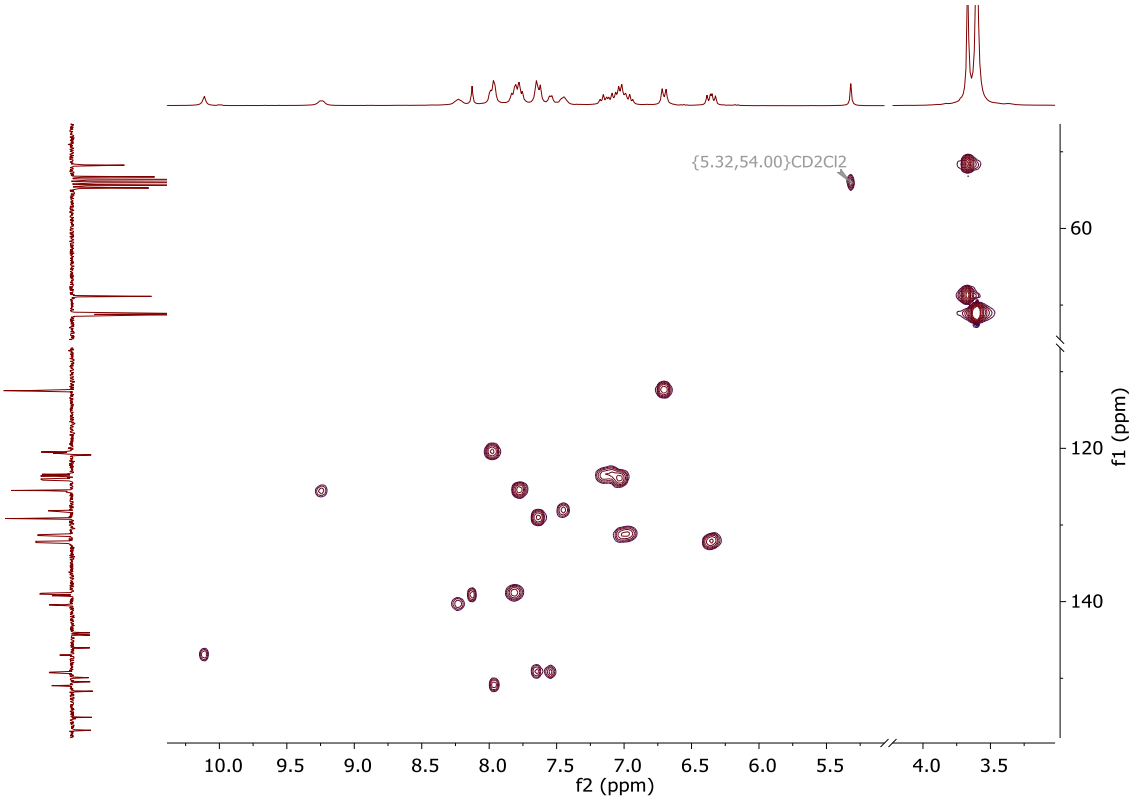


Figure S105. *HSQC NMR spectrum of compound* ***C7*** *(CD_2Cl_2, 300 MHz).*

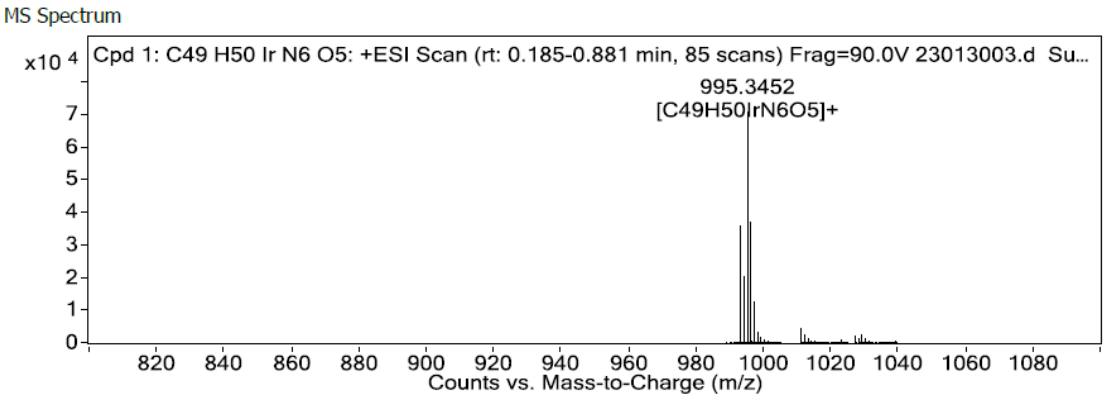


Figure S106. *Mass spectrum of compound* ***C7****.*

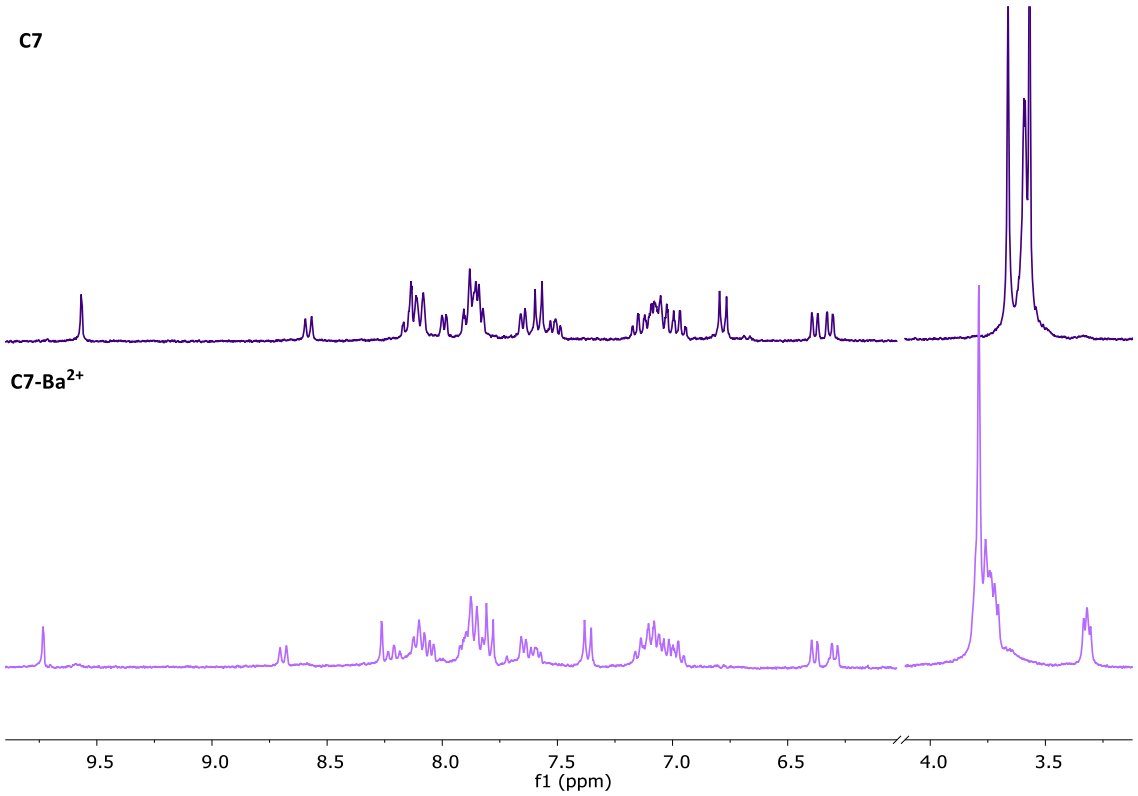
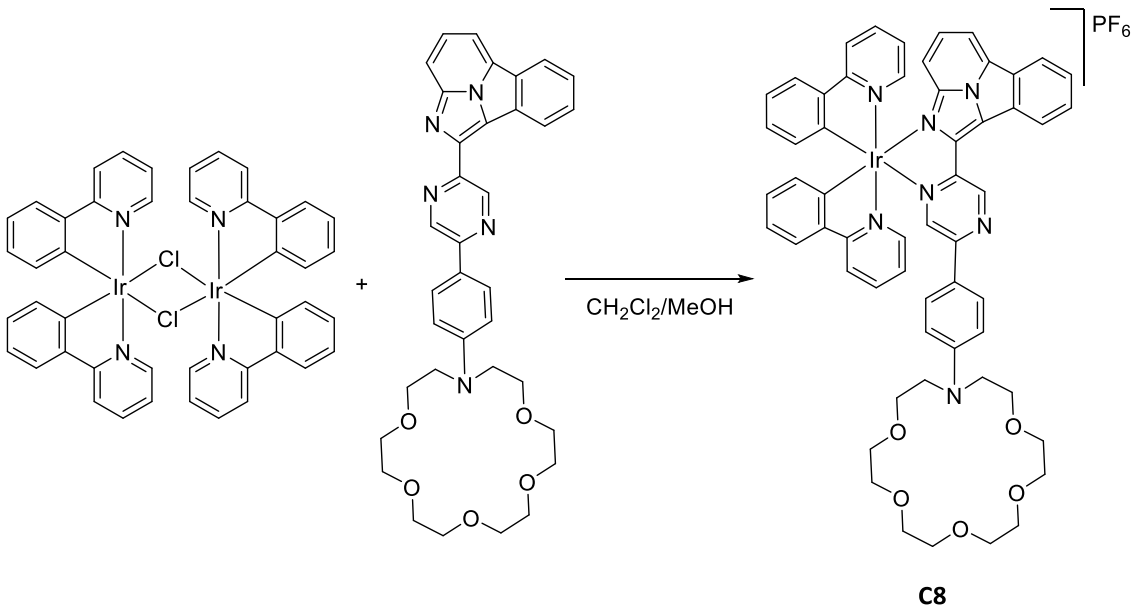


Figure S107. *^{1}H NMR of compound **C7** and **C7-Ba^{2+}**.*

3.1.4 Complex C8, $[Ir(ppy)_2(G3c)]PF_6$



C8

Under a N_2 atmosphere, to $[Ir(ppy)_2Cl]_2$ (19 mg, 18 µmol) and compound **G3c** (22 mg, 38 µmol) 5 mL of CH_2Cl_2/MeOH (2:1, v/v) was added. The reaction mixture was refluxed

overnight at 35°C. The solvents were evaporated and the title compound was precipitated by adding NH_4PF_6 in MeOH. A dark red solid with quantitative yield.

Exact mass: ESI-MS [$C_{57}H_{53}IrN_7O_5$]: calculated: m/z= 1106.3714, found: m/z= 1106.3738.

^{1}H NMR (500 MHz, acetone-*d*$_6$): δ 10.01 (s, 1H), 8.94 (d, J = 8.1 Hz, 1H), 8.74 (d, J = 8.0 Hz, 1H), 8.52 (d, J = 7.4 Hz, 1H), 8.38 (s, 1H), 8.33 (d, J = 5.6 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.11 (m, 2H), 8.06 – 7.98 (m, 4H), 7.91 (m, 3H), 7.68 (d, J = 8.7 Hz, 2H), 7.26 – 7.13 (m, 2H), 7.07 (m, 3H), 6.97 (t, J = 6.6 Hz, 1H), 6.89 (d, J = 8.6 Hz, 2H), 6.62 (t, J = 7.5 Hz, 2H), 6.53 (d, J = 8.6 Hz, 1H).

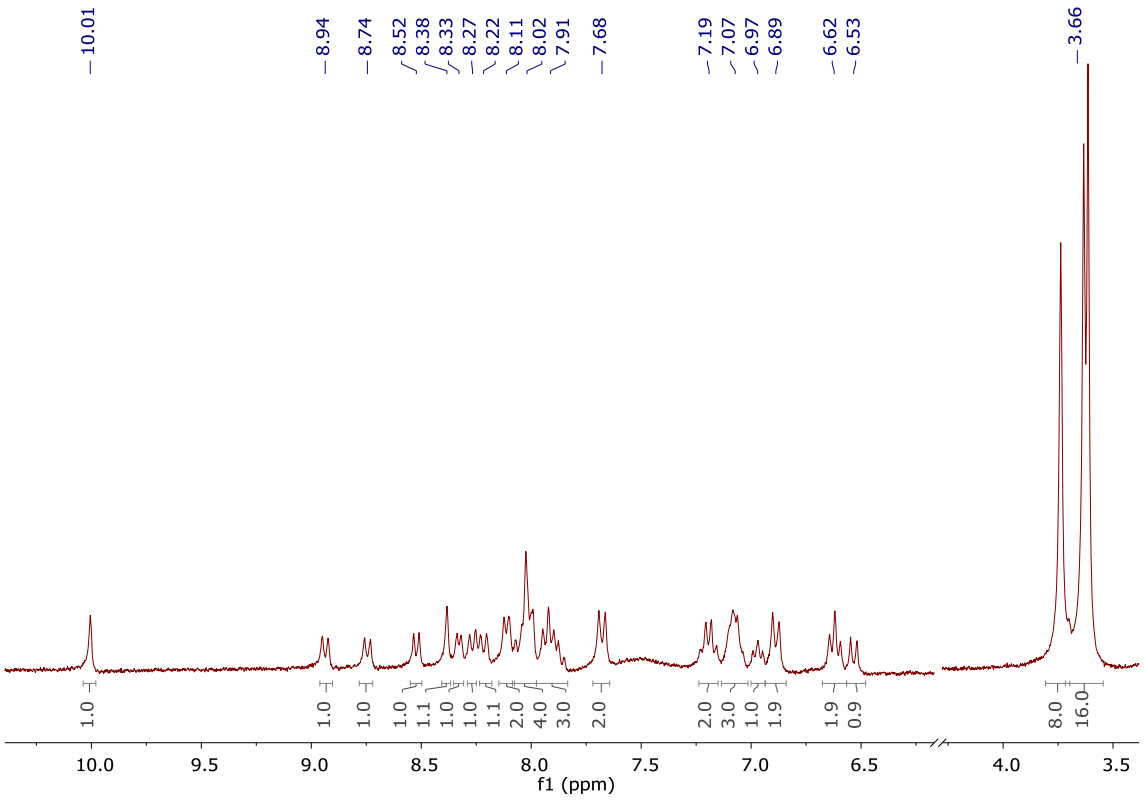


Figure S108. *^{1}H NMR spectrum of compound **C8** (acetone-d$_6$, 500 MHz).*

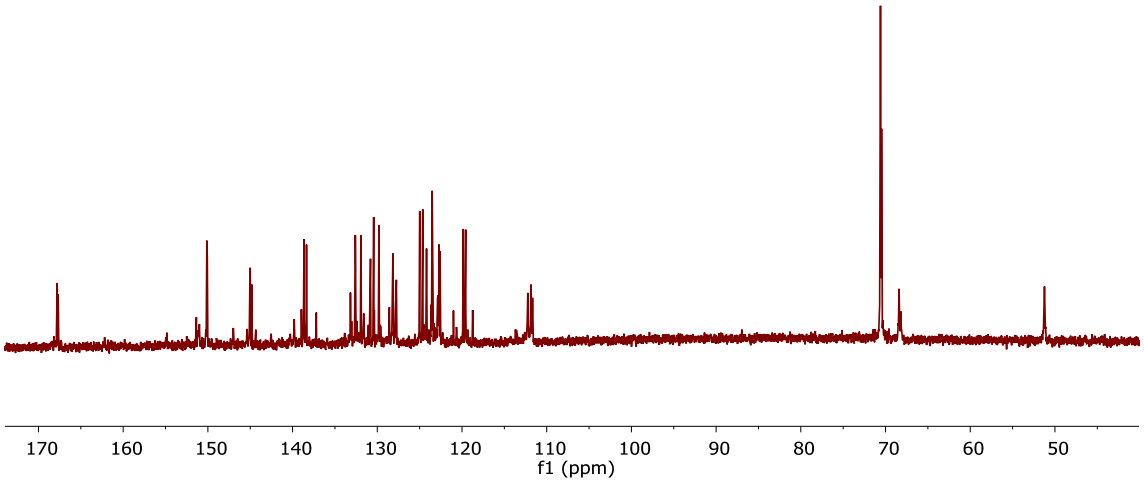


Figure S109. *^{13}C DEPT NMR spectrum of compound **C8** (acetone-d_6, 125 MHz).*

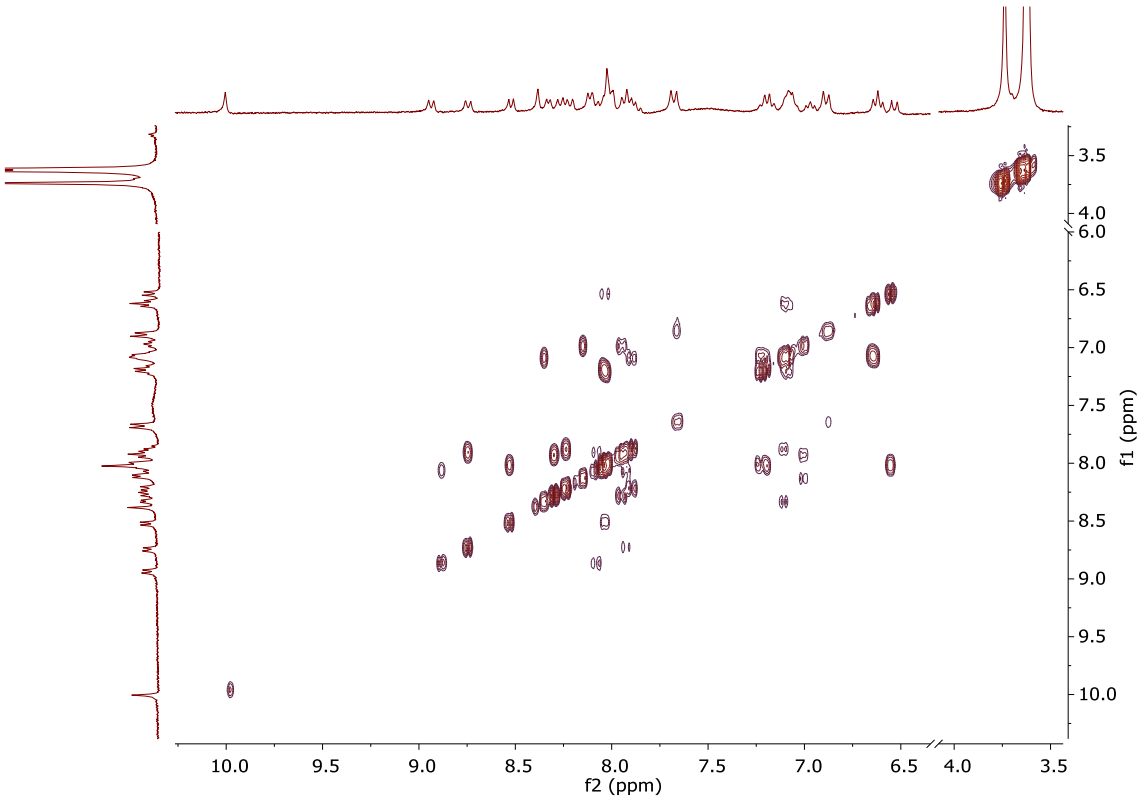


Figure S110. *COSY NMR spectrum of compound **C8** (acetone-d_6, 500 MHz).*

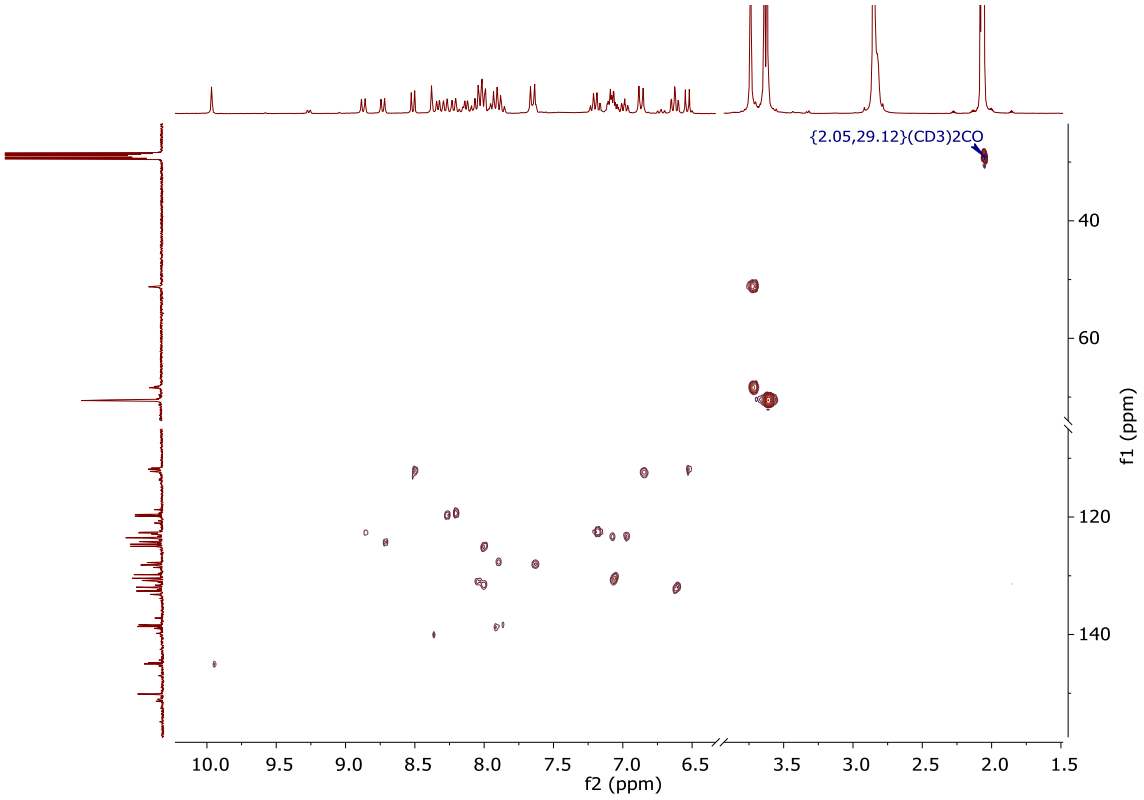


Figure S111. *HSQC NMR spectrum of compound* ***C8*** *(acetone-d_6, 500 MHz).*

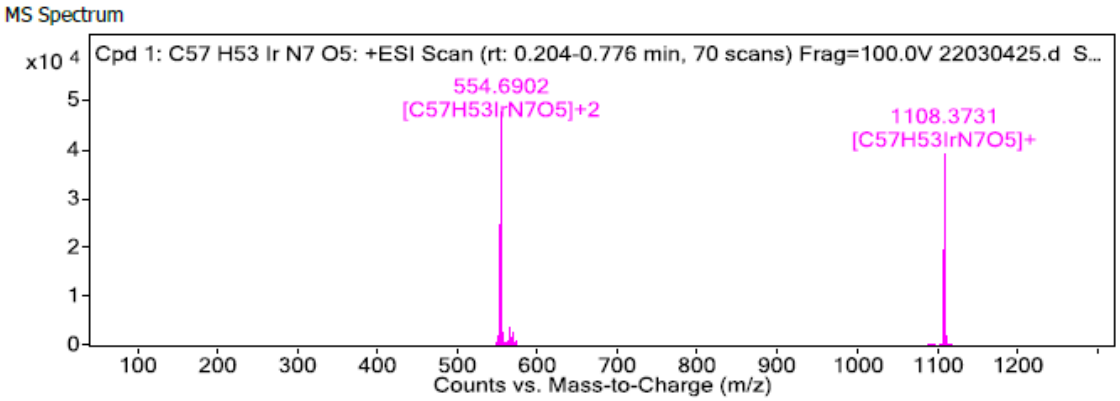


Figure S112. *Mass spectrum of compound* ***C8****.*

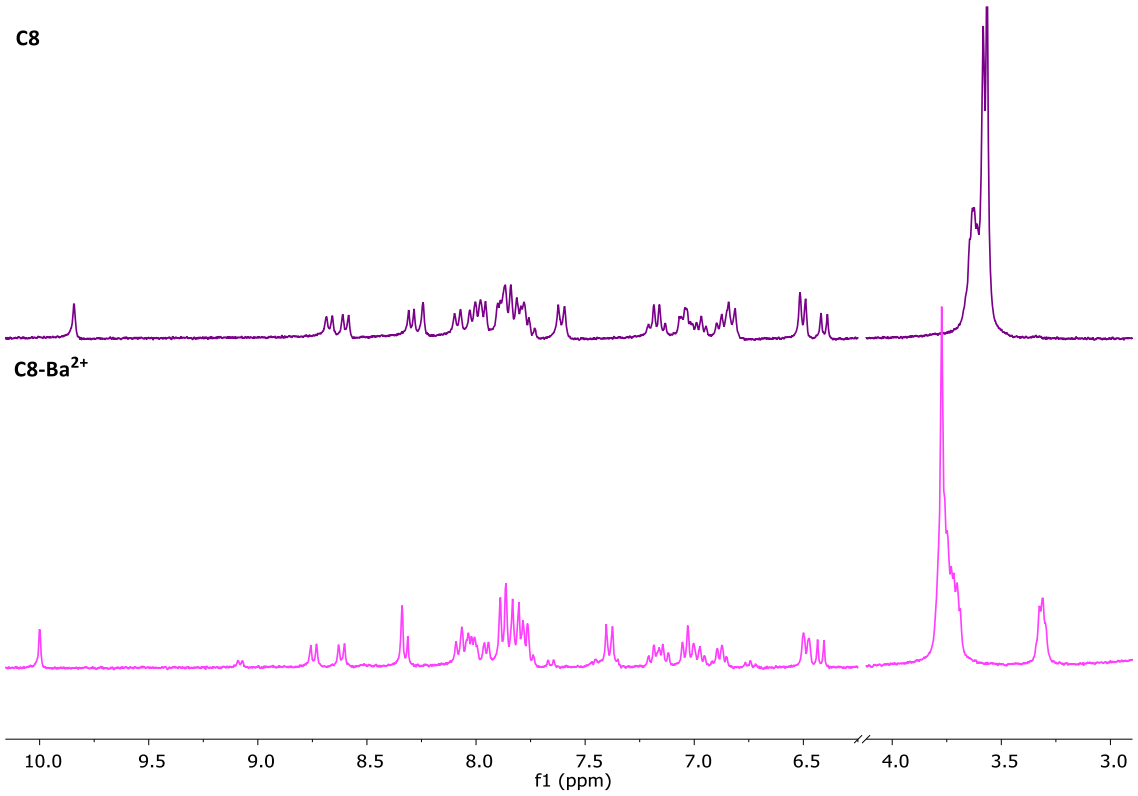


Figure S113. *^{1}H NMR of compound **C8** and **C8-Ba^{2+}**.*

3.2 PHOTOPHYSICAL CHARACTERIZATION

3.2.1 C5

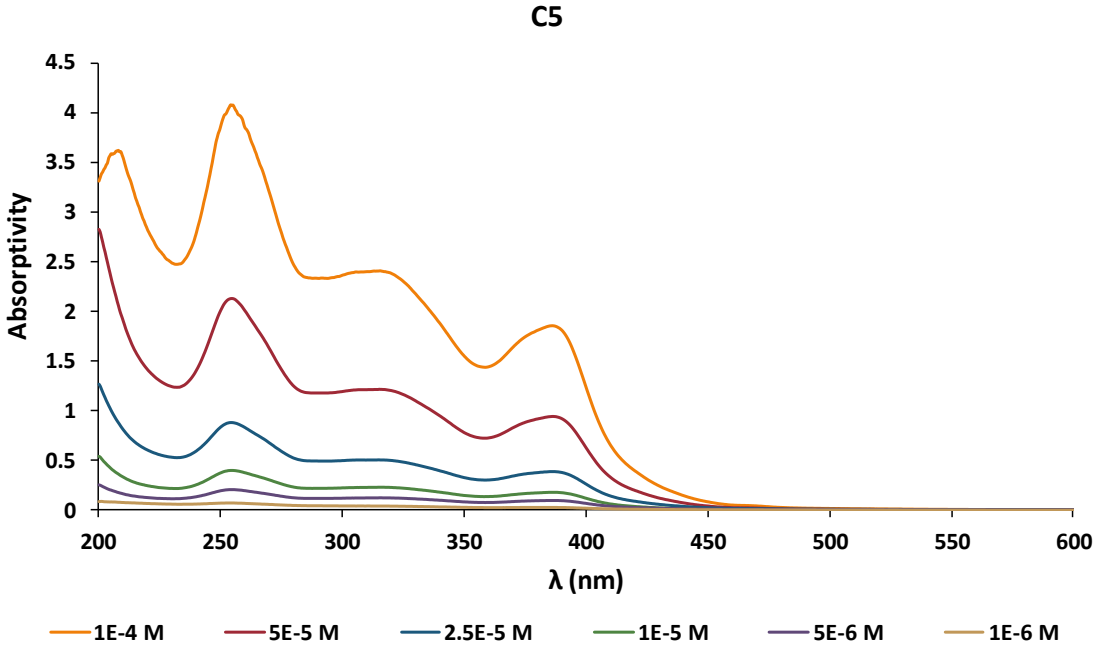
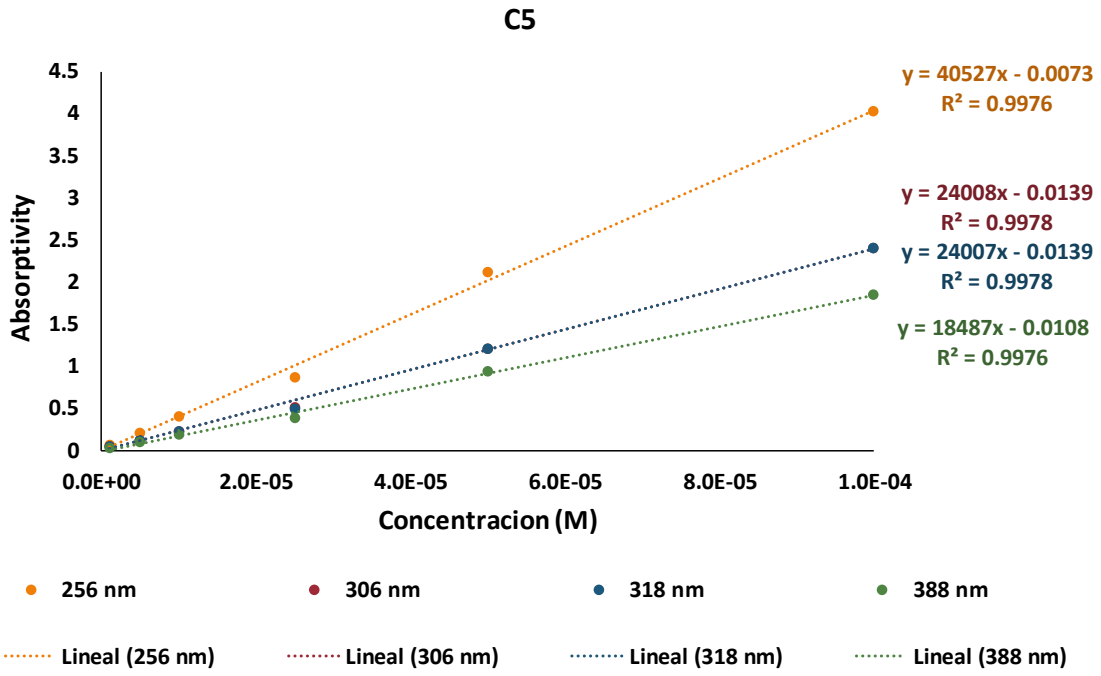


Figure S114. *UV-vis absorption spectra of free **C5** in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
256	40527
306	24008
318	24007
388	18487

Figure S115. *Calculated molar extinction coefficients of* ***C5*** *at selected absorption maxima.*

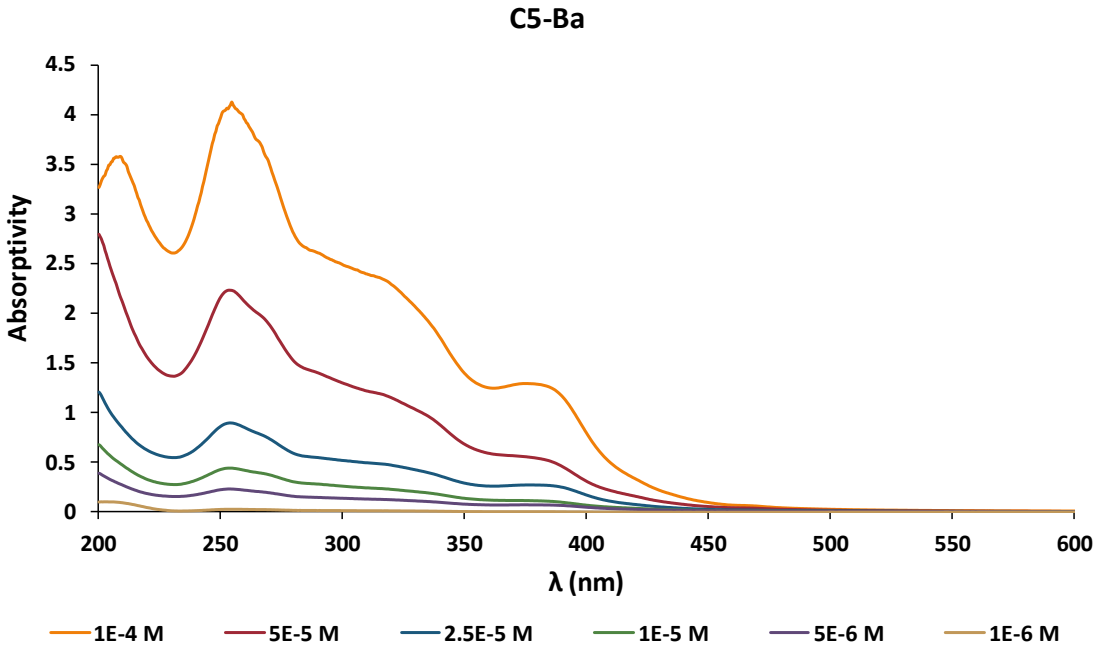
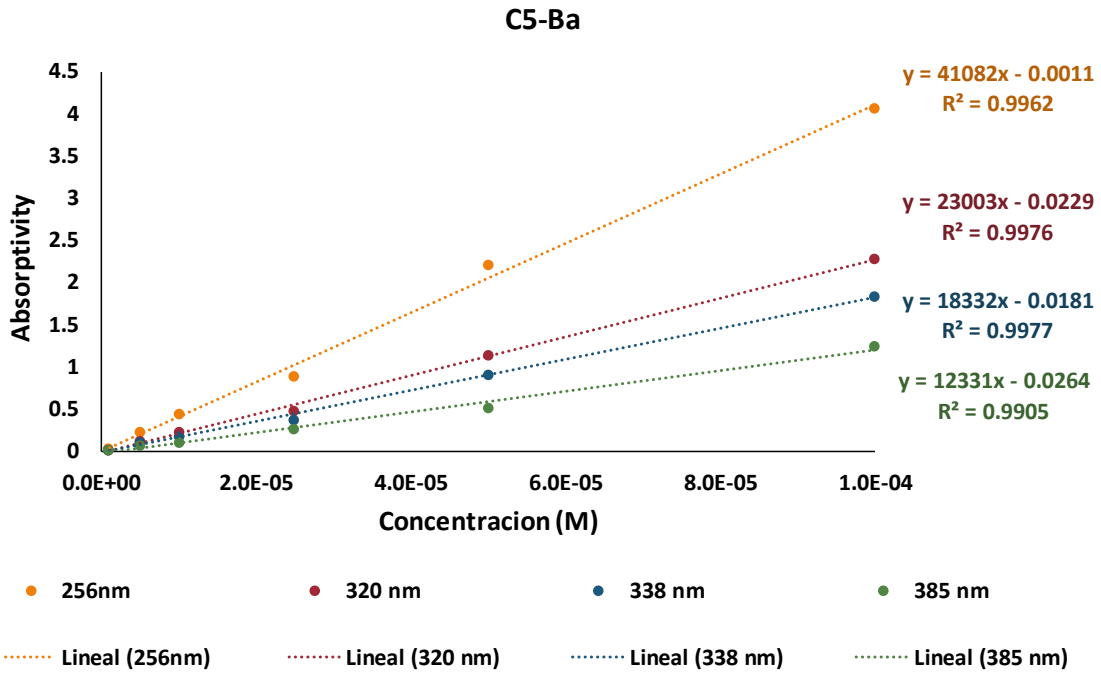


Figure S116. *UV-vis absorption spectra of free* ***C5-Ba*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
256	41082
320	23003
338	18332
385	12331

Figure S117. *Calculated molar extinction coefficients of* ***C5-Ba*** *at selected absorption maxima.*

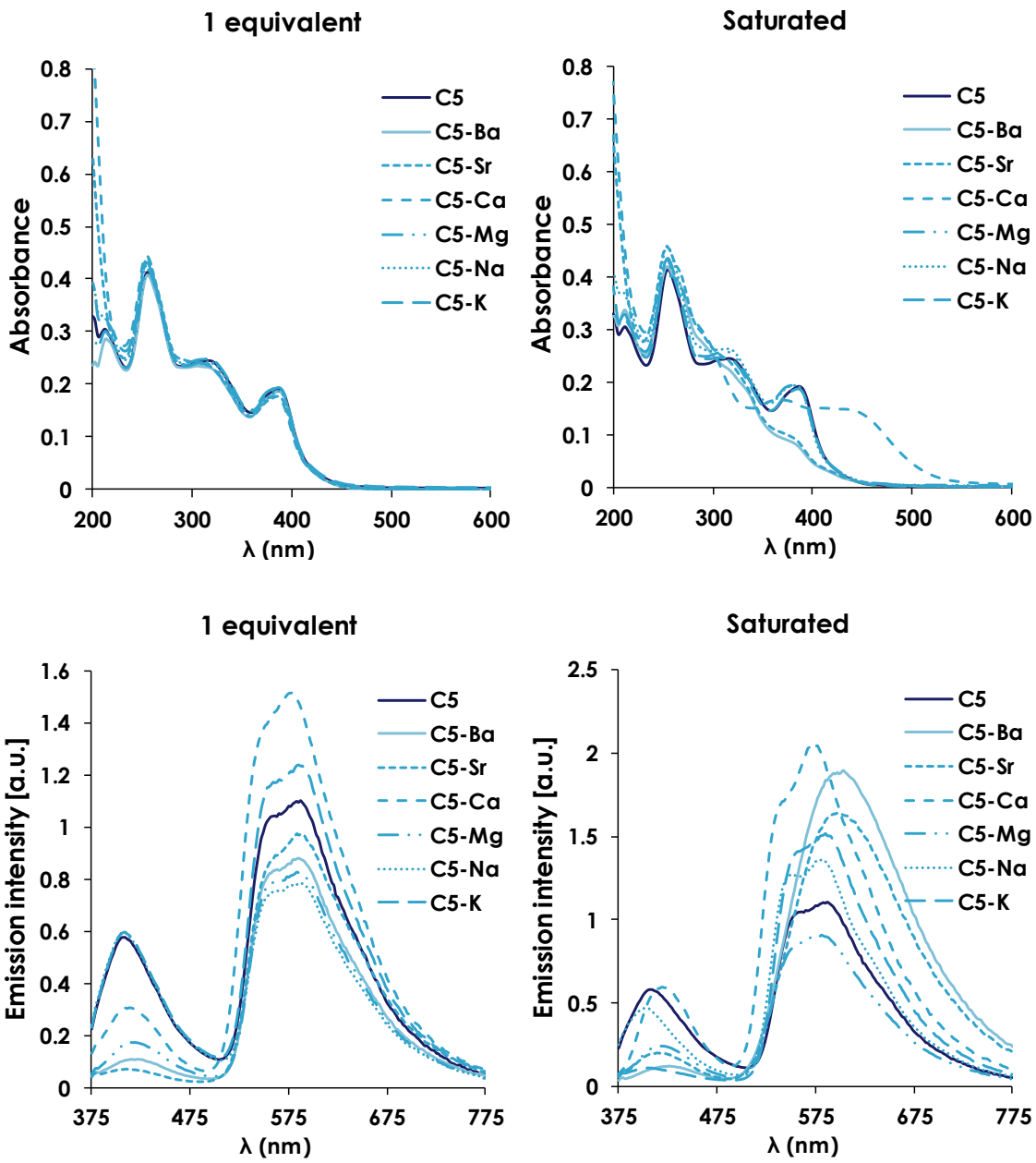


Figure S118. *Absorption and emission spectra of* ***C5*** *with 1 equivalent and saturated solutions of* Ba^{2+}*,* Sr^{2+}*,* Ca^{2+}*,* Mg^{2+}*,* Na^{+} *and* K^{+} *perchlorate salts.*

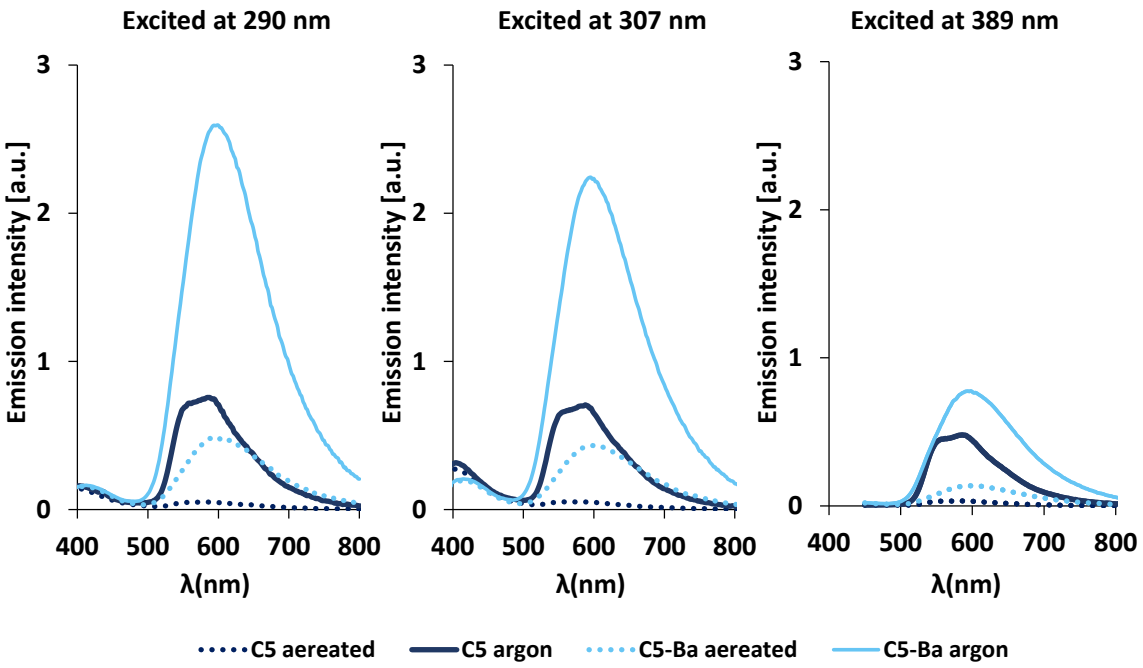


Figure S119. *Emission spectra of **C5** and **C5-Ba** excited at different wavelength, under aerated and argon conditions.*

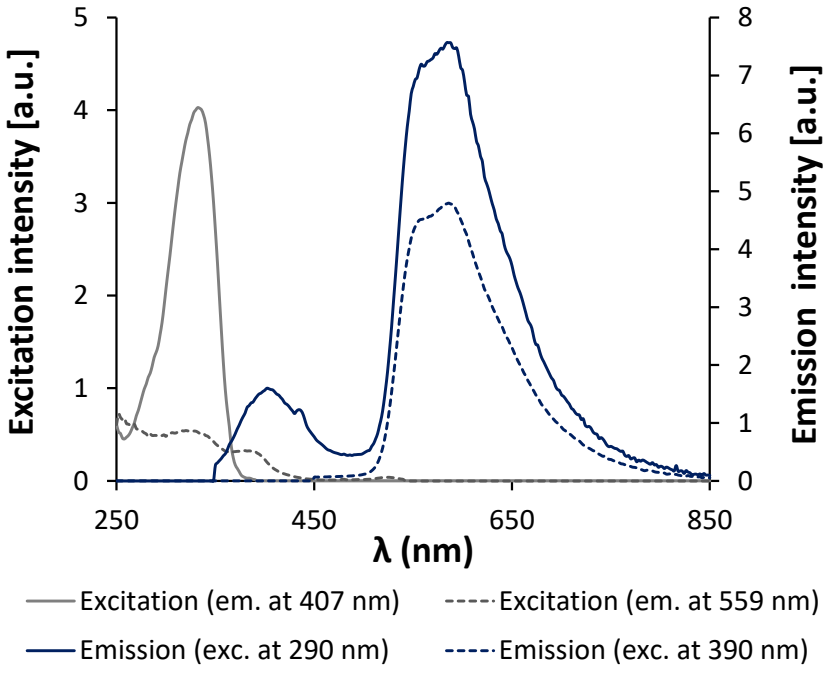
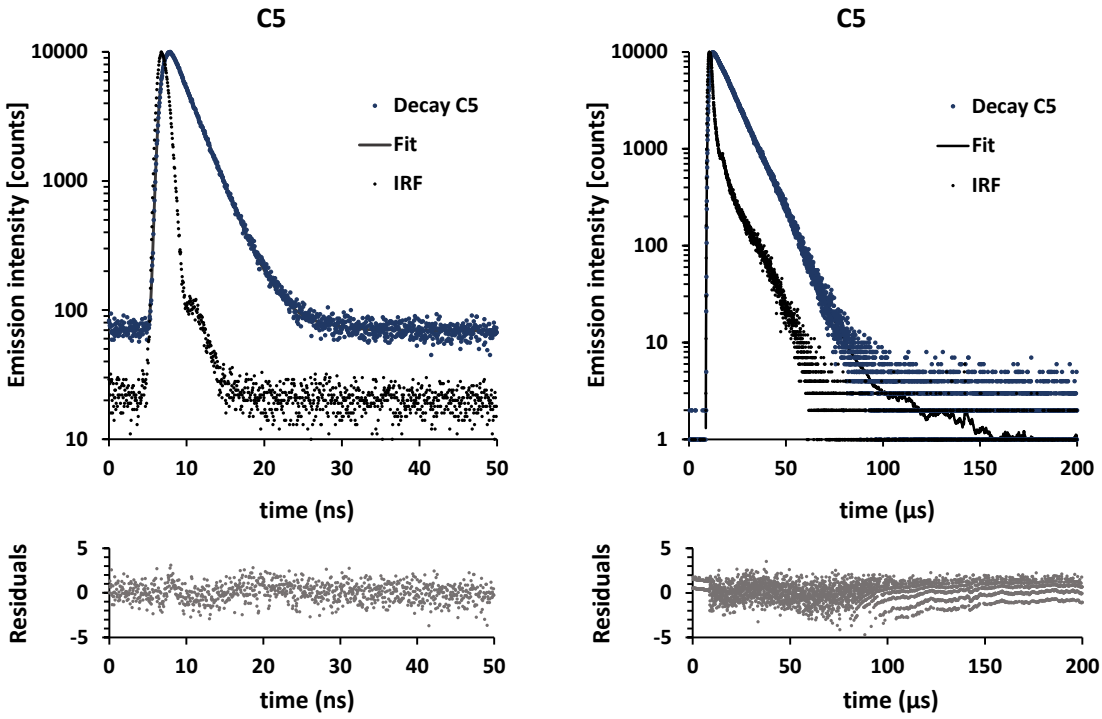


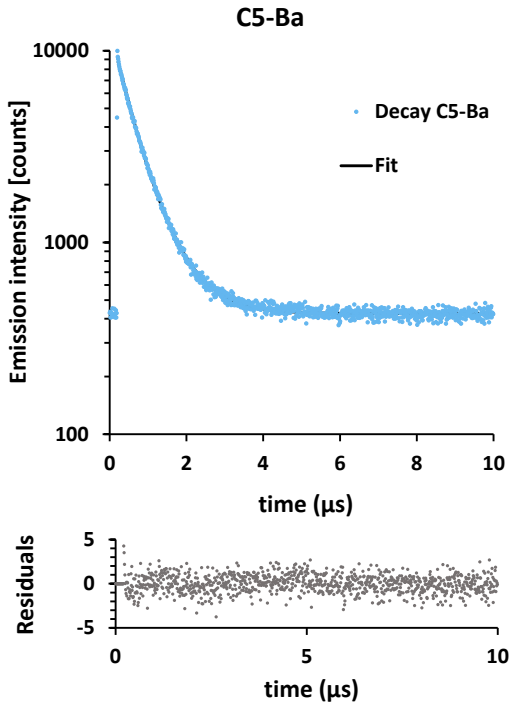
Figure S120. *Excitation and emission spectra of **C5** at different wavelength.*



Emission at 407 nm EPLED340 TCSPC 20MHz Slit 5, 1024 chanels, 10000 counts	
Result	
τ	χ^2
2.7 ns	1.1

Emission at 559 nm MicroF lamp MCS exc. 340 nm 100Hz Slit 1/2, 1000 chanels, 10000 counts	
Result	
τ	χ^2
388 ns (4%) 6735 ns (96%)	1.0

***Figure S121**. Lifetime decay and results of **C5**, excited at the two emission maxima.*



Emission at 599 nm EPLED340 MCS 100kHz Slit 10, 1000 chanels, 10000 counts	
Result	
τ	χ^2
414 ns (40%) 744 ns (60%)	1.1

***Figure S122.** Lifetime decay and result of **C5-Ba**, excited at the emission maximum.*

3.2.2 C6

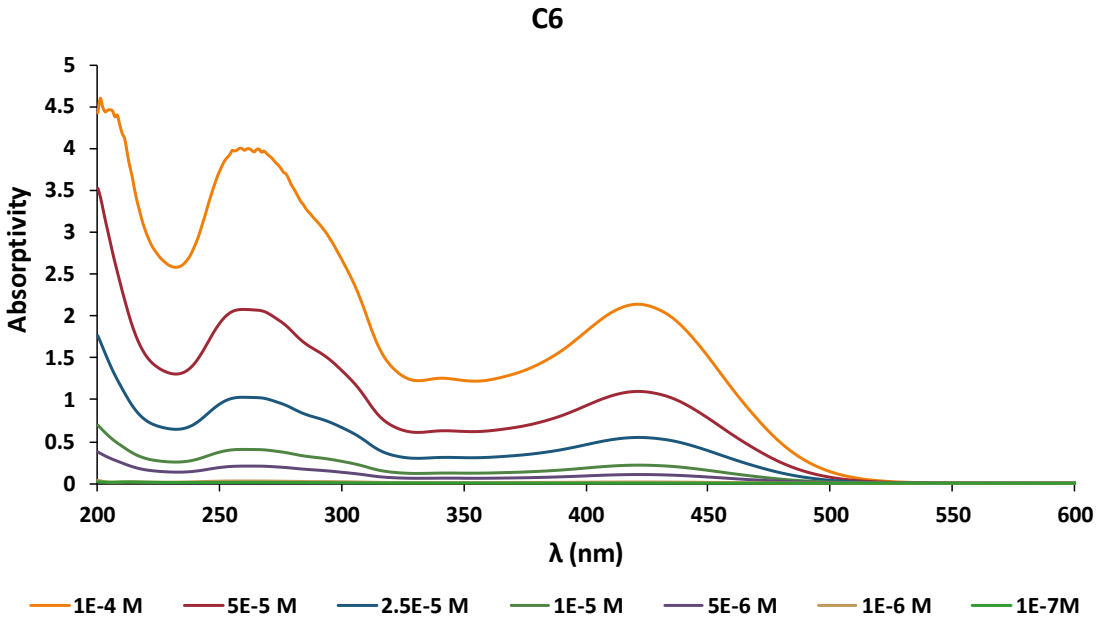
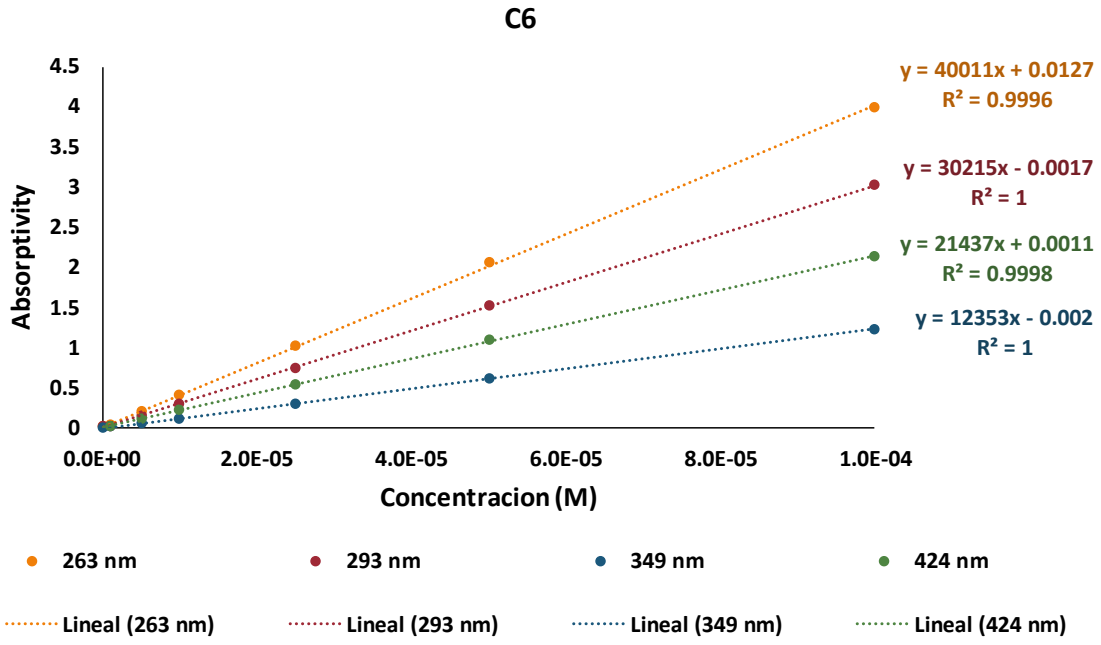


***Figure S123**. UV-vis absorption spectra of free **C6** in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
263	40011
293	30215
349	12353
424	21437

***Figure S124.** Calculated molar extinction coefficients of **C6** at selected absorption maxima.*

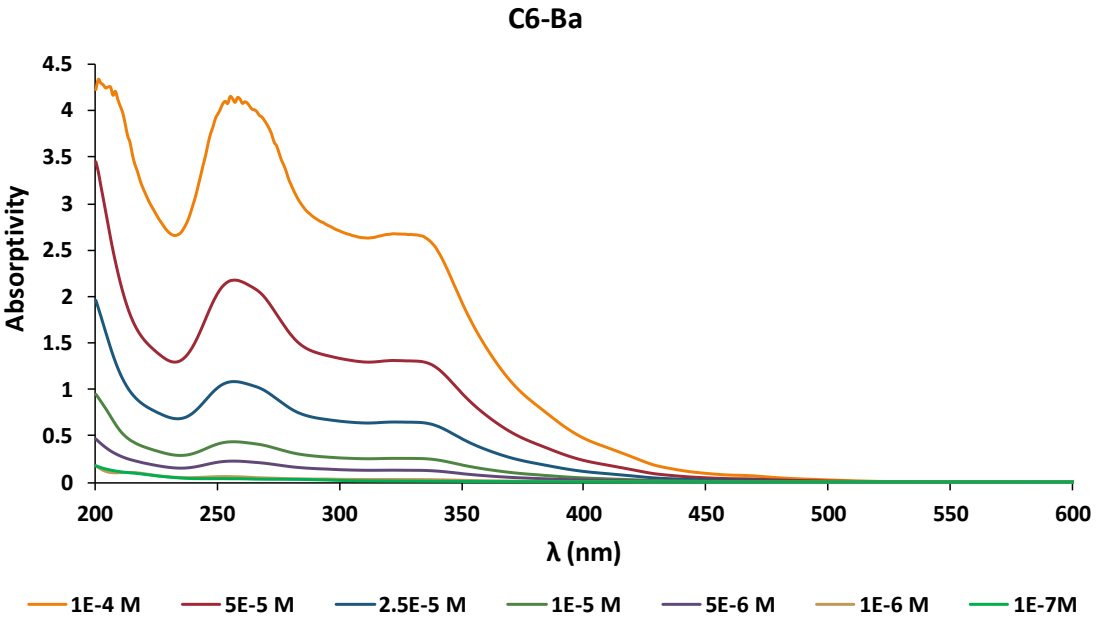
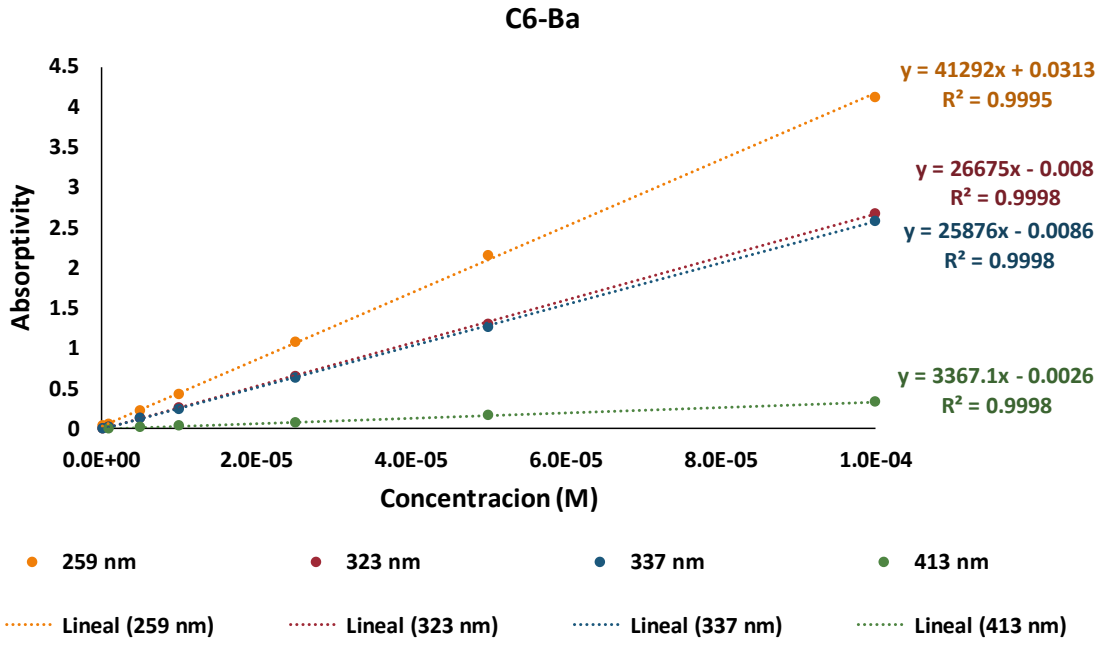


Figure S125. *UV-vis absorption spectra of free* ***C6-Ba*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
259	41292
323	26675
337	25876
413	3367.1

Figure S126. *Calculated molar extinction coefficients of* ***C6-Ba*** *at selected absorption maxima.*

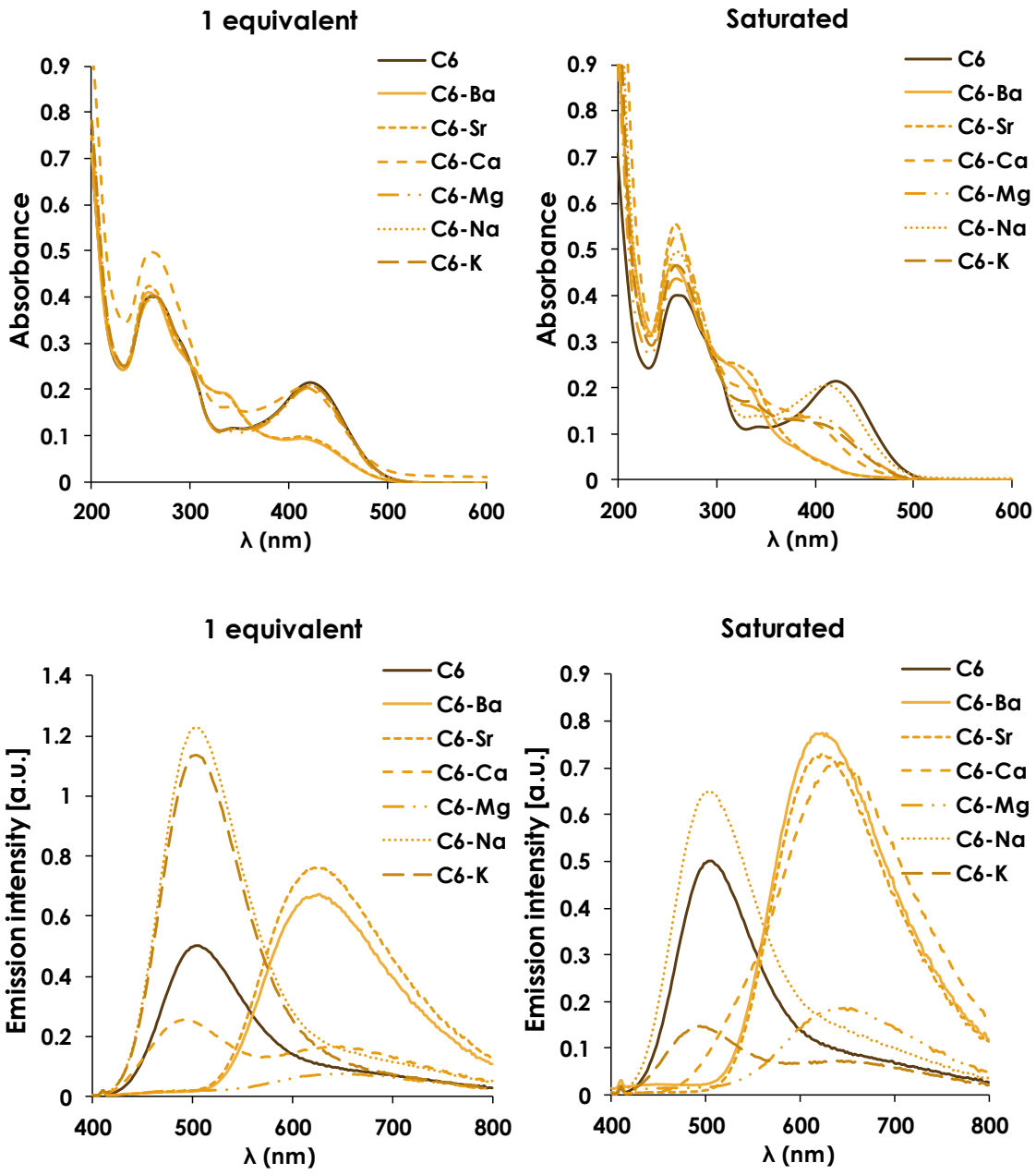


Figure S127. *Absorption and emission spectra of* ***C6*** *with 1 equivalent and saturated solutions of* Ba^{2+}*,* Sr^{2+}*,* Ca^{2+}*,* Mg^{2+}*,* Na^{+} *and* K^{+} *perchlorate salts.*

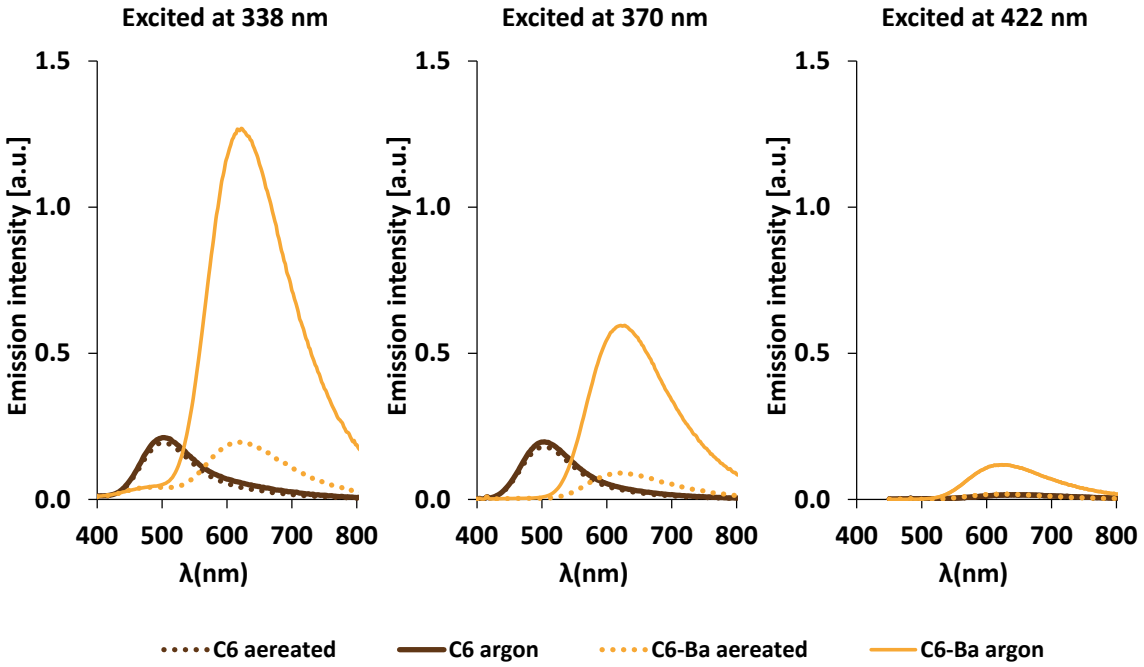


Figure S128. *Emission spectra of **C6** and **C6-Ba** excited at different wavelength, under aerated and argon conditions.*

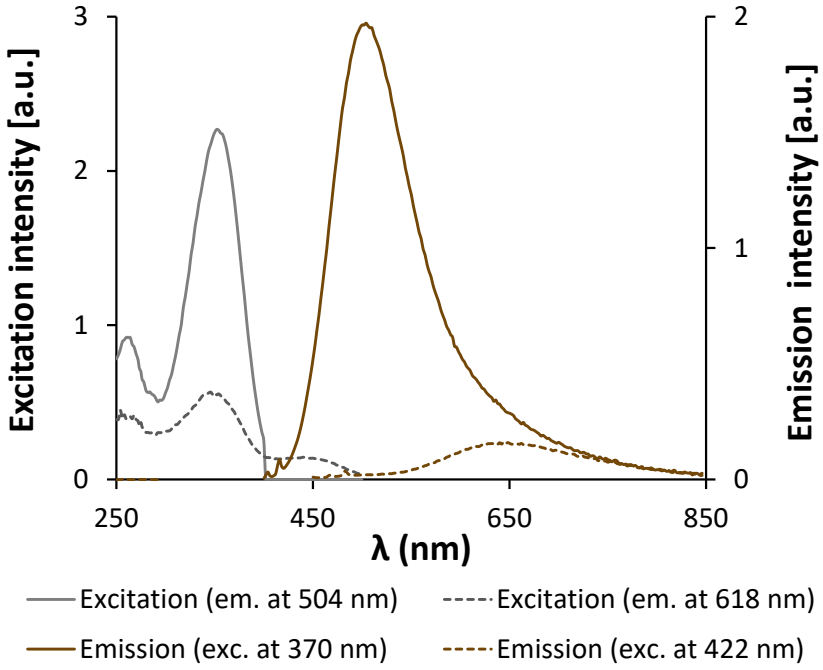
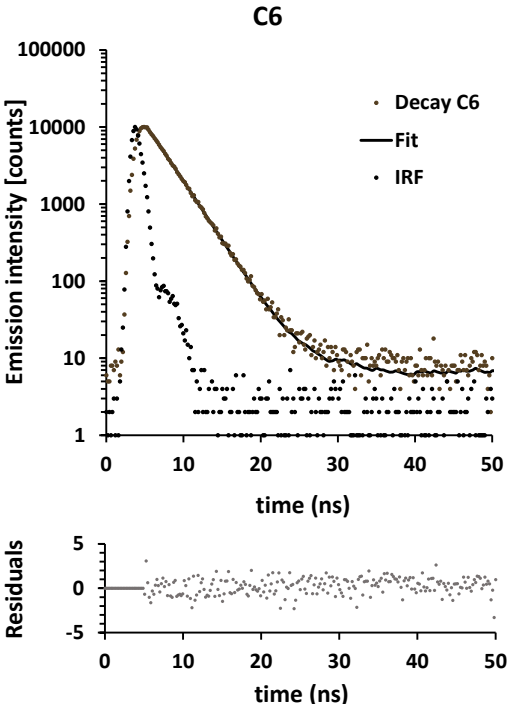
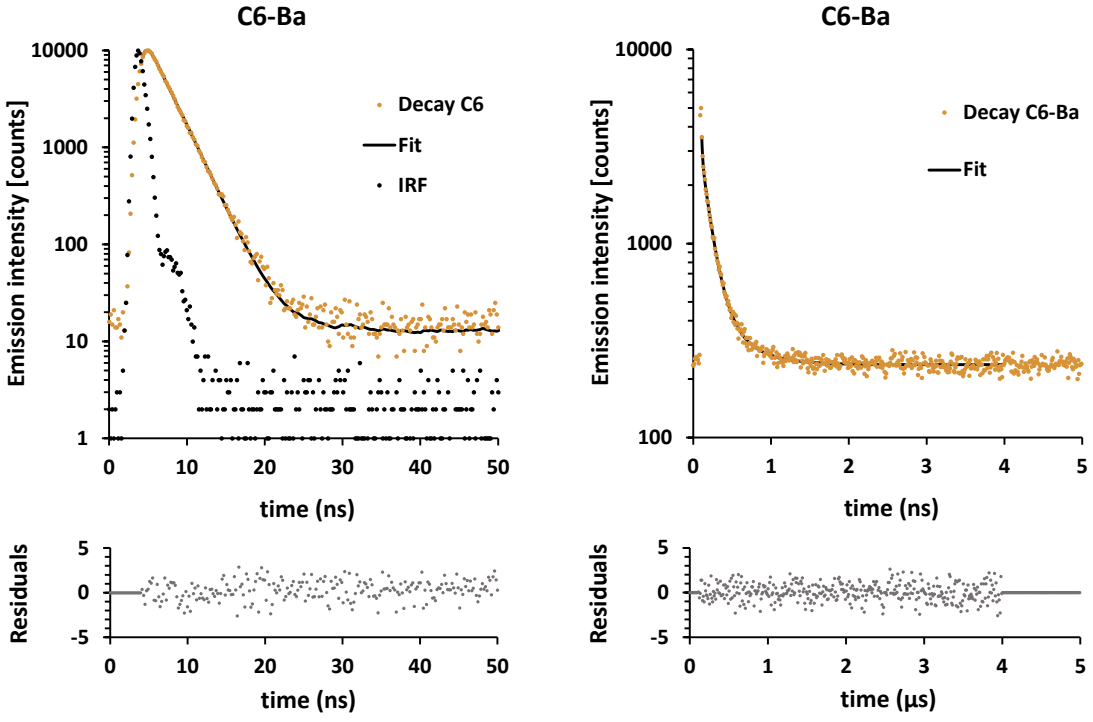


Figure S129. *Excitation and emission spectra of **C6** at different wavelength.*



Emission at 502 nm EPLED340 TCSPC 2MHz Slit 13, 1024 chanels, 10000 counts	
Result	
τ	χ^2
2.78 ns	1.1

Figure S130. *Lifetime decay and result of* ***C6****, excited at the emission maximum.*



Emission at 478 nm EPLED340 TCSPC 2MHz Slit 13, 1024 chanels, 10000 counts	
Result	
τ	χ^2
2.48 ns	1.2

Emission at 599 nm EPLED340 MCS 100kHz Slit 10, 1000 chanels, 10000 counts	
Result	
τ	χ^2
11ns (12%)	0.96
121 ns (64%)	
370 ns (24%)	

Figure S131. *Lifetime decay and results of* ***C6-Ba****, excited at the two emission maxima.*

3.2.3 C7

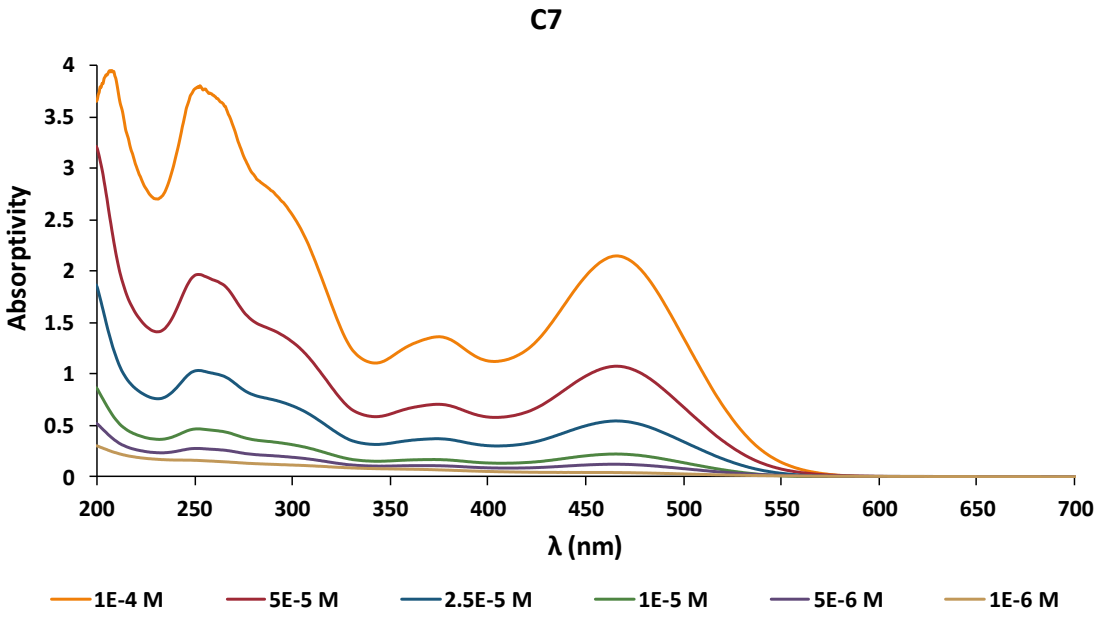
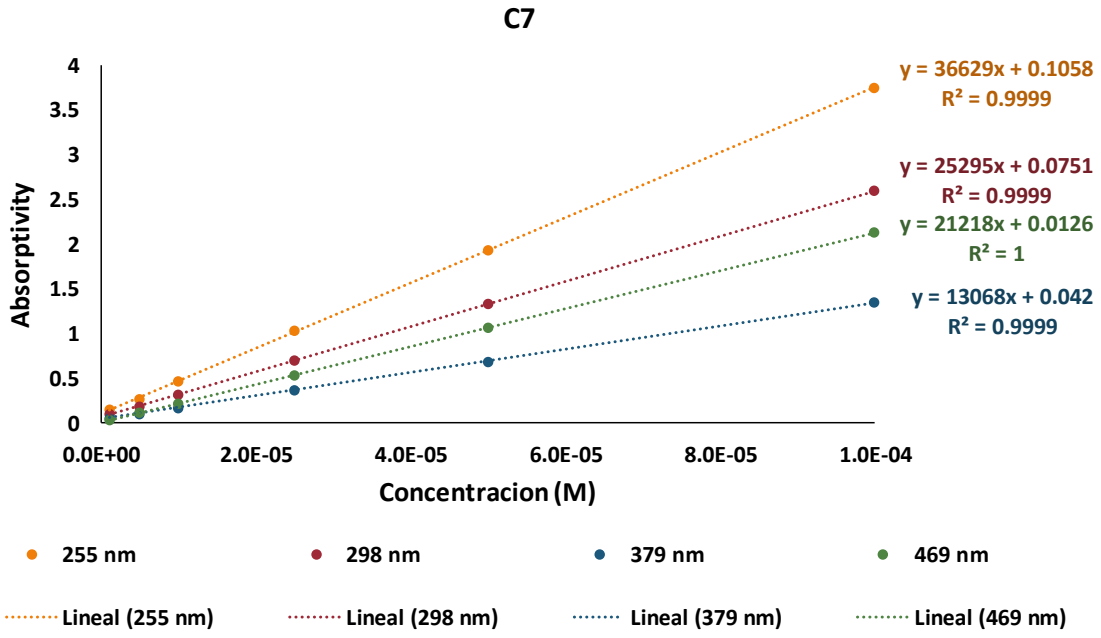


Figure S132. *UV-vis absorption spectra of free **C7** in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
255	36629
298	25295
379	13068
469	21218

Figure S133. *Calculated molar extinction coefficients of **C7** at selected absorption maxima.*

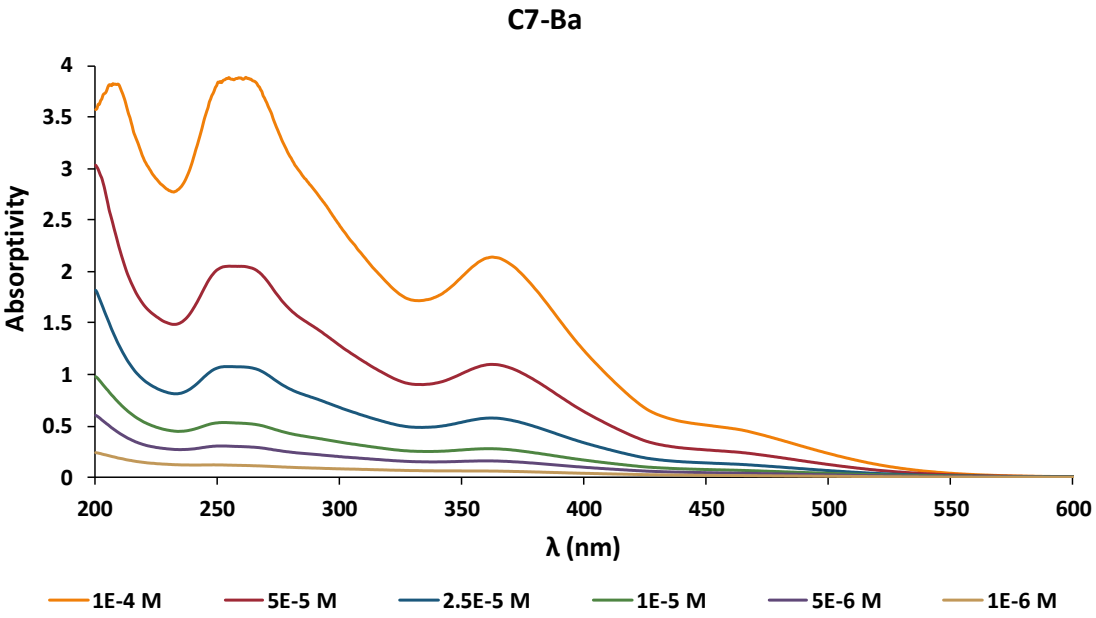
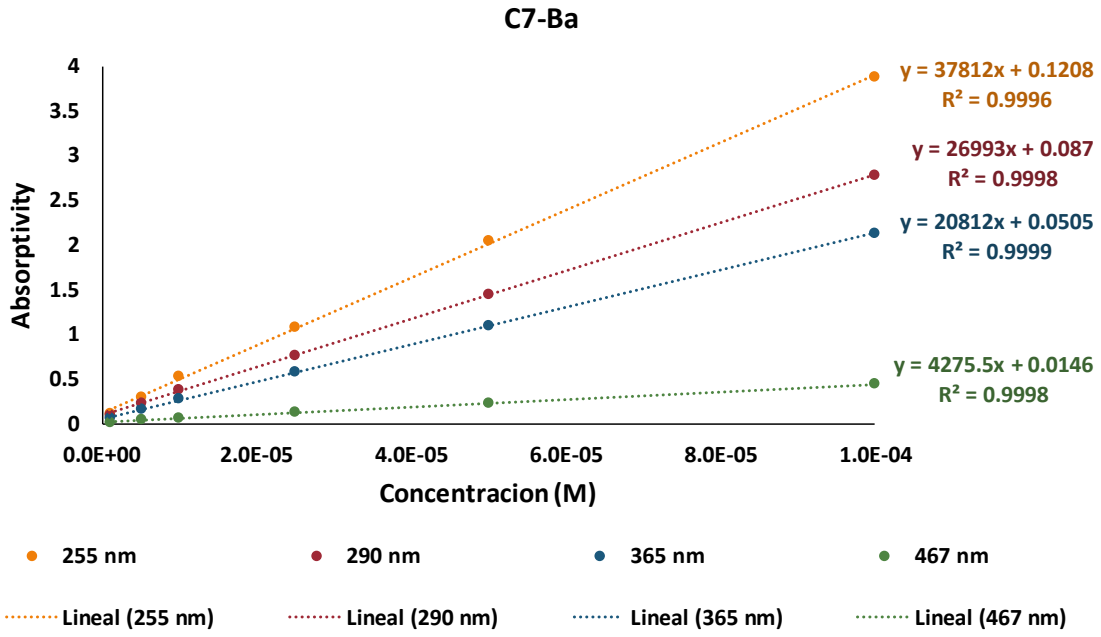


Figure S134. *UV-vis absorption spectra of free* ***C7-Ba*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
255	37812
290	26993
365	20812
567	4275.5

Figure S135. *Calculated molar extinction coefficients of* ***C7-Ba*** *at selected absorption maxima.*

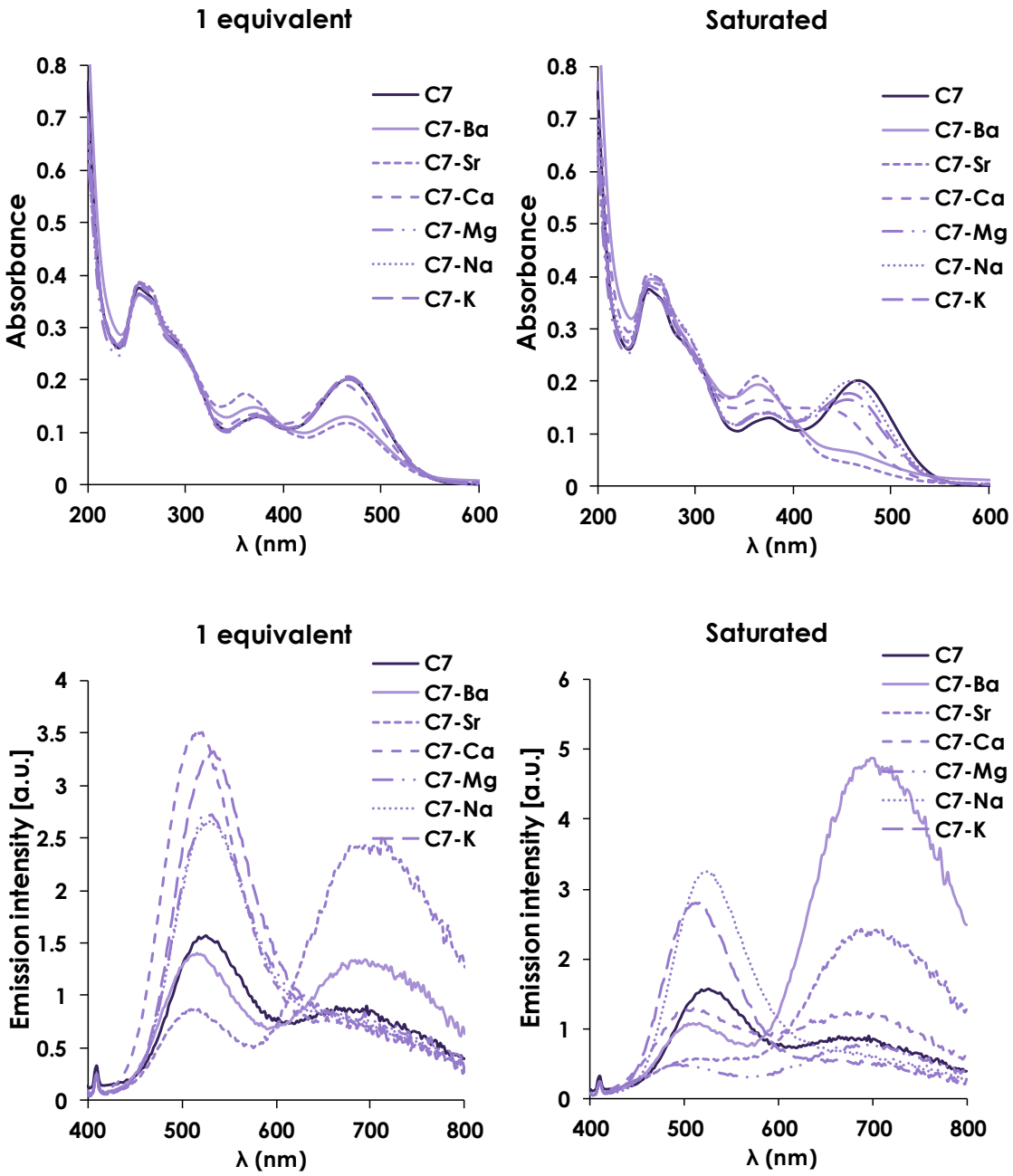


Figure S136. *Absorption and emission spectra of* ***C7*** *with 1 equivalent and saturated solutions of* Ba^{2+}*,* Sr^{2+}*,* Ca^{2+}*,* Mg^{2+}*,* Na^{+} *and* K^{+} *perchlorate salts.*

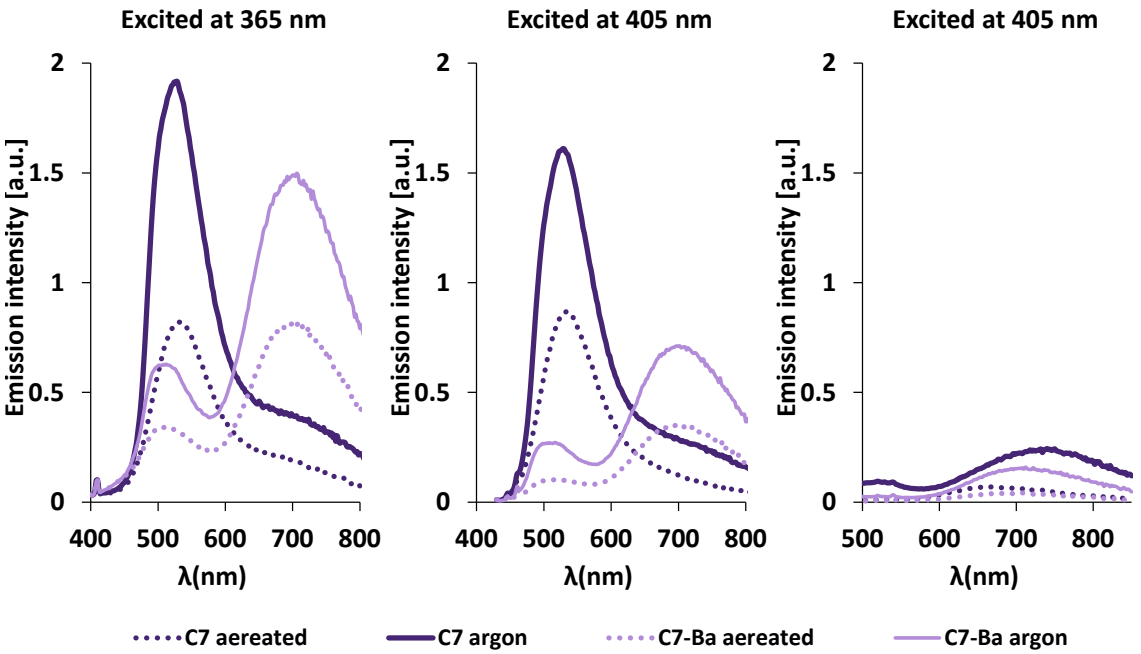


Figure S137. *Emission spectra of **C7** and **C7-Ba** excited at different wavelength, under aerated and argon conditions.*

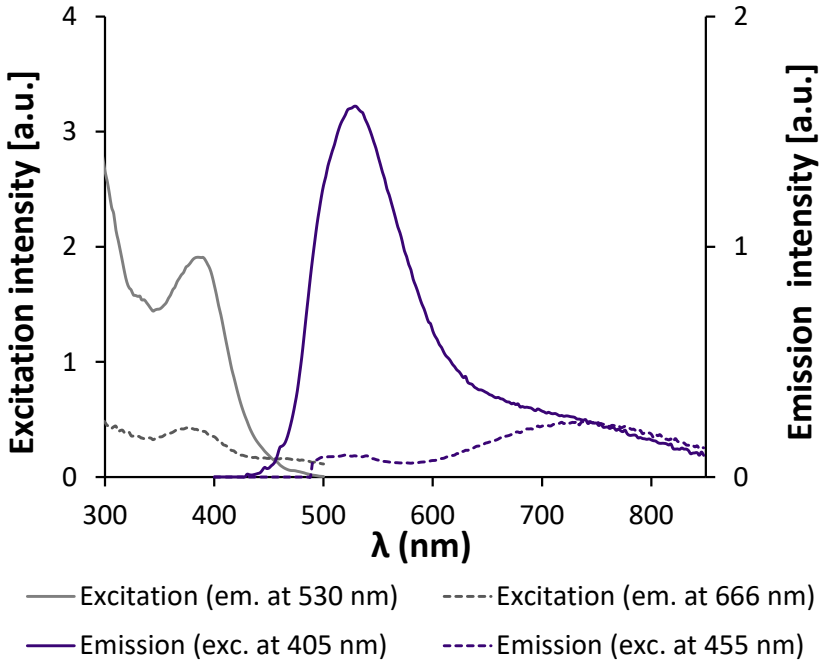
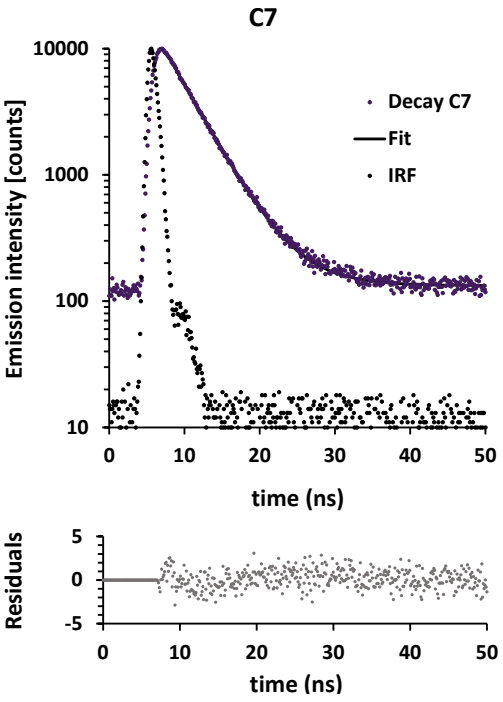
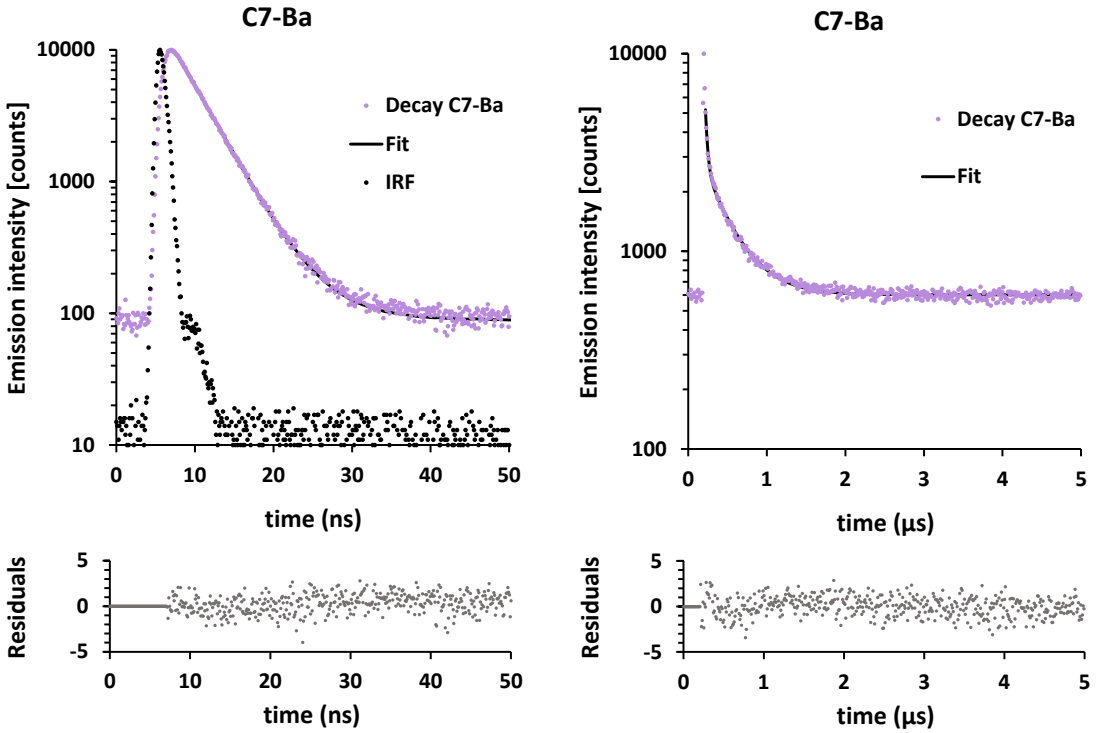


*Figure S138. Excitation and emission spectra of **C7** at different wavelength.*



Emission at 530 nm EPLED340 TCSPC 10MHz Slit 13, 1024 chanels, 10000 counts	
Result	
τ	χ^2
3.9 ns	1.2

Figure S139. *Lifetime decay and results of* ***C7****, excited at the emission maximum.*



Emission at 508 nm EPLED340 TCSPC 10MHz Slit 13, 1024 chanels, 10000 counts	
Result	
τ	χ^2
4.0 ns	1.1

Emission at 700 nm EPLED340 MCS 100kHz Slit 13, 1000 chanels, 10000 counts	
Result	
τ	χ^2
26.2 ns (17%) 341.6 ns (83%)	1.2

Figure S140. *Lifetime decay and results of* ***C5****, excited at the two emission maxima.*

3.2.4 C8

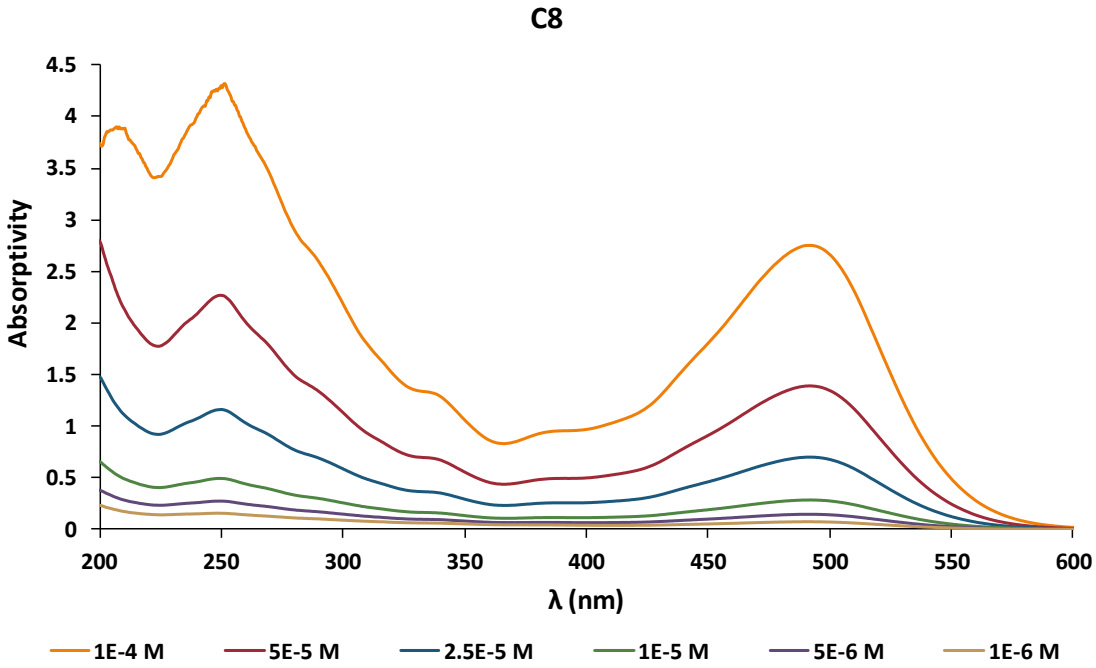
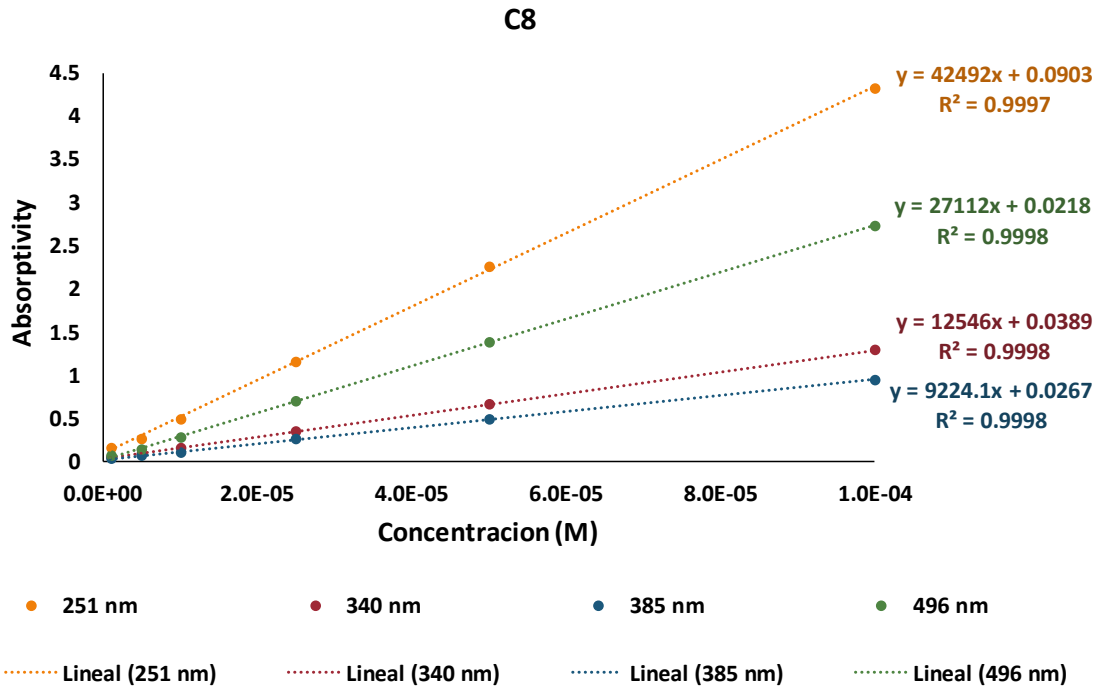


Figure S141. *UV-vis absorption spectra of free **C8** in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
251	42492
340	12546
385	9224.1
496	27112

Figure S142. *Calculated molar extinction coefficients of **C8** at selected absorption maxima.*

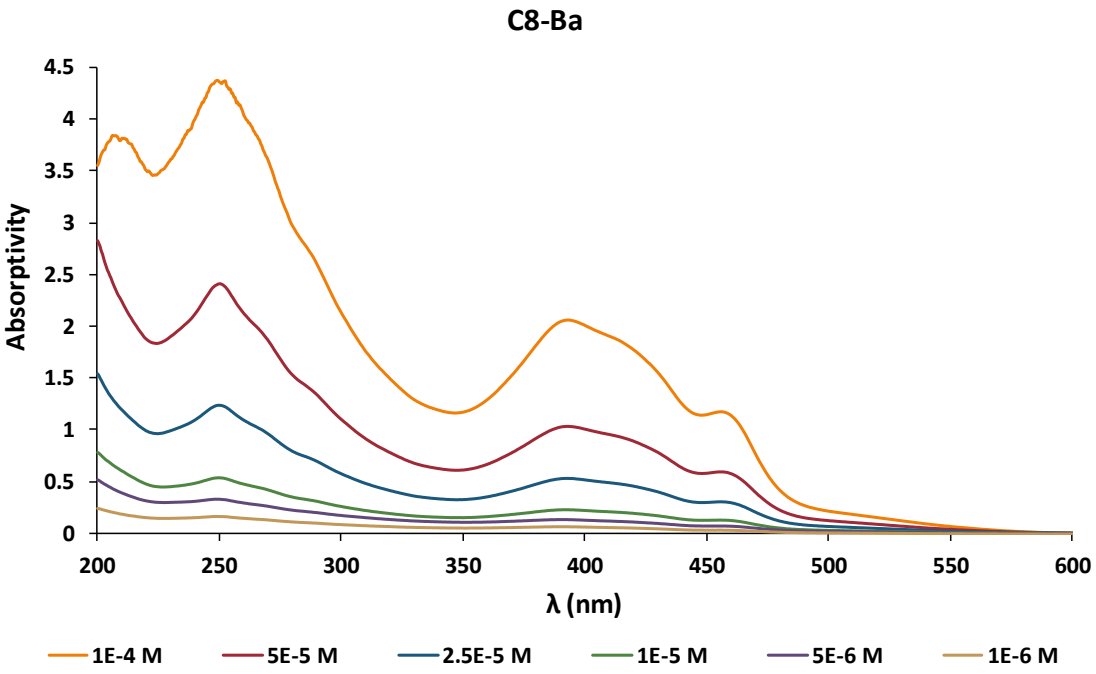
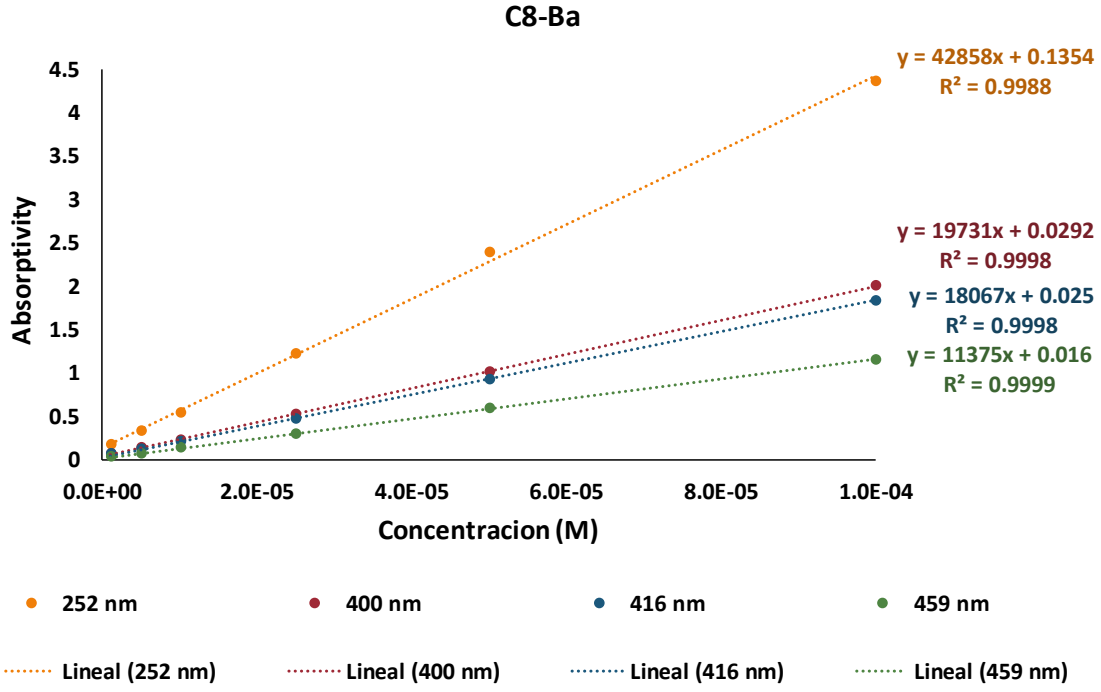


Figure S143. *UV-vis absorption spectra of free **C8-Ba** in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
252	42858
400	19731
416	1806
459	11375

Figure S144. *Calculated molar extinction coefficients of **C8-Ba** at selected absorption maxima.*

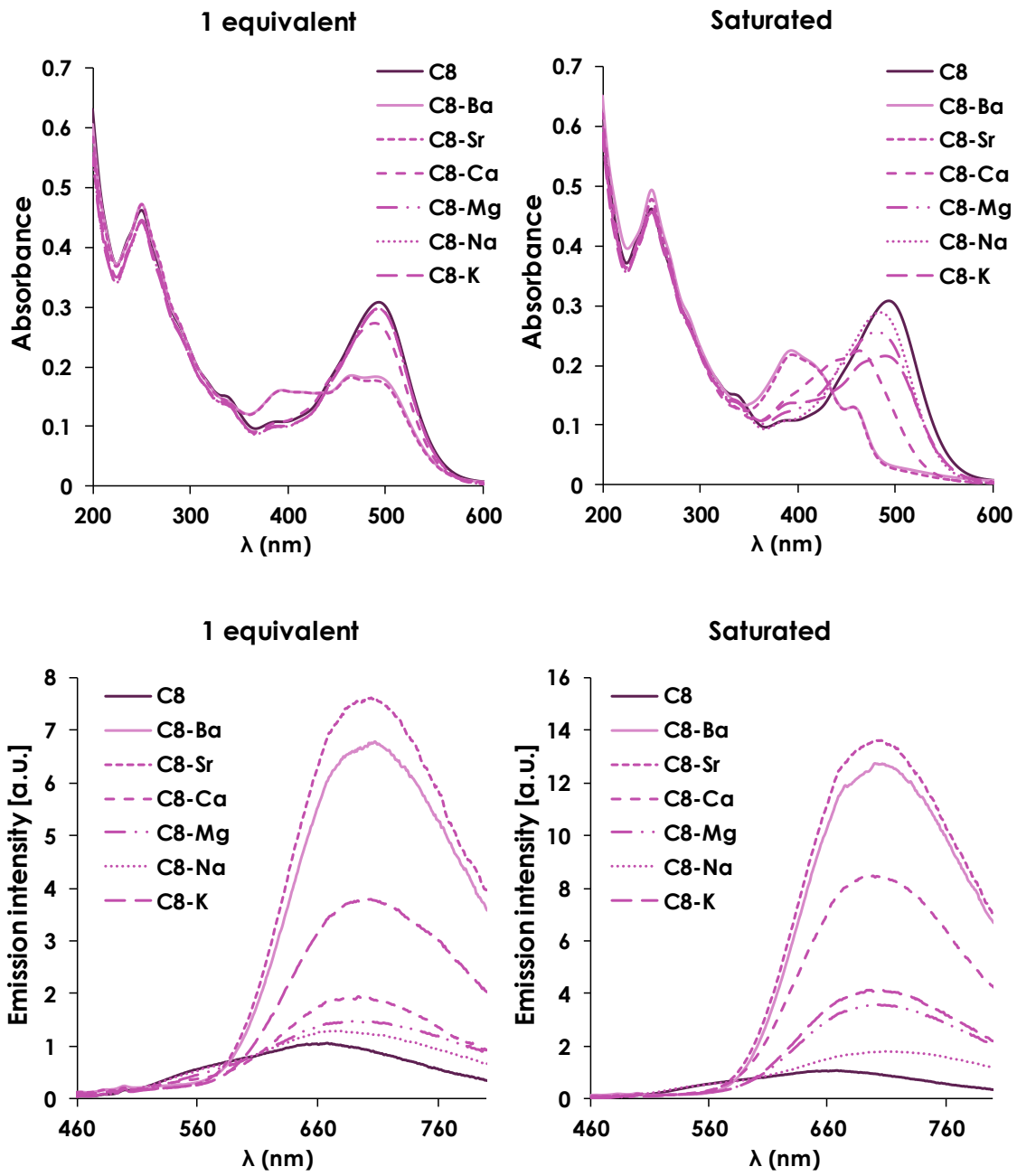


Figure S145. *Absorption and emission spectra of* ***C8*** *with 1 equivalent and saturated solutions of* Ba^{2+}*,* Sr^{2+}*,* Ca^{2+}*,* Mg^{2+}*,* Na^{+} *and* K^{+} *perchlorate salts.*

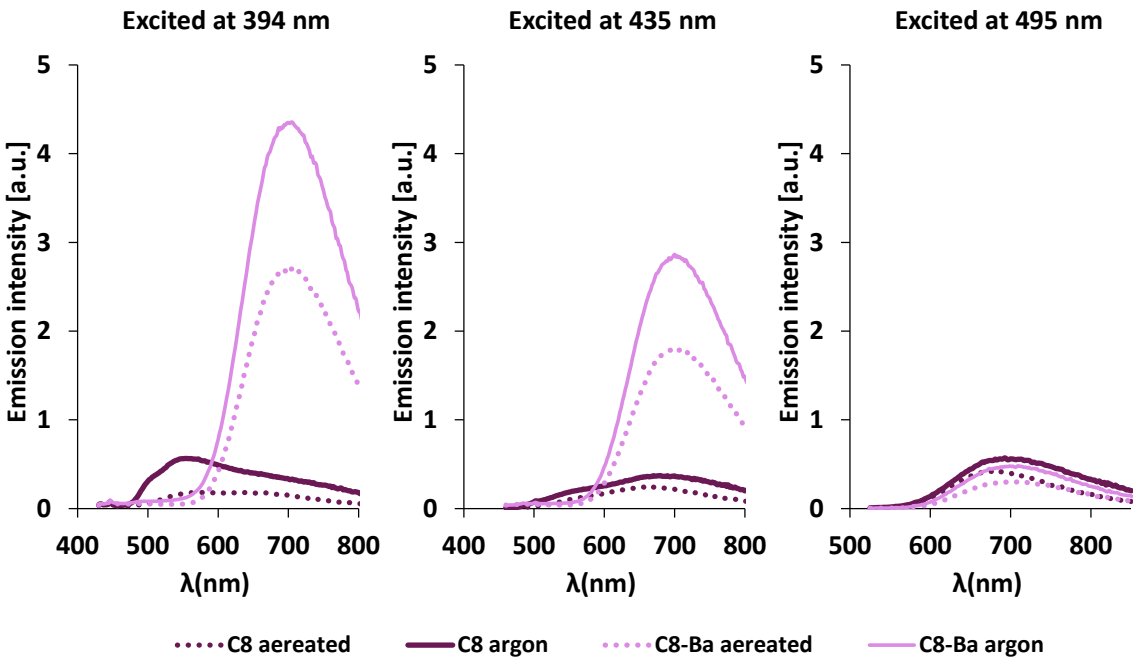
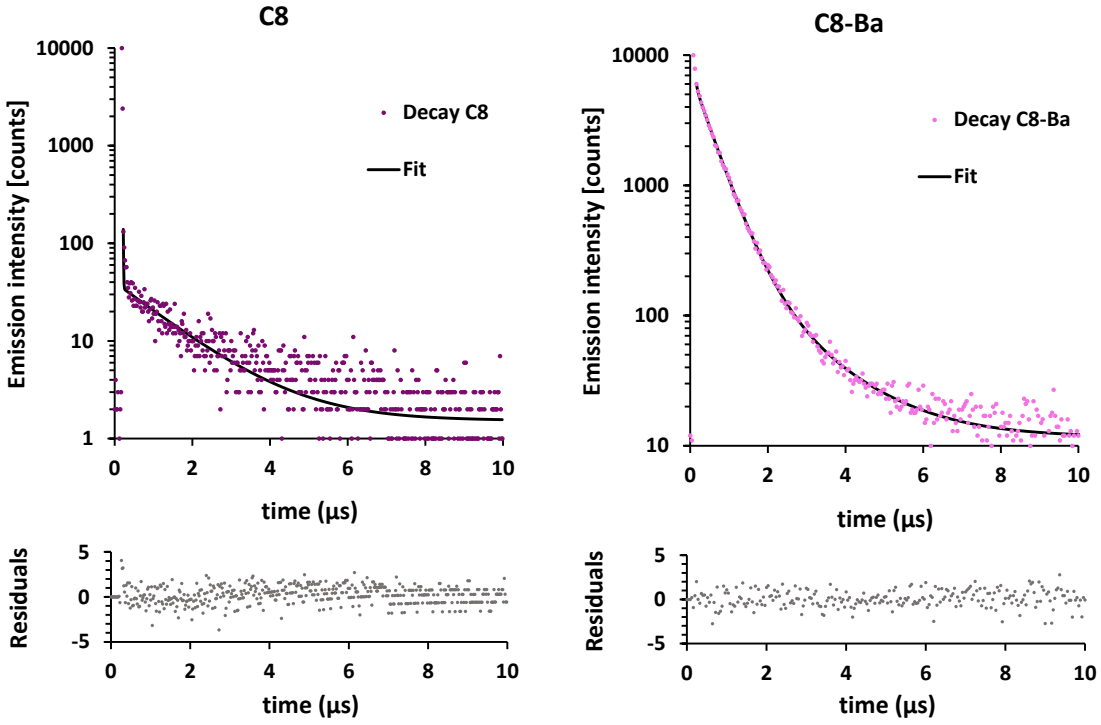


Figure S146. *Emission spectra of **C8** and **C8-Ba** excited at different wavelength, under aerated and argon conditions.*



Emission at 679 nm EPL485 MCS 100KHz Slit 13, 500 chanels, 10000 counts	
Result	
τ	χ^2
3.9 ns	1.1
1419 ns	

Emission at 700 nm EPL485 MCS 50kHz Slit 13, 500 chanels, 10000 counts	
Result	
τ	χ^2
34 ns (12%)	0.98
486 ns (64%)	
1534 ns (24%)	

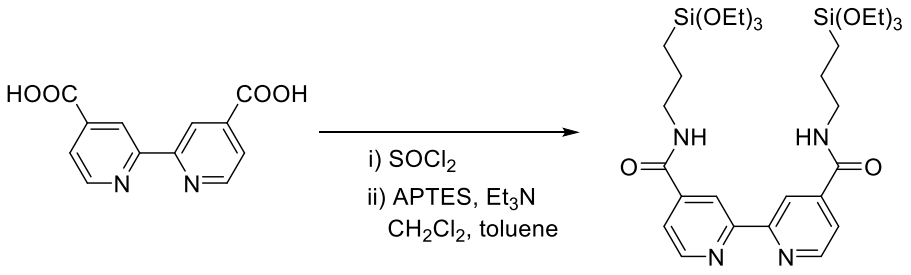
Figure S147. *Lifetime decay and results of **C8** and **C8-Ba** excited at their emission maxima.*

4 CHAPTER 4

4.1 SYNTHESIS AND CHARACTERIZATION

4.1.1 Compound 21, 2,2'-bipyridine-4,4'-diamidopropyltriethoxysilane

Compound **21** was synthesized according to the procedure described by Brennan et al.[8]



21

2,2'-bipyridine-4,4'-dicarboxylic acid (371 mg, 1.52 mmol) and thionyl chloride (4 mL, 55 mmol) were refluxed under nitrogen for 16 h, and any remaining unreacted thionyl chloride was removed under vacuum. To this, a solution containing Et_3N (450 µL, 3.23 mmol) and CH_2Cl_2 (5 mL, 78 mmol) was added. This mixture was then transferred to a solution of toluene (15 mL) containing APTES (712 mg, 3.06 mmol) and heated at 60°C for 1 h, and then stirred at ambient temperature for 16 h. The solvent was removed under vacuum and the dark yellow product was purified with a Soxhlet extraction using CH_2Cl_2 as the eluent. Yield 56%.

^{1}H NMR (300 MHz, DMSO-d_6): δ 8.95 (t, J = 5.6 Hz, 2H), 8.86 (dd, J = 5.0, 0.8 Hz, 2H), 8.79 (dd, J = 1.7, 0.8 Hz, 2H), 7.85 (dd, J = 5.0, 1.7 Hz, 2H), 3.76 (q, J = 7.0 Hz, 12H), 3.30 (m, 4H), 1.62 (p, J = 8.0 Hz, 4H), 1.16 (t, J = 7.0 Hz, 18H), 0.68 – 0.56 (m, 4H).

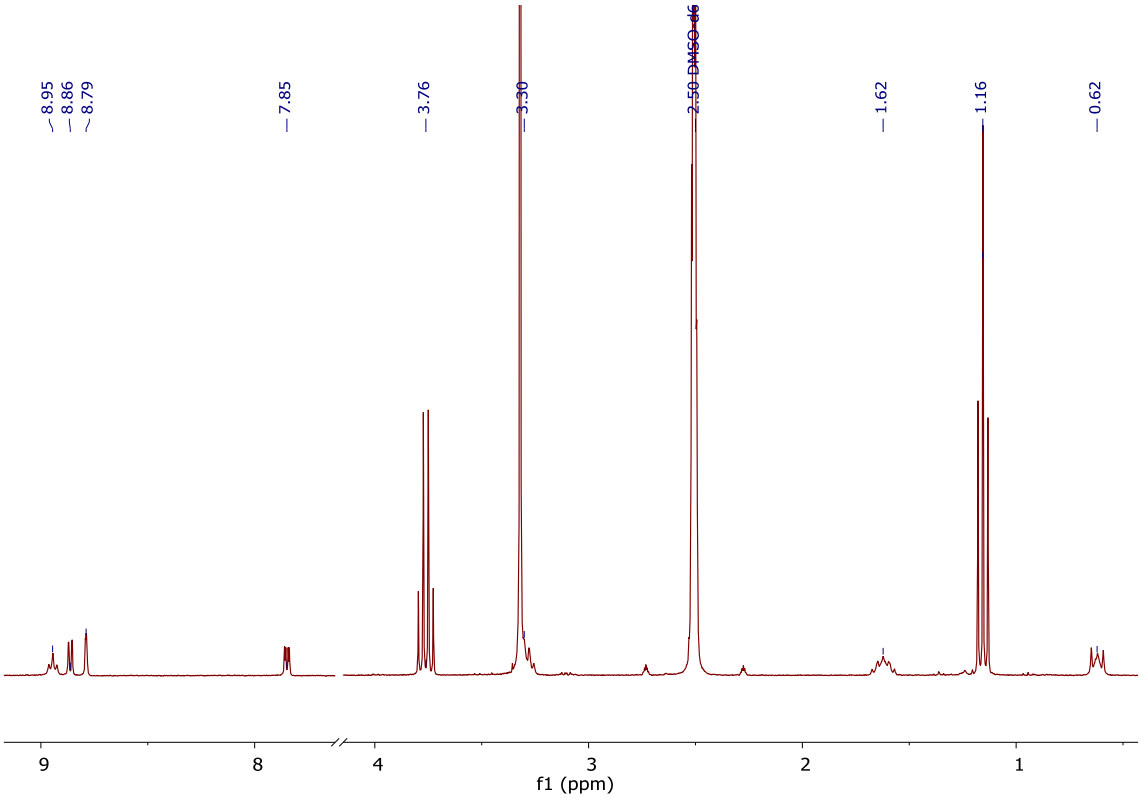
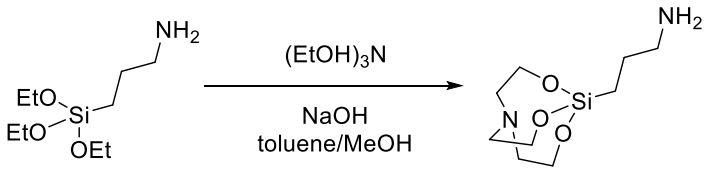


Figure S148. *^{1}H NMR spectrum of compound **21** (DMSO-d_6, 300 MHz).*

4.1.2 Compound 22, 3-aminopropylsilatrane

Compound **22** was synthesized by following a modified procedure described by Lämmerhofer et al.[9] The product contained a bit or triethanolamine.



22

APTES (5.30 mL, 22.6 mmol), triethanolamine (3.07mL, 22.6 mmol) and NaOH (3 mg, 75 µmol) was mixed in 30 mL of toluene and 14.2 mL MeOH and within a round bottom flask. The mixture was stirred for 24 h at 85˚C and then concentrated by rotary evaporator under reduced pressure. The resulting solid was used without further purification. Quantitative yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.78 (t, J = 5.8 Hz, 6H), 2.82 (t, J = 5.8 Hz, 6H), 2.64 (t, J = 6.9 Hz, 2H), 1.60 – 1.48 (m, 2H), 0.46 – 0.39 (m, 2H).

^{13}C NMR (125 MHz, MeOD-d_4): δ 58.54 (3C, CH_2), 51.74 (3C, CH_2), 45.86 (1C, CH_2), 29.49 (1C, CH_2), 14.60 (1C, CH_2).

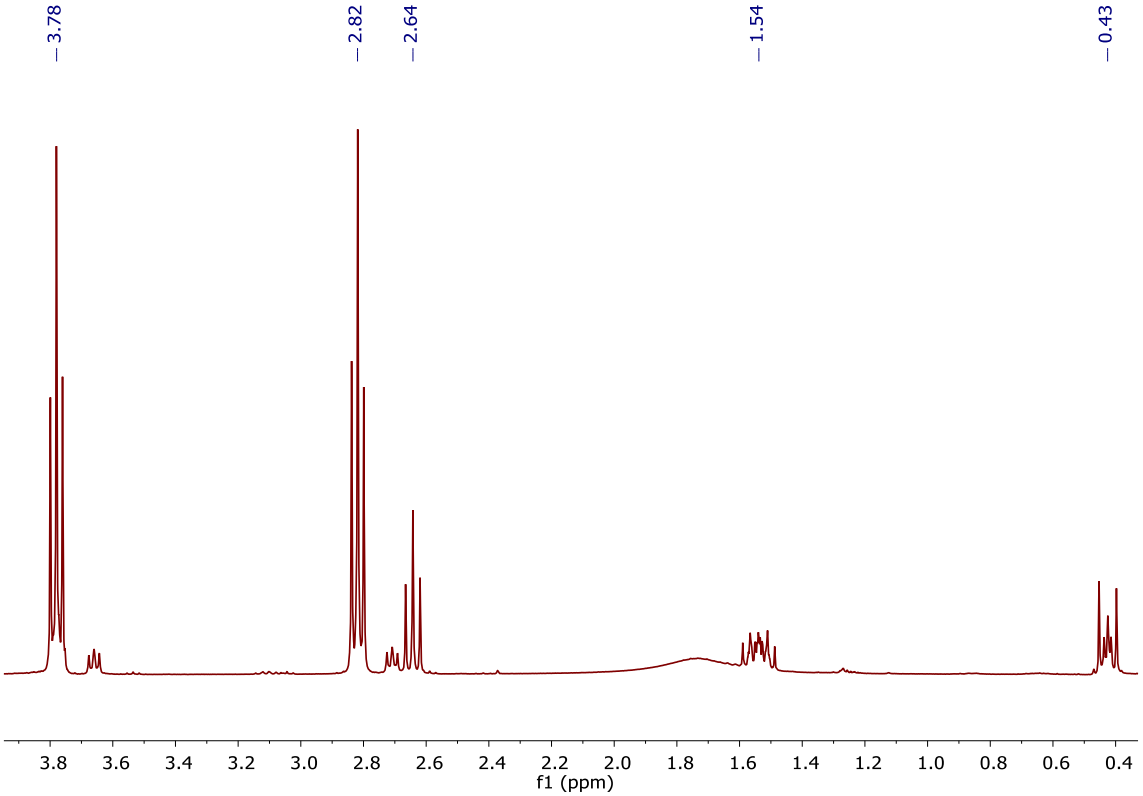


Figure S149. *^{1}H NMR spectrum of compound **22** ($CDCl_3$, 300 MHz).*

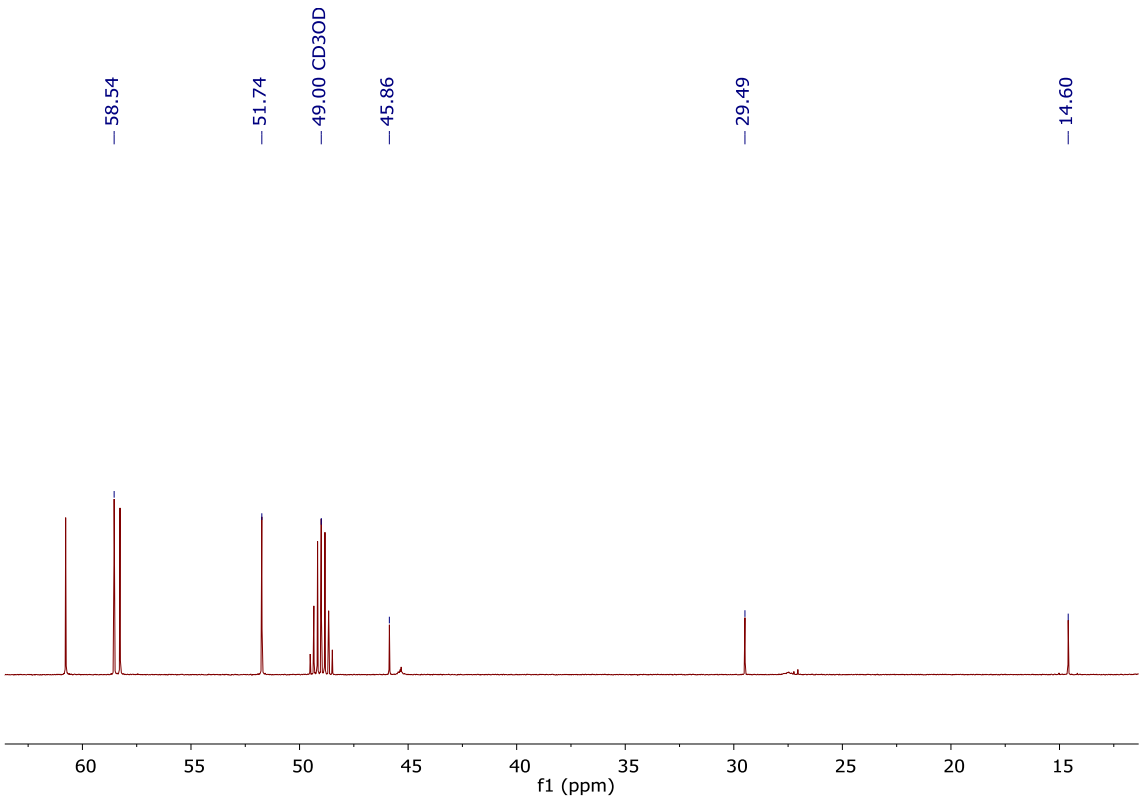


Figure S150. *^{13}C NMR spectrum of compound **22** (MeOD-d_4, 125 MHz).*

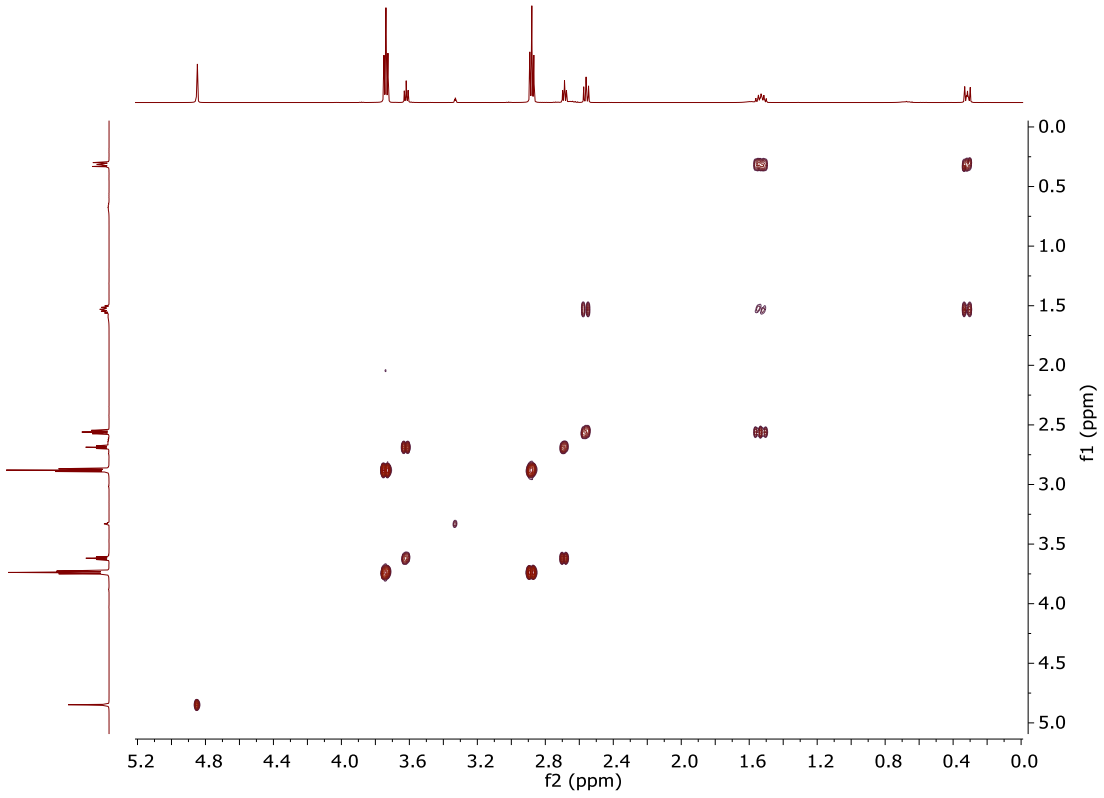


Figure S151. *COSY NMR spectrum of compound **22** (MeOD-d_4, 500 MHz).*

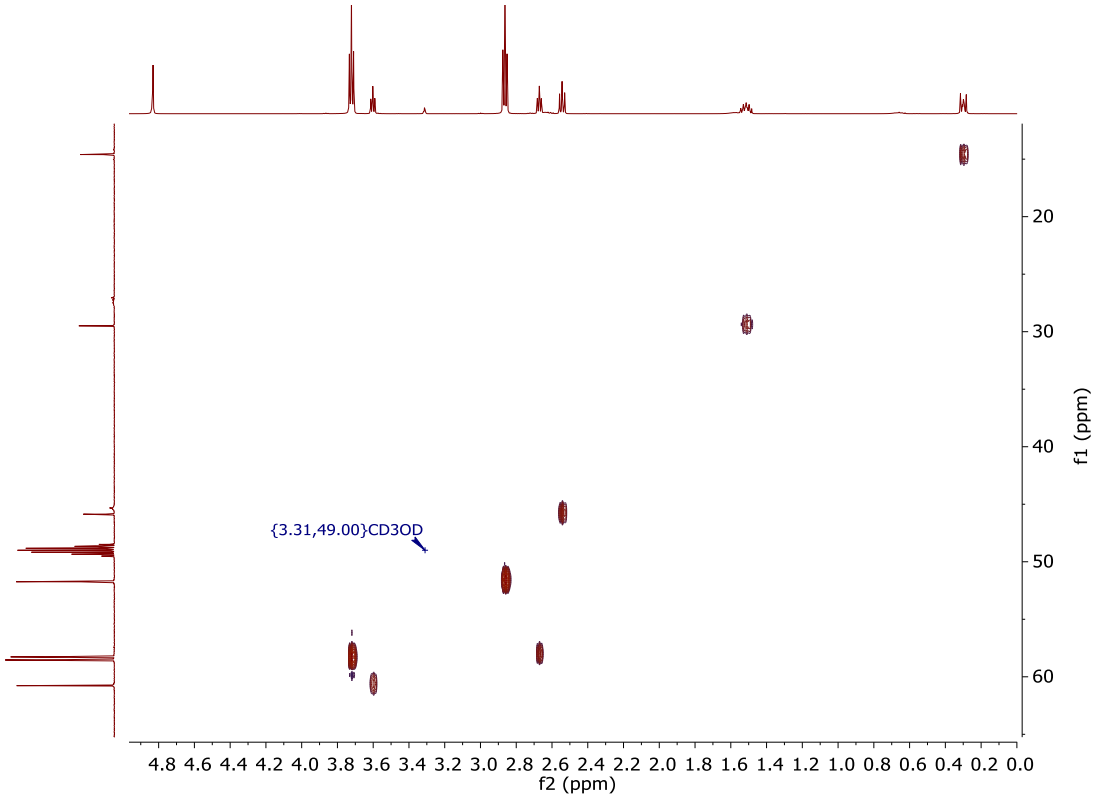


Figure S152. *HSQC NMR spectrum of compound* ***22*** *(MeOD-d₄, 500 MHz).*

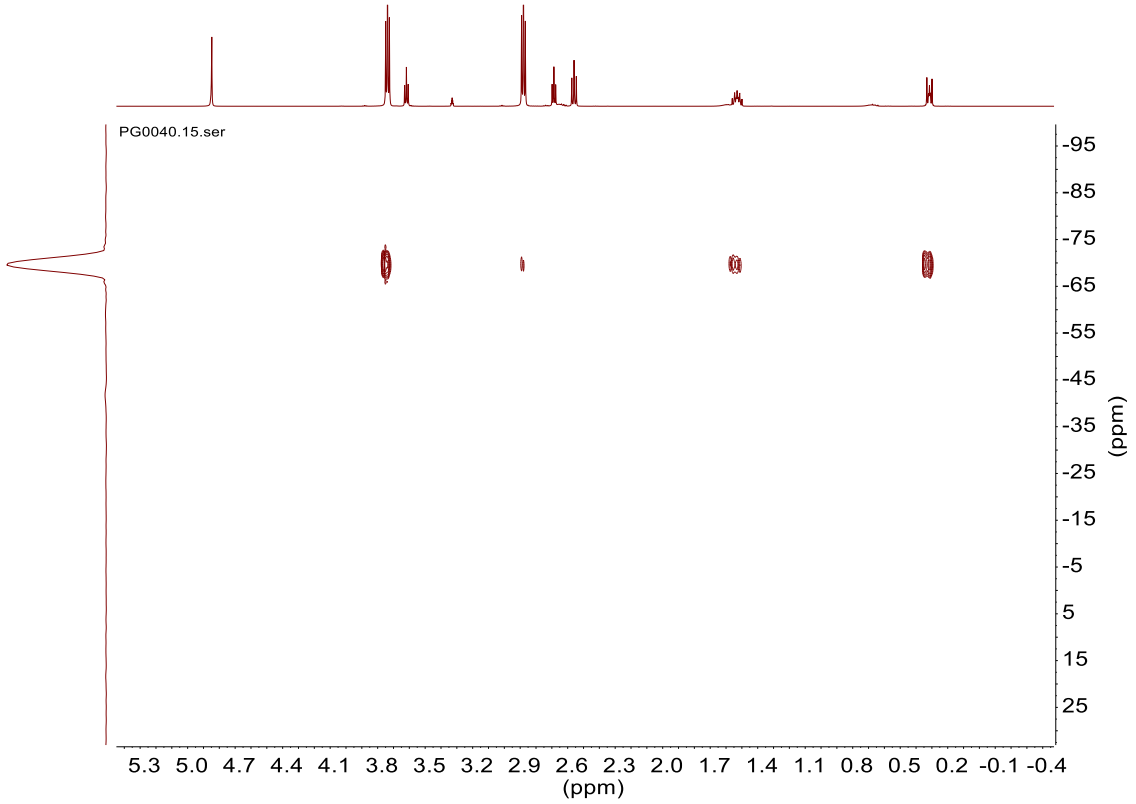
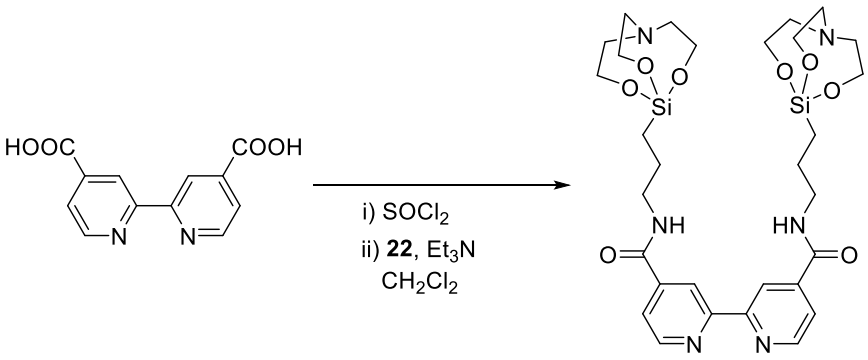


Figure S153. *^{1}H-^{29}Si HMBC NMR spectrum of compound* ***22*** *(MeOD-d₄, 500 MHz).*

4.1.3 Compound 23, 2,2'-bipyridine-4,4'-diamidopropylsilatrane

Compound **23** was synthesized according to the procedure described by Brudvig et al.[10]



23

To a dry round bottom flask 2,2'-bipyridine-4,4'-dicarboxylic acid (0.2 g, 0.82 mmol) and thionyl chloride (4 mL, 54 mmol) was added. The suspension was refluxed overnight under N_2. The solvent was removed under reduced pressure. To the crude dry CH_2Cl_2 (10 mL), Et_3N (0.560 mL, 4.01 mmol) and **20** (0.417 g, 1.79 mmol) was added. The solution was stirred at room temperature for 3 h, under N_2, over which time a pale pink precipitate normed. The reaction was cooled to 0°C overnight and filtered to afford a light pink solid. Yield 85%.

^{1}H NMR (300 MHz, MeOD-d_4): δ 8.79 (dd, J = 5.0, 0.9 Hz, 2H), 8.72 (dd, J = 1.7, 0.9 Hz, 2H), 7.76 (dd, J = 5.1, 1.7 Hz, 2H), 3.74 (t, J = 5.9 Hz, 12H), 3.37 (t, J = 6.9 Hz, 4H), 2.86 (t, J = 5.9 Hz, 12H), 1.71 (dq, J = 10.3, 7.1 Hz, 4H), 0.46 – 0.39 (m, 4H).

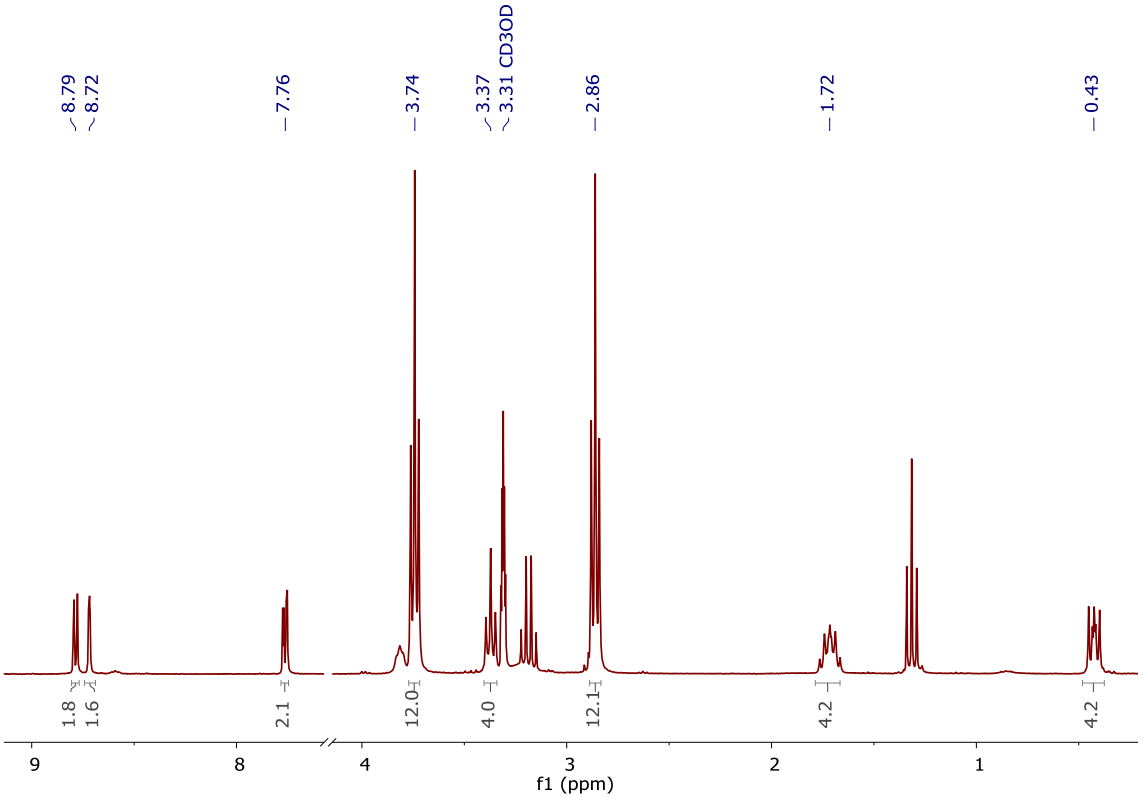
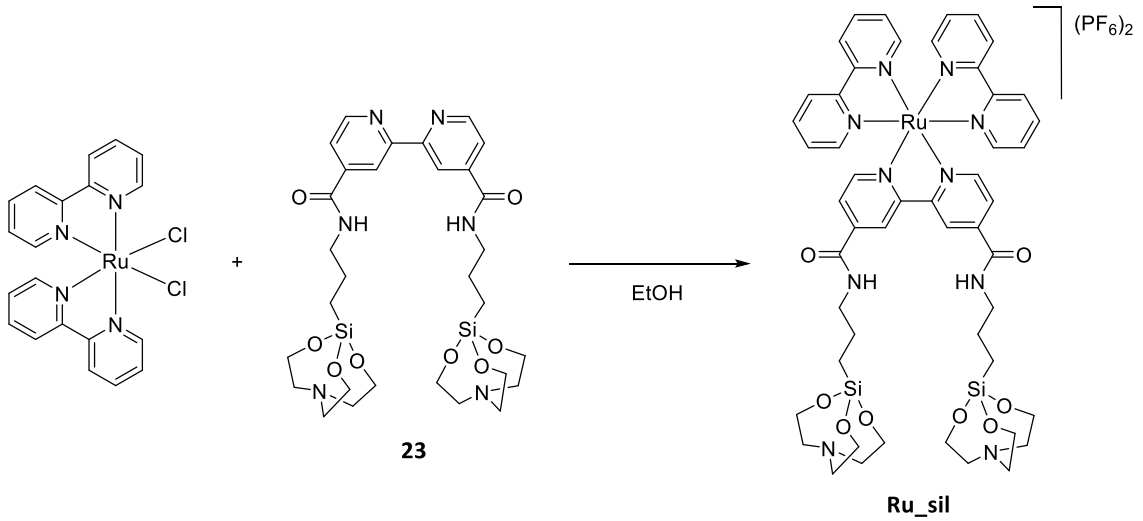


Figure S154. *^{1}H NMR spectrum of compound **23** (MeOD-d_4, 300 MHz).*

4.1.4 Compound Ru_sil, $[Ru(bpy)_2(23)](PF_6)_2$

Compound **Ru_sil** was synthesized by following a modified procedure by Willey et al.[11]



Under a N_2 atmosphere, $[Ru(bpy)_2Cl_2]$ (106.5 mg, 0.22 mmol) and compound **23** (148 mg, 0.22 mmol) were dissolved in 15 mL of EtOH. The reaction mixture was refluxed for 48 h at 50°C. The solvent was evaporated and to the crude MeOH was added. The

mixture was filtered and to the filtrate, KPF_6 was added for counter ion exchange. The precipitate formed was washed with Et_2O to obtain a red product. Yield 54%.

^{1}H NMR (500 MHz, MeOD-d_4): δ 9.11 (s, 2H), 8.71 (dd, J = 8.4, 3.7 Hz, 4H), 8.19 – 8.11 (m, 4H), 7.98 (d, J = 5.9 Hz, 2H), 7.88 – 7.74 (m, 6H), 7.50 (dt, J = 13.4, 6.8 Hz, 4H), 3.73 (t, J = 5.9 Hz, 12H), 3.37 (t, J = 6.9 Hz, 4H), 2.88 (t, J = 5.9 Hz, 12H), 1.75 – 1.62 (m, 4H), 0.39 – 0.30 (m, 4H).

^{13}C NMR (126 MHz, MeOD-d_4): δ 165.48 (2C, C_{quat}), 158.97 (2C, C_{quat}), 158.36 (2C, C_{quat}), 158.30 (2C, C_{quat}), 153.33 (2C, CH), 152.76 (2C, CH), 152.58 (2C, CH), 144.69 (2C, C_{quat}), 139.56 (2C, CH), 129.09 (2C, CH), 129.08 (2C, CH), 126.51 (2C, CH), 125.73 (2C, CH), 123.38 (2C, CH), 58.49 (6C, CH_2), 51.65 (6C, CH_2), 44.82 (2C, CH_2), 25.91 (2C, CH_2), 15.12 (2C, CH_2).

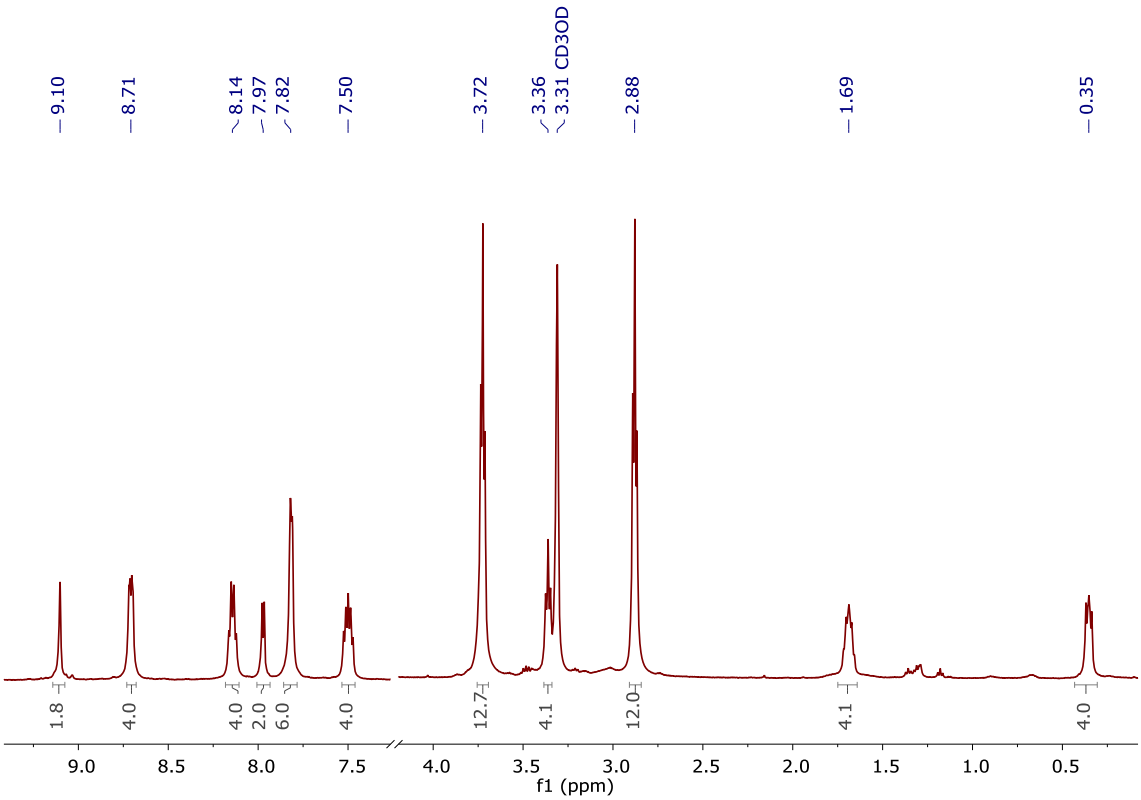


Figure S155. *^{1}H NMR spectrum of compound **Ru_sil** (MeOD-d_4, 300 MHz).*

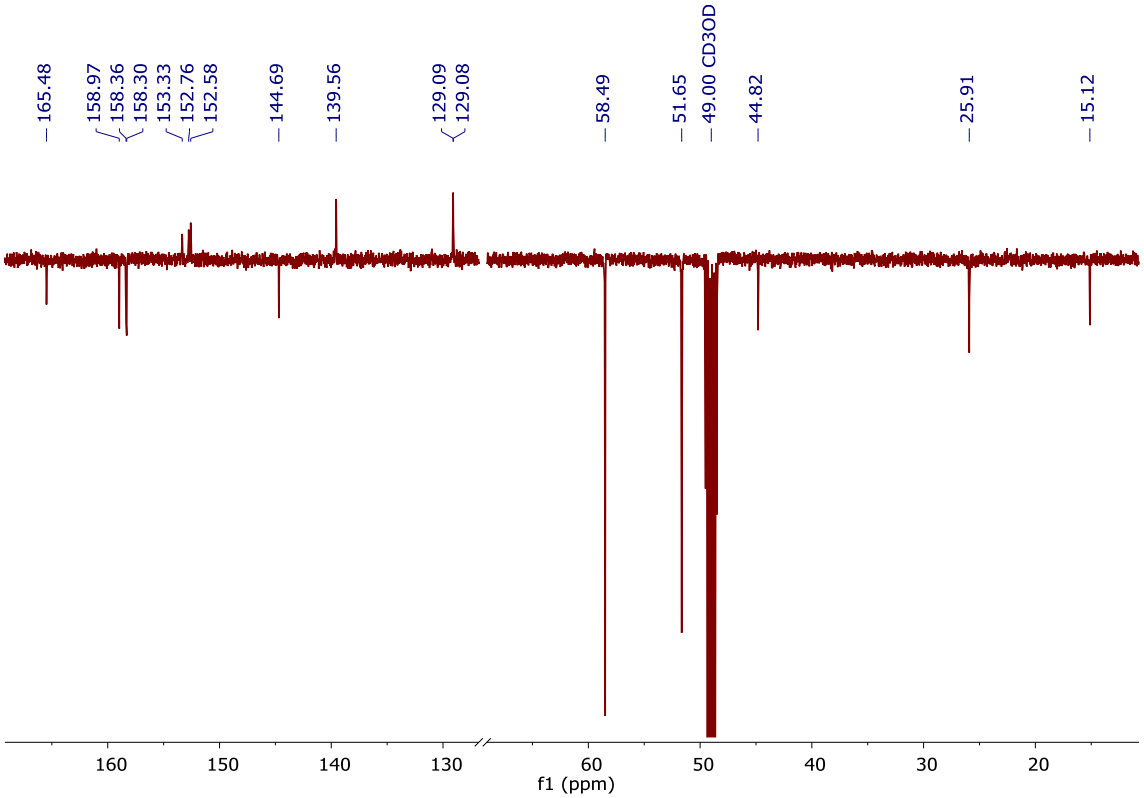


Figure S156. *^{13}C APT NMR spectrum of compound **Ru_sil** (MeOD-d_4, 300 MHz).*

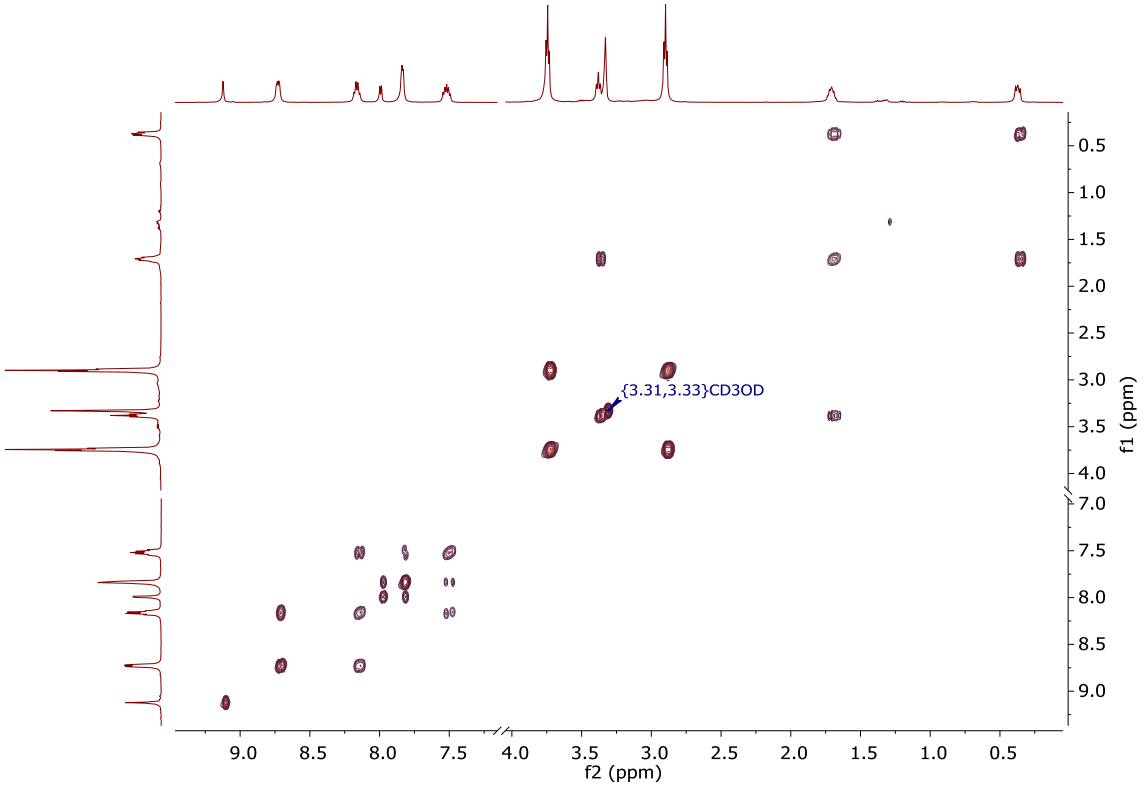


Figure S157. *COSY NMR spectrum of compound **Ru_sil** (MeOD-d_4, 300 MHz).*

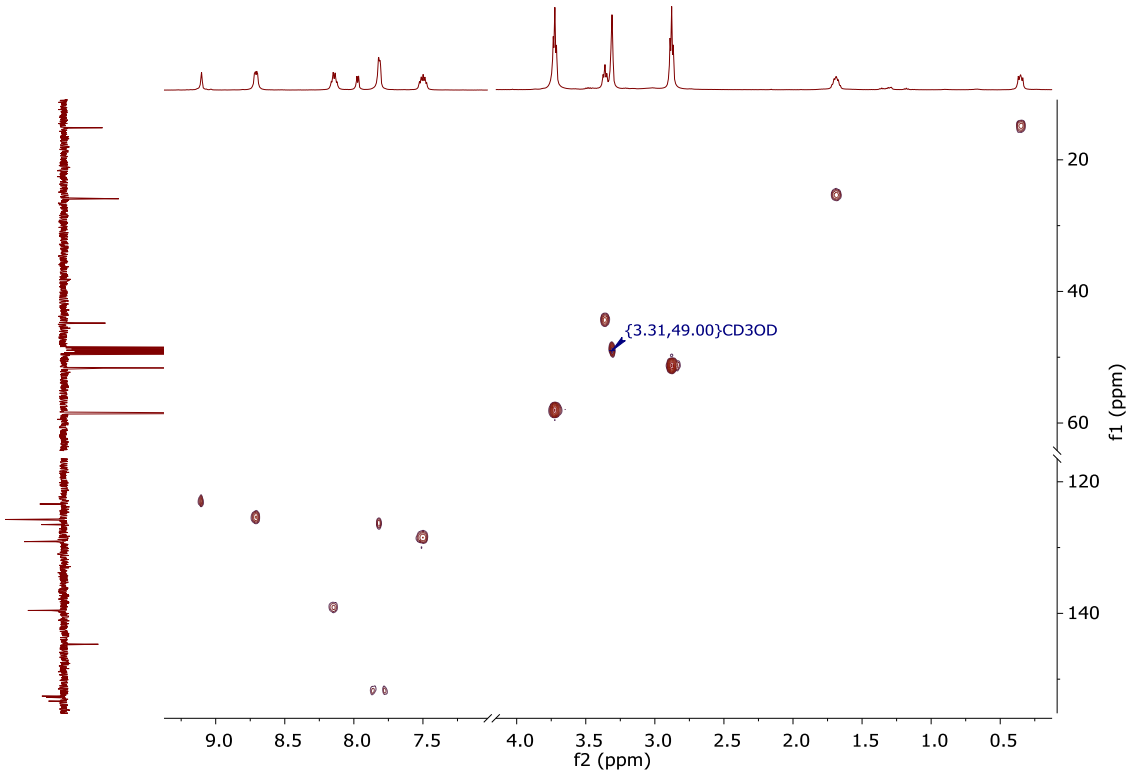
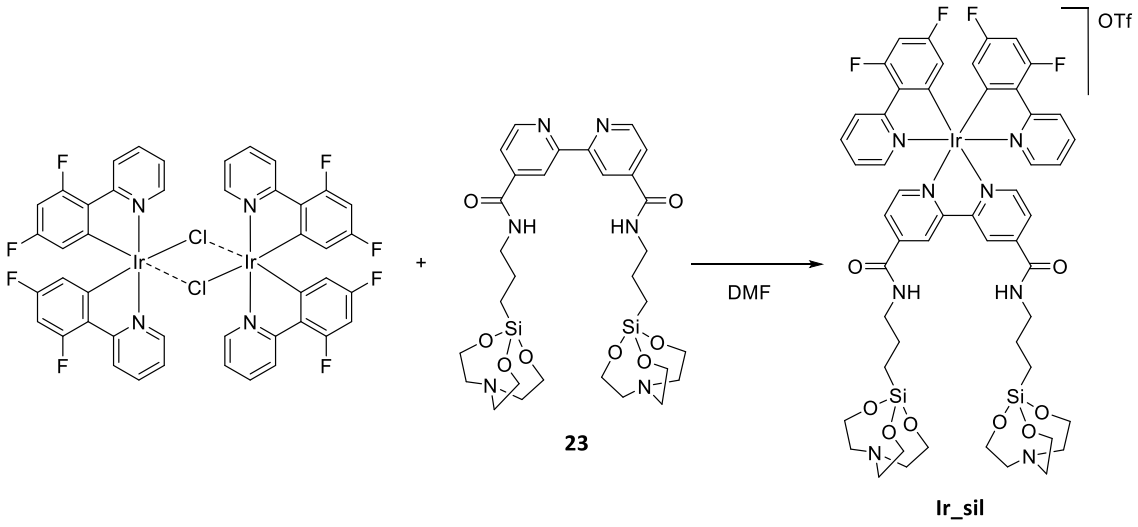


Figure S158. *HSQC NMR spectrum of compound* ***Ru_sil*** *(MeOD-d4, 300 MHz).*

4.1.5 Compound Ir_sil, [Ir(F_2-ppy)$_2$(23)]OTf



[Ir(F_2-ppy)$_2$Cl]$_2$ (100.0 mg, 0.082 mmol) and AgOTf (42.0 mg, 0.164 mmol) were added to a schlenk with acetone (9 mL), under N_2. The mixture was refluxed for 3 h. The reaction mixture is filtered over a celite pad and the filtrate is added to compound **23** in acetone (6 mL). The mixture is refluxed for 16 h, under N_2. The solvent was evaporated in vacuo and the residue was washed with H_2O to obtain a yellow solid. Yield: 37 %.

^{1}H NMR (500 MHz, MeOD-d_4): δ 9.14 (d, J = 1.8 Hz, 2H), 8.44 – 8.36 (m, 2H), 8.16 (d, J = 5.7 Hz, 2H), 8.04 – 7.93 (m, 4H), 7.71 (dd, J = 6.0, 1.5 Hz, 2H), 7.14 (ddd, J = 7.4, 5.9, 1.4 Hz, 2H), 6.81 – 6.67 (m, 2H), 5.78 – 5.71 (m, 2H), 3.72 (t, J = 5.9 Hz, 12H), 3.37 (t, J = 7.1 Hz, 4H), 2.87 (t, J = 5.9 Hz, 12H), 1.77 – 1.60 (m, 4H), 0.50 – 0.30 (m, 4H).

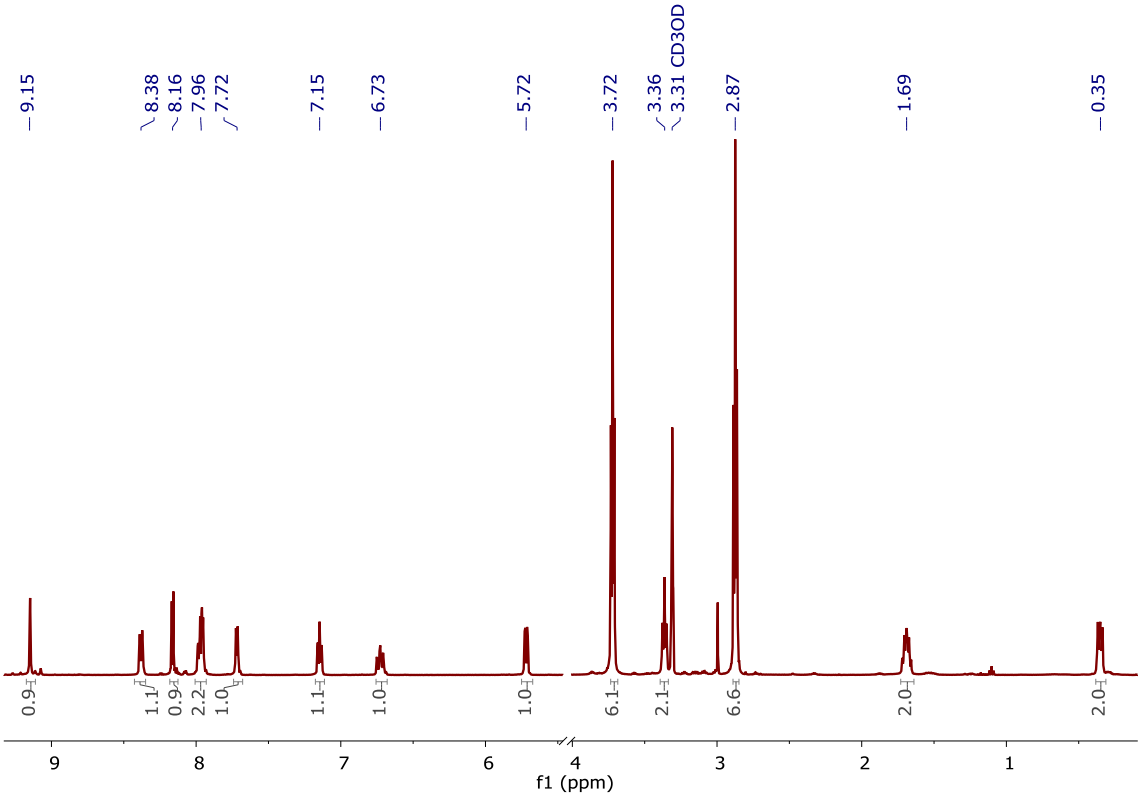


Figure S159. *^{1}H NMR spectrum of compound **Ir_sil** (MeOD-d_4, 300 MHz).*

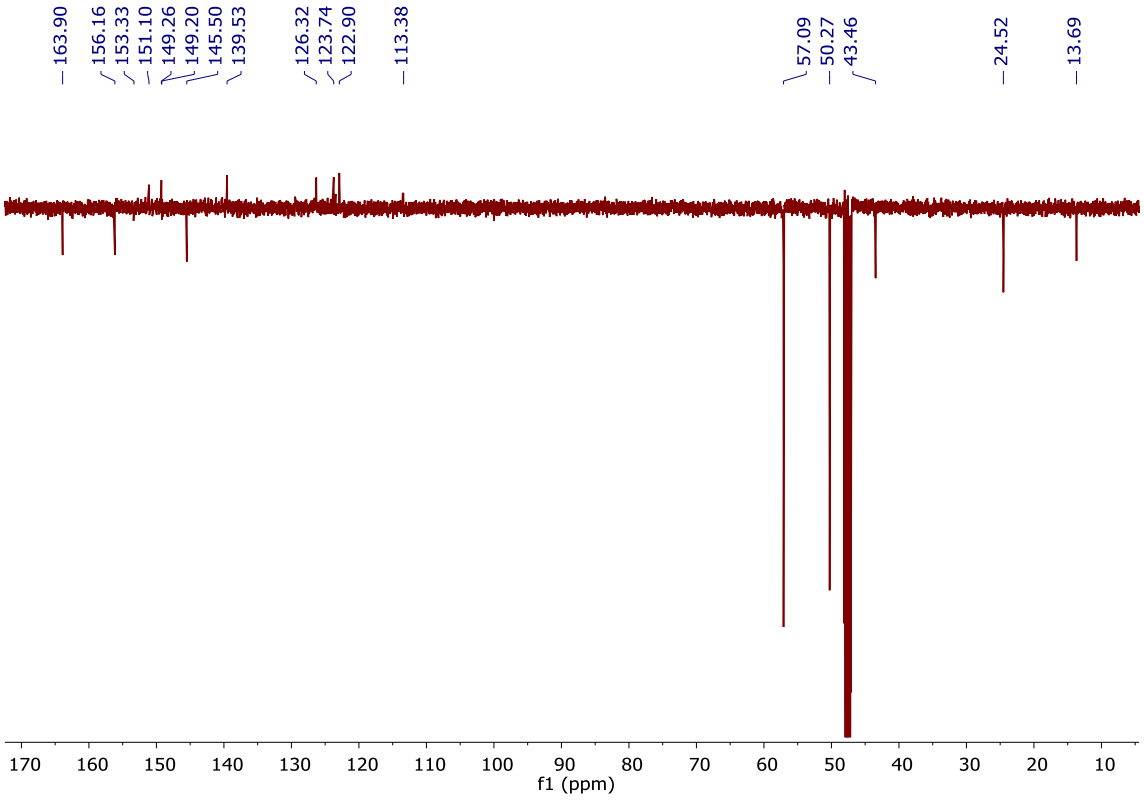


Figure S160. *APT ^{13}C NMR spectrum of compound* ***Ir_sil*** *(MeOD-d_4, 500 MHz).*

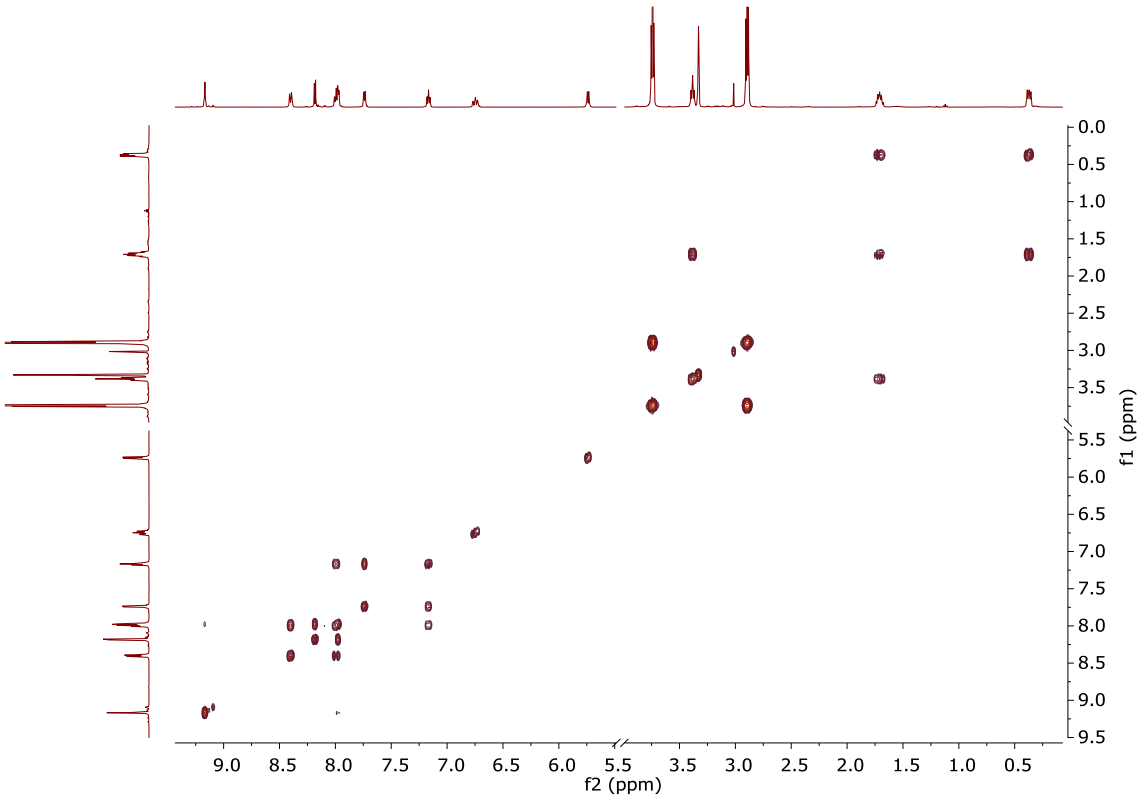


Figure S161. *COSY NMR spectrum of compound* ***Ir_sil*** *(MeOD-d_4, 500 MHz).*

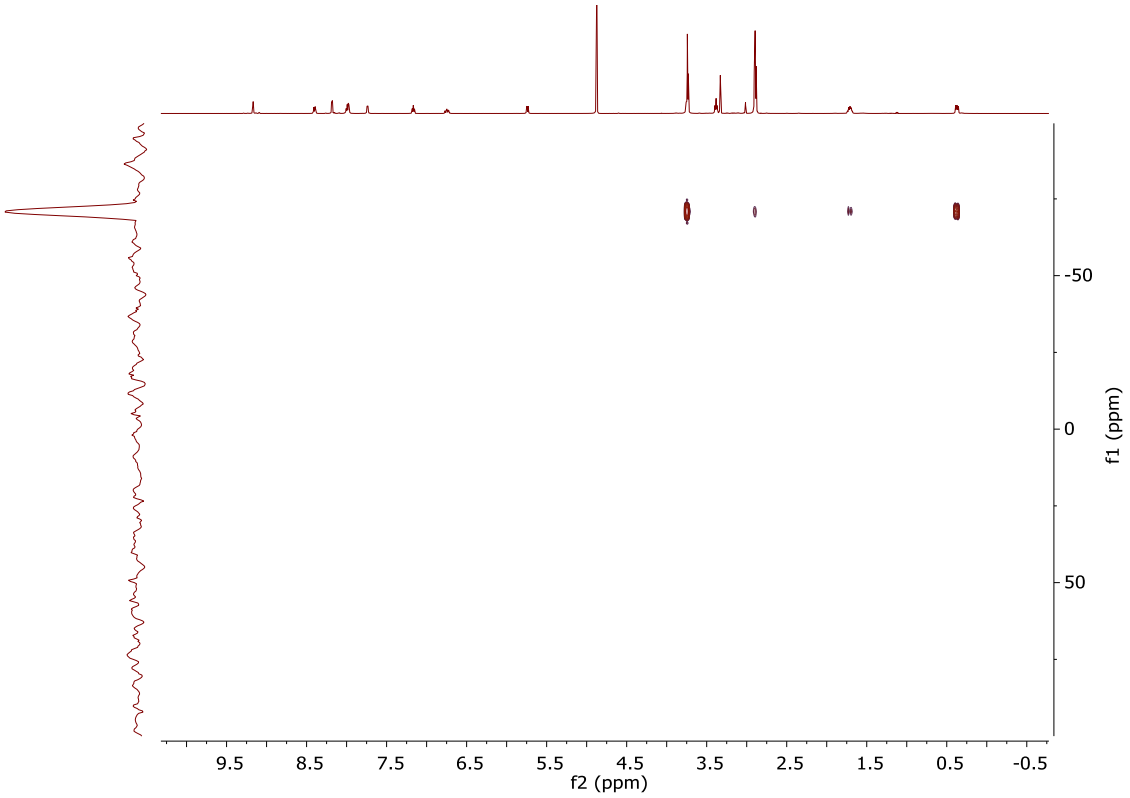
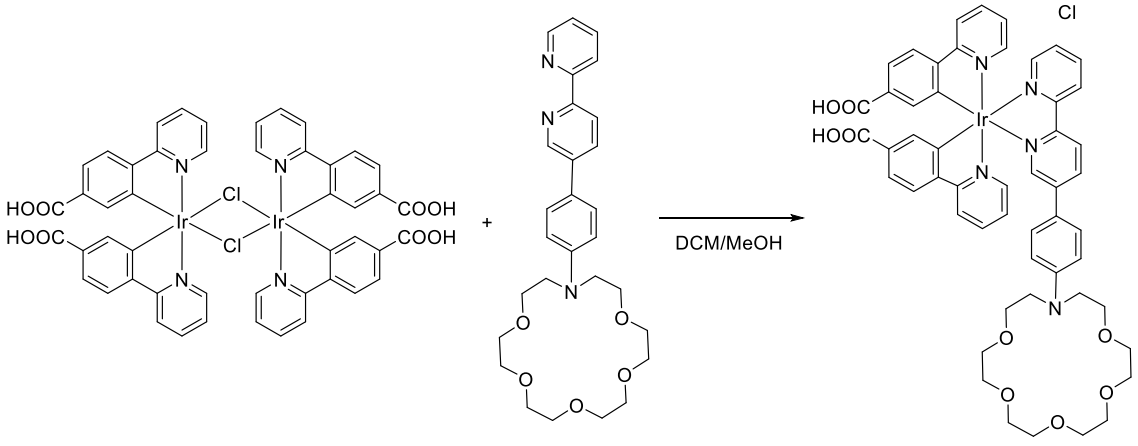


Figure S162. *^{1}H-^{29}Si HMBC NMR spectrum of compound* ***Ir_sil*** *(MeOD-d_4, 500 MHz).*

4.1.6 Compound C6_COOH, [Ir(HOOC-ppy)$_2$(L2)]Cl



Under a N_2 atmosphere, to [Ir(COOH-ppy)$_2$Cl]$_2$ (-) and AAN_160 (-) 8 mL of CH_2Cl_2/MeOH (2:1, v/v) was added. The reaction mixture was refluxed overnight at 35°C. The solvents were evaporated to obtain the desired product. An orange solid with quantitative yield.

Exact mass: ESI-MS [$C_{52}H_{51}IrN_5O_9$]: calculated: m/z= 1080.3293, found: m/z= 1080.3287.

^{1}H NMR (300 MHz, MeOD-*d*$_4$): δ 8.62 (d, J = 8.3 Hz, 1H), 8.58 (d, J = 8.7 Hz, 1H), 8.30–8.24 (m, 2H), 8.22–8.14 (m, 2H), 8.12 (d, J = 2.2 Hz, 1H), 8.02–7.87 (m, 5H), 7.88–7.83 (m, 1H), 7.78 (dd, J = 5.9, 1.4 Hz, 1H), 7.68 (ddd, J = 8.2, 4.6, 1.7 Hz, 2H), 7.51 (td, J = 5.9, 2.8 Hz, 1H), 7.25–7.12 (m, 4H), 7.04 (d, J = 1.7 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 3.68–3.56 (m, 24H).

^{13}C NMR (75 MHz, MeOD-*d*$_4$): δ 169.72 (1C, C_{quat}), 169.67 (1C, C_{quat}), 167.80 (1C, C_{quat}), 167.63 (1C, C_{quat}), 157.40 (1C, C_{quat}), 153.26 (1C, C_{quat}), 151.55 (1C, CH), 151.06 (1C, C_{quat}), 150.79 (1C, C_{quat}), 150.56 (1C, C_{quat}), 150.53 (1C, CH), 150.47 (1C, CH), 150.02 (1C, C_{quat}), 149.97 (1C, C_{quat}), 147.68 (1C, CH), 142.04 (1C, C_{quat}), 140.78 (1C, CH), 140.21 (1C, CH), 140.17 (1C, CH), 135.75 (1C, CH), 133.66 (1C, CH), 133.53 (1C, CH), 132.75 (1C, C_{quat}), 132.70 (1C, C_{quat}), 128.87 (1C, CH), 128.52 (2C, CH), 125.98 (3C, CH), 125.75 (1C, CH), 125.70 (1C, CH), 125.57 (1C, CH), 125.50 (1C, CH), 125.38 (1C, CH), 122.31 (2C, CH), 121.77 (1C, C_{quat}), 113.68 (2C, CH), 71.73 (8C, CH_2, crown), 69.69 (2C, CH_2, crown), 52.28 (2C, CH_2, crown).

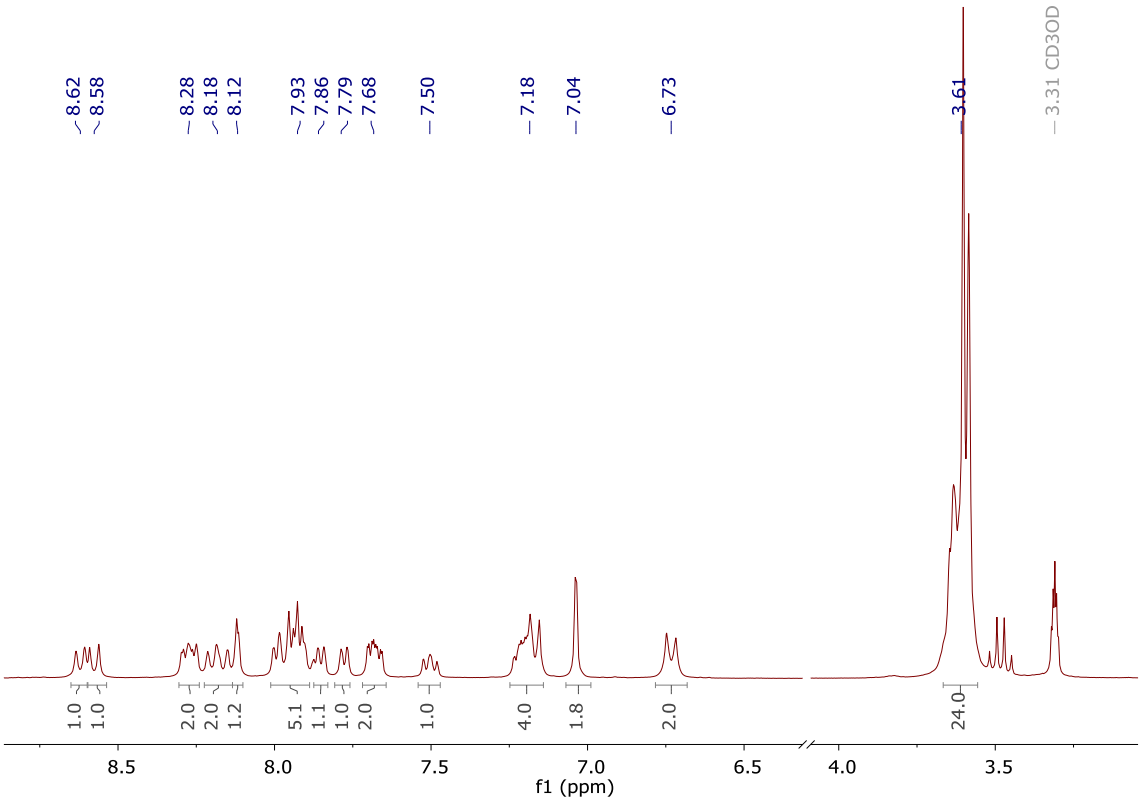


Figure S163. *^{1}H NMR spectrum of compound **C6_COOH** (MeOD-d$_4$, 300 MHz).*

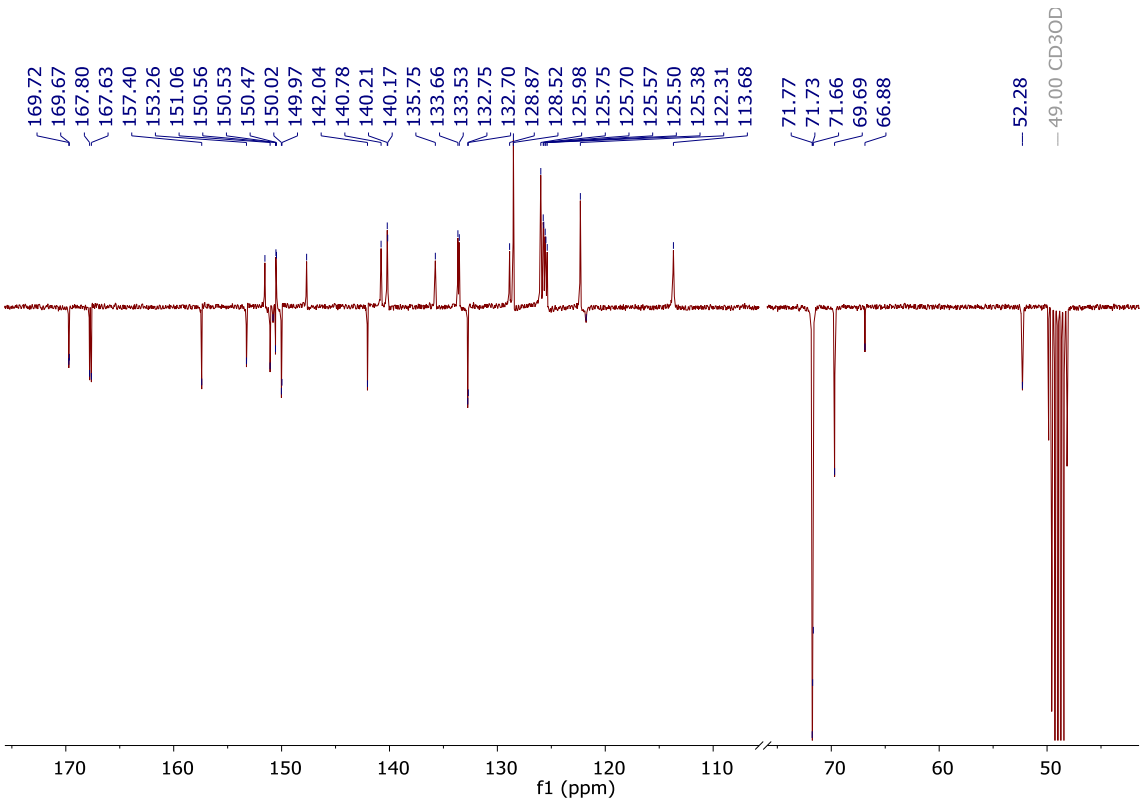


Figure S164. *^{13}C APT NMR spectrum of compound **C6_COOH** (MeOD-d$_4$, 300 MHz).*

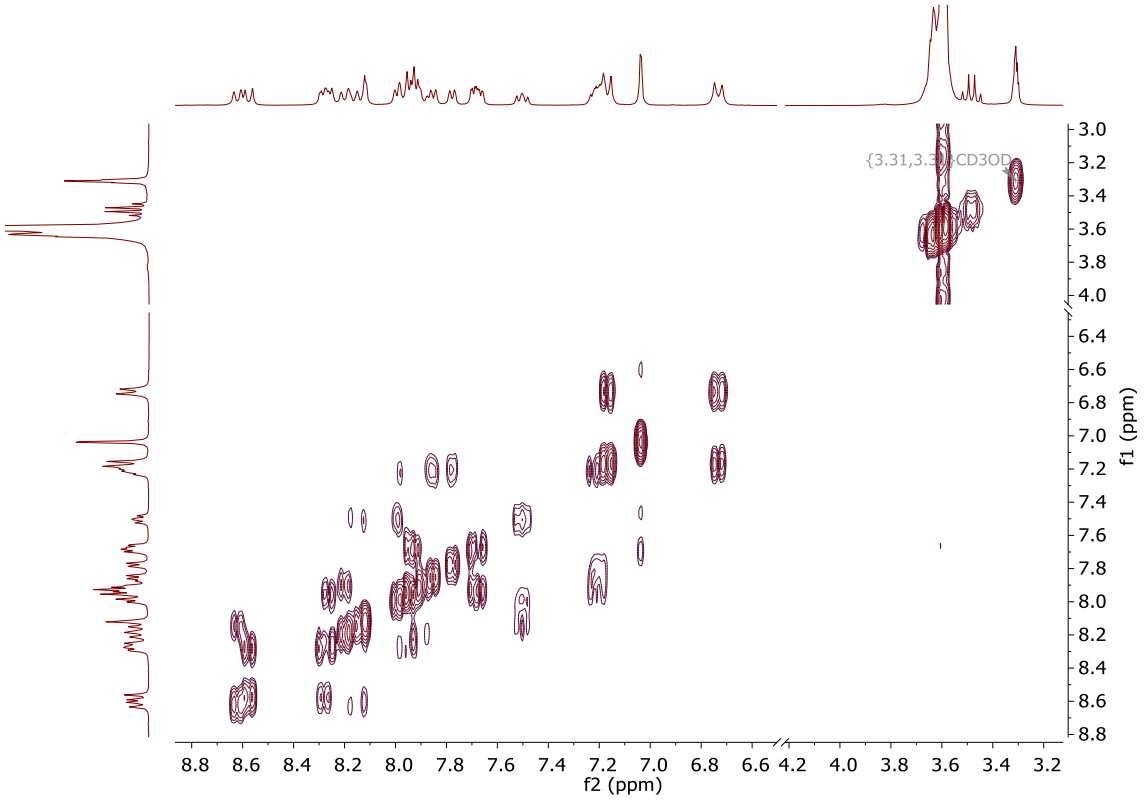


Figure S165. *COSY NMR spectrum of compound **C6_COOH** (MeOD-d$_4$, 300 MHz).*

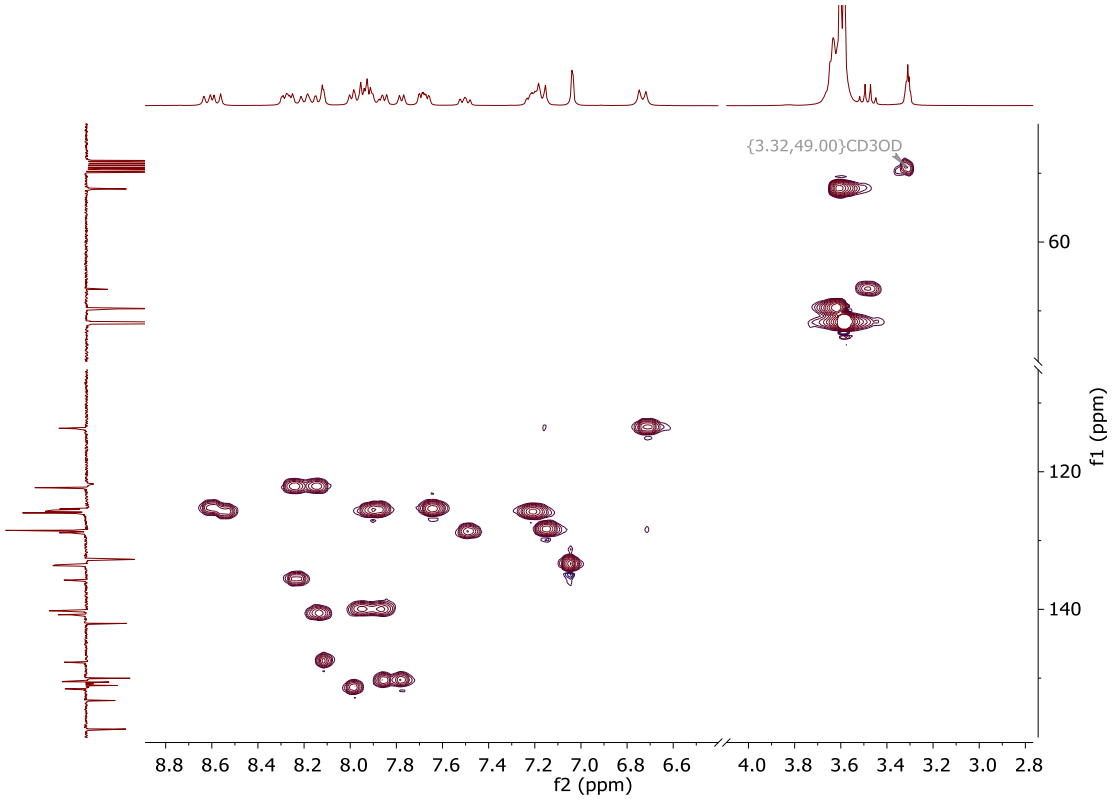


Figure S166.*HSQC NMR spectrum of compound* ***C6_COOH*** *(MeOD-d4, 300 MHz).*

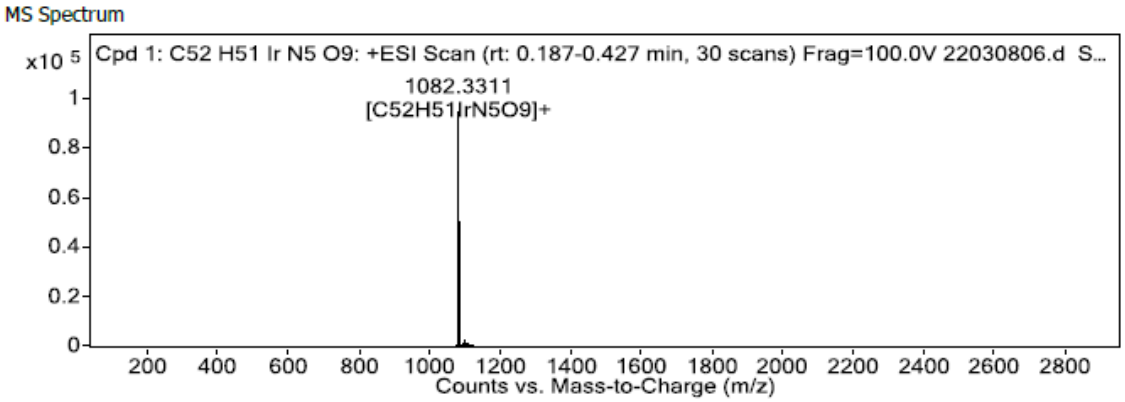
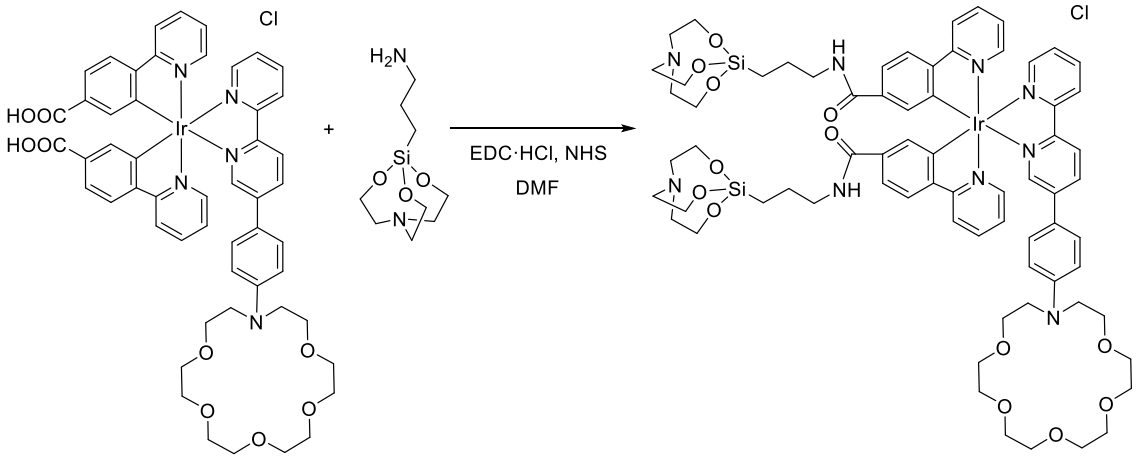


Figure S167. *Mass spectrum of compound* ***C6_COOH****.*

4.1.7 Compound C6_sil, [Ir(sil-ppy)$_2$(L2)]Cl



A solution of 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (86 mg, 0.45 mmol, 5 equiv.) and N-Hydroxysuccinimide (51 mg, 0.45 mmol, 5 equiv.) in DMF 1.5 mL were added to a DMF (1.5 mL) solution of **C6_COOH** (100 mg, 0.089 mmol, 1 equiv.). To this mixture, add the silatrane (207 mg, 0.89 mmol, 10 equiv.) and 4 mL of DMF. The reaction is stirred at room temperature overnight. After this time, extractions with CH_2Cl_2 and brine are performed and the organic phase is collected, dried over $MgSO_4$ and evaporated. DMF is completely removed by triturating the product in diethyl ether. The title compound was obtained as an orange solid. Yield 60%.

Exact mass: ESI-MS [$C_{70}H_{87}IrN_9O_{13}Si_2$]: calculated: m/z= 1508.5568, found: m/z= 1508.5608.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.36 (t, J = 7.9 Hz, 2H), 8.32 (dd, J = 8.6, 2.3 Hz, 1H), 8.22–8.15 (m, 1H), 8.06–7.94 (m, 3H), 7.88–7.80 (m, 3H), 7.79–7.68 (m, 2H), 7.62 (dd, J = 5.9, 1.4 Hz, 1H), 7.55 (dd, J = 6.0, 1.4 Hz, 1H), 7.43 (dd, J = 8.1, 1.7 Hz, 1H), 7.37–7.27 (m, 2H), 7.20–7.01 (m, 4H), 6.73–6.58 (m, 5H), 6.52 (t, J = 5.4 Hz, 1H), 3.64 (m, 36H), 3.34–3.18 (m, 4H), 2.75 (qd, J = 7.0, 5.9, 3.7 Hz, 12H), 1.59 (q, J = 7.3 Hz, 4H), 0.33 (td, J = 8.8, 6.6 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.68 (1C, C_{quat}), 167.34 (1C, C_{quat}), 166.75 (1C, C_{quat}), 166.69 (1C, C_{quat}), 156.33 (1C, C_{quat}), 152.05 (1C, C_{quat}), 150.46 (1C, C_{quat}), 150.30 (1C, C_{quat}), 150.05 (1C, CH), 149.27 (1C, C_{quat}), 148.97 (1C, CH), 148.89 (1C, CH), 146.44 (1C, C_{quat}), 146.39, 146.36 (1C, C_{quat}), 140.44 (1C, C_{quat}), 140.18 (1C, CH), 138.83 (1C, CH), 138.77 (1C, CH), 137.17 (1C, C_{quat}), 136.86 (1C, C_{quat}), 135.41 (1C, CH), 130.15 (1C, CH), 129.74 (1C, CH), 127.75 (3C, CH), 127.28 (1C, CH), 126.89 (1C, CH), 126.25 (1C, CH),

124.65 (1C, CH), 124.55 (1C, CH), 124.39 (2C, CH), 121.69 (1C, CH), 121.40 (1C, CH), 120.69 (1C, CH), 112.40 (2C, CH), 100.09 (1C, C_{quat}), 70.86 (8C, CH_2, crown), 68.59 (2C, CH_2, crown), 57.65 (6C, CH_2, silatrane), 51.33 (2C, CH_2, crown), 50.94 (6C, CH_2, silatrane), 42.61 (2C, CH_2, silatrane), 24.25 (2C, CH_2, silatrane), 13.56 (2C, CH_2, silatrane).

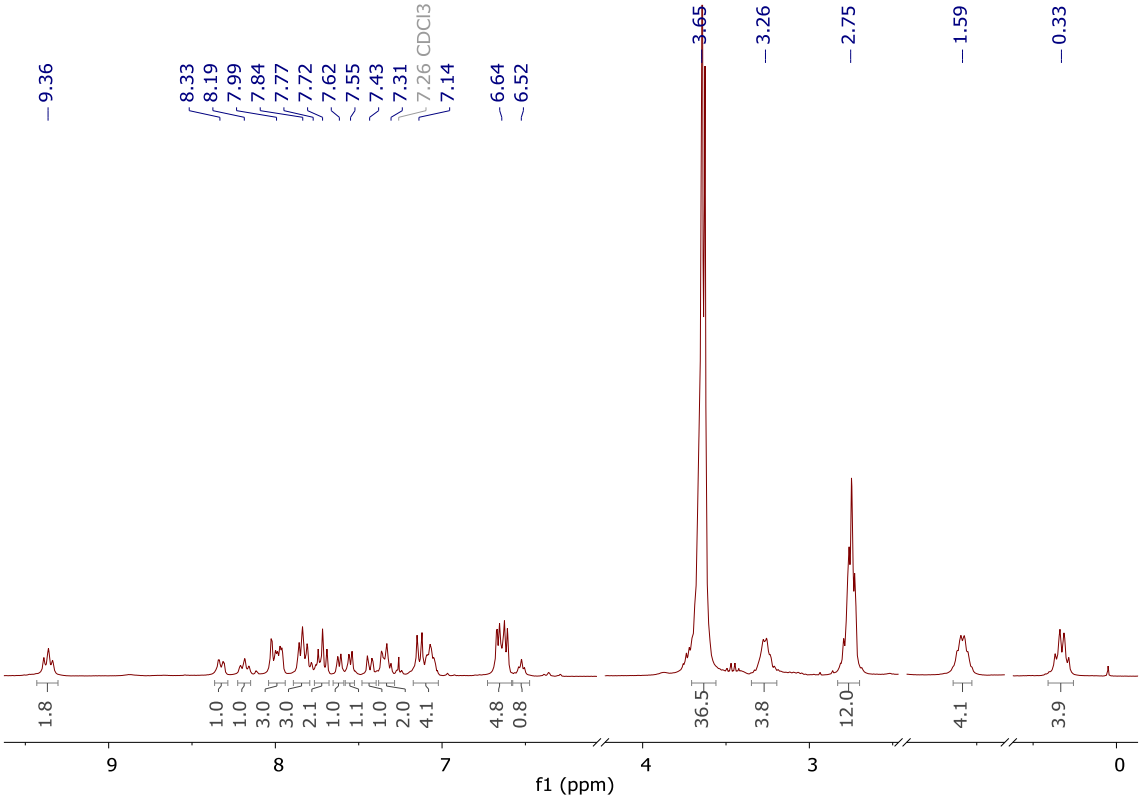


Figure S168. *^{1}H NMR spectrum of compound **C6_sil** (MeOD-d_4, 300 MHz).*

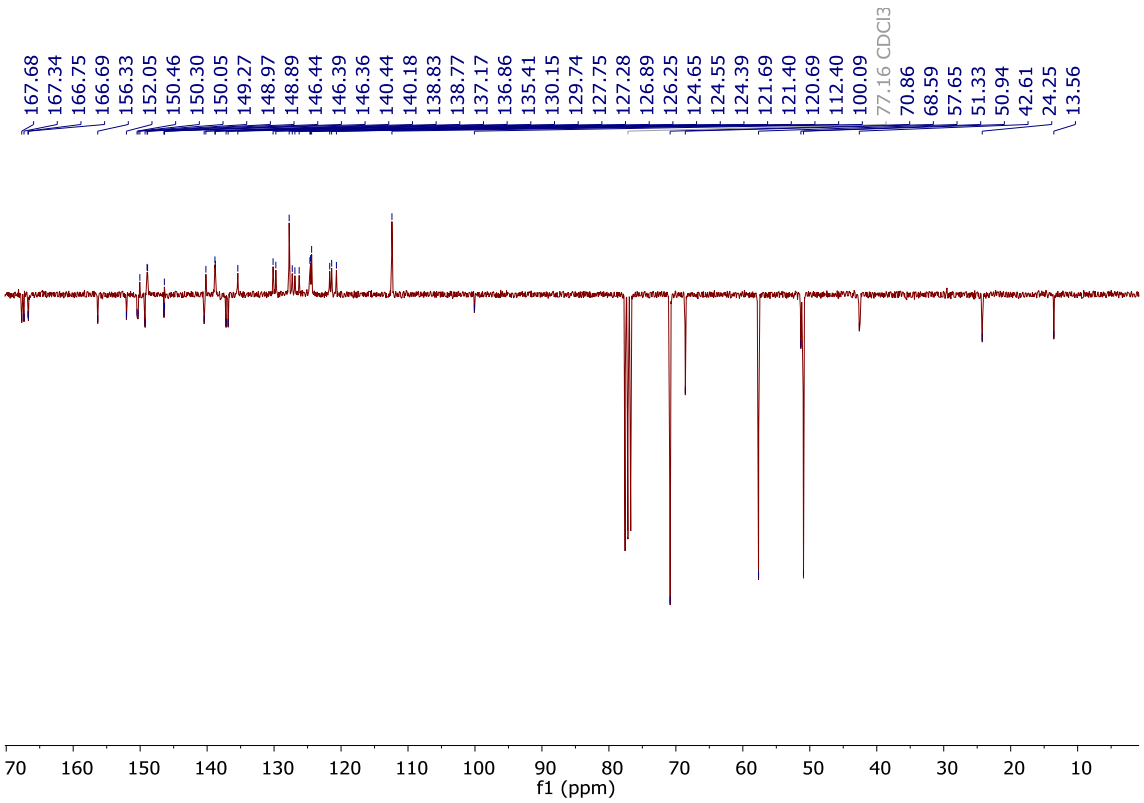


Figure S169. *^{13}C APT NMR spectrum of compound **C6_sil** (MeOD-d$_4$, 75 MHz).*

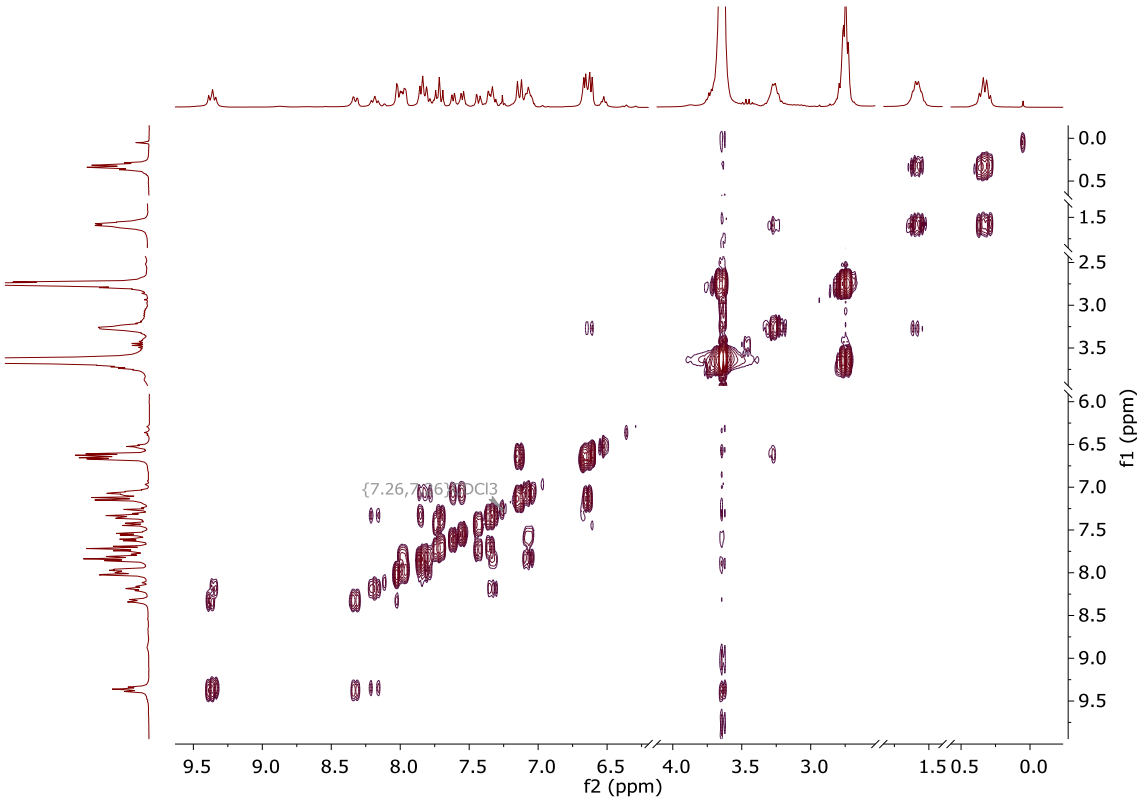


Figure S170. *COSY NMR spectrum of compound **C6_sil** (MeOD-d$_4$, 300 MHz).*

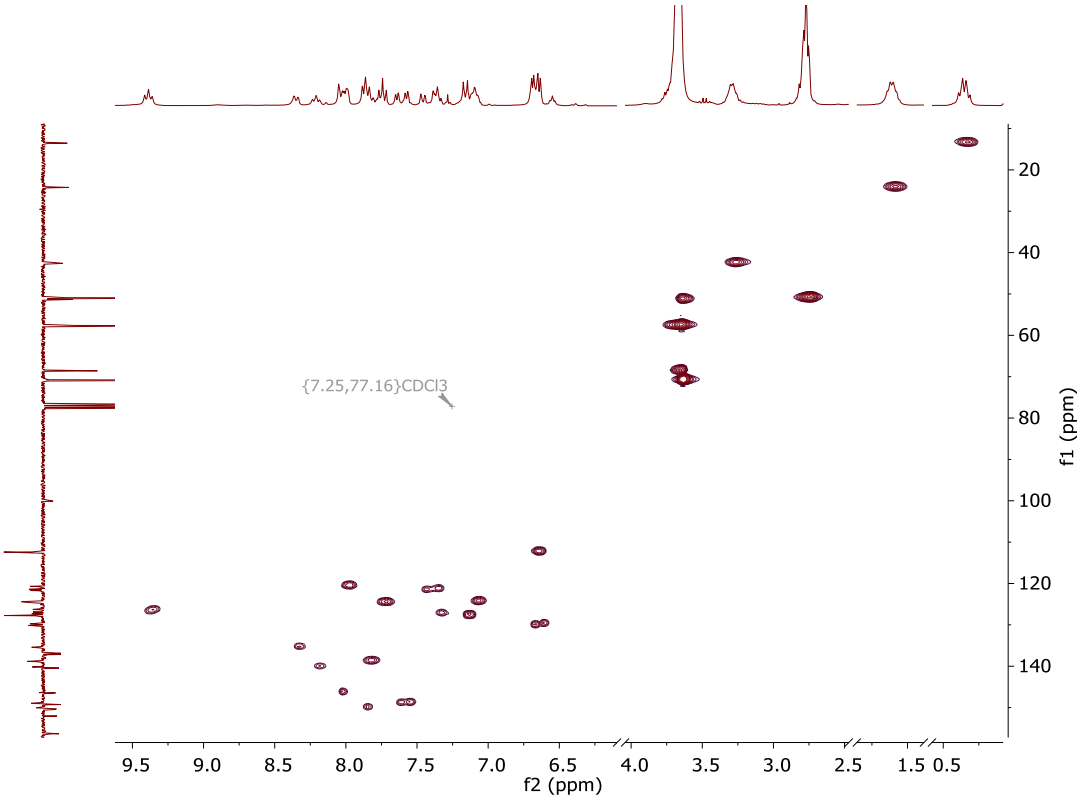


Figure S171. *HSQC NMR spectrum of compound* ***C6_sil*** *(MeOD-d4, 300 MHz).*

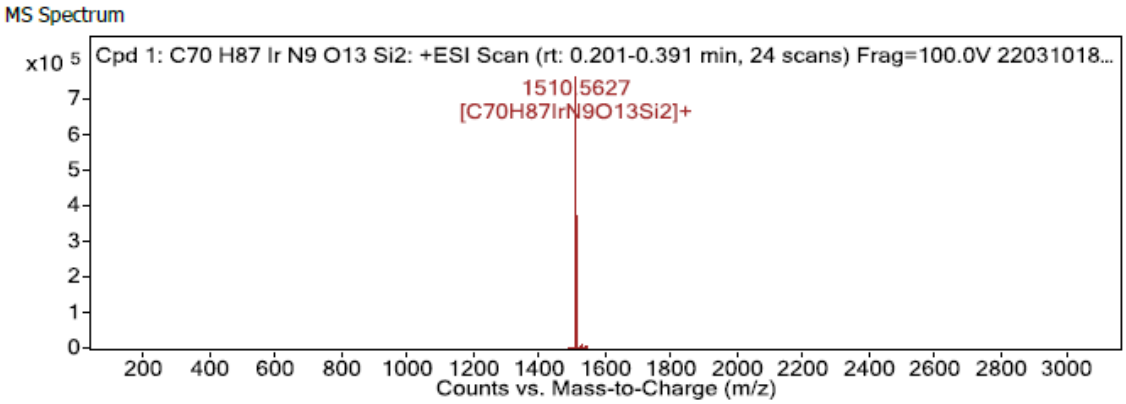


Figure S172. *Mass spectrum of compound* ***C6_sil****.*

4.2 PHOTOPHYSICAL CHARACTERIZATION

4.2.1 Ru_sil

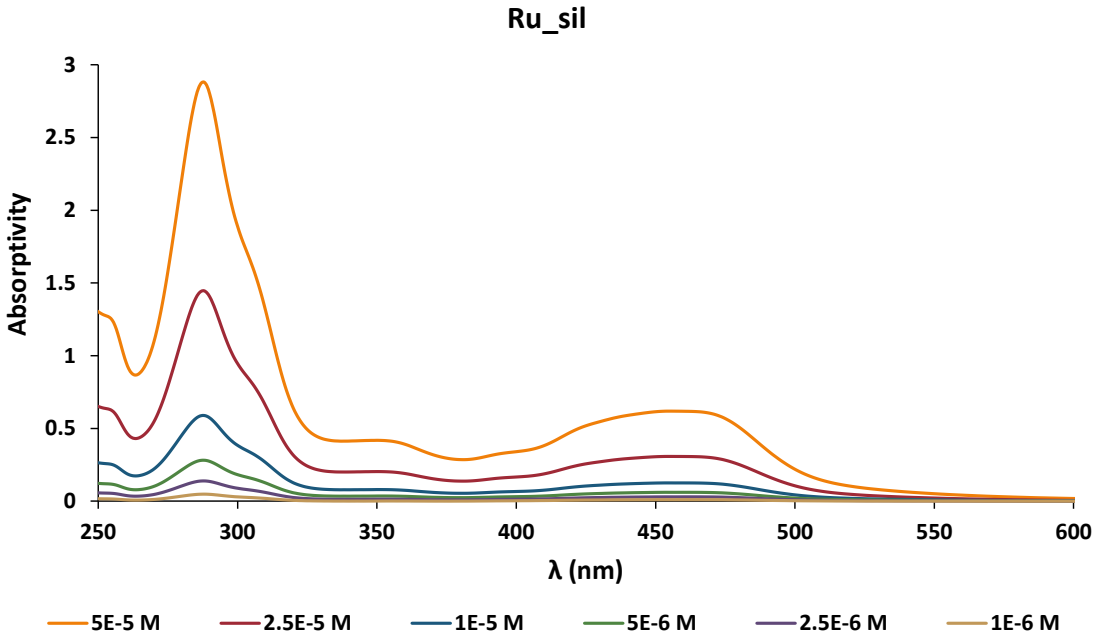
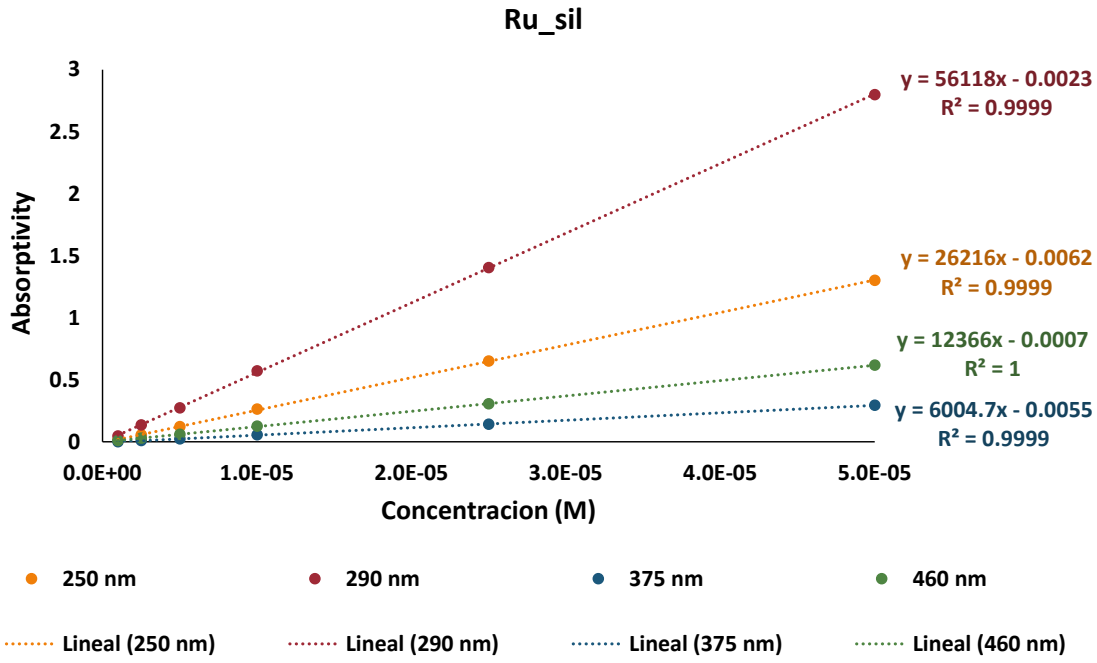


Figure S173. *UV-vis absorption spectra of* ***Ru_sil*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
250	26216
290	56118
375	6004.7
460	12366

Figure S174. *Calculated molar extinction coefficients of* ***Ru_sil*** *at selected absorption maxima.*

4.2.2 Ir_sil

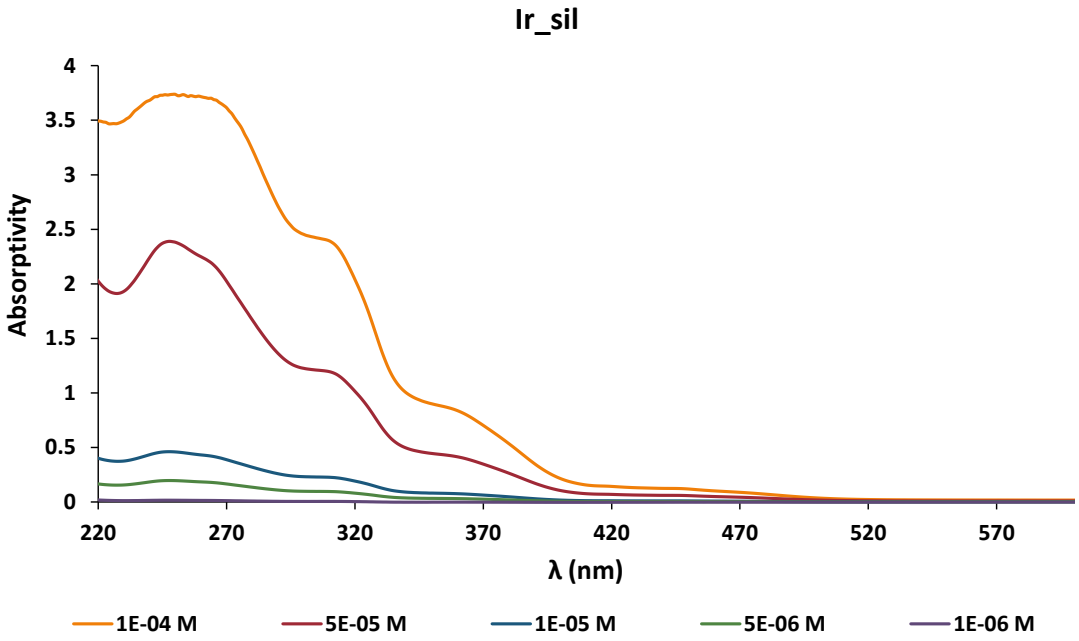
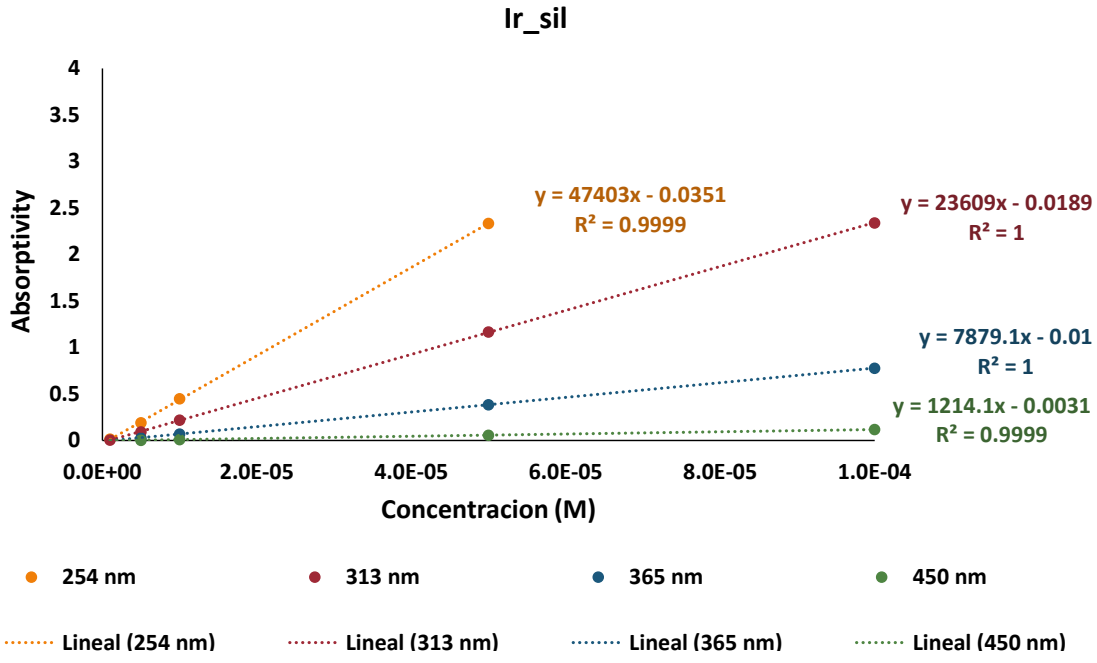


Figure S175. *UV-vis absorption spectra of* ***Ir_sil*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
254	47403
313	23609
365	7879.1
450	1214.1

Figure S176. *Calculated molar extinction coefficients of* ***Ir_sil*** *at selected absorption maxima.*

4.2.3 C6_COOH

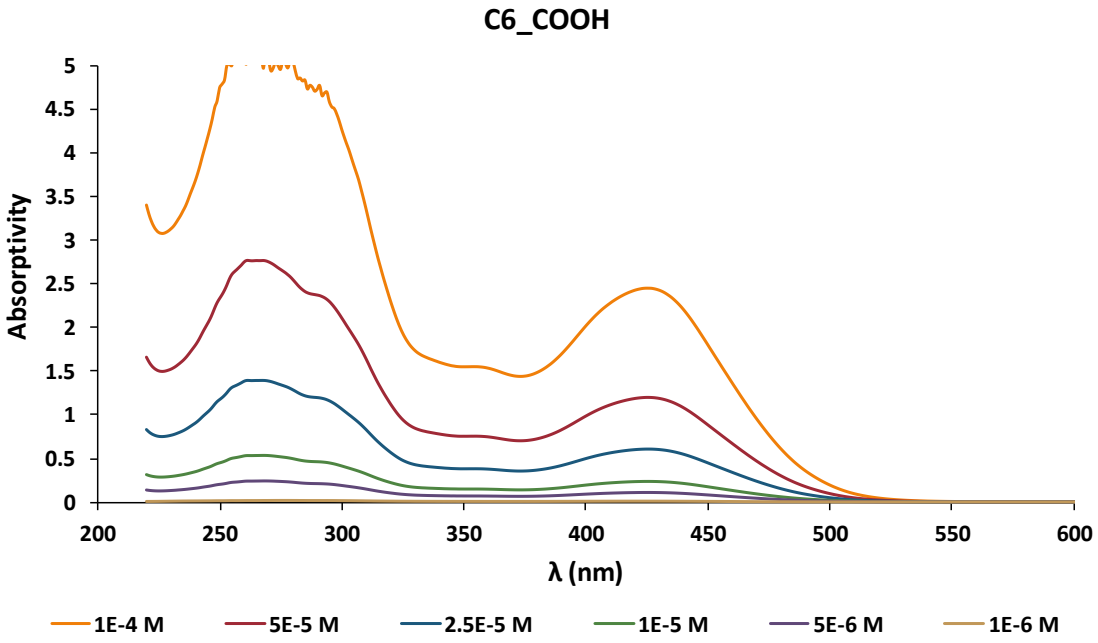
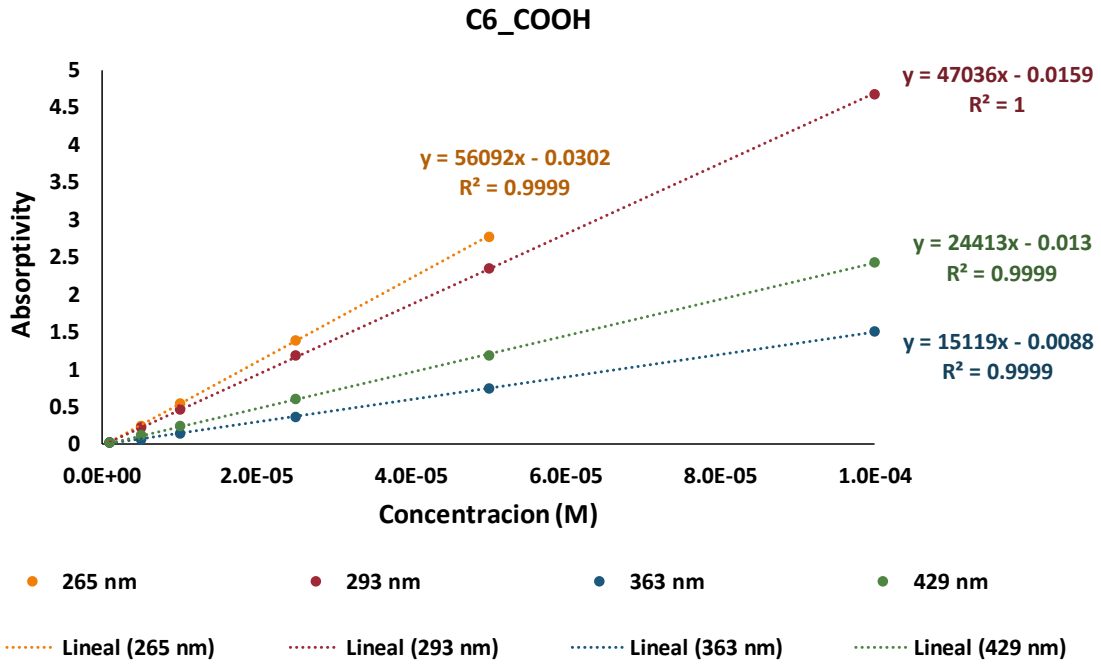


Figure S177. *UV-vis absorption spectra of free* ***C6_COOH*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
265	56092
293	47036
363	15119
429	24413

Figure S178. *Calculated molar extinction coefficients of* ***C6_COOH*** *at selected absorption maxima.*

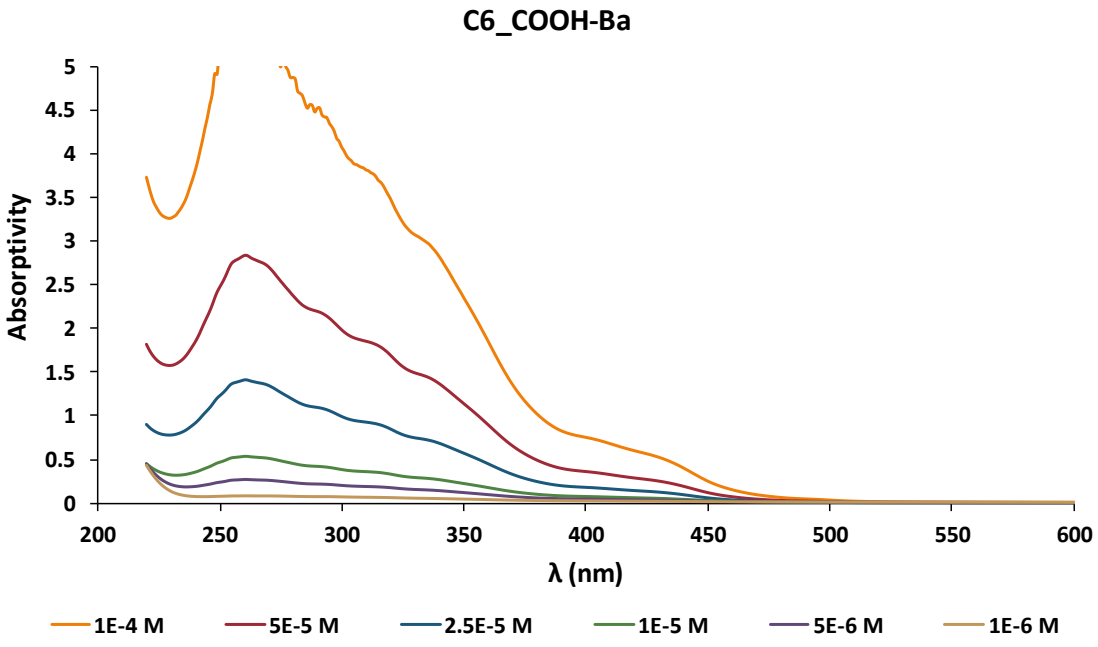
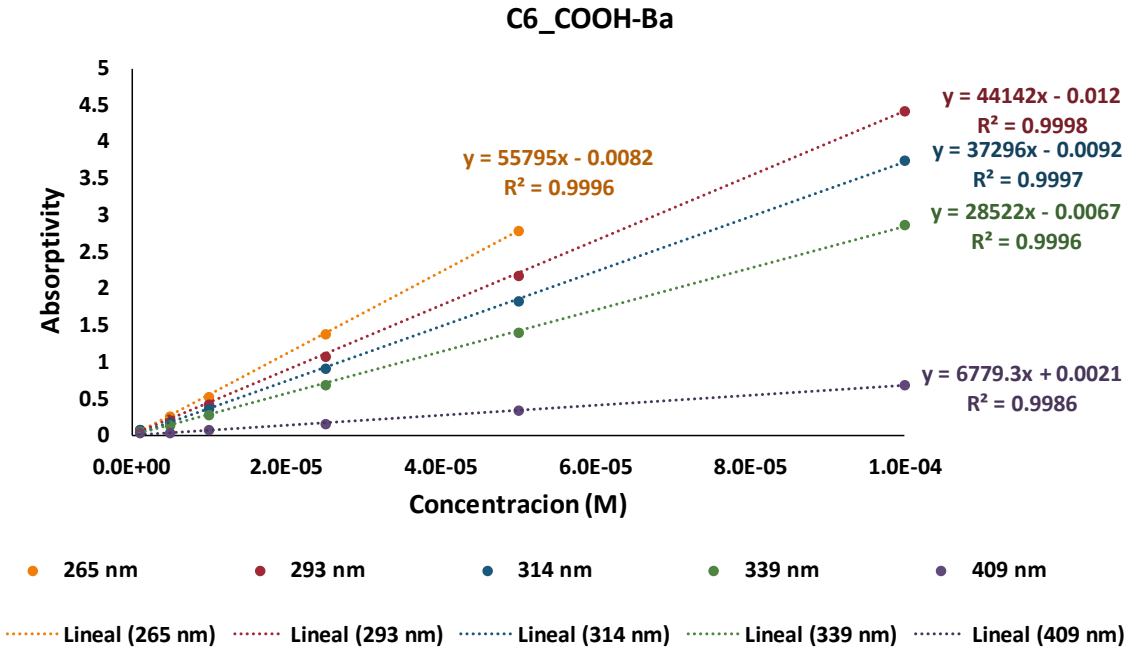


Figure S179. *UV-vis absorption spectra of free* ***C6_COOH-Ba*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
250	55795
277	44142
394	37296
428	28522
451	6779.3

Figure S180. *Calculated molar extinction coefficients of* ***C6_COOH-Ba*** *at selected absorption maxima.*

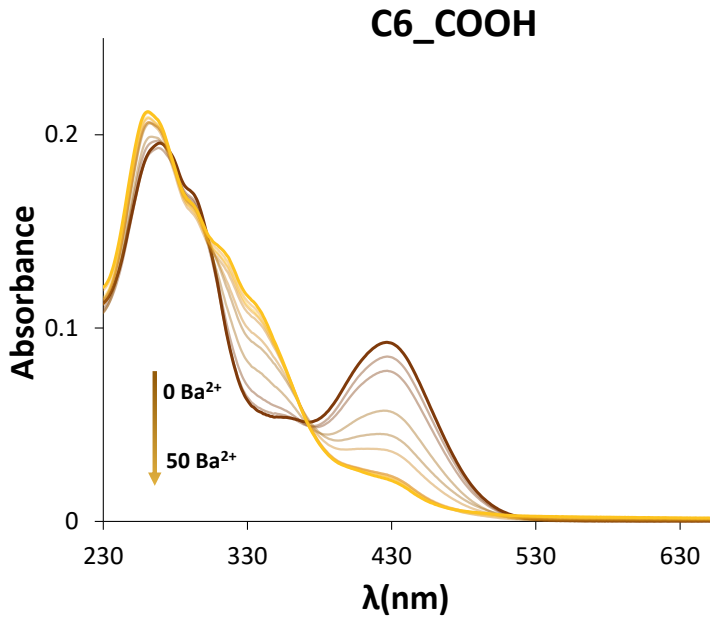
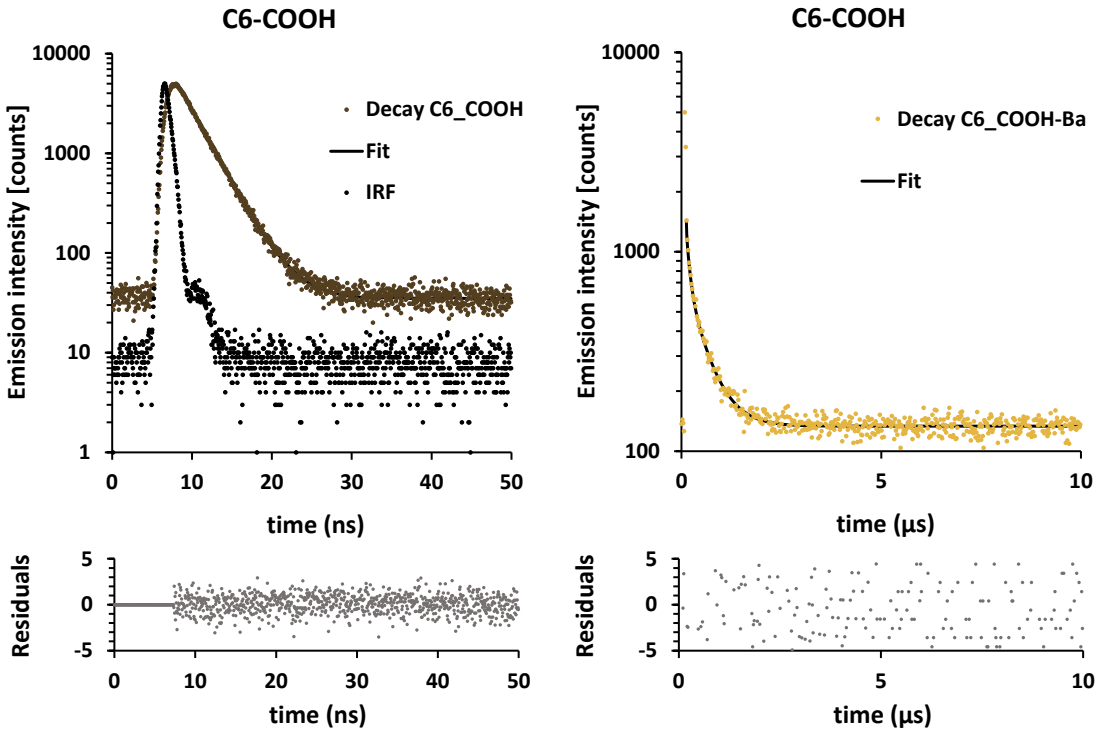


Figure S181. *Binding experiment of* ***C6_COOH****, in MeCN at a concentration of 5·10^{-6} M.*



Emission at 500 nm EPLED340 TCSPC 20MHz Slit 13, 1024 chanels, 5000 counts	
Result	
τ	χ^2
2.8 ns	1.1

Emission at 590 nm EPLED340 MCS 100kHz Slit 13, 1024 chanels, 5000 counts	
Result	
τ	χ^2
8.4ns (32%)	1.0
83.8 ns (14%)	
458.4 ns (53%)	

Figure S182. *Lifetime decay and results of* ***C6_COOH*** *and* ***C6_COOH-Ba*** *excited at their emission maxima.*

4.2.4 C6_sil

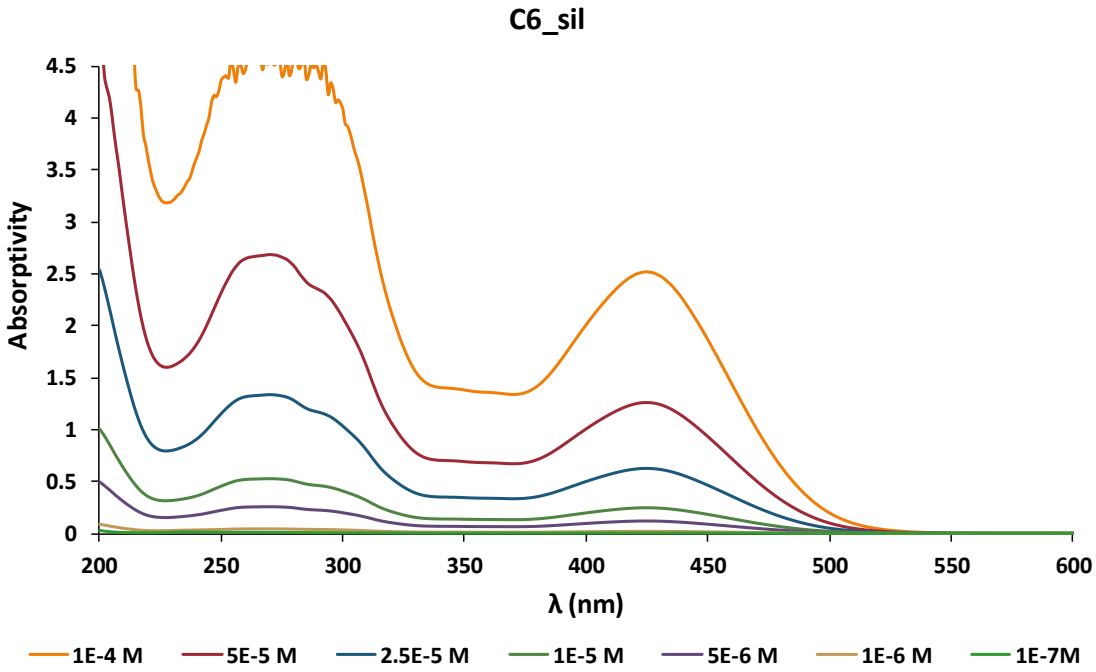
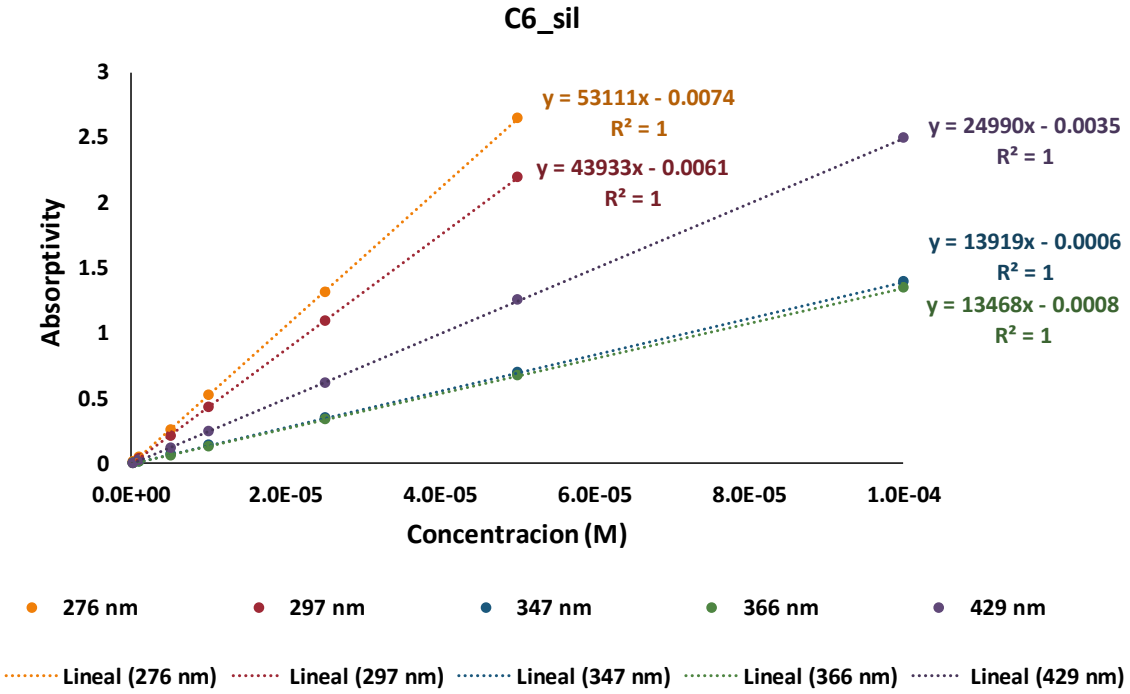


Figure S183. *UV-vis absorption spectra of free **C6_sil** in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
276	53111
297	43933
347	13919
366	13468
429	24990

Figure S184. *Calculated molar extinction coefficients of **C6_sil** at selected absorption maxima.*

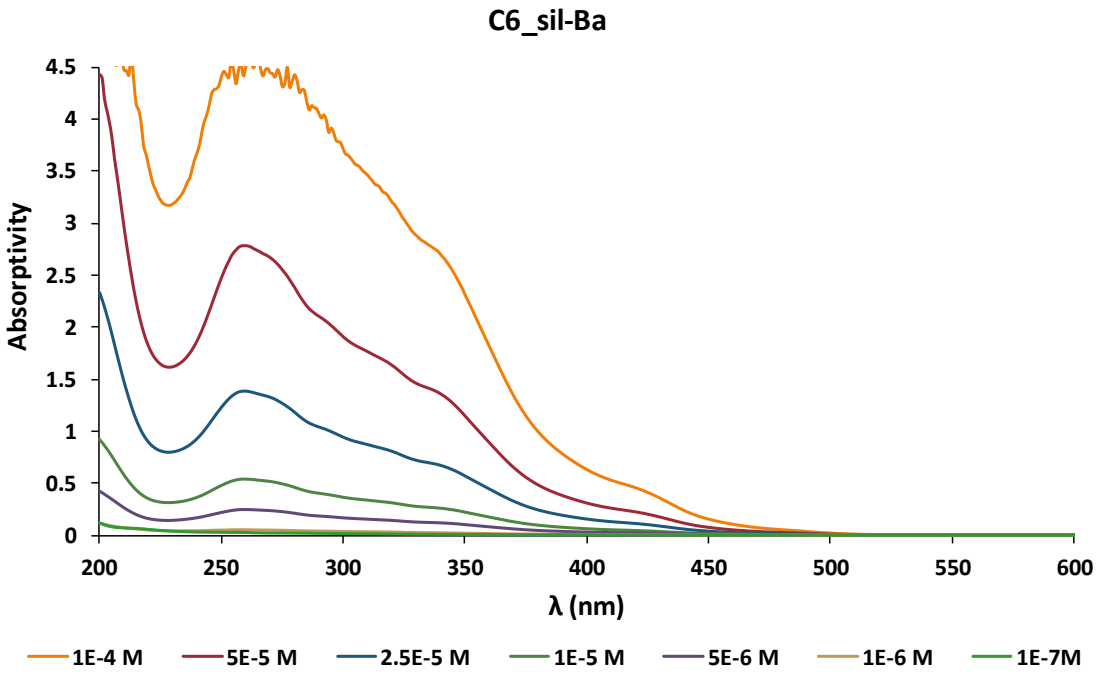
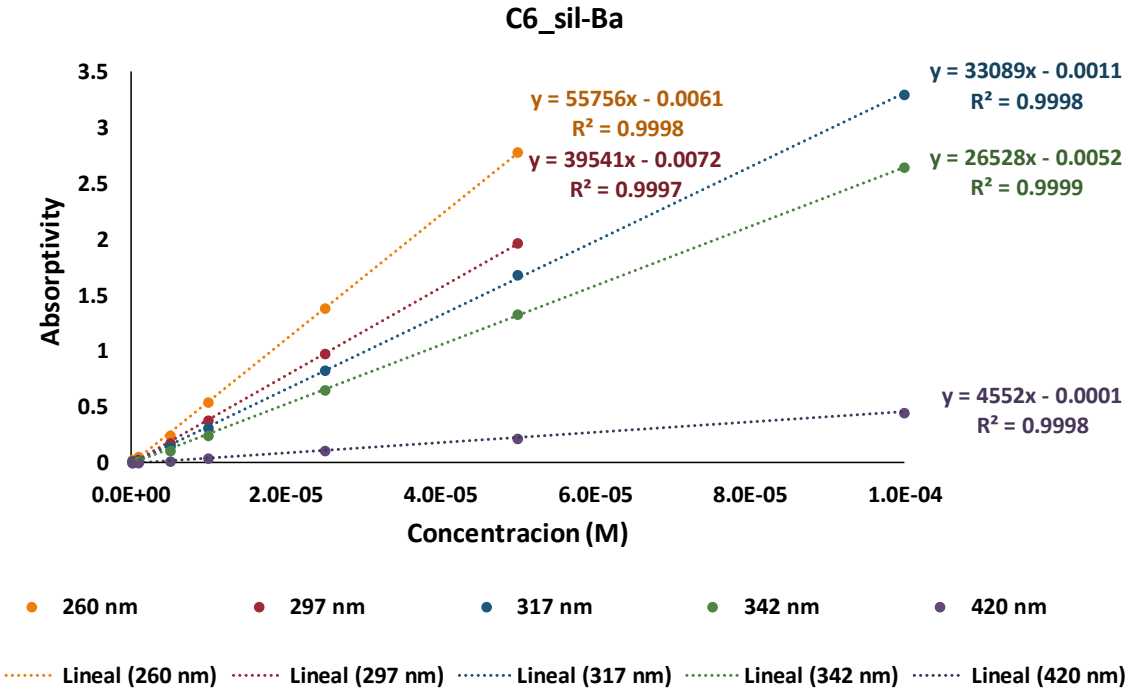


Figure S185. *UV-vis absorption spectra of free* ***C6_sil-Ba*** *in MeCN at different concentrations.*



λ (nm)	ε ($M^{-1}cm^{-1}$)
260	55756
297	39541
317	33089
342	26528
420	4552

Figure S186. *Calculated molar extinction coefficients of* ***C6_sil-Ba*** *at selected absorption maxima.*

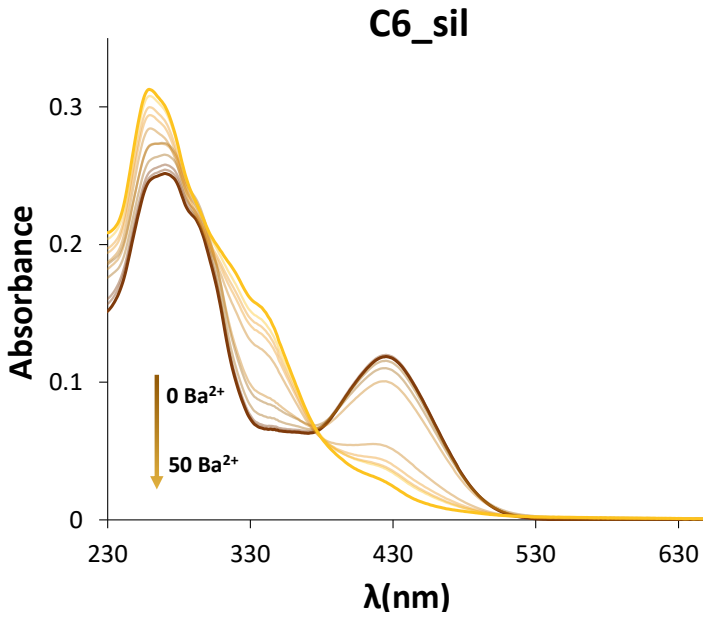


Figure S187. *Binding experiment of* ***C6_sil****, in MeCN at a concentration of* $5 \cdot 10^{-6}$ *M.*

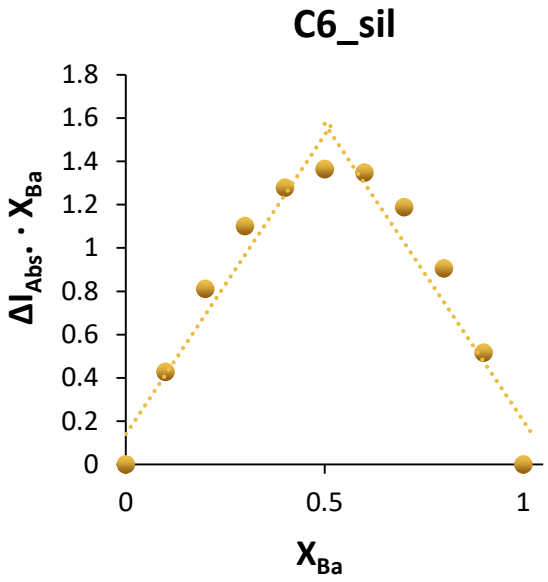
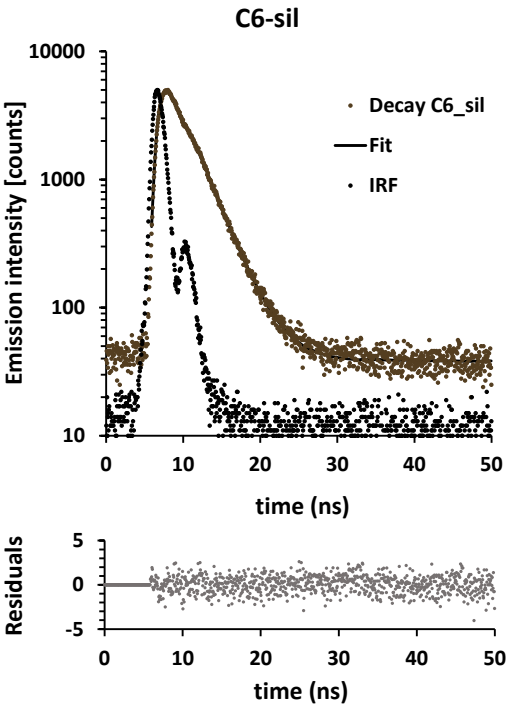
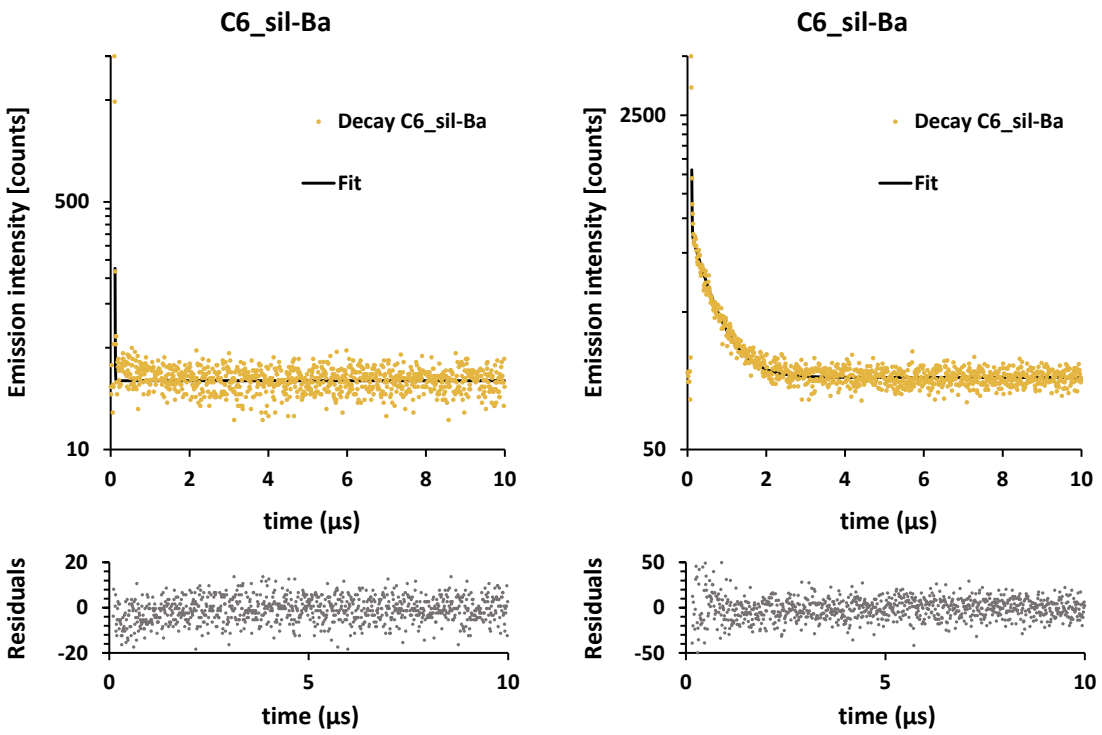


Figure S188. *Jobs Plot experiment of* ***C6_sil****, in MeCN at a concentration of* $1 \cdot 10^{-4}$ *M.*



Emission at 500 nm EPLED340 TCSPC 20MHz Slit 13, 1024 chanels, 5000 counts	
Result	
τ	χ^2
2.8 ns	1.0

Figure S189. *Lifetime decay and results of* ***C6_sil*** *excited at the emission maximum.*



Emission at 500 nm EPLED340 MCS 100KHz Slit 13, 1024 chanels, 5000 counts	
Result	
τ	χ^2
3.5 ns	1.1

Emission at 600 nm EPLED340 MCS 100KHz Slit 13, 1024 chanels, 5000 counts	
Result	
τ	χ^2
7.2 ns (23%) 499 ns (77%)	1.2

Figure S190. *Lifetime decay and results of* ***C6_sil-Ba*** *excited at the two emission maxima.*

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