Electronic supplementary information

Supramolecular Chemistry in Solution and Solid-Gas Interfaces: Synthesis and Photophysical Properties of Monocolor and Bicolor Sensors for Barium Tagging in Neutrinoless Double Beta Decay Nuclear Reactions

Fernando Auria-Luna,[a] Frank W. Foss Jr,[b] Juan Molina-Canteras,[a] Ivan Velazco-Cabral,[c] Aimar Marauri,[ad] Amaia Larumbe,[a] Borja Aparicio,[ae] Juan Luis Vázquez,[c] Nerea Alberro,[a] Iosune Arrastia,[a] Virginia San Nacianceno,[a] Adai Colom,[fg] Carlos Marcuello,[d] Benjamin J. P. Jones,[b] David Nygren,[b] Juan J. Gómez-Cadenas,[fh] Celia Rogero,[hi] Iván Rivilla,*[fh] Fernando P. Cossío,*[a] and the NEXT collaboration

[a]*Departamento de Química Orgánica I and Centro de Innovación y Química Avanzada (ORFEO-CINQA), Facultad de Química/Kimika Fakultatea, Universidad del País Vasco/Euskal Herriko Unibertsitatea (UPV/EHU), 20018 Donostia-San Sebastian, Spain*

[b]*Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, Texas 76019, United States*

[c]*Departament of Chemistry, University of Guanajuato, 36050 Guanajuato, Gto, Mexico*

[d]*Biofisika Institute (CSIC, UPV/EHU), 48940 Leioa, Spain.*

[e]*Present address: Centro de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela (Spain).*

[f]*Ikerbasque, Basque Foundation for Science, 48009 Bilbao, Spain.*

[g]*Department of Biochemistry and Molecular Biology, Faculty of Science and Technology, Campus Universitario, Universidad del País Vasco/Euskal Herriko Unibertsitatea (UPV/EHU), 48940 Leioa, Spain.*

[h]*Donostia International Physics Center (DIPC), 20018 Donostia-San Sebastian, Spain*

[i]*Materials Physics Center (CSIC-UPV/EHU), San Sebastián, E-20018, Spain*

NEXT Collaboration Author List:

C. Adams,[1] H. Almazán,[2] V. Álvarez,[3] B. Aparicio,[4] A.I. Aranburu,[5] L. Arazi,[6] I.J. Arnquist,[7] F. Auria-Luna,[4] S. Ayet,[8] C.D.R. Azevedo,[9] K. Bailey,[1] F. Ballester,[3] M. del Barrio-Torregrosa,[10] A. Bayo,[11] J.M. Benlloch-Rodríguez,[10] F.I.G.M. Borges,[12] A. Brodolin,[10] N. Byrnes,[13] S. Cárcel,[8] A. Castillo,[10] S. Cebrián,[14] E. Church,[7] L. Cid,[11] C.A.N. Conde,[12] T. Contreras,[15] F.P. Cossío,[4] E. Dey,[13] G. Díaz,[16] T. Dickel,[17] C. Echevarria,[10] M. Elorza,[10] J. Escada,[12] R. Esteve,[3] R. Felkai,[6,a] L.M.P. Fernandes,[18] P. Ferrario,[10,19] A.L. Ferreira,[9] F.W. Foss,[20] Z. Freixa,[5,19] J. García-Barrena,[3] J.J. Gómez-Cadenas,[10,19,b] R. González,[10] J. Grocott,[2] R. Guenette,[2] J. Hauptman,[21] C.A.O. Henriques,[18] J.A. Hernando Morata,[16] P. Herrero-Gómez,[22] V. Herrero,[2] C. Hervés Carrete,[16] Y. Ifergan,[6] B.J.P. Jones,[13] F. Kellerer,[8] L. Larizgoitia,[10] A. Larumbe,[4] P. Lebrun,[23] F. López,[10] N. López-March,[8] R. Madigan,[20] R.D.P. Mano,[18] A.P. Marques,[12] J. Martín-Albo,[8] G. Martínez-Lema,[6] M. Martínez-Vara,[10] R. Miller,[20] K. Mistry,[13] J. Molina-Canteras,[4] F. Monrabal,[10,19] C.M.B. Monteiro,[18] F.J. Mora,[3] K. Navarro,[13] P. Novella,[8] A. Nuñez,[11] D.R. Nygren,[13] E. Oblak,[10] J. Palacio,[11] B. Palmeiro,[2] A. Para,[23] I. Parmaksiz,[13] A. Pazos,[5] J. Pelegrin,[10] M. Pérez Maneiro,[16] M. Querol,[8] A.B. Redwine,[6] J. Renner,[16] I. Rivilla,[10,19] C. Rogero,[24] L. Rogers,[1] B. Romeo,[10] C. Romo-Luque,[8] F.P. Santos,[12] J.M.F. dos Santos,[18] M. Seemann,[10] I. Shomroni,[22] P.A.O.C. Silva,[18] V. San Nacienciano,[4] A. Simón,[10] S.R. Soleti,[10] M. Sorel,[8] J. Soto-Oton,[8] J.M.R. Teixeira,[18] S. Teruel-Pardo,[8] J.F. Toledo,[3] C. Tonnelé,[10] J. Torrent,[10,25] A. Trettin,[2] A. Usón,[8] P.R.G. Valle,[5,10] J.F.C.A. Veloso,[9] J. Waiton[2] and A. Yubero-Navarro.[10]

[1]*Argonne National Laboratory, Argonne, IL 60439, USA*

[2]*Department of Physics and Astronomy, Manchester University, Manchester. M13 9PL, United Kingdom*

[3]*Instituto de Instrumentación para Imagen Molecular (I3M), Centro Mixto CSIC - Universitat Politécnica de Valencia, Camino de Vera s/n, Valencia, E-46022, Spain*

[4]*Department of Organic Chemistry I, University of the Basque Country (UPV/EHU), Centro de Innovación en Química Avanzada (ORFEO-CINQA), San Sebastián / Donostia, E-20018, Spain*

[5]*Department of Applied Chemistry, Universidad del País Vasco (UPV/EHU), Manuel de Lardizabal 3, San Sebastian / Donostia, E-20018, Spain*

[6]*Unit of Nuclear Engineering, Faculty of Engineering Sciences, Ben-Gurion University of the Negev, P.O.B. 653, Beer-Sheva, 8410501, Israel*

[7]*Pacific Northwest National Laboratory (PNNL), Richland, WA 99352, USA*

[8]*Instituto de Física Corpuscular (IFIC), CSIC & Universitat de València, Calle Catedrático José Beltrán, 2, Paterna, E-46980, Spain*

[9]*Institute of Nanostructures, Nanomodelling and Nanofabrication (i3N), Universidade de Aveiro, Campus de Santiago, Aveiro, 3810-193, Portugal*

[10]*Donostia International Physics Center, BERC Basque Excellence Research Centre, Manuel de Lardizabal 4, San Sebastian / Donostia, E-20018, Spain*

[11]*Laboratorio Subterráneo de Canfranc, Paseo de los Ayerbe s/n, Canfranc Estación, E-22880, Spain*

[12]*LIP, Department of Physics, University of Coimbra, Coimbra, 3004-516, Portugal*

[13]*Department of Physics, University of Texas at Arlington, Arlington, TX 76019, USA*

[a] Now at Weizmann Institute of Science, Israel.
[b] NEXT spokesperson

[14]*Centro de Astropartículas y Física de Altas Energías (CAPA), Universidad de Zaragoza, Calle Pedro Cerbuna, 12, Zaragoza, E-50009, Spain*

[15]*Department of Physics, Harvard University, Cambridge, MA 02138, USA*

[16]*Instituto Gallego de Física de Altas Energías, Univ. de Santiago de Compostela, Campus sur, Rúa Xosé María Suárez Núñez, s/n, Santiago de Compostela, E-15782, Spain*

[17]*II. Physikalisches Institut, Justus-Liebig-Universitat Giessen, Giessen, Germany*

[18]*LIBPhys, Physics Department, University of Coimbra, Rua Larga, Coimbra, 3004-516, Portugal*

[19]*Ikerbasque (Basque Foundation for Science), Bilbao, E-48009, Spain*

[20]*Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX 76019, USA*

[21]*Department of Physics and Astronomy, Iowa State University, Ames, IA 50011-3160, USA*

[22] *Hebrew University, Edmond J. Safra Campus, Jerusalem, 9190401, Israel*

[23]*Fermi National Accelerator Laboratory, Batavia, IL 60510, USA*

[24]*Centro de Física de Materiales (CFM), CSIC & Universidad del País Vasco (UPV/EHU), Manuel de Lardizabal 5, San Sebastián / Donostia, E-20018, Spain*

[25]*Escola Politécnica Superior, Universitat de Girona, Av. Montilivi, s/n, Girona, E-17071, Spain*

Table of Contents

1. General Information

All experiments requiring a dry atmosphere were performed using conventional vacuum line and Schlenk techniques. The commercial reagents were purchased from Sigma MERK (Sigma-Aldrich), TCI (Tokio Chemical Industry CO), abcr Gmbh and ACROS organics: 1-aza-18-crown-6-ether (TCI, >98%); tris(dibenzylideneacetone)dipalladium(0) (Aldrich, 99.8%); 2-(dicyclohexylphosphino)-2'-(dimethylamino)biphenyl (abcr, >97%); *N*-iodosuccinimide (Aldrich, 95%); ammonium acetate (Aldrich, >98%); 1,1'-bis(diphenylphosphino)ferrocenepalladium (II) dichloride (Fluorochem, 98%); potassium phosphate tribasic (Aldrich, >98%);bromobenzene (Aldrich, 99%); sodium tert-butoxide (Aldrich, 97%); acetic acid, potassium salt (ACROS, 99%); bis(pinacolato)diboron (TCI, 99%); sodium hydroxide (Aldrich, 97%); *N*-hydroxysuccinimide (Aldrich, 98%); *N*-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (Aldrich, commercial grade); triethanolamine (Aldrich, 98%); (3-aminopropyl)triethoxysilane (Aldrich, 98%); kryptofix 22 (Aldrich); benzyl bromide (abcr, 99%); cesium carbonate (Aldrich, 99%); methyl 2-aminopyridine-4-carboxylate (Aldrich, 98%); methyl bromoacetate (Aldrich, 98%); phosphorous(V) oxychloride (Aldrich, 99%); hydriodic Acid (TCI, 57%); sodium iodide (Aldrich, 99%); potassium carbonate (Aldrich, 99%); 18-crown 6-ether (TCI, 99%); 1-fluoro-4-nitrobenzene (Aldrich, 98%), 4-bromo-1,8-naphthalic anhydride (TCI, 99%); 1-metil-2-pyrrolidinone (Aldrich, 99%); 11-aminoundecylethoxysilane (abcr, 99%); triethanolamine (Aldrich, 99%); and were used without further purification. MeOH (Methanol RA, Oppac); DMF (*N*,*N*-dimethylformamide, anhydrous 99,8%, MERCK); Hexane (95% alkanes mixture for synthesis, Panreac); CH_2Cl_2 (Diclorometano RA, Oppac); AcOEt (Etilo Acetato RA, Oppac); Acetone (VWR); MeCN (acetonitrile for HPLC, VWR); DMSO (dimethyl sulfoxide, VWR); toluene (VWR), acetone (VWR), ethanol (VWR).

2. Analytical Methods

Thin layer chromatographies (TLC) were performed on aluminum TLC plates (silica gel coated with flourescent indicator F254), and visualized either by exposure to UV light or staining with potassium permanganate or ninhydrine.

Column chromatographies were carried out with silica gel 60 (0.040- 0.063 mm).

Flash chromatographies were carried out using a Biotage Isolera four system, with Snap KP-Sil 10g cartridges.

Fourier Transform Infra-Red (FTIR) Spectroscopy spectra were recorded on an FT-IR spectrometer equipped with a diamond detection and single-reflection ATR module; wavenumbers are given in cm^{-1}.

Melting points (M.p.) were determined using a Büchi Melting Point B-560 apparatus.

Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR or ^{13}C NMR spectra were recorded at 400 or 500 MHz and 101 or 126 MHz for ^{13}C NMR, equipped with a z gradient BBOF probe, in $CDCl_3$. The data are reported as s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet or unresolved, br s = broad signal, coupling constant(s) in Hz, integration. The ^{1}H spectra were recorded using noesygppr1d sequence from Bruker's library at 500.13 MHz. A time domain of 64 k and a spectral width of 10000 Hz. Interpulse delay: 1 s. Adquistion time: 3 s. Number of scans: 64. Mixing time: 0.01 s.

Mass spectrometry (MS) and high-resolution mass spectrometry (HRMS). High-resolution mass spectra (HRMS) were recorded on HPLC Agilent 1200 Series system coupled to a hybrid quadrupole-time of flight (LC-QTOF) mass spectrometer Agilent 6530 from Agilent Technologies (Santa Clara, CA, USA). Mobile phase was composed by 0.1 % formic acid: acetonitrile 0.1% formic acid (50:50). Gas Temp. 325ºC; Drying gas: 5 l/min; Nebulizer: 40 psig; Shealt gas Temp. 375 ºC; Shealt gas flow: 11 l/min. Vcap: 3500 V(+).

Confocal Microscopy. Images were acquired using a Leica Stellaris5 confocal microscope (Leica Microsystems CMS GmbH, Germany) equipped with a TauSense module to acquire lifetime based images. Leica objective HC PL APO CS2 10x/0.40 DRY. Leica HyD detectors. Single-Photon counting mode (In photon counting mode, individual photons are resolved and counted with high fidelity, producing highly accurate and quantitative data). $\lambda_{exc.}$ = 405 nm, Line Average = 16, Scan Speed = 400 Hz. Pixel Size = 0.024 μm. Physical Length = 24.22 μm. The LAS-X software, version 4.5.0.25531, was used to analyze the images and the open version (Suite X; 3.30.16799) (Leica Microsystems CMS GmbH, Germany). Average emission spectra (Figure 11, panels C and F) were obtained with the same setup.

As a control experiment, the same images shown in Figure 12 were acquired for a sample of compound **15aa** deposited by means of spin coating over ITO without adding Ba^{2+}. Images were recorded in both wavelength ranges to make sure that no background signal at 410-470 nm could be miss assigned as the sensor−Ba^{2+} complex (Figure S1).

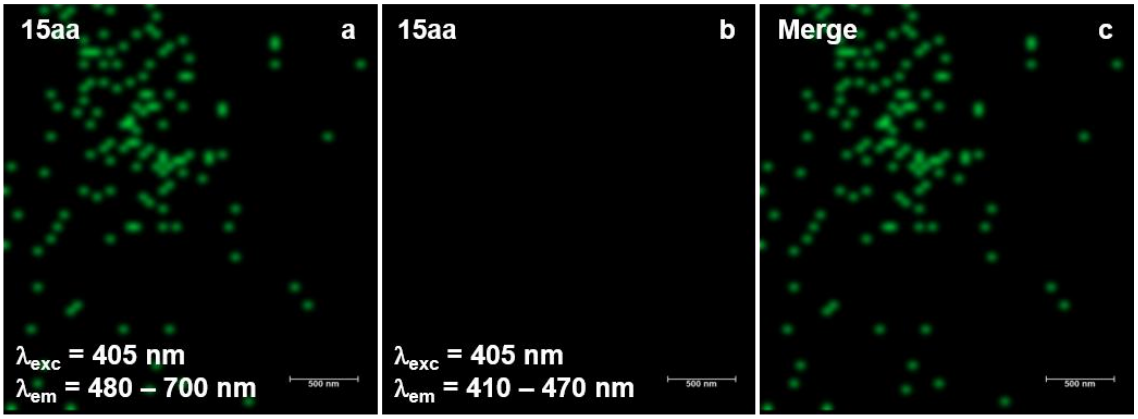


Figure S1. Confocal microscopy images of compound **15aa** at the unbound and Ba^{2+}-bound channels (see Figure 12, panels a to c, to compare).

Barium Sublimation. 3 g of $Ba(CF_3SO_3)_2$ (melting point: >300 ºC) were sublimated over indium tin oxide (ITO) surfaces with an Aldrich® sublimation apparatus Z221171 refrigerated with a water flow and connected to a vacuum pump providing 0.43 mbar, heating at ca. 280 ºC for 24 h. After completion, surfaces were kept under an Ar atmosphere until their characterization (Figure S2).

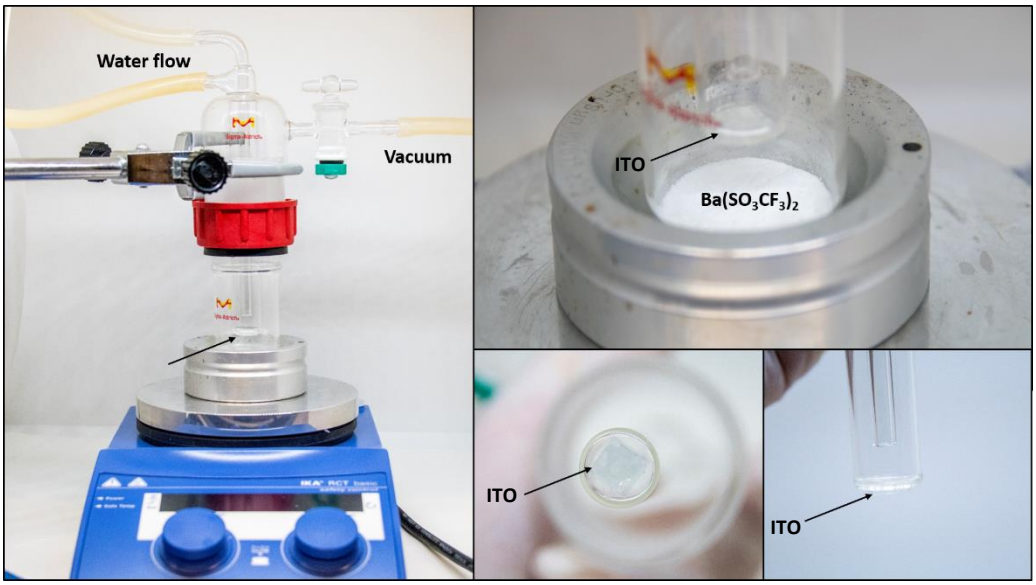


Figure S2. Sublimation system.

UV/Vis and Fluorescence Spectroscopy. Uv-vis spectra were acquired on a Cary 4000 UV-Vis Spectrophotometer. Emission spectra in solid state and in solution were acquired on an Edinburgh Instruments FLS1000 Spectrophotometer (Edinburgh, Scotland, UK), accuracy ± 0.2 nm. Quantum Yields were acquired with the Integrating Sphere accessory. Lifetimes were acquired with a picosecond pulsed diode laser EPL-485 nm (Edinburgh, Scotland, UK) and a picosecond pulsed light emitting diode EPLED-340 nm (Edinburgh, Scotland, UK). The spectra were recorded using Starna precision cell made of quartz with a path-length of 1 cm. All solutions were prepared with spectrophotometric grade MeCN in concentrations between $1 \cdot 10^{-4}$ and $1 \cdot 10^{-7}$ M, depending on linearity studies. Spectra of chelated fluorescent sensors were acquired by adding 1 equivalent of $Ba(ClO_4)_2$. To construct the Job´s plot different proportion of stock solutions of fluorescent sensors and $Ba(ClO_4)_2$ were mixed and registered, after 1 min of equilibration time.

Spin coating. Experiments were performed in a MB-SC-210 (MBRAUN) apparatus integrated into the Globe Box or in a NOVOSPIN C-series model SCC-200 apparatus coupled to a vacuum pump Linicon LV-125A.

Activation of ITO surfaces. ITO coating glass was activated by O_2-plasma-Ar (Diener Low pressure plasma machine of type Pico).

Binding constant determination. All the binding constants shown in Table 2 were calculated following the procedure described in the main manuscript. As an example, absorption data corresponding to compound **7ba**, together with its linear fitting using eq. (5), are shown below (Figure S3).

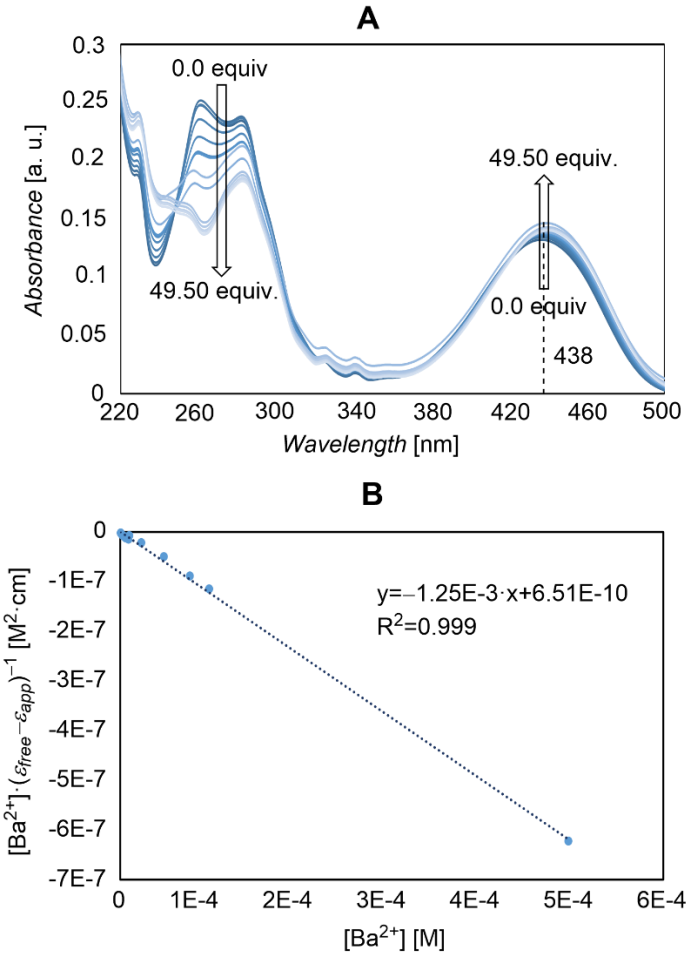


Figure S3. (A) Absorption spectra of compound **7ba** in the presence of different equivalents of Ba^{2+}. (B) Linear fitting of the terms included in eq. (5) to determine the binding constant K_b for **7ba**.

Limit of Detection (LOD). To obtain the LOD values of the sensors, titration experiments were performed, in which increasing concentrations of $Ba(ClO_4)_2$ were added to a solution 10 μM of the molecule under study. Then, ($I_{\lambda max}/I_{0\lambda max}$) vs. [$Ba^{2+}$] in the case of the monocolor series and ($I_{\lambda bound}/I_{\lambda free}$) vs. [$Ba^{2+}$] in the case of bicolor series were plotted. Finally, a linear fitting was performed and the slope values were used together with the pertinent standard deviation to obtain the detection limits shown below (Table S1).[1]

Table S1 Limits of Detection (LODs) for compounds **7aa-bb**, **14a,b** and **15aa-bb**.

Sensor	LOD [μM][a]	LOD [ppb]
7aa	0.228	31.37
7ab	0.351	48.24

7ba	0.077	10.53
7bb	0.059	8.14
14a	0.281	38.62
14b	0.392	53.81
15aa	0.226	31.09
15ab	0.127	17.50
15ba	0.187	25.69
15bb	0.194	26.61

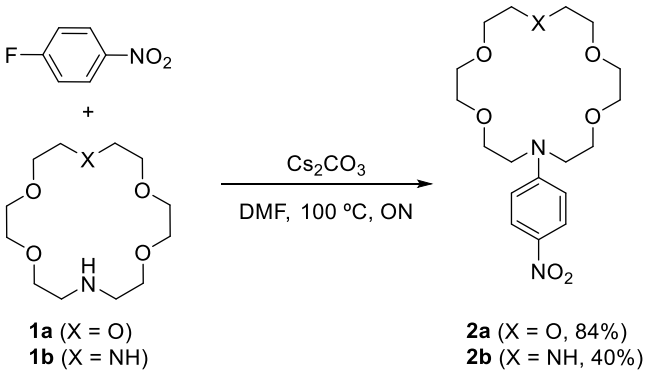
[a]Calculated as LOD = 3σ / k, where σ is the standard deviation and k is the slope of the linear fit, respectively.

Scratch test. The scratching experiments were carried out using a *JPK Nanowizard UltraSpeed AFM* equipped with a *Super Sharp Silicon*^{TM} (SSS-NCHR-10) AFM probe, with a nominal spring constant between 20 N/m. The AFM probe was calibrated to ascertain the deflection sensitivity and spring constant values by running force-distance curves on a stiff quartz surface and by the thermal tune.[2] The images were taken in contact mode, and the set point applied for the scratching experiment was 3500 nN, which is enough to remove the organic and ITO layers and maintain the quartz surface without damage. The resonance frequency of the AFM lever was settled at 60 KHz. Scratching was done by passing five times per area. Five different areas of 500 nm x 500 nm were scratched in each sample, and images after the experiment were 4 µm x 4 µm in a resolution of 256 x 256 pixels/frame. The raw gathered data was processed using ImageJ 2.14. software tool (Figure 4).[3]

3. Synthetic Procedures and Analytical Data

Synthesis of compounds 2a and 2b.

Compounds **2a** and **2b** were obtained following a modified procedure described by Sibert et al.[4] (**Scheme S1**) Spectral data for compound **2a** are consistent with the previously reported values.[4]



Scheme S1. Synthesis of compounds **2a** and **2b**.

To a microwave sealable glass vial equipped with a magnetic stirrer, the corresponding crown ether **1** (1.0 mmol, 1.0 equiv.), Cs_2CO_3 (325.8 mg, 1.0 mmol, 1.0 equiv.), 2.5 mL of DMF and 1-fluoro-4-nitrobenzene (106 μL, 1.0 mmol, 1.0 equiv.) were added sequentially. The vial was sealed, purged with argon, heated to 100 ºC in an oil bath and stirred overnight.

Purification: The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude was then dissolved in 50 mL of AcOEt and washed with Brine (3x50 mL). The organic fraction was collected, dried over $MgSO_4$, filtered and evaporated under reduced pressure. Finally, the resulting oil was further purified by column chromatography on silica gel and a gradient of polarity from CH_2Cl_2 to a CH_2Cl_2:MeOH mixture (9:1), affording the corresponding final adducts **2a** and **2b**.

16-(4-Nitrophenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane 2a.

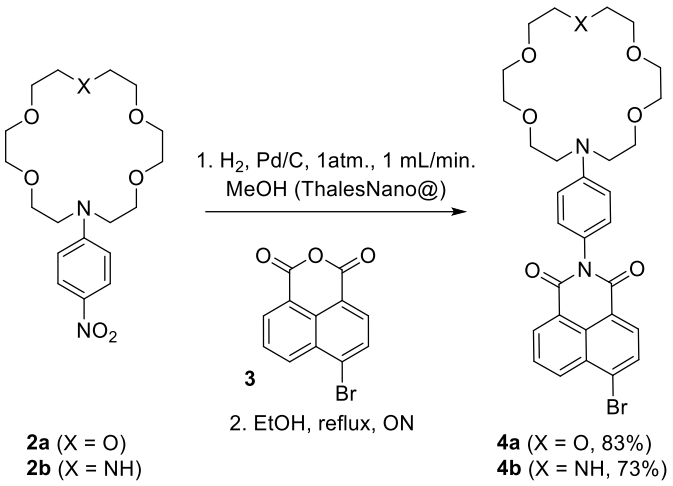
Following the general procedure, compound **2a** was obtained as a yellow oil in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 6.70 – 6.62 (m, 2H), 3.76 – 3.61 (m, 24H).

7-(4-Nitrophenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane 2b.

Following the general procedure, compound **2b** was obtained as a yellow oil in 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 2H), 6.65 – 6.58 (m, 2H), 3.83 – 3.58 (m, 20H), 2.88 (t, J = 4.7 Hz, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 152.9, 137.1, 126.5, 110.3, 70.5, 70.4, 69.5, 68.5, 51.1, 49.2. IR(solid) ν_{max} 2865, 1594, 1480, 1312, 1105, 824, 751. cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{18}H_{29}N_3O_6$, 383.2056; found, 383.2056.

Synthesis of compounds 4a and 4b.

Compounds **4a** and **4b** were obtained following a modified procedure described by Thapa et al.[5] (**Scheme S2**) Spectral data for compounds **4a** and **4b** are consistent with the previously reported values.[5]



Scheme S2. Synthesis of compounds **4a** and **4b**.

The corresponding nitro compound **2** (0.5 mmol, 1.1 equiv.) was reduced using a ThalesNano hydrogenation flow reactor (2.5 mM, Pd/C, 1 atm, 30 ºC, 1 mL/min) using methanol as the solvent and pouring the product directly over a round bottom flask charged with 4-bromo-1,8-naphthalic anhydride (124.7 mg, 0.45 mmol, 1.0 equiv.). The solvent was removed under reduced pressure and the crude was dissolved in 2 mL of EtOH, transferred to a microwave sealable glass vial equipped with a magnetic stirrer, sealed, heated to 77 ºC in an oil bath and stirred overnight.

Purification: The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. Then, the crude was further purified by column chromatography on silica gel and a gradient of polarity from CH_2Cl_2 to a CH_2Cl_2:MeOH mixture (9:1), affording the corresponding final adducts **4a** and **4b**.

2-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 4a.

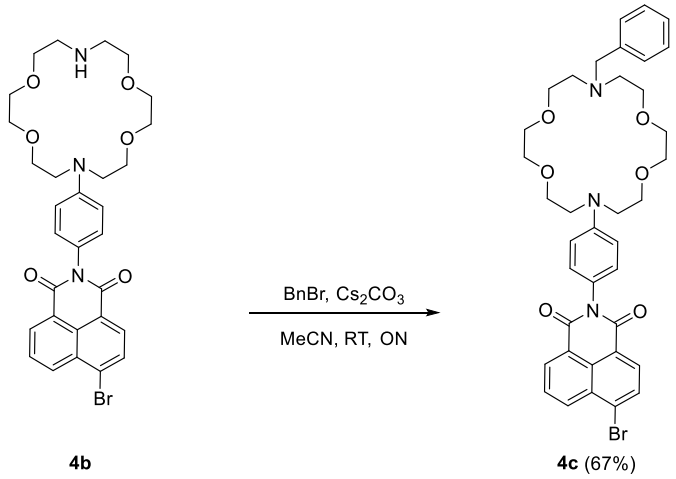
Following the general procedure, compound **4a** was obtained as a yellow solid in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.61 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.87 (dd, *J* = 8.6, 7.3 Hz, 1H), 7.10 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.1 Hz, 2H), 3.82 – 3.52 (m, 24H).

2-(4-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 4b.

Following the general procedure, compound **4b** was obtained as a yellow solid in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.62 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.45 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.87 (dd, *J* = 8.6, 7.3 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.1 Hz, 2H), 3.82 – 3.52 (m, 20H), 3.09 – 2.87 (m, 4H).

Synthesis of compound 4c.

Compound **4c** was obtained following a modified procedure described by Thapa et al.[5] (Scheme S3)



4b **4c** (67%)

Scheme S3. Synthesis of compound **4c**.

To a microwave sealable glass vial equipped with a magnetic stirrer, amine derivative **4b** (61.2 mg, 0.1 mmol, 1.0 equiv.), Cs_2CO_3 (32.5 mg, 0.1 mmol, 1.0 equiv.) and 1.0 mL of acetonitrile were added sequentially. The vial was sealed, purged with argon and benzyl bromide (13 μL, 0.11 mmol, 1.1 equiv.) was added dropwise to the mixture. The reaction was stirred at room overnight.

Purification: The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude was further purified by column chromatography on silica gel and a gradient of polarity from CH_2Cl_2 to a CH_2Cl_2:MeOH mixture (9:1), affording the corresponding final adduct **4c**.

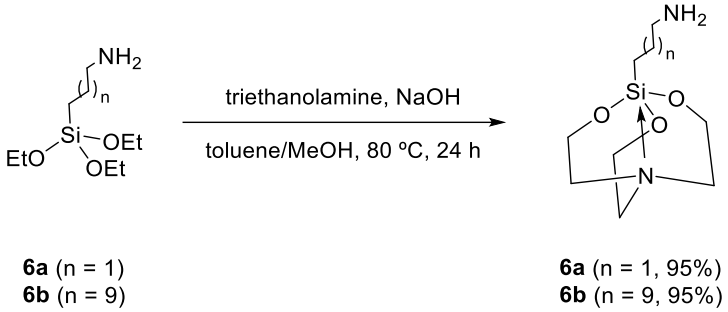
2-(4-(16-Benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 4c.

Following the general procedure, compound **4c** was obtained as a yellow solid in 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.62 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.46 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.87 (dd, *J* = 8.6, 7.3 Hz, 1H), 7.50 – 7.15 (m, 6H), 7.11

(d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.1 Hz, 2H), 3.83 – 3.54 (m, 20H), 2.84 (t, *J* = 5.8 Hz, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 164.3, 148.2, 139.8, 133.5, 132.5, 131.7, 131.3, 130.9, 130.5, 129.5, 129.2, 129.0, 128.3, 128.3, 127.0, 123.6, 123.0, 122.8, 111.9, 71.2, 70.8, 70.4, 68.9, 60.0, 53.9, 51.6. IR(solid) ν_{max} 2974, 2866, 1601, 1354, 1316, 1282, 1110, 812, 654. cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{37}H_{40}BrN_3O_6$, 701.2100; found, 701.2131. m.p.: 124-126 ºC.

Synthesis of compounds 6a and 6b.

Compounds **6a** and **6b** were obtained following a modified procedure described by Chen et al.[6] (**Scheme S4**)



6a (n = 1)
6b (n = 9)

6a (n = 1, 95%)
6b (n = 9, 95%)

Scheme S4. Synthesis of compounds **6a** and **6b**.

To a round bottom flask equipped with a magnetic stirrer, 30 mL of toluene, the corresponding triethoxysilane derivative **5** (18.80 mmol, 1.0 equiv.), triethanolamine (2.5 mL, 2800 mg, 18.80 mmol, 1.0 equiv.), 14.2 mL of MeOH and NaOH (7.5 mg, 0.19 mmol, 0.01 equiv.) were added sequentially. The reaction was heated to 80 ºC in an oil bath and stirred for 24 h.

Purification: The reaction mixture was cooled to room temperature and the solvent was removed under reduced presure. Then, the crude was washed with *n*-hexane (3x50 mL) and filtered. Finally, the residual solvent was evaporated under reduced pressure, affording the corresponding final adducts **6a** and **6b**.

3-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propan-1-amine 6a.

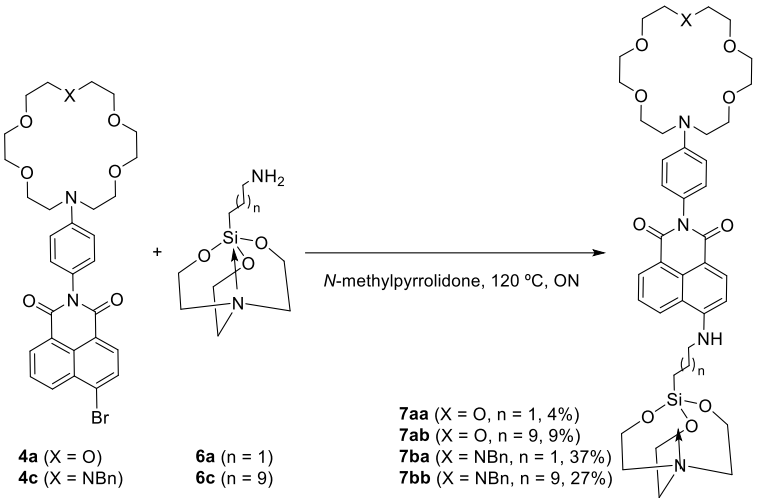
Following the general procedure, compound **6a** was obtained as a white solid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (t, *J* = 5.8 Hz, 6H), 2.79 (t, *J* = 5.8 Hz, 6H), 2.61 (t, *J* = 6.9 Hz, 2H), 1.59 – 1.44 (m, 2H), 0.44 – 0.34 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 57.9, 51.3, 45.6, 29.8, 13.1. IR(solid) ν_{max} 3355, 3287, 2921, 2876, 2857, 1276, 1118, 716, 612 cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_9H_{20}N_2O_3Si$, 232.1243; found, 232.1247. m.p.: 80-81 ºC.

11-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecan-1-amine 6b.

Following the general procedure, compound **6b** was obtained as a white solid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (t, *J* = 5.8 Hz, 6H), 2.79 (t, *J* = 5.8 Hz, 6H), 2.67 (t, *J* = 7.0 Hz, 2H), 1.56 – 1.10 (m, 20H), 0.51 – 0.32 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 58.1, 51.4, 42.5, 34.2, 29.9, 29.7, 27.1, 25.2, 16.6. IR(solid) ν_{max} 2919, 2851, 1567, 1466, 1088, 1026, 687 cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{17}H_{36}N_2O_3Si$, 344.2495; found, 344.2504. m.p.: 73-75 ºC.

Synthesis of compounds 7aa-7bb.

Compounds **7aa-7bb** were obtained following a modified procedure described by Thapa et al.[5] (**Scheme S5**)



Scheme S5. Synthesis of compounds **7aa-7bb**.

To a microwave sealable glass vial equipped with a magnetic stirrer, the corresponding naphtalimide derivative **4a** or **4c** (0.2 mmol, 1.0 equiv.), 0.25 mL of *N*-methylpyrrolidone and the corresponding silatrane derivative **6a** or **6b** (0.2 mmol, 2.0 equiv.) were added sequentially. The vial was sealed, purged with argon, heated to 120 ºC in an oil bath and stirred overnight.

Purification: The reaction mixture was cooled to room temperature. The crude was dissolved in 50 mL of AcOEt and washed with Brine (3x50 mL). The organic fraction was collected, dried over $MgSO_4$, filtered and evaporated under reduced pressure. Finally, the resulting solid was further purified by column chromatography on silica gel and a gradient of polarity from CH_2Cl_2 to a CH_2Cl_2:MeOH mixture (9:1), affording the corresponding final adducts **7aa-7bb**.

2-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-6-((3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)amino)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 7aa.

Following the general procedure, compound **7aa** was obtained as a yellow solid in 4% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 7.4, 1.1 Hz, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.16 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.57 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 9.3 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 1H), 5.96 (s, 1H), 3.81 (t, *J* = 5.8 Hz, 6H), 3.77 – 3.59 (m, 24H), 3.51 – 3.29 (m, 2H), 2.85 (t, *J* = 5.8 Hz, 6H), 1.93 (p, *J* = 6.6 Hz, 2H), 0.61 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 164.9, 150.5, 147.7, 135.2, 131.4, 130.5, 129.4, 128.4, 126.6, 124.2, 123.5, 120.5, 112.0, 109.5, 104.3, 71.0, 70.9, 70.8, 68.8, 57.8, 51.7, 51.2, 46.5, 29.8, 23.8, 13.3. IR(solid) ν_{max} 3359, 2865, 1688, 1645, 1574, 1516, 1385, 1093, 756 cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{39}H_{52}N_4O_{10}Si$, 764.3453; found, 764.3443. m.p.: 91-94 ºC.

2-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-6-((11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)amino)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 7ab.

Following the general procedure, compound **7ab** was obtained as a yellow solid in 9% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.11 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.64 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 9.2 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 5.26 (t, *J* = 10.2 Hz, 1H), 3.82 – 3.61 (m, 30H), 3.49 – 3.32 (m, 2H), 2.79 (t, *J* = 5.8 Hz, 6H), 1.81 (p, *J* = 7.6 Hz, 2H), 1.49 (p, *J* = 6.9 Hz, 2H), 1.40 – 1.24 (m, 14H), 0.50 – 0.36 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 164.9, 149.7, 147.7, 135.0, 131.6, 130.4, 129.3, 126.0, 124.8, 124.1, 123.7, 120.4, 112.0, 110.6, 104.5, 71.1, 71.0, 70.9, 68.8, 58.1, 51.7, 51.3, 43.9, 34.1, 29.7, 29.7, 29.6, 29.6, 29.5, 29.2, 27.3, 25.2, 16.6. IR(solid) ν_{max} 2920, 2853, 1654, 1578, 1518, 1357, 1100, 775 cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{47}H_{68}N_4O_{10}Si$, 876.4705; found, 876.4693. 95-100 ºC (dec.).

6-((3-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)amino)-2-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 7ba.

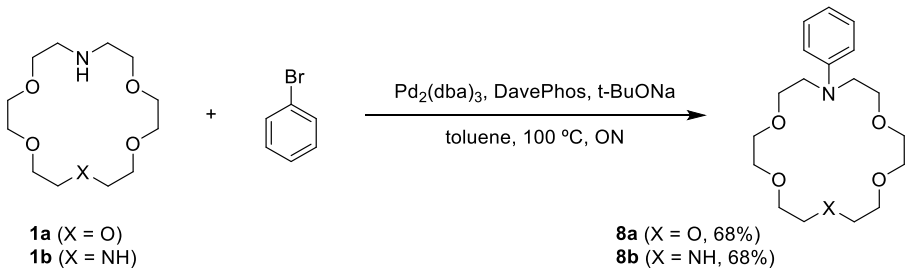
Following the general procedure, compound **7ba** was obtained as a yellow solid in 37% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 7.3, 1.1 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.16 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.57 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.43 – 7.23 (m, 5H), 7.11 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 9.1 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 1H), 5.97 (t, *J* = 4.8 Hz, 1H), 3.81 (t, *J* = 5.9 Hz, 6H), 3.77 – 3.55 (m, 22H), 3.40 (td, *J* = 6.7, 4.9 Hz, 2H), 2.85 (t, *J* = 5.8 Hz, 10H), 2.03 – 1.82 (m, 2H), 0.61 (t, *J* = 7.6 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.6, 164.9, 150.5, 147.7, 135.2, 131.4, 130.5, 129.4, 128.4, 127.2, 126.6, 124.4, 124.2, 123.5, 120.5, 111.9, 109.4, 104.3, 71.1, 70.7, 69.8, 69.0, 59.8, 57.8, 53.7, 51.6, 51.1, 46.5, 23.8, 13.3. IR(solid) ν_{max} 3321, 2870, 1638, 1577, 1518, 1360, 1094, 773. cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{46}H_{59}N_5O_9Si$, 853.4082; found, 853.4084. m.p.: 95-100 ºC (dec.).

6-((11-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)amino)-2-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 7bb.

Following the general procedure, compound **7bb** was obtained as a yellow solid in 27% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 7.3 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 2H), 7.47 – 7.19 (m, 5H), 7.11 (d, *J* = 8.9 Hz, 2H), 6.88 – 6.64 (m, 3H), 5.29 (t, *J* = 5.3 Hz, 1H), 3.85 – 3.53 (m, 22H), 3.49 – 3.32 (m, 2H), 2.87 (s, 4H), 2.79 (t, *J* = 5.8 Hz, 6H), 1.80 (q, *J* = 7.4 Hz, 2H), 1.47 – 1.24 (m, 16H), 0.54 – 0.31 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.5, 164.9, 149.7, 147.8, 135.0, 131.6, 130.4, 129.4, 129.2, 128.4, 127.1, 126.1, 124.8, 124.2, 123.7, 120.4, 111.9, 110.6, 104.5, 71.1, 70.8, 69.0, 58.1, 53.8, 51.6, 51.3, 43.9, 34.1, 29.8, 29.7, 29.7, 29.6, 29.5, 29.2, 27.3, 25.2, 16.6. IR(solid) ν_{max} 3361, 2921, 2853, 1688, 1646, 1576, 1518, 1357, 1100, 727. cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{54}H_{75}N_5O_9Si$, 965.5334; found, 965.5342. m.p.: 95-100 ºC (dec.).

Synthesis of compounds 8a and 8b.

Compounds **8a** and **8b** were obtained following a modified procedure described by Buchwald & Zhang.[7] (**Scheme S6**) Spectral data for compound **8a** are consistent with the previously reported values.[8]



Scheme S6. Synthesis of compounds **8a** and **8b**.

To a round bottom flask equipped with a magnetic stirrer, $Pd_2(dba)_3$ (232.6 mg, 0.254 mmol, 0.02 equiv.), DavePhos (300.8 mg, 0.764 mmol, 0.06 equiv.), the corresponding crown ether **1** (12.74 mmol, 1.0 equiv.), t-BuONa (1836.5 mg, 19.11 mmol, 1.5 equiv.), 100 mL of toluene and Bromobenzene (1333 µL, 12.74 mmol, 1.5 equiv.) were added sequentially. The mixture was heated to 100 ºC in an oil bath and stirred overnight.

Purification: The reaction mixture was cooled to room temperature, filtered through a celite pad and the solvent was removed under reduced pressure. The crude was then dissolved in 50 mL of

AcOEt and washed with Na_2CO_3 (sat.) (3x50 mL) and Brine (3x50 mL). The organic fraction was collected, dried over $MgSO_4$, filtered and evaporated under reduced pressure, affording the corresponding final adducts **8a** and **8b**.

***N*-Phenyl-1-aza-18-crown-6 8a.**

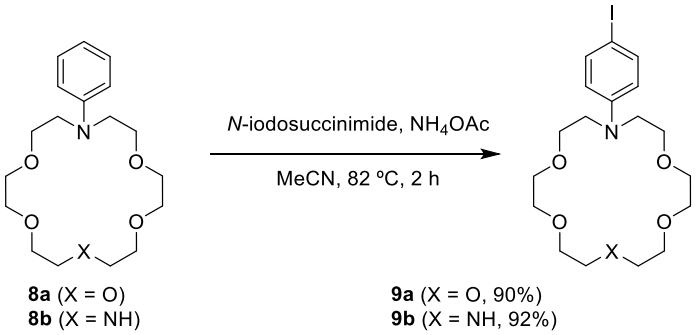
Following the general procedure, compound **8a** was obtained as a brown oil in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.8, 7.2 Hz, 2H), 6.72 – 6.61 (m, 3H), 3.74 – 3.57 (m, 24H).

***N*-Phenyl-1,10-diaza-18-crown-6 8b.**

Following the general procedure, compound **8b** was obtained as a brown oil in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.12 (m, 2H), 6.76 – 6.58 (m, 3H), 3.75 – 3.55 (m, 22H), 2.98 (s, 1H), 2.86 – 2.74 (m, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 148.02, 129.38, 116.11, 111.92, 70.65, 70.51, 70.37, 68.87, 50.81, 49.38. IR(solid) ν_{max} 2865, 1597, 1505, 1350, 1107, 908, 725. cm^{-1}. HRMS (ESI) (m/z): [M+H$^+$] calcd. for $C_{18}H_{31}N_2O_4$, 339.2278; found, 339.2273.

Synthesis of compounds 9a and 9b.

Compounds **9a** and **9b** were obtained following a modified procedure described by Das et al.[9] (**Scheme S7**)



Scheme S7. Synthesis of compounds **9a** and **9b**.

To a round bottom flask equipped with a magnetic stirrer, the corresponding crown ether derivative **8** (8.00 mmol, 1.0 equiv.), NH_4OAc (61.7 mg, 0.800 mmol, 0.1 equiv.), 100 mL of MeCN and *N*-iodosuccinimide (1889.9 mg, 8.40 mmol, 1.05 equiv.) were added sequentially. The reaction was heated in an oil bath to 82 ºC and stirred for 2 h.

Purification: The reaction mixture was cooled to room temperature and washed with Na_2CO_3 (sat.) (3x100 mL) and Brine (3x100 mL). The organic fraction was collected, dried over $MgSO_4$, filtered and evaporated under reduced pressure, affording the corresponding final adducts **9a** and **9b**.

***N*-(4-iodophenyl)-1-aza-18-crown-6 9a.**

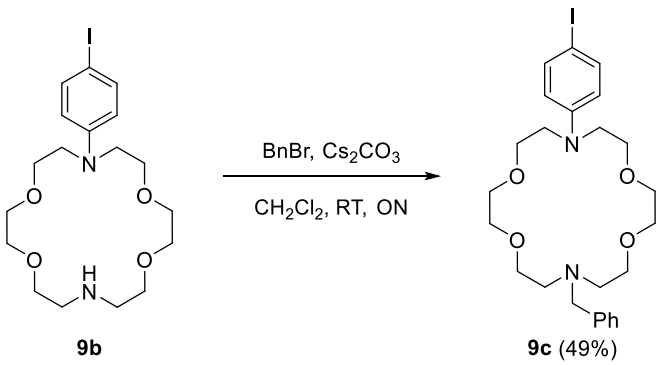
Following the general procedure, compound **9a** was obtained as a black oil in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 6.51 – 6.43 (m, 2H), 3.71 – 3.53 (m, 24H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 147.6, 137.8, 114.2, 76.5, 71.0, 68.6, 51.4. IR(solid) ν_{max} 2974, 2866, 1765, 1602, 1354, 1109, 813, 654 cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{18}H_{28}INO_5$, 465.1012; found, 465.1010.

***N*-(4-iodophenyl)-1,10-diaza-18-crown-6 9b.**

Following the general procedure, compound **9b** was obtained as a black oil in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 2H), 6.53 – 6.38 (m, 2H), 3.73 – 3.50 (m, 22H), 2.87 – 2.76 (m, 4H), 2.45 (s, 1H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 147.7, 137.9, 114.2, 76.7, 70.7, 70.6, 70.5, 68.6, 50.8, 49.4. IR(solid) ν_{max} 2866, 1586, 1495, 1107, 907, 725. cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{18}H_{29}IN_2O_4$, 464.1172; found, 464.1165.

Synthesis of compound 9c.

Compound **9c** was obtained following a modified procedure described by Thapa et al.[5] (**Scheme S8**)



9b **9c** (49%)

Scheme S8. Synthesis of compound **9c**.

To a microwave sealable glass vial equipped with a magnetic stirrer, *N*-(4-iodophenyl)-1,10-diaza-18-crown-6 **9b** (341.7 mg, 0.736 mmol, 1.0 equiv.), Cs_2CO_3 (239.8 mg, 0.736 mmol, 1.0

equiv.) and 7.5 mL of CH_2Cl_2 were added sequentially. The vial was sealed, purged with argon and benzyl bromide (87.5 μL, 0.736 mmol, 1.0 equiv.) was added dropwise to the mixture. The reaction was stirred at room temperature overnight.

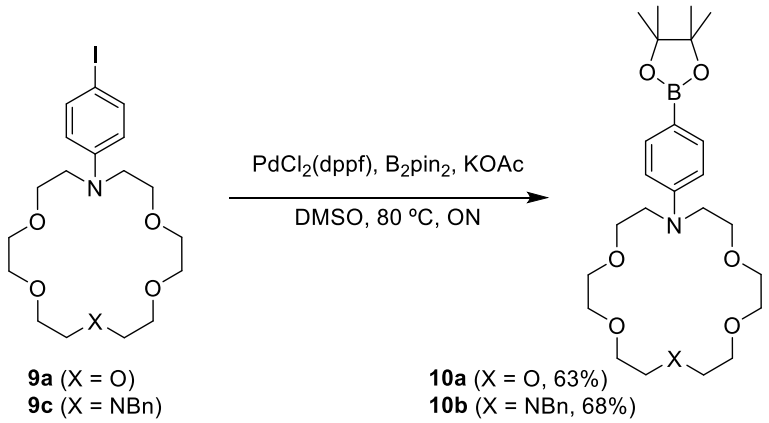
Purification: The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude was further purified by column chromatography on silica gel and a gradient of polarity from CH_2Cl_2 to a CH_2Cl_2:EtOAc mixture (1:1), affording the corresponding final adduct **9c**.

7-Benzyl-16-(4-iodophenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane 9c.

Following the general procedure, compound **9c** was obtained as a pale yellow oil in 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 2H), 7.38 – 7.13 (m, 5H), 6.54 – 6.38 (m, 2H), 3.71 – 3.53 (m, 22H), 2.81 (t, *J* = 5.9 Hz, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 163.5, 147.6, 139.7, 137.9, 129.0, 128.3, 127.0, 114.2, 71.2, 70.8, 70.3, 68.8, 60.0, 53.9, 51.4. IR(solid) ν_{max} 2861, 1585, 1494, 1350, 1110, 802, 733, 698. cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{25}H_{35}IN_2O_4$, 554.1642; found, 554.1633.

Synthesis of compounds 10a and 10b.

Compounds **10a** and **10b** were obtained following a modified procedure described by Ishiyama et al.[10] (**Scheme S9**)



Scheme S9. Synthesis of compounds **10a** and **10b**.

To a microwave sealable glass vial equipped with a magnetic stirrer, $PdCl_2$(dppf) (22.0 mg, 0.03 mmol, 0.03 equiv.), bis(pinacolato)diboron (279.3 mg, 1.00 mmol, 1.1 equiv.), KOAc (294.42 mg, 3.00 mmol, 3.0 equiv.), 6.0 mL of DMSO and the corresponding crown ether derivative **9**

(1.0 mmol, 1.0 equiv.) were added sequentially. The vial was sealed, purged with argon and stirred at 80 ºC overnight.

Purification: The reaction crude was cooled to room temperature, 50 mL of brine were added and the mixture was extracted with Et_2O (3x50 mL). The combined organic fractions were washed with Na_2CO_3 (sat.) (3x150 mL), NH_4Cl (sat.) (3x150 mL) and Brine (3x150 mL). Then, the organic fraction was collected, dried over $MgSO_4$ and filtered. Compound **10b** is used in the next step without further purification. Finally, the resulting oil was further purified by column chromatography on silica gel with a mixture of n-hexane:EtOAc and a gradient of polarity from (6:4) to pure EtOAc, affording the corresponding final adduct **10a**.

***N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1-aza-18-crown-6 10a.**

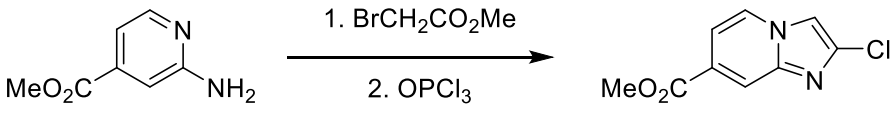
Following the general procedure, compound **10a** was obtained as a pale yellow oil in 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 6.67 – 6.62 (m, 2H), 3.71 – 3.62 (m, 24H), 1.30 (s, 12H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.2, 136.5, 114.7, 110.8, 83.3, 70.9, 68.7, 51.3, 25.0. IR(solid) ν_{max} 3055, 2857, 1585, 1494, 1349, 1110, 803, 700 cm^{-1}. HRMS (ESI) (m/z): $[M+H]^+$ calcd. for $C_{24}H_{41}BNO_7$, 466.2976; found, 466.2979.

7-Benzyl-16-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane 10b.

Following the general procedure, compound **10b** was obtained as a pale yellow oil in 63% yield (calculated from ^{1}H NMR, as the product comes with an inseparable impurity, assigned as the dehalogenation product from **9c**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.7 Hz, 2H), 7.54 – 7.06 (m, 5H), 6.65 (d, *J* = 8.7 Hz, 2H), 3.88 – 3.47 (m, 22H), 2.82 (t, *J* = 5.9 Hz, 4H), 1.32 (s, 12H). HRMS (ESI) (m/z): $[M+H^+]$ calcd. for $C_{31}H_{48}BN_2O_6$, 555.3605; found, 555.3599.

Synthesis of compound 12a.

Methyl 2-chloroimidazo[1,2-*a*]pyridine-7-carboxylate **12a** was obtained following a procedure described by Byun et al.[11] (**Scheme S10**) Spectral data for compound **12a** is consistent with the previously reported values.[11]



11 **12a** (51%)

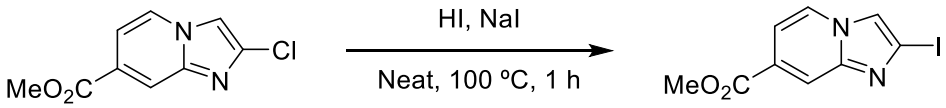
Scheme S10. Synthesis of compound **12a**.

Methyl 2-chloroimidazo[1,2-*a*]pyridine-7-carboxylate 12a.

Following the reported procedure, compound **12a** was obtained as a white solid in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.21 (m, 1H), 8.09 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.61 (d, *J* = 0.7 Hz, 1H), 7.46 (dd, *J* = 7.1, 1.7 Hz, 1H), 3.97 (s, 3H).

Synthesis of compound 12b.

Methyl 2-iodoimidazo[1,2-*a*]pyridine-7-carboxylate **12b** was obtained following a modified procedure described by Claiborne et al.[11] (**Scheme S11**)



12a **12b** (47%)

Scheme S11. Synthesis of compound **12b**.

To a microwave sealable glass vial equipped with a magnetic stirrer, methyl 2-chloroimidazo[1,2-*a*]pyridine-7-carboxylate **12a** (105.3 mg, 0.5 mmol, 1.0 equiv.), hydriodic acid 57% (1.7 mL, 12.5 mmol, 25.0 equiv.) and NaI (374.7 mg, 2.5 mmol, 5.0 equiv.) were added sequentially. The vial was sealed and stirred at 100 ºC for 1 h.

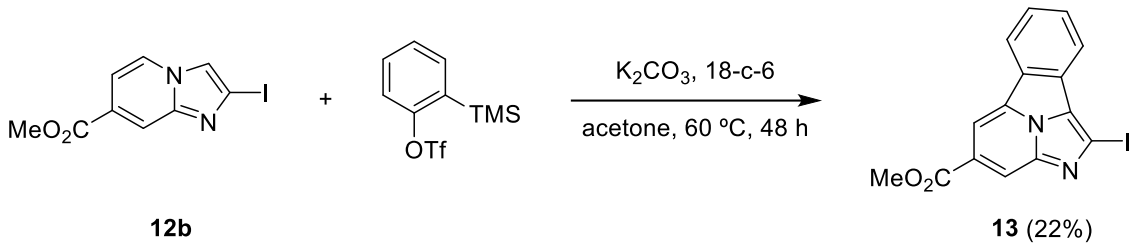
Purification: The reaction crude was cooled to room temperature and poured slowly over 50 mL of Na_2CO_3 (sat.). The aqueous solution was then extracted with EtOAc (3x50 mL) and the combined organic fractions were washed with Brine (3x150 mL). The organic fraction was collected, dried over $MgSO_4$, filtered and evaporated under reduced pressure, affording the corresponding final adduct **12b**.

Methyl 2-iodoimidazo[1,2-*a*]pyridine-7-carboxylate 12b.

Following the general procedure, compound **12b** was obtained as a brown solid in 47% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.24 (m, 1H), 8.11 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.78 (d, *J* = 0.7 Hz, 1H), 7.41 (dd, *J* = 7.1, 1.7 Hz, 1H), 3.96 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 165.4, 145.9, 126.7, 124.2, 119.5, 119.3, 112.4, 93.5, 52.9. IR(solid) ν_{max} 3139, 2950, 1703, 1430, 1346, 1308, 1267, 1242, 736. cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_9H_7IN_2O_2$, 301.9552; found, 301.9548. m.p.: 189-191 ºC.

Synthesis of compound 13.

Methyl 1-iodobenzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate **13** was obtained following a modified procedure described by Semwal et al.[13] (**Scheme S12**)



12b **13** (22%)

Scheme S12. Synthesis of compound **13.**

To a microwave sealable glass vial equipped with a magnetic stirrer, methyl 2-iodoimidazo[1,2-*a*]pyridine-7-carboxylate **12b** (30.2 mg, 0.1 mmol, 1.0 equiv.), K_2CO_3 (27.6 mg, 0.2 mmol, 2.0 equiv.), 18-Crown-6 (52.9 mg, 0.2 mmol, 2.0 equiv.), 1.0 mL of acetone and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (49 μL, 0.2 mmol, 2.0 equiv.) were added sequentially. The vial was sealed and stirred at 60 ºC for 48 h.

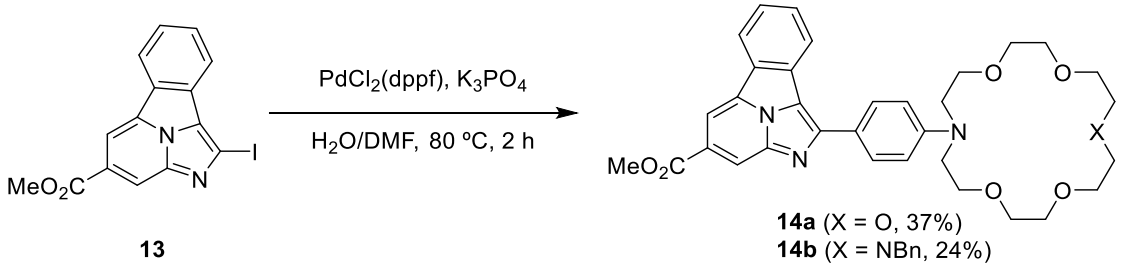
Purification: The reaction crude was cooled to room temperature and the solvent was removed under reduced pressure. The solid was dissolved in 50 mL of EtOAc and washed with Brine (3x50 mL). Then, the organic fraction was collected, dried over $MgSO_4$, filtered and evaporated under reduced pressure. Finally, the resulting solid was further purified by column chromatography on silica gel with a mixture of n-hexane:acetone and a gradient of polarity from (9.5:0.5) to (8:2), affording the corresponding final adduct **13**.

Methyl 1-iodobenzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate 13.

Following the general procedure, compound **13** was obtained as a brown solid in 22% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 11.4, 0.8 Hz, 2H), 8.45 – 8.32 (m, 2H), 7.83 (ddd, *J* = 8.1, 7.4, 1.2 Hz, 1H), 7.70 (ddd, *J* = 8.5, 7.4, 1.1 Hz, 1H), 4.10 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.5, 140.7, 131.7, 130.0, 129.2, 128.9, 128.6, 126.3, 123.5, 120.3, 116.2, 114.7, 110.0, 92.4, 53.2. IR(solid) ν_{max} 2955, 1714, 1232, 764, 731 cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{15}H_9IN_2$, 375.9709; found, 375.9706. m.p.: 148-151 ºC.

Synthesis of compounds 14a and 14b.

Compounds **14a** and **14b** were obtained following a modified procedure described by Lévesque et al.[14] (**Scheme S13**)



Scheme S13. Synthesis of compounds **14a** and **14b**.

To a microwave sealable glass vial equipped with a magnetic stirrer, $PdCl_2$(dppf) (3.7 mg, 0.005 mmol, 0.05 equiv.), the corresponding crown ether derivative **10** (0.1 mmol, 1.0 equiv.), K_3PO_4 (84.9 mg, 0.4 mmol, 4.0 equiv.), 1 mL of a mixture of DMF and H_2O (83:17) and methyl 1-iodobenzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate **13** (37.6 mg, 0.1 mmol, 1.0 equiv.) were added sequentially. The vial was sealed, heated to 80 ºC in an oil bath and stirred for 2 h.

Purification: The reaction crude was cooled to room temperature and the solvent was removed under reduced pressure. The solid was dissolved in 50 mL of EtOAc and washed with Na_2CO_3 (3x50 mL) and Brine (3x50 mL). Then, the organic fraction was collected, dried over $MgSO_4$, filtered and evaporated under reduced pressure. Finally, the resulting solid was further purified by column chromatography on silica gel with a mixture of EtOAc:MeOH and a gradient of polarity from pure EtOAc to (96:4), affording the corresponding final adducts **14a** and **14b**.

Methyl 1-(4-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate 14a.

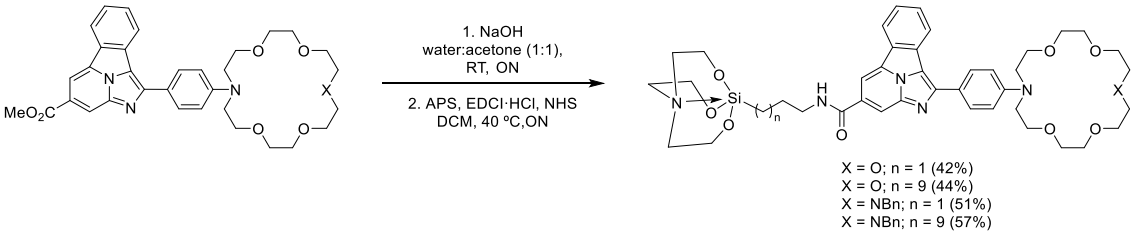
Following the general procedure, compound **14a** was obtained as a yellow oil in 37% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 7.0 Hz, 1H), 8.47 (dd, *J* = 15.8, 8.0 Hz, 2H), 8.29 (d, *J* = 8.9 Hz, 2H), 7.85 – 7.78 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.09 (s, 3H), 3.84 – 3.74 (m, 8H), 3.70 (d, *J* = 5.4 Hz, 16H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 167.2, 150.5, 149.2, 139.1, 131.7, 130.0, 129.4, 129.4, 128.9, 127.5, 125.1, 123.4, 121.6, 121.3, 121.2, 113.6, 112.1, 109.0, 71.1, 71.0, 70.9, 70.8, 68.8, 52.9, 51.6. IR(solid) ν_{max} 3404, 2911, 2869, 1714, 1647, 1602, 1113, 1092, 749 cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{33}H_{37}N_3O_7$, 587.2632; found, 587.2627.

Methyl 1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate 14b.

Following the general procedure, compound **14b** was obtained as a yellow oil in 24% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 6.9, 0.9 Hz, 2H), 8.58 – 8.40 (m, 2H), 8.30 (d, *J* = 8.9 Hz, 2H), 7.82 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 7.66 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1H), 7.41 – 7.27 (m, 5H), 6.94 (d, *J* = 9.0 Hz, 2H), 4.09 (s, 3H), 3.82 – 3.58 (m, 22H), 2.84 (s, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.2, 150.5, 149.3, 139.8, 132.1, 131.7, 130.1, 129.4, 129.3, 129.1, 128.9, 128.4, 127.8, 127.5, 127.2, 127.1, 125.1, 123.4, 121.2, 113.6, 112.0, 109.0, 71.2, 70.8, 70.3, 69.0, 60.0, 53.9, 53.0, 51.6. IR(solid) ν_{max} 2860, 1716, 1606, 1447, 1345 ,1231, 1109, 732 cm^{-1}. HRMS (ESI) (m/z): $[M]^+$ calcd. for $C_{40}H_{44}N_4O_6$, 676.3261; found, 676.3280.

Synthesis of compounds 15aa-bb.

Compounds **15aa-bb** were obtained after two reaction steps, being the first based on a modified procedure described by Sanchez-Sanchez et al.[15] and the second one based on a modified procedure described by Chinchilla et al.[16] (Scheme S14)



Scheme S14. Synthesis of compounds **15aa** and **15bb**.

To a round bottom flask equipped with a magnetic stirrer, the corresponding ester derivative **14** (0.1 mmol, 1.0 equiv.), 5 mL of a mixture of H_2O:acetone (1:1) and NaOH (13.2 mg, 0.33 mmol, 3.3 equiv.) were added sequentially. The reaction mixture was stirred overnight.

Purification: Acetone was removed under reduced pressure. Then, 20 mL of deionized water were added and the aqueous solution was washed with CH_2Cl_2 (3x20 mL) and 25 mL of a NH_4Cl saturated solution were added. The mixture was extracted CH_2Cl_2 (3x50 mL), and the combined organic layers were washed with 50 mL of deionized water. Finally, the solvent was evaporated under reduced pressure, giving rise to a yellow solid, which was used directly for the next reaction without further purification.

The last reaction product was charged in a microwave sealable glass vial equipped with a magnetic stirrer. Then, EDC·HCl (57.5 mg, 0.3 mmol, 3.0 equiv.), NHS (34.5 mg, 0.3 mmol, 3.0 equiv.), the corresponding silatrane derivative **6** (0.5 mmol, 5.0 equiv.) and 10 mL of CH_2Cl_2

were added sequentially. The vial was sealed, purged with argon, heated to 40 ºC in an oil bath and stirred overnight.

Purification: The reaction crude was cooled to room temperature and the solvent was removed under reduced pressure. Then, the solid was purified by flash chromatography in a Biotage Isolera Four system with a Biotage Snap Cartridge KP-Sil 10g, gradient of polarity from a CH_2Cl_2:AcOEt mixture (1:1) to a CH_2Cl_2:AcOEt:MeOH mixture (45:45:10), affording the corresponding final adducts **15aa-bb**.

1-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-*N*-(3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide 15aa.

Following the general procedure, compound **15aa** was obtained as a yellow oil in 42% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 0.8 Hz, 1H), 8.54 – 8.37 (m, 3H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.79 (ddd, *J* = 8.3, 5.3, 1.3 Hz, 2H), 7.71 – 7.59 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.85 – 3.66 (m, 24H), 3.58 (q, *J* = 6.1 Hz, 2H), 2.82 (t, *J* = 5.8 Hz, 6H), 1.85 (p, *J* = 7.1 Hz, 2H), 0.62 (t, *J* = 7.3 Hz, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 167.0, 149.3, 138.2, 135.0, 131.7, 130.1, 129.6, 129.6, 129.5, 125.4, 123.7, 121.1, 120.5, 120.2, 112.1, 109.6, 109.0, 71.1, 71.0, 70.9, 70.8, 68.8, 57.8, 51.6, 51.1, 43.6, 23.7, 13.3. IR(solid) ν_{max} 2915, 2866, 1708, 1603, 1459, 1347, 1209, 1097, 765. cm^{-1}. HRMS (ESI) (m/z): [M+H$^+$] calcd. for $C_{41}H_{54}N_5O_9Si$, 788.3691; found, 788.3697.

1-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-*N*-(11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide 15ab.

Following the general procedure, compound **15ab** was obtained as a yellow oil in 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.46 (dd, *J* = 14.3, 8.1 Hz, 2H), 8.36 – 8.19 (m, 3H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 5.1 Hz, 1H), 3.94 – 3.61 (m, 30H), 3.58 (q, *J* = 6.7 Hz, 2H), 2.78 (t, *J* = 5.7 Hz, 6H), 1.71 (p, *J* = 7.4 Hz, 2H), 1.47 – 1.41 (m, 2H), 1.33 – 1.19 (m, 14H), 0.55 – 0.31 (m, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 167.4, 150.0, 149.1, 139.0, 133.1, 131.5, 130.0, 129.6, 129.5, 129.3, 124.9, 123.6, 121.7, 121.1, 120.7, 112.1, 109.8, 107.6, 71.0, 68.8, 58.1, 51.6, 51.3, 40.8, 34.1, 29.9, 29.8, 29.7, 29.7, 29.5, 27.3, 25.2, 16.6. IR(solid) ν_{max} 3318, 2922, 2855, 1642, 1607, 1460, 1350, 1125, 1105, 770 cm^{-1}. HRMS (ESI) (m/z): [M+H$^+$] calcd. for $C_{49}H_{70}N_5O_9Si$, 900.4943; found, 900.4938.

***N*-(3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)-1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide 15ba.**

Following the general procedure, compound **15ba** was obtained as a yellow oil in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.44 (dd, *J* = 8.1, 4.6 Hz, 2H), 8.38 (s, 1H), 8.26 (d, *J* = 8.6 Hz, 2H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.37 – 7.17 (m, 5H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.85 – 3.54 (m, 30H), 2.88 (t, *J* = 5.7 Hz, 4H), 2.81 (d, *J* = 5.8 Hz, 6H), 1.85 (p, *J* = 7.0 Hz, 2H), 0.63 (t, *J* = 7.3 Hz, 2H).^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.3, 167.2, 149.2, 149.1, 138.8, 134.4, 131.6, 130.0, 129.5, 129.4, 129.2, 128.4, 127.6, 127.2, 125.0, 123.6, 121.5, 121.0, 120.5, 112.0, 109.8, 108.3, 71.2, 70.8, 70.0, 69.0, 59.8, 57.8, 53.7, 51.5, 51.1, 43.4, 23.7, 13.2. IR(solid) ν_{max} 2923, 1642, 1460, 1350, 1099, 769 cm^{-1}. HRMS (ESI) (m/z): [M+H$^+$] calcd. for $C_{48}H_{61}N_6O_8Si$, 877.4320; found, 877.4327.

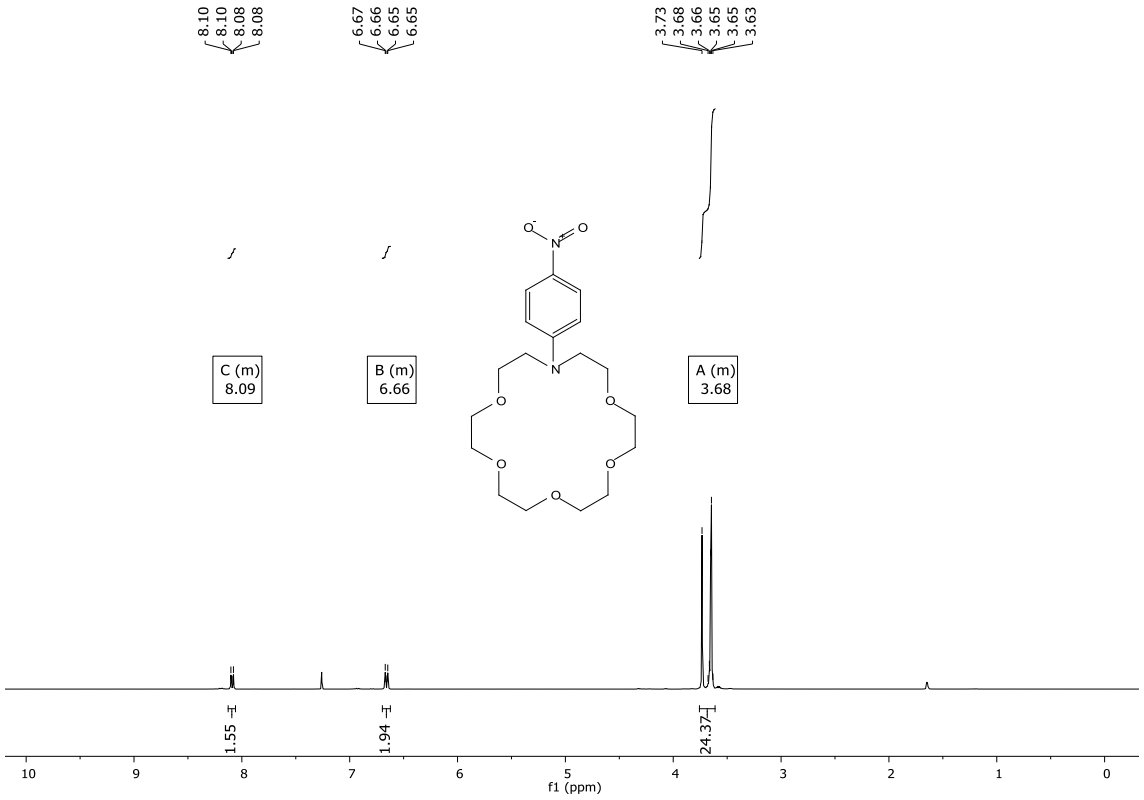
_N_-(11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)-1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide 15bb.

Following the general procedure, compound **15bb** was obtained as a yellow oil in 57% yield. ^{1}H NMR (500 MHz, $CDCl_{3\_10}$) δ 8.45 (s, 1H), 8.39 (d, *J* = 7.9 Hz, 1H), 8.37 – 8.30 (m, 1H), 8.27 (s, 1H), 8.26 – 8.21 (m, 2H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.15 (m, 5H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.67 (s, 1H), 3.81 – 3.62 (m, 28H), 3.55 (q, *J* = 6.8 Hz, 2H), 2.84 (t, *J* = 5.9 Hz, 4H), 2.76 (t, *J* = 5.8 Hz, 6H), 1.69 (p, *J* = 7.3 Hz, 2H), 1.48 – 1.17 (m, 16H), 0.46 – 0.37 (m, 2H). ^{13}C-NMR (126 MHz, $CDCl_{3\_10}$) δ 167.4, 149.8, 149.1, 138.9, 133.2, 131.4, 130.0, 129.4, 129.3, 129.1, 129.0, 128.3, 127.0, 124.8, 123.4, 121.7, 121.0, 120.6, 111.9, 109.9, 107.5, 71.2, 70.8, 70.3, 69.0, 60.0, 58.1, 53.9, 51.5, 51.3, 40.8, 34.1, 29.8, 29.8, 29.7, 29.6, 29.5, 25.2, 16.6. IR(solid) ν_{max} 2922, 2855, 1642, 1606, 1460, 1397, 1105, 770 cm^{-1}. HRMS (ESI) (m/z): [M]$^+$ calcd. for $C_{56}H_{76}N_6O_8Si$, 988.5494; found, 988.5486.

4. NMR Spectra

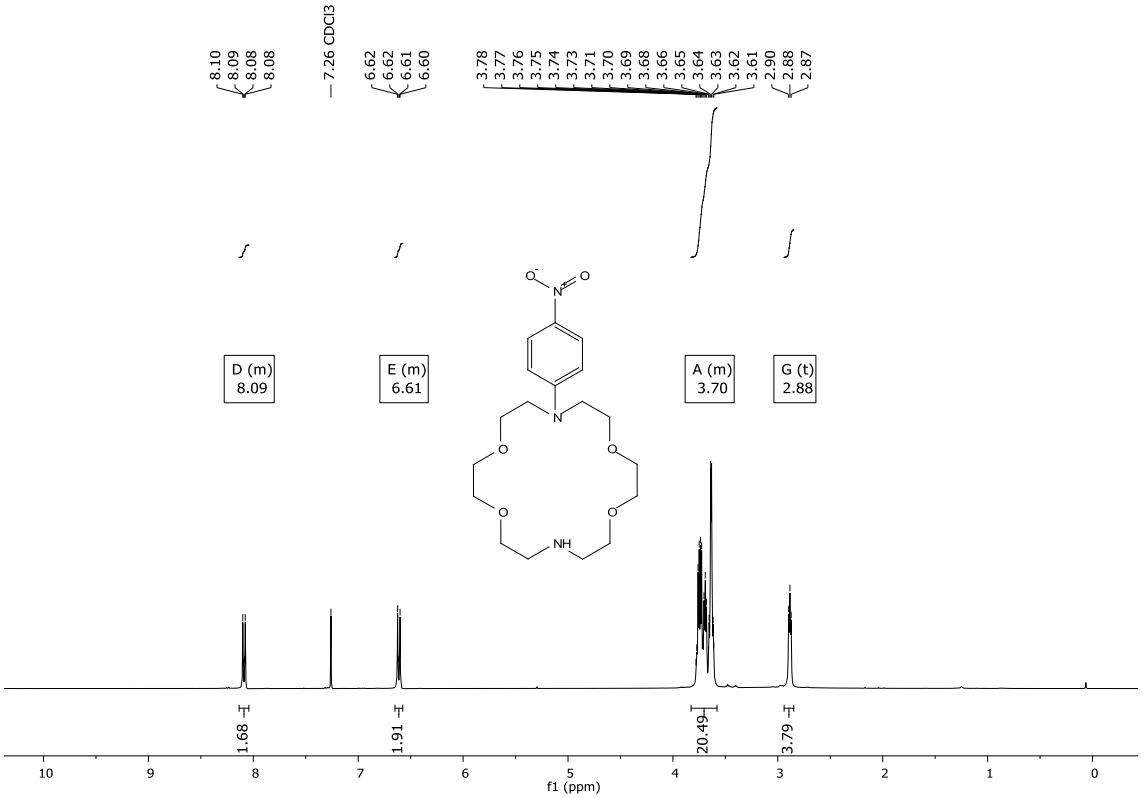
16-(4-Nitrophenyl)-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (2a)

^{1}H-NMR

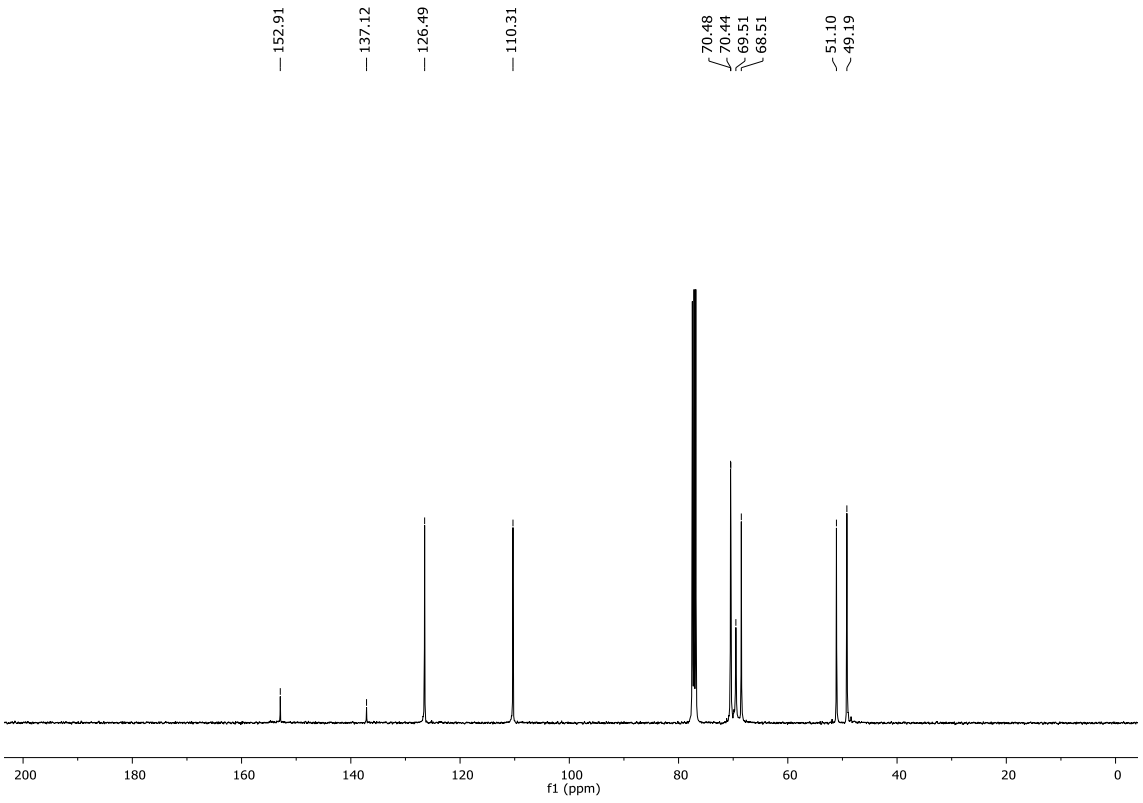


7-(4-Nitrophenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2b)

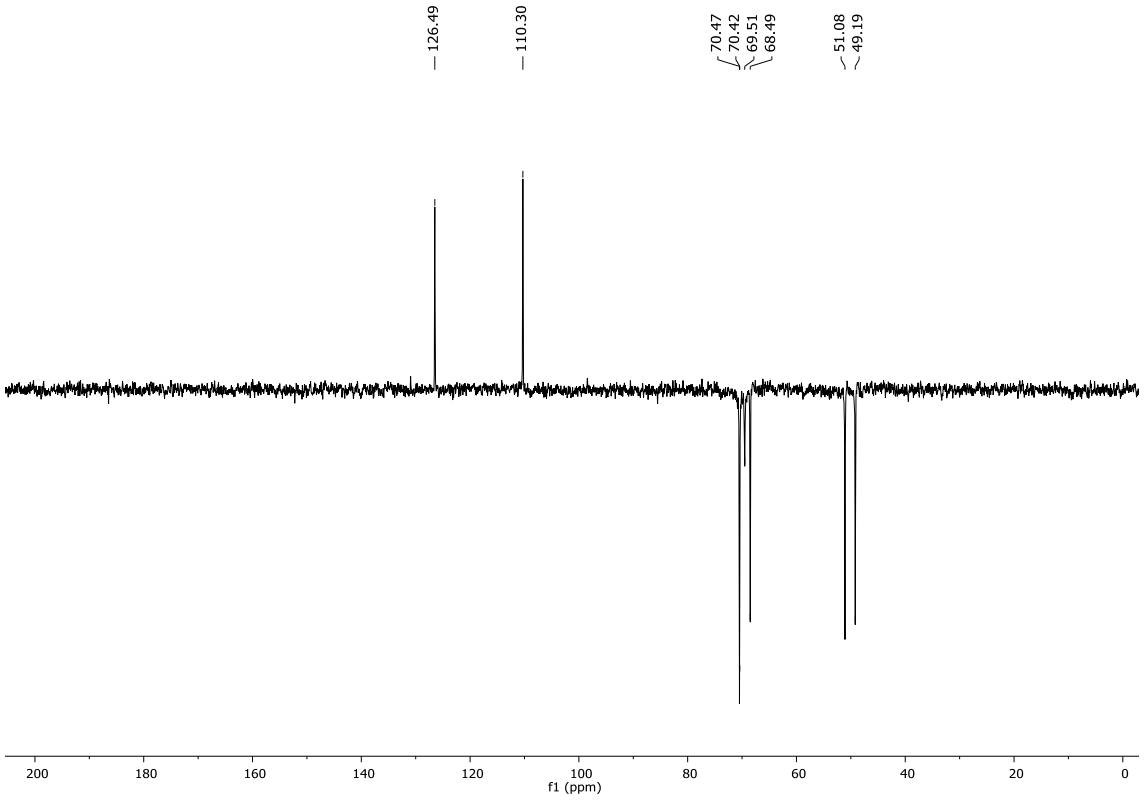
^{1}H-NMR



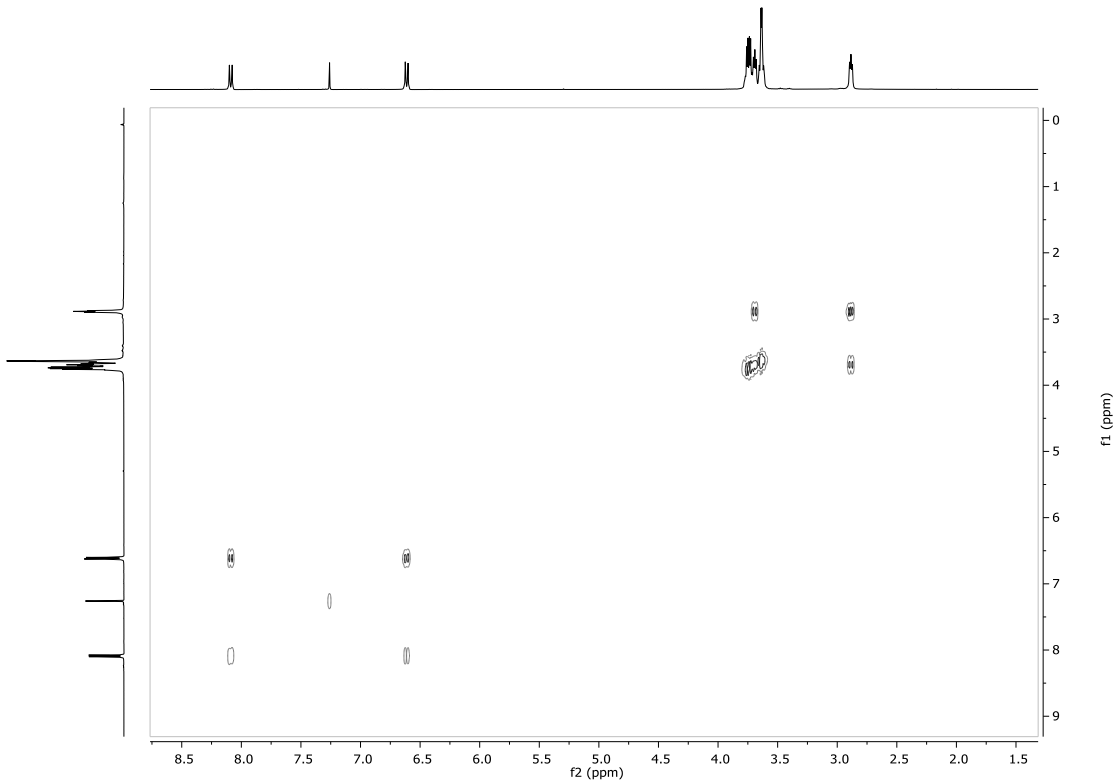
^{13}C-NMR



DEPT-135



g-COSY



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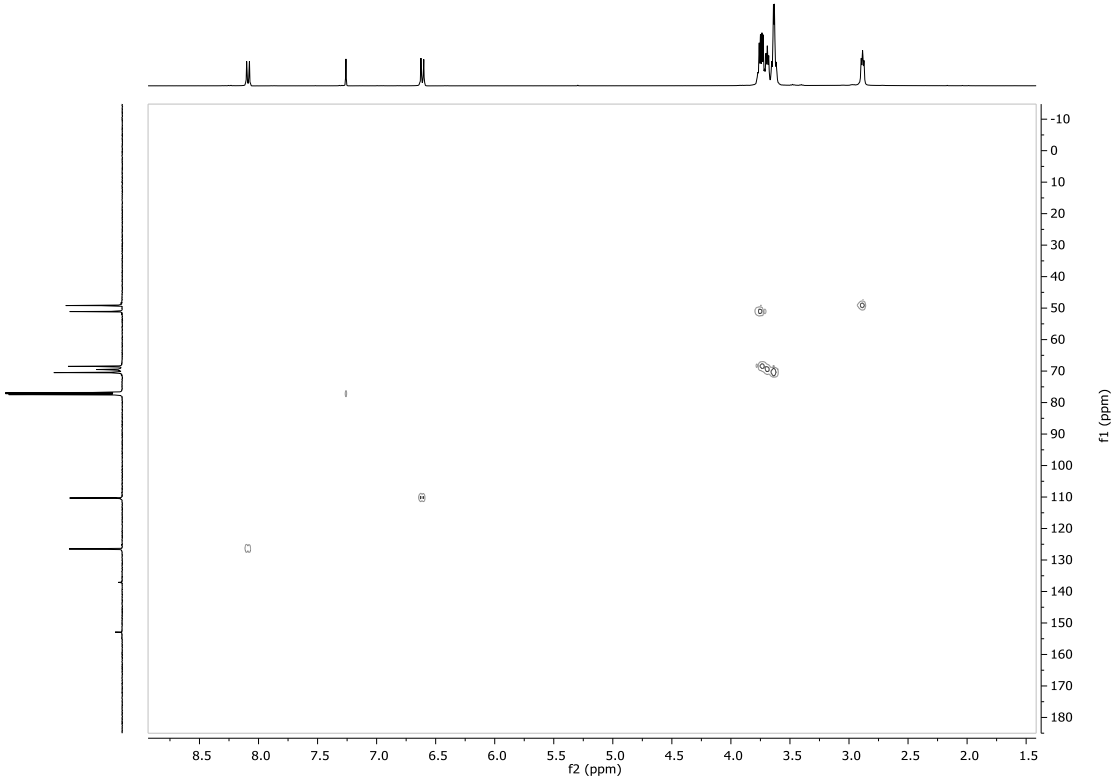
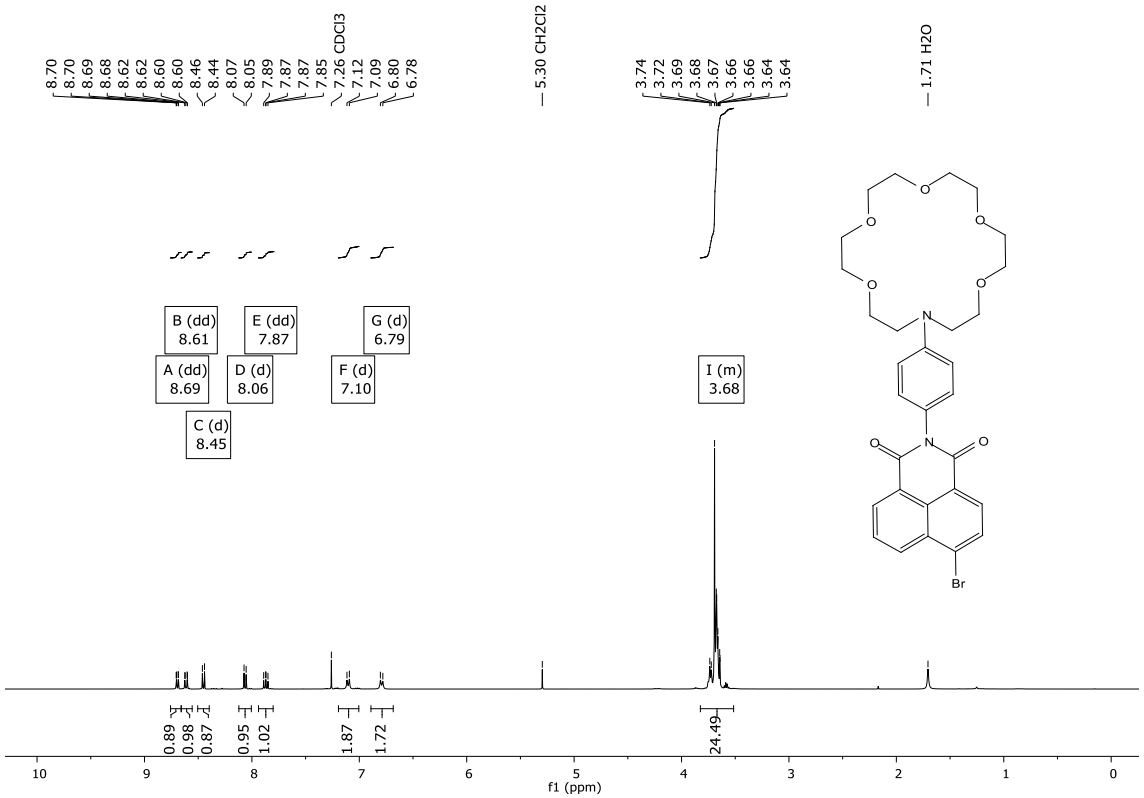

-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)

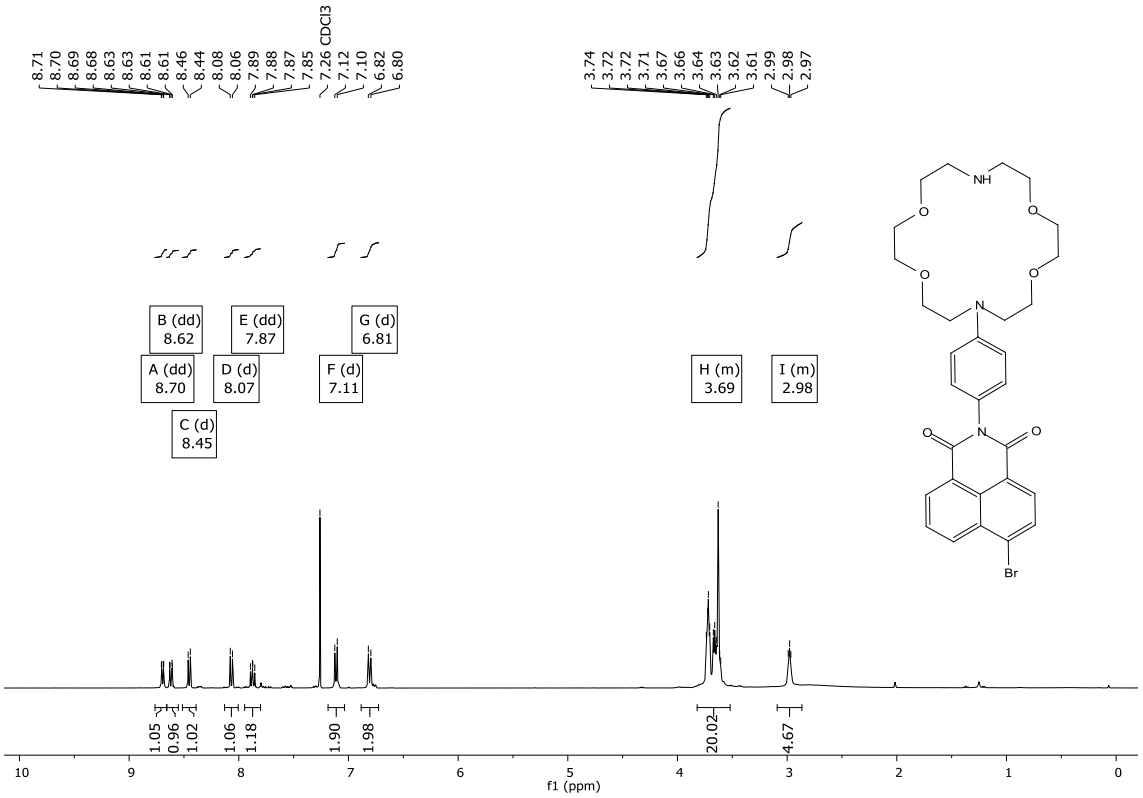
2-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (4a)

^{1}H-NMR



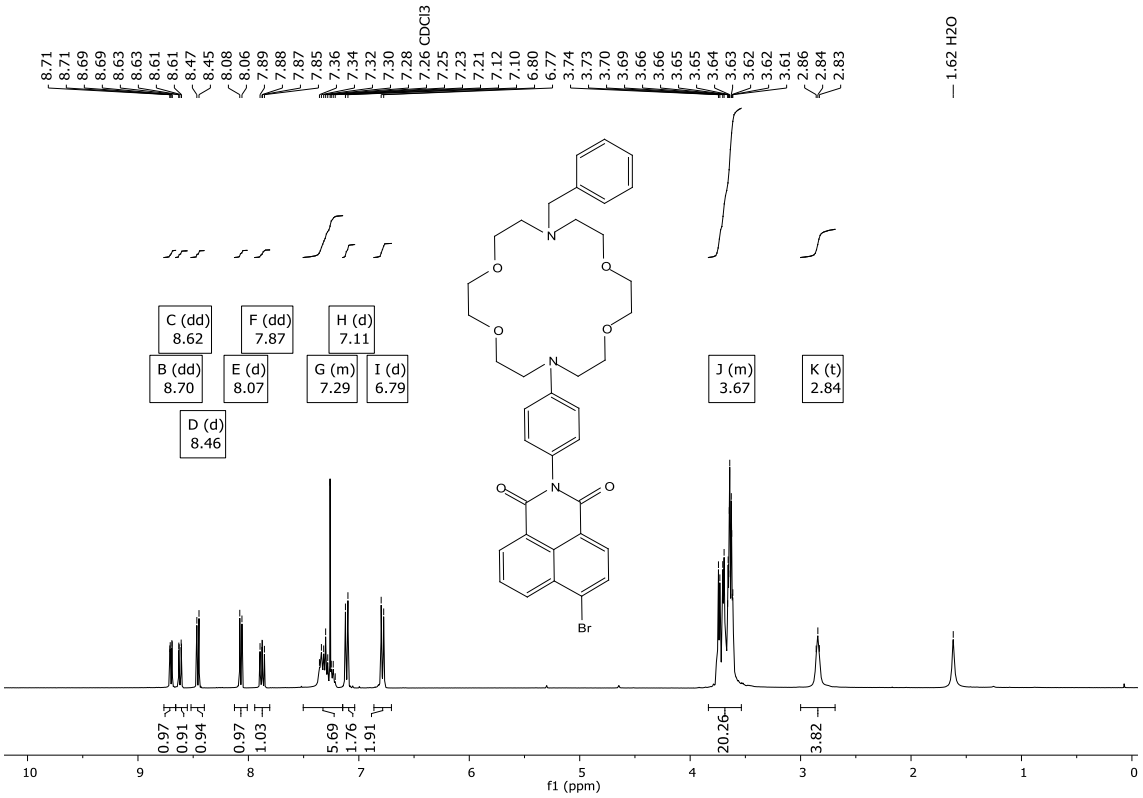
2-(4-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (4b)

^{1}H-NMR

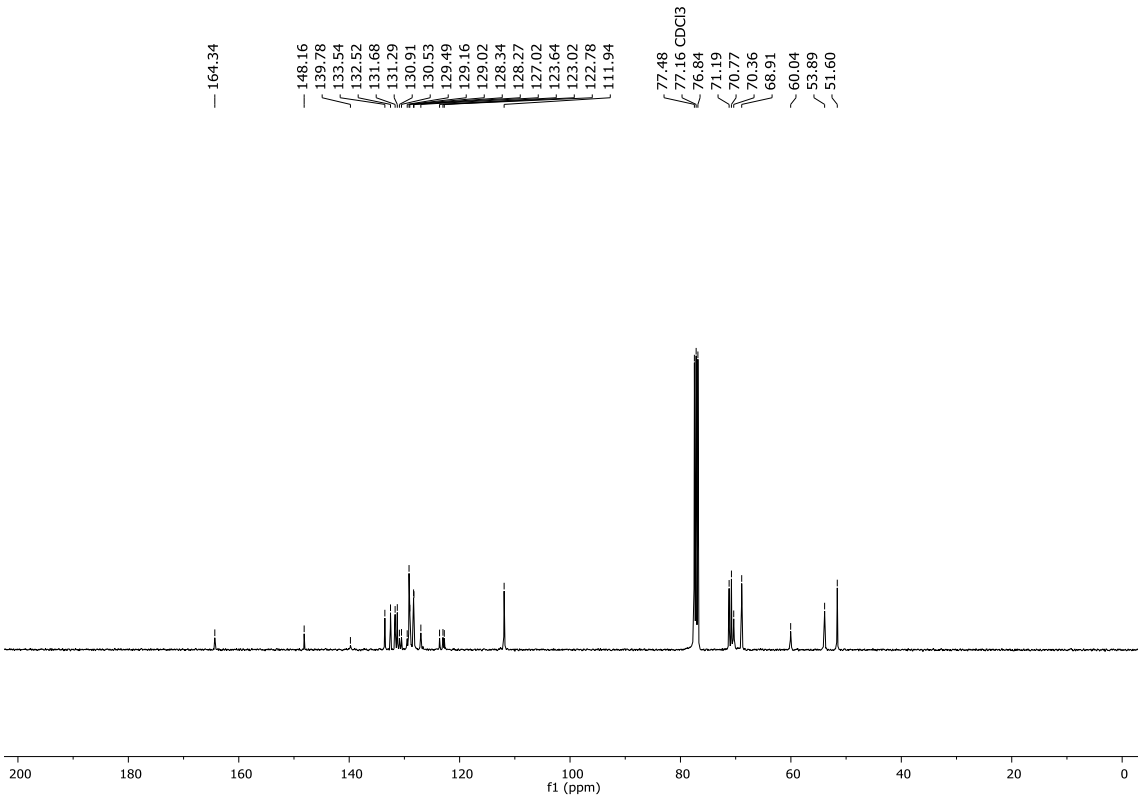


2-(4-(16-Benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-6-bromo-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (4c)

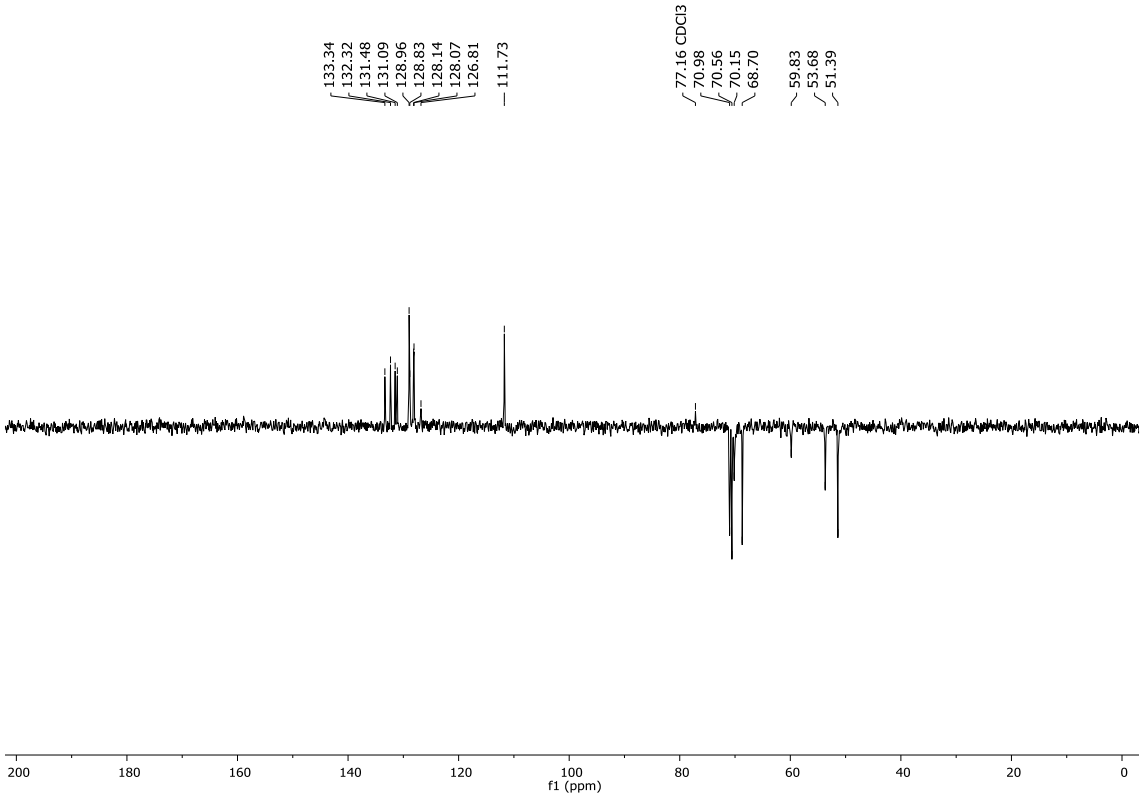
^{1}H-NMR



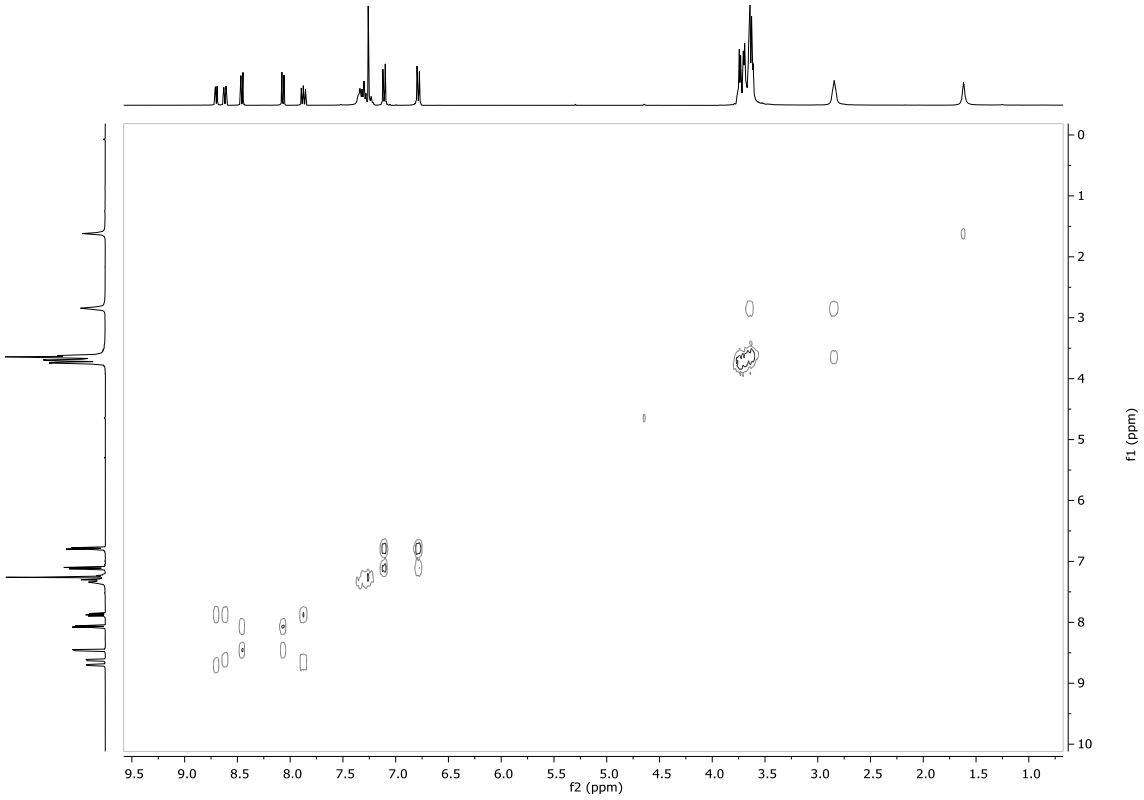
^{13}C-NMR



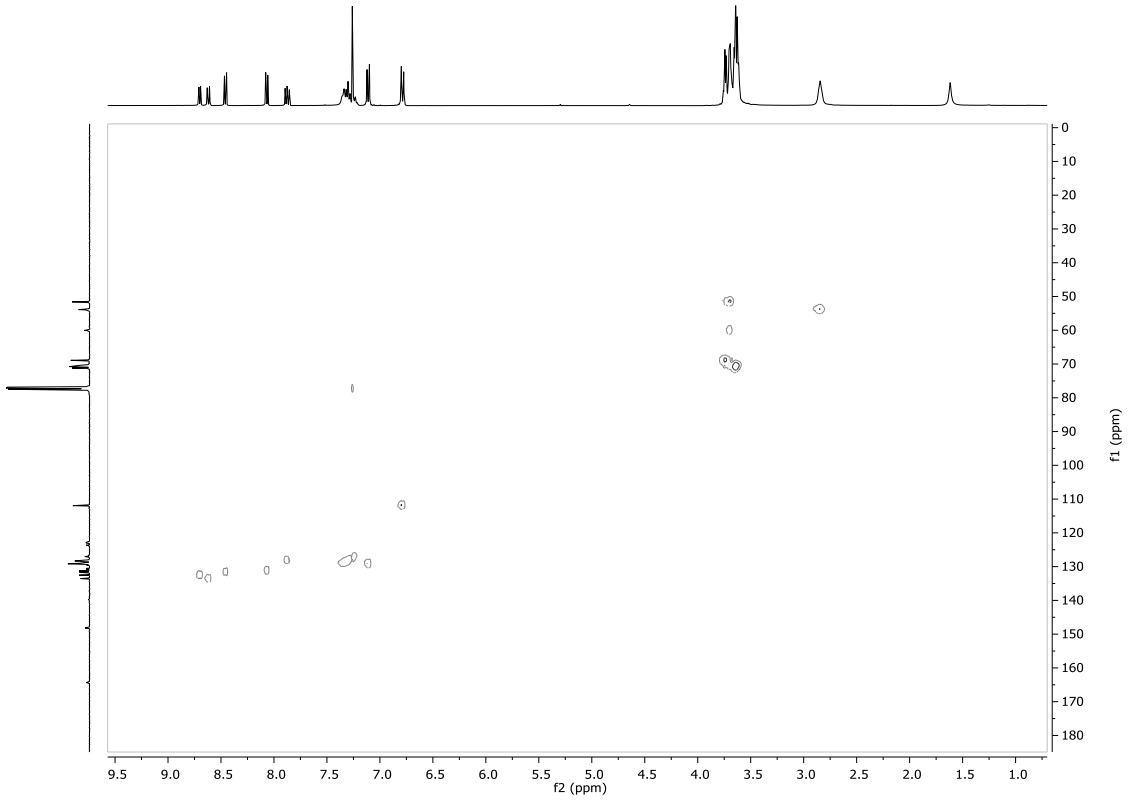
DEPT-135



g-COSY

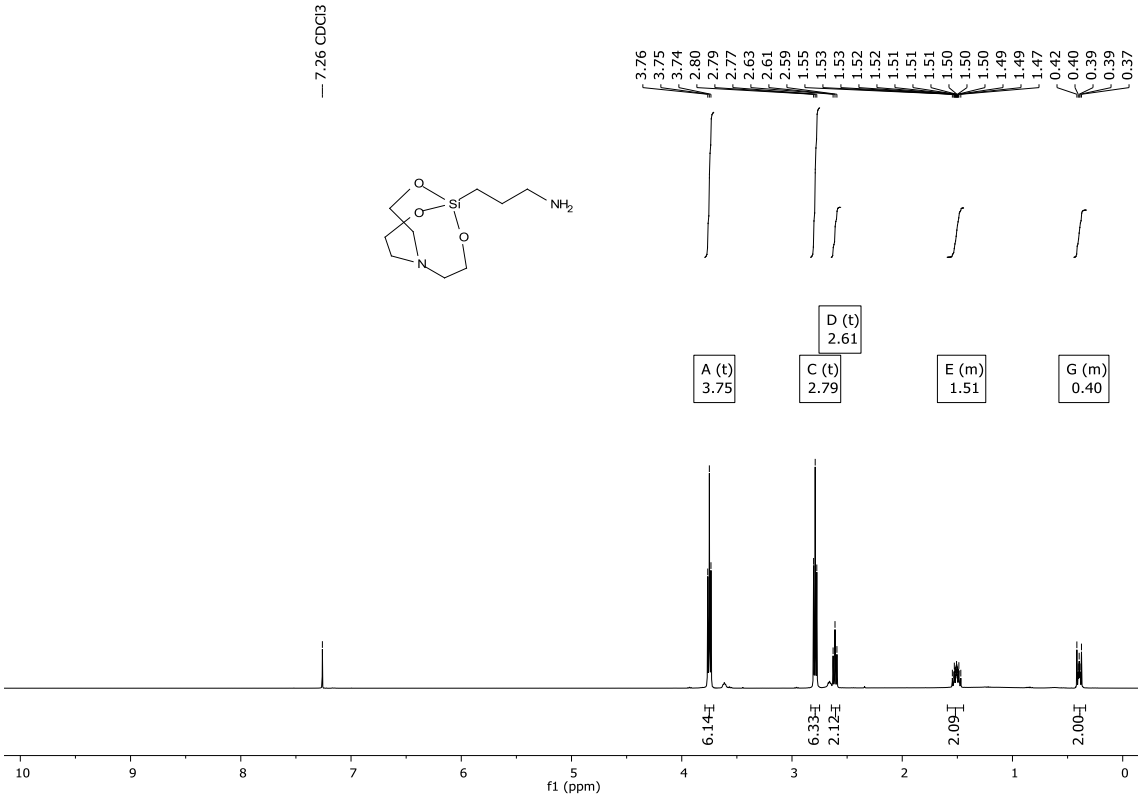


g-HSQC

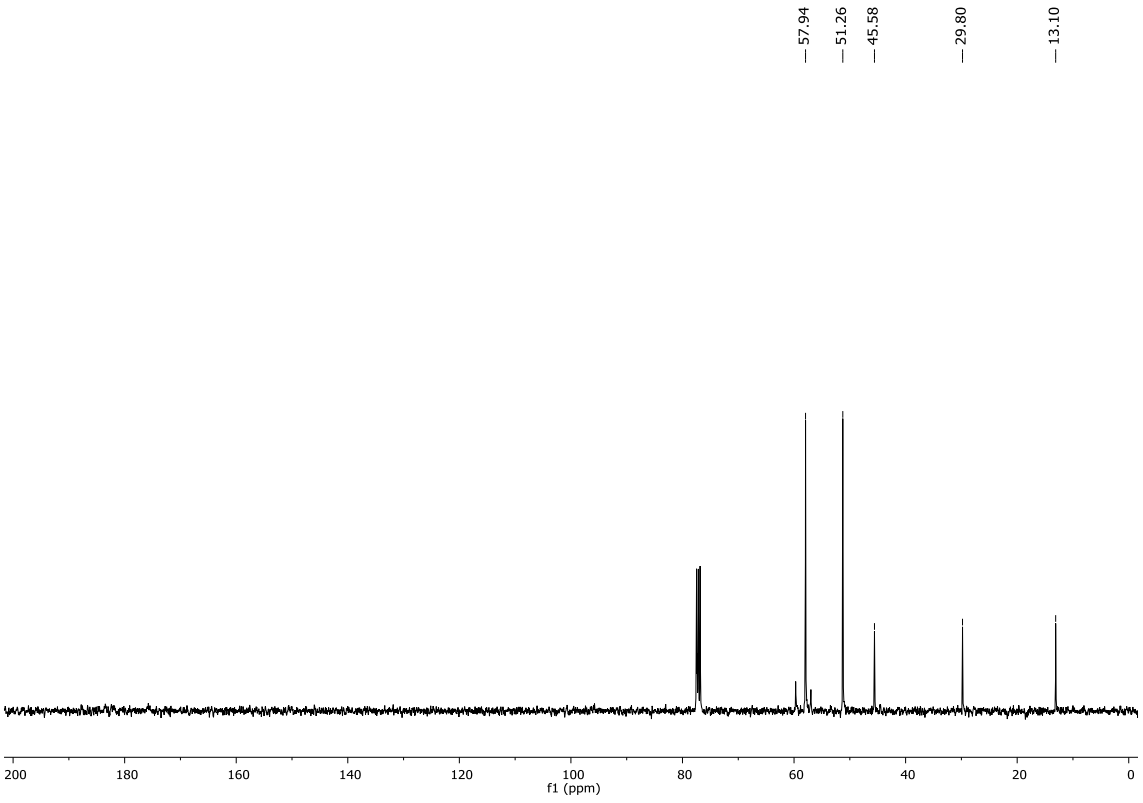


3-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propan-1-amine (6a)

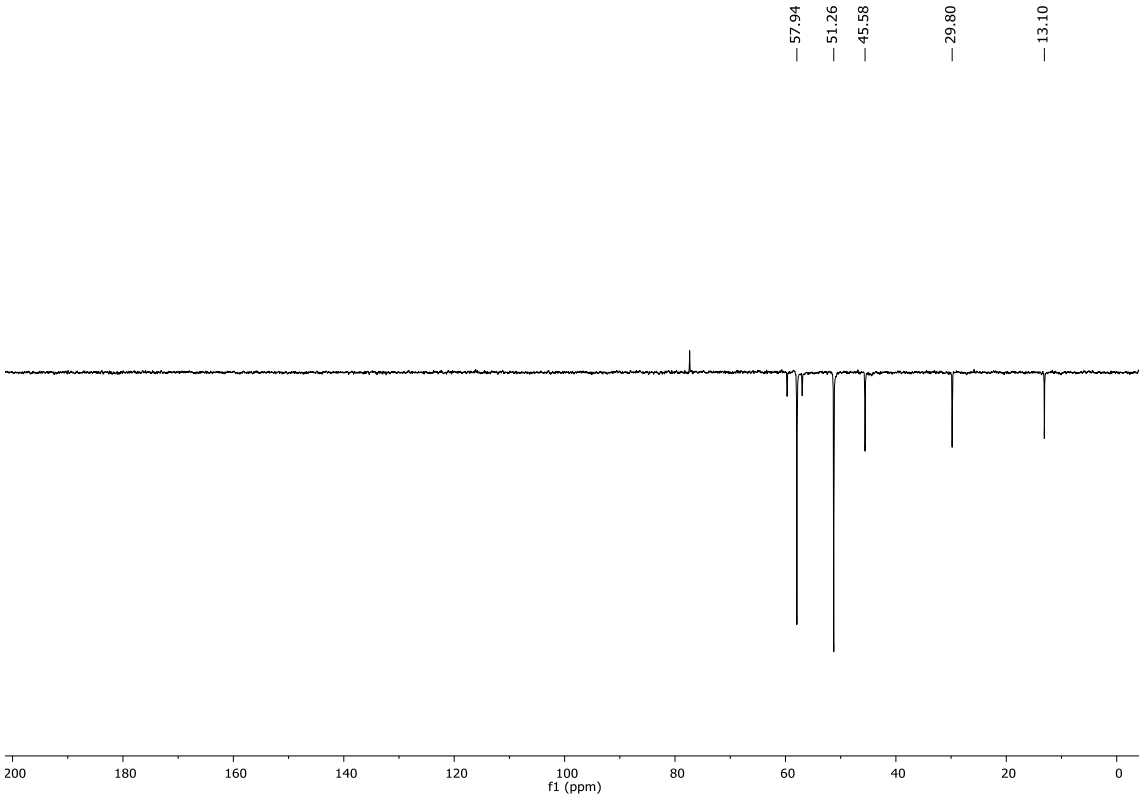
^{1}H-NMR



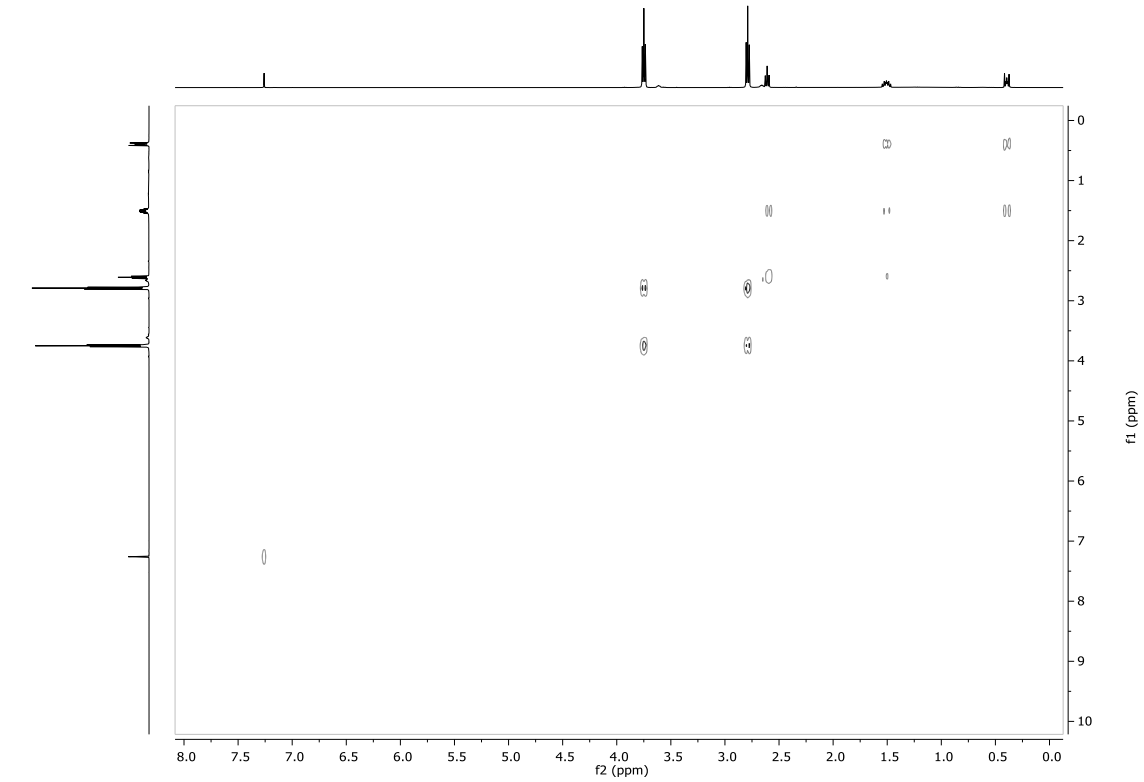
^{13}C-NMR



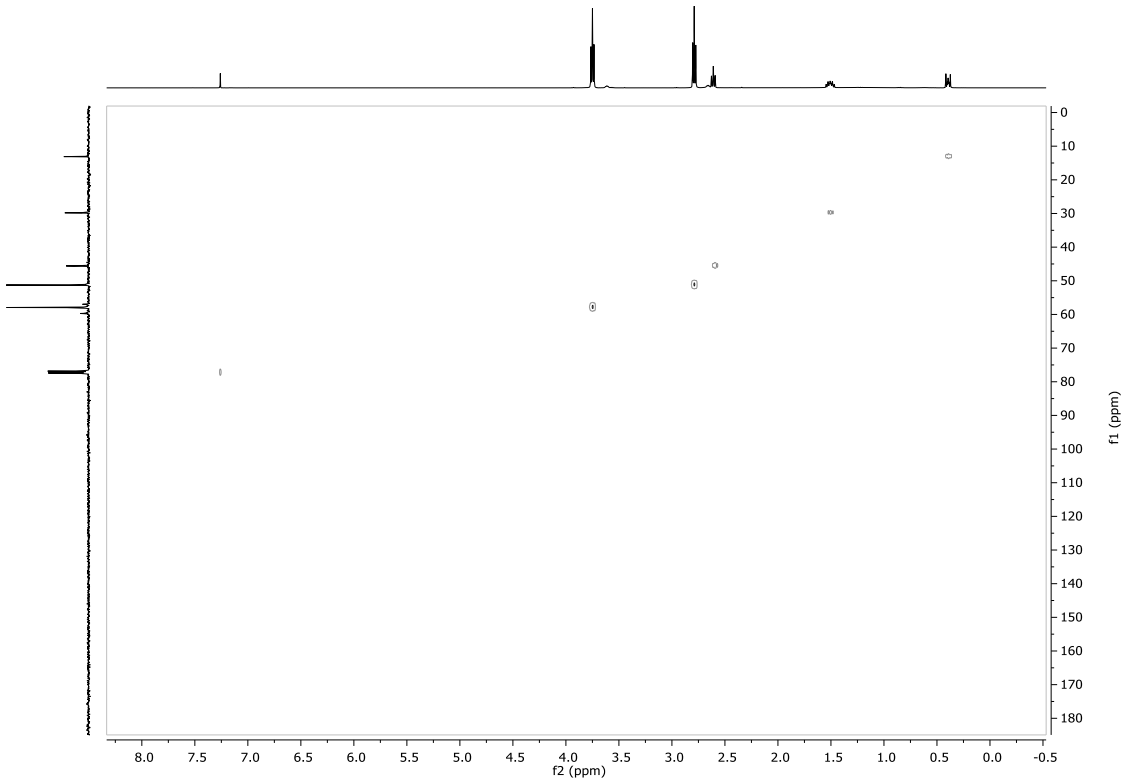
DEPT-135



g-COSY



g-HSQC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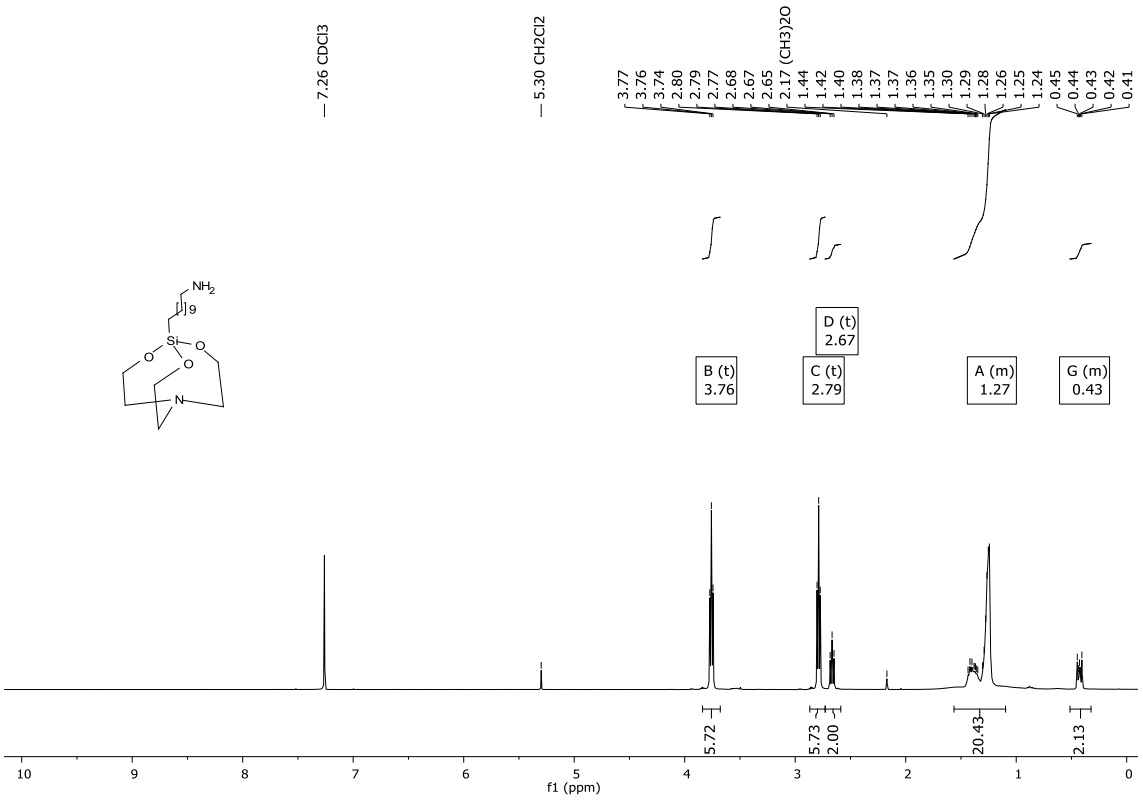
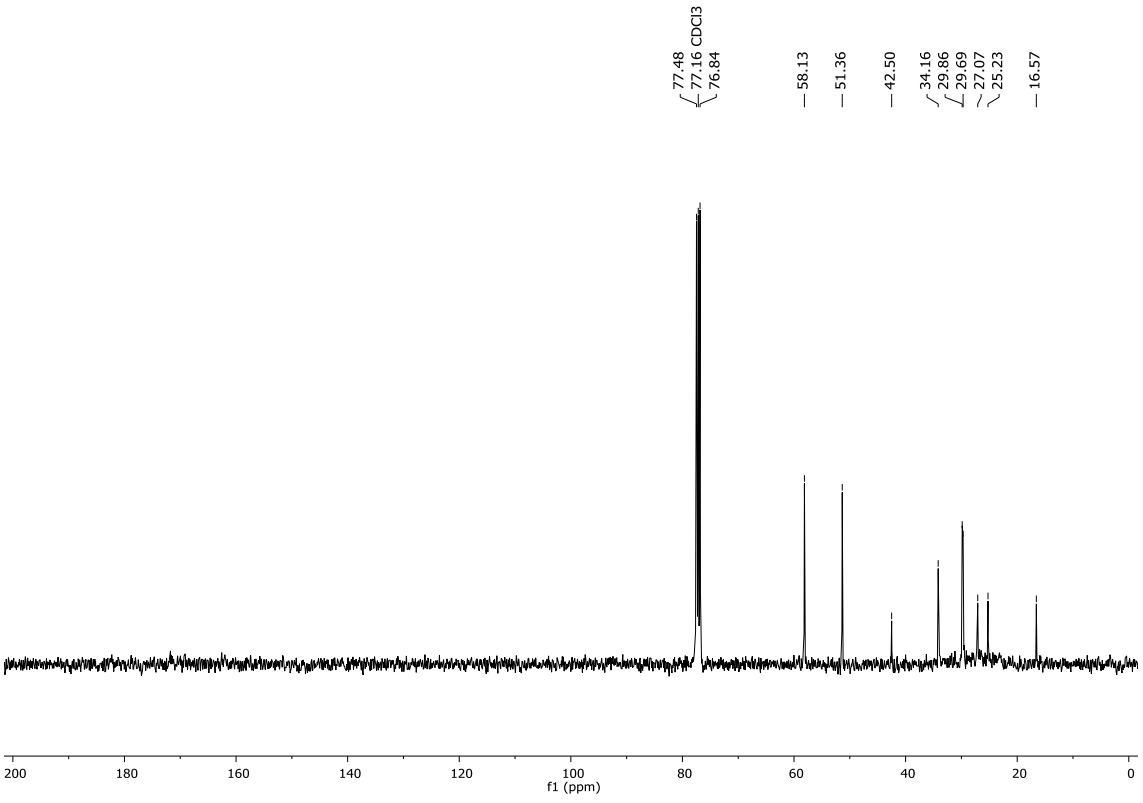
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

11-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecan-1-amine (6b)

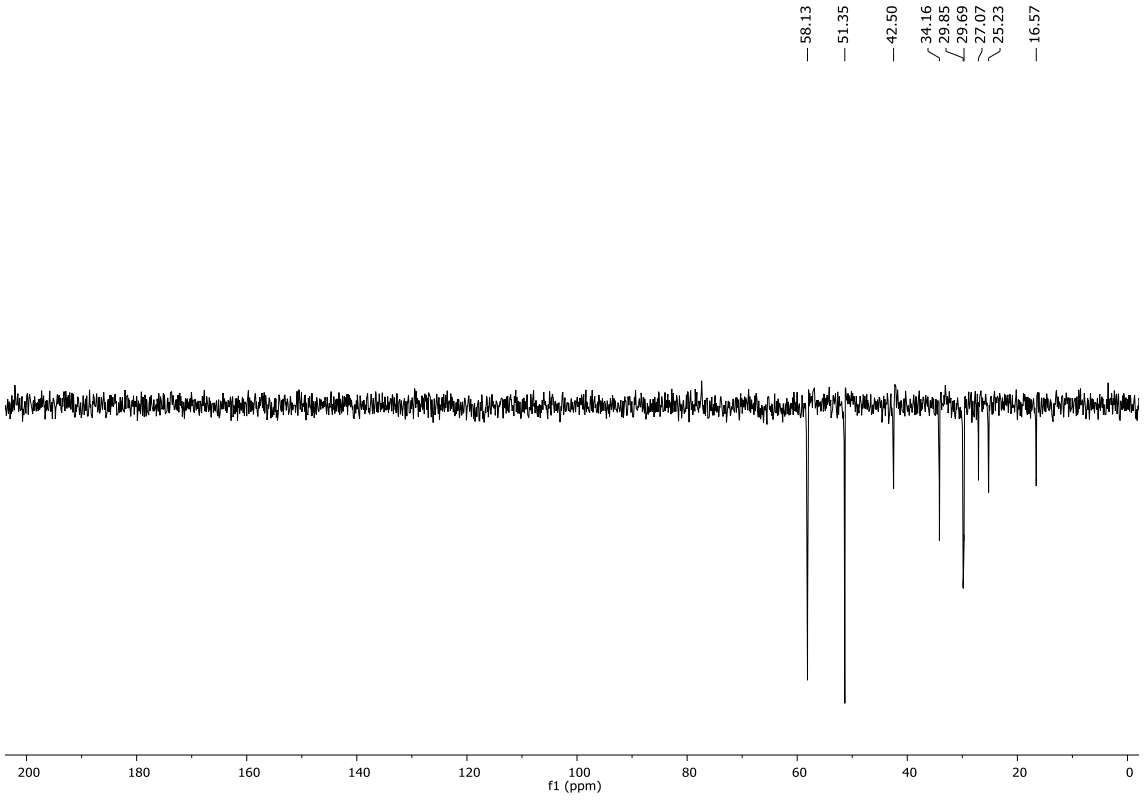
^{1}H-NMR



^{13}C-NMR



DEPT-135



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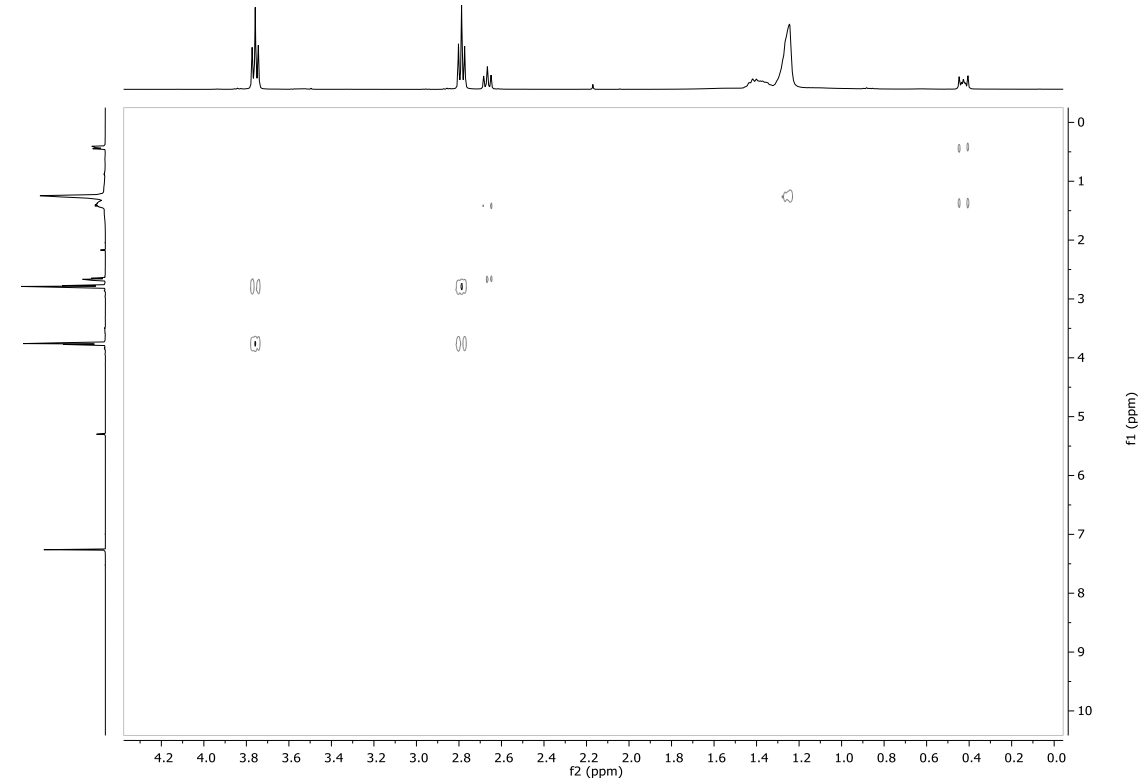
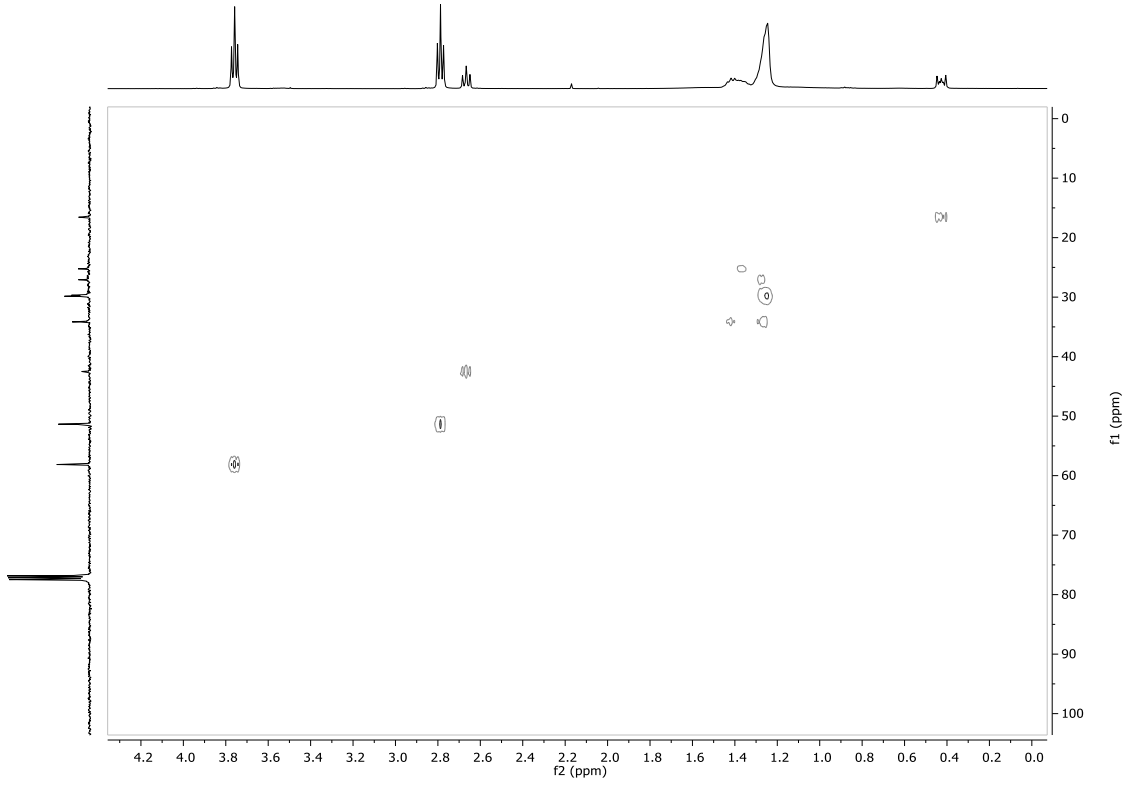


g-HSQC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f1 (ppm)
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3.2
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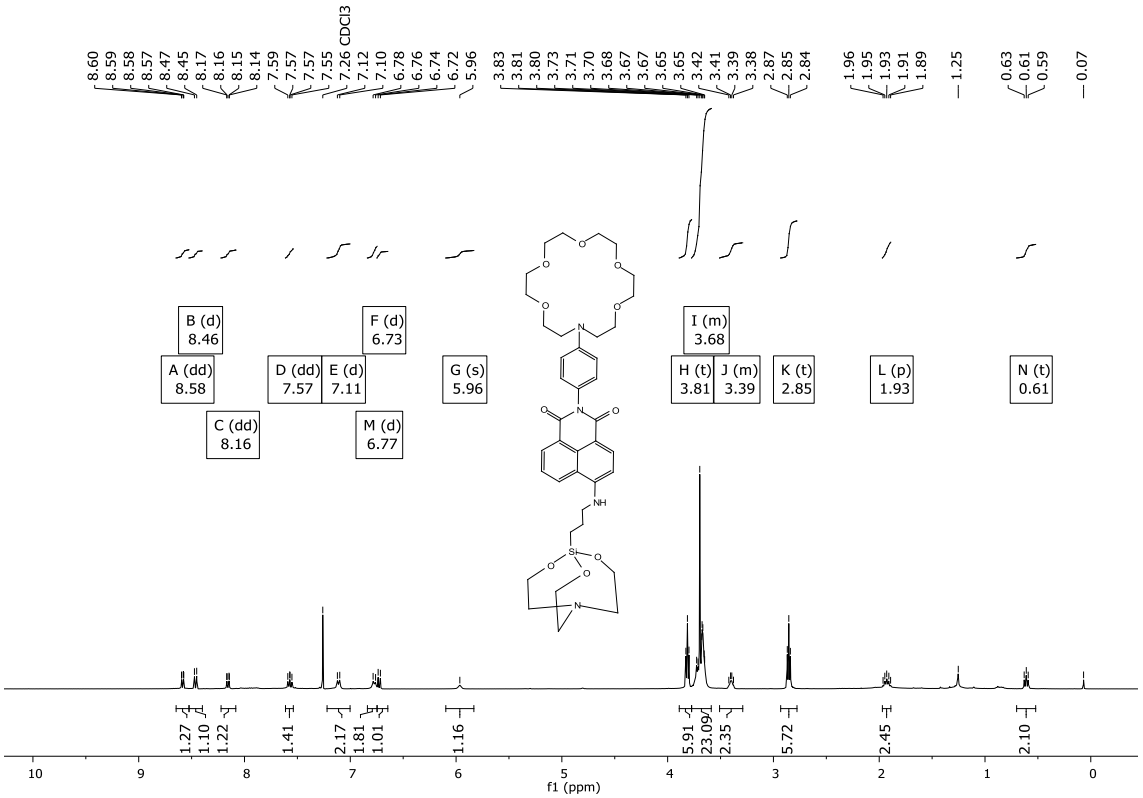
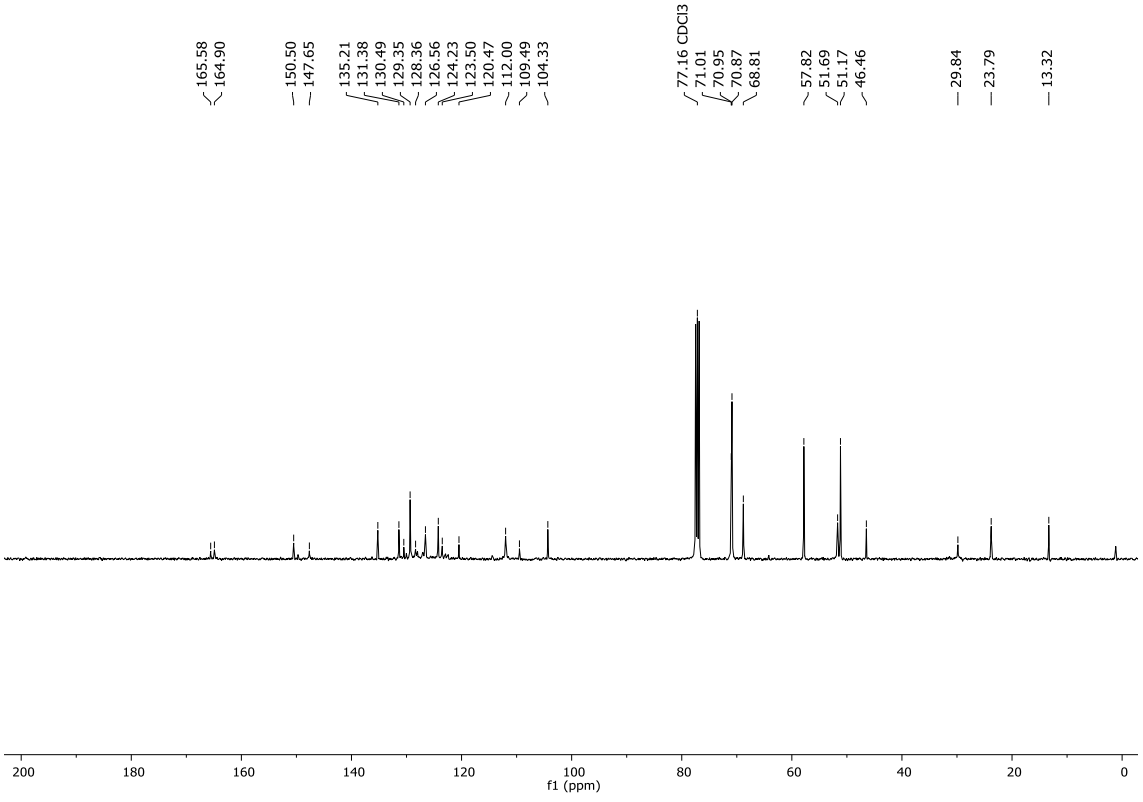
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f2 (ppm)

2-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-6-((3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)amino)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7aa)

^{1}H-NMR



^{13}C-NMR



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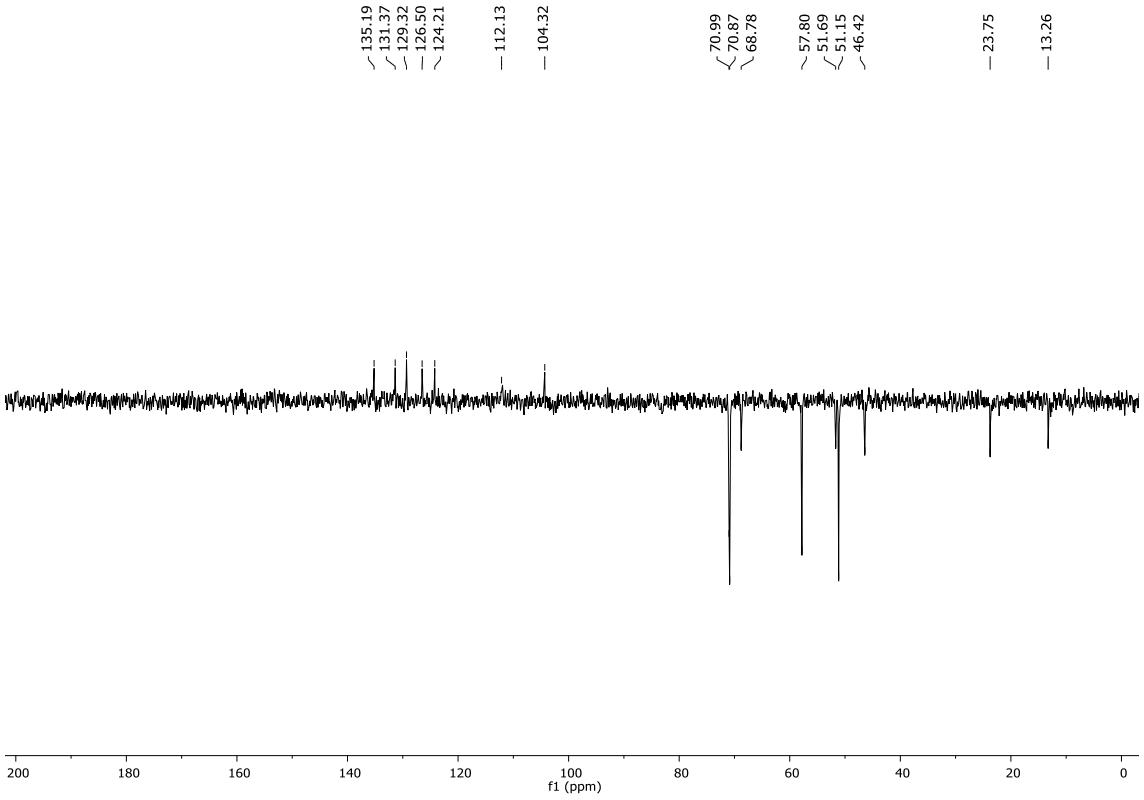
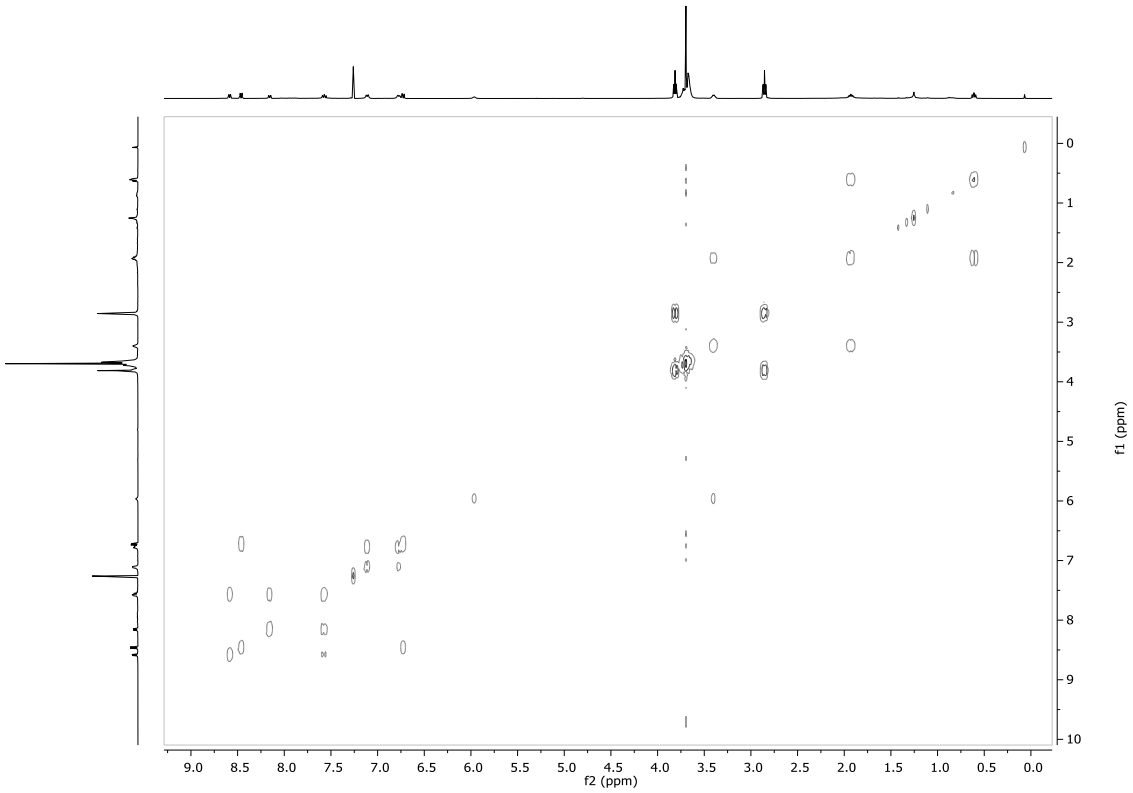
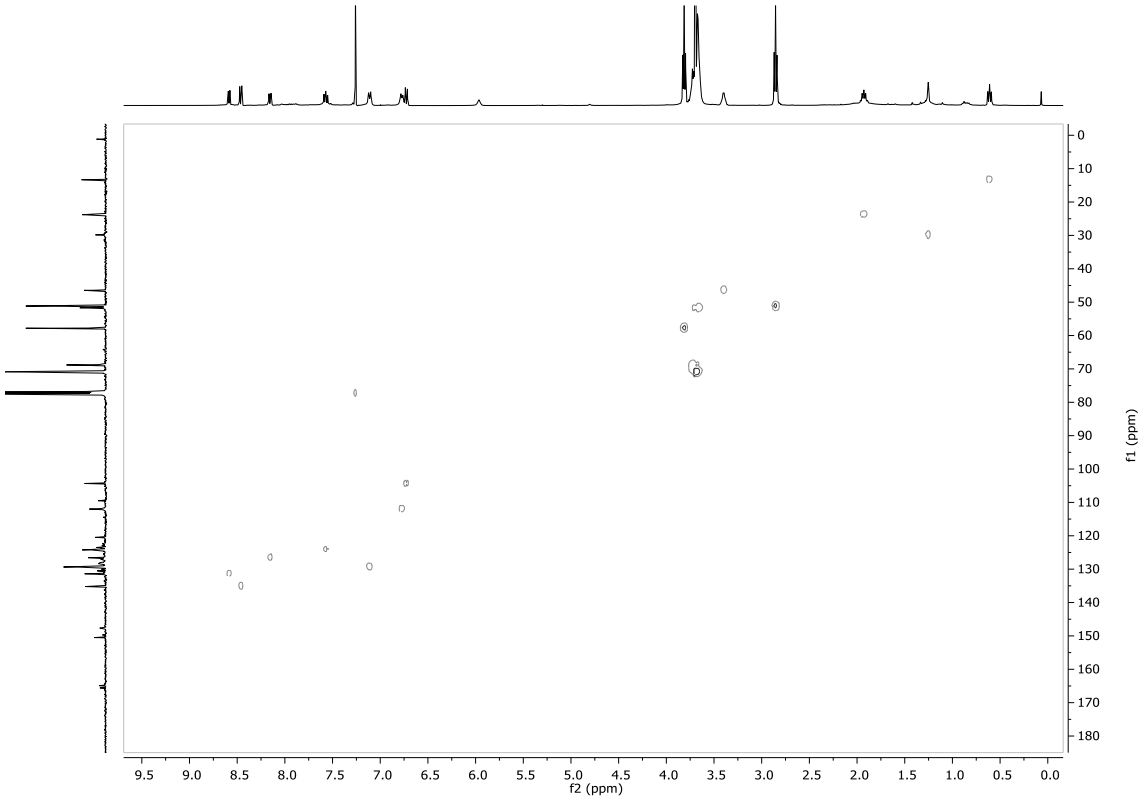


g-COSY



g-HSQC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f1 (ppm)
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8.0
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5.0
4.5
4.0
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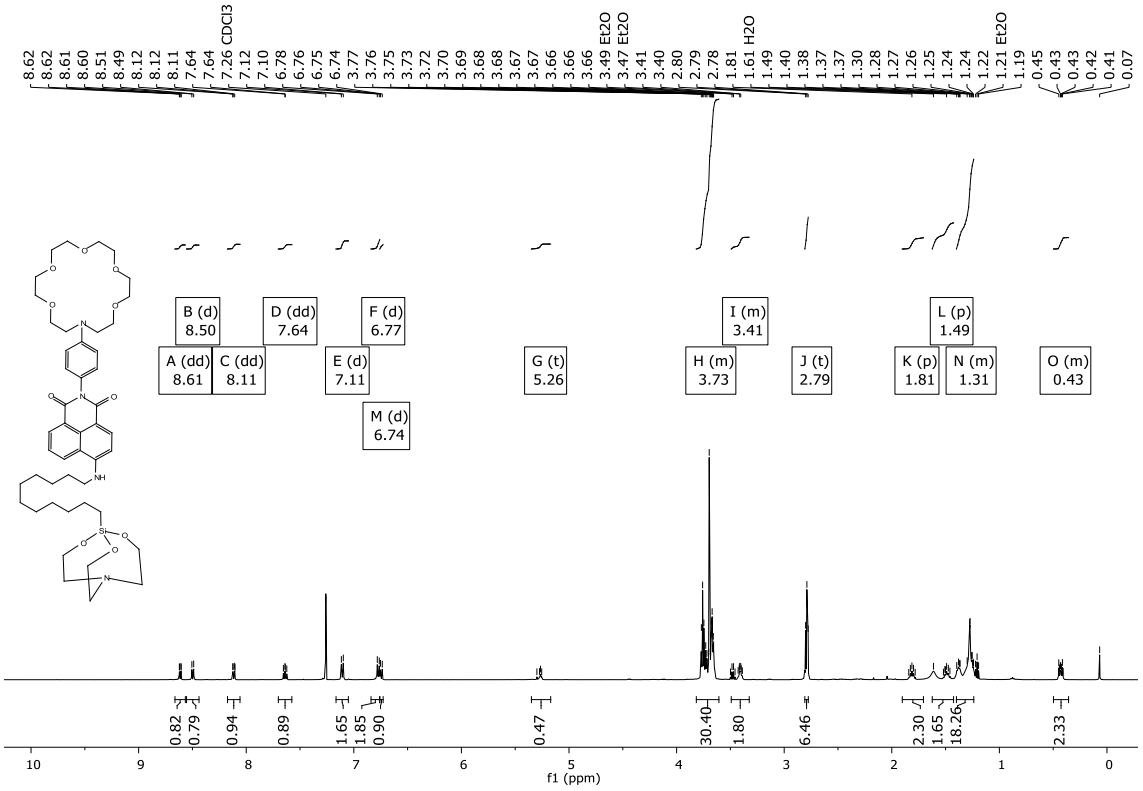
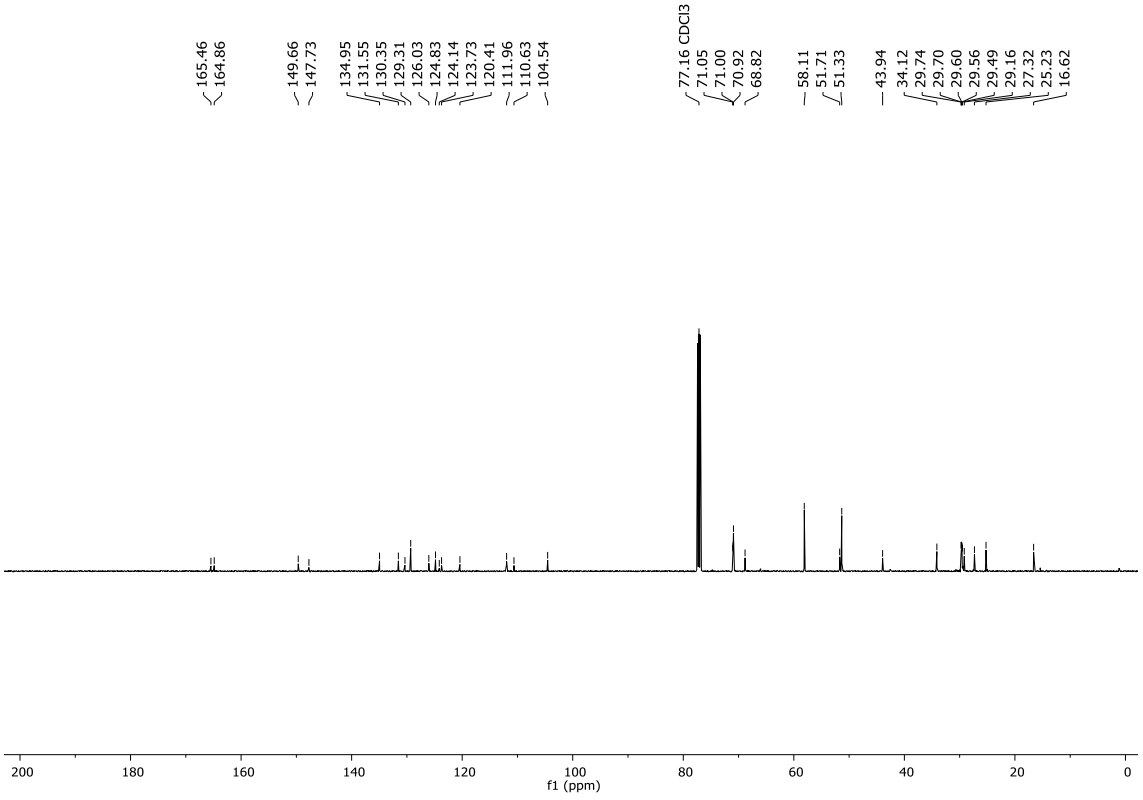
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

2-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-6-((11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)amino)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7ab)

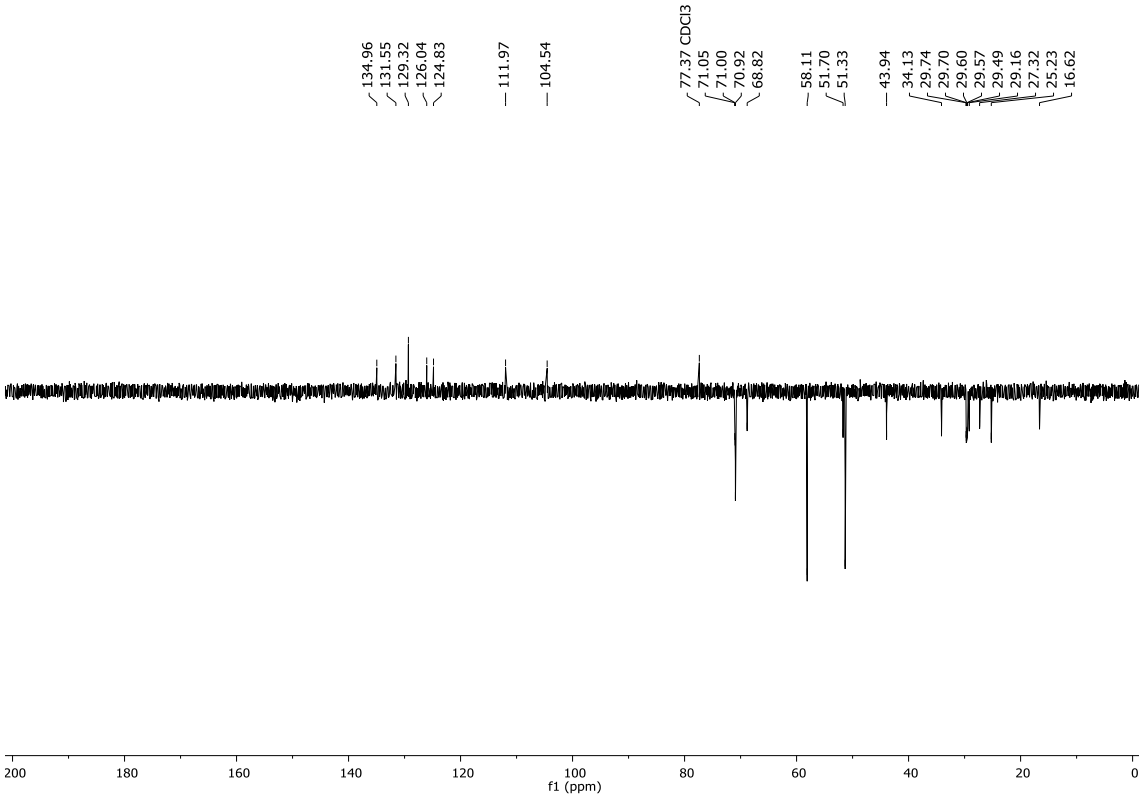
^{1}H-NMR



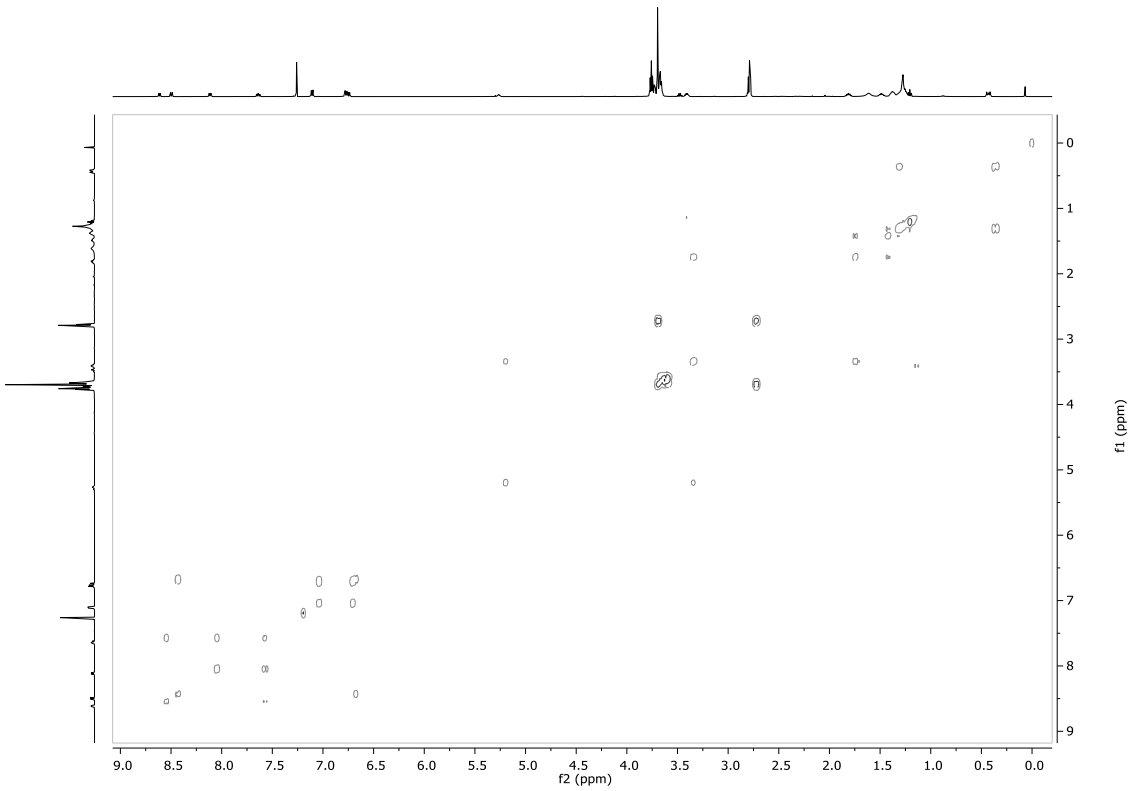
^{13}C-NMR



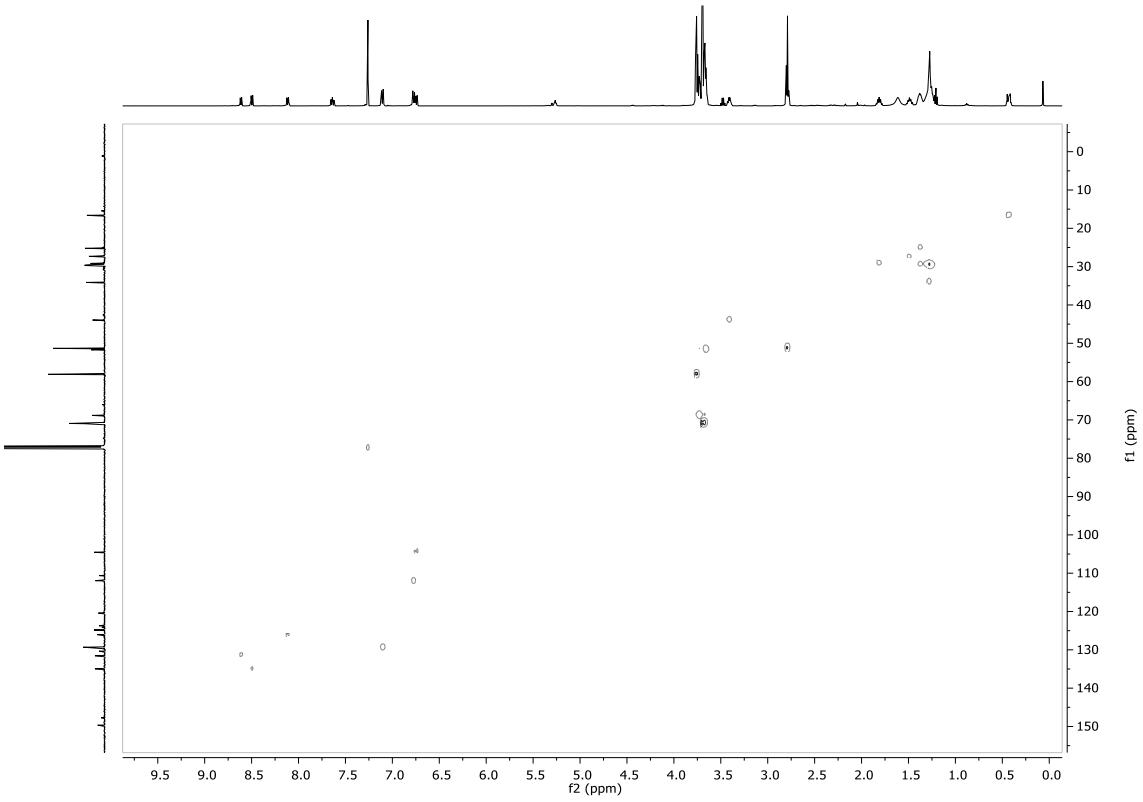
DEPT-135



g-COSY

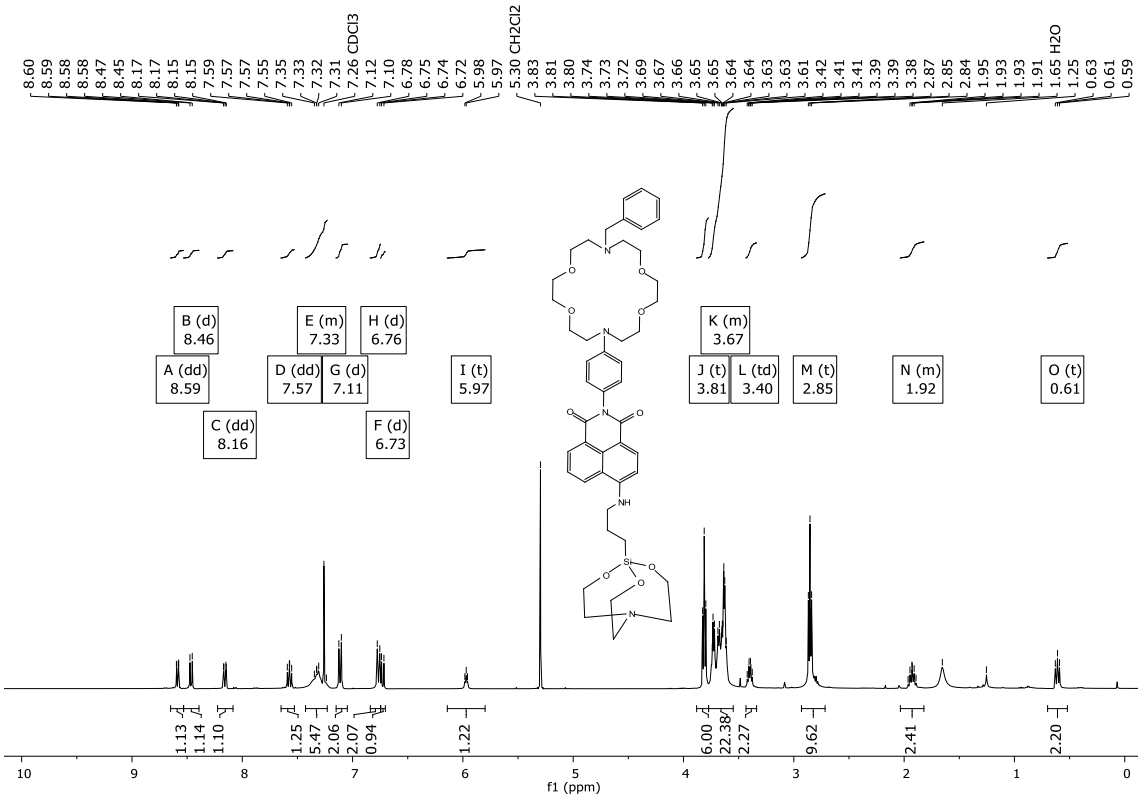


g-HSQC

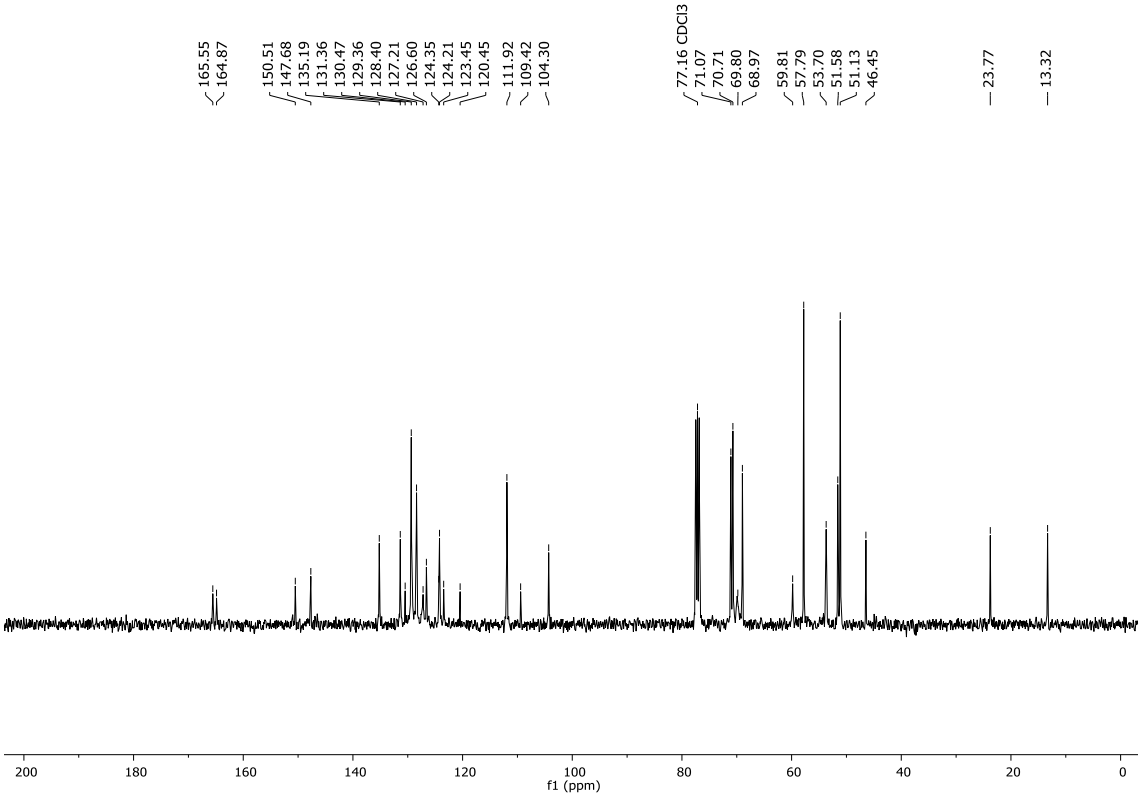


6-((3-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)amino)-2-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7ba)

^{1}H-NMR



^{13}C-NMR



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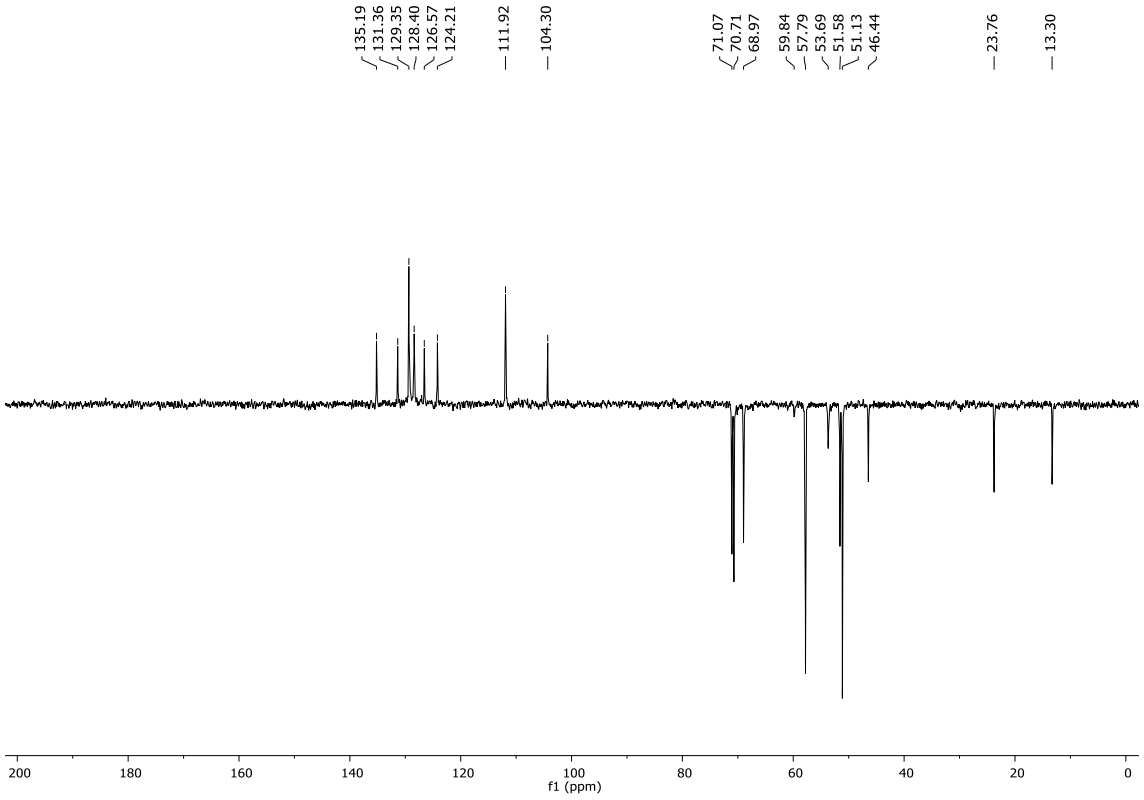

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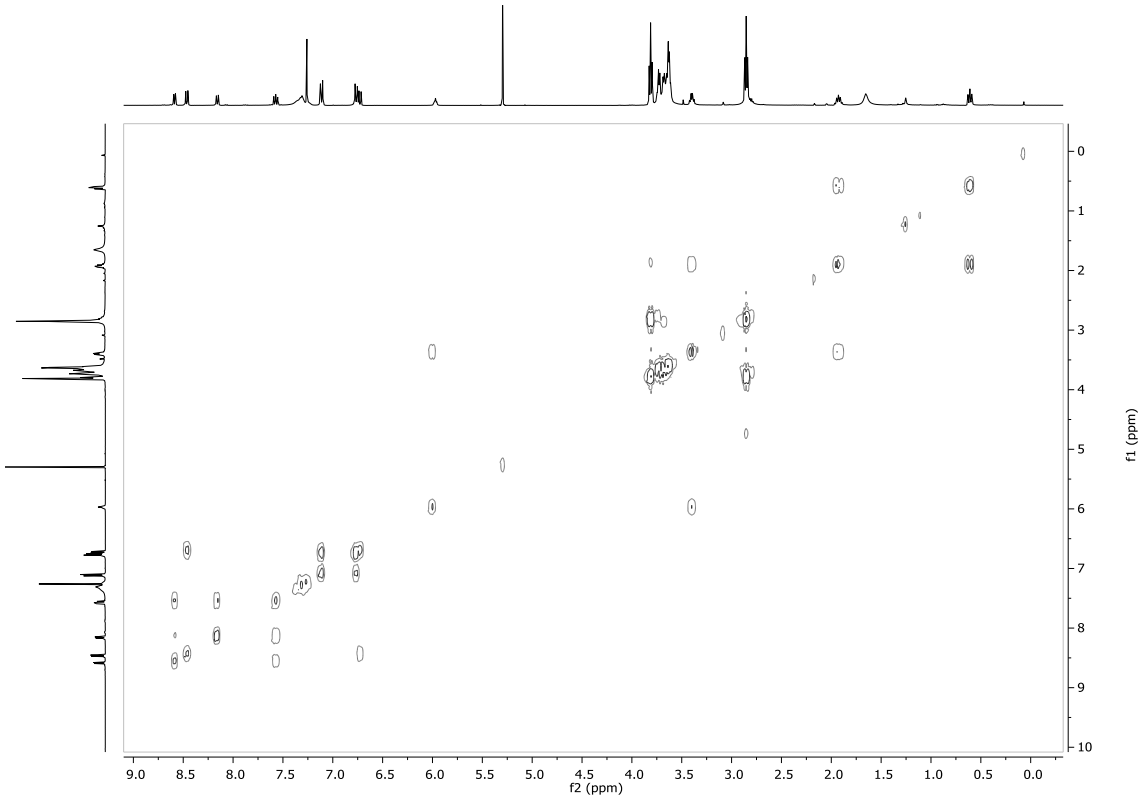
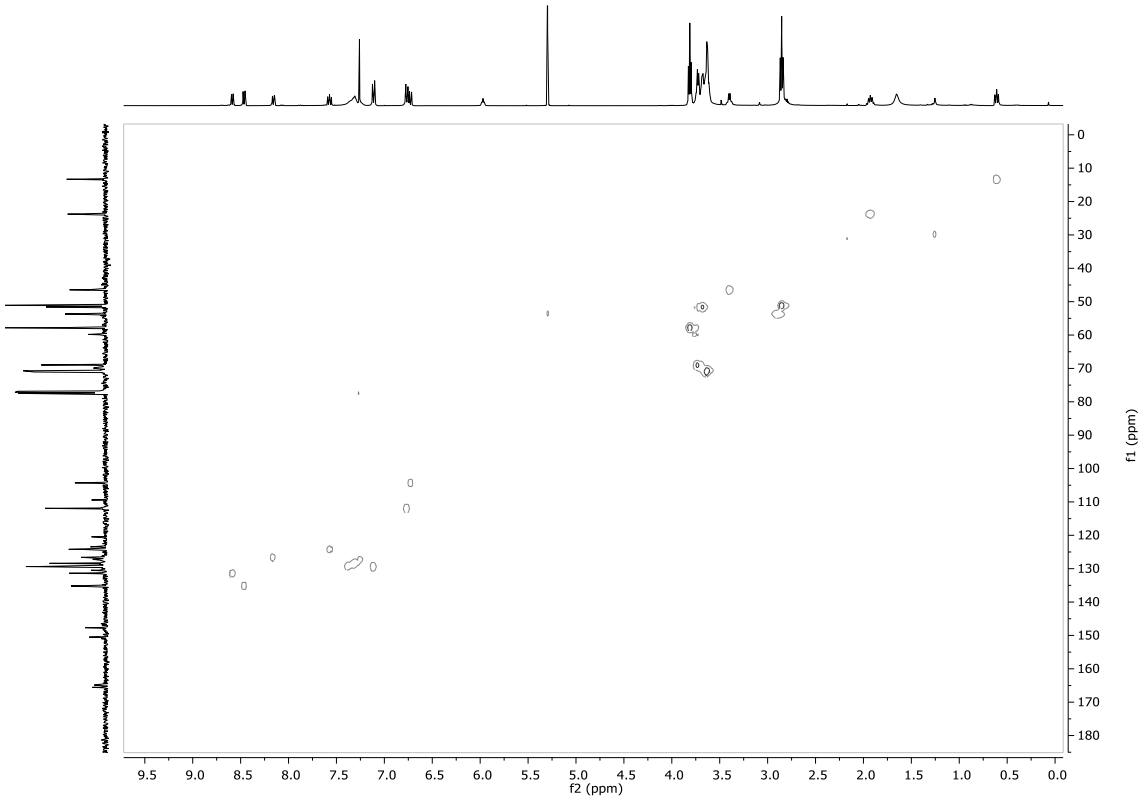
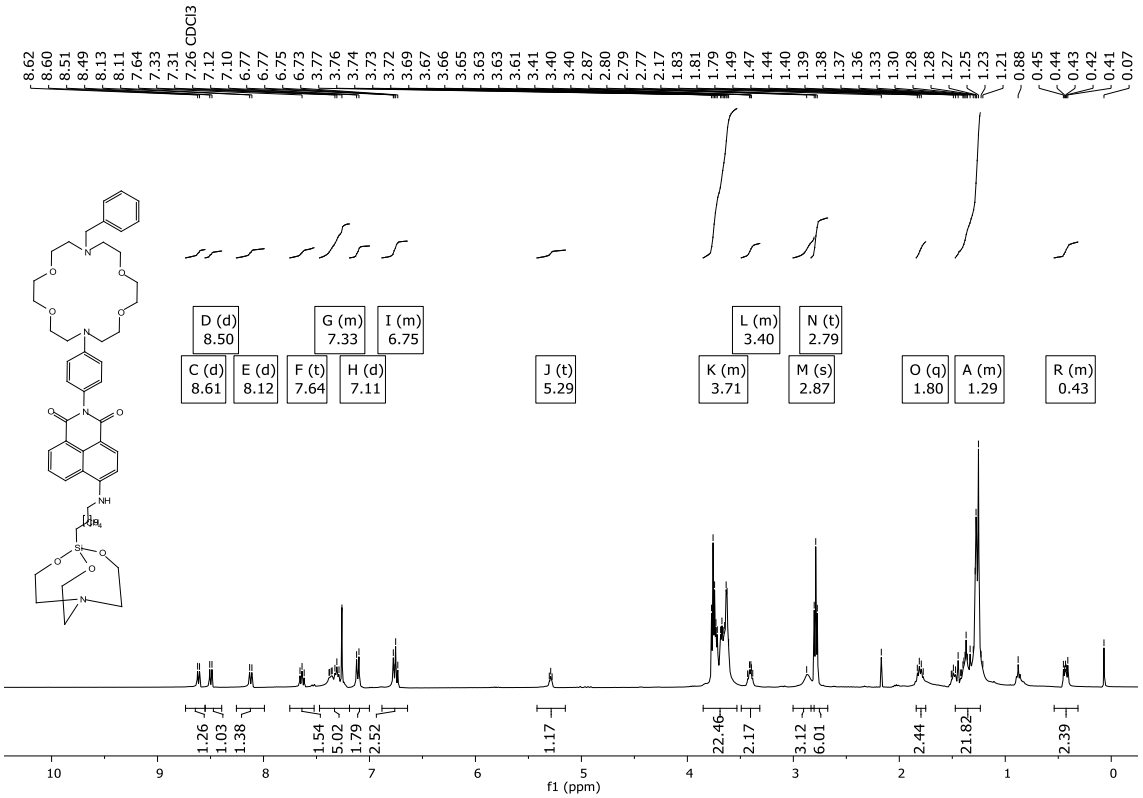


g-HSQC

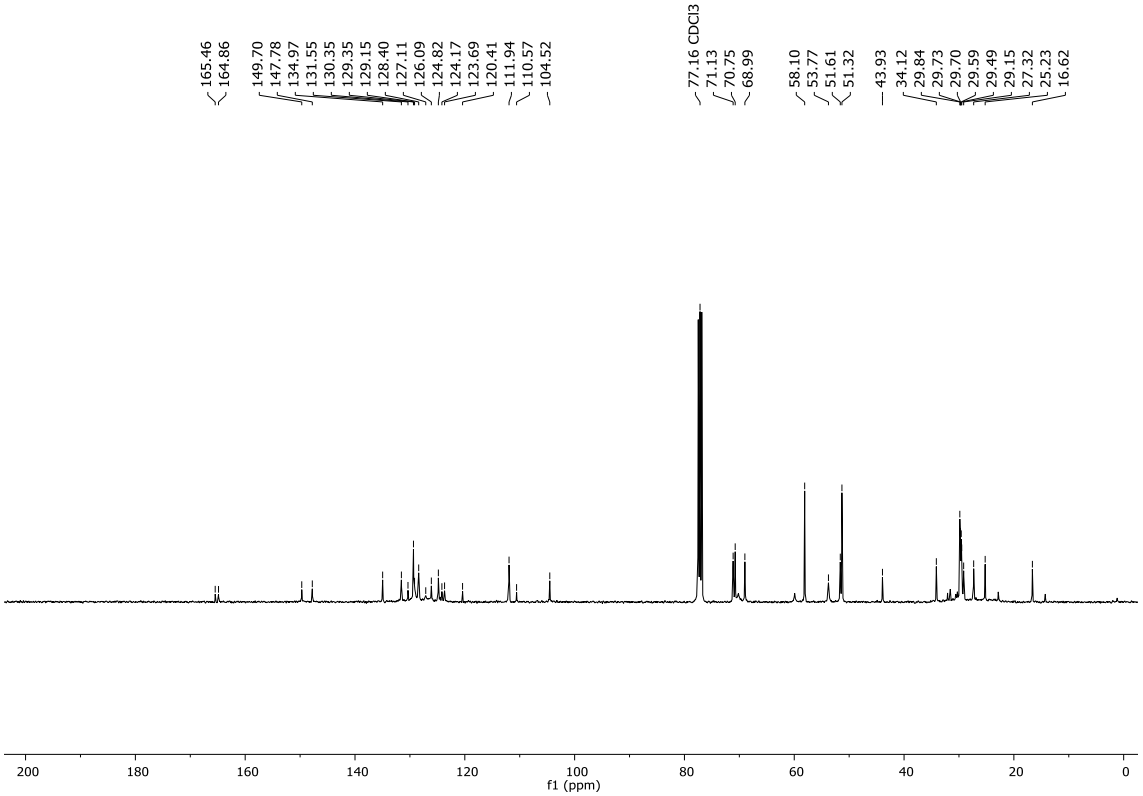


6-((11-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)amino)-2-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7bb)

^{1}H-NMR



^{13}C-NMR



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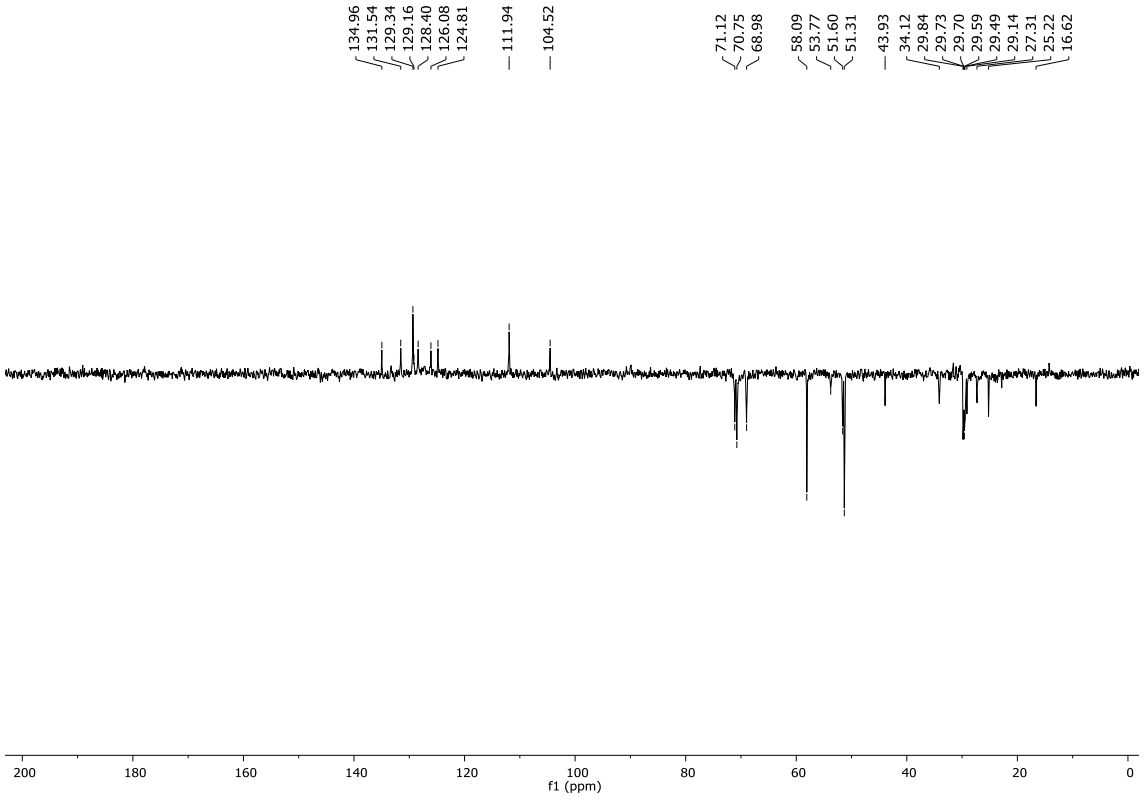

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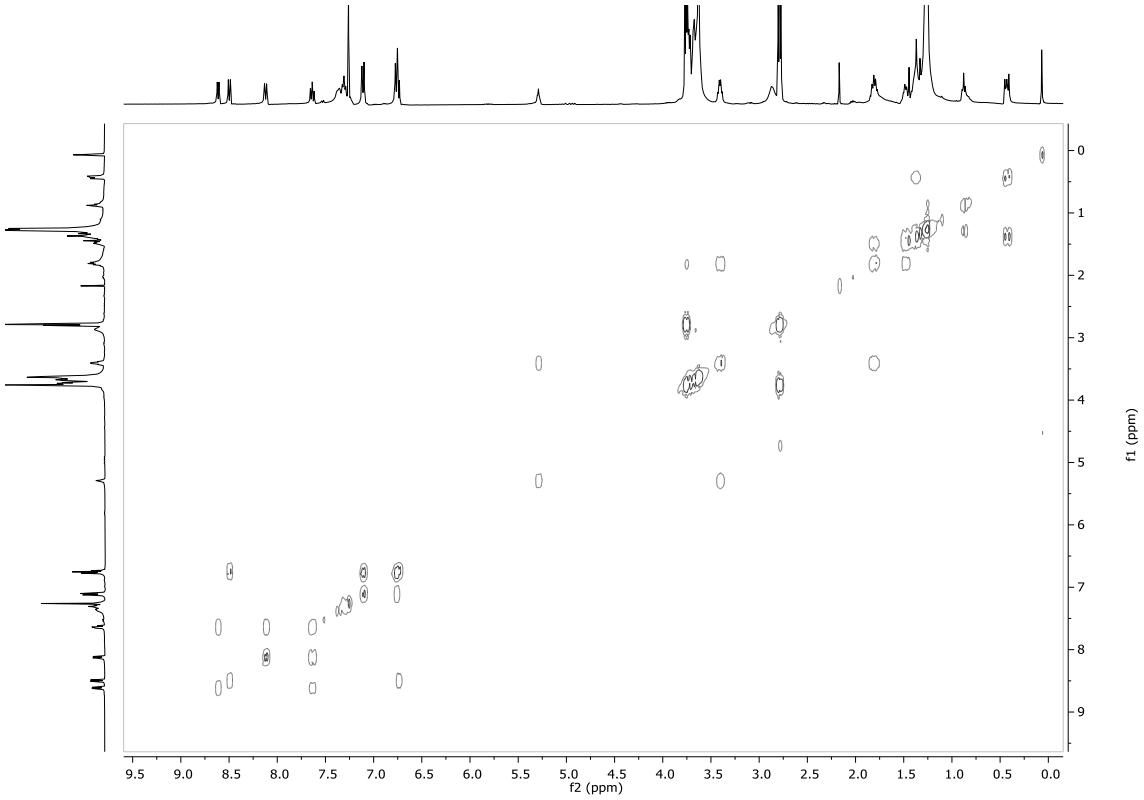
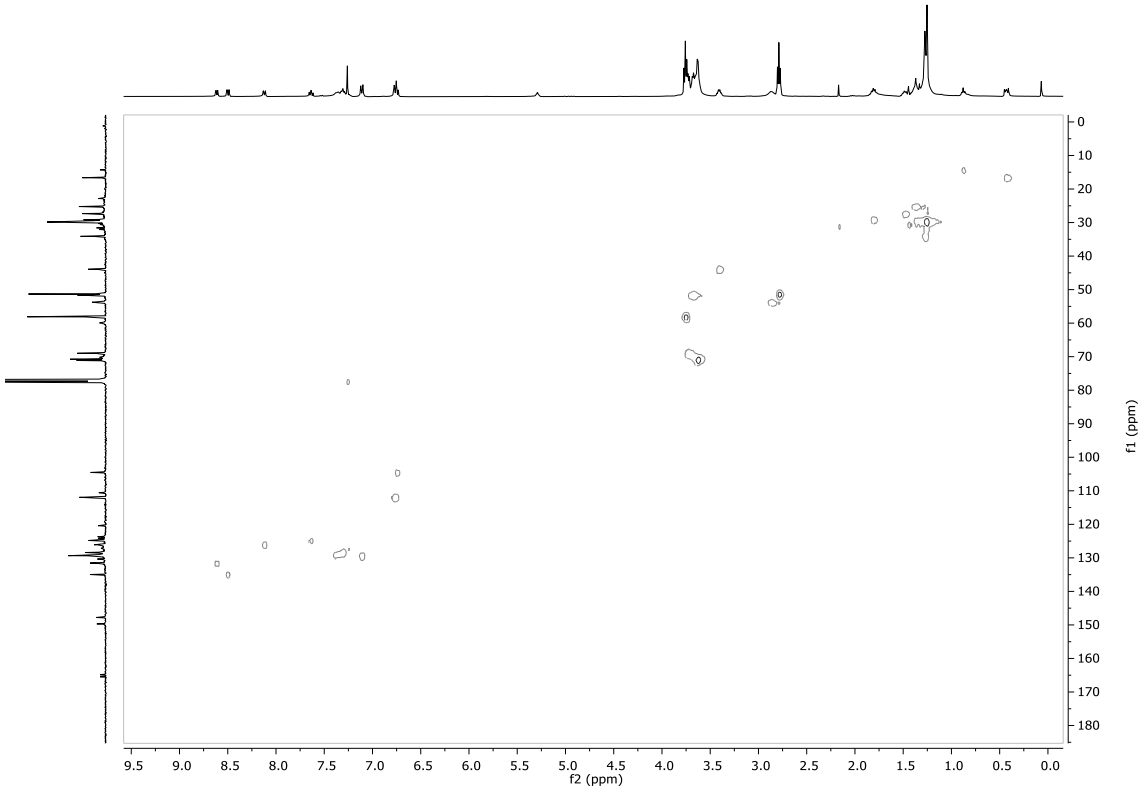
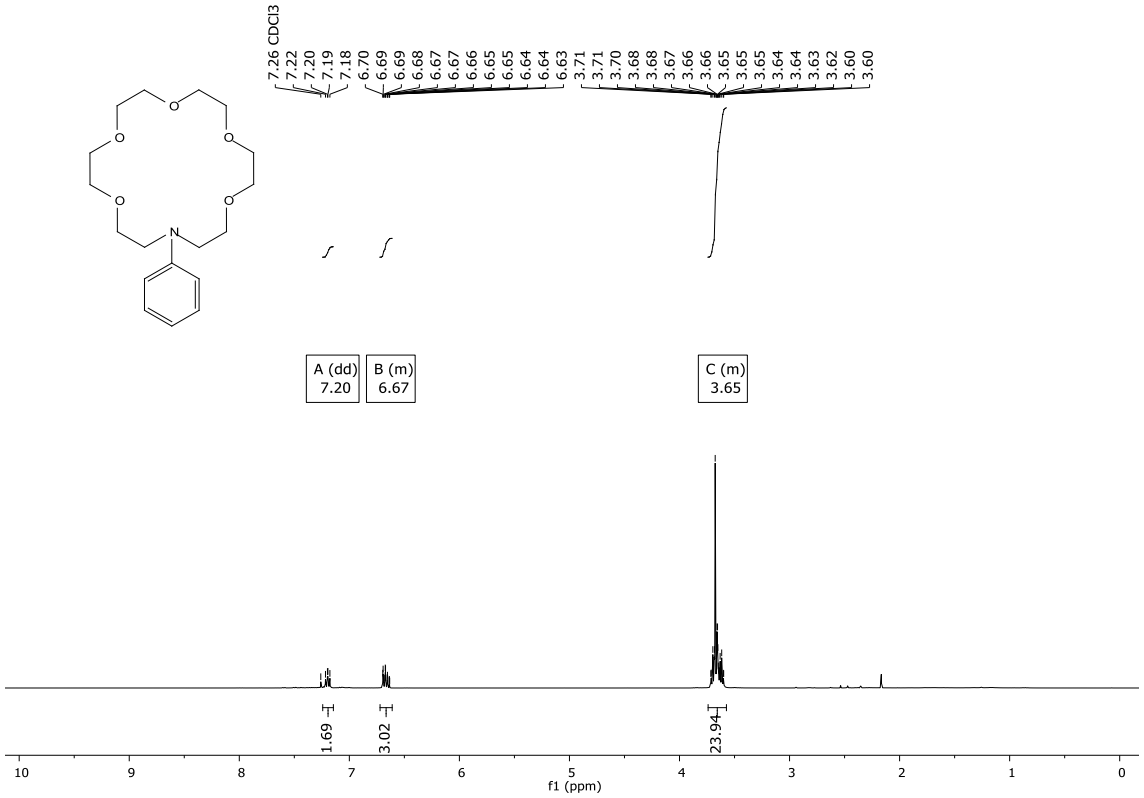


g-HSQC



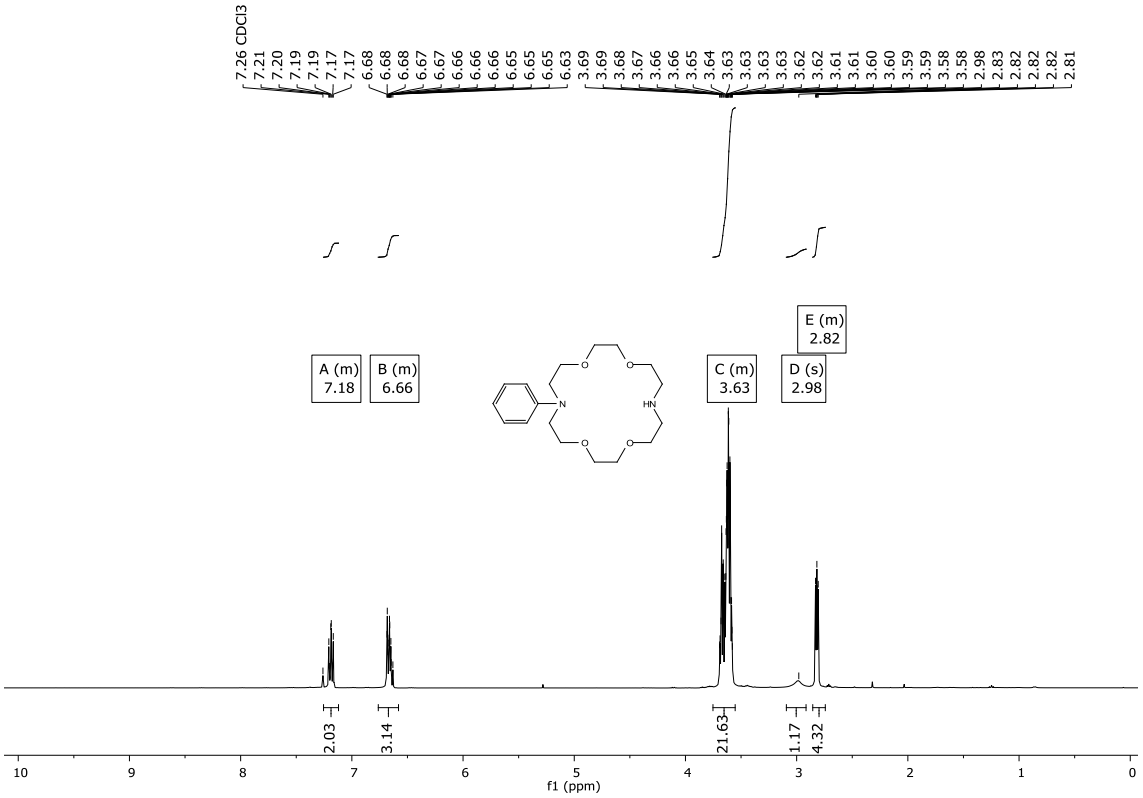
N-Phenyl-1-aza-18-crown (8a)

^{1}H-NMR

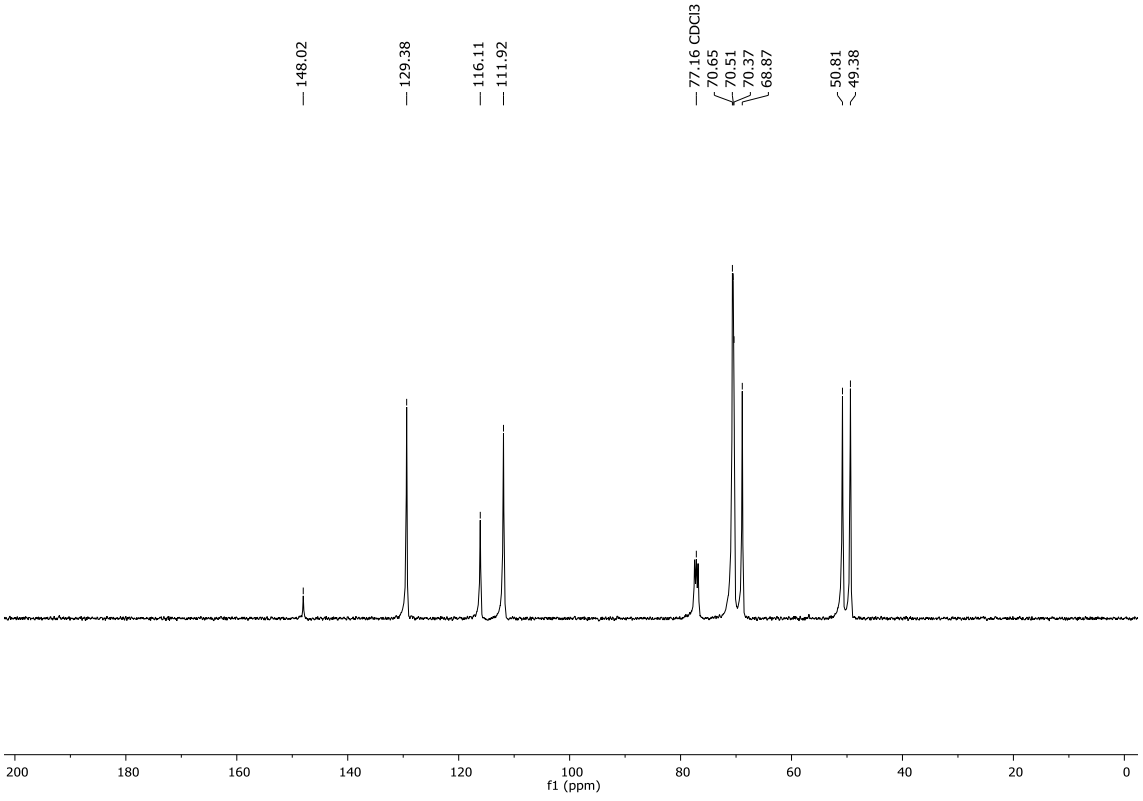


N-Phenyl-1,10-diaza-18-crown-6 (8b)

^{1}H-NMR



^{13}C-NMR



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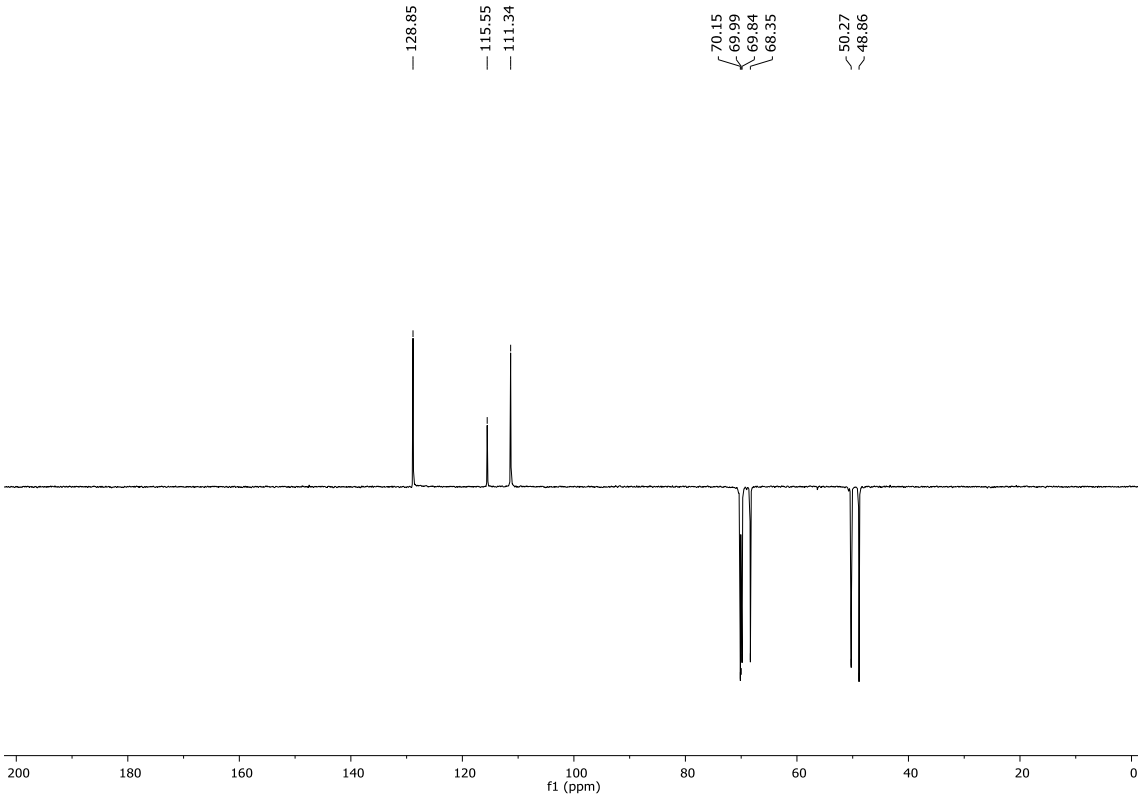
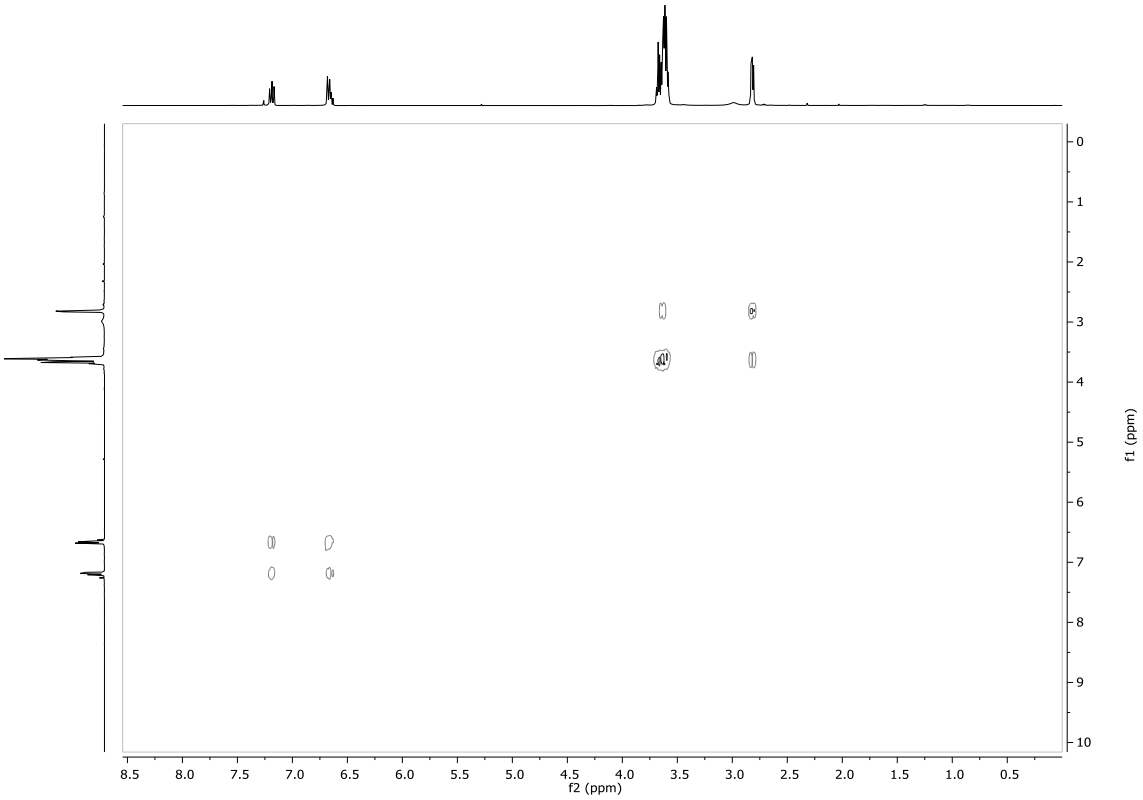
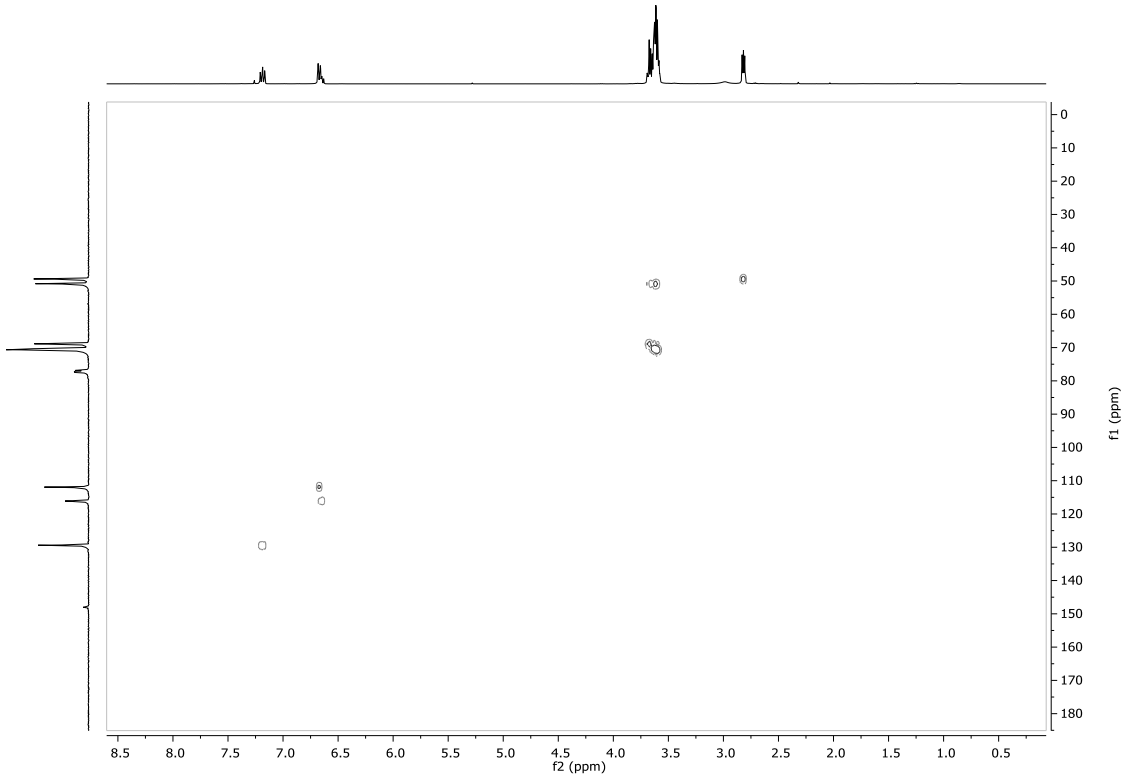


g-COSY



g-HSQC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f1 (ppm)
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7.5
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5.0
4.5
4.0
3.5
3.0
2.5
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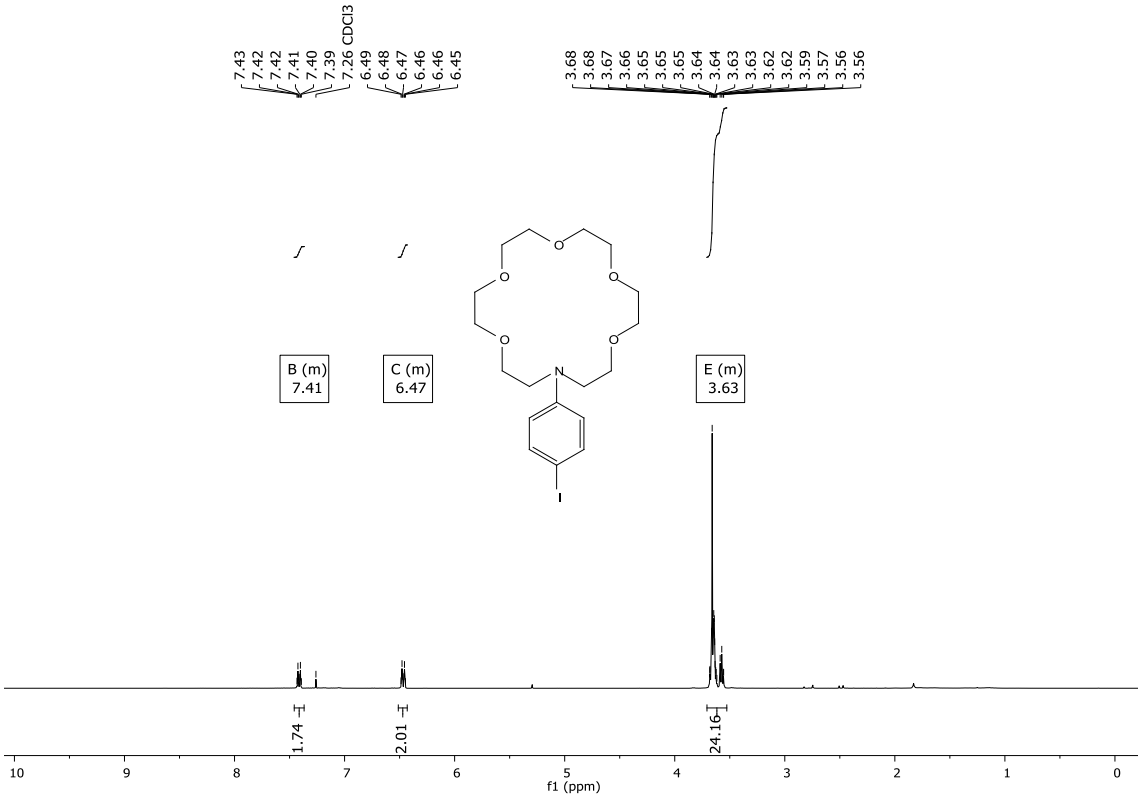
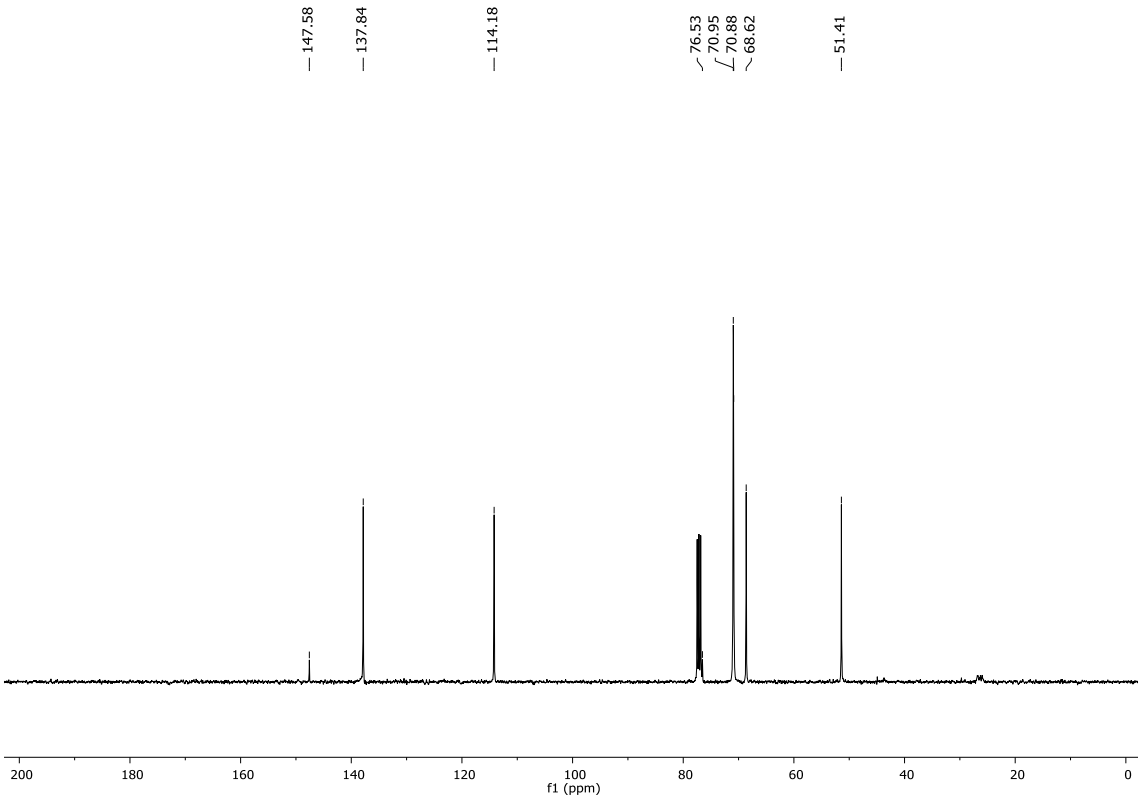
1.5
1.0
0.5
f2 (ppm)

N-(4-iodophenyl)-1-aza-18-crown-6 (9a)

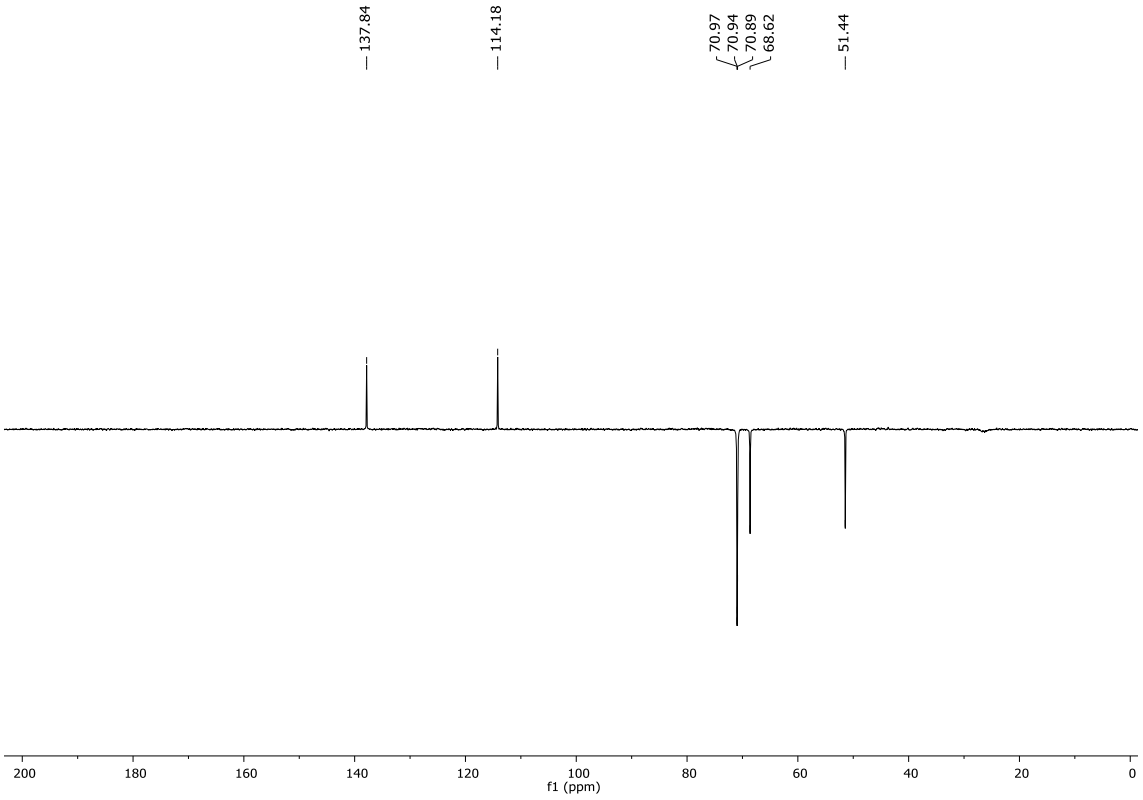
^{1}H-NMR



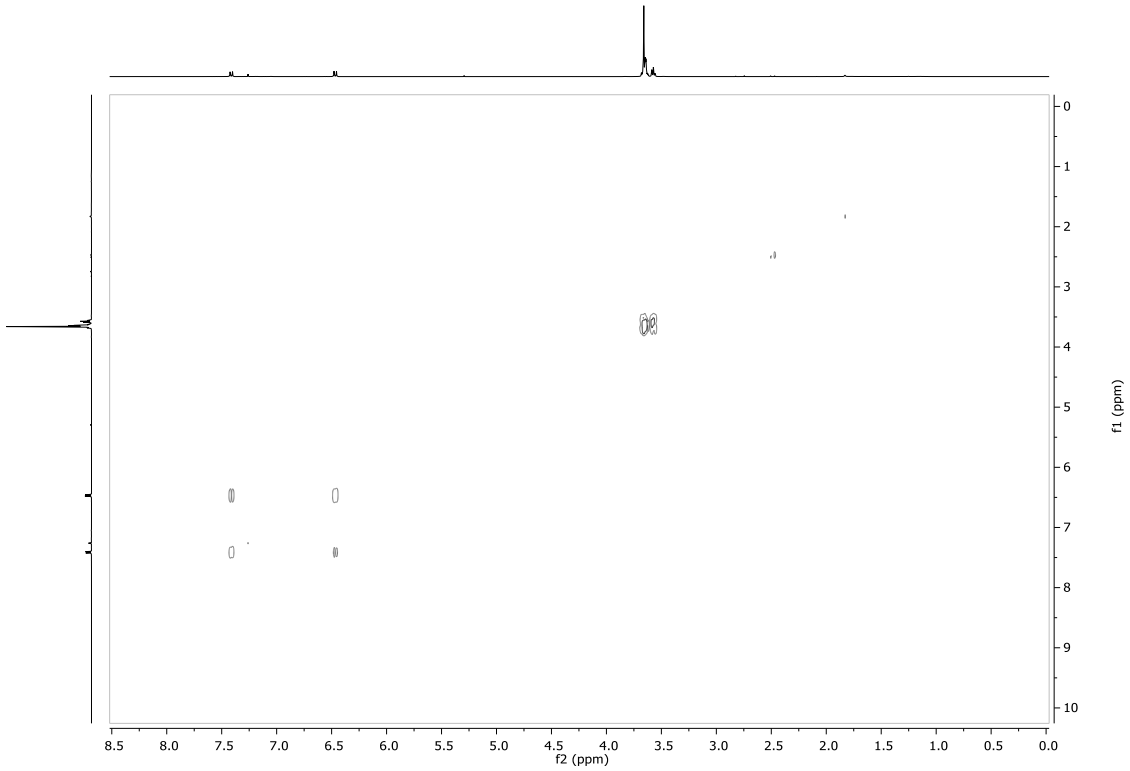
^{13}C-NMR



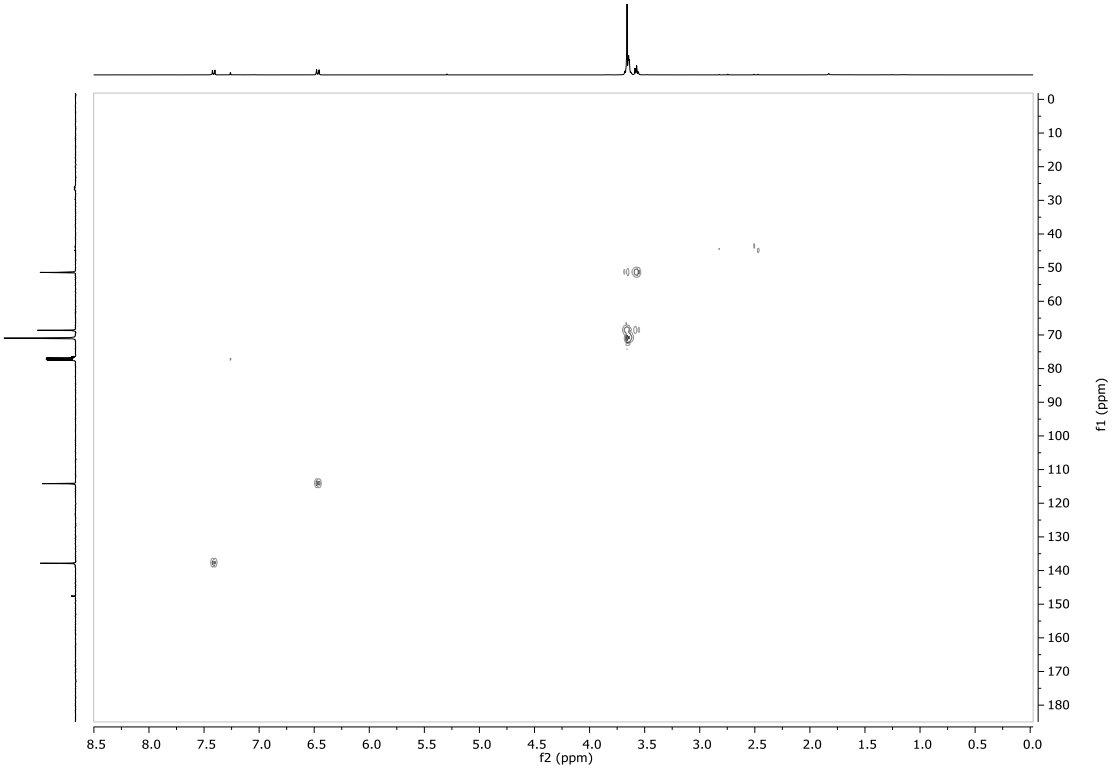
DEPT-135



g-COSY



g-HSQC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f1 (ppm)
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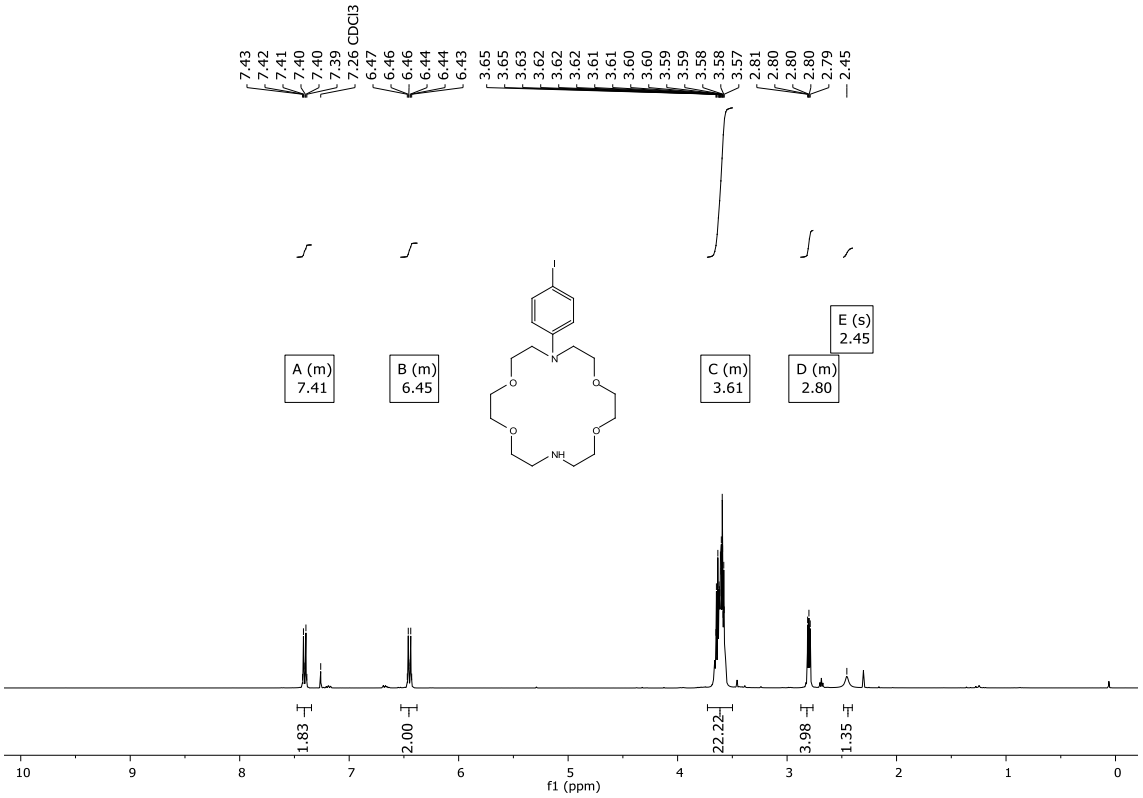
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

N-(4-iodophenyl)-1,10-diaza-18-crown-6 (9b)

^{1}H-NMR



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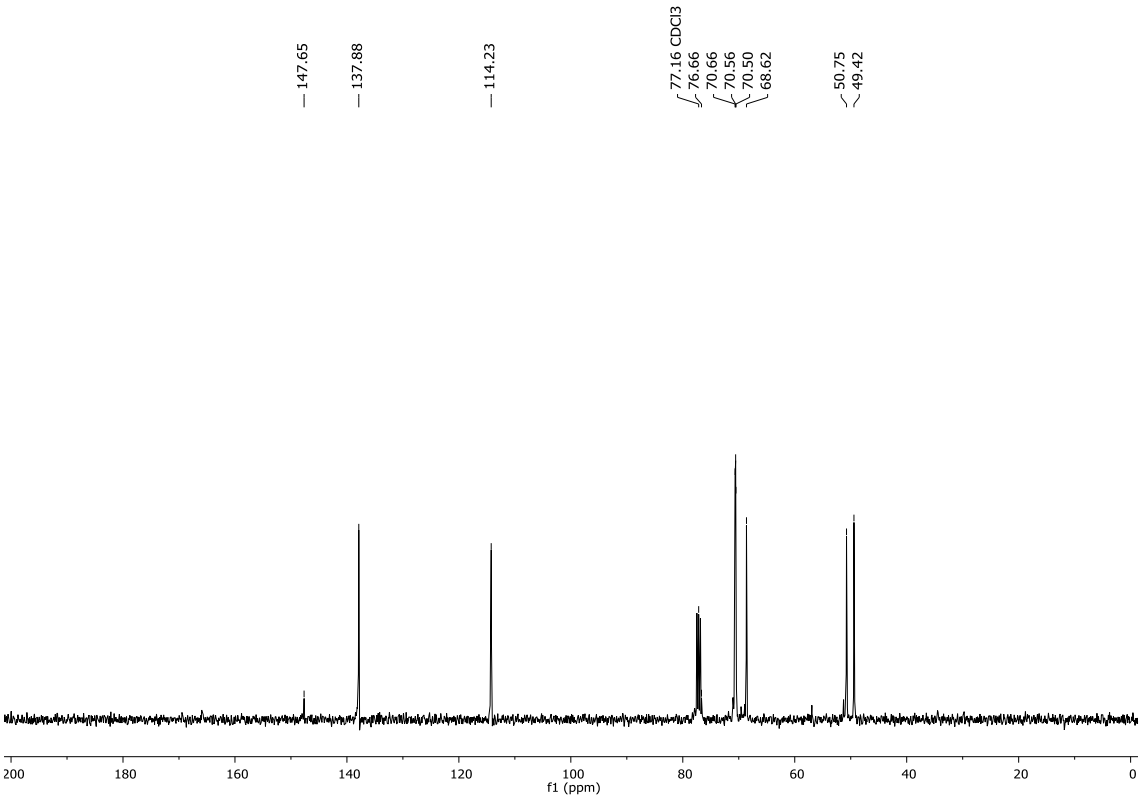
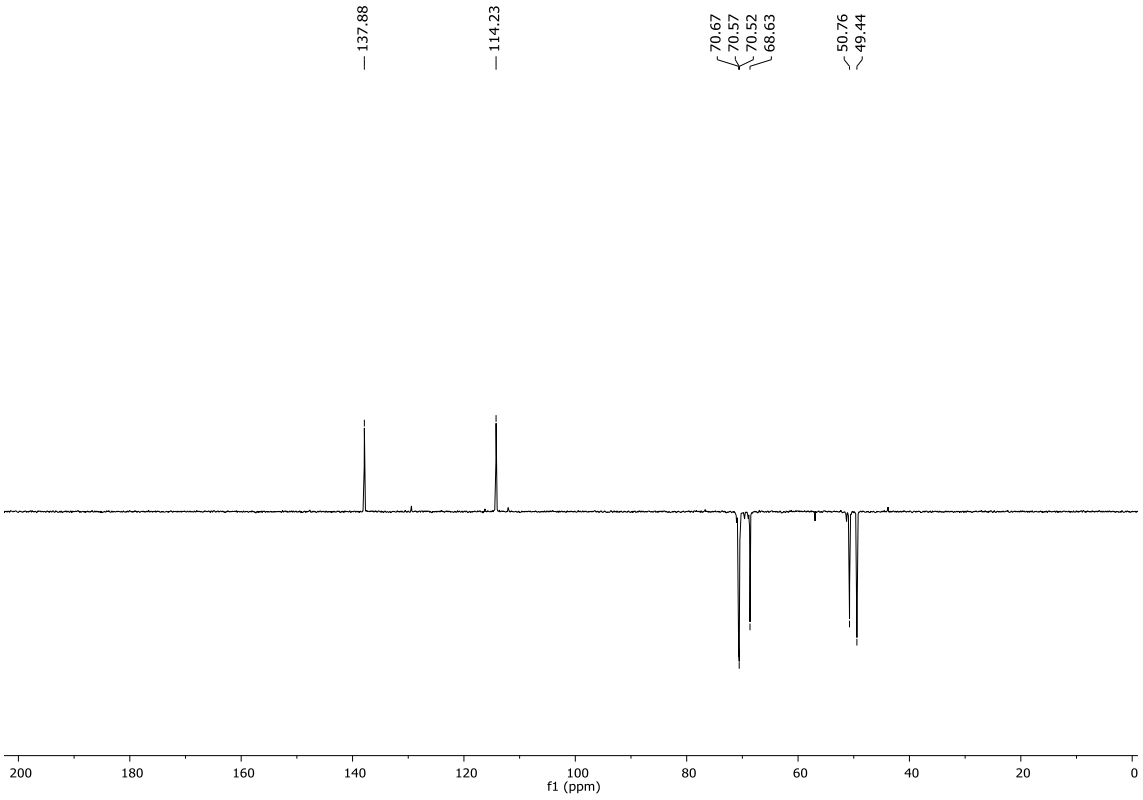
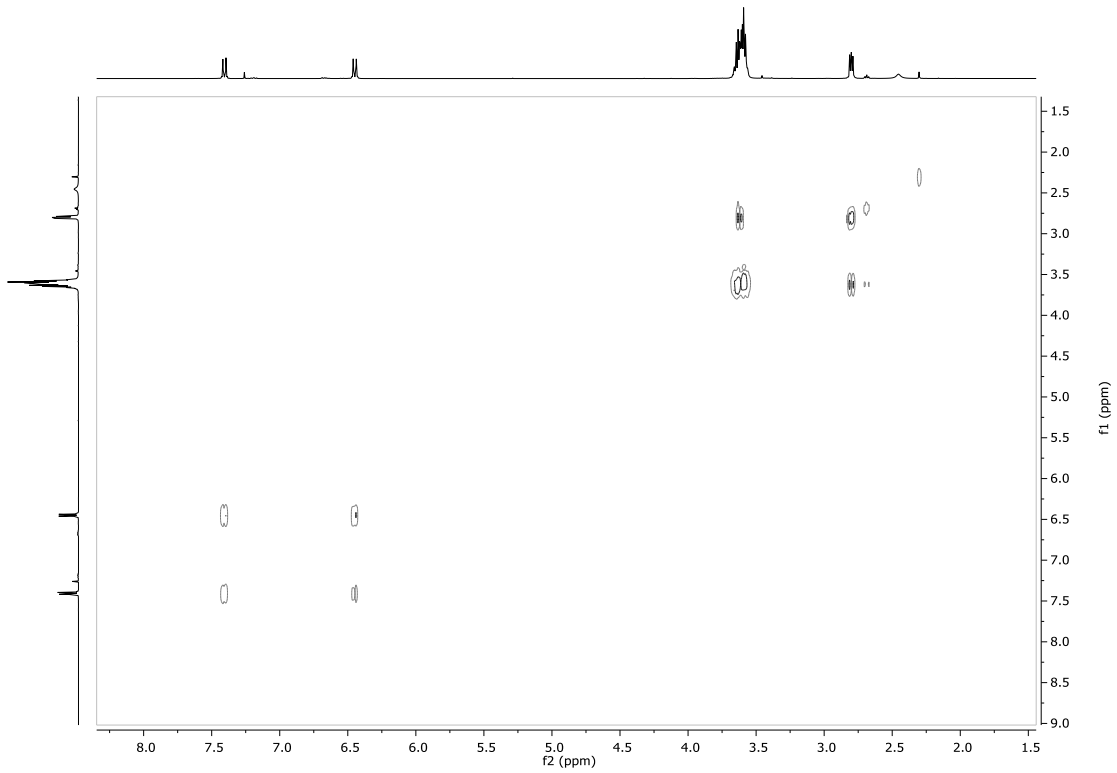


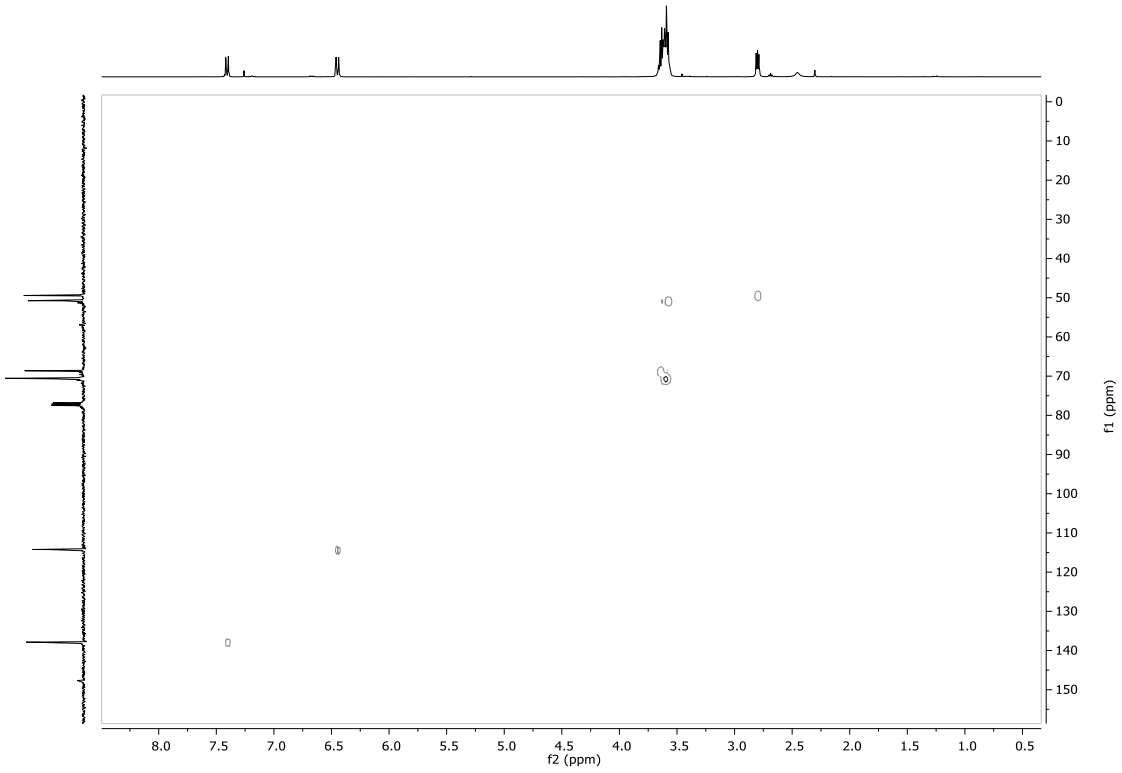
DEPT-135



g-COSY

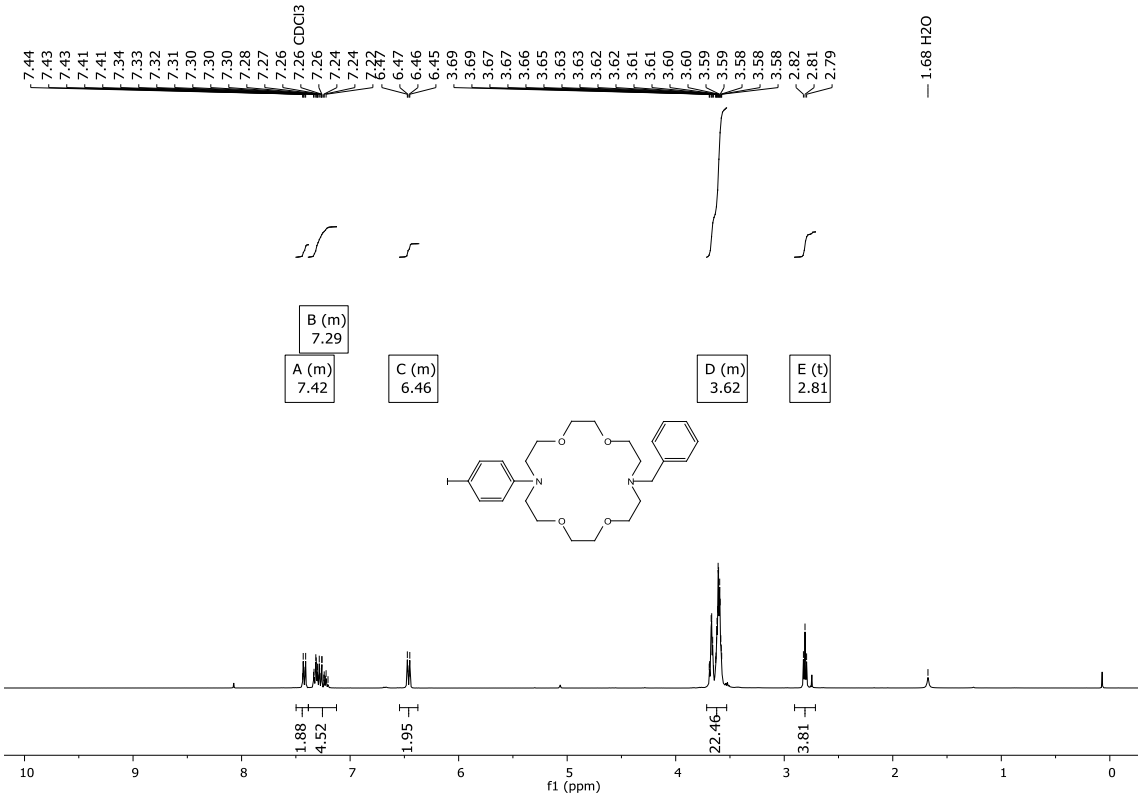


g-HSQC

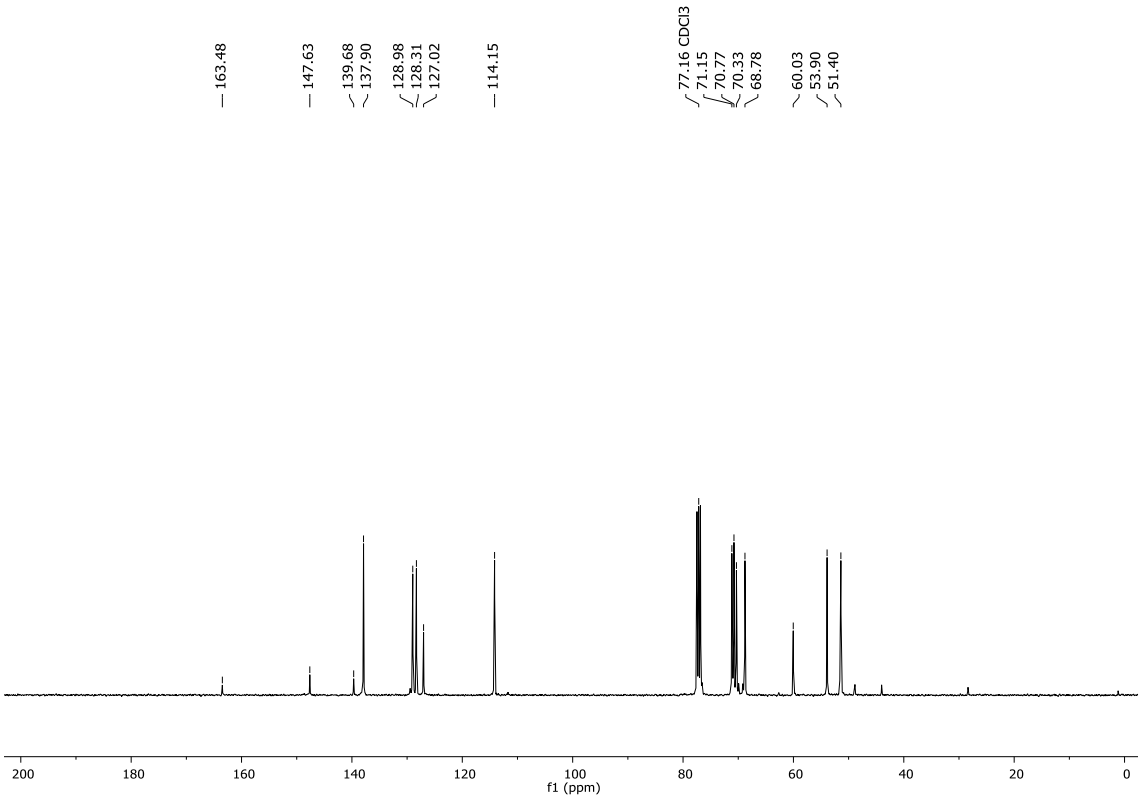


7-Benzyl-16-(4-iodophenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (9c)

^{1}H-NMR



^{13}C-NMR



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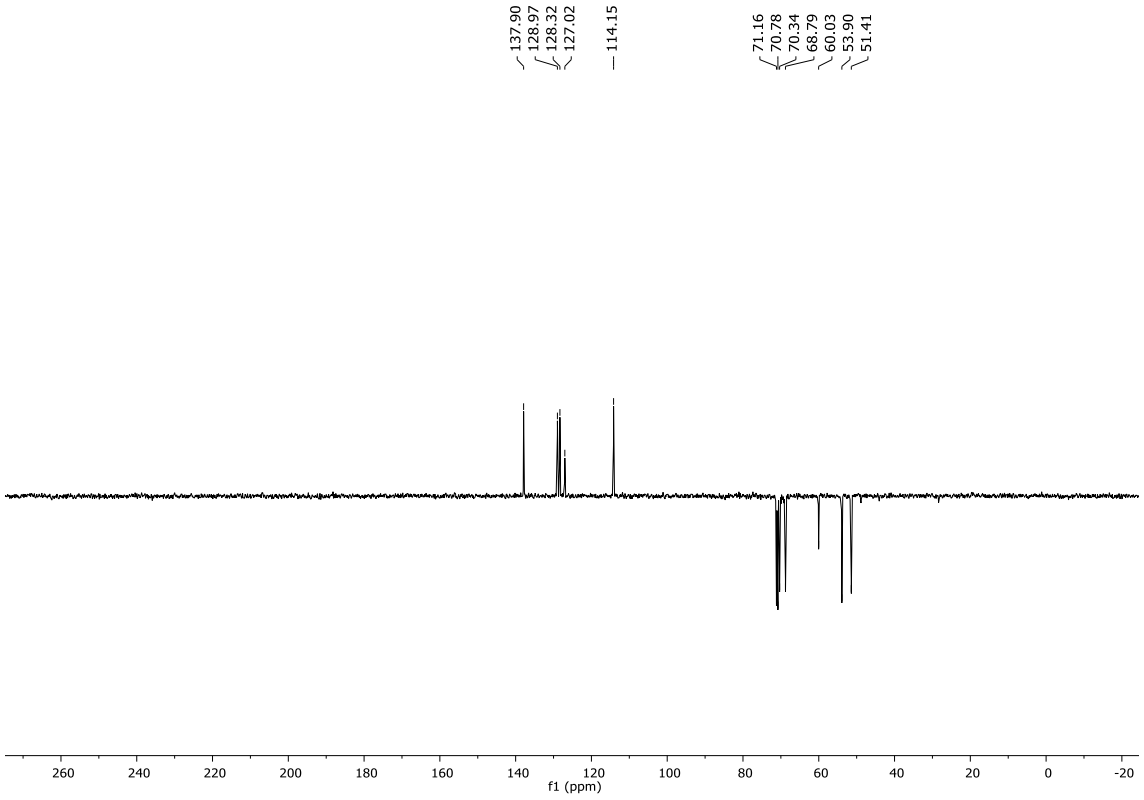
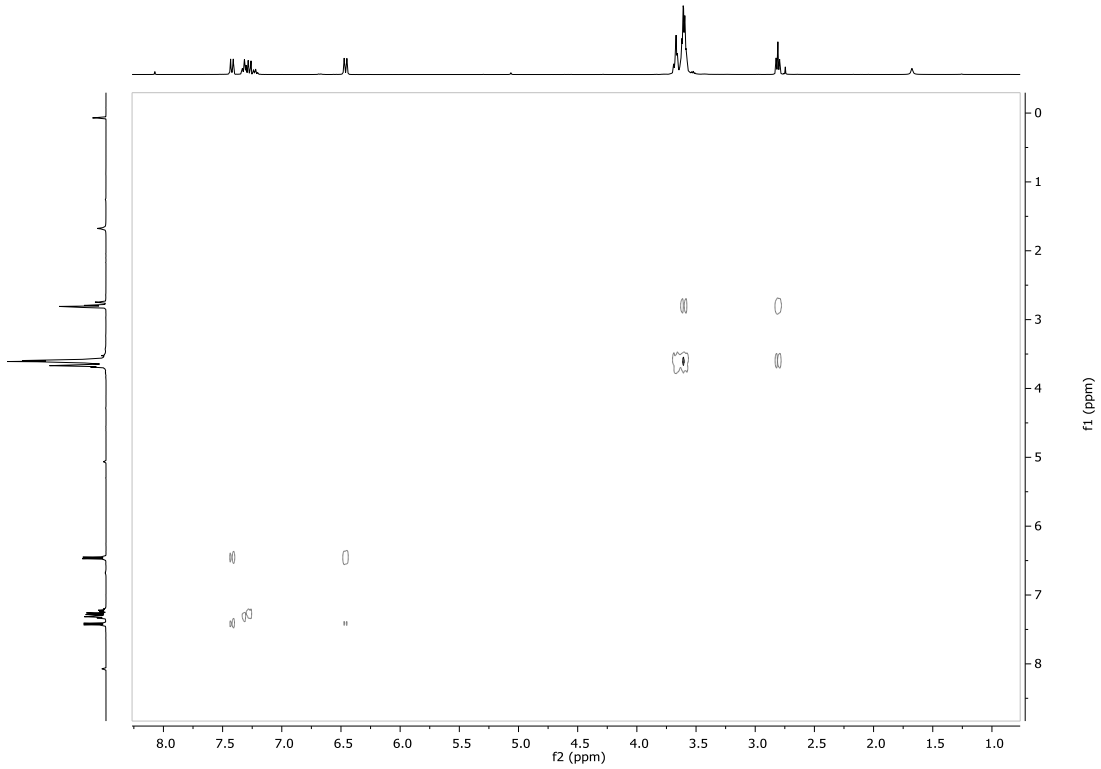
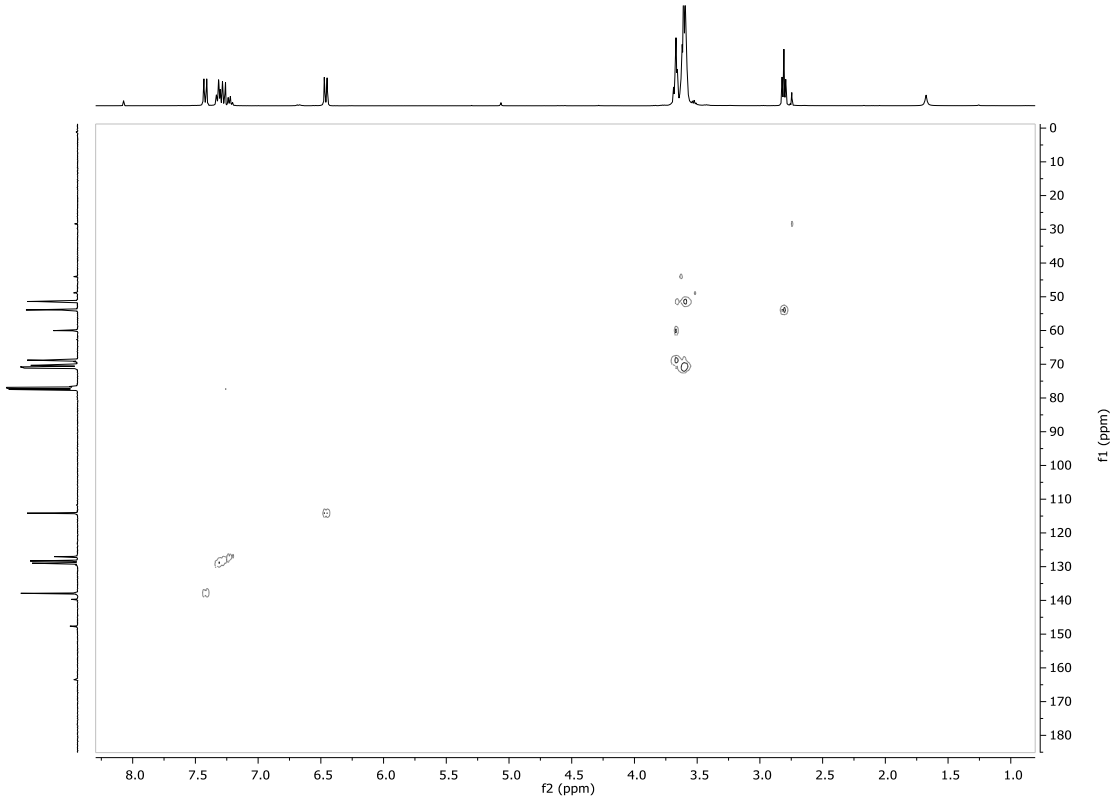


g-COSY

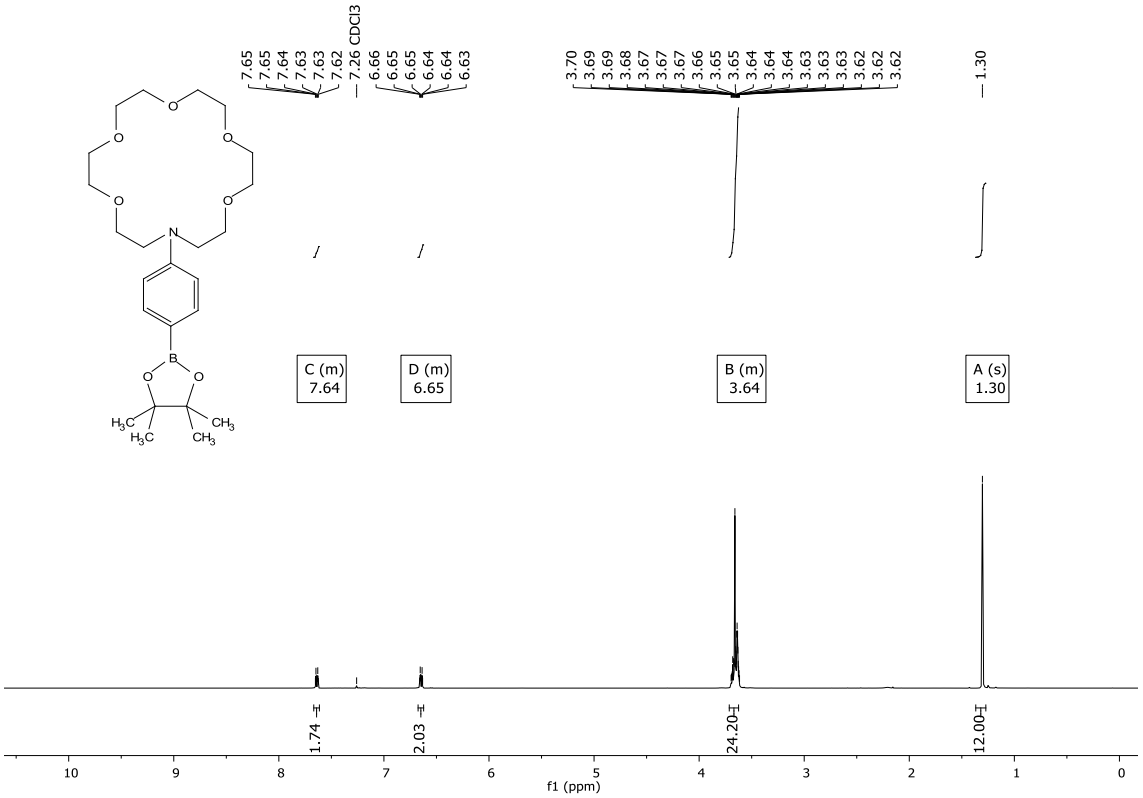


g-HSQC

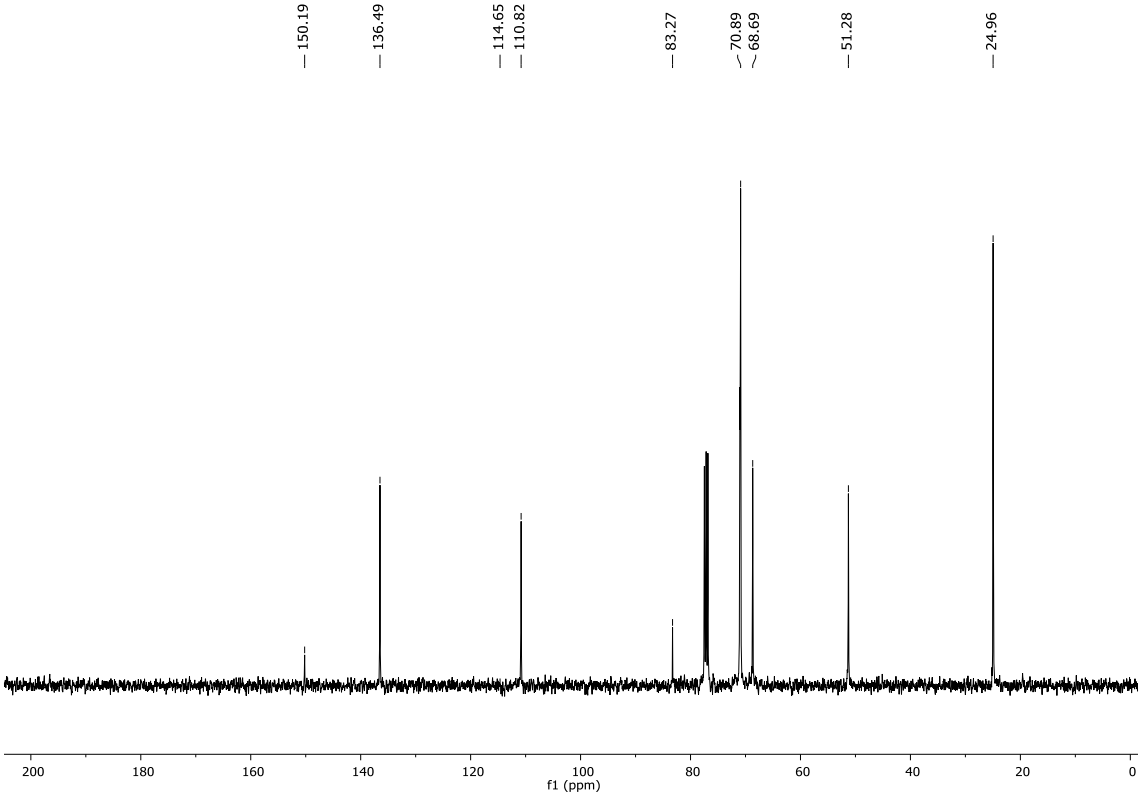


N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1-aza-18-crown-6 (10a)

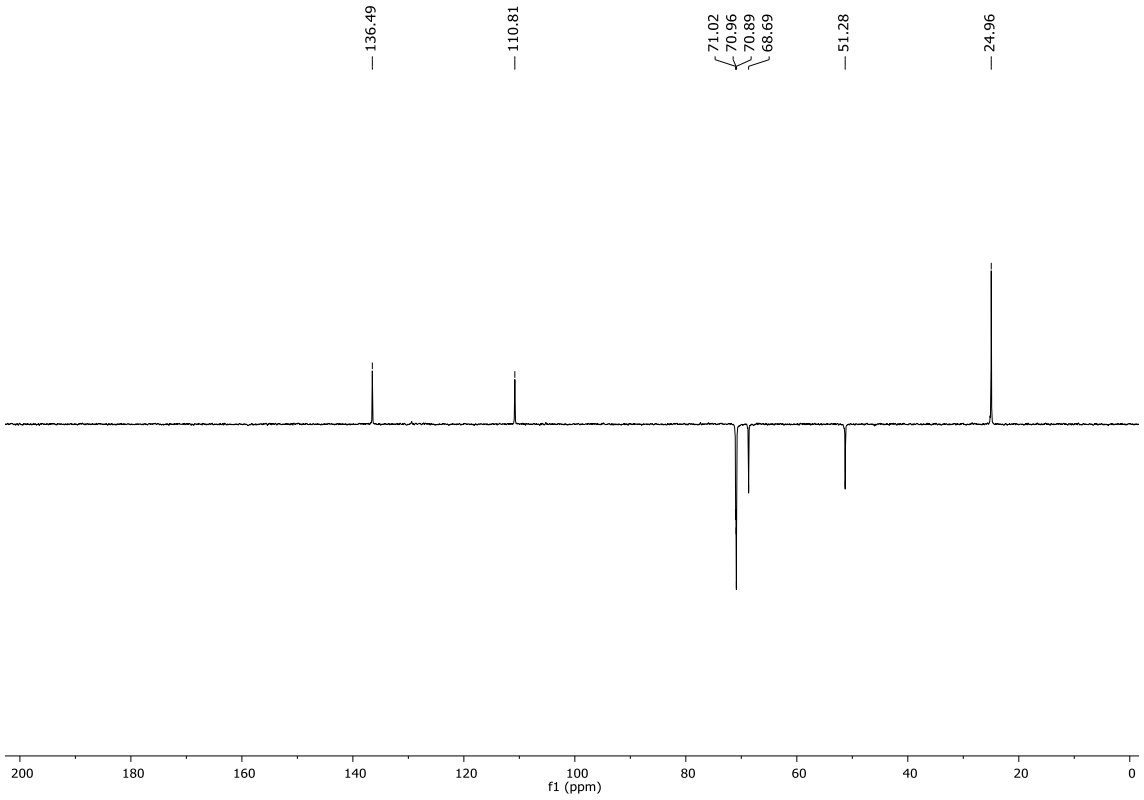
^{1}H-NMR



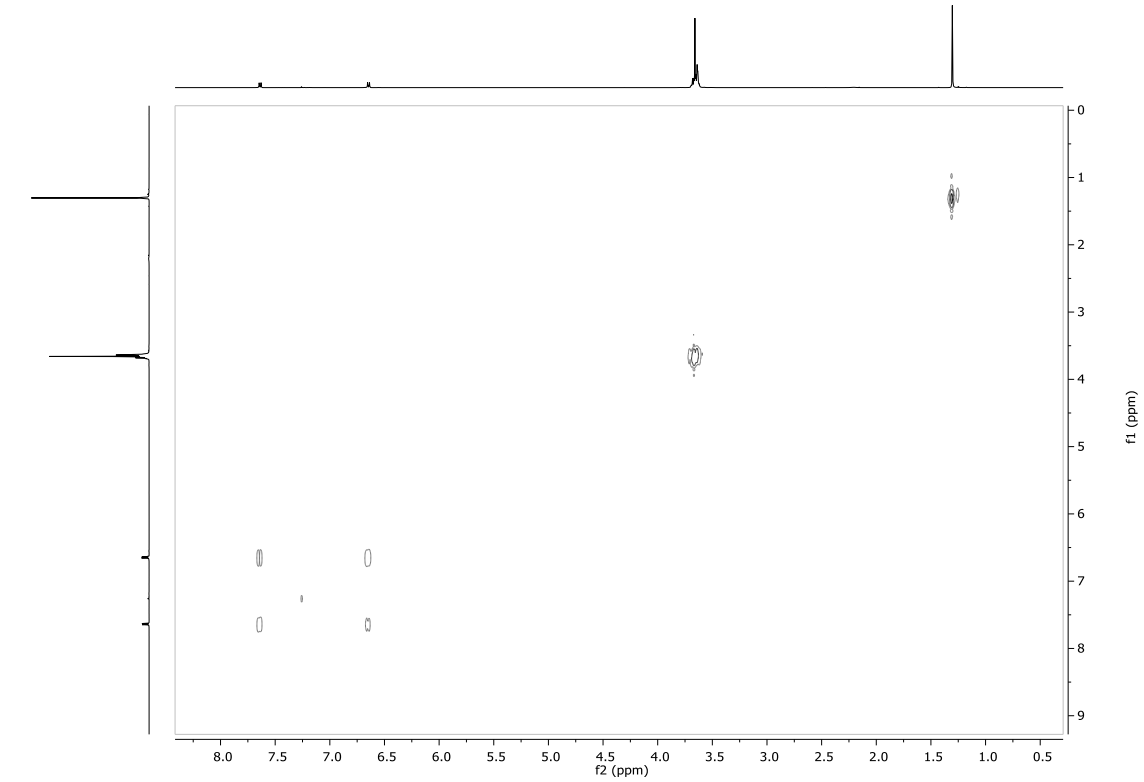
^{13}C-NMR



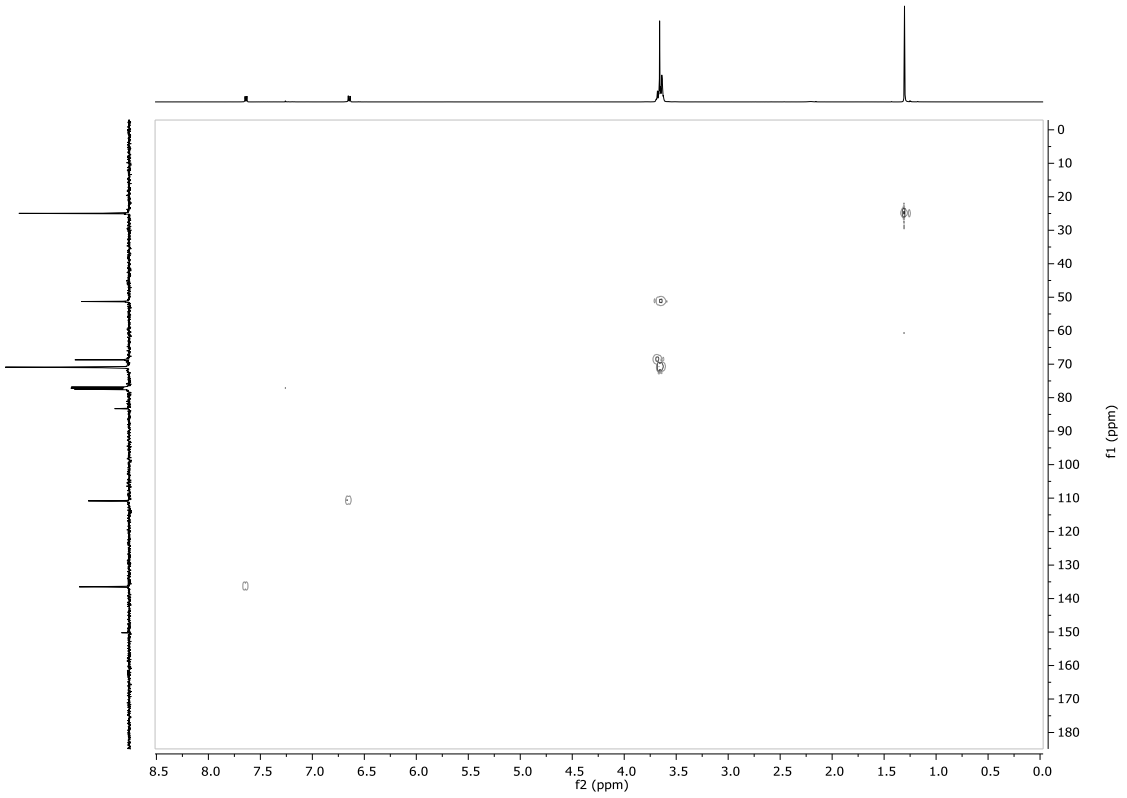
DEPT-135



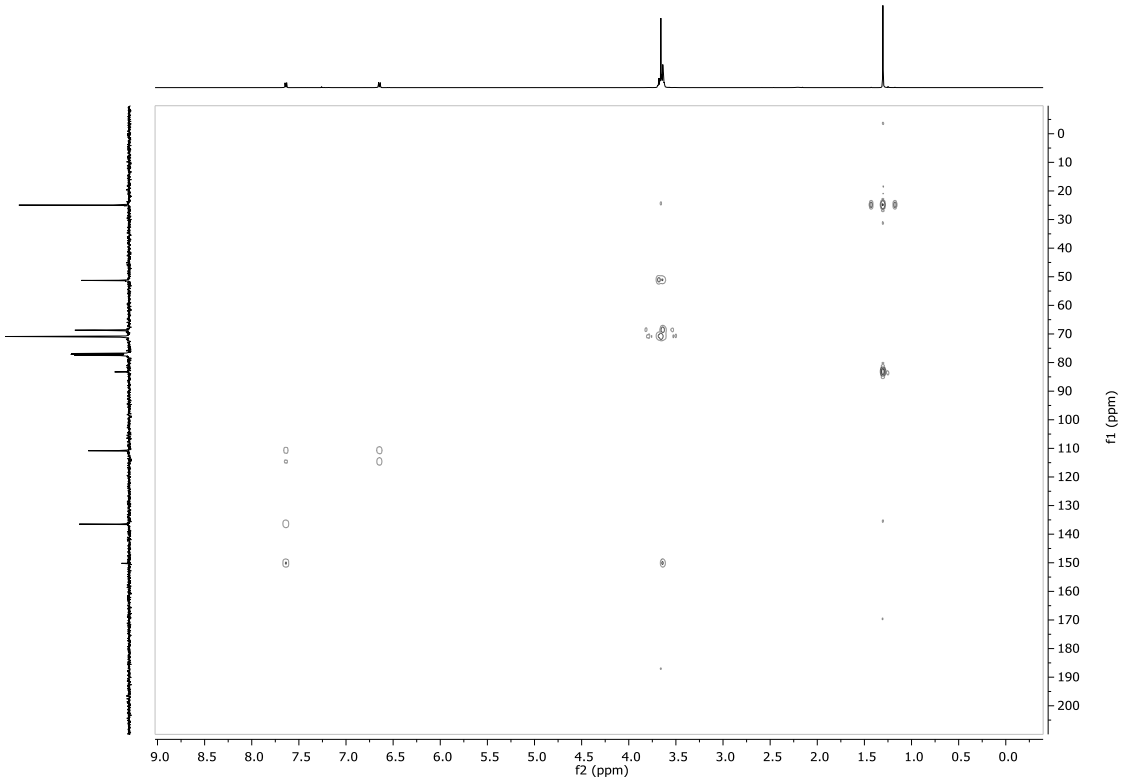
g-COSY



g-HSQC

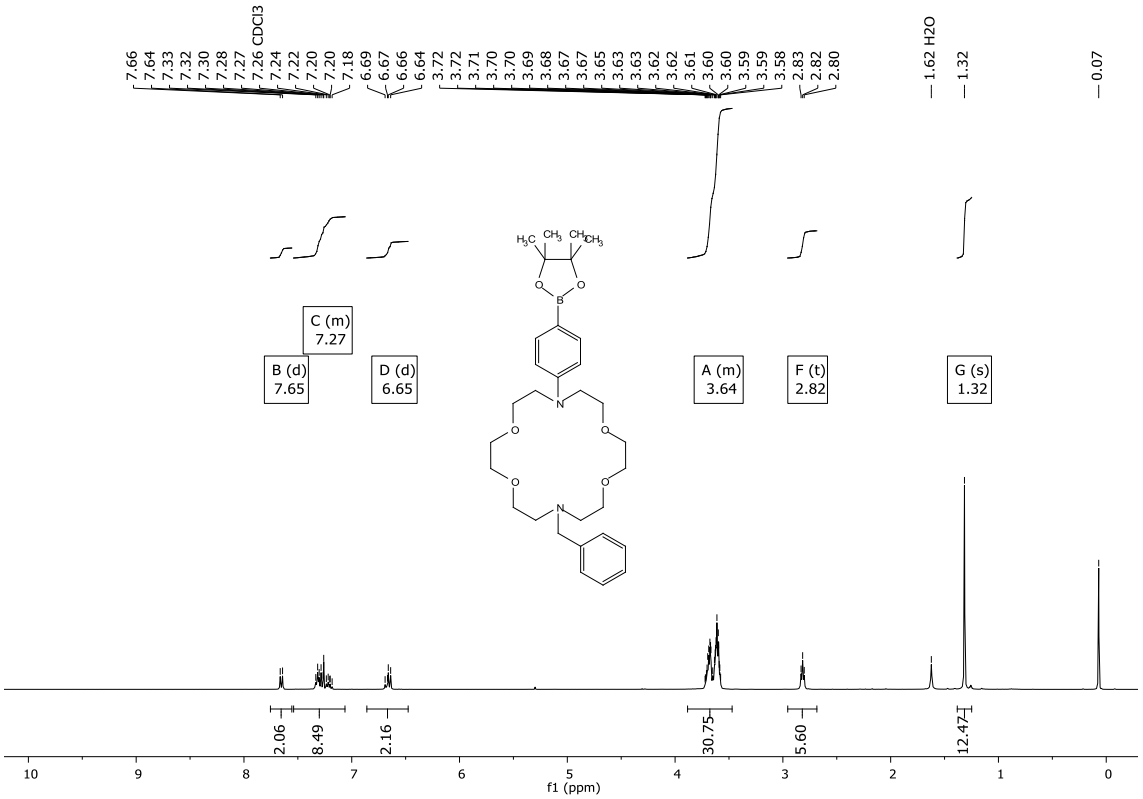


g-HMBC



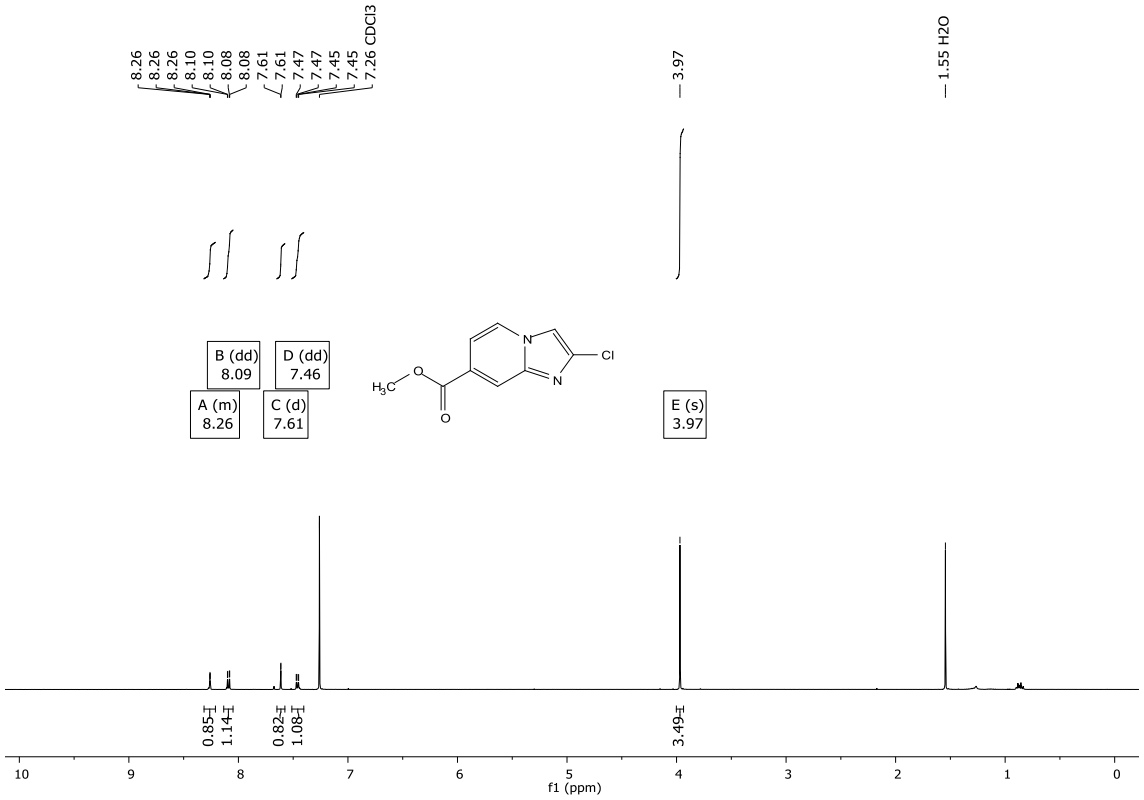
7-Benzyl-16-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (10b)

^{1}H-NMR



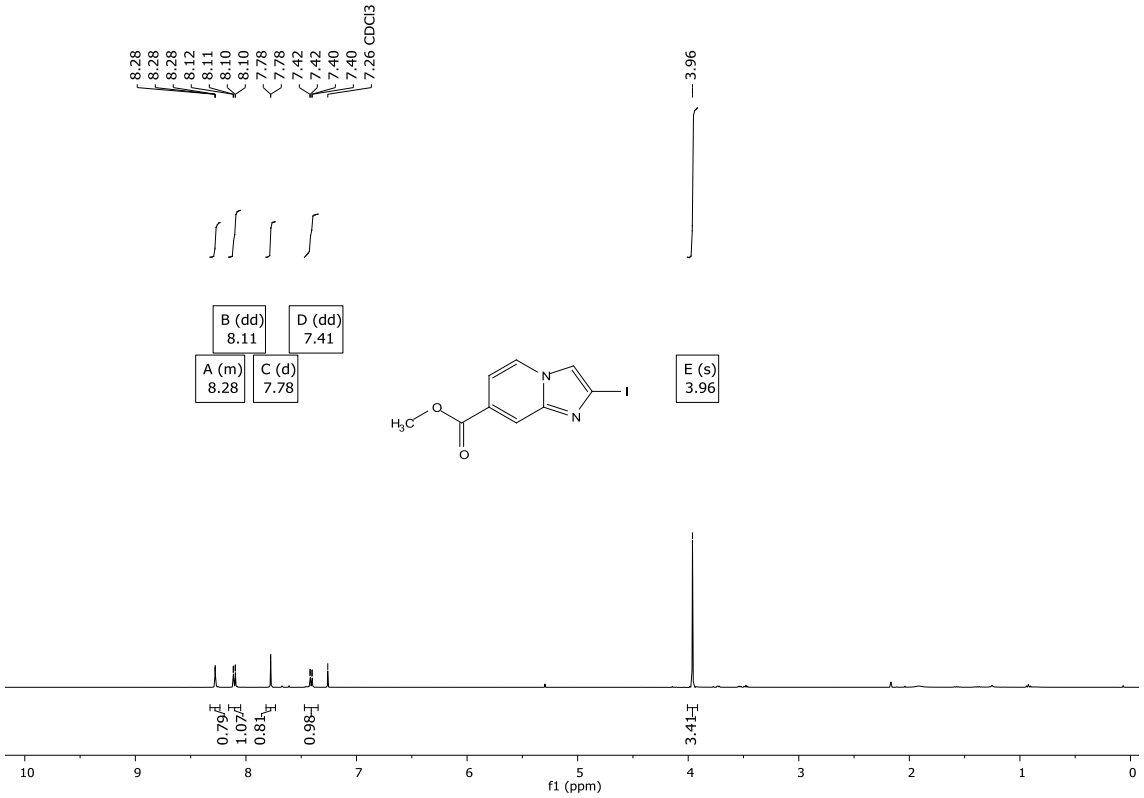
Methyl 2-chloroimidazo[1,2-*a*]pyridine-7-carboxylate (12a)

^{1}H-NMR

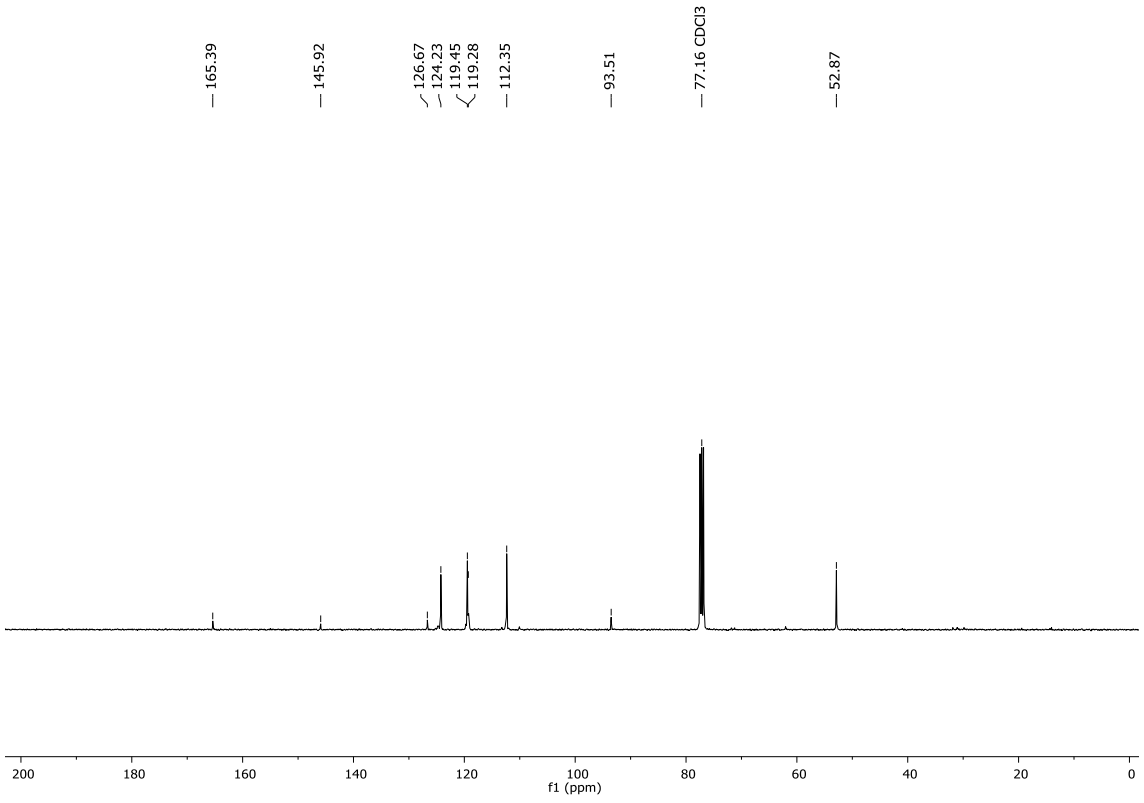


Methyl 2-iodoimidazo[1,2-*a*]pyridine-7-carboxylate (12b)

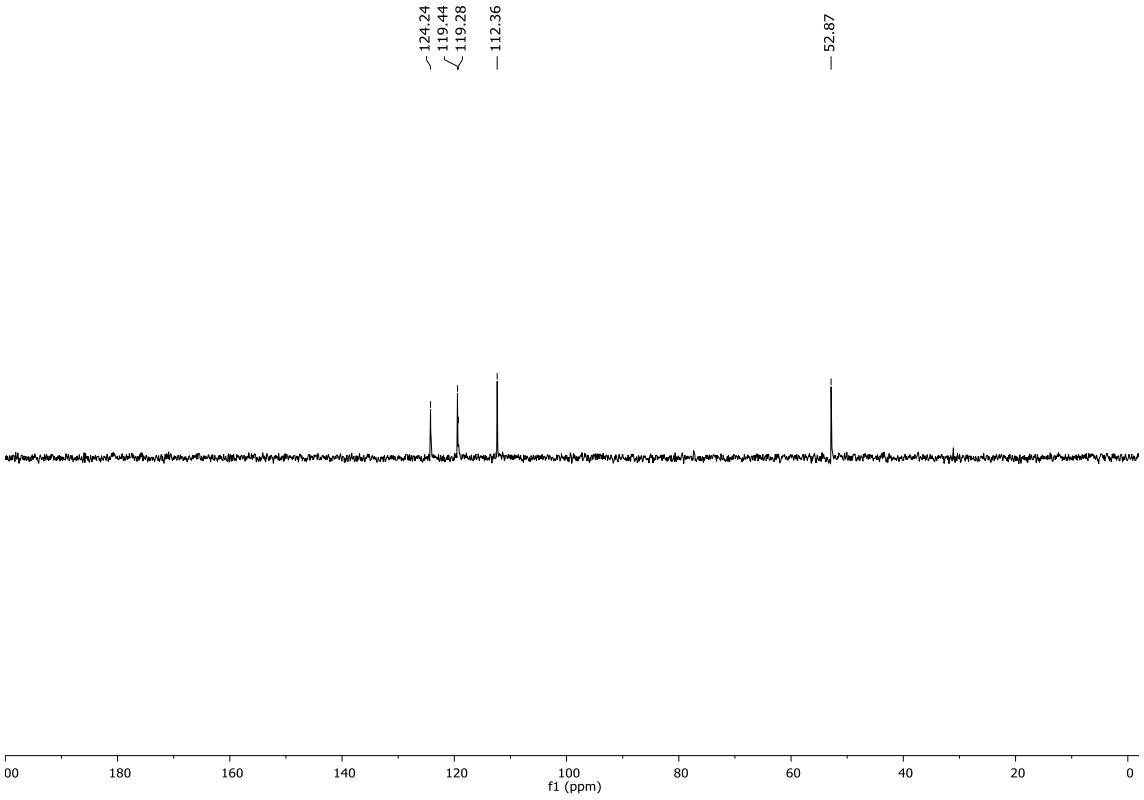
^{1}H-NMR



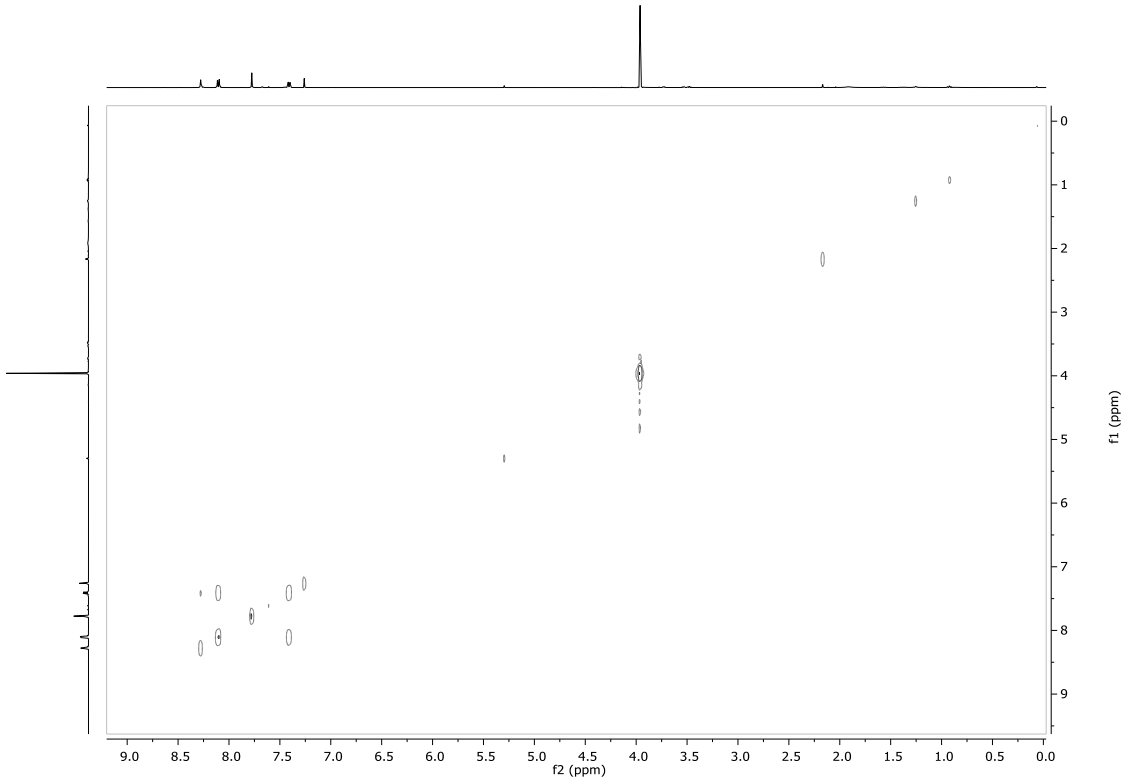
^{13}C-NMR



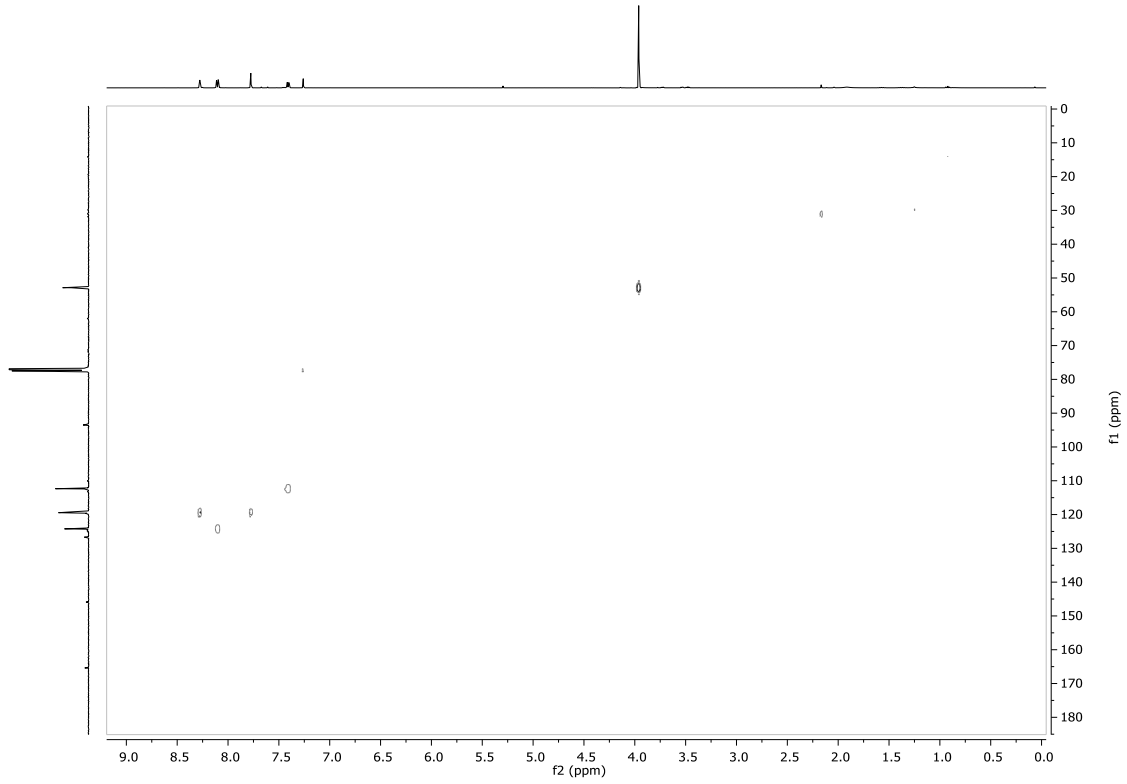
DEPT-135



g-COSY

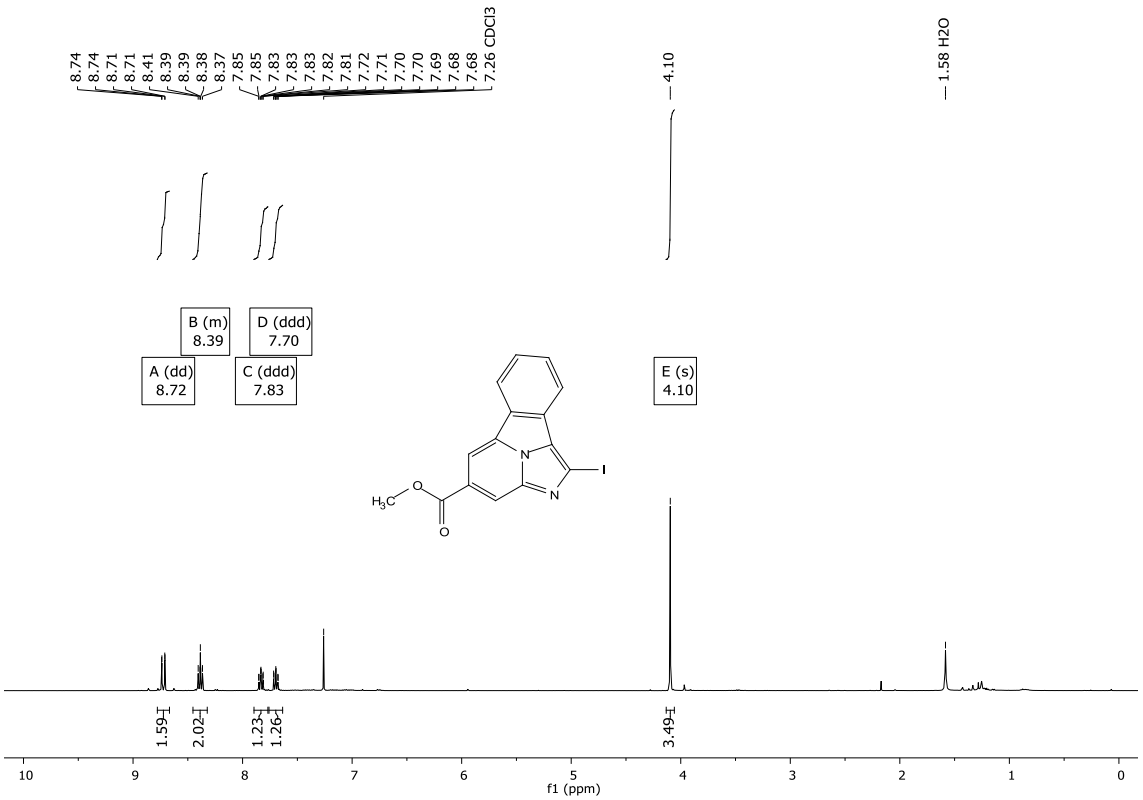


g-HSQC

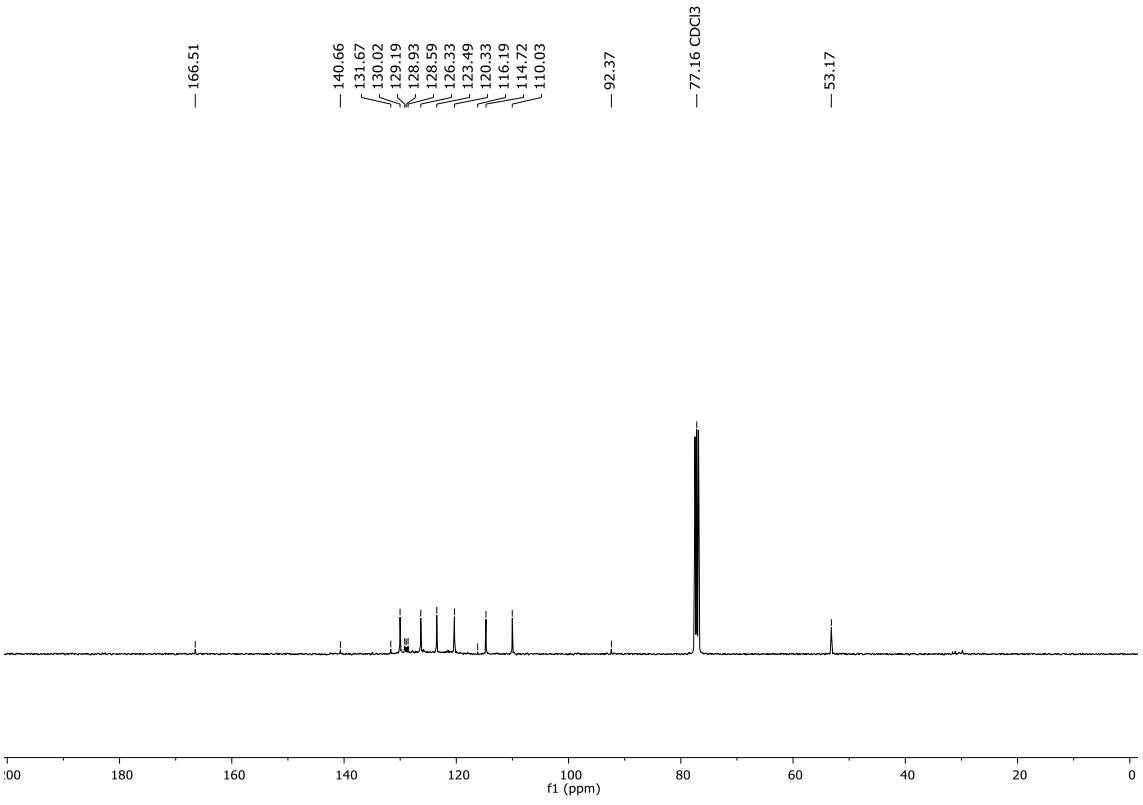


Methyl 1-iodobenzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate (13)

^{1}H-NMR



^{13}C-NMR



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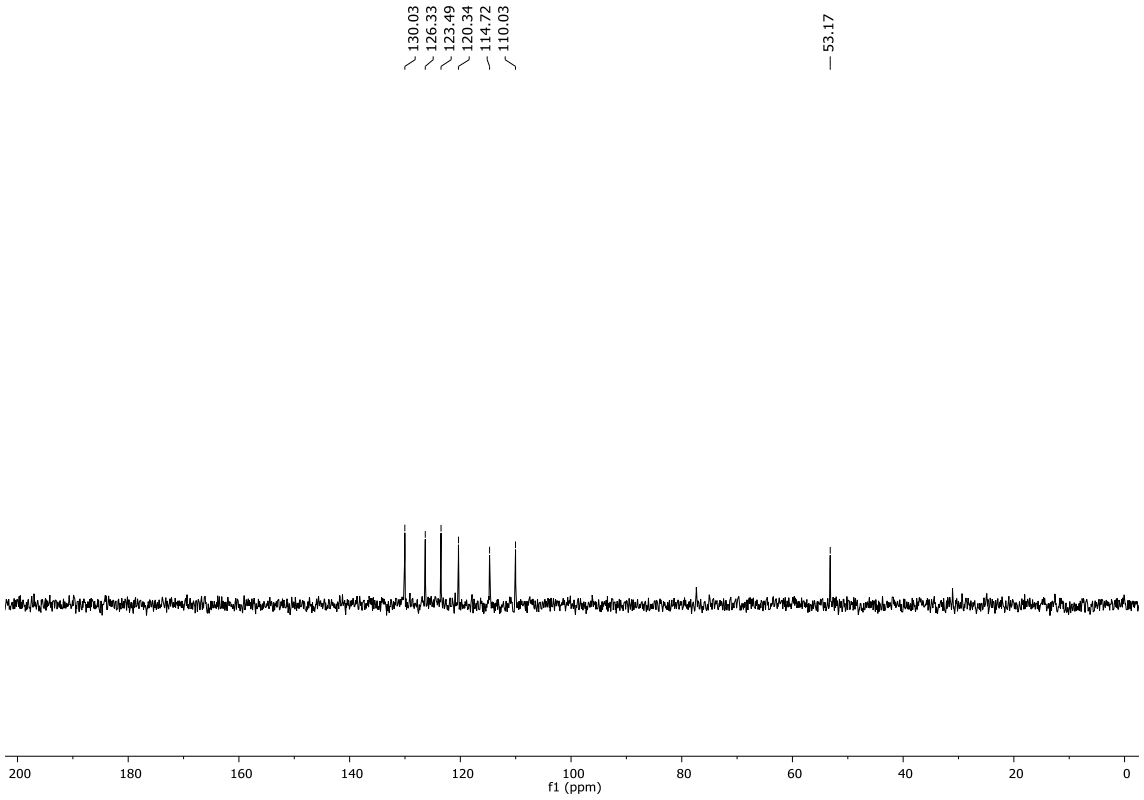
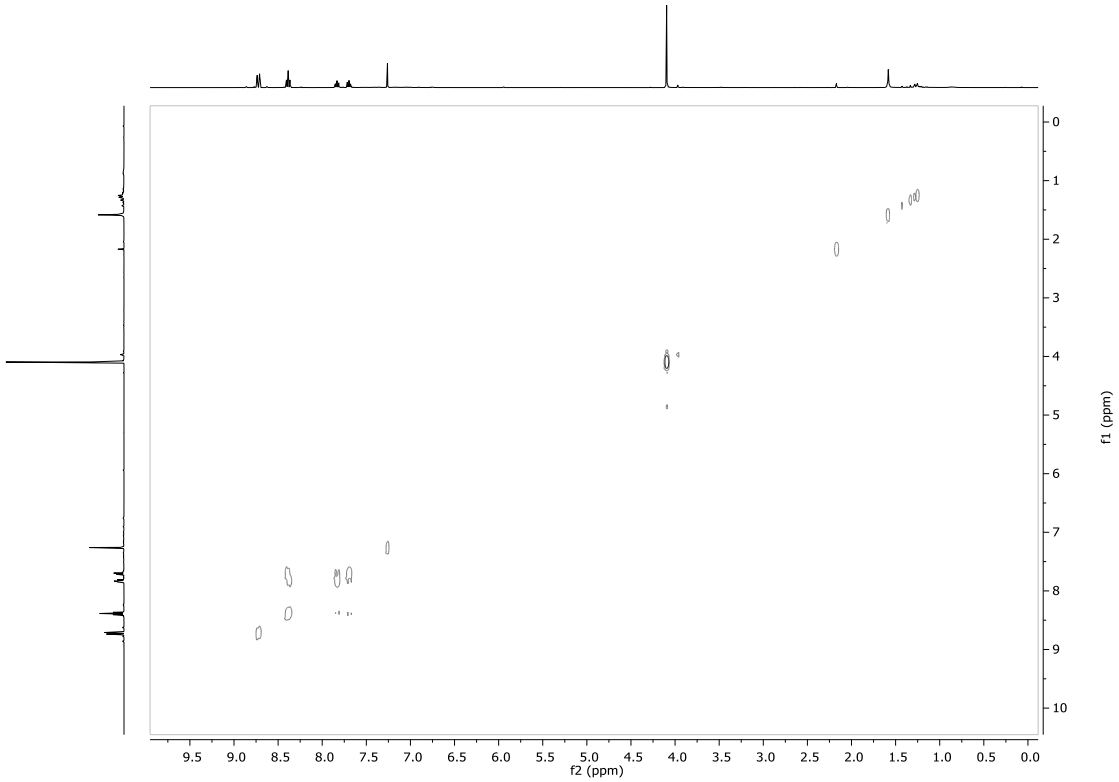
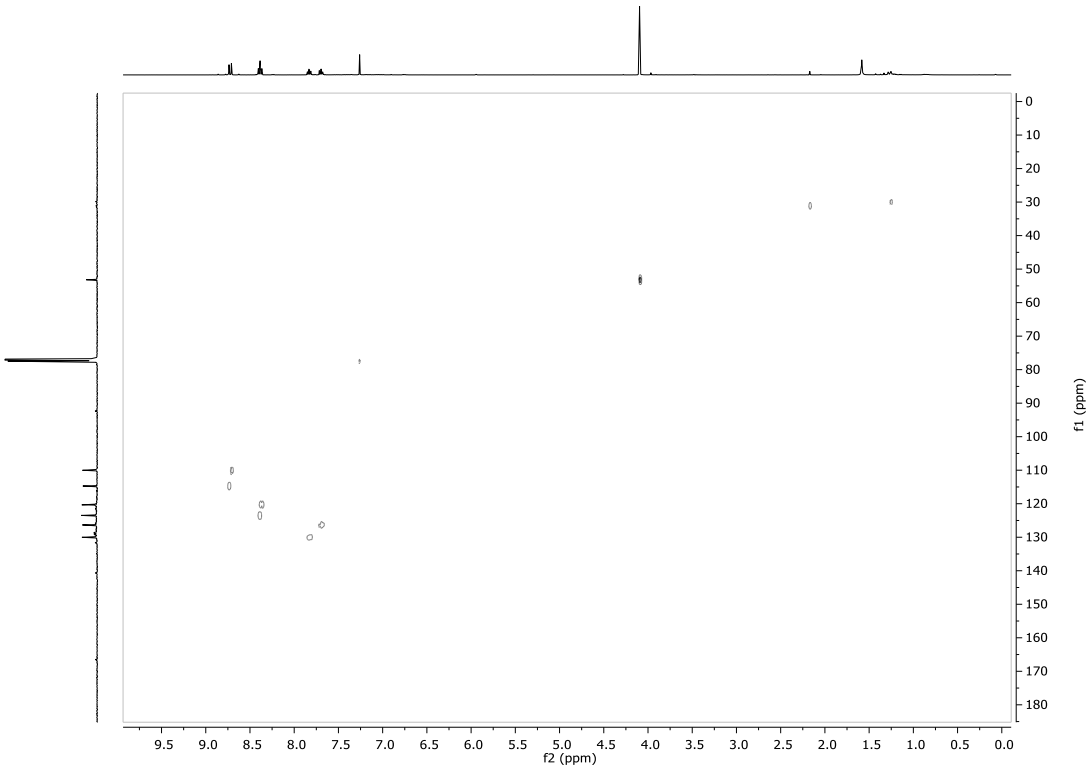


g-COSY

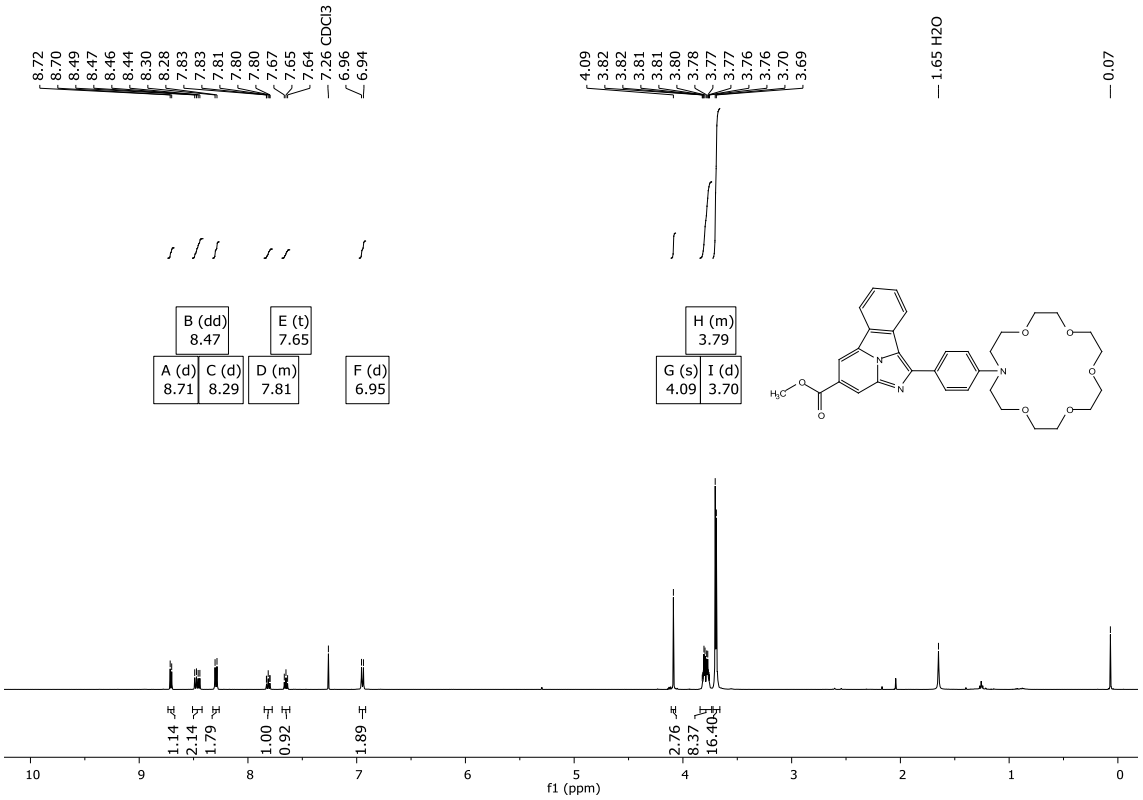


g-HSQC

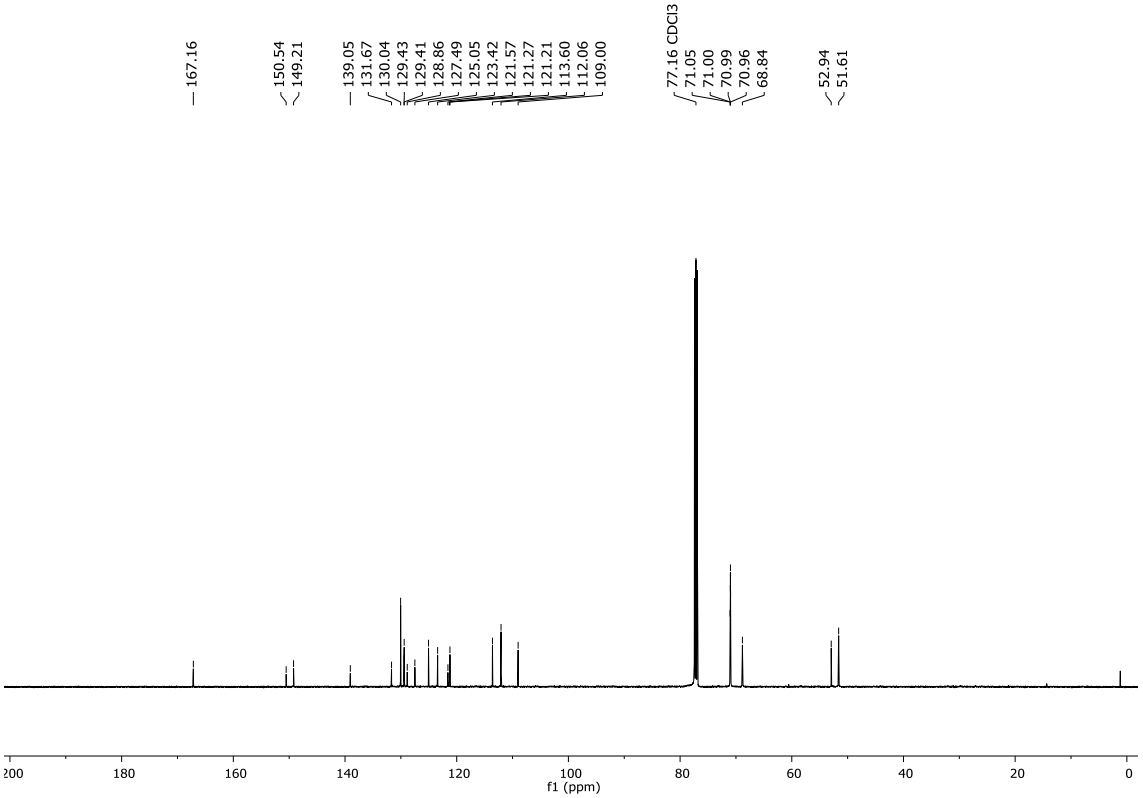


Methyl 1-(4-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate (14a)

^{1}H-NMR



^{13}C-NMR



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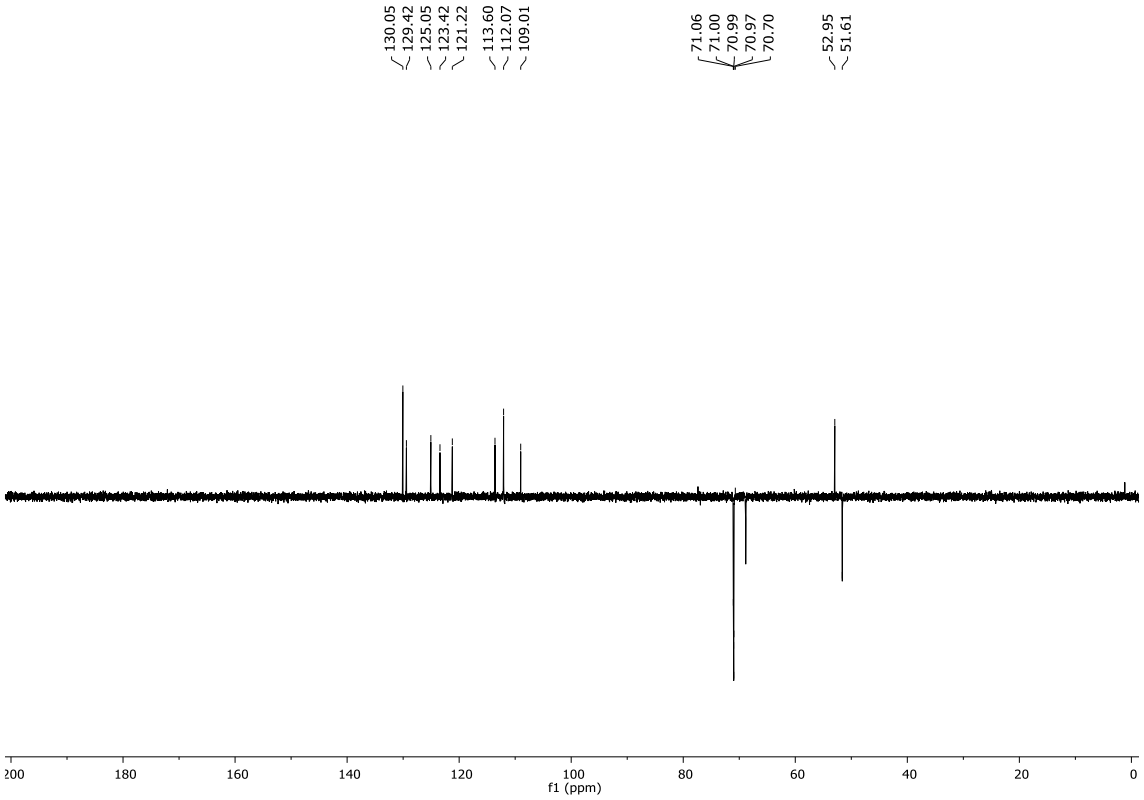
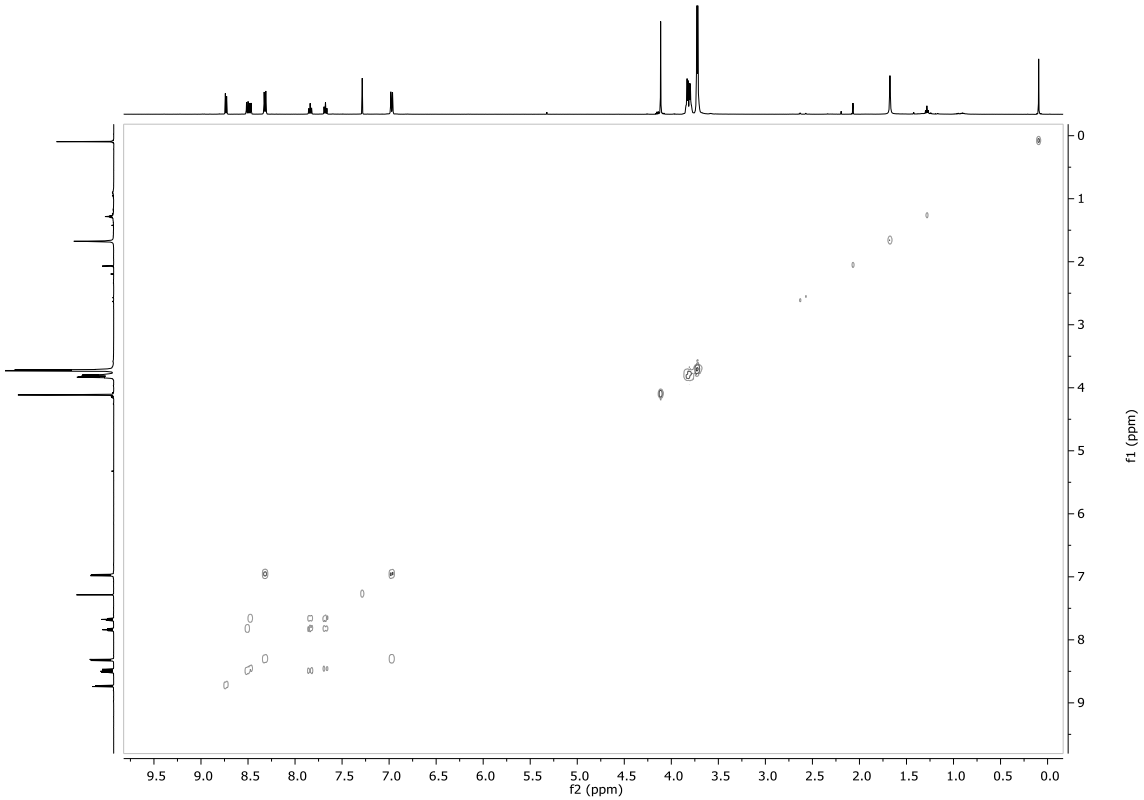
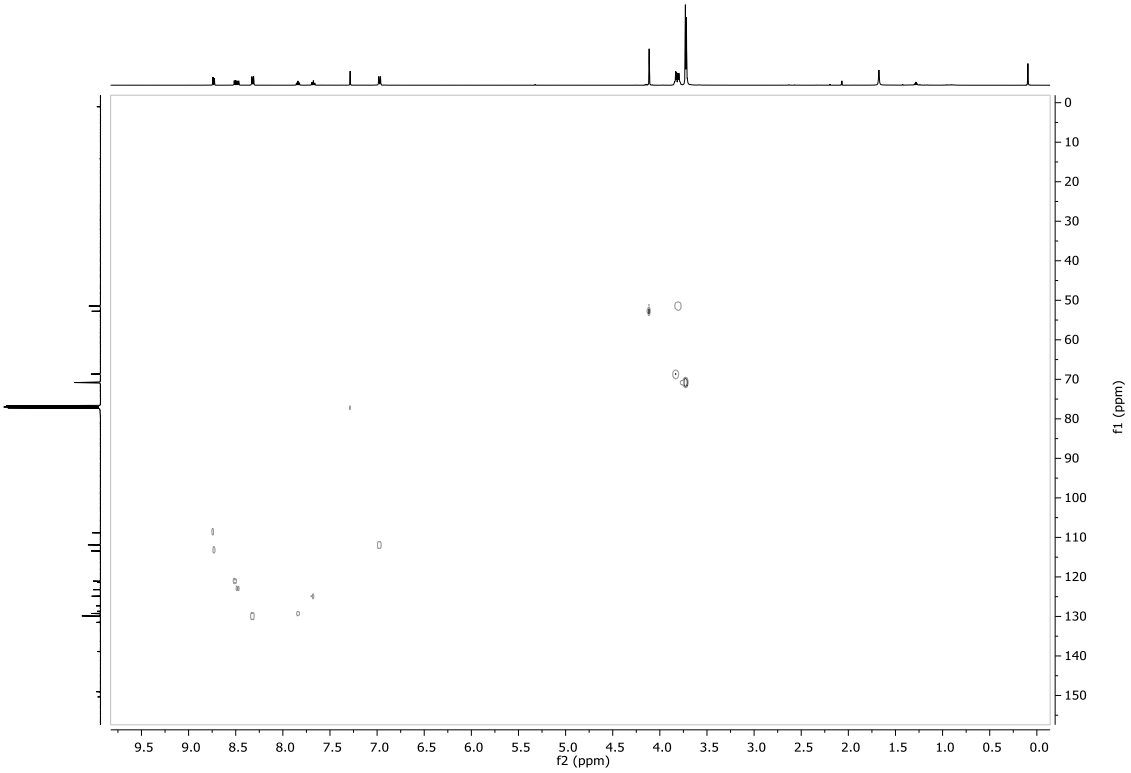


g-COSY

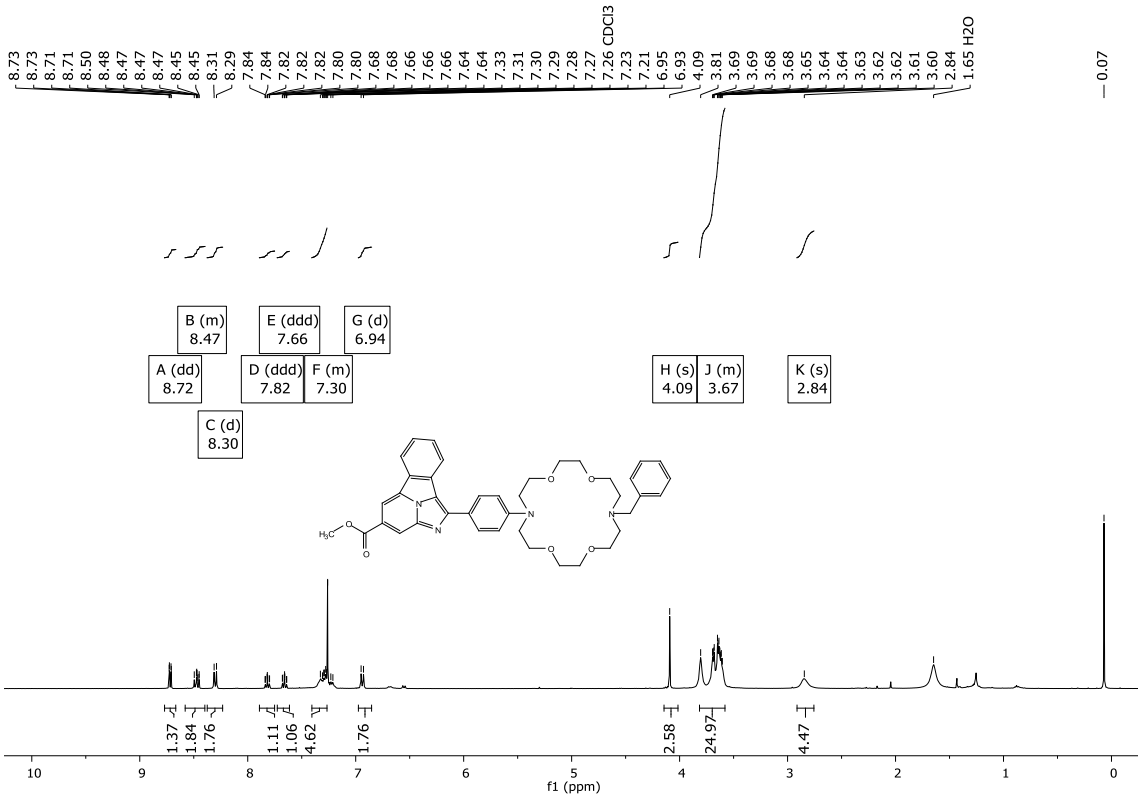


g-HSQC

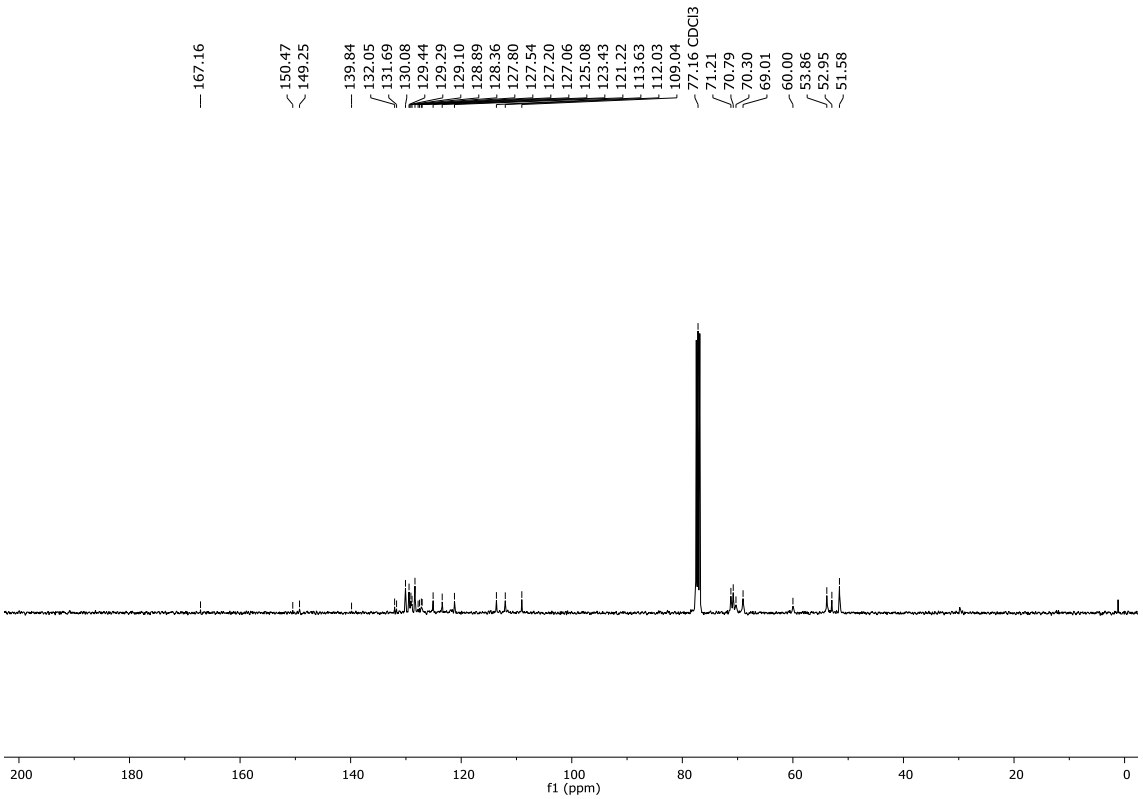


Methyl 1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate (14b)

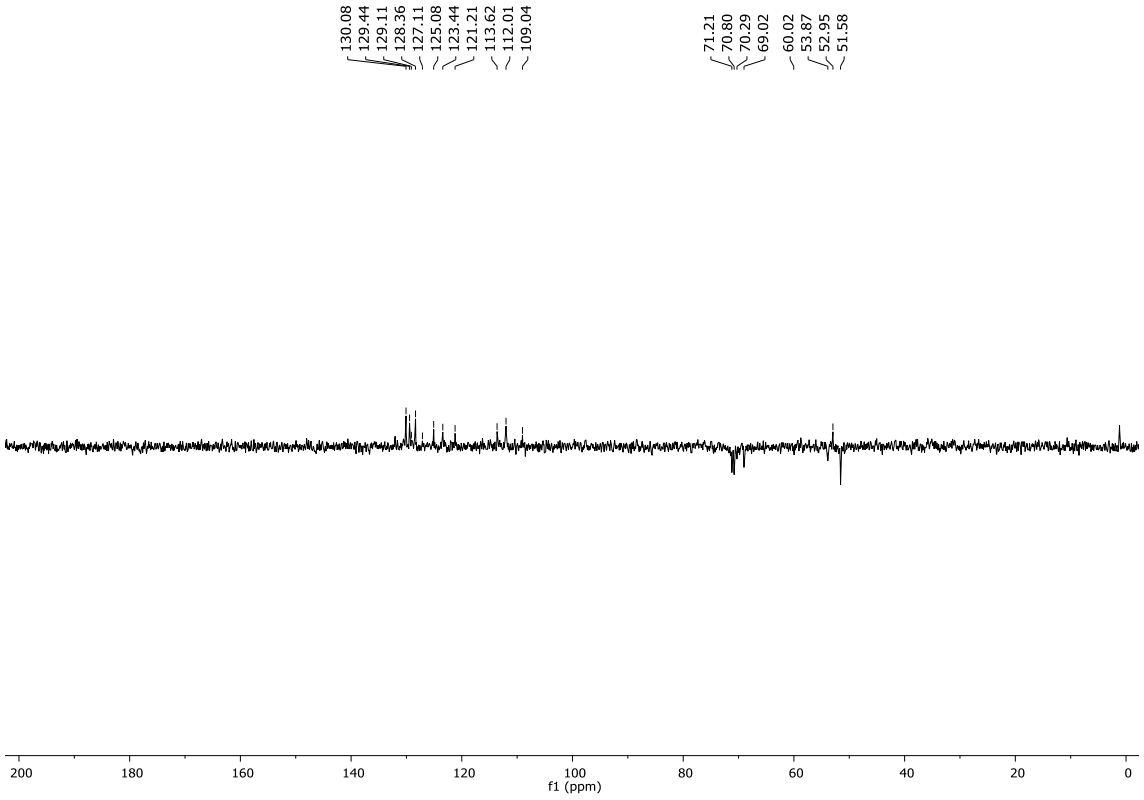
^{1}H-NMR



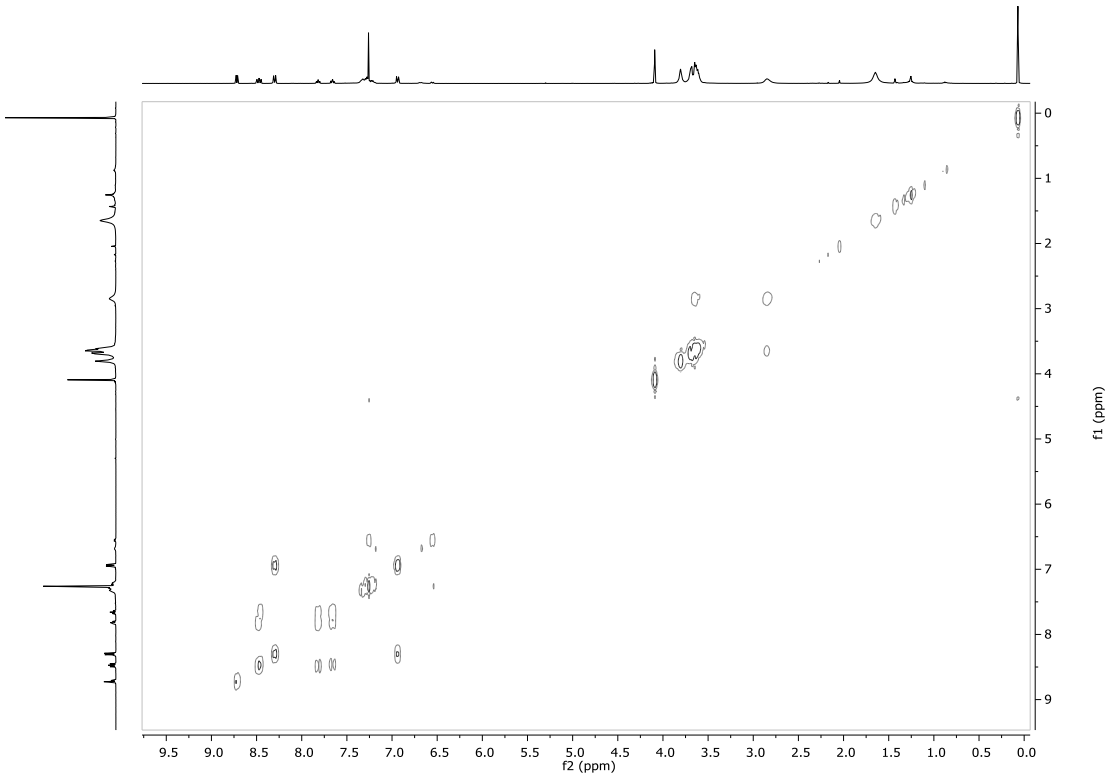
^{13}C-NMR



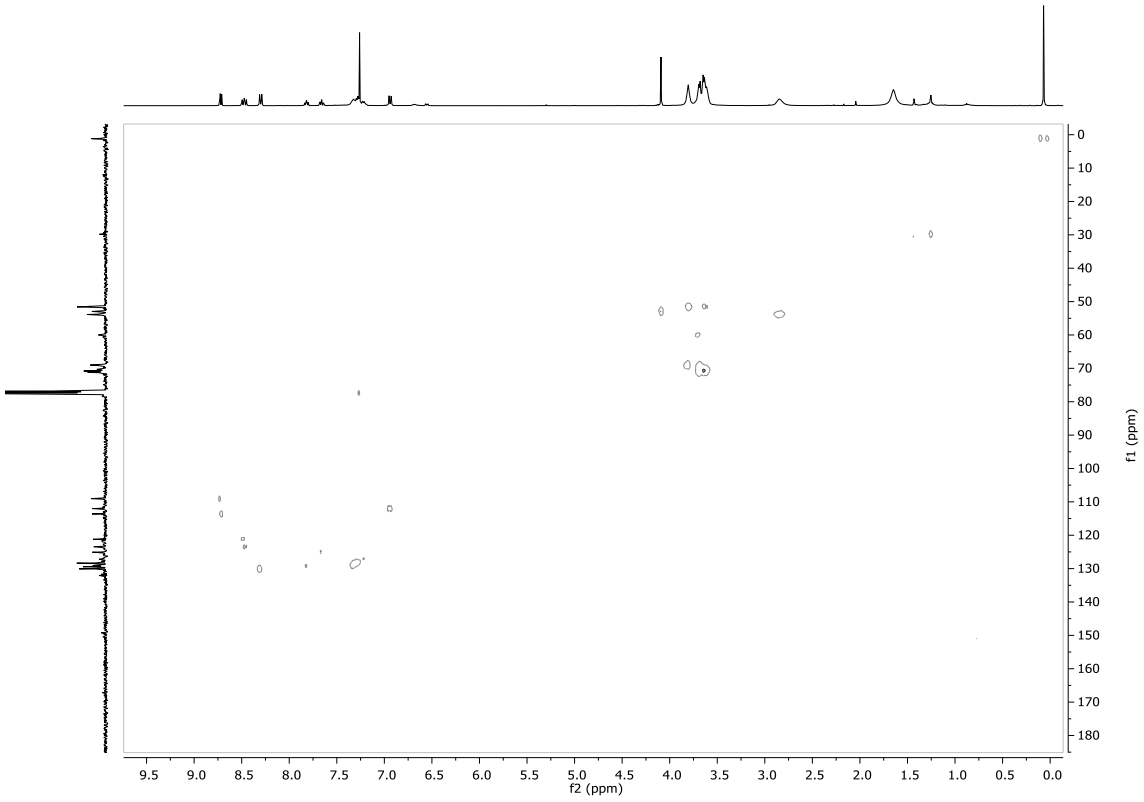
DEPT-135



g-COSY

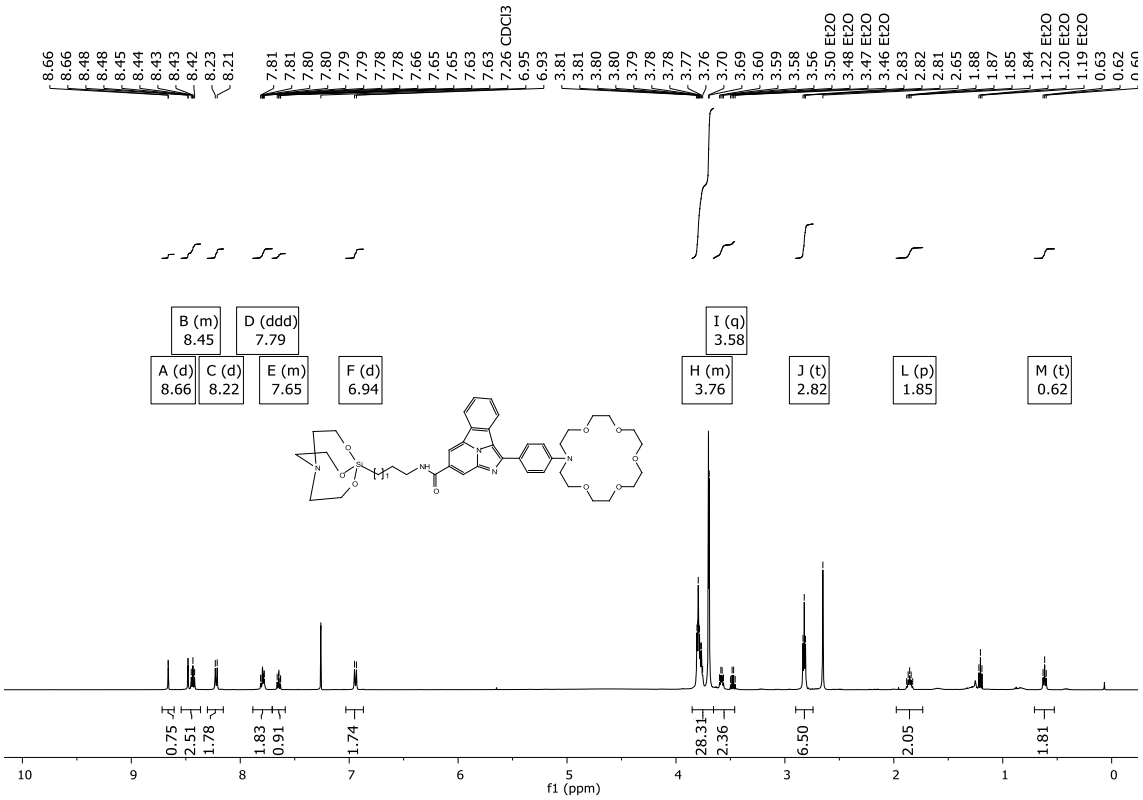


g-HSQC

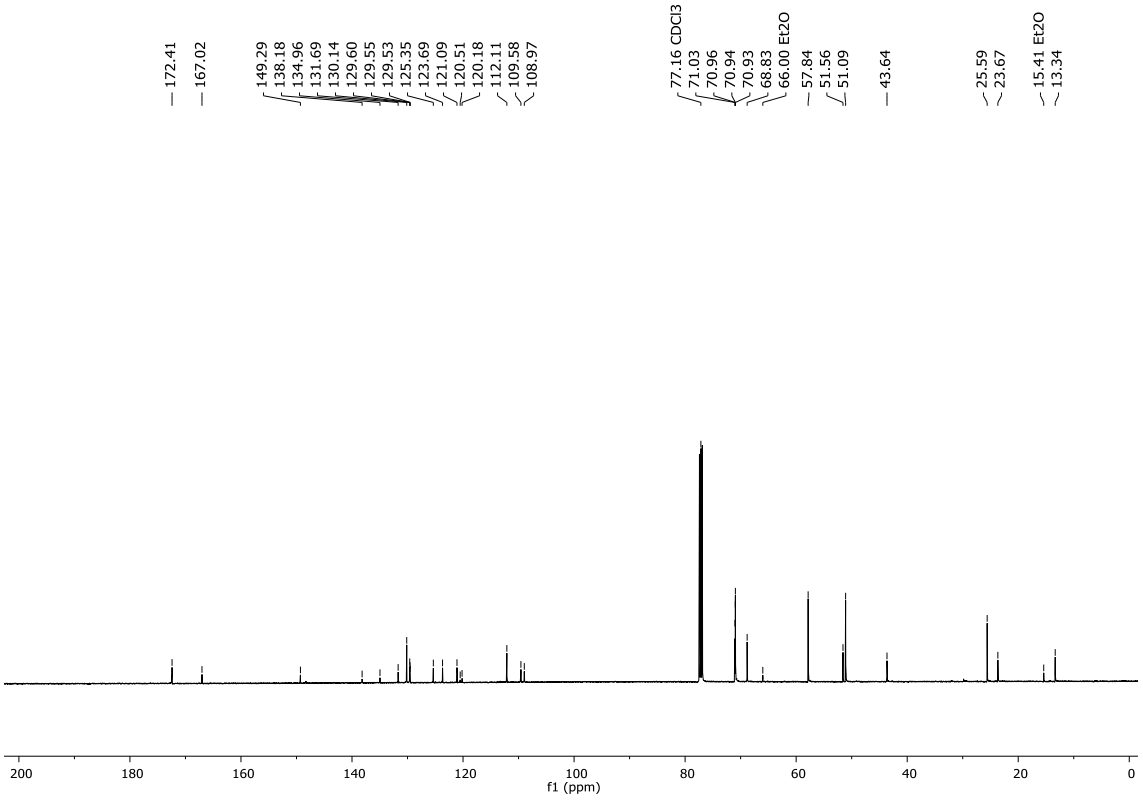


1-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-*N*-(3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide (15aa)

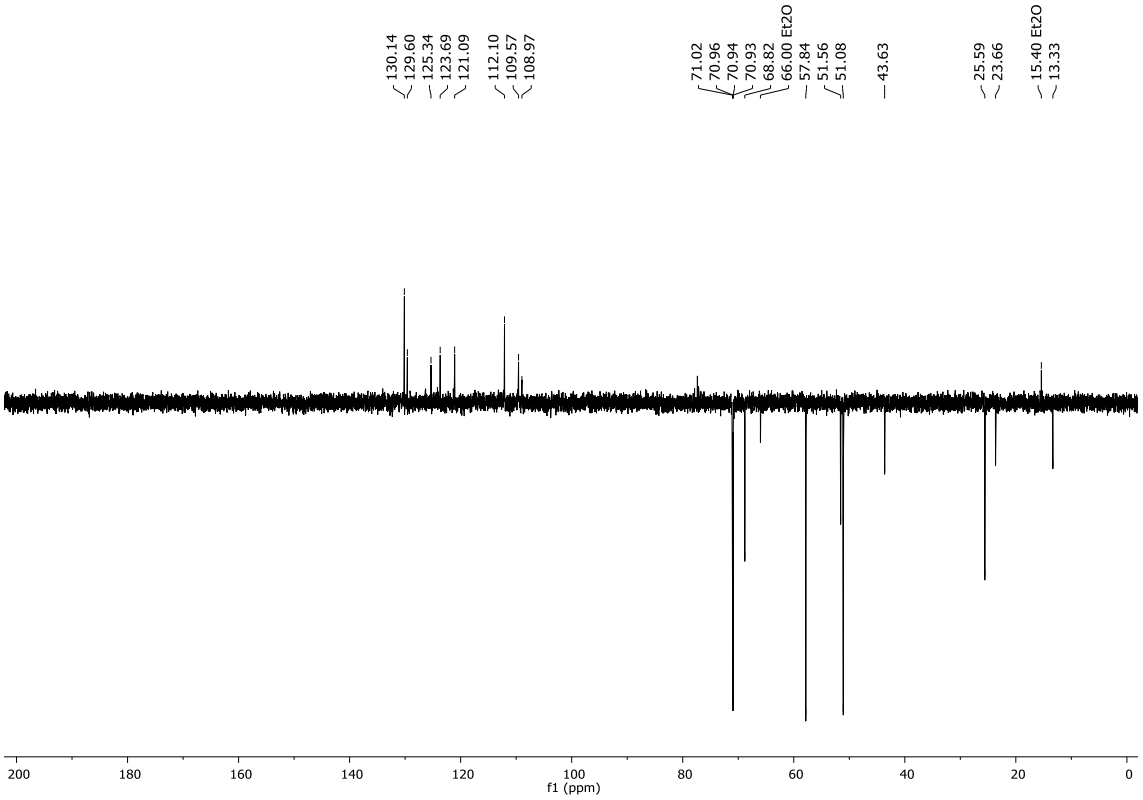
^{1}H-NMR



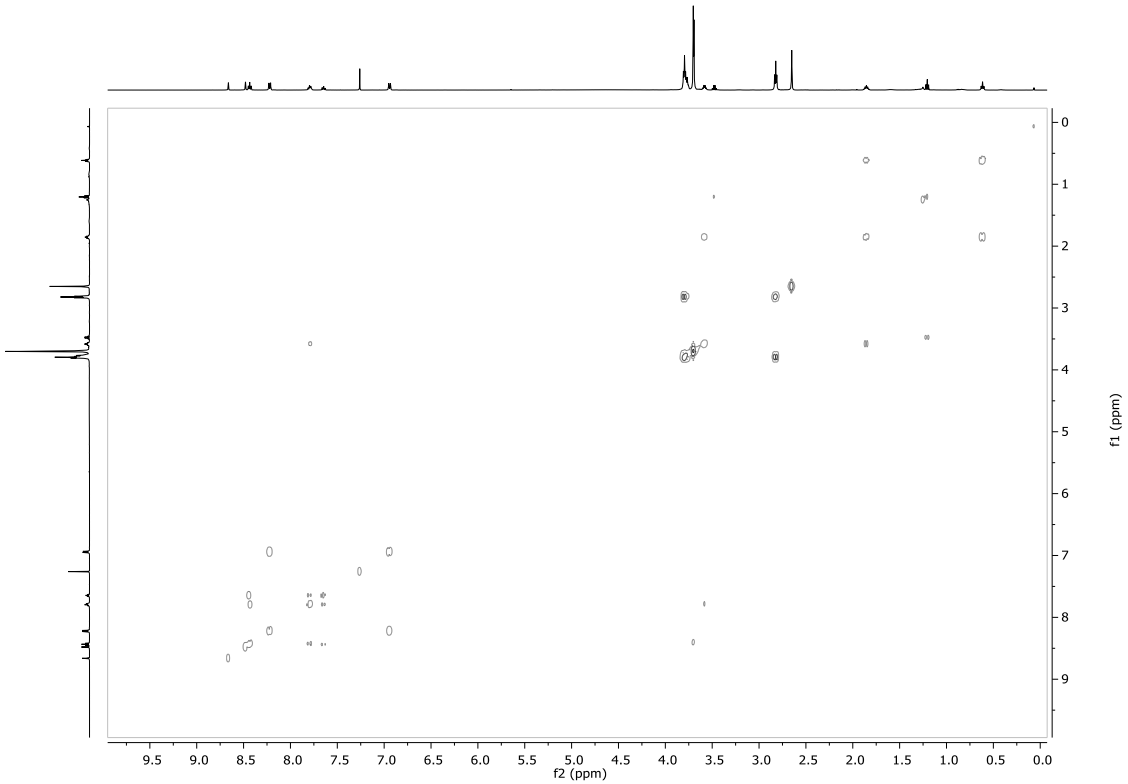
^{13}C-NMR



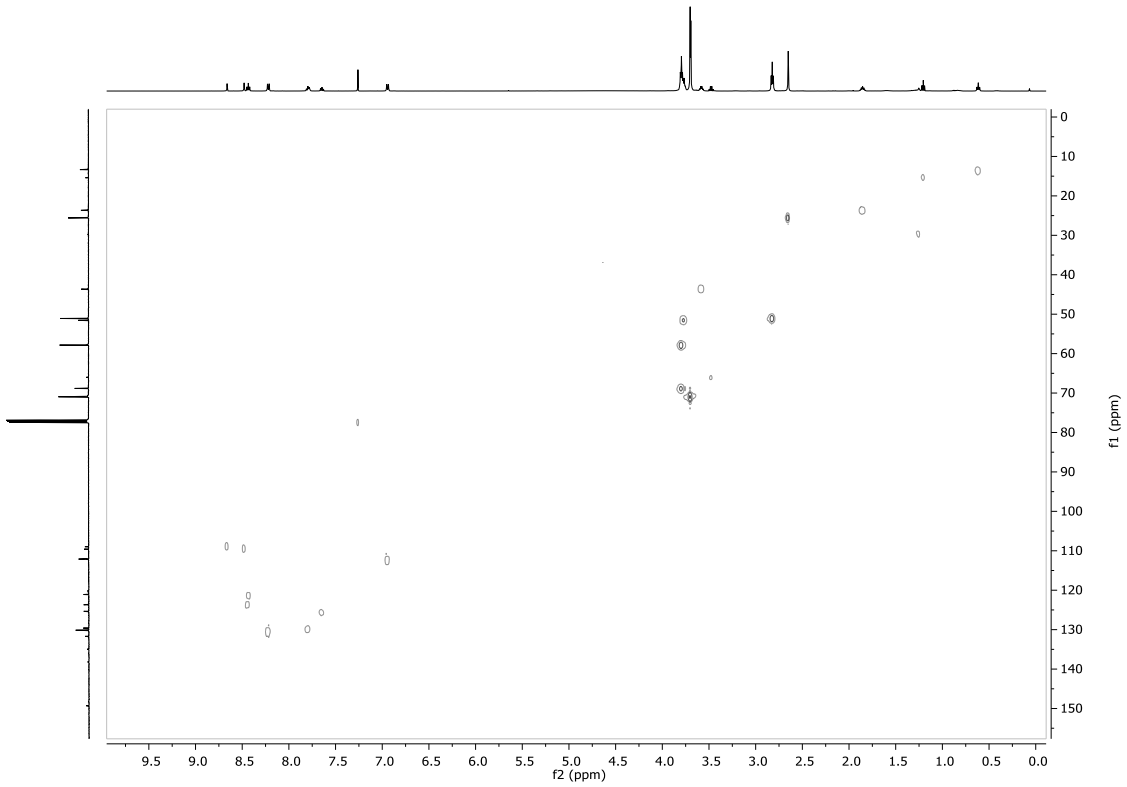
DEPT-135



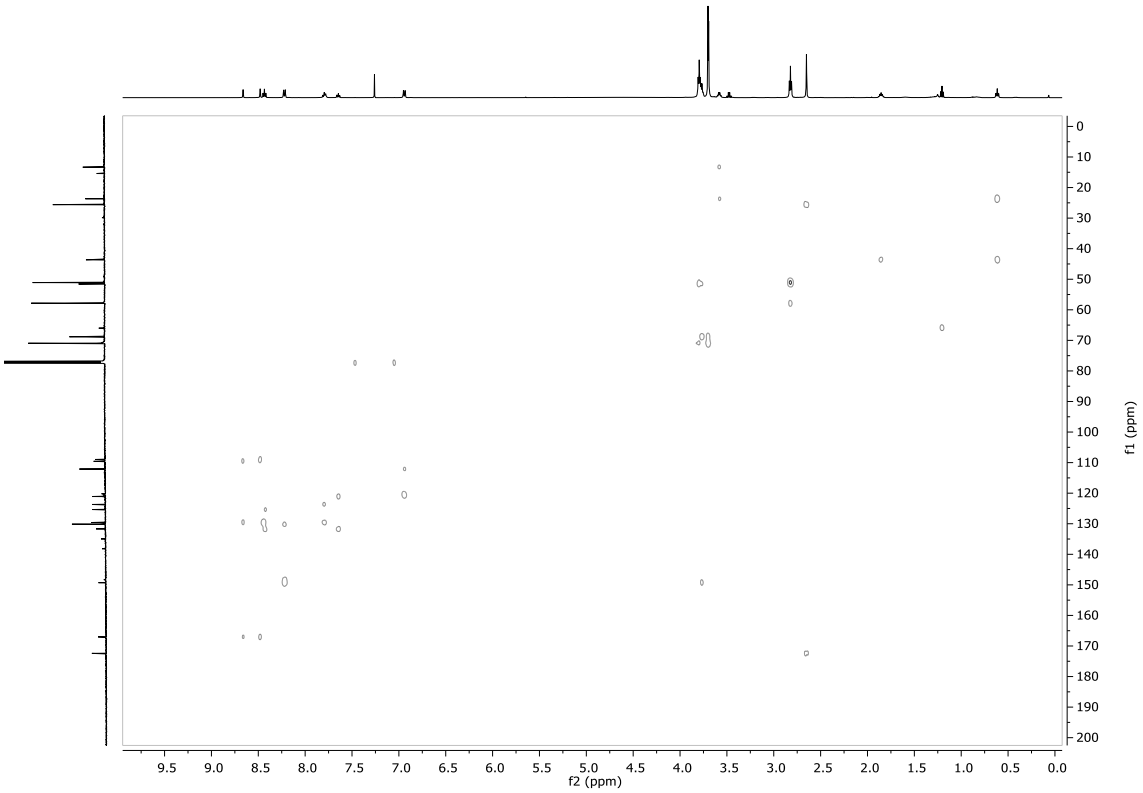
g-COSY



g-HSQC

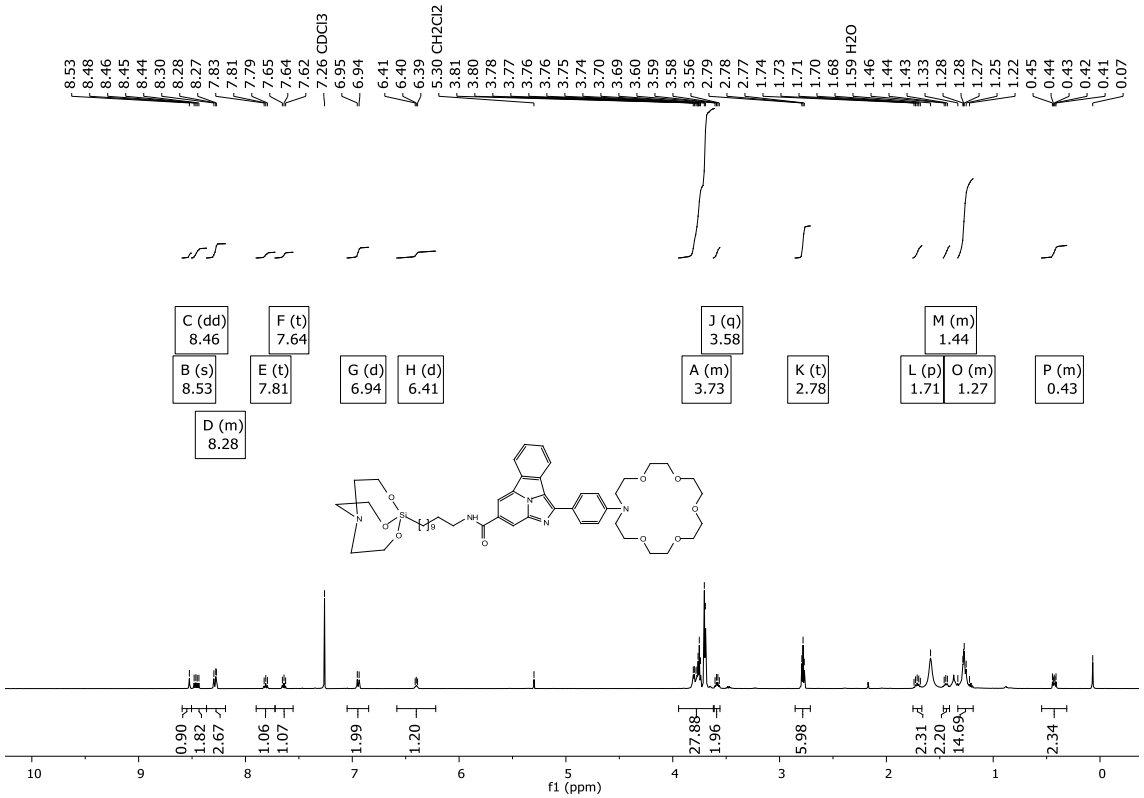


g-HMBC

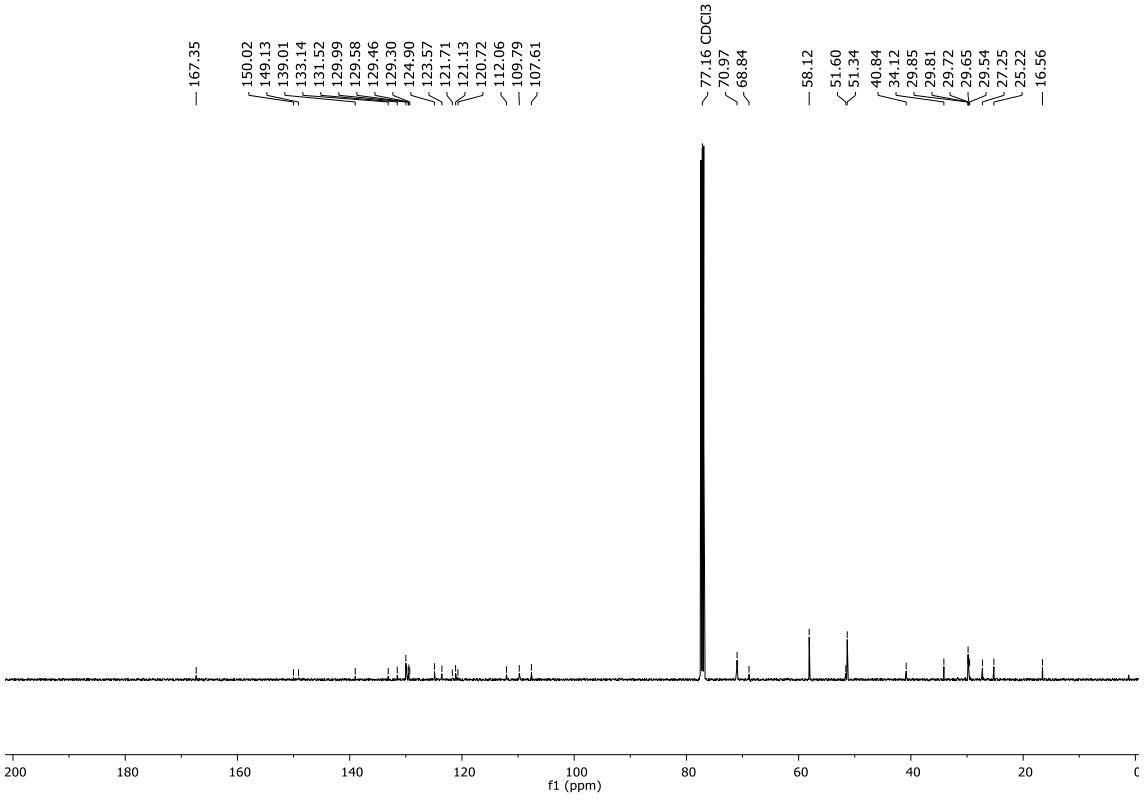


1-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-*N*-(11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide (15ab)

^{1}H-NMR



^{13}C-NMR



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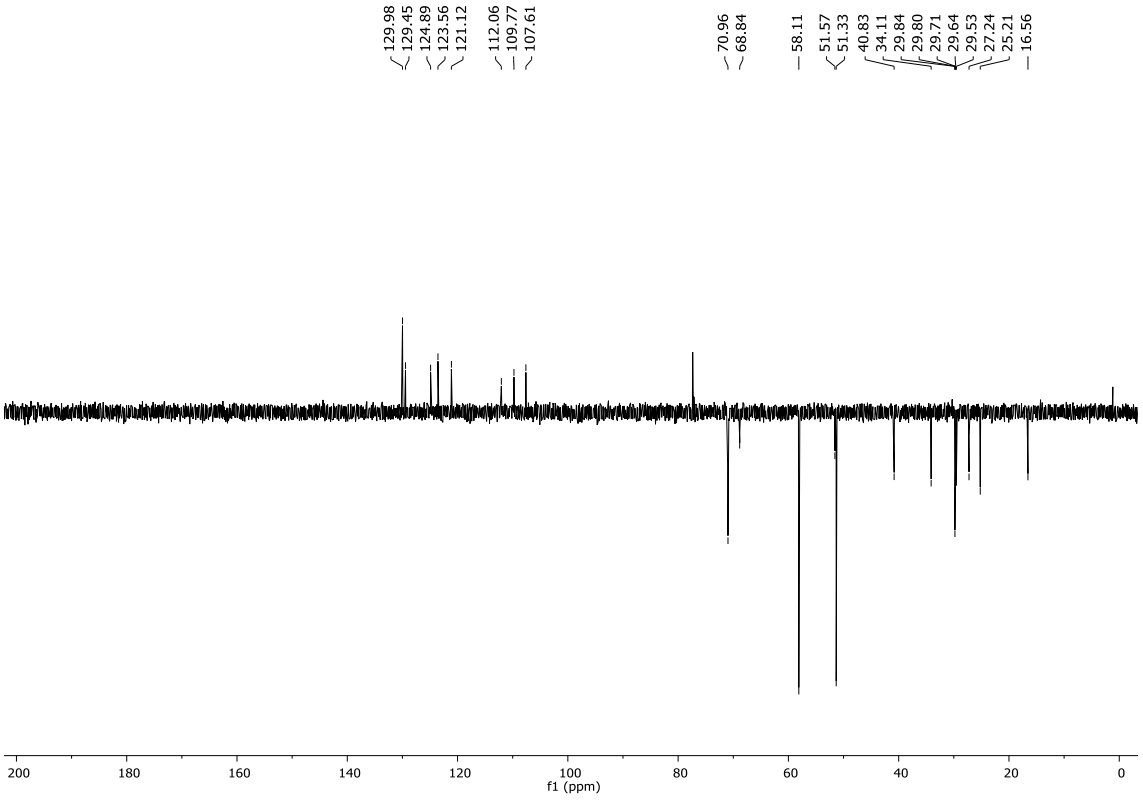
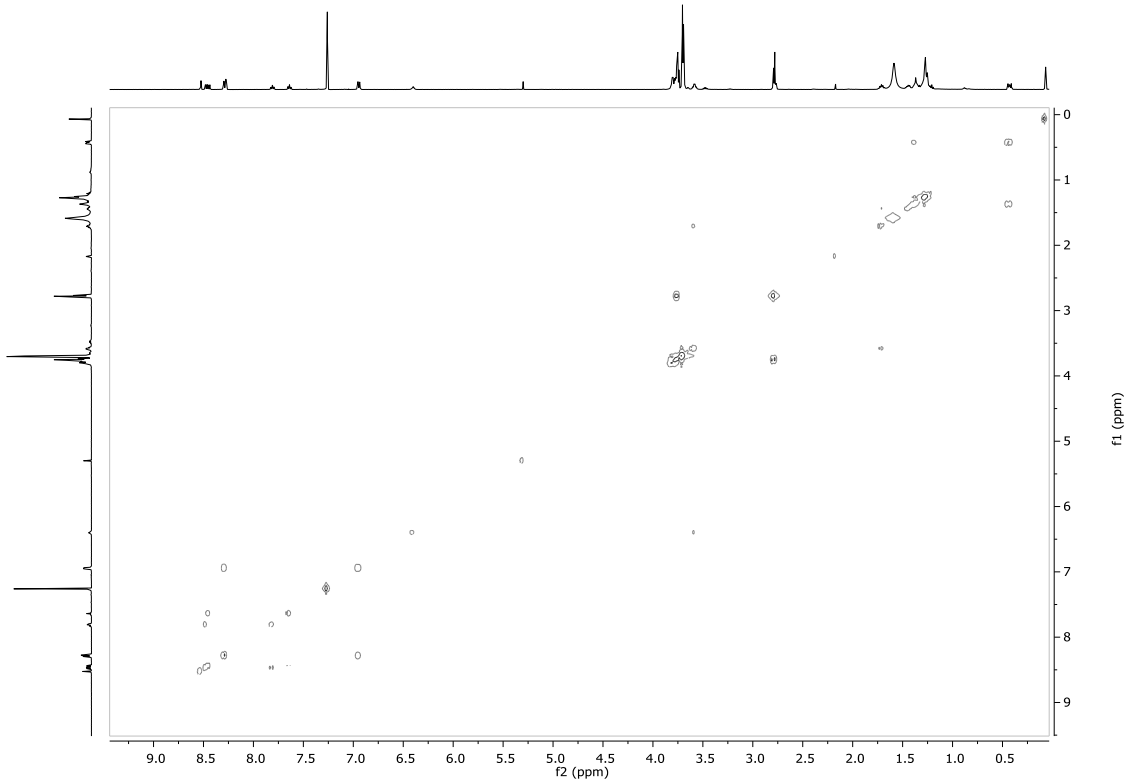
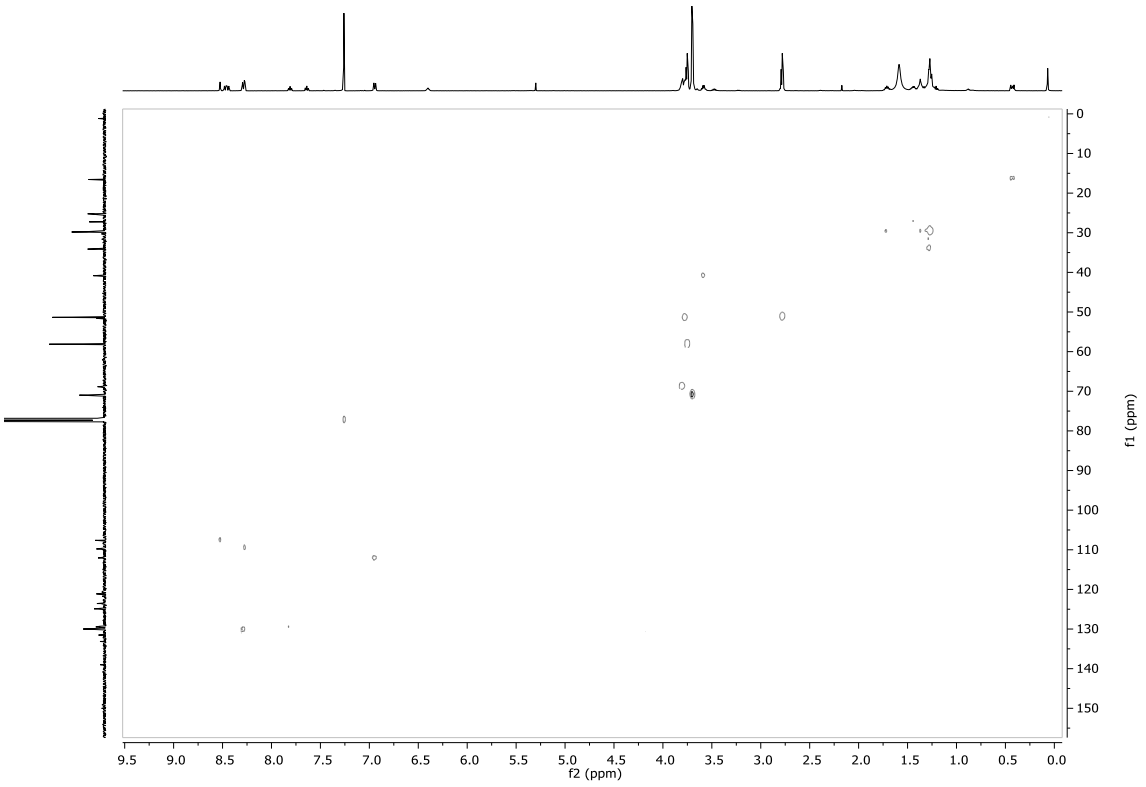


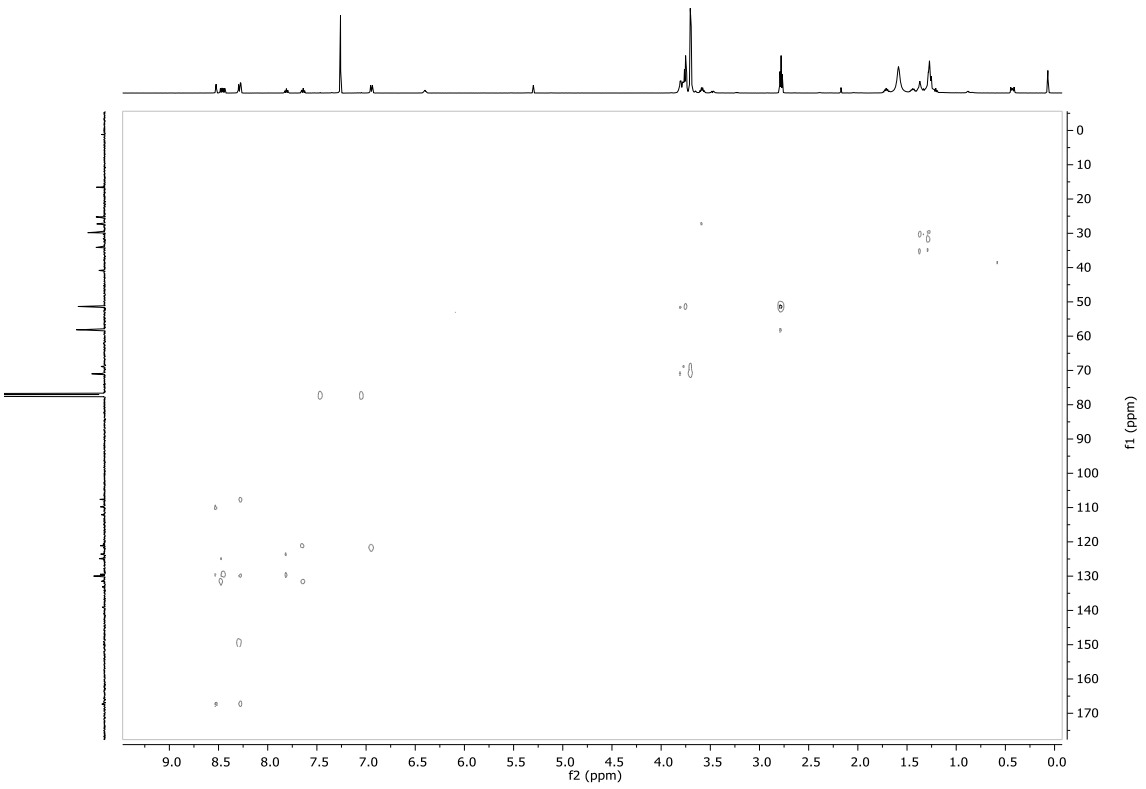
g-COSY



g-HSQC

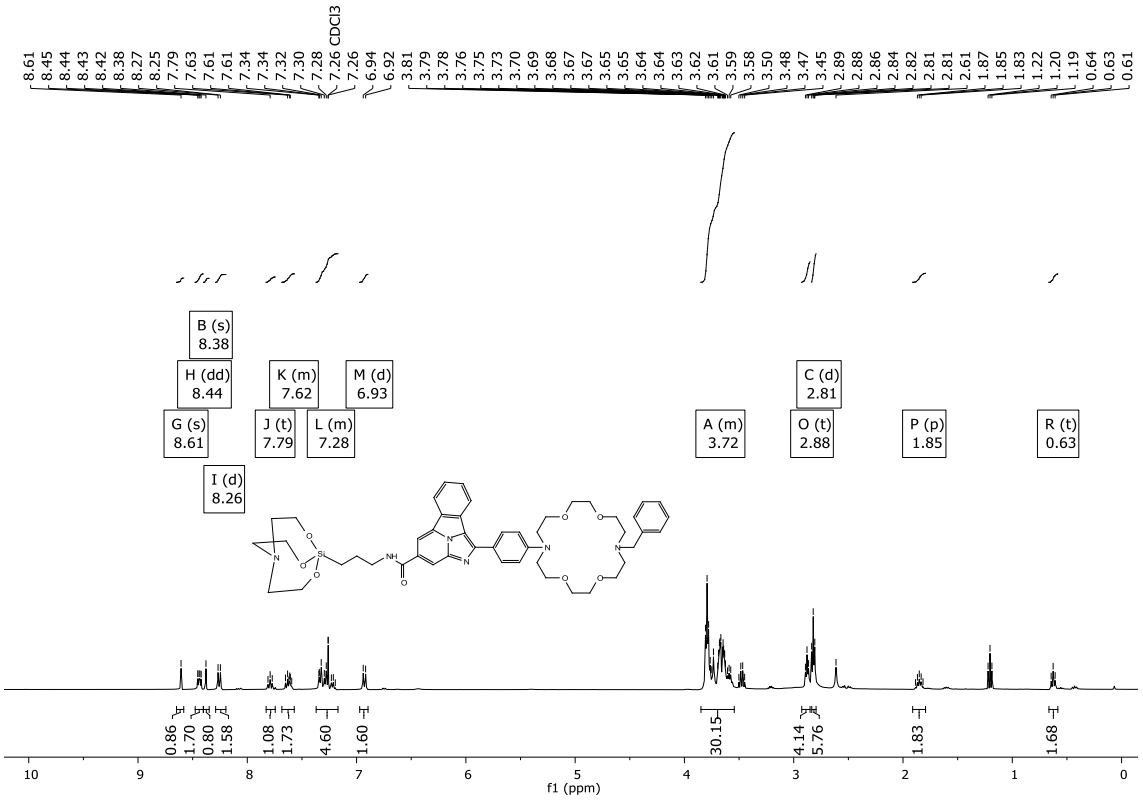


g-HMBC



_N_-(3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)-1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[_a_]imidazo[5,1,2-_cd_]indolizine-4-carboxamide (15ba)

^{1}H-NMR



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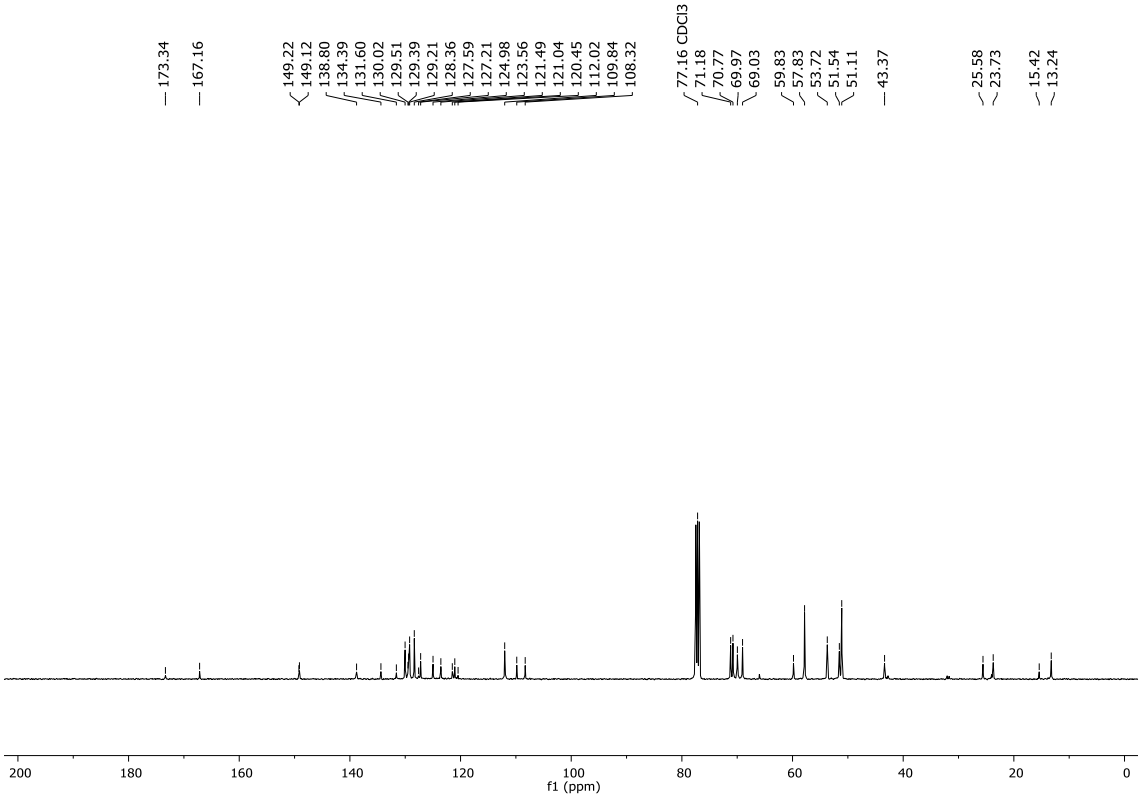

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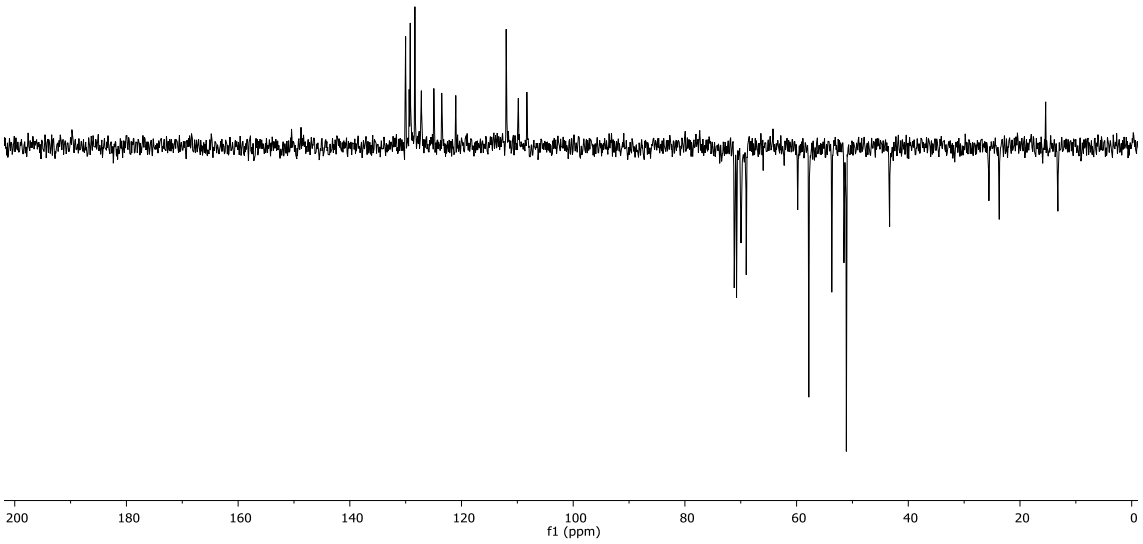

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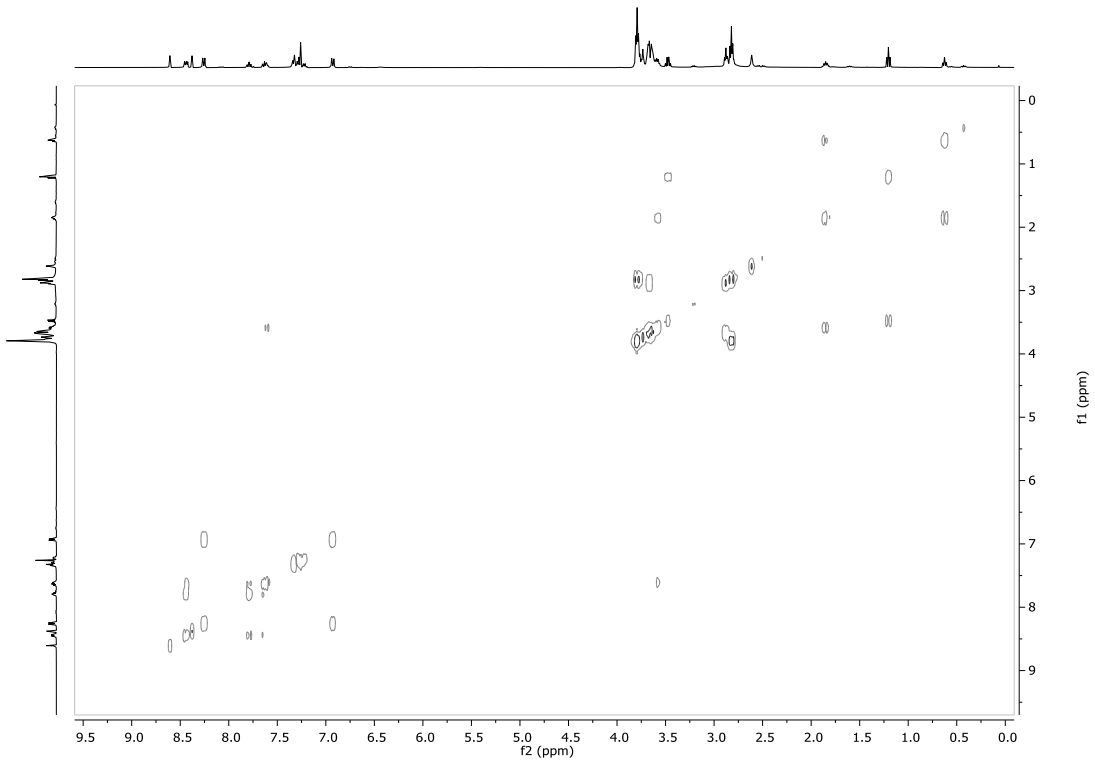
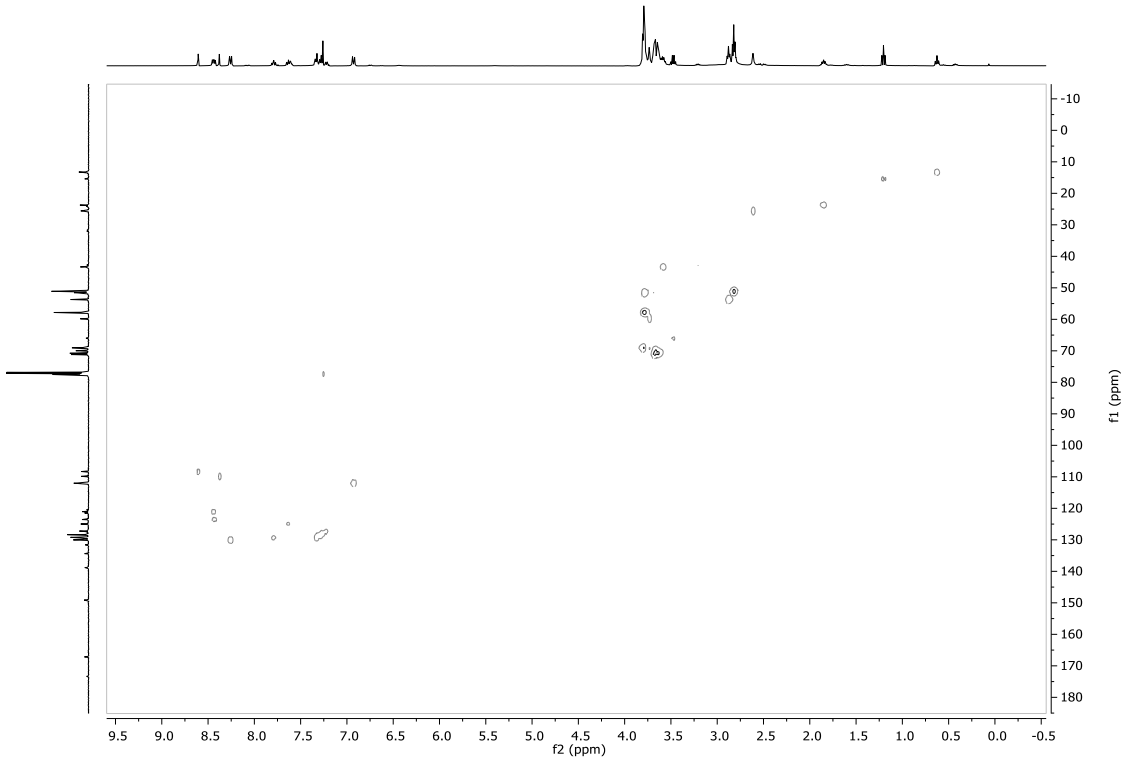
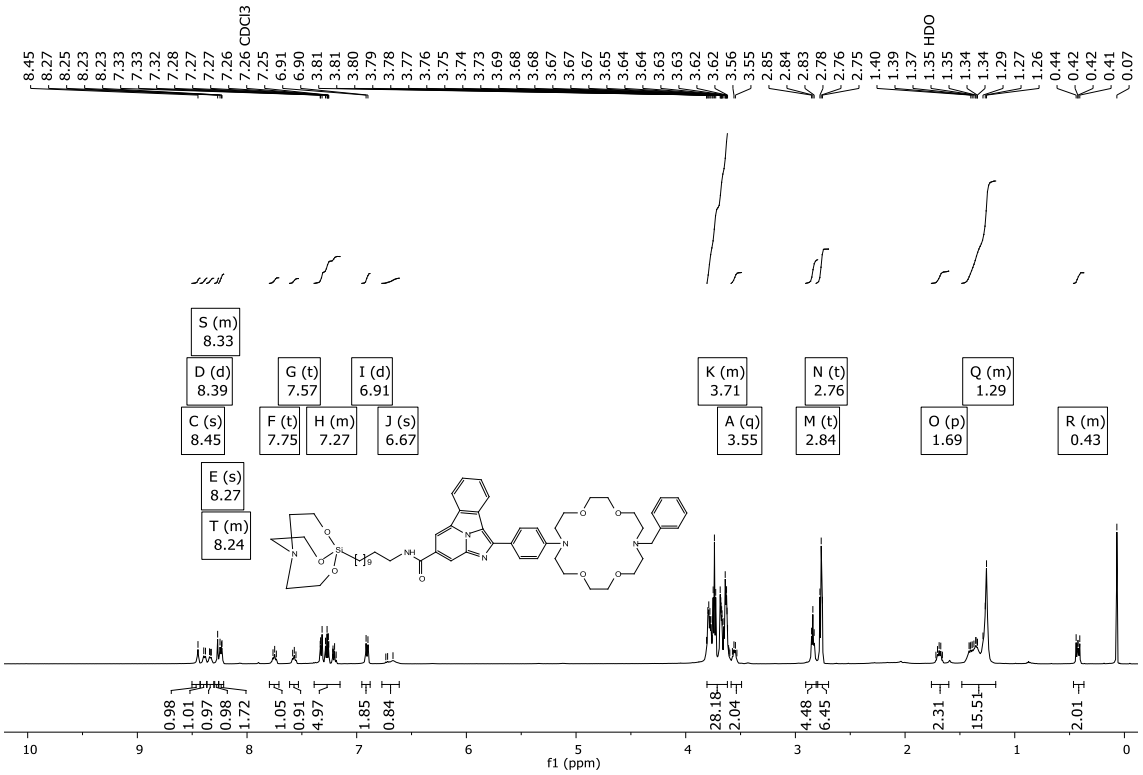


g-HSQC

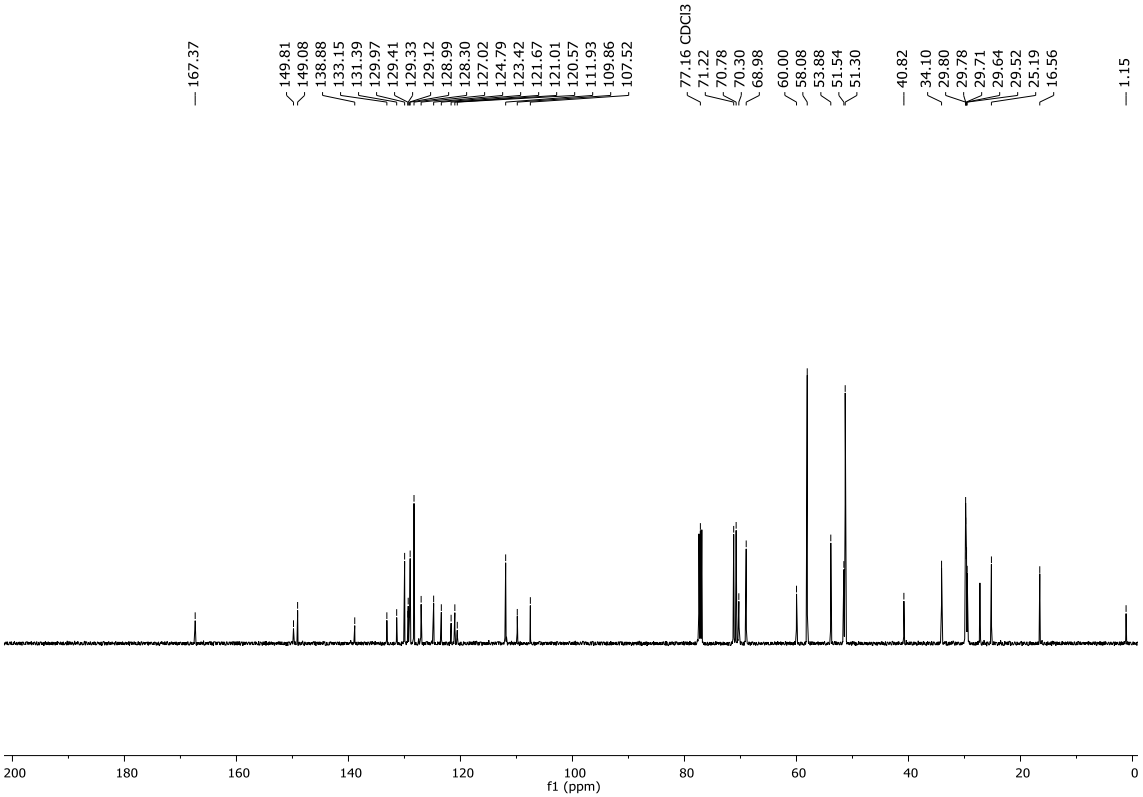

-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

_N_-(11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)-1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[_a_]imidazo[5,1,2-_cd_]indolizine-4-carboxamide (15bb)

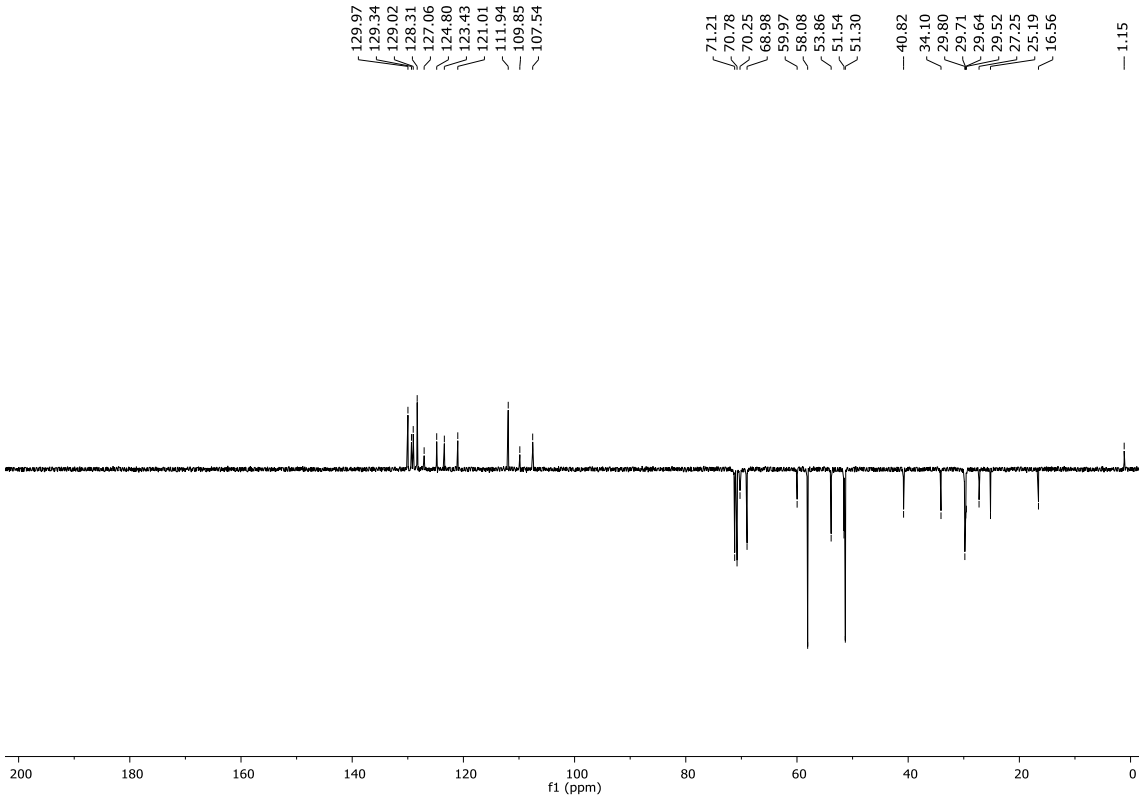
^{1}H-NMR



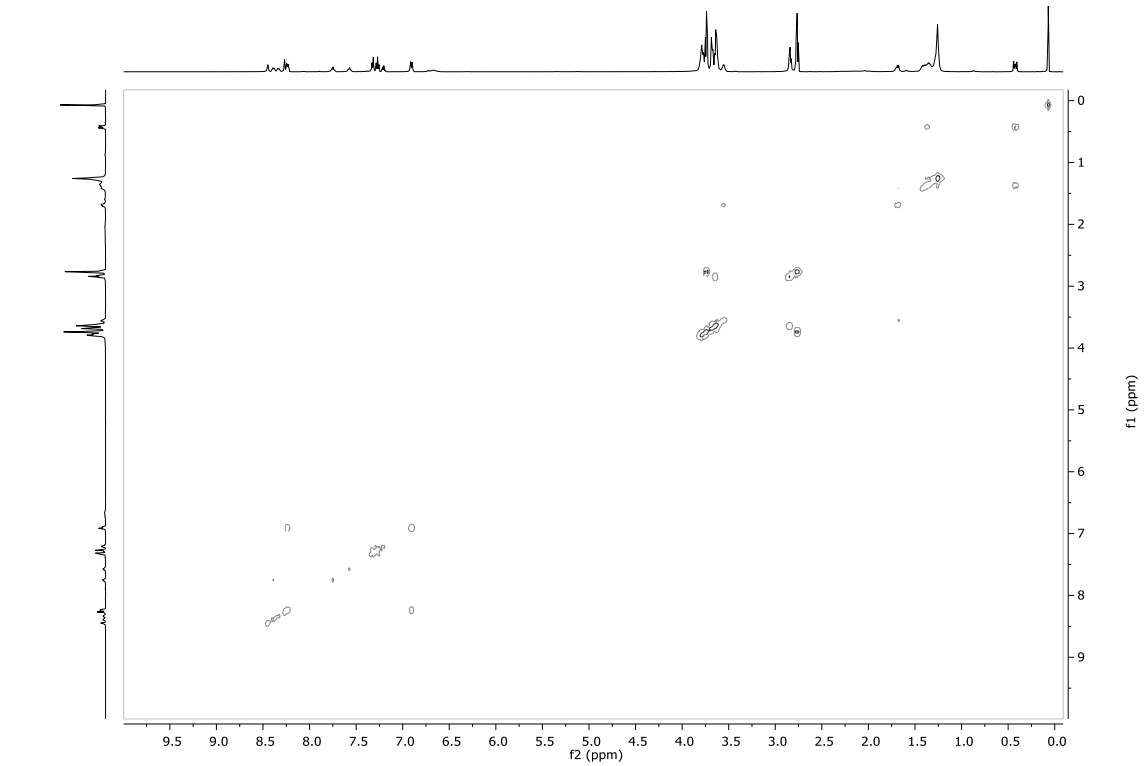
^{13}C-NMR



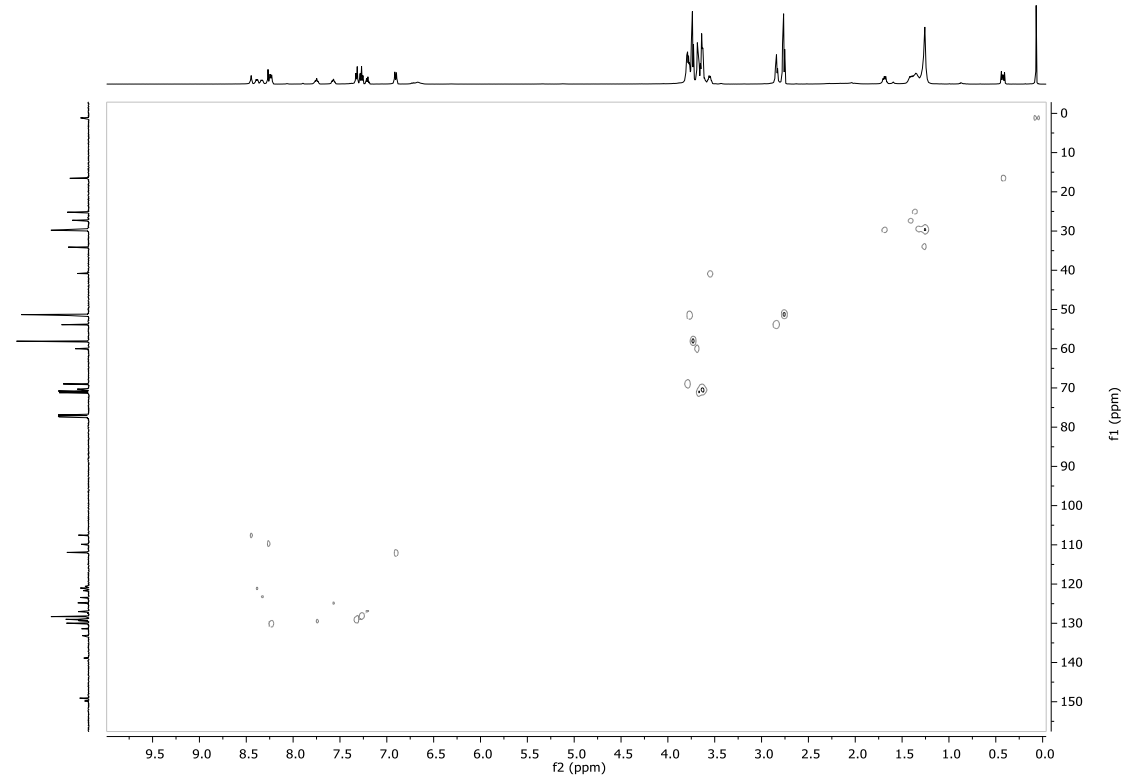
DEPT-135



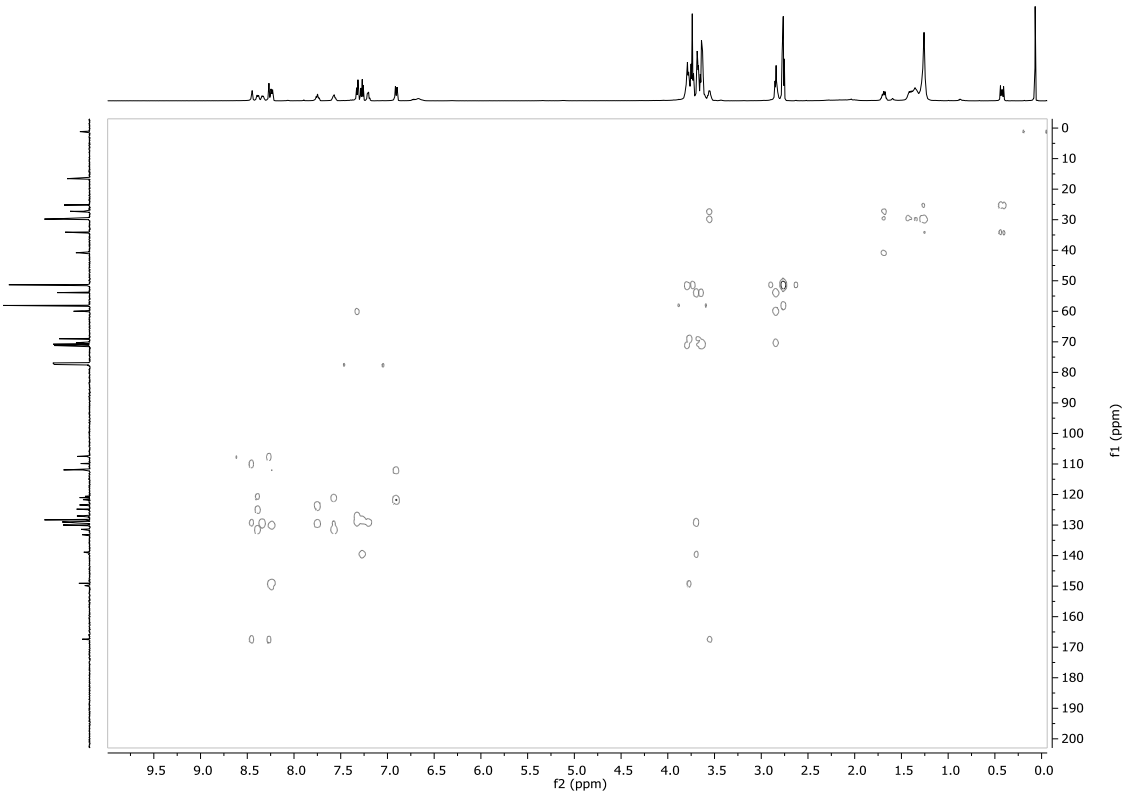
g-COSY



g-HSQC

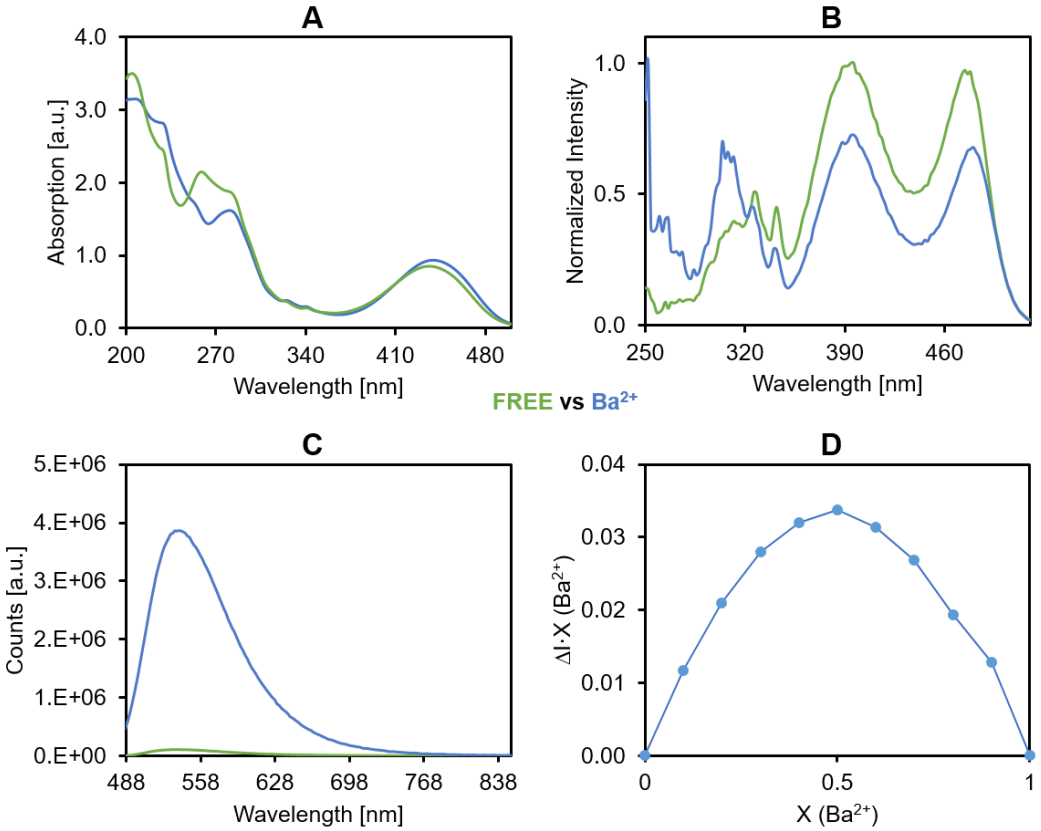


g-HMBC

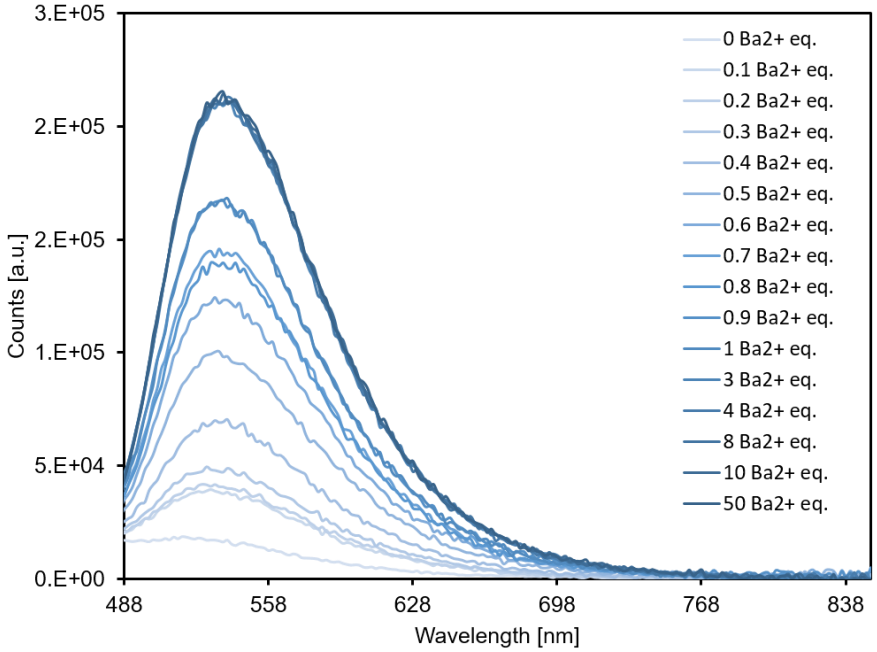


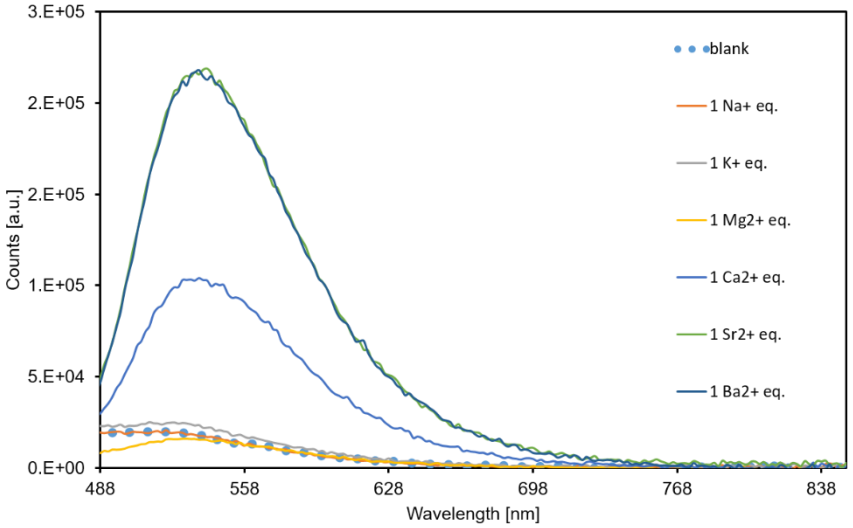
5. Photophysical Properties of Compounds 7aa-bb, 14a,b and 15aa-bb.

2-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-6-((3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)amino)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7aa)

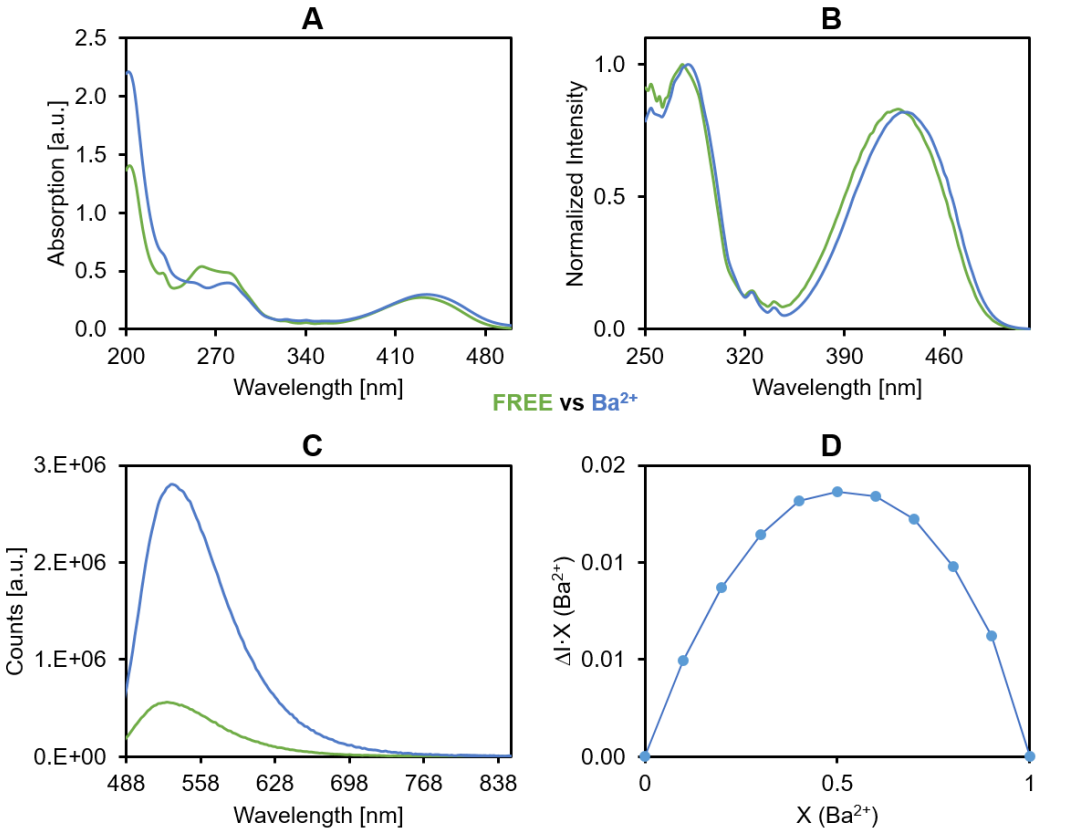


Lifetime (ns);	τ_{free} = 0.26 (19.72%), 1.92 (6.29%), 8.94 (73.99%); χ^2 = 1.1949 τ_{Ba} = 9.28 (100.00%); χ^2 = 1.1430
A = Absorption;	λ_{free} = 436 nm; λ_{Ba} = 440 nm
B = Normalized excitation;	λ_{free} = 396, 480 nm; λ_{Ba} = 396, 474 nm
C = Emission; (exc: λ_{free} = 396 nm; λ_{Ba} = 396 nm);	λ_{free} = 534 nm; λ_{Ba} = 538 nm
D = Job Plot;	

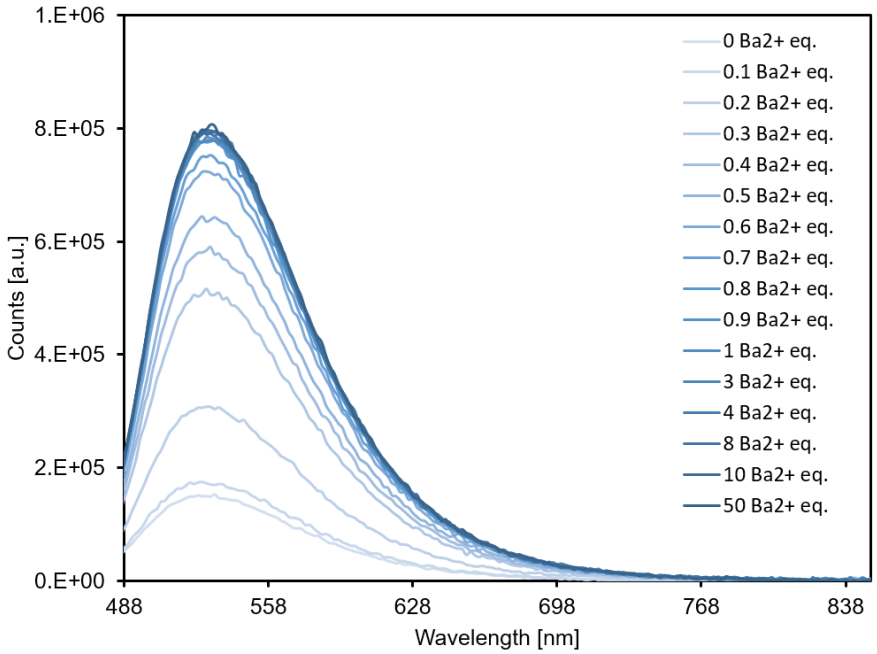

3.E+05
2.E+05
2.E+05
1.E+05
5.E+04
0.E+00
Counts [a.u.]
488
558
628
698
768
838
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.

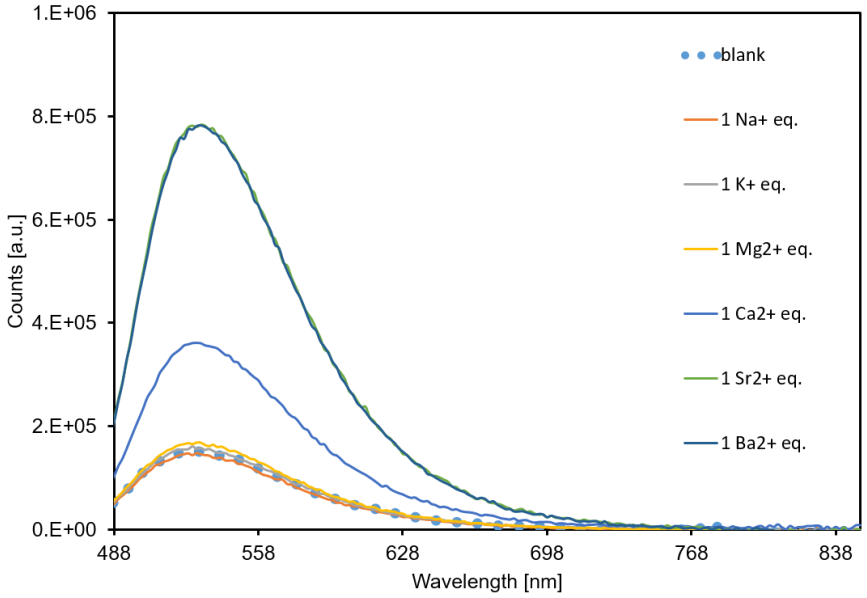

3.E+05
2.E+05
2.E+05
1.E+05
5.E+04
0.E+00
Counts [a.u.]
488
558
628
698
768
838
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

2-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-6-((11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)amino)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7ab)

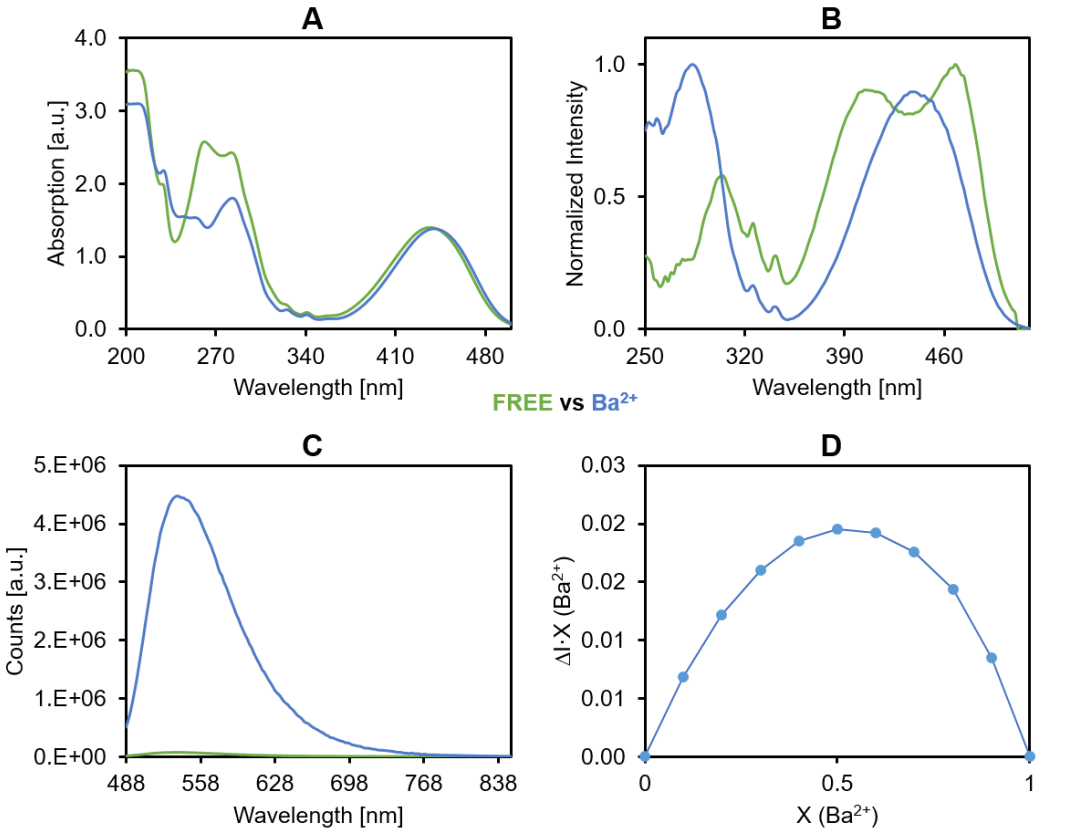


Lifetime (ns);	τ_{free} = 0.11 (1.76%), 1.68 (4.80%), 9.75 (93.44%); χ^2 = 1.2287 τ_{Ba} = 4.07 (3.95%), 9.57 (96.05%); χ^2 = 1.1984
A = Absorption;	λ_{free} = 430 nm; λ_{Ba} = 434 nm
B = Normalized excitation;	λ_{free} = 428 nm; λ_{Ba} = 432 nm
C = Emission; (exc: λ_{free} = 432 nm; λ_{Ba} = 432 nm);	λ_{free} = 528 nm; λ_{Ba} = 532 nm
D = Job Plot;	

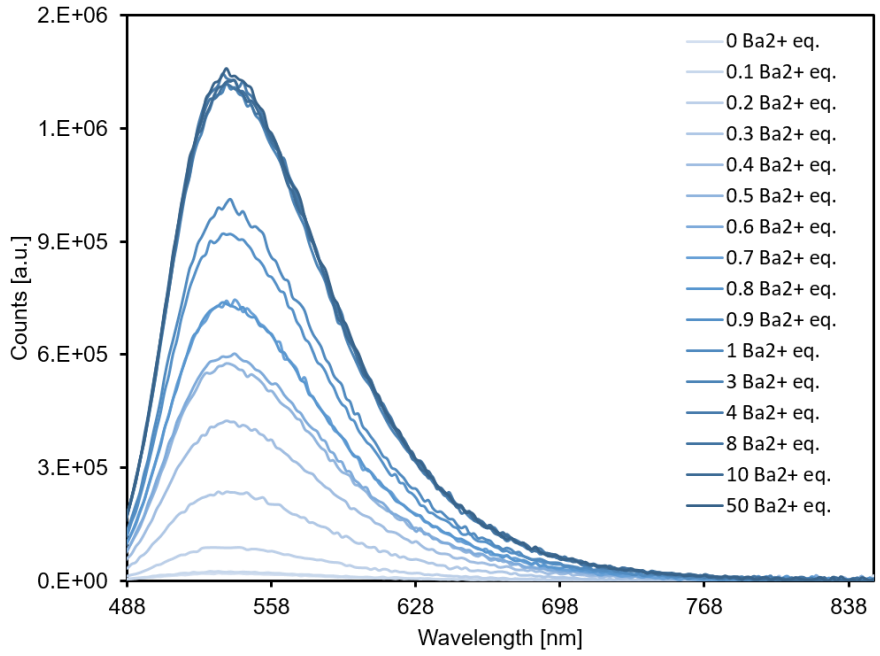

1.E+06
8.E+05
6.E+05
4.E+05
2.E+05
0.E+00
Counts [a.u.]
488
558
628
698
768
838
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.

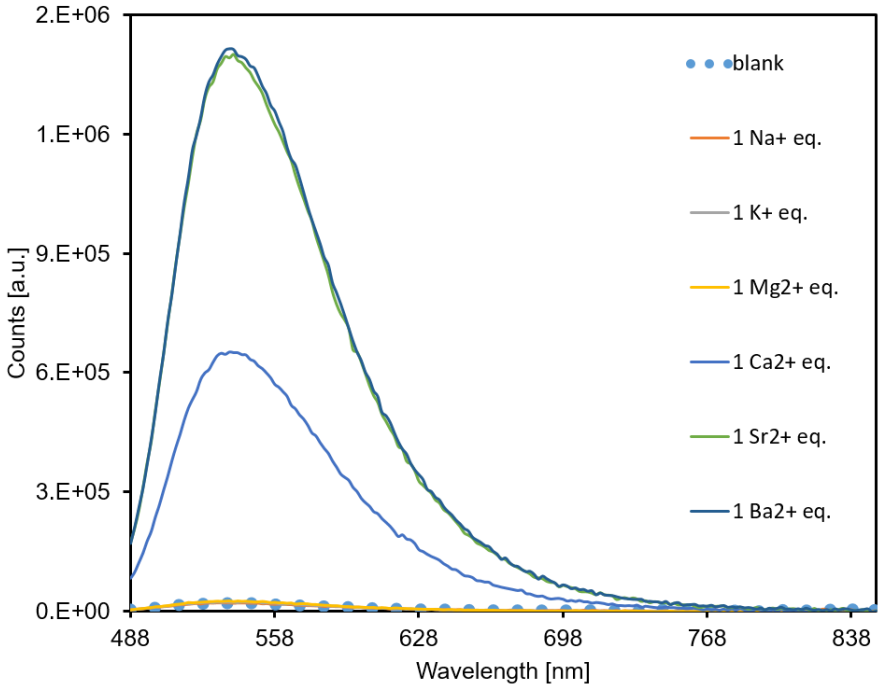

1.E+06
8.E+05
6.E+05
4.E+05
2.E+05
0.E+00
Counts [a.u.]
488
558
628
698
768
838
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

6-((3-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)amino)-2-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7ba)

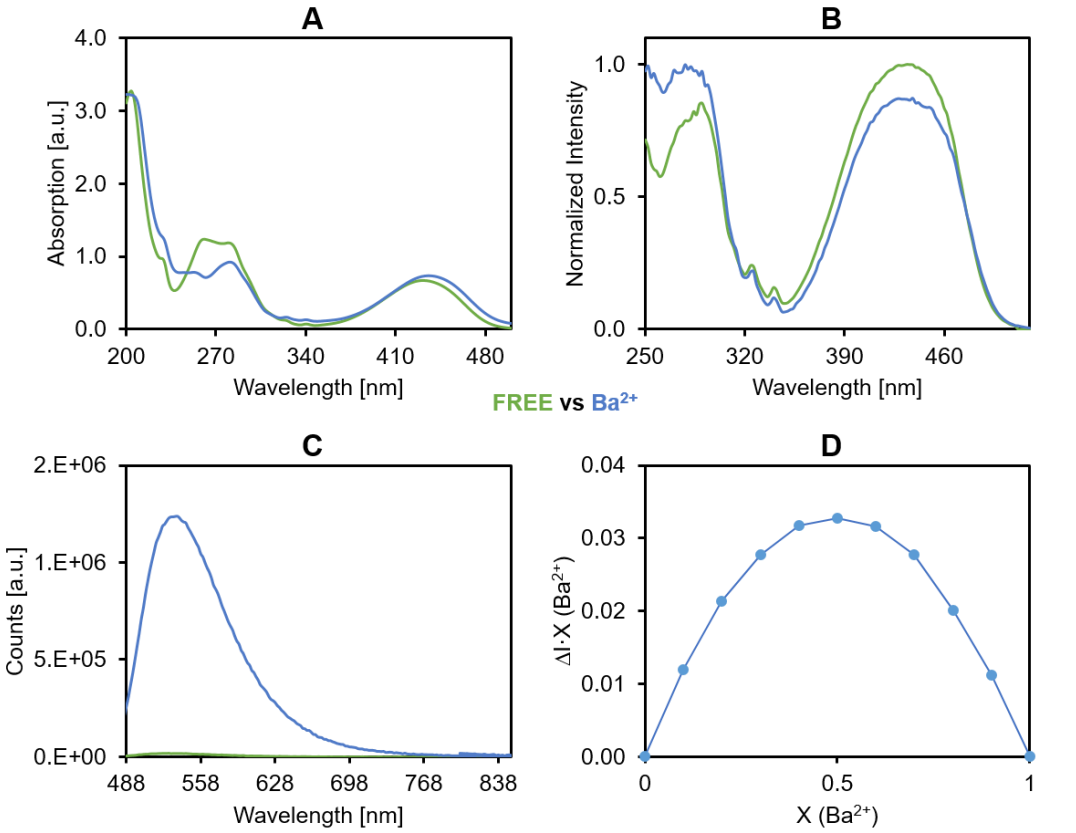


Lifetime (ns);	τ_{free} = 0.35 (45.20%), 8.72 (54.80%) χ^2 = 1.4777 τ_{Ba} = 8.89 (100.00%); χ^2 = 1.2602
A = Absorption;	λ_{free} = 437 nm; λ_{Ba} = 440 nm
B = Normalized excitation;	λ_{free} = 406, 468 nm; λ_{Ba} = 438 nm
C = Emission; (exc: λ_{free} = 468 nm; λ_{Ba} = 468 nm);	λ_{free} = 536 nm; λ_{Ba} = 540 nm
D = Job Plot;	

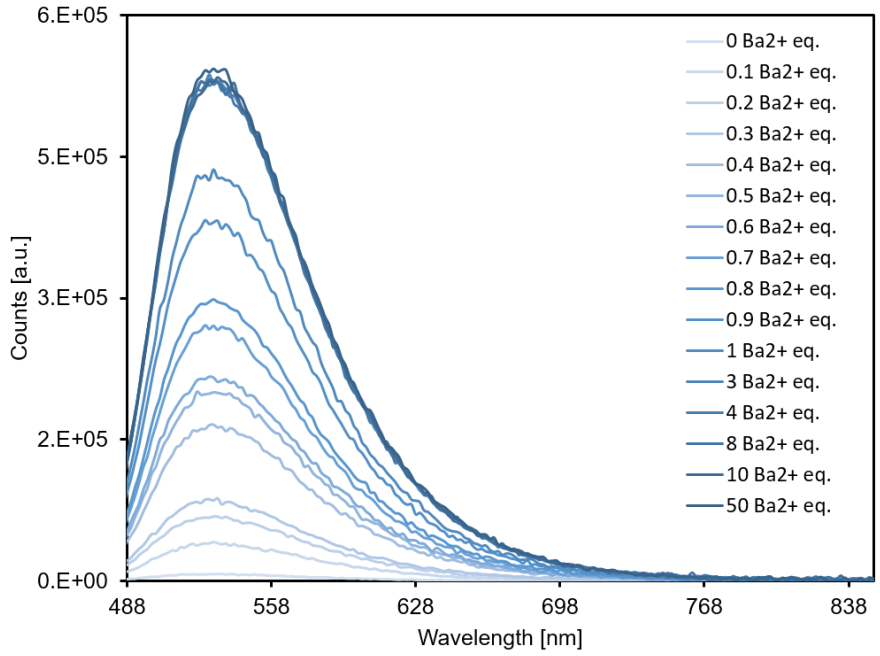

2.E+06
1.E+06
9.E+05
6.E+05
3.E+05
0.E+00
Counts [a.u.]
488
558
628
698
768
838
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.

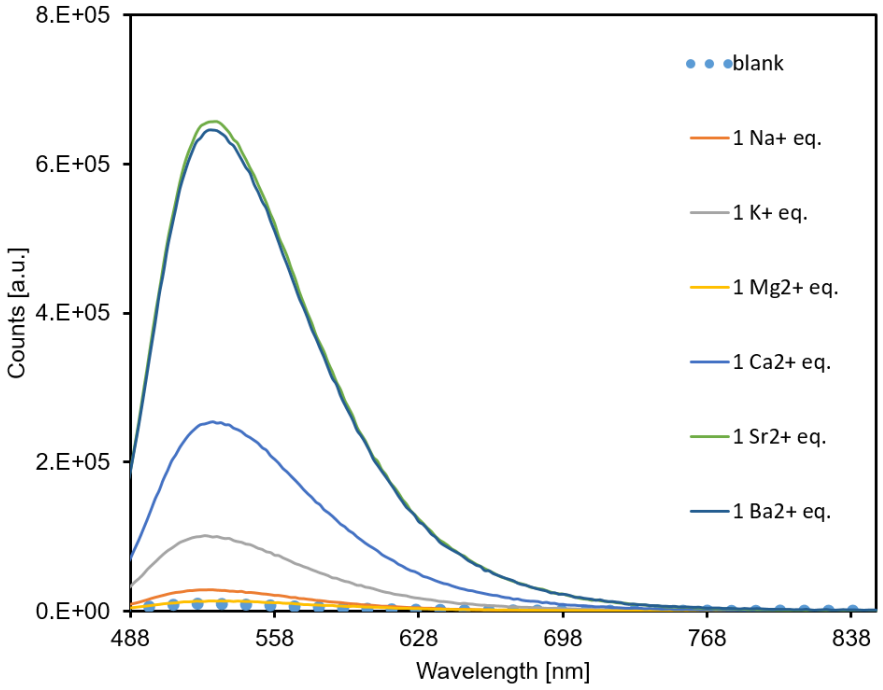

2.E+06
1.E+06
9.E+05
6.E+05
3.E+05
0.E+00
Counts [a.u.]
488
558
628
698
768
838
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

6-((11-(2,8,9-Trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)amino)-2-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (7bb)

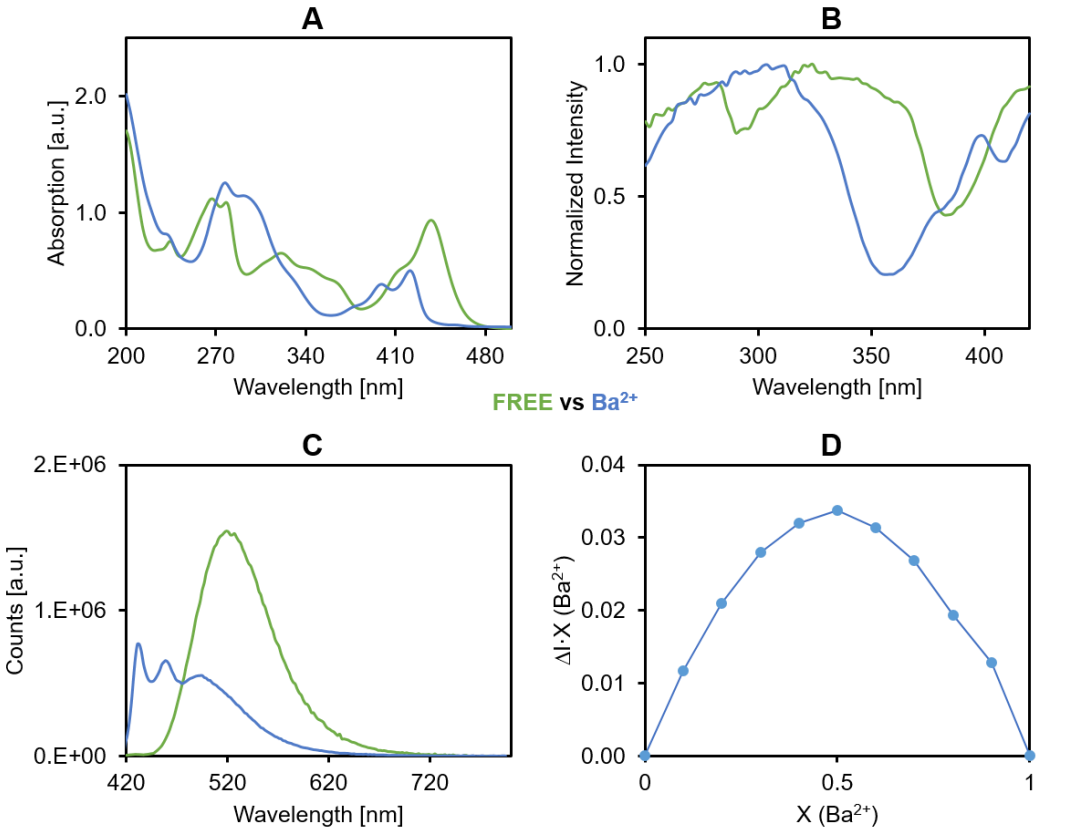


Lifetime (ns);	τ_{free} = 0.04 (16.53%), 0.59 (6.31%), 9.56 (77.17%); χ^2 = 1.0880 τ_{Ba} = 8.85 (100.00%); χ^2 = 1.1436
A = Absorption;	λ_{free} = 432 nm; λ_{Ba} = 436 nm
B = Normalized excitation;	λ_{free} = 434 nm; λ_{Ba} = 438 nm
C = Emission; (exc: λ_{free} = 438 nm; λ_{Ba} = 438 nm);	λ_{free} = 528 nm; λ_{Ba} = 534 nm
D = Job Plot;	

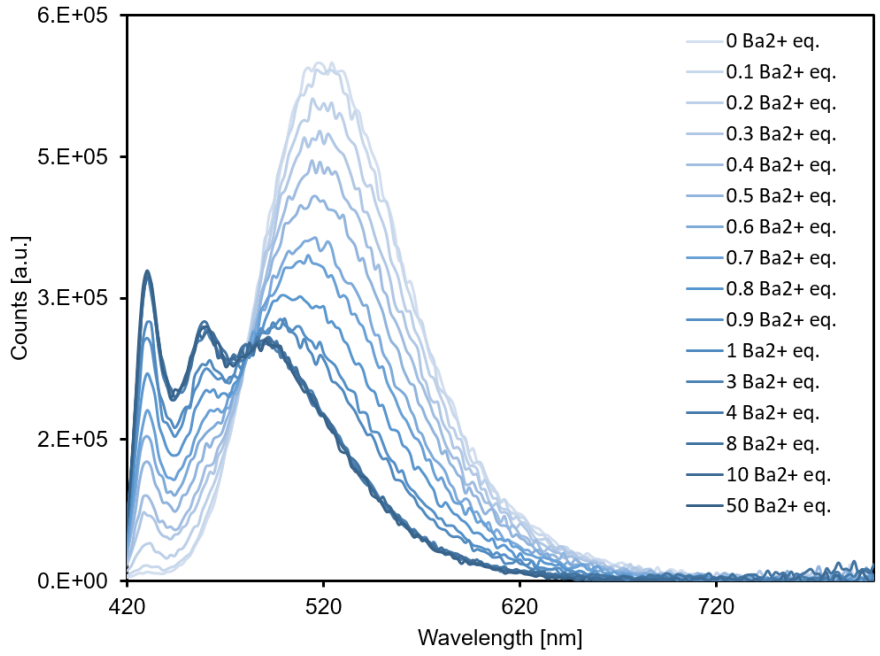

6.E+05
5.E+05
3.E+05
2.E+05
0.E+00
Counts [a.u.]
488
558
628
698
768
838
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.

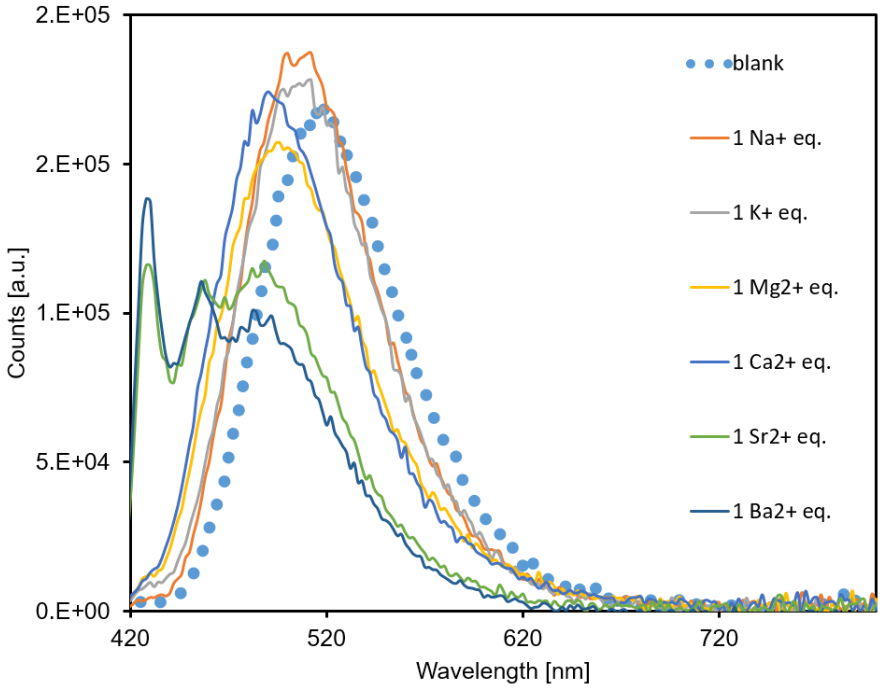

8.E+05
6.E+05
4.E+05
2.E+05
0.E+00
Counts [a.u.]
488
558
628
698
768
838
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

Methyl 1-(4-(1,4,7,10,13-pentaoxa-16-azacyclooctadecan-16-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate (14a)

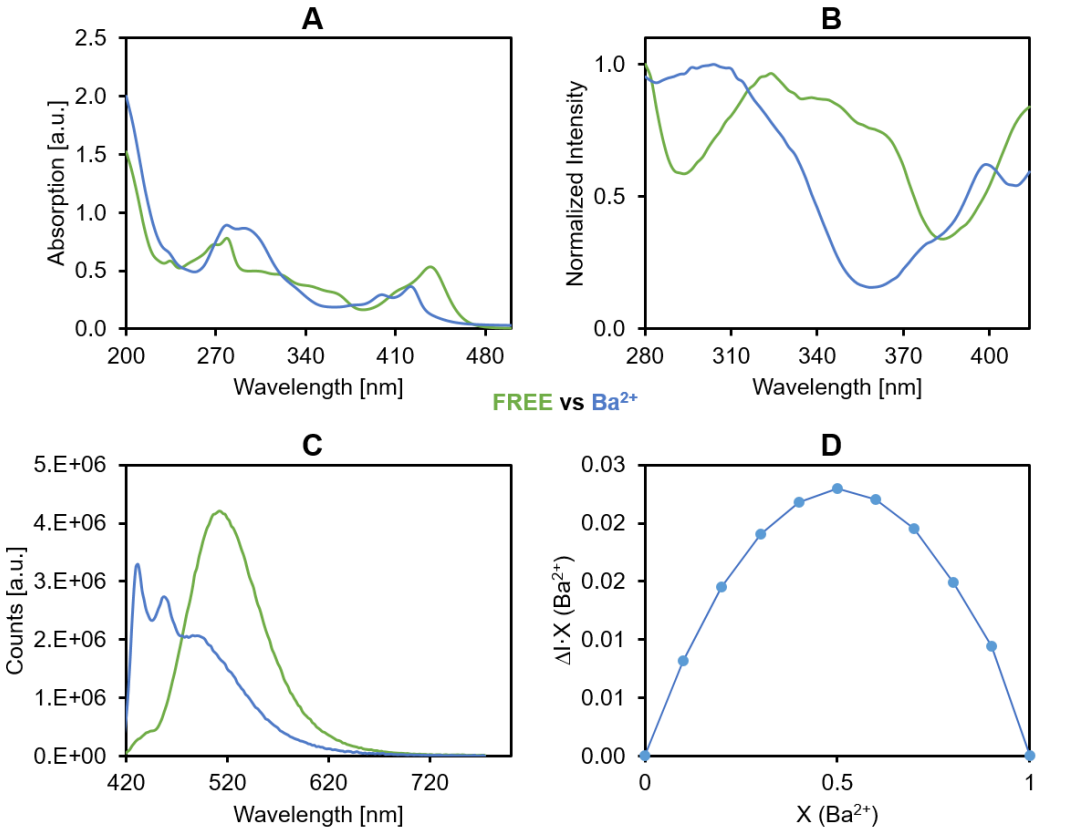


Lifetime (ns);	τ_{free} = 3.21 (74.57%), 4.33 (25.43%); χ^2 = 1.1898 τ_{Ba} = 3.26 (100.00%); χ^2 = 1.5850
A = Absorption;	λ_{free} = 438 nm; λ_{Ba} = 421 nm
B = Normalized excitation;	λ_{free} = 324 nm; λ_{Ba} = 400 nm
C = Emission; (exc: λ_{free} = 324 nm; λ_{Ba} = 400 nm);	λ_{free} = 520 nm; λ_{Ba} = 431, 463, 497 nm
D = Job Plot;	

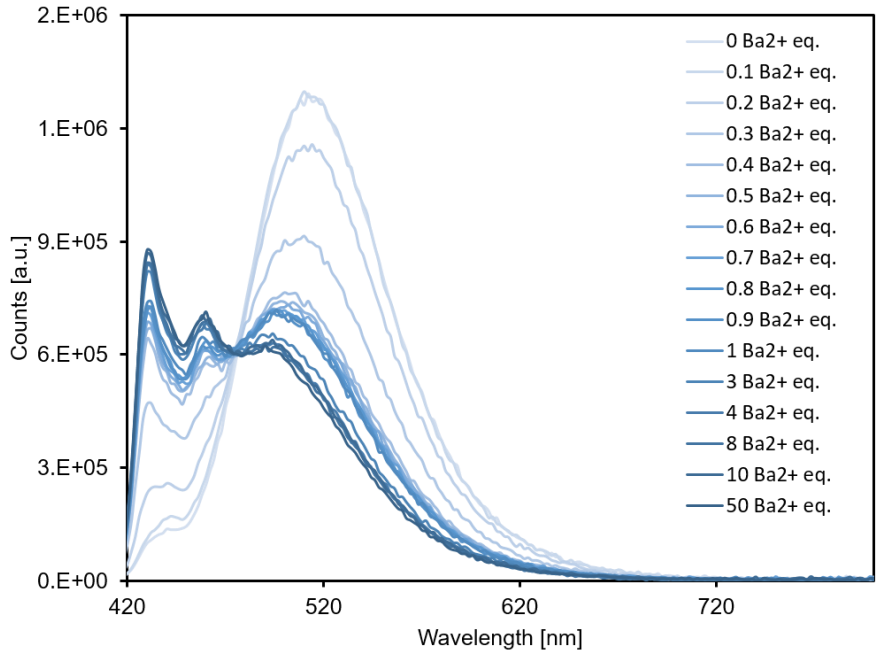

6.E+05
5.E+05
3.E+05
2.E+05
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.

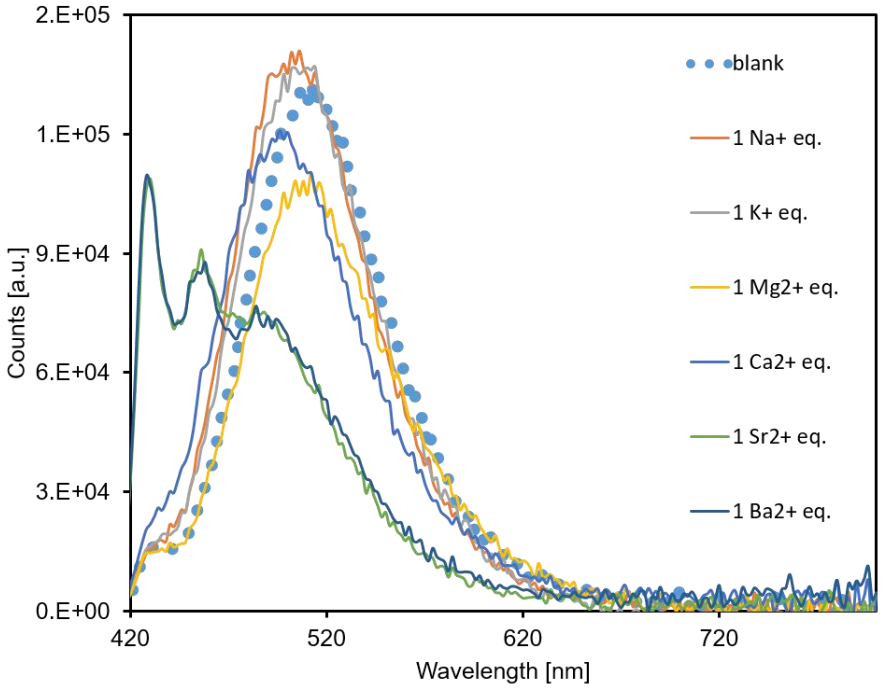

2.E+05
2.E+05
1.E+05
5.E+04
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

Methyl 1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxylate (14b)

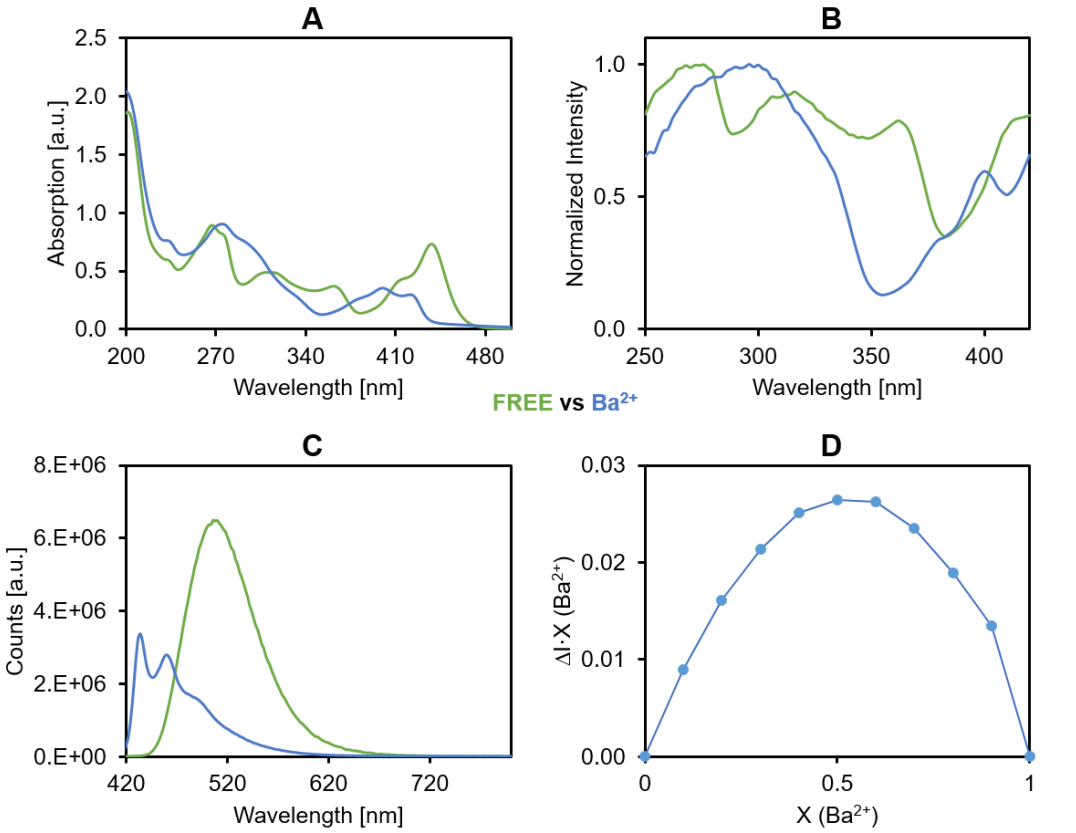


Lifetime (ns);	τ_{free} = 3.31 (97.12%), 9.19 (2.88%); χ^2 = 1.1130 τ_{Ba} = 2.07 (56.47%), 3.51 (43.53%); χ^2 = 1.2907
A = Absorption;	λ_{free} = 441 nm; λ_{Ba} = 424 nm
B = Normalized excitation;	λ_{free} = 324 nm; λ_{Ba} = 400 nm
C = Emission; (exc: λ_{free} = 324 nm; λ_{Ba} = 400 nm);	λ_{free} = 514 nm; λ_{Ba} = 432, 462, 494 nm
D = Job Plot;	

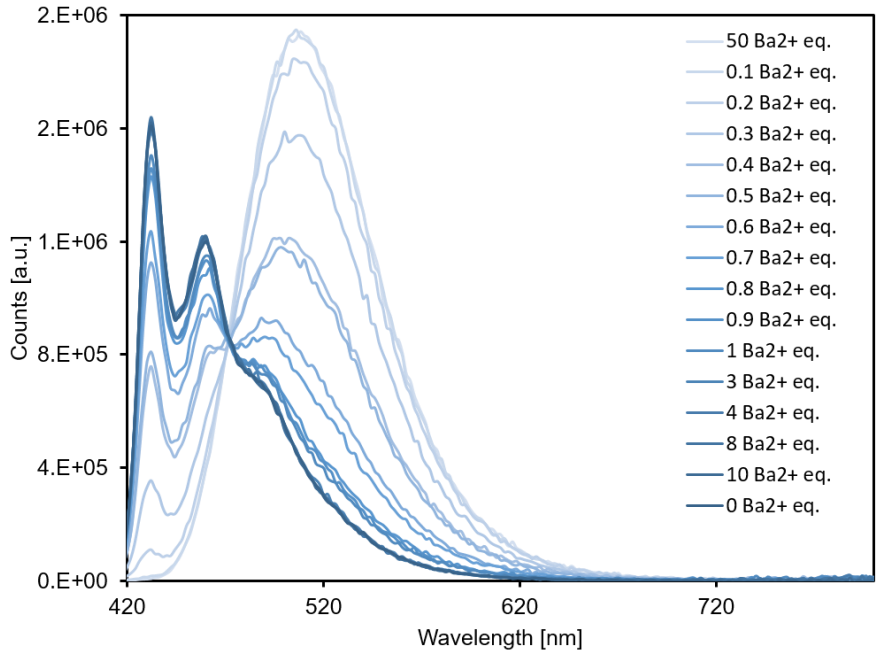

2.E+06
1.E+06
9.E+05
6.E+05
3.E+05
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.

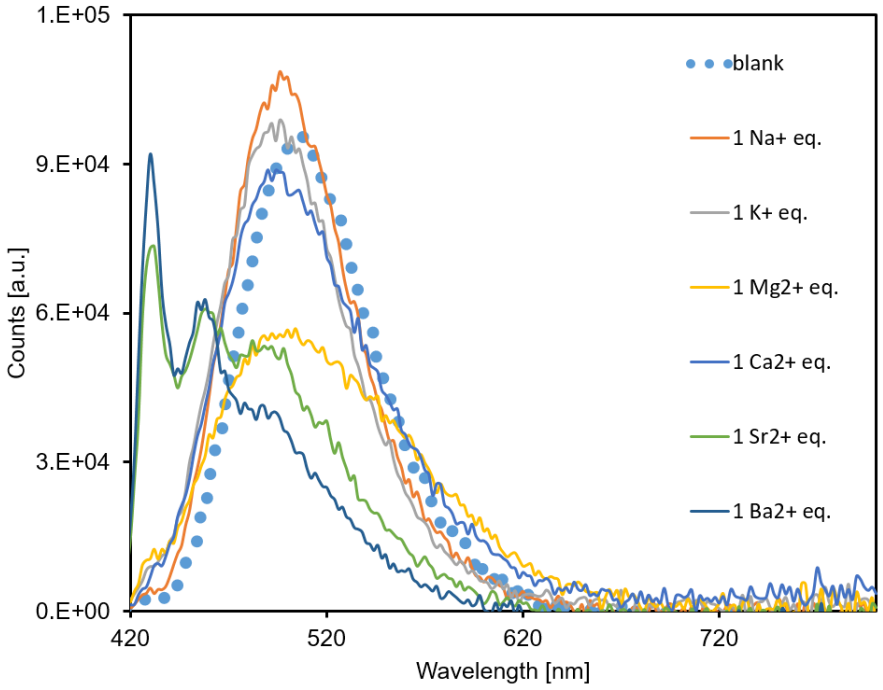

2.E+05
1.E+05
9.E+04
6.E+04
3.E+04
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

1-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-*N*-(3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide (15aa)

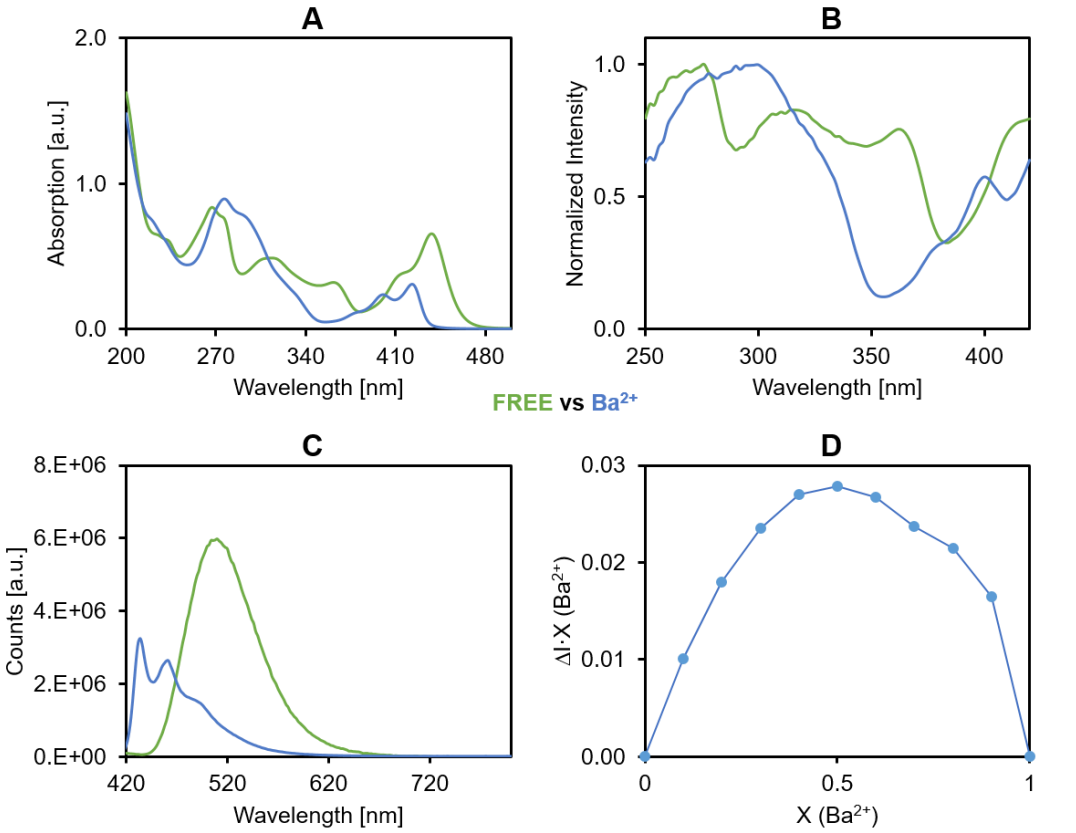


Lifetime (ns);	τ_{free} = 3.35 (98.00%), 14.53 (2.00%); χ^2 = 1.1758 τ_{Ba} = 3.71 (100.00%); χ^2 = 1.2310
A = Absorption;	λ_{free} = 442 nm; λ_{Ba} = 404 nm
B = Normalized excitation;	λ_{free} = 316 nm; λ_{Ba} = 400 nm
C = Emission; (exc: λ_{free} = 316 nm; λ_{Ba} = 400 nm);	λ_{free} = 508 nm; λ_{Ba} = 434, 462, 494 nm
D = Job Plot;	

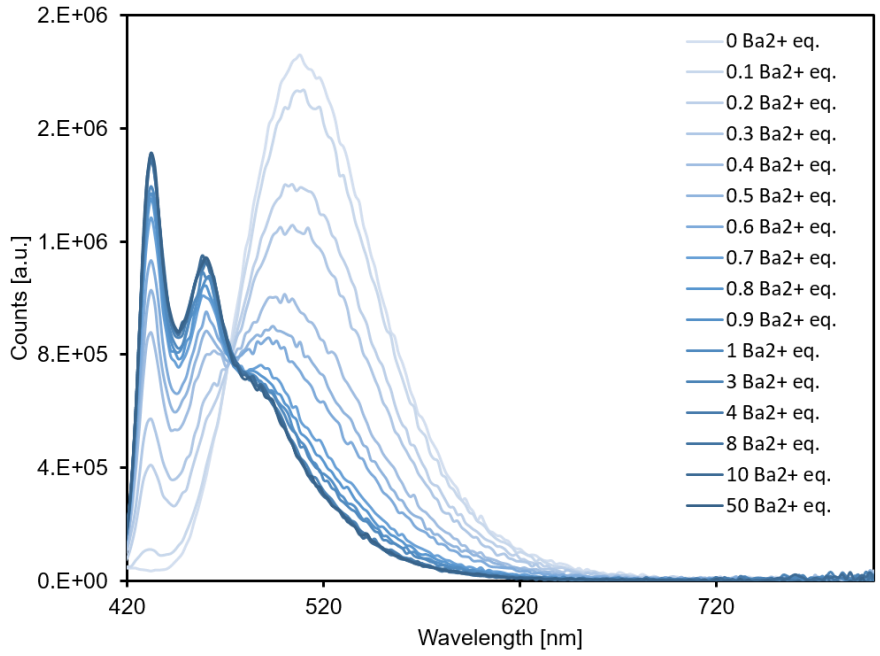

2.E+06
2.E+06
1.E+06
8.E+05
4.E+05
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
50 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
0 Ba2+ eq.


1.E+05
9.E+04
6.E+04
3.E+04
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

1-(4-(1,4,7,10,13-Pentaoxa-16-azacyclooctadecan-16-yl)phenyl)-*N*-(11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide (15ab)



Lifetime (ns);	τ_{free} = 3.38 (100.00%); χ^2 = 1.3521 τ_{Ba} = 3.53 (100.00%); χ^2 = 1.4100
A = Absorption;	λ_{free} = 442 nm; λ_{Ba} = 426 nm
B = Normalized excitation;	λ_{free} = 316 nm; λ_{Ba} = 400 nm
C = Emission; (exc: λ_{free} = 316 nm; λ_{Ba} = 400 nm);	λ_{free} = 504 nm; λ_{Ba} = 432, 464, 494 nm
D = Job Plot;	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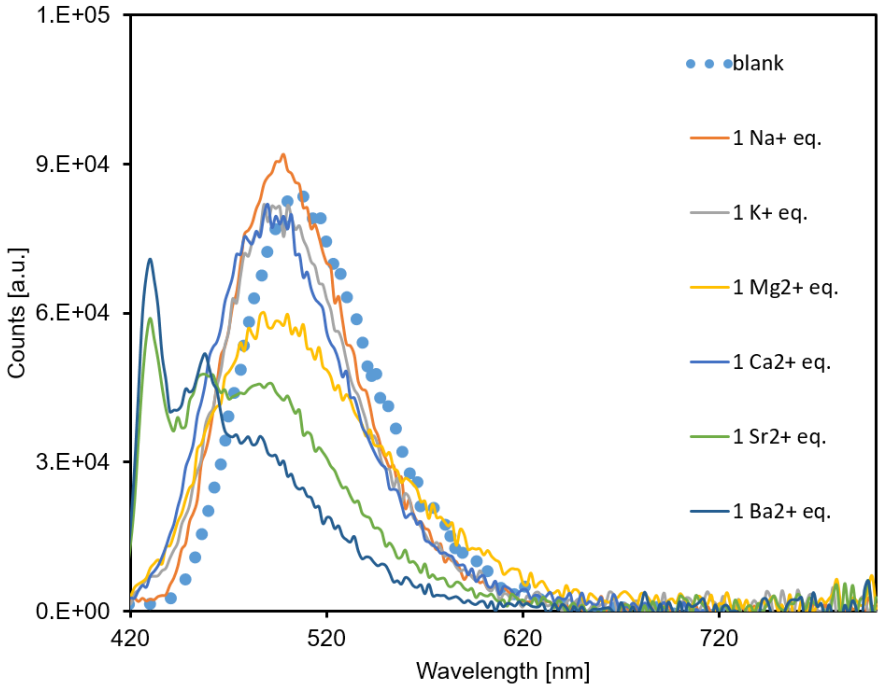
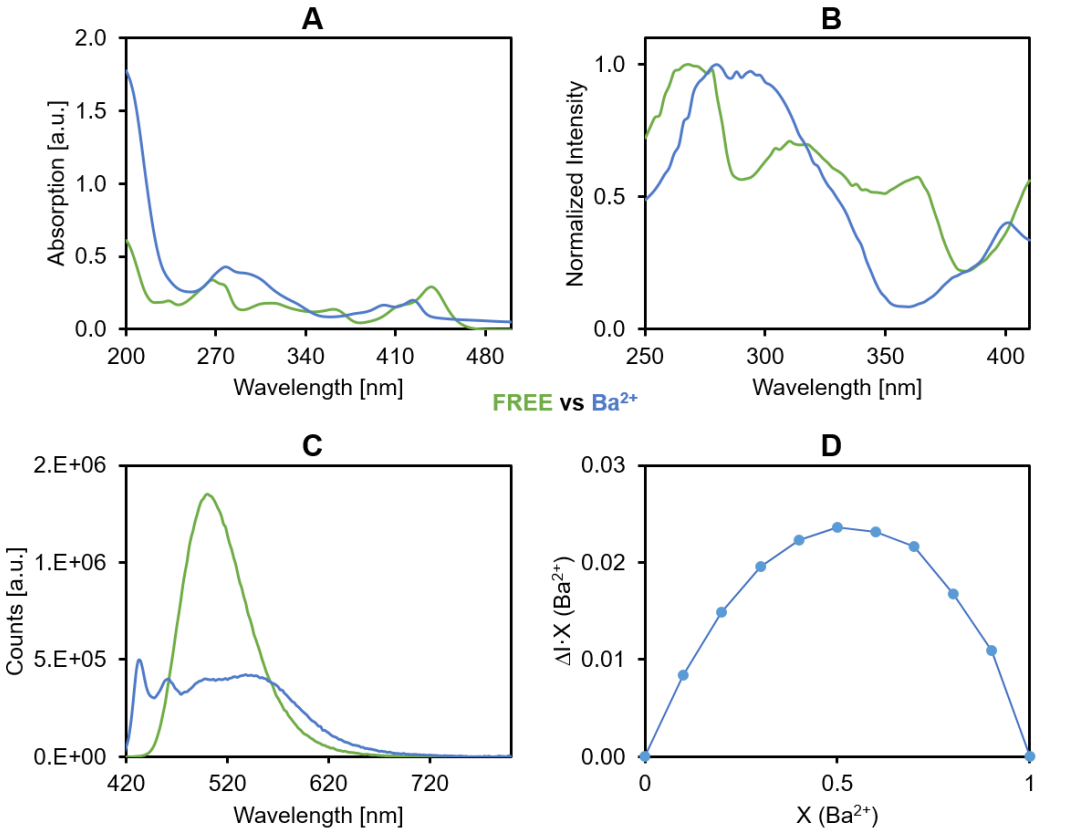
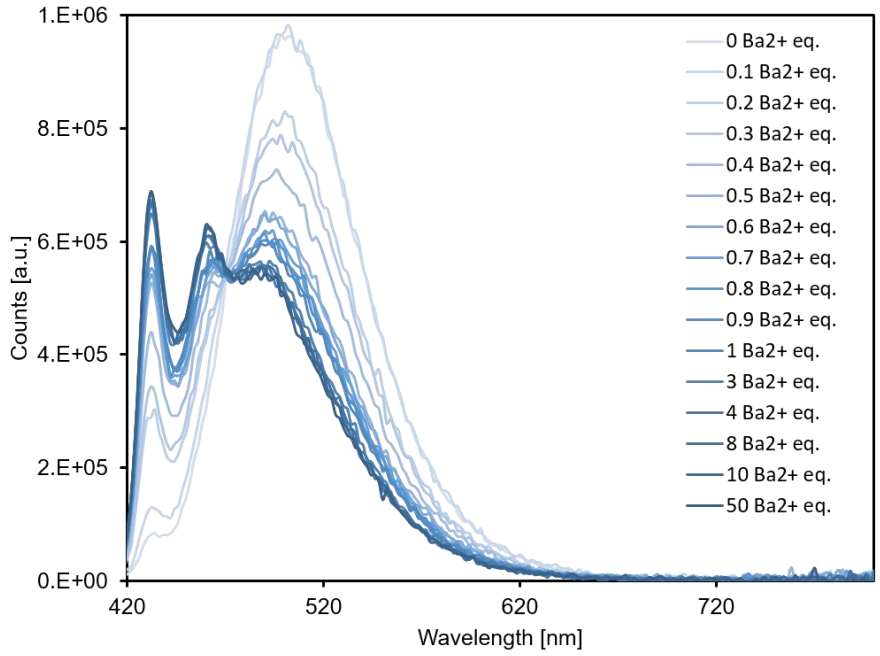
2.E+06
1.E+06
8.E+05
4.E+05
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.

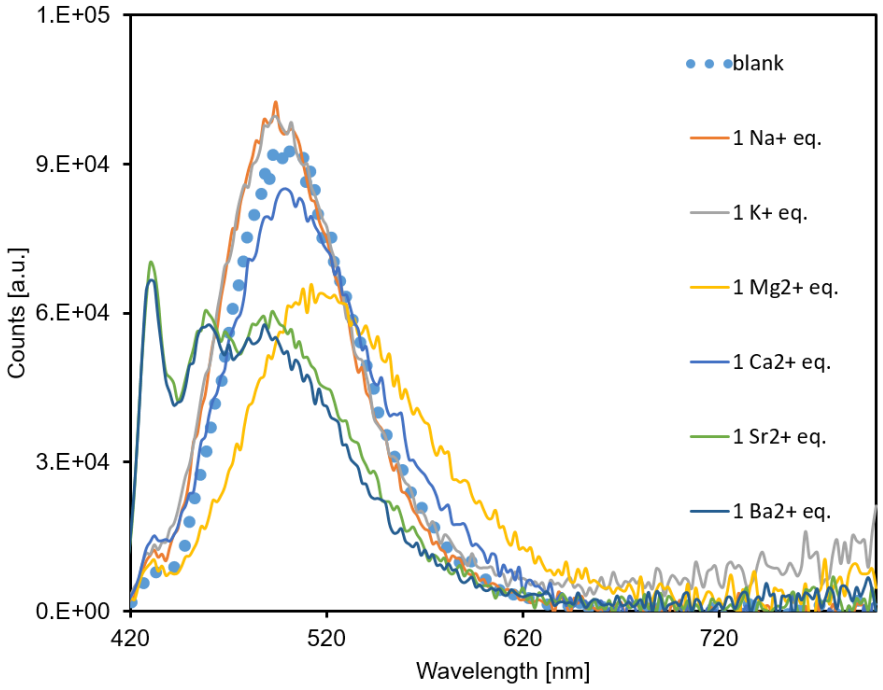

1.E+05
9.E+04
6.E+04
3.E+04
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

***N*-(3-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)propyl)-1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide (15ba)**

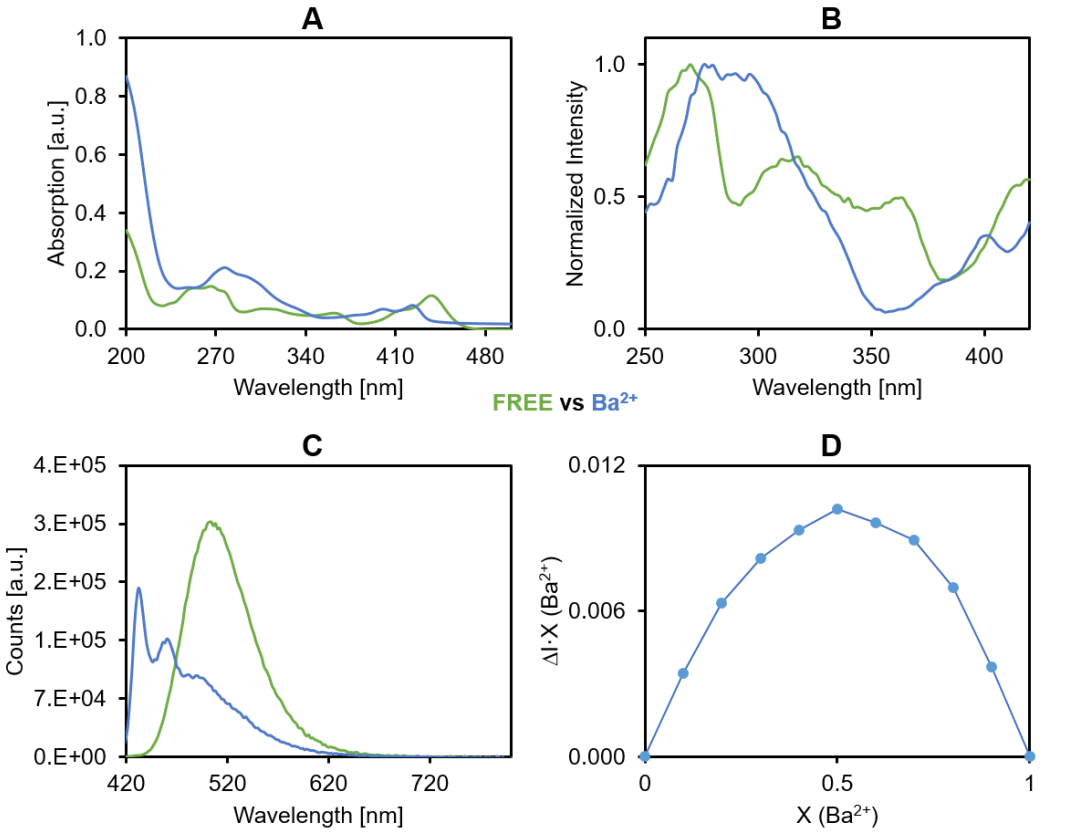


Lifetime (ns);	τ_{free} = 3.22 (100.00%); χ^2 = 1.2197 τ_{Ba} = 2.62 (80.59%), 4.25 (19.41%); χ^2 = 1.0968
A = Absorption;	λ_{free} = 442 nm; λ_{Ba} = 428 nm
B = Normalized excitation;	λ_{free} = 314 nm; λ_{Ba} = 400 nm
C = Emission; (exc: λ_{free} = 314 nm; λ_{Ba} = 400 nm);	λ_{free} = 502 nm; λ_{Ba} = 432, 464, 498 nm
D = Job Plot;	

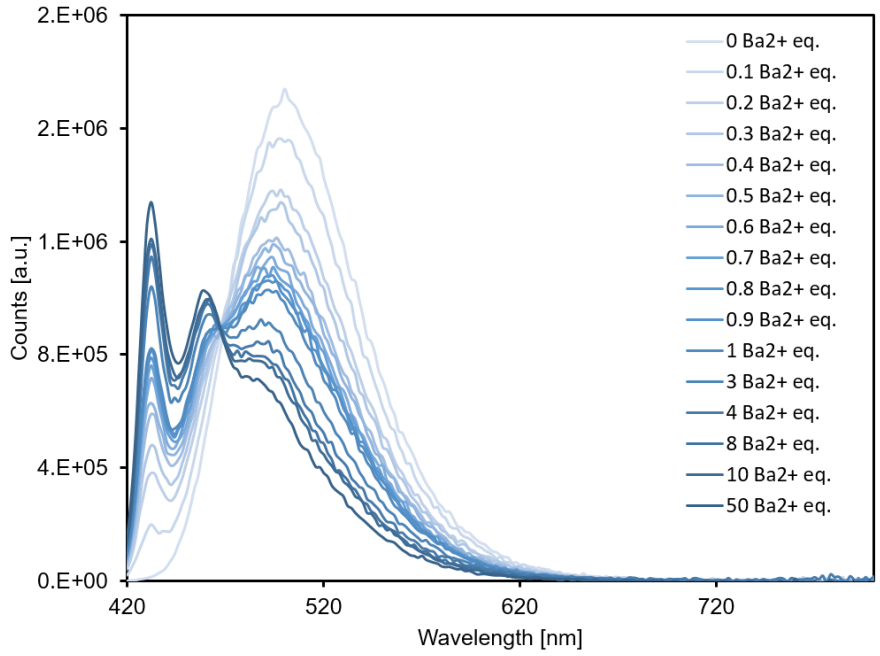

1.E+06
8.E+05
6.E+05
4.E+05
2.E+05
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.

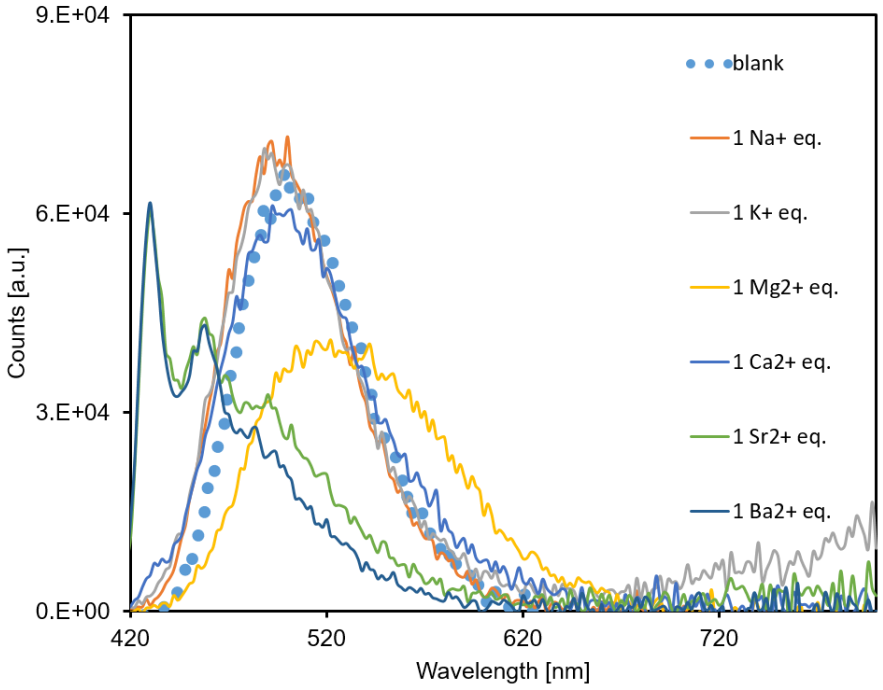

1.E+05
9.E+04
6.E+04
3.E+04
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

***N*-(11-(2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecan-1-yl)undecyl)-1-(4-(16-benzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)phenyl)benzo[*a*]imidazo[5,1,2-*cd*]indolizine-4-carboxamide (15bb)**



Lifetime (ns);	τ_{free} = 3.25 (100.00%); χ^2 = 1.1232 τ_{Ba} = 2.91 (100.00%); χ^2 = 1.1784
A = Absorption;	λ_{free} = 443 nm; λ_{Ba} = 428 nm
B = Normalized excitation;	λ_{free} = 316 nm; λ_{Ba} = 400 nm
C = Emission; (exc: λ_{free} = 316 nm; λ_{Ba} = 400 nm);	λ_{free} = 505 nm; λ_{Ba} = 432, 464, 496 nm
D = Job Plot;	

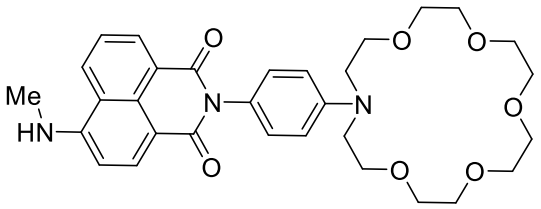

2.E+06
2.E+06
1.E+06
8.E+05
4.E+05
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
0 Ba2+ eq.
0.1 Ba2+ eq.
0.2 Ba2+ eq.
0.3 Ba2+ eq.
0.4 Ba2+ eq.
0.5 Ba2+ eq.
0.6 Ba2+ eq.
0.7 Ba2+ eq.
0.8 Ba2+ eq.
0.9 Ba2+ eq.
1 Ba2+ eq.
3 Ba2+ eq.
4 Ba2+ eq.
8 Ba2+ eq.
10 Ba2+ eq.
50 Ba2+ eq.


9.E+04
6.E+04
3.E+04
0.E+00
Counts [a.u.]
420
520
620
720
Wavelength [nm]
blank
1 Na+ eq.
1 K+ eq.
1 Mg2+ eq.
1 Ca2+ eq.
1 Sr2+ eq.
1 Ba2+ eq.

6. Computational data

Full ref. (34) of the main text: Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; S115 Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. and Fox, D. J Gaussian, Inc., Wallingford CT, 2009.

Cartesian coordinates (in Å) 7aa' (UV/Vis)



7aa'

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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3	6	0	1.299533	-0.167783	-1.396882
4	6	0	-0.108831	-0.643964	0.949114
5	1	0	1.797147	-0.552776	1.924278
6	6	0	-0.080032	-0.319667	-1.442206
7	1	0	1.848459	0.026453	-2.311033
8	6	0	-0.829257	-0.564113	-0.266724
9	1	0	-0.620870	-0.856884	1.876300
10	1	0	-0.573047	-0.223342	-2.398508
11	6	0	-6.698852	2.834301	0.880630
12	1	0	-7.203356	2.870055	-0.090326
13	1	0	-6.776561	3.835584	1.326687
14	6	0	-7.383485	1.827959	1.789145
15	1	0	-8.399899	2.176389	2.014440
16	1	0	-6.833441	1.753661	2.729771
17	6	0	-8.393093	0.282615	0.246291
18	1	0	-8.574543	1.187146	-0.346279
19	1	0	-9.341075	-0.003544	0.720653
20	6	0	-7.925162	-0.802667	-0.702771
21	1	0	-6.945662	-0.531177	-1.107571
22	1	0	-8.637775	-0.866433	-1.533058
23	6	0	-6.585320	-2.710417	-0.090627
24	1	0	-6.118730	-2.602795	-1.077412
25	1	0	-6.755602	-3.773755	0.089118
26	6	0	-5.670709	-2.119375	0.972871
27	1	0	-6.045653	-2.360062	1.976848
28	1	0	-5.669579	-1.033140	0.872657
29	6	0	-3.376950	-1.940944	1.552048
30	1	0	-2.502427	-2.591968	1.602406

31	1	0	-3.741939	-1.771710	2.574446
32	6	0	-3.004211	-0.601583	0.913583
33	1	0	-2.466225	0.004438	1.644180
34	1	0	-3.905977	-0.040717	0.664080
35	6	0	-2.911608	-0.875796	-1.562543
36	1	0	-3.755017	-1.547689	-1.396096
37	1	0	-2.257965	-1.370650	-2.280954
38	6	0	-3.442493	0.424330	-2.158161
39	1	0	-3.587831	0.315908	-3.241738
40	1	0	-2.726095	1.236142	-1.987888
41	6	0	-5.127541	2.067278	-1.685031
42	1	0	-4.718033	2.512658	-2.599679
43	1	0	-6.214037	2.038672	-1.795938
44	6	0	-4.731836	2.919282	-0.485486
45	1	0	-3.652979	2.858183	-0.326835
46	1	0	-4.987248	3.969727	-0.680457
47	7	0	-2.200522	-0.721334	-0.299590
48	8	0	-4.360917	-2.656123	0.800902
49	8	0	-7.867120	-2.087359	-0.070501
50	8	0	-7.404541	0.513476	1.244760
51	8	0	-5.330469	2.470997	0.727709
52	8	0	-4.695556	0.718082	-1.538718
53	6	0	3.904225	1.224546	0.042636
54	6	0	4.211222	-1.225613	-0.308259
55	6	0	5.372707	1.383077	0.079286
56	6	0	5.662569	-1.035416	-0.237398
57	6	0	6.216932	0.249646	-0.024087
58	6	0	7.632188	0.422522	0.045434
59	6	0	8.144423	1.739700	0.106977
60	6	0	5.912381	2.651559	0.195137
61	6	0	7.303896	2.831052	0.183202
62	1	0	9.213164	1.894617	0.060872
63	1	0	5.245796	3.501004	0.267363
64	1	0	7.717692	3.830830	0.221534
65	6	0	6.510274	-2.121270	-0.397319
66	6	0	8.476378	-0.739982	-0.023151
67	6	0	7.893530	-1.977686	-0.288565
68	1	0	6.080513	-3.098745	-0.575220
69	1	0	8.528974	-2.852298	-0.367847
70	7	0	3.413284	-0.074497	-0.146932
71	8	0	3.133563	2.166518	0.167354
72	8	0	3.681253	-2.313919	-0.493529
73	7	0	9.855625	-0.630755	0.113620
74	1	0	10.310105	-1.497739	-0.146228
75	6	0	10.438032	-0.116990	1.366219
76	1	0	10.336407	-0.843575	2.180723
77	1	0	11.496167	0.088663	1.204083
78	1	0	9.952100	0.805092	1.671807

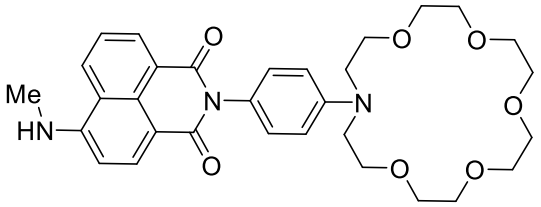
Zero-point correction=	0.649426(Hartree/Particle)
Thermal correction to Energy=	0.687289
Thermal correction to Enthalpy=	0.688234
Thermal correction to Gibbs Free Energy=	0.574695
Sum of electronic and zero-point Energies=	-1894.428451
Sum of electronic and thermal Energies=	-1894.390588
Sum of electronic and thermal Enthalpies=	-1894.389644
Sum of electronic and thermal Free Energies=	-1894.503183

Excitation energies and oscillator strengths 7aa' (UV/Vis).

```
 Excited State   1:      Singlet-A      2.6807 eV  462.50 nm  f=0.0001
                          <S**2>=0.000
                      150 -> 151        0.70355
      This state for optimization and/or second-order correction.
           Total Energy, E(TD-HF/TD-DFT) =  -1893.53203998
 Copying the excited state density for this state as the 1-particle RhoCI
                               density.

 Excited State   2:      Singlet-A      3.0956 eV  400.52 nm  f=0.3669
                          <S**2>=0.000
                      149 -> 151        0.69934

 Excited State   3:      Singlet-A      3.9601 eV  313.09 nm  f=0.0111
                          <S**2>=0.000
                      145 -> 151        0.56970
                      149 -> 154       -0.37211

 Excited State   4:      Singlet-A      3.9898 eV  310.75 nm  f=0.0056
                          <S**2>=0.000
                      150 -> 152        0.61332
                      150 -> 153       -0.23329
                      150 -> 155        0.14991
                      150 -> 156        0.11497
                      150 -> 158        0.11183

 Excited State   5:      Singlet-A      4.0866 eV  303.39 nm  f=0.0004
                          <S**2>=0.000
                      141 -> 151        0.64595
                      144 -> 151        0.15149

 Excited State   6:      Singlet-A      4.2020 eV  295.06 nm  f=0.0342
                          <S**2>=0.000
                      150 -> 163        0.63199
                      150 -> 165        0.11550
                      150 -> 166       -0.21115

 Excited State   7:      Singlet-A      4.2191 eV  293.87 nm  f=0.0345
                          <S**2>=0.000
                      150 -> 152       -0.11388
                      150 -> 153       -0.38324
                      150 -> 155       -0.15886
                      150 -> 156        0.40101
                      150 -> 157        0.12128
                      150 -> 158       -0.27726
                      150 -> 160       -0.15244

 Excited State   8:      Singlet-A      4.2330 eV  292.90 nm  f=0.0349
                          <S**2>=0.000
                      143 -> 151       -0.12054
                      150 -> 152       -0.11122
                      150 -> 153       -0.17373
                      150 -> 154        0.24545
                      150 -> 155        0.37542
                      150 -> 156       -0.18591
                      150 -> 157       -0.24171
                      150 -> 158       -0.31203
                      150 -> 161       -0.13638

 Excited State   9:      Singlet-A      4.2562 eV  291.30 nm  f=0.0103
                          <S**2>=0.000
```

```
                      143 -> 151       -0.41300
                      146 -> 151        0.50133
                      147 -> 151       -0.10529
                      148 -> 151        0.15104

     Excited State 10:      Singlet-A      4.2933 eV 288.79 nm f=0.0006
                             <S**2>=0.000
                      150 -> 154        0.15843
                      150 -> 155        0.25224
                      150 -> 156       -0.10905
                      150 -> 157        0.58118
                      150 -> 162        0.20093
SavETr:  write IOETrn=   770 NScale= 10 NData= 16 NLR=1 NState=   10 LETran=
                                  190.
```

Cartesian coordinates (in Å) 7aa' (Emission)



7aa'

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	0.056423	-0.088459	-1.111480
5	1	0	-1.819229	0.367393	-2.002084
6	6	0	-0.022464	-0.798290	1.222728
7	1	0	-1.951121	-0.819069	2.117071
8	6	0	0.745990	-0.525429	0.055217
9	1	0	0.593433	0.080221	-2.035062
10	1	0	0.464747	-1.081450	2.146125
11	6	0	6.790060	2.817275	0.182576
12	1	0	7.299150	2.497462	1.104490
13	1	0	6.845509	3.917246	0.152608
14	6	0	7.494160	2.240455	-1.019171
15	1	0	8.508573	2.663146	-1.086088
16	1	0	6.954378	2.523933	-1.929171
17	6	0	8.500652	0.260154	-0.152126
18	1	0	8.734842	0.920293	0.697163
19	1	0	9.436314	0.098799	-0.710443
20	6	0	7.988165	-1.042821	0.402819
21	1	0	7.042381	-0.864343	0.935059
22	1	0	8.717791	-1.428677	1.128122
23	6	0	6.491042	-2.504755	-0.745648
24	1	0	6.054452	-2.731994	0.240764
25	1	0	6.554144	-3.445081	-1.303331
26	6	0	5.601337	-1.523063	-1.473805
27	1	0	5.986201	-1.333545	-2.488296
28	1	0	5.599980	-0.564372	-0.937735
29	6	0	3.349088	-1.169138	-2.034401
30	1	0	2.477325	-1.752724	-2.349130
31	1	0	3.740092	-0.639209	-2.915912
32	6	0	2.930514	-0.121025	-1.005288

33	1	0	2.408878	0.699665	-1.496143
34	1	0	3.814016	0.308088	-0.519237
35	6	0	2.794080	-1.378896	1.125021
36	1	0	3.567045	-1.988143	0.644278
37	1	0	2.106663	-2.063104	1.618951
38	6	0	3.442574	-0.444011	2.127180
39	1	0	3.585216	-0.979414	3.077500
40	1	0	2.778229	0.412673	2.324590
41	6	0	5.203497	1.140925	2.238955
42	1	0	4.842762	1.222707	3.273714
43	1	0	6.292533	1.016338	2.286568
44	6	0	4.846067	2.385319	1.457892
45	1	0	3.761107	2.424892	1.298779
46	1	0	5.128128	3.282704	2.030068
47	7	0	2.088608	-0.669987	0.055356
48	8	0	4.300180	-2.077910	-1.542159
49	8	0	7.803819	-2.011004	-0.616135
50	8	0	7.527543	0.831993	-0.997552
51	8	0	5.444397	2.391157	0.179453
52	8	0	4.683882	-0.019692	1.613652
53	6	0	-3.929918	1.252350	-0.286002
54	6	0	-4.224993	-1.165313	0.410385
55	6	0	-5.354435	1.396514	-0.291759
56	6	0	-5.645246	-0.959877	0.392320
57	6	0	-6.192342	0.296932	0.030728
58	6	0	-7.612776	0.473909	0.011303
59	6	0	-8.131431	1.758851	-0.270686
60	6	0	-5.915616	2.653375	-0.598004
61	6	0	-7.287510	2.820679	-0.570687
62	1	0	-9.203103	1.914714	-0.222723
63	1	0	-5.251897	3.476862	-0.836449
64	1	0	-7.713959	3.797538	-0.781638
65	6	0	-6.497544	-2.024689	0.728339
66	6	0	-8.442500	-0.642562	0.306064
67	6	0	-7.868060	-1.858675	0.672547
68	1	0	-6.062135	-2.977035	1.009511
69	1	0	-8.524306	-2.694732	0.906237
70	7	0	-3.441549	-0.039303	0.058777
71	8	0	-3.117879	2.151141	-0.525343
72	8	0	-3.662351	-2.230585	0.675347
73	7	0	-9.847118	-0.500632	0.253800
74	1	0	-10.283934	-1.270893	0.749479
75	6	0	-10.419181	-0.410361	-1.088667
76	1	0	-10.177310	-1.286334	-1.710106
77	1	0	-11.506038	-0.323816	-1.015935
78	1	0	-10.045168	0.478073	-1.603596

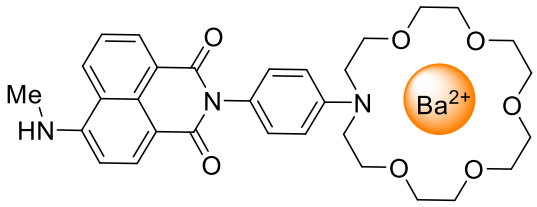
Excitation energies and oscillator strengths 7aa' (Emission).

```
 Excited State   1:      Singlet-A      2.0515 eV  604.35 nm  f=0.0067
                          <S**2>=0.000
                         150 -> 151        0.70334
      This state for optimization and/or second-order correction.
            Total Energy, E(TD-HF/TD-DFT) =  -1893.54611630
 Copying the excited state density for this state as the 1-particle RhoCI
                               density.

 Excited State   2:      Singlet-A      2.9388 eV  421.88 nm  f=0.5020
                          <S**2>=0.000
                         149 -> 151       -0.70082

 Excited State   3:      Singlet-A      3.5688 eV  347.41 nm  f=0.3635
                          <S**2>=0.000
```

```
                      150 -> 152       -0.59544
                      150 -> 153        0.29438
                      150 -> 154        0.18015

Excited State   4:      Singlet-A      3.6554 eV  339.18 nm  f=0.0176
                          <S**2>=0.000
                      150 -> 152       -0.24681
                      150 -> 153       -0.59979
                      150 -> 156        0.11741
                      150 -> 157       -0.21982

Excited State   5:      Singlet-A      3.7830 eV  327.74 nm  f=0.0024
                          <S**2>=0.000
                      140 -> 151        0.14317
                      141 -> 151       -0.51215
                      142 -> 151        0.12732
                      143 -> 151        0.20413
                      145 -> 151        0.21274
                      146 -> 151        0.10906
                      147 -> 151       -0.14800
                      148 -> 151       -0.20156

Excited State   6:      Singlet-A      3.8352 eV  323.28 nm  f=0.0330
                          <S**2>=0.000
                      138 -> 151        0.13746
                      144 -> 151        0.26663
                      146 -> 151       -0.34323
                      147 -> 151       -0.51692

Excited State   7:      Singlet-A      3.8702 eV  320.36 nm  f=0.0771
                          <S**2>=0.000
                      141 -> 151        0.23022
                      142 -> 151       -0.22528
                      143 -> 151        0.45760
                      144 -> 151       -0.30718
                      147 -> 151       -0.11847
                      149 -> 155        0.23561

Excited State   8:      Singlet-A      3.9196 eV  316.32 nm  f=0.0024
                          <S**2>=0.000
                      144 -> 151       -0.18884
                      146 -> 151       -0.10062
                      150 -> 155       -0.46660
                      150 -> 156       -0.33870
                      150 -> 157       -0.13999
                      150 -> 158        0.18112
                      150 -> 161       -0.16186

Excited State   9:      Singlet-A      3.9337 eV  315.18 nm  f=0.0069
                          <S**2>=0.000
                      141 -> 151        0.10076
                      143 -> 151        0.14814
                      144 -> 151        0.35321
                      145 -> 151        0.12136
                      146 -> 151        0.13156
                      148 -> 151       -0.13892
                      150 -> 154        0.11364
                      150 -> 155        0.18432
                      150 -> 156       -0.36096
                      150 -> 157       -0.14184
                      150 -> 158        0.20235
                      150 -> 161       -0.13748

Excited State  10:      Singlet-A      3.9483 eV  314.02 nm  f=0.0278
                          <S**2>=0.000
                      143 -> 151       -0.14139
                      144 -> 151       -0.32667
                      145 -> 151       -0.12013
```

146 -> 151	-0.12566
148 -> 151	0.14154
150 -> 155	0.47798
150 -> 156	-0.17921
150 -> 158	0.12543

Cartesian coordinates (in Å) 7aa'-Ba(ClO$_4$)$_2$ (UV/Vis).



7aa'-Ba(ClO$_4$)$_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.112822	-2.690667	-0.383232
2	6	0	-0.515793	-2.473141	-1.618306
3	6	0	-0.382446	-3.283288	0.635755
4	6	0	0.831547	-2.745332	-1.803636
5	1	0	-1.079359	-2.000814	-2.410830
6	6	0	0.960670	-3.583583	0.451668
7	1	0	-0.842316	-3.453163	1.601081
8	6	0	1.623393	-3.250821	-0.749329
9	1	0	1.270838	-2.492981	-2.755557
10	1	0	1.499623	-4.020398	1.277184
11	6	0	3.995581	2.885828	1.233636
12	1	0	4.538183	3.193891	0.330096
13	1	0	4.594843	3.179223	2.106031
14	6	0	2.644640	3.563819	1.347269
15	1	0	2.782744	4.650937	1.379551
16	1	0	2.157600	3.233739	2.264684
17	6	0	1.762894	4.013784	-0.888186
18	1	0	2.030877	5.047761	-0.643145
19	1	0	0.743211	3.983674	-1.265791
20	6	0	2.705678	3.476368	-1.952232
21	1	0	3.761972	3.615380	-1.684395
22	1	0	2.514515	4.015098	-2.889614
23	6	0	3.107493	1.504286	-3.226160
24	1	0	4.194435	1.620384	-3.106465
25	1	0	2.797961	1.997154	-4.157028
26	6	0	2.721122	0.040625	-3.276318
27	1	0	3.218787	-0.447225	-4.119817
28	1	0	1.641191	-0.041801	-3.401501
29	6	0	4.169990	-1.514398	-2.076688
30	1	0	4.767166	-1.321136	-1.187773
31	1	0	4.781397	-1.327613	-2.967826
32	6	0	3.709392	-2.973891	-2.070233
33	1	0	4.603830	-3.598909	-2.169124
34	1	0	3.095239	-3.185879	-2.946557
35	6	0	3.815486	-3.746117	0.286774
36	1	0	4.829016	-3.913612	-0.081650
37	1	0	3.474049	-4.701960	0.703918
38	6	0	3.879581	-2.742227	1.439330
39	1	0	4.632419	-3.114926	2.148815
40	1	0	2.933280	-2.646437	1.973317
41	6	0	4.731736	-0.620909	2.013309
42	1	0	3.994426	-0.560862	2.817258
43	1	0	5.665506	-1.036957	2.420170
44	6	0	5.020852	0.762248	1.488359
45	1	0	5.593780	1.295965	2.256195
46	1	0	5.627944	0.715370	0.574086

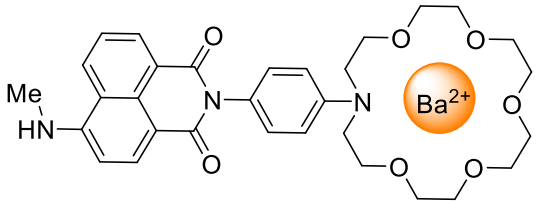
47	7	0	3.002561	-3.384732	-0.866772
48	8	0	3.070955	-0.596817	-2.041150
49	8	0	2.437425	2.091362	-2.118927
50	8	0	1.750900	3.212337	0.294049
51	8	0	3.809993	1.473714	1.233308
52	8	0	4.264465	-1.456302	0.959473
53	56	0	1.256374	0.460289	-0.000513
54	6	0	-2.355490	-0.773028	0.345655
55	6	0	-3.569213	-2.820100	-0.395203
56	6	0	-3.619840	-0.082364	0.513840
57	6	0	-4.844522	-2.095205	-0.181801
58	6	0	-4.841504	-0.743916	0.243989
59	7	0	-2.397305	-2.096567	-0.117231
60	8	0	-1.266307	-0.249544	0.578090
61	8	0	-3.509408	-3.968039	-0.791497
62	6	0	-6.079928	-0.055438	0.396433
63	6	0	-6.054068	1.336105	0.785749
64	6	0	-3.629713	1.246310	0.905859
65	6	0	-7.273680	-0.768664	0.155775
66	6	0	-6.034894	-2.754948	-0.425083
67	6	0	-4.824698	1.948717	1.039557
68	6	0	-7.255437	-2.090452	-0.245234
69	1	0	-2.682294	1.739053	1.081693
70	1	0	-4.789236	2.990302	1.324751
71	1	0	-8.237240	-0.293337	0.297932
72	1	0	-8.186693	-2.614842	-0.420643
73	1	0	-5.998302	-3.786344	-0.752060
74	7	0	-7.225775	2.028044	0.912016
75	1	0	-8.048188	1.619455	0.504734
76	6	0	-7.281578	3.452188	1.181833
77	1	0	-8.326408	3.760178	1.203611
78	1	0	-6.841182	3.679687	2.156352
79	1	0	-6.757854	4.039684	0.418069
80	17	0	1.165396	0.181215	3.468407
81	17	0	-1.080843	1.667834	-2.378825
82	8	0	2.364919	0.489392	4.286426
83	8	0	0.042111	-0.270324	4.301496
84	8	0	0.776349	1.394665	2.649569
85	8	0	1.525359	-0.889830	2.443635
86	8	0	-0.744832	2.290397	-1.042037
87	8	0	-0.651684	2.570846	-3.473640
88	8	0	-0.278711	0.376401	-2.436409
89	8	0	-2.520665	1.358530	-2.455999

Zero-point correction=	0.683640 (Hartree/Particle)
Thermal correction to Energy=	0.734729
Thermal correction to Enthalpy=	0.735674
Thermal correction to Gibbs Free Energy=	0.594183
Sum of electronic and zero-point Energies=	-3441.892932
Sum of electronic and thermal Energies=	-3441.841843
Sum of electronic and thermal Enthalpies=	-3441.840899
Sum of electronic and thermal Free Energies=	-3441.982389

Excitation energies and oscillator strengths 7aa'-$Ba(ClO_4)_2$ (UV/Vis)

```
 Excited State   1:      Singlet-A      3.0958 eV  400.49 nm  f=0.0001
                          <S**2>=0.000
                      204 -> 205        0.70302
     This state for optimization and/or second-order correction.
          Total Energy, E(TD-HF/TD-DFT) =  -3440.62265189
Copying the excited state density for this state as the 1-particle RhoCI
                              density.

 Excited State   2:      Singlet-A      3.1357 eV  395.39 nm  f=0.2715
                          <S**2>=0.000
                      203 -> 205        0.69660

 Excited State   3:      Singlet-A      3.7647 eV  329.33 nm  f=0.0192
                          <S**2>=0.000
                      204 -> 206        0.66761
                      204 -> 208        0.21565

 Excited State   4:      Singlet-A      3.9848 eV  311.14 nm  f=0.0005
                          <S**2>=0.000
                      201 -> 205       -0.15605
                      203 -> 207        0.66474
                      203 -> 215       -0.12625

 Excited State   5:      Singlet-A      4.0100 eV  309.19 nm  f=0.0018
                          <S**2>=0.000
                      201 -> 205        0.50953
                      203 -> 207        0.20570
                      203 -> 215        0.39579
                      203 -> 216        0.14597

 Excited State   6:      Singlet-A      4.0291 eV  307.72 nm  f=0.0114
                          <S**2>=0.000
                      204 -> 206       -0.22201
                      204 -> 208        0.58868
                      204 -> 209        0.10257
                      204 -> 210       -0.27725

 Excited State   7:      Singlet-A      4.0709 eV  304.56 nm  f=0.0002
                          <S**2>=0.000
                      197 -> 205        0.13080
                      200 -> 205        0.65064
                      200 -> 235       -0.10367

 Excited State   8:      Singlet-A      4.1132 eV  301.43 nm  f=0.0063
                          <S**2>=0.000
                      204 -> 208       -0.10052
                      204 -> 209        0.67173
                      204 -> 212       -0.17559

 Excited State   9:      Singlet-A      4.1454 eV  299.09 nm  f=0.0000
                          <S**2>=0.000
                      203 -> 206        0.70574

 Excited State  10:      Singlet-A      4.2495 eV  291.76 nm  f=0.0005
                          <S**2>=0.000
                      204 -> 207        0.69265
                      204 -> 210       -0.10899
```

Cartesian coordinates (in Å) 7aa'-Ba(ClO$_4$)$_2$ (Emission)



7aa'-Ba(ClO$_4$)$_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.834267	2.576876	0.603132
2	6	0	0.409172	2.975984	-0.659061
3	6	0	-0.066441	2.577956	1.654270
4	6	0	-0.923364	3.261521	-0.888584
5	1	0	1.120181	3.004570	-1.473788
6	6	0	-1.406807	2.876651	1.434430
7	1	0	0.255678	2.277698	2.644022
8	6	0	-1.882750	3.162491	0.141116
9	1	0	-1.211043	3.532635	-1.893094
10	1	0	-2.073443	2.841328	2.280848
11	6	0	-3.620992	-3.276519	-0.278716
12	1	0	-3.929460	-3.314999	-1.332525
13	1	0	-4.329419	-3.871275	0.311745
14	6	0	-2.234260	-3.840548	-0.075541
15	1	0	-2.204852	-4.881525	-0.416456
16	1	0	-1.986045	-3.800540	0.984422
17	6	0	-0.945987	-3.432840	-2.081353
18	1	0	-1.194098	-4.485465	-2.257988
19	1	0	0.125421	-3.294133	-2.200007
20	6	0	-1.675626	-2.569617	-3.097274
21	1	0	-2.732739	-2.848779	-3.201995
22	1	0	-1.182695	-2.693958	-4.069531
23	6	0	-1.990695	-0.319974	-3.710617
24	1	0	-2.988706	-0.598336	-4.077483
25	1	0	-1.270842	-0.365907	-4.537017
26	6	0	-2.010514	1.074691	-3.124131
27	1	0	-2.360342	1.790936	-3.874692
28	1	0	-0.998165	1.350294	-2.821135
29	6	0	-4.004378	1.916243	-2.026388
30	1	0	-4.762659	1.421554	-1.423083
31	1	0	-4.364535	1.993148	-3.060241
32	6	0	-3.748928	3.317536	-1.465980
33	1	0	-4.700042	3.857827	-1.480117
34	1	0	-3.081521	3.878665	-2.121115
35	6	0	-4.198937	3.265477	0.977693
36	1	0	-5.156262	3.577488	0.557039
37	1	0	-3.937916	4.001669	1.747687
38	6	0	-4.398044	1.911803	1.675792
39	1	0	-5.386954	1.943536	2.153362
40	1	0	-3.665219	1.709786	2.458507
41	6	0	-5.028338	-0.288186	1.230630
42	1	0	-4.588152	-0.613831	2.177818
43	1	0	-6.088066	-0.043994	1.391094
44	6	0	-4.946500	-1.404292	0.225405
45	1	0	-5.642366	-2.189358	0.543308
46	1	0	-5.244771	-1.055812	-0.772673
47	7	0	-3.236523	3.332146	-0.107344
48	8	0	-2.853238	1.085518	-1.974294
49	8	0	-1.597990	-1.216540	-2.688503
50	8	0	-1.249004	-3.071291	-0.742052

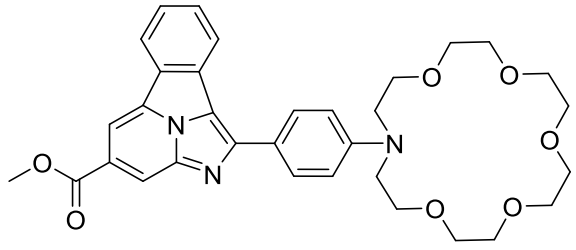
51	8	0	-3.632332	-1.933785	0.176310
52	8	0	-4.356940	0.856222	0.733685
53	56	0	-1.202070	-0.306300	-0.032564
54	6	0	2.181003	0.665784	1.018415
55	6	0	3.281105	2.819995	0.428682
56	6	0	3.490158	0.003740	0.940097
57	6	0	4.557482	2.144392	0.405437
58	6	0	4.651387	0.753117	0.620279
59	7	0	2.141772	2.012427	0.755485
60	8	0	1.165045	0.019575	1.275599
61	8	0	3.110420	4.002988	0.193648
62	6	0	5.901521	0.097902	0.521769
63	6	0	5.905136	-1.334605	0.656792
64	6	0	3.523896	-1.397467	1.131253
65	6	0	7.061499	0.858154	0.259538
66	6	0	5.733656	2.888329	0.118512
67	6	0	4.713425	-2.055238	0.992250
68	6	0	6.950435	2.249040	0.061525
69	1	0	2.597791	-1.911179	1.351910
70	1	0	4.756057	-3.130208	1.104557
71	1	0	8.048558	0.414082	0.241635
72	1	0	7.847439	2.821655	-0.143036
73	1	0	5.640047	3.953337	-0.047712
74	7	0	7.048579	-2.006488	0.443261
75	1	0	7.833784	-1.473670	0.102347
76	6	0	7.195397	-3.448359	0.498268
77	1	0	8.231001	-3.696380	0.277539
78	1	0	6.952154	-3.824004	1.494673
79	1	0	6.550497	-3.938727	-0.236265
80	17	0	-1.894138	-1.420393	3.154277
81	17	0	1.631997	-0.735204	-2.144954
82	8	0	-3.136019	-2.169974	3.355173
83	8	0	-1.161144	-1.263739	4.394963
84	8	0	-1.057503	-2.097651	2.123537
85	8	0	-2.220432	-0.074905	2.571559
86	8	0	1.177032	-1.684070	-1.096330
87	8	0	1.302528	-1.263614	-3.472343
88	8	0	0.870425	0.529038	-1.897381
89	8	0	3.061073	-0.478642	-2.013957

Excitation energies and oscillator strengths 7aa'-Ba(ClO_4)$_2$ (Emission)

```
 Excited State   1:      Singlet-A      2.9396 eV  421.77 nm  f=0.2606
                         <S**2>=0.000
                     204 -> 205       -0.69706
      This state for optimization and/or second-order correction.
           Total Energy, E(TD-HF/TD-DFT) =  -3441.14410968
 Copying the excited state density for this state as the 1-particle RhoCI
                              density.

 Excited State   2:      Singlet-A      3.8886 eV  318.84 nm  f=0.0150
                         <S**2>=0.000
                     199 -> 205        0.10721
                     203 -> 205       -0.66578

 Excited State   3:      Singlet-A      4.1967 eV  295.43 nm  f=0.0021
                         <S**2>=0.000
                     201 -> 205       -0.31203
                     202 -> 205        0.35014
                     204 -> 215        0.45035
                     204 -> 216        0.17666

 Excited State   4:      Singlet-A      4.3778 eV  283.21 nm  f=0.0002
                         <S**2>=0.000
                     187 -> 205       -0.12746
```

```
                      189 -> 205        0.21634
                      190 -> 205       -0.12903
                      191 -> 205       -0.15257
                      196 -> 205       -0.10445
                      198 -> 205       -0.43298
                      198 -> 234       -0.12271
                      199 -> 205        0.20575
                      203 -> 205        0.10369

Excited State   5:      Singlet-A      4.5784 eV  270.80 nm  f=0.0134
                           <S**2>=0.000
                      204 -> 207       -0.65868
```

Cartesian coordinates (in Å) 14a (UV/Vis)



14a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.670601	-0.277856	-0.340993
2	6	0	-0.937972	0.762678	0.250155
3	6	0	-0.943248	-1.257489	-1.037027
4	6	0	0.439523	0.840017	0.143243
5	1	0	-1.451792	1.520082	0.827902
6	6	0	0.433292	-1.194834	-1.154329
7	1	0	-1.477029	-2.083558	-1.489820
8	6	0	1.176377	-0.135975	-0.572649
9	1	0	0.942780	1.675535	0.607648
10	1	0	0.937314	-1.988619	-1.686491
11	6	0	7.227887	-1.300849	2.702754
12	1	0	7.721928	-2.069992	2.100645
13	1	0	7.357031	-1.578490	3.757965
14	6	0	7.875639	0.051127	2.458460
15	1	0	8.909963	0.028975	2.826035
16	1	0	7.334059	0.819826	3.014030
17	6	0	8.793775	-0.162827	0.246055
18	1	0	8.993936	-1.195776	0.555515
19	1	0	9.739987	0.392025	0.297126
20	6	0	8.275218	-0.200494	-1.177424
21	1	0	7.304038	-0.703828	-1.195298
22	1	0	8.977780	-0.779998	-1.787260
23	6	0	6.866120	1.466022	-2.197967
24	1	0	6.410589	0.637572	-2.754252
25	1	0	6.995396	2.304474	-2.885121
26	6	0	5.965776	1.854537	-1.033628
27	1	0	6.331217	2.774382	-0.557922
28	1	0	5.992188	1.061285	-0.285050
29	6	0	3.678069	2.170219	-0.482793
30	1	0	2.788846	2.609185	-0.938583
31	1	0	4.047032	2.858890	0.289570
32	6	0	3.335068	0.824689	0.159894
33	1	0	2.799358	1.000571	1.093530
34	1	0	4.247953	0.293366	0.430989
35	6	0	3.273993	-0.912440	-1.625646

36	1	0	4.087908	-0.324547	-2.052337
37	1	0	2.617092	-1.179318	-2.452377
38	6	0	3.862865	-2.174272	-1.005143
39	1	0	4.032879	-2.933250	-1.780820
40	1	0	3.169388	-2.589218	-0.264567
41	6	0	5.609808	-2.799889	0.518173
42	1	0	5.222865	-3.798008	0.281000
43	1	0	6.693366	-2.830840	0.381214
44	6	0	5.260105	-2.450928	1.959254
45	1	0	4.180094	-2.320861	2.057193
46	1	0	5.564437	-3.273822	2.620168
47	7	0	2.544214	-0.060686	-0.691740
48	8	0	4.643620	2.055227	-1.529427
49	8	0	8.169879	1.110604	-1.745822
50	8	0	7.828351	0.449989	1.093594
51	8	0	5.841749	-1.221082	2.384315
52	8	0	5.107398	-1.829591	-0.396154
53	6	0	-5.108171	-1.271110	-0.254755
54	6	0	-4.034806	0.691823	0.090325
55	7	0	-5.236493	0.053212	0.069342
56	6	0	-6.351043	0.811353	0.295644
57	6	0	-7.544926	0.120539	0.233453
58	6	0	-7.506431	-1.268067	-0.066857
59	6	0	-6.314110	-1.969810	-0.316753
60	1	0	-8.489879	0.614340	0.398206
61	1	0	-6.345826	-3.022214	-0.558109
62	6	0	-4.374543	2.074665	0.361797
63	6	0	-5.812009	2.144721	0.500818
64	6	0	-3.620418	3.248193	0.480657
65	6	0	-6.444918	3.359937	0.768407
66	6	0	-5.669674	4.505480	0.890868
67	6	0	-4.273375	4.446103	0.742678
68	1	0	-3.692174	5.356189	0.833131
69	1	0	-7.522289	3.406775	0.873736
70	1	0	-2.545652	3.234851	0.360395
71	7	0	-3.792865	-1.531069	-0.436535
72	6	0	-3.117366	-0.355285	-0.229171
73	1	0	-6.144572	5.456839	1.097333
74	6	0	-8.768937	-2.052732	-0.143995
75	8	0	-8.823649	-3.240447	-0.397520
76	8	0	-9.856863	-1.304414	0.098234
77	6	0	-11.129420	-1.982109	0.043131
78	1	0	-11.871388	-1.218329	0.259622
79	1	0	-11.289624	-2.402410	-0.949619
80	1	0	-11.166356	-2.775405	0.789620

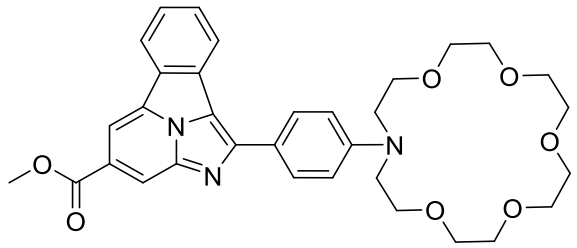
Excitation energies and oscillator strengths 14a (UV/Vis).

```
 Excited State   1:      Singlet-A      2.8755 eV  431.17 nm  f=0.7337
                             <S**2>=0.000
                      155 -> 157       -0.11179
                      156 -> 157        0.68352
     This state for optimization and/or second-order correction.
          Total Energy, E(TD-HF/TD-DFT) =  -1969.67149045
Copying the excited state density for this state as the 1-particle RhoCI
                              density.

 Excited State   2:      Singlet-A      3.2947 eV  376.31 nm  f=0.0602
                             <S**2>=0.000
                      155 -> 157        0.20380
                      156 -> 158        0.66111

 Excited State   3:      Singlet-A      3.5496 eV  349.29 nm  f=0.0912
                             <S**2>=0.000
                      154 -> 158       -0.10052
                      155 -> 157        0.62598
```

```
                      155 -> 158        0.13174
                      156 -> 157        0.14685
                      156 -> 158       -0.18566

Excited State   4:      Singlet-A      3.8314 eV  323.60 nm  f=0.2746
                           <S**2>=0.000
                      154 -> 157        0.27174
                      155 -> 157       -0.13656
                      155 -> 158        0.43641
                      156 -> 159       -0.32085
                      156 -> 160       -0.23078
                      156 -> 161        0.16674

Excited State   5:      Singlet-A      3.8384 eV  323.01 nm  f=0.0644
                           <S**2>=0.000
                      154 -> 157        0.17508
                      155 -> 158        0.26853
                      156 -> 159        0.56008
                      156 -> 160       -0.11120
                      156 -> 163        0.17017

Excited State   6:      Singlet-A      3.9021 eV  317.74 nm  f=0.0870
                           <S**2>=0.000
                      154 -> 157        0.19887
                      155 -> 158        0.19236
                      156 -> 160        0.55354
                      156 -> 161       -0.22790
                      156 -> 162        0.14289

Excited State   7:      Singlet-A      4.0755 eV  304.22 nm  f=0.0233
                           <S**2>=0.000
                      151 -> 157       -0.12058
                      156 -> 161        0.14169
                      156 -> 162        0.35561
                      156 -> 163        0.19986
                      156 -> 164       -0.10603
                      156 -> 166        0.21625
                      156 -> 168       -0.24052
                      156 -> 169       -0.34279
                      156 -> 172        0.13117

Excited State   8:      Singlet-A      4.1041 eV  302.10 nm  f=0.0149
                           <S**2>=0.000
                      156 -> 160       -0.15558
                      156 -> 161       -0.24484
                      156 -> 162        0.43185
                      156 -> 163        0.20193
                      156 -> 164       -0.11500
                      156 -> 166       -0.19500
                      156 -> 167        0.13863
                      156 -> 168        0.14844
                      156 -> 169        0.24089

Excited State   9:      Singlet-A      4.1489 eV  298.83 nm  f=0.0034
                           <S**2>=0.000
                      156 -> 159        0.15331
                      156 -> 160        0.22656
                      156 -> 161        0.53788
                      156 -> 162        0.17555
                      156 -> 167        0.11380
                      156 -> 168        0.11423
                      156 -> 169        0.20484

Excited State  10:      Singlet-A      4.1990 eV  295.27 nm  f=0.0007
                           <S**2>=0.000
                      156 -> 163        0.19540
                      156 -> 164        0.59063
                      156 -> 165        0.15746
```

156 -> 168	0.23386	
156 -> 169	-0.13004	

Cartesian coordinates (in Å) 14a (Emission)



14a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.707729	-0.321635	-0.328436
2	6	0	-0.955743	0.841748	-0.041755
3	6	0	-0.978983	-1.477836	-0.708976
4	6	0	0.408738	0.865065	-0.141772
5	1	0	-1.469561	1.740591	0.276319
6	6	0	0.384231	-1.462554	-0.821807
7	1	0	-1.529100	-2.391236	-0.905388
8	6	0	1.134472	-0.286538	-0.548284
9	1	0	0.927337	1.792665	0.067459
10	1	0	0.892152	-2.381154	-1.090909
11	6	0	7.244193	-0.483064	2.854946
12	1	0	7.747041	-1.394799	2.499177
13	1	0	7.330314	-0.479439	3.953414
14	6	0	7.927989	0.734820	2.287086
15	1	0	8.956832	0.792959	2.675081
16	1	0	7.397252	1.635943	2.613127
17	6	0	8.879438	-0.061488	0.253113
18	1	0	9.100825	-0.960369	0.849826
19	1	0	9.822553	0.496646	0.138069
20	6	0	8.365016	-0.513805	-1.088043
21	1	0	7.418772	-1.056085	-0.947104
22	1	0	9.092412	-1.209887	-1.528413
23	6	0	6.872751	0.733500	-2.471142
24	1	0	6.455048	-0.233646	-2.796149
25	1	0	6.939808	1.375725	-3.355657
26	6	0	5.959009	1.355858	-1.439615
27	1	0	6.322981	2.358021	-1.160506
28	1	0	5.962429	0.740007	-0.530124
29	6	0	3.700363	1.880984	-1.066228
30	1	0	2.826890	2.207054	-1.641315
31	1	0	4.080232	2.748141	-0.502640
32	6	0	3.294492	0.798947	-0.071156
33	1	0	2.746236	1.251255	0.757690
34	1	0	4.186544	0.333069	0.364483
35	6	0	3.221899	-1.317246	-1.357029
36	1	0	4.006428	-0.836332	-1.953257
37	1	0	2.552410	-1.814412	-2.059514
38	6	0	3.866128	-2.329689	-0.430145
39	1	0	4.013813	-3.281080	-0.964836
40	1	0	3.202091	-2.528234	0.426811
41	6	0	5.649756	-2.479974	1.125721
42	1	0	5.301554	-3.521763	1.173210
43	1	0	6.738160	-2.510721	0.987204
44	6	0	5.299865	-1.754851	2.406250

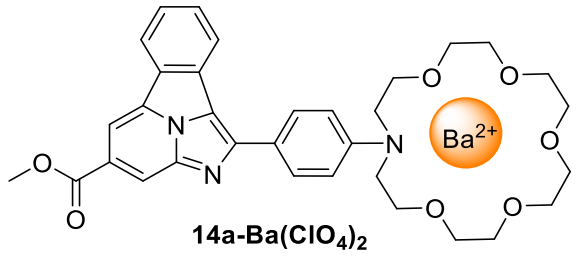
45	1	0	4.214495	-1.604685	2.461136
46	1	0	5.594096	-2.363871	3.275408
47	7	0	2.492338	-0.264339	-0.660888
48	8	0	4.662590	1.445241	-1.997658
49	8	0	8.182102	0.577361	-1.974411
50	8	0	7.911032	0.748748	0.878636
51	8	0	5.888010	-0.473012	2.465491
52	8	0	5.110065	-1.818658	-0.002225
53	6	0	-5.111643	-1.262349	-0.223416
54	6	0	-4.046162	0.712842	0.026961
55	7	0	-5.241615	0.074158	0.022749
56	6	0	-6.356786	0.855452	0.231459
57	6	0	-7.554694	0.154962	0.208473
58	6	0	-7.519399	-1.237739	-0.025391
59	6	0	-6.336517	-1.970661	-0.243147
60	1	0	-8.500512	0.657971	0.362073
61	1	0	-6.373880	-3.036489	-0.422488
62	6	0	-4.382278	2.102372	0.256768
63	6	0	-5.823769	2.168758	0.388850
64	6	0	-3.639003	3.278188	0.346873
65	6	0	-6.451731	3.397121	0.620925
66	6	0	-5.679985	4.539485	0.713155
67	6	0	-4.284470	4.484939	0.574429
68	1	0	-3.701953	5.397616	0.643805
69	1	0	-7.532214	3.447768	0.722982
70	1	0	-2.560501	3.275770	0.232332
71	7	0	-3.824616	-1.549568	-0.385458
72	6	0	-3.127259	-0.357059	-0.230582
73	1	0	-6.160012	5.496964	0.891771
74	6	0	-8.784039	-2.006002	-0.053976
75	8	0	-8.855063	-3.199061	-0.252801
76	8	0	-9.865735	-1.245394	0.165529
77	6	0	-11.121169	-1.919131	0.152113
78	1	0	-11.873692	-1.156170	0.343642
79	1	0	-11.298899	-2.386384	-0.819438
80	1	0	-11.157012	-2.685483	0.930083

Excitation energies and oscillator strengths 14a (Emission)

```
 Excited State   1:      Singlet-A      2.5926 eV  478.23 nm  f=1.0962
                          <S**2>=0.000
                        156 -> 157       -0.69325
      This state for optimization and/or second-order correction.
            Total Energy, E(TD-HF/TD-DFT) =  -1969.68137978
 Copying the excited state density for this state as the 1-particle RhoCI
                               density.

 Excited State   2:      Singlet-A      3.1928 eV  388.33 nm  f=0.0798
                          <S**2>=0.000
                        155 -> 157        0.19409
                        156 -> 158       -0.66664

 Excited State   3:      Singlet-A      3.4624 eV  358.08 nm  f=0.2660
                          <S**2>=0.000
                        155 -> 157        0.65102
                        156 -> 157       -0.10038
                        156 -> 158        0.19238

 Excited State   4:      Singlet-A      3.7223 eV  333.08 nm  f=0.2713
                          <S**2>=0.000
                        155 -> 158       -0.15604
                        156 -> 159       -0.27740
                        156 -> 160       -0.57321
                        156 -> 161        0.14173
```

```
Excited State   5:      Singlet-A      3.7320 eV  332.22 nm  f=0.0716
                        <S**2>=0.000
                       156 -> 159       -0.59049
                       156 -> 160        0.27546
                       156 -> 162        0.12362
                       156 -> 163       -0.17639

Excited State   6:      Singlet-A      3.8254 eV  324.11 nm  f=0.0473
                        <S**2>=0.000
                       154 -> 157       -0.47133
                       155 -> 158        0.44304
                       156 -> 160       -0.17536

Excited State   7:      Singlet-A      3.9762 eV  311.81 nm  f=0.0211
                        <S**2>=0.000
                       156 -> 160       -0.14046
                       156 -> 162        0.55699
                       156 -> 163        0.28400
                       156 -> 164       -0.11824
                       156 -> 167       -0.13864
                       156 -> 170        0.12008

Excited State   8:      Singlet-A      4.0154 eV  308.77 nm  f=0.0174
                        <S**2>=0.000
                       156 -> 159        0.11491
                       156 -> 161        0.63322
                       156 -> 166        0.16171
                       156 -> 169        0.11934

Excited State   9:      Singlet-A      4.0362 eV  307.18 nm  f=0.1409
                        <S**2>=0.000
                       150 -> 157       -0.12012
                       154 -> 157       -0.10389
                       156 -> 161       -0.15518
                       156 -> 162       -0.19324
                       156 -> 167        0.10836
                       156 -> 168       -0.17588
                       156 -> 169        0.34984
                       156 -> 170        0.31615
                       156 -> 171       -0.18501
                       156 -> 172        0.24751

Excited State  10:      Singlet-A      4.1110 eV  301.59 nm  f=0.0056
                        <S**2>=0.000
                       156 -> 163       -0.14428
                       156 -> 164       -0.60354
                       156 -> 165       -0.17283
                       156 -> 168       -0.24018
```

Cartesian coordinates (in Å) 14a-Ba(ClO$_4$)$_2$ (UV/Vis).



14a-Ba(ClO$_4$)$_2$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.368426	2.475186	-1.322086
2	6	0	0.007083	3.208431	-0.187168
3	6	0	0.587005	2.292291	-2.327565
4	6	0	1.332887	3.551111	0.025808
5	1	0	-0.718324	3.387760	0.595399
6	6	0	1.905101	2.683499	-2.143247
7	1	0	0.317807	1.756979	-3.229236
8	6	0	2.338264	3.185391	-0.898411
9	1	0	1.589477	4.017927	0.964546
10	1	0	2.606258	2.494443	-2.939017
11	6	0	3.516740	-3.323247	0.977044
12	1	0	3.855573	-3.195775	2.013850
13	1	0	4.148334	-4.087376	0.504955
14	6	0	2.079447	-3.795503	0.902631
15	1	0	1.977693	-4.748327	1.434557
16	1	0	1.800208	-3.935651	-0.141146
17	6	0	0.866924	-2.880523	2.819296
18	1	0	0.993658	-3.898410	3.204028
19	1	0	-0.176652	-2.588473	2.909043
20	6	0	1.729843	-1.918875	3.620258
21	1	0	2.771885	-2.257306	3.697130
22	1	0	1.315194	-1.845492	4.633826
23	6	0	2.262081	0.397521	3.764418
24	1	0	3.304264	0.149590	4.012255
25	1	0	1.694057	0.518451	4.695660
26	6	0	2.187237	1.676462	2.955573
27	1	0	2.611583	2.505268	3.530733
28	1	0	1.145020	1.900331	2.729439
29	6	0	4.163797	2.134724	1.610213
30	1	0	4.819690	1.419633	1.119946
31	1	0	4.553646	2.350954	2.612403
32	6	0	4.122286	3.430723	0.793512
33	1	0	5.134644	3.846883	0.784747
34	1	0	3.496713	4.173981	1.288576
35	6	0	4.699953	2.821544	-1.545685
36	1	0	5.667803	3.084888	-1.115774
37	1	0	4.604288	3.401388	-2.471972
38	6	0	4.742387	1.342782	-1.956631
39	1	0	5.674091	1.208594	-2.526214
40	1	0	3.914408	1.054433	-2.605036
41	6	0	5.136778	-0.838204	-1.172796
42	1	0	4.525351	-1.217013	-1.994984
43	1	0	6.190471	-0.831098	-1.489065
44	6	0	5.008316	-1.756066	0.016156
45	1	0	5.563035	-2.672984	-0.215357
46	1	0	5.453091	-1.301133	0.911453
47	7	0	3.690326	3.266287	-0.589369
48	8	0	2.877575	1.512828	1.711205

49	8	0	1.694542	-0.647551	2.984131
50	8	0	1.153735	-2.842178	1.419565
51	8	0	3.643379	-2.092889	0.268697
52	8	0	4.745021	0.485576	-0.821853
53	56	0	1.157387	-0.358529	0.155087
54	6	0	-2.919030	1.922261	-1.028762
55	6	0	-2.579515	-0.308866	-1.209843
56	6	0	-4.803868	0.622642	-0.627794
57	6	0	-3.082611	-1.603549	-1.089246
58	1	0	-2.453006	-2.471005	-1.223522
59	6	0	-5.306034	-0.654156	-0.506281
60	1	0	-6.326929	-0.836403	-0.208671
61	6	0	-4.433012	-1.752252	-0.747529
62	6	0	-5.162811	2.020662	-0.426225
63	6	0	-3.991216	2.823834	-0.671977
64	6	0	-6.360100	2.623408	-0.044090
65	1	0	-7.242428	2.023611	0.146205
66	6	0	-4.054873	4.210533	-0.526707
67	6	0	-5.260045	4.787955	-0.145947
68	1	0	-5.321801	5.863753	-0.029545
69	6	0	-6.400991	4.005629	0.093637
70	1	0	-3.179479	4.822333	-0.708262
71	7	0	-3.491748	0.684811	-1.000587
72	1	0	-7.324281	4.487617	0.391897
73	7	0	-1.372540	0.278298	-1.402050
74	6	0	-1.569903	1.637069	-1.302241
75	6	0	-4.926981	-3.149285	-0.601598
76	8	0	-4.250614	-4.139999	-0.753656
77	8	0	-6.238199	-3.199459	-0.272753
78	6	0	-6.784196	-4.517769	-0.104180
79	1	0	-7.829933	-4.367763	0.154709
80	1	0	-6.693616	-5.088302	-1.029387
81	1	0	-6.261397	-5.046311	0.693955
82	17	0	1.732565	-1.977750	-2.852297
83	17	0	-1.632866	0.117351	2.289092
84	8	0	2.929309	-2.842321	-2.991287
85	8	0	2.176615	-0.574609	-2.444474
86	8	0	0.878311	-2.465667	-1.697289
87	8	0	0.952136	-1.922026	-4.094278
88	8	0	-1.240104	-1.134499	1.534580
89	8	0	-0.686211	1.197084	1.787130
90	8	0	-1.434920	-0.086913	3.743253
91	8	0	-3.023865	0.488427	1.974072

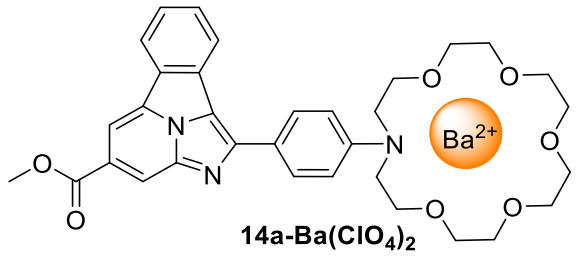
Excitation energies and oscillator strengths 14a- $Ba(ClO_4)_2$ (UV/Vis).

```
 Excited State   1:      Singlet-A      3.3230 eV  373.11 nm  f=0.2515
                             <S**2>=0.000
                      208 -> 214        0.11692
                      209 -> 211        0.18609
                      209 -> 214        0.13615
                      210 -> 211        0.63690
     This state for optimization and/or second-order correction.
          Total Energy, E(TD-HF/TD-DFT) =  -3516.74521275
Copying the excited state density for this state as the 1-particle RhoCI
                                density.

 Excited State   2:      Singlet-A      3.6696 eV  337.87 nm  f=0.0245
                             <S**2>=0.000
                      209 -> 211        0.48168
                      210 -> 211       -0.16587
                      210 -> 212       -0.33272
                      210 -> 214       -0.29375

 Excited State   3:      Singlet-A      3.7001 eV  335.08 nm  f=0.0036
                             <S**2>=0.000
```

```
                    209 -> 211        0.24248
                    209 -> 212       -0.16391
                    210 -> 212        0.55173
                    210 -> 213        0.16649
                    210 -> 214       -0.22585

Excited State   4:      Singlet-A      3.8240 eV  324.23 nm  f=0.0851
                         <S**2>=0.000
                    208 -> 211       -0.31795
                    209 -> 211        0.31564
                    209 -> 214        0.25924
                    210 -> 211       -0.20643
                    210 -> 212        0.11076
                    210 -> 214        0.38395

Excited State   5:      Singlet-A      3.9318 eV  315.33 nm  f=0.0023
                         <S**2>=0.000
                    209 -> 213       -0.11881
                    210 -> 212       -0.20304
                    210 -> 213        0.60472
                    210 -> 216        0.22958

Excited State   6:      Singlet-A      4.0155 eV  308.76 nm  f=0.0136
                         <S**2>=0.000
                    209 -> 215       -0.12730
                    210 -> 214        0.15864
                    210 -> 215        0.63628
                    210 -> 218       -0.12657

Excited State   7:      Singlet-A      4.1088 eV  301.76 nm  f=0.1639
                         <S**2>=0.000
                    208 -> 211       -0.22919
                    209 -> 211       -0.15499
                    209 -> 212        0.11264
                    209 -> 214        0.42216
                    209 -> 215       -0.10617
                    210 -> 214       -0.37675
                    210 -> 215        0.15839
                    210 -> 216        0.12207

Excited State   8:      Singlet-A      4.1706 eV  297.28 nm  f=0.0048
                         <S**2>=0.000
                    209 -> 211        0.12148
                    209 -> 212        0.53609
                    209 -> 214       -0.13144
                    210 -> 212        0.11181
                    210 -> 214        0.10805
                    210 -> 216        0.31484
                    210 -> 219        0.12536

Excited State   9:      Singlet-A      4.1941 eV  295.62 nm  f=0.0099
                         <S**2>=0.000
                    209 -> 212       -0.38251
                    210 -> 213       -0.21622
                    210 -> 216        0.42540
                    210 -> 217       -0.14254
                    210 -> 218        0.10587
                    210 -> 219        0.16796
                    210 -> 221        0.16008

Excited State  10:      Singlet-A      4.2659 eV  290.64 nm  f=0.0499
                         <S**2>=0.000
                    209 -> 225       -0.10100
                    210 -> 213        0.11636
                    210 -> 216       -0.22098
                    210 -> 217       -0.19508
                    210 -> 218        0.12504
                    210 -> 219        0.15173
```

210 -> 220	0.11005
210 -> 221	0.20574
210 -> 222	0.13792
210 -> 223	-0.15180
210 -> 224	-0.16349
210 -> 225	0.36954
210 -> 227	-0.13082

Cartesian coordinates (in Å) 14a-Ba(ClO$_4$)$_2$ (Emission)



14a-Ba(ClO$_4$)$_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.115104	-1.820811	-1.955880
2	6	0	-0.249072	-2.925752	-1.156141
3	6	0	-0.893291	-1.223360	-2.740466
4	6	0	-1.576028	-3.240665	-0.960816
5	1	0	0.506909	-3.434386	-0.569800
6	6	0	-2.217807	-1.576783	-2.586308
7	1	0	-0.631449	-0.412469	-3.410452
8	6	0	-2.611171	-2.502364	-1.593311
9	1	0	-1.806525	-4.038626	-0.270150
10	1	0	-2.949282	-1.064364	-3.189745
11	6	0	-2.843680	3.087131	1.970859
12	1	0	-3.077513	2.754915	2.991058
13	1	0	-3.446336	3.976404	1.748314
14	6	0	-1.382259	3.442580	1.815281
15	1	0	-1.100718	4.190067	2.565087
16	1	0	-1.212853	3.850810	0.820614
17	6	0	-0.151936	1.906957	3.225157
18	1	0	-0.132849	2.775630	3.892815
19	1	0	0.856148	1.513001	3.128685
20	6	0	-1.055404	0.837754	3.821778
21	1	0	-2.004857	1.246349	4.190664
22	1	0	-0.520555	0.375648	4.659439
23	6	0	-1.841215	-1.340965	3.405006
24	1	0	-2.700642	-1.099862	4.045447
25	1	0	-1.054034	-1.812606	4.005762
26	6	0	-2.266214	-2.284507	2.299068
27	1	0	-2.732775	-3.165843	2.752596
28	1	0	-1.391939	-2.607032	1.732055
29	6	0	-4.399082	-2.289671	1.175634
30	1	0	-5.132345	-1.518172	0.952111
31	1	0	-4.720536	-2.833998	2.073227
32	6	0	-4.321056	-3.273392	0.004157
33	1	0	-5.309109	-3.727980	-0.116579
34	1	0	-3.642473	-4.090991	0.243231
35	6	0	-4.975796	-1.938656	-1.980748
36	1	0	-5.925470	-2.327347	-1.610291
37	1	0	-4.924497	-2.193891	-3.045435
38	6	0	-5.000793	-0.400521	-1.866272
39	1	0	-6.040898	-0.087927	-2.034450

40	1	0	-4.386141	0.100043	-2.617290
41	6	0	-5.025629	1.320944	-0.291221
42	1	0	-4.658186	2.031993	-1.037675
43	1	0	-6.125097	1.333615	-0.290339
44	6	0	-4.542947	1.726999	1.076747
45	1	0	-5.117126	2.607422	1.385149
46	1	0	-4.713012	0.921561	1.803071
47	7	0	-3.939430	-2.664724	-1.260622
48	8	0	-3.177993	-1.616389	1.430882
49	8	0	-1.337906	-0.144496	2.836293
50	8	0	-0.547937	2.300158	1.918771
51	8	0	-3.161161	2.054950	1.049713
52	8	0	-4.578623	0.009024	-0.584120
53	56	0	-1.120289	0.256365	0.105595
54	6	0	2.642238	-1.629635	-1.312530
55	6	0	2.618753	0.627398	-1.381501
56	6	0	4.632062	-0.640268	-0.671152
57	6	0	3.276053	1.848384	-1.148933
58	1	0	2.796192	2.802101	-1.304462
59	6	0	5.303841	0.566841	-0.429839
60	1	0	6.316547	0.593462	-0.059495
61	6	0	4.602805	1.764177	-0.675031
62	6	0	4.786076	-2.067751	-0.590800
63	6	0	3.537767	-2.690144	-1.005869
64	6	0	5.846184	-2.876538	-0.190279
65	1	0	6.782217	-2.440113	0.137411
66	6	0	3.405305	-4.081275	-1.021172
67	6	0	4.481374	-4.862083	-0.621269
68	1	0	4.397307	-5.941123	-0.625673
69	6	0	5.683448	-4.259648	-0.209335
70	1	0	2.479993	-4.541410	-1.348184
71	7	0	3.354989	-0.478975	-1.123547
72	1	0	6.507382	-4.890100	0.103888
73	7	0	1.374610	0.231456	-1.769476
74	6	0	1.348595	-1.122938	-1.741838
75	6	0	5.281155	3.072625	-0.418489
76	8	0	4.761745	4.146289	-0.572319
77	8	0	6.547317	2.930318	0.006719
78	6	0	7.237835	4.151138	0.269119
79	1	0	8.232419	3.862613	0.598710
80	1	0	7.291736	4.757529	-0.635395
81	1	0	6.723163	4.717384	1.045822
82	17	0	-1.942572	2.805766	-2.068896
83	17	0	1.655770	-1.062351	1.997610
84	8	0	-2.960229	3.755757	-1.616365
85	8	0	-2.521030	1.419894	-2.060094
86	8	0	-0.822060	2.760194	-1.085262
87	8	0	-1.455972	3.134098	-3.393570
88	8	0	1.471836	0.247810	1.306037
89	8	0	0.643781	-1.972436	1.385772
90	8	0	1.384975	-0.912173	3.431868
91	8	0	3.000322	-1.565787	1.768510

Excitation energies and oscillator strengths 14a-Ba(ClO_4)$_2$ (Emission).

```
Excited State   1:      Singlet-A      3.0199 eV  410.56 nm  f=0.3328
                        <S**2>=0.000
                    209 -> 215        0.10989
                    210 -> 211        0.67571
     This state for optimization and/or second-order correction.
          Total Energy, E(TD-HF/TD-DFT) =  -3516.75124668
```

```
Copying the excited state density for this state as the 1-particle RhoCI
                              density.

 Excited State   2:      Singlet-A      3.5288 eV  351.35 nm  f=0.0603
                       <S**2>=0.000
                     208 -> 211        0.10922
                     209 -> 211        0.49835
                     210 -> 212       -0.10427
                     210 -> 215       -0.44317

 Excited State   3:      Singlet-A      3.6275 eV  341.79 nm  f=0.0102
                       <S**2>=0.000
                     209 -> 212        0.11460
                     210 -> 212        0.66336
                     210 -> 213        0.13656

 Excited State   4:      Singlet-A      3.7848 eV  327.58 nm  f=0.2718
                       <S**2>=0.000
                     208 -> 211       -0.35826
                     209 -> 211        0.37843
                     209 -> 215       -0.13203
                     210 -> 211        0.11297
                     210 -> 215        0.34941
                     210 -> 216       -0.11130
                     210 -> 217        0.10621
                     210 -> 219       -0.15021

 Excited State   5:      Singlet-A      3.8425 eV  322.66 nm  f=0.0155
                       <S**2>=0.000
                     209 -> 211       -0.14941
                     210 -> 212       -0.13188
                     210 -> 213        0.51096
                     210 -> 214        0.29233
                     210 -> 216       -0.22180
                     210 -> 217        0.16510
                     210 -> 219       -0.10353

 Excited State   6:      Singlet-A      3.9299 eV  315.49 nm  f=0.0184
                       <S**2>=0.000
                     210 -> 213       -0.40986
                     210 -> 214        0.47661
                     210 -> 217        0.12896
                     210 -> 219       -0.18030

 Excited State   7:      Singlet-A      3.9802 eV  311.50 nm  f=0.0446
                       <S**2>=0.000
                     210 -> 214        0.37375
                     210 -> 215        0.12180
                     210 -> 216        0.19835
                     210 -> 217       -0.21134
                     210 -> 219        0.43560

 Excited State   8:      Singlet-A      4.0357 eV  307.22 nm  f=0.0404
                       <S**2>=0.000
                     208 -> 211       -0.15520
                     209 -> 215       -0.16312
                     210 -> 215       -0.10358
                     210 -> 217        0.12684
                     210 -> 218       -0.11449
                     210 -> 219        0.23060
                     210 -> 220        0.14109
                     210 -> 221       -0.27122
                     210 -> 222       -0.24869
                     210 -> 223        0.36698

 Excited State   9:      Singlet-A      4.1260 eV  300.49 nm  f=0.0174
                       <S**2>=0.000
                     208 -> 211        0.10997
```

```
                        209 -> 212        0.10824
                        210 -> 213        0.10633
                        210 -> 215        0.13224
                        210 -> 216        0.47960
                        210 -> 217        0.16154
                        210 -> 218        0.22494
                        210 -> 219       -0.20520
                        210 -> 222       -0.14382
                        210 -> 223        0.19686

Excited State  10:      Singlet-A      4.1575 eV  298.22 nm  f=0.1962
                             <S**2>=0.000
                        208 -> 211        0.36244
                        209 -> 211        0.17931
                        209 -> 215        0.34626
                        210 -> 215        0.30002
                        210 -> 216       -0.19576
                        210 -> 218       -0.12625
                        210 -> 223        0.13722
```

Calculated Emission Spectrum 14a-Ba

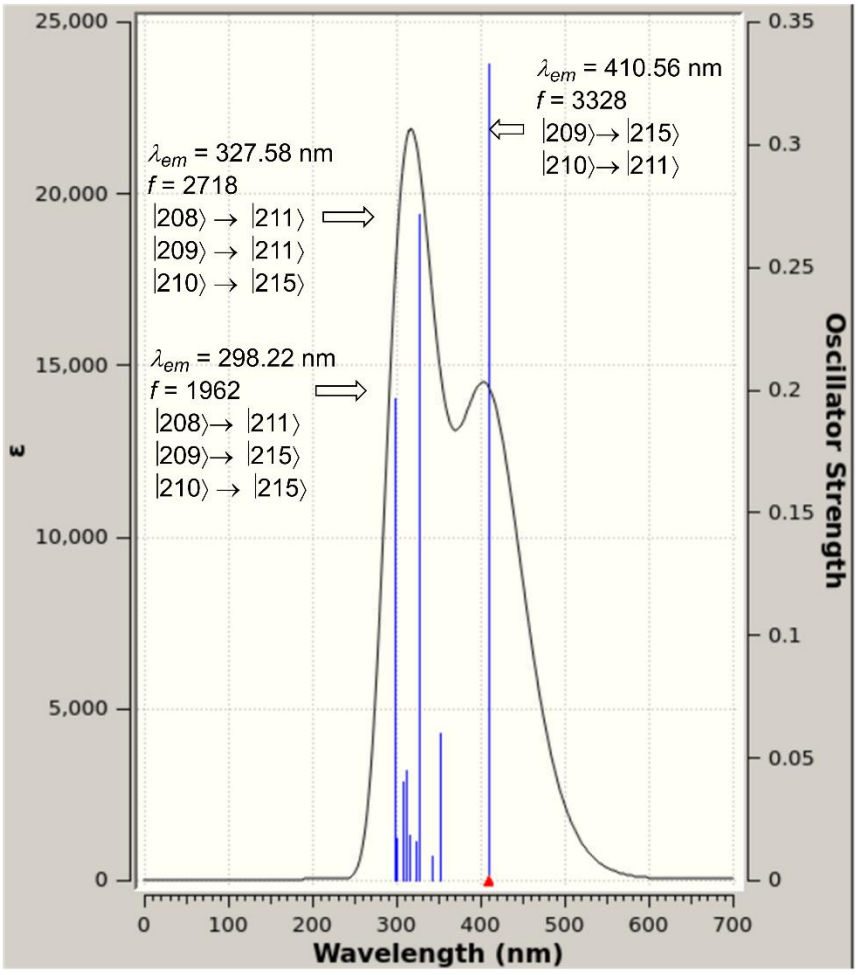
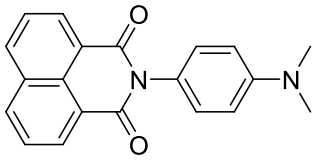


Figure S4. Emission spectrum of compound **14a-Ba(ClO$_4$)$_2$**, calculated at the TDDFT(Nstates=5) M06/6-311++G**&Def2TZVPP level of theory.The main transitions and the KS-MOs associated with them are indicated, as well as the respective emission wavelenghts (λ_{em}) and the oscillator strengths (*f*)

Cartesian coordinates (in Å) of model molecule 16.



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.383949	-0.087648	1.195175
2	6	0	-4.113615	-0.103943	-0.000268
3	6	0	-3.383934	-0.082630	-1.195692
4	6	0	-2.003072	-0.063285	-1.187964
5	6	0	-1.301587	-0.056822	-0.000214
6	6	0	-2.003011	-0.068293	1.187453
7	7	0	0.137920	-0.031272	-0.000155
8	6	0	0.802721	-1.257292	-0.001340
9	6	0	2.288569	-1.219654	-0.001054
10	6	0	2.969217	0.018879	0.000071
11	6	0	2.245033	1.232494	0.000938
12	6	0	0.758782	1.217362	0.000754
13	6	0	4.374763	0.043829	0.000305
14	6	0	5.030216	1.301192	0.001407
15	6	0	4.316229	2.460442	0.002220
16	6	0	2.905112	2.426572	0.001983
17	6	0	2.990572	-2.389566	-0.001906
18	6	0	4.402020	-2.373330	-0.001651
19	6	0	5.074433	-1.189494	-0.000580
20	8	0	0.197950	-2.285987	-0.002499
21	8	0	0.117964	2.224193	0.001366
22	7	0	-5.503515	-0.156028	-0.000645
23	6	0	-6.204752	0.135249	1.230808
24	6	0	-6.204363	0.148255	-1.229265
25	1	0	2.337655	3.337227	0.002630
26	1	0	4.821345	3.408739	0.003046
27	1	0	6.150185	-1.177106	-0.000396
28	1	0	6.105731	1.326982	0.001592
29	1	0	2.455748	-3.319766	-0.002774
30	1	0	4.940447	-3.303114	-0.002312
31	1	0	-1.470352	-0.057755	2.121284
32	1	0	-1.470427	-0.048908	-2.121750
33	1	0	-3.883676	-0.082157	-2.142935
34	1	0	-3.883564	-0.090800	2.142470
35	1	0	-5.954940	-0.566714	-2.003465
36	1	0	-5.989882	1.148855	-1.604372
37	1	0	-7.268276	0.071882	-1.055926
38	1	0	-7.268463	0.055982	1.057470
39	1	0	-5.994121	1.133510	1.614350
40	1	0	-5.951870	-0.585292	1.998659

7. References

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