Electronic Supplementary Information

A New Class of Customisable Stable Boronic Ester Assemblies

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1. Contents

1.1. NMR Spectroscopy

All ^{1}H, ^{13}C and ^{19}F spectra were collected on either a Bruker Ascend 400 MHz FT-NMR spectrometer or a BRUKER AVANCE III 500 MHz FT-NMR spectrometer where indicated. Samples were dissolved in $CDCl_3$, DMSO-d6, CD_3CN or CD_3OD where specified with the residual solvent peak used as the internal reference – $CDCl_3$; 7.26 (^{1}H), 77.16 (^{13}C), DMSO-d6; 2.50 (^{1}H), 39.5 (^{13}C), CD_3OD; 3.31 (^{1}H), 49.0 (^{13}C).[1]

Proton spectra are reported as chemical shift δ (ppm) (integral, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant) where appropriate. Carbon spectra are reported as chemical shift δ (ppm).

Fluorine NMR values are reported without internal reference.

1.2. Mass Spectrometry

MS for Synthetic Characterisation

For routine characterisation after synthesis, samples were typically prepared at a concentration of 1 ng/µL in acetonitrile (MS grade). The mass spectra were collected on a Shimadzu LCMS series 9030 quadrupole time-of-flight (Q-TOF) mass spectrometer using electrospray ionisation (ESI).

For macrocycle **$[2+2]_{Py}$**, the mass spectra were collected on a Orbitrap Elite spectrometer using electrosopray ionisation (ESI)

MS for hydrolytic stability studies and DEG substituted [4+4] macrocycle

For the hydrolytic stability study (see section 1.15), the samples analysed using mass spectrometry (MS) were diluted directly from the NMR samples by a factor of 5. For the stability test in acetic acid, the sample consisted of macrocycle **$[4+4]_{DEG}$** with a concentration of ~310 µM and acetic acid with a concentration of ~580 µM. For the stability test in TFA, the concentration of macrocycle **$[4+4]_{DEG}$** was as previous, whereas the concentration of TFA was ~430 µM with 1% of 2 mg/mL NaCl solution added to promote ionisation.

To preserve the structure of the macrocycles in these stability experiments and for characterisation of the DEG substituted [4+4] macrocycle, nanoelectrospray ionisation (nESI) experiments were performed on an LTQ-Orbitrap-XL (Thermo Fisher Scientific, MA, USA) using Pt-coated borosilicate tips (1.2 mm outer diameter, 0.69 inner diameter, Harvard Apparatus) that were pulled in-house. The tips have orifice sizes of ~2000 nm and were loaded with 10 µL of sample solution. The mass spectra were acquired in positive ionisation mode at *m/z* range of 100-2000 with the following ionisation conditions: capillary voltage of 1.2-1.5 kV, source temperature of 200 °C, and cone voltage of 68 V.

1.3. Melting Points

Melting points were determined using a Bibby Stuart Scientific SMP3.

1.4. X-ray Crystallography

X-ray crystallographic data was collected at the Australian Synchrotron on the MX1[2] and MX2[3] beamlines. Crystals were mounted from their respective mother liquors on to nylon loops with the assistance of paratone oil. Crystals of **$[4+4]_{Bn}$**, **$[2+2]_{BiPh}$**, and **$[3+2]_{TZ}$** were mounted using the ColdMountPro! system designed by Dr Michael Gardiner (ANU) at -20 °C. Data was collected under a stream of nitrogen gas at 100 K.

Cell refinement and data reduction were completed with XDS.[4] Crystal structures were solved using SHELXT[5] and refined using SHELXL[6] within the Olex 2 graphic interface.[7] Residual solvent was removed using the PLATON SQUEEZE[8] protocol.

Crystal data was visualised for presentation using Mercury[9] or ChimeraX[10-12]

A summary of the crystallographic parameters is provided in section 1.17.

The crystallographic information files were deposited to Cambridge Crystallographic Data base, CCDC Refcode: ULOWIF (**[2+2]$_{\mathbf{BiPh}}$**), ULOWEB (**[4+4]$_{\mathbf{Bn}}$**), ULOWAX (**[1+2]$_{\mathbf{H}}$**), ULOVUQ (**3$_{\mathbf{Me}}$**), ULOVOK (**[3+2]$_{\mathbf{TZ}}$**)

1.5. Microwave reactions

Microwave reactions were performed using a CEM Discover S-Class Explorer 48 microwave reactor, with continuous irradiation power ranging from 0–200 W, as specified, and an operational frequency of 50–60 Hz. All reactions were performed under “high” stirring in 10 mL vials sealed with ‘snap’ caps. For **general procedure C**, a staged heating protocol was implemented, heating from 60 to 100 °C in 10 °C increments.

1.6. Chromatography

Column chromatography was performed on SiliCycle brand silica gel 60 (230–400 mesh). Thin layer chromatography was performed on alumina backed silica plates (Chem-Supply), compounds were visualised either under 254 nm UV light and/or stained by alkaline $KMnO_4$ solution (1:1:100 $KMnO_4$: Na_2CO_3: H_2O).

1.7. Reagents

All solvents used were AR grade and used as supplied. Pet. spirits refer to the fraction boiling between 40–60 °C. Chemicals were purchased from a range of commercial sources (Merck, CombiBlocks, Ambeed, or AbaChemscene) and in most cases were used without further purification. Molecular sieves were activated by first heating at 80 °C for one day, then heating in a furnace at 300 °C for at least 18 hours.

Cyclopentadiene was prepared by distillation of commercially available dicyclopentadiene (‘cracking’ at ~140 °C under N_2) and stored at -80 °C. Dimethylacetylene dicarboxylate (DMAD) was purified by distillation of commercially available DMAD (80 °C, 0.01 mbar). Anhydrous *tert*-butyl hydroperoxide (*t*-BuOOH) was prepared in toluene from a commercial solution of *t*-BuOOH in water according to the method of Sharpless.[13]

Anhydrous dimethylformamide (DMF) was prepared by storing DMF over activated 4 Å sieves for 3 days. Anhydrous tetrahydrofuran (THF) was prepared by passing AR grade THF through a column of silica gel 60 (230–400 mesh), before storing over activated 4 Å sieves for 3 days. Anhydrous chloroform was prepared by short path distillation of acid free chloroform from phosphorous pentoxide (5% w/v), before storing over activated 4 Å sieves (adapted from Perrin[14]).

We thank Nemanja Djordjevic (Deakin University) for kindly donating the 3,6-dinitro-1,8-naphthalimide used in this project.

1.8. Characterisation

All novel compounds were characterised by ^1H and ^{13}C NMR spectroscopy, Electrospray Ionisation high-resolution mass spectrometry (ESI-HRMS) and in some cases X-Ray Crystallography.

Spectroscopic data for all previously reported compounds were compared to literature values and are referenced accordingly.

1.9. Diffusion NMR

Adapted from Ivanova *et al.*[15] ^{1}H-DOSY NMR experiments were obtained on a Bruker Avance III 500 spectrometer with a z-gradient coil delivering up to 53 G/cm. Sample was prepared in $CDCl_3$ (~ 10 mg/mL) and let temper at 20 °C for 30 minutes within the NMR instrument. The data set was acquired using the Bruker diffDste pulse program, and the gradient pulse length (δ) and diffusion delay (Δ) were set to 4.0 and 40.0 ms respectively. A linear gradient ramp from 2% to 100% of the gradient strength was used with 64 gradient steps.

The diffusion coefficients D were calculated with the T1/T2 relaxation module in TopSpin 4.1.1 (Bruker) using mono-exponential fitting with the Stejskal-Tanner Equation.[16] Diffusion coefficients with excellent goodness of fit ($R^2 > 0.999$) were normalised according to the method of Neufeld and Stalke[17] by using ratio between known diffusion coefficients ($D_{ref,lit}$) of residual solvent signal for $CDCl_3$ (2.45×10^{-9} m^2/s) and the measured diffusion coefficient (D_{ref}) of the internal standard ($CDCl_3$).

Normalised diffusion coefficients were transformed into solvodynamic radii using a modified Stokes-Einstein equation incorporating the Chen and Chen correction.

1.9.1. Chen and Chen correction

The Chen and Chen correction was applied using literature values for the solvodynamic radius of $CDCl_3$ ($r_{solv} = 0.325 \times 10^{-9}$ m). To apply the correction a solvent specific graph of cr_s versus r_s was generated according to equation 1, and the value of cr_s determined from the modified Stokes–Einstein equation. The corrected value of r_s was then determined using the solvent specific graph.

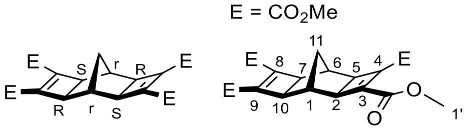
$$cr_s = \frac{r_s}{1 + 0.695(\frac{r_{solv}}{r_s})^{2.234}} \quad (1.)$$

1.10. Computational Details

Cage **[3+2]$_{\mathbf{Ph}}$** was modelled using Spartan '14 by building the molecular model before finding the equilibrium geometry using semi-empirical AM1 calculations. Notably semi-empirical AM1 calculations have been shown to effectively model fused [n]polynorbornane rods.[18, 19]

1.11. Naming

Where appropriate, compounds are named according to the extended von Bayer system.[20] The stereodescriptors R/S are used to describe the configuration of the substituents on the ring system.[21] For example, tetraester **7$_{\mathbf{Me}}$** contains four stereo centres and two pseudo asymmetric stereocentres, and is named accordingly.



Tetramethyl-(1r, 2S, 5R, 6r, 7S, 10R)-tetracyclo[4.4.1.0^{2,5}.0^{7,10}]deca-3,8-diene-3,4,8,9-tetracarboxylate

1.12. General Procedures

General reaction procedure A (Diels–Alder cycloaddition): Dienophile (1 eq.) and cyclopentadiene (8 eq.) were combined in minimum DMF and the solution left stirring at room temperature for the listed time (1–8 days) until the reaction was deemed complete (by ^{1}H NMR or TLC). The DMF was removed under reduced pressure and the crude product subjected to column chromatography or isolated by vacuum filtration (as specified).

General reaction procedure B (Upjohn Dihydroxylation): The diene was dissolved in acetone:H_2O (ratio as specified) and under nitrogen, N-methylmorpholine N-oxide and OsO_4 solution (4% in H_2O) were added and the solution left stirring at room temperature for three days. After this time, a 10% solution of NaS_2O_3 was added, before liquid-liquid extraction was performed (3 × 30 mL EtOAc). The organic layers were combined, dried (Na_2SO_4), filtered, and the solvent removed under reduced pressure.

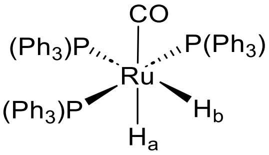
General reaction procedure C (Microwave mediated Mitsudo cycloaddition): The alkene, alkyne (1.5 eq), and $RuH_2(CO)(PPh_3)_3$ were combined in a microwave vial and suspended in acetone (2 mL). The suspension was irradiated in a microwave reactor (heated in stages as specified). After cooling the reaction, a fine powder precipitated from the solution and was collected by vacuum filtration. The precipitate was washed with acetone until no longer coloured.

General reaction procedure D (microwave mediated boronic ester formation): Bis-diol (1 eq.) and phenyl boronic acid (2 eq.) were combined in ethanol (0.5 mL) and the solution irradiated in a microwave reactor (130 °C, 150 W, 5 min). After reaction, the solution was cooled over ice, during which time a mass of precipitate formed. The precipitate was collected by vacuum filtration and washed with (1:1) EtOH:H_2O (2 mL), then ethanol (2 mL), before being allowed to dry under vacuum.

General isolation procedure A: The reaction mixture was concentrated to ~5 mL under reduced pressure, then transferred to a centrifuge tube. *n*-Hexane was added until precipitate formed. The fine suspension was compacted by centrifugation and the supernatant decanted. The solid material was triturated with additional *n*-hexane or diethyl ether (as specified), and the precipitate was again separated by centrifugation and the supernatant decanted.

1.13. Specific Synthesis

Carbonyldihydridotris(triphenylphosphine)ruthenium(II)[22] (18)

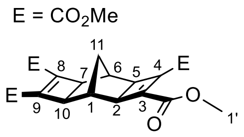


To a refluxing solution of ethanol (300 mL), triphenylphosphine (7.45 g, 28.4 mmol), ruthenium trichloride (0.987 g, 4.76 mmol), potassium hydroxide (1.74 g, 32.0 mmol) in ethanol (48mL) and 40% formaldehyde (45 mL) were added sequentially. The reaction was heated at reflux for 25 minutes before being removed from heat and allowed to stand overnight, during which time a grey precipitate formed. The precipitate was collected using vacuum filtration and washed with ethanol (1 × 25 mL), H_2O (1 × 25 mL), ethanol (1 × 25 mL) and pet. Spirits (1 × 25 mL). The light grey powder (3.0 g, 68%) was used without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 6.87 (m, 45H, 9 × Ph), −6.88 (tdd, *J* = 30.7, 15.1, 6.4 Hz, 1H, H_b), −8.84 (dtd, *J* = 74.0, 28.2, 6.4 Hz, 1H, H_a).

Spectral data matched that of the literature.[22]

Tetramethyl-(1r, 2S, 5R, 6r, 7S, 10R)-tetracyclo[4.4.1.0^{2,5}.0^{7,10}]deca-3,8-diene-3,4,8,9-tetracarboxylate (7_{Me})



Small Scale (< 2.0 grams): Norbornadiene (550 µL, 5.41 mmol), DMAD (1.69 mL, 13.50 mmol) and $RuH_2(CO)(PPh_3)_3$ (200 mg, 4 mol%) were added to a round bottom flask and dissolved in 3 mL of DMF. The reaction was heated in a sand bath at 100 °C for 15 hours and monitored by thin-layer chromatography (30% EtOAc: Pet. spirits, silica, R_f 0.22). Once complete, the reaction was let cool to room temperature and ice-cold water (~ 5 mL) added until a brown precipitate formed. The crude precipitate was collected by vacuum filtration and recrystalised from a minimum of hot ethanol (~ 2 mL). The crystalline powder was collected by vacuum filtration and washed with ice-cold ethanol (5 × 1mL) to afford methyl tetraester $\mathbf{7_{Me}}$ (1.85 g, 91%) as a slightly off-white powder.

Large Scale (40 grams): To a 1.0 L 3-neck round bottom flask, norbornadiene (17.0 mL, 0.167 mol) and DMF (75 mL) were added. The flask was equipped with a thermometer, a pressure equalising addition funnel, and a Liebig condenser. The solution of NBD was then heated until an internal thermometer reading of 90°C. The addition funnel was charged with a solution of DMAD (43.0 mL, 0.344 mol) in DMF (100 mL).

To the round-bottom flask, $RuH_2(CO)(PPh_3)_3$ (2.02 g, 1.31 mol%) was then added in a single portion, and slow addition of the DMAD solution was initiated. The addition was completed over a 1.5-hour period, during which time the internal temperature slowly rose to 110 °C. Once complete the addition funnel was replaced with a stopper, and the solution allowed to stir for an additional 18 hours at 110 °C.

After this time, the solution was let cool to room temperature, then poured into a beaker containing water (200 mL) whereupon a mass of precipitate formed. The suspension was let stir over ice for two hours, then let settle and the supernatant liquid decanted, before the bulk of the solid was collected by vacuum filtration and washed with ice-cold methanol (2 × 50 mL). The isolated solid was triturated in hot ethanol (60 mL), before again being collected by vacuum filtration and washed with additional ethanol (2 × 50 mL). The material was dried under vacuum to give methyl tetraester $\mathbf{7_{Me}}$ as an off-white powder (41 g, 0.11 mol, 65%)

Authors note: **The initial reaction generates a notable exotherm**. While the small-scale conditions have been performed routinely in our lab without incident, in reactions performed on a 5–10-gram scale bumping of the material was observed, and for the large-scale conditions dropwise addition of the DMAD reagent is essential to perform the reaction safely.

R_f 0.22 (30% EtOAc: Pet. Spirits, silica)

^{1}H NMR (400Hz, $CDCl_3$) δ 1.37 (2H, s, H_{11}), 2.42 (2H, s, $H_{1,6}$), 2.75 (4H, s, $H_{2,5,7,10}$), 3.78 (12H, s, $H_{1'}$)

HRMS (ESI, *m/z*) for $C_{19}H_{20}O_8$ $[M+H]^+ = 377.12309$, found 377.12306.

Spectral data matched that of literature.[23]

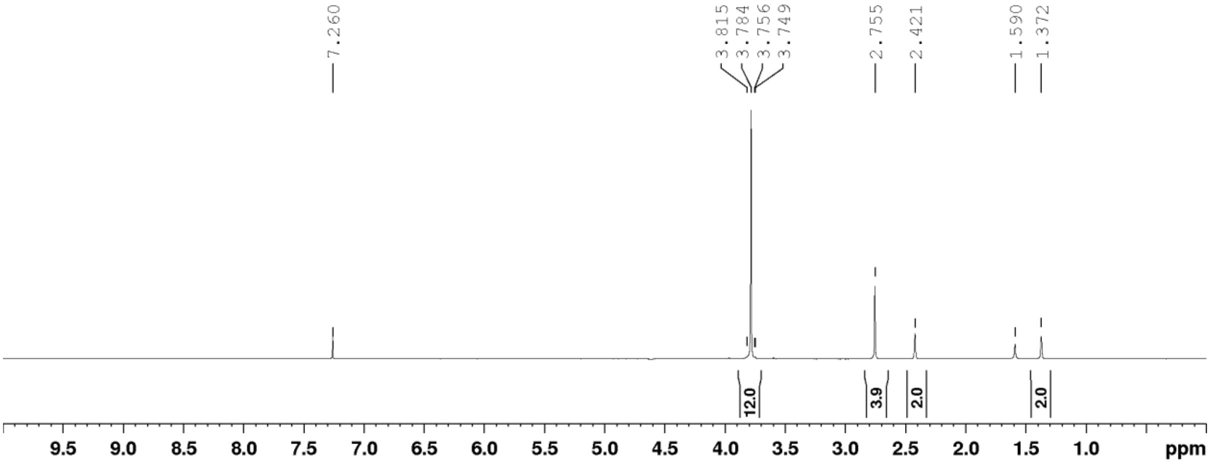
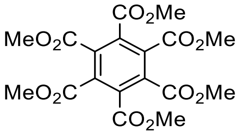


Figure S1. *^{1}H NMR spectrum of 7_{Me}.*

Benzenehexacarboxylic acid, hexamethyl ester (**19**)



In reactions where a vigorous exotherm was generated, a side product was noted. The product was likely the result of trimerization of dimethyl acetylene dicarboxylate (a known reaction[24]) and was assigned as benzenehexacarboxylic acid, hexamethyl ester on the basis of the single proton environment, and three carbon environments.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.29, 134.06, 53.63.

Spectral data matched that of literature.[25]

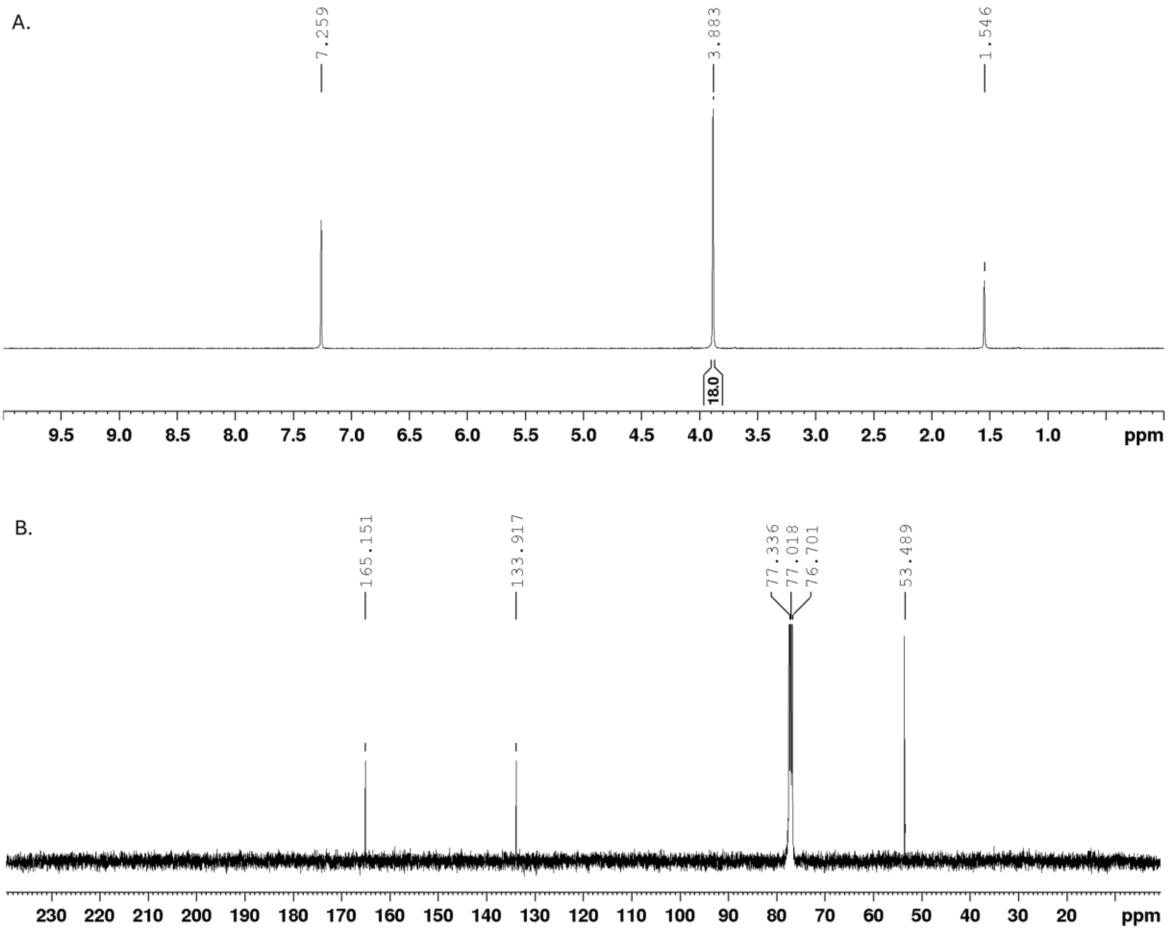
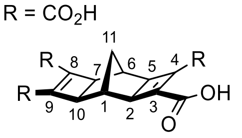


Figure S2. *A. ¹H NMR spectrum of **19**. B. ¹³C NMR spectrum of **19***

(1r, 2S, 5R, 6r, 7S, 10R)-tetracyclo[4.4.1.0^{2,5}.0^{7,10}]deca-3,8-diene-3,4,8,9-tetracarboxylic acid (7$_{H}$)[26]



Tetraester **7$_{Me}$** (1.0 g, 2.65 mmol) was added to a round-bottom flask and dissolved in MeOH/THF (1:1 mix, 10 mL). A solution of KOH (1.7 g in 8 mL H_2O) was added and the mix heated to reflux for 24 hours. After cooling, the solution was acidified to pH 1 with HCl (32% aq.). During this time a cloudy white precipitate formed that was collected by vacuum filtration, the solid was washed with H_2O (3 × 1 mL), acetone (3 × 1 mL), and was further dried under reduced pressure to yield the desired tetracarboxylate **7$_{H}$** as a fine white powder (850mg, 100%).

^{1}H NMR (500 MHz, DMSO) δ 2.60 (s, 4H, $H_{2,5,7,10}$), 2.07 (s, 2H, $H_{1,6}$), 1.13 (s, 2H, H_{11}).

^{13}C NMR (101 MHz, DMSO) δ 162.79, 143.32, 45.15, 31.06, 23.26.

Spectral data matched that of literature.[26]

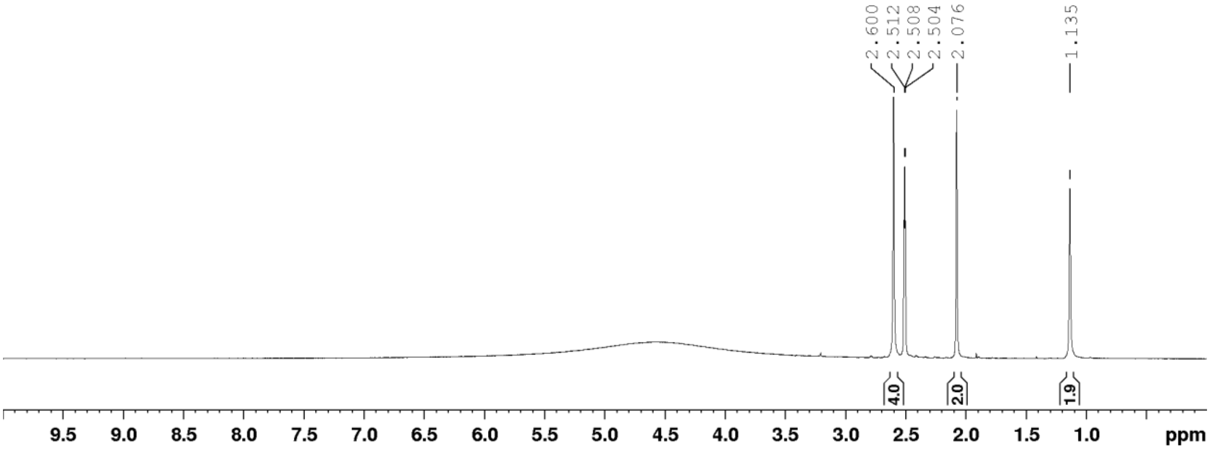
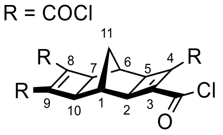


Figure S3. *^{1}H NMR spectrum of 7_H*

(1r, 2S, 5R, 6r, 7S, 10R)-Tetracyclo[4.4.1.$0^{2,5}$.$0^{7,10}$]deca-3,8-diene-3,4,8,9-tetracarboxyloyl chloride (20)[26]



Tetracarboxylate **X$_H$** (490 mg, 1.53 mmol) was added to 3-neck 100 mL round bottom flask and suspended in anhydrous chloroform (2.5 mL). Four drops of anhydrous DMF were added and the slurry placed over ice. Thionyl chloride (2.5 mL) was injected, and the solution was left for stirring for 10 minutes on ice. The flask was then transferred to a reflux setup and the solution heated at reflux under nitrogen for 2 hours. During this time the white slurry slowly became a clear, orange solution in this time. After cooling, the solvent was removed under reduced pressure to give the crude tetra-acyl chloride **X** as an orange solid (477 mg) with a small amount of DMF present (evident from analysis by ^{1}H NMR). This material was used in subsequent steps without additional purification.

A pure sample was obtained for analysis by performing the reaction without catalytic DMF.

^{1}H NMR (500 MHz, CDCl$_3$) δ 3.03 (s, 4H, $H_{2,5,7,10}$), 2.78 (s, 2H, $H_{1,6}$), 1.58 (s, 2H. H_{11}).

Spectral data matched that of literature.[26]

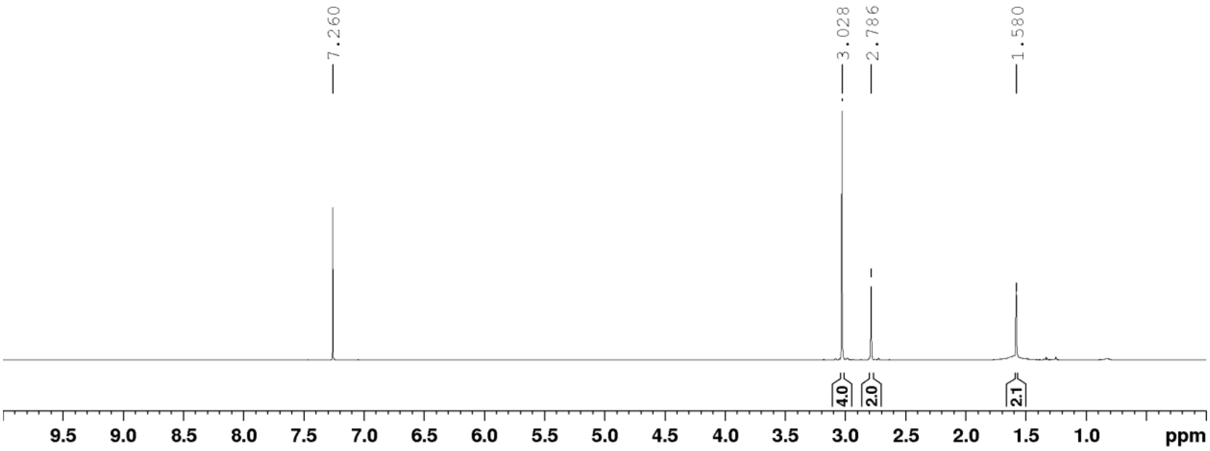
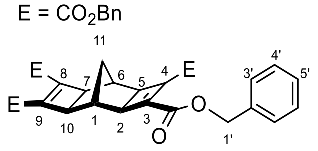


Figure S4. *^{1}H NMR spectrum of **20.***

Tetrabenzyl-(1r, 2S, 5R, 6r, 7S, 10R)-tetracyclo[4.4.1.0^{2,5}.0^{7,10}]deca-3,8-diene-3,4,8,9 tetracarboxylate ($\mathbf{7_{Bn}}$)



DMAP (321 mg, 2.63 mmol) was added to the flask containing tetra-acyl chloride **20** (prepared from $\mathbf{7_H}$ (2.01 g, 6.27 mmol)) under nitrogen, and the mix was suspended in anhydrous chloroform (20 mL). Anhydrous benzyl alcohol (2.8 mL, 27.1 mmol) was injected and the mix allowed to stir at room temperature for 20 minutes, then heated to reflux under nitrogen for 2 hours. After cooling, the mix was diluted with chloroform (20 mL) and washed sequentially with 1.0 M HCl (20 mL), saturated sodium carbonate (20 mL), then brine (20 mL). The organic phase was dried ($MgSO_4$), filtered through cotton wool, and the solvent removed *in vacuo* (chloroform portion removed 40 °C/300 mbar, benzyl alcohol was distilled from the reaction mix at 155 °C/0.2 mmHg). The crude material was purified by column chromatography (40% EtOAc: Pet. Spirits, silica, $\mathbf{R_f}$ 0.63) to afford benzyl tetraester $\mathbf{7_{Bn}}$ as a crystalline white powder (2.6 g, 60%).

$\mathbf{R_f}$ 0.63 (40% EtOAc: Pet. Spirits, silica)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 20H, $H_{3',4',5'}$), 5.17 (s, 8H, $H_{1'}$), 2.76 (s, 4H, $H_{2,5,7,10}$), 2.41 (s, 2H, $H_{1,6}$), 1.41 (s, 2H, H_{11}).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.78, 142.55, 135.57, 128.71, 128.44, 128.32, 66.75, 46.25, 31.89, 23.87.

HRMS (ESI, *m/z*) calculated for $C_{43}H_{36}O_8$ $[M+H]^+$ = 681.24829, found 681.24960.

M.p 115–117 °C

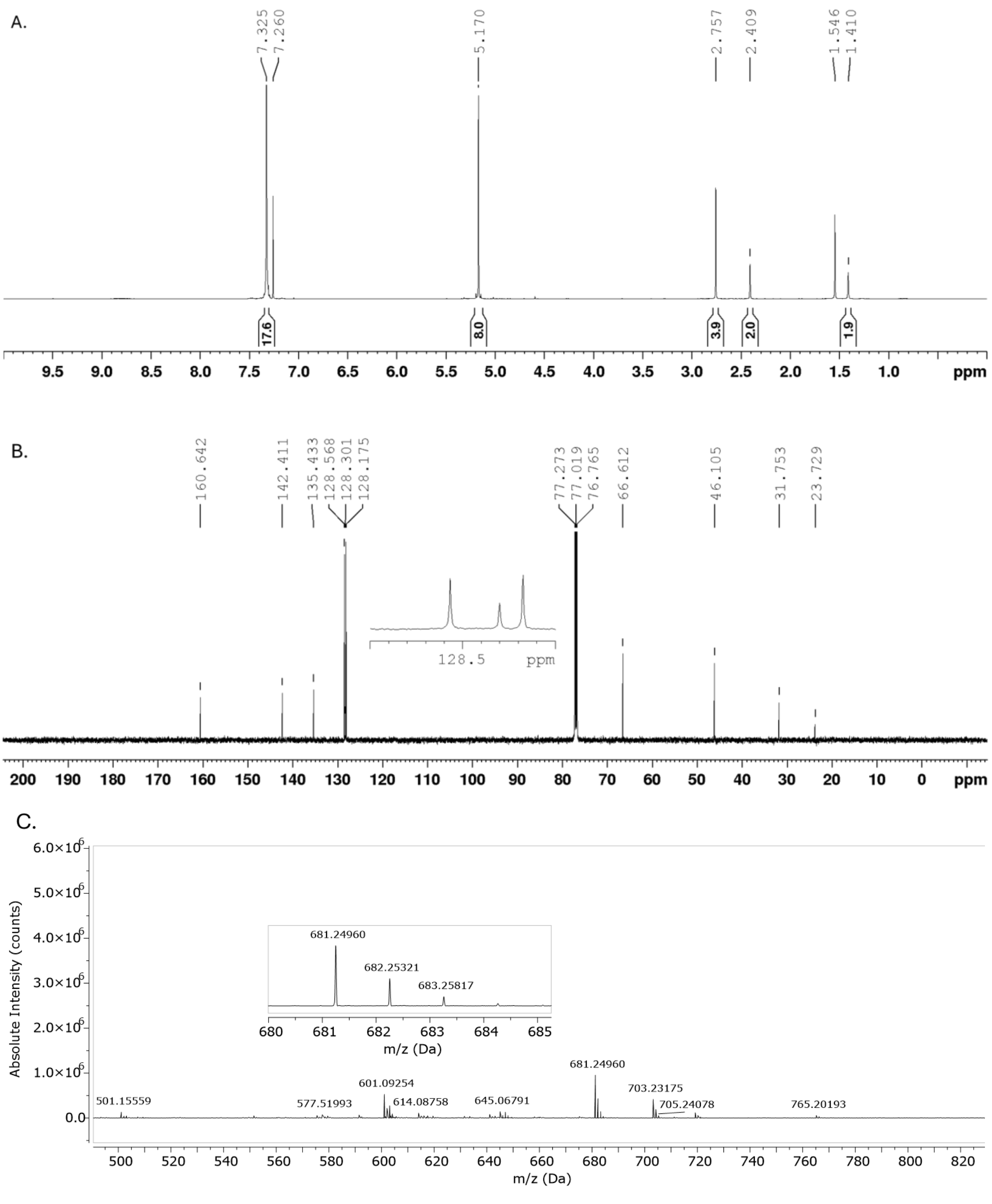
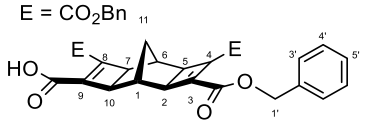


Figure S5. *A. ^{1}H NMR spectrum of 7_{Bn}. B. ^{13}C NMR spectrum of 7_{Bn}. C. HRMS spectrum of 7_{Bn}.*

In some reactions a small amount of the tri-benzyl ester, mono-carboxylate was isolated.

Tribenzyl-(1r, 2S, 5R, 6r, 7S, 10R)-tetracyclo[4.4.1.0^{2,5}.0^{7,10}]deca-3,8-diene-9-carboxylic acid-3,4,8-tricarboxylate ($7_{3Bn,H}$)



^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45 – 7.28 (m, 15H, $H_{3',4',5'}$), 5.31 (dd, *J* = 48.8, 12.5 Hz, 2H), 5.23 – 5.13 (m, 4H), 2.88 – 2.83 (m, 1H), 2.82 – 2.74 (m, 3H), 2.52 (s, 1H), 2.36 (s, 1H), 1.45 (d, *J* = 1.5 Hz, 1H), 1.26 (d, *J* = 1.5 Hz, 1H).

Coincident resonances led to a poorly resolved spectrum. As such not all hydrogen signals could be assigned.

^{13}C NMR (126 MHz, CDCl$_3$) δ 164.31, 160.81, 160.47, 160.00, 150.45, 142.77, 142.01, 141.64, 135.45, 135.37, 133.88, 129.26, 129.00, 128.82, 128.70, 128.66, 128.50, 128.42, 128.21, 68.72, 66.80, 46.61, 46.04, 46.00, 45.19, 31.42, 31.40, 23.96.

HRMS (ESI, *m/z*) calculated for $C_{36}H_{30}O_8$ $[M+H]^+$ = 591.20134, found 591.19974.

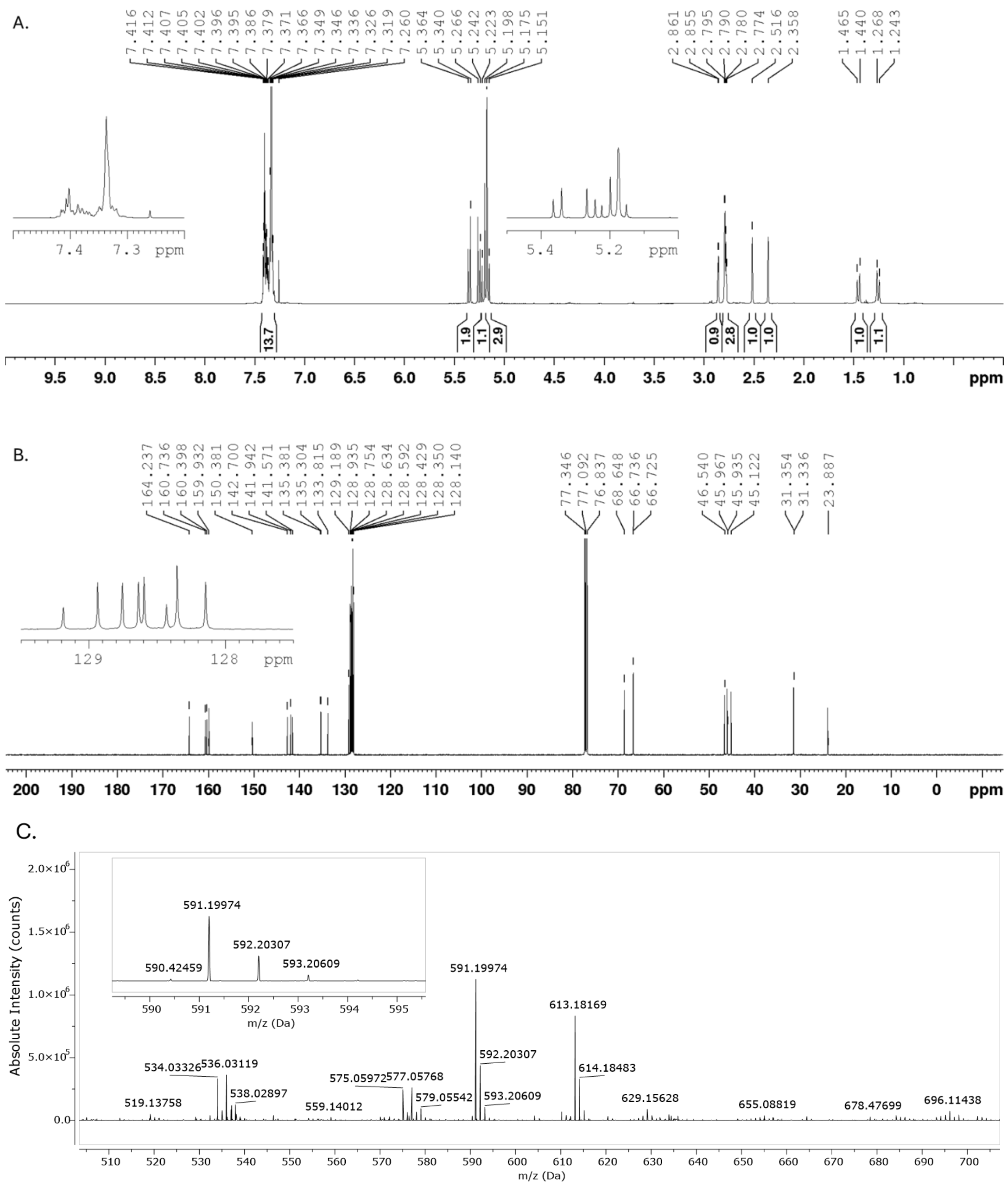
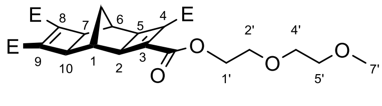


Figure S6. *A. ^{1}H NMR spectrum of $7_{3Bn,H}$. B. ^{13}C NMR spectrum of $7_{3Bn,H}$. C. HRMS spectrum of $7_{3Bn,H}$.*

Tetra(diethylene glycol monomethyl ether)-(1r, 2S, 5R, 6r, 7S, 10R)-tetracyclo[4.4.1.$0^{2,5}$.$0^{7,10}$]deca-3,8-diene-3,4,8,9-tetracarboxylate (7_{DEG})



DMAP (320 mg, 2.62 mmol) was added to the flask containing tetra-acyl chloride **20** (prepared from **7_H** (1.62 g, 5.06 mmol)) under nitrogen, and the mix was suspended in anhydrous chloroform (20 mL). Then, diethylene glycol monomethyl ether (2.67 mL, 22.7 mmol) was injected and the mix allowed to stir at room temperature for 20 minutes, then heated to reflux under nitrogen for 18 hours. After cooling the mix was diluted with ethyl acetate (20 mL) and washed sequentially with 1.0 M HCl (10 mL), saturated sodium carbonate (10 mL), then brine (10 mL). The organic phase was dried ($MgSO_4$), filtered, and solvent removed *in vacuo* (ethyl acetate portion removed 40 °C/150 mbar, residual diethylene glycol monomethyl ether was distilled from the reaction mix at 140 °C/0.2 mmHg) to give tetraester **7_{DEG}** as a brown oil (3.12 g, 4.37 mmol, 87%).

R_f 0.41 (5% MeOH: EtOAc, silica)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.32 (td, J = 4.9, 2.9 Hz, 8H, $H_{1'}$), 3.74 (t, J = 5.0 Hz, 8H, $H_{2'}$), 3.67 – 3.62 (m, 8H), 3.56 – 3.51 (m, 8H), 3.37 (s, 12H, $H_{7'}$), 2.75 (s, 4H, $H_{2,5,7,10}$), 2.40 (s, 2H, $H_{1,6}$), 1.38 (s, 2H, H_{11}).

Proton resonances $H_{4'}$ and $H_{5'}$ could not be resolved.

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.76, 142.62, 72.00, 70.64, 68.96, 64.03, 59.20, 46.16, 31.83, 23.78.

HRMS (ESI, *m/z*) calculated for $C_{35}H_{52}O_{16}$ $[M+H]^+$ = 729.33281, found 729.33060. $[M+Na]^+$ = 751.31476, found 751.29485.

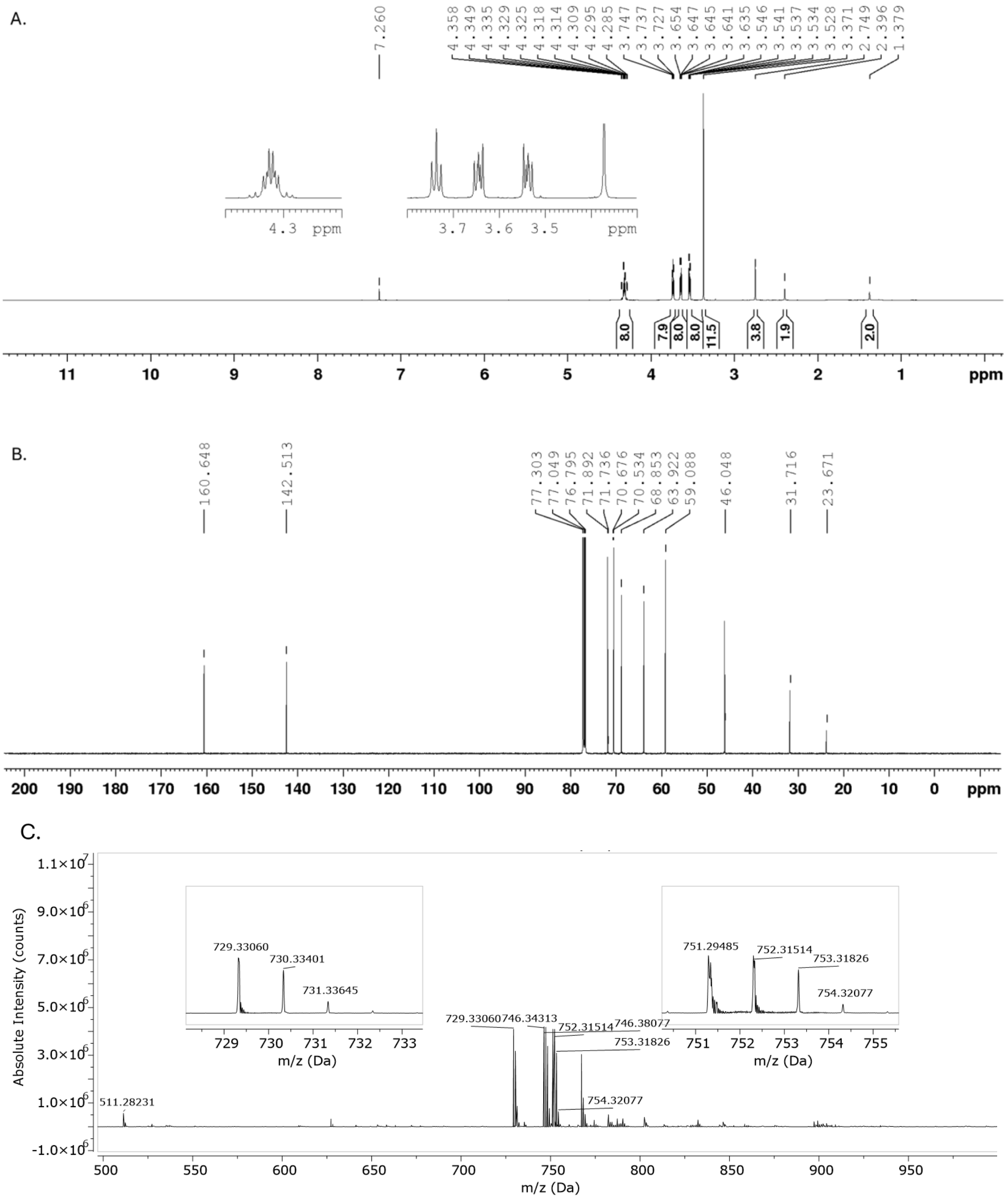
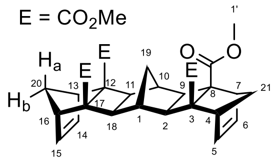


Figure S7. *A. ^{1}H NMR spectrum of 7_{DEG}. B. ^{13}C NMR spectrum of 7_{DEG}. C. HRMS spectrum of 7_{DEG}.*

Tetramethyl-(1r, 2S, 3S, 4R, 7S, 8R, 9R, 10r, 11S, 12S, 13R, 16S, 17R, 18R)-octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]henicosa-5,14-diene-3,8,11,18-tetracarboxylate (8_{Me})[27, 28]



Tetraester **7**$_{\mathbf{Me}}$ (5.53 g, 14.7 mmol) and CPD (10 mL, 120 mmol) were combined in DMF (25 mL) according to **general reaction procedure A**. After 7 days, a mass of clear, block crystals were deposited. The crystals were collected by vacuum filtration and washed with ice-cold DMF (3 × 5 mL), then ice-cold diethyl ether (2 × 5 mL). A second batch of crystals formed in the mother liquor, that was subsequently collected and washed by the same protocol. The clear crystals were combined and using ^{1}H NMR spectroscopy, found to be 9:1 *exo,exo* product **8**$_{\mathbf{Me}}$: *exo,endo* product **21** (5.07 g, 68%). Diene **8**$_{\mathbf{Me}}$ was isolated by column chromatography (**R**$_{\mathbf{f}}$ 0.43 in 60:40 Pet.Sp:EtOAc).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 6.42 (s, 4H, $H_{5,6,14,15}$), 3.68 (s, 12H, $H_{1'}$), 3.07 (s, 4H, $H_{4,7,13,16}$), 2.71 (s, 2H, $H_{1,10}$), 2.01 (d, J = 8.9 Hz, 2H, H_{20a}), 1.94 (s, 2H, H_{19}), 1.52 (d, J = 8.9 Hz, 2H, H_{20b}), 1.18 (s, 4H, $H_{2,9,11,18}$).

^{13}**C NMR** (101 MHz, $CDCl_3$) δ 172.93, 137.71, 60.51, 53.34, 51.49, 50.99, 46.78, 39.08, 35.12.

HRMS (ESI, *m/z*) calculated for $C_{29}H_{32}O_8$ $[M+H]^+$ = 509.21699, found 509.21682.

M.p 192–194°C

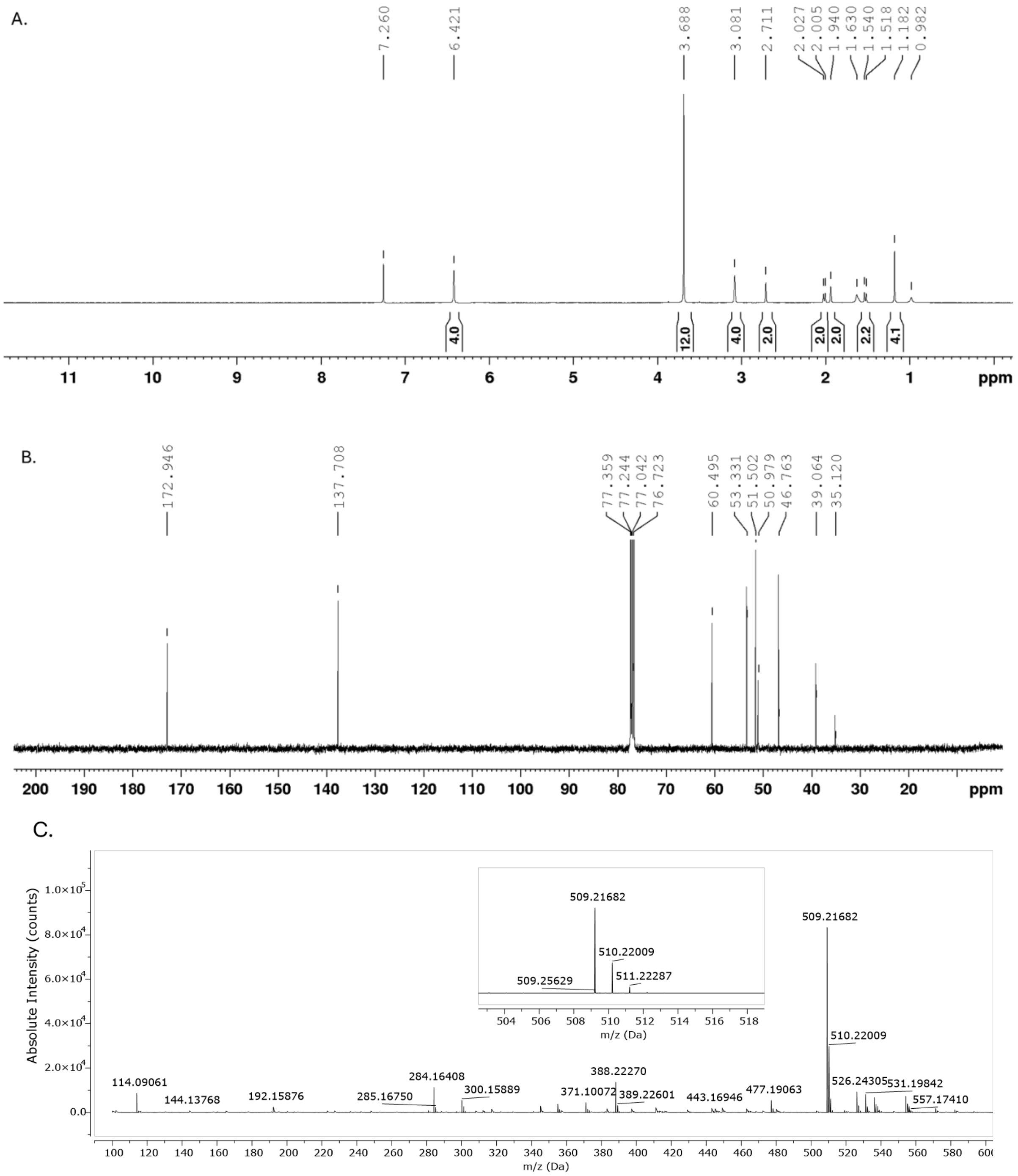
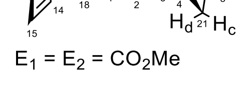


Figure S8. *A. ^{1}H NMR spectrum of* ***8$_{Me}$****. B. ^{13}C NMR spectrum of* ***8$_{Me}$****. C. HRMS spectrum of* ***8$_{Me}$****.*

Tetramethyl-(1r, 2S, 3S, 4S, 7R, 8R, 9R, 10r, 11S, 12S, 13R, 16S, 17R, 18R)-octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]henicosa-5,14-diene-3,8,11,18-tetracarboxylate (21)



$E_1 = E_2 = CO_2Me$

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (s, 2H, $H_{14,15}$), 6.09 (s, 2H, $H_{5,6}$), 3.68 (s, 6H, E_1-CO_2CH_3), 3.63 (s, 6H, E_2-CO_2CH_3), 3.11 (s, 2H, $H_{13,16}$), 2.92 (s, 2H, $H_{4,7}$), 2.60 (s, 2H, $H_{1,10}$), 2.04 (d, J = 9.6 Hz, 1H, H_{20a}), 2.01 – 1.93 (m, 2H, $H_{19e,\ 21d}$), 1.91 (d, J = 12.5 Hz, 1H, H_{19f}), 1.63 – 1.53 (m, H_2O, $H_{11,18,\ 20b}$), 1.38 (s, 2H, $H_{2,9}$), 1.26 (d, J = 9.3 Hz, 1H, H_{21c}).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.96, 171.69, 137.88, 135.86, 60.67, 59.26, 53.50, 51.71, 51.62, 51.23, 51.19, 47.76, 46.92, 41.98, 39.26, 33.08.

HRMS (ESI, *m/z*) calculated for $C_{29}H_{32}O_8$ $[M+H]^+$ = 509.21699, found 509.20869. $[M+Na]^+$ = 531.19894, found 531.19806.

M.p 207–209 °C

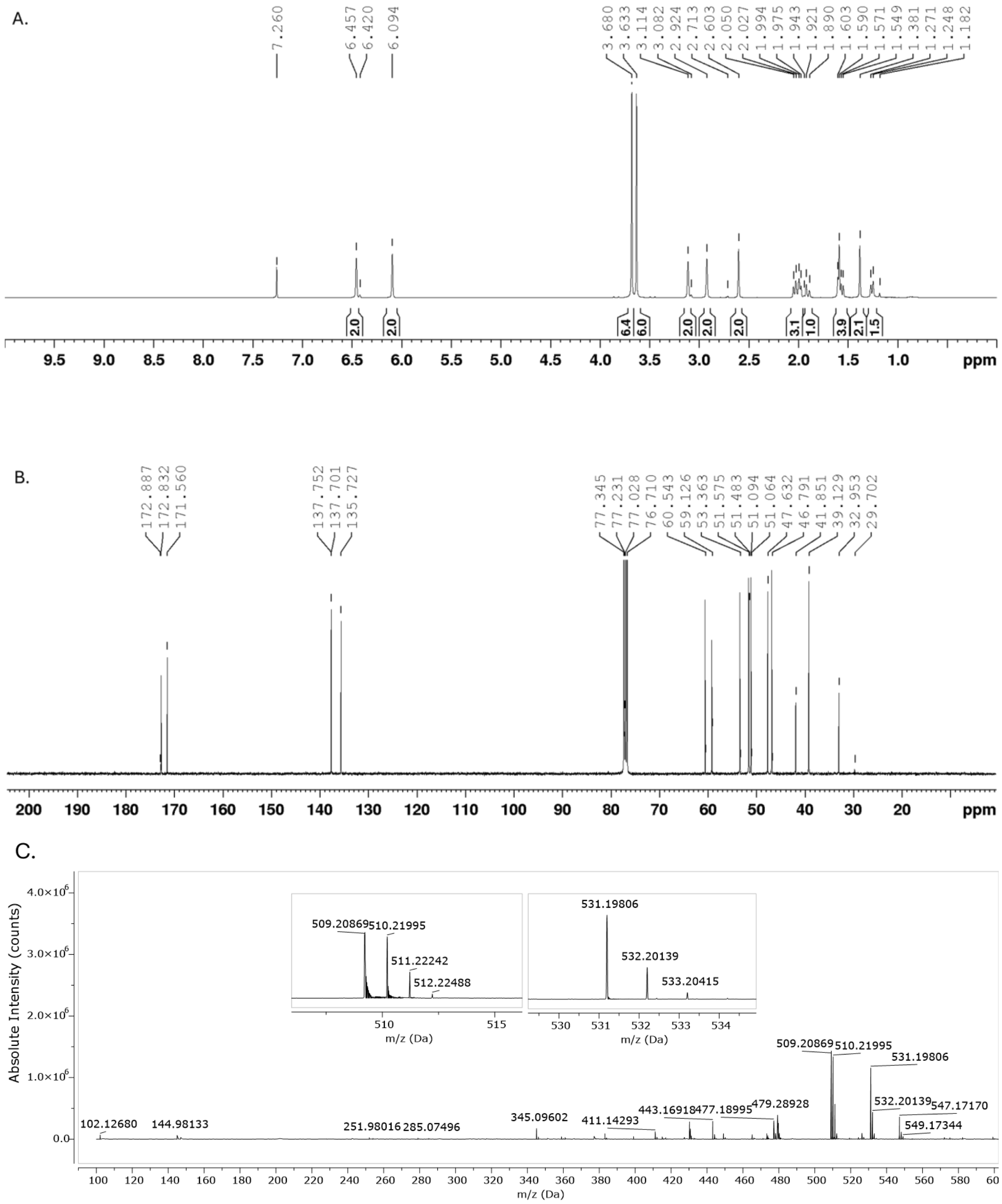
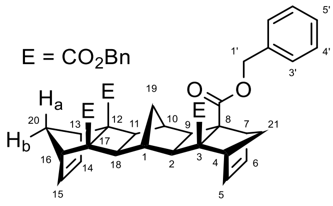


Figure S9. *A. ^{1}H NMR spectrum of **21**. B. ^{13}C NMR spectrum of **21**. C. HRMS spectrum of **21**.*

Tetrabenzyl-(1r, 2S, 3S, 4R, 7S, 8R, 9R, 10r, 11S, 12S, 13R, 16S, 17R, 18R)-octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]henicosa-5,14-diene-3,8,11,18-tetracarboxylate (8$_{Bn}$)



Tetraester **7_{Bn}** (410 mg, 0.585 mmol) and CPD (392 µL, 4.76 mmol) were combined in DMF (10 mL) according to **general reaction procedure A**. After 7 days, column chromatography (20% EtOAc: Pet. Spirits, Silica, **R_f** 0.59) afforded **8_{Bn}** as a crystalline white powder (268 mg, 55%)

R_f 0.59 (20% EtOAc: Pet. Spirits, Silica)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (q, J = 6.9 Hz, 20H, $H_{3',4',5'}$), 6.39 (t, J = 2.0 Hz, 4H, $H_{5,6,14,15}$), 5.00,4.97 (ABq, J_{AB} = 12.5 Hz, 8H, $H_{1'}$), 3.09 (s, 4H, $H_{4,7,13,16}$), 2.83 (s, 2H, $H_{1,10}$), 2.10 (s, 2H, H_{19}), 2.06 (d, J = 9.2 Hz, 2H, H_{20a}), 1.51 (d, J = 8.9 Hz, 2H, H_{20b}), 1.18 (s, 4H, $H_{2,9,11,18}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.24, 137.90, 136.33, 128.62, 128.47, 128.13, 66.50, 60.73, 53.60, 51.18, 47.08, 39.27, 35.63.

HRMS (ESI, *m/z*) calculated for $C_{53}H_{48}O_8$ $[M+Na]^+$ = 835.32414, found 835.33313.

M.p 51–52 °C

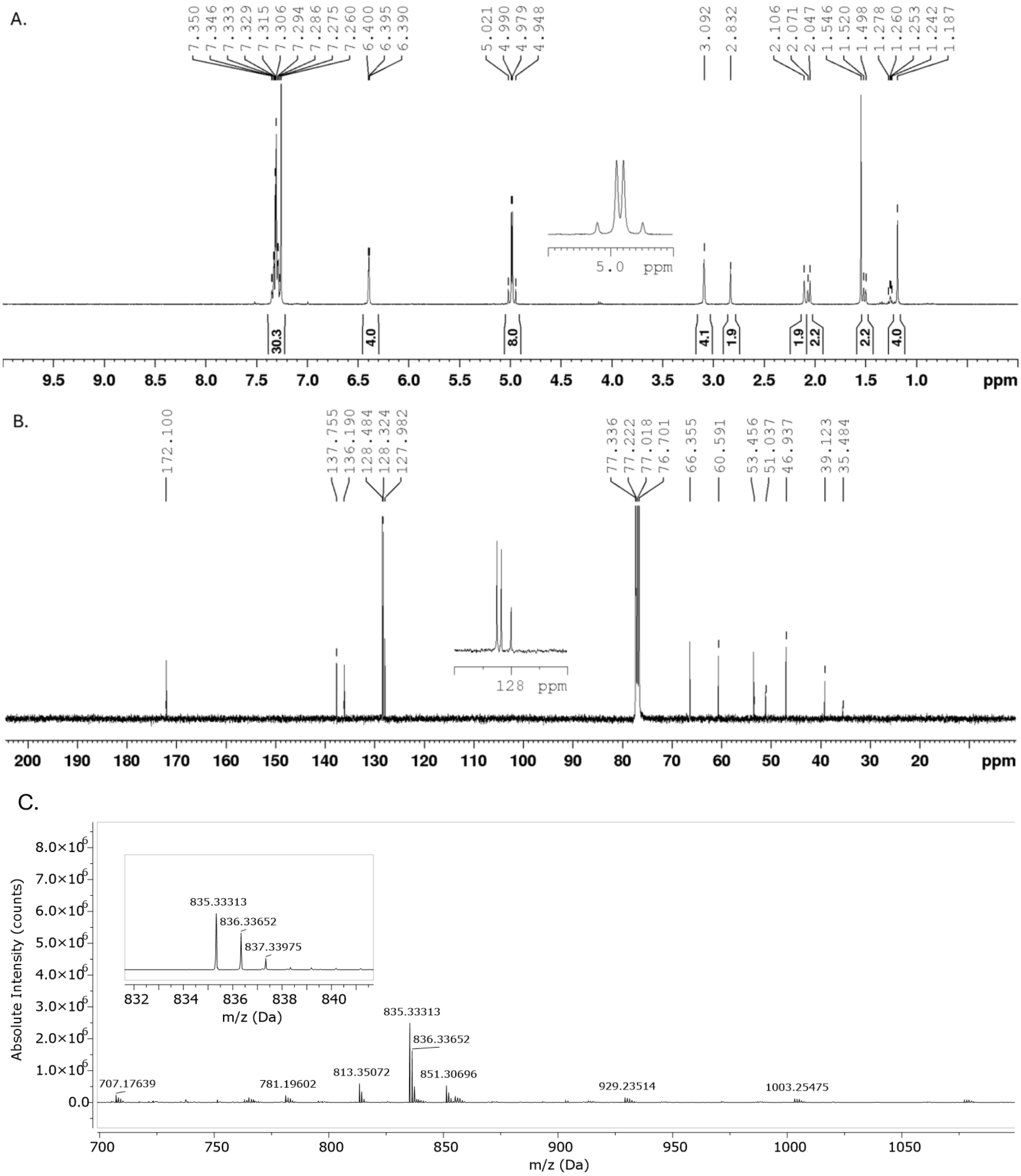
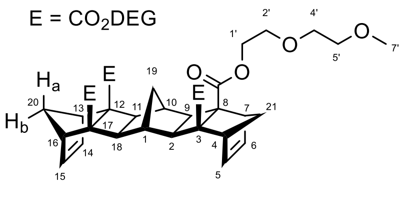


Figure S10. *A. ^{1}H NMR spectrum of **8_{Bn}**. B. ^{13}C NMR spectrum of **8_{Bn}**. C. HRMS spectrum of **8_{Bn}**.*

Tetra(diethylene glycol monomethyl ether)-(1r, 2S, 3S, 4R, 7S, 8R, 9R, 10r, 11S, 12S, 13R, 16S, 17R, 18R)-octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]henicosa-5,14-diene-3,8,11,18-tetracarboxylate (8_{DEG})



Tetraester **7_{DEG}** (500 mg, 0.70 mmol) and CPD (460 µL, 5.61 mmol) were combined in DMF (5 mL) according to **general reaction procedure A**. After 3 days, column chromatography (10% MeOH:EtOAc, Silica, R_f 0.43) afforded **8_{DEG}** as a clear oil (348 mg, 59%).

R_f 0.43 (10% MeOH:EtOAc, Silica)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.42 (t, J = 2.2 Hz, 4H, $H_{5,6,14,15}$), 4.25 (t, J = 5.1 Hz, 8H, $H_{1'}$), 3.75 – 3.66 (m, 8H, $H_{2'}$), 3.66 – 3.59 (m, 8H), 3.57 – 3.49 (m, 8H), 3.37 (s, 12H, $H_{7'}$), 3.11 (p, J = 1.7 Hz, 4H, $H_{4,7,13,16}$), 2.03 (dt, J = 8.9, 1.7 Hz, 2H, H_{20a}), 1.98 (s, 2H, H_{19}), 1.52 (dt, J = 8.9, 1.6 Hz, 2H, H_{20b}), 1.17 (s, 4H, $H_{2,9,11,16}$).

Proton resonances $H_{4'}$ and $H_{5'}$ could not be resolved.

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.24, 137.88, 72.04, 70.40, 69.26, 63.25, 60.58, 59.18, 53.44, 51.12, 46.92, 39.09, 35.42.

HRMS (ESI, *m/z*) calculated for $C_{45}H_{64}O_{15}$ $[M+H]^+$ = 861.42671, found 861.42569.

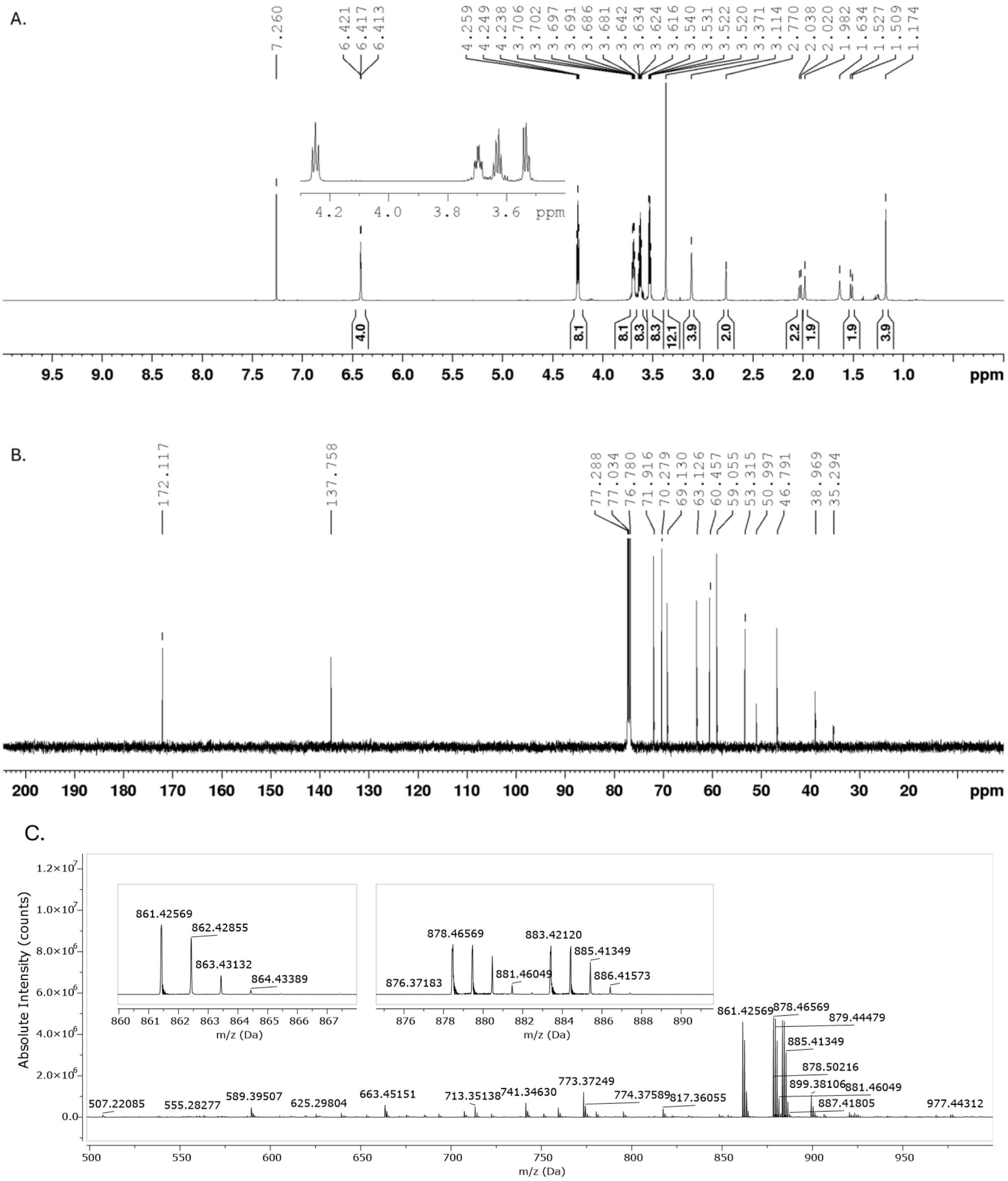
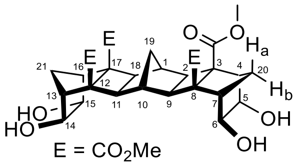


Figure S11. *A. ^{1}H NMR spectrum of* ***8$_{DEG}$****. B. ^{13}C NMR spectrum of* ***8$_{DEG}$****. C. HRMS spectrum of* ***8$_{DEG}$****.*

Tetramethyl-(1r, 2R, 3R, 4S, 5R, 6S, 7R, 8S, 9S, 10r, 11R, 12R, 13S, 14R, 15S, 16R, 17S, 18S)-octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]henicosa-5,6,14,15-tetraol-3,8,11,18-tetracarboxylate (3$_{Me}$)



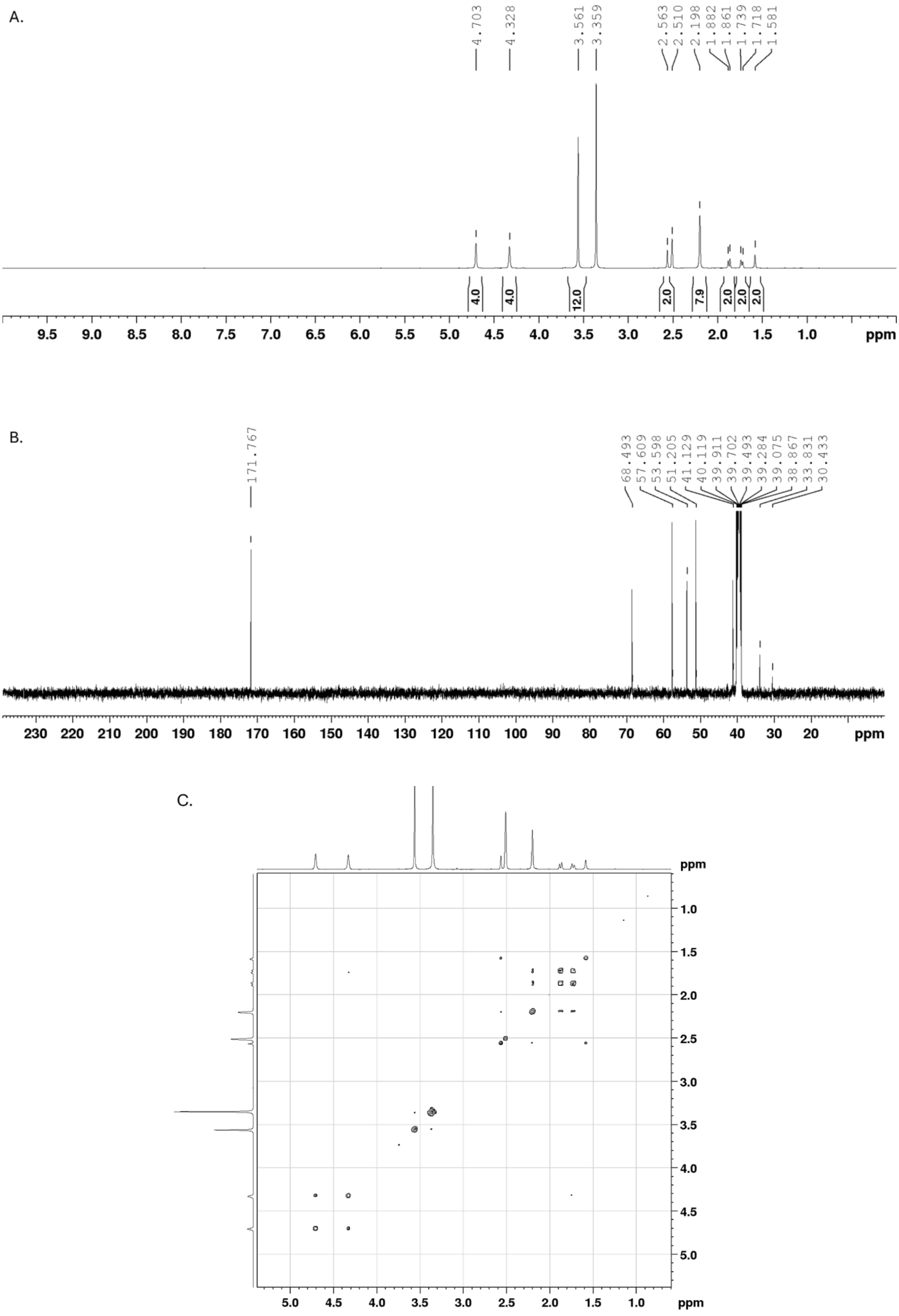
Diene **8_{Me}** (354 mg, 0.70 mmol), N-methylmorpholine N-oxide (291 mg, 2.48 mmol) and OsO_4 solution (4% in water, 100 µL) were combined in acetone:H_2O (19:1, 20 mL) according to **general reaction procedure B** to afford bis-diol **3_{Me}** as a fine white precipitate (394 mg, 98%)

^{1}H NMR (400 MHz, DMSO) δ 4.70 (s, 4H, O*H*), 4.32 (s, 4H, $H_{5,6,14,15}$), 3.55 (s, 12H, $H_{1'}$), 2.55 (s, 2H, $H_{1,10}$), 2.21 – 2.16 (m, 8H, $H_{2,4,7,9,11,12,17,18}$), 1.86 (d, J = 10.4 Hz, 2H, H_{20a}), 1.72 (d, J = 10.4 Hz, 2H, H_{20b}), 1.57 (s, 2H, H_{19}).

^{13}C NMR (101 MHz, DMSO) δ 171.77, 68.50, 57.61, 53.60, 51.21, 41.13, 33.83, 30.44.

HRMS (ESI, *m/z*) calculated for $C_{29}H_{36}O_{12}$ $[M+Na]^+$ = 599.20990, found 599.20969

M.p 117–119°C


A.
4.703
4.328
3.561
3.359
2.563
2.510
2.198
1.882
1.861
1.739
1.718
1.581
4.0
4.0
12.0
2.0
7.9
2.0
2.0
2.0
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 ppm
B.
171.767
68.493
57.609
53.598
51.205
41.129
40.119
39.911
39.702
39.493
39.284
39.075
38.867
33.831
30.433
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
C.
ppm
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

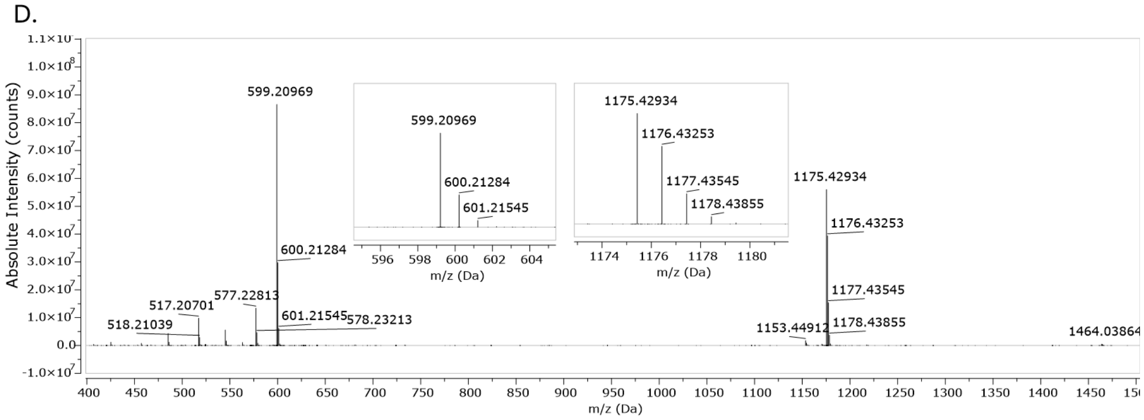
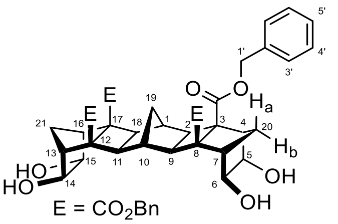


Figure S12. *A. ^1H NMR spectrum of* ***3_{Me}****. B. ^{13}C NMR spectrum of* ***3_{Me}****. C. ^1H-^1H COSY Spectrum of* ***3_{Me}****. D. HRMS spectrum of* ***3_{Me}****.*

Tetrabenzyl-(1r, 2R, 3R, 4S, 5R, 6S, 7R, 8S, 9S, 10r, 11R, 12R, 13S, 14R, 15S, 16R, 17S, 18S)-octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]henicosa-5,6,14,15-tetraol-3,8,11,18-tetracarboxylate (3_{Bn})



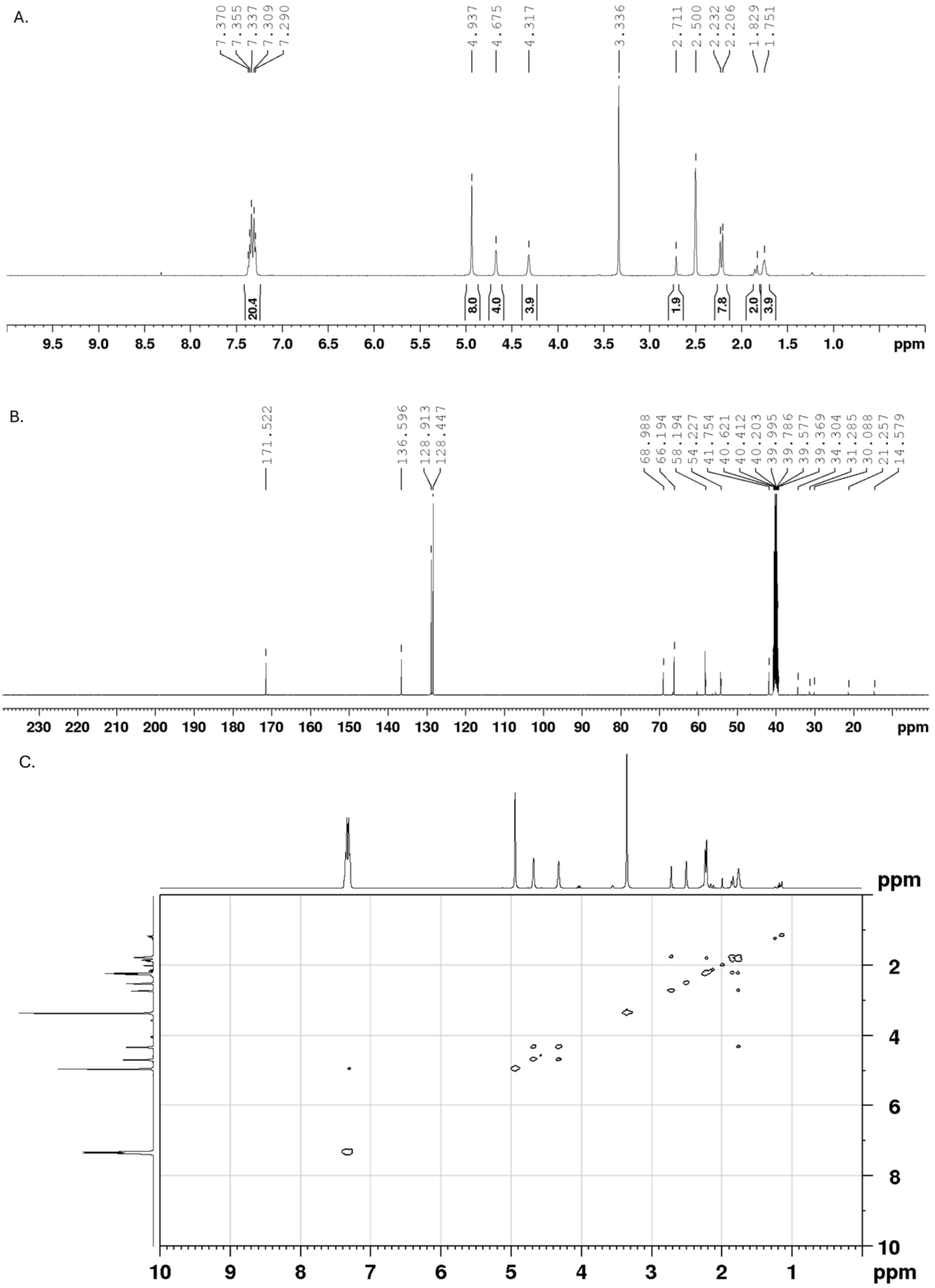
Diene **8_{Bn}** (240 mg, 0.29 mmol), N-methylmorpholine N-oxide (113 mg, 0.96 mmol) and OsO_4 solution (4% in water, 200 µL) were combined in acetone:H_2O (9:1, 10 mL) according to **general reaction procedure B** to afford bis-diol **3_{Bn}** as a crystalline powder (247 mg, 95%).

^{1}H NMR (400 MHz, DMSO) δ 7.40 – 7.27 (m, 20H, $H_{3',4',5'}$), 4.94 (s, 8H, $H_{1'}$), 4.67 (s, 4H,), 4.32 (s, 4H), 2.71 (s, 2H), 2.22 (d, J = 10.3 Hz, 8H), 1.84 (d, J = 10.4 Hz, 2H), 1.79 – 1.73 (m, 4H).

^{13}C NMR (101 MHz, DMSO) δ 171.05, 136.12, 128.44, 127.97, 68.51, 65.72, 57.72, 53.75, 41.28, 33.83, 30.81, 29.61, 20.78.

HRMS (ESI, *m/z*) calculated for $C_{53}H_{52}O_{12}$ $[M+H]^+$ = 881.35316, found 881.35324

M.p 215–217 °C


A.
7.370
7.355
7.337
7.309
7.290
4.937
4.675
4.317
3.336
2.711
2.500
2.232
2.206
1.829
1.751
20.4
8.0
4.0
3.9
1.9
7.8
2.0
3.9
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
ppm
B.
171.522
136.596
128.913
128.447
68.988
66.194
58.194
54.227
41.754
40.621
40.412
40.203
39.995
39.786
39.577
39.369
34.304
31.285
30.088
21.257
14.579
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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ppm
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7
6
5
4
3
2
1
ppm

D.

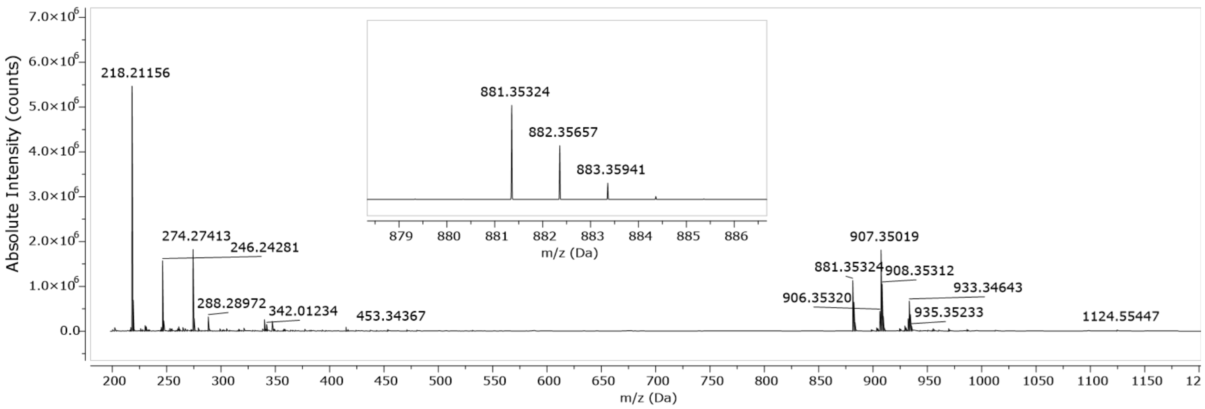
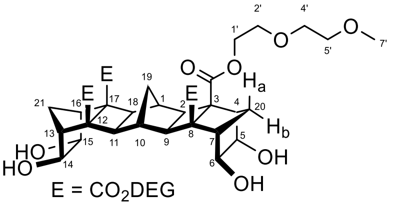


Figure S13. *A. ^{1}H NMR spectrum of **3**$_{Bn}$. B. ^{13}C NMR spectrum of **3**$_{Bn}$. C. ^{1}H-^{1}H COSY spectrum of **3**$_{Bn}$. D. HRMS spectrum of **3**$_{Bn}$.*

Tetra(diethylene gloycol monomethyl ether)-(1r, 2R, 3R, 4S, 5R, 6S, 7R, 8S, 9S, 10r, 11R, 12R, 13S, 14R, 15S, 16R, 17S, 18S)-octacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]henicosa-5,6,14,15-tetraol-3,8,11,18-tetracarboxylate (3$_{DEG}$)

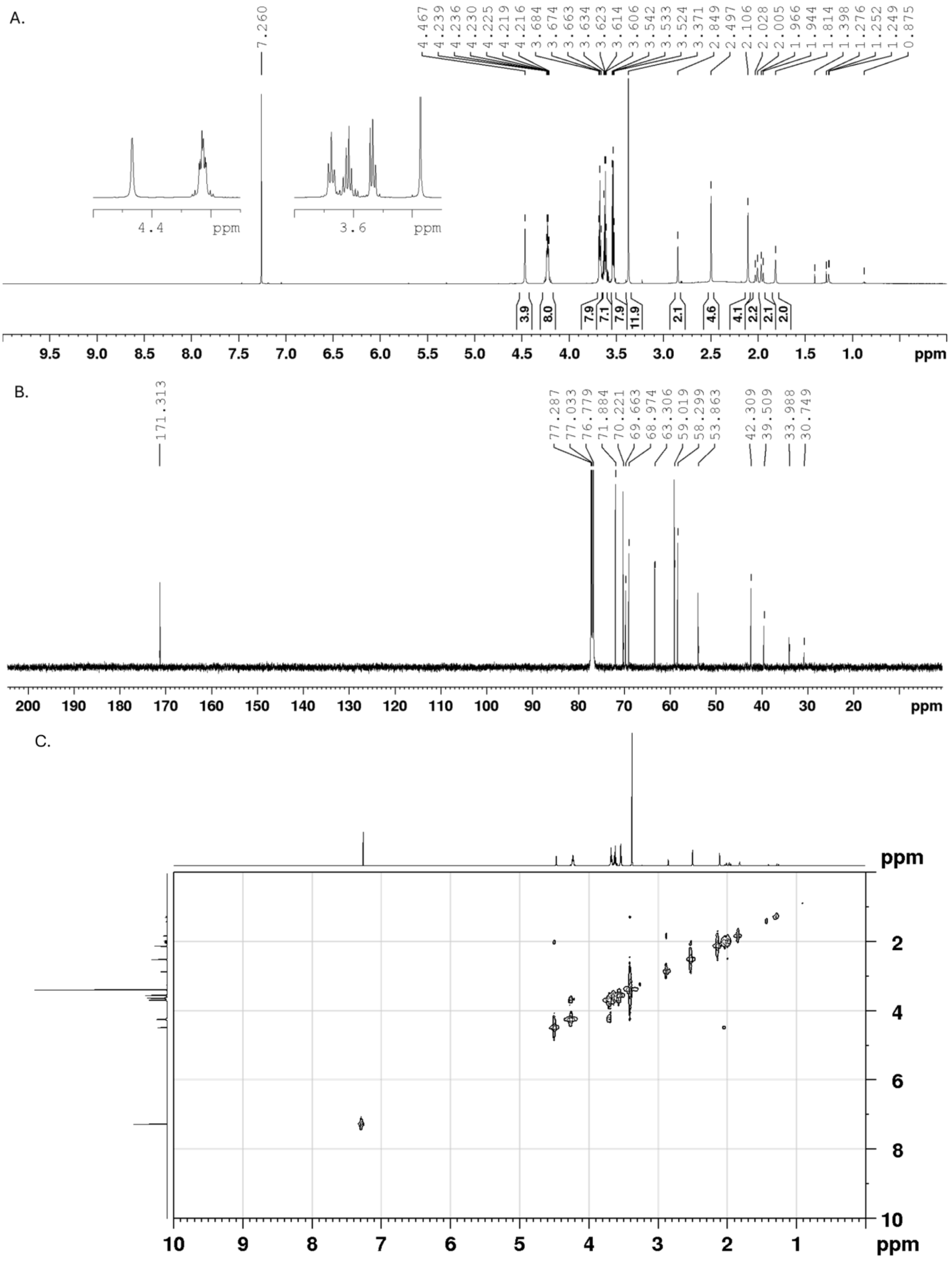


Diene **8**$_{DEG}$ (340 mg, 0.40 mmol), N-methylmorpholine N-oxide (122 mg, 1.04 mmol) and OsO_4 solution (4% in water, 200 µL) were combined in acetone:H_2O (4:1, 10 mL) according to **general reaction procedure B** to afford bis-diol **3**$_{DEG}$ as a clear, viscous oil (348 mg, 95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.47 (s, 4H, $H_{5,6,14,15}$), 4.28 – 4.17 (m, 8H, $H_{1'}$), 3.71 – 3.65 (m, 8H, $H_{2'}$), 3.65 – 3.58 (m, 8H), 3.56 – 3.51 (m, 8H), 3.37 (s, 12H, $H_{7'}$), 2.85 (s, 2H, $H_{1,10}$), 2.50 (s, 4H, $H_{4,7,13,17}$), 2.11 (s, 4H, $H_{2,9,11,18}$), 2.02 (d, J = 11.6 Hz, 2H, H_{20a}), 1.96 (dt, J = 11.3, 1.5 Hz, 2H, H_{20b}), 1.81 (s, 2H, H_{19}).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.31, 71.89, 70.22, 69.66, 68.98, 63.31, 59.02, 58.30, 53.86, 42.31, 39.51, 33.99, 30.75.

HRMS (ESI, *m/z*) calculated for $C_{45}H_{68}O_{20}$ [M+CH_3COO]$^-$ = 987.44425, found 987.44246.


A.
7.260
4.467
4.239
4.236
4.230
4.225
4.219
4.216
3.684
3.674
3.663
3.634
3.623
3.614
3.606
3.542
3.533
3.524
3.371
2.849
2.497
2.106
2.028
2.005
1.966
1.944
1.814
1.398
1.276
1.252
1.249
0.875
4.4
ppm
3.6
ppm
3.9
8.0
7.9
7.1
7.9
11.9
2.1
4.6
4.1
2.2
2.1
2.0
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
ppm
B.
171.313
77.287
77.033
76.779
71.884
70.221
69.663
68.974
63.306
59.019
58.299
53.863
42.309
39.509
33.988
30.749
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
C.
ppm
2
4
6
8
10
10
9
8
7
6
5
4
3
2
1
ppm

D.

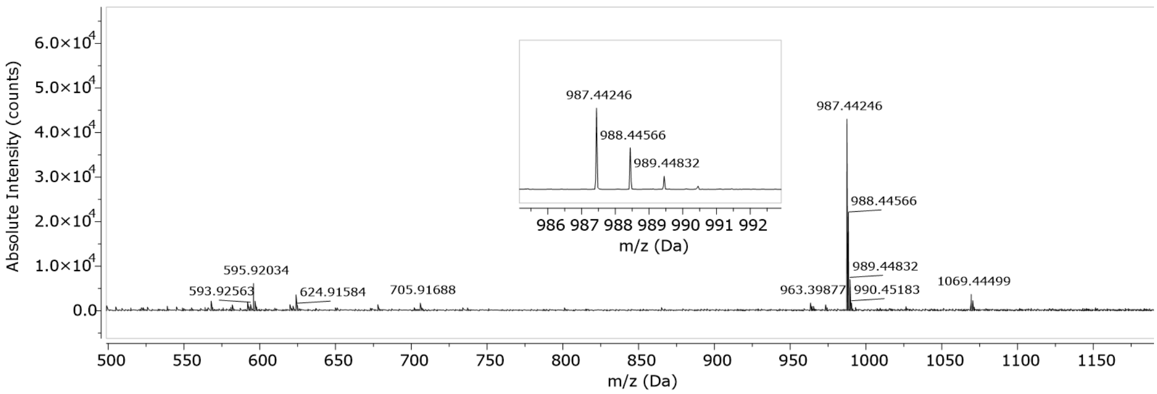
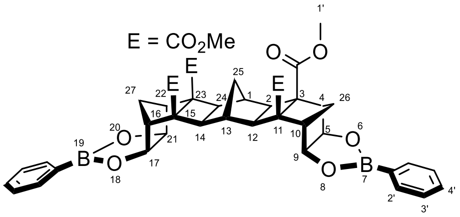


Figure S14. *A. ^1H NMR spectrum of* ***3_{DEG}****. B. ^{13}C NMR spectrum of* ***3_{DEG}****. C. ^1H-^1H COSY Spectrum of* ***3_{DEG}****. D. HRMS spectrum of* ***3_{DEG}****.*

Tetramethyl-(1r, 2R, 3R, 4S, 5R, 6S, 7R, 8S, 9S, 10r, 11R, 12R, 13S, 14R, 15S, 16R, 17S, 18S)-7,19-di(phenyl)-7,19-diboro-6,8,18,20-tetraoxadecacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]heptacosa-3,8,11,18-tetracarboxylate ([1+2]$_{Ph}$)



3_{Me} (40.9 mg, 0.0710 mmol) and phenyl boronic acid (18.7 mg, 0.153 mmol) were combined according to **general procedure D**. After drying, [1+2] assembly **[1+2]$_{Ph}$** was isolated as a fine white powder (33.4 mg, 63%)

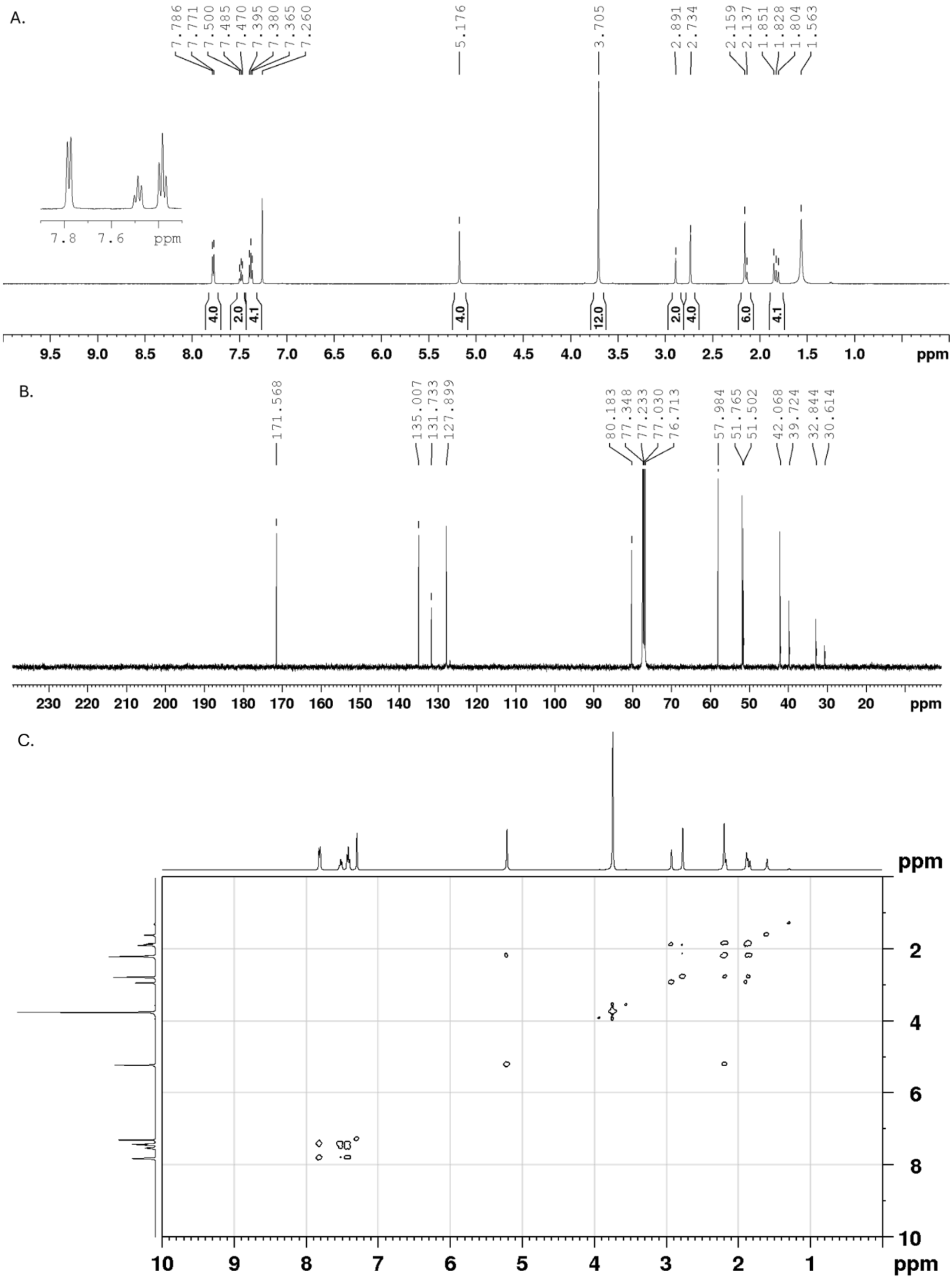
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 – 7.74 (m, 4H, $H_{2'}$), 7.53 – 7.44 (m, 2H, $H_{4'}$), 7.38 (t, J = 7.4 Hz, 4H, $H_{3'}$), 5.18 (s, 4H, $H_{5,9,17,21}$), 3.71 (s, 12H, $H_{1'}$), 2.89 (s, 2H, $H_{1,13}$), 2.74 (s, 4H, $H_{4,10,16,22}$), 2.18 – 2.12 (m, 8H, $H_{2,12,14,24,26a,}$), 1.87 – 1.78 (m, 4H, $H_{25,26b}$).

^{13}C NMR (101 MHz, CDCl$_3$) δ 171.56, 135.00, 131.73, 127.89, 80.18, 77.23, 57.99, 51.76, 51.50, 42.07, 39.72, 32.84, 30.61, 29.71.

HRMS (ESI, *m/z*) calculated for $C_{41}H_{42}B_2O_{12}$ [M+H]$^+$ = 749.29351, found 749.29272.

Note that within the mass spectrum (figure S15, D) a signal corresponding to the [1+1] adduct is present, given the stability evident from hydrolysis studies (see section **2.15**), the hydrolysis is reasoned to be due to fragmentation during ionisation. Calculated for $C_{35}H_{39}BO_{12}$ [M+H]$^+$ = 663.26074, found 663.25940.

M.p >350 °C


A.
7.786
7.771
7.500
7.485
7.470
7.395
7.380
7.365
7.260
5.176
3.705
2.891
2.734
2.159
2.137
1.851
1.828
1.804
1.563
7.8 7.6 ppm
4.0
2.0
4.1
4.0
12.0
2.0
4.0
6.0
4.1
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 ppm
B.
171.568
135.007
131.733
127.899
80.183
77.348
77.233
77.030
76.713
57.984
51.765
51.502
42.068
39.724
32.844
30.614
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
C.
ppm
2
4
6
8
10
10 9 8 7 6 5 4 3 2 1 ppm

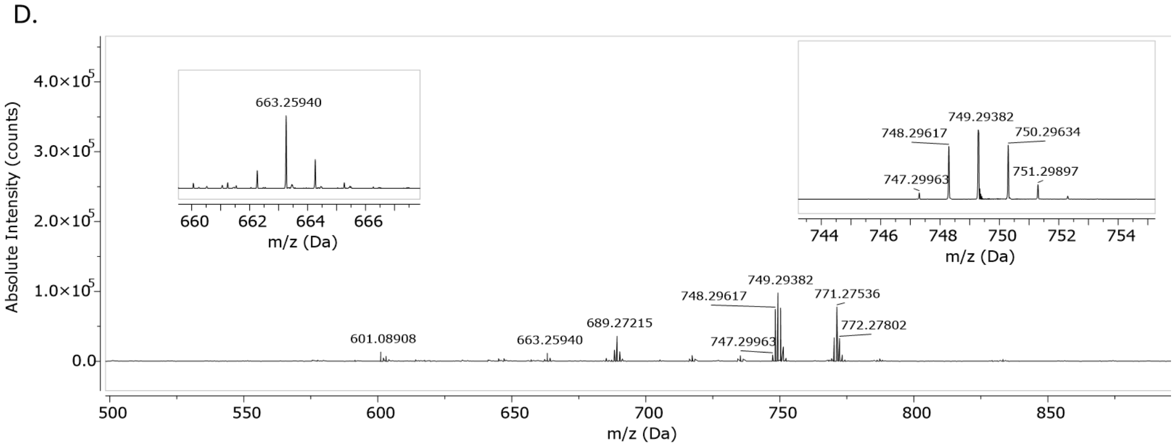
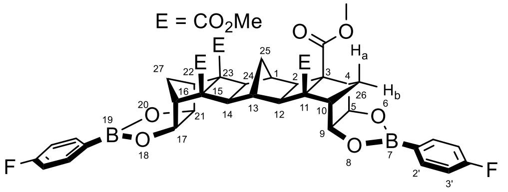


Figure S15. *A. ^{1}H NMR spectrum of **[1+2]$_{Ph}$**. B. ^{13}C NMR spectrum of **[1+2]$_{Ph}$**. C. ^{1}H-^{1}H COSY Spectrum of **[1+2]$_{Ph}$**. D. HRMS spectrum of **[1+2]$_{Ph}$**.*

Tetramethyl-(1r, 2R, 3R, 4S, 5R, 6S, 7R, 8S, 9S, 10r, 11R, 12R, 13S, 14R, 15S, 16R, 17S, 18S)-7,19-di(*p*-fluorophenyl)-7,19-diboro-6,8,18,20-tetraoxadecacyclo[8.8.1.1^{4,7}.1^{13,16}.0^{2,9}.0^{3,8}.0^{11,18}.0^{12,17}]heptacosa-3,8,11,18-tetracarboxylate ([1+2]$_F$)



3$_{Me}$ (38.7 mg, 0.0672 mmol) and 4-fluorophenyl boronic acid (22.6 mg, 0.162 mmol) were combined according to general procedure D. After drying, [1+2] assembly **[1+2]$_F$** was isolated as a fine white powder (26 mg, 49 %)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (t, *J* = 7.1 Hz, 4H, H$_{2'}$), 7.06 (t, *J* = 8.6 Hz, 4H, H$_{3'}$), 5.16 (s, 4H, H$_{5,9,17,21}$), 3.71 (s, 12H, H$_{1'}$), 2.89 (s, 2H, H$_{1,13}$), 2.73 (s, 4H, H$_{4,10,16,22}$), 2.15 (s, 8H, H$_{2,12,14,24,26a,}$), 1.85 (s, 2H, H$_{25}$), 1.79 (d, *J* = 12.0 Hz, 2H, H$_{26b}$).

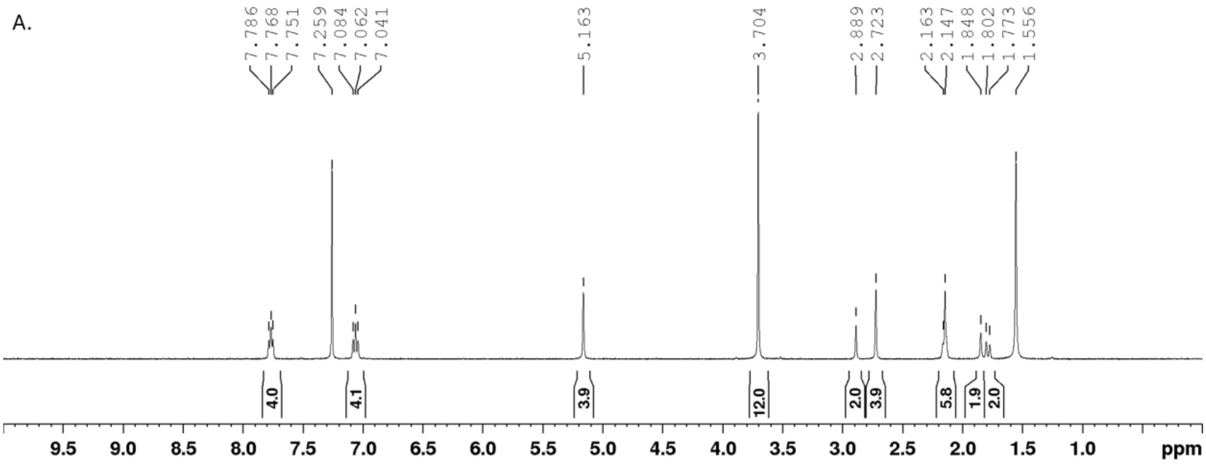
^{13}C NMR (101 MHz, CDCl$_3$) δ 171.66, 137.47, 137.39, 115.36, 115.15, 80.41, 58.11, 51.91, 51.61, 42.21, 39.86, 33.00, 30.76.

^{19}F NMR (376 MHz, CDCl$_3$) δ -107.39.

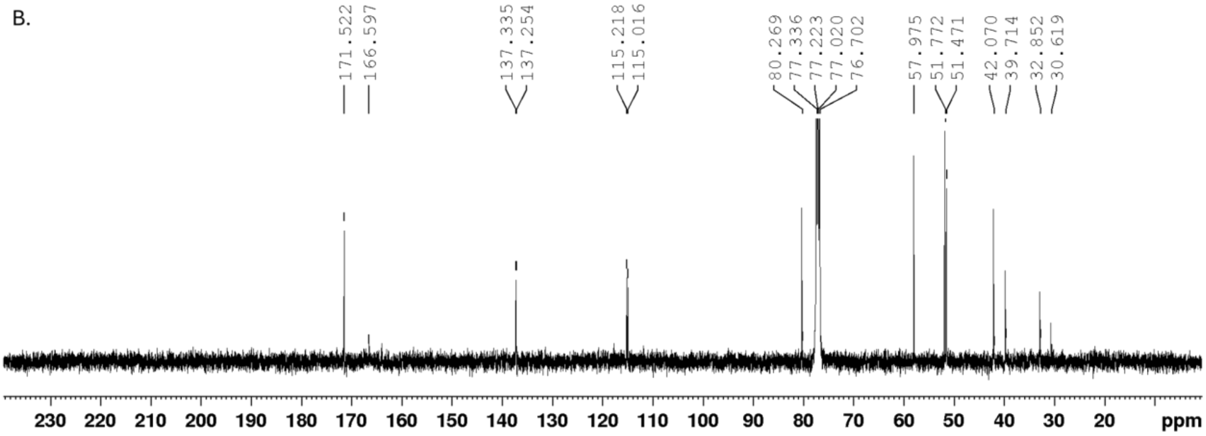
HRMS (ESI, *m/z*) calculated for $C_{41}H_{40}B_2F_2O_{12}$ [M+H]$^+$ = 785.27467, found 785.27492.

M.p 260–262 °C

A.


7.786
7.768
7.751
7.259
7.084
7.062
7.041
5.163
3.704
2.889
2.723
2.163
2.147
1.848
1.802
1.773
1.556
4.0
4.1
3.9
12.0
2.0
3.9
5.8
1.9
2.0
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
ppm

B.


171.522
166.597
137.335
137.254
115.218
115.016
80.269
77.336
77.223
77.020
76.702
57.975
51.772
51.471
42.070
39.714
32.852
30.619
230
220
210
200
190
180
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150
140
130
120
110
100
90
80
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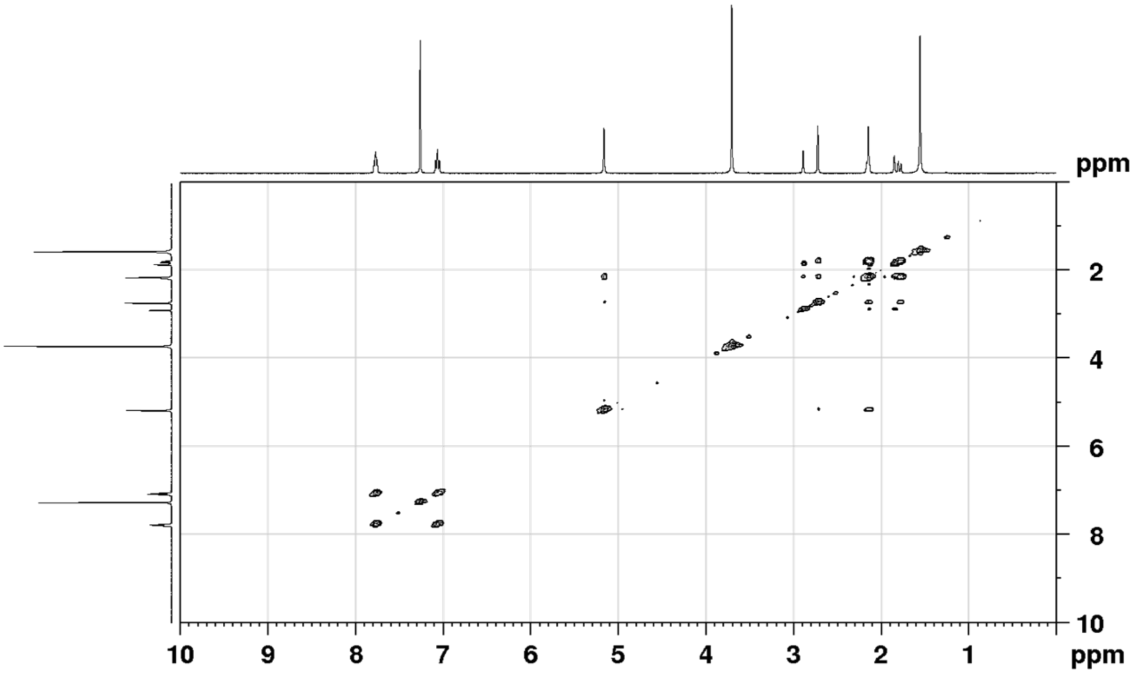
60
50
40
30
20
ppm

C.


ppm
2
4
6
8
10
10
9
8
7
6
5
4
3
2
1
ppm

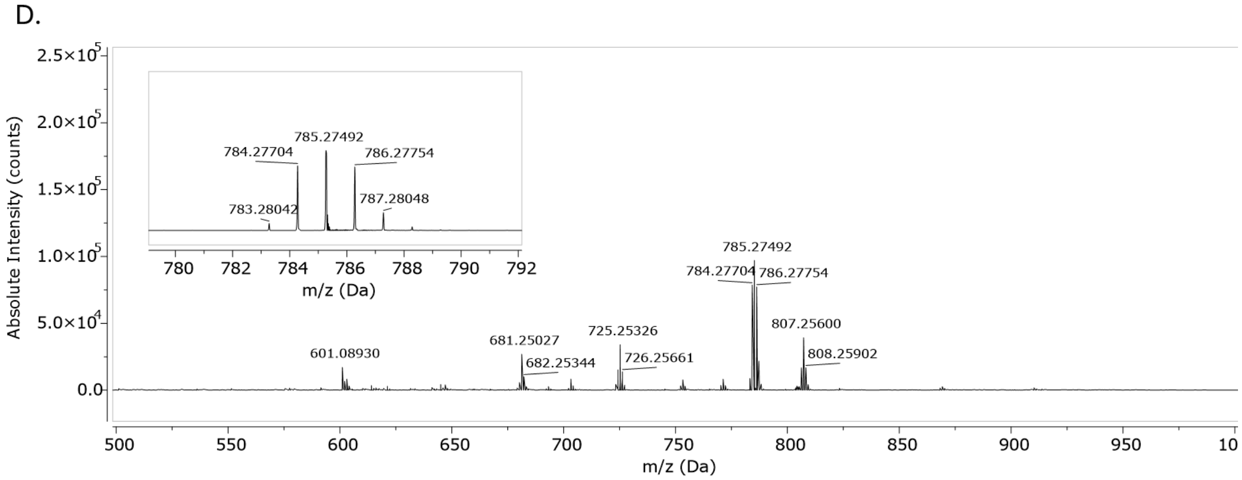
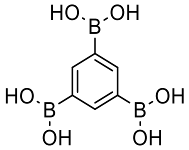


Figure S16. *A. ^{1}H NMR spectrum of **[1+2]$_F$**. B. ^{13}C NMR spectrum of **[1+2]$_F$**. C. ^{1}H-^{1}H COSY spectrum of **[1+2]$_F$**. D. HRMS spectrum of **[1+2]$_F$**.*

Benzene-1,3,5-triboronic acid (22)



To a 25 mL round bottom flask, benzene-1,3,5-triboronic acid tris(pinacol ester) (362 mg, 0.794 mmol) was added and suspended in 5.0 M HCl (15 mL). The suspension was left stirring at 70 °C for 5 days. After reaction, the suspension was filtered, and the filter cake washed with ice-cold water (3 × 1mL) and ice-cold Et_2O (3 × 2 mL) to give benzene-1,3,5-triboronic acid as a white powder (154 mg, 93%).

^{1}H NMR (500 MHz, DMSO) δ 8.20 (s, 3H, Aryl), 7.86 (s, 6H, B(O*H*)$_2$).

Spectral data matched with that of literature.[29]

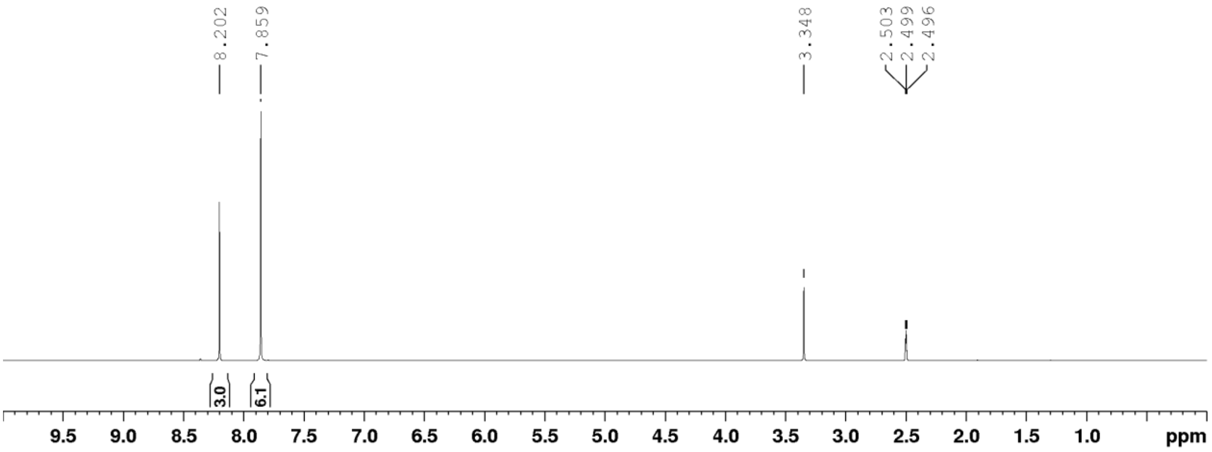
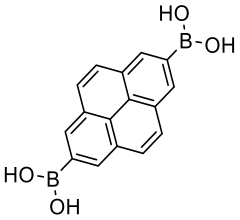


Figure S17. *A. ^{1}H NMR spectrum of **22**.*

Pyrene-2,7-diboronic acid (17)



To a 25 mL round bottom flask, pyrene-2,7-diboronic acid (pinacol ester) (145 mg, 0.320 mmol) was added and suspended in 5.0 M HCl (20 mL). The suspension was left stirring at 90 °C for 24 hours. After reaction, the suspension was filtered, and the filter cake washed with ice-cold water (2 × 4 mL) and ice-cold Et_2O (2 × 2 mL) to give pyrene-2,7-diboronic acid as a white powder (74.9 mg, 81%).

^{1}H NMR (400 MHz, DMSO) δ 8.67 (s, 4H), 8.43 (s, 4H), 8.15 (s, 4H).

Spectral data matched with that of literature.[30]

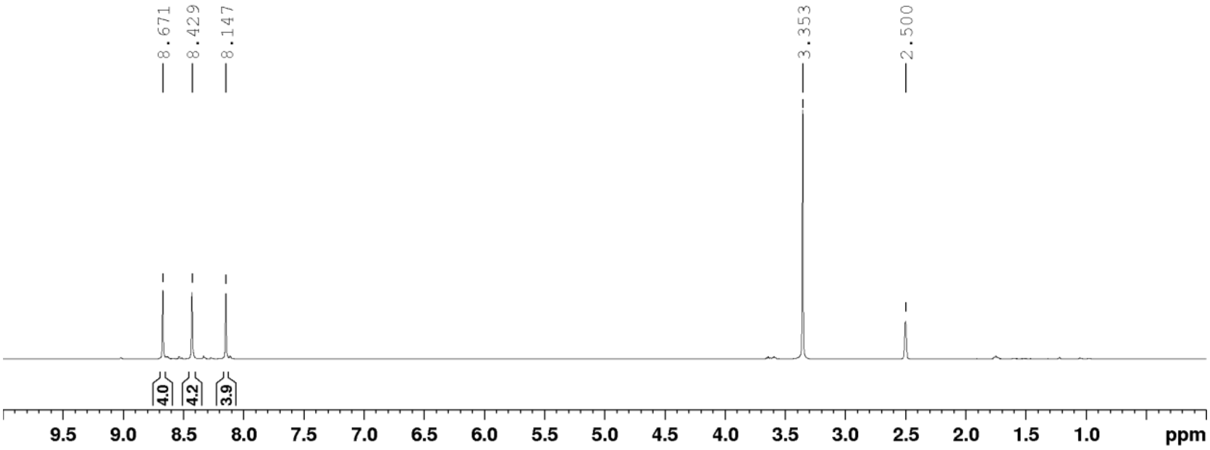
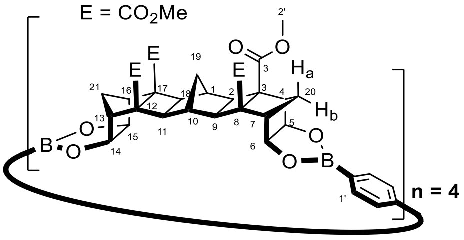


Figure S18. *A. ^{1}H NMR spectrum of **17**.*

Macrocycle: $\mathbf{3_{Me}}$ + benzene-1,4-diboronic acid ($\mathbf{[4+4]_{Me}}$)



Bis-diol $\mathbf{3_{Me}}$ (100 mg, 0.17 mmol) and benzene-1,4-diboronic acid (29 mg, 0.17 mmol) were added to a 100 mL pressure vessel and suspended in chloroform (60 mL). The vessel was sealed and heated at 100 °C for 24 hours. After cooling, the reaction mix was processed as per **general isolation procedure A**. After allowing the solid to air-dry overnight $\mathbf{[4+4]_{Me}}$ was isolated as a white powder (115 mg, 99%).

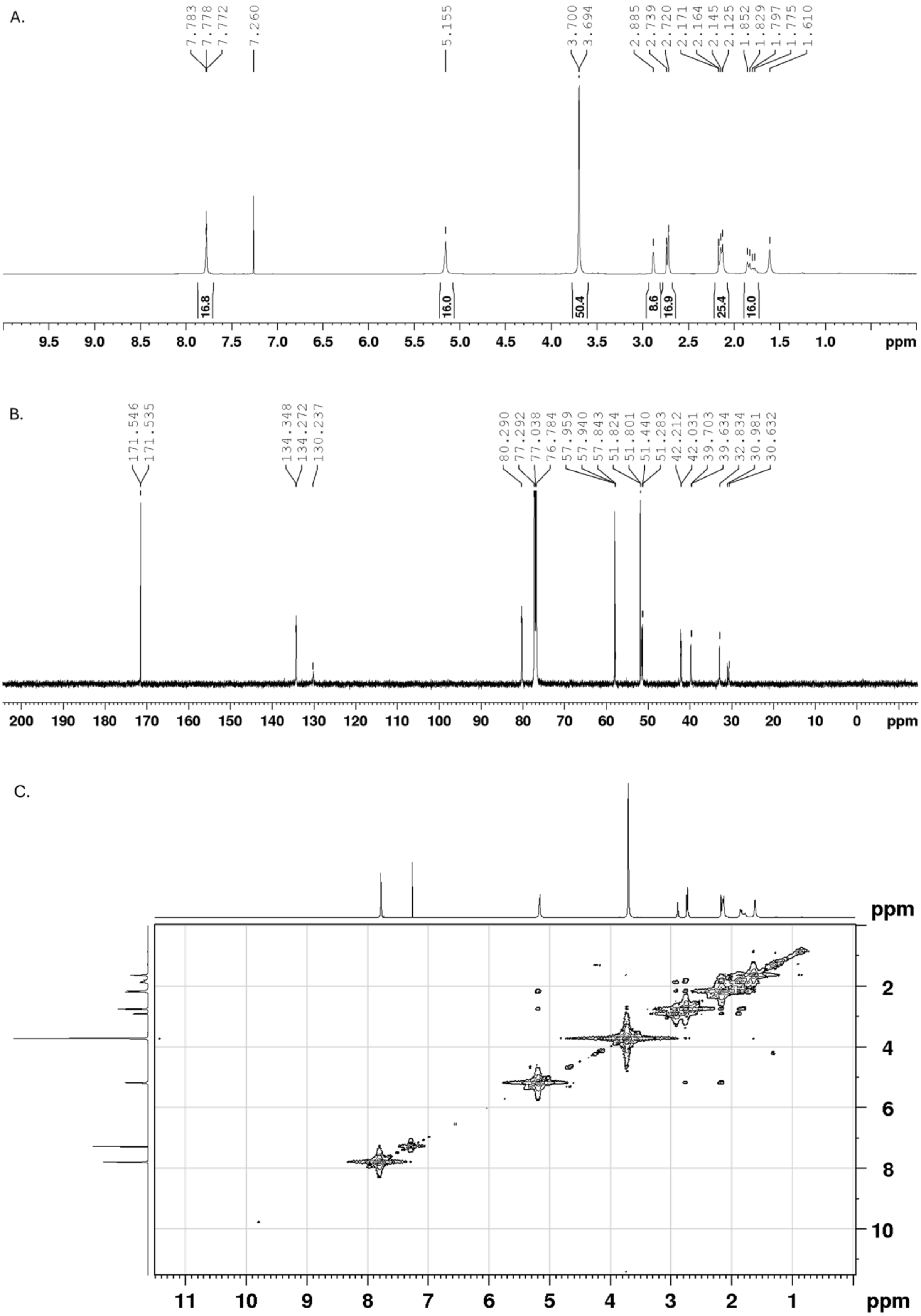
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (t, J = 3.2 Hz, 16H, $H_{1'}$), 5.16 (d, J = 6.9 Hz, 16H, $H_{5,6,14,15}$), 3.70 (s, 48H, $H_{2'}$), 2.91 – 2.86 (br, s, 8H, $H_{1,10}$), 2.75 – 2.71 (m, 16H, $H_{4,7,13,16}$), 2.14 (m, 24H, $H_{2,9,11,18,20a}$), 1.90 – 1.73 (m, 16H, $H_{19,20b}$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.66, 134.47, 80.39, 58.06, 51.92, 51.56, 42.15, 39.82, 32.96, 30.75.

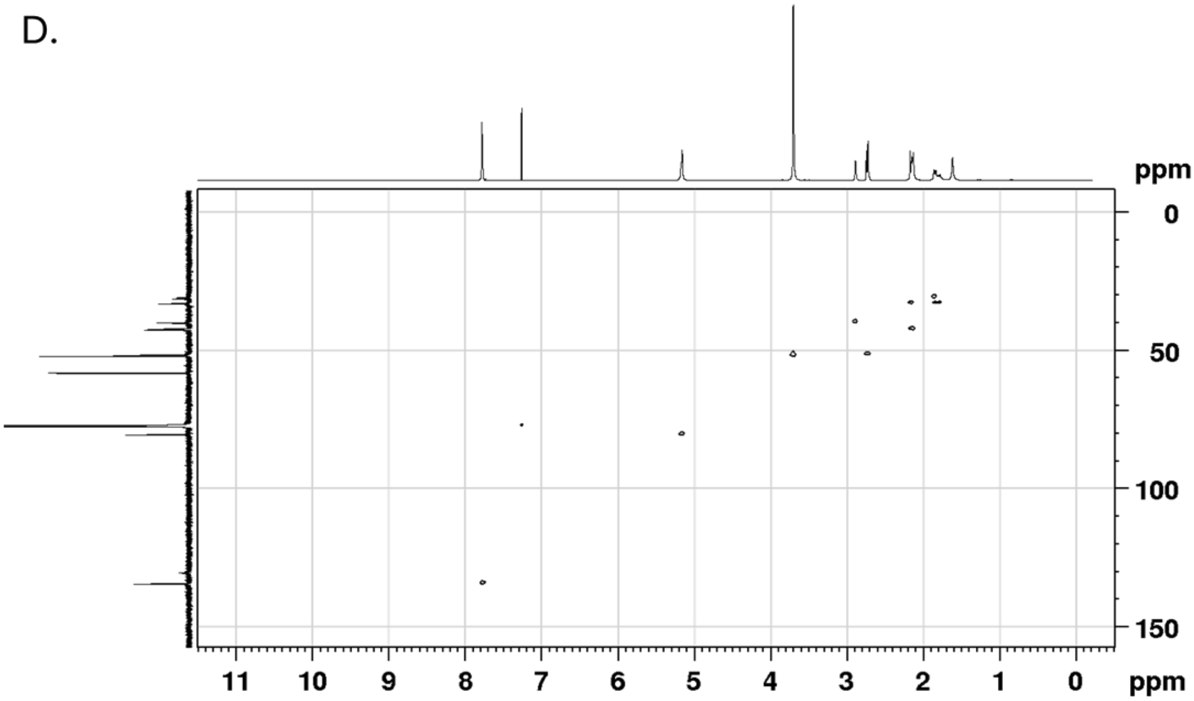
Carbon resonance corresponding to the carbon in the C–B bond was not apparent, a similar absence has been reported in the ^{13}C NMR spectra of similar assemblies.[31]

HRMS (ESI, *m/z*) calculated for $C_{140}H_{144}B_8O_{48}$ $[M+2Na]^{2+}$ = 1363.46780, found 1363.46632, $[M+3Na]^{3+}$ = 916.64160, found 916.64588.

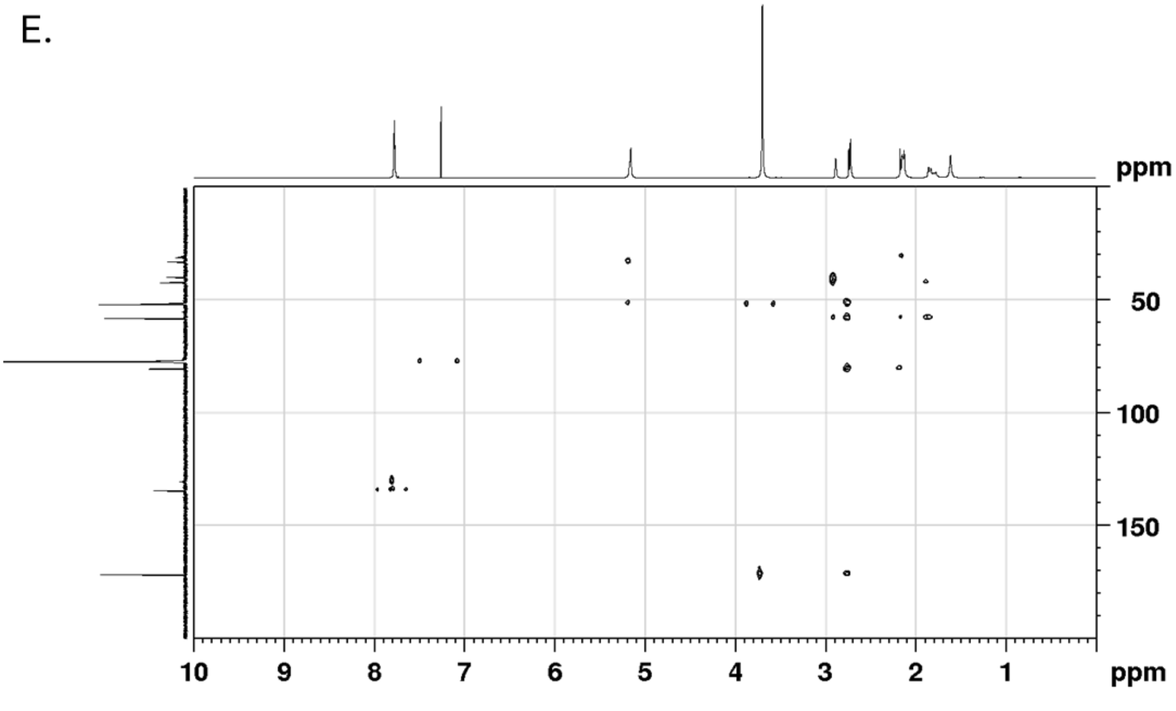
M.p > 350°C


A.
7.783
7.778
7.772
7.260
5.155
3.700
3.694
2.885
2.739
2.720
2.171
2.164
2.145
2.125
1.852
1.829
1.797
1.775
1.610
16.8
16.0
50.4
8.6
16.9
25.4
16.0
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 ppm
B.
171.546
171.535
134.348
134.272
130.237
80.290
77.292
77.038
76.784
57.959
57.940
57.843
51.824
51.801
51.440
51.283
42.212
42.031
39.703
39.634
32.834
30.981
30.632
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
C.
ppm
2
4
6
8
10
11 10 9 8 7 6 5 4 3 2 1 ppm

D.


ppm
0
50
100
150
11
10
9
8
7
6
5
4
3
2
1
0
ppm

E.


ppm
50
100
150
10
9
8
7
6
5
4
3
2
1
ppm

F.

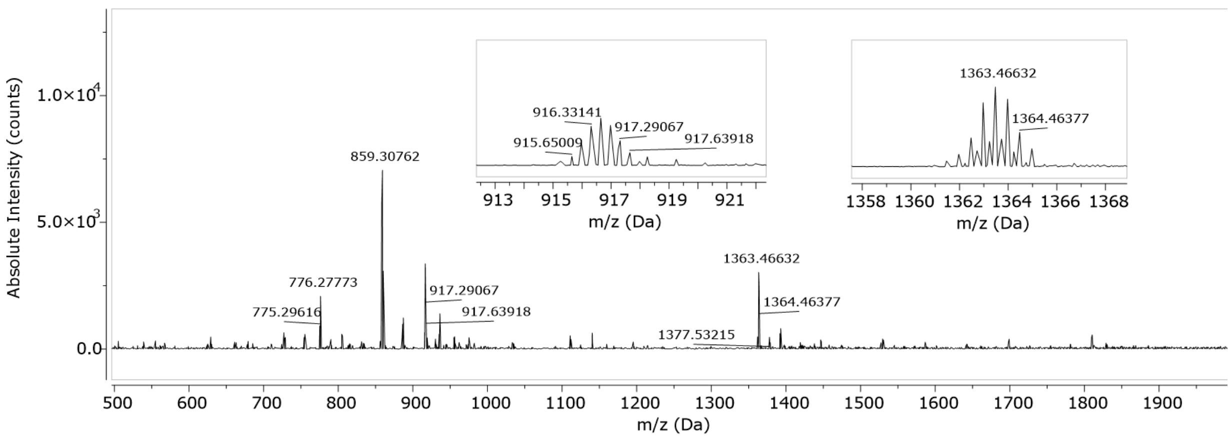
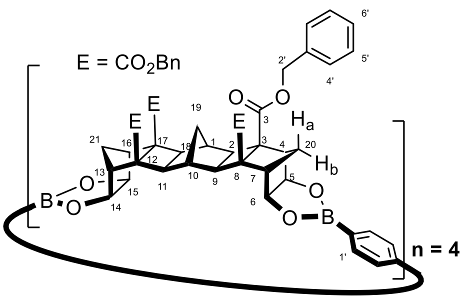


Figure S19. *A. ^{1}H NMR spectrum of **[4+4]$_{Me}$**. B. ^{13}C NMR spectrum of **[4+4]$_{Me}$**. C. ^{1}H-^{1}H COSY spectrum of **[4+4]$_{Me}$**. D. ^{1}H-^{13}C HSQC spectrum of **[4+4]$_{Me}$**. E. ^{1}H-^{13}C HMBC spectrum of **[4+4]$_{Me}$**. F. HRMS spectrum of **[4+4]$_{Me}$**.*

Macrocycle: 3$_{Bn}$ + benzene-1,4-diboronic acid ([4+4]$_{Bn}$)



Bis-diol **3$_{Bn}$** (70.2 mg, 0.0790 mmol) and benzene-1,4-diboronic acid (13.5 mg, 0.0814 mmol) were added to a pressure vessel and suspended in chloroform (70 mL). The vessel was sealed and heated at 100 °C for 18 hours. After cooling, the solution was processed as per **general isolation procedure A**. Macrocycle **[4+4]$_{Bn}$** was isolated as a clear, glass-like solid (75 mg, 93 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 16H, $H_{1'}$), 7.38 – 7.27 (m, 80H, $H_{4',5',6'}$), 5.12 (apparent d, 16H, $H_{5,6,14,15}$), 5.04 – 4.95 (m, 32H, $H_{2'}$), 2.98 (s, 8H, $H_{1,10}$), 2.71 (d, J = 7.9 Hz, 16H, $H_{4,7,13,16}$), 2.19 – 2.09 (m, 24H, $H_{2,9,11,18,20a}$), 2.01 (s, 8H, H_{19}), 1.83 – 1.69 (m, 8H, H_{20b}).

^{13}C NMR (400Hz, $CDCl_3$) δ 170.83, 135.78, 134.41, 128.73, 128.61, 128.39, 80.41, 66.96, 57.99, 51.41, 42.46, 39.87, 33.05, 31.15, 29.85.

M.p 297–300 °C

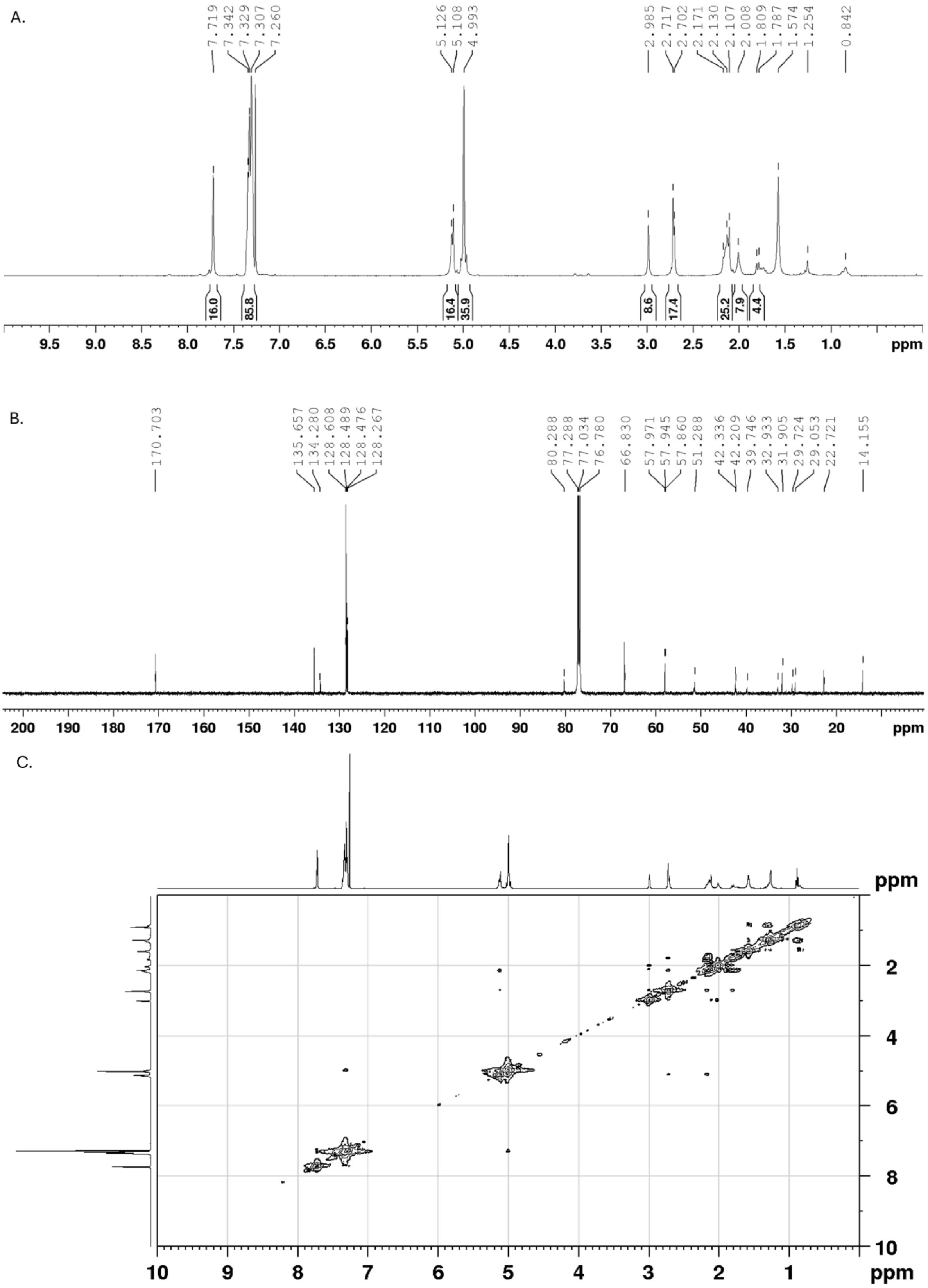
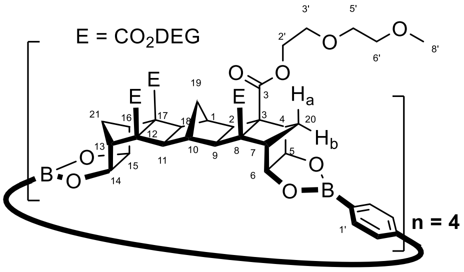


Figure S20. *A. ^{1}H NMR spectrum of* ***[4+4]$_{Bn}$****. B. ^{13}C NMR spectrum of* ***[4+4]$_{Bn}$****. C. ^{1}H-^{1}H COSY Spectrum of* ***[4+4]$_{Bn}$****.*

Macrocycle: 3$_{DEG}$ + benzene-1,4-diboronic acid ([4+4]$_{DEG}$)



Bis-diol **3**$_{\textbf{DEG}}$ (94.4 mg, 0.103 mmol) and benzene-1,4-diboronic acid (17.1 mg, 0.103 mmol) were added to a pressure vessel and suspended in chloroform (60 mL). The vessel was sealed and heated at 100 °C for 18 hours. After cooling, the solution was processed as per **general isolation procedure A**. Macrocycle **[4+4]**$_{\textbf{DEG}}$ was isolated as a fine white powder (105 mg, 98 %).

Large scale: Bis-diol **3**$_{\textbf{Deg}}$ (417 mg, 0.456 mmol) and benzene-1,4-diboronic acid (76 mg, 0.459 mmol) were combined in chloroform (170 mL) and the solution was heated to reflux for 48 hours. After cooling, the solution was processed as per **general isolation procedure A**. The precipitate was allowed to dry in air, before being further dried under vacuum to give macrocycle **[4+4]**$_{\textbf{DEG}}$ as a fine white powder (399 mg, 87 %)

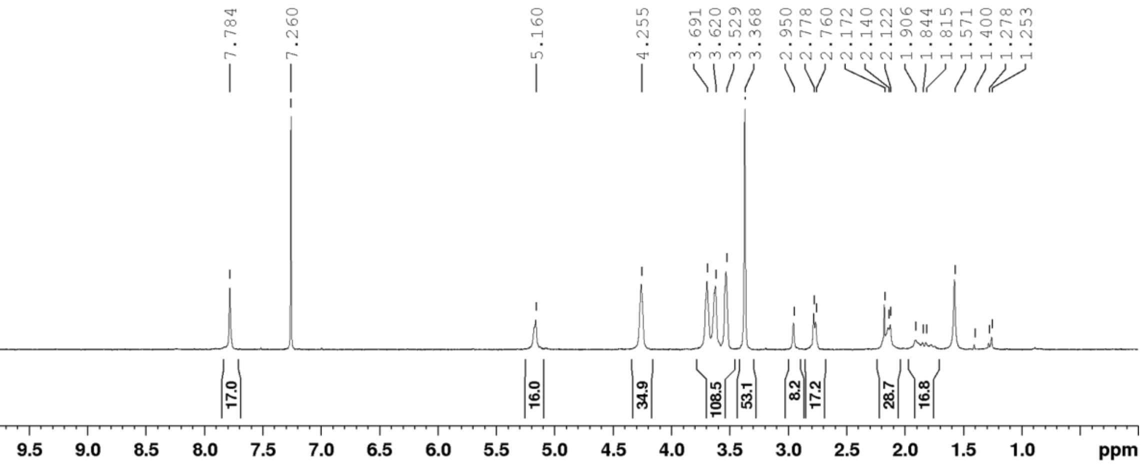
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 16H, $H_{1'}$), 5.16 (apparent d, J = 7.0 Hz, 16H, $H_{5,6,14,15}$), 4.28 – 4.22 (m, 32H, $H_{2'}$), 3.72 – 3.66 (m, 32H, H3’), 3.65 – 3.57 (m, 32H), 3.56 – 3.49 (m, 32H), 3.36 (s, 48H, $H_{8'}$), 2.94 (s, 8H, $H_{1,10}$), 2.79 – 2.72 (m, 16H, $H_{4,7,13,16}$), 2.19 – 2.10 (m, 24H, $H_{2,9,11,18,20a}$), 1.97 – 1.79 (m, 10H, H_{20b}, coincident with H_2O).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.81, 134.34, 80.35, 71.89, 70.29, 68.96, 63.48, 59.07, 57.92, 51.27, 42.24, 39.56, 32.82, 30.98.

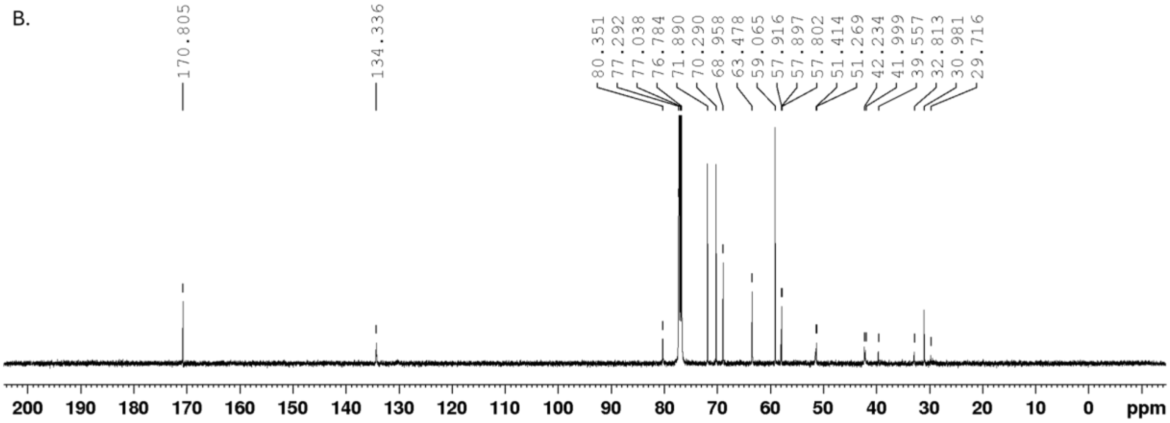
HRMS (ESI, *m/z*) calculated for $C_{204}H_{272}B_8O_{80}$ $[M + 3H]^{3+}$ = 1364.60981, found 1364.60961

M.p 254–260 °C

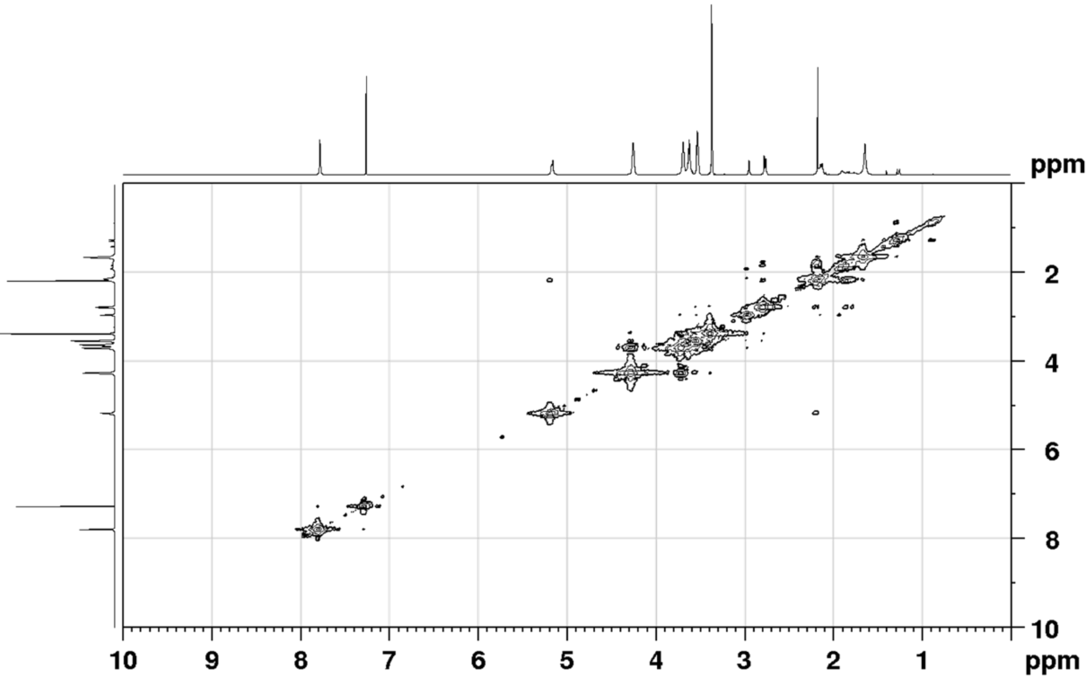
A.


7.784
7.260
5.160
4.255
3.691
3.620
3.529
3.368
2.950
2.778
2.760
2.172
2.140
2.122
1.906
1.844
1.815
1.571
1.400
1.278
1.253
17.0
16.0
34.9
108.5
53.1
8.2
17.2
28.7
16.8
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
ppm

B.


170.805
134.336
80.351
77.292
77.038
76.784
71.890
70.290
68.958
63.478
59.065
57.916
57.897
57.802
51.414
51.269
42.234
41.999
39.557
32.813
30.981
29.716
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

C.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ppm

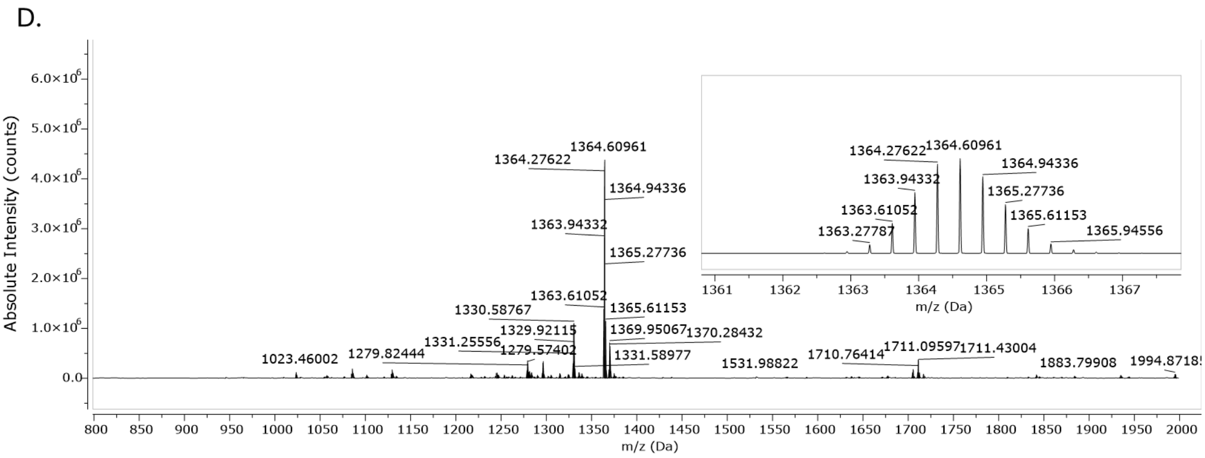
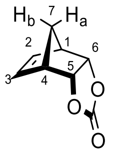


Figure S21. *A. ^{1}H NMR spectrum of* ***[4+4]$_{DEG}$****. B. ^{13}C NMR spectrum of* ***[4+4]$_{DEG}$****. C. ^{1}H-^{1}H COSY spectrum of* ***[4+4]$_{DEG}$****. D. HRMS spectrum of* ***[4+4]$_{DEG}$****.*

Endo-norborn-2-ene-5,6-carbonate (11)



CPD method: Vinylene carbonate (400 µL, 6.28 mmol) and cyclopentadiene (569 µL, 6.90 mmol) were dissolved in 3 mL of DMF, then heated in a microwave reactor (150 °C, 75 min, 200 W). The reaction was let cool before solvent was removed under reduced pressure. The crude material was subjected to column chromatography (80% DCM: Pet. Spirits, Silica, R$_f$ 0.45). Norbornene carbonate **11** was isolated as a white powder (572 mg, 60%).

DCPD method: Vinylene carbonate (1.29 g, 15.0 mmol) and dicyclopentadiene (1.20 mL, 8.95 mmol) were dissolved in toluene (1.5 mL) then heated in a microwave reactor (170 °C, 105 min, 200 W). After cooling, a mass of clear crystals formed that were collected by vacuum filtration. From the mother liquor, additional crystals formed upon standing that were also collected by vacuum filtration. The crude material was subjected to column chromatography (80% DCM: Pet. Spirits, Silica, R$_f$ 0.45) to give norbornene carbonate **11** (935 mg, 41%).

R$_f$ 0.45 (80% DCM: Pet. Spirits, Silica)

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.23 (s, 2H, $H_{2,3}$), 4.99 (s, 2H, $H_{5,6}$), 3.29 (s, 2H, $H_{1,4}$), 1.77 (dt, J = 10.5, 1.9 Hz, 1H, H), 1.27 (d, J = 10.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 155.61, 134.44, 79.01, 45.67, 42.62.

Spectral data matched that of literature.[32]

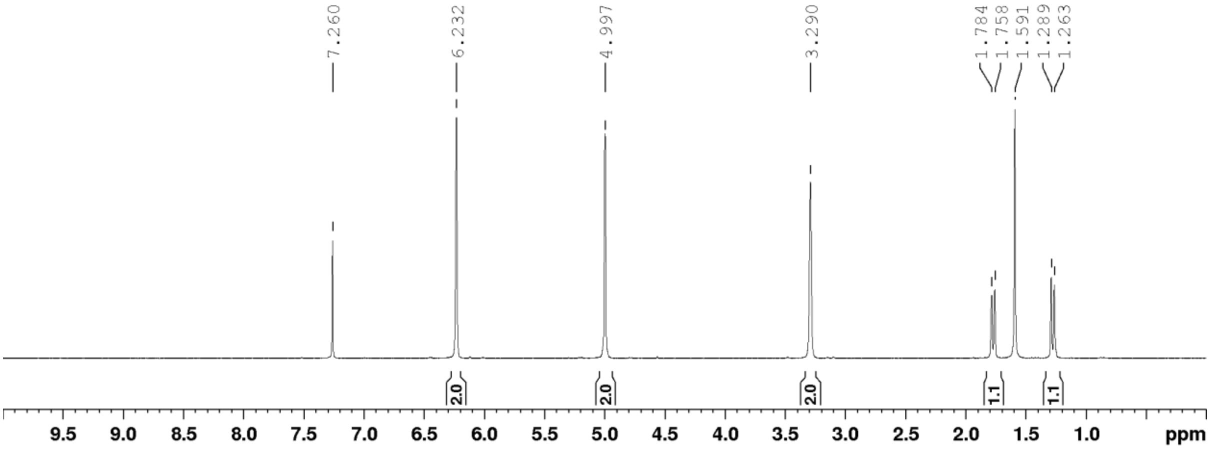
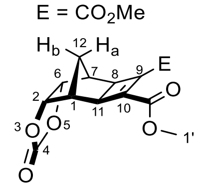


Figure S22. *A.* *^{1}H NMR spectrum of* ***11****.*

Dimethyl-(1R, 2S, 6R, 7S, 8S, 11R)-3,5-dioxatetracyclo[5.4.1.$0^{2,6}$.$0^{8,11}$]dodec-4-one-9-ene-9,10-dicarboxylate (12)



Norbornene carbonate **11** (528 mg, 3.47 mmol), DMAD (651 µL, 5.20 mmol), and $RuH_2(CO)(PPh_3)_3$ (80 mg, 2.5 mol%) were combined according to **general reaction procedure C** to give diester **12** as an off-white powder (774 mg, 2.63 mmol, 76 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.90 (dd, J = 3.2, 1.7 Hz, 2H, $H_{2,6}$), 3.80 (s, 6H, $H_{1'}$), 3.22 (s, 2H, $H_{8,11}$), 2.81 (dd, J = 3.3, 1.8 Hz, 2H, $H_{1,7}$), 1.64 (d, J = 12.7 Hz, 1H, H_{12a}), 1.21 (dt, J = 12.8, 1.4 Hz, 1H, H_{12b}).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.78, 155.09, 140.66, 77.71, 52.30, 39.15, 37.40, 26.58.

HRMS (ESI, *m/z*) calculated for $C_{14}H_{14}O_7$ $[M+Na]^+$ = 317.06318, found 317.06324. $[2M+Na]^+$ = 611.13713, found 611.13740.

M.p 166–167 °C

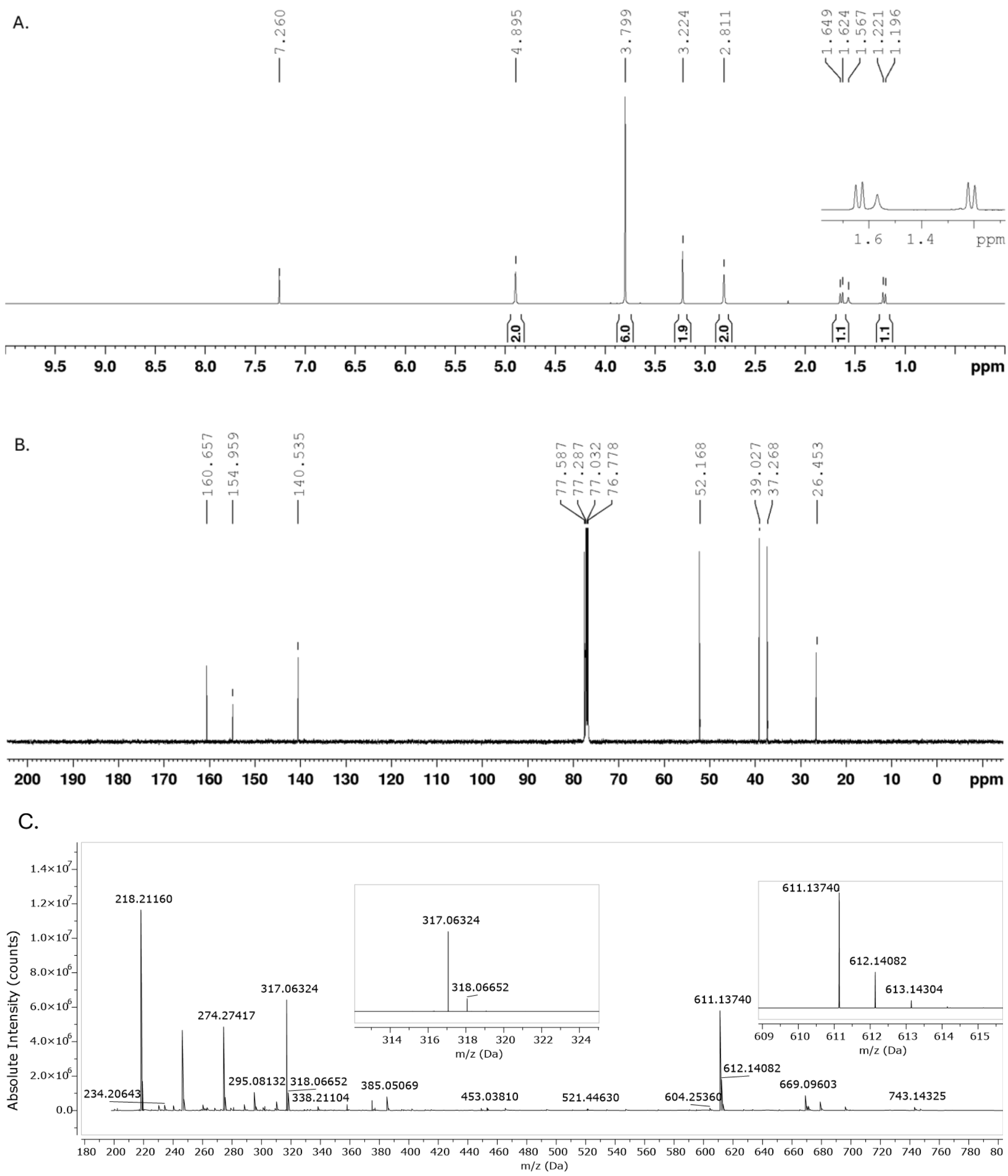
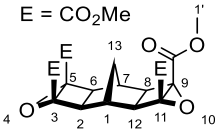


Figure S23. *A. ^{1}H NMR spectrum of **12**. B. ^{13}C NMR spectrum of **12**. C. HRMS spectrum of **12**.*

Tetramethyl-(2R, 3S, 5R, 6S, 8R, 9S, 11R, 12S)-4,10-dioxahexacyclo[5.5.1.0^{2,6}.0^{3,5}.0^{8,12}.0^{9,11}]tridecane-3,5,9,11-tetracarboxylate (13)



Tetraester **7$_{Me}$** (5.09 g, 13.5 mmol) was dissolved in anhydrous THF (450 mL) in a 3-neck RBF fitted with a nitrogen line, a stopper, and a septum. The solution was cooled over ice for 15 minutes, before a

3.824 M solution of *t*-BuOOH in toluene (7.7 mL, 29.5 mmol) was injected through the septum. After letting the solution let stir over ice for an additional 20 minutes, *t*-BuOK (840 mg, 7.49 mmol) was added to the solution in a single portion. The solution was left over ice for a further 10 minutes, before allowing the solution to come to room temperature and letting it stir for 12 hours. After reaction, a saturated solution of sodium sulfite (50 mL) was added, and the solution transferred to a 1.0 L RBF. The solution was concentrated *in vacuo* to ~1/3rd the original volume and transferred to a separatory funnel. A liquid-liquid extraction was performed with chloroform (4 × 50 mL), the organics were combined, dried ($MgSO_4$), filtered through cotton wool, and the solvent removed *in vacuo*. The crude material was triturated with hot isopropyl alcohol (15 mL), and the fine white powder collected by vacuum filtration. The solid was further dried under high-vacuum to give bis-epoxide **13** as a fine white powder (1.77 g, 4.34 mmol, 32%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 12H, $H_{1'}$), 3.29 (s, 2H), 2.27 (s, 4H, $H_{2,6,8,12}$), 1.91 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.37, 64.45, 52.99, 48.96, 36.57, 28.64.

HRMS (ESI, *m/z*) calculated for $C_{19}H_{20}O_{10}$ $[M+Na]^+$ = 431.09487, found 431.09491.

Spectral data matched that of literature.[33]

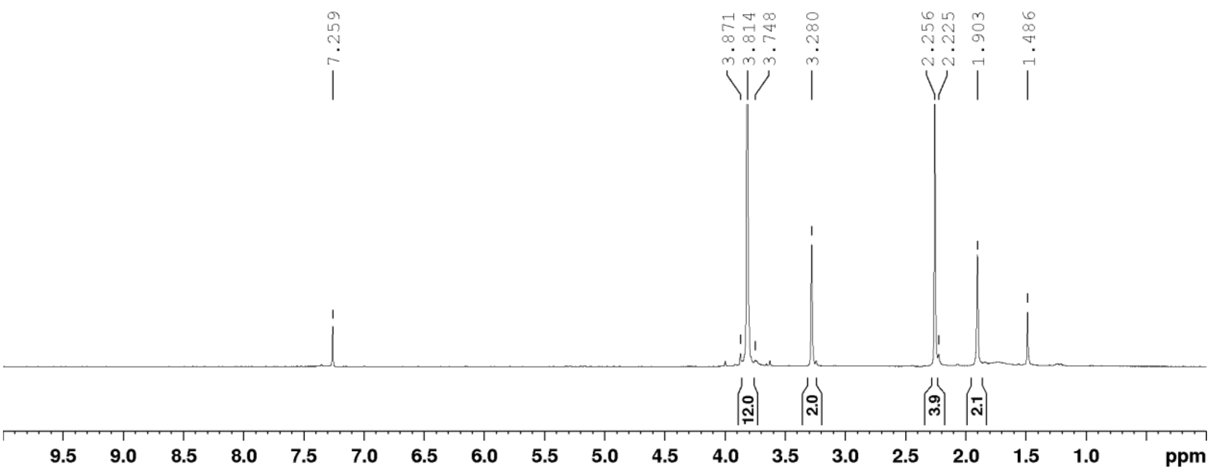
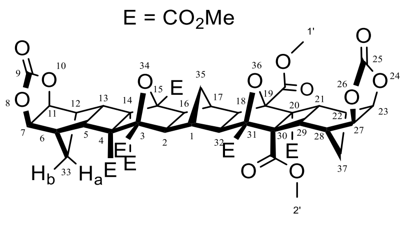


Figure S24. *^{1}H NMR spectrum of **13**.*

Octamethyl-(2R, 3R, 4R, 5S, 6S, 7R, 11S, 12R, 13R, 14S, 15S, 16S, 18R, 19R, 20R, 21S, 22S, 23R, 27S, 28R, 29R, 30S, 31S, 32S)-8,10,24,26,34,36-hexaoxatetradecacyclo[5.5.1.$0^{2,6}$.$0^{3,5}$.$0^{8,12}$.$0^{9,11}$]-heptatriaconta-9,25-dione-3,4,15,16,20,21,29,30-octacarboxylate (14)



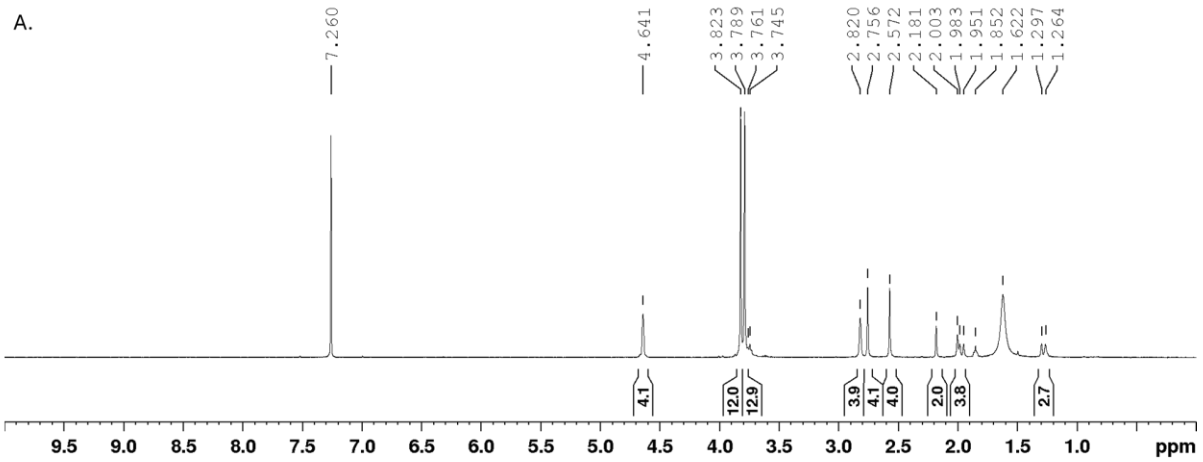
Bis-epoxide **13** (145 mg, 0.355 mmol) and diester carbonate **12** (209 mg, 0.710 mmol) were suspended in THF (1.5 mL) and heated in a microwave reactor (160 °C, 30 min, 200 W). The reaction was repeated two more times at a similar scale (total **13**: 382 mg, 0.936 mmol, **12**: 558 mg, 1.896 mmol). After cooling, a mass of precipitate formed in each solution that was collected by vacuum filtration and washed with THF (2 × 1.5 mL) and ethanol (1 × 2 mL) to give bis-carbonate **14** as a fine white powder (697 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (s, 4H. $H_{7,11,23,27}$), 3.82 (s, 12H, $H_{1'}$), 3.79 (s, 12H, $H_{2'}$), 2.82 (s, 4H, $H_{6,12,22,28}$), 2.75 (s, 4H, $H_{5,13,21,29}$), 2.57 (s, 4H, $H_{2,16,18,32}$), 2.18 (s, 2H, $H_{1,17}$), 2.02 – 1.92 (m, 4H, $H_{33a,35}$), 1.28 (d, J = 13.1 Hz, 2H, H_{33b}).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.84, 166.50, 154.89, 92.23, 64.60, 63.54, 52.71, 52.31, 49.34, 42.46, 41.40, 37.54, 30.58, 30.41.

HRMS (ESI, *m/z*) calculated for $C_{47}H_{48}O_{24}$ $[M+H+H_2O]^+$ = 1015.27139, found 1015.25885.

M.p >350 °C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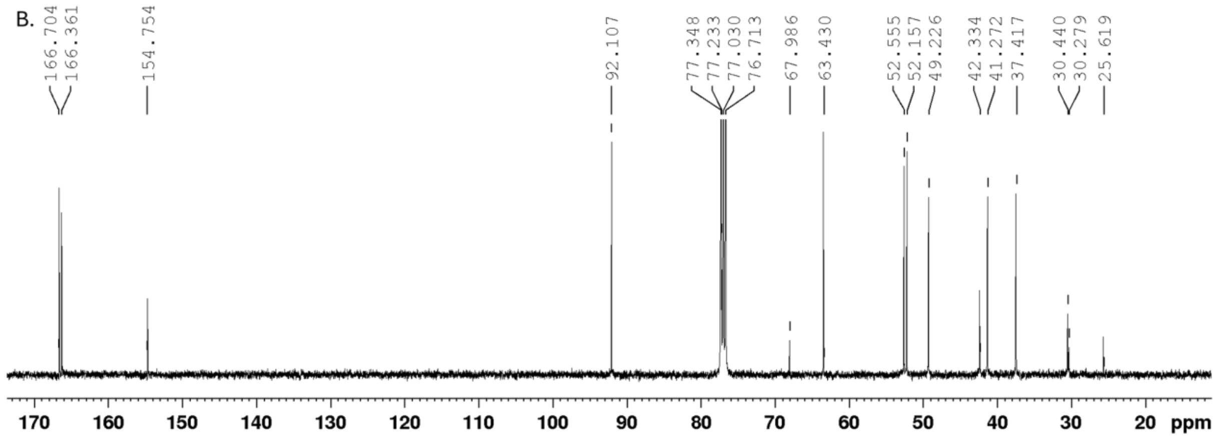
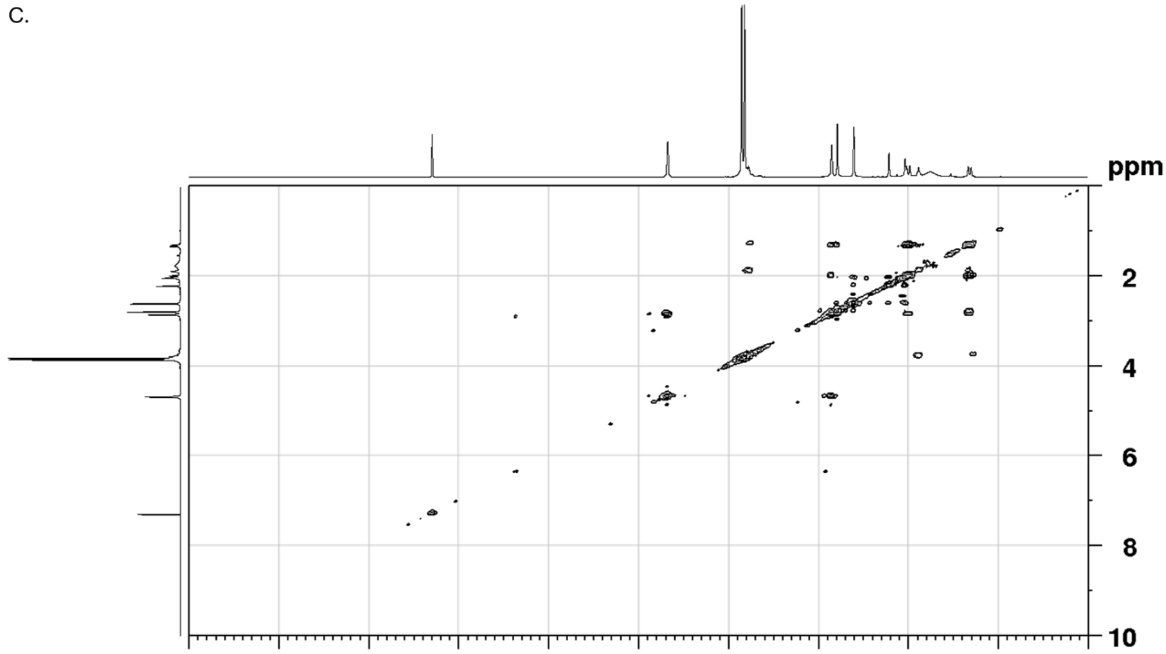
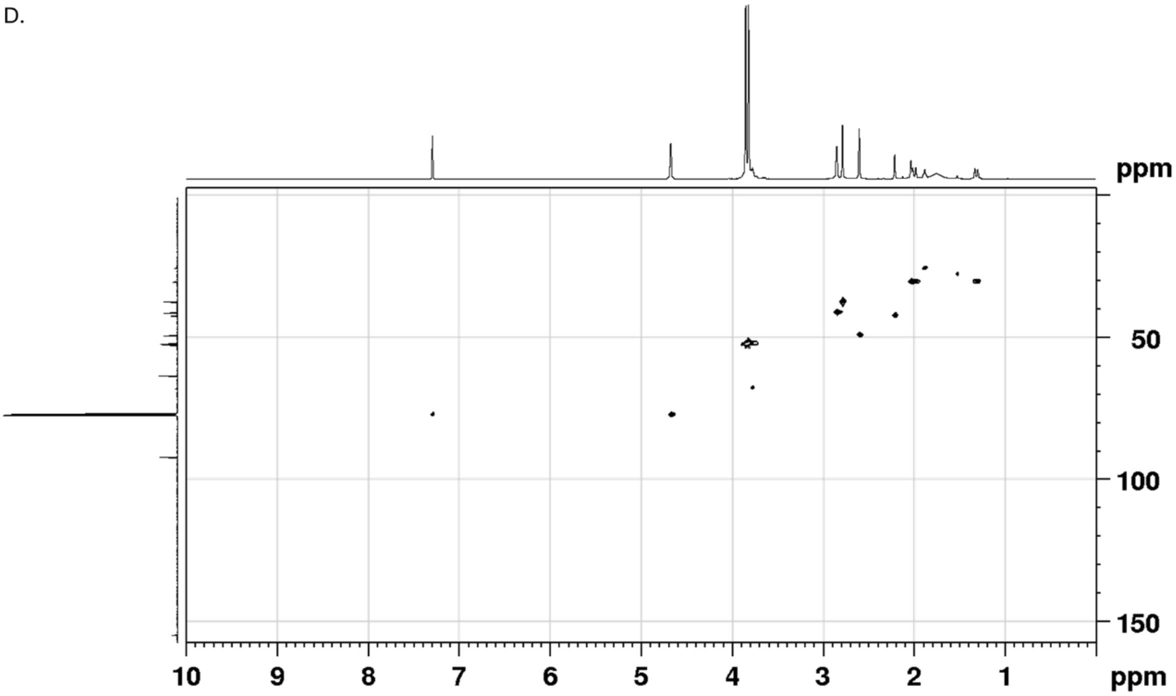
7.260
4.641
3.823
3.789
3.761
3.745
2.820
2.756
2.572
2.181
2.003
1.983
1.951
1.852
1.622
1.297
1.264
4.1
12.0
12.9
3.9
4.1
4.0
2.0
3.8
2.7
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

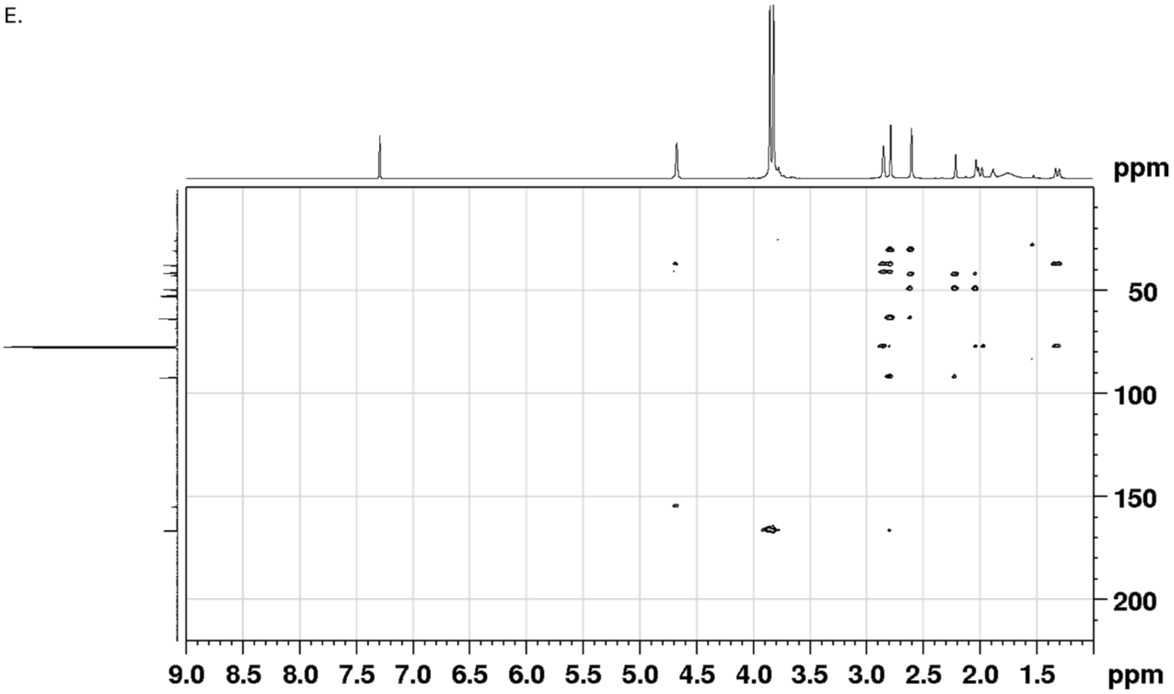

B.
166.704
166.361
154.754
92.107
77.348
77.233
77.030
76.713
67.986
63.430
52.555
52.157
49.226
42.334
41.272
37.417
30.440
30.279
25.619
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


C.
ppm
2
4
6
8
10
10 9 8 7 6 5 4 3 2 1 ppm

D.


ppm
50
100
150
10
9
8
7
6
5
4
3
2
1
ppm

E.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1.5
ppm

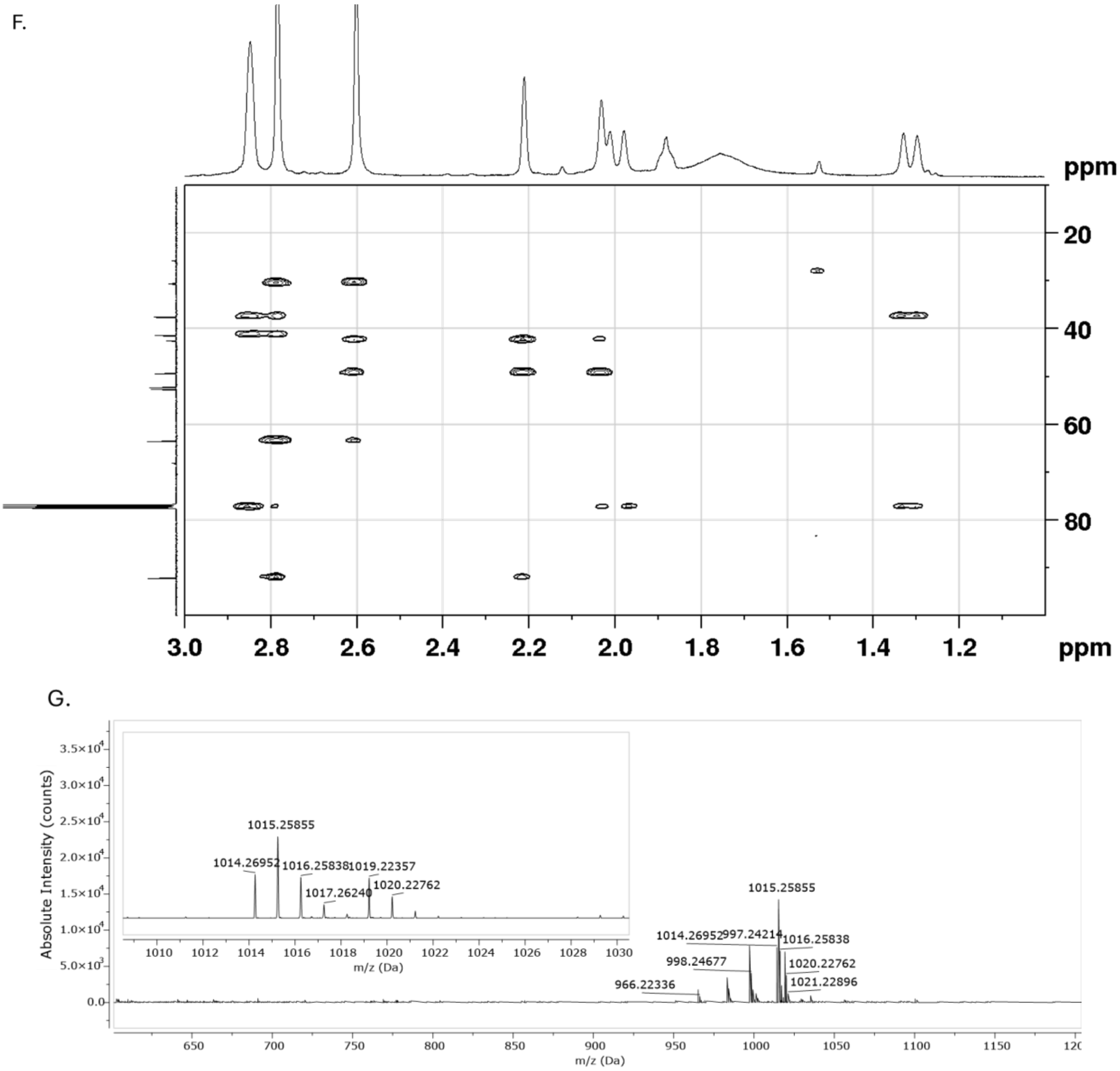
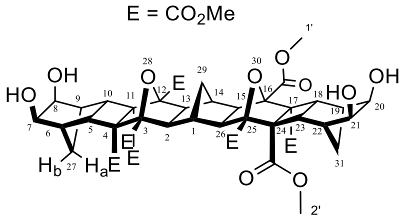


Figure S25. *A. ^{1}H NMR spectrum of **14**. B. ^{13}C NMR spectrum of **14**. C. ^{1}H-^{1}H COSY spectrum of **14**. D. ^{1}H-^{13}C HSQC spectrum of **14**. E. ^{1}H-^{13}C HMBC spectrum of **14**. F. Zoomed in ^{1}H-^{13}C HMBC spectrum of **14**. G. HRMS spectrum of **14**.*

Octamethyl-(2R, 3R, 4R, 5S, 6S, 7R, 8S, 9R, 10R, 11S, 12S, 13S, 15R, 16R, 17R, 18S, 19S, 20R, 21S, 22R, 23R, 24S, 25S, 26S)-28,30-dioxadodecacyclo-$[5.5.1.0^{2,6}.0^{3,5}.0^{8,12}.0^{9,11}]$- hentriaconta-7,8,20,21-tetraol-3,4,11,12,16,17,24,25-octacarboxylate (4)



Bis-carbonate **14** (153 mg, 0.154 mmol) was suspended in methanol (10 mL). A solution of caesium carbonate (189 mg, 0.580 mmol) in water (1 mL) was added and the mix heated to reflux for two hours. The solution initially became clear upon heating, before a mass of precipitate began to form. After cooling, the solution was concentrated to 1/3rd the original volume *in vacuo*, before the white precipitate was collected by vacuum filtration and washed with water (2 × 3 mL). Drying over vacuum gave bis-diol **4** as a fine white powder (96 mg, 0.101 mmol, 66%).

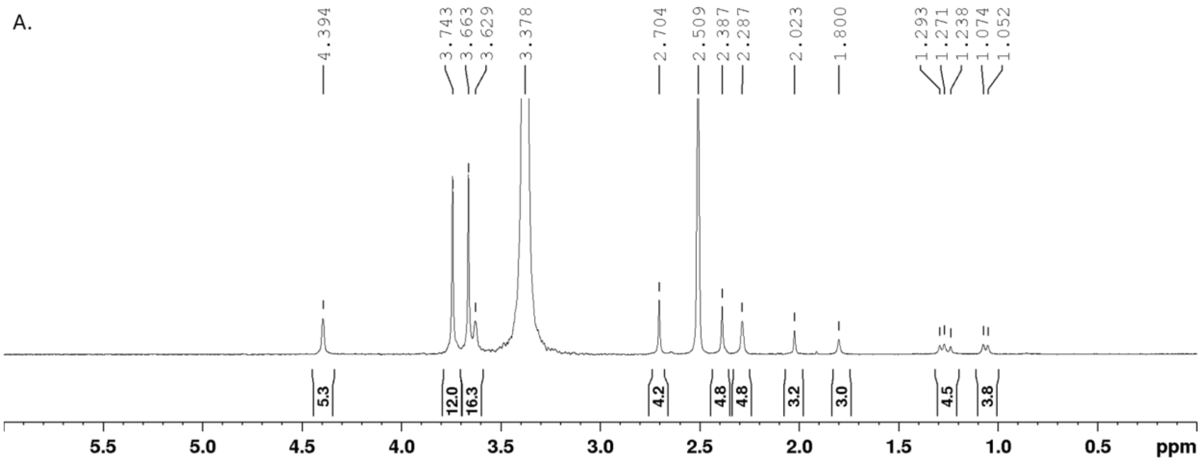
^{1}H NMR (400 MHz, DMSO) δ 4.39 (s, 4H, OH), 3.73 (s, 12H, $H_{1'}$), 3.65 (s, 12H, $H_{2'}$), 3.62 (s, 4H, $H_{7,8,20,21}$), 2.69 (s, 4H, $H_{5,10,18,23}$), 2.38 (s, 4H, $H_{2,13,15,26}$), 2.28 (s, 4H, $H_{6,9,19,22}$), 2.01 (s, 2H, $H_{1,14}$), 1.79 (s, 2H, H_{29}), 1.27 (d, J = 11.5 Hz, 2H, H_{27a}), 1.05 (d, J = 11.6 Hz, 2H, H_{27b}).

^{13}C NMR (126 MHz, DMSO) δ 166.75, 166.24, 91.35, 66.61, 63.12, 52.35, 51.63, 48.66, 43.15, 41.79, 36.75, 29.66, 27.33.

HRMS (ESI, *m/z*) calculated for $C_{45}H_{52}O_{22}$ $[M+H]^+$ = 945.30230, found 945.28533.

M.p °C > 300 °C

A.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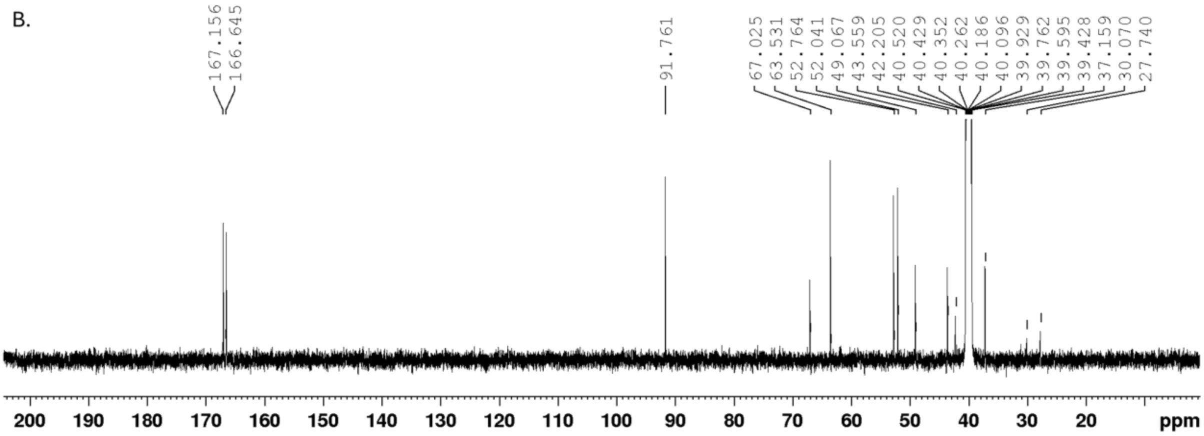
3.629
3.378
2.704
2.509
2.387
2.287
2.023
1.800
1.293
1.271
1.238
1.074
1.052
5.3
12.0
16.3
4.2
4.8
4.8
3.2
3.0
4.5
3.8
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

B.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91.761
67.025
63.531
52.764
52.041
49.067
43.559
42.205
40.520
40.429
40.352
40.262
40.186
40.096
39.929
39.762
39.595
39.428
37.159
30.070
27.740
200
190
180
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150
140
130
120
110
100
90
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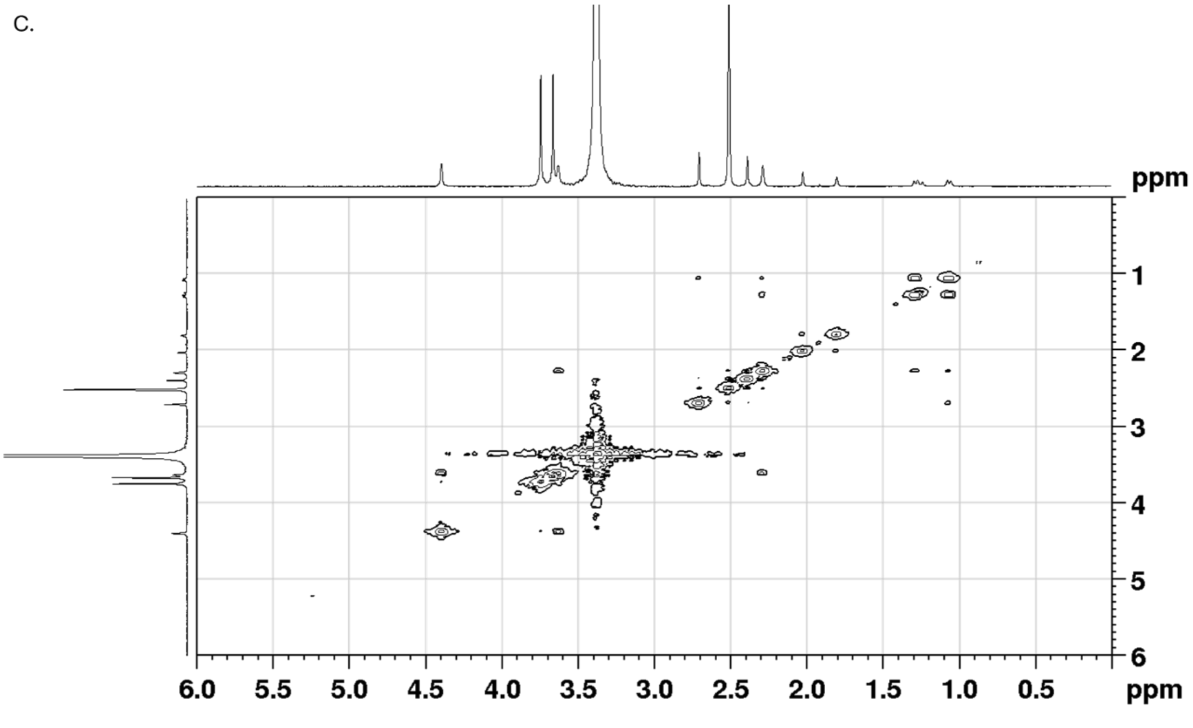
50
40
30
20
ppm

C.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6.0
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3.0
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1.5
1.0
0.5
ppm

D.

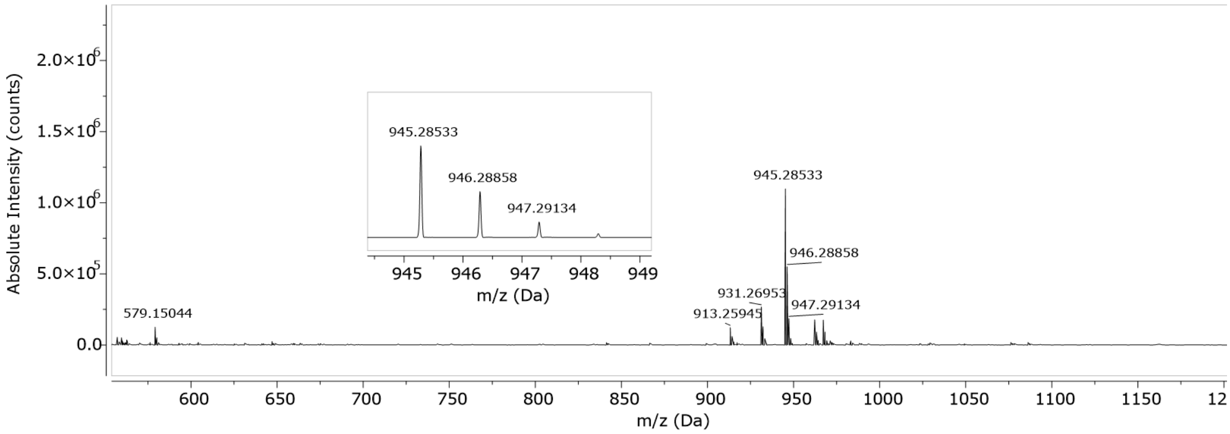
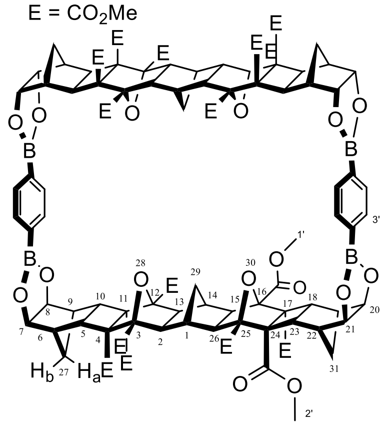


Figure S26. *A. ^1H NMR spectrum of **4**. B. ^{13}C NMR spectrum of **4**. C. ^1H-^1H COSY Spectrum of **4**. D. HRMS spectrum of **4**.*

Macrocycle: 4 + benzene-1,4-diboronic acid ($[2+2]_{Ph}$)



Bis-diol **4** (46 mg, 0.049 mmol) and benzene-1,4-diboronic acid (7.8 mg, 0.047 mmol) were added to a pressure vessel and suspended in anhydrous chloroform (60 mL). The vessel was sealed and heated at 100 °C for 24 hours. After cooling, the solution was processed as per **general isolation procedure A**. The solid was left to air-dry overnight before being further dried under reduced pressure for six hours to afford macrocycle **$[2+2]_{Ph}$** as a fine white powder (38.8mg, 79%).

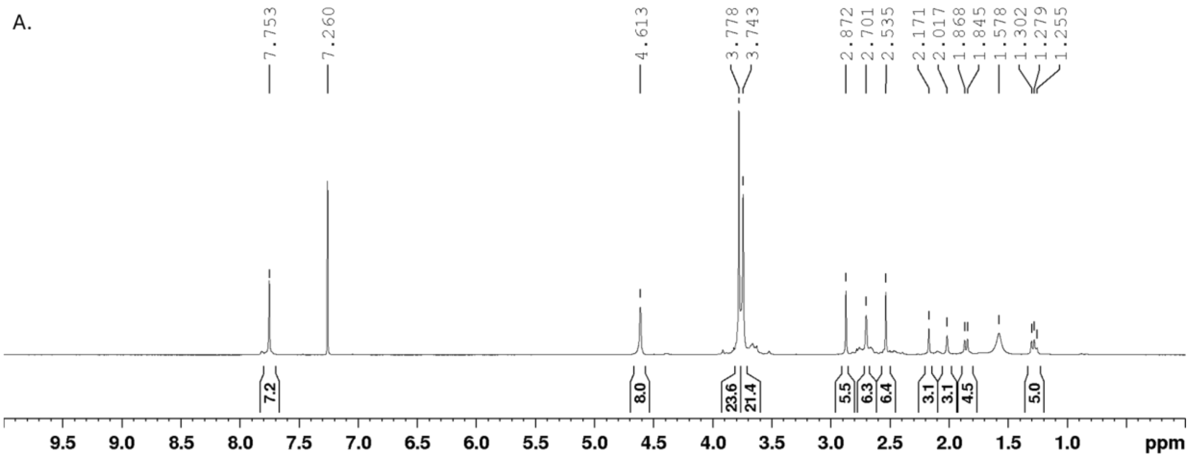
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.76 (s, 8H, $H_{3'}$), 4.62 (s, 8H, $H_{7,8,20,21}$), 3.78 (d, *J* = 1.5 Hz, 24H, $H_{2'}$), 3.75 (s, 24H, $H_{1'}$), 2.87 (s, 8H, $H_{5,10,18,23}$), 2.70 (s, 8H, $H_{6,9,15,23}$), 2.54 (s, 8H, $H_{2,13,15,26}$), 2.17 (s, 4H, $H_{1,14}$), 1.86 (d, *J* = 11.8 Hz, 4H, $H_{27a,29}$), 1.29 (d, *J* = 11.8 Hz, 4H, H_{27b}).

^{13}C NMR (126 MHz, CDCl$_3$) δ 167.28, 166.62, 134.41, 92.42, 80.31, 63.54, 52.36, 52.02, 49.03, 42.65, 41.95, 37.83, 31.28.

HRMS (ESI, *m/z*) calculated for $C_{102}H_{104}B_4O_{44}$ $[M + NH_4]^+$ = 2094.66607, found 2094.64793

M.p >350 °C

A.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3.743
2.872
2.701
2.535
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1.845
1.578
1.302
1.279
1.255
7.2
8.0
23.6
21.4
5.5
6.3
6.4
3.1
3.1
4.5
5.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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4.0
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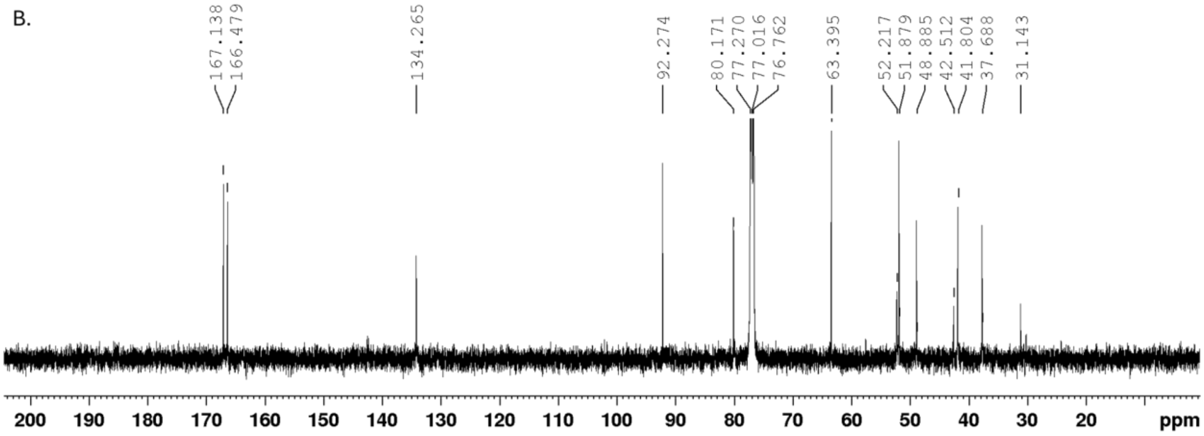
1.5
1.0
ppm

B.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92.274
80.171
77.270
77.016
76.762
63.395
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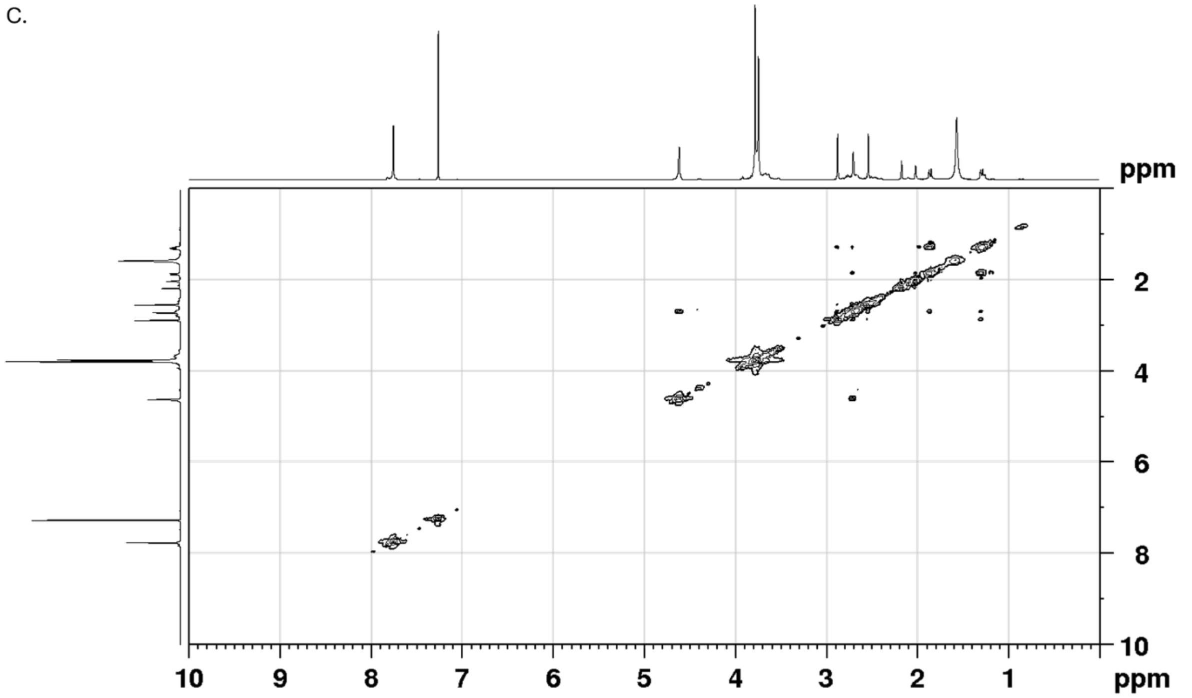
51.879
48.885
42.512
41.804
37.688
31.143
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

C.


ppm
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4
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8
10
10
9
8
7
6
5
4
3
2
1
ppm

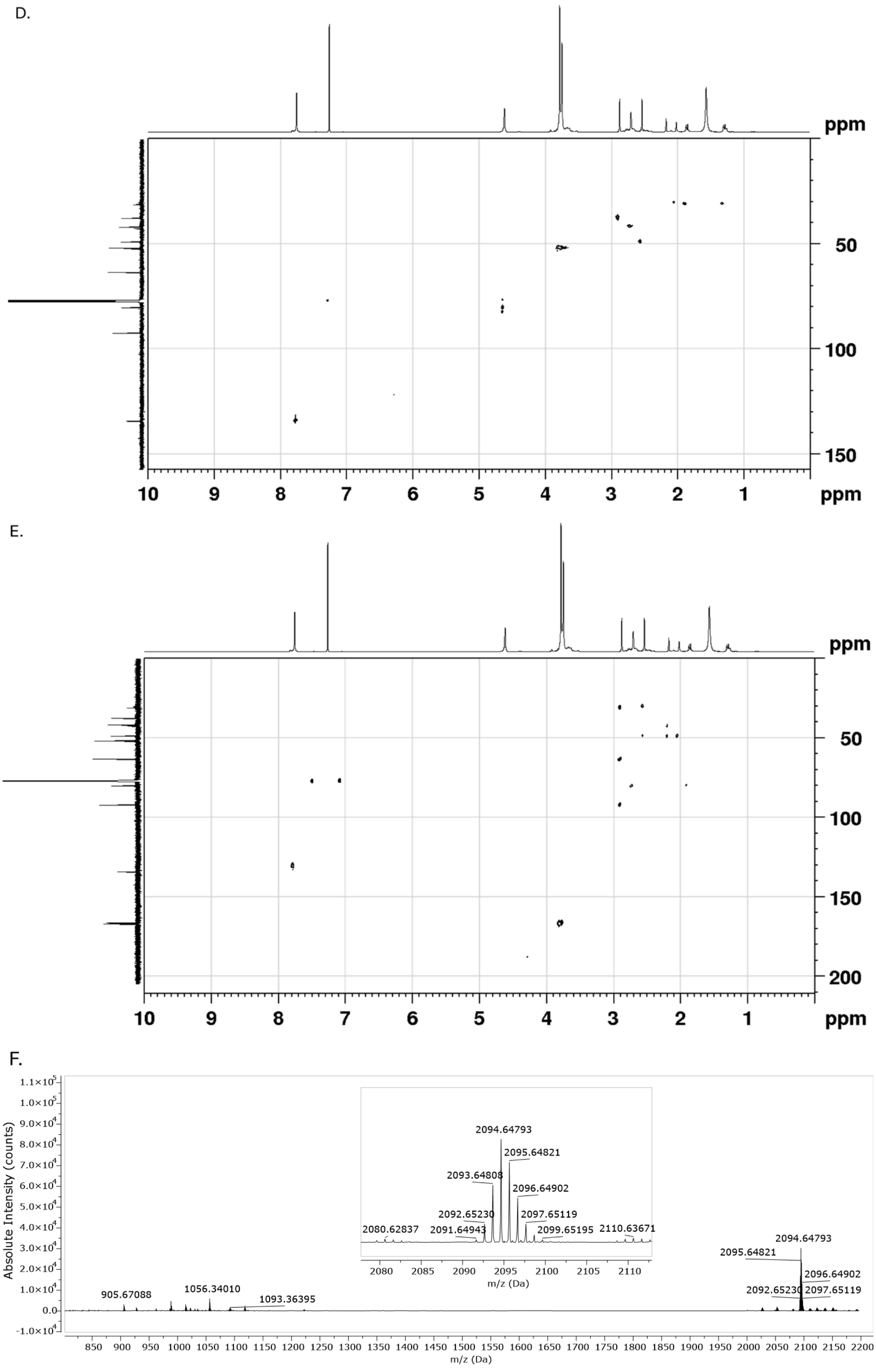
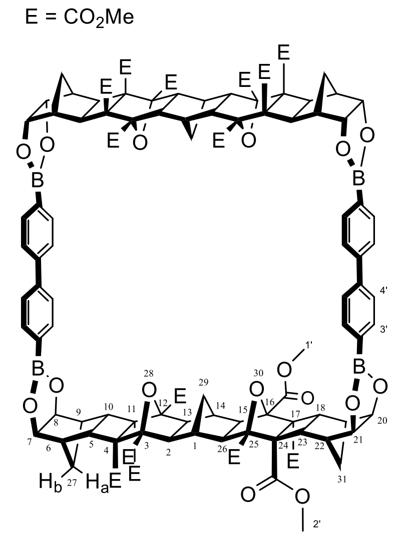

D.
ppm
50
100
150
10
9
8
7
6
5
4
3
2
1
ppm
E.
ppm
50
100
150
200
10
9
8
7
6
5
4
3
2
1
ppm
F.
1.1×10^5
1.0×10^5
9.0×10^4
8.0×10^4
7.0×10^4
6.0×10^4
5.0×10^4
4.0×10^4
3.0×10^4
2.0×10^4
1.0×10^4
0.0
-1.0×10^4
Absolute Intensity (counts)
2094.64793
2095.64821
2093.64808
2096.64902
2092.65230
2097.65119
2080.62837
2091.64943
2099.65195
2110.63671
2080
2085
2090
2095
2100
2105
2110
m/z (Da)
905.67088
1056.34010
1093.36395
2094.64793
2095.64821
2096.64902
2092.65230
2097.65119
850
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400
1450
1500
1550
1600
1650
1700
1750
1800
1850
1900
1950
2000
2050
2100
2150
2200
m/z (Da)

Figure S27. *A. ^{1}H NMR spectrum of* ***$[2+2]_{Ph}$****. B. ^{13}C NMR spectrum of* ***$[2+2]_{Ph}$****. C. ^{1}H-^{1}H COSY spectrum of* ***$[2+2]_{Ph}$****. D. ^{1}H-^{13}C HSQC spectrum of* ***$[2+2]_{Ph}$****. E. ^{1}H-^{13}C HMBC spectrum of* ***$[2+2]_{Ph}$****. F. HRMS spectrum of* ***$[2+2]_{Ph}$****.*

Macrocycle: 4 + biphenyl-4,4'-diboronic acid ([2+2]$_{BiPh}$)



Bis-diol **4** (28.2 mg, 0.0299 mmol) and biphenyl-4,4'-diboronic acid (7.8 mg, 0.0323 mmol) were added to a pressure vessel and suspended in chloroform (70 mL). The vessel was sealed and heated at 100 °C for 18 hours. After cooling, the solution was processed as per **general isolation procedure A**. Macrocycle **$[2+2]_{BiPh}$** was isolated as a fine white powder (30.1 mg, 90%).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, *J* = 7.5 Hz, 8H), 7.71 (d, *J* = 7.7 Hz, 8H), 4.66 – 4.61 (m, 8H, $H_{7,8,20,21}$), 3.79 (s, 24H, $H_{2'}$), 3.75 (s, 24H, $H_{1'}$), 2.84 (s, 8H, $H_{5,10,18,23}$), 2.71 (s, 8H, $H_{6,9,15,23}$), 2.53 (s, 8H, $H_{2,13,15,26}$), 2.15 (s, 4H, $H_{1,14}$), 1.86 (d, *J* = 10.5 Hz, 8H, $H_{27a,29}$), 1.34 – 1.26 (m, 11H, H_{27b}, coincident with grease).

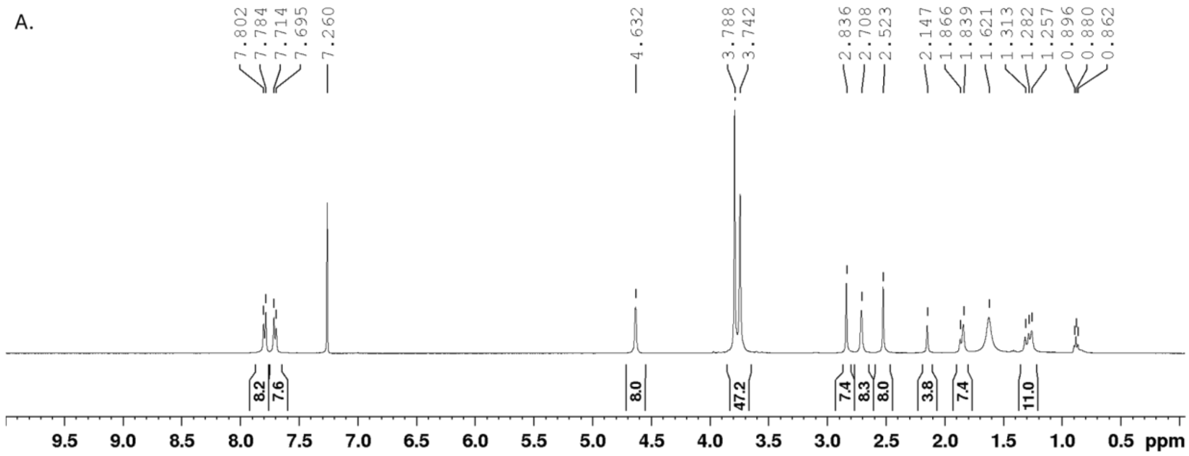
Esters assigned on the basis of an observed proton to carbon coupling in a HMBC experiment between $H_{5,10,18,23}$ and the carbonyl carbon of the methyl ester at δ = 3.79 ppm. The coupling is presumed to be caused by a W-type coupling to the $H_{2'}$ ester. Aromatic protons were unable to be resolved.

^{13}C NMR (101 MHz, CDCl$_3$) δ 167.14, 166.56, 143.04, 135.40, 126.32, 92.18, 80.20, 63.66, 52.56, 52.05, 49.29, 42.40, 42.04, 37.75, 31.10, 30.42.

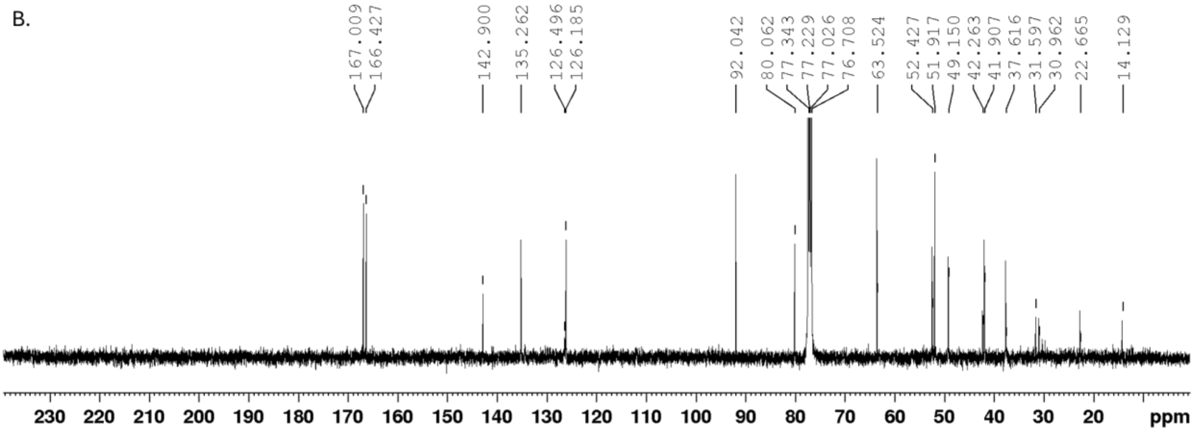
HRMS (ESI, *m/z*) calculated for $C_{102}H_{104}B_4O_{44}$ [M + 2H]$^{2+}$ = 1115.35487, found 1115.35460

M.p >350 °C

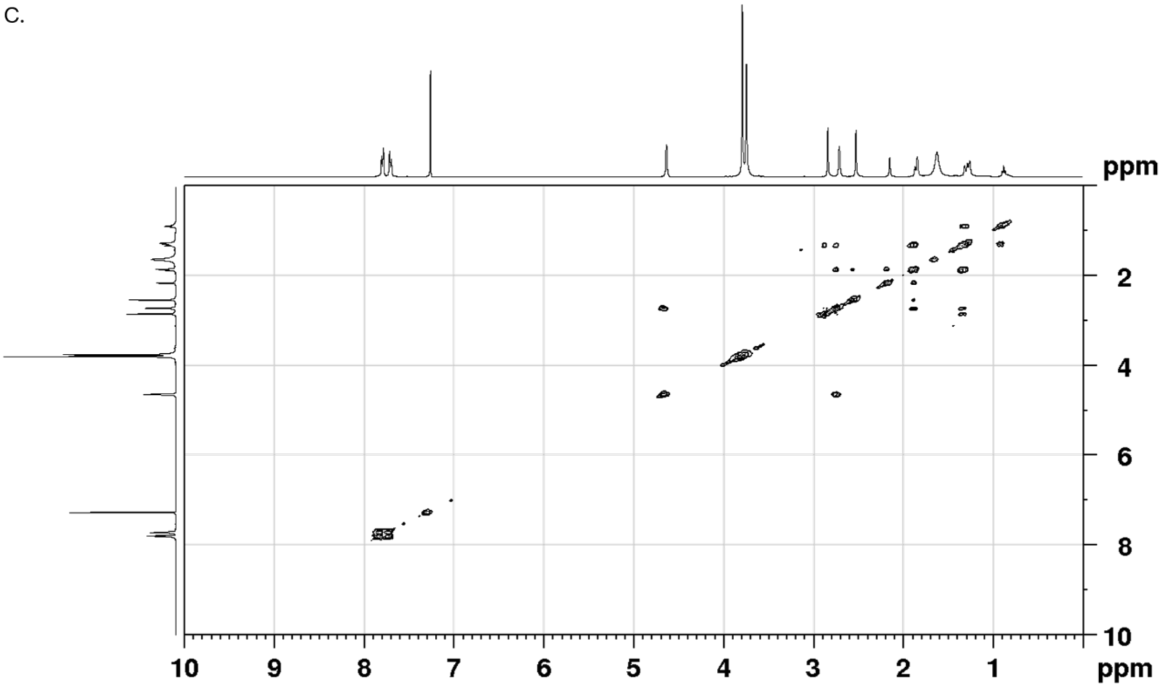
A.


7.802
7.784
7.714
7.695
7.260
4.632
3.788
3.742
2.836
2.708
2.523
2.147
1.866
1.839
1.621
1.313
1.282
1.257
0.896
0.880
0.862
8.2
7.6
8.0
47.2
7.4
8.3
8.0
3.8
7.4
11.0
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 ppm

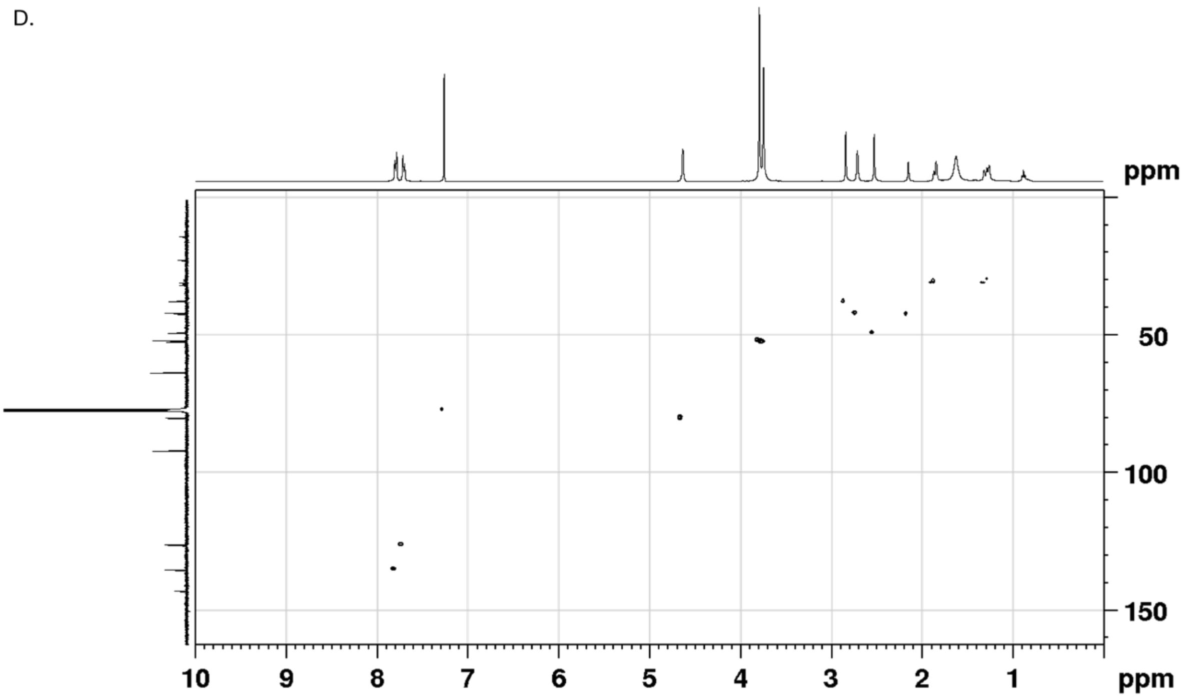
B.


167.009
166.427
142.900
135.262
126.496
126.185
92.042
80.062
77.343
77.229
77.026
76.708
63.524
52.427
51.917
49.150
42.263
41.907
37.616
31.597
30.962
22.665
14.129
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

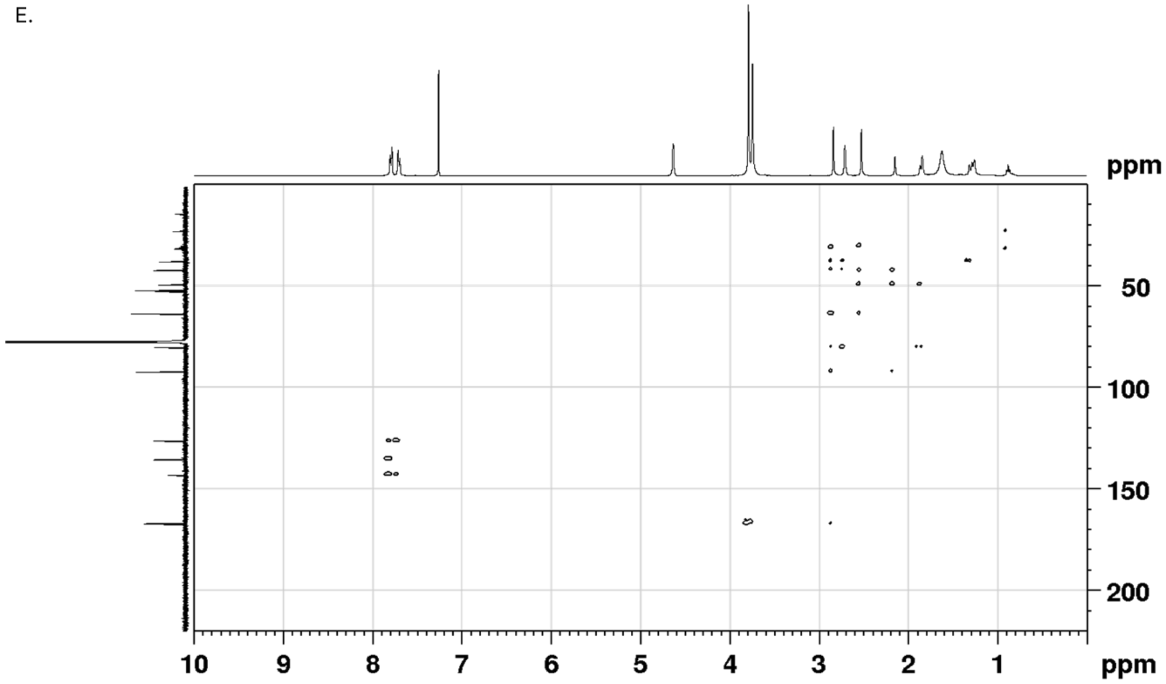
C.


ppm
2
4
6
8
10
10 9 8 7 6 5 4 3 2 1
ppm

D.


ppm
50
100
150
10
9
8
7
6
5
4
3
2
1
ppm

E.


ppm
50
100
150
200
10
9
8
7
6
5
4
3
2
1
ppm

F.

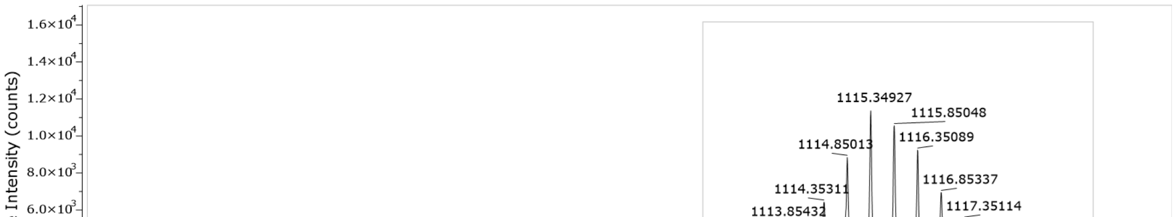
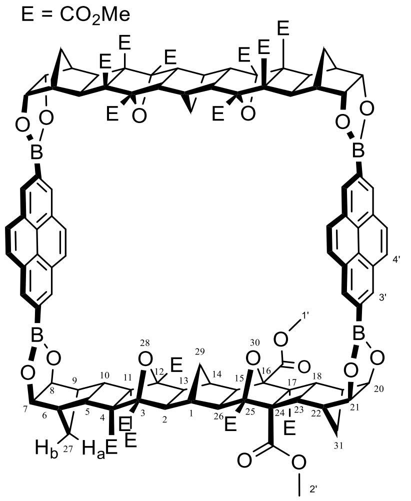

Absolute Intensity (counts)
1.6×10^4
1.4×10^4
1.2×10^4
1.0×10^4
8.0×10^3
6.0×10^3
4.0×10^3
2.0×10^3
0.0
801.81430
1116.35089
1115.34927
1115.85048
1108.33964
1116.85337
1201.83200
1263.85399
850
900
950
1000
1050
1100
1150
1200
1250
1300
1350
1400
1450
1500
1550
1600
1650
170
m/z (Da)
1115.34927
1115.85048
1114.85013
1116.35089
1114.35311
1116.85337
1113.85432
1117.35114
1112
1113
1114
1115
1116
1117
1118
1119
1120
m/z (Da)

Figure S28. *A. ^{1}H NMR spectrum of **[2+2]$_{BiPh}$**. B. ^{13}C NMR spectrum of **[2+2]$_{BiPh}$**. C. ^{1}H-^{1}H COSY spectrum of **[2+2]$_{BiPh}$**. D. ^{1}H-^{13}C HSQC spectrum of **[2+2]$_{BiPh}$**. E. ^{1}H-^{13}C HMBC spectrum of **[2+2]$_{BiPh}$**. F. HRMS spectrum of **[2+2]$_{BiPh}$**.*

Macrocycle: 4 + pyrene-2,7-diboronic acid ([2+2]$_{Py}$)



Bis-diol **4** (31.3 mg, 0.0332 mmol) and pyrene-2,7-diboronic acid (9.92 mg, 0.0342 mmol) were added to a pressure vessel and suspended in chloroform (60 mL). The vessel was sealed and heated at 100 °C for 18 hours. After cooling, the solution was processed as per **general isolation procedure A**. Macrocycle **[2+2]$_{Py}$** was isolated as a fine white powder (24.3 mg, 63%).

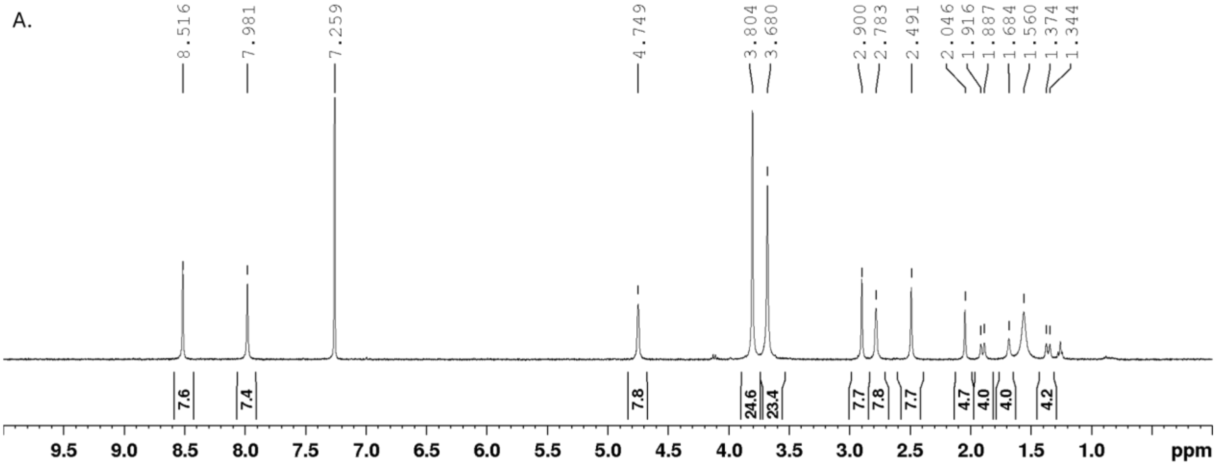
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 8H), 7.98 (s, 8H), 4.75 (s, 8H, $H_{7,8,20,21}$), 3.81 (s, 24H, $H_{2'}$), 3.68 (s, 24H, $H_{1'}$), 2.90 (s, 8H, $H_{5,10,18,23}$), 2.78 (s, 8H, $H_{6,9,15,23}$), 2.49 (s, 8H, $H_{2,13,15,26}$), 2.05 (s, 4H, $H_{1,14}$), 1.90 (d, J = 11.7 Hz, 4H, H_{27a}), 1.68 (s, 4H, H_{29}), 1.36 (d, J = 11.8 Hz, 4H, H_{27b}).

Low solubility in chloroform precluded collection of well resolved ^{13}C NMR spectra.

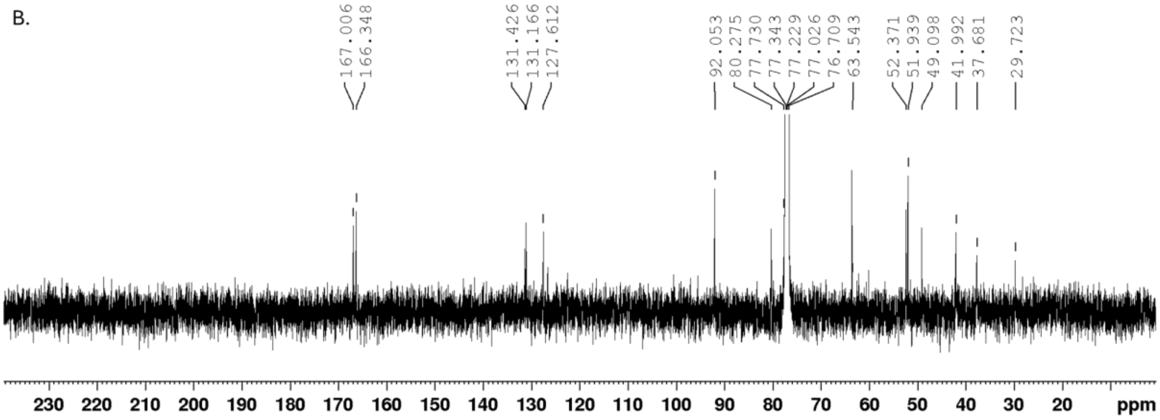
HRMS (ESI, *m/z*) calculated for $C_{122}H_{112}B_4O_{44}$ $[M + Na]^+$ = 2347.6882, found 2347.6860

M.p >350 °C

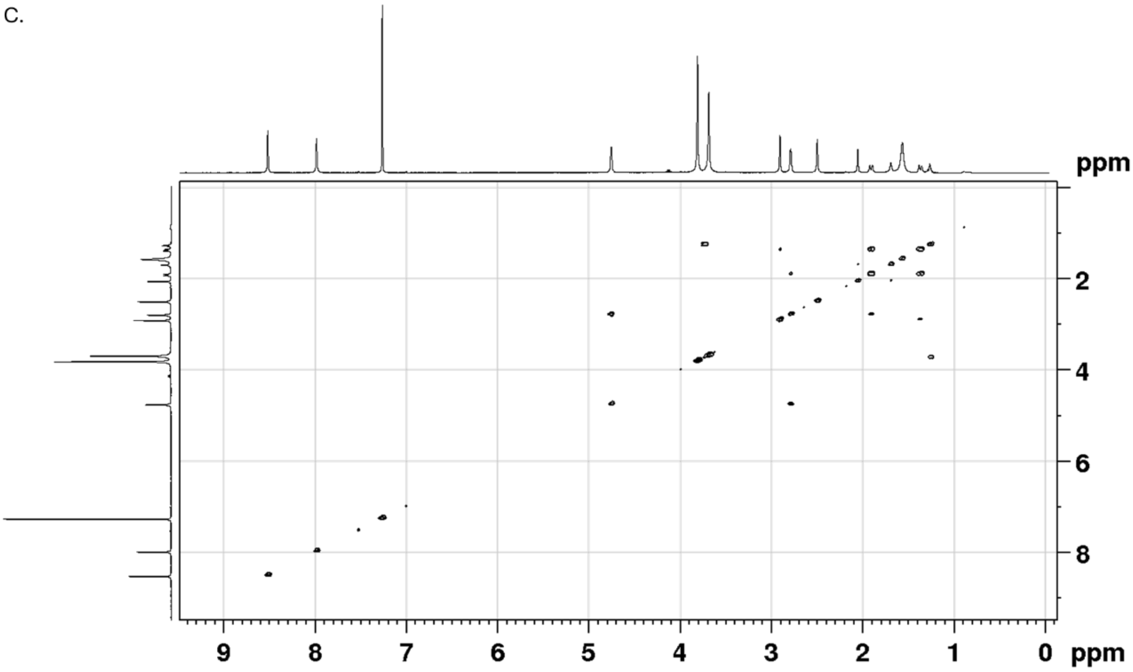
A.

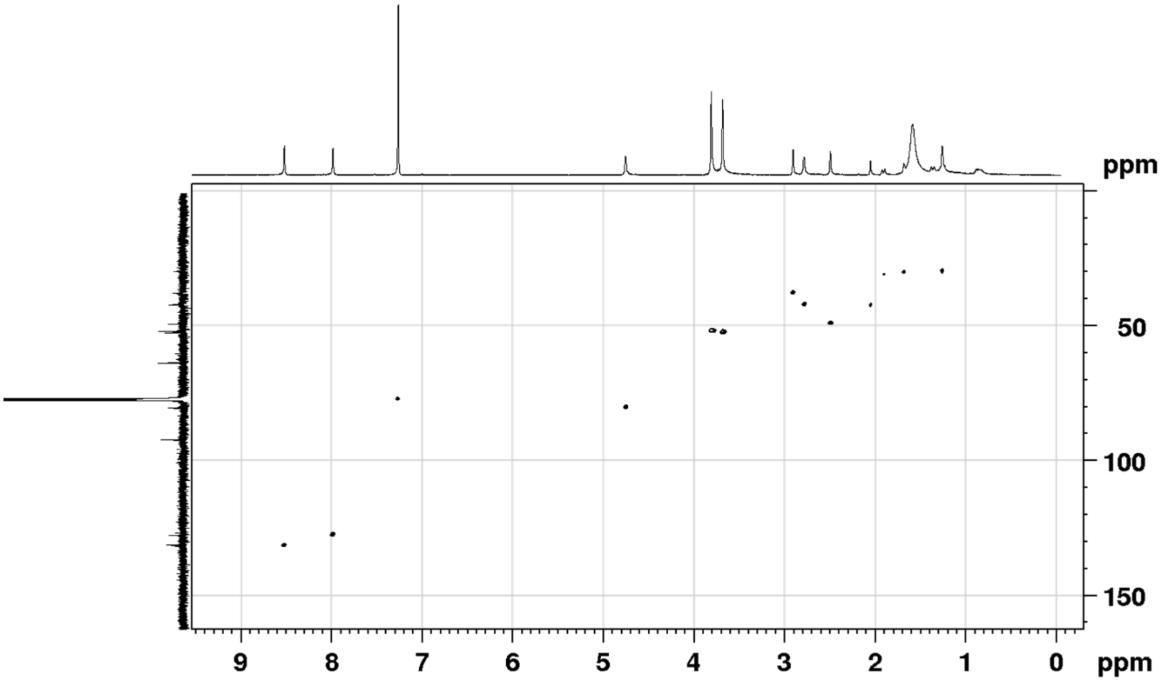

8.516
7.981
7.259
4.749
3.804
3.680
2.900
2.783
2.491
2.046
1.916
1.887
1.684
1.560
1.374
1.344
7.6
7.4
7.8
24.6
23.4
7.7
7.8
7.7
4.7
4.0
4.0
4.2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

B.

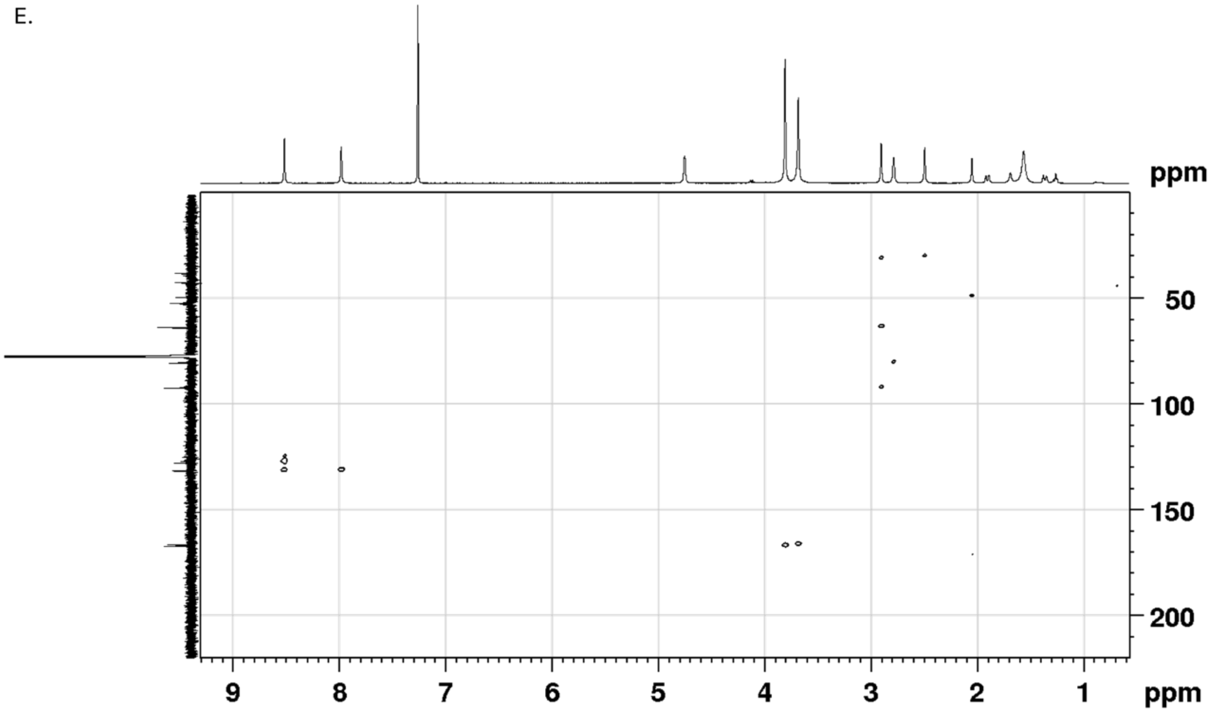

167.006
166.348
131.426
131.166
127.612
92.053
80.275
77.730
77.343
77.229
77.026
76.709
63.543
52.371
51.939
49.098
41.992
37.681
29.723
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
ppm

C.


ppm
2
4
6
8
9 8 7 6 5 4 3 2 1 0
ppm


ppm
50
100
150
9
8
7
6
5
4
3
2
1
0
ppm

E.


ppm
50
100
150
200
9
8
7
6
5
4
3
2
1
ppm

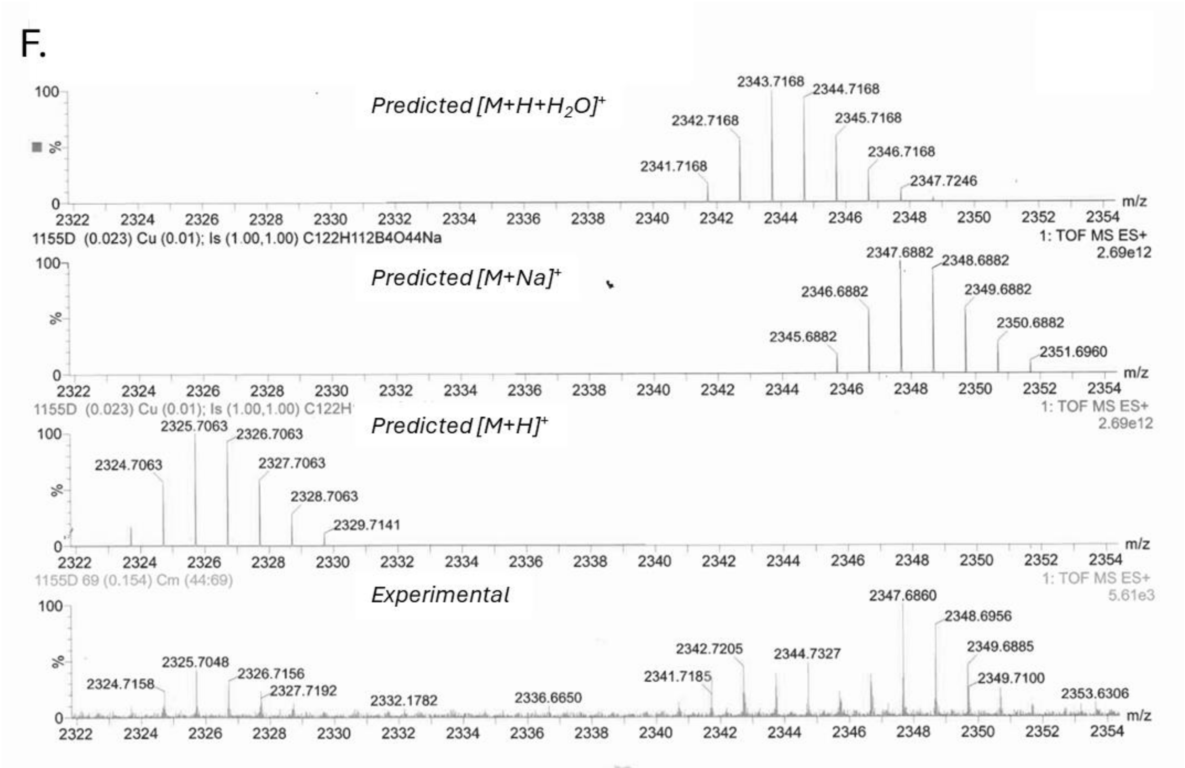
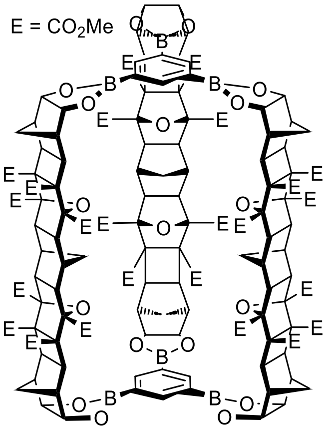


Figure S29. *A. ^{1}H NMR spectrum of* ***[2+2]$_{\mathrm{Py}}$****. B. ^{13}C NMR spectrum of* ***[2+2]$_{\mathrm{Py}}$****. C. ^{1}H-^{1}H COSY spectrum of* ***[2+2]$_{\mathrm{Py}}$****. D. ^{1}H-^{13}C HSQC spectrum of* ***[2+2]$_{\mathrm{Py}}$****. E. ^{1}H-^{13}C HMBC spectrum of* ***[2+2]$_{\mathrm{Py}}$****. F. HRMS spectrum of* ***[2+2]$_{\mathrm{Py}}$****.*

Cage: 4 + benzene-1,3,5-triboronic acid ([3+2]$_{\mathrm{Ph}}$)



Bis-diol **4** (59.1 mg, 0.0626 mmol) and benzene-1,3,5-triboronic acid (8.75 mg, 0.0417 mmol) were added to a pressure vessel and suspended in chloroform (60 mL). The vessel was sealed and heated at 100 °C for 60 hours. After cooling, the solution was processed as per **general isolation procedure A**. Cage **[3+2]$_{\mathrm{Ph}}$** was isolated as a fine white powder (16.2 mg, 25 %).

The resonances of the ^{1}H NMR spectrum were not assigned due to multiple coincident resonances.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 6H), 4.62 (dd, J = 8.7, 5.3 Hz, 6H), 4.55 – 4.47 (m, 6H), 3.87 (s, 18H), 3.80 – 3.72 (m, 36H), 3.60 (s, 18H), 2.93 (d, J = 6.9 Hz, 6H), 2.80 (d, J = 6.1 Hz, 12H), 2.39

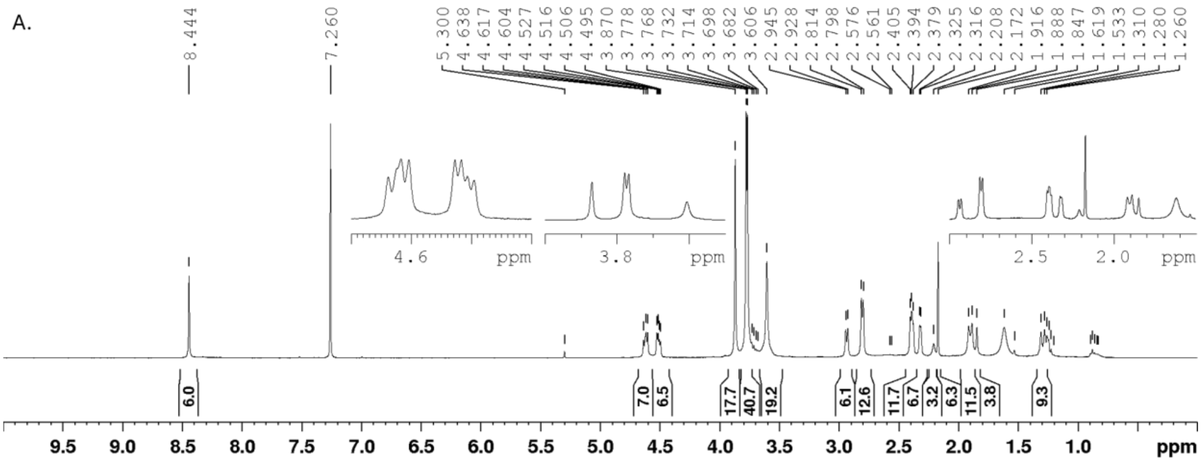
(dd, *J* = 6.8, 4.0 Hz, 12H), 2.32 (d, *J* = 4.5 Hz, 6H), 2.17 (d, *J* = 1.3 Hz, 6H), 1.94 – 1.81 (m, 12H), 1.33 – 1.20 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.50, 166.90, 166.49, 166.40, 145.73, 126.10, 93.23, 91.24, 80.97, 80.18, 63.22, 63.02, 58.65, 53.82, 52.72, 52.11, 52.08, 49.50, 48.37, 42.95, 42.34, 42.09, 41.60, 40.81, 36.66, 31.85, 31.08, 29.08, 18.60.

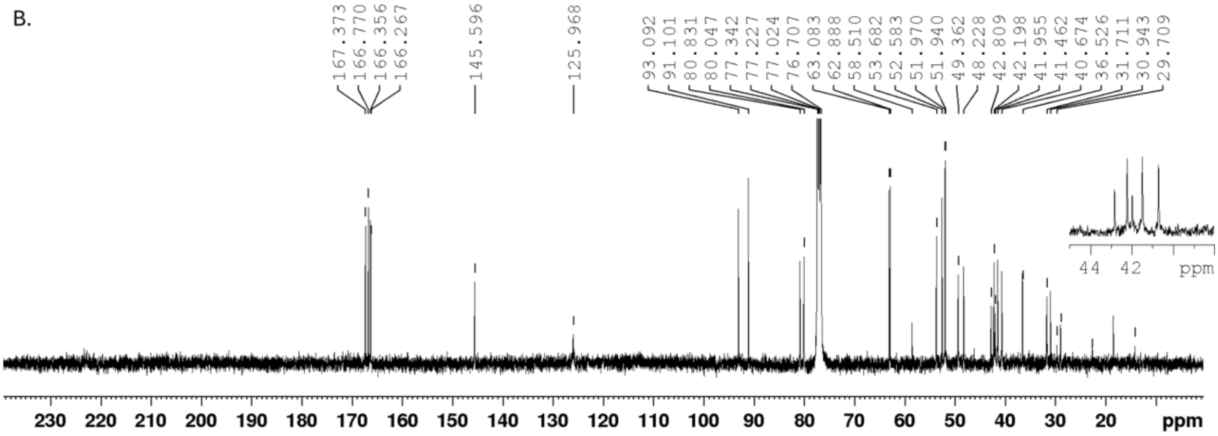
HRMS (ESI, *m/z*) calculated for $C_{147}H_{150}B_6O_{66}$ $[M + 2NH_4]^{2+}$ = 1536.48081, found 1536.47222

M.p >350 °C

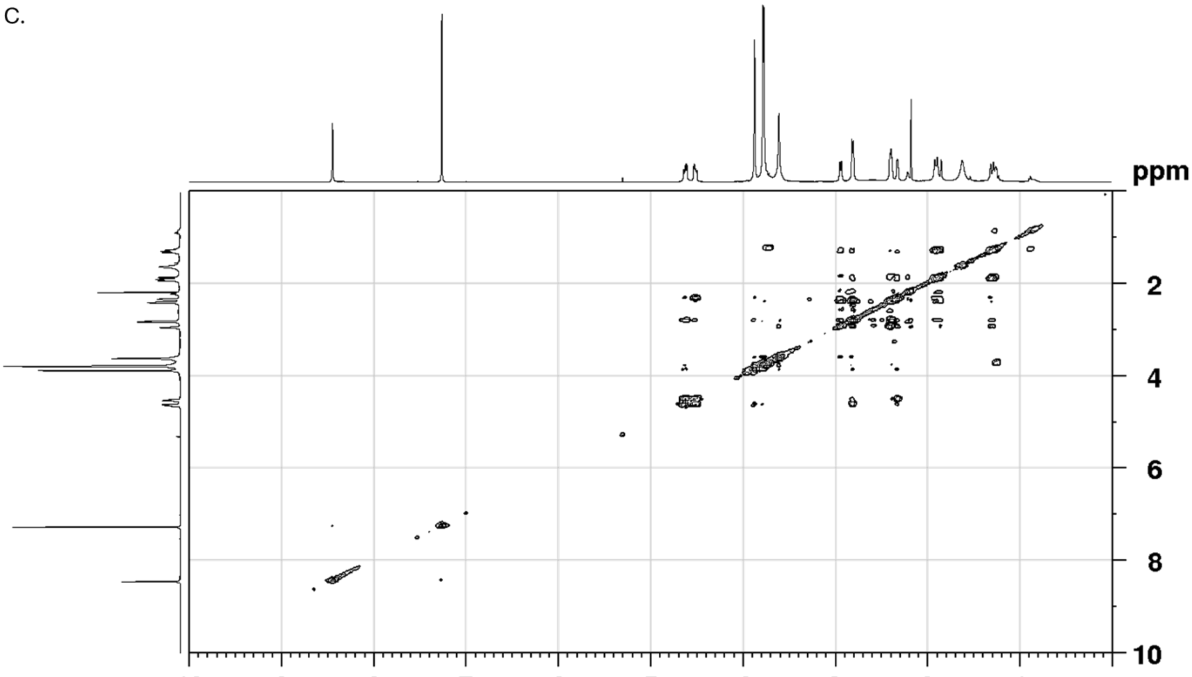
A.


8.444
7.260
5.300
4.638
4.617
4.604
4.527
4.516
4.506
4.495
3.870
3.778
3.768
3.732
3.714
3.698
3.682
3.606
2.945
2.928
2.814
2.798
2.576
2.561
2.405
2.394
2.379
2.325
2.316
2.208
2.172
1.916
1.888
1.847
1.619
1.533
1.310
1.280
1.260
4.6
ppm
3.8
ppm
2.5
2.0
ppm
6.0
7.0
6.5
17.7
40.7
19.2
6.1
12.6
11.7
6.7
3.2
6.3
11.5
3.8
9.3
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
ppm

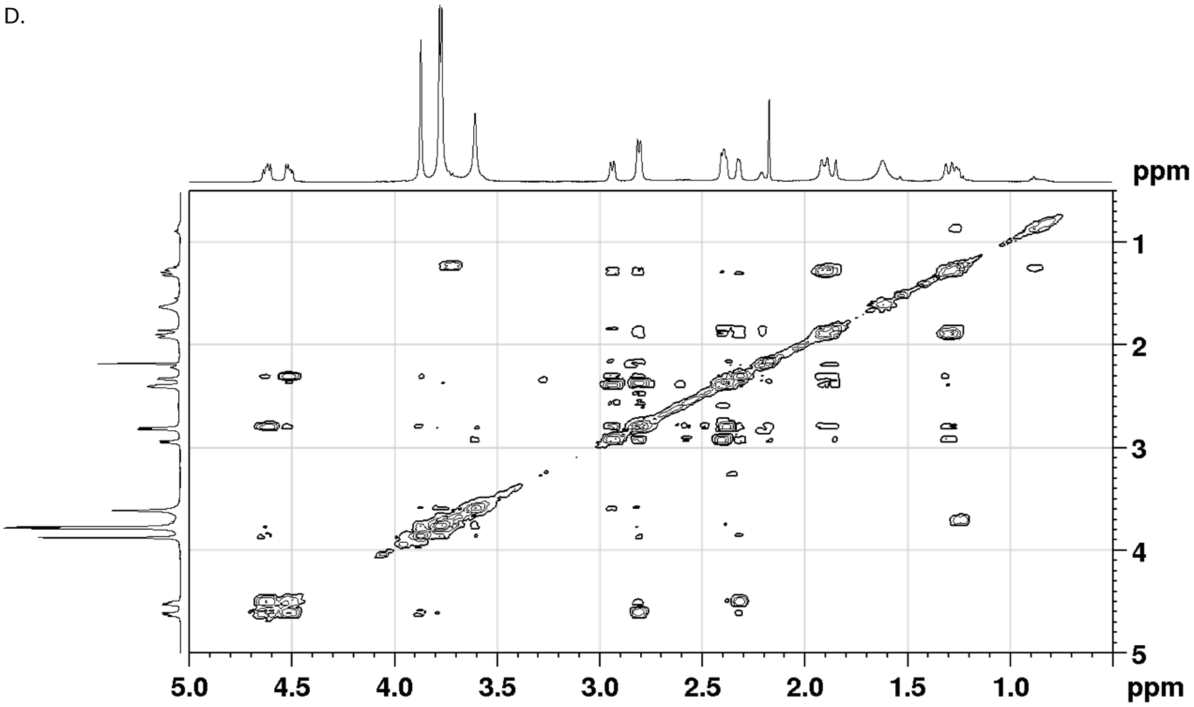
B.


167.373
166.770
166.356
166.267
145.596
125.968
93.092
91.101
80.831
80.047
77.342
77.227
77.024
76.707
63.083
62.888
58.510
53.682
52.583
51.970
51.940
49.362
48.228
42.809
42.198
41.955
41.462
40.674
36.526
31.711
30.943
29.709
44
42
ppm
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

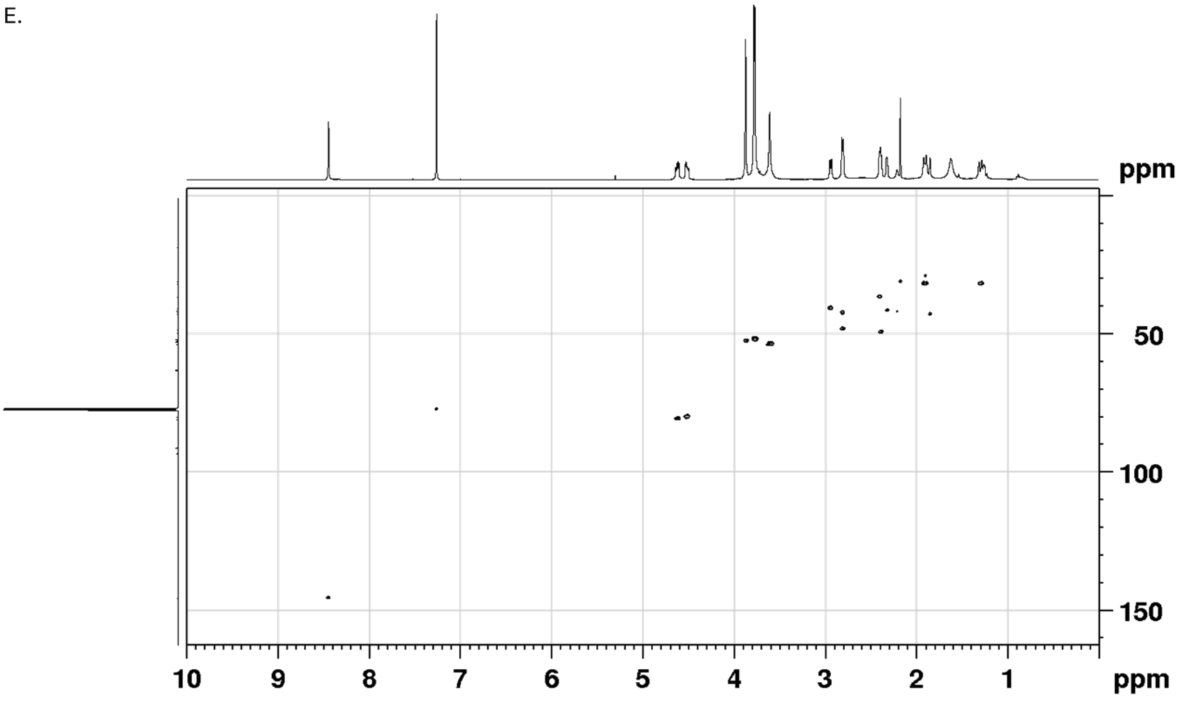
C.


ppm
2
4
6
8
10
ppm
10
9
8
7
6
5
4
3
2
1
ppm

D.


ppm
1
2
3
4
5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

E.


ppm
50
100
150
10
9
8
7
6
5
4
3
2
1
ppm

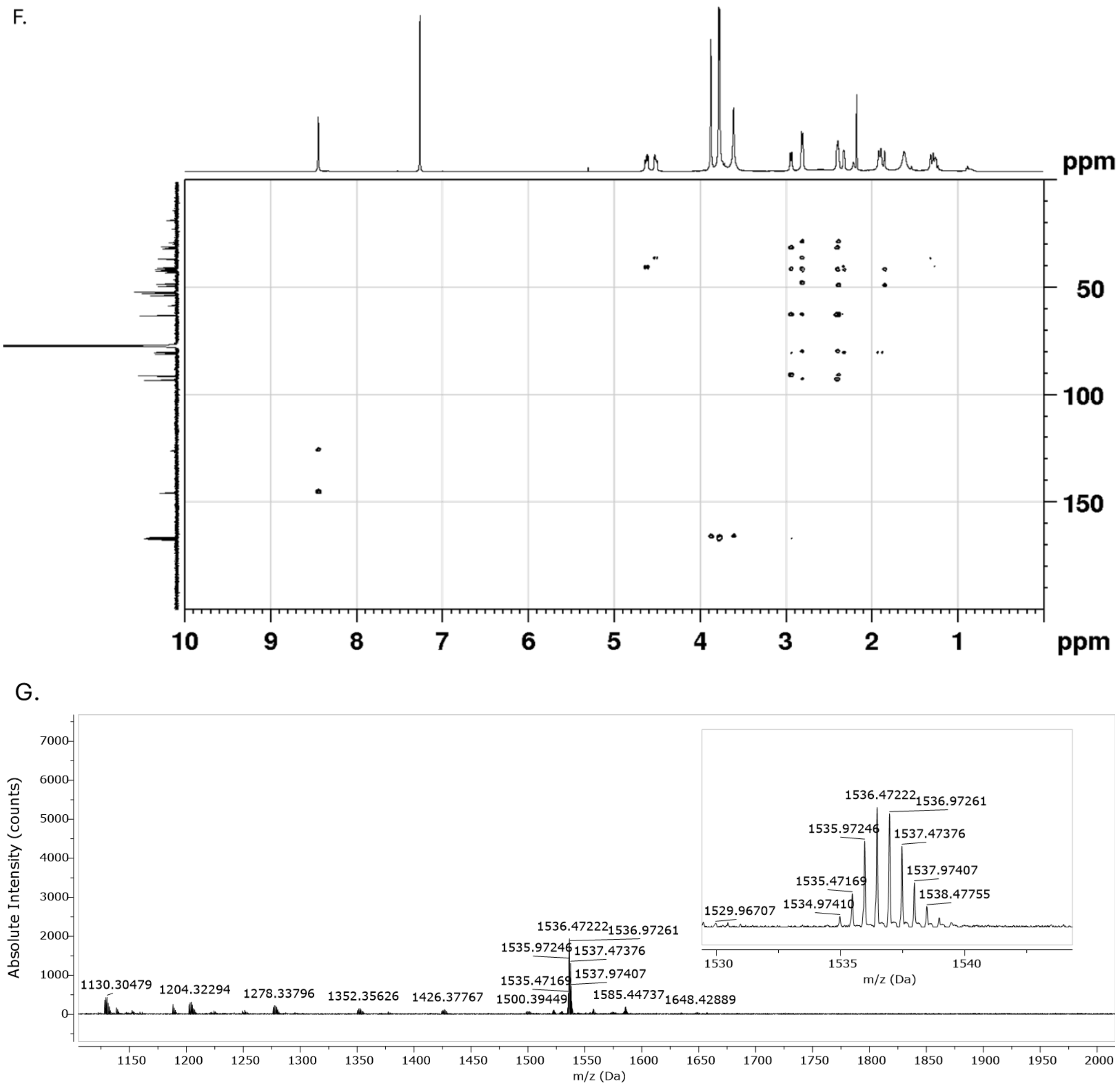
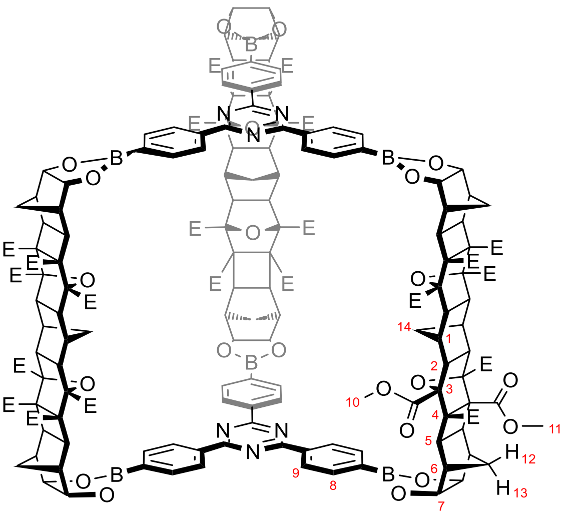


Figure S30. *A. ^{1}H NMR spectrum of* ***[3+2]$_{Ph}$****. B. ^{13}C NMR spectrum of* ***[3+2]$_{Ph}$****. C. ^{1}H-^{1}H COSY Spectrum of* ***[3+2]$_{Ph}$****. D. Zoomed in ^{1}H-^{1}H COSY Spectrum of* ***[3+2]$_{Ph}$****. E. ^{1}H-^{13}C HSQC spectrum of* ***[3+2]$_{Ph}$****. F. ^{1}H-^{13}C HMBC spectrum of* ***[3+2]$_{Ph}$****. G. HRMS spectrum of* ***[3+2]$_{Ph}$****.*

Cage: 4 + ((1,3,5-triazine-2,4,6-triyl)tris(benzene-4,1-diyl))triboronic acid ([3+2]$_{TZ}$)



Bis-diol **4** (83 mg, 0.088 mmol) and ((1,3,5-Triazine-2,4,6-triyl)tris(benzene-4,1-diyl))triboronic acid (27 mg, 0.061 mmol) were added to a pressure vessel and suspended in chloroform (100 mL). The vessel was sealed and heated at 100 °C for 60 hours. After cooling, the solution was processed as per **general isolation procedure A**. The solid was left to air-dry overnight before being further dried under reduced pressure for two hours to afford cage **[3+2]**$_{TZ}$ as a fine white powder (99 mg, 96%).

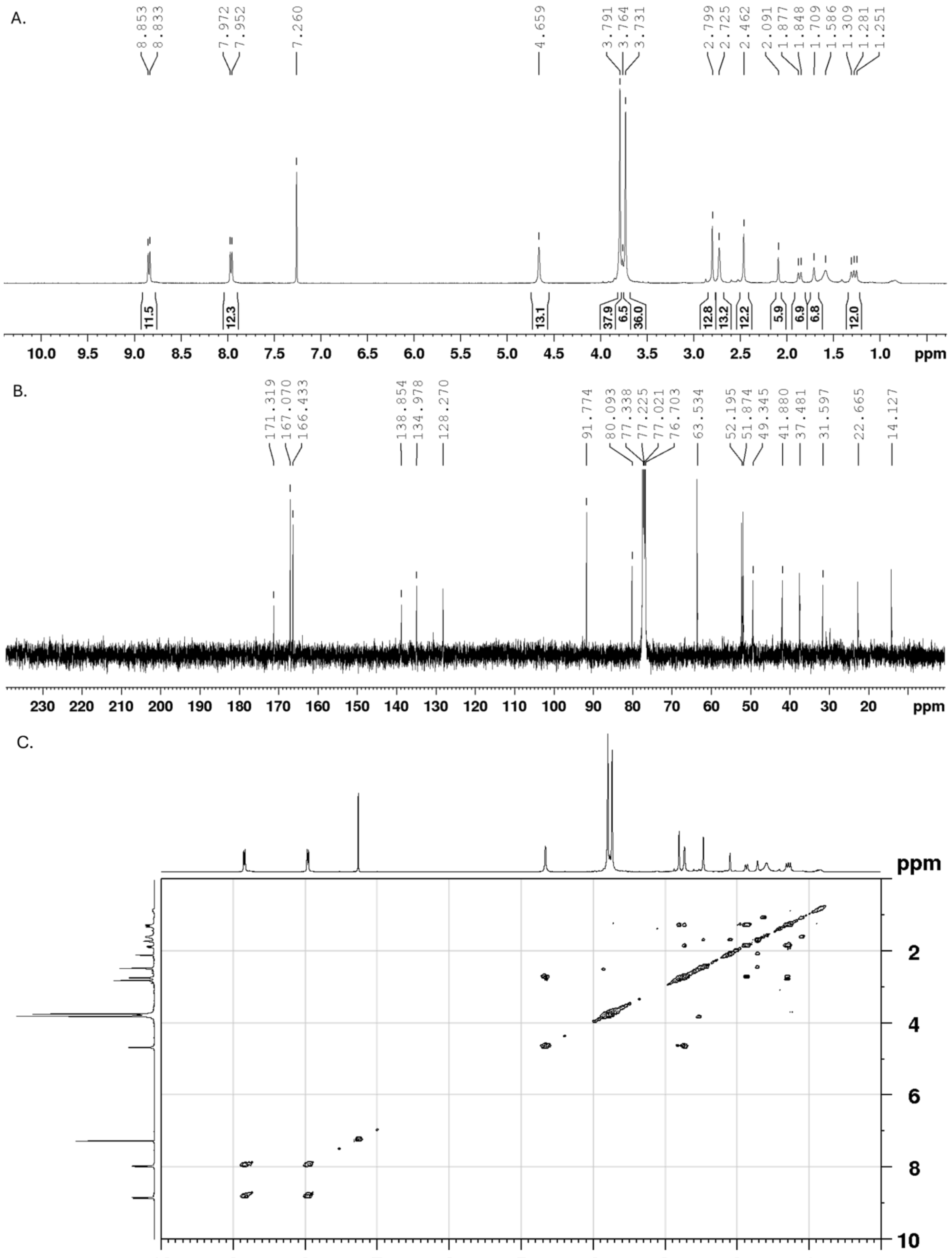
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 7.6 Hz, 12H, H_9), 7.95 (d, *J* = 7.5 Hz, 12H, H_8), 4.65 (s, 16H, H_7), 3.78 (s, 36H, H_{11}), 3.72 (s, 36H, H_{10}), 2.79 (s, 12H, H_5), 2.71 (s, 12H, H_6), 2.45 (s, 12H, H_2), 2.08 (s, 6H, H_1), 1.85 (d, *J* = 11.1 Hz, 6H, H_{12}), 1.71 (s, 6H, H_{14}), 1.33 – 1.23 (m, 6H, H_{13})

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.45, 167.20, 166.57, 138.99, 135.11, 128.40, 91.91, 80.23, 63.67, 52.34, 52.01, 49.49, 42.22, 42.02, 37.62, 30.89, 29.85. 17

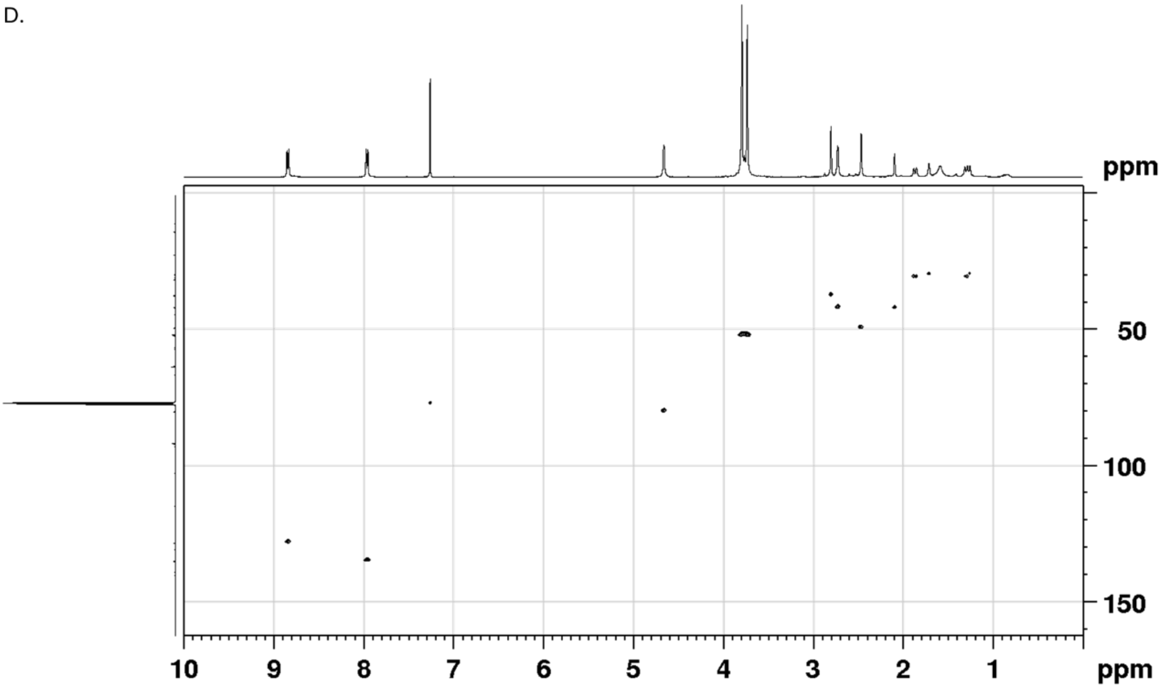
Diffusion Constant: 3.16×10^{-10} m^2/s (R_s = 11.42 ± 0.12 Å)

M.p >350 °C

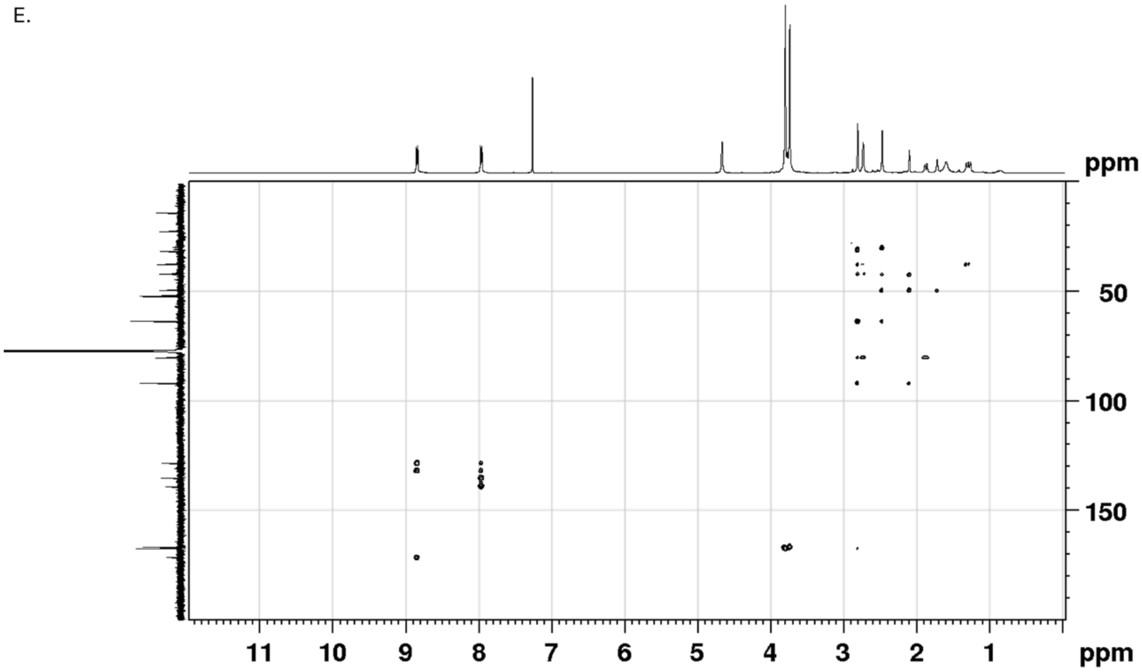
Despite some efforts, a satisfactory ESI-HRMS spectrum was not obtained.


A.
8.853
8.833
7.972
7.952
7.260
4.659
3.791
3.764
3.731
2.799
2.725
2.462
2.091
1.877
1.848
1.709
1.586
1.309
1.281
1.251
11.5
12.3
13.1
37.9
6.5
36.0
12.8
13.2
12.2
5.9
6.9
6.8
12.0
10.0 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 ppm
B.
171.319
167.070
166.433
138.854
134.978
128.270
91.774
80.093
77.338
77.225
77.021
76.703
63.534
52.195
51.874
49.345
41.880
37.481
31.597
22.665
14.127
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
C.
ppm
2
4
6
8
10
10 9 8 7 6 5 4 3 2 1 ppm

D.


ppm
50
100
150
10
9
8
7
6
5
4
3
2
1
ppm

E.


ppm
50
100
150
11
10
9
8
7
6
5
4
3
2
1
ppm

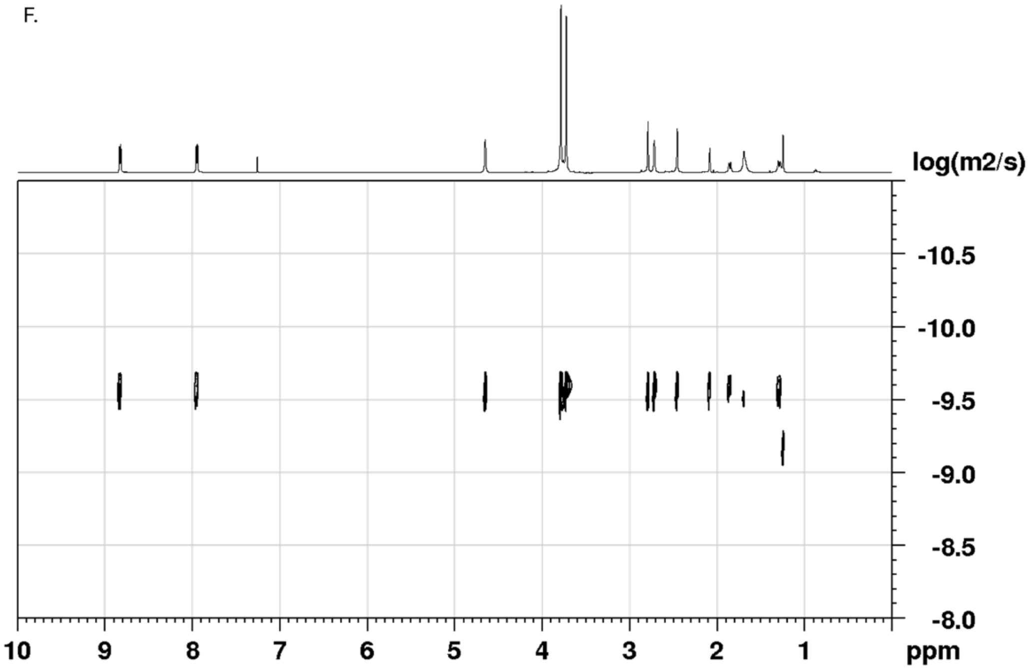


Figure S31. *A. ^{1}H NMR spectrum of* ***[3+2]$_{TZ}$****. B. ^{13}C NMR spectrum of* ***[3+2]$_{TZ}$****. C. ^{1}H-^{1}H COSY spectrum of* ***[3+2]$_{TZ}$****. D. ^{1}H-^{13}C HSQC spectrum of* ***[3+2]$_{TZ}$****. E. ^{1}H-^{13}C HMBC spectrum of* ***[3+2]$_{TZ}$****. F. ^{1}H DOSY NMR spectrum of* ***[3+2]$_{TZ}$****.*

1.14. Dynamics Study

A sample of **[1+2]$_F$** (1 eq.) and phenyl boronic acid (2 eq.) was prepared in (5:2) DMSO-*d6*:$CDCl_3$. The sample was monitored by ^{1}H and ^{19}F NMR spectroscopy over 6 days at 6-hour intervals at room temperature. The library of possible products from dynamic exchange is shown in Figure S32 (top).

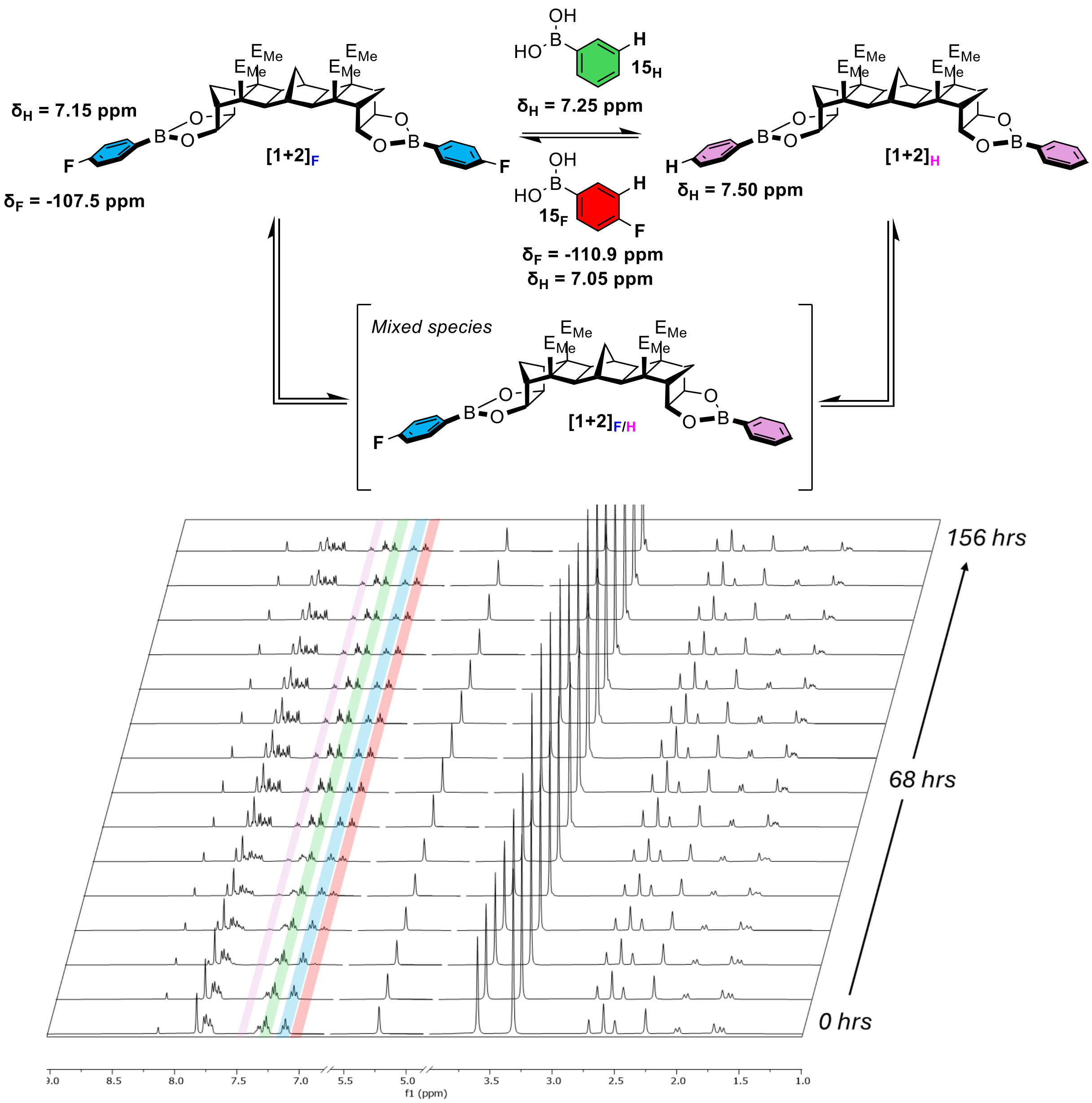


Figure S32. *Stacked* ^{1}*H NMR spectra of the mix of* ***[1+2]***$_{F}$ *and phenyl boronic acid* ***15***$_{H}$*. Coloured strips represent key resonances that change over time. (500 MHz,* $CDCl_3$*)*

In the ^{1}H NMR spectrum, four possible species have distinct resonances (figure S32) that could be used for determining the relative concentrations in solution. Four important considerations underpin the interpretation of the data:

1.) The mixed boronic ester species **[1+2]**$_{F/H}$ is presumed to form (figure S32, **[1+2]**$_{F/H}$), however analysis by ^{1}H and ^{19}F NMR spectroscopy cannot distinguish between the boronic esters of a mixed species **[1+2]**$_{F/H}$ and those of the homo-species (**[1+2]**$_{F}$ or **[1+2]**$_{H}$). As such integration of the formed boronic ester species is reflective of the amount of the respective boronic ester, rather than the concentration of the bis-boronic ester species (*ie.* Integration of the resonance at $\delta =$ 7.50 ppm reflects both **[1+2]**$_{H}$ and **[1+2]**$_{F/H}$).

2.) As the boronic ester substituent (H or F) does not notably affect the chemical shift of the framework resonances, the resonance corresponding to C<u>H</u>OB (δ = 5.22 ppm) serves as an internal standard, and integration is relative to this resonance.
3.) The potential side reaction involving boroxine formation was not observed in the ^{19}F NMR spectra (literature value: δ = -105.8 ppm[34]).
4.) The bis-diol species $\mathbf{3_{Me}}$ was never observed, as such the exchange is due to transesterification of the phenyl boronic acid species, rather than initial hydrolysis of the boronic ester followed by ester formation.

The relative integration of each resonance (with respect to the integration of the resonance corresponding to C<u>H</u>OB) was plotted over time (figure S33). Pleasingly, the ^{1}H NMR data confirmed that the system was undergoing transesterification. The decrease in the relative integration of the two starting compounds (**[1+2]**$_\mathbf{F}$ and **15**$_\mathbf{H}$) matches the increase in the relative integration of the other components (phenyl boronic ester (**[1+2]**$_\mathbf{H}$ and **[1+2]**$_\mathbf{F/H}$) and **15**$_\mathbf{F}$). The transesterification was slow (possibly due to sterics of the norbornane boronic ester), with the system taking ~120 hours to reach equilibrium at room temperature, however, the experiment confirms that the norbornane boronic ester system is suitably dynamic, and that supramolecular self-assembly with norbornane diols and boronic acids is likely proceeding under thermodynamic control, especially considering the high temperatures used in the synthesis.

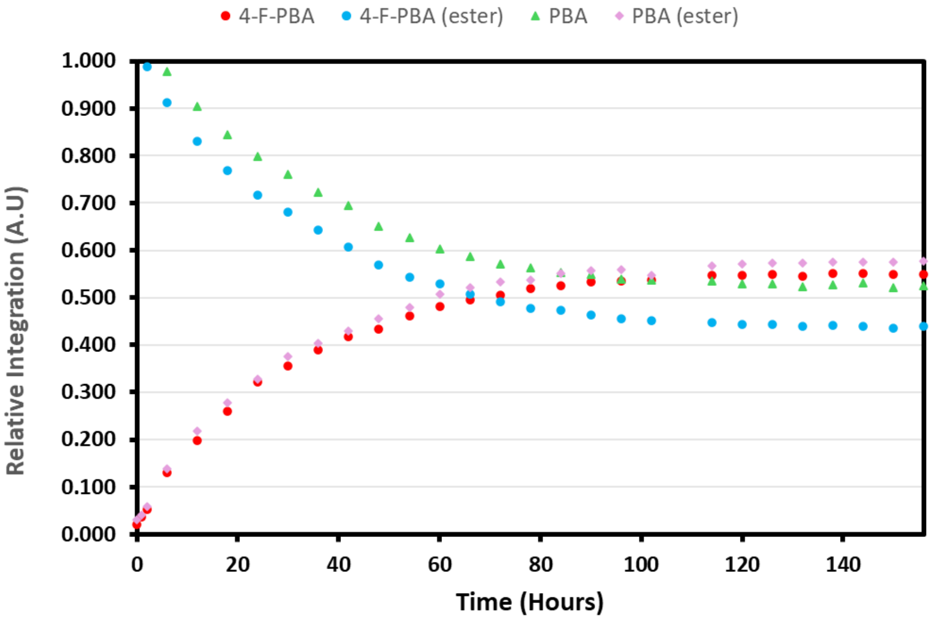


Figure S33. *Change in relative integration over time.*

The use of ^{19}F NMR spectroscopy similarly confirmed the equilibrium position. In this case, only two resonances are present, the added 4-fluorophenyl boronic ester (δ_F =-107.5 ppm) and the formed 4-fluorophenyl boronic acid (δ_F = -110.9 ppm). Note that the values are not referenced. Of interest, a smaller resonance was observed next to the 4-fluorophenyl boronic ester resonance and the exact nature of the species that gives rise to this signal is currently not understood. The change in the relative integration of the two ^{19}F resonances over time is displayed in Figure S34, and similar to the ^{1}H NMR data, appears to reach an equilibrium after ~120 hours.

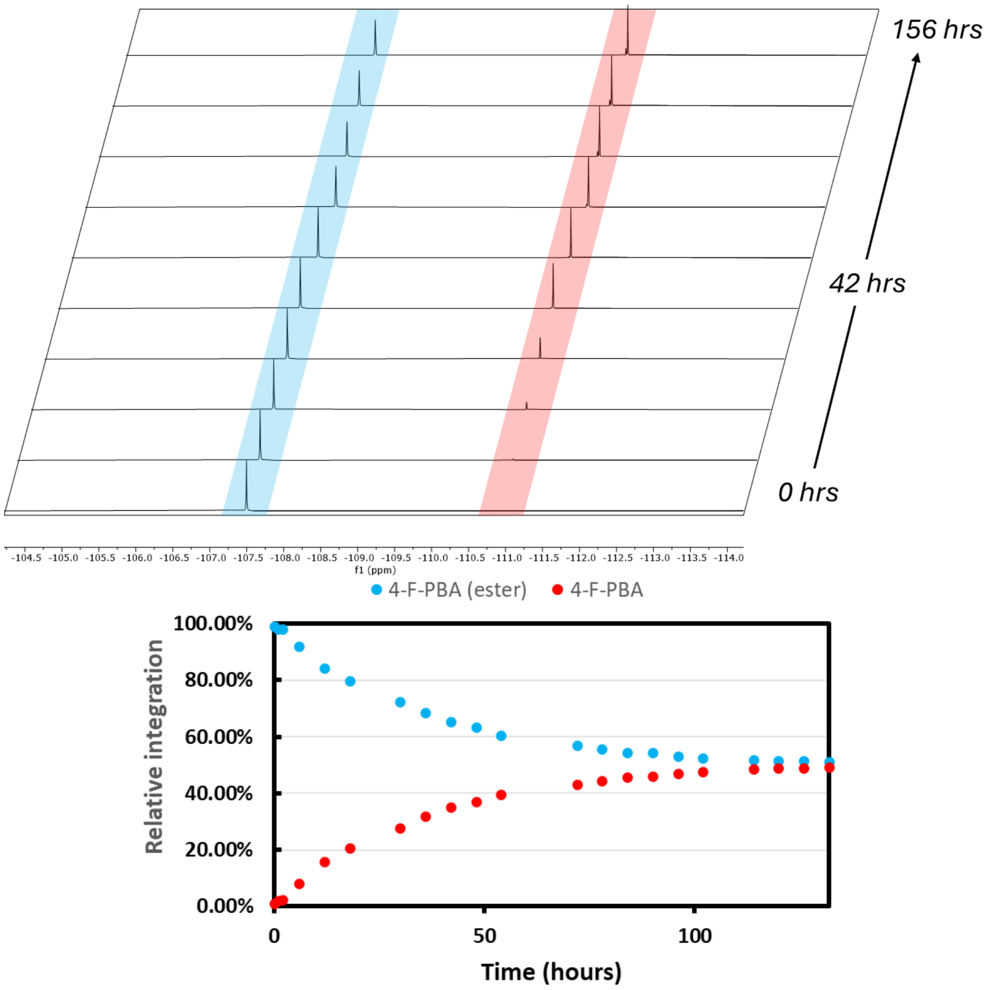


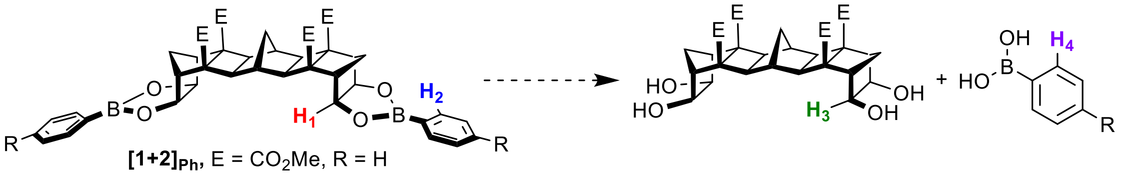
Figure S34. *Top: Stacked ^{19}F NMR spectra of spectra of the mix of* ***[1+2]***$_{F}$ *and phenyl boronic acid. Not referenced. Bottom: Change in relative integration of ^{19}F NMR spectra of the mix of* ***[1+2]***$_{F}$ *and phenyl boronic acid over time.*

1.15. Additional Hydrolysis Studies

1.15.1. *Exo*-norbornane systems

Hydrolysis of each compound (**[1+2]**$_{\mathbf{Ph}}$, **[4+4]**$_{\mathbf{Me}}$, **[4+4]**$_{\mathbf{DEG}}$) was monitored by ^{1}H NMR spectroscopy with the appearance of hydrolysis products (free diol resonance: *C<u>H</u>OH*, δ = 4.41 ppm, free boronic acid resonance: *Ar-<u>H</u>*, δ = 8.25 ppm) indicative of disassembly. A summary of the expected resonances is provided in Table S1. In the case of macrocycle models **[4+4]**$_{\mathbf{Me}}$ and **[4+4]**$_{\mathbf{DEG}}$, the appearance of resonances corresponding to an asymmetrical framework (*ie.* partially hydrolysed) would also be indicative of hydrolysis. The hydrolysis reaction of **[4+4]**$_{\mathbf{DEG}}$ was further monitored by nESI-HRMS.

Table S1. *Experimentally measured resonances relevant to monitoring hydrolysis of boronic ester assemblies.*



[1+2]$_{Ph}$, E = CO_2Me, R = H
[4+4]$_{Me}$, E = CO_2Me, R = Macrocycle
[4+4]$_{DEG}$, E = CO_2DEG, R = Macrocycle

Compound	Proton	$CDCl_3$ (ppm)	(1:1) $CDCl_3$:MeOD (ppm)
[1+2]$_{Ph}$	H_1	5.17	5.21
[4+4]$_{DEG}$	H_1	5.16	5.21
3_{Me}	H_3	-	4.40[b]
3_{DEG}	H_3	4.47	4.41
[1+2]$_{Ph}$	H_2	7.78	7.75
[4+4]$_{DEG}$	H_2	7.78	7.75
Phenyl boronic acid **15_H**	H_4	8.25[a]	-
Benzene-1,4-diboronic acid **5**	H_4	-	7.70

[a] Identical to literature values.[35] [b] Recorded in MeOD as insoluble in (1:1) $CDCl_3$:MeOD

Note that due to low solubility of bis-diol **3_{Me}** in (1:1) $CDCl_3$:MeOD a reference value **H_3** was not obtained. The reference value for bis-diol **3_{Me}** in MeOD is provided (δ = 4.40 ppm), otherwise the same proton in bis-diol **3_{DEG}** is expected to have an identical shift.

1.15.2. Stability: [1+2] 'Corner' Piece

A sample of **[1+2]$_{Ph}$** in both $CDCl_3$ or (1:1) $CDCl_3$:MeOD was prepared and analysed by ^1H NMR. Acetic acid (60 µL) was then added to the solution and a ^1H NMR spectrum was collected 30 minutes after addition. No hydrolysis products were observed in either case.

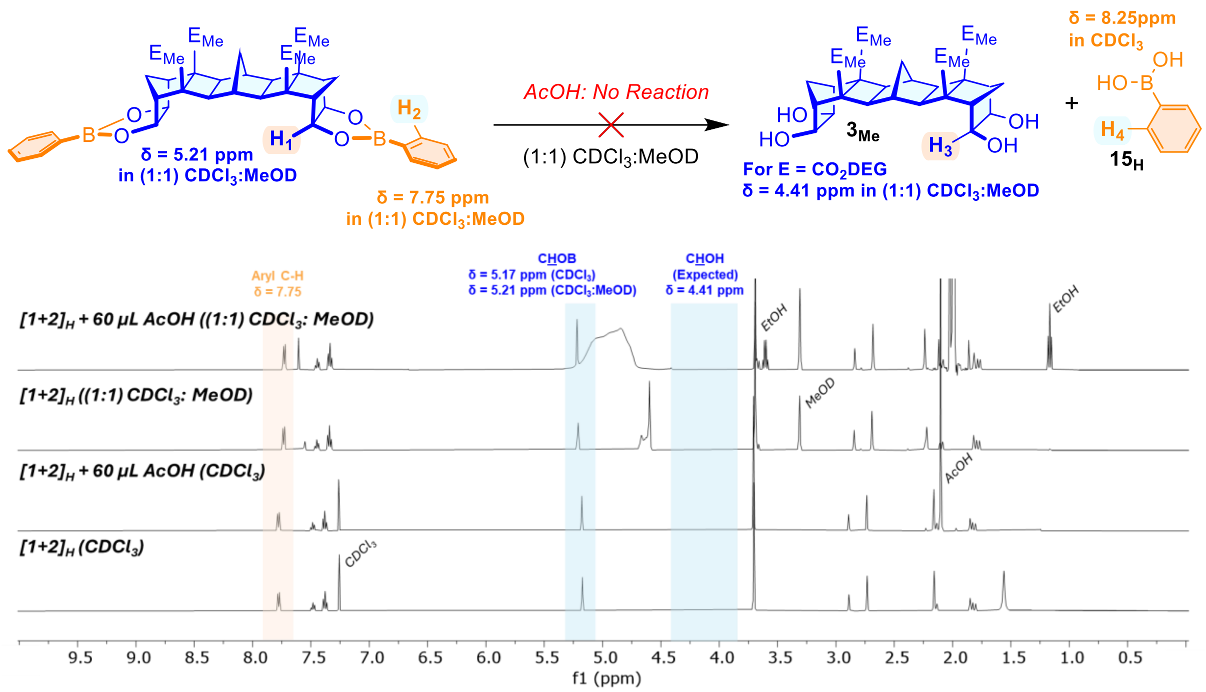


Figure S35. *Stacked ^{1}H NMR spectra of **[1+2]$_{Ph}$** and **[1+2]$_{Ph}$** + AcOH in $CDCl_3$ (bottom two spectra) or (1:1) $CDCl_3$:MeOD (top two spectra).*

1.15.3. Stability: Macrocycle [4+4]$_{Me}$

As macrocycle **[4+4]$_{Me}$** is largely insoluble in polar solvents, a 10 mg/mL sample of macrocycle **[4+4]$_{Me}$** in (9:1) $CDCl_3$:MeOD was prepared. To an NMR tube, 0.5 mL of the solution was added, followed by acetic acid (60 µL), and the reaction was monitored by ^{1}H NMR for 72 hours. After the 72 hours, the key resonances assigned to the macrocycle **[4+4]$_{Me}$** remained present (Ar–H singlet δ = 7.67 ppm) and *C<u>H</u>OB* δ = 5.08 ppm). Furthermore, no signals assignable to free diols or free boronic acids were noted. The experiment was repeated with addition of trifluoroacetic acid (20 µL), and after 72 hours resonances corresponding to the intact macrocycle were still clearly present.

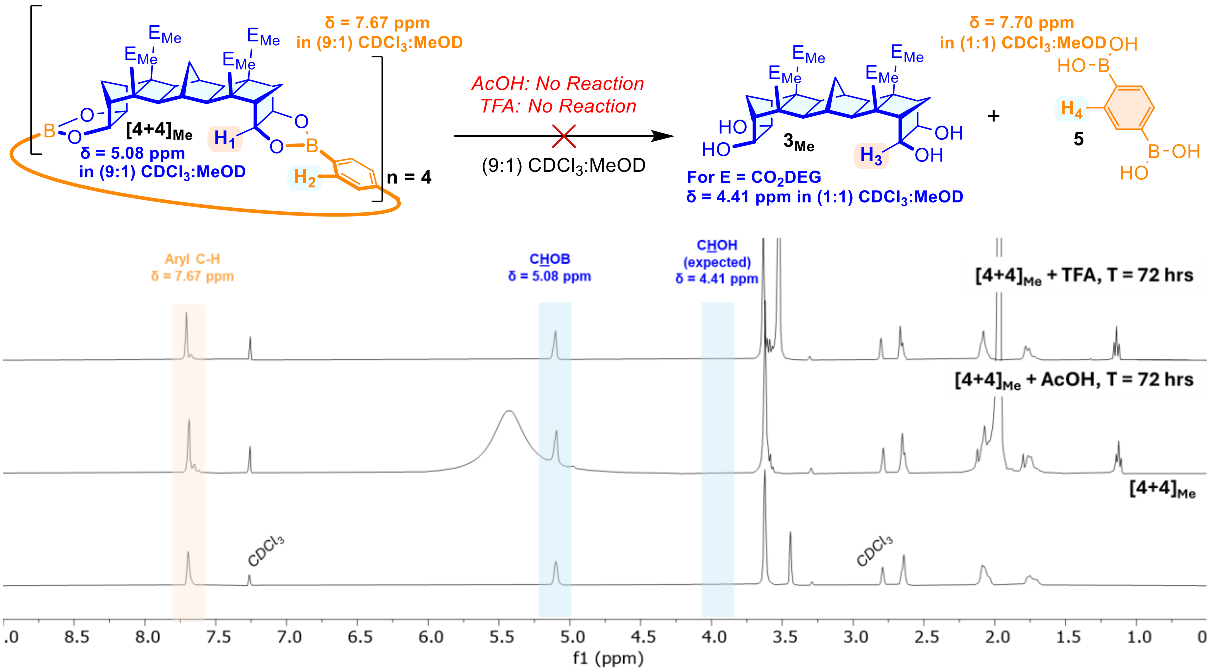


Figure S36. *Stacked ^{1}H NMR spectra of macrocycle* ***[4+4]$_{Me}$*** *,* ***[4+4]$_{Me}$*** *+ acetic acid, and* ***[4+4]$_{Me}$*** *+ trifluoroacetic acid. ((9:1) $CDCl_3$:MeOD, locked on $CDCl_3$, 400 MHz)*

1.15.4. Macrocycle [4+4]$_{DEG}$

A solution of macrocycle **[4+4]$_{DEG}$** was prepared at 7.5 mg/mL in (1:1) $CDCl_3$:MeOD (500 µL). Glacial acetic acid (100 µL) was added to give a 1.53 mM solution of macrocycle in (1:1) $CDCl_3$:MeOD with 2.92 mM acetic acid. The acidic solution was agitated, and analysed by both ^{1}H NMR and nESI-HRMS over a 24-hour period. Using the same methodology as with acetic acid, a solution of the macrocycle **[4+4]$_{DEG}$** was prepared at 7.5 mg/mL in (1:1) $CDCl_3$:MeOD with 2.18 mM trifluoroacetic acid.

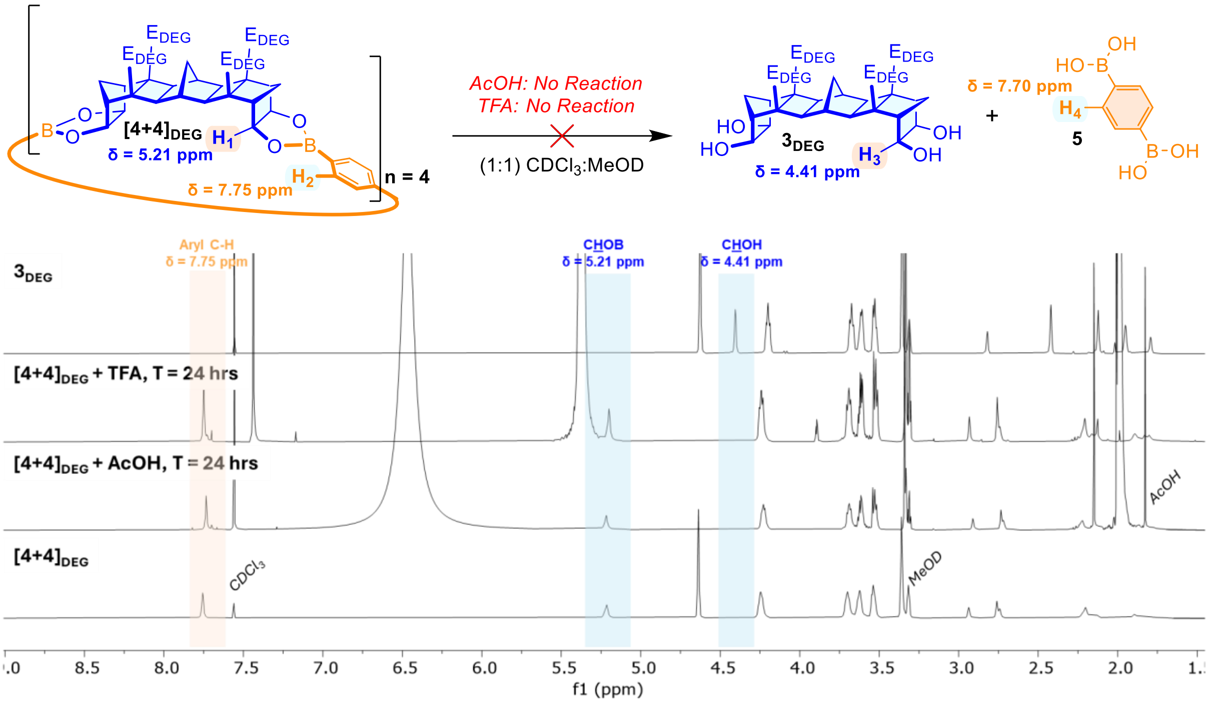


Figure S37. *Stacked ^{1}H NMR spectra of* ***3_{DEG}****,* ***$[4+4]_{DEG}$*** *+ AcOH,* ***$[4+4]_{DEG}$*** *+ TFA, and* ***$[4+4]_{DEG}$****. ((1:1) $CDCl_3$:MeOD, locked on MeOD, 400 MHz)*

For analysis by nESI-HRMS, a suitable sample was prepared at a 1:5 dilution from each ^{1}H NMR sample. For the sample comtaining acetic acid, after 24 hours the spectrum clearly showed the prescence of the macrocycle **$[4+4]_{DEG}$**, as the triply protonated species, as well as the quadruply protonated species. The other minor signals present were assigned to the [5+5] macrocycle ([(5+5) + 4H]$^{4+}$ = 1279.33, diff. = -7.8 ppm) and two [4+4] macrocycle ions (([2 × **$[4+4]_{DEG}$** + 5H]$^{5+}$ = 1637.34, diff. = 6.1 ppm). Whether the latter ion is mechanically interlocked (catenane) or an associative dimer would require further investigation. For all the major ions, the hydrates, and sometimes dihydrates were also present. Pleasingly, no signals were present that could be assigned to intermediate species or starting materials.

For the sample containing trifluoroacetic acid, the sample was initially prepared at a 1:5 dilution in acetonitrile, however no meaningful signal was obtained. Addition of 1 µL of a 2 mg/mL aq. NaCl solution was required to promote ionisation, and a signal was obtained, albiet significantly noisier than the related spectrum in which acetic acid was used. A signal coressponding to the [**$[4+4]_{DEG}$** + 3H]$^{3+}$ ion was observed at the expected 1364.61 *m/z*, as well as a signal coressponding to the [**$[4+4]_{DEG}$** + 4H]$^{4+}$ ion. A series of triply charged ions with similar isotopic splitting patterns to those of the previously observed ions for **$[4+4]_{DEG}$** appeared between 1364–1394 *m/z*, given that there are two ion sources are present (protons and sodium ions), the series is likely triply charged **$[4+4]_{DEG}$** as a distribution of the proton and sodium ion adducts. In support of the mixed cation hypothesis, the [**$[4+4]_{DEG}$** + Na + 2H]$^{3+}$ ion appeared to be present (1371.60681 *m/z*, diff = -5.01 ppm).

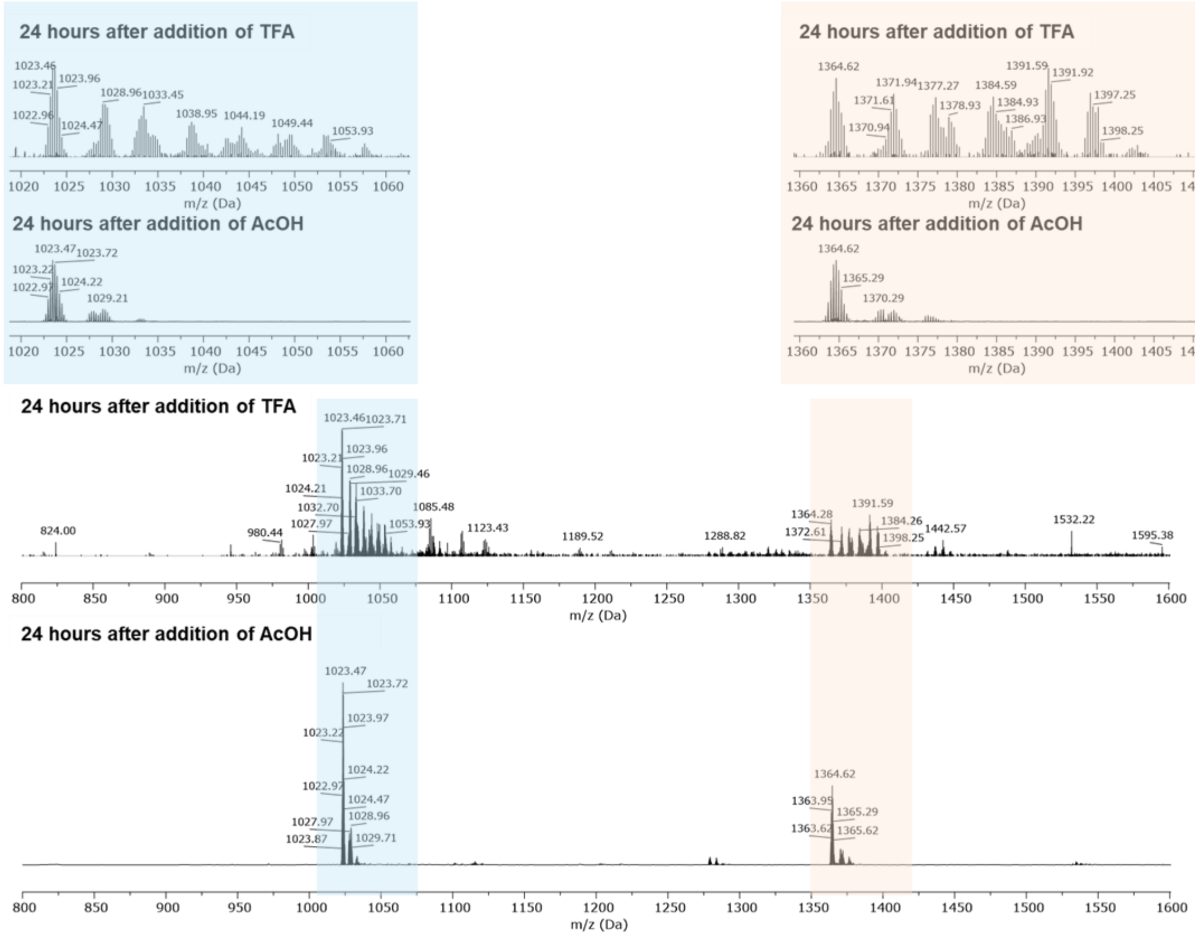


Figure S38. *nESI-HRMS spectrum of macrocycle* ***[4+4]***$_{\mathbf{DEG}}$ *in trifluoroacetic acid stability study after 24 hours.*

1.15.5. *Endo*-norbornane systems

As the structure of assemblies **[2+2]**$_{\mathbf{BiPh}}$ and **[3+2]**$_{\mathbf{TZ}}$ was confirmed by SC-XRD, they were selected for evaluation of stability to acids. Each assembly was prepared in a 35% MeOD:$CDCl_3$ solution at a concentration of 4 mg/mL. Then, samples for analysis were prepared from 550 µL of the assembly solution and 50 µL of either acetic acid or trifluoroacetic acid. The samples were monitored by ^{1}H NMR spectroscopy over a 24-hour period. The spectra of each assembly after the 24 hours are highlighted in figures **S39** and **S40**. In all cases no hydrolysis products were observed (*ie.* C$\underline{H}$OH at δ = 3.95 ppm), and resonances assigned to the intact products (*ie.* aryl protons and C$\underline{H}$OB at δ = 4.45 ppm) remained present.

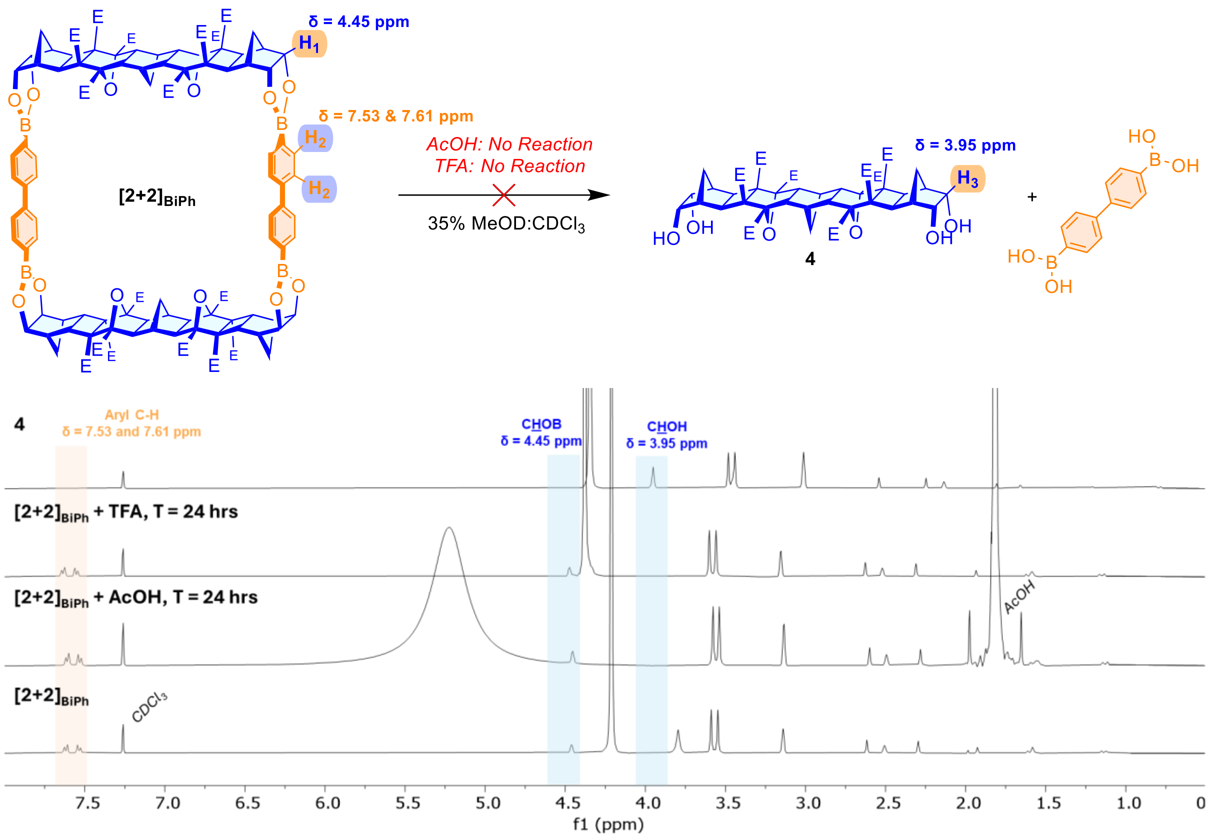


Figure S39. *Stacked ^{1}H NMR spectra of **[2+2]$_{BiPh}$**, **[2+2]$_{BiPh}$** + acetic acid, **[2+2]$_{BiPh}$** + trifluoracetic acid and starting bis(diol) **4**. (35% MeOD/CDCl$_3$, locked on CDCl$_3$).*

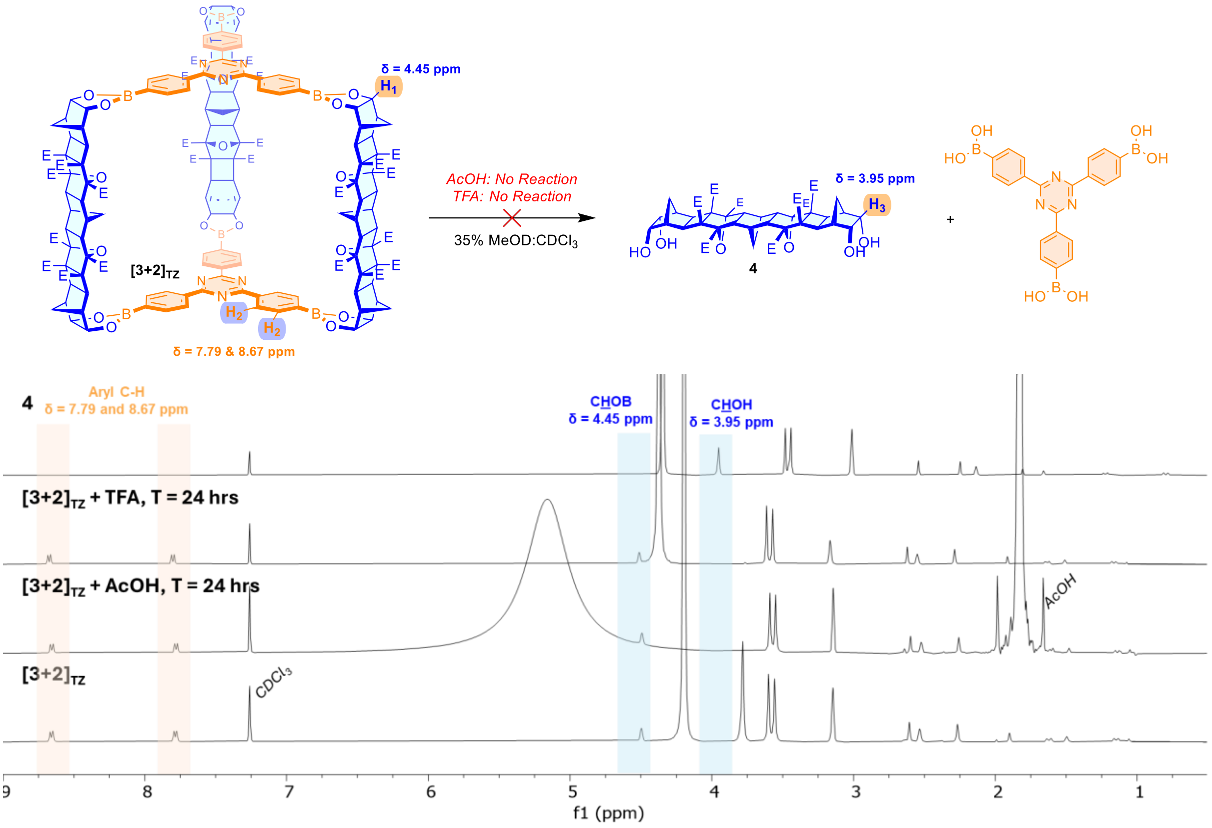


Figure S40. *Stacked ^{1}H NMR spectra of **[3+2]$_{TZ}$**, **[3+2]$_{TZ}$** + acetic acid, **[3+2]$_{TZ}$** + trifluoroacetic acid and starting bis(diol) **4**.*

1.16. Titration of [2+2]$_{Py}$

A 1.0 mM solution of **[2+2]$_{Py}$** in $CDCl_3$ was prepared and a solution containing **[2+2]$_{Py}$** (1.0 mM) and 3,6-dinitro-1,8-naphthalimide (40 mM) was titrated in. After each aliquot was added, a ^{1}H NMR spectrum was obtained, and a 1:1 binding ($K_a = 0.0196$ $M^{-1} \pm$ 0.186%) was determined from 40 data points using Bindfit.[36, 37] Binding within the cavity of the macrocycle was evident from the titration, as the resonances with the largest change in chemical shift were the central norbornane bridge protons ($\Delta\delta = 0.21$ ppm), and the pyrene protons ($\Delta\delta = 0.11$ and 0.10 ppm), while *exohedral* environments showed smaller changes, such as the *exo*-protons on the terminal norbornane boronic esters ($\Delta\delta = 0.021$ ppm) and the bridgehead protons of the terminal norbornanes ($\Delta\delta = 0.018$ ppm).

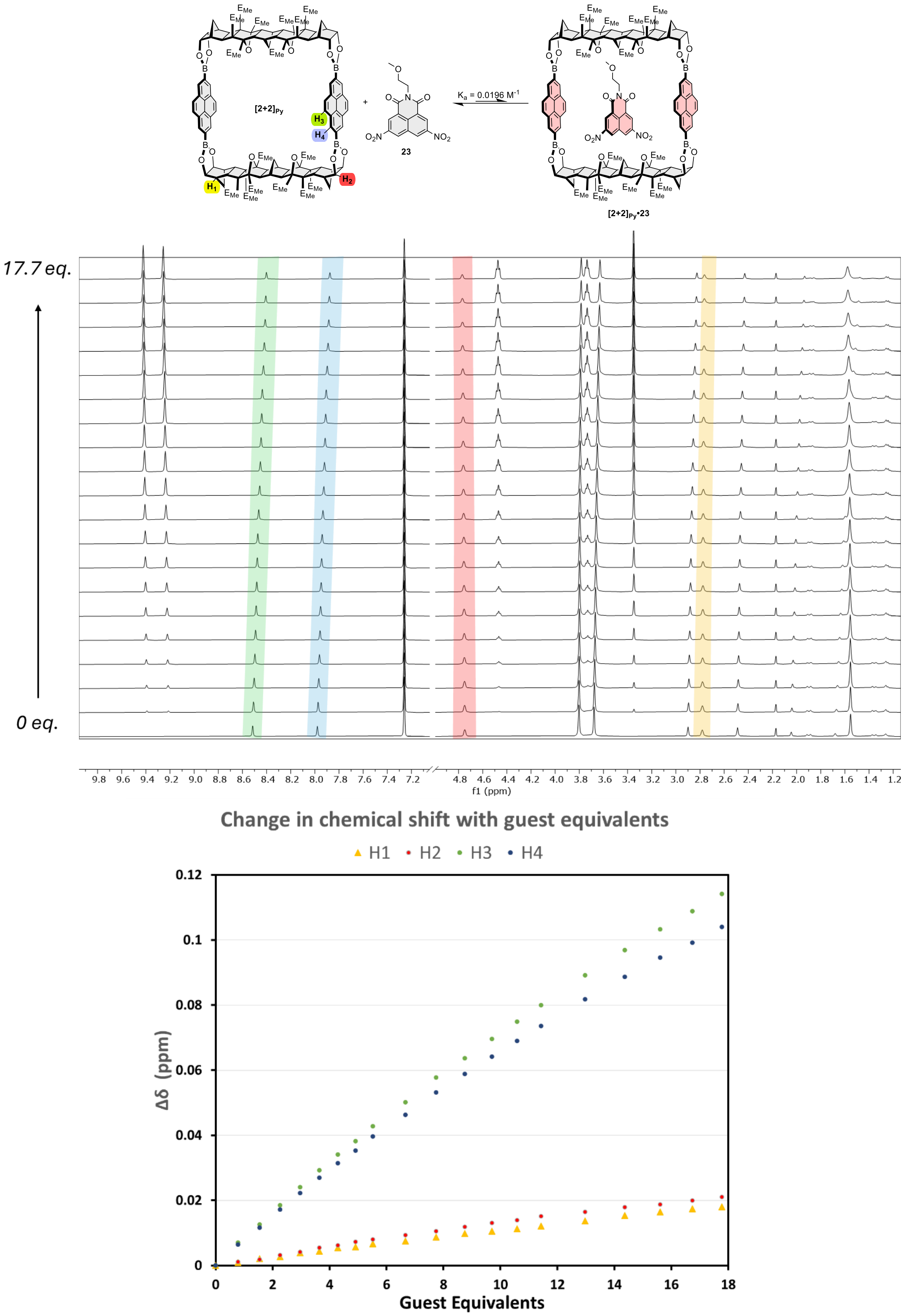
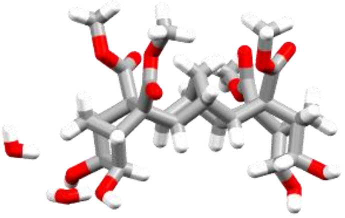


Figure S41. *Top: Stacked ^{1}H NMR spectra of the titration of **[2+2]$_{Py}$** with 3,6-dinitro-1,8-naphthalimide **23**. Bottom: Plot of guest equivalence against change in chemical shift for four resonances.*

1.17. X-Ray Crystallography

1.17.1. Bis(diol) 3_{Me}

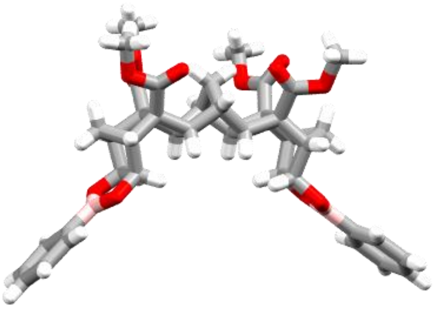
Table S2. *Crystallographic parameters of bis(diol) 3_{Me}*



Identification code	**Bis(diol) 3_{Me}**
Empirical formula	$C_{29}H_{40}O_{14}$
Formula weight	612.61
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.464(3)
b/Å	12.141(2)
c/Å	14.284(3)
α/°	90
β/°	92.34(3)
γ/°	90
Volume/Å^3	2679.6(9)
Z	4
ρ_{calc}g/cm^3	1.519
μ/mm^{-1}	0.121
F(000)	1304.0
Crystal size/mm^3	0.1 × 0.025 × 0.025
Radiation	Synchrotron (λ = 0.710754)
2Θ range for data collection/°	2.636 to 64.48
Index ranges	$-23 \leq h \leq 23$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$
Reflections collected	48763
Independent reflections	7856 [R_{int} = 0.0381, R_{sigma} = 0.0209]
Data/restraints/parameters	7856/0/402
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0379, wR_2 = 0.1021
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.1050
Largest diff. peak/hole / e Å^{-3}	0.44/-0.30

1.17.2. $[1+2]_{Ph}$

Table S3. *Crystallographic parameters of* ***$[1+2]_{Ph}$***



Identification code	**[1+2]Ph**
Empirical formula	$C_{41}H_{42}B_2O_{12}$
Formula weight	748.36
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	*Pbca*
a/Å	11.912(2)
b/Å	22.398(5)
c/Å	26.849(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7163(2)
Z	8
ρ_{calc}g/cm^3	1.388
μ/mm^{-1}	0.101
F(000)	3152.0
Crystal size/mm^3	0.1 × 0.03 × 0.03
Radiation	Synchrotron (λ = 0.710917)
2Θ range for data collection/°	3.034 to 64.218
Index ranges	$-15 \leq h \leq 15$, $-30 \leq k \leq 30$, $-37 \leq l \leq 37$
Reflections collected	125528
Independent reflections	11064 [R_{int} = 0.0696, R_{sigma} = 0.0247]
Data/restraints/parameters	11064/0/501
Goodness-of-fit on F^2	1.077
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1534
Final *R* indexes [all data]	R_1 = 0.0578, wR_2 = 0.1539
Largest diff. peak/hole / e Å^{-3}	1.09/-0.33

1.17.3. [4+4]Bn

A series of conditions were trialled to obtain high quality crystals of **[4+4]Bn**, after some tribulation use of DMSO as an anti-solvent was found to be essential. The best crystals (entry 14) were obtained by slow evaporation from a sealed vial with a needle pierced into the septum cap over the course of a week.

Table S4. *Summary of trialled crystallisation conditions for* ***[4+4]$_{Bn}$***

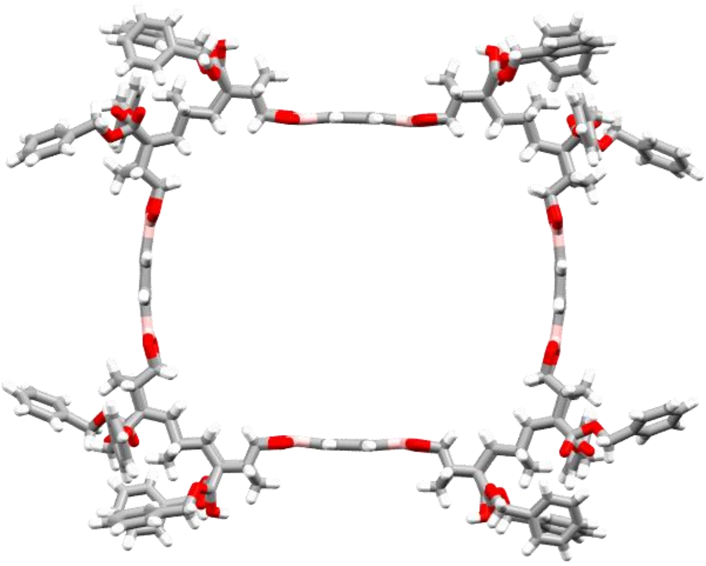
Entry	Solvent	Anti-solvent	Technique[a]	Material
1	Chloroform	Pentane	***i.***	Crystalline powder.
2	Chloroform	Diethyl Ether	***i.***	Clear solution.
3	Chloroform	Acetone	***i.***	Clear solution.
4	Chloroform	Heptane	***ii.***	Amorphous powder.
5	Chloroform	-	***iii.***	Glassy solid.
6	Dichloromethane	Ethyl Acetate	***iii.***	Crystalline powder.
7	Dichlorobenzene	Hexane	***i.***	Amorphous powder.
8	Dichlorobenzene	Pentane	***i.***	Amorphous powder.
9	Dichlorobenzene	Acetone	***i.***	Clear solution.
10	Dichlorobenzene	Ethyl Acetate	***i.***	Clear solution.
11	Chloroform	DMSO	***iii.***	Small crystals in fine precipitate.
12	Dichloromethane	DMSO	***iii.***	Glassy pieces, some crystals.
13	Dichloromethane	DMSO/Acetone	***iii.***	Cubic crystals.
14	Dichloromethane	DMSO/Ethyl Acetate	***iii.***	Cubic crystals.

[a] (i) Vapour Diffusion, **[4+4]$_{Bn}$** was dissolved in solvent in inner container, anti-solvent in outer container, (ii) Layered diffusion, **[4+4]$_{Bn}$** dissolved in solvent, anti-solvent carefully layered on top in a sealed vessel, (iii) Evaporation, a solution of **[4+4]$_{Bn}$** was made up in mix of solvent and anti-solvent and left in a vessel open to air for solvent to evaporate.

1.17.3.1 Data collection

The crystals were prone to rapid desolvation and loss of crystallinity upon exposure to air, however by cold mounting the crystals for analysis (-20 °C), they were amenable to SC-XRD analysis. The large unit cell ($a = b = c = 33.945$ Å) and rapid desolvation led to difficulty obtaining resolution beyond ~0.8 Å, and the reflections with higher resolution were cut prior to structure solution. Large amounts of disorder were present in two of the benzyl esters, and the benzene portions were fit using the fragment tool in Olex2.

Table S5. *Crystal data and structure refinement for macrocycle* ***[4+4]$_{Bn}$****.*



Identification code	**[4+4]$_{Bn}$**
Empirical formula	$C_{233.37}H_{206.28}B_8O_{48}$

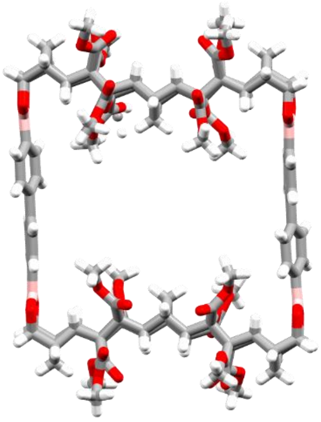
Formula weight	3865.19
Temperature/K	100(2)
Crystal system	cubic
Space group	I23
a/Å	33.899(4)
b/Å	33.899(4)
c/Å	33.899(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	38953(13)
Z	6
ρ_{calc}g/cm^3	0.989
μ/mm^{-1}	0.068
F(000)	12183.0
Crystal size/mm^3	0.3 × 0.3 × 0.3
Radiation	Synchrotron (λ = 0.710922)
2Θ range for data collection/°	1.7 to 56.568
Index ranges	$-45 \leq h \leq 45$, $-45 \leq k \leq 45$, $-44 \leq l \leq 44$
Reflections collected	314045
Independent reflections	16076 [R_{int} = 0.0640, R_{sigma} = 0.0264]
Data/restraints/parameters	16076/476/636
Goodness-of-fit on F^2	1.681
Final R indexes [I>=2σ (I)]	R_1 = 0.1543, wR_2 = 0.3829
Final R indexes [all data]	R_1 = 0.1715, wR_2 = 0.4208
Largest diff. peak/hole / e Å^{-3}	0.60/-0.42

1.17.4. [2+2]$_{\text{BiPh}}$

Crystals were grown from slow diffusion of hexane into a solution of **[2+2]$_{\text{BiPh}}$** in chloroform. The crystals were cold mounted (-20 °C) for analysis. The collected data was solved in the triclinic P-1 space group, and the crystal structure contained a large amount of disordered solvent that was removed during refinement by the Platon SQUEEZE protocol.[8]

The solvent mask was calculated and 649 electrons were found in a volume of 1635\%A^3^ in 1 void per unit cell. This is consistent with the presence of 11 $CHCl_3$ per Unit Cell which account for 638 electrons per unit cell.

Table S6. *Crystallographic parameters of macrocycle* ***[2+2]$_{\text{BiPh}}$***



Identification code	**[2+2]$_{\mathbf{BiPh}}$**
Empirical formula	$C_{124.99}H_{122.96}B_4Cl_{33}O_{44}$
Formula weight	3542.11
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.6260(19)
b/Å	18.312(4)
c/Å	22.349(5)
α/°	89.57(3)
β/°	88.27(3)
γ/°	78.50(3)
Volume/Å^3	3858.6(14)
Z	1
ρ_{calc}g/cm^3	1.524
μ/mm^{-1}	0.657
F(000)	1806.0
Crystal size/mm^3	0.1 × 0.05 × 0.03
Radiation	Synchrotron (λ = 0.710749)
2Θ range for data collection/°	1.822 to 64.378
Index ranges	$-13 \leq h \leq 14$, $-25 \leq k \leq 25$, $-30 \leq l \leq 30$
Reflections collected	70031
Independent reflections	19907 [R_{int} = 0.0675, R_{sigma} = 0.0601]
Data/restraints/parameters	19907/0/739
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0948, wR_2 = 0.2929
Final R indexes [all data]	R_1 = 0.1157, wR_2 = 0.3120
Largest diff. peak/hole / e Å^{-3}	0.83/-0.76

Offset π–π stacking

The stacking of **[2+2]$_{\mathbf{BiPh}}$** relied on offset π–π stacking, a motif characterised in literature[38] as having a distance between the ring centroids of approximately 3.8 Å, and a displacement of approximately 20° between the ring-centroid vector, and the normal vector of one of the ring planes. The crystal data measurements for macrocycle **[2+2]$_{\mathbf{BiPh}}$** were in agreement with these values (Figure S42).

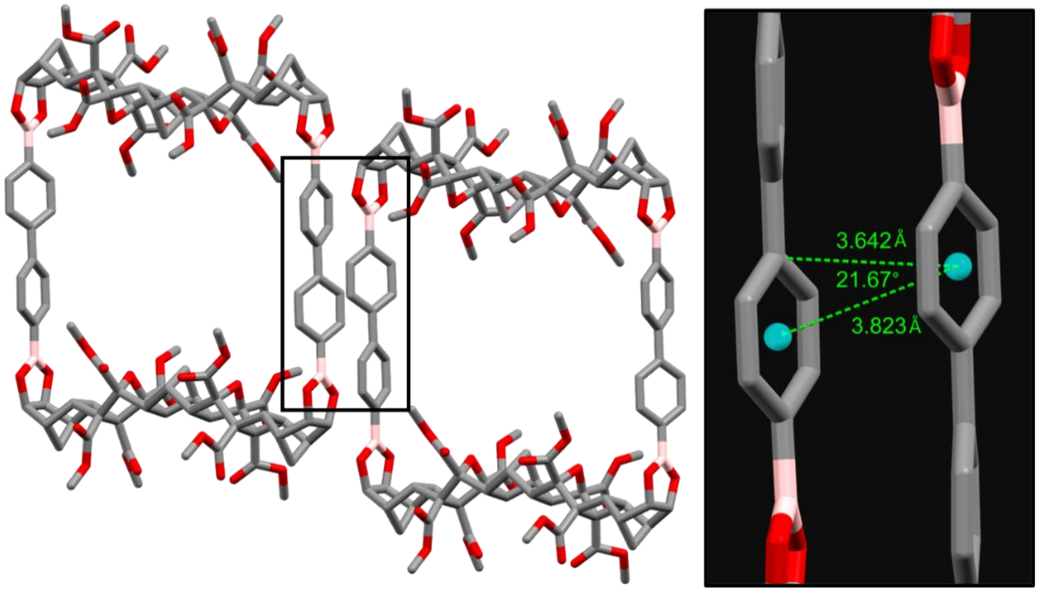
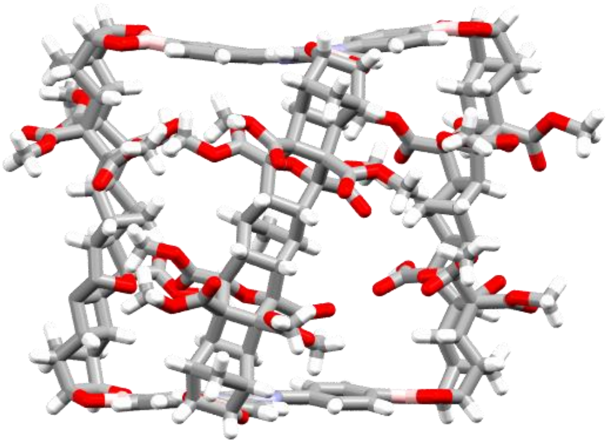


Figure S42. *Offset π–π stacking of two units in the [2+2] macrocycle* ***244***$_{\textbf{\textit{Biph}}}$ *crystal structure.*

1.17.5. [3+2]$_{\text{TZ}}$

Carefully cold mounting the crystals under a stream of nitrogen gas (-20 °C) proved necessary for obtaining reasonable data, and upon irradiation with X-rays the crystals tended to lose crystallinity. The collected data was solved in the monoclinic *C2/c* space group, and the crystal structure contained a large amount of disordered solvent that was removed during refinement by the Platon SQUEEZE protocol.[8] During the refinement process, large amounts of disorder were present in three of the 24 methyl ester substituents and as such they only partially modelled. Attempts to model the esters completely led to an unstable model. A solvent mask was calculated, and 3406 electrons were found in a volume of 22614 Å^3 in 1 void per unit cell. This is consistent with the presence of 7.625[$CHCl_3$] per Unit Cell which account for 3538 electrons per unit cell.

Table S7. *Crystal data and structure refinement for cage* ***[3+2]***$_{\textbf{\textit{TZ}}}$.



Identification code	**[3+2]**$_{\textbf{TZ}}$
Empirical formula	$C_{181.62}H_{165.62}B_6Cl_{22.88}N_6O_{66}$
Formula weight	4364.21
Temperature/K	100(2)
Crystal system	monoclinic

Space group	*C2/c*
a/Å	70.124(14)
b/Å	18.521(4)
c/Å	43.849(9)
α/°	90
β/°	119.40(3)
γ/°	90
Volume/Å^3	49617(21)
Z	8
ρ_{calc}g/cm^3	1.168
μ/mm^{-1}	0.323
F(000)	17954.0
Crystal size/mm^3	0.1 × 0.02 × 0.02
Radiation	Synchrotron (λ = 0.710922)
2Θ range for data collection/°	1.334 to 56.6
Index ranges	$-93 \leq h \leq 93$, $-24 \leq k \leq 24$, $-58 \leq l \leq 58$
Reflections collected	395038
Independent reflections	61092 [R_{int} = 0.1178, R_{sigma} = 0.0656]
Data/restraints/parameters	61092/0/2245
Goodness-of-fit on F^2	1.485
Final *R* indexes [I>=2σ (I)]	R_1 = 0.1758, wR_2 = 0.4594
Final *R* indexes [all data]	R_1 = 0.2286, wR_2 = 0.5001
Largest diff. peak/hole / e Å^{-3}	1.11/-0.67

1.18. Determination of dihedral angles

In all cases, dihedral angles between terminal diol or bis(boronic ester) assemblies were determined in Mercury[9] by generating two planes intersecting the 4 atoms of the diol group (HO-C-C-OH) or the five atoms of the boronic ester. The angle between the planes was taken as the dihedral angle between the two terminal groups.

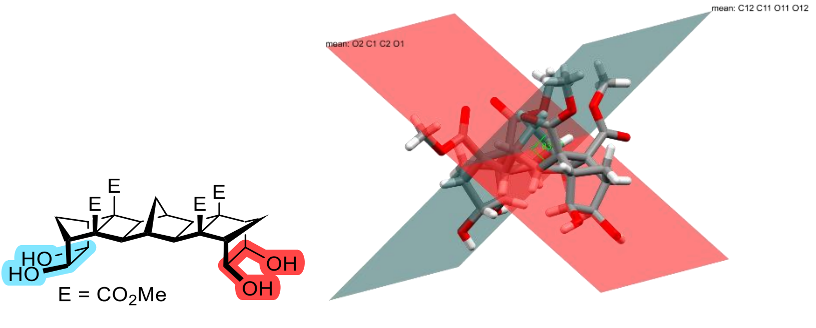


Figure S43. *Method for determination of dihedral angles.*

1.19. Density functional theory calculations

Density functional theory calculations were performed using ORCA 6.1.0.[39, 40] Geometry optimizations were carried out using the r2SCAN-3c composite method.[41] The resolution-of-identity (RI) approximation was employed for the Coulomb integrals using the def2-mTZVPP/J auxiliary basis set.[42]

All structures (bis(diol), benzene-1,4-diboronic acid, water, and the [3+3], [4+4], and [5+5] macrocycles) were optimised using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm with redundant internal coordinates. Convergence criteria were set to 1.0 × 10^{-6} Eh for the energy change,

1.0×10^{-4} Eh/bohr for the maximum gradient, and 3.0×10^{-5} Eh/bohr for the RMS gradient. The SCF convergence was achieved with tight criteria (TolE = 1.0×10^{-8} Eh) using the SOSCF procedure with L-BFGS Hessian updates. Integration grids were generated using the OptM3 radial grid and Lebedev-302 angular grid with adaptive pruning. All simulation input and output data are shared on Zenodo.

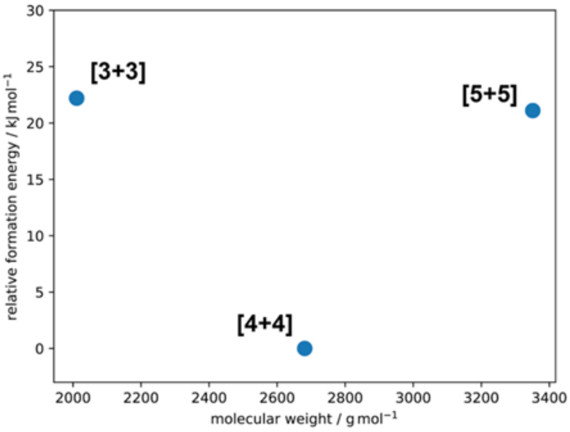


Figure S44. *Computed relative formation energies for the [3+3], [4+4] and [5+5] macrocycles using density functional theory.*

1.20. Model coordinates

The XYZ coordinates of the molecular model of cage **$[3+2]_{Ph}$** are provided.

Table S8. *XYZ coordinates of molecular model for cage* ***$[3+2]_{Ph}$****.*

Element	X	Y	Z
C	-5.61238	1.104229	1.127595
C	-4.68373	-0.11369	1.350569
C	-5.78257	1.145711	-0.43989
C	-5.00576	-0.10054	-0.91074
C	-5.82111	-1.32894	-0.44271
C	-5.56943	-1.35638	1.110644
C	-3.80775	-0.10178	0.072614
C	-5.23221	-2.69741	-0.88923
C	-4.85224	-2.7209	1.292686
C	-6.14335	-3.89078	-0.43563
C	-5.9	-3.88005	1.154951
C	-5.12766	2.512175	-0.79298
C	-4.96478	2.48203	1.421809
C	-6.12638	3.652479	-0.40799
C	-6.0116	3.634954	1.196293
O	-4.11221	2.678912	0.256636
O	-4.11468	-2.87208	0.038371
C	-5.34952	-5.23149	-0.52084
C	-5.16136	-5.23839	1.047639
C	-5.41117	5.030088	-0.42899
C	-5.27458	5.0024	1.145415

C	-5.85114	-6.527	1.502554
C	-4.93846	-7.70608	1.082728
C	-5.948	6.299956	1.591923
C	-5.03415	7.473979	1.153837
C	-6.16976	6.3285	-0.69958
C	-5.18238	7.493814	-0.41296
C	-6.05005	-6.56152	-0.79127
C	-5.03756	-7.69924	-0.48731
C	-6.97991	-6.69827	0.448489
C	-7.08649	6.465461	0.548861
O	-3.69146	-7.46395	-0.92964
O	-3.54691	-7.51907	1.361917
O	-3.84862	7.301504	-0.90358
O	-3.63415	7.274144	1.383482
C	-7.43361	3.521482	-1.11116
C	-7.24474	3.468307	2.01507
C	-7.52561	-3.7935	-0.98629
C	-7.03158	-3.83405	2.123159
C	-3.98447	-2.81565	2.51096
C	-4.8161	-2.73858	-2.3274
C	-4.42613	2.577406	-2.11875
C	-4.25602	2.589942	2.740483
O	-3.46956	1.883884	-2.46783
O	-4.91261	3.513987	-2.97555
O	-4.81163	2.367491	3.818892
O	-2.96875	3.005927	2.900907
O	-3.6012	-2.18402	-2.57419
O	-5.49199	-3.15858	-3.26841
O	-2.67628	-3.20145	2.523677
O	-4.39337	-2.55652	3.646042
O	-7.16333	-4.49811	3.153303
O	-8.02346	-2.95013	1.805193
O	-7.89096	-4.82947	-1.80151
O	-8.35106	-2.89135	-0.82432
O	-7.36551	4.363505	3.041492
O	-8.1272	2.615064	1.89401
O	-8.52752	3.908779	-0.38794
O	-7.63067	3.102403	-2.25367
C	-1.94248	-3.3891	1.319153
C	-3.24173	-2.04419	-3.95681
C	-4.35314	3.526235	-4.29654
C	-2.06709	3.019649	1.798846
C	-9.11749	-2.85601	2.721973
C	-9.15043	-4.70321	-2.46748
C	-8.46655	4.165386	3.933247
C	-9.80304	3.732847	-1.01188

B	-2.97398	7.226534	0.167747
B	-2.85073	-7.42414	0.169355
C	1.860091	1.075204	-5.44341
C	1.232531	-0.15215	-4.74012
C	3.298002	1.162331	-4.80128
C	3.347633	-0.07489	-3.88208
C	3.386236	-1.31163	-4.81127
C	1.915768	-1.38677	-5.36834
C	1.895627	-0.10894	-3.34032
C	3.518332	-2.6682	-4.06149
C	1.434434	-2.75536	-4.81358
C	3.604611	-3.87186	-5.06025
C	2.106902	-3.89648	-5.65001
C	3.234719	2.533628	-4.06887
C	1.241951	2.440755	-5.04527
C	3.375536	3.66903	-5.13501
C	1.93292	3.606998	-5.84411
O	1.811895	2.664679	-3.7232
O	2.164478	-2.87144	-3.54989
C	3.306392	-5.21122	-4.31948
C	1.864048	-5.26487	-4.96575
C	2.996952	5.042136	-4.51821
C	1.568824	4.970144	-5.19172
C	1.870135	-6.56547	-5.77179
C	1.783855	-7.72804	-4.74829
C	1.486556	6.259556	-6.00833
C	1.3754	7.439502	-5.00799
C	3.577854	6.351632	-5.04961
C	2.804018	7.503661	-4.35063
C	3.935403	-6.53245	-4.75511
C	3.180742	-7.67669	-4.02489
C	3.360443	-6.71655	-6.1873
C	2.955584	6.45997	-6.47051
O	2.860716	-7.42854	-2.6475
O	0.823653	-7.54444	-3.7022
O	2.564359	7.319724	-2.94881
O	0.479948	7.226287	-3.90993
C	4.644183	3.564979	-5.9097
C	1.852433	3.426333	-7.32034
C	4.748695	-3.75514	-6.00861
C	1.919732	-3.85003	-7.12694
C	-0.04883	-2.88351	-4.638
C	4.55938	-2.66789	-2.98474
C	4.020927	2.630612	-2.79347
C	-0.25663	2.506246	-5.09997
O	3.845351	1.951113	-1.78085

O	4.993347	3.580393	-2.79386
O	-0.90018	2.261951	-6.12343
O	-1.05758	2.900977	-4.07094
O	4.14826	-2.1173	-1.81325
O	5.724793	-3.05182	-3.09743
O	-0.66835	-3.35328	-3.51345
O	-0.86857	-2.595	-5.51221
O	2.661978	-4.29911	-8.00381
O	0.756971	-3.25305	-7.52006
O	5.700914	-4.72541	-5.88506
O	4.935099	-2.87343	-6.85208
O	1.007668	4.29733	-7.95052
O	2.421315	2.579563	-8.01345
O	4.559372	3.939383	-7.22205
O	5.74122	3.177934	-5.50179
C	0.032018	-3.51456	-2.28627
C	5.157883	-1.94706	-0.80761
C	5.848066	3.622742	-1.64237
C	-0.55926	2.945231	-2.73772
C	0.500997	-3.20511	-8.9264
C	6.857664	-4.58972	-6.71703
C	0.800822	4.083723	-9.34992
C	5.743195	3.783483	-8.01058
B	1.201109	7.213511	-2.7284
B	1.485506	-7.41942	-2.49195
C	0.550409	7.152686	-1.33989
C	-0.64993	7.179088	1.189342
C	-0.84543	7.144089	-1.22596
C	1.344234	7.171686	-0.18762
C	0.744909	7.187539	1.078027
C	-1.44643	7.159973	0.037565
C	0.755374	-7.33801	-1.14415
C	-0.5905	-7.3175	1.310486
C	-0.64557	-7.35012	-1.11226
C	1.480385	-7.31497	0.052317
C	0.807998	-7.30549	1.281473
C	-1.31901	-7.34064	0.113622
C	3.762459	1.213767	4.320416
C	3.487736	-0.0263	3.436796
C	2.490042	1.282773	5.249686
C	1.692974	0.024645	4.848342
C	2.506517	-1.19148	5.352355
C	3.720852	-1.24784	4.352379
C	1.942697	-0.01682	3.319055
C	1.820373	-2.56652	5.106575
C	3.508647	-2.62669	3.670771

C	2.672838	-3.74711	5.68564
C	3.929287	-3.74815	4.679927
C	1.857904	2.637803	4.818739
C	3.696428	2.571521	3.574424
C	2.689838	3.796837	5.459332
C	4.02327	3.75301	4.560729
O	2.261484	2.764674	3.41075
O	2.051831	-2.77619	3.679023
C	2.212721	-5.10351	5.06776
C	3.493319	-5.1326	4.140296
C	2.314969	5.156102	4.809906
C	3.611794	5.102073	3.907778
C	4.224964	-6.40924	4.56064
C	3.416058	-7.60064	3.984737
C	4.335017	6.409252	4.231292
C	3.500739	7.566658	3.623453
C	2.458572	6.477254	5.563783
C	2.215826	7.613014	4.531212
C	2.310635	-6.41722	5.839475
C	2.087686	-7.5754	4.82871
C	3.84277	-6.55798	6.060086
C	3.997817	6.618614	5.732701
O	1.05242	-7.36096	3.857256
O	2.990212	-7.44318	2.626888
O	1.126259	7.395172	3.624528
O	3.002792	7.329741	2.301016
C	2.733879	3.708323	6.946174
C	5.347486	3.604202	5.226129
C	2.922087	-3.61389	7.149376
C	5.30186	-3.66184	5.251986
C	4.097361	-2.75266	2.297915
C	0.37167	-2.59661	5.486008
C	0.358853	2.70397	4.868994
C	4.48765	2.642175	2.30084
O	-0.41948	2.000876	4.22257
O	-0.14195	3.652013	5.704474
O	5.701125	2.42619	2.254278
O	3.984613	3.012333	1.089982
O	-0.46477	-2.06611	4.55636
O	-0.08901	-2.9879	6.559909
O	3.438197	-3.23139	1.200079
O	5.260668	-2.45057	2.023846
O	5.702189	-4.08584	6.338899
O	6.20834	-3.05702	4.430413
O	2.366975	-4.59454	7.919955
O	3.536241	-2.71094	7.725078

O	6.296475	4.491571	4.799998
O	5.683028	2.770254	6.070568
O	3.908336	4.109127	7.520262
O	1.84213	3.312805	7.699777
C	2.029892	-3.42818	1.201137
C	-1.83637	-1.91997	4.955033
C	-1.56583	3.664318	5.879618
C	2.579727	3.017765	0.857814
C	7.553652	-2.97134	4.908258
C	2.505238	-4.44381	9.336641
C	7.617581	4.307842	5.317116
C	4.007983	3.967933	8.940736
B	1.619795	7.285098	2.335058
B	1.60894	-7.35234	2.590082
H	7.611157	4.428918	6.426724
H	8.205594	5.115771	4.816382
H	7.995467	3.294257	5.041232
H	3.239638	4.606154	9.439018
H	5.046068	4.317815	9.162348
H	3.866478	2.898128	9.22663
H	5.409074	6.425272	3.961023
H	1.850897	6.559711	6.484399
H	4.078441	8.52052	3.592998
H	2.037302	8.593606	5.031719
H	4.296758	7.622049	6.108575
H	4.449974	5.833715	6.377522
H	3.433444	4.99499	2.81315
H	1.341176	5.096133	4.272703
H	-1.74315	4.603909	6.45782
H	-2.08263	3.679677	4.888123
H	-1.87025	2.76158	6.460506
H	2.444042	7.18881	-0.27614
H	-1.12353	7.20192	2.18581
H	-1.47188	7.139338	-2.13437
H	-5.5517	8.45944	-0.83132
H	-5.3186	8.42857	1.656154
H	-6.24912	6.324344	2.657571
H	-4.23455	4.927103	1.53804
H	-4.45862	4.986043	-1.00449
H	-9.42855	4.26142	3.375477
H	-8.34075	4.98329	4.684562
H	-8.39389	3.157582	4.407891
H	-6.66703	6.383588	-1.68611
H	-7.85101	5.662375	0.631475
H	-7.58625	7.457689	0.60601
H	-10.5233	4.066783	-0.22511

H	-9.95269	2.658304	-1.27497
H	-9.86582	4.367361	-1.92813
H	-4.77546	4.45924	-4.74335
H	-4.69449	2.617147	-4.84629
H	-3.23629	3.553944	-4.24896
H	0.070524	4.882862	-9.62809
H	0.378273	3.064488	-9.51981
H	1.766472	4.197856	-9.89799
H	0.716134	6.257172	-6.80415
H	3.131001	7.453146	-6.93993
H	1.058399	8.381529	-5.51463
H	3.289329	5.659362	-7.16619
H	3.325484	8.482281	-4.47036
H	3.01635	5.008488	-3.40515
H	0.708726	4.876704	-4.48968
H	6.433664	4.56215	-1.79436
H	5.240754	3.655825	-0.704
H	2.510587	3.141188	-0.25501
H	2.106134	3.876163	1.393316
H	2.121422	2.049832	1.172643
H	-1.07227	3.180478	2.291548
H	-2.31989	3.859741	1.107354
H	-2.08252	2.041847	1.260662
H	1.524712	0.870825	2.794424
H	1.517954	-0.92145	2.831722
H	0.627158	0.028045	5.155569
H	4.716233	1.1132	4.889811
H	2.739817	1.289959	6.335878
H	2.820029	-1.07658	6.416031
H	8.084761	-2.44105	4.078988
H	7.582549	-2.38786	5.859689
H	7.964185	-3.9963	5.072315
H	2.028415	-3.48942	9.664819
H	1.965367	-5.33375	9.74379
H	3.586451	-4.45194	9.614303
H	4.259659	-5.75005	6.702895
H	4.13139	-7.54706	6.479164
H	1.677345	-6.47115	6.746747
H	1.855319	-8.53402	5.350013
H	3.986249	-8.55727	4.044473
H	1.238093	-5.00494	4.539156
H	3.304087	-5.11404	3.042996
H	1.741121	-4.23321	1.920311
H	-0.91314	-3.64145	1.687739
H	1.816625	-3.74082	0.14495
H	1.49761	-2.47663	1.443633

H	5.446256	-2.94412	-0.39551
H	4.642429	-1.33237	-0.0278
H	6.042878	-1.41894	-1.23449
H	-2.28409	-1.32288	4.121741
H	-1.89857	-1.38288	5.930762
H	-2.31643	-2.92626	5.019867
H	4.715822	-1.2066	4.853263
H	4.063172	-0.04995	2.4895
H	6.508215	2.723067	-1.64434
H	-4.15164	-0.11137	2.322944
H	-8.7465	-2.52515	3.721678
H	4.142417	-0.05178	-3.1087
H	-1.92449	-2.44823	0.717859
H	-2.36945	-4.22994	0.720366
H	0.494105	-2.54982	-1.96477
H	-0.77638	-3.82244	-1.57231
H	0.809863	-4.31207	-2.37332
H	3.333262	-5.08442	-3.21382
H	7.485047	-5.46929	-6.43057
H	7.375112	-3.62639	-6.49272
H	6.557644	-4.62693	-7.79173
H	-6.16154	-6.53411	2.566647
H	-5.24723	-8.66368	1.564049
H	-1.21736	-7.37962	-2.05576
H	-1.12185	-7.32189	2.278112
H	2.583829	-7.31679	0.028419
H	5.305363	-6.42826	4.324366
H	3.753517	-8.63338	-4.06168
H	5.038187	-6.57544	-4.65985
H	1.552795	-8.70028	-5.24344
H	3.584886	-7.7166	-6.61943
H	-5.36457	-8.66804	-0.93346
H	1.124961	-6.61371	-6.58777
H	3.703634	-5.92556	-6.89178
H	-7.48342	-7.68755	0.508537
H	-6.53674	-6.64003	-1.7832
H	-7.74285	-5.89001	0.499921
H	1.007062	-5.23088	-4.25532
H	-4.11317	-5.18294	1.417385
H	0.429744	-4.24154	-9.33429
H	-0.47804	-2.66819	-8.98862
H	-4.41844	-5.12297	-1.12047
H	-4.0543	-1.52169	-4.5145
H	-3.03841	-3.05121	-4.39467
H	-2.30457	-1.43438	-3.91842
H	-1.48986	3.086027	-2.12737

H	0.140435	3.807773	-2.61807
H	-0.05767	1.984798	-2.46926
H	-3.15408	-0.99395	-0.04065
H	-6.50976	-1.31627	1.708411
H	-6.58027	0.990612	1.670158
H	-6.84811	1.121097	-0.7659
H	-6.90166	-1.24435	-0.70488
H	-4.73676	-0.10557	-1.98681
H	-9.97491	-4.66418	-1.71586
H	-9.15763	-3.78119	-3.09683
H	-9.20504	-5.62785	-3.0933
H	-9.62721	-3.84528	2.808523
H	-9.78142	-2.08987	2.250243
H	1.685949	-1.00008	-2.7092
H	1.643926	0.791764	-2.73759
H	0.124655	-0.17983	-4.77022
H	4.117186	1.154272	-5.55702
H	1.881607	0.950886	-6.55157
H	1.856989	-1.372	-6.48132
H	4.153836	-1.21198	-5.61357
H	6.06549	2.714715	-8.00447
H	6.554877	4.434356	-7.60633
H	5.418856	4.108209	-9.02971
H	1.315969	-2.64323	-9.44239
H	4.678891	6.435927	-4.98476
H	-3.16426	0.799226	-0.03666

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