Supporting information for the article:

Rapid access to molecular complexity from bioderived 5-HMF derivatives via cascade cycloadditions

Gleb M. Averochkin, Evgeniy G. Gordeev, Fedor A. Kucherov, and Valentine P. Ananikov*

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky pr. 47, Moscow 119991, Russia.

Table of contents

1. General information

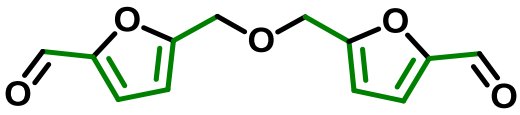
NMR spectra were recorded using Bruker Fourier 300 HD spectrometer at frequencies of 300.1 MHz (^{1}H) and 75.5 MHz (^{13}C) and Bruker Avance NEO at frequencies of 300.1 MHz (^{1}H) and 75.5 MHz (^{13}C) with the residual solvent peak as an internal standard for ^{1}H (Acetone d6 2.05, $CDCl_3$ 7.26, DMSO d6 2.50) and ^{13}C (Acetone d6 29.84, $CDCl_3$ 77.16, DMSO d6 39.52).

High-resolution mass spectra were obtained on a Bruker maXis Q-TOF instrument (Bruker Daltonik GmbH, Germany) equipped with an electrospray ionization (ESI) ion source. The experiments were performed in positive (+) MS ion mode (HV capillary, 4500 V; HV end plate offset, −500 V) with a scan range of m/z 50–1500. External calibration of the mass spectrometer was performed using a low-concentration tuning mix solution (Agilent Technologies). The direct syringe injection was applied to the analysed solutions in CH3CN (flow rate, 3 µl min^{-1}) for analytical characterization. Nitrogen was applied as the nebulizer gas (1 bar) and dry gas (4.0 L min^{-1}, 200 °C). The spectra were processed using the Bruker Data Analysis 4.0 software package.

X-ray diffraction data were collected at 100 K on a Bruker Quest D8 diffractometer equipped with a Photon-III areadetector (graphite monochromator, φ- and ω-scan technique), using Mo Kα-radiation (0.71073 Å).

2. Synthesis of 5-HMF derivatives

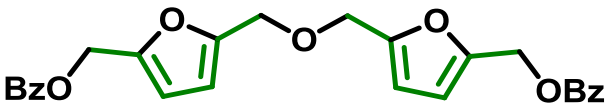
Synthesis of ((oxybis(methylene))bis(furan-5,2-diyl))dimethanol, **1**



This compound was synthesized according to a literature procedure[1] with 98% yield.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.58 (s, 2H), 7.50 (d, J = 3.5 Hz, 2H), 6.75 (d, J = 3.5 Hz, 2H), 4.62 (s, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.35, 157.25, 152.33, 123.68, 112.27, 63.71. HRMS (ESI) Calcd. for $C_{12}H_{10}O_5$ $[M + H]^+$: 235.0601, Found: 235.0609, Δ = 3.40 ppm.

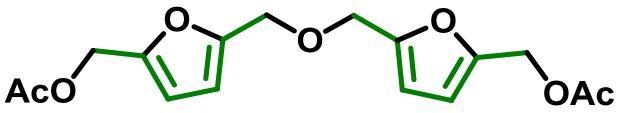
Synthesis of ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate, **1a**



((Oxybis(methylene))bis(furan-5,2-diyl))dimethanol **1c** (1.00 g, 4.2 mmol) was dissolved in pyridine (15 mL). The resulting solution was cooled to 0 °C in an ice bath, and benzoyl chloride (1220 µL, 10.5 mmol, 2.5 eq) was added dropwise via a syringe. The reaction mixture was stirred at room temperature for 24 hours. Volatiles were removed under reduced pressure. Then, 1 M HCl (15 mL) was added to the residue, and the crude mixture was washed with dichloromethane (3 x 15 mL). The combined organic phase was washed with saturated aqueous NaCl (2 x 15 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate (1.686 g, 90%) as a white powder.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.99 – 7.92 (m, 4H), 7.70 – 7.61 (m, 2H), 7.56 – 7.47 (m, 4H), 6.56 (d, J = 3.2 Hz, 2H), 6.45 (d, J = 3.2 Hz, 2H), 5.30 (s, 4H), 4.44 (s, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.28, 152.14, 149.47, 133.49, 129.27, 129.19, 128.78, 111.76, 110.68, 63.07, 58.32. HRMS (ESI) Calcd. for $C_{26}H_{22}O_7$ $[M + Na]^+$: 469.1258, Found: 469.1259, Δ = 0.21 ppm.

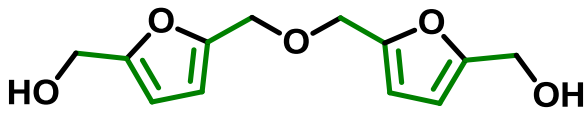
Synthesis of ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) diacetate, **1b**



((Oxybis(methylene))bis(furan-5,2-diyl))dimethanol **1c** (1.00 g, 4.2 mmol) was dissolved in pyridine (15 mL). The resulting solution was cooled to 0 °C in an ice bath, and acetic anhydride (990 µL, 10.5 mmol, 2.5 eq) was added dropwise via a syringe. The reaction mixture was stirred at room temperature for 24 hours. Volatiles were removed under reduced pressure. Then, 1 M HCl (15 mL) was added to the residue, and the crude mixture was washed with dichloromethane (3 x 15 mL). The combined organic phase was washed with saturated aqueous NaCl (2 x 15 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) diacetate (1.17 g, 92%) as a brown oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.38 (d, J = 3.2 Hz, 2H), 6.33 (d, J = 3.2 Hz, 2H), 5.05 (s, 4H), 4.50 (s, 4H), 2.10 (s, 6H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 170.61, 152.09, 149.86, 111.40, 110.63, 63.85, 58.15, 20.89. HRMS (ESI) Calcd. for $C_{16}H_{18}O_7$ $[M + K]^+$: 361.0684, Found: 361.0684, Δ = 0 ppm.

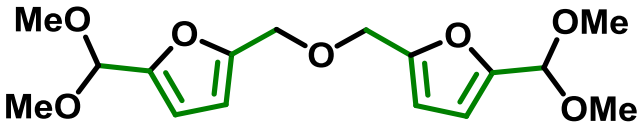
Synthesis of ((oxybis(methylene))bis(furan-5,2-diyl))dimethanol, **1c**



5,5'-(Oxybis(methylene))bis(furan-2-carbaldehyde) (7 g, 29.8 mmol) was dissolved in absolute methanol (120 mL). The resulting solution was cooled to 5 °C in an ice bath, and then sodium borohydride (1.131 g, 29.8 mmol) was added. The mixture was stirred at room temperature overnight, diluted with ethyl acetate (100 mL), washed with water (3 x 50 mL) and saturated aqueous NaCl (1 x 50 mL) and dried over sodium sulfate. The solvent was removed under reduced pressure to obtain ((oxybis(methylene))bis(furan-5,2-diyl))dimethanol (5.3 g, 89%) as a yellow powder.

^{1}H NMR (300 MHz, DMSO-d_6) δ 6.36 (d, J = 3.1 Hz, 2H), 6.23 (d, J = 3.1 Hz, 2H), 5.21 (t, J = 5.8 Hz, 2H), 4.39 (s, 4H), 4.37 (d, J = 5.8 Hz, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 155.74, 150.49, 110.33, 107.48, 63.02, 55.70. HRMS (ESI) Calcd. for $C_{12}H_{14}O_5$ $[M + Na]^+$: 261.0733, Found: 261.0745, Δ = 4.60 ppm.

Synthesis of 5,5'-(oxybis(methylene))bis(2-(dimethoxymethyl)furan), **1d**

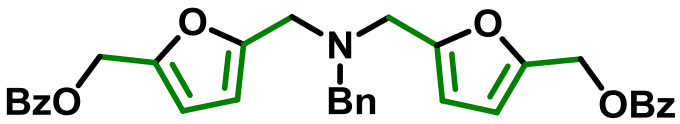


5,5'-(Oxybis(methylene))bis(furan-2-carbaldehyde) **1** (3.00 g, 12.82 mmol) was dissolved in methanol (100 mL), and then Amberlyst-15 (100 mg) and trimethyl orthoformate (4.2 ml, 38.46 mmol, 3 eq) were added. The reaction mixture was stirred at room temperature for 24 hours. Then, it was filtered through a Celite pad. Volatiles were removed under reduced pressure. The residue was dissolved in EtOAc (100 mL) and washed with water (3 x 50 mL). The organic phase was dried

over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give 5,5'-(oxybis(methylene))bis(2-(dimethoxymethyl)furan) (3.97 g, 95%) as a brown oil.

^{1}H NMR (300 MHz, DMSO-d_6) δ 6.43 – 6.38 (m, 4H), 5.42 (s, 2H), 4.40 (s, 4H), 3.25 (s, 12H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 151.15, 150.98, 110.19, 108.97, 97.35, 62.86, 52.57. HRMS (ESI) Calcd. for $C_{16}H_{22}O_7$ $[M + Na]^+$: 349.1258, Found: 349.1260, Δ = 0.57 ppm.

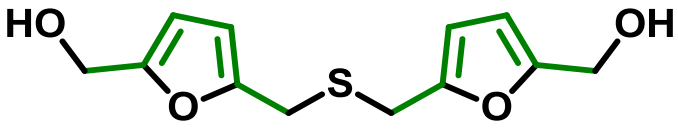
Synthesis of (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate, **1e**



Starting compound **1j** (335 mg, 1.02 mmol) was dissolved in dry pyridine (10 mL), the solution was cooled to 5°C, and benzyl chloride (275 µL, 2.37 mmol) was added dropwise. The reaction mixture was stirred at 24 °C for 16 h, the volatiles were evaporated under reduced pressure, 1 M HCl (20 mL) was added to the residue, and the product was extracted with ethyl acetate (3 × 8 mL). The combined organic phases were washed with brine, dried with sodium sulfate, evaporated and dried under high vacuum to give (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate as yellow oil (415 mg, 76%).

^{1}H NMR (300 MHz, Acetone-d_6) δ 8.05 – 7.99 (m, 4H), 7.66 – 7.58 (m, 2H), 7.52 – 7.45 (m, 4H), 7.42 – 7.36 (m, 2H), 7.30 – 7.17 (m, 3H), 6.52 (d, J = 3.1 Hz, 2H), 6.33 (d, J = 3.1 Hz, 2H), 5.33 (s, 4H), 3.67 (s, 4H), 3.62 (s, 2H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 166.39, 154.38, 150.10, 140.05, 134.02, 130.99, 130.24, 129.63, 129.43, 129.01, 127.75, 112.23, 110.52, 59.25, 57.72, 50.14. HRMS (ESI) Calcd. for $C_{33}H_{29}NO_6$ $[M + H]^+$: 536.2068, Found: 536.2066, Δ = 0.56 ppm.

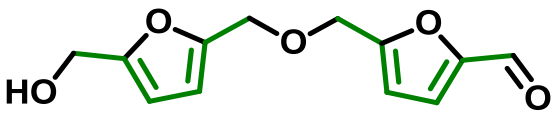
Synthesis of ((thiobis(methylene))bis(furan-5,2-diyl))dimethanol, **1f**



Starting compound **1i** (410 mg, 1.64 mmol) was dissolved in methanol (10 mL), and $NaBH_4$ (186 mg, 4.92 mmol) was added portionwise. The mixture was stirred at 24°C for 16 h, poured into brine, and extracted with ethyl acetate (3 × 5 mL). Combined organic phases were dried over sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by recrystallization from chloroform/hexanes to obtain ((thiobis(methylene))bis(furan-5,2-diyl))dimethanol as yellow crystals (330 mg, 79%).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.20 (d, *J* = 3.2 Hz, 2H), 6.12 (d, *J* = 3.2 Hz, 2H), 4.55 (s, 4H), 3.68 (s, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 153.89, 151.47, 108.80, 108.67, 57.54, 28.19. HRMS (ESI) Calcd. for $C_{12}H_{14}O_4S$ [M + Na]$^+$: 277.0505, Found: 277.0508, Δ = 1.08 ppm.

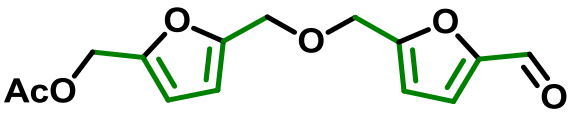
Synthesis of 5-(((5-(hydroxymethyl)furan-2-yl)methoxy)methyl)furan-2-carbaldehyde, **1g**



((Oxybis(methylene))bis(furan-5,2-diyl))dimethanol (1 g, 4.2 mmol) was dissolved in dry DCM (75 mL). MnO_2 (2.19 g, 25.2 mmol, 6 eq) was added to the solution. The reaction mixture was stirred at room temperature for 24 hours and then filtered through a small pad of Celite. Volatiles were removed under reduced pressure. The obtained residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate, which gave 5-(((5-(hydroxymethyl)furan-2-yl)methoxy)methyl)furan-2-carbaldehyde (0.694 g, 70%) as a yellow powder.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.59 (s, 1H), 7.19 (d, *J* = 3.5 Hz, 1H), 6.52 (d, *J* = 3.5 Hz, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.58 (s, 2H), 4.56 (s, 2H), 4.51 (s, 2H), 2.16 (s, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 177.87, 158.16, 154.95, 152.71, 150.81, 122.24, 111.64, 111.05, 108.58, 64.68, 63.88, 57.58. HRMS (ESI) Calcd. for $C_{12}H_{12}O_5$ $[M + Na]^+$: 259.0577, Found: 259.0573, Δ = 1.54 ppm.

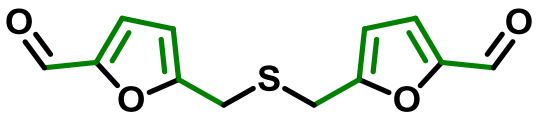
Synthesis of (5-(((5-formylfuran-2-yl)methoxy)methyl)furan-2-yl)methyl acetate, **1h**



5-(((5-(Hydroxymethyl)furan-2-yl)methoxy)methyl)furan-2-carbaldehyde (500 mg, 2.12 mmol) was dissolved in pyridine (5 ml). The solution was cooled to 0 °C, and acetyl chloride (189 mkl, 2.65 mmol, 1.25 eq) was added. The reaction mixture was stirred at room temperature for 24 hours. Then, it was poured into water (100 ml) and extracted with DCM (3 x 30 ml). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate, which gave (5-(((5-formylfuran-2-yl)methoxy)methyl)furan-2-yl)methyl acetate (498 mg, 97%) as a brown oil.

^{1}H NMR (300 MHz, Acetone-d_6) δ 9.63 (s, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 6.67 (d, *J* = 3.5, 1H), 6.45 – 6.41 (m, 2H), 5.02 (s, 2H), 4.60 (s, 2H), 4.54 (s, 2H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 177.45, 169.71, 157.98, 153.01, 152.20, 150.37, 122.27, 111.56, 111.14, 110.68, 63.93, 63.43, 57.55, 19.77. HRMS (ESI) Calcd. for $C_{14}H_{14}O_6$ $[M + Na]^+$: 301.0683, Found: 301.0682, Δ = 0.33 ppm.

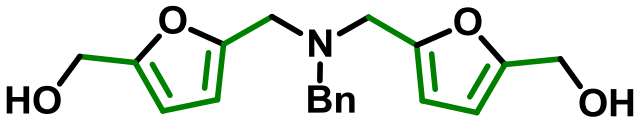
Synthesis of 5,5'-(thiobis(methylene))bis(furan-2-carbaldehyde), **1i**



5-(Bromomethyl)furan-2-carbaldehyde (BMF, 3.5 g, 18.5 mmol) was dissolved in dry DMF (25 mL) under Ar, and Na_2CO_3 (1.4 g, 13.2 mmol) was added. The mixture was cooled to 5 °C, and dry NaSH (0.52 g, 9.3 mmol) was added in small portions. After the full addition of the NaSH mixture, the mixture was stirred at 24 °C for 16 h, poured into aqueous ammonium chloride, and extracted with ethyl acetate (3 × 15 mL). The combined organic phases were washed with brine and dried with sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (eluted by ethyl acetate + hexanes, 1:1). The obtained mixture was additionally purified by recrystallization from acetone/diethyl ether to give 5,5'-(thiobis(methylene))bis(furan-2-carbaldehyde) as yellow crystals (495 mg, 51%).

^{1}H NMR (300 MHz, Chloroform-d) δ 9.56 (s, 2H), 7.16 (d, *J* = 3.5 Hz, 2H), 6.45 (d, *J* = 3.5 Hz, 2H), 3.78 (s, 4H). ^{13}C NMR (75 MHz, Chloroform-d) δ 177.29, 158.22, 152.60, 122.67, 110.93, 28.30. HRMS (ESI) Calcd. for $C_{12}H_{10}O_4S$ [M + H]$^+$: 251.0373, Found: 251.0382, Δ = 3.59 ppm.

Synthesis of (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))dimethanol, **1j**



5-HMF (3 g, 23.8 mmol) was dissolved in chloroform (50 ml), benzyl amine (1.37 ml, 12.6 mmol) was added to one portion followed by the portionwise addition of STAB (12.6 g, 59.4 mmol). The mixture was stirred at 24 °C for 16 h and then poured into brine. The organic layer was separated, water was additionally extracted with chloroform (3 × 10 mL), and the combined organic phases were dried over sodium sulfate. The solvent was removed under reduced pressure to

obtain (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))dimethanol as a light yellow oil (0.645 g, 47%).

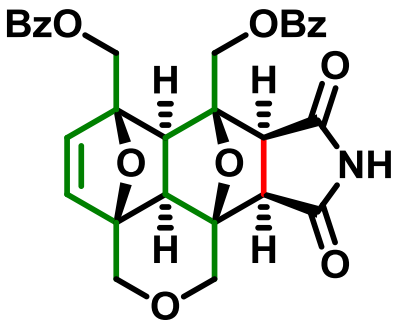
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.40 – 7.21 (m, 5H), 6.26 – 6.16 (m, 4H), 5.33 – 5.31 (m, 2H), 4.54 (s, 4H), 3.63 (s, 6H). ^{13}C NMR (75 MHz, Methylene Chloride-d_2) δ 154.46, 153.13, 139.58, 129.53, 128.78, 127.54, 110.06, 108.72, 58.00, 57.93, 50.27. HRMS (ESI) Calcd. for $C_{19}H_{21}NO_4$ $[M + H]^+$: 328.1543, Found: 328.1547, Δ = 1.22 ppm.

3. Cycloaddition reactions

Cycloaddition reaction with maleimide

((Oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate **1a** (223 mg, 0.5 mmol), maleimide (194 mg, 2 mmol) and EtOAc (2 mL) were placed in a screw cap test tube equipped with a magnetic stirring bar. The reaction mixture was heated to 80 °C and stirred for 48 h. During the reaction the white precipitate of cascade product **3ab** was formed. The reaction mixture was cooled to r.t. and the precipitate was filtered off, washed with 1 ml of EtOAc and dried under reduced pressure. *(8,10-Dioxo-3a*[1]*,6a,8,9,10,10a-hexahydro-1H,3H,6H-3a,6:7,10b-diepoxyisochromeno[4,5-ef]isoindole-6,7(7aH)-diyl)bis(methylene) dibenzoate* **3ab** was obtained as a mixture of exo-/endo-diastereomers in ratio 10:1 with 10% yield. The same procedure with heating to 100 °C gave **3ab** with 10:7 exo/endo ratio and 26% yield.

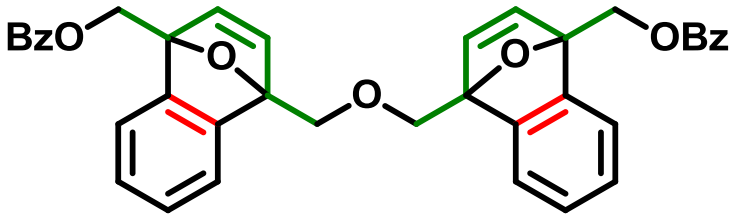
Spectra of exo-isomer:



^{1}H NMR (300 MHz, DMSO-d_6) δ 11.28 (s, 1H), 8.12 – 8.07 (m, 2H), 7.93 – 7.88 (m, 2H), 7.71 – 7.61 (m, 2H), 7.57 – 7.47 (m, 4H), 6.52 – 6.46 (m, 2H), 5.01 – 4.87 (m, 3H), 4.70 (d, *J* = 12.1 Hz, 1H), 4.17 (t, *J* = 12.9 Hz, 2H), 3.97 (d, *J* = 13.1 Hz, 1H), 3.80 (d, *J* = 9.5 Hz, 1H), 3.74 (d, *J* = 13.2 Hz, 1H), 3.23 (d, *J* = 9.6 Hz, 1H), 2.47 (d, *J* = 6.4 Hz, 1H), 1.96 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 176.26, 175.80, 165.22, 165.14, 138.50, 138.41, 133.59, 133.51, 129.54, 129.26, 129.20, 129.17, 128.77, 128.73, 90.58, 87.70, 83.81, 81.82, 65.17, 63.29, 62.75, 56.25, 54.04, 49.12, 46.44. HRMS (ESI) Calcd. for $C_{30}H_{25}NO_9$ [M + H]$^{+}$: 544.1602, Found: 544.1587, Δ = 2.76 ppm.

Cycloaddition reaction with benzyne

((Oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate **1a** (223 mg, 0.5 mmol), CsF (167 mg, 1.1 mmol) and MeCN (10 mL) were placed in a two necked round bottom flask equipped with a magnetic stirring bar, a reflux condenser and a dropping funnel. The reaction mixture was refluxed. The solution of 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (316 mkl, 2.6 eq) in MeCN (10 mL) was added dropwise for 6 h. Then the reaction mixture was cooled to r.t., poured into 100 mL of H_2O and extracted with DCM (3 x 30 ml). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. *((Oxybis(methylene))bis(1,4-epoxynaphthalene-4,1(4H)-diyl))bis(methylene) dibenzoate* **4ac** was obtained with quantitative yield.



^{1}H NMR (300 MHz, Acetone-d_6) δ 8.08 – 8.00 (m, 4H), 7.65 – 7.56 (m, 2H), 7.46 (m, 4H), 7.37 – 7.28 (m, 4H), 7.08 (d, J = 4.0 Hz, 4H), 7.03 – 6.92 (m, 4H), 5.31 – 5.08 (m, 4H), 4.68 – 4.38 (m, 4H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 166.55, 151.30, 150.53, 145.62, 144.14, 144.13, 134.02, 130.73, 130.28, 129.36, 125.76, 125.61, 120.75, 120.73, 120.03, 93.08, 91.74, 69.72, 62.47. HRMS (ESI) Calcd. for $C_{38}H_{30}O_7$ $[M + K]^+$: 637.1623, Found: 637.1628, Δ = 0.78 ppm.

Cascade cycloaddition reactions with alkynes

Procedure A

Dimeric 5-HMF derivative (0.5 mmol), alkyne (0.75 mmol) and toluene (2 ml) were placed in a screw cap test tube equipped with a magnetic stirring bar. The reaction mixture was heated to 110 °C and stirred for 12 h. The cascade product **3** was isolated by column chromatography with petroleum ether/EtOAc mixture as eluent.

Procedure B

Dimeric 5-HMF derivative (0.5 mmol), alkyne (0.75 mmol) and toluene (2 ml) were placed in a screw cap test tube equipped with a magnetic stirring bar. The reaction mixture was heated to 110 °C and stirred for 12 h. The cascade product **3** was isolated by recrystallization from methanol.

Procedure C

Dimeric 5-HMF derivative (0.5 mmol), alkyne (0.75 mmol) and toluene (2 ml) were placed in a screw cap test tube equipped with a magnetic stirring bar. The reaction mixture was heated to 110 °C and stirred for 12 h. Toluene was evaporated under reduced pressure, methanol (1 ml) was added to the residue and the mixture was stirred at r.t. for 6 h. The product **3** was isolated by recrystallization from methanol.

Procedure D

Dimeric 5-HMF derivative (0.5 mmol), alkyne (0.75 mmol) and toluene (2 ml) were placed in a screw cap test tube equipped with a magnetic stirring bar. The reaction mixture was heated to 140 °C and stirred for 24 h. The cascade product **3** was isolated by column chromatography with petroleum ether/EtOAc mixture as eluent.

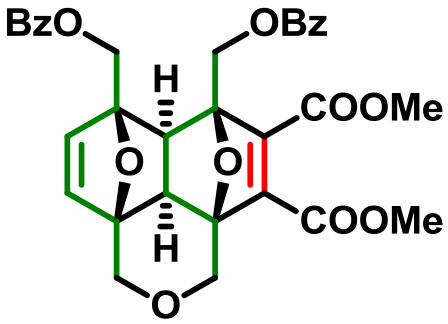
Procedure E (gram scale)

Dimeric 5-HMF derivative (17.65 mmol), alkyne (52.95 mmol, 3 eq) and toluene (40 ml) were placed in a round bottom flask equipped with a magnetic stirring bar and reflux condenser. The reaction mixture was refluxed and stirred for 24 h. The cascade product **3** was isolated by flash chromatography with petroleum ether/EtOAc mixture as eluent.

Procedure F (rearrangement of double cycloadducts)

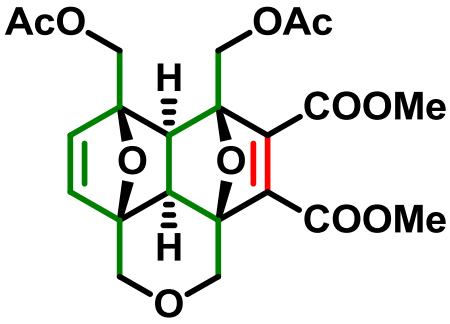
The corresponding double cycloadduct **4** (0.5 mmol) and toluene (2 ml) were placed in a screw cap test tube equipped with a magnetic stirring bar. The reaction mixture was heated to 150 °C and stirred for 24 h. The cascade product **3** was isolated by column chromatography with petroleum ether/EtOAc mixture as eluent.

Dimethyl 6,7-bis((benzoyloxy)methyl)-3a[1]*,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate* **3aa** (72% in procedure A, 70% in procedure E, 91% in procedure F)



[1]H NMR (300 MHz, DMSO-d_6) δ 8.04 – 7.95 (m, 2H), 7.92 – 7.83 (m, 2H), 7.74 – 7.64 (m, 2H), 7.62 – 7.50 (m, 4H), 6.65 – 6.54 (m, 2H), 5.12 – 4.84 (m, 4H), 4.30 – 3.92 (m, 4H), 3.75 (s, 3H), 3.60 (s, 3H), 2.64 (d, *J* = 6.1 Hz, 1H), 2.42 (d, *J* = 6.1 Hz, 1H). [13]C NMR (75 MHz, DMSO-d_6) δ 165.21, 164.83, 163.37, 161.86, 147.00, 146.69, 139.58, 139.41, 133.67, 133.59, 129.23, 129.08, 128.83, 91.53, 89.57, 84.75, 83.72, 65.07, 63.71, 62.84, 61.51, 54.07, 52.57, 52.15, 52.06. HRMS (ESI) Calcd. for $C_{32}H_{28}O_{11}$ $[M + Na]^+$: 611.1524, Found: 611.1515, Δ = 1.47 ppm.

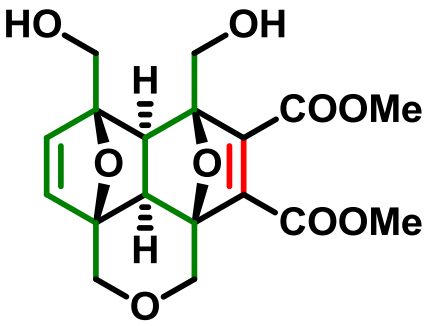
Dimethyl 6,7-bis(acetoxymethyl)-3a[1]*,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate* **3ba** (73% in procedure A, 87% in procedure F)



[1]H NMR (300 MHz, Acetone-d_6) δ 6.55 – 6.45 (m, 2H), 4.84 (d, *J* = 12.2 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.60 – 4.52 (m, 2H), 4.28 – 4.09 (m, 3H), 3.97 (d, *J* = 13.0 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.55 (d, *J* = 6.1 Hz, 1H), 2.39 (d, *J* = 6.1 Hz, 1H), 2.06 (s, 3H), 1.98 (s, 3H). [13]C NMR (75 MHz, Acetone-d_6) δ 169.78, 169.34, 163.56, 162.29, 147.55, 146.63, 139.84, 139.29, 91.74, 89.77, 84.97,

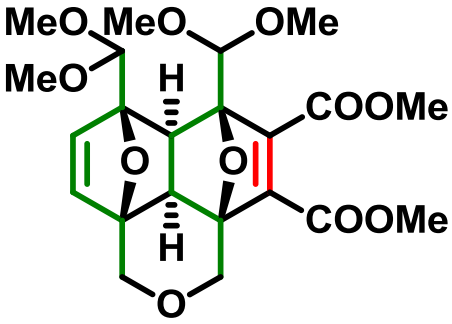
83.92, 65.46, 64.15, 62.42, 61.16, 54.76, 52.54, 51.84, 51.60, 19.74, 19.48. HRMS (ESI) Calcd. for $C_{22}H_{24}O_{11}$ $[M + Na]^+$: 487.1211, Found: 487.1216, Δ = 1.03 ppm.

Dimethyl 6,7-bis(hydroxymethyl)-3a1,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ca** (59%, procedure A)



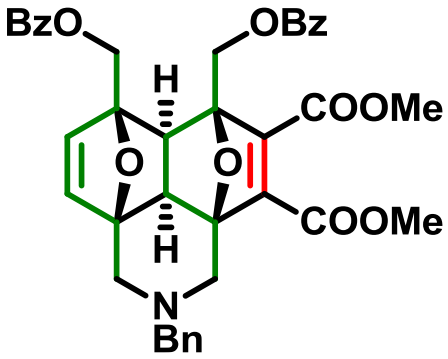
HRMS (ESI) Calcd. for $C_{18}H_{20}O_9$ $[M + Na]^+$: 403.1000, Found: 403.1011, Δ = 2.73 ppm.

Dimethyl 6,7-bis(dimethoxymethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3da** (53%, procedure A, 88% in procedure F)



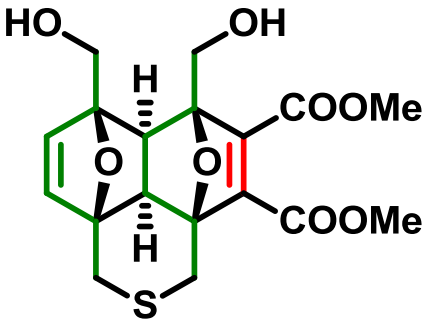
^{1}H NMR (300 MHz, Acetone-d_6) δ 6.49 – 6.37 (m, 2H), 5.21 (s, 1H), 5.04 (s, 1H), 4.24 – 4.13 (m, 3H), 3.94 (d, J = 13.0 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.47 (s, 3H), 3.46 (s, 3H), 3.44 (s, 3H), 3.39 (s, 3H), 2.51 (d, J = 6.1 Hz, 1H), 2.19 (d, J = 6.1 Hz, 1H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 165.40, 162.82, 153.04, 143.42, 140.81, 138.87, 104.38, 102.01, 96.43, 94.44, 85.40, 84.45, 66.61, 65.29, 57.29, 56.09, 55.59, 55.25, 54.92, 52.60, 52.48, 52.23. HRMS (ESI) Calcd. for $C_{22}H_{28}O_{11}$ $[M + Na]^+$: 491.1524, Found: 491.1522, Δ = 4.07 ppm.

Dimethyl 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a^1,6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea** (79%, procedure A)



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.73 – 7.62 (m, 2H), 7.60 – 7.50 (m, 4H), 7.39 – 7.18 (m, 5H), 6.54 (s, 2H), 5.15 – 4.83 (m, 4H), 3.78 – 3.68 (m, 5H), 3.57 (s, 2H), 3.32 (s, 3H), 2.82 (d, *J* = 13.4 Hz, 1H), 2.71 (d, *J* = 13.2 Hz, 1H), 2.60 (d, *J* = 6.0 Hz, 1H), 2.23 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.73, 165.36, 163.70, 163.09, 149.04, 145.77, 141.19, 139.73, 138.10, 134.10, 134.08, 129.73, 129.54, 129.33, 128.66, 127.50, 91.58, 89.74, 86.37, 85.11, 63.45, 62.15, 61.56, 55.36, 53.03, 53.00, 52.60, 51.78, 50.36. HRMS (ESI) Calcd. for $C_{39}H_{35}NO_{10}$ $[M + H]^+$: 678.2334, Found: 678.2346, Δ = 1.77 ppm.

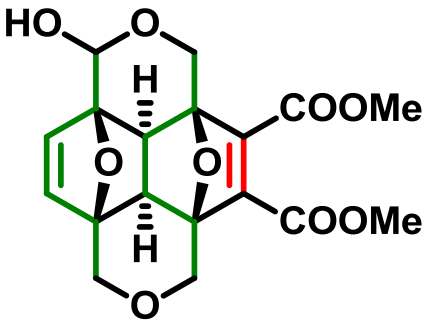
Dimethyl 6,7-bis(hydroxymethyl)-3a^1,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isothiochromene-4,5-dicarboxylate **3fa** (90%, procedure F)



^{1}H NMR (300 MHz, DMSO-d_6) δ 6.52 (d, *J* = 5.5 Hz, 1H), 6.35 (d, *J* = 5.5 Hz, 1H), 5.20 – 5.09 (m, 2H), 4.17 – 3.93 (m, 2H), 3.83 (d, *J* = 5.5 Hz, 2H), 3.75 – 3.63 (m, 6H), 3.46 (d, *J* = 14.6 Hz, 1H), 3.33 (d, *J* = 14.6 Hz, 1H), 2.95 – 2.78 (m, 2H), 2.30 (d, *J* = 6.1 Hz, 1H), 2.04 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (75 MHz,

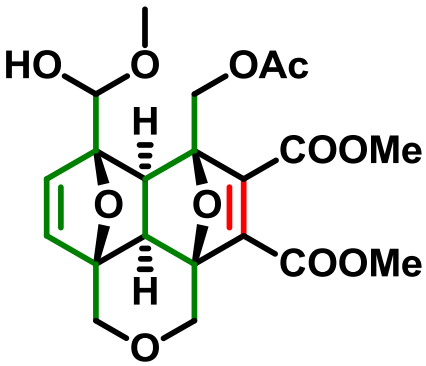
DMSO-d_6) δ 163.84, 162.85, 148.71, 146.47, 141.33, 140.46, 94.42, 91.10, 83.92, 82.53, 60.36, 58.47, 54.75, 52.98, 52.31, 51.93, 27.67, 26.40. HRMS (ESI) Calcd. for $C_{18}H_{20}O_8S$ $[M + H]^+$: 397.0952, Found: 397.0952, Δ = 0 ppm.

1-Hydroxy-1,3,3a,3a^1,5a,5a^1,6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-def]isochromene-4,5-dicarboxylic acid **3ga** (68%, procedure B)



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.06 (d, *J* = 4.6 Hz, 1H), 6.48 – 6.43 (m, 2H), 5.22 (d, *J* = 4.6 Hz, 1H), 4.47 (d, *J* = 12.7 Hz, 1H), 4.16 – 4.04 (m, 3H), 3.99 (d, *J* = 12.7 Hz, 1H), 3.85 (d, *J* = 12.8 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.19 (d, *J* = 6.2 Hz, 1H), 2.10 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.77, 162.54, 146.78, 146.41, 139.04, 138.75, 89.04, 86.12, 85.79, 85.69, 84.67, 65.04, 63.54, 55.79, 52.45, 52.41, 48.44, 46.63. HRMS (ESI) Calcd. for $C_{18}H_{18}O_9$ $[M + H]^+$: 379.1024, Found: 379.1031, Δ = 1.85 ppm.

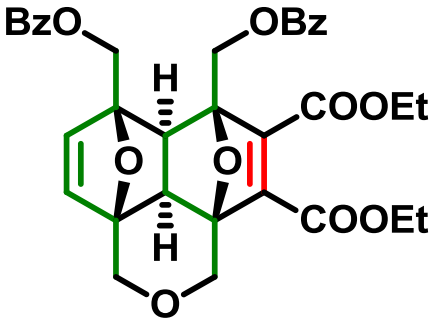
Dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a^1,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha** (54%, procedure C)



^{1}H NMR (300 MHz, DMSO-d_6) δ 6.60 (d, *J* = 6.4 Hz, 1H), 6.47 – 6.40 (m, 2H), 4.84 (d, *J* = 6.5 Hz, 1H), 4.79 (d, *J* = 12.6 Hz, 1H), 4.41 (d, *J* = 12.6 Hz, 1H), 4.17

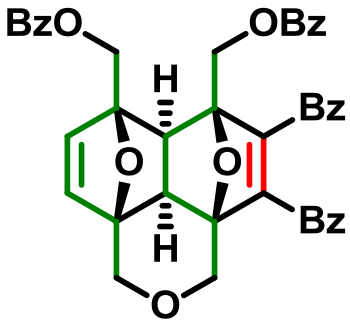
(d, *J* = 13.1 Hz, 1H), 4.13 – 3.98 (m, 2H), 3.91 (d, *J* = 12.9 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.37 (s, 3H), 2.30 (d, *J* = 6.1 Hz, 1H), 2.24 (d, *J* = 6.1 Hz, 1H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 170.24, 163.91, 162.57, 147.16, 147.14, 139.54, 138.80, 95.75, 93.89, 91.90, 85.00, 83.64, 65.58, 64.18, 61.98, 54.83, 53.84, 52.97, 52.67, 51.96, 20.74. HRMS (ESI) Calcd. for $C_{21}H_{24}O_{11}$ $[M + Na]^+$: 475.1211, Found: 475.1209, Δ = 0.42 ppm.

Diethyl 6,7-bis((benzoyloxy)methyl)-3a[1]*,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate* **3ad** (66%, procedure A)



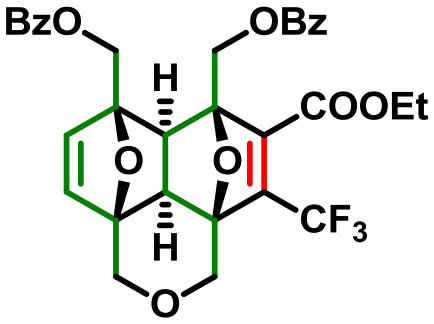
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.10 – 8.02 (m, 2H), 8.02 – 7.94 (m, 2H), 7.60 – 7.48 (m, 2H), 7.48 – 7.34 (m, 4H), 6.52 (d, *J* = 5.6 Hz, 1H), 6.44 (d, *J* = 5.6 Hz, 1H), 5.18 – 4.90 (m, 4H), 4.55 – 4.42 (m, 2H), 4.32 – 4.18 (m, 3H), 4.18 – 3.98 (m, 2H), 3.94 (d, *J* = 13.1 Hz, 1H), 2.78 (d, *J* = 6.1 Hz, 1H), 2.38 (d, *J* = 6.0 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.99, 165.57, 163.58, 162.09, 148.55, 145.37, 140.34, 139.07, 133.41, 133.30, 129.93, 129.52, 129.31, 128.57, 128.45, 92.13, 90.20, 85.24, 84.23, 66.28, 65.03, 63.00, 62.06, 61.87, 61.67, 55.16, 52.86, 14.12, 13.92. HRMS (ESI) Calcd. for $C_{34}H_{32}O_{11}$ $[M + Na]^+$: 639.1837, Found: 639.1826, Δ = 1.72 ppm.

(4,5-Dibenzoyl-3a[1]*,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate* **3ae** (50%, procedure D)



^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.23 – 8.12 (m, 2H), 7.72 – 7.65 (m, 2H), 7.65 – 7.58 (m, 1H), 7.51 (m, 2H), 7.42 (m, 6H), 7.27 (m, 3H), 7.16 (m, 2H), 7.04 (m, 2H), 6.64 (d, *J* = 5.6 Hz, 1H), 6.49 (d, *J* = 5.6 Hz, 1H), 5.36 – 5.18 (m, 2H), 5.17 – 5.02 (m, 2H), 4.78 (d, *J* = 13.4 Hz, 1H), 4.52 (d, *J* = 13.0 Hz, 1H), 3.91 (m, 2H), 3.21 (d, *J* = 6.1 Hz, 1H), 2.51 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 192.83, 190.80, 166.11, 165.50, 151.74, 151.11, 140.63, 139.03, 137.28, 136.62, 134.09, 133.54, 133.46, 132.92, 130.07, 129.70, 129.58, 129.34, 128.89, 128.81, 128.69, 128.65, 128.22, 128.06, 93.91, 90.52, 86.20, 84.15, 66.23, 65.66, 63.11, 61.63, 55.10, 52.97. HRMS (ESI) Calcd. for $C_{42}H_{32}O_9$ $[M + Na]^+$: 703.1939, Found: 703.1940, Δ = 0.14 ppm.

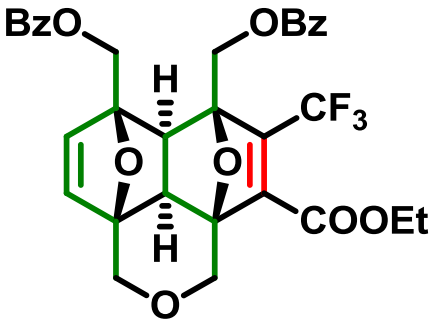
(5-(Ethoxycarbonyl)-4-(trifluoromethyl)-3a[1]*,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate* **3afA** (33%, procedure A)



^{1}H NMR (300 MHz, Acetone-d_6) δ 8.14 – 8.08 (m, 2H), 8.01 – 7.95 (m, 2H), 7.72 – 7.63 (m, 2H), 7.60 – 7.48 (m, 4H), 6.71 (d, *J* = 5.6 Hz, 1H), 6.65 (d, *J* = 5.6 Hz, 1H), 5.14 (s, 2H), 5.06 – 4.91 (m, 2H), 4.41 – 4.00 (m, 6H), 2.93 (d, *J* = 6.1 Hz,

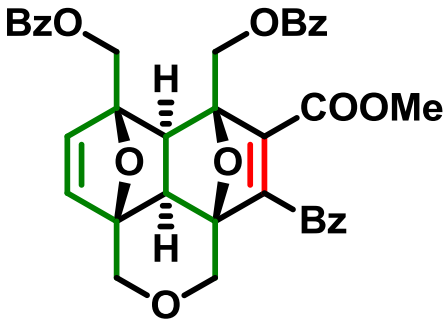
1H), 2.58 (d, *J* = 6.1 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 165.42, 164.98, 162.48 (q, *J* = 1.5 Hz), 148.42 (q, *J* = 4.4 Hz), 141.76 (q, *J* = 35.8 Hz), 140.05, 139.51, 133.49, 133.39, 129.83, 129.55, 129.48, 129.33, 128.65, 128.62, 121.37 (q, *J* = 270.3 Hz), 92.98, 89.82, 84.99, 84.13, 65.62, 63.50 (q, *J* = 1.9 Hz), 63.09, 61.73, 54.89, 52.68 (q, *J* = 1.1 Hz), 13.19. HRMS (ESI) Calcd. for $C_{32}H_{27}F_3O_9$ [M + Na]$^+$: 635.1499, Found: 635.1494, Δ = 0.79 ppm.

(4-(Ethoxycarbonyl)-5-(trifluoromethyl)-3a^1,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afB** (24%, procedure A)



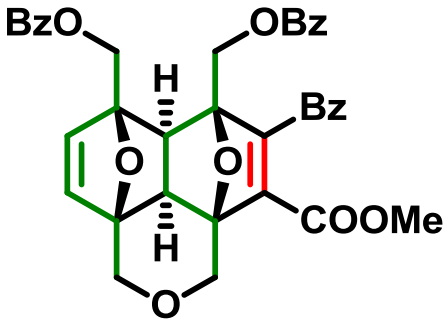
^{1}H NMR (300 MHz, Acetone-d_6) δ 8.11 – 7.99 (m, 4H), 7.74 – 7.62 (m, 2H), 7.60 – 7.48 (m, 4H), 6.72 – 6.61 (m, 2H), 5.20 (d, *J* = 12.6, 1H), 5.14 – 4.97 (m, 3H), 4.45 – 4.18 (m, 5H), 4.07 (d, *J* = 13.0 Hz, 1H), 2.81 (d, *J* = 6.1 Hz, 1H), 2.61 (d, *J* = 6.1 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 165.42, 165.13, 161.83, 149.36 (q, *J* = 4.4 Hz), 143.36 (q, *J* = 35.3 Hz), 140.03, 139.52, 133.41, 133.32, 129.87, 129.51, 129.48, 129.46, 128.61, 128.59, 121.65 (q, *J* = 271.1 Hz), 91.88, 90.03, 85.75, 84.24, 65.55, 63.48, 63.07, 61.93, 61.92, 61.86, 54.82, 53.40, 13.24. HRMS (ESI) Calcd. for $C_{32}H_{27}F_3O_9$ [M + Na]$^+$: 635.1499, Found: 635.1498, Δ = 0.16 ppm.

(4-Benzoyl-5-(methoxycarbonyl)-3a[1]*,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate* **3agA** (26%, procedure A)



[1]H NMR (300 MHz, DMSO-d_6) δ 8.06 – 8.00 (m, 2H), 7.91 – 7.84 (m, 2H), 7.81 – 7.64 (m, 5H), 7.62 – 7.50 (m, 6H), 6.64 (d, *J* = 5.5 Hz, 1H), 6.60 (d, *J* = 5.5 Hz, 1H), 5.23 (d, *J* = 12.1 Hz, 1H), 5.06 (d, *J* = 12.1 Hz, 1H), 5.02 – 4.90 (m, 2H), 4.21 – 4.11 (m, 2H), 3.98 (d, *J* = 13.0 Hz, 1H), 3.77 (d, *J* = 12.9 Hz, 1H), 3.26 (s, 3H), 2.78 (d, *J* = 6.1 Hz, 1H), 2.61 (d, *J* = 6.1 Hz, 1H). [13]C NMR (75 MHz, DMSO-d_6) δ 192.19, 165.75, 165.28, 162.88, 157.71, 142.82, 140.23, 139.83, 136.08, 135.12, 134.17, 134.13, 129.78, 129.61, 129.51, 129.43, 129.37, 129.06, 92.06, 90.00, 86.37, 84.36, 65.39, 63.66, 63.45, 62.45, 55.07, 52.28, 52.23. HRMS (ESI) Calcd. for $C_{37}H_{30}O_{10}$ $[M + Na]^+$: 657.1731, Found: 657.1726, Δ = 0.76 ppm.

(5-Benzoyl-4-(methoxycarbonyl)-3a[1]*,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate* **3agB** (30%, procedure A)



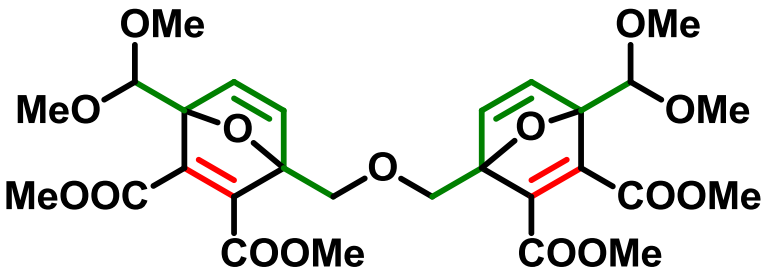
[1]H NMR (300 MHz, DMSO-d_6) δ 8.01 – 7.96 (m, 2H), 7.75 – 7.66 (m, 3H), 7.59 – 7.51 (m, 6H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.27 (m, 2H), 6.64 (d, *J* = 5.5 Hz, 1H), 6.60 (d, *J* = 5.5 Hz, 1H)., 5.03 – 4.88 (m, 4H), 4.38 (d, *J* = 13.1 Hz, 1H), 4.28 (d, *J* = 13.2 Hz, 1H), 4.22 (d, *J* = 12.9 Hz, 1H)., 4.01 (d, *J* = 13.0 Hz, 1H), 3.31 (s,

3H), 2.85 (d, *J* = 6.1 Hz, 1H), 2.54 (d, *J* = 6.1 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 193.12, 165.70, 165.17, 161.84, 155.57, 144.57, 140.07, 139.97, 135.70, 134.42, 134.07, 133.88, 129.74, 129.57, 129.32, 129.13, 129.05, 128.87, 128.75, 93.26, 90.28, 85.60, 84.23, 65.74, 64.64, 63.35, 61.48, 54.49, 53.10, 52.44. HRMS (ESI) Calcd. for $C_{37}H_{30}O_{10}$ [M + Na]$^+$: 657.1731, Found: 657.1737, Δ = 0.91 ppm.

Double cycloaddition reaction with dimethyl acetylenedicarboxilate

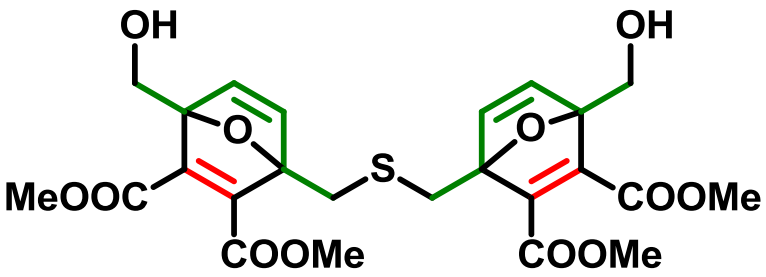
The HMF derivative (1 mmol) and dienophile (4 mmol) were placed in a 1.5 ml vial equipped with a magnetic stirring bar. The reaction mixture was heated to 80 °C and stirred for 12 h. The product was isolated by column chromatography with petroleum ether/EtOAc mixture as eluent.

Tetramethyl 4,4'-(oxybis(methylene))bis(1-(dimethoxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) **4da** (71%)



^{1}H NMR (300 MHz, Acetone-d_6) δ 7.14 (d, *J* = 5.2 Hz, 2H), 7.09 – 7.02 (m, 2H), 5.02 – 4.95 (s, 2H), 4.38 – 4.30 (m, 2H), 4.27 – 4.19 (m, 2H)., 3.78 – 3.70 (m, 12H), 3.48 – 3.41 (m, 12H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 165.29, 163.85, 157.14, 156.97, 150.27, 150.21, 144.71, 144.27, 101.75, 101.72, 97.96, 97.94, 96.98, 96.85, 69.32, 69.16, 56.12, 56.07, 56.04, 52.36. HRMS (ESI) Calcd. for $C_{28}H_{34}O_{15}$ [M + Na]$^+$: 633.1790, Found: 633.1791, Δ = 0.16 ppm.

Tetramethyl 4,4'-(thiobis(methylene))bis(1-(hydroxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) **4fa** (54%)

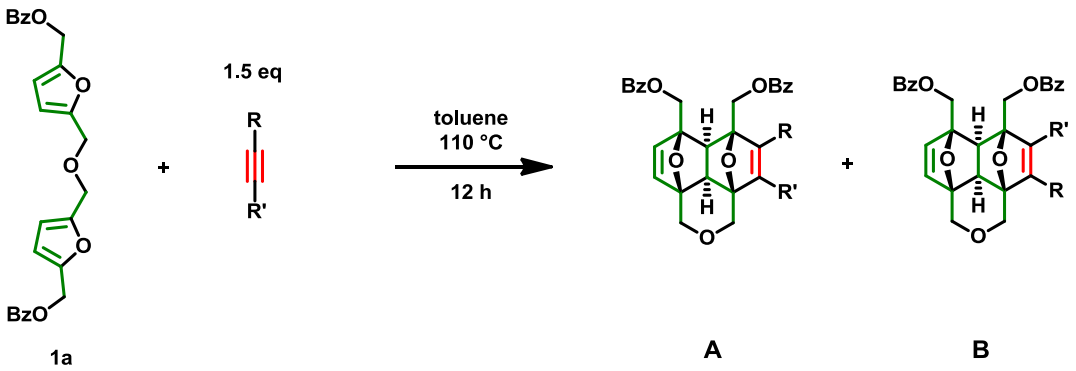


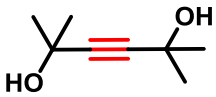
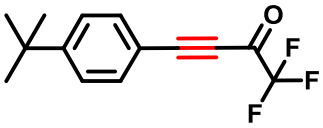
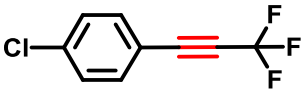
^{1}H NMR (300 MHz, Acetone-d_6) δ 7.16 – 7.05 (s, 4H), 4.28 – 4.10 (m, 4H), 3.96 (t, J = 6.1 Hz, 2H), 3.76 (s, 12H), 3.59 – 3.43 (m, 4H). ^{13}C NMR (75 MHz, Acetone-d_6) δ 164.21, 163.65, 154.31, 154.25, 152.56, 152.45, 145.74, 145.65, 144.25, 144.22, 97.57, 97.54, 97.04, 96.98, 59.07, 51.61, 32.14, 31.95. HRMS (ESI) Calcd. for $C_{24}H_{26}O_{12}S$ $[M + H]^+$: 539.1218, Found: 539.1219, Δ = 0.19 ppm.

The double cycloadducts **4aa - ca** were synthesized according to our previous study.[2]

4. Alkyne screening

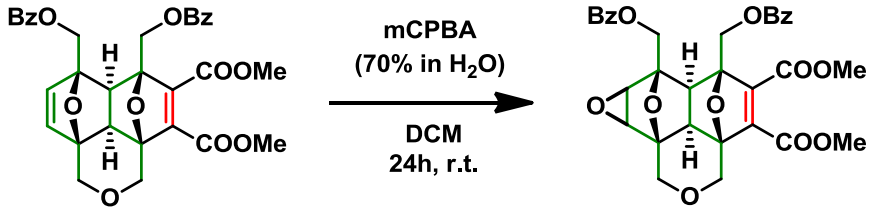
Table S1. Scope of the reaction with different alkynes.



Alkyne	Total yield of A and B(%)
H—≡—Bu	0
Ph—≡—COOEt	0
H—≡—COOMe	0
Pr—≡—Pr	0
HOH_2C—≡—Et	0
Me—≡—Ph	0
	0
Ph—≡—Ph	0
Ph—≡—Ac	0
	0
	0
MeOOC—≡—COOMe	72
EtOOC—≡—COOEt	66
F_3C—≡—COOEt	57
Bz—≡—COOMe	56
Bz—≡—Bz	50

5. Synthetic tranformations of cycloadducts

(3aS,3a1S,6R,6aR,7R,8bS)-dimethyl 6,7-bis((benzoyloxy)methyl)-1,3,3a1,6,6a,7,7a,8a-octahydro-3a,6:7,8b-diepoxybenzo[de]oxireno[2,3-h]isochromene-4,5-dicarboxylate (**7aa**)



3aa 7aa

A 70% suspension of meta-chloroperoxybenzoic acid (m-CPBA) (150 mg, 0.83 mmol) in water was added by portions to a solution of the adduct **3aa** (0.5 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred for 24 h at r.t. and then was poured into 30% solution of NH_3 in H_2O (20 mL), the organic layer was separated and the water layer was extracted with CH2Cl2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The resulting crystals of **7aa** were filtered and rinsed with ether.

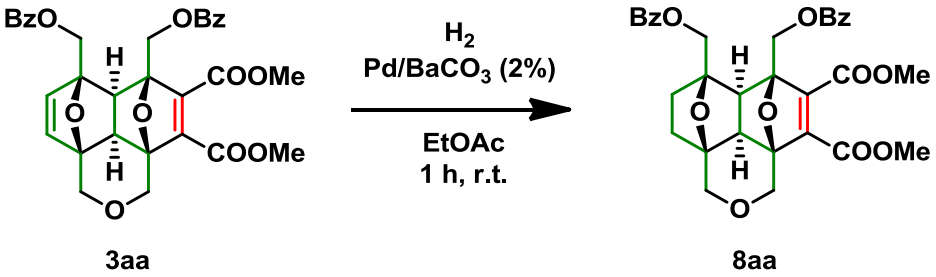
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.12 – 8.07 (m, 2H), 7.97 – 7.91 (m, 2H), 7.59 – 7.49 (m, 2H), 7.47 – 7.35 (m, 4H), 5.12 (d, *J* = 12.3 Hz, 1H), 5.02 – 4.92 (m, 2H), 4.86 (d, *J* = 12.1 Hz, 1H), 4.49 (d, *J* = 6.3 Hz, 1H), 4.45 (d, *J* = 6.3 Hz, 1H), 4.20 (d, *J* = 13.2 Hz, 1H), 3.87 (d, *J* = 13.2 Hz, 1H), 3.81 (s, 3H), 3.62 (s, 3H), 3.51 (d, *J* = 3.3 Hz, 1H), 3.32 (d, *J* = 3.3 Hz, 1H), 2.80 (d, *J* = 6.4 Hz, 1H), 2.31 (d, *J* = 6.3 Hz, 1H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 165.89, 165.44, 163.60, 162.14, 147.86, 144.74, 133.49, 133.36, 129.95, 129.83, 129.35, 129.13, 128.62, 128.48, 92.63, 85.56, 85.01, 79.20, 65.68, 64.89, 61.65, 61.58, 53.18, 52.99, 52.80, 52.47, 52.26, 51.63.

HRMS (ESI) Calcd. for $C_{32}H_{28}O_{12}$ $[M + Na]^+$: 627.1473, Found: 627.1460, Δ = 2.07 ppm.

Yield: 65%.

*(3aS,3a1R,6R,6aS,7R,9aS)-dimethyl 6,7-bis((benzoyloxy)methyl)-1,3,3a1,6,6a,7,8,9-octahydro-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate (***8aa***)*



3aa **8aa**

A continuous medium current of hydrogen was passed into the mixture of the adduct **3aa** (2g, 3.4 mmol) in EtOAc (20 mL) and 2 % $Pd/BaCO_3$ (140 mg) at r.t. The mixture was stirred for 1 h at r.t, filtered through a thin layer of Celite and concentrated under reduced pressure to give the desired product **8aa**.

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.06 – 8.01 (m, 2H), 7.86 – 7.81 (m, 2H), 7.74 – 7.61 (m, 2H), 7.61 – 7.48 (m, 4H), 5.10 – 4.98 (m, 2H), 4.83 (d, *J* = 11.6 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.24 (d, *J* = 13.0 Hz, 1H), 4.10 (d, *J* = 13.1 Hz, 1H)., 4.02 (d, *J* = 13.1 Hz, 1H), 3.80 – 3.71 (m, 4H), 3.59 (s, 3H), 2.71 (d, *J* = 6.5 Hz, 1H), 2.35 (d, *J* = 6.5 Hz, 1H), 1.94 – 1.71 (m, 2H), 1.61 – 1.37 (m, 2H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 165.10, 164.81, 163.32, 161.72, 145.51, 145.14, 133.66, 129.24, 129.20, 129.05, 128.91, 128.80, 92.20, 85.82, 85.06, 80.83, 66.39, 64.65, 63.91, 61.54, 53.55, 52.59, 52.13, 49.82, 33.93, 32.12.

HRMS (ESI) Calcd. for $C_{32}H_{30}O_{11}$ $[M + Na]^+$: 613.1680, Found: 613.1675, Δ = 0.81 ppm.

Yield: 95%.

6. NMR spectra of compounds

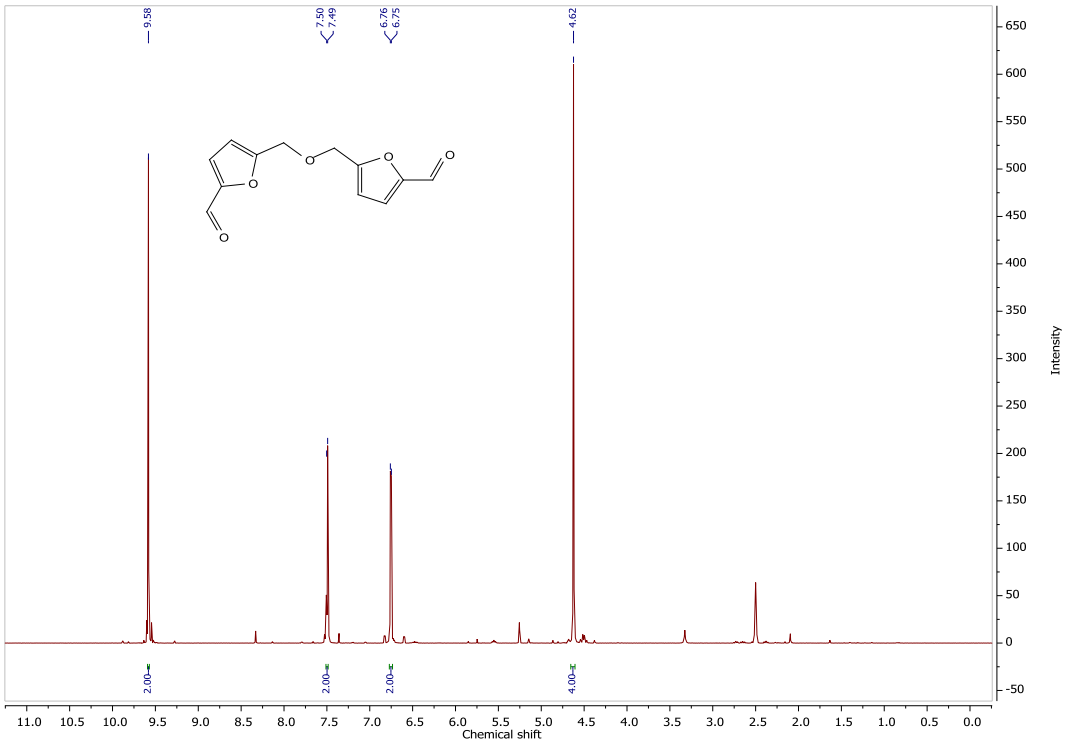


Figure S1. ^{1}H NMR spectrum of 5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde), **1** (300 MHz, DMSO-d_6).

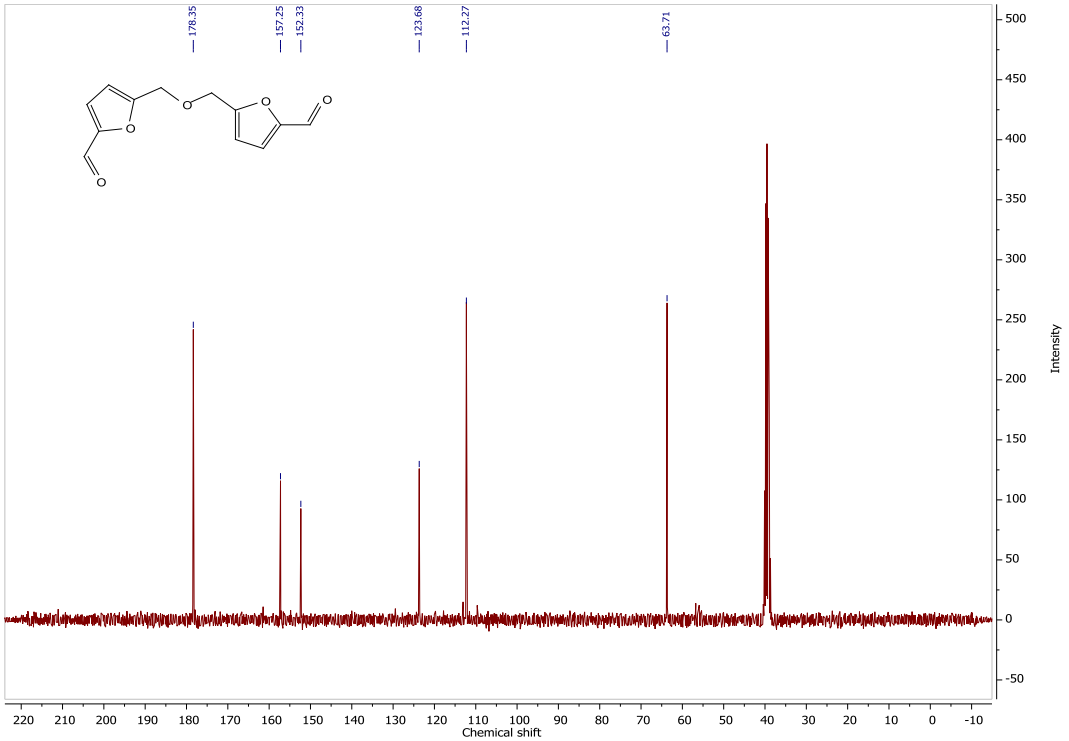


Figure S2. ^{13}C NMR spectrum of 5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde), **1** (75 MHz, DMSO-d_6).

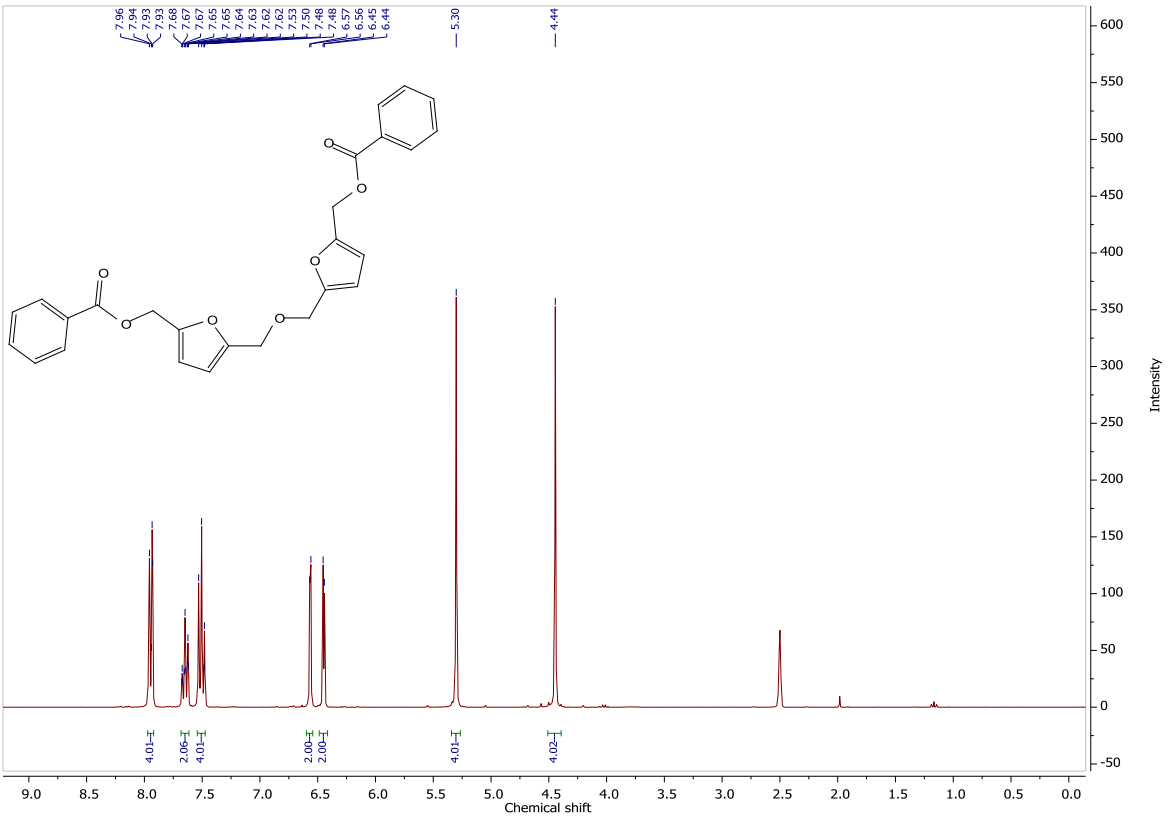


Figure S3. ^{1}H NMR spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate, **1a** (300 MHz, DMSO-d_6).

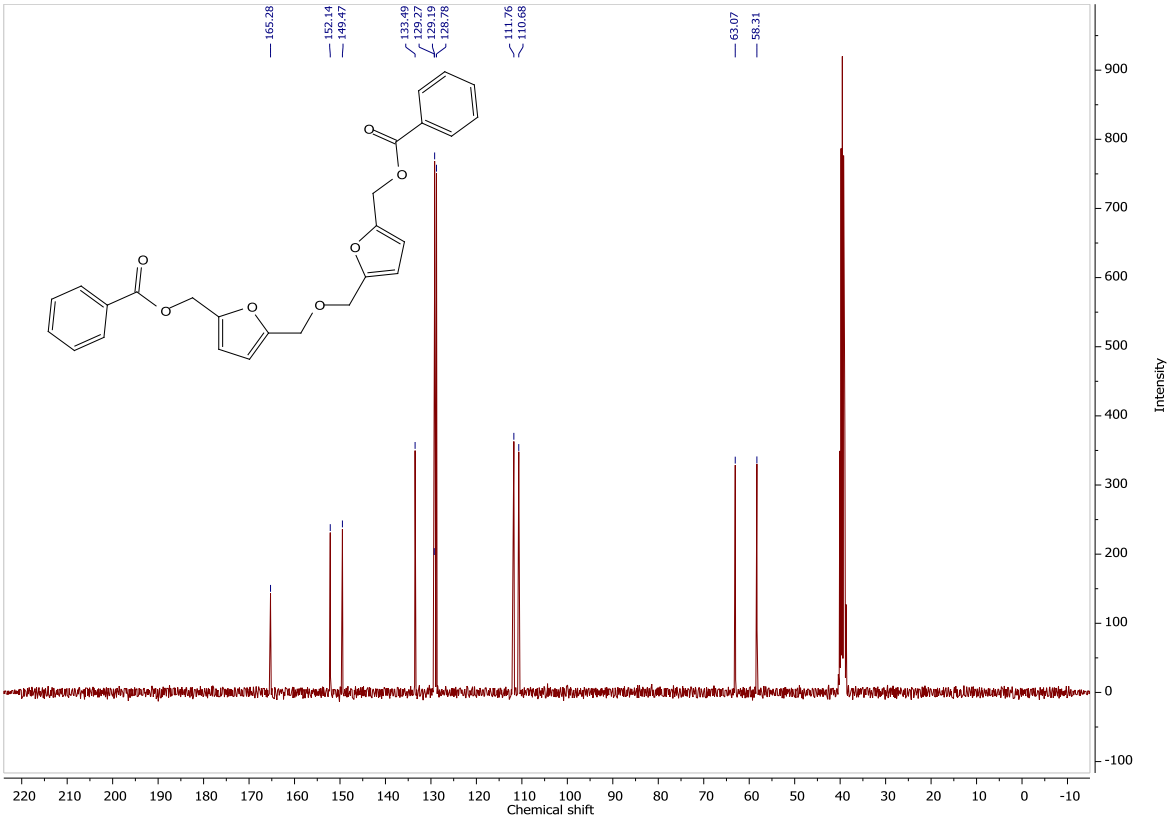


Figure S4. ^{13}C NMR spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate, **1a** (75 MHz, DMSO-d_6).

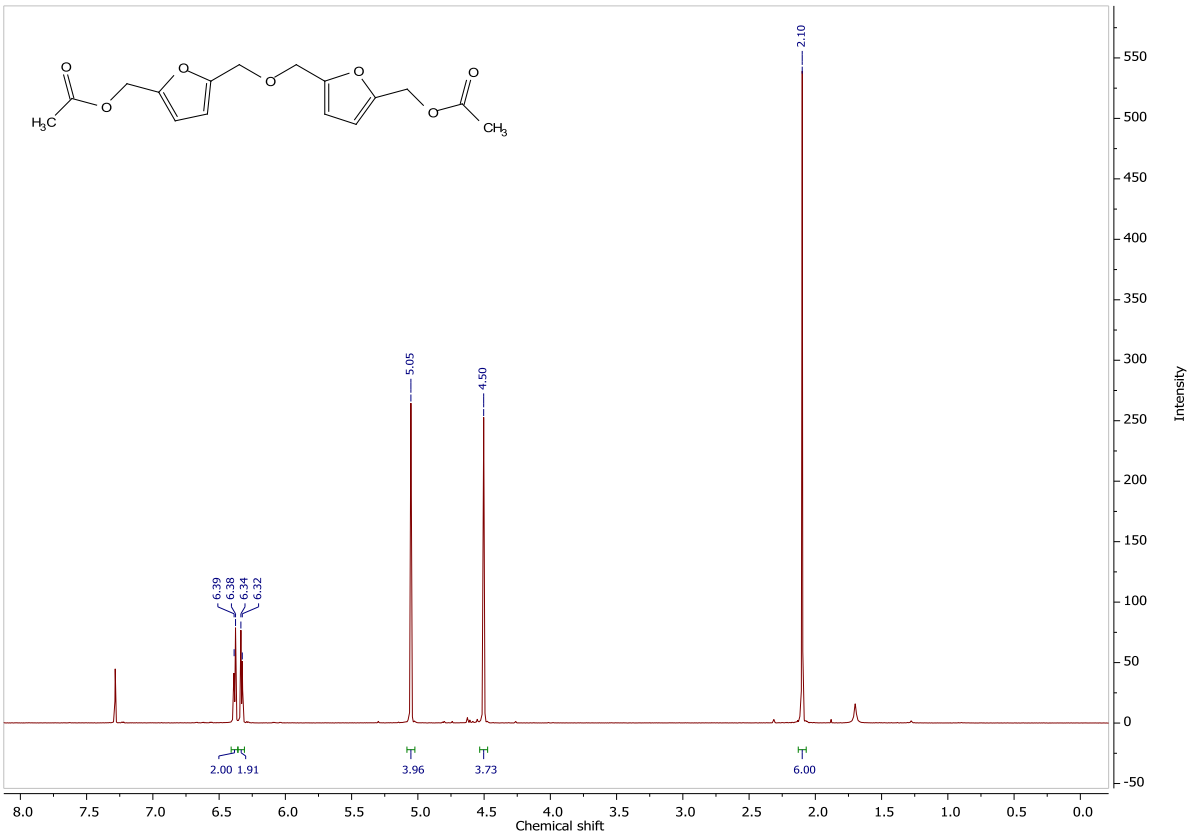


Figure S5. ^{1}H NMR spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) diacetate, **1b** (300 MHz, chloroform-*d*).

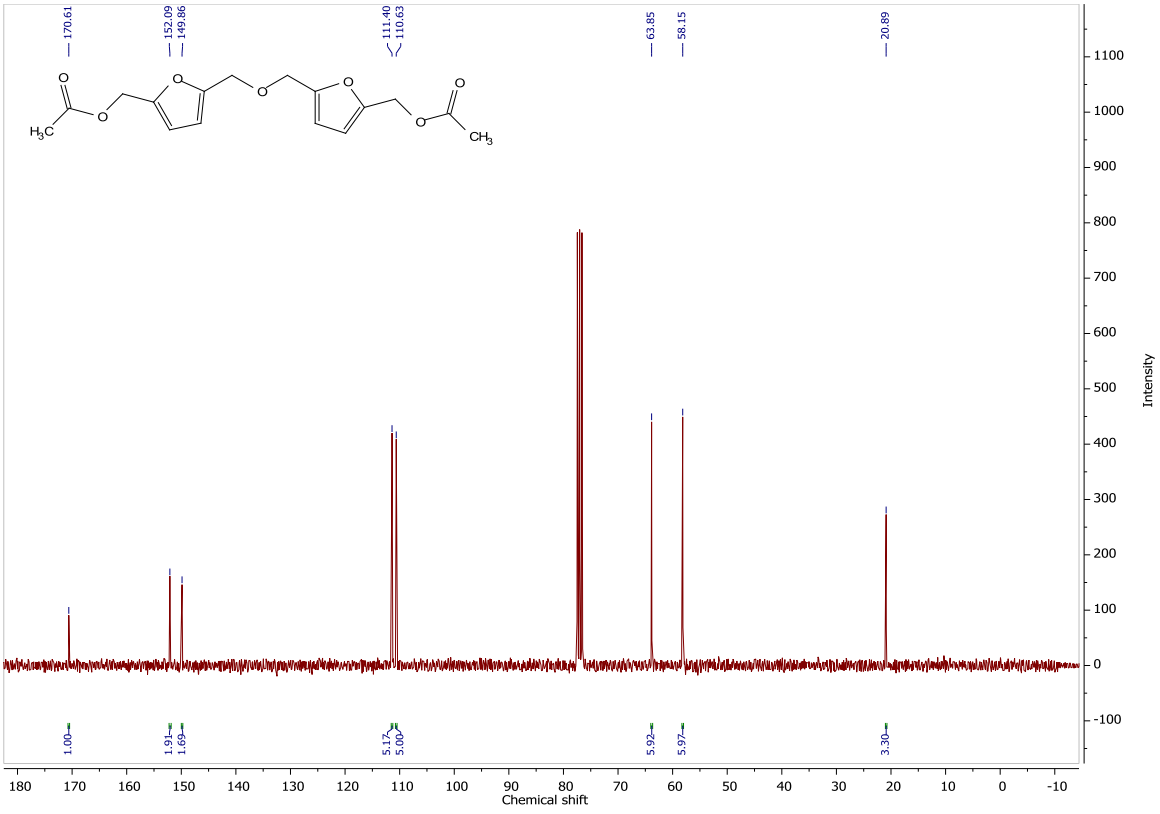


Figure S6. ^{13}C NMR spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) diacetate, **1b** (75 MHz, chloroform-*d*).

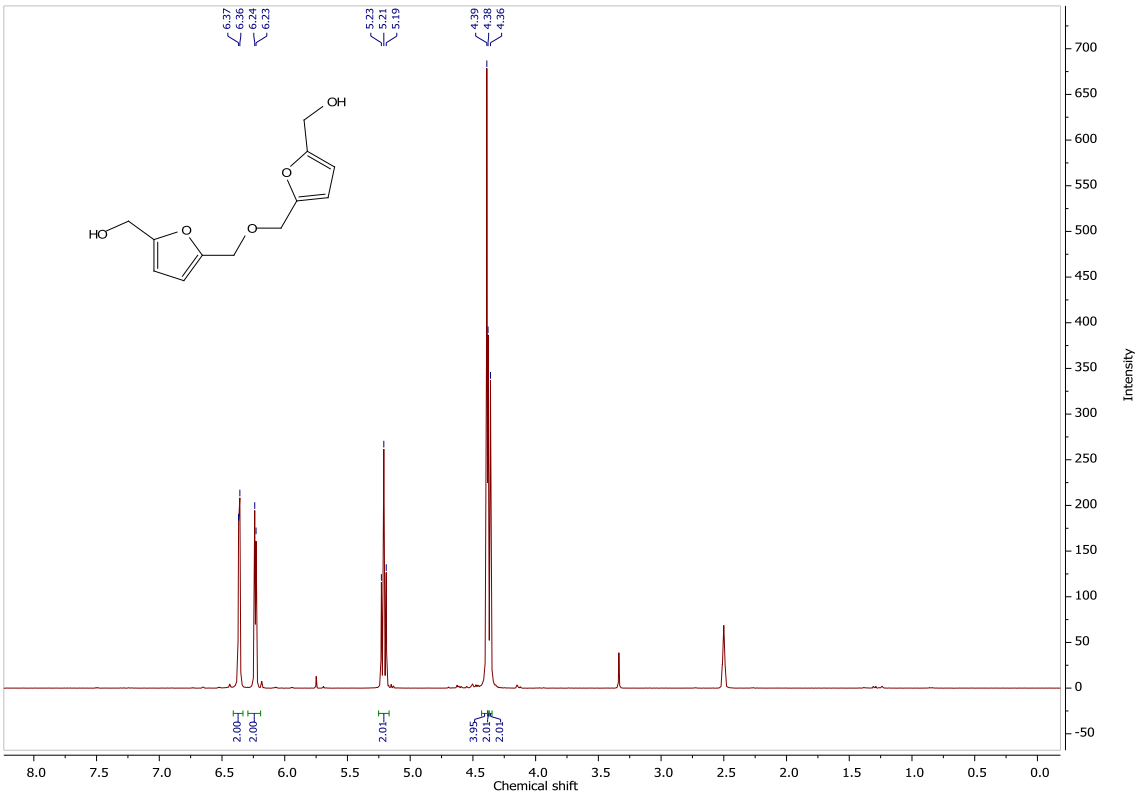


Figure S7. ^{1}H NMR spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))dimethanol, **1c** (300 MHz, DMSO-d_6).

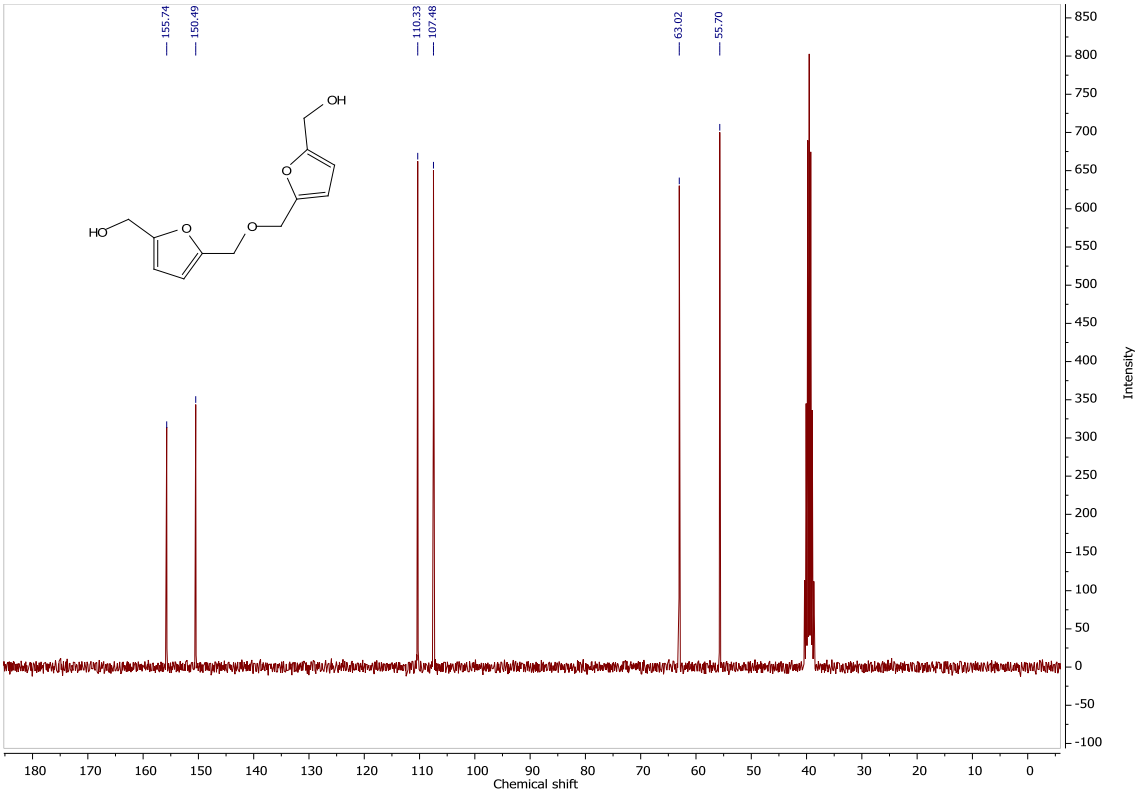


Figure S8. ^{13}C NMR spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))dimethanol, **1c** (75 MHz, DMSO-d_6).

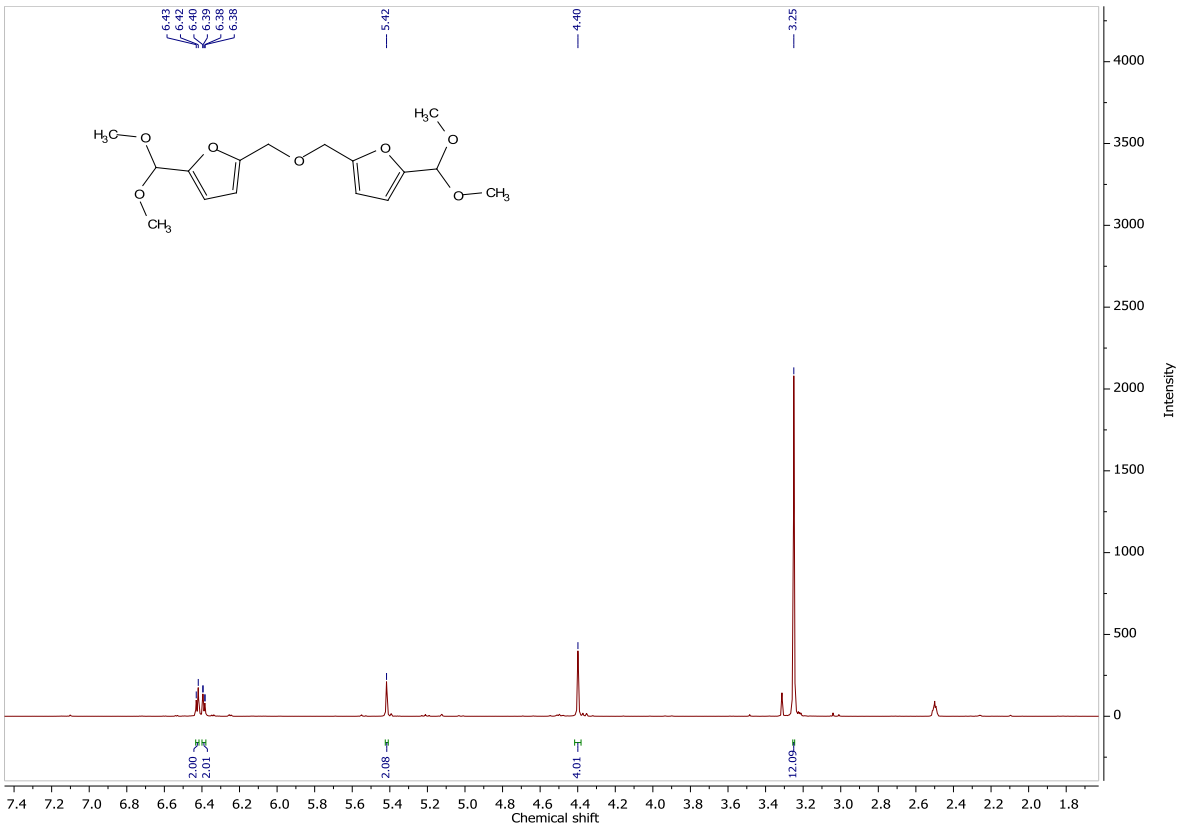


Figure S9. ^{1}H NMR spectrum of 5,5'-(oxybis(methylene))bis(2-(dimethoxymethyl)furan), **1d** (300 MHz, DMSO-d_6).

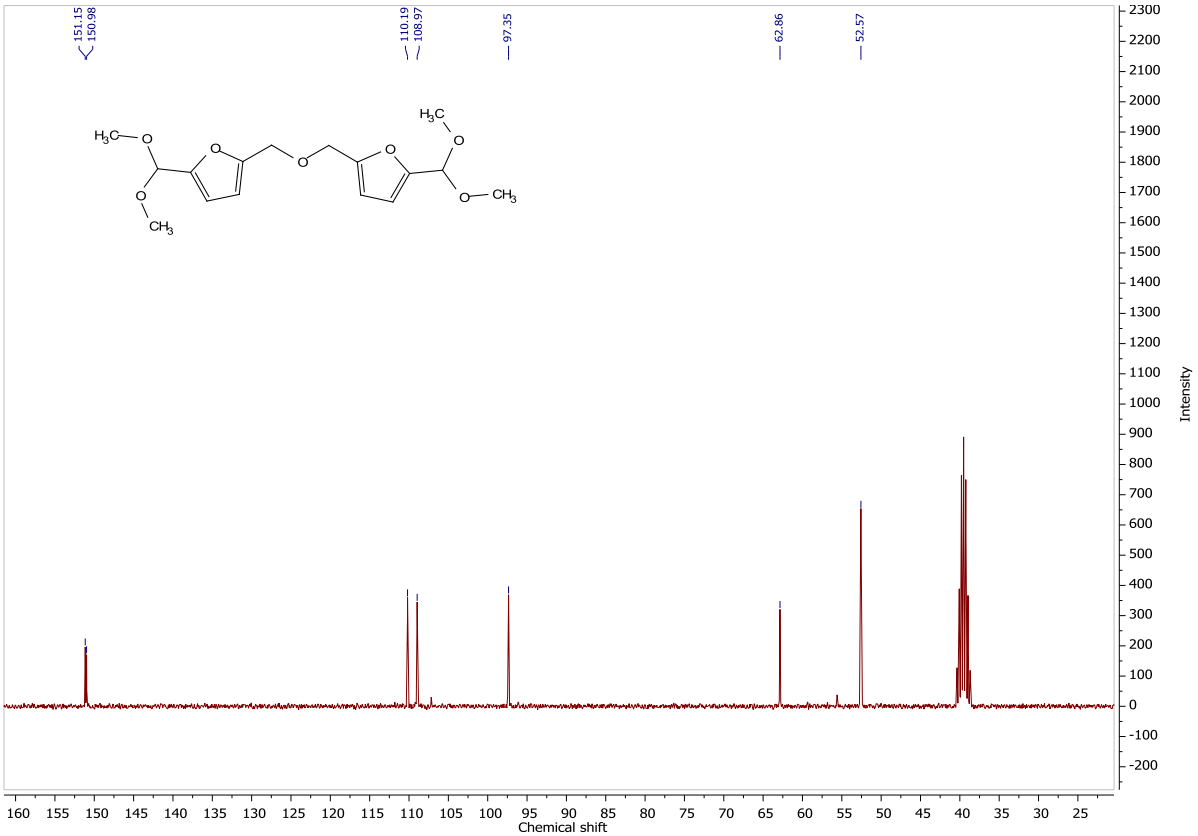


Figure S10. ^{13}C NMR spectrum of 5,5'-(oxybis(methylene))bis(2-(dimethoxymethyl)furan), **1d** (75 MHz, DMSO-d_6).

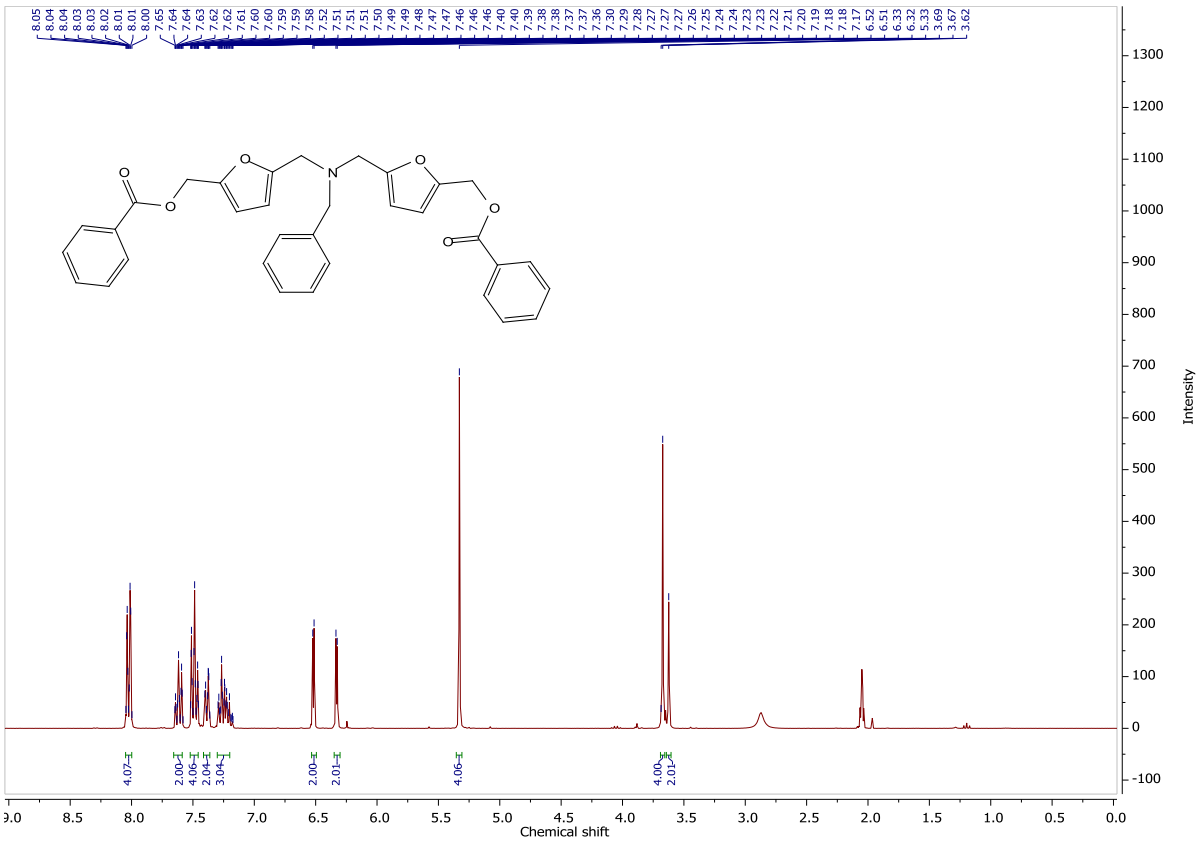


Figure S11. ^{1}H NMR spectrum of (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate, **1e** (300 MHz, Acetone-d_6).

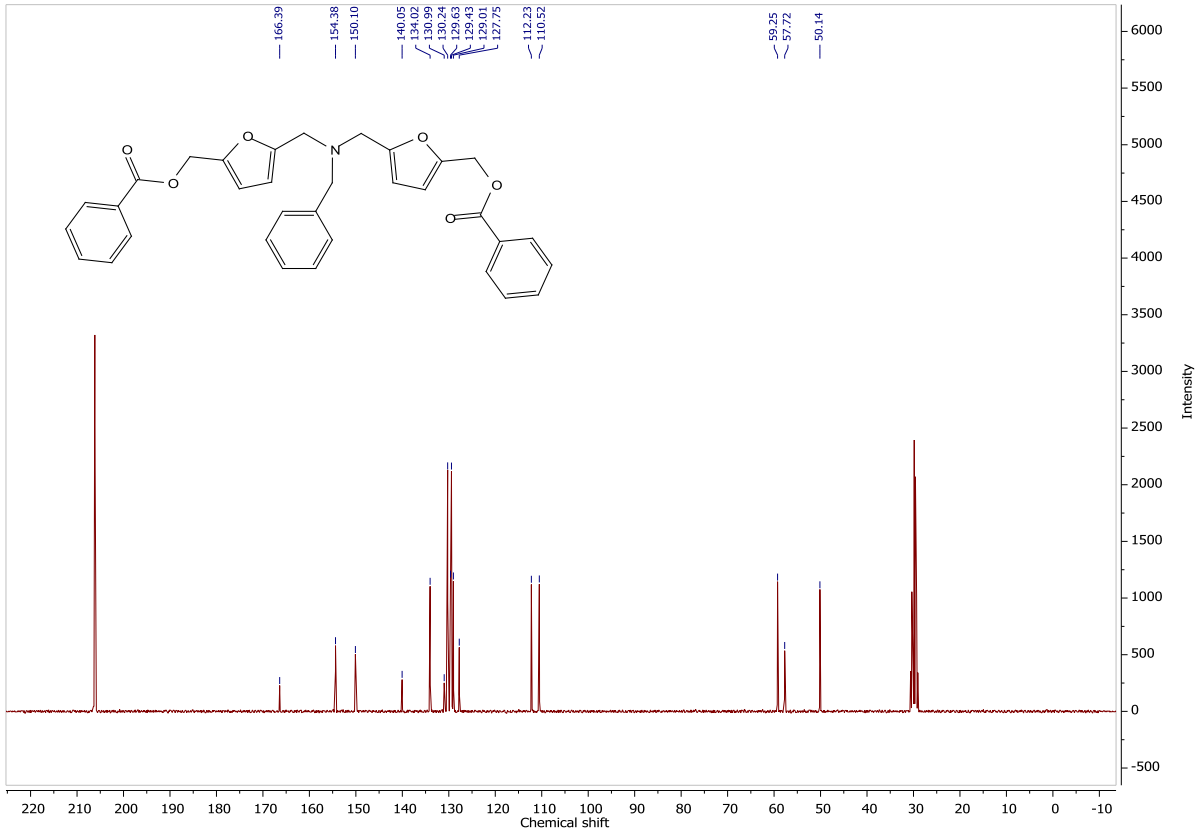


Figure S12. ^{13}C NMR spectrum of (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate, **1e** (75 MHz, Acetone-d_6).

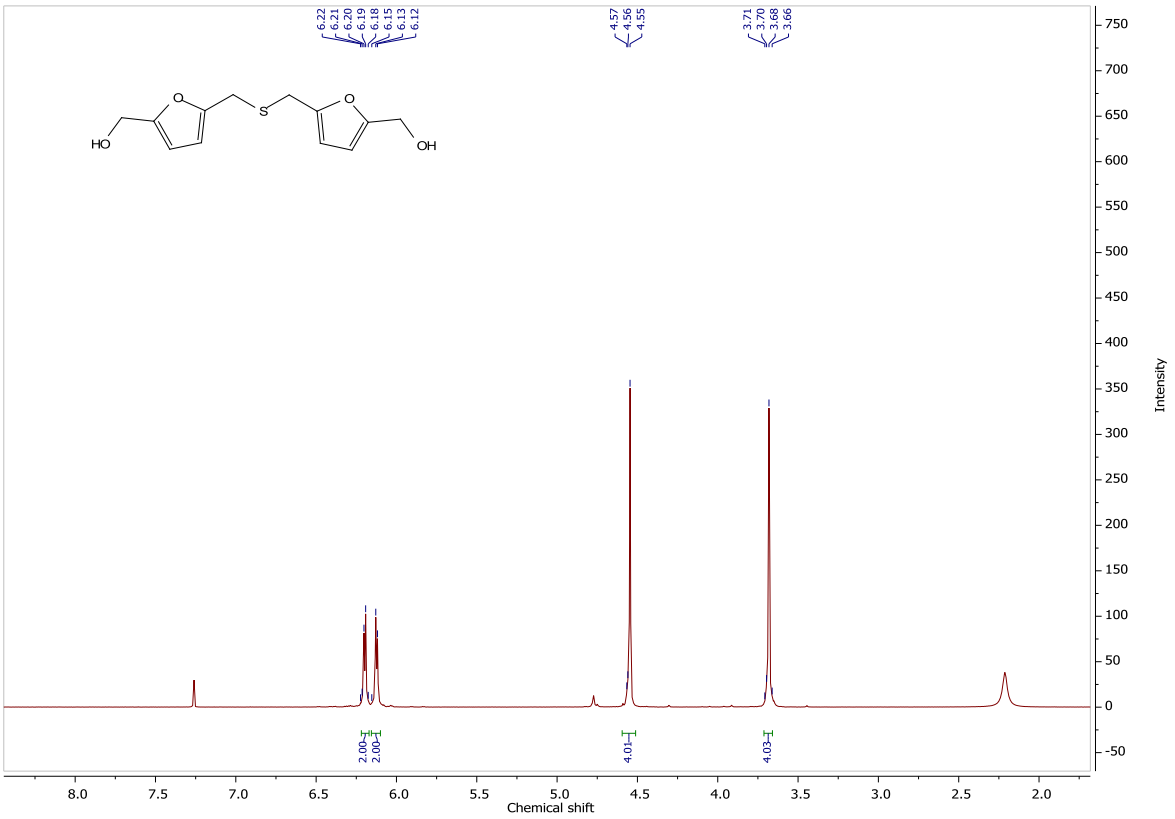


Figure S13. ^{1}H NMR spectrum of ((thiobis(methylene))bis(furan-5,2-diyl))dimethanol, **1f** (300 MHz, Chloroform-*d*).

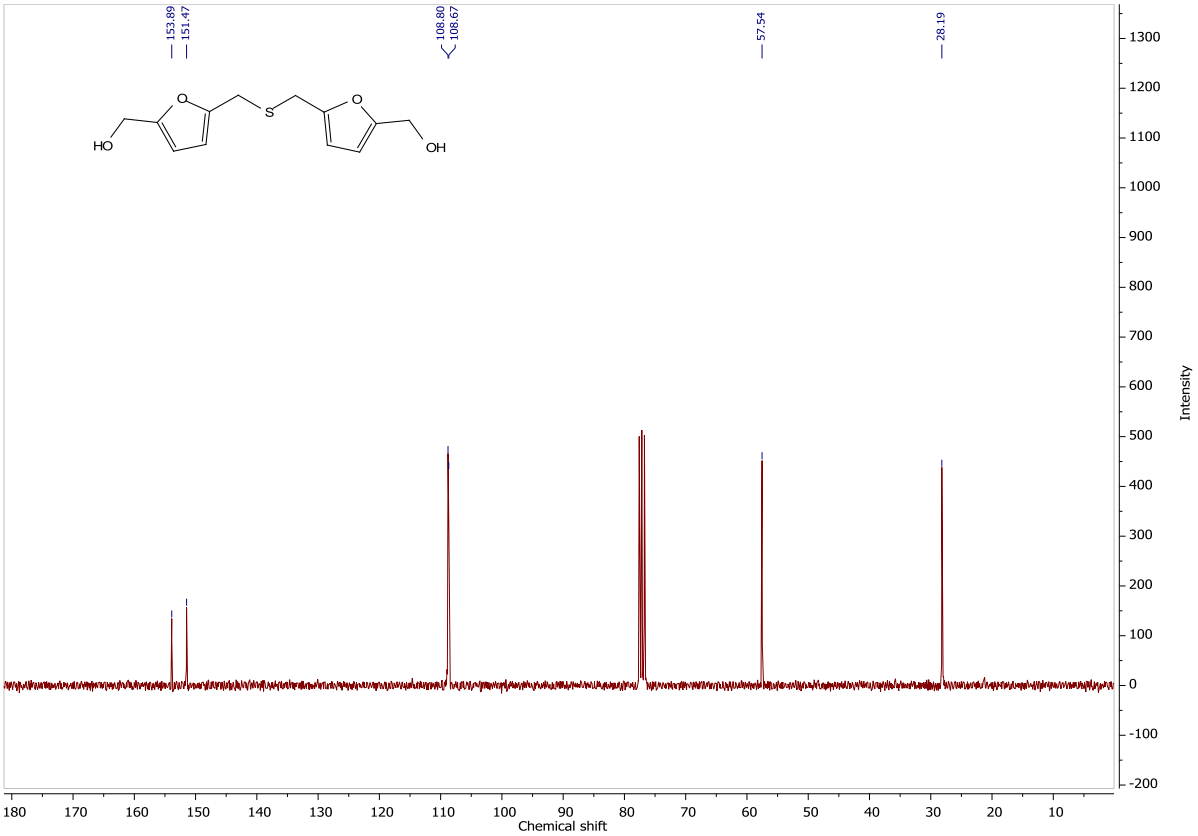


Figure S14. ^{13}C NMR spectrum of ((thiobis(methylene))bis(furan-5,2-diyl))dimethanol, **1f** (75 MHz, Chloroform-*d*).

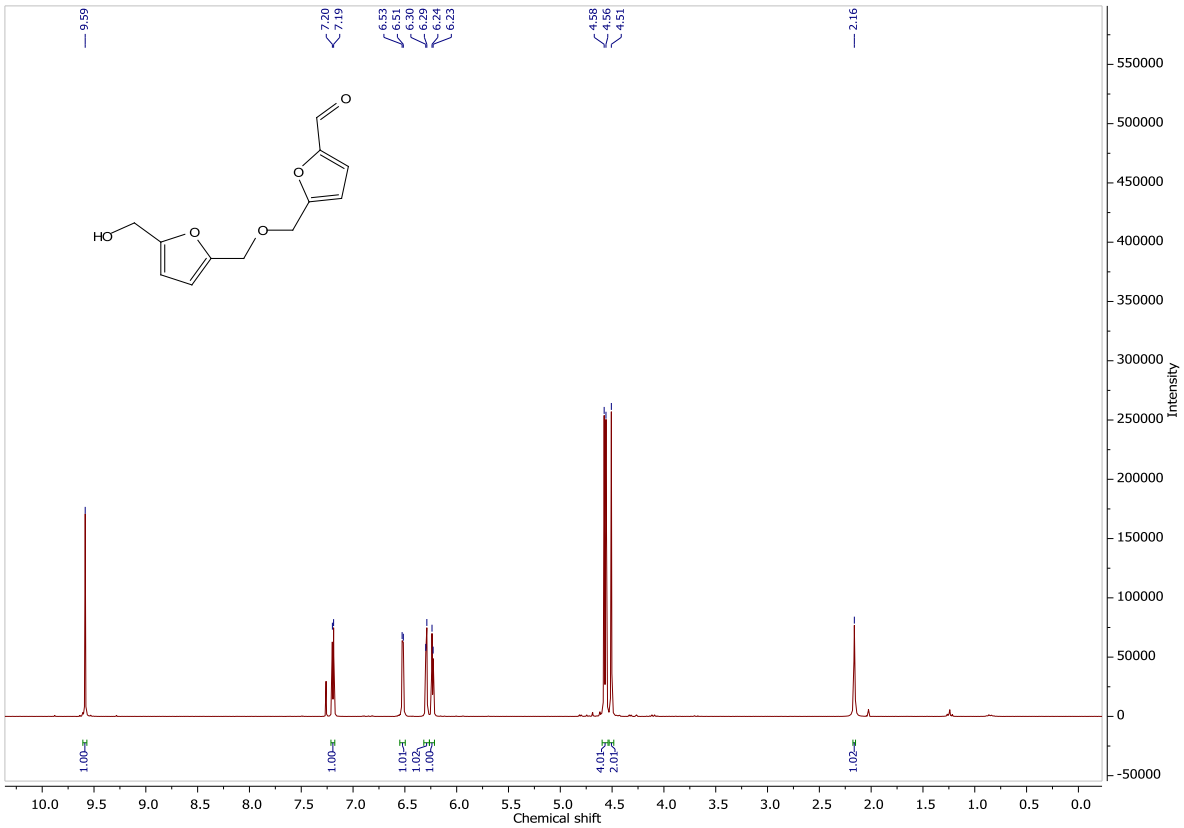


Figure S15. [1]H NMR spectrum of 5-(((5-(hydroxymethyl)furan-2-yl)methoxy)methyl)furan-2-carbaldehyde, **1g** (300 MHz, Chloroform-*d*).

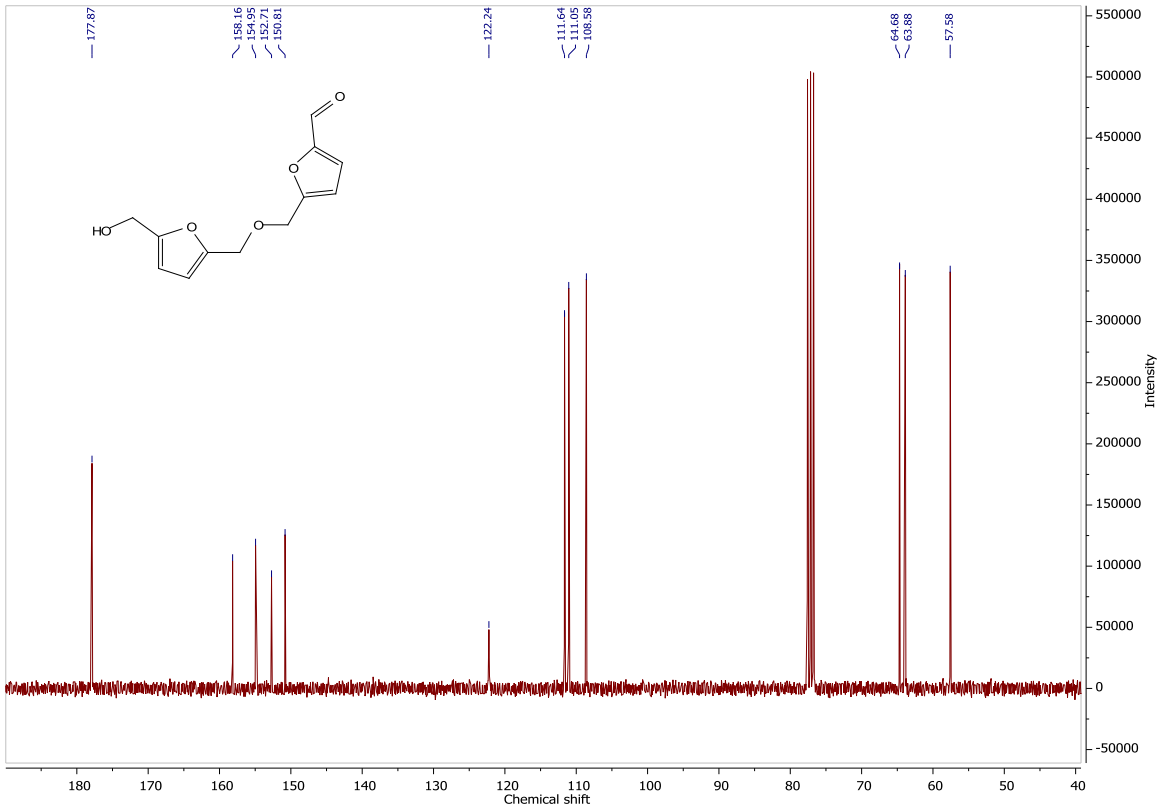


Figure S16. [13]C NMR spectrum of 5-(((5-(hydroxymethyl)furan-2-yl)methoxy)methyl)furan-2-carbaldehyde, **1g** (75 MHz, Chloroform-*d*).

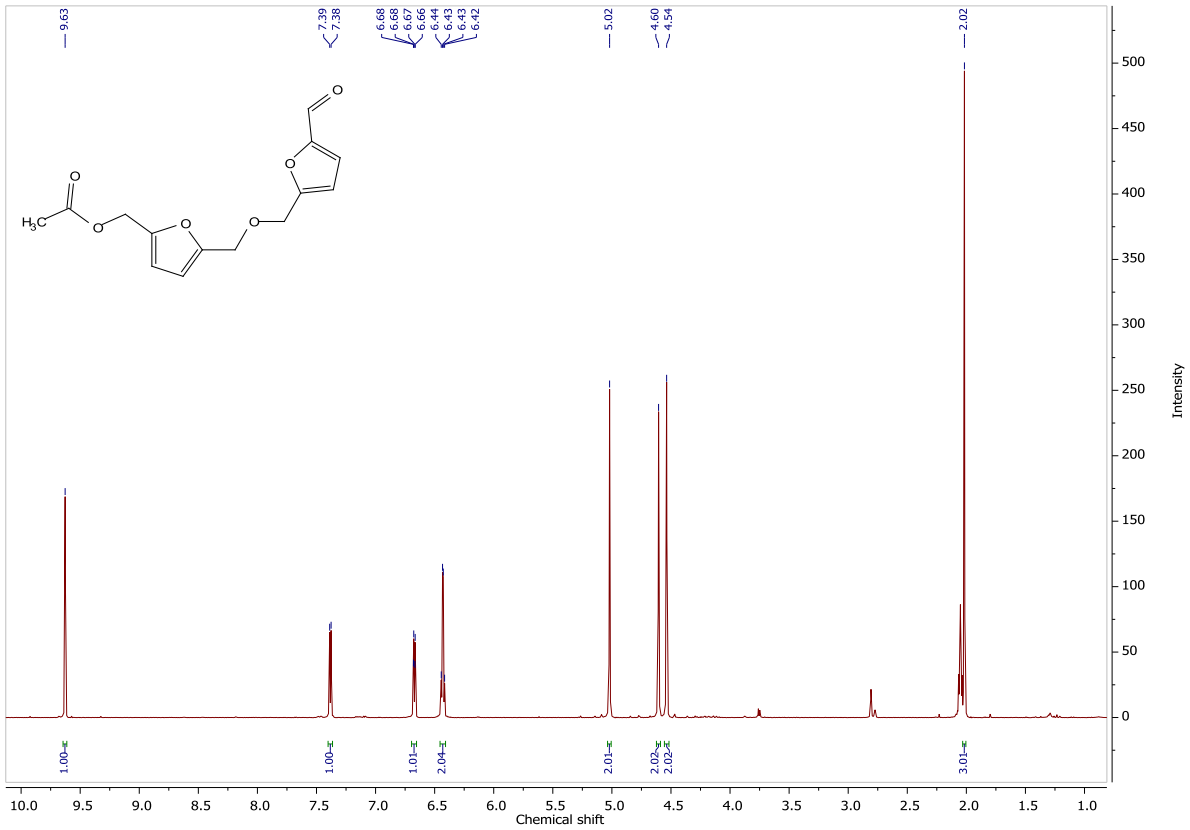


Figure S17. ^{1}H NMR spectrum of (5-(((5-formylfuran-2-yl)methoxy)methyl)furan-2-yl)methyl acetate, **1h** (300 MHz, Acetone-d_6).

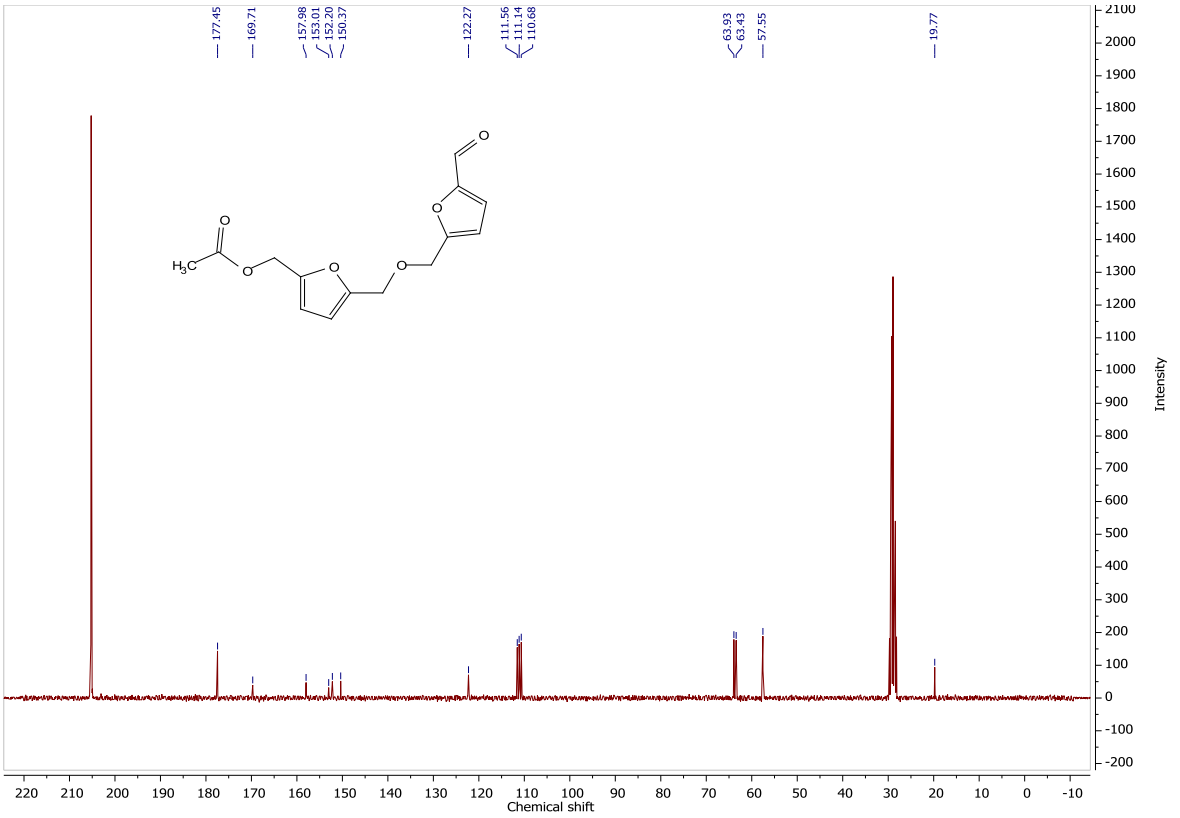


Figure S18. ^{13}C NMR spectrum of (5-(((5-formylfuran-2-yl)methoxy)methyl)furan-2-yl)methyl acetate, **1h** (75 MHz, Acetone-d_6).

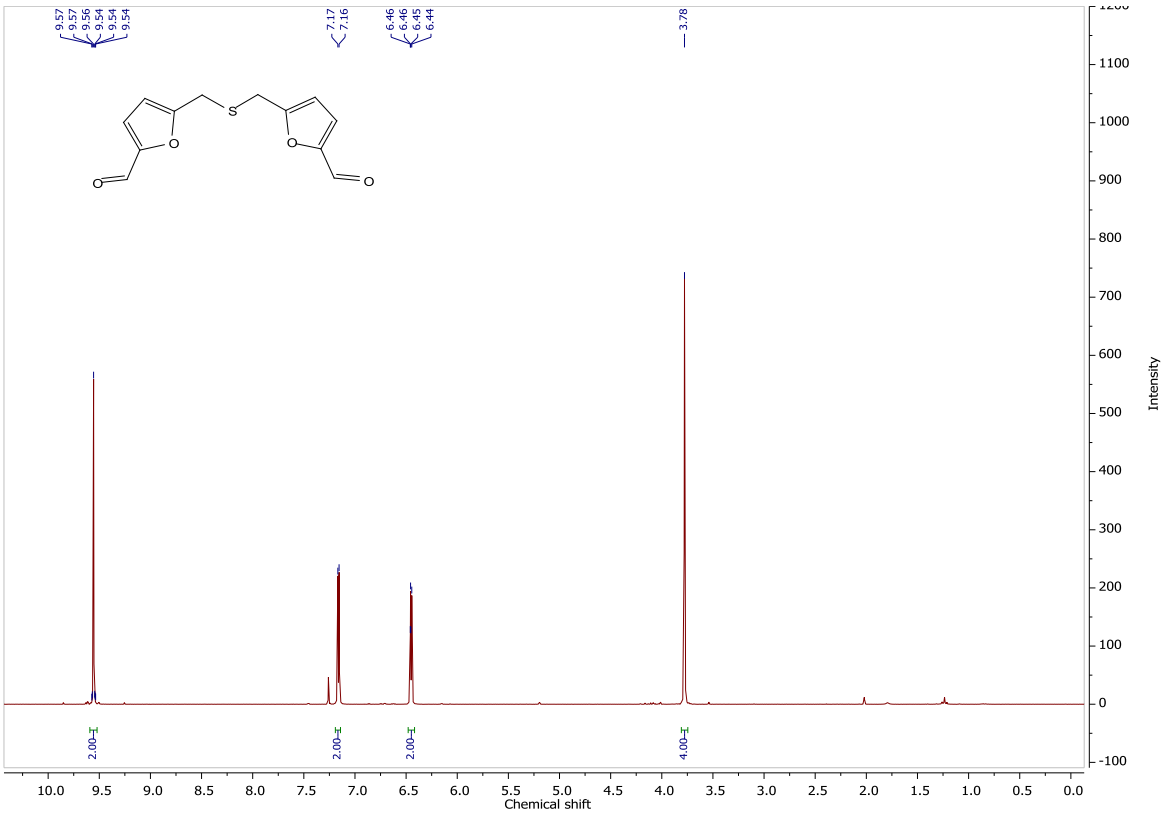


Figure S19. ^{1}H NMR spectrum of 5,5'-(thiobis(methylene))bis(furan-2-carbaldehyde) **1i** (300 MHz, Chloroform-*d*).

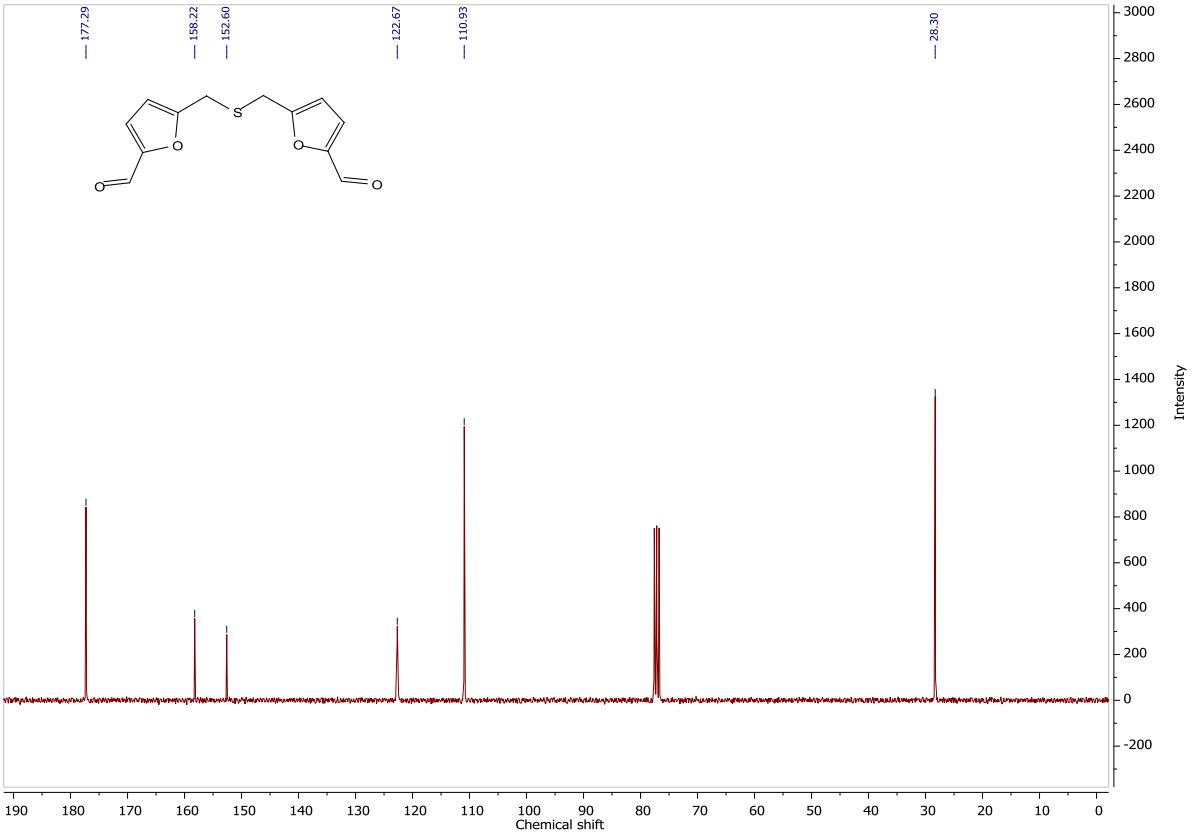


Figure S20. ^{13}C NMR spectrum of 5,5'-(thiobis(methylene))bis(furan-2-carbaldehyde) **1i** (75 MHz, Chloroform-*d*).

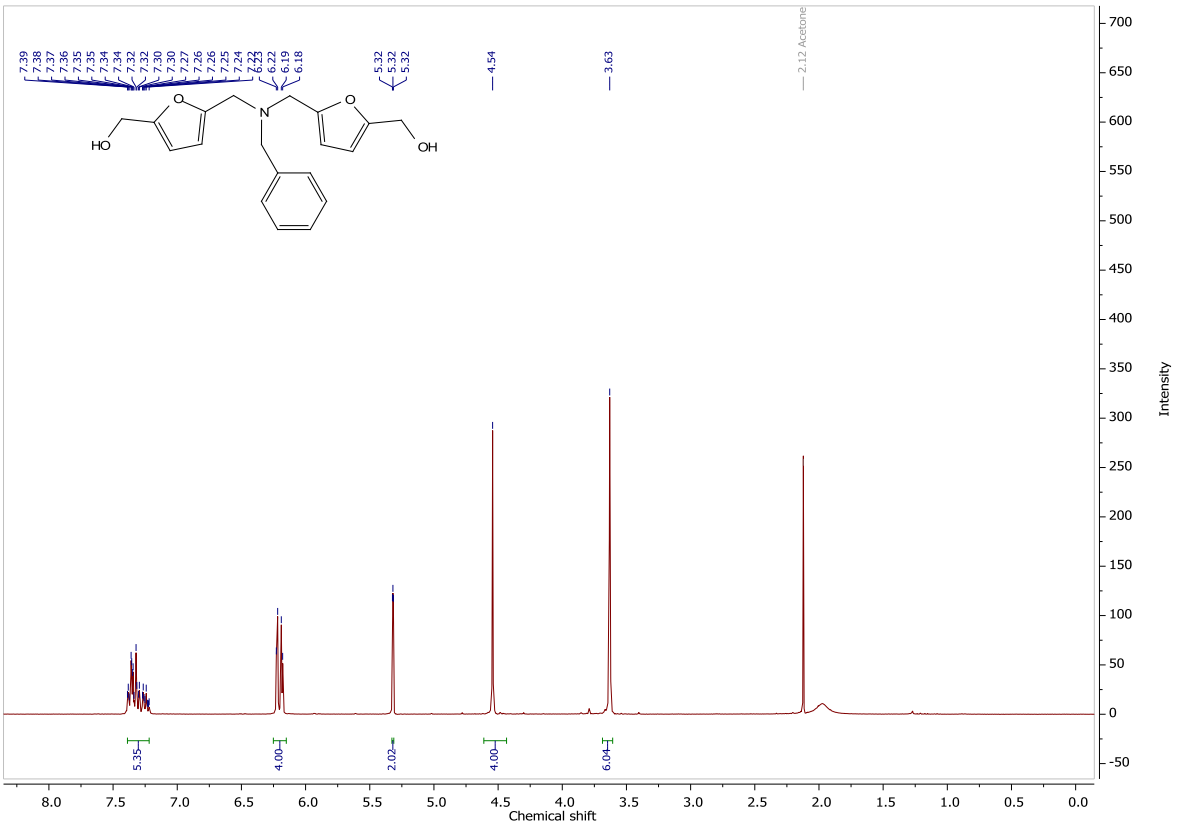


Figure S21. ^{1}H NMR spectrum of (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))dimethanol **1j** (300 MHz, Methylene Chloride-d_2).

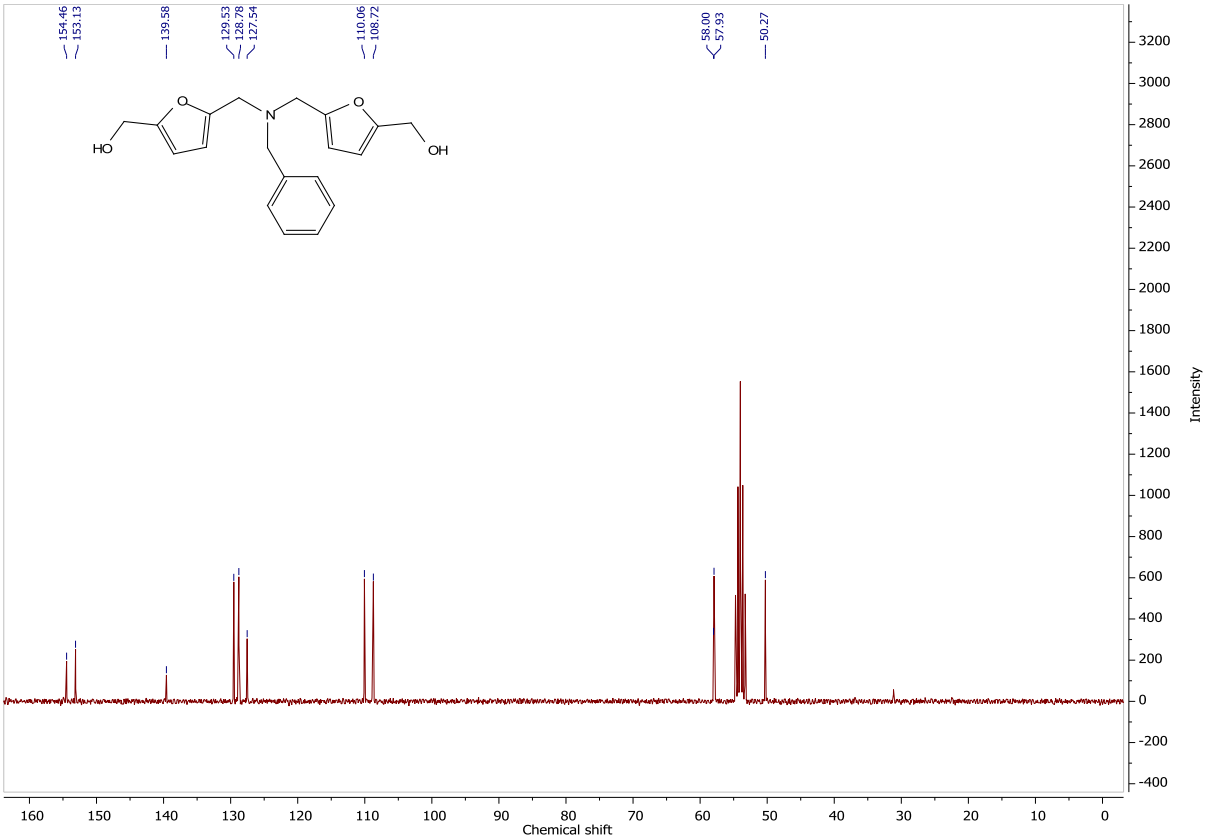


Figure S22. ^{1}H NMR spectrum of (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))dimethanol **1j** (75 MHz, Methylene Chloride-d_2).

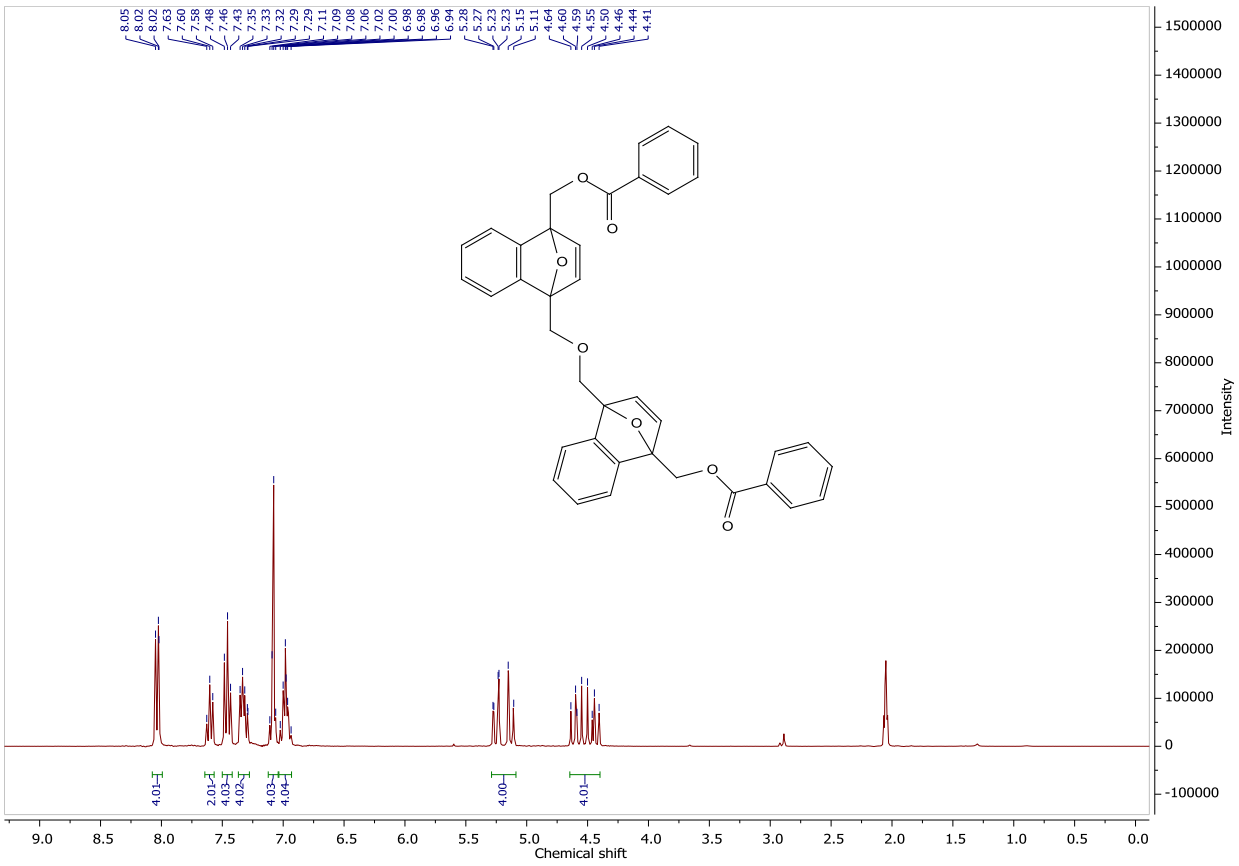


Figure S23. ^{1}H NMR spectrum of ((oxybis(methylene))bis(1,4-epoxynaphthalene-4,1(4H)-diyl))bis(methylene) dibenzoate **4ac** (300 MHz, Acetone-d_6).

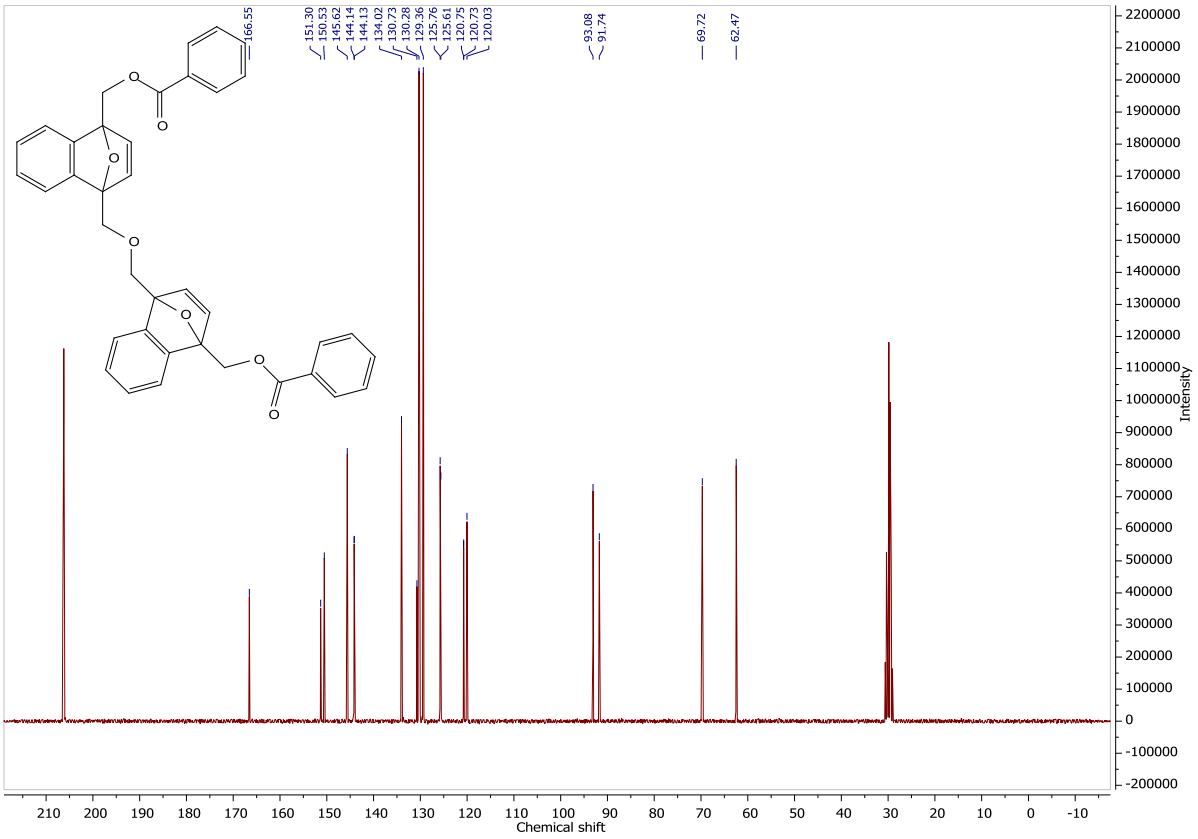


Figure S24. ^{13}C NMR spectrum of ((oxybis(methylene))bis(1,4-epoxynaphthalene-4,1(4H)-diyl))bis(methylene) dibenzoate **4ac** (75 MHz, Acetone-d_6).

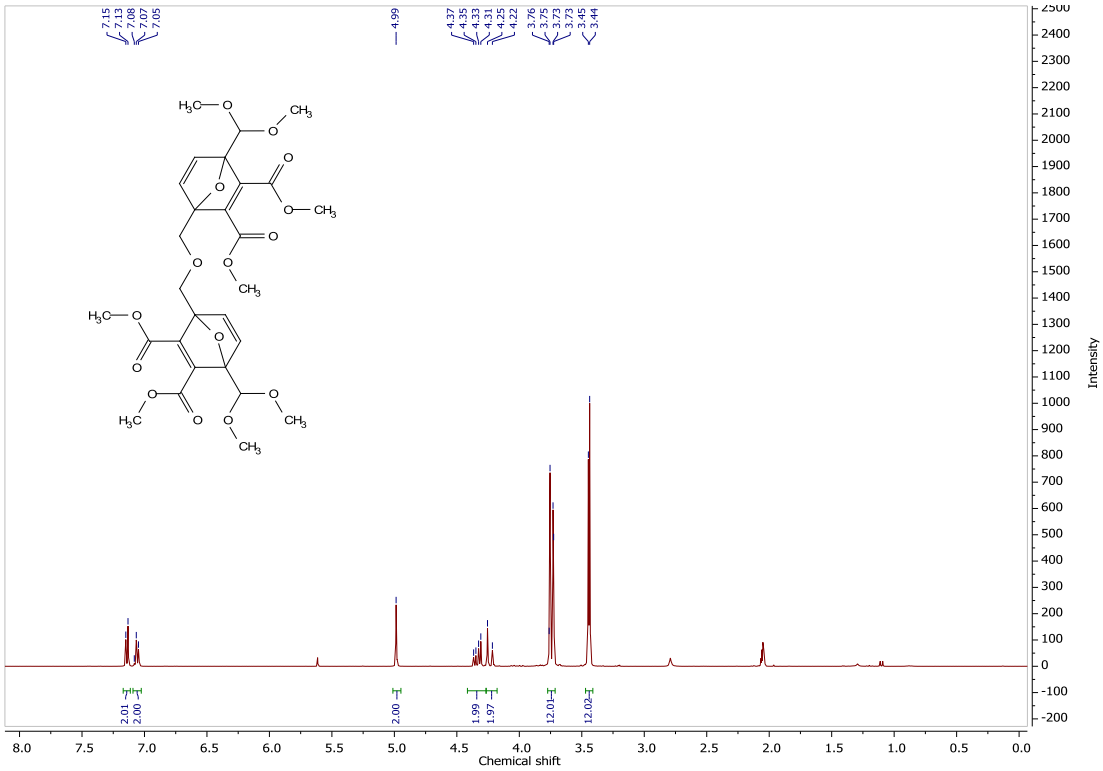


Figure S25. ^{1}H NMR spectrum of 4,4'-(oxybis(methylene))bis(1-(dimethoxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) **4da** (300 MHz, Acetone-d_6).

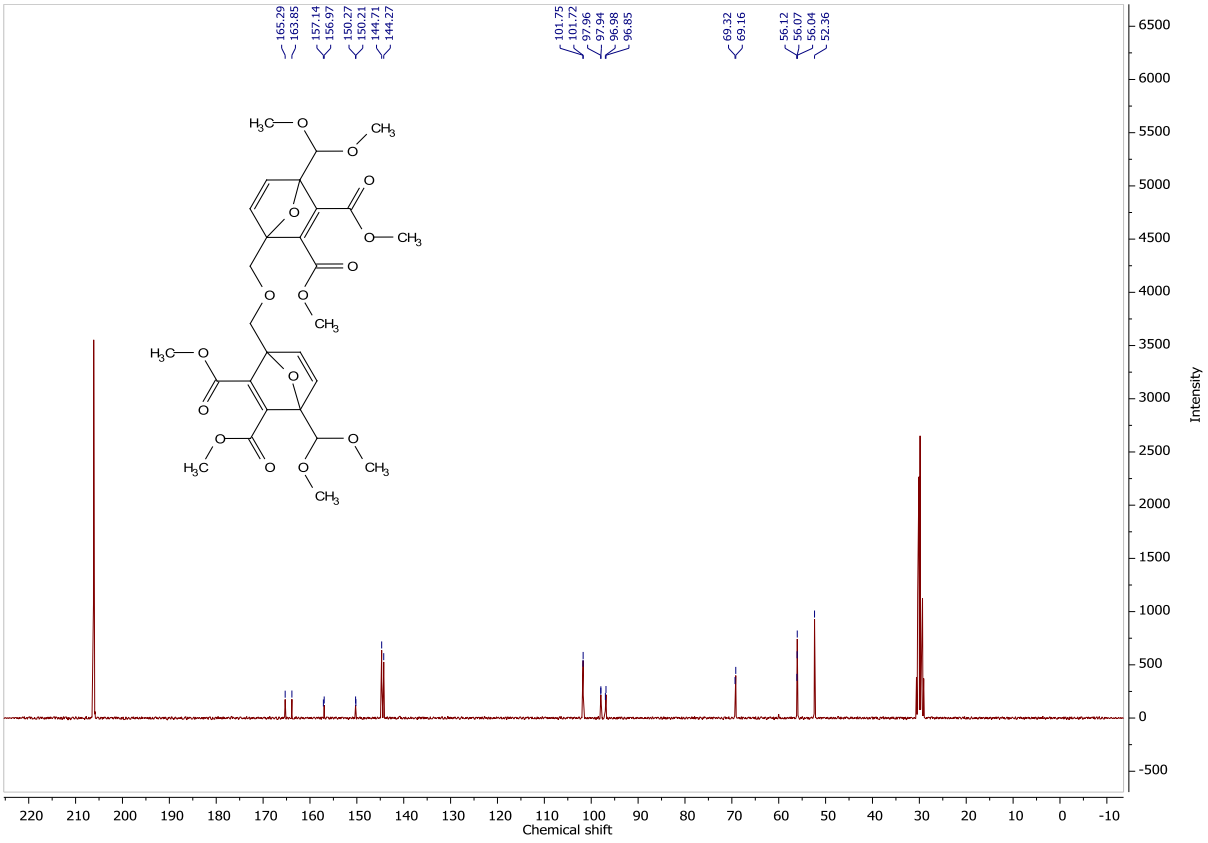


Figure S26. ^{13}C NMR spectrum of 4,4'-(oxybis(methylene))bis(1-(dimethoxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) **4da** (75 MHz, Acetone-d_6).

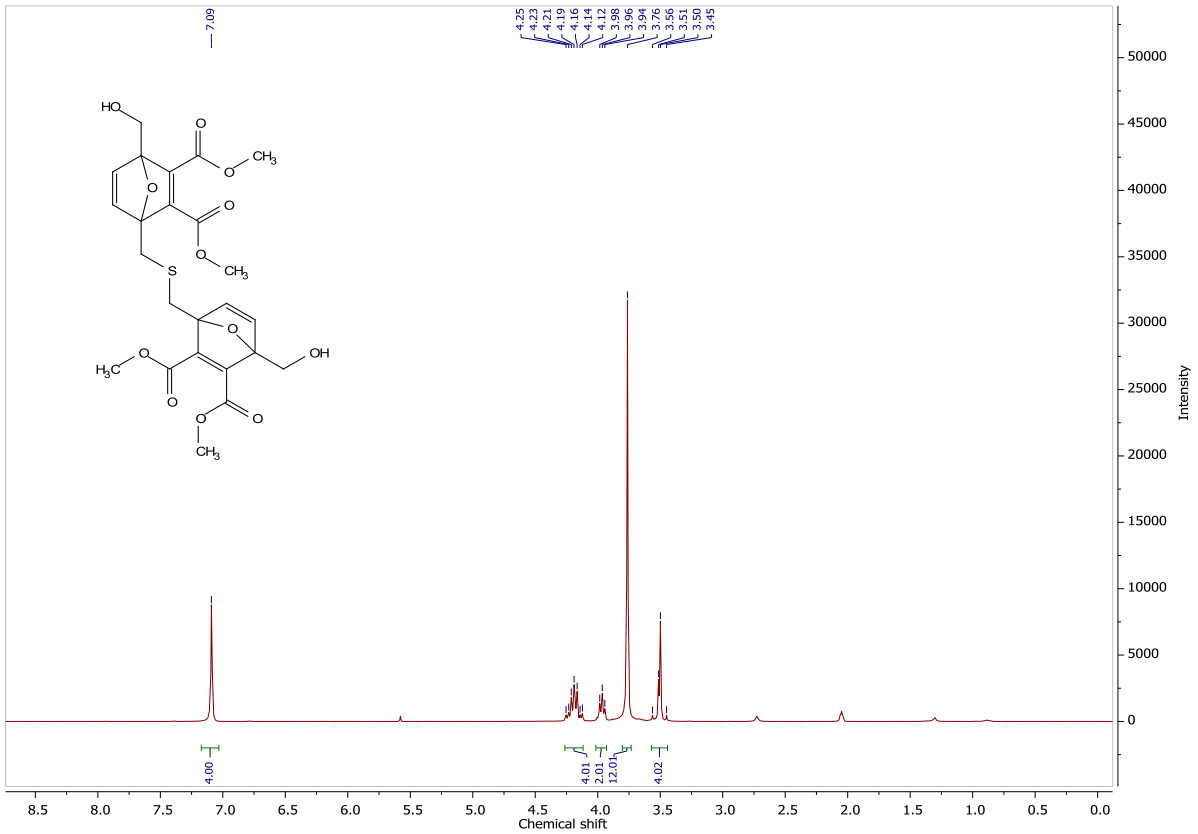


Figure S27. ^{1}H NMR spectrum of 4,4'-(thiobis(methylene))bis(1-(hydroxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) **4fa** (300 MHz, Acetone-d_6).

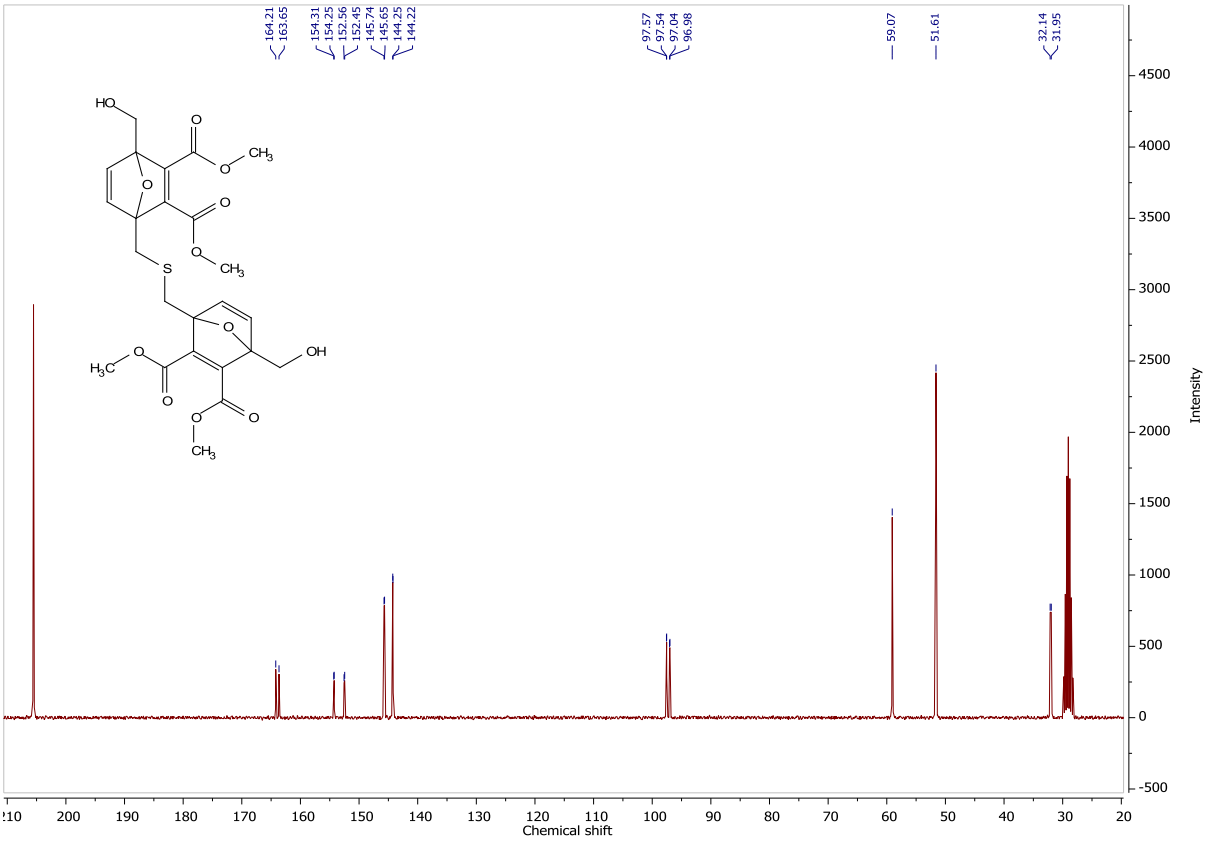


Figure S28. ^{1}H NMR spectrum of 4,4'-(thiobis(methylene))bis(1-(hydroxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) **4fa** (75 MHz, Acetone-d_6).

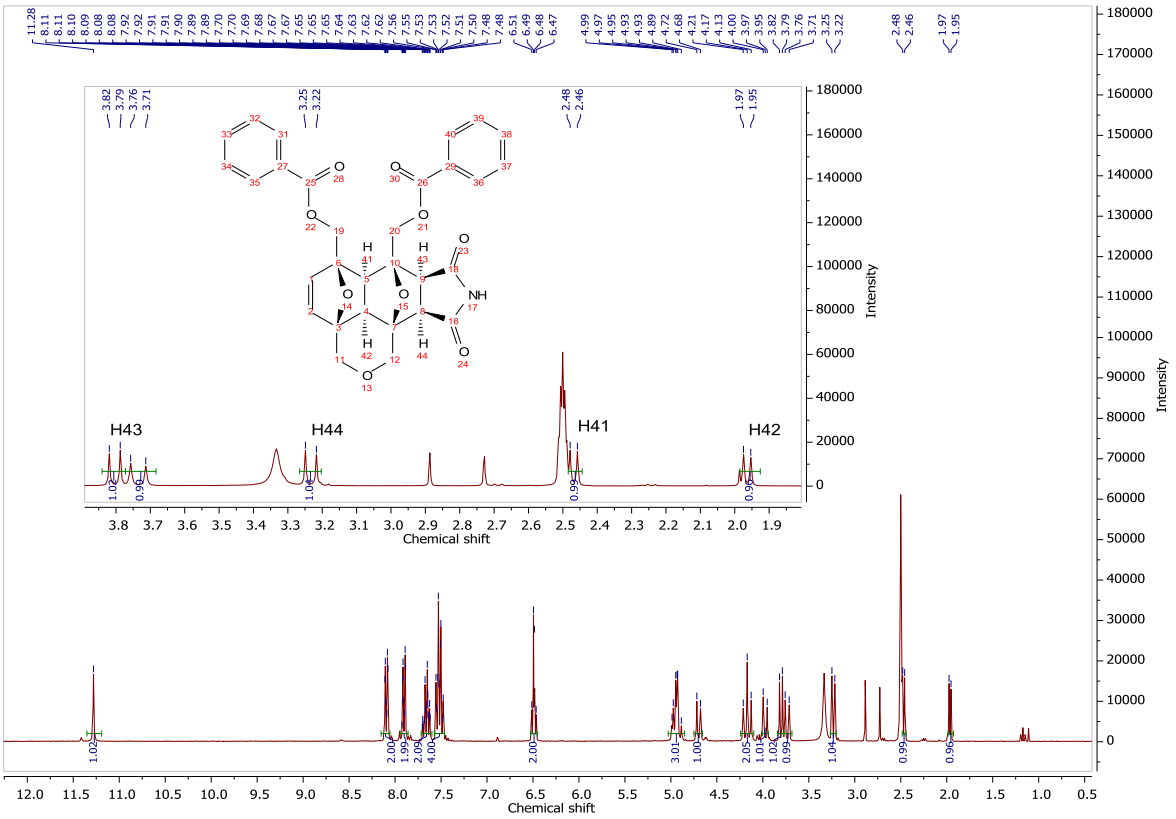


Figure S29. ^{1}H NMR spectrum of exo-(8,10-dioxo-3a^{1},6a,8,9,10,10a-hexahydro-1H,3H,6H-3a,6:7,10b-diepoxyisochromeno[4,5-ef]isoindole-6,7(7aH)-diyl)bis(methylene) dibenzoate **3ab** (300 MHz, DMSO-d_6).

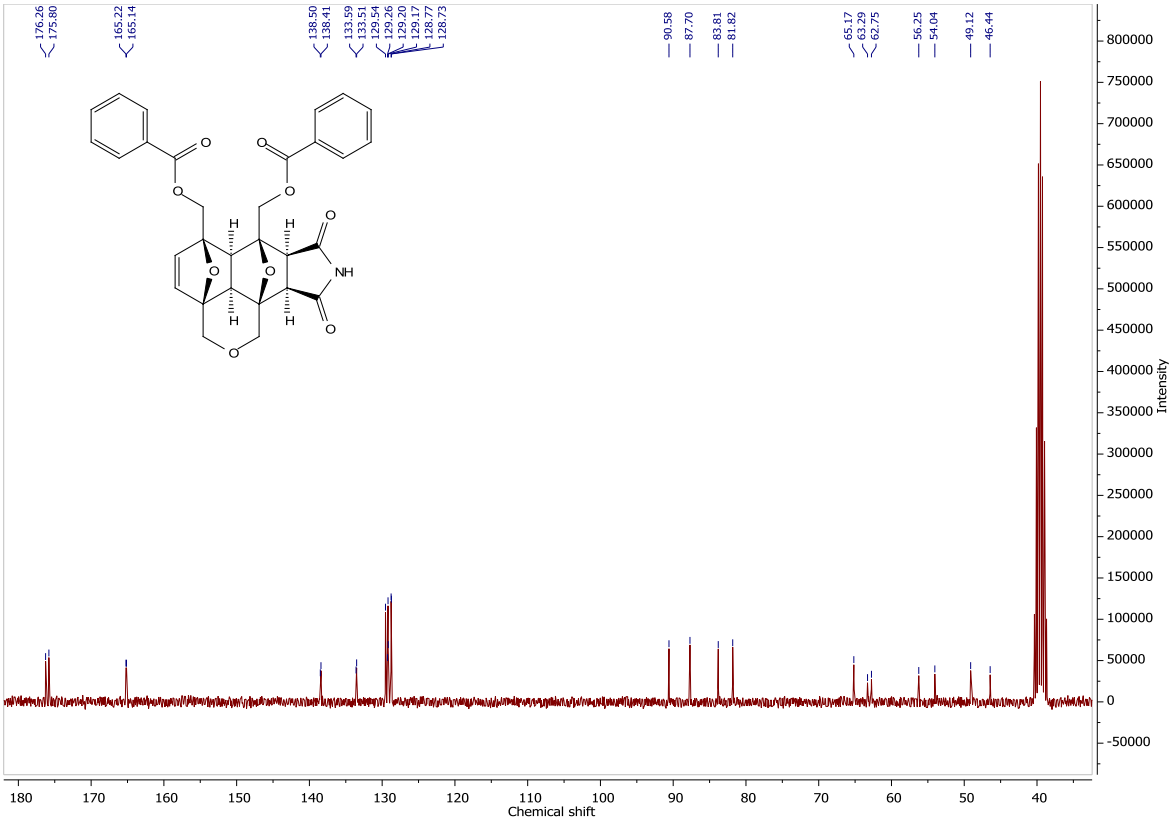


Figure S30. ^{13}C NMR spectrum of exo-(8,10-dioxo-3a^{1},6a,8,9,10,10a-hexahydro-1H,3H,6H-3a,6:7,10b-diepoxyisochromeno[4,5-ef]isoindole-6,7(7aH)-diyl)bis(methylene) dibenzoate **3ab** (75 MHz, DMSO-d_6).

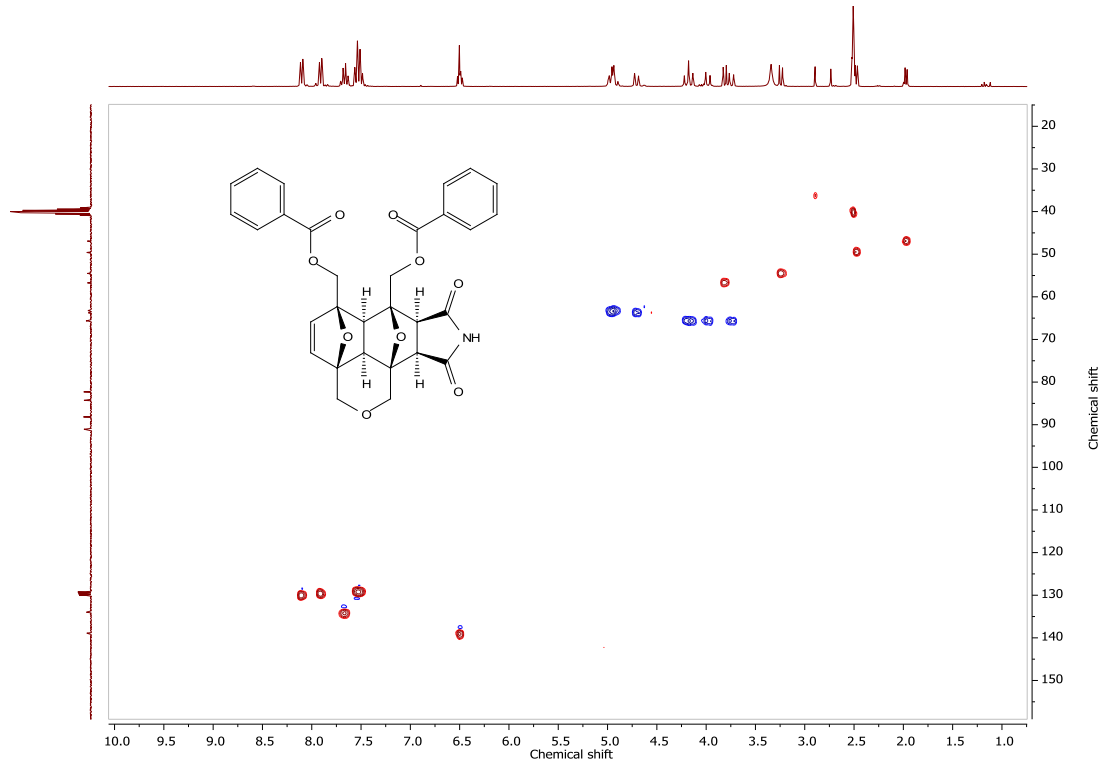


Figure S31. $^{1}H–^{13}C$ HSQC NMR spectrum of exo-(8,10-dioxo-3a[1],6a,8,9,10,10a-hexahydro-1H,3H,6H-3a,6:7,10b-diepoxyisochromeno[4,5-ef]isoindole-6,7(7aH)-diyl)bis(methylene) dibenzoate **3ab** (300 MHz, DMSO-d_6).

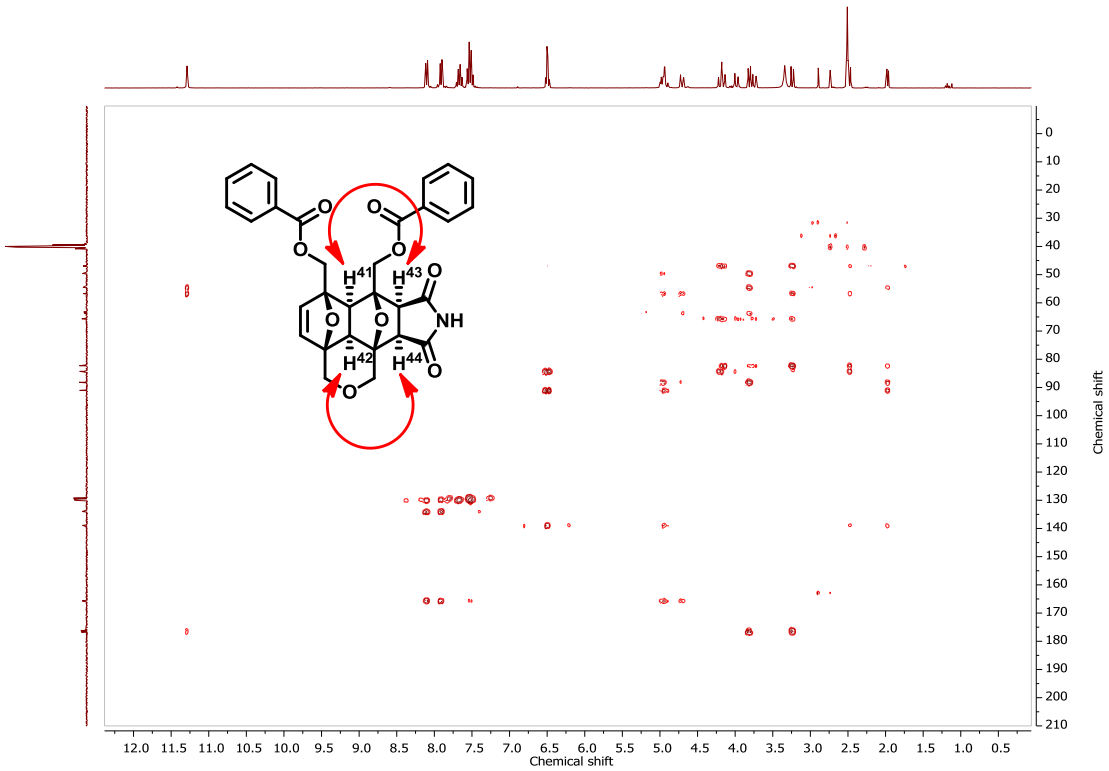


Fig. S32. ^{1}H-^{13}C HMBC NMR spectrum of exo-(8,10-dioxo-3a[1],6a,8,9,10,10a-hexahydro-1H,3H,6H-3a,6:7,10b-diepoxyisochromeno[4,5-ef]isoindole-6,7(7aH)-diyl)bis(methylene) dibenzoate **3ab** (300 MHz, DMSO-d_6).

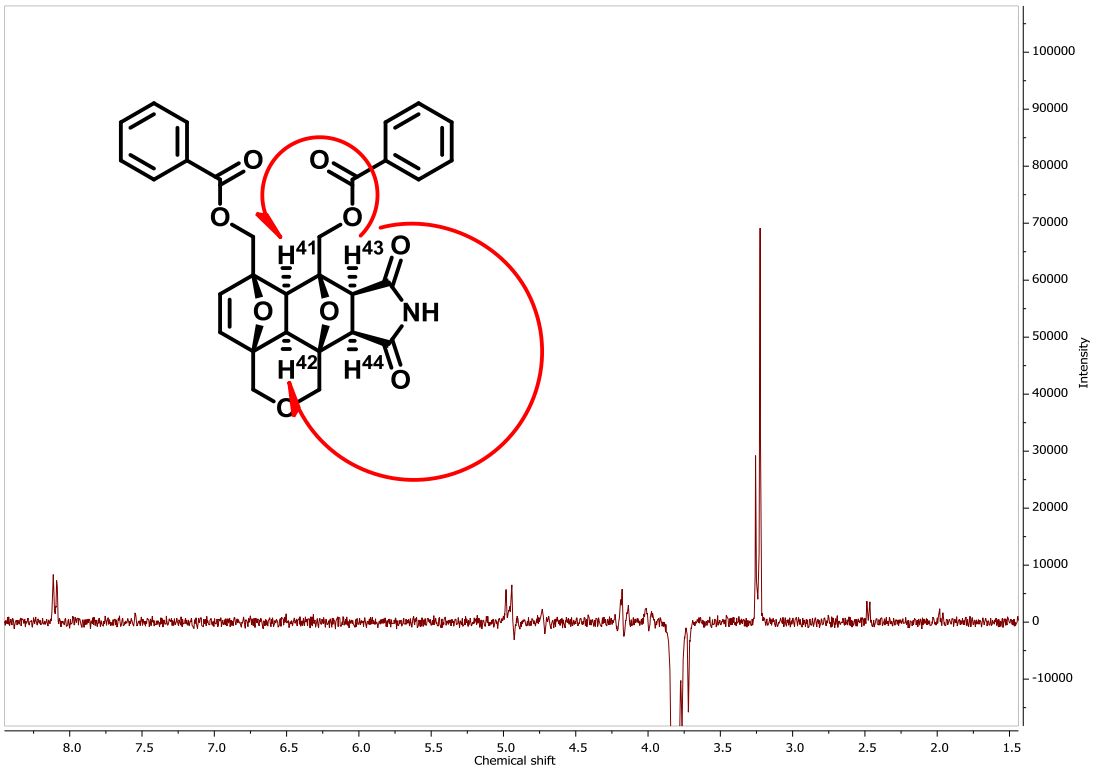


Fig. S33. NOE NMR spectrum of exo-(8,10-dioxo-3a[1],6a,8,9,10,10a-hexahydro-1H,3H,6H-3a,6:7,10b-diepoxyisochromeno[4,5-ef]isoindole-6,7(7aH)-diyl)bis(methylene) dibenzoate **3ab** (300 MHz, DMSO-d_6).

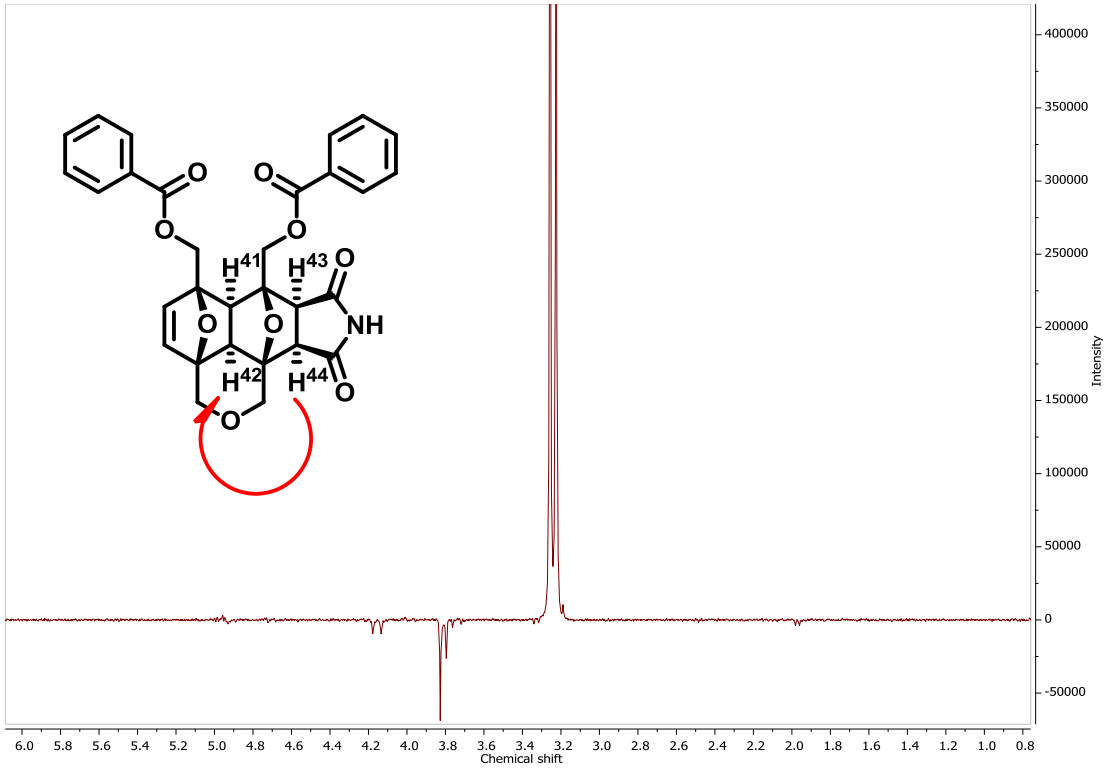


Fig. S34. NOE NMR spectrum of exo-(8,10-dioxo-3a[1],6a,8,9,10,10a-hexahydro-1H,3H,6H-3a,6:7,10b-diepoxyisochromeno[4,5-ef]isoindole-6,7(7aH)-diyl)bis(methylene) dibenzoate **3ab** (300 MHz, DMSO-d_6).

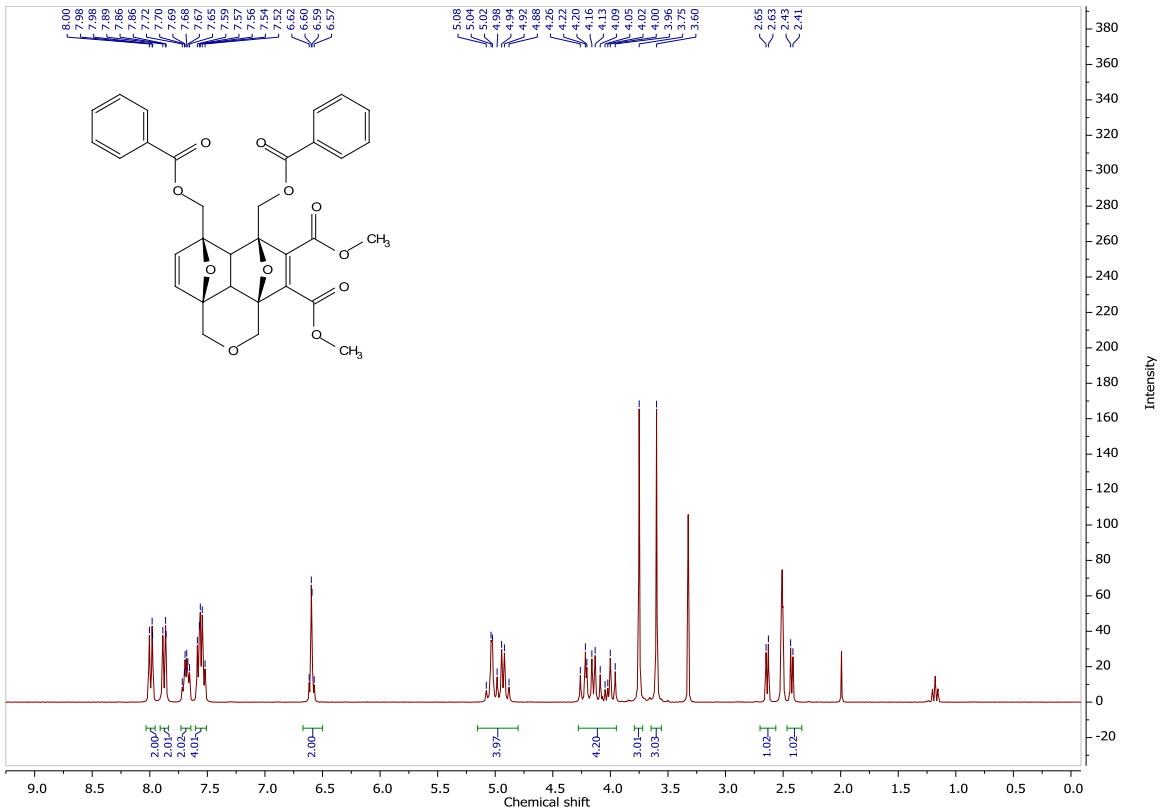


Figure S35. ^{1}H NMR spectrum of Dimethyl 6,7-bis((benzoyloxy)methyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3aa** (300 MHz, DMSO-d_6).

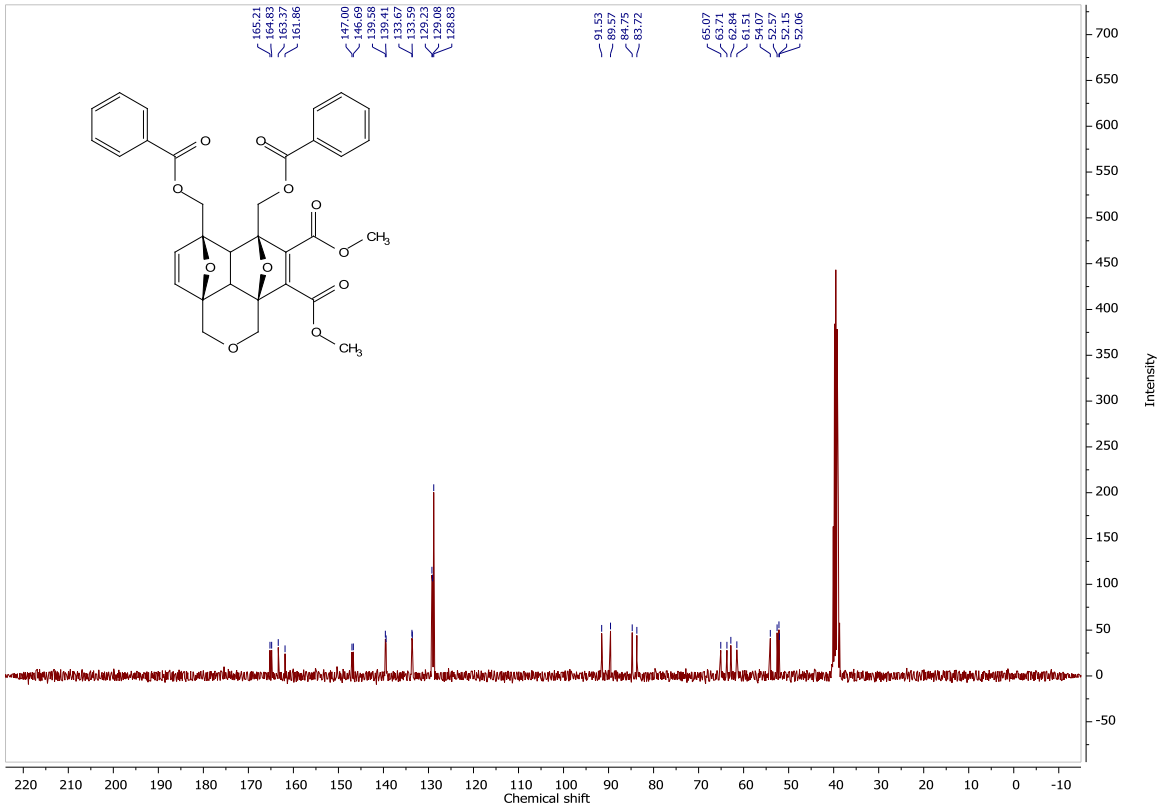


Figure S36. ^{13}C NMR spectrum of dimethyl 6,7-bis((benzoyloxy)methyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3aa** (75 MHz, DMSO-d_6).

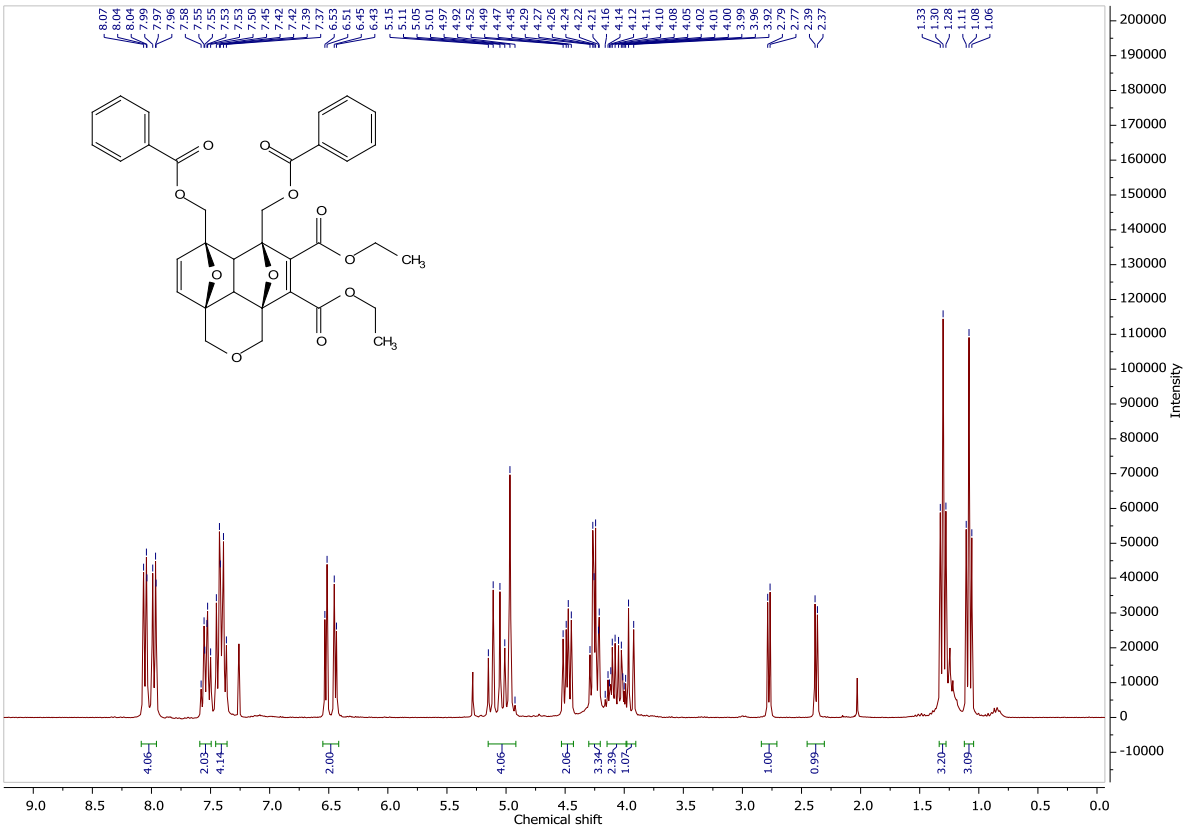


Figure S37. ^{1}H NMR spectrum of diethyl 6,7-bis((benzoyloxy)methyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ad** (300 MHz, Chloroform-*d*).

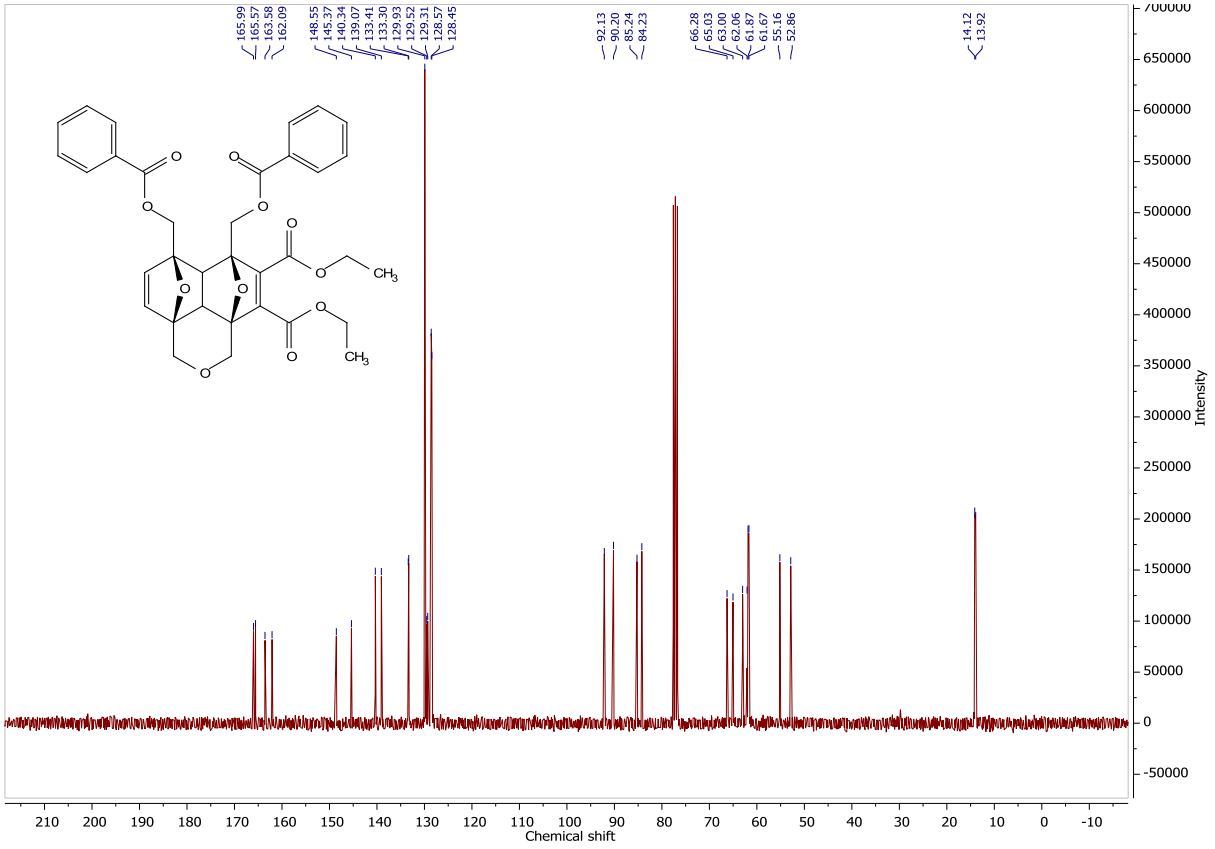


Figure S38. ^{13}C NMR spectrum of diethyl 6,7-bis((benzoyloxy)methyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ad** (75 MHz, Chloroform-*d*).

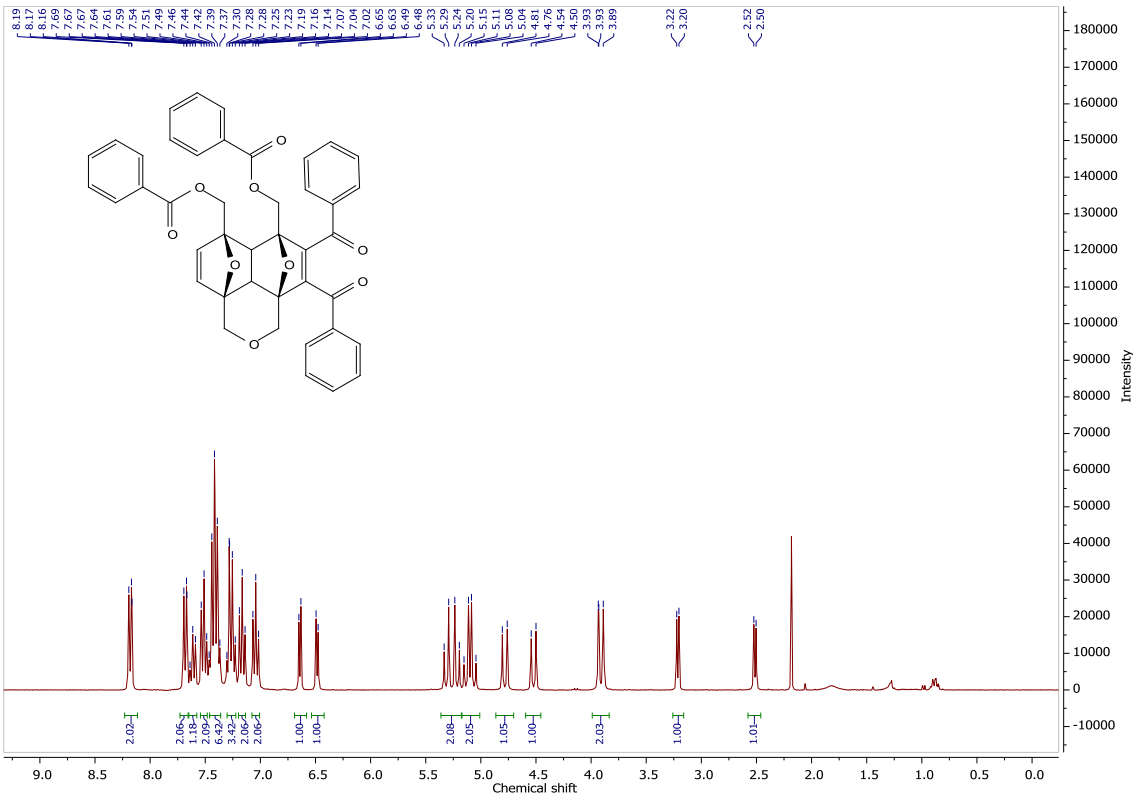


Figure S39. ^{1}H NMR spectrum of (4,5-dibenzoyl-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3ae** (300 MHz, Chloroform-*d*).

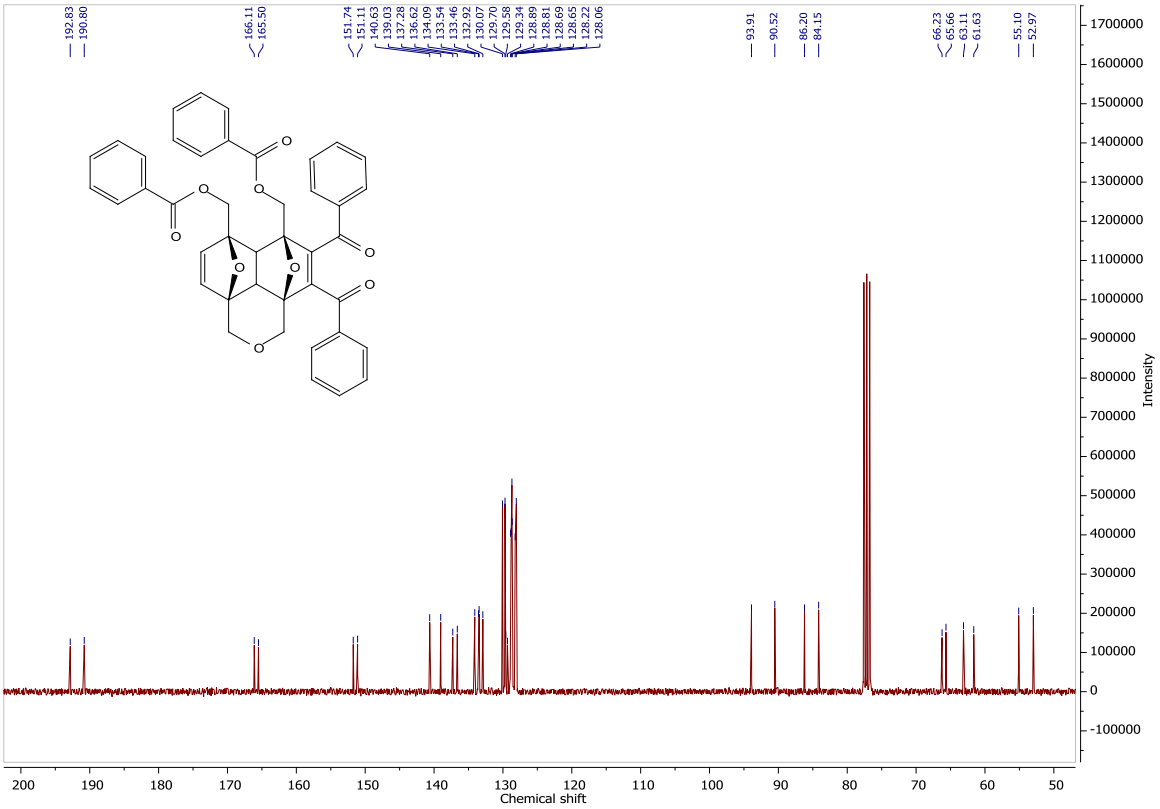


Figure S40. ^{13}C NMR spectrum of (4,5-dibenzoyl-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3ae** (75 MHz, Chloroform-*d*).

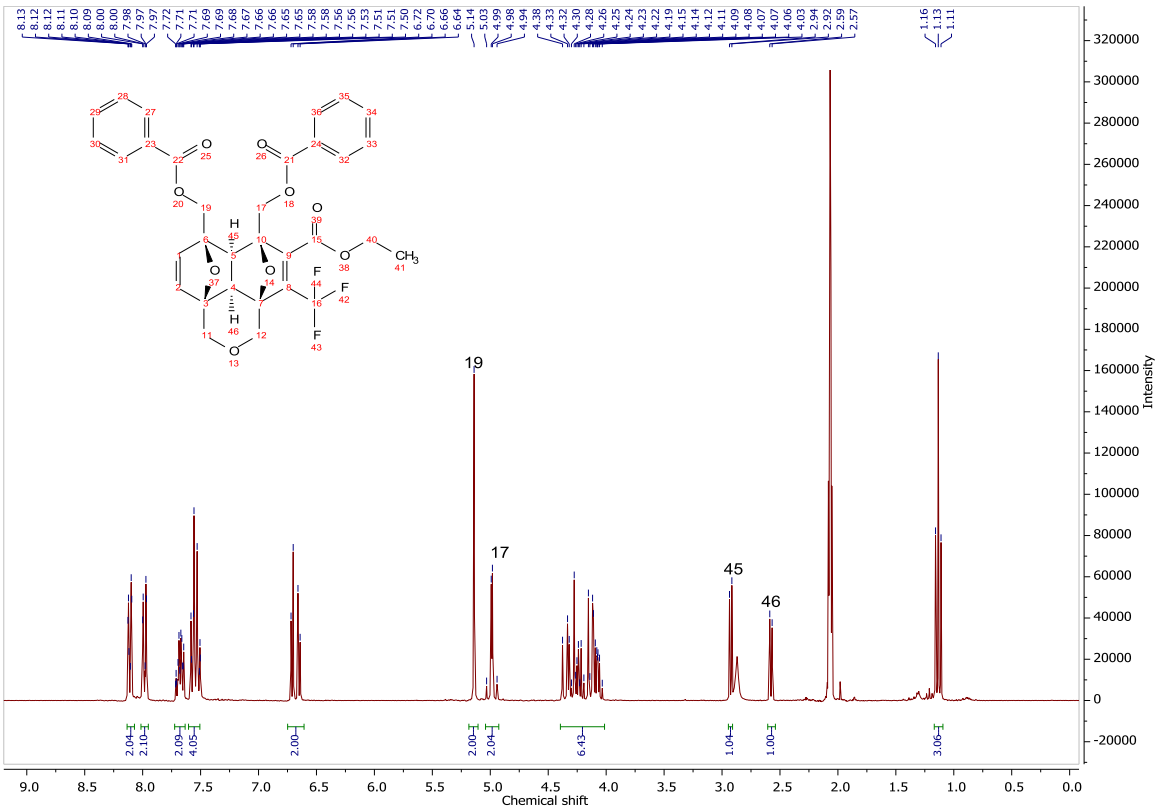


Figure S41. ^{1}H NMR spectrum of (5-(ethoxycarbonyl)-4-(trifluoromethyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afA** (300 MHz, Acetone-d_6).

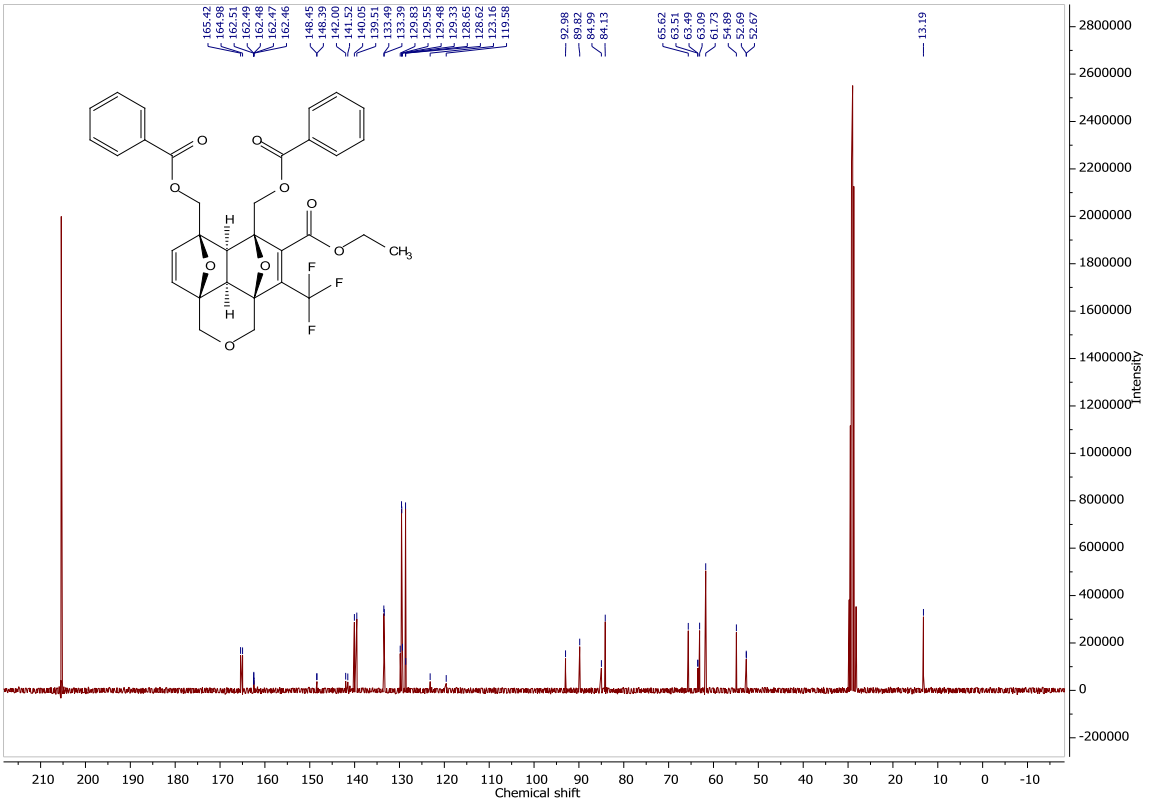


Figure S42. ^{13}C NMR spectrum of (5-(ethoxycarbonyl)-4-(trifluoromethyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afA** (75 MHz, Acetone-d_6).

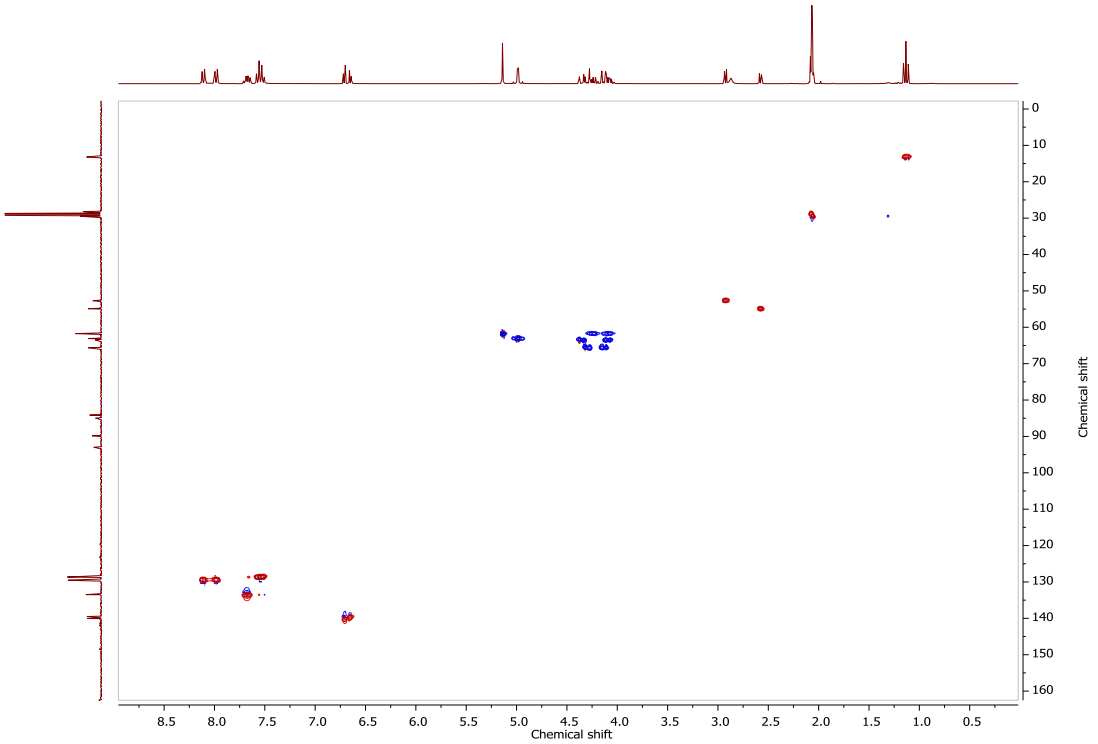


Figure S43. $^{1}H–^{13}C$ HSQC NMR spectrum of (5-(ethoxycarbonyl)-4-(trifluoromethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afA** (300 MHz, Acetone-d_6).

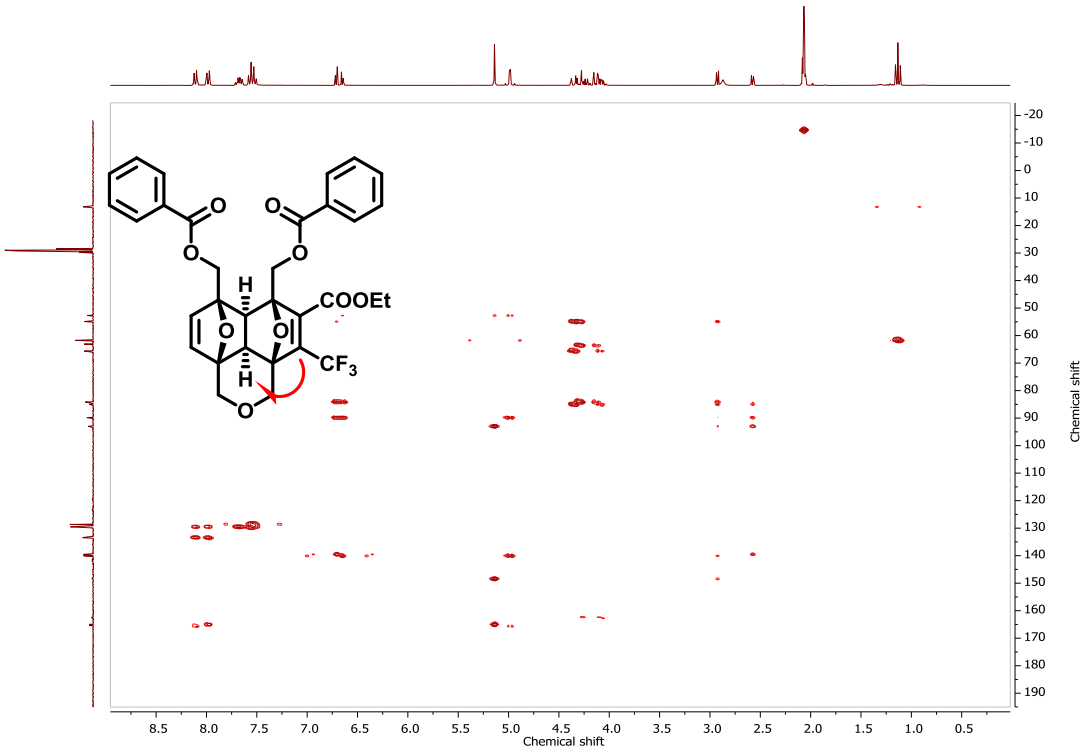


Figure S44. $^{1}H–^{13}C$ HMBC NMR spectrum of (5-(ethoxycarbonyl)-4-(trifluoromethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afA** (300 MHz, Acetone-d_6).

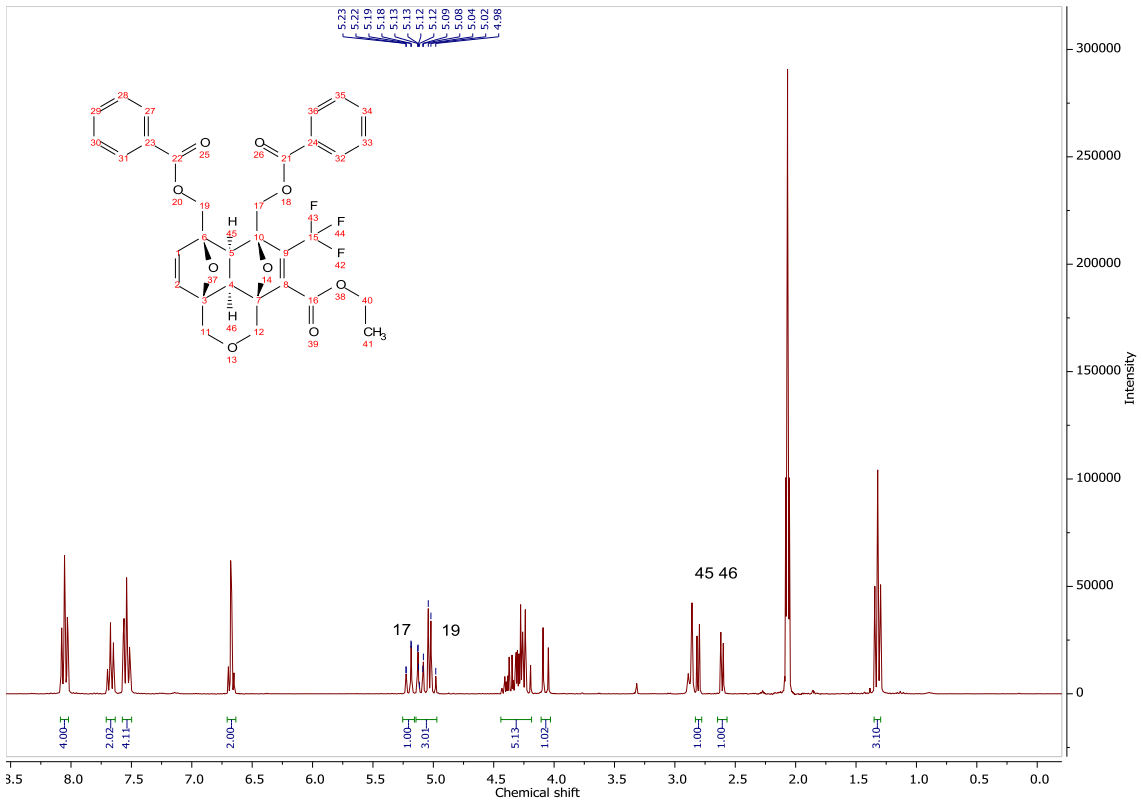


Figure S45. ^{1}H NMR spectrum of (4-(ethoxycarbonyl)-5-(trifluoromethyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afB** (300 MHz, Acetone-d_6).

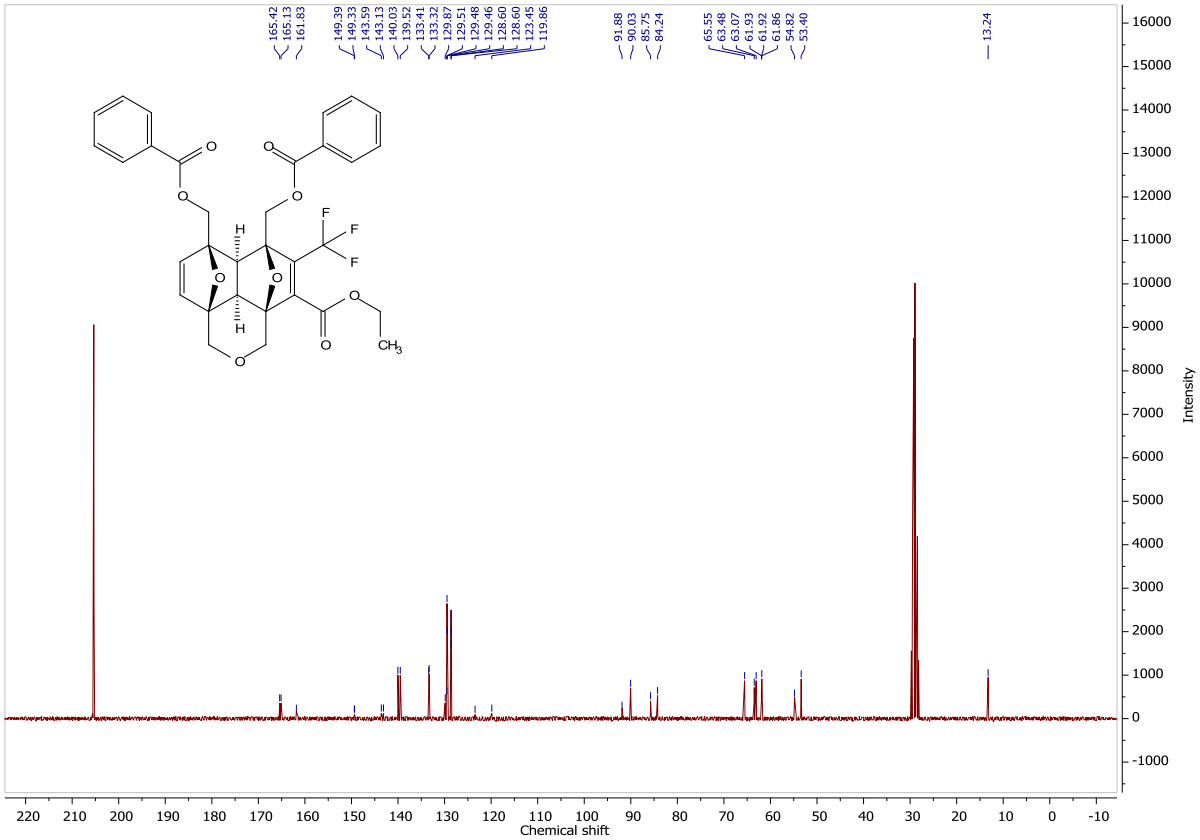


Figure S46. ^{13}C NMR spectrum of (4-(ethoxycarbonyl)-5-(trifluoromethyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afB** (75 MHz, Acetone-d_6).

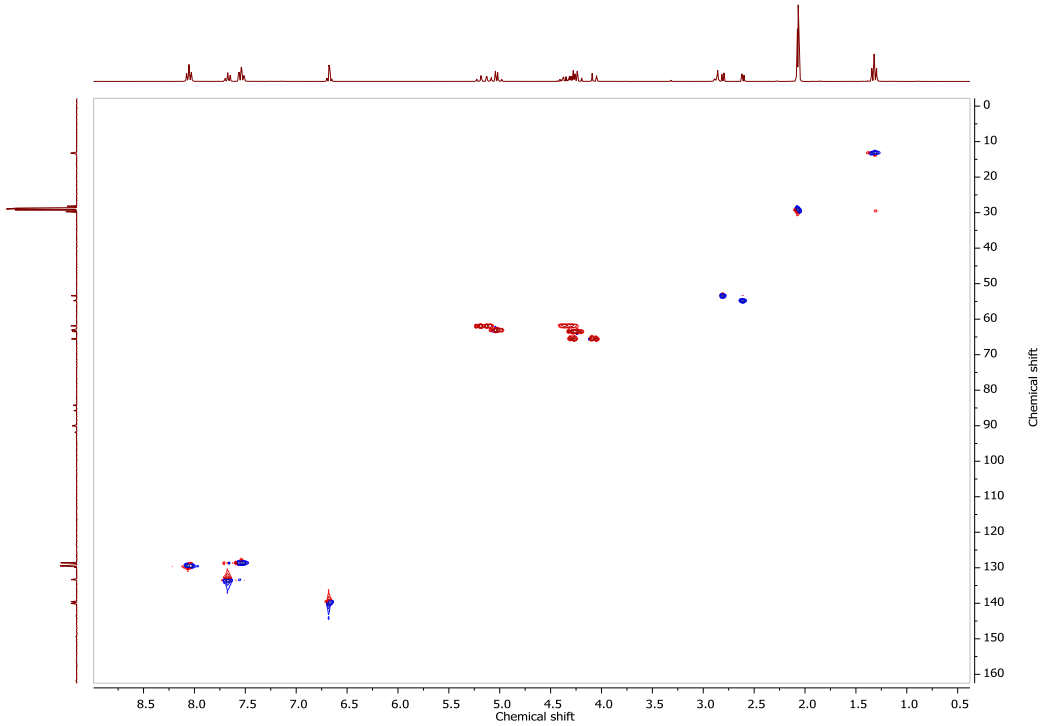


Figure S47. $^{1}H–^{13}C$ HSQC NMR spectrum of (4-(ethoxycarbonyl)-5-(trifluoromethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afB** (300 MHz, Acetone-d_6).

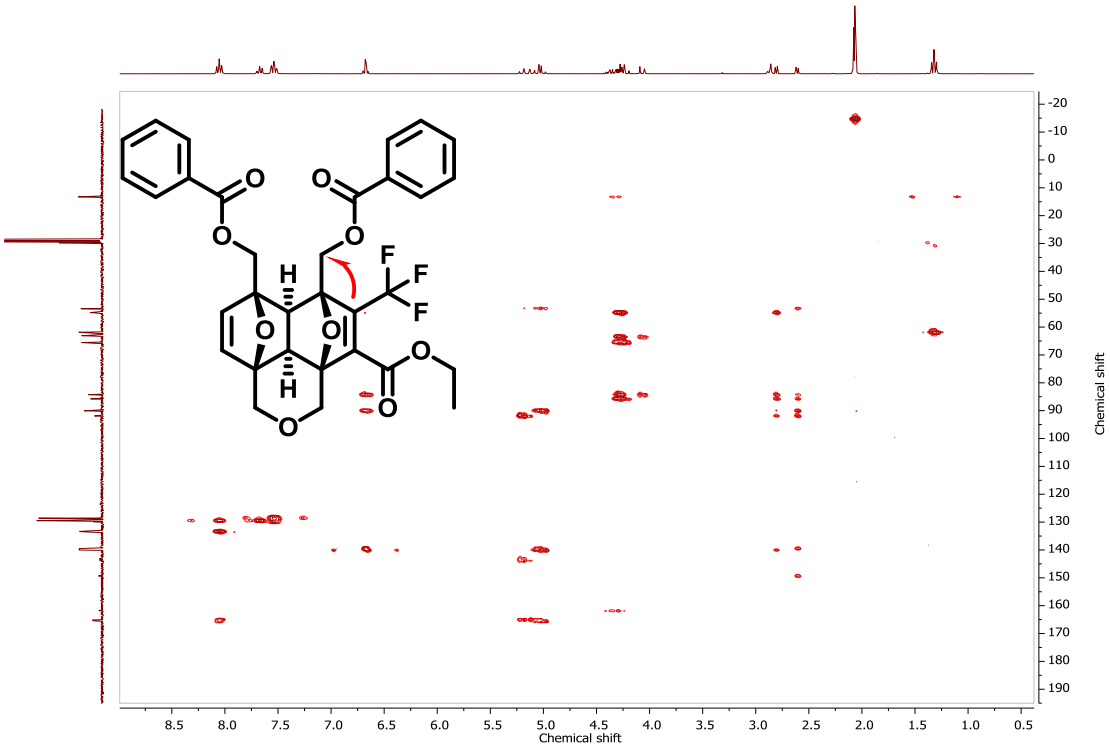


Figure S48. $^{1}H–^{13}C$ HMBC NMR spectrum of (4-(ethoxycarbonyl)-5-(trifluoromethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afB** (300 MHz, Acetone-d_6).

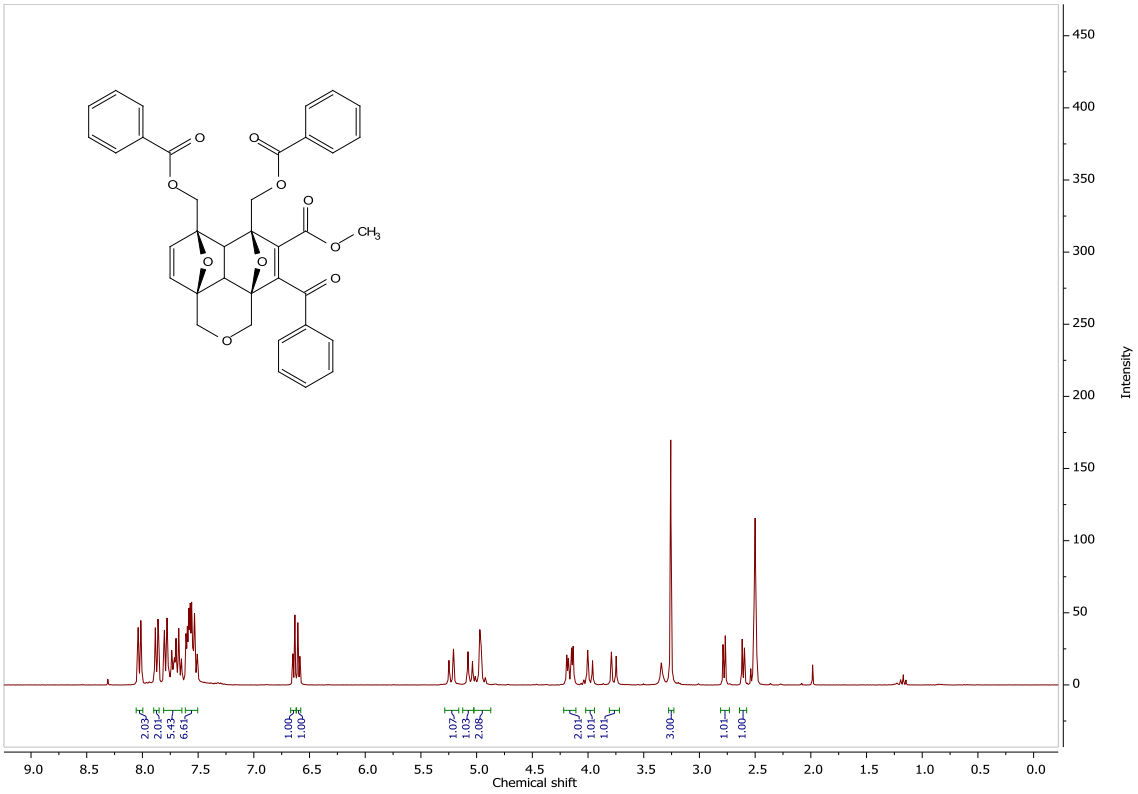


Figure S49. ^{1}H NMR spectrum of (4-benzoyl-5-(methoxycarbonyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agA** (300 MHz, DMSO-d_6).

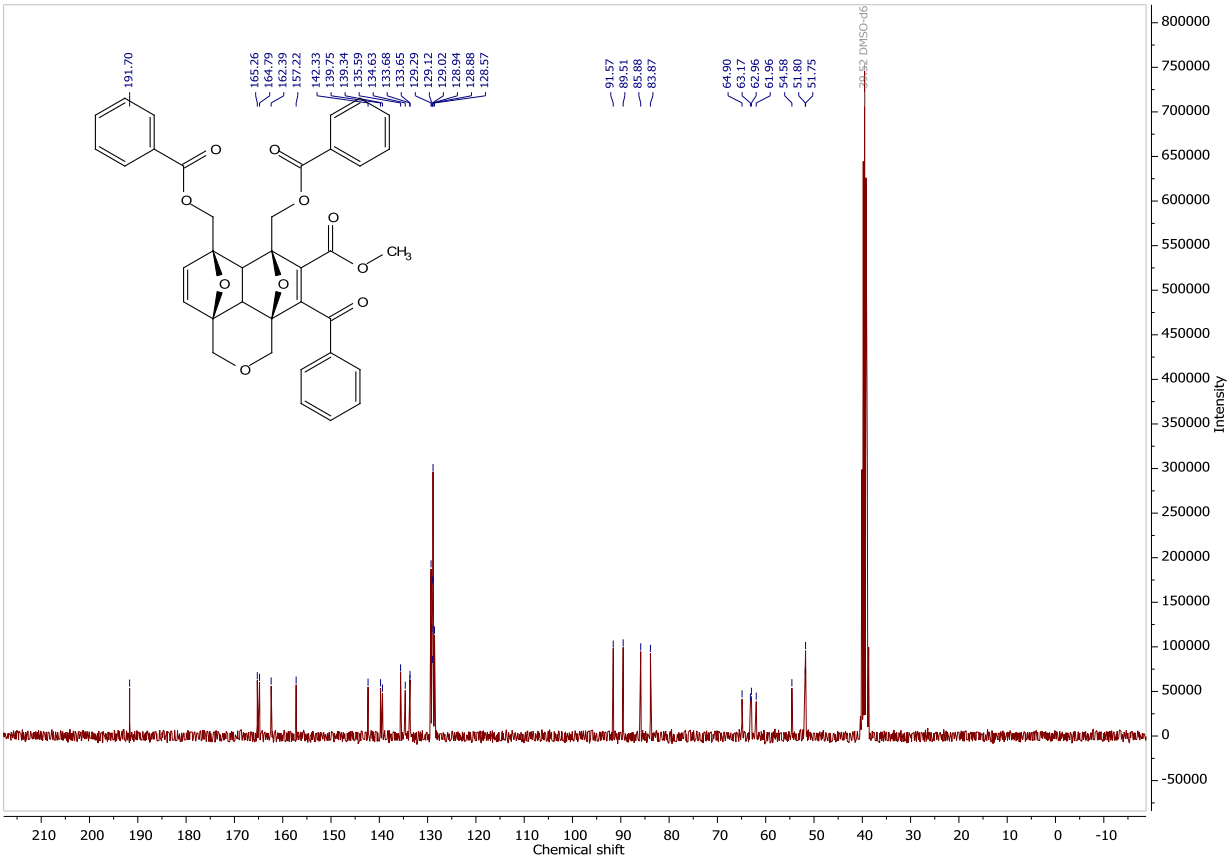


Figure S50. ^{1}H NMR spectrum of (4-benzoyl-5-(methoxycarbonyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agA** (300 MHz, DMSO-d_6).

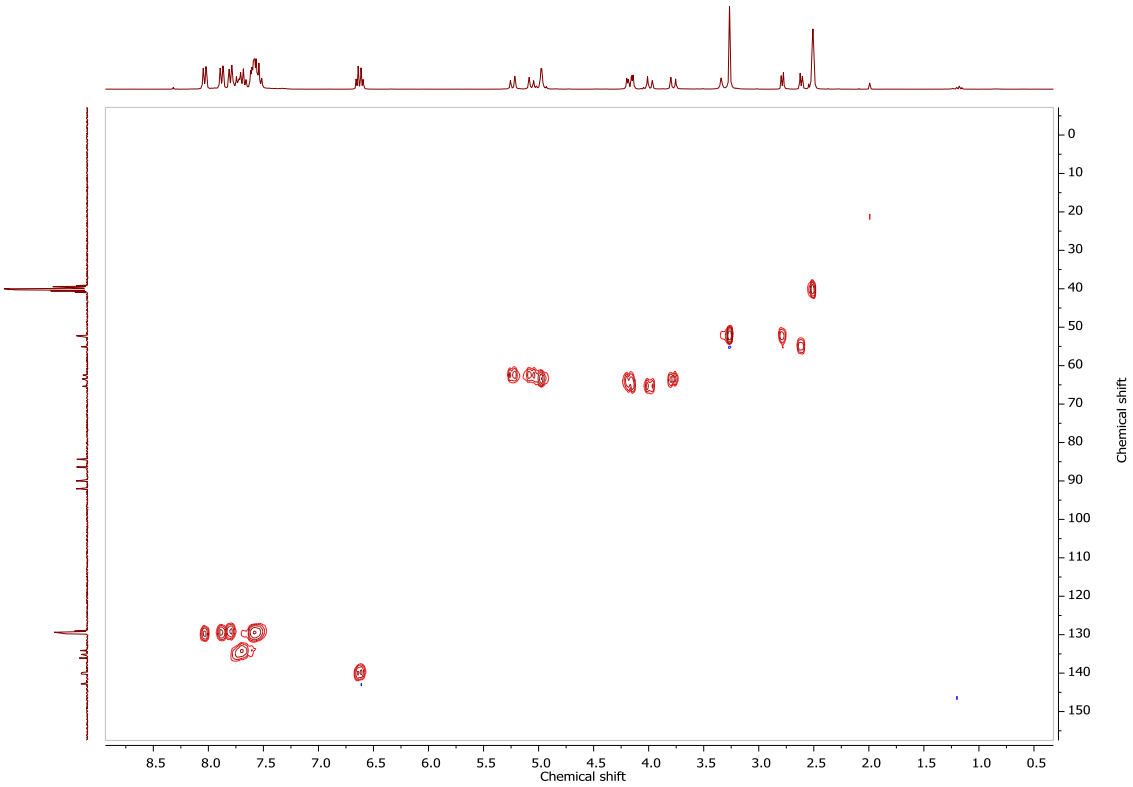


Figure S51. $^{1}H–^{13}C$ HSQC NMR spectrum of (4-benzoyl-5-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agA** (300 MHz, DMSO-d_6).

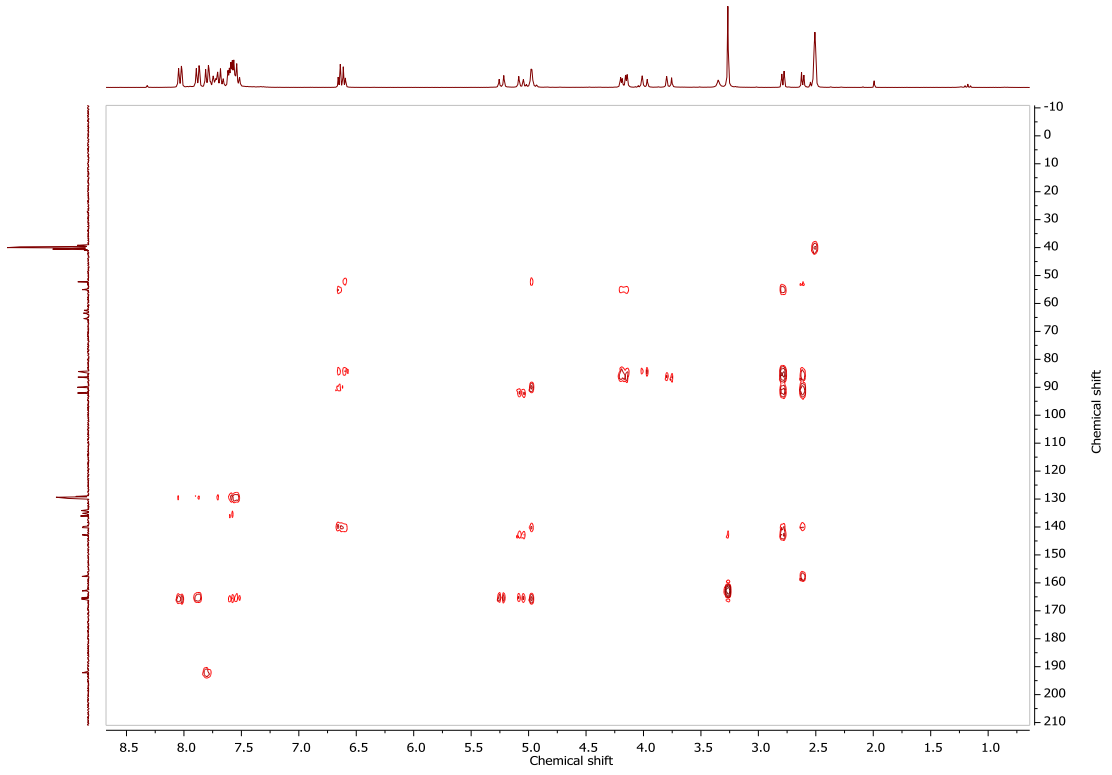


Figure S52. $^{1}H–^{13}C$ HMBC NMR spectrum of (4-benzoyl-5-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agA** (300 MHz, DMSO-d_6).

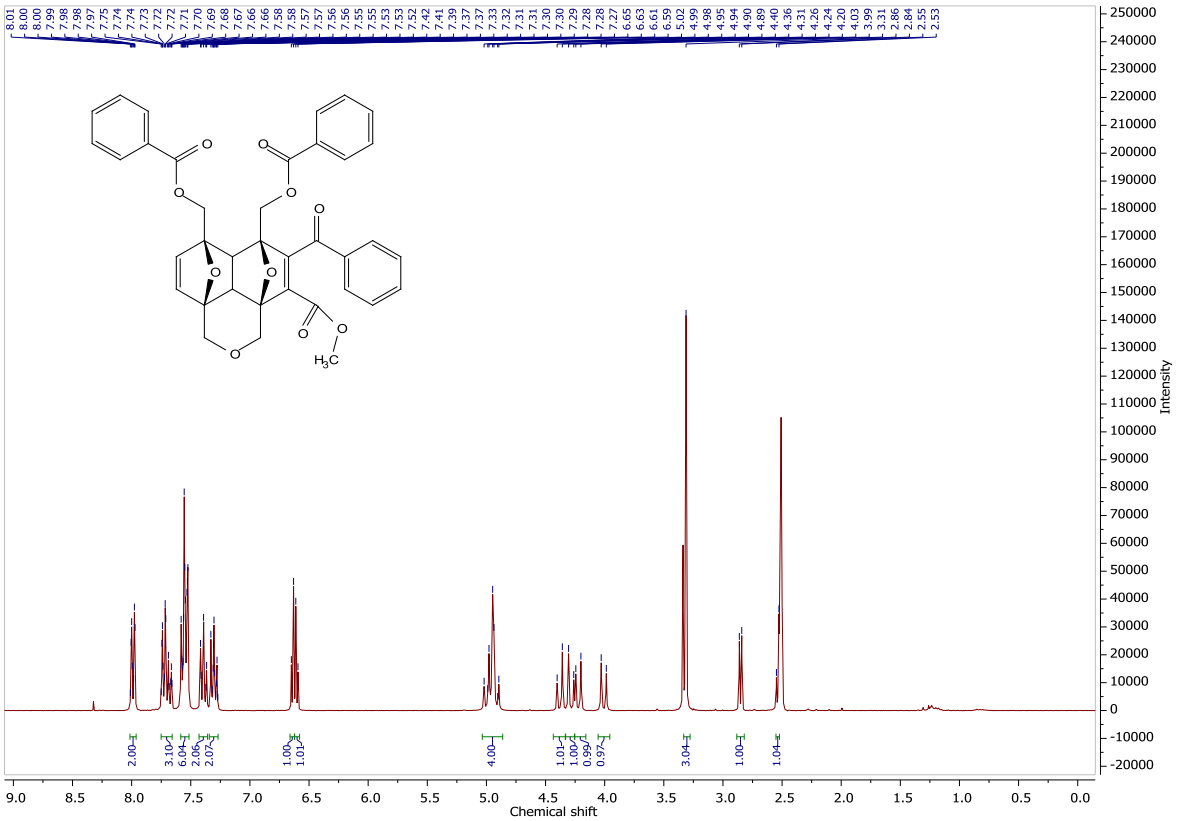


Figure S53. ^{1}H NMR spectrum of (5-benzoyl-4-(methoxycarbonyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB** (300 MHz, DMSO-d_6).

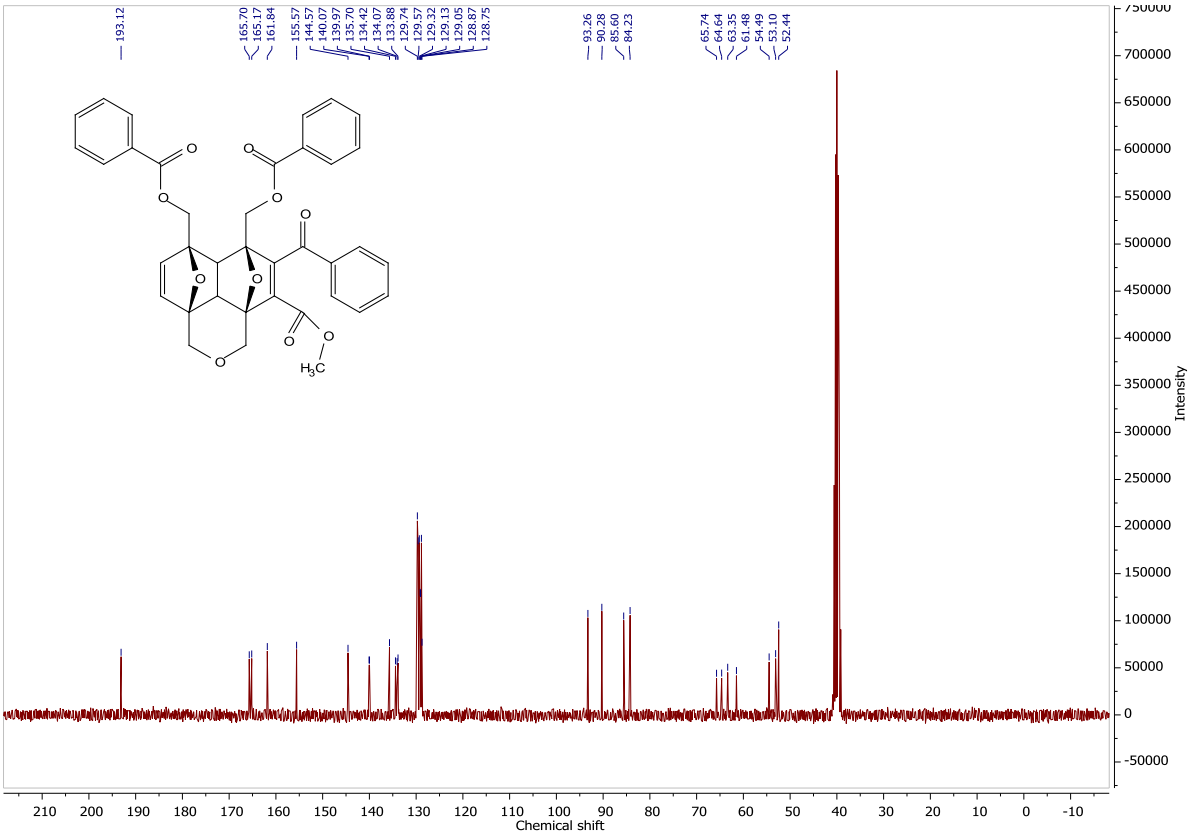


Figure S54. ^{13}C NMR spectrum of (5-benzoyl-4-(methoxycarbonyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB** (75 MHz, DMSO-d_6).

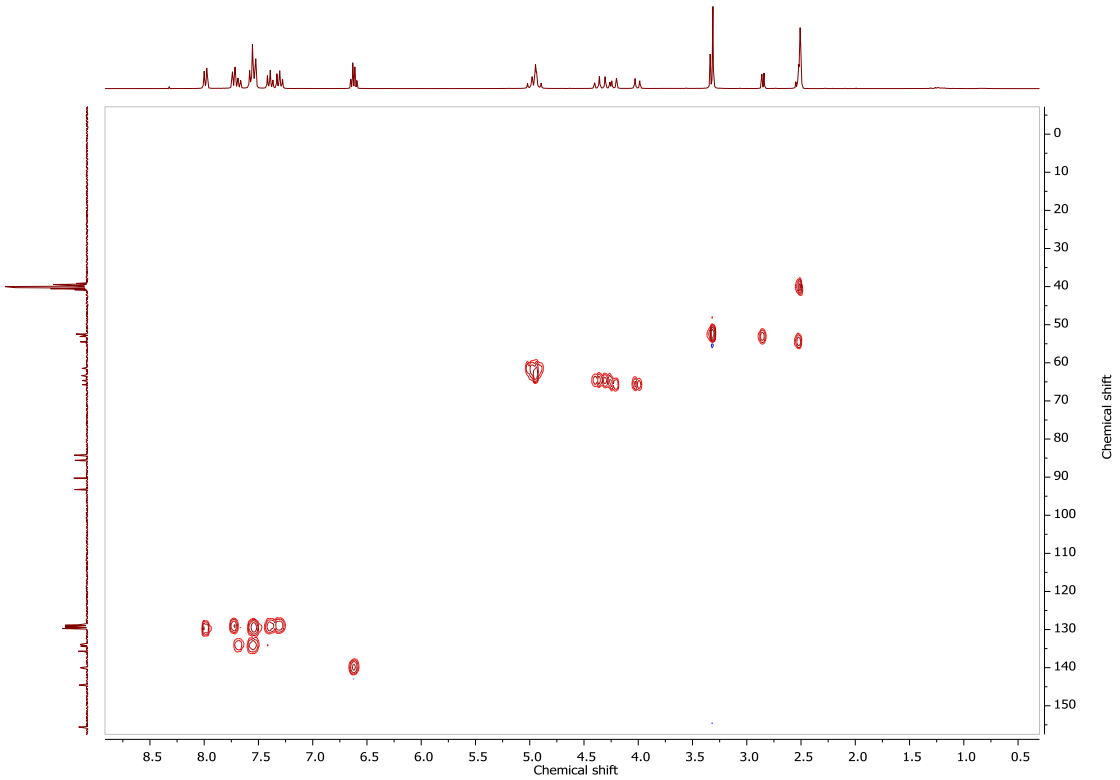


Figure S55. $^{1}H–^{13}C$ HSQC NMR spectrum of (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB** (300 MHz, DMSO-d_6).

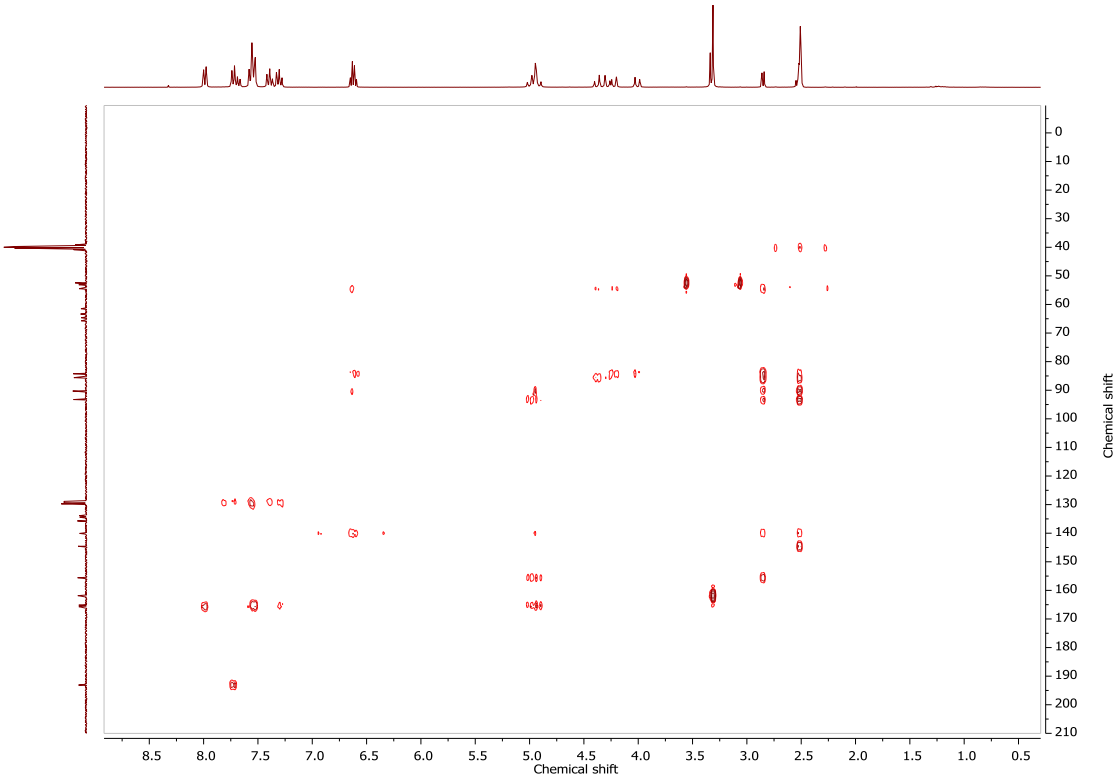


Figure S56. $^{1}H–^{13}C$ HMBC NMR spectrum of (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB** (300 MHz, DMSO-d_6).

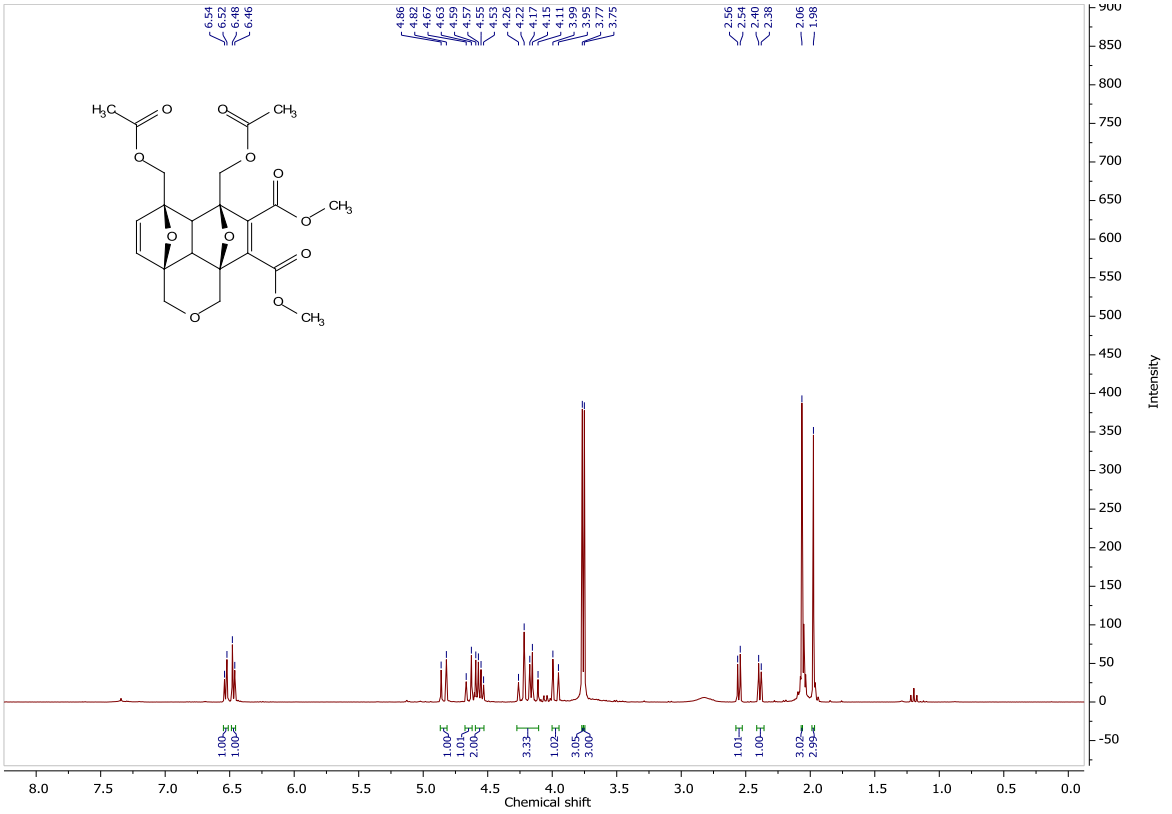


Figure S57. ^{1}H NMR spectrum of dimethyl 6,7-bis(acetoxymethyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ba** (300 MHz, Acetone-d_6).

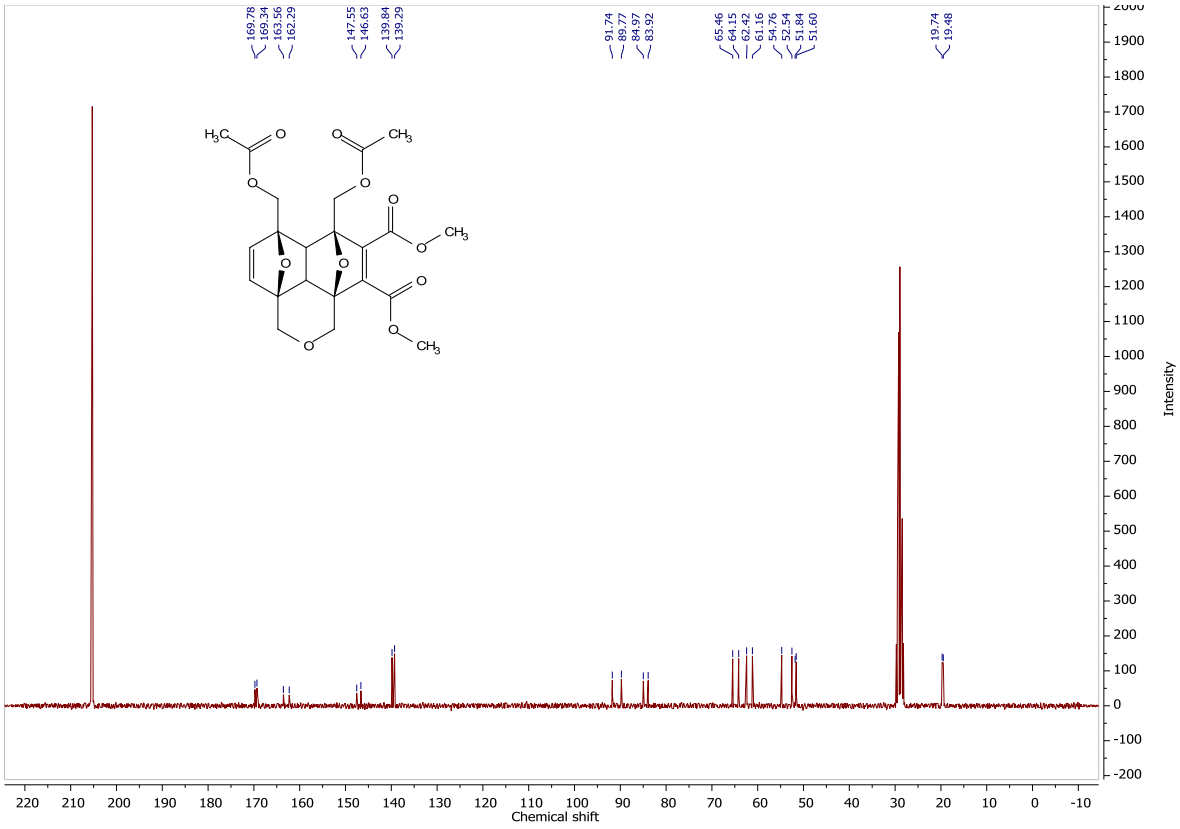


Figure S58. ^{13}C NMR spectrum of dimethyl 6,7-bis(acetoxymethyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ba** (75 MHz, Acetone-d_6).

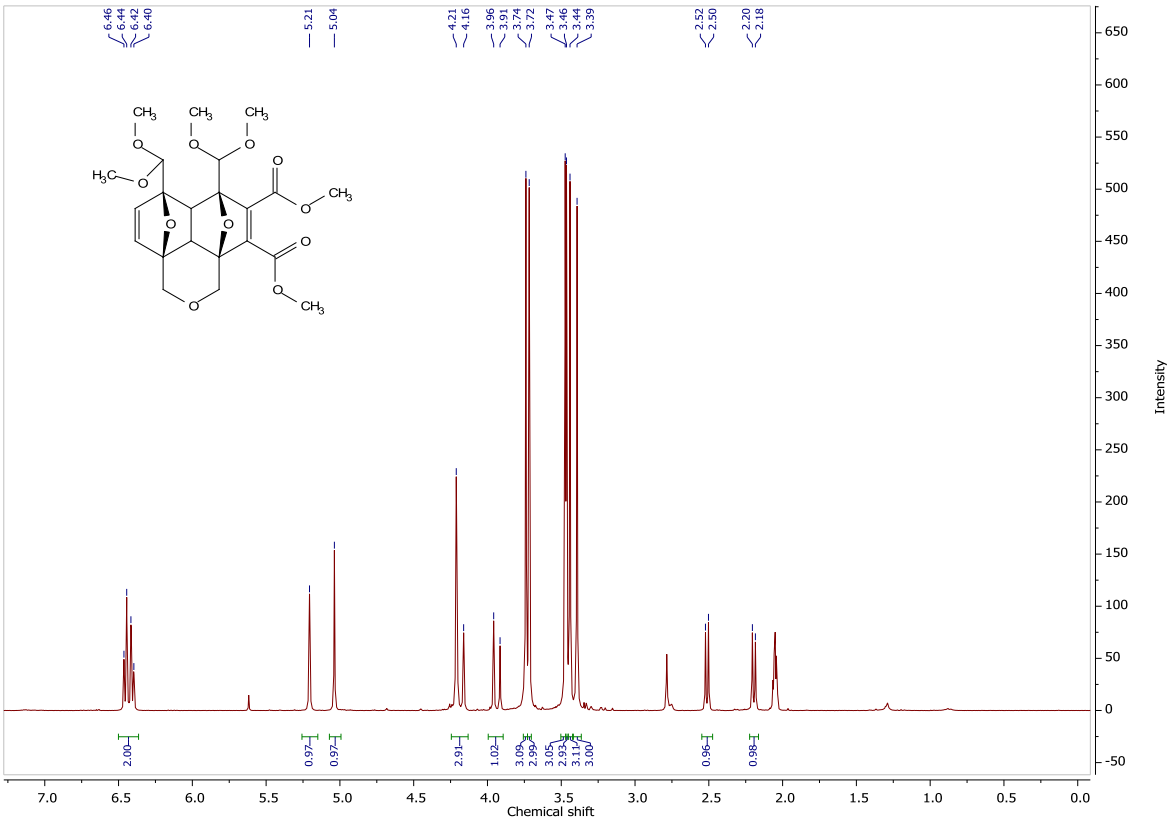


Figure S59. ^{1}H NMR spectrum of dimethyl 6,7-bis(dimethoxymethyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3da** (300 MHz, Acetone-d_6).

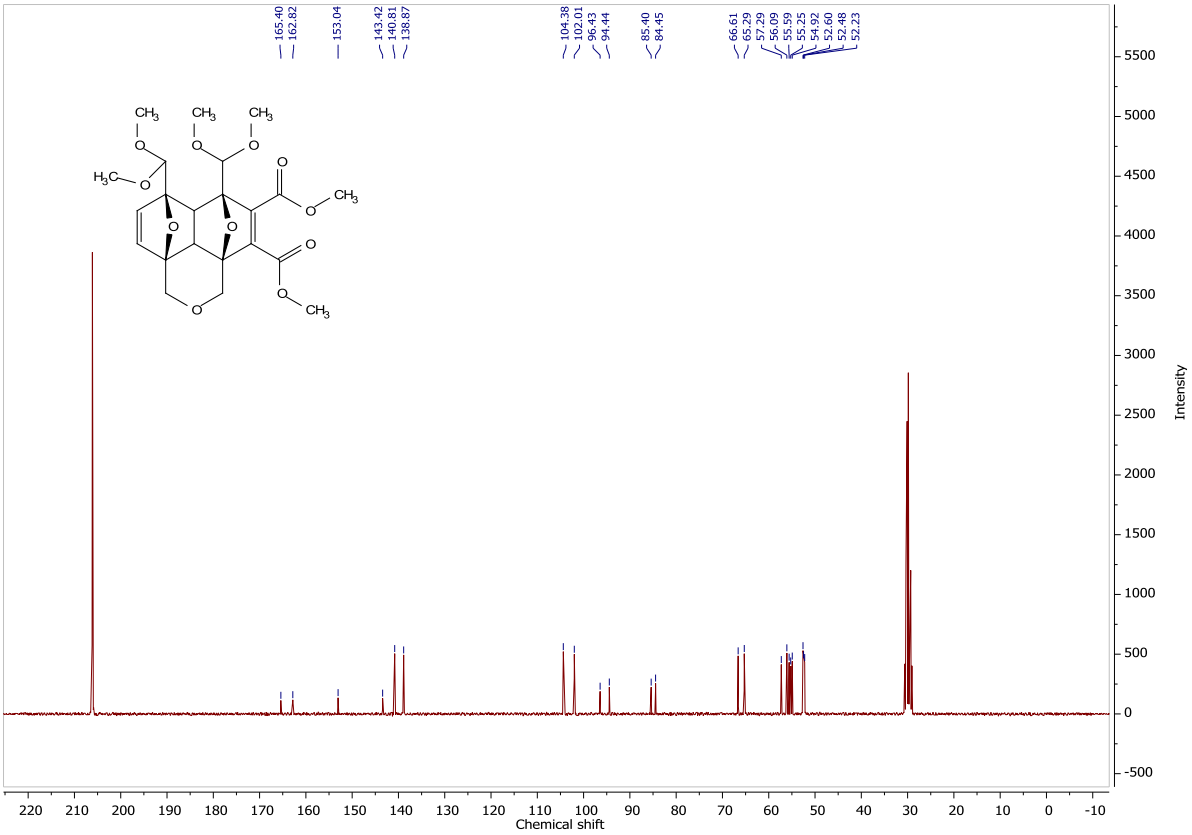


Figure S60. ^{13}C NMR spectrum of dimethyl 6,7-bis(dimethoxymethyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3da** (75 MHz, Acetone-d_6).

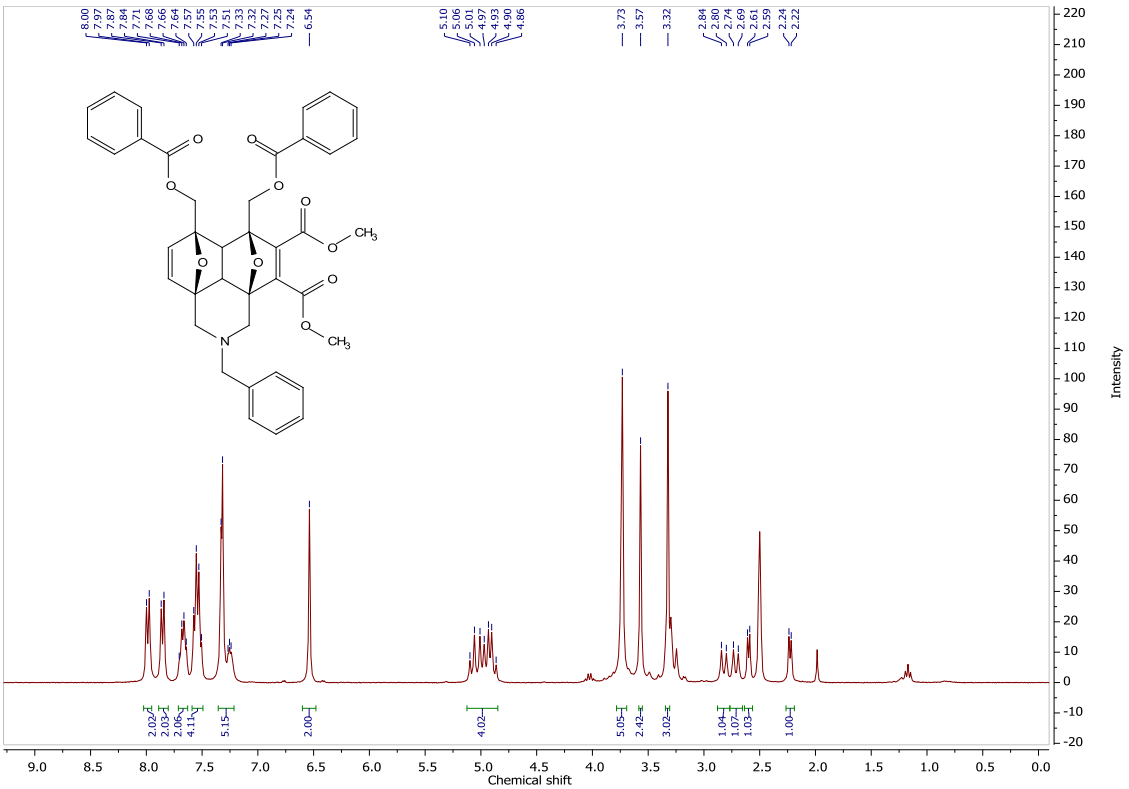


Figure S61. [1]H NMR spectrum of Dimethyl 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea** (300 MHz, DMSO-d_6).

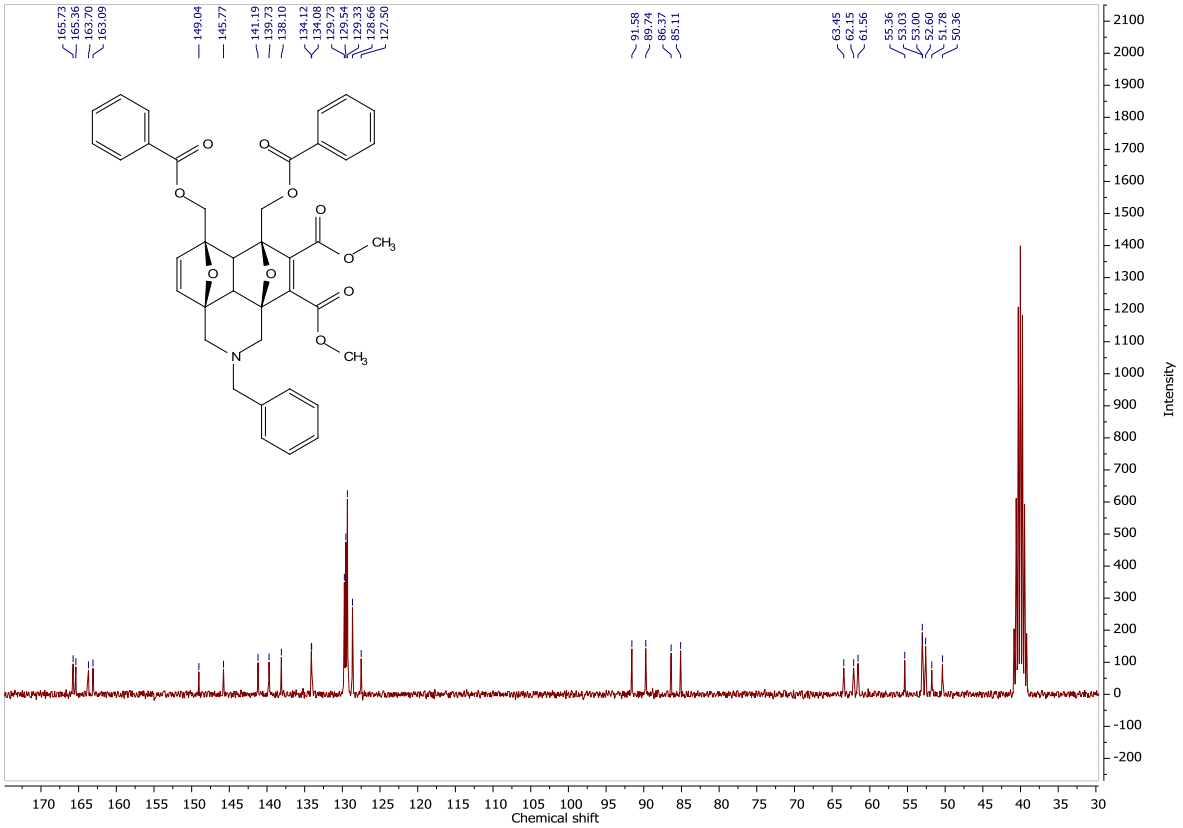


Figure S62. [13]C NMR spectrum of dimethyl 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea** (75 MHz, DMSO-d_6).

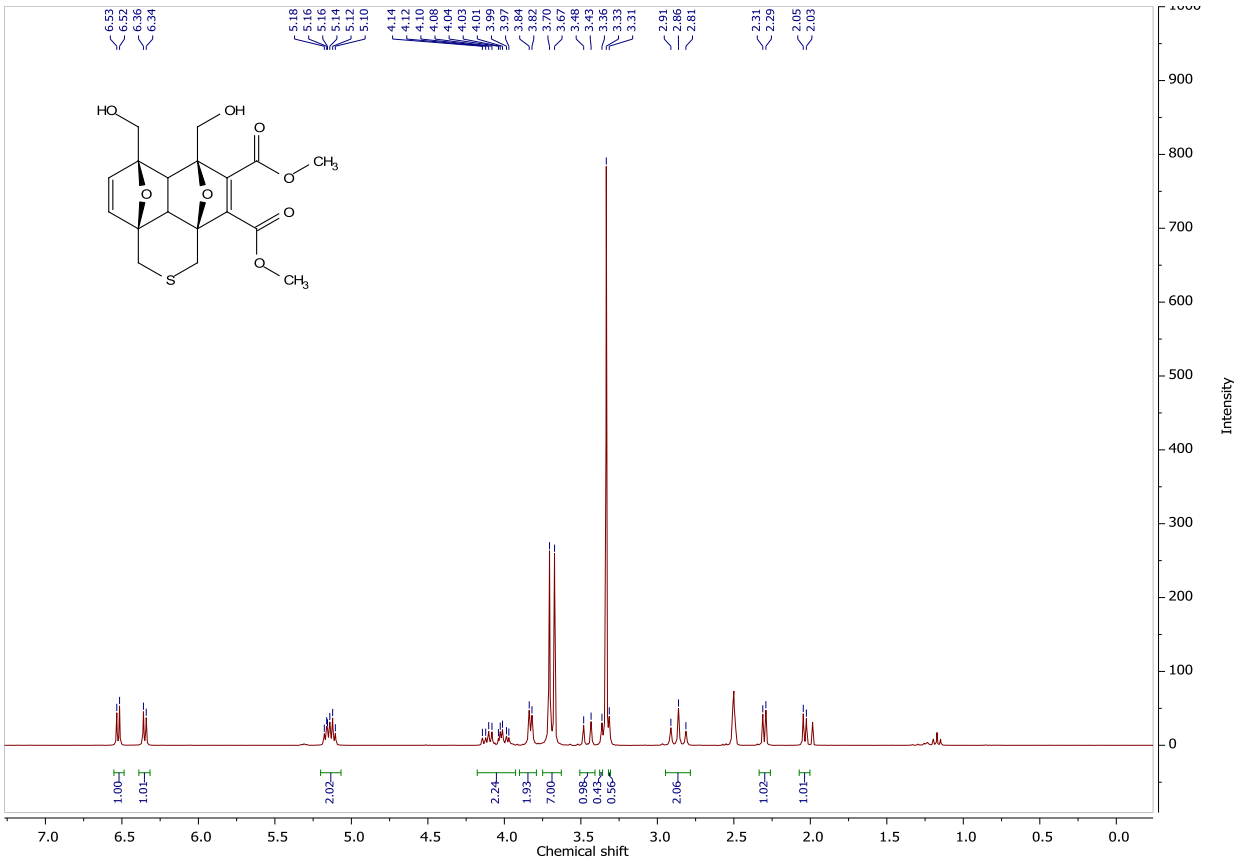


Figure S63. ^{1}H NMR spectrum of Dimethyl 6,7-bis(hydroxymethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isothiochromene-4,5-dicarboxylate **3fa** (300 MHz, DMSO-d_6).

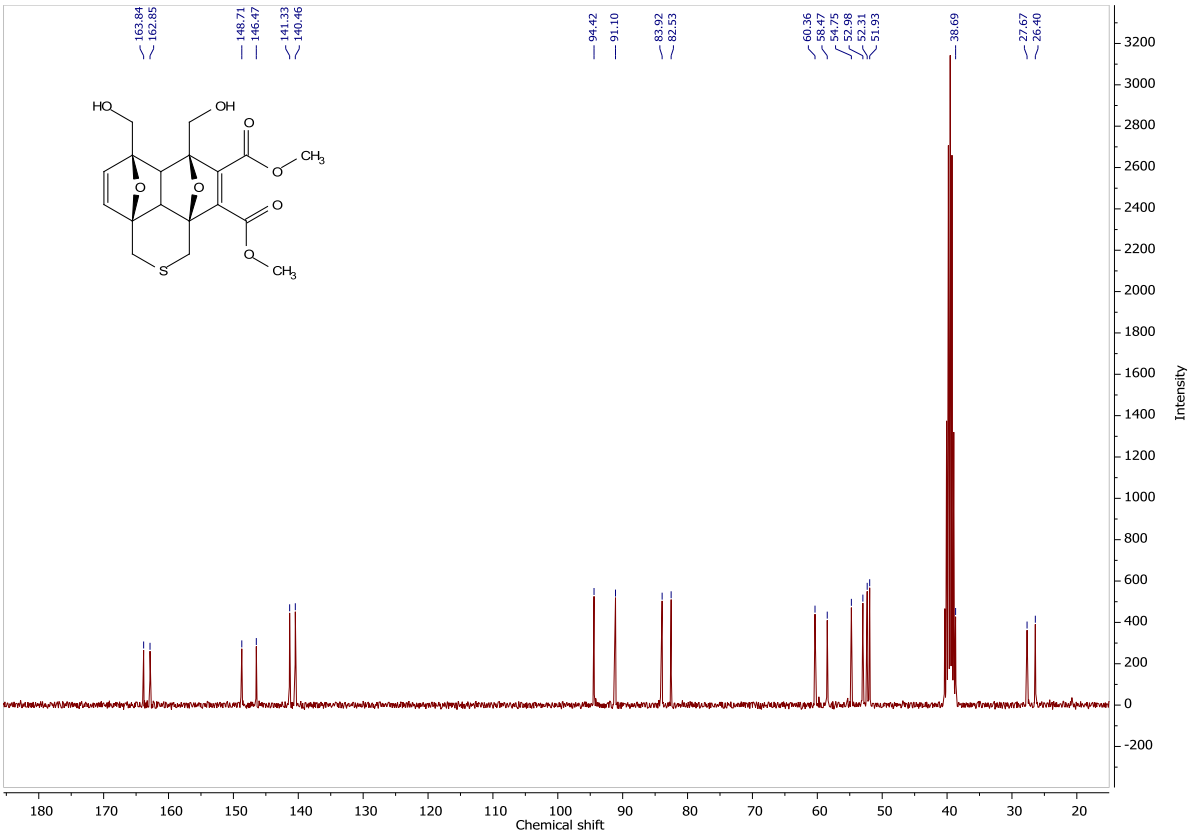


Figure S64. ^{13}C NMR spectrum of dimethyl 6,7-bis(hydroxymethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isothiochromene-4,5-dicarboxylate **3fa** (75 MHz, DMSO-d_6).

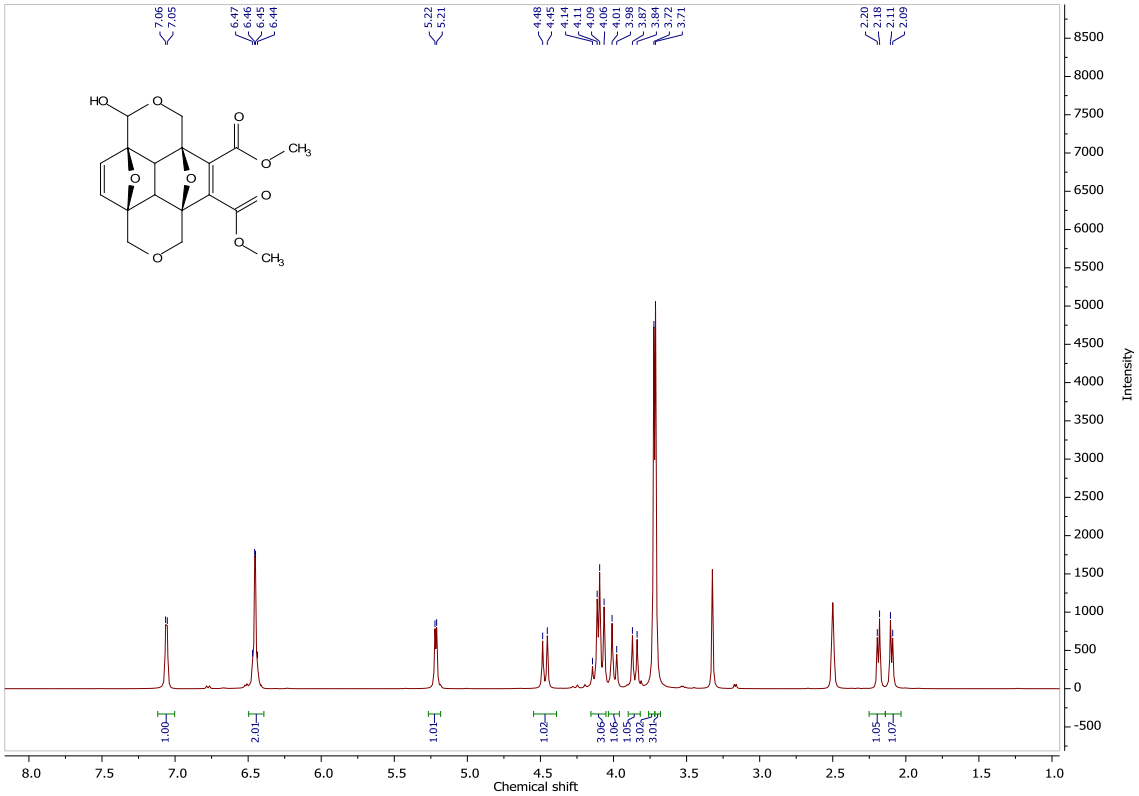


Figure S65. ^{1}H NMR spectrum of 1-hydroxy-1,3,3a,3a^{1},5a,5a^{1},6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga** (400 MHz, DMSO-d_6).

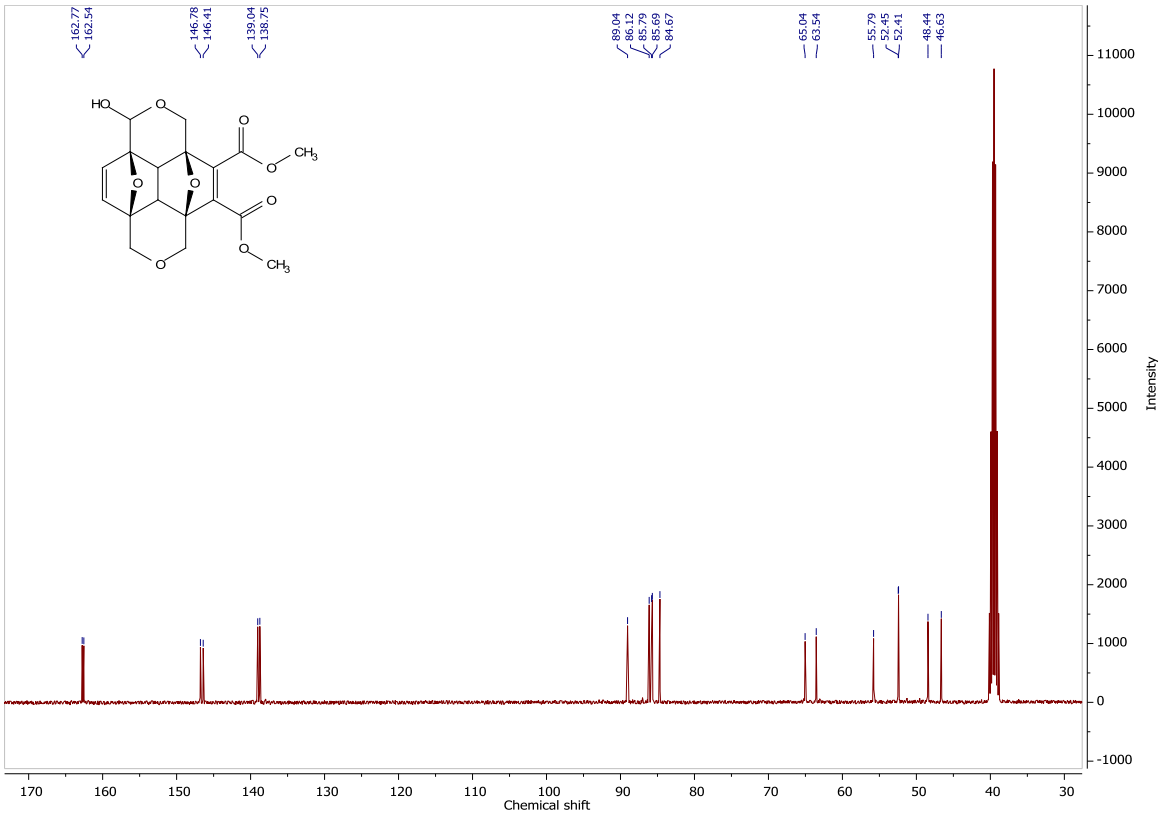


Figure S66. ^{13}C NMR spectrum of 1-hydroxy-1,3,3a,3a^{1},5a,5a^{1},6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga** (100 MHz, DMSO-d_6).

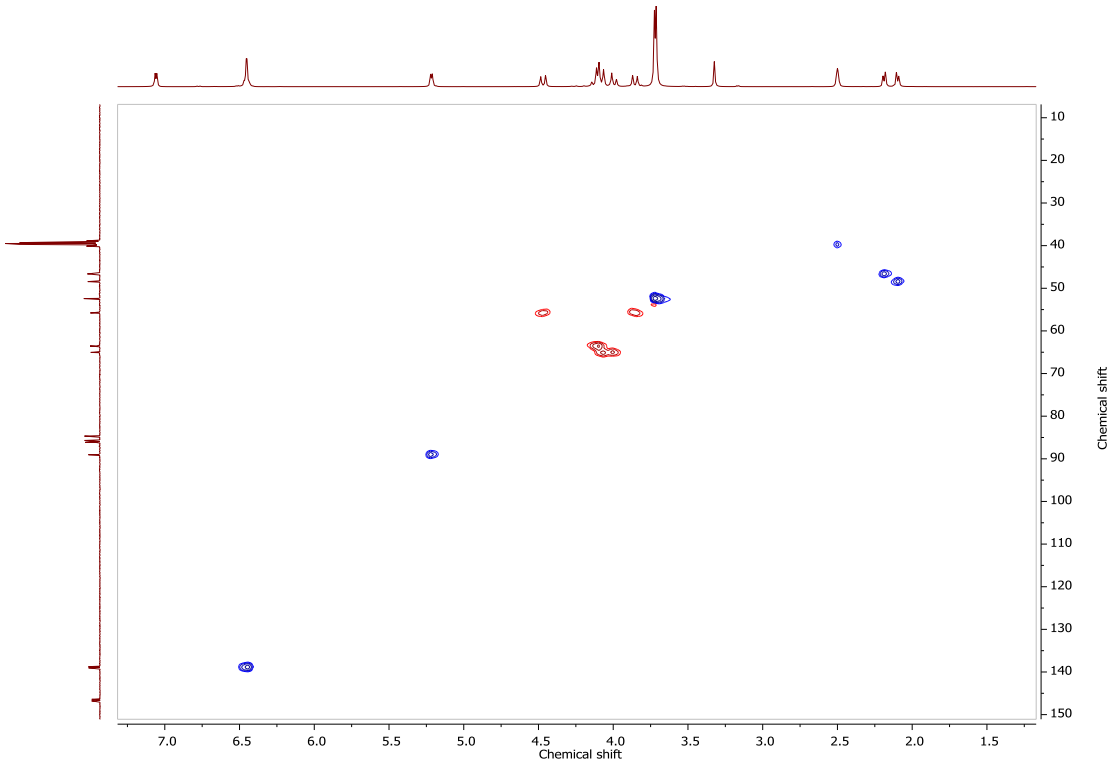


Fig. S67. ^{1}H–^{13}C HSQC NMR spectrum of 1-hydroxy-1,3,3a,3a^{1},5a,5a^{1},6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga** (400 MHz, DMSO-d_6).

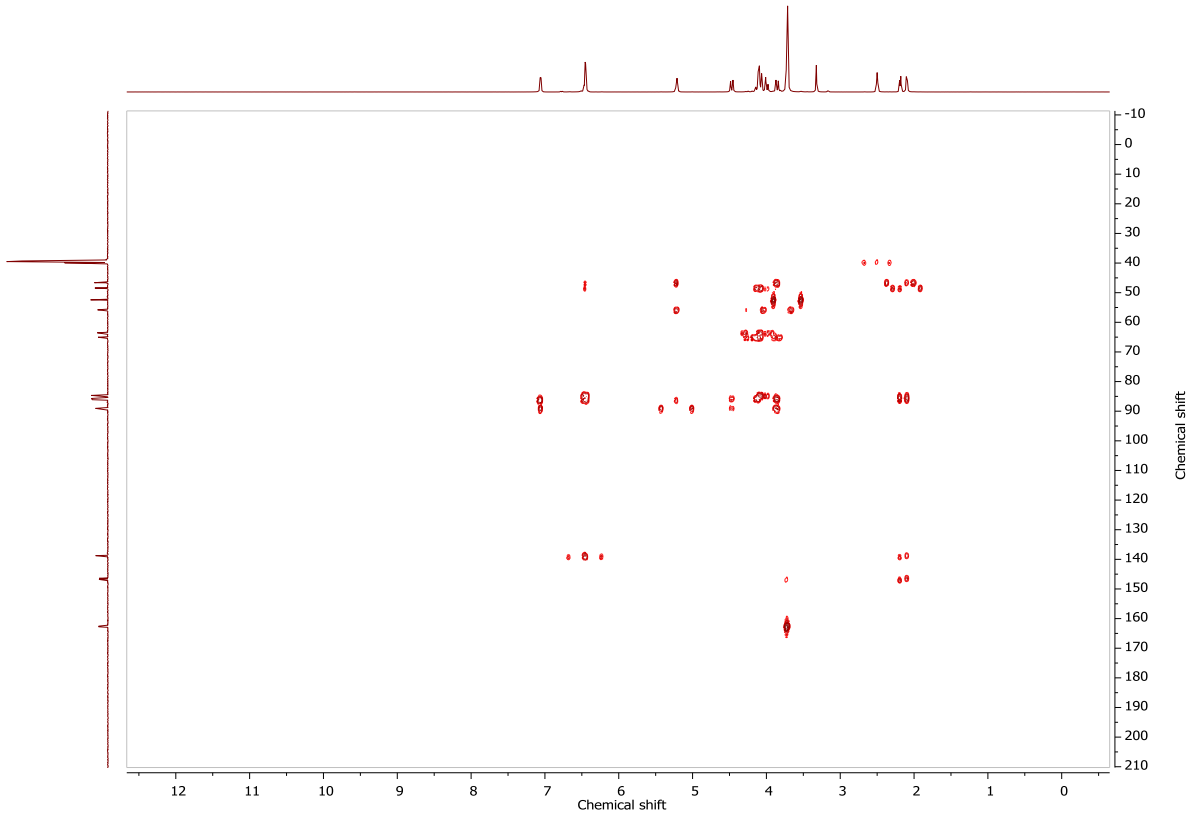


Fig. S68. ^{1}H-^{13}C HMBC NMR spectrum of 1-hydroxy-1,3,3a,3a^{1},5a,5a^{1},6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga** (400 MHz, DMSO-d_6).

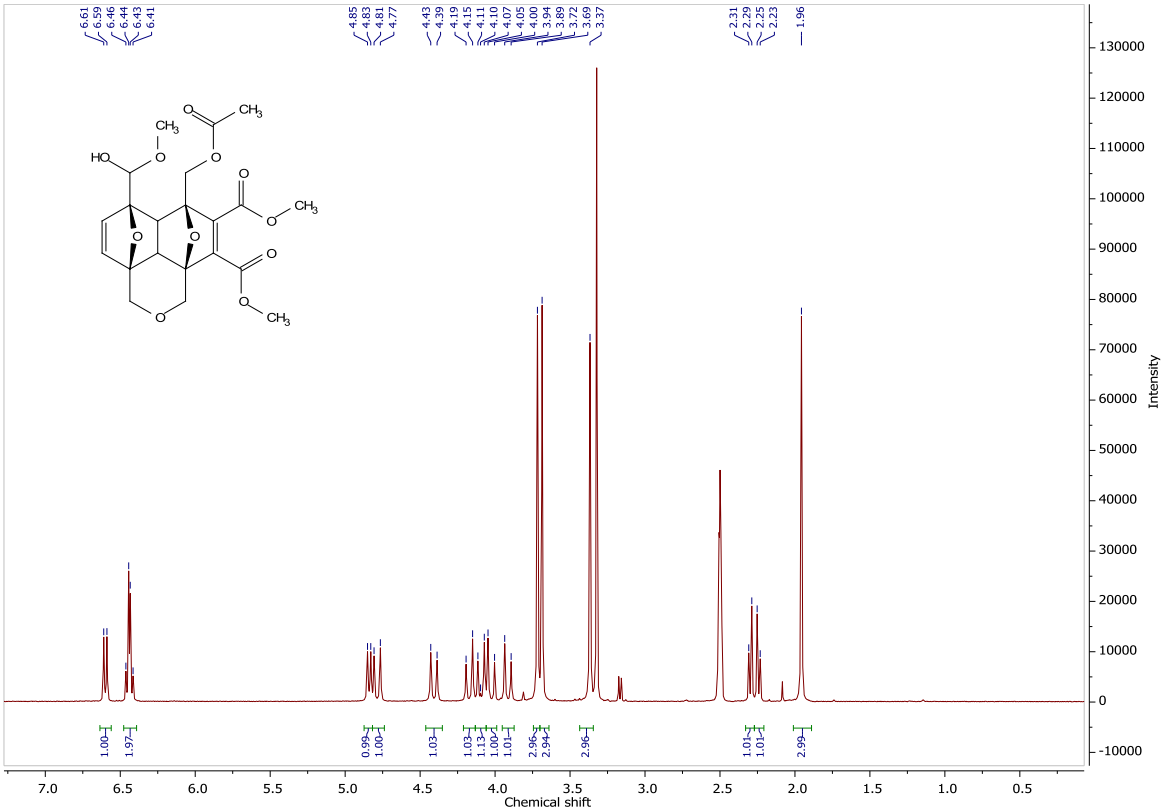


Figure S69. ^{1}H NMR spectrum of dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha** (300 MHz, DMSO-d_6).

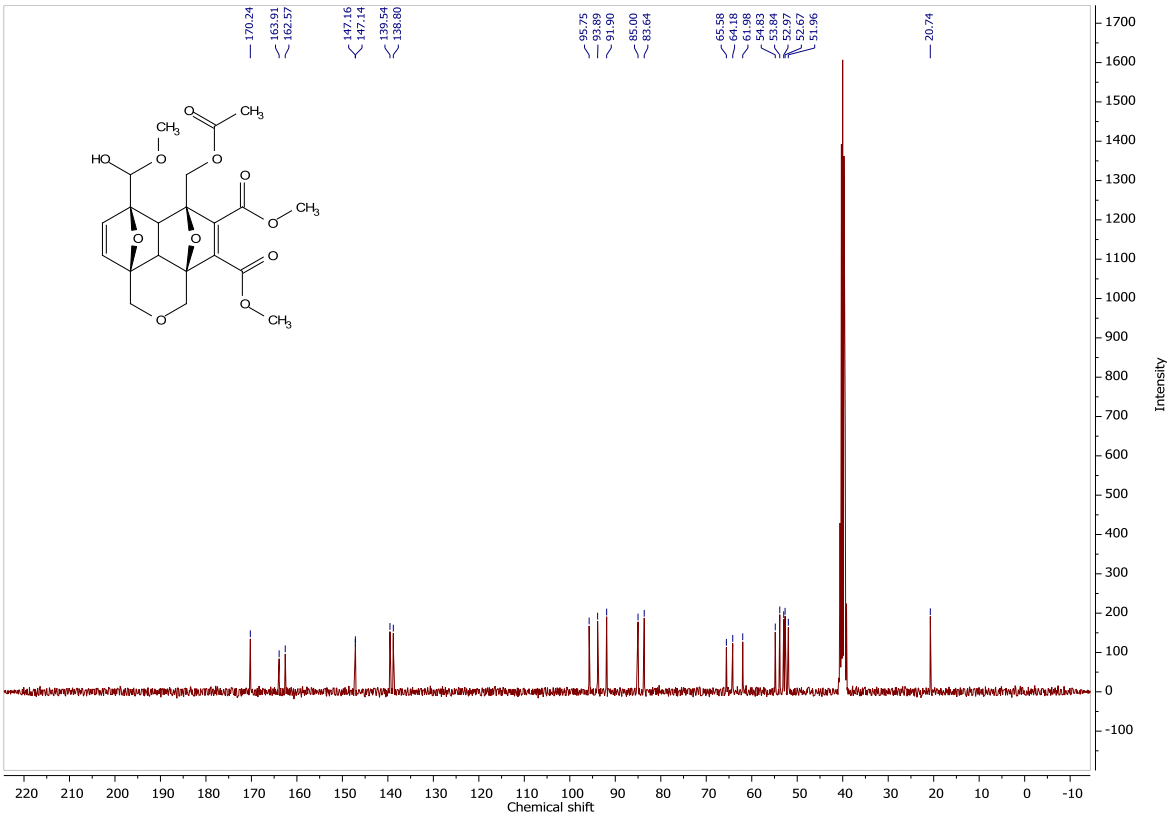


Figure S70. ^{13}C NMR spectrum of dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a^{1},6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha** (75 MHz, DMSO-d_6).

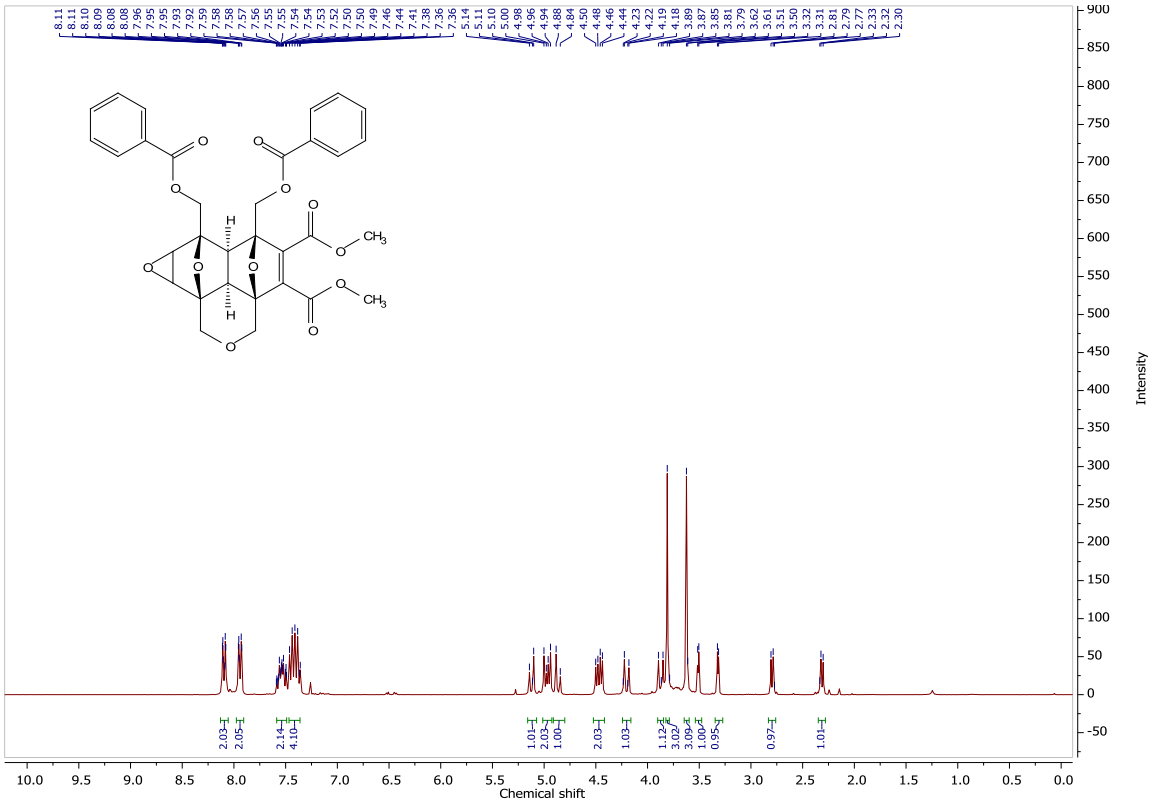


Figure S71. ^{1}H NMR spectrum of (3aS,3a1S,6R,6aR,7R,8bS)-dimethyl 6,7-bis((benzoyloxy)methyl)-1,3,3a1,6,6a,7,7a,8a-octahydro-3a,6:7,8b-diepoxybenzo[de]oxireno[2,3-h]isochromene-4,5-dicarboxylate **7aa** (300 MHz, Chloroform-*d*).

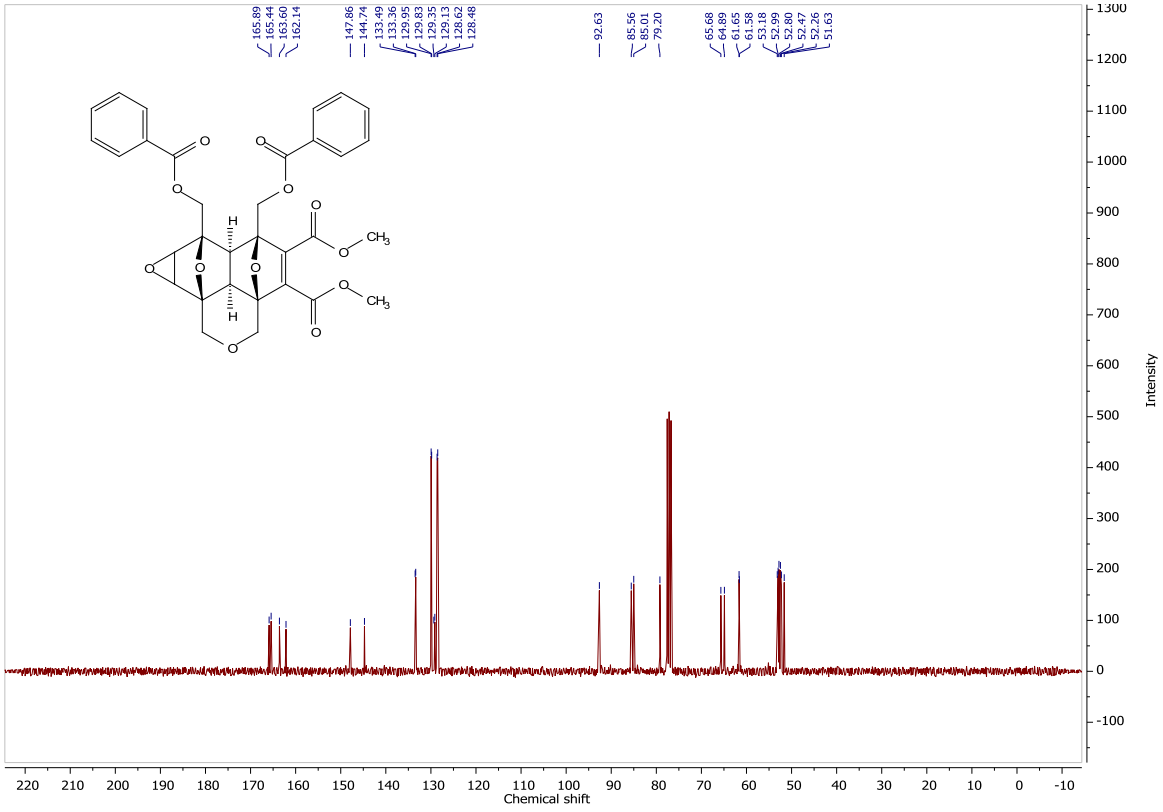


Figure S72. ^{13}C NMR spectrum of (3aS,3a1S,6R,6aR,7R,8bS)-dimethyl 6,7-bis((benzoyloxy)methyl)-1,3,3a1,6,6a,7,7a,8a-octahydro-3a,6:7,8b-diepoxybenzo[de]oxireno[2,3-h]isochromene-4,5-dicarboxylate **7aa** (75 MHz, Chloroform-*d*).

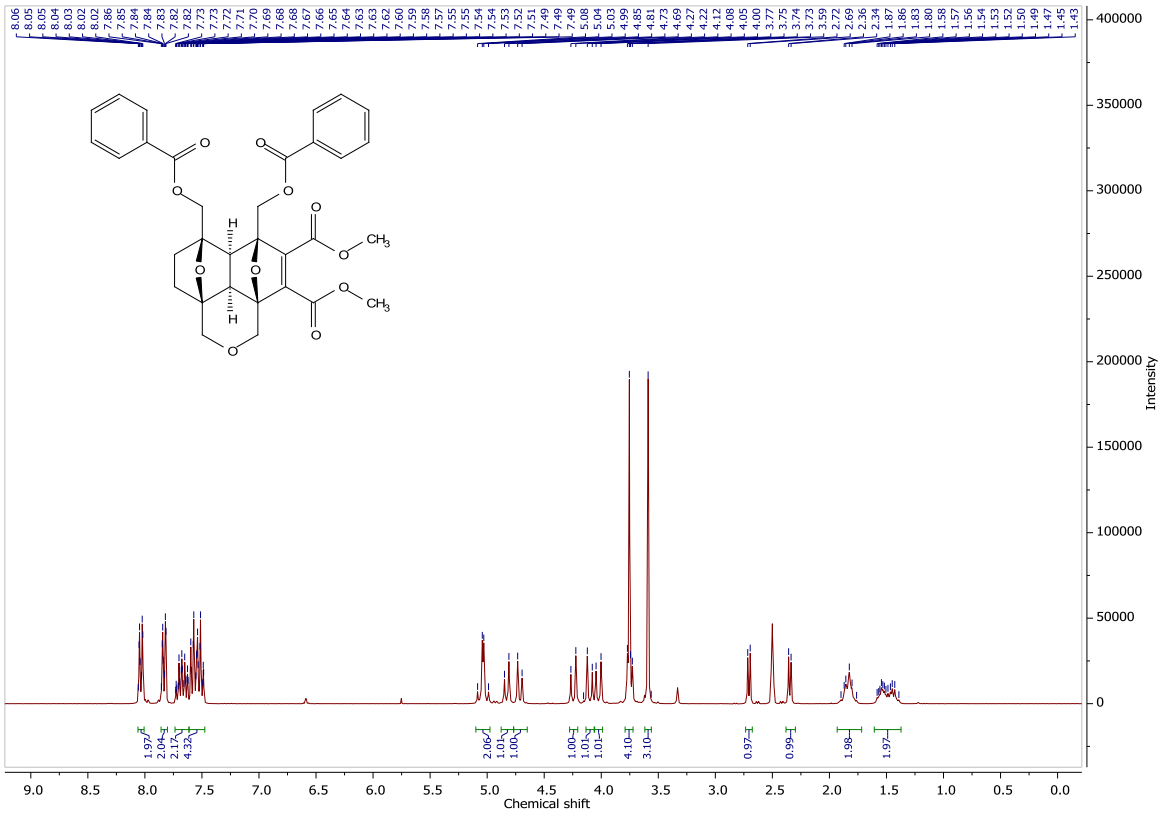


Figure S73. ^{1}H NMR spectrum of (3aS,3a1R,6R,6aS,7R,9aS)-dimethyl 6,7-bis((benzoyloxy)methyl)-1,3,3a1,6,6a,7,8,9-octahydro-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **8aa** (300 MHz, DMSO-d_6).

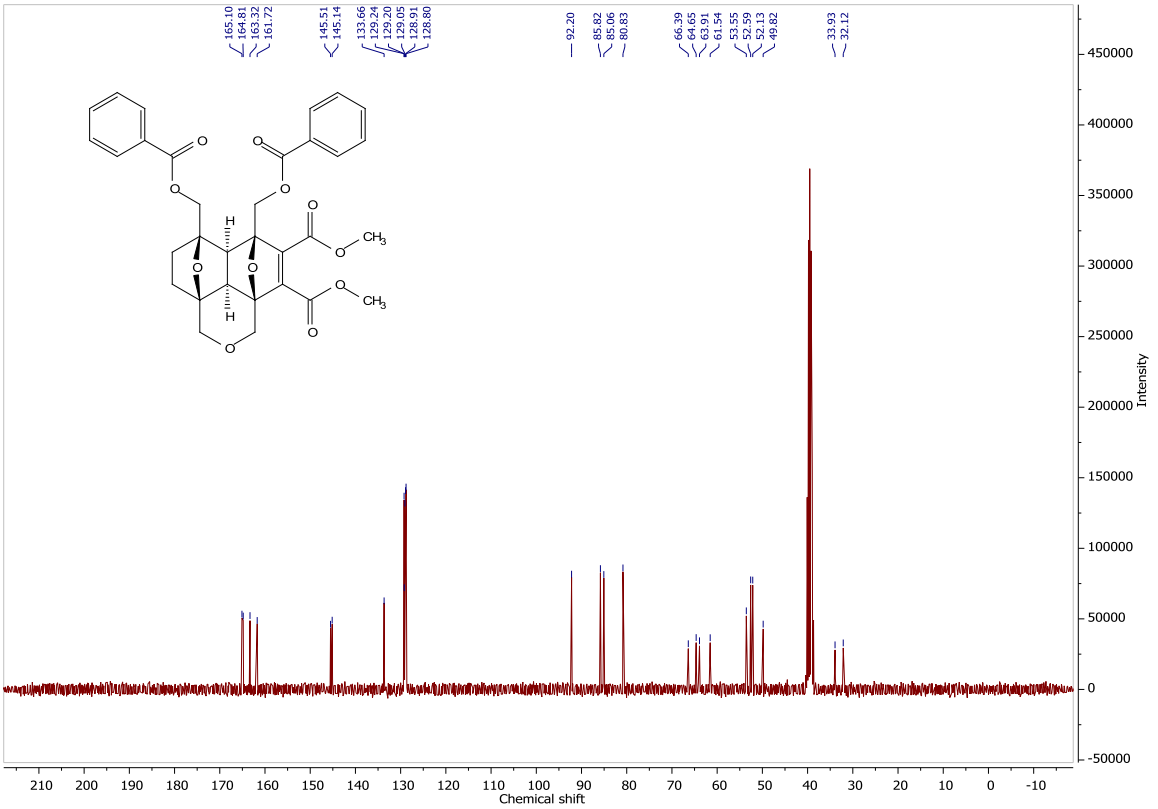


Figure S74. ^{13}C NMR spectrum of (3aS,3a1R,6R,6aS,7R,9aS)-dimethyl 6,7-bis((benzoyloxy)methyl)-1,3,3a1,6,6a,7,8,9-octahydro-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **8aa** (75 MHz, DMSO-d_6).

7. Mass spectra of compounds

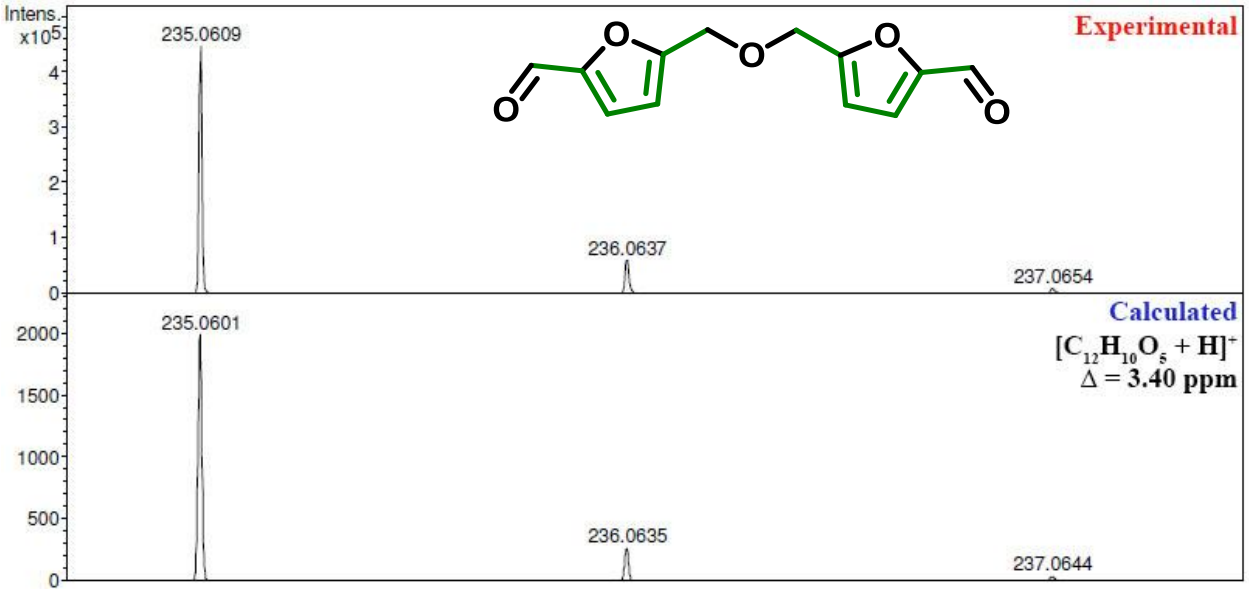


Figure S75. HRMS (ESI) spectrum of 5,5'-(oxybis(methylene))bis(furan-2-carbaldehyde) **1**.

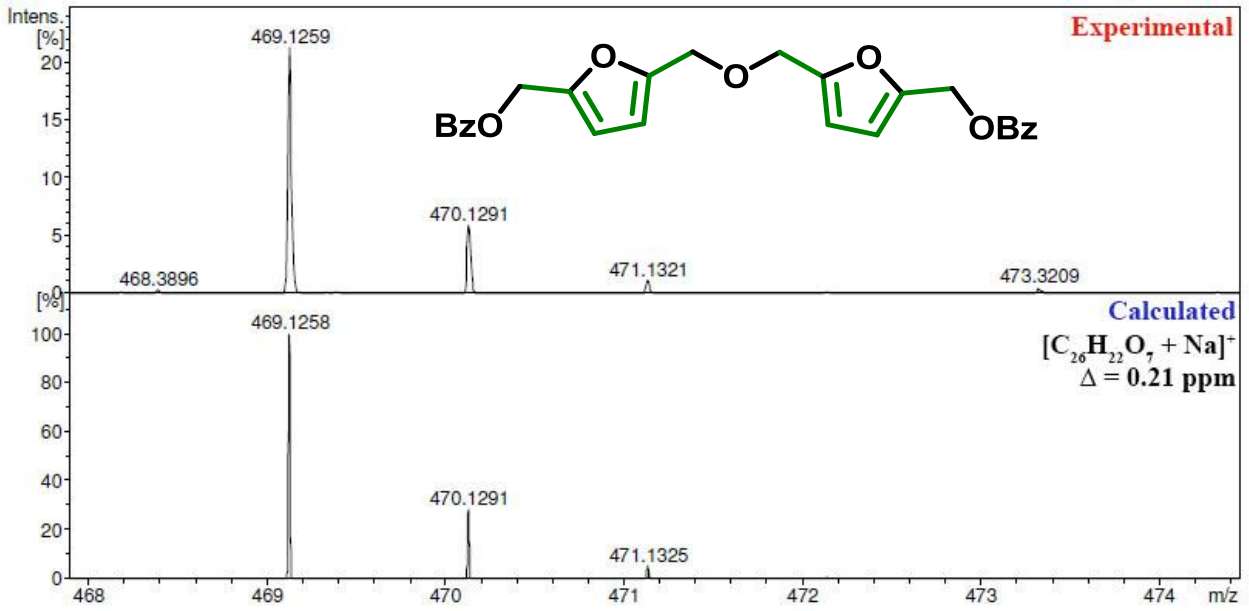


Figure S76. HRMS (ESI) spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate **1a**.

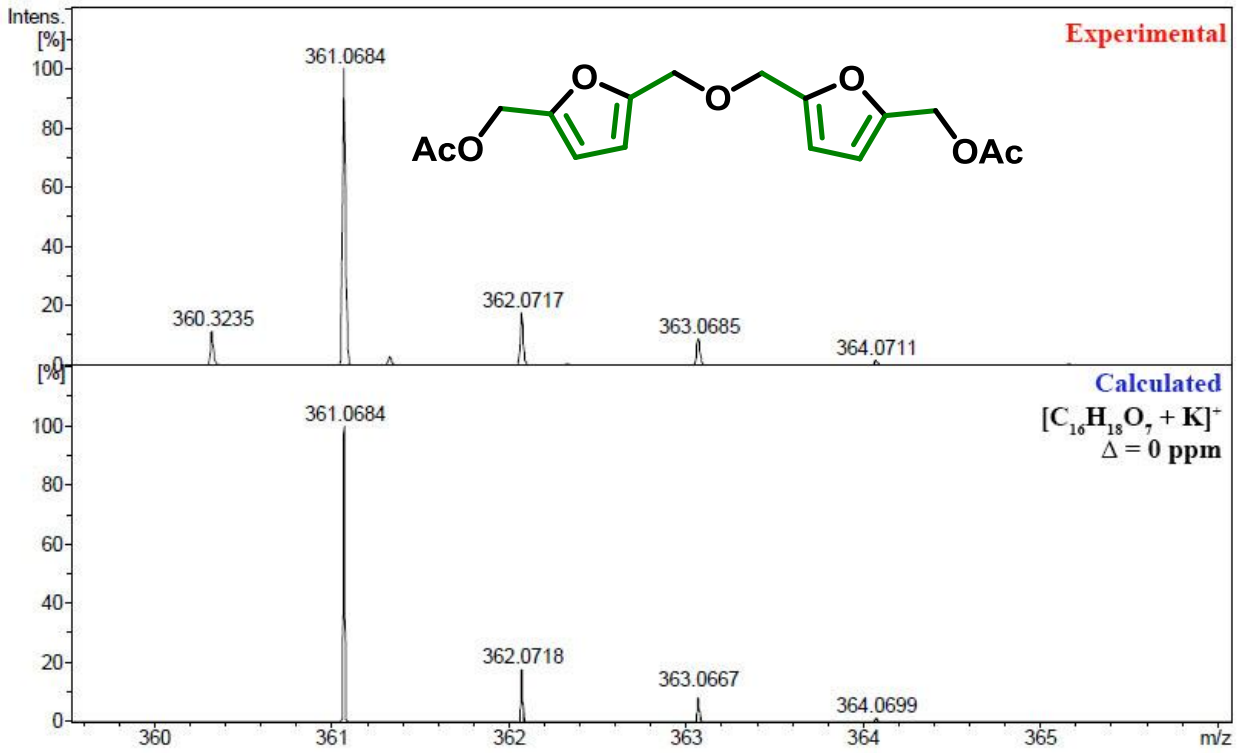


Figure S77. HRMS (ESI) spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))bis(methylene) diacetate **1b**.

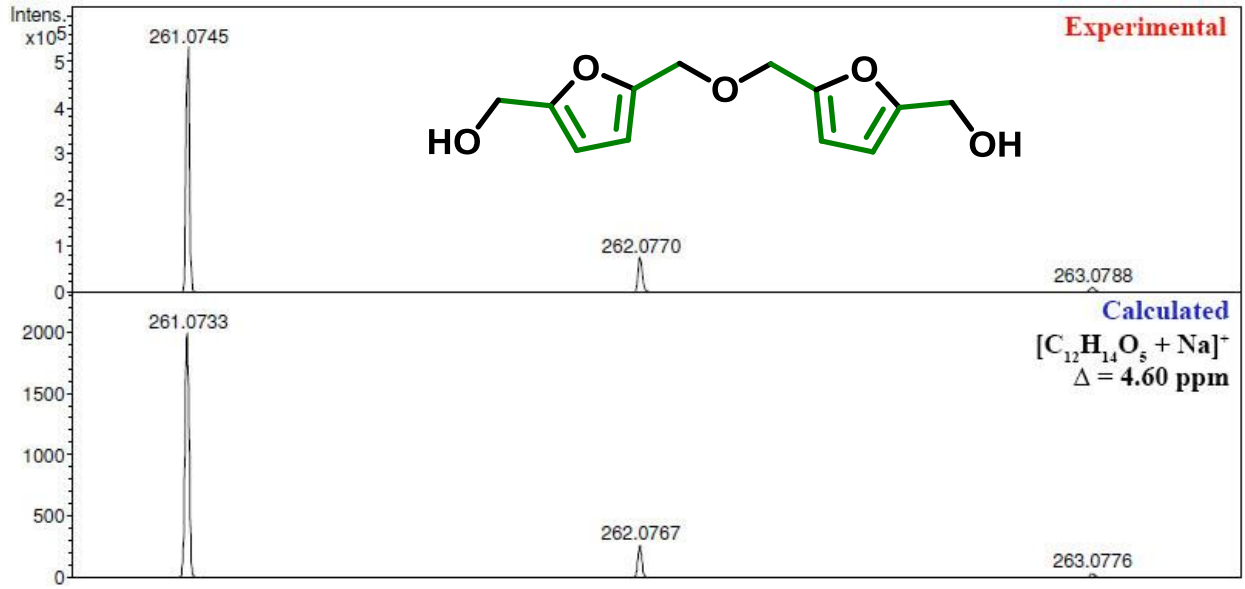


Figure S78. HRMS (ESI) spectrum of ((oxybis(methylene))bis(furan-5,2-diyl))dimethanol **1c**.

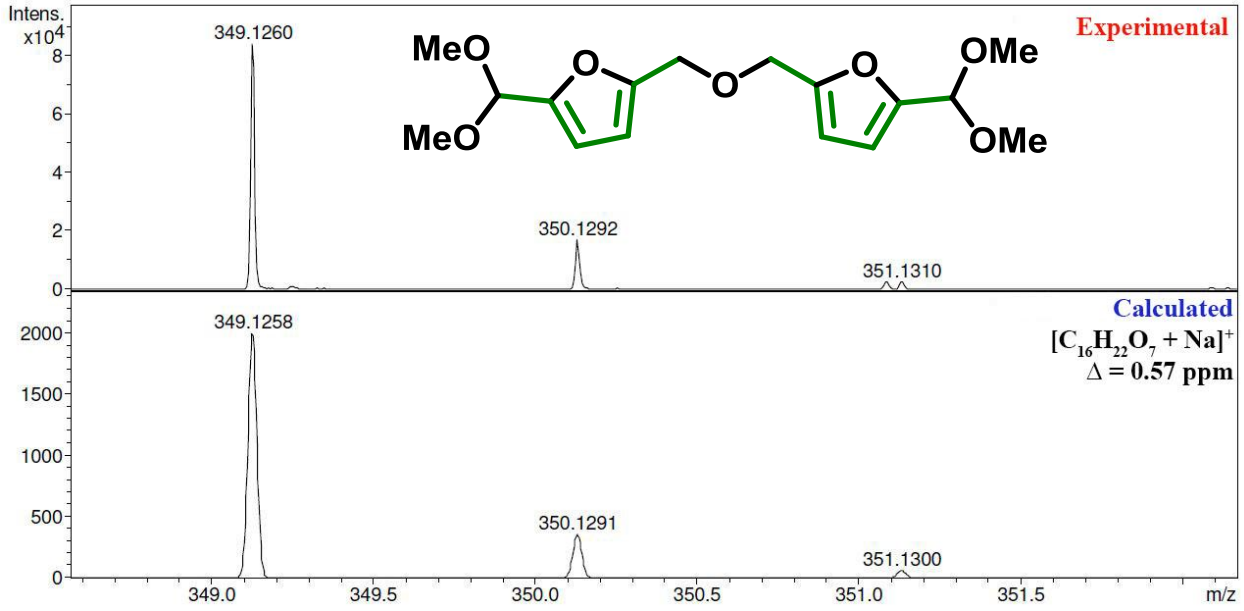


Figure S79. HRMS (ESI) spectrum of 5,5'-(oxybis(methylene))bis(2-(dimethoxymethyl)furan) **1d**.

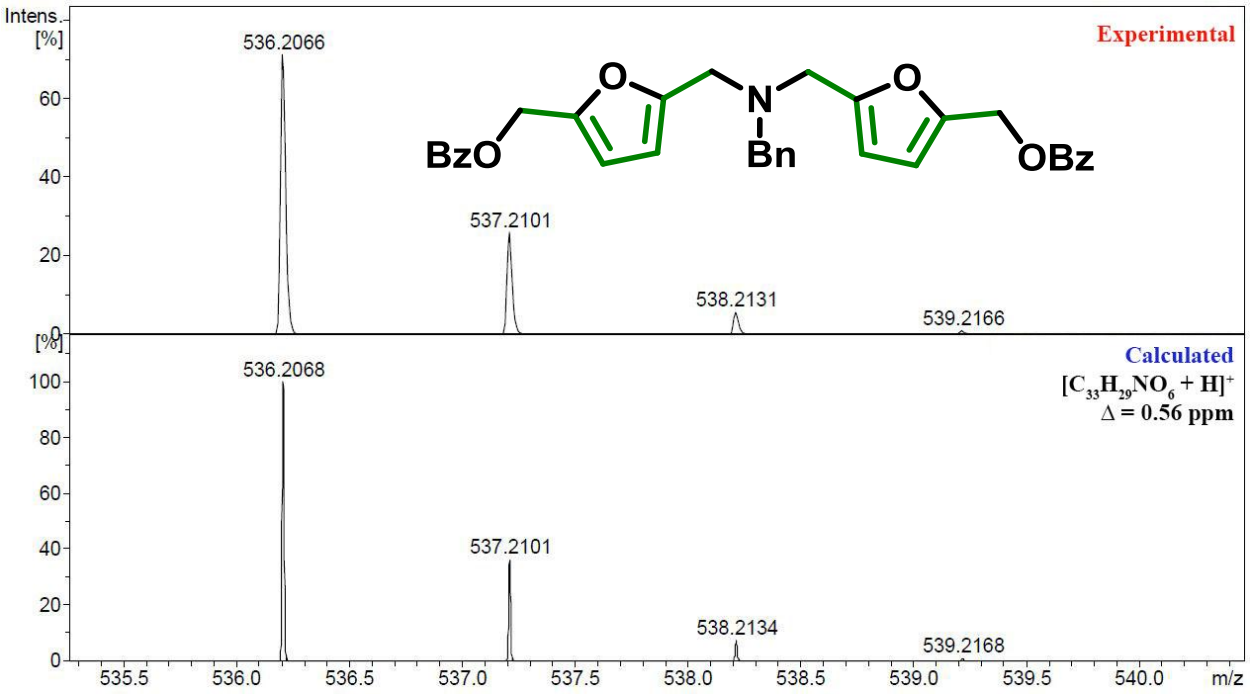


Figure S80. HRMS (ESI) spectrum of (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))bis(methylene) dibenzoate **1e**.

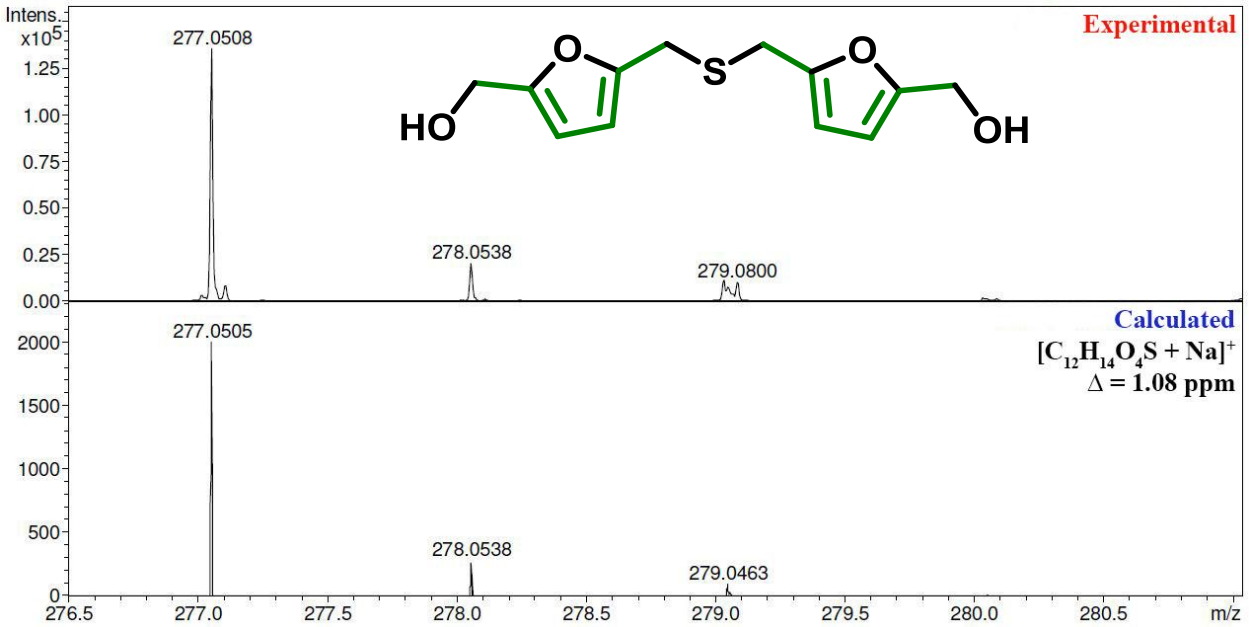


Figure S81. HRMS (ESI) spectrum of ((thiobis(methylene))bis(furan-5,2-diyl))dimethanol, **1f**.

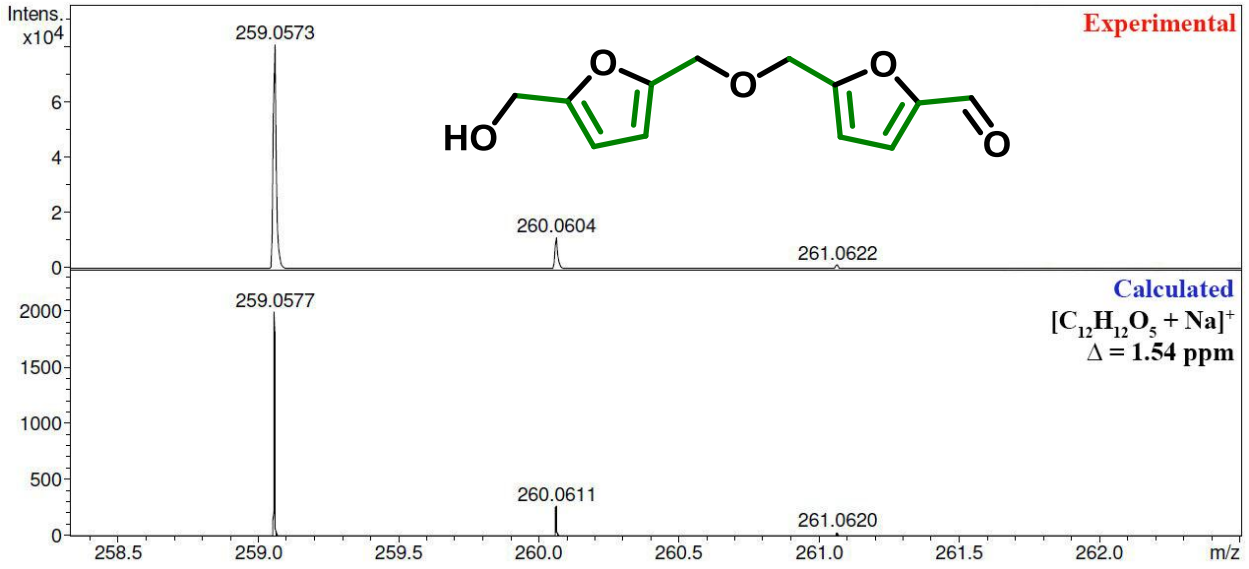


Figure S82. HRMS (ESI) spectrum of 5-(((5-(hydroxymethyl)furan-2-yl)methoxy)methyl)furan-2-carbaldehyde **1g**.

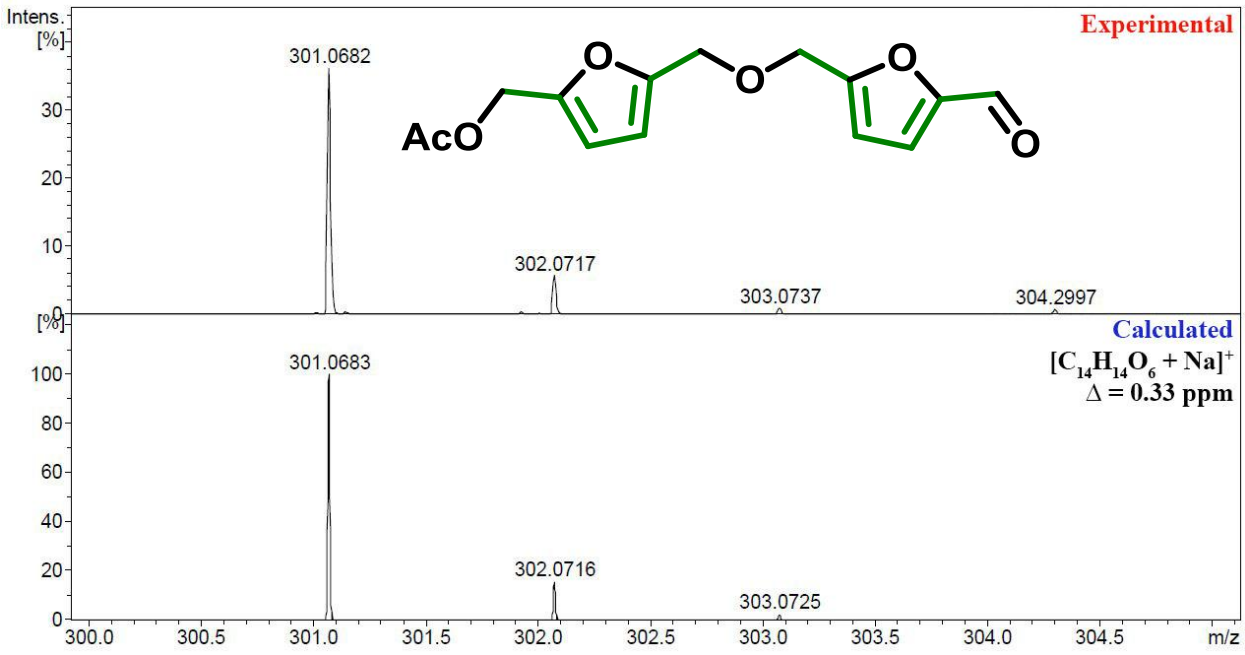


Figure S83. HRMS (ESI) spectrum of (5-(((5-formylfuran-2-yl)methoxy)methyl)furan-2-yl)methyl acetate **1h**.

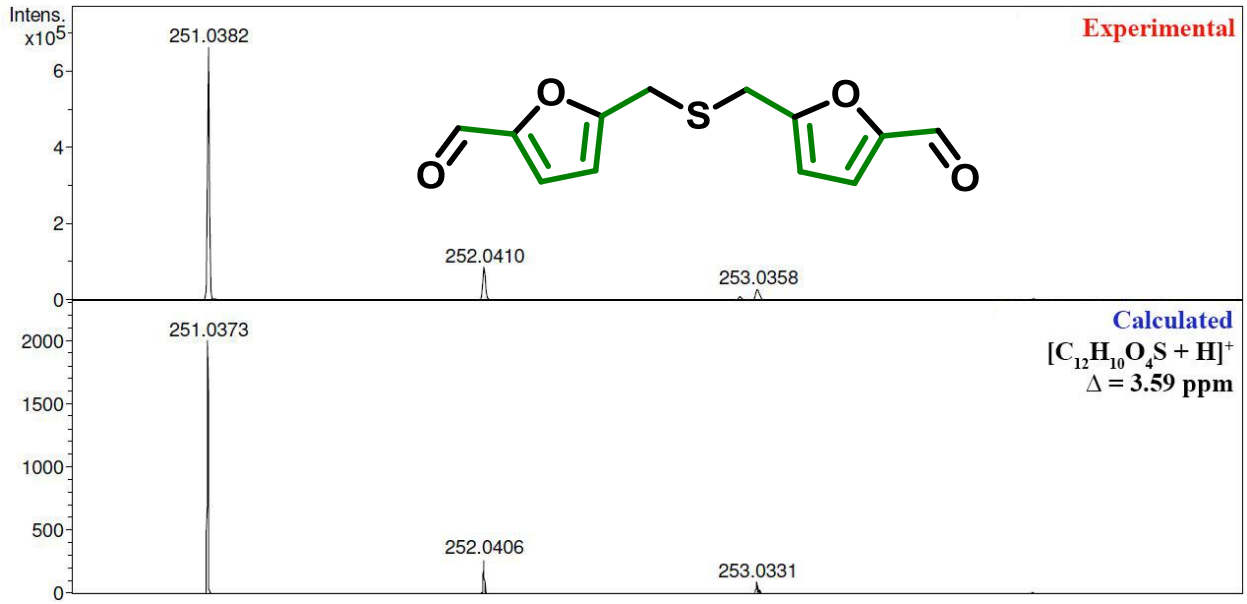


Figure S84. HRMS (ESI) spectrum of 5,5'-(thiobis(methylene))bis(furan-2-carbaldehyde) **1i**.

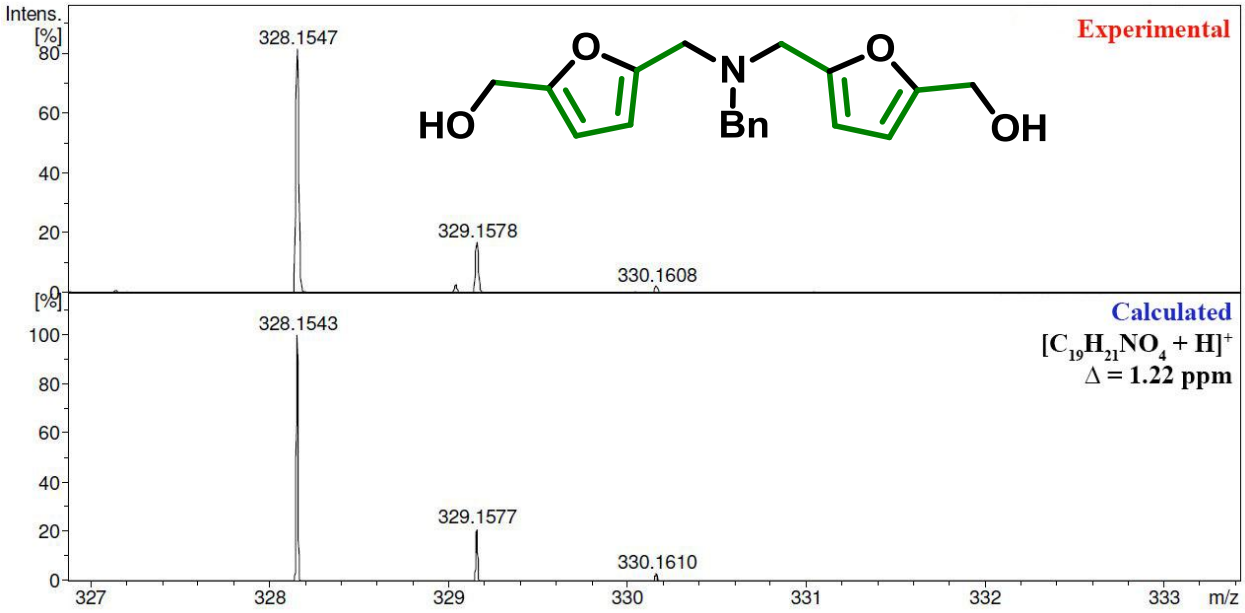


Figure S85. HRMS (ESI) spectrum of (((benzylazanediyl)bis(methylene))bis(furan-5,2-diyl))dimethanol **1j**.

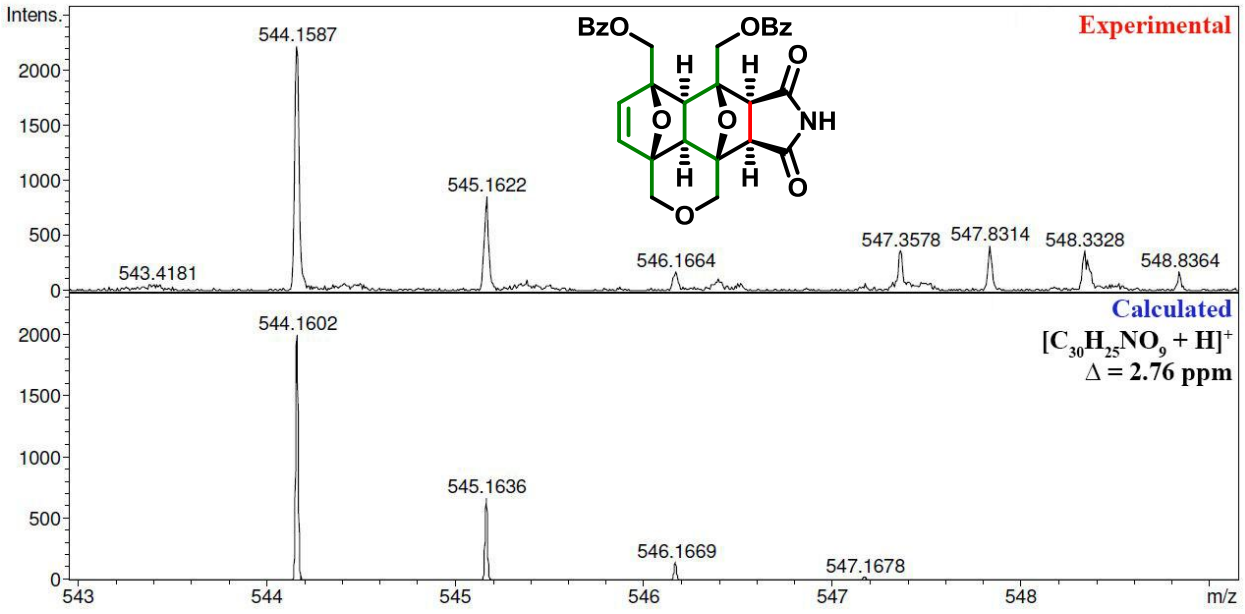


Figure S86. HRMS (ESI) spectrum of (8,10-Dioxo-3a[1],6a,8,9,10,10a-hexahydro-1H,3H,6H-3a,6:7,10b-diepoxyisochromeno[4,5-ef]isoindole-6,7(7aH)-diyl)bis(methylene) dibenzoate **3ab**.

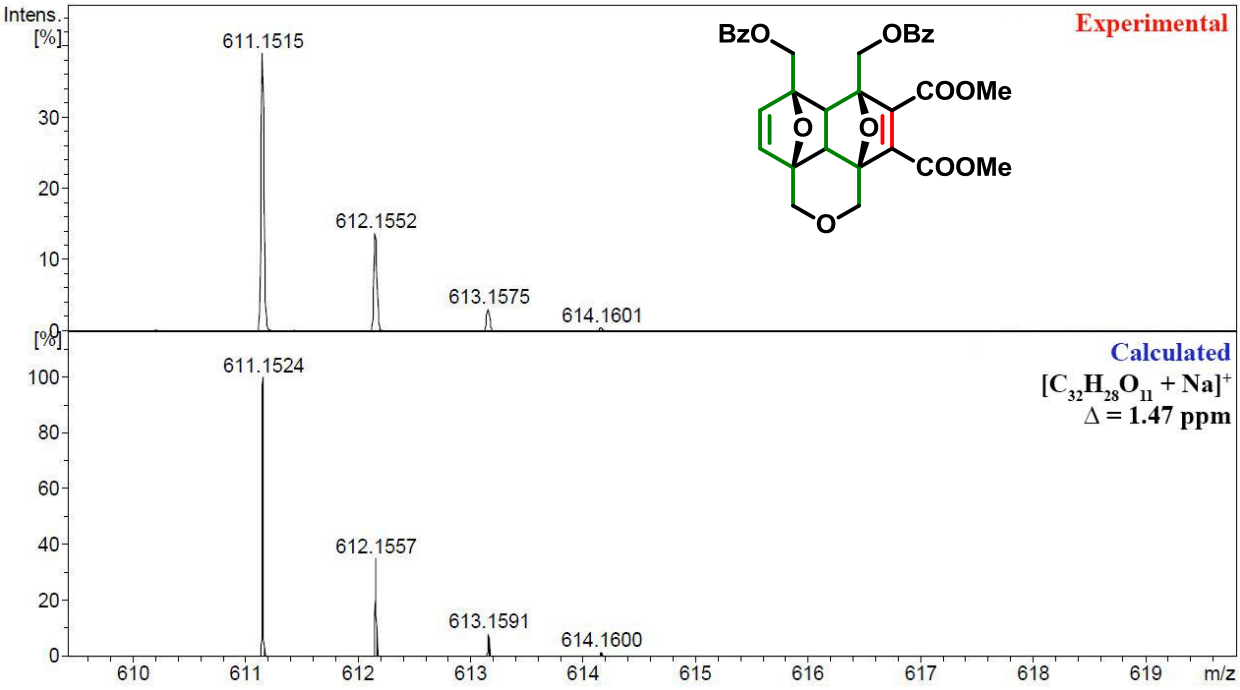


Figure S87. HRMS (ESI) spectrum of dimethyl 6,7-bis((benzoyloxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3aa**.

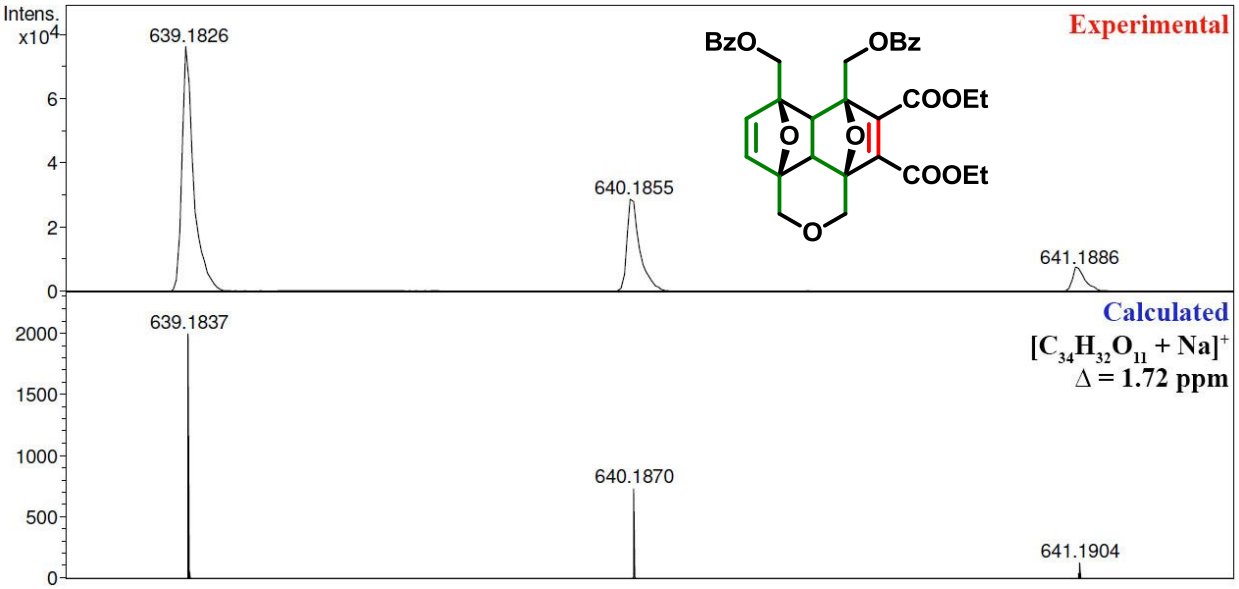


Figure S88. HRMS (ESI) spectrum of diethyl 6,7-bis((benzoyloxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ad**.

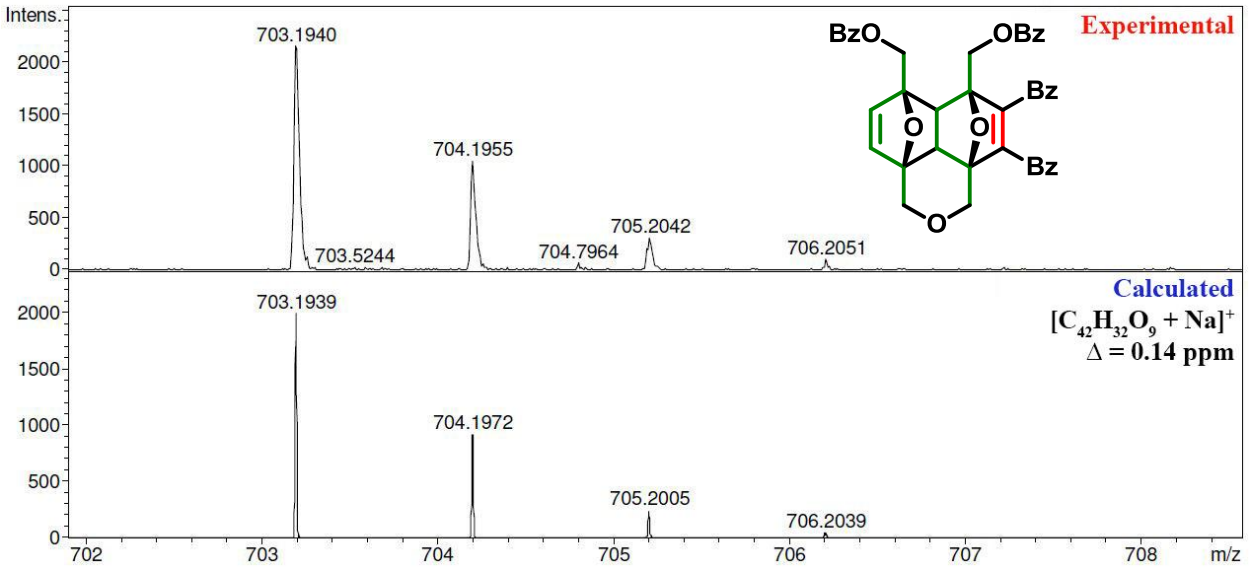


Figure S89. HRMS (ESI) spectrum of (4,5-dibenzoyl-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3ae**.

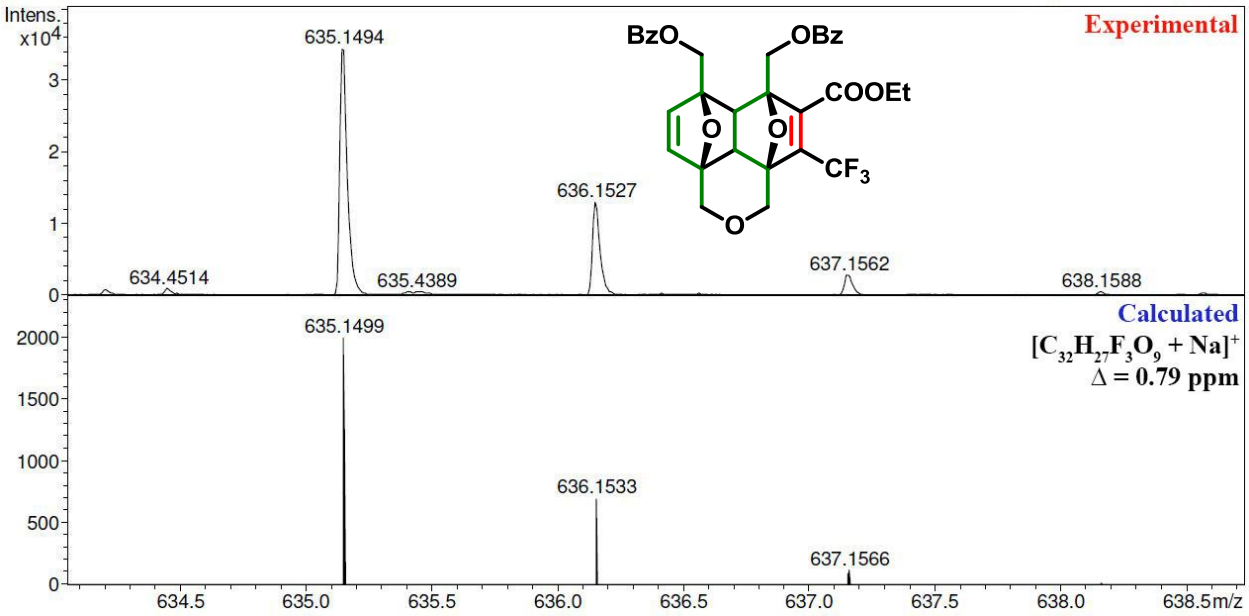


Figure S90. HRMS (ESI) spectrum of (5-(ethoxycarbonyl)-4-(trifluoromethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afA**.

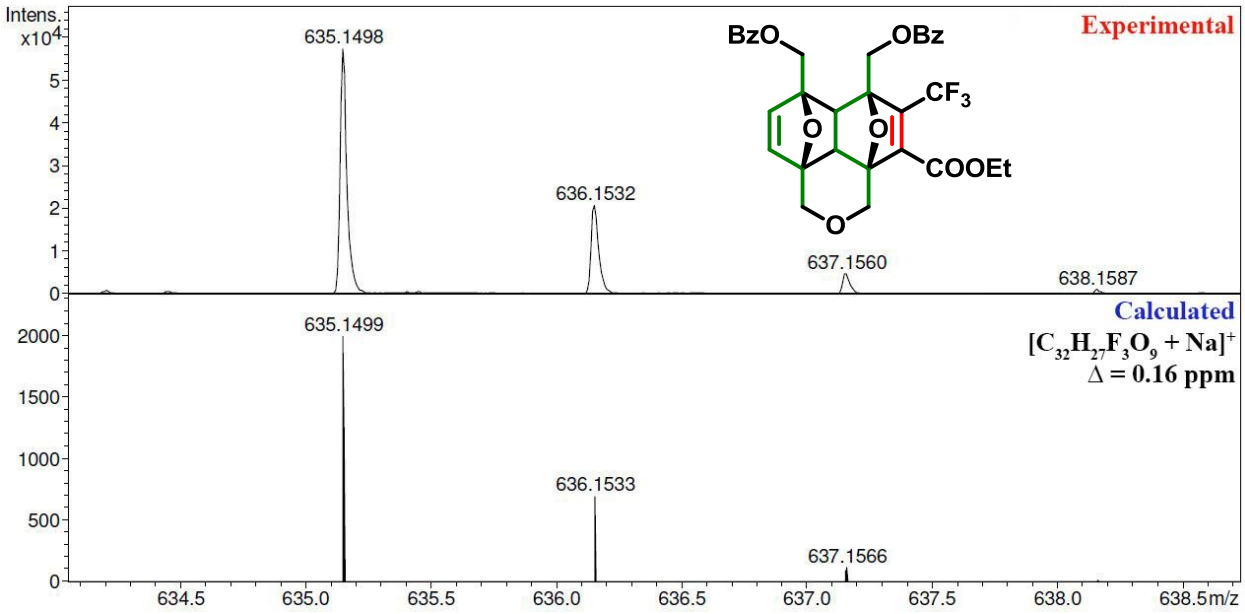


Figure S91. HRMS (ESI) spectrum of (4-(ethoxycarbonyl)-5-(trifluoromethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3afB**.

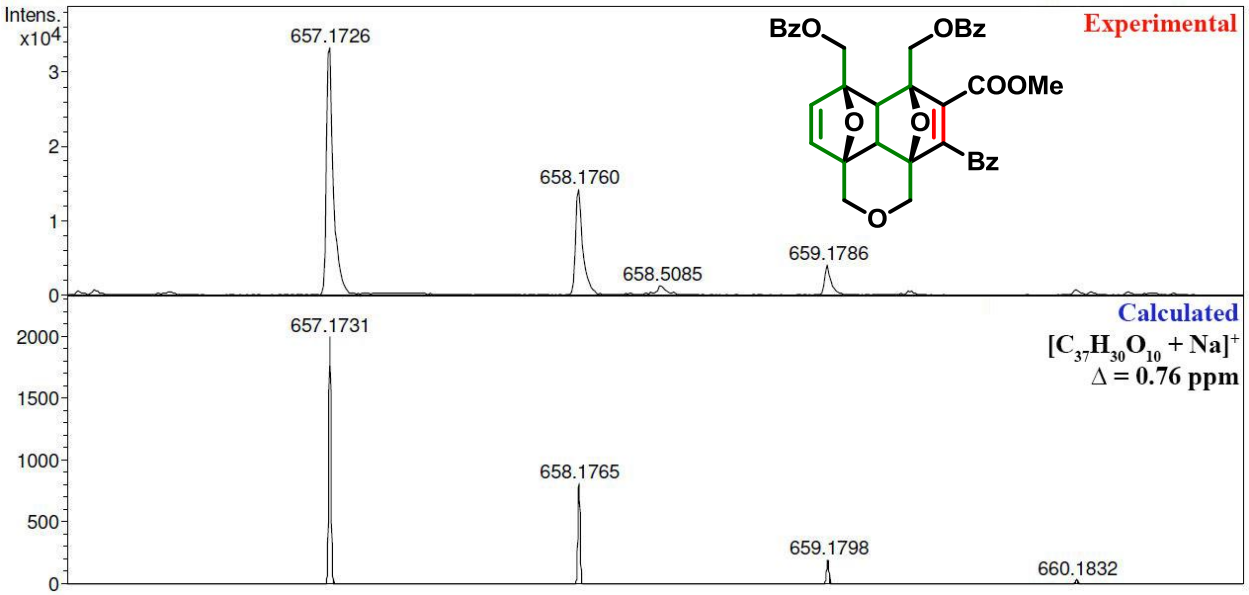


Figure S92. HRMS (ESI) spectrum of (4-benzoyl-5-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agA**.

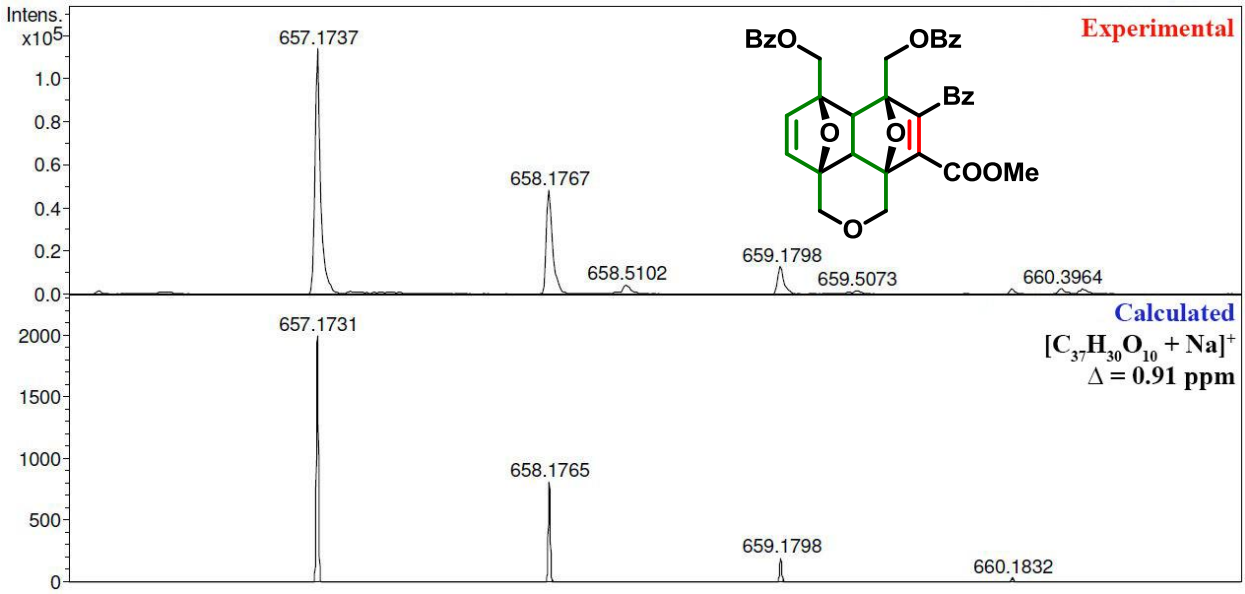


Figure S93. HRMS (ESI) spectrum of (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB**.

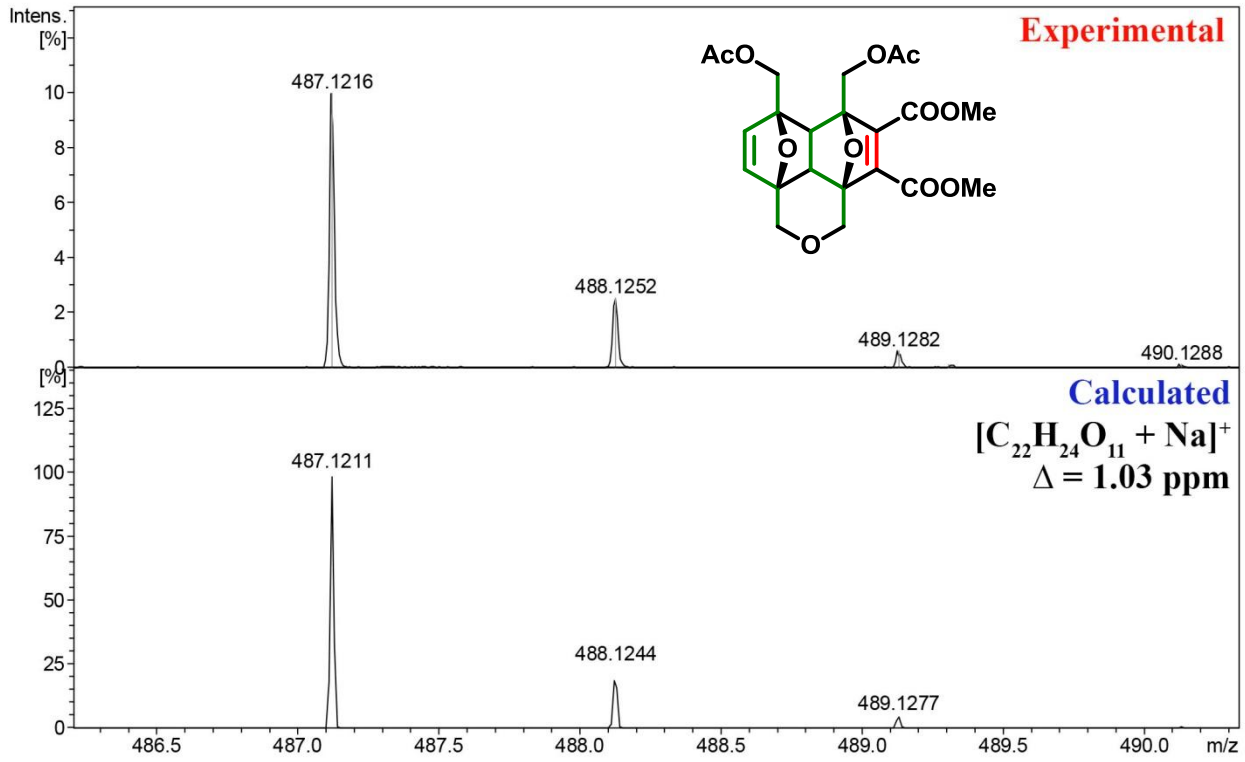


Figure S94. HRMS (ESI) spectrum of dimethyl 6,7-bis(acetoxymethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ba**.

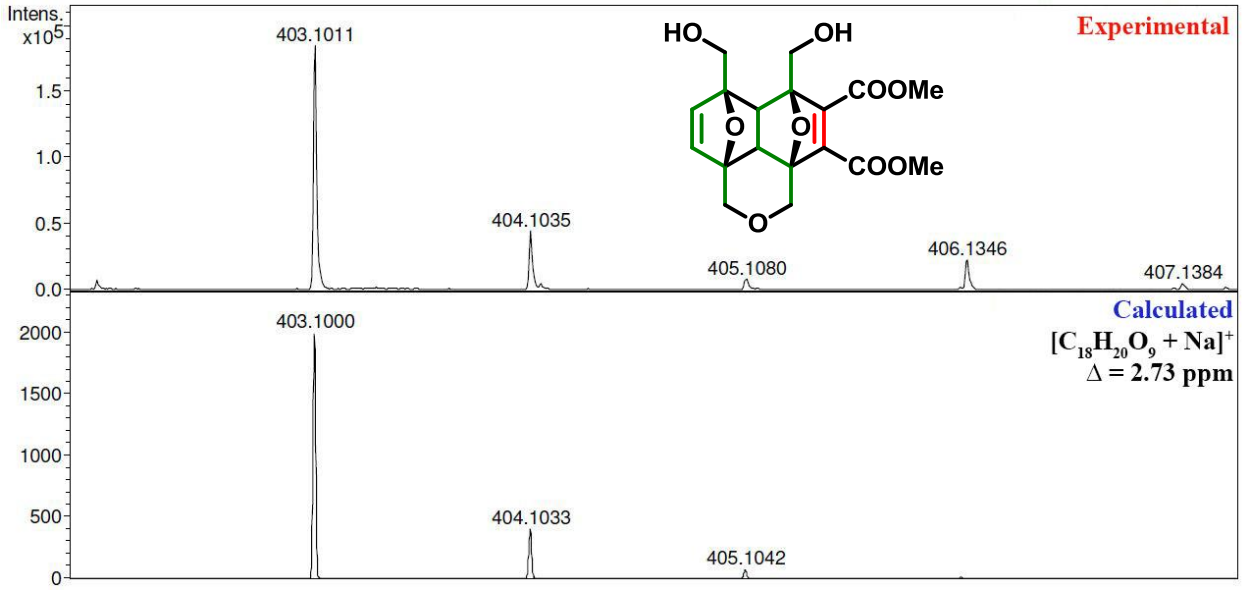


Figure S95. HRMS (ESI) spectrum of dimethyl 6,7-bis(hydroxymethyl)-3a1,6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ca**

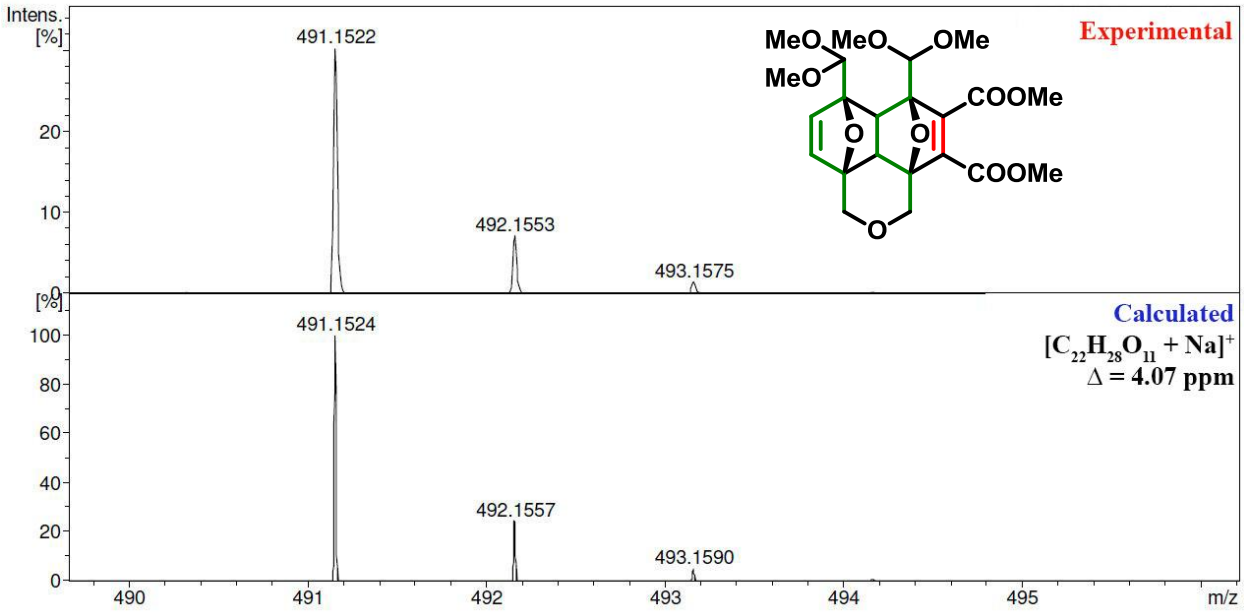


Figure S96. HRMS (ESI) spectrum of dimethyl 6,7-bis(dimethoxymethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3da**.

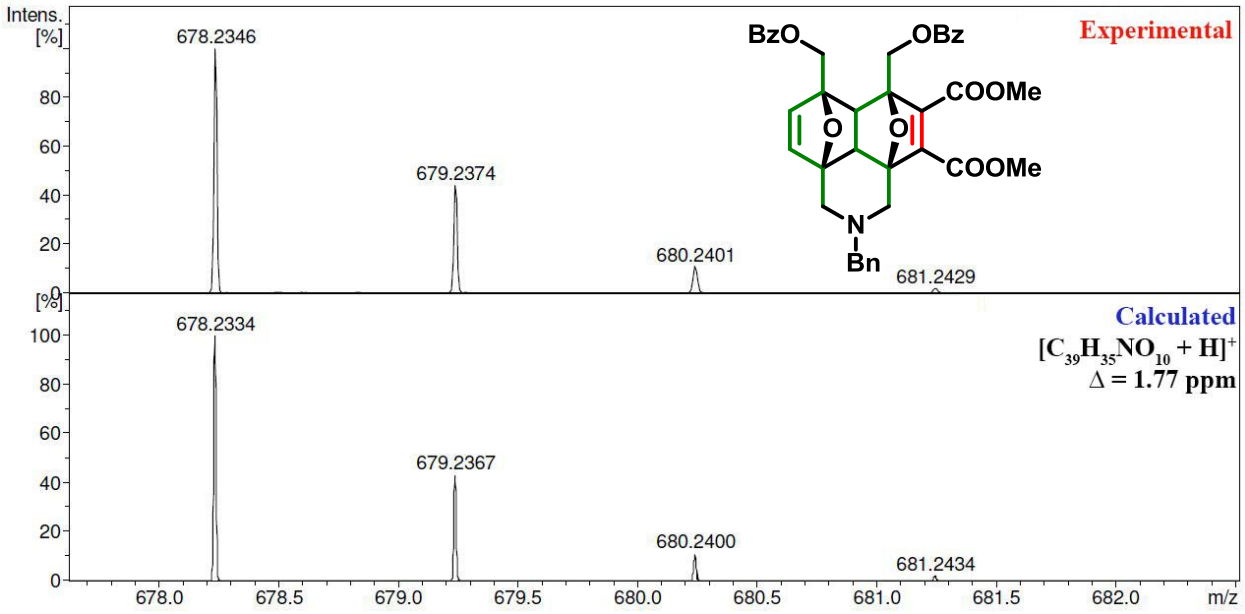


Figure S97. HRMS (ESI) spectrum of dimethyl 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea**.

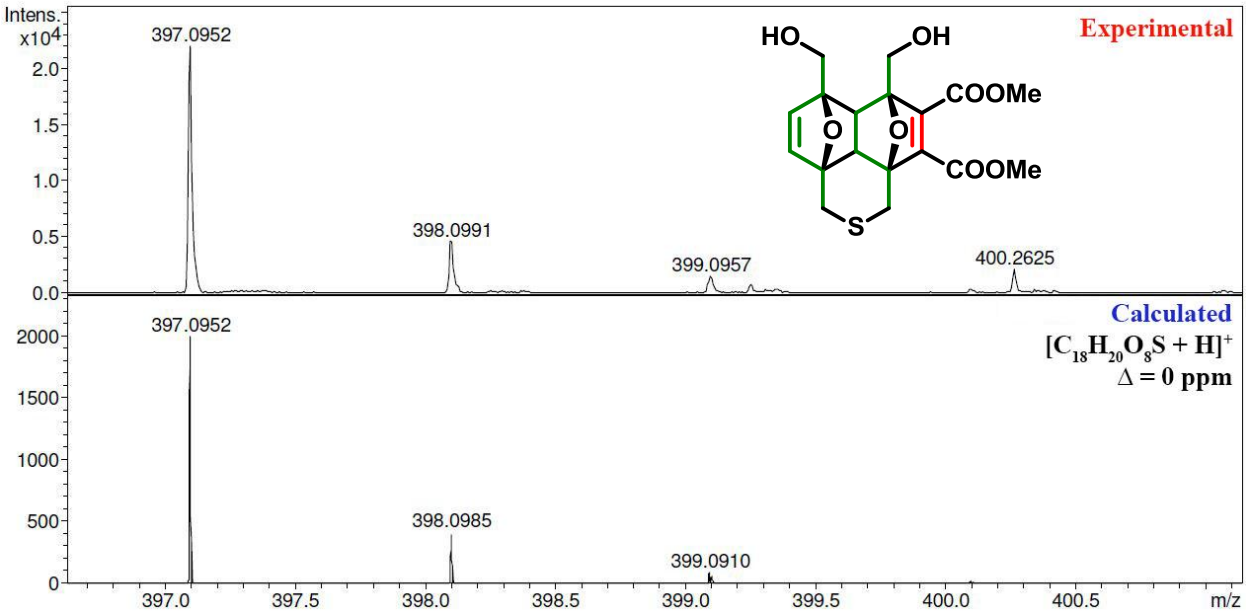


Figure S98. HRMS (ESI) spectrum of dimethyl 6,7-bis(hydroxymethyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isothiochromene-4,5-dicarboxylate **3fa**.

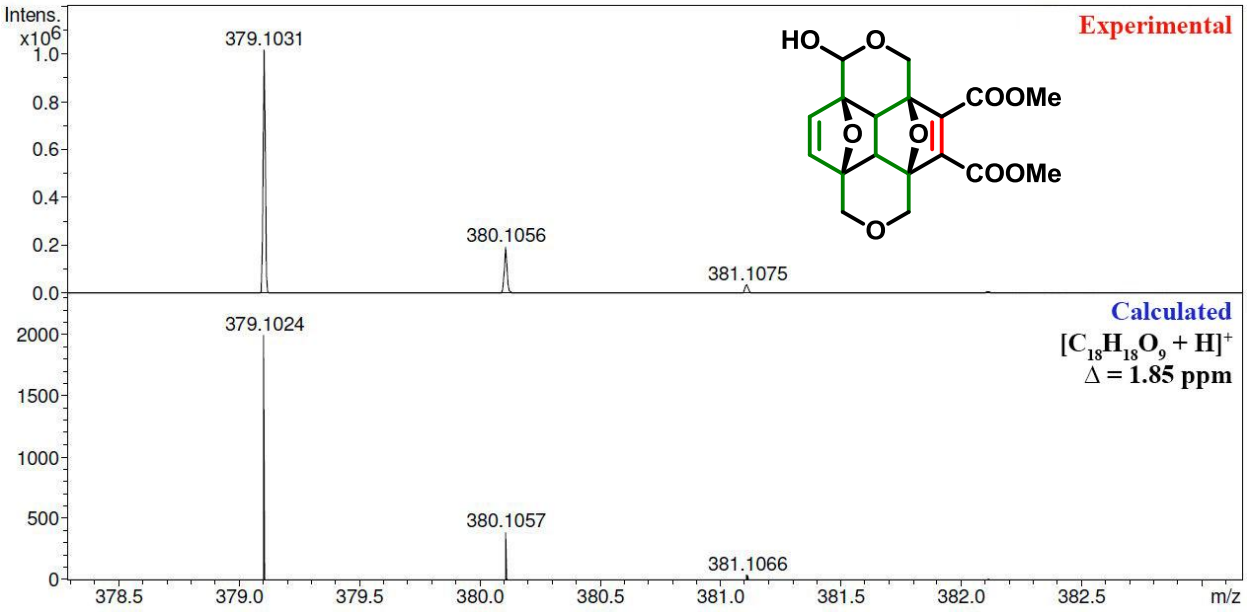


Figure S99. HRMS (ESI) spectrum of 1-hydroxy-1,3,3a,3a[1],5a,5a[1],6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga**.

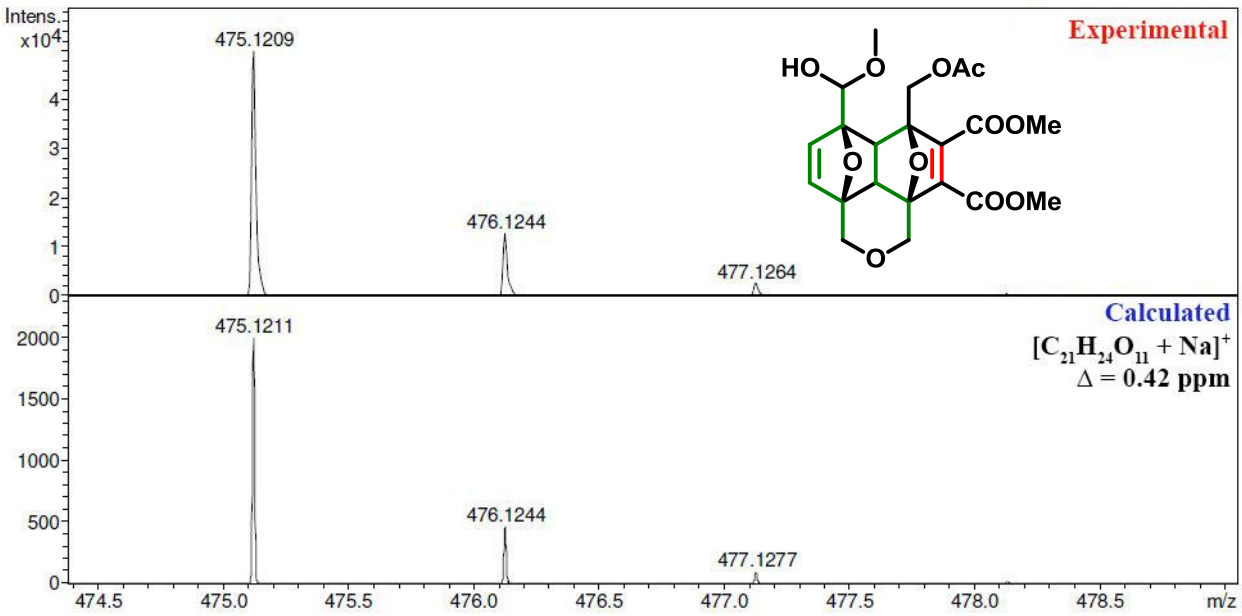


Figure S100. HRMS (ESI) spectrum of dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha**.

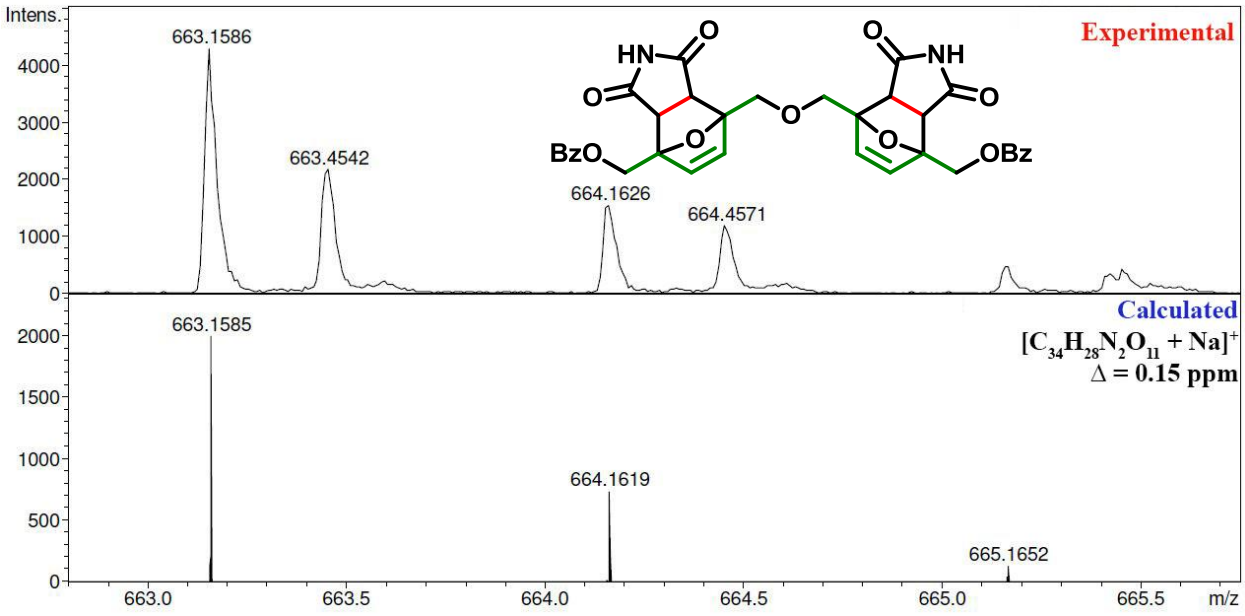


Figure S101. HRMS (ESI) spectrum of ((oxybis(methylene))bis(1,3-dioxo-1,2,3,3a,7,7a-hexahydro-4H-4,7-epoxyisoindole-7,4-diyl))bis(methylene) dibenzoate **4ab**.

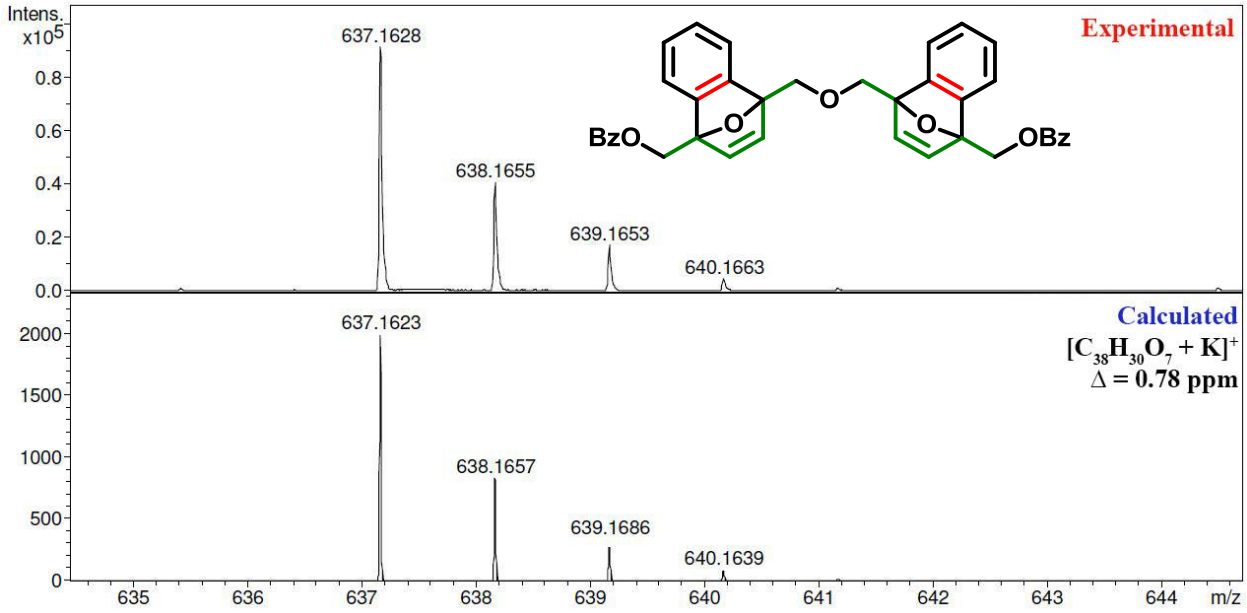


Figure S102. HRMS (ESI) spectrum of ((oxybis(methylene))bis(1,4-epoxynaphthalene-4,1(4H)-diyl))bis(methylene) dibenzoate **4ac**

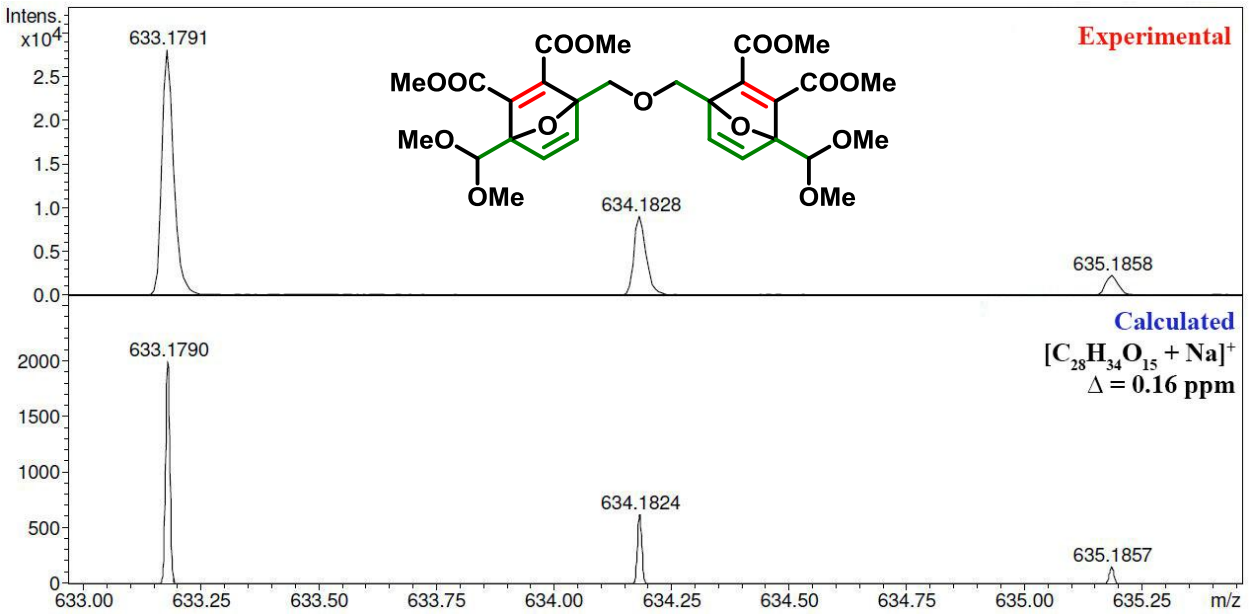


Figure S103. HRMS (ESI) spectrum of 4,4'-(oxybis(methylene))bis(1-(dimethoxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) **4da**.

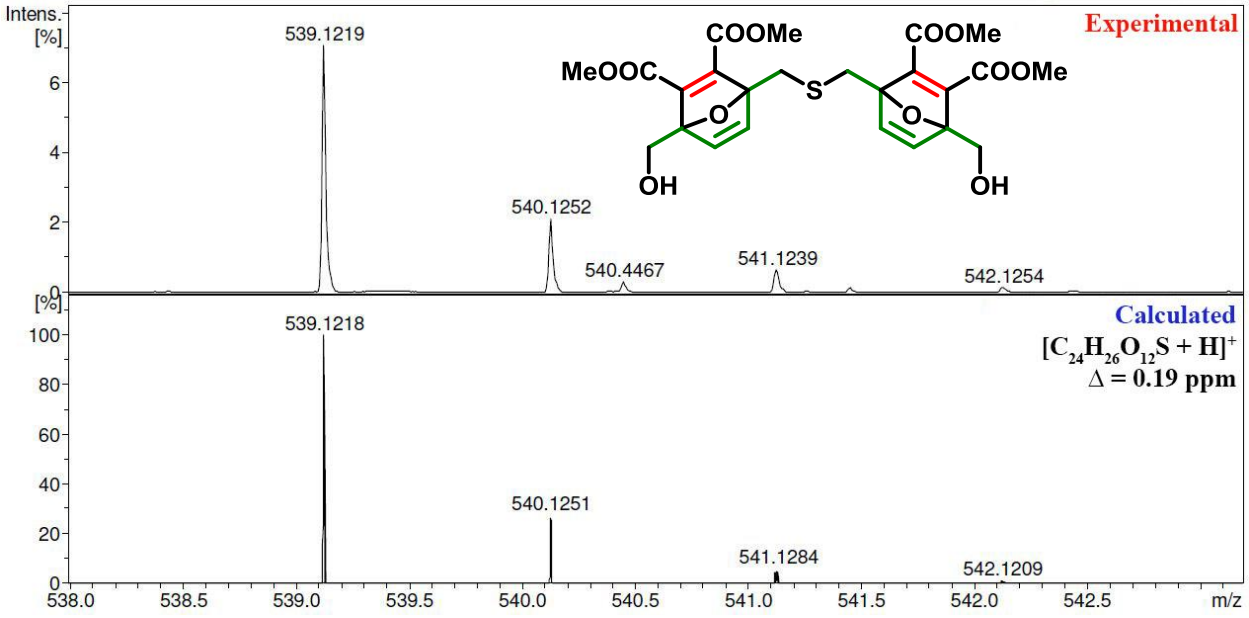


Figure S104. HRMS (ESI) spectrum of 4,4'-(thiobis(methylene))bis(1-(hydroxymethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate) **4fa**.

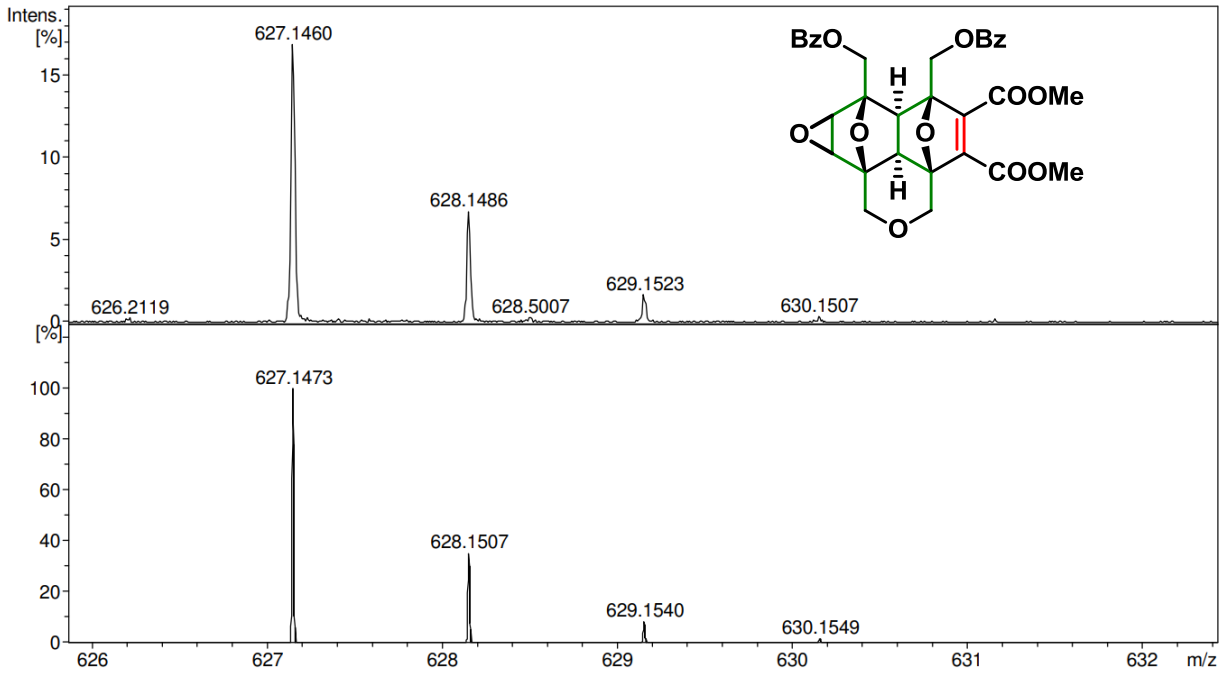


Figure S105. HRMS (ESI) spectrum of (3aS,3a1S,6R,6aR,7R,8bS)-dimethyl 6,7-bis((benzoyloxy)methyl)-1,3,3a1,6,6a,7,7a,8a-octahydro-3a,6:7,8b-diepoxybenzo[de]oxireno[2,3-h]isochromene-4,5-dicarboxylate **7aa**.

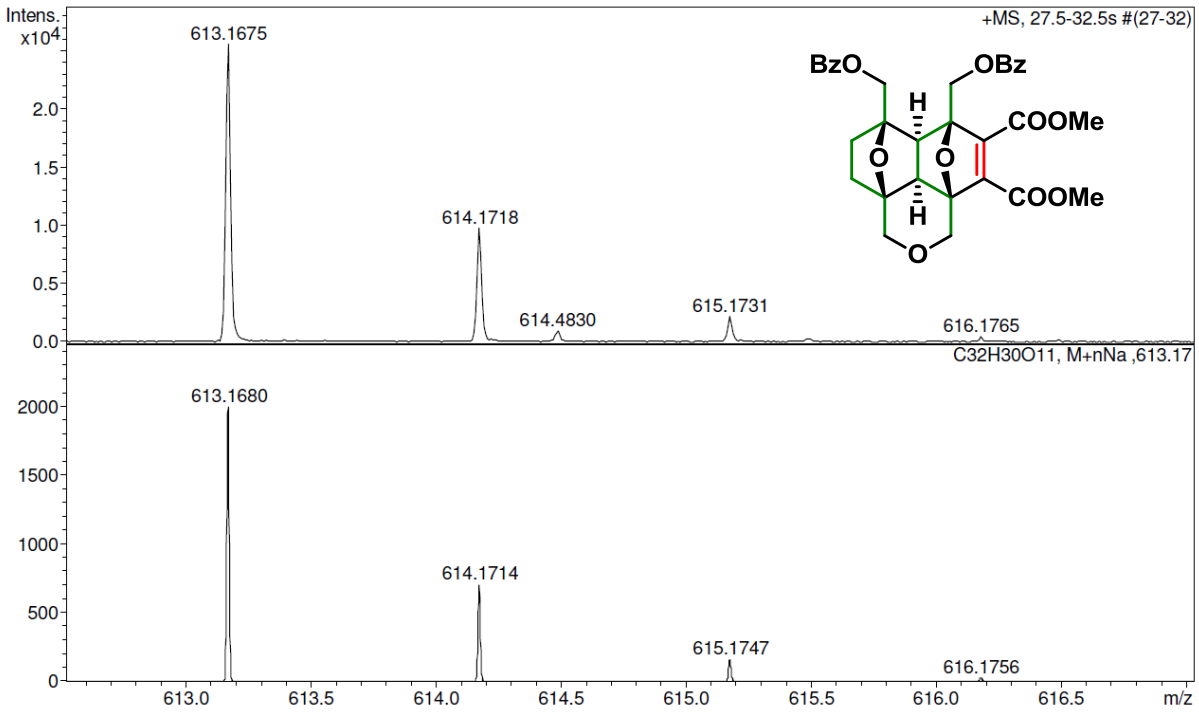


Figure S106. HRMS (ESI) spectrum of (3aS,3a1R,6R,6aS,7R,9aS)-dimethyl 6,7-bis((benzoyloxy)methyl)-1,3,3a1,6,6a,7,8,9-octahydro-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **8aa**.

8. X-Ray structure determination

X-Ray crystallographic data and refinement details

X-ray diffraction data were collected at 100 K on a Bruker Quest D8 diffractometer equipped with a Photon-III area detector (graphite monochromator, shutterless φ- and ω-scan technique) using Mo K_α radiation. The intensity data were integrated by the SAINT program[3] and were corrected for absorption and decay using SADABS[4]. The structure was solved by direct methods using SHELXT[5] and refined on F^2 using SHELXL-2018[6]. All nonhydrogen atoms were refined with individual anisotropic displacement parameters. The positions of all hydrogen atoms were found from the electron density-difference map, and these atoms were refined with individual isotropic displacement parameters. The SHELXTL program suite was used for molecular graphics.

Acknowledgment

Crystal structure determination was performed in the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow.

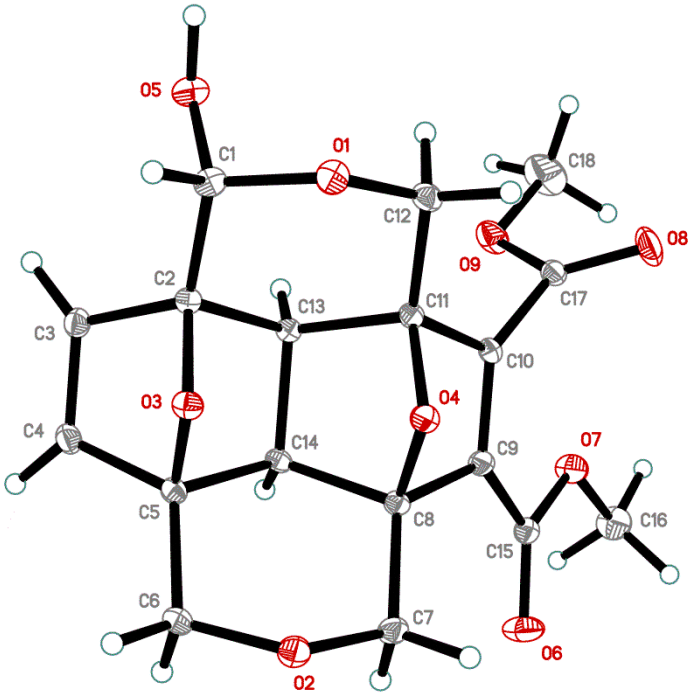


Figure S107. X-Ray structure of 1-hydroxy-1,3,3a,3a[1],5a,5a[1],6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga**.

Table S2. Crystal data and structure refinement for 1-hydroxy-1,3,3a,3a^{1},5a,5a^{1},6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga**.

Empirical formula	C18 H18 O9	
Formula weight	378.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 18.6508(3) Å	α= 90°.
	b = 5.87960(10) Å	β= 94.7151(7)°.
	c = 14.7464(3) Å	γ = 90°.
Volume	1611.61(5) Å^3	
Z	4	
Density (calculated)	1.559 g/cm^3	
Absorption coefficient	0.127 mm^{-1}	
F(000)	792	
Crystal size	0.40 x 0.07 x 0.05 mm^3	
Theta range for data collection	2.772 to 31.523°.	
Index ranges	-27<=h<=27, -8<=k<=8, -21<=l<=21	
Reflections collected	51521	
Independent reflections	5388 [R(int) = 0.0408]	
Observed reflections	4465	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8623 and 0.8256	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5388 / 0 / 319	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0647	
R indices (all data)	R1 = 0.0391, wR2 = 0.0707	
Largest diff. peak and hole	0.240 and -0.232 e.Å^{-3}	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for 1-hydroxy-1,3,3a,3a^1,5a,5a^1,6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga**. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	6973(1)	8194(1)	2951(1)	12(1)
O(2)	6460(1)	4566(1)	5998(1)	13(1)
O(3)	6048(1)	5660(1)	4106(1)	10(1)
O(4)	7434(1)	5691(1)	4604(1)	10(1)
O(5)	6392(1)	6182(1)	1732(1)	14(1)
O(6)	8342(1)	-228(1)	5941(1)	20(1)
O(7)	8953(1)	-391(1)	4683(1)	16(1)
O(8)	9341(1)	3871(1)	3398(1)	20(1)
O(9)	8591(1)	1309(1)	2695(1)	17(1)
C(1)	6345(1)	6987(1)	2618(1)	11(1)
C(2)	6213(1)	4949(1)	3213(1)	9(1)
C(3)	5607(1)	3255(1)	2977(1)	12(1)
C(4)	5475(1)	2291(1)	3771(1)	12(1)
C(5)	6002(1)	3405(1)	4484(1)	9(1)
C(6)	5879(1)	3446(1)	5480(1)	12(1)
C(7)	7154(1)	3531(1)	5951(1)	12(1)
C(8)	7354(1)	3451(1)	4980(1)	9(1)
C(9)	8054(1)	2343(1)	4716(1)	10(1)
C(10)	8181(1)	3307(1)	3917(1)	10(1)
C(11)	7560(1)	4975(1)	3700(1)	9(1)
C(12)	7629(1)	6920(1)	3053(1)	12(1)
C(13)	6898(1)	3470(1)	3418(1)	8(1)
C(14)	6749(1)	2383(1)	4328(1)	8(1)
C(15)	8447(1)	456(1)	5189(1)	11(1)
C(16)	9376(1)	-2232(2)	5089(1)	19(1)
C(17)	8774(1)	2874(1)	3324(1)	11(1)
C(18)	9152(1)	642(2)	2129(1)	28(1)

Table S4. Bond lengths [Å] and angles [°] for 1-hydroxy-1,3,3a,3a^1,5a,5a^1,6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga**.

O(1)-C(1)	1.4205(9)
O(1)-C(12)	1.4324(10)
O(2)-C(6)	1.4333(10)
O(2)-C(7)	1.4363(10)
O(3)-C(2)	1.4389(9)
O(3)-C(5)	1.4436(9)
O(4)-C(11)	1.4355(9)
O(4)-C(8)	1.4421(9)
O(5)-C(1)	1.3997(9)
O(5)-H(5)	0.947(16)
O(6)-C(15)	1.2107(10)
O(7)-C(15)	1.3450(10)
O(7)-C(16)	1.4402(10)
O(8)-C(17)	1.2064(10)
O(9)-C(17)	1.3306(10)
O(9)-C(18)	1.4443(11)
C(1)-C(2)	1.5172(11)
C(1)-H(1)	1.027(11)
C(2)-C(3)	1.5250(11)
C(2)-C(13)	1.5552(10)
C(3)-C(4)	1.3418(11)
C(3)-H(3)	1.023(12)
C(4)-C(5)	1.5268(11)
C(4)-H(4)	1.023(13)
C(5)-C(6)	1.5053(11)
C(5)-C(14)	1.5517(10)
C(6)-H(6A)	1.008(12)
C(6)-H(6B)	1.037(12)
C(7)-C(8)	1.5087(10)
C(7)-H(7A)	1.004(12)
C(7)-H(7B)	1.019(11)
C(8)-C(9)	1.5375(10)
C(8)-C(14)	1.5531(10)
C(9)-C(10)	1.3460(10)
C(9)-C(15)	1.4741(11)
C(10)-C(17)	1.4876(10)
C(10)-C(11)	1.5315(10)

C(11)-C(12)	1.5014(11)
C(11)-C(13)	1.5474(10)
C(12)-H(12A)	1.028(12)
C(12)-H(12B)	1.033(12)
C(13)-C(14)	1.5321(10)
C(13)-H(13)	1.006(11)
C(14)-H(14)	1.032(11)
C(16)-H(16A)	1.011(14)
C(16)-H(16B)	1.033(14)
C(16)-H(16C)	1.017(13)
C(18)-H(18A)	1.004(18)
C(18)-H(18B)	1.018(15)
C(18)-H(18C)	1.020(15)

C(1)-O(1)-C(12)	116.61(6)
C(6)-O(2)-C(7)	115.06(6)
C(2)-O(3)-C(5)	96.33(5)
C(11)-O(4)-C(8)	96.90(5)
C(1)-O(5)-H(5)	105.6(9)
C(15)-O(7)-C(16)	115.65(7)
C(17)-O(9)-C(18)	115.72(7)
O(5)-C(1)-O(1)	112.25(6)
O(5)-C(1)-C(2)	107.34(6)
O(1)-C(1)-C(2)	111.33(6)
O(5)-C(1)-H(1)	112.2(6)
O(1)-C(1)-H(1)	102.6(6)
C(2)-C(1)-H(1)	111.2(6)
O(3)-C(2)-C(1)	110.88(6)
O(3)-C(2)-C(3)	100.86(6)
C(1)-C(2)-C(3)	122.49(6)
O(3)-C(2)-C(13)	102.64(6)
C(1)-C(2)-C(13)	112.56(6)
C(3)-C(2)-C(13)	105.14(6)
C(4)-C(3)-C(2)	105.22(7)
C(4)-C(3)-H(3)	128.2(7)
C(2)-C(3)-H(3)	125.8(7)
C(3)-C(4)-C(5)	105.40(7)
C(3)-C(4)-H(4)	128.8(7)
C(5)-C(4)-H(4)	125.3(7)
O(3)-C(5)-C(6)	112.38(6)
O(3)-C(5)-C(4)	100.56(6)

C(6)-C(5)-C(4)	122.50(6)
O(3)-C(5)-C(14)	102.48(6)
C(6)-C(5)-C(14)	111.21(6)
C(4)-C(5)-C(14)	105.50(6)
O(2)-C(6)-C(5)	110.96(6)
O(2)-C(6)-H(6A)	105.3(7)
C(5)-C(6)-H(6A)	112.0(6)
O(2)-C(6)-H(6B)	111.2(6)
C(5)-C(6)-H(6B)	109.2(6)
H(6A)-C(6)-H(6B)	108.2(9)
O(2)-C(7)-C(8)	110.66(6)
O(2)-C(7)-H(7A)	109.4(7)
C(8)-C(7)-H(7A)	108.9(7)
O(2)-C(7)-H(7B)	104.6(6)
C(8)-C(7)-H(7B)	112.4(6)
H(7A)-C(7)-H(7B)	110.8(9)
O(4)-C(8)-C(7)	112.27(6)
O(4)-C(8)-C(9)	99.88(6)
C(7)-C(8)-C(9)	122.35(6)
O(4)-C(8)-C(14)	102.93(6)
C(7)-C(8)-C(14)	112.13(6)
C(9)-C(8)-C(14)	105.04(6)
C(10)-C(9)-C(15)	127.88(7)
C(10)-C(9)-C(8)	105.00(6)
C(15)-C(9)-C(8)	126.81(6)
C(9)-C(10)-C(17)	129.55(7)
C(9)-C(10)-C(11)	105.52(6)
C(17)-C(10)-C(11)	124.90(6)
O(4)-C(11)-C(12)	113.30(6)
O(4)-C(11)-C(10)	99.90(6)
C(12)-C(11)-C(10)	121.20(6)
O(4)-C(11)-C(13)	103.25(6)
C(12)-C(11)-C(13)	111.90(6)
C(10)-C(11)-C(13)	105.26(6)
O(1)-C(12)-C(11)	110.37(6)
O(1)-C(12)-H(12A)	106.2(7)
C(11)-C(12)-H(12A)	110.4(7)
O(1)-C(12)-H(12B)	111.8(6)
C(11)-C(12)-H(12B)	109.3(7)
H(12A)-C(12)-H(12B)	108.7(9)
C(14)-C(13)-C(11)	101.63(6)
C(14)-C(13)-C(2)	101.41(6)

C(11)-C(13)-C(2)	110.94(6)
C(14)-C(13)-H(13)	115.3(6)
C(11)-C(13)-H(13)	113.1(6)
C(2)-C(13)-H(13)	113.4(6)
C(13)-C(14)-C(5)	101.44(6)
C(13)-C(14)-C(8)	101.50(6)
C(5)-C(14)-C(8)	111.48(6)
C(13)-C(14)-H(14)	117.0(6)
C(5)-C(14)-H(14)	111.9(6)
C(8)-C(14)-H(14)	112.6(6)
O(6)-C(15)-O(7)	123.98(7)
O(6)-C(15)-C(9)	124.87(7)
O(7)-C(15)-C(9)	111.13(6)
O(7)-C(16)-H(16A)	104.6(8)
O(7)-C(16)-H(16B)	110.1(8)
H(16A)-C(16)-H(16B)	111.0(11)
O(7)-C(16)-H(16C)	110.0(8)
H(16A)-C(16)-H(16C)	111.4(10)
H(16B)-C(16)-H(16C)	109.7(10)
O(8)-C(17)-O(9)	124.90(7)
O(8)-C(17)-C(10)	123.49(7)
O(9)-C(17)-C(10)	111.58(6)
O(9)-C(18)-H(18A)	105.5(9)
O(9)-C(18)-H(18B)	109.7(8)
H(18A)-C(18)-H(18B)	112.9(13)
O(9)-C(18)-H(18C)	110.0(8)
H(18A)-C(18)-H(18C)	109.6(12)
H(18B)-C(18)-H(18C)	109.1(11)

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1-hydroxy-1,3,3a,3a[1],5a,5a[1],6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	14(1)	8(1)	15(1)	0(1)	0(1)	0(1)
O(2)	13(1)	15(1)	11(1)	-4(1)	2(1)	1(1)
O(3)	11(1)	10(1)	10(1)	-1(1)	2(1)	2(1)
O(4)	11(1)	9(1)	10(1)	-1(1)	1(1)	-1(1)
O(5)	18(1)	13(1)	11(1)	1(1)	1(1)	0(1)
O(6)	23(1)	24(1)	13(1)	6(1)	5(1)	8(1)
O(7)	13(1)	18(1)	16(1)	4(1)	3(1)	6(1)
O(8)	11(1)	28(1)	23(1)	-4(1)	6(1)	-7(1)
O(9)	17(1)	19(1)	16(1)	-5(1)	7(1)	-3(1)
C(1)	13(1)	8(1)	11(1)	0(1)	1(1)	2(1)
C(2)	10(1)	8(1)	9(1)	-1(1)	1(1)	0(1)
C(3)	10(1)	14(1)	11(1)	-1(1)	0(1)	-1(1)
C(4)	9(1)	14(1)	13(1)	-1(1)	1(1)	-2(1)
C(5)	9(1)	10(1)	9(1)	0(1)	2(1)	0(1)
C(6)	11(1)	16(1)	10(1)	-1(1)	3(1)	1(1)
C(7)	12(1)	15(1)	9(1)	-2(1)	1(1)	1(1)
C(8)	9(1)	9(1)	8(1)	0(1)	2(1)	0(1)
C(9)	9(1)	12(1)	10(1)	2(1)	1(1)	1(1)
C(10)	7(1)	11(1)	10(1)	0(1)	2(1)	0(1)
C(11)	9(1)	8(1)	9(1)	0(1)	1(1)	0(1)
C(12)	12(1)	10(1)	13(1)	2(1)	2(1)	-2(1)
C(13)	9(1)	7(1)	8(1)	-1(1)	2(1)	0(1)
C(14)	10(1)	7(1)	9(1)	0(1)	2(1)	0(1)
C(15)	10(1)	13(1)	11(1)	0(1)	0(1)	0(1)
C(16)	18(1)	18(1)	22(1)	4(1)	1(1)	7(1)
C(17)	9(1)	12(1)	12(1)	2(1)	2(1)	0(1)
C(18)	28(1)	33(1)	26(1)	-9(1)	16(1)	1(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 1-hydroxy-1,3,3a,3a^1,5a,5a^1,6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga**.

	x	y	z	U(eq)
H(5)	6411(8)	7500(30)	1363(10)	48(4)
H(1)	5948(6)	8187(19)	2653(7)	15(3)
H(3)	5412(6)	2790(20)	2335(8)	28(3)
H(4)	5151(7)	930(20)	3885(8)	29(3)
H(6A)	5435(6)	4340(20)	5601(8)	18(3)
H(6B)	5816(6)	1790(20)	5706(8)	19(3)
H(7A)	7142(6)	1940(20)	6194(8)	21(3)
H(7B)	7496(6)	4520(20)	6355(7)	17(3)
H(12A)	8020(6)	8030(20)	3307(8)	21(3)
H(12B)	7772(6)	6300(20)	2438(8)	21(3)
H(13)	6986(5)	2369(19)	2916(7)	12(2)
H(14)	6746(6)	629(19)	4356(7)	14(3)
H(16A)	9734(7)	-2600(20)	4632(9)	37(4)
H(16B)	9050(7)	-3620(20)	5190(9)	38(4)
H(16C)	9627(7)	-1730(20)	5694(9)	32(3)
H(18A)	8940(9)	-620(30)	1735(11)	61(5)
H(18B)	9597(8)	160(30)	2528(10)	42(4)
H(18C)	9281(8)	1970(30)	1730(9)	41(4)

Table S7. Torsion angles [°] for 1-hydroxy-1,3,3a,3a^1,5a,5a^1,6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga**.

C(12)-O(1)-C(1)-O(5)	-63.76(8)
C(12)-O(1)-C(1)-C(2)	56.61(8)
C(5)-O(3)-C(2)-C(1)	-176.65(6)
C(5)-O(3)-C(2)-C(3)	52.16(6)
C(5)-O(3)-C(2)-C(13)	-56.23(6)
O(5)-C(1)-C(2)-O(3)	-171.10(6)
O(1)-C(1)-C(2)-O(3)	65.68(8)
O(5)-C(1)-C(2)-C(3)	-52.29(9)
O(1)-C(1)-C(2)-C(3)	-175.51(6)
O(5)-C(1)-C(2)-C(13)	74.56(8)
O(1)-C(1)-C(2)-C(13)	-48.66(8)
O(3)-C(2)-C(3)-C(4)	-33.09(8)
C(1)-C(2)-C(3)-C(4)	-156.62(7)
C(13)-C(2)-C(3)-C(4)	73.33(7)
C(2)-C(3)-C(4)-C(5)	-0.07(8)
C(2)-O(3)-C(5)-C(6)	176.05(6)
C(2)-O(3)-C(5)-C(4)	-52.06(6)
C(2)-O(3)-C(5)-C(14)	56.59(6)
C(3)-C(4)-C(5)-O(3)	33.06(8)
C(3)-C(4)-C(5)-C(6)	158.37(7)
C(3)-C(4)-C(5)-C(14)	-73.19(8)
C(7)-O(2)-C(6)-C(5)	-60.59(8)
O(3)-C(5)-C(6)-O(2)	-60.99(8)
C(4)-C(5)-C(6)-O(2)	179.19(7)
C(14)-C(5)-C(6)-O(2)	53.24(8)
C(6)-O(2)-C(7)-C(8)	59.23(9)
C(11)-O(4)-C(8)-C(7)	-175.76(6)
C(11)-O(4)-C(8)-C(9)	53.08(6)
C(11)-O(4)-C(8)-C(14)	-54.99(6)
O(2)-C(7)-C(8)-O(4)	64.02(8)
O(2)-C(7)-C(8)-C(9)	-177.38(6)
O(2)-C(7)-C(8)-C(14)	-51.30(8)
O(4)-C(8)-C(9)-C(10)	-33.03(7)
C(7)-C(8)-C(9)-C(10)	-157.47(7)
C(14)-C(8)-C(9)-C(10)	73.35(7)
O(4)-C(8)-C(9)-C(15)	153.04(7)
C(7)-C(8)-C(9)-C(15)	28.60(12)

C(14)-C(8)-C(9)-C(15)	-100.58(8)
C(15)-C(9)-C(10)-C(17)	-4.70(14)
C(8)-C(9)-C(10)-C(17)	-178.54(7)
C(15)-C(9)-C(10)-C(11)	173.52(7)
C(8)-C(9)-C(10)-C(11)	-0.32(8)
C(8)-O(4)-C(11)-C(12)	176.37(6)
C(8)-O(4)-C(11)-C(10)	-53.27(6)
C(8)-O(4)-C(11)-C(13)	55.13(6)
C(9)-C(10)-C(11)-O(4)	33.75(7)
C(17)-C(10)-C(11)-O(4)	-147.92(7)
C(9)-C(10)-C(11)-C(12)	158.85(7)
C(17)-C(10)-C(11)-C(12)	-22.82(11)
C(9)-C(10)-C(11)-C(13)	-73.04(7)
C(17)-C(10)-C(11)-C(13)	105.29(8)
C(1)-O(1)-C(12)-C(11)	-59.28(8)
O(4)-C(11)-C(12)-O(1)	-62.55(8)
C(10)-C(11)-C(12)-O(1)	178.79(6)
C(13)-C(11)-C(12)-O(1)	53.69(8)
O(4)-C(11)-C(13)-C(14)	-33.78(7)
C(12)-C(11)-C(13)-C(14)	-155.96(6)
C(10)-C(11)-C(13)-C(14)	70.53(7)
O(4)-C(11)-C(13)-C(2)	73.38(7)
C(12)-C(11)-C(13)-C(2)	-48.80(8)
C(10)-C(11)-C(13)-C(2)	177.69(6)
O(3)-C(2)-C(13)-C(14)	34.17(7)
C(1)-C(2)-C(13)-C(14)	153.42(6)
C(3)-C(2)-C(13)-C(14)	-70.95(7)
O(3)-C(2)-C(13)-C(11)	-73.14(7)
C(1)-C(2)-C(13)-C(11)	46.11(8)
C(3)-C(2)-C(13)-C(11)	-178.25(6)
C(11)-C(13)-C(14)-C(5)	114.95(6)
C(2)-C(13)-C(14)-C(5)	0.50(7)
C(11)-C(13)-C(14)-C(8)	-0.04(7)
C(2)-C(13)-C(14)-C(8)	-114.49(6)
O(3)-C(5)-C(14)-C(13)	-34.90(7)
C(6)-C(5)-C(14)-C(13)	-155.18(6)
C(4)-C(5)-C(14)-C(13)	69.94(7)
O(3)-C(5)-C(14)-C(8)	72.46(7)
C(6)-C(5)-C(14)-C(8)	-47.83(8)
C(4)-C(5)-C(14)-C(8)	177.29(6)

O(4)-C(8)-C(14)-C(13)	33.64(7)
C(7)-C(8)-C(14)-C(13)	154.51(6)
C(9)-C(8)-C(14)-C(13)	-70.48(7)
O(4)-C(8)-C(14)-C(5)	-73.68(7)
C(7)-C(8)-C(14)-C(5)	47.19(8)
C(9)-C(8)-C(14)-C(5)	-177.80(6)
C(16)-O(7)-C(15)-O(6)	0.52(12)
C(16)-O(7)-C(15)-C(9)	179.36(7)
C(10)-C(9)-C(15)-O(6)	174.06(8)
C(8)-C(9)-C(15)-O(6)	-13.38(13)
C(10)-C(9)-C(15)-O(7)	-4.77(12)
C(8)-C(9)-C(15)-O(7)	167.79(7)
C(18)-O(9)-C(17)-O(8)	6.23(12)
C(18)-O(9)-C(17)-C(10)	-175.40(8)
C(9)-C(10)-C(17)-O(8)	-89.19(11)
C(11)-C(10)-C(17)-O(8)	92.91(10)
C(9)-C(10)-C(17)-O(9)	92.41(10)
C(11)-C(10)-C(17)-O(9)	-85.49(9)

Table S8. Hydrogen bonds for 1-hydroxy-1,3,3a,3a^1,5a,5a^1,6,8,8a,10a-decahydro-3a,5a:8a,10a-diepoxyisochromeno[6,5,4-*def*]isochromene-4,5-dicarboxylic acid **3ga** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D... A)	<(DHA)
O(5)-H(5)...O(2)#1	0.947(16)	1.814(17)	2.7311(8)	162.3(13)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+3/2,z-1/2

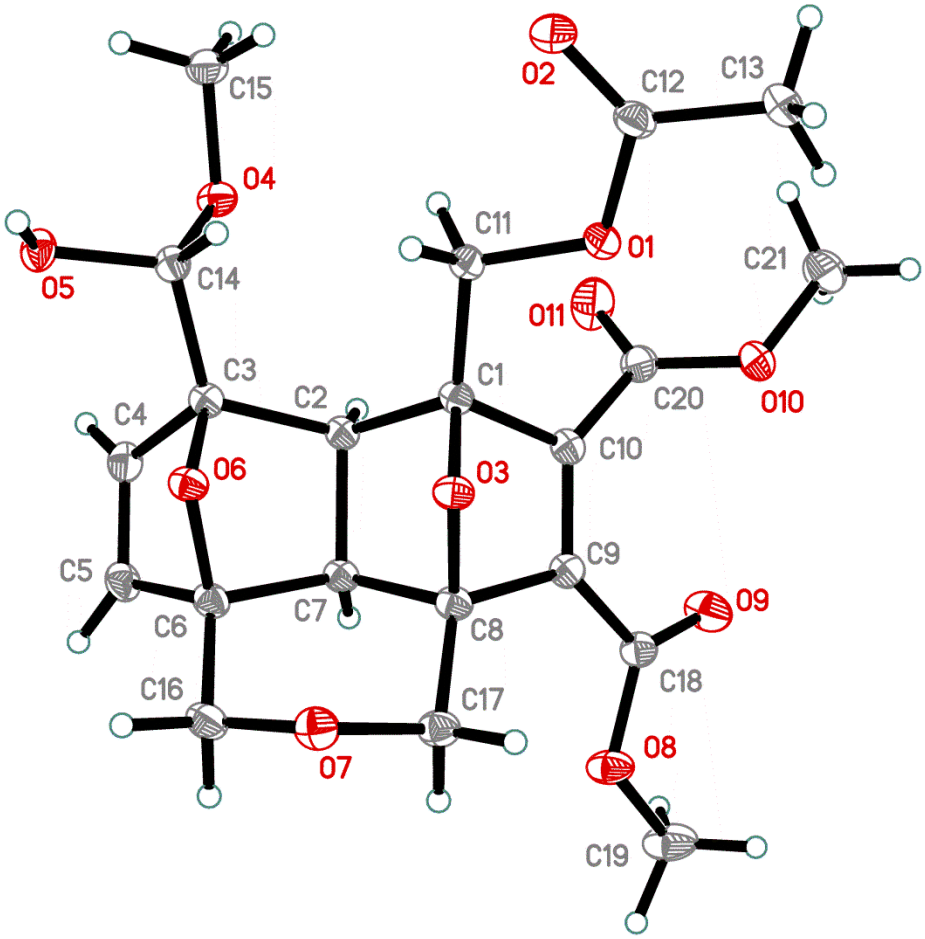


Figure S108. X-Ray structure of dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha**.

Table S9. Crystal data and structure refinement for dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha**.

Empirical formula	C21 H24 O11	
Formula weight	452.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.5648(3) Å	α= 90°.
	b = 16.2470(5) Å	β= 110.3080(10)°.
	c = 12.4776(4) Å	γ = 90°.
Volume	2008.60(11) $Å^3$	
Z	4	
Density (calculated)	1.496 g/cm^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	952	

Crystal size	0.570 x 0.510 x 0.440 mm^3
Theta range for data collection	2.145 to 34.970°.
Index ranges	-17<=h<=17, -26<=k<=26, -20<=l<=20
Reflections collected	67798
Independent reflections	8808 [R(int) = 0.0409]
Observed reflections	6915
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7469 and 0.6954
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8808 / 0 / 388
Goodness of fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0816
R indices (all data)	R1 = 0.0563, wR2 = 0.0912
Largest diff. peak and hole	0.293 and -0.257 $e.Å^{-3}$

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha**. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1750(1)	5908(1)	7173(1)	18(1)
O(2)	422(1)	5311(1)	8015(1)	24(1)
O(3)	4754(1)	6159(1)	8073(1)	13(1)
O(4)	3823(1)	3380(1)	8011(1)	16(1)
O(5)	5379(1)	3302(1)	9851(1)	17(1)
O(6)	6355(1)	4914(1)	9332(1)	14(1)
O(7)	7457(1)	6589(1)	9283(1)	18(1)
O(8)	6231(1)	7086(1)	5562(1)	20(1)
O(9)	4210(1)	6711(1)	4300(1)	23(1)
O(10)	1651(1)	6338(1)	4789(1)	19(1)
O(11)	2195(1)	4993(1)	4882(1)	29(1)
C(1)	3969(1)	5515(1)	7360(1)	12(1)
C(2)	5040(1)	4831(1)	7413(1)	12(1)
C(3)	5620(1)	4302(1)	8521(1)	13(1)
C(4)	6770(1)	3796(1)	8378(1)	16(1)
C(5)	7808(1)	4309(1)	8563(1)	17(1)
C(6)	7265(1)	5145(1)	8744(1)	14(1)
C(7)	6281(1)	5385(1)	7534(1)	13(1)
C(8)	5719(1)	6263(1)	7498(1)	13(1)
C(9)	4751(1)	6382(1)	6264(1)	13(1)
C(10)	3671(1)	5920(1)	6185(1)	13(1)
C(11)	2765(1)	5294(1)	7686(1)	15(1)
C(12)	595(1)	5836(1)	7394(1)	16(1)
C(13)	-401(1)	6481(1)	6778(1)	22(1)
C(14)	4653(1)	3832(1)	8957(1)	13(1)
C(15)	2739(1)	2970(1)	8225(1)	20(1)
C(16)	8184(1)	5840(1)	9342(1)	17(1)
C(17)	6794(1)	6874(1)	8145(1)	16(1)
C(18)	5004(1)	6744(1)	5267(1)	14(1)
C(19)	6567(1)	7407(1)	4612(1)	26(1)

C(20)	2452(1)	5696(1)	5200(1)	16(1)
C(21)	353(1)	6149(1)	3950(1)	28(1)

Table S11. Bond lengths [Å] and angles [°] for dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha**.

O(1)-C(12)	1.3460(10)
O(1)-C(11)	1.4414(10)
O(2)-C(12)	1.2091(11)
O(3)-C(1)	1.4356(10)
O(3)-C(8)	1.4450(9)
O(4)-C(14)	1.4076(10)
O(4)-C(15)	1.4277(11)
O(5)-C(14)	1.4066(10)
O(5)-H(1)	0.919(17)
O(6)-C(3)	1.4381(10)
O(6)-C(6)	1.4466(10)
O(7)-C(17)	1.4245(10)
O(7)-C(16)	1.4287(11)
O(8)-C(18)	1.3392(10)
O(8)-C(19)	1.4478(11)
O(9)-C(18)	1.2088(10)
O(10)-C(20)	1.3294(11)
O(10)-C(21)	1.4401(11)
O(11)-C(20)	1.2086(11)
C(1)-C(11)	1.5068(11)
C(1)-C(10)	1.5364(11)
C(1)-C(2)	1.5716(11)
C(2)-C(7)	1.5537(11)
C(2)-C(3)	1.5619(11)
C(2)-H(2)	1.014(13)
C(3)-C(14)	1.5194(11)
C(3)-C(4)	1.5289(11)
C(4)-C(5)	1.3322(12)
C(4)-H(4)	1.002(13)
C(5)-C(6)	1.5222(12)
C(5)-H(5)	1.004(13)

C(6)-C(16)	1.5062(12)
C(6)-C(7)	1.5566(11)
C(7)-C(8)	1.5408(11)
C(7)-H(7)	1.023(12)
C(8)-C(17)	1.5135(11)
C(8)-C(9)	1.5372(11)
C(9)-C(10)	1.3407(11)
C(9)-C(18)	1.4813(11)
C(10)-C(20)	1.4840(11)
C(11)-H(11A)	1.023(13)
C(11)-H(11B)	1.018(13)
C(12)-C(13)	1.4948(12)
C(13)-H(13A)	0.96(2)
C(13)-H(13B)	0.97(2)
C(13)-H(13C)	0.966(16)
C(14)-H(14)	1.016(12)
C(15)-H(15A)	1.027(15)
C(15)-H(15B)	1.023(14)
C(15)-H(15C)	1.023(14)
C(16)-H(16A)	1.001(14)
C(16)-H(16B)	1.026(13)
C(17)-H(17A)	1.008(13)
C(17)-H(17B)	1.033(13)
C(19)-H(19A)	0.998(16)
C(19)-H(19B)	1.008(15)
C(19)-H(19C)	1.026(17)
C(21)-H(21A)	1.015(16)
C(21)-H(21B)	1.022(16)
C(21)-H(21C)	0.998(16)

C(12)-O(1)-C(11)	115.94(7)
C(1)-O(3)-C(8)	97.67(5)
C(14)-O(4)-C(15)	113.15(6)
C(14)-O(5)-H(1)	108.5(10)
C(3)-O(6)-C(6)	96.64(5)
C(17)-O(7)-C(16)	113.44(6)
C(18)-O(8)-C(19)	114.44(7)
C(20)-O(10)-C(21)	115.54(8)
O(3)-C(1)-C(11)	111.55(6)
O(3)-C(1)-C(10)	99.37(6)

C(11)-C(1)-C(10)	116.57(6)
O(3)-C(1)-C(2)	103.68(6)
C(11)-C(1)-C(2)	118.86(7)
C(10)-C(1)-C(2)	104.35(6)
C(7)-C(2)-C(3)	100.04(6)
C(7)-C(2)-C(1)	99.55(6)
C(3)-C(2)-C(1)	118.77(6)
C(7)-C(2)-H(2)	116.1(7)
C(3)-C(2)-H(2)	112.1(7)
C(1)-C(2)-H(2)	109.6(7)
O(6)-C(3)-C(14)	111.23(6)
O(6)-C(3)-C(4)	101.33(6)
C(14)-C(3)-C(4)	115.59(7)
O(6)-C(3)-C(2)	101.10(6)
C(14)-C(3)-C(2)	119.24(6)
C(4)-C(3)-C(2)	105.99(6)
C(5)-C(4)-C(3)	106.43(7)
C(5)-C(4)-H(4)	128.5(7)
C(3)-C(4)-H(4)	124.9(7)
C(4)-C(5)-C(6)	104.77(7)
C(4)-C(5)-H(5)	129.9(7)
C(6)-C(5)-H(5)	124.8(7)
O(6)-C(6)-C(16)	111.83(6)
O(6)-C(6)-C(5)	101.17(6)
C(16)-C(6)-C(5)	122.07(7)
O(6)-C(6)-C(7)	102.66(6)
C(16)-C(6)-C(7)	113.07(7)
C(5)-C(6)-C(7)	103.77(6)
C(8)-C(7)-C(2)	103.26(6)
C(8)-C(7)-C(6)	112.36(6)
C(2)-C(7)-C(6)	101.92(6)
C(8)-C(7)-H(7)	111.3(7)
C(2)-C(7)-H(7)	115.8(7)
C(6)-C(7)-H(7)	111.6(7)
O(3)-C(8)-C(17)	109.91(6)
O(3)-C(8)-C(9)	99.99(6)
C(17)-C(8)-C(9)	124.56(7)
O(3)-C(8)-C(7)	102.06(6)
C(17)-C(8)-C(7)	112.41(6)
C(9)-C(8)-C(7)	105.11(6)

C(10)-C(9)-C(18)	123.91(7)
C(10)-C(9)-C(8)	104.86(7)
C(18)-C(9)-C(8)	129.78(7)
C(9)-C(10)-C(20)	132.04(7)
C(9)-C(10)-C(1)	106.39(6)
C(20)-C(10)-C(1)	121.15(7)
O(1)-C(11)-C(1)	106.40(6)
O(1)-C(11)-H(11A)	109.9(7)
C(1)-C(11)-H(11A)	110.4(8)
O(1)-C(11)-H(11B)	110.2(7)
C(1)-C(11)-H(11B)	110.5(7)
H(11A)-C(11)-H(11B)	109.5(10)
O(2)-C(12)-O(1)	122.76(8)
O(2)-C(12)-C(13)	126.08(8)
O(1)-C(12)-C(13)	111.16(7)
C(12)-C(13)-H(13A)	111.1(11)
C(12)-C(13)-H(13B)	109.6(13)
H(13A)-C(13)-H(13B)	106.8(17)
C(12)-C(13)-H(13C)	110.2(10)
H(13A)-C(13)-H(13C)	111.7(15)
H(13B)-C(13)-H(13C)	107.4(15)
O(5)-C(14)-O(4)	110.83(7)
O(5)-C(14)-C(3)	109.98(6)
O(4)-C(14)-C(3)	105.21(6)
O(5)-C(14)-H(14)	108.7(7)
O(4)-C(14)-H(14)	111.5(7)
C(3)-C(14)-H(14)	110.6(7)
O(4)-C(15)-H(15A)	110.5(8)
O(4)-C(15)-H(15B)	111.2(8)
H(15A)-C(15)-H(15B)	108.9(11)
O(4)-C(15)-H(15C)	106.4(8)
H(15A)-C(15)-H(15C)	110.4(11)
H(15B)-C(15)-H(15C)	109.5(11)
O(7)-C(16)-C(6)	111.73(7)
O(7)-C(16)-H(16A)	106.7(8)
C(6)-C(16)-H(16A)	110.8(8)
O(7)-C(16)-H(16B)	111.0(7)
C(6)-C(16)-H(16B)	108.6(7)
H(16A)-C(16)-H(16B)	108.0(11)
O(7)-C(17)-C(8)	109.69(7)

O(7)-C(17)-H(17A)	111.2(7)
C(8)-C(17)-H(17A)	109.3(7)
O(7)-C(17)-H(17B)	106.5(7)
C(8)-C(17)-H(17B)	110.6(7)
H(17A)-C(17)-H(17B)	109.5(10)
O(9)-C(18)-O(8)	124.24(8)
O(9)-C(18)-C(9)	123.77(8)
O(8)-C(18)-C(9)	111.96(7)
O(8)-C(19)-H(19A)	111.4(9)
O(8)-C(19)-H(19B)	106.4(9)
H(19A)-C(19)-H(19B)	112.3(12)
O(8)-C(19)-H(19C)	108.3(9)
H(19A)-C(19)-H(19C)	106.7(13)
H(19B)-C(19)-H(19C)	111.6(12)
O(11)-C(20)-O(10)	125.08(8)
O(11)-C(20)-C(10)	122.33(8)
O(10)-C(20)-C(10)	112.36(7)
O(10)-C(21)-H(21A)	104.0(9)
O(10)-C(21)-H(21B)	111.5(9)
H(21A)-C(21)-H(21B)	109.4(12)
O(10)-C(21)-H(21C)	108.7(9)
H(21A)-C(21)-H(21C)	111.2(13)
H(21B)-C(21)-H(21C)	111.8(12)

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	13(1)	20(1)	24(1)	6(1)	10(1)	3(1)
O(2)	19(1)	27(1)	30(1)	9(1)	14(1)	2(1)
O(3)	13(1)	15(1)	13(1)	-1(1)	6(1)	-1(1)
O(4)	16(1)	18(1)	13(1)	-1(1)	5(1)	-3(1)
O(5)	19(1)	20(1)	13(1)	2(1)	6(1)	2(1)
O(6)	13(1)	17(1)	12(1)	-1(1)	5(1)	-1(1)

O(7)	18(1)	20(1)	13(1)	-3(1)	4(1)	-4(1)
O(8)	20(1)	26(1)	14(1)	-1(1)	7(1)	-8(1)
O(9)	19(1)	38(1)	12(1)	1(1)	4(1)	-5(1)
O(10)	14(1)	21(1)	18(1)	2(1)	1(1)	0(1)
O(11)	32(1)	18(1)	27(1)	-4(1)	-4(1)	-3(1)
C(1)	11(1)	14(1)	12(1)	0(1)	4(1)	0(1)
C(2)	12(1)	14(1)	11(1)	-1(1)	4(1)	0(1)
C(3)	13(1)	14(1)	12(1)	-1(1)	5(1)	0(1)
C(4)	17(1)	17(1)	15(1)	1(1)	7(1)	3(1)
C(5)	13(1)	21(1)	18(1)	2(1)	7(1)	4(1)
C(6)	11(1)	18(1)	13(1)	0(1)	5(1)	0(1)
C(7)	12(1)	16(1)	12(1)	0(1)	6(1)	0(1)
C(8)	12(1)	15(1)	12(1)	-1(1)	6(1)	-1(1)
C(9)	14(1)	15(1)	12(1)	0(1)	5(1)	0(1)
C(10)	12(1)	15(1)	12(1)	-1(1)	4(1)	0(1)
C(11)	12(1)	17(1)	17(1)	3(1)	6(1)	2(1)
C(12)	13(1)	18(1)	20(1)	0(1)	8(1)	0(1)
C(13)	14(1)	22(1)	29(1)	4(1)	7(1)	4(1)
C(14)	14(1)	15(1)	12(1)	0(1)	5(1)	1(1)
C(15)	18(1)	22(1)	19(1)	1(1)	6(1)	-4(1)
C(16)	13(1)	23(1)	15(1)	0(1)	3(1)	-3(1)
C(17)	16(1)	18(1)	14(1)	-2(1)	5(1)	-4(1)
C(18)	15(1)	16(1)	13(1)	0(1)	6(1)	-1(1)
C(19)	29(1)	36(1)	16(1)	-1(1)	10(1)	-13(1)
C(20)	16(1)	17(1)	14(1)	1(1)	3(1)	-2(1)
C(21)	18(1)	34(1)	24(1)	5(1)	-3(1)	-4(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha**.

	x	y	z	U(eq)
H(1)	5237(16)	3463(10)	10506(14)	46(4)
H(2)	4704(12)	4478(8)	6700(11)	20(3)

H(4)	6697(12)	3206(8)	8129(11)	21(3)
H(5)	8715(13)	4214(8)	8492(11)	24(3)
H(7)	6716(12)	5305(7)	6925(10)	15(3)
H(11A)	2410(13)	4724(8)	7377(11)	24(3)
H(11B)	3016(13)	5299(8)	8550(11)	22(3)
H(13A)	-174(19)	6713(12)	6160(17)	65(6)
H(13B)	-380(20)	6928(14)	7295(19)	81(7)
H(13C)	-1304(16)	6257(10)	6516(14)	44(4)
H(14)	4105(12)	4227(7)	9254(10)	18(3)
H(15A)	2074(15)	3390(9)	8345(12)	35(4)
H(15B)	3088(13)	2603(9)	8932(12)	29(3)
H(15C)	2271(14)	2615(9)	7521(12)	30(3)
H(16A)	8643(14)	5713(8)	10172(12)	30(3)
H(16B)	8916(13)	5908(8)	8982(11)	26(3)
H(17A)	7454(13)	6950(8)	7732(11)	24(3)
H(17B)	6366(12)	7435(8)	8211(11)	22(3)
H(19A)	6380(15)	6995(10)	3982(14)	42(4)
H(19B)	7550(15)	7568(9)	4930(13)	38(4)
H(19C)	5959(17)	7904(11)	4283(14)	50(5)
H(21A)	-147(16)	6694(10)	3818(13)	44(4)
H(21B)	-158(16)	5727(10)	4252(13)	41(4)
H(21C)	489(15)	5953(10)	3239(14)	42(4)

Table S14. Torsion angles [°] for dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha**.

C(8)-O(3)-C(1)-C(11)	-175.75(6)
C(8)-O(3)-C(1)-C(10)	-52.21(6)
C(8)-O(3)-C(1)-C(2)	55.18(6)
O(3)-C(1)-C(2)-C(7)	-32.50(7)
C(11)-C(1)-C(2)-C(7)	-156.96(7)
C(10)-C(1)-C(2)-C(7)	71.11(7)
O(3)-C(1)-C(2)-C(3)	74.60(8)
C(11)-C(1)-C(2)-C(3)	-49.86(10)
C(10)-C(1)-C(2)-C(3)	178.21(6)
C(6)-O(6)-C(3)-C(14)	172.53(6)
C(6)-O(6)-C(3)-C(4)	49.13(7)
C(6)-O(6)-C(3)-C(2)	-59.87(6)

C(7)-C(2)-C(3)-O(6)	40.57(7)
C(1)-C(2)-C(3)-O(6)	-66.26(8)
C(7)-C(2)-C(3)-C(14)	162.75(7)
C(1)-C(2)-C(3)-C(14)	55.93(10)
C(7)-C(2)-C(3)-C(4)	-64.77(7)
C(1)-C(2)-C(3)-C(4)	-171.60(7)
O(6)-C(3)-C(4)-C(5)	-29.16(8)
C(14)-C(3)-C(4)-C(5)	-149.52(7)
C(2)-C(3)-C(4)-C(5)	76.01(8)
C(3)-C(4)-C(5)-C(6)	-3.58(8)
C(3)-O(6)-C(6)-C(16)	176.88(7)
C(3)-O(6)-C(6)-C(5)	-51.67(7)
C(3)-O(6)-C(6)-C(7)	55.37(7)
C(4)-C(5)-C(6)-O(6)	35.09(8)
C(4)-C(5)-C(6)-C(16)	159.90(8)
C(4)-C(5)-C(6)-C(7)	-71.07(8)
C(3)-C(2)-C(7)-C(8)	-123.13(6)
C(1)-C(2)-C(7)-C(8)	-1.43(7)
C(3)-C(2)-C(7)-C(6)	-6.44(7)
C(1)-C(2)-C(7)-C(6)	115.26(6)
O(6)-C(6)-C(7)-C(8)	80.72(7)
C(16)-C(6)-C(7)-C(8)	-39.93(9)
C(5)-C(6)-C(7)-C(8)	-174.24(6)
O(6)-C(6)-C(7)-C(2)	-29.17(7)
C(16)-C(6)-C(7)-C(2)	-149.83(7)
C(5)-C(6)-C(7)-C(2)	75.86(7)
C(1)-O(3)-C(8)-C(17)	-174.85(6)
C(1)-O(3)-C(8)-C(9)	52.58(7)
C(1)-O(3)-C(8)-C(7)	-55.37(6)
C(2)-C(7)-C(8)-O(3)	34.54(7)
C(6)-C(7)-C(8)-O(3)	-74.52(7)
C(2)-C(7)-C(8)-C(17)	152.24(6)
C(6)-C(7)-C(8)-C(17)	43.18(9)
C(2)-C(7)-C(8)-C(9)	-69.43(7)
C(6)-C(7)-C(8)-C(9)	-178.48(6)
O(3)-C(8)-C(9)-C(10)	-32.57(8)
C(17)-C(8)-C(9)-C(10)	-155.34(8)
C(7)-C(8)-C(9)-C(10)	72.93(8)
O(3)-C(8)-C(9)-C(18)	161.03(8)
C(17)-C(8)-C(9)-C(18)	38.25(13)

C(7)-C(8)-C(9)-C(18)	-93.47(9)
C(18)-C(9)-C(10)-C(20)	-5.16(14)
C(8)-C(9)-C(10)-C(20)	-172.59(8)
C(18)-C(9)-C(10)-C(1)	167.27(7)
C(8)-C(9)-C(10)-C(1)	-0.15(8)
O(3)-C(1)-C(10)-C(9)	33.01(8)
C(11)-C(1)-C(10)-C(9)	152.93(7)
C(2)-C(1)-C(10)-C(9)	-73.83(8)
O(3)-C(1)-C(10)-C(20)	-153.55(7)
C(11)-C(1)-C(10)-C(20)	-33.63(11)
C(2)-C(1)-C(10)-C(20)	99.61(8)
C(12)-O(1)-C(11)-C(1)	-177.91(7)
O(3)-C(1)-C(11)-O(1)	80.20(8)
C(10)-C(1)-C(11)-O(1)	-32.96(9)
C(2)-C(1)-C(11)-O(1)	-159.26(6)
C(11)-O(1)-C(12)-O(2)	2.53(12)
C(11)-O(1)-C(12)-C(13)	-177.49(7)
C(15)-O(4)-C(14)-O(5)	68.07(8)
C(15)-O(4)-C(14)-C(3)	-173.09(7)
O(6)-C(3)-C(14)-O(5)	-71.95(8)
C(4)-C(3)-C(14)-O(5)	42.87(9)
C(2)-C(3)-C(14)-O(5)	171.05(6)
O(6)-C(3)-C(14)-O(4)	168.65(6)
C(4)-C(3)-C(14)-O(4)	-76.53(8)
C(2)-C(3)-C(14)-O(4)	51.64(9)
C(17)-O(7)-C(16)-C(6)	-61.47(9)
O(6)-C(6)-C(16)-O(7)	-67.51(8)
C(5)-C(6)-C(16)-O(7)	172.68(7)
C(7)-C(6)-C(16)-O(7)	47.77(9)
C(16)-O(7)-C(17)-C(8)	64.29(9)
O(3)-C(8)-C(17)-O(7)	58.73(8)
C(9)-C(8)-C(17)-O(7)	176.99(7)
C(7)-C(8)-C(17)-O(7)	-54.21(9)
C(19)-O(8)-C(18)-O(9)	-1.38(13)
C(19)-O(8)-C(18)-C(9)	176.44(8)
C(10)-C(9)-C(18)-O(9)	6.03(14)
C(8)-C(9)-C(18)-O(9)	170.15(9)
C(10)-C(9)-C(18)-O(8)	-171.80(8)
C(8)-C(9)-C(18)-O(8)	-7.69(12)
C(21)-O(10)-C(20)-O(11)	3.77(13)

C(21)-O(10)-C(20)-C(10)	-170.86(8)
C(9)-C(10)-C(20)-O(11)	116.98(11)
C(1)-C(10)-C(20)-O(11)	-54.54(12)
C(9)-C(10)-C(20)-O(10)	-68.22(12)
C(1)-C(10)-C(20)-O(10)	120.26(8)

Table S15. Hydrogen bonds for dimethyl 6-(acetoxymethyl)-7-(hydroxy(methoxy)methyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-4,5-dicarboxylate **3ha** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D... A)	<(DHA)
O(5)-H(1)...O(3)#1	0.919(17)	1.873(17)	2.7839(8)	170.6(15)

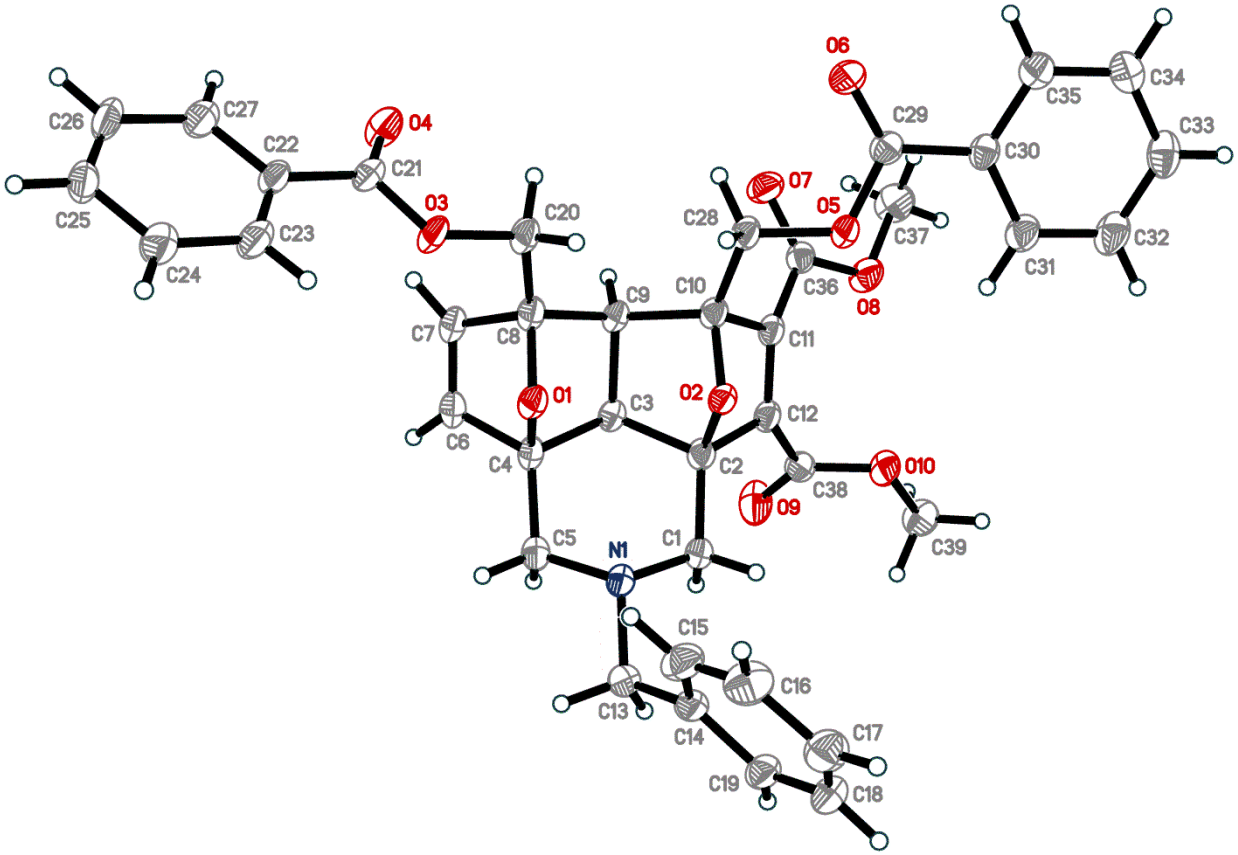


Figure S109. X-Ray structure of 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea**.

Table S16. Crystal data and structure refinement for 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea**.

Empirical formula	C39 H35 N O10	
Formula weight	677.68	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.19560(10) Å	α = 90°.
	b = 33.6799(5) Å	β= 97.8130(10)°.
	c = 10.50800(10) Å	γ = 90°.
Volume	3224.19(7) $Å^3$	
Z	4	
Density (calculated)	1.396 g/cm^3	
Absorption coefficient	0.836 mm^{-1}	
F(000)	1424	
Crystal size	0.05 x 0.03 x 0.02 mm^3	
Theta range for data collection	2.624 to 79.693°.	

Index ranges	-11<=h<=11, -34<=k<=42, -12<=l<=13
Reflections collected	33004
Independent reflections	6867 [R(int) = 0.0397]
Observed reflections	6100
Completeness to theta = 67.684°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.67883
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6867 / 0 / 454
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0640, wR2 = 0.1588
R indices (all data)	R1 = 0.0693, wR2 = 0.1613
Extinction coefficient	0.00065(11)
Largest diff. peak and hole	0.391 and -0.305 e.$Å^{-3}$

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea**. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5667(2)	7144(1)	7907(2)	24(1)
C(1)	6474(3)	6836(1)	8699(2)	23(1)
O(2)	7464(2)	6475(1)	6968(2)	20(1)
C(2)	6546(3)	6452(1)	7973(2)	21(1)
O(3)	4393(2)	6525(1)	2701(2)	25(1)
C(3)	5047(3)	6313(1)	7254(2)	21(1)
O(4)	3172(2)	5967(1)	2029(2)	33(1)
C(4)	4164(3)	6662(1)	6581(2)	22(1)
O(5)	9592(2)	5864(1)	6212(2)	24(1)
C(5)	4159(3)	7020(1)	7431(3)	27(1)
O(6)	10113(2)	5498(1)	4542(2)	32(1)
C(6)	2740(3)	6471(1)	5967(2)	25(1)
O(7)	7381(2)	5218(1)	6702(2)	31(1)
C(7)	3091(3)	6263(1)	4983(2)	24(1)
O(8)	8450(2)	5248(1)	8750(2)	31(1)
C(8)	4732(3)	6334(1)	4965(2)	23(1)
O(9)	6005(2)	6017(1)	10539(2)	40(1)
C(9)	5494(3)	6071(1)	6110(2)	21(1)
O(10)	8442(2)	5928(1)	10676(2)	29(1)
C(10)	7203(3)	6080(1)	6477(2)	21(1)
C(11)	7502(3)	5836(1)	7728(2)	21(1)
C(12)	7171(3)	6074(1)	8667(2)	21(1)
C(13)	5711(3)	7519(1)	8630(3)	28(1)
C(14)	7157(3)	7731(1)	8610(2)	25(1)
C(15)	7652(3)	7811(1)	7445(3)	33(1)
C(16)	8979(4)	8000(1)	7392(3)	38(1)
O(1)	4899(2)	6728(1)	5472(2)	23(1)
C(17)	9853(3)	8114(1)	8527(3)	36(1)
C(18)	9330(3)	8044(1)	9689(3)	31(1)
C(19)	8005(3)	7857(1)	9735(2)	27(1)
C(20)	5308(3)	6303(1)	3685(2)	25(1)

C(21)	3377(3)	6316(1)	1925(2)	24(1)
C(22)	2536(3)	6578(1)	935(2)	25(1)
C(23)	2773(3)	6983(1)	879(3)	35(1)
C(24)	1922(4)	7217(1)	-20(3)	37(1)
C(25)	825(3)	7040(1)	-892(3)	33(1)
C(26)	619(3)	6637(1)	-860(3)	32(1)
C(27)	1449(3)	6404(1)	65(2)	29(1)
C(28)	8192(3)	5974(1)	5496(2)	23(1)
C(29)	10404(3)	5599(1)	5652(2)	23(1)
C(30)	11679(3)	5450(1)	6552(2)	23(1)
C(31)	11933(3)	5571(1)	7833(2)	30(1)
C(32)	13157(3)	5431(1)	8630(3)	37(1)
C(33)	14110(3)	5168(1)	8157(3)	36(1)
C(34)	13852(3)	5044(1)	6881(3)	33(1)
C(35)	12641(3)	5186(1)	6078(3)	29(1)
C(36)	7767(3)	5407(1)	7672(2)	22(1)
C(37)	8774(4)	4828(1)	8632(3)	41(1)
C(38)	7107(3)	5997(1)	10051(2)	24(1)
C(39)	8527(3)	5873(1)	12053(2)	35(1)

Table S18. Bond lengths [Å] and angles [°] for 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea**.

N(1)-C(1)	1.467(3)
N(1)-C(5)	1.468(3)
N(1)-C(13)	1.472(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(1)-C(2)	1.509(3)
O(2)-C(2)	1.441(3)
O(2)-C(10)	1.437(3)
C(2)-C(3)	1.551(3)
C(2)-C(12)	1.538(3)
O(3)-C(20)	1.450(3)
O(3)-C(21)	1.350(3)
C(3)-H(3)	1.0000
C(3)-C(4)	1.543(3)
C(3)-C(9)	1.553(3)
O(4)-C(21)	1.199(3)
C(4)-C(5)	1.503(4)
C(4)-C(6)	1.522(3)
C(4)-O(1)	1.442(3)
O(5)-C(28)	1.448(3)
O(5)-C(29)	1.350(3)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
O(6)-C(29)	1.209(3)
C(6)-H(6)	0.9500
C(6)-C(7)	1.324(4)
O(7)-C(36)	1.213(3)
C(7)-H(7)	0.9500
C(7)-C(8)	1.530(3)
O(8)-C(36)	1.330(3)
O(8)-C(37)	1.454(3)
C(8)-C(9)	1.578(3)
C(8)-O(1)	1.432(3)
C(8)-C(20)	1.515(4)
O(9)-C(38)	1.198(3)
C(9)-H(9)	1.0000
C(9)-C(10)	1.567(3)

O(10)-C(38)	1.332(3)
O(10)-C(39)	1.450(3)
C(10)-C(11)	1.542(3)
C(10)-C(28)	1.507(3)
C(11)-C(12)	1.339(3)
C(11)-C(36)	1.467(3)
C(12)-C(38)	1.486(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(13)-C(14)	1.511(4)
C(14)-C(15)	1.390(4)
C(14)-C(19)	1.390(3)
C(15)-H(15)	0.9500
C(15)-C(16)	1.385(4)
C(16)-H(16)	0.9500
C(16)-C(17)	1.398(4)
C(17)-H(17)	0.9500
C(17)-C(18)	1.393(4)
C(18)-H(18)	0.9500
C(18)-C(19)	1.378(4)
C(19)-H(19)	0.9500
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.496(3)
C(22)-C(23)	1.384(4)
C(22)-C(27)	1.389(4)
C(23)-H(23)	0.9500
C(23)-C(24)	1.387(4)
C(24)-H(24)	0.9500
C(24)-C(25)	1.401(4)
C(25)-H(25)	0.9500
C(25)-C(26)	1.372(4)
C(26)-H(26)	0.9500
C(26)-C(27)	1.395(4)
C(27)-H(27)	0.9500
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(30)	1.491(3)
C(30)-C(31)	1.395(4)
C(30)-C(35)	1.391(4)

C(31)-H(31)	0.9500
C(31)-C(32)	1.391(4)
C(32)-H(32)	0.9500
C(32)-C(33)	1.385(4)
C(33)-H(33)	0.9500
C(33)-C(34)	1.393(4)
C(34)-H(34)	0.9500
C(34)-C(35)	1.388(4)
C(35)-H(35)	0.9500
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800

C(1)-N(1)-C(5)	112.0(2)
C(1)-N(1)-C(13)	109.68(19)
C(5)-N(1)-C(13)	112.2(2)
N(1)-C(1)-H(1A)	109.2
N(1)-C(1)-H(1B)	109.2
N(1)-C(1)-C(2)	111.86(19)
H(1A)-C(1)-H(1B)	107.9
C(2)-C(1)-H(1A)	109.2
C(2)-C(1)-H(1B)	109.2
C(10)-O(2)-C(2)	97.24(17)
C(1)-C(2)-C(3)	114.1(2)
C(1)-C(2)-C(12)	120.6(2)
O(2)-C(2)-C(1)	113.2(2)
O(2)-C(2)-C(3)	103.29(18)
O(2)-C(2)-C(12)	100.05(18)
C(12)-C(2)-C(3)	103.42(19)
C(21)-O(3)-C(20)	116.69(19)
C(2)-C(3)-H(3)	112.8
C(2)-C(3)-C(9)	102.93(19)
C(4)-C(3)-C(2)	111.79(19)
C(4)-C(3)-H(3)	112.8
C(4)-C(3)-C(9)	102.85(18)
C(9)-C(3)-H(3)	112.8
C(5)-C(4)-C(3)	112.6(2)

C(5)-C(4)-C(6)	121.3(2)
C(6)-C(4)-C(3)	103.97(19)
O(1)-C(4)-C(3)	102.36(18)
O(1)-C(4)-C(5)	113.2(2)
O(1)-C(4)-C(6)	101.20(19)
C(29)-O(5)-C(28)	116.66(18)
N(1)-C(5)-C(4)	110.6(2)
N(1)-C(5)-H(5A)	109.5
N(1)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	108.1
C(4)-C(6)-H(6)	127.3
C(7)-C(6)-C(4)	105.5(2)
C(7)-C(6)-H(6)	127.3
C(6)-C(7)-H(7)	127.1
C(6)-C(7)-C(8)	105.9(2)
C(8)-C(7)-H(7)	127.1
C(36)-O(8)-C(37)	113.5(2)
C(7)-C(8)-C(9)	103.85(19)
O(1)-C(8)-C(7)	101.29(19)
O(1)-C(8)-C(9)	102.87(18)
O(1)-C(8)-C(20)	111.2(2)
C(20)-C(8)-C(7)	117.7(2)
C(20)-C(8)-C(9)	117.7(2)
C(3)-C(9)-C(8)	99.15(18)
C(3)-C(9)-H(9)	112.1
C(3)-C(9)-C(10)	99.31(18)
C(8)-C(9)-H(9)	112.1
C(10)-C(9)-C(8)	120.25(19)
C(10)-C(9)-H(9)	112.1
C(38)-O(10)-C(39)	115.8(2)
O(2)-C(10)-C(9)	102.63(18)
O(2)-C(10)-C(11)	100.74(18)
O(2)-C(10)-C(28)	112.12(19)
C(11)-C(10)-C(9)	104.91(19)
C(28)-C(10)-C(9)	120.4(2)
C(28)-C(10)-C(11)	113.8(2)
C(12)-C(11)-C(10)	106.1(2)
C(12)-C(11)-C(36)	132.4(2)

C(36)-C(11)-C(10)	120.1(2)
C(11)-C(12)-C(2)	104.7(2)
C(11)-C(12)-C(38)	131.3(2)
C(38)-C(12)-C(2)	123.1(2)
N(1)-C(13)-H(13A)	109.4
N(1)-C(13)-H(13B)	109.4
N(1)-C(13)-C(14)	111.2(2)
H(13A)-C(13)-H(13B)	108.0
C(14)-C(13)-H(13A)	109.4
C(14)-C(13)-H(13B)	109.4
C(15)-C(14)-C(13)	119.8(2)
C(15)-C(14)-C(19)	118.5(3)
C(19)-C(14)-C(13)	121.7(2)
C(14)-C(15)-H(15)	119.3
C(16)-C(15)-C(14)	121.4(3)
C(16)-C(15)-H(15)	119.3
C(15)-C(16)-H(16)	120.0
C(15)-C(16)-C(17)	120.0(3)
C(17)-C(16)-H(16)	120.0
C(8)-O(1)-C(4)	96.77(17)
C(16)-C(17)-H(17)	120.8
C(18)-C(17)-C(16)	118.3(3)
C(18)-C(17)-H(17)	120.8
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-C(17)	121.3(3)
C(19)-C(18)-H(18)	119.3
C(14)-C(19)-H(19)	119.8
C(18)-C(19)-C(14)	120.4(3)
C(18)-C(19)-H(19)	119.8
O(3)-C(20)-C(8)	111.0(2)
O(3)-C(20)-H(20A)	109.4
O(3)-C(20)-H(20B)	109.4
C(8)-C(20)-H(20A)	109.4
C(8)-C(20)-H(20B)	109.4
H(20A)-C(20)-H(20B)	108.0
O(3)-C(21)-C(22)	111.3(2)
O(4)-C(21)-O(3)	124.1(2)
O(4)-C(21)-C(22)	124.6(2)
C(23)-C(22)-C(21)	122.7(2)
C(23)-C(22)-C(27)	119.5(2)

C(27)-C(22)-C(21)	117.8(2)
C(22)-C(23)-H(23)	119.6
C(22)-C(23)-C(24)	120.8(3)
C(24)-C(23)-H(23)	119.6
C(23)-C(24)-H(24)	120.2
C(23)-C(24)-C(25)	119.6(3)
C(25)-C(24)-H(24)	120.2
C(24)-C(25)-H(25)	120.2
C(26)-C(25)-C(24)	119.6(3)
C(26)-C(25)-H(25)	120.2
C(25)-C(26)-H(26)	119.6
C(25)-C(26)-C(27)	120.7(2)
C(27)-C(26)-H(26)	119.6
C(22)-C(27)-C(26)	119.8(3)
C(22)-C(27)-H(27)	120.1
C(26)-C(27)-H(27)	120.1
O(5)-C(28)-C(10)	106.35(18)
O(5)-C(28)-H(28A)	110.5
O(5)-C(28)-H(28B)	110.5
C(10)-C(28)-H(28A)	110.5
C(10)-C(28)-H(28B)	110.5
H(28A)-C(28)-H(28B)	108.7
O(5)-C(29)-C(30)	112.4(2)
O(6)-C(29)-O(5)	123.0(2)
O(6)-C(29)-C(30)	124.6(2)
C(31)-C(30)-C(29)	121.8(2)
C(35)-C(30)-C(29)	118.1(2)
C(35)-C(30)-C(31)	120.0(2)
C(30)-C(31)-H(31)	120.1
C(32)-C(31)-C(30)	119.9(3)
C(32)-C(31)-H(31)	120.1
C(31)-C(32)-H(32)	120.0
C(33)-C(32)-C(31)	120.0(3)
C(33)-C(32)-H(32)	120.0
C(32)-C(33)-H(33)	119.9
C(32)-C(33)-C(34)	120.2(3)
C(34)-C(33)-H(33)	119.9
C(33)-C(34)-H(34)	120.0
C(35)-C(34)-C(33)	120.0(3)
C(35)-C(34)-H(34)	120.0

C(30)-C(35)-H(35)	120.1
C(34)-C(35)-C(30)	119.9(3)
C(34)-C(35)-H(35)	120.1
O(7)-C(36)-O(8)	123.7(2)
O(7)-C(36)-C(11)	121.2(2)
O(8)-C(36)-C(11)	115.1(2)
O(8)-C(37)-H(37A)	109.5
O(8)-C(37)-H(37B)	109.5
O(8)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
O(9)-C(38)-O(10)	125.1(2)
O(9)-C(38)-C(12)	123.9(2)
O(10)-C(38)-C(12)	110.9(2)
O(10)-C(39)-H(39A)	109.5
O(10)-C(39)-H(39B)	109.5
O(10)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5

Table S19. Anisotropic displacement parameters ($Å^2$ x 10^3) for 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	22(1)	23(1)	25(1)	-2(1)	-4(1)	2(1)
C(1)	21(1)	26(1)	21(1)	-1(1)	-1(1)	2(1)
O(2)	19(1)	24(1)	17(1)	0(1)	0(1)	-1(1)
C(2)	21(1)	25(1)	18(1)	1(1)	1(1)	1(1)
O(3)	30(1)	26(1)	17(1)	2(1)	-7(1)	-3(1)
C(3)	20(1)	24(1)	18(1)	1(1)	-1(1)	-1(1)
O(4)	37(1)	30(1)	28(1)	0(1)	-6(1)	-6(1)
C(4)	18(1)	25(1)	22(1)	2(1)	-3(1)	1(1)
O(5)	21(1)	33(1)	18(1)	-3(1)	-3(1)	3(1)
C(5)	23(1)	27(1)	30(1)	-1(1)	-4(1)	4(1)
O(6)	35(1)	42(1)	16(1)	-3(1)	0(1)	8(1)
C(6)	20(1)	27(1)	26(1)	4(1)	-3(1)	1(1)
O(7)	41(1)	30(1)	21(1)	-4(1)	-2(1)	3(1)
C(7)	22(1)	24(1)	23(1)	4(1)	-5(1)	-2(1)
O(8)	41(1)	24(1)	23(1)	4(1)	-8(1)	3(1)
C(8)	22(1)	22(1)	22(1)	2(1)	-3(1)	-1(1)
O(9)	28(1)	70(2)	23(1)	5(1)	6(1)	6(1)
C(9)	20(1)	23(1)	18(1)	2(1)	-2(1)	-1(1)
O(10)	30(1)	42(1)	13(1)	3(1)	-1(1)	6(1)
C(10)	22(1)	21(1)	17(1)	2(1)	-1(1)	1(1)
C(11)	18(1)	27(1)	17(1)	2(1)	-1(1)	1(1)
C(12)	20(1)	25(1)	18(1)	1(1)	-1(1)	1(1)
C(13)	29(1)	24(1)	27(1)	-2(1)	-3(1)	4(1)
C(14)	29(1)	21(1)	25(1)	-2(1)	-2(1)	3(1)
C(15)	42(2)	33(2)	23(1)	-4(1)	0(1)	-1(1)
C(16)	45(2)	41(2)	30(2)	-1(1)	11(1)	-4(1)
O(1)	23(1)	23(1)	20(1)	3(1)	-2(1)	-1(1)
C(17)	35(2)	33(2)	41(2)	-3(1)	5(1)	-5(1)
C(18)	30(1)	33(1)	29(1)	-5(1)	-4(1)	-2(1)
C(19)	31(1)	28(1)	22(1)	-2(1)	-1(1)	0(1)
C(20)	26(1)	27(1)	20(1)	4(1)	-4(1)	1(1)

C(21)	25(1)	29(1)	17(1)	-2(1)	-2(1)	-3(1)
C(22)	24(1)	35(1)	15(1)	-3(1)	-1(1)	2(1)
C(23)	42(2)	34(2)	23(1)	-4(1)	-10(1)	3(1)
C(24)	45(2)	34(2)	29(1)	-1(1)	-6(1)	8(1)
C(25)	25(1)	52(2)	21(1)	1(1)	-1(1)	11(1)
C(26)	20(1)	54(2)	21(1)	-3(1)	-4(1)	1(1)
C(27)	25(1)	39(2)	22(1)	-3(1)	1(1)	-2(1)
C(28)	21(1)	30(1)	17(1)	1(1)	-1(1)	1(1)
C(29)	26(1)	26(1)	18(1)	1(1)	3(1)	-1(1)
C(30)	21(1)	28(1)	19(1)	4(1)	1(1)	-2(1)
C(31)	30(1)	40(2)	21(1)	0(1)	1(1)	1(1)
C(32)	34(2)	55(2)	20(1)	4(1)	-2(1)	-1(1)
C(33)	28(1)	45(2)	33(2)	12(1)	-2(1)	1(1)
C(34)	26(1)	33(2)	39(2)	3(1)	4(1)	3(1)
C(35)	29(1)	29(1)	27(1)	0(1)	2(1)	-1(1)
C(36)	21(1)	28(1)	18(1)	2(1)	3(1)	1(1)
C(37)	56(2)	24(1)	39(2)	4(1)	-7(1)	6(1)
C(38)	26(1)	25(1)	20(1)	1(1)	2(1)	2(1)
C(39)	45(2)	45(2)	14(1)	4(1)	-1(1)	9(1)

–

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a^1,6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea**.

	x	y	z	U(eq)
H(1A)	5988	6789	9470	27
H(1B)	7484	6931	8991	27
H(3)	4466	6153	7809	25
H(5A)	3636	7241	6940	33
H(5B)	3632	6958	8167	33
H(6)	1797	6495	6234	30
H(7)	2456	6103	4406	29
H(9)	5095	5795	6082	25
H(13A)	5570	7463	9530	33
H(13B)	4899	7693	8248	33
H(15)	7068	7734	6668	40
H(16)	9295	8053	6584	46
H(17)	10781	8236	8505	43
H(18)	9899	8126	10467	38
H(19)	7669	7814	10539	33
H(20A)	6324	6407	3773	30
H(20B)	5332	6021	3428	30
H(23)	3528	7102	1463	42
H(24)	2083	7495	-43	45
H(25)	226	7198	-1502	39
H(26)	-97	6516	-1475	39
H(27)	1271	6126	101	35
H(28A)	7775	5750	4955	28
H(28B)	8310	6205	4933	28
H(31)	11271	5748	8159	36
H(32)	13339	5516	9500	44
H(33)	14942	5071	8705	43
H(34)	14504	4863	6561	40
H(35)	12470	5104	5205	34
H(37A)	9279	4730	9453	62
H(37B)	9406	4791	7962	62

H(37C)	7857	4681	8403	62
H(39A)	9559	5860	12436	52
H(39B)	8033	5625	12228	52
H(39C)	8048	6096	12425	52

Table S21. Torsion angles [°] for 6,7-bis((benzoyloxy)methyl)-2-benzyl-2,3,3a[1],6a-tetrahydro-1H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isoquinoline-4,5-dicarboxylate **3ea**.

N(1)-C(1)-C(2)-O(2)	69.4(3)
N(1)-C(1)-C(2)-C(3)	-48.3(3)
N(1)-C(1)-C(2)-C(12)	-172.3(2)
N(1)-C(13)-C(14)-C(15)	53.6(3)
N(1)-C(13)-C(14)-C(19)	-127.5(3)
C(1)-N(1)-C(5)-C(4)	-62.2(3)
C(1)-N(1)-C(13)-C(14)	79.6(3)
C(1)-C(2)-C(3)-C(4)	42.1(3)
C(1)-C(2)-C(3)-C(9)	151.8(2)
C(1)-C(2)-C(12)-C(11)	-161.1(2)
C(1)-C(2)-C(12)-C(38)	28.6(3)
O(2)-C(2)-C(3)-C(4)	-81.2(2)
O(2)-C(2)-C(3)-C(9)	28.6(2)
O(2)-C(2)-C(12)-C(11)	-36.4(2)
O(2)-C(2)-C(12)-C(38)	153.3(2)
O(2)-C(10)-C(11)-C(12)	28.7(2)
O(2)-C(10)-C(11)-C(36)	-163.1(2)
O(2)-C(10)-C(28)-O(5)	80.4(2)
C(2)-O(2)-C(10)-C(9)	57.80(19)
C(2)-O(2)-C(10)-C(11)	-50.30(19)
C(2)-O(2)-C(10)-C(28)	-171.64(18)
C(2)-C(3)-C(4)-C(5)	-45.6(3)
C(2)-C(3)-C(4)-C(6)	-178.7(2)
C(2)-C(3)-C(4)-O(1)	76.2(2)
C(2)-C(3)-C(9)-C(8)	-117.18(19)
C(2)-C(3)-C(9)-C(10)	5.7(2)
C(2)-C(12)-C(38)-O(9)	51.7(4)
C(2)-C(12)-C(38)-O(10)	-124.5(2)
O(3)-C(21)-C(22)-C(23)	-1.8(4)
O(3)-C(21)-C(22)-C(27)	-180.0(2)
C(3)-C(2)-C(12)-C(11)	70.0(2)
C(3)-C(2)-C(12)-C(38)	-100.3(3)
C(3)-C(4)-C(5)-N(1)	55.6(3)
C(3)-C(4)-C(6)-C(7)	-72.8(2)
C(3)-C(4)-O(1)-C(8)	56.3(2)
C(3)-C(9)-C(10)-O(2)	-38.8(2)
C(3)-C(9)-C(10)-C(11)	66.1(2)

C(3)-C(9)-C(10)-C(28)	-164.1(2)
O(4)-C(21)-C(22)-C(23)	177.6(3)
O(4)-C(21)-C(22)-C(27)	-0.6(4)
C(4)-C(3)-C(9)-C(8)	-0.9(2)
C(4)-C(3)-C(9)-C(10)	122.04(19)
C(4)-C(6)-C(7)-C(8)	-1.4(3)
O(5)-C(29)-C(30)-C(31)	1.8(3)
O(5)-C(29)-C(30)-C(35)	-177.3(2)
C(5)-N(1)-C(1)-C(2)	58.4(3)
C(5)-N(1)-C(13)-C(14)	-155.2(2)
C(5)-C(4)-C(6)-C(7)	159.3(2)
C(5)-C(4)-O(1)-C(8)	177.8(2)
O(6)-C(29)-C(30)-C(31)	-178.3(3)
O(6)-C(29)-C(30)-C(35)	2.6(4)
C(6)-C(4)-C(5)-N(1)	179.6(2)
C(6)-C(4)-O(1)-C(8)	-50.8(2)
C(6)-C(7)-C(8)-C(9)	75.4(2)
C(6)-C(7)-C(8)-O(1)	-31.0(2)
C(6)-C(7)-C(8)-C(20)	-152.4(2)
C(7)-C(8)-C(9)-C(3)	-69.8(2)
C(7)-C(8)-C(9)-C(10)	-176.3(2)
C(7)-C(8)-O(1)-C(4)	49.8(2)
C(7)-C(8)-C(20)-O(3)	47.8(3)
C(8)-C(9)-C(10)-O(2)	67.6(2)
C(8)-C(9)-C(10)-C(11)	172.5(2)
C(8)-C(9)-C(10)-C(28)	-57.8(3)
C(9)-C(3)-C(4)-C(5)	-155.4(2)
C(9)-C(3)-C(4)-C(6)	71.5(2)
C(9)-C(3)-C(4)-O(1)	-33.5(2)
C(9)-C(8)-O(1)-C(4)	-57.4(2)
C(9)-C(8)-C(20)-O(3)	173.32(19)
C(9)-C(10)-C(11)-C(12)	-77.6(2)
C(9)-C(10)-C(11)-C(36)	90.6(2)
C(9)-C(10)-C(28)-O(5)	-158.8(2)
C(10)-O(2)-C(2)-C(1)	-177.15(19)
C(10)-O(2)-C(2)-C(3)	-53.3(2)
C(10)-O(2)-C(2)-C(12)	53.21(19)
C(10)-C(11)-C(12)-C(2)	4.6(2)
C(10)-C(11)-C(12)-C(38)	173.8(2)
C(10)-C(11)-C(36)-O(7)	-20.0(4)

C(10)-C(11)-C(36)-O(8)	159.9(2)
C(11)-C(10)-C(28)-O(5)	-33.1(3)
C(11)-C(12)-C(38)-O(9)	-115.8(3)
C(11)-C(12)-C(38)-O(10)	68.0(4)
C(12)-C(2)-C(3)-C(4)	174.91(19)
C(12)-C(2)-C(3)-C(9)	-75.4(2)
C(12)-C(11)-C(36)-O(7)	144.6(3)
C(12)-C(11)-C(36)-O(8)	-35.5(4)
C(13)-N(1)-C(1)-C(2)	-176.3(2)
C(13)-N(1)-C(5)-C(4)	173.9(2)
C(13)-C(14)-C(15)-C(16)	-179.2(3)
C(13)-C(14)-C(19)-C(18)	178.9(2)
C(14)-C(15)-C(16)-C(17)	0.3(5)
C(15)-C(14)-C(19)-C(18)	-2.2(4)
C(15)-C(16)-C(17)-C(18)	-2.1(5)
C(16)-C(17)-C(18)-C(19)	1.8(4)
O(1)-C(4)-C(5)-N(1)	-59.9(3)
O(1)-C(4)-C(6)-C(7)	33.1(2)
O(1)-C(8)-C(9)-C(3)	35.5(2)
O(1)-C(8)-C(9)-C(10)	-71.0(3)
O(1)-C(8)-C(20)-O(3)	-68.4(2)
C(17)-C(18)-C(19)-C(14)	0.4(4)
C(19)-C(14)-C(15)-C(16)	1.9(4)
C(20)-O(3)-C(21)-O(4)	2.1(4)
C(20)-O(3)-C(21)-C(22)	-178.6(2)
C(20)-C(8)-C(9)-C(3)	158.1(2)
C(20)-C(8)-C(9)-C(10)	51.6(3)
C(20)-C(8)-O(1)-C(4)	175.67(19)
C(21)-O(3)-C(20)-C(8)	-97.8(2)
C(21)-C(22)-C(23)-C(24)	-177.1(3)
C(21)-C(22)-C(27)-C(26)	178.9(2)
C(22)-C(23)-C(24)-C(25)	-0.9(5)
C(23)-C(22)-C(27)-C(26)	0.6(4)
C(23)-C(24)-C(25)-C(26)	-1.0(4)
C(24)-C(25)-C(26)-C(27)	2.7(4)
C(25)-C(26)-C(27)-C(22)	-2.5(4)
C(27)-C(22)-C(23)-C(24)	1.1(4)
C(28)-O(5)-C(29)-O(6)	10.6(4)
C(28)-O(5)-C(29)-C(30)	-169.5(2)
C(28)-C(10)-C(11)-C(12)	148.9(2)

C(28)-C(10)-C(11)-C(36)	-42.9(3)
C(29)-O(5)-C(28)-C(10)	150.8(2)
C(29)-C(30)-C(31)-C(32)	-178.5(3)
C(29)-C(30)-C(35)-C(34)	179.2(2)
C(30)-C(31)-C(32)-C(33)	-0.9(4)
C(31)-C(30)-C(35)-C(34)	0.1(4)
C(31)-C(32)-C(33)-C(34)	0.4(5)
C(32)-C(33)-C(34)-C(35)	0.3(4)
C(33)-C(34)-C(35)-C(30)	-0.6(4)
C(35)-C(30)-C(31)-C(32)	0.6(4)
C(36)-C(11)-C(12)-C(2)	-161.6(2)
C(36)-C(11)-C(12)-C(38)	7.6(5)
C(37)-O(8)-C(36)-O(7)	3.6(4)
C(37)-O(8)-C(36)-C(11)	-176.3(2)
C(39)-O(10)-C(38)-O(9)	0.2(4)
C(39)-O(10)-C(38)-C(12)	176.4(2)

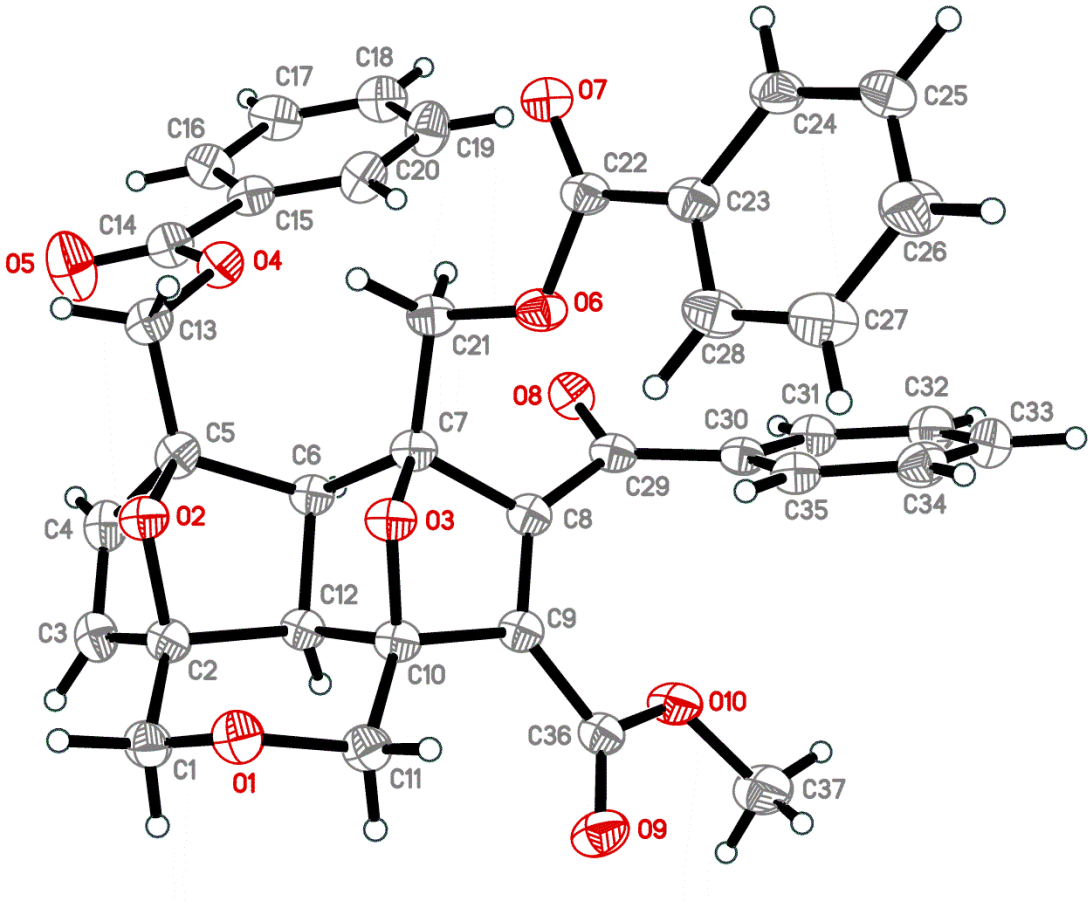


Figure S110. X-Ray structure of (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB**.

Table S22. Crystal data and structure refinement for (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB**.

Empirical formula	C37 H30 O10	
Formula weight	634.61	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3610(2) Å	α= 62.271(2)°.
	b = 13.3550(3) Å	β= 70.487(2)°.
	c = 13.4649(3) Å	γ = 70.729(2)°.
Volume	1520.04(7) Å^3	
Z	2	
Density (calculated)	1.387 Mg/m^3	
Absorption coefficient	0.840 mm^{-1}	
F(000)	664	

Crystal size	0.05 x 0.03 x 0.02 mm^3
Theta range for data collection	3.798 to 79.670°.
Index ranges	-11<=h<=13, -16<=k<=16, -17<=l<=17
Reflections collected	21798
Independent reflections	6239 [R(int) = 0.0533]
Completeness to theta = 67.684°	97.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.42700
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6239 / 0 / 425
Goodness of fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1665
R indices (all data)	R1 = 0.0585, wR2 = 0.1688
Largest diff. peak and hole	0.383 and -0.372 $e.Å^{-3}$

Table S23. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3)
for (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB**. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4825(1)	5758(1)	7475(1)	27(1)
C(1)	5951(2)	4791(2)	7795(1)	26(1)
O(2)	6396(1)	4362(1)	6108(1)	22(1)
C(2)	6994(2)	4642(1)	6755(1)	22(1)
O(3)	5552(1)	6698(1)	4998(1)	22(1)
C(3)	8335(2)	3720(1)	6876(1)	26(1)
O(4)	8414(1)	4320(1)	3318(1)	24(1)
C(4)	8750(2)	3561(1)	5903(1)	26(1)
C(5)	7624(2)	4346(1)	5201(1)	22(1)
O(5)	9919(2)	2593(1)	3810(1)	46(1)
O(6)	5333(1)	7780(1)	2745(1)	26(1)
C(6)	7851(2)	5613(1)	4704(1)	20(1)
C(7)	6746(2)	6653(1)	4075(1)	21(1)
O(7)	5262(1)	7565(1)	1202(1)	29(1)
O(8)	8978(1)	7819(1)	2156(1)	26(1)
C(8)	7226(2)	7756(1)	3794(1)	21(1)
O(9)	6595(1)	8897(1)	5924(1)	34(1)
C(9)	6889(2)	7870(1)	4793(1)	21(1)
C(10)	6239(2)	6830(1)	5683(1)	21(1)
O(10)	8088(1)	9324(1)	4200(1)	31(1)
C(11)	5281(2)	6827(1)	6808(1)	26(1)
C(12)	7482(2)	5777(1)	5846(1)	21(1)
C(13)	7423(2)	3925(1)	4402(1)	24(1)
C(14)	9624(2)	3580(2)	3138(2)	27(1)
C(15)	10552(2)	4129(2)	2005(1)	25(1)
C(16)	11798(2)	3436(2)	1668(2)	30(1)
C(17)	12654(2)	3885(2)	592(2)	33(1)
C(19)	11070(2)	5731(2)	214(2)	35(1)
C(18)	12296(2)	5032(2)	-139(2)	33(1)
C(20)	10192(2)	5284(2)	1279(2)	31(1)

C(21)	6311(2)	6686(1)	3096(1)	23(1)
C(22)	4824(2)	8078(1)	1824(1)	23(1)
C(23)	3672(2)	9126(1)	1687(1)	24(1)
C(24)	3258(2)	9750(2)	638(1)	27(1)
C(25)	2195(2)	10735(2)	492(2)	32(1)
C(26)	1538(2)	11084(2)	1388(2)	36(1)
C(27)	1938(2)	10465(2)	2438(2)	37(1)
C(28)	3007(2)	9488(2)	2590(2)	30(1)
C(29)	8025(2)	8390(1)	2632(1)	21(1)
C(30)	7601(2)	9663(1)	2040(1)	21(1)
C(31)	8596(2)	10269(2)	1167(1)	25(1)
C(32)	8215(2)	11445(2)	544(2)	31(1)
C(33)	6826(2)	12025(2)	777(2)	31(1)
C(34)	5837(2)	11421(2)	1646(2)	28(1)
C(35)	6219(2)	10250(1)	2287(1)	23(1)
C(36)	7159(2)	8734(1)	5057(1)	23(1)
C(37)	8304(3)	10281(2)	4309(2)	42(1)

Table S24. Bond lengths [Å] and angles [°] for (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB**.

O(1)-C(1)	1.427(2)
O(1)-C(11)	1.4269(19)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(1)-C(2)	1.508(2)
O(2)-C(2)	1.4483(18)
O(2)-C(5)	1.4421(17)
C(2)-C(3)	1.519(2)
C(2)-C(12)	1.555(2)
O(3)-C(7)	1.4396(17)
O(3)-C(10)	1.4354(18)
C(3)-H(3)	0.9500
C(3)-C(4)	1.330(2)
O(4)-C(13)	1.4505(18)
O(4)-C(14)	1.345(2)
C(4)-H(4)	0.9500
C(4)-C(5)	1.537(2)
C(5)-C(6)	1.571(2)
C(5)-C(13)	1.518(2)
O(5)-C(14)	1.208(2)
O(6)-C(21)	1.4437(19)
O(6)-C(22)	1.3468(19)
C(6)-H(6)	1.0000
C(6)-C(7)	1.568(2)
C(6)-C(12)	1.556(2)
C(7)-C(8)	1.549(2)
C(7)-C(21)	1.507(2)
O(7)-C(22)	1.205(2)
O(8)-C(29)	1.226(2)
C(8)-C(9)	1.341(2)
C(8)-C(29)	1.488(2)
O(9)-C(36)	1.204(2)
C(9)-C(10)	1.533(2)
C(9)-C(36)	1.482(2)
C(10)-C(11)	1.507(2)
C(10)-C(12)	1.546(2)

O(10)-C(36)	1.3386(19)
O(10)-C(37)	1.445(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.494(2)
C(15)-C(16)	1.393(2)
C(15)-C(20)	1.391(3)
C(16)-H(16)	0.9500
C(16)-C(17)	1.389(2)
C(17)-H(17)	0.9500
C(17)-C(18)	1.385(3)
C(19)-H(19)	0.9500
C(19)-C(18)	1.392(3)
C(19)-C(20)	1.389(2)
C(18)-H(18)	0.9500
C(20)-H(20)	0.9500
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.491(2)
C(23)-C(24)	1.395(2)
C(23)-C(28)	1.397(2)
C(24)-H(24)	0.9500
C(24)-C(25)	1.389(3)
C(25)-H(25)	0.9500
C(25)-C(26)	1.378(3)
C(26)-H(26)	0.9500
C(26)-C(27)	1.391(3)
C(27)-H(27)	0.9500
C(27)-C(28)	1.387(3)
C(28)-H(28)	0.9500
C(29)-C(30)	1.483(2)
C(30)-C(31)	1.397(2)
C(30)-C(35)	1.400(2)
C(31)-H(31)	0.9500
C(31)-C(32)	1.383(2)
C(32)-H(32)	0.9500
C(32)-C(33)	1.399(3)

C(33)-H(33)	0.9500
C(33)-C(34)	1.391(2)
C(34)-H(34)	0.9500
C(34)-C(35)	1.382(2)
C(35)-H(35)	0.9500
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800

C(11)-O(1)-C(1)	112.74(12)
O(1)-C(1)-H(1A)	109.3
O(1)-C(1)-H(1B)	109.3
O(1)-C(1)-C(2)	111.48(13)
H(1A)-C(1)-H(1B)	108.0
C(2)-C(1)-H(1A)	109.3
C(2)-C(1)-H(1B)	109.3
C(5)-O(2)-C(2)	96.49(11)
C(1)-C(2)-C(3)	121.12(14)
C(1)-C(2)-C(12)	112.93(13)
O(2)-C(2)-C(1)	112.41(12)
O(2)-C(2)-C(3)	101.23(12)
O(2)-C(2)-C(12)	102.31(12)
C(3)-C(2)-C(12)	104.66(12)
C(10)-O(3)-C(7)	97.28(10)
C(2)-C(3)-H(3)	127.5
C(4)-C(3)-C(2)	105.00(14)
C(4)-C(3)-H(3)	127.5
C(14)-O(4)-C(13)	118.17(13)
C(3)-C(4)-H(4)	126.8
C(3)-C(4)-C(5)	106.32(14)
C(5)-C(4)-H(4)	126.8
O(2)-C(5)-C(4)	100.78(12)
O(2)-C(5)-C(6)	101.56(12)
O(2)-C(5)-C(13)	111.02(12)
C(4)-C(5)-C(6)	106.31(12)
C(13)-C(5)-C(4)	115.96(14)
C(13)-C(5)-C(6)	118.83(13)
C(22)-O(6)-C(21)	117.17(12)
C(5)-C(6)-H(6)	112.4
C(7)-C(6)-C(5)	119.31(12)

C(7)-C(6)-H(6)	112.4
C(12)-C(6)-C(5)	99.51(11)
C(12)-C(6)-H(6)	112.4
C(12)-C(6)-C(7)	99.20(11)
O(3)-C(7)-C(6)	103.08(11)
O(3)-C(7)-C(8)	99.92(11)
O(3)-C(7)-C(21)	110.51(11)
C(8)-C(7)-C(6)	105.47(11)
C(21)-C(7)-C(6)	121.41(13)
C(21)-C(7)-C(8)	113.87(13)
C(9)-C(8)-C(7)	105.65(13)
C(9)-C(8)-C(29)	132.47(14)
C(29)-C(8)-C(7)	121.57(13)
C(8)-C(9)-C(10)	105.08(13)
C(8)-C(9)-C(36)	129.71(14)
C(36)-C(9)-C(10)	125.04(13)
O(3)-C(10)-C(9)	100.57(11)
O(3)-C(10)-C(11)	111.89(12)
O(3)-C(10)-C(12)	102.42(12)
C(9)-C(10)-C(12)	104.97(11)
C(11)-C(10)-C(9)	122.08(13)
C(11)-C(10)-C(12)	112.60(13)
C(36)-O(10)-C(37)	115.95(14)
O(1)-C(11)-C(10)	110.65(13)
O(1)-C(11)-H(11A)	109.5
O(1)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	108.1
C(2)-C(12)-C(6)	102.49(12)
C(2)-C(12)-H(12)	113.0
C(6)-C(12)-H(12)	113.0
C(10)-C(12)-C(2)	111.30(12)
C(10)-C(12)-C(6)	103.08(12)
C(10)-C(12)-H(12)	113.0
O(4)-C(13)-C(5)	108.10(12)
O(4)-C(13)-H(13A)	110.1
O(4)-C(13)-H(13B)	110.1
C(5)-C(13)-H(13A)	110.1
C(5)-C(13)-H(13B)	110.1

H(13A)-C(13)-H(13B)	108.4
O(4)-C(14)-C(15)	111.67(14)
O(5)-C(14)-O(4)	123.98(15)
O(5)-C(14)-C(15)	124.35(15)
C(16)-C(15)-C(14)	117.80(15)
C(20)-C(15)-C(14)	122.30(15)
C(20)-C(15)-C(16)	119.88(16)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-C(15)	120.07(17)
C(17)-C(16)-H(16)	120.0
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-C(16)	120.31(16)
C(18)-C(17)-H(17)	119.8
C(18)-C(19)-H(19)	119.6
C(20)-C(19)-H(19)	119.6
C(20)-C(19)-C(18)	120.74(18)
C(17)-C(18)-C(19)	119.43(17)
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
C(15)-C(20)-H(20)	120.2
C(19)-C(20)-C(15)	119.54(16)
C(19)-C(20)-H(20)	120.2
O(6)-C(21)-C(7)	103.93(12)
O(6)-C(21)-H(21A)	111.0
O(6)-C(21)-H(21B)	111.0
C(7)-C(21)-H(21A)	111.0
C(7)-C(21)-H(21B)	111.0
H(21A)-C(21)-H(21B)	109.0
O(6)-C(22)-C(23)	110.44(13)
O(7)-C(22)-O(6)	123.88(15)
O(7)-C(22)-C(23)	125.67(14)
C(24)-C(23)-C(22)	119.07(15)
C(24)-C(23)-C(28)	119.93(15)
C(28)-C(23)-C(22)	121.00(14)
C(23)-C(24)-H(24)	120.1
C(25)-C(24)-C(23)	119.80(16)
C(25)-C(24)-H(24)	120.1
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-C(24)	120.05(16)
C(26)-C(25)-H(25)	120.0

C(25)-C(26)-H(26)	119.7
C(25)-C(26)-C(27)	120.60(17)
C(27)-C(26)-H(26)	119.7
C(26)-C(27)-H(27)	120.1
C(28)-C(27)-C(26)	119.85(18)
C(28)-C(27)-H(27)	120.1
C(23)-C(28)-H(28)	120.1
C(27)-C(28)-C(23)	119.77(16)
C(27)-C(28)-H(28)	120.1
O(8)-C(29)-C(8)	117.82(14)
O(8)-C(29)-C(30)	121.43(14)
C(30)-C(29)-C(8)	120.58(13)
C(31)-C(30)-C(29)	118.50(14)
C(31)-C(30)-C(35)	119.89(15)
C(35)-C(30)-C(29)	121.48(14)
C(30)-C(31)-H(31)	119.9
C(32)-C(31)-C(30)	120.13(15)
C(32)-C(31)-H(31)	119.9
C(31)-C(32)-H(32)	120.1
C(31)-C(32)-C(33)	119.83(16)
C(33)-C(32)-H(32)	120.1
C(32)-C(33)-H(33)	120.0
C(34)-C(33)-C(32)	119.98(16)
C(34)-C(33)-H(33)	120.0
C(33)-C(34)-H(34)	119.8
C(35)-C(34)-C(33)	120.39(16)
C(35)-C(34)-H(34)	119.8
C(30)-C(35)-H(35)	120.1
C(34)-C(35)-C(30)	119.75(15)
C(34)-C(35)-H(35)	120.1
O(9)-C(36)-C(9)	124.21(14)
O(9)-C(36)-O(10)	124.31(15)
O(10)-C(36)-C(9)	111.48(13)
O(10)-C(37)-H(37A)	109.5
O(10)-C(37)-H(37B)	109.5
O(10)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5

Table S25. Anisotropic displacement parameters ($Å^2$ x 10^3) for (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	21(1)	33(1)	26(1)	-11(1)	3(1)	-12(1)
C(1)	26(1)	30(1)	22(1)	-9(1)	-1(1)	-12(1)
O(2)	15(1)	31(1)	24(1)	-13(1)	1(1)	-10(1)
C(2)	18(1)	28(1)	23(1)	-9(1)	-3(1)	-10(1)
O(3)	13(1)	31(1)	22(1)	-13(1)	0(1)	-8(1)
C(3)	20(1)	27(1)	29(1)	-6(1)	-6(1)	-9(1)
O(4)	18(1)	28(1)	26(1)	-14(1)	2(1)	-7(1)
C(4)	16(1)	27(1)	31(1)	-9(1)	-3(1)	-7(1)
C(5)	14(1)	27(1)	26(1)	-12(1)	1(1)	-8(1)
O(5)	38(1)	36(1)	36(1)	-7(1)	5(1)	2(1)
O(6)	21(1)	32(1)	29(1)	-15(1)	-10(1)	-2(1)
C(6)	14(1)	27(1)	22(1)	-10(1)	-2(1)	-8(1)
C(7)	14(1)	28(1)	22(1)	-12(1)	0(1)	-8(1)
O(7)	33(1)	31(1)	27(1)	-13(1)	-8(1)	-7(1)
O(8)	19(1)	29(1)	25(1)	-11(1)	-2(1)	-2(1)
C(8)	14(1)	26(1)	23(1)	-10(1)	-4(1)	-5(1)
O(9)	35(1)	40(1)	32(1)	-21(1)	4(1)	-18(1)
C(9)	16(1)	27(1)	22(1)	-10(1)	-3(1)	-7(1)
C(10)	16(1)	28(1)	21(1)	-11(1)	-2(1)	-9(1)
O(10)	34(1)	43(1)	24(1)	-12(1)	-2(1)	-25(1)
C(11)	24(1)	30(1)	23(1)	-11(1)	1(1)	-10(1)
C(12)	15(1)	27(1)	21(1)	-9(1)	-2(1)	-9(1)
C(13)	17(1)	31(1)	27(1)	-14(1)	2(1)	-11(1)
C(14)	21(1)	31(1)	28(1)	-15(1)	-2(1)	-4(1)
C(15)	19(1)	33(1)	28(1)	-16(1)	-1(1)	-8(1)
C(16)	22(1)	37(1)	29(1)	-15(1)	-4(1)	-3(1)
C(17)	20(1)	47(1)	32(1)	-21(1)	-1(1)	-5(1)
C(19)	31(1)	32(1)	37(1)	-12(1)	2(1)	-11(1)
C(18)	23(1)	44(1)	32(1)	-17(1)	2(1)	-14(1)
C(20)	22(1)	32(1)	36(1)	-17(1)	2(1)	-8(1)
C(21)	17(1)	29(1)	26(1)	-13(1)	-6(1)	-4(1)

C(22)	20(1)	29(1)	22(1)	-10(1)	-4(1)	-11(1)
C(23)	18(1)	30(1)	26(1)	-11(1)	-6(1)	-9(1)
C(24)	29(1)	32(1)	27(1)	-12(1)	-10(1)	-9(1)
C(25)	33(1)	35(1)	32(1)	-12(1)	-17(1)	-5(1)
C(26)	28(1)	41(1)	44(1)	-21(1)	-18(1)	3(1)
C(27)	28(1)	50(1)	37(1)	-25(1)	-10(1)	2(1)
C(28)	22(1)	42(1)	28(1)	-15(1)	-8(1)	-5(1)
C(29)	15(1)	30(1)	21(1)	-11(1)	-3(1)	-7(1)
C(30)	18(1)	29(1)	21(1)	-11(1)	-3(1)	-7(1)
C(31)	22(1)	32(1)	24(1)	-12(1)	-1(1)	-11(1)
C(32)	32(1)	33(1)	28(1)	-11(1)	-2(1)	-15(1)
C(33)	37(1)	26(1)	31(1)	-10(1)	-9(1)	-7(1)
C(34)	25(1)	32(1)	31(1)	-18(1)	-6(1)	-3(1)
C(35)	18(1)	31(1)	24(1)	-14(1)	-3(1)	-6(1)
C(36)	21(1)	28(1)	22(1)	-9(1)	-4(1)	-9(1)
C(37)	55(1)	50(1)	37(1)	-15(1)	-7(1)	-35(1)

Table S26. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB**.

	x	y	z	U(eq)
H(1A)	5572	4081	8286	32
H(1B)	6431	4904	8248	32
H(3)	8780	3339	7509	31
H(4)	9577	3062	5685	31
H(6)	8835	5680	4276	24
H(11A)	5780	6945	7244	31
H(11B)	4457	7473	6657	31
H(12)	8288	5898	5997	25
H(13A)	7588	3070	4744	29
H(13B)	6454	4238	4279	29
H(16)	12062	2654	2174	36
H(17)	13490	3403	356	40
H(19)	10830	6521	-279	42
H(18)	12882	5339	-874	39
H(20)	9353	5765	1511	37
H(21A)	7128	6652	2459	28
H(21B)	5858	6034	3354	28
H(24)	3703	9502	25	33
H(25)	1921	11168	-225	38
H(26)	805	11754	1286	43
H(27)	1479	10712	3051	44
H(28)	3288	9065	3305	36
H(31)	9535	9872	1003	30
H(32)	8894	11858	-42	37
H(33)	6558	12830	343	37
H(34)	4893	11815	1799	34
H(35)	5547	9845	2894	28
H(37A)	8781	10781	3564	63
H(37B)	8879	9983	4876	63
H(37C)	7396	10727	4562	63

Table S27. Torsion angles [°] for (5-benzoyl-4-(methoxycarbonyl)-3a[1],6a-dihydro-1H,3H,6H,7H-3a,6:7,9a-diepoxybenzo[de]isochromene-6,7-diyl)bis(methylene) dibenzoate **3agB**.

O(1)-C(1)-C(2)-O(2)	-64.55(17)
O(1)-C(1)-C(2)-C(3)	175.78(13)
O(1)-C(1)-C(2)-C(12)	50.59(17)
C(1)-O(1)-C(11)-C(10)	63.26(17)
C(1)-C(2)-C(3)-C(4)	159.65(14)
C(1)-C(2)-C(12)-C(6)	-151.78(13)
C(1)-C(2)-C(12)-C(10)	-42.20(17)
O(2)-C(2)-C(3)-C(4)	34.63(15)
O(2)-C(2)-C(12)-C(6)	-30.72(14)
O(2)-C(2)-C(12)-C(10)	78.86(14)
O(2)-C(5)-C(6)-C(7)	-67.01(16)
O(2)-C(5)-C(6)-C(12)	39.25(13)
O(2)-C(5)-C(13)-O(4)	159.26(12)
C(2)-O(2)-C(5)-C(4)	49.71(13)
C(2)-O(2)-C(5)-C(6)	-59.60(13)
C(2)-O(2)-C(5)-C(13)	173.10(13)
C(2)-C(3)-C(4)-C(5)	-2.63(16)
O(3)-C(7)-C(8)-C(9)	31.58(15)
O(3)-C(7)-C(8)-C(29)	-154.10(13)
O(3)-C(7)-C(21)-O(6)	60.88(15)
O(3)-C(10)-C(11)-O(1)	60.99(17)
O(3)-C(10)-C(12)-C(2)	-76.58(14)
O(3)-C(10)-C(12)-C(6)	32.62(13)
C(3)-C(2)-C(12)-C(6)	74.54(14)
C(3)-C(2)-C(12)-C(10)	-175.88(12)
C(3)-C(4)-C(5)-O(2)	-30.21(15)
C(3)-C(4)-C(5)-C(6)	75.35(15)
C(3)-C(4)-C(5)-C(13)	-150.12(13)
O(4)-C(14)-C(15)-C(16)	-175.35(14)
O(4)-C(14)-C(15)-C(20)	2.9(2)
C(4)-C(5)-C(6)-C(7)	-172.00(12)
C(4)-C(5)-C(6)-C(12)	-65.74(14)
C(4)-C(5)-C(13)-O(4)	-86.55(16)
C(5)-O(2)-C(2)-C(1)	177.37(13)
C(5)-O(2)-C(2)-C(3)	-51.95(13)
C(5)-O(2)-C(2)-C(12)	55.96(13)

C(5)-C(6)-C(7)-O(3)	71.09(16)
C(5)-C(6)-C(7)-C(8)	175.44(12)
C(5)-C(6)-C(7)-C(21)	-53.19(19)
C(5)-C(6)-C(12)-C(2)	-4.78(13)
C(5)-C(6)-C(12)-C(10)	-120.47(12)
O(5)-C(14)-C(15)-C(16)	4.5(3)
O(5)-C(14)-C(15)-C(20)	-177.27(18)
O(6)-C(22)-C(23)-C(24)	163.20(14)
O(6)-C(22)-C(23)-C(28)	-16.7(2)
C(6)-C(5)-C(13)-O(4)	42.10(18)
C(6)-C(7)-C(8)-C(9)	-75.09(14)
C(6)-C(7)-C(8)-C(29)	99.23(15)
C(6)-C(7)-C(21)-O(6)	-178.35(12)
C(7)-O(3)-C(10)-C(9)	52.85(13)
C(7)-O(3)-C(10)-C(11)	-176.05(13)
C(7)-O(3)-C(10)-C(12)	-55.22(13)
C(7)-C(6)-C(12)-C(2)	117.22(12)
C(7)-C(6)-C(12)-C(10)	1.54(13)
C(7)-C(8)-C(9)-C(10)	1.29(15)
C(7)-C(8)-C(9)-C(36)	176.71(15)
C(7)-C(8)-C(29)-O(8)	-43.7(2)
C(7)-C(8)-C(29)-C(30)	131.62(14)
O(7)-C(22)-C(23)-C(24)	-16.2(2)
O(7)-C(22)-C(23)-C(28)	163.94(16)
O(8)-C(29)-C(30)-C(31)	-26.3(2)
O(8)-C(29)-C(30)-C(35)	149.72(15)
C(8)-C(7)-C(21)-O(6)	-50.62(15)
C(8)-C(9)-C(10)-O(3)	-33.98(15)
C(8)-C(9)-C(10)-C(11)	-158.37(14)
C(8)-C(9)-C(10)-C(12)	72.06(14)
C(8)-C(9)-C(36)-O(9)	165.65(17)
C(8)-C(9)-C(36)-O(10)	-13.2(2)
C(8)-C(29)-C(30)-C(31)	158.55(14)
C(8)-C(29)-C(30)-C(35)	-25.5(2)
C(9)-C(8)-C(29)-O(8)	128.84(18)
C(9)-C(8)-C(29)-C(30)	-55.8(2)
C(9)-C(10)-C(11)-O(1)	-179.97(13)
C(9)-C(10)-C(12)-C(2)	178.75(12)
C(9)-C(10)-C(12)-C(6)	-72.06(13)
C(10)-O(3)-C(7)-C(6)	57.05(13)

C(10)-O(3)-C(7)-C(8)	-51.53(13)
C(10)-O(3)-C(7)-C(21)	-171.79(12)
C(10)-C(9)-C(36)-O(9)	-19.8(2)
C(10)-C(9)-C(36)-O(10)	161.40(14)
C(11)-O(1)-C(1)-C(2)	-61.81(17)
C(11)-C(10)-C(12)-C(2)	43.77(17)
C(11)-C(10)-C(12)-C(6)	152.97(12)
C(12)-C(2)-C(3)-C(4)	-71.42(15)
C(12)-C(6)-C(7)-O(3)	-35.34(13)
C(12)-C(6)-C(7)-C(8)	69.00(13)
C(12)-C(6)-C(7)-C(21)	-159.63(13)
C(12)-C(10)-C(11)-O(1)	-53.74(17)
C(13)-O(4)-C(14)-O(5)	2.4(2)
C(13)-O(4)-C(14)-C(15)	-177.76(13)
C(13)-C(5)-C(6)-C(7)	55.03(18)
C(13)-C(5)-C(6)-C(12)	161.29(13)
C(14)-O(4)-C(13)-C(5)	97.27(16)
C(14)-C(15)-C(16)-C(17)	175.93(16)
C(14)-C(15)-C(20)-C(19)	-177.06(17)
C(15)-C(16)-C(17)-C(18)	1.8(3)
C(16)-C(15)-C(20)-C(19)	1.2(3)
C(16)-C(17)-C(18)-C(19)	0.0(3)
C(18)-C(19)-C(20)-C(15)	0.6(3)
C(20)-C(15)-C(16)-C(17)	-2.4(3)
C(20)-C(19)-C(18)-C(17)	-1.2(3)
C(21)-O(6)-C(22)-O(7)	-9.6(2)
C(21)-O(6)-C(22)-C(23)	171.06(12)
C(21)-C(7)-C(8)-C(9)	149.37(13)
C(21)-C(7)-C(8)-C(29)	-36.31(19)
C(22)-O(6)-C(21)-C(7)	176.24(12)
C(22)-C(23)-C(24)-C(25)	-179.38(14)
C(22)-C(23)-C(28)-C(27)	-179.97(16)
C(23)-C(24)-C(25)-C(26)	-0.9(3)
C(24)-C(23)-C(28)-C(27)	0.1(3)
C(24)-C(25)-C(26)-C(27)	0.6(3)
C(25)-C(26)-C(27)-C(28)	0.0(3)
C(26)-C(27)-C(28)-C(23)	-0.4(3)
C(28)-C(23)-C(24)-C(25)	0.5(2)
C(29)-C(8)-C(9)-C(10)	-172.15(16)
C(29)-C(8)-C(9)-C(36)	3.3(3)

C(29)-C(30)-C(31)-C(32)	175.62(14)
C(29)-C(30)-C(35)-C(34)	-174.17(14)
C(30)-C(31)-C(32)-C(33)	-0.9(3)
C(31)-C(30)-C(35)-C(34)	1.8(2)
C(31)-C(32)-C(33)-C(34)	0.9(3)
C(32)-C(33)-C(34)-C(35)	0.4(3)
C(33)-C(34)-C(35)-C(30)	-1.8(2)
C(35)-C(30)-C(31)-C(32)	-0.4(2)
C(36)-C(9)-C(10)-O(3)	150.32(14)
C(36)-C(9)-C(10)-C(11)	25.9(2)
C(36)-C(9)-C(10)-C(12)	-103.63(16)
C(37)-O(10)-C(36)-O(9)	-5.8(2)
C(37)-O(10)-C(36)-C(9)	173.01(15)

9. Quantum chemical calculations

Computational Details

To analyze the potential energy surface of the cycloaddition process, all molecular structures were optimized by the PBE1PBE method[7] using the 6-311G(d) basis set.[8] For a more accurate description of the dispersion interaction, the empirical D3BJ corrections were used.[9] The Gibbs free energy for all optimized structures was calculated for a temperature of 373.15 K. All DFT calculations were performed using the Gaussian 16 software package.[10] Metadynamics modeling of cycloaddition processes for compound **1c** was performed by the GFN2-XTB method[11] using the Orca software package (temperature was 373.15 K, Nose-Hoover thermostat, the time integration step was 0.5 fs).[12] The hill spawning frequency were equal to 20 steps and height of each hill were equal to 2.0 $kJ \cdot mol^{-1}$ (0.478 $kcal \cdot mol^{-1}$). Since the metadynamics modeling was performed in the NVT ensemble, we calculate the Helmholtz free energy as a result.

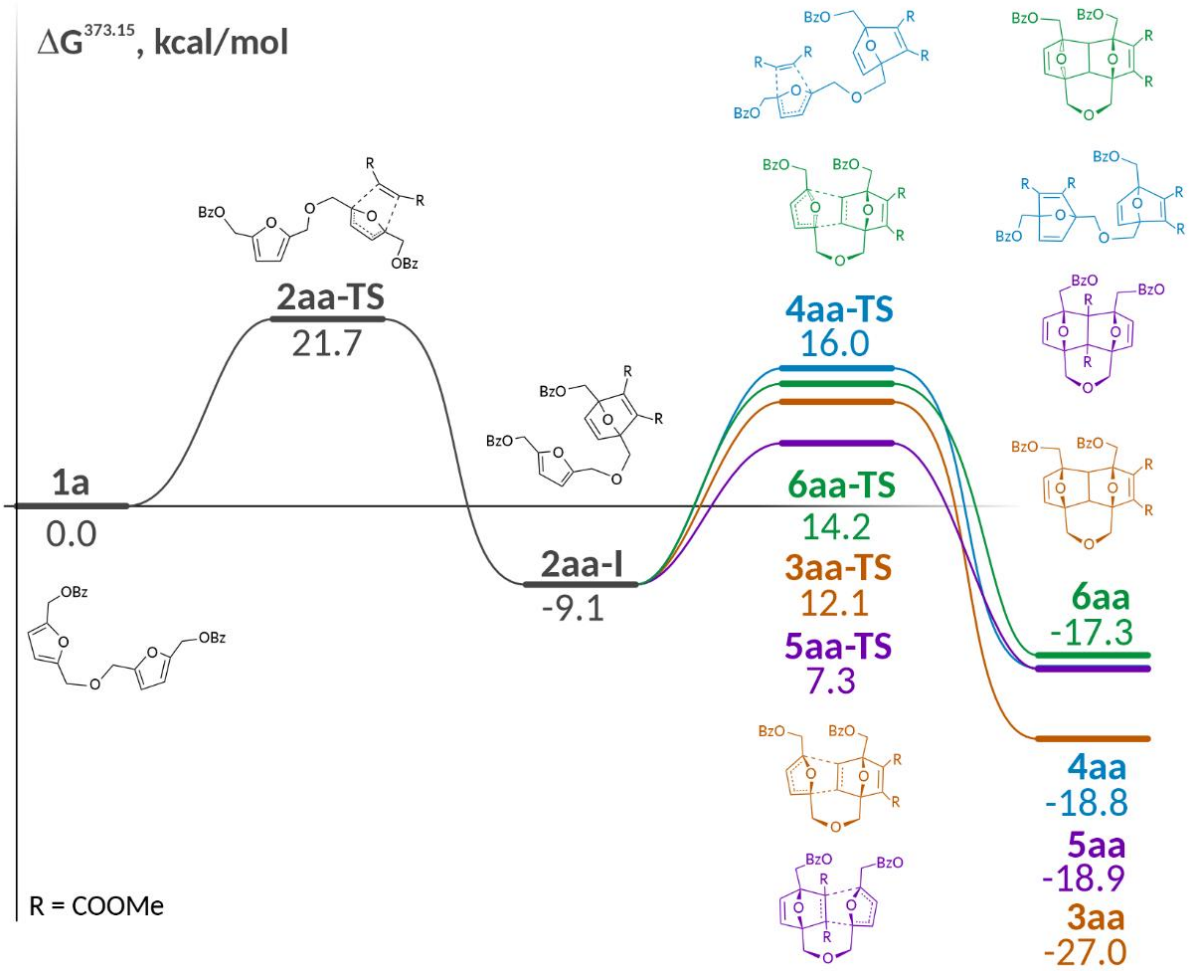


Figure S111. Gibbs free energy profile for the cycloaddition reaction involving substrate **1a**.

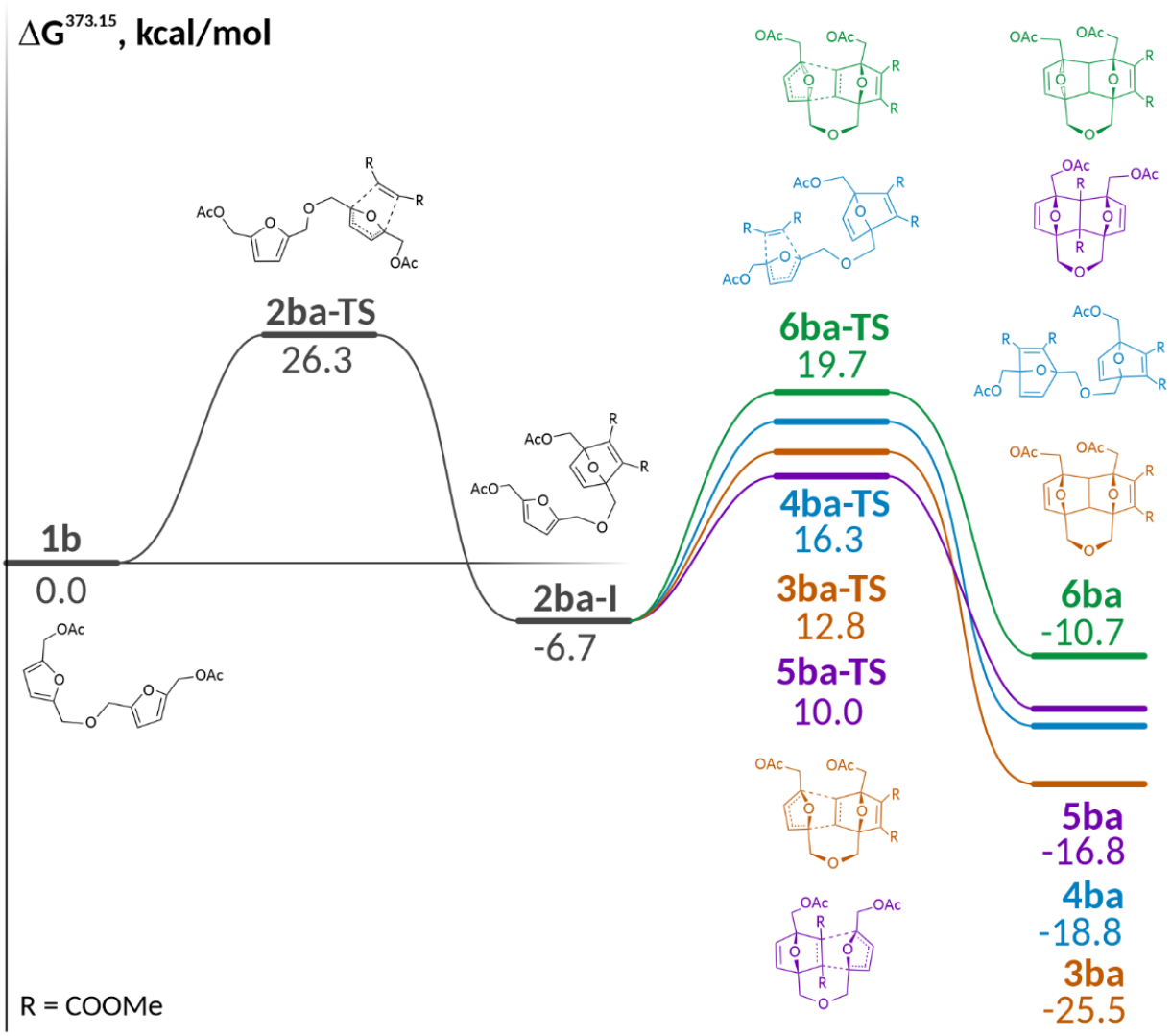


Figure S112. Gibbs free energy profile for the cycloaddition reaction involving substrate **1b**.

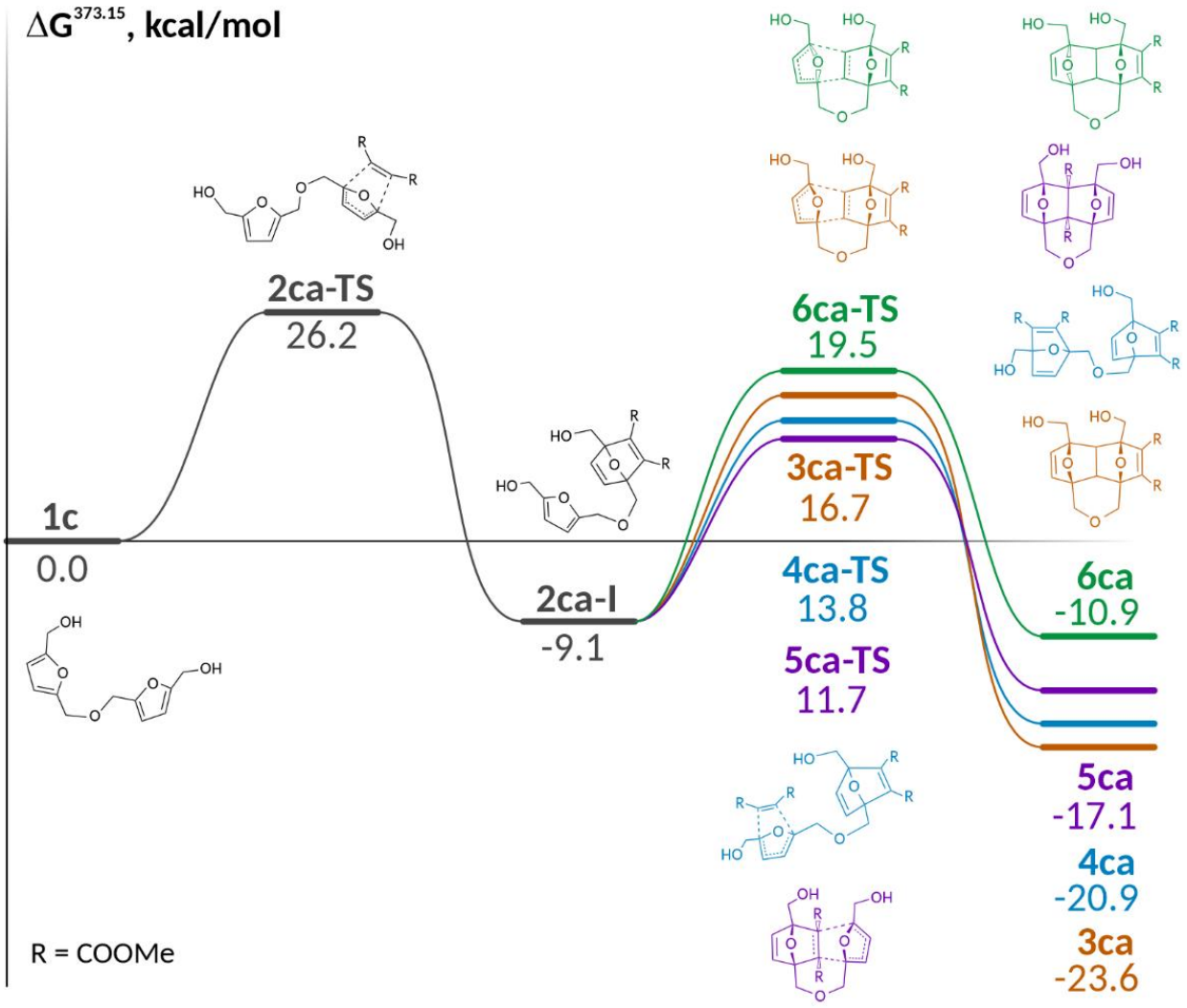


Figure S113. Gibbs free energy profile for the cycloaddition reaction involving substrate **1c**.

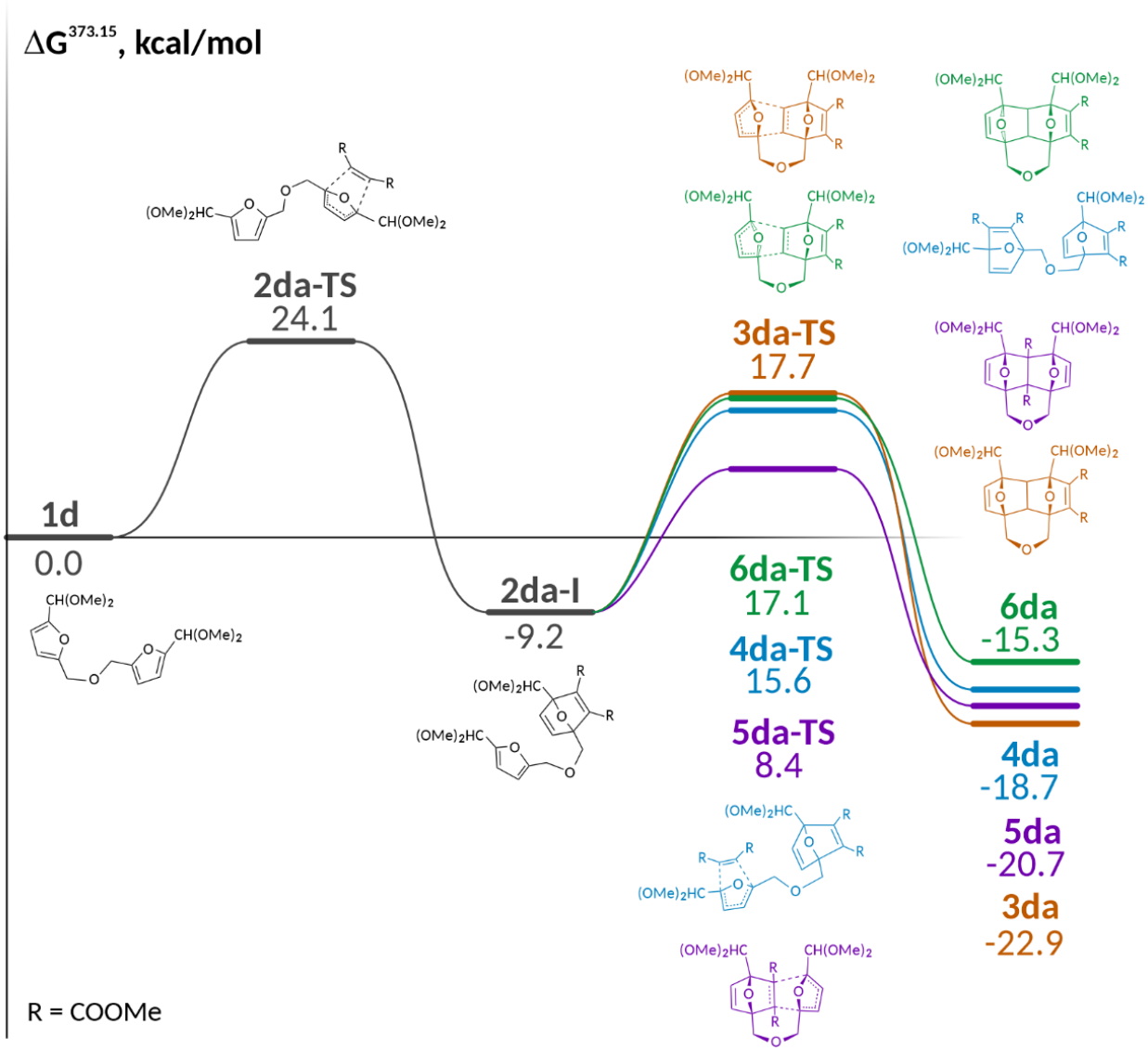


Figure S114. Gibbs free energy profile for the cycloaddition reaction involving substrate **1d**.

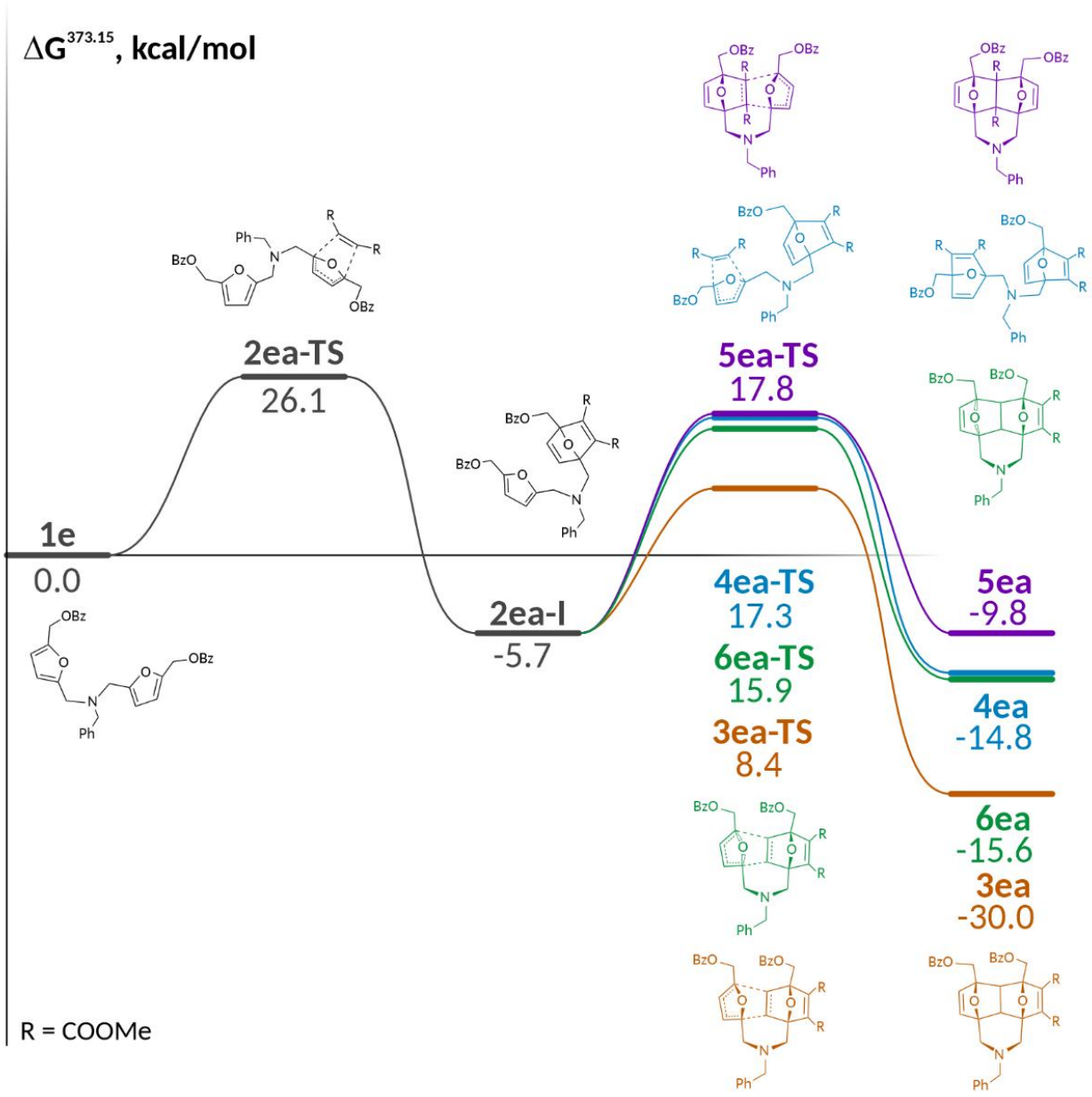


Figure S115. Gibbs free energy profile for the cycloaddition reaction involving substrate **1e**.

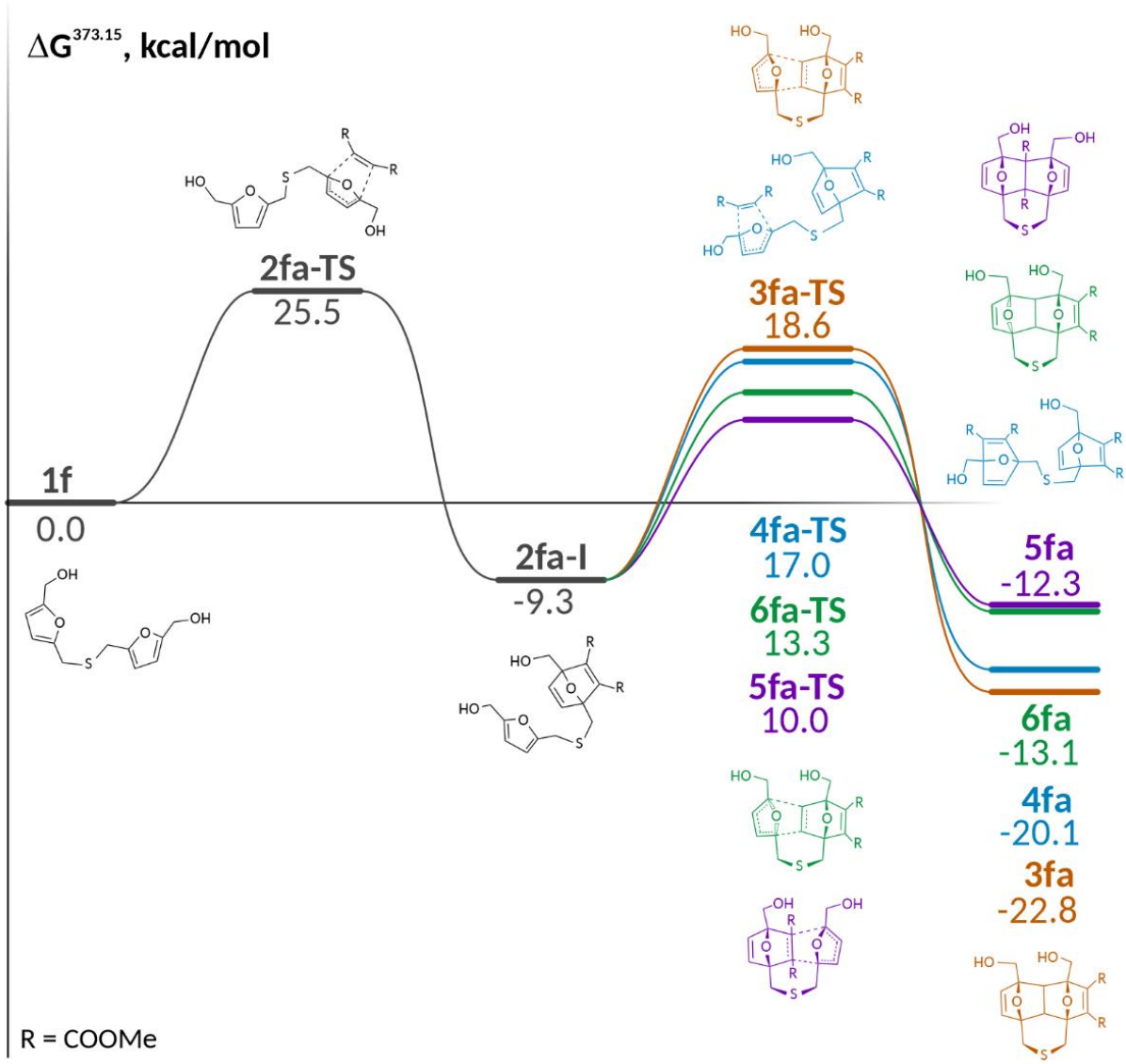


Figure S116. Gibbs free energy profile for the cycloaddition reaction involving substrate **1f**.

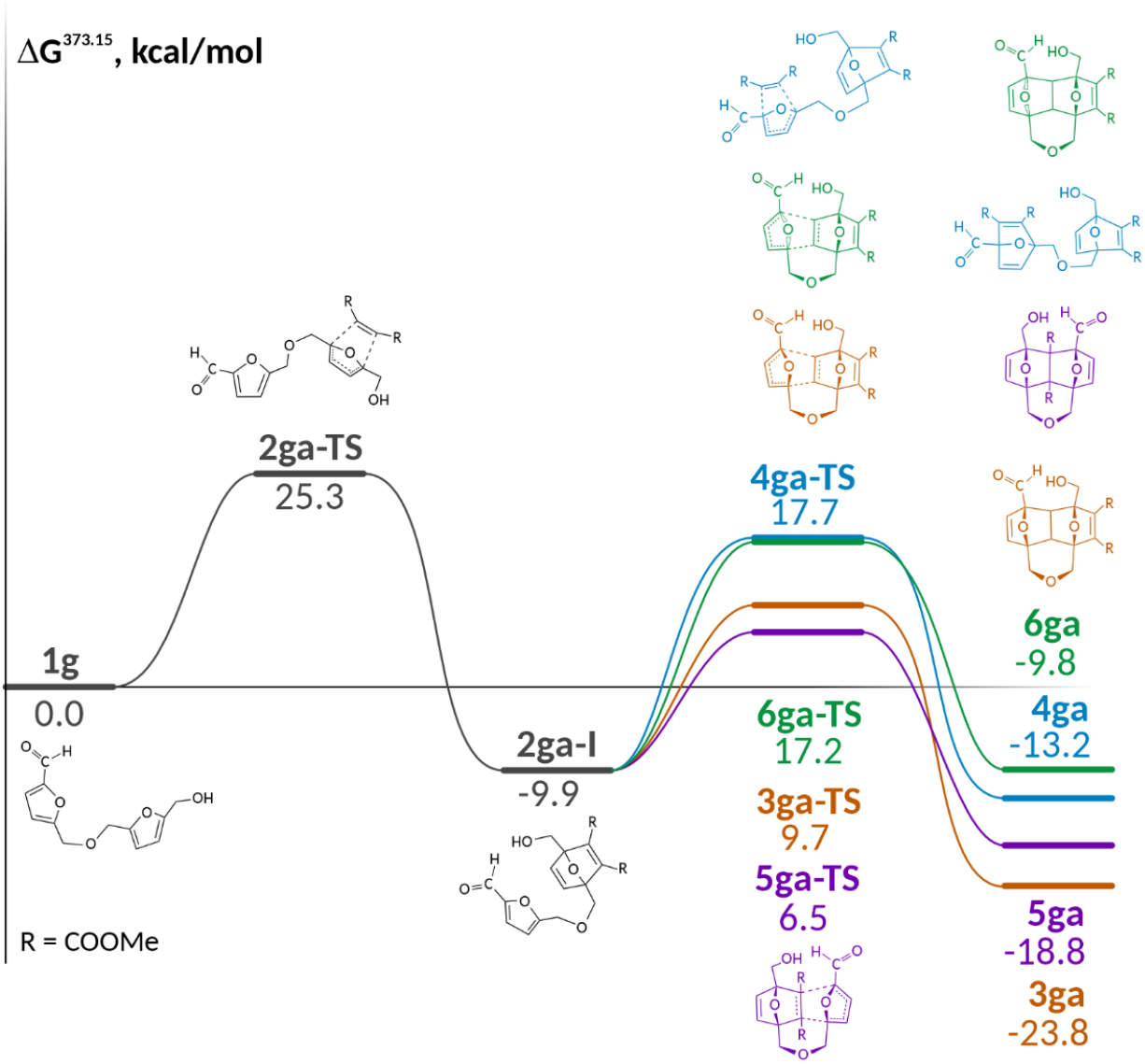


Figure S117. Gibbs free energy profile for the cycloaddition reaction involving substrate **1g**.

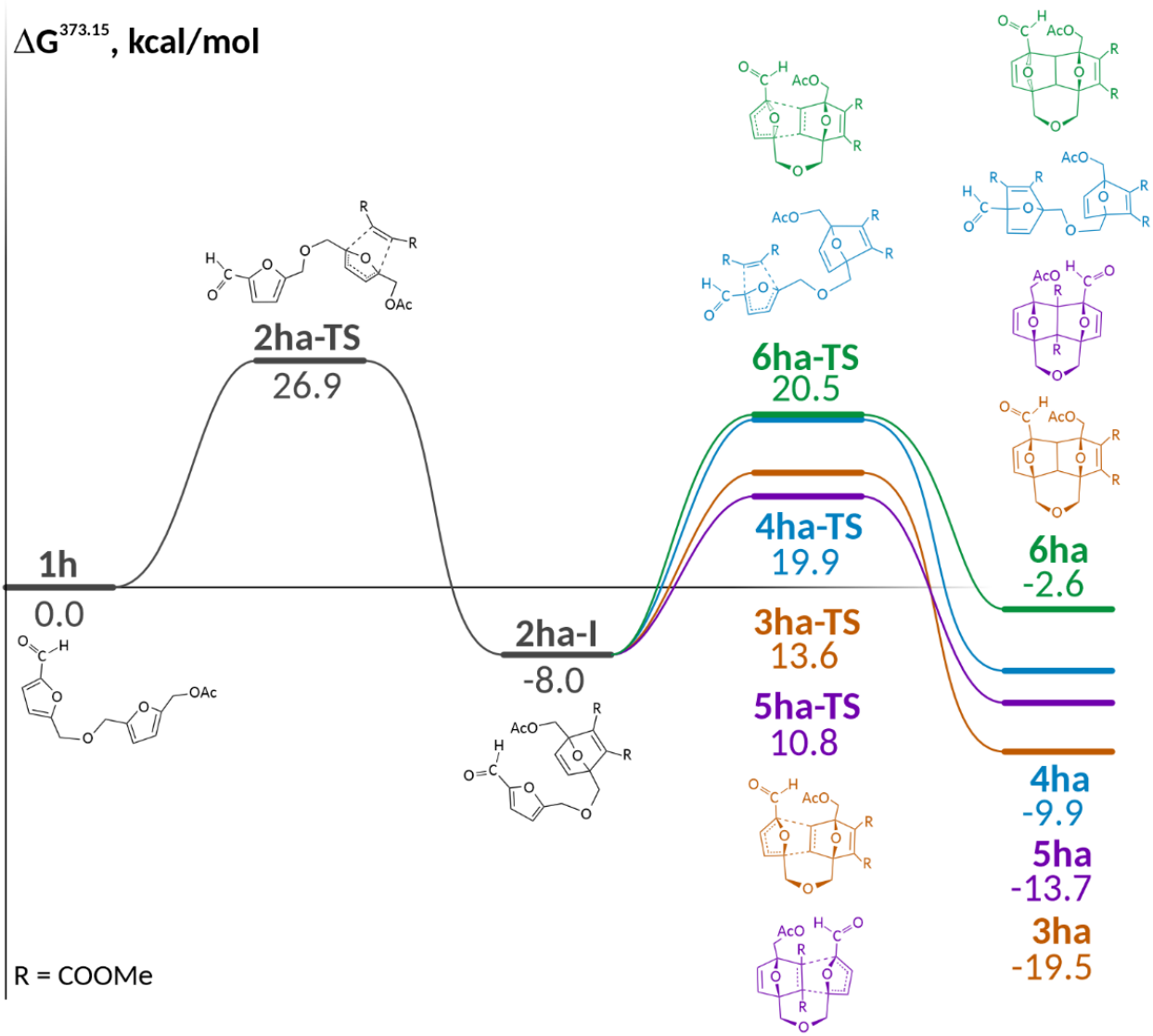


Figure S118. Gibbs free energy profile for the cycloaddition reaction involving substrate **1h**.

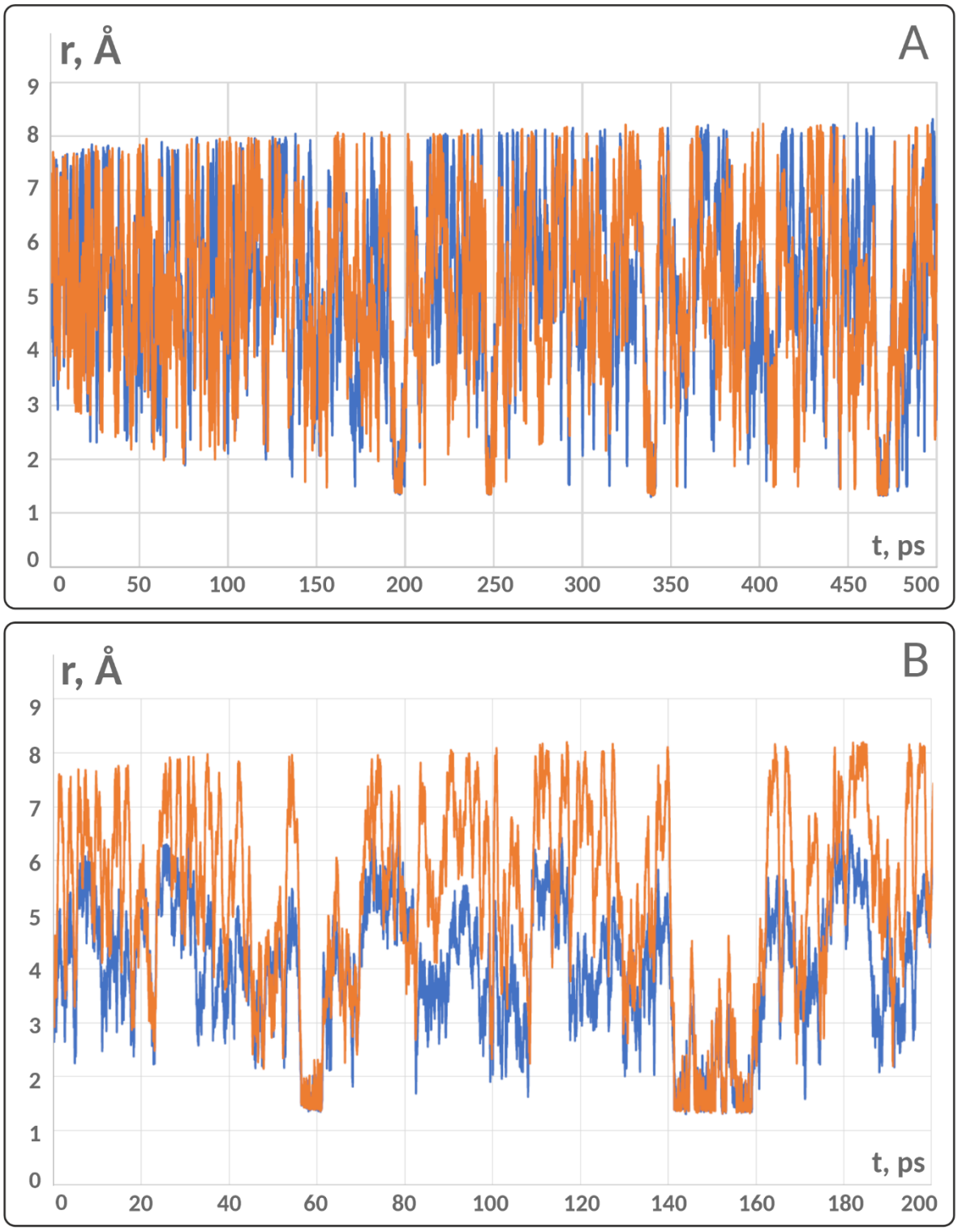


Figure S119. (A) The dependence of the values of collective variables on time for the product **4ca** formation process for substrate **1c**; (B) the dependence of the values of collective variables on time for the product **3ca** formation process for substrate **1c**; GFN2-XTB.

10. Molecular complexity indexes

Molecular complexity in organic chemistry is a rather subjective parameter. However, there are ways to mathematically characterize this property. For this purpose, various indexes based on the graph representation of molecules have been developed.[13] The most accurate results are shown by the augmented valence complexity index AVC[13d] (Equation 1) and the C_m index (Equation 2).[13f]

$$\mathrm{AVC} = \sum_{i=1} \sum_{j=1} n_j \left(\frac{1}{2}\right)^{d_{ij}} \tag{1}$$

Where i and j are the numbers of symmetrically nonequivalent vertices of the graph, n_j is the number of vertex connections, and d_{ij} is the minimal number of connections between vertices i and j. The authors define the AVC (augmented valence complexity) index as the sum of augmented valences of a single member of each equivalence class of vertices of the graph. The augmented valence of a vertex i is the sum of its valence n_1 and the valences of other vertices n_j with different weights $(1/2)^{dij}$ depending on d_{ij}, the minimal number of connections between vertices i and j. The equivalence class is a set of symmetrically equivalent vertices: if a number of vertices are symmetrically equivalent, they are assigned to one equivalence class, and only one of them is taken into account in the calculation of the AVC index. AVC is a useful measure of molecular complexity, and it takes into account the size, density and symmetry of the graph. Later, the C_m index was developed, taking into account additional factors such as heteroatoms and stereoisomers:

$$C_m = \sum_i d_i e_i s_i \log_2(V_i\, b_i) - \frac{1}{2} \sum_j d_j e_j s_j \log_2(V_j b_j) \tag{2}$$

Where i is the number of an atom, j is the number of an atom in the set of chemically equivalent atoms, V_i is the number of valence electrons of an atom, and b_i is the number of bonds of an atom. The bonding situation is described by the variables d_i for the number of chemically nonequivalent bonds to positions with $V_i b_i > 1$, e_i for the number of different elements or isotopes in the atom's microenvironment, and s_i for the number of isomeric possibilities at a given position. The unit of C_m is mcbit, which represents a bit of molecular complexity.

11. References

1. K. Mliki, M. Trabelsi, *Ind. Crops Prod.*, 2015, **78**, 91.
2. G. M. Averochkin, E. G. Gordeev, M. K. Skorobogatko, F. A. Kucherov, V. P. Ananikov, *ChemSusChem*, 2021, **14**, 3110.
3. Bruker AXS Inc., Madison, Wisconsin, USA, 2019.
4. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3.
5. G. M. Sheldrick, *Acta Crystallogr. A Found Adv.*, 2015, **71**, 3.
6. G. M. Sheldrick, *Acta Crystallogr. A Found Adv.*, 2015, **C 71**, 3.
7. (a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; (b) C. Adamo, V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.
8. (a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650; (b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639.
9. (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (b) H. Kruse, S. Grimme, *J. Chem. Phys.*, 2012, **136**, 154101.
10. M. J. Frisch, et al., in *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.
11. C. Bannwarth, S. Ehlert, S. Grimme, J Chem Theory Comput., 2019, **15**, 1652.
12. (a) F. Neese, *WIREs Comput. Mol. Sci.*, 2012, **2**, 73; (b) F. Neese, *WIREs Comput. Mol. Sci.*, 2018, **8**, e1327.
13. (a) S. H. Bertz, *J. Am. Chem. Soc.*, 1981, **103**, 3599; (b) S. H. Bertz, *Bull. Math. Biol.* 1983, **45**, 849; (c) J. B. Hendrickson, P. Huang, A. G. Toczko, *J. Chem. Inf. Comput. Sci.*, 1987, **27**, 63; (d) M. Randić, D. Plavšić, *Croat. Chem. Acta*, 2002, **75(1)**, 107; (e) M. Randić, D. Plavs□ić, *Int. J. Quantum Chem.*, 2003, **91**, 20; (f) T. Böttcher, *J. Chem. Inf. Model.*, 2016, **56**, 462.