Supporting Information

Synthesis of a Highly Aromatic and Planar [10]Annulene

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General Information

Common Experimental Variables

Unless otherwise noted, all reactions were performed under an inert atmosphere of argon. An inert argon atmosphere was established by either purging for 5 minutes with a high flow or by vacuum purging with hivac/Ar. Flash column chromatography was done with Geduran® Si 60 silica gel (40-63 µm). Fractions were monitored by analytical TLC using glass-backed plates pre-coated with (0.25mm) silica gel 60 F_{254}, plates were visualized with UV light (254 nm) and by staining with either a phosphomolybdic acid (5%) solution containing a trace of ceric sulfate in aqueous sulfuric acid (5% v/v) or with a basic $KMnO_4$ solution (1.5g $KMnO_4$, 10g K_2CO_3 and 1.25mL 10% aqueous NaOH in 200 mL H_2O). Concentration refers to removal of volatiles with a rotary evaporator (2-30 torr) or by rapid stirring under hi-vac (0.1-0.5 torr). Low temperatures (< -20 °C) were obtained with the help of a Neslab Cryotrol using absolute ethanol as the cooling bath solvent. Reactions using UV light were carried out in a Rayonet photochemical reactor

with Hg-vapour lamps coated to absorb light under 300 nm. The reactor was typically air cooled by passing filtered air through a coil immersed in the cryotrol bath at -78 °C. All reactions were stirred using a teflon coated magnetic stir bars at a rate sufficient to maintain homogeneity. All reaction solvent concentrations indicate the concentration of the limiting reagent.

Common Instrumental Variables

High resolution mass spectra (HRMS) and low-resolution mass spectra (LRMS) were obtained on a VG70E double focusing high resolution spectrometer. Electron impact (EI) ionization was accomplished at 70 eV. Alternatively, HRMS was obtained on a LC-MS/MS time-of-flight high resolution spectrometer with electrospray ionization (ESI). Infrared spectra were recorded on a Fourier transform interferometer using a diffuse reflectance cell (DRIFT) or an attenuated total reflectance Fourier transform infrared (ATR-IR) spectrometer. The latter required only a thin film of material.

Unless otherwise noted, NMR spectra were measured in $CDCl_3$ solution at either 500 MHz or 600 MHz for ^{1}H and 125 MHz or 150 MHz for ^{13}C. Residual non-deuterated solvent was used as the internal chemical shift standard [$CDCl_3$(7.26 δH, 77.0 δC); CD_3OD (3.31 δH, 49.00 δC]. ^{1}H NMR chemical shifts and coupling constants were determined by assuming first-order behaviour where appropriate. Clear deviations are specified by indicating an apparent (ap.) likeness to a signal (e.g. ap. t). Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), sep (septet), m (multiplet) and occasionally described as broad (br); the list of coupling constants (*J*) corresponds to the order of the multiplicity assignment and are reported to the nearest 0.1 Hz. ^{13}C NMR assignments were made on the basis of chemical shift. Quantitative ^{1}H-NMR was obtained with trichloroethylene and by setting pulse delay time to 10s to ensure complete relaxation.

Materials

Unless otherwise stated, all solvents were dried using a Braun Solvent Purification System (SPS) and stored over 4 Å sieves (pellets) that were activated by heating to 250-300 °C at 0.1-0.5 torr for 16 h. Typically solvents obtained from the SPS were exposed to the dried sieves for >3 days prior to use. Potassium *tert*-butoxide was either sublimed prior to use or purchased as a 1M solution in dry THF. Tertiary amine bases (diisopropylethylamine and triethylamine) were distilled and dried by storage over KOH pellets. Unless otherwise noted all other reagents were purchased and deemed to be of acceptable purity for direct use.

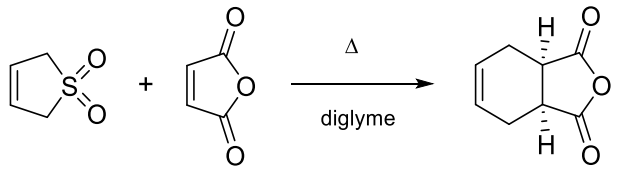
Computational methods

Unless otherwise stated, all geometry minimizations, frequency calculations and NMR predictions were done with either Gaussian09 or Gaussian16 packages. All single point energies and frequencies were computed at the M062X/6-31+G(d,p). Frequency calculations were done to confirm the absence of

negative frequencies. Natural bond orbital (NBO) calculations were done with either NBO6.0 or NBO7.0. Anisotropy of the induced ring current (AICD) images of the induced current density were obtained with AICD3.0.3 exclusively from the π-orbitals using the recommended isosurface parameters (0.05) and by positioning the magnetic field perpendicular to the plane of the aromatic ring. All computed isotropic chemical shifts were obtained with M062X/6-31+G(d,p) geometries at the B3LYP/6-311+G(2d,p) level of theory unless otherwise noted. Isotropic shifts were scaled according to either the Hoye *et al.* protocol[1] or the Cheshire database (http://cheshirenmr.info/index.htm). Coupling constants were computed at the B3LYP/6-31+G(d,p) level of theory and only considered Fermi contact contributions. Nucleus-independent chemical shifts (NICS) calculations were done at the M062X/6-31+G(d,p) geometries with Bqs that were placed using a python script that automatically locates aromatic rings (https://github.com/KarnParmar/NICS/).

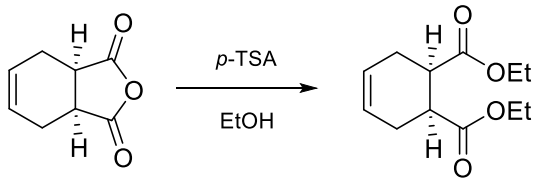
Experimental with spectra

Synthesis of 3a,4,7,7a-tetrahydroisobenofurane-1,3-dione (**14**)



Adapted from the literature.[2] Butadiene sulfone **12** (51.7 g, 437 mmol, 1 equiv.) and maleic anhydride **13** (42.9 g, 438 mmol, 1 equiv.) were heated in diglyme (48 mL) with a heat gun under atmospheric conditions until bubbling ensued. Careful intermittent heating was used to keep the solution bubbling. Heating stopped when the solvent was boiling, approximately 1.5 hours after beginning the reaction. A beige solid formed upon cooling the solution. Water was added and the solid was filtered. The solid was washed until the filtrate remained colourless, resulting in **14** as a light beige solid (45.7 g, 67%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.02– 5.97 (m, 2H), 3.40 – 3.35 (m, 2H), 3.40 – 3.34 (m, 2H), 2.63 (dddd, *J* = 15.5, 3.3, 3.3, 1.6 Hz, 2H), 2.31 (dddd, *J* = 14.8, 5.6, 5.6, 1.3 Hz, 2H).

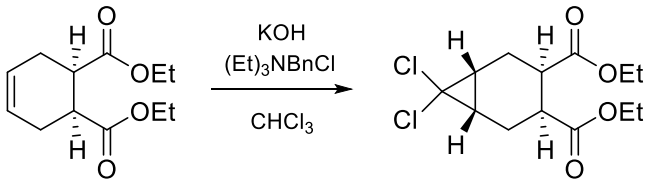
Synthesis of diethyl cyclohex-4-ene-1,2-carboxylate (**15**)



14 **15**

Adapted from the literature.[3] A round bottom flask containing anhydride **14** (45.4 g, 298 mmol, 1 equiv.), *p*-toluenesulfonic acid (4.56 g, 24.0 mmol, 0.08 equiv.) and ethanol (105 mL, 1.80 mol, 6 equiv.) was refluxed under atmospheric conditions for 17.5 hours at 100 °C. Toluene (54 mL) was added and the azeotrope was concentrated under reduced pressure. Ethanol (105 mL, 1.80 mol, 6 equiv.) was added and the solution was again refluxed at 100 °C for 23 hours under atmospheric conditions, after which toluene (54 mL) was added. The solution was again concentrated under reduced pressure. The resulting oil was diluted with diethyl ether and extracted twice with 3% Na_2CO_3(aq). The collected aqueous layers were washed with diethyl ether three times. The diethyl ether layers were then washed with water and dried over $MgSO_4$, filtered and concentrated. Purification *via* FCC (7:1 Hex:EtOAc) afforded **15** as a yellow oil (64.9 g, 96%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 5.39 – 5.65 (m, 2H), 4.16 (dq, *J* = 10.8, 7.1 Hz, 2H), 4.13 (dq, *J* = 10.8, 7.1 Hz, 2H), 3.03 – 3.02 (m, 2H), 2.57 – 2.52 (m, 2H), 2.36 – 2.32 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 6H).

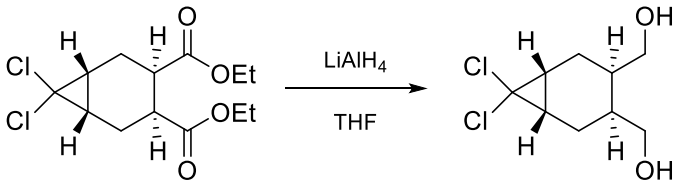
Synthesis of Diethyl (1*R*,6*S*)-7,7-dichlorobicyclo[4.1.0]heptane-3,4-dicarboxylate (**16**)



15 **16**

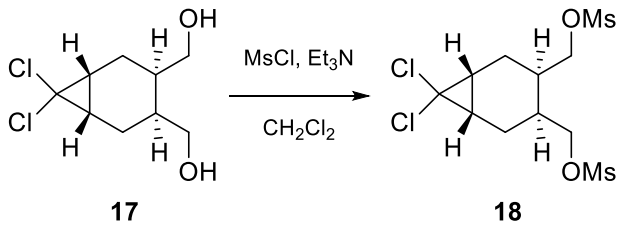
Adapted from the literature.[4] A 50% solution of NaOH(aq) (103 mL) was added to a solution of **15** (20.4 g, 90.4 mmol, 1 equiv.), chloroform (72.0 mL, 899 mmol, 10 equiv.) and triethylbenzyl ammonium chloride (11.1 g, 39.9 mmol, 0.44 equiv.) and stirred at room temperature under atmospheric conditions with a condenser. Any exotherms were controlled by an ice bath, which was necessary at larger scales. An additional 30 mL of chloroform was added once the solution was at room temperature. After 4 hours the reaction was quenched with water and 1 M HCl was added until pH 1. Dichloromethane was used to extract the aqueous layer three times. The organic layer was dried over magnesium sulfate, filtered, and concentrated. Purification *via* FCC (dichloromethane) resulted in **16** as a yellow oil (23.8 g, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.14 (dq, *J* = 7.2, 3.8 Hz, 2H), 4.13 (dq, *J* = 6.4, 4.5 Hz, 2H), 2.79 - 2.76 (m, 2H), 2.53 – 2.46 (m, 2H), 1.93 – 1.88 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 6H).

Synthesis of ((1*R*,6*S*)-7,7-dichlorobicyclo[4.1.0]heptane-3,4-diyl)dimethanol (**17**)



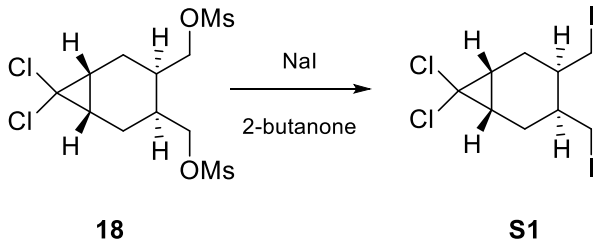
Adapted from the literature.[4] Bicyclo **16** (10.8 g, 34.9 mmol, 1 equiv.) was quantitatively transferred to a cooled round bottom flask containing $LiAlH_4$ (2.28 g, 60.2 mmol, 1.7 equiv.) and THF (174 mL). The flask was warmed to ambient temperature and stirred for 6 hours under inert atmosphere. The solution was cooled in an ice-water bath and quenched with cold water followed by 1 M HCl until the pH 2. The aqueous layer was extracted five times with dichloromethane and the organic layer was dried over $MgSO_4$ and concentrated, resulting in **17** as a yellow oil. Purification was achieved through FCC (EtOAc) affording **17** as a white solid (7.38 g, 94%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 3.63 (dd, *J* = 10.8, 7.2 Hz, 2H), 3.58 (dd, *J* = 11.4, 4.2 Hz, 2H), 2.43 (br s, OH), 2.09 – 2.04 (m, 2H), 1.81 – 1.77 (m, 2H), 1.73 – 1.70 (m, 4H).

Synthesis of ((1*R*,6*S*)-7,7-dichlorobicyclo[4.1.0]heptane-3,4-diyl)bis(methylene)dimethanesulfonate (**18**)



Adapted from the literature.[4] Triethylamine (13.7 mL, 98.2 mmol, 3 equiv.) was slowly added to a cooled flask containing **17** (7.38 g, 32.8 mmol, 1 equiv.), dichloromethane (30 mL) and methanesulfonyl chloride (6.1 mL, 79 mmol, 2.4 equiv.). The solution was stirred at room temperature under inert atmosphere and was quenched with distilled water after 5 hours. The aqueous layer was extracted once with dichloromethane and washed twice with brine. The collected organic layers were dried over $MgSO_4$, filtered and concentrated. Recrystallization (Hex:Dichloromethane) yielded **18** as an orange solid (12.0 g, 96%). Dimesylate **18** was also produced when diol **13** (41.8 mmol) was carried forward without purification (15.1 g, 95% over 2 steps). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.19 (dd, *J*= 10.0, 7.0 Hz, 2H), 4.11 (dd, *J* = 10.3, 6.8 Hz, 2H), 3.07 (s, 6H), 2.18 – 2.11 (m, 2H), 2.00 – 1.93 (m, 2H), 1.84 – 1.80 (m, 4H).

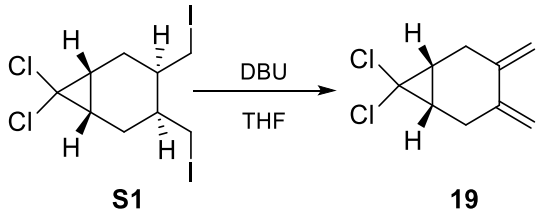
Synthesis of (1*R*,6*S*)-7,7-dichloro-3,4-bis(iodomethyl)bicyclo[4.1.0]heptane (**S1**)



18 **S1**

Adapted from the literature.[5] Dimesylate **18** (7.88 g, 20.7 mmol, 1 equiv.) was quantitatively transferred with 2-butanone (103 mL) to a round bottom flask containing sodium iodide (13.7 g, 158 mmol, 7.7 equiv.). The solution was refluxed at 80 °C for 22 hours under inert atmosphere. Dichloromethane was added once the solution had cooled and was extracted with water three times. The organic layer was dried over $MgSO_4$, filtered and concentrated, affording **S1** as a yellow-orange oil. The product was carried to the next step without purification. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.10 (dd, *J* = 5.3, 9.9 Hz, 2H), 2.97 (dd, *J* = 4.2, 4.2 Hz, 2H), 2.02 – 1.97 (m, 4H), 1.86 – 1.83 (m, 2H), 1.78 – 1.76 (m, 2H).

Synthesis of (1*R*,6*S*)-7,7-dichloro-3,4-dimethylenebicyclo[4.1.0]heptane (**19**)

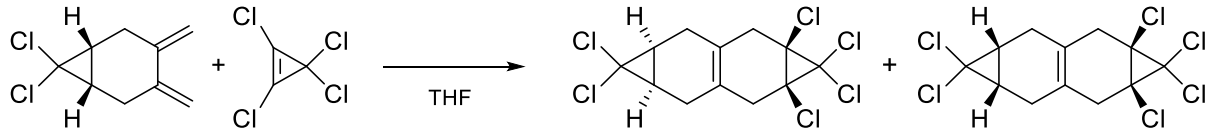


S1 **19**

Adapted from the literature.[5] DBU (15.7 mL, 105 mmol, 5.1 equiv.) was slowly added to a cold round bottom flask containing crude **S1** (20.7 mmol, 1 equiv.) and THF (207 mL) under inert atmosphere. The round bottom flask was removed from the ice-water bath and stirred at room temperature for 48.5 hours. Water was added to the solution and was subsequently extracted with dichloromethane three times. The organic layer was dried over $MgSO_4$, filtered and concentrated. Purification *via* flash column chromatography (7:3 Hex:EtOAc) produced **19** as a pungent, yellow oil (3.27 g, 84% over 2 steps). In practice, the sample was eluted through a silica plug with hexanes with no noticeable reduction in purity. The material was stored (up to several weeks) as a dilute solution in deoxygenated dichloromethane at -20 °C when it was not possible to use immediately. **^{1}H-NMR**[6] (600 MHz, $CDCl_3$): δ 5.26 – 5.25 (m, 2H), 4.82

– 4.81 (m, 2H), 2.79 – 2.74 (m, 2H), 2.26 (dddd, *J* = 16.1, 4.0, 3.8, 1.9 Hz, 2H), 1.85 – 1.80 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 93 140.0, 139.7, 111.4, 110.9, 69.4, 50.9, 39.4, 36.9, 29.1; **HRMS**: (FD) *m/z*: [M] Calcd for $C_9H_9Cl_3$ 221.9769; Found: 221.9772; **FTIR** (KBr thin film) ν_{max} (cm^{-1}) 2960, 2890, 2832, 1425, 1264, 1147, 973, 895, 823, 739.

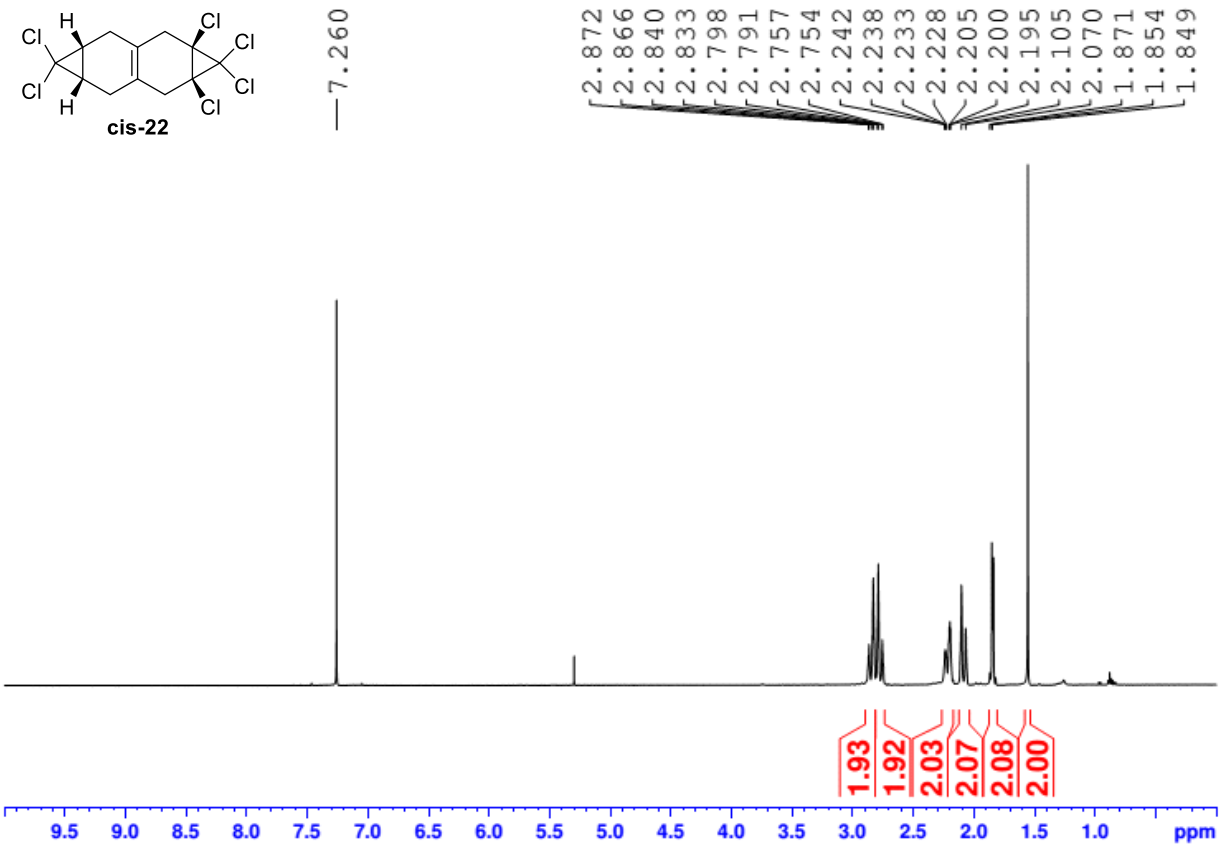
Synthesis of (1a*R*,3a*R*,4a*S*,6a*S*)-1,1,1a,4,4,6a-hexachloro-1,1a,2,3,3a,4,4a,5,6,6a-dodecahydrodicyclopropa[*b*,*g*]naphthalene and (1a*R*,3a*S*,4a*R*,6a*S*)-1,1,1a,4,4,6a-hexachloro1,1a,2,3,3a,4,4a,5,-6,6a-dodecahydrodicyclopro-pa[*b*,*g*]naphthalene (**22**)



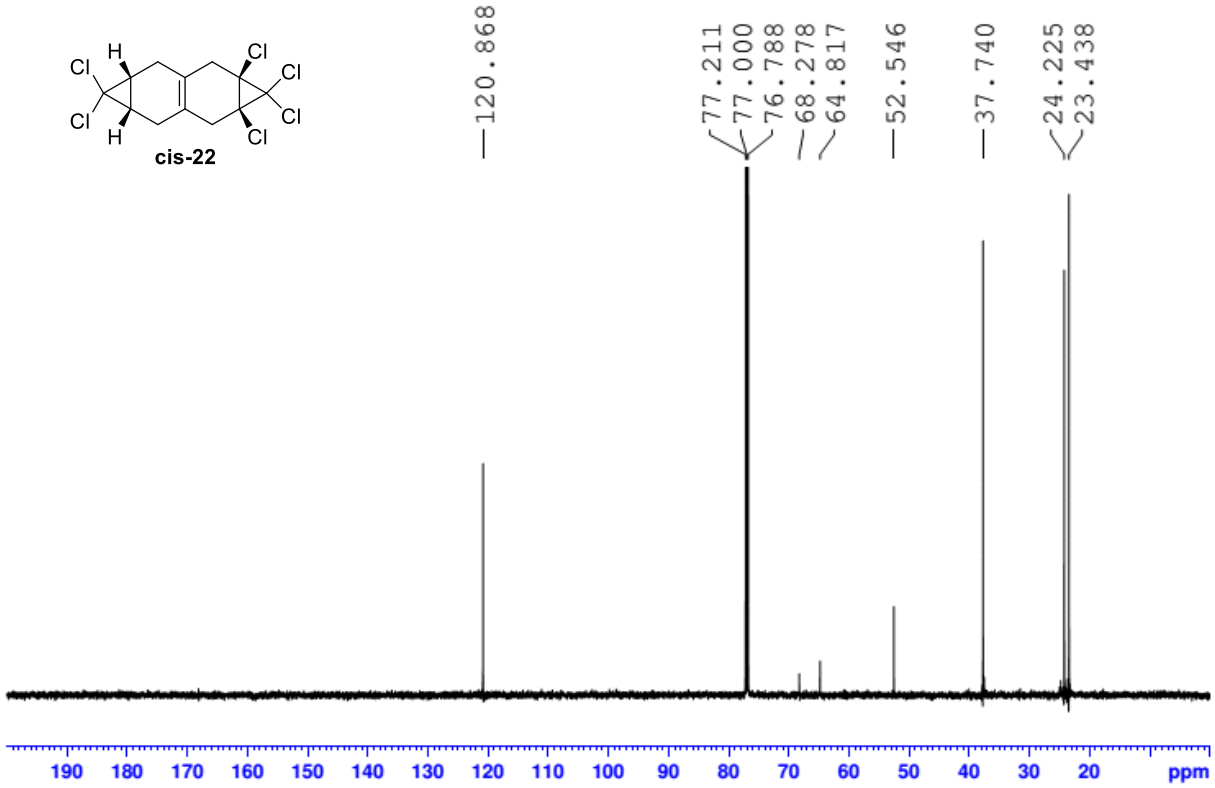
19 **21** ***trans*-22** ***cis*-22**

Tetrachlorocyclopropene (**21**)[7] (1.44 mL, 11.7 mmol, 1 equiv.) was added to a solution of diene **19** (2.22 g, 11.7 mmol, 1 equiv.) in THF (11.8 mL) and stirred at room temperature for 72 hours under inert atmosphere. The solution was concentrated and coevaporated with dichloromethane three times. Recrystallization (Hex:Dichloromethane) afforded white crystals containing ***trans*-22** and ***cis*-22** in a 3:1 ratio (2.62 g, 61%). In practice, 1.5 equivalents of crude tetrachlorocyclopropene was generally added and the reaction was allowed to proceed for 96 hours to afford greater yields (~79%). Major diastereomer ***cis*-22**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.91 (d, *J* = 16.8 Hz, 2H), 2.75 (d, *J* = 16.8 Hz, 2H), 2.32 (d, *J* = 20.3 Hz, 2H), 1.97 (d, *J* = 17.0 Hz, 2H), 1.86 – 1.82 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 121.1, 68.5, 52.8, 37.9, 24.4, 23.6; **HRMS**: (FD) *m/z*: [M] Calcd for $C_{12}H_{10}Cl_6$ 363.8914; Found: 363.8903; **FTIR** (KBr film) ν_{max} (cm^{-1}) 2895, 2828, 1431, 1424, 1075, 1045, 950, 870, 847, 782, 611, 552; **Melting range** = 157.2 - 157.8 °C. Minor diastereomer ***trans*-22**: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.84 (d, *J* = 16.5 Hz, 2H), 2.78 (d, *J* = 17.1 Hz, 2H), 2.22 (d, *J* = 18.0 Hz, 2H), 2.09 (d, *J* = 17.0 Hz, 2H), 1.87 – 1.82 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 121.0, 68.6, 64.7, 52.9, 37.6, 24.9, 23.7; **HRMS:** (FD) *m/z*: [M] Calcd for $C_{12}H_{10}Cl_6$ 363.89137; Found: 363.8921; **FTIR** (ATR) ν_{max} (cm^{-1}): 2921, 2896, 2851, 1718, 1426, 1325, 1219, 1157, 1046, 993, 914, 846, 804, 779, 610, 549, 505;
Melting range = 182.1 – 185.1 °C.

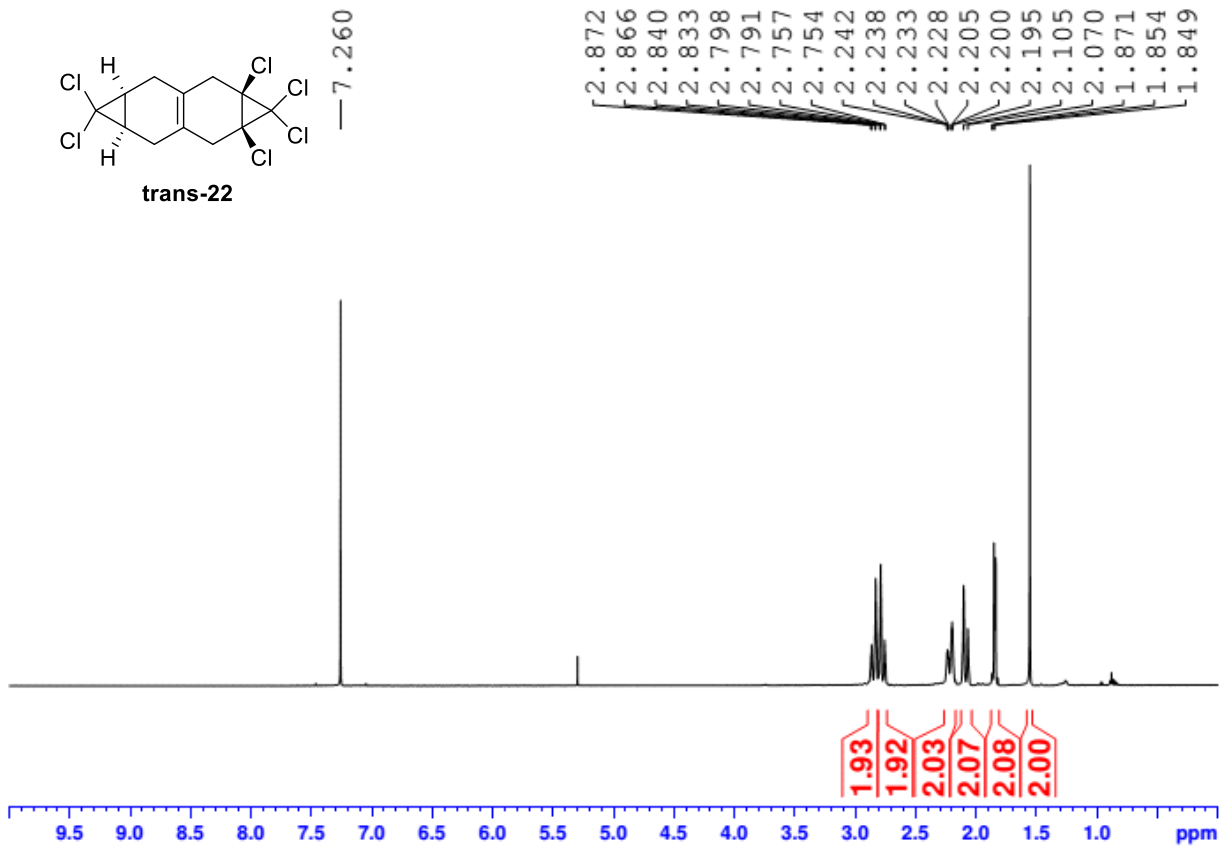
Compound *cis*-22, 500 MHz, ^{1}H-NMR, $CDCl_3$



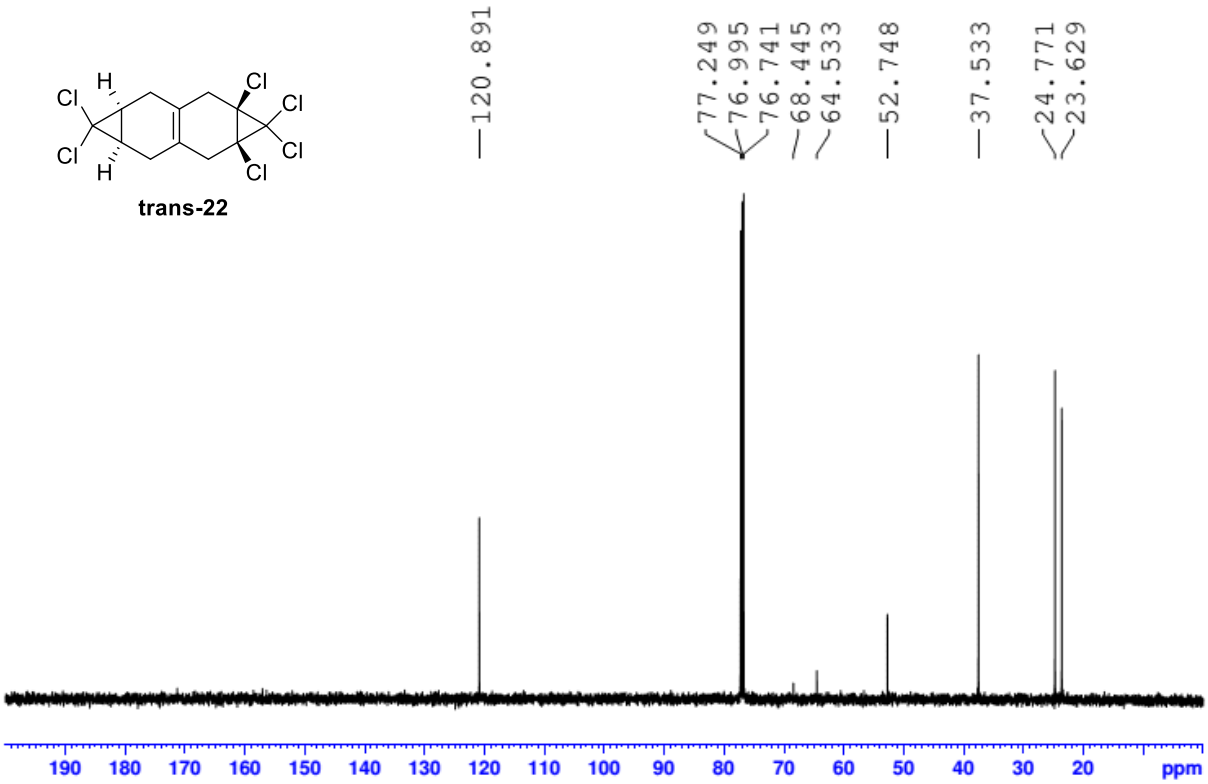
Compound *cis*-22, 150 MHz, ^{13}C-NMR, $CDCl_3$



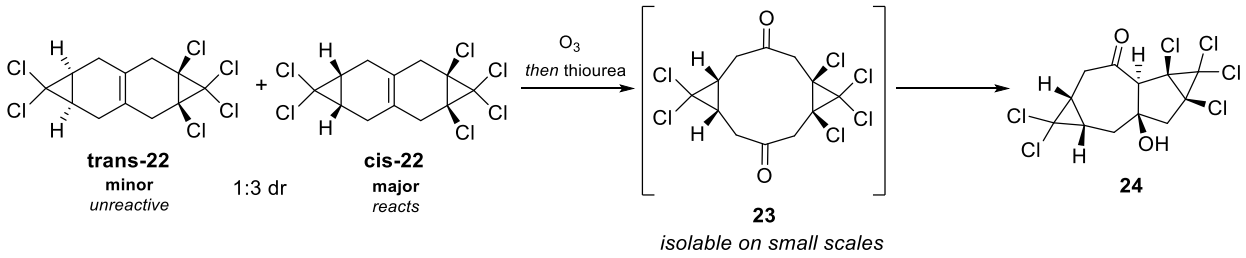
Compound *trans*-22, 500 MHz, ^{1}H-NMR, $CDCl_3$



Compound *trans*-22, 125 MHz, ^{13}C-NMR, $CDCl_3$



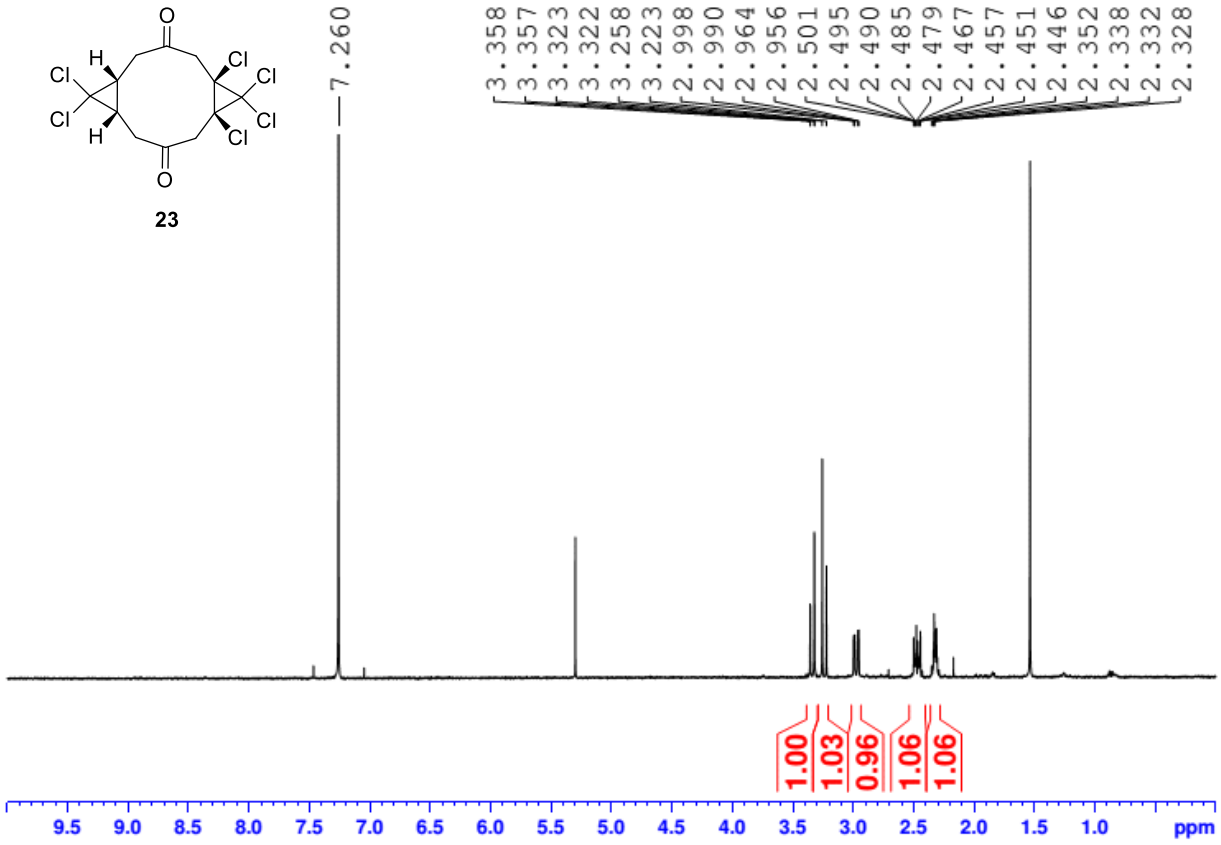
Synthesis of (1R,5R,7S,11S)-1,6,6,11,12,12-hexachlorotricyclo[9.1.0.05,7]dodecane-3,9-dione (19) and (1bS,5aR)-1,1,1a,4,4,6a-hexachloro-5a-hydroxydecahydrodicyclopropa[a,f]azulen-2(1H)-one (**23**)



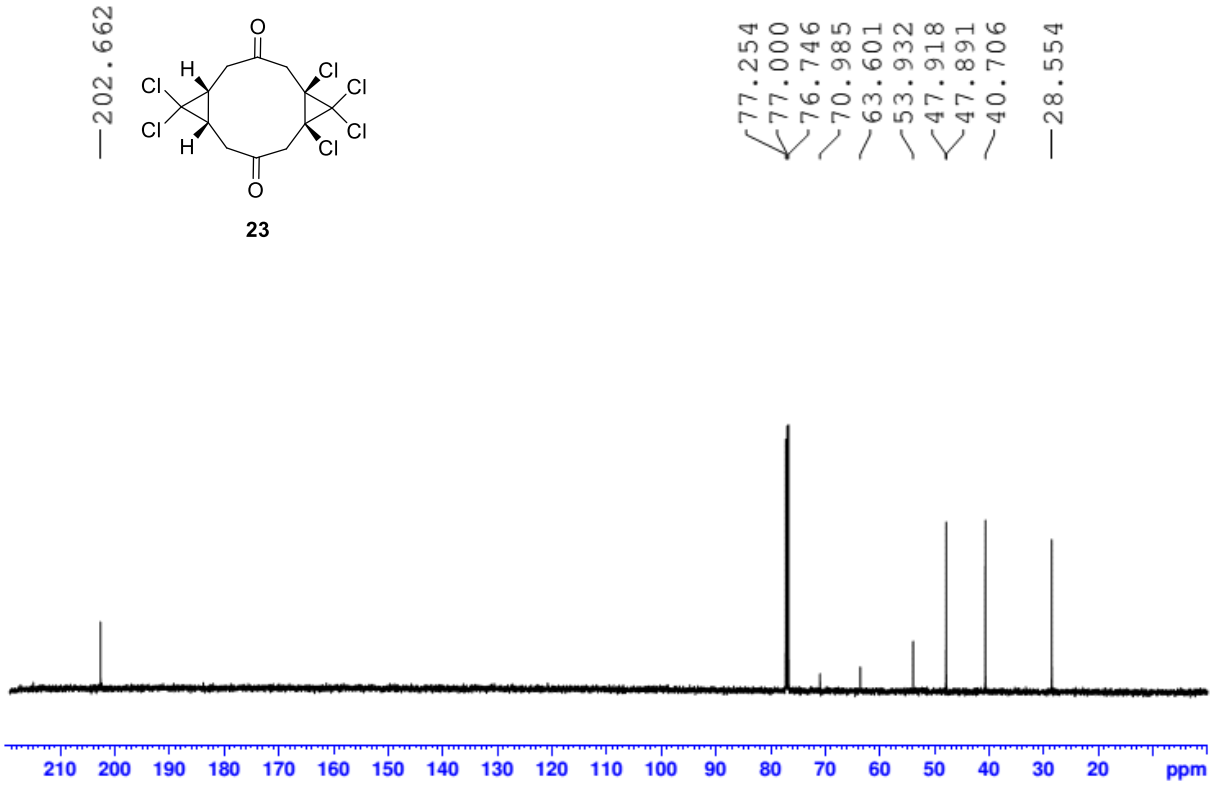
Ozone was bubbled through a solution of adduct **22** (***cis*-22**/***trans*-22** = 7.4:1) (200 mg, 0.55 mmol, 1 equiv.), 5:1 dichloromethane:MeOH (27.6 mL), and $NaHCO_{3(aq)}$ (5 mg, 0.06 mmol, 0.0013 equiv.) at -78 °C under atmospheric conditions. Oxygen was bubbled through the solution when a blue coloured appeared

and was discontinued when the colour disappeared. The solution was transferred *via* cannula to a round bottom flask at 0 °C containing thiourea (61 mg, 0.80 mmol, 1.2 equiv.), $NaHCO_3$ (37 mg, 0.44 mmol, 0.66 equiv.), and dichloromethane (10 mL). The solution was stirred at 0 °C for 1 hour and extracted twice with water. The collected aqueous layers were washed twice with dichloromethane and the organic layers were dried over $MgSO_4$, filtered and concentrated. Recrystallization (petroleum ether:Dichloromethane) yielded rectangular, transparent crystals of **23** (67 mg, 30%). **dione 23: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 3.41 (d, *J* = 14.5 Hz, 2H), 3.24 (d, *J* = 14.5 Hz, 2H), 2.98 (dd, *J* = 14.2, 3.4 Hz, 2H), 2.50 – 2.45 (m, 2H), 2.35 – 2.31 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 202.8, 71.1, 63.7, 54.0, 48.0, 40.8, 28.7; **HRMS**: (ESI) *m/z*: [M+Na] Calcd for $C_{12}H_{10}Cl_6O_2$ 418.8704; Found: 418.8723; **FTIR** (KBr film) ν_{max} (cm^{-1}) 2973, 2932, 2895, 1732, 1436, 1349, 1313, 1099, 1090, 1041, 924, 794, 745, 608, 569, 516; **Melting range** = 148.1 – 149.0 °C.

Compound 23, 600 MHz, ^{1}H-NMR, $CDCl_3$



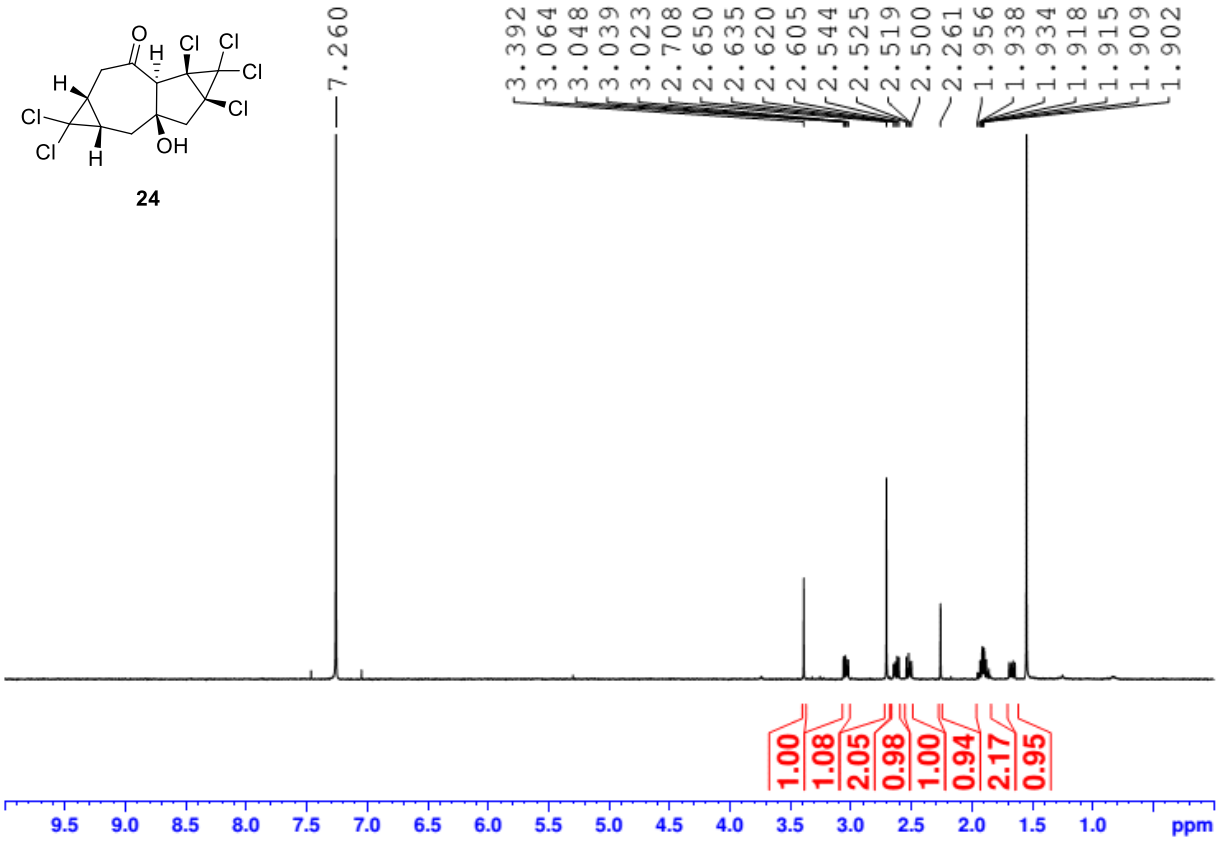
Compound 23, 125 MHz, ^{13}C-NMR, $CDCl_3$



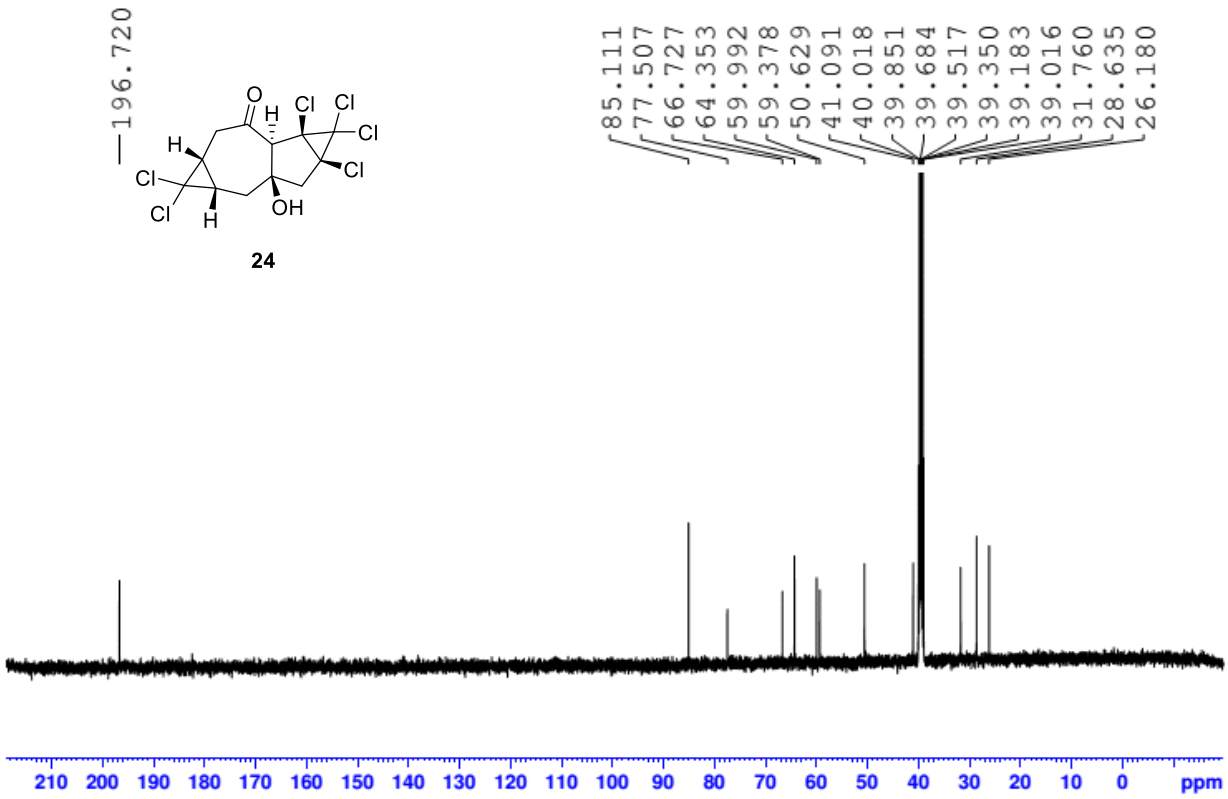
Larger batches (1–4 g) of this reaction gave larger amounts of aldol side product **24**. One experiment, for example, used 4.10 g of **22** and yielded products **23** and **24** as well as recovered starting material **22**. Aldol product **24** was separated from adducts **22** (***cis*-22**/***trans*-22** = 1:1.4) and dione **23** through filtration (dichloromethane) to yield **24** as a white solid (2.20 g, 49%).

transannular aldol adduct 24: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.39 (s, 1H), 3.04 (dd, *J* = 12.4, 7.7 Hz, 1H), 2.71 (s, 2H), 2.62 (dd, *J* = 15.2, 8.1 Hz, 1H), 2.52 (dd, *J* = 9.2, 6.2 Hz, 1H), 2.25 (s, OH), 1.96 – 1.86 (m, 2H), 1.67 (dd, *J* = 15.1, 8.4 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO): δ 196.7, 85.1, 77.5, 66.7, 64.4, 60.0, 59.4, 50.6, 41.1, 31.8, 28.6, 26.2; **HRMS**: (ESI) *m/z*: [M+Na] Calcd for $C_{12}H_{10}Cl_6O_2Na$ 418.8704; Found: 418.8720; **FTIR** (KBr Film) ν_{max} (cm^{-1}) 3438, 3039, 2944, 2927, 1711, 1432, 1383, 1286, 1117, 1046, 979, 902, 829, 791, 490; **Melting range** = 164.3 – 164.4 °C.

Compound 23, 500 MHz, ^{1}H-NMR, $CDCl_3$

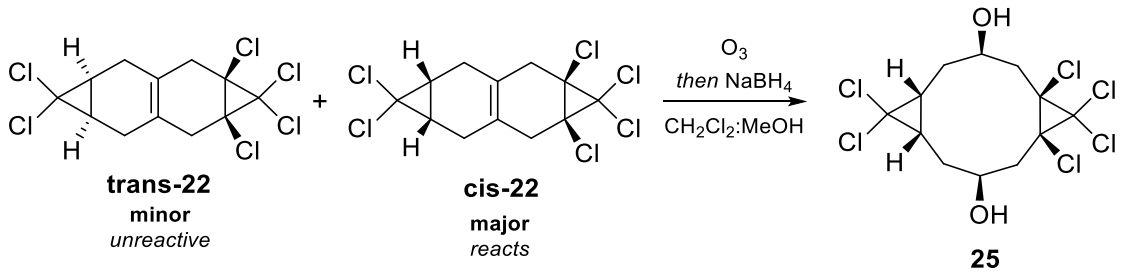


Compound 23, 125 MHz, ^{13}C-NMR, d_6-DMSO



24

Synthesis of (1*R*,3*R*,5*R*,7*S*,9*S*,11*S*)-1,6,6,11,12,12-hexachlorotricyclo[9.1.0.0^{5,7}]dodecane-3,9-diol (**25**)



trans-22
minor
unreactive

cis-22
major
reacts

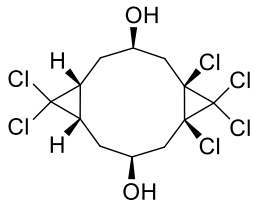
25

Ozone was bubbled through a solution of adduct **22** (***cis*-22**/***trans*-22** = 5.8:1) (358 mg, 0.97 mmol, 1 equiv.) and 3:1 Dichloromethane:MeOH (35.6 mL : 11.85 mL) at -78 °C under atmospheric conditions until the solution turned slightly pale blue (<3 min). Ozone flow was continued until the solution turned a darker blue (1-2 additional minutes). Excessive stirring (> 10 min) typically resulted in increasing amounts of aldol product **24** (*vide supra*). Nitrogen was bubbled through the solution rapidly until the solution became pale blue and clear (< 1 min). Sodium borohydride (212 mg, 5.5 mmol, 5.67 equiv.) was then added in one

portion at -78 °C. The solution was stirred vigorously for 45 minutes, warmed to room temperature, and stirred for an additional 30 min. An excess of a saturated NH_4Cl solution was added to quench excess sodium borohydride and the mixture was extracted three times with ethyl acetate (3 × 70 mL). The combined organic layers were dried with brine and passed through a column of sodium sulfate. The solvent was removed and a small amount of dichloromethane was added. The slurry was vacuum filtered, and the filter cake was washed with minimal amounts of dichloromethane to remove unreacted ***trans*-22**. The obtained white solid was then dried under hivac (<0.5 torr) at 75 °C for 5 hours to yield **25** as a pure white solid (276mg, 70%). Unreacted ***trans*-22** (CH_2Cl_2 layer) can typically be recovered with minor amounts of diol **25** and other side products. **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 4.39 (ddddd, J = 7.8, 4.4, 4.4, 4.4, 3.3 Hz, 2H), 2.85 (ddd, *J* = 14.8, 4.6, 1.5 Hz, 2H), 2.76 (d, *J* = 7.9 Hz, 2H), 2.37 (dd, *J* = 15.8, 4.5 Hz, 2H), 2.33-2.29 (m, 2H), 1.97 (dd, *J* = 16.4, 3.4 Hz), 1.43 (ddt, *J* = 16.0, 7.0, 3.0 Hz, 2H); **^{1}H NMR** (d_6-DMSO, 500 MHz): δ 4.98-4.97 (d, *J* = 3.64 Hz, 2H), 4.23-4.19 (m, 2H), 2.54-2.50 (dd, *J* = 16.15, 3.9 Hz, 2H)[i], 2.37-2.30 (ap t, *J* = 8.0 Hz, 2H), 2.13-2.09 (dd, *J* = 16.0, 3.0 Hz, 2H), 2.0-1.96 (dd, *J* = 15.2 4.4 Hz, 2H), 1.58-1.48 (m, 2H); **^{13}C NMR** (d_6-DMSO, 125 MHz): δ 73.5, 67.6, 66.4, 56.2, 37.9, 30.3, 26.9; **HRMS**: (ESI) *m/z*: [M+Na] Calcd for $C_{12}H_{14}Cl_6O_2Na$: 422.9023; Found: 422.9017; **FTIR** (ATR) ν_{max} (cm^{-1}) 3027, 2971, 2898, 1648, 1427, 1236, 1217, 1137, 1118, 1068, 1013, 948, 932, 919, 895, 877, 847, 819, 802, 778, 728, 694, 663, 616, 584; **Melting range** = 203.3 – 203.7 °C.

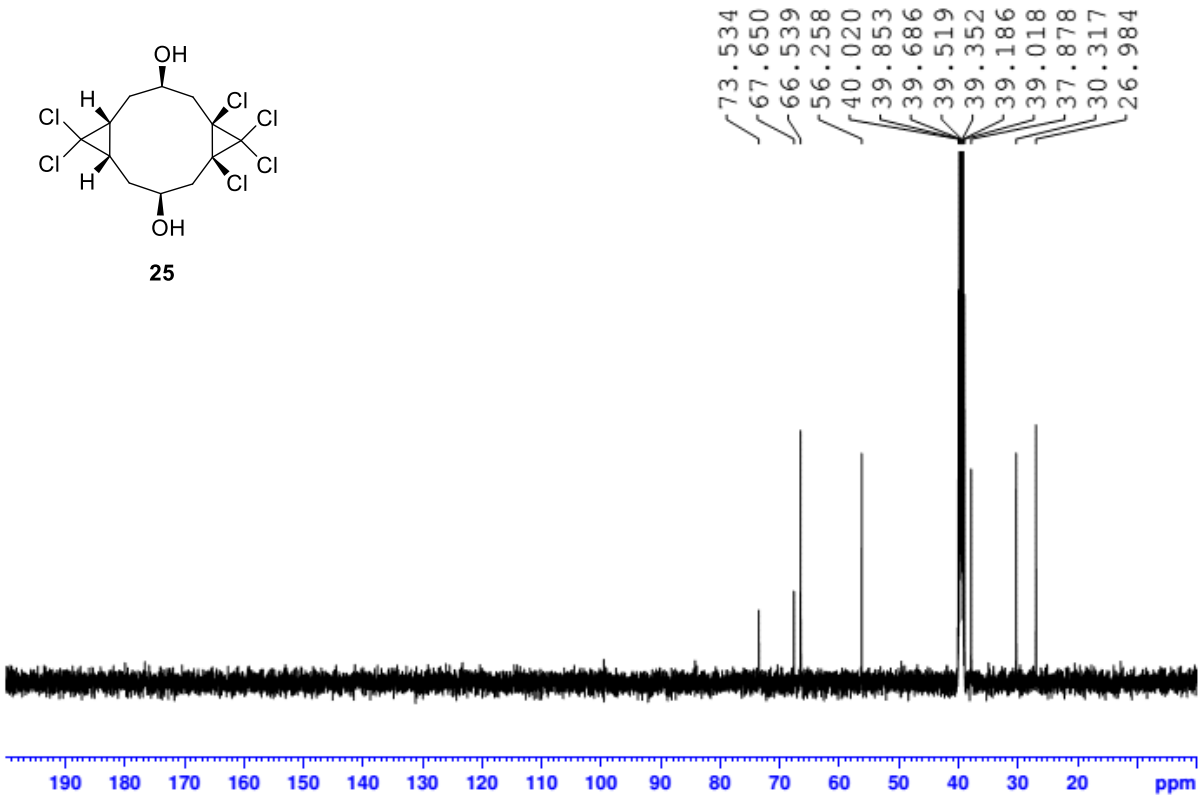
[i] Part of the signal is obscured by the solvent (d_6-DMSO)

Compound 25, 500 MHz, ^{1}H-NMR, $CDCl_3$

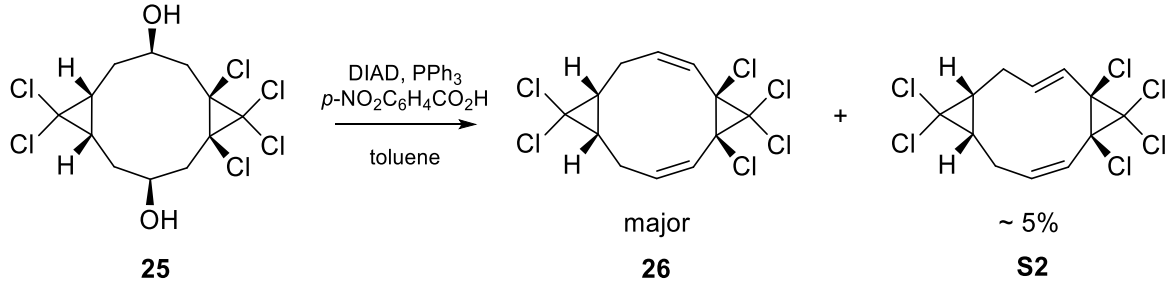


25

Compound 25, 125 MHz, ^{13}C-NMR, d_6-DMSO



Synthesis of (1R,2Z,5R,7S,9Z,11S)-1,6,6,11,12,12-hexachlorotricyclo[9.1.0.05,7]dodeca-2,9-diene (**26**)



Diol **25** (115 mg, 0.285 mmol, 1 equiv.)[ii] was added to a flame dried Schlenk tube with triphenylphosphine (373 mg, 1.42 mmol, 4.98 equiv.), *p*-nitrobenzoic acid (209 mg, 1.25 mmol, 4.38 equiv.) and a small stir bar. The tube was vacuum purged with argon and dry toluene (4.02 mL, 0.07 M) was added. The vessel

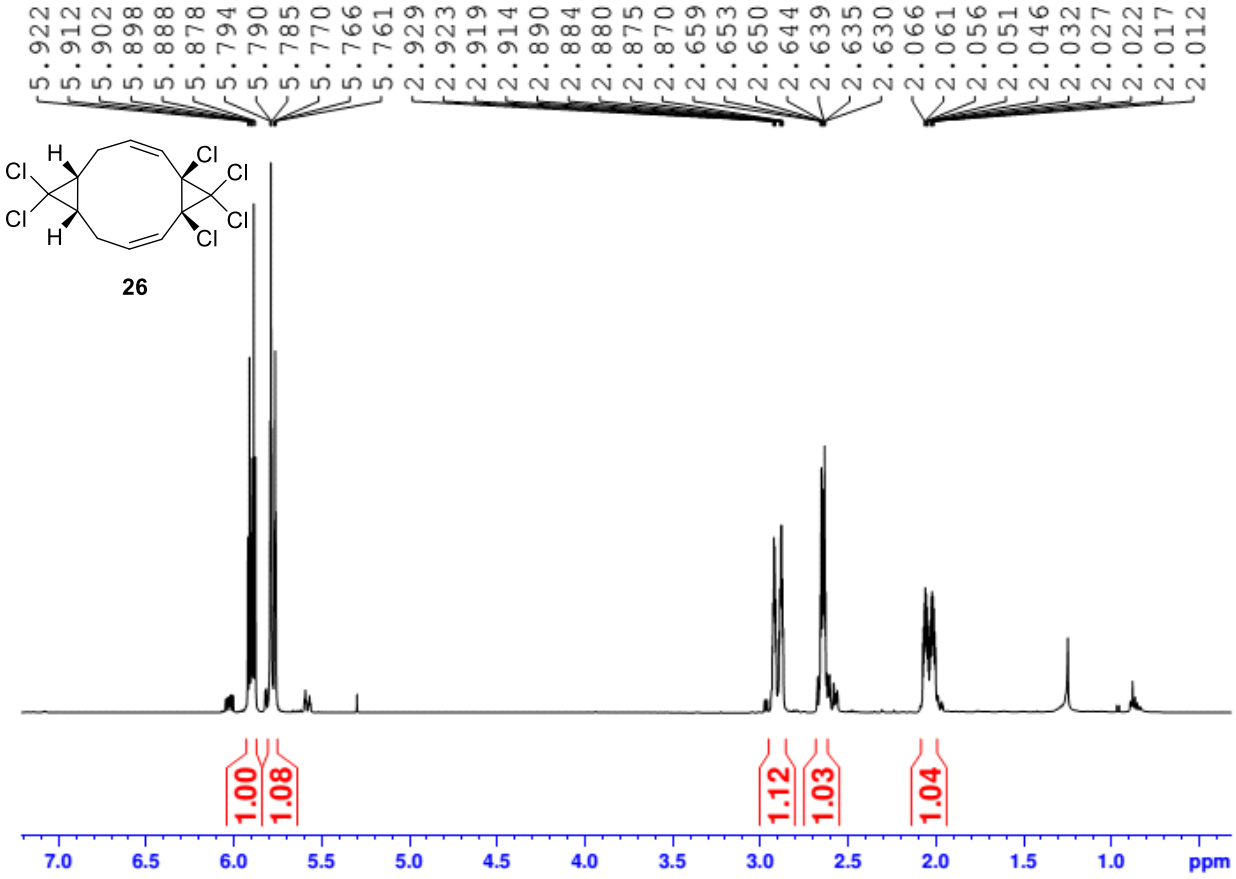
[ii] Note that scaling up the reaction past ~150 mg of **25** typically resulted in poor yields.

was sonicated for 5 minutes at room temperature, then cooled in an ice bath. Diisopropyl azodicarboxylate (0.276 mL, 1.40 mmol, 4.91 equiv.) was added dropwise slowly ensuring the formed yellow colour dissipated prior to further addition. After the addition was complete, the yellow-orange solution was sonicated for 10 minutes. During this time the solutions typically turned a lighter yellow or green colour. The reaction mixture was then allowed to stir overnight at room temperature, resulting in a clear yellow solution. Toluene was removed by rotary evaporation and the viscous oil was purified by eluting through a silica plug with 100% hexanes to obtain an inseparable mixture containing diene **26** and **S2** (~5%) as a white waxy solid (80 mg, 77%).

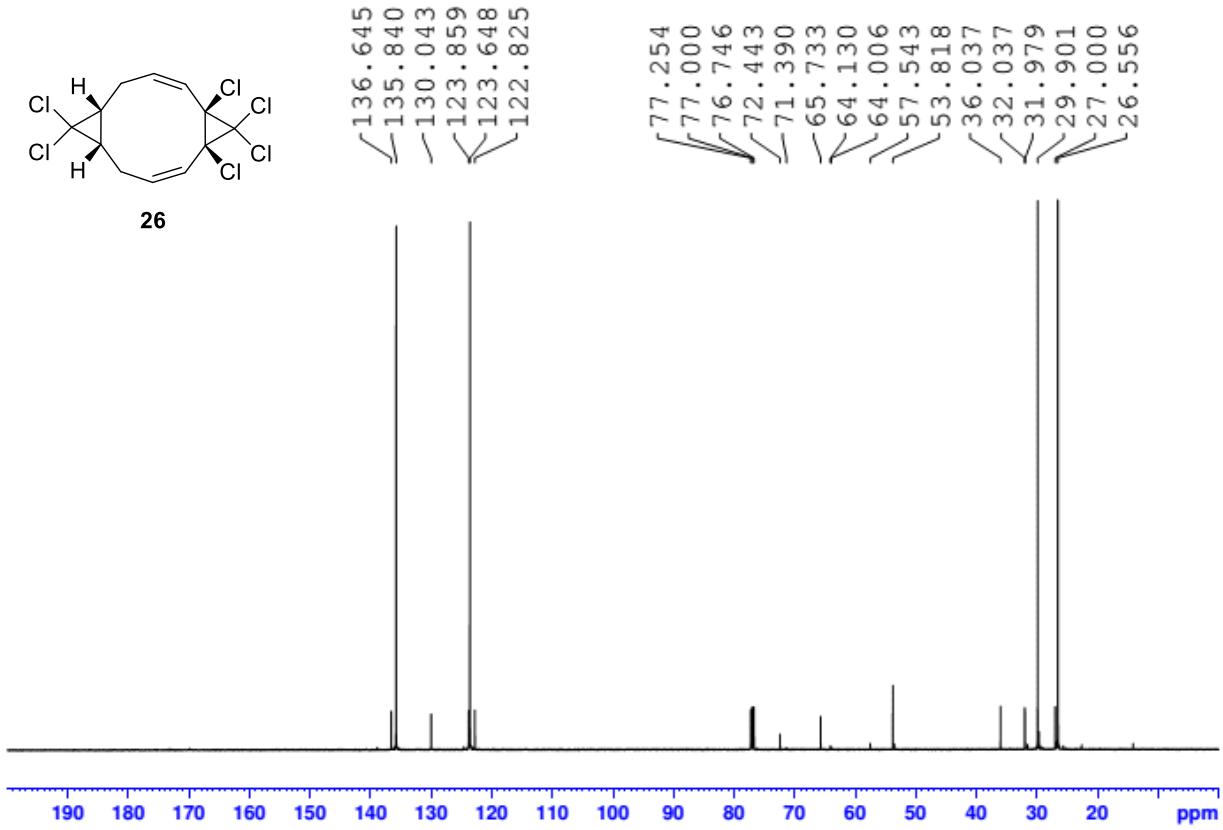
^{1}H NMR ($CDCl_3$, 500 MHz) mixture of regioisomers[iii]: (major) δ 5.92-5.87 (dt, J = 12.0, 4.8 Hz), 5.79-5.76 (dt, *J* = 12.0, 2.1 Hz, 2H), 2.93-2.87 (m, 2H), 2.65-2.62 (m, 2H), 2.07-2.00 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz) mixture of regioisomers: (major) δ 135.8, 123.6, 72.4, 65.7, 53.8, 29.9, 26.5, (minor) δ 136.6, 130.0, 123.8, 122.8, 71.3, 64.1, 57.5, 53.5, 36.0, 32.0, 31.9, 27.0; **HRMS:** (FD) *m/z*: [M]+ Calcd. For $C_{12}H_{10}Cl_6$: 363.8913; Found 363.8902. **FTIR** (ATR) ν_{max} (cm^{-1}) 3027, 2971, 2898, 1648, 1427, 1236, 1217, 1137, 1118, 1068, 1013, 948, 932, 919, 895, 877, 847, 819, 802, 778, 728, 694, 663, 616, 584; **Melting range** = 203.3 – 203.7 °C.

[iii] ^{1}H-NMR signals of minor species (**S2**) are mostly obscured by signals from **26**.

Compound 26, 500 MHz, ^{1}H-NMR, $CDCl_3$

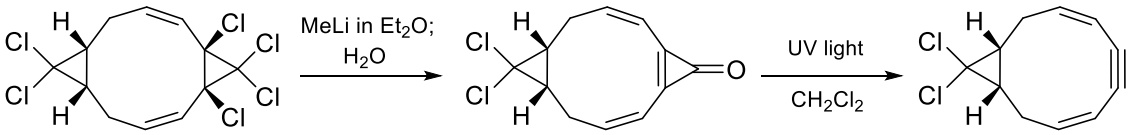


Compound 26, 500 MHz, ^{13}C-NMR, $CDCl_3$



26

Synthesis of (1R,3Z,7Z,10S)-11,11-dichlorobicyclo[8.1.0]undeca-3,7-dien-5-yne (**28**)



26 **27** **28**

Diene **26** (64 mg, 0.17 mmol, 1 equiv.)[iv] was added to a flame dried vial with a stir bar. The vessel was vacuum purged with argon and dry diethyl ether (6.25 mL, 0.01 M) was added. The solution was cooled

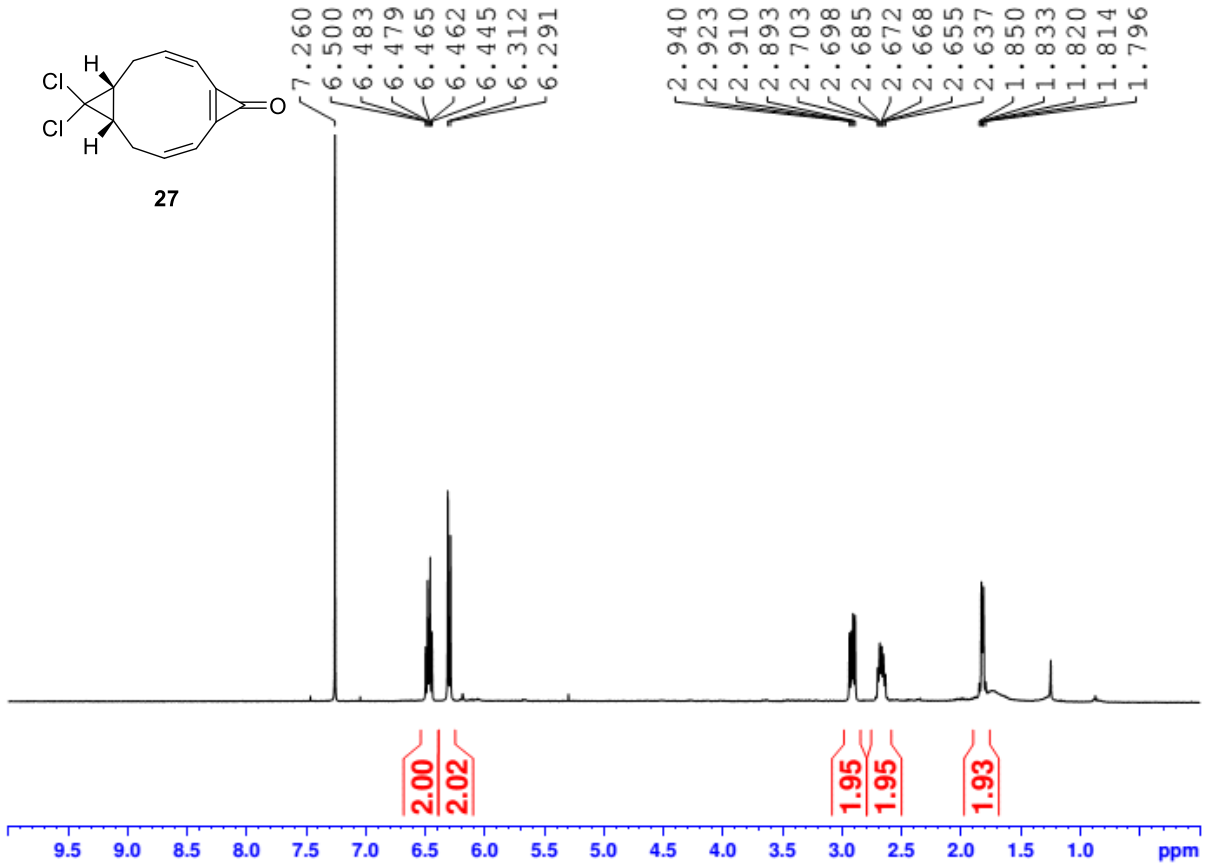
[iv] The reaction with methyl lithium was done on a maximum of 100 mg scale (**26**). Batches (50-100mg) were used when scale-up was desired.

in an ice bath and freshly quantified MeLi[v] (0.185 mL of a 1.2 M solution in Et_2O, 1 equiv.) was added carefully in one portion with vigorous stirring. The resulting brown solution was stirred for 2 minutes before being quenched with sat. NH_4Cl. The mixture was diluted with water and extracted with dichloromethane (3 × 5 mL). The combined organic layers were dried with sodium sulfate and concentrated to yield a crude black oil (60 mg) containing **27**. The oil was typically not purified, but a small amount of purified material could be obtained for analysis by eluting the oil onto a pipette column packed with Et_3N doped silica (with associated yield loss). The plug was washed with dichloromethane to remove non-polar impurifies and the compound then eluted with ethyl acetate. In practice the material (**27**) was carried to the next step without purification.

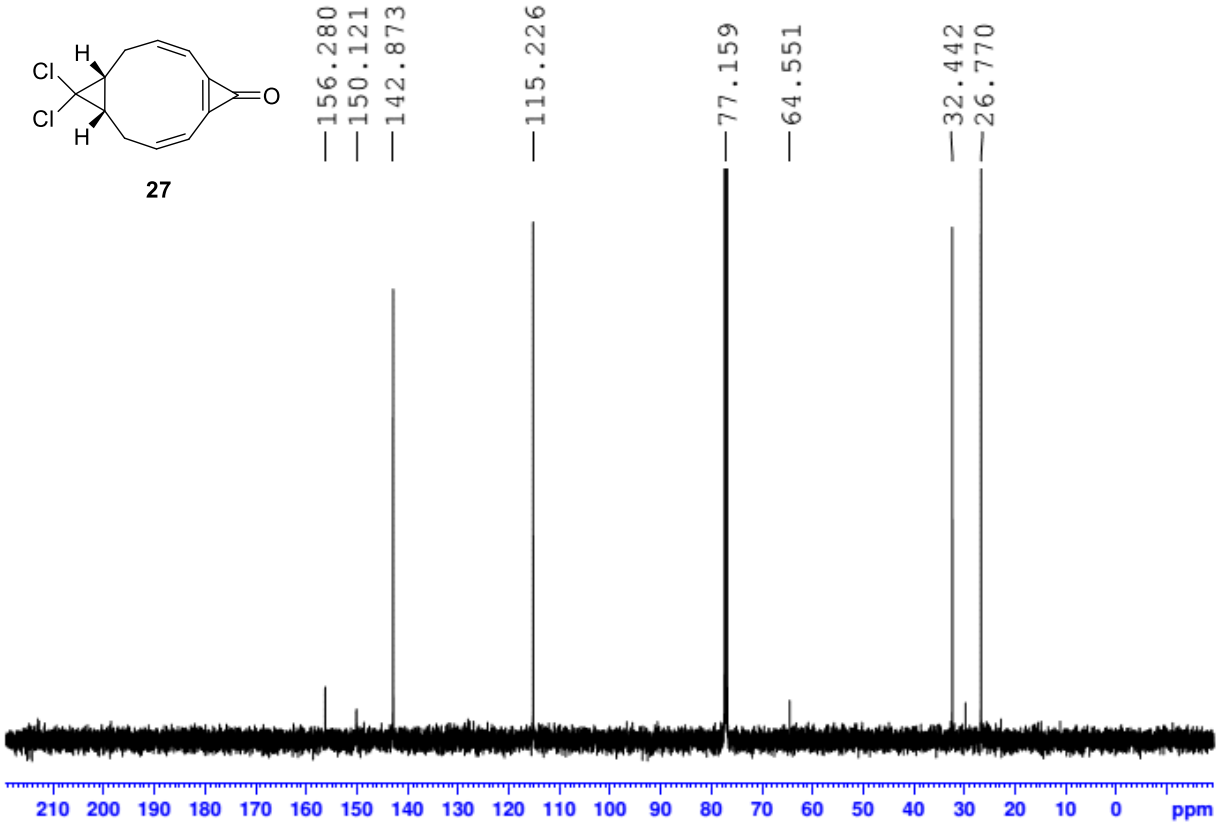
Cyclopropenone 27: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.49-6.44 (dt, J = 10.5 , 8.3 Hz, 2H), 6.31-6.29 (d, J = 10.6, 2H), 2.93-2.89 (dd, J = 15.0, 8.3 Hz, 2 H), 2.70-2.63 (m, 2H), 1.8-1.79 (m, 2H); **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 156.1, 149.9, 142.7, 115.0, 64.4, 32.2, 26.6; **HRMS:** [M+Na]+ Calcd. For $C_{12}H_{10}Cl_2ONa$: 263.0006; Found 263.0004; **FTIR** (ATR) ν_{max} (cm^{-1}): 3030, 2917, 2857, 1832, 1622, 1594, 1440, 1303, 1244, 1103, 1051, 946, 905, 814, 787

[v] Careful quantification of MeLi was absolutely necessary. Using an excess resulted in significant material degradation and using too little resulted in contamination of **27** with starting material **26**, which could not be removed easily and resulted in contamination of the final annulene (**7**).

Compound 27, 500 MHz, ^{1}H-NMR, $CDCl_3$



Compound 27, 125 MHz, ^{13}C-NMR, $CDCl_3$

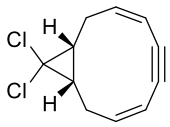


The crude cyclopropenone (**27**) was dissolved in 10 mL dichloromethane and placed into an air-cooled UV reactor. The sample was irradiated with 300 nm light for 4 hours. The sample was not allowed to exceed ~5 °C. After the reaction, the solvent was evaporated and the sample was purified by preparatory thin layer chromatography (PTLC) (hex, Rf = 0.15) to yield **28** as a clear and colourless oil (17.7 mg, 48%).

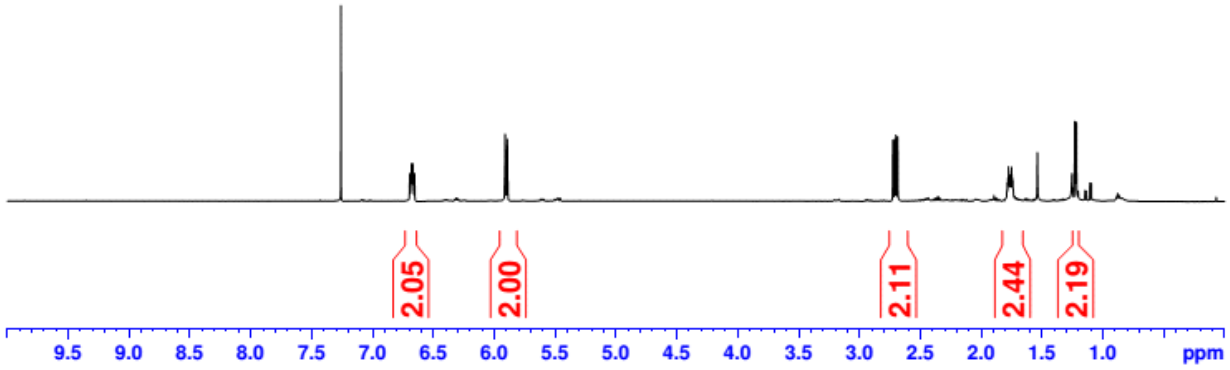
Dienyne 28: ^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.69-6.65 (m, 2H), 5.91-5.88 (d, J = 10.9 Hz, 2H), 2.72-2.68 (dd, J = 15.1, 8.4 Hz, 2H), 1.78-1.73 (m, 2H), 1.23-1.21 (ap. dd, J = 8.3, 3.6 Hz, 2H); **^{13}C NMR** (*d*$_6$-acetone, 125 MHz): δ 144.5, 113.9, 96.7, 67.6, 30-29[vi], 24.13; **HRMS:** (FD) [M]+ Calcd. for $C_{11}H_{10}Cl_2$: 212.0160; Found 212.0166 **FTIR** (ATR) ν_{max} (cm^{-1}): 3034, 2935, 2898, 2865, 2832, 1603, 1438, 1097, 1037, 835, 825, 813, 788

[vi] Signal is under *d*$_6$-acetone multiplet

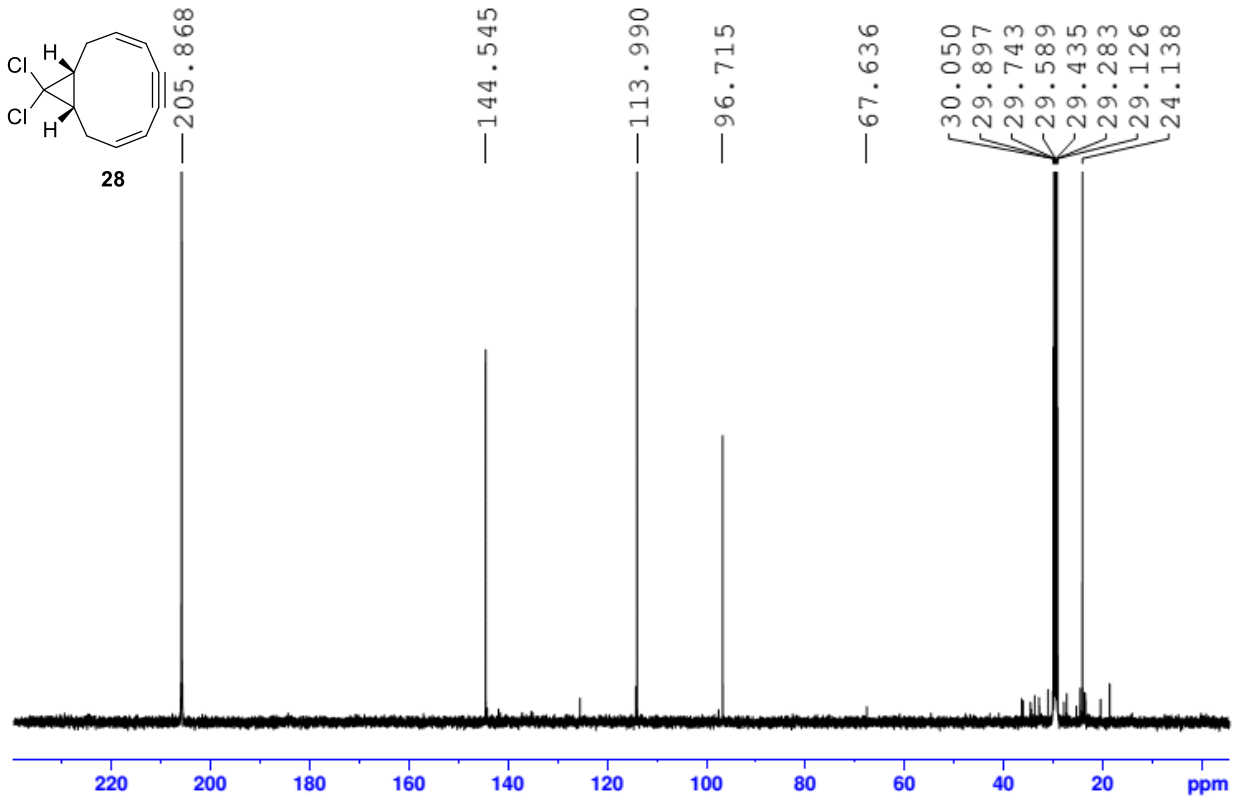
Compound 28, 600 MHz, ^{1}H-NMR, $CDCl_3$



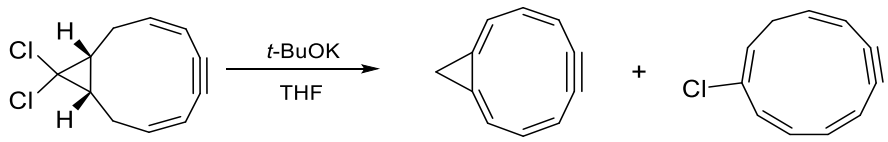
28



Compound 28, 125 MHz, ^{13}C-NMR, d_6-acetone



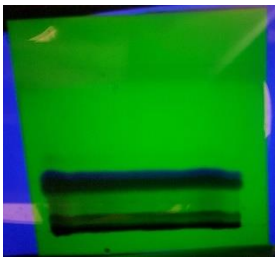
Synthesis of (1Z,3Z,7Z,9Z)-bicyclo[8.1.0]undeca-1,3,7,9-tetraen-5-yne ([10]annulene) (**7**)



Dienyne[vii] **24** (20 mg, 0.94 mmol) was added to a Schlenk tube and vacuum purged with argon three times. THF (1.47 mL) was added and the solution was cooled to -20 °C. In a separate vessel, freshly sublimed tBuOK was dissolved in THF (1.47 mL). The tBuOK solution was added to the dienyne and allowed to stir at -20 °C for 6 hours. The solution was then quenched with 1 mL sat. NH_4Cl, diluted with water and

[vii] The reaction does not go to completion if the starting material **28** is contaminated with diene **26** as several molar equivalents of tBuOK are consumed by **26**. Different inseparable side products are also observed with small amounts of diene (**26**) contaminants.

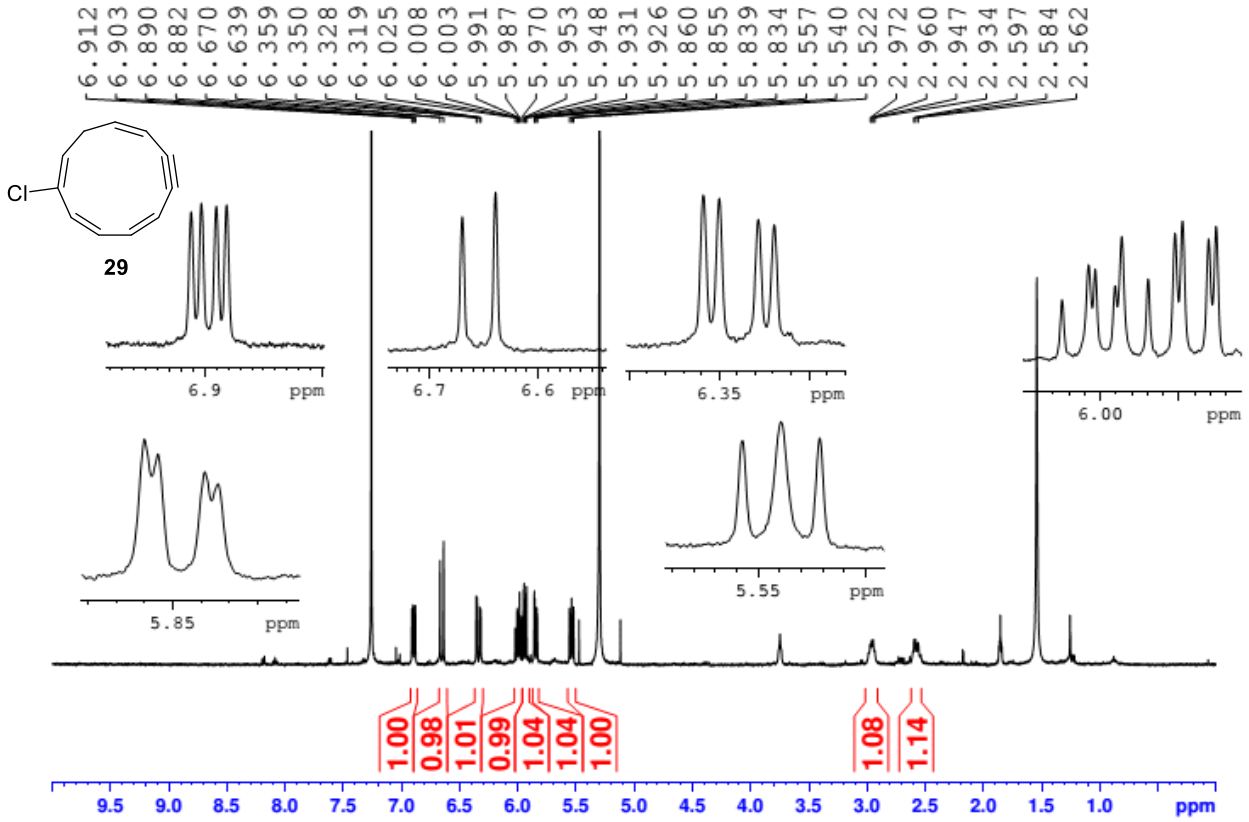
extracted with dichloromethane (3 × 30 mL). The combined organic extracts were concentrated at 250-300 mm Hg[viii] to yield a sweet smelling dark crude oil. Separately, an Ag-doped PTLC plate was prepared by exposing a standard PTLC plate to a solution of silver nitrate (3.2 g) in acetone:water (150 mL: 16 mL) in a plastic tub for 5 seconds (Note: extended exposure resulted in excess Ag^+ dopant on the PTLC plate, which causes material degradation during elution[8]). The plate was allowed to dry without heat or exposure to light and the crude oil was purified by elution with 100% hexanes (Rf = 0.33, fluorescent band). The band could be identified due to its blue fluorescence under UV light. Due to the high volatility of the material, it was not possible to separate from minor solvent impurities. An isolated yield was difficult to obtain.



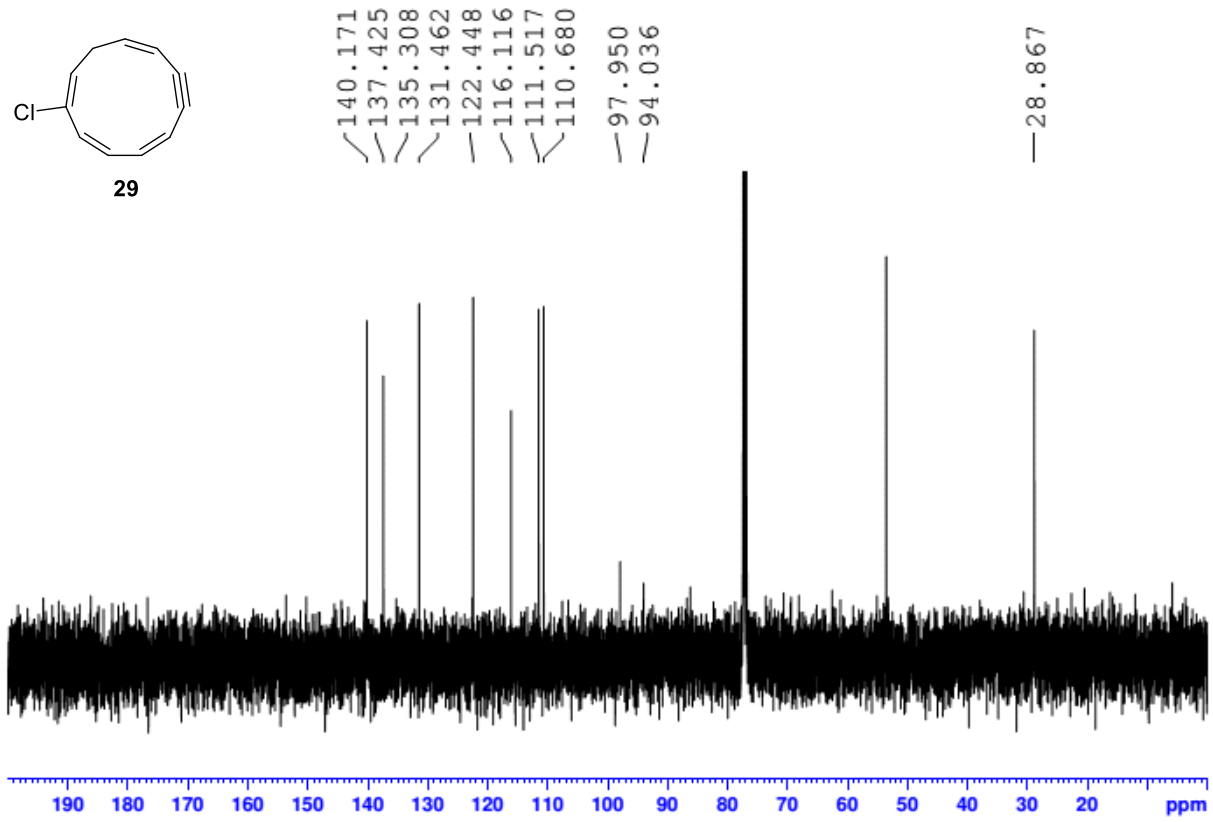
Side product 29: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.91-6.88 (dd, *J* = 10.7, 4.5 Hz, 1H), δ 6.66-6.63 (dd, *J* = 15.4Hz, 1H), δ 6.35-6.31 (dd, *J* = 15.4, 4.3 Hz, 1H), δ 6.02-5.97 (ap. q, *J* = 9.7 Hz, 1H), δ 5.95-5.92 (dd, *J* = 10.9, 2.4Hz, 1H), δ 5.86-5.83 (dd, *J* = 10.9, 1.89 Hz, 1H), δ 5.56-5.52 (ap. t, *J* = 8.9 Hz, 1H), δ 2.97-2.95 (m, 1H), δ 2.60-2.55 (m, 1H) [Note: minor amounts of product **7** visible in spectrum]; **^{13}C NMR** ($CDCl_3$, 150 MHz): 140.17, 137.42, 135.30, 131.46, 122.44, 116.11, 111.51, 110.68, 97.95, 94.04, 28.86; **HRMS:** (FD) [M]+ Calcd. for $C_{11}H_9Cl$: 176.0393; Found 176.0398; **FTIR** (ATR) ν_{max} (cm^{-1}): 3023, 2917, 2849, 2248, 2192, 2162, 1709, 1641, 1462, 1449, 1261, 1203, 1127, 1024, 950, 908, 841, 818, 732, 685, 649, 585, 530

[viii] Slow evaporation of solvent at low vacuum is critical to prevent loss of the volatile [10]annulene (**7**). Complete removal of solvent on at low vacuum or hivac (drying) was also avoided to ensure minimal yield loss. The PTLC plate had to be rinsed with minimal amounts of dichloromethane without vacuum filtration to avoid undesired material loss. The solvent was then evaporated very slowly in a large vial under a gentle vacuum (250-300 mmg Hg) at 15-20 °C to remove the solvent. The non-exhaustive solvent removal typically resulted in large amounts of dichloromethane and even trace THF (from the reaction mixture) in the final product.

Compound 29, 500 MHz, ^{1}H-NMR, $CDCl_3$

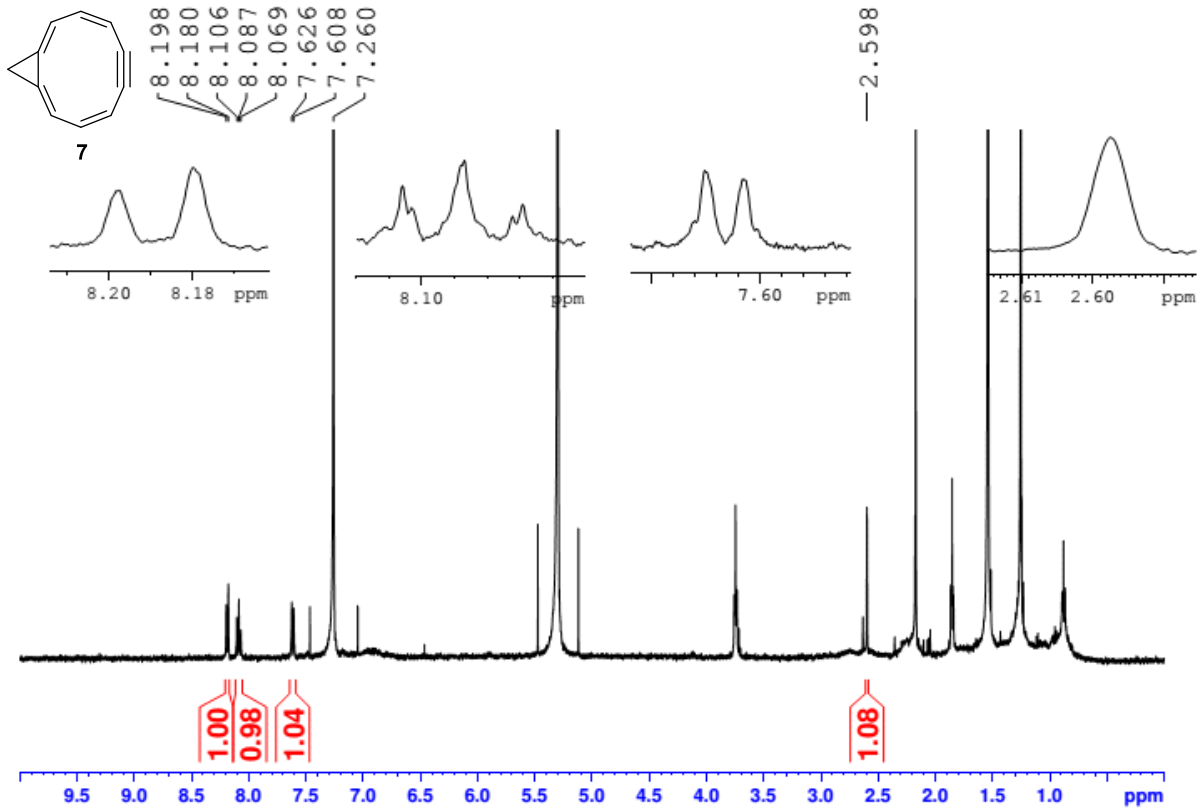


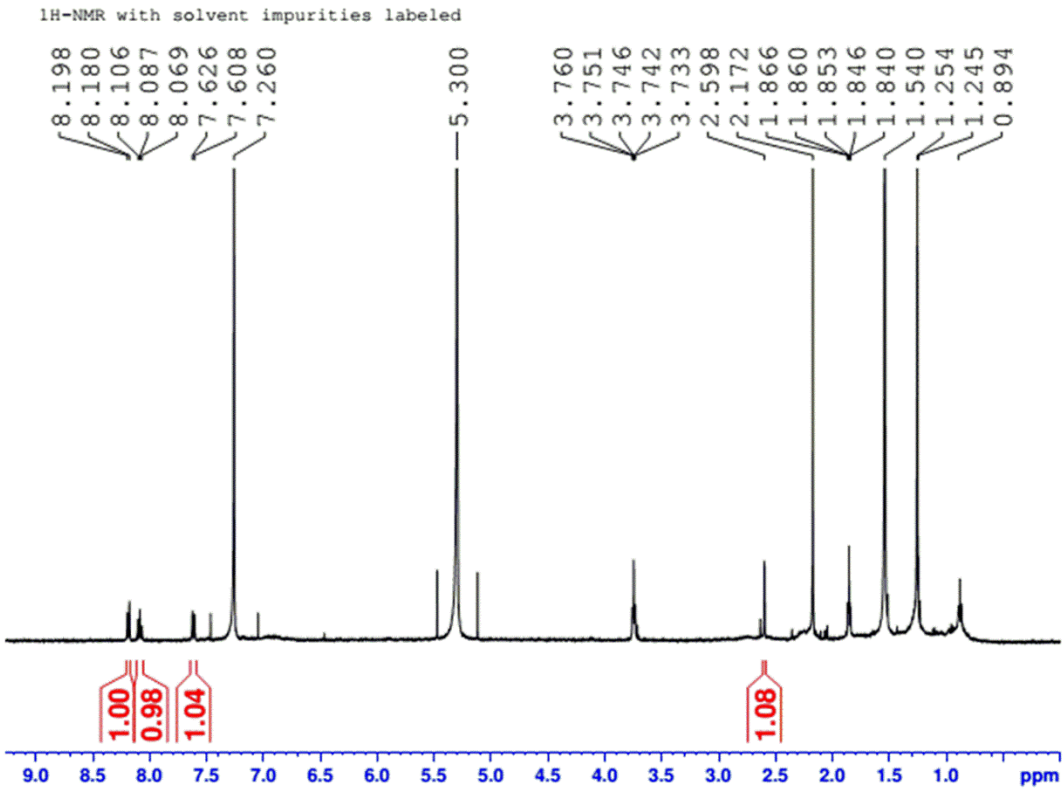
Compound 29, 125 MHz, ^{13}C-NMR, $CDCl_3$

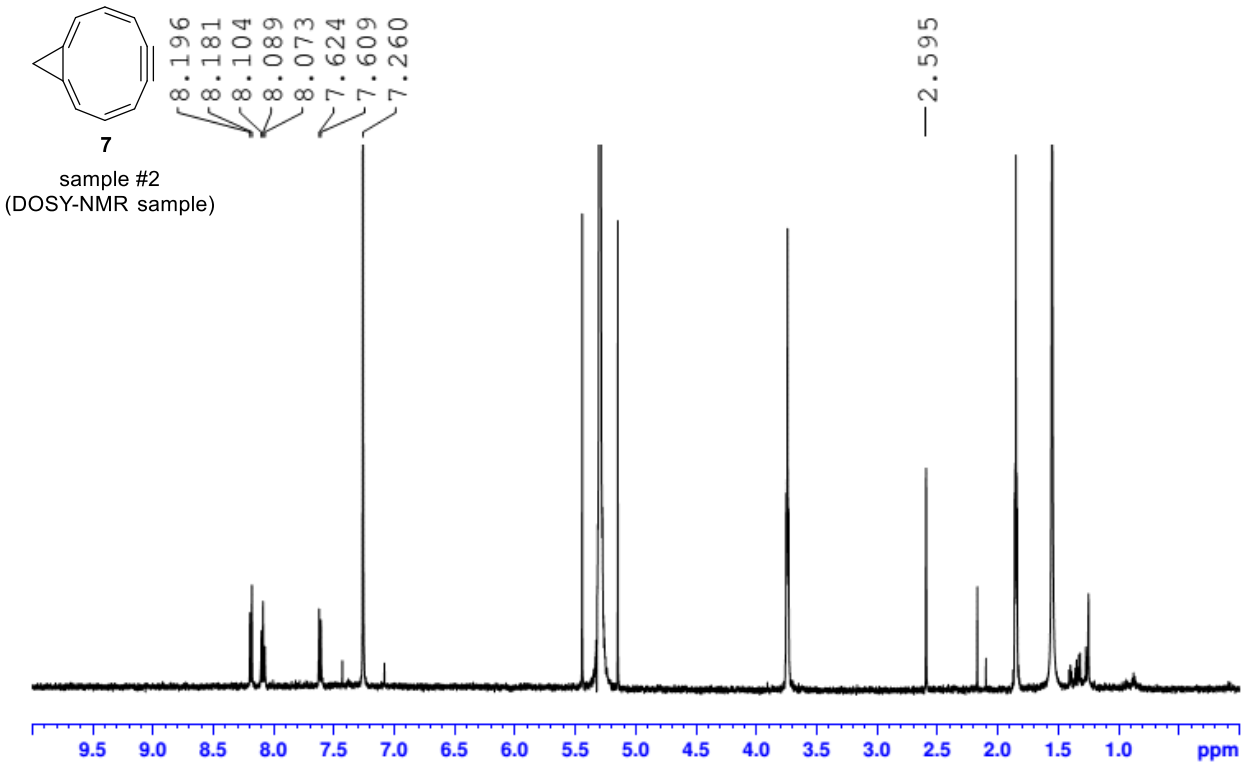


[10]annulene 7: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.19-8.18 (ap. d, ap. *J* = 9.2 Hz, 2H), 8.10-8.07 (ap. t, ap. *J* = 9.2, 2H), 7.62-7.60 (ap. d, ap. *J* = 8.3, 2H), 2.59 (ap. s, 2H); **^{13}C NMR** ($CDCl_3$, 150 MHz): 135.8, 118.6, 116.3, 115.6, 13.0; **MS:** (EI) [M]+ Calcd. for $C_{11}H_8$: 140.0626; Found 140.0623; **FTIR** (ATR) ν_{max} (cm^{-1}): 3041, 2957, 2957, 2924, 2852, 1726, 1708, 1692, 1463, 1427, 1409, 1371, 1257, 1102

Compound 7, 500 MHz, ^{1}H-NMR, $CDCl_3$



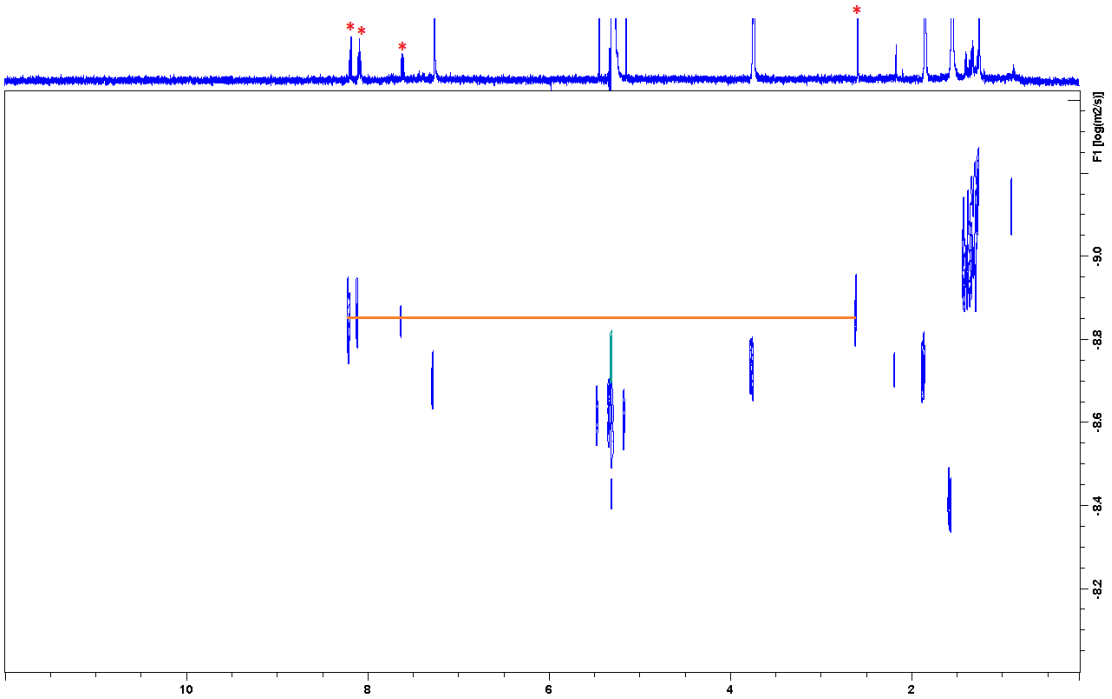




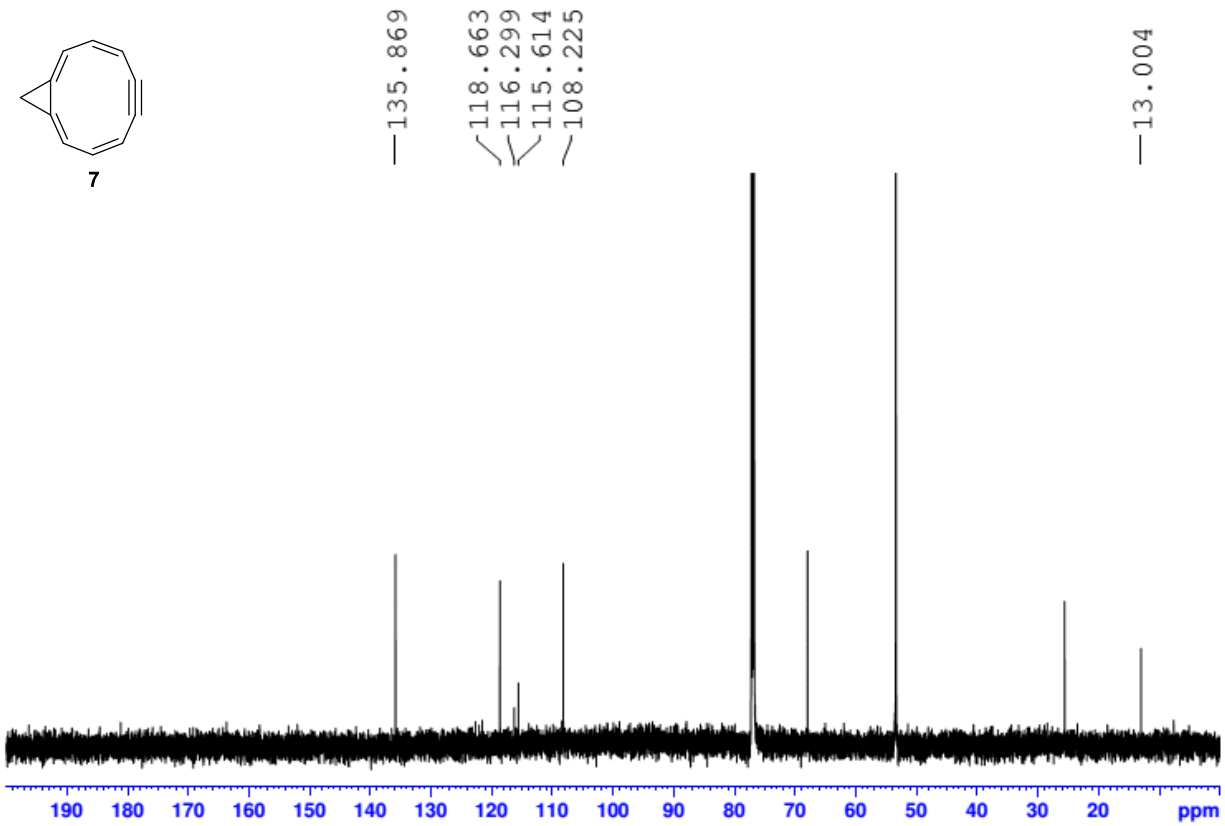
7

sample #2
(DOSY-NMR sample)

DOSY-NMR



Compound 7, 150 MHz, ^{13}C-NMR, $CDCl_3$



Computed NMR data

[10]Annulene (**7**) ^{1}H-NMR

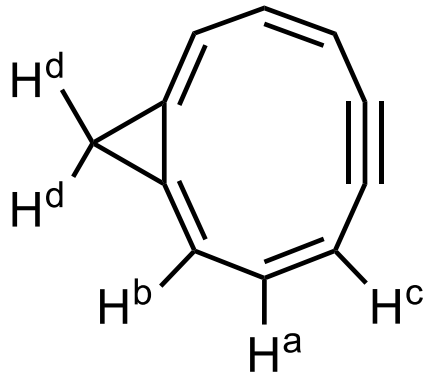


Table S1: Experimental and computed (^{1}H-NMR) chemical shifts of the prepared annulene (**7**)

			Proton shifts (a-d)[ii] (δ)					
entry	**geometry[i]**	**NMR**	**a**	**b**	**c**	**d**	**MAE[iii]**	**NICS(1)$_{zz}$[iv]**
1	**experimental**	**experimental**	**8.08**	**8.19**	**7.61**	**2.59**	**-**	**-**
2	**M062X**	**B3LYP/6-311+G(2d,p)**	8.193	8.260	7.698	2.740	**0.105**	-31.878
3	**wB97XD**	**B3LYP/6-311+G(2d,p)**	8.193	8.249	7.681	2.761	0.103	-32.024
4	**B3LYP**	**B3LYP/6-311+G(2d,p)**	8.318	8.347	7.791	2.840	0.206	-33.038
5	**MP2**	**B3LYP/6-311+G(2d,p)**	8.304	8.366	7.856	2.672	0.182	-33.656
6	**HF**	**B3LYP/6-311+G(2d,p)**	7.716	7.711	7.078	2.460	0.377	-25.570
7	**B3LYP**	**B3LYP/6-311+G(2d,p)**	8.442	8.477	7.909	2.872	0.308	-33.038
8	**MP2**	**MP2/6-31+G(d,p)**	8.423	8.487	7.926	2.533	0.253	-33.656

i. all geometries were calculated with the 6-31+G(d,p) basis set ii. NMR scaling factor for entries 2-6: (iso-31.9477)/(-1.0767) determined for the method described in entry 2, scaling factor for entry 7: (iso-31.9679)/(-1.0663), scaling factor for entry 8: (iso-31.9679)/(-1.0663) iii. Mean absolute error calculated by averaging the absolute differences between the computed (scaled) and experimental chemical shift. iv. NICS(1)$_{zz}$ values calculated using the corresponding geometry

The method described by Hoye *et al.*[1] using an M062X/6-31+G(d,p) geometry and isotropic shifts at B3LYP/6-311+G(d,p) (entry 2) gave results with an excellent mean absolute error (<0.2 ppm is recommended). Interestingly, using the geometry computed at wB97XD, a functional known to

incorporate long range correlation, gave similar results (entry 3). Interestingly, while NICS values were not significantly perturbed by changes in level of theory, the corresponding geometry often changed significantly.

[10]Annulene (**7**) ^{13}C-NMR

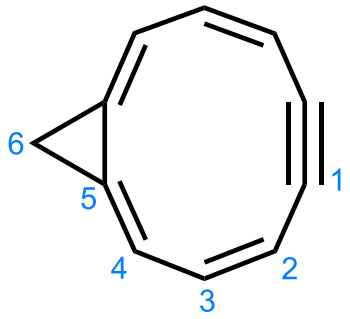


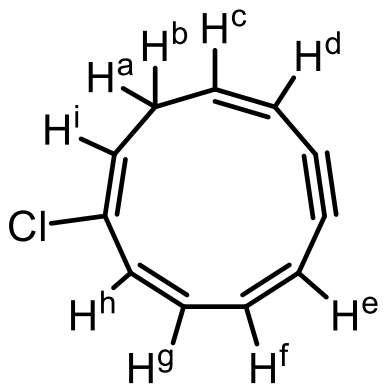
Table S2: Experimental and computed (^{13}C-NMR) chemical shifts of the prepared annulene (**7**)

			Carbon (^{13}C) shifts (1-6)[ii]						
entry	**geometry[i]**	**NMR**	**1**	**2**	**3**	**4**	**5**	**6**	**MAE[iii]**
1	**exp.**	**exp.**	**118.66**	**108.22**	**135.87**	**116.29**	**115.61**	**13.00**	**-**
2	**M062X**	**B3LYP/6-311+G(2d,p)**	118.45	105.54	134.81	116.92	114.98	13.65	0.97

i. all geometries were calculated with the 6-31+G(d,p) basis set ii. NMR scaling factor for entry 2: (iso-181.2412)/(-1.0522)) iii. Mean absolute error calculated by averaging the absolute differences between the computed (scaled) and experimental chemical shift.

The method described by Hoye *et al.*[1] using an M062X/6-31+G(d,p) geometry and isotropic shifts at B3LYP/6-311+G(d,p) (entry 2) gave results with an excellent mean absolute error (<2.0 ppm is recommended).

Side product (**29**) ^{1}H-NMR



			Proton (^{1}H) shifts (a-i)[ii] (δ)									
entry	**geometry**[i]	**NMR**	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**MAE**
1	**exp.**	**exp.**	**2.582**	**2.963**	**6.340**	**5.847**	**5.940**	**6.654**	**5.997**	**6.896**	**5.541**	-
2	**M062X**	**B3LYP/6-311+G(2d,p)**	2.710	2.920	6.427	5.866	5.885	6.622	6.236	6.764	5.639	0.093

i. all geometries were calculated with the 6-31+G(d,p) basis set ii. NMR scaling factor for entries 2-6: (iso-31.9477)/(-1.0767) iii. Mean absolute error calculated by averaging the absolute differences between the computed (scaled) and experimental chemical shift.

The method described by Hoye *et al.*[1] using an M062X/6-31+G(d,p) geometry and isotropic shifts at B3LYP/6-311+G(d,p) (entry 2) gave results with an excellent mean absolute error (<2.0 ppm is recommended).

Benzene ^{1}H-NMR

The method described by Hoye *et al.*[1] using an M062X/6-31+G(d,p) geometry and isotropic shifts at B3LYP/6-311+G(d,p) (entry 2) gave an average shift of 7.31 for benzene.

^{1}H-NMR simulation of aromatic region of **7**

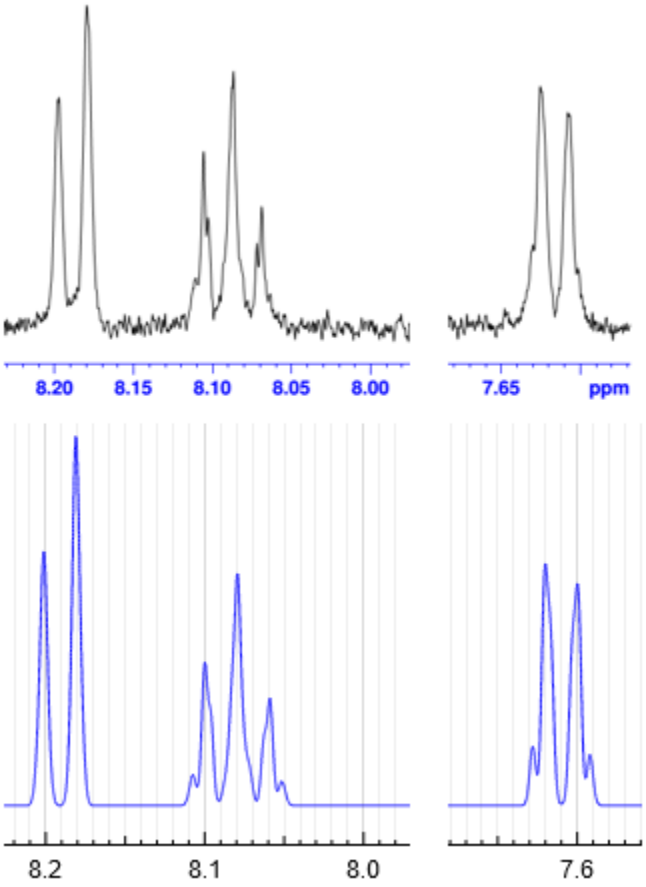


Figure S1: top: Experimental aromatic region of the ^{1}H-NMR of **7**; bottom: Simulated spectrum of aromatic region of ^{1}H-NMR of **7**.

Table S3: Computed coupling constants of **7** used to simulate the (^{1}H-NMR) spectrum

	delta (ppm)	J_{1-} (Hz)	J_{2-} (Hz)	J_{3-} (Hz)	J_{4-} (Hz)	J_{5-} (Hz)	J_{6-} (Hz)	J_{7-} (Hz)
1	8.19							
2	8.08	-0.404						
3	7.61	0.536	-0.20780					
4	8.19	1.424	10.3420	0.6570				
5	8.08	10.34	0.5580	10.87	-0.404			
6	7.61	0.6570	10.8829	5.6490	0.53590	-0.2070		
7	2.59	-1.1250	-0.0101230	-0.6425	1.125	0.0097	-0.64213	
8	2.59	-1.1250	0.0101230	0.6424	1.125	0.0097	-0.64213	4.9478

^{1}H-NMR data obtained via the Hoye *et al.* method (Table S1, entry 2) was used along with coupling constants computed at the B3LYP/6-31G(d,p) level of theory. The NMR spectrum was simulated using the method by Castillo *et al.* with the available web applet on nmrdb.org.[9]

Proposed pathway for the formation of **7** and **29**

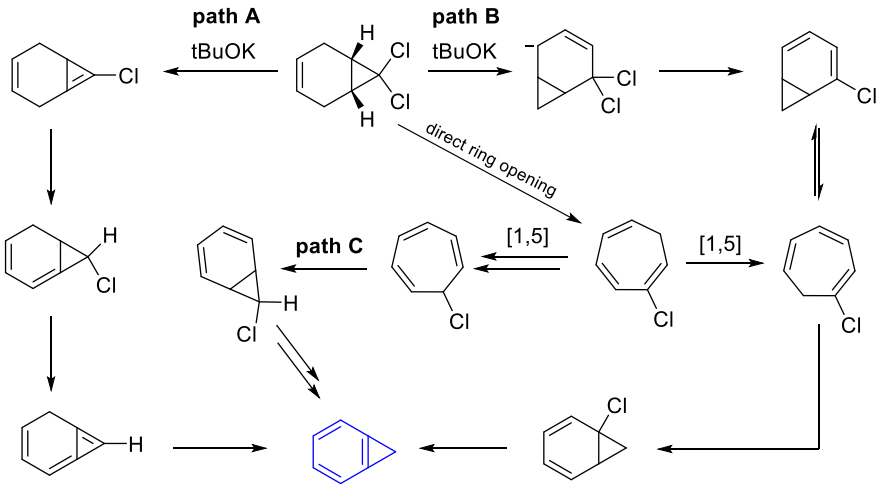


Figure S2: Possible pathways for the formation of benzocyclopropene (blue) from *cis*-7,7-dichlorobicyclo[4.1.0]hept-3-ene.

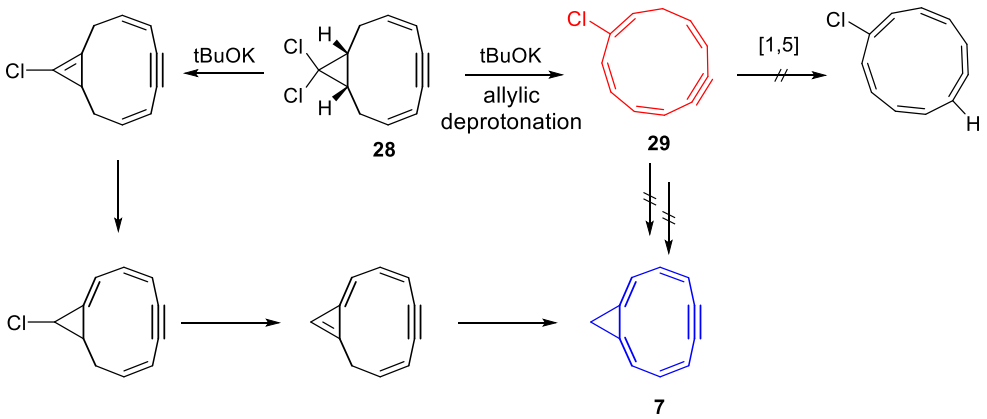


Figure S3: Proposed pathway for the formation of [10]annulene **7** and side product **29** from **28**. **29** cannot undergo a series of [1,5] shifts to generate **7**.

Two pathways are possible (Figure S3) for the formation of benzocyclopropene. The first (path A) involves direct elimination of HCl by tBuOK followed by an isomerization while the second (path B) depends on allylic deprotonation and a series of proton shifts/electrocyclizations. A third pathway (C) combines

elements of pathways A and B. ^{12}C-labelling experiments suggest pathway A/B is operational.[10] Direct HCl elimination and allylic deprotonation are also both possible with **28**. However, allylic deprotonation forms **29**, a dead-end material that cannot undergo [1,5] proton shifts to yield the desired product **7**. As the desired product (**7**) is ultimately observed, part of the material is likely proceeding through the pathway analogous to path A.

Strain visualization of **7**

[10]annulene (**7**) shows a total strain energy of 15.64 kcal/mol, which can be visualized with StrainViz. According to the procedure described by Jasti *et al.* C_{sp2}-C_{sp2} bonds were clipped symmetrically by removing carbon atoms and replacing them with hydrogen atoms. The resulting structures were minimized at M062X/6-31+G(d,p) and the strain was calculated using the StrainViz script. Analysis shows that strain is not highly localized near the alkyne or cyclopropane ring but instead is present to a higher degree on the flanks of the molecule (red bonds), likely due to the increased bond angles.

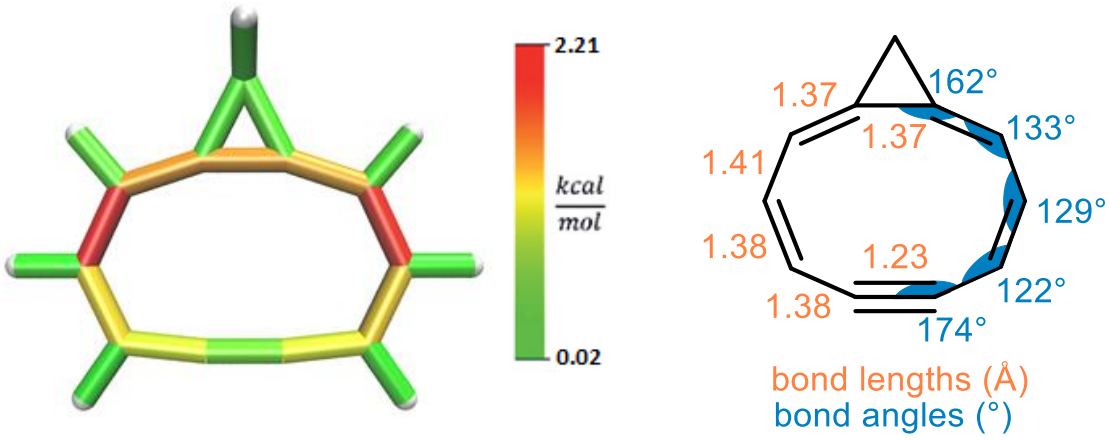


Figure S4: left: VMD generated image of StrainViz data showing the total strain in **7**; right: bond angles (°) and bond lengths (Å) of the aromatic ring in **7**.

Bond angle distortion diagrams

Angle distortion diagrams were created by constraining all bond angles, bond lengths, and dihedral angles except the two sets of CCC angles highlighted in blue. Symmetric distortions between 130° - 175° with constraints were computed at the M062X/6-31+G(d,p) level of theory.

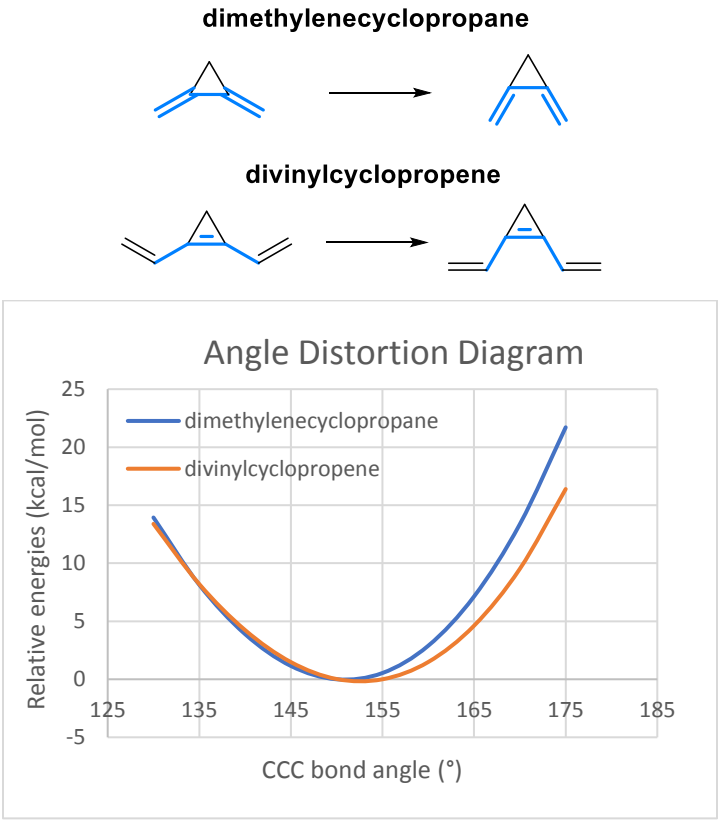


Figure S5: top: Distortion modes for divinylcyclopropene and dimethylenecyclopropane; bottom: Angle distortion curves.

Table S4: Energies of associated bond angle distortions for dimethylenecyclopropane and divinylcyclopropene

bond angle (°)	dimethylenecyclopropane (kcal/mol)	divinylcyclopropene (kcal/mol)
130	13.94	13.39
135	8.14	8.2
140	3.89	4.24
145	1.15	1.48
150	0	0.02
155	0.54	0
160	2.89	1.49
165	7.14	4.62
170	13.37	9.52
175	21.71	16.39

Molecular orbitals (HOMO/LUMO) of **7**

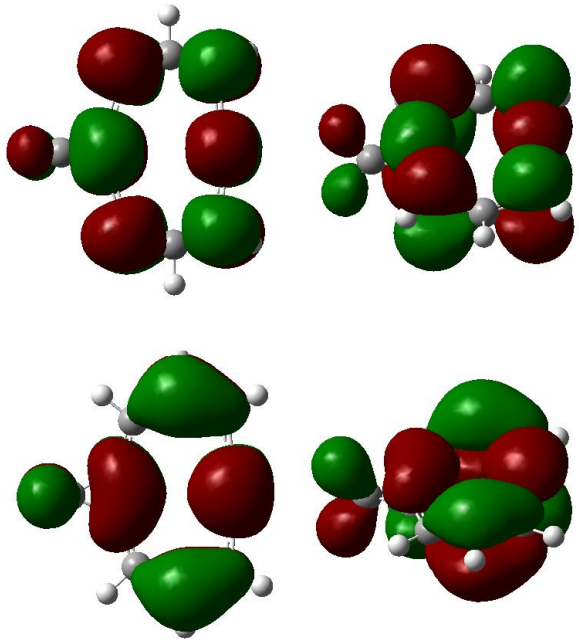


Figure S6: top: LUMO; bottom: HOMO; both calculated at M062X/6-31+G(d,p) level of theory.

X-Ray crystal structure and refinement data for ***trans*-22** and **24**

A specimen of $C_{24}H_{20}Cl_{12}O_2$, approximate dimensions 0.130 mm x 0.180 mm x 0.310 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

Axis	dx (mm)	2θ (°)	ω (°)	ϕ (°)	χ (°)	Width (°)	Frames	Time (s)	Wavelength (Å)	Voltage (kV)	Current (mA)	Temperature (K)
Phi	40.100	-27.00	18.84	-349.56	-24.38	0.50	739	5.0	0.71073	30.0	100	173
Phi	40.100	-27.00	343.09	129.70	-91.91	0.50	357	5.0	0.71073	30.0	100	173
Omega	40.100	-12.00	305.46	294.62	61.02	0.50	97	5.0	0.71073	30.0	100	173
Phi	40.100	-17.00	28.75	237.74	-90.93	0.50	127	5.0	0.71073	30.0	100	173
Phi	40.100	10.50	345.62	338.46	84.64	0.50	138	5.0	0.71073	30.0	100	173
Omega	40.100	-7.00	252.80	295.27	39.98	0.50	213	5.0	0.71073	30.0	100	173
Phi	40.100	-19.50	325.99	50.09	84.64	0.50	334	5.0	0.71073	30.0	100	173
Phi	40.100	0.50	4.92	72.80	-44.69	0.50	437	5.0	0.71073	30.0	100	173

A total of 2442 frames were collected. The total exposure time was 3.39 hours. The integration of the data using a triclinic unit cell yielded a total of 32732 reflections to a maximum θ angle of 27.60° (0.77 Å resolution), of which 6756 were independent (average redundancy 4.845, completeness = 98.9%, R_{int} = 2.61%, R_{sig} = 2.61%) and 5618 (83.16%) were greater than 2σ(F^2). The final cell constants of a = 9.9862(2) Å, b = 12.7443(3) Å, c = 13.1277(3) Å, α = 117.3680(10)°, β

= 94.9270(10)°, γ = 93.2760(10)°, volume = 1469.40(6) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7160 and 0.8640.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{24}H_{20}Cl_{12}O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 343 variables converged at R1 = 2.74%, for the observed data and wR2 = 6.34% for all data. The goodness-of-fit was 1.042. The largest peak in the final difference electron density synthesis was 0.375 $e^-/Å^3$ and the largest hole was -0.310 $e^-/Å^3$ with an RMS deviation of 0.055 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.731 g/cm^3 and F(000), 768 e^-.

Table S5: Sample and crystal data (1570)

Identification code	1570	
Chemical formula	$C_{24}H_{20}Cl_{12}O_2$	
Formula weight	765.80 g/mol	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal size	0.130 x 0.180 x 0.310 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9862(2) Å	α = 117.3680(10)°
	b = 12.7443(3) Å	β = 94.9270(10)°
	c = 13.1277(3) Å	γ = 93.2760(10)°
Volume	1469.40(6) $Å^3$	
Z	2	
Density (calculated)	1.731 g/cm^3	
Absorption coefficient	1.156 mm^{-1}	
F(000)	768	

Table S6: Data collection and structure refinement for 1570

Theta range for data collection	2.59 to 27.60°
Index ranges	-12<=h<=12, -16<=k<=16, -16<=l<=17

Reflections collected	32732	
Independent reflections	6756 [R(int) = 0.0261]	
Max. and min. transmission	0.8640 and 0.7160	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6756 / 0 / 343	
Goodness-of-fit on F^2	1.042	
Δ/σ_{max}	0.001	
Final R indices	5618 data; I>2σ(I)	R1 = 0.0274, wR2 = 0.0597
	all data	R1 = 0.0363, wR2 = 0.0634
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0268P)^2+0.4807P]$ where $P=(F_o+2F_c^2)/3$	
Largest diff. peak and hole	0.375 and -0.310 eÅ^{-3}	
R.M.S. deviation from mean	0.055 eÅ^{-3}	

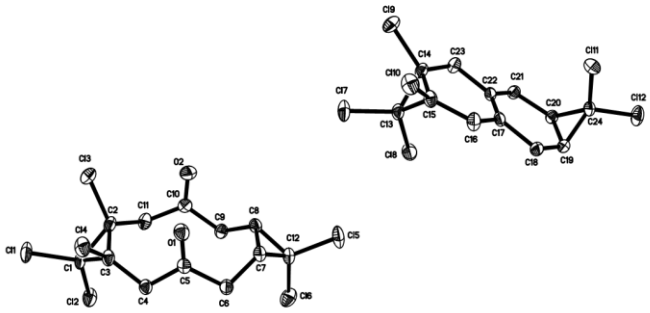
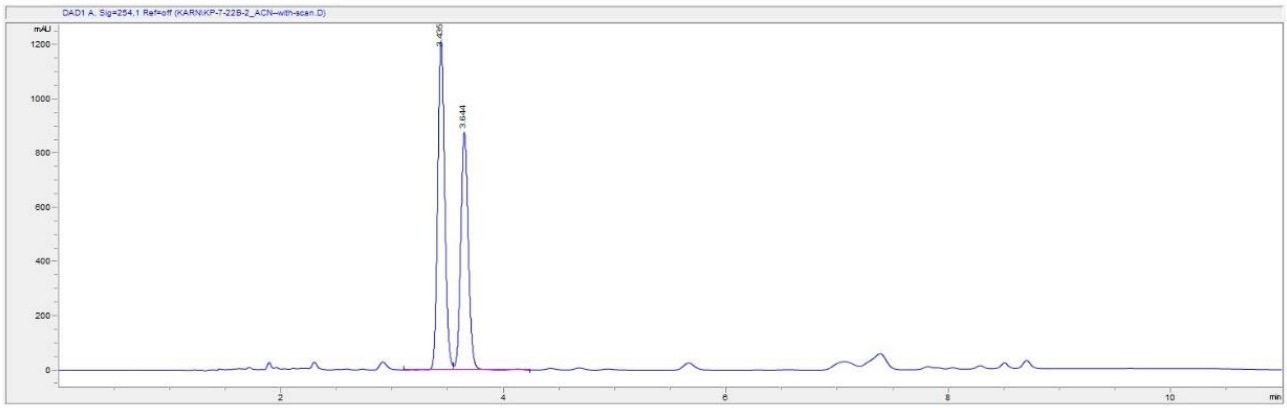
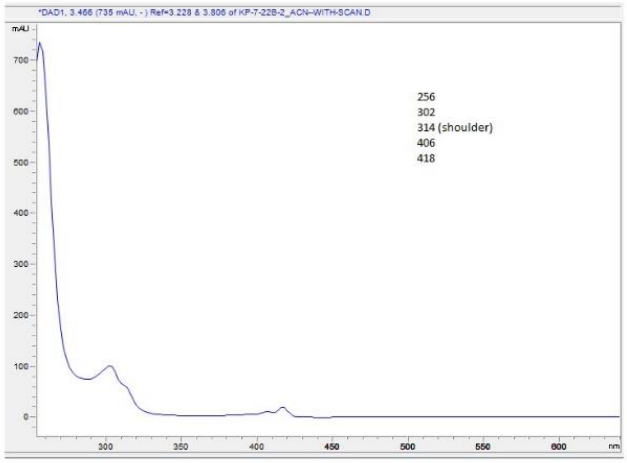


Figure S7: Structures of dione **23** and ***trans*-22**, thermal ellipsoids are at 50% probability.

HPLC chromatogram and UV-vis/fluorescence spectra of **7**:**29** mixture





Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,1 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.435	VV R	0.0675	5316.29395	1213.57874	56.1547
2	3.644	VV R	0.0729	4150.94043	877.41937	43.8453
Totals :				9467.23438	2090.99811	

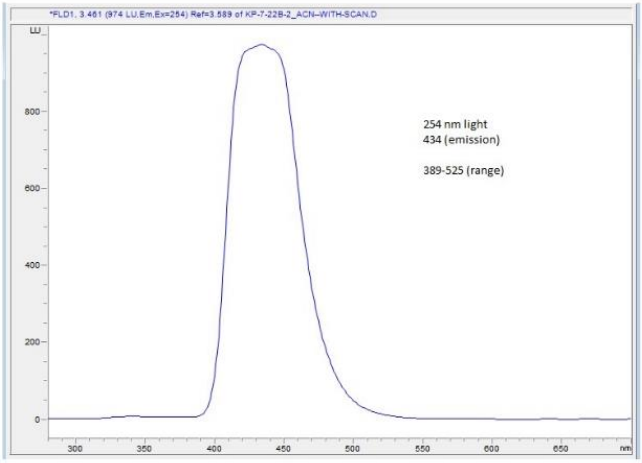
Signal 2: DAD1 B, Sig=280,1 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.435	BV	0.0701	622.07495	138.01361	39.7403
2	3.644	VB	0.0724	943.27594	202.32971	60.2597
Totals :				1565.35089	340.34332	

Signal 3: FLD1 A, Ex=254, Em=zero

Peak #	RetTime [min]	Type	Width [min]	Area [LU*s]	Height [LU]	Area %
1	3.511	BV R	0.1121	6556.57422	933.89539	99.7743
2	9.644	BB	0.0893	14.83493	2.53657	0.2257
Totals :				6571.40914	936.43196	

Data : KP-7-22B-2_ACN--with-scan.D



Timetable

Time min	A %	B %	C %	D %	Flow mL/min	Pressure bar
5.00	20.0	80.0	0.0	0.0	1.000	300.00
6.00	5.0	95.0	0.0	0.0	---	---
8.00	5.0	95.0	0.0	0.0	---	---
9.00	20.0	80.0	0.0	0.0	---	---
11.00	20.0	80.0	0.0	0.0	---	---

Figure S8: top: HPLC trace for the mixture containing **7** (t=3.43[UV-Vis]/3.51[Fluorescence]) and **29** (t=3.64); middle right: UV-Vis trace for **7**; middle left: Detector data; bottom right: Fluorescence emission spectrum for **7** (No fluorescence for **29**).

XYZ data

[10]annulene (**7**) NICS(1)$_{zz}$ geometry

M062X/6-31+G(d,p)

C	0.0	0.0	0.0
C	1.41267	0.0	0.0
C	-0.86763	0.0	1.07328
C	2.349	0.0	1.00584
C	-0.41974	0.0	2.37489
C	2.9289	0.0	2.2512
C	0.09957	0.0	3.48817
C	3.09598	0.0	3.61521
C	0.80686	0.0	4.66911
C	2.18664	0.0	4.69622
C	3.8462	0.0	1.06638
H	-0.45877	0.0	-0.98562
H	1.85908	0.0	-0.99234
H	-1.9377	0.0	0.88544
H	4.14272	0.0	3.91245
H	0.2617	0.0	5.60885
H	2.64546	0.0	5.68182
H	4.37983	-0.91817	0.81786
H	4.37983	0.91817	0.81786
Bq	1.1925	-1.00001	2.30406

Benzene NICS(1)$_{zz}$ geometry

M062X/6-31+G(d,p)

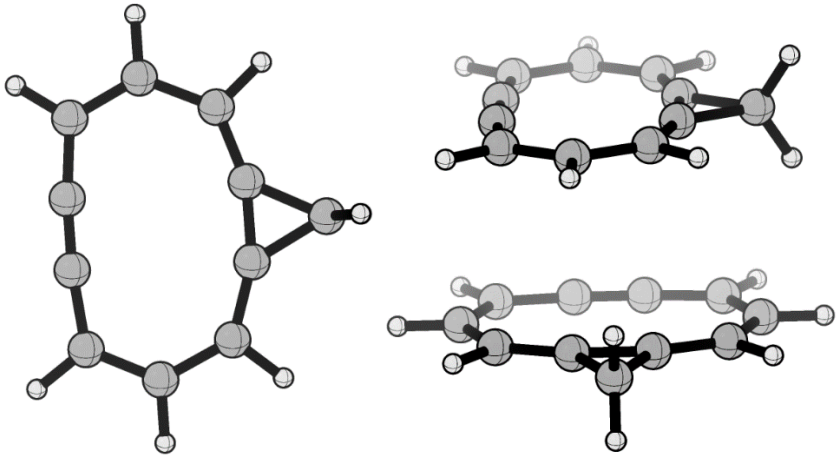
H	3.35552	0.0	1.93731
C	2.41532	0.0	1.39447
C	0.0	0.0	0.0
C	2.4153	0.0	0.0
C	1.20766	0.0	2.09171
C	0.0	0.0	1.39447
C	1.20766	0.0	-0.69725
H	3.35552	0.0	-0.54284
H	1.20768	0.0	3.17737
H	-0.94019	0.0	1.93731
H	1.20764	0.0	-1.78291
H	-0.9402	0.0	-0.54284
Bq	1.20766	-1.00	0.69723

Side product (**29**) geometry

M062X/6-31+G(d,p)

C	2.9984680	-0.1891090	0.1551310
C	1.9634660	-1.0345950	0.8646910
C	2.7165960	0.9493060	-0.5042990
C	1.3879790	1.4639690	-0.5701110
C	0.8399680	-1.4473520	-0.0516250
C	0.2164930	1.7897000	-0.5652100
C	-0.4371690	-1.1355730	0.1694130
C	-1.1709080	2.0952950	-0.5323550
C	-0.9800910	-0.4844010	1.3808110
C	-1.7156650	0.6388870	1.4419270
Cl	-1.6347330	-1.5635110	-1.0535720
C	-2.0385470	1.5740600	0.3624450
H	4.0332790	-0.5220490	0.1864920
H	1.5526800	-0.4655470	1.7100610
H	2.4505520	-1.9248580	1.2760600
H	3.5087810	1.5037070	-1.0011390
H	1.1113860	-1.9649880	-0.9695090
H	-1.5382110	2.8174070	-1.2583270
H	-0.8077420	-1.0254560	2.3104760
H	-2.1426410	0.8931300	2.4122270
H	-3.0611450	1.9472010	0.3394740

Cylview visualization of **7** at M062X/6-31+G(d,p)



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