A Step Toward Polytwistane: Synthesis and Characterization of C_2-Symmetric Tritwistane

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Supplementary Information

Contents

General Experimental Details

All reactions, unless stated otherwise, were carried out under a positive pressure of N_2 in flame-dried glassware. Commercial reagents and solvents were used as purchased with the following exceptions. Tetrahydrofuran (THF) and diethylether (Et_2O) were pre-dried over $CaCl_2$ and distilled over sodium and benzophenone under a nitrogen atmosphere immediately before use. *m*-CPBA was recrystallized from CH_2Cl_2 and stored at –25 °C.[1] Dichloromethane (CH_2Cl_2), Et_2O, ethyl acetate (EtOAc), hexanes and *n*-pentane for flash chromatography and workup were obtained in technical grade and distilled *in vacuo* prior to use. Hexanes refers to the fraction of petroleum that boils between 40 °C and 60 °C. All reactions were magnetically stirred and monitored by analytical thin-layer chromatography (TLC) using *Merck* silica gel 60 F_{254} glass-backed plates. Spots were visualized under UV light (254 nm) or by application of aqueous stains of basic potassium permanganate, ceric ammonium molybdate, anisaldehyde, dinitrophenylhydrazine or vanillin followed by heating with a heat gun. Flash column chromatography was performed on *Merck* silica gel 60 (0.040–0.063 mm). Column diameter, fraction size and amount of silica gel were chosen according to the parameters given by Still *et al.*.[2] Yields refer to chromatographically and spectroscopically pure material. Reactions under high pressure were performed in a 200 mL steel autoclave.The generation of high pressures was realized using a pressure generator by Andreas Hofer Hochdrucktechnik GmbH with a polytetrafluoroethene (teflon) inlet at the MPI für Kohlenforschung (Mülheim).

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or DMSO-d_6 on a *Varian* VNMRS 300, VNMRS 400, INOVA 400 or a VNMRS 600 spectrometer. Chemical shifts (δ) were calibrated using the residual undeuterated solvent as an internal reference and are according to the common convention reported in *parts per million* (ppm) downfield relative to tetramethylsilane (TMS). The chemical shifts of the reference solvents were defined concurrent with the data from Nudelman and coworkers[3] for $CHCl_3$: 7.26 ppm (^{1}H-NMR) and 77.16 ppm (^{13}C-NMR) and DMSO-d_6: 2.50 ppm (^{1}H-NMR) and 39.52 ppm (^{13}C-NMR). For the designation of multiplicities the following abbreviations were used: s (singlet), d (doublet), t (triplet), br (broad) and m (multiplet) or combinations thereof. Protons and carbons were assigned using 2D spectra (HSQC, COSY, NOESY, HMBC) and the assignment is corresponding to the numbering of the given structure. Analysis of all spectra was performed with MestReNova Version 5.2.5. by *Mestrec Laboratories*. Infrared (IR) spectra were recorded on a *Perkin Elmer* Spectrum BX-59343 instrument with a *Smiths Detection* DuraSampl*IR* II Diamond ATR sensor for detection in the range from 4500 cm^{-1} to 600 cm^{-1}. Samples were prepared as a film for liquid or neat for solid substances. Data in the experimental part are given

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(1) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770–2774.
(2) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
(3) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515.

in units of cm^{-1}. High resolution (HRMS) and low resolution (LRMS) mass spectra were recorded on a *Finnigan* MAT 90 and a *Finnigan* MAT 95 instrument. Ionization of the samples was achieved using electron spray ionization (ESI) or electron ionization (EI). In the experimental part only the high resolution mass peak is given and the used mode of ionization is stated.

Materials

The synthesis of known triene **9** from methyl acrylate (**S1**) in five steps according to previously reported procedures is enclosed in the experimental part.

Calculations

Calculations were carried out using Gaussian 03.[4]

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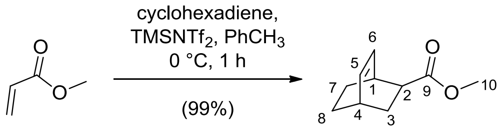
(4) Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Experimental Procedures

Methylbicyclo[2.2.2]oct-5-ene-2-*endo*-carboxylate (S2)[5]



S1 **S2**

Within a glovebox bis(trifluoromethane)sulfonamide (226 mg, 0.802 mmol, 0.150 eq.) was weighed into a one necked flask. Allyltrimethylsilane (0.128 mL, 91.7 mg, 1.60 mmol, 0.300 eq.) was added outside of the glovebox at 0 °C with stirring and stirring was continued at room temperature until the end of gas evolution. The reaction mixture was concentrated for 15 min in high vacuum. The residue was dissolved in toluene (14.5 mL) and methyl acrylate (**S1**) (0.482 mL, 461 mg, 5.35 mmol, 1.00 eq.) and cyclohexadiene (0.997 mL, 857 mg, 10.7 mmol, 2.00 eq.) were added successively at 0 °C to the solution. The reaction mixture was stirred at 0 °C for 1 h, after which time 10 mL of a saturated aqueous $NaHCO_3$ solution were added to the violet reaction mixture. The resulting mixture was stirred at room temperature for 1 h during which time it turned yellow. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (hexanes : EtOAc = gradient from 99 : 1 to 9 : 1) afforded bicycloester **S2** as a colorless oil (880 mg, 99%).

$C_{10}H_{14}O_2$	M_r = 166.22 g·mol^{-1}.	
TLC	R_f = 0.44 (hexanes : EtOAc = 9 : 1).	
^{1}H-NMR	(300 MHz, $CDCl_3$): δ = 6.35 – 6.27 (m, 1H), 6.18 – 6.11 (m, 1H), 3.63 – 3.62 (s, 3H), 2.96 – 2.88 (m, 1H), 2.67 – 2.56 (m, 2H), 1.79 – 1.64 (m, 2H), 1.60 – 1.45 (m, 2H), 1.33 – 1.19 (m, 2H) ppm.	
^{13}C-NMR	(75 MHz, $CDCl_3$): δ = 176.1 (C=O), 135.3 (CH), 131.5 (CH), 51.8 (CH_3), 42.8 (CH), 32.6 (CH), 30.0 (CH_2), 29.5 (CH), 25.5 (CH_2), 24.5 (CH_2) ppm.	
IR	(ATR): ν_{max} = 2943, 1733, 1434, 1195, 1171, 1054, 698 cm^{-1}.	
HRMS	(EI): m/z for $C_{10}H_{14}O_2^+$ $[M]^+$:	calcd.: 166.0994 found: 166.0982.

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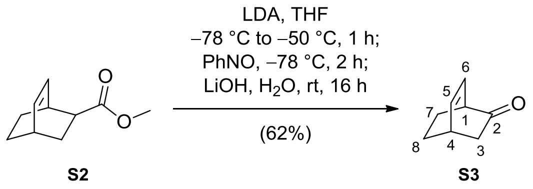
[5] Mathieu, B.; Ghosez, L. *Tetrahedron* **2002**, *58*, 8219–8226.

Bicyclo[2.2.2]oct-5-en-2-one (S3)[6]



To a solution of diisopropylamine (5.09 mL, 36.0 mmol, 1.20 eq.) in THF (80 mL) was added at –78 °C a solution of *n*-butyllithium in hexanes (2.36 M, 14.0 mL, 33.0 mmol, 1.10 eq.). The resulting mixture was stirred at –78 °C for 1 h before a solution of ester **S2** (4.99 g, 30.0 mmol, 1.00 eq.) in THF (20.0 mL) was added. During the addition the color of the reaction mixture turned yellow. The mixture was stirred for an additional 60 min and the reaction mixture was allowed to warm to –50 °C. The mixture was recooled to –78 °C and a solution of nitrosobenzene (3.37 g, 31.5 mmol, 1.05 eq.) in THF (15.0 mL) was added. The resulting mixture was stirred for 2 h at –78 °C and was then quenched with H_2O (30 mL) and allowed to warm to room temperature. The solvent was removed *in vacuo* and the orange residue was taken up in 1,4-dioxane (100 mL) and treated with a solution of LiOH in H_2O (2.00 M, 75.0 mL, 150 mmol, 5.00 eq.). The resulting solution was stirred at room temperature for 16 h and was then extracted with EtOAc (5 x 100 mL). The combined organic layer was washed with brine (2 x 100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by column chromatography (hexanes : Et_2O = 10 : 1) and subsequent sublimation (55 °C, 45 mbar) afforded the desired ketone **S3** (2.27 g, 62%) as a colorless solid.

$C_8H_{10}O$	$M_r = 122.16$ g·mol^{-1}.
TLC	$R_f = 0.55$ (hexanes : EtOAc = 3 : 1).
mp	80 – 82 °C.
^{1}H-NMR	(300 MHz, $CDCl_3$): $\delta = 6.47$ (ddd, J = 7.9, 6.5, 1.2 Hz, 1H), 6.19 (ddd, J = 8.1, 6.5, 1.7 Hz), 3.16 – 3.07 (m, 1H), 3.04 – 2.93 (m, 1H), 2.05 – 2.00 (m, 2H), 1.90 – 1.79 (m, 1H), 1.74 – 1.65 (m, 1H), 1.64 – 1.50 (m, 2H) ppm.
^{13}C-NMR	(75 MHz, $CDCl_3$): $\delta = 213.3$ (C=O), 137.2 (CH), 128.6 (CH), 48.7 (CH), 40.6 (CH_2), 32.5 (CH), 24.4 (CH_2), 22.6 (CH_2) ppm.
IR	(ATR): $\nu_{max} = 1725, 701$ cm^{-1}.
HRMS	(EI): m/z for $C_8H_{10}O^+$ $[M]^+$: calcd.: 122.0726 found: 122.0728.

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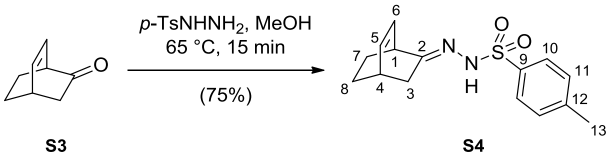
[6] Mukherjee, S.; Scopton, A. P.; Corey, E. J. *Org. Lett.* **2010**, *12*, 1836–1838.

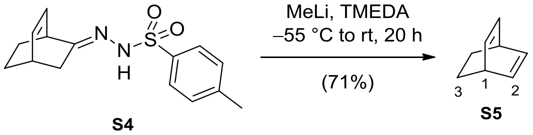
Bicyclo[2.2.2]oct-5-en-2-one tosylhydrazone (S4)[7]



To a solution of ketone **S3** (1.65 g, 13.5 mmol, 1.00 eq.) in MeOH (162 mL) was added tosylhydrazide (4.27 g, 22.9 mmol, 1.70 eq.). The resulting mixture was heated to 65 °C to dissolve all reagents. The resulting solution was allowed to cool to room temperature was left to stand to allow crystallization. Crystallization was completed by cooling to 0 °C and the precipitate was filtered and washed with cold MeOH and Et_2O to afford hydrazone **S4** (2.95 g, 75%) as colorless crystals.

$C_{15}H_{18}N_2O_2S$	$M_r = 290.38$ g·mol^{-1}.
TLC	$R_f = 0.43$ (hexanes : EtOAc = 3 : 1).
mp	215 °C (dec.).
^{1}H-NMR	(400 MHz, DMSO-d_6): $\delta = 9.81$ (s, 1H), 7.71 (d, $J = 8.1$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 6.40 – 6.28 (m, 1H), 6.25 – 6.16 (m, 1H), 3.05 – 3.00 (m, 1H), 2.87 – 2.80 (m, 1H), 2.37 (s, 3H), 2.16 – 1.96 (m, 2H), 1.56 – 1.43 (m, 2H), 1.37 – 1.19 (m, 2H) ppm.
^{13}C-NMR	(100 MHz, DMSO-d_6): $\delta = 164.5$ (C=N), 143.0 (C_{Ar}), 136.5 (C_{Ar}), 136.0 (CH), 130.8 (CH), 129.4 (C_{Ar}), 127.4 (C_{Ar}), 39.3 (CH), 32.6 (CH_2), 30.4 (CH), 24.0 (CH_2), 23.9 (CH_2), 21.0 (CH_3) ppm.
IR	(ATR): $\nu_{max} = 3212$, 1401, 1331, 1292, 1164, 1091, 1038, 1025, 969, 932, 814, 771, 702 cm^{-1}.
HRMS	(ESI+): m/z for $C_{15}H_{19}O_2N_2S^+$ $[M+H]^+$: calcd.: 291.1162 found: 291.1159.

Bicyclo[2.2.2]octa-2,5-diene – Dihydrobarrelene (S5)[7]



To a solution of tosylhydrazone **S4** (1.78 g, 6.12 mmol, 1.00 eq.) in TMEDA (12.2 mL, 81.1 mmol, 13.3 eq.) at –55 °C was added a solution of methyllithium in Et_2O (1.60 M, 16.8 mL, 26.9 mmol, 4.40 eq.). The resulting yellow mixture was allowed to warm to room temperature and stirred at this temperature for 20 h. The resulting red reaction mixture was cooled to –30 °C, quenched by addition

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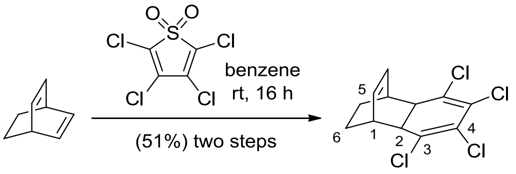
(7) Lightner, D. A.; Gawronski, J. K.; Bouman, T. D. *J. Am. Chem. Soc.* **1980**, *102*, 5749–5754.

of H_2O (0.75 mL) and subsequently allowed to warm to room temperature. The mixture was diluted with H_2O (50 mL) and extracted with *n*-pentane (5 x 100 mL). The combined organic layer was washed with HCl (2 m, 3 x 150 mL), NaOH (10 wt-%, 2 x 150 mL), dried (Na_2SO_4) and filtered over a silica plug. The solvent was removed by careful distillation from a water bath to afford a concentrated solution of dihydrobarrelene (**S5**) (~450 mg, 71%) in *n*-pentane. This solution was used for the next step without further purification, due to the volatility of the product. An analytically pure sample (colorless waxy solid) of the diene was obtained by sublimation (35 °C, 100 mbar) of a part of the product.

C_8H_{10}	M_r = 106.17 g·mol^{-1}.
TLC	R_f = 0.75 (hexanes).
mp	50 – 53 °C.
^{1}H-NMR	(300 MHz, $CDCl_3$): δ = 6.34 – 6.28 (m, 4H), 3.67 – 3.57 (m, 2H), 1.27 – 1.26 (m, 4H) ppm.
^{13}C-NMR	(75 MHz, $CDCl_3$): δ = 134.5 (CH), 37.1 (CH), 24.9 (CH_2) ppm.
IR	(ATR): ν_{max} = 2953, 1358, 908, 823, 700, 667 cm^{-1}.
HRMS	(EI): m/z for $C_8H_{10}^+$ $[M]^+$: calcd.: 106.0777 found: 106.0769.

Endo-3,4,5,6-Tetrachlorobicyclo[6.2.2.0^{2,7}]dodeca-3,4,9-triene (9)[8]



S5 **9**

To a solution of crude dihydrobarrelene (**S5**) (650 mg, 6.12 mmol, 1.00 eq.) in benzene (49.0 mL) at room temperature was added tetrachlorothiophene dioxide[9] (1.55 g, 6.12 mmol, 1.00 eq.) and the resulting mixture was stirred at room temperature for 12 h. The solvent was removed *in vacuo* and purification of the residue by flash column chromatography (hexanes) afforded triene **9** (897 mg, 51% over two steps) as a colorless solid.

$C_{12}H_{10}Cl_4$	M_r = 296.02 g·mol^{-1}.
TLC	R_f = 0.55 (hexanes).
mp	100 – 102 °C.

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[8] Grimme, W.; Wortmann, J.; Frowein, D.; Lex, J.; Chen, G.; Gleiter, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1893–1900.
[9] Lou, Y.; Chang, J.; Jorgensen, J.; Lemal, D. M. *J. Am. Chem. Soc.* **2002**, *154*, 15302–15307.

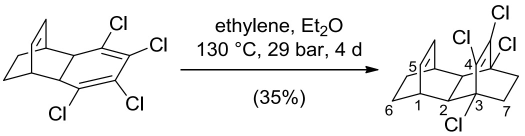
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 6.36 – 6.33 (m, 2H), 3.25 – 3.21 (m, 2H), 3.16 – 3.13 (m, 2H), 1.63 – 1.57 (m, 2H), 1.39 – 1.29 (m, 2H) ppm.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 134.1 (CH), 132.8 (C-Cl), 123.2 (C-Cl), 48.6 (CH), 33.8 (CH), 24.3 (CH_2) ppm.

IR (ATR): ν_{max} = 2937, 2937, 1616, 1215, 1168, 1098, 834, 782, 712 cm^{-1}.

HRMS (EI): m/z for $C_{12}H_{10}Cl_4^+$ $[M]^+$: calcd.: 293.9531
found: 293.9529.

syn-3,4,5,6-Tetrachlorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene (10)[8]



9 10

In the glass liner of an autoclave with 200 mL working space dodecatriene **9** (2.37 g, 8.00 mmol, 1.00 eq.) was dissolved in Et_2O (80.0 mL). The glass liner was furnished with a gas inlet and a gasoutlet and cooled to –110 °C and ethylene (1 L pressure tin) was condensed into the solution. The glass liner was put into a dry-ice cooled autoclave and the autoclave was sealed and heated slowly to 130 °C at which temperature the reaction mixture was stirred for 4 d at a pressure of approximately 29 bar. After cooling to room temperature excess ethylene was released and the reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography (hexanes) to afford tetradecadiene **10** (890 mg, 35%) as colorless crystals. Based on recovered starting material (1.455 g, 4.92 mmol) a yield of 89% was achieved. Recrystallization from hexanes afforded crystals suitable for X-ray analysis.

$C_{14}H_{14}Cl_4$ M_r = 324.08 g·mol^{-1}.

TLC R_f = 0.47 (hexanes).

mp 87 – 89 °C.

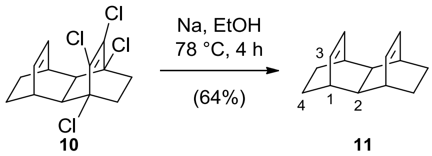
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.09 – 5.99 (m, 2H), 2.98 – 2.84 (m, 2H), 2.38 (br s, 2H), 2.20 – 2.10 (m, 2H), 2.00 – 1.90 (m, 2H), 1.54 – 1.44 (m, 2H), 1.29 – 1.18 (m, 2H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 129.8 (CH), 127.5 (C-Cl), 70.9 (C-Cl), 53.0 (CH), 39.0 (CH_2), 31.8 (CH), 25.5 (CH_2) ppm.

IR (ATR): ν_{max} = 992, 964, 846, 760, 719, 648, 578 cm^{-1}.

HRMS (EI): m/z for $C_{14}H_{14}Cl_4^+$ $[M]^+$: calcd.: 324.9844
found: 324.9851.

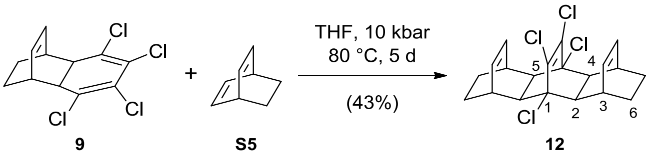
***syn*-3,4,5,6-Tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene (11)**[8]



A solution of chlorinated diene **10** (502 mg, 1.55 mmol, 1.00 eq.) in EtOH (30.0 mL) was heated to reflux. Sodium (1.78 g, 77.5 mmol, 50.0 eq.) was added in small pieces over a period of 3.5 h and after complete addition the reaction mixture was heated to reflux for an additional 45 min. After cooling to room temperature the reaction slurry was poured on an ice/H_2O mixture (75 g) and was extracted with *n*-pentane (3 x 125 mL). The combined organic phase was washed with H_2O (2 x 125 mL), brine (125 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (*n*-pentane) afforded diene **11** (186 mg, 64%) as a colorless solid.

$C_{14}H_{18}$	$M_r = 186.29$ g·mol^{-1}.
TLC	$R_f = 0.79$ (hexanes).
mp	55 – 56 °C.
^{1}H-NMR	(300 MHz, $CDCl_3$): $\delta = 5.81 - 5.74$ (m, 4H), 2.34 – 2.24 (m, 4H), 1.95 (br s, 2H), 1.53 – 1.42 (m, 4H), 1.14 – 1.03 (m, 4H) ppm.
^{13}C-NMR	(75 MHz, $CDCl_3$): $\delta = 132.1$ (CH), 43.8 (CH), 35.3 (CH), 27.3 (CH_2) ppm.
IR	(ATR): $\nu_{max} = 2948, 2931, 2900, 2876, 2861, 836, 683, 649$ cm^{-1}.
HRMS	(EI): m/z for $C_{14}H_{18}^+$ $[M]^+$: calcd.: 186.1403 found: 186.1402.

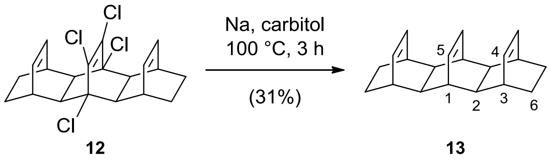
all-*syn*-1,8,15,16-Tetrachlorohexacyclo[6.6.2.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]icosa-4,11,15-triene (12)[8]



Dodecatriene **9** (828 mg, 2.80 mmol, 1.00 eq.) was placed in the teflon inlet (10 mL) of an autoclave together with a crystal of 4-*tert*-butylcatechol and was dissolved in THF (6.00 mL). Dihydrobarrelene (**S5**) (300 mg, 2.80 mmol, 1.00 eq.) was added. The lid was put on top of the surface of the liquid and the inlet was placed in the autoclave. The reaction mixture was submitted to a pressure of 10 kbar at 80 °C for five days. After cooling to room temperature the reaction mixture was concentrated *in vacuo*. Purification of the residue by flash column chromatography (hexanes) afforded chlorinated hexacycloicosatriene **12** (423 mg, 43%) as colorless crystals. Recrystallization from hexanes afforded crystals suitable for X-ray analysis.

$C_{20}H_{20}Cl_4$	M_r = 402.19 g·mol^{-1}.	
TLC	R_f = 0.52 (hexanes).	
mp	210°C (dec.).	
^{1}H-NMR	(300 MHz, $CDCl_3$): δ = 6.03 – 5.96 (m, 4H), 2.99 – 2.89 (m, 4H), 2.34 – 2.30 (m, 4H), 1.52 – 1.42 (m, 4H), 1.24 – 1.15 (m, 4H) ppm.	
^{13}C-NMR	(75 MHz, $CDCl_3$): δ = 130.5 (CH), 124.7 (C-Cl), 75.0 (C-Cl), 54.2 (CH), 31.6 (CH), 25.7 (CH_2) ppm.	
IR	(ATR): ν_{max} = 1028, 951, 867, 756, 719, 668, 646, 624 cm^{-1}.	
HRMS	(EI): m/z for $C_{20}H_{20}Cl_4^+$ [M^+]:	calcd.: 403.0314 found: 403.0311.

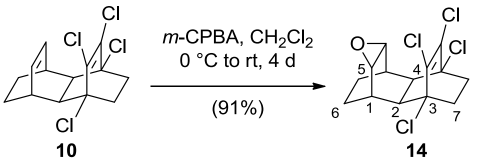
all-*syn*-Hexacyclo[6.6.2.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]icosa-4,11,15-triene (13)[8]



A solution of chlorinated triene **12** (567 mg, 1.41 mmol, 1.00 eq.) in diethylene glycol monoethyl ether (40.2 mL) was heated to 100 °C. Sodium (1.63 g, 71.0 mmol, 50.4 eq.) was added in small pieces over a period of 2.5 h and after complete addition the reaction mixture was heated to 100 °C for an additional 30 min. After cooling to room temperature the reaction slurry was poured on an ice/H_2O mixture (50 g) and was extracted with *n*-pentane (5 x 35 mL). The combined organic phase was washed with H_2O (2 x 50 mL), brine (25 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (*n*-pentane) afforded triene **13** (114 mg, 31%) as a colorless solid. Significant amounts of starting material **12** (175 mg) could be recovered.

$C_{20}H_{24}$	M_r = 264.41 g·mol^{-1}.	
TLC	R_f = 0.75 (hexanes).	
mp	141 – 143 °C.	
^{1}H-NMR	(600 MHz, $CDCl_3$): δ = 5.71 – 5.66 (m, 4H), 5.28 – 5.24 (m, 2H), 2.28 – 2.22 (m, 6H), 1.98 – 1.94 (m, 4H), 1.48 – 1.43 (m, 4H), 1.07 – 1.01 (m, 4H) ppm.	
^{13}C-NMR	(150 MHz, $CDCl_3$): δ = 132.4 (CH), 130.5 (CH), 45.8 (CH), 41.4 (CH), 34.9 (CH), 27.5 (CH_2) ppm.	
IR	(ATR): ν_{max} = 2923, 2902, 2867, 1426, 1376, 1152, 733, 692, 665 cm^{-1}.	
HRMS	(EI): m/z for $C_{20}H_{24}^+$ [M]$^+$:	calcd.: 264.1873 found: 264.1875.

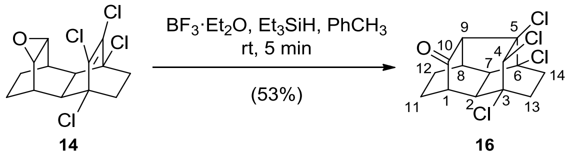
9,10-Epoxy-3,4,5,6-tetrachlorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-ene (14)



To a solution of chlorinated laticyclic diene **10** (250 mg, 0.770 mmol, 1.00 eq.) in CH_2Cl_2 (5 mL) at 0 °C was added *m*-CPBA (266 mg, 1.54 mmol, 2.00 eq.) and KF (89.5 mg, 1.54 mmol, 2.00 eq.). The resulting mixture was stirred at room temperature for 4 d. Then KF (89.5 mg, 1.54 mmol, 2.00 eq.) was added and the reaction mixture was filtered and the residue was washed with CH_2Cl_2. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography (hexanes : EtOAc = 9 : 1) to afford epoxide **14** (239 mg, 91%) as a colorless solid. Recrystallization from hexanes afforded crystals suitable for X-ray analysis.

$C_{14}H_{14}Cl_4O$	$M_r = 340.08$ g·mol^{-1}.
TLC	$R_f = 0.34$ (hexanes : EtOAc = 9 : 1).
mp	125 – 127 °C.
^{1}H-NMR	(600 MHz, $CDCl_3$): $\delta = 3.12 - 3.08$ (m, 2H), 2.67 – 2.63 (m, 2H), 2.42 – 2.40 (m, 2H), 2.26 – 2.21 (m, 2H), 2.09 – 2.04 (m, 2H), 1.84 – 1.79 (m, 2H), 1.18 – 1.13 (m, 2H) ppm.
^{13}C-NMR	(150 MHz, $CDCl_3$): $\delta = 129.0$ (C-Cl), 70.6 (C-Cl), 52.4 (CH), 49.8 (CH), 39.5 (CH_2), 30.2 (CH), 24.4 (CH_2) ppm.
IR	(ATR): $\nu_{max} = 996, 953, 946, 853, 805, 735$ cm^{-1}.
HRMS	(EI): m/z for $C_{14}H_{14}Cl_4O^+$ $[M]^+$: calcd.: 337.9793 found: 337.9799.

3,4,5,6-Tetrachloro-10-oxopentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{5,9}]tetradecane (16)

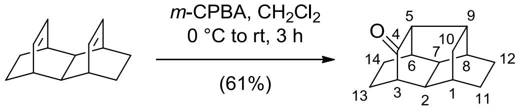


To a solution of epoxide **14** (20.1 mg, 59.0 µmol, 1.00 eq.) in toluene (2.00 mL) was added a solution of triethylsilane in toluene (0.114 mL of a 10 vol-% solution, 70.8 µmol, 1.20 eq.) and $BF_3{\cdot}OEt_2$ (0.174 mL of a 5 vol-% solution in toluene, 70.8 µmol, 1.20 eq.). The reaction mixture was stirred at room temperature for 5 min and was then quenched by addition of saturated aqueous $NaHCO_3$ (1 mL).

The reaction mixture was extracted with EtOAc (3 x 2 mL) and the combined organic layer was washed with brine (2 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was recrystallized from hexanes : Et_2O to afford ketone **16** (20 mg, 99%) as colorless crystals which were suitable for X-ray crystallography.

$C_{14}H_{14}Cl_4O$	M_r = 340.08 g·mol^{-1}.
TLC	R_f = 0.20 (hexanes : EtOAc = 9 : 1).
mp	154 – 158 °C.
^{1}H-NMR	(600 MHz, $CDCl_3$): δ = 4.53 (d, J = 1.6 Hz, 1H), 3.40 – 3.37 (m, 1H), 3.23 (dd, J = 6.4, 2.9 Hz, 1H), 2.85 – 2.82 (m, 2H), 2.78 (ddd, J = 14.1, 10.9, 8.8 Hz, 1H), 2.68 – 2.63 (m, 2H), 2.30 (ddd, J = 14.1, 10.8, 0.8 Hz, 1H), 2.19 – 2.14 (m, 1H), 2.14 – 2.08 (m, 1H), 1.83 – 1.75 (m, 2H), 1.69 – 1.61 (m, 1H) ppm.
^{13}C-NMR	(150 MHz, $CDCl_3$): δ = 214.2 (C=O), 78.0 (C-Cl), 76.3 (C-Cl), 72.8 (CH), 70.1 (CH), 69.1 (C-Cl), 48.8 (CH), 48.6 (CH), 42.6 (CH), 40.3 (CH), 34.9 (CH_2), 30.6 (CH_2), 28.2 (CH_2), 17.7 (CH_2) ppm.
IR	(ATR): ν_{max} = 1729, 1002, 921, 892 cm^{-1}.
HRMS	(EI): m/z for $C_{14}H_{14}Cl_4O^+$ $[M]^+$: calcd.: 337.9793 found: 337.9780.

Pentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{5,9}]tetradecan-4-one (19)



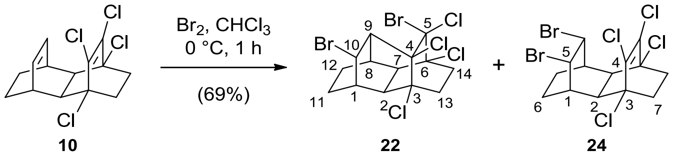
11 **19**

To a solution of tetracyclotetradecadiene **11** (30.0 mg, 0.161 mmol, 1.00 eq.) in CH_2Cl_2 (2.50 mL) at 0 °C was added *m*-CPBA (70-75 wt%, 37.5 mg, 0.161 mmol, 1.00 eq.). The reaction mixture was stirred at 0 °C for 1 h, was then allowed to warm to room temperature and stirred at room temperature for an additional 2 h. After dilution with CH_2Cl_2 (15 mL) the reaction mixture was poured into 10% aqueous NaOH (10 mL) and the organic layer was washed with H_2O (2 x 7.5 mL), brine (7.5 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (hexanes : EtOAc = 9 : 1) afforded ketone **19** (20.0 mg, 61%) as a colorless solid. Recrystallization from hexanes afforded crystals suitable for X-ray analysis.

$C_{14}H_{18}O$	M_r = 202.29 g·mol^{-1}.
TLC	R_f = 0.36 (hexanes : EtOAc = 9 : 1).
mp	95 – 97 °C.

^{1}H-NMR	(300 MHz, $CDCl_3$): δ = 2.80 – 2.71 (m, 1H), 2.40 – 2.29 (m, 1H), 2.27 – 2.19 (m, 1H), 2.17 – 2.10 (m, 1H), 2.07 – 2.01 (m, 1H), 2.00 – 1.88 (m, 2H), 1.85 – 1.72 (m, 4H), 1.67 – 1.53 (m, 5H), 1.52 – 1.37 (m, 2H) ppm.		
^{13}C-NMR	(100 MHz, $CDCl_3$): δ = 222.7 (C=O), 58.9 (CH), 47.1 (CH), 42.5 (CH), 40.6 (CH), 39.1 (CH), 38.3 (CH), 37.4 (CH), 29.5 (CH), 28.6 (CH_2), 28.3 (CH_2), 27.2 (CH_2), 19.8 (CH_2), 19.8 (CH_2) ppm.		
IR	(ATR): ν_{max} = 2925, 2859, 1721, 1260, 1090, 1063, 1025, 994, 909, 886, 858, 812, 798, 732 cm^{-1}.		
HRMS	(EI): m/z for $C_{14}H_{18}O^+$ [M$^+$]:	calcd.:	202.1352
		found:	202.1348.

Bromination of *syn*-3,4,5,6-Tetrachlorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene (10)



To a solution of chlorinated diene **10** (40.5 mg, 125 µmol, 1.00 eq.) in $CHCl_3$ (2.50 mL) at 0 °C was added a solution of bromine in $CHCl_3$ (0.700 mL of a 1.37 vol-% solution, 188 µmol, 1.50 eq.). The reaction mixture was stirred at 0 °C for 1 h and the reaction was then quenched by addition of diluted aqueous $Na_2S_2O_3$. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 x 5 mL). The combined organic layer was washed with $NaHCO_3$ (10 mL), brine (10 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (hexanes : EtOAc = 95 : 5) afforded 1,2-dibromide **24** (19 mg, 31%) as a colorless solid and hexahalogenated tritwistane **22** (23 mg, 38%) as an unseparable mixture of isomers at C5 (7 : 3 in favor of the displayed isomer) in form of a colorless solid. Recrystallization from hexanes (for 1,2-dibromide **24**) and $CHCl_3$ (for halogenated tritwistane **22**) respectively afforded crystals suitable for X-ray diffraction experiments.

Analytical Data for 5,10-Dibromo-3,4,5,6-tetrachloropentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{4,9}]tetradecane (22)

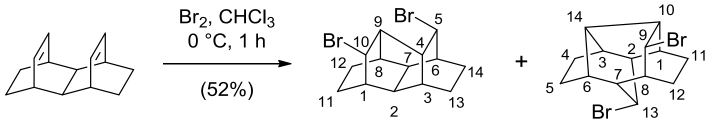
$C_{14}H_{14}Br_2Cl_4$	M_r = 483.88 g·mol^{-1}.
TLC	R_f = 0.34 (hexanes : EtOAc = 9 : 1).
^{1}H-NMR	(300 MHz, $CDCl_3$, both diastereomers): δ = 5.54 (d, J = 5.8 Hz, 1H), 3.27 – 3.19 (m, 1H), 3.06 – 2.91 (m, 2H), 2.68 – 2.24 (m, 6H), 2.14 – 1.91 (m, 2H), 1.63 – 1.42 (m, 2H) ppm.

^{13}C-NMR	(75 MHz, $CDCl_3$, major diastereomer): δ = 91.6 (C-Cl), 81.2 (C-Cl), 73.3 (C-Cl), 71.9 (C-Cl), 56.5 (CH), 50.6 (CH), 48.0 (CH), 47.4 (CH), 36.5 (CH_2), 35.7 (CH_2), 33.3 (CH), 26.6 (CH), 21.2 (CH_2), 19.9 (CH_2) ppm.
IR	(ATR): ν_{max} = 1463, 1018, 945, 906, 866, 849, 839, 806, 791, 738, 667, 649, 642, 603 cm^{-1}.
HRMS	(EI): m/z for $C_{14}H_{14}Br_2Cl_4^+$ [M]$^+$: calcd.: 479.8211 found: 479.8203.

Analytical Data for *syn*-9,10-Dibromo-3,4,5,6-tetrachlorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-ene (24)

$C_{14}H_{14}Br_2Cl_4$	M_r = 483.88 g·mol^{-1}.
TLC	R_f = 0.43 (hexanes : EtOAc = 9 : 1).
mp	152 – 155 °C.
^{1}H-NMR	(300 MHz, $CDCl_3$): δ = 4.58 – 4.51 (m, 2H), 2.56 – 2.50 (m, 2H), 2.44 – 2.40 (m, 2H), 2.40 – 2.34 (m, 2H), 2.26 – 2.18 (m, 2H), 2.13 – 2.04 (m, 2H), 1.48 – 1.40 (m, 2H) ppm.
^{13}C-NMR	(75 MHz, $CDCl_3$): δ = 129.4 (C-Cl), 69.3 (C-Cl), 52.9 (CH), 50.4 (CH), 39.6 (CH_2), 35.7 (CH), 21.2 (CH_2) ppm.
IR	(ATR): ν_{max} = 1465, 1311, 1059, 991, 956, 905, 877, 837, 811, 734, 713, 661, 610 cm^{-1}.
HRMS	(EI): m/z for $C_{14}H_{14}Br_2Cl_4^+$ [M]$^+$: calcd.: 479.8211 found: 479.8209.

Bromination of *syn*-3,4,5,6-Tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene (11)



11 **27** **30**

To a solution of diene **11** (49.9 mg, 268 µmol, 1.00 eq.) in $CHCl_3$ (3.00 mL) at 0 °C was added a solution of bromine in $CHCl_3$ (1.253 mL of a 1.37 vol-% solution, 335 µmol, 1.25 eq.). The reaction mixture was stirred at 0 °C for 1 h and the reaction was then quenched by addition of diluted aqueous $Na_2S_2O_3$. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 x 15 mL). The combined organic layer was washed with $NaHCO_3$ (30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by flash column chromatography (hexanes : Et_2O = 95 : 5) afforded rearranged dibromide **30** (15 mg, 14%) and dibromotritwistane **27**

(35 mg, 38%) as colorless solids. Recrystallization from hexanes afforded crystals suitable for X-ray diffraction experiments for both compounds.

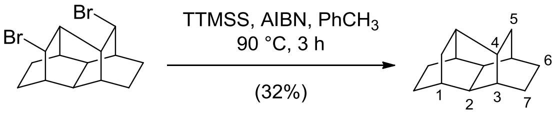
Analytical Data for 5,10-Dibromopentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{4,9}]tetradecane (27)

$C_{14}H_{18}Br_2$	M_r = 346.10 g·mol^{-1}.	
TLC	R_f = 0.25 (hexanes).	
^{1}H-NMR	(600 MHz, $CDCl_3$): δ = 4.63 (d, J = 5.9 Hz, 1H), 4.49 (d, J = 5.4 Hz, 1H), 2.67 – 2.63 (m, 1H), 2.50 – 2.46 (m, 1H), 2.43 – 2.38 (m, 1H), 2.33 – 2.26 (m, 1H), 2.18 – 2.12 (m, 2H), 2.02 – 1.95 (m, 2H), 1.82 – 1.76 (m, 2H), 1.73 – 1.66 (m, 2H), 1.61 – 1.52 (m, 2H), 1.48 – 1.38 (m, 2H) ppm.	
^{13}C-NMR	(150 MHz, $CDCl_3$): δ = 56.0 (CH), 54.9 (CH), 42.3 (CH), 39.8 (CH), 37.8 (CH), 37.7 (CH), 36.1 (CH), 35.6 (CH), 32.3 (CH), 27.5 (CH), 25.9 (CH_2), 21.5 (CH_2), 21.4 (CH_2), 21.2 (CH_2) ppm.	
IR	(ATR): ν_{max} = 2939, 2868, 745 cm^{-1}.	
HRMS	(EI): m/z for $C_{14}H_{18}Br_2^+$ $[M]^+$:	calcd.: 345.9750 found: 345.9568.

Analytical Data for 9,13-Dibromopentacyclo[6.2.2.1^{2,7}.1^{3,6}.0^{10,14}]tetradecane (30)

$C_{14}H_{18}Br_2$	M_r = 346.10 g·mol^{-1}.	
TLC	R_f = 0.35 (hexanes).	
mp	130 – 136 °C.	
^{1}H-NMR	(600 MHz, $CDCl_3$): δ = 5.12 (m, 1H), 4.78 (ddd, J = 5.4, 5.4, 1.3 Hz, 1H), 2.82 – 2.79 (m, 1H), 2.79 – 2.74 (ddd, J = 13.5, 9.6, 4.4 Hz, 1H), 2.52 – 2.46 (m, 2H), 2.43 – 2.38 (m, 2H), 2.38 – 2.31 (m, 4H), 2.27 (dddd, J = 14.4, 11.4, 4.7, 1.9 Hz, 1H), 2.11 (dddd, J = 14.9, 11.4, 6.0, 6.0 Hz, 1H), 1.83 – 1.76 (m, 2H), 1.75 – 1.68 (m, 1H), 1.56 – 1.53 (m, 1H) ppm.	
^{13}C-NMR	(150 MHz, $CDCl_3$): δ = 56.3 (CH), 53.2 (CH), 52.9 (CH), 51.9 (CH), 47.3 (CH), 47.0 (CH), 43.1 (CH), 41.5 (CH), 38.0 (CH), 37.2 (CH), 28.9 (CH_2), 26.9 (CH_2), 24.0 (CH_2), 18.8 (CH_2) ppm.	
IR	(ATR): ν_{max} = 2933, 823, 803, 770, 741, 719 cm^{-1}.	
HRMS	(EI): m/z for $C_{14}H_{18}Br^+$ $[M{-}Br]^+$:	calcd.: 265.0586 found: 265.0594.

Pentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{4,9}]tetradecane – C_2-Tritwistane (3)



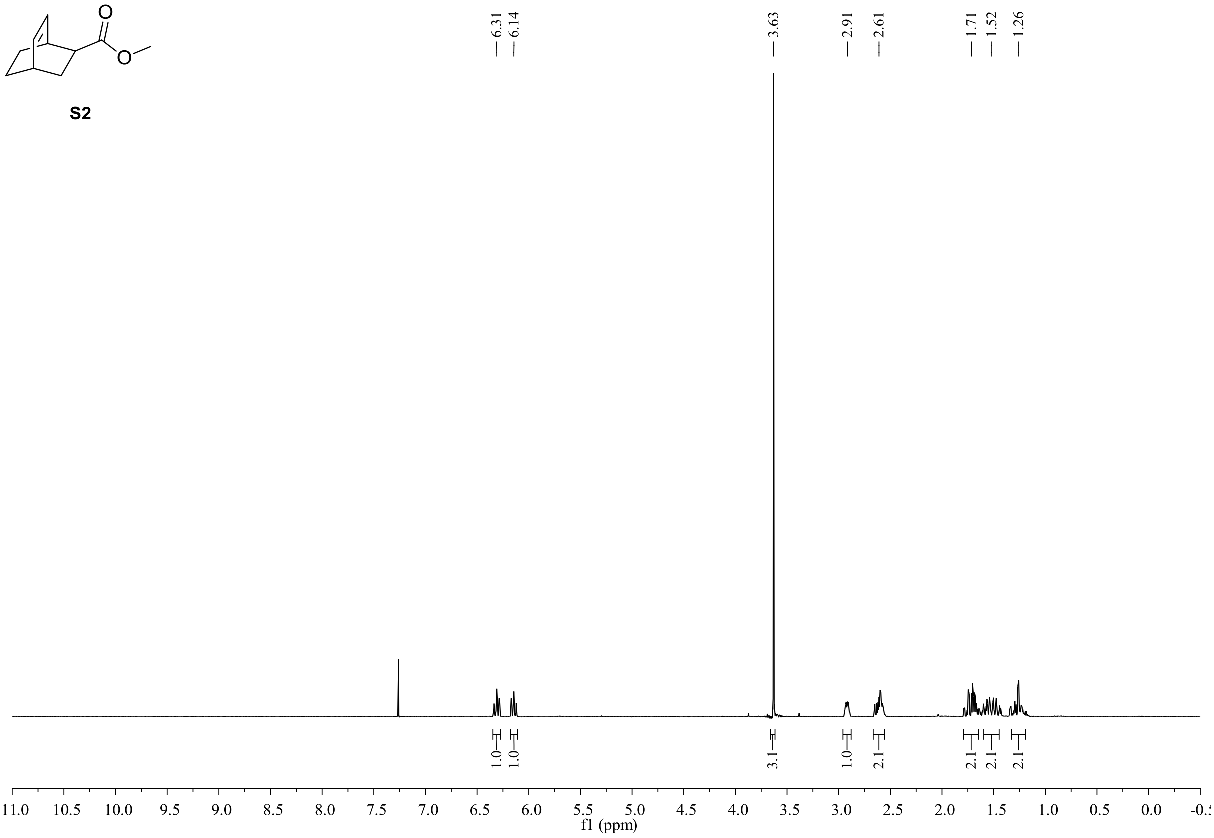
27 **3**

To a solution of dibromide **27** (34.6 mg, 0.100 mmol, 1.00 eq.) in toluene (3.00 mL) was added TTMSS (0.075 mL, 59.7 mg, 0.240 mmol, 2.40 eq.) and one crystal of AIBN (2.50 mg, 0.015 mmol, 0.150 eq.). The resulting mixture was heated to 90 °C for 3 h and was then allowed to cool to room temperature and was concentrated *in vacuo*. The residue was purified by flash column chromatography (2 x 20 cm, *n*-pentane, 8 mL) to afford tritwistane (**3**) contaminated with some silicon species as a colorless oil. A solution of this oil in $CDCl_3$ (1.50 mL) was stirred over a fluoride polymer at room temperature for 8 d. The solution was filtered over a short silica column and the solvent was removed *in vacuo* to afford tritwistane (**3**) (6 mg, 32%) as a waxy amorphous solid.

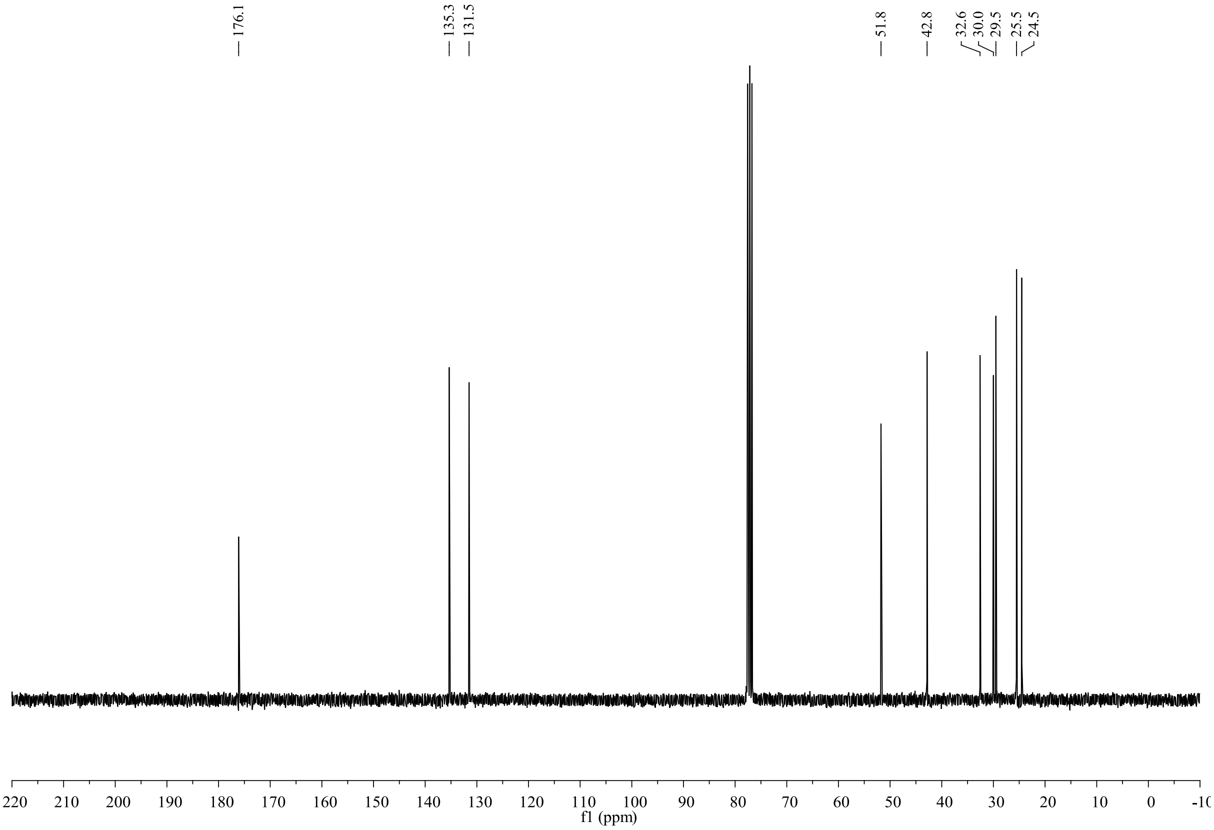
$C_{14}H_{20}$	M_r = 188.31 g·mol^{-1}.	
TLC	R_f = 0.92 (hexanes).	
^{1}H-NMR	(600 MHz, $CDCl_3$): δ = 1.72 (m, 2H), 1.70 – 1.63 (m, 6H), 1.52 – 1.44 (m, 10H), 1.36 (dd, J = 12.1, 5.0 Hz, 2H) ppm.	
^{13}C-NMR	(150 MHz, $CDCl_3$): δ = 35.4 (CH), 33.6 (CH), 29.1 (CH), 28.6 (CH), 27.3 (CH), 24.8 (CH_2), 22.8 (CH_2) ppm.	
IR	(ATR): $\nu_{\max}$ = 2921, 2908, 2871, 2860 cm^{-1}.	
HRMS	(EI): m/z for $C_{14}H_{20}^+$ [M]$^+$:	calcd.: 188.1560 found: 188.1549.

NMR Spectra

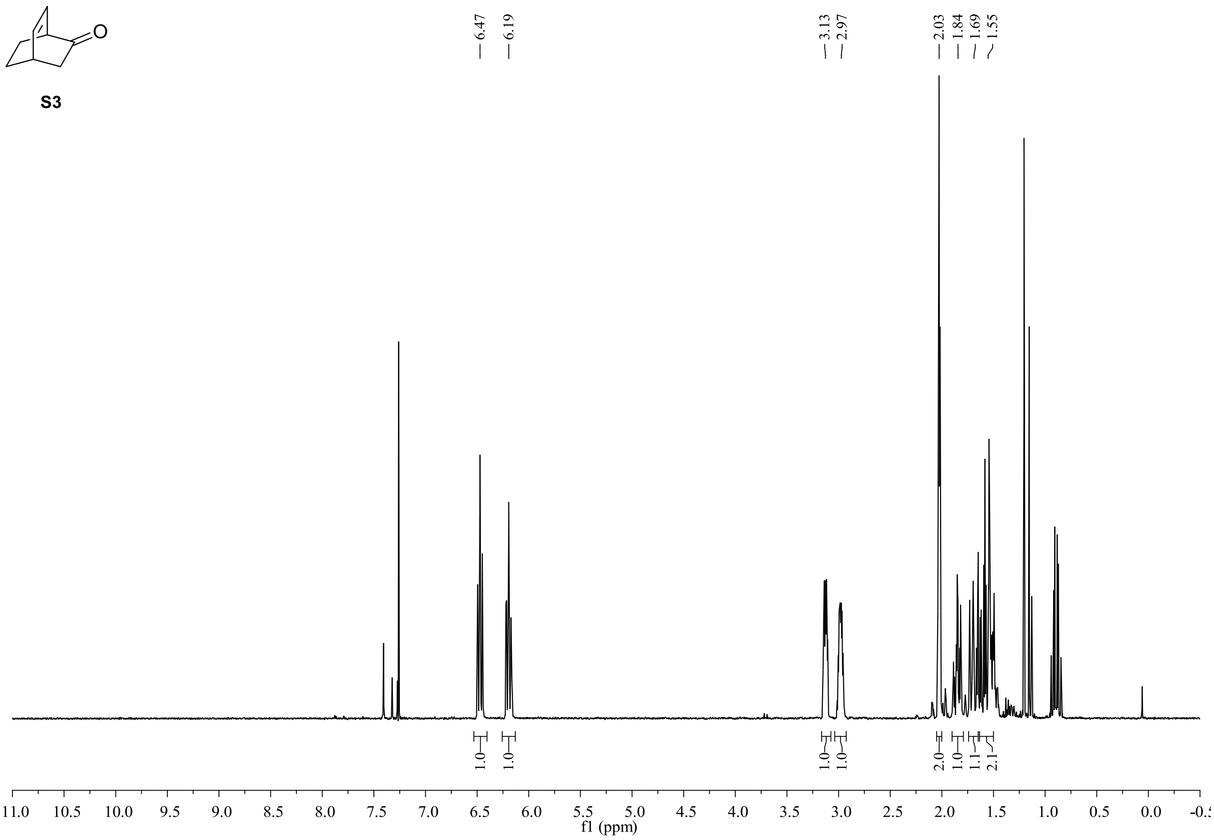
S2 (^{1}H-NMR, 300 MHz, CDCl$_3$)



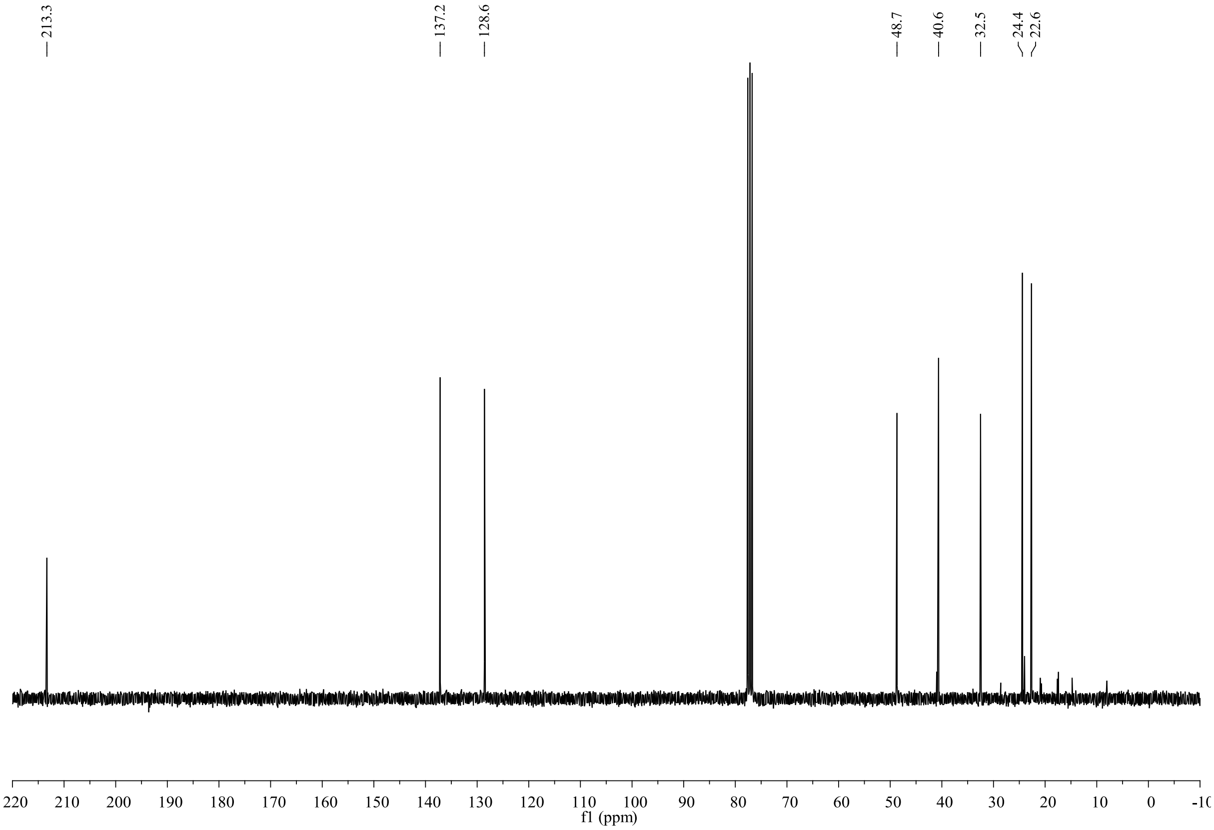
S2 (^{13}C-NMR, 75 MHz, CDCl$_3$)



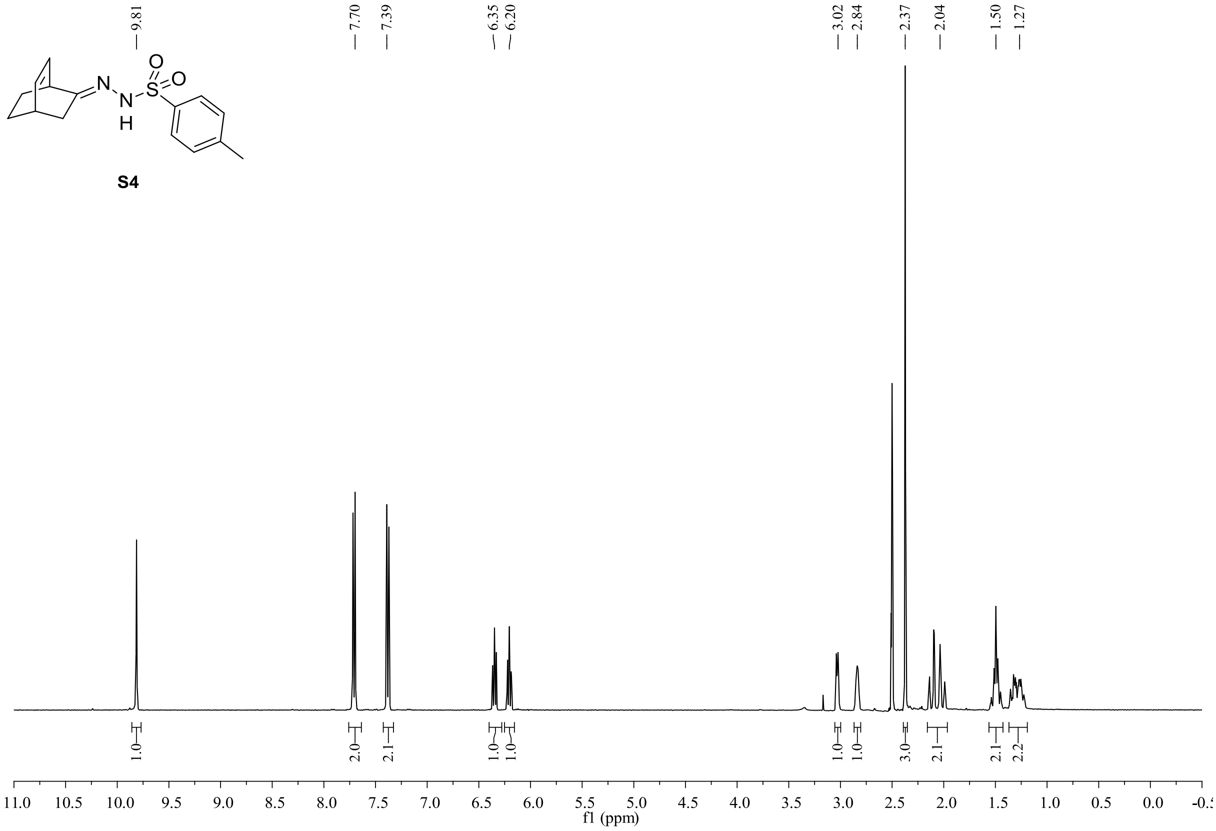
S3 (^{1}H-NMR, 300 MHz, $CDCl_3$)



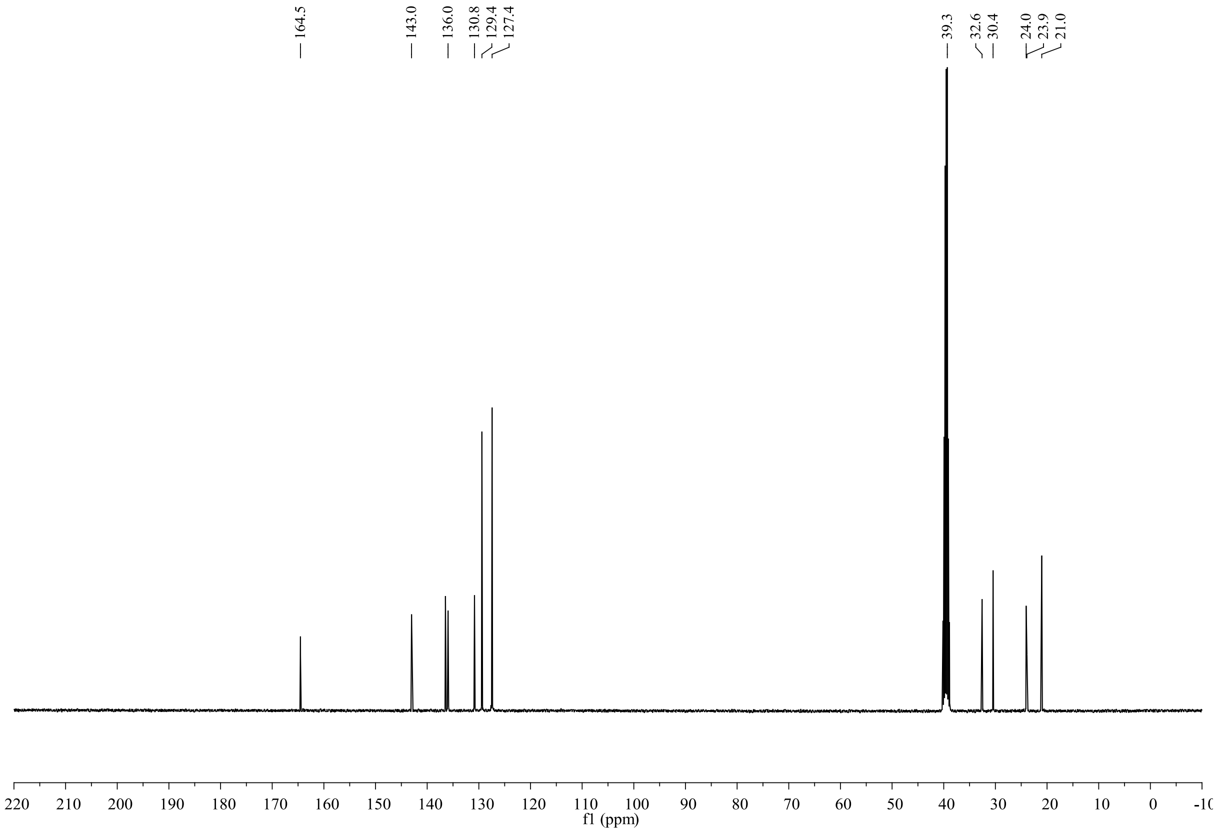
S3 (^{13}C-NMR, 75 MHz, $CDCl_3$)



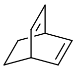
S4 (^{1}H-NMR, 400 MHz, DMSO-d_6)



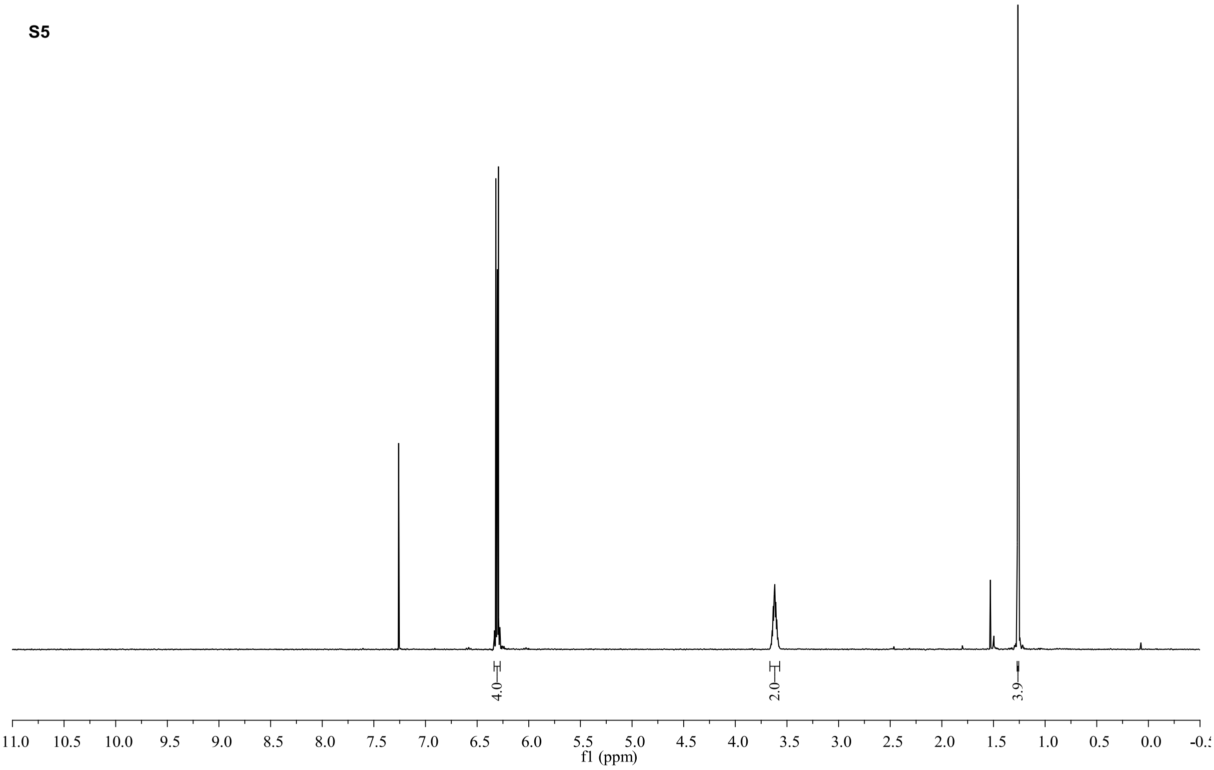
S4 (^{13}C-NMR, 100 MHz, DMSO-d_6)



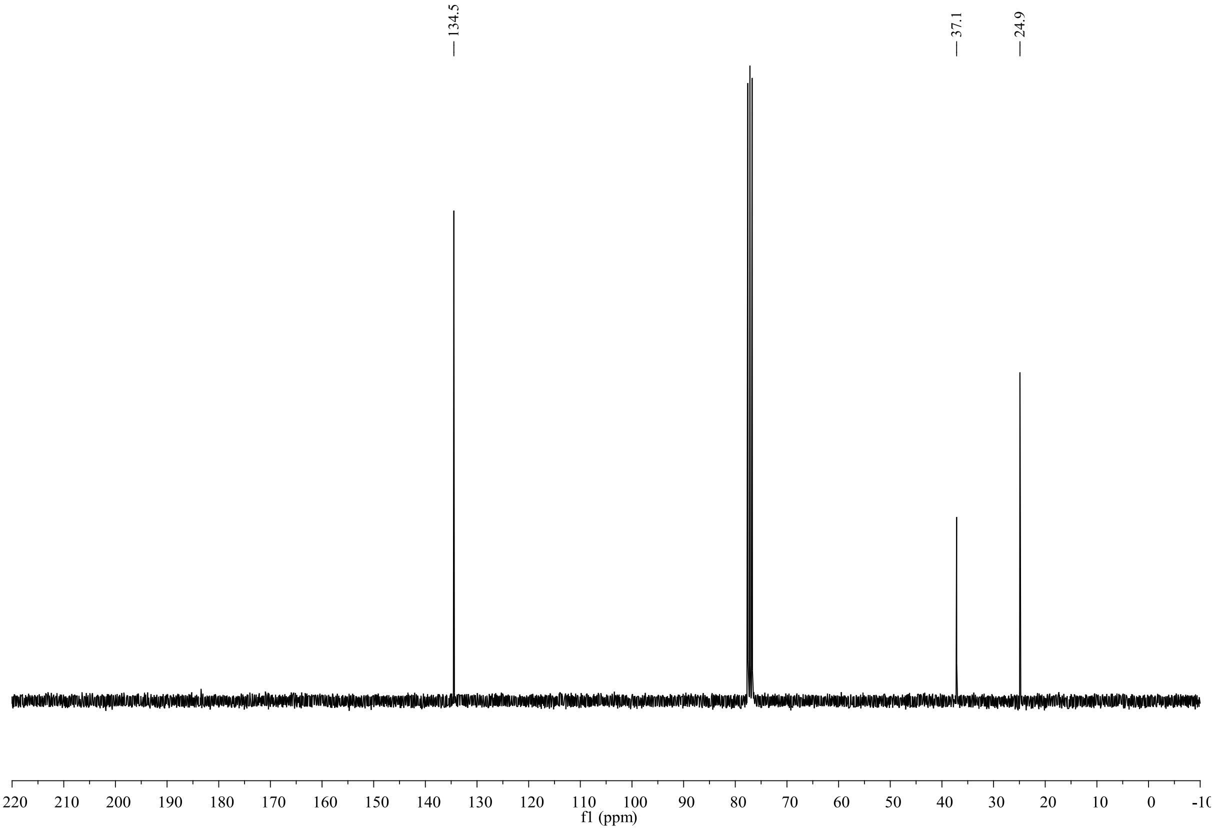
S5 (^{1}H-NMR, 300 MHz, CDCl$_3$)



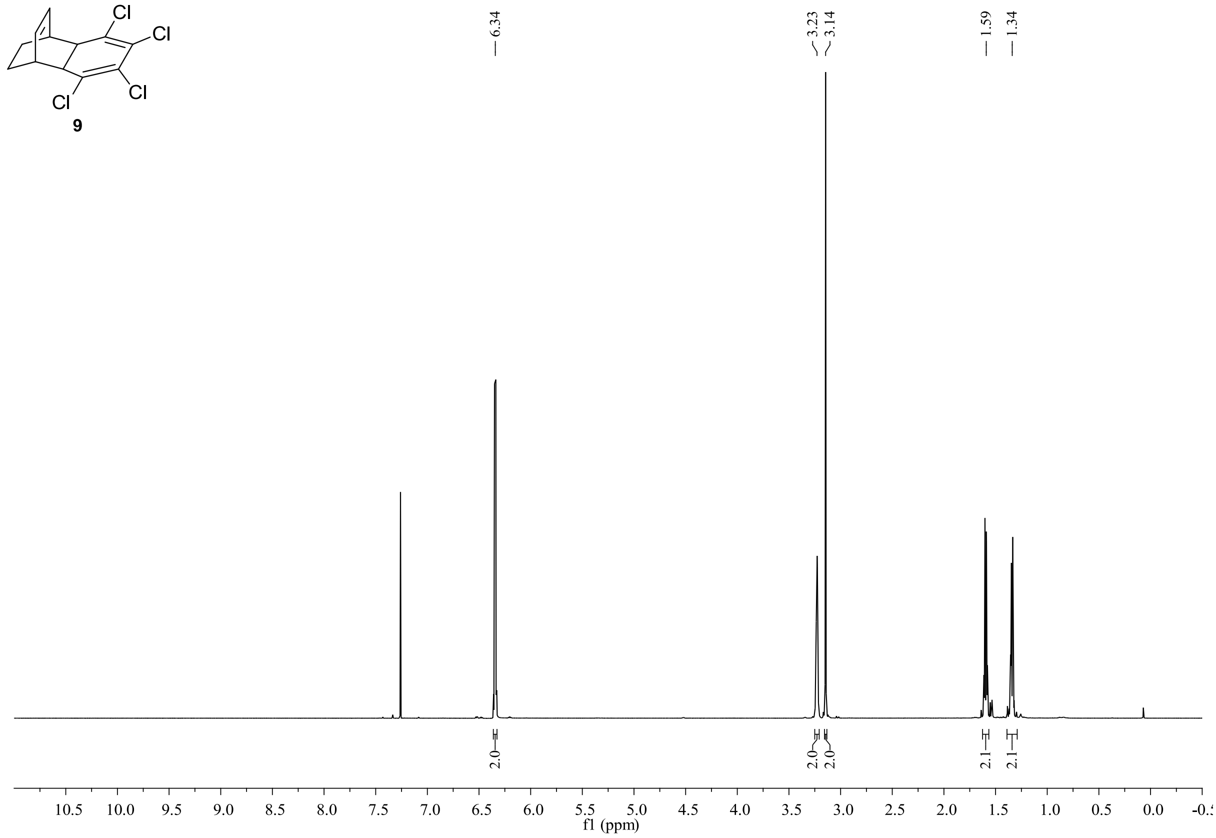
S5



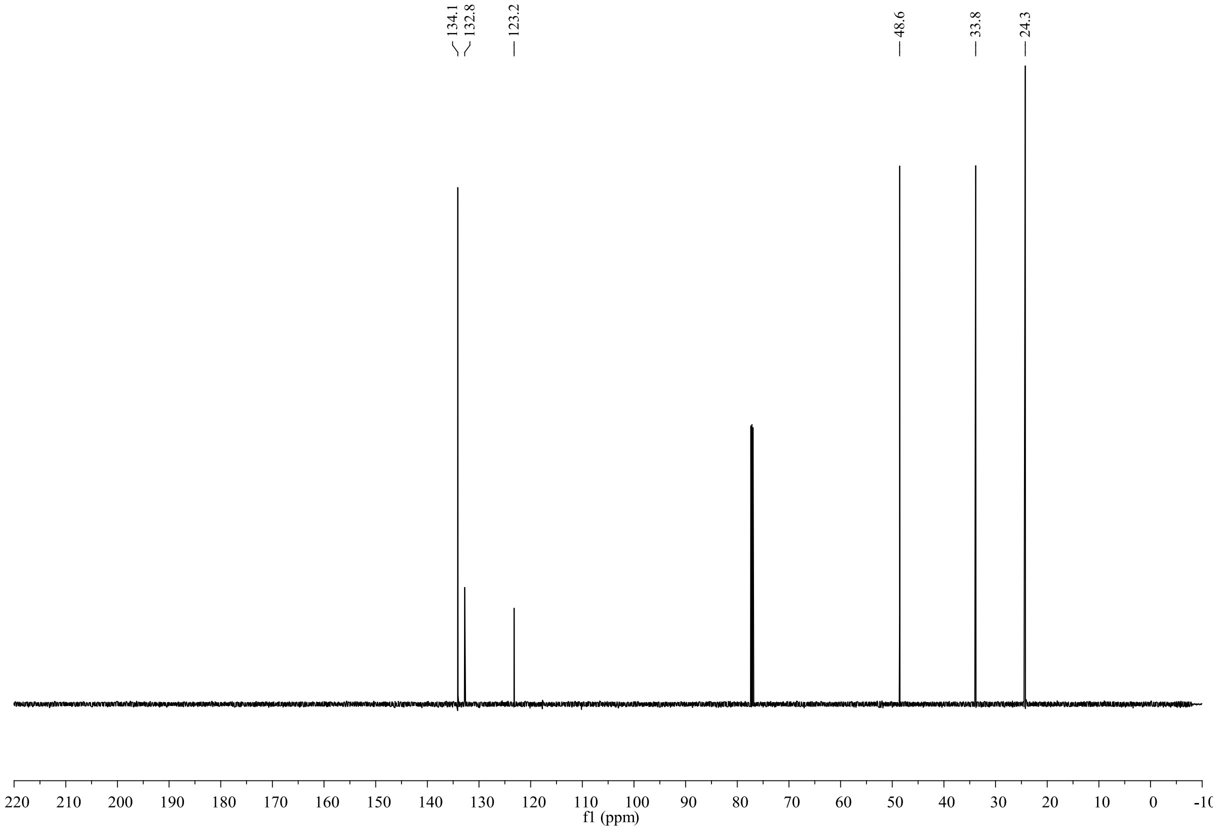
S5 (^{13}C-NMR, 75 MHz, CDCl$_3$)



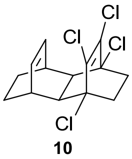
9 (^{1}H-NMR, 600 MHz, $CDCl_3$)



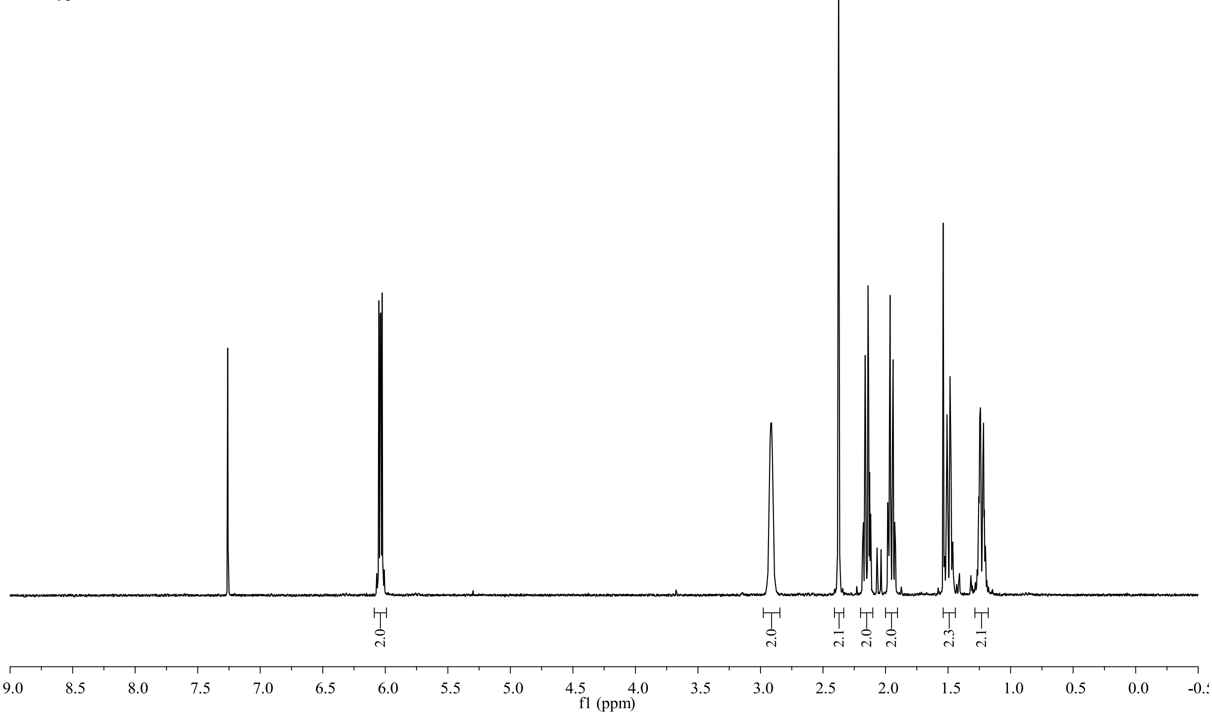
9 (^{13}C-NMR, 150 MHz, $CDCl_3$)



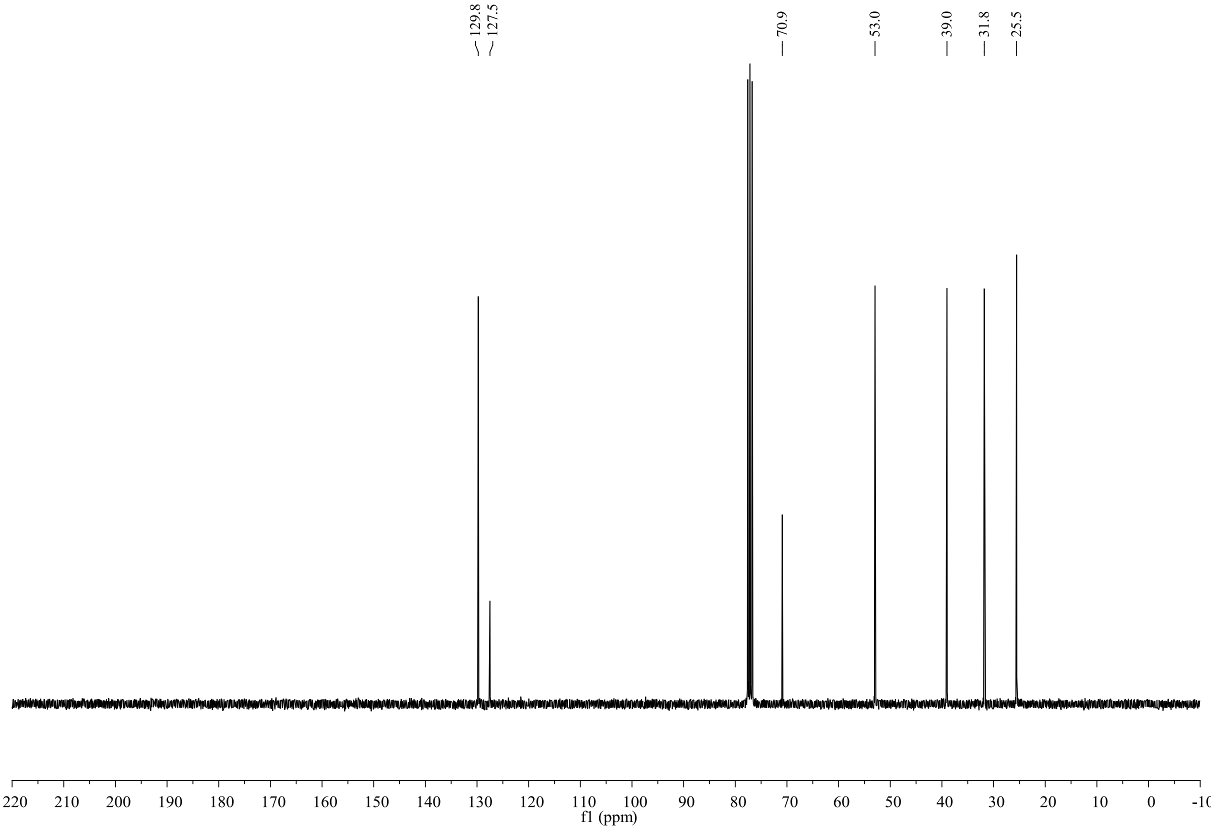
10 (^{1}H-NMR, 300 MHz, $CDCl_3$)



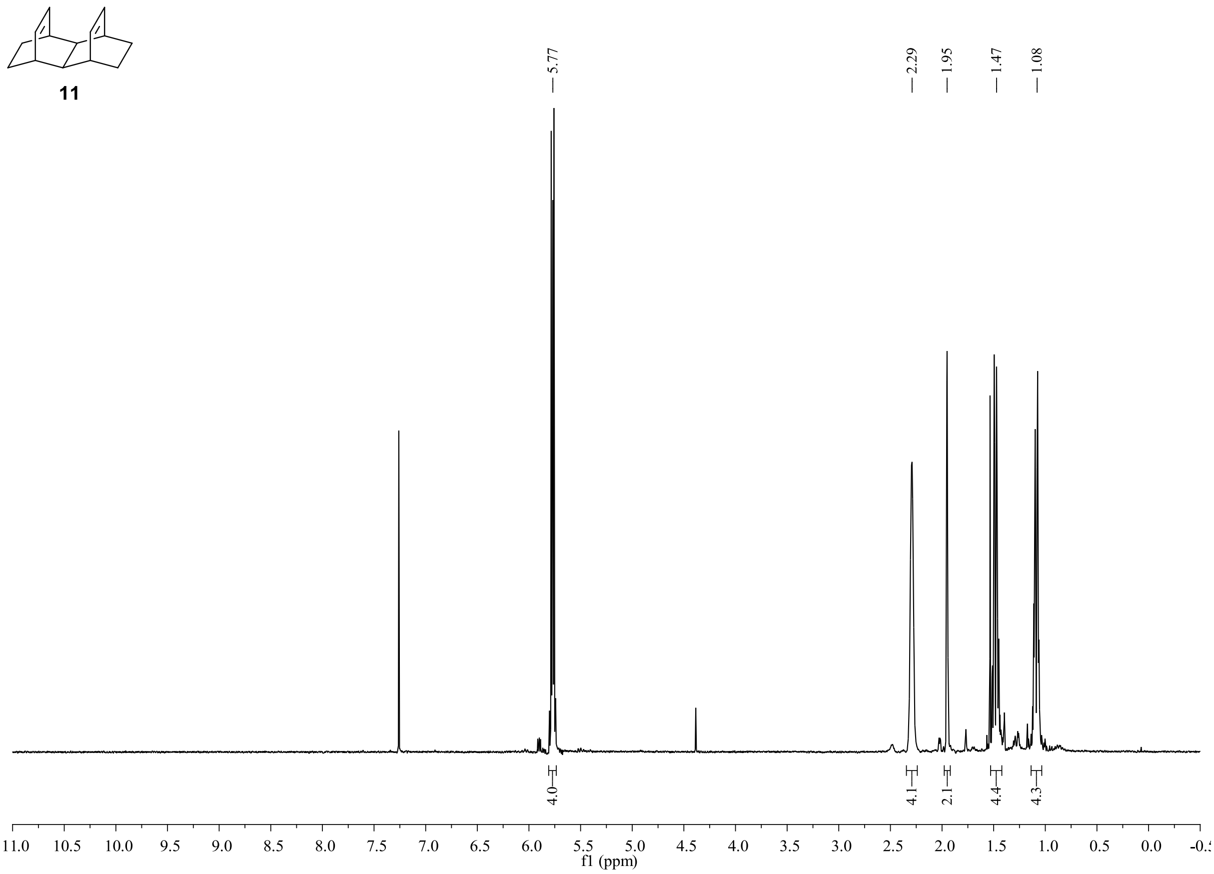
10



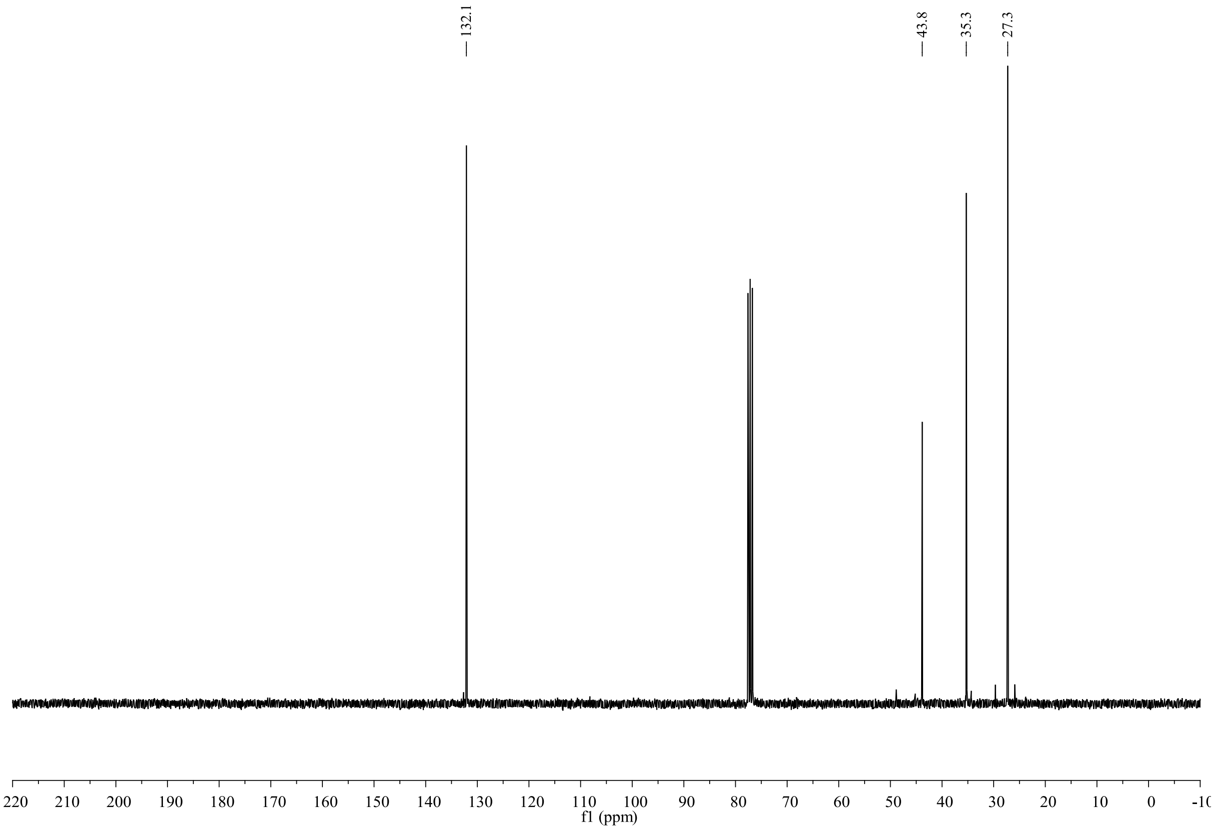
10 (^{13}C-NMR, 75 MHz, $CDCl_3$)



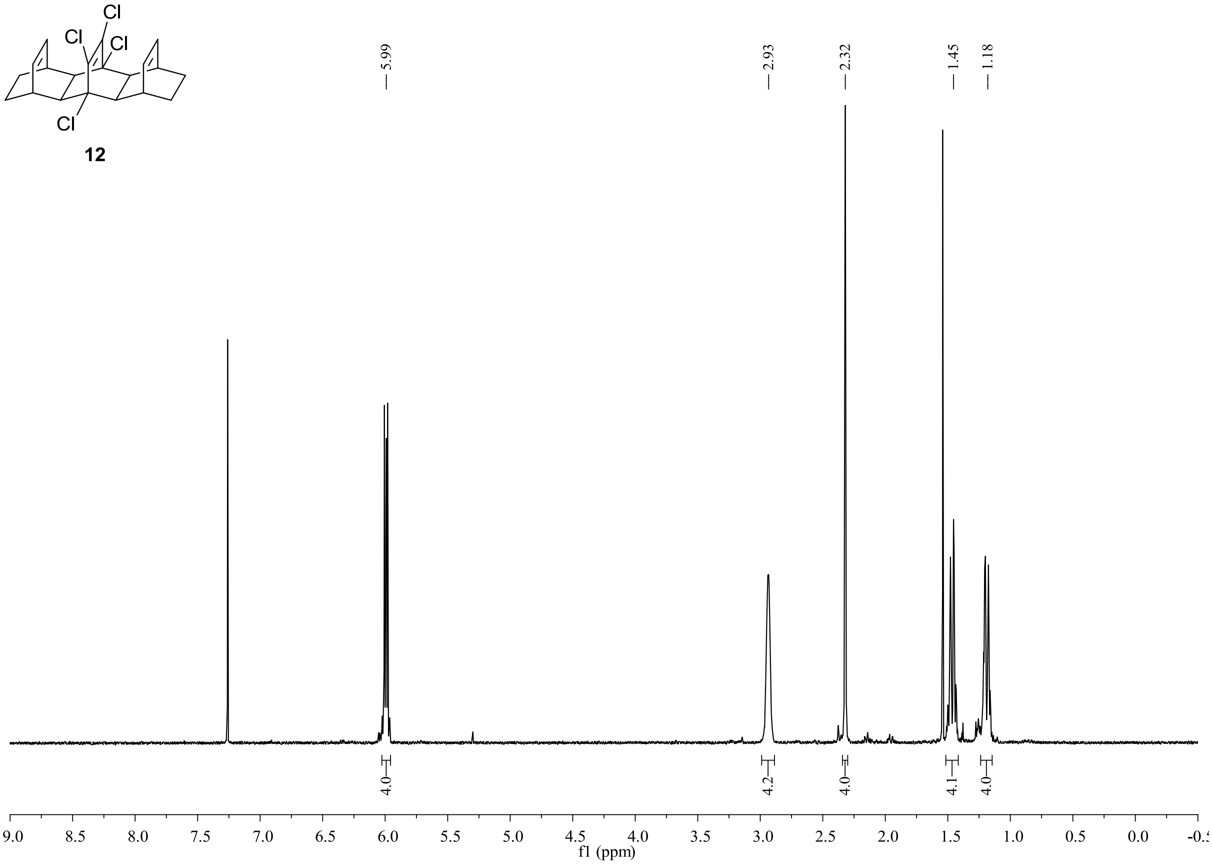
11 (^{1}H-NMR, 300 MHz, $CDCl_3$)



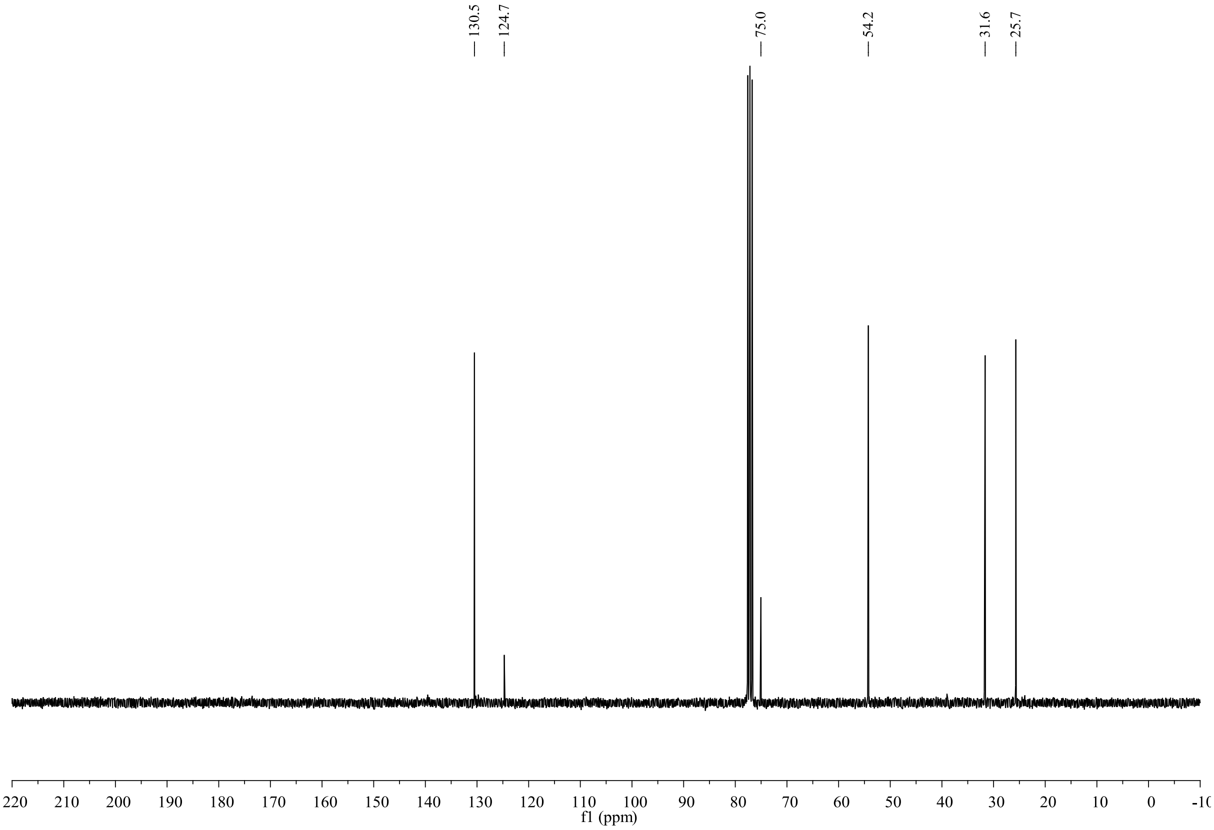
11 (^{13}C-NMR, 75 MHz, $CDCl_3$)



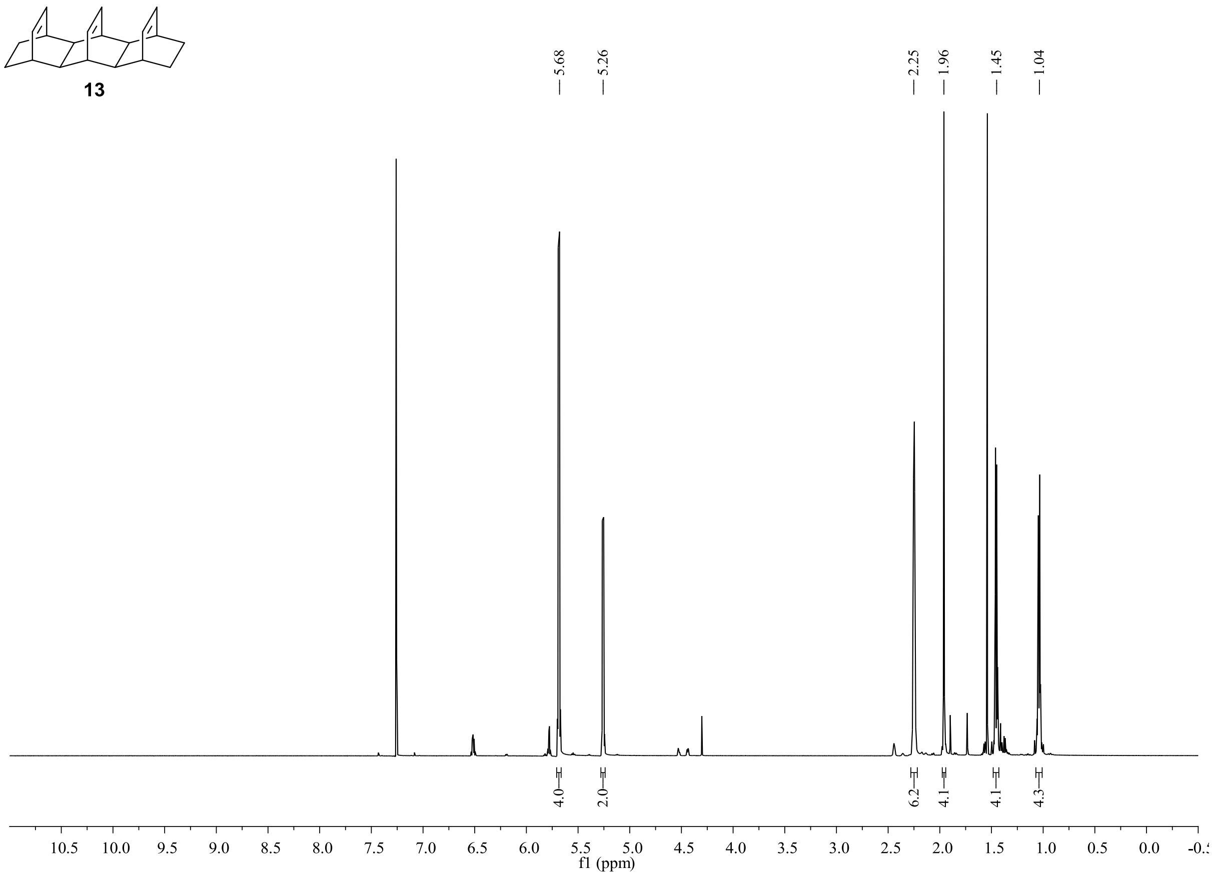
12 (^{1}H-NMR, 300 MHz, $CDCl_3$)



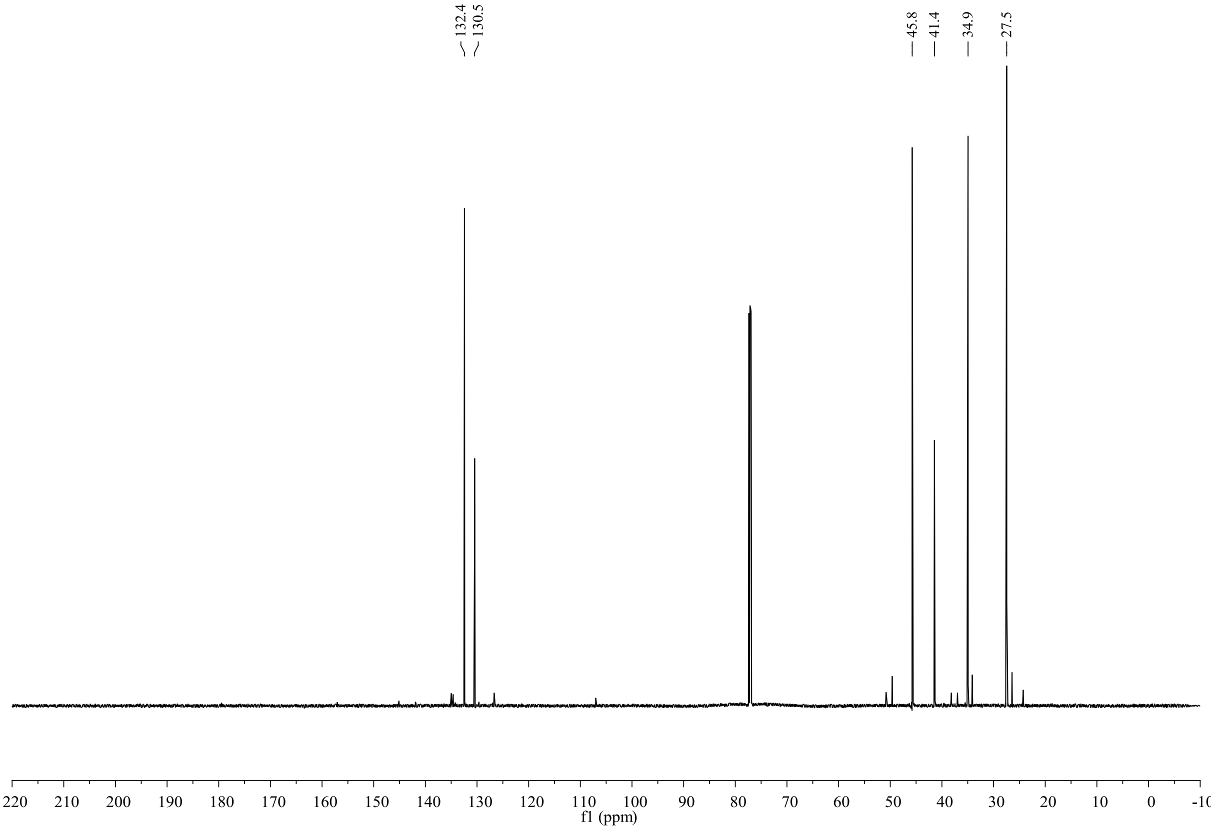
12 (^{13}C-NMR, 75 MHz, $CDCl_3$)



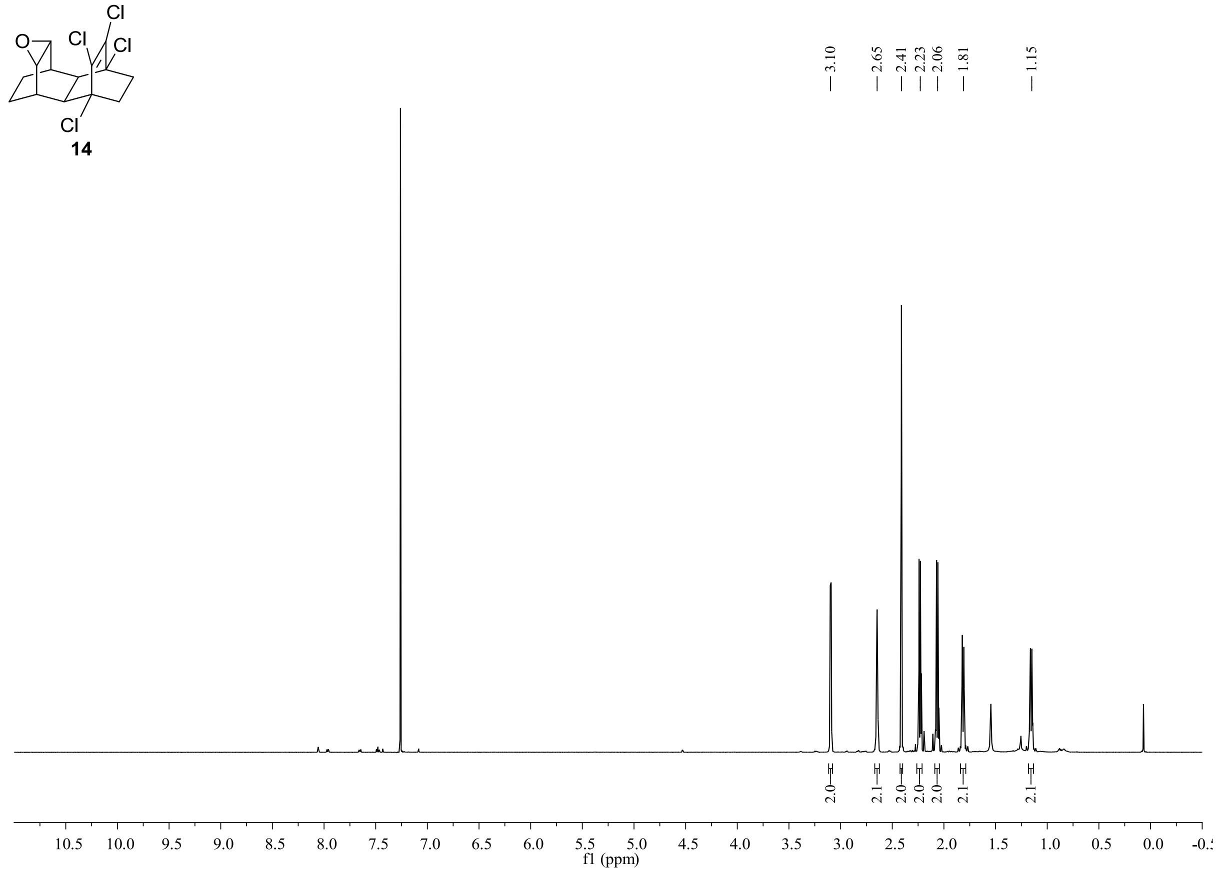
13 (^{1}H-NMR, 600 MHz, $CDCl_3$)



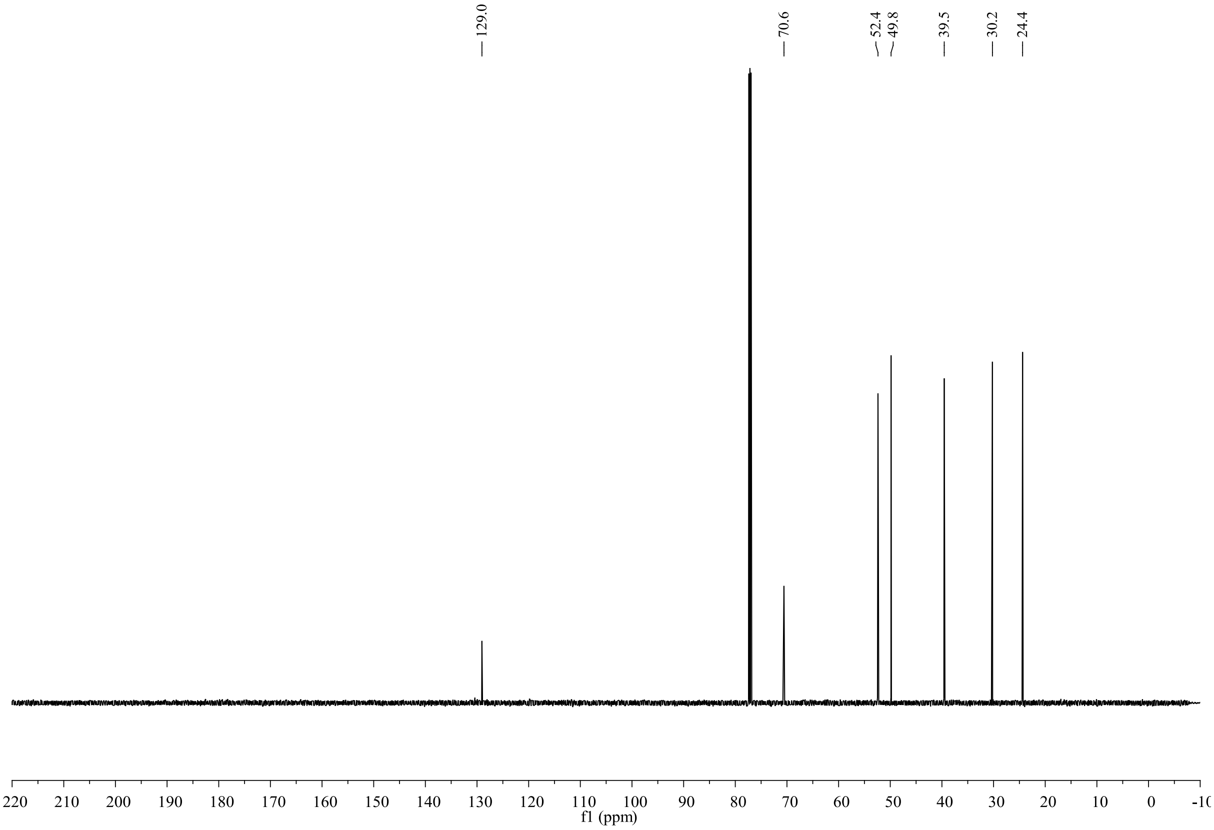
13 (^{13}C-NMR, 150 MHz, $CDCl_3$)



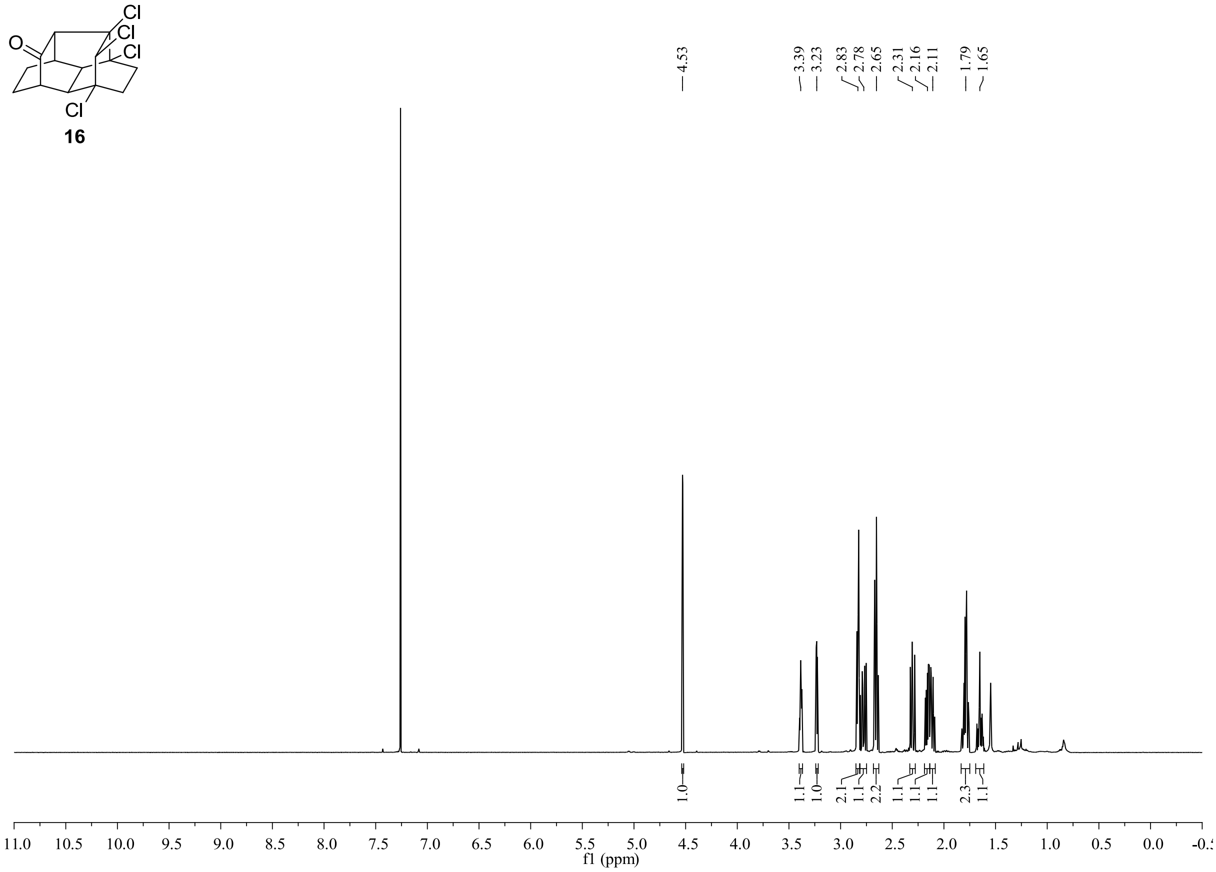
14 (^{1}H-NMR, 600 MHz, $CDCl_3$)



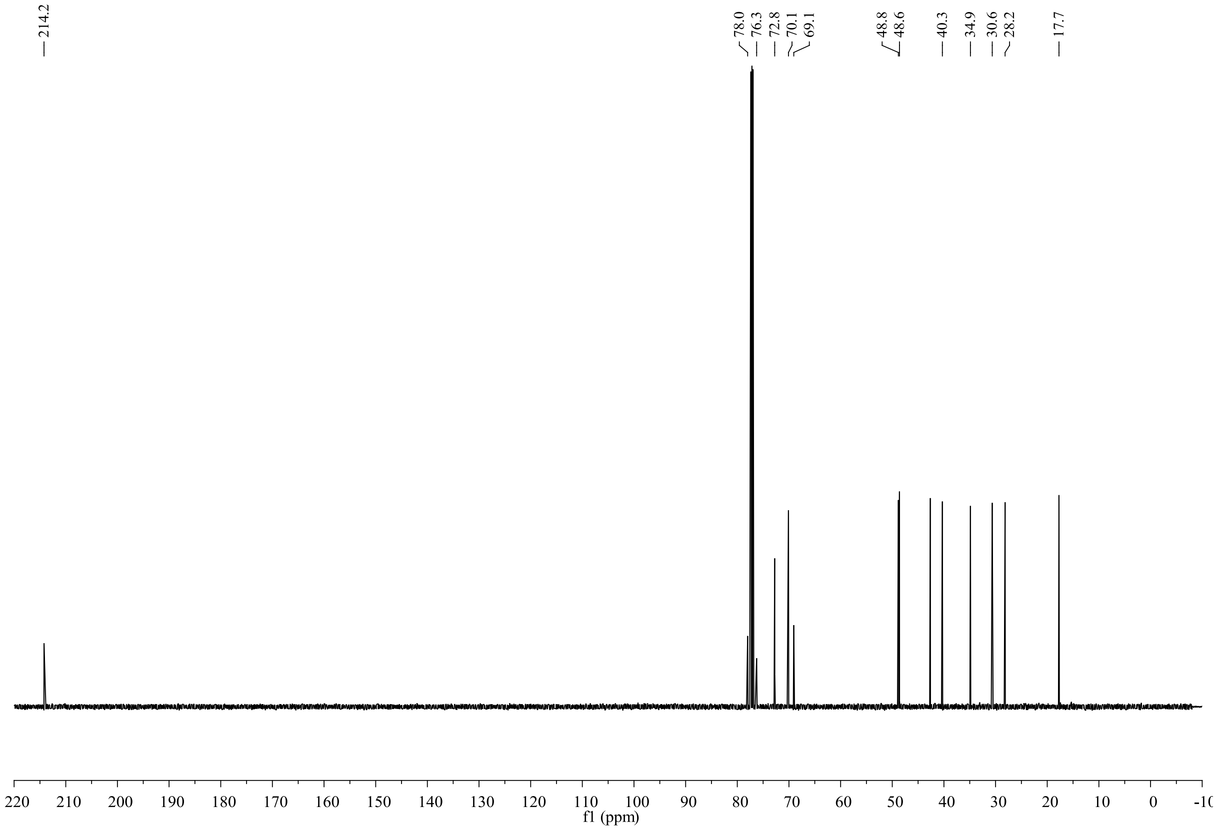
14 (^{13}C-NMR, 150 MHz, $CDCl_3$)



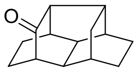
16 (^{1}H-NMR, 600 MHz, $CDCl_3$)



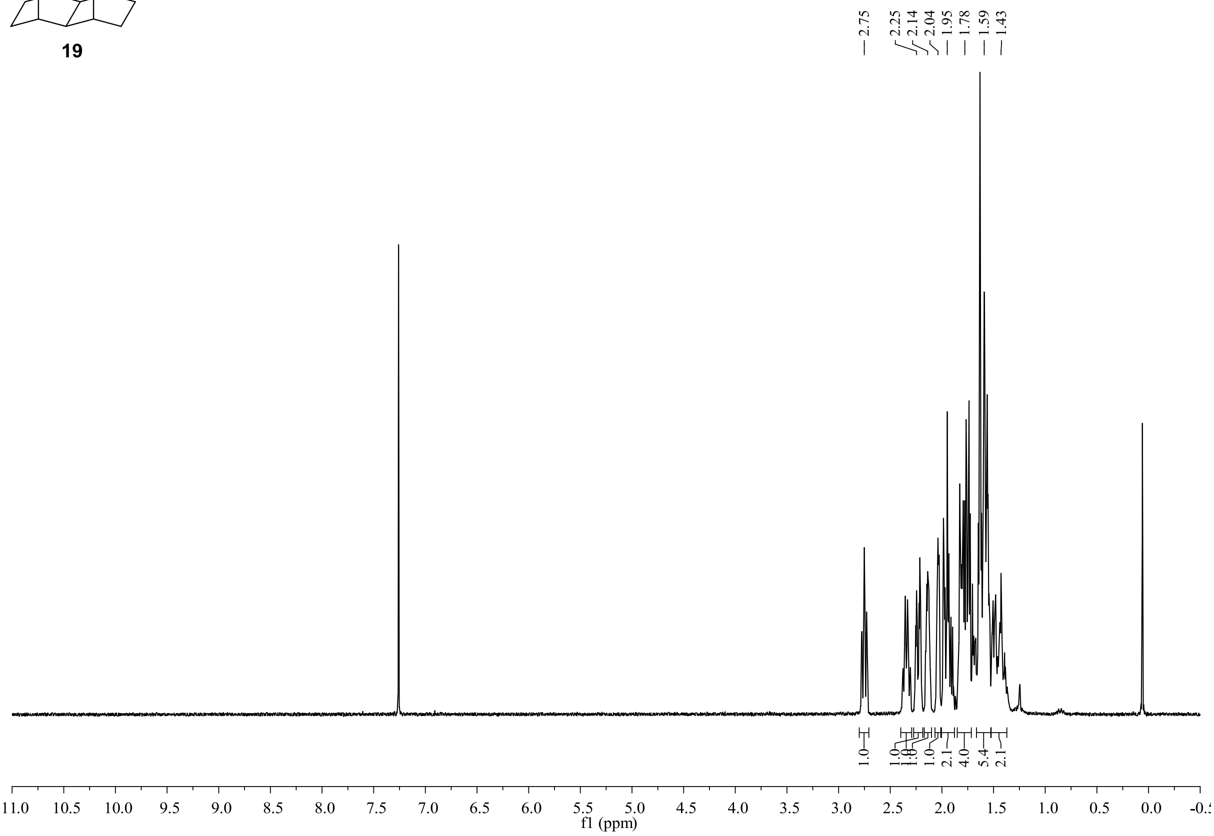
16 (^{13}C-NMR, 150 MHz, $CDCl_3$)



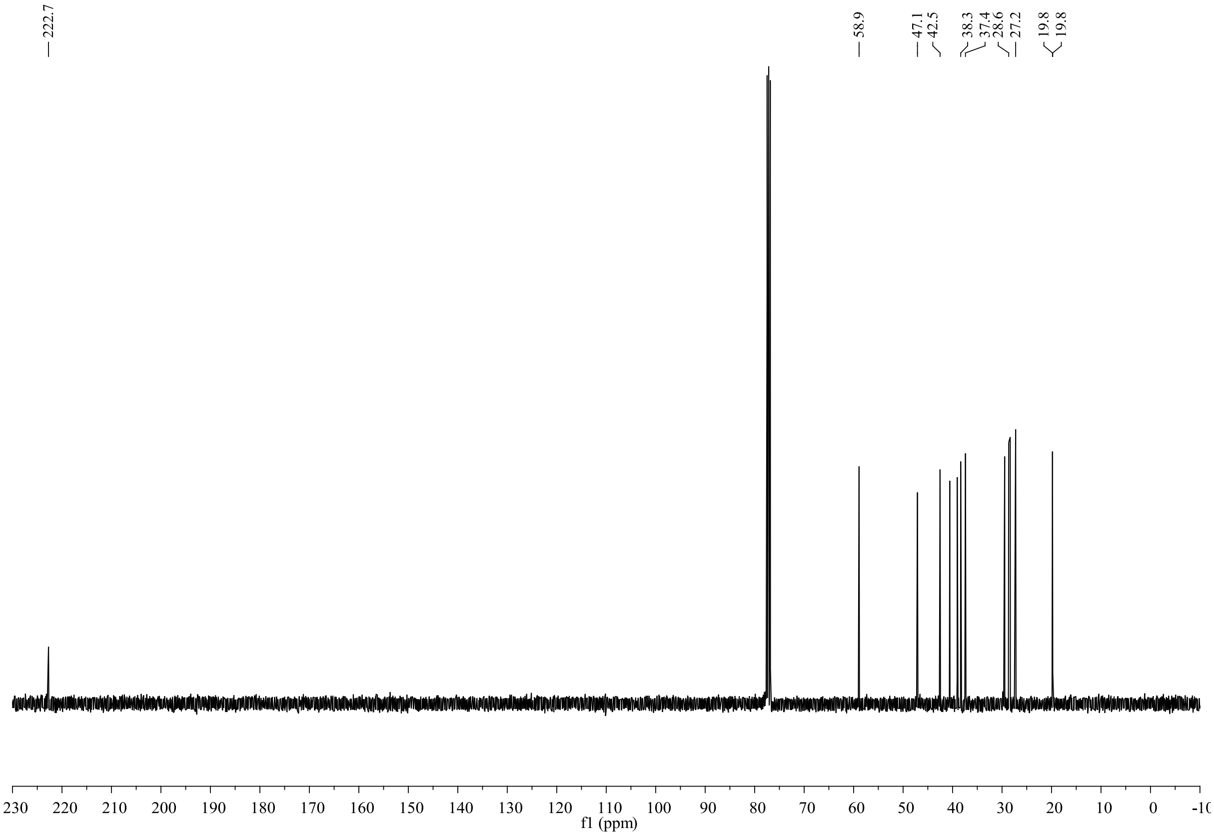
19 (^{1}H-NMR, 300 MHz, $CDCl_3$)



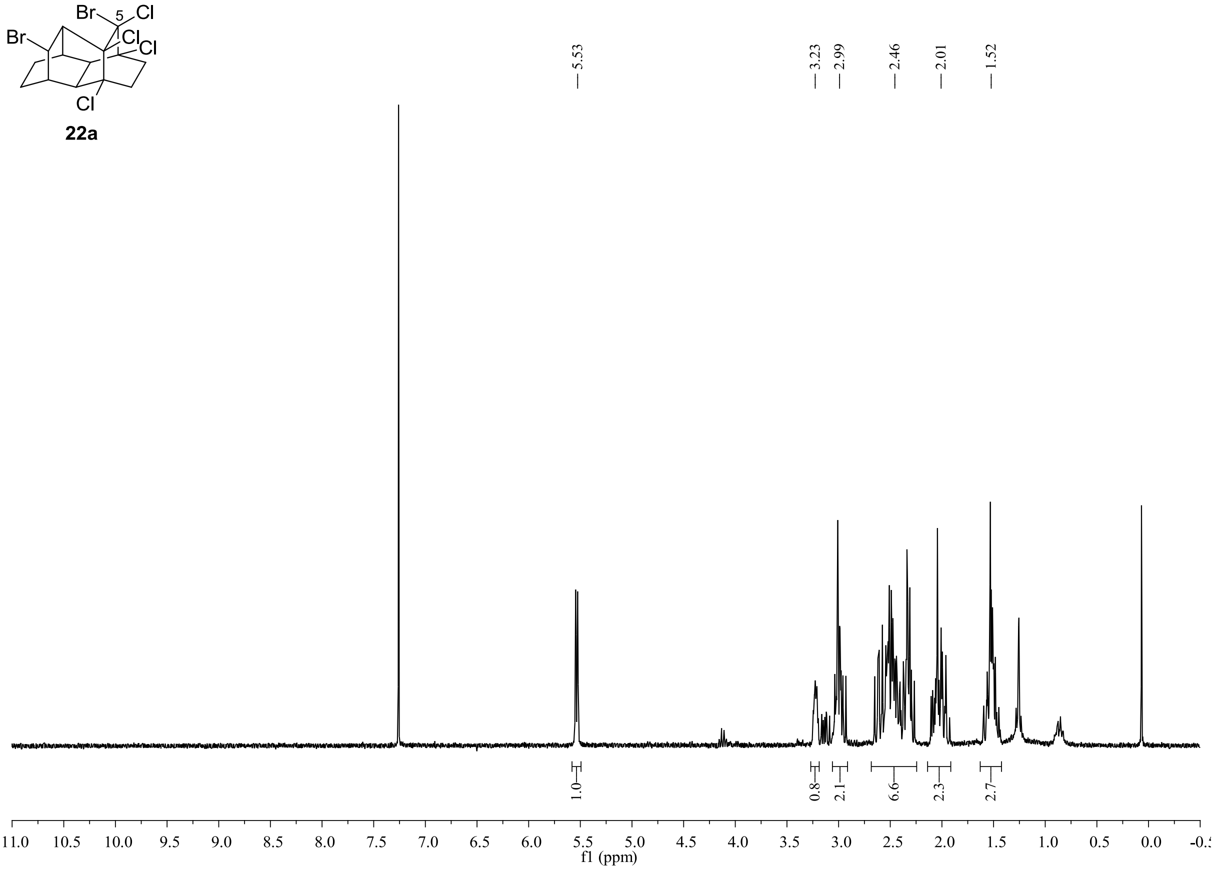
19



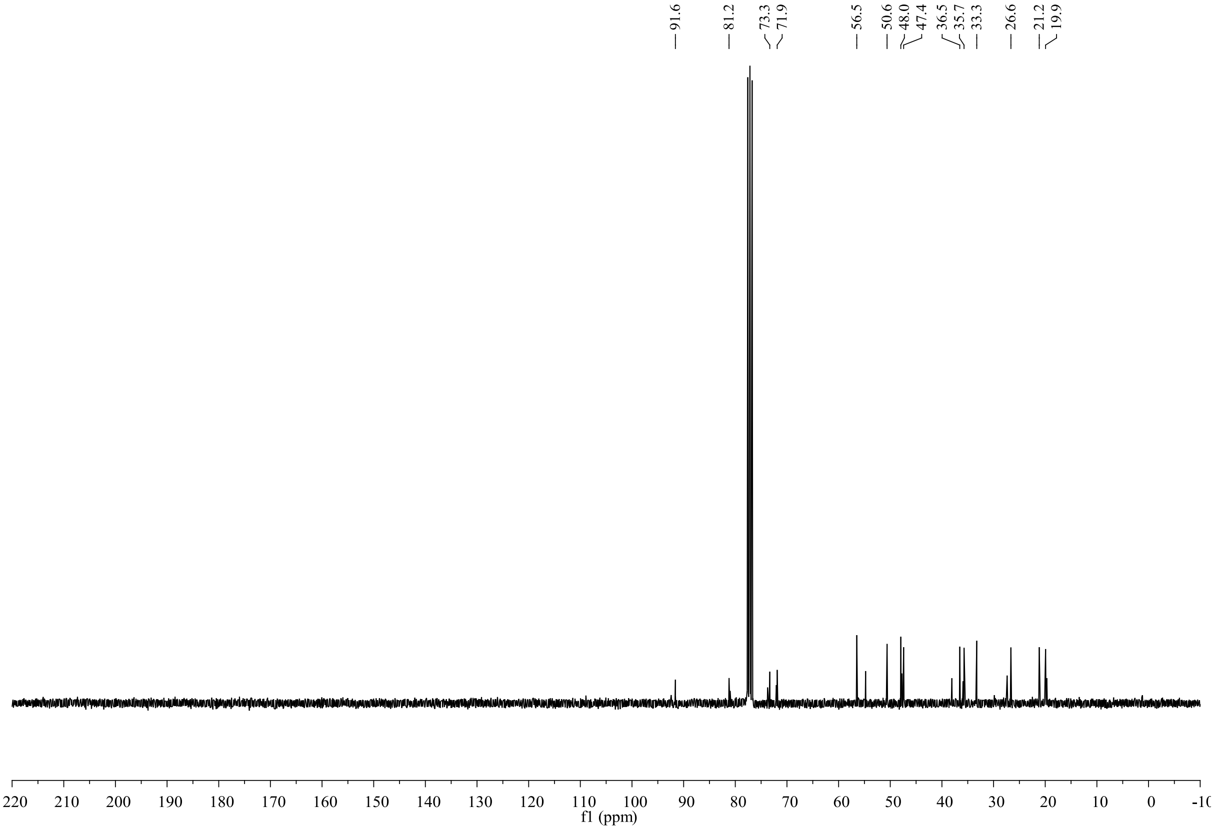
19 (^{13}C-NMR, 100 MHz, $CDCl_3$)



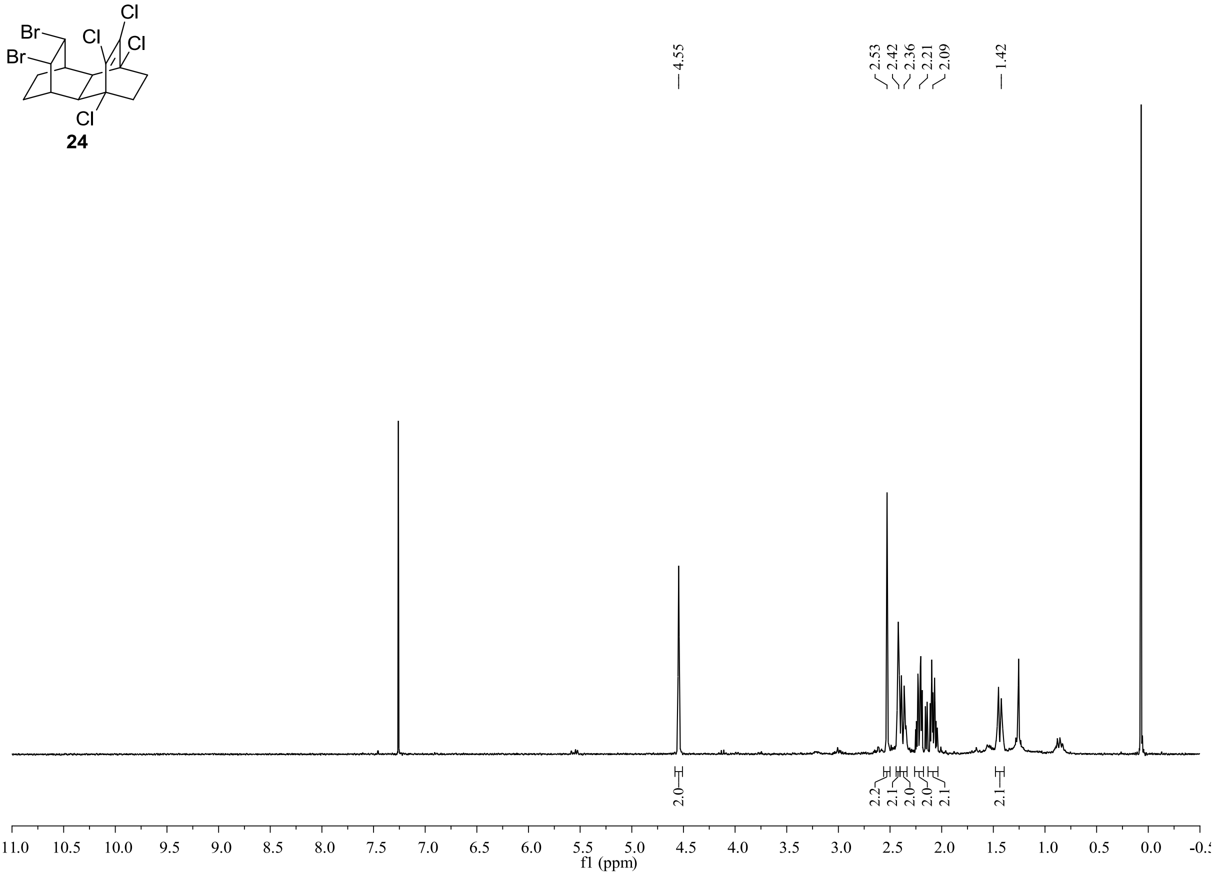
22 (^{1}H-NMR, 300 MHz, $CDCl_3$)



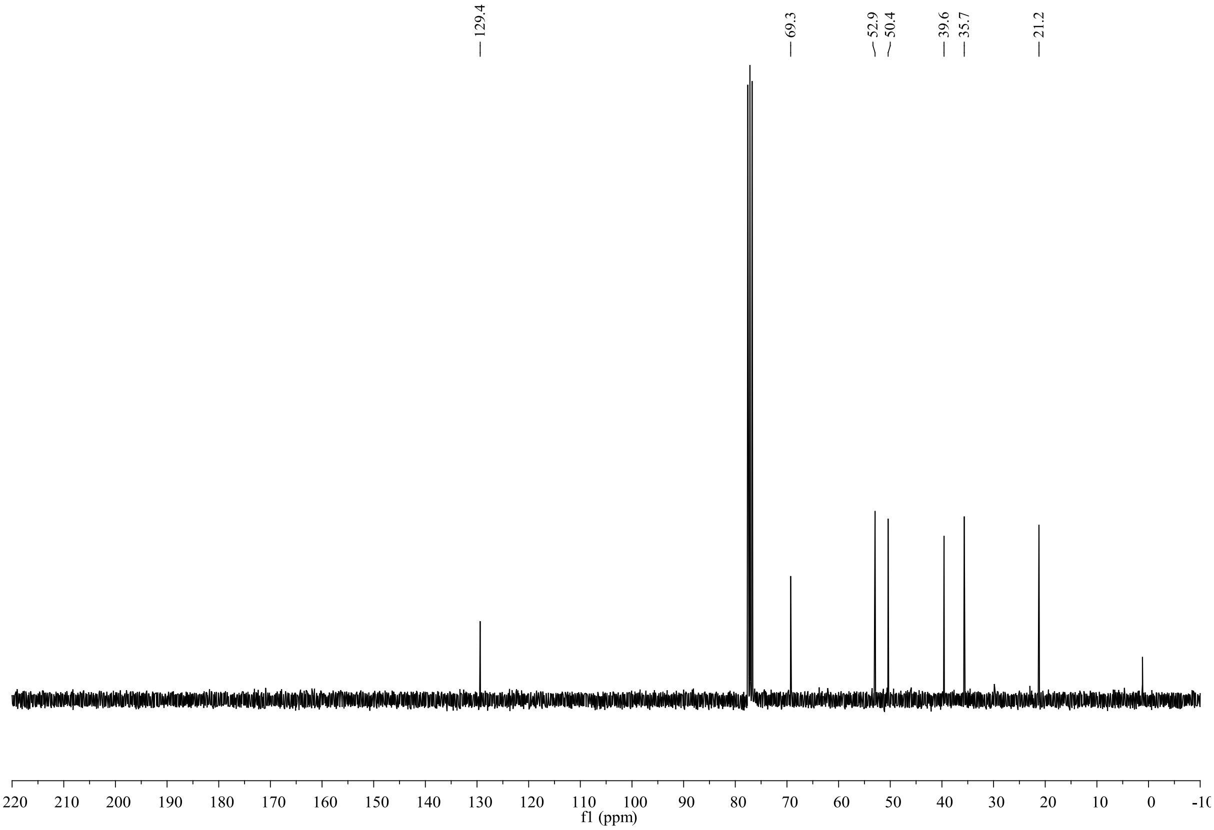
22 (^{13}C-NMR, 75 MHz, $CDCl_3$)



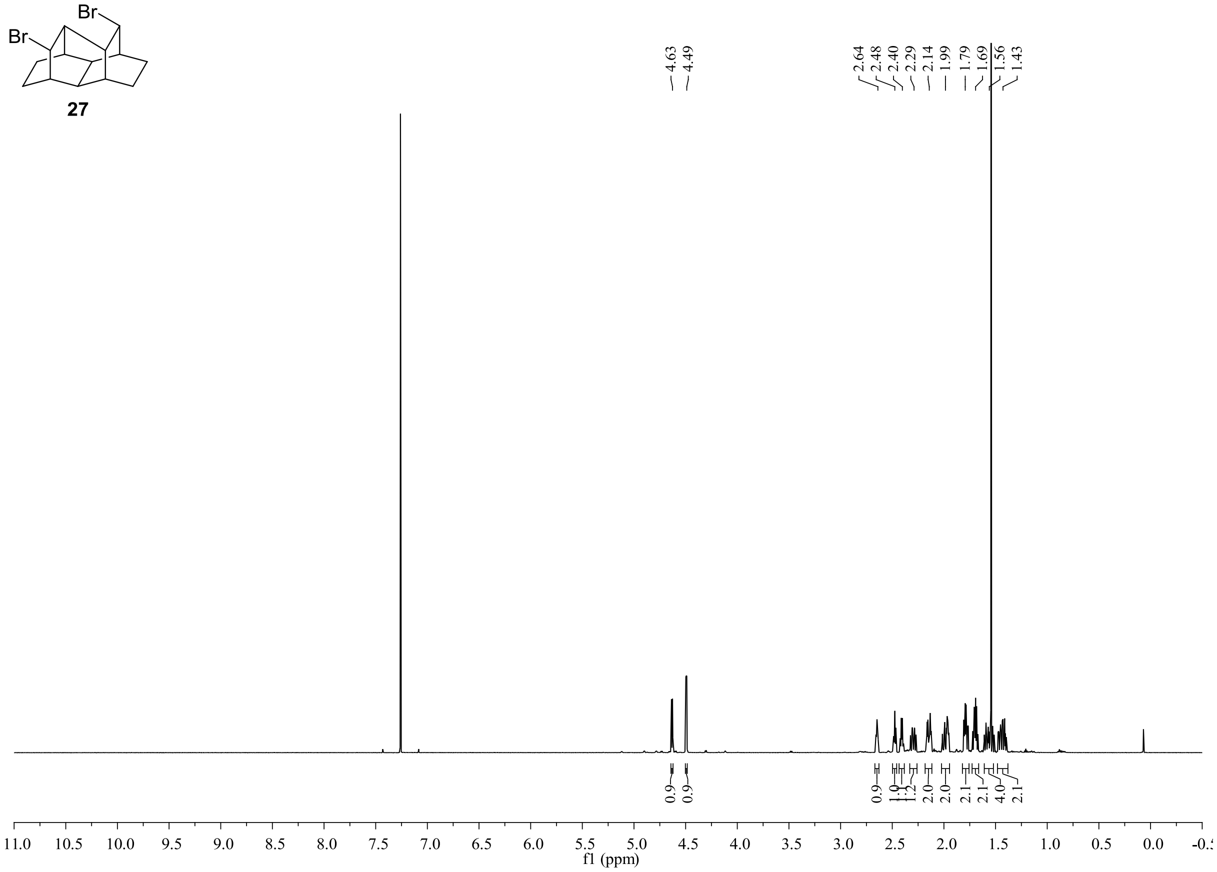
24 (^{1}H-NMR, 300 MHz, $CDCl_3$)



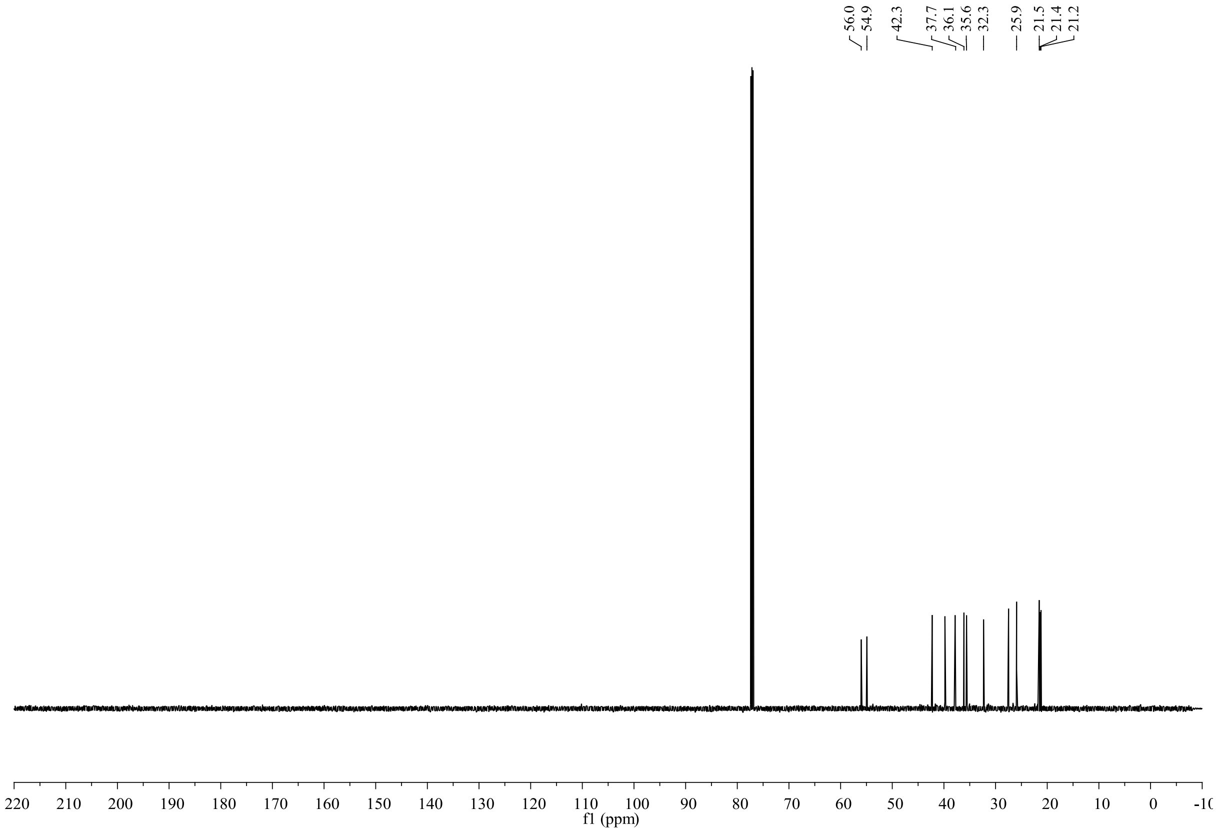
24 (^{13}C-NMR, 75 MHz, $CDCl_3$)



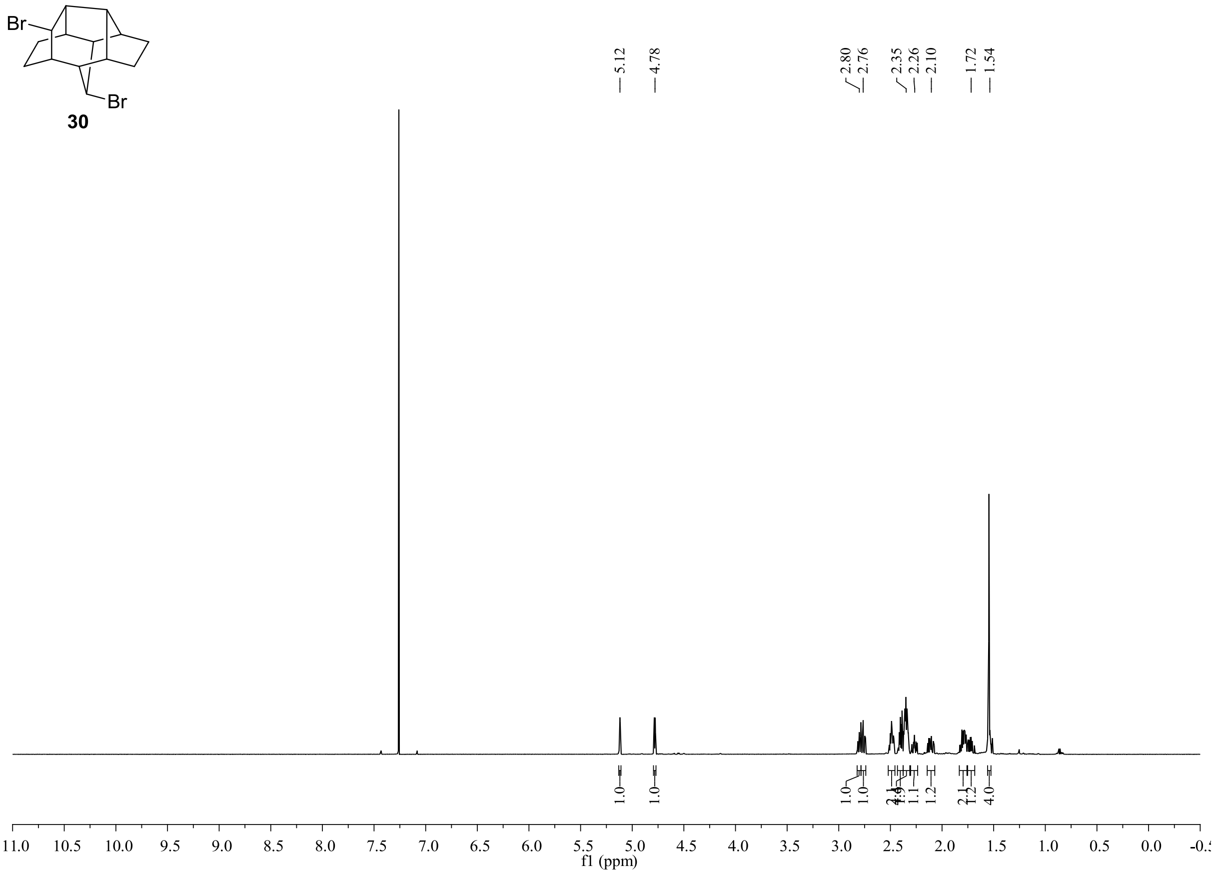
27 (^{1}H-NMR, 600 MHz, $CDCl_3$)



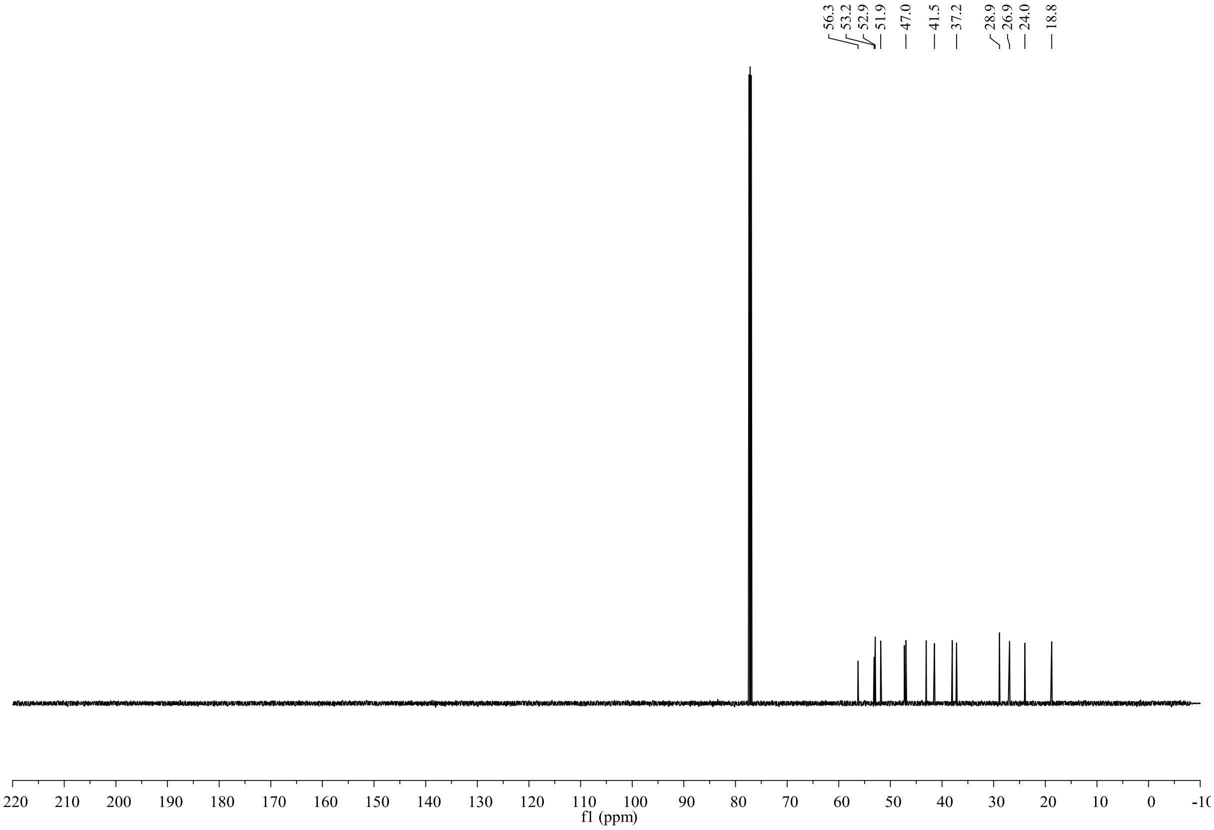
27 (^{13}C-NMR, 150 MHz, $CDCl_3$)



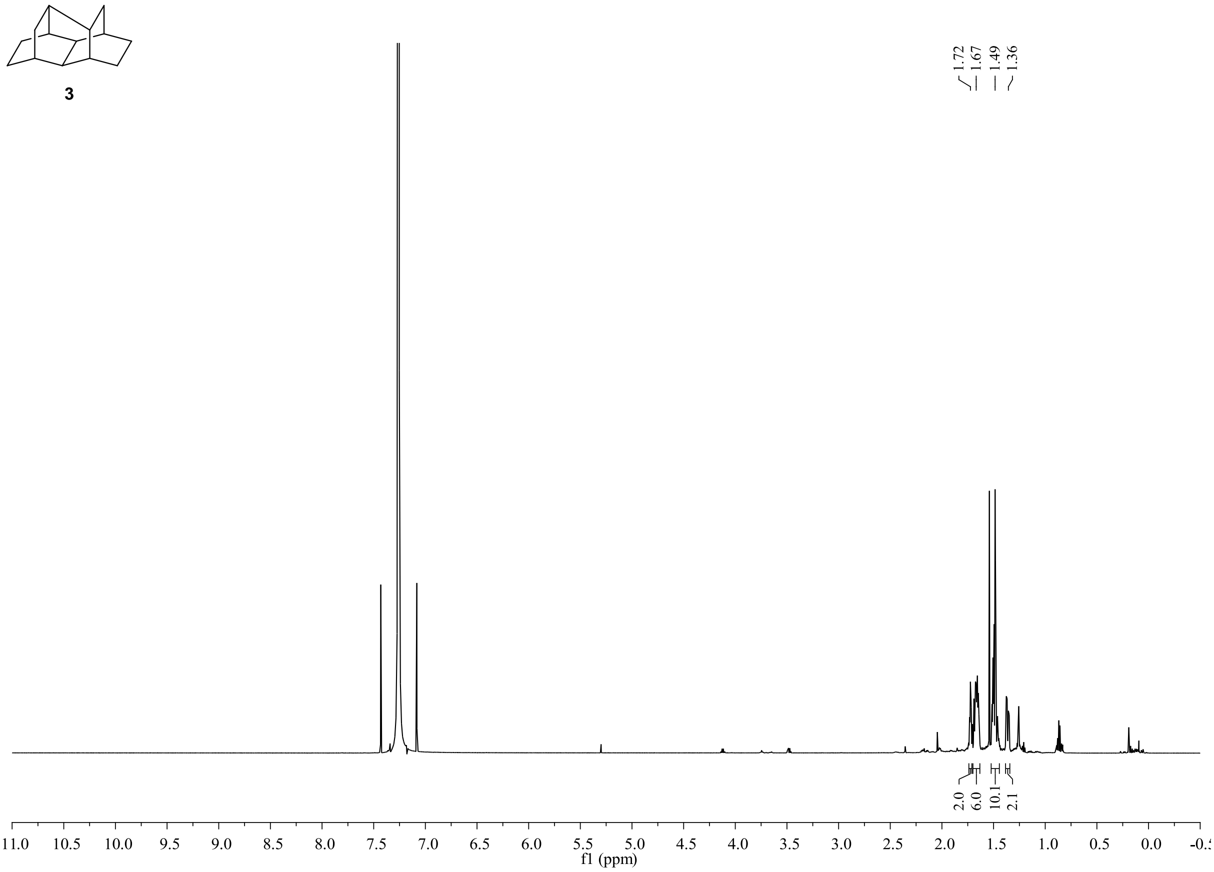
30 (^{1}H-NMR, 600 MHz, CDCl$_3$)



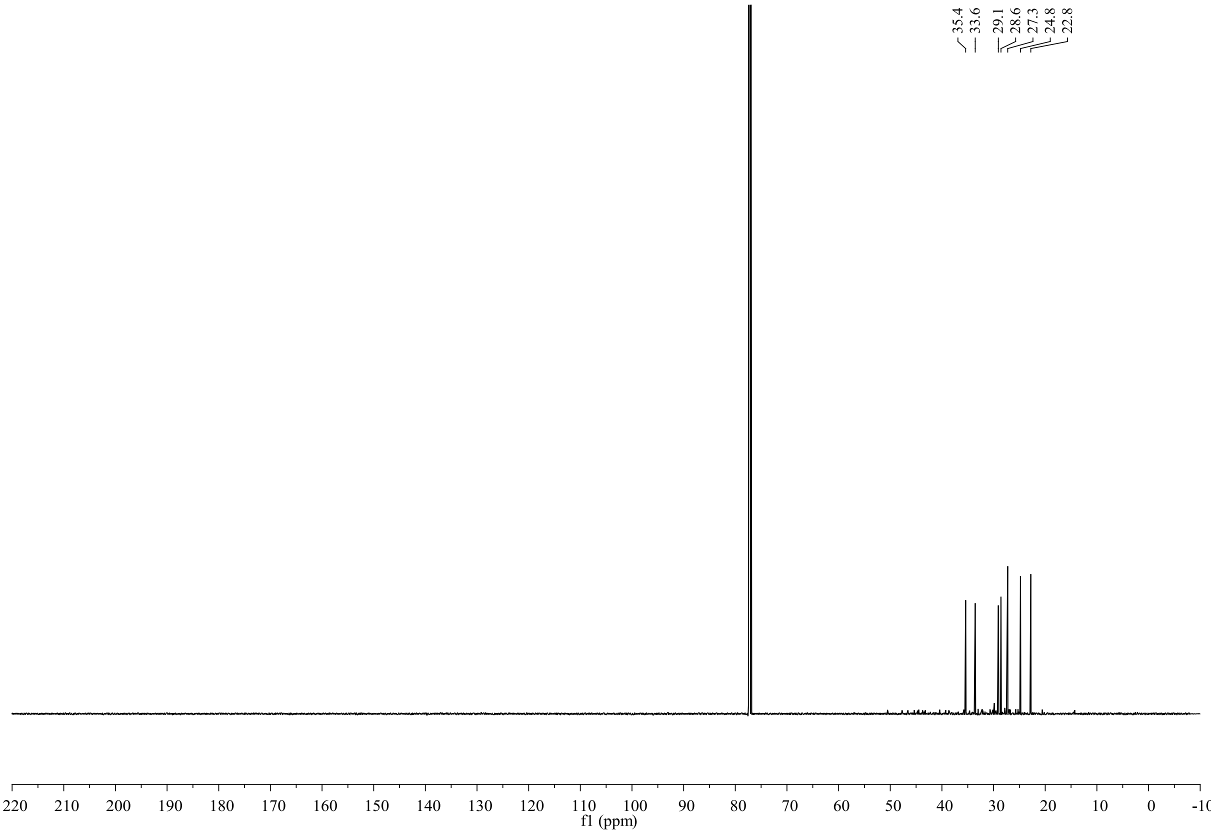
30 (^{13}C-NMR, 150 MHz, CDCl$_3$)



3 (^{1}H-NMR, 600 MHz, CDCl$_3$)



3 (^{13}C-NMR, 150 MHz, CDCl$_3$)

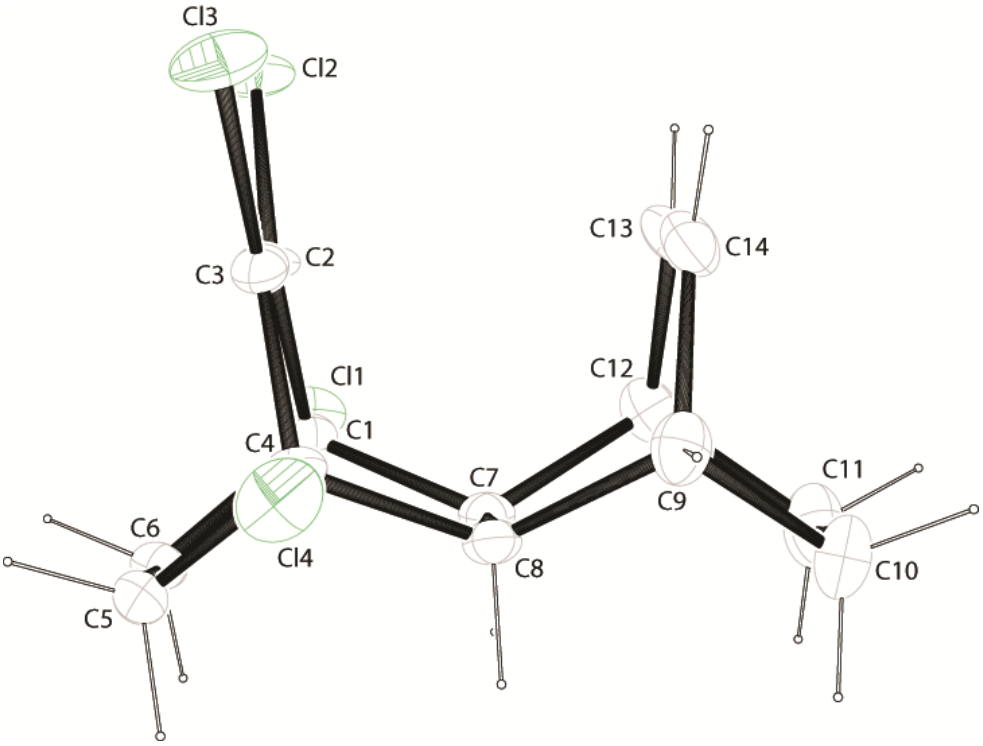


Crystallographic Data

Note: Crystallographic data for compounds **10**, **12**, **14**, **16**, **19**, **22**, **24**, **27**, **30** has also been deposited at the Cambridge Crystallographic Data Centre.

syn-3,4,5,6-Tetrachlorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9-diene (10) – CCDC 949955

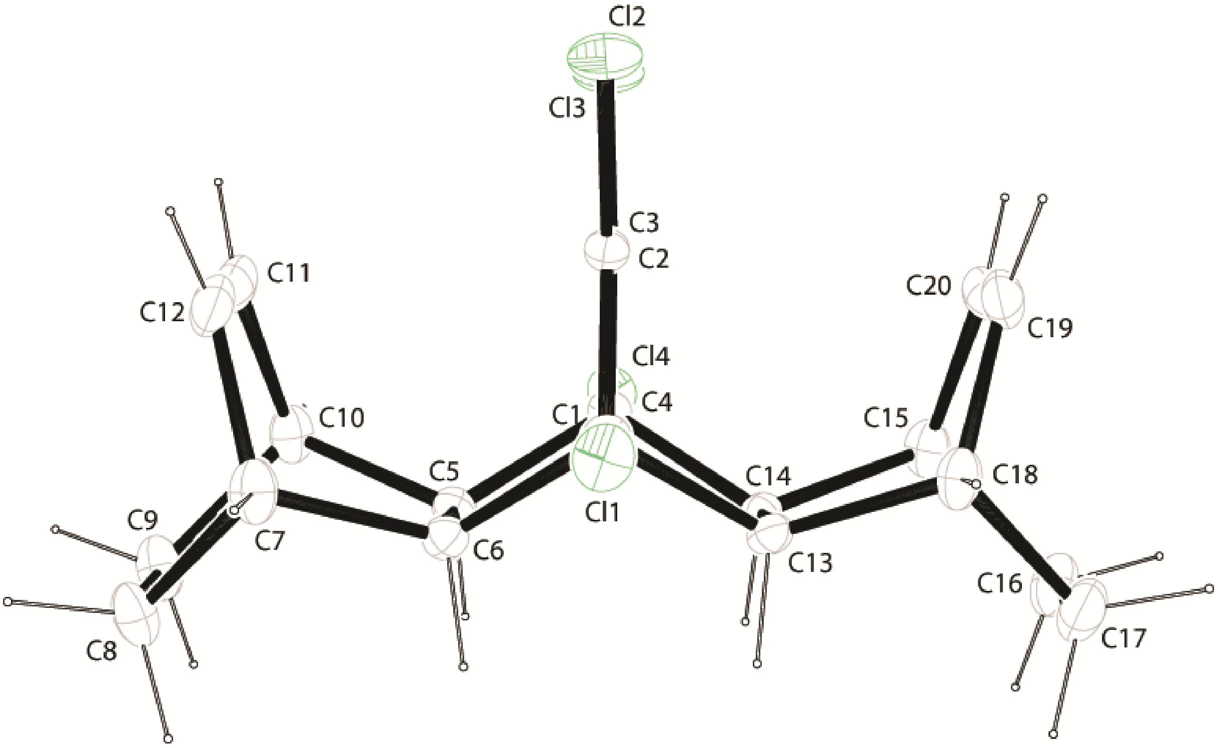
net formula	$C_{14}H_{14}Cl_4$
M_r/g mol^{-1}	324.072
crystal size/mm	0.096 × 0.049 × 0.023
T/K	123(2)
radiation	'Mo Kα
diffractometer	'Bruker D8Venture'
crystal system	triclinic
space group	*P*1bar
a/Å	7.0652(8)
b/Å	8.2217(9)
c/Å	13.0265(14)
α/°	92.900(3)
β/°	90.127(3)
γ/°	114.750(3)
V/Å^3	686.07(13)
Z	2
calc. density/g cm^{-3}	1.5688(3)
μ/mm^{-1}	0.840
absorption correction	multi-scan
transmission factor range	0.8682–0.9582
refls. measured	9118
R_{int}	0.0629
mean σ(*I*)/*I*	0.0579
θ range	3.07–25.36
observed refls.	1889
x, *y* (weighting scheme)	0.0277, 0.2364
hydrogen refinement	constr
refls in refinement	2522
parameters	163
restraints	0
$R(F_{obs})$	0.0360
$R_w(F^2)$	0.0750
S	1.033
shift/error$_{max}$	0.001
max electron density/e Å^{-3}	0.361
min electron density/e Å^{-3}	−0.284



all-*syn*-1,8,15,16-Tetrachlorohexacyclo[6.6.2.2^{3,6}.2^{10,13}.0^{2,7}.0^{9,14}]icosa-4,11,15-triene (12) – CCDC 949956

net formula	$C_{20}H_{20}Cl_4$
M_r/g mol^{-1}	402.184
crystal size/mm	0.151 × 0.089 × 0.081
T/K	123(2)
radiation	'Mo Kα
diffractometer	'Bruker D8Venture'
crystal system	triclinic
space group	*P*1bar
a/Å	7.0286(4)
b/Å	8.7167(5)
c/Å	15.6853(9)
α/°	83.186(2)
β/°	87.4669(19)
γ/°	66.2540(16)
V/Å^3	873.40(9)
Z	2
calc. density/g cm^{-3}	1.52931(16)
μ/mm^{-1}	0.677
absorption correction	multi-scan
transmission factor range	0.9197–0.9582
refls. measured	8310
R_{int}	0.0244
mean σ(I)/I	0.0296
θ range	3.17–25.03
observed refls.	2728
x, y (weighting scheme)	0.0276, 0.7769
hydrogen refinement	constr
refls in refinement	3057

parameters	217
restraints	0
$R(F_{\mathrm{obs}})$	0.0299
$R_{\mathrm{w}}(F^2)$	0.0766
S	1.116
shift/error$_{\mathrm{max}}$	0.001
max electron density/e Å^{-3}	0.364
min electron density/e Å^{-3}	−0.227

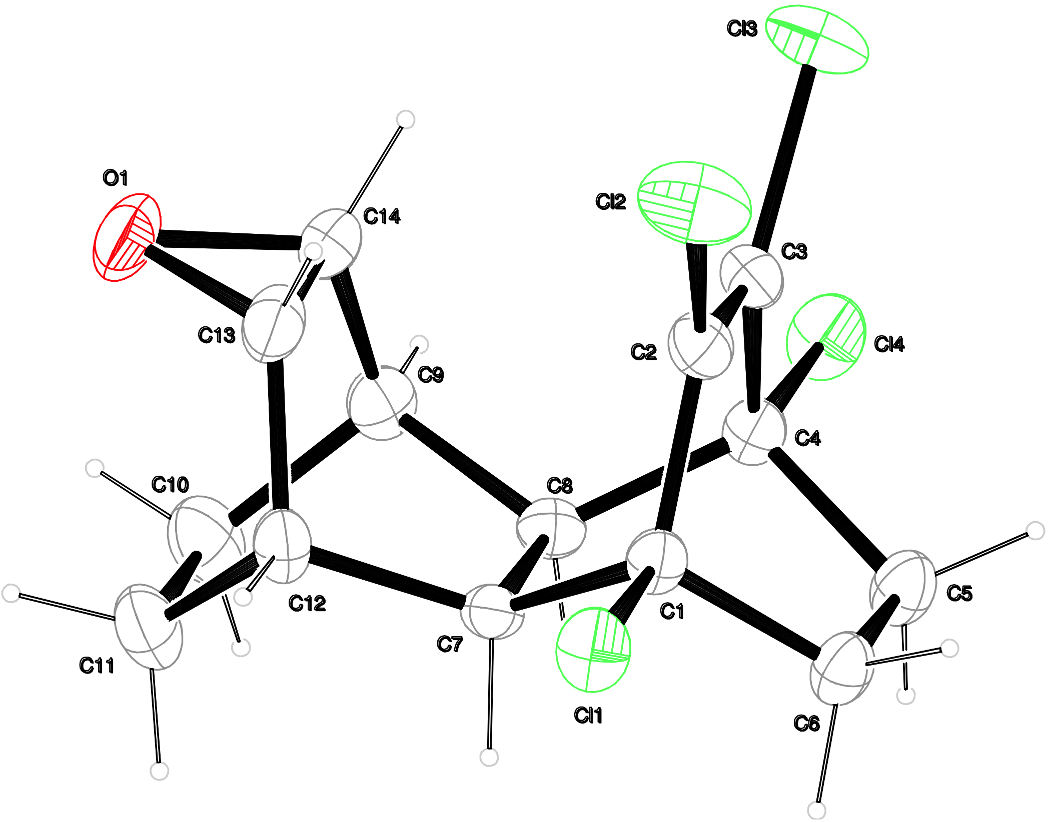


9,10-Epoxy-3,4,5,6-tetrachlorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-ene (14) – CCDC 948942

net formula	$C_{14}H_{14}Cl_4O$
M_r/g mol^{-1}	340.071
crystal size/mm	0.16 × 0.09 × 0.06
T/K	173(2)
radiation	MoKα
diffractometer	'KappaCCD'
crystal system	orthorhombic
space group	$P2_12_12_1$
a/Å	8.8558(2)
b/Å	12.1899(3)
c/Å	12.9536(3)
α/°	90
β/°	90
γ/°	90
V/Å^3	1398.36(6)
Z	4
calc. density/g cm^{-3}	1.61535(7)

μ/mm^{-1}	0.834
absorption correction	none
refls. measured	11150
R_{int}	0.0297
mean $\sigma(I)/I$	0.0279
θ range	3.15–27.43
observed refls.	2936
x, y (weighting scheme)	0.0313, 0.5754
hydrogen refinement	constr
Flack parameter	0.40(7)
refls in refinement	3189
parameters	173
restraints	0
$R(F_{\mathrm{obs}})$	0.0302
$R_{\mathrm{w}}(F^2)$	0.0720
S	1.065
shift/error$_{\mathrm{max}}$	0.001
max electron density/e Å^{-3}	0.380
min electron density/e Å^{-3}	−0.271

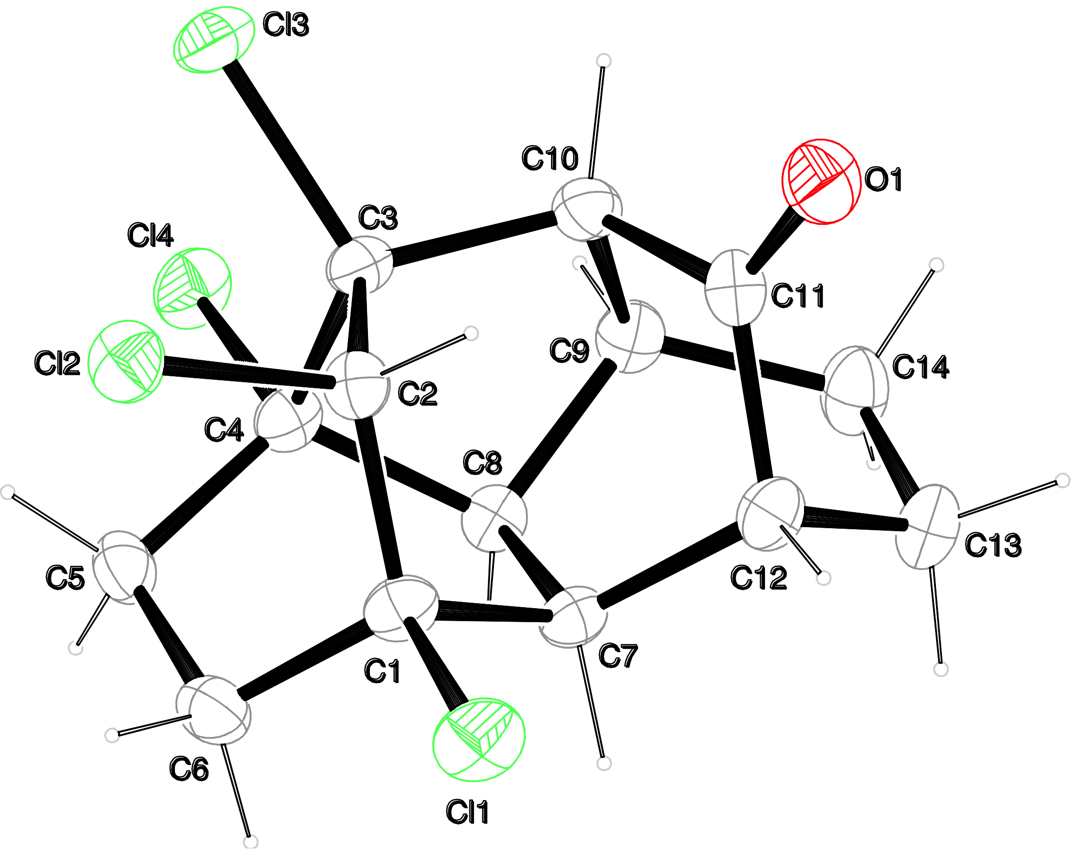
refined as a racemic twin, volume ratio 0.4/0.6.



3,4,5,6-Tetrachloro-10-oxopentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{5,9}]tetradecane (16) – CCDC 948943

net formula	$C_{14}H_{14}Cl_4O$
M_r/g mol^{-1}	340.071
crystal size/mm	0.23 × 0.12 × 0.09
T/K	173(2)

radiation	MoKα
diffractometer	'KappaCCD'
crystal system	triclinic
space group	*P*1bar
a/Å	6.5349(2)
b/Å	8.8020(4)
c/Å	11.7531(5)
α/°	89.290(2)
β/°	85.351(3)
γ/°	89.283(3)
V/Å^3	673.72(5)
Z	2
calc. density/g cm^{-3}	1.67639(12)
μ/mm^{-1}	0.865
absorption correction	none
refls. measured	5617
R_{int}	0.0208
mean $\sigma(I)/I$	0.0318
θ range	3.45–27.60
observed refls.	2682
x, y (weighting scheme)	0.0296, 0.6114
hydrogen refinement	constr
refls in refinement	3112
parameters	172
restraints	0
$R(F_{\text{obs}})$	0.0326
$R_w(F^2)$	0.0820
S	1.041
shift/error$_{\text{max}}$	0.001
max electron density/e Å^{-3}	0.681
min electron density/e Å^{-3}	−0.253



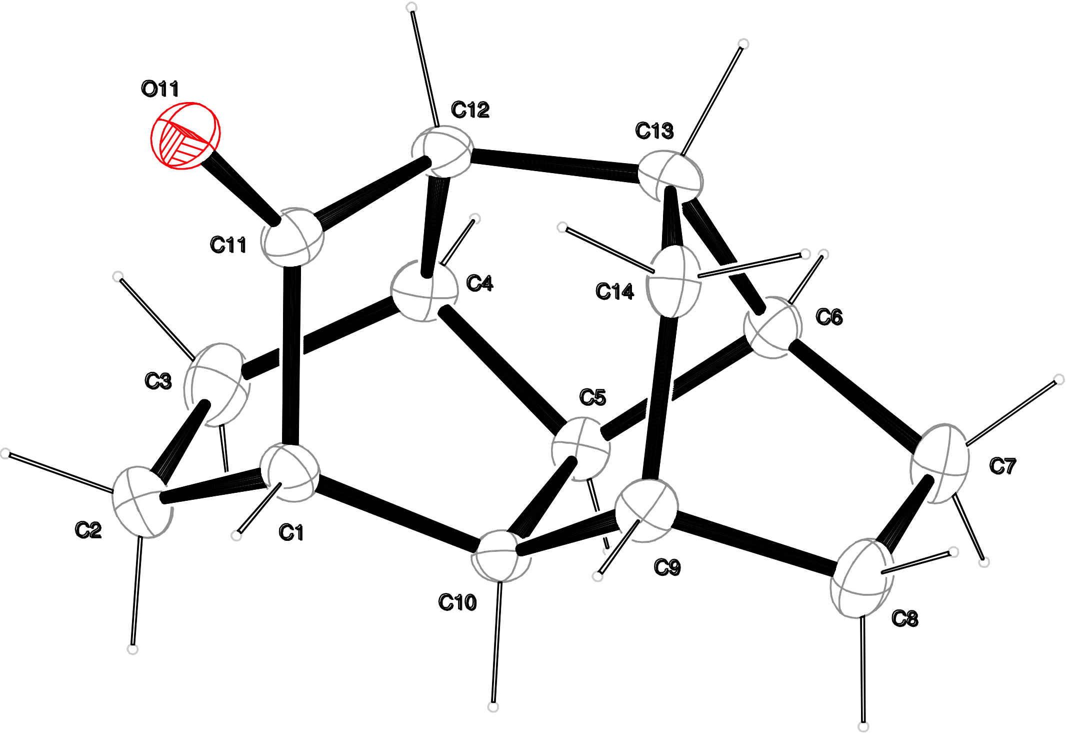
Pentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{5,9}]tetradecan-4-one (19) – CCDC 948941

net formula	$C_{14}H_{18}O$
M_r/g mol^{-1}	202.292
crystal size/mm	0.24 × 0.12 × 0.03
T/K	173(2)
radiation	MoKα
diffractometer	'KappaCCD'
crystal system	triclinic
space group	P1bar
a/Å	6.2093(4)
b/Å	8.3668(5)
c/Å	11.1450(5)
α/°	74.540(3)
β/°	89.252(3)
γ/°	68.175(3)
V/Å^3	515.66(5)
Z	2
calc. density/g cm^{-3}	1.30287(13)
μ/mm^{-1}	0.079
absorption correction	none
refls. measured	4338
R_{int}	0.0410
mean σ(I)/I	0.0552
θ range	3.55–27.55
observed refls.	1540
x, y (weighting scheme)	0.0579, 0.0876
hydrogen refinement	constr

refls in refinement	2364
parameters	200
restraints	0
$R(F_{\mathrm{obs}})$	0.0518
$R_w(F^2)$	0.1385
S	1.036
shift/error$_{\max}$	0.001
max electron density/e Å^{-3}	0.178
min electron density/e Å^{-3}	−0.161

O11, C11, C12, C13 and C14 are disordered over four sites with sof 0.39, 0..25, 0.28 and 0.08 resp., split model applied.

The following figure shows the main component of the disordered molecule:



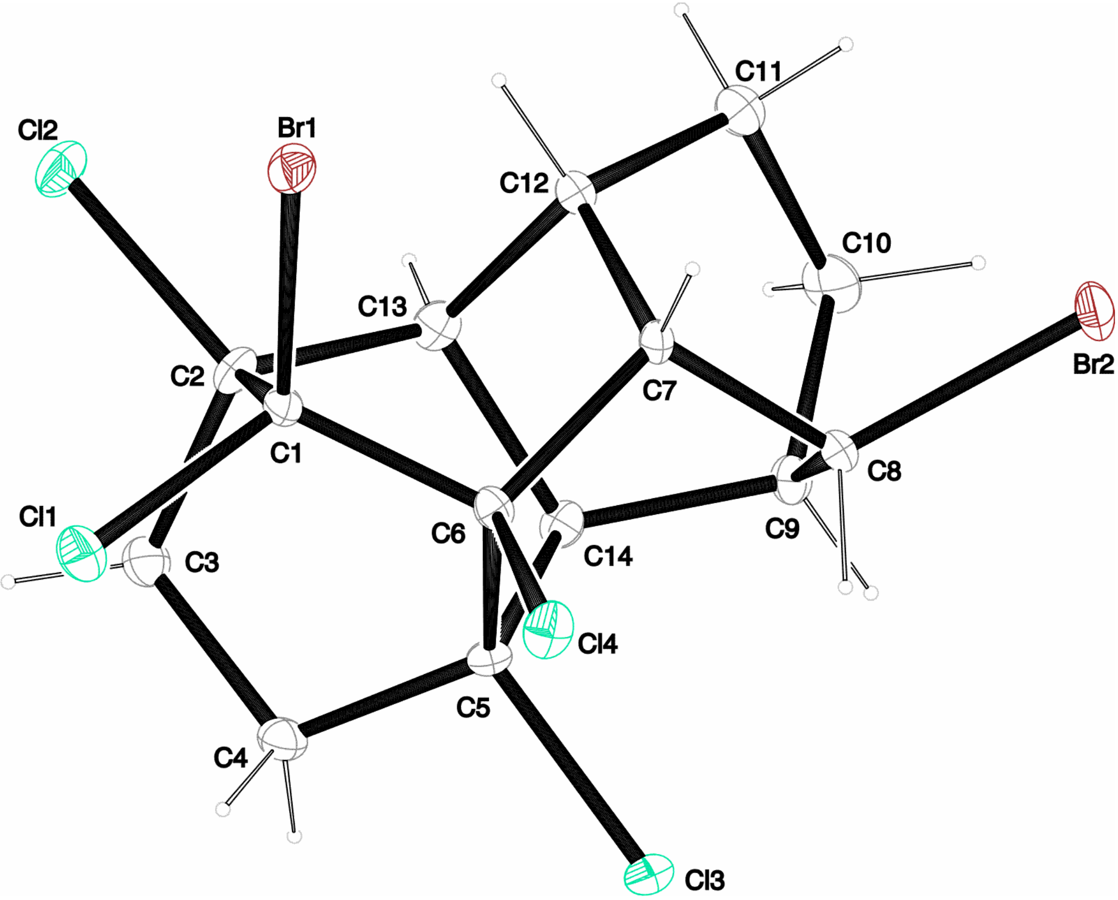
5,10-Dibromo-3,4,5,6-tetrachloropentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{4,9}]tetradecane (22) – CCDC 948945

net formula	$C_{14}H_{14}Br_2Cl_4$
M_r/g mol^{-1}	483.880
crystal size/mm	0.16 × 0.10 × 0.06
T/K	173(2)
radiation	MoKα
diffractometer	'Oxford XCalibur'
crystal system	monoclinic
space group	$P2_1/c$

a/Å	8.5158(3)
b/Å	12.1809(5)
c/Å	14.7928(5)
α/°	90
β/°	98.852(3)
γ/°	90
V/Å^3	1516.18(10)
Z	4
calc. density/g cm^{-3}	2.11983(14)
μ/mm^{-1}	6.037
absorption correction	'multi-scan'
transmission factor range	0.54047–1.00000
refls. measured	8102
R_{int}	0.0410
mean $\sigma(I)/I$	0.0415
θ range	4.24–26.36
observed refls.	2662
x, y (weighting scheme)	0.0771, 0.4065
hydrogen refinement	constr
refls in refinement	3084
parameters	182
restraints	0
$R(F_{\text{obs}})$	0.0424
$R_w(F^2)$	0.1162
S	1.025
shift/error$_{\text{max}}$	0.001
max electron density/e Å^{-3}	1.090
min electron density/e Å^{-3}	−1.433

Br1 and Cl1 bound to C1 are disordered: the site of Br1 is occupied by Cl11 as well and the site of Cl1 is occupied by Br11, sof ratio 0.7/0.3.

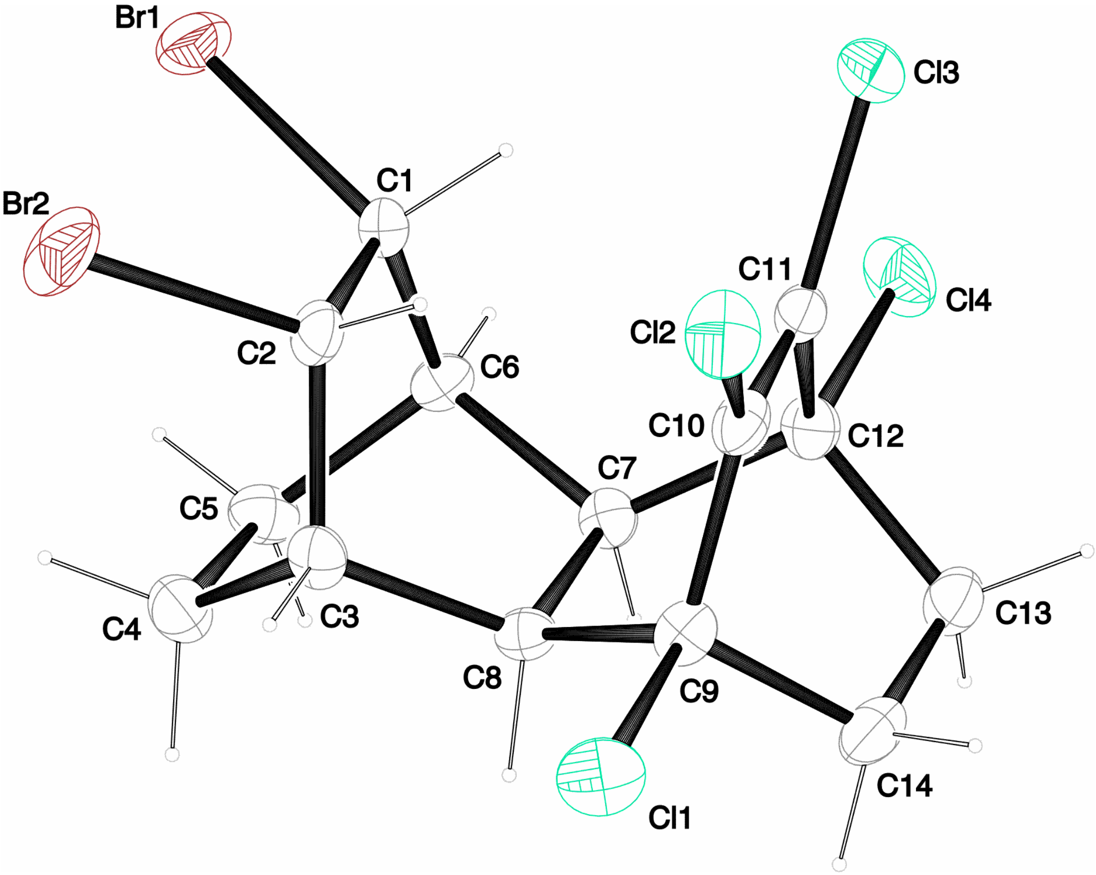
The following figure shows the main component of the disordered molecule:



syn-9,10-Dibromo-3,4,5,6-tetrachlorotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-ene (24) – CCDC 948944

net formula	$C_{14}H_{14}Br_2Cl_4$
M_r/g mol^{-1}	483.880
crystal size/mm	0.03 × 0.03 × 0.02
T/K	173(2)
radiation	MoKα
diffractometer	'KappaCCD'
crystal system	monoclinic
space group	$P2_1/c$
a/Å	14.7642(7)
b/Å	7.4391(3)
c/Å	14.5856(6)
α/°	90
β/°	91.061(2)
γ/°	90
V/Å^3	1601.70(12)
Z	4
calc. density/g cm^{-3}	2.00665(15)
μ/mm^{-1}	5.714
absorption correction	none
refls. measured	9823
R_{int}	0.0867
mean σ(I)/I	0.0662
θ range	3.14–25.35
observed refls.	2061
x, y (weighting scheme)	0.0395, 0.0737

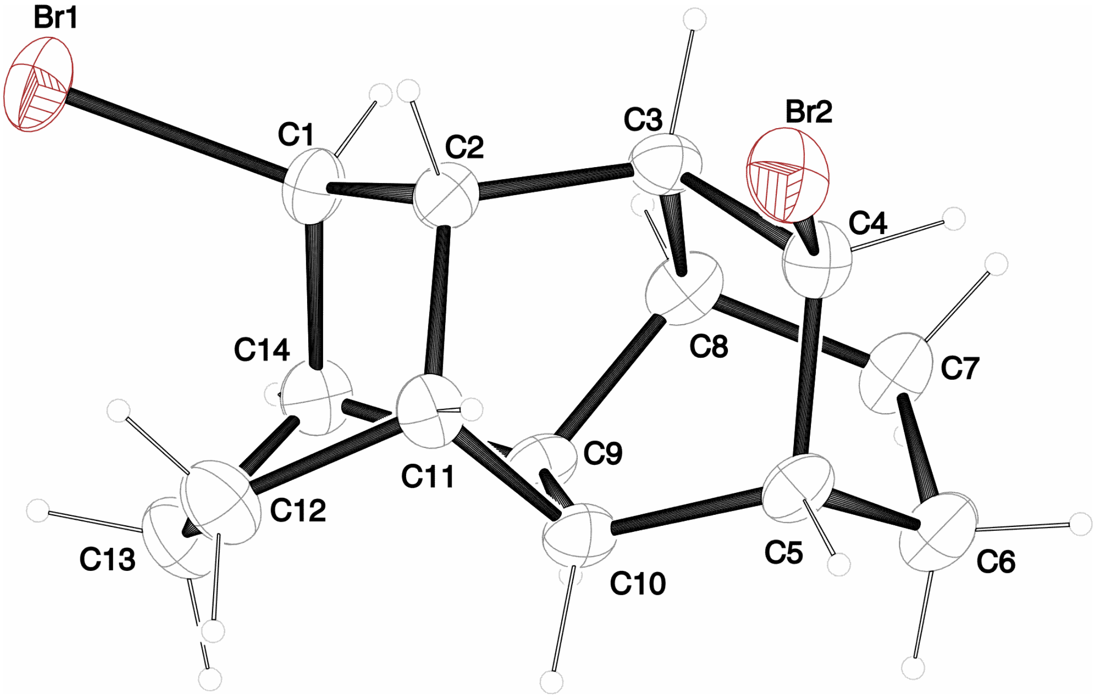
hydrogen refinement	constr
refls in refinement	2911
parameters	181
restraints	0
$R(F_{obs})$	0.0366
$R_w(F^2)$	0.0903
S	1.028
shift/error$_{max}$	0.001
max electron density/e Å^{-3}	0.827
min electron density/e Å^{-3}	−0.722



5,10-Dibromopentacyclo[6.2.2.2^{3,6}.0^{2,7}.0^{4,9}]tetradecane (27) – CCDC 948946

net formula	$C_{14}H_{18}Br_2$
M_r/g mol^{-1}	346.101
crystal size/mm	0.26 × 0.19 × 0.04
T/K	173(2)
radiation	MoKα
diffractometer	'Oxford XCalibur'
crystal system	monoclinic
space group	$P2_1/c$
a/Å	13.0330(10)
b/Å	7.7467(6)
c/Å	12.4282(9)
α/°	90
β/°	101.998(7)

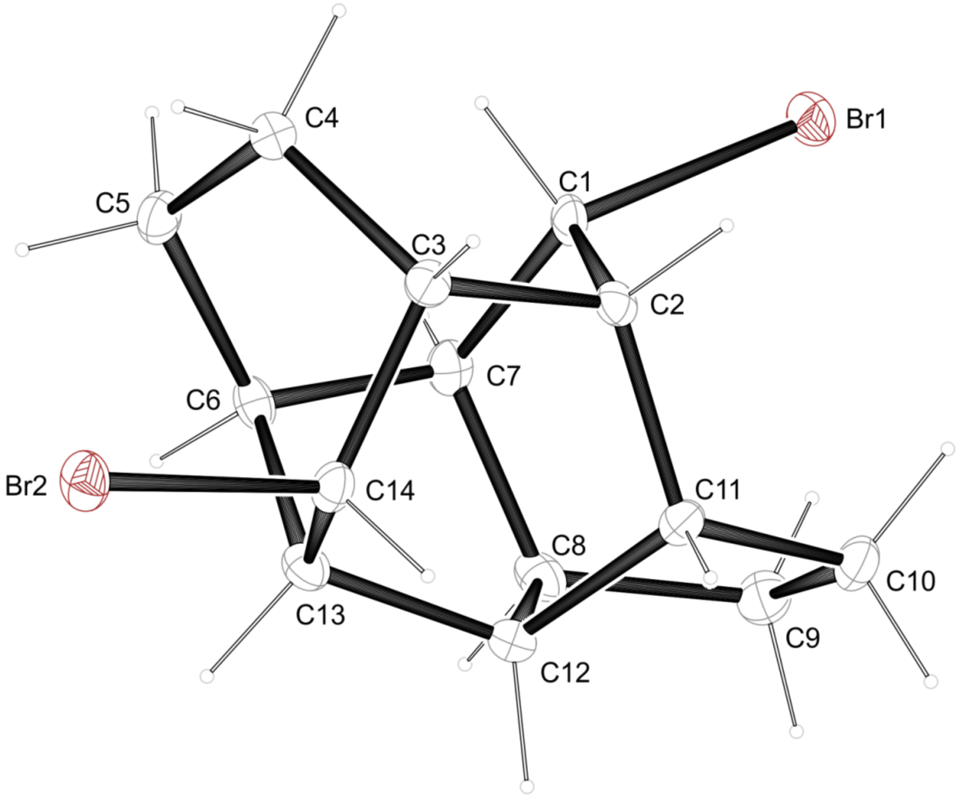
γ/°	90
V/Å^3	1227.37(16)
Z	4
calc. density/g cm^{-3}	1.8730(2)
μ/mm^{-1}	6.574
absorption correction	'multi-scan'
transmission factor range	0.41499–1.00000
refls. measured	4608
R_{int}	0.0303
mean $\sigma(I)/I$	0.0516
θ range	4.21–28.84
observed refls.	2166
x, y (weighting scheme)	0.0453, 0.2889
hydrogen refinement	constr
refls in refinement	2708
parameters	145
restraints	0
$R(F_{\mathrm{obs}})$	0.0390
$R_{\mathrm{w}}(F^2)$	0.1006
S	1.051
shift/error$_{\mathrm{max}}$	0.001
max electron density/e Å^{-3}	0.878
min electron density/e Å^{-3}	−0.977



9,13-Dibromopentacyclo[6.2.2.1^{2,7}.1^{3,6}.0^{10,14}]tetradecane (30) – CCDC 948947

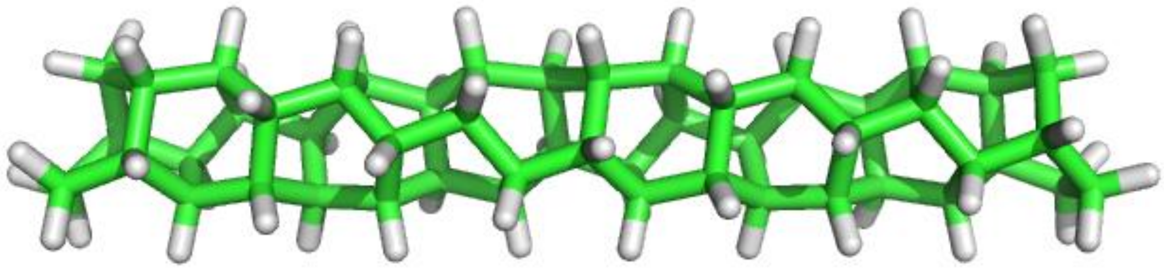
net formula	$C_{14}H_{18}Br_2$
M_r/g mol^{-1}	346.101
crystal size/mm	0.167 × 0.097 × 0.090
T/K	100(2)
radiation	'Mo Kα
diffractometer	'Bruker D8Venture'

crystal system	monoclinic
space group	$P2_1/c$
a/Å	14.3718(4)
b/Å	6.4978(2)
c/Å	12.7356(4)
α/°	90
β/°	94.731(2)
γ/°	90
V/Å^3	1185.26(6)
Z	4
calc. density/g cm^{-3}	1.93956(10)
μ/mm^{-1}	6.808
absorption correction	multi-scan
transmission factor range	0.6207–0.7457
refls. measured	22884
R_{int}	0.0451
mean σ(I)/I	0.0278
θ range	3.21–28.41
observed refls.	2534
x, y (weighting scheme)	0.0248, 0.6269
hydrogen refinement	constr
refls in refinement	2948
parameters	145
restraints	0
$R(F_{\text{obs}})$	0.0233
$R_w(F^2)$	0.0520
S	1.054
shift/error$_{\text{max}}$	0.001
max electron density/e Å^{-3}	0.508
min electron density/e Å^{-3}	−0.342



Computational Details

Oligotwistane $C_{52}H_{58}$ optimized at B3LYP/6-31G(d)



C	-10.08485800	-0.96247600	0.94554700
C	-8.66393100	-0.43398000	1.21994100
C	-10.30984700	-1.00470700	-0.59206300
C	-9.32762000	-0.00839000	-1.23940000
C	-8.50176800	1.06808800	0.79150100
C	-9.42124800	1.30583700	-0.42591600
C	-7.67204300	-1.19273000	0.31357000
C	-6.21914400	-0.97021500	0.79887100
C	-7.86803800	-0.54196600	-1.10307000
C	-6.85862200	0.62512300	-1.10472900
C	-6.03277000	0.53495800	1.20324300
C	-7.03752600	1.28764500	0.31229100
C	-5.22143700	-1.17714300	-0.35553600
C	-3.76899600	-1.22270000	0.18065600
C	-5.41028900	0.09732400	-1.25009500
C	-4.40659800	1.11298900	-0.67108800
C	-3.58051900	-0.11848800	1.28080900
C	-4.58446200	0.98042900	0.88321000
C	-2.77181300	-0.82353200	-0.92358500
C	-1.32004100	-1.13434800	-0.48407900
C	-2.95766800	0.72961500	-1.06016800
C	-1.95174400	1.31620100	-0.05126500
C	-1.12916700	-0.72962800	1.02059700
C	-2.13031400	0.42346200	1.22720700
C	-0.32278400	-0.23751300	-1.24231800
C	1.12917000	-0.72970700	-1.02052600
C	-0.50379400	1.17526900	-0.58255300
C	0.50379900	1.17531300	0.58247100
C	1.32004600	-1.13431000	0.48418200
C	0.32278700	-0.23741600	1.24234800
C	2.13031600	0.42336700	-1.22723000
C	3.58051900	-0.11858500	-1.28078900
C	1.95174900	1.31620700	0.05117200
C	2.95767300	0.72969900	1.06012000
C	3.76899700	-1.22271400	-0.18055200
C	2.77181800	-0.82345900	0.92366300
C	4.58446000	0.98036400	-0.88327700
C	6.03276800	0.53487500	-1.20327800
C	4.40660300	1.11304200	0.67101200
C	5.41029500	0.09741700	1.25009300
C	6.21913900	-0.97026900	-0.79880500

C	5.22144200	-1.17711500	0.35562600
C	7.03752200	1.28762700	-0.31237700
C	8.50176100	1.06804000	-0.79157300
C	6.85862900	0.62520000	1.10468900
C	7.86804000	-0.54189800	1.10309600
C	8.66391600	-0.43405300	-1.21992800
C	7.67203900	-1.19275000	-0.31350200
C	9.42124500	1.30586000	0.42582800
C	9.32762200	-0.00832100	1.23938800
C	10.30984400	-1.00467800	0.59209600
C	10.08484400	-0.96253100	-0.94551600
H	-10.20198700	-1.96122800	1.38410500
H	-10.82978100	-0.32018400	1.43213500
H	-8.40988900	-0.56503000	2.27898700
H	-11.34466000	-0.74122800	-0.84316000
H	-10.13768100	-2.01538800	-0.98401700
H	-9.57013100	0.15269800	-2.29688500
H	-8.73694700	1.74292800	1.62373400
H	-10.45955400	1.50451700	-0.13343100
H	-9.08503600	2.17842800	-0.99836700
H	-7.89485200	-2.26748500	0.29371200
H	-6.00443200	-1.64069400	1.64103600
H	-7.65358000	-1.25917900	-1.90529200
H	-7.06880000	1.33946900	-1.91033900
H	-6.24140300	0.69209600	2.26917300
H	-6.81885400	2.36276200	0.27934200
H	-5.43990500	-2.09571300	-0.91525700
H	-3.55032100	-2.22294100	0.57604000
H	-5.19851900	-0.11829800	-2.30527600
H	-4.62583900	2.13242300	-1.01387200
H	-3.79299100	-0.51196300	2.28317000
H	-4.36599900	1.92740600	1.39322500
H	-2.99178900	-1.33742800	-1.86812000
H	-1.10378800	-2.19864500	-0.64237500
H	-2.74508700	1.07010100	-2.08177600
H	-2.16759900	2.37073000	0.16336800
H	-1.34237900	-1.57154700	1.69179000
H	-1.91040300	0.98697200	2.14307100
H	-0.54582800	-0.20924600	-2.31665400
H	1.34238400	-1.57167800	-1.69165300
H	-0.28974000	1.98059800	-1.29689200
H	0.28974500	1.98069800	1.29674700
H	1.10379200	-2.19859400	0.64256200
H	0.54583100	-0.20906100	2.31668100
H	1.91040400	0.98680500	-2.14313900
H	3.79299200	-0.51213600	-2.28312100
H	2.16760400	2.37071900	-0.16354300
H	2.74509300	1.07026400	2.08170200
H	3.55032100	-2.22298500	-0.57585800
H	2.99179500	-1.33728000	1.86823800
H	4.36599600	1.92730200	-1.39336300
H	6.24140000	0.69194200	-2.26921900
H	4.62584600	2.13250200	1.01371800
H	5.19852700	-0.11812800	2.30528900
H	6.00442400	-1.64080900	-1.64092100
H	5.43991200	-2.09564400	0.91541300

H	6.81885200	2.36274600	-0.27950000
H	8.73693600	1.74283200	-1.62384600
H	7.06881300	1.33959600	1.91025300
H	7.65358400	-1.25906000	1.90536300
H	8.40986500	-0.56516800	-2.27896600
H	7.89484700	-2.26750300	-0.29358100
H	9.08503700	2.17848300	0.99823400
H	10.45955100	1.50452100	0.13333100
H	9.57013800	0.15282600	2.29686200
H	11.34466000	-0.74118800	0.84316900
H	10.13768000	-2.01533800	0.98410800
H	10.20196700	-1.96130600	-1.38402400
H	10.82976100	-0.32026500	-1.43214600

Energy: –2015.524023.