

**Supporting information for:**

**Natural chlordecone degradation revealed by numerous transformation products characterized in key French West Indies environmental compartments**

Marion L. Chevallier<sup>a,1</sup>, Oriane Della-Negra<sup>a,1</sup>, Sébastien Chaussonnerie<sup>a,2</sup>, Agnès Barbance<sup>a,2</sup>, Delphine Muselet<sup>a,2</sup>, Florian Lagarde<sup>a</sup>, Ekaterina Darii<sup>a</sup>, Edgardo Ugarte<sup>a</sup>, Ewen Lescop<sup>b</sup>, Nuria Fonknechten<sup>a</sup>, Jean Weissenbach<sup>a</sup>, Thierry Woignier<sup>c</sup>, Jean-François Gallard<sup>b</sup>, Stéphane Vuilleumier<sup>d</sup>, Gwenaél Imfeld<sup>e</sup>, Denis Le Paslier<sup>a,3</sup>, Pierre-Loïc Saaïdi<sup>a,3</sup>.

<sup>a</sup>Génomique Métabolique, Genoscope, Institut François Jacob, CEA, CNRS, Université d'Évry, Université Paris-Saclay, Evry, France.

<sup>b</sup>Institut de Chimie des Substances Naturelles. CNRS - UPR 2301 Bâtiment 27, 1 avenue de la Terrasse 91198 Gif-sur-Yvette Cedex, France.

<sup>c</sup>Institut Méditerranéen de Biodiversité et d'Ecologie marine et continentale (IMBE), Aix Marseille Université, CNRS, IRD, Avignon Université and IRD, UMR IMBE, Campus Agro Environnemental Caraïbes B. P. 214 Petit Morne, 97235, Le Lamentin, Martinique, France.

<sup>d</sup>Génétique Moléculaire, Génomique, Microbiologie (GMGM), Université de Strasbourg, UMR 7156 CNRS, 28 rue Goethe, 67000 Strasbourg Cedex, France.

<sup>e</sup>Laboratory of Hydrology and Geochemistry of Strasbourg (LHyGeS), Université de Strasbourg, UMR 7517 CNRS/EOST, 1 Rue Blessig, 67084 Strasbourg Cedex, France

<sup>1</sup>M.C. and O.D.N. contributed equally

<sup>2</sup>S.C., A.B. and D.M. also contributed equally

23 <sup>3</sup>To whom correspondence may be addressed: E-Mail: [plsaaidi@genoscope.cns.fr](mailto:plsaaidi@genoscope.cns.fr) or  
24 [denis@genoscope.cns.fr](mailto:denis@genoscope.cns.fr).  
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## **S1 Supporting Methods**

### **Chemicals and reagents**

Chlordecone was obtained from Cluzeau Info Labo (C.I.L.) (Dr. Ehrenstorfer, reference C11220000, batch number 10725, and purity 96.7%).  $^{13}\text{C}$ -enriched CLD was obtained from Azur Isotopes with a  $^{13}\text{C}/^{12}\text{C}$  ratio estimated to 80%. Vitamin B<sub>12</sub> ( $\geq 96\%$ ), palladium on carbon (12%), zinc powder, K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>S ( $\geq 98\%$ ) were purchased from Sigma Aldrich. Titanium (III) citrate was prepared from titanium (III) chloride ( $> 12\%$  in HCl) (Sigma-Aldrich) and sodium citrate and neutralized with Na<sub>2</sub>CO<sub>3</sub>[1]. Micrometric Fe<sup>0</sup> was obtained from Dousselin (iron powder NC 100.24; Dousselin & Geoffray Jacquet Réunis, 69270 Couzon au Mont d'Or, France). Dichloromethane (DCM), heptane and pentane (HPLC grade) were obtained from Fisher Chemical; cyclohexane (99.8%), ethyl acetate (EtOAc) (99.6%), chloroform (99.9%) and NMR solvents from Acros Organics; and acetonitrile (MeCN), ethanol (EtOH) and methanol (MeOH) (LC-MS grade) from VWR Chemicals. H<sub>2</sub>SO<sub>4</sub> (95-97%) was obtained from Fluka. Chemical products used for microbiological media were obtained from Sigma Aldrich.

### **Analytical methods**

#### **GC-FID analyses**

1 ml samples were collected, acidified to pH 3 with HCl (1 M) and extracted three times with dichloromethane (1:1 sample/DCM). After slow evaporation of the combined organic layers overnight, the crude residue was solubilized in an isooctane/acetone 85:15 mixture (350  $\mu\text{l}$ ) and 3  $\mu\text{l}$  were injected in duplicate using split mode (1:3; 350°C) on a Thermo Scientific Trace 1300 connected to a flame-ionization detector (320°C). The instrument was equipped with a non-polar 20 m  $\times$  0.15 mm  $\times$  0.15  $\mu\text{m}$  TG-5Sil column (Thermo Fisher Scientific). The

temperature program started at 150°C for 0.05 min, increased at a linear rate of 23°C/min until 290°C and remained 0.6 min at 290°C.

## GC-MS analyses

### *GC-MS 1*

500 µL samples were collected, acidified to pH 1 with HCl (6 M) and extracted with dichloromethane (1:1 sample/DCM). The organic layer was then analyzed using a Thermo Fisher Focus GC coupled to a single-quadrupole mass spectrometer (Thermo Fisher DSQ II). The instrument was equipped with a non-polar 30 m × 0.25 mm × 0.25 µm DB-5MS column (Agilent J&W) and a split/splitless injector. Ionization conditions and GC program were described elsewhere[2, 3].

### *GC-MS 2*

GC-MS analyses were performed using the instrument described in Chaussonnerie et al, 2016[2]. GC program started at 125°C (hold time 0.5 min), continued with 50°C min<sup>-1</sup> to 180°C, followed by 12.5°C min<sup>-1</sup> to 275°C (hold time 0.5 min). The study was done using the SIM (single ion monitoring) mode. Two ions were selected for CLD (m/z = 272; 237), B1 (m/z = 288; 253) and one for B2-3-4 (m/z = 217). Time ranges were also defined for these targeted ions.

## LC-HRMS analyses

### *LC-MS 1*

20 µl samples were collected and mixed with 480 µl of NH<sub>4</sub>OAc buffer (10 mM; pH 7 adjusted with NH<sub>4</sub>OH)/MeCN (38:10; V/V). The resulted mixture was filtered on 0.22 µm filters (Millex®-GV, Merck) and injected in a Dionex Ultimate 3000 LC system coupled to an

LTQ-OrbiElitemass spectrometer (Thermo Fisher Scientific) fitted with a heated electrospray ionization source (HESI) operating in negative ionization mode. Voltage optimization was described elsewhere[2]. The chromatographic separation was achieved using a Thermo Fisher Synchronis™ C<sub>18</sub> column (50 mm length, 2.1 mm inner diameter, 1.7 μm particle size) and carried out at 30°C with a flow rate of 0.5 mL/min using NH<sub>4</sub>OAc buffer (10 mM; pH 7 adjusted with NH<sub>4</sub>OH) as solvent A and MeCN as solvent B. The gradient started at 20% B for 1 min, followed by a linear gradient at 100% B for 7 min and remained 2 min at 100% B. The system returned to the initial solvent composition in 2 min and was re-equilibrated under these conditions for 2 min.

#### *LC-MS 2*

LC-MS analyses were performed using the instrument, column and ionization parameters described in material and methods section. The gradient started with a flowrate of 0.5 mL/min, at 12% B for 2 min, followed by a linear gradient at 20% B for 2 min, a second linear gradient at 100% B for 6 min and remained 2 min at 100% B. The system returned to the initial solvent composition in 4 min and was re-equilibrated under these conditions for 2 min. Carboxyindane references were purchased from Enamine Ltd. (1-*IH*-indane carboxylic acid, 2-*IH*-indane carboxylic acid, 4-*IH*-indane carboxylic acid, 5-*IH*-indane carboxylic acid), injected separately in LC-MS and mixed together.

#### Chloride analyses

Samples of 4 ml were collected, centrifuged (3050 x g), filtered (Millex®-GS, (0.22 μm, Merck) and sent for chloride analysis to the French public analysis laboratory of Drome (LDA26).

#### **Purification methods**

## Preparative Medium Pressure liquid Chromatography

Purification was carried out using a Combi Flash® Companion® (Teledyne ISCO) instrument equipped with a 40 g prepacked silica gel column (GraceResolv Flash Silica, Grace Davison, Discovery Sciences).

## Preparative High Performance Liquid Chromatography (HPLC)

A Shimadzu LC-20 AP preparative HPLC system coupled with an ultraviolet/visible detector (Shimadzu SPD-20AV) and an evaporative light scattering detector (Shimadzu ELSD-LT II) at 70°C and 3.4 bar was used. Chromatographic separation was achieved using a preparative HPLC column (X-Bridge Prep C18 5 µm OBD (150 x 19 mm) equipped with a security guard column (Cartridge Holder, 19 x 10 mm) and a prefilter (Guard Cartridge 19 x 20 mm).

## Nuclear Magnetic Resonance (NMR) analyses

Nuclear magnetic resonance spectroscopy (NMR) (<sup>1</sup>H-NMR; <sup>13</sup>C-NMR; <sup>1</sup>H-<sup>1</sup>H-COSY; <sup>1</sup>H-<sup>13</sup>C-HSQC; <sup>1</sup>H-<sup>13</sup>C-HMBC) was conducted on a Bruker Advance Ultra Shield 600 MHz spectrometer (UEVE, Evry, France). <sup>13</sup>C-enriched B1 was analyzed on a Bruker Advance III 800 MHz spectrometer (ICSN, Gif-sur-Yvette).

## Chemical protocols

### Compound <sup>13</sup>C-enriched B1

To a solution of <sup>13</sup>C-chlordecone (<sup>13</sup>C/<sup>12</sup>C = 80 %; 11 mg, 4.2 10<sup>-5</sup> mol, 1 eq.) and vitamin B<sub>12</sub> (4 mg, 2.9 10<sup>-6</sup> mol, 0.14 eq.) in degassed H<sub>2</sub>O/MeOH 7:3 (25 mL), was added titanium(III) citrate (5 mL, 3.2 10<sup>-4</sup> mol, 15 eq.) basified to pH 12.7 with NaOH (3 M). Reaction mixture was stirred under N<sub>2</sub> atmosphere at room temperature for 80 min and quenched by contact with O<sub>2</sub>. Extraction with pentane (5 x 30 mL) followed by concentration under reduced

pressure gave rise to a white crude solid. After purification (similar to TP B1)  $^{13}\text{C}$ -enriched B1 (2.7 mg;  $9.2 \cdot 10^{-6}$  mol; 22%) was obtained as a white solid. NMR data are available in Figures S33-S34.

#### Transformation products D1, D2, D3 and D4

To a solution of chlordecone (100 mg,  $1.9 \cdot 10^{-4}$  mol, 1 eq.) and vitamin B<sub>12</sub> (60 mg,  $5.8 \cdot 10^{-5}$  mol, 0.3 eq.) in degassed H<sub>2</sub>O/MeOH 1:4 (125 mL), was added titanium(III) citrate (25 mL,  $1.6 \cdot 10^{-3}$  mol, 8.4 eq.) basified to pH 12.7 with NaOH (3 M). Reaction mixture was stirred under N<sub>2</sub> atmosphere at room temperature for 4 h and, quenched by contact with O<sub>2</sub>. Extraction with pentane (5 x 250 mL) followed by concentration under reduced pressure gave rise to a white crude solid. A first purification step was carried out through PLC (Merck, PLC Silica gel, 1 mm, F<sub>254</sub>, 20 x 20) (cyclohexane/EtOAc 9:1); D1-4 retardation factor was 0.53. D1-D4 were then purified using a preparative HPLC system. Elution was performed at a flowrate of 25 mL/min using H<sub>2</sub>O as solvent A and MeCN as solvent B. Elution started at 50% B for 8 min, followed by a linear gradient reaching 60% B within 4 min, followed by a plateau within 43 min and a last linear gradient reaching 100% B within 7 min. Fractions containing respectively D1-D2 and D3-D4 (from 39 to 43 and 50 to 53 min respectively) were pooled separately, extracted 3 times with pentane and concentrated under reduced pressure to give the title compounds D1-D2 (3 mg;  $9.7 \cdot 10^{-6}$  mol; 5%) and D3-D4 (1.5 mg;  $5.4 \cdot 10^{-6}$  mol; 3%) as white solids. All NMR, GC-MS and LC-HRMS analyses for D1-D2 and D3-D4 are available in Figures 18-19, 22, 46-56.

#### Derivatization of C compounds

To a solution of C1-C2 or C3-C4 (250  $\mu\text{g}$ ,  $9 \cdot 10^{-7}$  mol) in ethanol or methanol (1 mL) was added concentrated sulfuric acid (10  $\mu\text{L}$ ). The reaction mixture was stirred for 1 h and



quenched with  $\text{K}_2\text{CO}_3$  (sat). Aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  and analysed in GC-MS. D1-D2 was obtained from C1-C2, D3-D4 from C3-C4 in presence of methanol. E1-E2 was obtained from C1-C2, E3-E4 from C3-C4 in presence of ethanol (**Figure S6**).

#### Degradation of CLD in presence of DTT or zero-valent zinc

CLD degradation tests were performed as described in Ranguin et al., 2017[4]. To a solution of chlordecone (0.25 mg,  $5.0 \cdot 10^{-7}$  mol, 1 eq.) in degassed ethanol (25 mL) were added either 1,4-dithiotreitol (231 mg,  $1.5 \cdot 10^{-3}$  mol, 3000 eq.) or zerovalent zinc (65.9 mg,  $1.0 \cdot 10^{-3}$  mol, 2015 eq.) and vitamin  $\text{B}_{12}$  (13.56 mg,  $1.0 \cdot 10^{-5}$  mol, 20 eq.). The reaction mixtures were carried out in triplicate, in a glove box ( $\text{N}_2$  98 %,  $\text{H}_2$  2 %) at room temperature (rt) for 4 h. Aliquots were acidified with HCl (6 M) to quench the reaction, filtered on 0.22  $\mu\text{m}$  filters (33 mm, Millex-GV, Merck), then analyzed in LC-MS and GC-MS according to the protocol GC-MS 2 (**Figure S7**).

#### Degradation of CLD in presence of hematin sodium and dithionite or sodium sulfide or zero-valent iron

To a solution of hematin (31.2 mg,  $4.9 \cdot 10^{-5}$  mol, 5 eq.) in degassed sodium carbonate solution (0.1 M, 2.5 mL) was added sodium dithionite or sodium sulfide or zero-valent iron (220 mg,  $1\text{-}3 \cdot 10^{-3}$  mol, 100 eq.) or titanium (III) citrate basified to pH 12.7 with NaOH (3 M) (5 mL,  $3.3 \cdot 10^{-4}$  mol, 32 eq.), and degassed water (30 mL). The solution was then added to chlordecone (5.0 mg,  $9.9 \cdot 10^{-6}$  mol, 1 eq.). The reaction mixture was stirred under  $\text{N}_2$  atmosphere at room temperature (rt) for several days; and followed by GC-MS and LC-MS analysis.

#### Degradation of CLD in presence of chlorophyll a and sodium sulfide

176 To a solution of sodium sulfide (220 mg,  $1.3 \times 10^{-3}$  mol, 100 eq.) in degassed water (30 mL)  
177 was added chlorophyll a (33.3 mg,  $3.7 \times 10^{-2}$  mol, 4 eq.). The solution was then added to  
178 chlordecone (5.0 mg,  $9.9 \times 10^{-6}$  mol, 1 eq.), and stirred under N<sub>2</sub> atmosphere at room  
179 temperature (rt) for several days; and followed by GC-MS and LC-MS analysis.

#### 180 Degradation of CLD adapted from Jablonski et al., 1996[5]

181 To a solution of chlordecone (0.3 mg,  $5.9 \times 10^{-7}$  mol, 1 eq.) and vitamin B<sub>12</sub> (0.05 mg,  $3.7 \times 10^{-8}$ ,  
182 0.06 eq) or rumen (0.05 mL), in degassed HEPES (50 mM, 5 mL) and ethylene glycol (0.8  
183 mL), was added titanium (III) citrate basified to pH 12.7 with NaOH (3 M) (1.3 mL,  $8.7 \times 10^{-5}$   
184 mol, 145 eq.). The reaction mixture was stirred under N<sub>2</sub> atmosphere at rt for 15 min and at 50  
185 °C for 4h. TLC was done on both reactions (Hexane/Acetone 3:1) and four spots were  
186 observed under UV lights with respective retardation factors (0.87, 0.97, 0.14, 0). These  
187 reactions were followed by GC-MS and LC-MS analysis.

#### 188 Degradation of CLD according to Schrauzer & Katz, 1978[6]

189 To a solution of chlordecone (0.5 mg,  $9.9 \times 10^{-7}$  mol, 1 eq.) and vitamin B<sub>12</sub> (20 mg,  $1.5 \times 10^{-5}$ , 15  
190 eq.) in degassed methanol (5 mL) was added acetoin (1.12 mL, basified to pH 12.7 with  
191 NaOH (3 M) (1.3 mL,  $1.3 \times 10^{-3}$  mol, 1000 eq.). The reaction mixture was stirred under N<sub>2</sub>  
192 atmosphere at room temperature (rt) for several days and followed by GC-MS and LC-MS  
193 analysis.

#### 194 Pd/C catalyzed hydrodehalogenation of C compounds (adapted from Chevallier et al, 195 2018)[3]

196 To a solution of C1-C2 or C3-C4 (1 mg,  $3.4 \times 10^{-6}$  mol, 1eq.) in degassed EtOH/THF/H<sub>2</sub>O (8 :  
197 2 : :1; 5 mL) was added palladium on carbon (10 % wt.; 1 mg;  $9 \times 10^{-7}$  mol, 0.25 eq.). The N<sub>2</sub>  
198 atmosphere of the round flask was removed by bubbling 3 volumes of H<sub>2</sub>. The reactor was

then filled with H<sub>2</sub>. The reaction was finally stirred for 3 hours under H<sub>2</sub> atmosphere; 3 samplings were performed (T0, T 1h, T 3h), and analyzed in LC-MS Orbitrap according to the protocol LC-MS 2 (**Figure S8**).

## **Anoxic microbiological experiments**

All bacterial cultures were performed at room temperature, anaerobically in a glove box (Unilab mBraun) under an N<sub>2</sub>/H<sub>2</sub> (98/2; V/V) atmosphere in MM+ medium[2] (otherwise mentioned) containing Na<sub>2</sub>S (0.4g/L) as reducing agent.

### **Chlordecone bacterial degradation in presence of Consortium 86 and *Citrobacter* sp. 86**

Modifications of previously described MM+ medium[2] were the following: MgCl<sub>2</sub> and NH<sub>4</sub>Cl were replaced by MgSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, respectively. NaCl, CaCl<sub>2</sub>, KCl were removed. Two liters of freshly prepared medium were inoculated with active consortium 86 culture (1/100 V/V). After 8h of incubation, three glass bottles were filled up with 650 ml of this growing bacterial culture and one filled up with medium as negative control. 162.5 µl of a chlordecone solution (200 mg of chlordecone in 1 ml dimethylformamide) were added to reach a final chlordecone concentration of 50 mg/L in each bottle. The same procedure was carried out for *Citrobacter* sp. 86. Cultures were incubated and monitored during 250 days using GC-FID, GC-MS, LC-HRMS and chloride analysis.

### **Chlordecone biodegradation in soil/liquid microcosms from Guadeloupe Island**

Soil microcosm were prepared from 0.5 g dry weight (dw) of andosol or 0.5 g dw of nitisol sampling in Guadeloupe Island. Each sample was inoculated under oxygen-free nitrogen atmosphere containing 5% H<sub>2</sub>, at 25 °C, in 12 mL M9 mineral medium or M9 mineral medium supplemented with vitamin B<sub>12</sub> (2 mg/L). Duplicate samples were taken over 36 months, using a sacrificial approach. A microcosm pair (duplicate samples) was retrieved

from each serie and analysed at  $t = 0$ ,  $t = 10$  months, and  $t = 36$  months. Two negative control series were conducted for each serie (again in duplicate, but only for  $t = 0$  and  $t = 36$  months), and consisted of (a) soil samples incubated aerobically and (b) irradiated soil samples soil samples ( $30 \pm 1.5$  kGy).

Duplicate samples from  $t = 0$ ,  $t = 10$  and  $t = 36$  months were first basified to pH 12 with NaOH (1M), extracted with pentane (6 x 15 mL) after vortex and decantation. Aqueous phases were then acidified to pH 1 with HCl (1 M) and extracted with  $\text{CH}_2\text{Cl}_2$  (12 x 15 mL) after vortex and decantation. Organic layers were then pooled, concentrated *in vacuo* and analyzed in duplicate using GC-MS and LC-MS protocols (**Figure S3, Table S2Table S3**).

#### Chlordecone degradation in presence of Martinique soil/liquid microcosms and liquid cultures

5 g of soil samples (Andosol 914, Nitisol 918, Ferralsol 919) were incubated in 50 mL MM+ medium[2] and amended with chlordecone at 40 mg/L. After one month, 500  $\mu\text{L}$  of each Martinique liquid supernatant was used to inoculate 50 mL of medium MM+ with chlordecone at 40 mg/L. Liquid cultures were monitored by GC-MS analysis (**Figure S9**).

#### Soil biodiversity analysis: 16S rRNA gene pyrosequencing and analysis

DNA extraction of 9 soils was performed on 10 g of sample using PowerMax® Soil DNA Isolation Kit (MoBio) according to the manufacturer's instructions. V4-V5 regions of 16S rRNA gene were amplified with the primers 515F GTGYCAGCMGCCGCGGTAA and 926R CCGYCAATTYMTTTRAGTTT then DNA libraries were sequenced using 250 bp paired end reads chemistry on a MiSeq Illumina sequencer. Illumina sequencing adapters and primer sequences were removed from the reads by in-house-designed software based on the FastX package. Reads were merged using `usearch v9.2.64 -fastq_mergepairs` command[7]. The merged reads were cleaned, dereplicated and clusterised using `usearch v9.2.64 (-fastq_filter, -`

derep\_fulllength and -cluster\_otus commands with default settings). The taxonomic assignment was performed on 200,000 sequences randomly selected with SortMeRNA v2.1[8] using Greengenes database gg\_13\_5 ([http://greengenes.secondgenome.com/downloads/database/13\\_5](http://greengenes.secondgenome.com/downloads/database/13_5)) or SILVA128 database[9] with --id 0.97 and --coverage 0.97. 16S sequences of bacterial species included in the consortia 86 and 92[2] were added to the databases. The OTU table was generated using usearch v9.2.64 -usearch\_global command with -id 0.97.

## Statistical methods

### Estimation of CLD and B1 extraction efficiency in andosol and nitisol

Extractions of one andosol (914) and one nitisol (918) were followed to determine CLD and B1 extraction efficiency. Samples were prepared as described before (4 g of crude sample and 15 mL of milliQ water acidified to pH 1) and were extracted with CH<sub>2</sub>Cl<sub>2</sub> (12 x 15 mL). Each extraction was injected in GC-MS (500 µL) (**Figure S10, Table S5**).

### Calibration curves

Chlordecone (CLD), chlordecol (CLD-OH), A1, B1 concentrations were estimated through GC-MS calibration curves (Figure SI). They were made using pure metabolites separately diluted in Hexane/Acetone (4/1). C1-C2 and C3-C4 concentrations were estimated through LC-MS calibration curves (Figure SI). They were made using pure metabolites separately diluted in NH<sub>4</sub>OAc buffer (10 mM; pH 7) /MeCN (4/1) (**Figure S11**).

Six successive dilutions enabled to build calibration curves with a concentration range from 0.01 to 25 mg/L. Each sample was injected in duplicate. B1, C1-C2, C3-C4 purity was estimated through NMR analysis (<sup>1</sup>H) by addition of chloroform as internal standard. Linear

267 regression was chosen as the calibration model. LOD (limit of detection) and LOQ (limit of  
268 quantification) were assumed according the AFNOR NF-T-90-210 requirement.

$$LOD = \frac{y_0 + 3 \times \sigma_{y_0}}{a}$$

$$LOQ = \frac{y_0 + 10 \times \sigma_{y_0}}{a}$$

269 Where a is the slope of the calibration curve,  $y_0$  the intercept and  $\sigma_{y_0}$  the standard deviation on  
270 the intercept (**Table S6**).

#### 271 Repeatability and uncertainty of the method

272 Uncertainty of measure was assumed according to the NF ISO/CEI GUIDE 98-3 (2014)  
273 requirement. This uncertainty included three parameters: (1) the uncertainty of reproducibility  
274 of extraction  $U_{\text{reproducibility}}$ , (2) the uncertainty of GC-MS or LC-MS instrument  $U_{\text{instrument}}$  and  
275 (3) the mean bias  $U_{\text{bias}}$  (corresponding to the difference between the calculated concentration  
276 and theoretical value) according to NF T 90-210 (2009) requirement (**Table S6**).

$$277 \quad U_{\text{reproducibility}} = \sqrt{\frac{\sum_i^n (x_i - \bar{x})^2}{n-1}} \text{ with } n = 2$$

$$278 \quad U_{\text{instrument}} = \sqrt{\frac{\sum_i^n (m_i - \bar{m})^2}{n-1}} \text{ with } n = 2$$

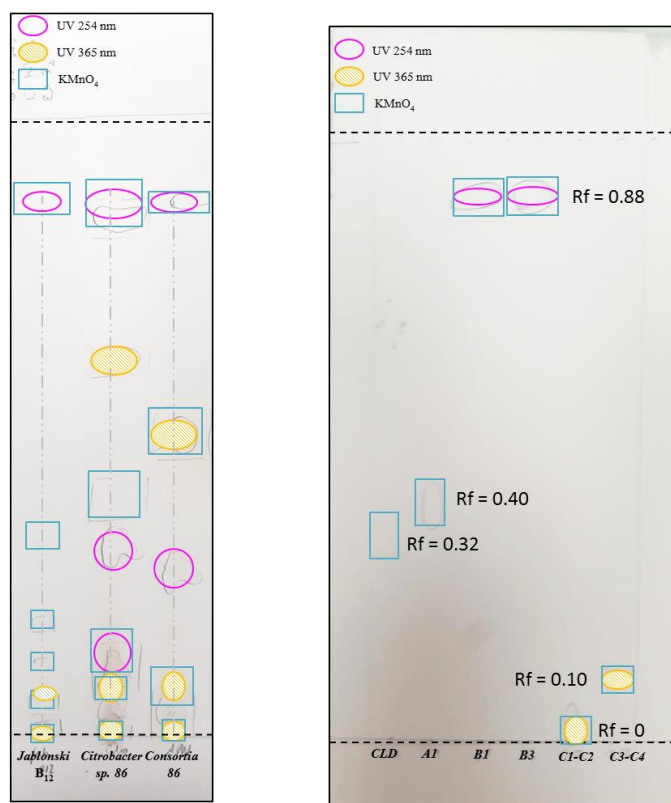
$$279 \quad U_{\text{bias}} = \sqrt{\frac{\sum_i^n b_i^2}{n}} \text{ with } n = 5; \text{ and } b_i, \text{ the difference between the calculated concentration with}$$

280 the calibration model and the theoretical value

281 The uncertainty U was a function of the three previous uncertainties with a confidence level  
282 of 68%.

$$U = \sqrt{U_{reproducibility}^2 + U_{intrument}^2 + U_{bias}^2}$$

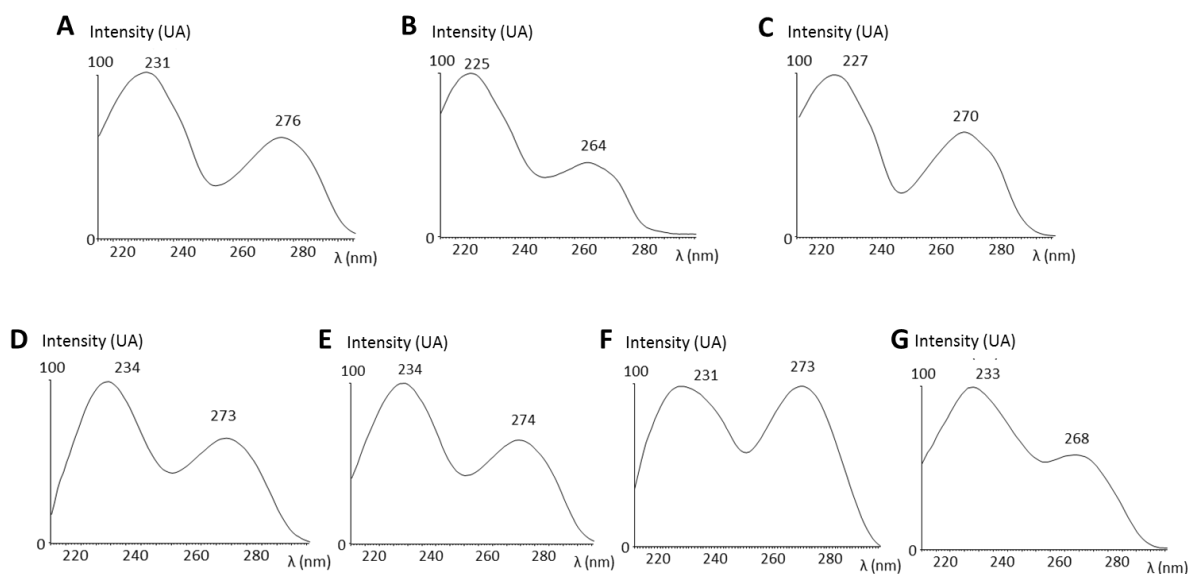
284 **S2 Supporting Figures**



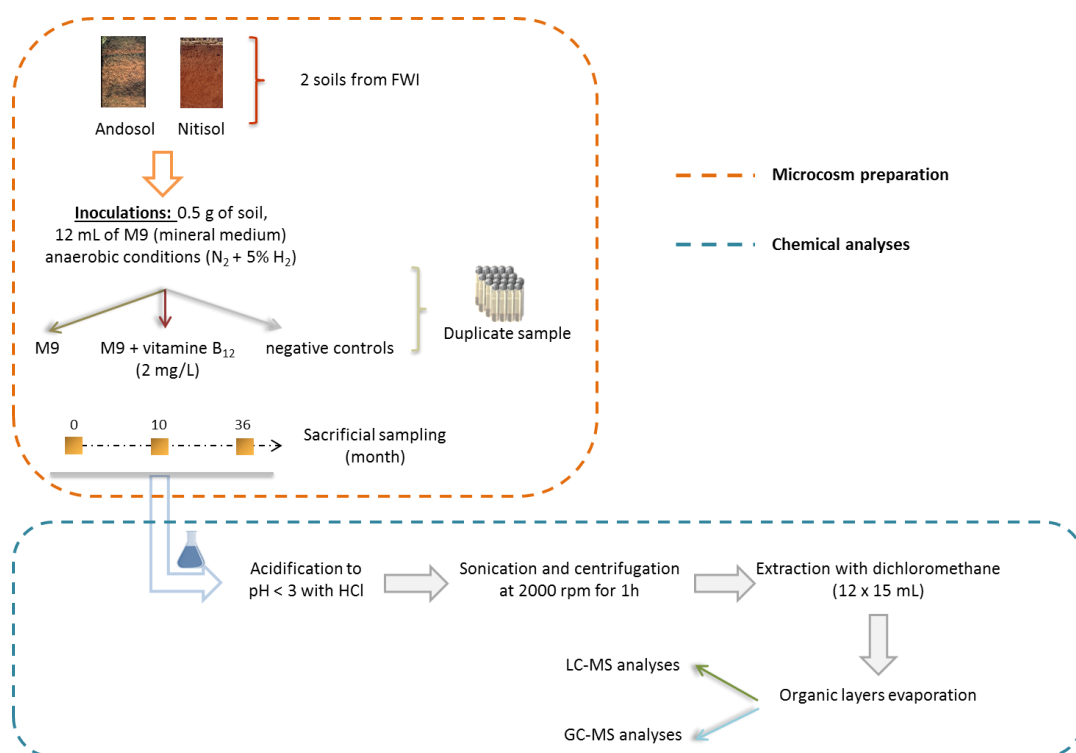
285  
286 **Figure S1.** Thin layer chromatography of extract cultures from *Citrobacter* sp. 86 and  
287 Consortia 86 in (hexane : acetone 3:1). After three months in culture, 1L was acidified each  
288 time, extracted three times with DCM (3 x 1L) and concentrated *in vacuo*. Retardation factors  
289 were then compared with purified standards.

290

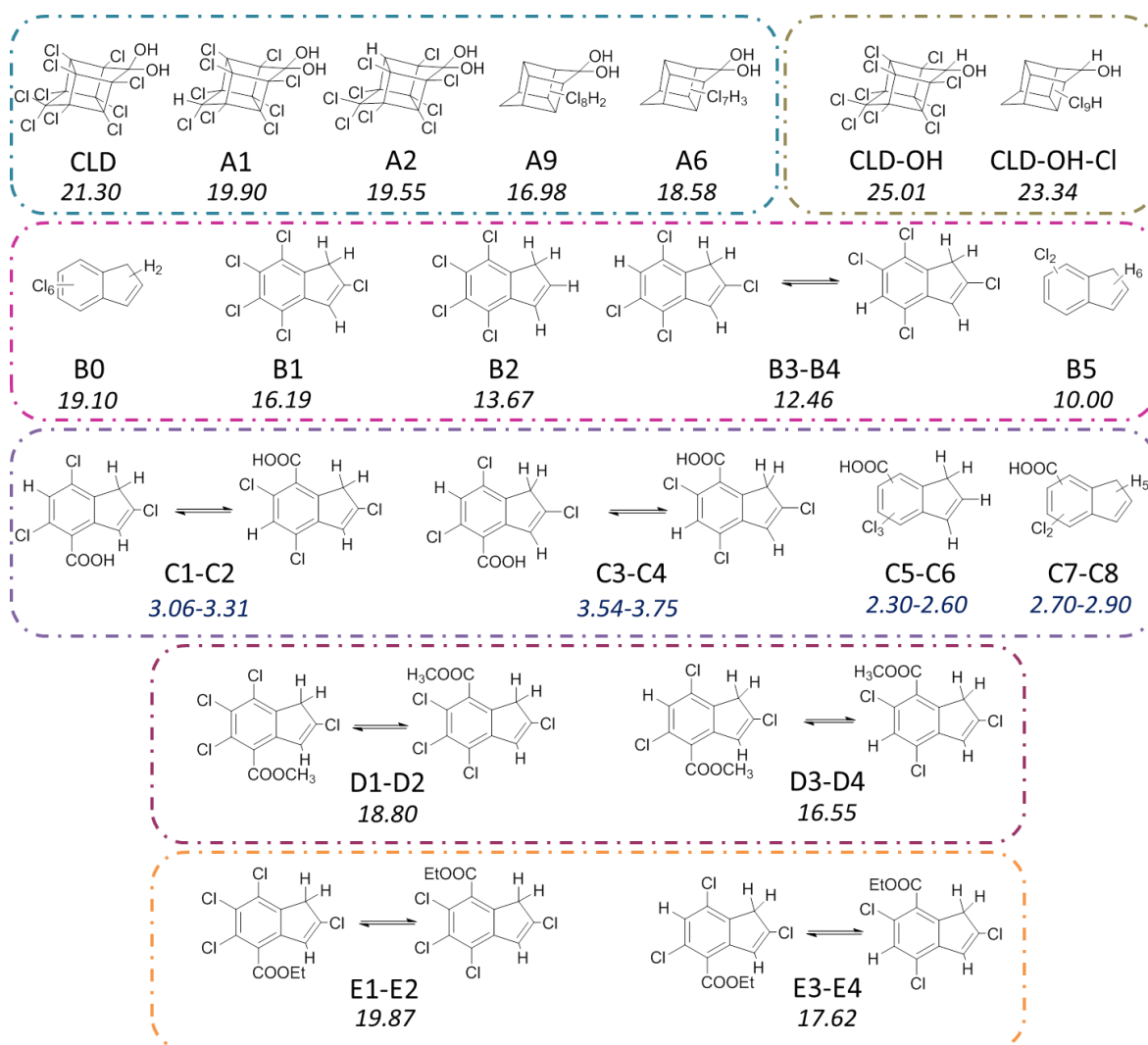




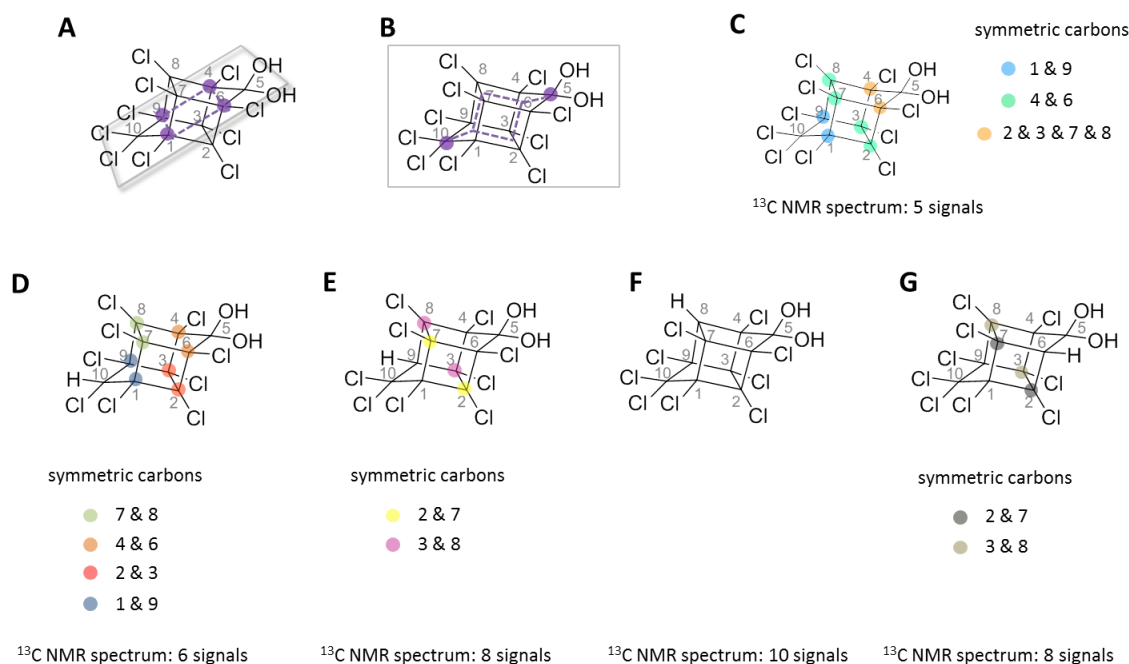
**Figure S2.** UV spectra of chlordecone bacterial metabolites extracted from liquid chromatography analysis. (A) UV spectrum of B1, (B) UV spectrum of B2, (C) UV spectrum of B3-B4, (D) UV spectrum of C1, (E) UV spectrum of C2, (F) UV spectrum of C3, (G) UV spectrum of C4



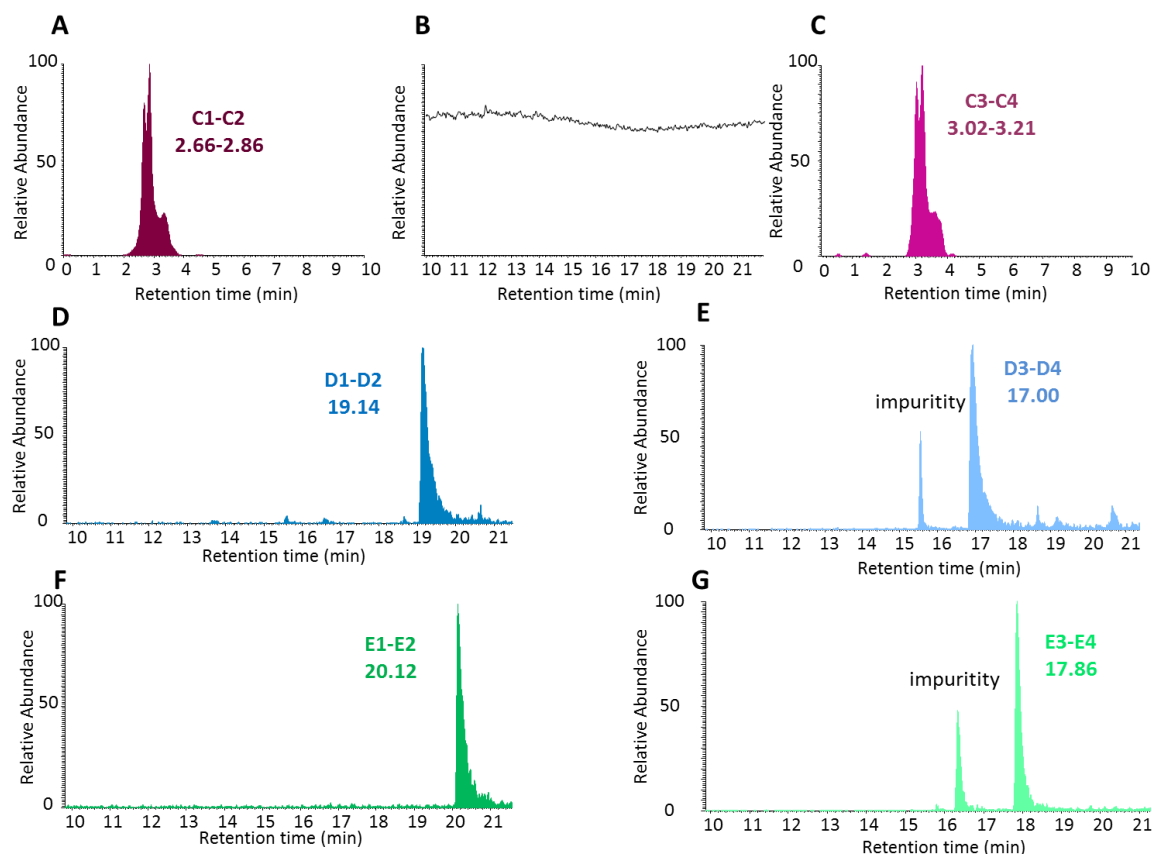
**Figure S3.** Microcosm preparation and extraction procedure enabling to find chlordecone TPs



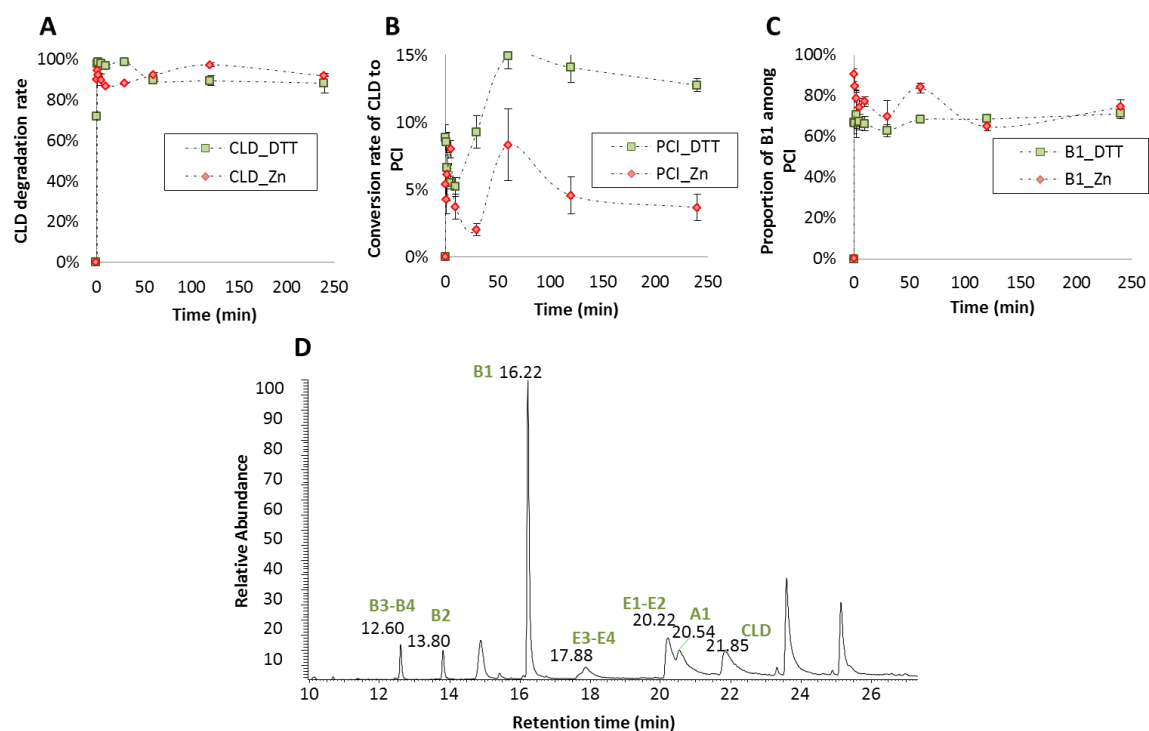
**Figure S4.** Structure of the 29 chlorodecone TP detected in environmental samples and/or in biodegradation processes. GC-MS retention time are indicated in black, in italics, in minute. LC-MS retention time are indicated in blue, in italics, in minute. Chromatographic methods are described in material and methods section.



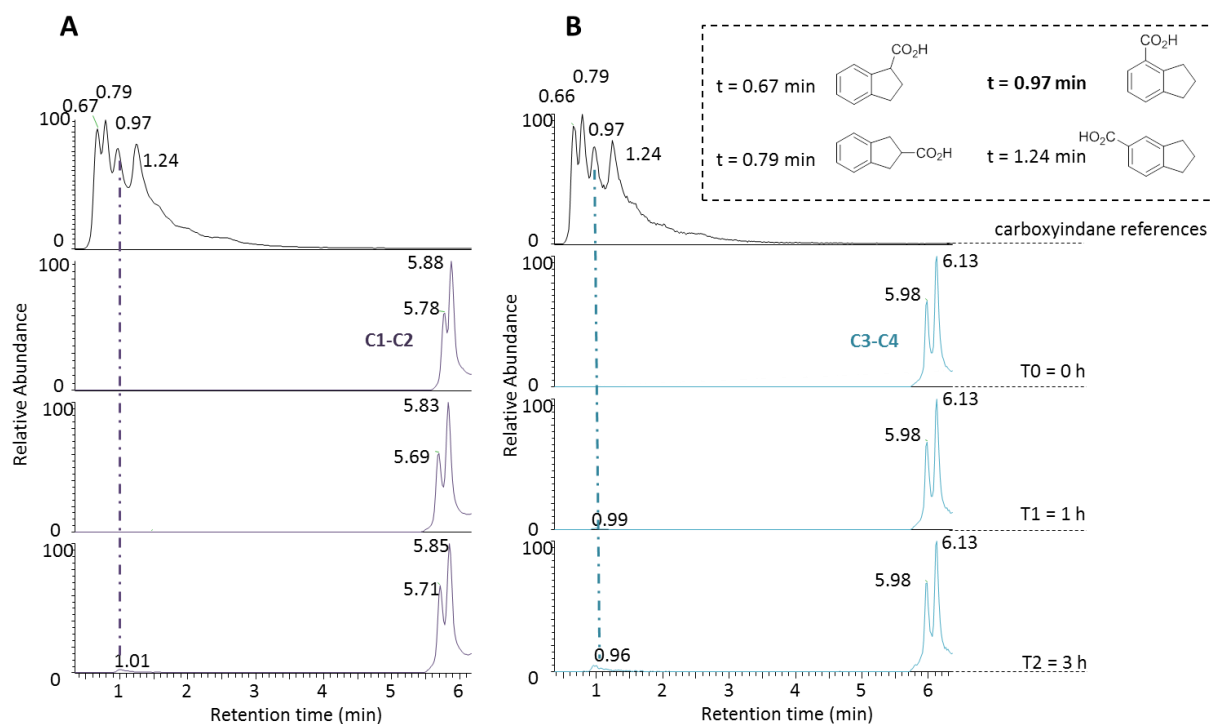
**Figure S5.** Chlordecone planes of symmetry and hydrochlordecone symmetric carbons according to the Hydrogen position. Number of expected signals in  $^{13}\text{C}$  NMR are also indicated. (A) Chlordecone horizontal plane of symmetry, (B) Chlordecone vertical plane of symmetry, Symmetric carbons for (C) chlordecone compared to (D) 10-monohydrochlordecone (E) 9 monohydrochlordecone (F) 8 monohydrochlordecone and (G) 6-monohydrochlordecone.



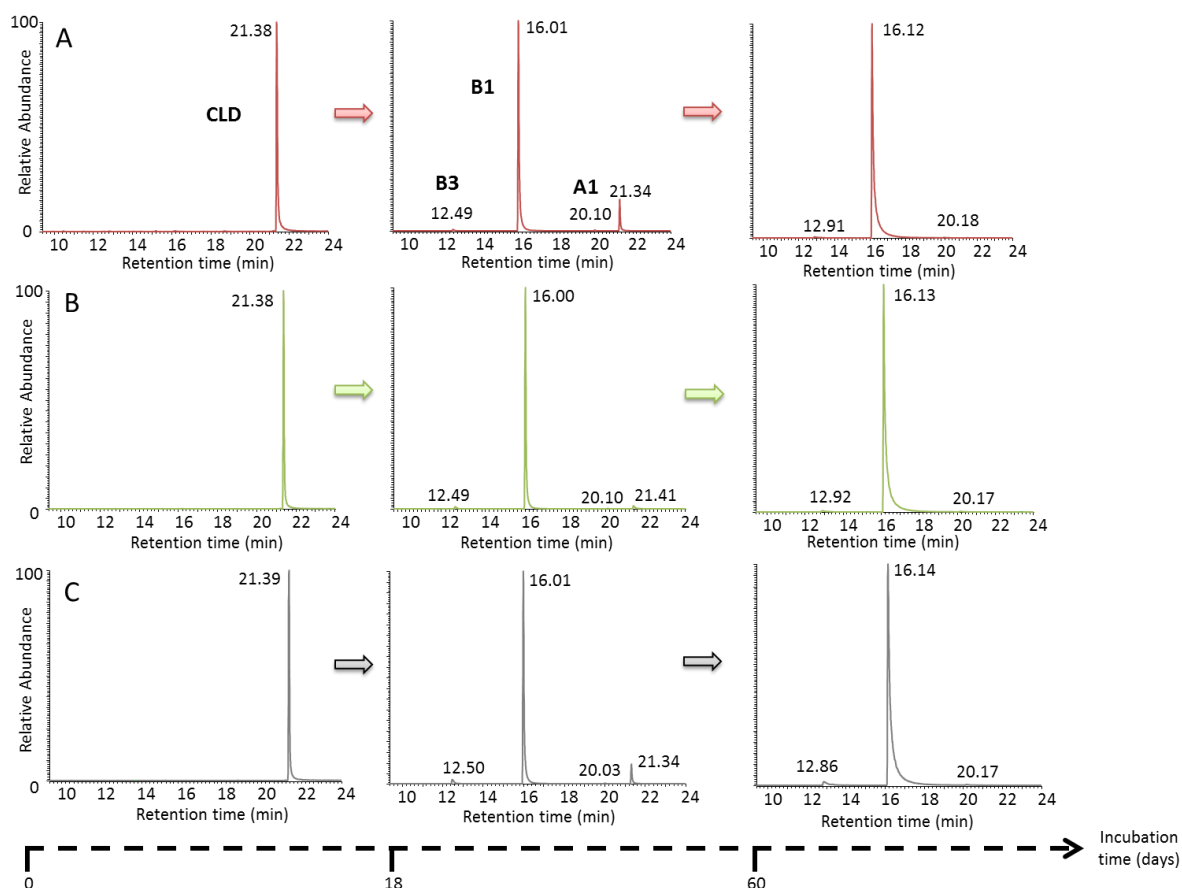
**Figure S6.** Derivatization of C compounds into D and E compounds and analysis of reactions by GC and LC-MS. Each figure represents extract ion chromatograms (A) LC-MS analysis of C1-C2 before reacting; (B) GC-MS analysis of C1-C2 and C3-C4 before reacting, no D or E compounds were present at this stage; (C) LC-MS analysis of C3-C4 before reacting, (D) GC-MS analysis of C1-C2 esterification in MeOH after 1h (E) GC-MS analysis of C3-C4 esterification in MeOH after 1h (F) GC-MS analysis of C1-C2 esterification in EtOH after 1h (G) GC-MS analysis of C3-C4 esterification in EtOH after 1h



**Figure S7.** Degradation of chlordecone with vitamin B<sub>12</sub> and DTT or zero valent zinc, according to Ranguin et al., 2017 protocol. (A) Degradation rate of CLD with vitamin B<sub>12</sub> and DTT (squares) or vitamin B<sub>12</sub> and zerovalent zinc (diamonds); (B) Conversion rate of CLD to PCI (polychloroindene) calculated as PCI peak area (C) Proportion of B1 among PCI (B1, B2, B3, B4) calculated as B1 peak area/PCI peak area (D) GC-MS (full scan) analysis of DTT experiment after 4h (C1-C2 were also observed in LC-MS Orbitrap, negative mode)

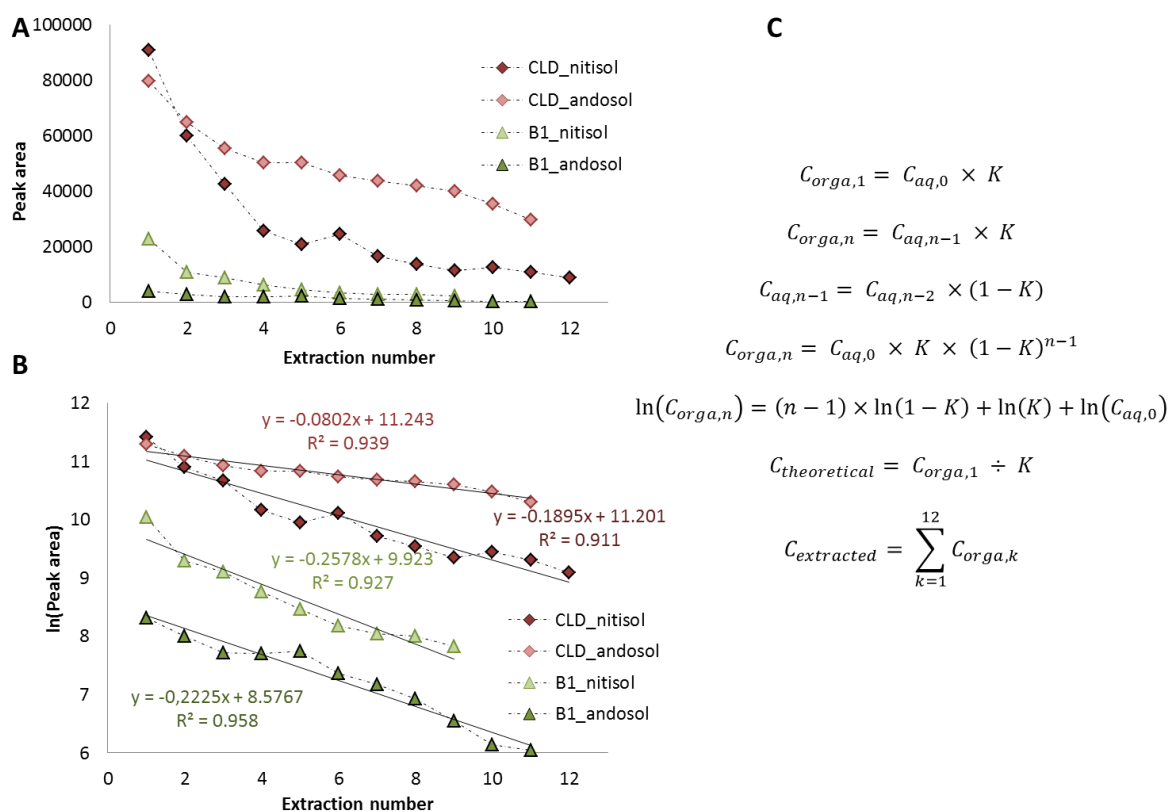


**Figure S8.** Hydrodehalogenation of C compounds and identification of the carboxyindane transformation product by LC-MS-Orbitrap (A) LC-MS spectra of C1-C2 Pd-catalyzed hydrodehalogenation over time (B) LC-MS spectra of C3-C4 Pd-catalyzed hydrodehalogenation over time (ESI, negative mode). All chromatograms correspond to extract ion chromatograms for C1, C2, C3, C4 and carboxyindane references.



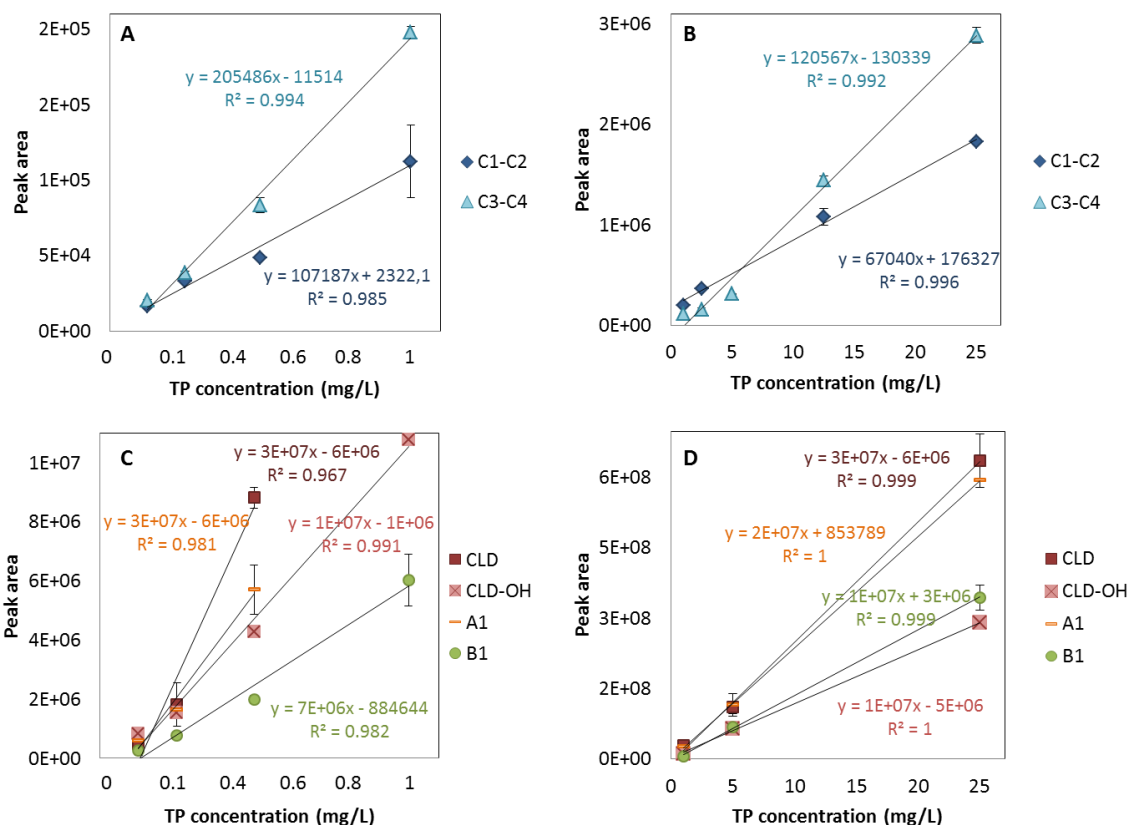
**Figure S9.** Liquid cultures from three soils (A) 914, (B) 918, (C) 919 supplemented with MM+ medium (Chaussonnerie et al., 2016), sodium sulfide as reding agent and chlordecone. Three samplings were taken for each soil at t = 0 day, t = 18 days and t = 60 days, extracted with isooctane and analyzed by GC-MS analysis.



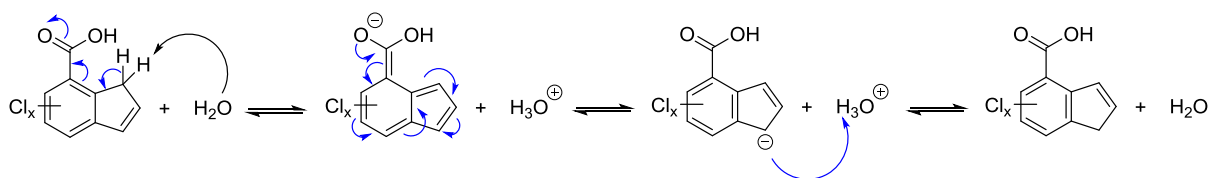


345

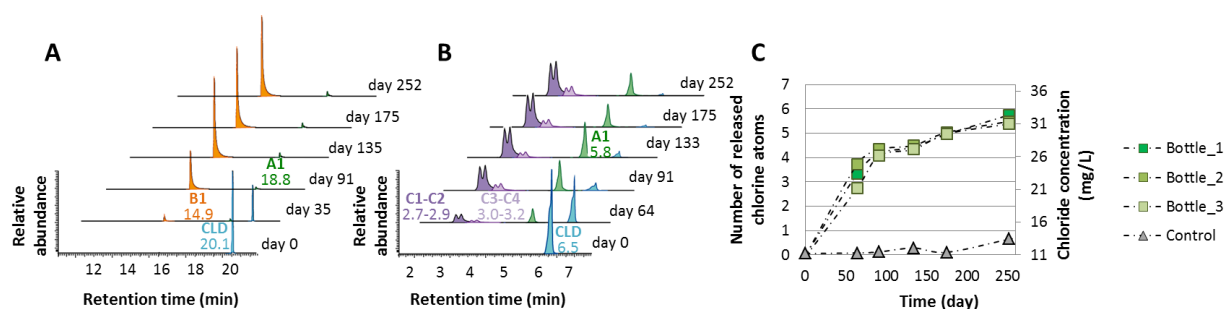
346 **Figure S10.** Estimation of CLD and B1 extraction efficiency by GC-MS analysis of each  
 347 extraction fraction (A) CLD and B1 peak area obtained from GC-MS analysis as a function of  
 348 extraction number and type of soil. (B) logarithm of CLD and B1 peak area as a function of  
 349 extraction number (C) Equations used to assume extraction efficiency of both metabolite;  
 350 with  $C_{x,y}$  the concentration of CLD or B1 in organic (orga) or aqueous (aq) layer at  $n^{th}$   
 351 extraction; K the partition coefficient and n the final number of extraction (12). These  
 352 equations were assessed considering that organic and aqueous layers contained the same  
 353 volume, thus the extracted fraction of B1 and CLD could be compared to the theoretical  
 354 concentration.



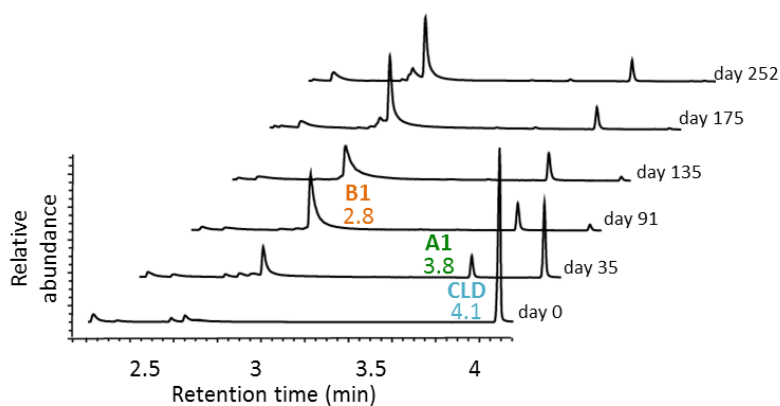
**Figure S11.** Calibration curves of CLD, CLD-OH, A1, B1, C1-C2 and C3-C4. (A) Calibration curve for 0.25-1 mg/L concentration range of C1-C2 and C3-C4 using LC-MS Orbitrap; (B) Calibration curve for 1-25 mg/L concentration range of C1-C2 and C3-C4 using LC-MS Orbitrap; (C) -Calibration curve for 0.25-1 mg/L concentration range of CLD, CLD-OH, A1 and B1 using GC-MS; (D) Calibration curve for 1-25 mg/L concentration range of CLD, CLD-OH, A1 and B1 using GC-MS.



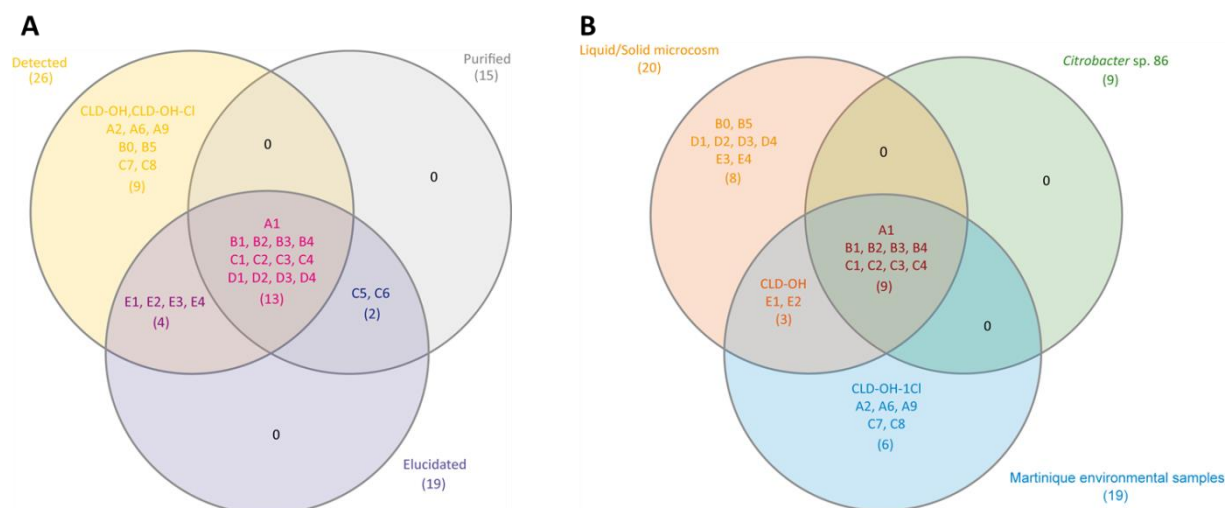
**Figure S12.** Proposed keto-enol mediated isomerization for polychloroindene carboxylic acids



**Figure S13.** TP production during chlordecone degradation by consortium 86 during 250 days examined by GC-MS analysis, LC-MS analysis and chloride concentration. (A) GC-MS monitoring of chlordecone degradation and detection of CLD (blue), A1 (green), B1 (orange) and B3 (yellow) TP. (B) TP production during chlordecone degradation by APW using LC-MS-Orbitrap analysis and detection of CLD (blue), A1 (green), C1 (purple), C2 (purple), C3 (magenta) and C4 (magenta) metabolites. Extract ion chromatograms for quasimolecular ion  $[M-H]^-$  of  $m/z = 506.6797$ ;  $472.7187$ ;  $296.8852$ ;  $260.9271$  (C) Chloride concentration monitoring during chlordecone degradation. The average number of released chlorine atoms per consumed chlordecone molecule is indicated.



**Figure S14.** TP production during chlordecone degradation by consortium 86 during 250 days examined by GC-FID analysis.



**Figure S15.** Venn diagrams representing the distribution of each observed TP. (A) Venn diagrams representing detected, purified and structure elucidated TP. (B) Venn diagrams distinguishing TP detected in liquid/solid microcosms, produced by *Citrobacter* sp. 86 (or consortium 86) and observed in Martinique environmental samples.

387 **S3 Supporting Tables**

Metal complex Reductant	Vitamin B <sub>12</sub> <sup>vi</sup>	Hematin <sup>iii</sup>	Chlorophyll a	Rumen <sup>vi</sup>	Without
Acetoin <sup>i</sup> (Methanol)	A, B, C, D (week)	/	/	/	X (week)
Sodium dithionite <sup>ii</sup>	Traces of A (week)	Traces of A (days)	/	/	X (week)
Sodium sulfide	A1, B1, C (days)	A1, B1, C (days)	Traces of A (days)	/	X (days)
1,4-dithiothreitol (Ethanol) <sup>iii</sup>	A, B, C, E (hours)	/	/	/	X (hours)
Zero valent iron (H <sub>2</sub> O-acetone) <sup>iv</sup>	A, B, C (week)	A (weeks)	/	/	A (weeks)
Zero valent zinc (Ethanol) <sup>iii</sup>	A, B, C, E (hours)	/	/	/	A, B, C, E (week)
Titanium citrate <sup>v</sup>	B, C (hours)	A (hours)	/	Traces of A (hours)	A (hours)
Titanium citrate (H <sub>2</sub> O-methanol)	B, C, D (hours)	/	/	/	A (hours)
Titanium citrate (H <sub>2</sub> O-ethanol)	B, C, E (hours)	/	/	/	A (hours)

388 **Table S1.** Screening of CLD transformation chemical conditions. Green cases meaning that  
389 the transformation was complete, orange cases that the transformation was partial and red  
390 cases that no transformation occurred. The slash / means that combinations have not been  
391 tested, and the green boxes show conditions retained for chemical synthesis of A1, B C, D  
392 and E compounds. Typical reaction time is indicated in brackets. Without reductant, no CLD  
393 transformation occurred. The solvent generally used is water otherwise indicated in brackets.  
394 This screening of degradation conditions has been established according to several already  
395 published protocols (i) Schrauzer & Katz 1978[6]; (ii) Holmstead et al., 1976[10]; (iii)  
396 Ranguin et al., 2017[4] (iv) Belghit et al., 2015[11]; (v) Chevallier et al., 2018[3]; (vi)  
397 Jablonski et al., 1996[5].

398

Conditions	Sample number	Incubation time (month)	B5	B3-B4	B2	B1	B0	D1-D2	D3-D4	E1-E2	E3-E4	CLD-OH	CLD	A1	
Nitrosol	-	57N	0	-	++	++	++	nd	+	+	nd	nd	+	--	nd
		65N	10	-	++	++	++	nd	+	+	nd	nd	+	nd	nd
		69N	36	--	+	++	+++	-	+	-	nd	nd	+	nd	nd
	Vitamin B <sub>12</sub>	71N	0	nd	+	++	++	-	+	+	nd	nd	+	--	nd
		79N	10	nd	-	nd	+	nd	nd	nd	nd	nd	+	nd	nd
		83N	36	-	++	+++	+++	+	++	+	-	+	-	nd	nd
Andosol	-	1A	0	nd	-	nd	+	nd	nd	nd	nd	+	-	nd	
		9A	10	nd	+	nd	+	nd	nd	nd	nd	+	-	--	
		13A	36	nd	+	nd	+	nd	nd	nd	nd	+	--	nd	
	Vitamin B <sub>12</sub>	15A	0	nd	nd	nd	-	nd	nd	nd	nd	+	--	nd	
		23A	10	nd	+	nd	+	nd	nd	nd	nd	+	--	nd	
		27A	36	nd	+	nd	+	nd	nd	nd	nd	+	nd	--	

nd	< 5 10 <sup>4</sup>	--	5 10 <sup>4</sup> - 4 10 <sup>5</sup>	-	5 10 <sup>5</sup> - 4 10 <sup>6</sup>	+	5 10 <sup>6</sup> - 4 10 <sup>7</sup>	++	5 10 <sup>7</sup> - 4 10 <sup>8</sup>	+++	5 10 <sup>8</sup> - 4 10 <sup>9</sup>
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**Table S2.** Analysis by GC-MS of soil/liquid microcosms. No quantification was done on this set of data, only peak area from full scan mode is represented here. (nd means not detected)

Conditions	Sample number	Incubation time (month)	C1-C2	C3-C4	A1	CLD
Nitrosol	-	57N	0	nd	nd	+
		65N	10	nd	-	-
		69N	36	+	++	-
	Vitamin B <sub>12</sub>	71N	0	nd	nd	++
		79N	10	nd	--	nd
		83N	36	nd	nd	nd
Andosol	-	1A	0	-	nd	++
		9A	10	nd	+	-
		13A	36	nd	nd	-
	Vitamin B <sub>12</sub>	15A	0	nd	nd	++
		23A	10	nd	+	-
		27A	36	nd	nd	+

nd	< 10 <sup>2</sup>	--	10 <sup>2</sup> - 10 <sup>3</sup>	-	10 <sup>3</sup> - 5 10 <sup>3</sup>	+	5 10 <sup>3</sup> - 10 <sup>4</sup>	++	> 10 <sup>5</sup>
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**Table S3.** Analysis by LC-MS (extract ion chromatograms, negative mode) of soil/liquid microcosms. No quantification was done on this set of data, only peak area is represented here. (nd means not detected)

Sample number	Type	Origin	Plot	GPS N	GPS W
914	Andosol	Maison rouge	Cacao 1	N 014°46.038	W 061°08.356
915	Andosol	Maison rouge	Cacao 2	N 014°45.802	W 061°08.323
918	Nitisol	Trinité	Montvert 3	N 014°41.626	W 060°57.507
920	Nitisol	Trinité	Montvert 4	N 014°41.774	W 060°57.505
919	Ferralsol	Trinité	Montvert 2	N 014°41.652	W 060°57.296
921	Ferralsol	Trinité	Montvert 1	N 014°41.635	W 060°57.154
922	Ashes and pumice stone	Basse pointe	H. Leyrits	N 014°37.272	W 060°58.112
923	Ashes and pumice stone	Basse pointe	H. Leyrits	N 014°50.598	W 061°07.258
926	Nitisol	Lamentin	R.LZ.Belème	N 014°39.924	W 061°00.361
927	Bed sediments	Trinité	Mangrove	N 014°43.250	W 060°56.462
928	Bed sediments	Trinité	Mangrove	N 014°43.260	W 060°56.480
929	River water	G. Trinité	Galion	N 014°42.008	W 060°57.067
930	River water	G. Trinité	Galion	N 014°42.008	W 060°57.067
931	Mangrove water	Trinité	Mangrove	N 014°43.250	W 060°56.462
932	Mangrove water	Trinité	Mangrove	N 014°43.260	W 060°56.480

**Table S4.** Environmental samples used for chlordecone TP investigation.

	Andosol	Nitisol
CLD	52 %	64 %
B1	94 %	65 %

411 **Table S5.** Estimated extraction efficiency of CLD and B1 in andosol and nitisol.

412

	CLD	A1	CLD-OH	B1	C1-C2	C3-C4
$U_{bias}$	33%	49%	13%	18%	28%	25%
LOD (m/L)	0.12	0.12	0.16	0.80	0.04	0.10
LOQ (mg/L)	0.66	0.65	0.85	0.15	0.21	0.50

413 **Table S6.** Mean bias, LOD (limit of detection) and LOQ (limit of quantification) of main  
414 chlordecone TPs.

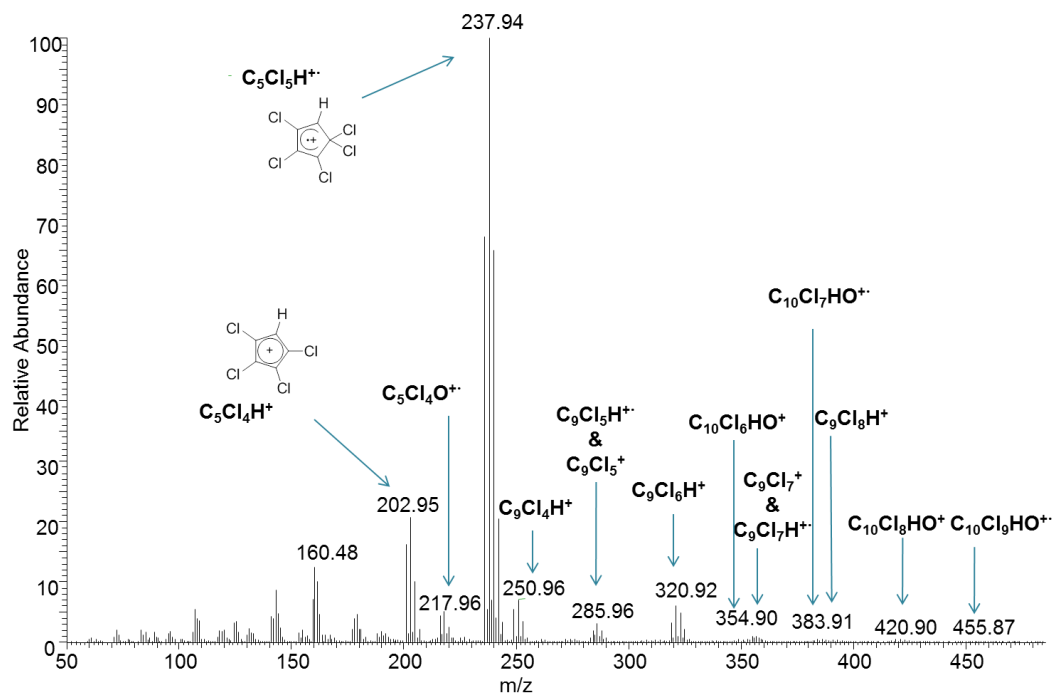
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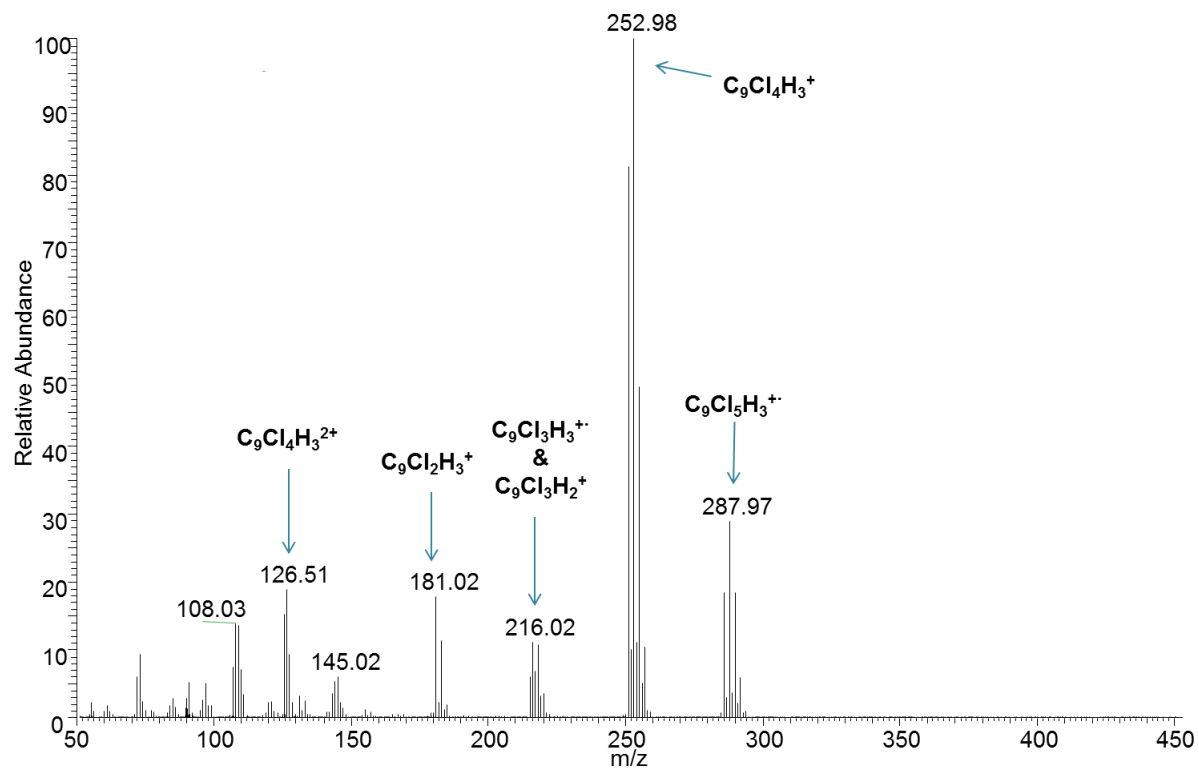
Sample type	Sample number	CLD	CLD-OH	A1	B1	C1-C2	C3-C4	Other detected TP
Andosol	914	0.11 ± 0.03	0.03 ± 0.01	0.28 ± 0.22	2.07 ± 1.84	nd	0.01 ± 0.004	A6, A9, A2, Monohydro-CLD-OH, B2, B3-B4
Andosol	915	0.15 ± 0.04	0.04 ± 0.01	0.07 ± 0.06	5.08 ± 2.20	0.45 ± 0.18	0.99 ± 0.50	A6, A9, A2, B2, B3-B4, C7-C8
Nitisol	918	0.04 ± 0.01	0.04 ± 0.01	nd	0.06 ± 0.01	0.01 ± 0.001	1.20 ± 1.18	Monohydro-CLD-OH, B2, B3-B4
Nitisol	920	0.05 ± 0.01	0.04 ± 0.01	nd	0.04 ± 0.01	nd	0.01 ± 0.002	B2, B3-B4
Ferralsol	919	0.08 ± 0.01	0.07 ± 0.01	nd	0.04 ± 0.01	0.02 ± 0.01	0.01 ± 0.002	B3-B4
Ferralsol	921	0.03 ± 0.01	0.03 ± 0.01	nd	0.17 ± 0.13	nd	nd	A9, B3-B4
Ashes and pumice stone	922	0.03 ± 0.01	0.05 ± 0.01	nd	0.04 ± 0.01	nd	nd	
Ashes and pumice stone	923	0.03 ± 0.01	0.03 ± 0.01	nd	0.12 ± 0.07	0.04 ± 0.02	0.30 ± 0.29	A9, B2, B3-B4
Nitisol Bed	926	nd	nd	nd	nd	nd	nd	B3-B4
Bed	927	nd	nd	nd	0.02 ± 0.01	nd	nd	B3-B4
sediments								
Bed	928	nd	nd	nd	0.02 ± 0.01	nd	nd	
sediments								
River water*	929	1.02 ± 0.35	nd	nd	1.81 ± 0.32	nd	nd	A6, A9, B2, B3-B4, E1-E2
River water*	930	0.44 ± 0.15	nd	nd	0.12 ± 0.02	0.04 ± 0.01	nd	B2, B3-B4
Mangrove water*	931	0.22 ± 0.20	nd	nd	0.13 ± 0.03	nd	nd	B3-B4
Mangrove water*	932	nd	nd	nd	0.14 ± 0.03	nd	nd	B3-B4

**Table S7.** Estimation of chlordecone TP concentration in environmental samples from Martinique. Other chlordecone nd means “not detected”. \*means that results are reported in µg/L otherwise they are in mg/kg

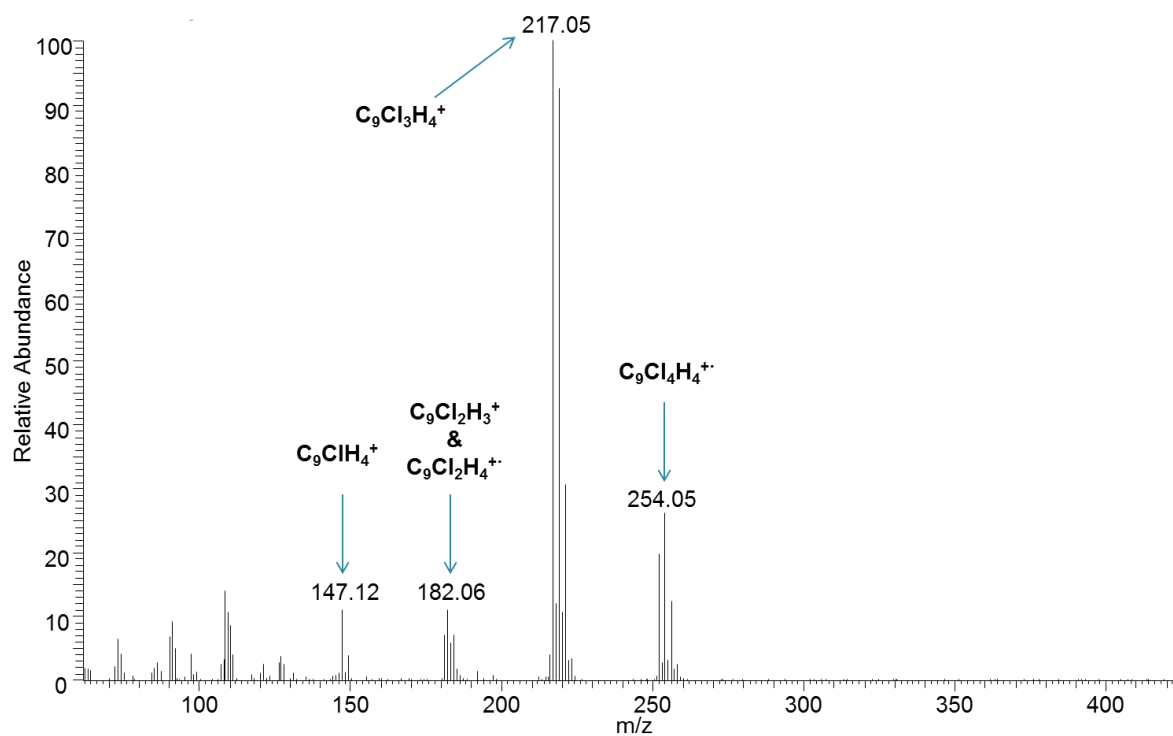
## S4 Supporting Mass Spectra



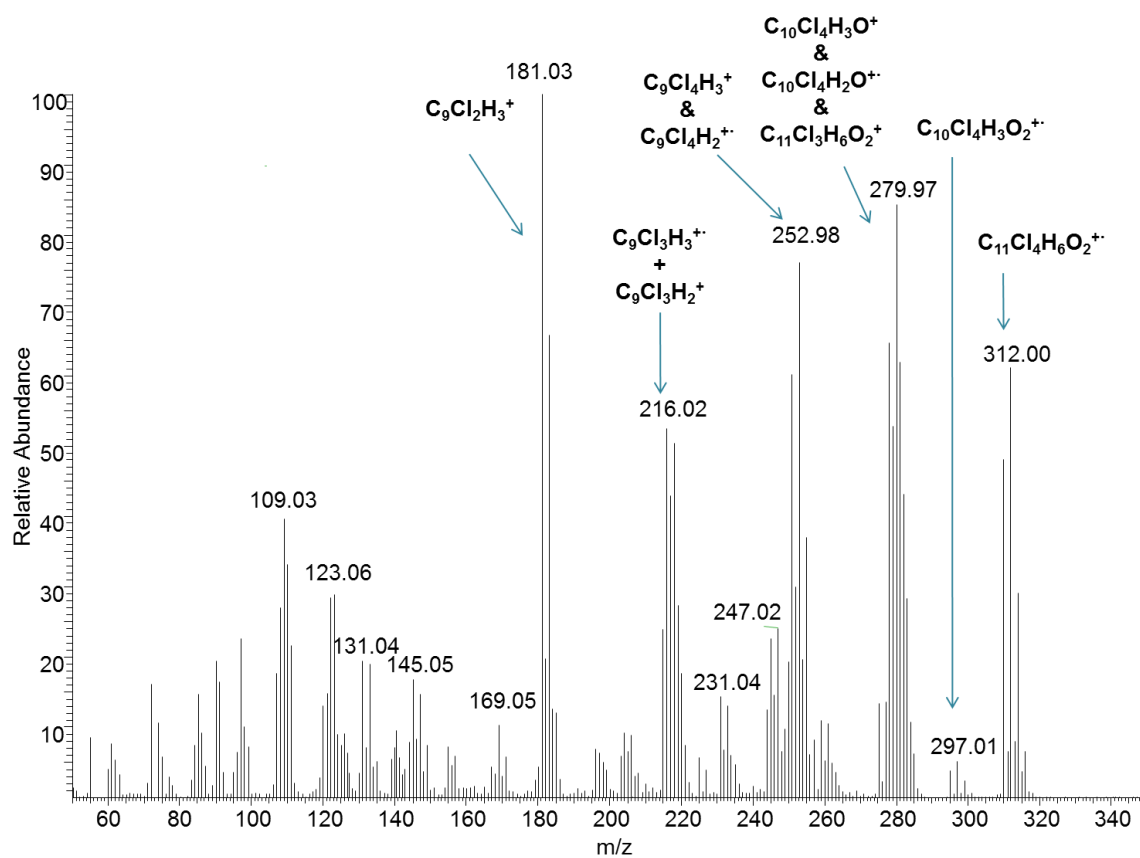
**Figure S16.** Mass spectrum analysis of A1 by GC-MS



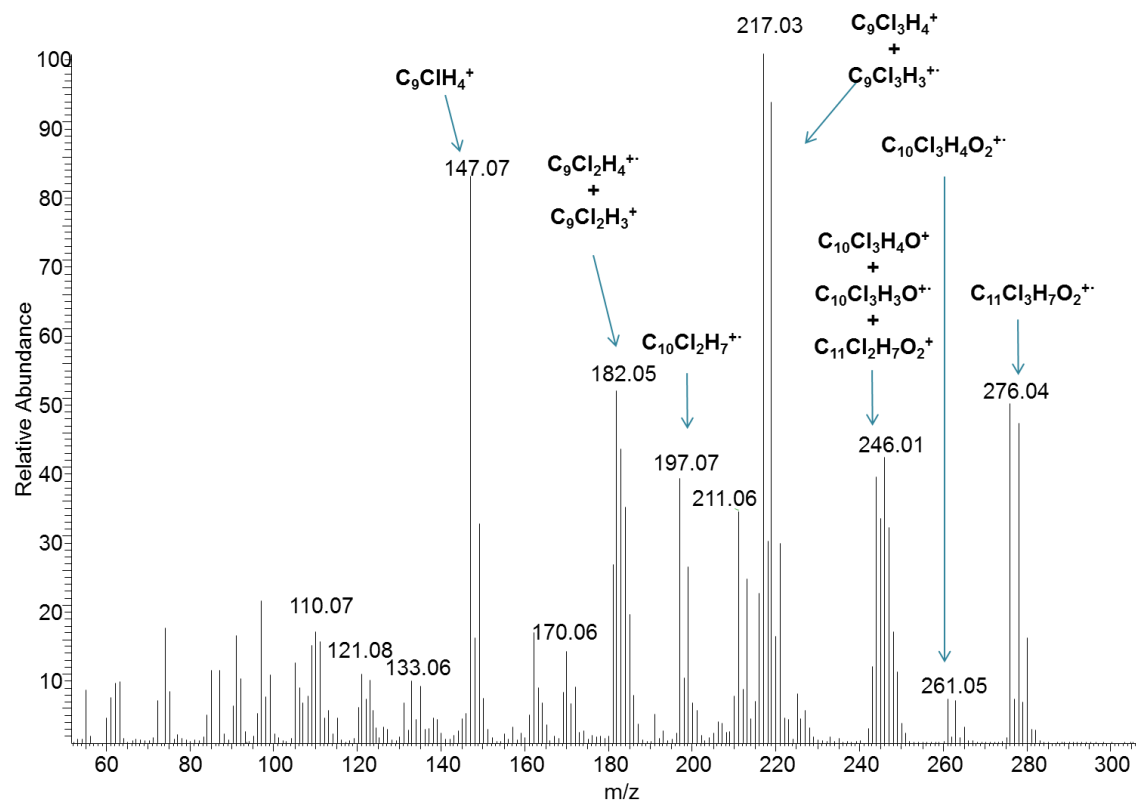
**Figure S17.** Mass spectrum analysis of B1 by GC-MS



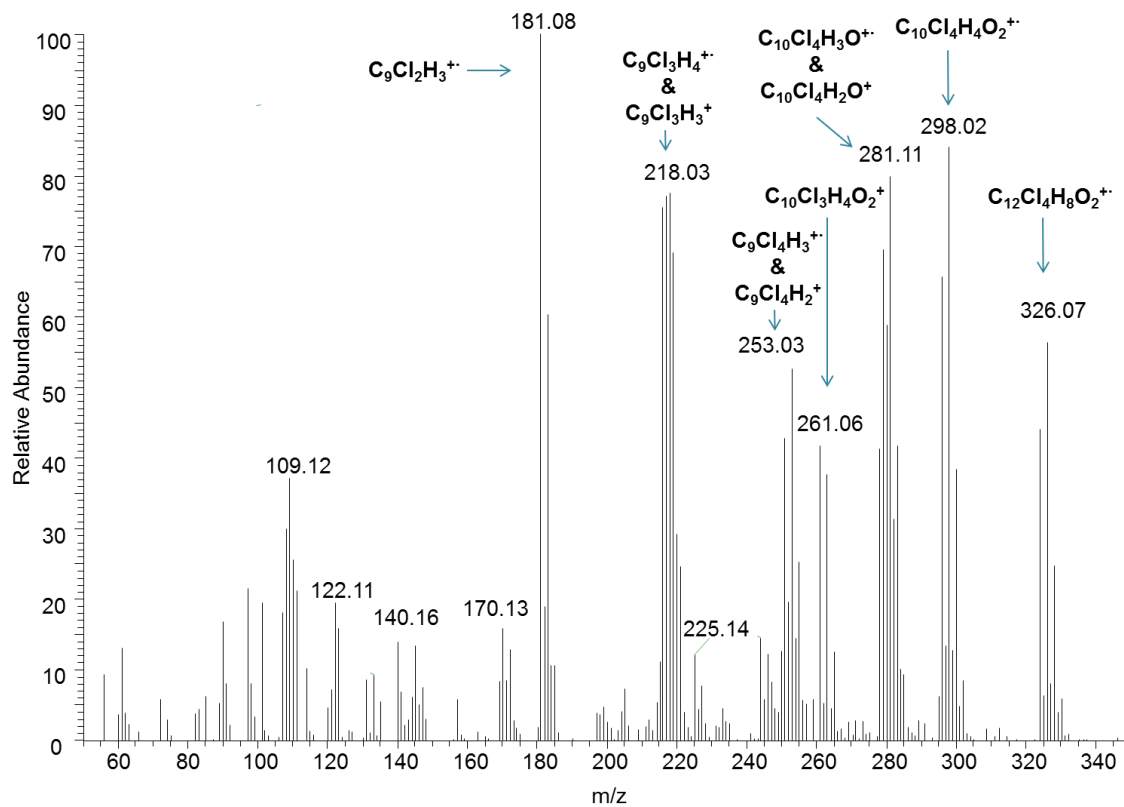
**Figure S18.** Mass spectrum analysis of B2 and B3-B4 by GC-MS



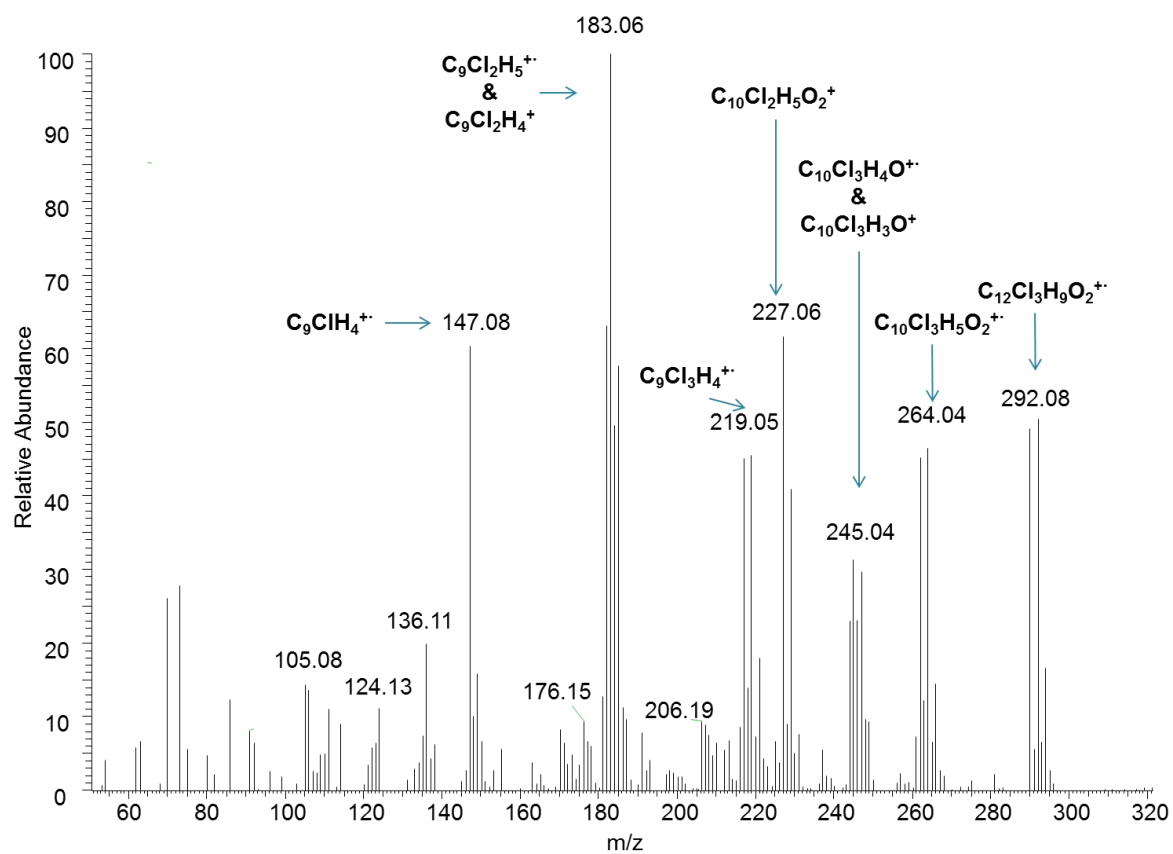
**Figure S19.** Mass spectrum analysis of D1-D2 by GC-MS



**Figure S20.** Mass spectrum analysis of D3-D4 by GC-MS

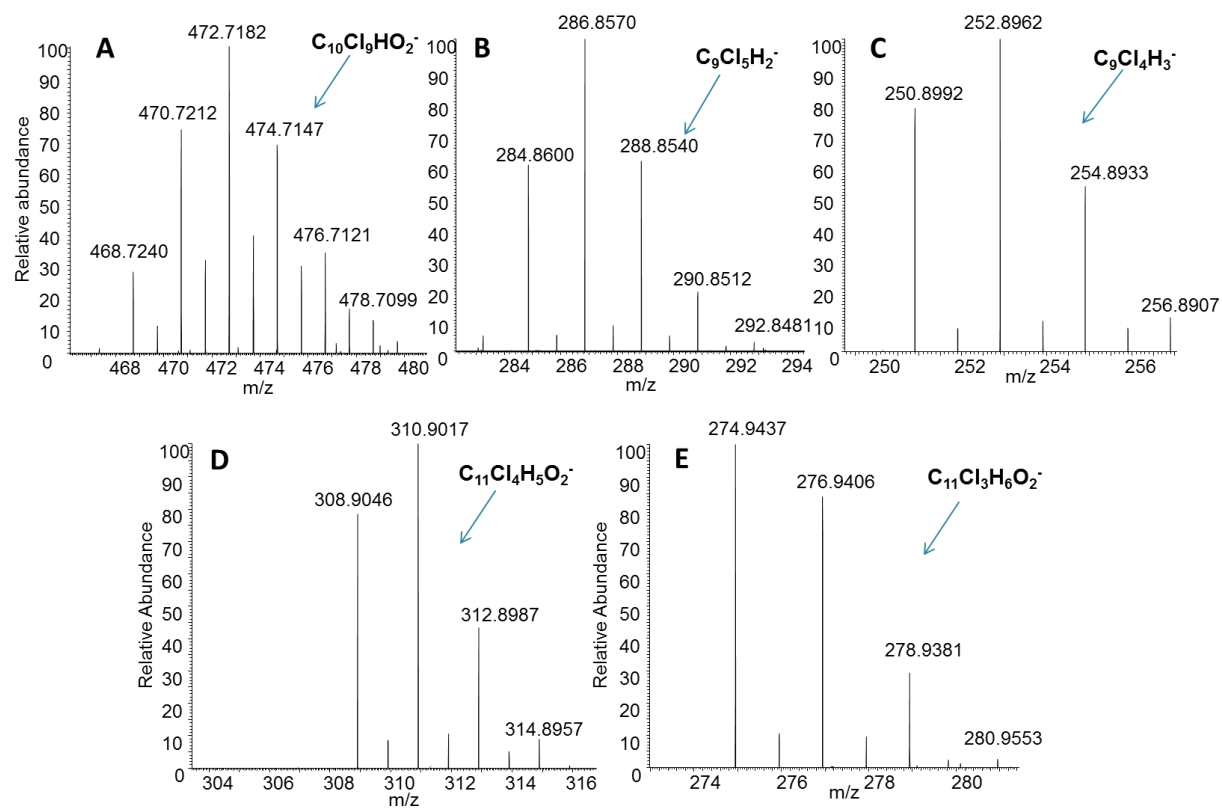


**Figure S21.** Mass spectrum analysis of E1-E2 by GC-MS

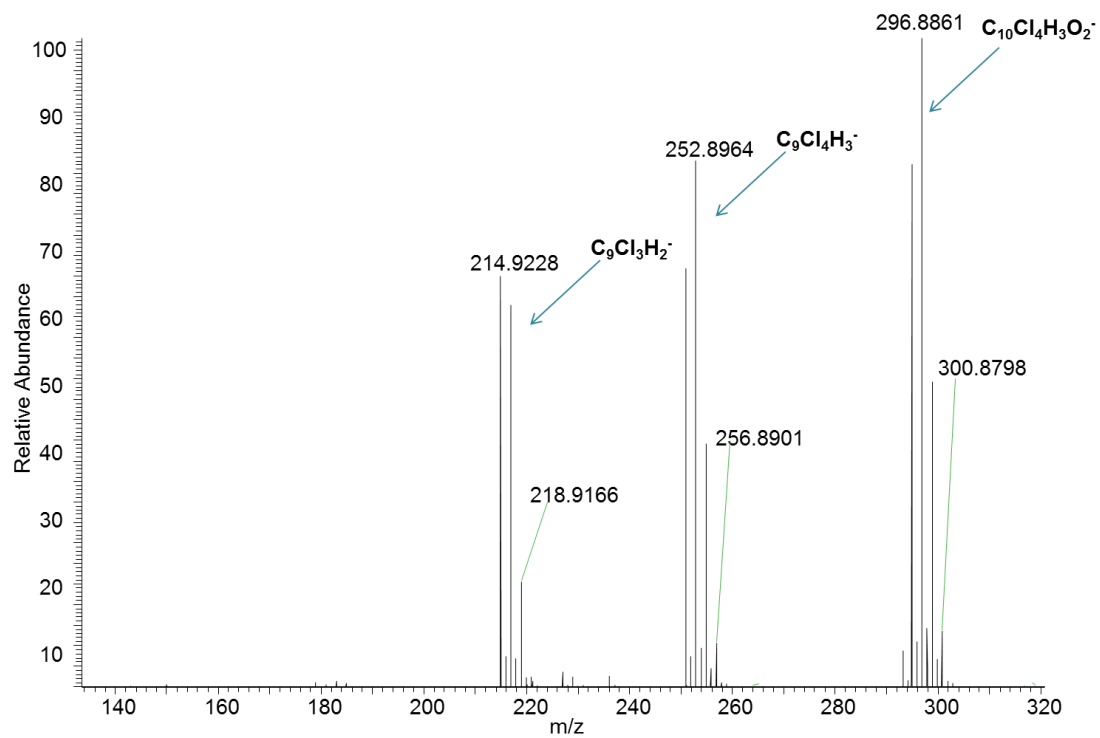


**Figure S22.** Mass spectrum analysis of E3-E4 by GC-MS

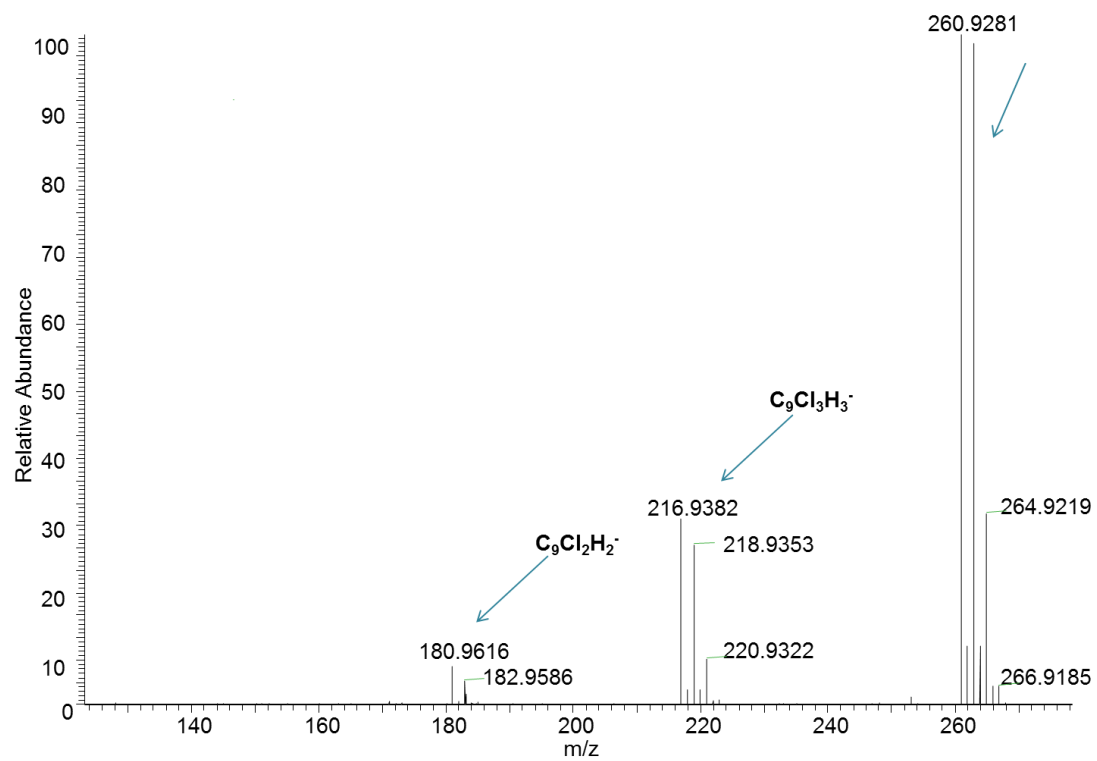




**Figure S23.** Mass spectra analysis of (A) A1, (B) B1, (C) B2 and B3-B4, (D) D1-D2 and (E) D3-D4 by LC-MS Orbitrap (negative mode)

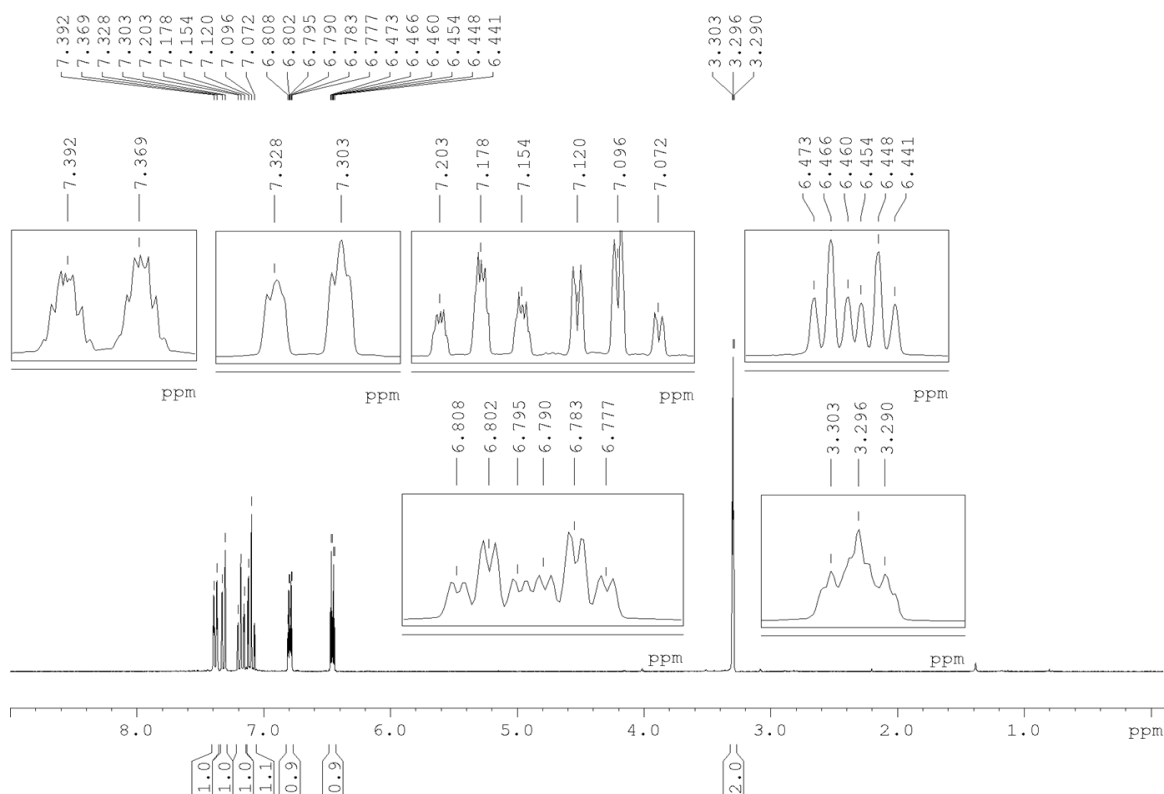


**Figure S24.** Mass spectrum analysis of C1-C2 by LC-MS Orbitrap (negative mode)

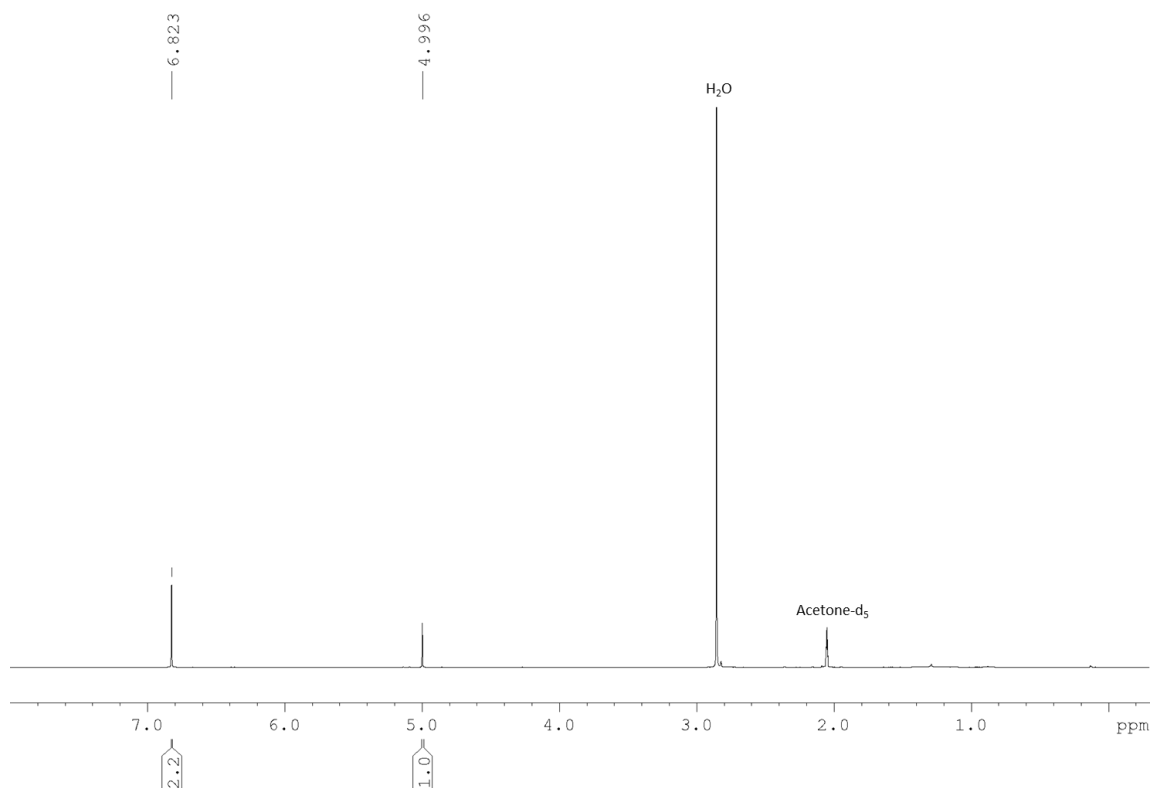


**Figure S25.** Mass spectrum analysis of C3-C4 by LC-MS Orbitrap (negative mode)

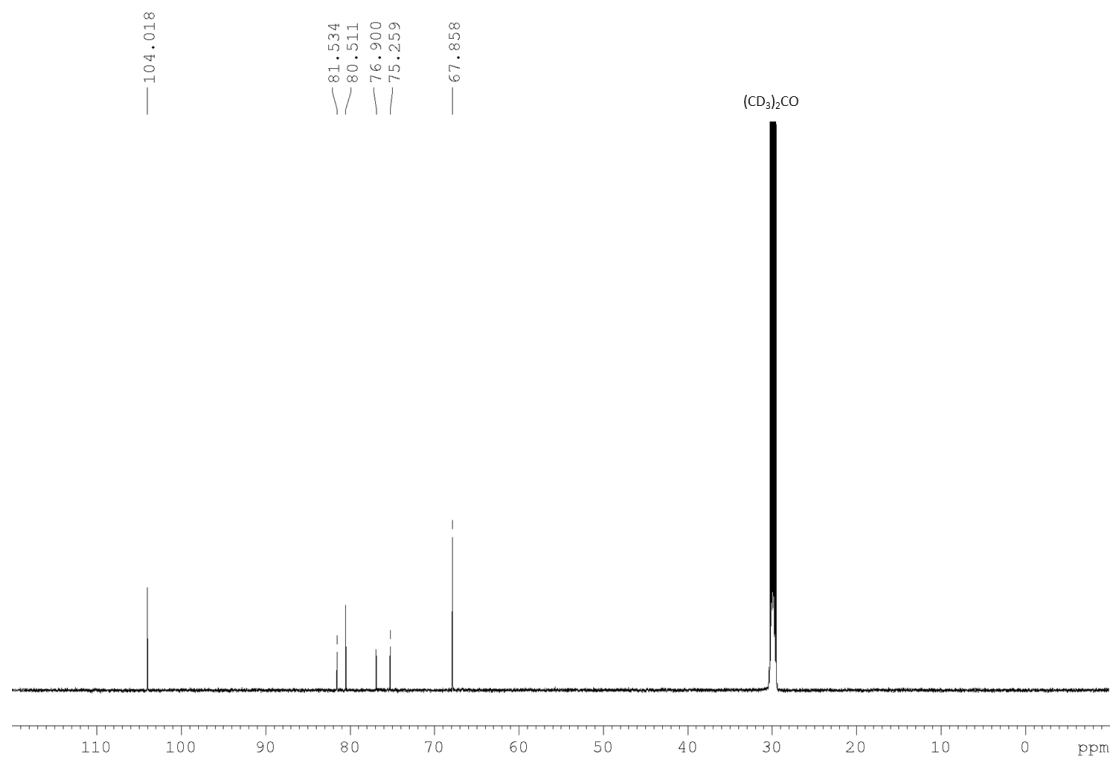
## S5 Supporting NMR Spectra



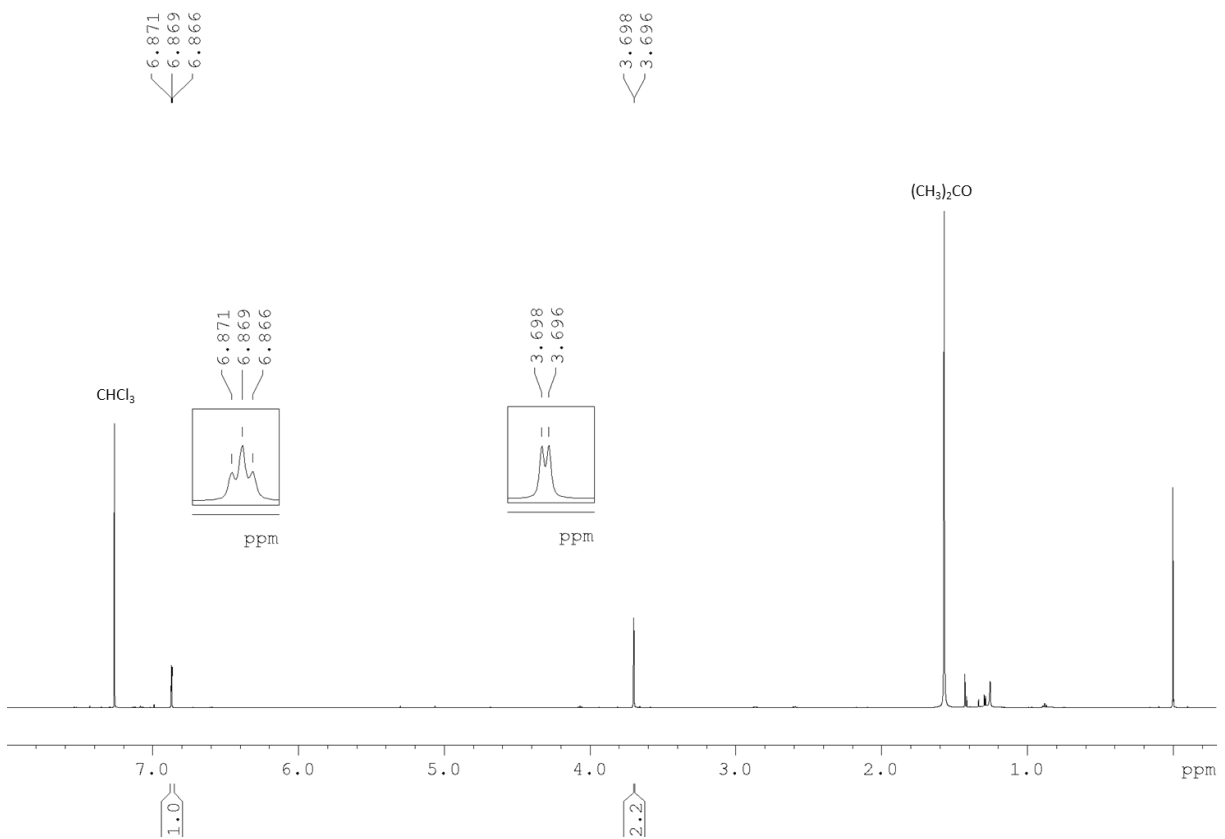
**Figure S26.**  $^1\text{H}$ -NMR spectrum of indene in  $\text{CDCl}_3$  (300 MHz)



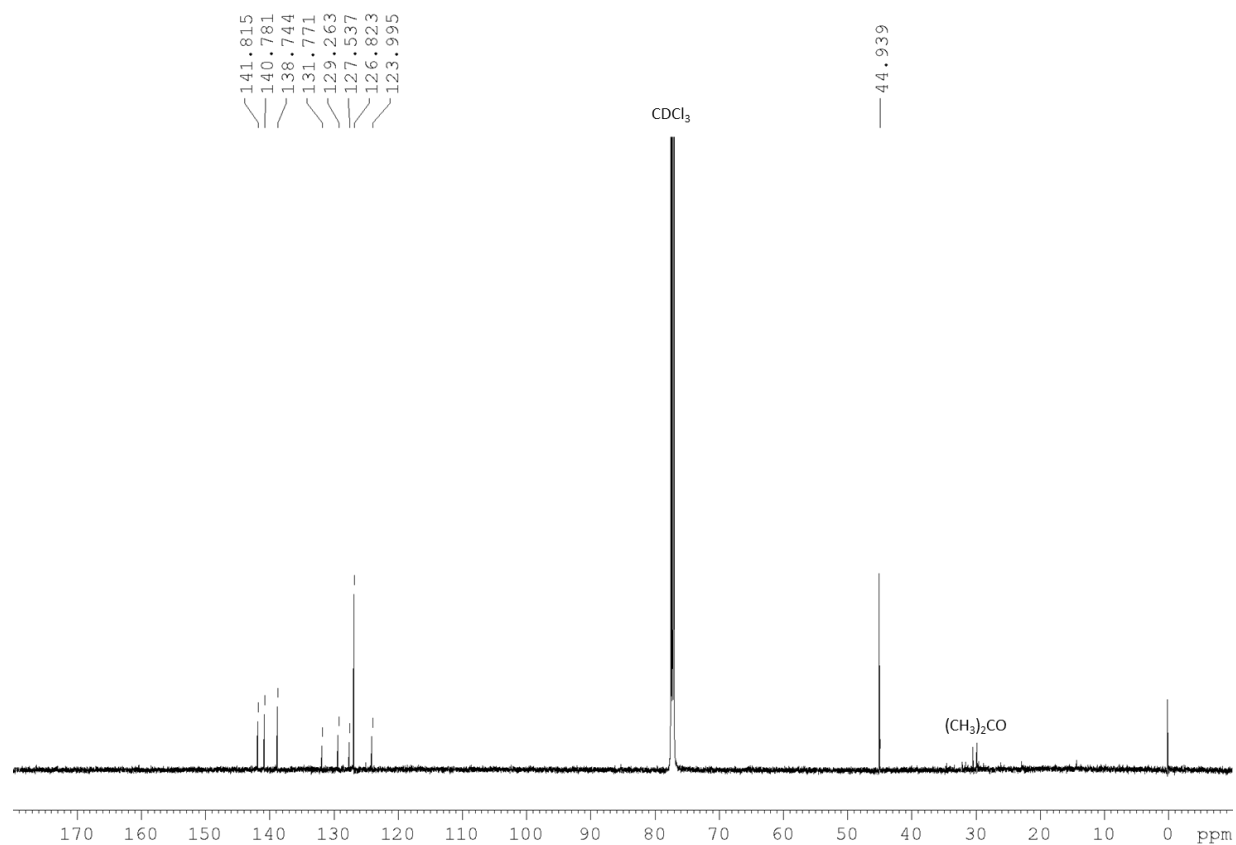
**Figure S27.**  $^1\text{H}$ -NMR spectrum of A1 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz).  $^1\text{H}$  NMR (600 MHz;  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  6.85 (s, 2 H,  $\text{C}_5\text{-(OH)}_2$ ), 5.00 (s, 1 H,  $\text{C}_{10}\text{-H}$ ).  $[\text{M-H}]^-$  calcd. for  $\text{C}_{10}\text{Cl}_9\text{O}_2\text{H}_2$ , 468.7246; found, 468.7242. TLC:  $R_f$  (hexane : acetone 3/1) = 0.32



**Figure S28.**  $^{13}\text{C}$ -NMR spectrum of A1 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz).  $^{13}\text{C}$  NMR (150 MHz;  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  103.0 ( $\text{C}_5$ ), 81.5 ( $\text{C}_{4-6}$ ), 80.5 ( $\text{C}_{1-9}$ ), 76.9 ( $\text{C}_{7-8}$ ), 75.2 ( $\text{C}_{2-3}$ ), 67.8 ( $\text{C}_{10}$ ).

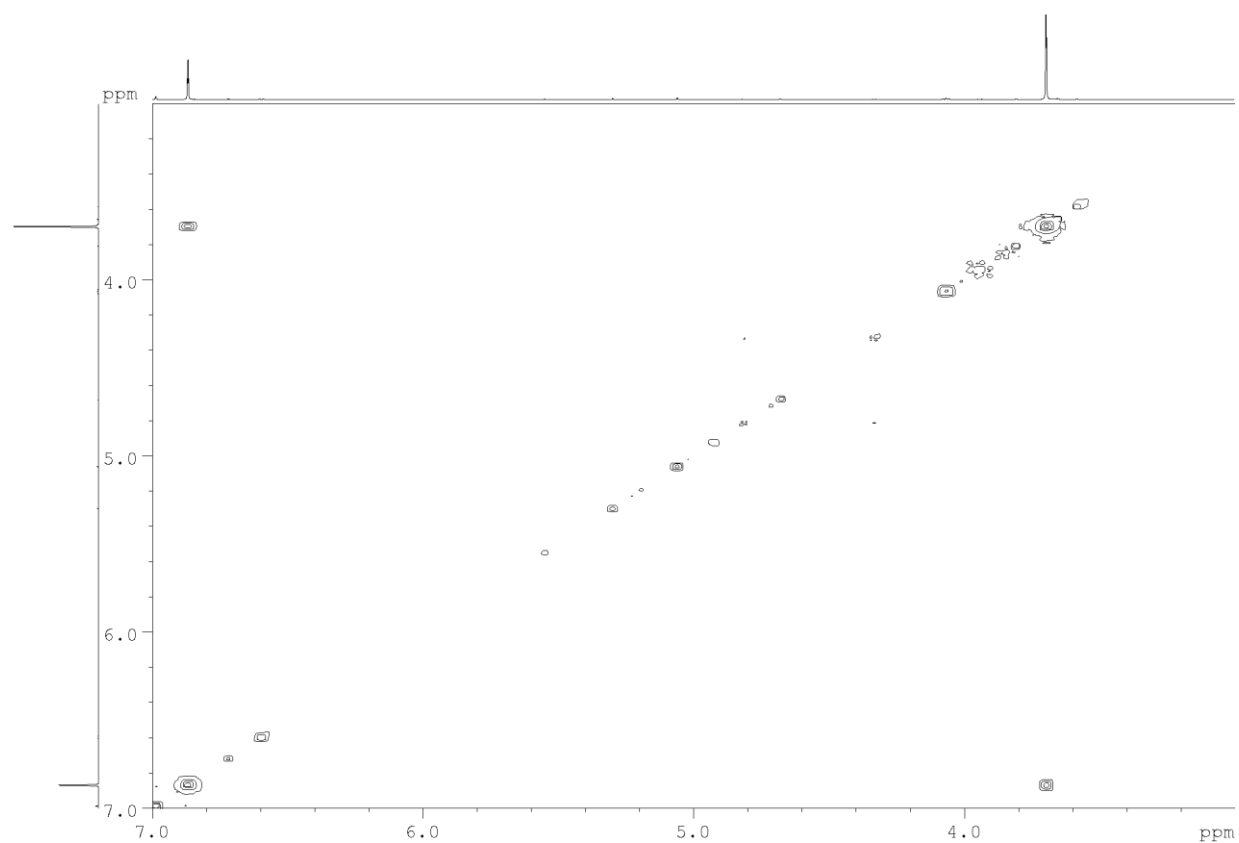


**Figure S29.**  $^1\text{H}$ -NMR spectrum of B1 in  $\text{CDCl}_3$  (600 MHz)

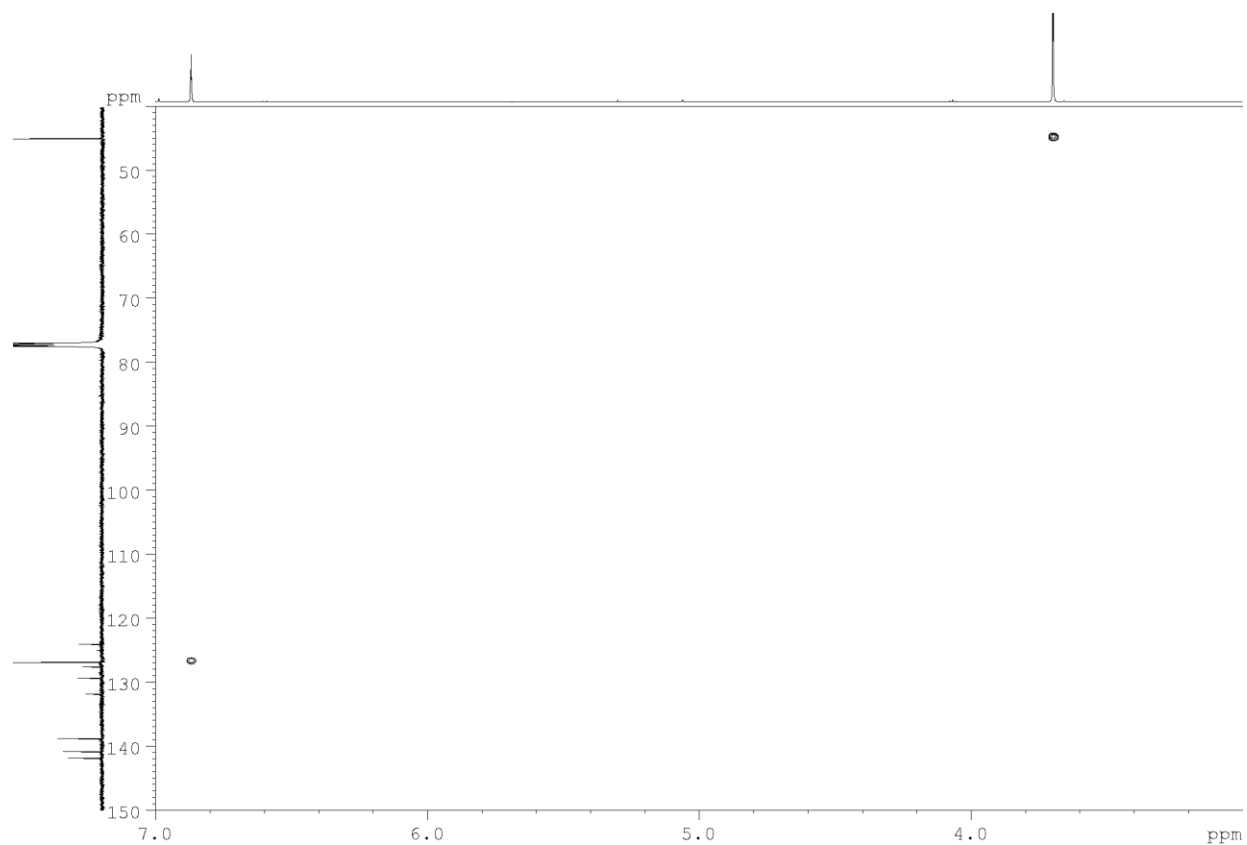


**Figure S30.** <sup>13</sup>C-NMR spectrum of B1 in CDCl<sub>3</sub> (600 MHz)

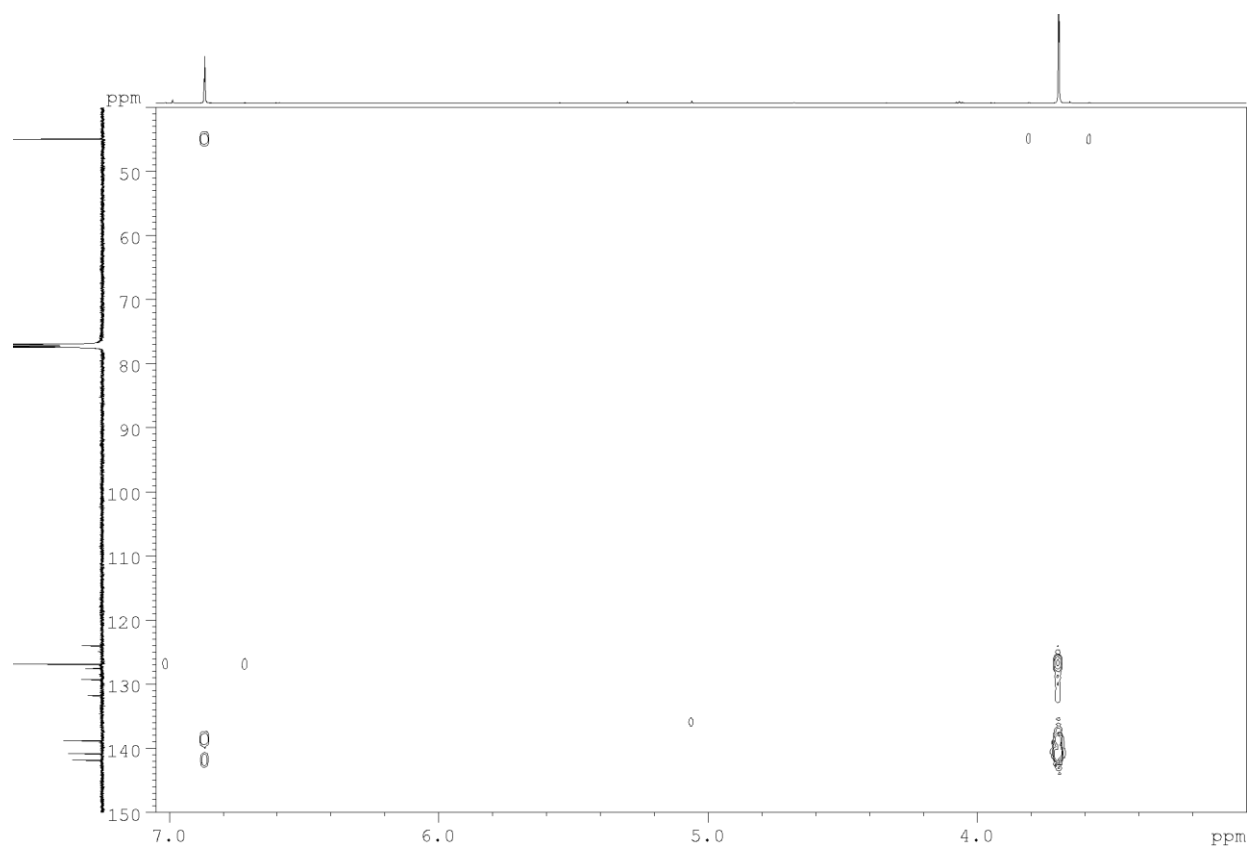




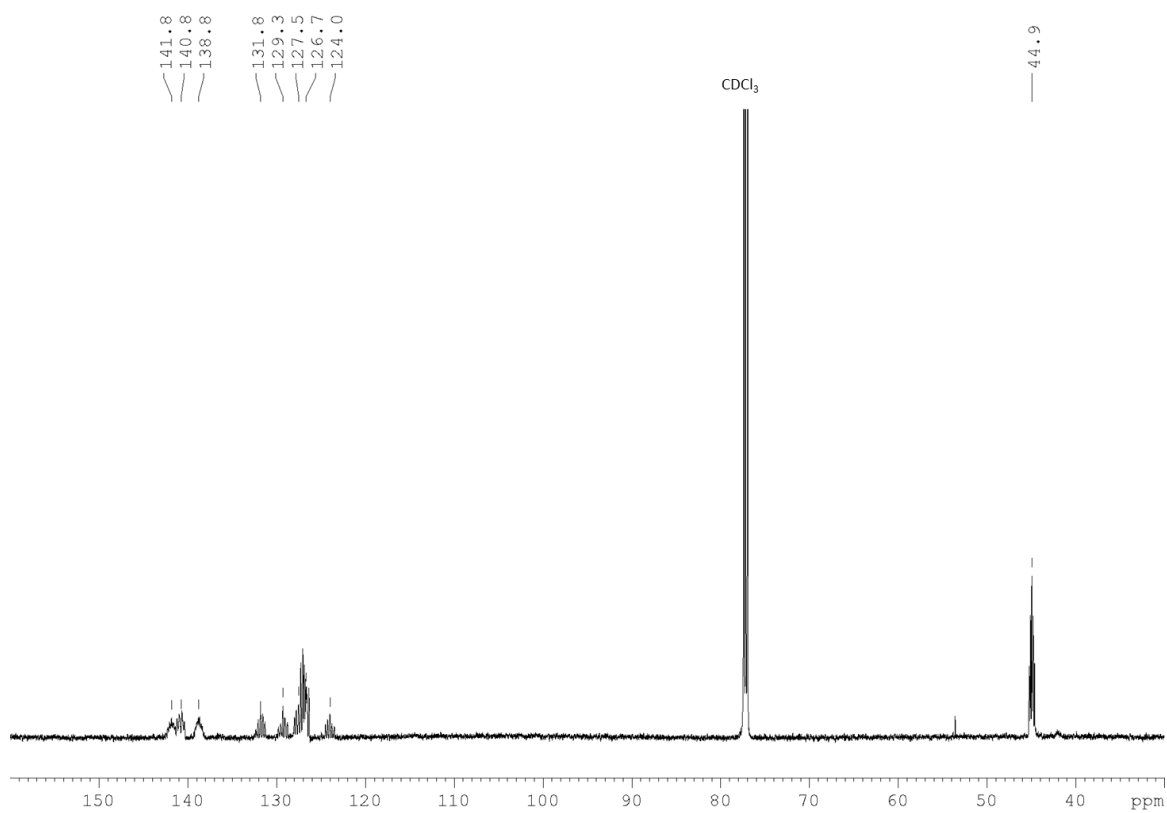
**Figure S31.** COSY spectrum of B1 in  $\text{CDCl}_3$  (600 MHz)



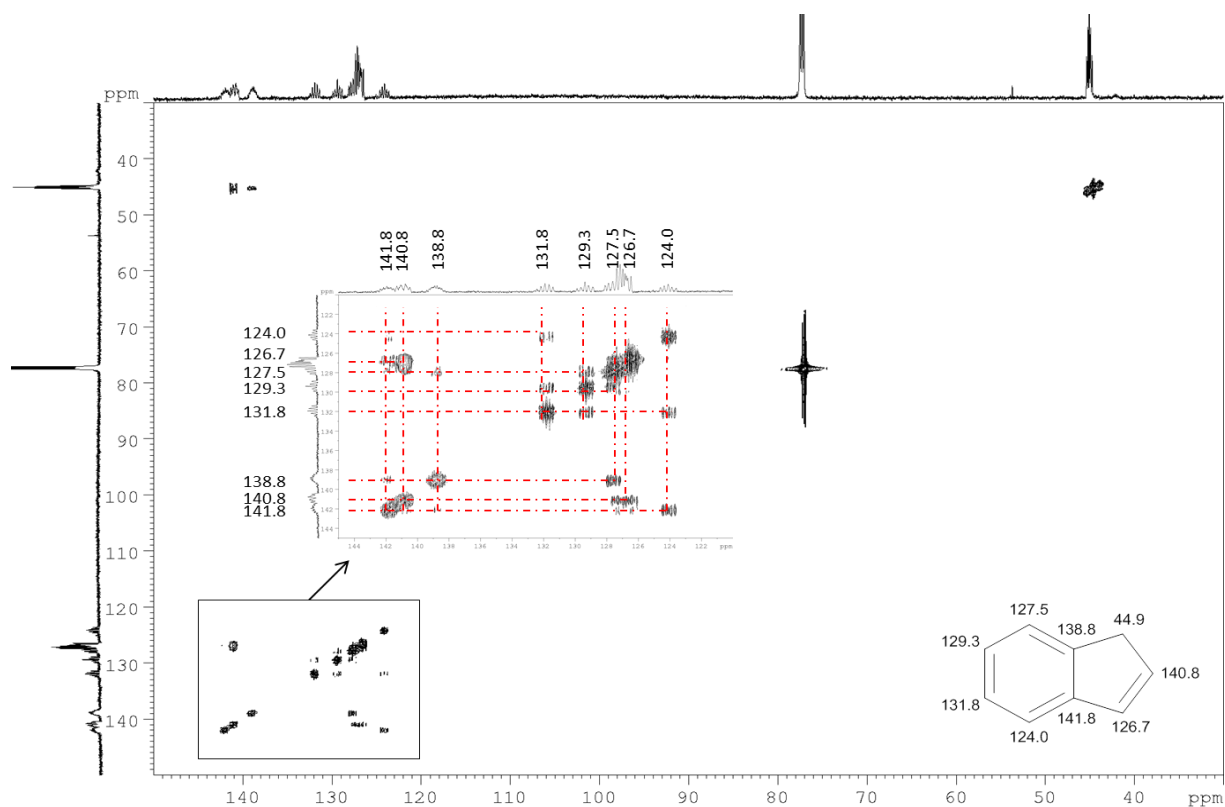
**Figure S32.** HSQC spectrum of B1 in CDCl<sub>3</sub> (600 MHz)



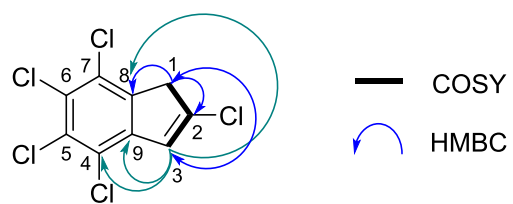
**Figure S33.** HMBC spectrum of B1 in CDCl<sub>3</sub> (600 MHz)



**Figure S34.**  $^{13}\text{C}$ -NMR spectrum of  $^{13}\text{C}$ -B1 in  $\text{CDCl}_3$  (600 MHz)

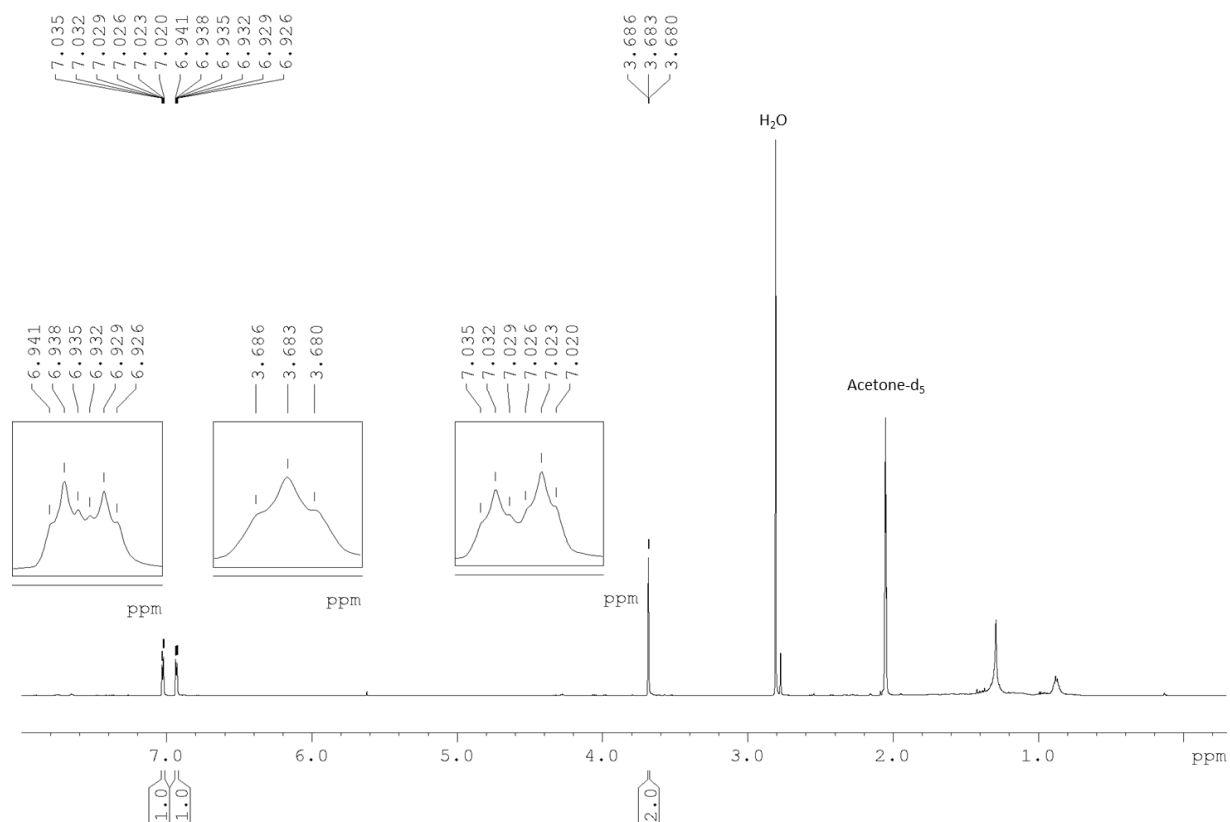


**Figure S35.**  $^{13}\text{C}$ - $^{13}\text{C}$  COSY spectrum of  $^{13}\text{C}$ -B1 in  $\text{CDCl}_3$  (800 MHz).  $^{13}\text{C}$  NMR (150 MHz;  $\text{CDCl}_3$ ):  $\delta$  141.9 ( $\text{C}_9$ ), 140.9 ( $\text{C}_2$ ), 138.8 ( $\text{C}_8$ ), 131.9 ( $\text{C}_5$ ), 129.4 ( $\text{C}_6$ ), 127.6 ( $\text{C}_7$ ), 127.0 ( $\text{C}_3$ ), 124.1 ( $\text{C}_4$ ), 45.0 ( $\text{C}_1$ ). HRMS ( $m/z$ ):  $[\text{M}-\text{H}]^-$  calcd. for  $\text{C}_2[^{13}]\text{C}_7\text{Cl}_5\text{H}_2$ , 291.8828; found, 291.8838.

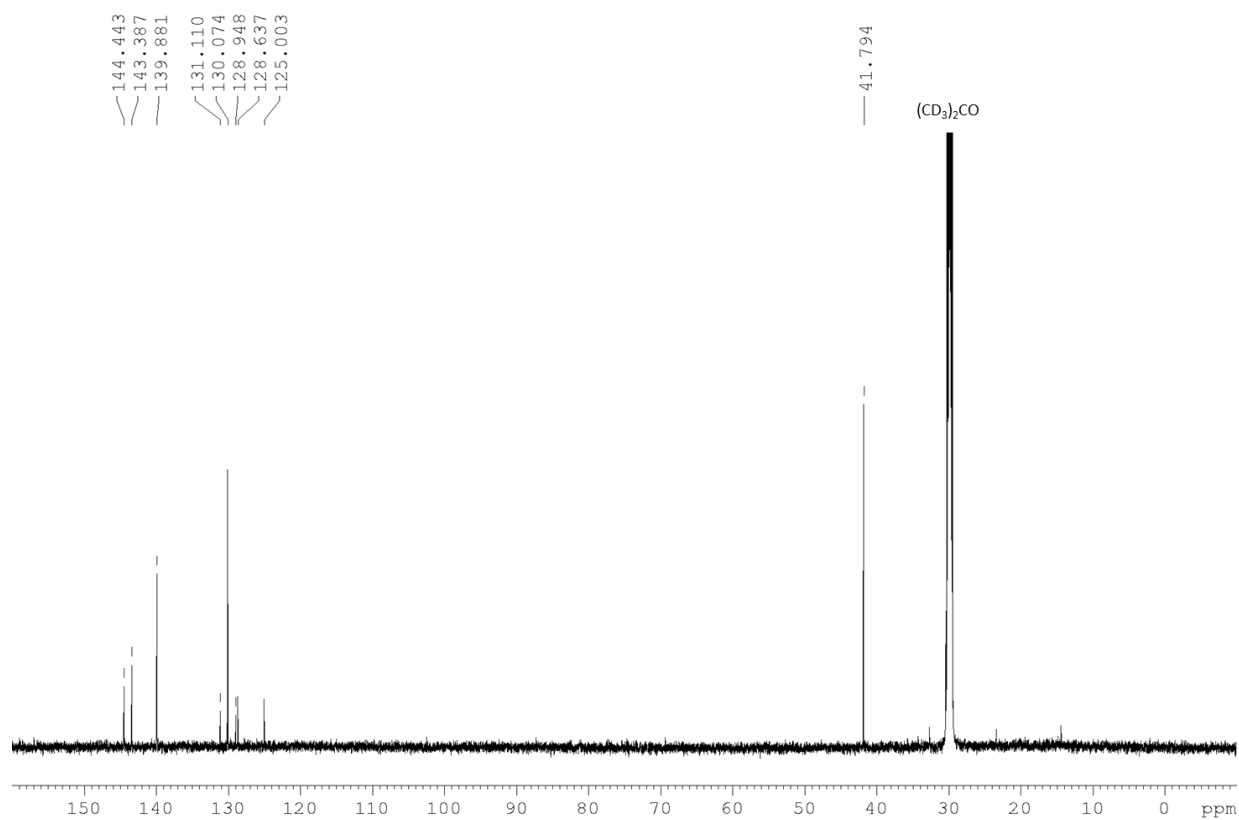


#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	<i>J</i> Coupling (Hz)	Protons	HMBC	COSY
1	44.9	CH <sub>2</sub>	3.70	d, 1.4	2H	C2, C3, C8	H-3
2	140.8						
3	126.8	CH	6.87	t, 1.4	1H	C1, C4, C8, C9	H-1
4	124.0						
5	131.8						
6	129.8						
7	127.5						
8	138.7						
9	141.8						

**Table S8.** NMR data assignment of B1 in CDCl<sub>3</sub>. HRMS (m/z): [M-H]<sup>-</sup> calcd. for C<sub>9</sub>Cl<sub>5</sub>H<sub>2</sub>, 284.8594; found, 284.860. TLC: R<sub>f</sub> (cyclohexane : ethyl acetate 9/1) = 0.78

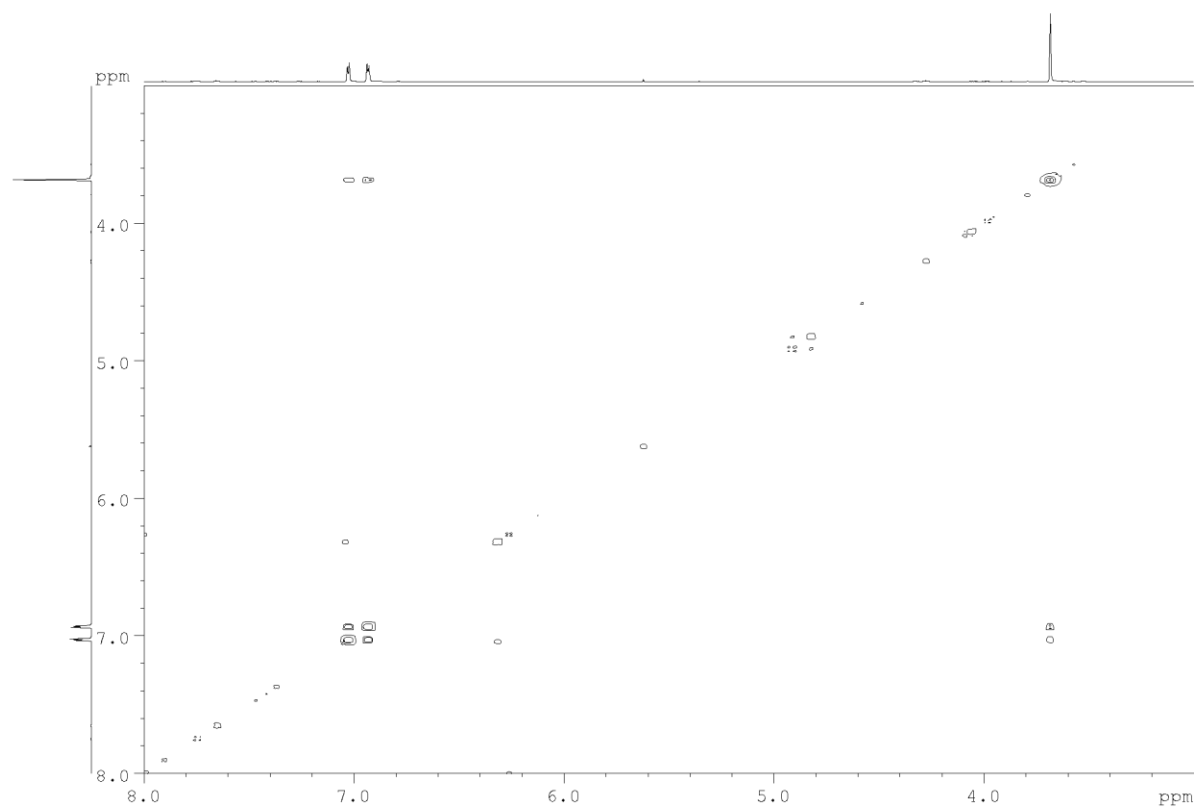


**Figure S36.**  $^1\text{H}$ -NMR spectrum of B2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)

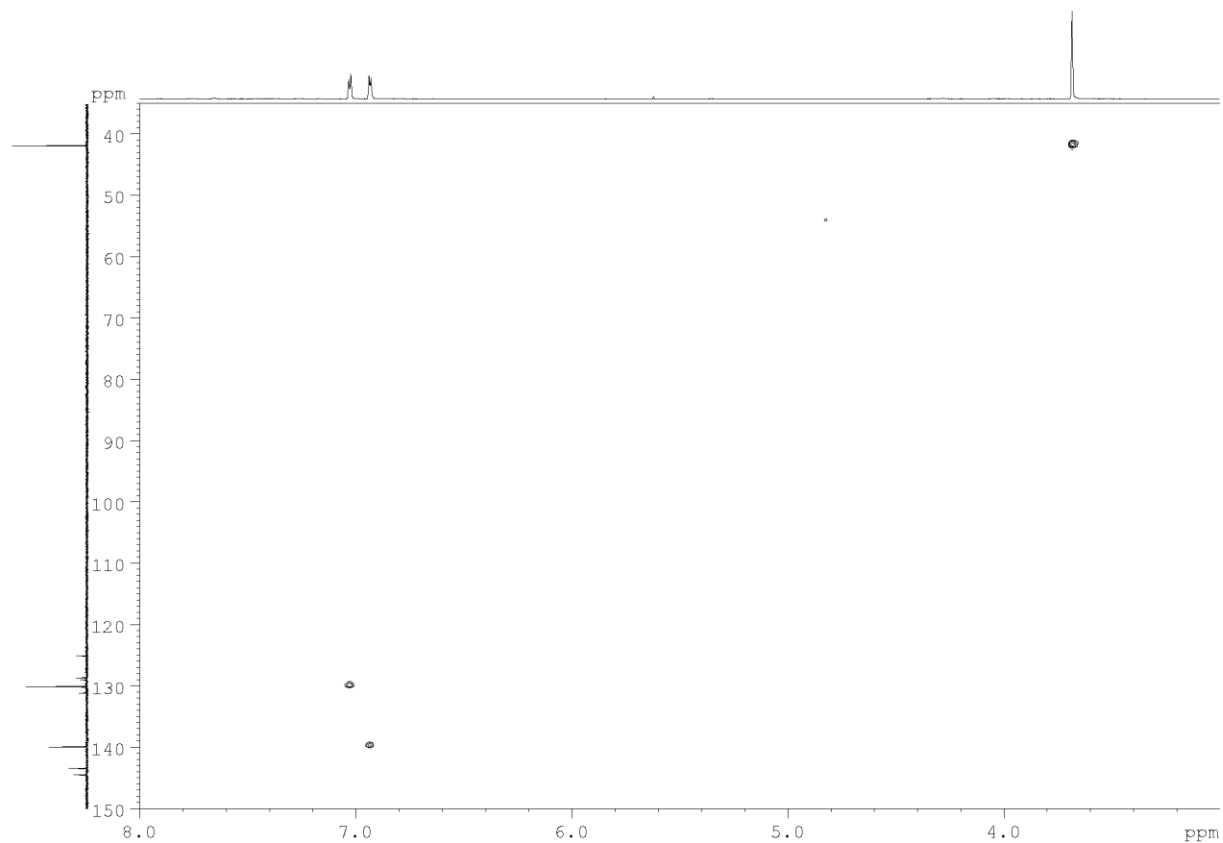


**Figure S37.** <sup>13</sup>C-NMR spectrum of B2 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)

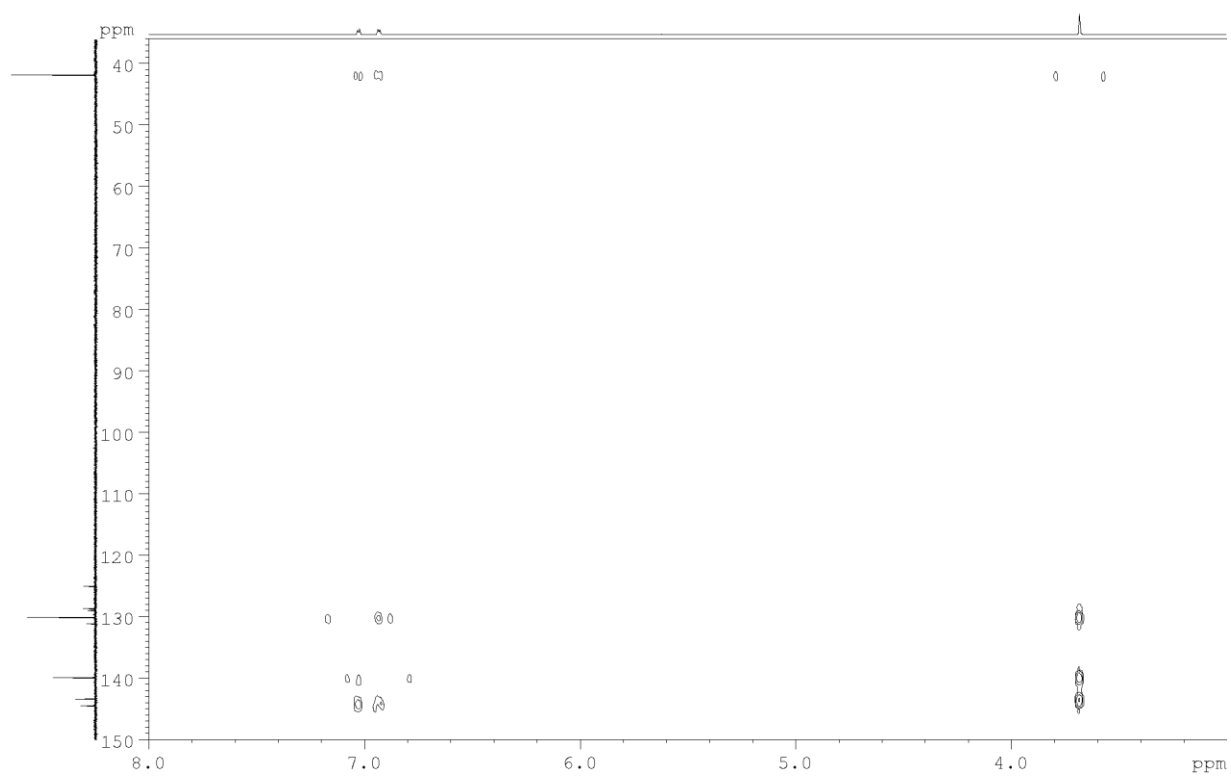




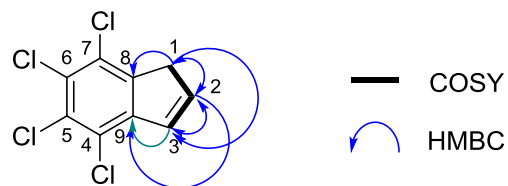
**Figure S38.** COSY spectrum of B2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



**Figure S39.** HSQC spectrum of B2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)

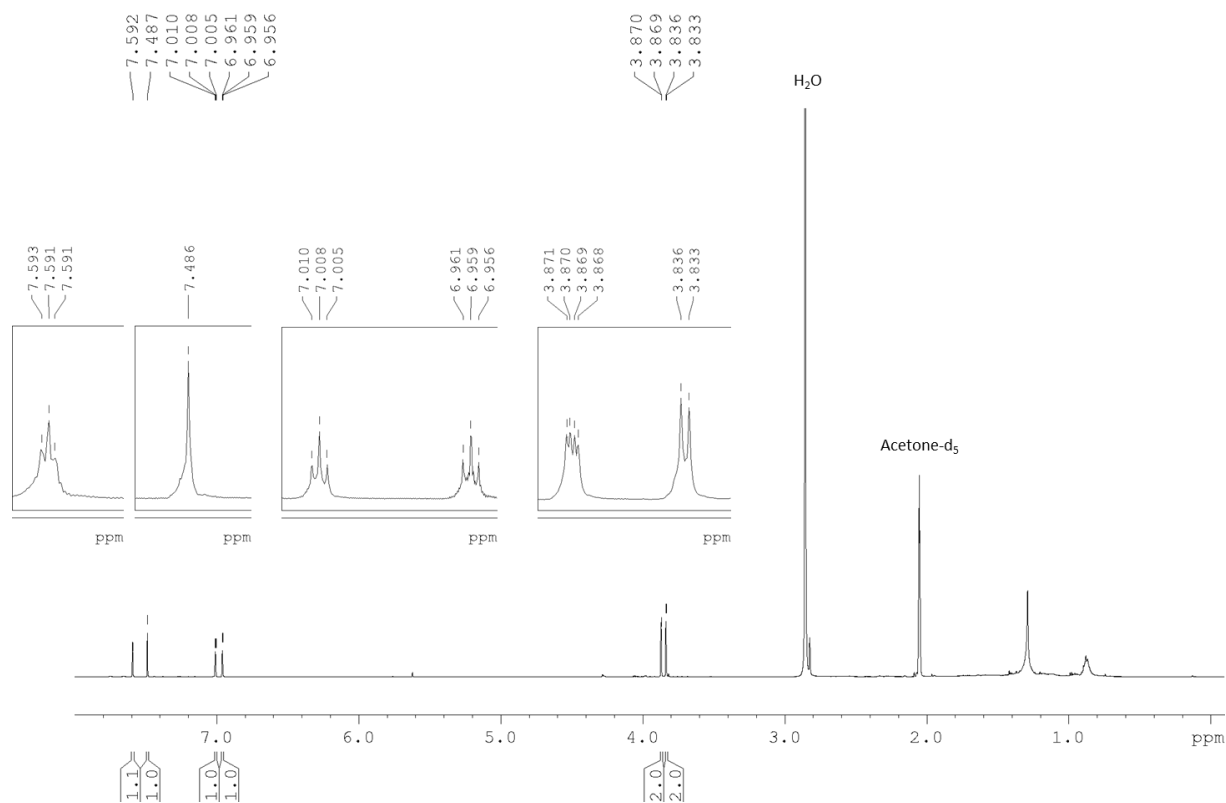


**Figure S40.** HMBC spectrum of B2 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)

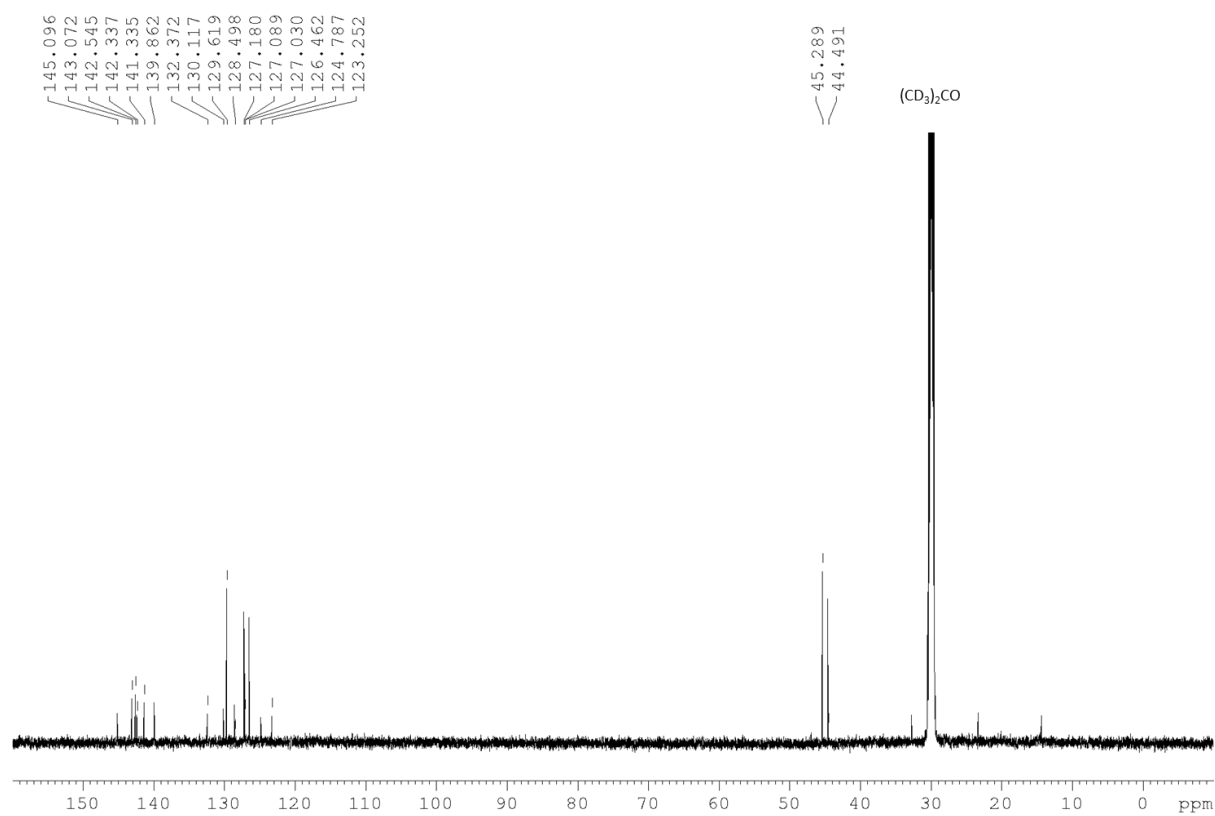


#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	$J$ Coupling (Hz)	Protons	HMBC	COSY
1	41.8	CH <sub>2</sub>	3.68	t, 1.9	2H	C2, C3, C8	H-2, H-3
2	139.9	CH	6.93	dt, 5.5, 1.9	1H	C1, C3, C9	H-1
3	130.1	CH	7.03	dt, 5.5, 1.7	1H	C1, C2, C9	H-1
4	125.0						
5	131.1						
6	128.9						
7	128.6						
8	143.4						
9	144.4						

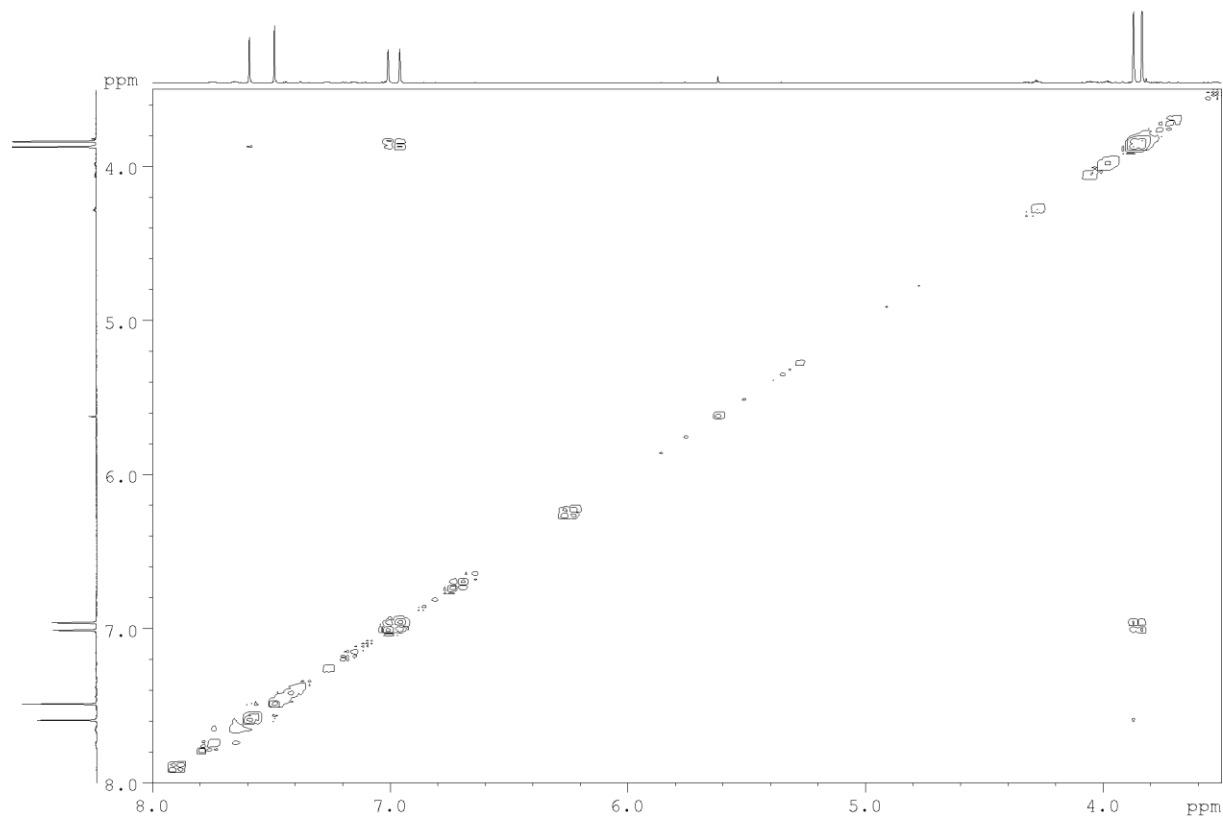
**Table S9.** NMR data assignment of B2 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}-\text{H}]^-$  calcd. for  $\text{C}_9\text{Cl}_4\text{H}_3$ , 250.8983; found, 250.8993. TLC:  $R_f$  (cyclohexane : ethyl acetate 9/1) = 0.68



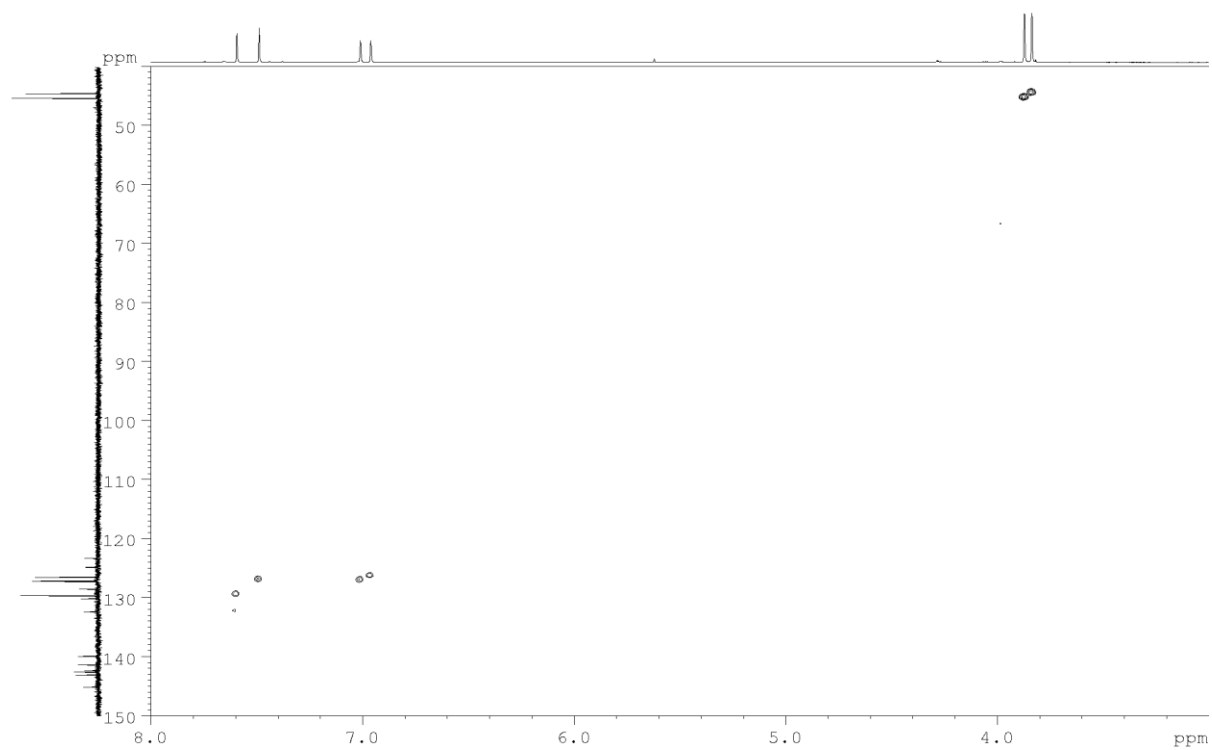
**Figure S41.**  $^1\text{H}$ -NMR spectrum of B3-B4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



**Figure S42.** <sup>13</sup>C-NMR spectrum of B3-B4 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)

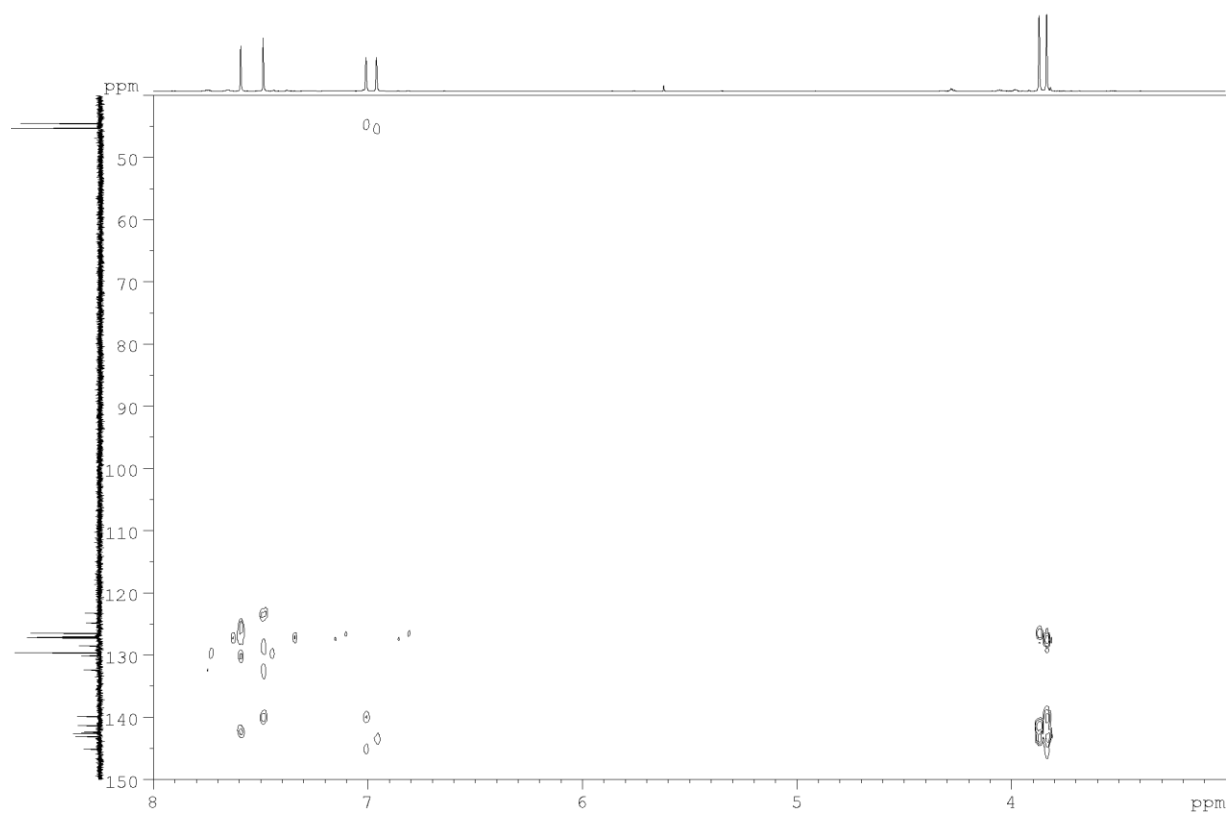


**Figure S43.** COSY spectrum of B3-B4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)

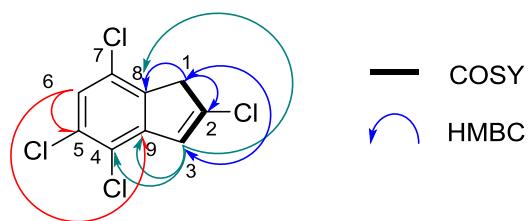


**Figure S44.** HSQC spectrum of B3-B4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)





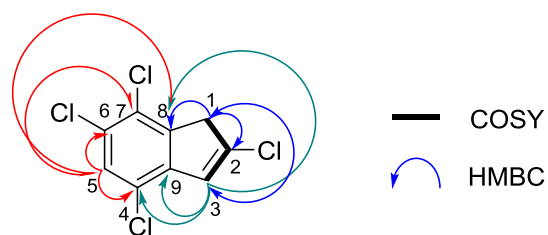
**Figure S45.** HMBC spectrum of B3-B4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	$J$ Coupling (Hz)	Protons	HMBC	COSY
1	45.3	CH <sub>2</sub>	3.87	dd, 1.3, 0.6		C2, C3, C8	H-3, H-6
2	143.1						
3	126.5	CH	6.96	t, 1.4		C1, C4, C8, C9	H-1
4	124.8						
5*	130.1						
6*	129.6	CH	7.59	t, 0.6		C5, C9	H-1
7*	127.0						
8	141.3						
9	142.3						

**Table S10.** NMR data assignment of B3 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}-\text{H}]^-$  calcd. for  $\text{C}_9\text{Cl}_4\text{H}_3$ , 250.8983; found, 250.8993. TLC:  $R_f$  (cyclohexane : ethyl acetate 9/1) = 0.88

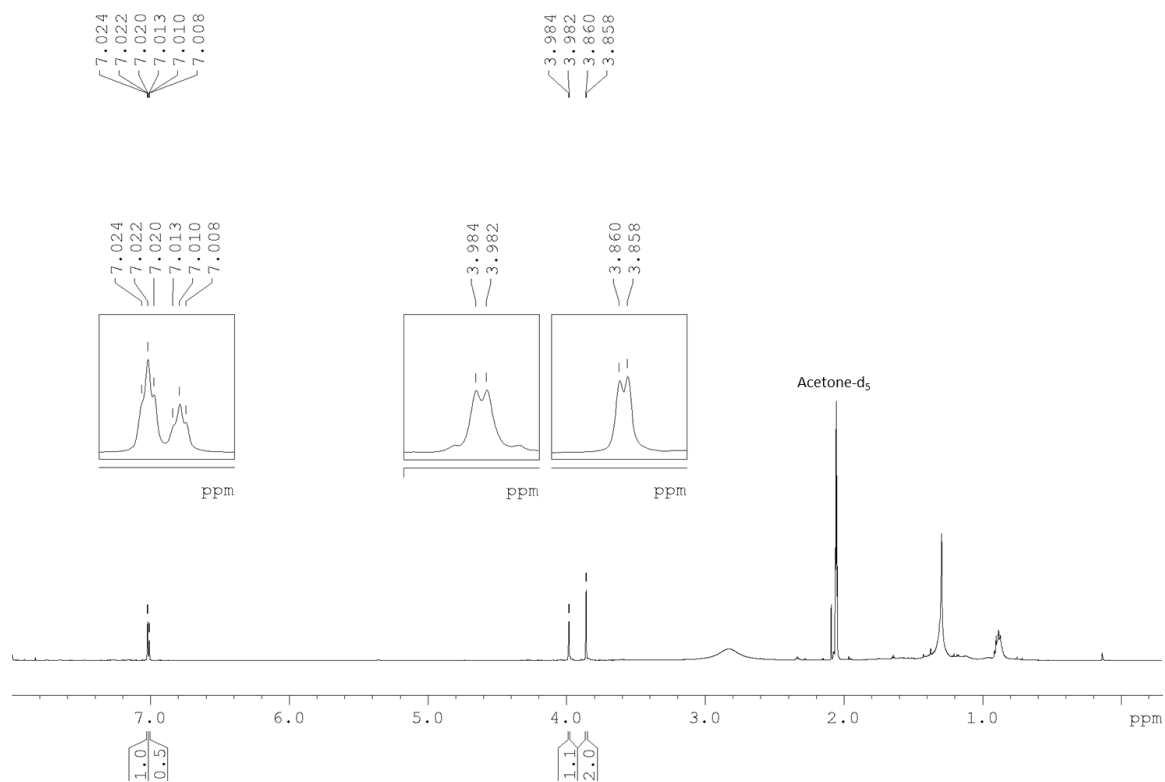
\* means that carbon position is assumed but not confirmed



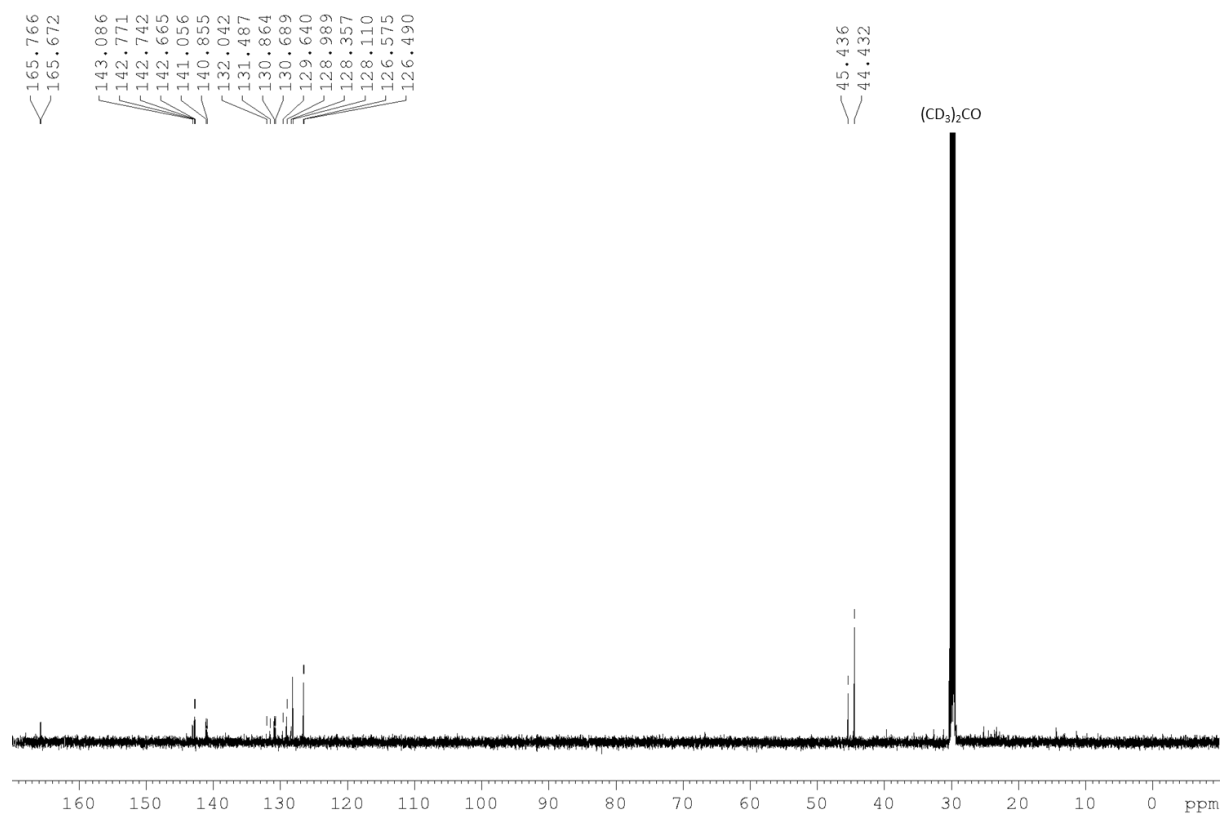
#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	$J$ Coupling (Hz)	Protons	HMBC	COSY
1	44.5	CH <sub>2</sub>	3.83	d, 1.4	2H	C2, C3, C8	H-3, H-5
2	142.5						
3	127.2	CH	7.01	t, 1.5	1H	C1, C4, C8, C9	H-1
4	123.3						
5*	127.1	CH	7.49	s	1H	C4, C6, C7, C8	
6*	132.4						
7*	128.5						
8	139.9						
9	145.1						

**Table S11.** NMR data assignment of B4 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}-\text{H}]^-$  calcd. for  $\text{C}_9\text{Cl}_4\text{H}_3$ , 250.8983; found, 250.8993. TLC:  $R_f$  (cyclohexane : ethyl acetate 9/1) = 0.88

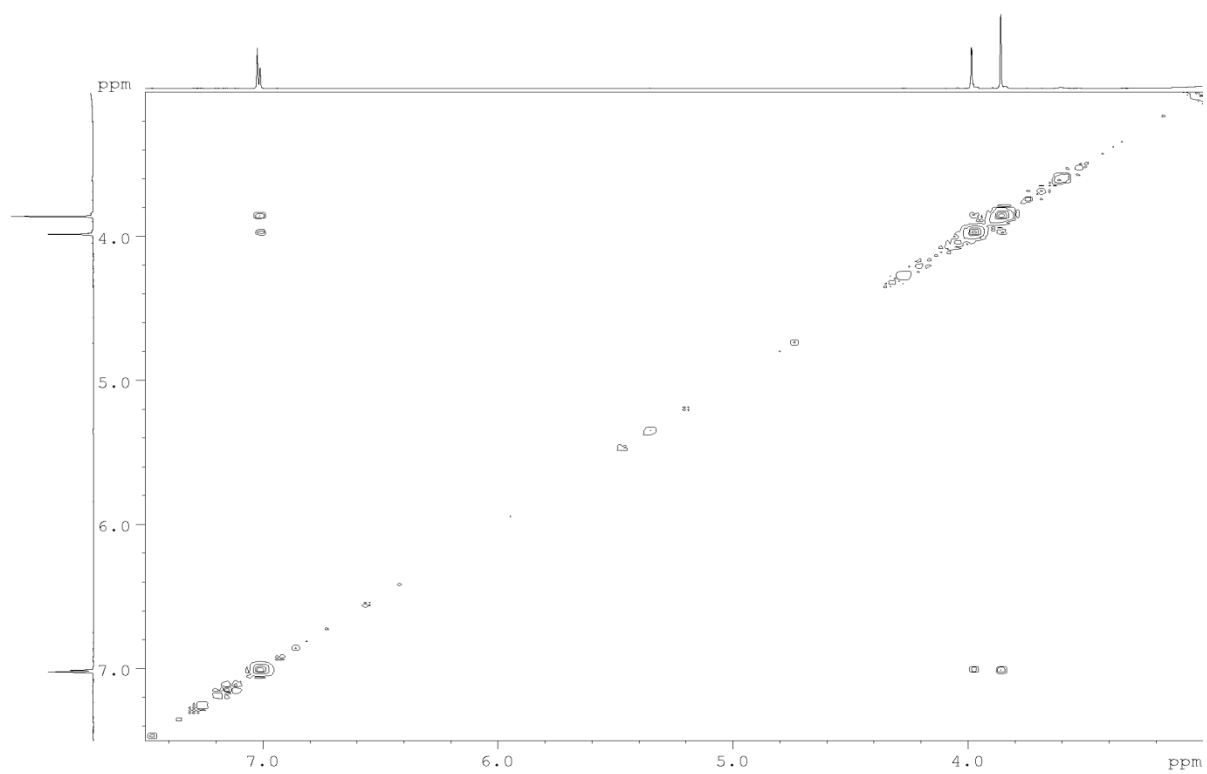
\* means that carbon position is assumed but not confirmed



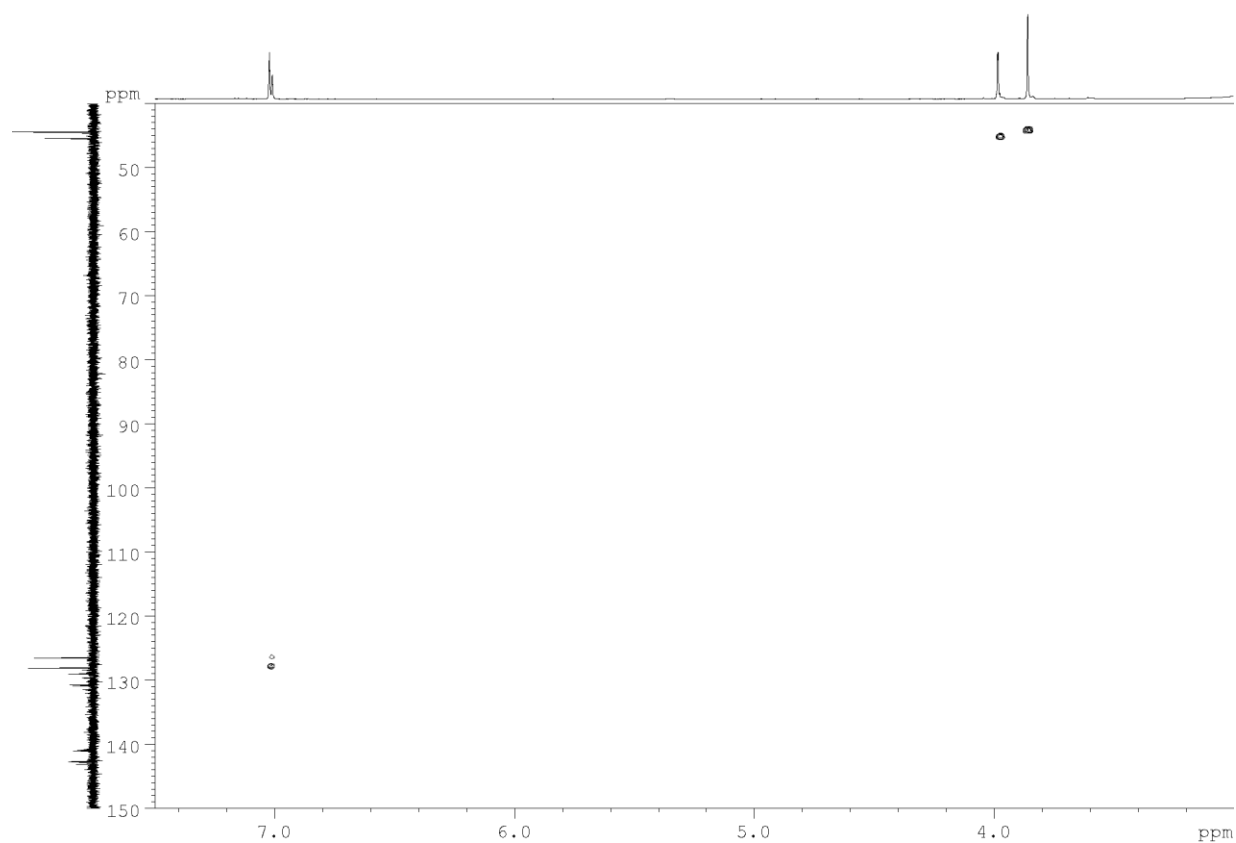
**Figure S46.**  $^1\text{H}$ -NMR spectrum of C1-C2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



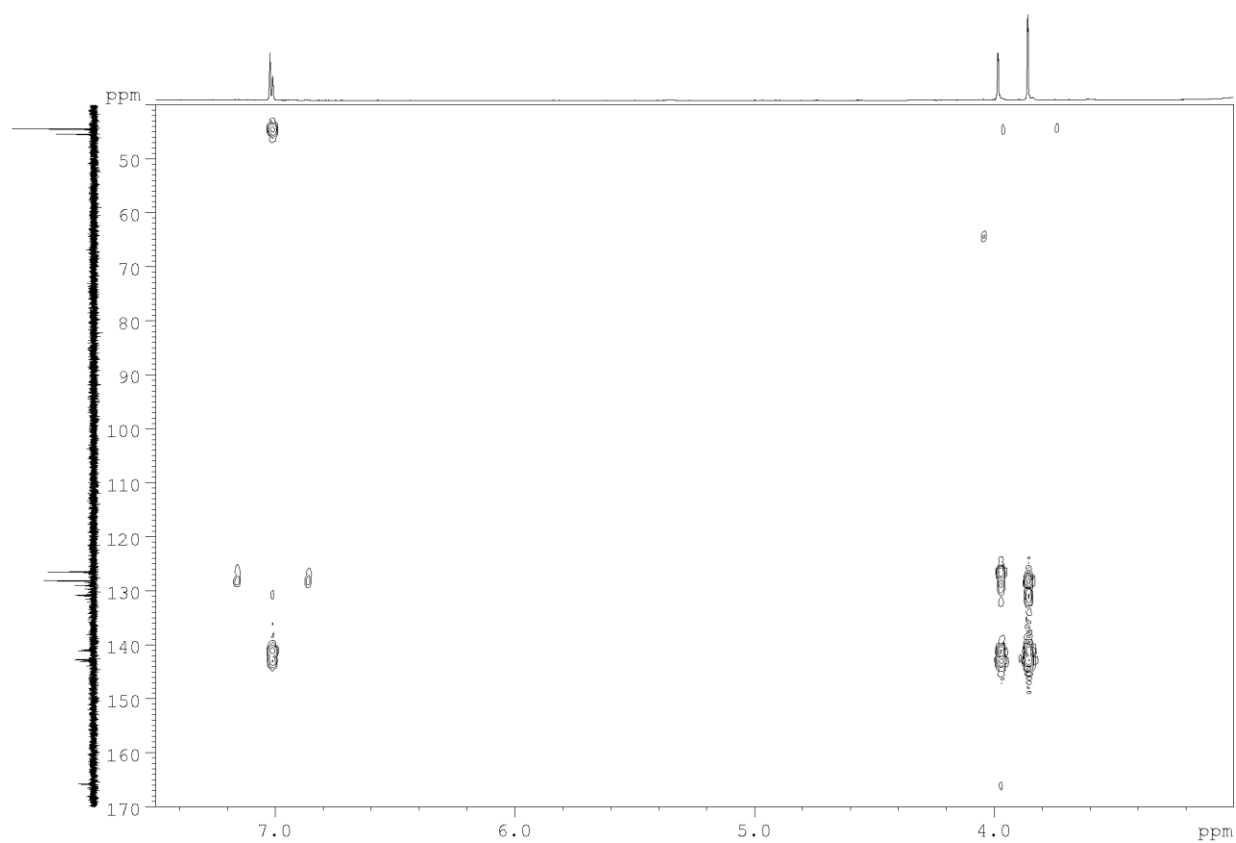
**Figure S47.**  $^{13}\text{C}$ -NMR spectrum of C1-C2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



**Figure S48.** COSY spectrum of C1-C2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)

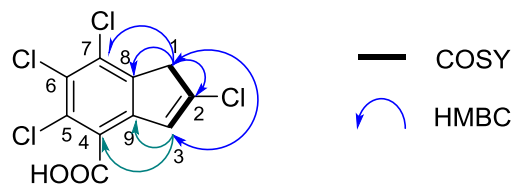


**Figure S49.** HSQC spectrum of C1-C2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



**Figure S50.** HMBC spectrum of C1-C2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)

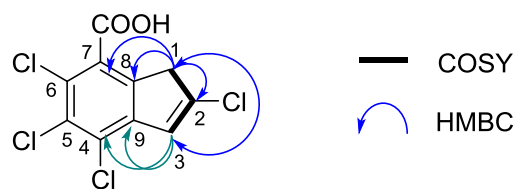




#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	<i>J</i> Coupling (Hz)	Protons	HMBC	COSY
1	44.4		3.86	d, 1.4	2H	C2, C3, C7, C8	H-3
2	142.7						
3	128.4		7.02	t, 1.4	1H	C1, C4, C9	H-1
4	130.7						
5*	132.0						
6*	131.5						
7*	130.9						
8	140.9						
9	142.7						
10	165.7						

**Table S12.** NMR data assignment of C1 (major isomer) in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M-H}]^-$  calcd. for  $\text{C}_{10}\text{Cl}_4\text{O}_2\text{H}_3$ , 294.8882; found, 294.8888. TLC:  $R_f$  (methanol : dichloromethane : formic acid 1/9/0.05) = 0.5

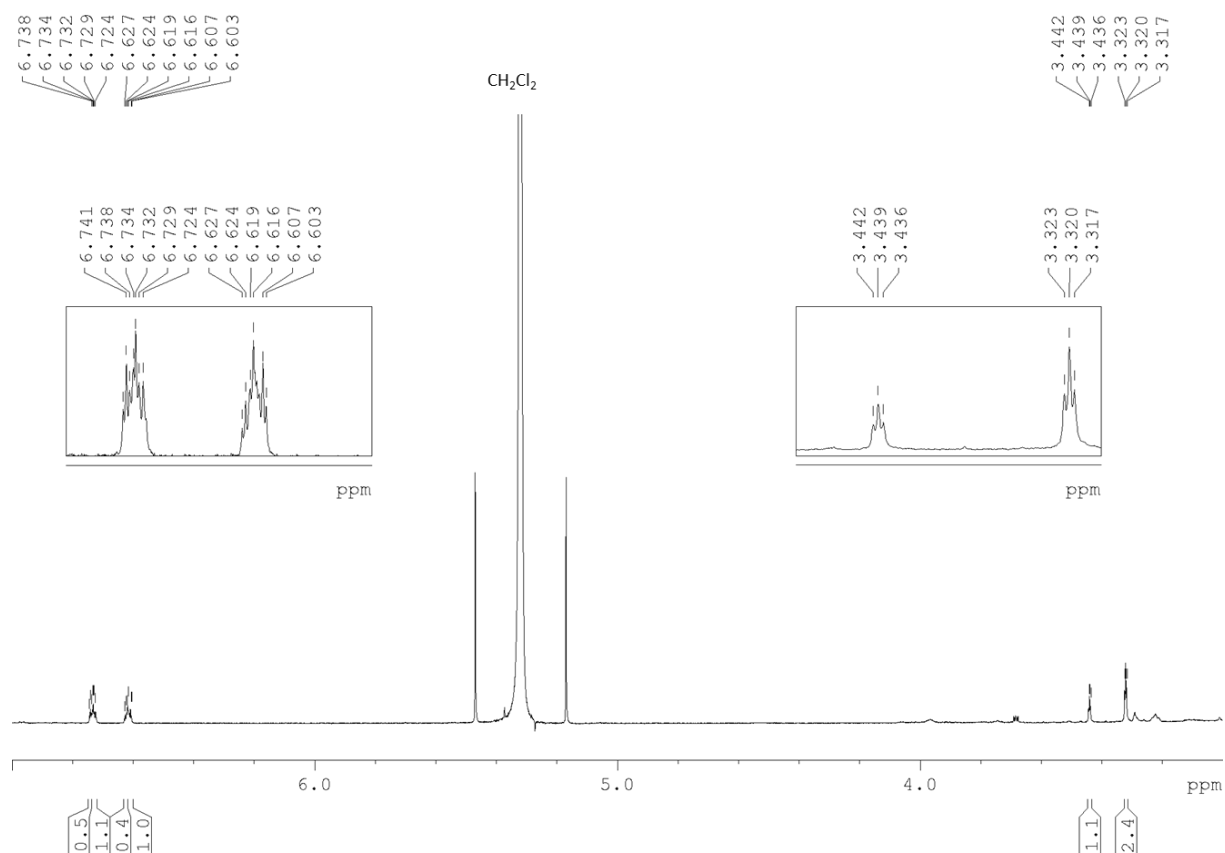
\* means that carbon position is assumed but not confirmed



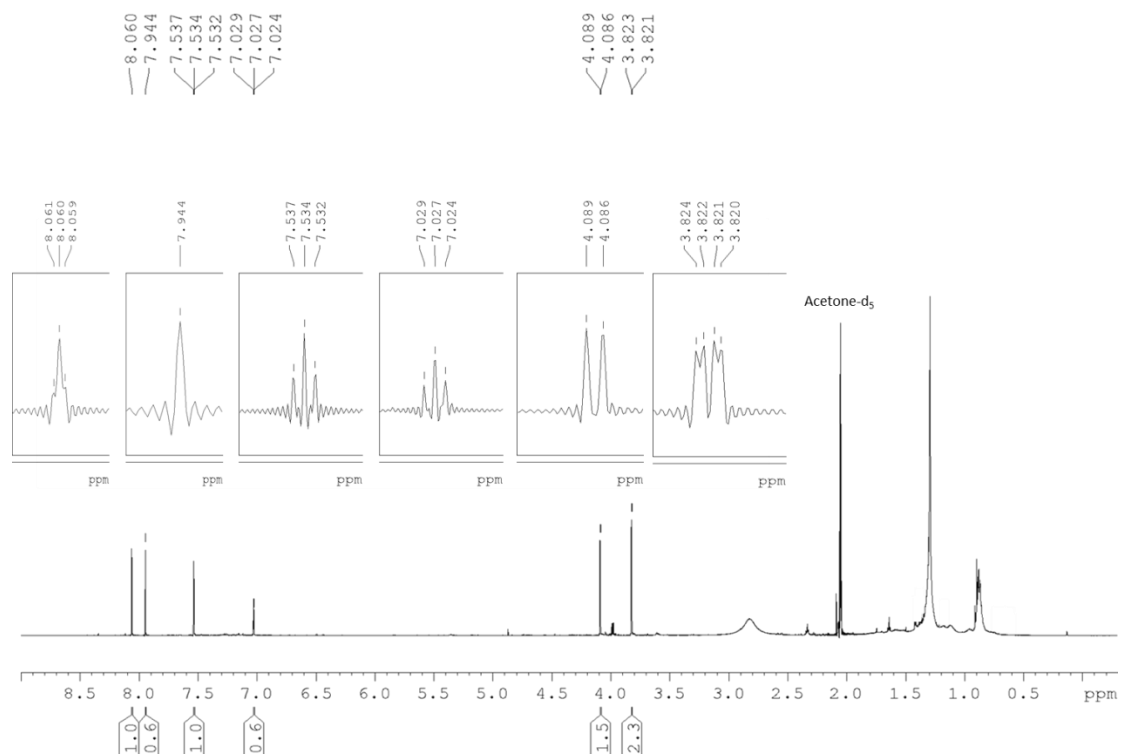
#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	$J$ Coupling (Hz)	Protons	HMBC	COSY
1	45.4		3.98	d, 1.5	2H	C2, C3, C7, C8	H-3
2	142.8						
3	126.5		7.01	t, 1.5	1H	C1, C4, C9	H-1
4	126.6						
5*	128.1						
6*	129.0						
7*	129.6						
8	141.1						
9	143.2						
10	165.8						

**Table S13.** NMR data assignment of C2 (minor isomer) in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}-\text{H}]^-$  calcd. for  $\text{C}_{10}\text{Cl}_4\text{O}_2\text{H}_3$ , 294.8882; found, 294.8888. TLC:  $R_f$  (methanol : dichloromethane : formic acid 1/9/0.05) = 0.5

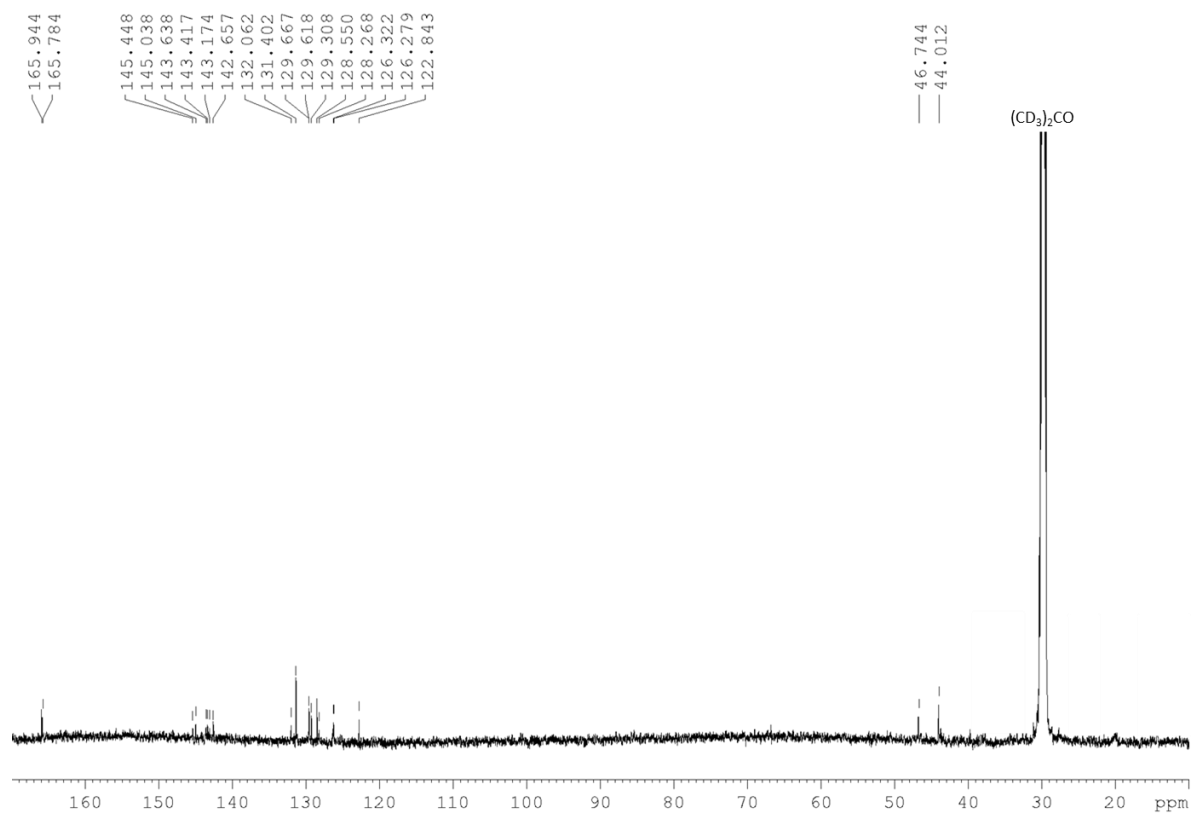
\* means that carbon position is assumed but not confirmed



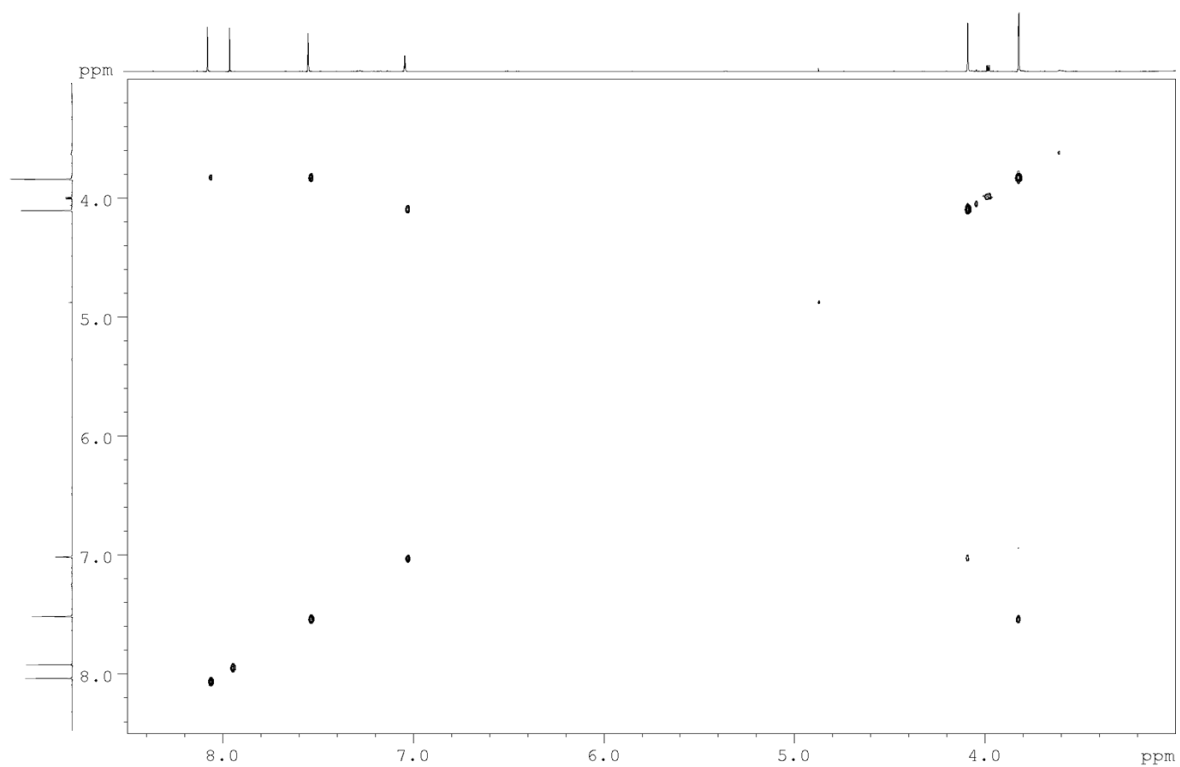
**Figure S51.** <sup>1</sup>H-NMR spectrum of C5-C6 in CD<sub>2</sub>Cl<sub>2</sub> (600 MHz)



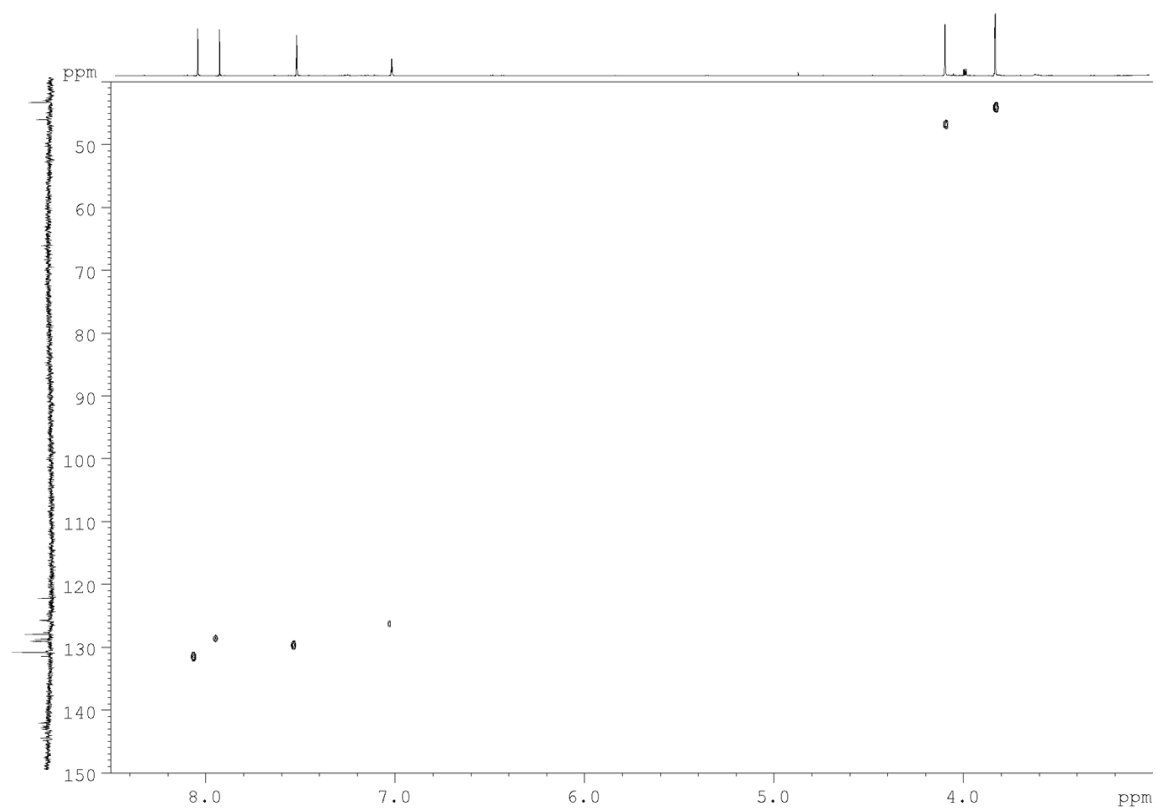
**Figure S52.** full  $^1\text{H}$ -NMR spectrum of C3-C4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz, exponential apodization parameter: Hz) including enlargement windows (exponential apodization parameter: -0.3 Hz).



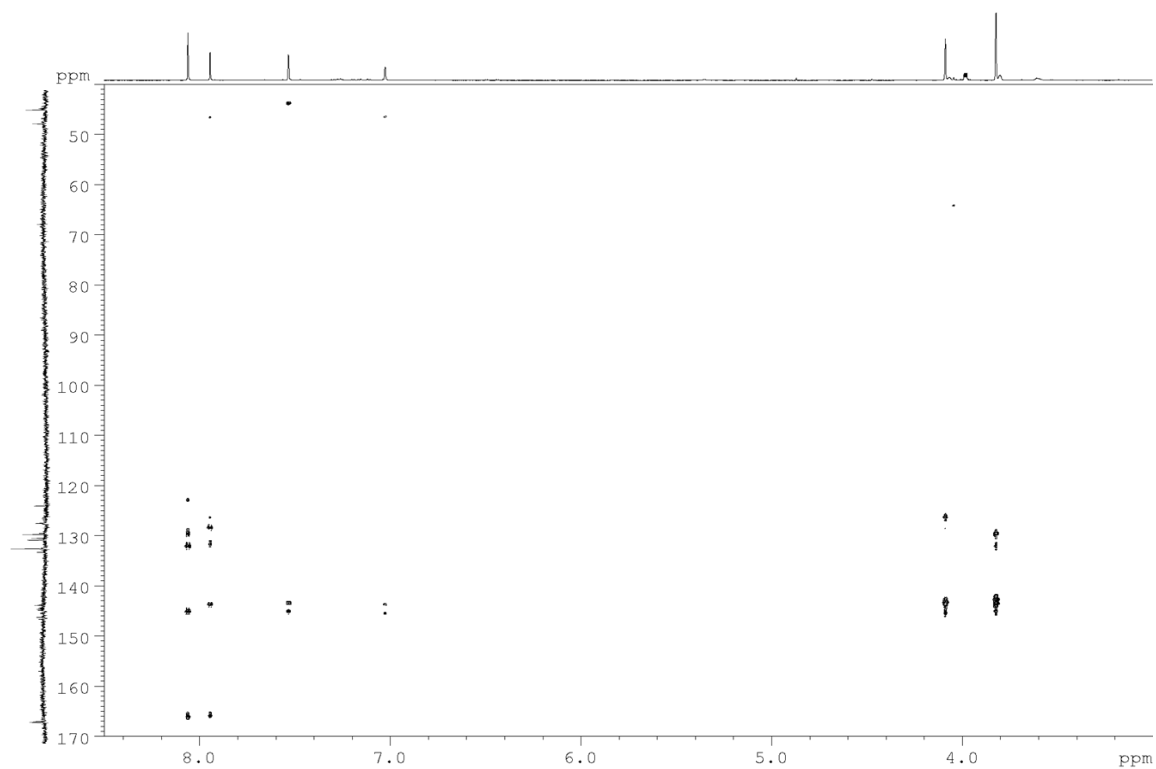
**Figure S53.** <sup>13</sup>C-NMR spectrum of C3-C4 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)



**Figure S54.** COSY spectrum of C3-C4 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)

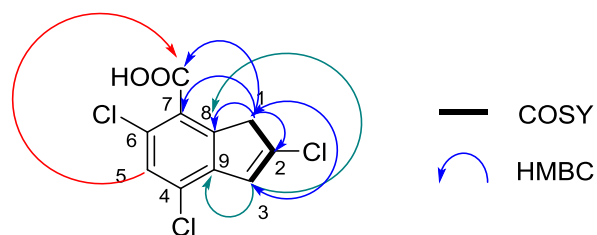


**Figure S55.** HSQC spectrum of C3-C4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



**Figure S56.** HMBC spectrum of C3-C4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



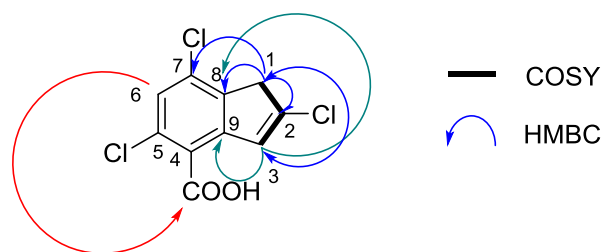


#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	$J$ Coupling (Hz)	Protons	HMBC	COSY
1	46.7		4.09	d, 1.5	2H	C2, C3, C7, C8, C10	H-3
2	145.4						
3	126.3		7,03	t, 1.5	1H	C1, C8, C9	H-1
4*	126.3						
5*	128.6		7,94	s	1H	C10 <sup>i</sup>	
6*	129.7						
7*	128.3						
8	143.2						
9	143.6						
10	165.8						

**Table S14.** NMR data assignment of C3 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}-\text{H}]^-$  calcd. for  $\text{C}_{10}\text{Cl}_3\text{O}_2\text{H}_4$  260.9271; found, 260.9278. TLC:  $R_f$  (methanol : dichloromethane : formic acid 1/9/0.05) = 0.69

\* means that carbon position is assumed but not confirmed

<sup>i</sup> means that others HMBC couplings were observed but were not attributed due to the incertitude on carbon position

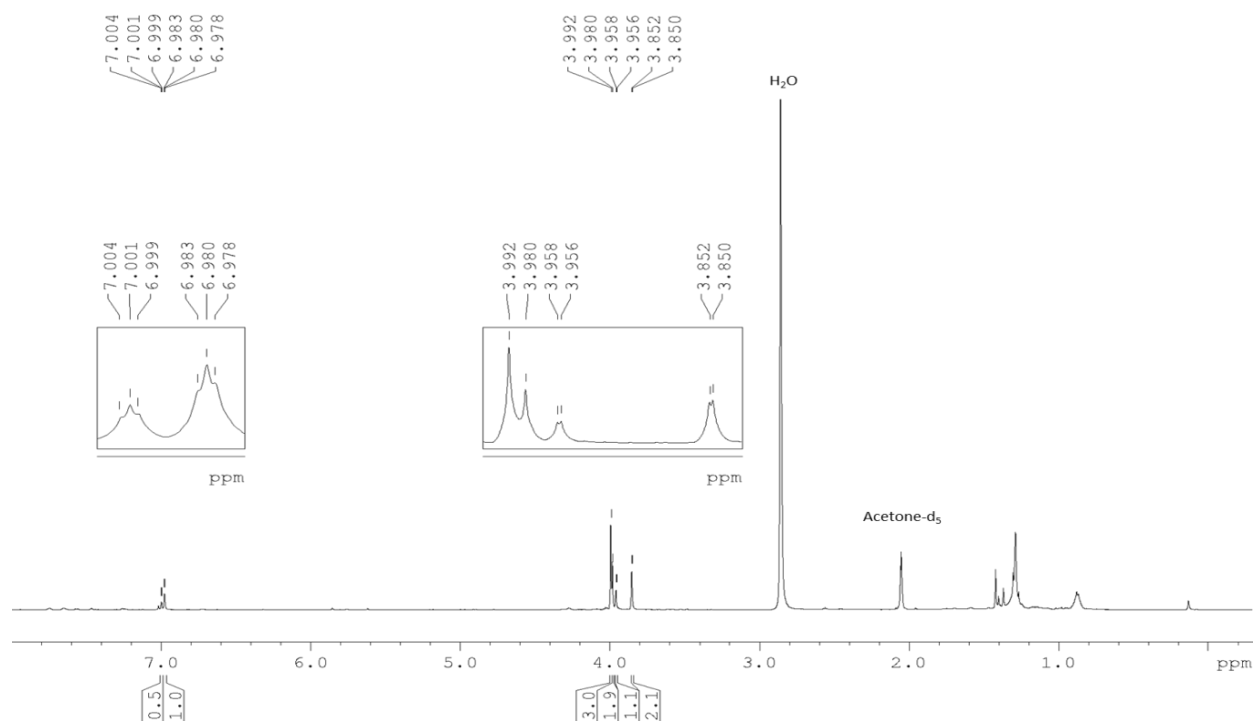


#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	$J$ Coupling (Hz)	Protons	HMBC	COSY
1	44.0		3.82	dd, 1.6, 0.6	2H	C2, C3, C7, C8	H-3, H6
2	143.4						
3	129.3		7.53	t, 1.5	1H	C1, C8, C9	H-1
4*	132.1						
5*	131.4						
6*	122.8		8.06	t, 0.6	1H	C10 <sup>i</sup>	H-1
7*	129.6						
8	142.7						
9	145.0						
10	165.9						

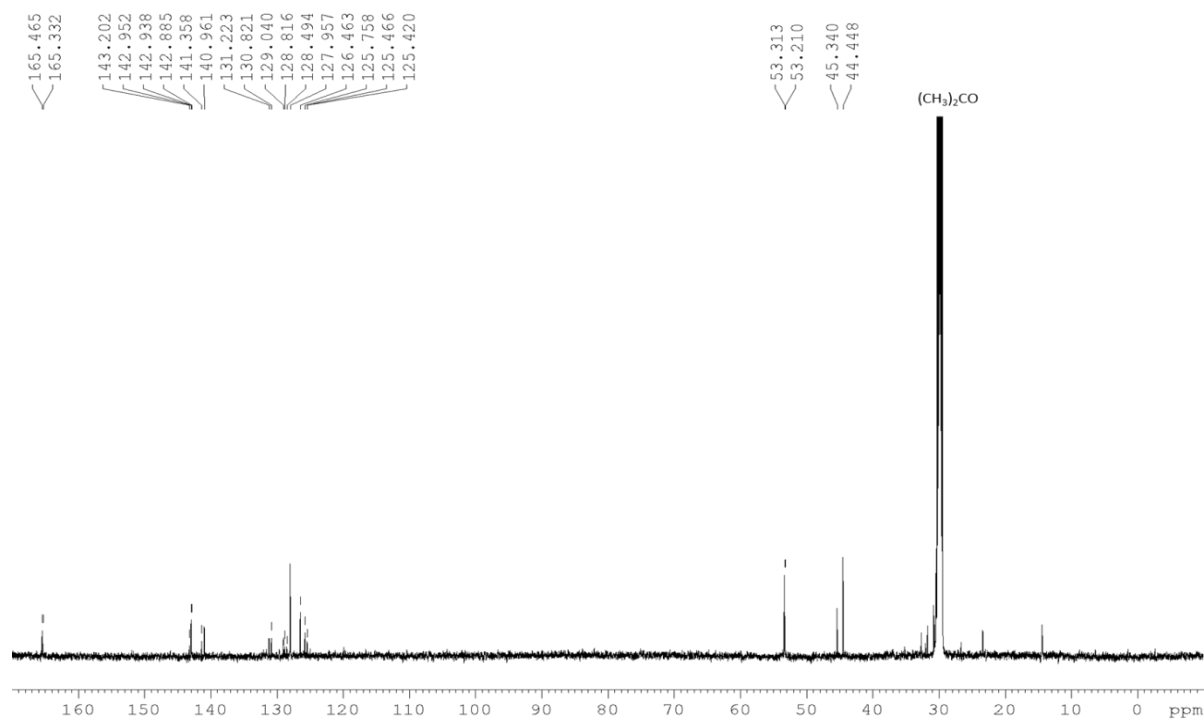
**Table S15.** NMR data assignment of C4 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}-\text{H}]^-$  calcd. for  $\text{C}_{10}\text{Cl}_3\text{O}_2\text{H}_4$  260.9271; found, 260.9278. TLC:  $R_f$  (methanol : dichloromethane : formic acid 1/9/0.05) = 0.69

\* means that carbon position is assumed but not affirmed

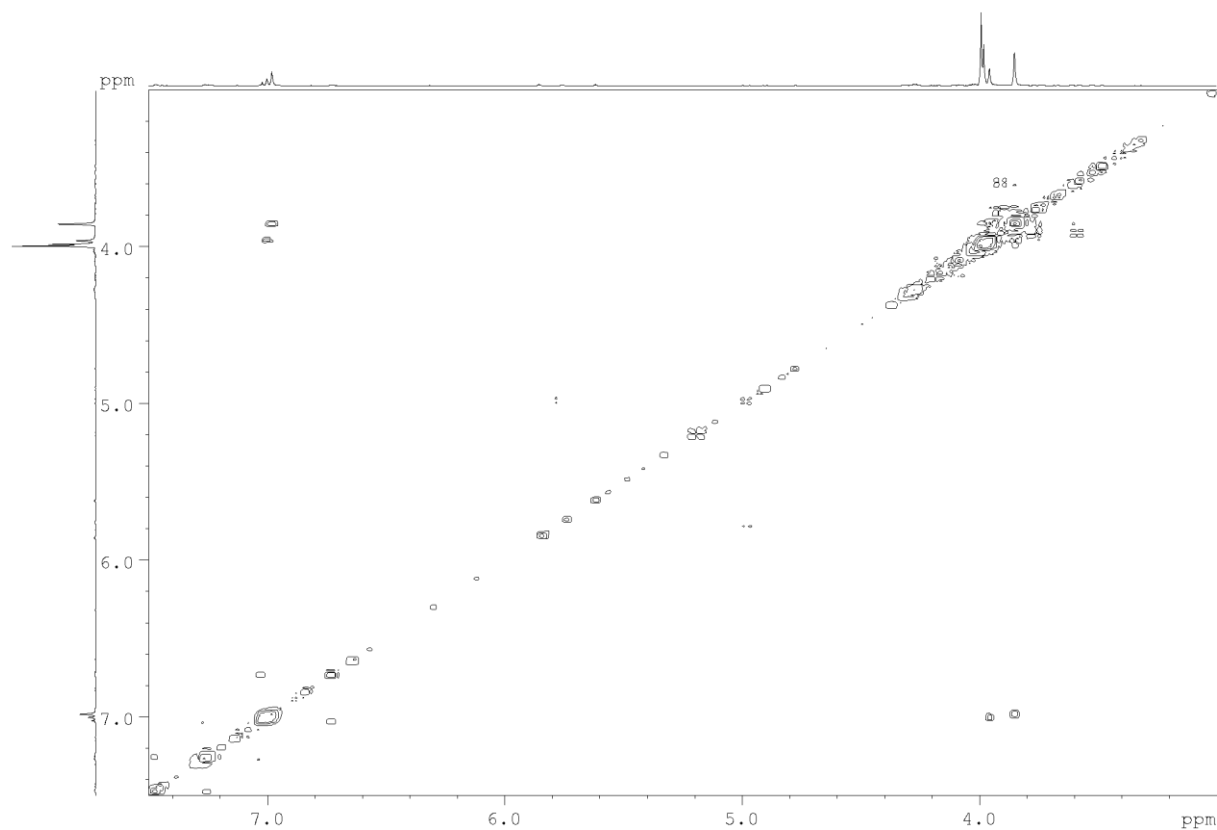
<sup>i</sup> means that others HMBC couplings were observed but were not attributed due to the incertitude on carbon position



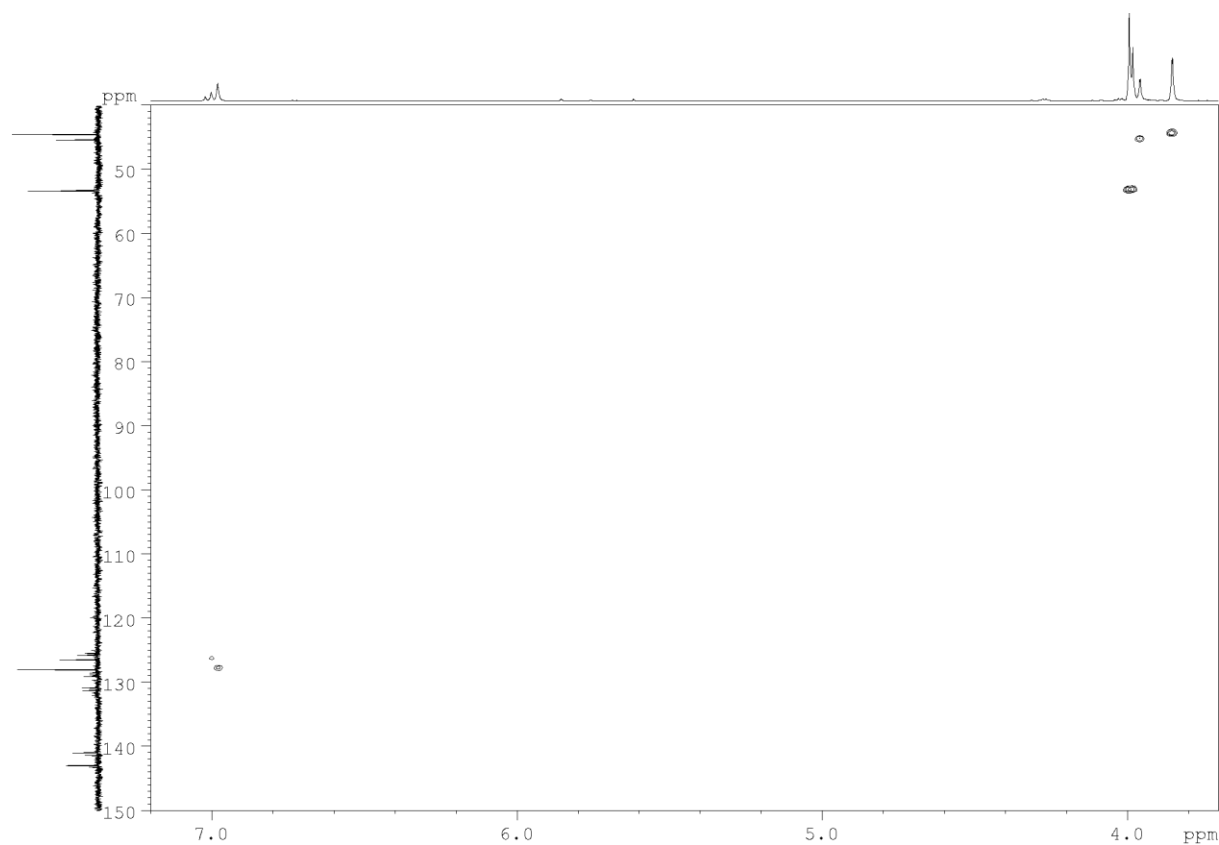
**Figure S57.** <sup>1</sup>H-NMR spectrum of D1-D2 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)



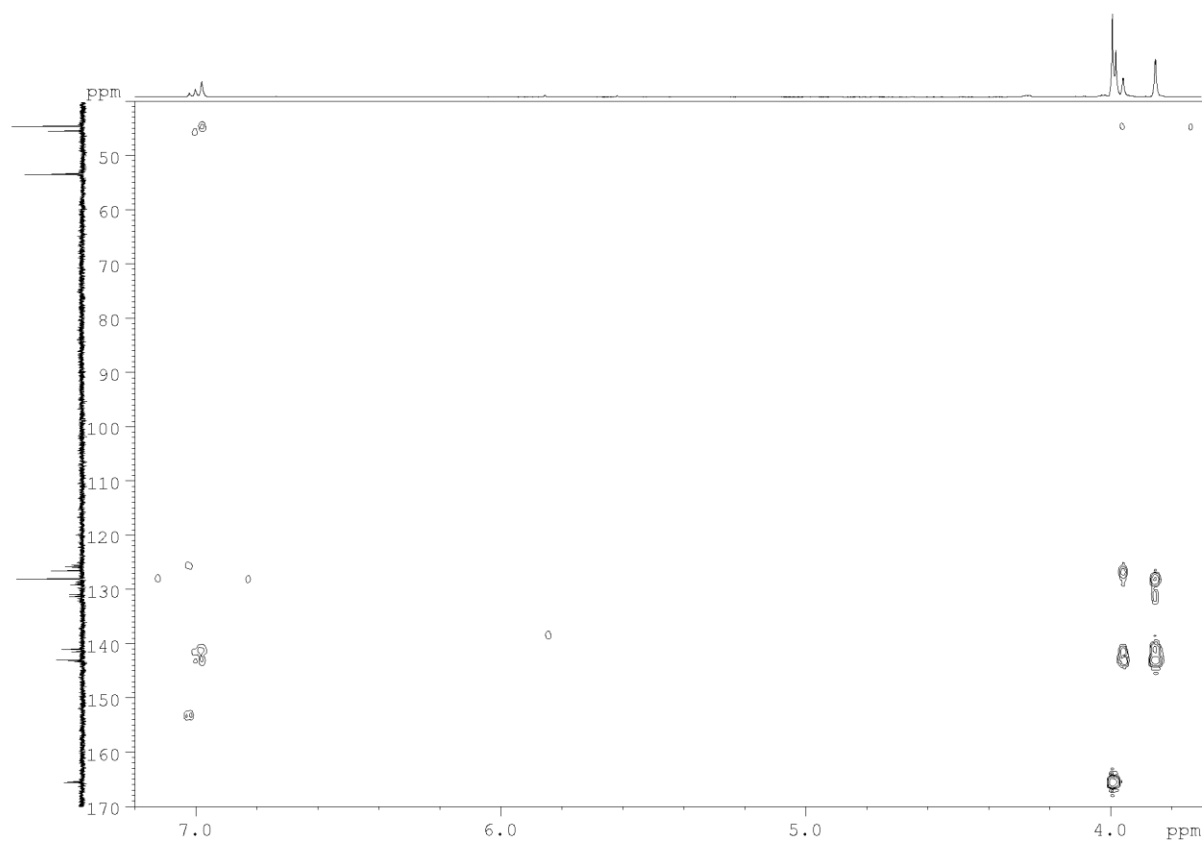
**Figure S58.** <sup>13</sup>C-NMR spectrum of D1-D2 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)



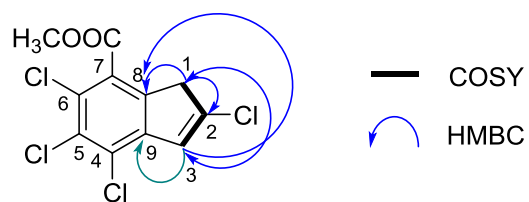
**Figure S59.** COSY spectrum of D1-D2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



**Figure S60.** HSQC spectrum of D1-D2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



**Figure S61.** HMBC spectrum of D1-D2 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)

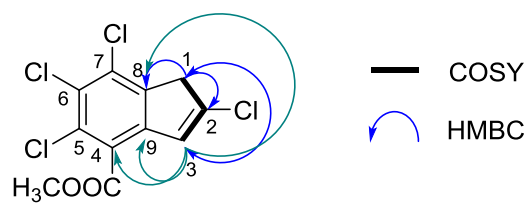


#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	<i>J</i> Coupling (Hz)	Protons	HMBC	COSY
1	45.3		3.95	d, 1.5	2H	C2, C3, C8	H-3
2	143.2						
3	126.5		7.00	t, 1.5	1H	C1, C9	H-1
4*	125.5						
5*	129.0						
6*	128.8						
7*	128.5						
8	141.4						
9	143.2142.9						
10	165.3						
11	53.2		3.98	s	3H		

**Table S16.** NMR data assignment of D1 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}]^-$  calcd. for  $\text{C}_{11}\text{Cl}_4\text{O}_2\text{H}_5$ , 308.9038; found, 308.9046.

\* means that carbon position is assumed but not confirmed

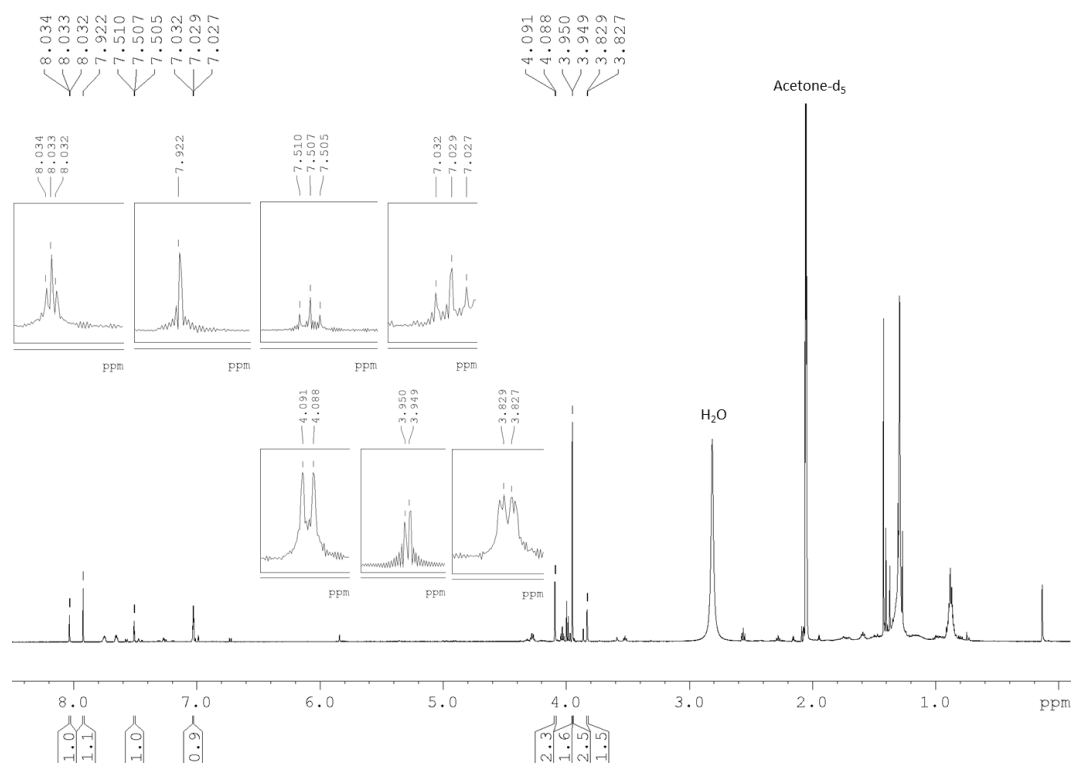




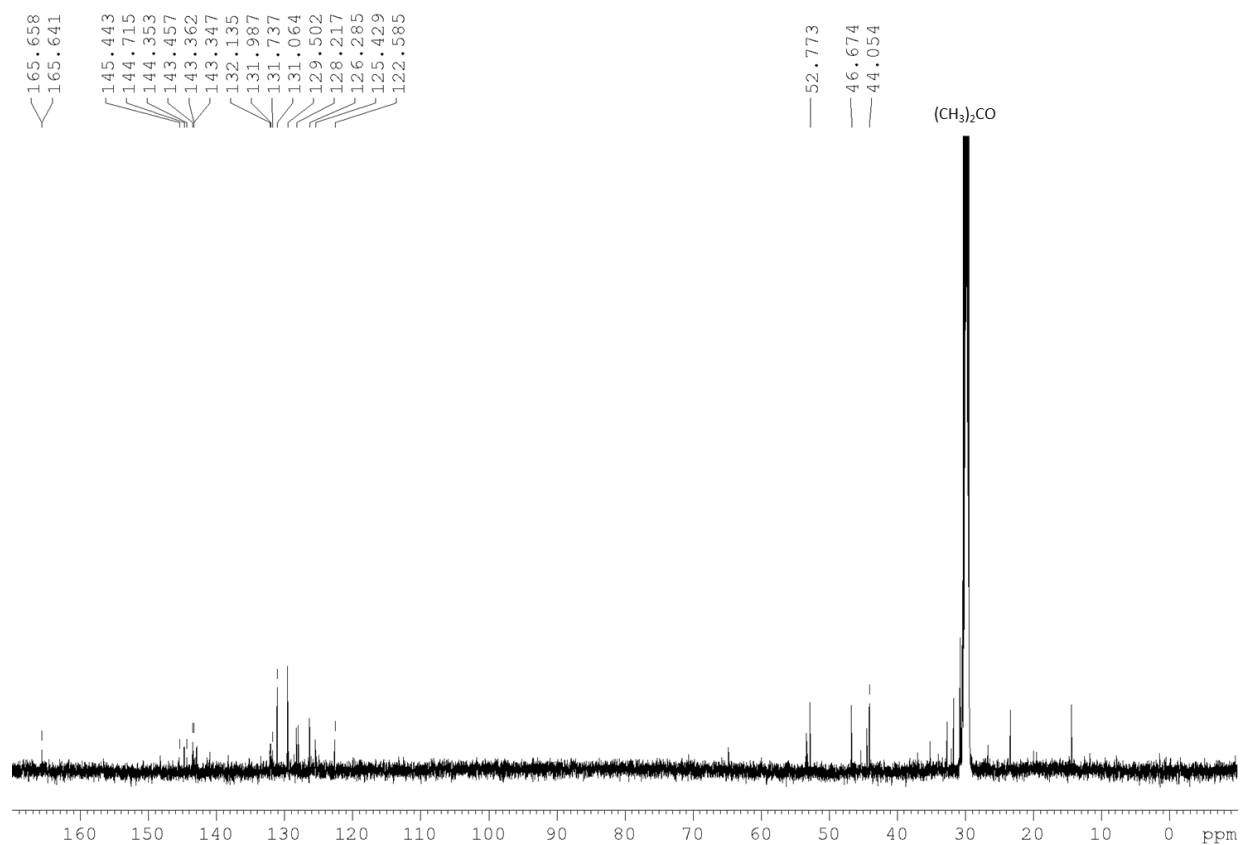
#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	<i>J</i> Coupling (Hz)	Protons	HMBC	COSY
1	44.4		3.85	d, 1.4	2H	C2, C3, C7, C8	H-3
2	142.9						
3	128.0		6.98	t, 1.4	1H	C1, C9	H-1
4*	130.7						
5*	125.8						
6*	125.4						
7*	131.2						
8	141.1						
9	142.9						
10	165.5						
11	53.3		3.99	s	3H		

**Table S17.** NMR data assignment of D2 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}]^-$  calcd. for  $\text{C}_{11}\text{Cl}_4\text{O}_2\text{H}_5$ , 308.9038; found, 308.9046.

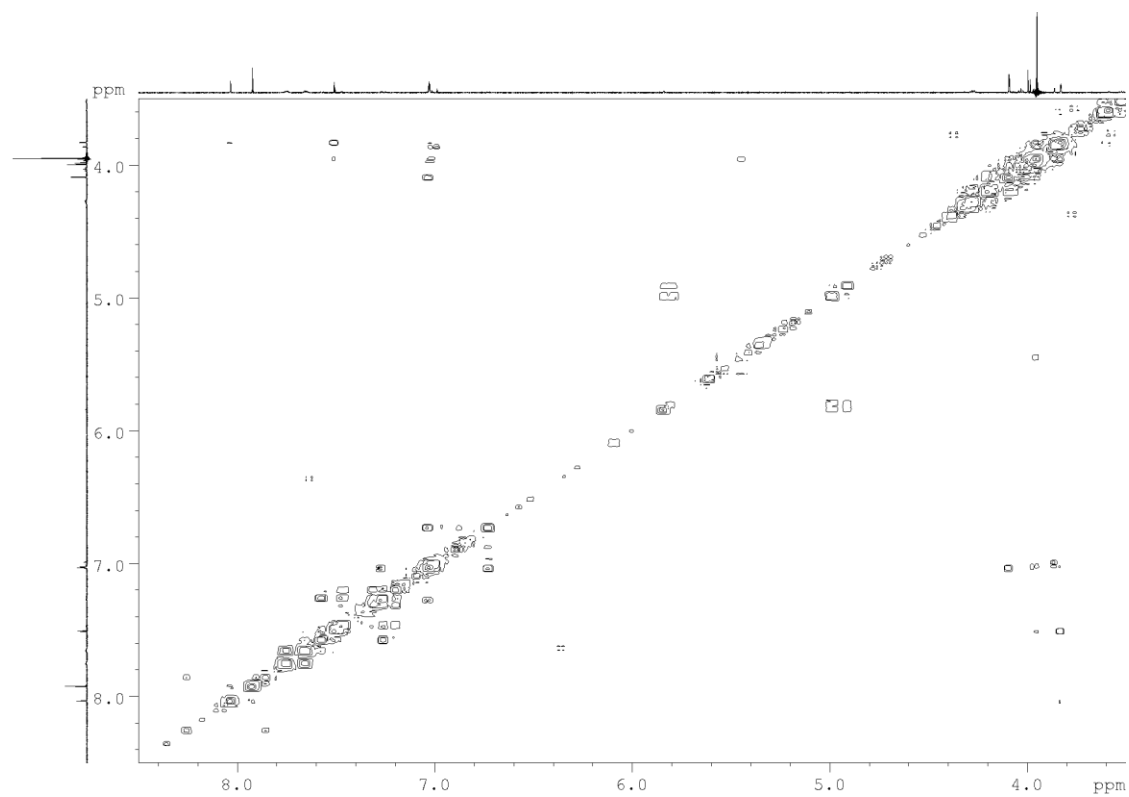
\* means that carbon position is assumed but not confirmed



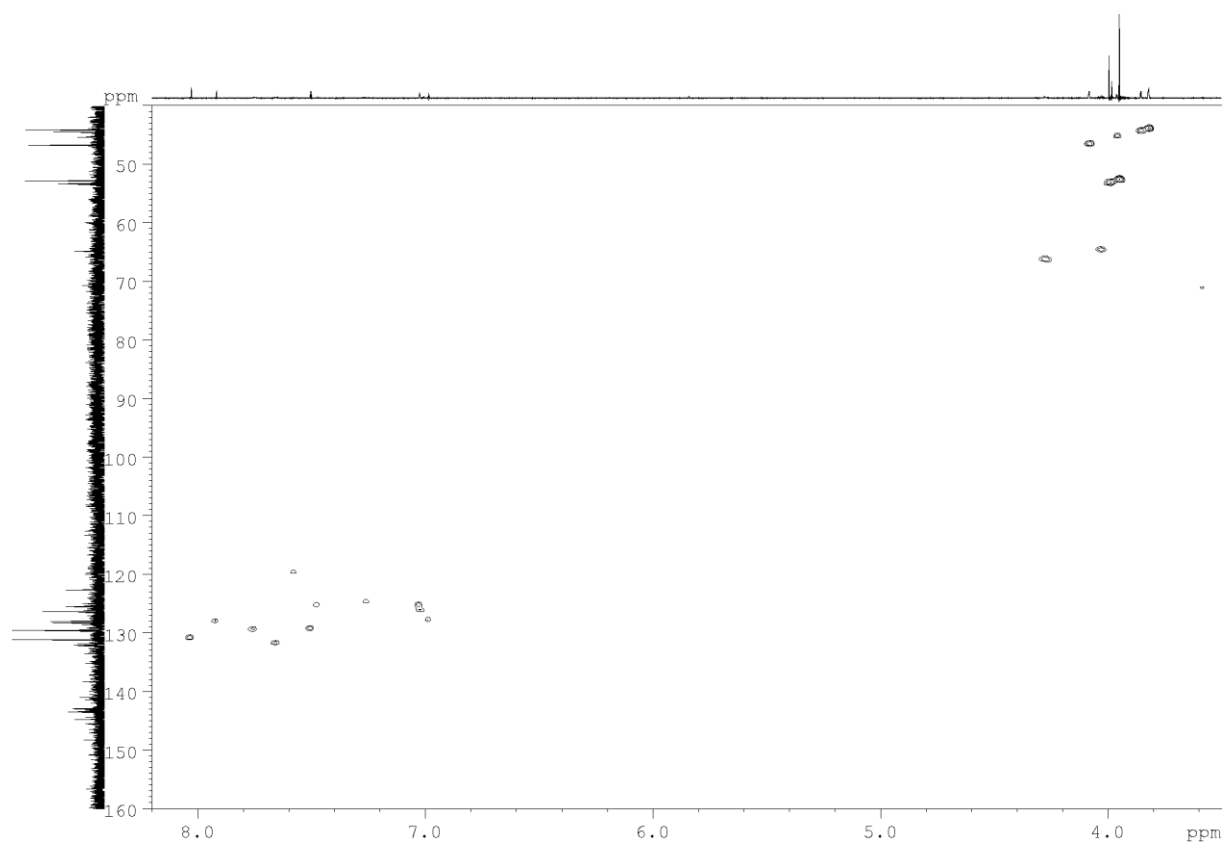
**Figure S62.**  $^1\text{H}$ -NMR spectrum of D3-D4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz, exponential apodization parameter: Hz) including enlargement windows (exponential apodization parameter: -0.3 Hz).



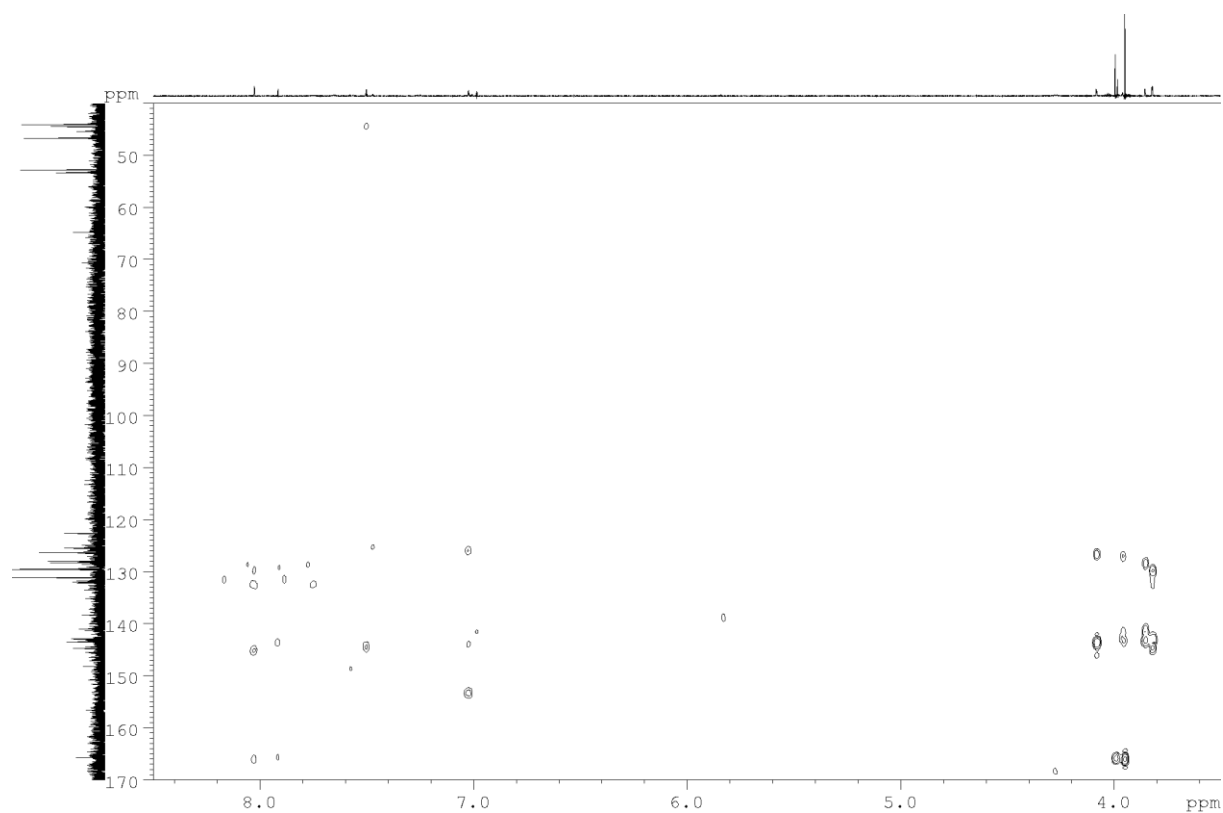
**Figure S63.** <sup>13</sup>C-NMR spectrum of D3-D4 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)



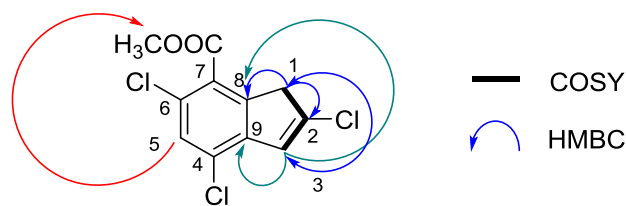
**Figure S64.** COSY spectrum of D3-D4 in (CD<sub>3</sub>)<sub>2</sub>CO (600 MHz)



**Figure S65.** HSQC spectrum of D3-D4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)



**Figure S66.** HMBC spectrum of D3-D4 in  $(\text{CD}_3)_2\text{CO}$  (600 MHz)

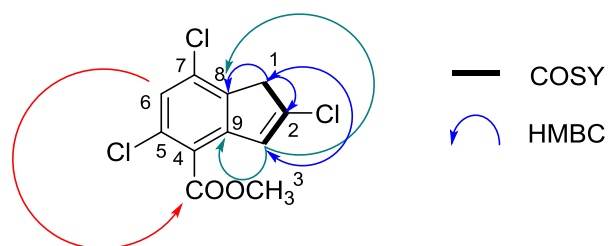


#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	$J$ Coupling (Hz)	Protons	HMBC	COSY
1	46.7		4.08	d, 1.6	2H	C2, C3, C8	H-3
2	143.3						
3	125.4		7.02	t, 1.7	1H	C1, C8, C9	H-1
4*	128.2						
5*	128.3		7.92	s	1H	C10 <sup>i</sup>	
6*	131.1						
7*	131.7						
8	143.5						
9	145.4						
10	165.6						
11	52.8		3.95	s	3H		

**Table S18.** NMR data assignment of D3 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}]^-$  calcd. for  $\text{C}_{11}\text{Cl}_3\text{O}_2\text{H}_6$  274.9428; found, 274.9437.

\* means that carbon position is assumed but not confirmed

<sup>i</sup> means that others HMBC couplings were observed but were not attributed due to the incertitude on carbon position



#	$^{13}\text{C}(\delta)$	HSQC	$^1\text{H}(\delta)$	<i>J</i> Coupling (Hz)	Protons	HMBC	COSY
1	44.1		3.82	dd. 1.5 : 0.6	2H	C2. C3. C8	H-3. H6
2	143.4						
3	129.5		7.5	t, 1.6	1H	C1, C8, C9	H-1
4*	122.6						
5*	132.1						
6*	132.0		8.03	t, 0.6	1H	C10 <sup>i</sup>	H-1
7*	129.7						
8	144.4						
9	144.7						
10	165.7						
11	52.8		3.95	s	3H		

**Table S19.** NMR data assignment of D4 in  $(\text{CD}_3)_2\text{CO}$ . HRMS ( $m/z$ ):  $[\text{M}]^-$  calcd. for  $\text{C}_{11}\text{Cl}_3\text{O}_2\text{H}_6$  274.9428; found, 274.9437.

\* means that carbon position is assumed but not confirmed

<sup>i</sup> means that others HMBC couplings were observed but were not attributed due to the incertitude on carbon position



## S6 Supporting References

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