Table of Contents

Chemicals and enzymes

All chemicals and medium ingredients used in this work were purchased from Sigma Aldrich, ABCR, Fisher Scientific or TCI, respectively. All enzymes used were purchased from NEB, Zymo Research or Thermo Fisher Scientific, respectively, and were used according to the manufacturer's instructions using the supplied buffers.

Reverse transcriptase PCR for cloning of CpTS1 and CpTS2

Clitopilus passeckerianus DSM 1602 was obtained from the German strain collection DSMZ and grown on potato dextrose agar (PDA, Carl Roth, Germany) at 24 °C for 7 days. The spores were collected and frozen with liquid nitrogen, followed by grinding in a mortar. The total RNA was extracted using TRIzol (Thermo Fisher Scientific, USA) following the manufacturer's protocol. DNase I (1 μL, New England Biolabs, USA) was used to remove genomic DNA from the RNA solution following the supplier's protocol. A cDNA library was constructed using the SuperScript IV Reverse Transkriptase kit (Thermo Fisher Scientific, USA). CpTS1 was amplified from the cDNA library using Q5 High-Fidelity DNA polymerase (New England Biolabs) and primers CpTS1_short-Fw and CpTS1_short-Rv (Table S1). The amplificate was used as the template in another PCR amplification using primers CpTS1_long-Fw and CpTS1_long-Rv with homology arm extensions for cloning through homologous recombination in yeast. The DNA fragment was homologously recombined to the linearised (HindIII and EcoRI digestion) expression plasmid pYE-Express in yeast.[1,2] The yeast cells were plated on SM-URA agar plates (425 mg yeast nitrogen base, 1.25 g ammonium sulfate, 5 g glucose, 192.5 mg nutritional supplement minus uracil, 5 g agar, 250 mL water) and grown at 28 °C for 3 days. Plasmid DNA was isolated (Zymoprep Yeast Plasmid Miniprep II kit; Zymo Research, Irvine, CA, USA) and used for electroporation of *E. coli* BL21(DE3) electrocompetent cells. After growth overnight at 37 °C on LB (Lennox) agar amended with kanamycin sulfate (50 μg mL^{-1}), single colonies were selected to inoculate LB (Lennox) medium (5 mL) with kanamycin sulfate. Cultures were grown overnight at 37 °C followed by isolation of plasmid DNA to yield plasmid pYE-CpTS1. The correct insertion of the desired gene was confirmed through DNA sequencing. CpTS2 was cloned using the same method with different primers as listed in Table S1, yielding plasmid pYE-CpTS2.

Table S1. Primers used in this study.

Primer	Nucleotide sequence (5'→3')
CpTS1_short-Fw	ATGGTTTCCGTTCTATCTAC
CpTS1_short-Rv	GTCGATACAATCCTGCATGA
CpTS2_short-Fw	ATGCTCAATACACCGTACTTC
CpTS2_short-Rv	CAGCTGGGATAATAGTTTGA
CpTS1_long-Fw	GGCAGCCATATGGCTAGCATGACTGGTGGAATGGTTTCCGTTCTATCTAC
CpTS1_long-Rv	TCTCAGTGGTGGTGGTGGTGGTGCTCGAGTGTCATGCAGGATTGTATCGAC
CpTS2_long-Fw	GGCAGCCATATGGCTAGCATGACTGGTGGAATGCTCAATACACCGTACTTC
CpTS2_long-Rv	TCTCAGTGGTGGTGGTGGTGGTGCTCGAGTGTCAAACTATTATCCCAGCTG

Gene expression and purification of CpTS1 and CpTS2

Small scale cultures of *Escherichia coli* BL21 (DE3) transformed with pYE-CpTS1 or pYE-CpTS2 were grown in LB (Lennox) medium (10 mL) containing kanamycin sulfate (50 μg/mL) overnight with shaking at 37 °C. The gene expression cultures in LB (Lennox) medium containing kanamycin sulfate (50 μg/mL) were inoculated with the grown overnight culture (2 %). Culturing was continued with shaking at 37 °C until an OD_{600} = 0.4 – 0.6 was reached. After cooling the culture to 18 °C, enzyme expression was induced by the addition of IPTG solution (100 mM, 1 ‰, v/v). The cultures were shaken at 18 °C for 18 h. Cells were harvested via centrifugation (1,500 g, 40 min, 4 °C), resuspended in binding buffer (30 mL/L culture; 20 mM Na_2HPO_4, 500 mM NaCl, 20 mM imidazole, 1 mM $MgCl_2$, adjusted with 1 N HCl to pH = 7.4, stored after preparation at 4 °C) and lysed by ultrasonication (10x 1 min) on ice. The cell debris was removed by centrifugation (14,600 g, 7 min, 4 °C) and the supernatant was loaded on a Ni^{2+}-NTA superflow affinity chromatography column (Qiagen, Venlo, Netherlands) equilibrated with binding buffer. The column was washed with binding buffer (2 column volumes, CV) and washing buffer (2 CV; 20 mM Na_2HPO_4, 500 mM NaCl, 100 mM imidazole, 1 mM $MgCl_2$, adjusted with 1 N HCl to pH = 7.4, stored after preparation at 4 °C). The desired protein was eluted with elution buffer (1 CV; 20 mM Na_2HPO_4, 500 mM NaCl, 500 mM imidazole, 1 mM $MgCl_2$, adjusted with 1 N HCl to pH = 7.4, stored after preparation at 4 °C). Protein purity was checked by SDS-PAGE analysis (Figure S1) and protein concentrations were determined through Bradford assay.[3] Typical protein yields were 2.0 mg/mL (CpTS1) and 2.3 mg/mL (CpTS2).
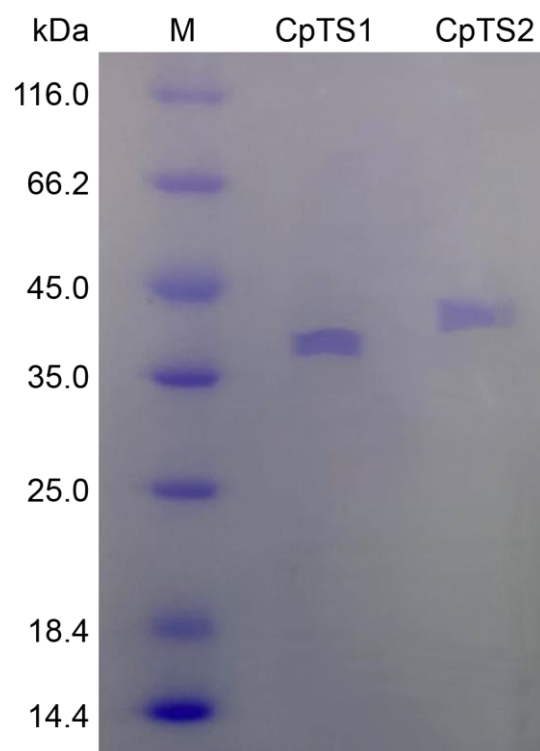
Figure S1. SDS-PAGE analysis of purified recombinant CpTS1 and CpTS2. M = protein marker.

```
MVSVLSTALCKRPNFVSRFPANEHFDRGVIAENVQWYLSEKWPWKSDAERERYLTKDFEGWGLMI

LGDAPSDRTEAACLWFSWLFLWDDMVEKMSSSEARLSLVQLAEIFSDTRIPKDPTPIERIALAIR

DMLLEVDDDDLRDLGRSILTQVCHFFTAIGSKQDRARAFAGGFDSFIKYRLNDVGGRLALELLLW

ARGCIIPPNAKSTGLADLVNISLLHATLINDFFSYEVEAEVLRELEFSGRKKHGYMVFNTVAVLM

AEKSMSRTDAYVELIEKIKVVEKRYVKALDDLRIRHRESGEDLTRIEEVSDVLVDLMGGNSVWSE

TCGRYNPA
```

Figure S2. Amino acid sequence of CpTS1 from *Clitopilus passeckerianus* (accession number PP777465). Highly conserved motifs are highlighted in bold.

Test incubations for determination of the substrate scope of CpTS1 and CpTS2

For test enzymatic conversions the substrates GPP, FPP, GGPP and GFPP (trisammonium salts, 1 mg each) were dissolved in incubation buffer (0.8 mL; 50 mM Tris/HCl, 10 mM MgCl$_2$, 10% glycerol (v/v), 20 mM β-cyclodextrin, adjusted with 1 N HCl to pH = 8.2), followed by vortexing of the solutions to remove micelles. Enzyme preparations were obtained as mentioned above and added to the substrate solutions (0.2 mL, enzyme concentration: 2.0 mg/mL (CpTS1) and 2.3 mg/mL (CpTS2)), followed by incubation for 16 h at 30 °C. The reaction mixtures were extracted with n-hexane, the extracts were dried with MgSO$_4$ and analysed by GC/MS.

Preparative scale incubations with CpTS1 and CpTS2 and compound isolations

A preparative scale enzymatic conversion of trisammonium GGPP (60 mg, 120 μmol) was done in incubation buffer (100 mL). An enzyme preparation of CpTS1 (20 mL, 2.0 mg mL^{-1}) was added (final substrate concentration of 1 mmol L^{-1}, final enzyme concentration of 0.3 mg L^{-1}), followed by incubation for 16 h at 30 °C. The reaction mixture were extracted with n-hexane (3x 100 mL), the combined extracts were dried with MgSO$_4$ and the solvent was evaporated. The crude product was purified via column chromatography on silica gel with pentane yield pure **1** (1.2 mg, 4.4 μmol, 3.7%).

Analogously, a preparative scale enzymatic conversion of trisammonium FPP (100 mg, 231 μmol) was done in incubation buffer (80 mL). An enzyme preparation of CpTS2 (30 mL, 2.3 mg mL^{-1}) was added (final substrate concentration of 2.1 mmol L^{-1}, final enzyme concentration of 0.6 mg L^{-1}), followed by incubation for 16 h at 30 °C. The reaction mixture were extracted with n-hexane (3x 100 mL), the combined extracts were dried with MgSO$_4$ and the solvent was evaporated. The crude product was purified via column chromatography on silica gel with n-pentane, followed by column chromatography on activated silica gel with pentane to yield pure **2** (1.5 mg, 7.3 μmol, 3.2%).

For the preparation of activated silica gel, 10 g of silica gel were dissolved in sat. AgNO$_3$ solution in methanol overnight, followed by rigorous evaporation of the solvent.

Clitopilene (1). TLC (pentane): R_f = 0.91. GC (HP5-MS): I = 1845. IR (diamond ATR): $\tilde{v}$ / cm^{-1} = 2945 (s), 2923 (s), 2856 (m), 1654 (w), 1636 (w), 1458 (m), 1373 (w), 1271 (w), 1260 (w), 1093 (w), 1082 (w), 1028 (w), 810 (w). HR-MS (APCI): calc. for [C$_{20}$H$_{32}$]$^+$ m/z = 272.2499; found: m/z = 272.2498.. Optical rotation: [α]$_D^{25}$ = -26.7 (c 0.12, acetone). NMR data are given in Table S2.

Isopentalenene (2). TLC (pentane): R_f = 0.90. activated TLC (pentane): R_f = 0.90. GC (HP5-MS): I = 1362. IR (diamond ATR): $\tilde{v}$ / cm^{-1} = 2953 (s), 2923 (s), 2687 (s), 2003 (w), 1735 (w), 1461 (w), 1440 (w), 1379 (w), 1365 (w), 1093 (w), 1021 (w). HR-MS (APCI): calc. for [C$_{15}$H$_{24}$]$^+$ m/z = 204.1878; found: m/z = 204.1885. Optical rotation: [α]$_D^{25}$ = 9.3 (c 0.15, acetone). NMR data are given in Table S5.

GC/MS

GC/MS analyses were carried out on a 7890B/5977A series gas chromatography/mass selective detector (Agilent, Santa Clara, CA, USA). The GC was equipped with an HP5-MS fused silica capillary column (30 m, 0.25 mm i. d., 0.50 μm film; Agilent) and operated using the settings 1) inlet pressure: 77.1 kPa, He at 23.3 mL min⁻¹, 2) injection volume: 1 – 2 μL, 3) temperature program: 5 min at 50 °C then increasing 5 °C min⁻¹ to 320 °C, 4) 60 s valve time, and 5) carrier gas: He at 1.2 mL min⁻¹. The MS was operated with settings 1) source: 230 °C, 2) transfer line: 250 °C, 3) quadrupole: 150 °C and 4) electron energy: 70 eV.

HRMS

High resolution mass spectra using APCI were recorded on an Orbitrap XL instrument (Thermo Fisher Scientific, Waltham, MA, USA).

NMR spectroscopy

NMR spectra were recorded at 298 K on a Bruker (Billerica, MA, USA) Avance III HD Cryo (700 MHz) NMR spectrometer. Spectra were measured in C_6D_6 and referenced against solvent signals (¹H-NMR, residual proton signal: δ = 7.16 ppm; ¹³C-NMR: δ = 128.06 ppm).[4] Coupling constants are given in Hz.

IR spectroscopy

IR spectra were recorded on a Bruker α infrared spectrometer with a diamond ATR probehead. Peak intensities are given as s (strong), m (medium), w (weak) and br (broad).

Optical rotations

Optical rotations were recorded on a Modular Compact Polarimeter MCP 100 (Anton Paar, Graz, Austria). The temperature setting was 25 °C; the wavelength of the light used was 589 nm (sodium D line); the path-length was 10 cm, the compound concentrations c are given in g 100 mL⁻¹.
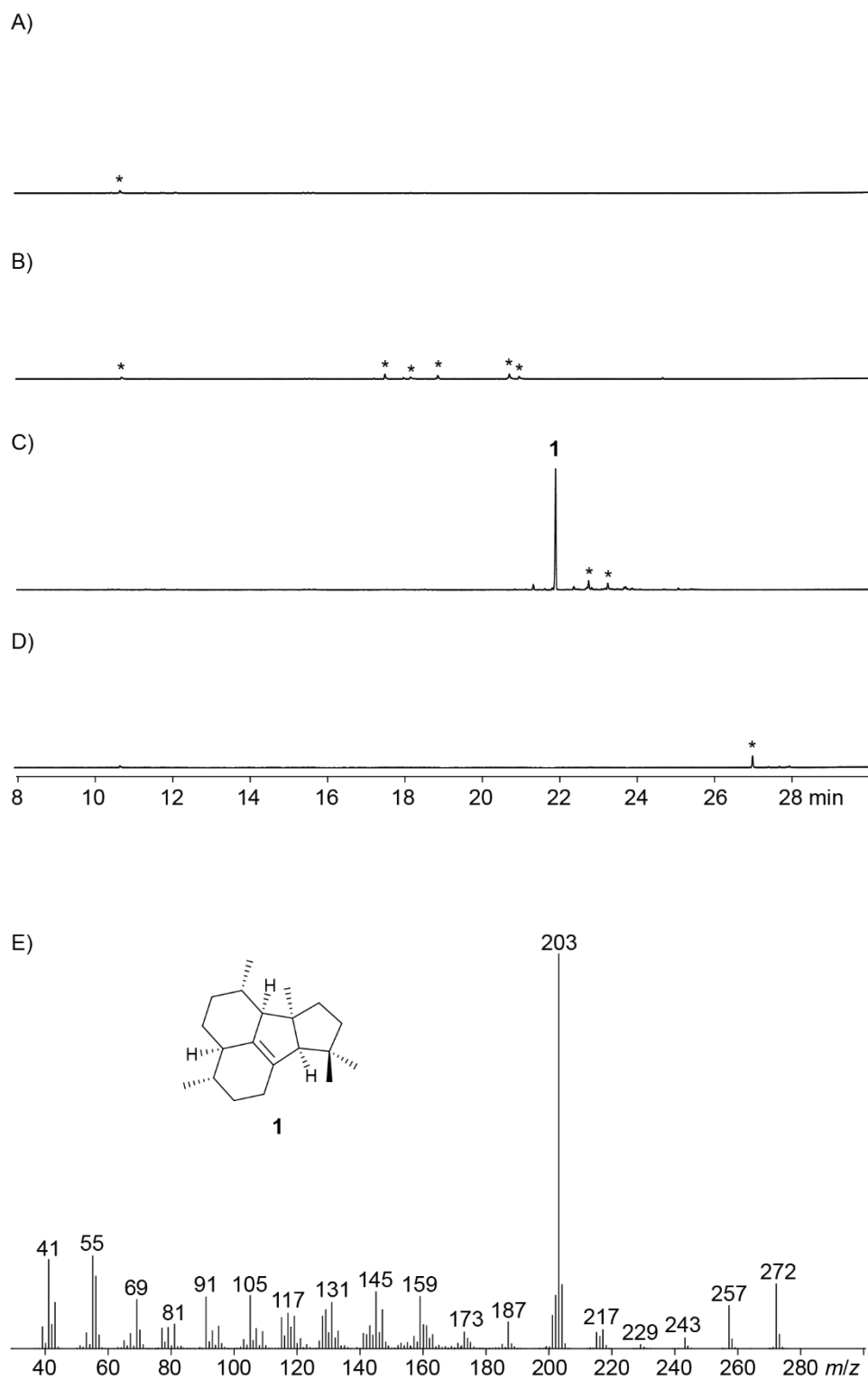
A)

B)

C)

1

D)

8   10   12   14   16   18   20   22   24   26   28 min

E)

203

41 55

69   91 105   131 145 159
    81   117   173 187   217   257 272
                                    229 243

40   60   80   100   120   140   160   180   200   220   240   260   280 m/z

1

Figure S3. Substrate screening for CpTS1. Chromatograms of extracts obtained from an incubation of A) GPP, B) FPP, C) GGPP, and D) GFPP with CpTS1. E) EI mass spectrum of clitopilene (**1**). Asterisks indicate spontaneous hydrolysis products and contaminants such as plasticisers.
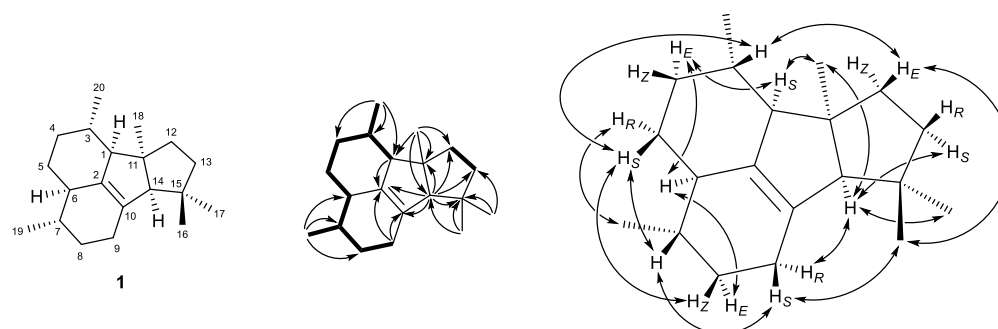
Figure S4. Structure elucidation of **1**. Bold bonds indicate ^{1}H,^{1}H-COSY correlations, single headed arrows indicate key HMBC correlations, and double headed arrows indicate key NOESY correlations.

Table S2. NMR data of clitopilene (**1**) in C_6D_6 recorded at 298 K.

C[a]	type	^{13}C[b]	^{1}H[b]
1	CH	62.90	1.57 (m)
2	C_q	139.30	–
3	CH	35.47	1.25 (m)
4	CH_2	35.71	1.67 (dddd, J = 13.1, 3.3, 3.3, 3.3, H$_Z$)
			1.03 (m, H$_E$)
5	CH_2	32.40	1.97 (dddd, J = 12.7, 5.1, 3.3, 3.3, H$_R$)
			0.71 (dddd, J = 13.1, 13.1, 12.0, 3.1, H$_S$)
6	CH	43.40	1.54 (m)
7	CH	36.72	1.15 (m)
8	CH_2	32.50	1.57 (m, H$_Z$)
			1.25 (m, H$_E$)
9	CH_2	27.14	2.02 (m, H$_S$)
			1.85 (m, H$_R$)
10	C_q	131.43	–
11	C_q	51.55	–
12	CH_2	34.02	1.82 (ddd, J = 12.6, 12.6, 6.1, H$_E$)
			1.30 (ddd, J = 12.6, 6.4, 1.5, H$_Z$)
13	CH_2	43.12	1.61 (m, H$_S$)
			1.40 (ddd, J = 11.7, 6.1, 1.3, H$_R$)
14	CH	73.72	2.14 (br d, J = 2.6)
15	C_q	41.82	–
16	CH_3	30.71	1.17 (br s)
17	CH_3	23.21	0.82 (s)
18	CH_3	34.26	1.21 (br s)
19	CH_3	19.98	0.98 (d, J = 6.6)
20	CH_3	21.36	0.92 (d, J = 6.2)

[a] Carbon numbering as shown in Figure S4. [b] Chemical shifts δ in ppm, multiplicity: s = singlet, d = doublet, m = multiplet, br = broad, coupling constants J are given in Hertz.
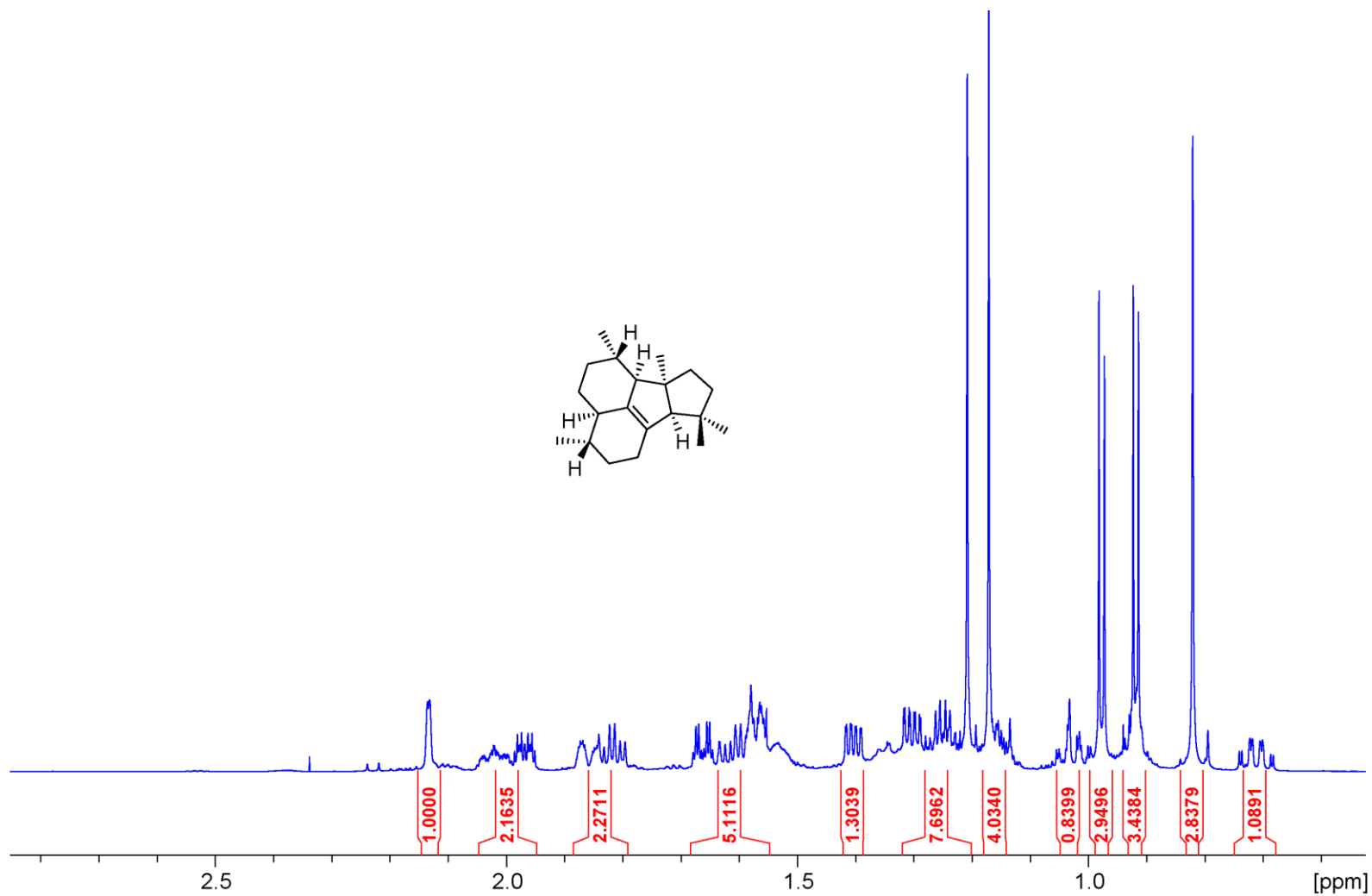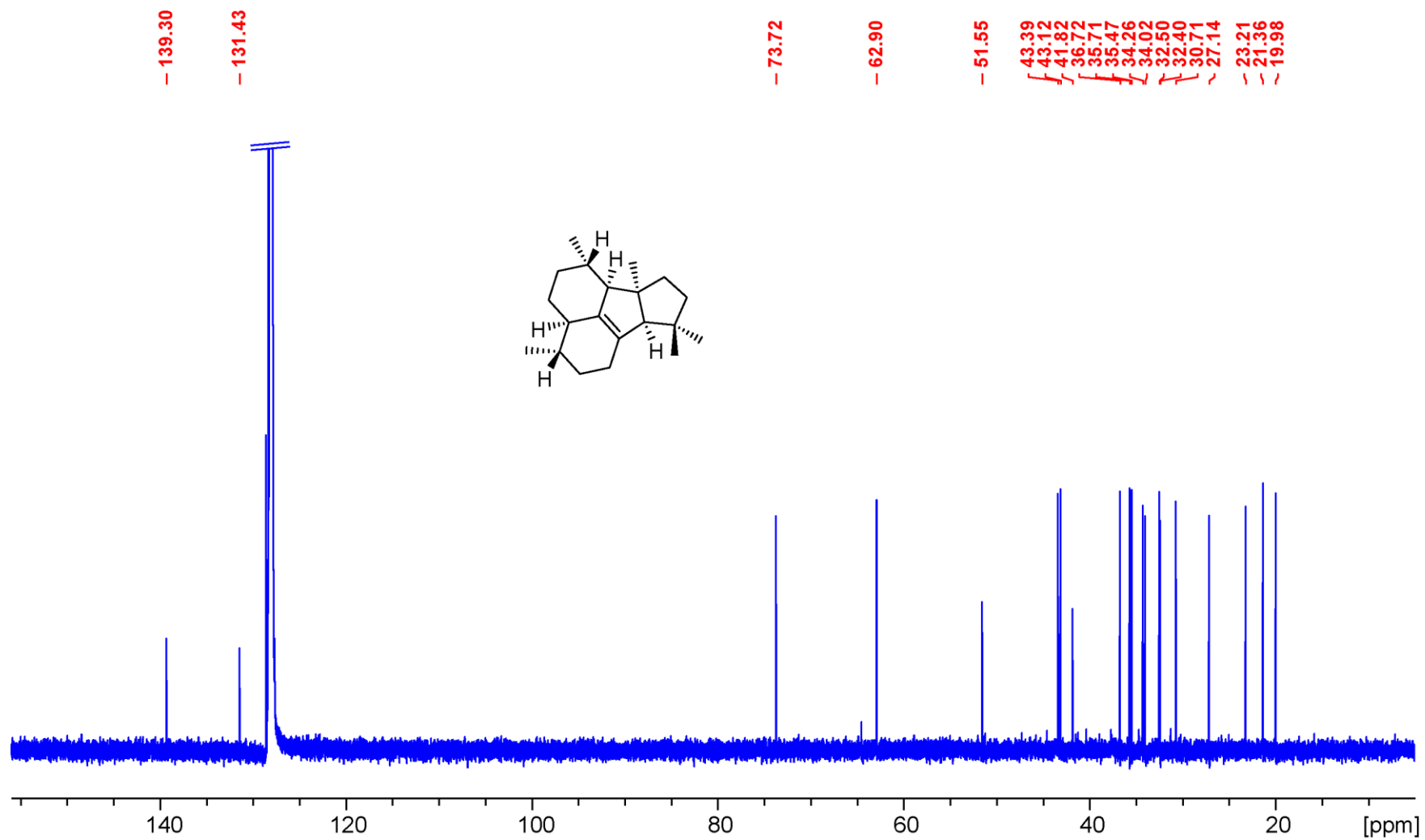
Figure S5. ^{1}H-NMR spectrum of **1** (700 MHz, C$_6$D$_6$).

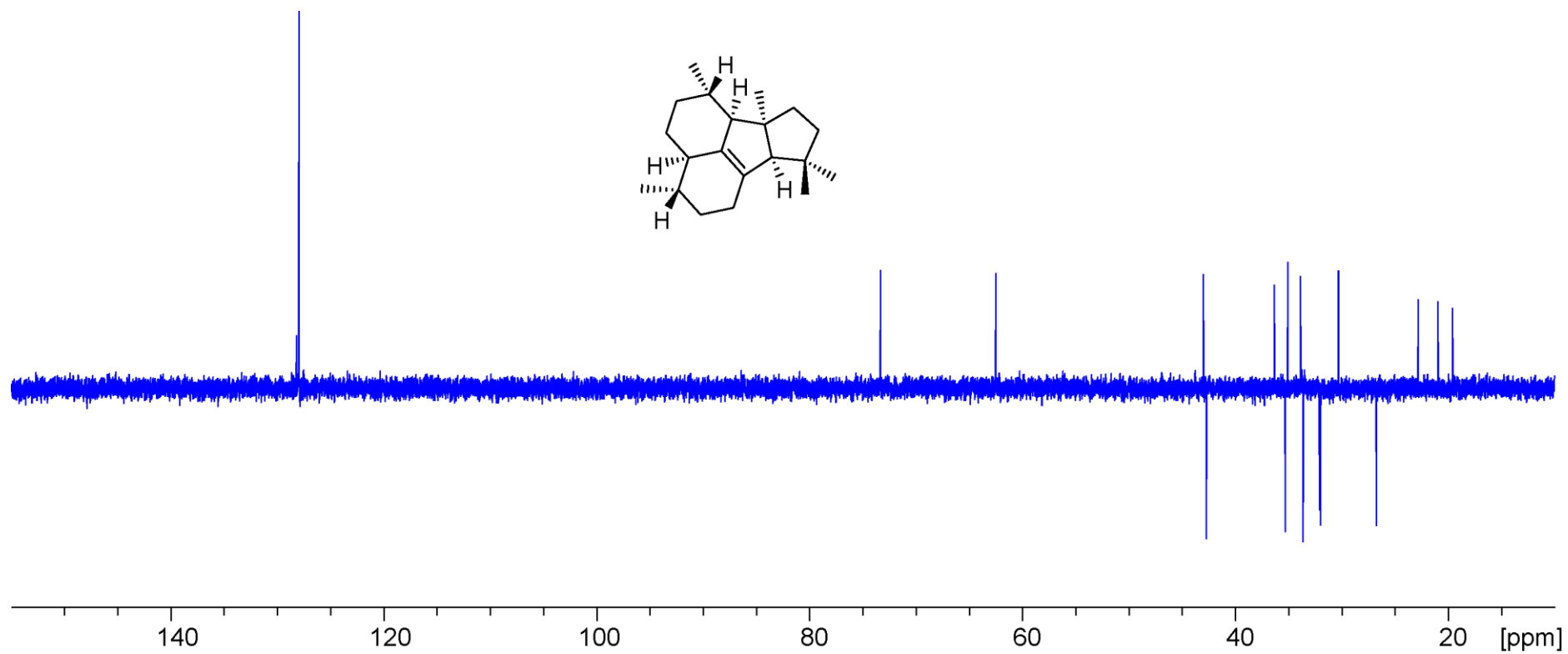**Figure S6.** ^{13}C-NMR spectrum of **1** (176 MHz, C$_6$D$_6$).

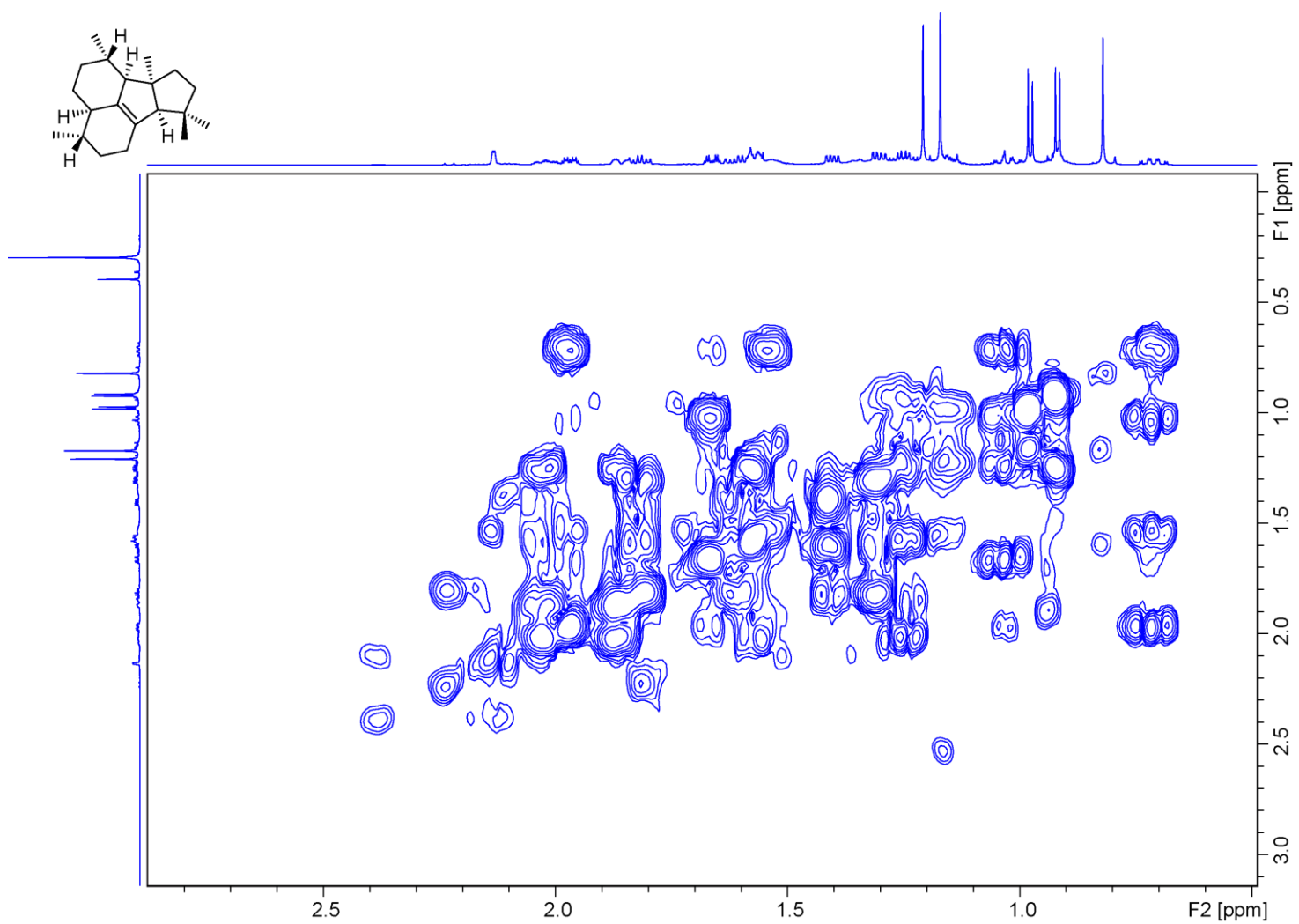**Figure S7.** ^{13}C-DEPT spectrum of **1** (176 MHz, C_6D_6).

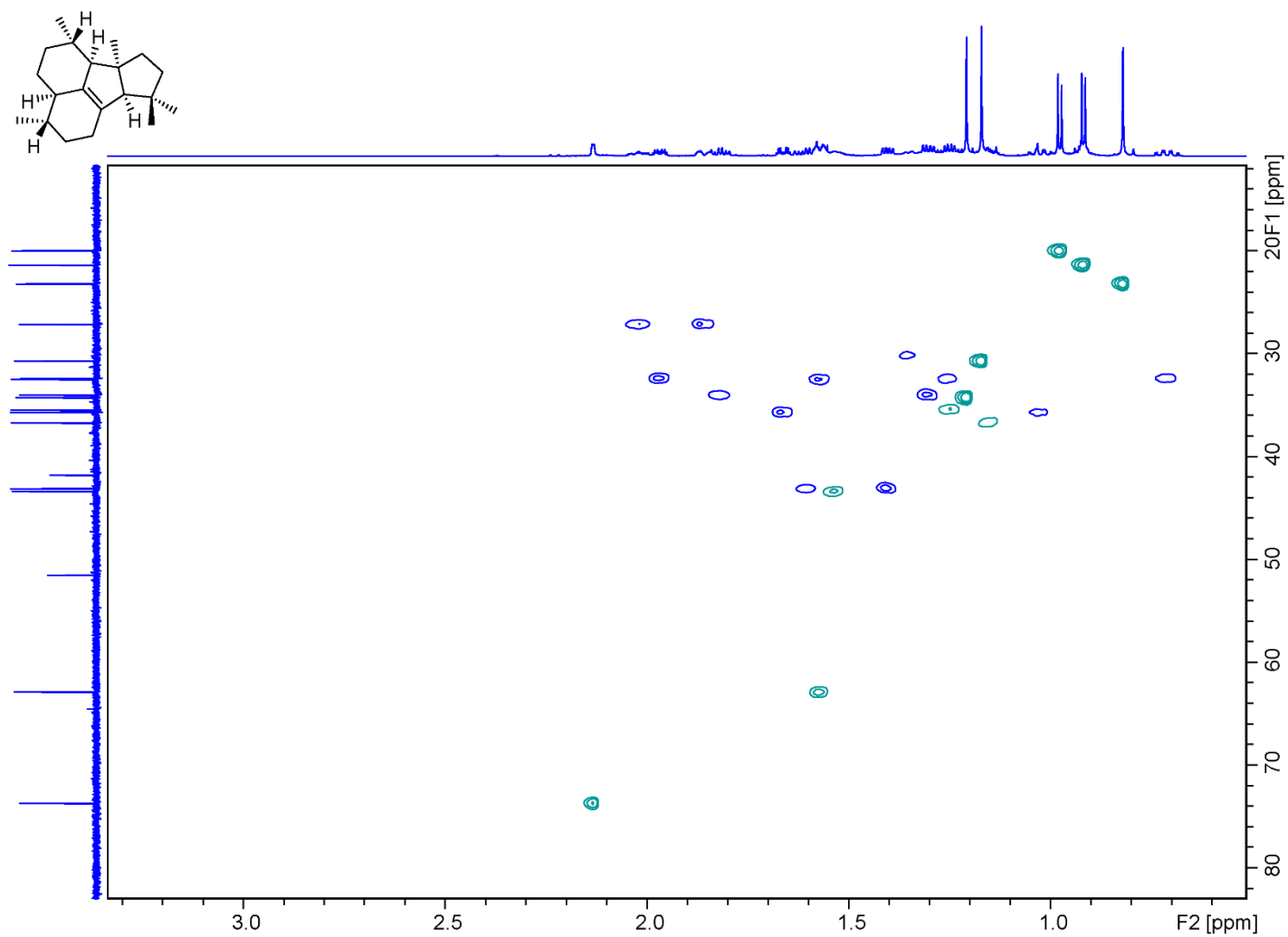**Figure S8.** $^1H,^1H$-COSY spectrum of **1** (700 MHz, C_6D_6).
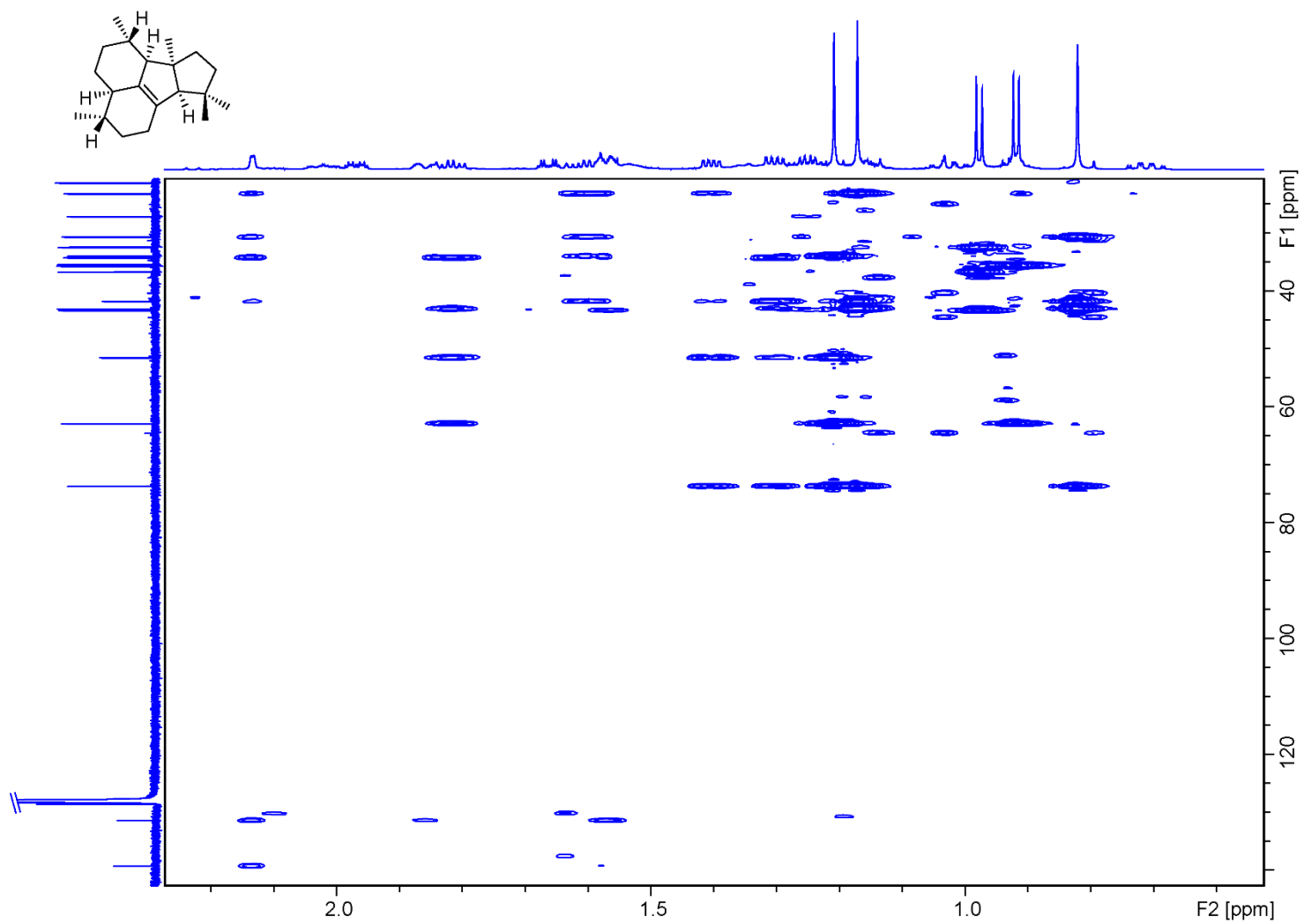
Figure S9. HSQC spectrum of **1** (C_6D_6).

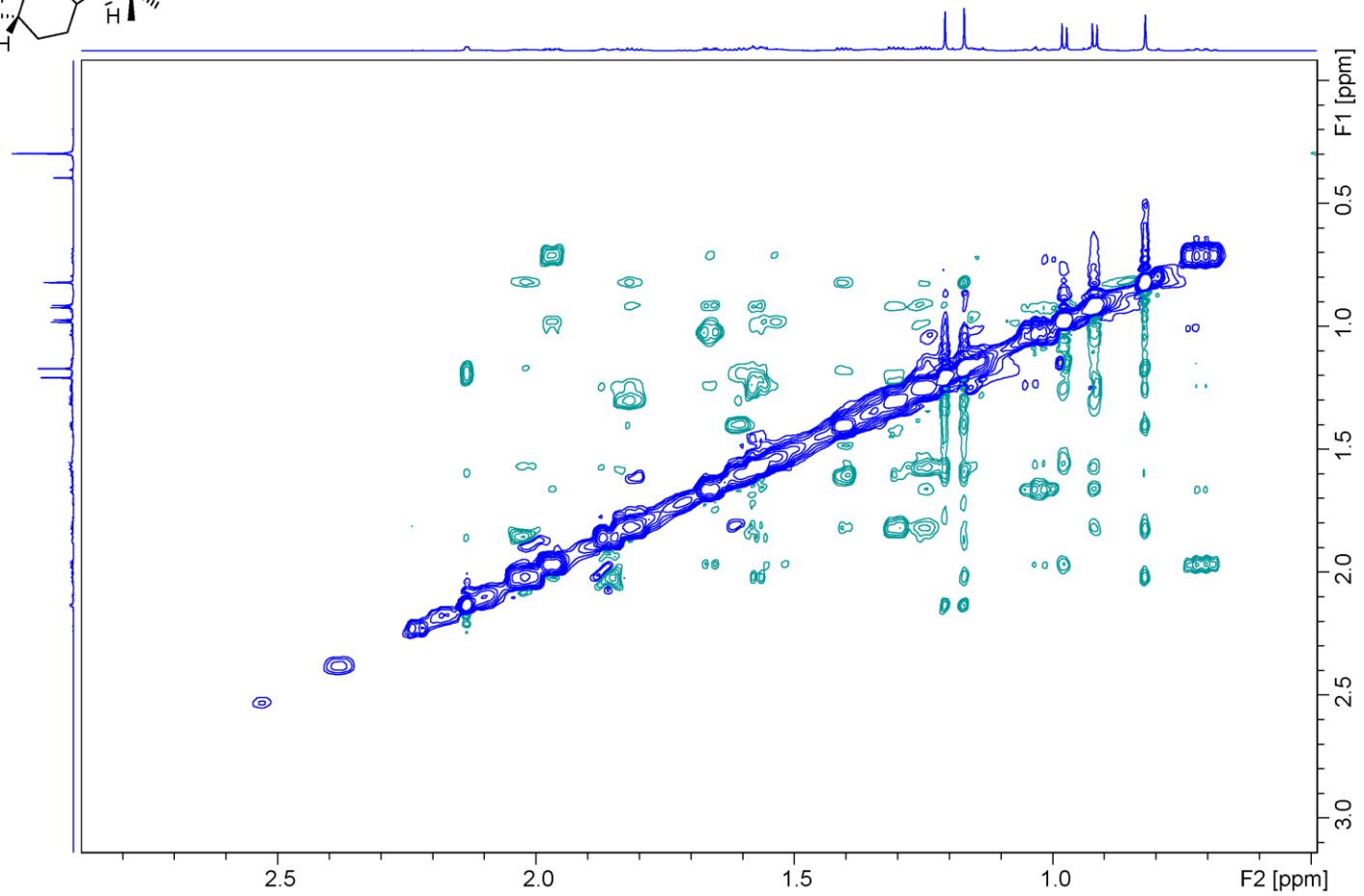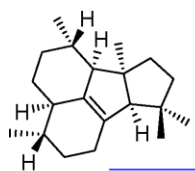**Figure S10.** HMBC spectrum of **1** (C_6D_6).

Figure S11. NOESY spectrum of **1** (C$_6$D$_6$).

15

Computational methods

All computed structures were geometry optimized without restrictions and were characterized as minima or as transition state structures by frequency analyses using the B97D3/6-31g(d,p) method with the density fitting approximation for s- and p-functions, including Grimme's empirical D3-dispersion correction[5] in Gaussian16.[6] Frequency computations also provided Gibbs corrections, which include Grimme's quasi-RRHO approach with a frequency cut-off value of 100.0 wave numbers using GoodVibes.[7,8] For single point energies, the mPW1PW91 functional was applied with the 6-311+G(d,p) basis set without density fitting and the ultra-fine integration grid, as this method was shown to be very reliable for examining carbocation cyclization and rearrangement reactions.[9-13] Conformational analyses were performed with xTB-GFN2 in the CREST 2.12 program (github.com/crest-lab), developed by the Grimme group.[14-18] Additionally, Orca 5.0.4[19] was used to localize transition state structures.

Table S3. Results of DFT calculations for the cyclisation cascade from GGPP to **1**.

Structure	Gibbs energy (298.15K) in Hartree	energy relative to A in kcal/mol	reaction barrier in kcal/mol	Gibbs free energy in kcal/mol
A	−781.709854	0.0		
A-TS	−781.690804	12.0	12.0	
B	−781.704738	3.2		3.2
B	−781.707534	1.5		
B-TS	−781.700262	6.0	4.6	
C	−781.698414	7.2		5.7
C	−781.700102	6.1		
C-TS	−781.701853	5.0	−1.1	
D	−781.709977	−0.1		−6.2
D	−781.709977	−0.1		
D-TS	−781.707568	1.4	1.5	
E	−781.741035	−19.6		−19.5
E	−781.741033	−19.6		
E-TS	−781.727775	−11.3	8.3	
F	−781.749734	−25.0		−5.5
F	−781.749731	−25.0		
F-TS	−781.753429	−27.3	−2.3	
G	−781.768851	−37.0		−12.0
G	−781.770143	−37.8		
G-TS	−781.768362	−36.7	0.3	
H	−781.778527	−43.1		−5.3
H	−781.778527	−43.1		
H-TS	−781.767828	−36.4	6.7	
I	−781.775876	−41.4		1.7
I	−781.762206	−32.9		
I-TS	−781.754193	−27.8	5.0	
J	−781.791289	−51.1		−18.3

E / kcal mol⁻¹

A-TS +12.0
B-TS +6.0
C-TS +5.0
D-TS +1.4
E-TS −11.3
F-TS −27.3
G-TS −36.7
H-TS −36.4
I-TS −27.8

+0.0 A
3.2 B
+1.5 B
+7.2 C
+6.1 C
−0.1 D
−19.6 E
−25.0 F
−37.0 G
−37.8 G
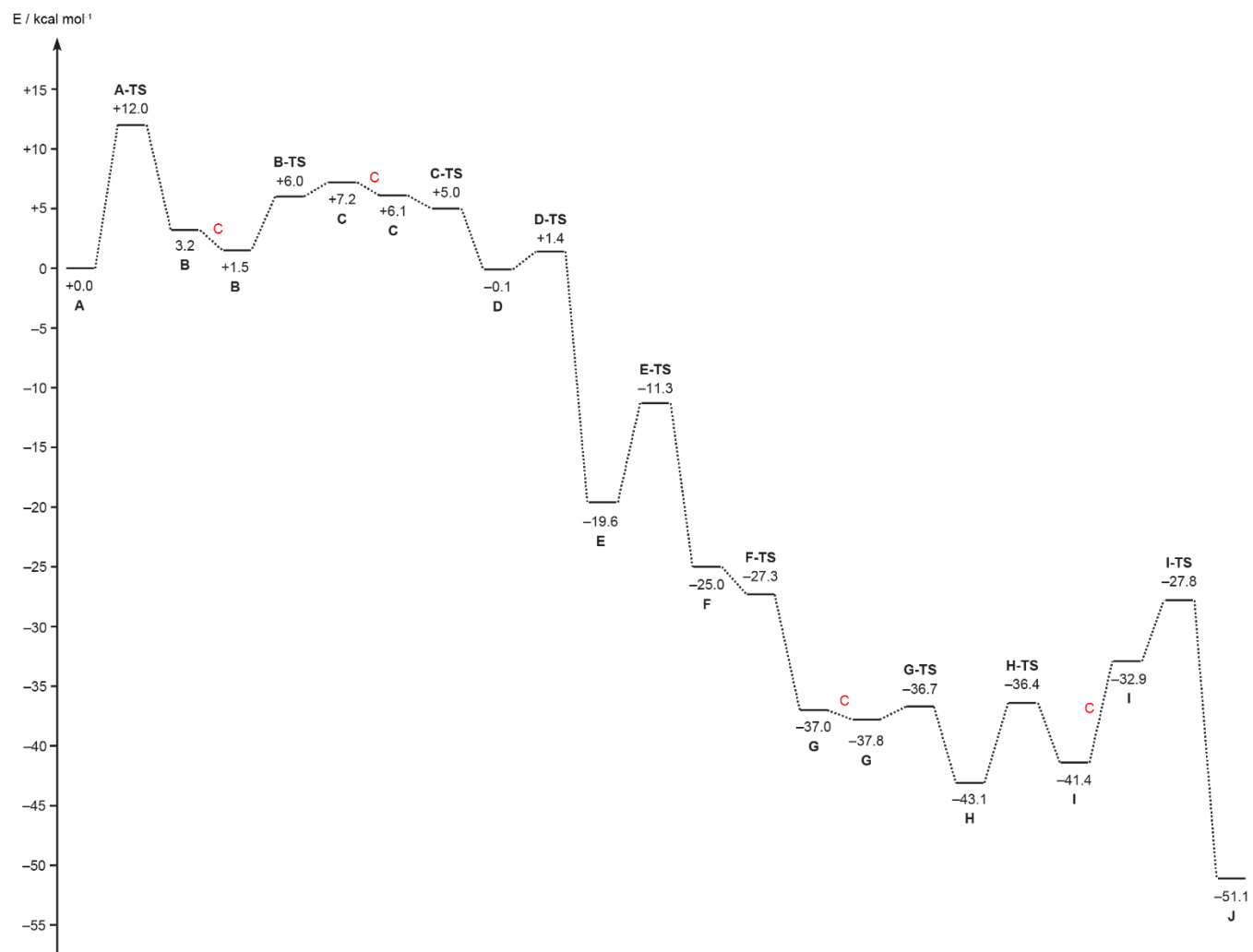−43.1 H
−41.4 I
−32.9 I
−51.1 J

Figure S12. Computed energy profile for the cyclisation of GGPP to **1**. Red letters C indicate required conformational changes of intermediates.

Isotopic labelling experiments

Isotopic labelling experiments were performed with the substrates and enzymes as listed in Table S4. Isotopic labelling experiments were carried out with ca. 1 mg labelled GGPP or its precursors in aqueous NH_4HCO_3 (0.5 mL; 25 mM), incubation buffer (up to 5 mL) and purified enzyme solutions (GGPPS: 1 mL, CpTS1: 1 mL, IDI: 0.5 mL) as listed in Table S4. The reaction mixtures were incubated at 30 °C overnight, and the products were extracted with C_6D_6 (200 μL, three times) or hexane (200 μL), and then analysed by NMR and/or GC/MS.

Table S4. Labelling experiments with CpTS1 and CpTS2.

entry	substrate	enzymes	results shown in
1	(1-^{13}C)GGPP[20]	CpTS1	Figures S13 and S14
2	(2-^{13}C)GGPP[21]	CpTS1	Figures S13 and S14
3	(3-^{13}C)GGPP[20]	CpTS1	Figures S13 and S14
4	(4-^{13}C)GGPP[20]	CpTS1	Figures S13 and S14
5	(1-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
6	(2-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
7	(3-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
8	(4-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
9	(1-^{13}C)GPP[23] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
10	(6-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
11	(7-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
12	(8-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
13	(9-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
14	(10-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
15	(11-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
16	(12-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
17	(9-^{13}C)GPP[24] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
18	(14-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
19	(15-^{13}C)FPP[22] + IPP	GGPPS,[21] CpTS1	Figures S13 and S14
20	(20-^{13}C)GGPP[21]	CpTS1	Figures S13 and S14
21	(3-^{13}C,2-^{2}H)GGPP[21]	CpTS1	Figure 1A
22	(3-^{13}C,2-^{2}H)FPP[15] + IPP	GGPPS,[21] CpTS1	Figure 1B
23	(2-^{13}C)FPP[22] + (1,1-^{2}H$_2$)IPP[26]	GGPPS,[21] CpTS1	Figure 1C
24	(R)-(1-^{13}C,1-^{2}H)IPP[27]	IDI,[28] GGPPS,[21] CpTS1	Figures S15 and S16
25	(S)-(1-^{13}C,1-^{2}H)IPP[27]	IDI,[28] GGPPS,[21] CpTS1	Figures S15 and S16
26	DMAPP + (E)-(4-^{13}C,4-^{2}H)IPP[29]	GGPPS,[21] CpTS1	Figure S17
27	DMAPP + (Z)-(4-^{13}C,4-^{2}H)IPP[29]	GGPPS,[21] CpTS1	Figure S17
28	DMAPP + (E)-(4-^{13}C,4-^{2}H)IPP[29]	FPPS,[30] CpTS2	Figure S28
29	DMAPP + (Z)-(4-^{13}C,4-^{2}H)IPP[29]	FPPS,[30] CpTS2	Figure S28
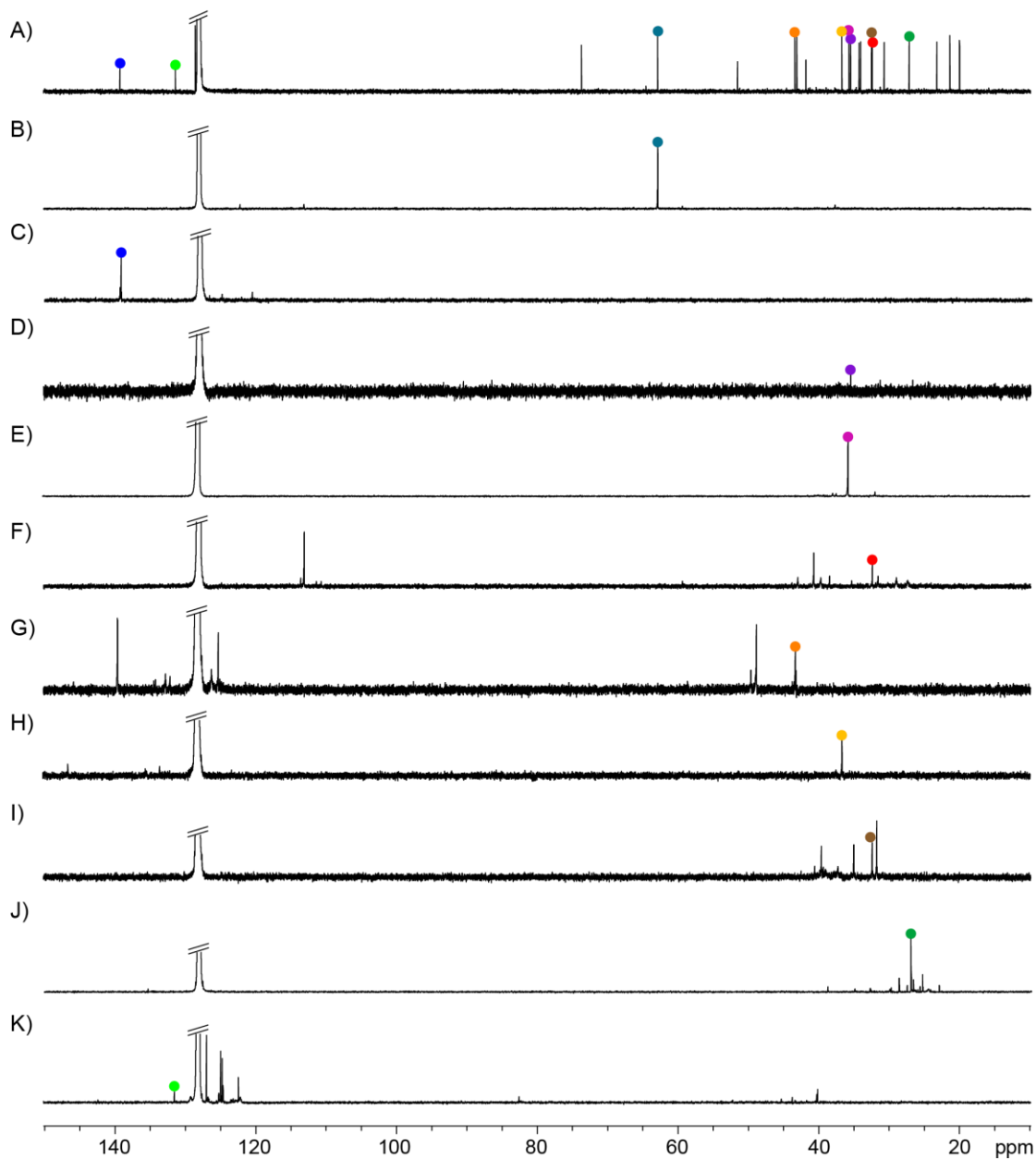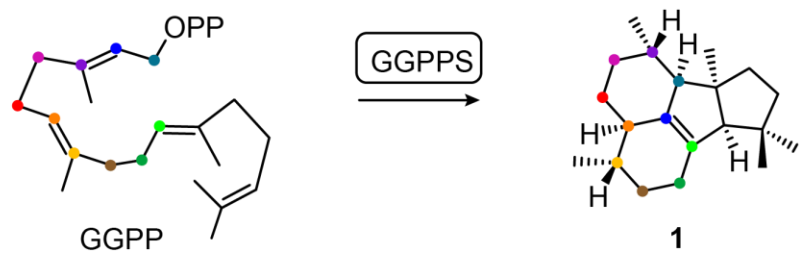
Figure S13. ^{13}C-NMR spectra of A) unlabelled **1**, and B) to K) labelled **1** from the ten isotopomers of (^{13}C)GGPP labelled at C1 – C10. Coloured dots correlate peaks to the individual carbons of **1**.
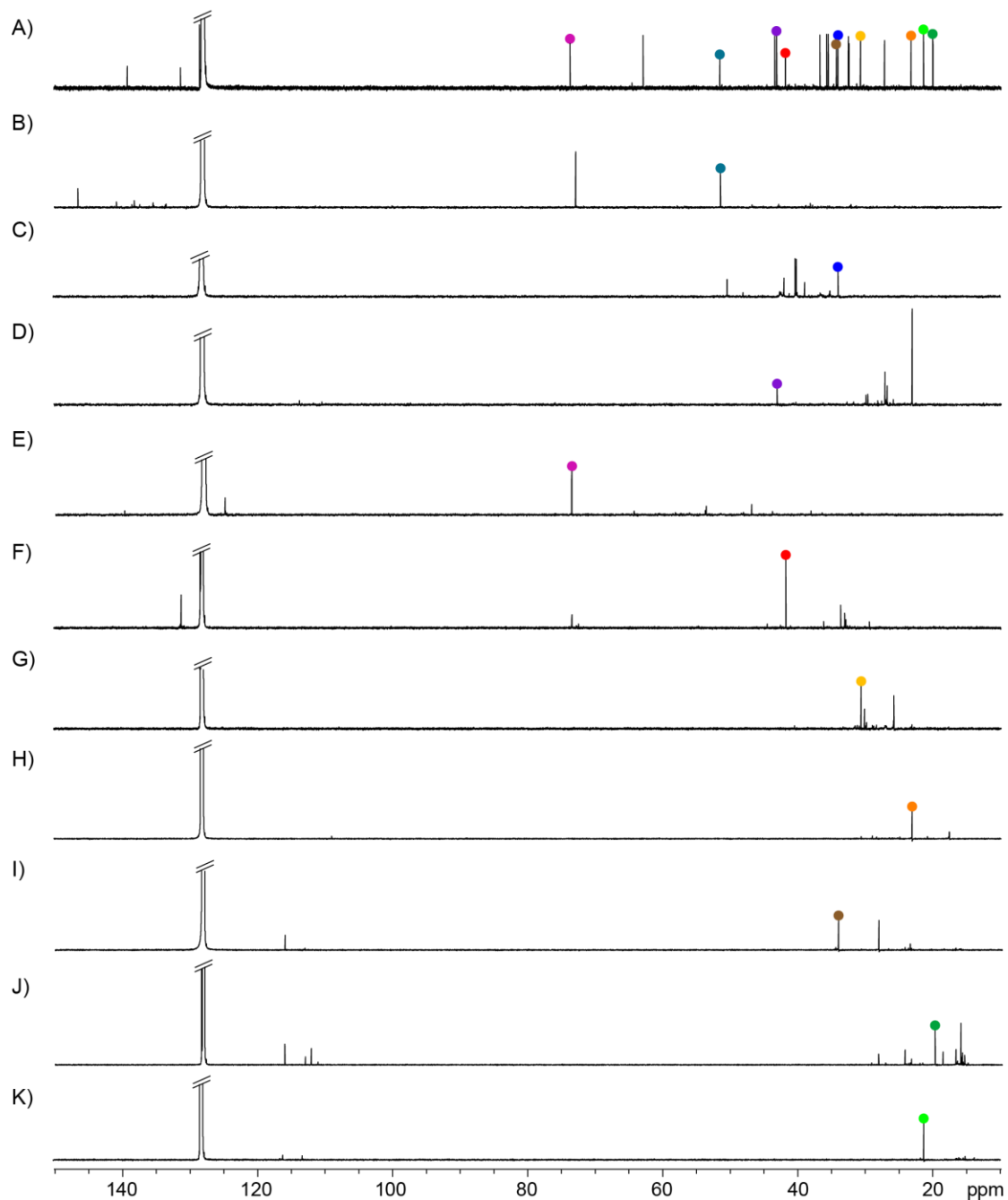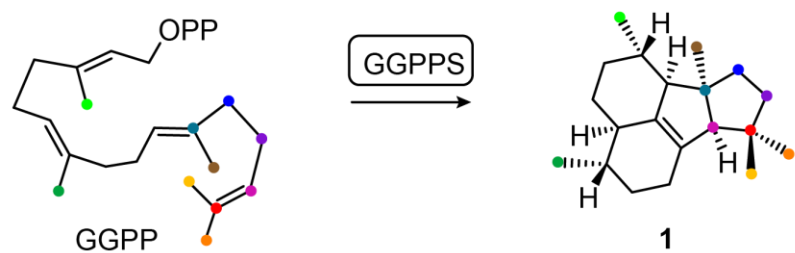
Figure S14. ^{13}C-NMR spectra of A) unlabelled **1**, and B) to K) labelled **1** from the ten isotopomers of (^{13}C)GGPP labelled at C11 – C20. Coloured dots correlate peaks to the individual carbons of **1**.
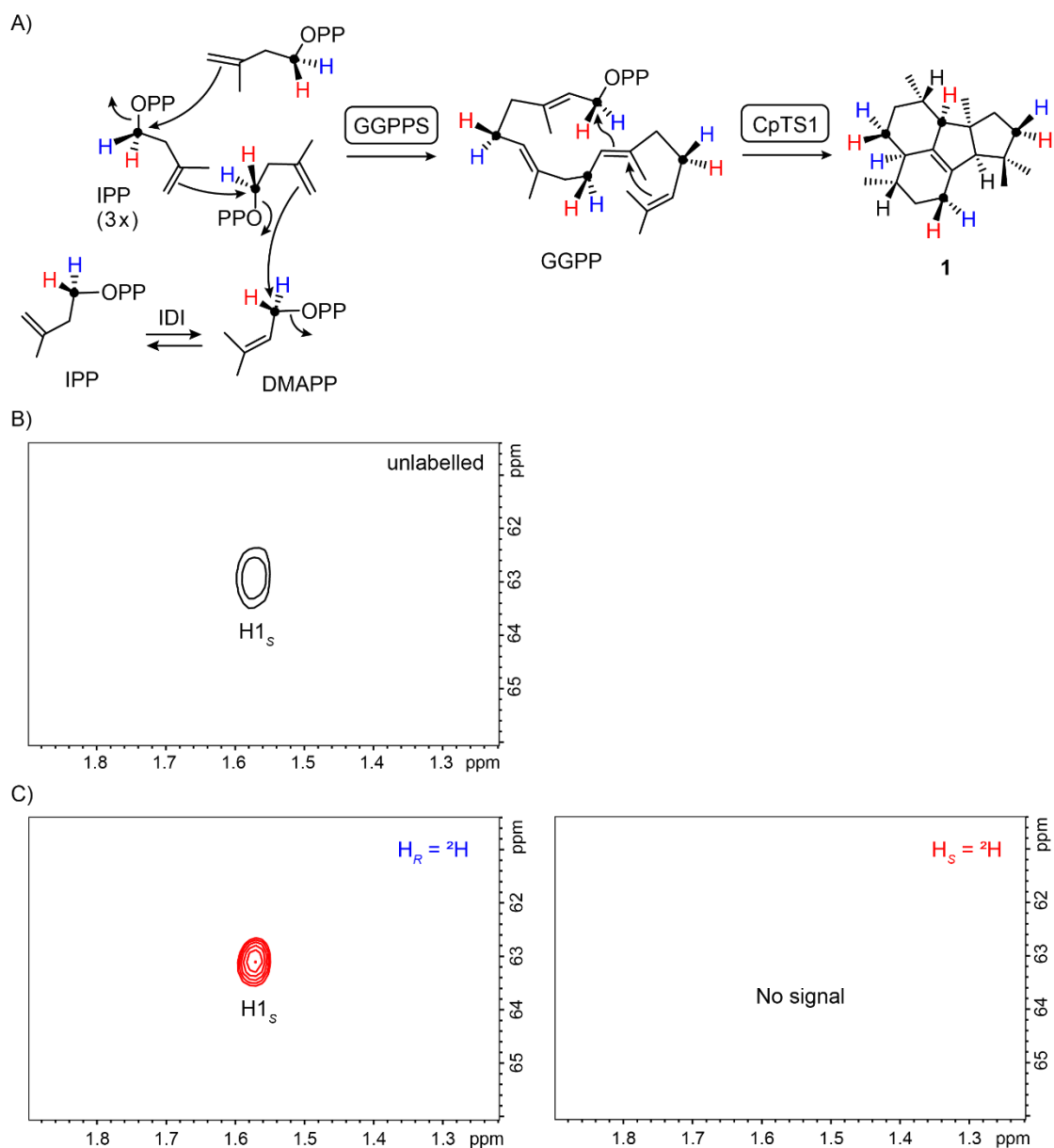
Figure S15. The 1,3-hydride shift from **H** to **I**. A) Formation of labelled **1** from (*R*)- or (*S*)-(1-^{13}C,1-^{2}H)IPP with IDI, GGPPS and CpTS1. Partial HSQC spectra of B) unlabelled **1** showing the crosspeak for the hydrogen bound to C1, C) labelled **1** obtained from (*R*)-(1-^{13}C,1-^{2}H)IPP, and D) labelled **1** obtained from (*S*)-(1-^{13}C,1-^{2}H)IPP. The observed signal for H1 in the experiment with (*R*)-(1-^{13}C,1-^{2}H)IPP and the missing signal in the experiment with (*S*)-(1-^{13}C,1-^{2}H)IPP confirm the selective migration of the 1-*pro-R* hydrogen in the hydride shift from **H** to **I**.
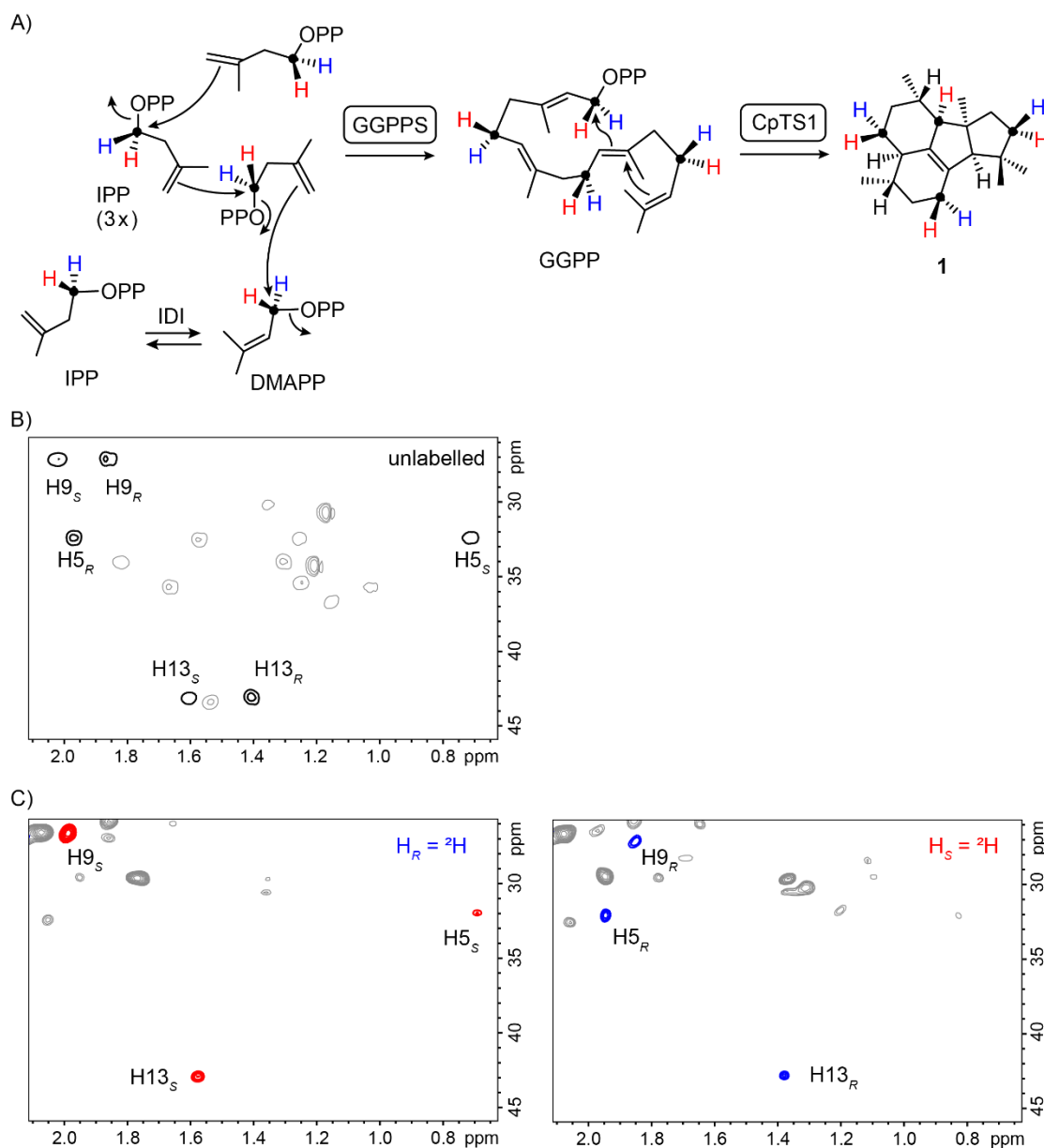
Figure S16. The absolute configuration of **1**. A) Formation of labelled **1** from (*R*)- or (*S*)-(1-^{13}C,1-^{2}H)IPP with IDI, GGPPS and CpTS1. B) Partial HSQC spectrum of unlabelled **1** showing the crosspeaks for the hydrogens at C5, C9 and C13. C) HSQC spectra for labelled **1** obtained from (*R*)- and (*S*)-(1-^{13}C,1-^{2}H)IPP. As a result of the enantioselective deuteration, in each labelling experiment one of the two crosspeaks is vanished, while the second crosspeak shows slight upfield shifts in both dimensions (^{1}H and ^{13}C chemical shifts). From the known absolute configuration at the deuterated carbons C5, C9 and C13 the absolute configuration of **1** can be inferred. Black dots represent ^{13}C-labelled carbons.
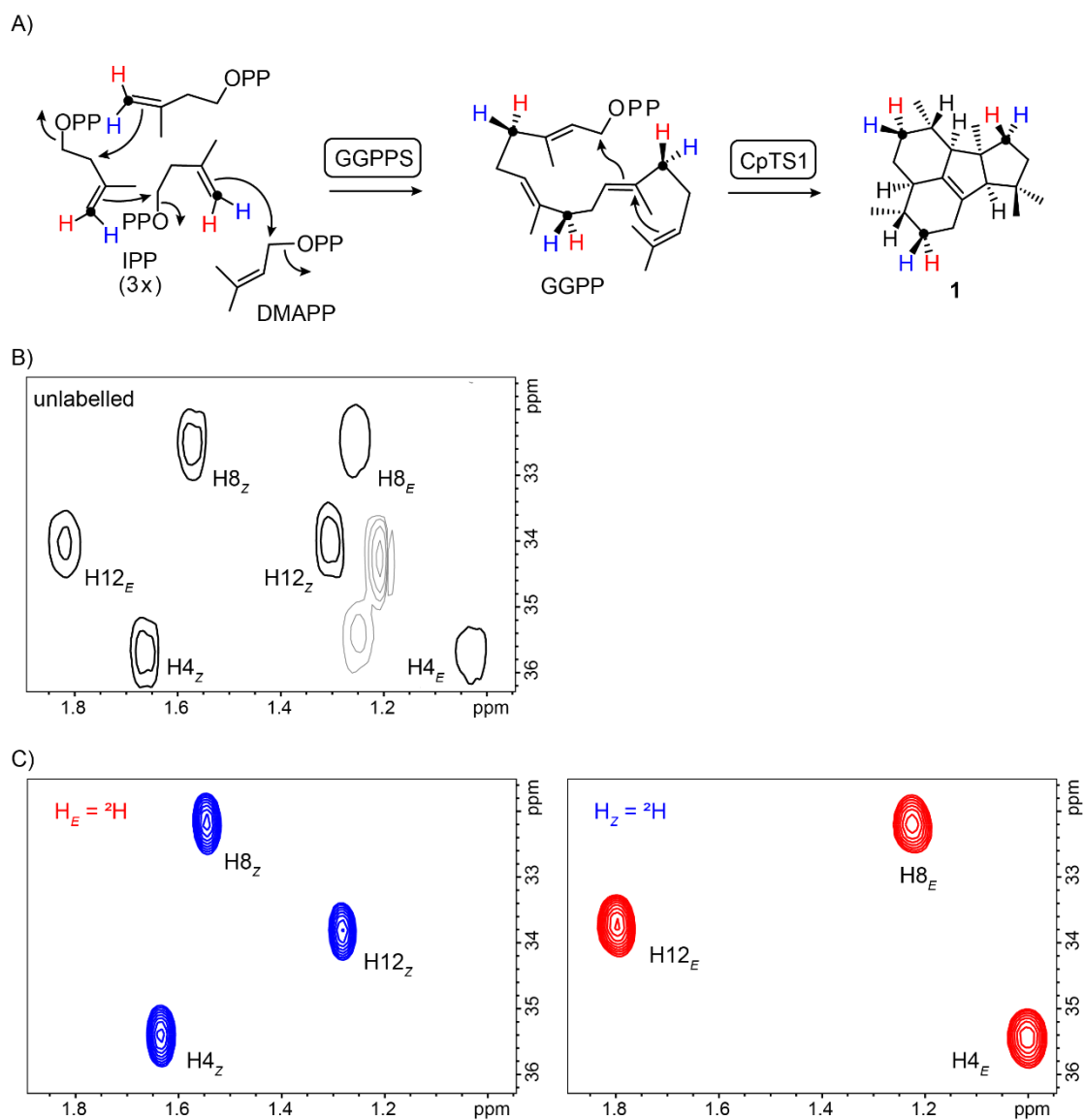
Figure S17. The absolute configuration of **1**. A) Formation of labelled **1** from DMAPP and (*E*)- or (*Z*)-(4-^{13}C,4-^{2}H)IPP with GGPPS and CpTS1. B) Partial HSQC spectrum of unlabelled **1** showing the crosspeaks for the hydrogens at C4, C8 and C12. C) HSQC spectra for labelled **1** obtained from (*E*)- and (*Z*)-(4-^{13}C,4-^{2}H)IPP. As a result of the enantioselective deuteration, in each labelling experiment one of the two crosspeaks is vanished, while the second crosspeak shows slight upfield shifts in both dimensions (^{1}H and ^{13}C chemical shifts). From the known absolute configuration at the deuterated carbons C4, C8 and C12 the absolute configuration of **1** can be inferred. Black dots represent ^{13}C-labelled carbons.

```
MLNTPYFIIPNTLRNWPWKRVLNPHQKVCEEEAADWMRSCGAFTPKSQDAFDRCAFGLLGSLAYP

HLGRDGLRIACDLMNMFFVIDEYSDVASGREARLQADIVMDALHTPLEPRPAGEWIGGEVTRQFW

ANAIRTATPSSQRRFVRNFQRYVDAVVQQAQDREIHCIRDVKSYFILRRQTIGAIPSLDLLTLEM

DLEDEVLDHPIVAKLLELCVDMILIGNDLYSYNVEQARGDDTHNFVRIVKDERKCNLNDALQWIS

DYHDRLADEFLNLMHNLPSFGSDLIDEQVKIYVDGLGNWVRANECWSFESERYFGKKGKLYLKSR

RIRLLPSSIALQGQNIDSQAAVDISDLPAAAGIIV
```

Figure S18. Amino acid sequence of CpTS2 from *Clitopilus passeckerianus* (accession number PP777466). Highly conserved motifs are highlighted in bold.
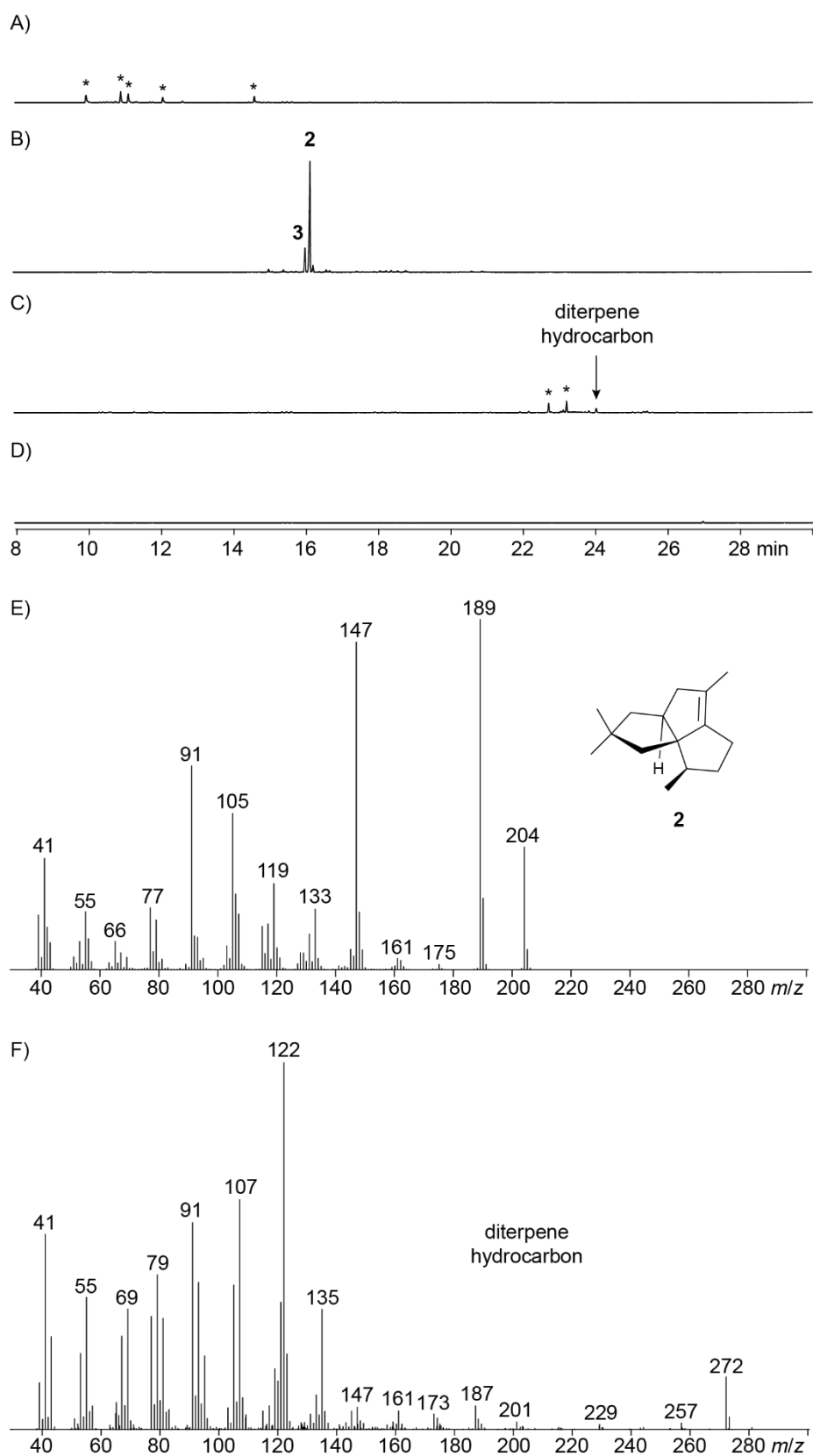
Figure S19. Substrate screening for CpTS2. Chromatograms of extracts obtained from an incubation of A) GPP, B) FPP, C) GGPP, and D) GFPP with CpTS2. EI mass spectra of E) isopentalenene (**1**) and F) an unidentified diterpene hydrocarbon. Asterisks indicate spontaneous hydrolysis products and contaminants such as plasticisers.

26

Table S5. GC/MS identification of terpenes formed from FPP by CpTS2.

Compound	I[a]	I (lit.)[b]	MS match[c]
$C_{15}H_{24}$ (unknown)	1281	–	–
$C_{15}H_{24}$ (unknown)	1308	–	–
pentalenene	1351	1339[31]	922
isopentalenene	1361	–	–
$C_{15}H_{24}$ (unknown)	1368	–	–
protoillud-6-ene	1388	1367[32]	842
asterisca-2(9),6-diene	1393	1381[30]	839
$C_{15}H_{24}$ (unknown)	1401	–	–

[a] Retention index on a HP5-MS GC column. [b] Retention index data from the literature on the same or a similar GC column. [c] Mass spectral match factor (0 – 999, 999 indicates identical mass spectra).
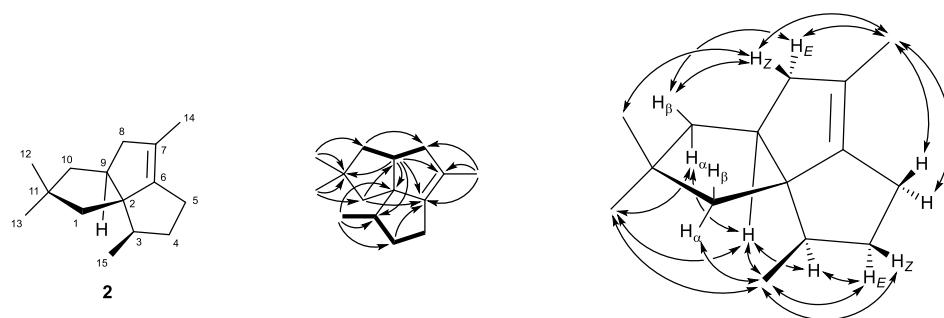
Figure S20. Structure elucidation of **2**.

Table S6. NMR data of isopentalenene (**2**) in C_6D_6 recorded at 298 K.

C[a]	type	^{13}C[b]	^{1}H[b]
1	CH_2	42.29	1.43 (m, H_α)
			1.21 (d, J = 13.0, H_β)
2	C_q	71.31	–
3	CH	41.66	1.50 (m)
4	CH_2	34.71	1.87 (dddd, J = 12.4, 8.6, 7.6, 3.2, H_E)
			1.36 (dddd, J = 12.4, 11.4, 11.4, 6.8, H_Z)
5	CH_2	21.56	2.07 (m, 2H)
6	C_q	149.24	–
7	C_q	124.87	–
8	CH_2	50.03	2.70 (ddm, J = 16.3, 10.0, H_E)
			2.43 (m, H_Z)
9	CH	43.88	2.38 (m)
10	CH_2	49.87	1.69 (dd, J = 12.8, 8.7, H_α)
			1.43 (m, H_β)
11	C_q	40.66	–
12	CH_3	31.10	1.05 (s)
13	CH_3	29.29	1.17 (s)
14	CH_3	14.26	1.53 (br s)
15	CH_3	14.77	0.89 (d, J = 6.7)

[a] Carbon numbering as shown in Figure S20. [b] Chemical shifts δ in ppm, multiplicity: s = singlet, d = doublet, m = multiplet, br = broad, coupling constants J are given in Hertz.
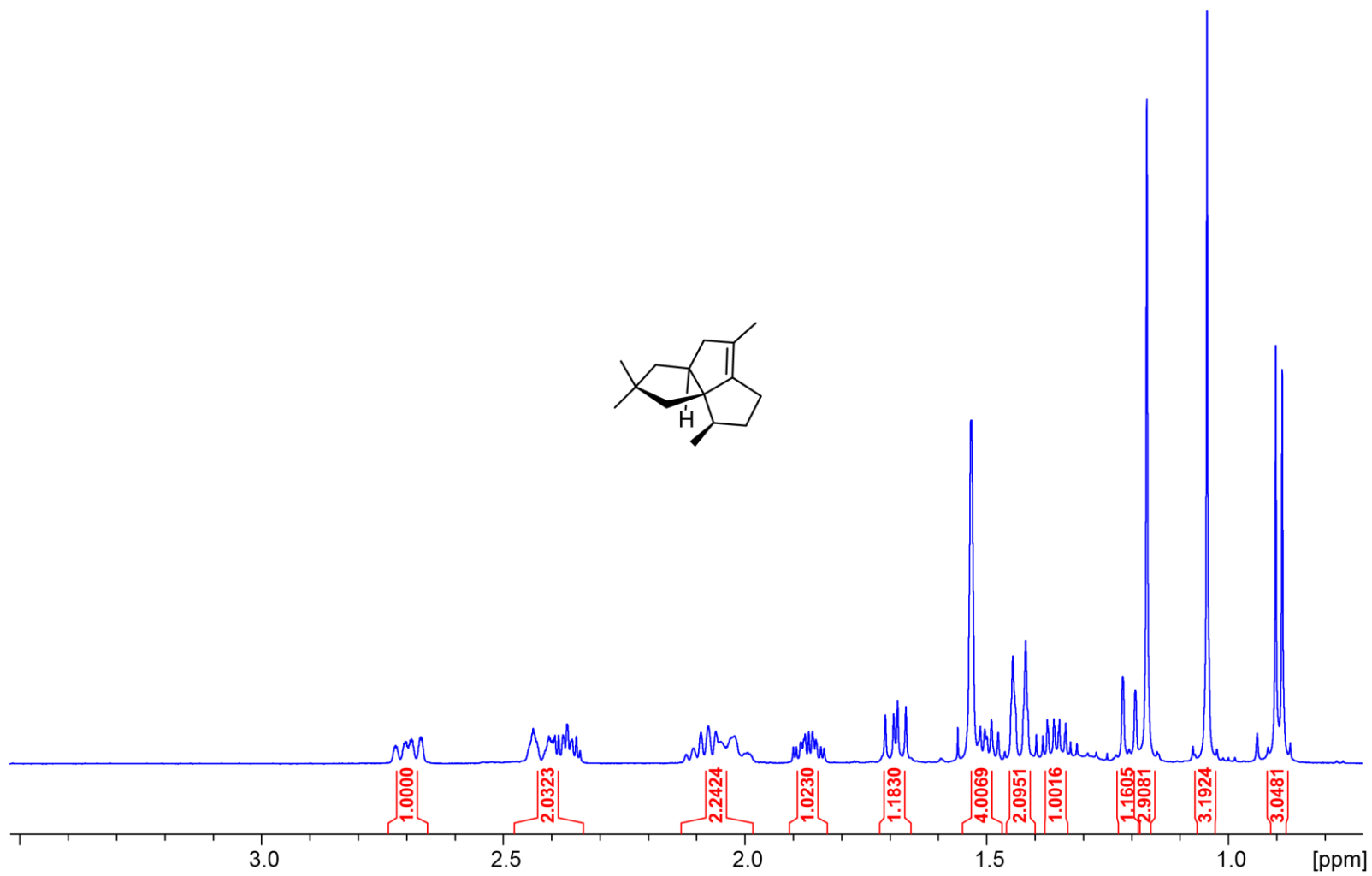
Figure S21. ^{1}H-NMR spectrum of **2** (500 MHz, C$_6$D$_6$).

29
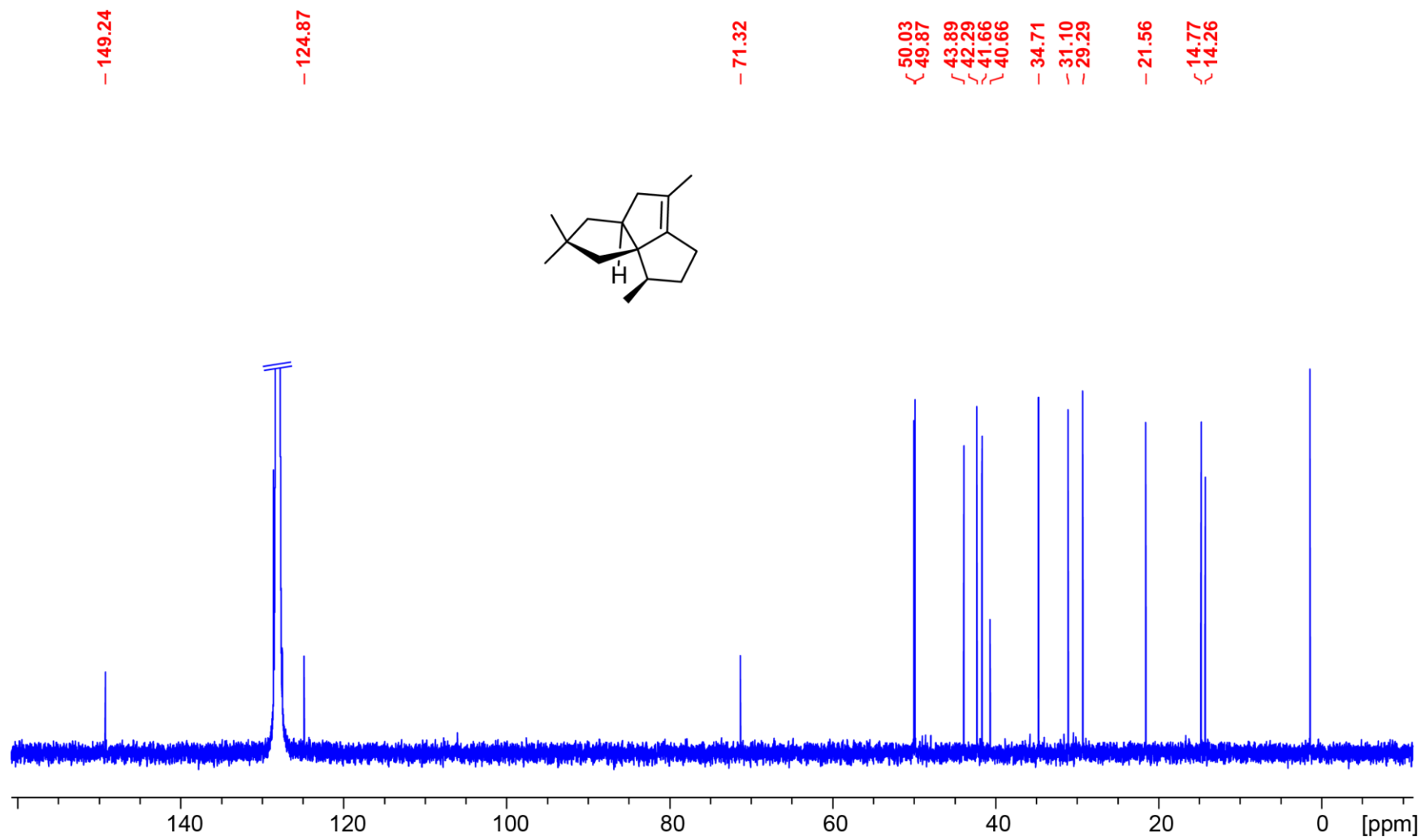
Figure S22. ^{13}C-NMR spectrum of **1** (125 MHz, C_6D_6).
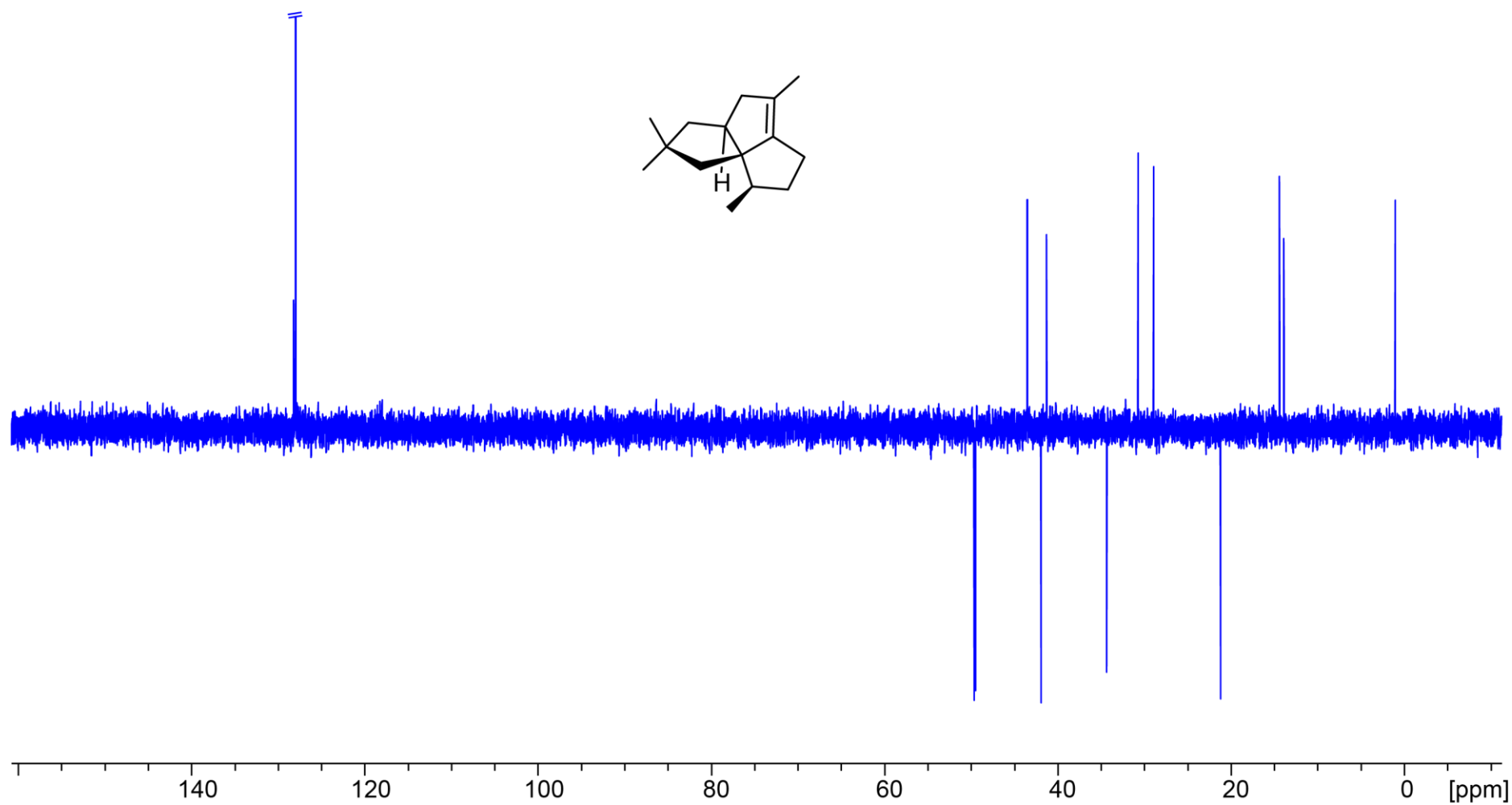
Figure S23. ^{13}C-DEPT spectrum of **1** (125 MHz, C_6D_6).
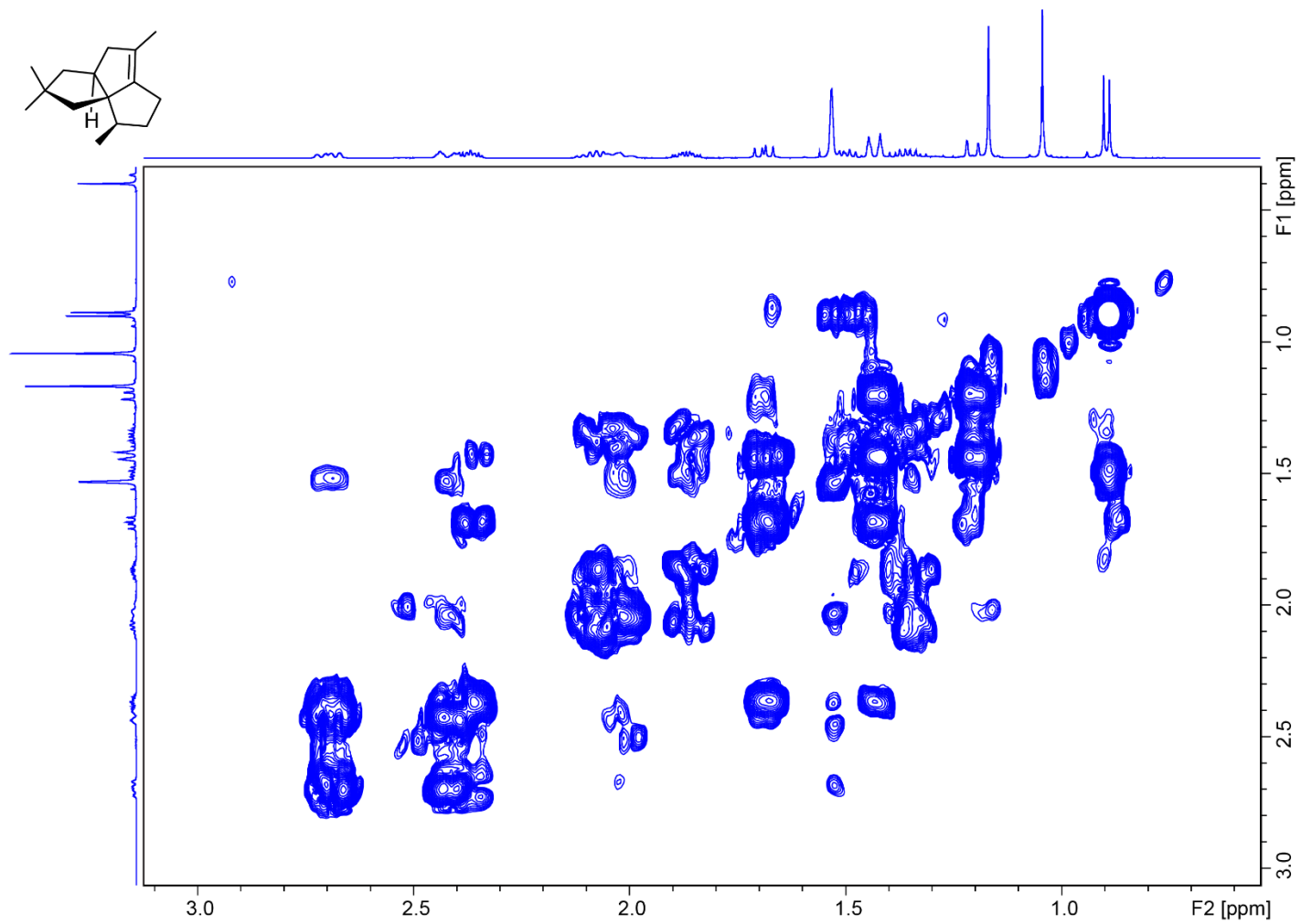
Figure S24. ^{1}H,^{1}H-COSY spectrum of **1** (500 MHz, C$_6$D$_6$).
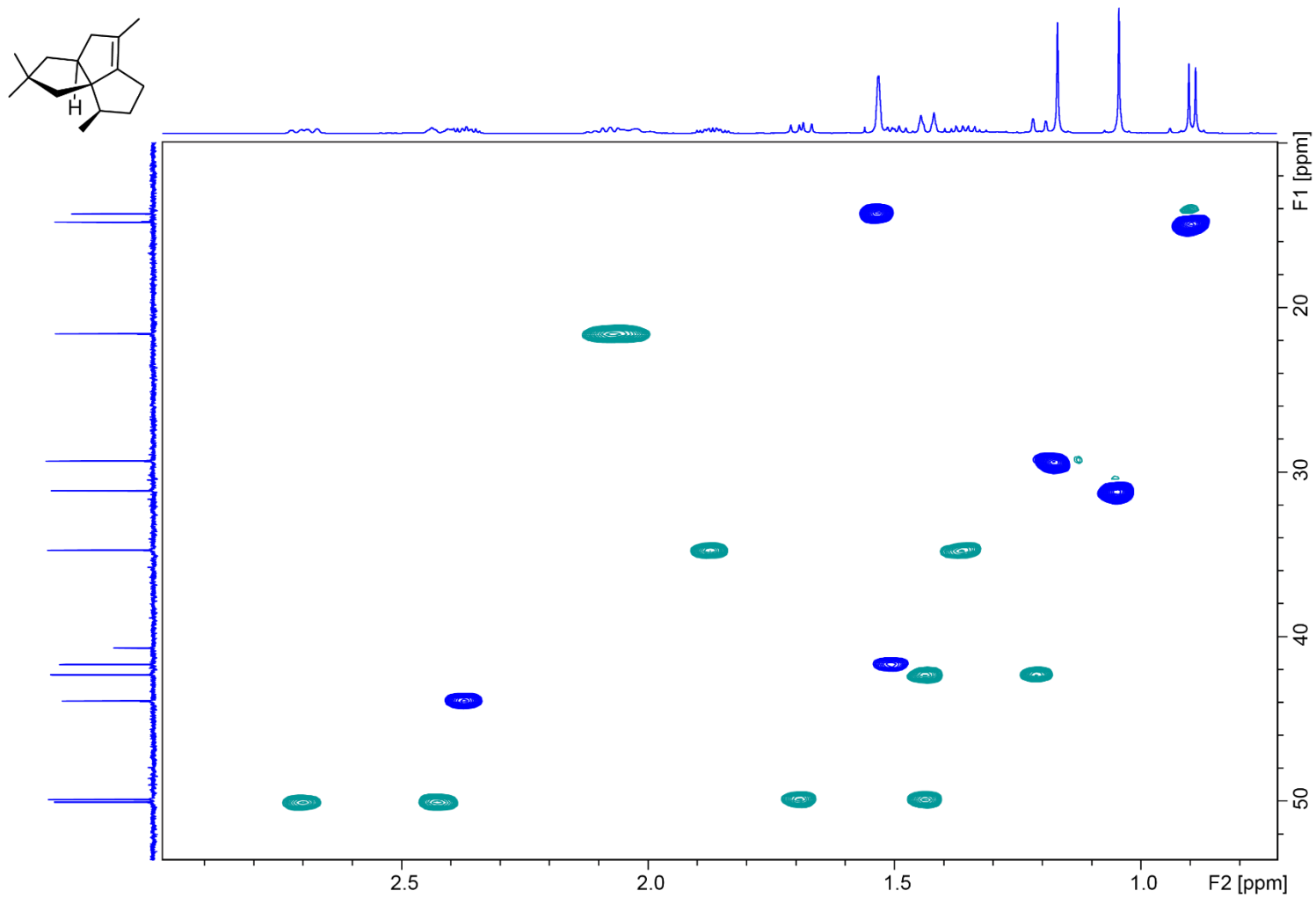
Figure S25. HSQC spectrum of **1** (C_6D_6).
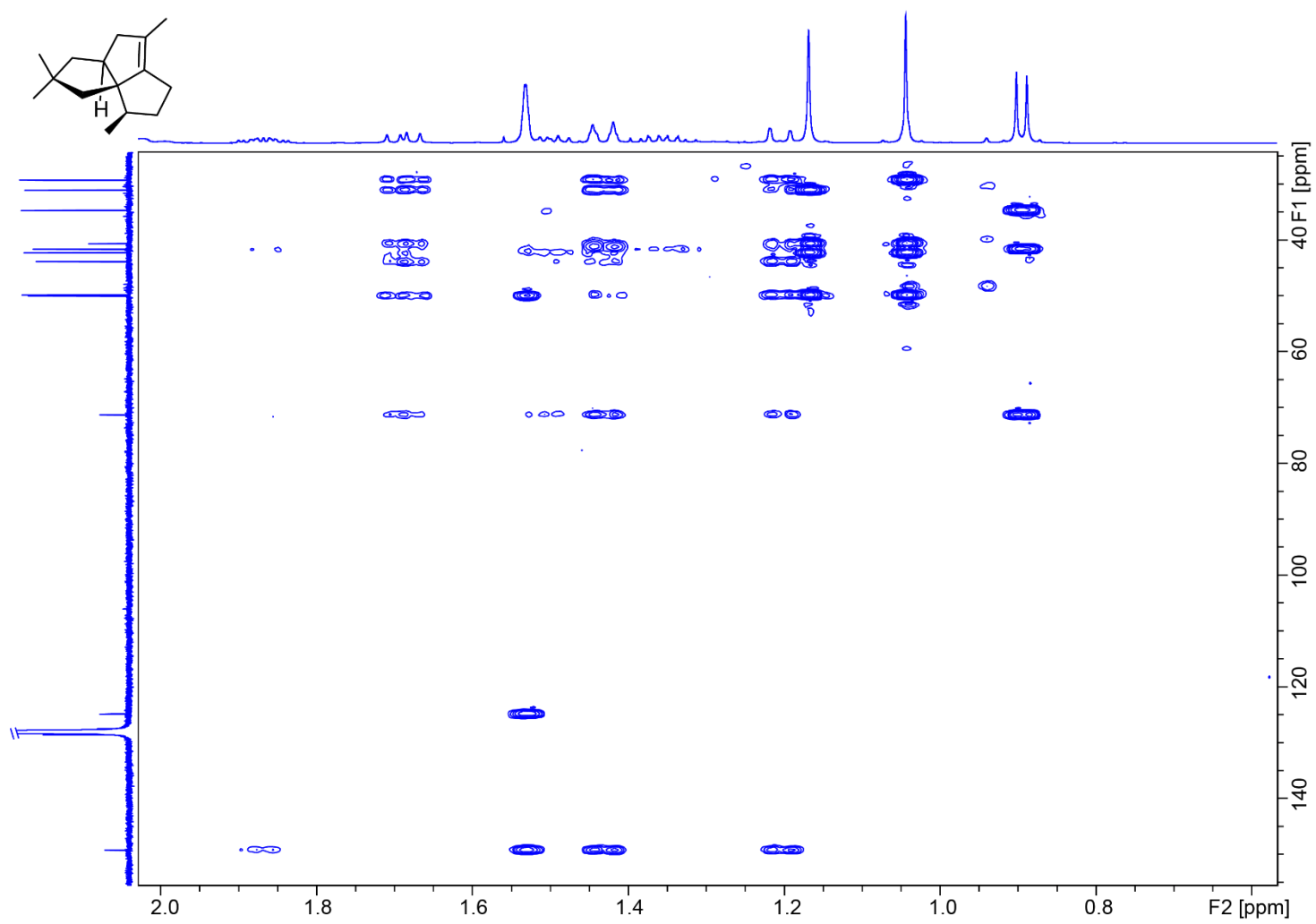
Figure S26. HMBC spectrum of **1** (C_6D_6).
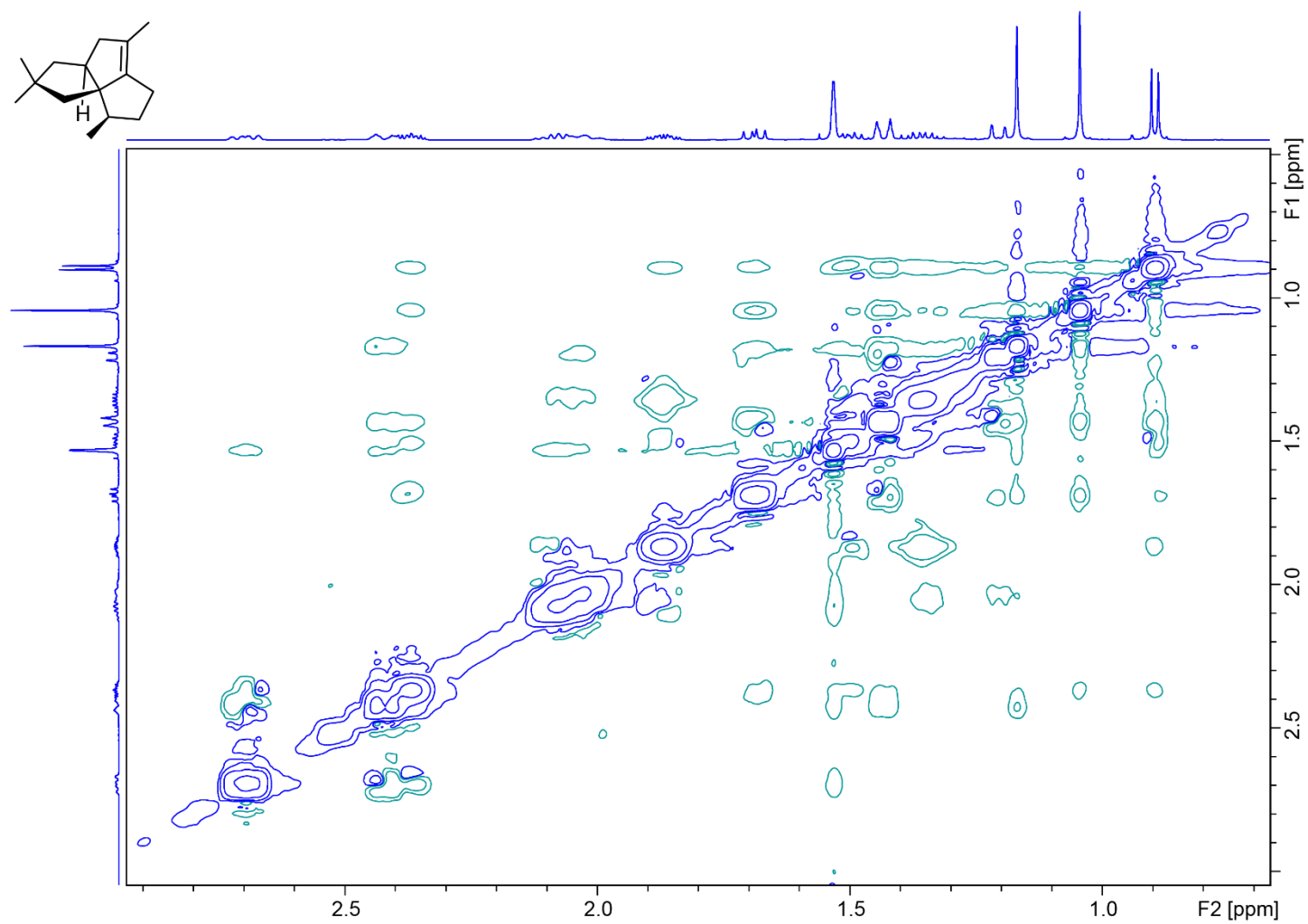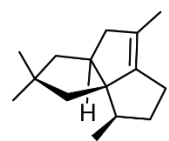
Figure S27. NOESY spectrum of **1** (C_6D_6).
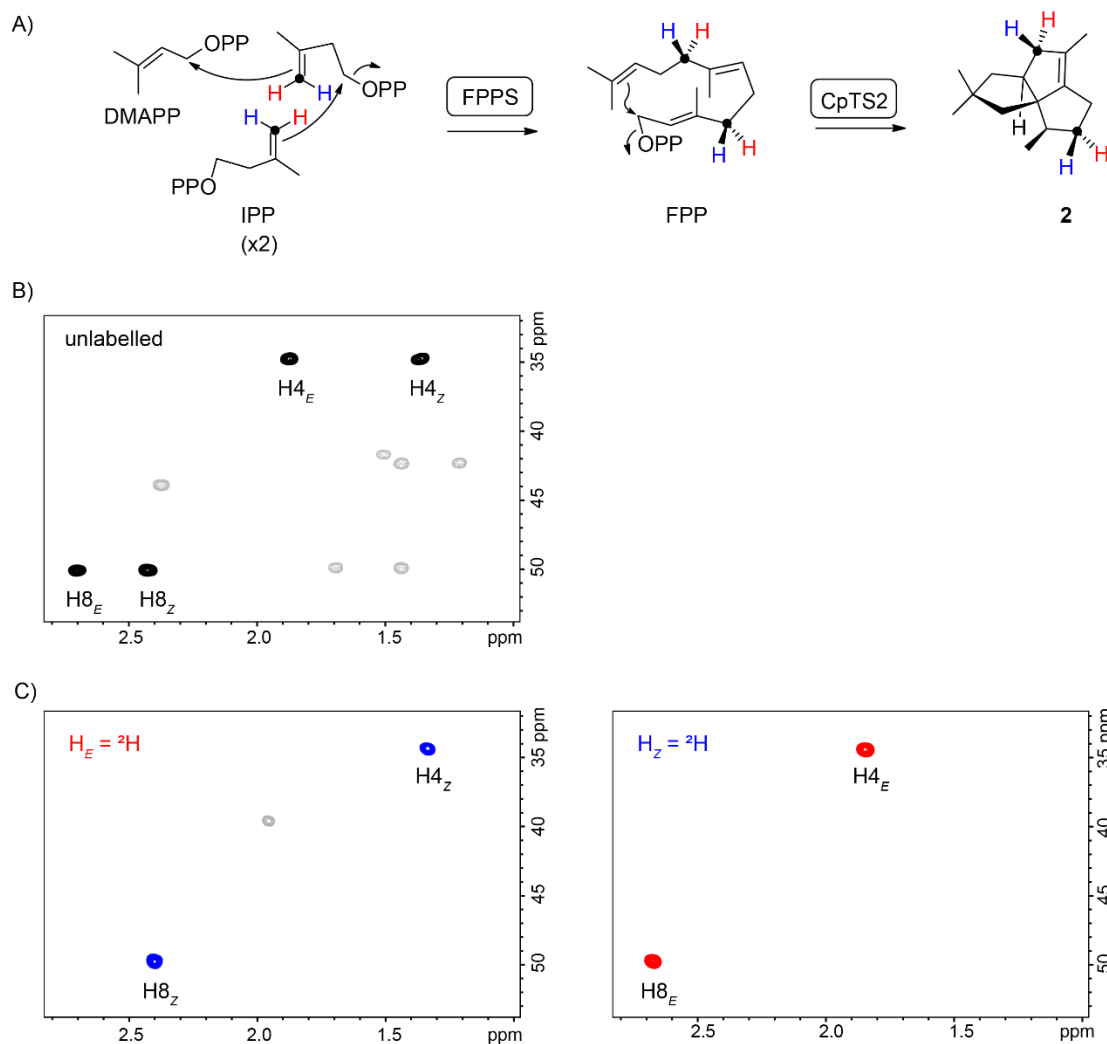
Figure S28. The absolute configuration of **2**. A) Formation of labelled **2** from DMAPP and (*E*)- or (*Z*)-(4-^{13}C,4-^{2}H)IPP with FPPS and CpTS2. B) Partial HSQC spectrum of unlabelled **2** showing the crosspeaks for the hydrogens at C4 and C8. C) HSQC spectra for labelled **2** obtained from (*E*)- and (*Z*)-(4-^{13}C,4-^{2}H)IPP. As a result of the enantioselective deuteration, in each labelling experiment one of the two crosspeaks is vanished, while the second crosspeak shows slight upfield shifts in both dimensions (^{1}H and ^{13}C chemical shifts). From the known absolute configuration at the deuterated carbons C4 and C8 the absolute configuration of **2** can be inferred. Black dots represent ^{13}C-labelled carbons.

Cartesian coordinates

Cartesian coordinates, Gibbs energies (G"..." in Hartree) and imagininary frequencies of transition states (T-"..." in cm^{-1}) (mPW1PW91/6-311+G(d,p)//B97D3/6-31G(d,p)-sp-density-fitting, 1 bar, 298.15 K)

A (G781.709854E_MeAcr11qn_mAPW)

C	-0.710983	1.769821	-1.001870
C	0.353692	2.597518	-0.224624
C	1.749170	2.009437	-0.207357
C	1.022583	-1.441218	0.954112
C	-0.048457	-1.966626	0.038603
C	-0.538973	-0.938571	-1.049725
H	1.569070	1.476880	1.806742
H	-1.616960	2.394833	-1.040214
H	-0.005669	2.738309	0.807797
C	2.222794	1.442240	0.925818
C	2.366633	-1.523586	0.814879
H	-0.907881	-2.286360	0.653476
C	3.253742	-0.708273	1.739487
C	3.517463	0.709496	1.145567
H	4.217696	-1.210647	1.908310
H	4.096602	0.621518	0.215892
H	0.672020	-0.875163	1.823811
C	3.077359	-2.292135	-0.269732
H	3.805515	-2.986175	0.177536
H	2.405287	-2.870456	-0.911991
H	3.656891	-1.613515	-0.916037
H	2.770221	-0.592039	2.722077
H	0.285881	-2.867674	-0.496872
H	4.151818	1.266969	1.855270
H	0.380851	3.597129	-0.690564
H	-0.402918	1.645287	-2.048397
C	-1.063250	0.391703	-0.360012
H	-0.657395	0.423537	0.660298
C	0.589344	-0.737831	-2.070121
H	0.871038	-1.705253	-2.506081
H	0.286209	-0.086702	-2.899307
H	1.474741	-0.309065	-1.593778
C	-1.800944	-1.511743	-1.738496
H	-1.706917	-2.583836	-1.965266
H	-1.991047	-0.977600	-2.682466
C	-2.617148	0.248211	-0.300425
H	-3.104448	0.889577	-1.051739
C	-2.972412	-1.255543	-0.782562
H	-2.966473	-1.961971	0.058186
H	-3.965025	-1.277234	-1.244399
C	-3.322516	0.337579	0.964562
C	-4.751383	0.728745	0.989365
H	-4.841599	1.657109	1.584840
H	-5.174519	0.906212	-0.004042
H	-5.350859	-0.014033	1.539499
C	-2.664133	0.003565	2.250513

H	-1.895491	-0.771688	2.135557
H	-2.121075	0.908370	2.584688
H	-3.376098	-0.263069	3.039127
C	2.538806	2.152431	-1.488691
H	1.920983	1.945399	-2.373502
H	2.893778	3.190563	-1.592926
H	3.417452	1.499462	-1.531270

A-TS (TS_G781.690804T-152_MeAcr11_mABPW)

C	0.327505	2.161519	0.549079
C	-0.833944	2.652728	-0.354671
C	-2.118988	1.861157	-0.199707
C	-0.856745	-1.604602	-0.632102
C	0.303012	-1.788902	0.303777
C	0.764008	-0.523493	1.115050
H	-1.898667	0.997021	-2.089317
H	1.115417	2.930458	0.512367
H	-0.500699	2.637193	-1.404236
C	-2.520870	1.032852	-1.185669
C	-2.172579	-1.800753	-0.387615
H	1.154208	-2.193673	-0.262243
C	-3.186394	-1.384216	-1.436291
C	-3.680533	0.076742	-1.193190
H	-4.055389	-2.058917	-1.432732
H	-4.254533	0.123996	-0.257809
H	-0.609035	-1.261376	-1.642636
C	-2.743334	-2.325503	0.905742
H	-3.386593	-3.196065	0.707195
H	-1.983790	-2.625646	1.635330
H	-3.387256	-1.569689	1.382700
H	-2.735090	-1.438197	-2.438846
H	0.071569	-2.547901	1.066537
H	-4.382551	0.334727	-2.002969
H	-1.012746	3.709752	-0.095328
H	-0.000288	2.130841	1.593645
C	0.940613	0.791133	0.107240
H	0.456927	0.468904	-0.827469
C	-0.259282	-0.236165	2.215783
H	-0.374729	-1.134375	2.837498
H	0.053908	0.577485	2.880737
H	-1.236824	0.004109	1.787360
C	2.156720	-0.802553	1.730987
H	2.124660	-1.757798	2.277810
H	2.392314	-0.024880	2.471896
C	2.386983	0.930914	-0.071559
H	2.881657	1.683488	0.559511
C	3.294486	-0.902025	0.701460
H	3.313797	-1.881179	0.209582
H	4.265466	-0.678003	1.149346
C	3.279317	0.067883	-0.774393
C	4.714112	0.568003	-0.978174
H	4.763675	1.176760	-1.890667
H	5.065476	1.175751	-0.134921

H	5.397309	-0.280728	-1.107234
C	2.771653	-0.737817	-1.971354
H	1.734812	-1.067029	-1.876646
H	2.845612	-0.107096	-2.867602
H	3.405741	-1.617504	-2.136330
C	-2.889669	2.111414	1.078305
H	-2.233004	2.126270	1.960545
H	-3.371076	3.101665	1.037773
H	-3.676706	1.371740	1.260953

B (G781.704738E_MeAcr11qp_mBPW)

C	0.453625	1.924018	0.704469
C	-0.672896	2.686529	-0.029062
C	-1.992762	1.946811	0.013865
C	-0.904881	-1.699533	-0.781921
C	0.232820	-2.041576	0.152308
C	0.750339	-0.813142	1.003609
H	-1.808131	1.360521	-1.991683
H	1.371351	2.528479	0.701452
H	-0.365623	2.871147	-1.070207
C	-2.415818	1.265926	-1.081947
C	-2.237909	-1.701405	-0.541608
H	1.055136	-2.439234	-0.459456
C	-3.170123	-1.109140	-1.577522
C	-3.599585	0.352830	-1.209728
H	-4.085224	-1.712723	-1.674488
H	-4.206440	0.340350	-0.295347
H	-0.604642	-1.376929	-1.785436
C	-2.882316	-2.188175	0.731973
H	-3.662849	-2.927360	0.495674
H	-2.174218	-2.651410	1.426049
H	-3.389152	-1.368347	1.265129
H	-2.681975	-1.092468	-2.563518
H	-0.034665	-2.843908	0.854740
H	-4.255472	0.713586	-2.018598
H	-0.759226	3.672636	0.457347
H	0.219463	1.745373	1.760235
C	0.697430	0.447955	0.081247
H	-0.239076	0.356197	-0.542088
C	-0.163342	-0.648986	2.233126
H	-0.214763	-1.596626	2.784029
H	0.219917	0.104138	2.935124
H	-1.182145	-0.369335	1.945104
C	2.203963	-1.063135	1.477160
H	2.237287	-1.987386	2.072356
H	2.498025	-0.249720	2.162487
C	1.838356	0.657113	-0.755676
H	1.752324	1.450554	-1.512514
C	3.212797	-1.166874	0.323638
H	3.021524	-2.074742	-0.266244
H	4.233083	-1.275502	0.717365
C	3.174058	0.053126	-0.627086
C	4.027768	1.246123	-0.024055

H	3.974226	2.150896	-0.641894
H	3.716076	1.486618	0.998338
H	5.070112	0.901167	-0.005562
C	3.753441	-0.282618	-2.030379
H	3.159603	-1.062201	-2.523652
H	3.788205	0.601641	-2.680360
H	4.777476	-0.657584	-1.904798
C	-2.741206	2.010079	1.325464
H	-2.079418	1.836124	2.185229
H	-3.167326	3.016990	1.459761
H	-3.566024	1.293497	1.388182

B (G781.707534E_mBmCqp_mBPW)

C	0.202582	0.492572	2.053283
C	1.098136	-0.726044	2.398756
C	2.237888	-0.853690	1.400590
C	0.430637	0.763108	-1.585947
C	-0.277525	1.985586	-1.058272
C	-1.273384	1.617182	0.108385
H	1.162417	-2.180616	0.181009
H	-0.434058	0.753626	2.911883
H	0.509013	-1.653721	2.443987
C	2.084321	-1.593160	0.279544
C	1.781829	0.542845	-1.654981
H	-0.837548	2.489355	-1.861110
C	2.297254	-0.800586	-2.110277
C	2.970383	-1.597617	-0.935942
H	3.044294	-0.667745	-2.909320
H	3.956965	-1.170044	-0.718797
H	-0.198014	-0.000248	-2.054468
C	2.808299	1.571276	-1.262235
H	3.031279	2.198895	-2.140786
H	2.466969	2.242258	-0.466447
H	3.752456	1.112960	-0.951881
H	1.472506	-1.397416	-2.527068
H	0.452728	2.717549	-0.689616
H	3.144394	-2.622169	-1.296766
H	1.492685	-0.568710	3.413241
H	0.849180	1.361206	1.876347
C	-0.713640	0.323516	0.817829
H	0.070339	-0.072678	-0.061358
C	-1.364326	2.807999	1.087829
H	-1.791514	3.671560	0.559408
H	-2.018577	2.584492	1.940779
H	-0.384928	3.114488	1.473746
C	-2.708153	1.349740	-0.423852
H	-2.991045	2.180765	-1.085231
H	-3.406894	1.386350	0.428124
C	-1.465611	-0.863099	0.735992
H	-1.179721	-1.692211	1.393623
C	-2.882164	0.015042	-1.152192
H	-2.247995	-0.021425	-2.049998
H	-3.914765	-0.088004	-1.514058

40

C	-2.556865	-1.176354	-0.220828
C	-3.791030	-1.539481	0.675251
H	-3.566006	-2.362574	1.365650
H	-4.137193	-0.678236	1.258703
H	-4.605027	-1.861381	0.012392
C	-2.155656	-2.442488	-1.032653
H	-1.255718	-2.264366	-1.636209
H	-1.973126	-3.304523	-0.377515
H	-2.978022	-2.697969	-1.713923
C	3.467403	-0.045577	1.746572
H	3.229757	1.020342	1.886983
H	3.877389	-0.398094	2.705670
H	4.265515	-0.116330	1.001900

B-TS (G781.700262T-398_mBmCPW)

C	0.102847	-1.035008	1.749442
C	0.963444	-2.220199	1.197170
C	2.208173	-1.710851	0.484455
C	0.862372	1.681869	-0.649308
C	0.127779	2.070614	0.600037
C	-1.255381	1.427907	0.787602
H	1.255082	-1.652710	-1.379947
H	-0.520696	-1.374254	2.590074
H	0.342112	-2.833315	0.525998
C	2.177411	-1.415880	-0.832933
C	2.197367	1.483384	-0.769682
H	-0.116844	3.153212	0.600264
C	2.738810	0.773628	-1.992672
C	3.218202	-0.677437	-1.633920
H	3.589854	1.321427	-2.426969
H	4.172204	-0.621031	-1.094530
H	0.252482	1.490447	-1.536725
C	3.207386	1.876226	0.276685
H	3.803344	2.719781	-0.107246
H	2.764307	2.198115	1.225679
H	3.918134	1.067292	0.483230
H	1.958042	0.711946	-2.765810
H	0.742053	1.907037	1.494676
H	3.425925	-1.200522	-2.579950
H	1.246178	-2.860560	2.045438
H	0.774865	-0.257464	2.137439
C	-0.778211	-0.484384	0.644490
H	-0.219686	-0.247593	-0.276747
C	-1.808869	1.630096	2.188317
H	-1.919614	2.711998	2.364303
H	-2.795564	1.170267	2.313484
H	-1.132532	1.242678	2.959716
C	-2.251026	1.723560	-0.348540
H	-1.895839	2.613068	-0.888430
H	-3.220828	1.990387	0.095159
C	-2.070237	-0.981930	0.491983
H	-2.489047	-1.597150	1.300179
C	-2.476872	0.592857	-1.373335

41

H	-1.553562	0.396570	-1.935612
H	-3.228992	0.905781	-2.110519
C	-2.950679	-0.700309	-0.671689
C	-4.431918	-0.616988	-0.225905
H	-4.748269	-1.547637	0.263328
H	-4.605952	0.209317	0.475182
H	-5.073558	-0.459516	-1.102101
C	-2.780291	-1.921237	-1.643294
H	-1.739952	-2.025918	-1.975939
H	-3.097168	-2.857620	-1.168216
H	-3.416841	-1.748213	-2.521364
C	3.399856	-1.512558	1.393790
H	3.171948	-0.812733	2.214064
H	3.666829	-2.468732	1.870190
H	4.290608	-1.144519	0.875555

C (G781.698414E_mBmCqn_mCPW)

C	0.124587	-1.421370	1.559095
C	1.129313	-2.438196	0.912266
C	2.344933	-1.724519	0.343020
C	0.838388	1.619429	-0.505896
C	0.080141	1.878366	0.768369
C	-1.357043	1.428427	0.843304
H	1.519245	-1.608063	-1.578454
H	-0.489945	-1.911990	2.327986
H	0.605185	-3.017522	0.137698
C	2.370467	-1.323341	-0.946104
C	2.183242	1.587456	-0.627327
H	-0.047390	2.973672	0.932317
C	2.803083	1.003380	-1.879282
C	3.384873	-0.427799	-1.608430
H	3.618149	1.642088	-2.253977
H	4.297466	-0.339955	-1.004870
H	0.252319	1.371511	-1.392924
C	3.137851	2.025510	0.454011
H	3.680887	2.921312	0.113369
H	2.649848	2.281217	1.401593
H	3.899936	1.262261	0.655888
H	2.046646	0.935685	-2.675978
H	0.636313	1.531835	1.650575
H	3.693264	-0.847171	-2.578417
H	1.432251	-3.150211	1.694200
H	0.706916	-0.633259	2.062492
C	-0.753067	-0.842081	0.489310
H	-0.232633	-0.528680	-0.418203
C	-1.950060	1.464597	2.226913
H	-1.966644	2.519108	2.554739
H	-2.979643	1.095961	2.255475
H	-1.339063	0.915242	2.953107
C	-2.255949	1.777125	-0.325944
H	-1.801093	2.629804	-0.852673
H	-3.227347	2.106995	0.067338
C	-2.118781	-0.963285	0.483260

42

H	-2.591393	-1.382929	1.379782
C	-2.499499	0.655156	-1.362651
H	-1.572099	0.439444	-1.910373
H	-3.226492	1.004478	-2.108665
C	-3.021325	-0.628599	-0.675944
C	-4.479249	-0.458889	-0.189446
H	-4.841744	-1.383300	0.279554
H	-4.588098	0.350879	0.544430
H	-5.137582	-0.232672	-1.037923
C	-2.956857	-1.809810	-1.691772
H	-1.932892	-1.965579	-2.055872
H	-3.307065	-2.743302	-1.233776
H	-3.605013	-1.588019	-2.550085
C	3.440140	-1.468478	1.354042
H	3.078633	-0.860314	2.199433
H	3.782675	-2.421851	1.785218
H	4.315274	-0.965144	0.932209

C (G781.700102E_mCmDqp_mCPW)

C	0.069558	2.463952	0.421822
C	-1.322575	2.858233	-0.111315
C	-2.380273	1.801961	0.150604
C	-0.745705	-1.443194	-0.857224
C	0.533522	-1.859101	-0.187658
C	1.120856	-1.038118	0.946266
H	-2.473565	1.302555	-1.876196
H	0.739627	3.348375	0.372954
H	-1.247274	3.066533	-1.189144
C	-2.863825	1.074432	-0.876001
C	-2.001589	-1.827212	-0.532131
H	1.301171	-2.049307	-0.946822
C	-3.172448	-1.368307	-1.380278
C	-3.834428	-0.069225	-0.833292
H	-3.933442	-2.161759	-1.426186
H	-4.224800	-0.243351	0.178635
H	-0.621521	-0.857301	-1.772422
C	-2.356476	-2.679046	0.661903
H	-2.905121	-3.576783	0.339891
H	-1.493995	-3.008033	1.253160
H	-3.032577	-2.131021	1.336873
H	-2.837311	-1.180976	-2.411414
H	0.382970	-2.839408	0.308476
H	-4.705663	0.156064	-1.469467
H	-1.603854	3.805897	0.375928
H	0.042579	2.216807	1.496747
C	0.819705	1.408335	-0.322950
H	0.532348	1.207780	-1.358669
C	0.180073	-0.646927	2.044930
H	-0.045546	-1.555862	2.628792
H	0.622408	0.075692	2.740417
H	-0.767932	-0.272485	1.645661
C	2.545184	-1.425630	1.314176
H	2.538176	-2.496267	1.585072

H	2.859334	-0.878431	2.213794
C	1.933518	0.793271	0.224392
H	2.188820	1.154020	1.229365
C	3.499632	-1.163720	0.134944
H	3.419565	-1.968291	-0.608434
H	4.539041	-1.177683	0.487339
C	3.145445	0.222221	-0.529919
C	4.307886	1.225605	-0.303762
H	4.065473	2.218268	-0.707049
H	4.544805	1.334873	0.764040
H	5.211238	0.864430	-0.813404
C	2.906387	0.074112	-2.046288
H	2.038500	-0.555848	-2.281702
H	2.755031	1.051899	-2.523826
H	3.784445	-0.388299	-2.514924
C	-2.845247	1.684310	1.585157
H	-2.002169	1.678602	2.293213
H	-3.461708	2.556552	1.854897
H	-3.444249	0.787053	1.774150

C-TS (G781.701853T-241_mCmDPW)

C	0.023759	2.437397	0.456067
C	-1.366388	2.848407	-0.066574
C	-2.414705	1.775266	0.162286
C	-0.694701	-1.446356	-0.846740
C	0.577081	-1.863926	-0.164075
C	1.178529	-1.015487	0.950368
H	-2.486561	1.322540	-1.876877
H	0.707117	3.313384	0.417602
H	-1.290469	3.089303	-1.137423
C	-2.879050	1.064467	-0.884845
C	-1.957172	-1.821304	-0.531469
H	1.340610	-2.074406	-0.922340
C	-3.114716	-1.381295	-1.406746
C	-3.823416	-0.101125	-0.872703
H	-3.855849	-2.191948	-1.476028
H	-4.237018	-0.289045	0.127271
H	-0.560728	-0.882788	-1.774848
C	-2.329431	-2.655495	0.669453
H	-2.868847	-3.560275	0.351244
H	-1.475926	-2.971027	1.279908
H	-3.019814	-2.100516	1.323736
H	-2.757260	-1.181209	-2.427902
H	0.415118	-2.831902	0.349253
H	-4.681460	0.105527	-1.532338
H	-1.651143	3.779272	0.449819
H	0.000542	2.177434	1.528414
C	0.759550	1.385850	-0.301691
H	0.458161	1.189261	-1.334031
C	0.251106	-0.674304	2.083686
H	0.071120	-1.595815	2.661898
H	0.686527	0.055981	2.776136
H	-0.718591	-0.322957	1.716128

C	2.613218	-1.406696	1.296376
H	2.620488	-2.478686	1.558285
H	2.939734	-0.861749	2.193434
C	1.881578	0.760318	0.234918
H	2.153570	1.147970	1.225781
C	3.534178	-1.115775	0.097840
H	3.464210	-1.922036	-0.644754
H	4.582294	-1.090770	0.422816
C	3.109989	0.255500	-0.552976
C	4.224991	1.312319	-0.339577
H	3.927123	2.295653	-0.728922
H	4.477991	1.423985	0.724299
H	5.134945	1.000411	-0.869709
C	2.849522	0.107304	-2.065331
H	2.007999	-0.560960	-2.289881
H	2.646488	1.079893	-2.534617
H	3.739382	-0.311923	-2.552061
C	-2.882230	1.613685	1.591192
H	-2.040147	1.586190	2.300229
H	-3.498610	2.477586	1.886708
H	-3.481134	0.711132	1.752020

D (G781.709977E_mCmDqn_mDPW)

C	-0.218198	2.225420	0.665755
C	-1.580445	2.743992	0.177473
C	-2.605474	1.626795	0.228523
C	-0.422942	-1.453765	-0.821833
C	0.815567	-1.903139	-0.100759
C	1.462961	-0.930837	0.925845
H	-2.540051	1.392368	-1.850157
H	0.535948	3.046618	0.701178
H	-1.477718	3.130994	-0.846884
C	-2.957395	1.000312	-0.913996
C	-1.722358	-1.767645	-0.531145
H	1.559839	-2.169413	-0.863222
C	-2.814990	-1.423372	-1.518088
C	-3.752600	-0.259767	-1.060571
H	-3.437171	-2.318011	-1.681221
H	-4.274166	-0.537813	-0.135827
H	-0.255529	-1.004005	-1.805019
C	-2.159256	-2.502123	0.707824
H	-2.698817	-3.420322	0.428994
H	-1.336301	-2.776864	1.373456
H	-2.872689	-1.895058	1.285342
H	-2.373572	-1.153944	-2.488687
H	0.615994	-2.832450	0.454905
H	-4.522663	-0.140028	-1.837712
H	-1.875885	3.589815	0.817270
H	-0.256087	1.888768	1.717719
C	0.450227	1.198074	-0.162454
H	0.135650	1.096089	-1.202370
C	0.655453	-0.881463	2.225286
H	0.670574	-1.866884	2.710887

H	1.081448	-0.160552	2.936395
H	-0.393227	-0.616480	2.040610
C	2.954843	-1.283841	1.134731
H	3.080529	-2.360582	1.318909
H	3.330758	-0.756866	2.025090
C	1.655643	0.559865	0.319733
H	1.962387	1.115203	1.223897
C	3.677007	-0.800215	-0.134816
H	3.664495	-1.579958	-0.909102
H	4.733412	-0.573319	0.060390
C	2.912691	0.473901	-0.643638
C	3.747051	1.753920	-0.419236
H	3.181985	2.658356	-0.689695
H	4.070077	1.849629	0.627245
H	4.650256	1.727209	-1.044045
C	2.562865	0.360367	-2.138985
H	1.919697	-0.500201	-2.361743
H	2.073738	1.268456	-2.520011
H	3.487707	0.228744	-2.715749
C	-3.112356	1.274902	1.606003
H	-2.288969	1.025618	2.295518
H	-3.627331	2.141264	2.049788
H	-3.814069	0.435346	1.609941

D (G781.709977E_mCmDqn_mDPW)

C	-0.218198	2.225420	0.665755
C	-1.580445	2.743992	0.177473
C	-2.605474	1.626795	0.228523
C	-0.422942	-1.453765	-0.821833
C	0.815567	-1.903139	-0.100759
C	1.462961	-0.930837	0.925845
H	-2.540051	1.392368	-1.850157
H	0.535948	3.046618	0.701178
H	-1.477718	3.130994	-0.846884
C	-2.957395	1.000312	-0.913996
C	-1.722358	-1.767645	-0.531145
H	1.559839	-2.169413	-0.863222
C	-2.814990	-1.423372	-1.518088
C	-3.752600	-0.259767	-1.060571
H	-3.437171	-2.318011	-1.681221
H	-4.274166	-0.537813	-0.135827
H	-0.255529	-1.004005	-1.805019
C	-2.159256	-2.502123	0.707824
H	-2.698817	-3.420322	0.428994
H	-1.336301	-2.776864	1.373456
H	-2.872689	-1.895058	1.285342
H	-2.373572	-1.153944	-2.488687
H	0.615994	-2.832450	0.454905
H	-4.522663	-0.140028	-1.837712
H	-1.875885	3.589815	0.817270
H	-0.256087	1.888768	1.717719
C	0.450227	1.198074	-0.162454
H	0.135650	1.096089	-1.202370

C	0.655453	-0.881463	2.225286
H	0.670574	-1.866884	2.710887
H	1.081448	-0.160552	2.936395
H	-0.393227	-0.616480	2.040610
C	2.954843	-1.283841	1.134731
H	3.080529	-2.360582	1.318909
H	3.330758	-0.756866	2.025090
C	1.655643	0.559865	0.319733
H	1.962387	1.115203	1.223897
C	3.677007	-0.800215	-0.134816
H	3.664495	-1.579958	-0.909102
H	4.733412	-0.573319	0.060390
C	2.912691	0.473901	-0.643638
C	3.747051	1.753920	-0.419236
H	3.181985	2.658356	-0.689695
H	4.070077	1.849629	0.627245
H	4.650256	1.727209	-1.044045
C	2.562865	0.360367	-2.138985
H	1.919697	-0.500201	-2.361743
H	2.073738	1.268456	-2.520011
H	3.487707	0.228744	-2.715749
C	-3.112356	1.274902	1.606003
H	-2.288969	1.025618	2.295518
H	-3.627331	2.141264	2.049788
H	-3.814069	0.435346	1.609941

D-TS (G781.707568T5-58_mDmEtsPW)

C	-0.583980	1.631380	1.064329
C	-1.843600	2.391892	0.582166
C	-2.940023	1.395947	0.278831
C	-0.145301	-1.331842	-0.782482
C	1.024200	-1.911845	-0.032829
C	1.765843	-0.935542	0.933683
H	-2.390744	1.349626	-1.737812
H	0.112342	2.334056	1.561483
H	-1.587902	2.990212	-0.304808
C	-3.018343	0.886169	-0.965709
C	-1.487666	-1.602949	-0.573363
H	1.728980	-2.271633	-0.795605
C	-2.473493	-1.383494	-1.697724
C	-3.648694	-0.408326	-1.378099
H	-2.890395	-2.375108	-1.950395
H	-4.298138	-0.829935	-0.600200
H	0.090314	-0.967152	-1.785056
C	-2.024754	-2.186593	0.696312
H	-2.728536	-3.003573	0.481606
H	-1.249564	-2.551026	1.376737
H	-2.607378	-1.418280	1.226542
H	-1.943834	-1.024703	-2.591808
H	0.718687	-2.799154	0.539099
H	-4.254663	-0.311351	-2.290841
H	-2.137284	3.094334	1.376627
H	-0.841237	0.920855	1.868698

C	0.251133	0.952561	0.018864
H	-0.000170	1.174504	-1.019304
C	1.219079	-1.076241	2.360176
H	1.446222	-2.079061	2.747526
H	1.679825	-0.346225	3.039170
H	0.129157	-0.949345	2.406637
C	3.297651	-1.121658	0.864631
H	3.577593	-2.180958	0.954806
H	3.766309	-0.590333	1.707877
C	1.624700	0.543538	0.369229
H	1.886317	1.150768	1.254330
C	3.715782	-0.494809	-0.473738
H	3.578680	-1.215963	-1.293540
H	4.775351	-0.207822	-0.486649
C	2.785460	0.744664	-0.693021
C	3.520861	2.053214	-0.321873
H	2.848062	2.921778	-0.380981
H	3.932573	2.009718	0.696806
H	4.357574	2.230528	-1.011126
C	2.333425	0.836212	-2.161618
H	1.807717	-0.065464	-2.502579
H	1.693142	1.710237	-2.350705
H	3.217548	0.947125	-2.803275
C	-3.775186	0.968982	1.461756
H	-4.387370	1.819452	1.800626
H	-4.459396	0.141953	1.243153
H	-3.152357	0.684390	2.325838

E (G781.741035E_mDmEtsqp_mEPW)

C	0.594127	0.099108	1.847018
C	1.902919	-0.692993	2.129450
C	2.941037	-0.554406	1.036940
C	0.182840	0.307126	-0.747934
C	-0.625222	1.631486	-0.691285
C	-1.965926	1.306335	0.045102
H	1.934421	-1.966341	-0.166371
H	-0.036575	-0.038132	2.735935
H	1.635846	-1.754963	2.247596
C	2.739933	-1.226162	-0.149526
C	1.632722	0.471697	-1.089984
H	-0.781651	2.043367	-1.697906
C	2.277626	-0.336989	-2.227167
C	3.437148	-1.047920	-1.487545
H	2.598254	0.320546	-3.050658
H	4.328102	-0.412742	-1.422746
H	-0.246122	-0.343972	-1.525624
C	2.324253	1.765276	-0.800158
H	1.928099	2.474774	-1.549917
H	2.100098	2.188325	0.183260
H	3.405655	1.717710	-0.958138
H	1.564146	-1.071356	-2.623016
H	-0.075298	2.390955	-0.119561
H	3.727165	-1.997108	-1.954455

H	2.325042	-0.354107	3.085145
H	0.799001	1.179241	1.793676
C	-0.198806	-0.389520	0.616227
H	-0.025704	-1.470317	0.524516
C	-2.286548	2.414166	1.063828
H	-2.434496	3.380868	0.560841
H	-3.207259	2.181011	1.615486
H	-1.476939	2.538371	1.798373
C	-3.136046	1.094629	-0.954227
H	-3.076686	1.780492	-1.810972
H	-4.090718	1.307237	-0.450633
C	-1.722616	-0.101474	0.706896
H	-2.001260	-0.079553	1.772176
C	-3.070733	-0.384253	-1.347552
H	-2.303278	-0.547256	-2.124179
H	-4.015252	-0.761005	-1.764341
C	-2.680141	-1.120826	-0.036446
C	-3.937292	-1.313644	0.846106
H	-3.678779	-1.818469	1.787977
H	-4.412751	-0.357295	1.102673
H	-4.684754	-1.929631	0.327142
C	-2.078105	-2.506257	-0.327111
H	-1.215063	-2.458807	-1.008748
H	-1.764793	-3.021406	0.593168
H	-2.830337	-3.141736	-0.814192
C	4.121070	0.319260	1.329106
H	4.679057	-0.136252	2.163771
H	4.812330	0.438911	0.490079
H	3.807055	1.310798	1.689210

E (G781.741033E_mE12HmFqp_mEPW)

C	0.594097	0.095618	1.847209
C	1.902890	-0.697023	2.128228
C	2.941040	-0.556381	1.036005
C	0.182963	0.308518	-0.747444
C	-0.625069	1.632804	-0.688352
C	-1.965872	1.306253	0.047189
H	1.934384	-1.965936	-0.170008
H	-0.036693	-0.043399	2.735783
H	1.635785	-1.759198	2.244379
C	2.739980	-1.225878	-0.151702
C	1.632773	0.473740	-1.089202
H	-0.781313	2.046636	-1.694196
C	2.277689	-0.332897	-2.227777
C	3.437205	-1.045128	-1.489390
H	2.598314	0.326124	-3.050080
H	4.328136	-0.410035	-1.423400
H	-0.245928	-0.341118	-1.526385
C	2.324280	1.766801	-0.797013
H	2.100089	2.188000	0.187196
H	3.405660	1.719561	-0.955100
H	1.928082	2.477707	-1.545408
H	1.564232	-1.066556	-2.624987

49

H	-0.075185	2.391125	-0.115055
H	3.727285	-1.993445	-1.958026
H	2.324950	-0.359923	3.084579
H	0.798940	1.175849	1.795991
C	-0.198753	-0.390618	0.615429
H	-0.025691	-1.471241	0.521648
C	-2.286778	2.412319	1.067752
H	-2.434794	3.379852	0.566387
H	-3.207530	2.178097	1.618889
H	-1.477278	2.535379	1.802606
C	-3.135806	1.096177	-0.952738
H	-3.076146	1.783296	-1.808452
H	-4.090555	1.308189	-0.449045
C	-1.722581	-0.102646	0.706647
H	-2.001120	-0.082437	1.771990
C	-3.070650	-0.382130	-1.348258
H	-2.303178	-0.544070	-2.125090
H	-4.015196	-0.758126	-1.765666
C	-2.680231	-1.120742	-0.038249
C	-3.937433	-1.314690	0.843971
H	-3.679025	-1.820991	1.785076
H	-4.412757	-0.358663	1.101983
H	-4.684982	-1.929766	0.324050
C	-2.078406	-2.505822	-0.330999
H	-1.215595	-2.457504	-1.012860
H	-1.764839	-3.022265	0.588470
H	-2.830849	-3.140567	-0.818711
C	4.121053	0.316770	1.329848
H	3.807022	1.307381	1.692456
H	4.679423	-0.140737	2.163170
H	4.812023	0.438512	0.490882

E-TS (G781.727775T-730_mE12HmFPW)

C	-0.580120	1.897633	-0.857543
C	-2.016463	1.986112	-1.438518
C	-2.911262	1.027563	-0.695505
C	-0.342488	-0.201083	0.608593
C	0.489194	0.507789	1.670286
C	1.839934	0.881902	0.960712
H	-2.771934	-0.343094	-2.268931
H	0.094926	2.465554	-1.512261
H	-1.990842	1.730812	-2.507678
C	-3.110809	-0.191147	-1.238137
C	-1.262032	-1.258849	0.899863
H	0.655063	-0.098464	2.567574
C	-2.000048	-2.074027	-0.139711
C	-3.403085	-1.449351	-0.485866
H	-2.129074	-3.093506	0.250990
H	-3.985775	-1.295413	0.431924
H	0.119471	-1.393082	0.606366
C	-1.558683	-1.647436	2.326900
H	-1.174371	-0.952639	3.075589
H	-2.654120	-1.684419	2.420490

H	-1.202535	-2.664388	2.542401
H	-1.425146	-2.137007	-1.072433
H	-0.060188	1.404613	1.995558
H	-3.937617	-2.191765	-1.093360
H	-2.348165	3.032979	-1.355756
H	-0.552200	2.411587	0.112174
C	0.036963	0.457459	-0.722537
H	-0.277174	-0.136898	-1.589284
C	2.239047	2.335157	1.258304
H	2.420571	2.477128	2.333485
H	3.164239	2.596151	0.727521
H	1.463908	3.050210	0.951782
C	2.958693	-0.111334	1.379578
H	2.915858	-0.360221	2.449189
H	3.941823	0.349795	1.206218
C	1.582559	0.575419	-0.573465
H	1.929929	1.410400	-1.198913
C	2.783231	-1.320226	0.456976
H	1.957755	-1.969772	0.818030
H	3.667036	-1.971549	0.414164
C	2.433750	-0.708120	-0.927448
C	3.731890	-0.244278	-1.631117
H	3.502711	0.206342	-2.606899
H	4.276816	0.504552	-1.041105
H	4.407190	-1.093990	-1.801284
C	1.731623	-1.730233	-1.837772
H	0.842290	-2.181194	-1.368529
H	1.423070	-1.285757	-2.794402
H	2.414577	-2.559601	-2.066034
C	-3.352842	1.440489	0.688268
H	-2.503413	1.726957	1.329593
H	-3.990046	2.335389	0.620267
H	-3.928941	0.669669	1.212391

F (G781.749734E_mE12HmFqn_mFPW)

C	-0.537976	1.405948	-1.829826
C	-1.705519	2.067480	-1.061584
C	-2.578257	1.048353	-0.360078
C	-0.599199	-0.194562	0.184576
C	-0.064539	0.750448	1.236123
C	1.413941	1.097890	0.807425
H	-2.349667	-0.246358	-2.007584
H	-0.892359	1.070306	-2.813894
H	-2.316929	2.657643	-1.764228
C	-2.767392	-0.156332	-1.000615
C	-0.993156	-1.603228	0.592409
H	-0.126741	0.335563	2.246476
C	-1.978719	-2.303859	-0.366475
C	-3.276095	-1.445254	-0.481638
H	-2.210782	-3.311267	0.003110
H	-3.791700	-1.370787	0.482967
H	-0.033729	-2.148697	0.486753
C	-1.449882	-1.741112	2.060654

51

H	-0.622672	-1.599328	2.765217
H	-2.239551	-1.024645	2.319284
H	-1.845424	-2.750170	2.227411
H	-1.532270	-2.418969	-1.365114
H	-0.643103	1.683371	1.269850
H	-3.954537	-1.920290	-1.204775
H	-1.337791	2.794364	-0.322550
H	0.227873	2.163917	-2.031689
C	0.118094	0.153610	-1.109619
H	0.098241	-0.688301	-1.812922
C	1.647435	2.615783	0.859534
H	1.530248	2.998133	1.883777
H	2.665322	2.858396	0.526320
H	0.947361	3.165152	0.213524
C	2.435843	0.328016	1.688721
H	2.105661	0.247928	2.733917
H	3.385094	0.883245	1.706221
C	1.570055	0.481622	-0.638627
H	1.986623	1.225753	-1.333833
C	2.633536	-1.028345	1.001489
H	1.827352	-1.728668	1.279841
H	3.572354	-1.518659	1.293342
C	2.599746	-0.706005	-0.518204
C	3.984383	-0.167321	-0.958313
H	3.981235	0.085940	-2.027966
H	4.274560	0.735940	-0.404864
H	4.762757	-0.924708	-0.793587
C	2.280121	-1.944552	-1.372725
H	1.339271	-2.437767	-1.088458
H	2.220483	-1.694102	-2.441847
H	3.076199	-2.692584	-1.257096
C	-3.320834	1.466516	0.877477
H	-2.649149	1.884087	1.640377
H	-4.015018	2.276811	0.604599
H	-3.908725	0.658185	1.323197

F (G781.749731E_fgsctsqpFPW)

C	-0.537816	1.405863	-1.829818
C	-1.705627	2.067346	-1.061870
C	-2.578308	1.048180	-0.360266
C	-0.599147	-0.194390	0.184697
C	-0.064386	0.750735	1.236064
C	1.414105	1.098003	0.807280
H	-2.349657	-0.246540	-2.007745
H	-0.891882	1.070346	-2.814031
H	-2.317092	2.657157	-1.764761
C	-2.767425	-0.156506	-1.000794
C	-0.993292	-1.602896	0.592795
H	-0.126561	0.336023	2.246499
C	-1.978470	-2.303795	-0.366255
C	-3.275986	-1.445441	-0.481740
H	-2.210452	-3.311191	0.003398
H	-3.791690	-1.370931	0.482817

H	-0.033851	-2.148456	0.487761
C	-1.450645	-1.740232	2.060902
H	-0.623677	-1.598365	2.765727
H	-2.240254	-1.023505	2.318987
H	-1.846442	-2.749159	2.227828
H	-1.531780	-2.418945	-1.364782
H	-0.642901	1.683695	1.269633
H	-3.954278	-1.920676	-1.204886
H	-1.338162	2.794453	-0.322941
H	0.228031	2.163921	-2.031378
C	0.118118	0.153530	-1.109569
H	0.098187	-0.688448	-1.812793
C	1.647723	2.615880	0.859156
H	1.530533	2.998408	1.883332
H	2.665641	2.858355	0.525942
H	0.947726	3.165219	0.213038
C	2.435974	0.328197	1.688692
H	2.105772	0.248264	2.733893
H	3.385231	0.883413	1.706107
C	1.570137	0.481477	-0.638664
H	1.986737	1.225443	-1.334025
C	2.633657	-1.028272	1.001649
H	1.827549	-1.728614	1.280204
H	3.572525	-1.518489	1.293505
C	2.599720	-0.706243	-0.518103
C	3.984354	-0.167803	-0.958498
H	3.981127	0.085240	-2.028204
H	4.274686	0.735541	-0.405261
H	4.762683	-0.925223	-0.793699
C	2.279830	-1.944947	-1.372304
H	1.338896	-2.437894	-1.087861
H	2.220227	-1.694774	-2.441490
H	3.075771	-2.693098	-1.256492
C	-3.320831	1.466347	0.877302
H	-2.648997	1.883043	1.640560
H	-4.014301	2.277330	0.604658
H	-3.909451	0.658259	1.322520

F-TS (G781.753429T-330_fgsctsPW)

C	0.596319	-1.522594	-1.799476
C	1.645968	-2.215994	-0.912748
C	2.580993	-1.256602	-0.237680
C	0.735144	0.361388	-0.019845
C	0.332587	-0.337461	1.286430
C	-1.179971	-0.723179	1.129495
H	2.280451	0.155078	-1.765799
H	1.080453	-1.185195	-2.727453
H	2.250294	-2.909292	-1.527262
C	2.581302	0.050719	-0.718896
C	0.890507	1.922105	0.021209
H	0.524726	0.268380	2.176160
C	2.259625	2.374834	-0.577422
C	3.286332	1.281037	-0.230522

H	2.543148	3.360924	-0.190152
H	3.491668	1.249280	0.849215
H	0.092998	2.302542	-0.637179
C	0.720248	2.561645	1.411064
H	-0.226698	2.308950	1.896895
H	1.539112	2.287935	2.091140
H	0.744619	3.652676	1.294437
H	2.188472	2.463568	-1.671989
H	0.884534	-1.270095	1.439635
H	4.241648	1.433887	-0.752997
H	1.185416	-2.857513	-0.144132
H	-0.153501	-2.260445	-2.109554
C	-0.114936	-0.293457	-1.123905
H	-0.289235	0.433436	-1.927674
C	-1.412618	-2.109019	1.759543
H	-1.203205	-2.090731	2.838944
H	-2.453872	-2.429976	1.627237
H	-0.768681	-2.876971	1.304339
C	-2.155754	0.329612	1.742427
H	-1.697232	0.892320	2.567392
H	-3.018088	-0.192598	2.180416
C	-1.456199	-0.694785	-0.424304
H	-1.731110	-1.701454	-0.777070
C	-2.625068	1.213949	0.579343
H	-1.911904	2.031234	0.384369
H	-3.593850	1.693230	0.777078
C	-2.688544	0.259398	-0.639993
C	-3.974939	-0.600748	-0.571320
H	-4.022918	-1.297357	-1.420284
H	-4.038417	-1.195536	0.349191
H	-4.865815	0.040755	-0.611852
C	-2.700214	1.027172	-1.973435
H	-1.886835	1.763476	-2.046457
H	-2.630629	0.348552	-2.836266
H	-3.640503	1.586595	-2.071929
C	3.382729	-1.706244	0.933457
H	2.847087	-2.438440	1.551467
H	4.276744	-2.222785	0.539501
H	3.740047	-0.875074	1.550115

G (G781.768851E_fgsctsqnGPW)

C	0.333692	-1.264059	-1.972561
C	1.116936	-2.307405	-1.148388
C	2.098693	-1.706205	-0.209784
C	0.969767	0.493956	-0.206472
C	0.513425	0.456523	1.268478
C	-0.963813	-0.039134	1.327474
H	2.513311	-0.193279	-1.540837
H	0.966313	-0.866819	-2.780760
H	1.699183	-2.969204	-1.823121
C	2.417558	-0.334121	-0.451965
C	1.561931	1.877924	-0.635478
H	0.619645	1.443581	1.735871

54

C	2.921674	1.973449	0.107582
C	3.444637	0.512887	0.290611
H	2.782727	2.449556	1.087929
H	3.494989	0.247647	1.355182
H	1.758250	1.804266	-1.720458
C	0.650547	3.087824	-0.416535
H	-0.275455	3.009770	-0.998947
H	0.384576	3.228569	0.638526
H	1.174069	3.995924	-0.745589
H	3.628572	2.599992	-0.450741
H	1.156012	-0.195507	1.879470
H	4.448369	0.362795	-0.129460
H	0.468707	-3.003245	-0.590389
H	-0.514274	-1.759041	-2.462912
C	-0.166788	-0.114487	-1.062814
H	-0.536634	0.680953	-1.726926
C	-1.090758	-1.108054	2.430677
H	-0.826094	-0.688218	3.411892
H	-2.110387	-1.503210	2.503866
H	-0.423223	-1.964420	2.241107
C	-1.991064	1.127558	1.554186
H	-1.504957	2.046001	1.910387
H	-2.706271	0.837518	2.336861
C	-1.300894	-0.588402	-0.104965
H	-1.323426	-1.692688	-0.096166
C	-2.726100	1.337166	0.216339
H	-2.183894	2.056697	-0.418886
H	-3.739957	1.740166	0.347806
C	-2.731382	-0.054934	-0.462310
C	-3.808002	-0.962438	0.180360
H	-3.749842	-1.985044	-0.219724
H	-3.725496	-1.025914	1.271668
H	-4.809903	-0.572627	-0.045286
C	-3.032297	0.020452	-1.971235
H	-2.377625	0.718896	-2.509970
H	-2.949357	-0.967158	-2.448680
H	-4.061832	0.369905	-2.127757
C	2.570503	-2.462511	0.965819
H	2.376720	-3.538326	0.890347
H	3.623659	-2.257519	1.195673
H	1.993930	-2.085971	1.835906

G (G781.770143E_gh12htsqpGPW)

C	-0.442005	-0.972240	2.153675
C	-1.265947	-2.047618	1.425973
C	-2.211324	-1.497672	0.423189
C	-0.887848	0.584809	0.158153
C	-0.384201	0.283351	-1.271969
C	0.906205	-0.589596	-1.200636
H	-2.499442	0.212601	1.522351
H	-1.076819	-0.444790	2.882443
H	-1.877135	-2.630647	2.146244
C	-2.395977	-0.080341	0.463588

55

C	-1.378089	2.061629	0.343960
H	-0.162802	1.233666	-1.776076
C	-2.691773	2.143155	-0.473642
C	-3.352208	0.730325	-0.406649
H	-2.464892	2.402717	-1.517089
H	-3.459596	0.298509	-1.410805
H	-1.624476	2.163390	1.416579
C	-0.366154	3.159286	0.006491
H	0.543721	3.076408	0.614054
H	-0.078468	3.157985	-1.052293
H	-0.817109	4.138679	0.218153
H	-3.350939	2.930367	-0.087011
H	-1.151824	-0.185341	-1.906628
H	-4.355077	0.749808	0.041772
H	-0.643154	-2.815813	0.935731
H	0.353028	-1.455931	2.735902
C	0.172049	0.040887	1.148590
H	0.538789	0.884196	1.751041
C	0.668820	-2.000496	-1.769517
H	0.408552	-1.953478	-2.837116
H	1.572828	-2.616686	-1.675460
H	-0.142408	-2.536800	-1.257118
C	2.082976	0.103922	-1.951089
H	1.733993	0.672008	-2.825020
H	2.782911	-0.654080	-2.331896
C	1.327557	-0.597368	0.318674
H	1.456574	-1.637310	0.663020
C	2.769657	0.970642	-0.890571
H	2.202400	1.902355	-0.727998
H	3.790294	1.266216	-1.170288
C	2.739954	0.103189	0.394030
C	3.825523	-0.998777	0.317075
H	3.814787	-1.617421	1.226137
H	3.684565	-1.670173	-0.540366
H	4.824857	-0.551146	0.227576
C	3.000672	0.939100	1.659160
H	2.364365	1.833377	1.717432
H	2.855509	0.350124	2.576980
H	4.040529	1.293636	1.660867
C	-2.828518	-2.361155	-0.602570
H	-2.509590	-1.999914	-1.597294
H	-2.567989	-3.419420	-0.503923
H	-3.922193	-2.227289	-0.595390

G-TS (G781.768362T-731_gh12htsPW)
C	0.431128	-1.140486	-1.953539
C	1.207053	-2.179997	-1.121372
C	2.282046	-1.535195	-0.281614
C	0.849587	0.635336	-0.141998
C	0.094395	0.819087	1.215784
C	-0.985115	-0.282291	1.321204
H	2.646554	-0.406411	-1.045679
H	1.122419	-0.696013	-2.691755

H	1.655029	-2.961497	-1.749828
C	2.118279	-0.174576	0.093717
C	1.512729	1.968595	-0.628417
H	-0.388829	1.804671	1.177446
C	2.690475	2.156826	0.368733
C	3.140413	0.721178	0.784090
H	2.344435	2.714912	1.248969
H	3.091145	0.561237	1.870743
H	1.937701	1.757274	-1.630784
C	0.610755	3.195729	-0.764114
H	-0.249461	2.999365	-1.417767
H	0.233804	3.541667	0.207216
H	1.176908	4.027135	-1.204591
H	3.515803	2.728885	-0.072088
H	0.754167	0.838264	2.094481
H	4.168771	0.488005	0.479009
H	0.527300	-2.696943	-0.421731
H	-0.351919	-1.649818	-2.529992
C	-0.198623	-0.046568	-1.071425
H	-0.595139	0.727888	-1.742710
C	-0.475461	-1.487690	2.129564
H	-0.329341	-1.214043	3.184350
H	-1.194814	-2.317561	2.096674
H	0.490235	-1.869668	1.762261
C	-2.288722	0.299956	1.930480
H	-2.078554	1.018760	2.735839
H	-2.889309	-0.506843	2.376144
C	-1.338090	-0.621136	-0.173022
H	-1.359476	-1.715799	-0.309859
C	-3.024616	0.915764	0.734110
H	-2.573492	1.886264	0.464655
H	-4.088733	1.105314	0.930266
C	-2.808547	-0.097629	-0.421480
C	-3.777182	-1.294575	-0.260687
H	-3.632076	-2.023563	-1.071419
H	-3.630677	-1.824693	0.690328
H	-4.821979	-0.956656	-0.296281
C	-3.059989	0.543200	-1.797136
H	-2.506434	1.483104	-1.933951
H	-2.798360	-0.136725	-2.621617
H	-4.125910	0.787556	-1.903676
C	3.471312	-2.349349	0.129623
H	3.100171	-3.078283	0.869572
H	3.877722	-2.928316	-0.708490
H	4.261379	-1.764536	0.609266

H (G781.778527E_gh12htsqnHPW)

C	0.456279	-1.270696	-1.959088
C	1.268700	-2.228117	-1.073075
C	2.470475	-1.507017	-0.431915
C	0.921013	0.580947	-0.276647
C	0.505675	0.354747	1.280011
C	-0.929230	-0.264421	1.291764

57

H	3.259090	-1.404600	-1.211523
H	1.112176	-0.850992	-2.741402
H	1.649399	-3.078161	-1.655144
C	2.209718	-0.078949	-0.128073
C	1.287818	2.070323	-0.588898
H	0.591025	1.320025	1.792185
C	2.587568	2.288809	0.223278
C	3.281015	0.907870	0.212073
H	2.351612	2.592132	1.253416
H	3.830425	0.640760	1.128404
H	1.546078	2.083519	-1.664441
C	0.215864	3.130879	-0.351079
H	-0.644351	2.993306	-1.016146
H	-0.145056	3.130849	0.686008
H	0.630873	4.126753	-0.554398
H	3.220087	3.074853	-0.204973
H	1.195431	-0.316390	1.823800
H	4.031361	0.829372	-0.597484
H	0.632468	-2.660444	-0.284918
H	-0.343385	-1.816293	-2.477652
C	-0.168181	-0.131904	-1.122611
H	-0.569589	0.622754	-1.813351
C	-0.937921	-1.455561	2.269989
H	-0.702789	-1.127255	3.292791
H	-1.921324	-1.938764	2.293582
H	-0.201455	-2.220960	1.982141
C	-2.003146	0.808037	1.696725
H	-1.559906	1.692577	2.175668
H	-2.673966	0.365478	2.446805
C	-1.287657	-0.667860	-0.179694
H	-1.307685	-1.766368	-0.267807
C	-2.781238	1.155522	0.415739
H	-2.293929	1.980775	-0.124636
H	-3.808233	1.484275	0.627559
C	-2.739831	-0.132116	-0.443139
C	-3.768913	-1.160480	0.086508
H	-3.700360	-2.106339	-0.469512
H	-3.640981	-1.390614	1.151597
H	-4.788415	-0.771598	-0.039662
C	-3.067985	0.135582	-1.923522
H	-2.474180	0.953729	-2.353173
H	-2.914028	-0.762549	-2.539088
H	-4.122954	0.424199	-2.024949
C	3.130300	-2.298927	0.728087
H	2.422594	-2.414828	1.559142
H	3.399534	-3.298424	0.368071
H	4.038483	-1.810774	1.100494

H (G781.778527E_hi13hqnHPW)

C	0.456387	-1.270584	-1.959187
C	1.268866	-2.227962	-1.073183
C	2.470591	-1.506795	-0.432013
C	0.920957	0.581030	-0.276716

C	0.505687	0.354514	1.280019
C	-0.929128	-0.264814	1.291699
H	3.259092	-1.404175	-1.211724
H	1.112267	-0.850811	-2.741476
H	1.649623	-3.077969	-1.655274
C	2.209693	-0.078755	-0.128086
C	1.287584	2.070489	-0.588706
H	0.591000	1.319743	1.792293
C	2.587267	2.289007	0.223563
C	3.280906	0.908172	0.212101
H	2.351213	2.592088	1.253753
H	3.830604	0.641046	1.128239
H	1.545893	2.083854	-1.664236
C	0.215476	3.130864	-0.350800
H	-0.644719	2.993202	-1.015876
H	-0.145436	3.130687	0.686290
H	0.630323	4.126820	-0.554036
H	3.219701	3.075225	-0.204488
H	1.195518	-0.316602	1.823751
H	4.031007	0.829925	-0.597720
H	0.632665	-2.660362	-0.285044
H	-0.343227	-1.816230	-2.477777
C	-0.168181	-0.131840	-1.122703
H	-0.569619	0.622795	-1.813449
C	-0.937647	-1.456237	2.269583
H	-0.702554	-1.128207	3.292483
H	-1.920994	-1.939554	2.293028
H	-0.201094	-2.221462	1.981510
C	-2.003137	0.807414	1.697080
H	-1.559953	1.691832	2.176300
H	-2.673870	0.364533	2.447044
C	-1.287656	-0.667894	-0.179848
H	-1.307750	-1.766381	-0.268188
C	-2.781302	1.155279	0.416238
H	-2.294085	1.980773	-0.123844
H	-3.808322	1.483857	0.628207
C	-2.739833	-0.132050	-0.443112
C	-3.768906	-1.160619	0.086153
H	-3.700336	-2.106287	-0.470189
H	-3.640984	-1.391109	1.151166
H	-4.788414	-0.771713	-0.039894
C	-3.067974	0.136200	-1.923392
H	-2.474149	0.954494	-2.352737
H	-2.914038	-0.761700	-2.539301
H	-4.122935	0.424882	-2.024709
C	3.130641	-2.298717	0.727819
H	2.423032	-2.414839	1.558930
H	3.400043	-3.298127	0.367692
H	4.038758	-1.810436	1.100224

H-TS (G781.767828T-498_hi13hPW)

C	-0.449609	-0.968780	2.144388
C	-1.218376	-2.047978	1.369038

C	-2.359718	-1.448931	0.533919
C	-0.812053	0.715761	0.265776
C	-0.466226	0.321231	-1.134078
C	0.819505	-0.485424	-1.212631
H	-3.108575	-1.069865	1.255515
H	-1.141425	-0.438527	2.819722
H	-1.659219	-2.777620	2.062435
C	-1.997041	-0.141237	-0.191323
C	-1.353036	2.131032	0.531627
H	-0.766192	0.950000	-1.979158
C	-2.544635	2.257760	-0.446096
C	-3.130563	0.833959	-0.582452
H	-2.190372	2.629772	-1.419746
H	-3.557673	0.623711	-1.571262
H	-1.738627	2.123927	1.567045
C	-0.319770	3.252439	0.397493
H	0.497896	3.142222	1.121393
H	0.114993	3.272417	-0.612835
H	-0.788163	4.228805	0.576084
H	-3.295446	2.975534	-0.094455
H	-1.518503	-0.549449	-1.292186
H	-3.934908	0.665874	0.148379
H	-0.538838	-2.625282	0.722841
H	0.318613	-1.432309	2.778983
C	0.225051	0.040337	1.192918
H	0.687306	0.829162	1.800834
C	0.669835	-1.784745	-2.020984
H	0.334153	-1.576814	-3.046982
H	1.629615	-2.309282	-2.081699
H	-0.052069	-2.470229	-1.555360
C	1.874766	0.490323	-1.873270
H	1.410938	1.267230	-2.498237
H	2.505086	-0.105063	-2.547347
C	1.292635	-0.655549	0.281608
H	1.339846	-1.722906	0.544934
C	2.694601	1.066717	-0.710260
H	2.193582	1.950929	-0.284990
H	3.694185	1.391234	-1.030360
C	2.747470	-0.068531	0.340190
C	3.748779	-1.164794	-0.099838
H	3.768004	-1.987950	0.628135
H	3.514643	-1.598815	-1.080678
H	4.763693	-0.749444	-0.161811
C	3.181600	0.435532	1.728216
H	2.622096	1.322238	2.054585
H	3.067598	-0.346208	2.492723
H	4.242062	0.720769	1.705870
C	-3.055947	-2.466911	-0.380015
H	-2.359914	-2.868812	-1.130983
H	-3.426545	-3.313389	0.211080
H	-3.911454	-2.025121	-0.907825

I (G781.775876E_hi13hqpIPW)

C	0.372741	-1.484557	-1.702320
C	1.271756	-2.314809	-0.784549
C	2.441343	-1.484584	-0.244680
C	0.803555	0.588651	-0.208605
C	0.190577	0.931142	1.039187
C	-1.074414	0.249440	1.312931
H	2.992050	-1.069178	-1.107248
H	0.961442	-1.135888	-2.565990
H	1.677576	-3.176387	-1.333219
C	2.010536	-0.260891	0.619361
C	1.636156	1.642157	-0.974806
H	0.634847	1.632181	1.755051
C	2.749601	2.062529	0.001737
C	3.125716	0.801720	0.817424
H	2.375996	2.858433	0.664905
H	3.270248	1.033405	1.880260
H	2.085253	1.117972	-1.835611
C	0.795850	2.814901	-1.495942
H	0.030763	2.493703	-2.214729
H	0.293140	3.336791	-0.667507
H	1.439259	3.543049	-2.006300
H	3.610300	2.486853	-0.529699
H	1.663948	-0.667052	1.586407
H	4.072033	0.375329	0.459480
H	0.697796	-2.732879	0.059891
H	-0.443436	-2.097888	-2.108374
C	-0.230222	-0.278647	-0.969325
H	-0.670266	0.388500	-1.726104
C	-1.139792	-0.397171	2.710573
H	-0.900900	0.330618	3.497978
H	-2.142336	-0.791873	2.904544
H	-0.428980	-1.231477	2.782489
C	-2.145384	1.455838	1.163825
H	-1.690169	2.457289	1.191437
H	-2.798001	1.391163	2.044424
C	-1.337412	-0.663177	0.067718
H	-1.243632	-1.726229	0.342750
C	-2.878503	1.183761	-0.160798
H	-2.385130	1.724476	-0.983002
H	-3.915671	1.545144	-0.118242
C	-2.796721	-0.346397	-0.397678
C	-3.819021	-1.084359	0.498774
H	-3.679402	-2.172561	0.437875
H	-3.759126	-0.799582	1.556702
H	-4.840964	-0.860282	0.164736
C	-3.086877	-0.730383	-1.860144
H	-2.432773	-0.219512	-2.579066
H	-2.981890	-1.813527	-2.012572
H	-4.120155	-0.462623	-2.118969
C	3.396824	-2.351955	0.595553
H	2.864699	-2.812121	1.440732
H	3.799922	-3.160810	-0.028399

| H | 4.245716 | -1.784274 | 0.995950 |

I (G781.762206E_ijsctsqnIPW)

C	0.615136	0.926587	1.985038
C	1.253269	2.124291	1.268697
C	2.312566	1.738968	0.192929
C	0.888457	-0.449057	-0.195097
C	0.195564	-0.034931	-1.389219
C	-1.149949	0.454399	-1.186959
H	3.315673	1.957476	0.598779
H	1.361545	0.393809	2.592459
H	1.700869	2.804945	2.005048
C	2.340542	0.236595	-0.150267
C	1.307226	-1.990082	-0.166229
H	0.627056	-0.135285	-2.391930
C	2.349045	-1.993865	0.975116
C	3.153214	-0.688521	0.810978
H	2.976779	-2.893753	0.922770
H	4.143518	-0.868048	0.370978
H	0.408898	-2.566549	0.103299
C	1.866965	-2.542534	-1.484388
H	1.124442	-2.537275	-2.293581
H	2.754521	-1.996529	-1.830273
H	2.170338	-3.586103	-1.331133
H	1.840858	-2.013341	1.949356
H	2.771403	0.135685	-1.158289
H	3.321634	-0.191624	1.774089
H	0.456729	2.708919	0.778353
H	-0.149555	1.281844	2.691234
C	-0.051103	-0.046340	0.994667
H	-0.302890	-0.965183	1.540181
C	-1.576288	1.631723	-2.079258
H	-1.302780	1.455175	-3.128068
H	-2.657706	1.788893	-2.028764
H	-1.083995	2.553275	-1.743277
C	-1.956254	-0.928674	-1.601302
H	-1.337907	-1.680669	-2.113819
H	-2.706481	-0.598137	-2.330659
C	-1.355662	0.553460	0.357314
H	-1.470057	1.606320	0.660353
C	-2.538704	-1.453698	-0.279596
H	-1.870293	-2.212268	0.154422
H	-3.504639	-1.947147	-0.462581
C	-2.665653	-0.239273	0.673645
C	-3.910491	0.604391	0.306892
H	-3.927247	1.544599	0.874894
H	-3.972488	0.857537	-0.758608
H	-4.824291	0.048498	0.555479
C	-2.802074	-0.657871	2.149603
H	-2.012011	-1.344660	2.479755
H	-2.787474	0.220884	2.809280
H	-3.759913	-1.171312	2.307591
C	2.135940	2.580570	-1.077022

H	1.199264	2.305364	-1.598254
H	2.063694	3.651633	-0.845801
H	2.962014	2.436194	-1.786537

I-TS (G781.754193T-303_ijsctsPW)

C	0.741539	-1.670528	-1.523890
C	1.667718	-2.306302	-0.482543
C	2.834716	-1.368101	-0.102305
C	0.879656	0.293829	0.093433
C	0.178709	0.401216	1.296260
C	-1.175044	-0.199455	1.286696
H	3.564980	-1.405241	-0.929162
H	1.336934	-1.361903	-2.397772
H	2.078998	-3.254941	-0.854044
C	2.401926	0.133149	0.022171
C	0.787487	2.227100	-0.278526
H	0.615002	0.840343	2.200098
C	2.227233	2.408990	-0.750187
C	2.849026	1.061268	-1.122471
H	2.811543	2.883955	0.051912
H	3.942385	1.116650	-1.202001
H	0.058565	2.098572	-1.083851
C	0.331353	3.232047	0.756524
H	-0.715690	3.116172	1.051013
H	0.969701	3.235478	1.648787
H	0.433444	4.226716	0.292054
H	2.200686	3.113090	-1.599254
H	2.826373	0.540689	0.956479
H	2.466708	0.698015	-2.088244
H	1.090909	-2.563775	0.425344
H	-0.000083	-2.391766	-1.894165
C	-0.003744	-0.449168	-0.932746
H	-0.240697	0.227211	-1.766339
C	-1.183756	-1.236678	2.452660
H	-1.146526	-0.736030	3.428995
H	-2.116416	-1.811176	2.389898
H	-0.344929	-1.941588	2.385939
C	-2.354669	0.827616	1.443910
H	-2.058625	1.735329	1.985971
H	-3.146407	0.355415	2.040705
C	-1.311870	-0.822411	-0.153351
H	-1.358752	-1.921277	-0.082733
C	-2.830658	1.080309	0.005641
H	-2.201449	1.843497	-0.484487
H	-3.863114	1.454136	-0.029862
C	-2.671489	-0.282498	-0.720680
C	-3.804309	-1.248509	-0.294710
H	-3.688673	-2.220767	-0.793274
H	-3.824979	-1.435084	0.787310
H	-4.784447	-0.840558	-0.576825
C	-2.721320	-0.133166	-2.251125
H	-2.038676	0.642870	-2.624510
H	-2.475017	-1.078349	-2.755000

H	-3.733063	0.155375	-2.567158
C	3.529378	-1.848095	1.179720
H	2.846643	-1.780855	2.041905
H	3.842715	-2.896664	1.088710
H	4.420666	-1.247231	1.406676

J (G781.791289E_ijsctsqpJPW)

C	0.652031	-2.506028	0.428775
C	2.151705	-2.402217	0.760331
C	2.892056	-1.396021	-0.148410
C	0.864119	0.040087	0.283844
C	0.087462	1.262115	0.522319
C	-1.427868	0.828213	0.630286
H	2.674440	-1.650652	-1.203124
H	0.491773	-3.194707	-0.409783
H	2.615347	-3.394247	0.679867
C	2.327314	0.017298	0.123356
C	0.530349	2.429820	-0.445502
H	0.432072	1.610078	1.522379
C	2.065984	2.471674	-0.555767
C	2.682550	1.123928	-0.936861
H	2.495503	2.820246	0.398335
H	3.775821	1.187807	-0.998405
H	0.125439	2.183830	-1.442052
C	-0.039456	3.775759	0.018580
H	-1.132301	3.762389	0.097642
H	0.367425	4.051072	1.002222
H	0.233661	4.565308	-0.693822
H	2.338792	3.223437	-1.311651
H	2.739623	0.395534	1.082911
H	2.319896	0.792587	-1.922823
H	2.282698	-2.080308	1.808529
H	0.094010	-2.918871	1.281184
C	0.026933	-1.126989	0.086255
H	0.031810	-1.052142	-1.043165
C	-1.986828	1.336211	1.973930
H	-1.999504	2.434762	2.005334
H	-3.014586	0.988964	2.134332
H	-1.380531	0.980616	2.820346
C	-2.339941	1.261826	-0.568062
H	-1.942876	2.107958	-1.139053
H	-3.308877	1.595402	-0.172149
C	-1.406539	-0.755776	0.549523
H	-1.563739	-1.211125	1.542035
C	-2.531498	0.010518	-1.439787
H	-1.688172	-0.097205	-2.146658
H	-3.442955	0.048221	-2.051579
C	-2.536066	-1.177016	-0.444432
C	-3.887531	-1.261935	0.302231
H	-3.862008	-2.055392	1.062086
H	-4.159909	-0.327314	0.807101
H	-4.694482	-1.499347	-0.403871
C	-2.289820	-2.523677	-1.146724

H	-1.378170	-2.518060	-1.763488
H	-2.214298	-3.351351	-0.427787
H	-3.124299	-2.749939	-1.823829
C	4.411515	-1.447803	0.063535
H	4.670036	-1.211268	1.106378
H	4.794656	-2.452564	-0.154273
H	4.944874	-0.743650	-0.587676

References

1   R. D. Gietz and R. H. Schiestl, *Nat. Protoc.* 2007, **2**, 31-34.

2   J. S. Dickschat, K. A. K. Pahirulzaman, P. Rabe and T. A. Klapschinski, *ChemBioChem* 2014, **15**, 810-814.

3   M. M. Bradford, *Anal. Biochem.* 1976, **72**, 248-254.

4   G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics* 2010, **29**, 2176-2179.

5   S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem.* 2011, **32**, 1456-1465.

6   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, 2019.

7   S. Grimme, *Chem. Eur. J.* 2012, **18**, 9955-9964.

8   G. Luchini, J. V. Alegre-Requena, Y. Guan, I. Funes-Ardoiz, R. S. Paton, GoodVibes v3.0.1, 2019.

9   C. Adamo, V. Barone, *J. Chem. Phys.* 1998, **108**, 664-675.

10   S. P. T. Matsuda, W. K. Wilson, Q. Xiong, *Org. Biomol. Chem.* 2006, **4**, 530-543.

11   Y. J. Hong, D. J. Tantillo, *J. Org. Chem.* 2018, **83**, 3780-3793.

12   L. Lauterbach, B. Goldfuss, J. S. Dickschat, *Angew. Chem. Int. Ed.* 2020, **59**, 11943-11947.

13   H. Xu, B. Goldfuss, J. S. Dickschat, *Chem. Eur. J.* 2021, **27**, 9758-9762.

14   P. Pracht, F. Bohle, S. Grimme, *Phys. Chem. Chem. Phys.* 2020, **22**, 7169-7192.

15   S. Grimme, *J. Chem. Theory Comput.* 2019, **155**, 2847-2862.

16   P. Pracht, S. Grimme, *Chem. Sci.* 2021, **12**, 6551-6568.

17   P. Pracht, C.A. Bauer, S. Grimme, *J. Comput. Chem.* 2017, **38**, 2618-2631.

18   S. Spicher, C. Plett, P. Pracht, A. Hansen, S. Grimme, *J. Chem. Theory Comput.* 2022, **18**, 3174-3189.

19   F. Neese, "The ORCA program system" Wiley Interdisciplinary Reviews: Computational Molecular Science, 2012, **2**, 73-78.

20   Z. Quan and J. S. Dickschat, *Org. Biomol. Chem.* 2020, **18**, 6072-6076.

21   P. Rabe, J. Rinkel, E. Dolja, T. Schmitz, B. Nubbemeyer, T. H. Luu and J. S. Dickschat, *Angew. Chem. Int. Ed.* 2017, **56**, 2776-2779.

22   P. Rabe, L. Barra, J. Rinkel, R. Riclea, C. A. Citron, T. A. Klapschinski, A. Janusko and J. S. Dickschat, *Angew. Chem. Int. Ed.* 2015, **54**, 13448-13451.

23   H. Li and J. S. Dickschat, *Org. Chem. Front.* 2022, **9**, 795-801.

24   G. Bian, J. Rinkel, Z. Wang, L. Lauterbach, A. Hou, Y. Yuan, Z. Deng, T. Liu and J. S. Dickschat, *Angew. Chem. Int. Ed.* 2018, **57**, 15887-15890.

25   T. A. Klapschinski, P. Rabe and J. S. Dickschat, *Angew. Chem. Int. Ed.* 2016, **55**, 10141-10144.

26   J. Rinkel, P. Rabe, X. Chen, T. G. Köllner, F. Chen and J. S. Dickschat, *Chem. Eur. J.* 2017, **23**, 10501-10505.

27   J. Rinkel and J. S. Dickschat, *Org. Lett.* 2019, **21**, 2426-2429.

28   F. M. Hahn, A. P. Hurlburt and C. D. Poulter, *J. Bacteriol.* 1999, **181**, 4499-4504.

29   L. Lauterbach, J. Rinkel and J. S. Dickschat, *Angew. Chem. Int. Ed.* 2018, **57**, 8280-8283.

30   P. Rabe, J. Rinkel, B. Nubbemeyer, T. G. Köllner, F. Chen and J. S. Dickschat, *Angew. Chem. Int. Ed.*, 2016, **55**, 15420-15423.

31   C. A. Citron, J. Gleitzmann, G. Laurenzano, R. Pukall and J. S. Dickschat, *ChemBioChem*, 2012, **13**, 202-214.

32   H. Utsunomia, J. Kawata, W. Chanoki, N. Shirakawa and M. Miyazawa, *J. Oleo Sci.*, 2005, **54**, 609-612.