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Supporting Information

Biosynthesis of *Pseudomonas*-Derived Butenolides

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General Microbiological and Molecular Biology Methods

Pseudomonas fluorescens HKI0874 was previously isolated as described by Klapper *et al.*[1] *P. fluorescens* HKI0874 was propagated on SM/5 solid agar or liquid medium (Formedium™, UK) at 22 °C. When grown in liquid culture, *P. fluorescens* HKI0874 was cultured in 1 L baffled Erlenmeyer flasks containing 250 mL SM/5 medium or in 5 mL SM/5 in culture tubes at 22 °C on a gyratory shaker at 135 rpm unless otherwise noted. *Pseudomonas jessenii* EC-S101[2] was a kind gift of Prof. Hashidoko (Hokkaido University, Japan) and was propagated on SM/5 solid agar or liquid medium (Formedium™, UK) at 22 °C. *Escherichia coli* strains were cultured at 37 °C in LB liquid or solid agar medium (Carl Roth, Germany). When required, media were supplemented with gentamicin (15 µg/mL, Carl Roth, Germany), kanamycin (50 µg/mL, Carl Roth, Germany), chloramphenicol (50 µg/mL, Carl Roth, Germany), and ampicillin (100 µg/mL, Carl Roth, Germany). For selection on sucrose, LB agar was prepared without NaCl (10 g/L tryptone, 5 g/L yeast extract, 50 g/L sucrose, 15 g/L agar agar, Carl Roth, Germany). Glycerol stocks of bacterial strains were prepared by mixing 1 mL overnight culture of the respective strain with 0.5 mL of 60% (v/v) *aq.* glycerol and stored at –80 °C.
Oligonucleotides used in this study were purchased from Invitrogen (ThermoFisher Scientific, Darmstadt). PCR reactions were carried out in a peqSTAR PCR cycler (Peqlab) using Q5® High-Fidelity 2x Master Mix (New England Biolabs) for applications requiring high fidelity such as sequencing and cloning, for other applications DreamTaq Green PCR Master Mix 2x (Thermo Scientific, Darmstadt) was used. PCR reaction products were purified for subsequent cloning and sequencing by gel extraction using GeneJET Gel Extraction Kit (Thermo Scientific). Plasmid constructs were cloned using the Gibson Assembly method (New England Biolabs, software: http://nebuilder.neb.com). Plasmids were isolated using QIAprep® Spin Miniprep Kit (Qiagen). PCR products were treated with ExoSAP-IT (Thermo Scientific) before sequencing. DNA Sanger sequencing was performed by LGC Genomics, Berlin. Sequences were mapped to reference sequences using Geneious 11.0.3.

Instrumentation and General Synthetic Methods

All 1D (^{1}H, ^{13}C, selective NOESY) and 2D NMR spectra (^{1}H-^{1}H COSY, HSQC, HMBC) were recorded in deuterated solvents (VWR, Germany) on Bruker AVANCE DRX 300, 500, and 600 MHz (600 MHz with Bruker cryo probe) instruments. Chemical shifts (δ) are reported in parts per million relatively to the resonance of the residual solvent. Coupling constants (*J*) are reported in Hertz (Hz). HRESI-MS measurements were conducted on a Thermo Fisher Exactive Orbitrap equipped with an electrospray ion source and a Betasil 100-3 C_{18} column (150 × 2.1 mm). The following elution gradient was used: 5% B for 1 min, 5% to 98% B in 15 min, 98% B for 3 min, solvent A: H_2O + 0.1% HCOOH, solvent B: acetonitrile, flow rate: 0.2 mL min^{-1}, injection volume: 5 µL. Optical rotation measurements were performed using a 0.5 dm cuvette on a JASCO P-1020 polarimeter at 25 °C (unless otherwise noted).

UHPLC-ESI-MS analysis was performed on a Shimadzu System (LC-30AD, SPD-M30A, LCMS-2020). The system is equipped with an electrospray ion source. The following elution gradient was used on a Kinetex® C18 column (50 × 2.1 mm, 1.7 µm, 100 Å, Phenomenex) if not otherwise stated: solvent A: H_2O + 0.1% HCOOH, solvent B: acetonitrile + 0.1% HCOOH, flow rate: 0.7 mL min^{-1}, gradient: 10% B for 0.5 min, 10% to 100% B in 8 min, 100% B for 3 min, injection: 1 to 10 µL. The column was equilibrated prior each injection with 10% B for 2.5 min.

Flash chromatography was performed on normal phase silica gel (NORMASIL 60 VWR, 40-63 µm) or on reverse phase silica gel (Biotage® KP-C18-HS) on a Biotage® IsoleraTM Prime using the indicated solvents. Semi-preparative HPLC purification was conducted on a Shimadzu HPLC System (LC-20AD, SPD-M20A) using a Luna® C18(2) column (250 × 10 mm, 5 µm, 100 Å, Phenomenex). Acetonitrile and H_2O was used as mobile phase with a flow rate of 5 mL min^{-1}.

All chemicals used were reagent grade and used as supplied except where noted (Sigma-Aldrich, TCI, Carl Roth, Alfa Aesar, VWR, Merck abcr). Solvents for chromatography and workup procedures were obtained from VWR (Chromanorm, HPLC grade). Anhydrous tetrahydrofuran (THF) was obtained from a solvent purification system. Reactions were performed under an argon atmosphere where noted. Analytical thin-layer chromatography was performed on *E. Merck* silica gel 60 F_{254} plates (0.25 mm). Compounds were visualized either by UV absorption (254 nm) or by staining using permanganate, ninhydrin, or cerium-ammonium-molybdate (CAM) stain.

Genome Sequencing and Annotation

For whole genome sequencing, genomic DNA of *P. fluorescens* HKI0874 and *Pseudomonas jessenii* EC-S101[2] was isolated from 3 mL overnight cultures in SM/5 medium using the QIAamp DNA Mini Kit (Qiagen). Illumina sequencing (Illumina HiSeq sequencer with NovaSeq 6000 S2 PE150 XP sequencing mode) as well as assembly of the genome was performed by GATC (Konstanz, Germany). The fastq files obtained were subjected to *de novo* assembly using CLC mapper (v4.22.107090). For *P. fluorescens* HKI0874 this resulted in 130 contigs with an N50 value of 148,257 bp. The Whole Genome Shotgun project for *P. fluorescens* HKI0874 has been deposited at DDBJ/ENA/GenBank under the accession VCNJ00000000. The version described in this paper is version VCNJ01000000. For *P. jessenii* EC-S101 35 contigs with an N50 value of 328341 bp were obtained. The Whole Genome Shotgun project for *P. jessenii* EC-S101 has been deposited at DDBJ/ENA/GenBank under the accession VDDB00000000. The version described in this paper is version VDDB01000000. Genomic data with annotations according to this report can be retrieved from: https://doi.org/10.6084/m9.figshare.10259870.v1. The genome sequence was mined for biosynthetic gene clusters using AntiSmash 5.0.[3] The contigs from genome sequencing were annotated using Rapid prokaryotic genome annotation Prokka (v1.13.3).[4]

Phylogenetic Placement of *P. fluorescens* HKI0874 and *P. jessenii* EC-S101

The phylogenetic placement of the strain was carried out using the phylogenomics pipeline in anvio (v5.4 margaret).[5] The dataset used for the phylogenomic analysis was obtained from NCBI with reference genomes downloaded using ncbi-genome-download script described in https://github.com/kblin/ncbi-genome-download. Briefly, the multifasta file from the assembly and reference genomes downloaded from NCBI (as .fasta) were converted into contig databases using anvi-script-FASTA-to-contigs-db command. For each contig database custom hidden Markov model (hmm) profiles were created by searching for single copy genes (N = 139) identified by Campbell *et al.*[6] The single copy genes (amino acid sequences) that were common to all the genomes were subsequently concatenated and aligned using MUSCLE.[7] A genome wide maximum likelihood phylogenetic tree was constructed from the alignment using FastTree (v2.1.10)[8] using JTT model. The obtained newick tree was visualized and modified in itol tree manipulation suit (v4.4).[9] *P. fluorescens* HKI0874 and *P. jessenii* EC-S101 grouped under the

Fluorescens clade and were found to be closely related to each other, as well as related to *Pseudomonas fluorescens* Pf01 and *Pseudomonas jessenii* LBp-160603 (Figure S1).

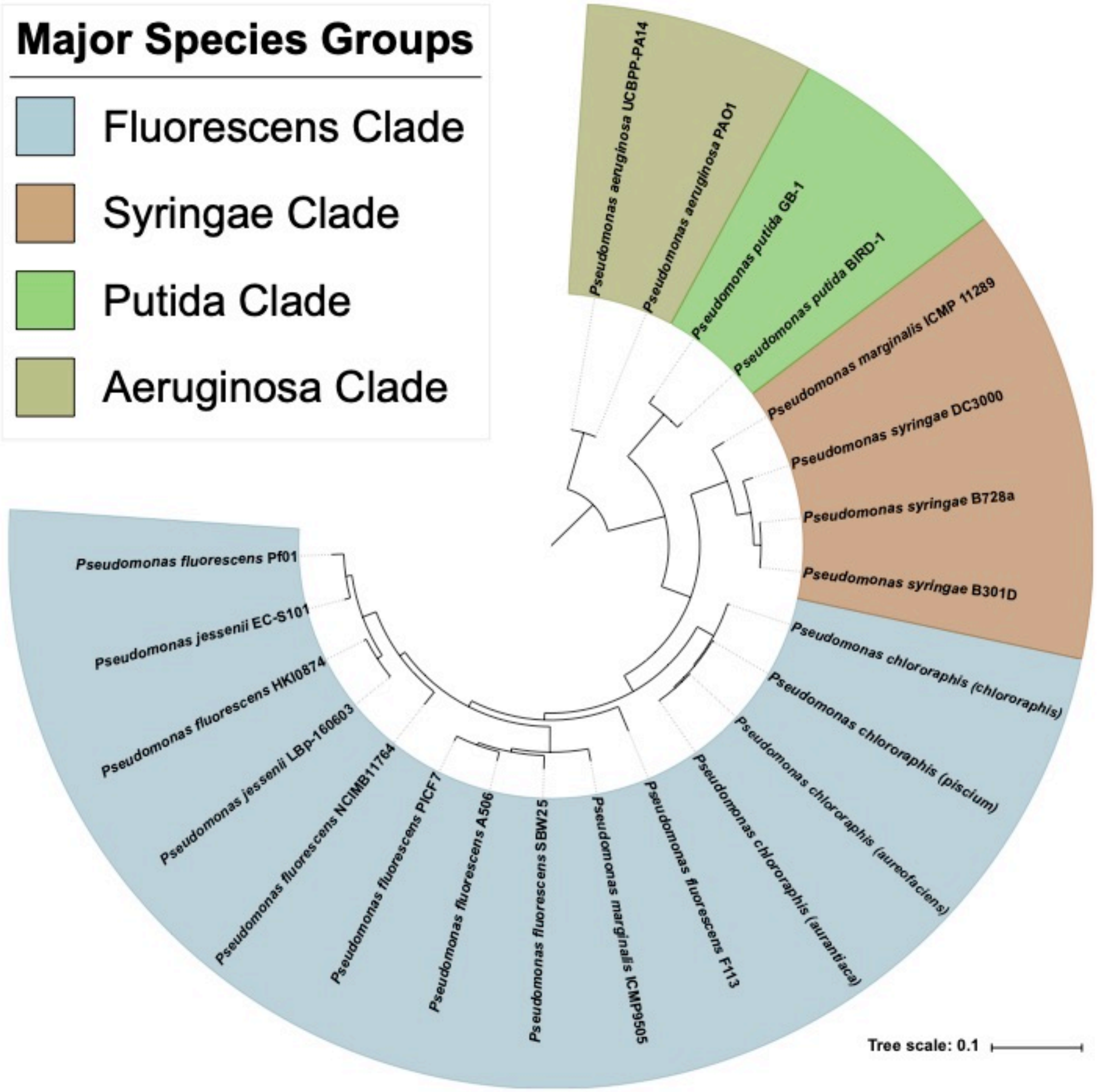


Figure S1: Phylogenetic placement of *P. fluorescens* HKI0874 and *P. jessenii* EC-S101 amongst different pseudomonads. Species name and strain designation is given. Names in brackets denote subspecies.

Isolation of Styrolide A (1) and Styrolide B (2)

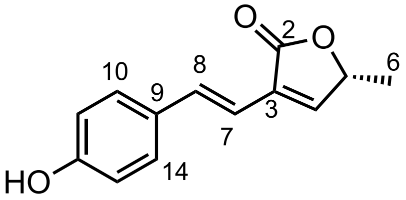
A 5 mL SM/5 (Formedium™, UK) liquid culture of *P. fluorescens* HKI0874 was inoculated from a single colony grown overnight on SM/5 agar at 22 °C and incubated at 22 °C overnight while shaking on a gyratory shaker at 180 rpm. A 200 mL pre-culture in SM/5 medium was inoculated from the 5 mL pre-culture and shaken for 24 h at 22 °C. A 40 L batch fermenter containing SM/5 medium was inoculated with 200 mL pre-culture and fermented at 22 °C. After 13.5 h the bottom-aeration of the fermenter was changed to head-aeration only, due to extensive foaming caused by lipopeptide production. After 19.5 h the culture was centrifuged and the supernatant was extracted with an equal amount of ethyl acetate. The solvent was removed *in vacuo*, until approximately 500 mL solvent was left. The organic phase was dried over Na_2SO_4, decanted and 15 g Isolute® HM-N (Biotage) was added before the solvent was removed *in vacuo* to obtain 7.7 g of absorbed crude extract. For isolation of styrolide A (**1**) 6 g of Isolute-extract (*i.e.* approximately 2 g of crude extract) were fractionated on 60 g normal phase silica gel by flash chromatography using an Isolera™ Prime (Biotage), flow rate 50 mL min^{-1}, with 25% ethyl acetate in hexane (1:3). Styrolide A (**1**) eluted after 1.2 L in approximately 300 mL of solvent. Fractions containing styrolide A (**1**) were combined (9 mg) and re-purified by semi-preparative reverse-phase HPLC (PDA lamp turned off) using the following elution gradient: solvent A: H_2O, solvent B: acetonitrile, 35% B for 15 min (t_R = 14 – 15 min). The solvent was removed *in vacuo* at 30 °C, avoiding light exposure, to yield 4 mg styrolide A (**1**). Extensive drying of styrolide A (**1**) led to partly decomposition.

Styrolide B (**2**) was purified from 1 g of Isolute-extract (*i.e.* approximately 0.34 g of crude extract) on normal phase silica (60 g) with forced flow using the following elution gradient: A: hexane, B: ethyl acetate, 20% B for 1 L, 25 % B for 0.3 L. Styrolide B (**2**) eluted after 1 L in approximately 200 mL of solvent. Fractions containing styrolide B (**2**) were combined and the organic phase was quickly removed *in vacuo* at 25 °C, avoiding light exposure, to yield 0.2 mg styrolide B (**2**). NMR experiments were conducted immediately due to instability of styrolide B (**2**). Complete drying or reverse-phase purification (requires prolonged removal of aqueous organic phase) of styrolide B (**2**) led to decomposition.

Analytical Data of Isolated Styrolides

For styrolide A (**1**) NMR data match those of the respective synthetic compound (c.f. **Total Synthesis of Styrolide A (1)**).

Table S1: NMR signal assignment for styrolide A (**1**) measured in *d₄-MeOD* (500 MHz).

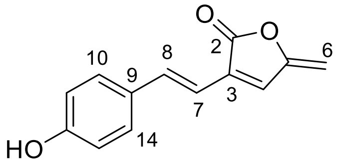


Position	δC [ppm]	δH [ppm] (m, *J* [Hz])
2	174.3	-
3	130.2	-
4	150.2	7.42 (d, 1.5, 1H)
5	79.3	5.14 (q, 6.8, 1H)
6	19.3	1.42 (d, 6.9, 3H)
7	114.9	6.69 (d, 16.4, 1H)
8	135.5	7.54 (d, 16.3, 1H)
9	129.5	-
10, 14	129.4	7.36 (d, 8.5, 2H)
11, 13	116.6	6.78 (d, 8.5, 2H)
12	159.4	4.57 (s, OH)

HR-ESI-MS: $[M+H]^+$ *m/z* = 217.0860 (calculated for $C_{13}H_{13}O_3^+$ 217.0859).

The coupling constant between proton H7 and H8 (*J* = 16.4 Hz) suggests an *E*-configuration of the corresponding double bond. The absolute configuration was determined by retention time comparison with synthetic styrolide A **1** enantiomers (see **ECD Spectrum Calculation for (*R*/*S*)-Styrolide A 1 for Determination of Absolute Configuration of Styrolide A**).

Table S2: NMR signal assignment for styrolide B (**2**) measured in *d_4-MeOD* (500 MHz).



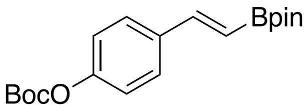
Position	δ_C [ppm]	δ_H [ppm] (m, *J* [Hz])
2	170.6	-
3	131.9	-
4	134.2	7.41 (s, 1H)
5	156.1	-
6	96.8	4.96 (d, 2.3, 1H), 5.15 (d, 2.3, 1H)
7	114.8	6.81 (d, 16.4, 1H)
8	137.8	7.63 (d, 16.3, 1H)
9	129.4	-
10, 14	129.8	7.40 (d, 8.4, 2H)
11, 13	116.8	6.79 (d, 8.5, 2H)
12	159.9	4.55 (s, OH)

HR-ESI-MS: $[M+H]^+$ *m/z* = 215.0705 (calculated for $C_{13}H_{11}O_3^+$ 215.0703)

The coupling constant between proton H7 and H8 (*J* = 16.4 Hz) suggests an *E*-configuration of the corresponding double bond.

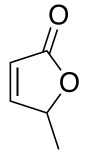
Total Synthesis of Styrolide A (1)

(*E*)-*tert*-Butyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-phenyl) carbonate (4)



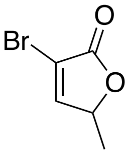
2M *N*-Lithiumdiisopropyl amide in THF (1.08 mL, 2.16 mmol, 1.2 eq.) was added under argon atmosphere to 1 mL anhydrous THF and cooled to 0 °C. $(Bpin)_2CH_2$ (572 mg, 2.16 mmol, 1.2 eq.) in 4 mL anhydrous THF was slowly added and the reaction mixture was stirred for 15 min at 0 °C and cooled to –78 °C.[10] *Tert*-butyl-(4-formylphenyl) carbonate **3** (0.4 g, 1.8 mmol, 1 eq.) in 2 mL anhydrous THF was added slowly and the reaction suspension was stirred for 4 h at –78 °C. The reaction mixture was warmed to r.t. and the solvent was removed *in vacuo*. After flash chromatography on reverse phase silica gel (solvent A: acetonitrile + 0.1% HCOOH, solvent B: H_2O + 0.1% HCOOH, stepwise gradient: 40% A for 9 min, 50% A for 9 min, 60% for 9 min, 70% A for 9 min, SNAP ultra C18 30 g Biotage®, flow rate: 25 mL min^{-1}, t_R = 26 – 33 min) **4** was obtained as a yellow oil (255 mg, 0.74 mmol). 41% yield; ^{1}H NMR (300 MHz, *CDCl₃*) δ 7.48 (app d, 8.6, 2H), 7.36 (d, 18.7, 1H), 7.14 (app d, 8.6, 2H), 6.10 (d, 18.4, 1H), 1.55 (s, 9H), 1.31 (s, 12H); ^{13}C NMR (75 MHz, *CDCl₃*) δ 151.6, 151.4, 148.3, 135.1, 128.0 (2C), 121.3 (2C), 116.7 (from HSQC), 83.7, 83.4 (2C), 27.7 (3C), 24.8 (4C); ESI-MS: $[M\text{-}Boc+H]^+$ *m/z* = 247.15, $\lambda_{max,1}$ = 216 nm, $\lambda_{max,2}$ = 265 nm, t_R = 8.70 min (Boc-group was removed upon ESI-ionisation)[11]; HR-ESI-MS: $[M\text{-}H]^-$ *m/z* = 309.1148 (calculated for $C_{14}H_{18}O_7B^-$ 309.1140, free boronic acid with 1 eq. HCOOH).

β-Angelica lactone (6)



β-Angelica lactone **6** was synthesized according to a known literature procedure.[12] A catalytic amount of NEt_3 (140 µL, 1.02 mmol, 0.1 eq.) was added to α-angelica lactone **5** (1 g, 10.2 mmol, 1 eq.). The reaction was carried out without solvents. The reaction mixture was heated to 75 °C and after 2 h cooled to r.t. Subsequent flash chromatography on normal phase silica gel (solvent A: EtOAc, solvent B: hexane, 50% A) yielded β-angelica lactone **6** as a colorless oil (550 mg, 0.56 mmol). 55% yield; ^{1}H NMR (500 MHz, *$CDCl_3$*) δ 7.44 (d, 5.7, 1H), 6.07 (dd, 5.6, 1.6, 1H), 5.12 (app q, 6.9, 1H), 1.43 (d, 6.9, 3H); ^{13}C NMR (125 MHz, *$CDCl_3$*) δ 173.0, 157.4, 121.2, 79.6, 18.8; ESI-MS: $[M+H]^+$ *m/z* = 99.05, λ_{max} = 223 nm, t_R = 0.48 min. Analytical data match reported literature values.[13]

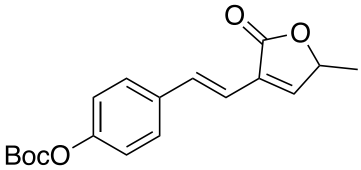
3-Bromo-5-methylfuran-2(5*H*)-one (7)



Bromination of β-angelica lactone **6** was adapted from a literature-known procedure[14] and performed in benzotrifluoride (BTF).[15] A solution of bromine (300 µL, 5.81 mmol, 1.5 eq.) in 4 mL BTF was slowly added to β-angelica lactone **6** (380 mg, 3.78 mmol, 1 eq.) in 10 mL BTF. The reaction mixture was stirred for 2 h at 90 °C and cooled to r.t. NEt_3 (800 µL, 5.81 mmol, 1.5 eq.) was added and the reaction mixture was stirred for 18 h at r.t. The precipitating $HNEt_3Br$ was removed by filtration using Celite and washed with DCM. The combined filtrate was washed with 1.2 M aqueous HCl solution and H_2O, dried over Na_2SO_4 and the solvent was removed *in vacuo*. After flash chromatography on normal phase silica gel (solvent A: Et_2O, solvent B: hexane, 25% A) 3-bromo-5-methylfuran-2(5*H*)-one **7** was obtained as an off-yellow oil (300 mg, 1.69 mmol). 43% yield; ^{1}H NMR (600 MHz, *$CDCl_3$*) δ 7.51 (s, 1H), 5.08 (q, 6.8, 1H), 1.48 (d, 6.9, 3H); ^{13}C NMR (150 MHz, *$CDCl_3$*) δ 168.2, 153.6, 113.2, 79.1, 18.8. ESI-MS:

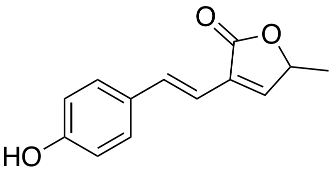
$[M+H]^+$ *m/z* = 177.05, λ_{max} = 226 nm, t_R = 0.97 min. Analytical data match reported literature values.[14]

(*E*)-*tert*-Butyl(4-(2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)vinyl)phenyl) carbonate (8)



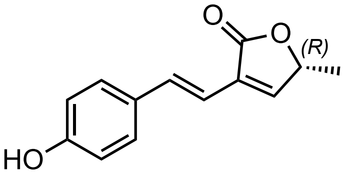
(*E*)-*tert*-Butyl-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl) carbonate **4** (61 mg, 0.18 mmol, 1.3 eq.) and 3-bromo-5-methylfuran-2(5*H*)-one **7** (24 mg, 0.14 mmol, 1 eq.) were dissolved in 1.2 mL oxygen-free THF. K_2CO_3 (38 mg, 0.27 mmol, 2 eq.) in 300 µL oxygen-free water and $Pd(PPh_3)_4$ (16 mg, 14 µmol, 0.1 eq.) were added and the reaction suspension was stirred 48 h at 50 °C under argon atmosphere.[16-17] The reaction was stopped by the addition of aqueous saturated ammonium chloride solution. The suspension was extracted three times with EtOAc. The combined organic phases were washed twice with water, dried over Na_2SO_4 and the solvent was removed *in vacuo*. After flash chromatography on reverse phase silica gel (solvent A: acetonitrile + 0.1% HCOOH, solvent B: H_2O + 0.1% HCOOH, stepwise gradient: 40% A for 7.1 min, 50% A for 7.1 min, 60% for 7.1 min, SNAP ultra C18 10 g Biotage®, flow rate: 12 mL min^{-1}, t_R = 16 – 19 min) **8** was obtained as an off-yellow solid (14.5 mg, 0.046 mmol). 34% yield; ^{1}H NMR (300 MHz, *CDCl₃*) δ 7.67 (d, 16.3, 1H), 7.48 (app d, 8.7, 2H), 7.23 (app d, 1.8, 1H), 7.16 (app d, 8.7, 2H), 6.74 (d, 16.4, 1H) 5.10 (qd, 6.8, 1.8, 1H), 1.56 (s, 9H), 1.47 (d, 6.8, 3H); ^{13}C NMR (75 MHz, *CDCl₃*) δ 171.7, 151.7, 151.2, 148.7, 134.1, 134.0, 129.2, 127.9 (2C), 121.6 (2C), 116.9, 83.8, 77.2, 27.7 (3C), 19.2; ESI-MS: $[M-Boc+H]^+$ *m/z* = 217.25, $\lambda_{max,1}$ = 223 nm, $\lambda_{max,2}$ = 290 nm, t_R = 6.08 min (Boc-group was removed upon ESI-ionisation)[11]; HR-ESI-MS: $[M+H]^+$ *m/z* = 317.1385 (calculated for $C_{18}H_{21}O_5^+$ 317.1384).

Synthetic styrolide A ((*E*)-3-(4-Hydroxystyryl)-5-methylfuran-2(5H)-one) (*rac*-1)

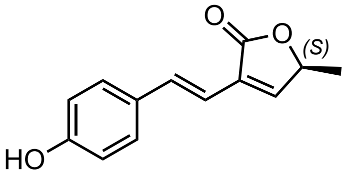


(*E*)-*tert*-Butyl(4-(2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)vinyl)phenyl) carbonate **8** (14.5 mg, 47 µmol, 1 eq.) was dissolved in 1 mL of a mixture of DCM and trifluoroacetic acid (TFA) (v/v, 9:1) and stirred for 18 h at r.t. The mixture was co-evaporated with toluene three times to obtain styrolide A (*rac*-**1**) as a yellow solid (9 mg, 42 µmol). 90% yield; ^{1}H NMR (300 MHz, *d₄-MeOD*) δ 7.54 (d, 16.2, 1H), 7.43 (d, 1.8, 1H), 7.36 (app d, 8.5, 2H), 6.77 (app d, 8.5, 2H), 6.69 (d, 16.2, 1H), 5.14 (q, 6.7, 1H), 1.42 (d, 6.9, 3H); ^{13}C NMR (75 MHz, *d₄-MeOD*) δ 174.4, 159.3, 150.2, 135.6, 130.2, 129.5, 129.3 (2C), 116.6 (2C), 114.9, 79.2, 19.3; ESI-MS: $[M+H]^+$ *m/z* = 217.25, λ_{max} = 312 nm, t_R = 3.99 min; HR-ESI-MS: $[M+H]^+$ *m/z* = 217.0860 (calculated for $C_{13}H_{13}O_3^+$ 217.0859). Analytical data are in agreement with isolated styrolide A (see **Analytical Data of Isolated Styrolides**).

HPLC purification of styrolide A *rac*-1 using a chiral stationary phase



(*R*)-**1**

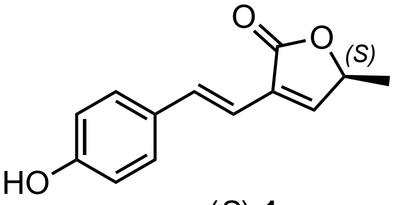


(*S*)-**1**

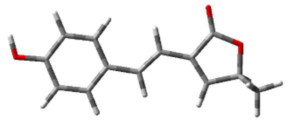
Synthetic styrolide A ((*E*)-3-(4-Hydroxystyryl)-5-methylfuran-2(5H)-one) *rac*-**1** (1.8 mg) was dissolved in a 1:1 mixture of isopropanol/*n*-hexane, filtered (PTFE) and subjected to analytical HPLC purification using a chiral stationary phase (0.46x25 cm, DAIC 14325, Chiralcel OD-H, Daicel Chemical Industries, Ltd.). *n*-Hexane (75%) and isopropanol (25%) was used as mobile phase with a flow rate of 0.7 mL min^{-1}. Fractions with t_R = 12.5 – 16.5 min were combined to yield 0.8 mg of (*R*)-**1** (44% yield, *ee* = 100%, $[\alpha]_D^{25}$ = +10 (c = 0.1 in *MeOH*)) and fractions with t_R = 21.0 – 29.0 min were combined to yield 0.7 mg of (*S*)-**1** (39% yield, *ee* = 100%, $[\alpha]_D^{25}$ = –9 (c = 0.1 in *MeOH*)).

ECD Spectrum Calculation for (*R*/*S*)-Styrolide A 1 for Determination of the Absolute Configuration of Styrolide A 1

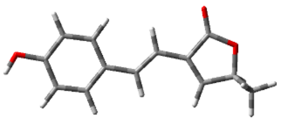
Conformation searches based on molecular mechanics with MMFF94s force field were performed to give stable conformers with populations higher than 1%.[18-19] All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level in Gaussian 09 program package,[20] led to optimized conformers within a 2.5 kcal/mol energy threshold from global minimum. These predominant conformers were subjected to theoretical calculation of ECD using time-dependent density functional theory (TDDFT) at CAM-B3LYP/6-311+G (d,p) level in air. The calculated ECD spectra were generated using SpecDis 1.60 with $\sigma = 0.3$ eV (Figure S4).[21-23] Experimental ECD spectra (Figure S4) of (*R*)-**1** and (*S*)-**1** were recorded on a JASCO J-815 CD spectrometer in a 1 mm quartz glass cuvette. The enantiomers were dissolved in MeOH (c = 0.3).



(*S*)-**1**



(*S*)-**1-1**



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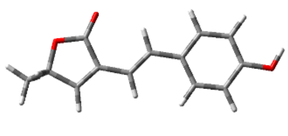
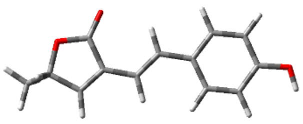


(*S*)-**1-3**

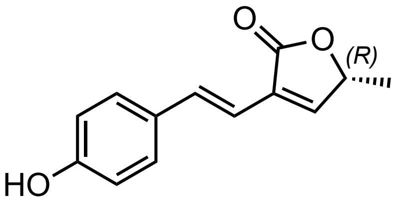


(*S*)-**1-4**

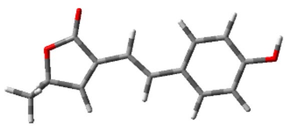
Figure S2. Optimized conformers of (*S*)-**1** ((*S*)-**1-1** to (*S*)-**1-4**).

Table S3. Energy analysis for conformers of (*S*)-**1-1** to (*S*)-**1-4** at B3LYP/6-31G(d) level in gas phase.

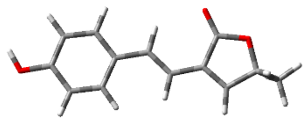
Species	$E'=E+ZPE$	E	H	G	ΔE(kal/mol)	P_E%
(*S*)-**1-1**	-728.296811	-728.253628	-728.239266	-728.238321	0.8239075	10.95%
(*S*)-**1-2**	-728.296676	-728.253468	-728.239109	-728.238165	0.90862	9.49%
(*S*)-**1-3**	-728.298124	-728.255630	-728.241403	-728.240459	0	43.98%
(*S*)-**1-4**	-728.297924	-728.255339	-728.241095	-728.240151	0.1255	35.58%



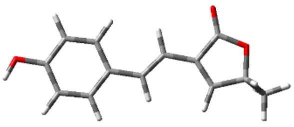
(*R*)-**1**



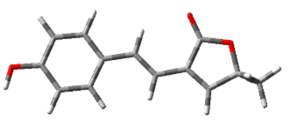
(*R*)-**1-1**



(*R*)-**1-2**



(*R*)-**1-3**



(*R*)-**1-4**

Figure S3. Optimized conformers of (*R*)-**1** ((*R*)-**1-1** to (*R*)-**1-4**).

Table S4. Energy analysis for conformers of (*R*)-**1-1** to (*R*)-**1-4** at B3LYP/6-31G(d) level in gas phase.

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔE*(kal/mol)	P_E%
(*R*)-**1-1**	-728.296811	-728.253628	-728.239266	-728.238321	0.8239075	10.94%
(*R*)-**1-2**	-728.298124	-728.255630	-728.241403	-728.240459	0	43.97%
(*R*)-**1-3**	-728.296679	-728.253468	-728.239109	-728.238164	0.9067375	9.52%
(*R*)-**1-4**	-728.297924	-728.255339	-728.241095	-728.240151	0.1255	35.57%

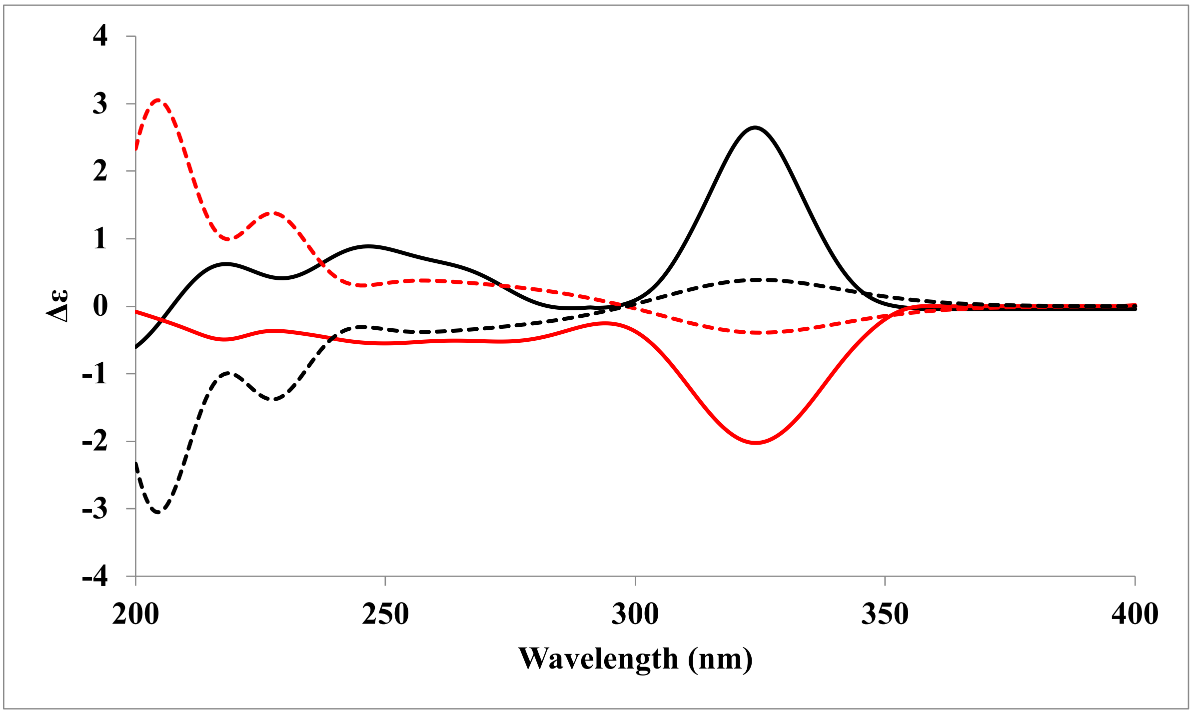


Figure S4: Comparison of experimental (solid lines) and calculated (dashed lines, in gas phase) ECD spectra of (*R*)-**1** (black) and (*S*)-**1** (red).

Table S5: Z-Matrix of optimized conformers, optimized at the B3LYP/6-31g(d) level in gas phase.

nuclei	Z-Matrix of ***(S)*-1-1**			Z-Matrix of ***(S)*-1-2**			Z-Matrix of ***(S)*-1-3**			Z-Matrix of ***(S)*-1-4**		
C	3.77806	-1.87912	0.19228	4.07835	0.48557	0.16687	3.989	-0.08542	0.28044	3.64978	-2.4252	-0.09726
C	4.59994	-0.76253	0.11239	4.58823	-0.80619	0.15238	4.47676	-1.3765	0.12371	4.49647	-1.33527	0.05827
C	4.06226	0.51913	0.14066	3.74112	-1.90544	0.23391	3.60811	-2.45668	0.01765	3.9835	-0.06261	0.28367
C	2.67729	0.68186	0.24585	2.36062	-1.70335	0.32719	2.2285	-2.23519	0.06451	2.59844	0.11905	0.34818
C	1.82844	-0.4328	0.31164	1.82419	-0.40758	0.32711	1.71516	-0.93787	0.20488	1.7268	-0.96627	0.17801
C	2.39481	-1.71475	0.29754	2.6987	0.68572	0.25929	2.60997	0.13395	0.32711	2.26665	-2.24221	-0.03087
O	5.94352	-0.96814	0.01122	5.93997	-0.95503	0.06103	5.82886	-1.54469	0.0841	5.83935	-1.55853	-0.01161
C	0.37077	-0.30262	0.45413	0.36908	-0.24146	0.45686	0.25749	-0.75781	0.27564	0.26687	-0.8201	0.26758
C	-0.35896	0.63994	-0.16456	-0.33355	0.70477	-0.1872	-0.39636	0.26631	-0.29562	-0.41299	0.19558	-0.28802
C	-1.78391	0.80086	-0.04511	-1.75528	0.9026	-0.08315	-1.8204	0.48185	-0.26817	-1.84066	0.38244	-0.24521
C	-2.72022	-0.07569	0.31729	-2.71275	0.06589	0.3165	-2.46436	1.51017	-0.82173	-2.51227	1.39084	-0.80257
C	-4.07017	0.52298	0.24786	-4.04833	0.69143	0.2142	-3.92257	1.41559	-0.60857	-3.96549	1.26954	-0.56941
O	-3.83904	1.85438	-0.21361	-3.78545	1.99395	-0.30794	-4.08594	0.20767	0.13202	-4.09465	0.06928	0.18995
C	-2.50343	2.04029	-0.411	-2.44529	2.14011	-0.5085	-2.86606	-0.36397	0.35266	-2.86066	-0.47439	0.4027
O	-1.99069	3.06658	-0.82147	-1.90874	3.13442	-0.96445	-2.69794	-1.40545	0.96136	-2.66324	-1.50129	1.02698
C	-4.98771	-0.19462	-0.72826	-4.9796	-0.04991	-0.73068	-4.48263	2.57845	0.19349	-4.53914	2.43202	0.22356
H	4.21117	-2.87509	0.17353	4.75108	1.33675	0.1112	4.67899	0.74826	0.37386	4.06244	-3.41565	-0.26629
H	4.69631	1.39843	0.0883	4.13025	-2.91844	0.2279	3.97843	-3.47008	-0.09866	4.63755	0.79288	0.41756
H	2.27196	1.69042	0.28646	1.70566	-2.56946	0.39043	1.55422	-3.08557	-0.01652	2.20881	1.11436	0.54675
H	1.76507	-2.59914	0.35883	2.32094	1.70506	0.2877	2.24762	1.14804	0.47347	1.61438	-3.10466	-0.15055
H	6.38552	-0.10503	-0.04373	6.14864	-1.9033	0.05339	6.01971	-2.49178	-0.01512	6.30177	-0.7165	0.12965
H	-0.09985	-1.04111	1.09815	-0.1227	-0.95458	1.11322	-0.27597	-1.53818	0.81445	-0.24288	-1.61827	0.80334
H	0.12489	1.36755	-0.81613	0.17344	1.40618	-0.85023	0.17246	1.0124	-0.84812	0.13589	0.95613	-0.84097
H	-2.53952	-1.09634	0.62084	-2.55702	-0.94284	0.66939	-1.99639	2.31725	-1.36729	-2.06808	2.19958	-1.36519
H	-4.52901	0.57086	1.24107	-4.50854	0.79609	1.20241	-4.45232	1.31662	-1.56188	-4.50504	1.14638	-1.51437
H	-5.94911	0.32606	-0.79649	-5.9286	0.48882	-0.82667	-5.55055	2.42668	0.38471	-5.60122	2.26127	0.43063
H	-5.17213	-1.22785	-0.41743	-5.18851	-1.063	-0.37261	-4.35483	3.52769	-0.33643	-4.43754	3.37605	-0.32112
H	-4.56631	-0.20452	-1.74023	-4.55592	-0.11676	-1.73954	-3.99896	2.65826	1.17403	-4.04487	2.53553	1.19657

nuclei	Z-Matrix of **(*R*)-1-1**			Z-Matrix of **(*R*)-1-2**			Z-Matrix of **(*R*)-1-3**			Z-Matrix of **(*R*)-1-4**		
C	3.77701	-1.74478	0.72901	3.98929	-0.21403	-0.19456	4.0491	0.13569	-0.65804	3.64531	-2.07145	1.27777
C	4.59962	-0.70507	0.31553	4.47596	-1.25405	0.58701	4.57754	-0.80876	0.21238	4.49524	-1.18109	0.63442
C	4.0651	0.42596	-0.29077	3.60644	-2.13674	1.21738	3.74325	-1.60868	0.98479	3.98671	-0.16968	-0.17309
C	2.6825	0.51637	-0.48031	2.22704	-1.96833	1.06415	2.35718	-1.45442	0.88357	2.60282	-0.04717	-0.33231
C	1.83268	-0.51548	-0.05552	1.71476	-0.91473	0.2936	1.80361	-0.49578	0.02261	1.72776	-0.92667	0.32145
C	2.39613	-1.65292	0.5387	2.61046	-0.04736	-0.34657	2.66396	0.28942	-0.757	2.26336	-1.94866	1.11628
O	5.94083	-0.83589	0.51994	5.82789	-1.37991	0.70729	5.93403	-0.92462	0.27726	5.83684	-1.33791	0.81759
C	0.37797	-0.47128	-0.2651	0.25731	-0.79415	0.14026	0.34051	-0.38925	-0.07495	0.26928	-0.84765	0.15609
C	-0.3605	0.64397	-0.14436	-0.39654	0.37838	0.12244	-0.31486	0.77489	-0.21387	-0.41639	0.30663	0.15607
C	-1.78284	0.72616	-0.34652	-1.8204	0.55134	-0.01107	-1.74434	0.92024	-0.29932	-1.84318	0.44379	0.01299
C	-2.71447	-0.22555	-0.29484	-2.46433	1.71866	-0.0463	-2.68156	0.02467	-0.60968	-2.52063	1.59254	0.01807
C	-4.06421	0.33311	-0.52219	-3.92235	1.5302	-0.18577	-4.02645	0.63802	-0.62277	-3.9709	1.36801	-0.14692
O	-3.83845	1.73183	-0.69989	-4.08563	0.11383	-0.22394	-3.78799	2.01009	-0.30869	-4.09181	-0.04938	-0.24844
C	-2.50611	1.99426	-0.58431	-2.86587	-0.49156	-0.12769	-2.45262	2.20651	-0.11878	-2.85586	-0.62281	-0.16362
O	-1.99851	3.09889	-0.6668	-2.69771	-1.69785	-0.13432	-1.93287	3.27491	0.15077	-2.65173	-1.82191	-0.22446
C	-5.00002	0.12124	0.65637	-4.48061	2.1367	-1.46237	-4.96265	0.03855	0.41328	-4.53298	2.01319	-1.40272
H	4.20772	-2.62503	1.19754	4.67996	0.46146	-0.69107	4.71147	0.74962	-1.26174	4.05459	-2.86154	1.90076
H	4.69991	1.23992	-0.62603	3.97591	-2.95644	1.82502	4.14638	-2.35202	1.66493	4.64346	0.52351	-0.68859
H	2.27997	1.39831	-0.97356	1.55207	-2.66447	1.5583	1.7122	-2.084	1.4926	2.21695	0.73332	-0.98334
H	1.76578	-2.47541	0.86832	2.249	0.75792	-0.98057	2.26981	1.02263	-1.45633	1.60858	-2.65471	1.62259
H	6.38354	-0.0364	0.19106	6.01796	-2.15073	1.26674	6.15679	-1.60397	0.93436	6.30204	-0.661	0.29971
H	-0.08288	-1.42238	-0.51935	-0.27602	-1.73936	0.0627	-0.19921	-1.32976	-0.00157	-0.23456	-1.80691	0.05646
H	0.11341	1.58879	0.12171	0.17211	1.30074	0.22903	0.23908	1.71359	-0.24102	0.1263	1.24111	0.28912
H	-2.53058	-1.27328	-0.10779	-1.99649	2.69038	0.02366	-2.50324	-1.01462	-0.84327	-2.08267	2.57351	0.13557
H	-4.50562	-0.07014	-1.43971	-4.45335	1.9208	0.6887	-4.4724	0.58097	-1.62136	-4.5226	1.70456	0.73715
H	-5.96141	0.61188	0.46917	-5.54839	1.90966	-1.55369	-5.92012	0.57079	0.41105	-5.59253	1.75944	-1.5167
H	-5.18109	-0.94317	0.83651	-4.35281	3.22374	-1.47746	-5.15231	-1.0211	0.21485	-4.43719	3.1031	-1.36918
H	-4.5963	0.56662	1.57311	-3.99565	1.7159	-2.35091	-4.55429	0.13637	1.42591	-4.02621	1.64584	-2.30272

The absolute configuration of isolated styrolide A **1** was determined by retention time comparison with synthetic styrolide A **1** enantiomers (Figure S5). Therefore, isolated **1** and synthetic *rac*-**1** were analyzed by HPLC using a chiral stationary phase (0.46x25 cm, DAIC 14325, Chiralcel OD-H, Daicel Chemical Industries, Ltd.). *n*-Hexane (85%) and isopropanol (15%) was used as mobile phase with a flow rate of 1 mL min^{-1}.

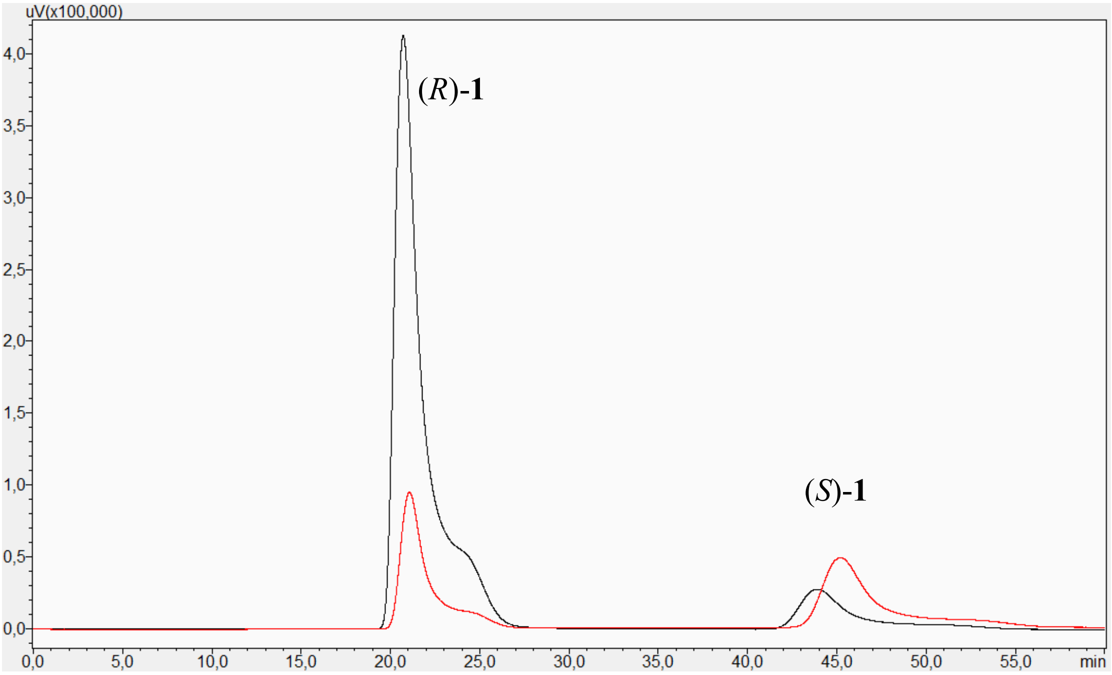


Figure S5: HPLC profiles of isolated styrolide A **1** (black) and synthetic *rac*-**1** (red). Isolated styrolide A matches with (*R*)-**1** (*ee* = 78%, determined by peak area calculation).

Transposon Mutagenesis and Transposon Mutant Screen

For the generation of Tn5-insertion mutants a pUTmini-Tn5 Km vector (PANC-1plus miniTn5 package, Biomedal) was used.[24-25] The vector was transformed into chemically competent *E. coli* S17-1 λ pir cells *via* heat shock at 42 °C. For subsequent intergenic conjugation using a standard protocol[1, 26] overnight donor (*E. coli* S17-1 λ pir pUTmini-Tn5 Km) and acceptor (*P. fluorescens* HKI0874) strain cultures were mixed in various ratios (3:1 → 9:1) and washed with sterile, deionized water. Mating spots (30 µL) were spotted on dry LB agar plates and incubated at 28 °C overnight. The mating spots were then suspended in LB medium (200 µL) and plated on LB plates (100 µL, 15 µg/mL kanamycin and 50 µg/mL chloramphenicol). 2300 single insertion mutants were selected and used to inoculate SM/5 medium cultures in 96 well plates (200 µL, 22 °C) for temporary storage, from which 5 µL were used to inoculate SM/5 medium cultures in 96 deep well plates (500 µL). These cultures were incubated for 20 h at 22 °C before all liquid was removed *in vacuo*. Each pellet was suspended in 25 µL acetone and 10 µL were immediately used for TLC analysis (*E. Merck* silica gel 60 F_{254} plates, 0.25 mm) with hexane/ethylacetate 1:1 (v/v) as mobile phase. Green fluorescence of styrolide B (**2**) was detected using UV light (254 nm, $R_f = 0.62$, Figure S6).

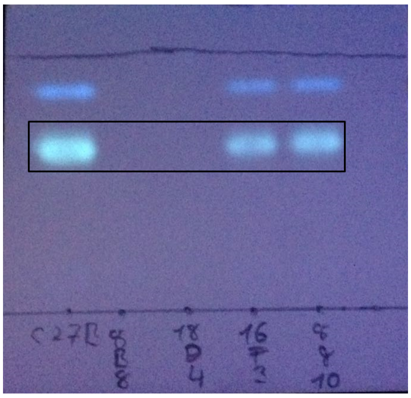


Figure S6: TLC plate showing the green fluorescence of styrolide B **2** (highlighted box) produced by *P. fluorescens* HKI0874 (1st lane fltr) and most Tn5 insertion mutants (*e.g.*, 16F3 and 8G10, 4th and 5th lane fltr). Two out of 2300 Tn5 insertion mutants did not produce any styrolides (8B8 and 18D4, 2nd and 3rd lane fltr).

Mutants lacking the characteristic band were cultivated in 5 mL SM/5 medium for 20 h at 22 °C, 180 rpm. Ethyl acetate culture extracts were analyzed *via* LC-MS (see LC-MS-Based Metabolomic Profiling) for the absence of styrolides.

hiTAIL-PCR for Insertion Site Analysis

Two *P. fluorescens* HKI0874 pUTmini-Tn5 Km insertion mutants which did not produce styrolides were culture in LB medium for gDNA isolation using the QIAamp DNA Mini Kit (Qiagen). The hiTAIL-PCR was performed following the procedure and PCR protocol described by Liu and Chen[27] using Dreamtaq 2x Mastermix (Thermo Fisher). Target-specific and sequencing primers (Table S6) were designed to bind close to the I end (U primers) or the O end (D primers) of the Tn5 transposon of pUTminiTn5 Km, however, these primers can also be used for pUTminiTn5 vectors with other selection markers. Briefly, pre-amplification was performed using 30 ng of gDNA, the degenerated primer mix LAD1–4 (1 µM)[27], and either transposon-specific primer pUTminiTn5_0_D (0.3 µM, for amplification of the genomic region downstream of Tn5) or pUTminiTn5_0_U (0.3 µM, for amplification of the genomic region upstream of Tn5). The primary-TAIL PCR was conducted using 40-fold diluted pre-amplification product, primer ACI (0.3 µM)[27], and either transposon-specific primer pUTminiTn5_1_D (0.3 µM) or pUTminiTn5_1_U (0.3 µM, with respect to the PCR product generated during pre-amplification). The secondary-TAIL PCR was conducted using ten-fold diluted primary-TAIL PCR product, primer ACI (0.3 µM), and transposon-specific primer pUTminiTn5_2_D/U (0.3 µM). If more than a single band was visible on the agarose gel, a gel extraction was done prior sequencing, otherwise ExoSAP-IT (Thermo Fisher) digestion was performed prior sequencing. PCR products generated using the D-primers (downstream) were sequenced using ACI, pUTminiTn5_seqD1/U1, and pUTminiTn5_seqD2 to determine the downstream region of the Tn5 insertion site, whereas PCR products generated using the U-primers were sequenced using ACI, pUTminiTn5_Km_seqD1/U1, and pUTminiTn5_seqU2 to determine the upstream region of the Tn5 insertion site.

The transposon insertion sites 29562 → 29570 and 34115 → 34123 were both found on contig 15, CDS coordinates 26882 → 30532 and 33608 → 34426, respectively.

Table S6: Primers used for hiTAIL-PCR and sequencing of hiTAIL-PCR-products.

Primer	Sequence 5’ → 3’
LAD1	**ACGATGGACTCCAGAGCGGCC**GC(G/C/A)N(G/C/A)NNNGGAA
LAD2	**ACGATGGACTCCAGAGCGGCC**GC(G/C/T)N(G/C/T)NNNGGTT
LAD3	**ACGATGGACTCCAGAGCGGCC**GC(G/C/A)(G/C/A)N(G/C/A)NNNCCAA
LAD4	**ACGATGGACTCCAGAGCGGCC**GC(G/C/T)(G/A/T)N(G/C/T)NNNCGGT
pUTminiTn5_0_D	GGCTCCAAGGATCGGGCCTTGATG
pUTminiTn5_0_U	GTTGGCGAAGTAATCGCAACATCCGC
ACI	**ACGATGGACTCCAGAG**
pUTminiTn5_1_D	**ACGATGGACTCCAGTCCGGCC**TTGATGTTACCCGAGAGCTTGGC
pUTminiTn5_1_U	**ACGATGGACTCCAGTCCGGCC**GCATTAAAATCTAGCGAGGGCTTTACTAAGC
pUTminiTn5_2_D/U	GCTCAATCAATCACCGGATCCCCGGG
pUTminiTn5_seqD1/U1	GGATGACCTTTTGAATGACC
pUTminiTn5_seqD2	GAATTCGTCGACAAGCTTCG
pUTminiTn5_seqU2	GGATCCCCGGGAATTCGG

InterProScan Analysis of Biosynthetic Gene Cluster Region *sto*

An InterProScan v5 analysis[28] was conducted to analyze the amino acid sequences of the gene coding sequences surrounding the transposon insertion sites for putative functions. Note that alignment lengths for StoC, StoF, and StoH are too short to reliably predict a putative function.

Genomic data with annotations according to this report (Table S7 and Table S9) can be retrieved from: https://doi.org/10.6084/m9.figshare.10259870.v1

Table S7: Gene location (start and end) on contig 15 (*stoA-stoI*) and on contig 30 (*stoR*), amino acid length and InterProScan v5 results for *stoX*.

Gene	Start	End	Orien-tation	aa length	db	family	Domain description	Matching stats		Interpro family	GO terms
								alignment length	e-value		
stoA	26882	30532	+	1216	SUPERFAMILY	SSF53323	Pyruvate-flavodoxin oxidoreductase, central domain	747	5,23E-24	IPR002869	GO:0016491|GO:0055114
stoA	26882	30532	+	1216	Gene3D	G3DSA:3.40.920.10	Pyruvate-flavodoxin oxidoreductase, central domain	744	7,70E-17	IPR002869	GO:0016491|GO:0055114
stoA	26882	30532	+	1216	SUPERFAMILY	SSF52518	Thiamin diphosphate-binding fold	463	2,30E-05	IPR029061	
stoA	26882	30532	+	1216	Pfam	PF01558	Pyruvate ferredoxin/flavodoxin/ketoisovalerate oxidoreductase, catalytic domain	755	7,80E-20	IPR019752	GO:0016903|GO:0055114
stoB	30596	31660	+	354	Pfam	PF03756	A-factor biosynthesis hotdog domain	127	1,30E-09	IPR005509	
stoC	31657	32838	+	393	Pfam	PF00724	NADH:flavin oxidoreductase / NADH oxidase family, N-terminal	24	1,90E-38	IPR001155	GO:0010181|GO:0016491|GO:0055114
stoD	32835	33608	+	257	PRINTS	PR00081	Short-chain dehydrogenase/reductase SDR, Glucose/ribitol dehydrogenase family signature	216	7,50E-28	IPR002347	
stoE	33608	34426	+	272	Pfam	PF00106	short chain dehydrogenase/reductase SDR	20	4,90E-16	IPR002347	
stoE	33608	34426	+	272	SUPERFAMILY	SSF51735	NAD(P)-binding domain superfamily	18	1,44E-29	IPR036291	
stoE	33608	34426	+	272	PRINTS	PR00081	Short-chain dehydrogenase/reductase SDR, Glucose/ribitol dehydrogenase family signature	161	2,70E-06	IPR002347	
stoF	34468	34782	+	104	Gene3D	G3DSA:1.10.1200.10	ACP-like superfamily	2	1,20E-07	IPR036736	
stoG	34801	36156	+	451	Pfam	PF00501	AMP-dependent synthetase/ligase, AMP-binding enzyme	14	1,30E-28	IPR000873	GO:0003824
stoG	34801	36156	+	451	Pfam	PF13193	AMP-binding enzyme C-terminal domain	364	5,20E-06	IPR025110	
stoH	36193	36435	+	80	SUPERFAMILY	SSF47336	ACP-like superfamily	5	2,09E-10	IPR036736	
stoI	36432	37505	+	357	Pfam	PF08545	3-Oxoacyl-[acyl-carrier-protein (ACP)] synthase III	115	8,00E-17	IPR013751	GO:0004315|GO:0006633 KEGG: 00061+2.3.1.180
stoR	28054	27278	–	258	Pfam	PF02525	Flavodoxin-like fold	208	6.8E-58	IPR003680	

Identification of the Acaterin Biosynthetic Gene Cluster

BLASTp v2.9[29] was used to search for homologues proteins of StoB, StoC, and StoD, putatively involved in the formation of butenolide moiety (shared motif in styrolides and acaterin), in *Pseudomonas jessenii* EC-S101. *Vice versa*, StoR was found by protein homology search using acaR.

Table S8: BLASTp v2.9 results of protein homology search for StoB, StoC, StoD, acaR. Only hits with highest similarity are listed (AcaA, AcaB, AcaC, StoR).

query	subject	% identity	alignment length	mismatches	gap opens	query start	query end	subject start	subject end	e-value	bit score
StoB	AcaA	29.907	321	164	6	5	281	7	310	4.50e-33	128
StoC	AcaB	42.175	377	217	1	6	381	3	379	3.17e-99	301
StoD	AcaC	49.609	256	127	1	2	257	3	256	8.30e-84	252
AcaR	StoR	84.375	256	40	0	1	256	1	256	1.16e-170	469

Table S9: Gene location (start and end) on contig 6 (*acaA*, *acaB*, *acaC*) and on contig 14 (*acaR*), amino acid length and InterProScan v5 results for *acaA*, *acaB*, *acaC*, and *acaR*.

Gene	Start	End	Orien-tation	aa length	db	family	Domain description	Matching stats		Interpro family	GO terms
								alignment length	e-value		
acaA	161646	162890	+	414	Pfam	PF03756	A-factor biosynthesis hotdog domain	132	1.8E-9	IPR005509	
acaB	162887	164035	+	382	Pfam	PF00724	NADH:flavin oxidoreductase / NADH oxidase family	10	7.0E-43	IPR001155	GO:0010181|GO:0016491|GO:0055114
acaC	164049	164819	+	256	ProSitePatterns	PS00061	Short-chain dehydrogenases/reductases family signature.	140	-	IPR020904	GO:0016491
acaC	164049	164819	+	256	PRINTS	PR00081	Glucose/ribitol dehydrogenase family signature, Short-chain dehydrogenase/reductase SDR	215	2.1E-34	IPR002347	
acaC	164049	164819	+	256	PRINTS	PR00080	Short-chain dehydrogenase/reductase (SDR) superfamily signature	153	3.7E-7	IPR002347	
acaR	84885	84109	–	258	Pfam	PF02525	Flavodoxin-like fold	211	9.4E-57	IPR003680	

Genus-Wide Prevalence of Potential Butenolide Biosynthetic Gene Clusters

In order to determine the genus-wide prevalence of potential butenolide biosynthetic gene clusters we scanned a phylogenomic tree of all 503 complete *Pseudomonas* genomes deposited and available from the NCBI genome assembly database for Pfam domain PF03756 present in StoB, which is critical for the formation of the butenolide motif, using GtoTree.[30] This identified 44 candidate genomes with a putative butenolide biosynthetic gene cluster. Cross referencing the genome accession numbers with the NCBI biosample database revealed that most of these *Pseudomonas* species were isolated from plant and soil. For all 44 genomes the proteome was extracted from the assemblies using prodigal v2.6.3.[31] Subsequently, using the *stoB*, *stoC* and *stoD* as baits, we reduced the number of genomes to 11 genomes that contained all three genes and manually checked the synteny around *stoB* (10 genes/predicted ORFs up- and downstream, Figure S7).

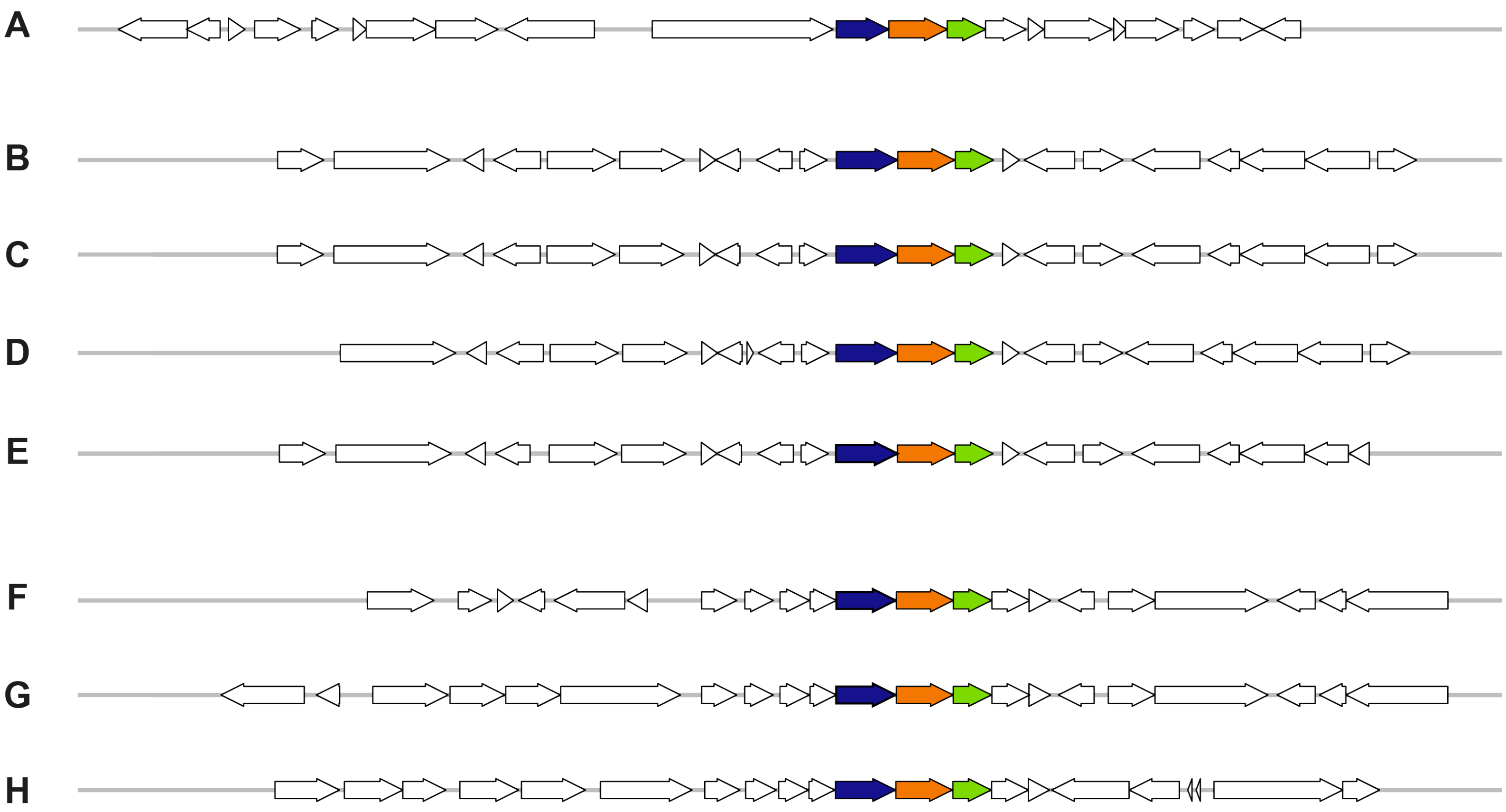


Figure S7: Genomic region of the styrolide (A: *P. fluorescens* HKI0770) and acaterin (B: *P. jessenii* EC-S101) biosynthetic gene cluster and of other potential butenolide biosynthetic gene clusters (C: *P. fluorescens* LBUM677, D: *P. koreensis* P19E3, E: *P.* sp. S150, F: *P.* sp. TKP, G: *P. fluorescens* L321 and *P. fluorescens* L111, H: *P.* sp. VLB120, *P. putida* PC2, *P.* sp. SWI44, *P.* sp. SWI6, *P. putida* NX-1). Highlighted are genes corresponding to StoB (blue), StoC (orange), and StoD (green) homologs. For the potential butenolide biosynthetic gene cluster, regions with similar gene synteny were grouped and are representative for more strains, if the gene synteny was identical for all 21 genes/predicted ORFs.

Gene Deletion via Homologous Recombination

For the generation of marker-less genomic deletion mutants a gentamicin-resistance (*gent*^{R}) selection and sucrose counterselection (*sacB*) approach was used. The corresponding pEXG2-based suicide vectors[32-33] were constructed using the Gibson Assembly method. The parent plasmid pEXG2 was linearized by HindIII and EcoRI digestion. Left and right homology arms (LA, RA) were PCR amplified (touchdown PCR, 30 s annealing, 2 min elongation) from genomic DNA using primer pairs LA_*xxxX*_F/LA_*xxxX*_R and RA_*xxxX*_F/RA_*xxxX*_R, respectively (Table S10). These primers include a sequence of about 20 bp that overlap with the adjacent PCR fragment and the linearized vector (the primers were designed using: http://nebuilder.neb.com). The LA and RA were ligated into the pEXG2 vector using the standard Gibson Assembly protocol to yield the respective deletion constructs pEXG2Δ*xxxX*.

Table S10: Primers for amplification of left and right homology arms.

Primer	Sequence 5' → 3'	T_a [°C]
LA_*stoA*_F1	ggaagcataaatgtaaagcaGGTTTGGGCATTGATCTCG	64.8
LA_*stoA*_R1	caacttcgtaGATCACCGACAGGCAGTTG	
RA_*stoA*_F1	gtcggtgatcTACGAAGTTGCACGGCTG	64.2
RA_*stoA*_R1	ggaaattaattaaggtaccgGTAATTGCCTACCAACGGG	
LA_*stoA*_F2	ggaagcataaatgtaaagcaTGTTACAACGATTGACAAG	57.8
LA_*stoA*_R2	cttcgatgatCACAGTTTCAAGTCCTTATG	
RA_*stoA*_F2	tgaaactgtgATCATCGAAGAGAAGCAG	59.2
RA_*stoA*_R2	ggaaattaattaaggtaccgCAACTGCACTTCTTCGAG	
LA_*stoB*_F	ggaagcataaatgtaaagcaGGCTACCAGAATGCAGCG	62.8
LA_*stoB*_R	aggccgcaagATTCATCGTTATCAGCTCATCTG	
RA_*stoB*_F	aacgatgaatCTTGCGGCCTTGCAGCAA	67.3
RA_*stoB*_R	ggaaattaattaaggtaccgGACGACATCACCCAACAGC	
LA_*stoC*_F	ggaagcataaatgtaaagcaGATAGCCTGGAAGCCGCC	65.5
LA_*stoC*_R	tttcctcgtaGATCATTGCTGCAAGGCC	

RA_*stoC*_F	agcaatgatcTACGAGGAAAACCTGAAATGAACTTCAC	67.5
RA_*stoC*_R	ggaaattaattaaggtaccgCGGTGCCGGTGACAAACG	
LA_*stoD*_F	ggaagcataaatgtaaagcaGGCGATGAGCGAGGCACA	67.7
LA_*stoD*_R	cggccgaaaaGTTCATTTCAGGTTTTCCTCGTAGTACTG	
RA_*stoD*_F	tgaaatgaacTTTTCGGCCGGTAAATTCTGATG	66.4
RA_*stoD*_R	ggaaattaattaaggtaccgCATCGGGCGCGTCAATCAC	
LA_*stoE*_F	ggaagcataaatgtaaagcaACCGCCAAGATCGCTCTC	65.1
LA_*stoE*_R	acaatggcggGTGCATCAGAATTTACCGGC	
RA_*stoE*_F	tctgatgcacCCGCCATTGTCTCAAGCG	64.3
RA_*stoE*_R	ggaaattaattaaggtaccgGTGGCAAGACAGAGTTGG	
LA_*stoG*_F	ggaagcataaatgtaaagcaGGGCGTACGCTTTCGCGC	70.8
LA_*stoG*_R	cgagagcgccTTGCATACCCAACCCCTCGTTC	
RA_*stoG*_F	gggtatgcaaGGCGCTCTCGCCCAGTCG	72.0
RA_*stoG*_R	ggaaattaattaaggtaccgTTCGCGTGGTCACGTCCC	
LA_*stoH*_F	ggaagcataaatgtaaagcaCTGGCGTTTCTGCTGTTC	61.8
LA_*stoH*_R	cctcgattttAACCATTTGTCATTTCCTTATAACG	
RA_*stoH*_F	acaaatggttAAAATCGAGGTCGCCGCATG	65.6
RA_*stoH*_R	ggaaattaattaaggtaccgACAACACGATCGGAATCGAG	
LA_*stoI*_F	ggaagcataaatgtaaagcaAAGATCGAAGACCCGAACTACAGC	69.4
LA_*stoI*_R	aacgctcactACTCATGCGGCGACCTCG	
RA_*stoI*_F	ccgcatgagtAGTGAGCGTTTGCAGGCC	65.6
RA_*stoI*_R	ggaaattaattaaggtaccgTTTACACCACCCGTTCTGTC	
LA_*stoJ*_F	gaagcataaatgtaaagcaAGGAAAATCCTGCTGTGC	58.6
LA_*stoJ*_R	tctgtcgaCTTCATGAAACAGCTGTC	
RA_*stoJ*_F	ttcatgaagTCGACAGAACGGGTGGTG	67.9
RA_*stoJ*_R	gaaattaattaaggtaccgCGCAGATGCTCGAACGTTG	
LA_*stoK*_F	gaagcataaatgtaaagcaGGATCGACCTCAAAGGTGCCAC	71.6
LA_*stoK*_R	atcggcggGGCCATGGCGGGACTCGG	
RA_*stoK*_F	ccatggccCCGCCGATTGTCAGCGCTTG	72.0
RA_*stoK*_R	gaaattaattaaggtaccgTCGCCGGTCTCGCGTTCA	
LA_*stoM*_F	gaagcataaatgtaaagcaAGTCCGGTGGCCTGCACG	71.5
LA_*stoM*_R	tcccacacGCCTGAGGAAAACTCGCCATGAAAAAC	

RA_*stoM*_F	cctcaggcGTGTGGGATTGAGGCTGTC	65.6
RA_*stoM*_R	gaaattaattaaggtaccgACCGGTTTCATCTCGACAATC	
LA_*stoN*_F	gaagcataaatgtaaagcaCTCCTCACCATCAGTCAG	60.0
LA_*stoN*_R	gcggcctcCTCATACGATCACCTCTTG	
RA_*stoN*_F	cgtatgagGAGGCCGCTGCCCATGAG	71.4
RA_*stoN*_R	gaaattaattaaggtaccgACTCGCTCAGATCCGCCG	
LA_*stoO*_F	ggaagcataaatgtaaagcaGCTGCACGGCATCCCGATG	72.0
LA_*stoO*_R	ccagttccagACTCATGGGCAGCGGCCT	
RA_*stoO*_F	gcccatgagtCTGGAACTGGAACTGGTCTGAC	68.4
RA_*stoO*_R	ggaaattaattaaggtaccgACCCCGCGTGTGGTGATC	
LA_*stoP*_F	ggaagcataaatgtaaagcaCATCACGGCAGCCGTGTAAC	68.6
LA_*stoP*_R	aggcaatctgTCTTGAGCCACACCCGATTG	
RA_*stoP*_F	tggctcaagaCAGATTGCCTTCATGGGG	60.1
RA_*stoP*_R	ggaaattaattaaggtaccgTTCAAGAAGATAAACTCGTCTG	
LA_*clp*_F	ggaagcataaatgtaaagcaACAGCCGCTTGAGCCAGC	69.1
LA_*clp*_R	cgatgatgacgcgGAGCGTCTGACCGTTGAAAATCAG	
RA_*clp*_F	tcagacgctcCGCGTCATCATCGTTCCTGACAAC	71.3
RA_*clp*_R	ggaaattaattaaggtaccgTCGCCGTGCACGTCCTGC	
LA_*acaA*_F	ggaagcataaatgtaaagcagaatctgtgatggattacttg	58.6
LA_*acaA*_R	tcctttgttcgatcatgatcatccctctg	
RA_*acaA*_F	gatcatgatcgaacaaaggaaggaagcatg	62.2
RA_*acaA*_R	ggaaattaattaaggtaccgggtccggatattgcagcc	
LA_*acaB*_F	ggaagcataaatgtaaagcaccacgagcacgtgcccgg	72.0
LA_*acaB*_R	cggggcgtaacatcatgcttccttcctttgttcgggc	
RA_*acaB*_F	aagcatgatgttacgccccgcgttggca	70.4
RA_*acaB*_R	ggaaattaattaaggtaccgtaagcggattgatcgctgagcag	
LA_*acaC*_F	ggaagcataaatgtaaagcaatcgcgtgcggatcatgg	65.9
LA_*acaC*_R	cgctggcgtagtacatatgtcgcatctccttatgc	
RA_*acaC*_F	acatatgtactacgccagcggcaagttc	66.7
RA_*acaC*_R	ggaaattaattaaggtaccgctgtcgaagatcagttcgcg	

The vectors were transformed into chemically competent *E. coli* Top10 cells *via* heat shock at 42 °C. Plasmids were purified using the QIAprep® Spin Miniprep Kit and sequenced. For subsequent intergenic conjugation, chemically competent *E. coli* ET12567 pUZ8002 or *E. coli* S17-1 λ pir was transformed with the respective deletion vector constructs. Biparental mating was performed using a standard protocol.[1, 26] Briefly, overnight donor (*E. coli* ET12567 pUZ8002 pEXG2Δ*xxx* or *E. coli* S17-1 λ pir pEXG2Δ*xxx*) and acceptor (*P. fluorescens* HKI0874 for *stoX* deletions, or a respective deletion mutant for *clp*, *stoX* double knockouts, or *P. jessenii* EC-S101 for *acaX* deletions) strain cultures were mixed in various ratios (3:1 → 9:1) and washed with sterile, deionized water. Mating spots (30 µL) were spotted on dry LB agar plates and incubated at 28 °C overnight. The mating spots were then suspended in LB medium (200 µL) and plated on LB plates (100 µL, 15 µg/mL gentamicin and 100 µg/mL ampicillin). Single transformants were selected and used to inoculate LB medium cultures. After 4-6 hours, cultures were plated on 5% sucrose LB plates (without NaCl) for selection of double crossover mutants. Deletion mutants were identified by PCR (touchdown PCR, $T_a = 60.0$ °C) using primer pairs including both up- and downstream regions of the homology arms: KOC_LA_*xxxX*_F/KOC_LA_*xxxX*_R and KOC_RA_*xxxX*_F/ KOC_RA_*xxxX*_R (Table S11). PCR products were sequenced and aligned using Geneious software to confirm deletions.

Table S11: Primers for knockout-control (KOC) amplification and sequencing of KOC-PCR products.

Primer	Sequence 5'→3'
KOC_LA_*stoA*_F	CACTGTCGCCTGTTCTGGAG
KOC_LA_*stoA*_R	GCGCGATCTTTTTCGGCTC
KOC_RA_*stoA*_F	GTGGCGTCAGCGTACTGATT
KOC_RA_*stoA*_R	AGGCTATCGCTGCGGATTC
KOC_LA_*stoB*_F	CCAACCATTTGGCTTTCGCC
KOC_LA_*stoB*_R	CCGAGAAAACCAAACCCTGC
KOC_RA_*stoB*_F	GGTCATTCACGGTGTCGAGT
KOC_RA_*stoB*_R	ATTTCATCTGCTTGCGCCAC
KOC_LA_*stoC*_F	GGGTGGCGATGATGAATGGA

KOC_LA_*stoC*_R	TTGTCGTTGATGAGGCGGAA
KOC_RA_*stoC*_F	TTCATCTACTGCAACGACTGGT
KOC_RA_*stoC*_R	CGAAGTGCCGAAAACCGTAT
KOC_LA_*stoD*_F	GATGCACGTTACAACAGCCG
KOC_LA_*stoD*_R	AAACCGTATGCCCGTTTTGC
KOC_RA_*stoD*_F	CGAGGCGATGCGTTTTGTTT
KOC_RA_*stoD*_R	TCTTCGCCACGGGACAAATC
KOC_LA_*stoE*_F	GATGCGTTTTGTTTCCGCGA
KOC_LA_*stoE*_R	CGCAGTTTGTCCTCGACATC
KOC_RA_*stoE*_F	GGTGGCATGAACTCGGAAGA
KOC_RA_*stoE*_R	GATCGAACAGCAGAAACGCC
KOC_LA_*stoG*_F	GATGGACGAGCTGTTCGAGG
KOC_LA_*stoG*_R	CGAGTCCCAGTTATCGCTGT
KOC_RA_*stoG*_F	CGATGTCGAGGACAAACTGC
KOC_RA_*stoG*_R	CCATCCATCTGCAAACGCTG
KOC_LA_*stoH*_F	TTCTGGCGTTTCTGCTGTTC
KOC_LA_*stoH*_R	GTCCTCTTCAGTCACCCGAC
KOC_RA_*stoH*_F	CAAGAAAATGCGTCACCCCG
KOC_RA_*stoH*_R	AAACCGCACAACACAACGTG
KOC_LA_*stoI*_F	TCCAGAAGTGGAACACGAGC
KOC_LA_*stoI*_R	GTCTTCACGCATGTCCAACG
KOC_RA_*stoI*_F	AGCATCGCTGAAATCCTGCT
KOC_RA_*stoI*_R	CAACACTGGGCATGAAACCG
KOC_LA_*stoJ*_F	TTGCTCCGGCTATATCTCTGC
KOC_LA_*stoJ*_R	TGTGGTGCGTTCGAAGAGTTT
KOC_RA_*stoJ*_F	TTGCGAAGTGCCGGAGAAAA
KOC_RA_*stoJ*_R	CTTGATGATGCCGACACTGC
KOC_LA_*stoK*_F	CGTTGTGTTGTGCGGTTTCG
KOC_LA_*stoK*_R	AATTGGGCTTCCAGCAGGTC
KOC_RA_*stoK*_F	TGCTCTTCACCCCGTATTGG
KOC_RA_*stoK*_R	GTTTCTCCCTCGCCTACAGC
KOC_LA_*stoM*_F	CTGACCGATCCGCAAGTGAT

KOC_LA_*stoM*_R	TTTGCAGGTGCCACGAAAAC
KOC_RA_*stoM*_F	AGAATCTTGTAGGCGGCAGTG
KOC_RA_*stoM*_R	AACCAACGGAGCACGTCTT
KOC_LA_*stoN*_F	CTGCTGGTTGTGTTGACCTG
KOC_LA_*stoN*_R	GAAGAAAATCACTCCGCAGCC
KOC_RA_*stoN*_F	CAGCGTTATCCAGTCCCTCG
KOC_RA_*stoN*_R	TGCCAATCAGGATCTCACCG
KOC_LA_*stoO*_F	CACGAGATCGAGTATCCGCA
KOC_LA_*stoO*_R	CAAGCATCACGACGAACAGG
KOC_RA_*stoO*_F	GCTTGAGCATGGGCGATTG
KOC_RA_*stoO*_R	TTCGCCTCGGTATCGTCTTG
KOC_LA_*stoP*_F	GCGCTGGAGTTTCTCTGTGA
KOC_LA_*stoP*_R	GTCCGCAAAGCAATCCCAAG
KOC_RA_*stoP*_F	GGTTATCTGAATGCCTGCGG
KOC_RA_*stoP*_R	AGCAGTGTGACGGATTGACA
KOC_LA_*clp*_F	GACATTGACGAGCCGACAC
KOC_LA_*clp*_R	TCCTGCACATTGGCGATACC
KOC_RA_*clp*_F	GCAGGCCCGACCAGACG
KOC_RA_*clp*_R	GACACCCAACCGCCGTG
KOC_LA_*acaA*_F	CAACTCGACATCCGTTGCAGA
KOC_LA_*acaA*_R	CACAGAAACGCCATGGAGCAA
KOC_RA_*acaA*_F	GTTCTGGACAACCGAACCCT
KOC_RA_*acaA*_R	CATCCCCACCCAATCGCATA
KOC_LA_*acaB*_F	GGAAAGCACCGAAGCCAAAC
KOC_LA_*acaB*_R	CGATAAAGCGGCAGTGTTCA
KOC_RA_*acaB*_F	TCGCTTACTTCTCCCACGAA
KOC_RA_*acaB*_R	CCATTCACCACCTCACATGC
KOC_LA_*acaC*_F	GTTTCTGTGCAACGCCACG
KOC_LA_*acaC*_R	CACCACCTCACATGCCTTCA
KOC_RA_*acaC*_F	ATGCGATTGGGTGGGGATGTC
KOC_RA_*acaC*_R	CAATCAACTGACGCATCTGGACG

The *clp* deletion mutant was created to avoid extensive foam formation during fermentation. Therefore, the third module A-PCP (A_{Thr}) domain of the lipopeptide producing NRPS was deleted. The deletion mutants in the styrolide (*stoX*) and acaterin (*acaX*) biosynthetic gene cluster region were created by marker-less, in-frame deletion of the single genes. Typically, the sequence between the first 6 and the last 21 bases of a gene was deleted to prevent polar effects. Due to its large size two subsequent deletions were conducted for *stoA*.

LC-MS-Based Metabolomic Profiling

Metabolite production of *P. fluorescens* HKI0874, *P. jessenii* EC-S101, respective deletion mutants, and HKI0874 Tn5 insertion mutants in SM/5 medium was analyzed *via* UHPLC-MS (Shimadzu). For *P. fluorescens* HKI0874 and respective mutants, overnight liquid cultures (5 mL) were extracted with 10 mL ethyl acetate. For *P. jessenii* EC-S101 and corresponding mutants, cultures grown on solid SM/5 agar were extracted with 10 mL ethyl acetate. The organic phase was dried over sodium sulfate and solvents were removed using a speedvac Savant SPD1010 (Thermo). LC-MS samples were prepared by dissolving the crude bacterial extracts in 200 µL methanol and filtration through PTFE filter membranes (0.2 µm). LC-MS results were analyzed using the LabSolutions Postrun and LabSolutions Browser software (v.5.60). UV-chromatograms at 354 nm (absorption of styrolide B **2**) were compared for Δ*stoX* gene deletion mutants and Tn5 insertion mutants (Figure S8).

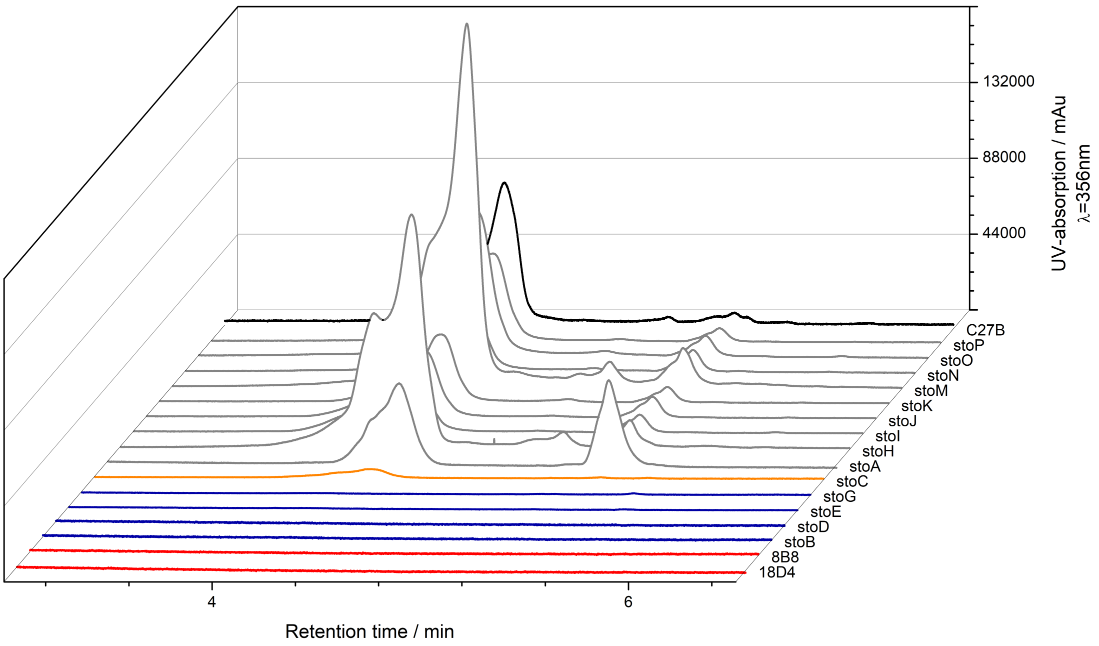


Figure S8. HPLC profiles of *P. fluorescens* HKI0874 (black), *P. fluorescens* HKI0874 Tn5 mutants (8B8 and 18D4, red), and *P. fluorescens* HKI0874 Δ*stoX* gene deletion mutants (blue: mutants deficient in styrolide production, orange: mutant with reduced styrolide production, grey: mutants which still produce styrolides).

UV-chromatograms at 190 nm (absorption of acaterin **9** and 4,5-didehydroacaterin **10**) were compared for *P. jessenii* EC-S101 and *P. jessenii* EC-S101 Δ*acaX* gene deletion mutants (Figure S9). Here, LC-MS analysis was performed on a Luna® C18 column (150 × 2 mm, 5 µm, 100 Å, Phenomenex®), solvent A: H_2O + 0.1% HCOOH, solvent B: acetonitrile + 0.1% HCOOH, flow rate: 0.2 mL min^{-1}, injection: 10 µL, gradient: 10% B for 0.5 min, 10% to 100% B over 20 min, 100% B for 8 min. The column was equilibrated prior each injection with 10% B for 10 min. Peak identity was confirmed by LC-ESI-MS (**10**: *m/z* = 225 $[M+H]^+$, **9**: *m/z* = 227 $[M+H]^+$).[2]

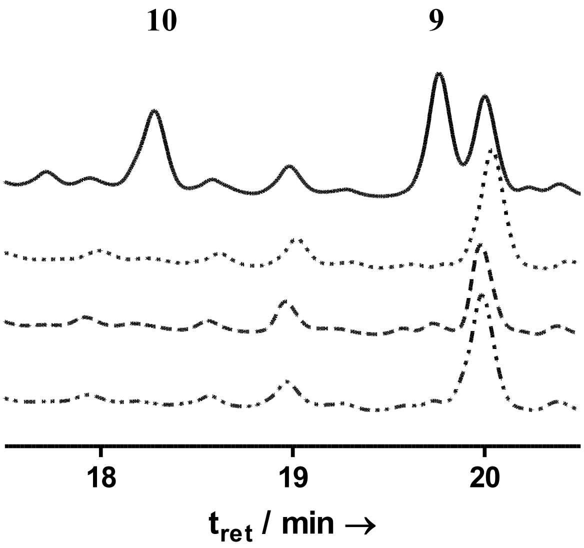


Figure S9. HPLC profiles of *P. jessenii* EC-S101 (solid line), *P. jessenii* EC-S101 Δ*acaA* (dotted line), *P. jessenii* EC-S101 Δ*acaB* (dashed line), and *P. jessenii* EC-S101 Δ*acaC* (dashed-dotted line).

Intermediate/shunt product analyses of styrolide deletion mutants in SM/5 medium was conducted *via* UHPLC-MS (Shimadzu) with the above-mentioned method, taking advantage of the aromatic moiety as UV-visible chromophore. The column was equilibrated prior each injection with 10% B for 10 min. Chromatograms of culture extracts of 50 mL cultures (1 day in SM/5 medium) were compared with the wildtype *P. fluorescens* HKI0874 by overlaying the UV-trace at different wavelengths (*e.g.* 190 nm, 254 nm) and searching for differences in the metabolite profiles. The HPLC profile of culture extracts of *P. fluorescens* HKI0874 Δ*stoC* and Δ*stoE* deletion mutant each showed an additional peak with *m/z* = 233 $[M+H]^+$ / *m/z* = 231 $[M-H]^-$, eluting at different retention times and showing different UV-spectra (Figure S10).

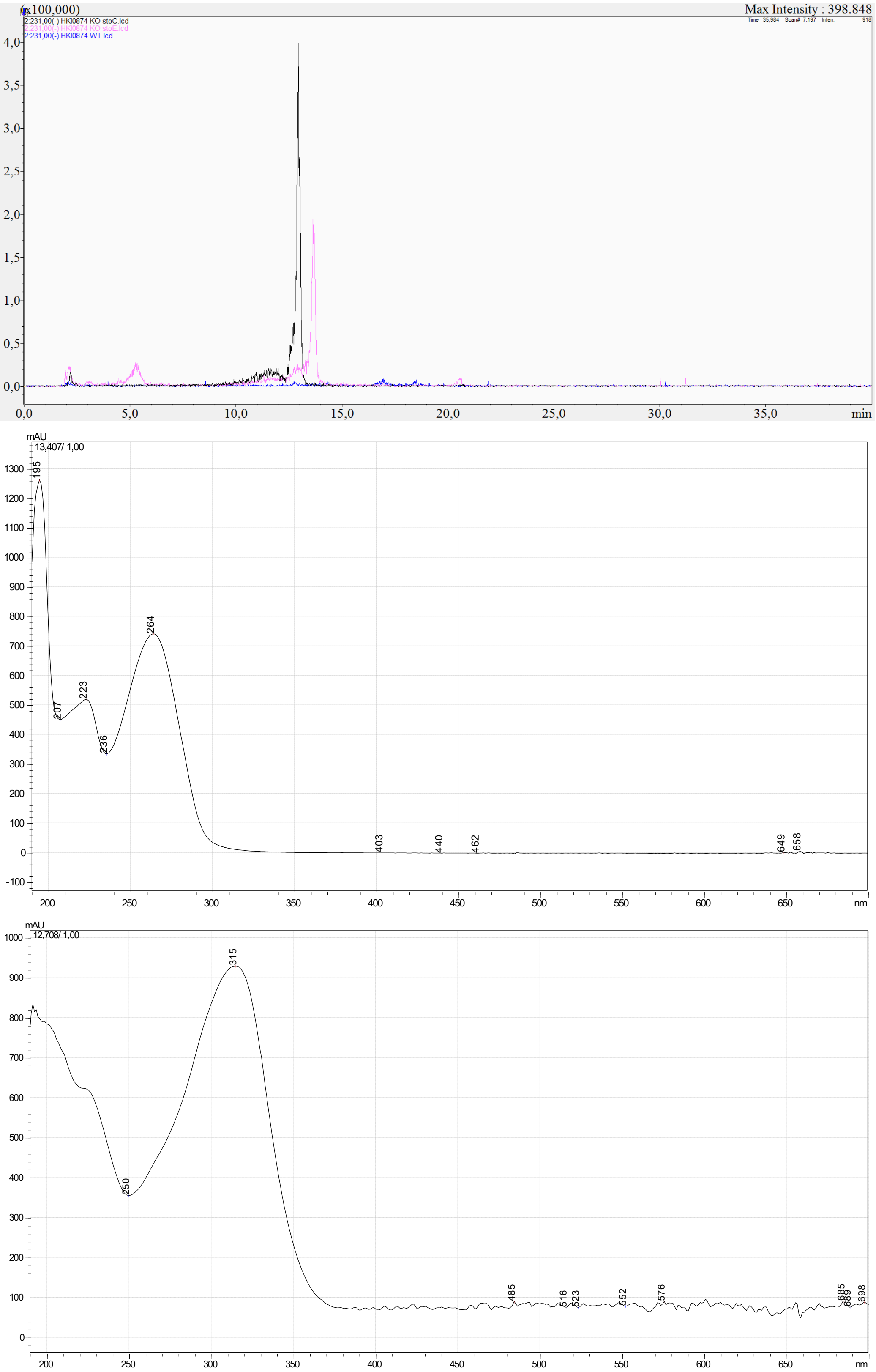


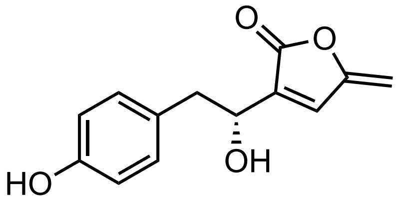
Figure S10: Selected ion monitoring (top) on m/z = 231 $[M-H]^-$ of *P. fluorescens* HKI0874 (blue), Δ*stoC* (black), and Δ*stoE* (pink); and UV-spectra of the corresponding shunt product **11** (middle, Δ*stoE*) and intermediate product **12** (bottom, Δ*stoC*).

UV Chromatogram Calculation for Potential Shunt/Intermediate Products

Intermediate/shunt products of *P. fluorescens* HKI0874 Δ*stoC* and Δ*stoE* were speculated to be different hydration products of styrolide B. UV spectra of all likely candidates **11** – **16** were thus computed for comparison with experimental data.

Conformation searches based on molecular mechanics with MMFF94s force field were performed to give stable conformers with populations higher than 1%.[18-19] All these conformers were further optimized by the density functional theory method at the B3LYP/6-31G(d) level in Gaussian 09 program package,[20] led to optimized conformers within a 2.5 kcal/mol energy threshold from global minimum. These predominant conformers were subjected to theoretical calculation of UV using time-dependent density functional theory (TDDFT) at CAM-B3LYP/6-311+G (d,p) level in air. The calculated UV spectra were generated using SpecDis 1.60 with $\sigma = 0.3$ eV.[21-23]

Comparing UV spectra calculations with experimental data (Figure S10), for shunt product **11** the additional hydroxyl group would be at position 7 in place of the E-double bond connecting the aromatic moiety with the butenolide moiety, while for intermediate **12** the 6-position of the exo-double bond in the butenolide moiety would be hydroxylated.



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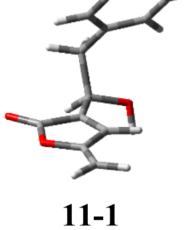
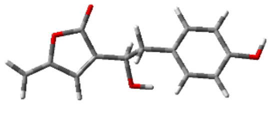


11-1



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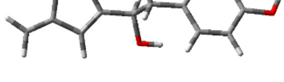
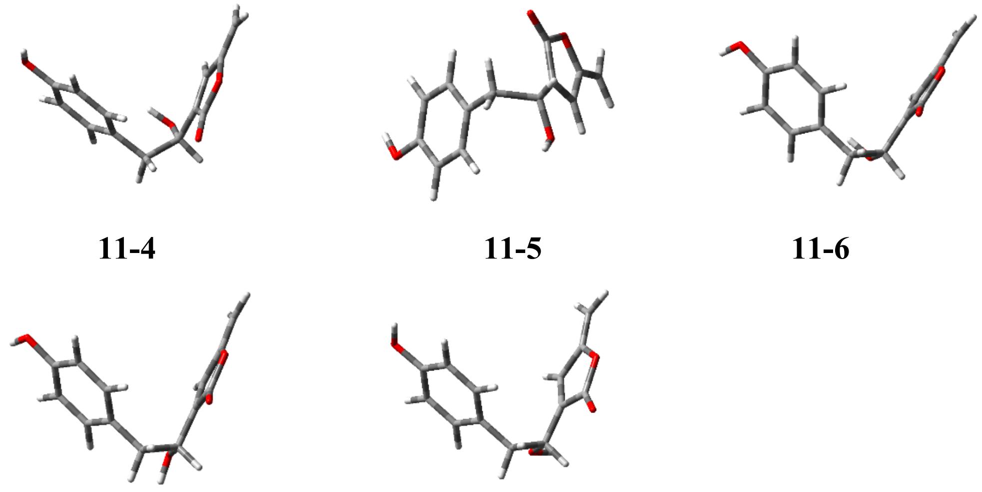


11-3



11-4 **11-5** **11-6**

11-7 **11-8**

Figure S11. Optimized conformers of **11** (**11-1** to **11-8**).

Table S12. Energy analysis for conformers of **11-1** to **11-8** at B3LYP/6-31G(d) level in gas phase.

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔE*(kal/mol)	P_E%
11-1	-803.246568	-803.231575	-803.230631	-803.29012	0	43.97%
11-2	-803.246445	-803.231446	-803.230502	-803.290022	0.061495	39.64%
11-3	-803.245346	-803.230578	-803.229634	-803.28833	1.123225	6.60%
11-4	-803.242842	-803.227816	-803.226872	-803.28654	2.24645	0.99%
11-5	-803.24512	-803.230355	-803.229411	-803.288131	1.2480975	5.35%
11-6	-803.242557	-803.227523	-803.226579	-803.286282	2.408345	0.75%
11-7	-803.242823	-803.227752	-803.226807	-803.286973	1.9747425	1.57%
11-8	-803.242686	-803.227627	-803.226683	-803.286656	2.17366	1.12%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

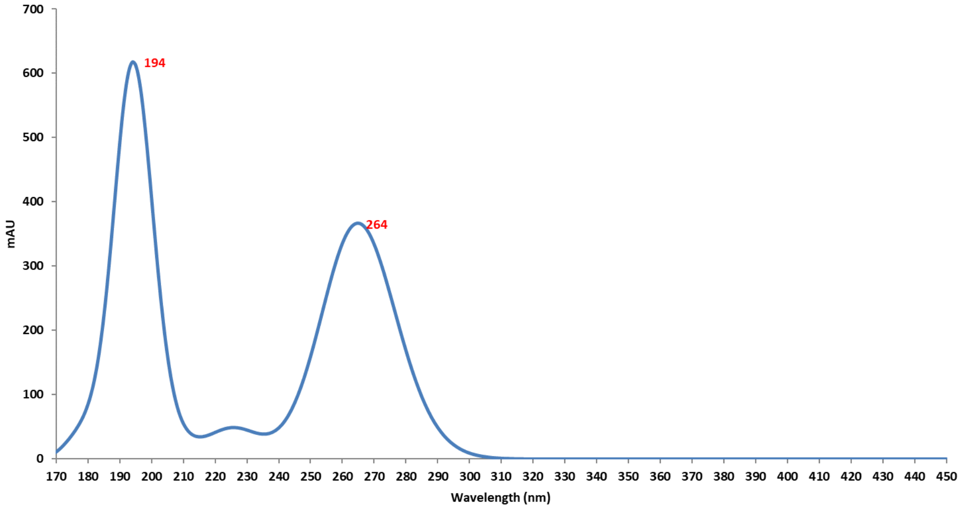
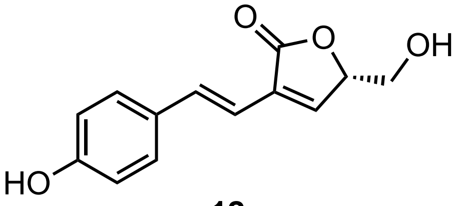


Figure S12. Calculated UV spectrum of **11**. UV maximum matches with experimental UV maximum for shunt product **11** (Figure S10, middle).



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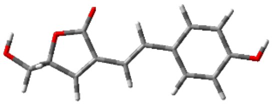

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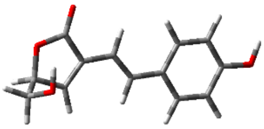

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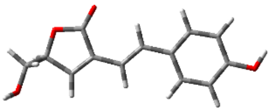

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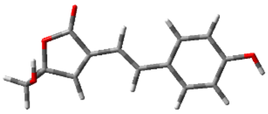

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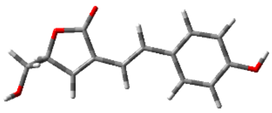

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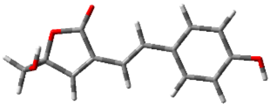

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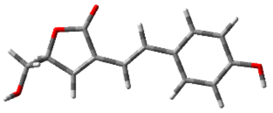

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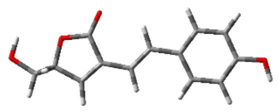

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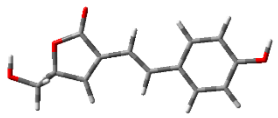

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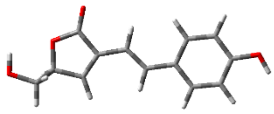


12-10

Figure S13. Optimized conformers of **12** (**12-1** to **12-10**).

Table S13. Energy analysis for conformers of **12-1** to **12-10** at B3LYP/6-31G(d) level in gas phase.

Species	$E'=E+ZPE$	E	H	G	ΔE(kal/mol)	P_E%
12-1	-803.244423	-803.229226	-803.228282	-803.289073	1.605145	2.42%
12-2	-803.244813	-803.22953	-803.228586	-803.289048	1.620833	2.36%
12-3	-803.24432	-803.229132	-803.228188	-803.288949	1.682955	2.12%
12-4	-803.244813	-803.229528	-803.228584	-803.289062	1.612048	2.39%
12-5	-803.246316	-803.231232	-803.230288	-803.290458	0.736058	10.49%
12-6	-803.244567	-803.229265	-803.228321	-803.28891	1.707428	2.04%
12-7	-803.247464	-803.232422	-803.231478	-803.291412	0.137423	28.82%
12-8	-803.245593	-803.230435	-803.229491	-803.290048	0.993333	6.80%
12-9	-803.245491	-803.230335	-803.229391	-803.289964	1.046042	6.22%
12-10	-803.247744	-803.232711	-803.231767	-803.291631	0.000000	36.35%

E, E', H, G: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

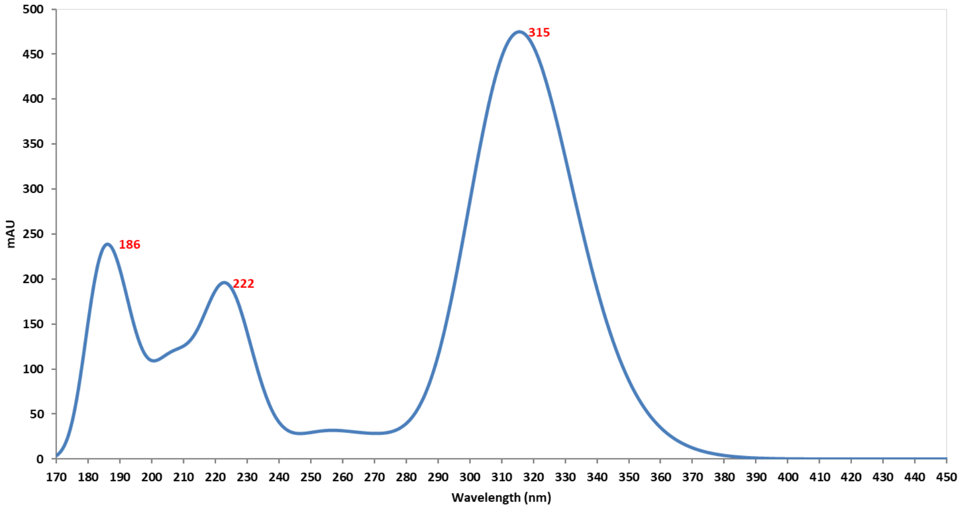
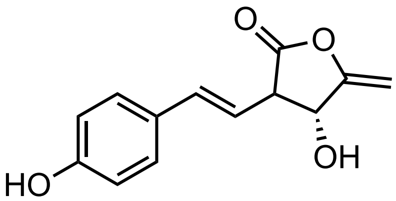


Figure S14. Calculated UV spectrum of **12**. UV maximum matches with experimental UV maximum for intermediate product **12** (Figure S10, bottom).



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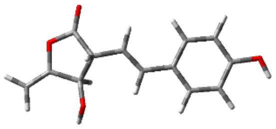

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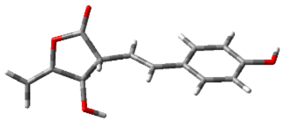

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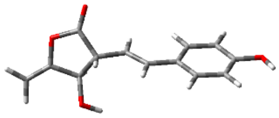

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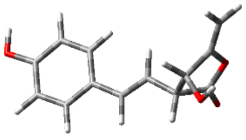

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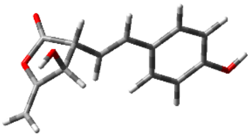

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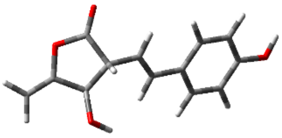

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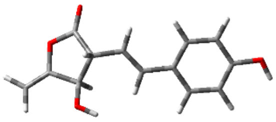

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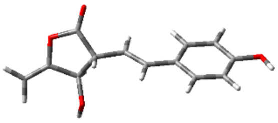

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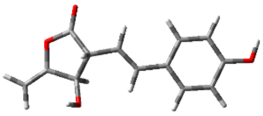

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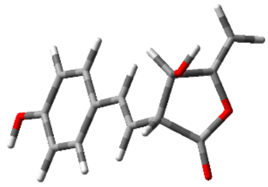

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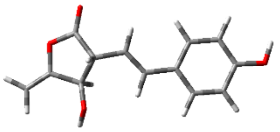

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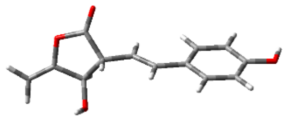

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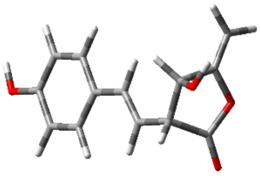

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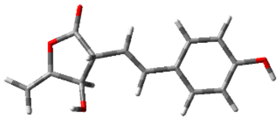

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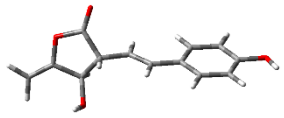


13-15

Figure S15. Optimized conformers of **13** (**13-1** to **13-15**).

Table S14. Energy analysis for conformers of **13-1** to **13-15** at B3LYP/6-31G(d) level in gas phase.

Species	*E*'=*E*+*ZPE*	*E*	*H*	*G*	*ΔE*(kal/mol)	P_E%
13-1	-803.229642	-803.214298	-803.213354	-803.274288	0.252255	11.06%
13-2	-803.229656	-803.214329	-803.213385	-803.274193	0.311867	10.00%
13-3	-803.228057	-803.212766	-803.211822	-803.272605	1.308337	1.86%
13-4	-803.228169	-803.21288	-803.211936	-803.27277	1.204800	2.21%
13-5	-803.227682	-803.212345	-803.211401	-803.272205	1.559337	1.22%
13-6	-803.227571	-803.212252	-803.211308	-803.271962	1.711820	0.94%
13-7	-803.227882	-803.212126	-803.211181	-803.274321	0.231547	11.45%
13-8	-803.230509	-803.215306	-803.214362	-803.27469	0.000000	16.92%
13-9	-803.22649	-803.21121	-803.210266	-803.271213	2.181817	0.43%
13-10	-803.228052	-803.212693	-803.211749	-803.272371	1.455172	1.45%
13-11	-803.229661	-803.214337	-803.213393	-803.274384	0.192015	12.24%
13-12	-803.226437	-803.211163	-803.210219	-803.271187	2.198132	0.41%
13-13	-803.230497	-803.215306	-803.214362	-803.274634	0.035140	15.95%
13-14	-803.229662	-803.214349	-803.213405	-803.274411	0.175072	12.59%
13-15	-803.227969	-803.212622	-803.211678	-803.272247	1.532982	1.27%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

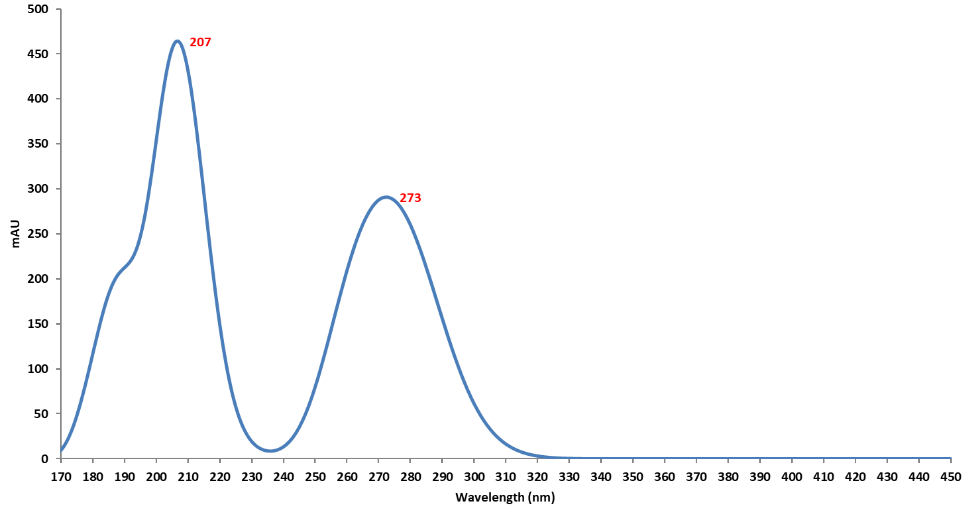
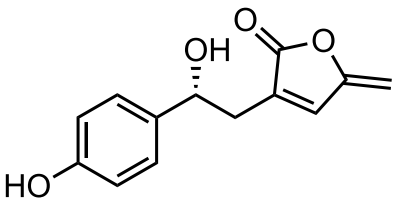


Figure S16. Calculated UV spectrum of **13**.



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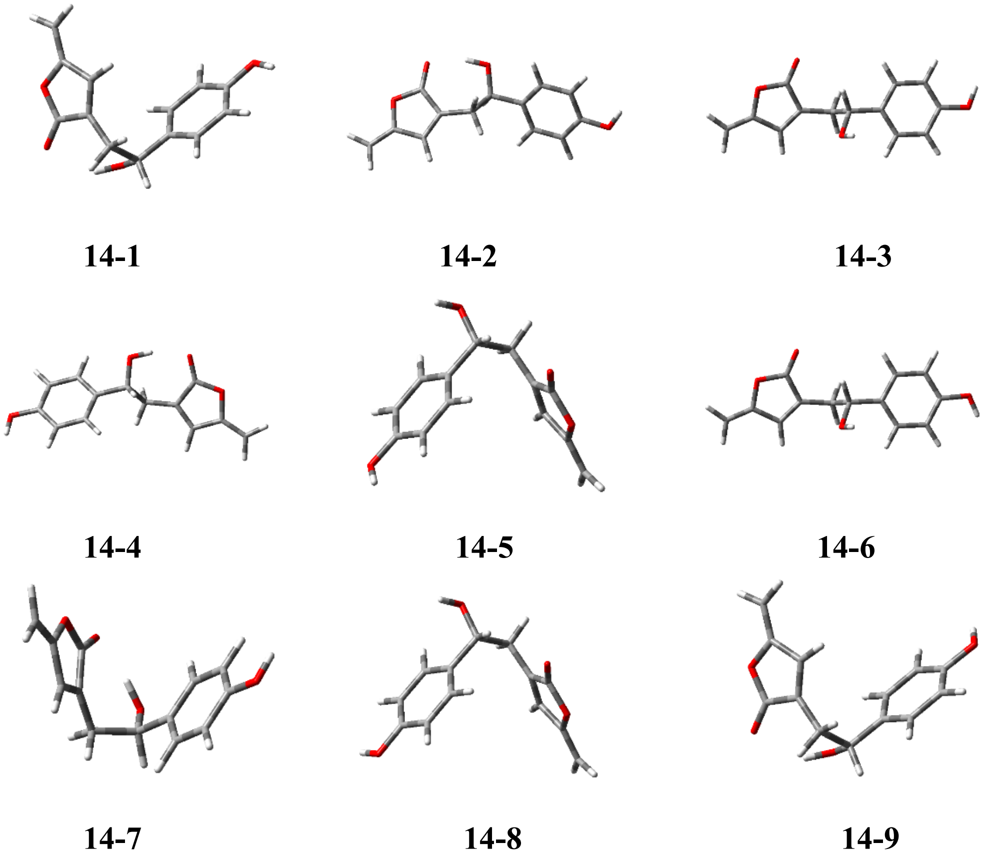


14-1 **14-2** **14-3**

14-4 **14-5** **14-6**

14-7 **14-8** **14-9**

Figure S17. Optimized conformers of **14** (**14-1** to **14-9**).

Table S15. Energy analysis for conformers of **14-1** to **14-9** at B3LYP/6-31G(d) level in gas phase.

Species	*E'*=*E*+*ZPE*	*E*	*H*	*G*	*ΔE*(kal/mol)	P_E%
14-1	-803.247514	-803.232789	-803.231845	-803.290894	0.325045	28.60%
14-2	-803.246062	-803.230937	-803.229992	-803.29035	0.666405	16.08%
14-3	-803.247142	-803.232406	-803.231461	-803.290495	0.575418	18.74%
14-4	-803.245107	-803.230071	-803.229127	-803.288762	1.662875	2.99%
14-5	-803.245946	-803.230821	-803.229877	-803.290257	0.724763	14.57%
14-6	-803.246747	-803.232154	-803.23121	-803.289881	0.960702	9.78%
14-7	-803.244846	-803.229823	-803.228879	-803.288473	1.844223	2.20%
14-8	-803.245923	-803.231196	-803.230252	-803.289122	1.436975	4.38%
14-9	-803.245572	-803.230847	-803.229903	-803.28865	1.733155	2.66%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

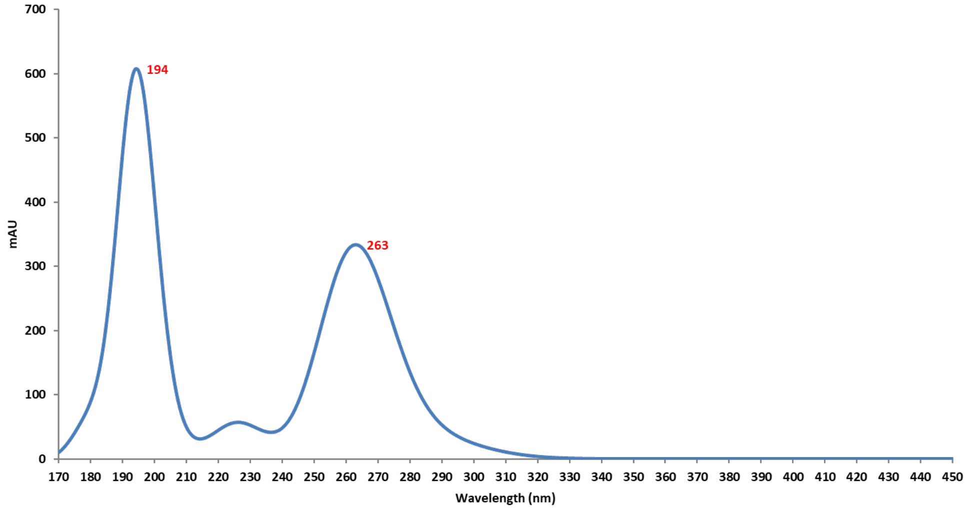
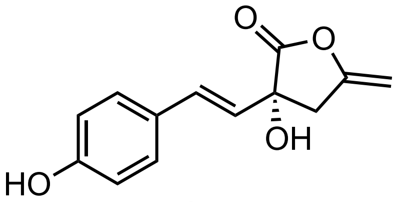


Figure S18. Calculated UV spectrum of **14**.



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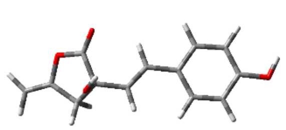

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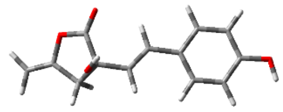

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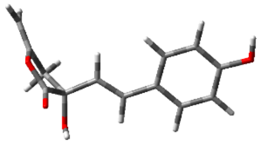

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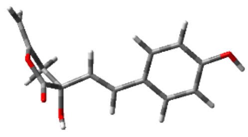

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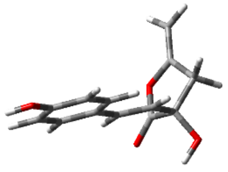
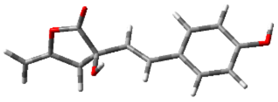
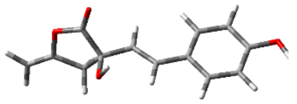


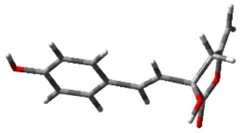
15-5



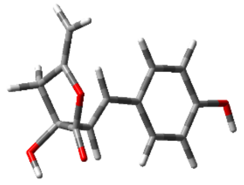
15-6



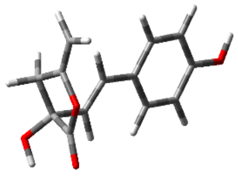
15-7



15-8



15-9



15-10

Figure S19. Optimized conformers of **15** (**15-1** to **15-10**).

Table S16. Energy analysis for conformers of **15-1** to **15-10** at B3LYP/6-31G(d) level in gas phase.

Species	*E'=E+ZPE*	*E*	*H*	*G*	*ΔE*(kal/mol)	P_E%
15-1	-803.233888	-803.218724	-803.217779	-803.27777	0.051455	23.95%
15-2	-803.233983	-803.218831	-803.217887	-803.277852	0.000000	26.12%
15-3	-803.233025	-803.217788	-803.216844	-803.277048	0.504510	11.15%
15-4	-803.232305	-803.2171	-803.216156	-803.276516	0.838340	6.35%
15-5	-803.232349	-803.217146	-803.216201	-803.276545	0.820142	6.54%
15-6	-803.232813	-803.217563	-803.216619	-803.276931	0.577928	9.85%
15-7	-803.231579	-803.216352	-803.215408	-803.276088	1.106910	4.03%
15-8	-803.231579	-803.216366	-803.215422	-803.275918	1.213585	3.37%

15-9	-803.231921	-803.216654	-803.21571	-803.276229	1.018433	4.68%
15-10	-803.231694	-803.216417	-803.215472	-803.276069	1.118833	3.95%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

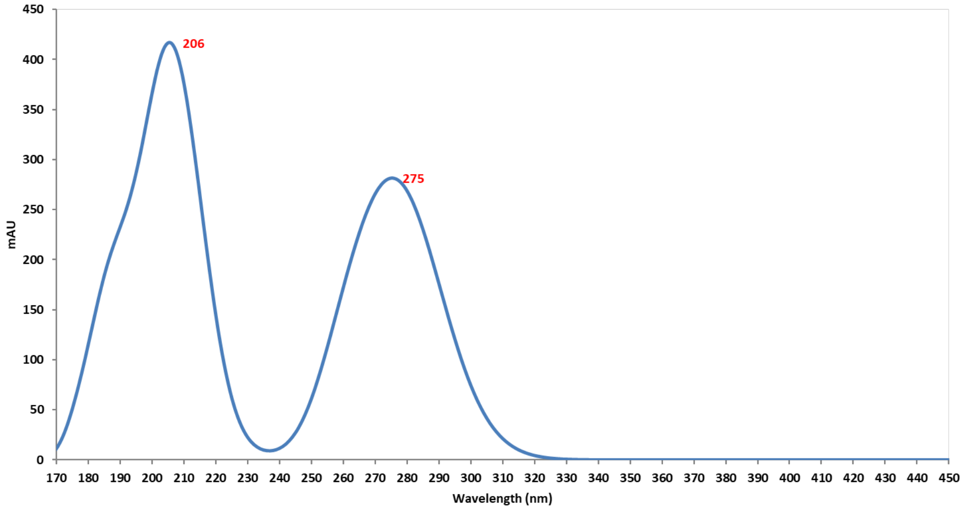
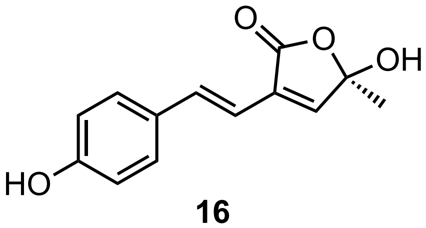
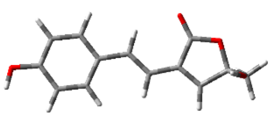


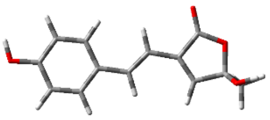
Figure S20. Calculated UV spectrum of **15**.



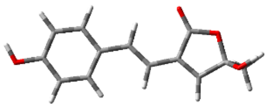
16



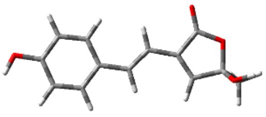
16-1



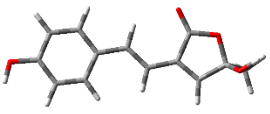
16-2



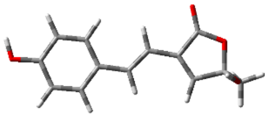
16-3



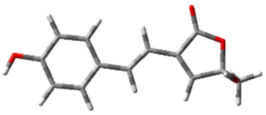
16-4



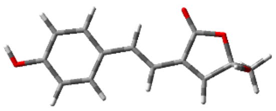
16-5



16-6



16-7



16-8

Figure S21. Optimized conformers of **16** (**16-1** to **16-8**).

Table S17. Energy analysis for conformers of **16-1** to **16-8** at B3LYP/6-31G(d) level in gas phase.

Species	$E'=E+ZPE$	E	H	G	ΔE(kal/mol)	P_E%
16-1	-803.258233	-803.242879	-803.241935	-803.302429	1.917013	1.51%
16-2	-803.260323	-803.245077	-803.244133	-803.303929	0.975762	7.41%
16-3	-803.258139	-803.242782	-803.241838	-803.302335	1.975998	1.37%
16-4	-803.260075	-803.24482	-803.243876	-803.303745	1.091222	6.10%
16-5	-803.259797	-803.244458	-803.243514	-803.303924	0.978900	7.37%
16-6	-803.259699	-803.244358	-803.243414	-803.303833	1.036002	6.69%
16-7	-803.261876	-803.246639	-803.245695	-803.305484	0.000000	38.48%
16-8	-803.261607	-803.24636	-803.245415	-803.305282	0.126755	31.06%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

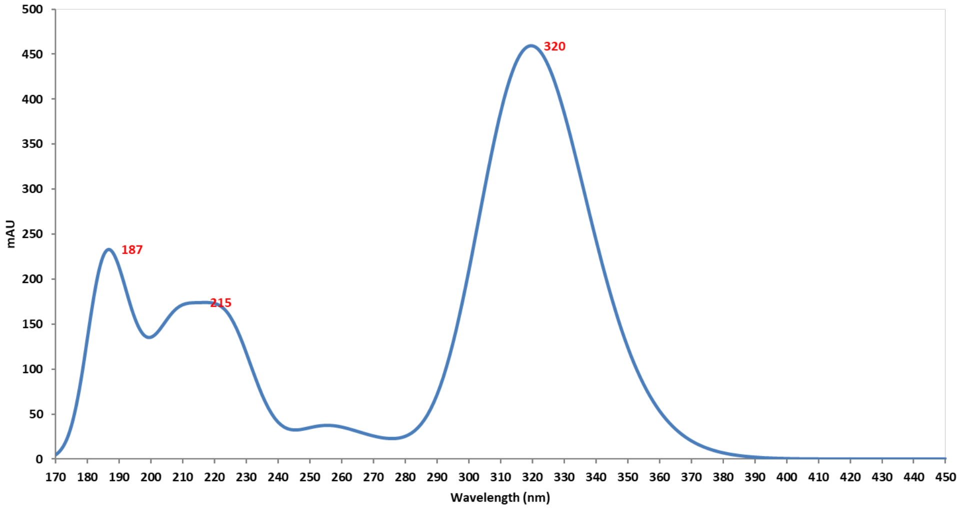
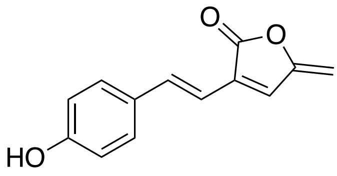
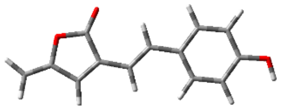


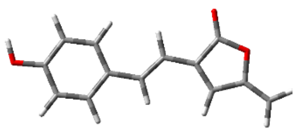
Figure S22. Calculated UV spectrum of **16**.



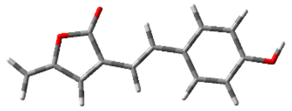
2



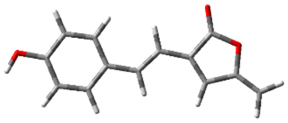
2-1



2-2



2-3



2-4

Figure S23. Optimized conformers of **2**(**2-1** to **2-4**).

Table S18. Energy analysis for conformers of **2-1** to **2-4** at B3LYP/6-31G(d) level in gas phase.

Species	$E'=E+ZPE$	E	H	G	ΔE(kal/mol)	P_E%
2-1	-726.845429	-726.831851	-726.830906	-726.887482	1.018432	8.45%
2-2	-726.847551	-726.834065	-726.833121	-726.889105	0.000000	47.14%
2-3	-726.845315	-726.831738	-726.830794	-726.887356	1.097498	7.39%
2-4	-726.847278	-726.833785	-726.832841	-726.888877	0.143070	37.02%

E, *E'*, *H*, *G*: total energy, total energy with zero point energy (ZPE), enthalpy, and Gibbs free energy

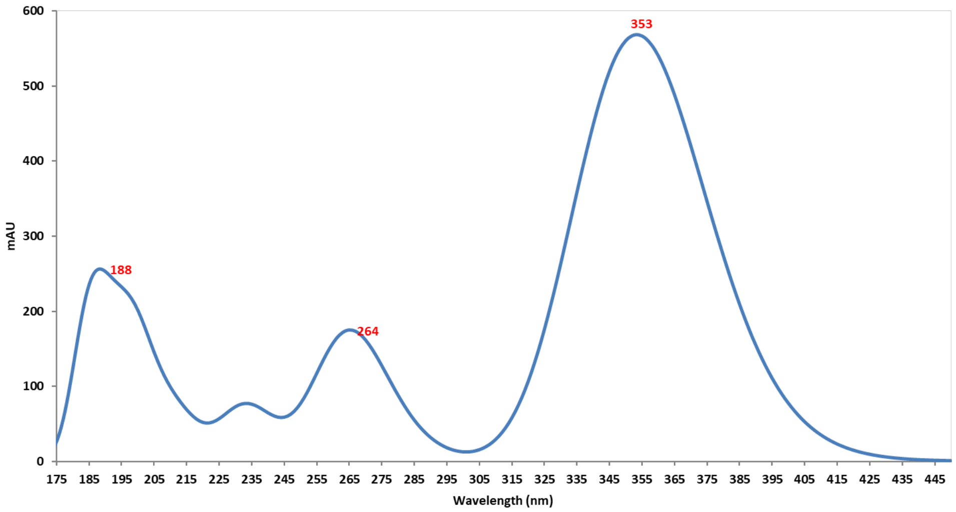


Figure S24. Calculated UV spectrum of **2** (control). UV maximum matches with experimental UV maximum for styrolide B **2**.

Table S19: Z-Matrix of optimized conformers, optimized at the B3LYP/6-31g(d) level in gas phase.

nuclei	Z-Matrix of **11-1**			Z-Matrix of **11-2**			Z-Matrix of **11-3**			Z-Matrix of **11-4**			Z-Matrix of **11-5**		
C	3.42097	-1.8954	-0.22648	3.67682	0.29049	0.8906	2.24007	-0.00787	2.32455	2.32944	0.10017	1.81137	1.73562	-1.87468	0.82056
C	4.21879	-0.89054	0.30688	4.23804	-0.81585	0.26501	2.65026	-1.1177	1.59674	2.66877	-1.17032	1.36424	2.62784	-1.17151	1.62
C	3.65084	0.21782	0.92594	3.43423	-1.82561	-0.2535	1.73644	-1.86572	0.86279	1.68586	-2.07658	0.98242	2.19994	-0.09312	2.38647
C	2.2607	0.32014	1.00951	2.0457	-1.72296	-0.1436	0.39123	-1.49054	0.85406	0.34225	-1.7015	1.05047	0.85711	0.2885	2.34509
C	1.43966	-0.68487	0.47617	1.46178	-0.61303	0.48466	-0.04077	-0.36568	1.57297	-0.02085	-0.42155	1.49795	-0.05782	-0.40384	1.53658
C	2.0319	-1.79487	-0.14213	2.2899	0.39327	1.00211	0.896	0.36652	2.31708	0.98682	0.47523	1.87895	0.39326	-1.49567	0.78133
O	5.57085	-1.03056	0.20186	5.59734	-0.87505	0.17902	3.97262	-1.44706	1.63238	3.99232	-1.49397	1.3125	3.92905	-1.57783	1.6287
C	-0.06651	-0.555	0.54859	-0.04328	-0.48706	0.58497	-1.49525	0.05552	1.53904	-1.47985	-0.02017	1.55271	-1.50836	0.02811	1.4743
C	-0.61907	0.37672	-0.54651	-0.61773	0.47165	-0.47509	-1.84474	1.09548	0.45018	-1.91809	1.01343	0.49118	-1.82374	1.0846	0.39119
C	-2.04008	0.7297	-0.30334	-2.05055	0.77125	-0.22858	-1.50809	0.70768	-0.94502	-1.47705	0.70549	-0.89209	-1.50986	0.68495	-1.00578
C	-3.16785	0.40343	-0.92616	-3.16278	0.43911	-0.87593	-0.71384	1.25265	-1.86167	-0.66711	1.33738	-1.73531	-0.68583	1.1849	-1.92168
C	-4.25198	1.05633	-0.28605	-4.27179	1.02913	-0.21778	-0.77647	0.47677	-3.0472	-0.59068	0.59678	-2.94208	-0.79694	0.41836	-3.1099
O	-3.79752	1.8318	0.76902	-3.85014	1.76953	0.87527	-1.64536	-0.58925	-2.88407	-1.38415	-0.53694	-2.86729	-1.73009	-0.59253	-2.94999
C	-2.43866	1.65192	0.76603	-2.48631	1.6316	0.87726	-2.11132	-0.45882	-1.60153	-1.93757	-0.48456	-1.61415	-2.18552	-0.43898	-1.66644
O	-1.65694	2.17816	1.5426	-1.72817	2.14577	1.68441	-2.90825	-1.21337	-1.06733	-2.7106	-1.3103	-1.15327	-3.02976	-1.14181	-1.13441
C	-5.54173	0.97276	-0.61549	-5.55559	0.92143	-0.56306	-0.1159	0.70039	-4.18409	0.12785	0.90359	-4.02308	-0.12411	0.60425	-4.24639
O	-0.52646	-0.27505	-1.82032	-0.49837	-0.12612	-1.77347	-1.2348	2.35547	0.76329	-1.45627	2.32217	0.85407	-1.16335	2.319	0.70438
H	3.88007	-2.75667	-0.70371	4.31731	1.06985	1.29402	2.96418	0.56003	2.90204	3.10778	0.79882	2.10422	2.08213	-2.72099	0.23393
H	4.26697	1.00594	1.34708	3.8658	-2.69372	-0.74153	2.04687	-2.7392	0.29812	1.94116	-3.0709	0.63047	2.88942	0.45607	3.01981
H	1.8198	1.18835	1.4973	1.42119	-2.51608	-0.55043	-0.31977	-2.08886	0.28666	-0.42146	-2.41522	0.74546	0.52596	1.12808	2.95404
H	1.41737	-2.58944	-0.56035	1.86099	1.26176	1.49916	0.58502	1.22955	2.90274	0.73598	1.47562	2.22346	-0.29656	-2.06594	0.16217
H	5.99493	-0.27389	0.63876	5.84533	-1.71025	-0.2497	4.10332	-2.2585	1.11484	4.07338	-2.40366	0.98254	4.4217	-1.02985	2.26111
H	-0.51571	-1.55284	0.45582	-0.49253	-1.4829	0.4725	-2.12131	-0.83808	1.42511	-2.10135	-0.91968	1.45732	-2.13837	-0.8595	1.33803
H	-0.32625	-0.19227	1.55103	-0.28796	-0.15177	1.60063	-1.74914	0.4724	2.52295	-1.6786	0.37599	2.55731	-1.78095	0.43747	2.45639
H	-0.0317	1.30039	-0.61593	-0.0575	1.41413	-0.50316	-2.92528	1.27594	0.50064	-3.01343	1.07339	0.50188	-2.8964	1.30593	0.44718
H	-3.24461	-0.24749	-1.78422	-3.21262	-0.17453	-1.76291	-0.11996	2.14528	-1.7376	-0.19172	2.25517	-1.52987	-0.03825	2.03891	-1.79574
H	-6.29076	1.52114	-0.05334	-6.32561	1.42104	0.01596	-0.24278	0.03792	-5.03439	0.11247	0.2597	-4.89629	-0.29152	-0.04726	-5.09819
H	-5.8816	0.3631	-1.44571	-5.86979	0.34001	-1.42307	0.56025	1.5408	-4.29806	0.74573	1.79408	-4.06391	0.60354	1.4007	-4.35806
H	0.4246	-0.3788	-2.00684	0.4563	-0.17511	-1.96381	-0.27324	2.20825	0.79479	-1.84849	2.5344	1.71822	-0.20814	2.13368	0.72531

nuclei	Z-Matrix of **11-6**			Z-Matrix of **11-7**			Z-Matrix of **11-8**		
C	1.62765	-2.15083	0.96985	2.31928	0.09571	1.87154	1.65742	-2.10671	0.93014
C	2.61614	-1.26971	1.38852	2.67257	-1.15332	1.37695	2.62756	-1.23878	1.41533
C	2.2884	0.00018	1.8507	1.69978	-2.05627	0.96131	2.27591	-0.00376	1.94926
C	0.94816	0.39174	1.89306	0.35186	-1.69954	1.04213	0.93003	0.36571	1.99571
C	-0.06473	-0.48289	1.47373	-0.02442	-0.44118	1.53644	-0.06413	-0.4962	1.51048
C	0.28874	-1.75984	1.01243	0.97262	0.45189	1.95257	0.31233	-1.7382	0.97835
O	3.91125	-1.69197	1.32928	3.99974	-1.46029	1.31351	3.92946	-1.63908	1.34934
C	-1.51859	-0.06033	1.50294	-1.48634	-0.04969	1.60188	-1.52213	-0.08685	1.54394
C	-1.91785	0.99275	0.44559	-1.93134	0.99262	0.55337	-1.92496	0.97637	0.4999
C	-1.46638	0.68536	-0.93419	-1.48925	0.69337	-0.83266	-1.48344	0.6698	-0.88449
C	-0.62204	1.29636	-1.75874	-0.61742	1.282	-1.64516	-0.5771	1.22358	-1.68353
C	-0.55674	0.56706	-2.97313	-0.57265	0.5641	-2.86762	-0.55738	0.517	-2.9133
O	-1.39439	-0.53592	-2.92316	-1.45006	-0.50803	-2.83421	-1.48819	-0.50965	-2.89923
C	-1.9634	-0.47676	-1.67751	-2.0199	-0.44611	-1.58917	-2.06534	-0.43231	-1.65862
O	-2.7782	-1.2736	-1.23836	-2.85948	-1.22212	-1.16105	-2.95	-1.16591	-1.24696
C	0.18825	0.8581	-4.04051	0.19023	0.83786	-3.92683	0.22778	0.76271	-3.96306
O	-1.42851	2.28634	0.82758	-1.46876	2.29158	0.94806	-1.42234	2.25748	0.90499
H	1.89719	-3.13957	0.60977	3.08866	0.79123	2.19356	1.94628	-3.06866	0.51662
H	3.05437	0.6959	2.1774	1.96669	-3.03417	0.57387	3.02638	0.68118	2.32988
H	0.70012	1.38924	2.2487	-0.40441	-2.40997	0.71298	0.65632	1.33502	2.40855
H	-0.47513	-2.45932	0.67749	0.70377	1.43367	2.33743	-0.43789	-2.42721	0.59539
H	4.48343	-0.97683	1.65143	4.08951	-2.36445	0.97105	4.48356	-0.94758	1.74621
H	-2.15156	-0.94898	1.38421	-2.10129	-0.95274	1.49659	-2.14605	-0.9802	1.41207
H	-1.73196	0.32782	2.50768	-1.68541	0.33612	2.61048	-1.7416	0.28907	2.5521
H	-3.0115	1.07946	0.44217	-3.02663	1.04777	0.58043	-3.01803	1.06726	0.51966
H	-0.06858	2.19565	-1.53513	-0.01781	2.14792	-1.40843	0.06162	2.05682	-1.43289
H	0.16061	0.22422	-4.92081	0.1451	0.21474	-4.81423	0.15944	0.15082	-4.85686
H	0.84062	1.72414	-4.06295	0.87662	1.67766	-3.93616	0.95609	1.56628	-3.95806
H	-1.85535	2.51303	1.67151	-1.92126	2.93963	0.38136	-1.85161	2.92201	0.3391

nuclei	Z-Matrix of **12-1**			Z-Matrix of **12-2**			Z-Matrix of **12-3**			Z-Matrix of **12-4**			Z-Matrix of **12-5**		
C	3.23866	-2.83913	0.91344	3.6185	-0.5583	1.5928	4.12619	-0.69632	0.37843	3.9942	-0.65749	1.32111	3.18368	-2.78345	1.36853
C	4.3199	-1.99006	0.71666	3.8617	-1.6908	2.2712	4.2935	-2.02158	0.75851	4.1873	-2.01492	1.54329	4.23065	-1.87256	1.42348
C	4.12398	-0.6604	0.36133	2.7969	-2.4041	2.6695	3.19325	-2.84563	0.96576	3.11031	-2.89387	1.55338	3.99564	-0.50953	1.28036
C	2.82211	-0.17731	0.19604	1.5458	-2.0007	2.3998	1.90579	-2.33115	0.78385	1.82063	-2.40174	1.33162	2.68948	-0.05484	1.07337
C	1.71705	-1.02244	0.3744	1.2923	-0.8641	1.7182	1.71523	-1.0004	0.38432	1.60573	-1.03753	1.08833	1.62098	-0.96009	0.99911
C	1.93881	-2.35474	0.74848	2.3671	-0.1538	1.3223	2.83908	-0.18402	0.19669	2.70458	-0.16756	1.09977	1.87955	-2.32742	1.163
O	5.57078	-2.50338	0.88879	5.1278	-2.1038	2.5469	5.56649	-2.47939	0.92475	5.46176	-2.44934	1.75552	5.48721	-2.35994	1.6273
C	0.33345	-0.54401	0.23959	0.0075	-0.5169	1.4807	0.34304	-0.49434	0.23339	0.22825	-0.56345	0.88732	0.231	-0.51924	0.81224
C	-0.06563	0.33073	-0.69805	-0.4435	0.5673	0.8234	-0.03131	0.37599	-0.71854	-0.11164	0.39342	0.00894	-0.13361	0.44746	-0.04517
C	-1.40808	0.82348	-0.85483	-1.7098	0.9451	0.5678	-1.36209	0.89492	-0.89037	-1.44374	0.88363	-0.23476	-1.47793	0.9087	-0.27881
C	-2.56854	0.28823	-0.47714	-2.0402	2.0565	-0.1037	-2.53589	0.38799	-0.51463	-1.77494	1.84948	-1.09144	-1.83497	1.87906	-1.12086
C	-3.71184	1.13018	-0.89588	-3.5312	2.1884	-0.2219	-3.65873	1.24874	-0.95015	-3.23308	2.10186	-1.09543	-3.29839	2.09232	-1.11902
O	-3.10209	2.2245	-1.58866	-4.0027	1.0443	0.4558	-3.02199	2.32279	-1.64995	-3.74134	1.17672	-0.13389	-3.78356	1.13436	-0.17518
C	-1.74794	2.06393	-1.58256	-2.8943	0.3565	0.8919	-1.67152	2.13369	-1.63456	-2.71511	0.43586	0.37752	-2.73555	0.41715	0.32751
O	-0.95406	2.8328	-2.09491	-3.0423	-0.6802	1.506	-0.85932	2.87945	-2.15203	-2.8586	-0.45185	1.19894	-2.85663	-0.48262	1.13884
C	-4.55704	1.67051	0.26396	-4.0167	2.1817	-1.6596	-4.50077	1.81829	0.19794	-3.88929	1.84373	-2.45524	-3.97365	1.85549	-2.47533
O	-3.78252	2.4681	1.16023	-3.5193	3.3232	-2.3271	-3.71558	2.60457	1.0948	-3.4848	2.824	-3.40634	-3.75794	0.52694	-2.95236
H	3.40521	-3.87469	1.19582	4.4733	0.0506	1.2518	4.9935	-0.05954	0.22873	4.84307	0.02018	1.32723	3.37884	-3.84533	1.4876
H	4.96165	0.01394	0.21481	2.9581	-3.3407	3.2298	3.31345	-3.88097	1.2678	3.24907	-3.95516	1.73225	4.80593	0.21036	1.33274
H	2.68253	0.87001	-0.06235	0.7242	-2.6436	2.7619	1.05096	-2.98318	0.94902	0.98191	-3.09508	1.34349	2.51482	1.01445	0.98441
H	1.10278	-3.03181	0.90694	2.2756	0.7884	0.7606	2.72913	0.86145	-0.08148	2.571	0.90068	0.95066	1.06812	-3.0511	1.12467
H	6.21966	-1.80117	0.71802	5.0873	-2.9377	3.0426	5.52905	-3.41335	1.1877	5.4403	-3.40845	1.90665	6.10921	-1.61472	1.65054
H	-0.3726	-0.95694	0.9559	-0.7478	-1.2111	1.8762	-0.37653	-0.88094	0.9508	-0.52271	-1.06402	1.49501	-0.50451	-1.0554	1.40836
H	0.65144	0.73211	-1.41388	0.3068	1.2683	0.4227	0.69902	0.75306	-1.43439	0.66625	0.85333	-0.59862	0.63265	0.93669	-0.64443
H	-2.6845	-0.64205	0.05915	-1.3432	2.795	-0.523	-2.67466	-0.53337	0.03141	-1.08705	2.40073	-1.71748	-1.15594	2.44693	-1.74077
H	-4.34988	0.58589	-1.60062	-3.8843	3.0975	0.3184	-4.30302	0.71037	-1.65375	-3.43976	3.12297	-0.75587	-3.53955	3.0959	-0.75218
H	-5.00394	0.85215	0.83719	-5.1278	2.2245	-1.7092	-4.97143	1.01519	0.77372	-4.97977	1.88313	-2.35621	-3.59342	2.55252	-3.22873
H	-5.36259	2.30588	-0.1189	-3.6611	1.2843	-2.2132	-5.28801	2.46911	-0.19687	-3.63253	0.84926	-2.83845	-5.0563	1.99528	-2.38868
H	-3.41677	3.20568	0.637	-3.844	3.3407	-3.2298	-3.32683	3.32857	0.56911	-3.95003	2.62148	-4.23731	-4.12583	-0.07733	-2.28056

nuclei	Z-Matrix of **12-6**			Z-Matrix of **12-7**			Z-Matrix of **12-8**			Z-Matrix of **12-9**			Z-Matrix of **12-10**		
C	3.17257	-2.89825	1.43598	3.20278	-2.89534	1.33661	3.369	-2.78301	0.95687	4.19203	-0.68792	0.48838	4.06328	-0.57778	1.26179
C	4.2235	-1.99127	1.47931	4.2645	-2.00186	1.39553	4.43209	-1.90893	0.77123	4.36705	-2.02539	0.81907	4.27153	-1.93672	1.45993
C	3.99303	-0.62811	1.33039	4.05186	-0.63455	1.25843	4.20829	-0.58068	0.42751	3.27232	-2.86767	0.97608	3.20603	-2.82941	1.44122
C	2.68742	-0.16933	1.12913	2.75337	-0.15772	1.05323	2.89665	-0.12437	0.26288	1.98258	-2.35902	0.7939	1.91254	-2.34965	1.21465
C	1.61485	-1.07065	1.06641	1.6704	-1.04528	0.97511	1.80959	-0.99484	0.43012	1.78474	-1.01546	0.4439	1.68286	-0.98386	0.9952
C	1.86895	-2.43808	1.23637	1.90624	-2.41729	1.13329	2.05939	-2.32555	0.79227	2.90278	-0.18142	0.30591	2.76997	-0.10013	1.0356
O	5.47941	-2.48256	1.67781	5.51279	-2.51073	1.59736	5.69319	-2.39673	0.94231	5.64197	-2.47678	0.98758	5.54918	-2.35866	1.67781
C	0.22564	-0.62507	0.88523	0.28838	-0.58032	0.7889	0.41584	-0.54562	0.29652	0.41012	-0.5163	0.29162	0.30198	-0.52312	0.78728
C	-0.13941	0.34008	0.02631	-0.05899	0.38509	-0.07702	0.00095	0.33506	-0.62867	0.04153	0.37844	-0.63975	-0.03979	0.43674	-0.0871
C	-1.48267	0.8066	-0.20181	-1.39452	0.87058	-0.31237	-1.35113	0.80128	-0.78614	-1.28975	0.89502	-0.81791	-1.37485	0.91513	-0.33931
C	-1.84055	1.76694	-1.05397	-1.73478	1.82706	-1.17729	-2.50042	0.24654	-0.40161	-2.46302	0.39842	-0.42614	-1.70753	1.88118	-1.19648
C	-3.30288	1.99365	-1.04107	-3.18967	2.07964	-1.16432	-3.65857	1.06077	-0.82681	-3.58432	1.2495	-0.87708	-3.16447	2.12155	-1.20645
O	-3.78342	1.06122	-0.0725	-3.68861	1.16862	-0.17861	-3.07095	2.15673	-1.5405	-2.94863	2.30215	-1.61388	-3.67372	1.19045	-0.24491
C	-2.73847	0.33901	0.42763	-2.65643	0.43289	0.32803	-1.71432	2.02737	-1.5293	-1.59849	2.11726	-1.59187	-2.64474	0.45515	0.26877
O	-2.85633	-0.54725	1.2545	-2.78832	-0.43934	1.16695	-0.93367	2.80525	-2.04782	-0.78452	2.84976	-2.12483	-2.78495	-0.43446	1.08801
C	-3.97024	1.72222	-2.39282	-3.87842	1.78484	-2.4997	-4.48118	1.61707	0.33865	-4.38805	1.86769	0.27023	-3.82589	1.84244	-2.55892
O	-3.59342	2.70786	-3.34983	-5.27013	2.0923	-2.41642	-5.60031	2.35442	-0.1535	-5.47492	2.63647	-0.24553	-5.22209	2.13407	-2.49604
H	3.36427	-3.96016	1.56017	3.3807	-3.96071	1.45177	3.55742	-3.81746	1.22959	5.05518	-0.0377	0.37689	4.90337	0.11021	1.2907
H	4.80634	0.08898	1.37392	4.87387	0.07172	1.31441	5.03172	0.11276	0.28932	3.39875	-3.913	1.23878	3.35674	-3.89212	1.60127
H	2.51639	0.90028	1.03587	2.59598	0.91471	0.96951	2.73596	0.92197	0.01299	1.13236	-3.02586	0.9188	1.08289	-3.05386	1.20403
H	1.05431	-3.15856	1.20807	1.08305	-3.12742	1.09303	1.23836	-3.0229	0.94101	2.78676	0.87272	0.06551	2.62415	0.96899	0.90597
H	6.1036	-1.73905	1.69852	6.14626	-1.77563	1.632	6.32796	-1.6812	0.77371	5.61116	-3.42245	1.20588	5.53891	-3.32058	1.81157
H	-0.5091	-1.15533	1.4876	-0.45498	-1.09694	1.39262	-0.28289	-0.98887	1.00148	-0.31372	-0.93265	0.98727	-0.44793	-1.03703	1.38511
H	0.62549	0.82517	-0.57815	0.71671	0.85296	-0.68134	0.71234	0.76202	-1.33578	0.77943	0.77734	-1.33636	0.74021	0.90732	-0.68372
H	-1.17007	2.32936	-1.68881	-1.04611	2.36785	-1.81119	-2.5982	-0.68693	0.13341	-2.60257	-0.51599	0.13183	-1.01175	2.43775	-1.80868
H	-3.52338	3.01147	-0.70035	-3.41808	3.09625	-0.82657	-4.29894	0.51285	-1.52646	-4.24397	0.71161	-1.56654	-3.40794	3.13061	-0.8568
H	-5.06002	1.74321	-2.28127	-3.79244	0.72736	-2.7729	-3.8893	2.29714	0.96111	-3.7716	2.53901	0.87819	-3.72393	0.79062	-2.84801
H	-3.70097	0.7317	-2.77765	-3.45053	2.39019	-3.30496	-4.86492	0.80953	0.97	-4.8063	1.09242	0.91984	-3.38979	2.46549	-3.34607
H	-4.06483	2.49592	-4.17499	-5.62487	1.58109	-1.66408	-5.24395	3.03632	-0.75438	-5.0889	3.28981	-0.85974	-5.58425	1.6097	-1.75643

nuclei	Z-Matrix of **13-1**			Z-Matrix of **13-2**			Z-Matrix of **13-3**			Z-Matrix of **13-4**			Z-Matrix of **13-5**		
C	-4.01854	-0.76299	1.07384	-3.84377	0.70785	-0.76632	-4.05803	-0.51241	1.03557	-3.55081	-1.15509	-0.94617	-1.72876	-2.72326	2.5245
C	-4.5907	0.12258	0.16937	-4.59049	0.00997	0.17413	-4.49538	0.43745	0.12107	-3.99908	-2.09794	-0.03	-3.07681	-2.49064	2.28594
C	-3.82614	0.70838	-0.83331	-3.99312	-0.94364	0.99073	-3.64528	0.91533	-0.87014	-3.11224	-2.72067	0.84118	-3.47988	-1.58925	1.30751
C	-2.46458	0.40446	-0.92524	-2.62356	-1.19576	0.86414	-2.33395	0.4357	-0.94035	-1.75524	-2.38693	0.7945	-2.51405	-0.9077	0.56004
C	-1.86557	-0.47492	-0.01181	-1.84903	-0.48932	-0.06683	-1.87003	-0.51223	-0.01716	-1.28576	-1.42545	-0.11124	-1.14734	-1.11619	0.79591
C	-2.65847	-1.06709	0.97959	-2.47564	0.45477	-0.89151	-2.74825	-0.99217	0.96272	-2.19467	-0.8229	-0.99139	-0.76539	-2.04114	1.77741
O	-5.92132	0.38917	0.29656	-5.92188	0.28816	0.26186	-5.78159	0.87633	0.22681	-5.32995	-2.39236	-0.02054	-3.98286	-3.17713	3.03775
C	-0.44523	-0.83597	-0.09934	-0.41879	-0.80161	-0.18607	-0.50828	-1.05569	-0.08248	0.15053	-1.12177	-0.14536	-0.10056	-0.44502	0.00899
C	0.53107	0.05342	-0.34378	0.53138	0.12637	-0.38696	0.58191	-0.29733	-0.28245	0.64593	0.11699	-0.30029	-0.18165	0.8299	-0.40867
C	1.98959	-0.31842	-0.44755	1.99896	-0.19888	-0.51786	1.9833	-0.85956	-0.35414	2.12623	0.42203	-0.33366	0.84181	1.60326	-1.21288
C	2.83449	0.32042	0.63137	2.83473	0.4223	0.57849	2.91188	-0.32022	0.71357	2.57392	1.38361	0.74729	2.19965	0.96845	-1.42757
C	4.12018	0.50818	-0.09847	4.10907	0.6721	-0.15239	3.70664	0.68789	-0.03489	2.69821	2.66381	0.00303	3.06577	2.17881	-1.50701
O	3.93994	0.59594	-1.47542	3.91532	0.80721	-1.52365	3.6425	0.51372	-1.41076	2.77813	2.48434	-1.37132	2.52039	3.2641	-0.83052
C	2.63936	0.22347	-1.70375	2.62365	0.40745	-1.75726	2.65019	-0.40568	-1.63461	2.46749	1.16934	-1.60462	1.22627	2.91074	-0.5459
O	2.10971	0.28735	-2.80578	2.08498	0.49579	-2.85304	2.31957	-0.76308	-2.75928	2.42562	0.6879	-2.73077	0.47122	3.61789	0.11003
C	5.34802	0.54301	0.43133	5.33978	0.71989	0.36966	4.38288	1.7125	0.49623	2.67991	3.89104	0.53481	4.21864	2.3015	-2.17445
O	2.99157	-0.53626	1.75288	3.02305	-0.47082	1.66641	3.77313	-1.35606	1.17817	3.85123	0.9957	1.24604	2.2502	0.21736	-2.63206
H	-4.62914	-1.21864	1.84814	-4.3244	1.44163	-1.40717	-4.73429	-0.88182	1.8011	-4.25163	-0.6846	-1.62987	-1.42691	-3.43241	3.29005
H	-4.26601	1.39244	-1.55195	-4.56978	-1.49861	1.72367	-3.98072	1.64891	-1.59609	-3.45182	-3.46288	1.5563	-4.53093	-1.40654	1.10795
H	-1.87961	0.85026	-1.72696	-2.1654	-1.9456	1.50507	-1.68234	0.79832	-1.73226	-1.06726	-2.87959	1.47801	-2.84438	-0.21887	-0.21363
H	-2.22571	-1.76517	1.69204	-1.91144	0.99306	-1.64963	-2.41953	-1.73789	1.68265	-1.85675	-0.10059	-1.73056	0.28565	-2.23377	1.97947
H	-6.18254	1.00566	-0.40705	-6.31459	-0.28078	0.94376	-5.9496	1.5163	-0.48412	-5.49216	-3.074	0.65175	-4.87633	-2.89777	2.77907
H	-0.2152	-1.88758	0.05979	-0.15618	-1.85317	-0.08913	-0.42011	-2.13095	0.0598	0.81723	-1.97247	-0.01851	0.76994	-1.06037	-0.20099
H	0.28565	1.10455	-0.49187	0.25717	1.17707	-0.47565	0.47941	0.78024	-0.40421	-0.03038	0.96373	-0.41012	-1.06715	1.41418	-0.15105
H	2.11146	-1.40987	-0.45236	2.15173	-1.28548	-0.56458	1.97643	-1.95646	-0.34647	2.72578	-0.49627	-0.30979	0.37912	1.85492	-2.17726
H	2.4487	1.29064	0.96661	2.42565	1.36864	0.95221	2.38305	0.10104	1.57506	1.87789	1.44179	1.59076	2.53087	0.34327	-0.5912
H	6.22561	0.66115	-0.19551	6.20869	0.88555	-0.25853	4.91737	2.41182	-0.14038	2.75472	4.76972	-0.09952	4.76227	3.24033	-2.1857
H	5.49867	0.44395	1.50191	5.50176	0.5846	1.43459	4.41966	1.87976	1.56754	2.58878	4.05003	1.60411	4.63583	1.46678	-2.72929
H	2.11463	-0.62754	2.16552	2.15214	-0.59874	2.08188	4.49947	-0.93375	1.66953	4.21616	1.75346	1.73597	1.56538	-0.47144	-2.57643

nuclei	Z-Matrix of **13-6**			Z-Matrix of **13-7**			Z-Matrix of **13-8**			Z-Matrix of **13-9**			Z-Matrix of **13-10**		
C	-3.95691	-0.56133	-0.67538	-3.8736	0.50216	-0.98741	-1.7393	-2.84135	2.44417	-2.86953	-2.43542	0.9577	-1.78686	-2.78566	2.44117
C	-4.26326	-1.63381	0.15219	-4.63445	-0.03018	0.04563	-3.08437	-2.51242	2.34126	-3.99165	-1.87357	0.36281	-3.13123	-2.46094	2.31658
C	-3.26687	-2.28396	0.87131	-4.04769	-0.8233	1.02552	-3.50845	-1.52408	1.46051	-3.87822	-0.75309	-0.45229	-3.54617	-1.48615	1.41657
C	-1.94312	-1.84756	0.75969	-2.67468	-1.08125	0.96915	-2.56643	-0.85218	0.67469	-2.61877	-0.18557	-0.66977	-2.59562	-0.82376	0.63321
C	-1.61532	-0.75689	-0.05837	-1.88683	-0.53949	-0.05589	-1.20125	-1.15711	0.77489	-1.47537	-0.72846	-0.06599	-1.23137	-1.12479	0.75501
C	-2.63411	-0.12549	-0.78465	-2.5019	0.24354	-1.04201	-0.80009	-2.16884	1.65846	-1.61228	-1.86699	0.73962	-0.83898	-2.12272	1.65776
O	-5.56659	-2.02495	0.22899	-5.96906	0.24692	0.0603	-3.96729	-3.19272	3.12578	-5.1986	-2.45984	0.60218	-4.02261	-3.13185	3.09963
C	-0.20615	-0.35152	-0.17238	-0.45353	-0.85511	-0.09441	-0.18039	-0.4968	-0.05329	-0.13055	-0.17969	-0.29755	-0.20363	-0.47347	-0.07126
C	0.19312	0.93073	-0.22342	0.49681	0.04025	-0.40917	-0.2257	0.79428	-0.42449	0.1334	1.13612	-0.36507	-0.23823	0.81955	-0.4365
C	1.60921	1.45302	-0.33796	1.96939	-0.29216	-0.45528	0.80556	1.51566	-1.26538	1.47689	1.80219	-0.58606	0.79387	1.54156	-1.27854
C	2.74266	0.45522	-0.22682	2.77528	0.4334	0.60134	2.20521	0.93211	-1.30558	2.69577	0.94824	-0.87309	2.18615	0.94342	-1.33932
C	3.81089	1.31074	0.36344	4.04437	0.70592	-0.13191	3.03252	2.16299	-1.45706	3.32551	0.84837	0.46828	3.02043	2.16923	-1.49653
O	3.29198	2.37813	1.08769	3.87459	0.68579	-1.51286	2.37763	3.30048	-1.00128	2.94081	1.87809	1.31598	2.39263	3.2978	-0.98059
C	1.95691	2.42257	0.7761	2.61331	0.19573	-1.73528	1.08405	2.91703	-0.75254	1.88314	2.49607	0.69818	1.09399	2.92781	-0.73925
O	1.17652	3.20824	1.29932	2.11297	0.13523	-2.85128	0.25398	3.66734	-0.25455	1.30636	3.46662	1.1763	0.28034	3.6754	-0.21023
C	5.13254	1.16607	0.21546	5.25862	0.90959	0.39237	4.25568	2.24809	-1.99243	4.13268	-0.1294	0.89392	4.21418	2.27762	-2.09143
O	3.12927	-0.05437	-1.49488	2.99192	-0.40181	1.73024	2.37612	0.036	-2.39619	3.57603	1.64357	-1.75522	2.31697	0.06476	-2.4466
H	-4.7439	-0.06603	-1.23704	-4.34551	1.11067	-1.75349	-1.42063	-3.61883	3.13246	-2.97147	-3.31257	1.59023	-1.47592	-3.55241	3.14484
H	-3.49606	-3.12492	1.51789	-4.63451	-1.24824	1.83334	-4.5582	-1.26577	1.3656	-4.74781	-0.3116	-0.9284	-4.59508	-1.2312	1.30461
H	-1.1709	-2.36172	1.32757	-2.22218	-1.70325	1.73833	-2.91506	-0.09516	-0.02335	-2.54084	0.67984	-1.32352	-2.93585	-0.0772	-0.08038
H	-2.41216	0.7059	-1.44891	-1.92414	0.64859	-1.86956	0.24936	-2.43885	1.75078	-0.74397	-2.31717	1.21483	0.20954	-2.3888	1.76748
H	-5.63355	-2.76306	0.85649	-6.36977	-0.19912	0.82406	-4.85994	-2.85018	2.95566	-5.88676	-1.95089	0.14325	-4.91363	-2.79322	2.91346
H	0.50147	-1.17534	-0.19641	-0.18498	-1.87509	0.17301	0.64727	-1.13512	-0.35727	0.65484	-0.92503	-0.38318	0.61417	-1.11989	-0.38115
H	-0.56101	1.71889	-0.17074	0.21969	1.06405	-0.65607	-1.06831	1.41032	-0.10865	-0.68405	1.84666	-0.22965	-1.07598	1.44041	-0.11661
H	1.67837	2.00709	-1.2844	2.12535	-1.37754	-0.39702	0.39492	1.62125	-2.27877	1.36453	2.56557	-1.36597	0.37524	1.67007	-2.28594
H	2.53195	-0.37691	0.45371	2.30246	1.3688	0.92357	2.47867	0.41989	-0.37631	2.46848	-0.01936	-1.32747	2.46271	0.41894	-0.41724
H	5.82703	1.86315	0.67244	6.11682	1.07763	-0.25191	4.76841	3.20251	-2.06355	4.5239	-0.12078	1.90731	4.71069	3.24141	-2.1594
H	5.54411	0.35211	-0.37338	5.433	0.90695	1.46213	4.77768	1.36722	-2.35392	4.42031	-0.95465	0.25122	4.72222	1.42618	-2.52903
H	2.3439	-0.46398	-1.89754	3.38824	0.15132	2.42453	2.38836	0.55425	-3.21961	4.4472	1.21271	-1.69859	3.19801	-0.34209	-2.39031

nuclei	Z-Matrix of **13-11**			Z-Matrix of **13-12**			Z-Matrix of **13-13**			Z-Matrix of **13-14**			Z-Matrix of **13-15**		
C	-4.06325	-0.77979	1.09028	-3.87029	-0.82292	-0.5159	-4.04518	-0.5177	-0.48704	-3.67074	-1.44234	-0.83654	-4.05021	-0.47119	-0.52813
C	-4.64017	0.1044	0.18734	-3.9775	-1.90311	0.35066	-4.29895	-1.65816	0.26363	-3.95583	-2.42227	0.10585	-4.317	-1.59241	0.24667
C	-3.88014	0.69169	-0.8182	-2.8566	-2.4074	1.00061	-3.25739	-2.37325	0.84331	-2.95969	-2.91933	0.93917	-3.28444	-2.30099	0.8503
C	-2.51856	0.38985	-0.9152	-1.60959	-1.8151	0.77896	-1.94166	-1.93282	0.66933	-1.65824	-2.421	0.82684	-1.96443	-1.87365	0.6759
C	-1.91563	-0.48934	-0.00435	-1.48323	-0.71437	-0.08005	-1.66438	-0.7745	-0.07135	-1.35452	-1.42079	-0.10679	-1.67463	-0.73459	-0.08913
C	-2.70305	-1.08151	0.99108	-2.62401	-0.23113	-0.73493	-2.72973	-0.07895	-0.65911	-2.37015	-0.94491	-0.94688	-2.73071	-0.0453	-0.7004
O	-5.97089	0.36921	0.31907	-5.21262	-2.4491	0.53567	-5.5966	-2.0504	0.40547	-5.23802	-2.87914	0.17986	-5.61829	-1.97256	0.38812
C	-0.49589	-0.84876	-0.09978	-0.1501	-0.13935	-0.31004	-0.26222	-0.36853	-0.25121	0.0286	-0.94089	-0.21321	-0.26976	-0.33972	-0.26992
C	0.48021	0.04873	-0.31274	0.08055	1.18289	-0.37266	0.15155	0.90913	-0.30621	0.35255	0.35516	-0.35131	0.1501	0.93621	-0.31548
C	1.93965	-0.31805	-0.42618	1.40641	1.88258	-0.59406	1.57976	1.37703	-0.4839	1.77266	0.85172	-0.47022	1.57845	1.40724	-0.49694
C	2.79254	0.25613	0.68619	2.6324	1.06075	-0.93884	2.68419	0.40391	-0.11738	2.20054	1.72869	0.68851	2.68568	0.42414	-0.16914
C	4.03966	0.6192	-0.04594	3.29407	0.92291	0.38372	3.75048	1.33451	0.35093	3.02538	2.76149	-0.00123	3.75939	1.34602	0.30076
O	3.84849	0.72103	-1.41888	2.90895	1.9119	1.27848	3.23811	2.55358	0.77749	2.77855	2.82465	-1.36752	3.24257	2.53641	0.80069
C	2.57039	0.28854	-1.66216	1.82769	2.53426	0.70714	1.91475	2.55408	0.41448	1.94223	1.77738	-1.65669	1.9197	2.55328	0.43738
O	2.04988	0.34659	-2.76888	1.24514	3.47491	1.23514	1.14334	3.45409	0.72188	1.45401	1.60561	-2.7662	1.14883	3.43827	0.78808
C	5.25168	0.80721	0.48866	4.12976	-0.05358	0.75368	5.06921	1.10901	0.35596	3.94578	3.55273	0.56178	5.0834	1.16075	0.24267
O	3.04147	-0.70743	1.70369	3.48122	1.80206	-1.81409	3.10361	-0.3715	-1.23275	2.96325	0.99694	1.64212	3.07745	-0.30821	-1.32025
H	-4.66919	-1.2349	1.8684	-4.75259	-0.44265	-1.02279	-4.86688	0.02789	-0.94208	-4.4553	-1.06953	-1.48872	-4.86474	0.06948	-1.00159
H	-4.32338	1.37572	-1.53463	-2.93007	-3.25282	1.67701	-3.44438	-3.26844	1.42746	-3.17171	-3.68791	1.67529	-3.48227	-3.18096	1.45364
H	-1.9353	0.83739	-1.71707	-0.73815	-2.21431	1.29302	-1.13311	-2.49961	1.12579	-0.88378	-2.81349	1.48208	-1.16321	-2.43452	1.15158
H	-2.26347	-1.77529	1.70378	-2.55562	0.60388	-1.42775	-2.55112	0.80525	-1.26546	-2.15772	-0.19268	-1.70304	-2.54042	0.82378	-1.32515
H	-6.23237	0.99273	-0.37807	-5.1391	-3.17312	1.1786	-5.62046	-2.84886	0.95757	-5.28607	-3.55636	0.87408	-5.65227	-2.75662	0.95985
H	-0.26491	-1.90322	0.03437	0.65152	-0.8667	-0.39797	0.44674	-1.18956	-0.33876	0.80077	-1.70446	-0.15185	0.43115	-1.16479	-0.37024
H	0.23271	1.10403	-0.42058	-0.75528	1.87133	-0.23339	-0.58341	1.71055	-0.21987	-0.43249	1.10955	-0.38855	-0.58205	1.73947	-0.22025
H	2.0618	-1.40721	-0.49327	1.26498	2.67211	-1.34255	1.6901	1.72341	-1.52054	2.4672	0.01193	-0.60468	1.67883	1.78541	-1.52339
H	2.34561	1.14532	1.14507	2.40946	0.1064	-1.42285	2.40275	-0.26954	0.69993	1.35186	2.19603	1.20065	2.41225	-0.2699	0.63416
H	6.10378	1.06056	-0.13472	4.54426	-0.07491	1.75756	5.76305	1.8648	0.71126	4.50339	4.2706	-0.03206	5.76341	1.92791	0.602
H	5.4158	0.72749	1.55919	4.41914	-0.84742	0.07332	5.48259	0.16181	0.02285	4.15081	3.51195	1.6274	5.52462	0.25882	-0.16517
H	3.70253	-1.3403	1.37351	4.35921	1.38202	-1.7957	3.57525	0.21277	-1.85166	3.85669	0.86065	1.28185	3.73859	-0.9618	-1.03662

nuclei	Z-Matrix of **14-1**			Z-Matrix of **14-2**			Z-Matrix of **14-3**			Z-Matrix of **14-4**			Z-Matrix of **14-5**		
C	-3.32192	0.04034	1.59938	-3.28906	-1.94178	0.19395	-3.29994	-2.08482	0.29694	-2.21985	-1.59017	-1.16306	-3.33708	-0.21357	1.99864
C	-3.90431	-1.1811	1.28564	-3.91022	-1.3469	1.28469	-3.91471	-1.24647	1.21758	-3.06807	-0.82503	-0.37268	-3.88234	-1.33663	1.38925
C	-3.37483	-1.98595	0.28332	-3.39528	-0.18656	1.85244	-3.41344	0.02668	1.46704	-2.73967	0.48305	-0.03381	-3.3024	-1.88027	0.24844
C	-2.24262	-1.55783	-0.41392	-2.24	0.3874	1.3158	-2.27616	0.46481	0.78282	-1.54091	1.03212	-0.49499	-2.15862	-1.28575	-0.28949
C	-1.63944	-0.32405	-0.11869	-1.59974	-0.19357	0.20958	-1.63941	-0.36501	-0.15473	-0.66837	0.27609	-1.2941	-1.59454	-0.14514	0.30677
C	-2.19196	0.46898	0.90025	-2.13468	-1.36925	-0.34169	-2.16547	-1.64612	-0.3875	-1.02178	-1.04247	-1.62291	-2.19415	0.38086	1.46113
O	-5.00755	-1.55944	1.99203	-5.03475	-1.94022	1.77657	-5.02109	-1.71345	1.86345	-4.22705	-1.4005	0.05646	-4.99863	-1.88379	1.94875
C	-0.38922	0.13759	-0.84309	-0.33856	0.43364	-0.35098	-0.38543	0.10884	-0.86381	0.63985	0.87706	-1.76866	-0.34575	0.50151	-0.25903
C	0.86932	-0.48701	-0.20488	0.91463	-0.36081	0.05159	0.87106	-0.52976	-0.23514	1.8819	0.25182	-1.1077	0.91264	-0.31948	0.06685
C	2.10372	0.32562	-0.39702	2.17355	0.36429	-0.26655	2.1086	0.28158	-0.41222	1.89277	0.29936	0.37789	2.16764	0.40057	-0.27758
C	2.98899	0.76658	0.49072	3.14203	0.09554	-1.1348	2.99814	0.69787	0.48316	1.99097	-0.67997	1.27038	3.09885	0.14595	-1.18984
C	4.00025	1.49383	-0.18937	4.13516	1.10462	-1.03811	4.01123	1.43574	-0.18256	1.9425	-0.12028	2.57311	4.10769	1.14018	-1.1029
O	3.74817	1.51926	-1.55152	3.78916	2.03774	-0.07285	3.75569	1.4941	-1.54302	1.80924	1.25731	2.50567	3.81057	2.04896	-0.09904
C	2.58367	0.81408	-1.69592	2.5859	1.59808	0.41449	2.58775	0.79742	-1.70084	1.77047	1.53408	1.16366	2.6213	1.6094	0.42175
O	1.9964	0.62503	-2.75035	1.93861	2.14441	1.29409	1.99718	0.63579	-2.75791	1.64001	2.6474	0.68063	2.01539	2.13774	1.34071
C	5.06237	2.08708	0.35731	5.25967	1.18933	-1.7505	5.0779	2.01065	0.37477	2.00928	-0.78148	3.72957	5.20524	1.2324	-1.85528
O	-0.49582	-0.24378	-2.21556	-0.42775	0.48785	-1.77857	-0.4943	-0.24776	-2.24203	0.74644	0.69833	-3.1857	-0.48015	0.62124	-1.67927
H	-3.74864	0.65891	2.38365	-3.70083	-2.84995	-0.23711	-3.70427	-3.07451	0.10574	-2.4905	-2.61019	-1.42083	-3.79867	0.19765	2.89213
H	-3.82368	-2.94029	0.02807	-3.8722	0.28203	2.70755	-3.88972	0.68793	2.18365	-3.39603	1.08708	0.58477	-3.72029	-2.75904	-0.23218
H	-1.83296	-2.18599	-1.20321	-1.83885	1.29198	1.77057	-1.89202	1.46237	0.98381	-1.28777	2.05545	-0.22032	-1.70515	-1.71535	-1.18125
H	-1.74871	1.42863	1.15554	-1.6529	-1.84513	-1.19384	-1.69591	-2.30347	-1.1169	-0.36387	-1.64882	-2.24267	-1.77394	1.25624	1.95349
H	-5.32521	-2.40441	1.63375	-5.35174	-1.42234	2.53454	-5.36752	-1.00726	2.4324	-4.71651	-0.75147	0.58797	-5.26141	-2.65733	1.4239
H	-0.34895	1.23369	-0.81547	-0.27254	1.47226	-0.00745	-0.33986	1.20393	-0.81579	0.63299	1.96019	-1.60342	-0.26071	1.52227	0.13078
H	1.04259	-1.48633	-0.62441	0.92106	-1.33025	-0.46393	1.04239	-1.52251	-0.67075	2.77609	0.76199	-1.48941	0.88665	-1.27108	-0.48037
H	0.717	-0.61703	0.87487	0.89875	-0.57606	1.12766	0.71597	-0.67606	0.84219	1.98924	-0.78827	-1.44492	0.93563	-0.57091	1.13489
H	2.95972	0.59802	1.55673	3.17183	-0.7449	-1.81106	2.97102	0.50435	1.54496	2.08616	-1.7324	1.05066	3.09236	-0.67473	-1.89047
H	5.77628	2.61899	-0.26388	5.95113	2.01061	-1.59173	5.79297	2.55297	-0.236	1.96083	-0.24697	4.67288	5.9125	2.04078	-1.69976
H	5.24917	2.05961	1.42536	5.51733	0.45267	-2.50354	5.26773	1.95704	1.44128	2.11154	-1.86054	3.7675	5.42488	0.51492	-2.63826
H	0.29817	0.09698	-2.67933	-1.33969	0.75527	-1.99083	0.30161	0.09515	-2.70061	-0.1399	0.85723	-3.55595	-1.37751	0.9624	-1.84276

nuclei	Z-Matrix of **14-6**			Z-Matrix of **14-7**			Z-Matrix of **14-8**			Z-Matrix of **14-9**		
C	-2.40222	0.82704	1.52201	-2.74057	0.48745	0.11169	-2.58885	1.22809	1.57318	-2.68965	-0.17089	-0.48141
C	-3.15226	0.19528	0.53934	-3.09668	-0.79266	-0.29387	-3.25795	0.31084	0.77347	-3.29113	0.34039	0.66079
C	-2.70968	0.15641	-0.77747	-2.28668	-1.51627	-1.16203	-2.72416	-0.09393	-0.44433	-2.67186	1.33843	1.40486
C	-1.49343	0.75753	-1.11289	-1.10057	-0.94585	-1.62924	-1.49851	0.42861	-0.86456	-1.42813	1.8284	0.99715
C	-0.71267	1.39758	-0.13663	-0.72236	0.34816	-1.23347	-0.8019	1.35773	-0.07418	-0.7998	1.32706	-0.15596
C	-1.18786	1.42814	1.18607	-1.55643	1.05862	-0.35673	-1.36521	1.75148	1.15139	-1.44887	0.32136	-0.8898
O	-4.33153	-0.3793	0.91037	-4.2624	-1.31	0.18775	-4.45016	-0.17419	1.22311	-4.5031	-0.16796	1.0235
C	0.62765	2.03001	-0.46623	0.57188	0.96899	-1.72021	0.54886	1.90933	-0.49548	0.56924	1.84657	-0.55717
C	1.84092	1.294	0.14951	1.83011	0.31527	-1.12094	1.7158	1.23412	0.25751	1.70433	1.17442	0.24521
C	1.86523	-0.18421	-0.03969	1.89724	0.33725	0.36359	1.9015	-0.20522	-0.0685	1.90524	-0.26619	-0.06547
C	1.90999	-1.17077	0.8493	1.9926	-0.6579	1.23862	1.63606	-1.30993	0.61861	1.60998	-1.36908	0.61225
C	1.90859	-2.41128	0.15957	2.01575	-0.1153	2.54936	2.02386	-2.43268	-0.15922	2.03401	-2.49377	-0.14371
O	1.86416	-2.20691	-1.21024	1.93485	1.26737	2.50477	2.56634	-2.02562	-1.3692	2.63274	-2.08978	-1.32793
C	1.82874	-0.84579	-1.34846	1.85584	1.56467	1.16911	2.50435	-0.65893	-1.32683	2.56591	-0.72324	-1.29349
O	1.76524	-0.24086	-2.40858	1.75546	2.68876	0.70438	2.89605	0.1035	-2.19825	2.99649	0.03737	-2.14809
C	1.9424	-3.62803	0.70491	2.10032	-0.7948	3.69398	1.90508	-3.71723	0.17977	1.89875	-3.77751	0.19211
O	0.79669	2.23532	-1.8688	0.63511	0.84387	-3.14565	0.69366	1.83748	-1.91354	0.74664	1.7323	-1.96798
H	-2.76391	0.85547	2.54585	-3.38275	1.04047	0.79163	-3.02079	1.53839	2.52032	-3.18523	-0.94645	-1.0582
H	-3.29027	-0.33036	-1.55464	-2.55807	-2.51644	-1.48433	-3.23986	-0.80739	-1.07888	-3.13669	1.74485	2.29732
H	-1.16203	0.72398	-2.14925	-0.46854	-1.51358	-2.31015	-1.08787	0.11012	-1.82132	-0.95148	2.60983	1.58521
H	-0.61622	1.92505	1.96671	-1.28822	2.06133	-0.02733	-0.85582	2.47253	1.78671	-0.99122	-0.08158	-1.79145
H	-4.75596	-0.74746	0.118	-4.38785	-2.19624	-0.18871	-4.82036	-0.75793	0.54073	-4.8244	0.32048	1.79854
H	0.6114	3.04375	-0.04589	0.57112	2.04485	-1.51256	0.56271	2.97948	-0.25409	0.59554	2.9227	-0.34519
H	1.86506	1.50388	1.22702	2.71595	0.82104	-1.52723	1.57653	1.34945	1.3399	1.52288	1.29698	1.32059
H	2.76398	1.7111	-0.27235	1.91061	-0.71977	-1.48029	2.64642	1.76139	0.01062	2.64386	1.70057	0.03164
H	1.93704	-1.06039	1.92258	2.03942	-1.70978	1.00204	1.18708	-1.35722	1.59901	1.11576	-1.41453	1.5706
H	1.93563	-4.51317	0.07676	2.10813	-0.27162	4.6449	2.23645	-4.49818	-0.49721	2.26033	-4.56004	-0.46738
H	1.97427	-3.77444	1.77905	2.16098	-1.87734	3.71495	1.47749	-4.02214	1.12873	1.42545	-4.08041	1.11973
H	1.14104	1.40844	-2.26592	-0.24427	1.08946	-3.48403	1.6332	1.68804	-2.13748	1.6944	1.59972	-2.16629

nuclei	Z-Matrix of **15-1**			Z-Matrix of **15-2**			Z-Matrix of **15-3**			Z-Matrix of **15-4**			Z-Matrix of **15-5**		
C	1.47955	0.87237	3.73298	-0.60667	-1.67805	3.25123	-1.165	1.31828	3.19215	1.77219	-3.29814	1.9578	-0.20813	-2.62444	2.90169
C	0.39239	1.68494	4.02833	0.28283	-2.73333	3.40789	-0.22857	1.07904	4.18966	1.01719	-3.16832	3.11654	0.84311	-3.5214	2.76105
C	-0.74201	1.67546	3.22432	1.01237	-3.21488	2.32675	0.97252	0.44223	3.89917	-0.07214	-2.30544	3.16293	1.6004	-3.55242	1.59542
C	-0.78296	0.84077	2.1033	0.84908	-2.62376	1.07028	1.23825	0.04378	2.5856	-0.40502	-1.5574	2.02957	1.29982	-2.6653	0.55739
C	0.3105	0.02444	1.78041	-0.03119	-1.54687	0.89504	0.31323	0.29045	1.56109	0.35437	-1.66354	0.85545	0.25369	-1.74117	0.68669
C	1.43645	0.03799	2.61365	-0.76836	-1.08836	1.99516	-0.89755	0.92002	1.87999	1.43748	-2.55127	0.82592	-0.50691	-1.7385	1.86376
O	0.4759	2.48203	5.13087	0.40895	-3.2789	4.65059	-0.53096	1.48415	5.45545	1.37765	-3.91712	4.19696	1.09938	-4.36771	3.79833
C	0.28921	-0.88535	0.62821	-0.19248	-0.9724	-0.44693	0.62221	-0.17303	0.20068	0.0136	-0.91505	-0.36072	-0.04666	-0.845	-0.4372
C	-0.1848	-0.54145	-0.58217	-0.30657	0.34613	-0.68494	0.31956	0.52161	-0.90994	-0.34405	0.38112	-0.35895	-0.37316	0.45101	-0.28907
C	-0.22982	-1.43214	-1.80756	-0.46841	0.99592	-2.0445	0.61108	0.13133	-2.34066	-0.71089	1.20471	-1.57333	-0.69408	1.42125	-1.40417
C	0.63001	-0.92907	-2.94795	0.68188	1.90874	-2.41414	-0.64366	-0.02144	-3.17759	0.33441	2.25337	-1.8962	0.37845	2.47855	-1.57362
C	-0.36003	-0.17386	-3.76284	0.16291	3.23645	-1.9869	-0.82533	-1.49789	-3.17708	-0.50352	3.44847	-2.18449	-0.4281	3.7194	-1.72524
O	-1.67776	-0.53759	-3.50568	-1.22171	3.27135	-1.85807	0.34489	-2.19529	-2.89959	-1.80348	3.34585	-1.70508	-1.74232	3.58587	-1.29504
C	-1.63265	-1.37727	-2.42346	-1.64619	1.97648	-2.00433	1.26002	-1.25032	-2.51652	-1.96593	2.04648	-1.30495	-1.94134	2.25028	-1.06877
O	-2.6068	-1.98111	-1.9869	-2.82597	1.64698	-2.06454	2.44385	-1.49367	-2.30552	-3.01297	1.61232	-0.83634	-3.01131	1.78346	-0.69267
C	-0.072	0.79495	-4.63707	0.90749	4.30873	-1.7012	-1.97941	-2.14181	-3.37543	-0.10491	4.53033	-2.86062	0.00988	4.87009	-2.24541
O	0.13406	-2.765	-1.46461	-0.65433	0.00348	-3.04835	1.43187	1.16466	-2.87851	-0.92537	0.35598	-2.7006	-0.89326	0.71733	-2.62999
H	2.35765	0.88516	4.37227	-1.17884	-1.31842	4.10172	-2.1035	1.80865	3.43444	2.61742	-3.97997	1.93313	-0.79923	-2.61775	3.81307
H	-1.60049	2.29878	3.4529	1.70566	-4.04234	2.43775	1.70871	0.2462	4.67206	-0.67458	-2.20502	4.06003	2.42004	-4.2532	1.47391
H	-1.68305	0.82528	1.4932	1.42256	-3.00652	0.22874	2.18052	-0.45458	2.36694	-1.27164	-0.90125	2.06942	1.89597	-2.6962	-0.35207
H	2.29375	-0.59453	2.39502	-1.4849	-0.27804	1.88653	-1.65057	1.09883	1.11704	2.03579	-2.66414	-0.07521	-1.3469	-1.05821	1.98214
H	-0.35319	2.98036	5.21692	1.05215	-4.00514	4.60694	0.21056	1.25577	6.03957	0.76017	-3.731	4.9231	1.84849	-4.93664	3.55719
H	0.71848	-1.87057	0.79931	-0.18334	-1.68639	-1.26802	1.14812	-1.12443	0.14873	0.09716	-1.46934	-1.29344	0.04047	-1.28687	-1.42776
H	-0.56676	0.46879	-0.72968	-0.26993	1.0378	0.15684	-0.16984	1.49006	-0.8096	-0.3761	0.91848	0.58882	-0.41223	0.87431	0.71467
H	1.04461	-1.75834	-3.53325	0.86401	1.90617	-3.49534	-0.48818	0.338	-4.20183	0.95509	1.97469	-2.75461	1.01133	2.29543	-2.44868
H	1.46139	-0.3006	-2.61031	1.61722	1.64211	-1.90995	-1.50836	0.50595	-2.75998	0.98456	2.47314	-1.04102	1.01511	2.57478	-0.68607
H	-0.86032	1.30595	-5.18175	0.44555	5.23807	-1.38146	-2.02403	-3.22632	-3.34269	-0.78596	5.35684	-3.03973	-0.64987	5.72813	-2.33231
H	0.95179	1.09604	-4.83467	1.98935	4.28803	-1.78437	-2.90151	-1.60693	-3.57826	0.90354	4.61574	-3.25209	1.03012	4.98241	-2.59748
H	-0.62308	-3.12642	-0.9638	-1.56311	-0.33302	-2.92242	2.31108	1.04672	-2.46938	-1.70404	-0.1905	-2.48231	-1.69273	0.17251	-2.49976

nuclei	Z-Matrix of **15-6**			Z-Matrix of **15-7**			Z-Matrix of **15-8**			Z-Matrix of **15-9**			Z-Matrix of **15-10**		
C	2.66725	2.2431	2.09186	0.91053	1.50968	3.36033	-0.51709	-2.36329	3.00649	0.676	3.46829	1.52915	2.24954	-1.3016	3.33696
C	1.75748	3.2829	2.23233	-0.17495	2.33929	3.61109	0.5965	-3.17754	2.84377	1.98797	3.55576	1.97669	1.46681	-0.60628	4.24932
C	0.48787	3.19705	1.67222	-1.2806	2.33847	2.76801	1.41734	-3.0459	1.72917	2.85207	2.47298	1.86117	0.37629	0.14392	3.82385
C	0.1282	2.05115	0.9557	-1.29413	1.49471	1.65318	1.11695	-2.07868	0.76532	2.39178	1.286	1.28328	0.07009	0.20062	2.46039
C	1.03786	0.99691	0.78916	-0.20155	0.66099	1.37501	0.00671	-1.23707	0.91976	1.0757	1.18227	0.81053	0.85736	-0.48171	1.52164
C	2.30614	1.09909	1.3763	0.89529	0.66695	2.24653	-0.81521	-1.39656	2.04338	0.21791	2.28154	0.9514	1.94193	-1.24424	1.97563
O	2.15061	4.38017	2.93885	-0.11859	3.14466	4.7093	0.85024	-4.10688	3.80805	2.39222	4.73217	2.53383	1.80162	-0.69016	5.56787
C	0.68744	-0.23688	0.07058	-0.196	-0.26009	0.23009	-0.29178	-0.25125	-0.12784	0.62868	-0.09574	0.23763	0.5514	-0.47373	0.08356
C	-0.0446	-0.26192	-1.05682	-0.62503	0.08359	-0.99678	-0.66163	1.01391	0.13669	-0.19526	-0.19262	-0.81985	0.12133	0.61096	-0.58353
C	-0.43549	-1.47685	-1.86657	-0.64899	-0.77675	-2.24118	-0.97768	2.11073	-0.8565	-0.69478	-1.45488	-1.4793	-0.20223	0.7133	-2.05417
C	-1.93678	-1.66937	-1.95255	-0.24407	-2.23346	-2.13831	-1.00218	1.77975	-2.33523	-2.19531	-1.60917	-1.31477	-1.67843	0.98406	-2.27827
C	-2.1638	-2.71314	-0.91728	1.20729	-2.15663	-2.45493	0.39703	2.09488	-2.72943	-2.34195	-3.06497	-1.04981	-1.9908	0.12022	-3.44747
O	-1.02401	-3.45356	-0.62488	1.54187	-1.0313	-3.20115	1.01154	3.00268	-1.8731	-1.15294	-3.69308	-0.70427	-1.02224	-0.83966	-3.70834
C	0.00608	-2.82332	-1.27227	0.41505	-0.25045	-3.21281	0.1555	3.14382	-0.81126	-0.15193	-2.79089	-0.94365	0.05361	-0.53212	-2.92021
O	1.14731	-3.26903	-1.33381	0.28471	0.75883	-3.89808	0.29567	3.97724	0.07801	1.03725	-3.0577	-0.8007	1.11144	-1.15247	-2.96058
C	-3.3126	-2.93472	-0.27148	2.14276	-3.02345	-2.05605	1.0588	1.56221	-3.76092	-3.48063	-3.75833	-1.14636	-3.07299	0.2307	-4.22422
O	0.10477	-1.27937	-3.17029	-1.9639	-0.68313	-2.78296	-2.23076	2.66976	-0.47209	-0.36525	-1.33784	-2.86658	0.5756	1.8031	-2.55829
H	3.65464	2.31995	2.53813	1.76646	1.51744	4.02911	-1.15514	-2.48219	3.87755	0.00865	4.31899	1.63373	3.09627	-1.88817	3.68187
H	-0.23304	4.00036	1.78484	-2.13737	2.97606	2.96082	2.2871	-3.68018	1.5916	3.87751	2.52911	2.21197	-0.24669	0.68287	4.53035
H	-0.874	1.98821	0.53934	-2.17167	1.48724	1.01081	1.76426	-1.98111	-0.10339	3.07431	0.44278	1.19697	-0.79649	0.77507	2.14317
H	3.02945	0.29284	1.27537	1.75252	0.02365	2.06248	-1.70029	-0.7792	2.17642	-0.81709	2.22668	0.6247	2.56392	-1.79456	1.27281
H	1.42051	5.02029	2.95061	-0.93494	3.66902	4.75163	1.65743	-4.59071	3.56859	3.32374	4.64735	2.79525	1.17467	-0.15621	6.08241
H	1.09224	-1.14963	0.50393	0.20918	-1.24645	0.43835	-0.16735	-0.6107	-1.14539	1.03863	-0.98157	0.71892	0.7271	-1.41911	-0.42644
H	-0.39305	0.67919	-1.48108	-0.98203	1.10156	-1.15539	-0.72943	1.32657	1.17926	-0.55618	0.72107	-1.29177	-0.00769	1.54678	-0.04036
H	-2.23657	-2.04552	-2.938	-0.75495	-2.83842	-2.89787	-1.69384	2.43895	-2.87464	-2.74857	-1.30221	-2.20904	-1.8836	2.03951	-2.48804
H	-2.50208	-0.75248	-1.75251	-0.45582	-2.68536	-1.16509	-1.29623	0.74926	-2.5542	-2.57733	-1.05388	-0.44958	-2.29317	0.66228	-1.42891
H	-3.38505	-3.71199	0.48345	3.18519	-2.87844	-2.32383	2.08765	1.84295	-3.96574	-3.50071	-4.82546	-0.94663	-3.22119	-0.43489	-5.06929
H	-4.20458	-2.35373	-0.48171	1.89307	-3.89679	-1.46241	0.59139	0.84404	-4.42668	-4.41395	-3.28168	-1.42766	-3.83102	0.98462	-4.0389
H	1.06778	-1.4197	-3.08345	-2.0193	0.18857	-3.21991	-2.05549	3.22453	0.31232	0.60949	-1.36499	-2.91524	1.50756	1.51688	-2.50278

nuclei	Z-Matrix of **16-1**			Z-Matrix of **16-2**			Z-Matrix of **16-3**			Z-Matrix of **16-4**			Z-Matrix of **16-5**		
C	-3.48718	2.65828	-0.4432	-2.56359	3.16226	1.0372	-2.30874	3.28168	1.49872	-3.67486	2.52927	-0.98582	-3.41166	2.67477	-0.46207
C	-3.15476	3.66779	0.45072	-3.55954	3.34666	0.0867	-3.23383	3.58098	0.50702	-3.50745	3.41062	0.07439	-3.08433	3.65758	0.46286
C	-2.02984	3.55834	1.26016	-3.70756	2.4556	-0.97004	-3.31691	2.80643	-0.6444	-2.5175	3.19695	1.02722	-1.97552	3.51481	1.28905
C	-1.2234	2.41969	1.16671	-2.83834	1.36572	-1.07574	-2.45454	1.71723	-0.80321	-1.67913	2.08377	0.91029	-1.18025	2.36951	1.18129
C	-1.53262	1.39611	0.25901	-1.8156	1.17087	-0.13646	-1.50244	1.40763	0.1788	-1.82198	1.1909	-0.16168	-1.4843	1.37256	0.24261
C	-2.68079	1.52127	-0.53488	-1.6957	2.07264	0.92978	-1.44716	2.19362	1.33797	-2.8374	1.41727	-1.10033	-2.61637	1.53124	-0.56834
O	-3.96911	4.75926	0.50853	-4.38407	4.42253	0.23054	-4.05435	4.65112	0.70521	-4.34707	4.48183	0.1492	-3.88742	4.75648	0.53351
C	-0.72691	0.17086	0.15333	-0.94322	-0.00475	-0.2742	-0.63655	0.23544	-0.01586	-0.98014	-0.00603	-0.30354	-0.69132	0.14021	0.12019
C	0.61339	0.14949	0.23551	0.37557	0.0117	-0.02304	0.65627	0.19532	0.3461	0.34275	-0.0166	-0.07475	0.64621	0.09883	0.23422
C	1.43198	-1.02962	0.14082	1.27538	-1.1048	-0.15523	1.53769	-0.92712	0.16156	1.21585	-1.15349	-0.21239	1.45388	-1.08653	0.12432
C	1.17257	-2.2181	-0.40119	2.58023	-1.09584	0.11467	1.26432	-2.20921	-0.07385	2.52749	-1.16713	0.02219	1.18806	-2.25913	-0.44906
C	2.34063	-3.11188	-0.30595	3.19133	-2.41091	-0.13999	2.49815	-3.01207	-0.14504	3.10482	-2.49842	-0.2272	2.35297	-3.16059	-0.36754
O	3.33065	-2.3441	0.35727	2.12853	-3.21173	-0.6237	3.54371	-2.09241	0.11831	2.01325	-3.28492	-0.6681	3.3343	-2.42538	0.34625
C	2.83338	-1.10096	0.60332	0.97995	-2.47691	-0.62395	3.008	-0.85307	0.29303	0.87969	-2.52739	-0.64734	2.85048	-1.17961	0.6036
O	3.45866	-0.18879	1.11591	-0.1076	-2.91483	-0.95567	3.65118	0.15829	0.51417	-0.22588	-2.94967	-0.9367	3.46896	-0.28717	1.15642
C	2.85568	-3.56196	-1.66593	3.79268	-3.03939	1.10908	2.70535	-3.66344	-1.50509	3.72803	-3.11894	1.01509	2.90367	-3.54218	-1.73387
O	1.97471	-4.22608	0.48074	4.17675	-2.24806	-1.13819	2.44065	-3.99123	0.87097	4.0654	-2.37174	-1.25433	2.00759	-4.33862	0.33269
H	-4.37164	2.75378	-1.06647	-2.46594	3.85995	1.86395	-2.2591	3.8896	2.39765	-4.45554	2.70333	-1.72073	-4.28336	2.79657	-1.09872
H	-1.76662	4.33694	1.96897	-4.48584	2.58681	-1.71482	-4.03921	3.02959	-1.42293	-2.38634	3.87419	1.86489	-1.71651	4.27271	2.02153
H	-0.35763	2.33791	1.82008	-2.96105	0.67097	-1.90438	-2.52653	1.1171	-1.70758	-0.92289	1.91518	1.67281	-0.32723	2.26271	1.84761
H	-2.95491	0.73934	-1.23912	-0.93682	1.93264	1.69498	-0.74229	1.96512	2.13365	-2.98087	0.73318	-1.93406	-2.88657	0.77148	-1.29795
H	-3.61382	5.37578	1.16958	-5.02781	4.41786	-0.49667	-4.63384	4.74578	-0.06816	-4.11951	5.00005	0.93814	-3.53462	5.35555	1.21174
H	-1.29194	-0.74351	-0.01056	-1.44053	-0.90698	-0.62412	-1.10838	-0.61411	-0.50264	-1.50436	-0.89871	-0.63861	-1.26478	-0.75976	-0.08727
H	1.16739	1.07496	0.39204	0.84019	0.94277	0.298	1.1239	1.07043	0.79809	0.83289	0.9073	0.22832	1.20714	1.01306	0.42967
H	0.23913	-2.51505	-0.85396	3.14273	-0.24223	0.46243	0.27862	-2.63588	-0.17816	3.11678	-0.31966	0.33912	0.26411	-2.5303	-0.93728
H	3.7514	-4.18288	-1.54777	4.19049	-4.03513	0.88087	3.65608	-4.20889	-1.52552	4.09965	-4.12599	0.79245	3.79093	-4.17644	-1.6219
H	2.11121	-4.16573	-2.1963	4.62335	-2.44067	1.49842	1.91287	-4.38622	-1.72782	4.58083	-2.53099	1.37163	2.17123	-4.11188	-2.31639
H	3.13824	-2.70965	-2.29385	3.04353	-3.16779	1.89829	2.74667	-2.91911	-2.30809	2.99865	-3.21963	1.82653	3.20929	-2.6611	-2.30912
H	2.74214	-4.82148	0.47645	4.59249	-3.11896	-1.24871	3.24039	-4.53264	0.7671	4.45484	-3.25453	-1.3667	1.49545	-4.06936	1.11194

nuclei	Z-Matrix of **16-6**			Z-Matrix of **16-7**			Z-Matrix of **16-8**		
C	-2.04985	3.50798	1.22503	-2.51448	3.13234	1.05041	-3.63981	2.49333	-0.95973
C	-3.16613	3.59051	0.40289	-3.52327	3.30845	0.11199	-3.46781	3.37346	0.10083
C	-3.46767	2.56904	-0.49047	-3.68718	2.40676	-0.93326	-2.47908	3.15435	1.05366
C	-2.63244	1.44981	-0.56151	-2.82075	1.31471	-1.03993	-1.6464	2.037	0.93627
C	-1.49142	1.35424	0.24832	-1.7851	1.12813	-0.1131	-1.79411	1.14542	-0.13611
C	-1.21586	2.38941	1.15231	-1.64965	2.04036	0.94234	-2.80839	1.37689	-1.0746
O	-3.95166	4.69935	0.50734	-4.34428	4.38682	0.25647	-4.30202	4.44878	0.17585
C	-0.65838	0.14564	0.16138	-0.91561	-0.04974	-0.25166	-0.95724	-0.05477	-0.27843
C	0.68137	0.15596	0.25531	0.40588	-0.03288	-0.01507	0.36838	-0.06405	-0.06616
C	1.53036	-1.00314	0.17913	1.30318	-1.1513	-0.14863	1.23927	-1.2025	-0.20451
C	1.28897	-2.2165	-0.31487	2.61232	-1.1371	0.10111	2.55628	-1.20835	0.00016
C	2.48975	-3.0688	-0.22734	3.21353	-2.46193	-0.13316	3.12388	-2.54976	-0.22327
O	3.46748	-2.25857	0.40499	2.14624	-3.26387	-0.60857	2.02578	-3.34162	-0.64156
C	2.94616	-1.01794	0.60917	0.99624	-2.53197	-0.59035	0.89078	-2.58752	-0.59943
O	3.55054	-0.07349	1.08567	-0.09611	-2.96605	-0.90924	-0.22069	-3.0088	-0.86446
C	3.00414	-3.5094	-1.59005	3.79099	-3.08377	1.1298	3.73419	-3.15295	1.03328
O	2.21492	-4.2156	0.55148	4.23448	-2.36645	-1.10555	4.11134	-2.4964	-1.23263
H	-1.82962	4.30899	1.92515	-2.40512	3.83802	1.86894	-4.42019	2.67156	-1.69404
H	-4.34012	2.62236	-1.13369	-4.47605	2.5313	-1.66804	-2.3449	3.83051	1.8918
H	-2.87684	0.65588	-1.26376	-2.95697	0.61143	-1.85921	-0.89149	1.86385	1.69916
H	-0.35751	2.33627	1.81778	-0.88159	1.90694	1.69953	-2.95654	0.69333	-1.9079
H	-4.68294	4.62394	-0.12706	-5.00309	4.37225	-0.45701	-4.07777	4.9616	0.96931
H	-1.20297	-0.78101	-0.00041	-1.419	-0.95384	-0.58818	-1.48845	-0.94903	-0.59819
H	1.211	1.09736	0.40516	0.87317	0.90046	0.29579	0.86062	0.86307	0.22412
H	0.35864	-2.55038	-0.74891	3.178	-0.28358	0.44542	3.14997	-0.3583	0.30325
H	3.9184	-4.10382	-1.47662	4.18716	-4.08303	0.91393	4.10391	-4.16444	0.82774
H	2.27309	-4.13801	-2.1104	4.6194	-2.48728	1.52765	4.58708	-2.56346	1.38745
H	3.25478	-2.65297	-2.22592	3.0299	-3.20164	1.9092	2.99916	-3.23787	1.84147
H	1.73382	-3.91711	1.3399	3.88778	-1.82353	-1.8316	3.74428	-1.97336	-1.96334

nuclei	Z-Matrix of **2-1**			Z-Matrix of **2-2**			Z-Matrix of **2-3**			Z-Matrix of **2-4**		
C	-0.88628	-3.38482	-1.79134	0.37281	-3.7027	-0.13639	0.16458	-3.7582	0.32756	-1.03041	-3.31374	-2.05022
C	-0.48321	-4.2399	-0.77398	-0.37855	-4.16752	-1.2082	-0.46511	-4.23004	-0.81686	-0.42712	-4.18355	-1.15105
C	0.12054	-3.74233	0.37512	-0.9717	-3.27995	-2.0987	-0.89602	-3.35151	-1.80431	0.34718	-3.69856	-0.10279
C	0.31808	-2.36416	0.50671	-0.81161	-1.90452	-1.90598	-0.69478	-1.97789	-1.63707	0.51344	-2.31829	0.048
C	-0.09618	-1.48211	-0.50211	-0.07147	-1.4143	-0.82059	-0.07561	-1.47963	-0.4816	-0.10044	-1.42351	-0.84036
C	-0.68797	-2.00843	-1.65843	0.53172	-2.32784	0.05464	0.36418	-2.38538	0.49352	-0.86197	-1.93544	-1.89914
O	-0.69516	-5.5754	-0.94489	-0.50684	-5.51637	-1.35689	-0.63908	-5.57646	-0.93732	-0.61574	-5.52074	-1.33634
C	0.12202	-0.03064	-0.41446	0.09109	0.03972	-0.67406	0.142	-0.0305	-0.36129	0.07421	0.03194	-0.73138
C	-0.00473	0.67575	0.72072	0.06914	0.6764	0.50778	0.02768	0.64645	0.79305	0.03302	0.69853	0.43326
C	0.20445	2.09401	0.84444	0.20938	2.09612	0.70751	0.23577	2.06161	0.95161	0.18279	2.12142	0.60066
C	0.18088	3.05771	-0.07123	0.20438	2.733	1.87567	0.22808	3.04572	0.05753	0.13851	2.7897	1.75031
C	0.39945	4.30899	0.56197	0.36584	4.12441	1.65672	0.44026	4.28206	0.72145	0.32743	4.17259	1.5014
O	0.5502	4.1442	1.92872	0.47626	4.39183	0.30407	0.57107	4.08649	2.08607	0.49856	4.40168	0.14806
C	0.42268	2.79297	2.1317	0.38084	3.1642	-0.3074	0.43793	2.73131	2.25717	0.41344	3.15906	-0.43397
O	0.48229	2.24387	3.22137	0.43006	3.00177	-1.51663	0.48084	2.15868	3.33534	0.51591	2.96273	-1.6347
C	0.45464	5.50384	-0.02858	0.41109	5.08029	2.586	0.50686	5.48961	0.15855	0.34591	5.15287	2.40584
H	-1.35289	-3.78682	-2.6861	0.84055	-4.40739	0.54517	0.50458	-4.45541	1.08814	-1.62763	-3.70484	-2.86893
H	0.44772	-4.40278	1.17181	-1.55543	-3.63242	-2.94291	-1.3849	-3.71088	-2.70405	0.83148	-4.37099	0.59786
H	0.80932	-1.99069	1.40242	-1.27663	-1.21549	-2.60835	-1.03544	-1.29829	-2.41507	1.13882	-1.95103	0.85791
H	-1.00949	-1.3525	-2.46399	1.14216	-1.98371	0.88535	0.87575	-2.03788	1.38797	-1.33687	-1.26511	-2.61237
H	-0.37255	-6.04359	-0.15745	-1.04294	-5.69077	-2.14774	-1.09522	-5.75752	-1.77519	-0.12757	-6.00155	-0.64834
H	0.38751	0.45514	-1.35013	0.21059	0.58466	-1.60816	0.39629	0.4786	-1.2874	0.21712	0.54951	-1.67774
H	-0.28296	0.17656	1.64881	-0.07915	0.09592	1.4171	-0.23917	0.12204	1.7108	-0.14278	0.14218	1.35268
H	0.01346	2.93091	-1.12947	0.09619	2.27722	2.84823	0.07703	2.94343	-1.00572	-0.01677	2.36212	2.72923
H	0.6257	6.40047	0.55897	0.53905	6.11965	2.29994	0.6717	6.37233	0.76854	0.4994	6.1824	2.09761
H	0.33255	5.6212	-1.09984	0.32316	4.85781	3.64382	0.40072	5.63128	-0.91142	0.21011	4.96064	3.46451

Isolation and Analytical Data of Shunt Product (11) and Intermediate (12)

A 5 mL SM/5 (Formedium^{TM}, UK) liquid culture of *P. fluorescens* HKI0874 Δ*stoE* Δ*clp* (for isolation of shunt product **11**) and *P. fluorescens* HKI0874 Δ*stoC* Δ*clp* (for isolation of intermediate **12**) was inoculated from a single colony grown overnight on SM/5 agar at 22 °C and incubated at 22 °C overnight while shaking on a gyratory shaker at 180 rpm. A 100 mL pre-culture in SM/5 medium was inoculated with 0.5 mL pre-culture of the respective mutant strain and shaken for 24 h at 22 °C. A 20 L batch fermenter containing SM/5 medium was inoculated with 100 mL pre-culture of the respective mutant strain and fermented at 22 °C. After 22 h the culture was centrifuged and the supernatant was extracted with an equal amount of ethyl acetate. The solvent was removed *in vacuo*, until approximately 500 mL solvent was left. The organic phase was dried over Na_2SO_4, decanted and Isolute® HM-N (Biotage) was added before the solvent was removed *in vacuo*. For isolation of shunt product **11** the whole extract was fractionated on 75 g normal phase silica gel by flash chromatography with forced flow, using the following elution gradient: A: hexane, B: ethyl acetate, 33% B for 0.4 L, 50% B for 0.2 L. Shunt product **11** eluted after 0.5 L in approximately 0.1 L of solvent. Fractions containing shunt product **11** were combined (50 mg) and re-purified by semi-preparative reverse-phase HPLC using the following elution gradient: solvent A: H_2O, solvent B: acetonitrile, 22.5% B for 18 min (t_R = 15.5 min). The solvent was removed *in vacuo* at 30 °C, avoiding light exposure, to yield 30 mg shunt product **11**.

For isolation of intermediate **12** the whole extract was fractionated on 90 g normal phase silica gel by flash chromatography with forced flow, using the following elution gradient: A: hexane, B: ethyl acetate, 10% B for 0.3 L, 15% B for 0.4 L, 30% B for 0.4 L, 50% B for 2.5 L. Intermediate **12** eluted after 1 L 50% B in approximately 0.8 L of solvent. Fractions containing intermediate **12** were combined (56 mg) and partly re-purified by semi-preparative reverse-phase HPLC using the following elution gradient: solvent A: H_2O, solvent B: acetonitrile, 22.5% B for 14 min (t_R = 10.7 min). The solvent was removed *in vacuo* at 30 °C, to yield 2.1 mg intermediate **12**.

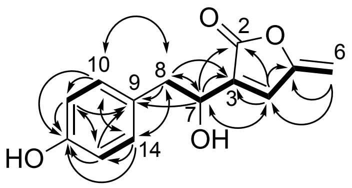


Figure S25. Chemical structure of shunt product **11** with selected correlations observed by 2D NMR spectroscopy. Bold lines: ^{1}H-^{1}H COSY correlations; solid arrows: HMBC correlations.

Table S20: NMR signal assignment for shunt product **11** measured in *d_4-MeOD* (300 MHz).

Position	δ$_C$ [ppm]	δ$_H$ [ppm] (m, *J* [Hz])
2	170.6	-
3	139.5	-
4	138.9	7.32 (app d, 1.3,1H)
5	155.5	-
6	97.6	4.94 (d, 2.6, 1H), 5.14 (d, 2.6, 1H)
7	68.7	4.67 (app t, 6.2, 1H)
8	42.0	2.81 (dd, 13.9, 7.4, 1H), 3.03 (dd, 13.9, 4.9, 1H)
9	129.6	-
10, 14	131.6	7.01 (dt, 9.2, 2.4, 2H)
11, 13	116.0	6.68 (dt, 9.2, 2.4, 2H)
12	157.0	-

$[\alpha]_D^{25}$ = +39 (c = 0.3 in *MeOH*); HR-ESI-MS: $[M+H]^+$ m/z = 233.0813 (calculated for $C_{13}H_{13}O_4^+$ 233.0808).

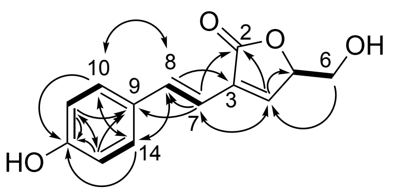


Figure S26. Chemical structure of intermediate **12** with selected correlations observed by 2D NMR spectroscopy. Bold lines: ^{1}H-^{1}H COSY correlations; solid arrows: HMBC correlations.

Table S21: NMR signal assignment for intermediate **12** measured in *d_4-MeOD* (500 MHz).

Position	δ_C [ppm]	δ_H [ppm] (m, *J* [Hz])
2	174.3	-
3	131.8	-
4	145.9	7.38 (d, 1.7, 1H)
5	83.8	5.09 (m, 1H)
6	63.0	3.71 (dd, 12.2, 4.8, 1H), 3.87 (dd, 12.2, 3.8, 1H)
7	115.0	6.72 (d, 16.4, 1H)
8	135.7	7.56 (d, 16.4, 1H)
9	129.5	-
10, 14	129.4	7.36 (d, 8.7, 2H)
11, 13	116.6	6.78 (d, 8.6, 2H)
12	159.4	-

$[\alpha]_D^{25}$ = +1.7 (c = 0.3 in *MeOH*); HR-ESI-MS: $[M+H]^+$ m/z = 233.0807 (calculated for $C_{13}H_{13}O_4^+$ 233.0808).

Heterologous Expression of Styrolide and Acaterin BGC

The biosynthetic gene cluster borders were determined by heterologous expression of different sets of genes. For heterologous expression, a modified pMQ72 vector, pMQ72*rbs*, containing a ribosomal binding site was used.[34] Different expression sequences of the styrolide BGC and the acaterin BGC were amplified from genomic DNA of *Pseudomonas fluorescens* HKI0874 and *Pseudomonas jessenii* ESC101, respectively. Primers for PCR amplification were designed using: http://nebuilder.neb.com (Table S22). Due to their size or separate genomic location, constructs *stoA–stoH* and *stoA–stoI*, or *acaABCR*, respectively, were split into two fragments. Construct *stoB–stoI* and *acaABC* was amplified as single fragment. Amplified fragments were cloned into the SalI/HindIII linearized pMQ72*rbs* vector using the standard Gibson Assembly protocol. The vectors were transformed into chemically competent *E. coli* Top10 cells *via* heat shock at 42 °C. Plasmids were purified from overnight cultures (LB 15 µg/mL gentamicin) of single colonies using the QIAprep® Spin Miniprep Kit and sequenced. For heterologous gene expression, *Pseudomonas protegens* Pf-5 Δ*gacA* was used as host. Briefly, electro competent *P. protegens* Pf-5 Δ*gacA* (200µL) were transformed with plasmids (750–1000 ng) containing the desired sequence using a standard protocol (30 min incubation on ice prior electroporation). Electroporation (1.8 kV) was conducted using an electroporation cuvette (1 mm, Biozyme) and an Eppendorf Eporator®. SOC medium (2 mL) was added and outgrow was performed for 2 h under shaking conditions at 28°C. For selection of transformants, 200 µL of the outgrow was spread on selective LB agar plates containing 50 µg/mL gentamicin and cultivated overnight at 28°C. For heterologous expression, a single colony was inoculated in selective LB medium with 50 µg/mL gentamicin. Expression was induced at OD = 0.6 with L–arabinose (100 mM final conc.). *P. protegens* Pf-5 Δ*gacA* pMQ72*rbs* was cultivated as negative control. After 24 h, the cultures were extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 and the solvent was removed in *vacuo*. Samples were analyzed *via* LC-MS to monitor compound production. Whereas *stoA–stoH* and *stoB–stoI* did not allow styrolide production in the heterologous host, expression of *stoA–stoI* led to styrolide production (Figure S27). Expression of *acaABC* led to 4,5-didehydroacaterin **10** production and *acaABCR* allowed production of 4,5-didehydroacaterin **10** and acaterin **9** (Figure S28).

Table S22: Primers for amplification of expression constructs for styrolides and acaterin.

Primer	Sequence 5' → 3'	T_a [°C]
*stoA–stoI*_1_F	ccggggaaggagatatacagGTGTACTTGGATTCCATTG	58.4
*stoA–stoI*_1_R	ggaagctgctGATCAAATAACCGTTGGAC	
*stoA–stoI*_2_F	ttatttgatcAGCAGCTTCCTTTCGCCAAAG	69.5
*stoA–stoI*_2_R	ctcatccgccaaaacagccaTCAGGCCTGCAAACGCTC	
*stoB–stoI*_F	ccggggaaggagatatacagATGAATAACGACAGCATTGCGC	67.1
*stoB–stoI*_R	ctcatccgccaaaacagccaTCAGGCCTGCAAACGCTC	
*stoA–stoH*_1_F	ccggggaaggagatatacagGTGTACTTGGATTCCATTG	56.8
*stoA–stoH*_1_R	gcggtgaagtTCATTTCAGGTTTTCCTC	
*stoA–stoH*_2_F	cctgaaatgaACTTCACCGCCAAGATCGC	69.3
*stoA–stoH*_2_R	ctcatccgccaaaacagccaTCATGCGGCGACCTCGATTTTC	
*acaABC*_F	ccggggaaggagatatacagATGATCGACATGCACAGGAAAG	66.0
*acaABC*_R	ctcatccgccaaaacagccaTCAGAACTTGCCGCTGGC	
*acaABCR_acaABC*_F	ccggggaaggagatatacagATGATCGACATGCACAGGAAAG	66.0
*acaABCR_acaABC*_R	gcacattcatTCAGAACTTGCCGCTGGC	
*acaABCR_acaR*_F	caagttctgaATGAATGTGCTACTGGTCTAC	62.2
*acaABCR_acaR*_R	ctcatccgccaaaacagccaTTACAAAGTGTGGGCGGC	

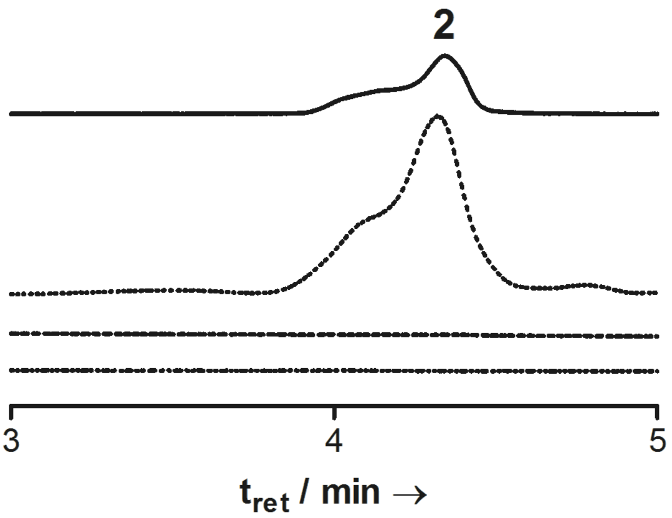


Figure S27. HPLC profiles at 356 nm of *P. fluorescens* HKI0874 (solid line, top), *P. protegens* Pf-5 Δ*gacA* pMQ72 *stoA–stoI* (dotted line, top-middle), *P. protegens* Pf-5 Δ*gacA* pMQ72 *stoB–stoI* (dashed line, bottom-middle), and *P. protegens* Pf-5 Δ*gacA* pMQ72 *stoA–stoH* (dashed-dotted line, bottom) with/without styrolide B **2** production.

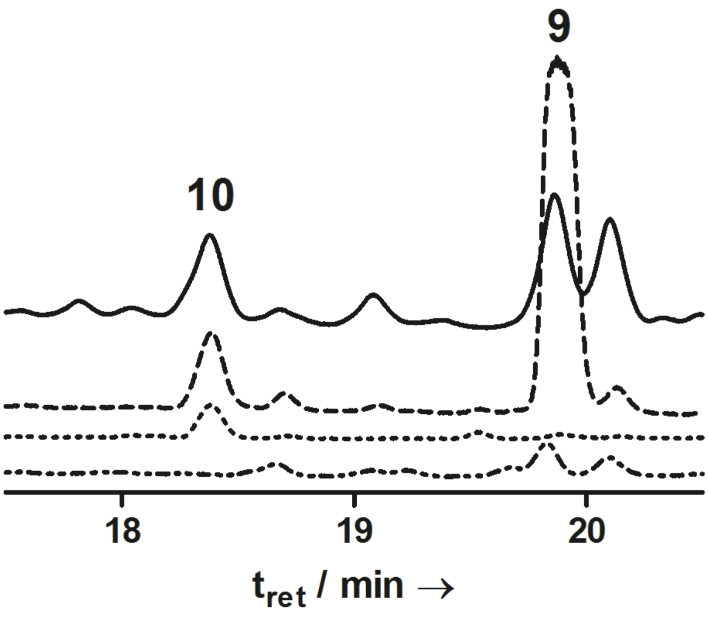


Figure S28. HPLC profiles at 190 nm of *P. jessenii* EC-S101 (solid line, top), *P. protegens* Pf-5 Δ*gacA* pMQ72 *acaABCR* (dashed line, top-middle), *P. protegens* Pf-5 Δ*gacA* pMQ72 *acaABC* (dotted line, bottom-middle), *P. protegens* Pf-5 Δ*gacA* pMQ72*rbs* (negative control, dashed-dotted line, bottom) with/without 4,5-didehydroacaterin **10** and acaterin **9** production.

Transcriptomics on *P. fluorescens* HKI0874 WT and *P. fluorescens* HKI0874Δ*stoE*

5 mL SM/5 (Formedium^{TM}, UK) liquid cultures of *P. fluorescens* HKI0874 wildtype (3 replicates) and *P. fluorescens* HKI0874 Δ*stoE* (3 replicates) were inoculated from single colonies grown overnight on SM/5 agar at 22 °C (3 individual colonies on 3 individual plates for each strain) and incubated at 22 °C for 22 h while shaking on a gyratory shaker at 180 rpm. The OD was set to 1.0 using SM/5 medium and 250 mL SM/5 medium was inoculated with 250 µL pre-culture for each replicate and shaken for 16 h at 22 °C, 180 rpm. All cultures were centrifuged with 4,000 *g* for 10 min at room temperature. The supernatant was decanted and the cell pellets (approx. 1.5 g) were resuspended in 1.5 mL PBS, after which 15 mL RNA*later* Stabilization Solution (Thermo Fisher) was added immediately. The samples were incubated for 10 min at room temperature before they were snap-frozen in liquid nitrogen and shipped on dry ice for RNA-seq analysis (RNA isolation, rRNA depletion and RNA-seq done by GATC Konstanz).

The contigs from genome sequencing of *Pseudomonas fluorescens* HKI0874 were annotated using rapid prokaryotic genome annotation Prokka (v1.13.3).[4] The assembled genome was used as a reference genome for mapping the fastq reads from the transcriptome analysis on WT and Δ*stoE* strains of *Pseudomonas fluorescens* HKI0874. Alignment to the reference genome was carried out using Bowtie2.[35] Approximately 99.5% of the quality-filtered reads from three replicates of WT and Δ*stoE* strains were mapped to the reference genome. Cufflinks tool[36] was used to subsequently identify and quantify transcripts from the RNA-seq alignment assembly. Cuffmerge was then used to identify and annotate full length transcripts with a gtf file for the reference genome. Briefly, the .gff file obtained from the Prokka workflow was converted into .gtf file using the gffread command. The .gtf annotations were then used to identify transcripts. Subsequently, Cuffdiff was used to identify differential gene expression at the gene/transcript level and reported as log2 fold change and FDR corrected qvalue between the WT and Δ*stoE* strains. The ORFs that were differentially expressed were then assigned COG categories using eggNOG mapper.[37] The hierarchical categories of differentially expressed genes with their fold changes were visualized as a circular packaging plot using R (v3.5.3, Figure S29).

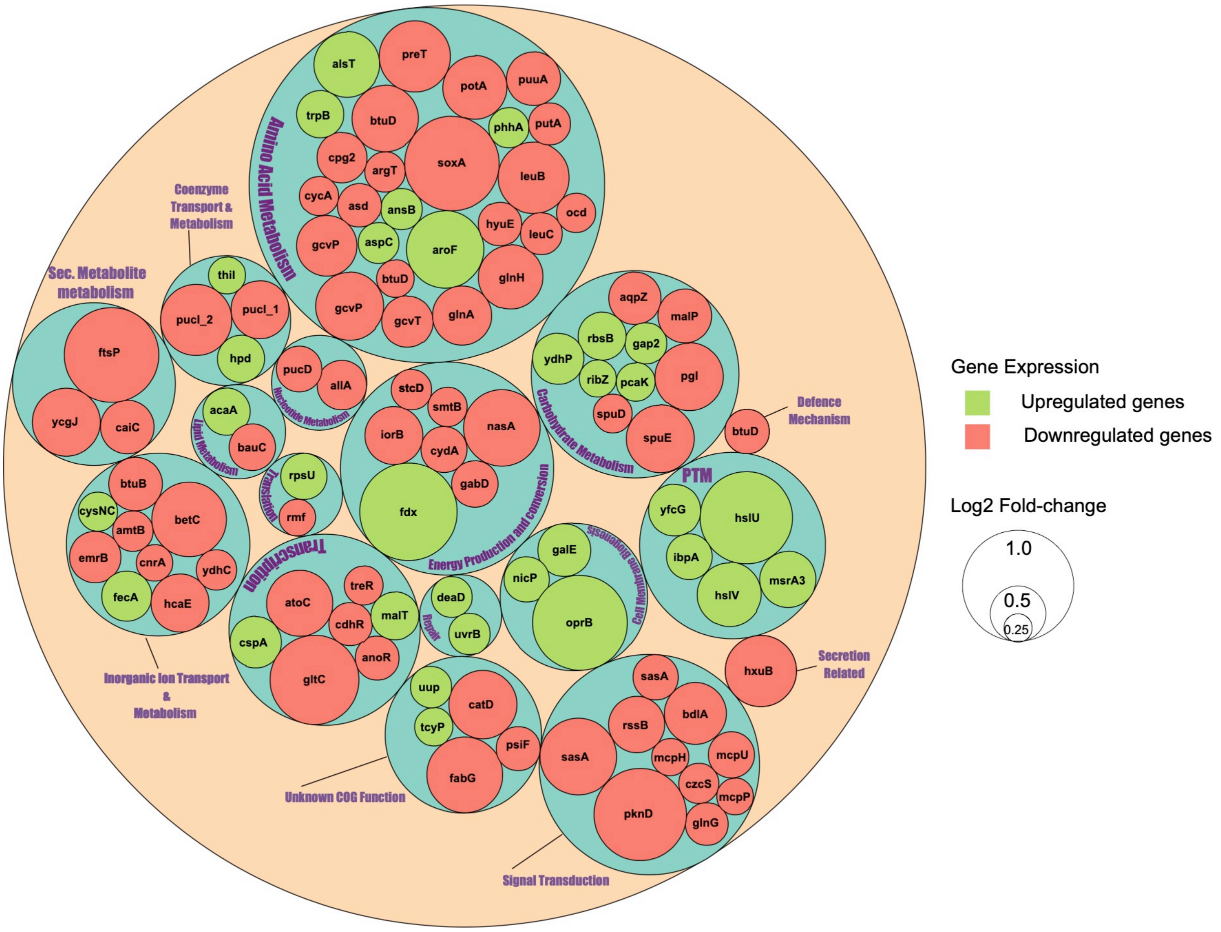


Figure S29: Hierarchical categories (metabolic pathways) of differentially expressed genes with their fold changes.

Phenotypic Analysis of *P. fluorescens* HKI0874 WT and *P. fluorescens* HKI0874Δ*stoE*

Phenotypic analyses were performed to evaluate potential signaling functions with regard to swarming ability and effects on bacterial growth of the styrolides.

Growth Curve Assay

SM/5 overnight cultures of *P. fluorescens* HKI0874 wildtype and *P. fluorescens* HKI0874 Δ*stoE*, were diluted to OD_{600} = 0.5, of which 5 µL were added to SM/5 medium (95 µL) in 96 well plates (twelve technical replicates for each strain). The plates were incubated at 28°C in a TECAN plate reader and shaken for 10 s before OD_{600} measurements. This process was repeated every 15 min for 24 h. The assay was performed in triplicates (Figure S30).

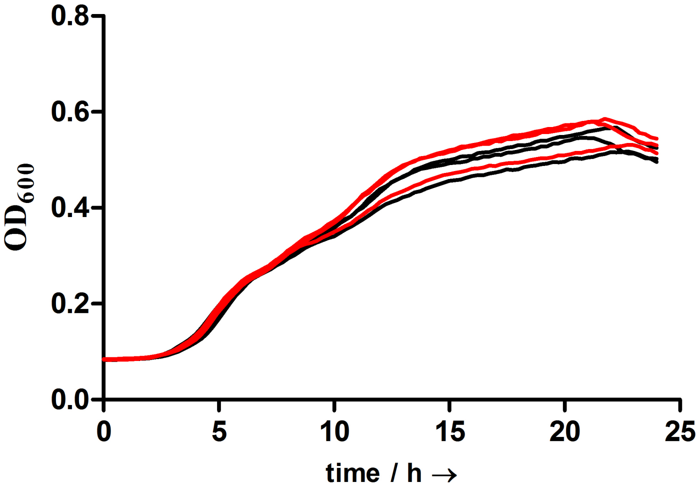


Figure S30: Growth curves for *P. fluorescens* HKI0874 wildtype (black) and *P. fluorescens* HKI0874 Δ*stoE* (red). Shown are three biological replicates each, which are the mean of 12 technical replicates.

Swarming Assay

2 µL of SM/5 overnight cultures of *P. fluorescens* HKI0874 wildtype and *P. fluorescens* HKI0874 Δ*stoE* were spot in the middle of SM/5 agar plates (0.7 % agar). The plates were incubated for 20 h at 22 °C. The assay was performed in triplicates (Figure S31).

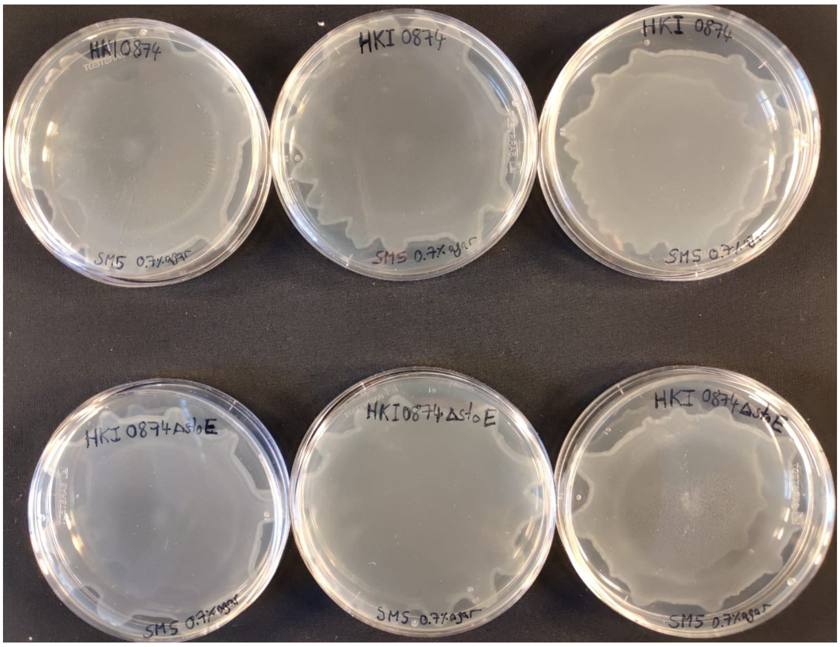


Figure S31: Swarming assay of *P. fluorescens* HKI0874 wildtype (top row) and *P. fluorescens* HKI0874 Δ*stoE* (bottom row). The swarming ability was unaffected by the deletion of *stoE*.

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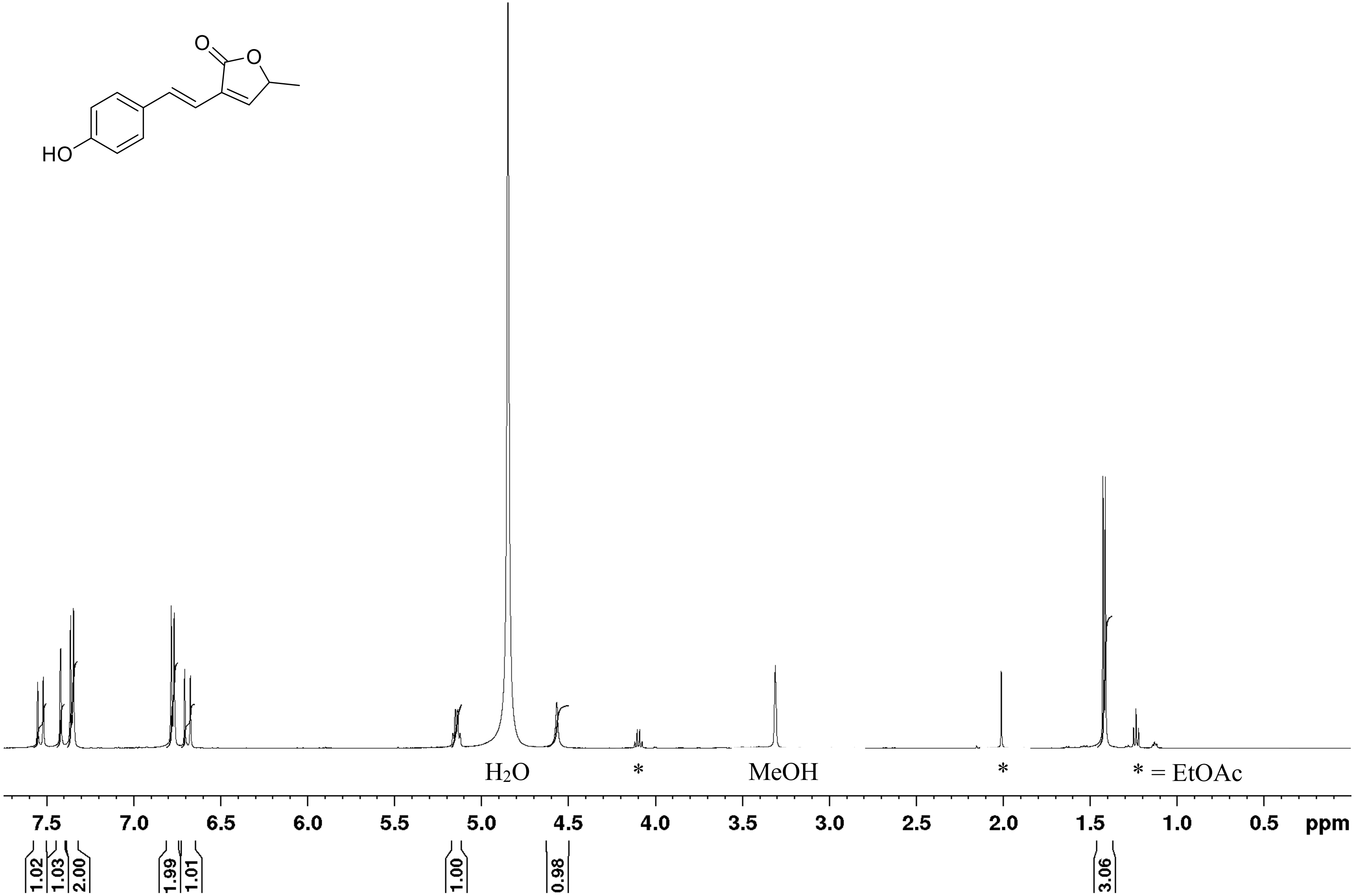
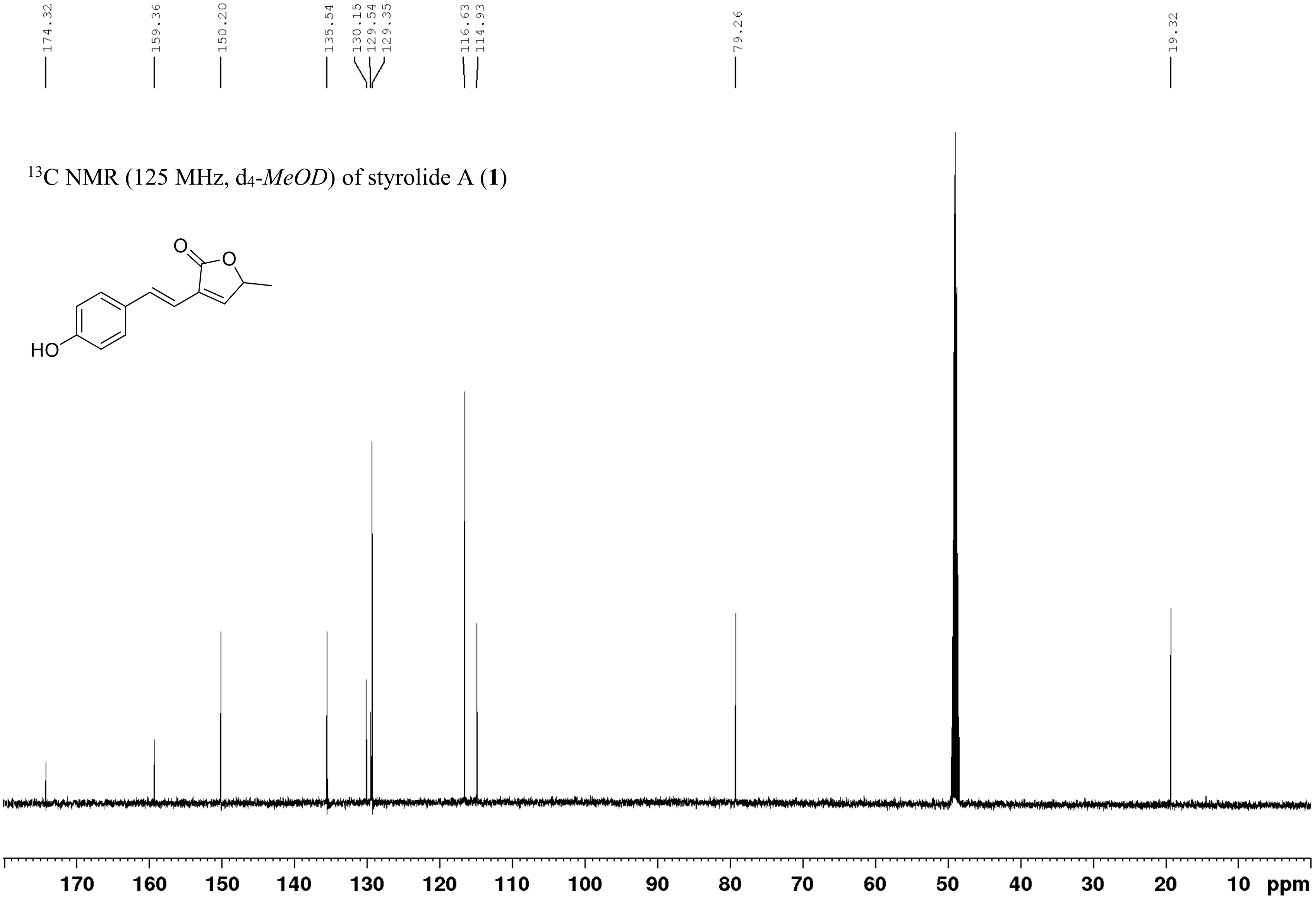
NMR Spectra

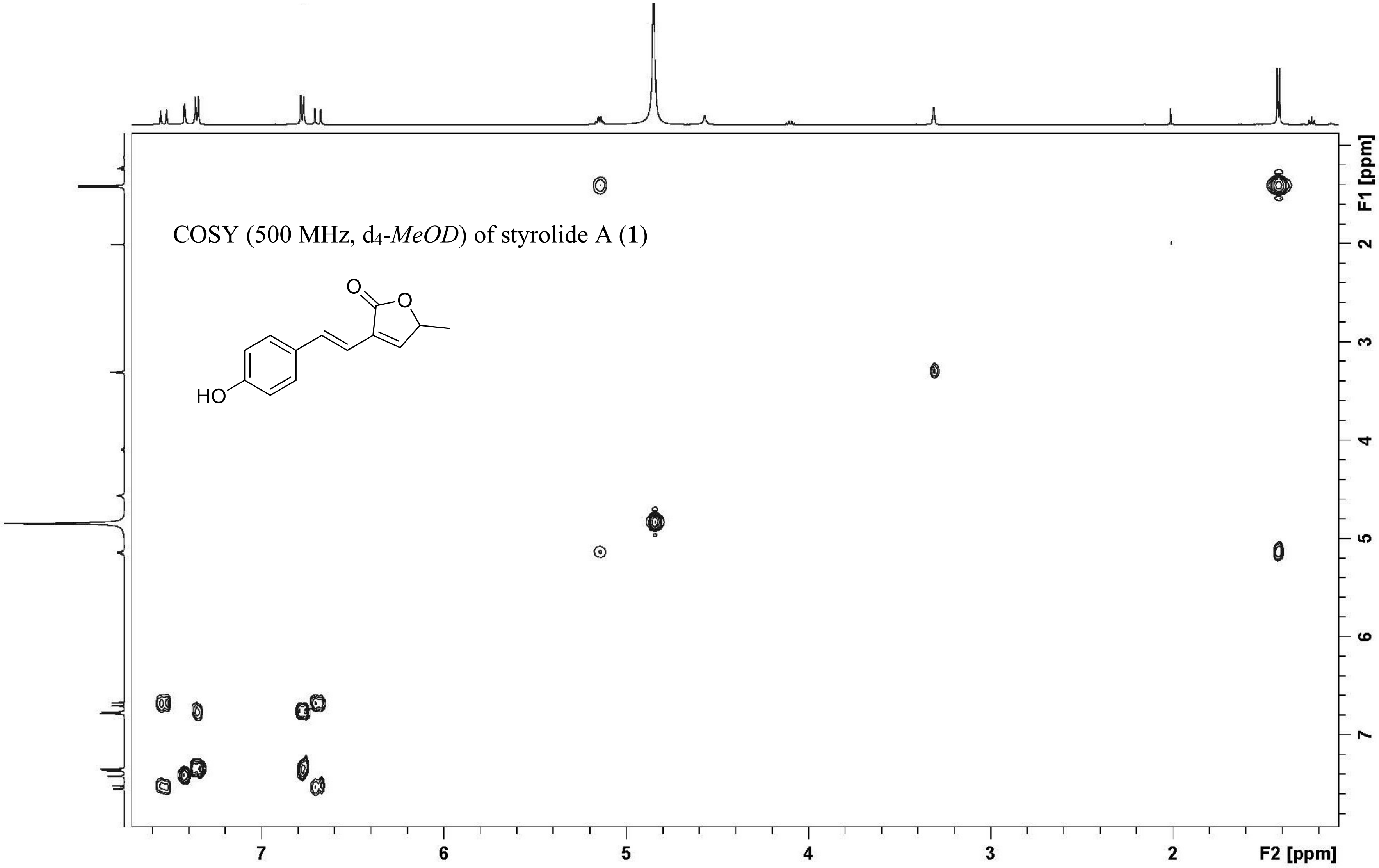
- ^{1}H, ^{13}C, ^{1}H ^{1}H COSY, HSQC, HMBC NMR spectra of styrolide A (**1**)
- ^{1}H, ^{13}C, ^{1}H ^{1}H COSY, HSQC, HMBC NMR spectra of styrolide B (**2**)
- ^{1}H, ^{13}C, ^{1}H ^{1}H COSY, HSQC, HMBC NMR spectra of shunt product (**11**)
- ^{1}H, ^{13}C, ^{1}H ^{1}H COSY, HSQC, HMBC NMR spectra of intermediate (**12**)
- ^{1}H, ^{13}C, HSQC, HMBC NMR spectra of (*E*)-*tert*-butyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-phenyl) carbonate (**4**)
- ^{1}H and ^{13}C NMR spectra of β-angelica lactone (**6**)
- ^{1}H and ^{13}C NMR spectra of 3-bromo-5-methylfuran-2(5*H*)-one (**7**)
- ^{1}H, ^{13}C, ^{1}H ^{1}H COSY, HSQC, HMBC NMR spectra of (*E*)-*tert*-butyl(4-(2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)vinyl)phenyl) carbonate (**8**)
- ^{1}H, ^{13}C, ^{1}H ^{1}H COSY, HSQC, HMBC NMR spectra of synthetic styrolide A (*rac*-**1**)

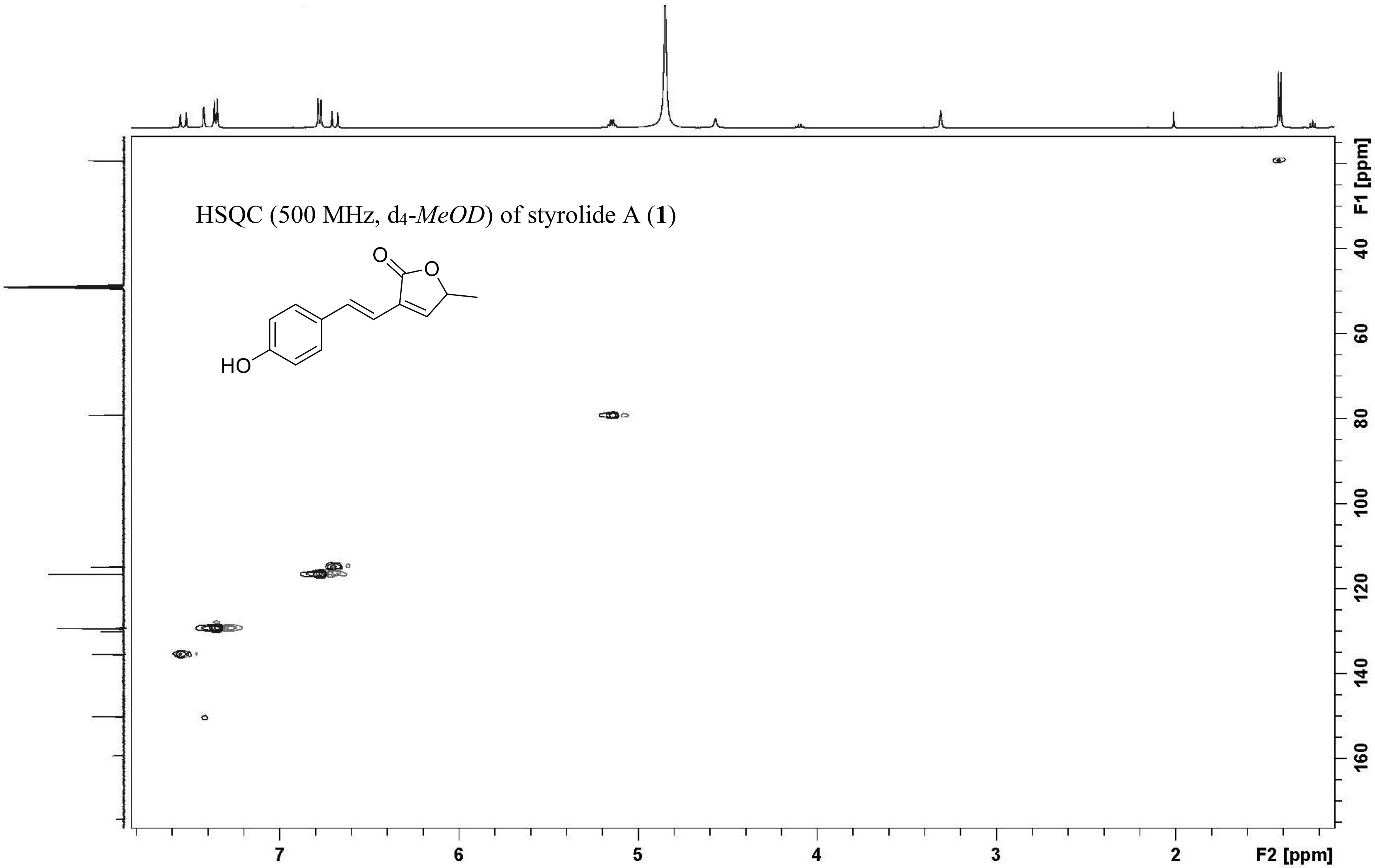
^{1}H NMR (500 MHz, d$_4$-*MeOD*) of styrolide A (**1**)

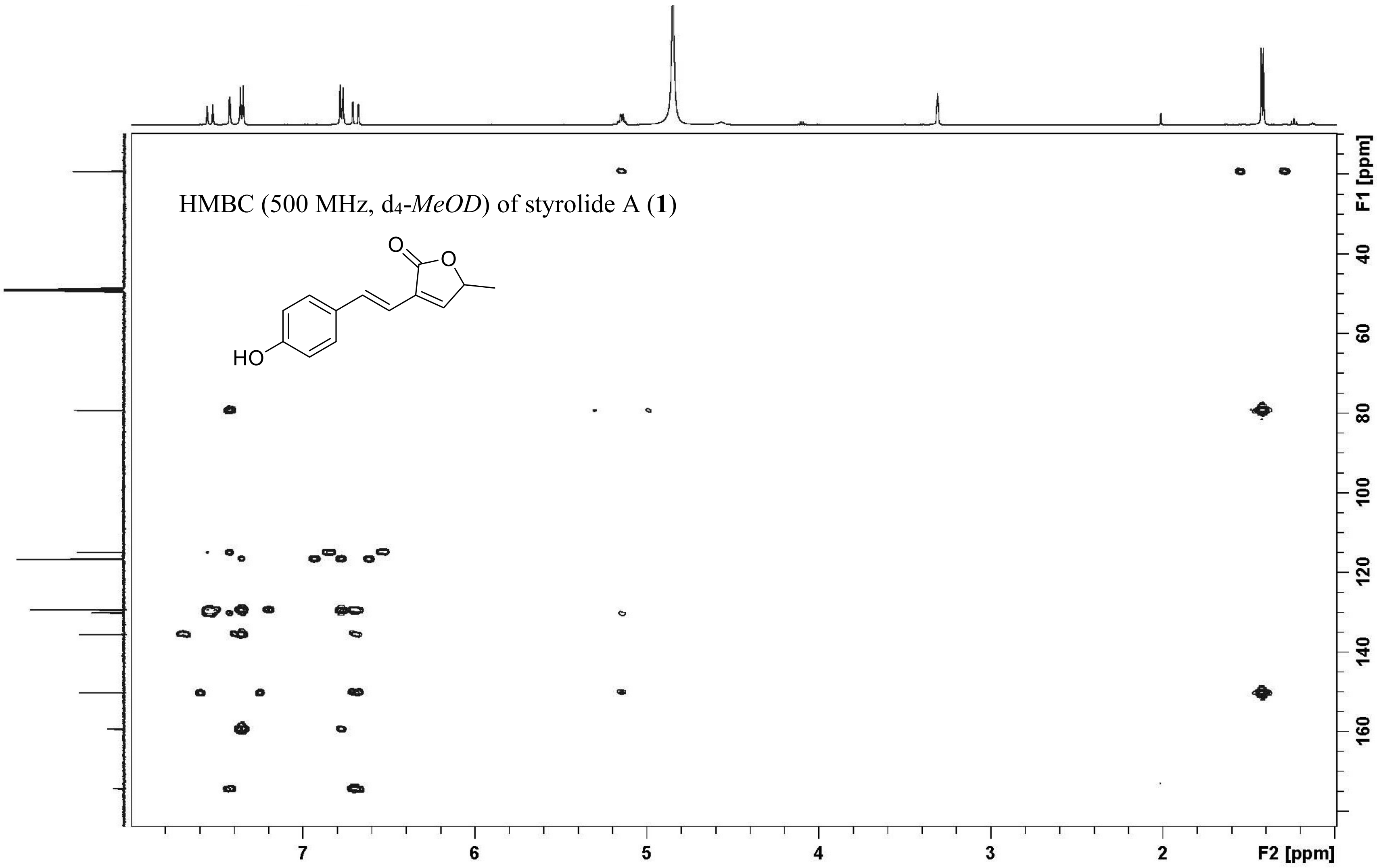




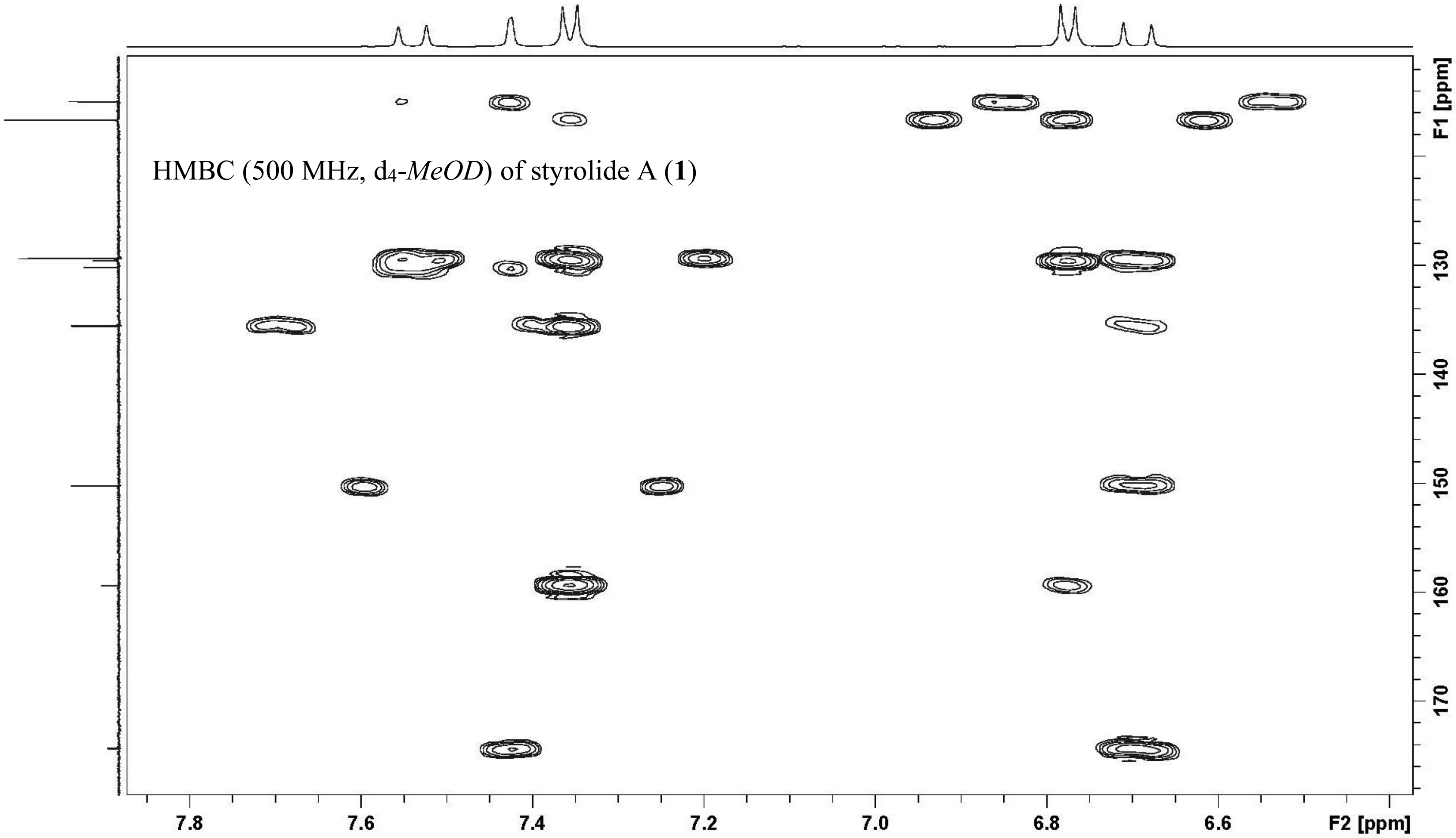
^{13}C NMR (125 MHz, d$_4$-*MeOD*) of styrolide A (**1**)


COSY (500 MHz, d_4-*MeOD*) of styrolide A (**1**)

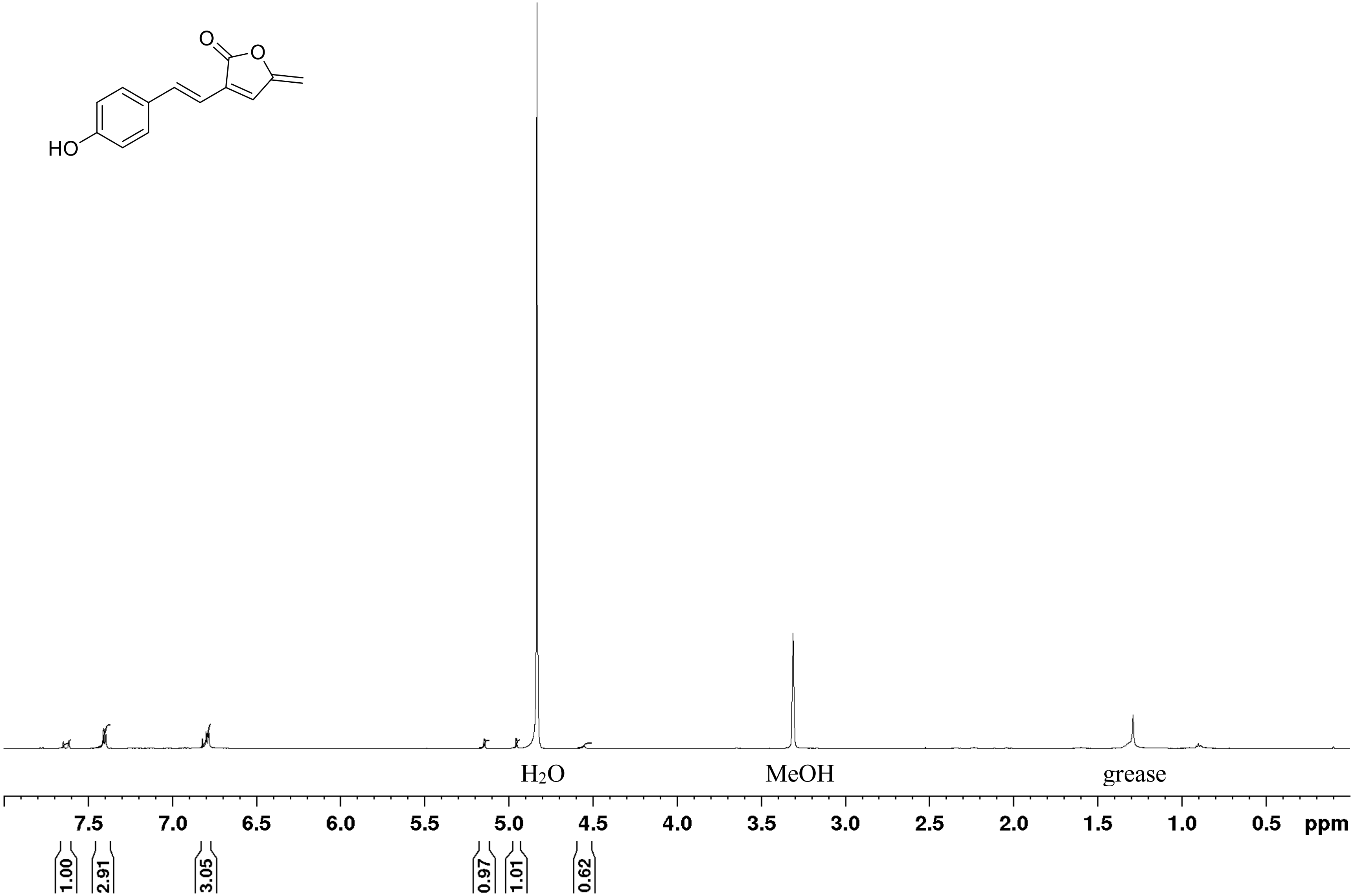

HSQC (500 MHz, d_4-*MeOD*) of styrolide A (**1**)

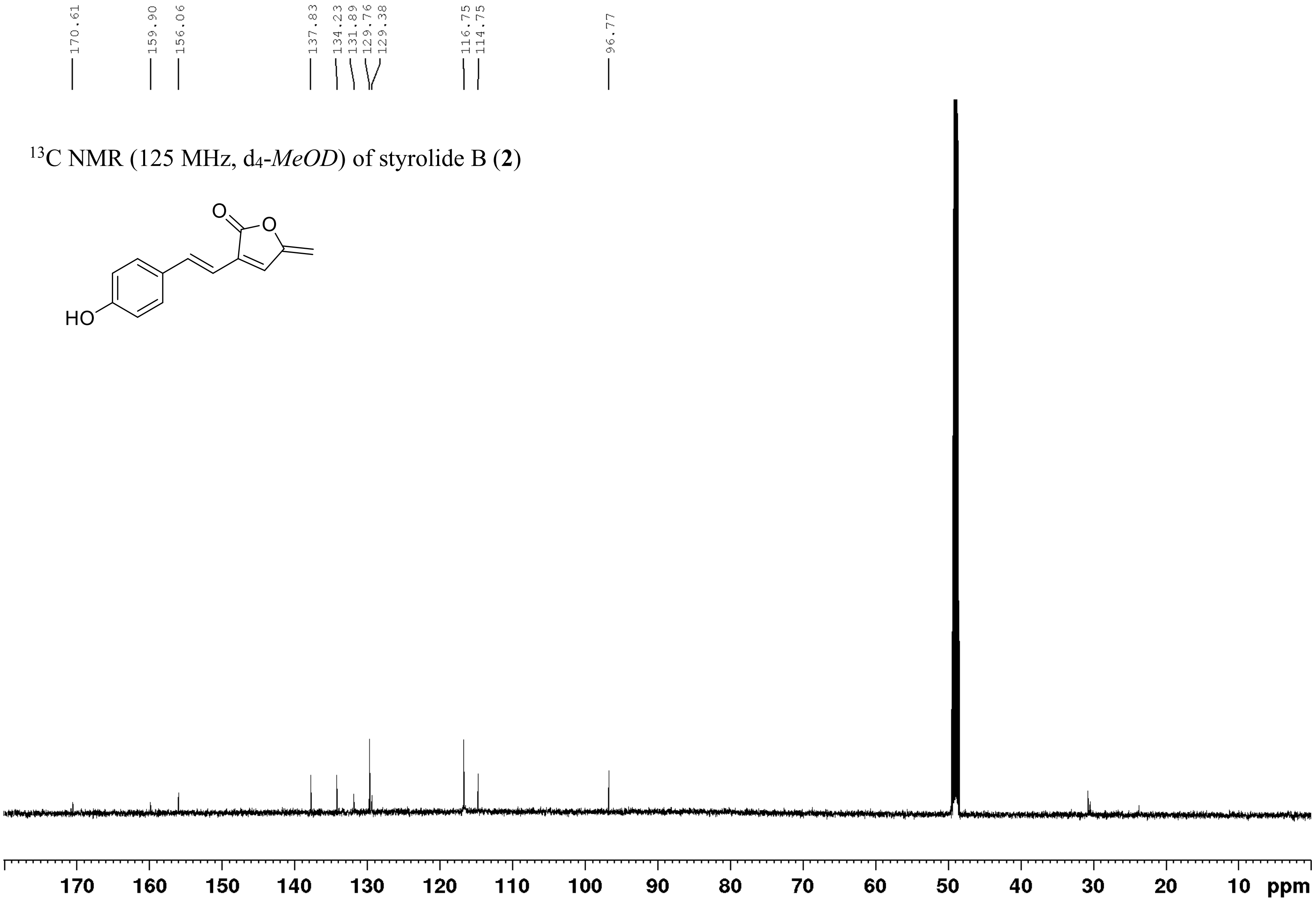


HMBC (500 MHz, d_4-*MeOD*) of styrolide A (**1**)

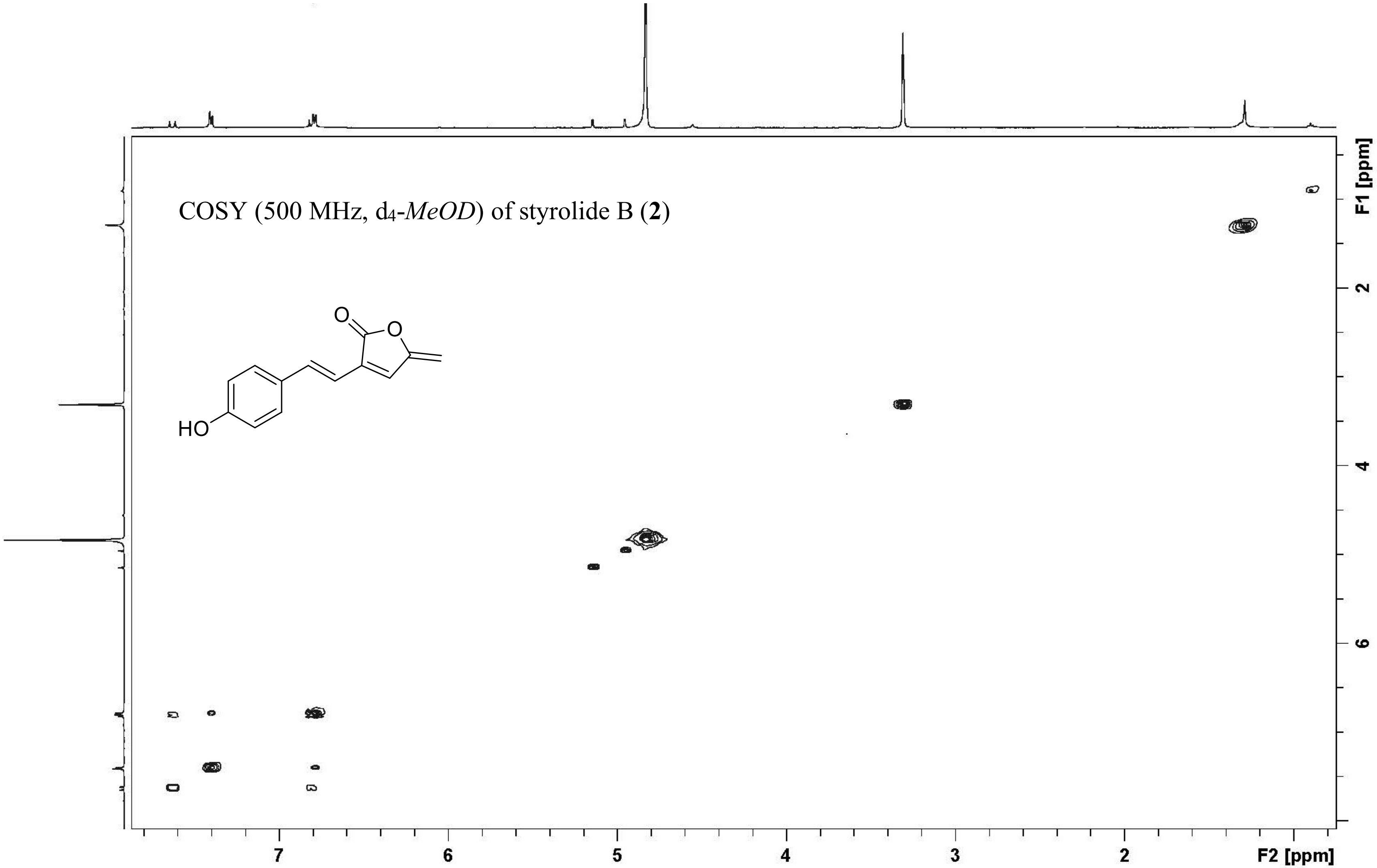

HMBC (500 MHz, d4-MeOD) of styrolide A (1)
F1 [ppm]
130
140
150
160
170
7.8
7.6
7.4
7.2
7.0
6.8
6.6
F2 [ppm]

^{1}H NMR (500 MHz, d$_4$-*MeOD*) of styrolide B (**2**)

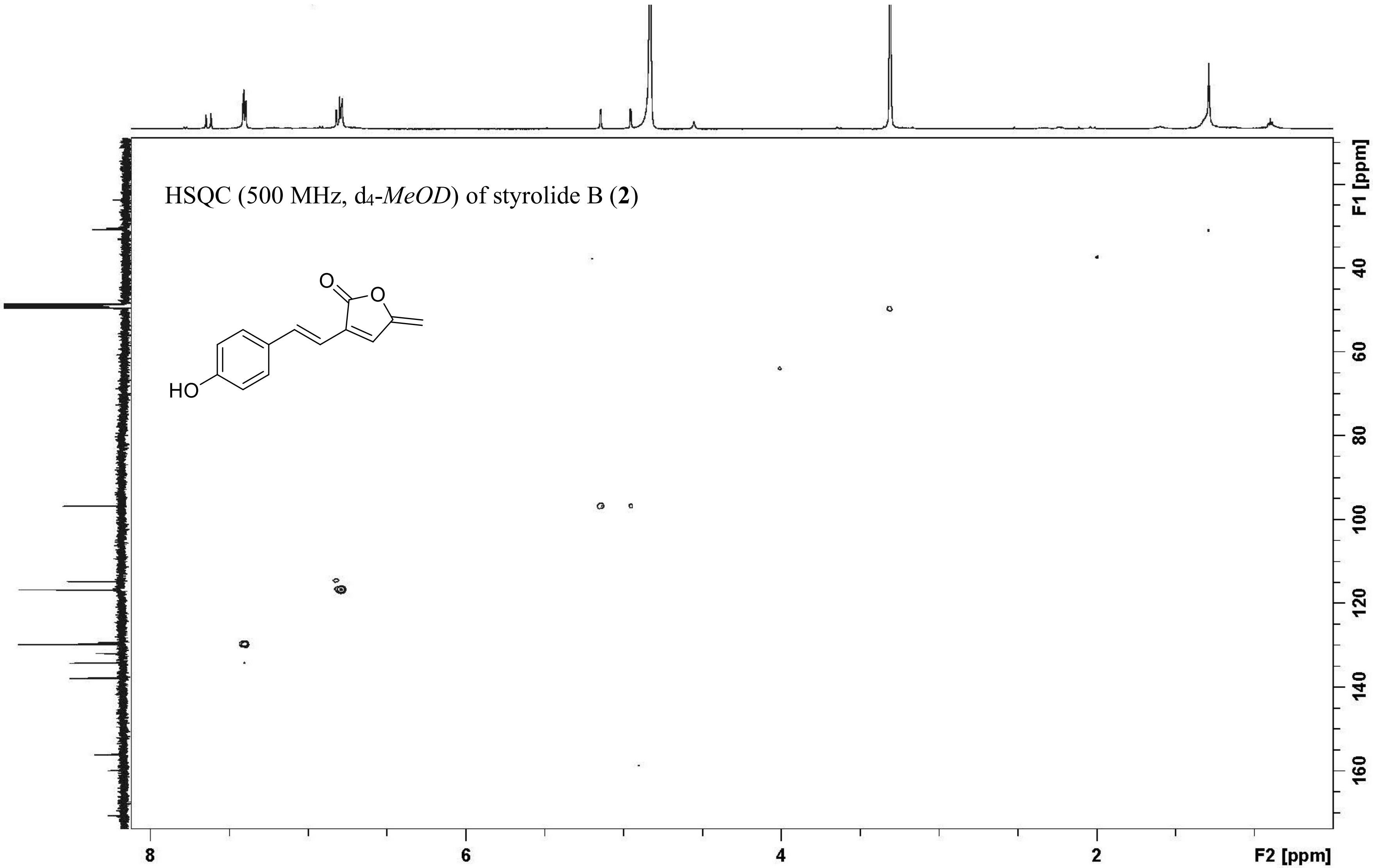




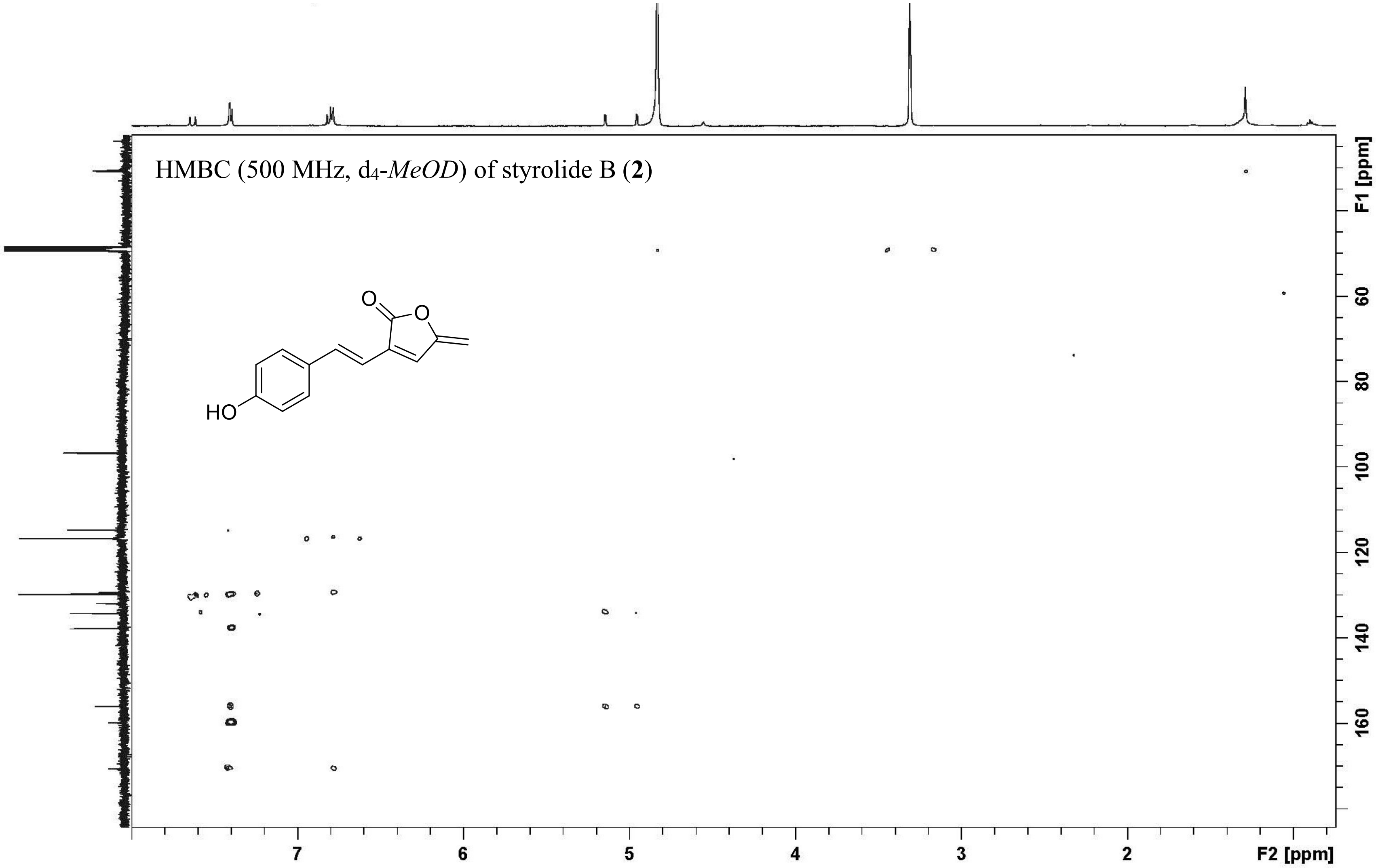
^{13}C NMR (125 MHz, d$_4$-*MeOD*) of styrolide B (**2**)



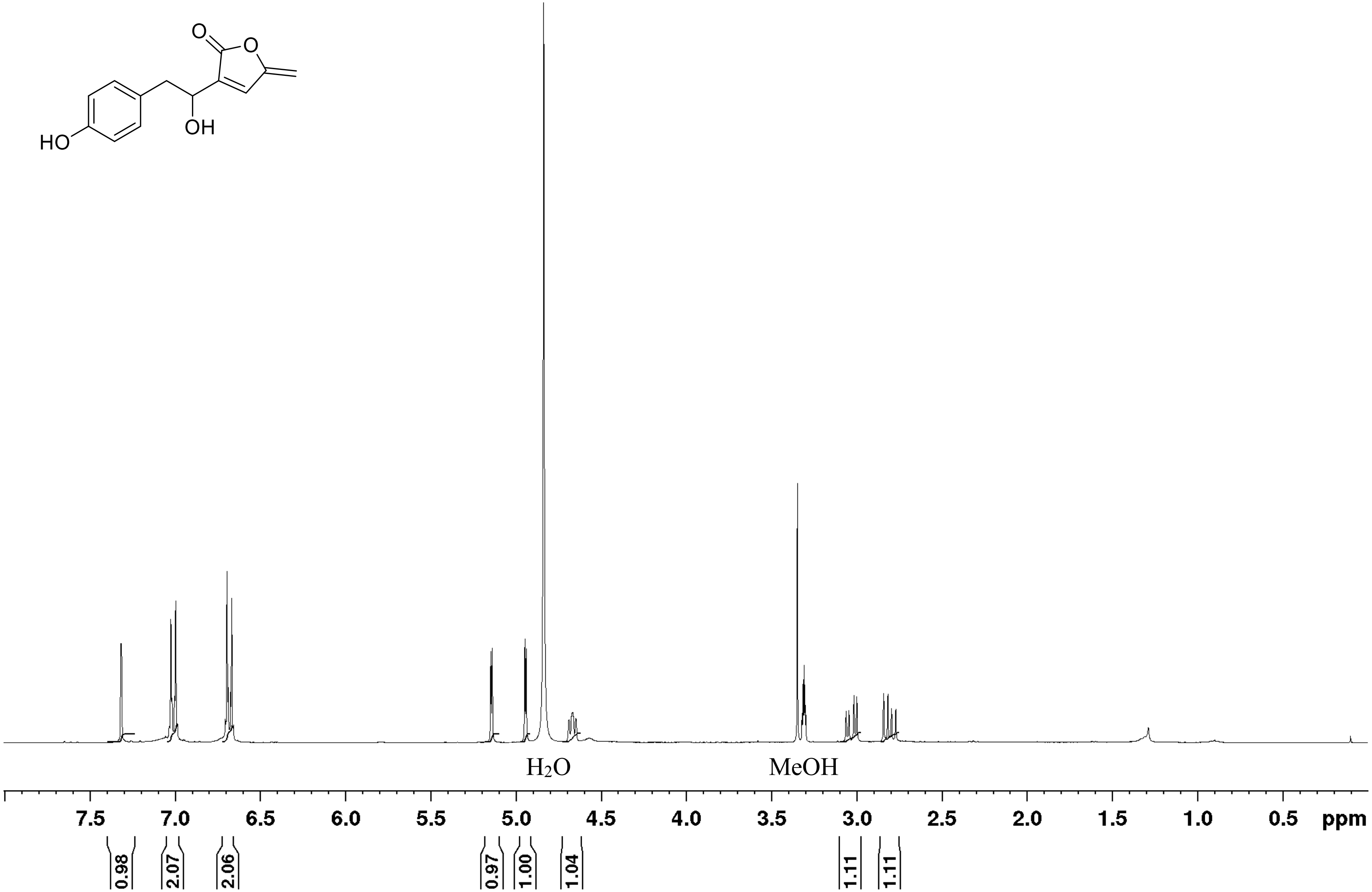
COSY (500 MHz, d_4-*MeOD*) of styrolide B (**2**)



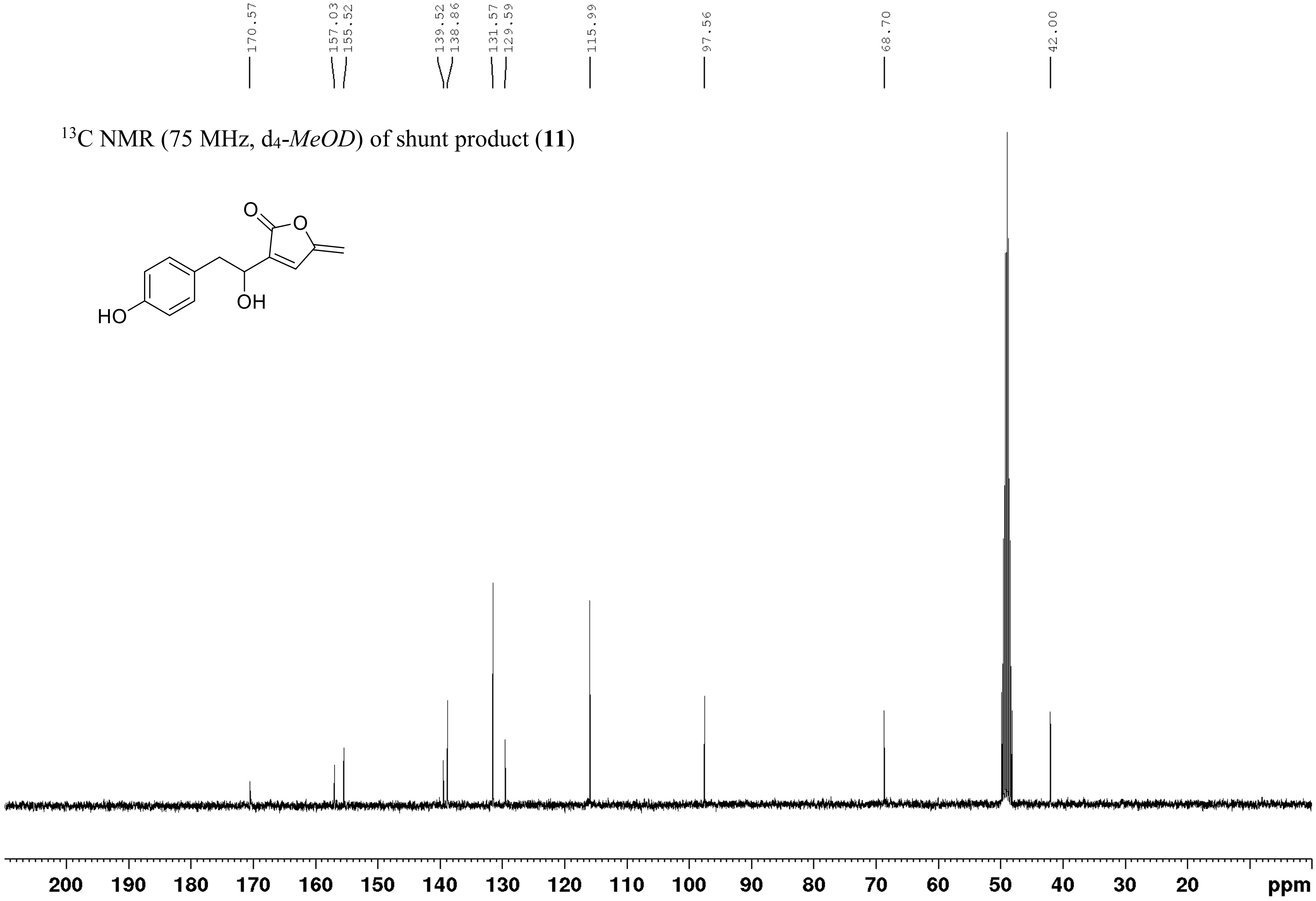
HSQC (500 MHz, d$_4$-*MeOD*) of styrolide B (**2**)

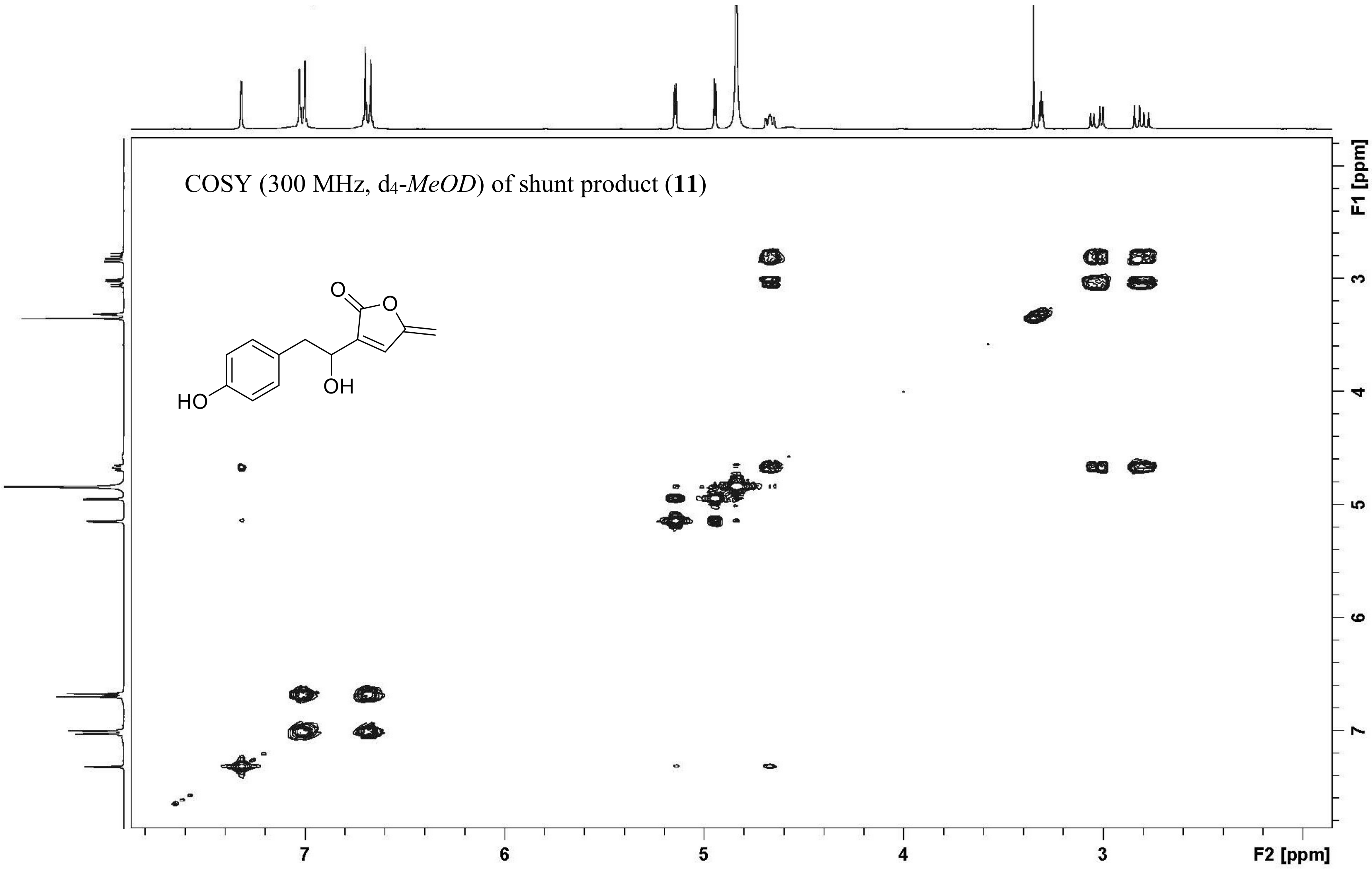

HMBC (500 MHz, d₄-MeOD) of styrolide B (2)
O
O
HO
F1 [ppm]
60
80
100
120
140
160
7
6
5
4
3
2
F2 [ppm]

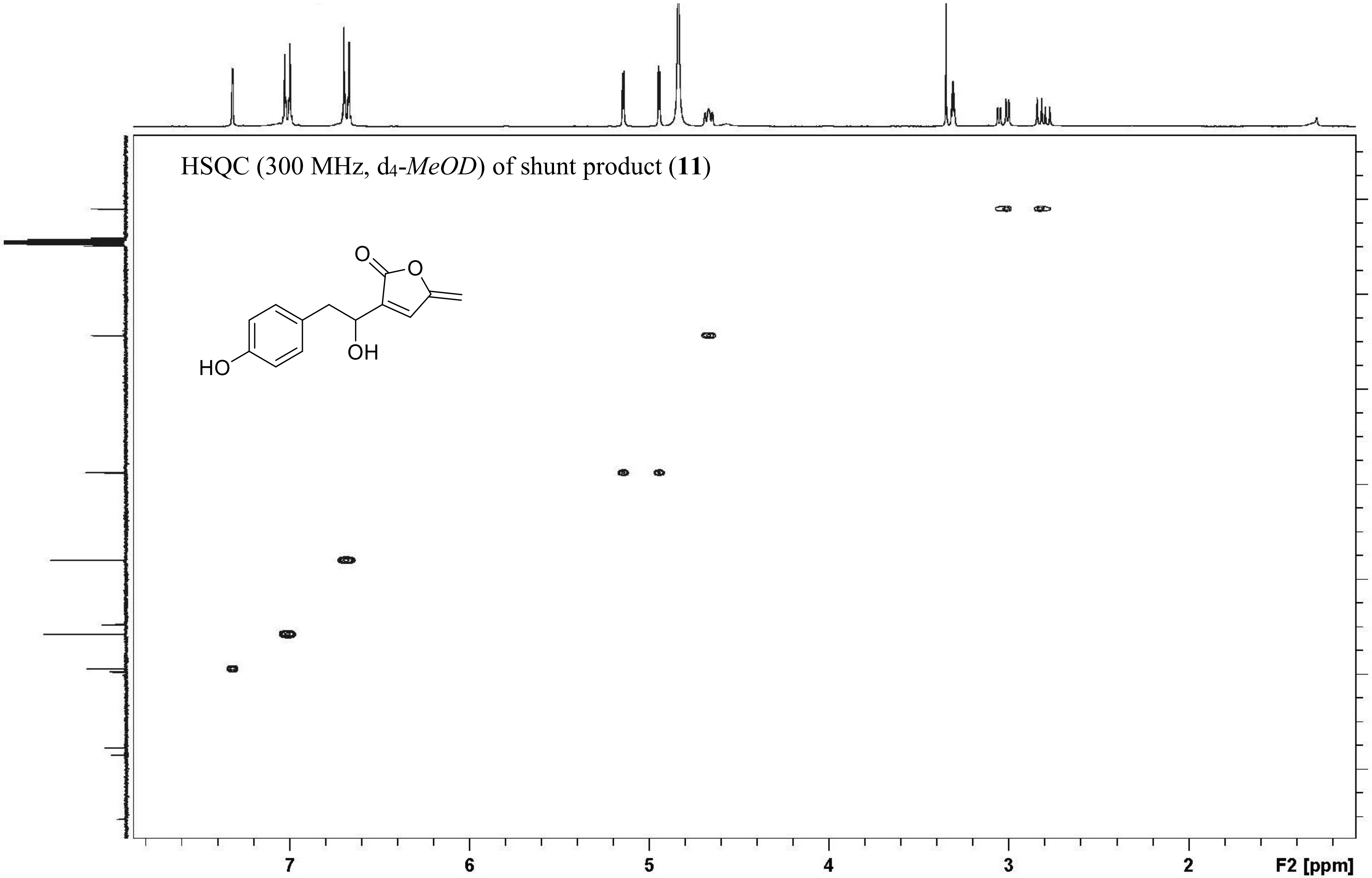
^{1}H NMR (300 MHz, d$_4$-*MeOD*) of shunt product (**11**)



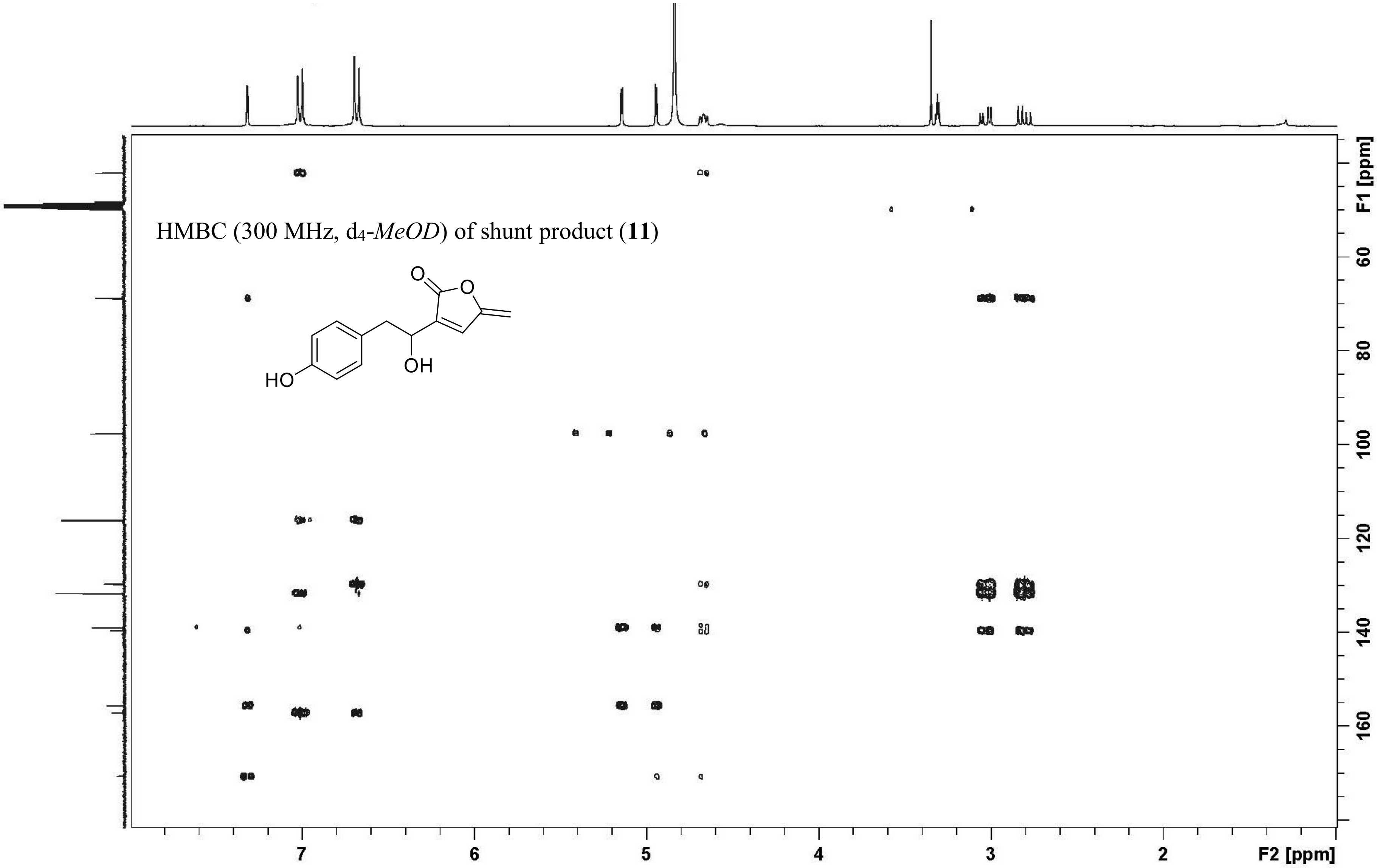
^{13}C NMR (75 MHz, d$_4$-*MeOD*) of shunt product (**11**)



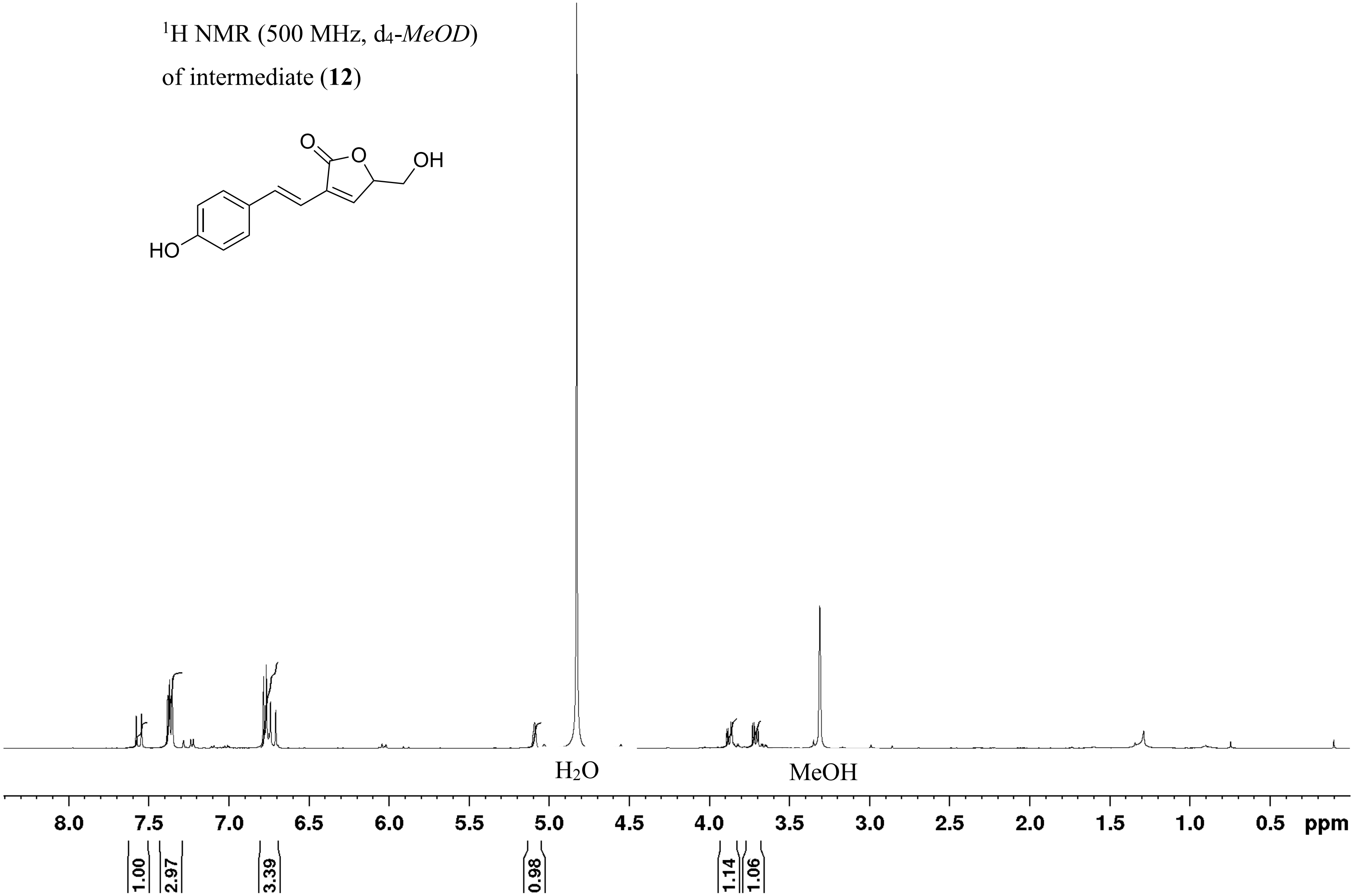

COSY (300 MHz, d$_4$-*MeOD*) of shunt product (**11**)

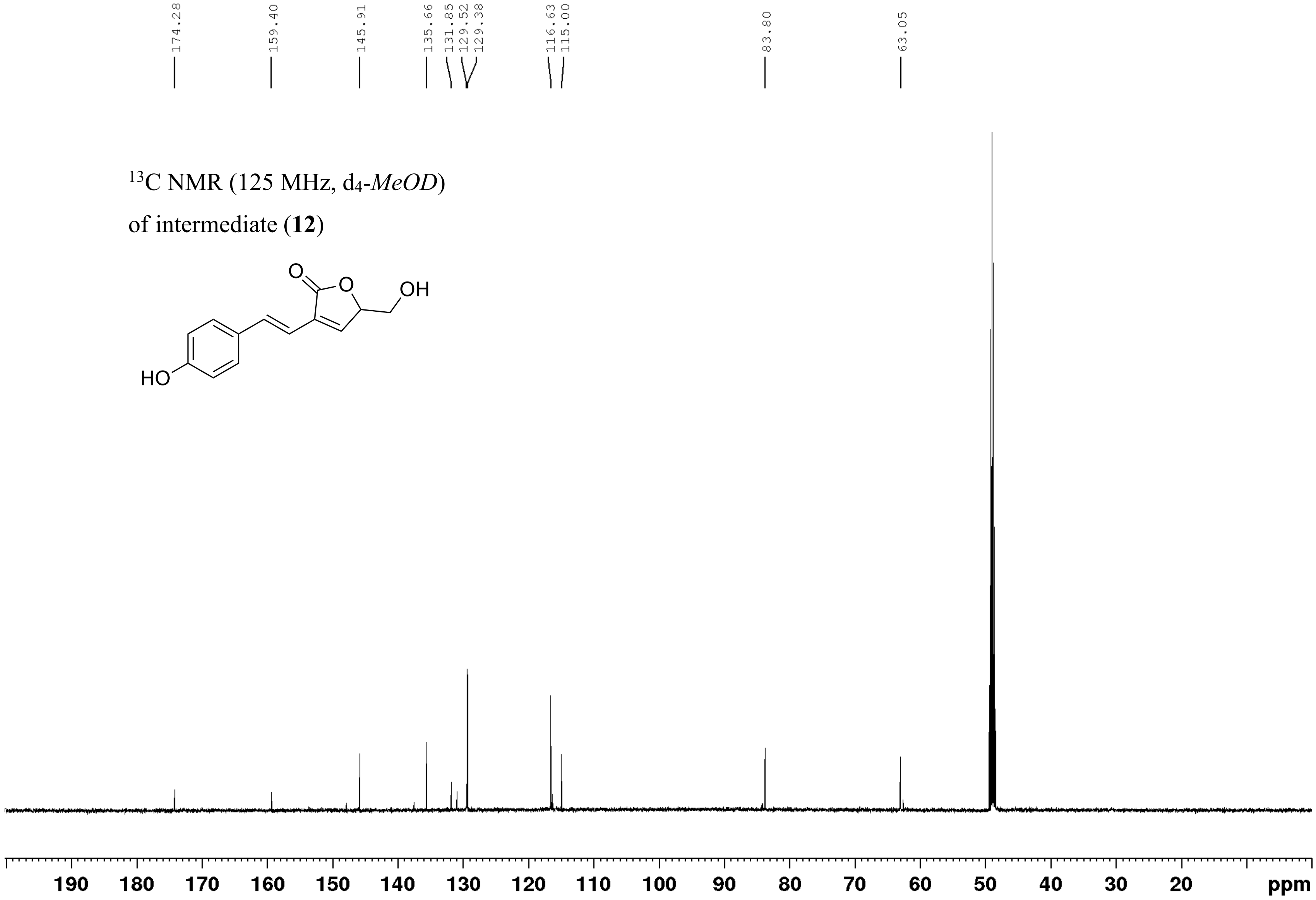


HSQC (300 MHz, d_4-*MeOD*) of shunt product (**11**)


HMBC (300 MHz, d$_4$-*MeOD*) of shunt product (**11**)

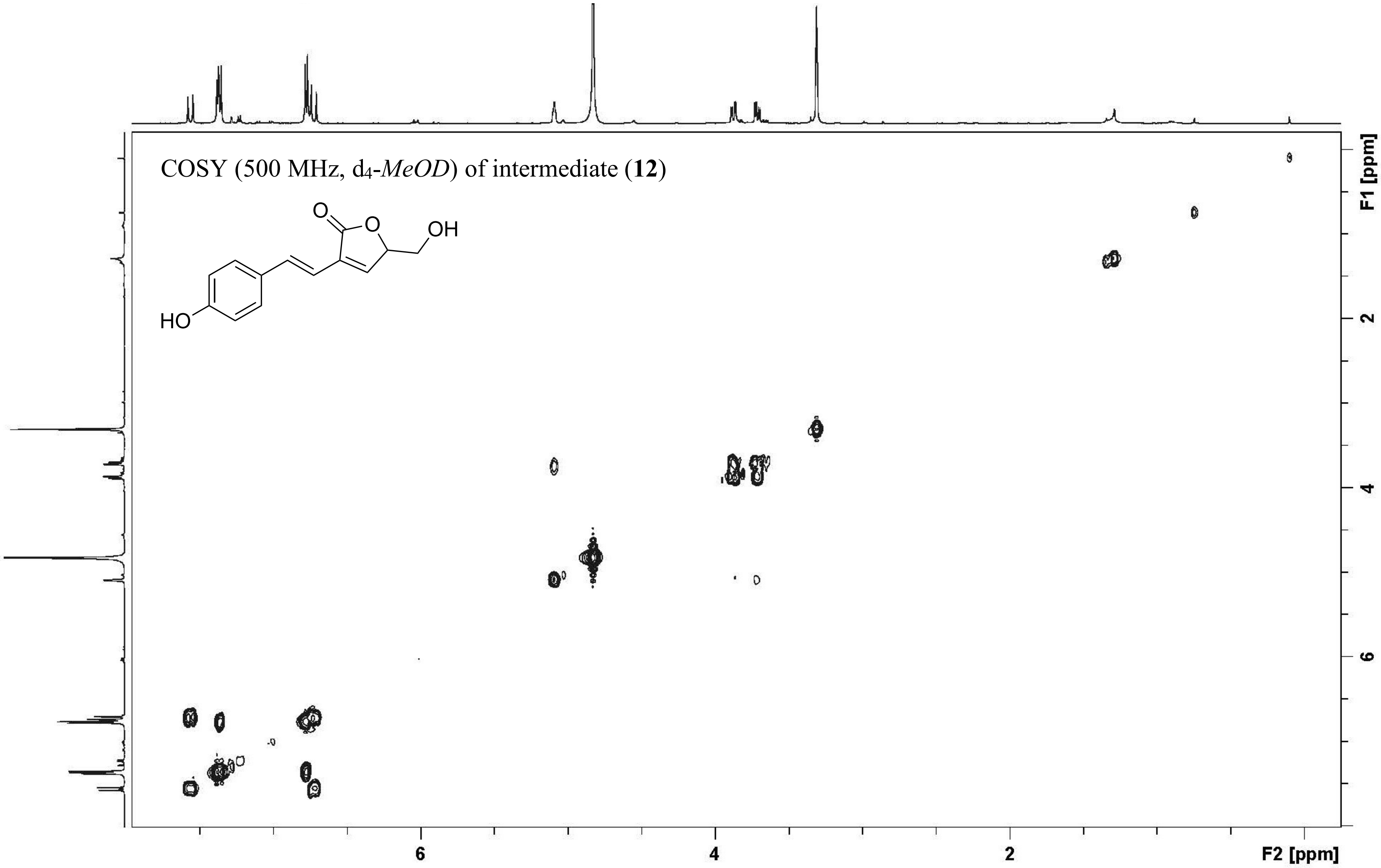
^{1}H NMR (500 MHz, d$_4$-*MeOD*)
of intermediate (**12**)



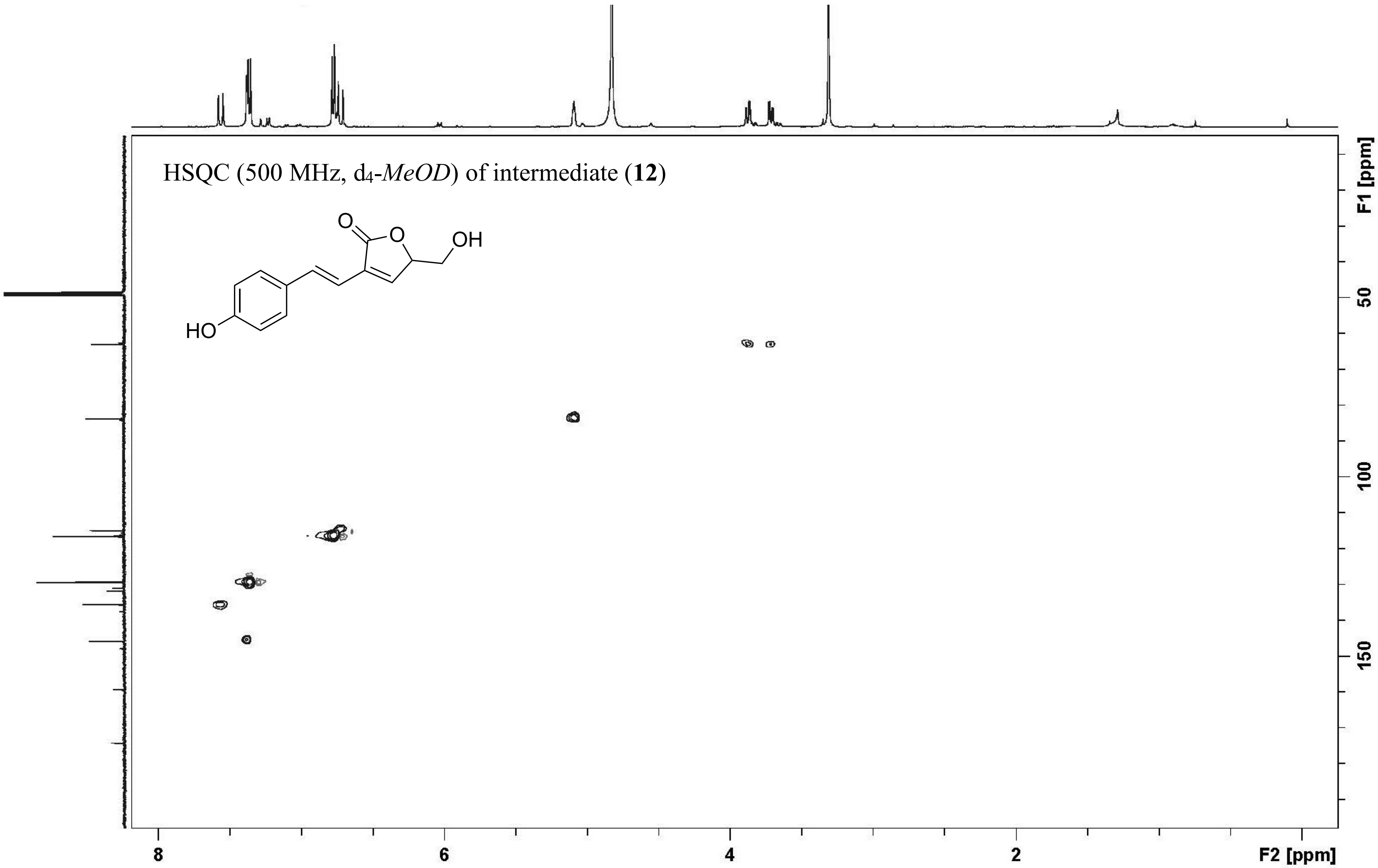


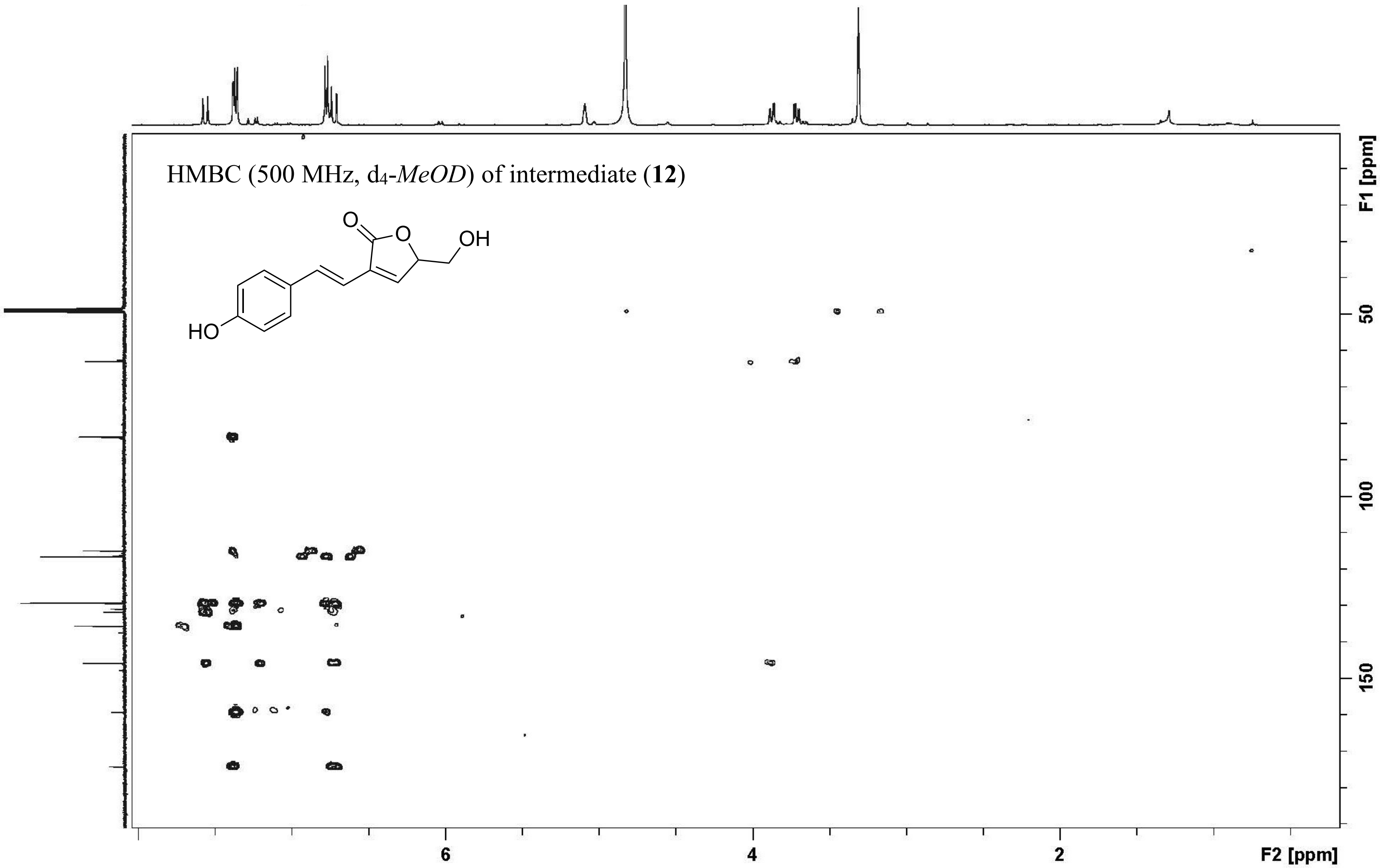
^{13}C NMR (125 MHz, d$_4$-*MeOD*)

of intermediate (**12**)

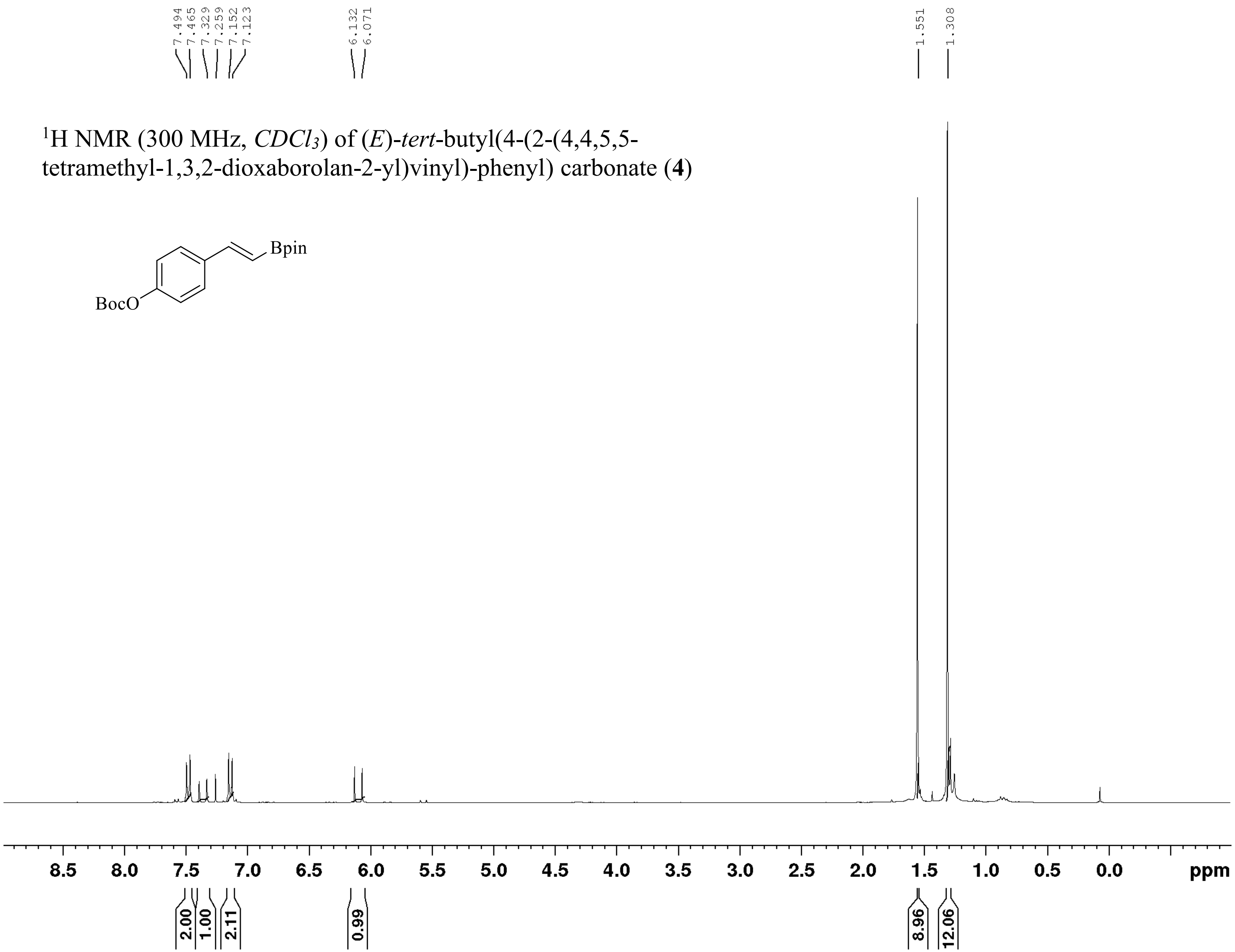


COSY (500 MHz, d_4-*MeOD*) of intermediate (**12**)


HSQC (500 MHz, d_4-*MeOD*) of intermediate (**12**)

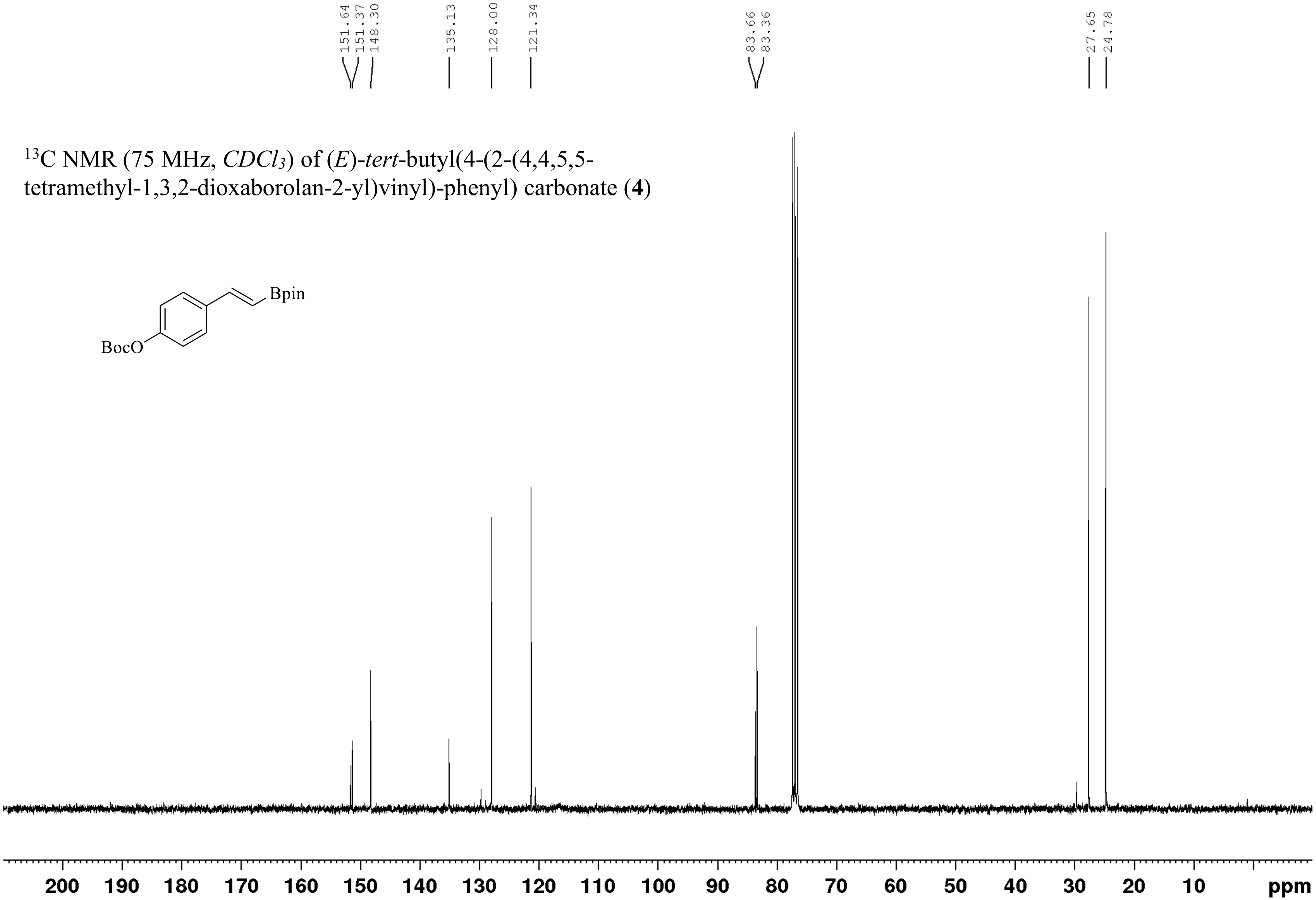


HMBC (500 MHz, d_4-*MeOD*) of intermediate (**12**)

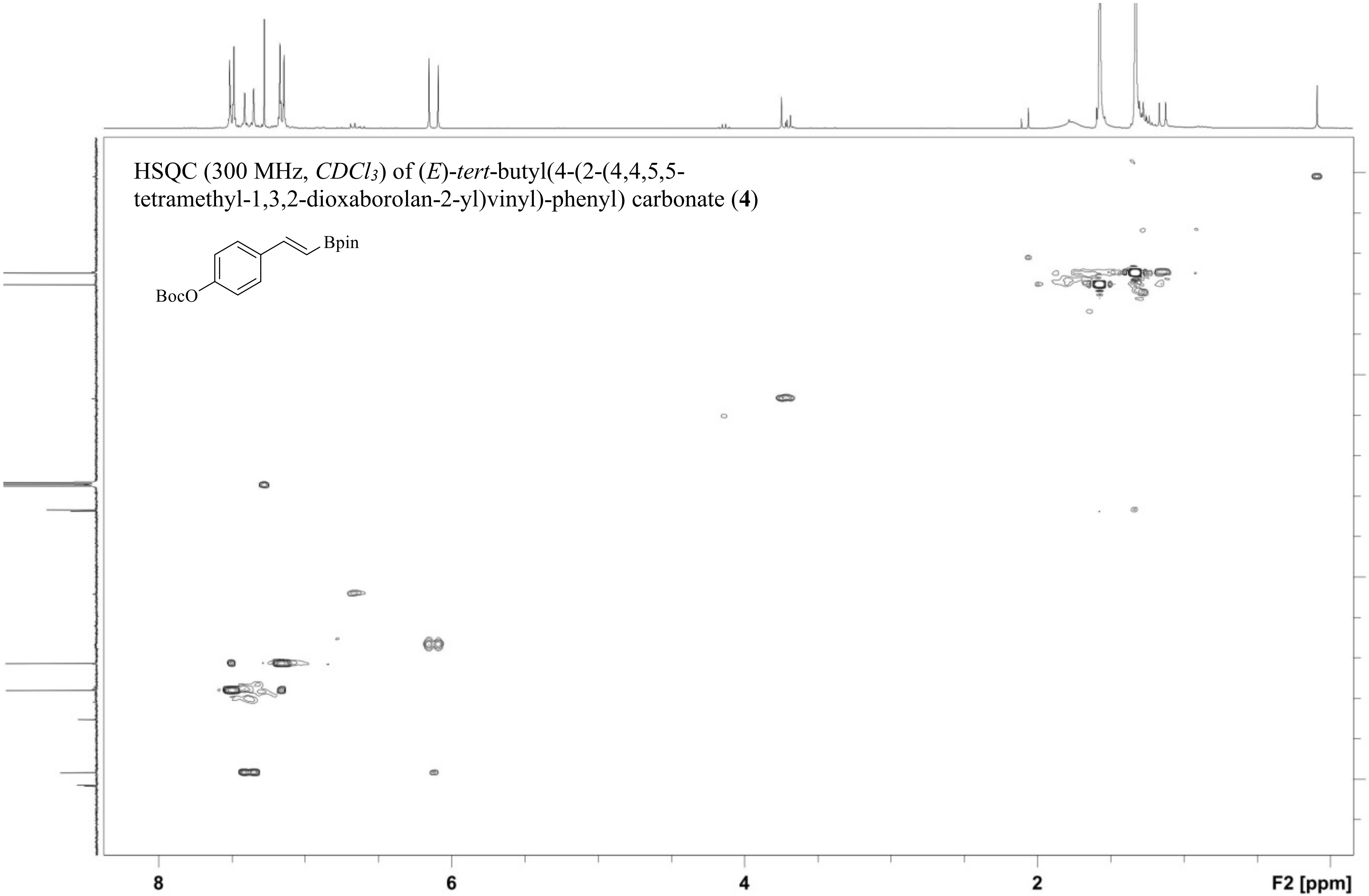


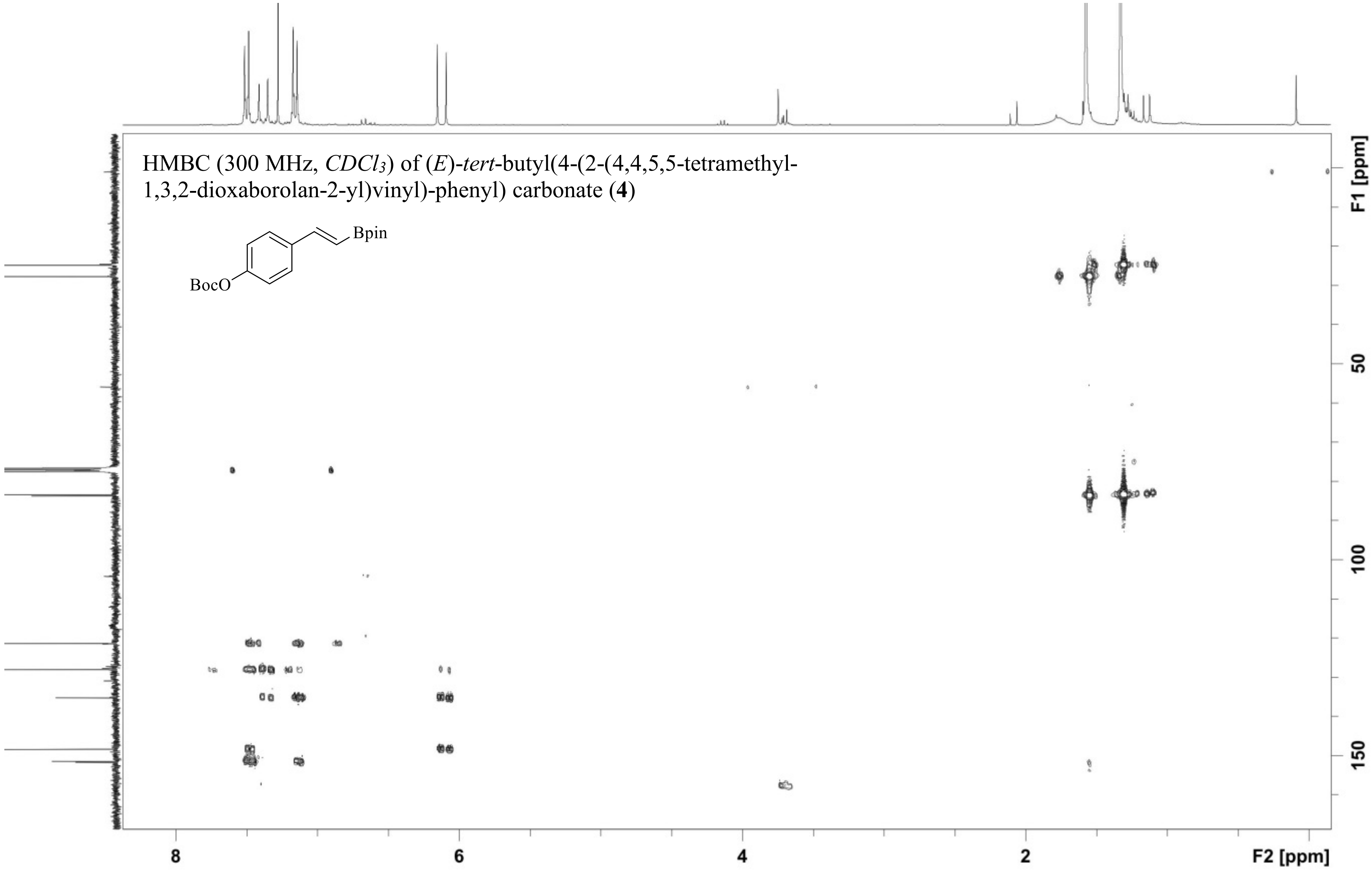
^{1}H NMR (300 MHz, *CDCl$_3$*) of (*E*)-*tert*-butyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-phenyl) carbonate (**4**)

^{13}C NMR (75 MHz, *$CDCl_3$*) of (*E*)-*tert*-butyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-phenyl) carbonate (**4**)



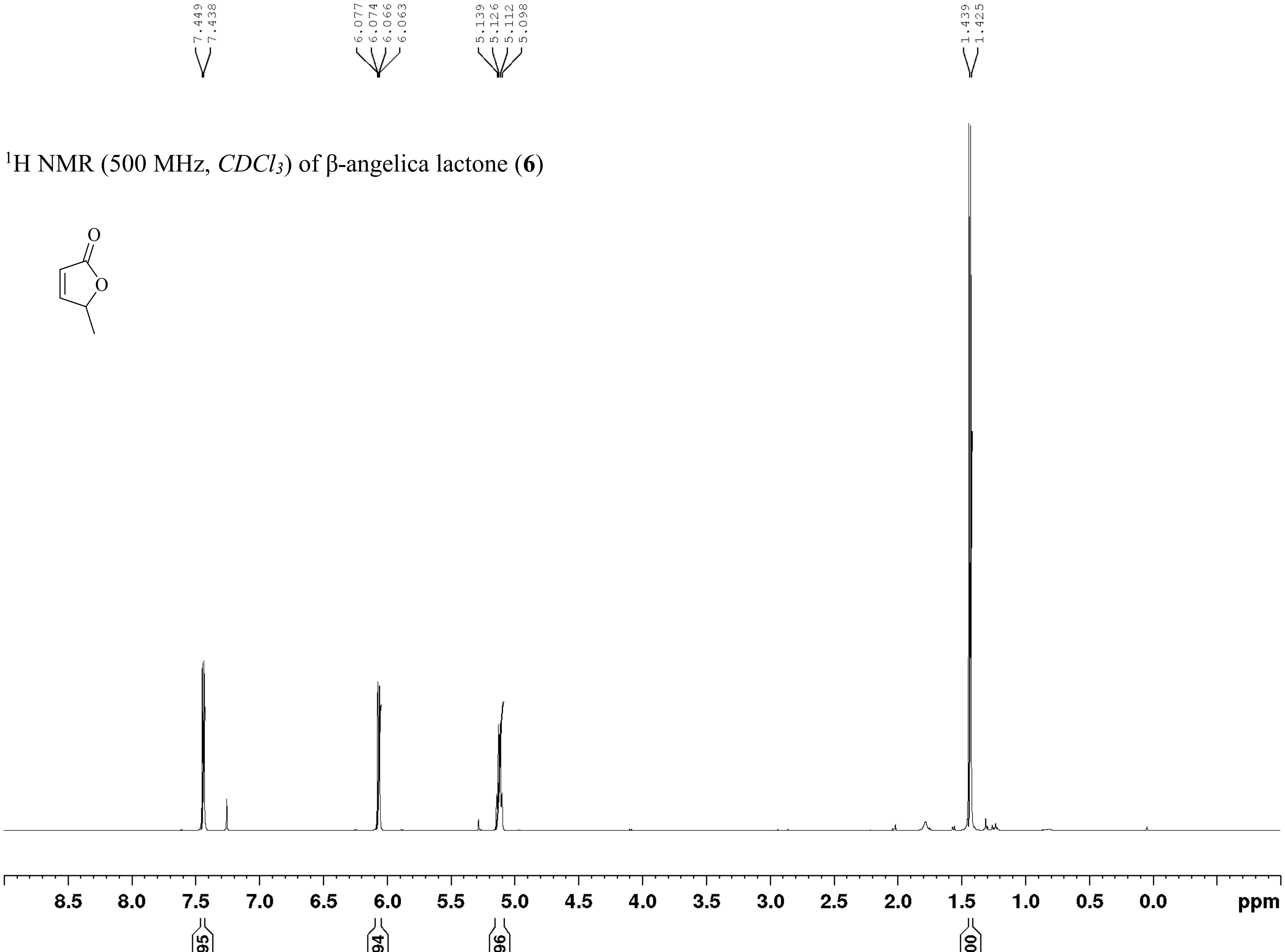
HSQC (300 MHz, *CDCl$_3$*) of (*E*)-*tert*-butyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-phenyl) carbonate (**4**)

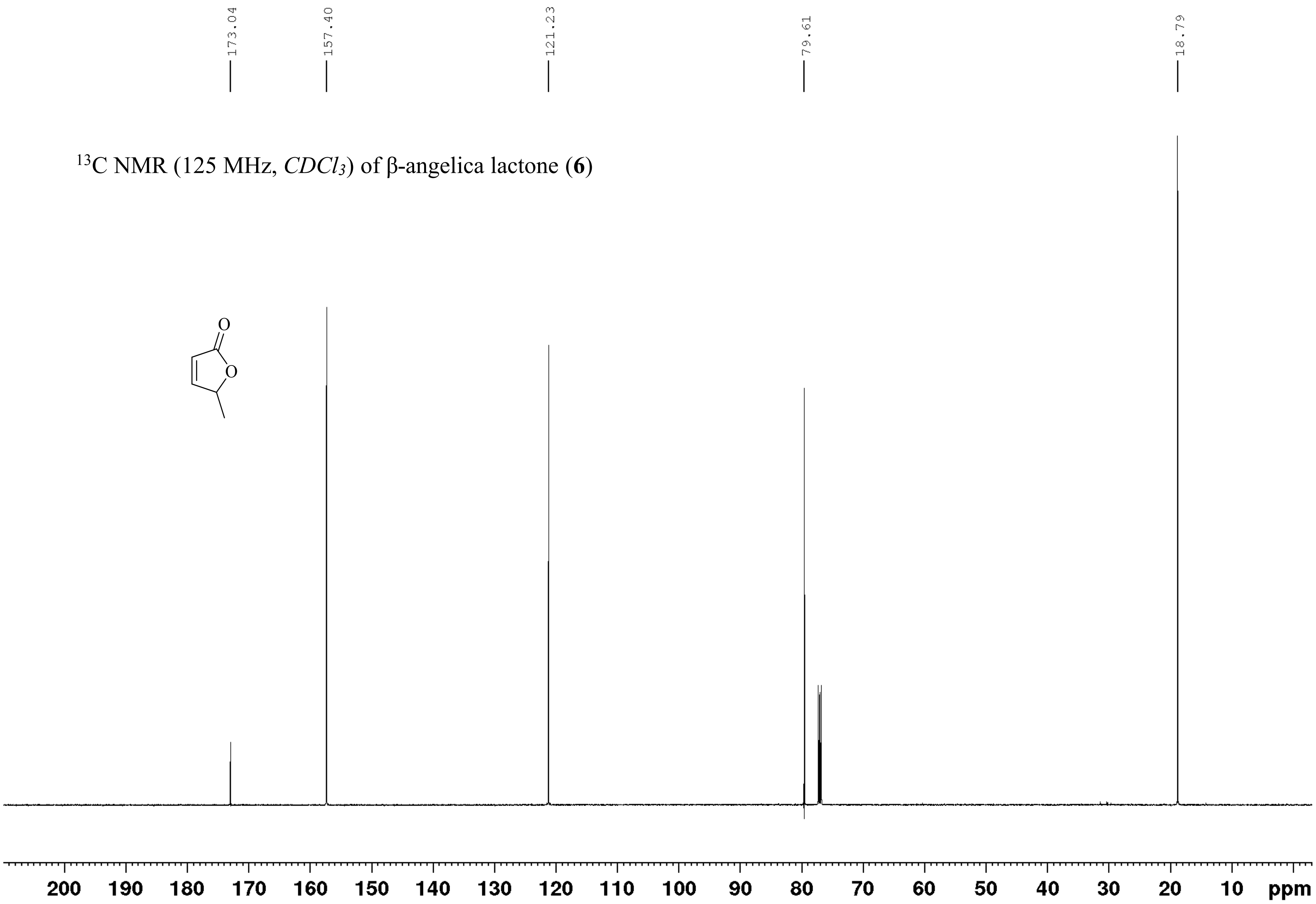




HMBC (300 MHz, *CDCl₃*) of (*E*)-*tert*-butyl(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-phenyl) carbonate (**4**)

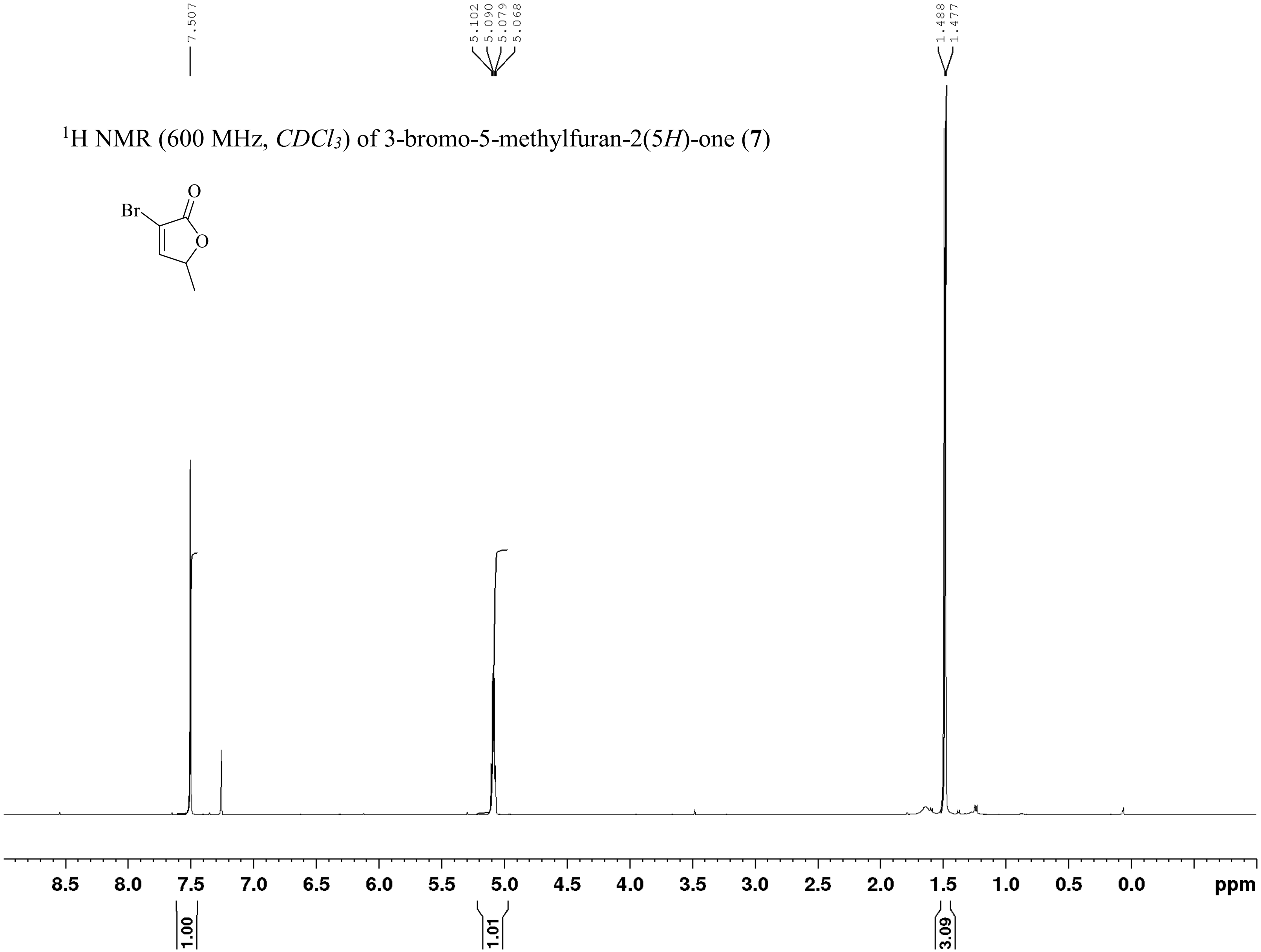
^{1}H NMR (500 MHz, *CDCl$_3$*) of β-angelica lactone (**6**)



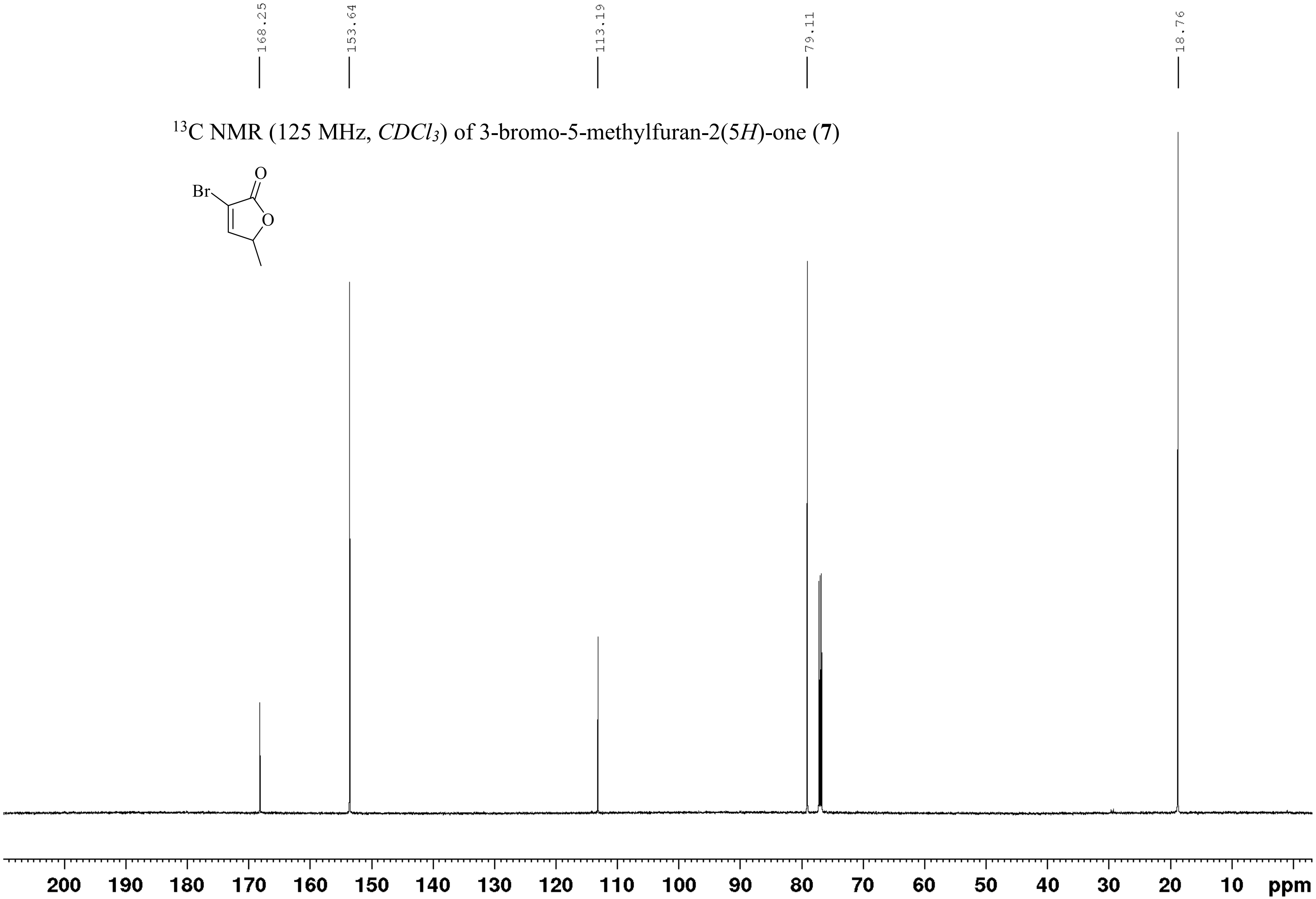


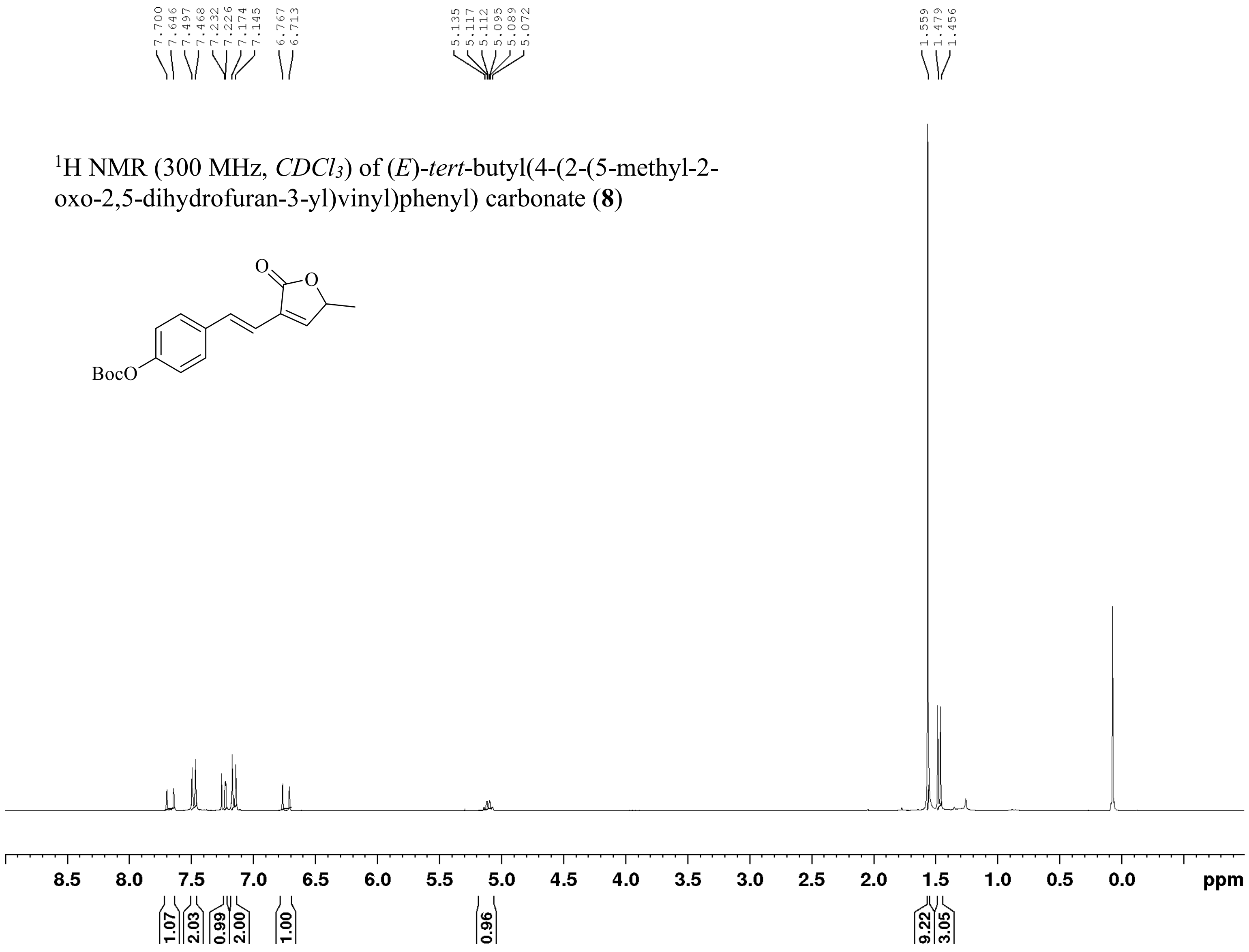
^{13}C NMR (125 MHz, *$CDCl_3$*) of β-angelica lactone (**6**)

^{1}H NMR (600 MHz, *CDCl$_3$*) of 3-bromo-5-methylfuran-2(5*H*)-one (**7**)

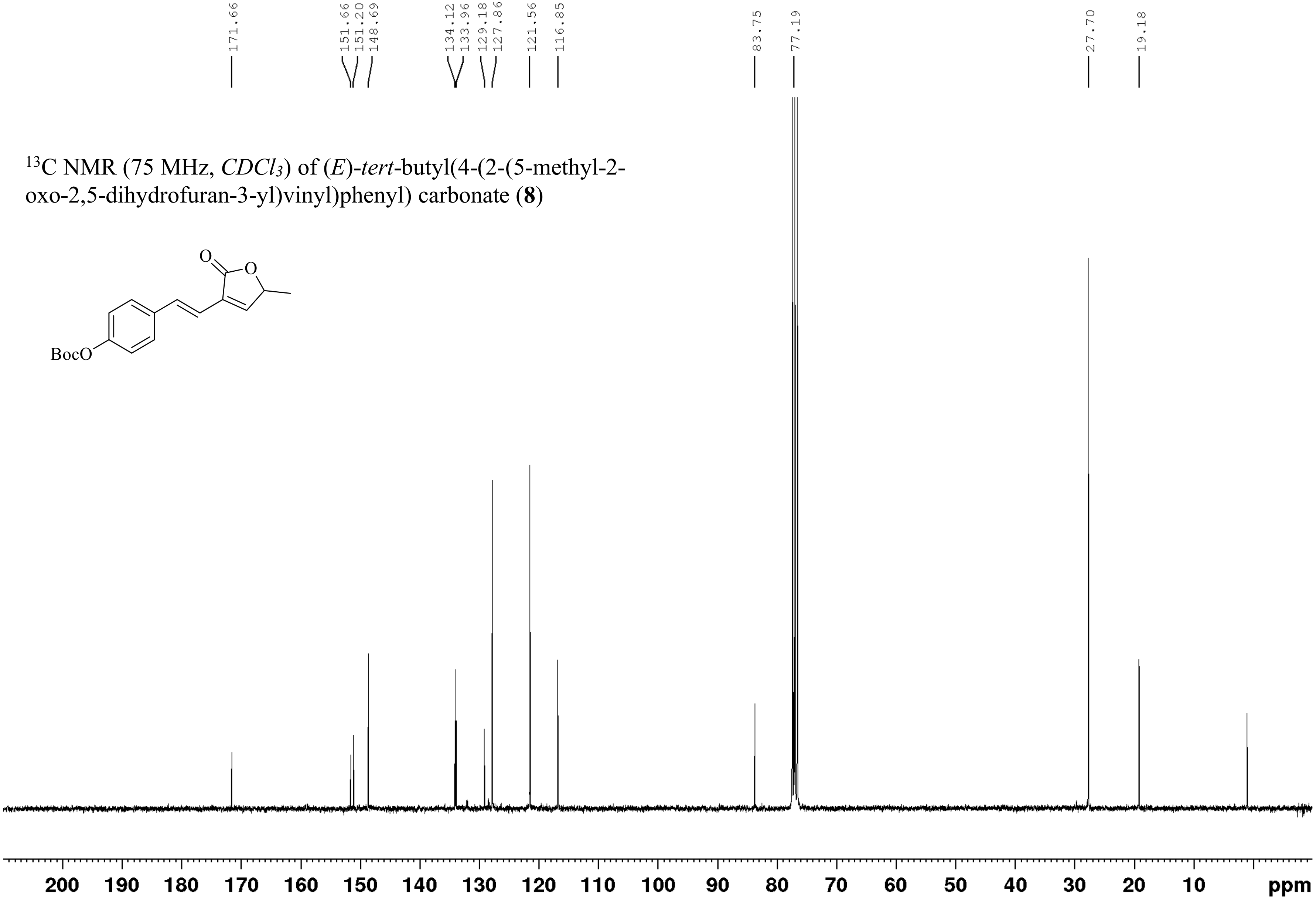


^{13}C NMR (125 MHz, *CDCl$_3$*) of 3-bromo-5-methylfuran-2(5*H*)-one (**7**)

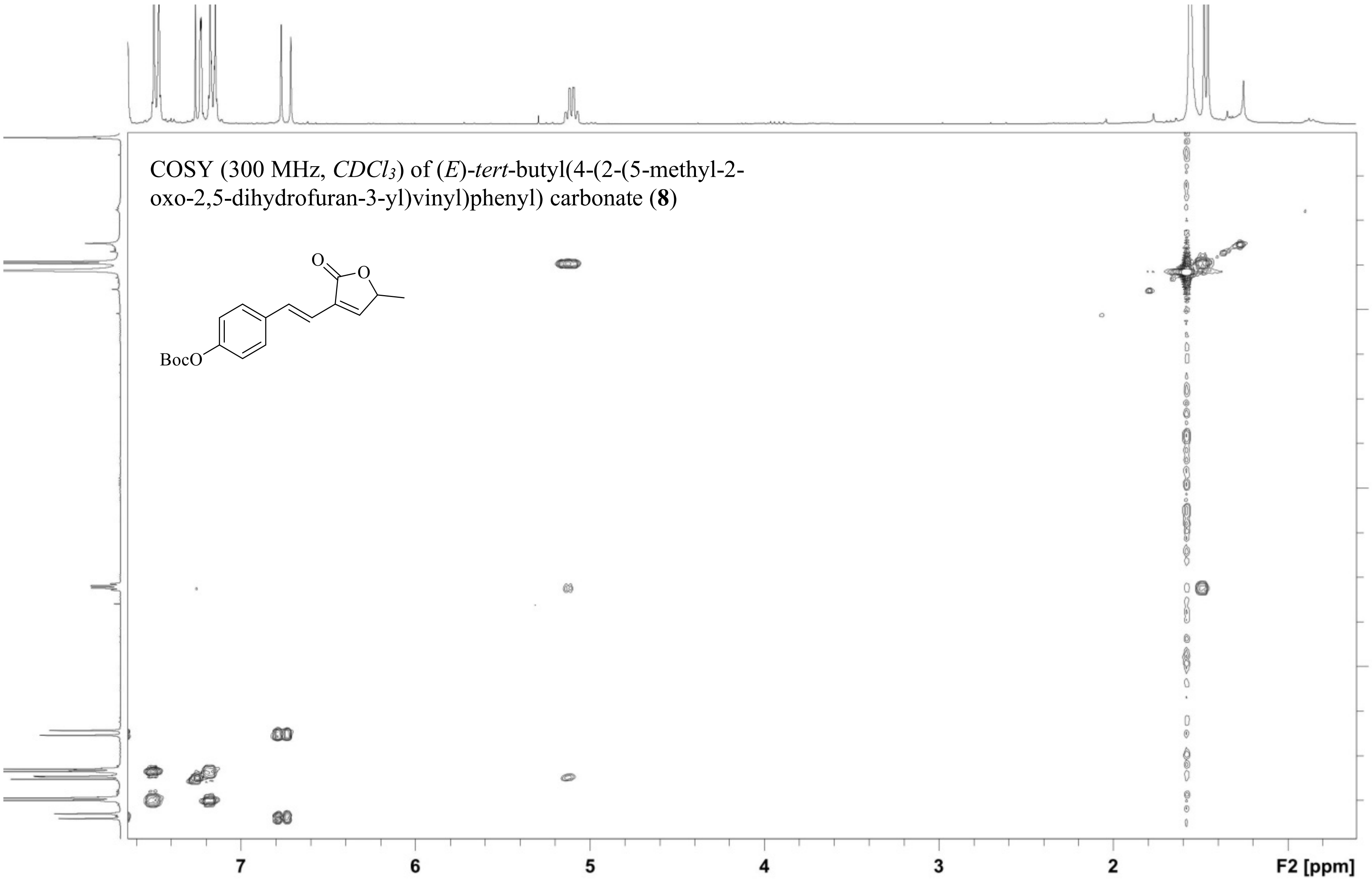




^{1}H NMR (300 MHz, *CDCl$_3$*) of (*E*)-*tert*-butyl(4-(2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)vinyl)phenyl) carbonate (**8**)

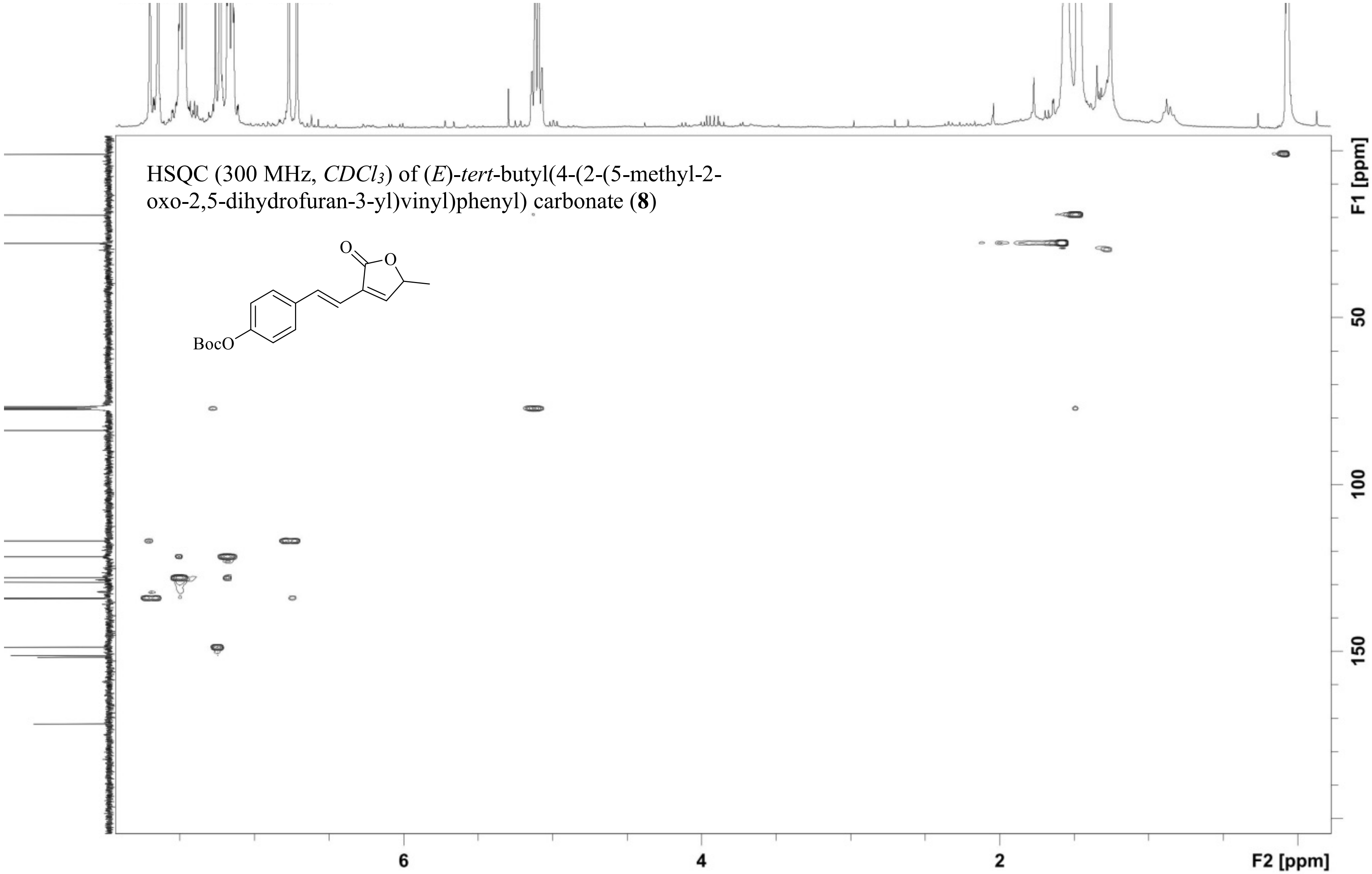


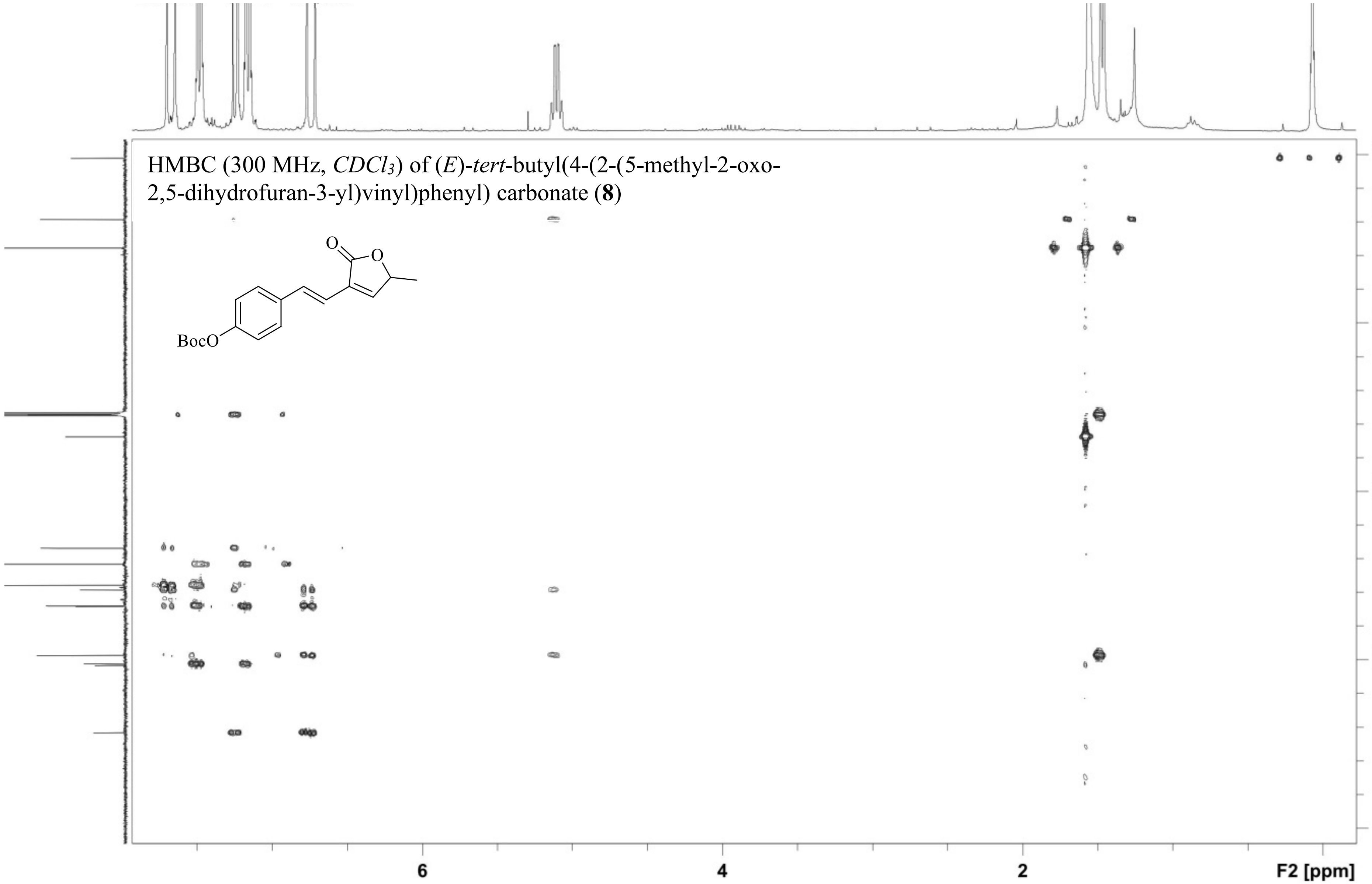
^{13}C NMR (75 MHz, *CDCl$_3$*) of (*E*)-*tert*-butyl(4-(2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)vinyl)phenyl) carbonate (**8**)



COSY (300 MHz, *CDCl₃*) of (*E*)-*tert*-butyl(4-(2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)vinyl)phenyl) carbonate (**8**)

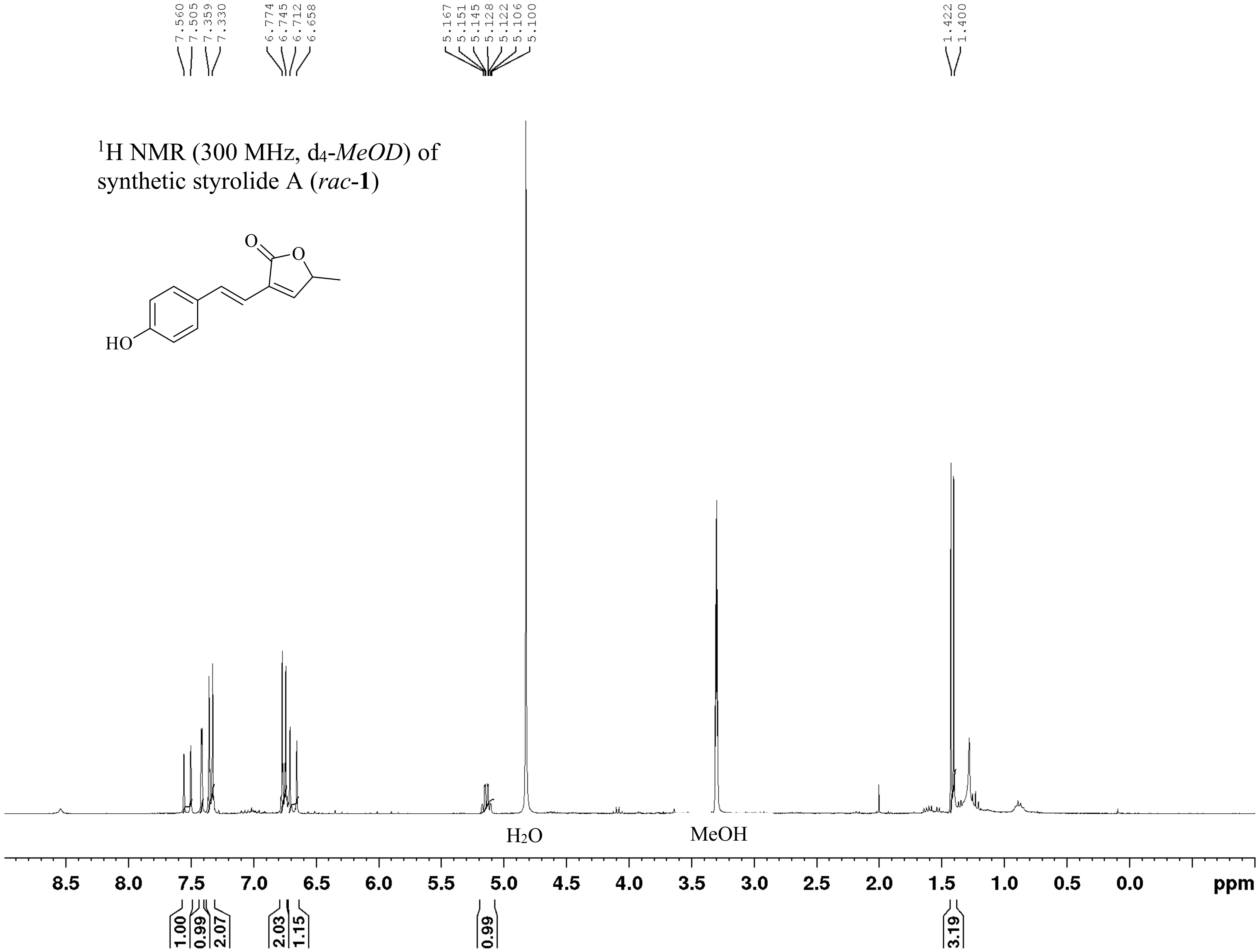
HSQC (300 MHz, *CDCl₃*) of (*E*)-*tert*-butyl(4-(2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)vinyl)phenyl) carbonate (**8**)



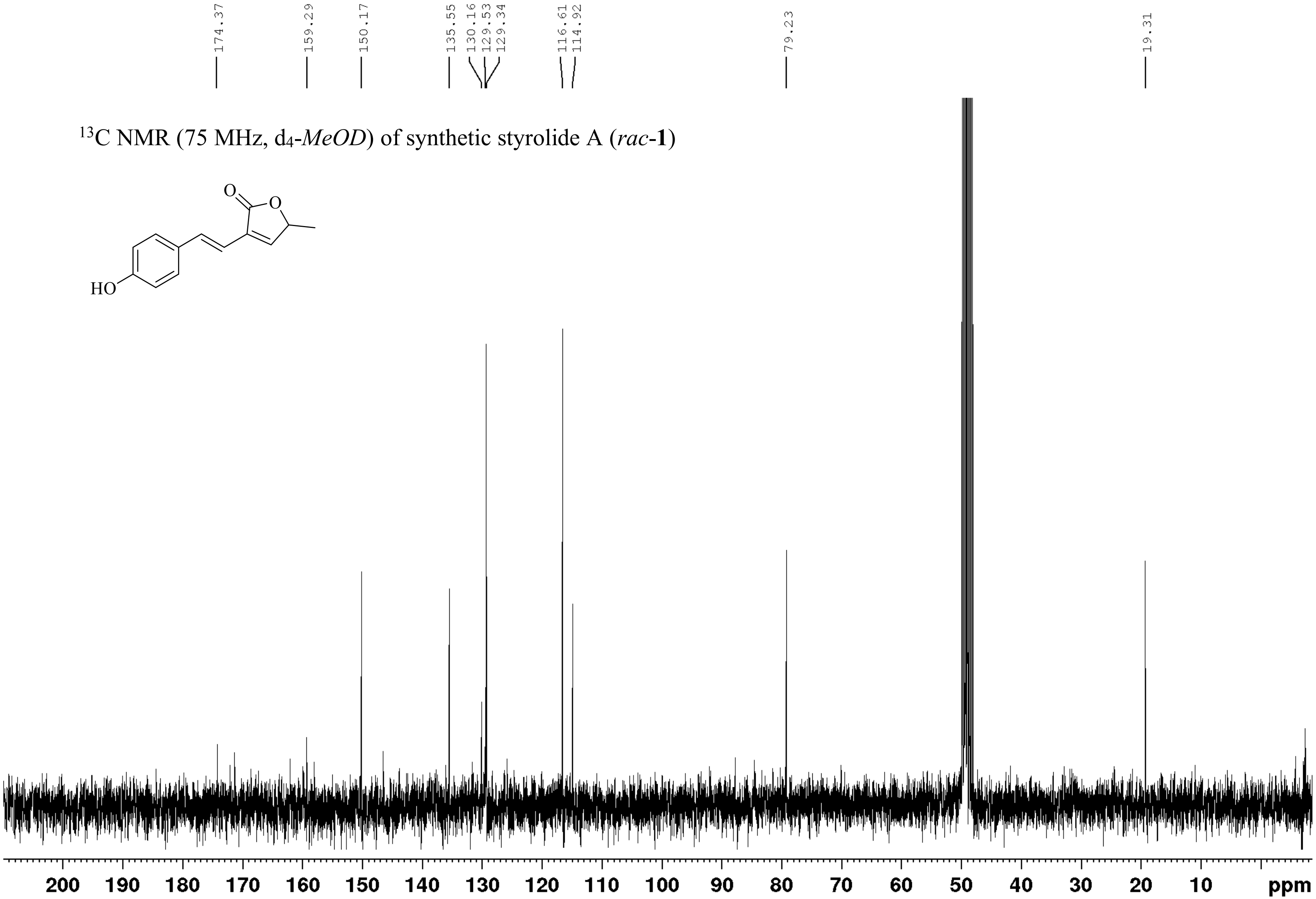


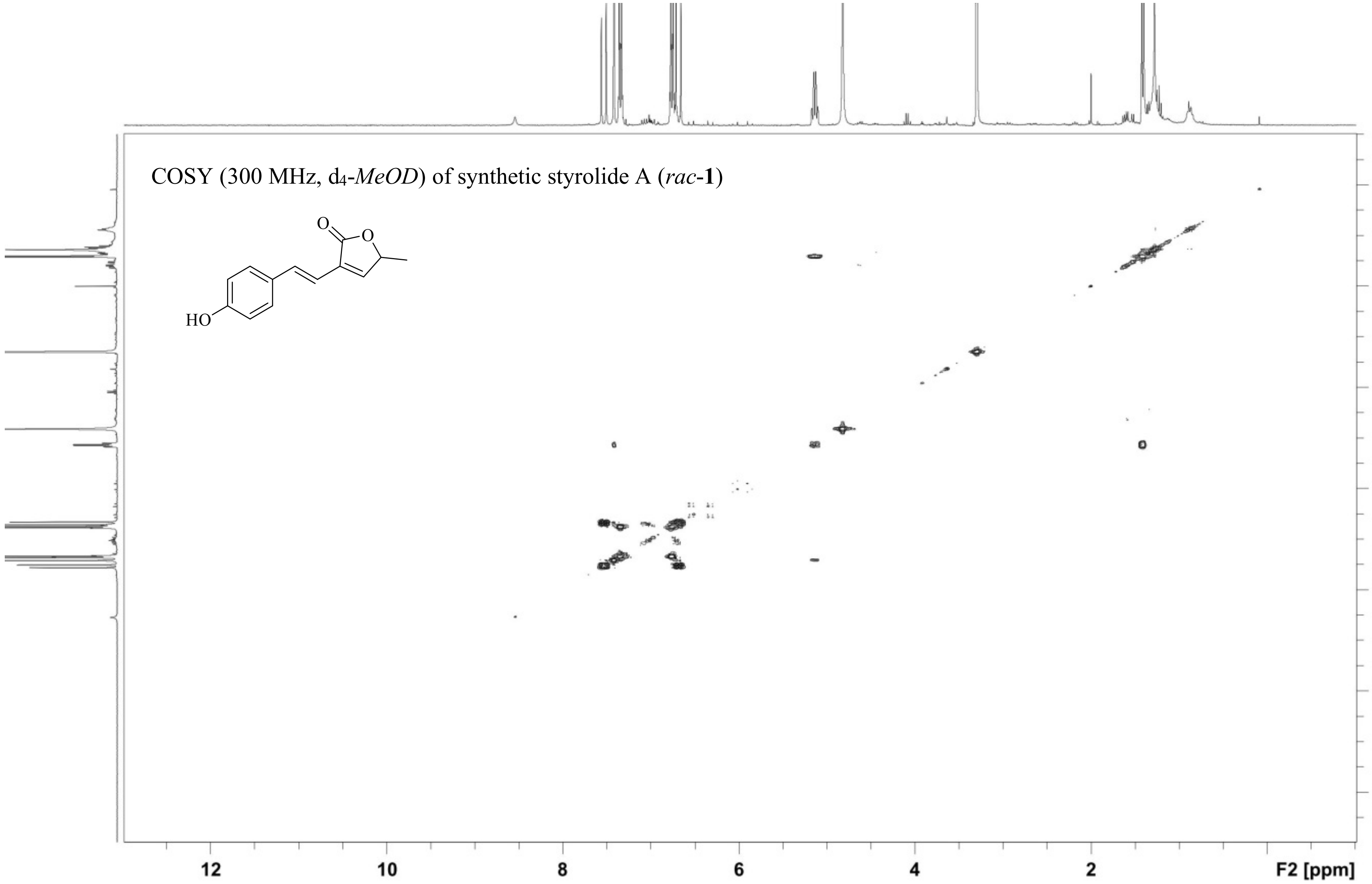
HMBC (300 MHz, *CDCl₃*) of (*E*)-*tert*-butyl(4-(2-(5-methyl-2-oxo-2,5-dihydrofuran-3-yl)vinyl)phenyl) carbonate (**8**)

^{1}H NMR (300 MHz, d_4-*MeOD*) of synthetic styrolide A (*rac*-**1**)



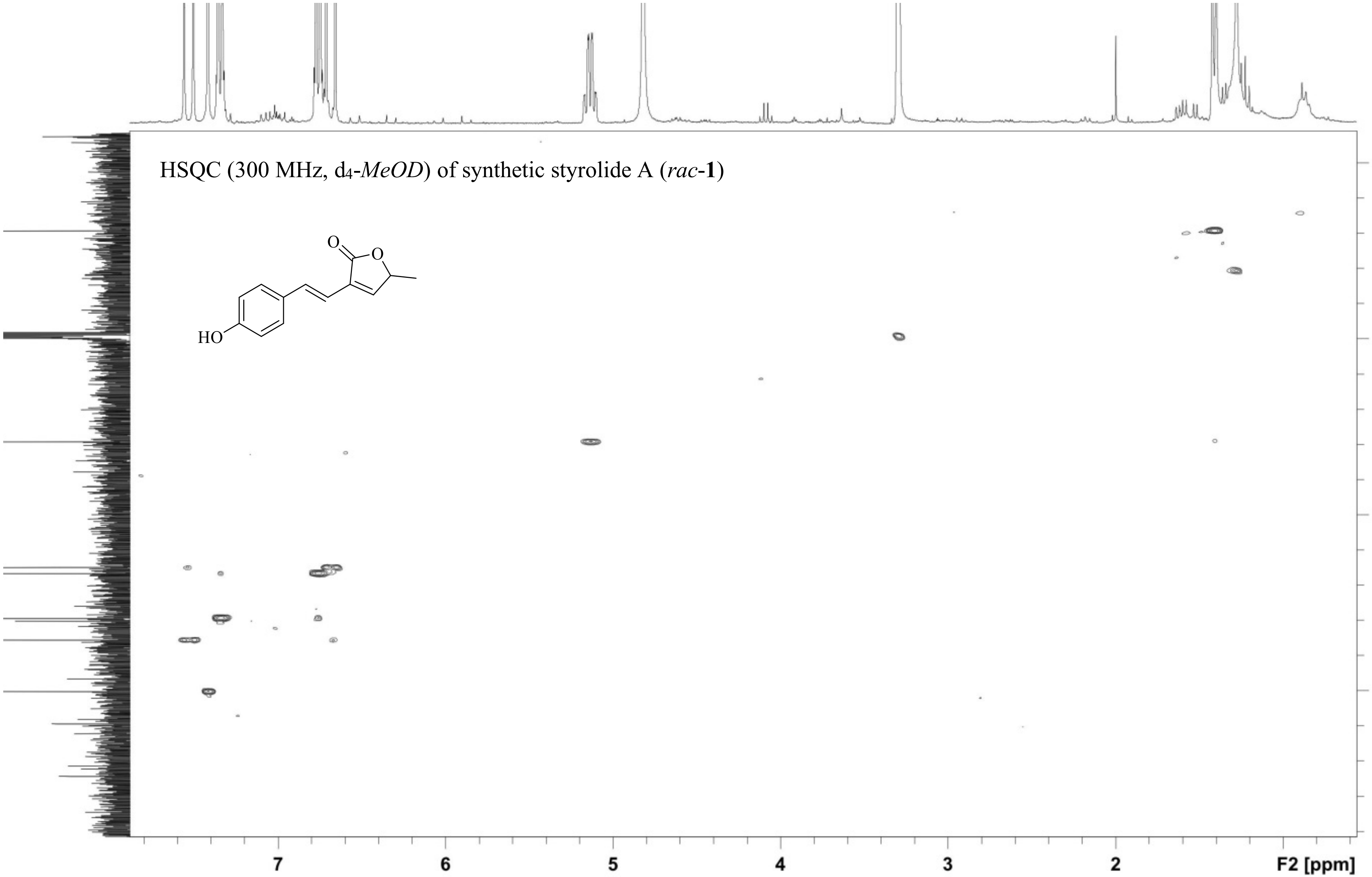
^{13}C NMR (75 MHz, d$_4$-*MeOD*) of synthetic styrolide A (*rac*-**1**)

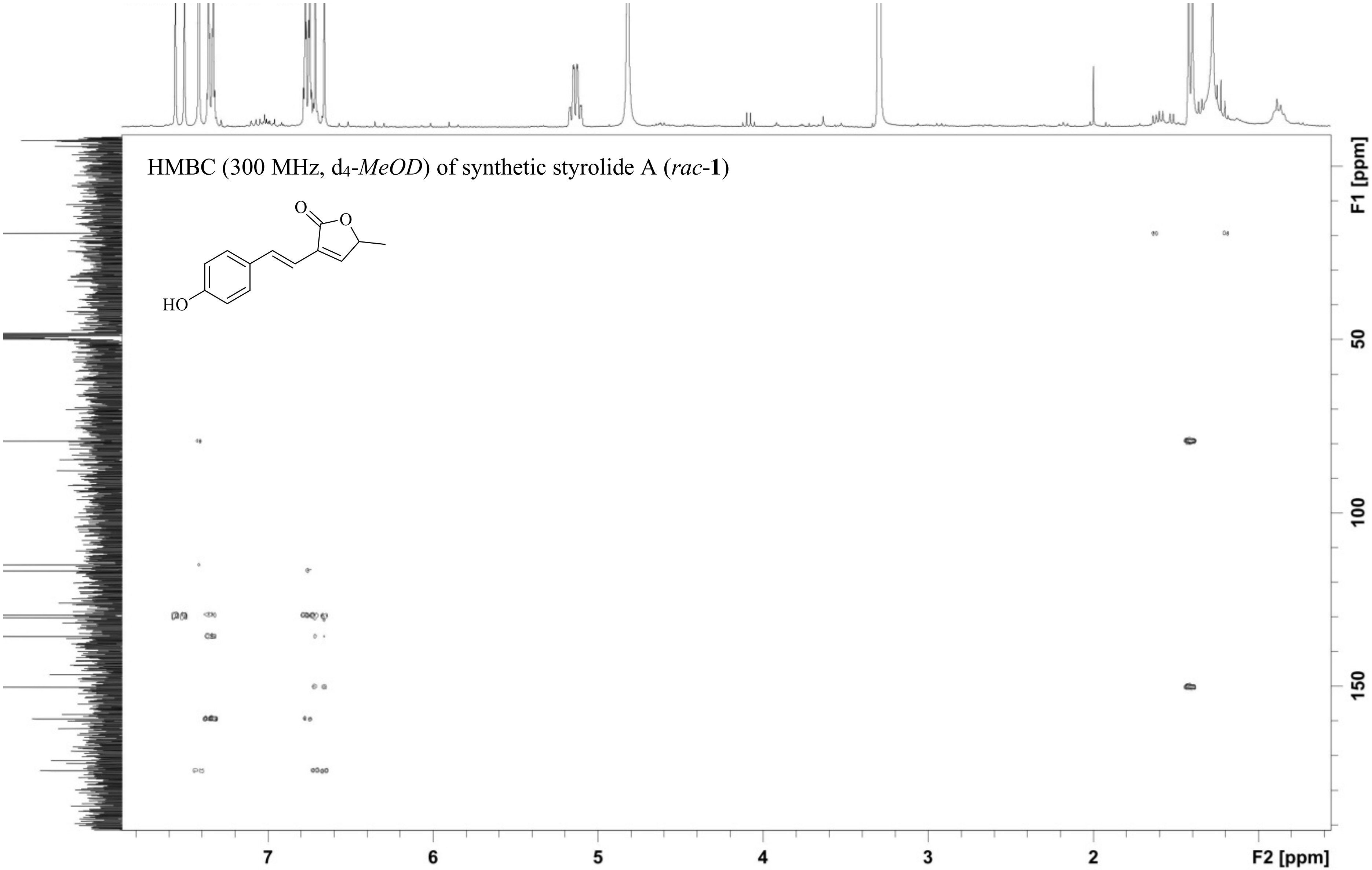




COSY (300 MHz, d$_4$-*MeOD*) of synthetic styrolide A (*rac*-**1**)

HSQC (300 MHz, d$_4$-*MeOD*) of synthetic styrolide A (*rac*-**1**)





HMBC (300 MHz, d$_4$-*MeOD*) of synthetic styrolide A (*rac*-**1**)