Supporting Information

Syntheses of (+)-30-*epi*-, (-)-6-*epi*-, (+/-)-6,30-*epi*-13,14-Didehydroxyisogarcinol and (+/-)-6,30-*epi*-Garcimultiflorone A Utilizing Highly Diastereoselective, Lewis Acid-Controlled Cyclizations

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I. General Information

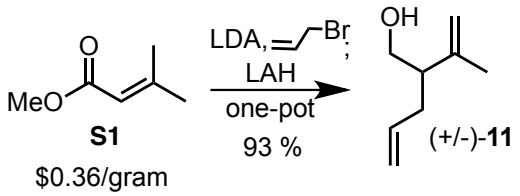
A. Instrumentation and Methods

^{1}H NMR spectra were recorded at 400 MHz or 500 MHz at ambient temperature with $CDCl_3$, MeOD, or CD_3CN (Cambridge Isotope Laboratories, Inc.) as solvents unless otherwise stated. Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, br = broad, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants. ^{13}C NMR were recorded at 100 MHz or 125.0 MHz at ambient temperature with the same solvents unless otherwise stated. Chemical shifts are reported in parts per million relative to $CDCl_3$ (^{1}H, δ 7.26; ^{13}C, δ 77.0), C_6D_6 (^{1}H, δ 7.16), DMSO-D_6 (^{1}H, δ 2.50; ^{13}C δ 39.4), CD_3OD (^{1}H, δ 3.31, 4.78; ^{13}C, δ 49.3) or CD_2O_2 (^{1}H, δ 10.35; ^{13}C δ 165.5). All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer. High-resolution mass spectra were obtained in the Boston University Chemical Instrumentation Center using a Waters Q-TOF mass spectrometer. Melting points were recorded on a Mel-temp (Laboratory Devices). Analytical thin layer chromatography was performed using 200-400 mesh silica gel (Scientific Absorbents, Inc.). Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise noted. Analytical LC-MS experiments were performed using a Waters Acquity UPLC (Ultra Performance Liquid Chromatography) with a Binary solvent manager, SQ mass spectrometer, Water 2996 PDA (PhotoDiode Array) detector, and Evaporative Light Scattering Detector (ELSD). An Acquity UPLC BEH C18 1.7 μm column was used for analytical UPLC-MS. Preparative HPLC purification was performed on a Gilson PLC 2020 Personal Purification System. Optical rotations were recorded on an AUTOPUL III digital polarimeter at 589 nm and are recorded as $[\alpha]_D^{22}$ (concentration in grams/100 mL solvent). A CHIRALPAK® AD-H [Chiral Technologies Inc., 150 x 4.60 mm (L x I.D.)] column was used for enantiomeric excess determination. A Scilligence ELN was used for experimental procedure planning.

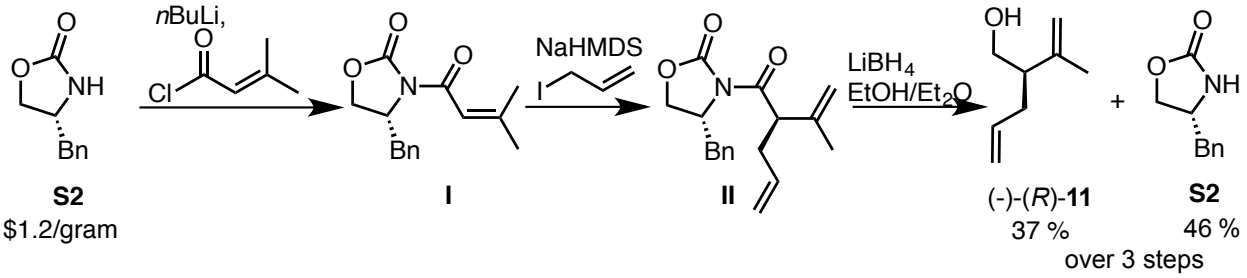
B. Reagents and Solvents

HPLC grade tetrahydrofuran, methylene chloride, diethyl ether, toluene, acetonitrile, and benzene were purchased from Fisher and VWR and were purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology, Inc.). Other ACS grade solvents for chromatography were purchased from Clean Harbors. All other reagents and relevant catalysts were purchased from Sigma-Aldrich, Acros, Alfa Aesar, and Strem Chemicals. Diisopropylamine was distilled over KOH before use. Phloroglucinol was purchased from Sigma-Aldrich. 3,3-Dimethylacrylate was purchased from eNovation Chemicals and (*R*)-4-benzyl-2-oxazolidinone was purchased from AK Scientific.

II. Experimental Procedures and Compound Characterization

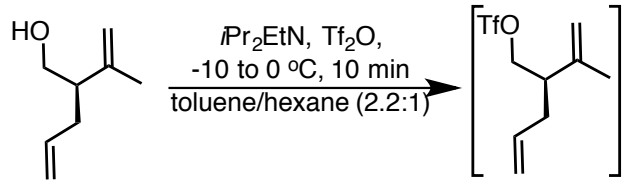


2-(Prop-1-en-2-yl)pent-4-en-1-ol (+/-)-11: Racemic alcohol (+/-)-**11** was prepared according to a known protocol;[S1] spectroscopic data for (+/-)-**11** were found to be identical with those reported in the literature.[S1]



(-)-(*R*)-2-(Prop-1-en-2-yl)pent-4-en-1-ol (-)-(*R*)-11:[S1,S2] *n*-Butyllithium (82.7 mL, 2.5 M in THF) was added dropwise to a stirred solution of oxazolidinone **S2** (34.9 g, 197 mmol) in THF (643 mL). The orange reaction mixture was stirred for 10 min which was followed by dropwise addition of 3,3-dimethylacryloylchloride (23.7 mL, 213 mmol). The reaction mixture [now yellow in color] was warmed to 0 ^{o}C and then stirred for 30 min at which point TLC analysis indicated completion. Excess acid chloride was hydrolyzed by the addition of aqueous 1 M K_2CO_3 (125 mL). The reaction was then warmed to room temperature and allowed to stir for 1.5 h. Water (100 mL) was added and THF was removed *in vacuo*. The aqueous solution was then poured into a separatory funnel and extracted with CH_2Cl_2 (3 x 250 mL). The combined organic layers were washed with water (1 x 200 mL) and brine (1 x 200 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford intermediate **I** (51.1 g, >98 % purity by ^{1}H NMR analysis) as a white solid. Compound **I** was then dissolved in THF (656 mL), and the solution was cooled to -78 ^{o}C. A solution of NaHMDS (200 mL, 1.0 M in THF) was added dropwise via cannula, and

the reaction mixture was then stirred for 45 min. Allyl iodide (18 mL, 197 mmol) was added *via* syringe, and the reaction mixture was stirred for an additional 3 h. The reaction was then quenched with a saturated aqueous solution of NH_4Cl (500 mL), warmed to room temperature, and extracted with Et_2O (3 x 500 mL). The combined organic extracts were washed with water (1 x 500 mL) and brine (1 x 500 mL), dried ($MgSO_4$), and concentrated *in vacuo* to provide a crude oil (50 g). Purification by column chromatography (silica gel, 2-9 % EtOAc/hexanes) afforded allylation adduct **II** as a crude oil (45.5 g, >65 % purity as determined by ^{1}H NMR analysis, product **II** $\mathbf{R_f}$ = 0.54 and byproduct $\mathbf{R_f}$ = 0.36 in 10 % EtOAc/pentane). Crude allylation adduct **II** was dissolved in Et_2O (560 mL), and the solution was cooled to 0 ^{o}C. A solution of $LiBH_4$ (169 mL, 2.0 M in Et_2O) was then added dropwise followed by EtOH (17.8 mL), and the reaction mixture was stirred at 0 ^{o}C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl (500 mL), poured into a separatory funnel, and extracted with Et_2O (3 x 500 mL). The combined organic layers were then dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford (-)-(*R*)-**11** as a crude oil. Purification by column chromatography (silica gel, 2-12 % EtOAc/hexanes) provided alcohol (-)-(*R*)-**11** (9.22 g, 37 % over three steps, >98 % purity as determined by ^{1}H NMR analysis) as a clear oil in >99 % ee as determined by chiral HPLC analysis of its benzoylated derivative (100 % hexanes using a Lux® 5u Cellulose-2 column).[S1] Oxazolidinone **S2** (16.0 g, 46 %) was also recovered and stored for future use. Spectroscopic data for (-)-(*R*)-**11** were found to be identical with those reported in the literature.[S1] Alcohol (-)-(*R*)-**11** was further dried by vacuum distillation (12.3 mm Hg, oil bath temperature: 95 ^{o}C, b.p. 61 ^{o}C) before use in subsequent reactions.



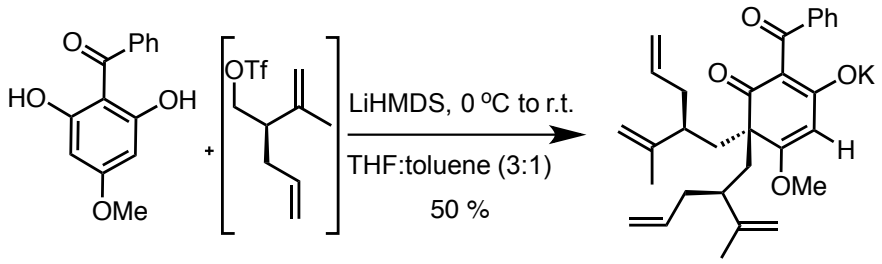
(-)-(*R*)-**11** (-)-(*R*)-**S3**

Triflate (-)-(*R*)-S3: To a flame-dried, 250-mL round-bottom flask under argon containing alcohol (-)-(*R*)-**11** (3.9 mL, 27.4 mmol) was added toluene (21.6 mL), hexane (48 mL), and diisopropylethylamine (6.0 mL, 34.5 mmol). The solution was cooled to -10 ^{o}C, and trifluoromethansulfonic anhydride (4.19 mL, 24.9 mmol) was added dropwise over the course of 20 seconds. The reaction mixture was allowed to stir for 5 min before filtering under argon into

a 250-mL round-bottom flask using a custom-made 150-mL ChemGlass Büchner funnel with a 24/40 joint pictured in **Figure S1**. The fritted funnel was removed and quickly replaced with a septum and argon balloon. The clear solution of triflate (-)-(*R*)-**S3** was then used immediately in the next reaction (*vide infra*).

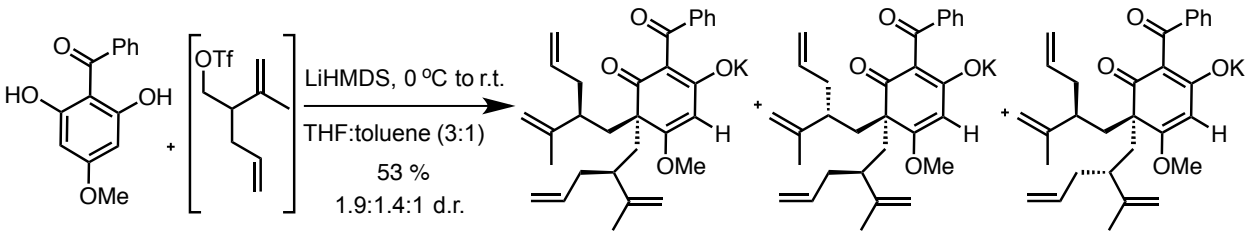
Figure S1. 150-mL ChemGlass Filtration Büchner Funnel with a 24/40 Joint

Regioselective Alkylative Dearomatization



10 (-)-(*R*)-**S3** (+)-(*S*,*S*)-**9A-K**

(+)-2-Benzoyl-3-hydroxy-5-methoxy-6,6-bis((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)cyclohexa-2,4-dien-1-one (+)-(*S*,*S*)-9A: To a flame-dried, round-bottom flask fitted with a stir bar was added acylphloroglucinol **10** (1.5 g, 6.14 mmol). The flask was charged with argon, THF (20.4 mL), and toluene (6.6 mL), and the solution was then cooled to 0 ^{o}C in an ice-water bath. LiHMDS (39 mL, 1.0 M in THF) was added over the course of 5 min, and the reaction mixture was allowed to stir until a homogeneous solution was formed. The solution of triflate (-)-(*R*)-**S3** (7.07 g, 27.4 mmol) was then added to the reaction mixture *via* syringe over the course of 3 min. The reaction mixture was warmed to 20 ^{o}C in a water bath and stirred for 20 min. The water bath was removed and the reaction was warmed to room temperature and stirred for 4.5 h. The reaction mixture was quenched with 1 M HCl (300 mL), diluted with water (600 mL), and extracted into Et_2O (3 x 300 mL). The combined organic layers were washed with 1 M HCl (1 x 400 mL), water (1 x 400 mL), and brine (1 x 300 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo* to provide a crude orange oil. Purification by the *General Purification Procedure for Dearomatized Phloroglucinols and PPAP Derivatives* (see below) provided potassium salt (+)-(*S*,*S*)-**9A-K** (1.53 g, 50 % from the first crop). Crops 2 and 3 provided impure potassium salt (+)-(*S*,*S*)-**9A-K** (134.6 mg, 4 %), which was further purified by dissolving in Et_2O and triturating with pentane. The potassium salt (+)-(*S*,*S*)-**9A-K** was converted to enol (+)-(*S*,*S*)-**9A** with 97 % recovery *via* extraction with 1M HCl (*vide infra*).

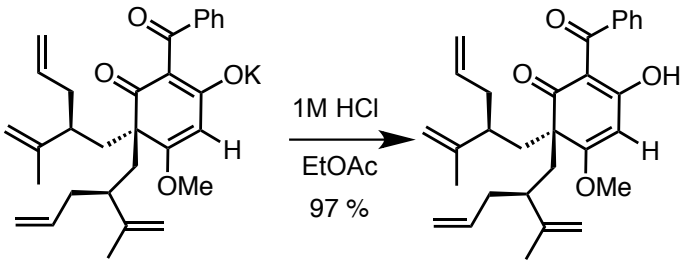


2-Benzoyl-3-hydroxy-5-methoxy-6,6-bis(2-(prop-1-en-2-yl)pent-4-en-1-yl)cyclohexa-2,4-dien-1-one (+/-)-9A, (*meso*)-9B, and (*meso*)-9C:[S3] Potassium salts (+/-)-**9A-K**, (*meso*)-**9B-K**, and (*meso*)-**9C-K** were prepared from acylphloroglucinol **10** (1.5 g, 6.14 mmol), LiHMDS (39 mL, 1.0 M in THF), and racemic triflate **S3** (7.07 g, 27.4 mmol) in the same manner described above for the preparation of potassium salt (+)-(*S*,*S*)-**9A-K**. Purification of the resulting crude oil by the *General Purification Procedure for Dearomatized Phloroglucinols and PPAP Derivatives* (see below) provided potassium salts (+/-)-**9A-K**, (*meso*)-**9B-K**, and (*meso*)-**9C-K** (1.62 g, 53 %, 1.9:1.4:1 d.r. as determined by ^{1}H NMR analysis). The potassium salts were converted to enols (+/-)-**9A**, (*meso*)-**9B**, and (*meso*)-**9C** with 97 % recovery *via* extraction with 1M HCl (*vide infra*).

General Purification Procedure for Dearomatized Phloroglucinols and PPAP Derivatives:[S1,S4]

Pentane (150 mL) was added to the crude oil containing enol (+)-(*S*,*S*)-**9A** or enols (+/-)-**9A**, (*meso*)-**9B**, and (*meso*)-**9C** and was stirred vigorously for 30 min. The resulting solution was decanted to a separatory funnel and vigorously mixed with saturated aqueous K_2CO_3 (40 mL). Water (10 mL) was then added to the biphasic mixture, and upon shaking vigorously, a precipitate crashed out of solution (**Figure S2**). The layers were separated, and the precipitate remained in the separatory funnel. The precipitate was rinsed with pentane to remove impurities and was then dissolved in acetone. Additional precipitate was obtained by repeating the extraction process with the initial crude pentane solution two additional times. The acetone solutions of precipitate were dried (Na_2SO_4), filtered, and concentrated *in vacuo* to provide potassium salt (+)-(*S*,*S*)-**9A-K** (1.53 g, 50 % from the first extraction) or potassium salts (+/-)-**9A-K**, (*meso*)-**9B-K**, and (*meso*)-**9C-K** (1.62 g, 53 %, 1.9:1.4:1 d.r. as determined by ^{1}H NMR analysis). If the 2nd and 3rd crops proved impure, the impure precipitates were further purified by dissolving in Et_2O and triturating with pentane.

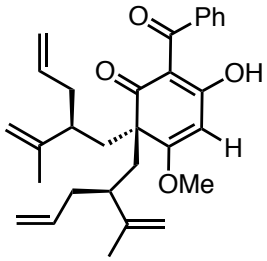
Figure S2. Potassium salts (+/-)-**9A-K**, (*meso*)-**9B-K**, and (*meso*)-**9C-K** Formed as Precipitates in the *General Purification Procedure for Dearomatized Phloroglucinols and PPAP Derivatives.*



(+)-(*S*,*S*)-**9A-K** (+)-(*S*,*S*)-**9A**

General Procedure to Convert Potassium Salts to Enols with up to 97 % Recovery: A solution of (+)-(*S*,*S*)-**9A-K** (510.1 mg) in EtOAc (30 mL) was extracted with 1M HCl (1 x 20 mL), washed with H_2O (1 x 20 mL) and brine (1 x 20 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo* to provide enol (+)-(*S*,*S*)-**9A** (454.9 mg, 97 % yield) as a red solid.

[Enols (+/-)-**9A** (red solid), (*meso*)-**9B** (pink solid), and (*meso*)-**9C** (yellow oil) can be separated *via* preparative thin layer chromatography (silica gel, 3 elutions in 7 % EtOAc/hexanes with 1 % AcOH, Elution 1: 12 hours; Elution 2: 1 h, and Elution 3: 1 h).]



(+)-(*S*,*S*)-**9A**

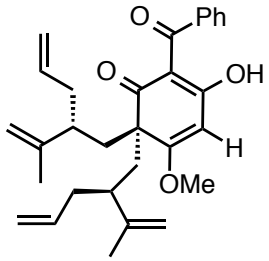
(+)-2-Benzoyl-3-hydroxy-5-methoxy-6,6-bis((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)cyclohexa-2,4-dien-1-one (+)-(*S*,*S*)-9A: R_f = 0.20 (10 % EtOAc/hexanes); **m.p.** 79 – 84 °C (CH_2Cl_2); IR ν_{max} 3074, 2978, 2932, 2851, 1661, 1645, 1621, 1593, 1519, 1447, 1374, 1218, 1176, 913, 893, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ~ 3:1 mixture of enol tautomers as determined by ^1H NMR analysis) δ 17.95 (s, 0.6H)*, 17.28 (s, 0.2H)**, 7.56 – 7.33 (m, 5H), 5.67 – 5.48 (m, 3H), 5.05 – 4.85 (m, 4H), 4.70 – 4.64 (m, 1.1H), 4.64 – 4.60 (m, 0.7H), 4.60 – 4.54 (m, 2.2H), 3.80 (s, 2.25H)*, 3.69 (s, 0.75H)**, 2.30 – 1.85 (m, 9H), 1.73 (dd, *J* = 13.3, 2.4 Hz, 1H), 1.62 – 1.55 (m, 4H), 1.48 (s, 2H);

*denotes conjugated enol tautomer (major)

** denotes cross-conjugated enol tautomer (minor)

^{13}C NMR (100 MHz, $CDCl_3$, 3:1 mixture of enol tautomers as determined by ^1H NMR analysis) δ 197.0*, 194.9**, 193.5*, 189.1*, 188.1**, 183.9**, 178.3*, 170.4**, 146.6, 146.4, 146.2, 146.0, 139.3, 138.1, 136.6, 136.4, 136.4, 136.2, 131.6, 130.6, 128.3, 127.5, 127.4, 127.3, 127.3, 116.1, 115.9, 115.7, 113.3, 113.1, 112.1, 112.1, 108.6, 104.8, 98.3, 98.0, 56.6, 56.6, 55.7, 55.1, 52.1, 44.3, 43.9, 43.8, 43.5, 43.4, 42.6, 41.3, 40.4, 39.7, 39.4, 39.1, 18.3**, 18.1*, 17.7**, 17.5*;

HR-MS: *m/z* Calcd. for $C_{30}H_{36}O_4$ [M+H$^+$]: 461.2692, Found 461.2693; $[\alpha]_D^{25}$ = +28.1 (c. 0.250, $CHCl_3$).



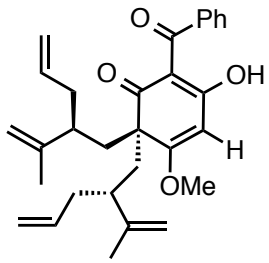
(*meso*)-**9B**

[*meso*]-(*r*)-2-Benzoyl-3-hydroxy-5-methoxy-6-((*R*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-6-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)cyclohexa-2,4-dien-1-one (*meso*)-9B: R_f = 0.23 (10 % EtOAc/hexanes); **m.p.** 81 – 84 ºC (CH_2Cl_2); IR ν_{max} 3072, 2977, 2934, 1658, 1644, 1618, 1590, 1519, 1446, 1373, 1288, 1218, 1177, 1114, 992, 912, 893, 831 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ~ 5:1 mixture of enol tautomers as determined by ^{1}H NMR analysis) δ 17.70 (s, 0.8H)*, 17.04 (s, 0.1H)**, 7.62 – 7.34 (m, 5H), 5.65 – 5.50 (m, 2H), 5.41 (s, 0.8H)*, 5.35 (s, 0.2H)**, 4.99 – 4.88 (m, 4H), 4.66 (app dd, *J* = 1.8, 1.4 Hz, 2H), 4.57 (app d, *J* = 2.2 Hz, 2H), 3.68 (s, 2.5H)*, 3.57 (s, 0.5H)**, 2.23 – 1.87 (m, 10H), 1.64 – 1.55 (m, 6H);

*denotes conjugated enol tautomer (major)

** denotes cross-conjugated enol tautomer (minor)

^{13}C NMR (100 MHz, $CDCl_3$, ~ 5:1 mixture of enol tautomers as determined by ^{1}H NMR analysis) δ 198.3**, 197.6*, 194.6*, 193.6**, 188.6*, 183.7**, 178.8*, 170.6**, 146.3, 146.2, 139.2, 138.3, 136.4, 136.2, 131.9, 131.1, 128.5, 127.7, 127.6, 127.6, 116.1, 115.7, 112.2, 112.0, 107.9, 104.6, 98.0, 57.0, 55.0, 54.5, 52.1, 44.2, 43.7, 42.9, 41.0, 39.6, 39.4, 18.3, 17.9; **HR-MS**: *m/z* Calcd. for $C_{30}H_{36}O_4$ 461.2692 [M+H$^+$]: Found 461.2686.



(*meso*)-**9C**

[*meso*]-(*s*)-2-Benzoyl-3-hydroxy-5-methoxy-6-((*R*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-6-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)cyclohexa-2,4-dien-1-one (*meso*)-9C: R_f = 0.33 (14 % EtOAc/hexanes); IR ν_{max} 3072, 2979, 2929, 2848, 1661 1644, 1621, 1517, 1448, 1373, 1216, 1174, 1111, 992, 912, 890, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, ~1.7:1 mixture of enol tautomers as determined by ^{1}H NMR analysis) δ 18.11 (s, 0.5H)*, 17.38 (s, 0.3H)**, 7.54 – 7.32 (m, 5H), 5.74 (s, 0.6H)*, 5.66 (s, 0.4H)**, 5.65 – 5.52 (m, 2H), 5.03 – 4.90 (m, 4H), 4.62 (dd, *J* = 1.7, 1.7 Hz, 1.3H), 4.57 (dd, *J* = 1.6, 1.6 Hz, 2.7H), 3.91 (s, 1.9H)*, 3.80 (s, 1.1H)**, 2.25 (dd, *J* = 13.5, 7.9 Hz, 1H), 2.18 – 1.88 (m, 8H), 1.72 (dd, *J* = 13.4, 2.4 Hz, 1H), 1.59 (br s, 3H), 1.47 (br s, 3H);

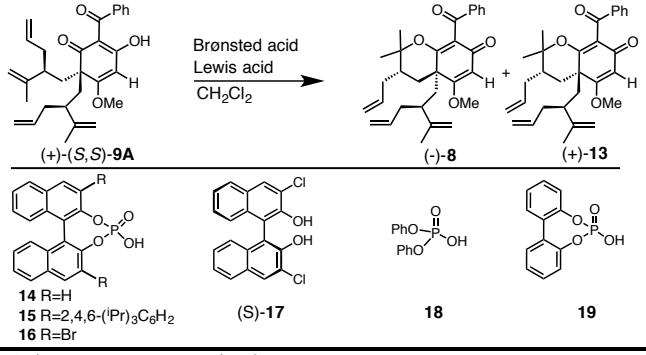
*denotes conjugated enol tautomer (major)

** denotes cross-conjugated enol tautomer (minor)

^{13}C NMR (100 MHz, $CDCl_3$; ~1.7:1 mixture of enol tautomers as determined by ^{1}H NMR analysis) δ 196.4, 195.9, 195.7, 192.4, 189.2, 183.9, 177.8, 170.3, 146.7, 146.1, 139.3, 138.1, 136.8, 136.6, 136.4, 131.4, 130.2, 129.0, 128.2, 127.5, 127.2, 127.1, 127.1, 115.9, 115.7, 113.1, 113.0, 109.5, 104.9, 98.7, 98.4, 65.8, 56.6, 56.3, 55.7, 52.3, 44.5, 44.0, 43.3, 40.8, 39.4, 39.2, 17.7, 17.6, 15.3; **HR-MS**: *m/z* Calcd. for $C_{30}H_{36}O_4$ [M+H$^+$]: 461.2692, Found 461.2680.

Diastereoselective Oxycyclization Studies (Tables 1 and 2):

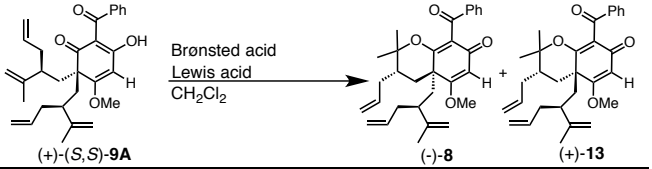
Table 1. *Diastereoselective Oxycyclization and Chelation Studies.*



Entry	Brønsted Acid	Lewis Acid	Conditions	Yield	d.r. (**8**:**13**)[b]
1	HCl[a]	none	-10 °C to r.t., 72h	25%[b]	1:1.1
2	**19** (10 equiv)	LiBr (10 equiv)	0 °C, 48 h	99%	1:1.8
3	**18** (5 equiv)	LiBr (5 equiv)	r.t., 1.5 h	91%	1:1.8
4	(*R*)-**14** (10 equiv)	LiBr (10 equiv)	0 °C, 48 h	91%	1:2
5	(*S*)-**14** (10 equiv)	LiBr (10 equiv)	0 °C, 48 h	91%	1:3
6	(*R*)-**15** (5 equiv)	LiBr (5 equiv)	r.t., 48 h	89%	1:2.2
7	(*S*)-**15** (5 equiv)	LiBr (5 equiv)	r.t., 48 h	86%	1:1.8
8	(*S*)-**16** (10 equiv)	LiBr (10 equiv)	0 °C, 48 h	99%	1:1.5
9	(*S*)-**17** (1 equiv)	$SbCl_5$ (1 equiv)	-78 °C, 2 h	18%	9:1
10	(*S*)-**14** (5 equiv)	none	-5 to 10 °C, 48 h	0%	none
11	none	LiBr (10 equiv)	r.t., 5 d	19%	1:1.6
12	none	$SnCl_4$ (2 equiv)	-78 to -20 °C, 48 h	36%	7:1
13[c]	(+/-)-**14** (2 equiv)	$SnCl_4$ (1 equiv)	-78 to 50 °C, 36 h	58%	1:1.1
14	*p*TsOH (10 equiv)	BF_3OEt_2 (79 equiv)	-78 to -5 °C, 1 h	32%[d] (57% brsm)	1:2

[a] CH_2Cl_2/4M HCl in dioxane (1:1). [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] $SnCl_4$ saturated with (+/-)-**14** prior to addition of substrate (+)-(*S*,*S*)-**9A**. [d] 54 % starting material also recovered.

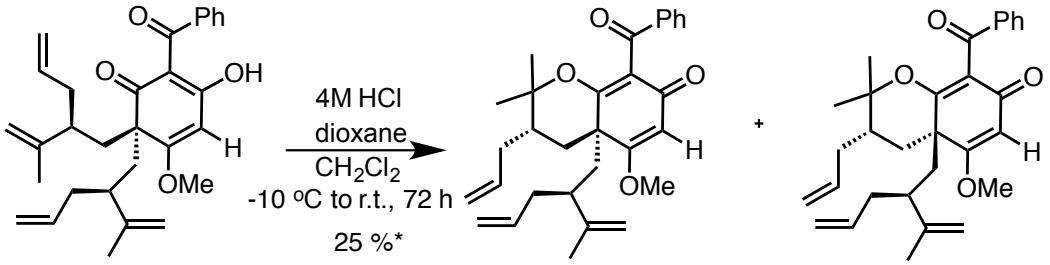
Table 2. Optimized Lewis/Brønsted Acid Combinations for Diastereoselective Cyclization.



(+)-(*S*,*S*)-**9A** (-)-**8** (+)-**13**

Entry	Brønsted Acid	Lewis Acid	Conditions	Yield	d.r. (**8**:**13**)[b]
1	(*S*)-**14** (2 equiv)	$SnCl_4$ (2 equiv)	-78 to -30 °C, 6 d	68 %	14:1
2	(*R*)-**14** (2 equiv)	$SnCl_4$ (2 equiv)	-78 to -30 °C, 6 d	9 %	1:0
3[a]	(+/-)-**14** (2 equiv)	$SnCl_4$ (2 equiv)	-78 to -20 °C, 17 h	52 %	14:1
4	**18** (2 equiv)	$SnCl_4$ (2 equiv)	-78 to 0 °C, 19 h	47 %	10:1
5	**18** (10 equiv)	$InCl_3$ (10 equiv)	r.t., 1 h	99 %	5.4:1
6	*p*TsOH (10 equiv)	BF_3OEt (79 equiv)	-15 to -5 °C, 2 h; -40 to -5 °C, 2 h	42 %	1:5

[a] Substrate (+/-)-**9A** was used. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture.



(+)-(*S*,*S*)-**9A** (***Table 1**, entry 1*) (-)-**8** (+)-**13**

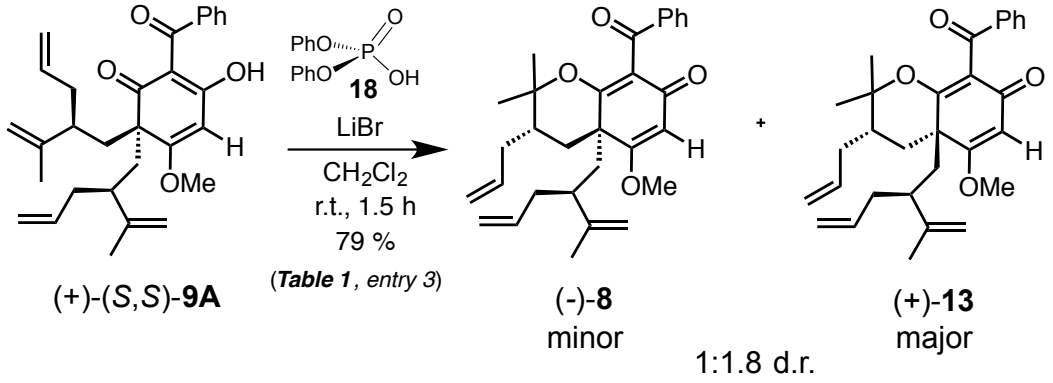
1:1.1 d.r.

*Yield determined by ^{1}H NMR analysis of the crude reaction mixture.

(***Table 1**, entry 1*) To a flame-dried 10-mL round-bottom flask under an argon atmosphere containing enol (+)-(*S*,*S*)-**9A** (2.3 mg, 0.00499 mmol) was added CH_2Cl_2 (0.33 mL). The solution was cooled to -10 °C, and 4 M HCl in dioxane (0.3 mL) was added. The reaction mixture was allowed to slowly warm to room temperature and was stirred for 72 h. The reaction was then quenched with saturated aqueous $NaHCO_3$ (2 mL), poured into water (2 mL), and extracted into CH_2Cl_2 (3 x 4 mL). The combined organic layers were washed with water (1 x 5 mL) and brine (1 x 5 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo* to afford

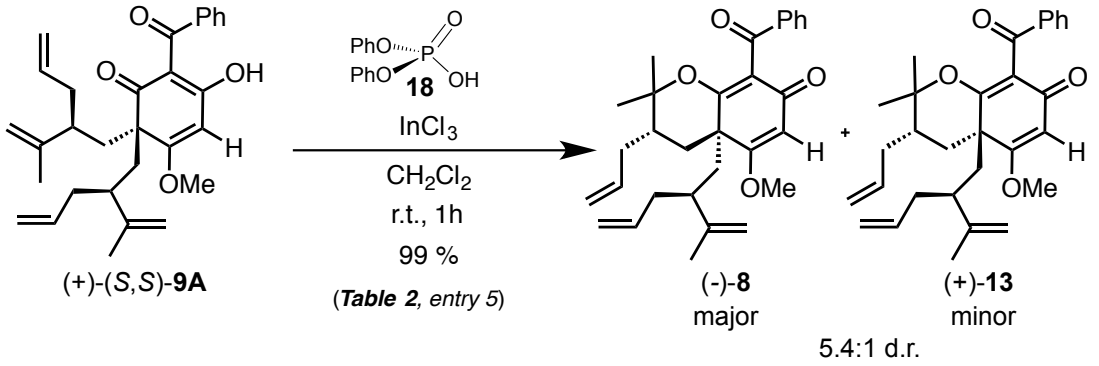
oxycyclization products (+)-**13** and (-)-**8** (25 %, 1:1.1 d.r. based on ^{1}H NMR analysis of the crude reaction mixture).

General Procedure A



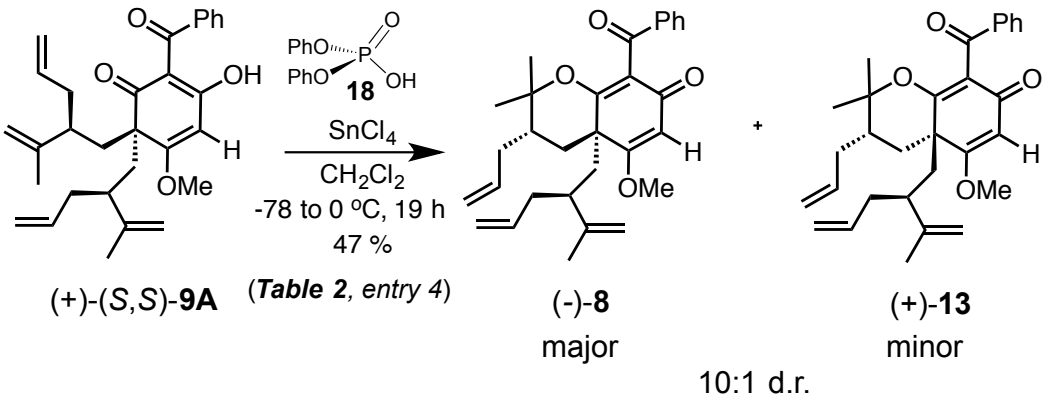
(+)-(3*S*,4a*R*)-3-Allyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one (+)-13 and (-)-(3*S*,4a*S*)-3-Allyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one (-)-8: (***Table 1****, entry 3*) To a 250-mL round-bottom flask containing a solution of enol (+)-(*S*,*S*)-**9A** (1.39 g, 3.02 mmol) in CH_2Cl_2 (101 mL) was added LiBr (1.31 g, 15.1 mmol) in a single portion. After the suspension was stirred for one minute, diphenyl phosphate **18** (3.79 g, 15.1 mmol) was added in a single portion. The reaction mixture was allowed to stir vigorously for 1.5 h and was then quenched with saturated aqueous $NaHCO_3$ (100 mL), poured into water (20 mL), and extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with water (1 x 100 mL) and brine (1 x 100 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography (silica gel, 10 – 40 % EtOAc/hexanes) provided oxycyclization products (-)-**8** and (+)-**13** (1.1 g, 79 %, 1:1.8 d.r. as determined by ^{1}H NMR analysis) as a red oil. Diphenyl phosphate **18** was re-isolated following extraction of the combined aqueous layers (pH<7) with EtOAc.

(***Table 1****, entries 2-8, entry 11*) All reactions in Table 1 using LiBr were carried out according to general procedure A to provide oxycyclization products (-)-**8** and (+)-**13**.



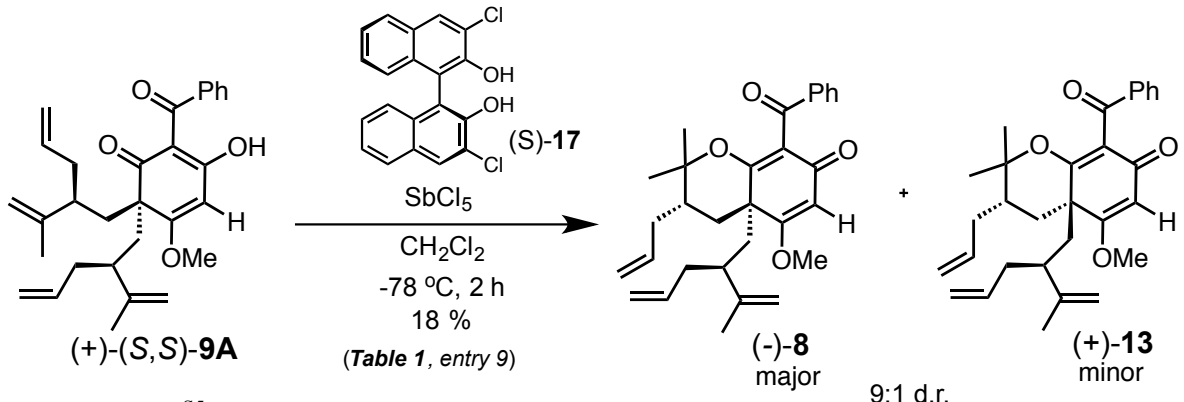
(***Table 2****, entry 5*) Oxycyclization product (-)-**8** (3.6 mg, 99 %, 5.4:1 d.r. as determined by ^{1}H NMR analysis) was prepared according to general procedure A from a solution of enol (+)-(*S*,*S*)-**9A** (3.6 mg, 0.00782 mmol) in CH_2Cl_2 (0.53 mL) using $InCl_3$ (17.3 mg, 0.0782 mmol) and phosphoric acid **18** (19.6 mg, 0.0782 mmol). After 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted into Et_2O (3 x 3 mL). The combined organic layers were washed with H_2O (1 x 3 mL) and brine (1 x 3 mL), dried (Na_2SO_4), filtered, and concentrated. Purification by column chromatography (silica gel, 10 – 40 % EtOAc/hexanes) provided oxycyclization product (-)-**8** (3.6 mg, 99 %, 5.4:1 d.r. as determined by ^{1}H NMR analysis).

General Procedure B



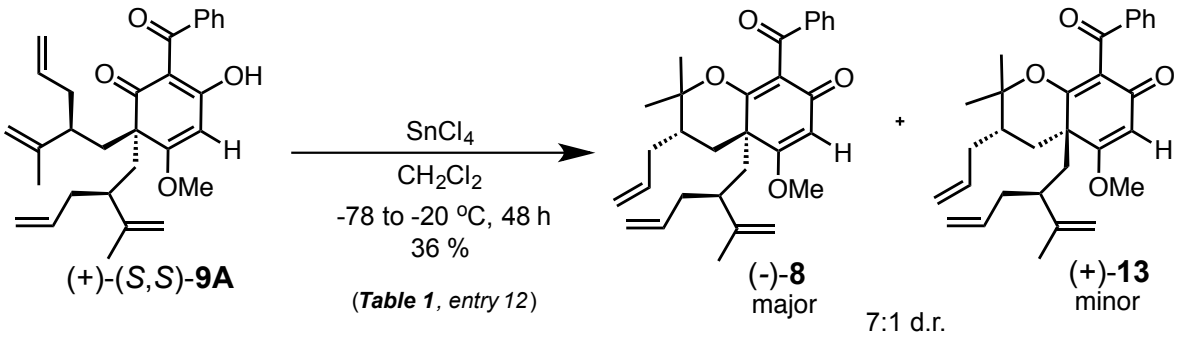
(-)-(3*S*,4a*S*)-3-Allyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one (-)-8: (***Table 2****, entry 4*) To a flame-dried, round-bottom flask was added diphenyl phosphate **18** (10.2 mg, 0.0408 mmol) and the flask was then purged with argon. Methylene chloride (0.29 mL) and $SnCl_4$ (0.2 mL, 0.2 M in CH_2Cl_2, 0.0408 mmol) were then added sequentially at room temperature, and the clear solution was cooled to -78 ^{o}C. A solution of enol (+)-(*S*,*S*)-**9A** (9.4 mg, 0.0204 mmol) in CH_2Cl_2 (0.2 mL) was

transferred to the $SnCl_4$/diphenyl phosphate mixture *via* syringe over the course of 2 min, and the reaction mixture was allowed to stir for 19 h at 0 °C (temperature controlled by a Cryocool™). The reaction was quenched with saturated aqueous $NaHCO_3$ (3 mL), poured into water (2 mL), and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with water (1 x 5 mL) and brine (1 x 5 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by silica gel chromatography (10 – 40 % EtOAc/hexanes) afforded oxycyclization product (-)-**8** (4.4 mg, 47 %, 10:1 d.r. as determined by ^{1}H NMR analysis) as a white amorphous solid. [Compounds (-)-**8** and (+)-**13** can be separated by preparative plate chromatography with ~ 8 elutions in 10 % EtOAc/hexanes]. (-)-**8:** $\mathbf{R}_f$ = 0.24 (35 % EtOAc/hexanes); IR ν_{max} 3074, 2980, 2941, 1677, 1650, 1621, 1598, 1448, 1387, 1374, 1350, 1265, 1225, 1170, 1137, 1129, 1084, 994, 914, 839, 782, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.55 – 7.50 (m, 1H), 7.45 – 7.39 (m, 2H), 5.72 – 5.58 (m, 2H), 5.49 (s, 1H), 5.09 – 4.95 (m, 4H), 4.69 (br s, 1H), 4.63 (br s, 1H), 3.64 (s, 3H), 2.45 (dd, *J* = 14.3, 4.4 Hz, 1H), 2.23 – 2.12 (m, 2H), 2.11 – 1.94 (m, 4H), 1.80 – 1.69 (m, 1H), 1.68 – 1.60 (m, 1H), 1.62 (s, 3H), 1.55 (t, *J* = 13.3 Hz, 2H), 1.26 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.4, 186.0, 174.8, 169.6, 146.7, 137.7, 136.5, 135.8, 133.1, 129.2, 128.4, 126.3, 117.3, 116.3, 111.6, 103.1, 88.4, 55.3, 47.6, 44.6, 42.4, 42.3, 39.8, 36.1, 35.6, 28.8, 21.7, 19.1; **HR-MS**: *m/z* Calcd. for $C_{30}H_{36}O_4$ [M+H$^+$]: 461.2692, Found 461.2701; $[\alpha]_D^{25}$ = -79.1 (c. 0.250, $CHCl_3$).

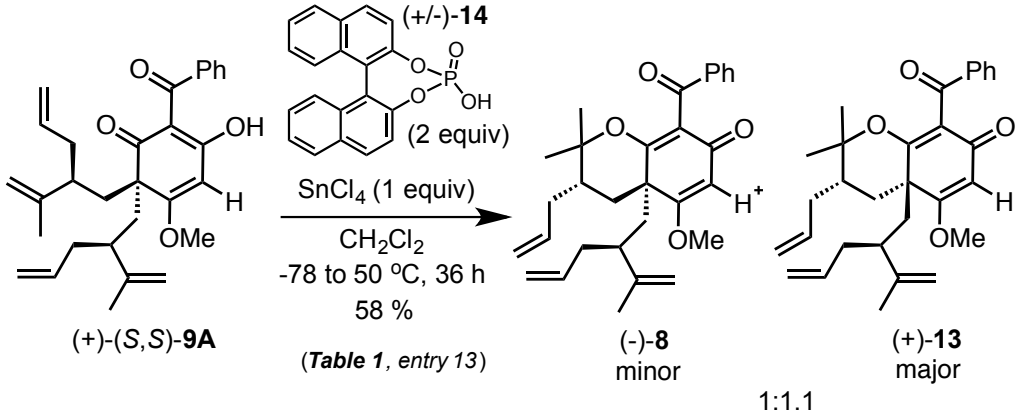


(***Table 1**, entry 9*)[S5] Oxycyclization product (-)-**8** was prepared according to general procedure B from a solution of enol (+)-(*S*,*S*)-**9A** (9.5 mg, 0.0206 mmol) in CH_2Cl_2 (0.05 mL) which was added to a solution of (*S*)-*o*,*o*'-dichloro-BINOL (*S*)-**17** (7.3 mg, 0.0206 mmol) and $SbCl_5$ (21 μL,

1.0 M in CH_2Cl_2) in CH_2Cl_2 (0.1 mL) at -78 °C. The reaction mixture was stirred at this temperature for 4 h and was then quenched with saturated aqueous $NaHCO_3$ and extracted into Et_2O (3 x 4 mL). The combined organic layers were washed with water (1 x 5 mL) and brine (1 x 5 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by preparative thin layer chromatography (silica gel, 19 % EtOAc/hexanes with 3 % AcOH) provided oxycyclization product (-)-**8** (1.7 mg, 18 %, 9:1 d.r. as determined by ^{1}H NMR analysis).

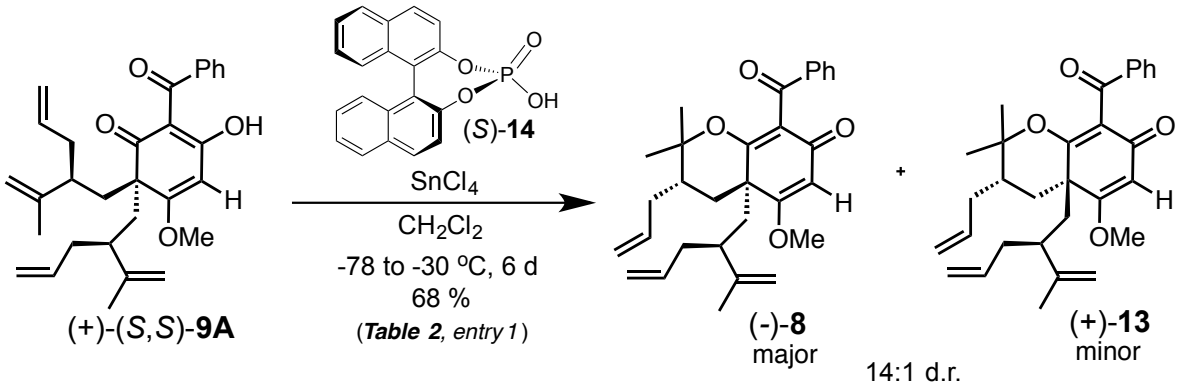


(***Table 1**, entry 12*) To a solution enol (+)-(*S*,*S*)-**9A** (11.8 mg, 0.0256 mmol) in CH_2Cl_2 (0.56 mL) in a flame-dried, round-bottom flask at -78 °C was added $SnCl_4$ (0.25 mL, 0.2 M in CH_2Cl_2). The reaction mixture was warmed to -20 °C for 48 h and then quenched and purified according to general procedure B to provide oxycyclization product (-)-**8** (4.3 mg, 36 %, 7:1 d.r. as determined by ^{1}H NMR analysis).

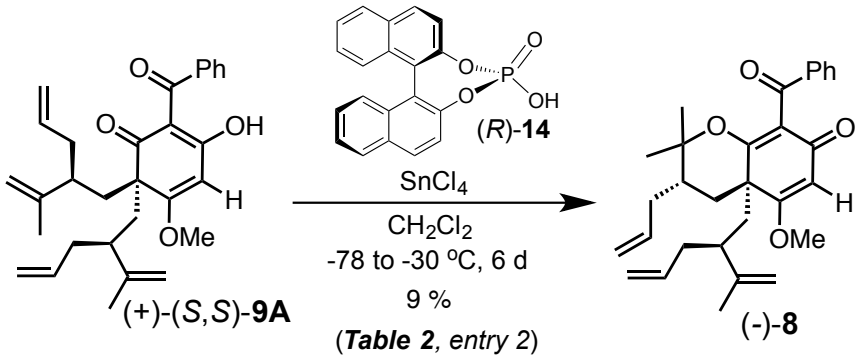


(***Table 1**, entry 13*) Oxycyclization products (+)-**13** and (-)-**8** were prepared according to general

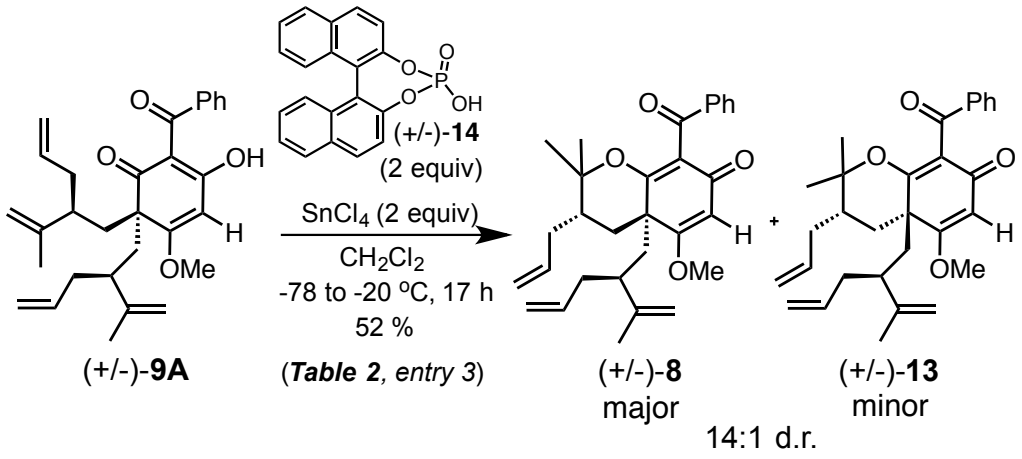
procedure B from a solution of enol (+)-(*S*,*S*)-**9A** (4.0 mg, 0.00868 mmol) in CH_2Cl_2 (0.09 mL) which was added to a solution of phosphoric acid (+/-)-**14** (6.0 mg, 0.0174 mmol) and $SnCl_4$ (40 μL, 0.2 M in CH_2Cl_2) in CH_2Cl_2 (0.12 mL) at -78 °C. The reaction mixture was warmed to -20 °C for 24 h and then heated to 50 °C for 12 h. The reaction was quenched with 1M HCl and extracted into CH_2Cl_2 (3 x 4 mL). The combined organic layers were washed with water (1 x 3 mL) and brine (1 x 3 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by silica gel chromatography (10 – 40 % EtOAc/hexanes) provided oxycyclization products (+)-**13** and (-)-**8** (2.3 mg, 58 %, 1:1.1 d.r. as determined by ^{1}H NMR analysis).



(***Table 2**, entry 1*) Oxycyclization product (-)-**8** was prepared according to general procedure B from a solution of (+)-(*S*,*S*)-**9A** (3.7 mg, 0.00803 mmol) in CH_2Cl_2 (0.15 mL) which was added to a solution of (*S*)-**14** (5.6 mg, 0.0161 mmol) and $SnCl_4$ (0.08 mL, 0.2 M in CH_2Cl_2) in CH_2Cl_2 (0.11 mL) at -78 °C. The reaction mixture was warmed to -45 °C for 3 h and then allowed to stir for 6 d at -30 °C. The reaction was quenched with pyridine (1.3 μL) and saturated aqueous $NaHCO_3$ (2 mL), poured into water (2 mL), and extracted with CH_2Cl_2 (3 x 3 mL). The combined organic layers were washed with water (1 x 3 mL) and brine (1 x 3 mL). The organic solution was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by column chromatography (silica gel, 10 – 40 % EtOAc/hexanes) afforded oxycyclization product (-)-**8** (2.5 mg, 68 %, 14:1 d.r. as determined by ^{1}H NMR analysis).



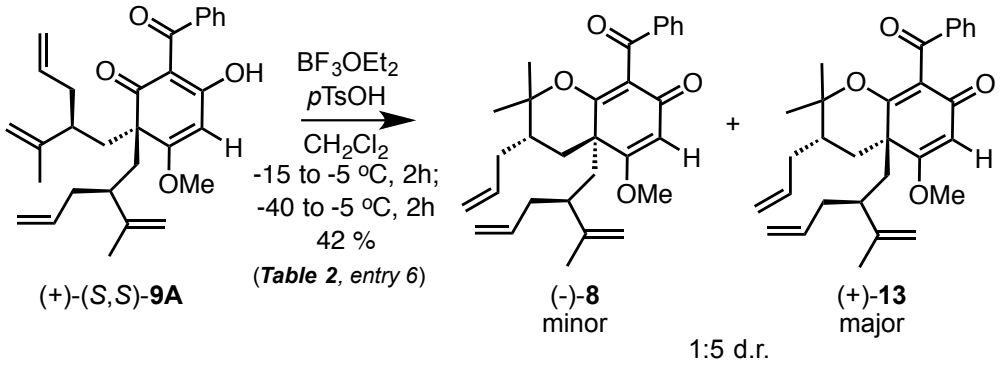
(***Table 2**, entry 2*) Oxycyclization product (-)-**8** was prepared according to general procedure B from a solution of enol (+)-(*S*,*S*)-**9A** (3.4 mg, 0.00738 mmol) in CH_2Cl_2 (0.15 mL) which was added to a solution of phosphoric acid (*R*)-**14** (5.7 mg, 0.0162 mmol) and $SnCl_4$ (0.07 mL, 0.2 M in CH_2Cl_2) in CH_2Cl_2 (0.11 mL) at -78 °C. The reaction mixture was warmed to -45 °C for 3 h and then allowed to stir for 6 d at -30 °C. The reaction was quenched with pyridine (1.2 μL) and saturated aqueous $NaHCO_3$ (2 mL), poured into water (2 mL), and extracted with CH_2Cl_2 (3 x 3 mL). The combined organic layers were washed with water (1 x 3 mL) and brine (1 x 3 mL). The organic solution was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by column chromatography (silica gel, 10 – 40 % EtOAc/hexanes) afforded oxycyclization product (-)-**8** (0.3 mg, 9 %) as a single diastereomer.



(***Table 2**, entry 3*) Oxycyclization product (+/-)-**8** was prepared according to general procedure B from a solution of enol (+/-)-**9A** (6.0 mg, 0.013 mmol) in CH_2Cl_2 (0.13 mL) which was added to

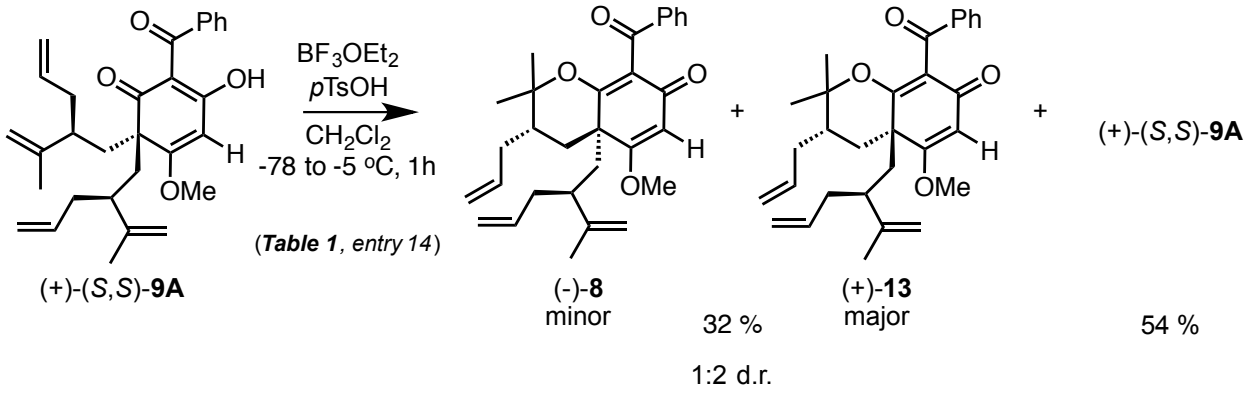
a solution of phosphoric acid (+/-)-**14** (9.1 mg, 0.0261 mmol) and $SnCl_4$ (0.13 mL, 0.2 M in CH_2Cl_2) in CH_2Cl_2 (0.19 mL) at -78 °C. The reaction mixture was then warmed to -20 °C and was stirred at this temperature for 17 h. The reaction mixture was then warmed to room temperature for 5 minutes before it was quenched and purified according to general procedure B to afford (+/-)-**8** (3.1 mg, 52 %, 14:1 d.r. as determined by ^{1}H NMR analysis).

General Procedure C



(+)-(3*S*,4a*R*)-3-Allyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one (+)-13: (***Table 2, entry 6***) To a 100-mL flame-dried round-bottom flask under an argon atmosphere containing a solution of enol (+)-(*S*,*S*)-**9A** (107 mg, 0.232 mmol) in CH_2Cl_2 (23 mL) at -15 °C was added BF_3OEt_2 (2.3 mL, 18.5 mmol). The reaction was stirred and allowed to warm to -10 °C over 10 min. *p*TsOH (444 mg, 2.33 mmol) was then added to the reaction mixture in a single portion and the reaction mixture was allowed to warm to -5 °C until the *p*TsOH completely dissolved. The reaction vessel was then transferred to an acetone bath at -5 °C (the temperature was controlled by Cryocool™) and stirred at this temperature for 2 h. The reaction mixture was cooled to -40 °C and then allowed to warm to -5 °C over the course of 2 h. The reaction was quenched with 1 M HCl (30 mL) and stirred vigorously for 1 h. The biphasic mixture was then poured into H_2O (10 mL) and extracted into CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (1 x 20 mL), water (1 x 20 mL) and brine (1 x 20 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography (silica gel, 5 – 30 % EtOAc/hexanes with 4 % AcOH) afforded oxycyclization product (+)-**13** (45.4 mg, 42 %, 1:5 d.r. as determined by ^{1}H NMR analysis) as a solid. (+)-**13:** $\mathbf{R}_f$ = 0.21 (35 % EtOAc/hexanes);

m.p. 154 – 156 °C (CH_2Cl_2); IR ν_{max} 3073, 2979, 2926, 2851, 1677, 1653, 1624, 1599, 1449, 1384, 1375, 1225, 1174, 1132, 1082, 1015, 993, 913, 840, 733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 2H), 7.53 – 7.48 (m, 1H), 7.42 – 7.37 (m, 2H), 5.74 (dddd, *J* = 17.3, 10.0, 7.8, 5.7 Hz, 1H), 5.68 – 5.59 (m, 1H), 5.61 (s, 1H), 5.13 – 5.03 (m, 2H), 5.01 – 4.94 (m, 2H), 4.76 (br s, 1H), 4.67 (br s, 1H), 3.73 (s, 3H), 2.32 (dd, *J* = 13.7, 6.8 Hz, 1H), 2.23 (dd, *J* = 13.9, 3.8 Hz, 1H), 2.18 – 2.11 (m, 2H), 2.10 – 1.94 (m, 3H), 1.80 (dd, *J* = 13.8, 3.3 Hz, 1H), 1.71 – 1.62 (m, 1H), 1.66 (s, 3H), 1.49 (t, *J* = 13.2 Hz, 1H), 1.29 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 186.4, 175.0, 168.5, 146.0, 137.6, 136.6, 135.8, 133.0, 129.3, 128.1, 125.8, 117.3, 116.0, 112.1, 102.5, 87.4, 55.8, 45.3, 43.2, 39.7, 39.6, 39.5, 36.0, 35.8, 28.2, 20.7, 19.3; **HR-MS**: *m/z* Calcd. for $C_{30}H_{36}O_4$ $[M+H^+]$: 461.2692, Found 461.2681; $[\alpha]_D^{25}$ = +34.1 (c. 0.250, $CHCl_3$).

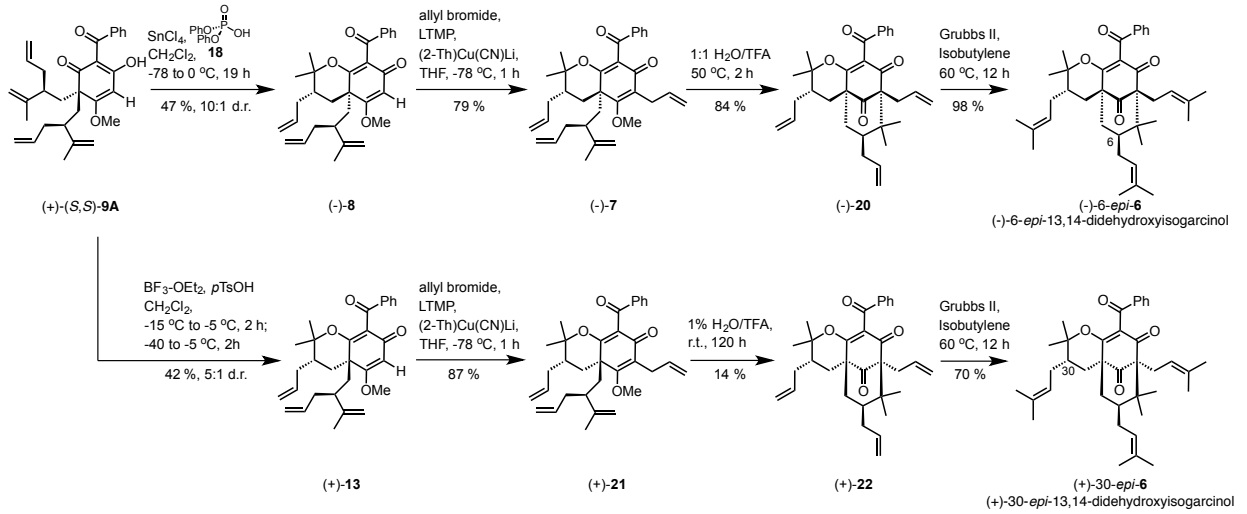


(***Table 1**, entry 14*) Oxycyclization products (-)-**8** and (+)-**13** were prepared according to general procedure C from a solution of (+)-(*S*,*S*)-**9A** (50.7 mg, 0.11 mmol) in CH_2Cl_2 (10.8 mL) using BF_3OEt_2 (1.08 mL, 8.74 mmol) and *p*TsOH (209 mg, 1.1 mmol). After the *p*TsOH completely dissolved, the reaction mixture was allowed to stir vigorously for 1 h. The reaction mixture was then quenched and purified according to general procedure C to provide oxycyclization products (-)-**8** and (+)-**13** (16.4 mg, 32 %, 1:2 d.r. as determined by ^1H NMR analysis) and starting enol (+)-(*S*,*S*)-**9A** (27.4 mg, 54 %).

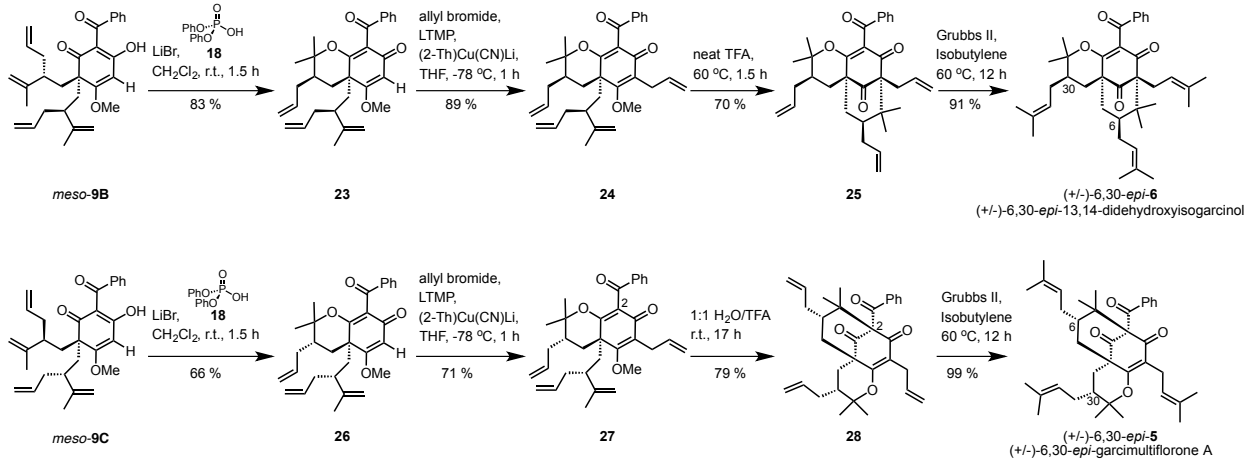
Total Synthesis of (-)-6-*epi*-, (+)-30-*epi*-, (+/-)-6,30-*epi*-13,14-Didehydroxyisogarcinol and (+/-)-6,30-*epi*-Garcimultiflorone A (Schemes S1 and S2).

Scheme S1. Asymmetric Syntheses of (-)-6-*epi*-**6** and (+)-30-*epi*-**6** and Racemic Syntheses of (+/-)-6,30-*epi*-**6** and (+/-)-6,30-*epi*-**5**.

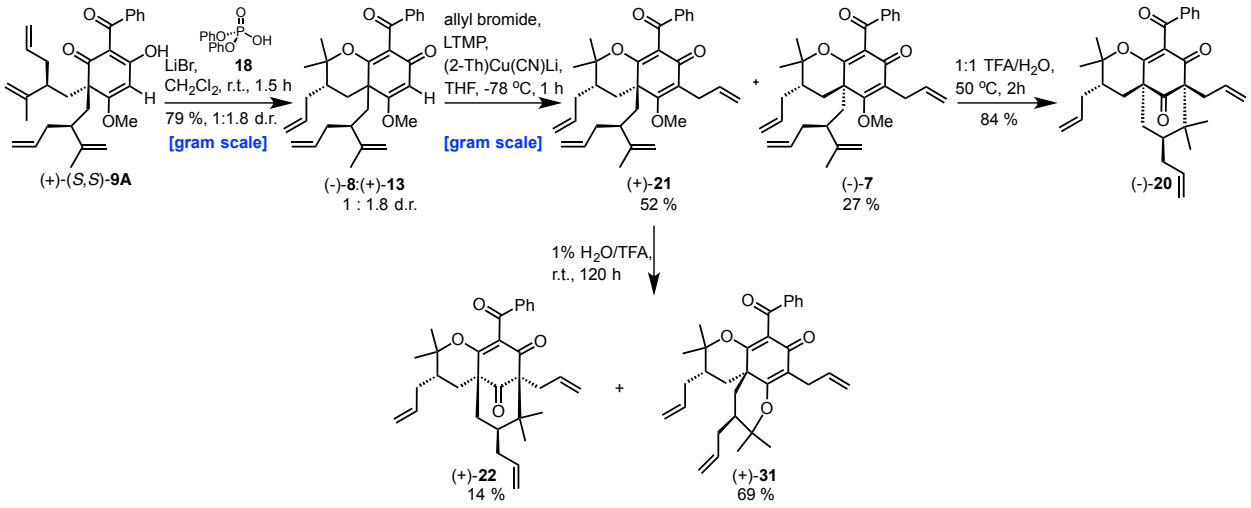
A. Synthesis of the Type B PPAPs (-)-*epi*-**6** and (+)-30-*epi*-**6**.



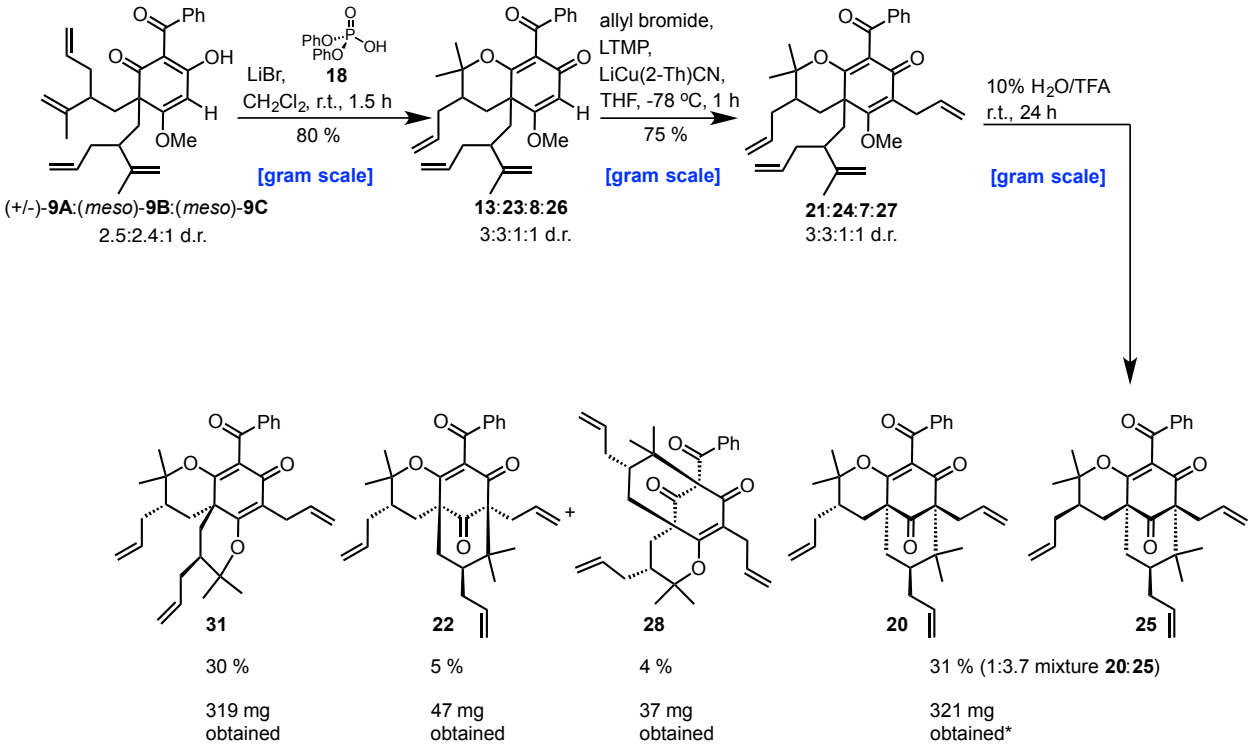
B. *Meso* Diastereomers **9B** and **9C** Provide Access to Type B PPAP (+/-)-6,30-*epi*-**6** and Type A PPAP (+/-)-6,30-*epi*-**5**.



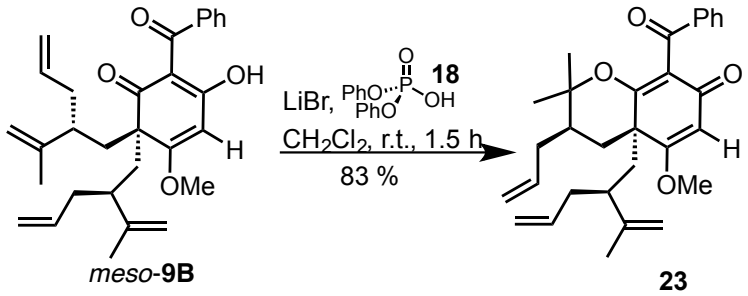
Scheme S2A. Scalable Strategy for Production of Enantioenriched Isomers (-)-**20** and (+)-**22**.



Scheme S2B. Gram Scale Synthesis of Racemic Stereoisomers **20**, **22**, **25**, and **28** in 4 Synthetic Operations from Acylphloroglucinol **10**.

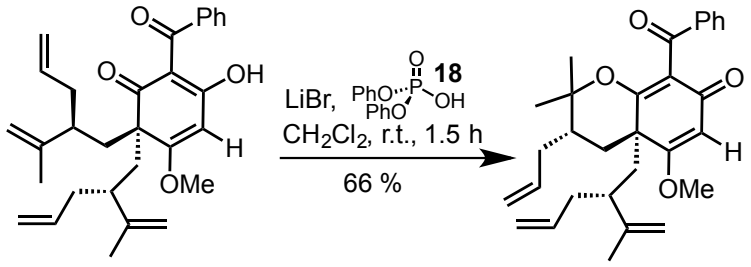


*Column chromatography provided compounds **20** and **25** as a 1:3.7 mixture as determined by ^{1}H NMR analysis.[14]



meso-**9B** **23**

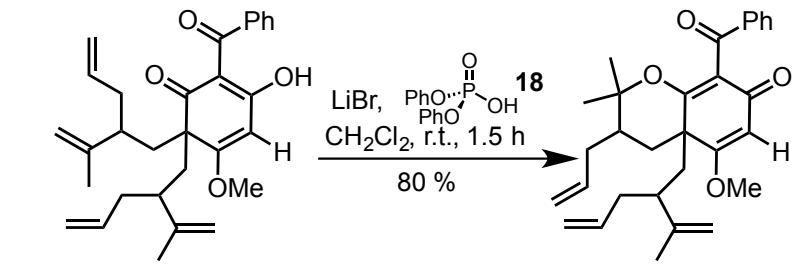
(+/-)-(3*R*,4a*R*)-3-Allyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one 23: Oxycyclization product **23** (167 mg, 83 %) was provided as an amorphous solid and was prepared according to general procedure A from enol (*meso*)-**9B** (201 mg, 0.436 mmol) using LiBr (379 mg, 4.36 mmol) and diphenyl phosphate **18** (1.09 g, 4.36 mmol) in CH_2Cl_2 (30 mL). **23**: $\mathbf{R}_f$ = 0.23 (30 % EtOAc/hexanes); IR ν_{max} 3073, 2977, 2940, 2845, 1677, 1652, 1622, 1598, 1449, 1389, 1374, 1262, 1226, 1174, 1133, 1078, 994, 914, 839, 778, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.82 (m, 2H), 7.58 – 7.47 (m, 1H), 7.47 – 7.37 (m, 2H), 5.83 – 5.59 (m, 2H), 5.51 (s, 1H), 5.18 – 4.94 (m, 4H), 3.64 (s, 3H), 2.30 – 2.05 (m, 7H), 2.00 (dd, *J* = 13.3, 6.3 Hz, 1H), 1.72 (ddd, *J* = 13.6, 9.4, 9.4 Hz, 1H), 1.67 (s, 3H), 1.52 (dd, *J* = 13.0, 13.0 Hz, 1H), 1.33 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 186.2, 174.9, 168.2, 146.8, 137.6, 136.6, 135.8, 133.1, 129.2, 128.3, 126.1, 117.3, 116.2, 111.7, 102.9, 87.4, 55.2, 45.4, 42.6, 39.9, 39.8, 39.4, 36.1, 35.1, 28.2, 20.6, 18.9; **HR-MS**: *m/z* Calcd. for $C_{30}H_{36}O_4$ $[M+H^+]$: 461.2692, Found 461.2701.



meso-**9C** **26**

(+/-)-(3*S*,4a*R*)-3-Allyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*R*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one 26: Oxycyclization product **26** (63.6 mg, 66 %) was synthesized as an amorphous solid and was prepared according to general procedure A from enol (*meso*)-**9C** (95.8 mg, 0.208 mmol), LiBr (182 mg, 2.1 mmol), diphenyl phosphate **18** (525 mg, 2.1 mmol) in CH_2Cl_2 (14 mL). **26**: $\mathbf{R}_f$ = 0.31 (35 % EtOAc/hexanes); IR ν_{max} 3075,

2979, 2933, 2920, 2857, 1678, 1650, 1622, 1598, 1449, 1374, 1349, 1259, 1226, 1169, 1126, 1075, 1006, 915, 839, 781, 733 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.55 – 7.48 (m, 1H), 7.44 – 7.37 (m, 2H), 5.67 (dddd, *J* = 16.4, 10.0, 8.0, 5.8 Hz, 1H), 5.65 – 5.57 (m, 1H), 5.60 (s, 1H), 5.14 – 4.91 (m, 4H), 4.76 (t, *J* = 1.5 Hz, 1H), 4.67 (s, 1H), 3.75 (s, 3H), 2.48 (dd, *J* = 13.7, 3.7 Hz, 1H), 2.24 – 2.09 (m, 2H), 2.08 – 1.88 (m, 4H), 1.74 (ddd, *J* = 13.9, 8.8, 8.8 Hz, 1H), 1.66 (s, 3H), 1.64 – 1.57 (m, 1H), 1.54 (dd, *J* = 13.3 Hz, 1H), 1.27 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.1, 186.0, 175.1, 170.0, 146.1, 137.7, 136.5, 135.8, 133.0, 129.3, 128.3, 126.0, 117.3, 116.1, 111.7, 102.5, 88.3, 55.8, 47.6, 45.3, 42.7, 42.4, 39.5, 36.0, 35.5, 28.8, 21.6, 19.9; **HR-MS**: *m/z* Calcd. for $C_{30}H_{36}O_4$ $[M+H^+]$: 461.2692, Found 461.2690.



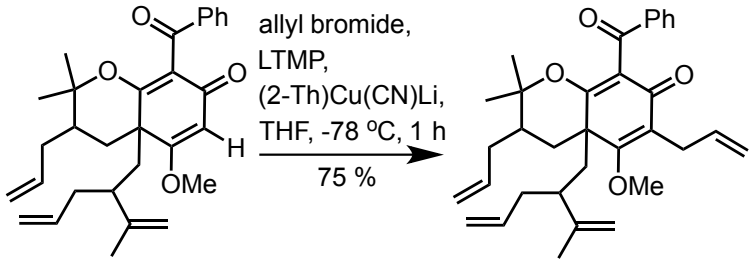
(+/-)-**9A**:(*meso*)-**9B**:(*meso*)-**9C**
2.5:2.4:1 d.r.

13:**23**:**8**:**26**
3:3:1:1 d.r.

(+/-)-3-Allyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-(2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one 13:23:8:26: Oxycyclization products **13**:**23**:**8**:**26** (1.7 g, 3:3:1:1 d.r. as determined by ^1H NMR analysis) were prepared according to general procedure A from enols (+/-)-**9A**:(*meso*)-**9B**:(*meso*)-**9C** (2.0 g, 4.34 mmol, 2.5:2.4:1 d.r. as determined by ^1H NMR analysis), LiBr (3.77 g, 43.4 mmol), diphenyl phosphate **18** (10.9 g, 43.4 mmol) in CH_2Cl_2 (289 mL).

Vinylic Allylation:

General Procedure D



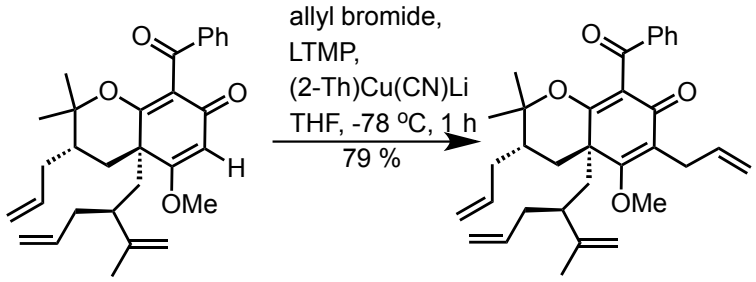
13:**23**:**8**:**26**
3:3:1:1 d.r.

21:**24**:**7**:**27**
3:3:1:1 d.r.

(Lithium Tetramethylpiperidine [LTMP] Preparation): To a flame-dried 10-mL round-bottom flask under an argon atmosphere containing a solution of 2,2,6,6-tetramethylpiperidine (2.08 mL, 12.3 mmol) in THF (24 mL) at -78 °C was added *n*BuLi (4.96 mL, 2.5 M in THF) in a dropwise fashion over the course of 15 min. The LTMP solution was allowed to stir for 15 min at -78 °C prior to use.

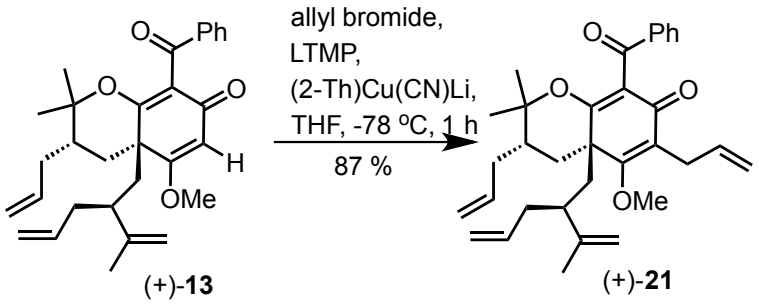
(+/-)-3,6-Diallyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-(2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one 21:**24**:**7**:**27:** To a flame-dried 1-L round-bottom flask under an argon atmosphere containing pyranodienones **13**:**23**:**8**:**26** (1.04 g, 2.27 mmol, 3:3:1:1 d.r. as determined by ^{1}H NMR analysis) was added THF (86.4 mL). The solution was cooled to -78 °C, and a freshly prepared solution (at -78 °C) of LTMP (22.7 mL, 0.5 M in THF) was added along the side of the flask in a dropwise fashion over the course of an hour. Lithium 2-thienylcyanocuprate (49.9 mL, 0.25 M in THF) was then added in a dropwise manner along the side of the flask over the course of an hour. [Note: Lithium 2-thienylcyanocuprate should be bright yellow in color and should not contain any visible copper salts for optimal yields.] Allyl bromide (0.98 mL, 11.3 mmol) was added dropwise into the center of the reaction mixture over the course of 10 min. [Note: Allyl bromide was filtered through a pad of basic Al_2O_3 under an argon atmosphere prior to use.] The reaction was allowed to stir for 1 h and was then quenched with 30 % NH_4OH (432 mL), diluted with Et_2O (200 mL), and vigorously stirred for 5 min at room temperature. The mixture was poured into a separatory funnel and extracted into Et_2O (3 x 400 mL). The combined organic extracts were washed with water (1 x 400 mL) and brine (1 x

400 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography (silica gel, 2 – 10 % EtOAc/hexanes) provided vinylic allylation products **21**:**23**:**7**:**27** (853 mg, 75 %, 3:3:1:1 d.r. as determined by ^{1}H NMR analysis) as a brown oil.

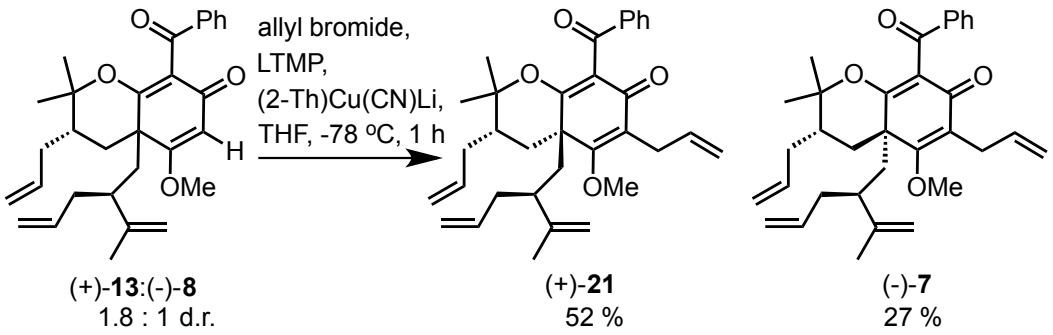


(-)-**8** (-)-**7**

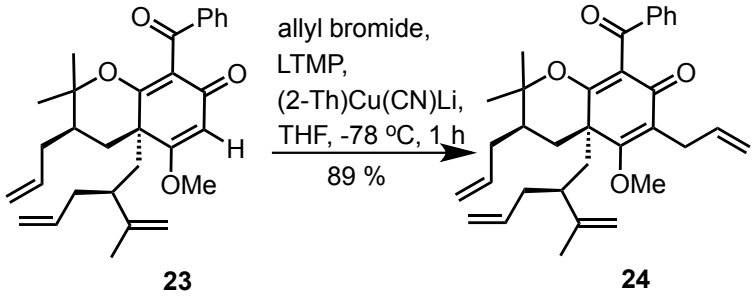
(-)-(3*S*,4a*R*)-3,6-Diallyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one (-)-7: Vinylic allylation product (-)-**7** (17.4 mg, 79 %) was prepared according to general procedure D from a solution of pyranodineone (-)-**8** (20.3 mg, 0.0441 mmol) in THF (1.68 mL) at -78 °C using LTMP (0.44 mL, 0.5 M in THF), lithium 2-thienylcyanocuprate (0.97 mL, 0.25 M in THF), and allyl bromide (19 μL, 0.22 mmol). (-)-**7**: $\mathbf{R}_f$ = 0.38 (20 % EtOAc/hexanes); IR ν_{max} 2982, 2917, 2848, 1677, 1656, 1618, 1598, 1449, 1373, 1229, 1174, 1129, 998, 916, 739 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.55 – 7.48 (m, 1H), 7.41 (m, 2H), 5.93 (dddd, *J* = 16.5, 10.2, 6.3, 6.1 Hz, 1H), 5.69 (dddd, *J* = 16.4, 10.4, 8.3, 5.8 Hz, 1H), 5.62 (dddd, *J* = 17.1, 10.2, 6.8, 6.6 Hz, 1H), 5.12 – 4.90 (m, 6H), 4.68 (t, *J* = 1.4 Hz, 1H), 4.54 (br s, 1H), 3.93 (s, 3H), 3.26 (dddd, *J* = 15.6, 5.7, 1.8, 1.8 Hz, 1H), 3.06 (dddd, *J* = 15.7, 6.4, 1.6, 1.6 Hz, 1H), 2.44 (dd, *J* = 14.5, 4.5 Hz, 1H), 2.22 (dd, *J* = 13.5, 5.8 Hz, 1H), 2.19 – 1.95 (m, 4H), 1.92 (dd, *J* = 13.5, 3.4 Hz, 1H), 1.74 (ddd, *J* = 13.8, 10.2, 9.6 Hz, 1H), 1.66 – 1.59 (m, 1H), 1.60 (br s, 3H), 1.49 (dd, *J* = 14.6, 13.0 Hz, 1H), 1.27 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.4, 186.4, 171.8, 169.9, 146.7, 137.7, 136.6, 136.5, 135.9, 133.0, 129.1, 128.4, 126.0, 119.9, 117.2, 116.1, 115.0, 111.7, 88.1, 62.1, 49.1, 45.2, 42.5, 39.4, 35.7, 35.5, 28.8, 28.5, 21.7, 18.9; **HR-MS**: *m/z* Calcd. for $C_{33}H_{40}O_4$ [M+H$^+$]: 501.3005, Found 501.3013; $[\alpha]_D^{27}$ = -140.6 (c. 0.250, $CHCl_3$).



(+)-(3*S*,4a*S*)-3,6-Diallyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one (+)-21: Vinylic allylation product (+)-**21** (93.8 mg, 87 %) was prepared according to general procedure D from a solution of pyranodineone (+)-**13** (98.7 mg, 0.2143 mmol) in THF (8.2 mL) at -78 ºC using LTMP (2.14 mL, 0.5 M in THF), lithium 2-thienylcyanocuprate (4.7 mL, 0.25 M in THF), and allyl bromide (0.1 mL, 1.16 mmol). (+)-**21**: $\mathbf{R}_f$ = 0.28 (15 % EtOAc/hexanes); IR ν_{max} 3072, 2976, 2928, 2848, 1678, 1656, 1622, 1449, 1387, 1372, 1229, 1178, 1130, 995, 912, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.53 – 7.47 (m, 1H), 7.42 – 7.35 (m, 2H), 5.95 (dddd, *J* = 16.7, 10.1, 6.0, 6.0 Hz, 1H), 5.80 – 5.69 (m, 1H), 5.67 – 5.56 (m, 1H), 5.15 – 4.91 (m, 6H), 4.73 (qd, *J* = 1.5, 1.4 Hz, 1H), 4.59 (br s, 1H), 3.97 (s, 3H), 3.27 (dddd, *J* = 15.4, 5.7, 1.6, 1.6 Hz, 1H), 3.20 (dddd, *J* = 15.7, 6.4, 1.6, 1.6 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.23 (dd, *J* = 13.5, 3.8 Hz, 1H), 2.20 – 2.12 (m, 2H), 2.11 – 1.97 (m, 3H), 1.79 – 1.72 (m, 1H), 1.72 – 1.63 (m, 1H), 1.62 (s, 3H), 1.47 (dd, *J* = 12.9, 12.9 Hz, 1H), 1.31 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 186.7, 172.0, 168.5, 145.9, 137.7, 136.7, 136.2, 135.9, 132.9, 129.3, 128.1, 125.9, 121.4, 117.2, 115.7, 115.3, 112.3, 87.3, 62.4, 46.8, 43.5, 39.7, 39.5, 39.3, 36.6, 36.1, 28.2, 28.2, 20.7, 18.8; **HR-MS**: *m/z* Calcd. for $C_{33}H_{40}O_4$ [M+H^+]: 501.3005, Found 501.3006; $[\alpha]_D^{27}$ = +41.1 (c. 0.250, $CHCl_3$).

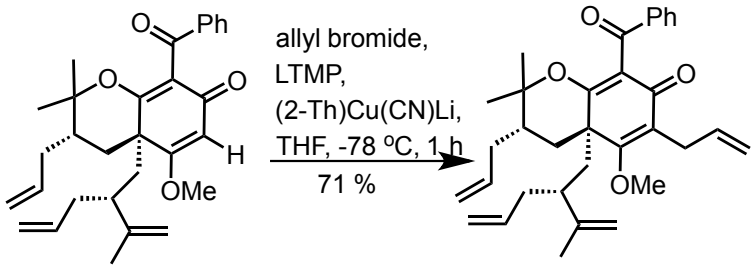


(+)-(3*S*,4a*S*)-3,6-Diallyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one (+)-21 and (-)-(3*S*,4a*R*)-3,6-Diallyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one (-)-7: Vinylic allylation products (+)-**21** (621 mg, 52 %) and (-)-**7** (323 mg, 27 %) were prepared according to general procedure D from a solution of pyranodineones (+)-**13**:(-)-**8** (1.1 g, 2.39 mmol) in THF (91 mL) at -78 ºC using LTMP (23.9 mL, 0.5 M in THF), lithium 2-thienylcyanocuprate (52.5 mL, 0.25 M in THF), and allyl bromide (1.03 mL, 11.9 mmol). Purification by column chromatography (silica gel, 2 – 14 % EtOAc/hexanes) provided 306 mg of (+)-**21** and 159 mg of (-)-**7**. Purification of remaining impure fractions by preparative thin layer chromatography (silica gel, 4 elutions in 15 % EtOAc/hexanes) afforded an additional 315 mg of (+)-**21** and 164 mg of (-)-**7**. Reaction yield:[(+)-**21** (621 mg, 52 %) and (-)-**7** (323 mg, 27 %)]



(+/-)-(3*R*,4a*R*)-3,6-Diallyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*S*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one 24: Vinylic allylation product **24** (19.3 mg, 89 %) was prepared as a yellow oil according to general procedure D from a solution of pyranodienone **23** (20.0 mg, 0.0434 mmol) in THF (1.65 mL) at -78 ºC using LTMP (0.43 mL, 0.5 M in THF), lithium 2-thienylcyanocuprate (0.96 mL, 0.25 M in THF), and allyl bromide (20

μL, 0.231 mmol). **24:** $\mathbf{R}_f$ = 0.26 (14 % EtOAc/hexanes); IR ν_{max} 3075, 2977, 2924, 2852, 1678, 1656, 1621, 1449, 1372, 1229, 1175, 1130, 1074, 995, 912, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.55 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 5.93 (dddd, *J* = 16.7, 10.0, 6.1, 6.1 Hz, 1H), 5.81 – 5.69 (m, 1H), 5.64 (dddd, *J* = 17.0, 10.1, 6.6, 6.6 Hz, 1H), 5.14 – 4.92 (m, 6H), 4.68 (dd, *J* = 1.3, 1.3 Hz, 1H), 4.56 (s, 1H), 3.91 (s, 3H), 3.25 (dddd, *J* = 15.5, 5.5, 2.0, 2.0 Hz, 1H), 3.06 (dddd, *J* = 15.9, 6.8, 1.7, 1.7 Hz, 1H), 2.27 – 2.00 (m, 7H), 1.97 (dd, *J* = 13.3, 6.0 Hz, 1H), 1.69 (ddd, *J* = 14.0, 9.6, 9.6 Hz, 1H), 1.61 (s, 3H), 1.47 (dd, *J* = 13.2, 13.2 Hz, 1H), 1.31 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 186.6, 172.1, 168.6, 146.9, 137.6, 136.7, 136.5, 135.9, 133.0, 129.1, 128.3, 125.9, 120.3, 117.2, 116.1, 115.0, 111.8, 87.1, 62.0, 46.8, 42.6, 39.9, 39.5, 39.4, 36.2, 35.0, 28.2, 28.2, 20.8, 18.8; **HR-MS**: *m/z* Calcd. for $C_{33}H_{40}O_4$ [M+H^+]: 501.3005, Found 501.2999.

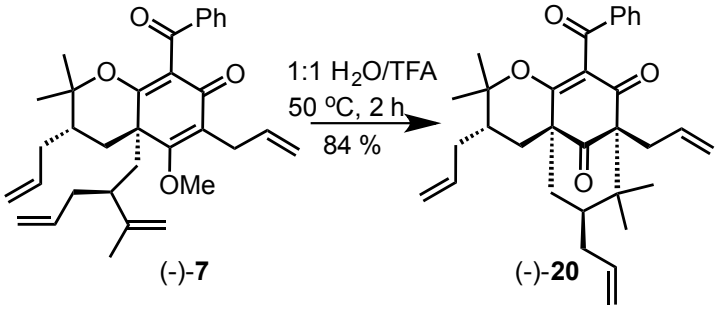


26 **27**

(+/-)-(3*S*,4a*R*)-3,6-Diallyl-8-benzoyl-5-methoxy-2,2-dimethyl-4a-((*R*)-2-(prop-1-en-2-yl)pent-4-en-1-yl)-2,3,4,4a-tetrahydro-7*H*-chromen-7-one 27: Vinylic allylation product **27** (48.9 mg, 71 %) was prepared according to general procedure D from a solution of pyranodienone **26** (63.6 mg, 0.138 mmol) in THF (5.3 mL) at -78 °C using LTMP (1.4 mL, 0.5 M in THF), lithium 2-thienylcyanocuprate (3.0 mL, 0.25 M in THF), and allyl bromide (60 μL, 0.691 mmol). **27:** $\mathbf{R}_f$ = 0.42 (25 % EtOAc/hexanes); IR ν_{max} 3082, 2978, 2935, 2849, 1679, 1654, 1620, 1449, 1373, 1229, 1172, 1123, 1068, 996, 913, 740 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 – 7.37 (m, 2H), 5.95 (dddd, *J* = 16.5, 10.4, 6.1, 6.1 Hz, 1H), 5.69 (dddd, *J* = 16.7, 10.3, 8.6, 5.6 Hz, 1H), 5.60 (dddd, *J* = 16.0, 12.0, 6.9, 6.7 Hz, 1H), 5.14 – 4.90 (m, 6H), 4.74 (br s, 1H), 4.62 (br s, 1H), 4.01 (s, 3H), 3.24 (ddd, *J* = 37.9, 15.8, 5.9 Hz, 2H), 2.45 (dd, *J* = 14.1, 4.2 Hz, 1H), 2.16 (dddd, *J* = 31.6, 13.8, 8.6, 8.6 Hz, 2H), 2.06 – 1.95 (m, 4H), 1.74 (ddd, *J* = 14.2, 9.4, 9.4 Hz, 1H), 1.63 (s, 3H), 1.61 – 1.55 (m, 1H), 1.51 (dd, *J* = 14.1 Hz, 1H), 1.27 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 186.3, 171.9,

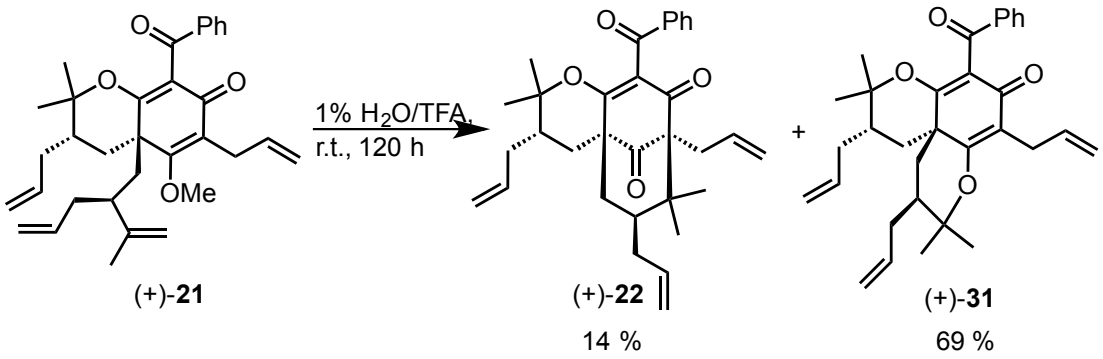
170.0, 146.1, 137.8, 136.7, 136.4, 135.9, 132.9, 129.2, 128.2, 126.3, 120.7, 117.3, 115.8, 115.2, 112.0, 88.2, 62.4, 49.1, 45.2, 42.9, 42.3, 39.1, 36.2, 35.4, 28.7, 28.5, 21.7, 19.5; **HR-MS**: *m/z* Calcd. for $C_{33}H_{40}O_4$ [M+H$^+$]: 501.3005, Found 501.3021.

Cationic *C*-Cyclization to a [3.3.1]-Bicyclic Framework

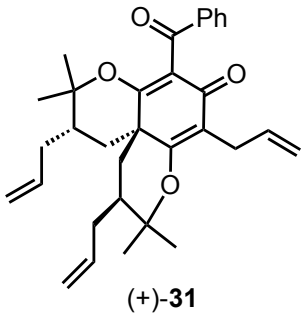


(-)-(3*S*,4a*R*,6*S*,8*S*)-3,6,8-Triallyl-10-benzoyl-2,2,7,7-tetramethyl-3,4,5,6,7,8-hexahydro-2*H*,9*H*-4a,8-methanocycloocta[*b*]pyran-9,11-dione (-)-20: Trifluoroacetic acid (1.0 mL) and water (1.0 mL) were added to a 20-mL scintillation vial. After the mixture cooled to room temperature, the TFA/H_2O (2.0 mL) mixture was added to a 20-mL scintillation vial containing pyranodienone (-)-**7** (7.1 mg, 0.0141 mmol). The reaction mixture was then heated to 50 °C for 2 h, cooled to room temperature, and concentrated *in vacuo*. Purification by column chromatography provided *C*-cyclization product (-)-**20** (5.8 mg, 84 %) as a white amorphous solid. (-)-**20**: $\mathbf{R}_f$ = 0.43 (20 % EtOAc/hexanes); IR ν_{max} 3078, 2978, 2935, 1728, 1682, 1641, 1600, 1449, 1391, 1374, 1351, 1305, 1120, 993, 917, 733 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.55 – 7.48 (m, 1H), 7.42 – 7.35 (m, 2H), 5.85 – 5.77 (m, 1H), 5.73 (dddd, *J* = 16.5, 9.8, 8.8, 5.2 Hz, 1H), 5.64 (dddd, *J* = 16.6, 10.2, 7.6, 6.2 Hz, 1H), 5.17 – 4.98 (m, 6H), 3.02 (dd, *J* = 14.2, 3.6 Hz, 1H), 2.69 (dddd, *J* = 13.1, 7.5, 1.2, 1.2 Hz, 1H), 2.58 (dddd, *J* = 12.9, 6.3, 1.3, 1.3 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.18 (dd, *J* = 13.9, 4.7 Hz, 1H), 2.21 – 2.05 (m, 2H), 1.79 (ddd, *J* = 14.1, 10.3, 8.4 Hz, 1H), 1.70 (ddd, *J* = 13.9, 9.6, 9.6 Hz, 1H), 1.53 – 1.42 (m, 2H), 1.21 (s, 3H), 1.09 (s, 3H), 1.00 (dd, *J* = 13.9, 13.9 Hz 1H), 0.93 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 193.7, 193.2, 171.0, 137.3, 136.8, 135.5, 134.4, 133.1, 129.0, 128.3, 127.1, 119.2, 117.4, 116.8, 87.0, 70.7, 52.9, 46.1, 42.0, 41.9, 39.7, 35.5, 33.7, 30.0, 28.4, 27.3, 22.0, 21.3, 16.1; **HR-MS**: *m/z* Calcd. for $C_{32}H_{38}O_4$ [M+Na$^+$]: 509.2668, Found 509.2674; $[\alpha]_D^{27}$

= -110.9 (c. 0.250, $CHCl_3$).

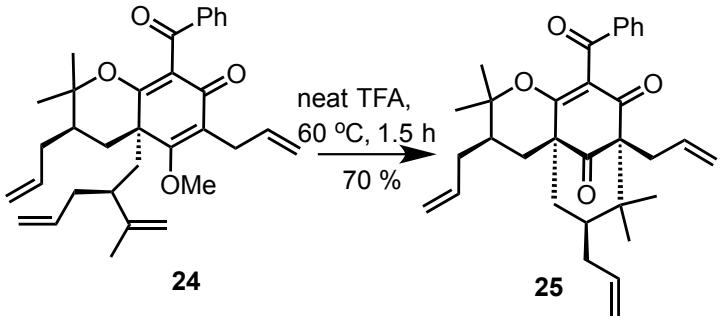


(+)-(3*S*,4a*R*,6*S*,8*S*)-3,6,8-Triallyl-10-benzoyl-2,2,7,7-tetramethyl-3,4,5,6,7,8-hexahydro-2*H*,9*H*-4a,8-methanocycloocta[*b*]pyran-9,11-dione (+)-22: To a 25-mL round-bottom flask containing pyranodienone (+)-**21** (10.0 mg, 0.01997 mmol) and a stir bar was added TFA (5.0 mL) and the solution was allowed to stir at room temperature for 1 h. Water (0.05 mL) was then added and the reaction mixture was allowed to stir for 24 hours. The solvent was removed *in vacuo*. This process was repeated 5x before purification by column chromatography (silica gel, 2 – 12 % EtOAc/hexanes) to provide *C*-cyclization product (+)-**22** (1.4 mg, 14 %) as a yellow solid and *O*-cyclization product (+)-**31** (6.7 mg, 69 %) as a white amorphous solid. (+)-**22**: $\mathbf{R}_f$ = 0.31 (15 % EtOAc/hexanes); **m.p.** 95 – 100 ^{o}C (CH_2Cl_2); IR ν_{max} 3085, 2981, 2934, 2858, 1727, 1682, 1640, 1607, 1449, 1390, 1353, 1230, 1173, 1137, 1120, 1002, 922, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.54 – 7.48 (m, 1H), 7.37 (m, *J* = 7.7 Hz, 2H), 5.77 – 5.55 (m, 3H), 5.27 (ddd, *J* = 17.0, 2.0 Hz, 1H), 5.13 – 5.05 (m, 4H), 5.02 (dd, *J* = 10.2, 2.1 Hz, 1H), 2.73 – 2.64 (m, 3H), 2.60 (dd, *J* = 12.9, 6.6 Hz, 1H), 2.36 (ddd, *J* = 14.4, 4.3 Hz, 1H), 2.20 (br dd, *J* = 14.2, 5.7 Hz, 1H), 1.98 – 1.87 (m, 2H), 1.80 – 1.66 (m, 3H), 1.65 – 1.57 (m, 1H), 1.30 (s, 3H), 1.15 (s, 3H), 1.03 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 193.7, 193.2, 170.5, 138.1, 137.4, 135.2, 134.2, 133.2, 128.9, 128.2, 123.6, 119.3, 117.8, 117.8, 85.4, 69.7, 48.2, 46.6, 44.4, 38.6, 36.2, 35.9, 34.7, 30.3, 28.7, 27.9, 26.7, 22.1, 21.4; **HR-MS**: *m/z* Calcd. for $C_{32}H_{38}O_4$ [M+H$^+$]: 487.2770, Found 487.2762; $[\alpha]_D^{24.6}$ = +24.4 (c. 0.250, $CHCl_3$).



(+)-**31**

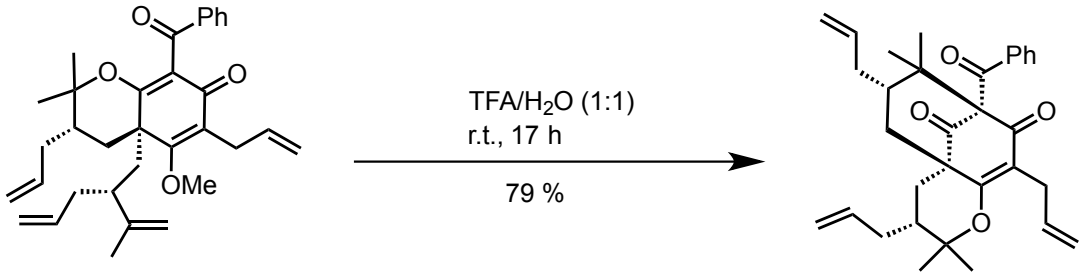
(+)-(3*S*,4a*S*,6*S*)-3,6,9-Triallyl-11-benzoyl-2,2,7,7-tetramethyl-3,4,6,7-tetrahydro-2*H*,5*H*,10*H*-pyrano[3,2-*e*]chromen-10-one (+)-31: $\mathbf{R}_f$ = 0.16 (15 % EtOAc/hexanes); IR ν_{max} 3077, 2979, 2932, 2851, 1686, 1659, 1622, 1449, 1396, 1374, 1270, 1226, 1195, 1123, 995, 914, 841, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.56 – 7.48 (m, 1H), 7.46 – 7.38 (m, 2H), 5.85 (dddd, *J* = 16.7, 10.0, 6.5 Hz, 1H), 5.78 – 5.64 (m, 2H), 5.19 – 4.89 (m, 6H), 3.18 (dddd, *J* = 14.2, 6.7, 1.4 Hz, 1H), 3.08 (dddd, *J* = 14.2, 6.3, 1.6 Hz, 1H), 2.49 (ddd, *J* = 14.5, 11.3, 3.7 Hz, 2H), 2.02 – 1.89 (m, 2H), 1.76 – 1.62 (m, 2H), 1.54 (s, 3H), 1.36 (d, *J* = 13.7 Hz, 1H), 1.33 (s, 3H), 1.30 (d, *J* = 14.0 Hz, 1H), 1.14 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 185.7, 170.4, 168.3, 137.5, 136.0, 135.6, 135.6, 133.0, 129.1, 128.4, 128.1, 124.1, 122.2, 117.7, 115.1, 88.6, 87.1, 41.8, 40.0, 39.9, 35.4, 35.4, 33.4, 32.7, 28.5, 28.2, 27.1, 20.6, 20.2; **HR-MS**: *m/z* Calcd. for $C_{32}H_{38}O_4$ [$M+H^+$]: 487.2828, Found 487.2836. ; $[\alpha]_D^{22.7}$ = +91.6 (c. 0.161, $CHCl_3$).



24 **25**

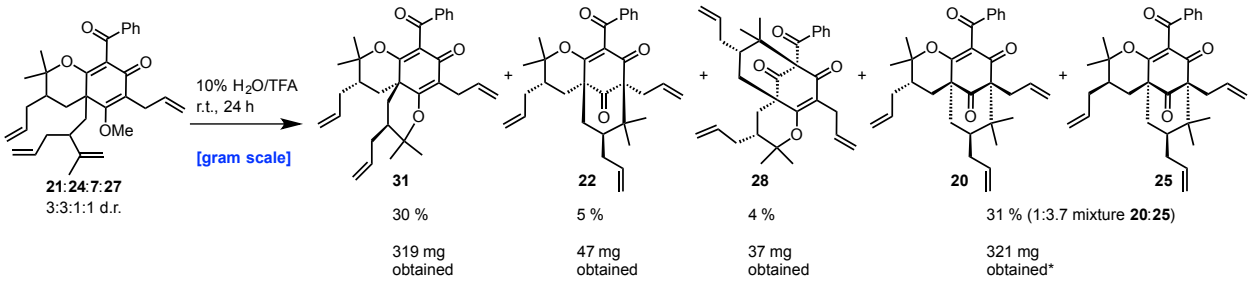
(+/-)-(3*R*,4a*S*,6*S*,8*R*)-3,6,8-Triallyl-10-benzoyl-2,2,7,7-tetramethyl-3,4,5,6,7,8-hexahydro-2*H*,9*H*-4a,8-methanocycloocta[*b*]pyran-9,11-dione 25: To a 20-mL scintillation vial containing pyranodienone **24** (55.1 mg, 0.110 mmol) was added TFA (4 mL). The vessel was then sealed and placed in a oil bath at 60 °C and stirred vigorously for 1.5 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and purified by column chromatography (silica gel, 2-10 % EtOAc/hexanes) to provide 37.4 mg (70 %) of *C*-cyclization product **25** as a white solid. **25**: $\mathbf{R}_f$ = 0.29 (14 % EtOAc/hexanes); **m.p.** 137 – 139 °C (CH_2Cl_2); IR ν_{max} 2975, 2922, 2857, 1727, 1683, 1641, 1606, 1449, 1390, 1353, 1137, 1121, 915, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.55 – 7.48 (m, 1H), 7.42 – 7.34 (m, 2H), 5.83 – 5.66 (m, 2H), 5.61 (dddd, *J* = 17.1, 10.2, 6.9, 6.9 Hz, 1H), 5.16 – 4.96 (m, 6H), 2.68 (dd, *J*

= 13.1, 7.2 Hz, 1H), 2.58 (dd, *J* = 12.8, 6.5 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.41 (dd, *J* = 13.8, 4.5 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.02 (dd, *J* = 14.0 Hz, 2H), 2.08 – 2.00 (m, 1H), 1.87 (dddd, *J* = 13.4, 10.3, 2.9, 2.9 Hz, 1H), 1.72 (dd, *J* = 14.6, 3.4 Hz, 1H) 1.80 – 1.68 (m, 2H), 1.31 – 1.23 (m, 1H), 1.27 (s, 3H), 1.09 (s, 3H), 0.84 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.9, 193.7, 193.0, 169.8, 137.4, 136.8, 135.2, 134.4, 133.1, 128.9, 128.3, 126.1, 119.1, 117.8, 116.8, 85.4, 71.5, 49.7, 46.3, 40.3, 40.1, 38.6, 35.9, 33.7, 29.6, 28.4, 27.9, 22.2, 21.2, 15.9; **HR-MS**: *m/z* Calcd. for $C_{32}H_{38}O_4$ [M+Na$^+$]: 487.2848, Found 487.2849.



27 **28**

(+/-)-(3*R*,4a*S*,6*S*,8*R*)-3,6,10-Triallyl-8-benzoyl-2,2,7,7-tetramethyl-3,4,5,6,7,8-hexahydro-2*H*,9*H*-4a,8-methanocycloocta[*b*]pyran-9,11-dione 28: To a 20-mL scintillation vial containing pyranodienone **27** (5.1 mg, 0.0102 mmol) was added water (4.5 mL) and TFA (4.5 mL). The reaction mixture was allowed to stir for 17 h before concentrating *in vacuo* to provide *C*-cyclization product **28** (3.9 mg, 79 %) as a clear oil. **28**: $\mathbf{R}_f$ = 0.33 (15 % EtOAc/hexanes); IR ν_{max} 3078, 2978, 2927, 2854, 1722, 1698, 1641, 1604, 1448, 1392, 1374, 1348, 1243, 1224, 1186, 1134, 1115, 995, 915, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.41 – 7.35 (m, 1H), 7.26 – 7.21 (m, 2H), 5.81 – 5.61 (m, 3H), 5.15 – 4.91 (m, 6H), 3.17 (dd, *J* = 13.5, 6.4 Hz, 1H), 3.12 (dd, *J* = 13.5, 7.4 Hz, 1H), 2.42 – 2.28 (m, 3H), 2.01 (dd, *J* = 13.9 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.80 (ddd, *J* = 13.9, 9.2 Hz, 1H), 1.77 – 1.70 (m, 3H), 1.54 (s, 3H), 1.34 (s, 3H), 1.30 – 1.24 (m, 1H), 1.20 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 193.5, 192.5, 167.5, 136.9, 136.8, 135.3, 135.2, 132.0, 128.2, 127.9, 123.3, 117.7, 116.7, 115.6, 84.1, 79.1, 50.9, 47.7, 41.4, 40.1, 38.8, 36.0, 32.6, 28.9, 28.2, 27.1, 23.0, 21.5, 16.1; **HR-MS**: *m/z* Calcd. for $C_{32}H_{38}O_4$ [M+H$^+$]: 487.2848, Found 487.2853.

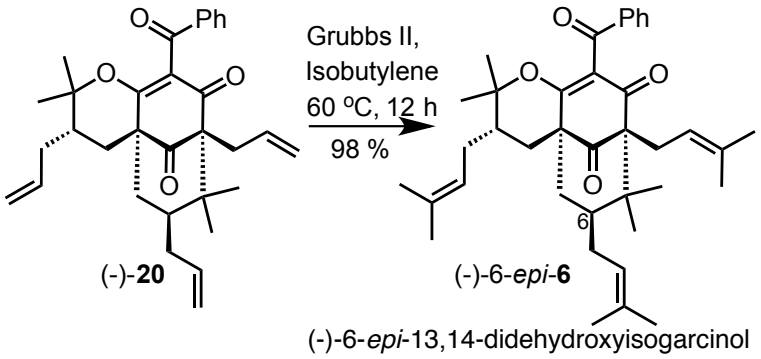


*Column chromatography provided compounds **20** and **25** as a 1:3.7 mixture determined by ^{1}H NMR analysis.[14]

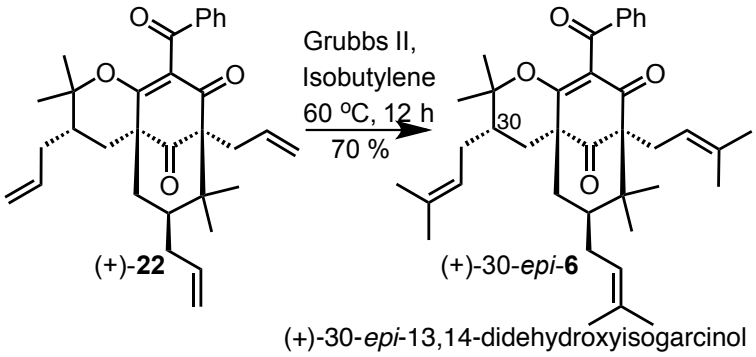
Cyclization Products 20:25:22:28:31: To a 500-mL round-bottom flask containing pyranodienones **21**:**24**:**7**:**27** (1.08 g, 2.16 mmol, 3:3:1:1 d.r. as determined by ^{1}H NMR analysis), was added TFA (120 mL). After 10 min, compounds **21**:**24**:**7**:**27** were fully dissolved in TFA, and water (12 mL) was then added dropwise over the course of 10 min. The reaction mixture stirred at room temperature for 24 h and was then concentrated *in vacuo*. Purification by column chromatography (silica gel, 0 – 12 % EtOAc/hexanes) provided 30-*epi*-13,14-didehydroxyisogarcinol core **22** (47 mg, 5 %) as a yellow solid, *O*-cyclization product **31** (319 mg, 30 %) as a white amorphous solid, and a mixture of cyclization products **20** and **25** (321 mg, 31 %, 1:3.7 mixture as determined by ^{1}H NMR analysis) as a white crystalline solid. Type A cyclization product **28** (90.5 mg, 41 % purity) was further purified by preparative thin layer chromatography (silica gel, ~2 elutions in 15 % EtOAc/hexanes) to provide 37 mg (4 %, 100 % purity) of **28** as a yellow oil. [Cyclization products **25** and **20** were separated by preparative thin layer chromatography (silica gel, ~10 elutions in 5 % EtOAc/hexanes; A single spot is cut into five sections, with the bottom two sections (compound **25**) and top two sections (compound **20**) are in most cases 100 % pure)].

Olefin Metathesis:

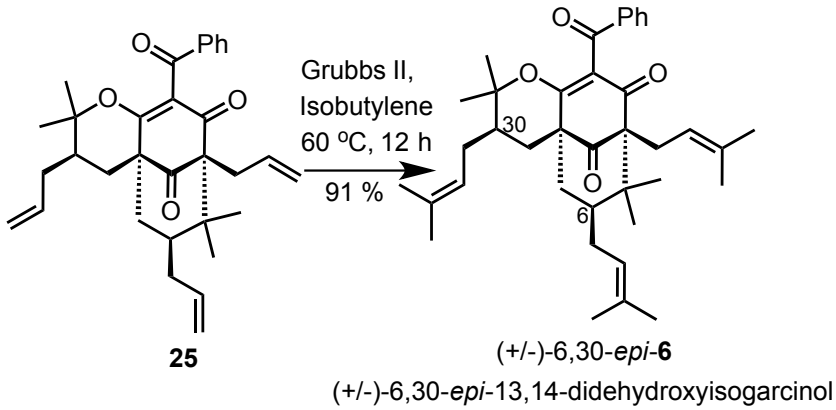
General Procedure E



(-)-6-*epi*-13,14-Didehydroxyisogarcinol (-)-6-*epi*-6: To a flame-dried 30-mL glass pressure tube containing (-)-**20** (16.8 mg, 0.0345 mmol) was added Grubbs 2nd generation catalyst (5.9 mg, 0.0069 mmol). The vessel was purged with argon, cooled to -78 ^{o}C, and filled with isobutylene (7 mL) which was condensed along the side of the tube. The reaction vessel was then sealed and warmed to 60 ^{o}C with vigorous stirring for 12 h. The reaction mixture was then re-cooled to -78 ^{o}C and opened to the air. The dry ice bath was then removed which allowed for the evaporation of isobutylene. Purification by column chromatography (silica gel, 2 – 10 % EtOAc/hexanes) provided 19.3 mg (98 %) of (-)-6-*epi*-13,14-didehyroxyisogarcinol [(-)-6-*epi*-**6**] as a clear oil. (-)-6-*epi*-**6**: $\mathbf{R}_f$ = 0.24 (9 % EtOAc/hexanes); IR ν_{max} 2973, 2928, 2858, 1728, 1683, 1643, 1605, 1449, 1374, 1348, 1308, 1231, 1172, 1125, 1095, 984, 955, 831, 755 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.66 (m, 2H), 7.56 – 7.46 (m, 1H), 7.43 – 7.32 (m, 2H), 5.22 – 5.15 (m, 1H), 5.06 (ddt, *J* = 8.6, 5.4, 1.7 Hz, 1H), 4.87 (ddt, *J* = 8.2, 5.5, 1.6 Hz, 1H), 3.03 (dd, *J* = 14.2, 3.7 Hz, 1H), 2.68 (dd, *J* = 13.8, 8.0 Hz, 1H), 2.52 – 2.31 (m, 1H), 2.23 – 2.15 (m, 1H), 2.15 (dd, *J* = 14.0, 4.7 Hz, 1H), 2.06 – 1.97 (m, 2H), 1.84 – 1.67 (m, 2H), 1.77 (s, 3H), 1.70 (s, 3H), 1.64 (s, 3H), 1.60 (s, 6H), 1.58 (s, 3H), 1.47 (dd, *J* = 13.9, 12.4 Hz, 1H), 1.41 (dddd, *J* = 9.9, 9.9, 3.7, 3.7 Hz, 1H), 1.21 (s, 3H), 1.11 (s, 3H), 0.96 (dd, *J* = 14.2, 13.0 Hz, 1H), 0.89 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.4, 194.0, 193.6, 170.9, 137.5, 134.3, 133.6, 133.2, 132.9, 128.8, 128.3, 126.8, 122.5, 121.4, 120.1, 86.8, 70.4, 52.8, 46.1, 42.9, 42.4, 40.8, 29.7, 28.5, 27.7, 27.7, 26.1, 25.8, 25.8, 24.8, 22.1, 21.3, 18.1, 18.0, 18.0, 16.2; **HR-MS**: *m/z* Calcd. for $C_{38}H_{50}O_4$ [M+Na^{+}]: 593.3607, Found 593.3607; $[\alpha]_D^{26}$ = -144.59 (c. 0.250, $CHCl_3$).

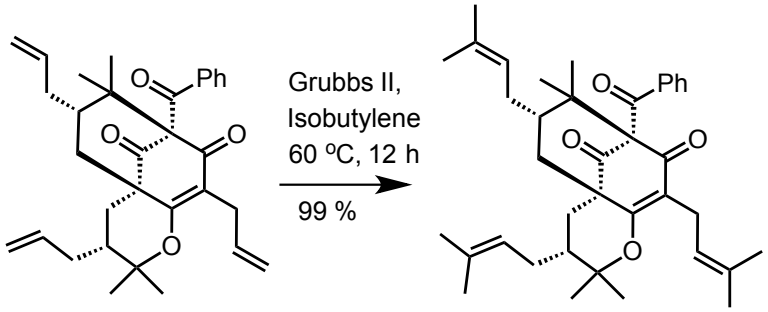


(+)-30-*epi*-13,14-Didehydroxyisogarcinol (+)-30-*epi*-6: Polyprenylated product (+)-30-*epi*-**6** (21.4 mg, 70 %) was afforded as a yellow oil and prepared according to general procedure E from Type B PPAP core (+)-**22** (26.0 mg, 0.0534 mmol) using Grubbs 2nd generation catalyst (18.2 mg, 0.0214 mmol) and isobutylene (10 mL) in a sealed pressure tube. (+)-30-*epi*-**6**: $\mathbf{R}_f$ = 0.29 (12 % EtOAc/hexanes); IR ν_{max} 2975, 2924, 2892, 2851, 1728, 1685, 1642, 1607, 1448, 1393, 1347, 1229, 1169, 1124, 959, 842, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 7.52 – 7.45 (m, 1H), 7.38 – 7.30 (m, 2H), 5.08 – 5.02 (m, 1H), 4.97 – 4.84 (m, 2H), 2.67 – 2.40 (m, 4H), 2.24 – 2.16 (m, 1H), 2.09 – 2.01 (m, 1H), 1.97 (dd, *J* = 14.4, 13.8 Hz, 1H), 1.88 – 1.74 (m, 3H), 1.72 (s, 3H), 1.70 (s, 6H), 1.70 (s, 3H), 1.69 (s, 3H), 1.65 (dd, *J* = 14.5, 3.0 Hz, 1H), 1.61 (s, 6H), 1.60 (s, 3H), 1.52 – 1.46 (m, 1H), 1.30 (s, 3H), 1.16 (s, 3H), 1.00 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.5, 193.8, 193.6, 170.4, 137.6, 134.5, 134.3, 133.1, 133.0, 128.7, 128.3, 125.0, 123.9, 121.2, 119.8, 85.4, 69.2, 48.4, 46.7, 46.4, 39.7, 38.0, 30.0, 29.2, 29.1, 28.0, 26.8, 26.1, 26.0, 25.8, 25.2, 22.3, 21.5, 18.2, 18.1, 17.9; **HR-MS**: *m/z* Calcd. for $C_{38}H_{50}O_4$ [M+H$^+$]: 571.3787, Found 571.3787; $[\alpha]_D^{26}$ = -144.59 (c. 0.250, $CHCl_3$).



(+/-)-6,30-*epi*-13,14-didehydroxyisogarcinol (+/-)-6,30-*epi*-6: Polyprenylated product (+/-)-6,30-*epi*-**6** (10.7 mg, 91 %) was prepared according to general procedure E from Type B PPAP

core **25** (10.0 mg, 0.0206 mmol) using Grubbs 2nd generation catalyst (3.5 mg, 0.00411 mmol) and isobutylene (5 mL) in a sealed pressure tube. (+/-)-6,30-*epi*-**6**: $\mathbf{R}_f$ = 0.28 (15 % EtOAc/hexanes); IR ν_{max} 2977, 2929, 2857, 1726, 1683, 1644, 1609, 1449, 1377, 1347, 1310, 1226, 1173, 1124, 964, 917, 839, 763, 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.65 (m, 2H), 7.57 – 7.45 (m, 1H), 7.42 – 7.32 (m, 2H), 5.17 – 5.02 (m, 2H), 4.86 (app t, *J* = 6.5 Hz, 1H), 2.66 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.49 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.41 (dd, *J* = 13.6, 4.5 Hz, 1H), 2.31 – 2.19 (m, 1H), 2.18 – 2.02 (m, 2H), 2.02 – 1.92 (m, 1H), 1.90 – 1.61 (m, 13H), 1.77 (s, 6H), 1.64 (s, 3H), 1.36 – 1.25 (m, 1H), 1.32 (s, 3H), 1.15 (s, 3H), 0.89 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 193.9, 193.5, 169.8, 137.6, 134.2, 134.1, 133.3, 133.0, 128.8, 128.3, 125.8, 122.6, 121.2, 120.1, 85.4, 71.3, 49.8, 46.3, 41.5, 40.5, 39.6, 29.9, 28.6, 28.0, 27.8, 26.1, 25.8, 25.8, 24.4, 22.3, 21.3, 18.1, 18.0, 17.9, 16.0; **HR-MS**: *m/z* Calcd. for $C_{38}H_{50}O_4$ [M+Na^+]: 593.3607, Found 593.3611.



28 (+/-)-6,30-*epi*-**5**

(+/-)-6,30-*epi*-garcimultiflorone A

6,30-*epi*-garcimultiflorone A 6,30-*epi*-5: Polyprenylated product (+/-)-6,30-*epi*-**5** (18.9 mg, 99 %) was afforded as a white amorphous solid and was prepared according to general procedure E from **28** (16.3 mg, 0.0335 mmol) with Grubbs 2nd generation catalyst (5.7 mg, 0.0067 mmol), and isobutylene (5 mL). 6,30-*epi*-**5:** $\mathbf{R}_f$ = 0.51 (10 % EtOAc/hexanes); IR ν_{max} 2973, 2923, 2857, 1721, 1697, 1643, 1604, 1447, 1389, 1373, 1344, 1243, 1222, 1125, 1065, 1024, 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.40 – 7.35 (m, 1H), 7.25 – 7.20 (m, 2H), 5.11 – 5.06 (m, 1H), 5.06 – 4.95 (m, 1H), 3.12 (dd, *J* = 13.6, 7.2 Hz, 1H), 3.07 (dd, *J* = 13.6, 7.7 Hz, 1H), 2.27 (dd, *J* = 13.5, 4.3 Hz, 1H), 2.24 – 2.12 (m, 2H), 1.98 (dd, *J* = 14.3, 13.2 Hz, 1H), 1.90 – 1.76 (m, 2H), 1.73 (s, 3H), 1.71 (s, 3H), 1.70 – 1.55 (unresolved m, 3H), 1.66 (br d, *J* = 1.4 Hz, 3H), 1.64 (br d, *J* = 1.3 Hz, 3H), 1.62 (s, 3H), 1.58 (s, 3H), 1.54 (s, 3H), 1.35 (s, 3H), 1.27 (dd, *J* = 13.6, 12.5 Hz, 1H), 1.19 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 193.6, 192.8, 167.0, 136.8, 134.2, 133.2, 131.9, 131.8, 128.2, 127.8, 124.5, 122.6, 121.3, 121.3, 84.0,

79.1, 51.0, 47.8, 42.7, 40.5, 39.8, 30.0, 29.0, 28.2, 26.7, 25.9, 25.8, 25.8, 23.0, 21.8, 21.2, 18.0, 17.9, 17.9, 16.1; **HR-MS**: *m/z* Calcd. for $C_{38}H_{50}O_4$ [M+H$^+$]: 571.3787, Found 571.3789.

III. References Cited

S1. (a) Boyce, J. H.; Porco, J. A., Jr. *Angew. Chem. Int. Ed.* **2014**, *53,* 7832.

S2. Kwon, M. S.; Sim, S. H.; Chung, Y. K.; Lee, E. *Tetrahedron*. 2011, *67*, 10179.

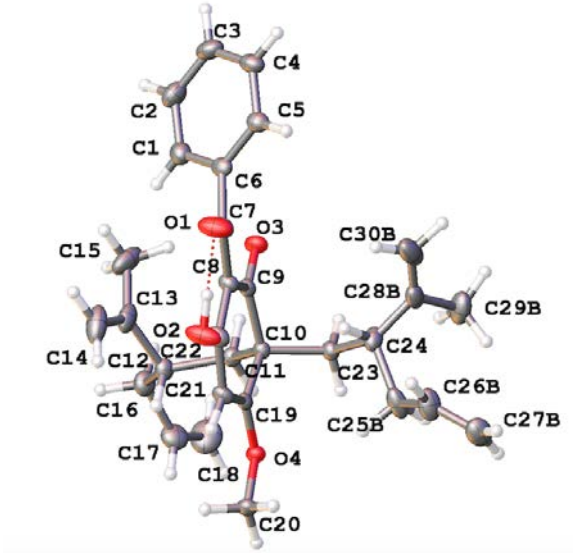
S3. Only one enantiomer of (+/-)-**9A** is shown for clarity.

S4. Grenning, A. J.; Boyce, J. H.; Porco, J. A., Jr. *J. Am. Chem. Soc.* **2014**, *136*, 11799.

S5. (a) Surendra, K.; Corey, E. J. *J. Am. Chem. Soc.* 2012, *134*, 11992. (b) Surendra, K.; Rajendar, G.; Corey, E. J. *J. Am. Chem. Soc.* 2014, *136*, 642.

IV. X-Ray Crystallographic Data

X-ray crystallographic data for compound (*meso*)-**9C**:



Crystals of compound (*meso*)-**9C** suitable for X-ray analysis were obtained in isooctane at -20 ^{o}C over the course of 48 h. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC # 1508478). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data

$C_{30}H_{36}O_4$	$F(000)$ = 1984
M_r = 460.59	D_x = 1.151 Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, λ = 1.54178 Å
Hall symbol: -P 2yn	Cell parameters from 9698 reflections
a = 14.1854 (2) Å	θ = 3.2–66.5°
b = 19.4283 (3) Å	μ = 0.59 mm^{-1}
c = 19.7516 (3) Å	T = 100 K
β = 102.419 (1)°	Block, colorless
V = 5316.13 (14) Å^3	0.24 × 0.20 × 0.15 mm
Z = 8	

Data collection

Bruker Proteum-R diffractometer	9331 independent reflections
Radiation source: rotating anode	8667 reflections with $I > 2\sigma(I)$
Montel	$R_{int} = 0.040$
ω and ϕ scans	$\theta_{max} = 66.6°$, $\theta_{min} = 3.2°$
Absorption correction: multi-scan *SADABS* (Sheldrick, 2015)	$h = -16 \rightarrow 16$
$T_{min} = 0.702$, $T_{max} = 0.753$	$k = -23 \rightarrow 23$
53021 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	8 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.041$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 2.449P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
9331 reflections	$\Delta\rangle_{max} = 0.43$ e Å^{-3}
645 parameters	$\Delta\rangle_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. A two component disorder was refined on one of the two independent residues. The conformation of the minor component is a close match with the conformation of the second (non-disordered) residue. Pseudo-symmetry between the two residues is evident, with slight conformational variability seen in the pendant -C(=CH2)Me groups, leading to elongated atomic displacement ellipsoids. Refinement of these slight distortions as disorders would not improve the model significantly with regard to the goals of the study – unequivocal

identification of the bonding and determination of the relative stereochemistry.

CheckCIF Alerts and Discussion:

PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.2 Ratio
PLAT220_ALERT_2_C Non-Solvent Resd 2 C Ueq(max)/Ueq(min) Range 3.1 Ratio

The pseudosymmetric distortion of the -C(=CH2)Me group ADPs, discussed above, give rise to these PLAT220 alerts.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O4	1.09297 (6)	0.15715 (4)	0.20805 (4)	0.01925 (19)	
O104	0.64233 (6)	0.32305 (5)	0.35483 (4)	0.02131 (19)	
O103	0.35885 (6)	0.24222 (5)	0.20792 (5)	0.0232 (2)	
O3	0.88681 (6)	0.32151 (5)	0.27426 (5)	0.0232 (2)	
O1	1.12602 (7)	0.42870 (6)	0.38743 (6)	0.0372 (3)	
O101	0.51998 (7)	0.16489 (6)	0.06906 (6)	0.0398 (3)	
O2	1.22521 (7)	0.34941 (6)	0.33734 (6)	0.0372 (3)	
H2	1.2010 (15)	0.3822 (10)	0.3624 (10)	0.056*	
O102	0.65948 (7)	0.21588 (6)	0.14434 (6)	0.0378 (3)	
H102	0.6157 (14)	0.1927 (10)	0.1111 (10)	0.057*	
C19	1.08626 (9)	0.21714 (6)	0.23984 (6)	0.0169 (2)	
C109	0.44664 (9)	0.24816 (6)	0.21797 (7)	0.0182 (3)	
C119	0.60427 (9)	0.29128 (6)	0.29524 (6)	0.0180 (2)	
C10	0.98338 (8)	0.23316 (6)	0.24247 (6)	0.0173 (2)	
C108	0.50429 (9)	0.22348 (6)	0.16996 (7)	0.0211 (3)	
C8	1.05439 (9)	0.34271 (7)	0.30989 (7)	0.0208 (3)	
C123	0.45015 (9)	0.35309 (6)	0.29421 (6)	0.0188 (3)	
H12A	0.3792	0.3470	0.2836	0.023*	
H12B	0.4695	0.3676	0.3433	0.023*	
C121	0.65401 (9)	0.27063 (7)	0.24785 (7)	0.0220 (3)	
H121	0.7214	0.2790	0.2554	0.026*	
C122	0.60532 (10)	0.23608 (7)	0.18619 (7)	0.0245 (3)	
C22	1.14657 (9)	0.31777 (7)	0.30554 (7)	0.0240 (3)	
C110	0.49696 (9)	0.28217 (6)	0.28684 (6)	0.0175 (2)	

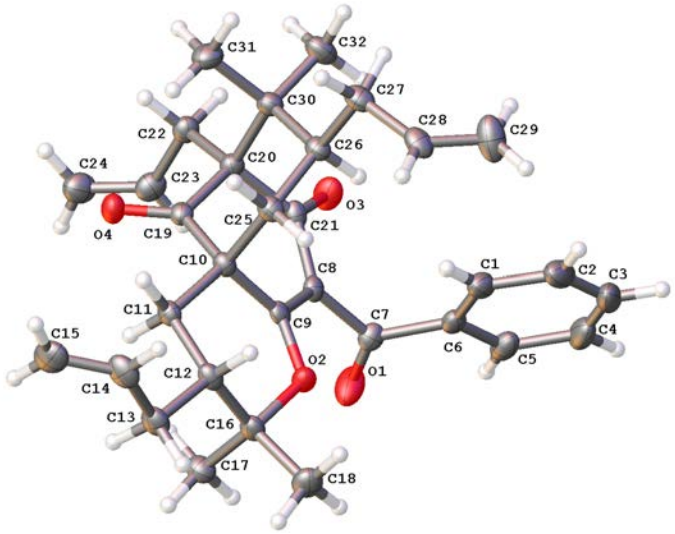
C5	0.94034 (10)	0.46233 (7)	0.41489 (7)	0.0248 (3)	
H5	0.9784	0.4444	0.4567	0.030*	
C107	0.46492 (10)	0.18645 (7)	0.10778 (7)	0.0251 (3)	
C106	0.36103 (9)	0.16794 (7)	0.08309 (6)	0.0209 (3)	
C20	1.18870 (9)	0.13223 (7)	0.20766 (7)	0.0216 (3)	
H20A	1.1841	0.0880	0.1833	0.032*	
H20B	1.2249	0.1262	0.2555	0.032*	
H20C	1.2221	0.1656	0.1839	0.032*	
C9	0.96987 (9)	0.30364 (6)	0.27532 (6)	0.0182 (3)	
C21	1.16168 (9)	0.25772 (7)	0.26770 (6)	0.0209 (3)	
H21	1.2247	0.2464	0.2622	0.025*	
C113	0.43687 (10)	0.10766 (7)	0.33501 (7)	0.0250 (3)	
C101	0.28868 (10)	0.21723 (7)	0.06578 (7)	0.0237 (3)	
H101	0.3036	0.2646	0.0735	0.028*	
C112	0.51596 (9)	0.16169 (6)	0.34855 (7)	0.0218 (3)	
H112	0.5531	0.1576	0.3110	0.026*	
C7	1.04977 (9)	0.40372 (7)	0.35035 (7)	0.0246 (3)	
C11	0.91784 (9)	0.22771 (6)	0.16877 (6)	0.0194 (3)	
H11A	0.9117	0.1784	0.1558	0.023*	
H11B	0.8527	0.2443	0.1712	0.023*	
C124	0.47444 (9)	0.41173 (6)	0.24891 (7)	0.0223 (3)	
H124	0.5461	0.4123	0.2537	0.027*	
C6	0.96015 (9)	0.44358 (6)	0.35126 (7)	0.0226 (3)	
C1	0.90411 (11)	0.46971 (7)	0.29041 (7)	0.0293 (3)	
H1	0.9164	0.4562	0.2469	0.035*	
C4	0.86474 (10)	0.50724 (7)	0.41709 (8)	0.0295 (3)	
H4	0.8504	0.5193	0.4604	0.035*	
C111	0.47551 (9)	0.23594 (6)	0.34615 (7)	0.0207 (3)	
H11C	0.5026	0.2586	0.3910	0.025*	
H11D	0.4047	0.2333	0.3413	0.025*	
C105	0.33829 (10)	0.09856 (7)	0.07217 (7)	0.0246 (3)	
H105	0.3875	0.0647	0.0833	0.030*	
C12	0.95032 (10)	0.26691 (7)	0.11027 (7)	0.0237 (3)	
H12	1.0173	0.2516	0.1092	0.028*	
C23	0.94394 (9)	0.17787 (6)	0.28671 (6)	0.0203 (3)	
H23A	0.8737	0.1857	0.2812	0.024*	
H23B	0.9520	0.1322	0.2665	0.024*	

C117	0.62860 (10)	0.07897 (7)	0.42745 (8)	0.0288 (3)	
H117	0.6547	0.0605	0.3909	0.035*	
C102	0.19481 (10)	0.19705 (8)	0.03718 (7)	0.0283 (3)	
H10A	0.1457	0.2308	0.0245	0.034*	
C116	0.58725 (10)	0.14998 (7)	0.41830 (7)	0.0264 (3)	
H11E	0.6409	0.1834	0.4224	0.032*	
H11F	0.5537	0.1595	0.4564	0.032*	
C114	0.42338 (11)	0.06856 (7)	0.27879 (8)	0.0346 (3)	
H11G	0.3736	0.0349	0.2709	0.042*	
H11H	0.4635	0.0742	0.2464	0.042*	
C120	0.74388 (9)	0.33981 (8)	0.36805 (7)	0.0263 (3)	
H12C	0.7562	0.3707	0.3317	0.039*	
H12D	0.7816	0.2975	0.3682	0.039*	
H12E	0.7628	0.3626	0.4132	0.039*	
C104	0.24385 (11)	0.07889 (8)	0.04513 (7)	0.0299 (3)	
H104	0.2282	0.0314	0.0390	0.036*	
C125	0.44502 (11)	0.48058 (7)	0.27786 (7)	0.0292 (3)	
H12F	0.4450	0.5173	0.2431	0.035*	
H12G	0.3785	0.4764	0.2855	0.035*	
C16	0.88347 (11)	0.24729 (8)	0.04002 (7)	0.0298 (3)	
H16A	0.8165	0.2608	0.0410	0.036*	
H16B	0.9033	0.2739	0.0026	0.036*	
C118	0.63140 (12)	0.04026 (8)	0.48258 (8)	0.0376 (4)	
H11I	0.6060	0.0571	0.5201	0.045*	
H11J	0.6589	-0.0045	0.4848	0.045*	
C13	0.95213 (12)	0.34425 (8)	0.12025 (7)	0.0341 (3)	
C115	0.37547 (11)	0.10088 (8)	0.38799 (8)	0.0342 (3)	
H11K	0.4165	0.0893	0.4331	0.051*	
H11L	0.3276	0.0644	0.3738	0.051*	
H11M	0.3423	0.1445	0.3916	0.051*	
C128	0.42852 (11)	0.40433 (7)	0.17257 (7)	0.0295 (3)	
C2	0.83020 (12)	0.51563 (8)	0.29312 (9)	0.0368 (3)	
H2A	0.7929	0.5344	0.2514	0.044*	
C103	0.17244 (10)	0.12788 (8)	0.02709 (7)	0.0316 (3)	
H103	0.1080	0.1142	0.0078	0.038*	
C3	0.81042 (11)	0.53434 (8)	0.35642 (9)	0.0350 (3)	
H3	0.7596	0.5657	0.3580	0.042*	

C24	0.98847 (11)	0.17426 (7)	0.36466 (7)	0.0286 (3)	
H24	1.0013	0.2224	0.3823	0.034*	0.882 (2)
H24A	1.0321	0.2153	0.3710	0.034*	0.118 (2)
C17	0.88491 (12)	0.17269 (8)	0.02320 (8)	0.0368 (4)	
H17	0.9454	0.1525	0.0216	0.044*	
C130	0.32064 (13)	0.40750 (9)	0.15178 (9)	0.0412 (4)	
H13A	0.2927	0.3702	0.1746	0.062*	
H13B	0.3004	0.4024	0.1014	0.062*	
H13C	0.2982	0.4519	0.1658	0.062*	
C126	0.51127 (13)	0.50079 (7)	0.34441 (9)	0.0396 (4)	
H126	0.5750	0.5142	0.3423	0.048*	
C28A	0.91265 (13)	0.14225 (10)	0.40038 (9)	0.0301 (4)	0.882 (2)
C127	0.48875 (17)	0.50156 (9)	0.40542 (9)	0.0536 (5)	
H12H	0.4258	0.4885	0.4098	0.064*	
H12I	0.5354	0.5151	0.4452	0.064*	
C26B	1.1339 (16)	0.1081 (11)	0.4460 (9)	0.0387 (6)	0.118 (2)
H26B	1.1647	0.1494	0.4647	0.046*	0.118 (2)
C30A	0.87404 (15)	0.17554 (12)	0.44499 (10)	0.0480 (5)	0.882 (2)
H30A	0.8279	0.1534	0.4660	0.058*	0.882 (2)
H30B	0.8921	0.2219	0.4564	0.058*	0.882 (2)
C14	1.03420 (16)	0.37891 (9)	0.13193 (8)	0.0503 (5)	
H14A	1.0339	0.4275	0.1374	0.060*	
H14B	1.0936	0.3552	0.1349	0.060*	
C25A	1.08282 (13)	0.13442 (12)	0.38212 (11)	0.0353 (5)	0.882 (2)
H25A	1.0729	0.0883	0.3604	0.042*	0.882 (2)
H25B	1.1319	0.1587	0.3622	0.042*	0.882 (2)
C27A	1.13524 (18)	0.06682 (14)	0.49160 (14)	0.0400 (6)	0.882 (2)
H27A	1.1224	0.0249	0.4665	0.048*	0.882 (2)
H27B	1.1590	0.0660	0.5404	0.048*	0.882 (2)
C15	0.85652 (15)	0.37957 (9)	0.11521 (9)	0.0483 (5)	
H15A	0.8177	0.3747	0.0680	0.072*	
H15B	0.8672	0.4285	0.1263	0.072*	
H15C	0.8223	0.3585	0.1481	0.072*	
C129	0.48330 (15)	0.39616 (8)	0.12619 (8)	0.0424 (4)	
H12J	0.4541	0.3921	0.0783	0.051*	
H12K	0.5516	0.3943	0.1410	0.051*	
C18	0.80813 (16)	0.13267 (10)	0.01038 (10)	0.0542 (5)	

H18A	0.7465	0.1511	0.0115	0.065*	
H18B	0.8144	0.0854	0.0000	0.065*	
C29A	0.88496 (14)	0.06859 (10)	0.38154 (11)	0.0436 (5)	0.882 (2)
H29A	0.8644	0.0645	0.3311	0.065*	0.882 (2)
H29B	0.8319	0.0549	0.4032	0.065*	0.882 (2)
H29C	0.9407	0.0386	0.3981	0.065*	0.882 (2)
C30B	0.9546 (11)	0.2325 (8)	0.4587 (7)	0.0480 (5)	0.118 (2)
H30C	0.9941	0.2702	0.4518	0.058*	0.118 (2)
H30D	0.9216	0.2333	0.4958	0.058*	0.118 (2)
C28B	0.9457 (9)	0.1809 (7)	0.4182 (6)	0.0301 (4)	0.118 (2)
C29B	0.8756 (11)	0.1212 (8)	0.4126 (9)	0.0436 (5)	0.118 (2)
H29D	0.8419	0.1155	0.3641	0.065*	0.118 (2)
H29E	0.8284	0.1306	0.4411	0.065*	0.118 (2)
H29F	0.9111	0.0790	0.4289	0.065*	0.118 (2)
C25B	1.0652 (12)	0.1121 (9)	0.3762 (9)	0.0353 (5)	0.118 (2)
H25C	1.0289	0.0682	0.3684	0.042*	0.118 (2)
H25D	1.1039	0.1155	0.3402	0.042*	0.118 (2)
C26A	1.12007 (17)	0.12617 (13)	0.45869 (11)	0.0387 (6)	0.882 (2)
H26A	1.1338	0.1669	0.4856	0.046*	0.882 (2)
C27B	1.1535 (18)	0.0528 (12)	0.4818 (13)	0.0400 (6)	0.118 (2)
H27C	1.1240	0.0105	0.4646	0.048*	0.118 (2)
H27D	1.1976	0.0541	0.5254	0.048*	0.118 (2)

X-ray crystallographic data for compound **25**:



Crystals of compound **25** suitable for X-ray analysis were obtained by slow evaporation from isooctane. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC # 1508479). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data

$C_{32}H_{38}O_4$	$F(000) = 1048$
$M_r = 486.62$	$D_x = 1.172$ Mg m^{-3}
Orthorhombic, $Pca2_1$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Hall symbol: P 2c -2ac	Cell parameters from 9398 reflections
$a = 23.1187$ (4) Å	$\theta = 3.8–66.5°$
$b = 7.8379$ (2) Å	$\mu = 0.60$ mm^{-1}
$c = 15.2175$ (3) Å	$T = 100$ K
$V = 2757.44$ (10) Å^3	Prism, colorless
$Z = 4$	0.19 × 0.14 × 0.08 mm

Data collection

Bruker Proteum-R diffractometer	4823 independent reflections
Radiation source: rotating anode	4762 reflections with $I > 2\sigma(I)$
Montel	$R_{int} = 0.049$
ω and ϕ scans	$\theta_{max} = 66.7°$, $\theta_{min} = 3.8°$
Absorption correction: multi-scan *SADABS* (Sheldrick, 2015)	$h = -27 \rightarrow 27$
$T_{min} = 0.793$, $T_{max} = 0.864$	$k = -9 \rightarrow 9$
71181 measured reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.691P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.077$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rangle_{max} = 0.19$ e Å^{-3}
4823 reflections	$\Delta\rangle_{min} = -0.13$ e Å^{-3}
330 parameters	Absolute structure: Refined as an inversion twin.
1 restraint	Flack parameter: 0.49 (19)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

CheckCIF Alert and Discussion:

Alert level C STRVA01_ALERT_4_C Flack test results are ambiguous. From the CIF: _refine_ls_abs_structure_Flack 0.490 From the CIF: _refine_ls_abs_structure_Flack_su 0.190

Discussion: Since the structure is composed of only light atoms, the anomalous dispersion 'signal' is weak, resulting in the relatively large s.u. for the Flack parameter. Nonetheless, refinement of the structure as an inversion twin significantly improved all of the relevant metrics for model quality including R1, wR2 and the GOOF. Despite high s.u.'s, the Flack parameter, the Hooft y and the refined twin fraction all agree fairly well. Since the structure is racemic, identification of the absolute structure has no relevance to the results.

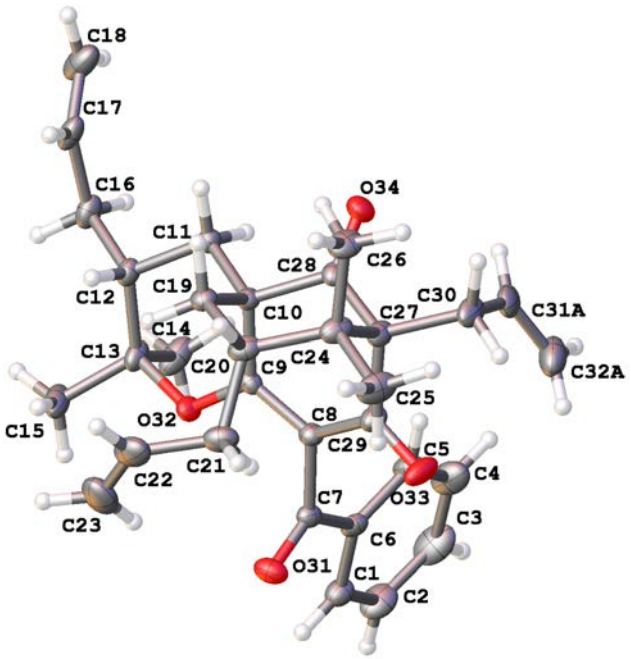
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	0.41587 (6)	0.57164 (18)	0.63038 (9)	0.0228 (3)
O4	0.26372 (5)	0.55694 (18)	0.44008 (10)	0.0276 (3)
O3	0.41522 (6)	0.19463 (18)	0.39632 (11)	0.0306 (3)
O1	0.43755 (7)	0.1629 (2)	0.61676 (13)	0.0416 (4)
C10	0.35369 (8)	0.6453 (2)	0.50397 (13)	0.0189 (4)
C19	0.31561 (8)	0.5411 (2)	0.44236 (13)	0.0197 (4)
C9	0.39375 (7)	0.5256 (2)	0.55223 (13)	0.0189 (4)
C21	0.39550 (8)	0.3256 (2)	0.42847 (14)	0.0213 (4)
C8	0.41377 (7)	0.3805 (2)	0.51564 (13)	0.0194 (4)
C26	0.42174 (8)	0.6715 (2)	0.36698 (13)	0.0217 (4)
H26	0.4508	0.5930	0.3940	0.026*
C7	0.45546 (8)	0.2645 (2)	0.56343 (13)	0.0230 (4)
C16	0.38173 (8)	0.6750 (3)	0.69382 (13)	0.0238 (4)
C6	0.51833 (8)	0.2759 (3)	0.54256 (13)	0.0254 (4)
C12	0.35278 (9)	0.8211 (3)	0.64295 (14)	0.0228 (4)
H12	0.3843	0.8925	0.6169	0.027*
C25	0.39072 (8)	0.7628 (2)	0.44318 (13)	0.0225 (4)
H25A	0.3652	0.8519	0.4182	0.027*
H25B	0.4202	0.8210	0.4797	0.027*
C11	0.31685 (8)	0.7515 (2)	0.56749 (13)	0.0213 (4)
H11A	0.2990	0.8476	0.5351	0.026*
H11B	0.2853	0.6797	0.5913	0.026*
C20	0.34878 (8)	0.4285 (2)	0.37886 (13)	0.0207 (4)
C17	0.33976 (9)	0.5523 (3)	0.73804 (15)	0.0291 (5)
H17A	0.3128	0.5071	0.6942	0.044*
H17B	0.3181	0.6129	0.7838	0.044*

H17C	0.3614	0.4580	0.7646	0.044*
C13	0.31620 (9)	0.9380 (3)	0.70229 (14)	0.0283 (5)
H13A	0.2826	0.8733	0.7249	0.034*
H13B	0.3397	0.9748	0.7532	0.034*
C22	0.30803 (9)	0.3014 (3)	0.33305 (14)	0.0250 (4)
H22A	0.2779	0.3660	0.3011	0.030*
H22B	0.3304	0.2355	0.2892	0.030*
C23	0.27924 (10)	0.1793 (3)	0.39519 (15)	0.0292 (5)
H23	0.3032	0.1185	0.4351	0.035*
C14	0.29518 (10)	1.0924 (3)	0.65330 (15)	0.0326 (5)
H14	0.3236	1.1666	0.6292	0.039*
C28	0.50541 (9)	0.8776 (3)	0.36545 (15)	0.0286 (5)
H28	0.4967	0.9610	0.4087	0.034*
C30	0.37978 (9)	0.5584 (3)	0.31189 (14)	0.0239 (4)
C5	0.55341 (9)	0.1354 (3)	0.56228 (15)	0.0342 (5)
H5	0.5370	0.0359	0.5878	0.041*
C1	0.54274 (9)	0.4214 (3)	0.50662 (14)	0.0334 (5)
H1	0.5192	0.5173	0.4931	0.040*
C27	0.45603 (10)	0.8054 (3)	0.31318 (14)	0.0275 (5)
H27A	0.4712	0.7515	0.2591	0.033*
H27B	0.4297	0.8990	0.2955	0.033*
C31	0.33416 (10)	0.6675 (3)	0.26447 (15)	0.0319 (5)
H31A	0.3110	0.7295	0.3080	0.048*
H31B	0.3089	0.5934	0.2296	0.048*
H31C	0.3535	0.7492	0.2256	0.048*
C32	0.41365 (10)	0.4580 (3)	0.24271 (15)	0.0328 (5)
H32A	0.4321	0.5376	0.2017	0.049*
H32B	0.3872	0.3830	0.2105	0.049*
H32C	0.4434	0.3890	0.2717	0.049*
C18	0.42750 (10)	0.7368 (3)	0.75764 (15)	0.0332 (5)
H18A	0.4494	0.6389	0.7799	0.050*
H18B	0.4089	0.7959	0.8068	0.050*
H18C	0.4538	0.8154	0.7274	0.050*
C15	0.24075 (11)	1.1329 (3)	0.64120 (16)	0.0389 (6)
H15A	0.2111	1.0620	0.6643	0.047*
H15B	0.2310	1.2331	0.6094	0.047*
C24	0.22383 (10)	0.1505 (3)	0.39844 (17)	0.0372 (5)

H24A	0.1985	0.2090	0.3596	0.045*
H24B	0.2087	0.0712	0.4397	0.045*
C4	0.61223 (10)	0.1417 (4)	0.54450 (17)	0.0475 (7)
H4	0.6360	0.0457	0.5569	0.057*
C29	0.55912 (11)	0.8339 (3)	0.3556 (2)	0.0468 (7)
H29A	0.5694	0.7508	0.3129	0.056*
H29B	0.5882	0.8850	0.3911	0.056*
C2	0.60231 (11)	0.4264 (4)	0.49030 (17)	0.0467 (7)
H2	0.6193	0.5264	0.4663	0.056*
C3	0.63625 (11)	0.2871 (5)	0.50889 (17)	0.0525 (8)
H3	0.6766	0.2910	0.4971	0.063*

X-ray crystallographic data for compound (+/-)-**22**:



Crystals of compound (+/-)-**22** suitable for X-ray analysis were obtained by slow evaporation from isooctane. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC # 1508480). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data

C32H38O4	V = 2727.8 (4) Å3
Mr = 486.62	Z = 4
Monoclinic, P21/n	Cu Ka radiation, l = 1.54178 Å
a = 10.9732 (10) Å	m = 0.60 mm-1
b = 16.0101 (14) Å	T = 100 K
c = 15.5863 (14) Å	0.4 × 0.3 × 0.25 mm
b = 94.993 (3)°	

Data collection

Bruker Proteum-R diffractometer	4803 independent reflections
Absorption correction: multi-scan SADABS (Sheldrick, 2015)	4745 reflections with I > 2s(I)
Tmin = 0.829, Tmax = 0.861	Rint = 0.049
88704 measured reflections	

Refinement

R[F2 > 2s(F2)] = 0.039	0 restraints
wR(F2) = 0.096	H-atom parameters constrained
S = 1.05	Dρmax = 0.25 e Å-3
4803 reflections	Dρmin = -0.22 e Å-3
348 parameters	

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT (Bruker, 2006); program(s) used to solve structure: SHELXT (Sheldrick, 2015); program(s) used to refine structure: SHELXL2014/7 (Sheldrick, 2014); molecular graphics: Olex2 (Dolomanov et al., 2009); software used to prepare material for publication: Olex2 (Dolomanov et al., 2009).

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Bruker (2006). SADABS. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Dolmanov, O. V., et al. (2009). OLEX2: A complete structure solution, refinement and analysis program. J. Appl. Cryst. 42, 339-341 (2009).
Document origin: publCIF [Westrip, S. P. (2010). J. Apply. Cryst., 43, 920-925].

supporting information

S1. Introduction
S2. Experimental
S2.1. Synthesis and crystallization
S2.2. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 1.
S3. Results and discussion
(boyce6_0m)

Crystal data

C32H38O4	F(000) = 1048
Mr = 486.62	Dx = 1.185 Mg m-3
Monoclinic, P21/n	Cu Ka radiation, l = 1.54178 Å
a = 10.9732 (10) Å	Cell parameters from 9577 reflections
b = 16.0101 (14) Å	q = 2.8–66.3°
c = 15.5863 (14) Å	m = 0.60 mm-1
b = 94.993 (3)°	T = 100 K
V = 2727.8 (4) Å3	Prism, colorless
Z = 4	0.4 × 0.3 × 0.25 mm

Data collection

Bruker Proteum-R diffractometer	4803 independent reflections
Radiation source: rotating anode	4745 reflections with I > 2s(I)
Montel monochromator	Rint = 0.049
/w and /f scans	qmax = 66.7°, qmin = 4.9°
Absorption correction: multi-scan SADABS (Sheldrick, 2015)	h = -13®13
Tmin = 0.829, Tmax = 0.861	k = -17®18
88704 measured reflections	l = -18®18

Refinement

Refinement on F2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
R[F2 > 2s(F2)] = 0.039	H-atom parameters constrained
wR(F2) = 0.096	w = 1/[s2(Fo2) + (0.042P)2 + 1.182P] where P = (Fo2 + 2Fc2)/3
S = 1.05	(D/s)max = 0.001
4803 reflections	Dρmax = 0.25 e Å-3
348 parameters	Dρmin = -0.22 e Å-3

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are

estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. CheckCIF Alert and Discussion: PLAT230_ALERT_2_C Hirshfeld Test Diff for C2 – C3 .. 5.4 s.u. Discussion: The disorder at C31—C32 most likely creates two slightly different orientations of the phenyl ring containing C2—C3. Refinement of this disorder would only increase the number of parameters without any significant effect on either model quality or on the structural information needed for this study.

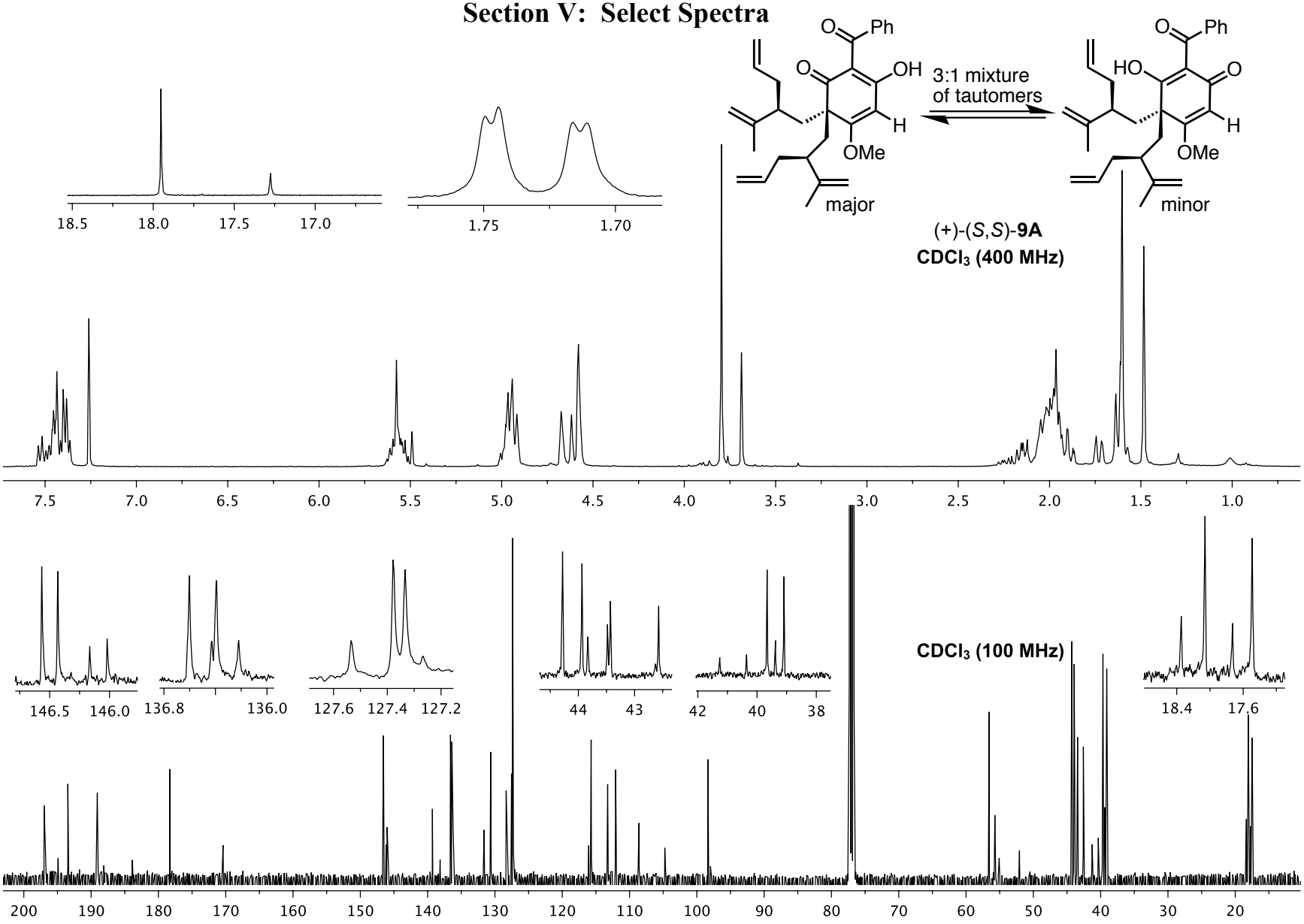
Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å2) for (boyce6_0m)

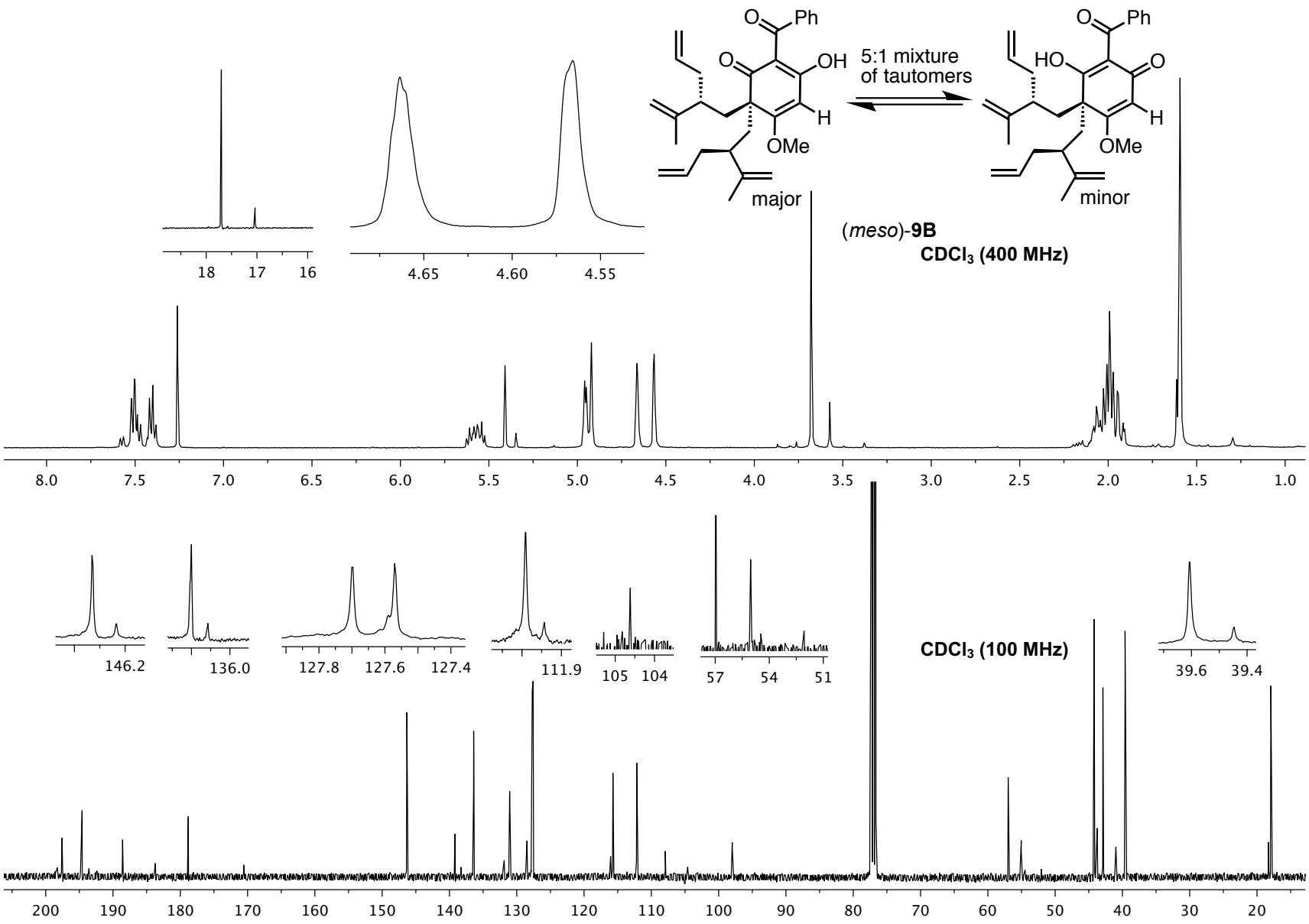
	x	y	z	Uiso*/Ueq	Occ. (<1)
O32	0.40162 (7)	0.61725 (5)	0.75037 (5)	0.02160 (19)	
O34	0.20176 (8)	0.61749 (5)	0.48014 (5)	0.0258 (2)	
O31	0.33969 (8)	0.78687 (6)	0.83505 (5)	0.0263 (2)	
O33	0.14828 (8)	0.83476 (5)	0.66303 (6)	0.0326 (2)	
C9	0.31575 (9)	0.64635 (7)	0.69214 (7)	0.0162 (2)	
C10	0.24796 (10)	0.58712 (7)	0.62971 (7)	0.0165 (2)	
C28	0.19072 (10)	0.63780 (7)	0.55396 (7)	0.0187 (2)	
C7	0.36261 (10)	0.78331 (7)	0.76035 (7)	0.0180 (2)	
C11	0.33705 (10)	0.52147 (7)	0.60060 (7)	0.0187 (2)	
H11A	0.2907	0.4783	0.5659	0.022*	
H11B	0.3945	0.5484	0.5635	0.022*	
C8	0.28892 (10)	0.72829 (7)	0.69641 (7)	0.0177 (2)	
C6	0.46616 (10)	0.83072 (7)	0.72841 (7)	0.0191 (2)	
C12	0.40968 (10)	0.47981 (7)	0.67707 (7)	0.0201 (2)	
H12	0.3497	0.4513	0.7120	0.024*	
C19	0.13752 (10)	0.54612 (7)	0.67000 (7)	0.0196 (2)	
H19A	0.1021	0.5030	0.6296	0.024*	
H19B	0.1687	0.5172	0.7236	0.024*	
C29	0.18159 (11)	0.76347 (7)	0.64889 (8)	0.0223 (3)	
C1	0.55286	0.86663 (8)	0.78825 (8)	0.0248 (3)	

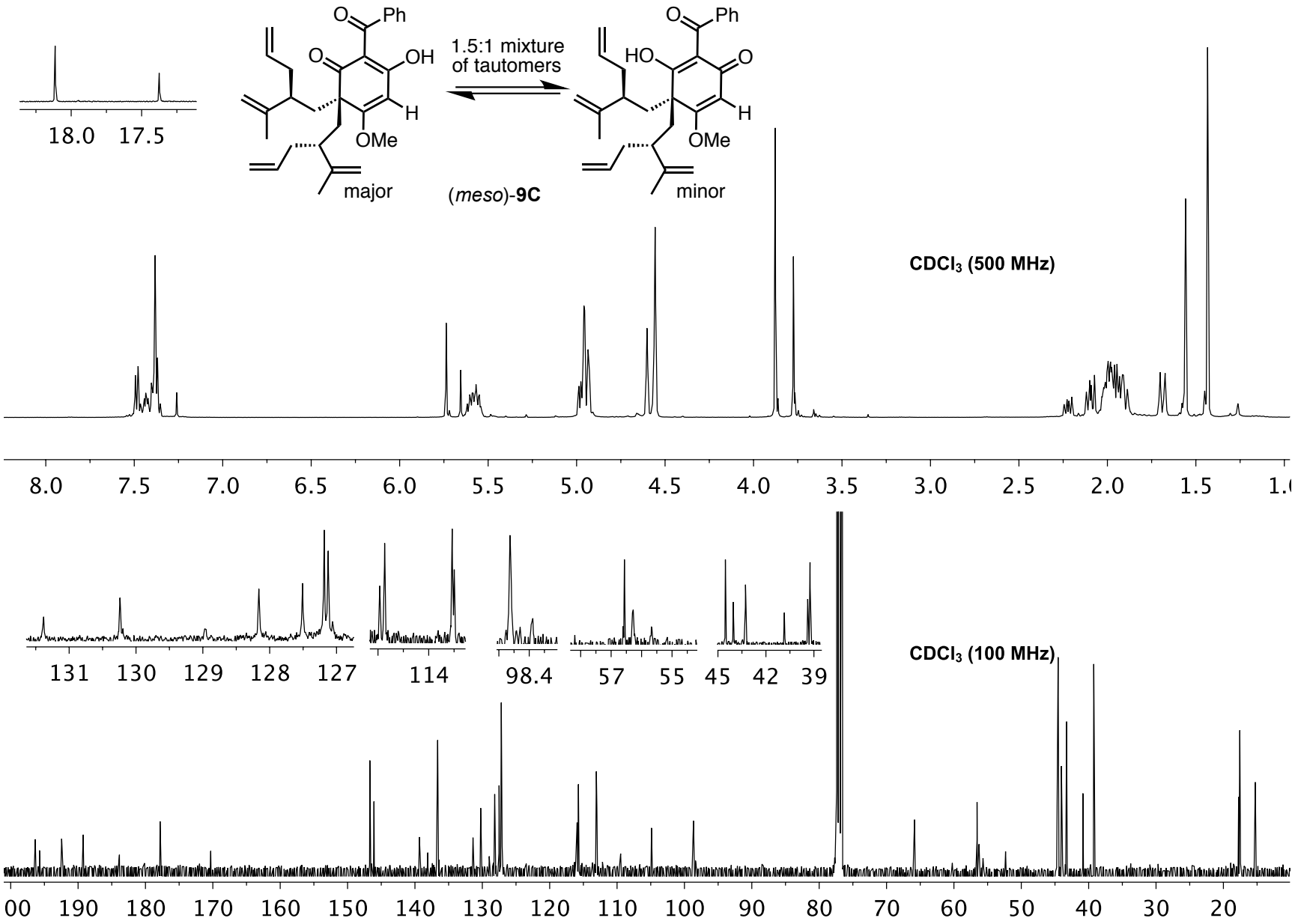
	(11)				
H1	0.5437	0.8620	0.8481	0.030*	
C27	0.11072 (11)	0.70999 (7)	0.57876 (8)	0.0222 (3)	
C13	0.47956 (11)	0.54418 (7)	0.73566 (8)	0.0237 (3)	
C20	0.03386 (10)	0.60604 (8)	0.69144 (8)	0.0234 (3)	
H20	-0.0386	0.5688	0.6955	0.028*	
C24	-0.00591 (10)	0.66690 (8)	0.61546 (8)	0.0252 (3)	
C5	0.47908 (12)	0.83864 (8)	0.64078 (8)	0.0267 (3)	
H5	0.4209	0.8137	0.5998	0.032*	
C16	0.49586 (11)	0.41234 (8)	0.64639 (9)	0.0263 (3)	
H16A	0.5530	0.4384	0.6085	0.032*	
H16B	0.5449	0.3887	0.6969	0.032*	
C17	0.42798 (12)	0.34324 (7)	0.59842 (8)	0.0273 (3)	
H17	0.3547	0.3240	0.6202	0.033*	
C30	0.07728 (12)	0.76840 (8)	0.50066 (9)	0.0303 (3)	
H30A	0.0205	0.7387	0.4583	0.036*	0.691 (6)
H30B	0.0341	0.8181	0.5206	0.036*	0.691 (6)
H30C	0.0539	0.7339	0.4491	0.036*	0.309 (6)
H30D	0.0057	0.8028	0.5124	0.036*	0.309 (6)
C26	-0.07497 (11)	0.61515 (8)	0.54294 (9)	0.0305 (3)	
H26A	-0.1055	0.6524	0.4960	0.046*	
H26B	-0.1440	0.5862	0.5657	0.046*	
H26C	-0.0192	0.5740	0.5211	0.046*	
C21	0.05471 (11)	0.64684 (8)	0.78203 (8)	0.0275 (3)	
H21A	0.1166	0.6916	0.7803	0.033*	
H21B	-0.0226	0.6728	0.7968	0.033*	
C2	0.65170 (12)	0.90870 (9)	0.76059 (10)	0.0357 (3)	
H2	0.7118	0.9318	0.8014	0.043*	
C14	0.59189 (12)	0.58149 (8)	0.69945 (10)	0.0344 (3)	
H14A	0.5700	0.6012	0.6406	0.052*	
H14B	0.6558	0.5388	0.6989	0.052*	
H14C	0.6221	0.6285	0.7355	0.052*	

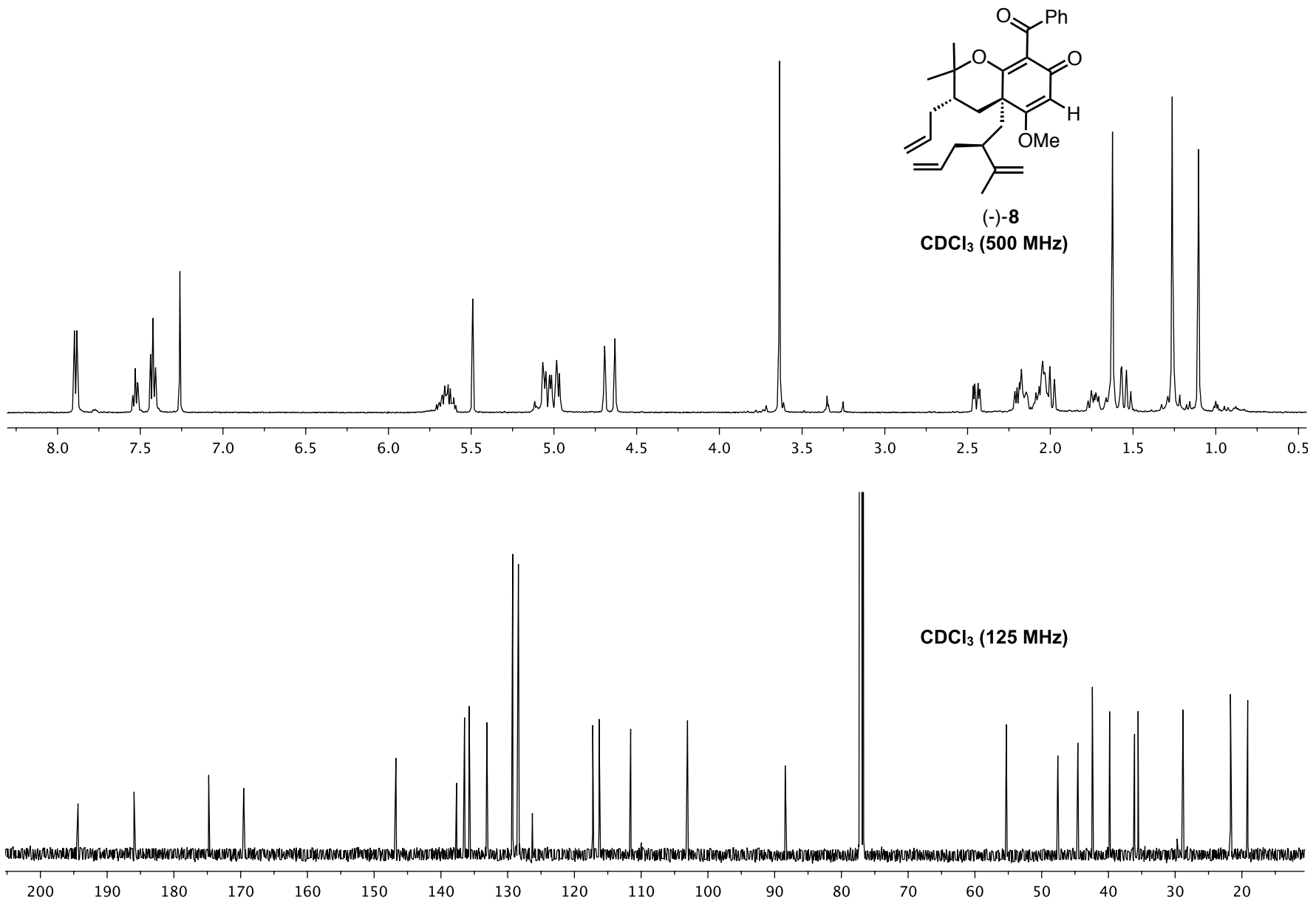
C4	0.57699 (14)	0.88291 (9)	0.61335 (10)	0.0386 (3)	
H4	0.5848	0.8896	0.5535	0.046*	
C15	0.50789 (14)	0.51033 (8)	0.82657 (9)	0.0356 (3)	
H15A	0.5505	0.5532	0.8627	0.053*	
H15B	0.5600	0.4608	0.8247	0.053*	
H15C	0.4314	0.4952	0.8508	0.053*	
C22	0.09661 (14)	0.58548 (9)	0.85049 (9)	0.0366 (3)	
H22	0.0464	0.5381	0.8579	0.044*	
C25	-0.09582 (12)	0.73319 (9)	0.64336 (10)	0.0364 (3)	
H25A	-0.0528	0.7715	0.6846	0.055*	
H25B	-0.1625	0.7057	0.6705	0.055*	
H25C	-0.1295	0.7646	0.5928	0.055*	
C3	0.66347 (13)	0.91739 (9)	0.67319 (11)	0.0425 (4)	
H3	0.7311	0.9471	0.6542	0.051*	
C23	0.19857 (16)	0.59254 (11)	0.90143 (9)	0.0453 (4)	
H23A	0.2509	0.6391	0.8958	0.054*	
H23B	0.2196	0.5511	0.9437	0.054*	
C18	0.46165 (15)	0.30709 (9)	0.52873 (10)	0.0405 (4)	
H18A	0.5343	0.3245	0.5050	0.049*	
H18B	0.4133	0.2635	0.5020	0.049*	
C31A	0.1896 (4)	0.7971 (2)	0.4562 (2)	0.0323 (9)	0.691 (6)
H31A	0.2245	0.7592	0.4183	0.039*	0.691 (6)
C32A	0.2403 (3)	0.87139 (16)	0.46782 (16)	0.0446 (9)	0.691 (6)
H32A	0.2074	0.9105	0.5054	0.054*	0.691 (6)
H32B	0.3098	0.8858	0.4386	0.054*	0.691 (6)
C32B	0.2431 (6)	0.8101 (3)	0.4155 (5)	0.0420 (18)	0.309 (6)
H32C	0.2235	0.7639	0.3786	0.050*	0.309 (6)
H32D	0.3085	0.8463	0.4045	0.050*	0.309 (6)
C31B	0.1792 (8)	0.8239 (5)	0.4825 (5)	0.032 (2)	0.309 (6)
H31B	0.1993	0.8702	0.5192	0.038*	0.309 (6)

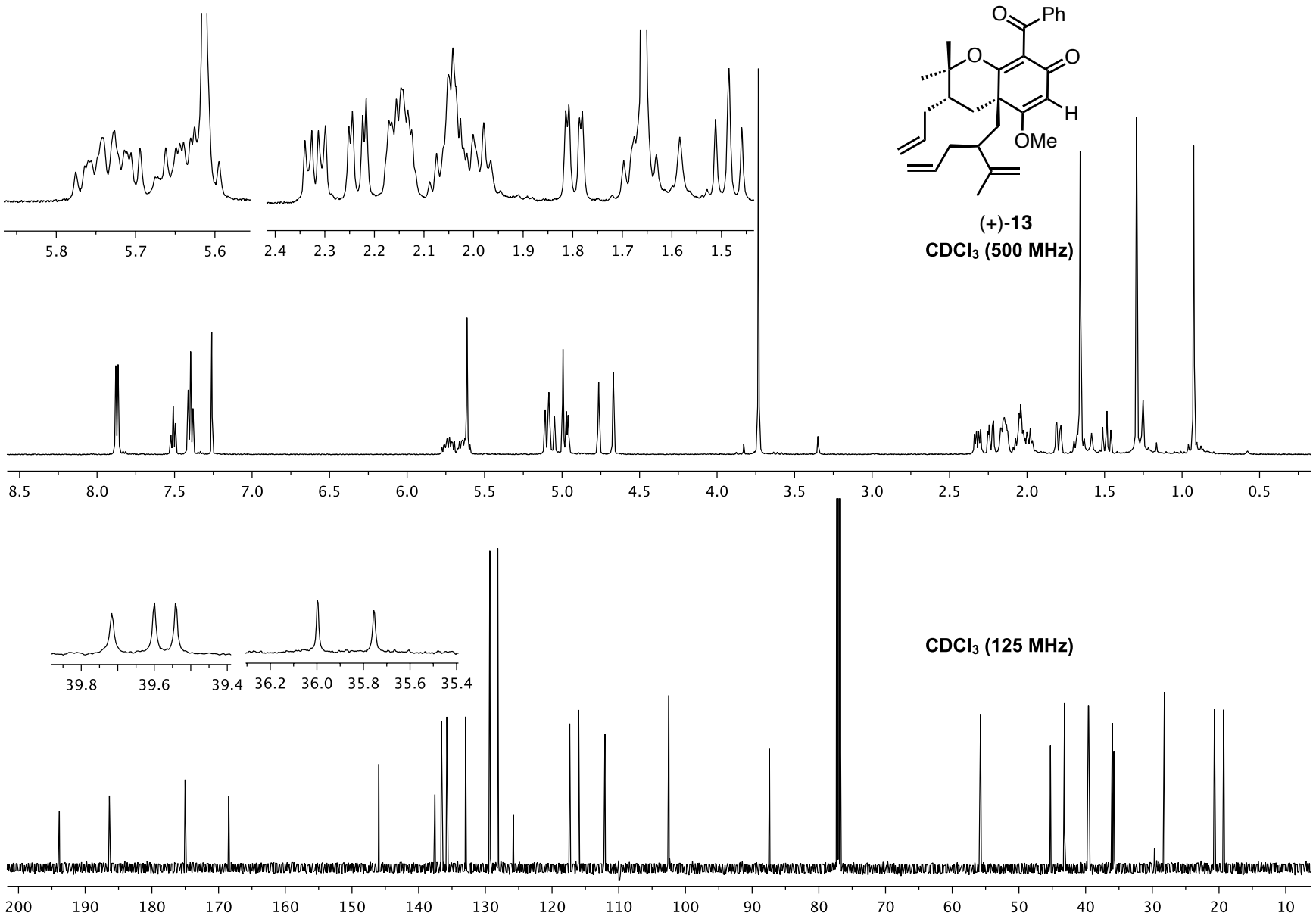
Section V: Select Spectra

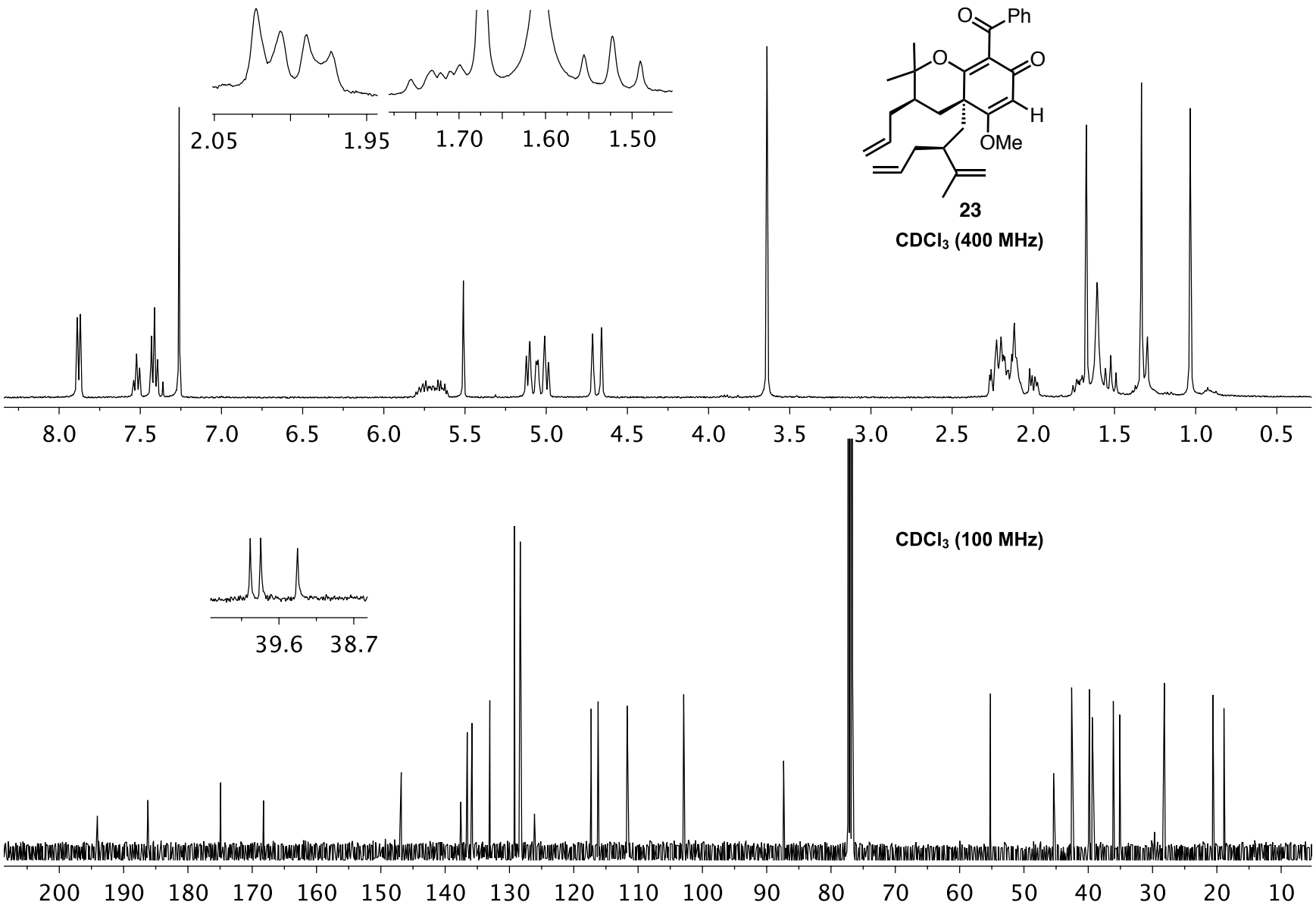


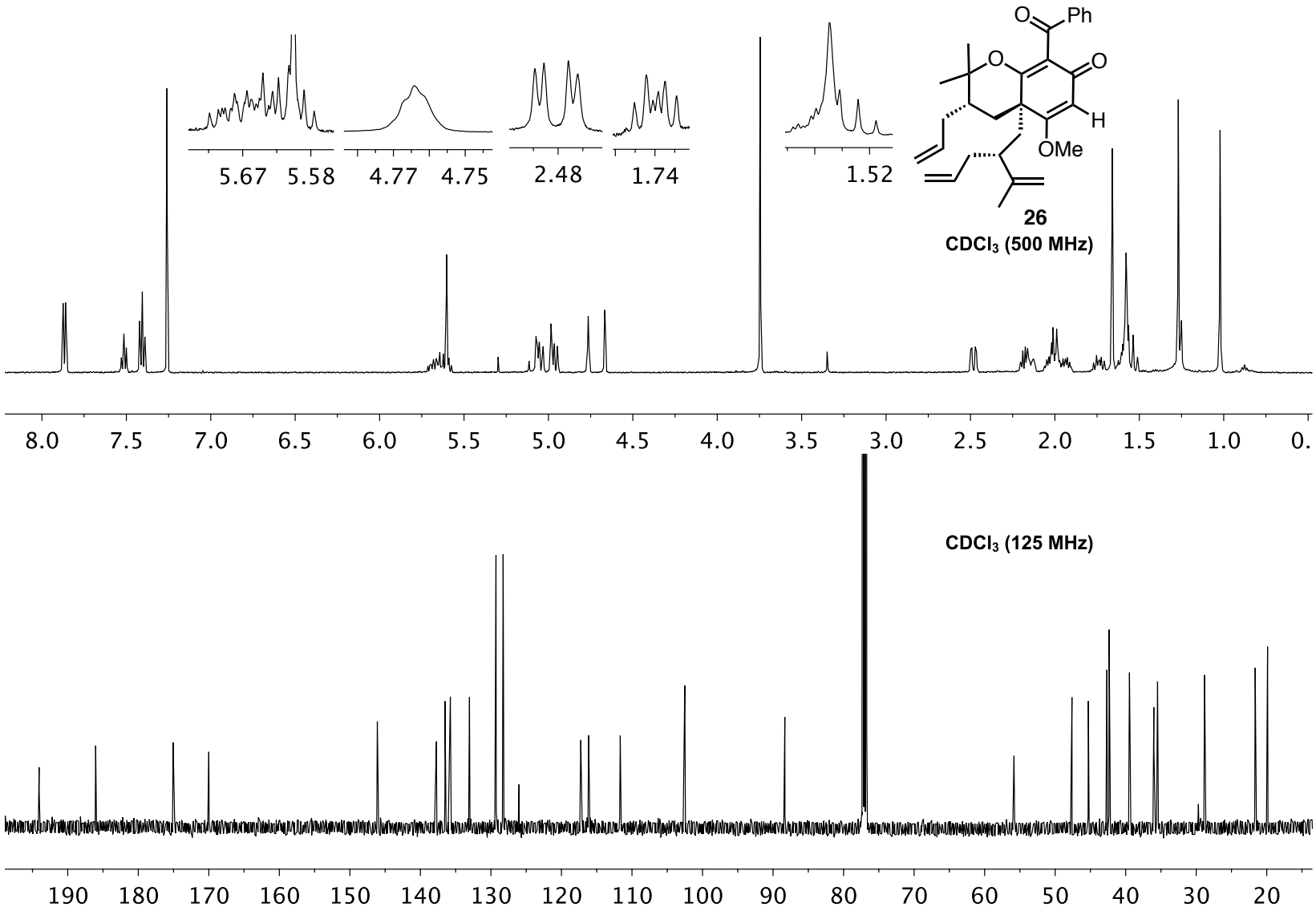

O
Ph
O
OH
H
OMe
major
5:1 mixture
of tautomers
HO
minor
(meso)-9B
CDCl3 (400 MHz)
CDCl3 (100 MHz)


18.0
17.5
O
Ph
O
OH
H
OMe
major
1.5:1 mixture
of tautomers
(meso)-9C
HO
O
Ph
O
H
OMe
minor
CDCl3 (500 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
131
130
129
128
127
114
98.4
57
55
45
42
39
CDCl3 (100 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

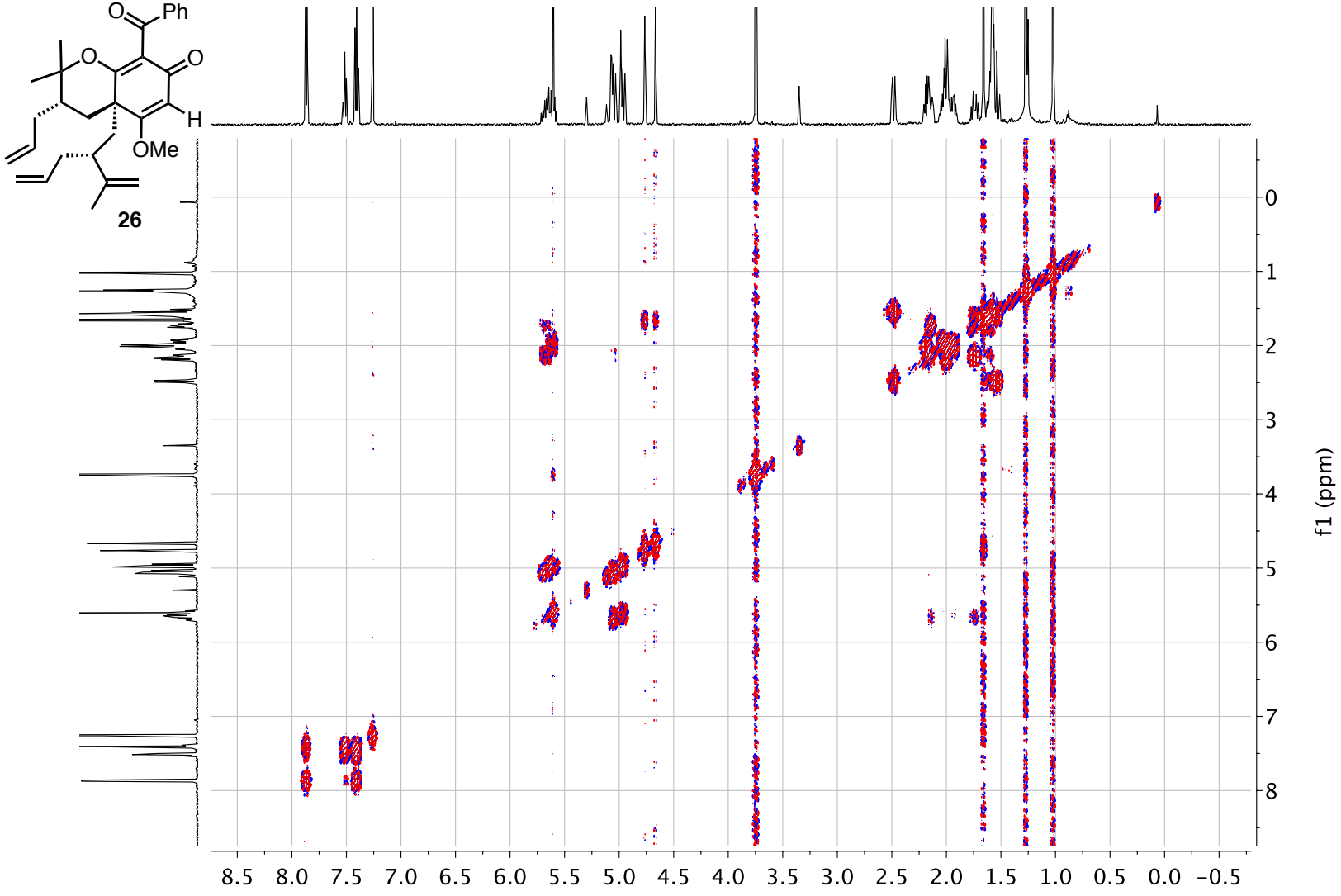

O
Ph
O
O
H
OMe
(-)-8
CDCl3 (500 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
CDCl3 (125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


O
Ph
O
O
H
OMe
(+)-13
CDCl3 (500 MHz)
CDCl3 (125 MHz)

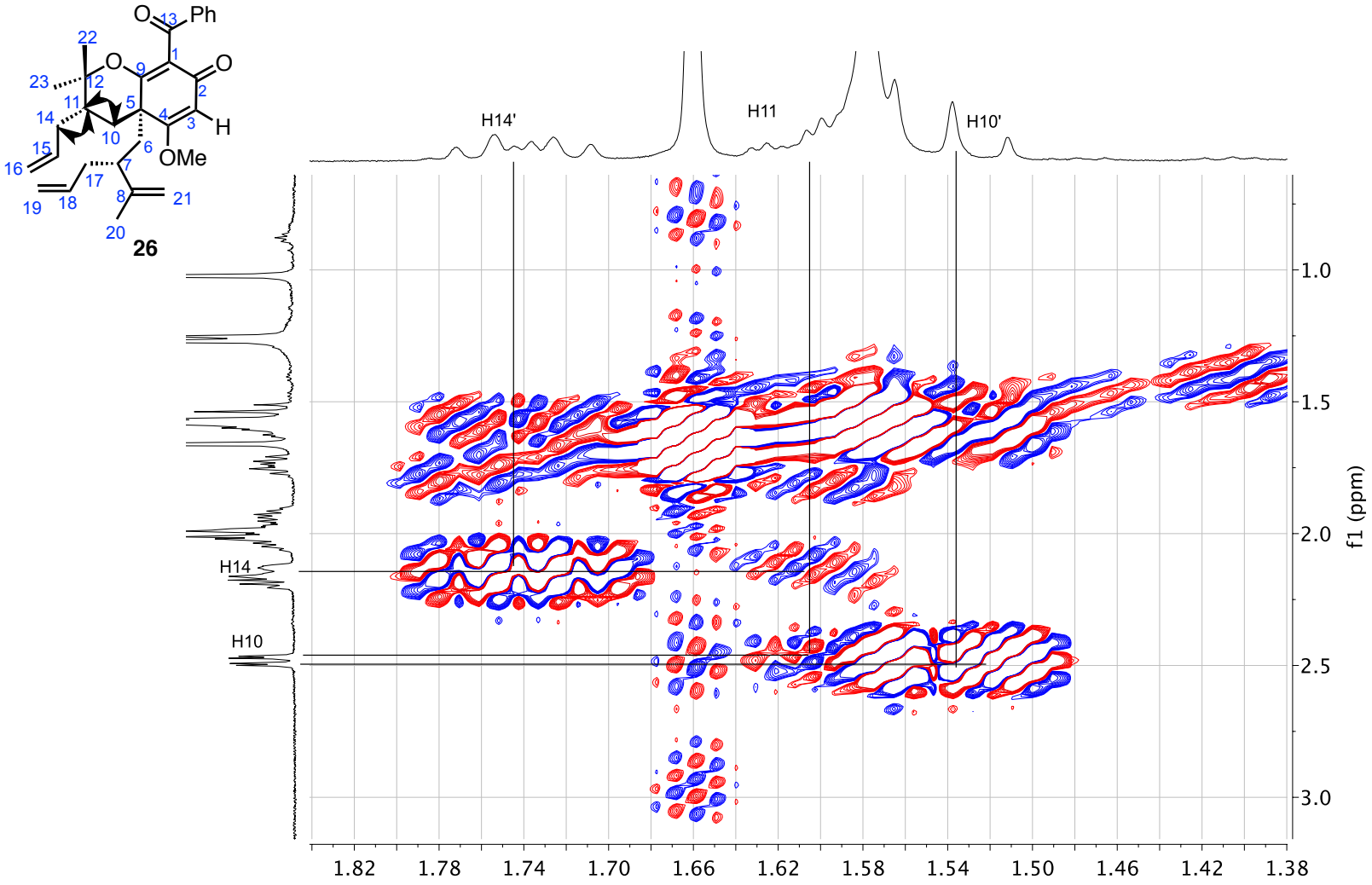

2.05
1.95
1.70
1.60
1.50
O
Ph
O
O
H
OMe
23
CDCl3 (400 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
CDCl3 (100 MHz)
39.6
38.7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


5.67
5.58
4.77
4.75
2.48
1.74
1.52
O
Ph
O
O
H
OMe
26
CDCl3 (500 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
CDCl3 (125 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

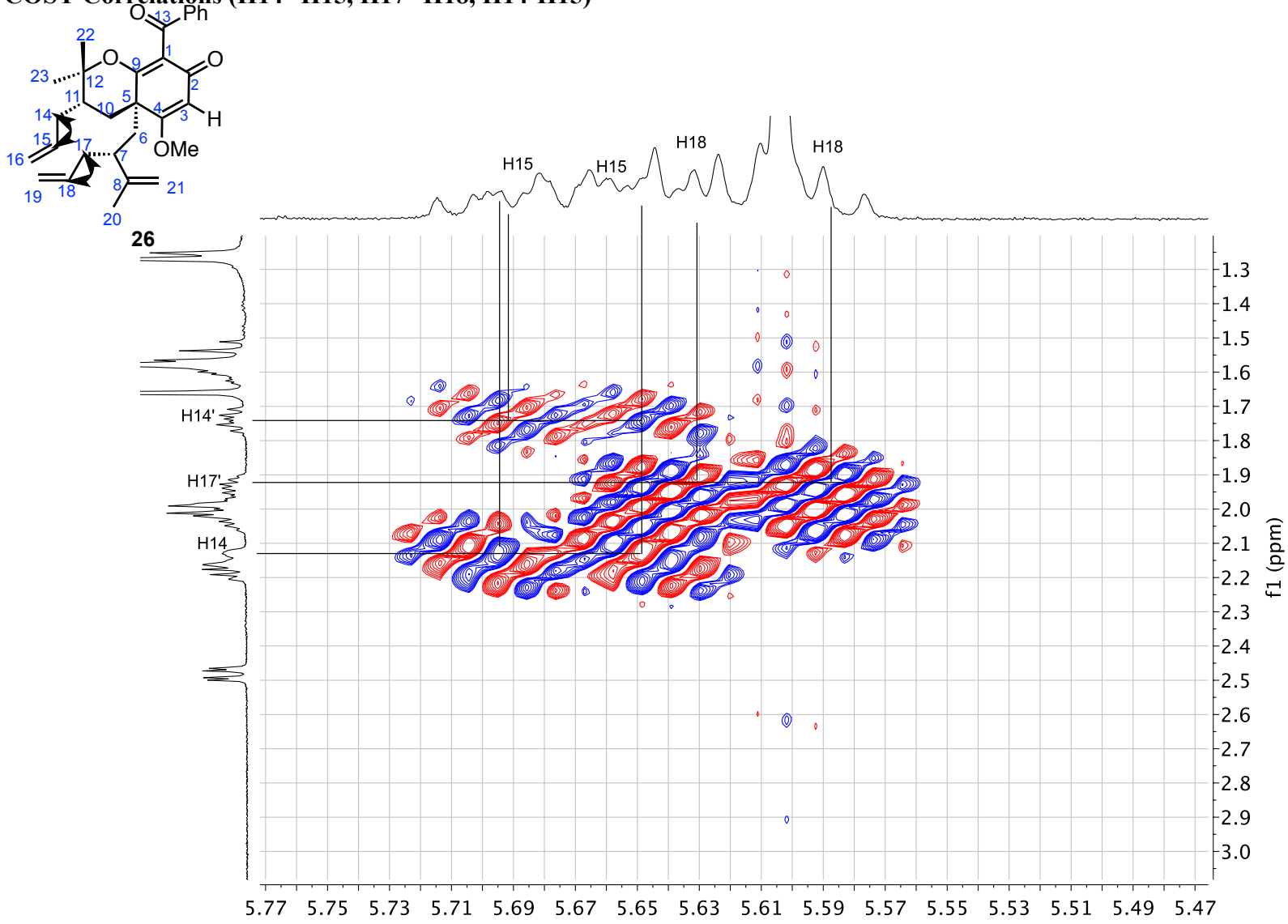
COSY Correlations for Compound 26



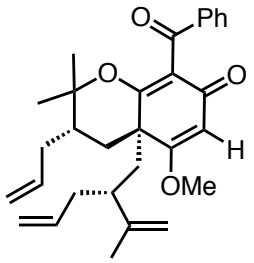
COSY Correlations (H14-H14', H14-H11, H10-H11, H10-H10')



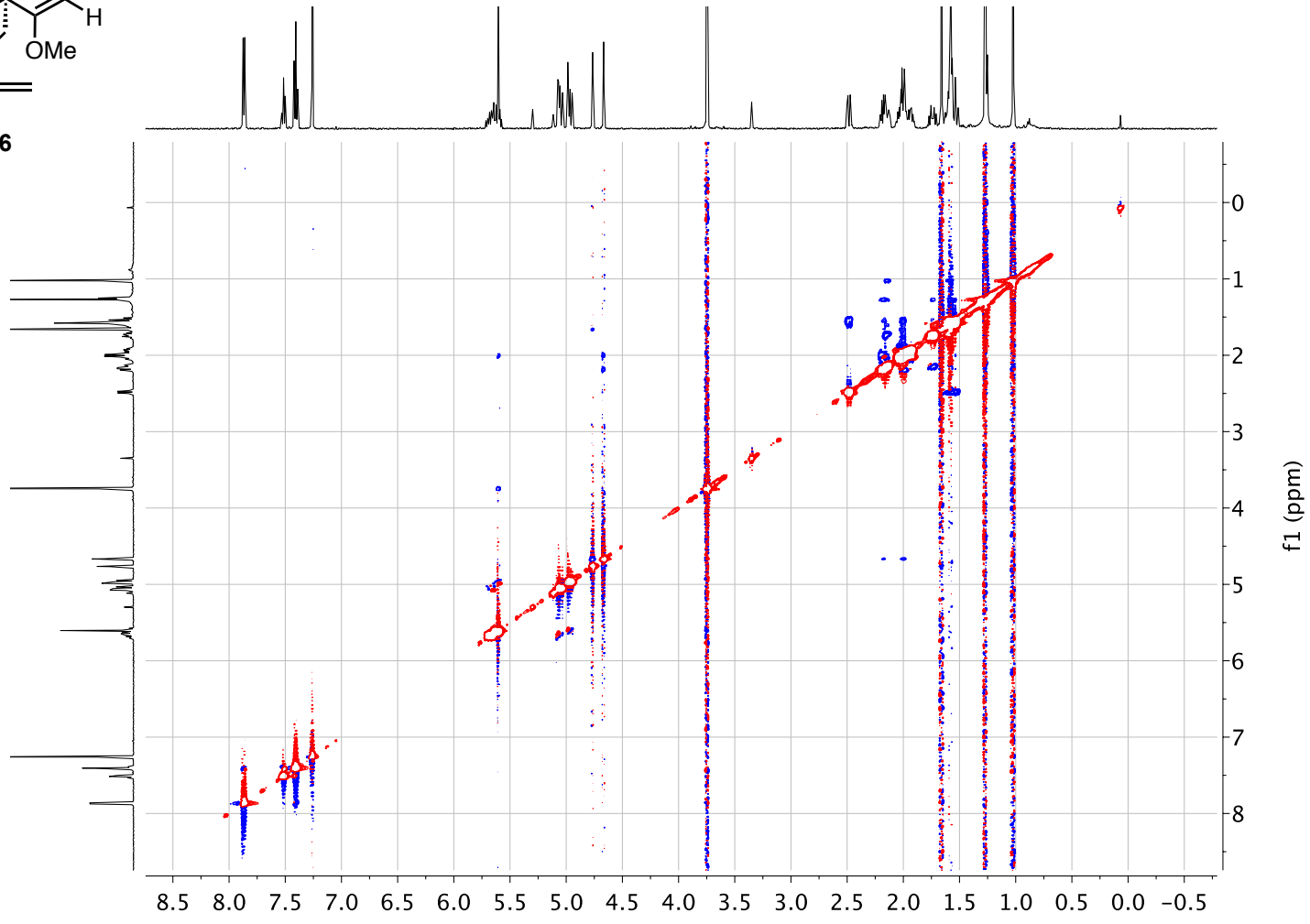
COSY Correlations (H14'-H15, H17'-H18, H14-H15)



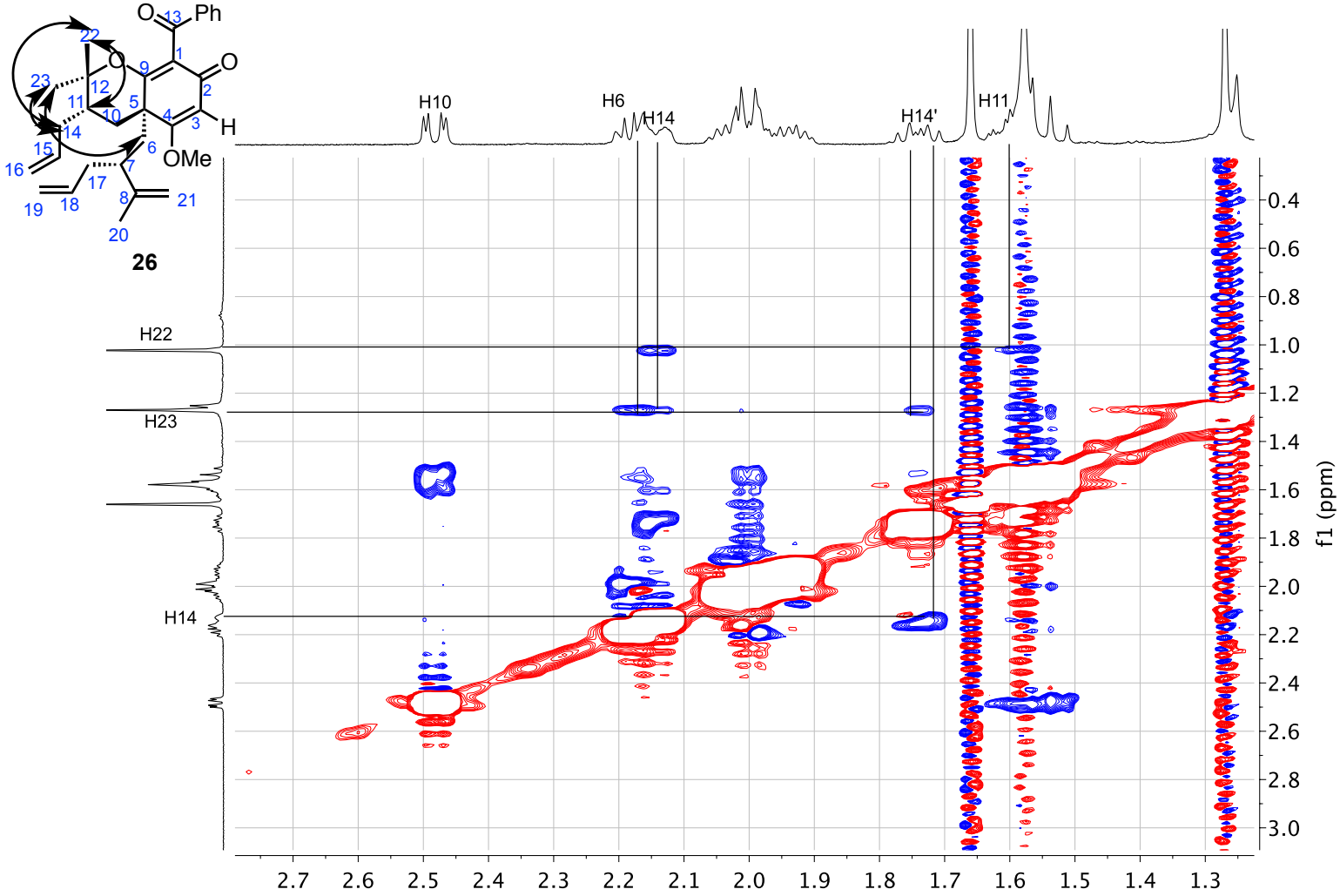
NOESY Correlations for Compound 26



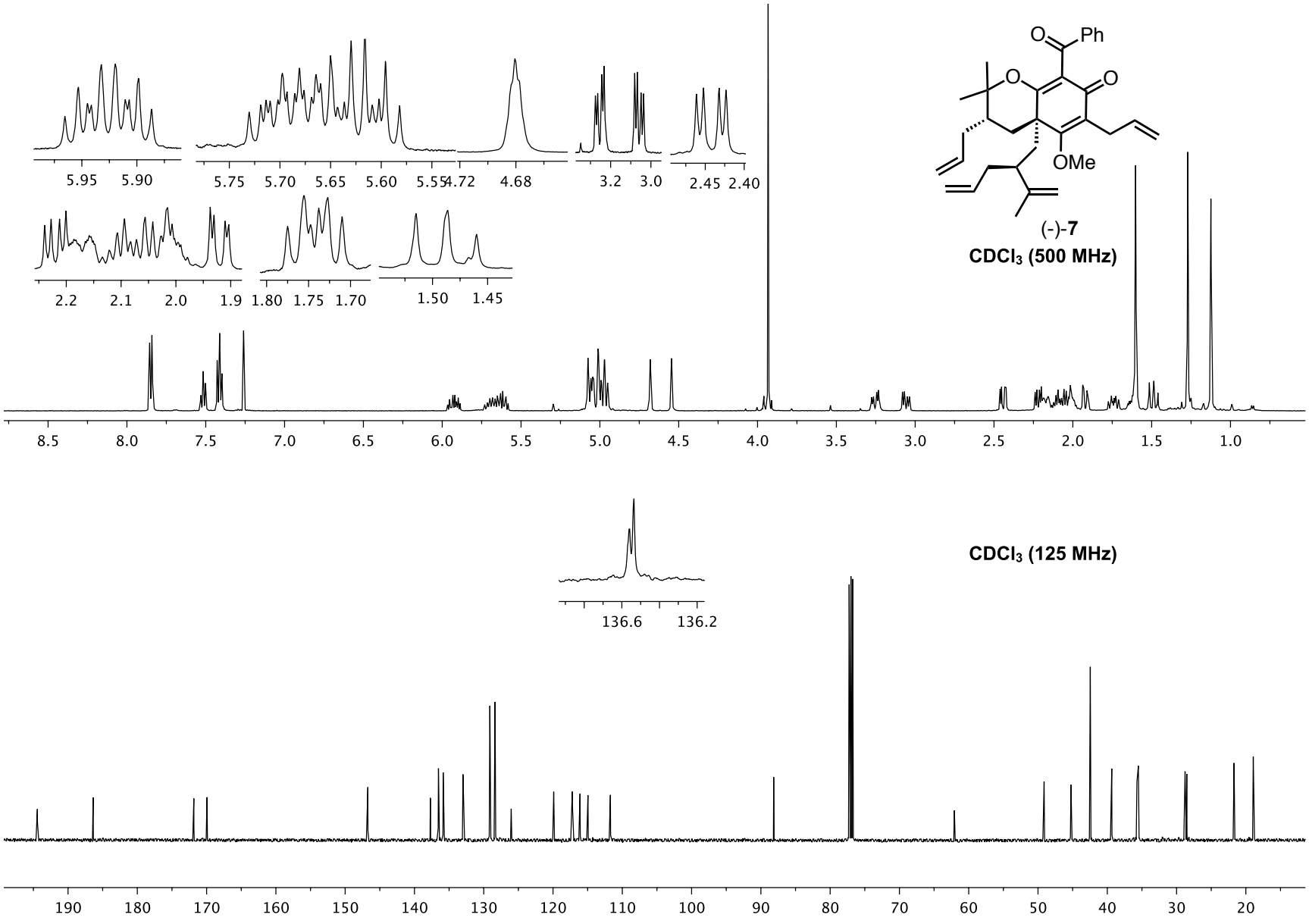
26

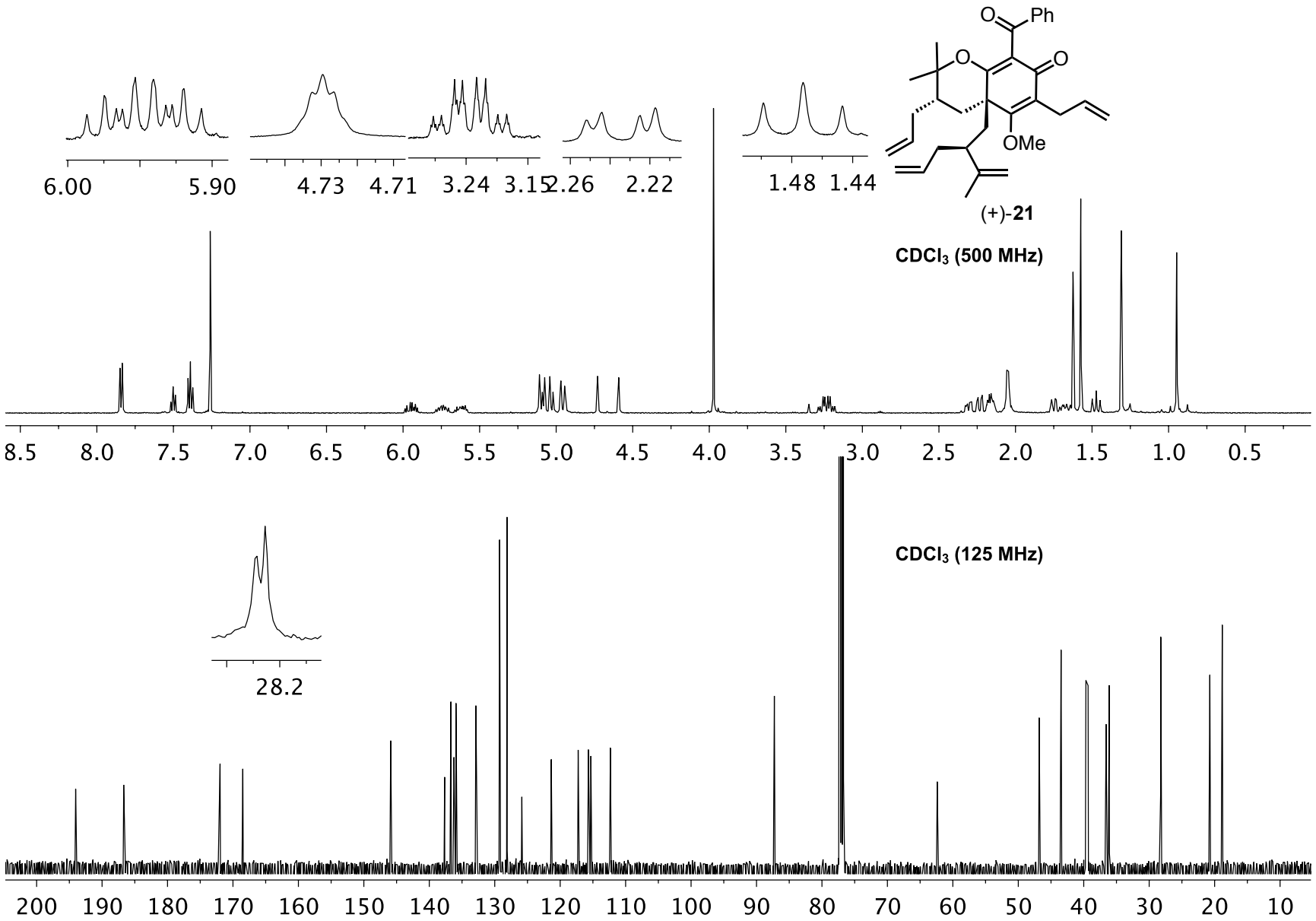


NOESY Correlations (H22-H14, H22-H11 (orientation of H22), H23-H6 (orientation of H23), H23-H14, H14-H14')

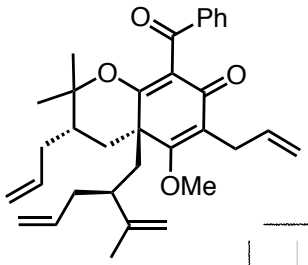


Diagnostic Information: H11 does not come into proximity with H6.


O
Ph
O
O
OMe
(-)-7
CDCl3 (500 MHz)
CDCl3 (125 MHz)

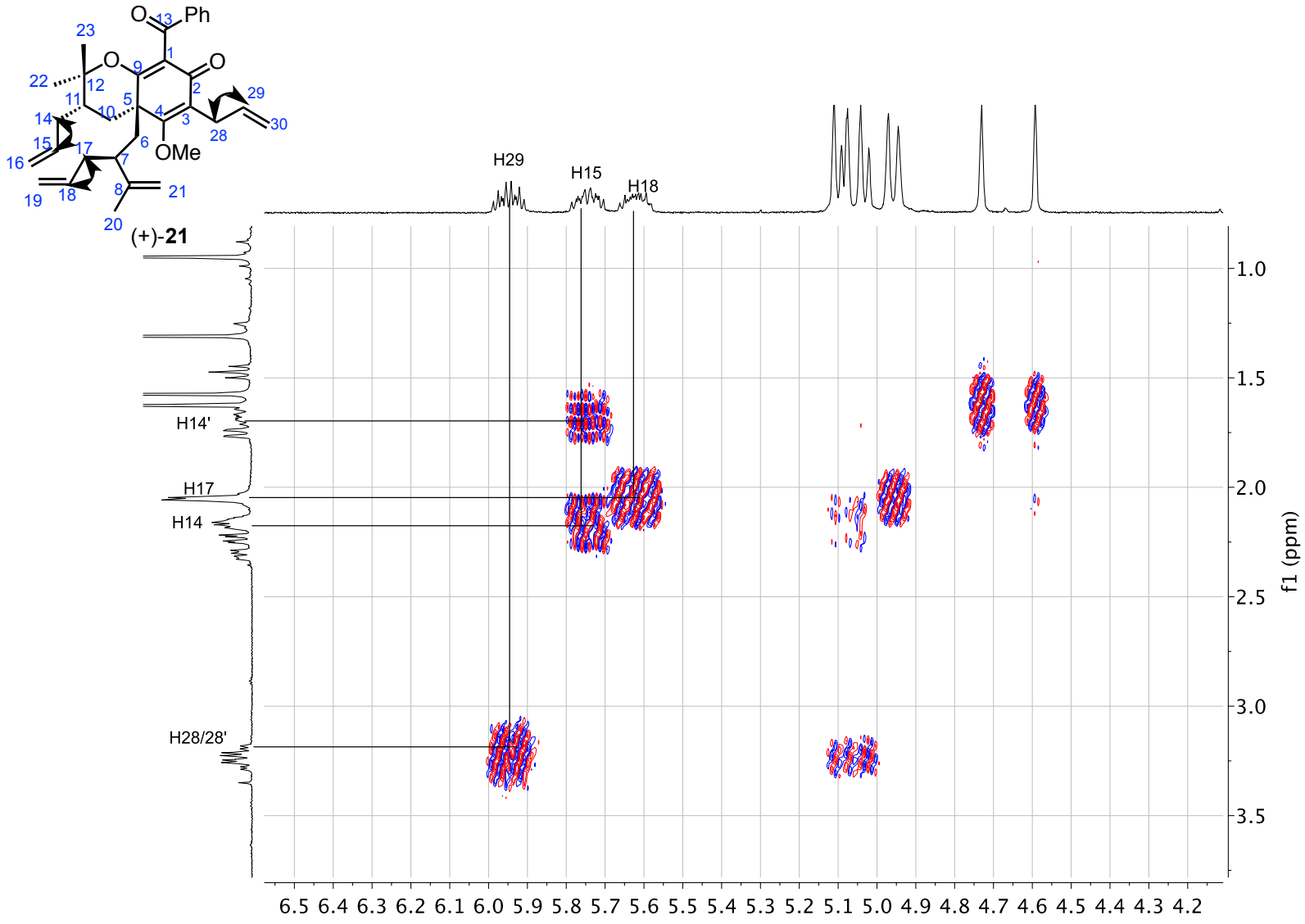

6.00
5.90
4.73
4.71
3.24
3.15
2.26
2.22
1.48
1.44
O
Ph
O
O
OMe
(+)-21
CDCl3 (500 MHz)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
28.2
CDCl3 (125 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

COSY Correlations for Compound (+)-21

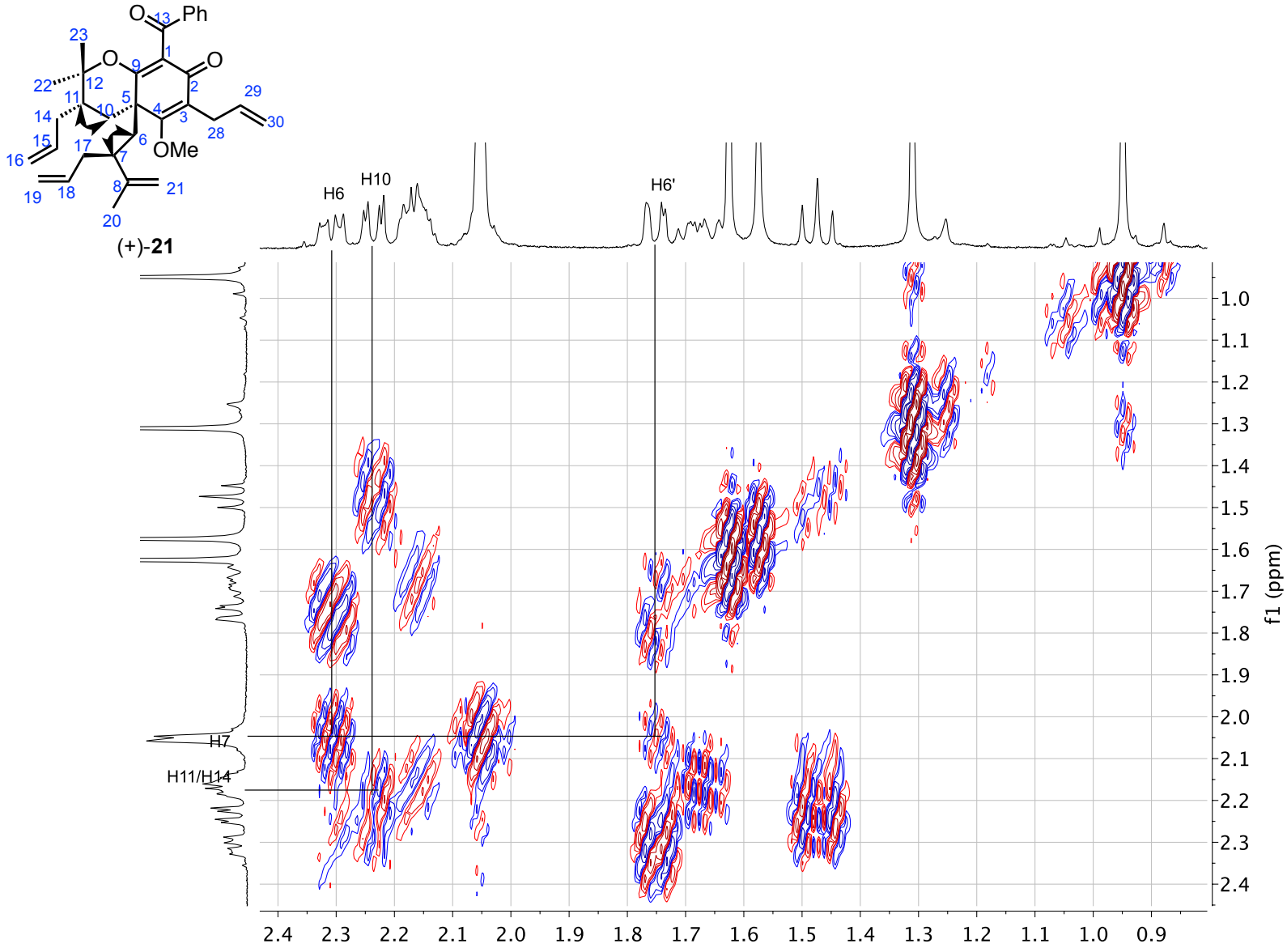


(+)-**21**

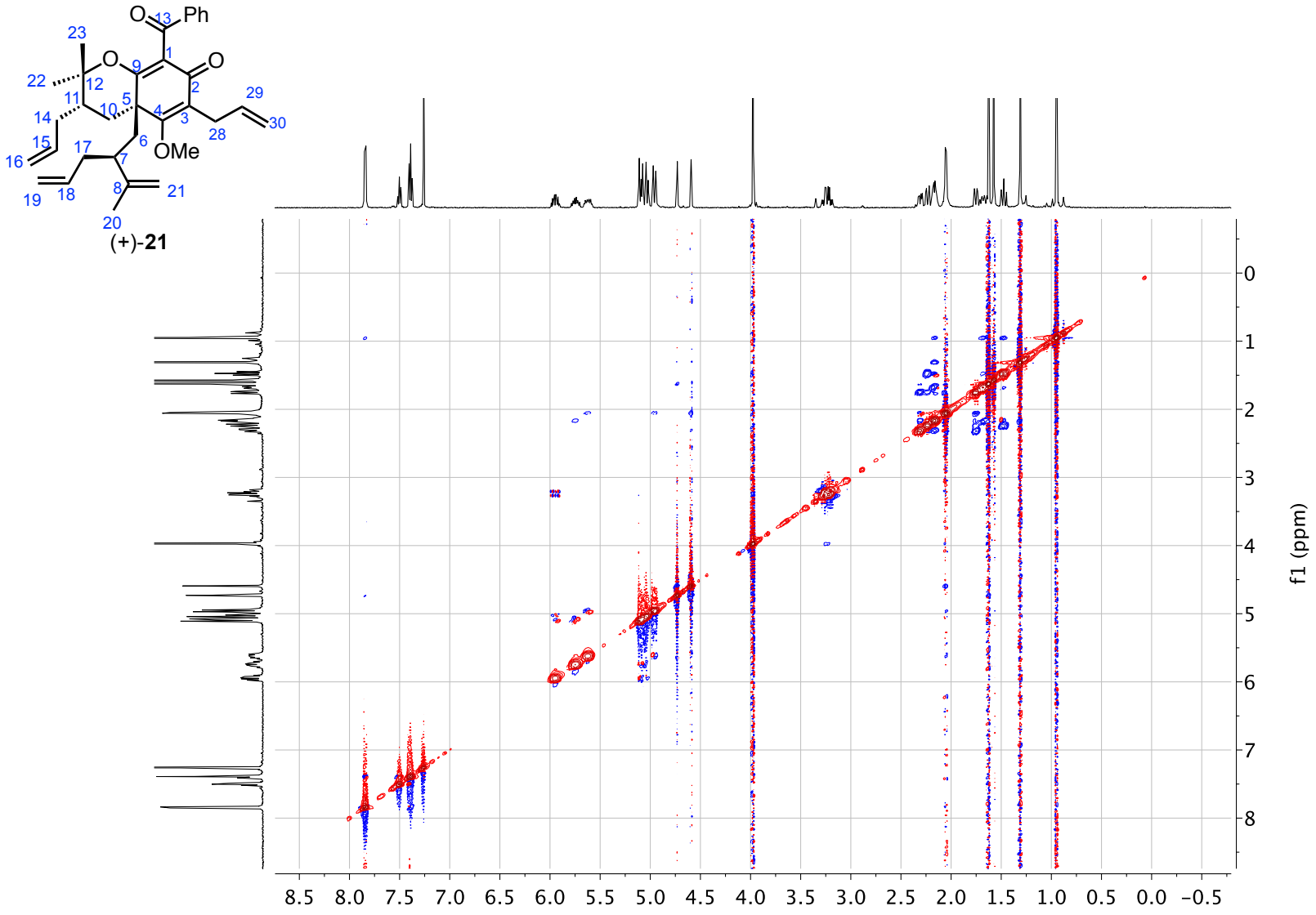
COSY Correlations (H14'-H15, H17-H18, H14-H15, H28/28'-H29)



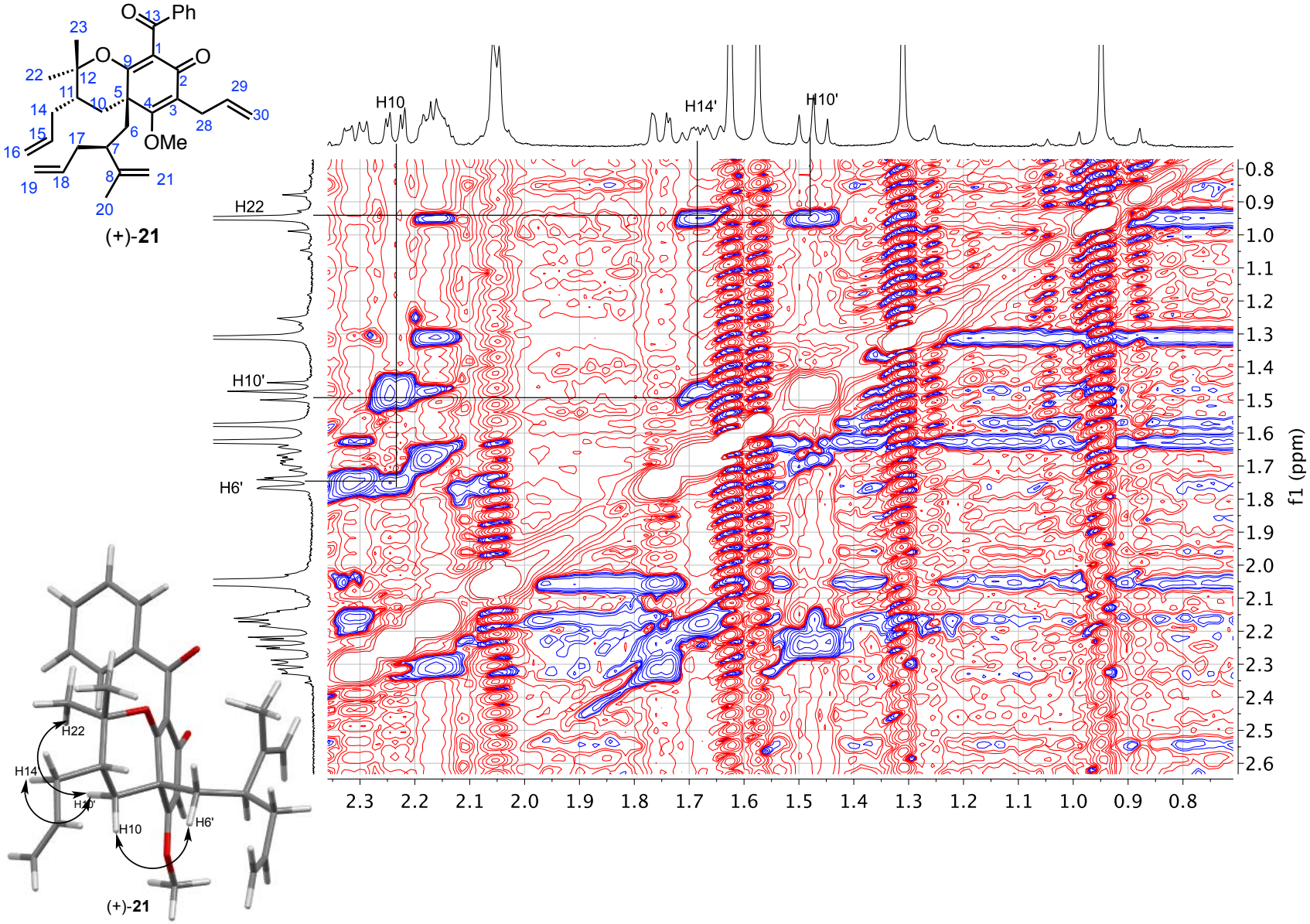
COSY Correlations (H7-H6, H7-H6', H11-H10)

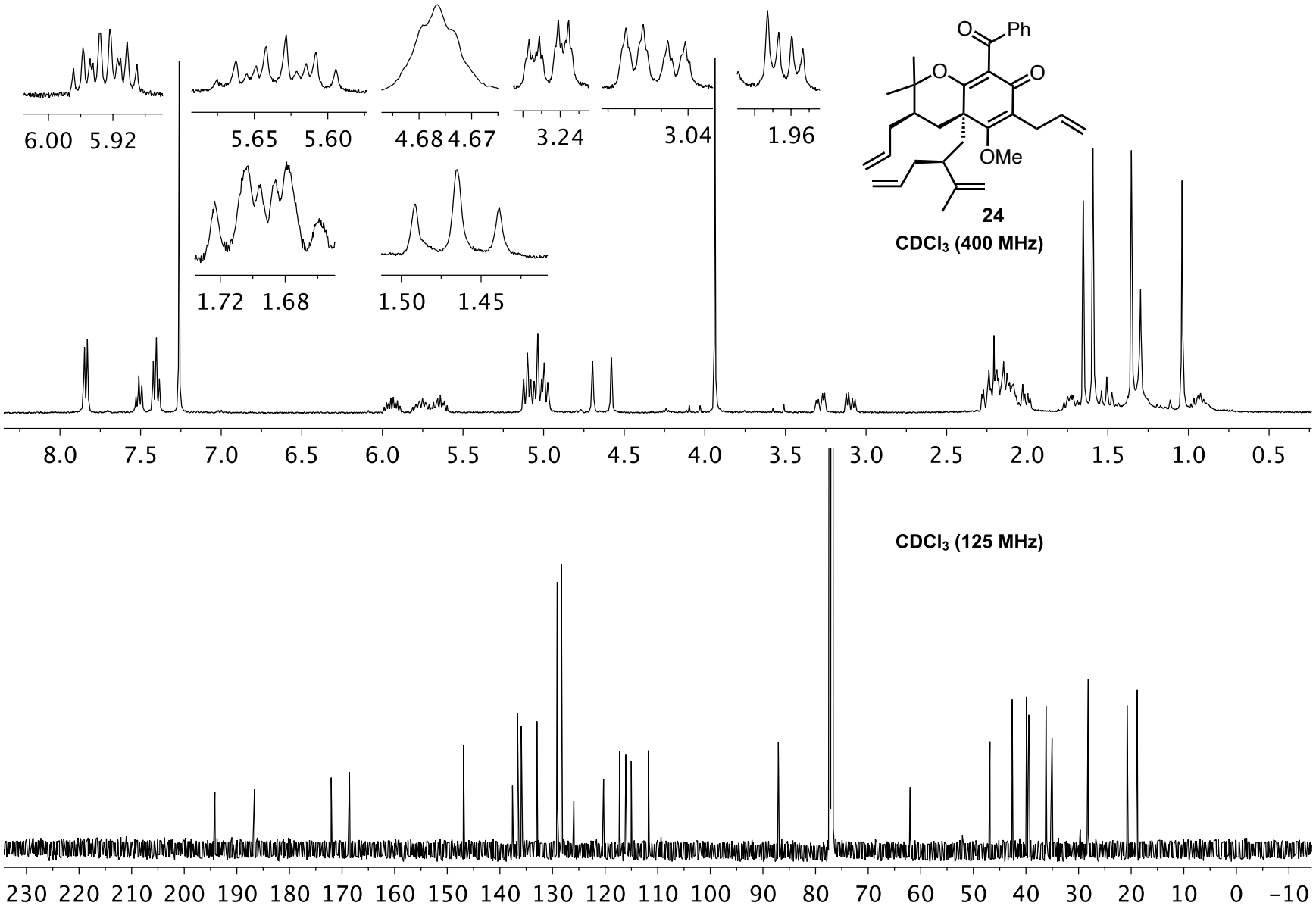


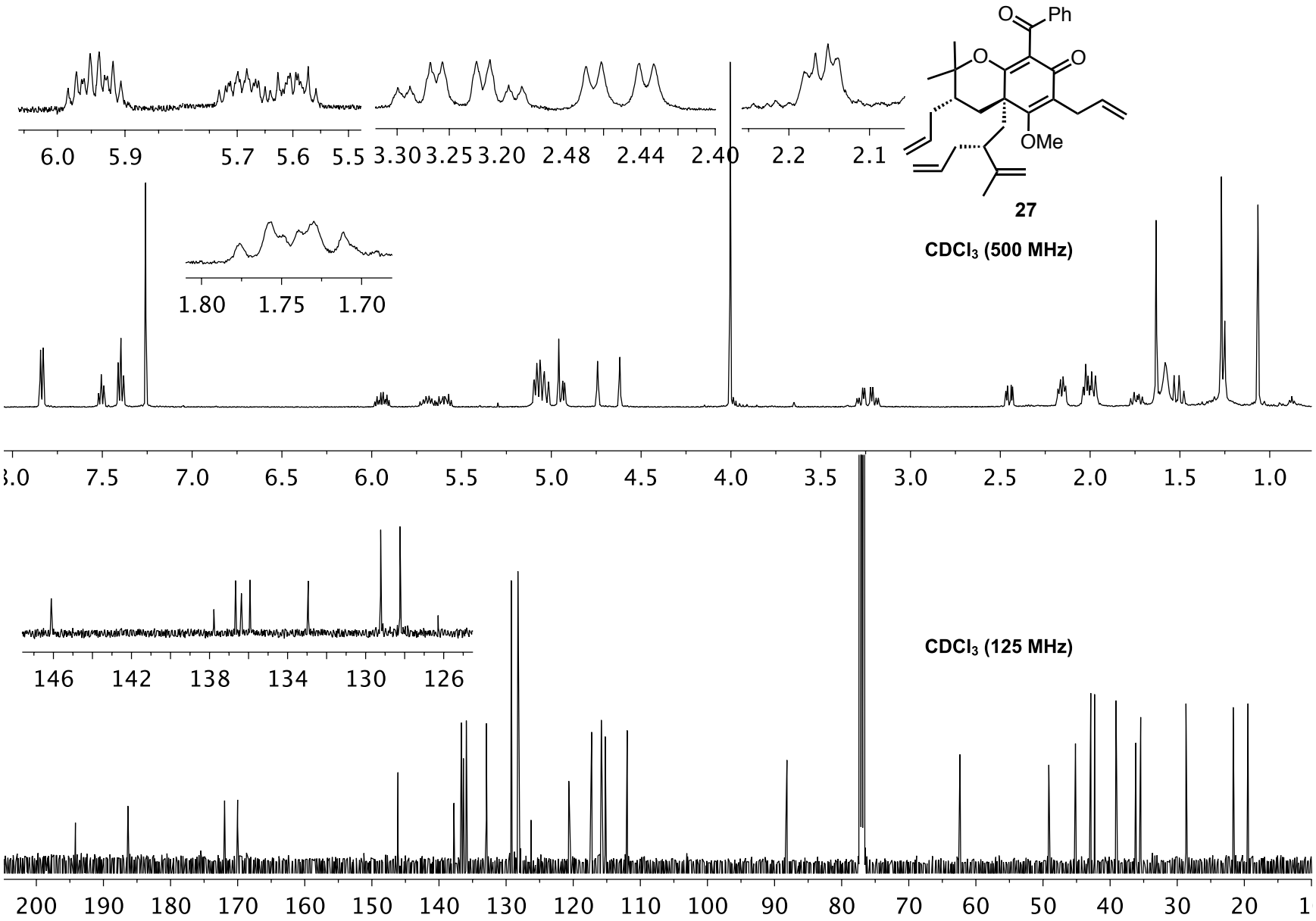
NOESY Correlations for Compound (+)-21

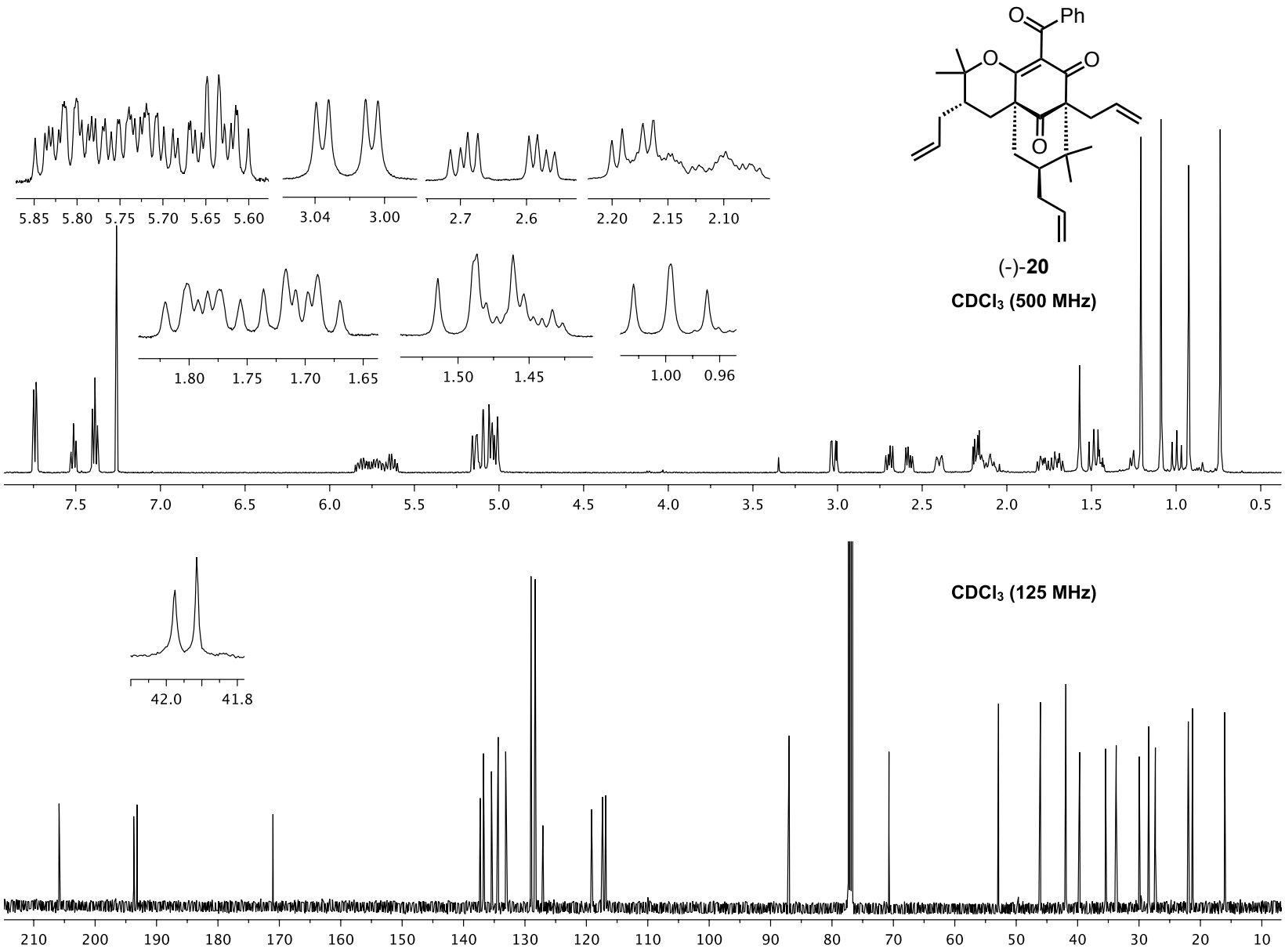


NOESY Correlations (H22-H10', H10'-H14', H6'-H10)

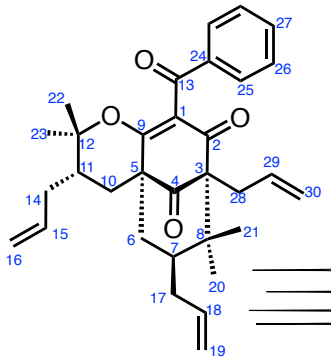



6.00
5.92
5.65
5.60
4.68
4.67
3.24
3.04
1.96
1.72
1.68
1.50
1.45
O
Ph
O
O
OMe
24
CDCl3 (400 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
CDCl3 (125 MHz)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

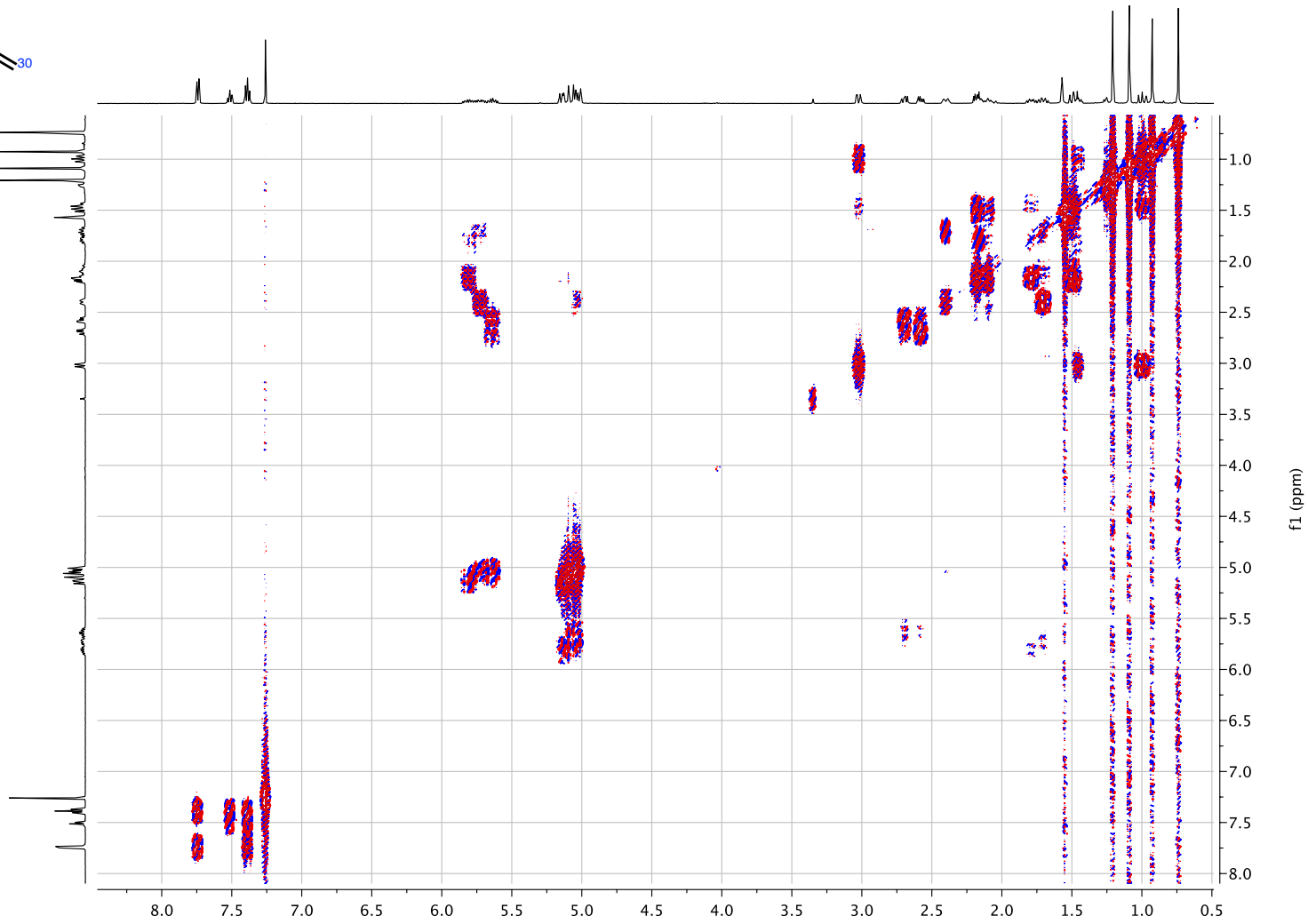

O
Ph
O
O
OMe
27
CDCl3 (500 MHz)
CDCl3 (125 MHz)


O
Ph
O
O
O
(-)-20
CDCl3 (500 MHz)
5.85 5.80 5.75 5.70 5.65 5.60
3.04 3.00
2.7 2.6
2.20 2.15 2.10
1.80 1.75 1.70 1.65
1.50 1.45
1.00 0.96
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
CDCl3 (125 MHz)
42.0 41.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

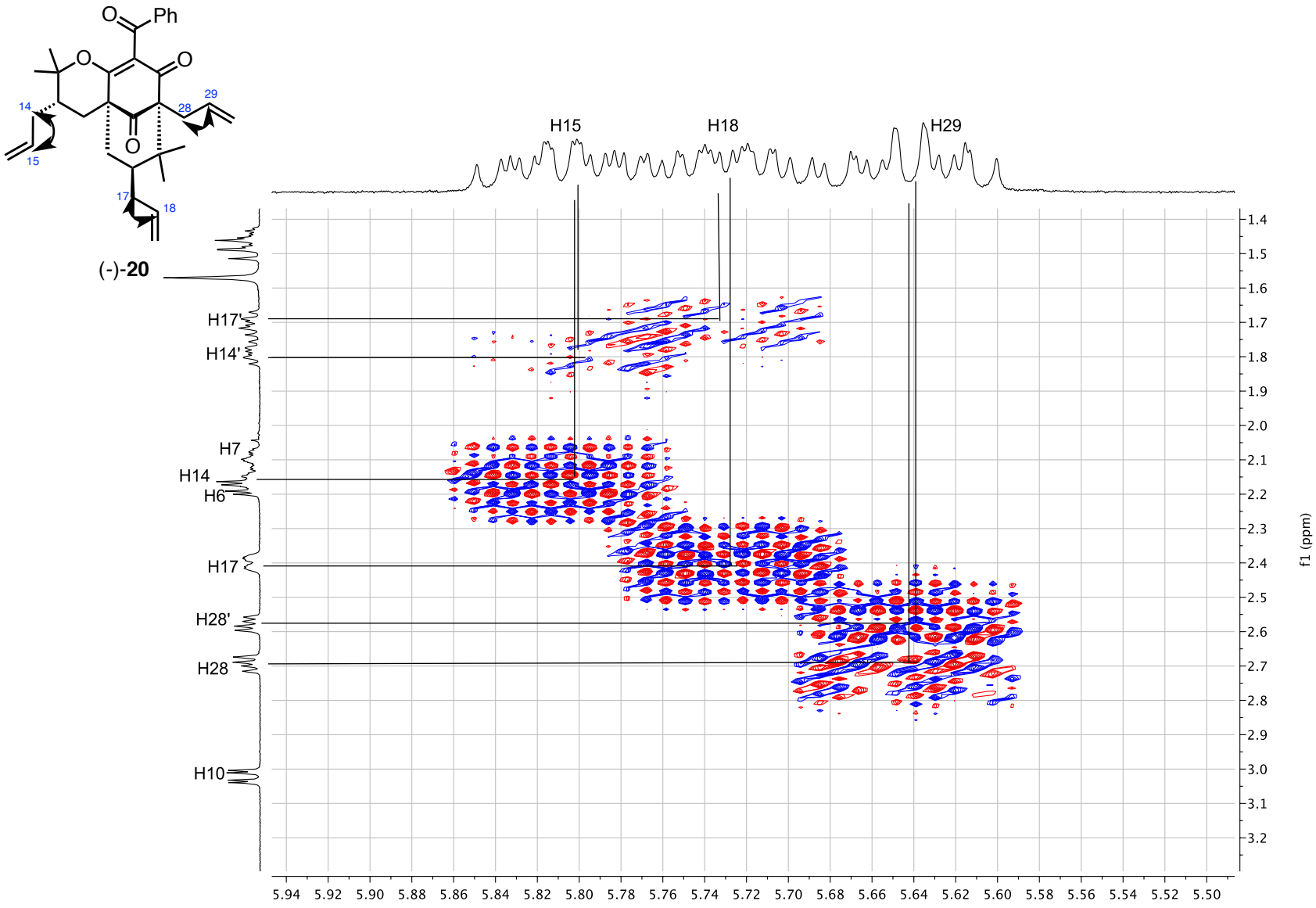
COSY Correlations for Compound (-)-20



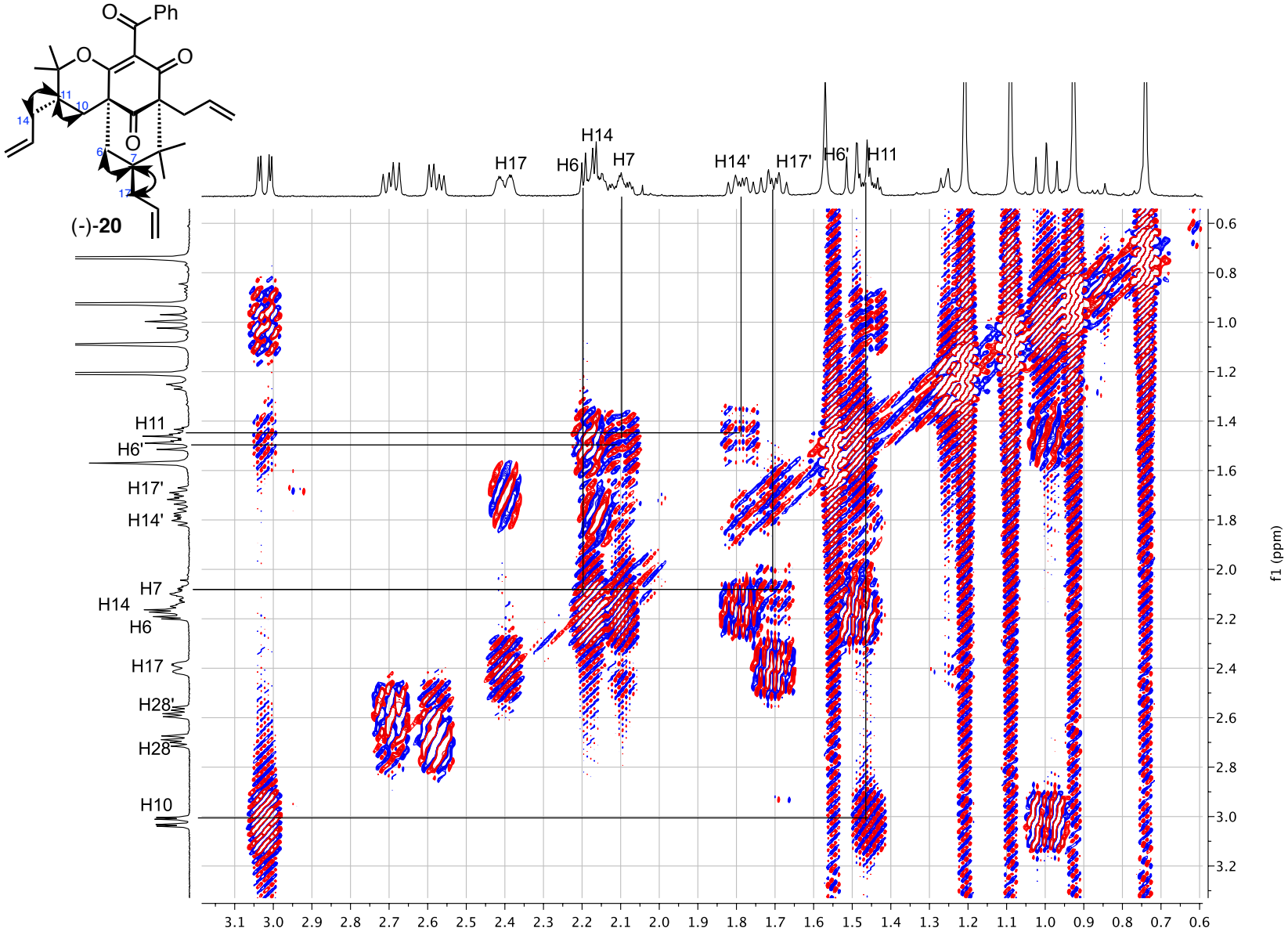
(-)-**20**



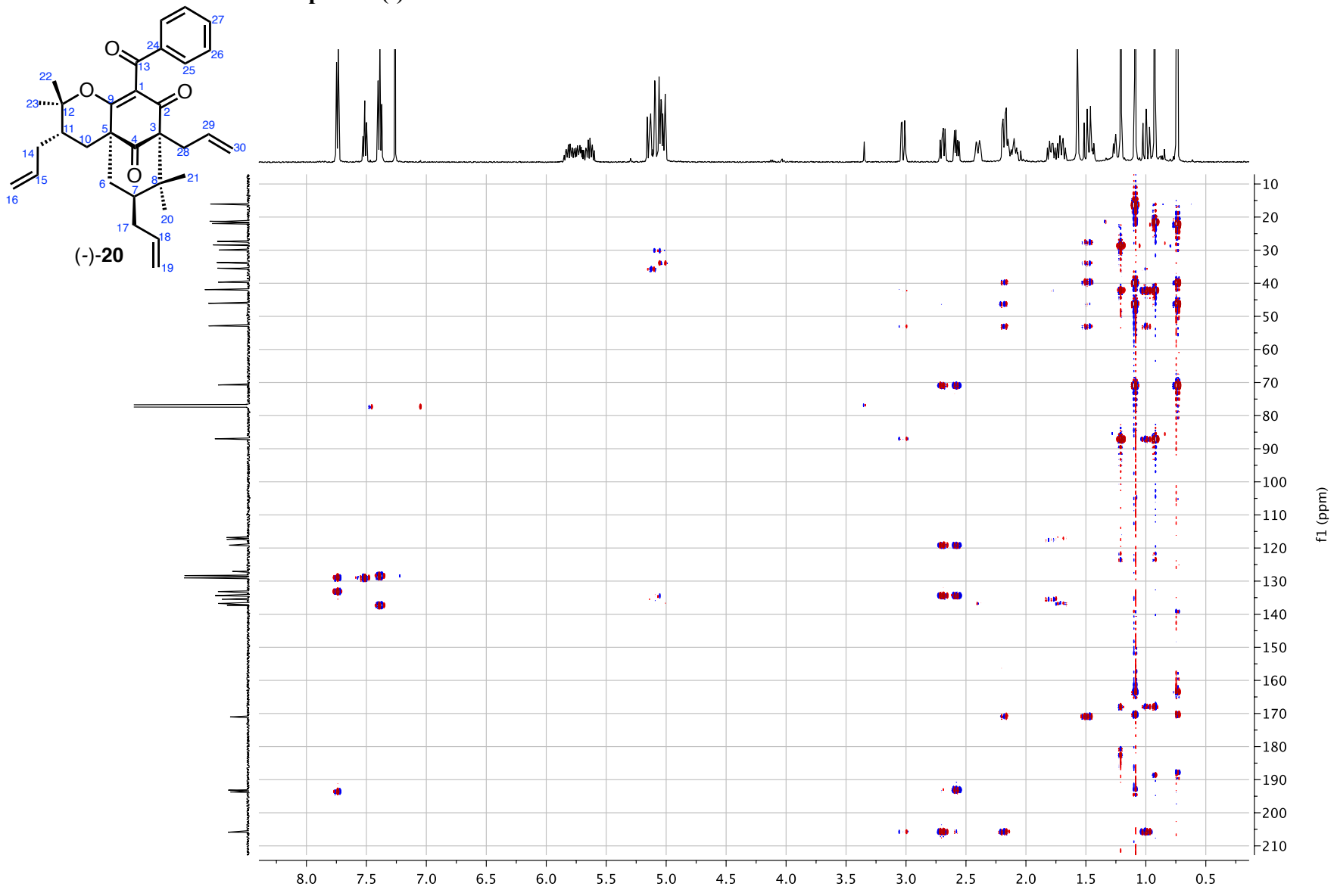
COSY Correlations (H17'-H18, H14'-H15, H14-H15, H17-H18, H28'-H29, H28-H29)



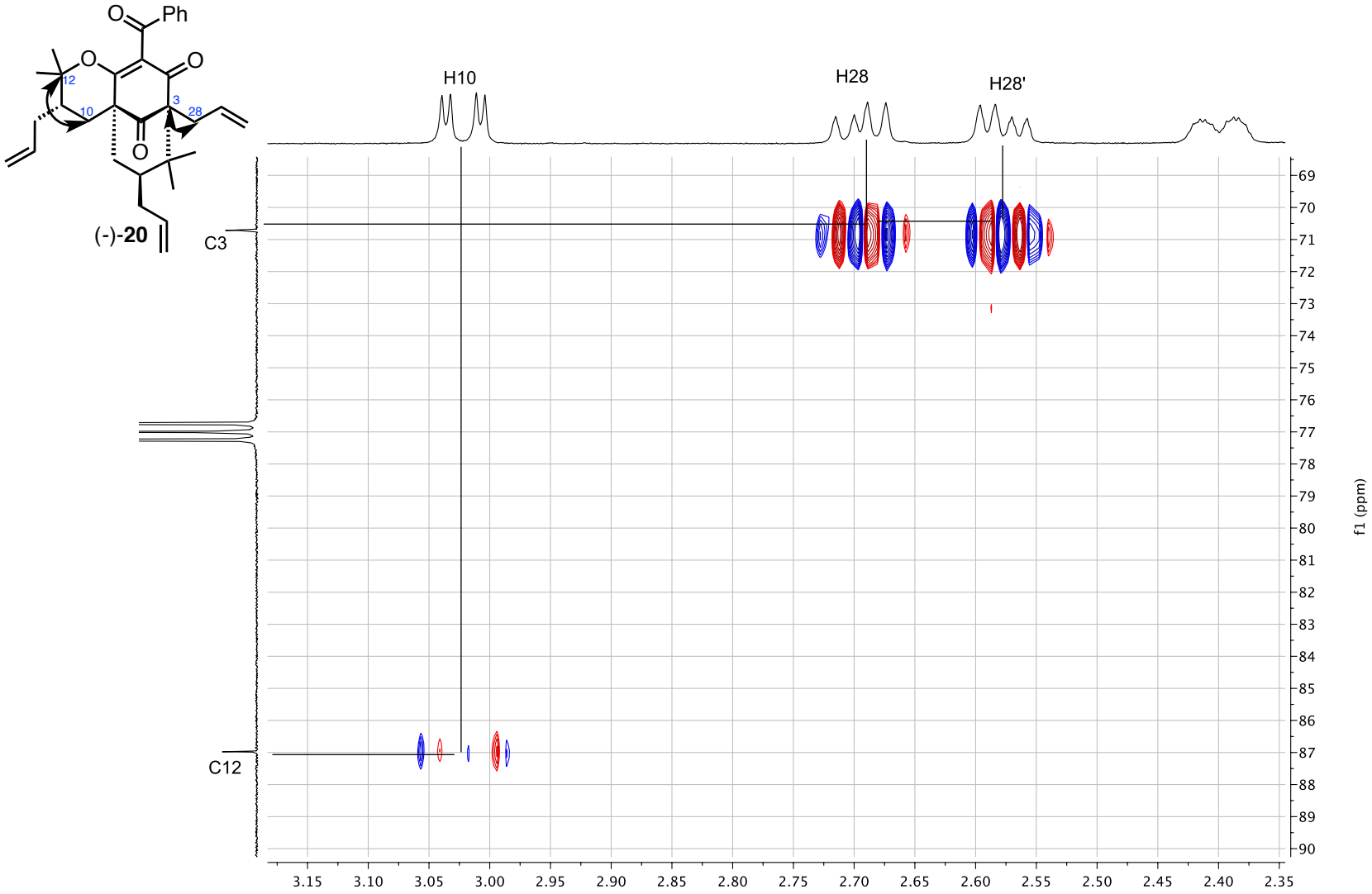
COSY Correlations (H11-H14', H6'-H7, H7-H6, H7-H17', H10-H11)



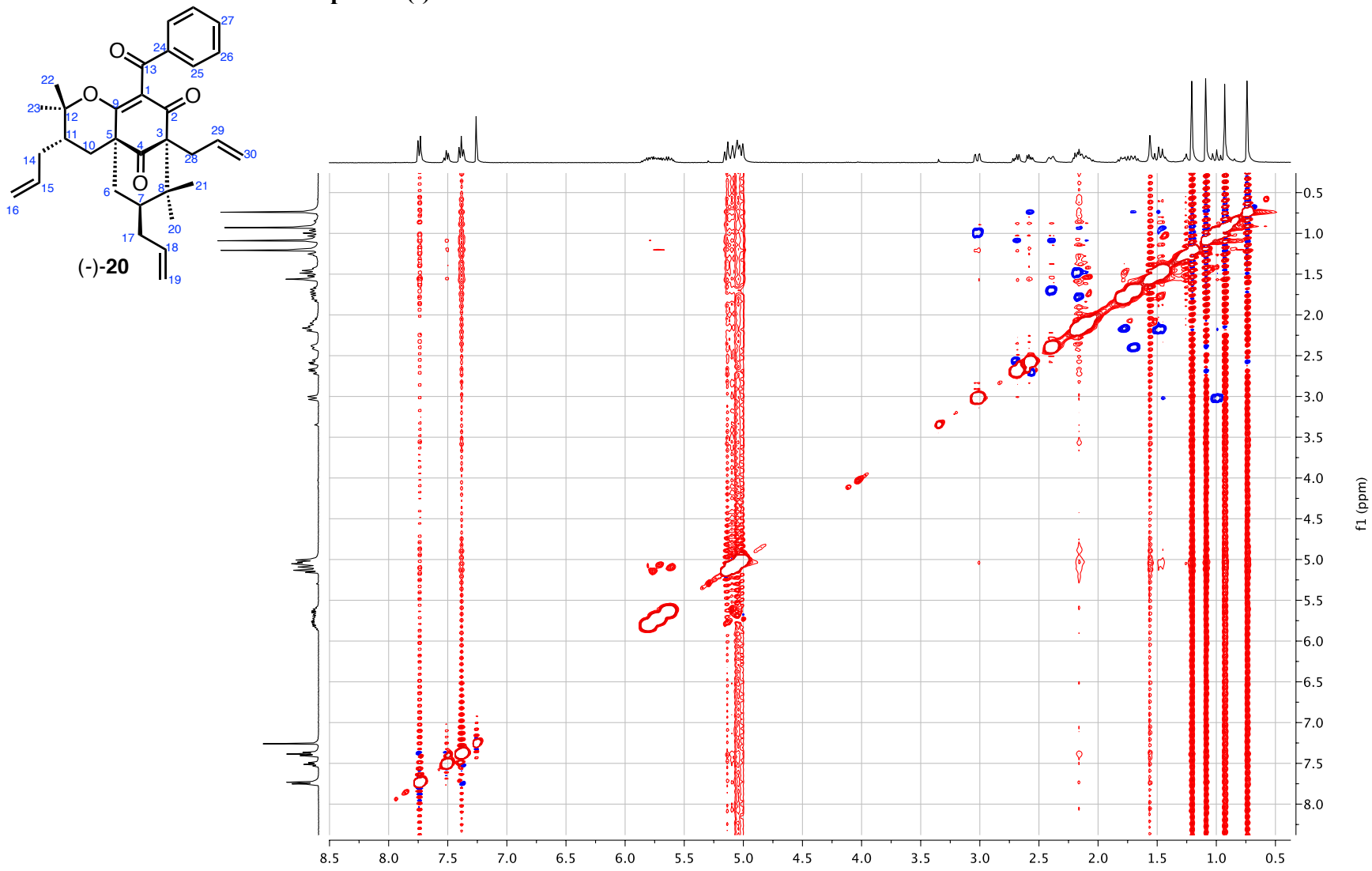
HMBC Correlations for Compound (-)-20



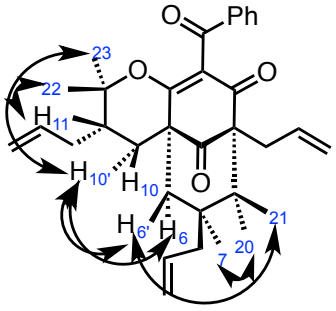
HMBC Correlations (C3-H28, C3-H28', C12-H10)



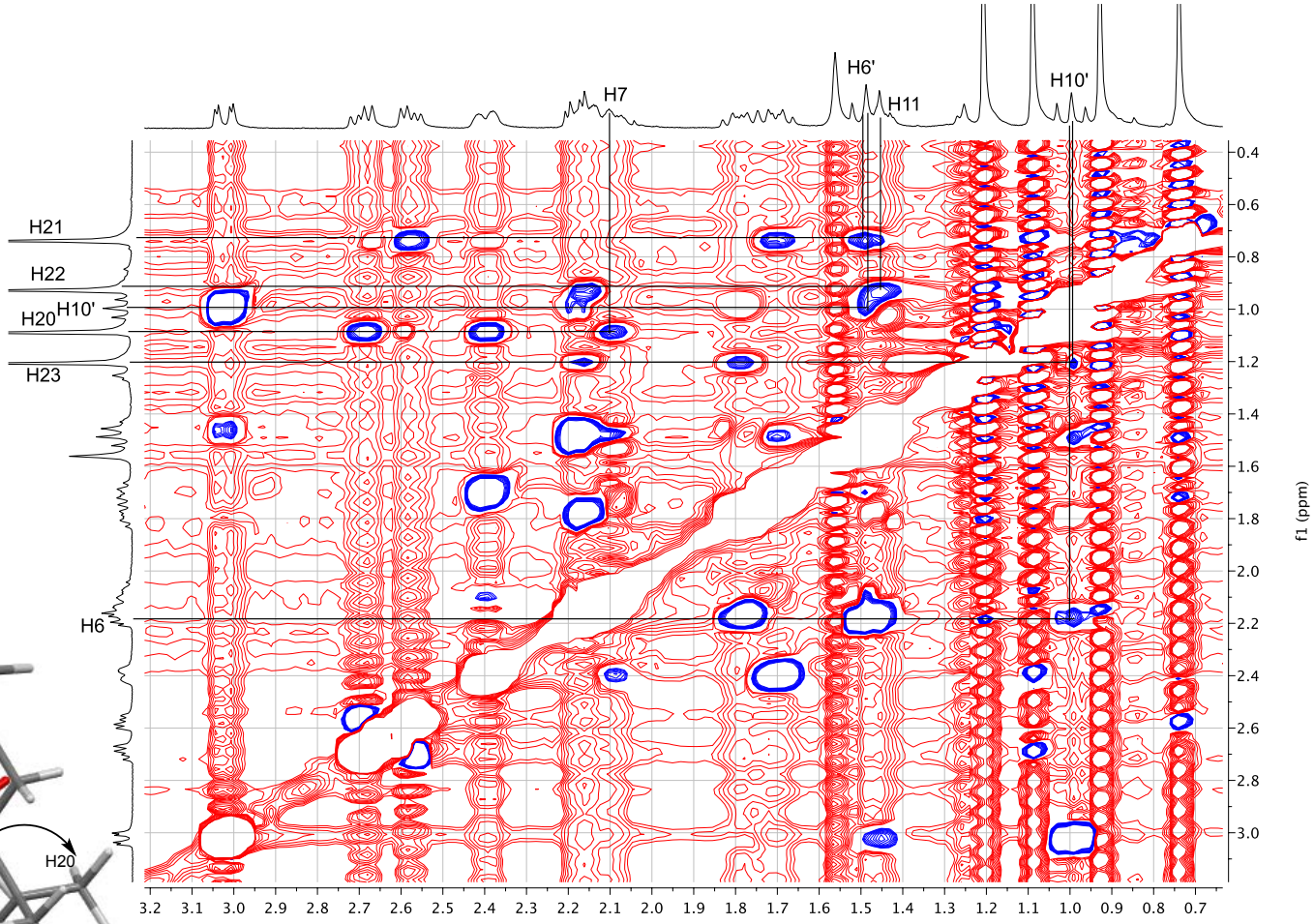
NOESY Correlations for Compound (-)-20

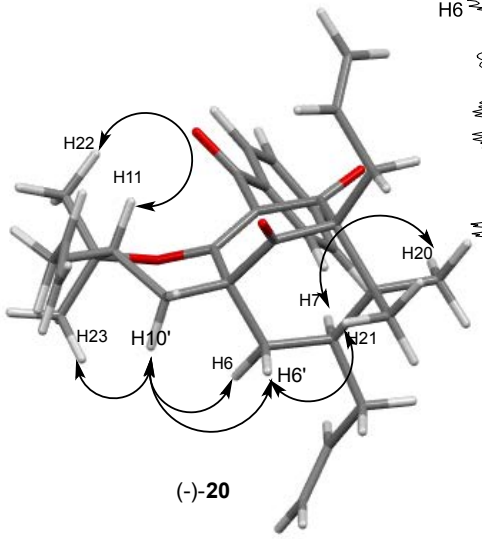


NOESY Correlations (H21-H6', H22-H11, H10'-H6', H20-H7, H23-H10', H6-H10')



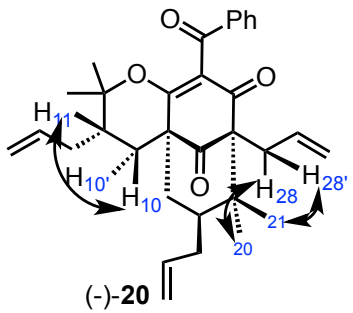
(-)-**20**



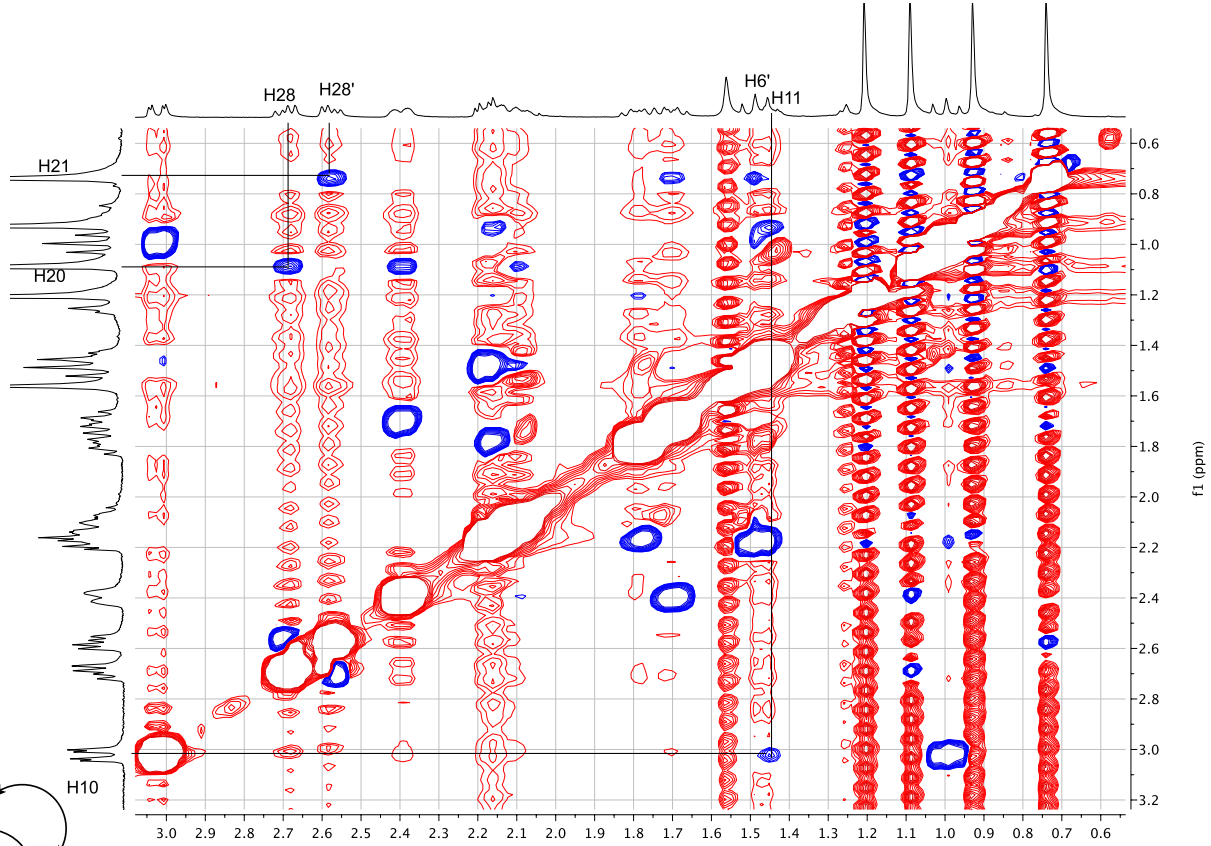


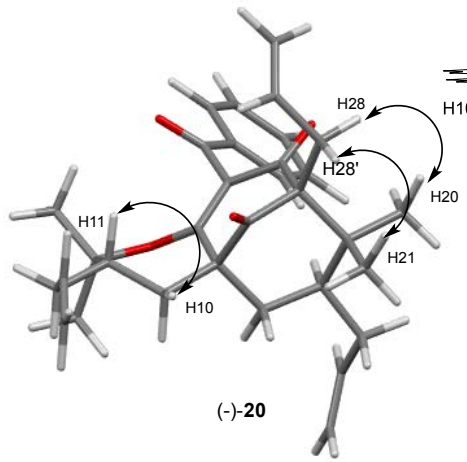
(-)-**20**

NOESY Correlations (H10-H11, H28-H20, H28'-H21)



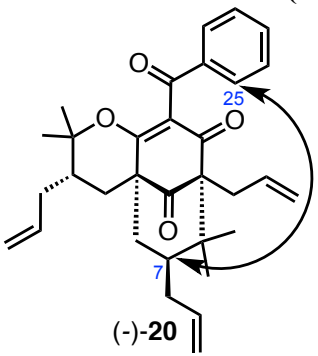
(-)-**20**



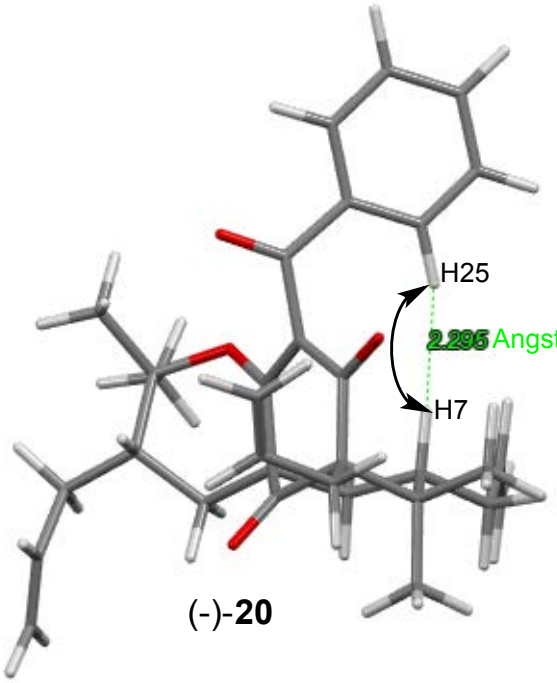


(-)-**20**

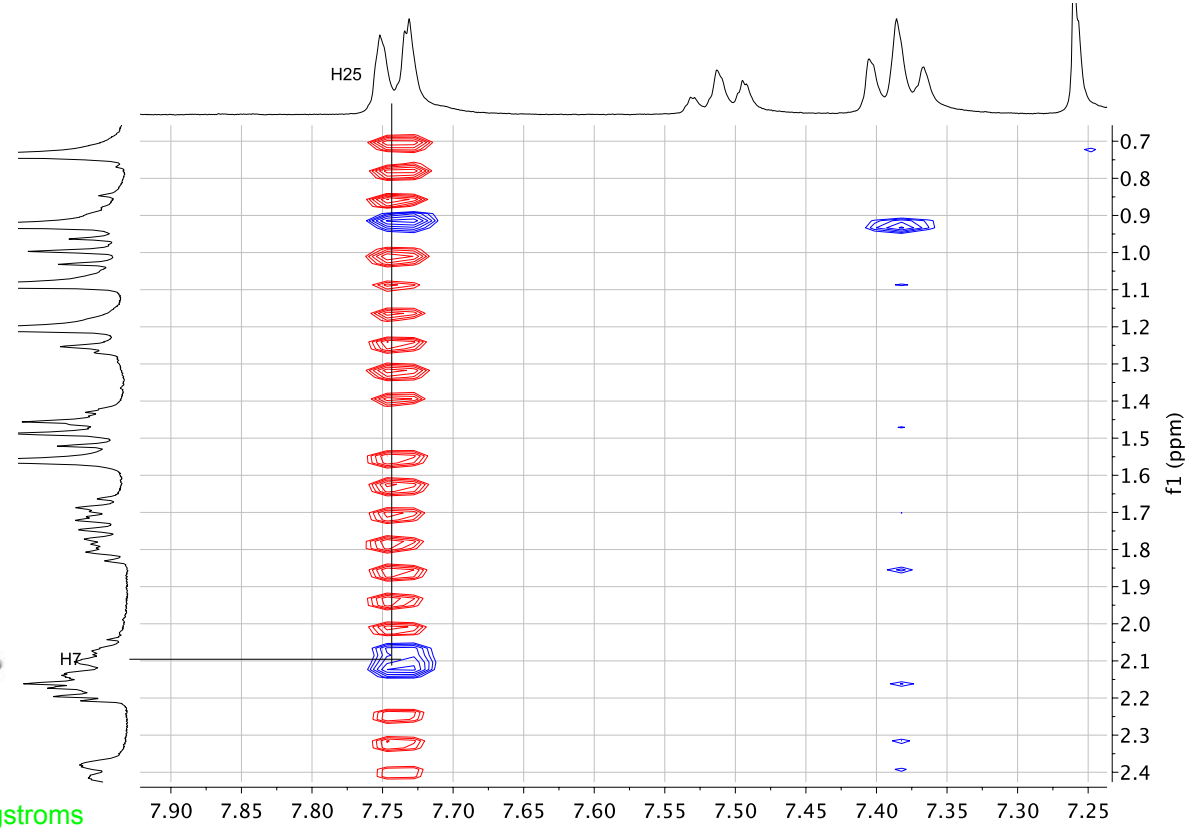
NOESY Correlation (H7-H25)
NOESY Correlation (H25-H7)

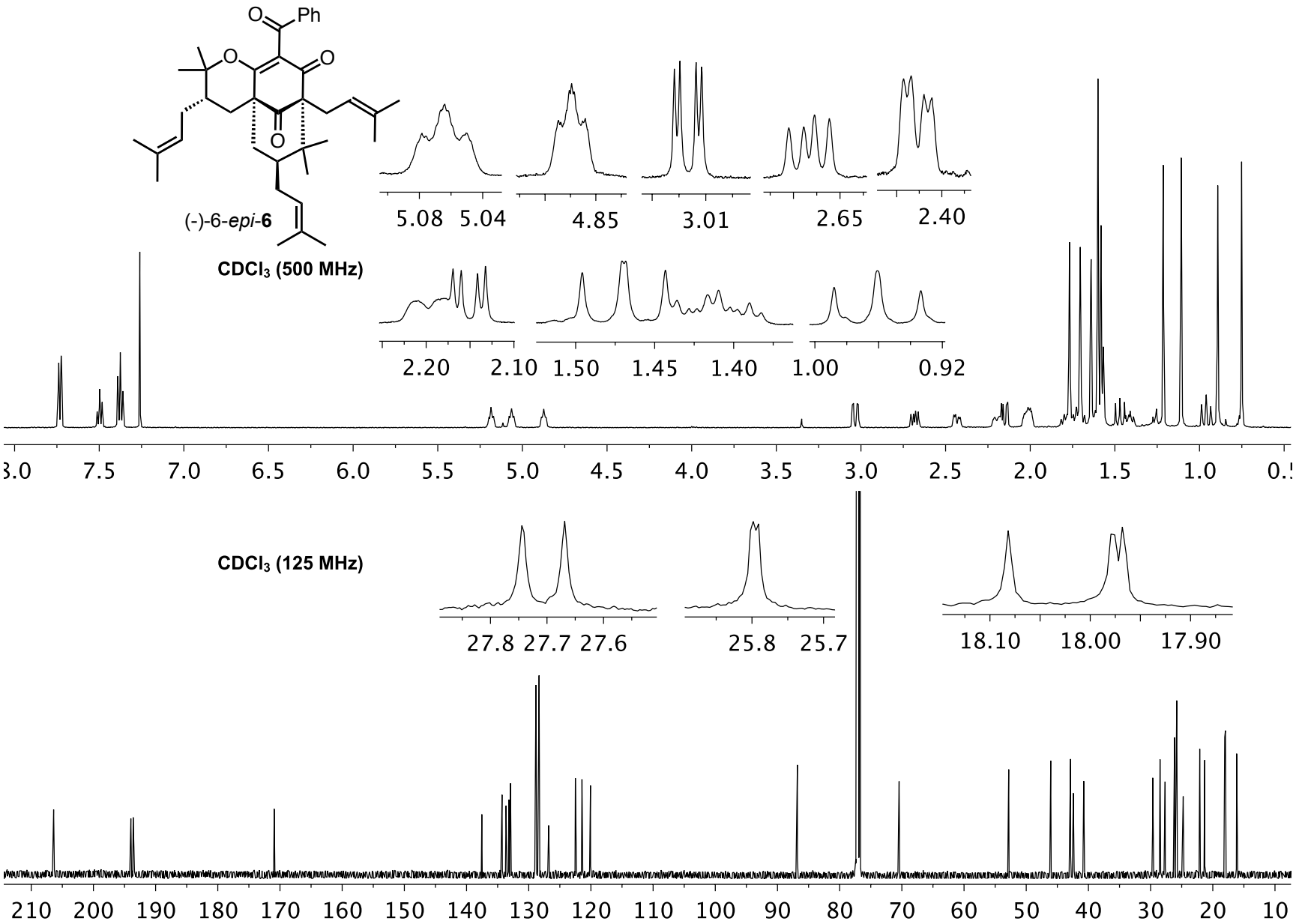


(-)-**20**

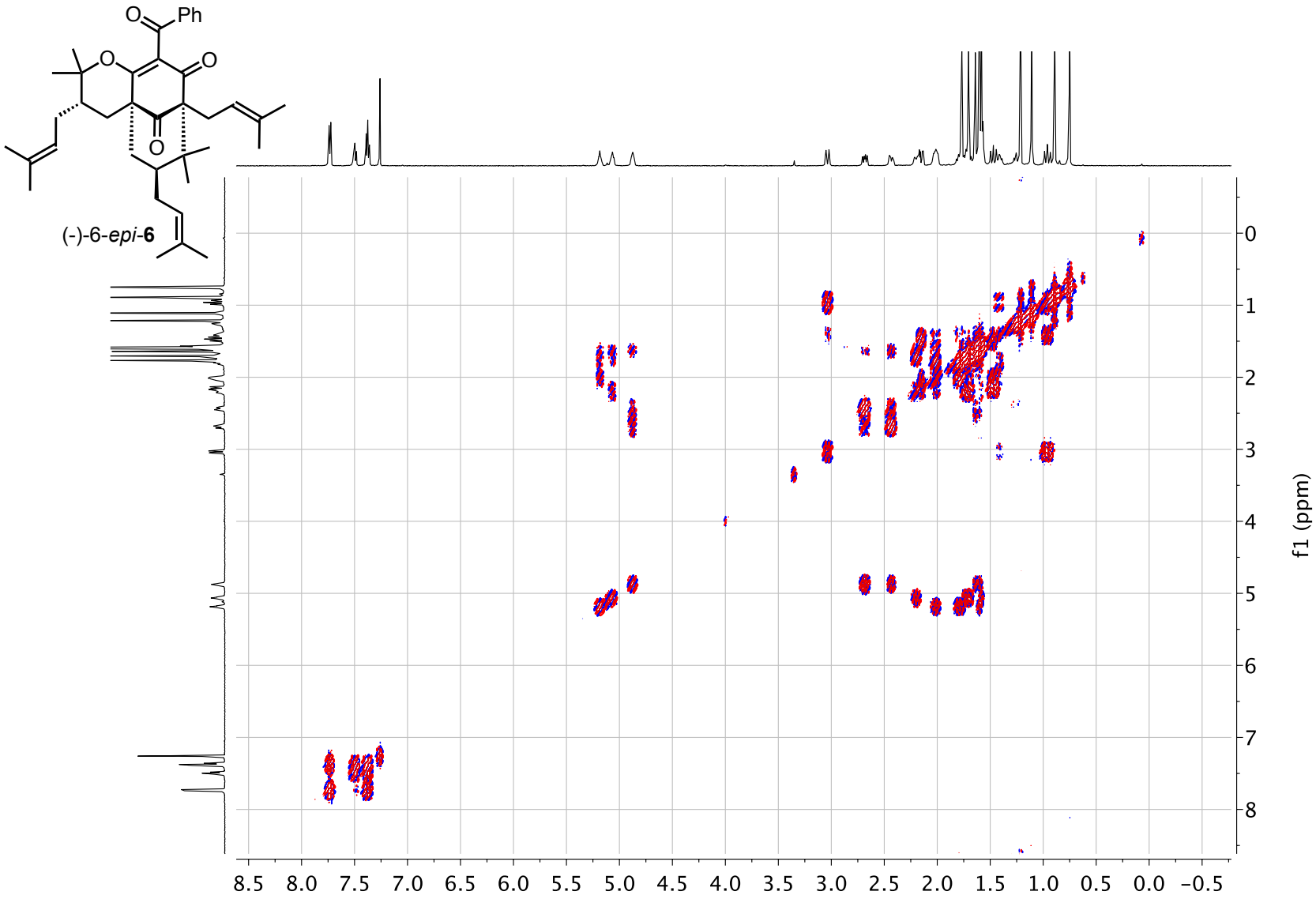


(-)-**20**

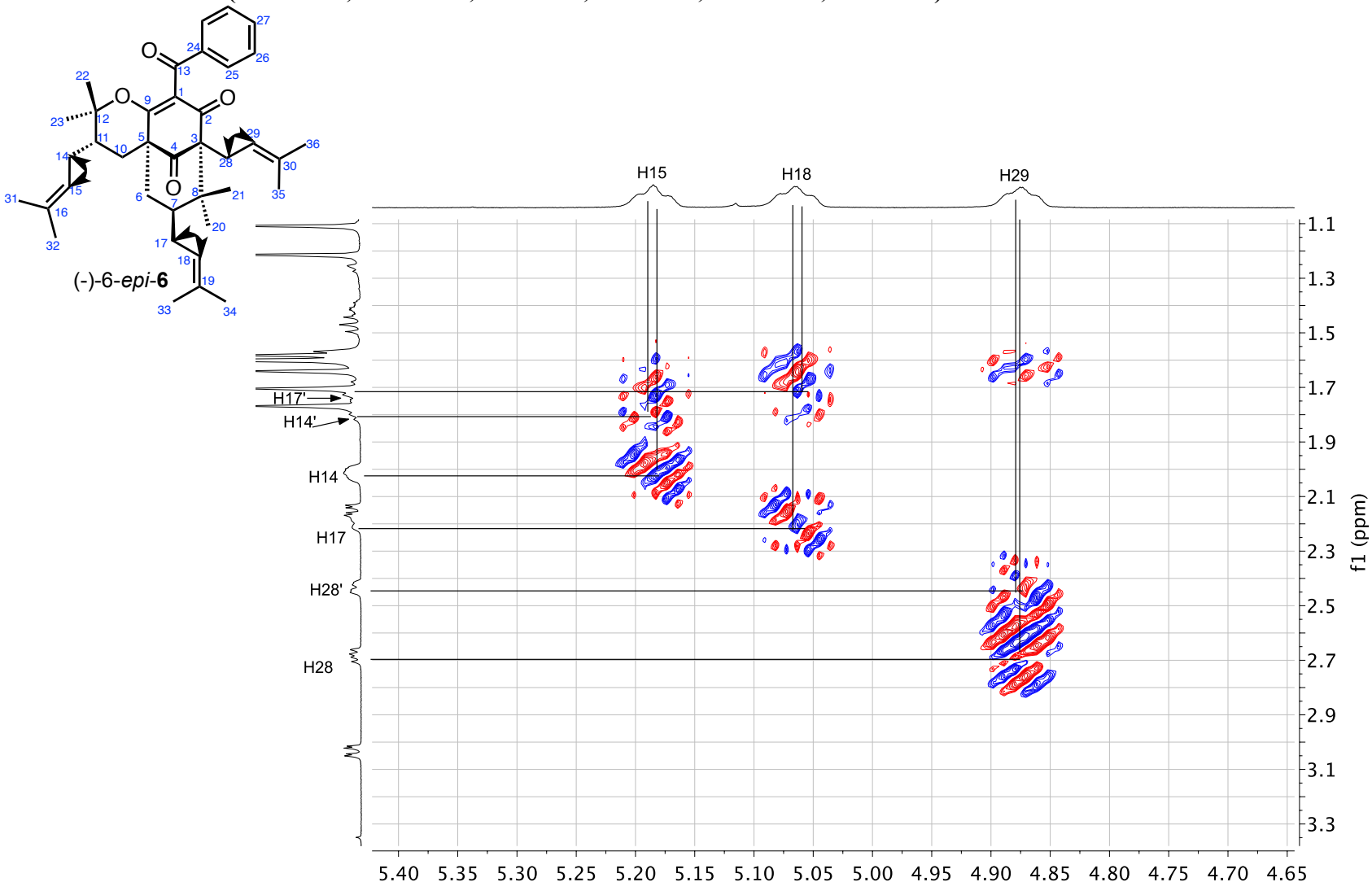



O
Ph
O
O
O
(-)-6-*epi*-**6**
CDCl$_3$ (500 MHz)
5.08 5.04
4.85
3.01
2.65
2.40
2.20 2.10
1.50 1.45 1.40
1.00
0.92
3.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
CDCl$_3$ (125 MHz)
27.8 27.7 27.6
25.8 25.7
18.10 18.00 17.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

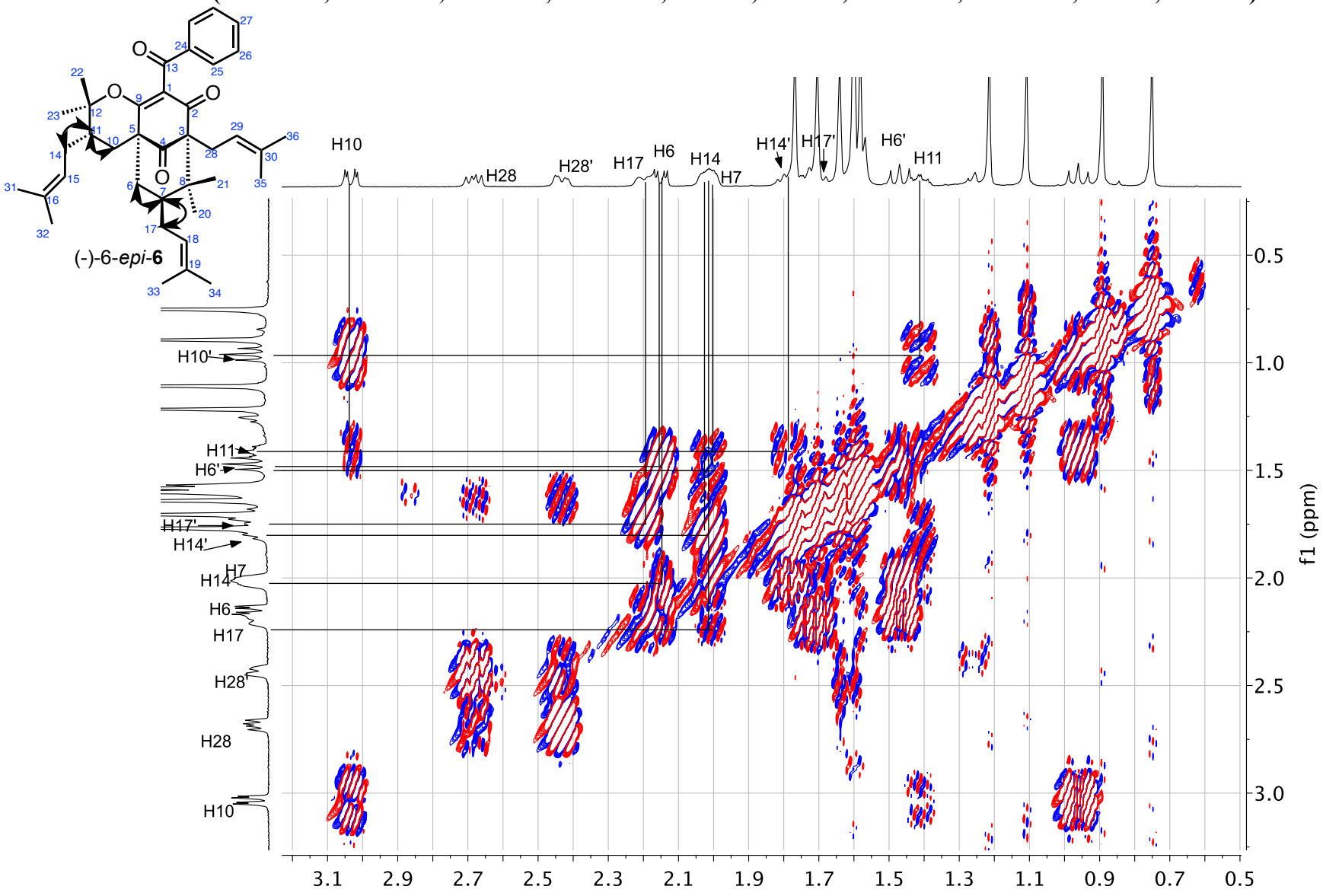
COSY Correlations for Compound (-)-6-*epi*-6



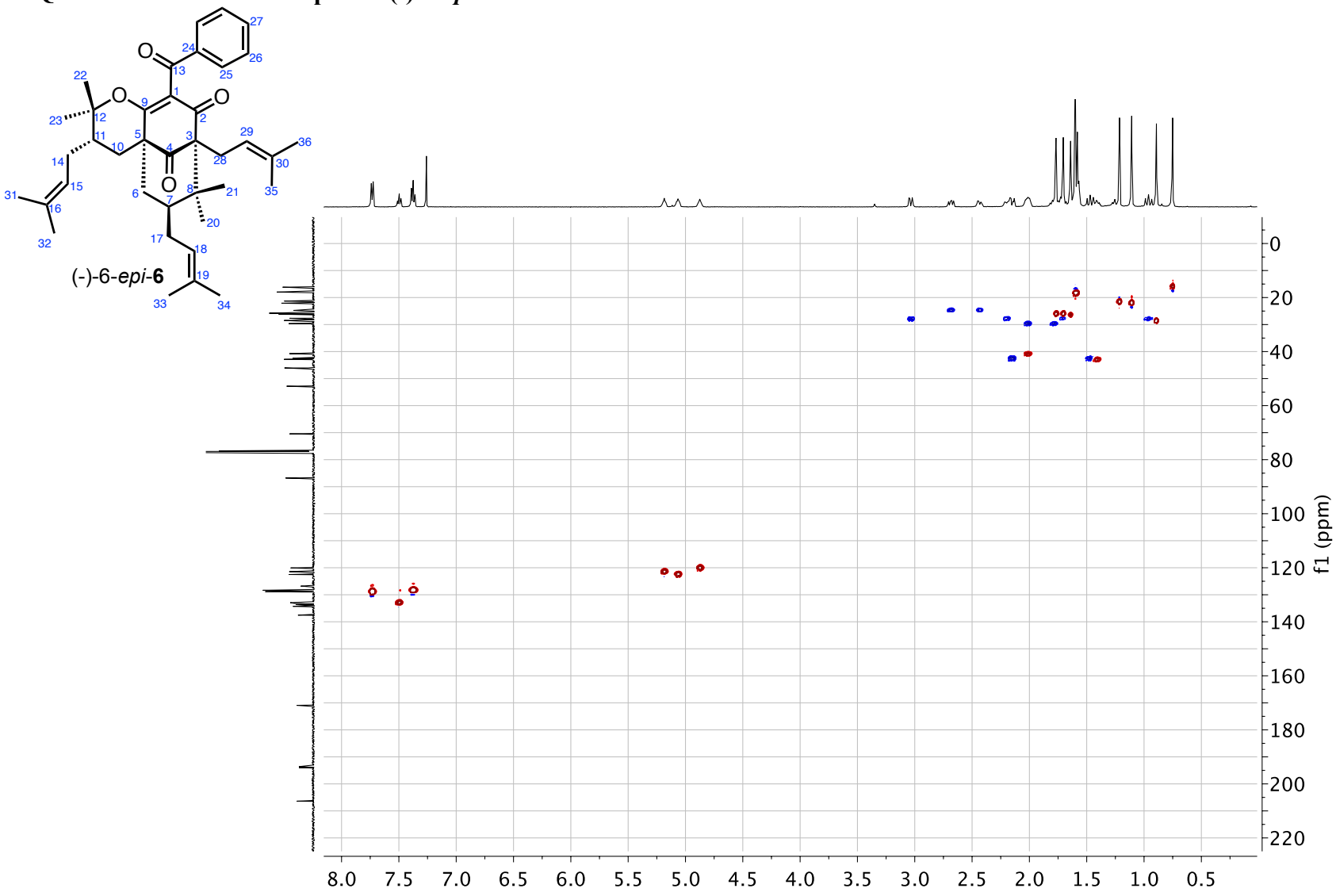
COSY Correlations (H17'-H18, H14'-H15, H14-H15, H17-H18, H28'-H29, H28-H29)



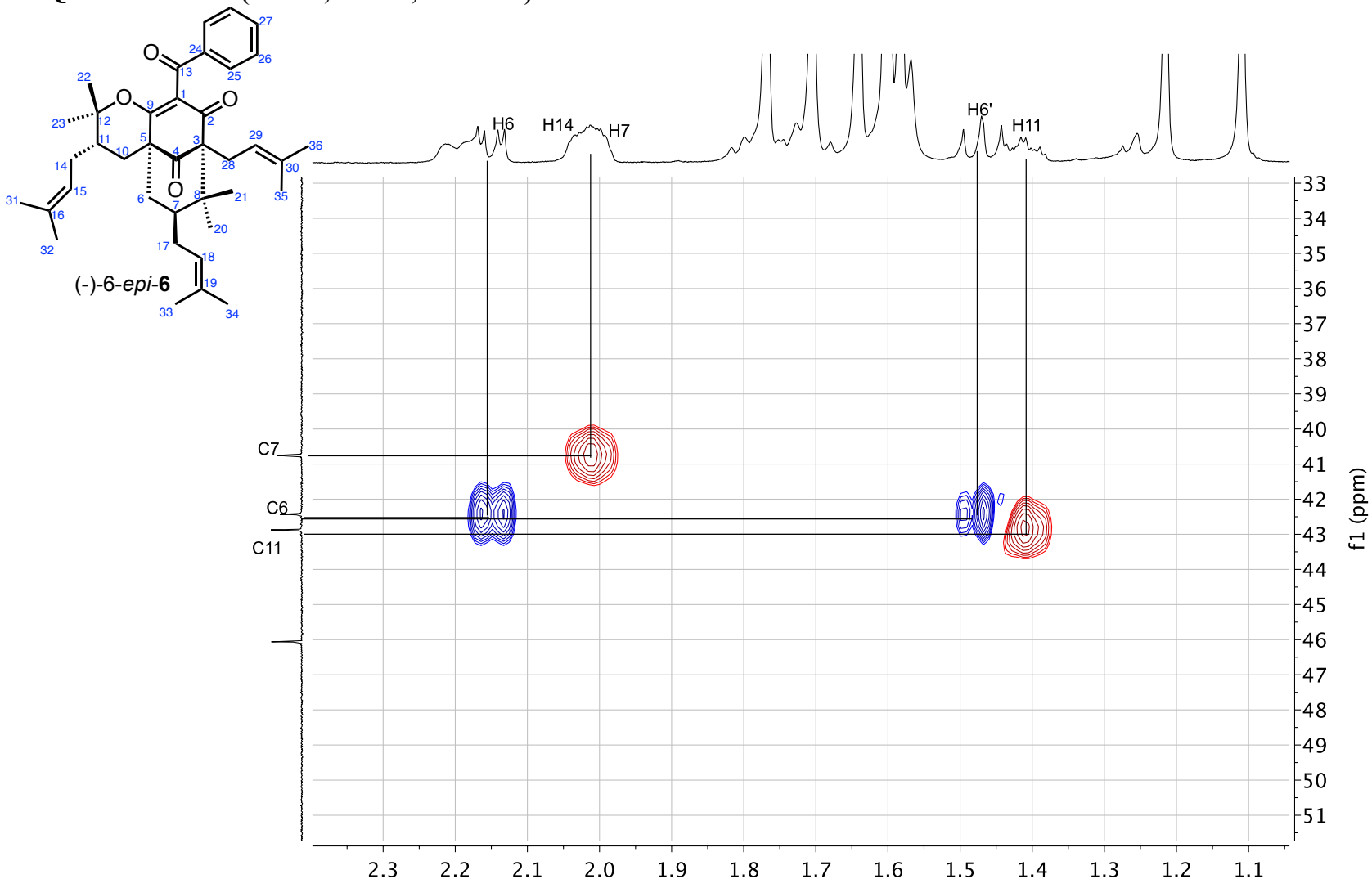
COSY Correlations (H10'-H10, H10'-H11, H11-H10, H11-H14', H6'-H6, H6'-H7, H17'-H17, H14'-H14, H7-H6, H17-H7)



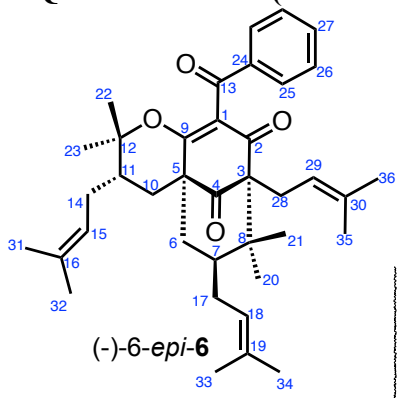
HSQC Correlations for Compound (-)-6-*epi*-6

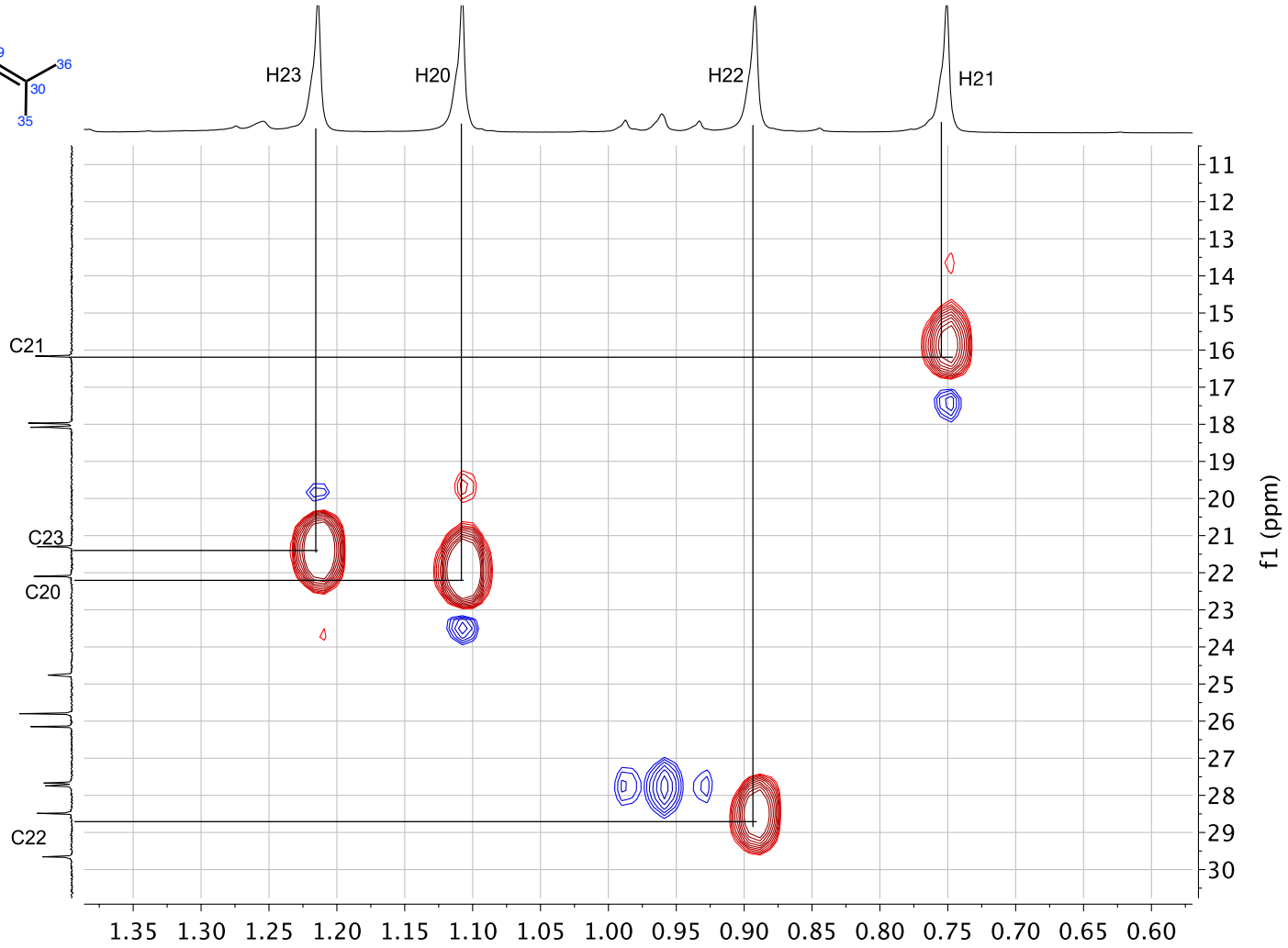


HSQC Correlations (C7-H7, C6-H6, C11-H11)

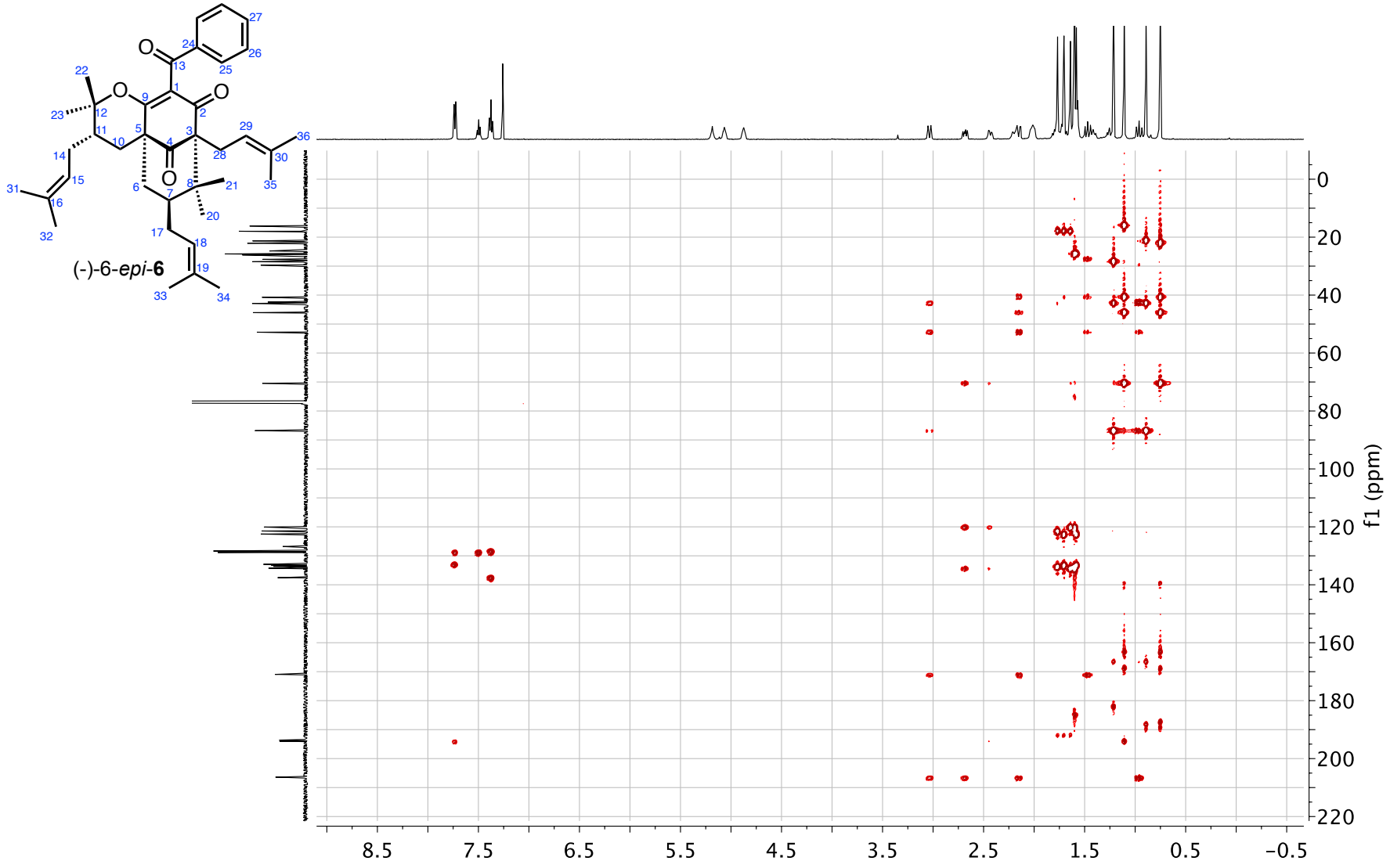


HSQC Correlations (C21-H21, C23-H23, C20-H20, C22-H22)

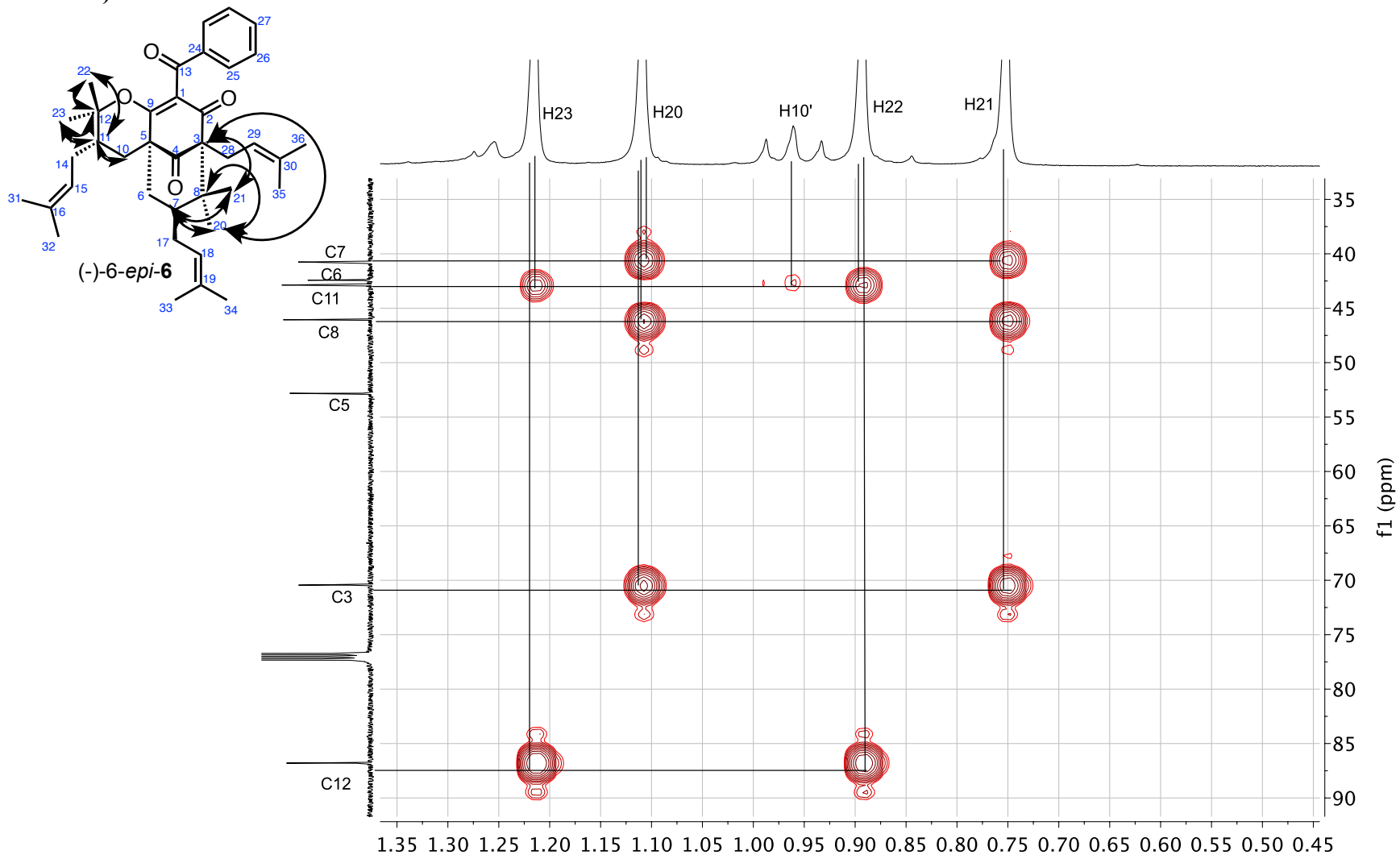




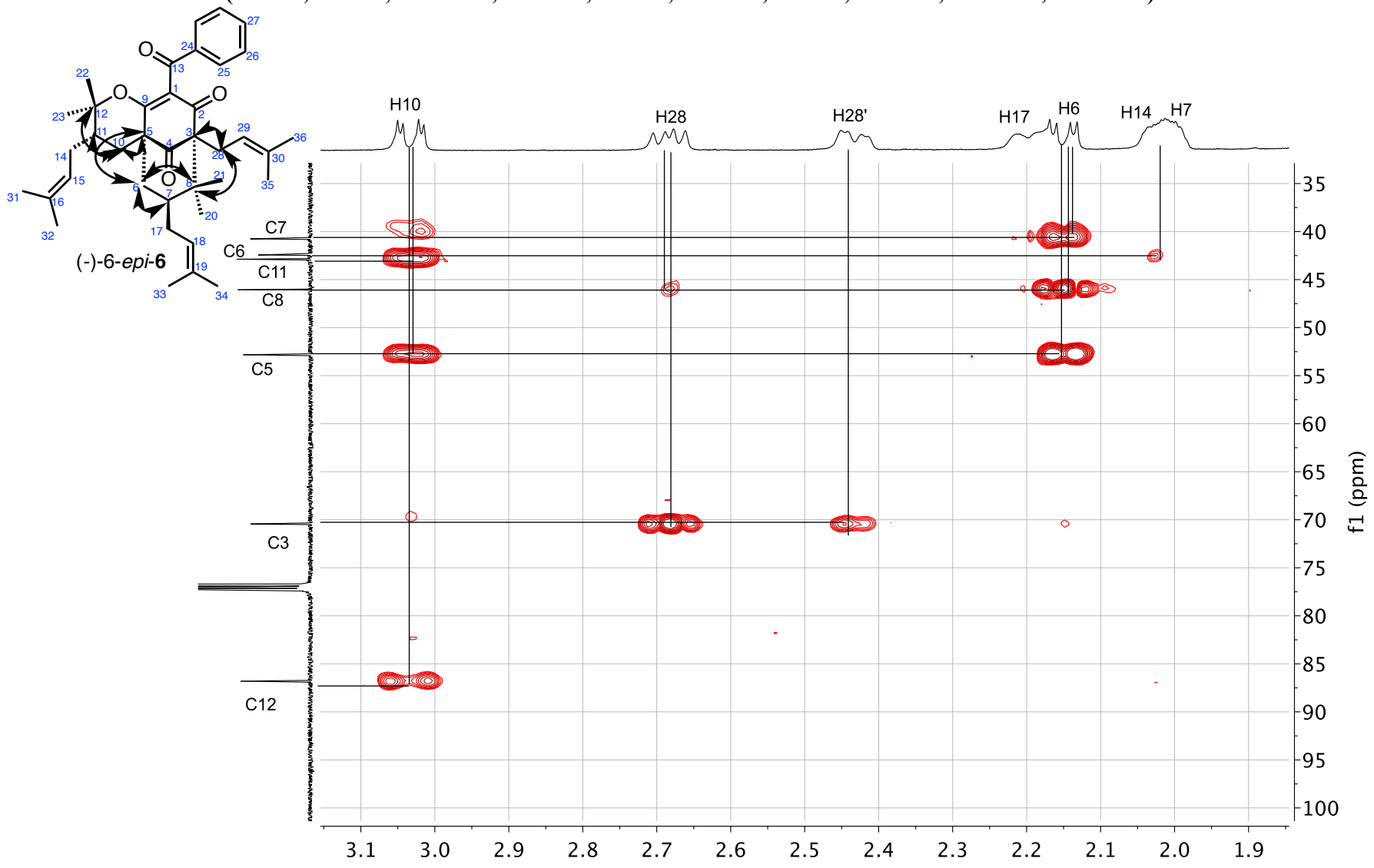
HMBC Correlations for Compound (-)-6-*epi*-6



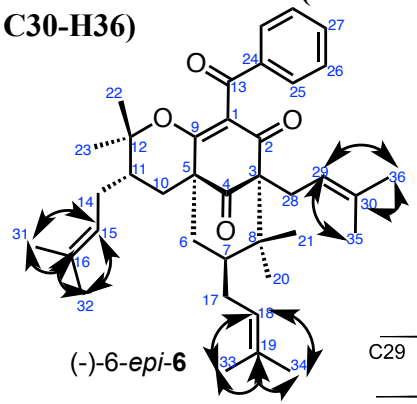
HMBC Correlations (C7-H20, C7-H21, C11-H23, C11-H10', C11-H22, C8-H20, C8-H21, C3-H20, C3-H21, C12-H23, C12-H22)

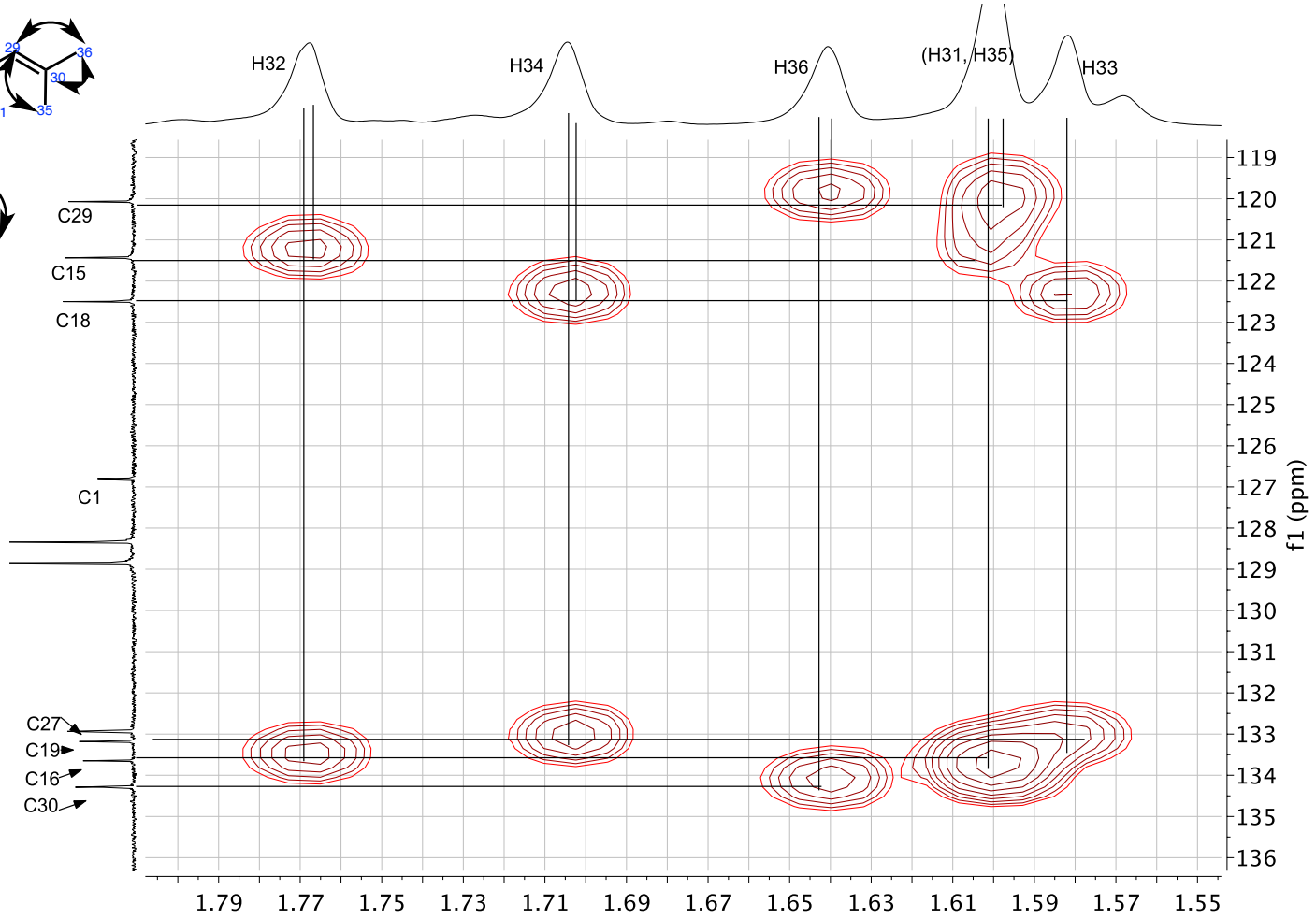


HMBC Correlations (C7-H6, C6-H7, C11-H10, C8-H28, C8-H6, C5-H10, C5-H6, C3-H28, C3-H28', C12-H10)

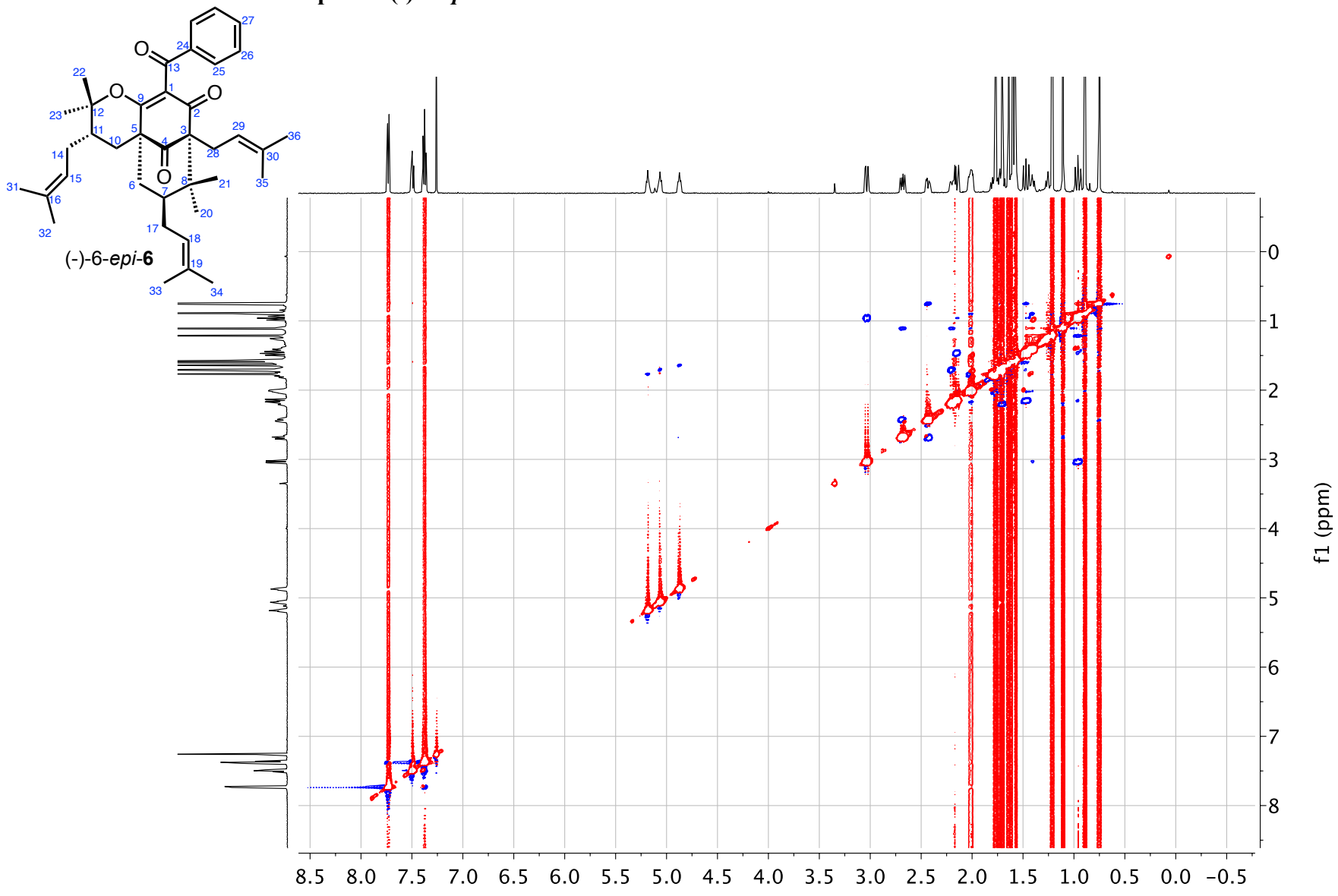


HMBC Correlations (C29-H36, C29-H35, C15-H32, C15-H31, C18-H34, C18-H33, C19-H34, C19-H33, C16-H32, C16-H31, C30-H36)

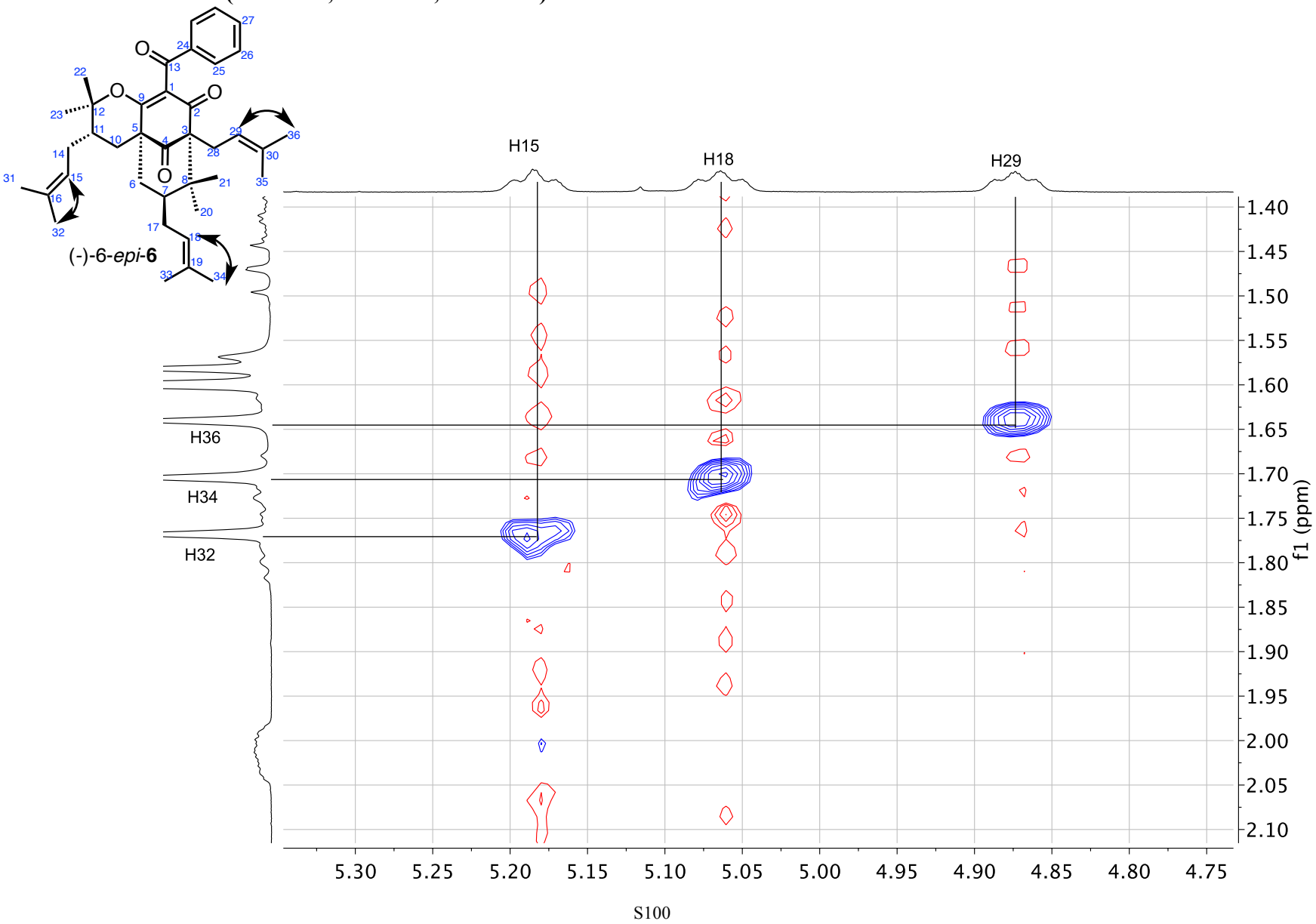




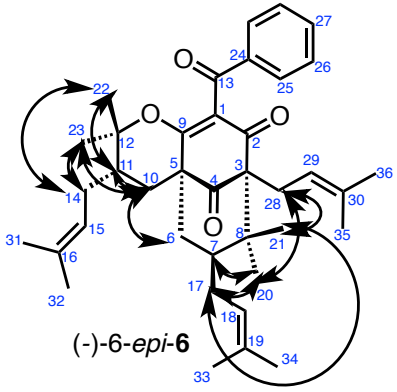
NOESY Correlations for Compound (-)-6-*epi*-6

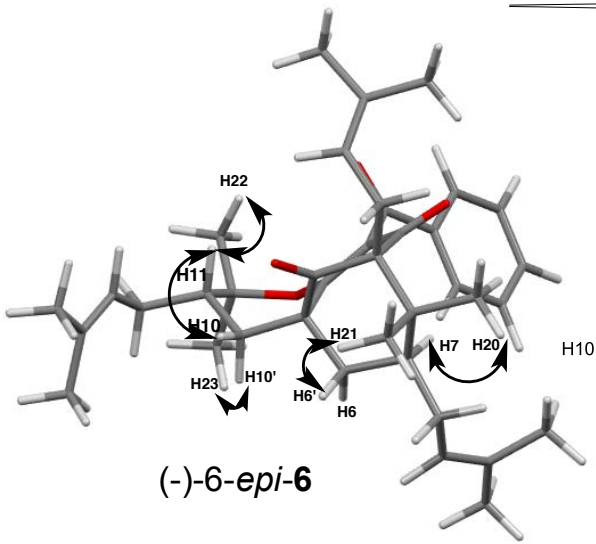


NOESY Correlations (H36-H29, H34-H18, H32-H15)

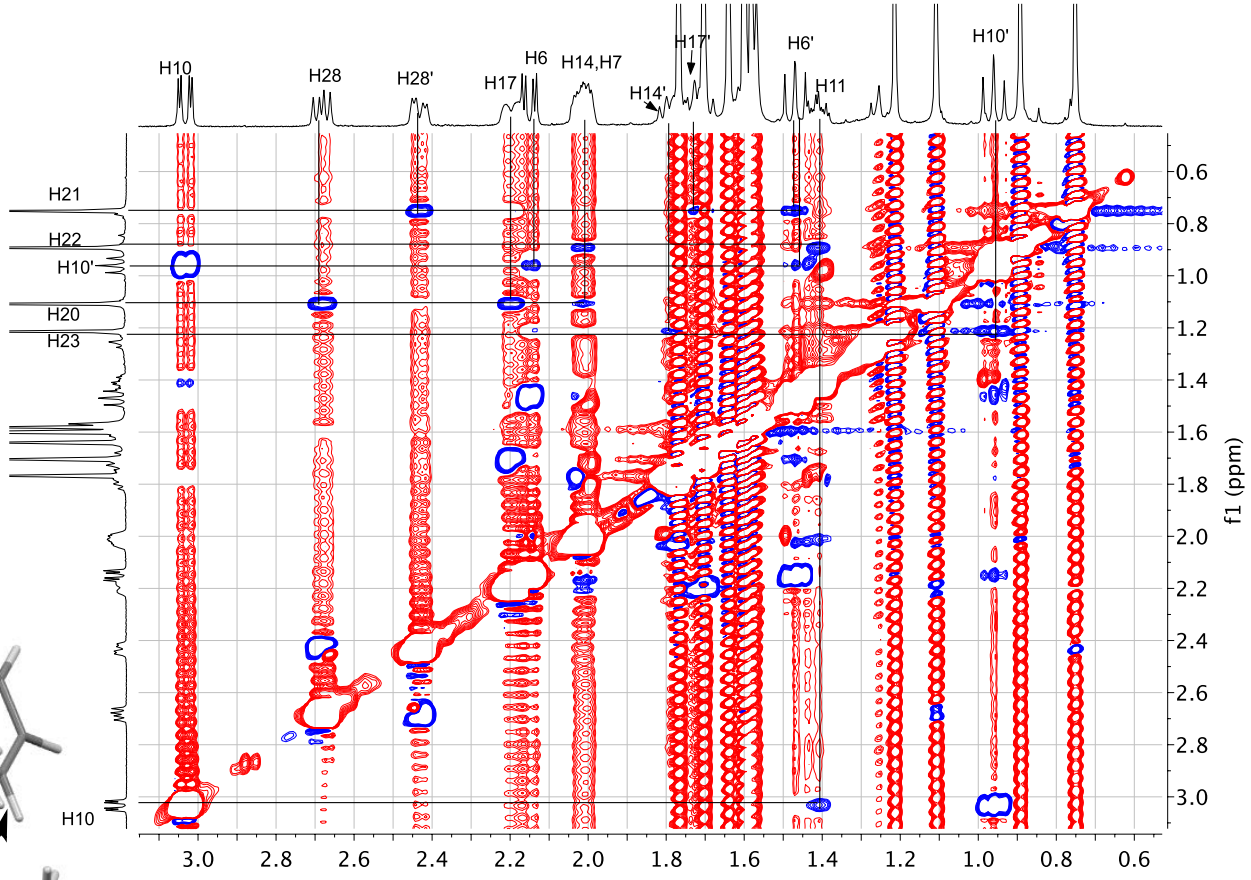


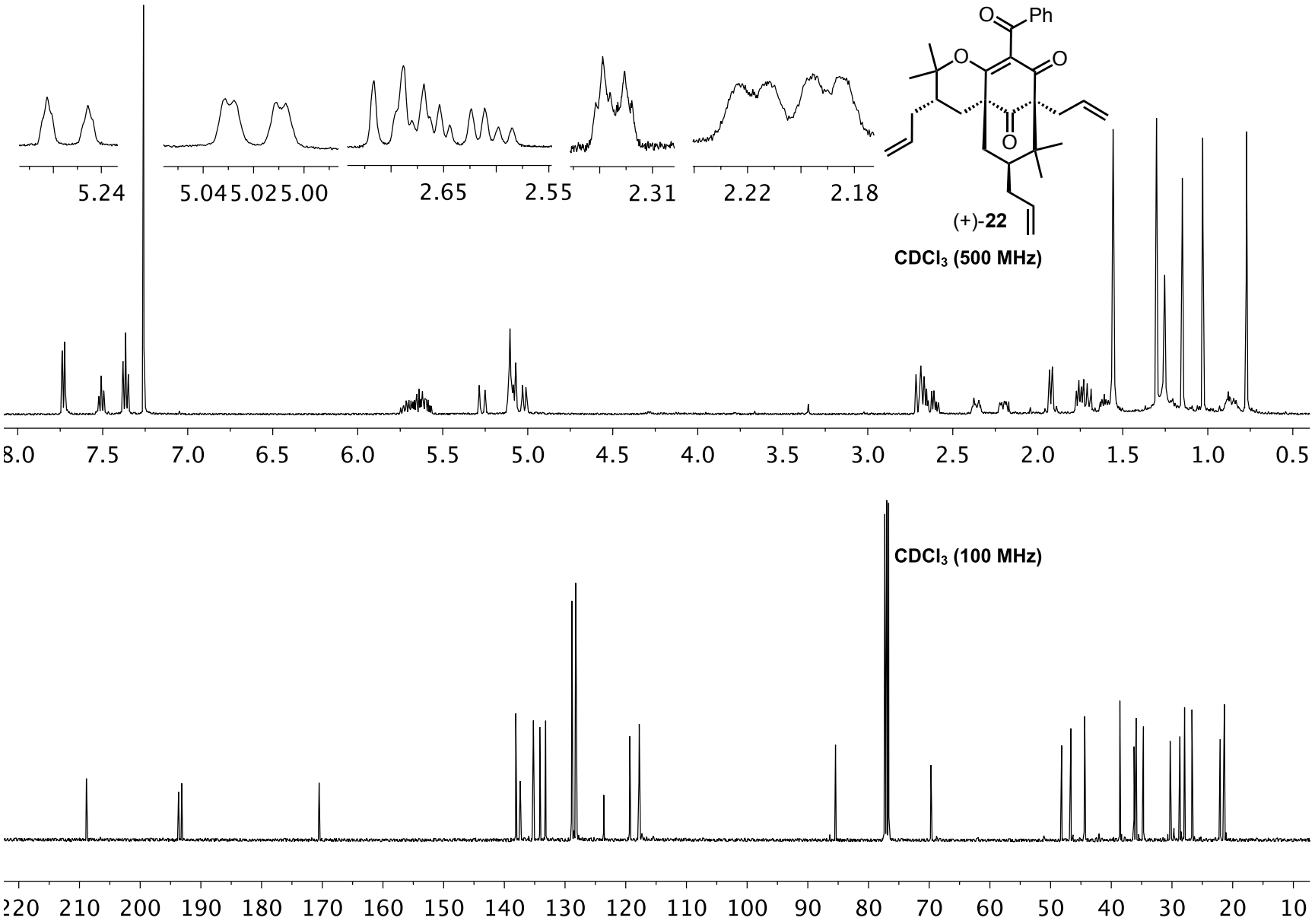
NOESY Correlations (H21-H28', H21-H17', H21-H6', H22-H11 (indicates orientation of H22), H22-H14, H10'-H6, H10'-H6', H20-H28, H20-H17, H20-H7 (directionality of H20), H23-H14', H23-H10' (indicates orientation of H10'), H10-H11 (indicates orientation of H10).

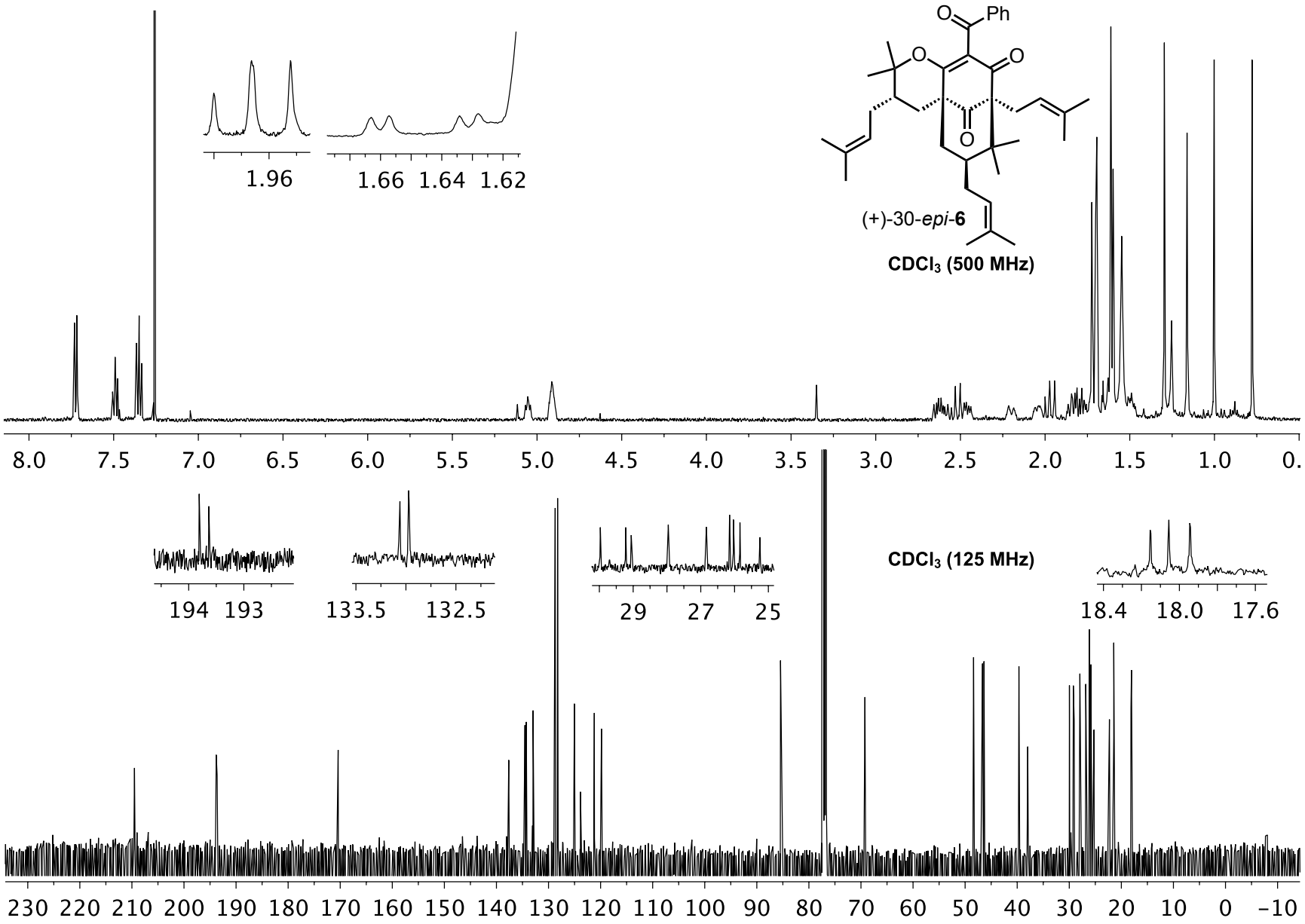


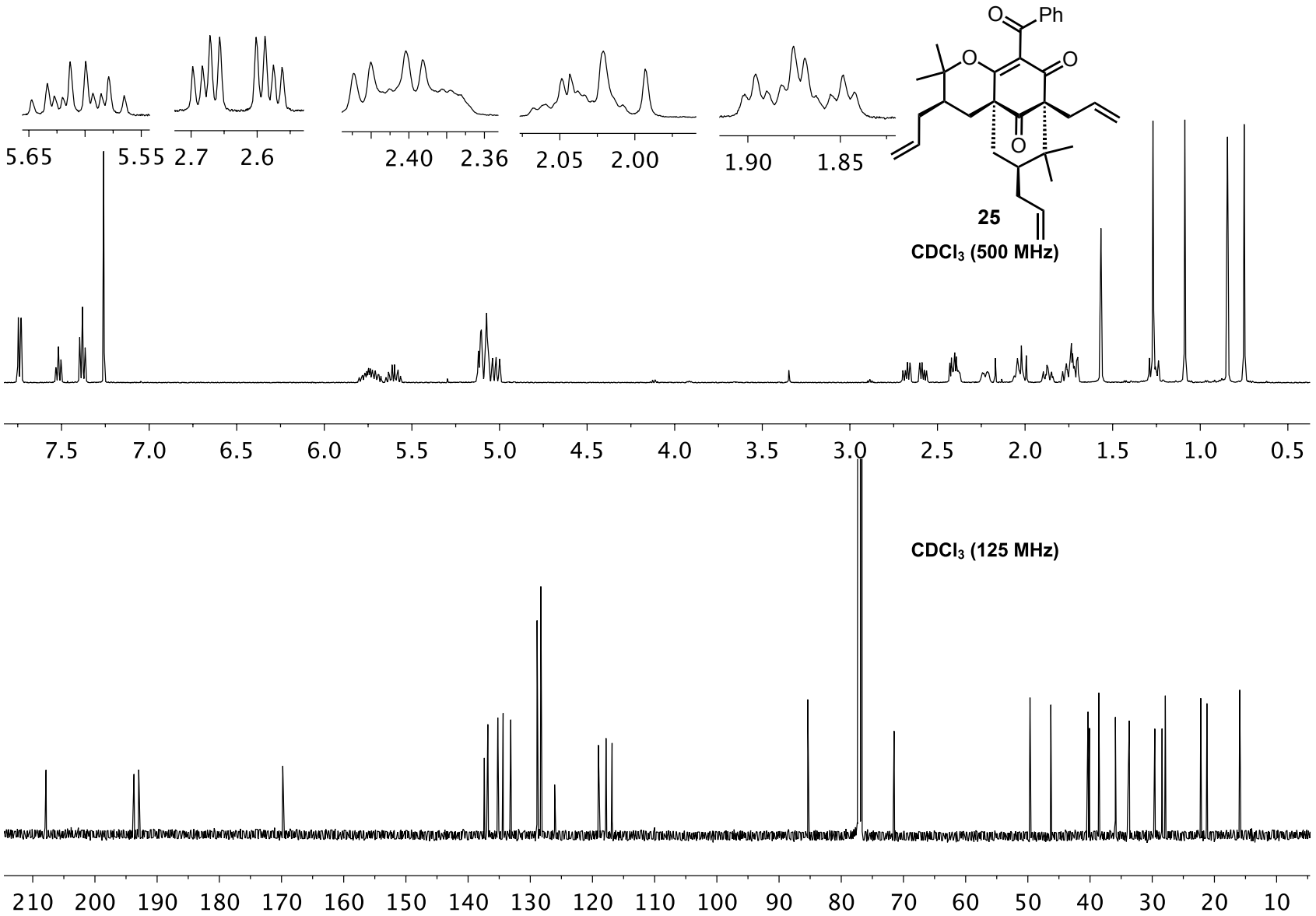


H22-H11, H23-H10', H10-H11, H20-H7, H21-H6'
Key Diagnostic Evidence: H11 does not come into proximity with H6.

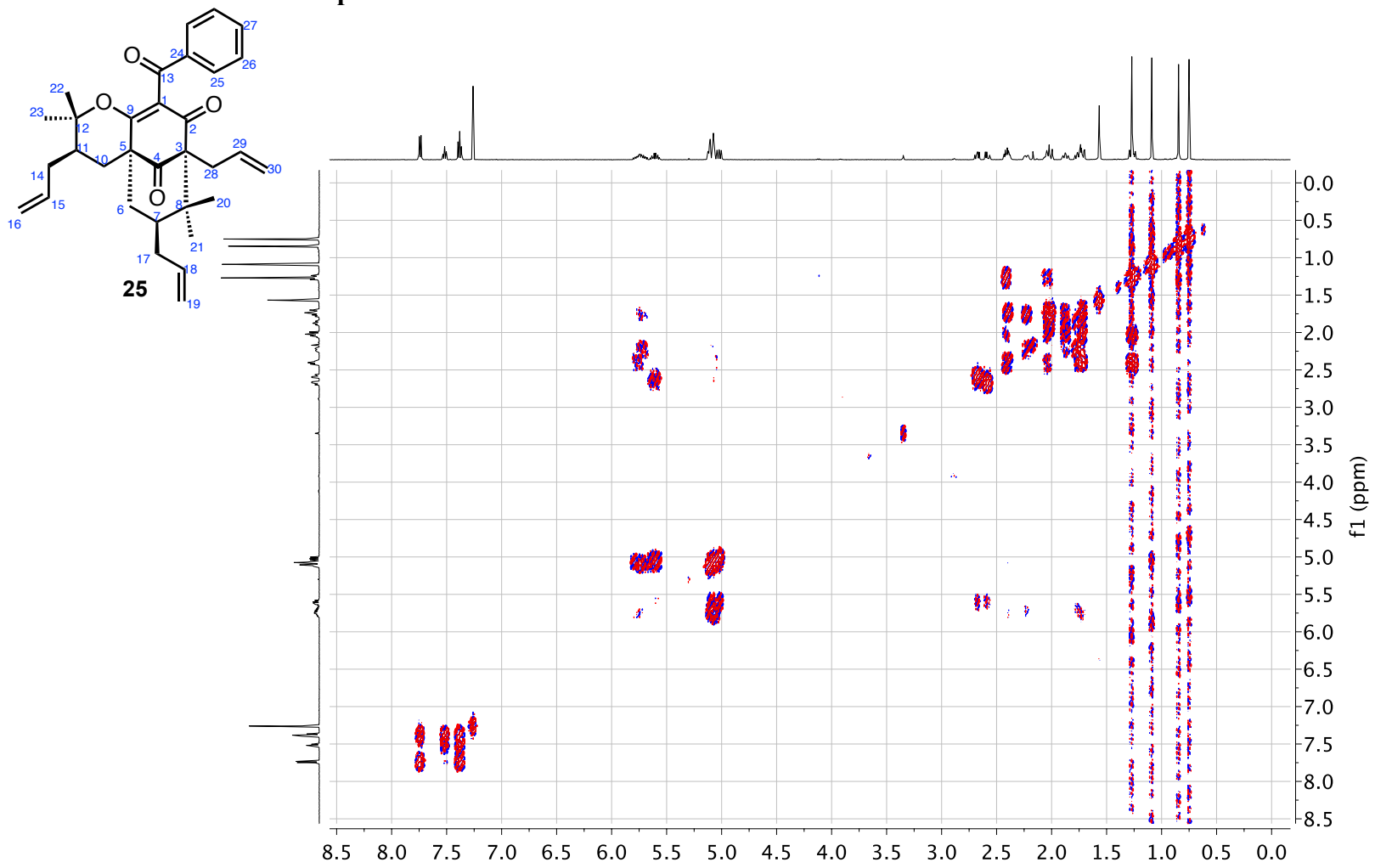



5.24
5.045.025.00
2.65
2.55
2.31
2.22
2.18
O
Ph
O
O
O
(+)-22
CDCl3 (500 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
CDCl3 (100 MHz)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

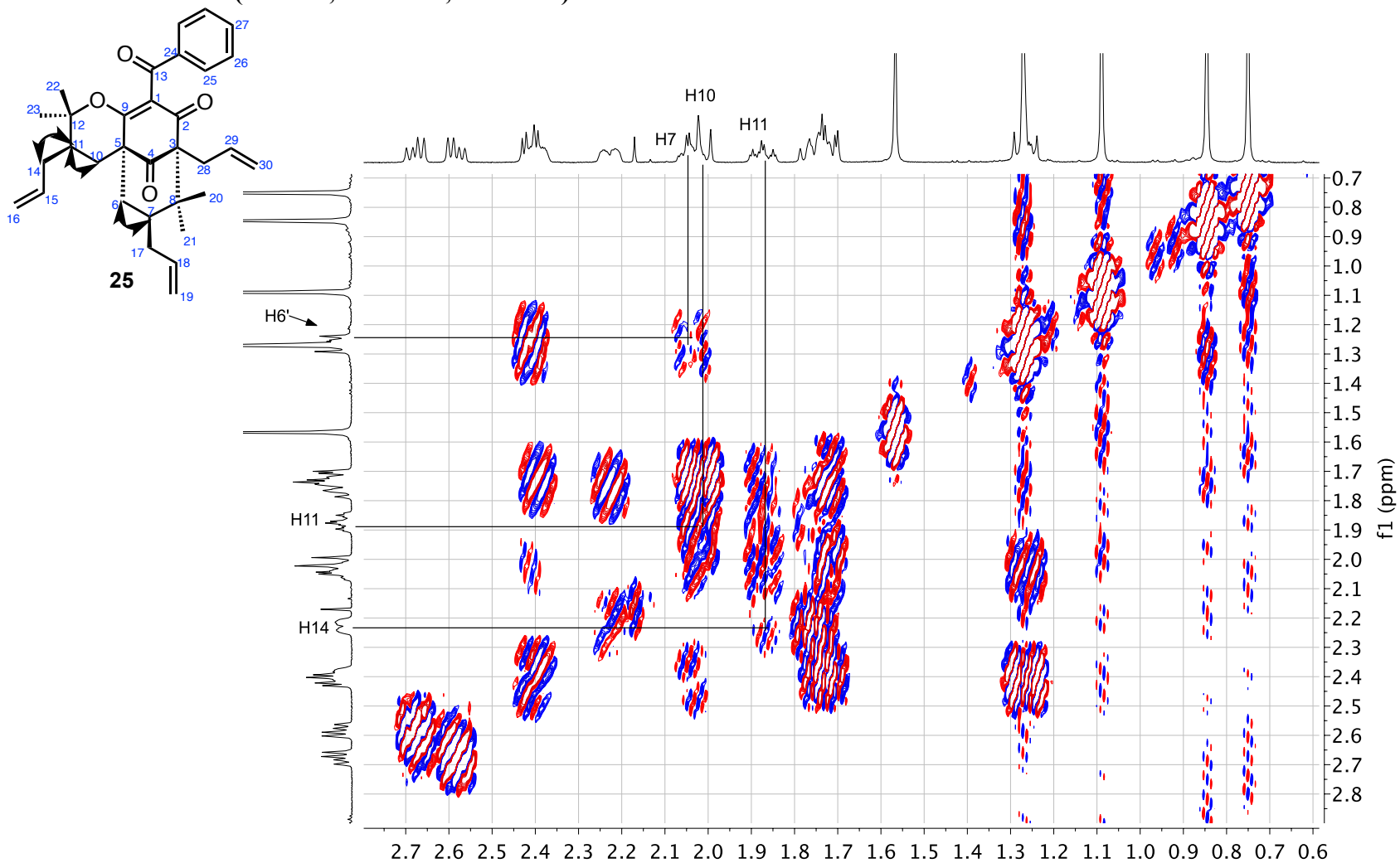

1.96
1.66 1.64 1.62
O
Ph
O
O
O
(+)-30-*epi*-**6**
$CDCl_3$ (500 MHz)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.
194 193
133.5 132.5
29 27 25
$CDCl_3$ (125 MHz)
18.4 18.0 17.6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


5.65
5.55
2.7
2.6
2.40
2.36
2.05
2.00
1.90
1.85
O
Ph
O
O
O
25
CDCl3 (500 MHz)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
CDCl3 (125 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

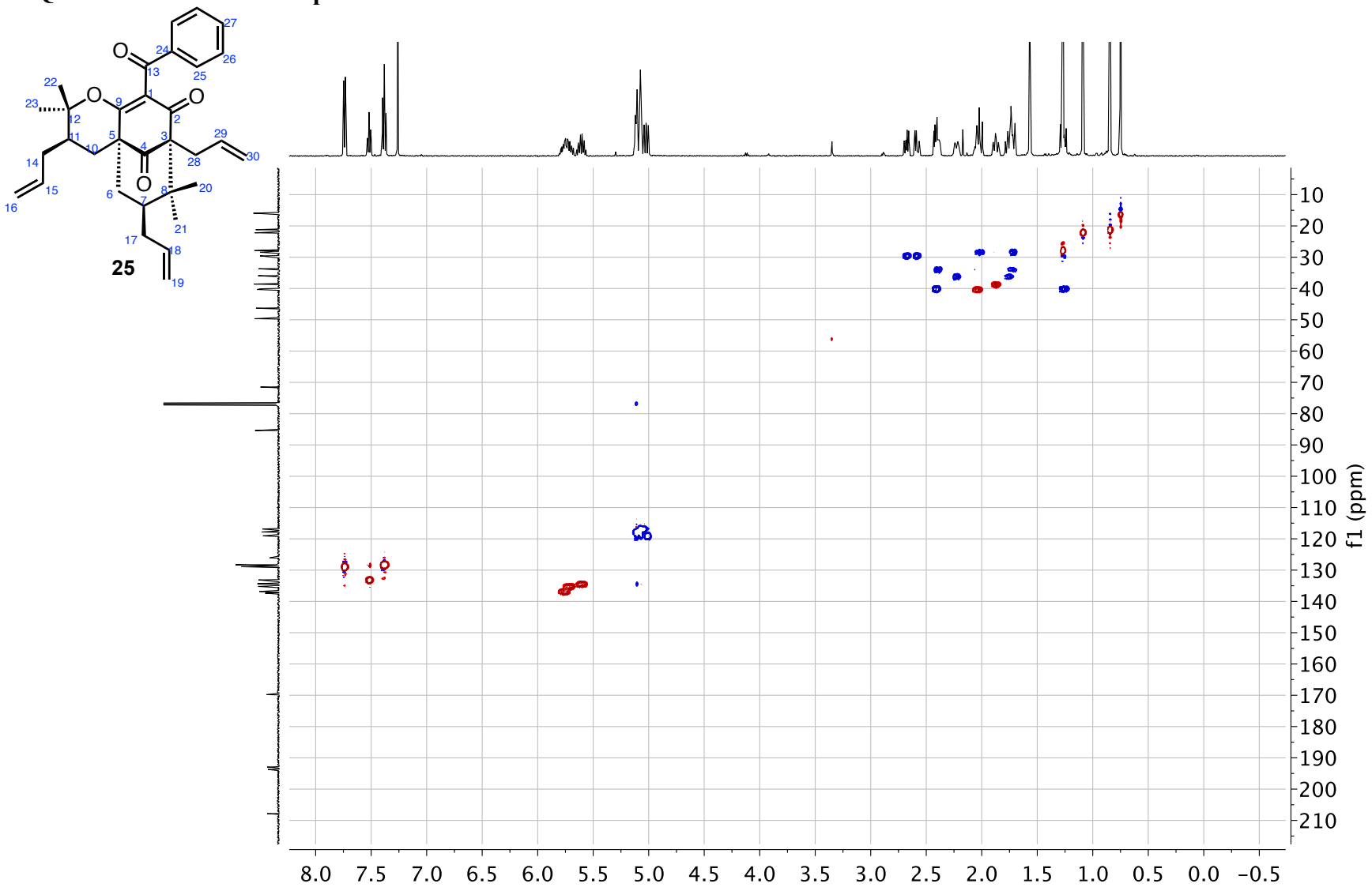
COSY Correlations for Compound 25



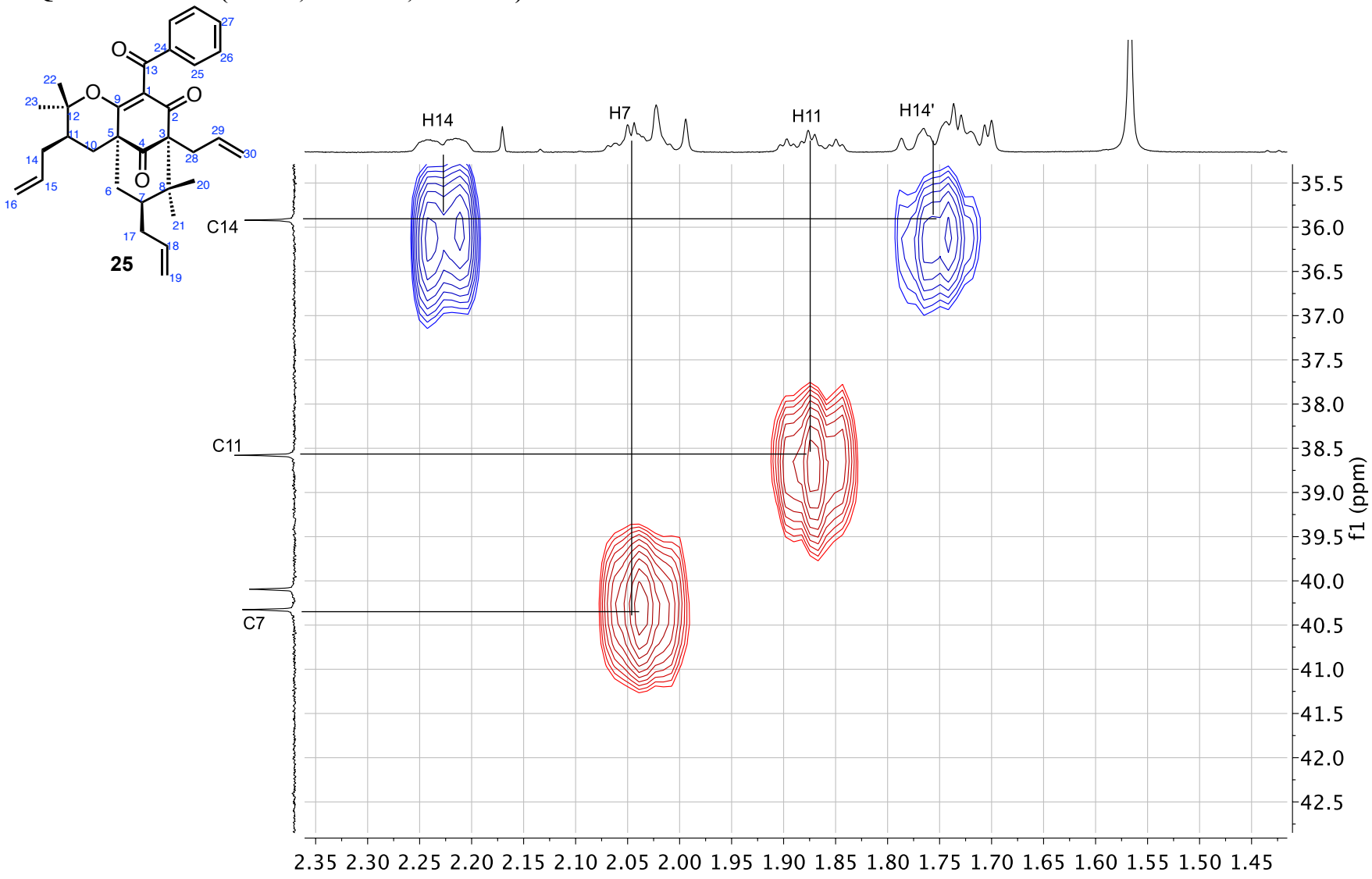
COSY Correlations (H6'-H7, H11-H10, H14-H11)



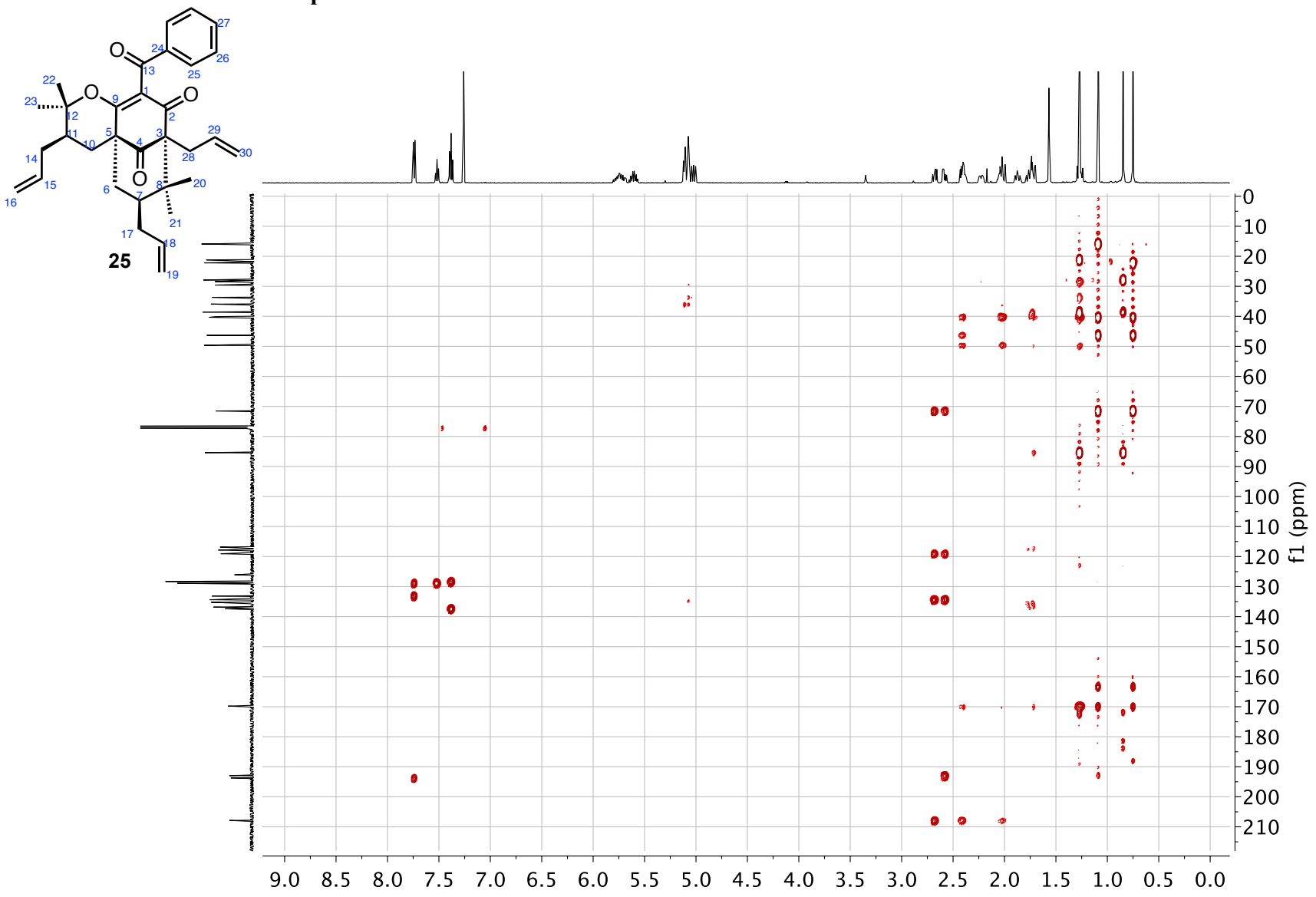
HSQC Correlations for Compound 25



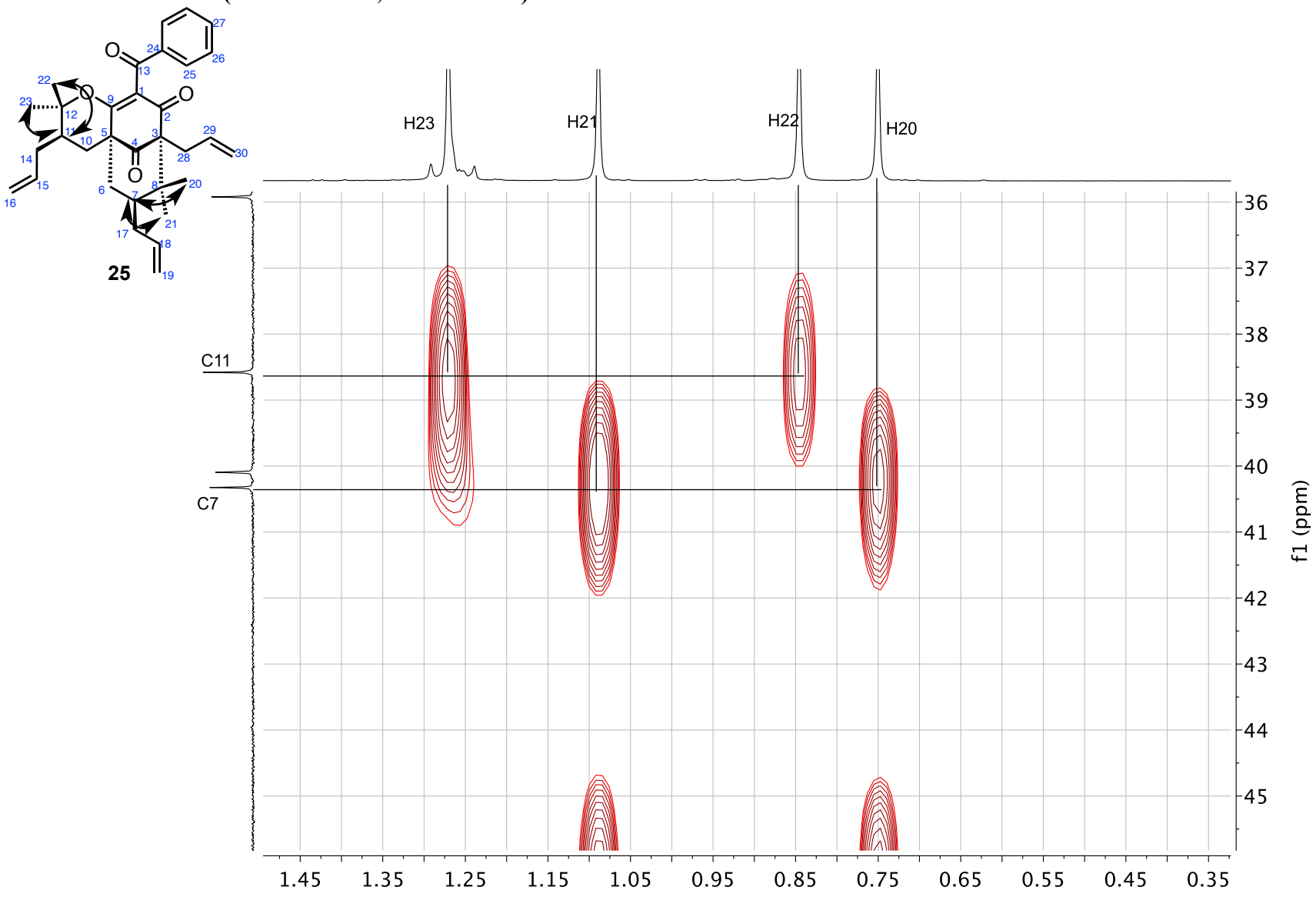
HSQC Correlations (C7-H7, C11-H11, C14-H14)



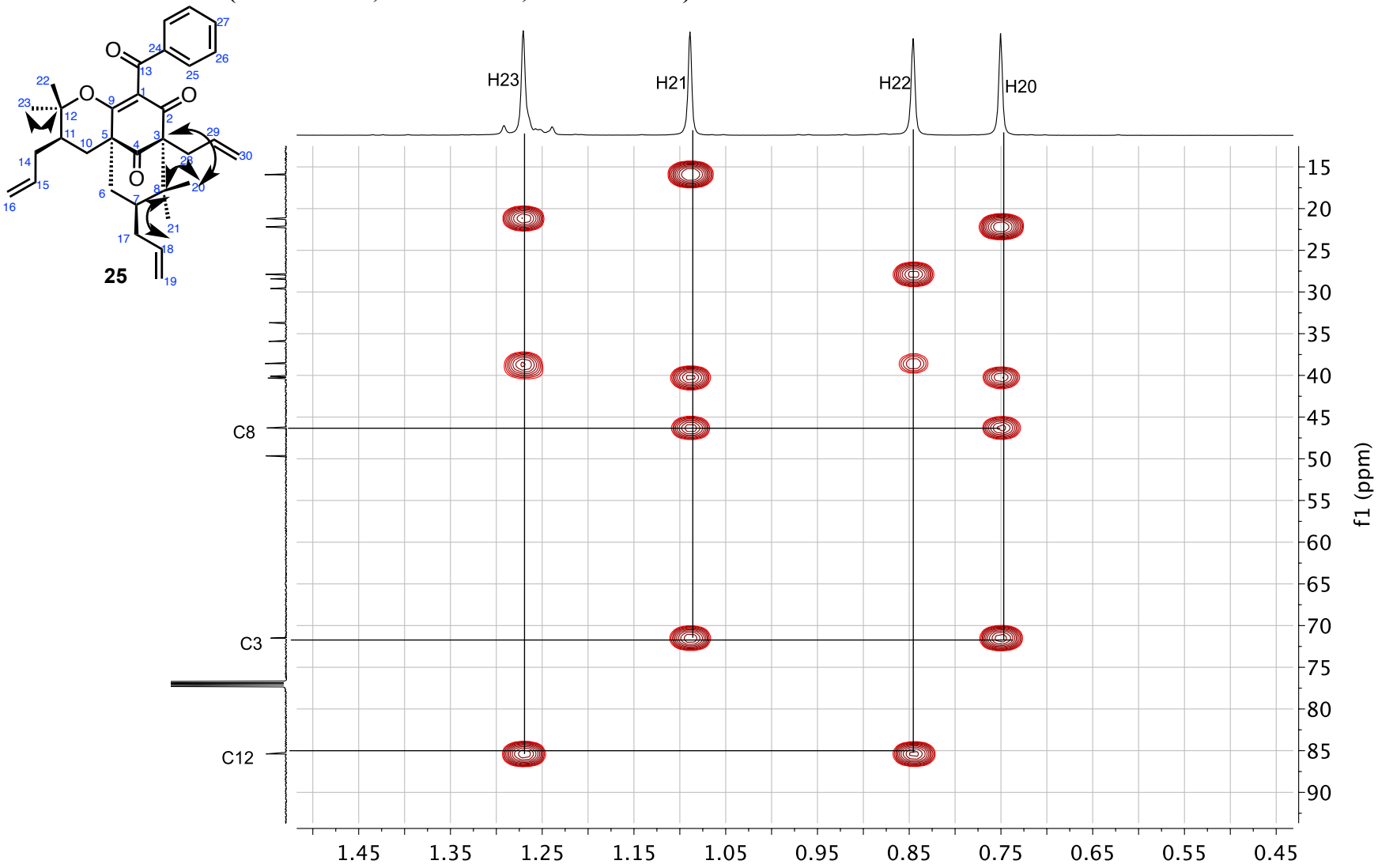
HMBC Correlations for Compound 25



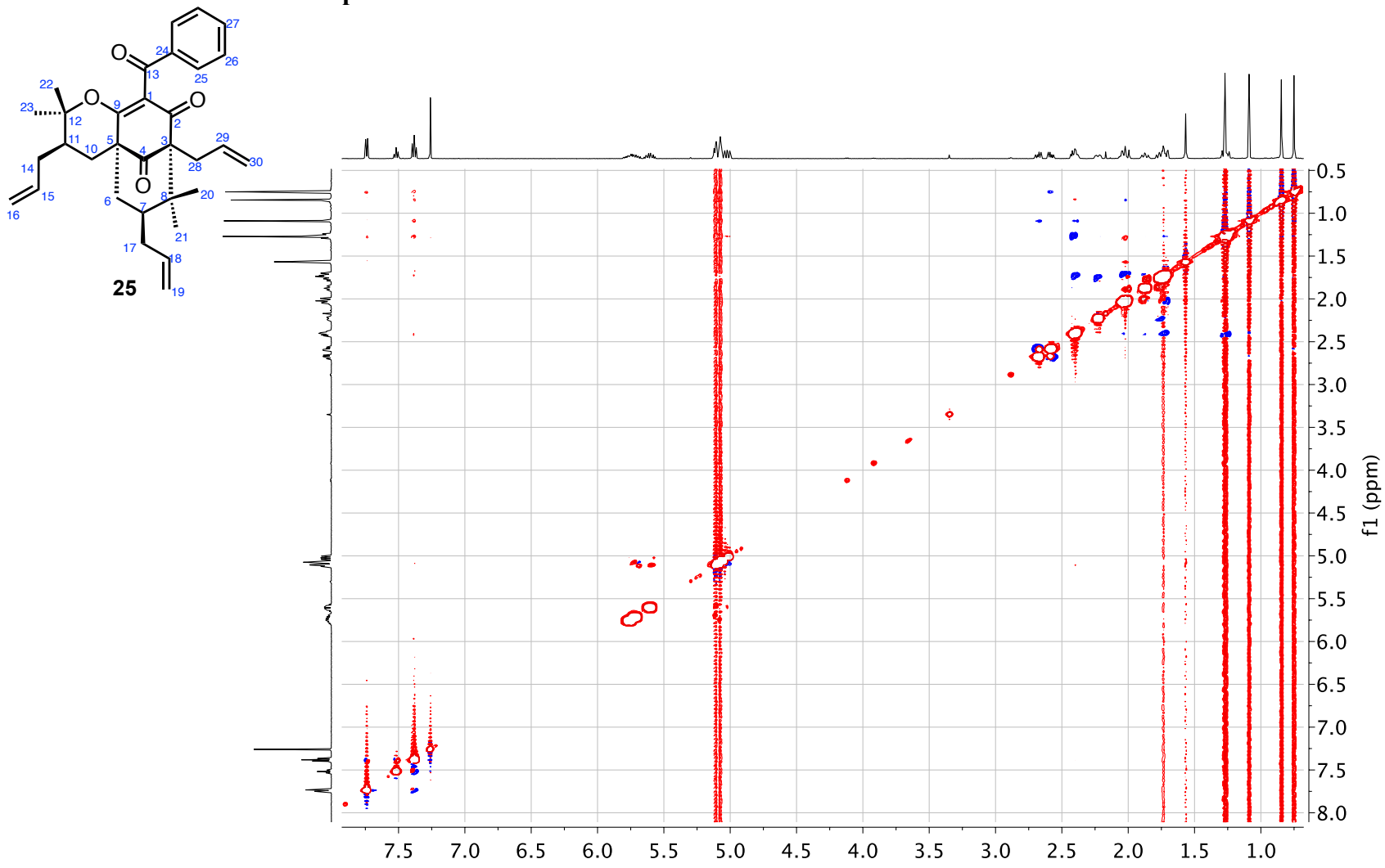
HMBC Correlations (C11-H23/H22, C7-H21/H20)



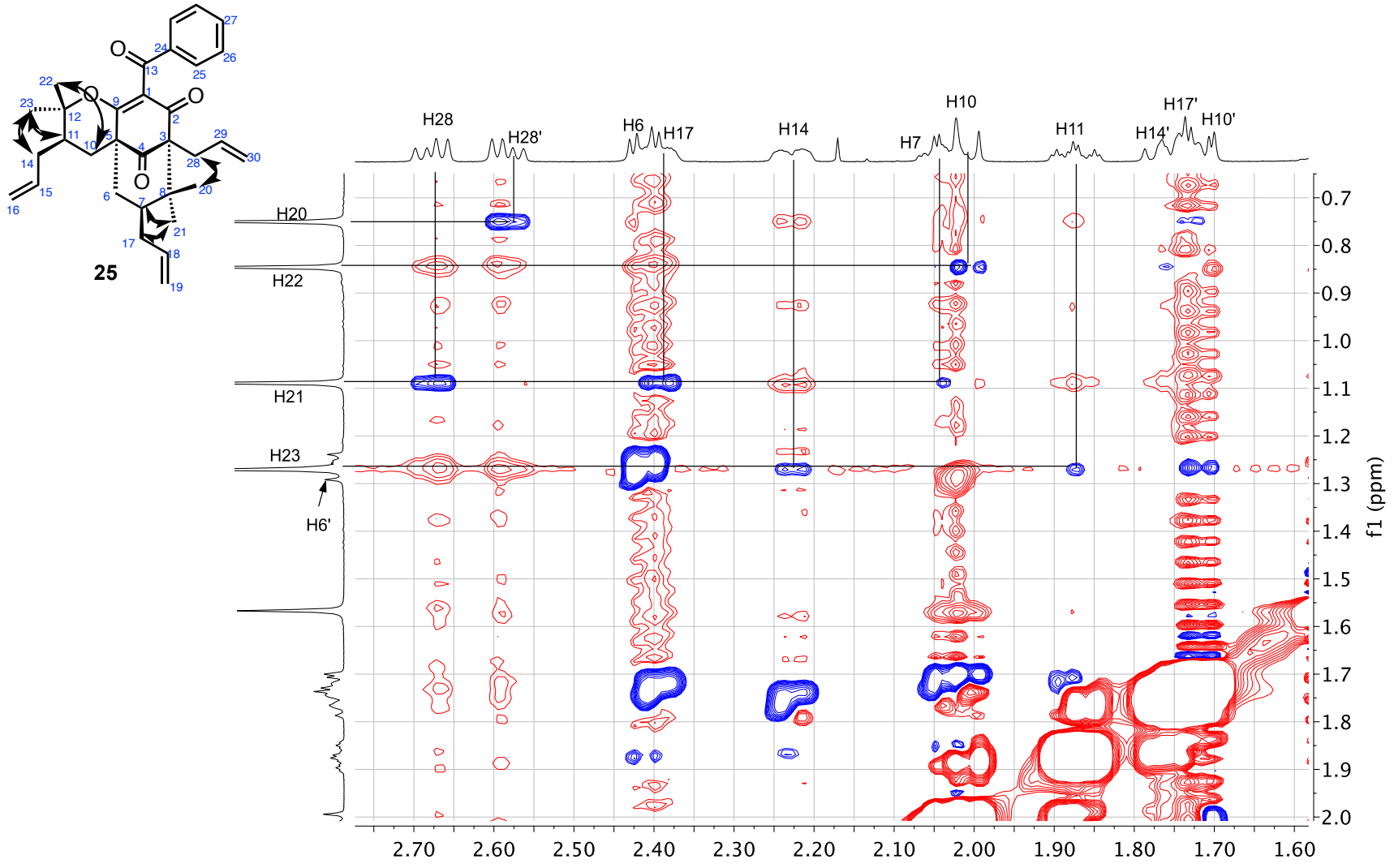
HMBC Correlations (C8-H20/H21, C3-H20/H21, C12-H23/H22)



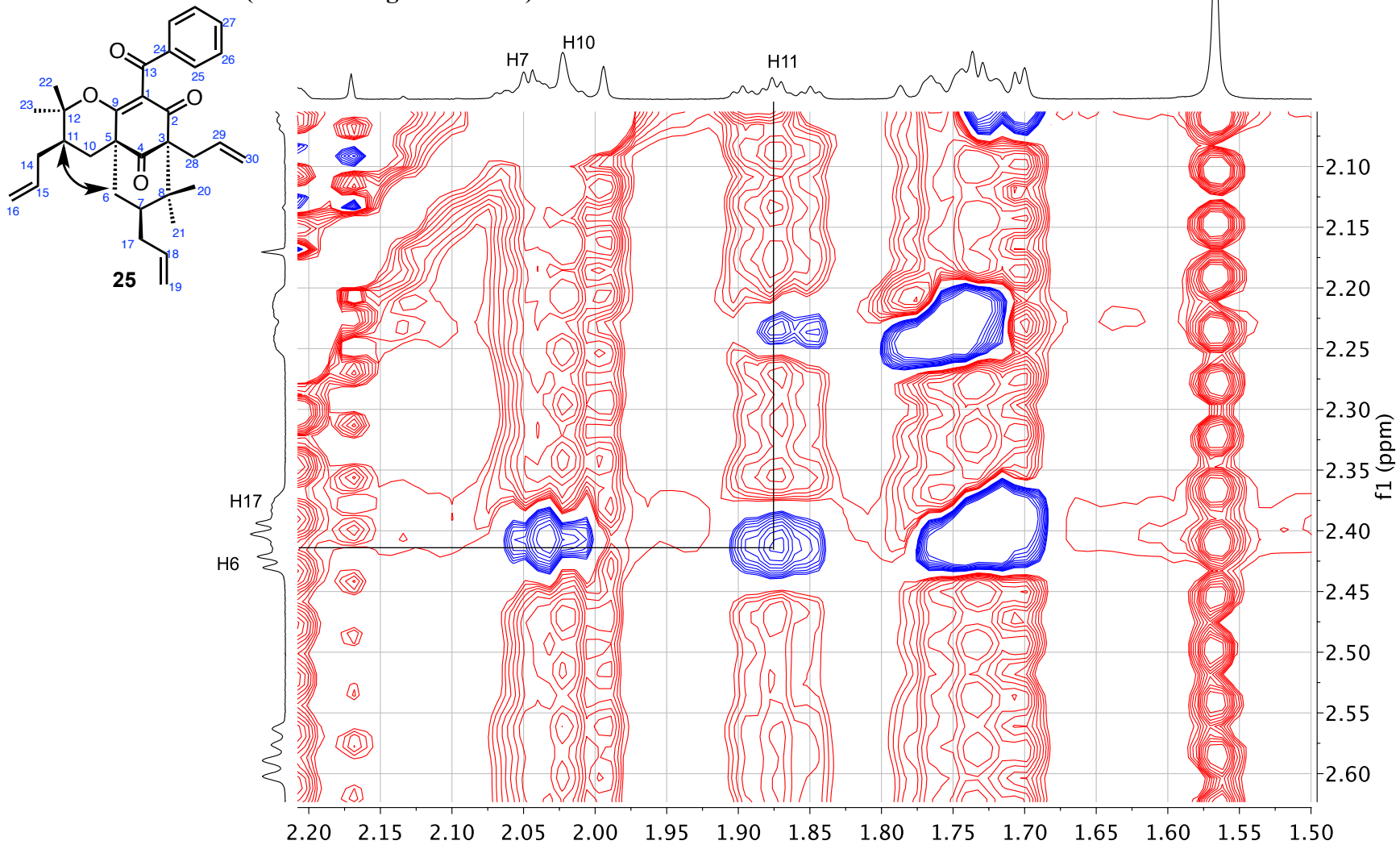
NOESY Correlations for Compound 25

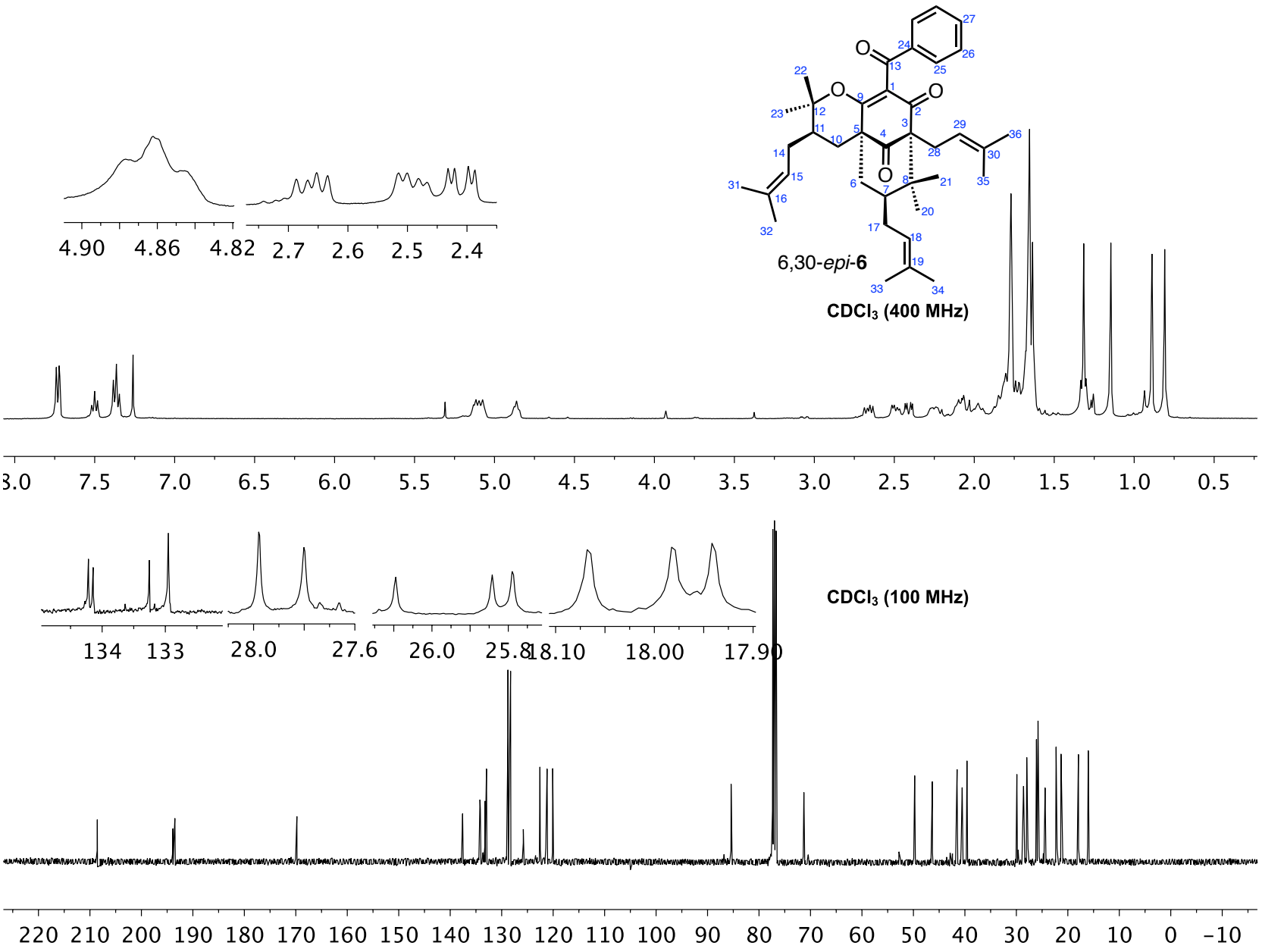


NOESY Correlations (H20-H28', H22-H10, H21-H28, H21-H17, H21-H7 (indicates orientation of H21), H23-H14, H23-H11 (indicates orientation of H23)

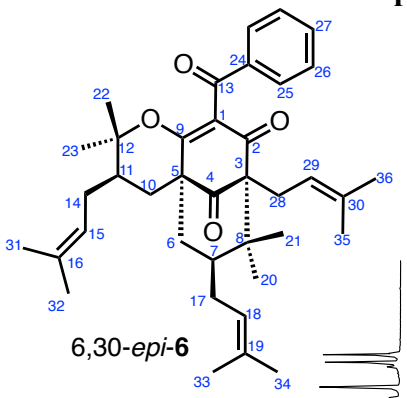


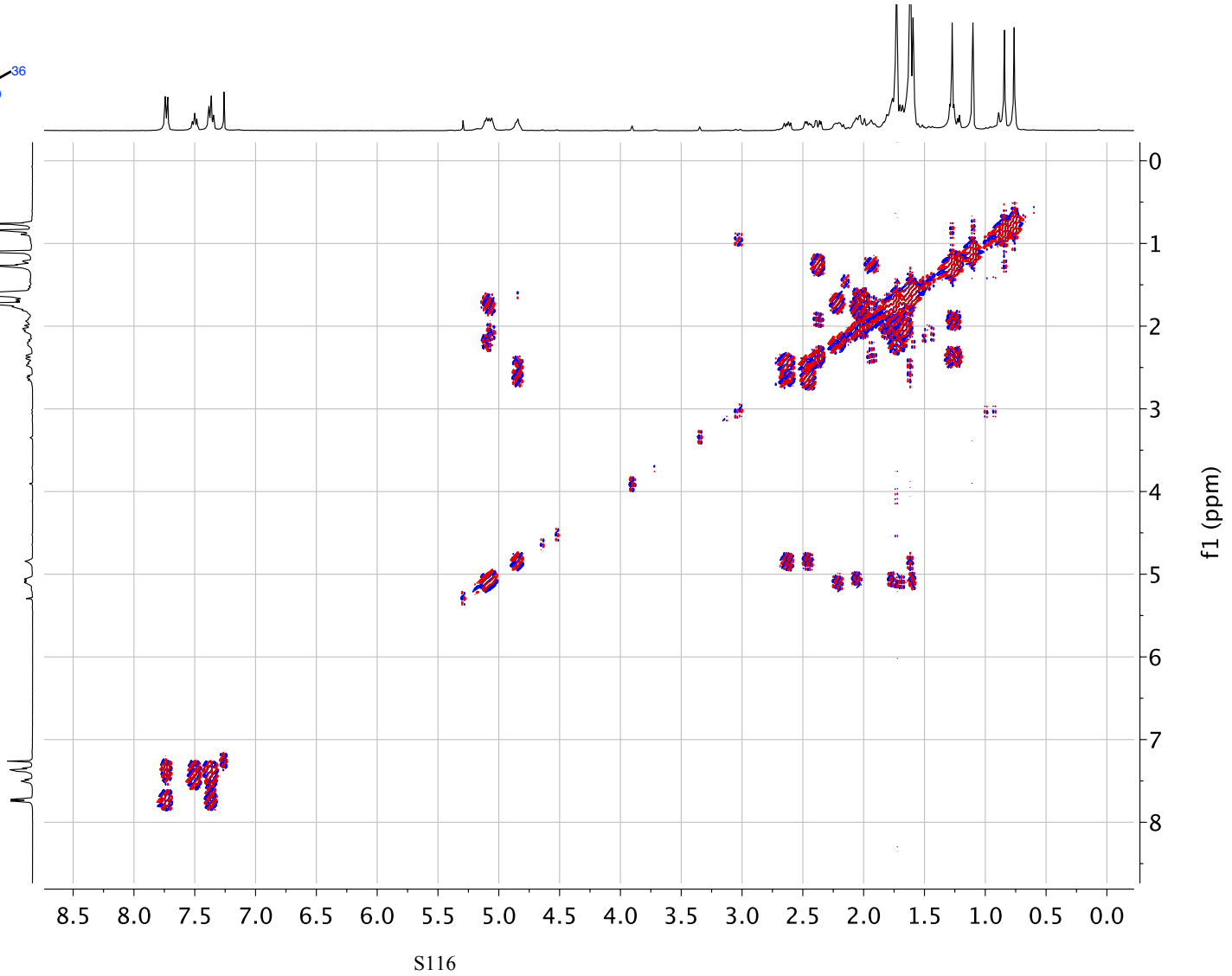
NOESY Correlations (H6-H11 Diagnostic NOE)



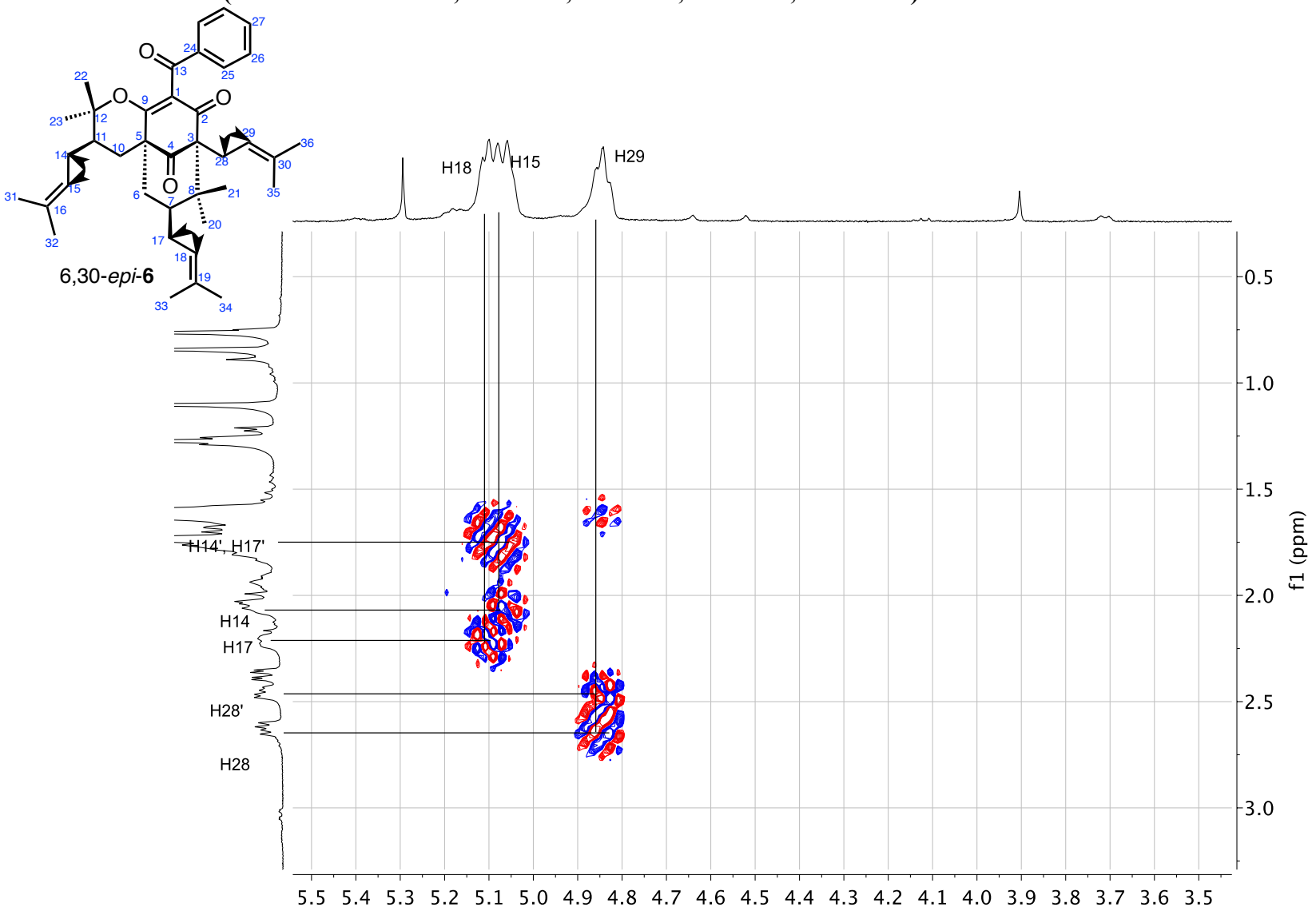

6,30-epi-6
CDCl3 (400 MHz)
CDCl3 (100 MHz)

COSY Correlations for Compound 6,30-*epi*-6

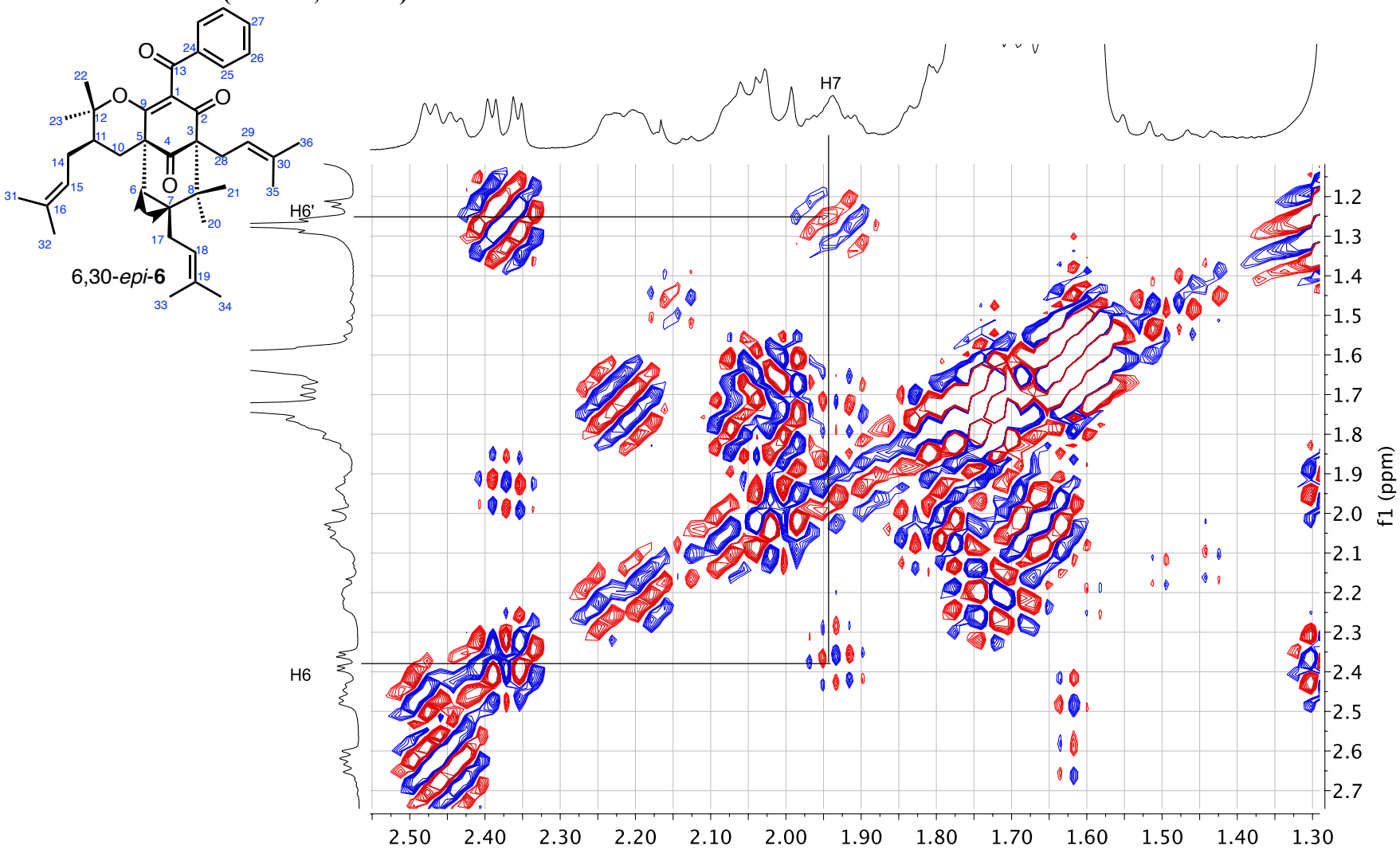




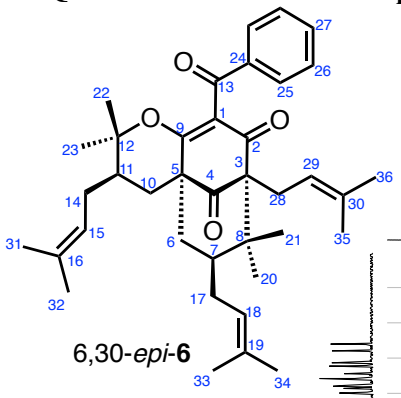
COSY Correlations (H14'/H17'-H15/H18, H14-H15, H17-H18, H28-H29, H28'-H29)

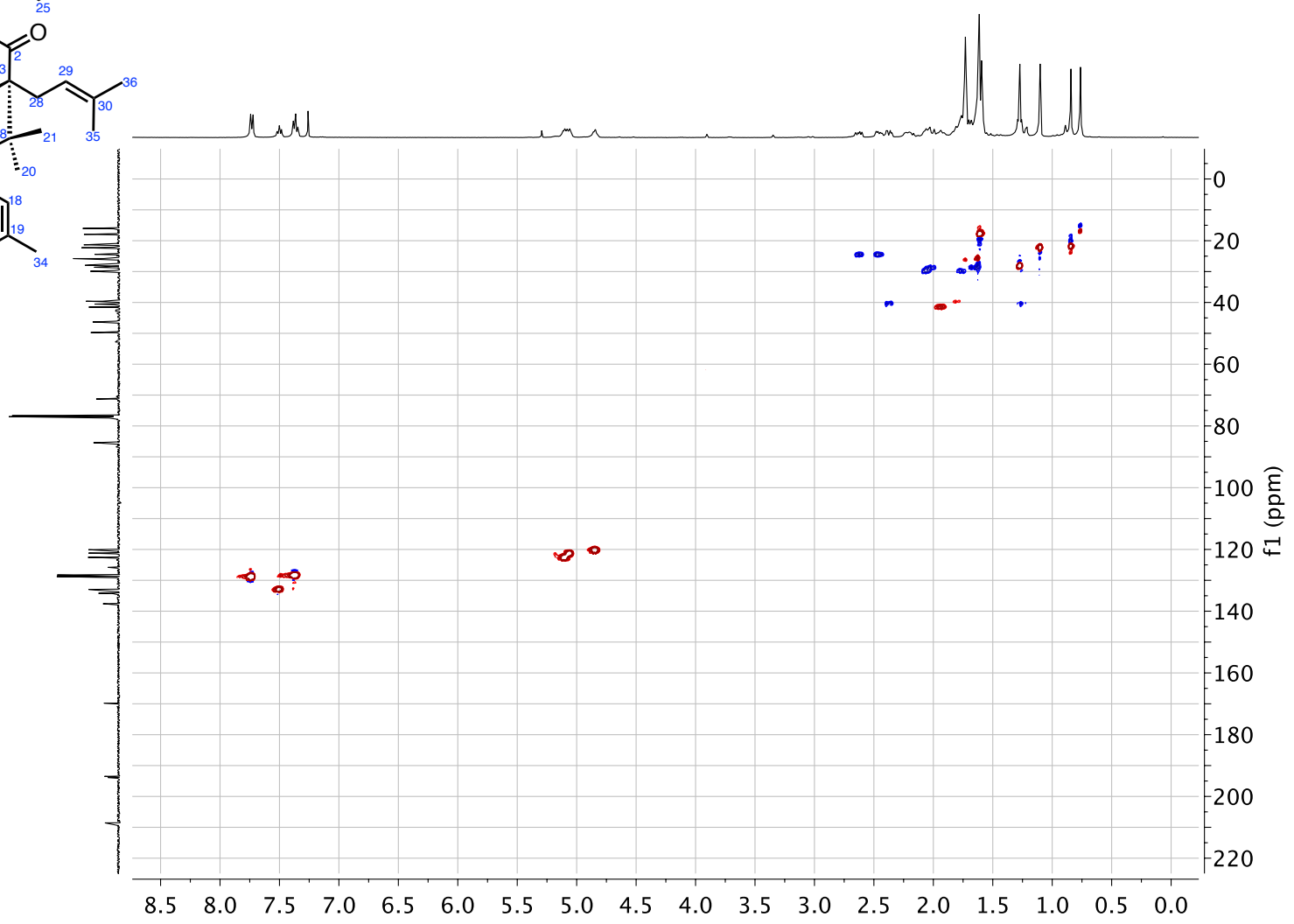


COSY Correlations (H6'-H7, H6-H7)

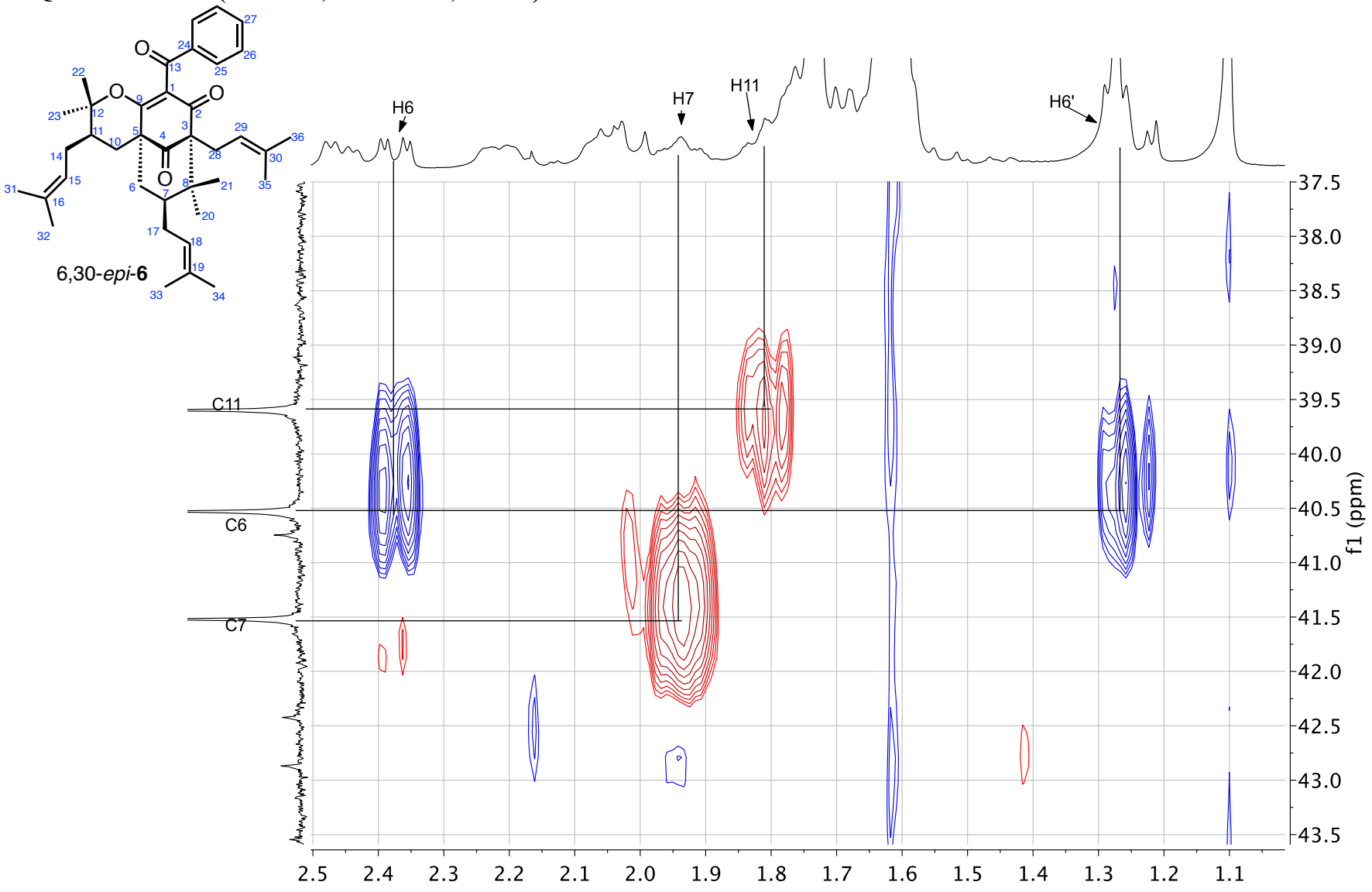


HSQC Correlations for Compound 6,30-*epi*-6

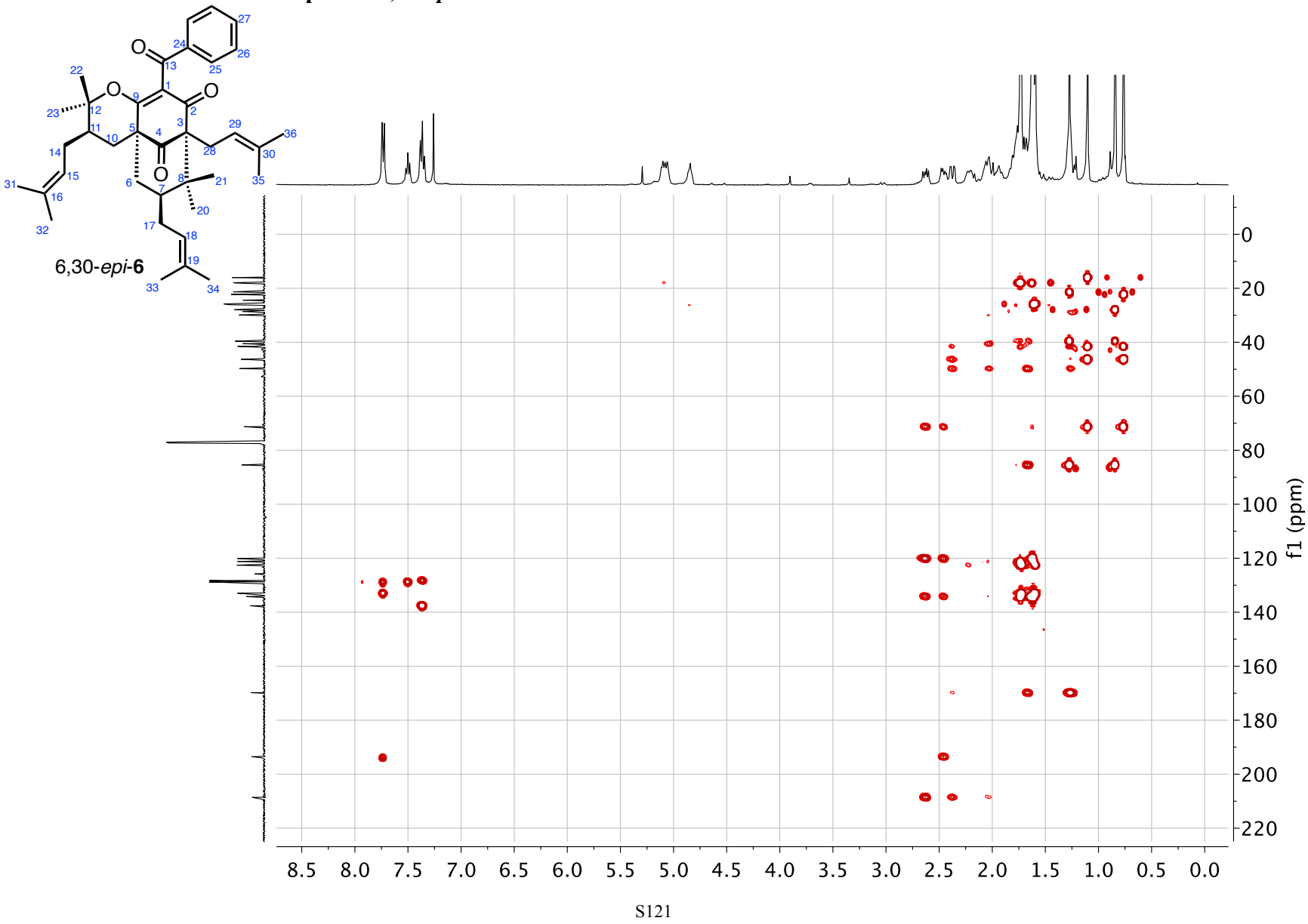




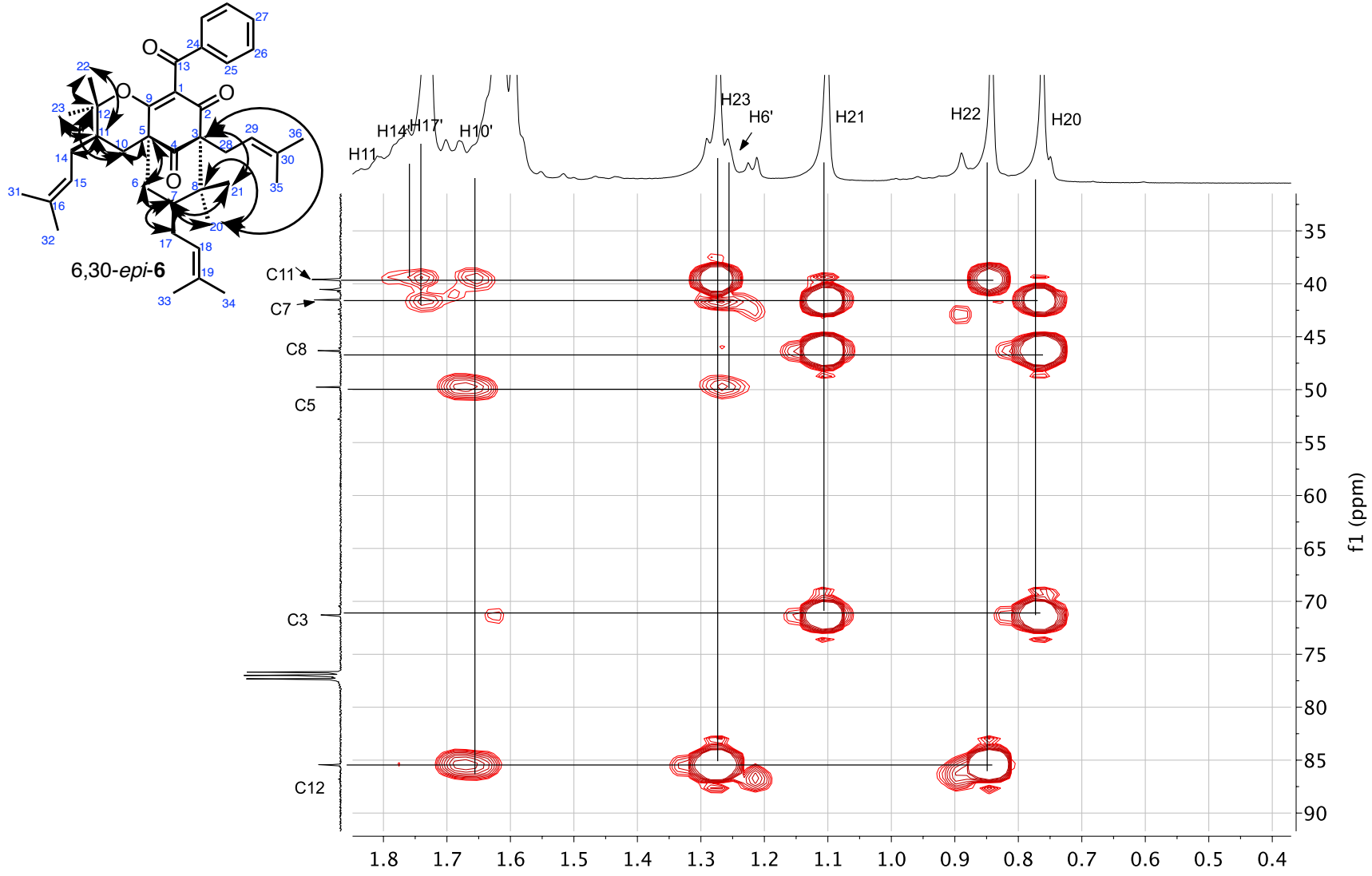
HSQC Correlations (C11-H11, C6-H6/H6', C7-H7)



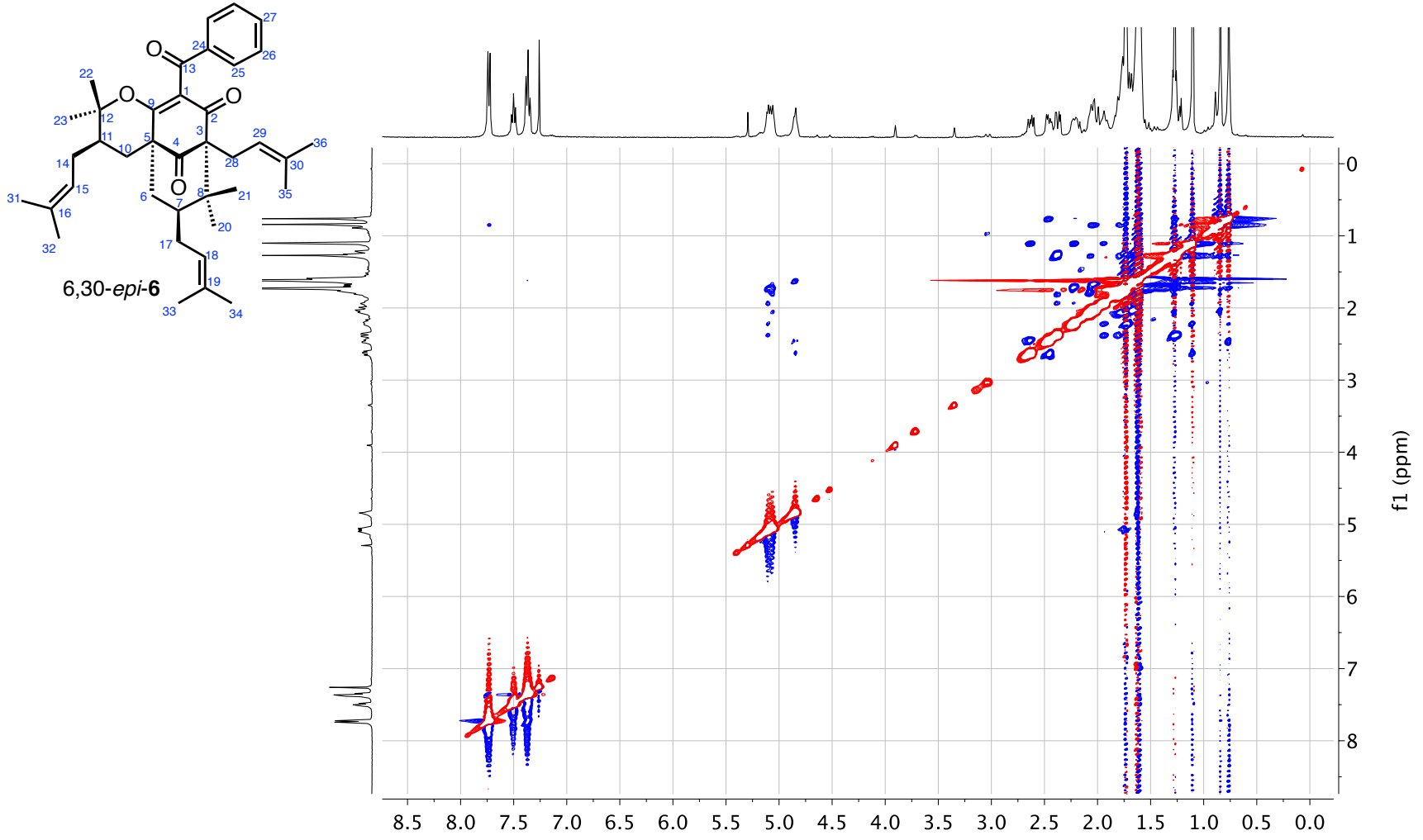
HMBC Correlations for Compound 6,30-*epi*-6



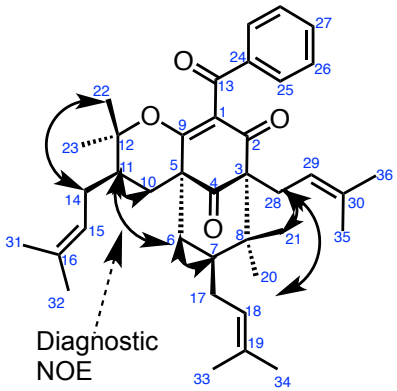
HMBC Correlations (C11-H14', C11-H10', C11-H23, C11-H22, C7-H17', C7-H6', C7-H21, C7-H20, C8-H21, C8-H20, C5-H10', C5-H6', C3-H21, C3-H20, C12-H10', C12-H23, C12-H22)



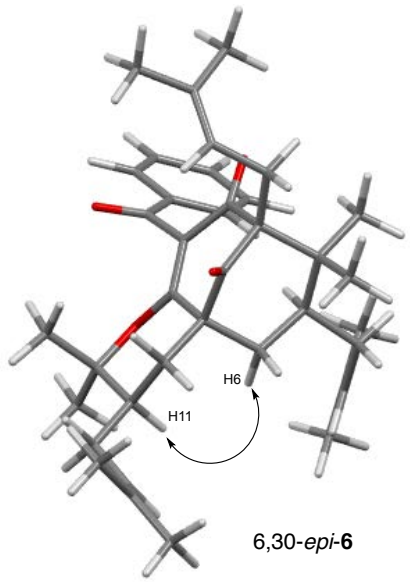
NOESY Correlations for Compound 6,30-*epi*-6



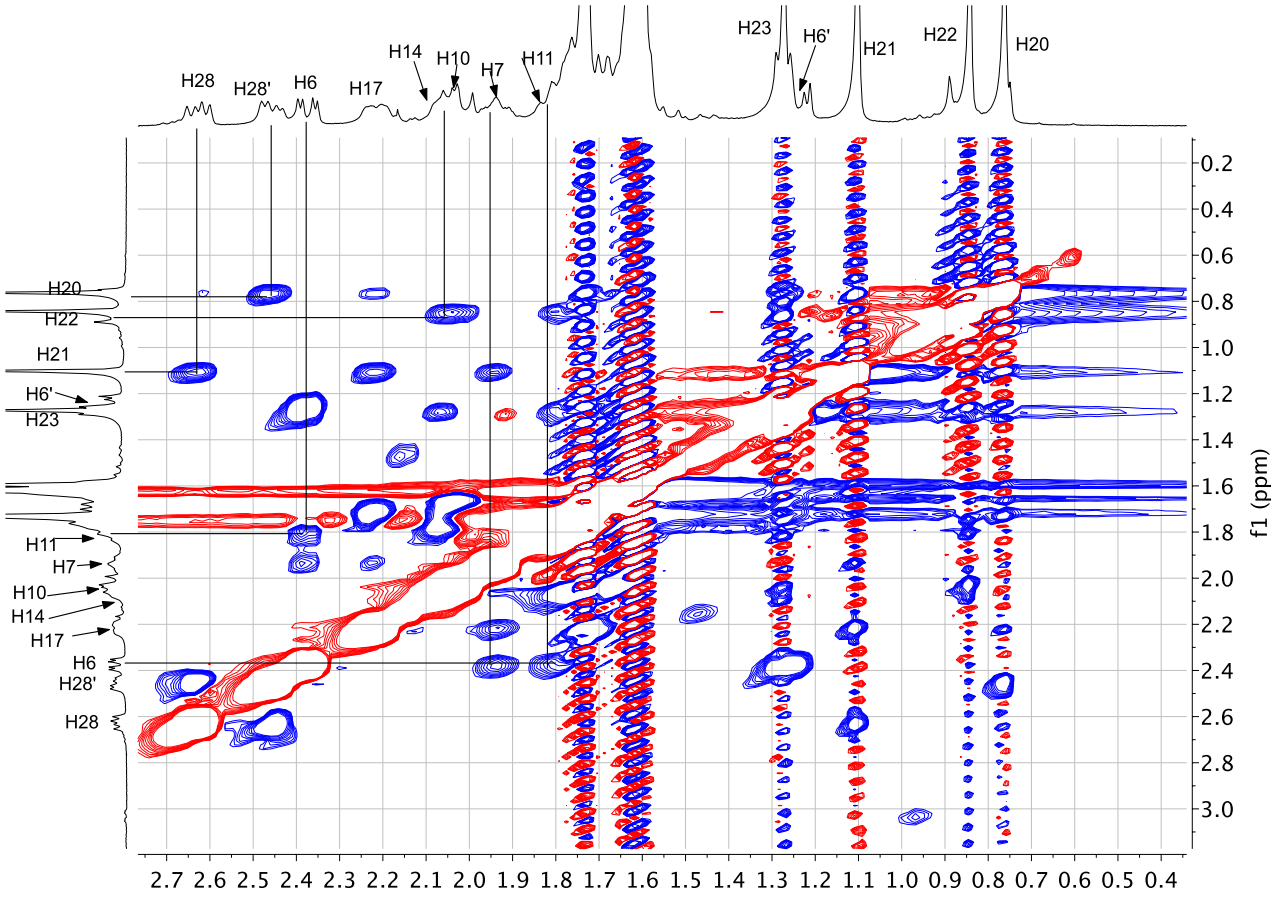
NOESY Correlations (H20-H28', H22-H14, H21-H28, H11-H6 Diagnostic NOE, H6-H11 Diagnostic NOE, H6-H7)

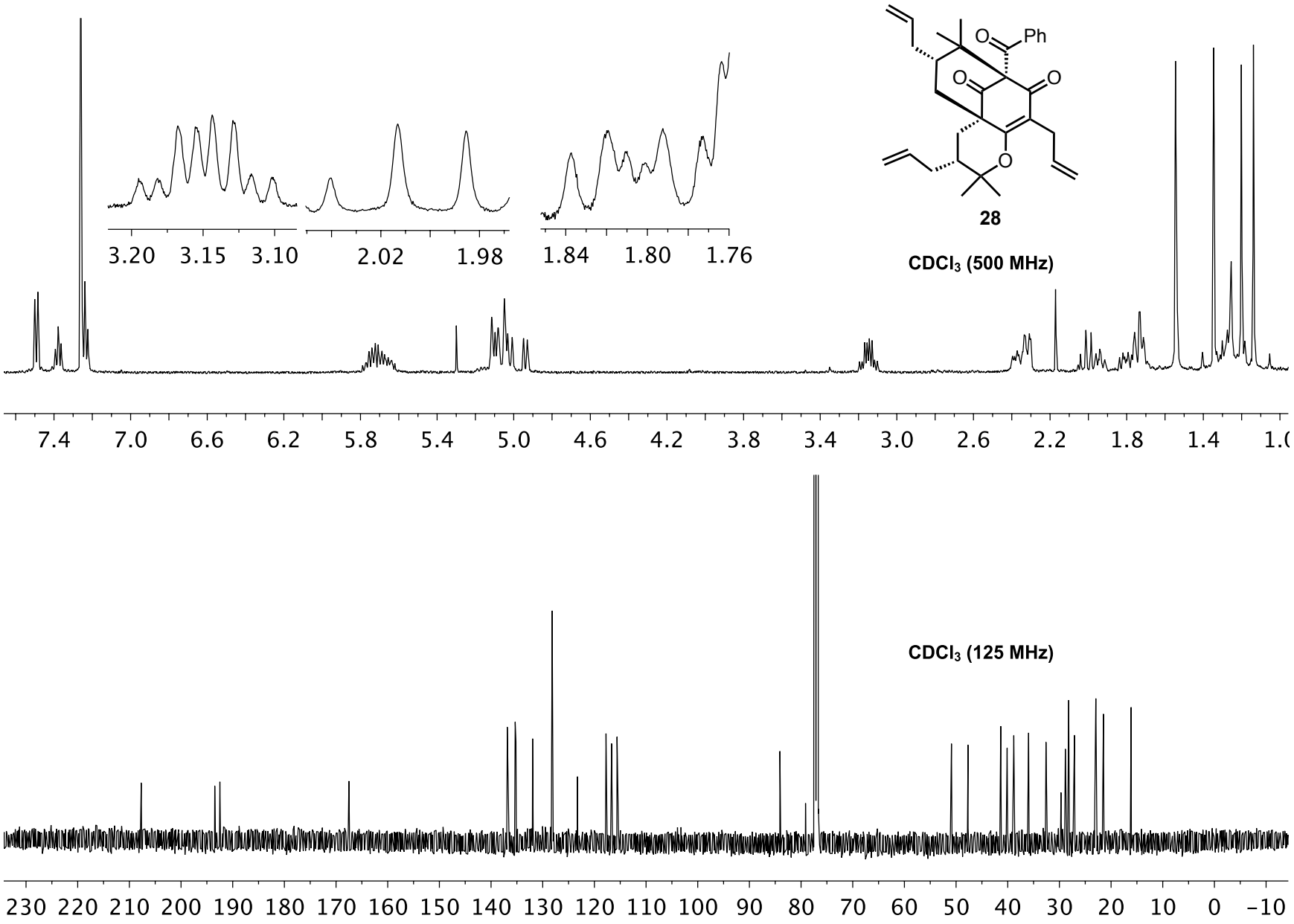


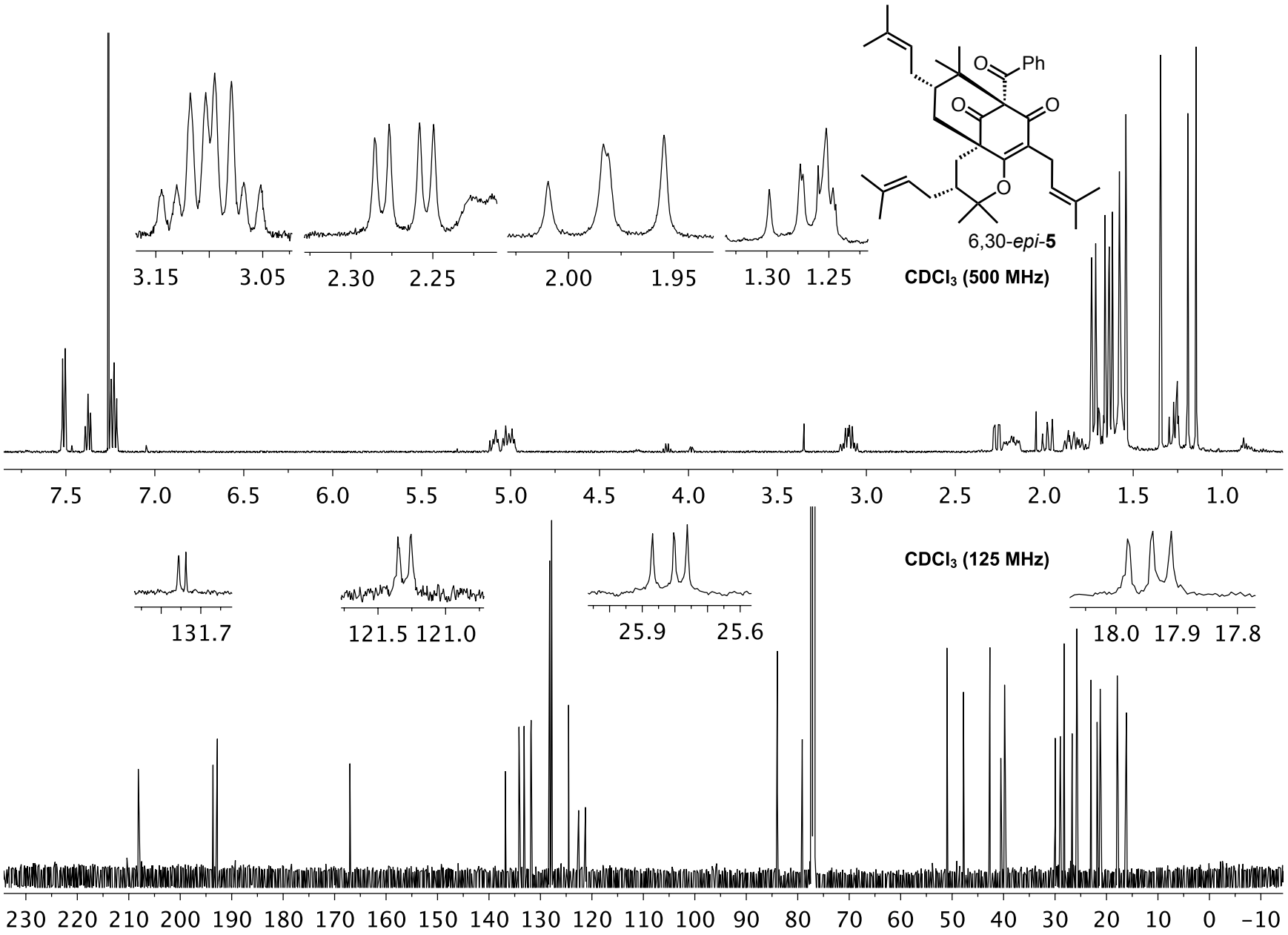
6,30-*epi*-**6**

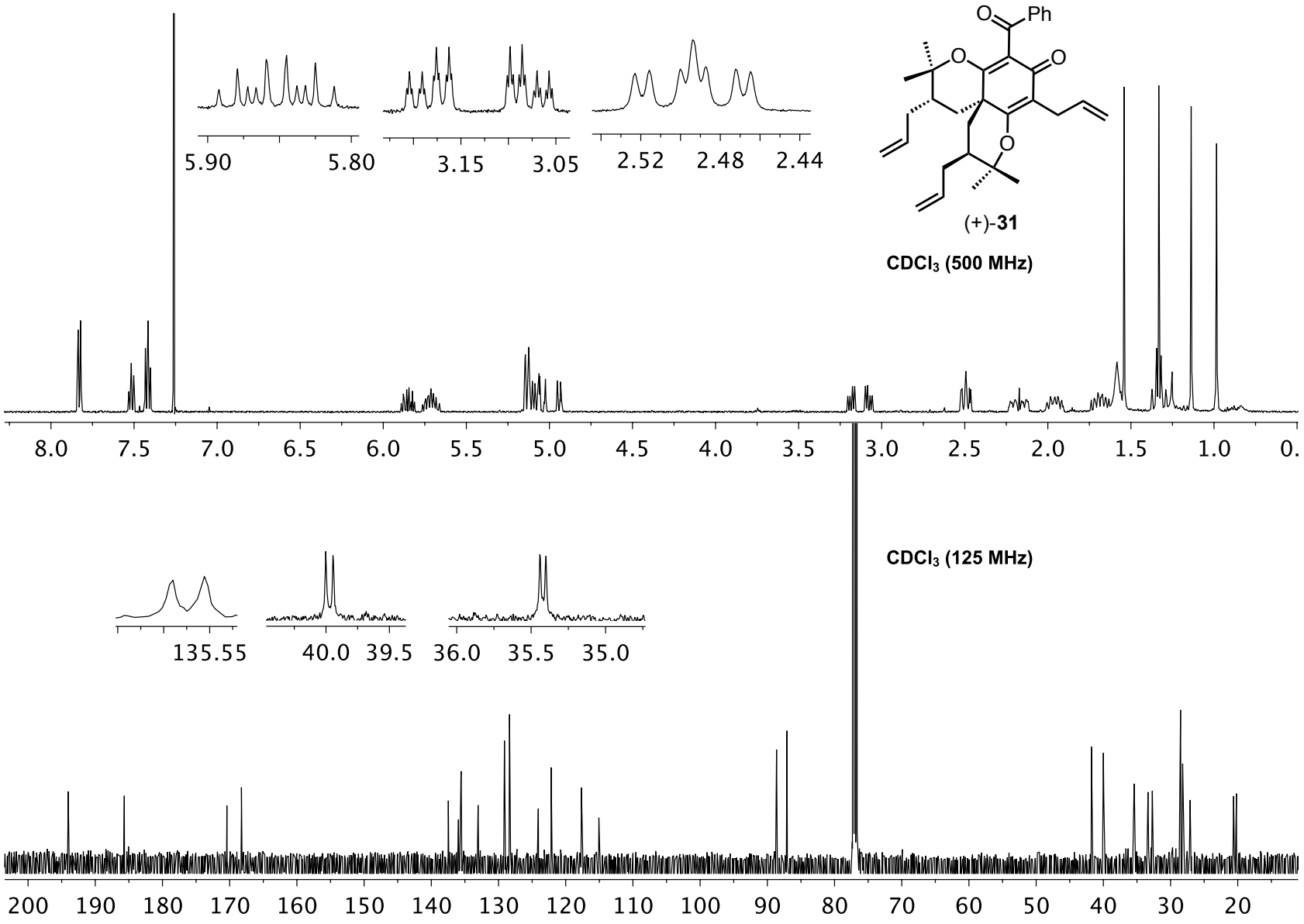


6,30-*epi*-**6**

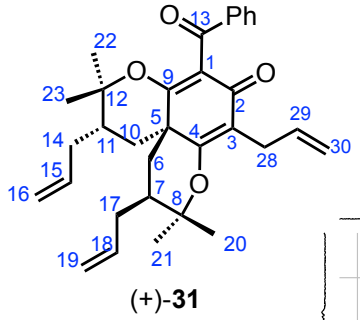



O
Ph
O
O
O
O
28
CDCl3 (500 MHz)
3.20 3.15 3.10
2.02 1.98
1.84 1.80 1.76
7.4 7.0 6.6 6.2 5.8 5.4 5.0 4.6 4.2 3.8 3.4 3.0 2.6 2.2 1.8 1.4
CDCl3 (125 MHz)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

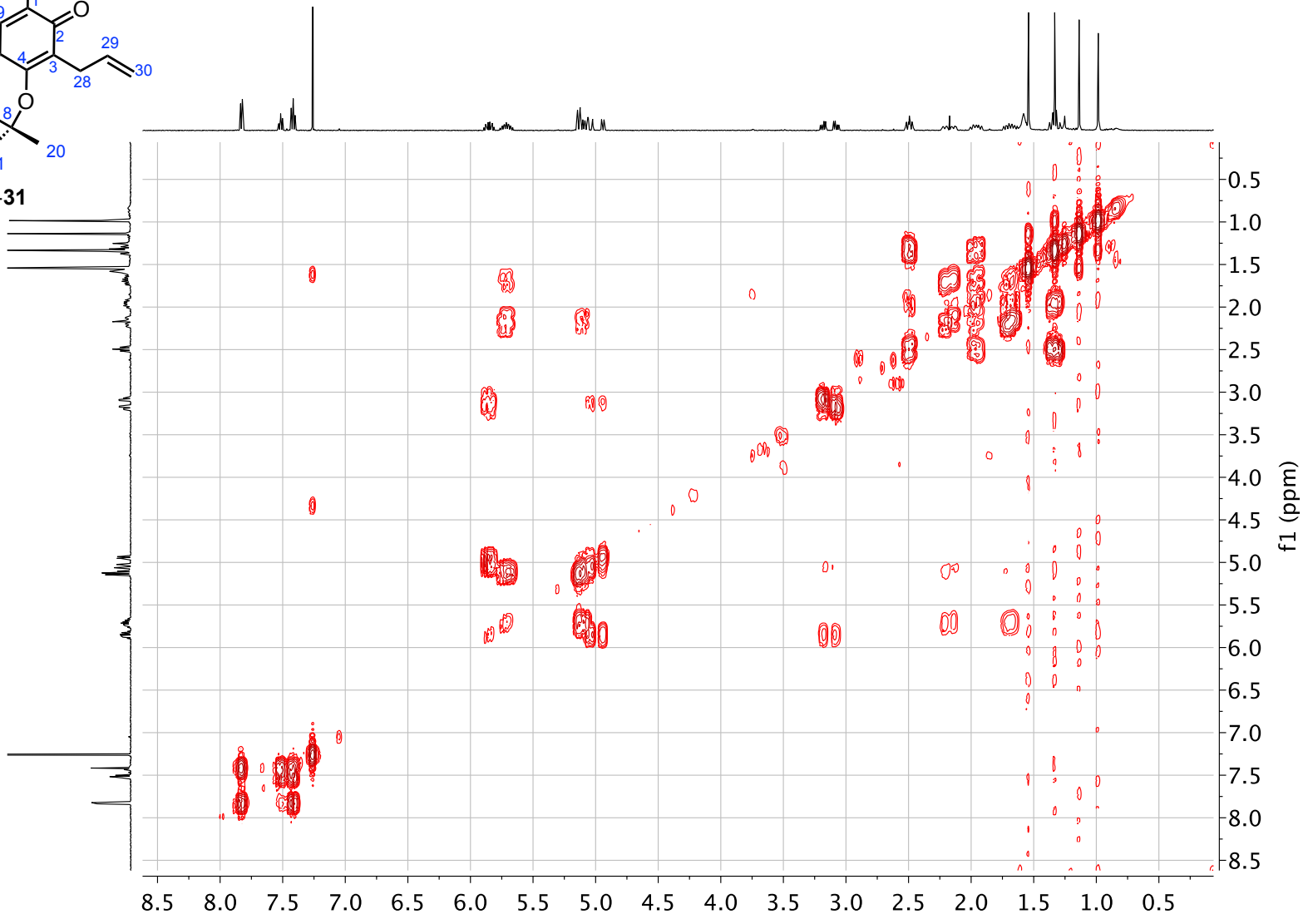

O
Ph
O
O
O
6,30-epi-5
CDCl3 (500 MHz)
3.15
3.05
2.30
2.25
2.00
1.95
1.30
1.25
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
CDCl3 (125 MHz)
131.7
121.5
121.0
25.9
25.6
18.0
17.9
17.8
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


O
Ph
O
O
O
(+)-31
CDCl3 (500 MHz)
5.90
5.80
3.15
3.05
2.52
2.48
2.44
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
CDCl3 (125 MHz)
135.55
40.0
39.5
36.0
35.5
35.0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

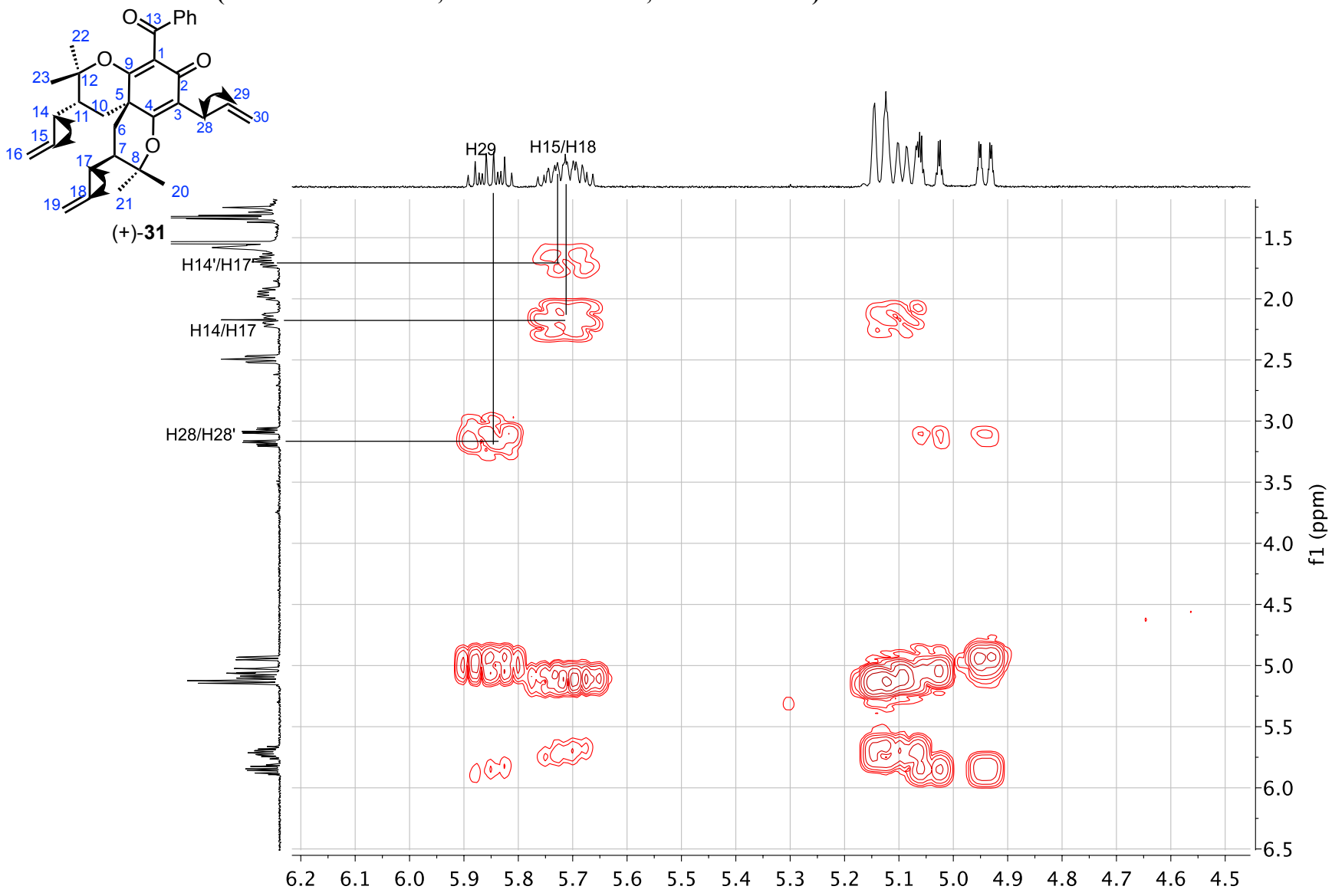
COSY Correlations for Compound (+)-31



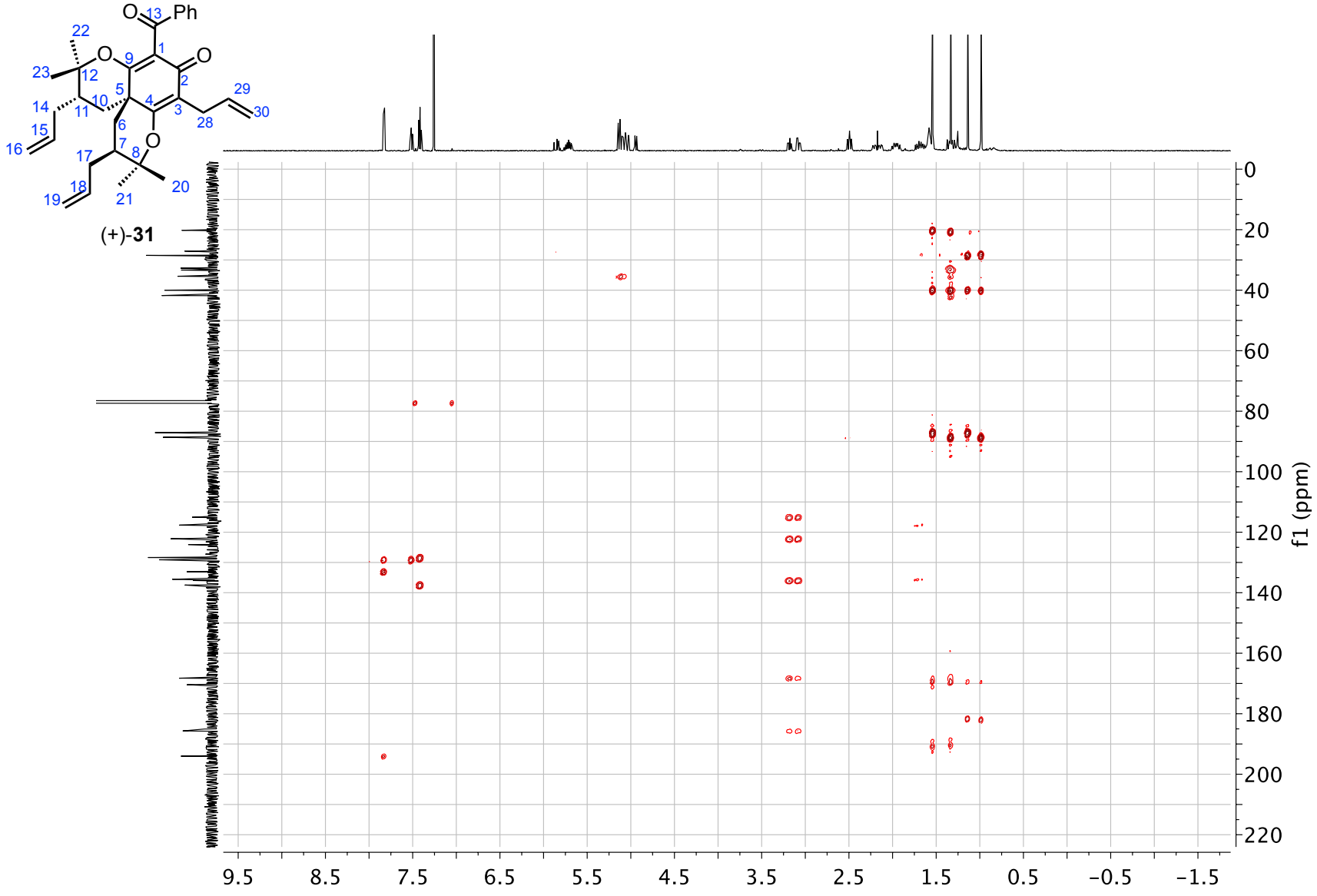
(+)-**31**



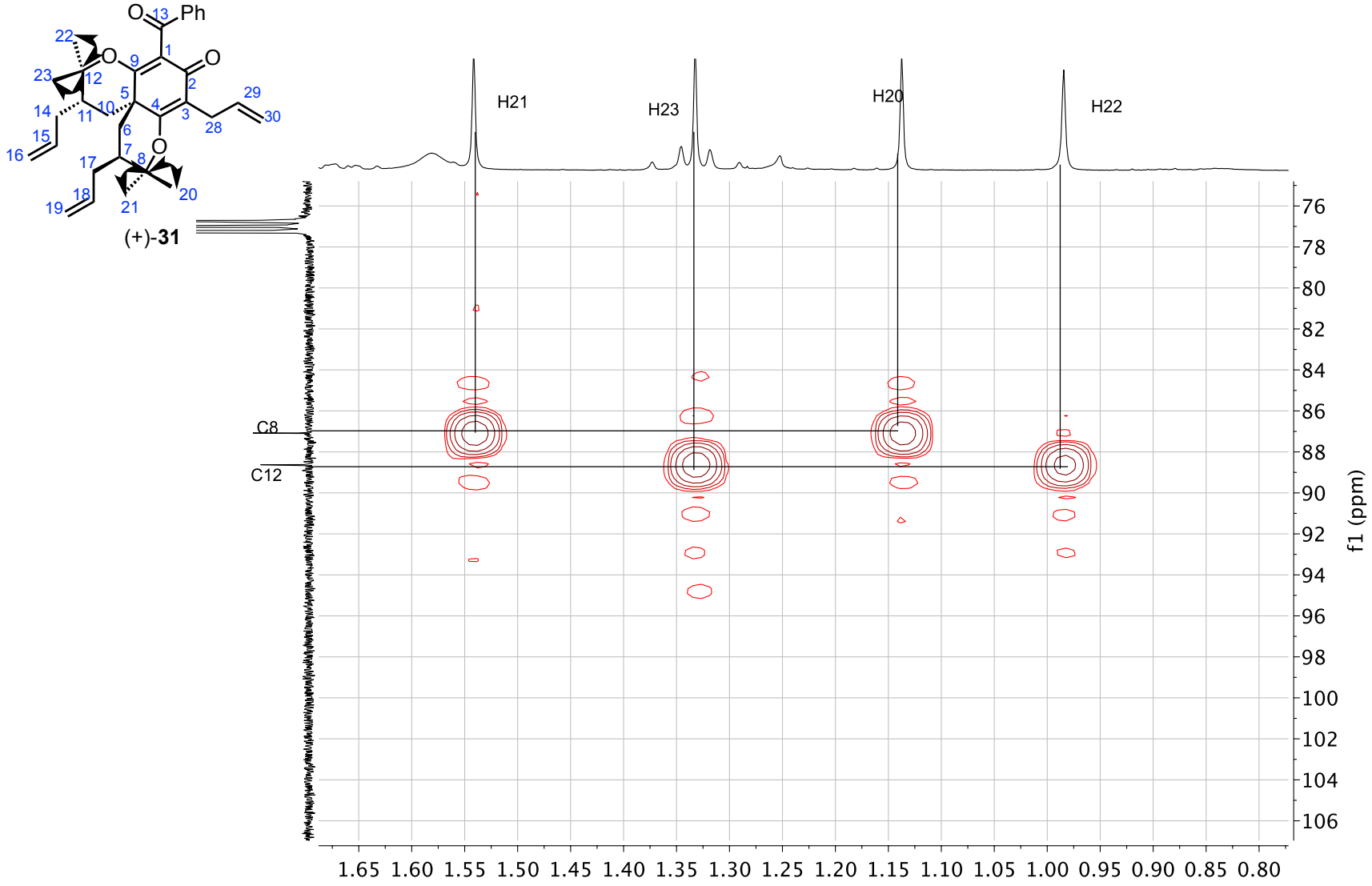
COSY Correlations (H14'/H17'-H15/H18, H14/H17-H15/H18, H28/H28'-H29)



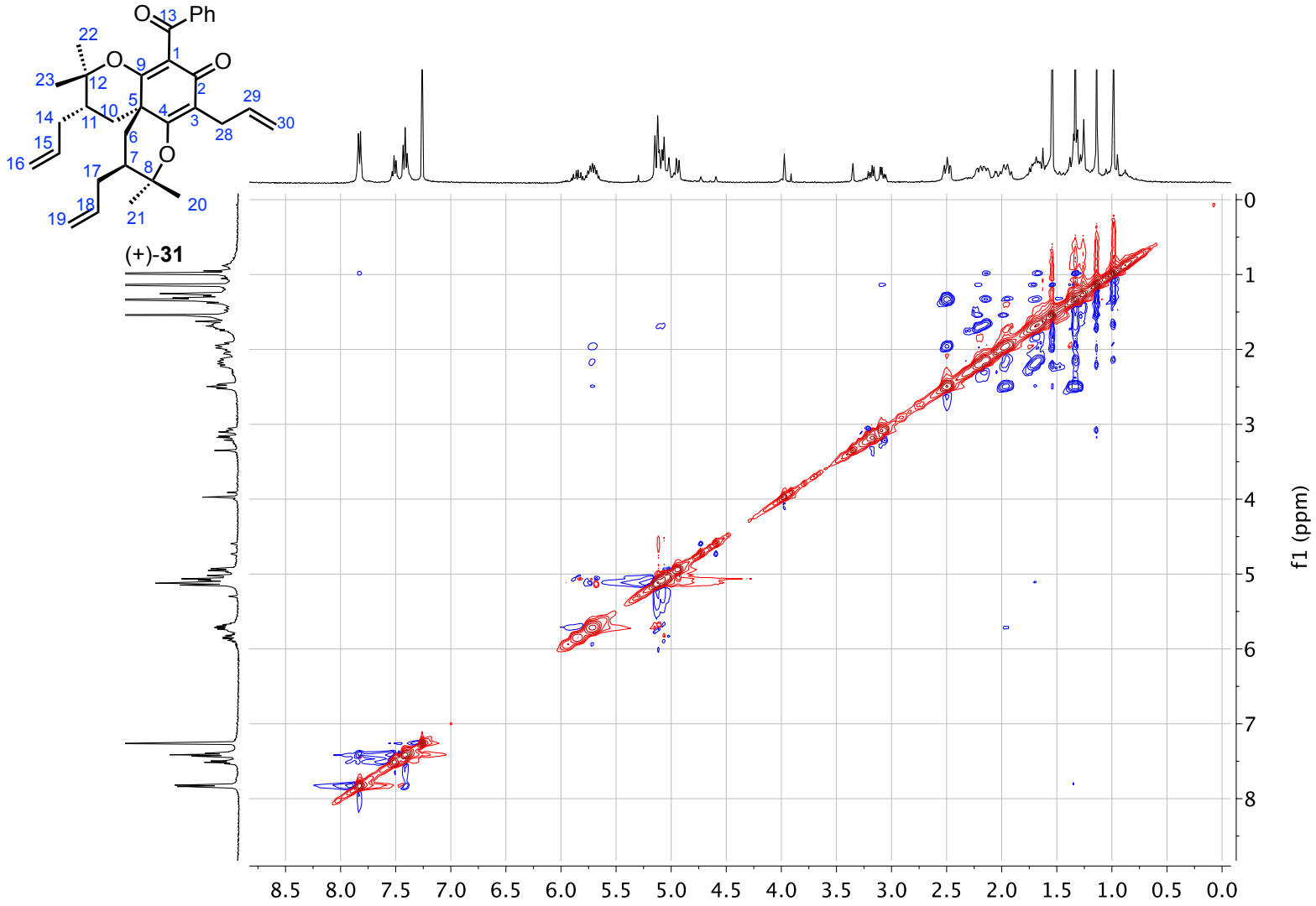
HMBC Correlations for Compound (+)-31



HMBC Correlations (C8-H21, C8-H20, C12-H23, C12-H22)

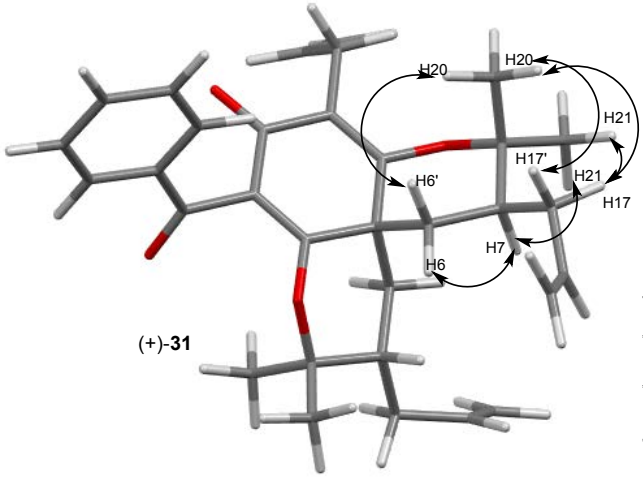


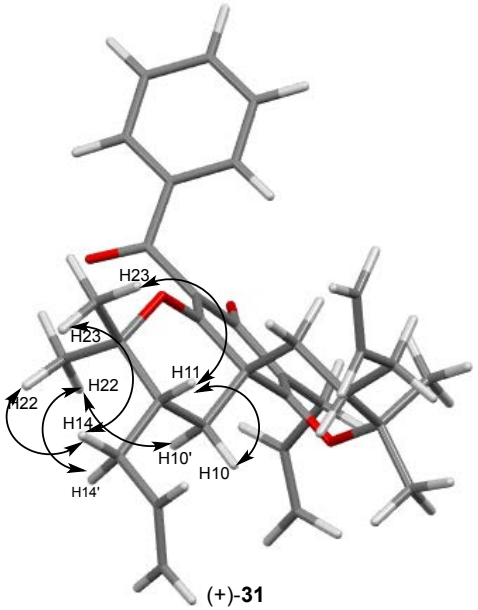
NOESY Correlations for Compound (+)-31

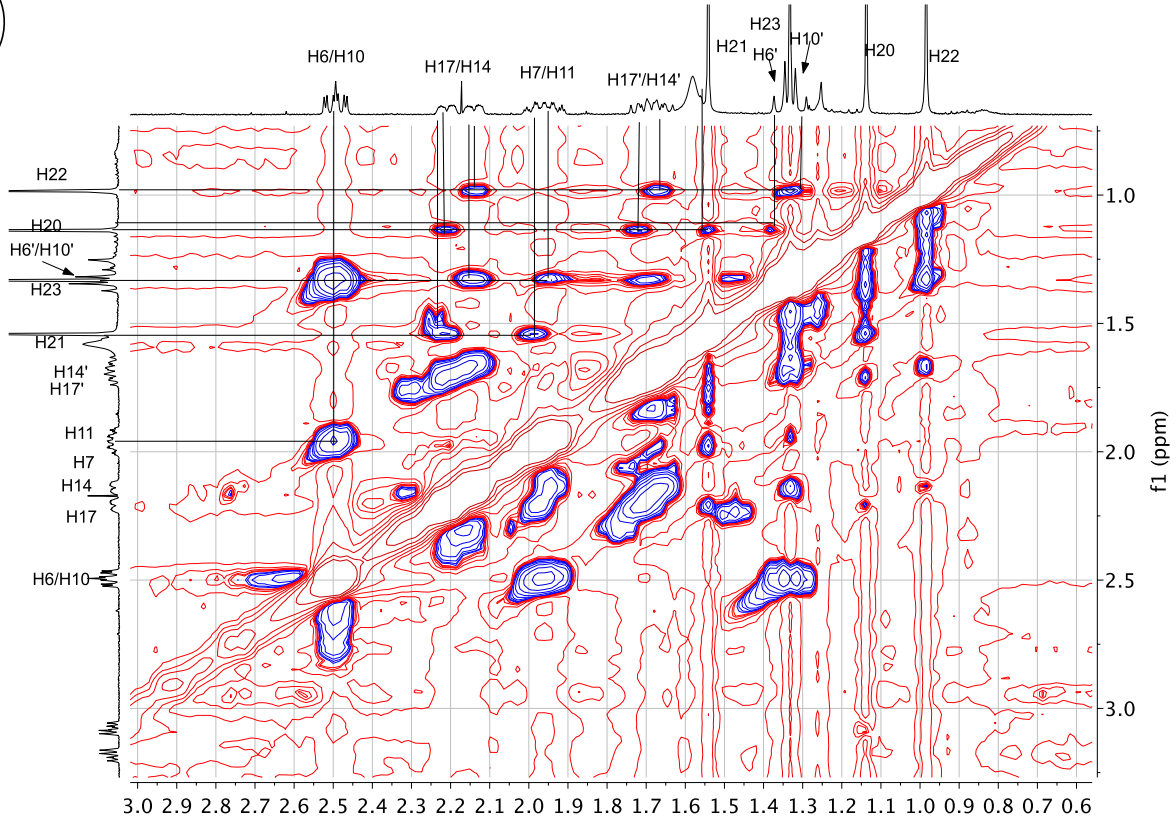


NOESY Correlations (H22-H14, H22-H14', H22-H23, H22-H10', H20-H17, H20-H17', H20-H6', H23-H14, H23-H11, H21-H17, H21-H7, H11/H7-H6/H10, H22-H10')

KEY EVIDENCE: H10 or H10' are not proximal to H17 or H17', a feature that would be required for the alternative diastereomer (not shown).







VI. Computational Studies

Figure S3. Energy profiles for the transformation of **9A** to (-)-**8** or (+)-**13**, in presence of $SnCl_4$ (top), and in presence of BF_3-OEt_2 (bottom).

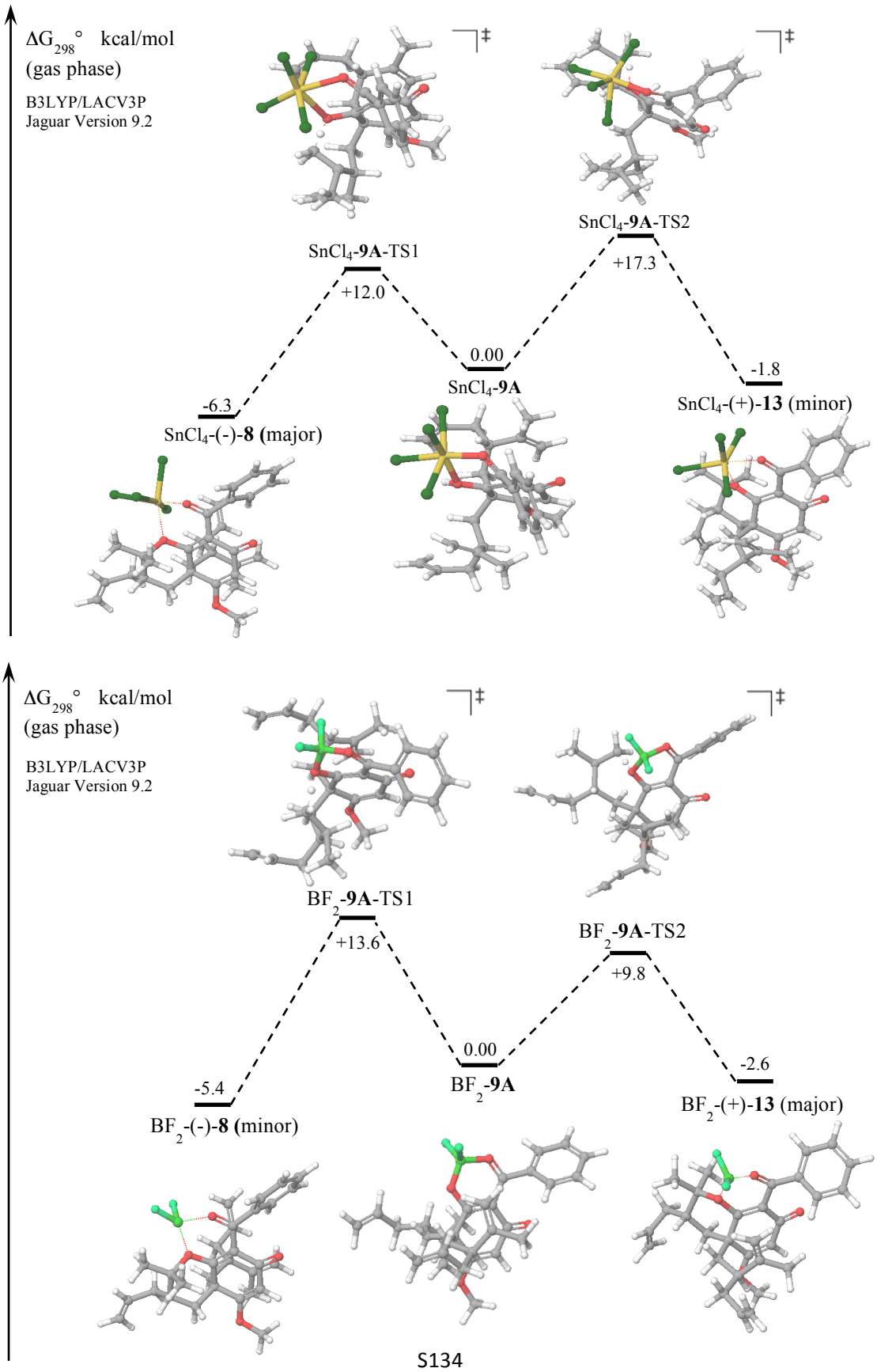
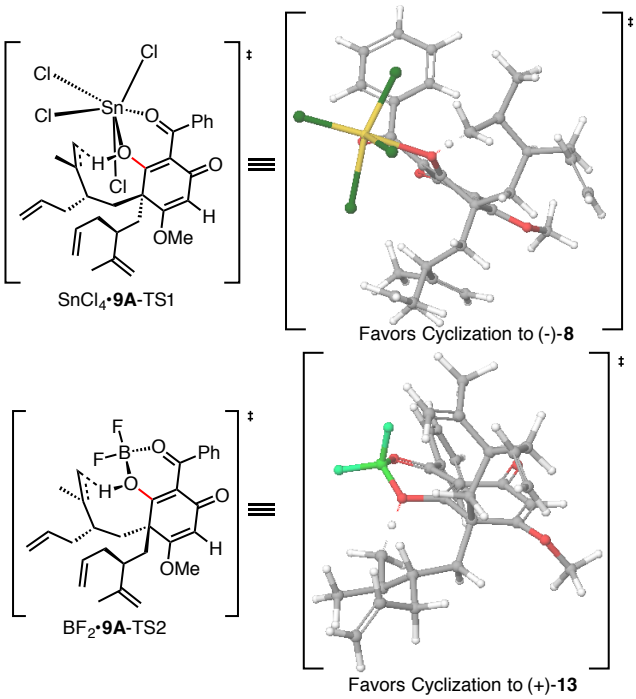


Figure S4. Transition State Models for Sn-9A-TS1 and BF_2-9A-TS2.



All structures were fully optimized by using Density Functional Theory (DFT) in Jaguar 9.2 (Schrodinger 2016-2) with the B3LYP functional. All calculations were carried out with the Los Alamos Effective Core Potentials Double Zeta (LACV3P) pseudospectral basis set for all atoms. Structures were evaluated by optimized energy values at the same level of theory. Transition state searches were performed using the QST method on Jaguar Version 9.2 (Schrodinger Maestro), using the same function and basis set.

$SnCl_4$-**9A**

C1	0.1161780000000	-1.2742290000000	-1.0971500000000
C2	-0.3409010000000	-2.5455230000000	-1.0322000000000
C3	-1.0892830000000	-3.0214930000000	0.1332210000000
C4	-1.4869090000000	-2.0285350000000	1.1605750000000
C5	-1.0178870000000	-0.7547140000000	1.0934660000000
C6	-0.1034970000000	-0.1996940000000	-0.0201550000000
O7	-1.3206260000000	-4.2112050000000	0.2932430000000
H8	-0.1650780000000	-3.2698560000000	-1.8152260000000
O9	0.8263810000000	-0.7628250000000	-2.1590520000000
C10	1.1009160000000	-1.6127780000000	-3.2693340000000
C11	-2.3151960000000	-2.4900340000000	2.3201830000000
O12	-2.0035710000000	-2.1614420000000	3.4590540000000
C13	-3.5729670000000	-3.2611400000000	2.1019820000000
C14	-4.0787250000000	-4.0746580000000	3.1472280000000
C15	-5.2710030000000	-4.8012470000000	2.9727080000000
C16	-5.9735390000000	-4.7251010000000	1.7579470000000
C17	-5.4809450000000	-3.9247400000000	0.7129550000000
C18	-4.2879590000000	-3.1981520000000	0.8817960000000

O19	-1.3297970000000	0.1847820000000	2.0149790000000
C20	1.2890030000000	0.2260890000000	0.5555620000000
C21	-0.7183780000000	1.0716860000000	-0.7031860000000
C22	-1.9362360000000	0.8936500000000	-1.6521340000000
C23	-3.2484770000000	0.4976890000000	-0.9812250000000
C24	-4.0378580000000	-0.5679420000000	-1.7141380000000
C25	-3.7142740000000	1.0625670000000	0.1464140000000
C26	-2.1292600000000	2.1320470000000	-2.5547540000000
C27	-2.4412670000000	3.4133500000000	-1.8021730000000
C28	-1.5888210000000	4.4407760000000	-1.6670190000000
C29	1.9521250000000	-0.6266240000000	1.6781120000000
C30	2.3041840000000	-2.0562270000000	1.2804690000000
C31	2.8629660000000	-2.3774210000000	0.1016930000000
C32	2.0091970000000	-3.1162320000000	2.3257740000000
C33	3.2174660000000	0.0688390000000	2.2183810000000
C34	2.9367570000000	1.3384760000000	3.0007170000000
C35	3.1285120000000	2.5775860000000	2.5237590000000
H36	1.6645760000000	-1.0539130000000	-4.0172020000000
H37	1.7081290000000	-2.4718850000000	-2.9794410000000
H38	0.1835790000000	-1.9610300000000	-3.7468570000000
H39	-3.5740030000000	-4.1887410000000	4.0967700000000
H40	-5.6513560000000	-5.4316110000000	3.7665250000000
H41	-6.8870780000000	-5.2900730000000	1.6238910000000
H42	-6.0226330000000	-3.8806100000000	-0.2230750000000
H43	-3.9483600000000	-2.6081740000000	0.0467170000000
H44	-0.7994020000000	0.9674860000000	2.0183700000000
H45	1.2076890000000	1.2475250000000	0.9274920000000
H46	2.0020010000000	0.3384230000000	-0.2646750000000
H47	0.0713020000000	1.4973850000000	-1.3281750000000
H48	-0.9221490000000	1.8756100000000	0.0021190000000
H49	-1.6930140000000	0.0921930000000	-2.3511370000000
H50	-4.3243280000000	-0.1987310000000	-2.7006440000000
H51	-3.4454420000000	-1.4706080000000	-1.8642850000000
H52	-4.9574000000000	-0.8338680000000	-1.1908100000000
H53	-4.6639340000000	0.7579740000000	0.5685170000000
H54	-3.1868620000000	1.8633390000000	0.6415350000000
H55	-2.9352950000000	1.9575330000000	-3.2701160000000
H56	-1.2343710000000	2.2871390000000	-3.1606110000000
H57	-3.4266250000000	3.4885380000000	-1.3634080000000
H58	-1.8724150000000	5.3355060000000	-1.1294980000000
H59	-0.5978000000000	4.4155380000000	-2.0985690000000
H60	1.2718070000000	-0.7046960000000	2.5154050000000
H61	3.1119600000000	-3.4010230000000	-0.1452540000000
H62	3.0981000000000	-1.6316160000000	-0.6450020000000
H63	0.9476590000000	-3.1874330000000	2.5468600000000
H64	2.3412140000000	-4.1004610000000	1.9885890000000
H65	2.5486590000000	-2.8963490000000	3.2487460000000
H66	3.9001490000000	0.2915380000000	1.3951540000000
H67	3.7717070000000	-0.5991490000000	2.8812070000000
H68	2.5808280000000	1.2217850000000	4.0141160000000
H69	2.9319520000000	3.4509690000000	3.1315160000000
H70	3.5004360000000	2.7477660000000	1.5218290000000

Sn71	-1.5586980000000	-0.2966440000000	3.9337700000000
Cl72	0.6340240000000	-0.4545900000000	5.1388150000000
Cl73	-2.5005390000000	-1.0310690000000	6.0862560000000
Cl74	-1.2091420000000	2.0880850000000	4.3564170000000
Cl75	-3.8663200000000	0.3278560000000	3.5059650000000

$SnCl_4$-**9A**-TS1

C1	0.4582040000000	-1.4473880000000	-1.0121860000000
C2	0.1765530000000	-2.7458900000000	-0.7525210000000
C3	-0.4926540000000	-3.1332680000000	0.4919510000000
C4	-1.1058500000000	-2.0603470000000	1.3036350000000
C5	-0.8669710000000	-0.7547500000000	1.0226970000000
C6	0.1222240000000	-0.2703980000000	-0.0771860000000
O7	-0.5507060000000	-4.3039180000000	0.8499750000000
H8	0.4327970000000	-3.5469970000000	-1.4305640000000
O9	1.0573610000000	-1.0137270000000	-2.1730400000000
C10	1.3403020000000	-1.9606130000000	-3.1991270000000
C11	-2.0567480000000	-2.4626410000000	2.3832270000000
O12	-1.9734330000000	-1.9668360000000	3.5033310000000
C13	-3.2187650000000	-3.3286940000000	2.0429690000000
C14	-3.7364120000000	-4.2088870000000	3.0240260000000
C15	-4.8658820000000	-4.9984890000000	2.7417690000000
C16	-5.4918960000000	-4.9123970000000	1.4865260000000
C17	-4.9796110000000	-4.0495690000000	0.5014480000000
C18	-3.8410140000000	-3.2658590000000	0.7721940000000
O19	-1.6428000000000	0.2047400000000	1.6151080000000
C20	1.4482430000000	0.2603930000000	0.5621400000000
C21	-0.4019960000000	0.9016450000000	-0.9626140000000
C22	-1.7814890000000	0.7139580000000	-1.6495980000000
C23	-2.9507470000000	0.6525390000000	-0.6309410000000
C24	-4.3372370000000	1.0049240000000	-1.1938850000000
C25	-2.5683490000000	1.3635930000000	0.5855370000000
C26	-1.9475950000000	1.7305400000000	-2.8070650000000
C27	-1.7626390000000	3.1806510000000	-2.4059140000000
C28	-0.7075990000000	3.9261650000000	-2.7696840000000
C29	2.2624840000000	-0.6102290000000	1.5685160000000
C30	2.8855900000000	-1.8810940000000	0.9995140000000
C31	3.4687600000000	-1.9467330000000	-0.2094920000000
C32	2.8450970000000	-3.0893620000000	1.9185560000000
C33	3.4022200000000	0.2164710000000	2.2062960000000
C34	2.9456370000000	1.2968200000000	3.1671200000000
C35	2.9678390000000	2.6112420000000	2.8990870000000
H36	1.7977450000000	-1.4407220000000	-4.0431730000000
H37	2.0460980000000	-2.7237010000000	-2.8667930000000
H38	0.4289120000000	-2.4360870000000	-3.5664200000000
H39	-3.2789100000000	-4.3260280000000	3.9967200000000
H40	-5.2525630000000	-5.6857280000000	3.4818740000000
H41	-6.3602910000000	-5.5227090000000	1.2726550000000
H42	-5.4625910000000	-4.0040540000000	-0.4642690000000
H43	-3.4841720000000	-2.6260130000000	-0.0216900000000
H45	1.2158420000000	1.1943020000000	1.0749360000000
H46	2.1221170000000	0.5740990000000	-0.2377010000000

H47	0.3253210000000	1.1057690000000	-1.7519530000000
H48	-0.3581000000000	1.8483380000000	-0.4229740000000
H49	-1.7681060000000	-0.2489280000000	-2.1622540000000
H50	-4.4247840000000	2.0556570000000	-1.4716130000000
H51	-4.5611180000000	0.4140680000000	-2.0846880000000
H52	-5.1338000000000	0.7963780000000	-0.4789920000000
H53	-2.9066990000000	1.6264460000000	-3.3153150000000
H54	-1.2094570000000	1.5015070000000	-3.5800830000000
H55	-2.5381280000000	3.6277380000000	-1.8021050000000
H56	-0.6129580000000	4.9606750000000	-2.4685930000000
H57	0.0836640000000	3.5208070000000	-3.3839750000000
H58	1.6007750000000	-0.9322710000000	2.3638540000000
H59	3.9123720000000	-2.8662670000000	-0.5676400000000
H60	3.5265490000000	-1.0902010000000	-0.8657870000000
H61	3.4151770000000	-2.8920840000000	2.8276960000000
H62	1.8275770000000	-3.3478610000000	2.2053410000000
H63	3.2855510000000	-3.9654150000000	1.4398610000000
H64	4.0196270000000	0.6643900000000	1.4243790000000
H65	4.0766050000000	-0.4338570000000	2.7677630000000
H66	2.6054010000000	0.9651380000000	4.1369940000000
H67	2.6500970000000	3.3401680000000	3.6320300000000
H68	3.3181020000000	2.9865610000000	1.9478680000000
Sn69	-2.4245440000000	0.0980470000000	3.9271890000000
Cl72	0.0862020000000	-0.1266750000000	4.3631470000000
Cl73	-3.0080270000000	-0.6543320000000	6.0320810000000
Cl74	-2.0702020000000	2.4576740000000	3.5823320000000
Cl75	-4.4859240000000	-0.2087620000000	2.7828710000000
H74	-3.5079040000000	1.5645960000000	1.1035460000000
H75	-2.3330180000000	2.3572870000000	0.1940170000000

$SnCl_4$-**9A**-TS2

C1	-0.3852460000000	-2.1990140000000	-1.1034550000000
C2	-1.2104580000000	-3.2202520000000	-1.4120640000000
C3	-2.0508830000000	-3.8433280000000	-0.3942770000000
C4	-1.7128320000000	-3.5958050000000	1.0351120000000
C5	-0.8486530000000	-2.5837790000000	1.3507060000000
C6	-0.2349160000000	-1.5932440000000	0.3110150000000
O7	-3.0189790000000	-4.5134440000000	-0.7234250000000
H8	-1.2968000000000	-3.6204150000000	-2.4120340000000
O9	0.4516950000000	-1.6000420000000	-2.0191660000000
C10	0.3673450000000	-1.9901680000000	-3.3877500000000
C11	-2.4457650000000	-4.3968470000000	2.0736300000000
O12	-2.7243370000000	-3.9119930000000	3.1599540000000
C13	-2.8304440000000	-5.8059380000000	1.8251200000000
C14	-1.8579200000000	-6.8213360000000	1.6703450000000
C15	-2.2674990000000	-8.1591570000000	1.4966350000000
C16	-3.6364400000000	-8.4842870000000	1.4634760000000
C17	-4.6044620000000	-7.4744630000000	1.6066360000000
C18	-4.2048340000000	-6.1395420000000	1.7972150000000
O19	-0.4146540000000	-2.3012610000000	2.6246450000000
C20	1.2939900000000	-1.3098320000000	0.5075010000000
C21	-0.9922170000000	-0.2184940000000	0.4047050000000

C22	-2.1807510000000	0.0595680000000	-0.5724950000000
C23	-3.4360280000000	0.6501070000000	0.0713670000000
C24	-4.7389290000000	0.2436510000000	-0.5917750000000
C25	-3.4292480000000	1.4854170000000	1.1254740000000
C26	-1.7333750000000	0.9296230000000	-1.7719150000000
C27	-1.3929450000000	2.3615130000000	-1.3929390000000
C28	-0.1581570000000	2.8863440000000	-1.4160790000000
C29	1.7780420000000	-0.6911680000000	1.8470860000000
C30	2.2669140000000	-1.8232060000000	2.7870500000000
C31	1.9192900000000	-2.7076950000000	3.1788520000000
C32	2.7445420000000	-1.3415650000000	4.1690130000000
C33	2.8681630000000	0.3827470000000	1.5928160000000
C34	2.9704740000000	1.4356230000000	2.6819200000000
C35	4.1000140000000	1.7428650000000	3.3372760000000
H36	1.0500600000000	-1.3795970000000	-3.9809470000000
H37	0.6560410000000	-3.0330970000000	-3.5273440000000
H38	-0.6368760000000	-1.8328300000000	-3.7851860000000
H39	-0.7969070000000	-6.6161680000000	1.6891820000000
H40	-1.5365050000000	-8.9501290000000	1.3831470000000
H41	-3.9486970000000	-9.5105380000000	1.3176810000000
H42	-5.6559840000000	-7.7294600000000	1.5614550000000
H43	-4.9793150000000	-5.3884610000000	1.8858480000000
H44	0.8162270000000	-2.5911660000000	2.9468700000000
H45	1.5900130000000	-0.6124010000000	-0.2780810000000
H46	1.8794180000000	-2.1970870000000	0.2560790000000
H47	-0.2720860000000	0.5851610000000	0.2480350000000
H48	-1.3013680000000	-0.0455460000000	1.4301450000000
H49	-2.5324520000000	-0.8834940000000	-0.9837920000000
H50	-4.7487730000000	0.5749120000000	-1.6313560000000
H51	-4.8708660000000	-0.8381890000000	-0.5813430000000
H52	-5.6018180000000	0.6934500000000	-0.0992010000000
H53	-4.3558810000000	1.8734320000000	1.5274310000000
H54	-2.5161940000000	1.8163350000000	1.5960750000000
H55	-2.5190410000000	0.9694580000000	-2.5277450000000
H56	-0.8720540000000	0.4852660000000	-2.2685450000000
H57	-2.2209740000000	2.9876490000000	-1.0878080000000
H58	0.0096530000000	3.9180380000000	-1.1389710000000
H59	0.7024330000000	2.3047940000000	-1.7126950000000
H60	0.9492420000000	-0.1526280000000	2.3036810000000
H61	2.1519790000000	-0.5212890000000	4.5689820000000
H62	2.7866570000000	-2.1373170000000	4.9131660000000
H63	3.7628160000000	-0.9558180000000	4.1015380000000
H64	2.6438690000000	0.9608490000000	0.6950730000000
H65	3.8439060000000	-0.0731360000000	1.4139980000000
H66	2.0683950000000	1.9808630000000	2.9206400000000
H67	4.1181280000000	2.5197670000000	4.0892620000000
H68	5.0301080000000	1.2317480000000	3.1334200000000
Sn69	-1.5833050000000	-2.5825750000000	4.3834160000000
Cl72	-0.5926150000000	-4.6482380000000	4.9418960000000
Cl73	-3.5326960000000	-2.5499300000000	5.7657450000000
Cl74	-0.2741900000000	-0.9250970000000	5.4552850000000
Cl75	-3.1100630000000	-1.1801720000000	3.0972080000000

H74	2.3107560000000	-3.3643670000000	3.9603300000000
H75	2.0696200000000	-3.3301130000000	2.2873730000000

$SnCl_4$-(-)-**8**

C1	-1.8408264699815	1.9390034351428	-1.3379512121356
C2	-1.4552376803146	0.4516131157535	-1.1970689164244
C3	-1.5872934406807	2.7753184139349	-0.0892891329643
C4	-1.9279484560748	-0.1297835726714	0.1621062682167
C5	-2.1027137922815	-0.2695546867486	-2.3754201749126
C6	0.0947725177119	0.2668984579085	-1.3046911612268
O7	-1.7114979767714	0.7031875216725	1.2778342670668
C8	-2.5090104618686	-1.3652393199210	0.2695830892823
C9	-2.1976383466042	2.0668537049882	1.1508819494030
C10	-1.8848768779173	2.9511941489001	2.3773328134222
C11	-3.7424167744383	1.9896736399998	1.0649844358223
C12	-0.0966340311482	3.2026789371077	0.0343737023379
C13	-2.8232506403164	-1.3980926299296	-2.2623960056789
O14	-1.8814769357198	0.3915549163499	-3.5661238158735
C15	-3.0201648421113	-2.0458609093225	-0.9683380661524
O16	-3.6672354987965	-3.0902861188131	-0.9688763254772
C17	-2.6725873216415	-2.0324463642117	1.6030747560908
O18	-2.4889644690398	-1.4189598653353	2.6337497195938
C19	-2.9755279582206	-3.4855382918084	1.7414248248898
C20	-2.1632740879845	-4.4744433831742	1.1389901088059
C21	-4.0734097632858	-3.8814236442841	2.5370176085016
C22	-4.3855486105697	-5.2465596436428	2.6909434909388
C23	-3.5922957226829	-6.2250643119144	2.0624139847195
C24	-2.4788108594521	-5.8395372923510	1.2912012103697
C25	0.0899167236685	4.6617428031720	0.4058179785359
C26	0.6316156777272	5.5842760311599	-0.4032127161795
C27	0.6936973929491	-1.1741347636596	-1.3523864817989
C28	2.1778006780836	-1.1592473020352	-0.9204825226883
C29	0.5378184579251	-1.8872480725627	-2.6998114169326
C30	2.7695590552254	-2.5498878964746	-0.7797566444511
C31	3.1789622615526	-3.0868405772789	0.3796471791213
C32	1.1093594909375	-1.1973571289688	-3.9272962063912
C33	-0.0613536824790	-3.0866061146035	-2.7994581690402
C34	-2.3793229527772	-0.1902106371330	-4.7641568146094
Sn35	-1.2044460925045	-0.2211468622247	3.3130010455776
Cl36	0.0447713300096	1.4467864730457	4.6449406388938
Cl37	-0.9586286656158	-1.7520071897523	5.2138504371347
Cl38	-3.1760981779392	0.5989145216210	4.5618657125587
H39	-2.9016396612980	2.0081671597310	-1.5810887933520
H40	-1.3391125967923	2.3926495773698	-2.1941244108574
H41	-2.1490304094851	3.6978502963992	-0.2481628551331
H42	0.5324422266748	0.7342407360275	-0.4279029536324
H43	0.4778724744773	0.8485332067565	-2.1421796425172
H44	-0.8238346174492	2.9704439402808	2.6144998717581
H45	-2.1898178060900	3.9821394868634	2.1970328312130
H46	-2.4183614132409	2.6592840551771	3.2738284698889
H47	-4.1834767854023	2.9835633900685	0.9822380500954
H48	-4.1042279072390	1.4108615151734	0.2172274882540

H49	-4.1616856591612	1.5275647352991	1.9588396179479
H50	0.4218523192729	3.0493119088768	-0.9120480083102
H51	0.4364792054332	2.5918714760148	0.7633375131216
H52	-3.2746142795704	-1.8866547995974	-3.1108875248072
H53	-1.3053418230133	-4.1944030762185	0.5458694522380
H54	-4.6867506238143	-3.1389117140515	3.0285275812550
H55	-5.2341704419396	-5.5430870578312	3.2915935066172
H56	-3.8350579899070	-7.2723718149704	2.1775932765959
H57	-1.8686019773107	-6.5931758468991	0.8144424440693
H58	-0.2343106363997	4.9596651792461	1.3918321290260
H59	0.7461862362467	6.6084299379276	-0.0785128156549
H60	0.9700366589941	5.3333254831538	-1.3980839478275
H61	0.1769310465181	-1.7696138407611	-0.6002981454232
H62	2.2878208692626	-0.6463109039883	0.0350705620441
H63	2.7814593696438	-0.5908918191039	-1.6281750681303
H64	2.8581555908157	-3.1289438565903	-1.6885184062882
H65	3.5938692989089	-4.0837801259438	0.4155506660341
H66	3.1065906382341	-2.5411545352379	1.3097352802994
H67	0.6281543364190	-0.2362762944184	-4.1011715536245
H68	2.1800808112724	-1.0295263764597	-3.8149489047837
H69	0.9652330109511	-1.8009512264954	-4.8238139253844
H70	-0.1625949812531	-3.5865557496855	-3.7517805007502
H71	-0.4587455857235	-3.5947589412192	-1.9331794654028
H72	-2.0880316196474	0.4318444896317	-5.6107696854193
H73	-1.9615281790418	-1.1843320922578	-4.9311105991974
H74	-3.4685015473557	-0.2496427910009	-4.7601153158664
Cl75	0.5874311381569	-0.4540290266261	2.2709832283111

$SnCl_4$-(+)-**13**

C1	-0.8753333868541	1.7868849175251	0.1816132823996
C2	-0.5600405435324	0.2831494017005	0.2631781399715
C3	-1.1355799105008	-0.4717221884916	-0.9779523647083
O4	-0.8974929727461	0.1577845274753	-2.2231341354384
C5	-1.2901631167369	1.5726986132519	-2.2746322088379
C6	-0.5171543447010	2.3639680264148	-1.1812388940879
C7	-1.2008268394292	-0.1901002032333	1.5665266167628
C8	-2.1022568249350	-1.1823063022925	1.6447053356097
C9	-2.4971164064013	-1.9495993559289	0.4644503211600
C10	-1.8685280701530	-1.6262552864745	-0.8614193079941
C11	-2.0768115591020	-2.5605304114565	-2.0273598624061
O12	-1.6252200183300	-2.3248128891922	-3.1348797128853
C13	-2.7060738677448	-3.9039429900217	-1.8805610362973
C14	-3.8137088107947	-4.2328198022777	-2.6936404927757
C15	-4.3842319128891	-5.5194141590725	-2.6317772539755
C16	-3.8426652651391	-6.4876914260764	-1.7651126240891
C17	-2.7236385535062	-6.1753672259957	-0.9666039215840
C18	-2.1488976660376	-4.8904976231551	-1.0337911529201
O19	-3.3802394686896	-2.7894914644288	0.6226927333480
C20	-0.9434495981895	2.2414858419186	-3.6289643335263
C21	-2.8309602583506	1.6822673395671	-2.0865255006270
C22	-0.7069579922672	3.9068349598203	-1.1921711867421
C23	0.1853220107211	4.6208831723858	-0.1951549973441

C24	-0.2621101280886	5.4006197304816	0.8006945365105
C25	1.0059369997172	0.1011227752862	0.3089087406695
C26	1.7288085409028	-0.8279598610398	1.3428127895350
C27	3.2020351570601	-0.3570510617963	1.4683079877607
C28	4.0379675739238	-1.1797461690189	2.4323911002455
C29	5.1535368472234	-1.8408581725775	2.0853643548552
C30	1.6645129226034	-2.3329360307372	1.0474536057267
C31	0.7518888789241	-3.1712799783639	1.9213247813158
C32	2.4198315249661	-2.9243922333737	0.1072925295193
O33	-0.7814776496121	0.5605314528167	2.6438354741115
C34	-1.2252917259290	0.1823159468305	3.9405903869699
H35	-0.3459847021650	2.3206756545729	0.9703824346923
H36	-1.9272858244204	1.9703519506204	0.3986607238407
H37	0.5458025894848	2.1948018715305	-1.3606939252775
H38	-2.5618521351223	-1.4788703670773	2.5762049553125
H39	-4.2199393022299	-3.5020301429663	-3.3780399871065
H40	-5.2295222624611	-5.7660978699714	-3.2578172021555
H41	-4.2785050972154	-7.4763818436466	-1.7205398933912
H42	-2.3022197628309	-6.9237787820374	-0.3132271312533
H43	-1.2781809691400	-4.6681892434920	-0.4338076877371
H44	-1.4588572403513	3.1958254803825	-3.7410411974051
H45	0.1204448955387	2.4603709252640	-3.7135905612496
H46	-1.2325497806947	1.6763332263416	-4.5058931589196
H47	-3.1523973206809	2.7184117515151	-1.9776889630895
H48	-3.3806438447083	1.2970393825839	-2.9396898925931
H49	-3.2070389903911	1.1492620701538	-1.2156200364448
H50	-1.7459347509066	4.1751555148432	-1.0029938188221
H51	-0.4463253936915	4.3343038969069	-2.1590803764637
H52	1.2500420293897	4.4774336838863	-0.3154571597234
H53	0.4252784577448	5.8830834890646	1.4811907345800
H54	-1.3181423667328	5.5701375810675	0.9534770759620
H55	1.4183597738630	1.0879589693100	0.5146575054763
H56	1.3872932571210	-0.1090795184887	-0.6889523459997
H57	1.3019929087546	-0.6750563237404	2.3323963131076
H58	3.2332952801535	0.6743447690503	1.8224088125593
H59	3.6828167526257	-0.3500713426742	0.4887284891874
H60	3.6922279929491	-1.2205239898376	3.4550096628666
H61	5.7130023838795	-2.4137318186637	2.8101155684663
H62	5.5229779586173	-1.8224626368287	1.0700656950011
H63	-0.2901962512446	-3.0035577491361	1.6881077996543
H64	0.9388191639778	-4.2361736060077	1.7778753240802
H65	0.9154690702098	-2.9476680860870	2.9756845552242
H66	2.3762691044088	-3.9893625647650	-0.0666022420792
H67	3.0991127656384	-2.3559191175920	-0.5101927432640
H68	-0.7477111532766	0.8251956762850	4.6808376907615
H69	-2.3048410666204	0.3013805669980	4.0458123712222
H70	-0.9471664450654	-0.8474976777756	4.1726993688663
Sn71	-0.3455371717523	-1.1124033447613	-3.9630909132588
Cl72	0.1661093889741	-2.9088675439404	-5.5229741056269
Cl73	-2.6997109106446	-0.4124134258402	-4.7732715268905
Cl74	1.4240043599574	0.3712484880344	-4.7157305068770
Cl75	1.1155832664949	-2.0309660459719	-2.5849919406208

BF_2-**9A**

C1	-0.1014890000000	-1.2607560000000	-0.3973720000000
C2	-0.6668500000000	-2.4790910000000	-0.5411530000000
C3	-1.7079580000000	-2.9556580000000	0.3774090000000
C4	-2.1465230000000	-2.0494590000000	1.4718970000000
C5	-1.5287950000000	-0.8597990000000	1.6497940000000
C6	-0.4734750000000	-0.2607600000000	0.7042310000000
O7	-2.1419730000000	-4.0971000000000	0.2305870000000
H8	-0.3884350000000	-3.1557450000000	-1.3316720000000
O9	0.8479170000000	-0.7409990000000	-1.2547100000000
C10	1.2176990000000	-1.5043960000000	-2.3947880000000
C11	-3.2529220000000	-2.4239300000000	2.3961300000000
O12	-3.4885630000000	-1.7774440000000	3.4166640000000
C13	-4.2585620000000	-3.4973750000000	2.1636150000000
C14	-4.5406290000000	-4.4501280000000	3.1714210000000
C15	-5.5171570000000	-5.4433680000000	2.9623980000000
C16	-6.2237310000000	-5.4937490000000	1.7461770000000
C17	-5.9552200000000	-4.5485010000000	0.7394480000000
C18	-4.9805800000000	-3.5548710000000	0.9482690000000
O19	-1.8062950000000	-0.0724440000000	2.7465400000000
C20	0.8037100000000	0.1829530000000	1.4844040000000
C21	-1.0567550000000	1.0176650000000	0.0141590000000
C22	-2.0946630000000	0.8309720000000	-1.1395520000000
C23	-3.4904370000000	0.3744660000000	-0.7163020000000
C24	-4.1887320000000	-0.5602760000000	-1.6854800000000
C25	-4.0869580000000	0.7636780000000	0.4234380000000
C26	-2.1713500000000	2.0772530000000	-2.0459450000000
C27	-2.5488770000000	3.3491870000000	-1.3102280000000
C28	-1.7820240000000	4.4489090000000	-1.2587980000000
C29	1.4833550000000	-0.7907370000000	2.4920180000000
C30	1.9095770000000	-2.1273990000000	1.8911550000000
C31	2.7098580000000	-2.2183610000000	0.8152260000000
C32	1.3983780000000	-3.3622420000000	2.6045480000000
C33	2.7169360000000	-0.1397980000000	3.1591880000000
C34	2.4166520000000	1.1672620000000	3.8659880000000
C35	2.9903570000000	2.3396580000000	3.5529230000000
H36	1.9454460000000	-0.9415800000000	-2.9795480000000
H37	1.6826360000000	-2.4487910000000	-2.1105350000000
H38	0.3585610000000	-1.6984070000000	-3.0378850000000
H39	-4.0054870000000	-4.4406800000000	4.1117860000000
H40	-5.7226990000000	-6.1727970000000	3.7332660000000
H41	-6.9675440000000	-6.2596180000000	1.5825370000000
H42	-6.4930350000000	-4.5870330000000	-0.1975360000000
H43	-4.7856640000000	-2.8401020000000	0.1606660000000
H44	0.5231810000000	1.0784170000000	2.0409350000000
H45	1.5542060000000	0.5297850000000	0.7738430000000
H46	-0.2118070000000	1.5528900000000	-0.4244230000000
H47	-1.4359880000000	1.7089470000000	0.7679460000000
H48	-1.7188950000000	0.0531630000000	-1.8027130000000
H49	-4.2903700000000	-0.0877940000000	-2.6624270000000
H50	-3.6185210000000	-1.4805320000000	-1.8113420000000

H51	-5.1874890000000	-0.8257160000000	-1.3391320000000
H52	-5.0776330000000	0.4277150000000	0.6890620000000
H53	-3.5971880000000	1.4351200000000	1.1134170000000
H54	-2.8955170000000	1.9159310000000	-2.8452410000000
H55	-1.2088240000000	2.2227830000000	-2.5391980000000
H56	-3.5030030000000	3.3458900000000	-0.8029190000000
H57	-2.1053010000000	5.3272950000000	-0.7201710000000
H58	-0.8216290000000	4.4890600000000	-1.7507650000000
H59	0.7613760000000	-0.9962070000000	3.2841640000000
H60	3.0134160000000	-3.1737880000000	0.4137340000000
H61	3.0747800000000	-1.3315720000000	0.3166180000000
H62	0.3106280000000	-3.3590730000000	2.6519920000000
H63	1.7136970000000	-4.2758190000000	2.0993750000000
H64	-0.4353150000000	-1.0362680000000	3.8747630000000
H65	1.7855960000000	-3.3874630000000	3.6230320000000
H66	3.5004210000000	0.0297810000000	2.4181030000000
H67	3.1396670000000	-0.8243260000000	3.8954870000000
H68	1.6889070000000	1.1248230000000	4.6650380000000
H69	2.7396170000000	3.2443130000000	4.0856830000000
H70	3.7172390000000	2.4133290000000	2.7568300000000
H71	-1.0534720000000	5.0945960000000	-1.9088560000000
B72	-2.8249790000000	-0.4566900000000	3.7739510000000
F73	-2.2543740350454	-0.6570850737105	5.1902319708535
F74	-3.9479769323172	0.5963953068604	3.8125123859455

BF_2-**9A**-TS1

C1	0.5856870000000	-1.4117740000000	-1.0640430000000
C2	0.1381500000000	-2.6617030000000	-0.8162170000000
C3	-0.7635560000000	-2.9398410000000	0.3027560000000
C4	-1.2797940000000	-1.8237430000000	1.1236980000000
C5	-0.7579530000000	-0.5767260000000	0.9939110000000
C6	0.2638570000000	-0.2468420000000	-0.1163510000000
O7	-1.0125880000000	-4.1041330000000	0.5942010000000
H8	0.4663560000000	-3.4986550000000	-1.4231990000000
O9	1.4926680000000	-1.1552330000000	-2.0949320000000
C10	1.0928160000000	-1.7465540000000	-3.3143780000000
C11	-2.3931520000000	-1.9986080000000	2.1199010000000
O12	-2.6379160000000	-1.1185110000000	3.0160190000000
C13	-3.3287960000000	-3.1442470000000	2.0347140000000
C14	-3.7149690000000	-3.8228610000000	3.2023210000000
C15	-4.6302230000000	-4.8781680000000	3.1348790000000
C16	-5.1786380000000	-5.2528000000000	1.9053170000000
C17	-4.8172160000000	-4.5689130000000	0.7416580000000
C18	-3.9021060000000	-3.5136460000000	0.8045200000000
O19	-1.3330690000000	0.4914430000000	1.7075580000000
C20	1.6002050000000	0.2447650000000	0.5393470000000
C21	-0.2900500000000	0.9372500000000	-0.9828420000000
C22	-1.6305930000000	0.7150200000000	-1.7621260000000
C23	-2.9102670000000	0.4916940000000	-0.8677560000000
C24	-4.2422890000000	0.6782390000000	-1.6119630000000

C25	-2.9121550000000	1.2785200000000	0.4593610000000
C26	-1.7831120000000	1.8254950000000	-2.8395190000000
C27	-1.9143660000000	3.2105980000000	-2.2564440000000
C28	-0.9218360000000	4.1025100000000	-2.3278230000000
C29	2.2364770000000	-0.6812790000000	1.6229340000000
C30	2.8136970000000	-1.9744760000000	1.0612410000000
C31	3.7010680000000	-1.9703930000000	0.0500760000000
C32	2.5133920000000	-3.2659680000000	1.7787270000000
C33	3.3390440000000	0.0631710000000	2.4092330000000
C34	2.7603340000000	1.1263570000000	3.3078590000000
C35	3.0665090000000	2.4188880000000	3.1634770000000
H36	1.5637560000000	-1.1851240000000	-4.1466270000000
H37	1.4572700000000	-2.7937370000000	-3.3736580000000
H38	-0.0086470000000	-1.7064620000000	-3.4726150000000
H39	-3.3010900000000	-3.5411250000000	4.1628080000000
H40	-4.9172190000000	-5.4033420000000	4.0365350000000
H41	-5.8885890000000	-6.0682280000000	1.8554470000000
H42	-5.2510990000000	-4.8522450000000	-0.2086170000000
H43	-3.6490840000000	-2.9801550000000	-0.1030830000000
H45	1.4121450000000	1.2322030000000	1.0094020000000
H46	2.3472700000000	0.4689490000000	-0.2507110000000
H47	0.4966120000000	1.1976890000000	-1.7264800000000
H48	-0.3856330000000	1.8538460000000	-0.3636490000000
H49	-1.5085550000000	-0.2229970000000	-2.3451740000000
H50	-4.4352330000000	1.7471340000000	-1.8362800000000
H51	-4.2404060000000	0.0943620000000	-2.5568970000000
H52	-5.0813830000000	0.3028550000000	-0.9877340000000
H53	-2.6554120000000	1.6277050000000	-3.4949120000000
H54	-0.9040490000000	1.7816980000000	-3.5210950000000
H55	-2.8469700000000	3.5051850000000	-1.7877120000000
H56	-1.0534720000000	5.0945960000000	-1.9088560000000
H57	0.0270000000000	3.8522260000000	-2.7928530000000
H58	1.4459620000000	-0.9526690000000	2.3554610000000
H59	4.1479100000000	-2.8933200000000	-0.3063050000000
H60	4.0121290000000	-1.0483350000000	-0.4278390000000
H61	2.9678790000000	-3.2358610000000	2.7909570000000
H62	1.4190710000000	-3.3939620000000	1.8909210000000
H63	2.9134040000000	-4.1492020000000	1.2358070000000
H64	4.0809530000000	0.4953370000000	1.7011290000000
H65	3.8840100000000	-0.6549590000000	3.0601740000000
H66	2.0789820000000	0.8302640000000	4.0999320000000
H67	2.6322110000000	3.1562310000000	3.8307430000000
H68	3.7429010000000	2.7531130000000	2.3825510000000
B68	-1.7820350000000	0.0826320000000	3.0447720000000
F69	-2.4918190000000	1.1352780000000	3.6647090000000
F70	-0.6694380000000	-0.1654770000000	3.8847530000000
H71	-3.8782500000000	1.1386480000000	0.9916850000000
H72	-2.7586660000000	2.3629120000000	0.2881120000000
H73	-2.0805560000000	0.8635590000000	1.1323850000000
H74	-2.9111000000000	-0.5821120000000	-0.5890320000000

BF_2-**9A**-TS1

C1	-0.2776250000000	-2.0178020000000	-1.3673170000000
C2	-1.0729890000000	-3.0588420000000	-1.6925530000000
C3	-1.8075100000000	-3.8065440000000	-0.6693600000000
C4	-1.6365070000000	-3.4573000000000	0.7576820000000
C5	-0.9534700000000	-2.3405610000000	1.1103790000000
C6	-0.1642000000000	-1.5035390000000	0.0818960000000
O7	-2.6321170000000	-4.6431870000000	-1.0190940000000
H8	-1.2147650000000	-3.3385390000000	-2.7314840000000
O9	0.3444720000000	-1.2604140000000	-2.3603890000000
C10	1.1156170000000	-2.0705920000000	-3.2224990000000
C11	-2.2391100000000	-4.2685220000000	1.8686070000000
O12	-2.3794430000000	-3.7926060000000	3.0468550000000
C13	-2.6109950000000	-5.6889760000000	1.6749860000000
C14	-1.7338030000000	-6.5841350000000	1.0364330000000
C15	-2.0809240000000	-7.9327370000000	0.8989760000000
C16	-3.2959560000000	-8.3998730000000	1.4071650000000
C17	-4.1602170000000	-7.5220680000000	2.0666190000000
C18	-3.8170180000000	-6.1738380000000	2.2088940000000
O19	-0.7856660000000	-2.0101160000000	2.4619600000000
C20	1.3697590000000	-1.5717920000000	0.4320710000000
C21	-0.6930960000000	-0.0313800000000	0.1086730000000
C22	-2.1517310000000	0.1474710000000	-0.4399490000000
C23	-3.1744590000000	0.5273330000000	0.6268020000000
C24	-4.4769740000000	-0.2320560000000	0.6654630000000
C25	-2.9772310000000	1.5519010000000	1.4771460000000
C26	-2.2240890000000	1.0831450000000	-1.6684470000000
C27	-1.7755150000000	2.4947950000000	-1.3847820000000
C28	-0.6521870000000	2.9970300000000	-1.9067110000000
C29	1.8525400000000	-0.9208250000000	1.7837110000000
C30	2.2150060000000	-2.0145670000000	2.8516040000000
C31	1.0314910000000	-2.9824590000000	3.0780260000000
C32	2.6438520000000	-1.4086050000000	4.2018490000000
C33	3.0339080000000	0.0586560000000	1.5124920000000
C34	3.1042080000000	1.1737070000000	2.5260760000000
C35	4.2412140000000	1.4905330000000	3.1526490000000
H36	1.9226000000000	-1.4478360000000	-3.6593320000000
H37	1.6067170000000	-2.9201850000000	-2.6951960000000
H38	0.4909940000000	-2.4407050000000	-4.0626280000000
H39	-0.7789630000000	-6.2423430000000	0.6547650000000
H40	-1.4053590000000	-8.6179270000000	0.4032590000000
H41	-3.5670010000000	-9.4405680000000	1.2912120000000
H42	-5.0956600000000	-7.8859140000000	2.4722270000000
H43	-4.4946680000000	-5.5062200000000	2.7243240000000
H44	0.0586780000000	-2.4762700000000	2.7624240000000
H45	1.9339880000000	-1.1258620000000	-0.4148080000000
H46	1.6832420000000	-2.6386760000000	0.4019600000000
H47	0.0138660000000	0.5998060000000	-0.4735640000000
H48	-0.6475450000000	0.3640620000000	1.1393160000000
H49	-2.4931910000000	-0.8331510000000	-0.8296990000000
H50	-5.0075970000000	-0.0965210000000	-0.2999140000000
H51	-4.2729240000000	-1.3138370000000	0.8090180000000
H52	-5.1432180000000	0.1099820000000	1.4873540000000

H53	-3.7270320000000	1.8197950000000	2.2152000000000
H54	-2.0688660000000	2.1437510000000	1.4510290000000
H55	-3.2704890000000	1.1216350000000	-2.0423220000000
H56	-1.6150700000000	0.6406980000000	-2.4876180000000
H57	-2.4099510000000	3.1412830000000	-0.7873830000000
H58	-0.3803200000000	4.0304630000000	-1.7172070000000
H59	0.0034870000000	2.3887270000000	-2.5225460000000
H60	1.0350230000000	-0.3158900000000	2.2153890000000
H61	1.9171420000000	-0.6401760000000	4.5400350000000
H62	2.7193890000000	-2.1937480000000	4.9850220000000
H63	3.6559680000000	-0.9643580000000	4.1228930000000
H64	2.8931990000000	0.5710700000000	0.5371120000000
H65	3.9923350000000	-0.5046910000000	1.4483470000000
H66	2.2109940000000	1.7574810000000	2.7296840000000
H67	4.2553870000000	2.3068260000000	3.8675800000000
H68	5.1576490000000	0.9410390000000	2.9648840000000
H69	0.9506430000000	-3.3330440000000	4.1298610000000
H70	1.1633120000000	-3.8853210000000	2.4421100000000
H71	3.0747800000000	-2.6108940000000	2.4756650000000
B72	-1.9308590000000	-2.4089960000000	3.2888770000000
F73	-1.6071860000000	-2.2731500000000	4.6572430000000
F74	-3.0102760000000	-1.5263620000000	3.0726410000000

BF_2-(-)-**8**

C1	-1.8408264699815	1.9390034351428	-1.3379512121356
C2	-1.4552376803146	0.4516131157535	-1.1970689164244
C3	-1.5872934406807	2.7753184139349	-0.0892891329643
C4	-1.9279484560748	-0.1297835726714	0.1621062682167
C5	-2.1027137922815	-0.2695546867486	-2.3754201749126
C6	0.0947725177119	0.2668984579085	-1.3046911612268
O7	-1.7114979767714	0.7031875216725	1.2778342670668
C8	-2.5090104618686	-1.3652393199210	0.2695830892823
C9	-2.1976383466042	2.0668537049882	1.1508819494030
C10	-1.8848768779173	2.9511941489001	2.3773328134222
C11	-3.7424167744383	1.9896736399998	1.0649844358223
C12	-0.0966340311482	3.2026789371077	0.0343737023379
C13	-2.8232506403164	-1.3980926299296	-2.2623960056789
O14	-1.8814769357198	0.3915549163499	-3.5661238158735
C15	-3.0201648421113	-2.0458609093225	-0.9683380661524
O16	-3.6672354987965	-3.0902861188131	-0.9688763254772
C17	-2.6725873216415	-2.0324463642117	1.6030747560908
O18	-2.4889644690398	-1.4189598653353	2.6337497195938
C19	-2.9755279582206	-3.4855382918084	1.7414248248898
C20	-2.1632740879845	-4.4744433831742	1.1389901088059
C21	-4.0734097632858	-3.8814236442841	2.5370176085016
C22	-4.3855486105697	-5.2465596436428	2.6909434909388
C23	-3.5922957226829	-6.2250643119144	2.0624139847195
C24	-2.4788108594521	-5.8395372923510	1.2912012103697

C25	0.0899167236685	4.6617428031720	0.4058179785359
C26	0.6316156777272	5.5842760311599	-0.4032127161795
C27	0.6936973929491	-1.1741347636596	-1.3523864817989
C28	2.1778006780836	-1.1592473020352	-0.9204825226883
C29	0.5378184579251	-1.8872480725627	-2.6998114169326
C30	2.7695590552254	-2.5498878964746	-0.7797566444511
C31	3.1789622615526	-3.0868405772789	0.3796471791213
C32	1.1093594909375	-1.1973571289688	-3.9272962063912
C33	-0.0613536824790	-3.0866061146035	-2.7994581690402
C34	-2.3793229527772	-0.1902106371330	-4.7641568146094
B35	-1.1387782539207	0.1743338719820	2.9566290378768
F36	-1.2069463225514	0.7948276695490	4.3144966151270
F37	0.1088899026267	-0.2560155311476	3.4672706011479
H38	-2.9016396612980	2.0081671597310	-1.5810887933520
H39	-1.3391125967923	2.3926495773698	-2.1941244108574
H40	-2.1490304094851	3.6978502963992	-0.2481628551331
H41	0.5324422266748	0.7342407360275	-0.4279029536324
H42	0.4778724744773	0.8485332067565	-2.1421796425172
H43	-0.8238346174492	2.9704439402808	2.6144998717581
H44	-2.1898178060900	3.9821394868634	2.1970328312130
H45	-2.4183614132409	2.6592840551771	3.2738284698889
H46	-4.1834767854023	2.9835633900685	0.9822380500954
H47	-4.1042279072390	1.4108615151734	0.2172274882540
H48	-4.1616856591612	1.5275647352991	1.9588396179479
H49	0.4218523192729	3.0493119088768	-0.9120480083102
H50	0.4364792054332	2.5918714760148	0.7633375131216
H51	-3.2746142795704	-1.8866547995974	-3.1108875248072
H52	-1.3053418230133	-4.1944030762185	0.5458694522380
H53	-4.6867506238143	-3.1389117140515	3.0285275812550
H54	-5.2341704419396	-5.5430870578312	3.2915935066172
H55	-3.8350579899070	-7.2723718149704	2.1775932765959
H56	-1.8686019773107	-6.5931758468991	0.8144424440693
H57	-0.2343106363997	4.9596651792461	1.3918321290260
H58	0.7461862362467	6.6084299379276	-0.0785128156549
H59	0.9700366589941	5.3333254831538	-1.3980839478275
H60	-0.4353150000000	-1.0362680000000	3.8747630000000
H61	0.1769310465181	-1.7696138407611	-0.6002981454232
H62	2.2878208692626	-0.6463109039883	0.0350705620441
H63	2.7814593696438	-0.5908918191039	-1.6281750681303
H64	2.8581555908157	-3.1289438565903	-1.6885184062882
H65	3.5938692989089	-4.0837801259438	0.4155506660341
H66	3.1065906382341	-2.5411545352379	1.3097352802994
H67	0.6281543364190	-0.2362762944184	-4.1011715536245
H68	2.1800808112724	-1.0295263764597	-3.8149489047837
H69	0.9652330109511	-1.8009512264954	-4.8238139253844
H70	-0.1625949812531	-3.5865557496855	-3.7517805007502
H71	-0.4587455857235	-3.5947589412192	-1.9331794654028
H72	-2.0880316196474	0.4318444896317	-5.6107696854193
H73	-1.9615281790418	-1.1843320922578	-4.9311105991974
H74	-3.4685015473557	-0.2496427910009	-4.7601153158664

BF_2-(+)-**13**

C1	-0.9109090000000	1.7894970000000	-0.0255870000000
C2	-0.4228070000000	0.3423690000000	0.1681770000000
C3	-0.9140380000000	-0.4217020000000	-1.0667420000000
O4	-0.4706590000000	0.0746270000000	-2.3516390000000
C5	-0.9568940000000	1.4315180000000	-2.6029610000000
C6	-0.5569740000000	2.3846810000000	-1.4028550000000
C7	-0.9972040000000	-0.1140510000000	1.5227600000000
C8	-1.9249800000000	-1.1005430000000	1.5856950000000
C9	-2.3358740000000	-1.8428040000000	0.3954850000000
C10	-1.7362230000000	-1.5277080000000	-0.9150780000000
C11	-2.0239830000000	-2.3509890000000	-2.1178660000000
O12	-1.4254480000000	-1.8988960000000	-3.0573370000000
C13	-2.4697030000000	-3.7598580000000	-2.1335300000000
C14	-3.3301570000000	-4.2033810000000	-3.1491290000000
C15	-3.7269320000000	-5.5439790000000	-3.2026510000000
C16	-3.2546390000000	-6.4521920000000	-2.2502670000000
C17	-2.3832750000000	-6.0214320000000	-1.2465230000000
C18	-1.9881490000000	-4.6828890000000	-1.1907270000000
O19	-3.2620830000000	-2.6409840000000	0.4821040000000
C20	-0.2510900000000	2.0233470000000	-3.8765830000000
C21	-2.5075800000000	1.4581100000000	-2.8012600000000
C22	-1.1736410000000	3.8186470000000	-1.4807470000000
C23	-0.3158500000000	4.8151170000000	-0.7433120000000
C24	-0.7252600000000	5.4137400000000	0.3776820000000
C25	1.1474490000000	0.3111620000000	0.2213120000000
C26	1.8171430000000	-0.9209540000000	0.8980970000000
C27	3.3536450000000	-0.7442130000000	0.9050090000000
C28	4.0345640000000	-1.8078590000000	1.7271280000000
C29	4.7996320000000	-2.7505590000000	1.1697530000000
C30	1.4401640000000	-2.2540760000000	0.2640160000000
C31	0.9676730000000	-3.3710710000000	1.1599000000000
C32	1.6725600000000	-2.4968210000000	-1.0364410000000
O33	-0.6064910000000	0.6505430000000	2.6344560000000
C34	-0.8018630000000	0.0152870000000	3.8798290000000
H35	-0.4797820000000	2.4428240000000	0.7651110000000
H36	-2.0147090000000	1.8198040000000	0.1129660000000
H37	0.5519530000000	2.4874280000000	-1.4354240000000
H38	-2.4102820000000	-1.3744790000000	2.5154290000000
H39	-3.6970160000000	-3.5100680000000	-3.8961270000000
H40	-4.4012940000000	-5.8781410000000	-3.9797360000000
H41	-3.5563850000000	-7.4912070000000	-2.2922900000000
H42	-2.0154230000000	-6.7212820000000	-0.5068420000000
H43	-1.2999550000000	-4.3696860000000	-0.4209830000000
H44	0.0413820000000	3.0858420000000	-3.7858560000000
H45	0.7005570000000	1.4913280000000	-4.0781820000000
H46	-0.8945020000000	1.9640970000000	-4.7789940000000
H47	-2.8511700000000	2.4609910000000	-3.1325390000000
H48	-2.8482160000000	0.7382860000000	-3.5685470000000
H49	-3.0418370000000	1.2054390000000	-1.8641680000000
H50	-2.2098140000000	3.8161990000000	-1.0750950000000
H51	-1.2756150000000	4.1833820000000	-2.5192540000000
H52	0.6676340000000	5.0546430000000	-1.1376530000000

H53	-0.0817450000000	6.1332580000000	0.8730540000000
H54	-1.6932850000000	5.1863630000000	0.8129820000000
H55	1.4903030000000	1.2012260000000	0.7923920000000
H56	1.5708920000000	0.4391800000000	-0.7989110000000
H57	1.4964500000000	-0.9290170000000	1.9630630000000
H58	3.6181560000000	0.2395190000000	1.3489150000000
H59	3.7431790000000	-0.7415730000000	-0.1373250000000
H60	3.8975460000000	-1.8046340000000	2.8045160000000
H61	5.2801250000000	-3.4982440000000	1.7920090000000
H62	4.9459820000000	-2.7941260000000	0.0954140000000
H63	0.0149330000000	-3.0875500000000	1.6477220000000
H64	0.8141240000000	-4.3203430000000	0.6035800000000
H65	1.7232490000000	-3.5607080000000	1.9496060000000
H66	1.4623850000000	-3.4673090000000	-1.4745720000000
H67	2.0993050000000	-1.7339200000000	-1.6782280000000
H68	-0.2142840000000	0.5634690000000	4.6453530000000
H69	-1.8679570000000	0.0758520000000	4.1847360000000
H70	-0.4353150000000	-1.0362680000000	3.8747630000000
B71	-0.5613150000000	-0.9116200000000	-3.4957360000000
F72	0.7103420000000	-1.4289300000000	-3.8176370000000
F73	-1.1174200000000	-0.3951790000000	-4.6862130000000
H74	0.5029100000000	-1.3489980000000	-3.7563800000000