Supporting Information

Regiodivergent Photocyclization of Dearomatized Acylphloroglucinols: Asymmetric Syntheses of (–)-Nemorosone and (–)-6-*epi*-Garcimultiflorone A

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I. General Information

A. Instrumentation and Methods

All NMR spectra were obtained in chloroform-*d* ($CDCl_3$) or methanol-d_4 (CD_3OD) from Cambridge Isotope Laboratories, Inc. at ambient temperatures using a Varian 400 MHz or 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the internal solvent peak (Chloroform-*d*: δ 7.26 for ^{1}H; δ 77.16 for ^{13}C. Methanol-d_4: δ 3.31 for ^{1}H; δ 49.00 for ^{13}C). Data for ^{1}H NMR are reported as follows: chemical shift, multiplicity (*br* = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, and integration. All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared spectra were recorded on a Bruker ALPHA P FT-IR spectrometer equipped with a diamond ATR module. High-resolution mass spectra were obtained at the Boston University Chemical Instrumentation Center using a Waters Q-TOF mass spectrometer. Melting points were recorded on a Mel-temp apparatus (Laboratory Devices) and are uncorrected. Analytical LCMS was performed on a Waters Acquity UPLC (Ultra Performance Liquid Chromatography (Waters MassLynx Version 4.1) with a Binary solvent manager, SQ mass spectrometer, Waters 2996 PDA (PhotoDiode Array) detector, and ELSD (Evaporative Light Scattering Detector). An Acquity UPLC BEH C18 1.7 μm column was used for analytical UPLC-MS. Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F plates (Merck KGaA). Preparative HPLC was performed on a Gilson PLC2020 using a Waters SunFire™ Prep C18 OBD™ 5 μm 19 × 50 mm column. Flash chromatography was performed using ZEOprep 60 Eco 40–63 μm silica gel (Zeochem AG). Preparative TLC was conducted with glass-backed 250 μm silica gel 60-F plates (Merck KGaA). Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Optical rotations were recorded on an AUTOPUL III digital polarimeter at 589 nm and are recorded as $[\alpha]_D^{temp.}$ (concentration in grams/100 mL solvent). Chiral HPLC analysis of enantioenriched compounds was performed using a Waters 1525 Binary HPLC Pump with a Waters 2487 diode array detector. A CHIRAL® OD-H [Chiral Technologies Inc., 150 × 4.60 mm

(L × I.D.)] column was used for enantiomeric excess determination. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise noted. The Scilligence ELN Reaction Planner (Scilligence Corp.) was used for experimental procedure planning.

B. Reagents and Solvents

HPLC grade methylene chloride and acetonitrile were purchased from Fisher and methylene chloride was purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology, Inc.). Anhydrous acetonitrile for photoreactions was purchased from Sigma Aldrich and was used as received. Spectrophotometric grade solvents for photophysical experiments were purchased from Sigma Aldrich and was used as received, including acetonitrile, methylcyclohexane, and ethanol. All other reagents were purchased and used as received from Alfa Aesar, Oakwood Chemical, Sigma Aldrich, Strem, and TCI America.

C. Photoreaction Setup

Rayonet Recirculating Flow Reactor:

The flow system is described in detail in our literature reference.[S1]

Plain Flow Photoreactor I:

An LED flow reactor was constructed using PTFE tubing (Cole-Parmer Instrument Company, 1/32"ID x 1/16"OD) twined into a plate shape on an aluminum support (**Figure S1A**). Available tubing volume was measured to be 2.7 mL. The reactor was placed in a flammable cabinet equipped with a purple LED lamp (Kessil®, 40 W, λ_{em} = 370–420 nm, λ_{peak} = 390 nm) and a fan (**Figure S1B**). The inlet of tubing was connected to a syringe pump (KD Scientific, LEGATO 100 Syringe Pump). Connecting parts were all purchased from IDEX Health & Science.

Temperature-Controlled Flow Photoreactor II:

A temperature-controlled flow reactor was constructed using PTFE tubing twined onto a beaker (**Figures S2A** and **B**). The beaker was placed in a slightly larger plastic container and the top was sealed with hot glue. The available tubing volume was measured to be 6.0 mL. The interlayer is connected to a circular chiller with glycol controlling the reactor temperature. A small convex mirror was placed at the bottom of the reactor in order to improve light focusing efficiency. The reactor was placed in a flammable cabinet equipped with a purple LED lamp (**Figure S2C**) on top. The tubing inlet was finally connected to a syringe pump.

Batch Reactor III:

A batch photochemical reactor was built in a flammable cabinet with a stirring plate and a purple LED lamp (**Figure S3**). A fan was placed above the lamp to prevent overheating. Meanwhile, a large piece of aluminum foil was placed behind the test tubes to enhance light focusing. Reaction Pyrex® tubes were placed on the stirring plate with a tube rack; the distance between the tubes and lamp was kept within 5 cm.

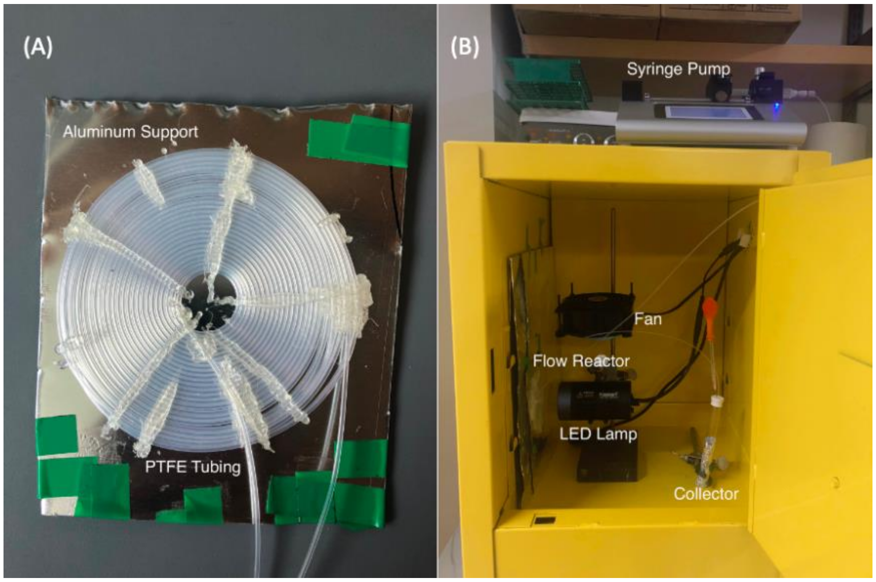


Figure S1. Plain flow photoreactor I.

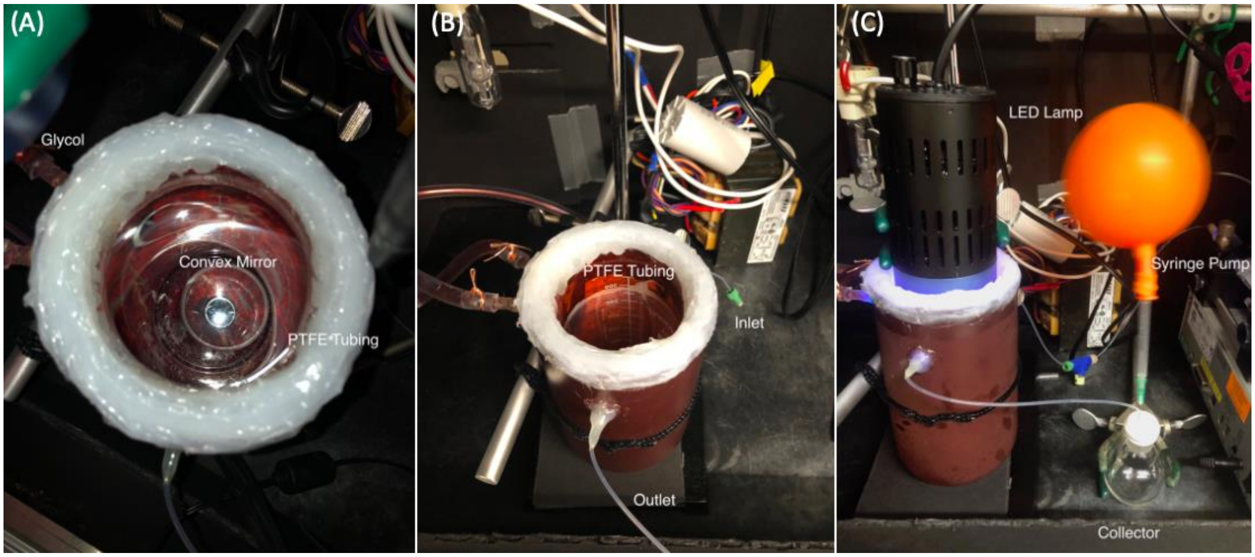


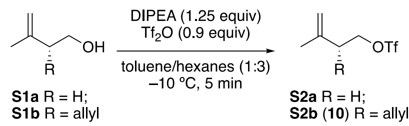
Figure S2. Temperature-controlled flow photoreactor II.

Figure S3. Batch reactor III.

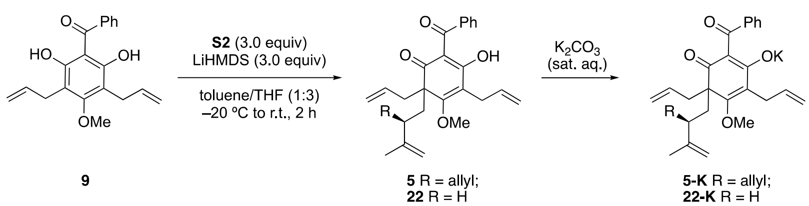
II. Experimental Procedures and Compound Characterization

A. Dearomatization

Experimental Procedure: The procedure was followed and modified according to literature references.[S2–4]

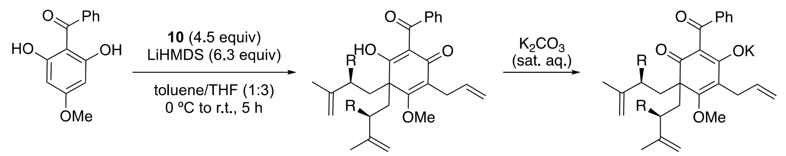


General Procedure for the Synthesis of Alkyl Triflates:[S2,3] To a flame-dried flask containing alcohol **S1** (1.0 equiv) was added toluene and hexane (1:3, 0.4 M) and diisopropylethylamine (DIPEA, 1.25 equiv) under argon. The solution was cooled to –10 ºC, and trifluoromethanesulfonic anhydride (Tf_2O, 0.9 equiv) was then added in one portion. The reaction mixture was allowed to stir for 5 min before it was quickly filtered through a cotton plug. The clear solution of primary alkyl triflate **S2** was then used immediately without further purification.



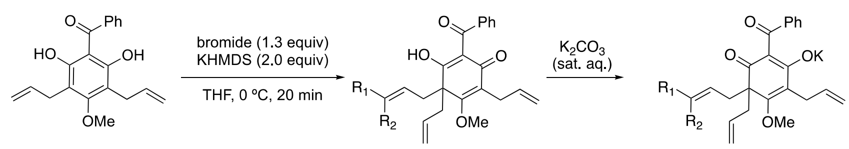
General Dearomatization Procedure A:[S2] To a flame-dried 50-mL round-bottom flask with benzoylated phloroglucinol derivative **9**[S2] (162 mg, 0.5 mmol) was added a mixture of toluene and THF (8 mL, 1:3, 62.5 mM) under argon, and the mixture was then cooled to –20 ºC. A solution of LiHMDS (1.0 M in THF, 1.47 mL, 3.0 equiv) was added over the course of 2 min leading to a homogeneous dark-red solution. After the mixture was stirred for 5 min, the solution of triflate **S2** (3.0 equiv) was added dropwise at a steady rate. The reaction was allowed to warm to r.t. and was stirred for 2 h. After completion, the reaction was quenched with 1 *N* HCl solution, poured into water, and extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The dearomatized compound was then dissolved in *n*-pentane and was washed with saturated K_2CO_3

aqueous solution to afford its potassium salt as a yellow precipitate. This potassium salt was used for characterization purposes.



S3 **14** R = allyl **14-K** R = allyl

General Dearomatization Procedure B:[S3] To a flame-dried, argon-charged 50-mL round-bottom flask with phloroglucinol derivative **S3**[S2] (244 mg, 1.0 mmol) was added a mixture of toluene and THF (16 mL, 1:3, 62.5 mM) under argon, and the mixture was then cooled to 0 ºC. A solution of LiHMDS (1.0 M in THF, 6.3 mL, 6.3 equiv) was added over the course of 5 min. To the mixture was then added triflate **10** (4.5 equiv) in two portions at a steady rate. The mixture was allowed to warm to room temperature after the completion of addition and stirred for 5 h. The reaction was quenched with 1 *N* HCl solution (50 mL), diluted with water (100 mL), and was extracted with diethyl ether (50 mL × 3). The combined organic layers were washed with 1 *N* HCl solution, water, and brine. The organic solution was then dried over anhydrous Na_2SO_4, filtered, and was concentrated *in vacuo*. Purification by silica flash chromatography (EtOAc/hexanes) provided the desired dearomatized compound. The dearomatized compound was then dissolved in *n*-pentane and washed with saturated K_2CO_3 aqueous solution to afford its potassium salt as a yellow precipitate which was used for characterization purposes.



9

25 R_1 = Ph, R_2 = H
27 R_1 = R_2 = Me

25-K R_1 = Ph, R_2 = H
27-K R_1 = R_2 = Me

General Dearomatization Procedure C:[S4] To a solution of **9** (150 mg, 0.46 mmol, 1.0 equiv) in THF (5 mL) was added KHMDS (1 M, 0.92 mL, 2.0 equiv) at 0 ºC under argon. After 2 min, an allylic bromide (1.3 equiv) was added dropwise as a solution in benzene (450 mg/mL). After 20 min, the reaction was poured into saturated aqueous NH_4Cl (10 mL) and the mixture was extracted three times with diethyl ether (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (EtOAc/hexanes: 5/95 to 25/75) to afford desired product. The dearomatized product was then dissolved in *n*-pentane and washed with saturated K_2CO_3

aqueous solution to afford its potassium salt as a yellow precipitate. This potassium salt was used for characterization purposes.

Dearomatized Substrate 5:[S2] 180 mg, 83% yield; slightly yellow oil; R_f = 0.32 (EtOAc/hexanes: 10/90); ^{1}H NMR (*potassium enolate form; 1.3:1 mixture of diastereomers as determined by ^{1}H NMR analysis*, CD_3OD, 400 MHz): δ 7.77–7.73 (m, 1.8H), 7.40–7.37 (m, 1.0H), 7.31–7.28 (m, 1.9H), 6.00–5.93 (m, 1.1H), 5.78–5.69 (m, 1.1H), 5.65–5.56 (m, 1.1H), 5.10–5.01 (m, 2.1H), 4.95–4.93 (m, 2.2H), 4.89–4.80 (m, 2.6 H), 4.60–4.56 (m, 1.7H), 3.96 (s, 1.0H), 3.91 (s, 1.3H), 3.22–3.12 (m, 2.0H), 2.62–2.56 (m, 1.2H), 2.50–2.42 (m, 1.2H), 2.24–2.18 (m, 1.8H), 2.07–1.92 (m, 2.8H), 1.84–1.65 (m, 1.2H), 1.60–1.57 (m, 2.5H), 1.29–1.25 (m, 1.2H).

Dearomatized Substrate 14:[S3] 217 mg, 46% yield; beige amorphous solid; R_f = 0.20 (EtOAc/hexanes: 10/90); ^{1}H NMR (*potassium enolate form*, CD_3OD, 500 MHz): δ 7.77 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 7.5 Hz, 2H), 5.64–5.56 (m, 2H), 5.21 (s, 1H), 4.91–4.82 (m, 4H), 4.61 (d, J = 3.6 Hz, 2H), 3.52 (s, 3H), 2.24–2.19 (m, 2H), 2.15–2.10 (m, 2H), 2.00–1.94 (m, 2H), 1.88 (dd, J = 13.5, 7.5 Hz, 2H), 1.82 (dd, J = 13.0, 2.0 Hz, 2H), 1.59 (s, 6H).

Dearomatized Substrate 22: 133 mg, 69% yield; slightly yellow oil; R_f = 0.45 (EtOAc/hexanes: 10/90); ^{1}H NMR (*potassium enolate form*, CD_3OD, 400 MHz): δ 7.79 (d, J = 7.2 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.2 Hz, 2H), 6.01–5.91 (m, 1H), 5.79–5.69 (m, 1H), 5.05 (td, J = 15.2, 2.0 Hz, 2H), 4.96 (td, J = 9.6, 1.6 Hz, 2H), 4.63 (s, 2H), 3.91 (s, 3H), 3.20 (d, J = 5.6 Hz, 2H), 2.64–2.58 (m, 1H), 2.53–2.48 (m, 1H), 2.04–1.95 (m, 2H), 1.88–1.81 (m, 2H), 1.68 (s, 3H); ^{13}C NMR (CD_3OD, 101 MHz): δ 201.1, 192.0, 187.5, 169.6, 147.2, 142.5, 139.0, 135.9, 132.2, 130.1, 128.7, 123.3, 117.3, 116.9, 114.7, 109.9, 62.7, 57.6, 43.9, 37.5, 34.0, 29.4, 22.8; $IR_{\upsilon max}$ (Diamond ATR): 2930, 1634, 1600, 1516, 1429, 1343, 1225, 1133, 993, 917, 696, 634 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{25}H_{29}O_4$: 393.2066, Found: 393.2055.

Dearomatized Substrate 25:[S4] 144 mg, 71% yield; colorless oil; R_f = 0.44 (EtOAc/hexanes: 25/75); ^{1}H NMR (*potassium enolate form*, CD_3OD, 500 MHz): δ 7.70 (t, J = 7.5 Hz, 2H), 7.31–7.24 (m, 5H), 7.18 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 2H), 6.42 (d, J = 16.0 Hz, 1H), 6.17 (dt, J = 16.0, 7.0 Hz, 1H), 5.94–5.86 (m, 1H), 5.77–5.69 (m, 1H), 5.04 (td, J = 14.0, 1.5 Hz, 2H), 4.95 (d, *J* = 10.5 Hz, 1H), 4.86 (dd, *J* = 9.5, 2.0 Hz, 1H), 3.97 (s, 3H), 3.19 (ddd, *J* = 30.5, 16, 5.5 Hz, 2H), 2.77–2.66 (m, 3H), 2.55 (dd, *J* = 13.0, 8.0 Hz, 1H); ^{13}C NMR (CD_3OD, 126 MHz) δ 201.4, 191.4, 187.4, 169.5, 142.3, 139.1, 138.9, 135.9, 133.4, 132.1, 130.2, 129.4, 128.7, 128.0, 127.3, 127.2, 122.8, 117.2, 117.0, 114.7, 62.7, 58.1, 43.3, 42.5, 29.2.

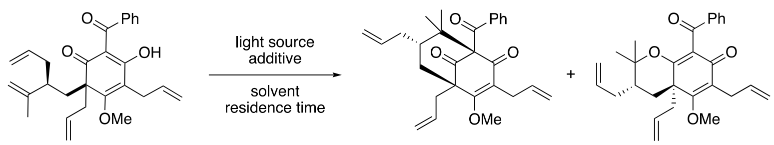
Dearomatized Substrate 27: 87 mg, 48% yield; colorless oil; R_f = 0.54 (EtOAc/hexanes: 25/75); ^{1}H NMR (*potassium enolate form*, CD_3OD, 500 MHz): δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.30 (t, *J* = 7.0 Hz, 2H), 5.86–5.89 (m, 1H), 5.74–5.65 (m, 1H), 5.09–5.00 (m, 3H), 4.92 (d, *J* = 10 Hz, 2H), 3.23–3.14 (m, 2H), 2.64 (dd, *J* = 12.5, 5.5 Hz, 1H), 2.56–2.45 (m, 3H), 1.66 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (CD_3OD, 126 MHz): δ 201.0, 192.2, 187.7, 169.9, 142.6, 139.0, 136.1, 133.7, 132.0, 130.2, 128.6, 122.8, 121.7, 117.1, 116.8, 114.5, 62.5, 57.6, 43.3, 37.9, 29.3, 26.1, 18.3; $IR_{\upsilon max}$ (Diamond ATR): 2917, 1640, 1516, 1428, 1228, 1134, 993, 918, 696 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{25}H_{29}O_4$: 393.2066, Found: 393.2051.

B. Photocyclization of Dearomatized Substrate and Condition Optimization

General Experimental Procedure A using Flow Photoreactor I: Dearomatized substrate (20 mg) and additive were dissolved in anhydrous solvent and the mixture was degassed using sonication for 30 min before being taken up into a syringe. The reaction mixture was then injected in the flow photoreactor **I** with a syringe pump at a constant rate which was followed by a flush of the corresponding solvent at the same rate until all of the reaction solution was eluted from the flow reactor and collected. The solvent was then removed *in vacuo* and the resulting residue was purified by silica flash chromatography or preparative thin-layer chromatography (EtOAc/hexanes). Unless otherwise noted, all the photoreactions were conducted using these general conditions.

General Experimental Procedure B using Flow Reactor II: Dearomatized substrate (20 mg) was dissolved in anhydrous acetonitrile (5 mM) and the mixture was degassed using sonication for 30 min before taken into a syringe. The reaction mixture was then injected in the flow photoreactor **II** with a syringe pump at a constant rate (16.67 μL/min, t_R = 6 h) which was followed by a flush with acetonitrile at the same rate until all of the reaction solution was eluted from the flow reactor and collected. The chiller was able to keep the reaction temperature at 10 ºC. The solvent was then removed *in vacuo* and the resulting residue was purified by silica flash chromatography or preparative thin-layer chromatography (EtOAc/hexanes).

Table S1. Condition screening for the photocyclization of 5.



Entry	Light Source λ_{max} (nm)	Solvent (mM)	Additive (mol%)	Residence Time t_R (h)	Yield[a] (%)
1[b]	350	CH_3CN (0.5)	n/a	12	(–)-**8**: 16, **11**: 12
2	390	CH_3CN (5)	n/a	2	(–)-**8**: 22.5, **11**: 7
3	427	CH_3CN (5)	n/a	2	n.r.[c]
4	metal halide	CH_3CN (5)	n/a	2	(–)-**8**: 9
5	390	toluene (5)	n/a	2	n.r.
6	390	CH_2Cl_2 (5)	n/a	2	(–)-**8**: 5
7	390	CH_2Cl_2/TFE (5)	n/a	2	trace
8	390	THF (5)	n/a	2	n.r.
9	390	CH_3CN (5)	n/a	1	trace
10	390	CH_3CN (5)	n/a	4	(–)-**8**: 24, **11**: 6
11	390	CH_3CN (5)	n/a	8	decomp.
12[d]	370	CH_3CN (5)	thioxanthone[e] (5)	0.5	decomp.
13[d]	390	CH_3CN (5)	dibromothioxanthone[e] (5)	0.5	decomp.
14	**390**	**CH_3CN (1)**	**n/a**	**4**	(–)-**8: **29**, 11: **10
15	390	CH_3CN (10)	n/a	4	(–)-**8**: 19, **11**: 9
16[f]	n/a	1,4-dioxane	n/a	36	n.r.

[a]Isolated yield; [b]Reaction was conducted in Rayonet flow system (see S1) around –20 ºC for 12 h; [c]n.r.: No reaction; [d]Reaction was conducted as a batch process for 0.5 h (see general procedure C); [e]For more details about thioxanthone and its derivatives, see reference S5; [f]Thermal control conditions.

General Experimental Procedure C in Batch: To a flame-dried test tube was added dearomatized substrate (20 mg) and anhydrous acetonitrile (5 mM) and the mixture was degassed using sonication for 30 min. After degassing, the test tube was placed in front of a Kessil® LED lamp and was allowed to stir for 36 h at room temperature. After the completion, the solvent was removed *in vacuo* and the residue was purified by silica flash chromatography or preparative thin-layer chromatography (EtOAc/hexanes).

Control Experiment under Thermal Conditions (Conia-Ene Conditions): To an oven-dried microwave reaction vial was added dearomatized substrate **5** (20 mg) and anhydrous 1,4-dioxane (5 mM) and the mixture was degassed using sonication for 10 min. After degassing, the vial was sealed with a polyethylene snap cap was placed in microwave (CEM Discover SP, 300 W) and was heated to 100 ºC/300 psi for 1 h. After cooling of the microwave reactor, the solvent was removed *in vacuo* and the residue was purified by preparative thin-layer chromatography (EtOAc/hexanes).

PPAP Core (–)-8: colorless oil; R_f = 0.30 (EtOAc/hexanes: 10/90); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (dd, J = 8.5, 1.0 Hz, 2H), 7.38 (tt, J = 7.5, 1.0 Hz, 1H), 7.24 (td, J = 7.5, 0.5 Hz, 2H), 5.86–5.74 (m, 2H), 5.69–5.61 (m, 1H), 5.17 (dd, J = 17.5, 2.0 Hz, 1H), 5.11–5.01 (m, 5H), 4.08 (s, 3H), 3.37 (ddt, J = 16.0, 6.5, 1.5 Hz, 1H), 3.24 (ddt, J = 16.0, 6.0, 1.5 Hz, 1H), 2.71 (dd, J = 14.0, 6.0 Hz, 1H), 2.51 (dd, J = 13.5, 7.5 Hz, 1H), 2.38–2.34 (m, 1H), 2.06 (dd, J = 14.0, 4.0 Hz, 1H), 1.77–1.07 (m, 2H), 1.54–1.47 (m, 1H), 1.34 (s, 3H), 1.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 206.7, 193.7, 192.9, 173.0, 136.7, 136.2, 135.4, 133.5, 132.0, 128.4, 127.9, 123.4, 118.8, 117.0, 115.8, 79.1, 62.4, 59.4, 48.7, 42.3, 40.2, 35.1, 32.8, 28.2, 23.3, 15.8; IR$_{\upsilon max}$ (Diamond ATR): 2942, 1724, 1699, 1642, 1597, 1447, 1341, 1240, 917, 735 cm^{-1}; HRMS (ESI): [M + H]$^+$ Calcd. For $C_{28}H_{33}O_4$: 433.2379, Found: 433.2384; $[\alpha]_D^{23}$ = –74.9 (c = 0.200, $CHCl_3$).

***O*-Cyclized Byproduct 11:**[S2] colorless oil; R_f = 0.15 (EtOAc/hexanes: 10/90); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (dd, J = 8.0, 1.6 Hz, 2H), 7.51 (tt, J = 7.2, 2.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 2H), 5.95–5.85 (m, 1H), 5.75–5.58 (m, 2H), 5.17–4.98 (m, 6H), 3.98 (s, 3H), 3.22 (d, J = 6.4 Hz, 2H), 2.76–2.66 (m, 2H), 2.47 (dd, J = 14.4, 4.0 Hz, 1H), 2.22–2.16 (m, 1H), 1.81–1.73 (m, 1H), 1.67–1.59 (m, 1H), 1.55–1.50 (m, 1H), 1.28 (s, 3H), 1.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 194.6, 186.4, 171.4, 169.9, 137.8, 136.5, 136.0, 133.2, 132.4, 129.5, 128.4, 126.0, 121.0, 119.8, 117.4, 115.2, 88.3, 62.3, 49.8, 46.6, 42.7, 35.6, 33.9, 28.7, 28.4, 21.8.

PPAP Core (–)-15: 10.9 mg, 54% yield; white solid, m. p.: 133–135 ºC (EtOAc/hexanes: 20/80); R_f = 0.50 (EtOAc/hexanes: 25/75); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.63 (dd, J = 7.5, 1.0 Hz, 2H), 7.43 (tt, J = 7.0, 1.0 Hz, 1H), 7.31 (t, J = 7.5 Hz, 2H), 5.88 (s, 1H), 5.65–5.56 (m, 2H), 5.03–4.90 (m, 4H), 4.64 (dd, J = 23.0, 2.0 Hz, 2H), 3.74 (s, 3H), 2.39–2.32 (m, 2H), 2.17–1.98 (m, 4H), 1.84–1.78 (m, 2H), 1.74–1.67 (m, 1H), 1.65 (s, 3H), 1.44–1.36 (m, 1H), 1.39 (s, 3H), 1.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 207.5, 193.1, 177.0, 148.4, 136.97, 136.96, 136.4, 132.4, 128.6, 128.1, 117.0, 115.7, 110.8, 105.6, 79.7, 57.7, 55.8, 48.9, 44.7, 42.2, 41.7, 39.5, 33.6, 33.0, 23.7, 17.3, 15.9; $IR_{\upsilon max}$ (Diamond ATR): 2936, 1721, 1697, 1642, 1600, 1449, 1373, 1238, 910, 735 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{30}H_{37}O_4$: 461.2692, Found: 461.2693; $[\alpha]_D^{24}$ = –59.3 (c = 0.100, $CHCl_3$).

***O*-Cyclized Byproduct 16:**[S3] 2.2 mg, 11% yield; white amorphous solid; R_f = 0.16 (EtOAc/hexanes: 25/75); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.53 (tt, *J* = 7.0, 1.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 5.71–5.59 (m, 2H), 5.49 (s, 1H), 5.07–4.96 (m, 4H), 4.66 (d, *J* = 32.0 Hz, 2H), 3.63 (s, 3H), 2.45 (dd, *J* = 14.0 Hz, 1H), 2.21–2.14 (m, 2H), 2.09–1.97 (m, 4H), 1.77–1.71 (m, 1H), 1.67–1.61 (m, 1H), 1.62 (s, 3H), 1.57–1.51 (m, 1H), 1.26 (s, 3H), 1.10 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 194.5, 186.1, 175.0, 169.7, 146.9, 137.8, 136.6, 135.9, 133.3, 129.4, 128.6, 126.5, 117.4, 116.5, 111.7, 103.2, 88.6, 55.5, 47.7, 44.7, 42.6, 42.5, 40.0, 36.2 35.7, 29.0, 21.9, 19.3.

de Mayo Product 17: 1.4 mg, 7%; 4.0 mg, 80% yield (from further treatment of 5.0 mg of the *O*-cyclized byproduct **16**); white solid, m. p.: 155–158 ºC (EtOAc/hexanes: 20/80); R_f = 0.27 (EtOAc/hexanes: 25/75); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 5.79–5.70 (m, 2H), 5.62 (s, 1H), 5.10–4.96 (m, 4H), 3.85 (s, 3H), 2.86 (d, *J* = 12.5 Hz, 1H), 2.59 (dd, *J* = 14.5, 2.5 Hz, 1H), 2.23–2.18 (m, 1H), 2.14–2.10 (m, 2H), 1.94–1.88 (m, 1H), 1.82–1.76 (m, 1H), 1.62–1.54 (m, 3H), 1.32–1.25 (m, 1H), 1.21 (s, 3H), 1.15 (t, *J* = 13.5 Hz, 1H), 0.92 (s, 3H), 0.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 196.4, 182.4, 138.2, 136.8, 136.5, 131.7, 129.4, 127.3, 116.4, 115.8, 101.7, 87.2, 75.0, 61.6, 56.7, 52.3, 48.0, 46.8, 44.9, 42.0, 35.6, 33.1, 28.6, 28.4, 27.9, 22.1, 19.8; $IR_{\upsilon max}$ (Diamond ATR): 3368, 2960, 1712, 1655, 1608, 1361, 1221, 1205, 913, 809, 720 cm^{-1}; HRMS (ESI): $[M + Na]^+$ Calcd. For $C_{30}H_{36}O_4Na$: 483.2511, Found: 483.2493; $[\alpha]_D^{23}$ = 130.2 (c = 0.100, $CHCl_3$).

PPAP Core 23: 5.4 mg, 27% yield; colorless oil; R_f = 0.40 (EtOAc/hexanes: 10/90); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.6

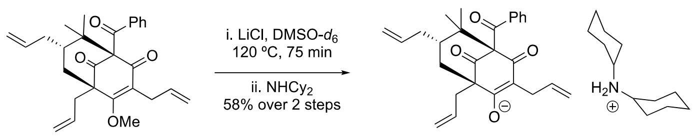
Hz, 2H), 5.90–5.74 (m, 2H), 5.19–5.04 (m, 4H), 4.12 (s, 3H), 3.40 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.26 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.74 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.53 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.93–1.78 (m, 3H), 1.35 (d, *J* = 13.2 Hz, 1H), 1.27 (s, 3H), 1.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 206.7, 193.6, 192.9, 172.2, 136.0, 135.6, 133.6, 132.0, 128.5, 127.9, 123.1, 118.7, 115.8, 78.9, 62.4, 59.4, 45.4, 36.7, 35.2, 34.6, 28.3, 25.8, 22.0; $IR_{\upsilon max}$ (Diamond ATR): 2927, 1721, 1696, 1642, 1596, 1238, 1225, 917, 688 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{25}H_{29}O_4$: 393.2066, Found: 393.2068.

de Mayo Product 26:[S4] 4.8 mg, 24% yield; colorless oil; R_f = 0.45 (EtOAc/hexanes: 25/75); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46–7.41 (m, 4H), 7.38–7.26 (m, 6H), 5.93–5.79 (m, 2H), 5.64 (s, 1H), 5.14 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 2H), 4.98 (dd, *J* = 17.5, 1.5 Hz, 1H), 4.03 (s, 3H), 3.61 (d, *J* = 9.0 Hz, 1H), 3.50 (td, *J* = 9.5, 4.5 Hz, 1H), 3.22 (ddd, *J* = 31.5 16.5, 5.5 Hz, 2H), 2.64 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.55 (dd, *J* = 15.0, 7.0 Hz, 1H), 2.31 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.05 (dd, *J* = 13.5, 4.5 Hz, 1H).

de Mayo Product 28: 2.6 mg, 13% yield; beige amorphous solid; R_f = 0.47 (EtOAc/hexanes: 25/75); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (d, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.0 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 5.93–5.78 (m, 2H), 5.17–5.06 (m, 4H), 4.98 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.01 (s, 3H), 3.18 (ddd, *J* = 38.5, 16.0, 5.0 Hz, 2H), 3.04–3.01 (m, 1H), 2.60 (ddd, *J* = 40.5, 14.5, 6.0 Hz, 2H), 2.07 (dd, *J* = 13.5, 5.0 Hz, 1H), 1.95 (dd, *J* = 13.5, 10.0 Hz, 1H), 1.41 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 201.7, 197.7, 178.4, 140.6, 135.6, 133.5, 127.7, 127.6, 127.5, 120.1, 118.9, 115.4, 83.3, 69.8, 63.8, 62.1, 48.7, 45.0, 32.7, 27.6, 27.2, 23.5, 21.3; $IR_{\upsilon max}$ (Diamond ATR): 2917, 1760, 1639, 1582, 1447, 1333, 1234, 988, 920, 700 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{25}H_{29}O_4$: 393.2066, Found: 393.2067.

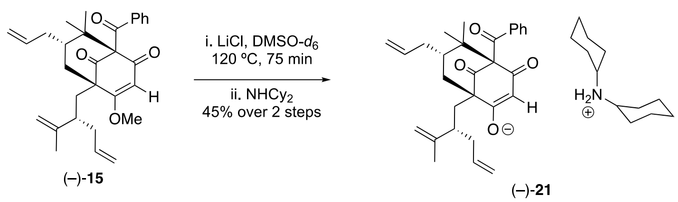
Rearomatized Product 29: 3.4 mg, 17% yield; yellow oil; R_f = 0.75 (EtOAc/hexanes: 25/75); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 11.09 (s, 1H), 7.73 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.53 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.42 (td, *J* = 8.0, 0.5 Hz, 2H), 6.11–5.96 (m, 2H), 5.09–4.94 (m, 4H), 4.59 (td, *J* = 7.0, 1.0 Hz, 1H), 3.93 (d, *J* = 7.5 Hz, 2H), 3.80 (s, 3H), 3.46 (dt, *J* = 6.0, 1.5 Hz, 2H), 3.36 (dt, *J* = 6.0, 1.5 Hz, 2H), 1.54 (s, 3H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 199.6, 163.2, 159.6, 157.3, 139.4, 138.1, 137.7, 136.6, 132.3, 129.6, 127.7, 119.2, 118.5, 117.3, 114.8, 114.5, 111.9, 110.0, 72.7, 62.1, 28.3, 25.7, 17.7; IR$_{\upsilon max}$ (Diamond ATR): 2918, 1597, 1578, 1416, 1330, 1282, 1118, 910 cm^{-1}; HRMS (ESI): $[M + Na]^+$ Calcd. For $C_{25}H_{28}O_4Na$: 415.1885, Found: 415.1895.

C. Confirmation of the Type A Scaffolds



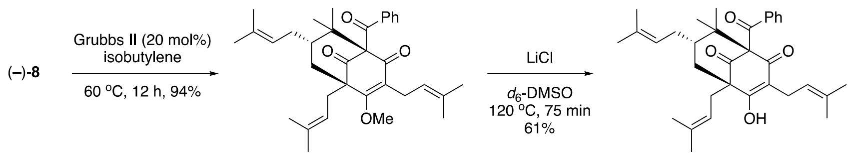
(–)-**8** (–)-**12**

To a flame-dried 1-dram vial charged with argon and compound (–)-**8** (5 mg, 11.6 μmol) was added deuterated DMSO (DMSO-d_6, 0.2 mL) and LiCl (10 mg, 0.24 mmol, 20 equiv). The reaction was then heated to 120 ºC for 75 min. After completion, the reaction was cooled to room temperature and to the mixture was added water (5 mL), followed by a mixture of diethyl ether and hexanes (1:1, 10 mL) and 1 *N* HCl (5 mL). The resulting mixture was extracted by diethyl ether and hexanes (1:1) (10 mL × 3), washed with water and brine, and dried over anhydrous Na_2SO_4. Solvent was removed *in vacuo* and the residue was purified by preparative plate chromatography (silica gel, EtOAc/hexanes/AcOH: 20:80:3) to afford the demethylated compound. To the demethylated compound was added diethyl ether (2 mL) and dicyclohexylamine ($NHCy_2$, 3 μL, 14 μmol, 1.2 equiv). The solution immediately turned bright yellow after the addition of the amine. The solvent was removed *in vacuo* and diethyl ether (2 mL) was added and removed *in vacuo*. The resulting salt was recrystallized from chloroform and isooctane to afford a yellow solid; 4.1 mg, 58% yield; m. p.: 175–176 ºC (diethyl ether); R_f = 0.44 (EtOAc/hexanes: 50/50); ^{1}H NMR (CD_3OD, 400 MHz): δ 7.76 (dd, J = 8.4, 1.2 Hz, 2H), 7.35 (td, J = 8.0, 1.2 Hz, 1H), 7.20 (td, J = 8.4, 1.2 Hz, 2H), 5.89–5.73 (m, 2H), 5.72–5.63 (m, 1H), 5.04–4.90 (m, 5H), 4.78 (d, J = 10.0 Hz, 1H), 3.19–3.03 (m, 4H), 2.54 (d, J = 13.6, 6.4 Hz, 1H), 2.42 (d, J = 12.0, 7.2 Hz, 1H), 2.34–2.92 (m, 1H), 2.10–1.95 (m, 6H), 1.90–1.85 (m, 4H), 1.74–1.64 (m, 3H), 1.43–1.15 (m, 11H), 1.36 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (CD_3OD, 101 MHz): δ 212.3, 196.3, 187.9, 185.6, 138.1, 137.6, 125.4, 131.0, 128.3, 127.0, 116.0, 115.0, 114.8, 111.8, 78.1, 61.8, 53.1, 45.8, 41.6, 40.9, 35.1, 33.3, 29.2, 27.5, 24.7, 24.0, 23.1, 15.3; IR$_{\upsilon max}$ (Diamond ATR): 2935, 2858, 1706, 1690, 1488, 1386, 1223, 910, 689 cm^{-1}; HRMS (ESI): $[M^- + 2H]^+$ Calcd. For Anion $C_{27}H_{31}O_4$: 419.2222, Found: 419.2219; $[\alpha]_D^{23}$ = –150.9 (c = 0.100, $CHCl_3$).



To a flame-dried 1-dram vial charged with argon and compound (–)-**15** (11.7 mg, 25.4 μmol) was added DMSO-d_6 (0.18 mL) and LiCl (20 mg, 0.47 mmol, 18 equiv). The reaction was then heated to 120 ºC for 75 min. After completion, the reaction was cooled to room temperature and the mixture was added water (10 mL), diethyl ether and hexanes (1:1, 20 mL) and 1 *N* HCl (10 mL). The resulting mixture was extracted by diethyl ether and hexanes (1:1) (10 mL × 3), washed with water and brine, and dried over anhydrous Na_2SO_4. Solvent was removed *in vacuo* and the residue was purified by preparative plate chromatography (silica gel, EtOAc/hexanes/AcOH: 20:80:3) to afford the demethylated compound. To the demethylated compound was added diethyl ether (2 mL) and $NHCy_2$ (6 μL, 0.30 mmol, 1.2 equiv). The solvent was removed *in vacuo* and diethyl ether (2 mL) was added and removed *in vacuo* again. The resulting salt was recrystallized from chloroform and isooctane to afford a white solid; 7.2 mg, 45% yield; m. p.: 187–189 ºC (diethyl ether); R_f = 0.10 (EtOAc/hexanes: 50/50); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.95 (*br*, 2H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.38 (tt, *J* = 7.0, 1.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 2H), 5.64–5.52 (m, 2H), 5.49 (s, 1H), 4.98–4.84 (m, 4H), 4.59 (d, *J* = 46.0 Hz, 2H), 2.60 (*br*, 2H), 2.55–2.50 (m, 1H), 2.32–2.28 (m, 1H), 2.14–2.09 (m, 1H), 2.05–1.89 (m, 4H), 1,75–1.57 (m, 12H), 1.63 (s, 3H), 1.39 (s, 3H), 1.25–1.20 (m, 5H), 1.12–0.99 (m, 6H), 1.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 212.2, 195.8, 191.3, 186.9, 149.2, 138.2, 138.0, 137.8, 131.3, 128.5, 127.5, 115.9, 114.5, 110.4, 104.3, 78.2, 61.2, 52.2, 46.6, 44.3, 43.3, 41.6, 38.9, 34.07, 34.01, 28.6, 28.3, 25.0, 24.69, 24.66, 24.3, 18.3, 16.0; $IR_{\upsilon max}$ (Diamond ATR): 2938, 2859, 1707, 1572, 1536, 1260, 1053, 802 cm^{-1}; HRMS (ESI): $[M^- + 2H]^+$ Calcd. For Anion $C_{29}H_{35}O_4$: 447.2535, Found: 447.2523; $[\alpha]_D^{25}$ = –188.2 (c = 0.200, $CHCl_3$).

D. Synthesis of (–)-Nemorosone



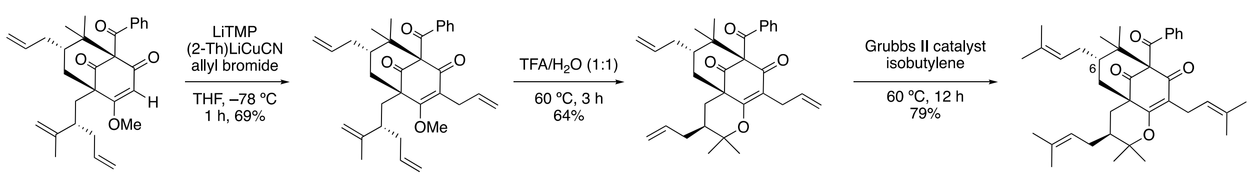
(–)-13   2 (–)-nemorosone

***O*-Methyl Nemorosone (–)-13:** To a 15-mL glass pressure tube charged with argon was added compound **8** (18.8 mg, 43.5 μmol) and Grubbs 2nd generation catalyst (7.2 mg, 8.4 μmol). The tube was then cooled to –78 ºC and isobutylene (5.0 mL) was added along the side of the tube. The tube was sealed and heated to 60 ºC for 12 h. The reaction was then cooled back to –78 ºC for 5 min and was opened to air for removal of isobutylene. The crude product was dissolved in CH_2Cl_2 (2.0 mL) and purified by preparative plate chromatography (silica gel, EtOAc/hexanes: 10/90) to obtain **13** as a colorless oil. Spectroscopic data for **13** were found to be identical with those reported in the literature:[S6] 21.2 mg, 94% yield; R_f = 0.51 (EtOAc/hexanes: 20/80); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44 (dd, J = 7.5, 1.0 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 2H), 5.04–4.99 (m, 3H), 4.00 (s, 3H), 3.25 (dd, J = 15.0, 7.0 Hz, 1H), 3.16 (dd, J = 15.5, 7.0 Hz, 1H), 2.59 (dd, J = 14.5, 6.5 Hz, 1H), 2.43 (dd, J = 14.0, 6.0 Hz, 1H), 2.16 (dd, J = 12.0, 6.5 Hz, 1H), 2.02 (dd, J = 12.5, 4.0 Hz, 1H), 1.76–1.67 (m, 2H), 1.69 (s, 3H), 1.68 (s, 3H), 1.65 (s, 6H), 1.63 (s, 3H), 1.58 (s, 3H), 1.47 (dd, J = 13.5, 12.0 Hz, 1H, CH2), 1.35 (s, 3H), 1.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 207.4, 194.2, 193.2, 173.2, 136.4, 134.5, 133.6, 133.2, 132.0, 128.7, 127.9, 126.9, 122.7, 121.5, 119.7, 79.4, 62.6, 60.0, 49.0, 43.9, 40.4, 29.9, 26.9, 26.2, 26.0, 25.8, 23.6, 23.5, 18.3, 18.0, 15.9; $IR_{\upsilon max}$ (Diamond ATR): 2920, 1723, 1699, 1648, 1598, 1447, 1375, 1237, 1066, 850, 806 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{34}H_{45}O_4$: 517.3318, Found: 517.3300. $[\alpha]_D^{22}$ = –50.2 (c = 0.250, $CHCl_3$).

(–)-Nemorosone 2: To a flame-dried 5-mL round-bottom flask charged with argon and **13** (12.3 mg, 21.3 μmol) was added anhydrous DMSO-d_6 (0.25 mL, 85 mM) and LiCl (17 mg, 0.39 mmol, 18 equiv). The reaction was then heated to 120 ºC for 75 min. After completion, the reaction was cooled down to room temperature and the mixture was added water (2 mL), diethyl ether and hexanes mixture (1:1, 5 mL) and 1 *N* HCl (2 mL). The resulting mixture was extracted by diethyl ether/hexanes mixture (1:1, 5 mL × 3), washed with water and brine and dried over anhydrous

Na_2SO_4. Solvents were removed *in vacuo* and the residue was purified by preparative thin-layer chromatography (silica gel, EtOAc/hexanes/AcOH: 20/80/3) to afford natural product nemorosone as a slightly yellow oil. Spectroscopic data for **13** were found to be identical with those reported in the literature:[S6] 7.3 mg, 61% yield; R_f = 0.47 (EtOAc/hexanes: 40/60); ^{1}H NMR (CD_3OD, 500 MHz): δ 7.54 (dd, J = 7.0, 0.8 Hz, 2H), 7.43 (td, J = 7.5, 1.0 Hz, 1H), 7.25 (t, J = 8.0, 0.5 Hz, 2H), 5.08 (tt, J = 7.5, 1.0 Hz, 1H), 5.02–4.99 (m, 2H), 3.10 (ddd, J = 26.5, 14.5, 7.0 Hz, 2H), 2.50 (ddd, J = 26.0, 14.5, 7.0 Hz, 2H), 2.18–2.13 (m, 1H), 2.01 (dd, J = 13.5, 7.0 Hz, 1H), 1.75–1.69 (m, 2H), 1.69 (s, 3H), 1.66 (s, 3H), 1.65 (s, 9H), 1.59 (s, 3H), 1.44 (t, J = 12.5 Hz, 1H), 1.34 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (CD_3OD, 126 MHz): δ 209.3, 194.9, 138.2, 135.2, 134.2, 133.6, 133.1, 129.6, 128.8, 124.0, 122.2, 121.1, 120.8, 44.6, 42.3, 30.4, 28.2, 26.3, 26.04, 26.02, 24.3, 22.3, 18.3, 18.1, 18.0, 16.2; IR$_{\upsilon max}$ (Diamond ATR): 3314, 2914, 1723, 1698, 1580, 1446, 1393, 1371, 1219, 839, 687 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{33}H_{43}O_4$: 503.3161, Found: 503.3170; $[\alpha]_D^{23}$ = –74.3 (c = 0.250, $CHCl_3$).

E. Synthesis of (–)-6-e*pi*-Garcimultiflorone

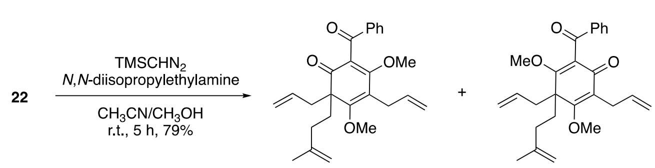


Allyl derivative (–)-18 (lithium tetramethylpiperidine [LiTMP] preparation[S3]): To a flame-dried 10-mL round-bottom flask under an argon atmosphere containing a solution of 2,2,6,6-tetramethylpiperidine (420 μL, 12.3 mmol) in THF (4.8 mL) at –78 ºC was added *n*-BuLi (1 mL, 2.5 M in hexanes) dropwise. The LiTMP solution was allowed to stir for 15 min at –78 ºC prior to use. Then, to a flame-dried 25-mL round-bottom flask containing compound **15** (26.8 mg, 58.2 μmol) was added THF (2.2 mL) under argon. The solution was then cooled to –78 ºC. The freshly made LiTMP solution (0.58 mL, 0.5 M in THF) was added dropwise along the side of the flask which was followed by dropwise addition of lithium 2-thienylcyanocuprate (1.3 mL, 0.25 M in THF). Allyl bromide (30 μL, 0.35 mmol) was then slowly added into the reaction mixture over the course of 1 min. The reaction was allowed to stir for 1 h at –78 ºC. After completion, the mixture was warmed to room temperature and was quenched with 30 % NH_4OH aqueous solution (10 mL), diluted with Et_2O (10 mL), and vigorously stirred for 5 min. The mixture was poured into a separatory funnel and further extracted into Et_2O (4 mL × 3). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by silica flash chromatography (EtOAc/hexanes: 0/100 to 10/90) provided the vinylic allylation product **18** as a slightly yellow oil. 20 mg, 69% yield; R_f = 0.29 (EtOAc/hexanes: 10/90); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 8.0 Hz, 2H), 5.89–5.81 (m, 1H), 5.67–5.55 (m, 2H), 5.08–5.00 (m, 4H), 4.92–4.89 (m, 2H), 4.67 (d, J = 33.5 Hz, 2H), 4.06 (s, 3H), 3.35–3.24 (m, 2H), 2.35–2.33 (m, 2H), 2.15–2.12 (m, 1H), 2.05–2.02 (m, 2H), 2.00–1.95 (m, 1H), 1.87–1.84 (m, 1H), 1.79–1.70 (m, 2H), 1.66 (s, 3H), 1.40 (t, J = 12.0 Hz, 1H), 1.34 (s, 3H), 1.11 (s, 3H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 207.7, 193.4, 192.8, 173.4, 148.2, 137.0, 136.8, 136.1, 136.0, 132.0, 128.6, 127.9, 120.3, 116.9, 115.9, 115.3, 111.1, 79.3, 61.2, 59.4, 48.9, 44.7, 42.2, 41.9, 39.2, 34.6, 32.8, 28.6, 23.4, 17.5, 15.6; $IR_{\upsilon max}$ (Diamond ATR): 2932, 1720, 1700, 1642, 1590, 1448, 1241, 1222, 994, 913 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{33}H_{41}O_4$: 501.3005, Found: 501.3008; $[\alpha]_D^{24}$ = –138.2 (c = 0.250, $CHCl_3$).

***O*-Cyclized Compound 19:** To a scintillation vial containing **18** (9.0 mg, 0.018 mmol) was added a 1:1 mixture of water and TFA (5.0 mL). The resulting mixture was allowed to stir for 17 h before being concentrating *in vacuo*. The residue was purified by preparative thin-layer chromatography (EtOAc/hexanes: 10/90) to provide *O*-cyclized product **19** as a colorless oil. 5.6 mg, 64% yield; R_f = 0.28 (EtOAc/hexanes: 10/90); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (dd, J = 8.5, 1.0 Hz, 2H), 7.38 (tt, J = 7.5, 1.0 Hz, 1H), 7.24 (td, J = 8.0, 0.5 Hz, 2H), 5.78–5.60 (m, 3H), 5.12–4.99 (m, 5H), 4.92 (dd, J = 10.0, 2.0 Hz, 1H), 3.19–3.10 (m, 2H), 2.87 (dd, J = 14.5, 3.5 Hz, 1H), 2.41–2.37 (m, 1H), 2.27–2.22 (m, 1H), 2.07 (dd, J = 13.5, 4.5 Hz, 1H), 1.92–1.86 (m, 1H), 1.82–1.76 (m, 1H), 1.75–1.69 (m, 1H), 1.54–1.47 (m, 2H), 1.46 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H), 1.14 (s, 3H), 1.10–1.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 206.1, 193.8, 193.2, 168.8, 137.0, 137.0, 135.7, 135.2, 132.1, 128.2, 128.1, 125.3, 117.4, 116.8, 115.8, 86.6, 78.8, 54.9, 47.7, 42.4, 41.9, 40.8, 35.5, 32.8, 29.6, 27.6, 27.4, 22.9, 22.0, 16.5; $IR_{\upsilon max}$ (Diamond ATR): 2925, 1722, 1696, 1640, 1598, 1371, 1346, 1226, 915 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{32}H_{39}O_4$: 487.2848, Found: 487.2860; $[\alpha]_D^{24}$ = –219.5 (c = 0.250, $CHCl_3$).

(–)-6-*Epi*-Garcimultiflorone 20: To a flame-dried 30-mL glass pressure tube containing **19** (3.2 mg, 6.58 μmol) was added Grubbs catalyst 2nd generation (2.5 mg, 1.94 μmol). The pressure tube was then purged with argon, cooled to –78 ºC, and filled with isobutylene (2 mL). The reaction vessel was sealed and heated to 60 ºC with vigorous stirring. After 12 h, the reaction was then cooled back to –78 ºC for 5 min and was opened to the air to remove isobutylene. The residue was purified by preparative thin-layer chromatography (EtOAc/hexanes: 10/90) to provide (–)-6-*epi*-garcimultiflorone A **20** as a clear oil. 3.0 mg, 79% yield; colorless oil; R_f = 0.44 (EtOAc/hexanes: 10/90); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.49 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 8.0 Hz, 2H), 5.11–5.08 (m, 1H), 5.02–4.95 (m, 2H), 3.13–3.03 (m, 2H), 2.82 (dd, J = 14.0, 3.5 Hz, 1H), 2.21–2.17 (m, 1H), 2.10–2.08 (m, 1H), 2.02 (dd, J = 13.5, 3.5 Hz, 1H), 1.91–1.84 (m, 1H), 1.73–1.69 (m, 2H), 1.69 (s, 6H), 1.64 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H), 1.57 (s, 3H), 1.48–1.43 (m, 2H), 1.45 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H), 1.15 (s, 3H), 1.04 (t, J = 13.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 206.4, 194.0, 193.5, 168.2, 137.1, 133.8, 133.3, 132.2, 132.0, 128.3, 128.0, 126.7, 122.7, 121.7, 121.4, 86.4, 78.9, 55.0, 47.9, 43.3, 42.2, 42.0, 29.7, 29.3, 27.7, 26.7, 25.9, 23.0, 22.1, 18.1, 18.0, 16.5; $IR_{\upsilon max}$ (Diamond ATR): 2927, 1723, 1696, 1644, 1598, 1447, 1371, 1343, 1123 cm^{-1}; HRMS (ESI): $[M + H]^+$ Calcd. For $C_{38}H_{51}O_4$: 571.3787, Found: 571.3806; $[\alpha]_D^{24}$ = –190.6 (c = 0.200, $CHCl_3$).

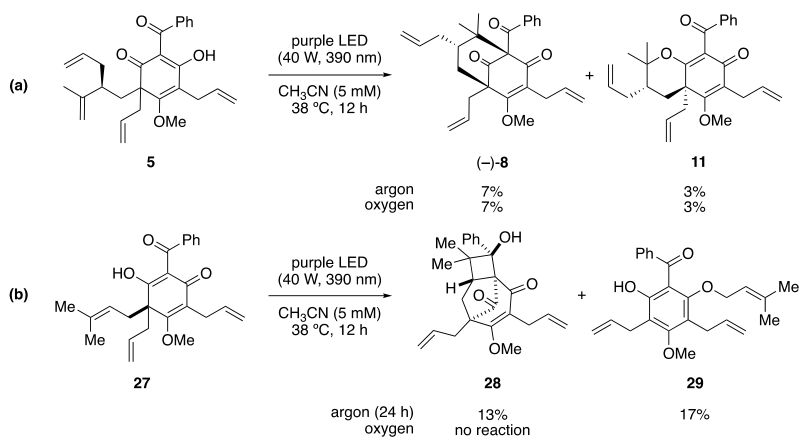
F. Derivatization of Dearomatized Compound 22



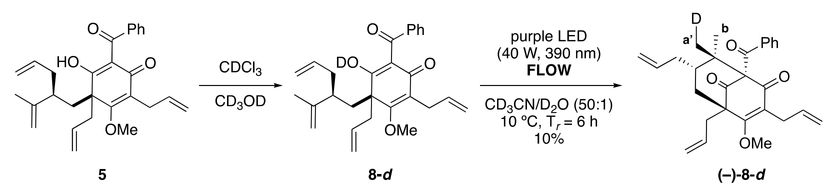
Methylation of 22: To a solution of dearomatized compound **22** (26 mg, 55 μmol) in acetonitrile and methanol (9:1, 1 mL) under argon was added *N*, *N*-diisopropylethylamine (14 μL, 80 μmol) and trimethylsilyldiazomethane ($TMSCHN_2$, 2 M in hexanes, 0.12 mmol). The resulting mixture was stirred at room temperature for 5 h and was then quenched with 3 *N* HCl solution and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was further purified by silica flash chromatography (EtOAc/hexanes: 5/95 to 10/90) to afford a pair of regioisomers (ratio = 1:2) as a slightly yellow oil. 17.6 mg, 79% yield; R_f = 0.19 (EtOAc/hexanes: 10/90); ^{1}H NMR (*2:1 mixture of diastereomers as determined by ^{1}H NMR analysis,* $CDCl_3$, 400 MHz): δ 7.92–7.89 (m, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 6.02–5.83 (m, 1.6H), 5.72–5.58 (m, 1.4H), 5.13–4.98 (m, 4.8H), 4.72–4.62 (m, 2.6H), 3.98 (s, 2H), 3.93 (s, 1H), 3.68 (s, 1H), 3.64 (s, 2H), 3.23–3.20 (m, 2.4H), 2.74–2.56 (m, 2.7H), 2.11–1.98 (m, 2.2H), 1.96–1.80 (m, 3H), 1.72 (s, 2H), 1.66 (s, 1H); ^{13}C NMR (*2:1 mixture of regioisomers as determined by ^{1}H NMR analysis,* $CDCl_3$, 101 MHz): δ 199.2, 196.5, 196.2, 187.3, 171.4, 170.0, 169.5, 168.1, 145.1, 144.9, 138.6, 138.3, 136.6, 136.3, 133.1, 133.02, 132.96, 129.3, 129.2, 128.6, 128.4, 121.3, 118.7, 118.3, 118.2, 117.9, 115.3, 115.0, 114.5, 110.1, 110.0, 63.1, 62.2, 60.7, 59.9, 59.0, 53.6, 44.1, 42.0, 37.3, 35.2, 32.8, 32.6, 29.0, 28.0, 22.6, 22.5. $IR_{\upsilon max}$ (Diamond ATR): 2945, 1672, 1649, 1612, 1550, 1449, 1362, 1220, 1129, 992, 736, 690 632 cm^{-1}; HRMS (ESI): [M + H]$^+$ Calcd. For $C_{26}H_{31}O_4$: 407.2222, Found: 407.2227.

G. Argon/Oxygen-Bubbling Experiments

To a flame-dried vial was added dearomatized substrate (20 mg) and anhydrous acetonitrile (5 mM) and the mixture was degassed in sonication for 30 min. After degassing, a 4-inch needle connected to a balloon (oxygen or argon) was inserted to the bottom of the vial. The reaction was then placed in front of the Kessil® LED lamp (390 nm) and another short needle was inserted to allow gas to bubble through the reaction mixture. The reactions were allowed to stir for 12 h at room temperature. Balloons were recharged if the gas ran out during the period. After reaction completion, the solvent was removed *in vacuo* and the residue was purified by preparative thin-layer chromatography (EtOAc/hexanes: 10/90). As indicated by the results listed below, for dearomatized compound **5** the reactions showed no observable difference when bubbling with argon or oxygen. Meanwhile, for prenylated compound **27**, oxygen completely hindered the reaction in a time period of 12 h.



H. Deuterium-Labeling Experiment



To a solution of **5** (20 mg) in deuterated chloroform ($CDCl_3$, 2 mL) was added several drops of deuterated methanol (CD_3OD). Place the mixture in sonication for 10 min and then remove all the solvent *in vacuo*. The photoreaction was conducted with the resulting residue in flow photoreactor II (Procedure B) in a mixture of deuterated acetonitrile and deuterium oxide (CD_3CN/D_2O: 50/1, 5 mM). After completion, the solvent was removed *in vacuo* and the resulting residue was purified by preparative thin-layer chromatography (EtOAc/hexanes: 10/90), affording a mixture of (–)-***8-d*** and (–)-**8** (3.3:1, 2.0 mg, 10 % yield). To test the reversibility of deuteration, the non-deuterated product (–)-**8** was treated under the same conditions. However, after work-up, the recovered product (–)-**8** did not show any evidence of deuterium incorporation.

I. Photophysical Studies

Unless otherwise mentioned, whenever necessary spectrophotometric grade 2-methyl tetrahydrofuran (2-MeTHF) was used for photophysical experiments. UV/VIS absorbances were obtained with Agilent Technologies Cary 60 UV/VIS® instrument. Fluorescence emission, luminescence emission, excitation, phosphorescence emission, and lifetime experiments were carried out using Edinburgh instruments FLS 1000® photoluminescence Spectrometer. A continuous wave Xenon lamp source was used for recording fluorescence, luminescence at 77 K, and excitation spectra. A microsecond-pulsed Xenon lamp source was used to record phosphorescence spectra and phosphorescence lifetimes. Fluorescence, luminescence, phosphorescence and excitation spectra were reported as the average of three scans with a dwell time of 0.2 s.

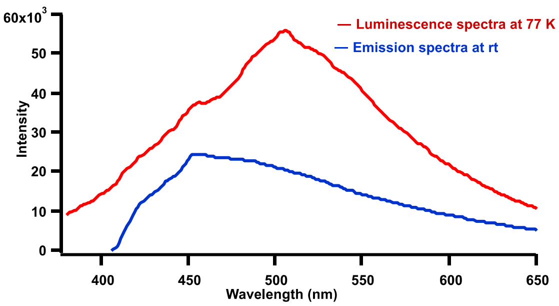


Figure S4. Luminescence of **5** at 77 K (*red*) and its room temperature fluorescence (*blue*) in 2-MeTHF.

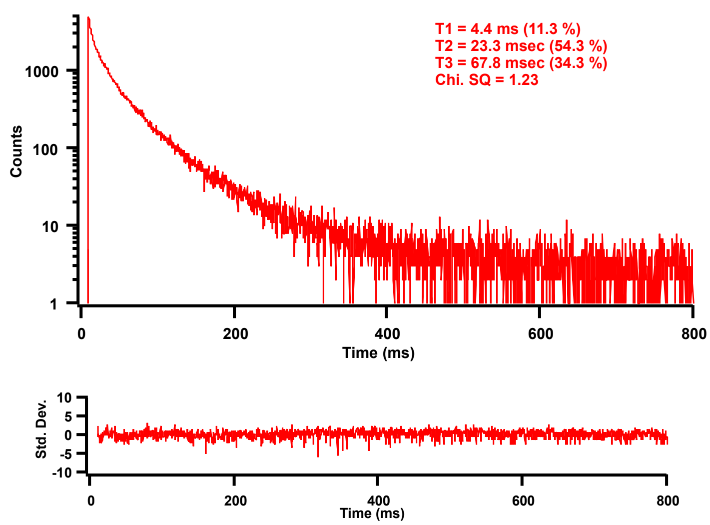


Figure S5. Phosphorescence lifetime decay of compound **5** in 2-MeTHF glass at 77 K. (τ_1 = 4.4 ms, τ_2 = 23.3 ms and τ_3 = 67.8 ms).

Photophysical studies of compounds 5 and 25. For photophysical studies of compounds **5** and **25**, 30 μM solution in 2-MeTHF was used. Concentration was adjusted to have optical density (O.D) ~ 0.15 at the excitation wavelength. Normalized UV spectra of compound **5** matched with its normalized excitation spectra (**Figure 2** for compound **5** and **Figure S4** for compound **25)** indicating that the compounds are optically pure for photophysical experiments. For compound **5**, UV/VIS absorption spectra and excitation spectra were recorded from 300 nm to 415 nm that showed maxima around 354 nm (**Figure 2**). Fluorescence was recorded with excitation and emission arm slit width of 6 nm by excitation at 350 nm. The fluorescence signal had maximum intensity at 454 nm (**Figure S4**). Excitation spectra were monitored at room temperature from the fluorescence signal at 454 nm with an excitation and emission arm slit width of 6 nm. Phosphorescence spectra were recorded at 77 K with an excitation and emission arm slit width of 6 nm and 4 nm, respectively. Phosphorescence spectra had maximum intensity around 510 nm corresponding to a triplet energy ~ 56 kcal/mol. Luminescence spectra were recorded at 77 K using a continuous wave Xenon lamp source without time gating to record the signal from both fluorescence and phosphorescence. Excitation and emission arm slit widths were used to record luminescence spectra at 77 K and were 1 nm and 4 nm, respectively.

The phosphorescence emission lifetime for compound **5** was determined using a microsecond pulsed Xenon lamp source of 1.3 Hz with detector gating delay of 9 ms and gate width of 790 ms (**Figure S5**). Tri-exponential decay was observed with lifetimes of τ_1 = 4.4 ms, τ_2 = 23.3 ms, and τ_3 = 67.8 ms. χ^2 = 1.23.

For compound **25** (**Figure S6**), UV/VIS absorption spectra and excitation spectra were monitored from 250 nm to 420 nm with a maximum around 352 nm. Fluorescence spectra were recorded with an excitation and emission arm slit width of 5 nm by excitation at 375 nm. The fluorescence signal had a maximum intensity around 450 nm. Excitation spectra were monitored from the fluorescence signal at room temperature with a slit width of 5 nm at both the excitation and emission arms. Phosphorescence spectra were recorded at 77 K with an excitation and emission arm slit width of 5 nm with a detector gating delay of 0.2 ms. Phosphorescence spectra had maximum intensity around 536 nm corresponding to the triplet energy of 53.3 kcal/mol. Luminescence spectra were recorded at 77 K using continuous wave Xenon lamp source without time gating to record the signal from fluorescence and phosphorescence.

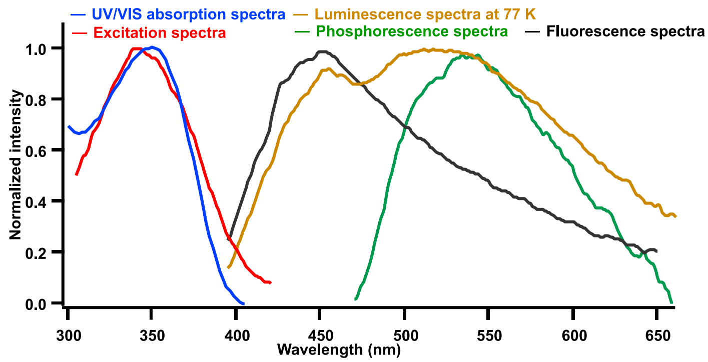


Figure S6. UV/VIS absorption (*blue*), excitation (*red*), fluorescence (*black*), phosphorescence (*green*) and emission spectra at 77 K (*orange*) of compound **25** in 2-MeTHF. UV/VIS absorption, fluorescence and excitation spectra were recorded at room temperature. Phosphorescence spectra and emission spectra were recorded at 77 K in 2-MeTHF glass.

The phosphorescence emission lifetime for compound **25** was determined using a microsecond pulsed Xenon lamp source of 0.1 Hz with a detector gating delay of 1 ms and gate width of 10 s (**Figure S7**). Bi-exponential decay was observed with a lifetime of τ_1 = 9.4 ms and τ_2 = 40.5 ms. χ^2 = 1.07.

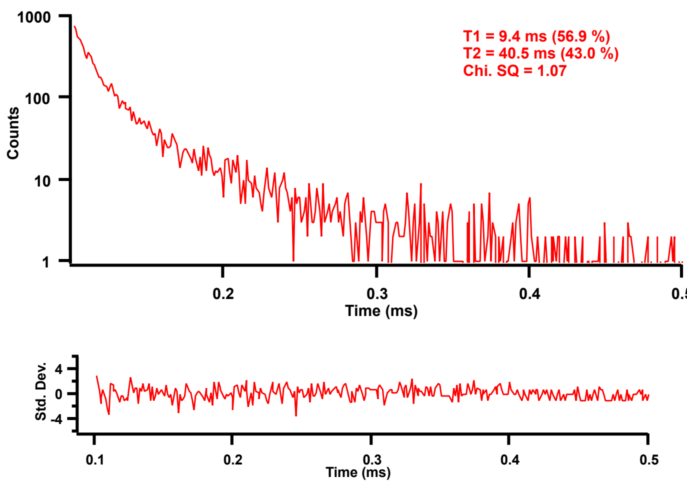
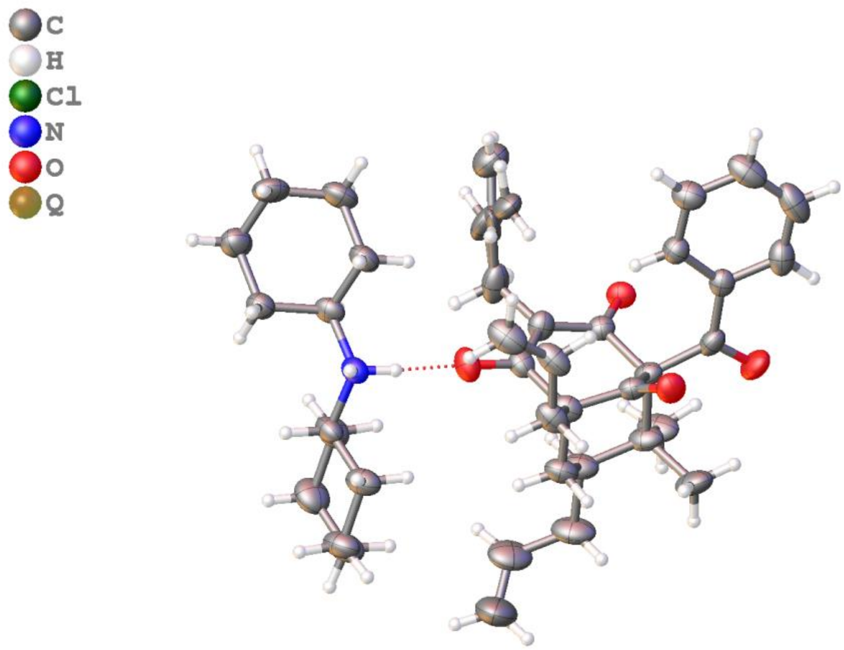
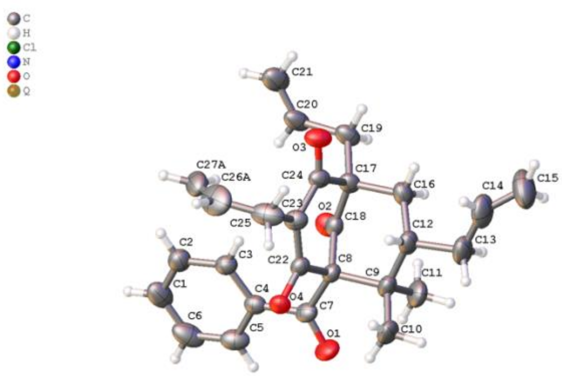


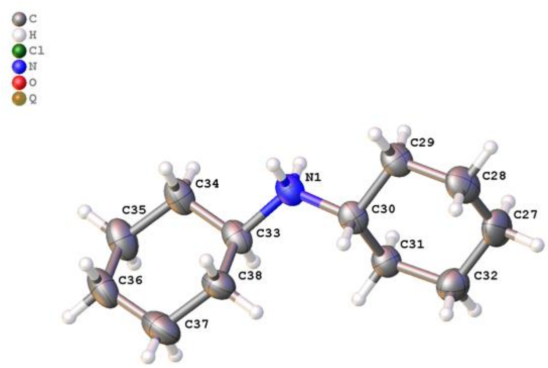
Figure S7. Phosphorescence lifetime decay of compound **25** in 2-MeTHF glass at 77 K. (τ_1 = 9.4 ms and τ_2 = 40.5 ms).

III. X-ray Crystallographic Data

A. Compound 12







Crystals of compound **12** suitable for X-ray analysis were obtained by layering a $CHCl_3$ solution with isooctane at ambient temperature followed by storage in a sealed vial. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC # 1913293). Copies of the data can be obtained free of charge through application to the

CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computing details

Cell refinement: *SAINT* V8.38A (Bruker, 2016); data reduction: *SAINT* V8.38A (Bruker, 2016); program(s) used to solve structure: ShelXT (Sheldrick, 2015); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

Table S2. Crystal data.

$C_{27}H_{29}O_4{\cdot}C_{12}H_{24}N{\cdot}0.87(CHCl_3)$	$F(000) = 753$
$M_r = 704.09$	$D_x = 1.208$ Mg m^{-3}
Monoclinic, $P2_1$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 10.3691$ (5) Å	Cell parameters from 9447 reflections
$b = 17.1035$ (8) Å	$\theta = 4.1$–$66.4°$
$c = 11.0229$ (5) Å	$\mu = 2.21$ mm^{-1}
$\beta = 97.966$ (2)°	$T = 296$ K
$V = 1936.02$ (16) Å^3	Block, colourless
$Z = 2$	0.38 × 0.12 × 0.08 mm

Table S3. Data collection.

Bruker APEX-II CCD diffractometer	6555 reflections with $I > 2\sigma(I)$
ϕ and ω scans	$R_{int} = 0.051$
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for	$\theta_{max} = 67.2°$, $\theta_{min} = 4.1°$

absorption correction. wR2(int) was 0.1286 before and 0.0812 after correction. The Ratio of minimum to maximum transmission is 0.7824. The λ/2 correction factor is Not present.	
T_{min} = 0.589, T_{max} = 0.753	h = -12∅12
64642 measured reflections	k = -20∅20
6845 independent reflections	l = -13∅12

Table S4. Refinement parameters.

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.042	$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 0.376P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.119	$(\Delta/\sigma)_{max}$ < 0.001
S = 1.04	$\Delta\rangle_{max}$ = 0.37 e Å^{-3}
6845 reflections	$\Delta\rangle_{min}$ = -0.18 e Å^{-3}
515 parameters	Absolute structure: Flack x determined using 3008 quotients [(I+)–(I–)]/[(I+)+(I–)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
807 restraints	Absolute structure parameter: 0.060 (5)
Primary atom site location: dual	

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.

Table S5. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for 12.

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O4	0.3074 (2)	0.21222 (11)	0.40127 (18)	0.0358 (4)	
O2	0.07159 (19)	0.43266 (12)	0.3732 (2)	0.0438 (5)	
O3	0.5114 (2)	0.45709 (13)	0.4206 (2)	0.0458 (5)	
O1	-0.0094 (2)	0.23884 (15)	0.2827 (2)	0.0522 (6)	
N1	0.7017 (2)	0.56622 (14)	0.4807 (2)	0.0375 (5)	
H1A	0.6880	0.6121	0.5149	0.045*	
H1B	0.6250	0.5420	0.4665	0.045*	
C22	0.3100 (3)	0.28452 (16)	0.3822 (2)	0.0317 (6)	
C24	0.4141 (3)	0.41435 (16)	0.3954 (3)	0.0347 (6)	
C4	0.0514 (3)	0.27323 (16)	0.4877 (3)	0.0344 (6)	
C18	0.1715 (3)	0.40534 (16)	0.3460 (2)	0.0338 (6)	
C3	0.1380 (3)	0.30661 (17)	0.5811 (3)	0.0373 (6)	
H3	0.2124	0.3316	0.5622	0.045*	

C30	0.7878 (3)	0.51884 (16)	0.5735 (3)	0.0391 (6)	
H30	0.7982	0.4666	0.5396	0.047*	
C7	0.0687 (3)	0.27395 (17)	0.3550 (3)	0.0377 (6)	
C17	0.2893 (3)	0.45266 (16)	0.3313 (3)	0.0369 (6)	
C23	0.4171 (3)	0.33331 (17)	0.4186 (3)	0.0381 (6)	
C5	-0.0584 (3)	0.23531 (19)	0.5206 (3)	0.0479 (7)	
H5	-0.1176	0.2120	0.4602	0.057*	
C31	0.9213 (3)	0.55567 (18)	0.6044 (3)	0.0416 (7)	
H31A	0.9119	0.6093	0.6306	0.050*	
H31B	0.9645	0.5565	0.5318	0.050*	
C20	0.2744 (4)	0.54438 (17)	0.5108 (3)	0.0481 (8)	
H20	0.2090	0.5177	0.5433	0.058*	
C33	0.7456 (3)	0.58264 (19)	0.3579 (3)	0.0422 (7)	
H33	0.8250	0.6144	0.3713	0.051*	
C9	0.1851 (4)	0.31796 (18)	0.1677 (3)	0.0450 (7)	
C38	0.7753 (3)	0.5076 (2)	0.2944 (3)	0.0480 (7)	
H38A	0.7002	0.4732	0.2874	0.058*	
H38B	0.8479	0.4810	0.3423	0.058*	
C8	0.1834 (3)	0.31967 (15)	0.3135 (2)	0.0340 (6)	
C2	0.1150 (3)	0.3032 (2)	0.7010 (3)	0.0480 (7)	
H2	0.1738	0.3263	0.7620	0.058*	
C19	0.2764 (3)	0.53743 (17)	0.3755 (3)	0.0443 (7)	

H19A	0.3486	0.5679	0.3536	0.053*	
H19B	0.1967	0.5597	0.3328	0.053*	
C29	0.7191 (3)	0.51088 (19)	0.6863 (3)	0.0450 (7)	
H29A	0.6360	0.4849	0.6642	0.054*	
H29B	0.7025	0.5624	0.7176	0.054*	
C37	0.8095 (4)	0.5265 (3)	0.1661 (4)	0.0641 (10)	
H37A	0.8899	0.5562	0.1744	0.077*	
H37B	0.8238	0.4780	0.1243	0.077*	
C34	0.6412 (4)	0.6290 (2)	0.2833 (3)	0.0482 (7)	
H34A	0.6286	0.6777	0.3252	0.058*	
H34B	0.5601	0.6000	0.2757	0.058*	
C16	0.2984 (3)	0.45156 (18)	0.1914 (3)	0.0439 (7)	
H16A	0.2243	0.4795	0.1484	0.053*	
H16B	0.3767	0.4790	0.1768	0.053*	
C10	0.2049 (4)	0.2332 (2)	0.1268 (3)	0.0588 (9)	
H10A	0.1418	0.1999	0.1567	0.088*	
H10B	0.2909	0.2160	0.1593	0.088*	
H10C	0.1943	0.2309	0.0390	0.088*	
C27	0.9363 (4)	0.5006 (2)	0.8187 (3)	0.0567 (9)	
H27E	0.9891	0.4681	0.8782	0.068*	
H27F	0.9269	0.5514	0.8558	0.068*	
C12	0.3010 (4)	0.3689 (2)	0.1391 (3)	0.0470 (7)	

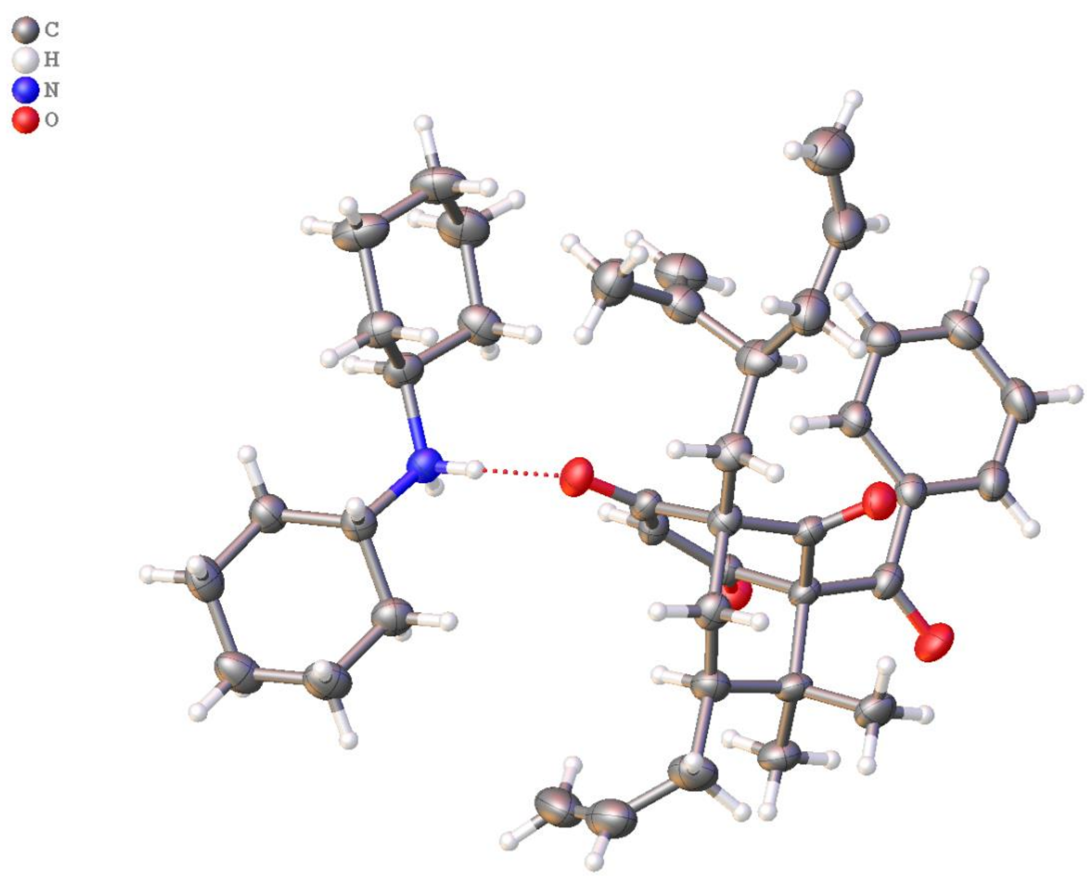
H12	0.3811	0.3438	0.1781	0.056*	
C32	1.0046 (3)	0.5103 (2)	0.7058 (3)	0.0522 (8)	
H32A	1.0242	0.4591	0.6752	0.063*	
H32B	1.0863	0.5377	0.7285	0.063*	
C1	0.0068 (4)	0.2663 (2)	0.7320 (4)	0.0568 (9)	
H1	-0.0080	0.2643	0.8132	0.068*	
C25	0.5417 (3)	0.2976 (2)	0.4794 (4)	0.0584 (9)	
H25A	0.5450	0.2440	0.4511	0.070*	0.755 (13)
H25B	0.6134	0.3254	0.4511	0.070*	0.755 (13)
H25C	0.5454	0.2430	0.4564	0.070*	0.245 (13)
H25D	0.6153	0.3243	0.4526	0.070*	0.245 (13)
C6	-0.0801 (4)	0.2321 (2)	0.6404 (4)	0.0608 (10)	
H6	-0.1536	0.2068	0.6604	0.073*	
C11	0.0570 (4)	0.3515 (2)	0.1019 (3)	0.0616 (10)	
H11A	0.0491	0.4052	0.1249	0.092*	
H11B	-0.0148	0.3222	0.1247	0.092*	
H11C	0.0566	0.3481	0.0149	0.092*	
C35	0.6748 (4)	0.6470 (2)	0.1552 (3)	0.0578 (9)	
H35A	0.6020	0.6735	0.1075	0.069*	
H35B	0.7496	0.6816	0.1619	0.069*	
C28	0.8029 (4)	0.4636 (2)	0.7860 (3)	0.0552 (9)	
H28A	0.7597	0.4611	0.8585	0.066*	

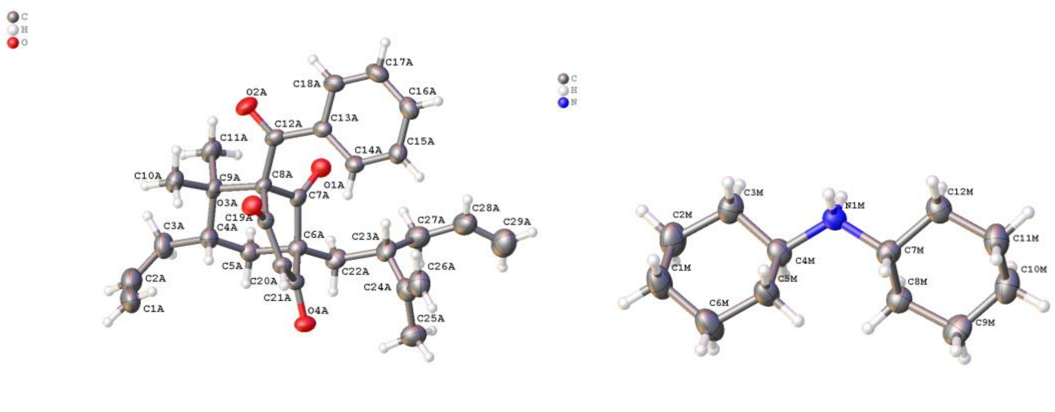
H28B	0.8128	0.4107	0.7572	0.066*	
C36	0.7051 (4)	0.5720 (2)	0.0904 (3)	0.0580 (9)	
H36A	0.6270	0.5403	0.0747	0.070*	
H36B	0.7328	0.5847	0.0123	0.070*	
C13	0.3092 (5)	0.3737 (3)	-0.0001 (3)	0.0646 (10)	
H13A	0.3110	0.3211	-0.0327	0.077*	
H13B	0.2315	0.3993	-0.0406	0.077*	
C21	0.3560 (4)	0.5845 (2)	0.5866 (4)	0.0593 (9)	
H21A	0.4230	0.6121	0.5580	0.071*	
H21B	0.3475	0.5855	0.6695	0.071*	
C14	0.4250 (5)	0.4168 (3)	-0.0289 (3)	0.0713 (11)	
H14	0.5053	0.4042	0.0154	0.086*	
C27A	0.5001 (5)	0.3354 (3)	0.6809 (5)	0.0544 (16)	0.755 (13)
H27A	0.4325	0.3675	0.6463	0.065*	0.755 (13)
H27B	0.5202	0.3319	0.7656	0.065*	0.755 (13)
C26A	0.5642 (14)	0.2968 (9)	0.6133 (8)	0.076 (3)	0.755 (13)
H26A	0.6311	0.2653	0.6512	0.091*	0.755 (13)
C15	0.4222 (6)	0.4713 (4)	-0.1123 (4)	0.0968 (18)	
H15A	0.3436	0.4853	-0.1582	0.116*	
H15B	0.4989	0.4960	-0.1257	0.116*	
Cl2B	0.725 (2)	0.2912 (18)	-0.040 (2)	0.067 (2)	0.292 (7)
Cl3A	0.6037 (5)	0.2166 (5)	0.1336 (6)	0.095 (2)	0.395 (7)

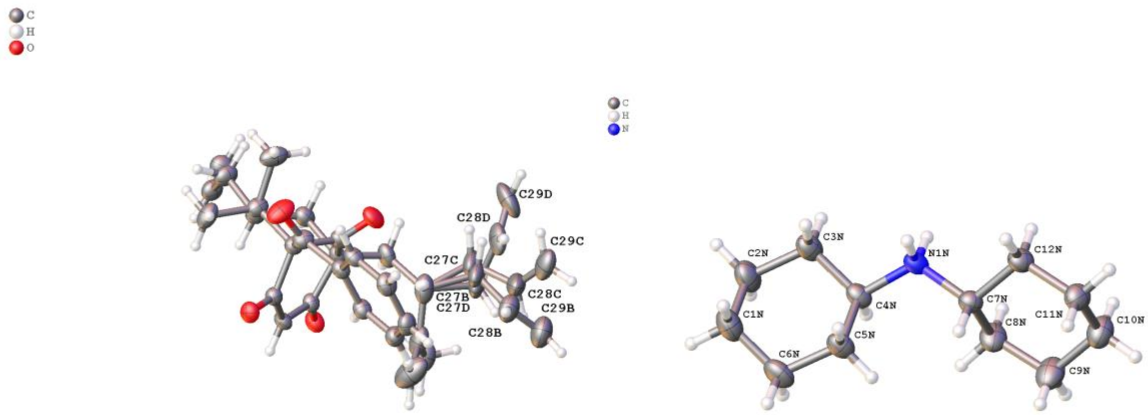
Cl1B	0.6463 (7)	0.2599 (4)	0.1795 (5)	0.078 (2)	0.292 (7)
Cl3B	0.6956 (7)	0.1241 (3)	0.0456 (5)	0.0750 (19)	0.292 (7)
Cl2A	0.7838 (9)	0.1355 (3)	0.0000 (6)	0.137 (3)	0.395 (7)
C1SB	0.7446 (6)	0.2217 (3)	0.0764 (5)	0.0551 (12)	0.292 (7)
H1SB	0.8355	0.2221	0.1151	0.066*	0.292 (7)
C1SA	0.7446 (6)	0.2217 (3)	0.0764 (5)	0.0551 (12)	0.395 (7)
H1SA	0.8154	0.2347	0.1416	0.066*	0.395 (7)
Cl1A	0.7488 (14)	0.2853 (13)	-0.0501 (16)	0.067 (2)	0.395 (7)
Cl3C	0.7739 (9)	0.1852 (6)	0.0273 (8)	0.0551 (12)	0.110 (2)
Cl1C	0.5442 (10)	0.1970 (5)	0.1415 (10)	0.052 (2)	0.110 (2)
Cl2C	0.7120 (9)	0.3240 (5)	0.1564 (12)	0.077 (3)	0.110 (2)
C1SC	0.702 (2)	0.2230 (14)	0.150 (3)	0.0551 (12)	0.110 (2)
H1SC	0.7489	0.2019	0.2260	0.066*	0.110 (2)
C27B	0.5741 (17)	0.2716 (12)	0.7310 (14)	0.072 (6)	0.245 (13)
H27C	0.6005	0.2197	0.7405	0.087*	0.245 (13)
H27D	0.5646	0.3017	0.7994	0.087*	0.245 (13)
C26B	0.549 (4)	0.304 (2)	0.6142 (16)	0.070 (8)	0.245 (13)
H26B	0.5247	0.3555	0.6275	0.083*	0.245 (13)
Cl3D	0.8970 (16)	0.1341 (12)	-0.0529 (16)	0.095 (2)	0.077 (3)
Cl2D	0.7449 (19)	0.2470 (10)	-0.0543 (15)	0.0750 (19)	0.077 (3)
C1SD	0.802 (3)	0.1674 (19)	0.046 (3)	0.0551 (12)	0.077 (3)
H1SD	0.8479	0.1831	0.1264	0.066*	0.077 (3)

Cl1D	0.6871 (18)	0.0974 (11)	0.051 (2)	0.077 (3)	0.077 (3)

B. Compound 21







Crystals of compound **21** suitable for X-ray analysis were obtained by layering a $CHCl_3$ solution with isooctane at ambient temperature followed by storage in a sealed vial. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC # 1913294). Copies of the data can be obtained free of charge through application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computing details

Data collection: *APEX2* (Bruker, 2016); cell refinement: *SAINT* V8.38A (Bruker, 2016); data reduction: *SAINT* V8.38A (Bruker, 2016); program(s) used to solve structure: SHELXT 2018/2 (Sheldrick, 2018); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

Table S6. Crystal data.

$1(C_{29}H_{33}O_4)\cdot C_{12}H_{24}N$	$F(000) = 2736$
$M_r = 627.87$	$D_x = 1.142$ Mg m^{-3}
Monoclinic, *C*2	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 33.1205$ (10) Å	Cell parameters from 9835 reflections
$b = 11.3921$ (3) Å	$\theta = 2.3–66.3°$

c = 25.2617 (13) Å	μ = 0.56 mm^{-1}
β = 129.951 (2)°	T = 100 K
V = 7306.8 (5) $Å^3$	Plate
Z = 8	0.12 × 0.10 × 0.04 mm

Table S7. Data collection.

Bruker X8 Proteum-R diffractometer	12802 independent reflections
Radiation source: rotating anode	11261 reflections with $I > 2\sigma(I)$
Montel monochromator	R_{int} = 0.056
ϕ and ω scans	θ_{max} = 66.8°, θ_{min} = 2.3°
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.0803 before and 0.0660 after correction. The Ratio of minimum to maximum transmission is 0.8755. The λ/2 correction factor is Not present.	h = -39∅39
T_{min} = 0.659, T_{max} = 0.753	k = -13∅13
89574 measured reflections	l = -29∅29

Table S8. Refinement parameters.

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained

$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 2.1555P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rangle_{max} = 0.25$ e Å^{-3}
12802 reflections	$\Delta\rangle_{min} = -0.24$ e Å^{-3}
880 parameters	Absolute structure: Flack x determined using 4686 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
27 restraints	Absolute structure parameter: -0.02 (6)

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.

Table S9. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for 21.

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O3B	0.58378 (8)	0.72429 (18)	1.10783 (10)	0.0316 (4)	
O4B	0.54578 (7)	0.60028 (19)	0.90265 (10)	0.0319 (4)	
O1A	0.87535 (8)	0.97255 (19)	1.59035 (11)	0.0348 (5)	
O3A	1.01190 (7)	0.87127 (19)	1.59905 (10)	0.0350 (5)	

O4A	0.84063 (8)	0.89348 (19)	1.38435 (10)	0.0347 (5)	
O1B	0.71402 (7)	0.7183 (2)	1.09701 (11)	0.0383 (5)	
O2A	1.00607 (9)	0.8640 (2)	1.72490 (11)	0.0447 (6)	
O2B	0.69361 (10)	0.8749 (2)	1.20209 (11)	0.0485 (6)	
N1N	0.56069 (9)	0.5808 (2)	1.17251 (12)	0.0277 (5)	
H1NA	0.525984	0.582742	1.148134	0.033*	
H1NB	0.567693	0.623647	1.149809	0.033*	
N1M	0.87884 (9)	0.8802 (2)	1.31406 (12)	0.0309 (5)	
H1MA	0.867865	0.884960	1.338209	0.037*	
H1MB	0.913664	0.871466	1.344223	0.037*	
C21B	0.57574 (10)	0.6444 (2)	0.96207 (14)	0.0264 (6)	
C7B	0.66650 (10)	0.7262 (3)	1.06181 (14)	0.0284 (6)	
C19B	0.59316 (10)	0.7168 (3)	1.06689 (14)	0.0267 (6)	
C20B	0.56338 (10)	0.6536 (3)	1.00560 (14)	0.0268 (6)	
H20B	0.533479	0.615023	0.992661	0.032*	
C7A	0.88700 (11)	0.9168 (2)	1.56077 (15)	0.0286 (6)	
C20A	0.92727 (11)	0.8927 (3)	1.49042 (14)	0.0305 (6)	
H20A	0.941302	0.904739	1.468654	0.037*	
C13A	0.98840 (11)	1.0500 (3)	1.67422 (15)	0.0304 (6)	
C18B	0.74783 (11)	0.6785 (3)	1.27784 (15)	0.0321 (6)	
H18B	0.760868	0.751242	1.299154	0.038*	
C13B	0.70568 (10)	0.6720 (3)	1.20680 (14)	0.0288 (6)	

C14A	0.96886 (12)	1.1197 (3)	1.61666 (16)	0.0339 (7)	
H14A	0.949410	1.085511	1.573153	0.041*	
C2B	0.53003 (13)	1.0096 (3)	0.86072 (16)	0.0378 (7)	
H2B	0.498405	0.982134	0.847953	0.045*	
C6B	0.62764 (10)	0.6959 (3)	0.98541 (14)	0.0276 (6)	
C4N	0.58618 (11)	0.6395 (3)	1.24070 (14)	0.0304 (6)	
H4N	0.573636	0.601469	1.262570	0.037*	
C12N	0.54973 (12)	0.4196 (3)	1.09964 (15)	0.0337 (7)	
H12A	0.511797	0.426463	1.071117	0.040*	
H12B	0.561032	0.471636	1.080952	0.040*	
C7N	0.57592 (11)	0.4565 (3)	1.17360 (15)	0.0293 (6)	
H7N	0.614196	0.453268	1.201074	0.035*	
C19A	0.96231 (11)	0.8756 (2)	1.56189 (14)	0.0286 (6)	
C9B	0.62468 (12)	0.9136 (3)	1.05441 (15)	0.0338 (7)	
C14B	0.68770 (11)	0.5614 (3)	1.17638 (15)	0.0311 (6)	
H14B	0.660262	0.555389	1.129040	0.037*	
C21A	0.87238 (11)	0.8929 (2)	1.44953 (14)	0.0289 (6)	
C8A	0.94046 (11)	0.8596 (2)	1.59973 (14)	0.0273 (6)	
C15A	0.97836 (12)	1.2393 (3)	1.62420 (17)	0.0378 (7)	
H15A	0.965443	1.285121	1.585760	0.045*	
C22B	0.65269 (12)	0.6199 (3)	0.96360 (16)	0.0364 (7)	
H22A	0.681455	0.663726	0.972085	0.044*	

H22B	0.626690	0.606721	0.914210	0.044*	
C4B	0.58936 (11)	0.9005 (3)	0.97385 (15)	0.0323 (6)	
H4B	0.556112	0.864555	0.957075	0.039*	
C5N	0.64595 (11)	0.6292 (3)	1.28887 (15)	0.0361 (7)	
H5NA	0.658476	0.657655	1.265474	0.043*	
H5NB	0.655983	0.547365	1.300540	0.043*	
C12B	0.68175 (11)	0.7858 (3)	1.16882 (15)	0.0322 (6)	
C8B	0.64185 (10)	0.7857 (3)	1.08855 (14)	0.0273 (6)	
C6A	0.84765 (11)	0.8855 (3)	1.48464 (14)	0.0303 (6)	
C17B	0.77014 (12)	0.5767 (3)	1.31642 (16)	0.0371 (7)	
H17B	0.798368	0.581758	1.363538	0.045*	
C11N	0.56406 (13)	0.2937 (3)	1.09767 (17)	0.0374 (7)	
H11G	0.601674	0.288120	1.123111	0.045*	
H11H	0.546015	0.270906	1.050239	0.045*	
C7M	0.85574 (12)	0.7715 (3)	1.27094 (16)	0.0337 (7)	
H7M	0.817421	0.773658	1.243236	0.040*	
C4M	0.86712 (12)	0.9948 (3)	1.27786 (17)	0.0358 (7)	
H4M	0.882976	0.993876	1.255844	0.043*	
C5B	0.61341 (11)	0.8201 (3)	0.95235 (16)	0.0332 (7)	
H5BA	0.645034	0.856732	0.965152	0.040*	
H5BB	0.588714	0.811962	0.902491	0.040*	
C16B	0.75113 (12)	0.4682 (3)	1.28601 (17)	0.0376 (7)	

H16B	0.765793	0.400395	1.312653	0.045*	
C12A	0.98054 (11)	0.9195 (3)	1.67094 (15)	0.0328 (7)	
C18A	1.01702 (12)	1.1032 (3)	1.73859 (16)	0.0377 (7)	
H18A	1.030361	1.058080	1.777404	0.045*	
C8M	0.86809 (13)	0.7618 (3)	1.22253 (17)	0.0382 (7)	
H8MA	0.905828	0.767875	1.248958	0.046*	
H8MB	0.851365	0.825936	1.189608	0.046*	
C12M	0.87759 (13)	0.6673 (3)	1.32019 (18)	0.0412 (7)	
H12C	0.915764	0.668859	1.351136	0.049*	
H12D	0.866829	0.673171	1.347887	0.049*	
C1B	0.53067 (14)	1.0363 (3)	0.81108 (19)	0.0492 (9)	
H1BA	0.561450	1.064034	0.821464	0.059*	
H1BB	0.500335	1.027565	0.765280	0.059*	
C9A	0.92991 (12)	0.7235 (3)	1.60328 (16)	0.0342 (7)	
C3N	0.56837 (12)	0.7662 (3)	1.22605 (16)	0.0373 (7)	
H3NA	0.530479	0.769130	1.198887	0.045*	
H3NB	0.576615	0.801878	1.199133	0.045*	
C15B	0.71017 (12)	0.4604 (3)	1.21574 (16)	0.0349 (7)	
H15B	0.697656	0.387224	1.194826	0.042*	
C2N	0.59506 (13)	0.8362 (3)	1.29282 (18)	0.0467 (8)	
H2NA	0.584541	0.917866	1.281562	0.056*	
H2NB	0.583533	0.806327	1.317169	0.056*	

C5A	0.83682 (12)	0.7546 (3)	1.48643 (16)	0.0348 (7)	
H5AA	0.819937	0.747104	1.506498	0.042*	
H5AB	0.812504	0.725249	1.439467	0.042*	
C17A	1.02577 (13)	1.2231 (3)	1.74523 (18)	0.0453 (8)	
H17A	1.044563	1.258127	1.788418	0.054*	
C10B	0.59221 (14)	0.9739 (3)	1.07041 (18)	0.0438 (8)	
H10A	0.585376	1.053776	1.054606	0.066*	
H10B	0.611488	0.972723	1.119325	0.066*	
H10C	0.559430	0.933141	1.047304	0.066*	
C3B	0.57569 (13)	1.0191 (3)	0.93651 (16)	0.0408 (7)	
H3BA	0.567296	1.075551	0.956908	0.049*	
H3BB	0.606184	1.047921	0.943051	0.049*	
C8N	0.56098 (14)	0.3742 (3)	1.20575 (17)	0.0403 (7)	
H8NA	0.523514	0.380361	1.181176	0.048*	
H8NB	0.579719	0.396387	1.253453	0.048*	
C10N	0.54849 (15)	0.2113 (3)	1.12931 (19)	0.0454 (8)	
H10G	0.510535	0.212313	1.101677	0.055*	
H10H	0.559016	0.131809	1.129368	0.055*	
C3M	0.89298 (13)	1.0915 (3)	1.33147 (19)	0.0424 (8)	
H3MA	0.930764	1.079061	1.364071	0.051*	
H3MB	0.880100	1.089149	1.356759	0.051*	
C5M	0.80826 (12)	1.0139 (3)	1.22225 (17)	0.0415 (8)	

H5MA	0.791495	1.011061	1.242617	0.050*	
H5MB	0.793360	0.952021	1.188007	0.050*	
C9N	0.57460 (18)	0.2482 (3)	1.2027 (2)	0.0517 (9)	
H9NA	0.612495	0.240721	1.231062	0.062*	
H9NB	0.563266	0.196276	1.221364	0.062*	
C23B	0.67402 (14)	0.4999 (3)	0.99948 (18)	0.0484 (9)	
H23B	0.691252	0.513770	1.048133	0.058*	0.433 (11)
H23A	0.692991	0.512430	1.048761	0.058*	0.407 (11)
H23C	0.694758	0.510989	1.049274	0.058*	0.160 (8)
C23A	0.79941 (12)	1.0883 (3)	1.44784 (17)	0.0428 (8)	
H23D	0.832941	1.110371	1.492515	0.051*	
C6N	0.67173 (12)	0.7000 (3)	1.35501 (17)	0.0430 (8)	
H6NA	0.662311	0.665834	1.380957	0.052*	
H6NB	0.709721	0.695820	1.383383	0.052*	
C24A	0.79936 (13)	1.1379 (3)	1.39347 (19)	0.0442 (8)	
C4A	0.88648 (13)	0.6788 (3)	1.52765 (17)	0.0382 (7)	
H4A	0.901305	0.684430	1.504405	0.046*	
C16A	1.00686 (13)	1.2909 (3)	1.68837 (18)	0.0428 (8)	
H16A	1.013294	1.371291	1.693260	0.051*	
C9M	0.84848 (14)	0.6452 (3)	1.18396 (19)	0.0458 (8)	
H9MA	0.810339	0.642749	1.153825	0.055*	
H9MB	0.858502	0.638695	1.155462	0.055*	

C1N	0.65448 (13)	0.8277 (3)	1.33921 (18)	0.0469 (8)	
H1NC	0.670328	0.869562	1.381943	0.056*	
H1ND	0.666405	0.863902	1.316639	0.056*	
C22A	0.79583 (11)	0.9533 (3)	1.44650 (17)	0.0375 (7)	
H22C	0.779605	0.930883	1.466105	0.045*	
H22D	0.772433	0.928099	1.398647	0.045*	
C24B	0.63366 (16)	0.4065 (3)	0.9754 (2)	0.0513 (9)	
C11A	0.91225 (14)	0.7094 (3)	1.64586 (18)	0.0429 (8)	
H11D	0.940325	0.732599	1.692702	0.064*	
H11E	0.903336	0.628792	1.644901	0.064*	
H11F	0.881997	0.757921	1.626747	0.064*	
C11B	0.67312 (14)	0.9877 (3)	1.08210 (17)	0.0475 (8)	
H11A	0.693617	0.948804	1.072670	0.071*	
H11B	0.694060	0.997733	1.131044	0.071*	
H11C	0.662103	1.063096	1.059973	0.071*	
C2M	0.88128 (14)	1.2110 (3)	1.2977 (2)	0.0531 (9)	
H2MA	0.898801	1.217292	1.278482	0.064*	
H2MB	0.895387	1.271611	1.332550	0.064*	
C10A	0.98024 (13)	0.6519 (3)	1.63639 (18)	0.0426 (8)	
H10D	0.992851	0.665635	1.611719	0.064*	
H10E	0.972715	0.569949	1.634511	0.064*	
H10F	1.006654	0.675460	1.683664	0.064*	

C10M	0.87133 (15)	0.5421 (3)	1.2340 (2)	0.0498 (9)	
H10I	0.857361	0.469201	1.208187	0.060*	
H10J	0.909304	0.540814	1.261727	0.060*	
C1M	0.82230 (15)	1.2314 (3)	1.2406 (2)	0.0554 (10)	
H1MC	0.805272	1.235739	1.260534	0.066*	
H1MD	0.816733	1.305502	1.217829	0.066*	
C25B	0.60136 (16)	0.3641 (4)	0.90246 (19)	0.0555 (9)	
H25A	0.582565	0.428935	0.871403	0.083*	
H25B	0.576722	0.306081	0.893818	0.083*	
H25C	0.624098	0.330056	0.895403	0.083*	
C11M	0.85779 (15)	0.5519 (3)	1.2804 (2)	0.0495 (9)	
H11I	0.873514	0.486920	1.312754	0.059*	
H11J	0.819892	0.547167	1.252845	0.059*	
C6M	0.79786 (15)	1.1325 (3)	1.1878 (2)	0.0569 (10)	
H6MA	0.812506	1.133066	1.164661	0.068*	
H6MB	0.760176	1.145068	1.153257	0.068*	
C26A	0.84075 (15)	1.1976 (3)	1.4116 (2)	0.0543 (9)	
H26C	0.869548	1.208241	1.458130	0.065*	
H26D	0.841103	1.229020	1.377961	0.065*	
C27B	0.7168 (10)	0.4480 (15)	0.9991 (18)	0.058 (3)	0.433 (11)
H27A	0.702274	0.433599	0.951923	0.070*	0.433 (11)
H27B	0.745758	0.502859	1.020005	0.070*	0.433 (11)

C28A	0.75919 (17)	1.2727 (4)	1.4529 (2)	0.0602 (10)	
H28A	0.790754	1.301969	1.492656	0.072*	
C3A	0.87098 (16)	0.5493 (3)	1.5231 (2)	0.0526 (9)	
H3AA	0.889222	0.520930	1.569644	0.063*	
H3AB	0.833544	0.546412	1.499082	0.063*	
C27A	0.75436 (15)	1.1445 (4)	1.4442 (2)	0.0536 (9)	
H27G	0.720610	1.125691	1.399880	0.064*	
H27H	0.755087	1.110177	1.479902	0.064*	
C26B	0.6275 (2)	0.3584 (4)	1.0177 (3)	0.0803 (15)	
H26A	0.603155	0.298436	1.002082	0.096*	
H26B	0.647575	0.384807	1.063051	0.096*	
C2A	0.88188 (18)	0.4677 (4)	1.4885 (2)	0.0629 (11)	
H2A	0.864179	0.396273	1.475090	0.075*	
C25A	0.75076 (15)	1.1213 (4)	1.31900 (19)	0.0539 (9)	
H25D	0.745740	1.039179	1.307845	0.081*	
H25E	0.754971	1.162474	1.289665	0.081*	
H25F	0.720639	1.151590	1.312107	0.081*	
C29A	0.72250 (19)	1.3502 (4)	1.4089 (2)	0.0688 (12)	
H29G	0.690344	1.324703	1.368485	0.083*	
H29H	0.728891	1.429991	1.418558	0.083*	
C1A	0.9133 (2)	0.4819 (4)	1.4740 (2)	0.0713 (13)	
H1AA	0.932211	0.551339	1.485989	0.086*	

H1AB	0.916627	0.422565	1.451698	0.086*	
C28B	0.7362 (5)	0.3341 (10)	1.0393 (6)	0.053 (3)	0.433 (11)
H28B	0.748945	0.333574	1.084507	0.063*	0.433 (11)
C29B	0.7354 (4)	0.2378 (9)	1.0119 (6)	0.068 (3)	0.433 (11)
H29A	0.722700	0.237554	0.966661	0.082*	0.433 (11)
H29B	0.747480	0.168589	1.037307	0.082*	0.433 (11)
C29C	0.7995 (4)	0.3647 (9)	1.0801 (5)	0.061 (3)	0.407 (11)
H29C	0.819187	0.433649	1.096854	0.074*	0.407 (11)
H29D	0.815993	0.293011	1.099933	0.074*	0.407 (11)
C28C	0.7499 (5)	0.3686 (12)	1.0298 (8)	0.067 (4)	0.407 (11)
H28C	0.732286	0.297083	1.015230	0.080*	0.407 (11)
C28D	0.7607 (9)	0.485 (2)	1.0268 (12)	0.056 (8)	0.160 (8)
H28D	0.782925	0.477002	1.074562	0.068*	0.160 (8)
C29D	0.7796 (10)	0.543 (3)	1.0034 (15)	0.074 (10)	0.160 (8)
H29E	0.759442	0.553874	0.956131	0.089*	0.160 (8)
H29F	0.813387	0.574017	1.033854	0.089*	0.160 (8)
C27C	0.7164 (11)	0.477 (2)	0.9911 (18)	0.058 (3)	0.407 (11)
H27C	0.698679	0.468235	0.942390	0.070*	0.407 (11)
H27D	0.739214	0.545313	1.007828	0.070*	0.407 (11)
C27D	0.7072 (13)	0.427 (3)	0.987 (3)	0.058 (3)	0.160 (8)
H27E	0.711306	0.346833	1.003533	0.070*	0.160 (8)
H27F	0.689627	0.424056	0.938453	0.070*	0.160 (8)

Table S10. Atomic displacement parameters (Å^2) for 21

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3B	0.0358 (10)	0.0377 (11)	0.0271 (10)	0.0024 (9)	0.0228 (9)	-0.0014 (8)
O4B	0.0264 (10)	0.0448 (12)	0.0231 (10)	-0.0007 (8)	0.0152 (9)	-0.0048 (9)
O1A	0.0359 (11)	0.0395 (11)	0.0332 (11)	0.0043 (9)	0.0240 (10)	0.0016 (9)
O3A	0.0272 (10)	0.0415 (12)	0.0330 (11)	0.0049 (9)	0.0179 (9)	0.0043 (9)
O4A	0.0351 (11)	0.0385 (12)	0.0231 (11)	-0.0070 (9)	0.0154 (9)	-0.0027 (9)
O1B	0.0224 (10)	0.0533 (13)	0.0322 (11)	0.0001 (9)	0.0144 (9)	0.0041 (10)
O2A	0.0475 (13)	0.0464 (13)	0.0253 (11)	0.0061 (11)	0.0167 (10)	0.0088 (10)
O2B	0.0575 (14)	0.0363 (13)	0.0260 (11)	-0.0051 (11)	0.0150 (11)	-0.0077 (10)
N1N	0.0234 (11)	0.0370 (13)	0.0229 (12)	0.0010 (10)	0.0150 (10)	-0.0003 (10)
N1M	0.0289 (12)	0.0322 (13)	0.0300 (13)	-0.0029 (10)	0.0183 (11)	0.0008 (11)
C21B	0.0225 (13)	0.0314 (15)	0.0220 (14)	0.0021 (11)	0.0128 (12)	-0.0002 (12)
C7B	0.0239 (14)	0.0356 (16)	0.0244 (14)	0.0001 (12)	0.0149 (12)	0.0038 (12)
C19B	0.0260 (13)	0.0298 (14)	0.0245 (14)	0.0019 (11)	0.0163 (12)	0.0014 (12)
C20B	0.0209 (12)	0.0354 (15)	0.0238 (14)	-0.0023 (11)	0.0142 (11)	-0.0015 (12)
C7A	0.0311 (14)	0.0264 (14)	0.0281 (15)	0.0017 (11)	0.0189 (13)	0.0057 (12)
C20A	0.0335 (15)	0.0341 (16)	0.0272 (15)	-0.0013 (12)	0.0211 (13)	-0.0006 (12)
C13A	0.0270 (14)	0.0357 (16)	0.0254 (15)	0.0029 (12)	0.0154 (12)	-0.0005 (12)
C18B	0.0246 (14)	0.0431 (17)	0.0253 (15)	-0.0044 (12)	0.0145 (12)	-0.0050 (13)
C13B	0.0245 (13)	0.0370 (16)	0.0237 (14)	-0.0006 (12)	0.0149 (12)	-0.0012 (12)

C14A	0.0325 (15)	0.0356 (17)	0.0260 (15)	0.0015 (12)	0.0153 (13)	-0.0014 (12)
C2B	0.0388 (16)	0.0340 (16)	0.0328 (17)	0.0039 (13)	0.0194 (14)	0.0067 (13)
C6B	0.0234 (13)	0.0373 (16)	0.0242 (14)	0.0026 (11)	0.0162 (12)	0.0030 (12)
C4N	0.0265 (14)	0.0424 (17)	0.0233 (14)	-0.0013 (12)	0.0164 (12)	-0.0026 (12)
C12N	0.0372 (15)	0.0393 (17)	0.0274 (15)	0.0031 (13)	0.0220 (14)	0.0009 (13)
C7N	0.0285 (14)	0.0328 (15)	0.0259 (15)	0.0023 (12)	0.0172 (12)	0.0013 (12)
C19A	0.0312 (15)	0.0256 (14)	0.0289 (15)	0.0003 (11)	0.0193 (13)	0.0004 (12)
C9B	0.0331 (15)	0.0324 (16)	0.0247 (15)	-0.0011 (12)	0.0134 (13)	0.0002 (12)
C14B	0.0252 (14)	0.0386 (17)	0.0248 (15)	-0.0007 (12)	0.0139 (12)	-0.0038 (13)
C21A	0.0330 (14)	0.0255 (14)	0.0240 (15)	-0.0039 (12)	0.0164 (13)	-0.0005 (11)
C8A	0.0287 (14)	0.0277 (15)	0.0234 (14)	0.0028 (11)	0.0158 (12)	0.0052 (11)
C15A	0.0369 (16)	0.0333 (17)	0.0369 (17)	0.0041 (13)	0.0208 (15)	0.0027 (13)
C22B	0.0321 (15)	0.053 (2)	0.0322 (16)	0.0079 (14)	0.0243 (14)	0.0034 (14)
C4B	0.0289 (14)	0.0337 (16)	0.0254 (15)	0.0006 (12)	0.0133 (12)	0.0035 (12)
C5N	0.0250 (14)	0.0484 (19)	0.0299 (16)	0.0006 (13)	0.0154 (13)	-0.0023 (14)
C12B	0.0315 (15)	0.0343 (17)	0.0225 (15)	-0.0041 (13)	0.0135 (13)	-0.0026 (13)
C8B	0.0241 (13)	0.0301 (15)	0.0219 (14)	-0.0003 (11)	0.0121 (12)	0.0002 (11)
C6A	0.0264 (14)	0.0334 (16)	0.0269 (14)	-0.0015 (12)	0.0151 (12)	0.0012 (12)
C17B	0.0305 (15)	0.0482 (19)	0.0240 (15)	0.0059 (14)	0.0136 (13)	0.0029 (14)
C11N	0.0443 (17)	0.0383 (18)	0.0351 (17)	0.0022 (14)	0.0281 (15)	-0.0013 (14)
C7M	0.0332 (15)	0.0341 (16)	0.0355 (17)	-0.0053 (13)	0.0229 (14)	-0.0041 (13)
C4M	0.0355 (16)	0.0337 (17)	0.0407 (18)	-0.0040 (13)	0.0255 (15)	0.0031 (14)

C5B	0.0282 (14)	0.0401 (17)	0.0282 (15)	0.0015 (12)	0.0166 (13)	0.0051 (13)
C16B	0.0356 (16)	0.0402 (18)	0.0345 (17)	0.0107 (14)	0.0213 (14)	0.0078 (14)
C12A	0.0317 (15)	0.0406 (17)	0.0253 (16)	0.0044 (13)	0.0180 (13)	0.0042 (13)
C18A	0.0380 (16)	0.0457 (19)	0.0288 (16)	0.0058 (14)	0.0212 (14)	-0.0005 (14)
C8M	0.0397 (17)	0.0377 (17)	0.0425 (18)	-0.0025 (13)	0.0289 (15)	-0.0015 (14)
C12M	0.0424 (17)	0.0375 (17)	0.0461 (19)	-0.0024 (14)	0.0294 (16)	0.0025 (15)
C1B	0.0432 (19)	0.057 (2)	0.040 (2)	0.0027 (16)	0.0232 (16)	0.0098 (17)
C9A	0.0403 (16)	0.0255 (15)	0.0344 (16)	0.0036 (13)	0.0230 (14)	0.0083 (12)
C3N	0.0323 (15)	0.0475 (19)	0.0308 (16)	0.0036 (14)	0.0196 (14)	-0.0057 (14)
C15B	0.0307 (15)	0.0358 (16)	0.0347 (17)	0.0021 (12)	0.0194 (14)	0.0006 (13)
C2N	0.0444 (19)	0.054 (2)	0.0382 (18)	-0.0016 (16)	0.0249 (16)	-0.0139 (16)
C5A	0.0343 (16)	0.0353 (17)	0.0333 (16)	-0.0074 (12)	0.0210 (14)	-0.0016 (13)
C17A	0.0461 (18)	0.047 (2)	0.0365 (18)	-0.0006 (16)	0.0239 (16)	-0.0127 (16)
C10B	0.0536 (19)	0.0338 (17)	0.0351 (18)	0.0106 (15)	0.0245 (16)	-0.0002 (14)
C3B	0.0411 (17)	0.0342 (17)	0.0332 (17)	0.0008 (14)	0.0175 (15)	0.0056 (14)
C8N	0.055 (2)	0.0409 (18)	0.0367 (17)	-0.0043 (15)	0.0351 (16)	-0.0005 (15)
C10N	0.061 (2)	0.0368 (18)	0.052 (2)	-0.0037 (16)	0.0429 (19)	-0.0029 (16)
C3M	0.0371 (16)	0.0376 (18)	0.051 (2)	-0.0075 (14)	0.0274 (16)	-0.0067 (15)
C5M	0.0348 (16)	0.0365 (18)	0.0394 (18)	-0.0039 (14)	0.0175 (15)	0.0031 (15)
C9N	0.082 (3)	0.038 (2)	0.054 (2)	-0.0039 (17)	0.053 (2)	0.0026 (16)
C23B	0.0462 (19)	0.058 (2)	0.0356 (18)	0.0199 (17)	0.0238 (16)	0.0054 (16)
C23A	0.0329 (16)	0.0419 (19)	0.0356 (18)	0.0061 (14)	0.0138 (15)	0.0041 (15)

C6N	0.0267 (15)	0.062 (2)	0.0303 (16)	-0.0050 (15)	0.0139 (14)	-0.0060 (16)
C24A	0.0412 (18)	0.0388 (18)	0.050 (2)	0.0032 (15)	0.0283 (16)	-0.0030 (16)
C4A	0.0450 (17)	0.0283 (16)	0.0402 (18)	-0.0011 (13)	0.0269 (15)	0.0016 (13)
C16A	0.0410 (17)	0.0351 (18)	0.047 (2)	0.0012 (14)	0.0255 (16)	-0.0076 (15)
C9M	0.0476 (18)	0.050 (2)	0.055 (2)	-0.0035 (16)	0.0394 (18)	-0.0101 (17)
C1N	0.0416 (19)	0.058 (2)	0.0385 (19)	-0.0093 (16)	0.0244 (16)	-0.0155 (16)
C22A	0.0269 (14)	0.0435 (18)	0.0325 (17)	0.0009 (13)	0.0146 (13)	0.0040 (14)
C24B	0.069 (2)	0.044 (2)	0.052 (2)	0.0196 (17)	0.044 (2)	0.0051 (17)
C11A	0.0521 (19)	0.0386 (18)	0.0443 (19)	0.0012 (15)	0.0338 (17)	0.0103 (15)
C11B	0.0472 (19)	0.0387 (19)	0.0322 (18)	-0.0095 (15)	0.0142 (15)	0.0038 (14)
C2M	0.051 (2)	0.0387 (19)	0.067 (2)	-0.0112 (16)	0.036 (2)	-0.0036 (18)
C10A	0.0474 (18)	0.0337 (17)	0.0424 (19)	0.0081 (14)	0.0269 (16)	0.0099 (15)
C10M	0.055 (2)	0.0357 (18)	0.074 (3)	-0.0067 (15)	0.048 (2)	-0.0084 (17)
C1M	0.051 (2)	0.0360 (19)	0.067 (3)	-0.0063 (16)	0.032 (2)	0.0079 (17)
C25B	0.062 (2)	0.055 (2)	0.044 (2)	0.0161 (19)	0.0313 (19)	0.0033 (18)
C11M	0.056 (2)	0.0355 (18)	0.067 (2)	-0.0035 (15)	0.044 (2)	0.0004 (16)
C6M	0.049 (2)	0.044 (2)	0.056 (2)	-0.0034 (16)	0.0240 (18)	0.0139 (18)
C26A	0.050 (2)	0.044 (2)	0.063 (2)	0.0028 (17)	0.034 (2)	0.0021 (18)
C27B	0.040 (4)	0.040 (11)	0.081 (7)	0.012 (6)	0.033 (4)	-0.005 (6)
C28A	0.066 (2)	0.065 (3)	0.046 (2)	0.021 (2)	0.035 (2)	0.007 (2)
C3A	0.059 (2)	0.0322 (18)	0.059 (2)	-0.0027 (16)	0.034 (2)	0.0017 (16)
C27A	0.054 (2)	0.063 (3)	0.046 (2)	0.0100 (19)	0.0334 (18)	0.0042 (18)

C26B	0.142 (5)	0.051 (3)	0.079 (3)	0.000 (3)	0.085 (3)	-0.006 (2)
C2A	0.074 (3)	0.040 (2)	0.055 (2)	0.0019 (19)	0.032 (2)	0.0024 (18)
C25A	0.058 (2)	0.059 (2)	0.044 (2)	-0.0048 (18)	0.0321 (19)	0.0004 (17)
C29A	0.071 (3)	0.069 (3)	0.073 (3)	0.018 (2)	0.049 (2)	0.011 (2)
C1A	0.098 (3)	0.042 (2)	0.062 (3)	0.018 (2)	0.046 (3)	0.002 (2)
C28B	0.048 (6)	0.048 (7)	0.048 (6)	0.013 (5)	0.024 (5)	0.000 (5)
C29B	0.070 (7)	0.058 (7)	0.074 (7)	0.020 (5)	0.046 (6)	0.003 (5)
C29C	0.088 (9)	0.050 (6)	0.071 (7)	0.023 (5)	0.063 (7)	0.006 (5)
C28C	0.055 (8)	0.037 (7)	0.117 (12)	0.004 (5)	0.059 (8)	-0.006 (6)
C28D	0.048 (15)	0.070 (18)	0.052 (14)	0.015 (12)	0.032 (13)	-0.018 (12)
C29D	0.039 (13)	0.13 (3)	0.069 (18)	0.008 (15)	0.040 (14)	-0.011 (17)
C27C	0.040 (4)	0.040 (11)	0.081 (7)	0.012 (6)	0.033 (4)	-0.005 (6)
C27D	0.040 (4)	0.040 (11)	0.081 (7)	0.012 (6)	0.033 (4)	-0.005 (6)

Table S11. Geometric parameters (Å, º) for 21

O3B—C19B	1.259 (3)	C5N—C6N	1.529 (5)
O4B—C21B	1.256 (3)	C12B—C8B	1.555 (4)
O1A—C7A	1.217 (4)	C6A—C5A	1.542 (4)
O3A—C19A	1.265 (3)	C6A—C22A	1.532 (4)
O4A—C21A	1.262 (3)	C17B—C16B	1.377 (5)
O1B—C7B	1.216 (3)	C11N—C10N	1.522 (5)
O2A—C12A	1.222 (4)	C7M—C8M	1.522 (4)

O2B—C12B	1.212 (4)	C7M—C12M	1.524 (5)
N1N—C4N	1.503 (4)	C4M—C3M	1.514 (5)
N1N—C7N	1.497 (4)	C4M—C5M	1.518 (4)
N1M—C7M	1.496 (4)	C16B—C15B	1.381 (5)
N1M—C4M	1.495 (4)	C18A—C17A	1.383 (5)
C21B—C20B	1.402 (4)	C8M—C9M	1.524 (5)
C21B—C6B	1.531 (4)	C12M—C11M	1.523 (5)
C7B—C6B	1.520 (4)	C9A—C4A	1.565 (5)
C7B—C8B	1.513 (4)	C9A—C11A	1.527 (4)
C19B—C20B	1.388 (4)	C9A—C10A	1.534 (4)
C19B—C8B	1.543 (4)	C3N—C2N	1.532 (4)
C7A—C8A	1.513 (4)	C2N—C1N	1.515 (5)
C7A—C6A	1.518 (4)	C5A—C4A	1.528 (4)
C20A—C19A	1.398 (4)	C17A—C16A	1.378 (5)
C20A—C21A	1.400 (4)	C8N—C9N	1.521 (5)
C13A—C14A	1.398 (4)	C10N—C9N	1.517 (5)
C13A—C12A	1.502 (4)	C3M—C2M	1.518 (5)
C13A—C18A	1.390 (4)	C5M—C6M	1.522 (5)
C18B—C13B	1.399 (4)	C23B—C24B	1.498 (6)
C18B—C17B	1.384 (5)	C23B—C27B	1.541 (12)
C13B—C14B	1.395 (4)	C23B—C27C	1.569 (14)
C13B—C12B	1.501 (4)	C23B—C27D	1.560 (17)

C14A—C15A	1.384 (5)	C23A—C24A	1.484 (5)
C2B—C1B	1.304 (5)	C23A—C22A	1.542 (5)
C2B—C3B	1.499 (4)	C23A—C27A	1.570 (5)
C6B—C22B	1.526 (4)	C6N—C1N	1.520 (5)
C6B—C5B	1.555 (4)	C24A—C26A	1.321 (5)
C4N—C5N	1.523 (4)	C24A—C25A	1.509 (5)
C4N—C3N	1.512 (5)	C4A—C3A	1.541 (5)
C12N—C7N	1.529 (4)	C9M—C10M	1.523 (5)
C12N—C11N	1.522 (4)	C24B—C25B	1.497 (5)
C7N—C8N	1.517 (4)	C24B—C26B	1.328 (6)
C19A—C8A	1.536 (4)	C2M—C1M	1.527 (5)
C9B—C4B	1.573 (4)	C10M—C11M	1.505 (5)
C9B—C8B	1.600 (4)	C1M—C6M	1.521 (6)
C9B—C10B	1.533 (5)	C27B—C28B	1.513 (15)
C9B—C11B	1.528 (5)	C28A—C27A	1.470 (6)
C14B—C15B	1.384 (5)	C28A—C29A	1.325 (6)
C21A—C6A	1.548 (4)	C3A—C2A	1.471 (6)
C8A—C12A	1.549 (4)	C2A—C1A	1.318 (7)
C8A—C9A	1.604 (4)	C28B—C29B	1.287 (12)
C15A—C16A	1.378 (5)	C29C—C28C	1.279 (13)
C22B—C23B	1.538 (5)	C28C—C27C	1.526 (15)
C4B—C5B	1.524 (4)	C28D—C29D	1.286 (18)

C4B—C3B	1.540 (4)	C28D—C27D	1.516 (18)
C7N—N1N—C4N	117.7 (2)	C5A—C6A—C21A	106.8 (2)
C4M—N1M—C7M	117.9 (2)	C22A—C6A—C21A	113.8 (2)
O4B—C21B—C20B	124.2 (2)	C22A—C6A—C5A	108.5 (2)
O4B—C21B—C6B	116.3 (2)	C16B—C17B—C18B	120.9 (3)
C20B—C21B—C6B	119.4 (2)	C12N—C11N—C10N	110.3 (3)
O1B—C7B—C6B	123.7 (2)	N1M—C7M—C8M	111.7 (2)
O1B—C7B—C8B	121.5 (3)	N1M—C7M—C12M	107.3 (2)
C8B—C7B—C6B	114.1 (2)	C8M—C7M—C12M	111.6 (3)
O3B—C19B—C20B	125.3 (3)	N1M—C4M—C3M	108.2 (3)
O3B—C19B—C8B	115.3 (2)	N1M—C4M—C5M	111.5 (2)
C20B—C19B—C8B	119.4 (2)	C3M—C4M—C5M	112.1 (3)
C19B—C20B—C21B	123.9 (2)	C4B—C5B—C6B	113.8 (2)
O1A—C7A—C8A	121.7 (3)	C17B—C16B—C15B	119.6 (3)
O1A—C7A—C6A	123.2 (3)	O2A—C12A—C13A	118.6 (3)
C8A—C7A—C6A	114.6 (2)	O2A—C12A—C8A	122.1 (3)
C19A—C20A—C21A	124.1 (3)	C13A—C12A—C8A	119.3 (2)
C14A—C13A—C12A	123.8 (3)	C17A—C18A—C13A	120.3 (3)
C18A—C13A—C14A	118.8 (3)	C7M—C8M—C9M	110.6 (3)
C18A—C13A—C12A	117.4 (3)	C11M—C12M—C7M	110.8 (3)
C17B—C18B—C13B	120.1 (3)	C4A—C9A—C8A	108.0 (2)

C18B—C13B—C12B	117.2 (3)	C11A—C9A—C8A	109.7 (3)
C14B—C13B—C18B	118.4 (3)	C11A—C9A—C4A	111.0 (3)
C14B—C13B—C12B	124.4 (3)	C11A—C9A—C10A	109.5 (3)
C15A—C14A—C13A	120.2 (3)	C10A—C9A—C8A	110.2 (2)
C1B—C2B—C3B	125.8 (3)	C10A—C9A—C4A	108.5 (3)
C21B—C6B—C5B	105.3 (2)	C4N—C3N—C2N	111.6 (3)
C7B—C6B—C21B	113.7 (2)	C16B—C15B—C14B	120.1 (3)
C7B—C6B—C22B	112.0 (2)	C1N—C2N—C3N	111.3 (3)
C7B—C6B—C5B	101.1 (2)	C4A—C5A—C6A	113.4 (2)
C22B—C6B—C21B	112.3 (2)	C16A—C17A—C18A	120.5 (3)
C22B—C6B—C5B	111.7 (2)	C2B—C3B—C4B	112.2 (3)
N1N—C4N—C5N	111.5 (2)	C7N—C8N—C9N	110.3 (3)
N1N—C4N—C3N	107.5 (2)	C9N—C10N—C11N	110.6 (3)
C3N—C4N—C5N	111.8 (3)	C4M—C3M—C2M	110.9 (3)
C11N—C12N—C7N	110.8 (3)	C4M—C5M—C6M	109.9 (3)
N1N—C7N—C12N	108.5 (2)	C10N—C9N—C8N	111.6 (3)
N1N—C7N—C8N	111.9 (2)	C22B—C23B—C27B	114.4 (7)
C8N—C7N—C12N	111.1 (2)	C22B—C23B—C27C	100.3 (7)
O3A—C19A—C20A	124.7 (3)	C22B—C23B—C27D	118 (2)
O3A—C19A—C8A	116.1 (2)	C24B—C23B—C22B	116.1 (3)
C20A—C19A—C8A	119.2 (2)	C24B—C23B—C27B	108.0 (10)
C4B—C9B—C8B	108.8 (2)	C24B—C23B—C27C	118.1 (13)

C10B—C9B—C4B	108.6 (2)	C24B—C23B—C27D	95.6 (11)
C10B—C9B—C8B	109.5 (2)	C24A—C23A—C22A	113.9 (3)
C11B—C9B—C4B	109.5 (3)	C24A—C23A—C27A	110.7 (3)
C11B—C9B—C8B	110.6 (2)	C22A—C23A—C27A	110.4 (3)
C11B—C9B—C10B	109.8 (3)	C1N—C6N—C5N	111.5 (3)
C15B—C14B—C13B	120.8 (3)	C23A—C24A—C25A	118.2 (3)
O4A—C21A—C20A	124.2 (3)	C26A—C24A—C23A	119.4 (3)
O4A—C21A—C6A	116.3 (2)	C26A—C24A—C25A	122.4 (4)
C20A—C21A—C6A	119.4 (2)	C5A—C4A—C9A	113.0 (3)
C7A—C8A—C19A	111.5 (2)	C5A—C4A—C3A	109.2 (3)
C7A—C8A—C12A	109.7 (2)	C3A—C4A—C9A	113.8 (3)
C7A—C8A—C9A	104.3 (2)	C17A—C16A—C15A	119.8 (3)
C19A—C8A—C12A	106.0 (2)	C10M—C9M—C8M	111.2 (3)
C19A—C8A—C9A	110.9 (2)	C2N—C1N—C6N	110.3 (3)
C12A—C8A—C9A	114.6 (2)	C6A—C22A—C23A	116.7 (3)
C16A—C15A—C14A	120.4 (3)	C25B—C24B—C23B	118.4 (3)
C6B—C22B—C23B	116.2 (2)	C26B—C24B—C23B	121.6 (4)
C5B—C4B—C9B	113.2 (2)	C26B—C24B—C25B	120.0 (4)
C5B—C4B—C3B	108.9 (2)	C3M—C2M—C1M	112.2 (3)
C3B—C4B—C9B	113.0 (3)	C11M—C10M—C9M	110.5 (3)
C4N—C5N—C6N	111.1 (2)	C6M—C1M—C2M	110.7 (3)
O2B—C12B—C13B	118.5 (3)	C10M—C11M—C12M	111.2 (3)

O2B—C12B—C8B	122.0 (3)	C1M—C6M—C5M	111.0 (3)
C13B—C12B—C8B	119.4 (2)	C28B—C27B—C23B	108.7 (11)
C7B—C8B—C19B	110.8 (2)	C29A—C28A—C27A	125.7 (5)
C7B—C8B—C9B	105.9 (2)	C2A—C3A—C4A	116.9 (3)
C7B—C8B—C12B	109.4 (2)	C28A—C27A—C23A	112.8 (3)
C19B—C8B—C9B	110.1 (2)	C1A—C2A—C3A	128.8 (4)
C19B—C8B—C12B	106.4 (2)	C29B—C28B—C27B	121.1 (15)
C12B—C8B—C9B	114.4 (2)	C29C—C28C—C27C	127.4 (18)
C7A—C6A—C21A	111.9 (2)	C29D—C28D—C27D	129 (3)
C7A—C6A—C5A	102.5 (2)	C28C—C27C—C23B	113.1 (13)
C7A—C6A—C22A	112.5 (2)	C28D—C27D—C23B	108.1 (16)

IV. References

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[S5] Iyer, A.; Clay, A.; Jockusch, S.; Sivaguru, J. *J. Phys. Org. Chem.* **2017**, *30*, 3738–3742.

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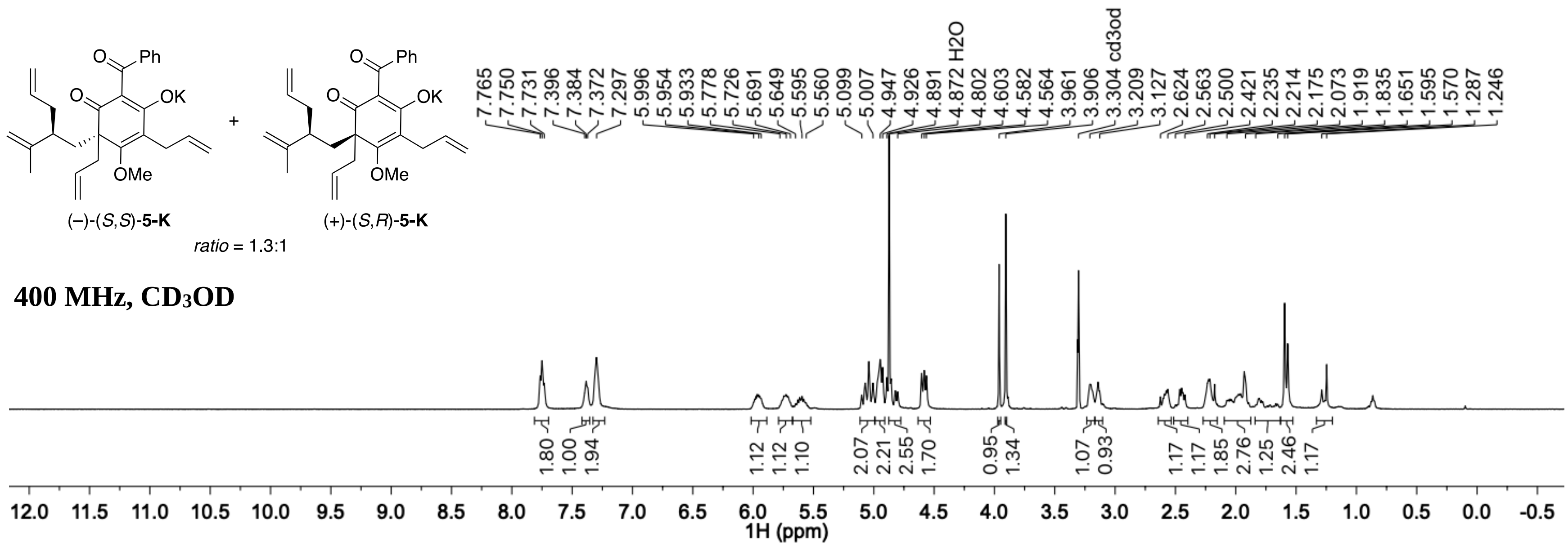
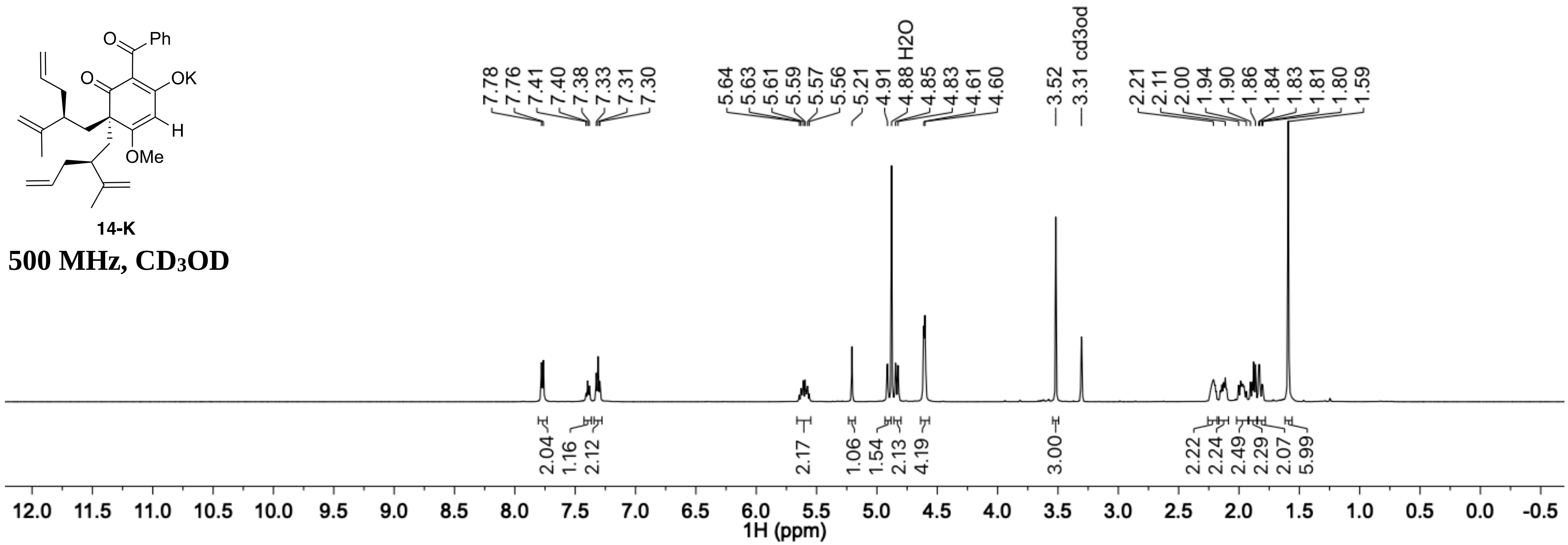
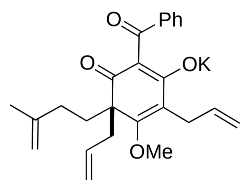
V. Select NMR Spectra

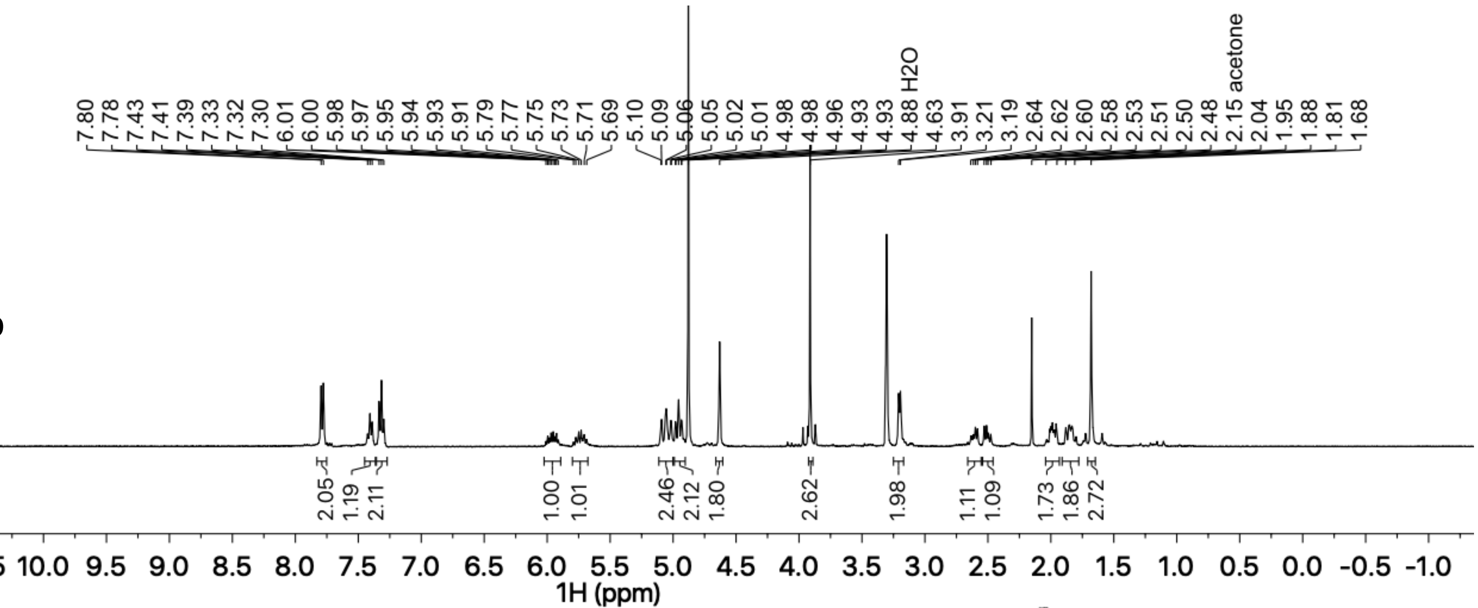

O
Ph
O
OK
OMe
+
O
Ph
O
OK
OMe
(–)-(S,S)-5-K
(+)-(S,R)-5-K
ratio = 1.3:1
400 MHz, CD3OD
7.765 7.750 7.731 7.396 7.384 7.372 7.297 5.996 5.954 5.933 5.778 5.726 5.691 5.649 5.595 5.560 5.099 5.007 4.947 4.926 4.891 4.872 H2O 4.802 4.603 4.582 4.564 3.961 3.906 3.304 cd3od 3.209 3.127 2.624 2.563 2.500 2.421 2.235 2.214 2.175 2.073 1.919 1.835 1.651 1.595 1.570 1.287 1.246
1.80 1.00 1.94 1.12 1.12 1.10 2.07 2.21 2.55 1.70 0.95 1.34 1.07 0.93 1.17 1.17 1.85 2.76 1.25 2.46 1.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 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 0.0 -0.5
1H (ppm)


O
Ph
O
OK
H
OMe
14-K
500 MHz, CD3OD
7.78 7.76 7.41 7.40 7.38 7.33 7.31 7.30 5.64 5.63 5.61 5.59 5.57 5.56 5.21 4.91 4.88 H2O 4.85 4.83 4.61 4.60 3.52 3.31 cd3od 2.21 2.11 2.00 1.94 1.90 1.86 1.84 1.83 1.81 1.80 1.59
2.04 1.16 2.12 2.17 1.06 1.54 2.13 4.19 3.00 2.22 2.24 2.49 2.29 2.07 5.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 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 0.0 -0.5
1H (ppm)

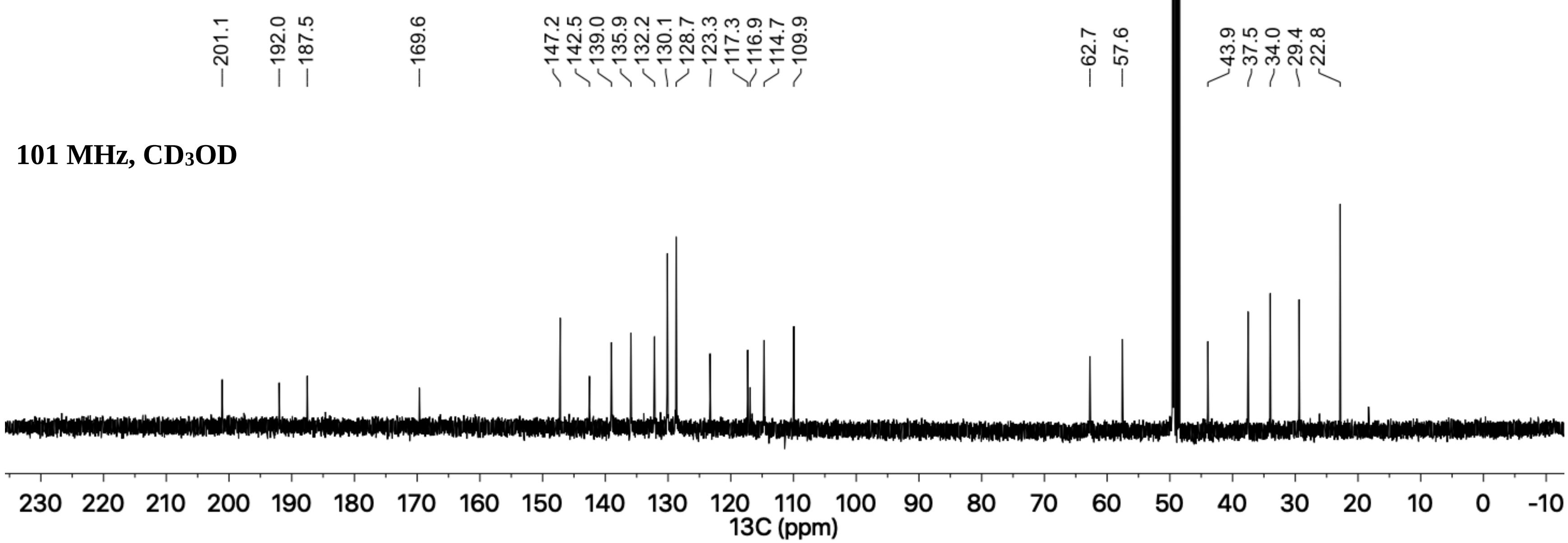


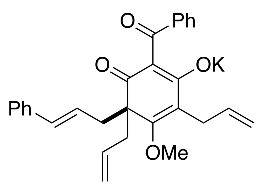
22-K

400 MHz, CD_3OD



101 MHz, CD_3OD





25-K

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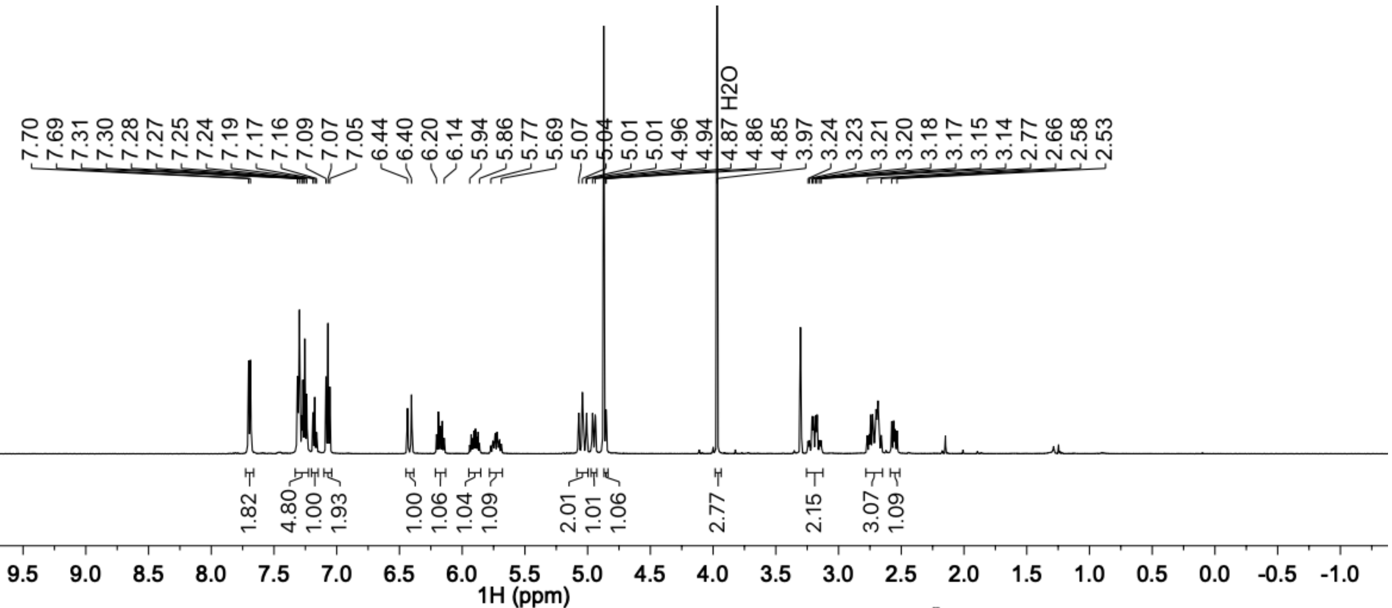
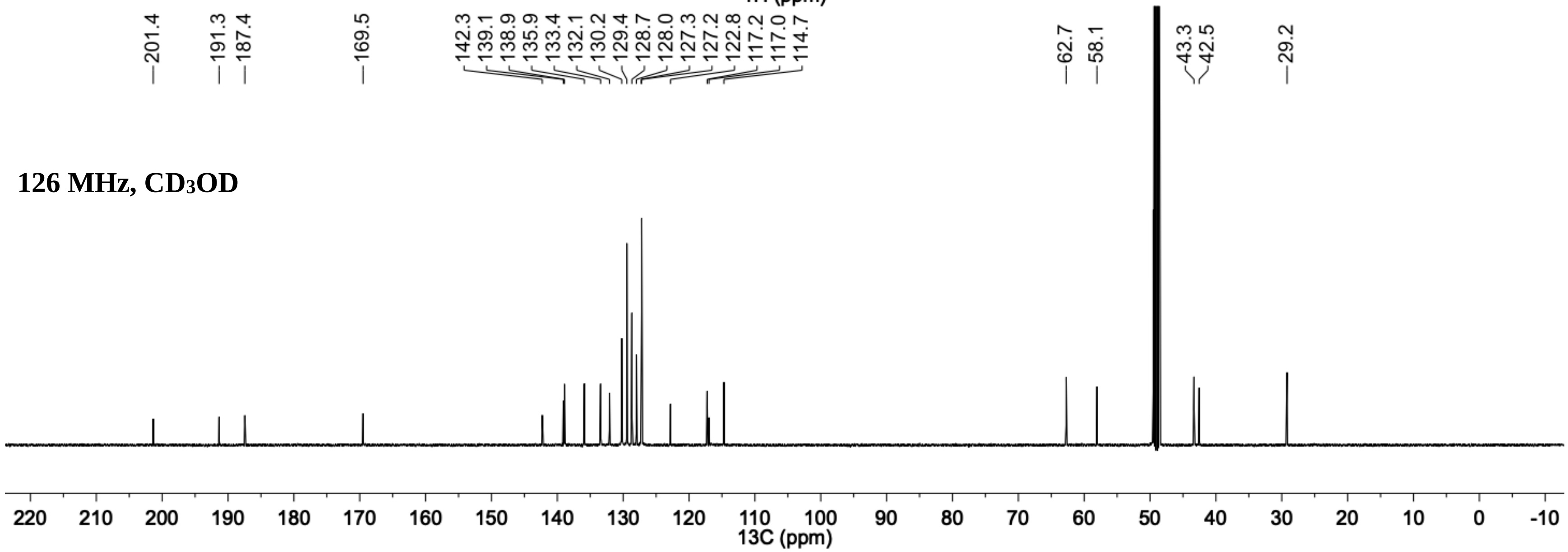
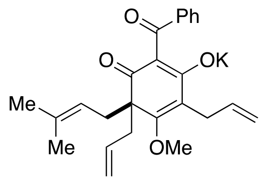


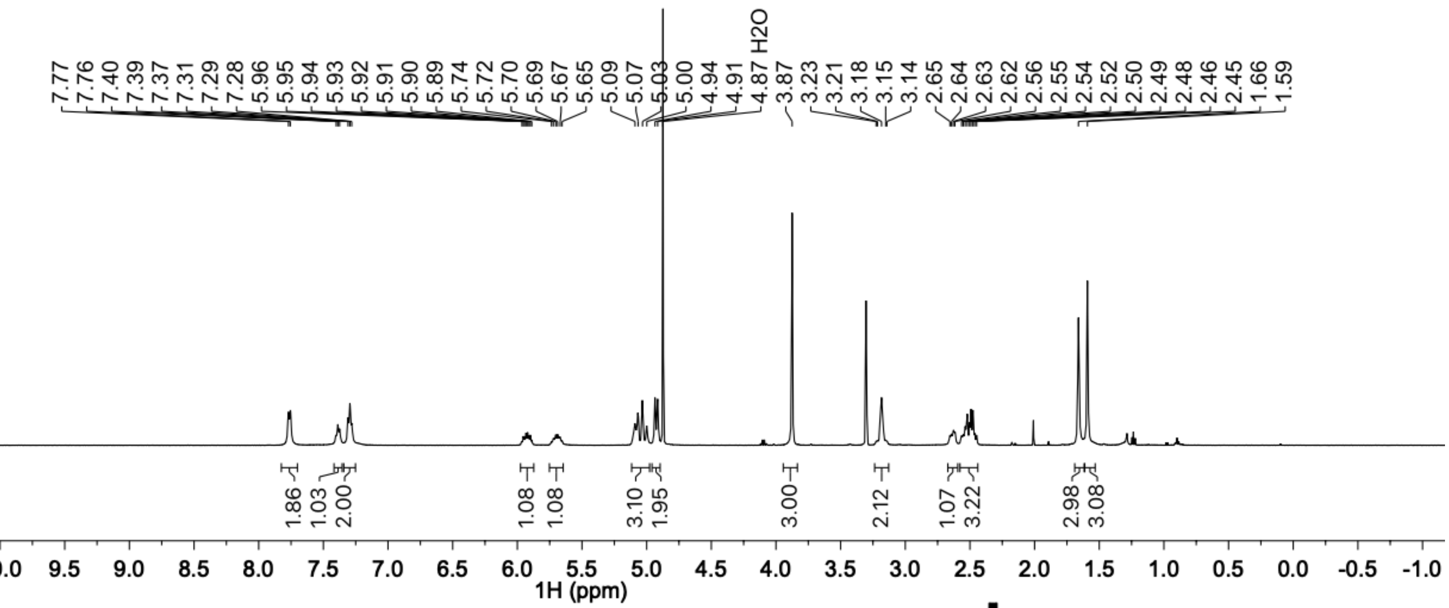
126 MHz, CD$_3$OD



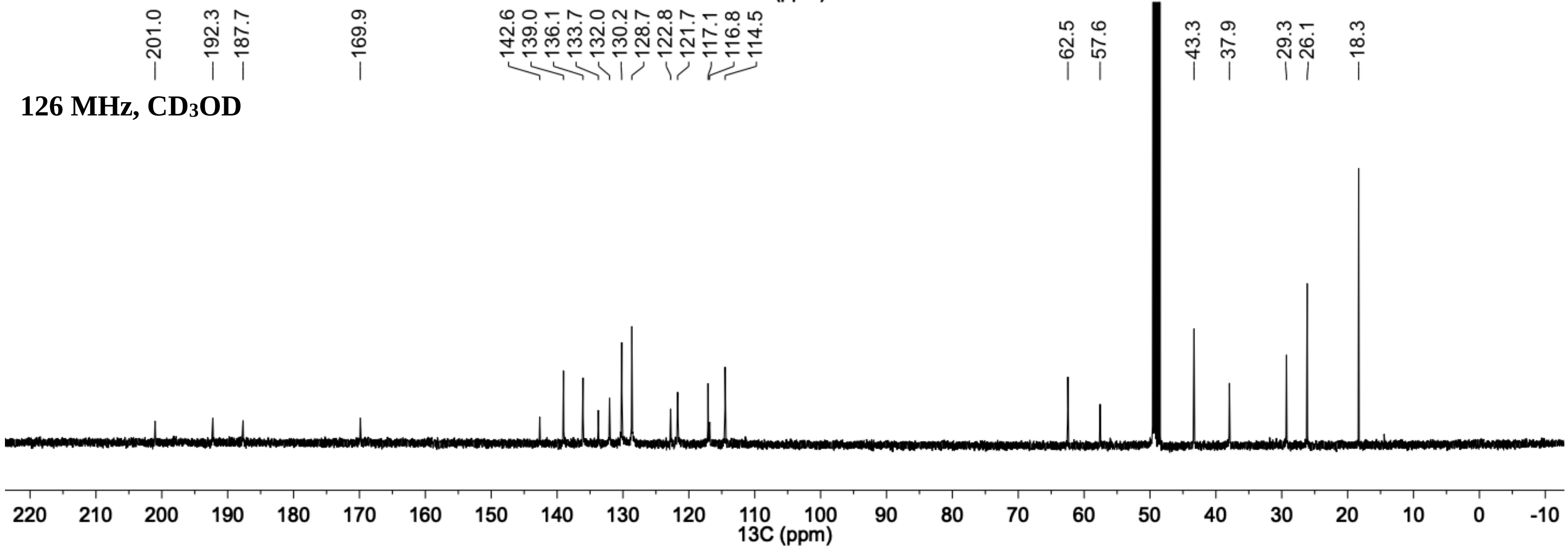


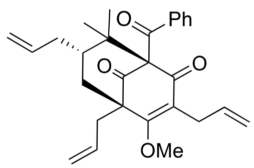
27-K

500 MHz, CD3OD



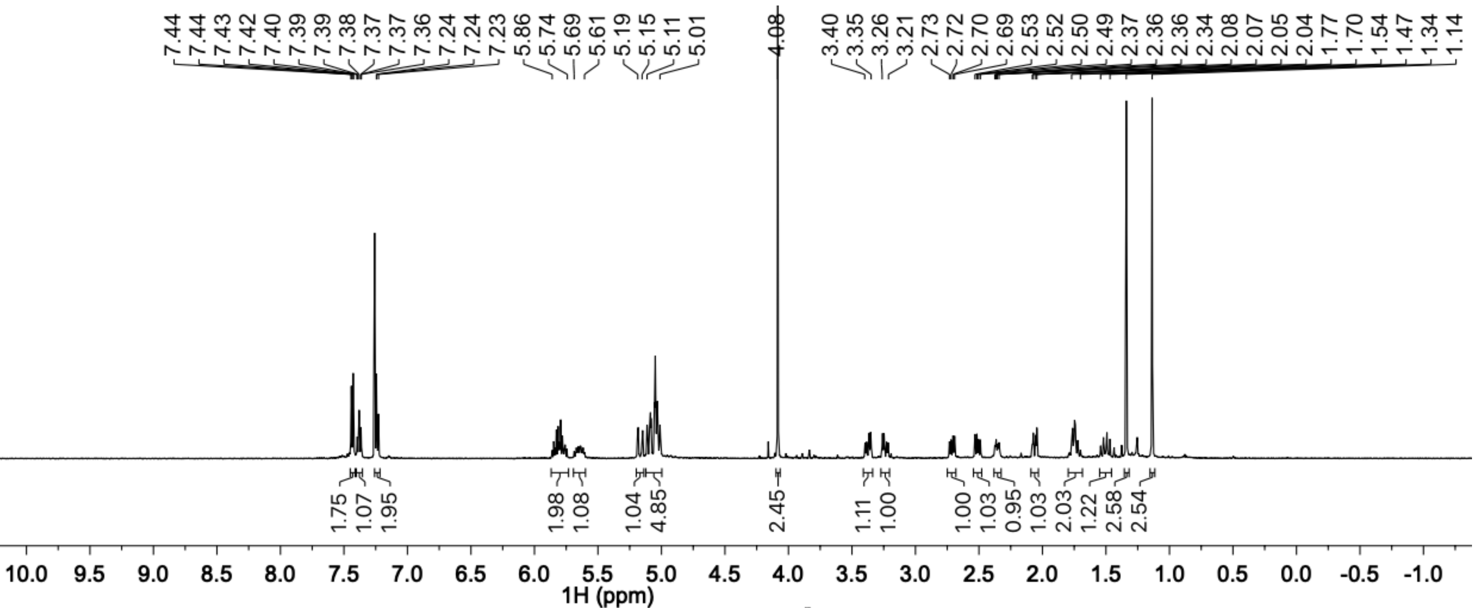
126 MHz, CD3OD



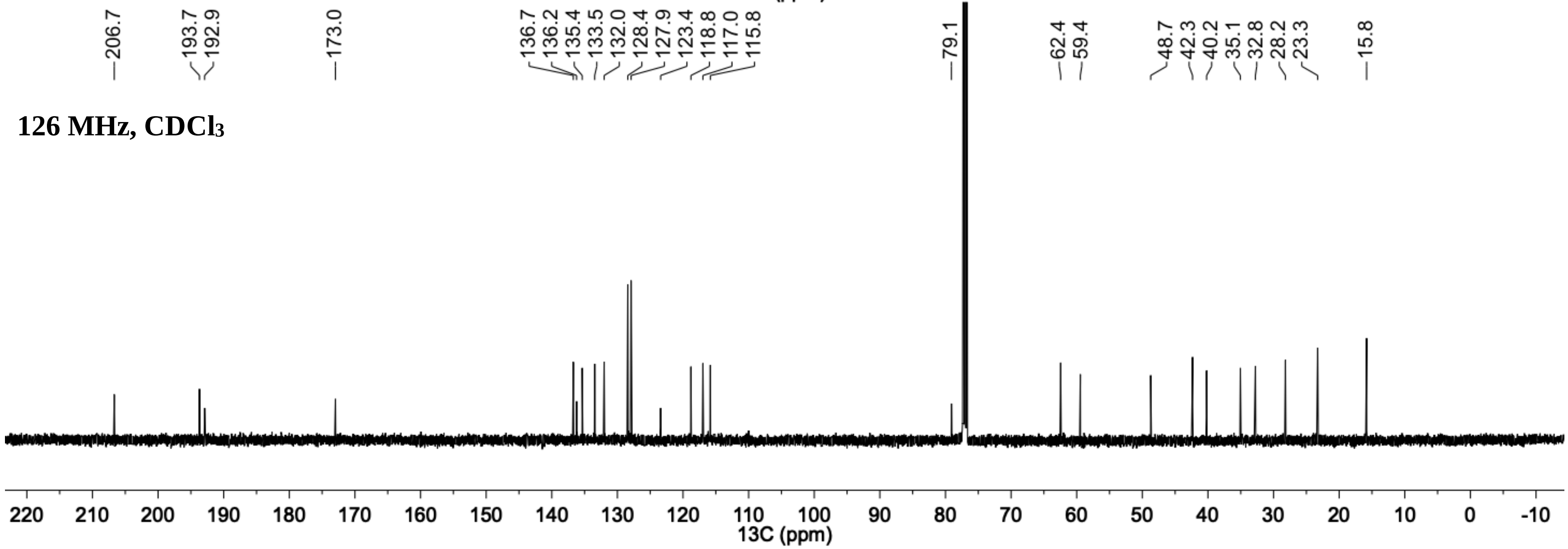


(–)-**8**

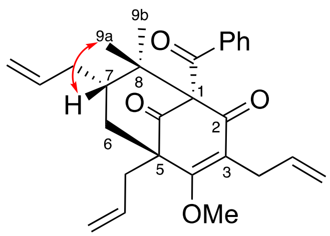
500 MHz, $CDCl_3$

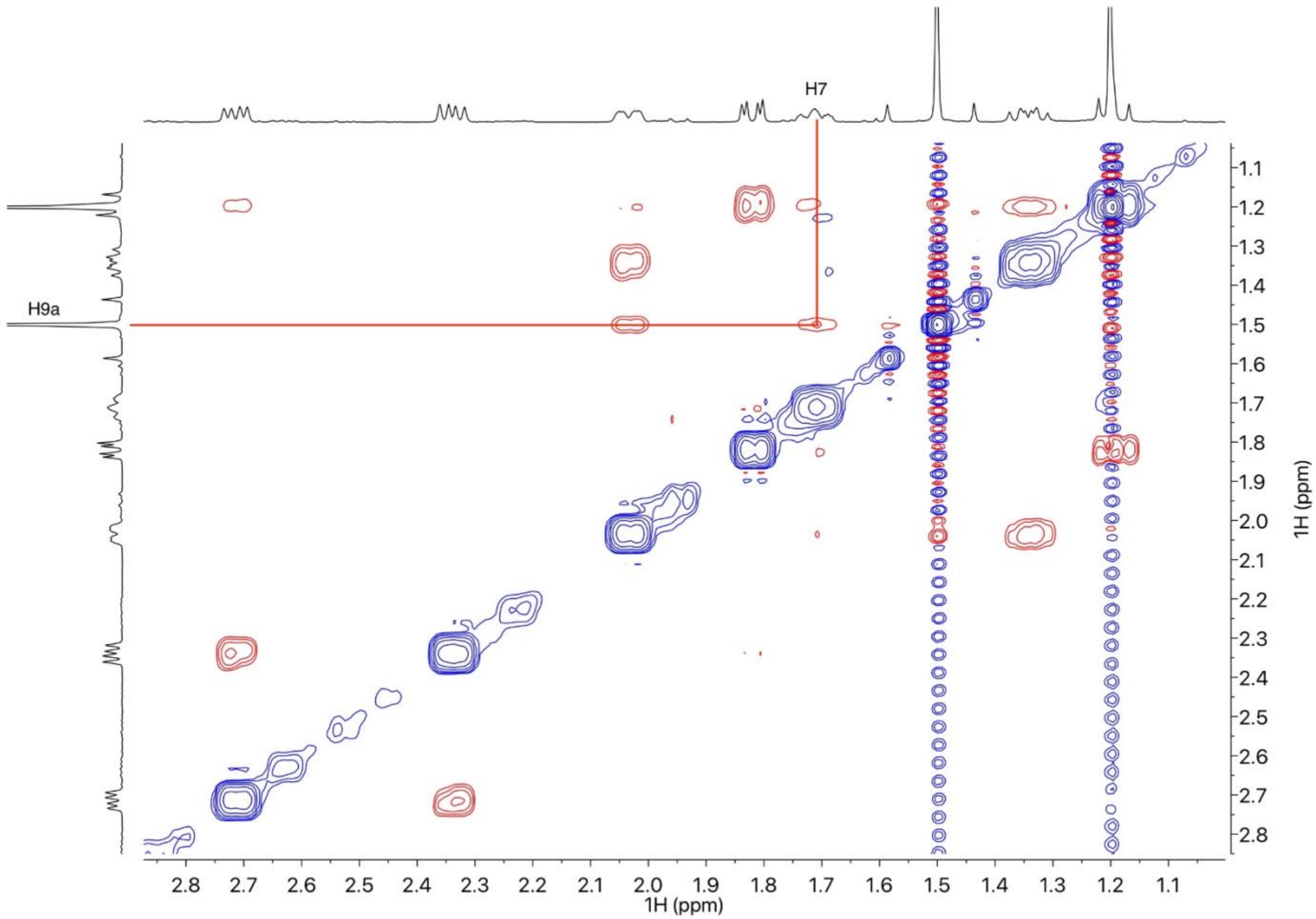


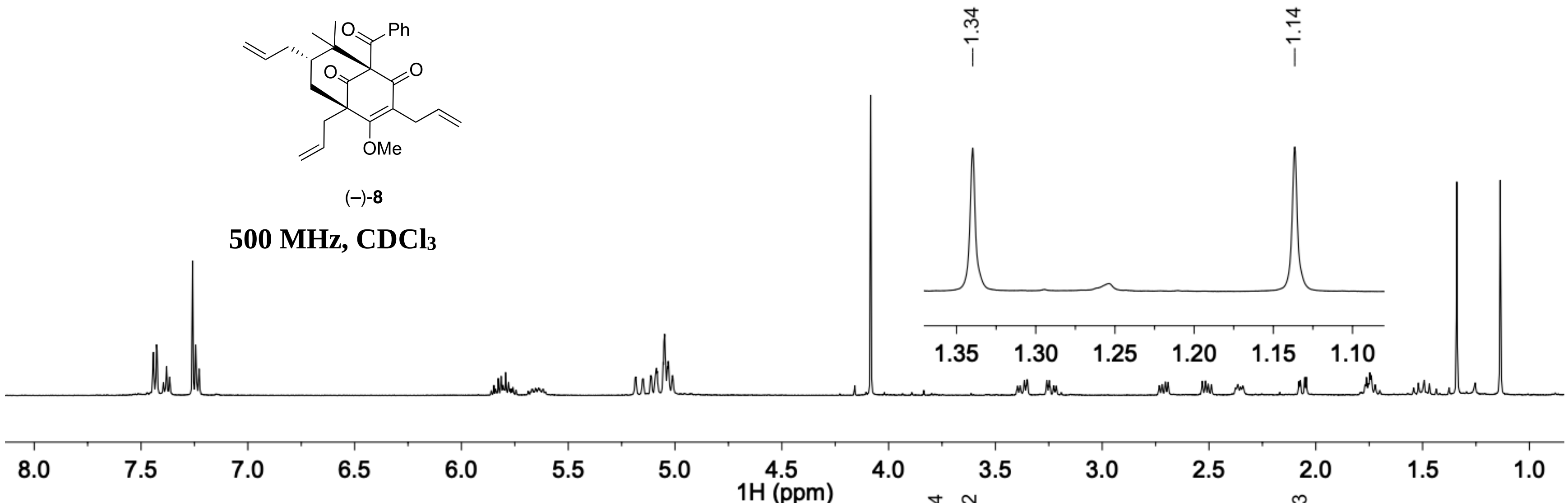
126 MHz, $CDCl_3$



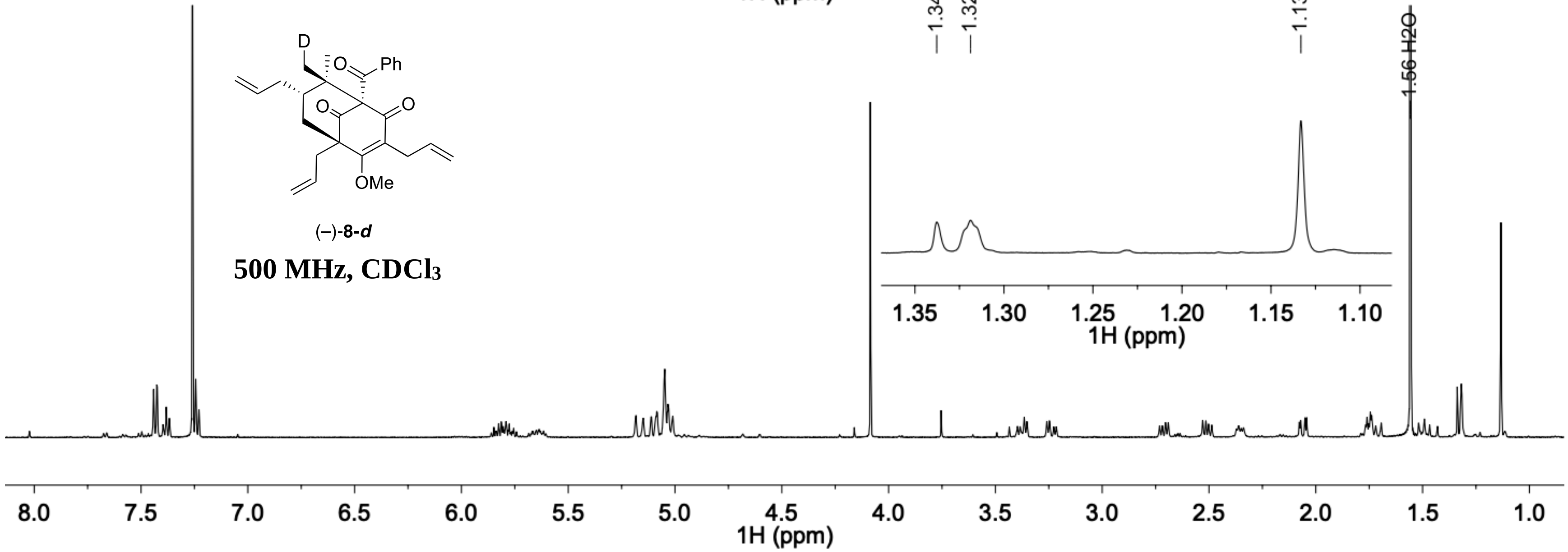
Partial NOESY Spectrum of **(–)-8** (500 MHz, benzene-d_6), Key ^1H-^1H Correlation Highlighted



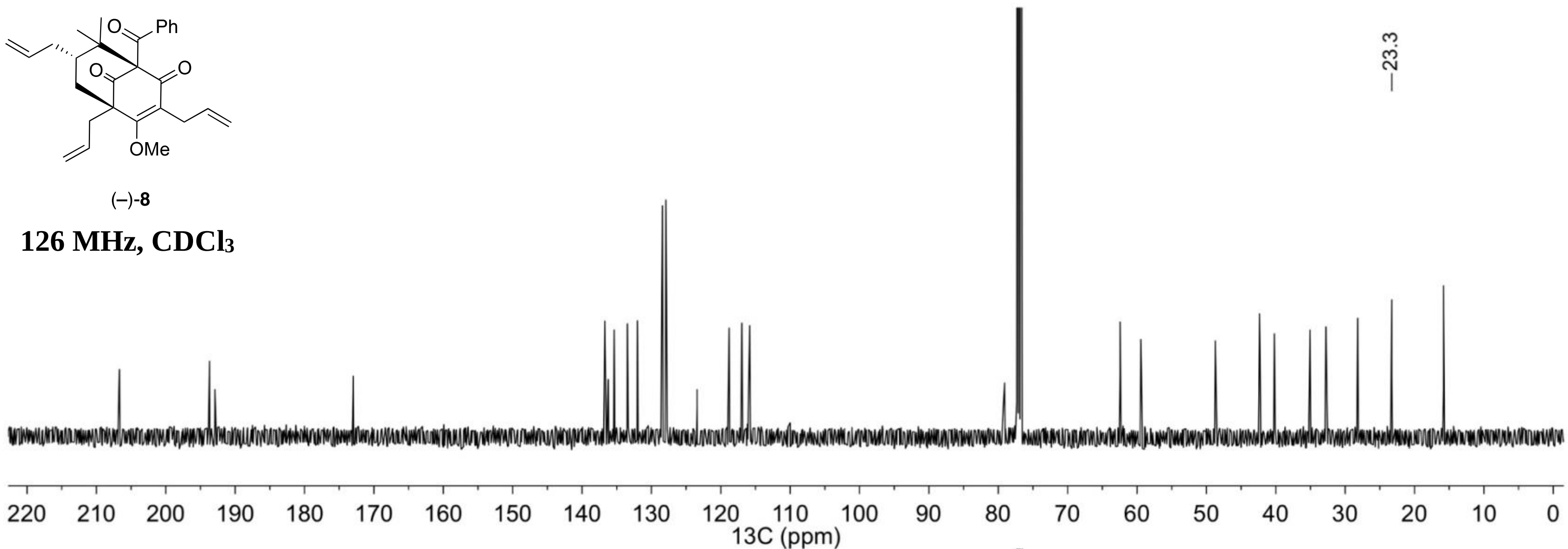


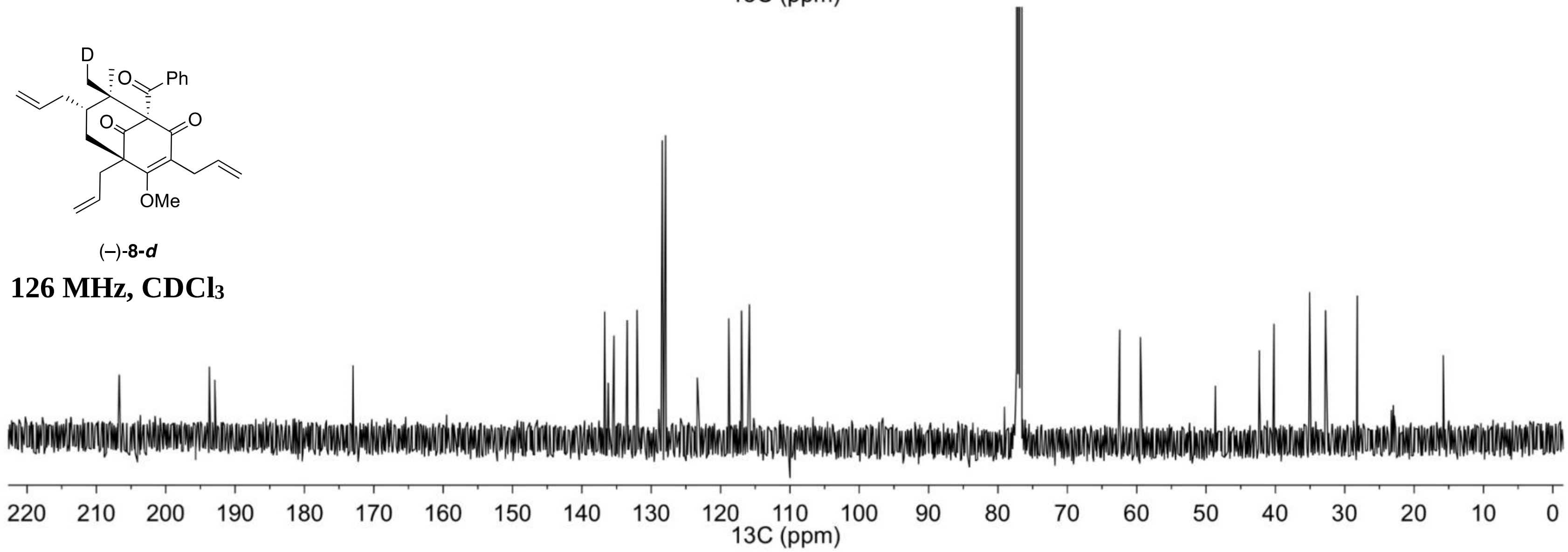


Ph
O
O
O
OMe
(–)-8
500 MHz, CDCl3
1.34
1.14
1.35 1.30 1.25 1.20 1.15 1.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
1H (ppm)

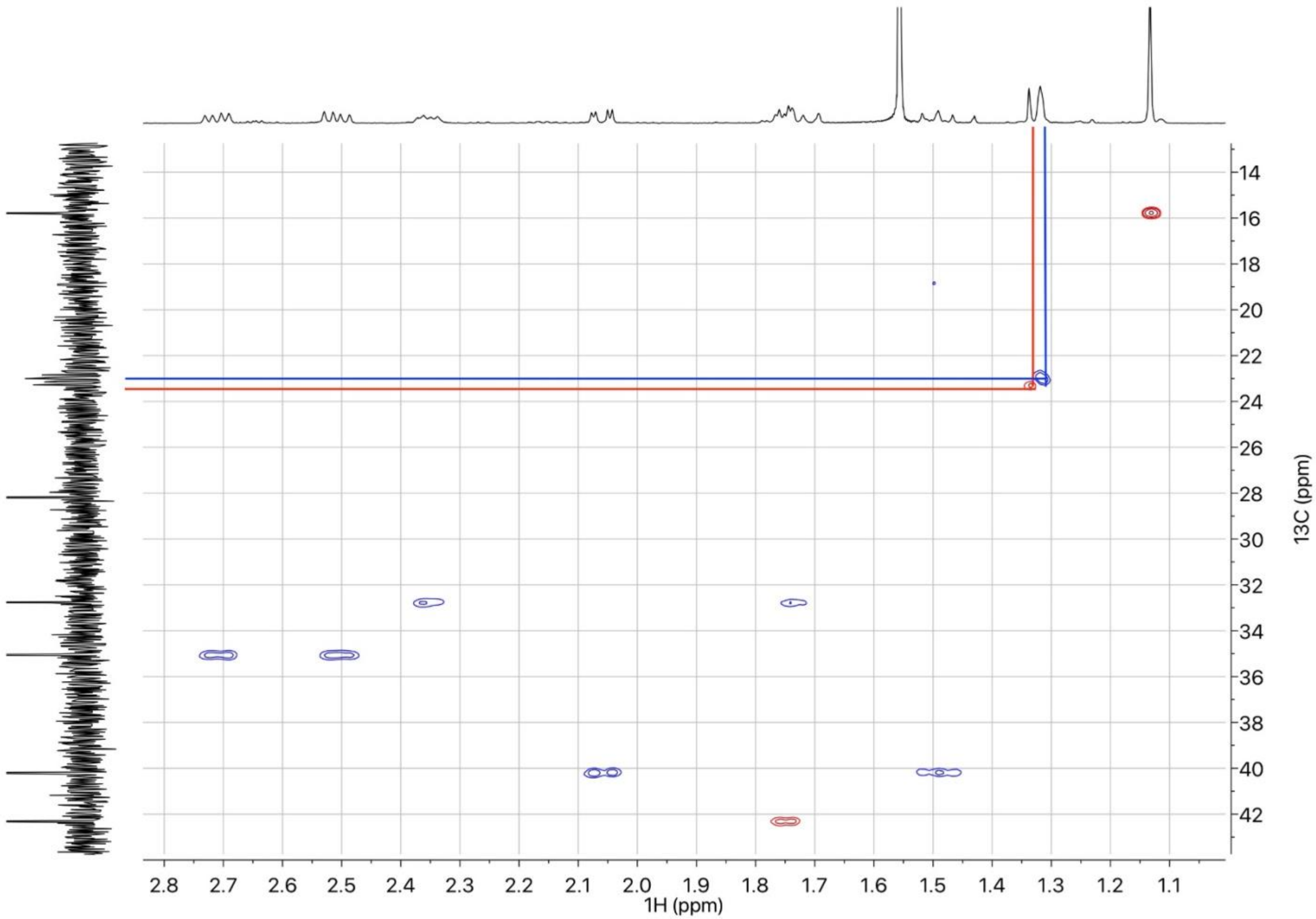


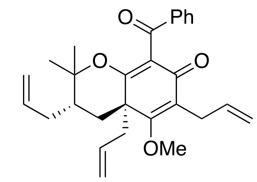
D
Ph
O
O
O
OMe
(–)-8-d
500 MHz, CDCl3
1.34
1.32
1.13
1.56 H2O
1.35 1.30 1.25 1.20 1.15 1.10
1H (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
1H (ppm)


O
Ph
O
O
OMe
(–)-8
126 MHz, CDCl3
—23.3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)


D
O
Ph
O
O
OMe
(–)-8-d
126 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C (ppm)

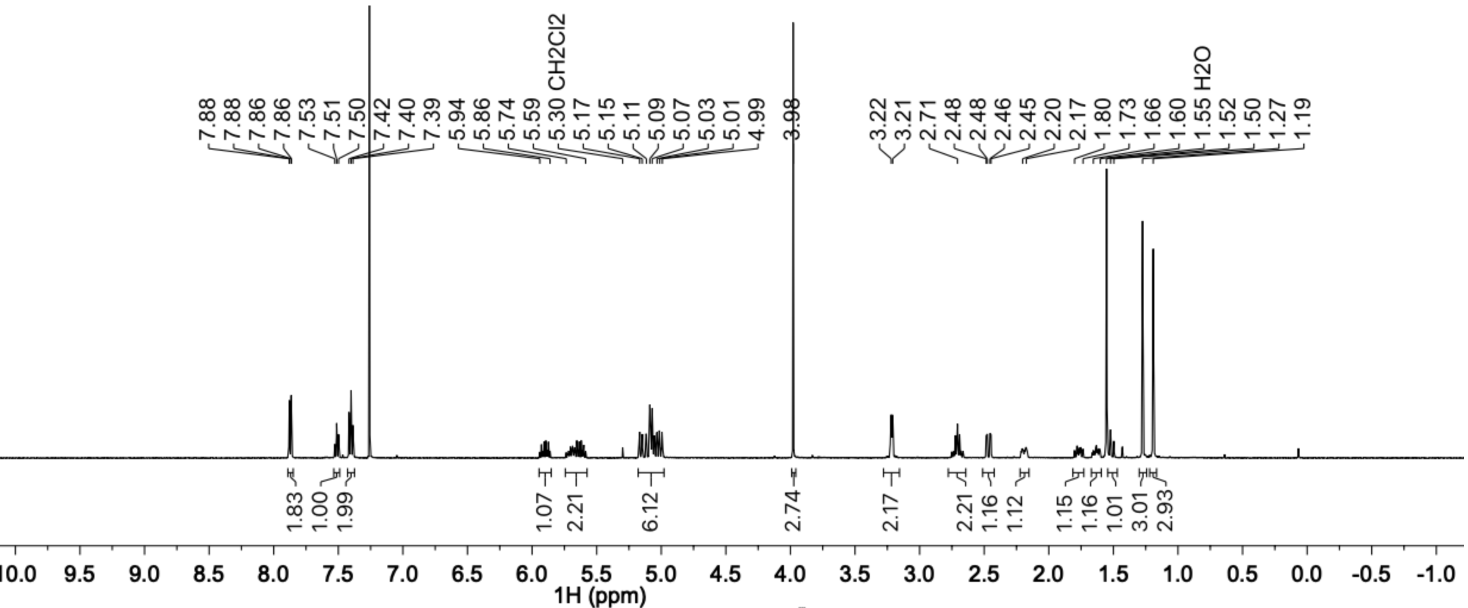
Partial gHSQC Spectrum of **(–)-8-*d*** (500 MHz), Key ^{1}H-^{13}C Correlations Highlighted



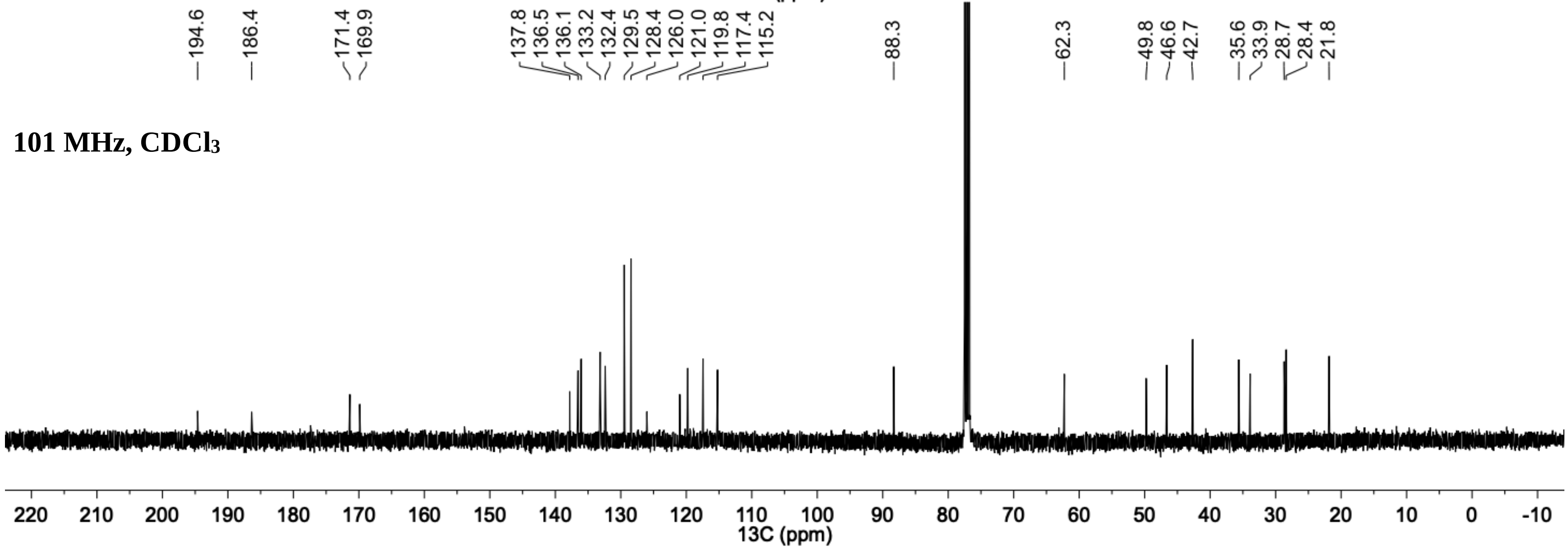


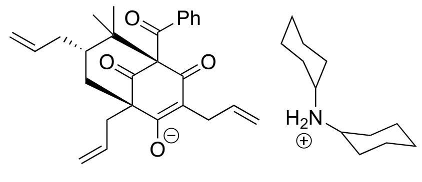
11

400 MHz, CDCl₃



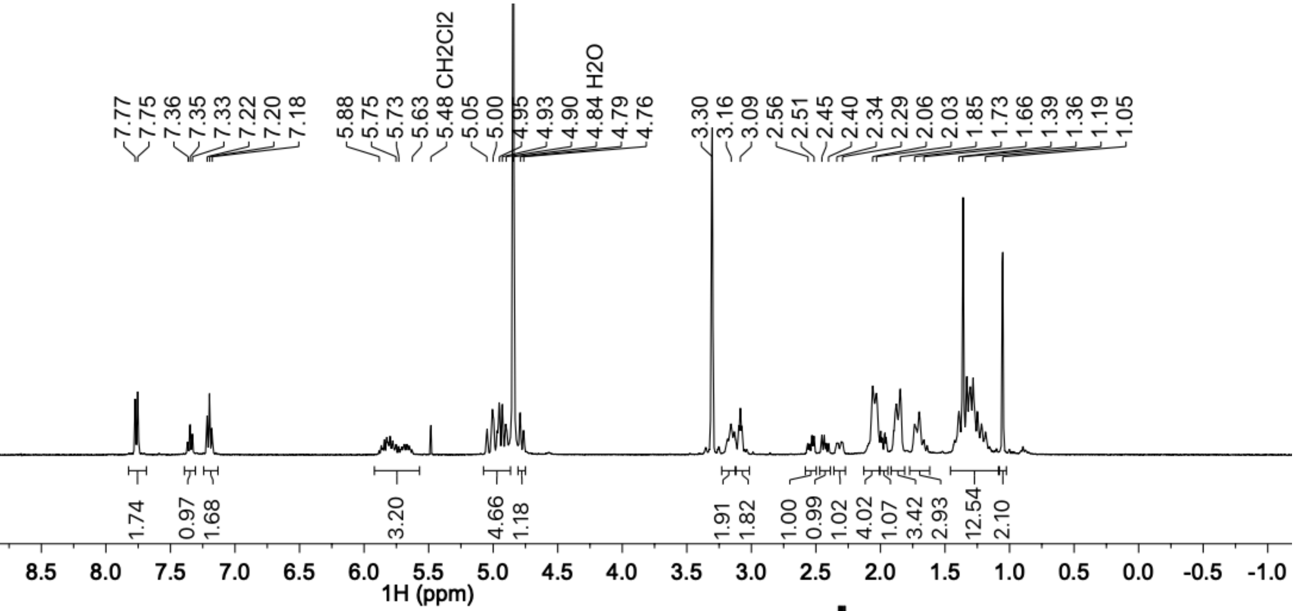
101 MHz, CDCl₃



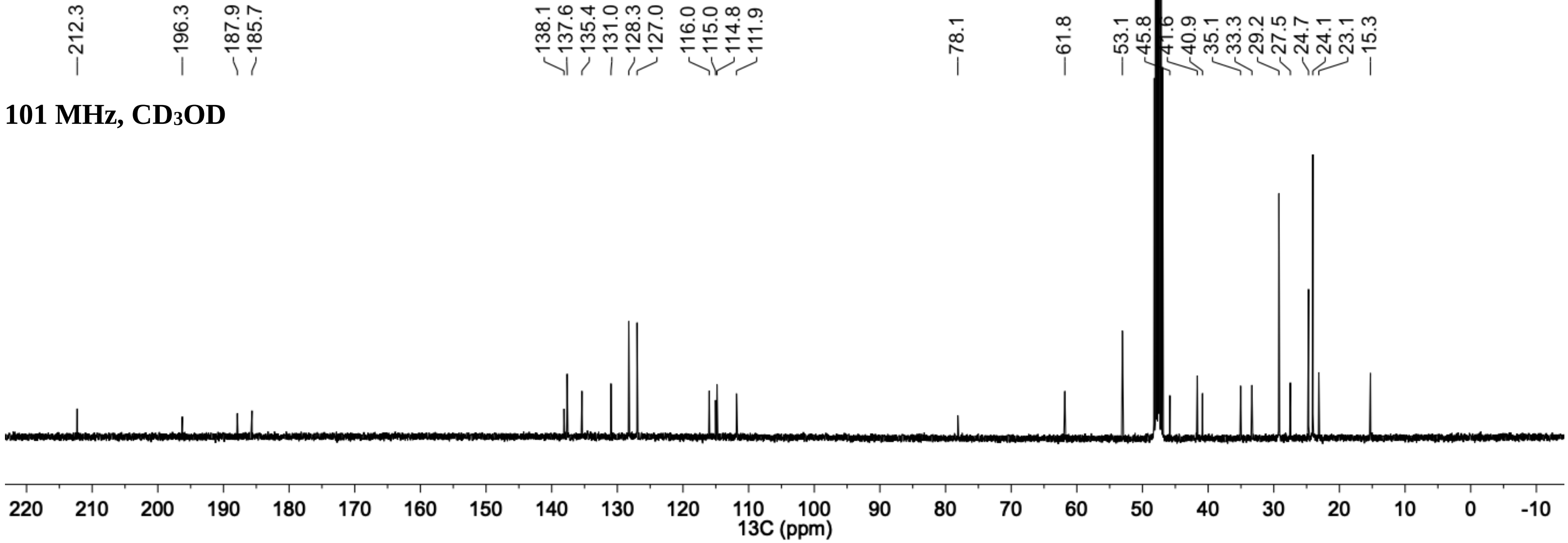


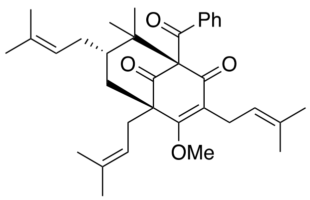
(–)-**12**

400 MHz, CD$_3$OD



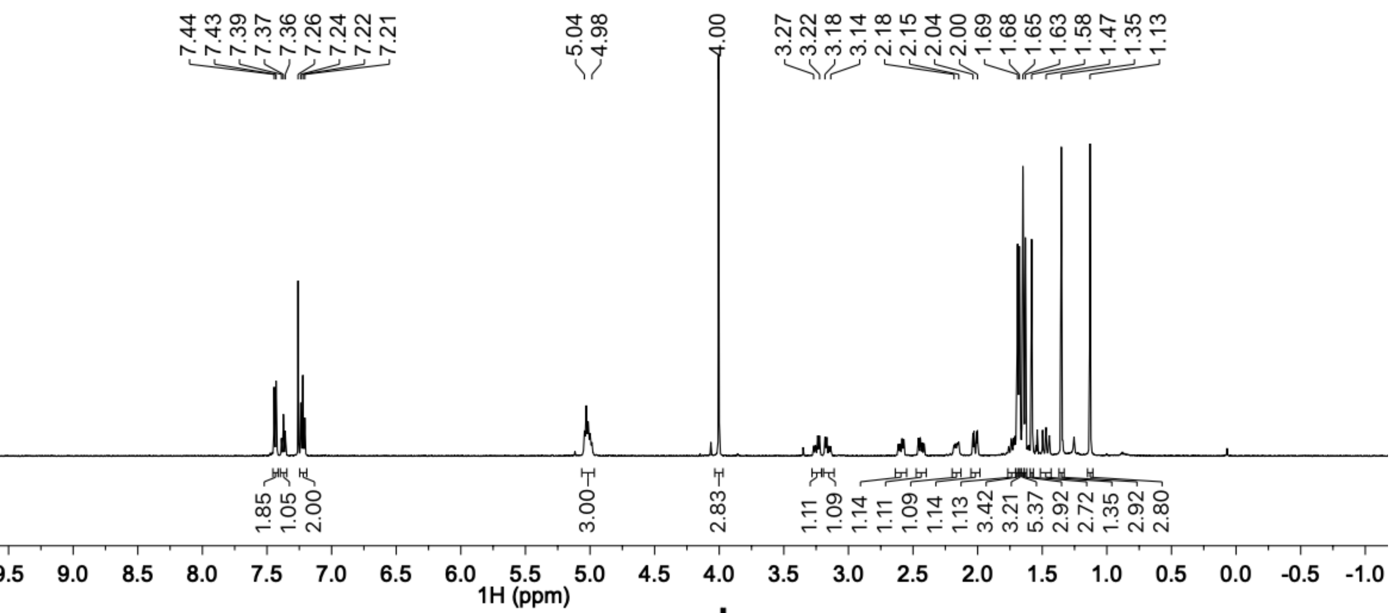
101 MHz, CD$_3$OD



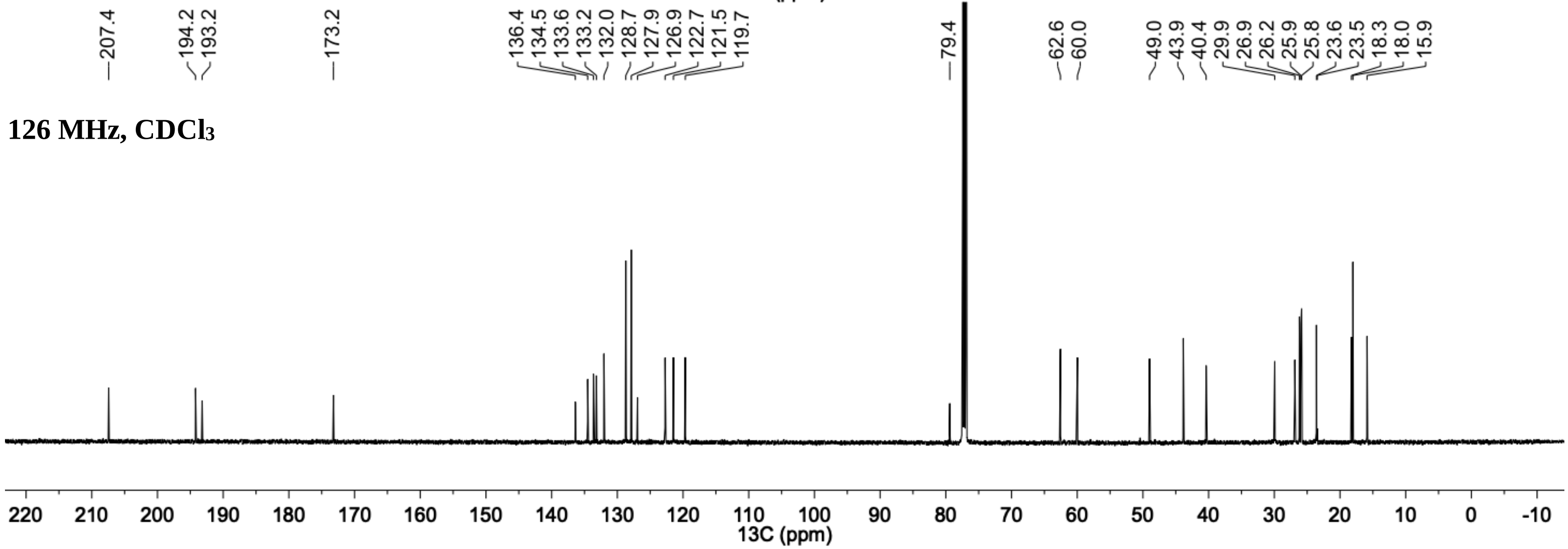


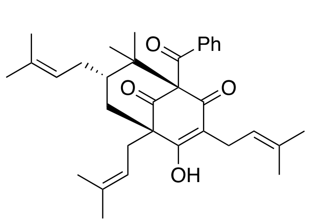
(–)-**13**

500 MHz, CDCl₃

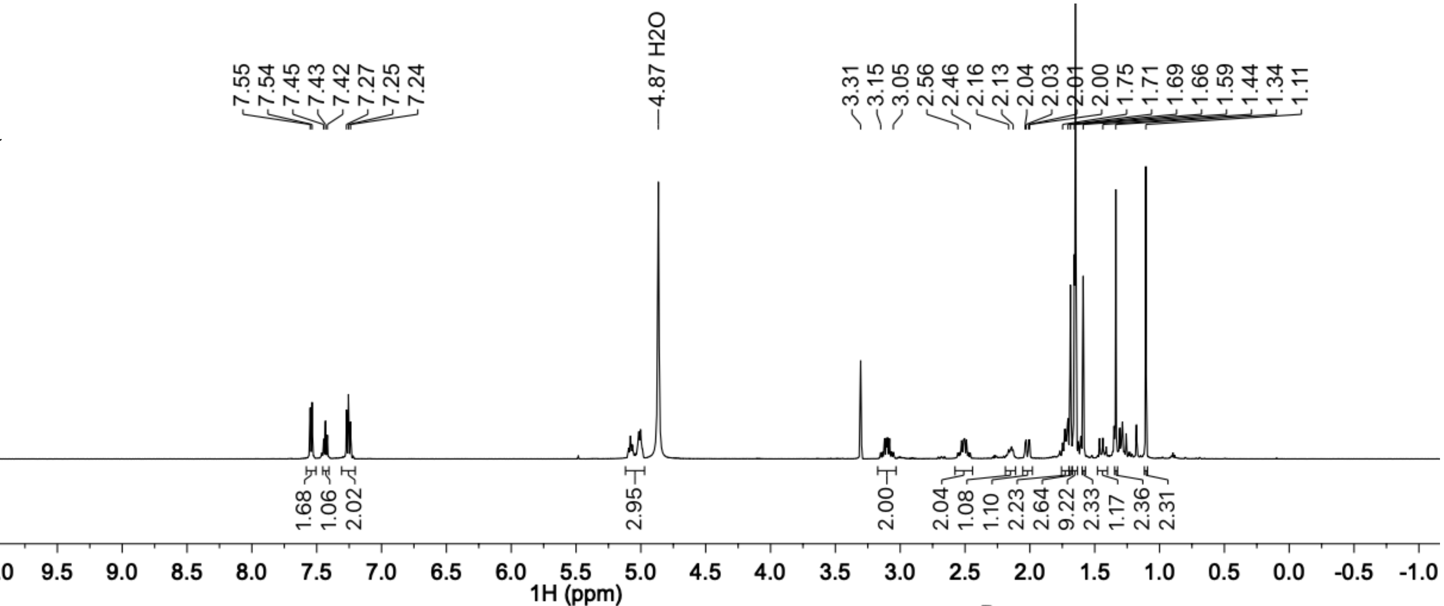


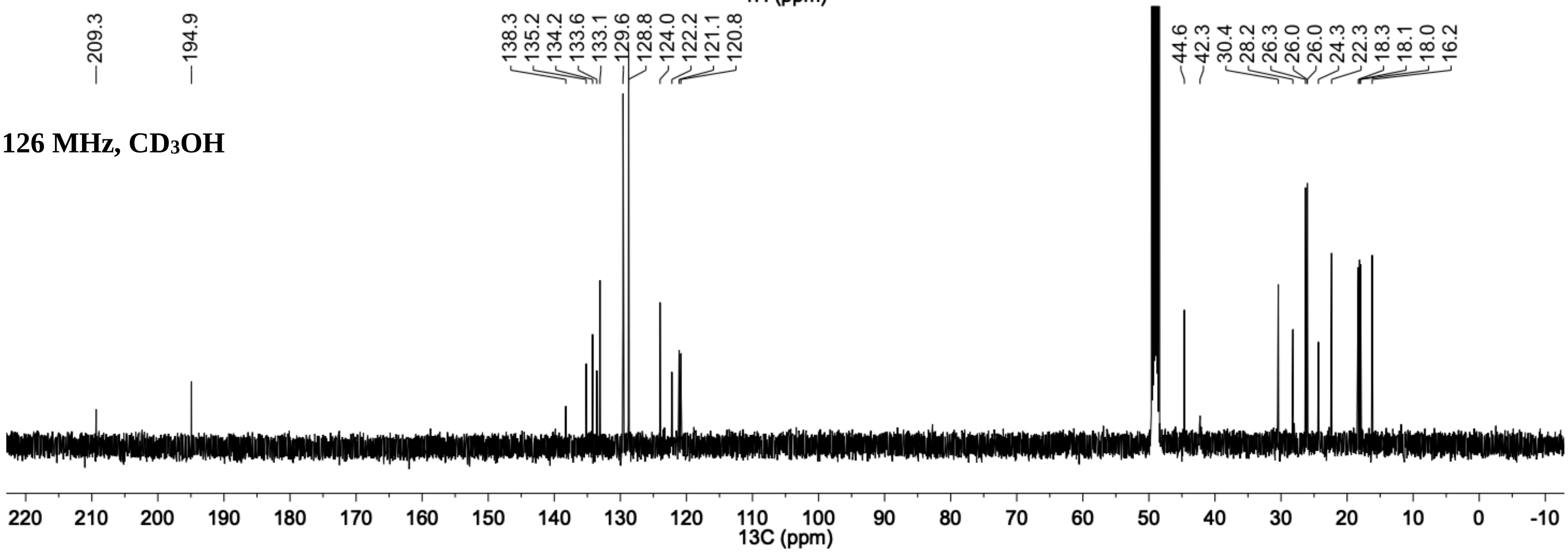
126 MHz, CDCl₃

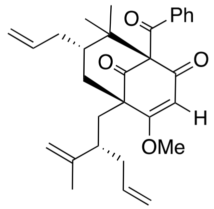




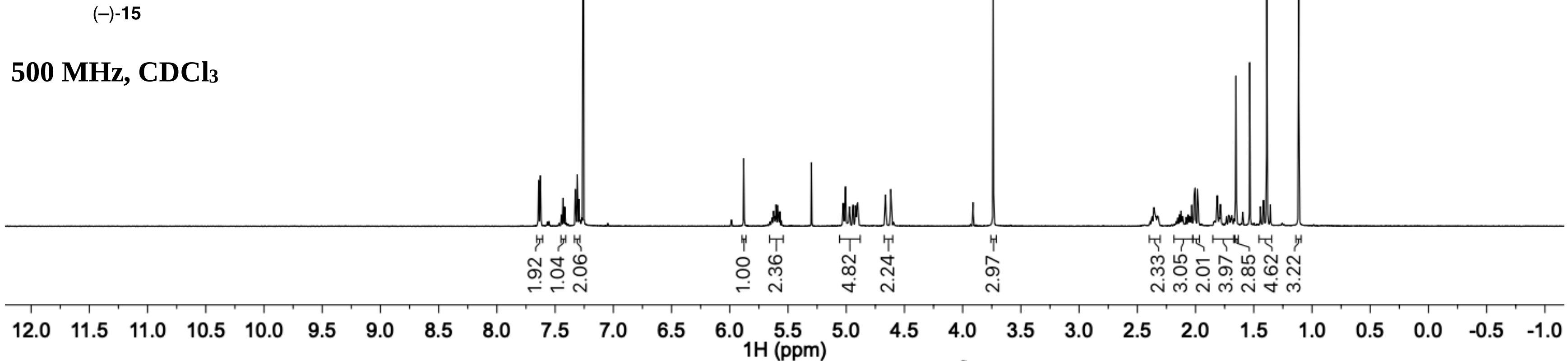
2 (–)-nemorosone

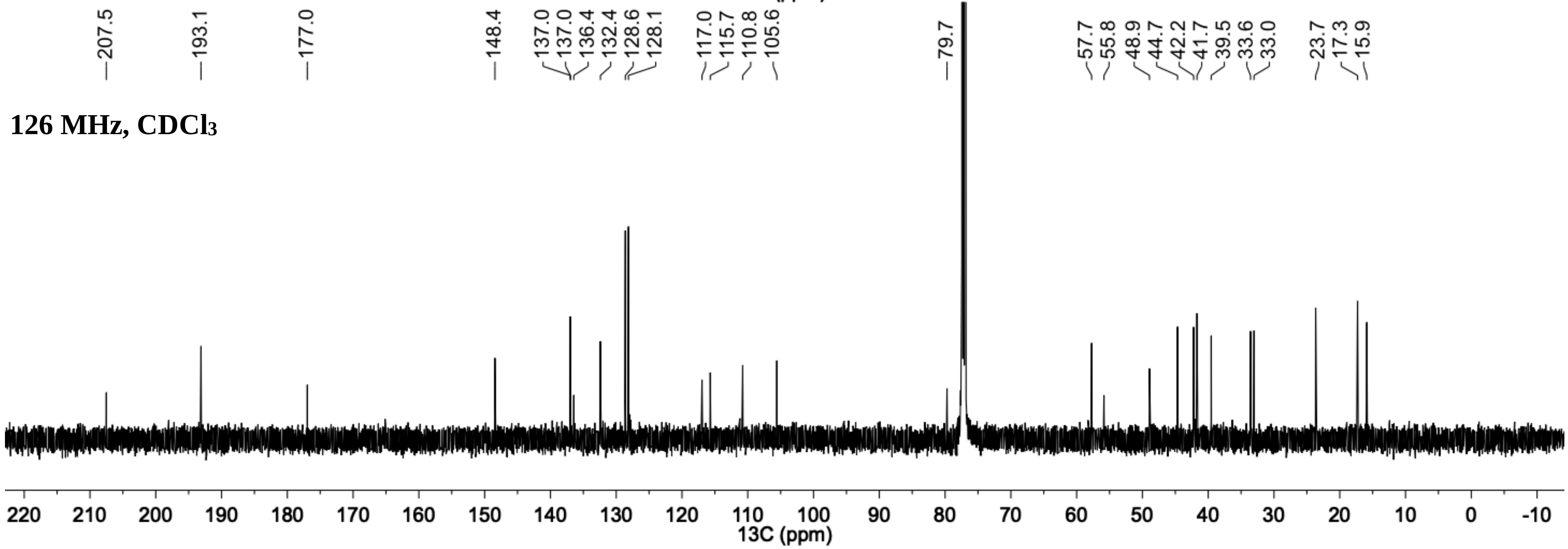


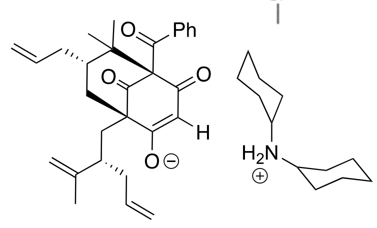



O
Ph
O
O
H
OMe

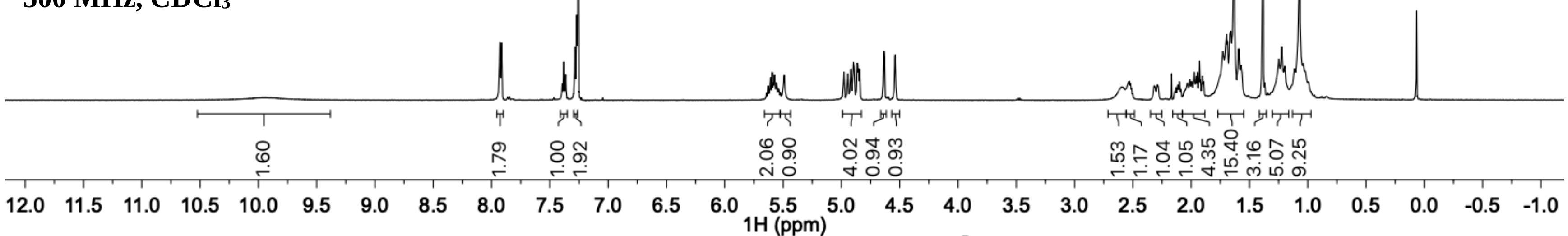
(–)-**15**


500 MHz, $CDCl_3$
7.64 7.64 7.63 7.62 7.45 7.43 7.42 7.33 7.31 7.30
5.88 5.65 5.56 5.30 CH2Cl2 5.03 4.90 4.66 4.61
3.74
2.39 2.32 2.17 2.03 2.01 1.98 1.81 1.78 1.73 1.68 1.65 1.53 H2O 1.44 1.42 1.39 1.36 1.11
1.92 1.04 2.06 1.00 2.36 4.82 2.24 2.97 2.33 3.05 2.01 3.97 2.85 4.62 3.22
12.0 11.5 11.0 10.5 10.0 9.5 9.0 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 0.0 -0.5 -1.0
1H (ppm)

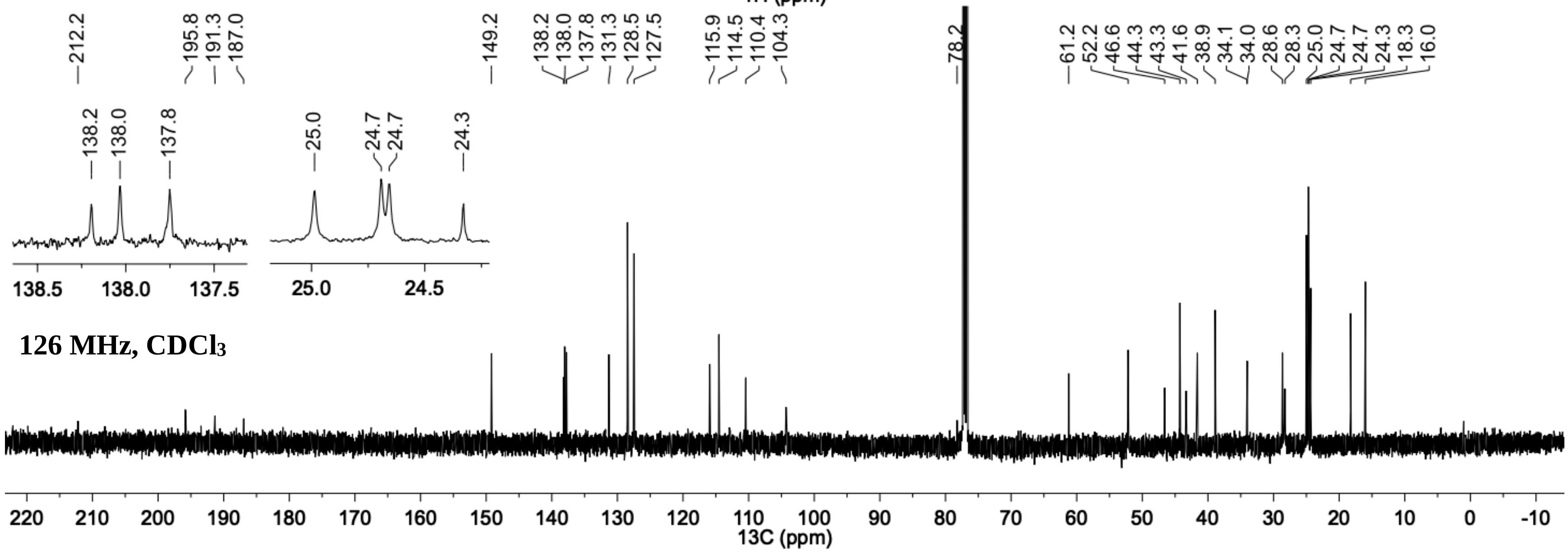

126 MHz, $CDCl_3$
207.5 193.1 177.0 148.4 137.0 137.0 136.4 132.4 128.6 128.1 117.0 115.7 110.8 105.6 79.7 57.7 55.8 48.9 44.7 42.2 41.7 39.5 33.6 33.0 23.7 17.3 15.9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
13C (ppm)



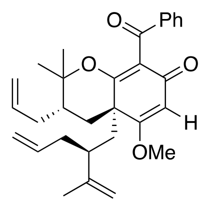
(–)-**21**



500 MHz, CDCl3

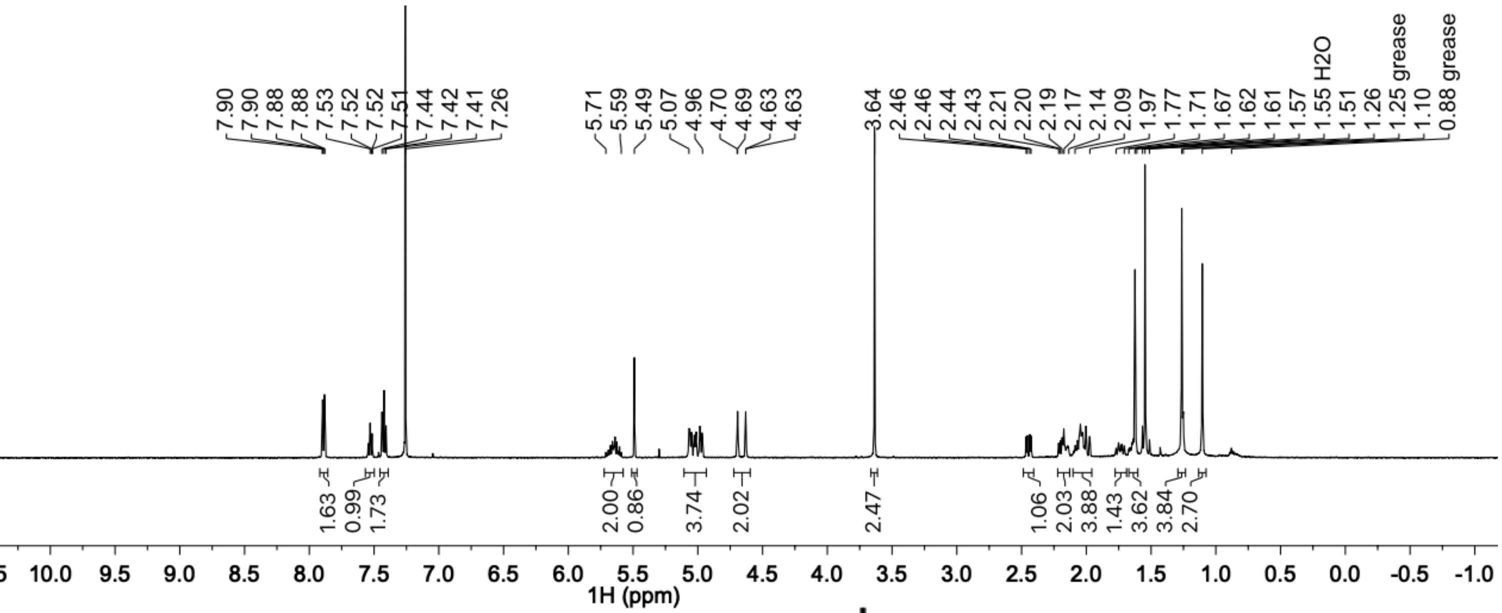


126 MHz, CDCl3

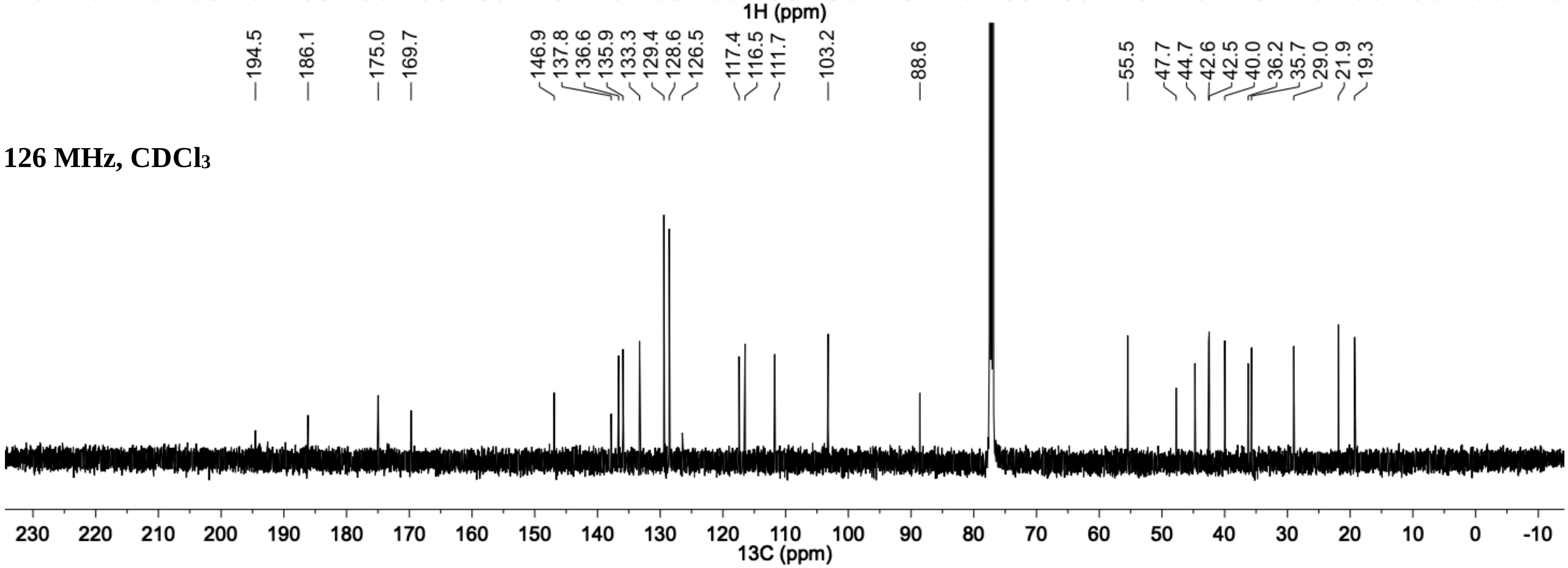


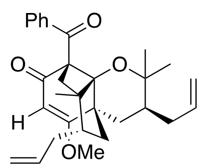
16

500 MHz, $CDCl_3$



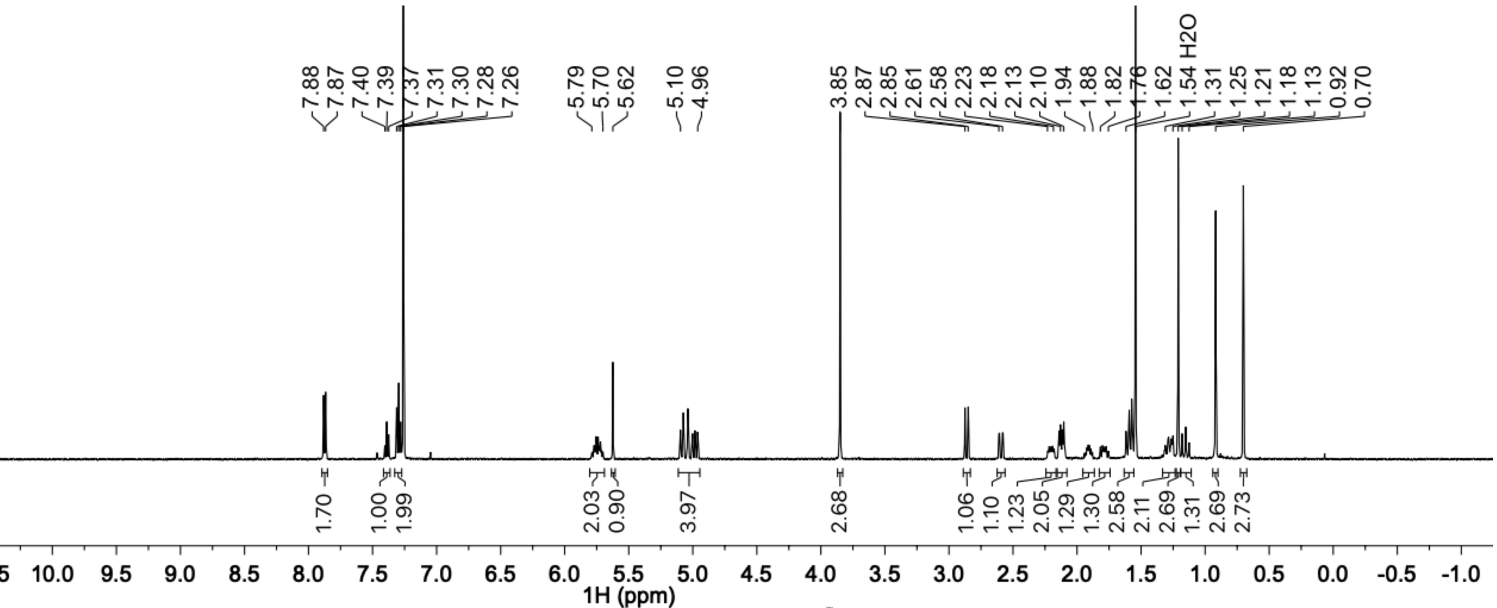
126 MHz, $CDCl_3$



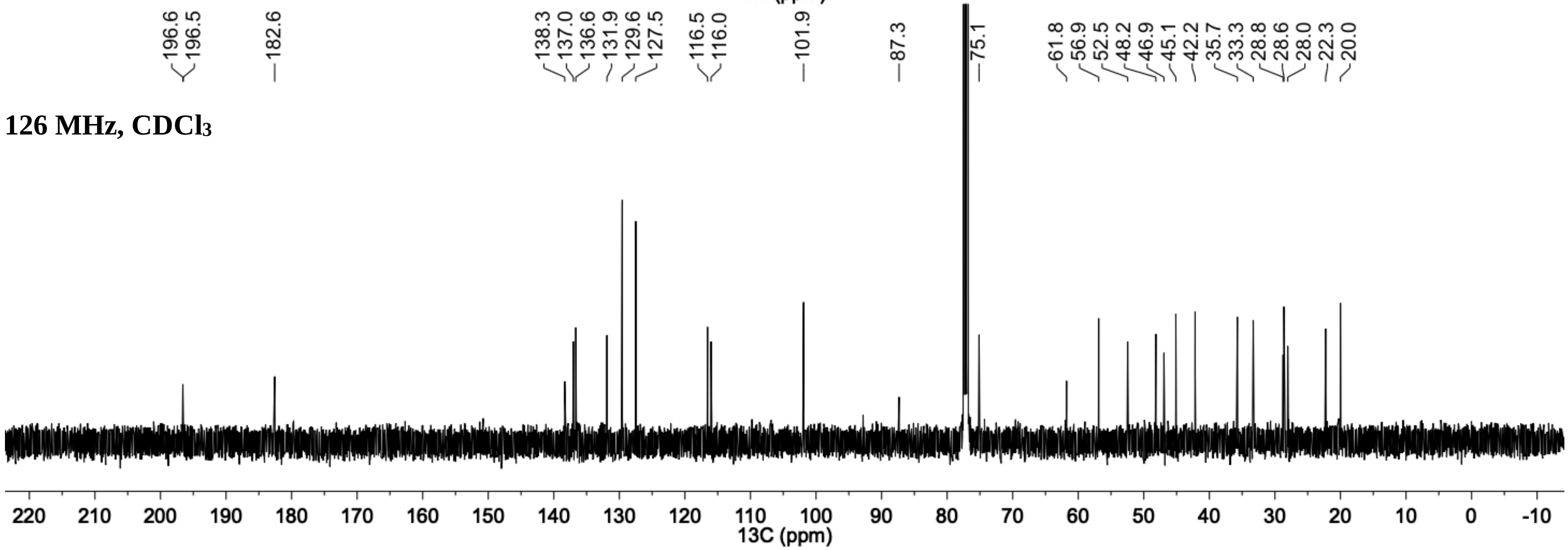


17

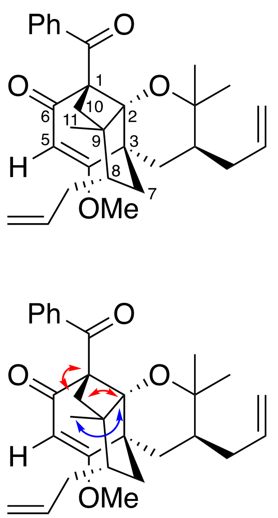
500 MHz, $CDCl_3$

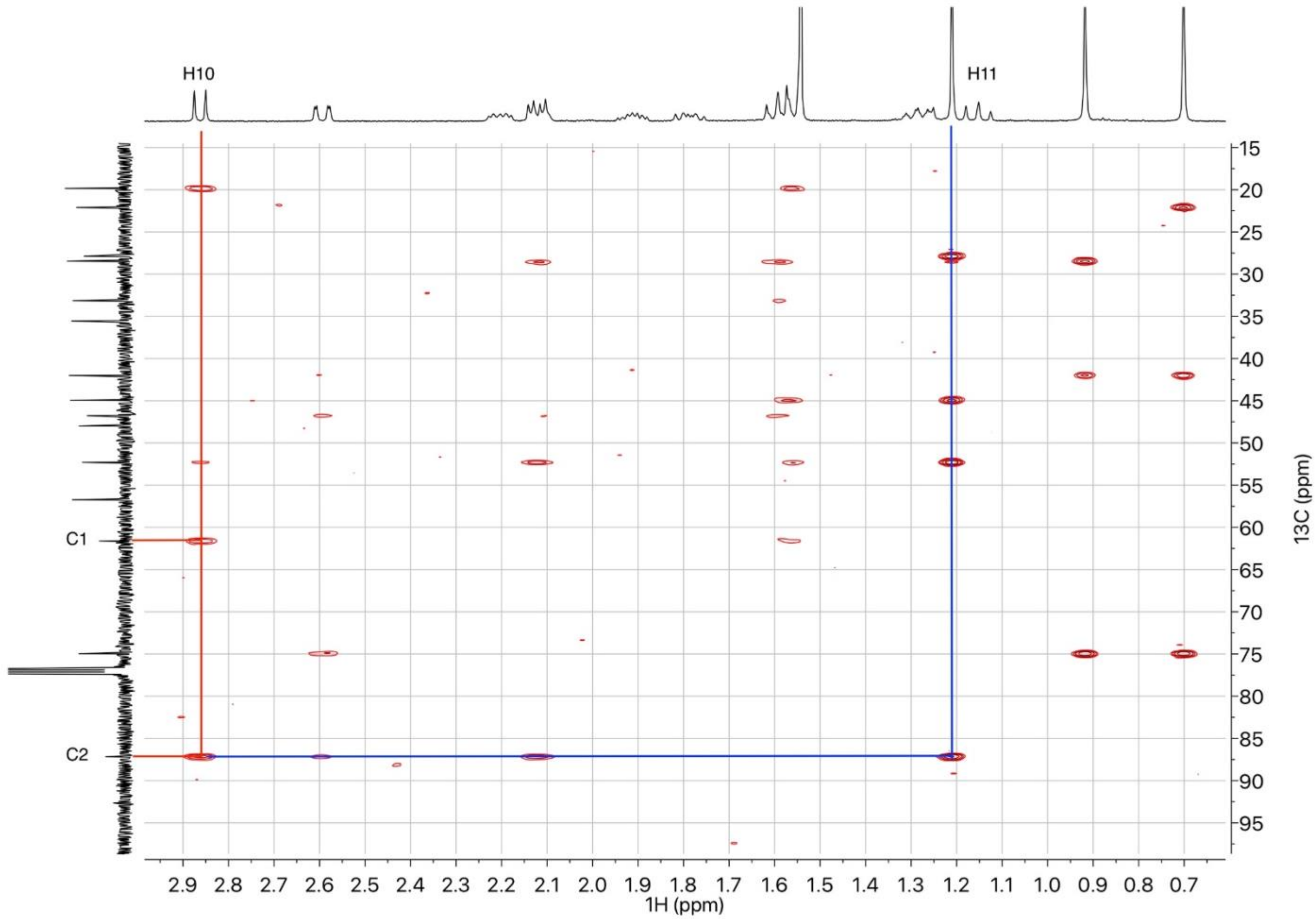


126 MHz, $CDCl_3$

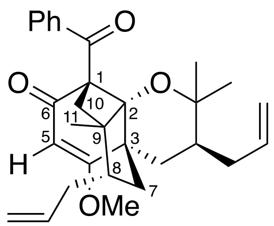


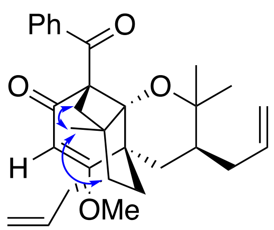
Partial gHMBC Spectrum of **17** (500/126 MHz), Key ^{1}H-^{13}C Correlations Highlighted

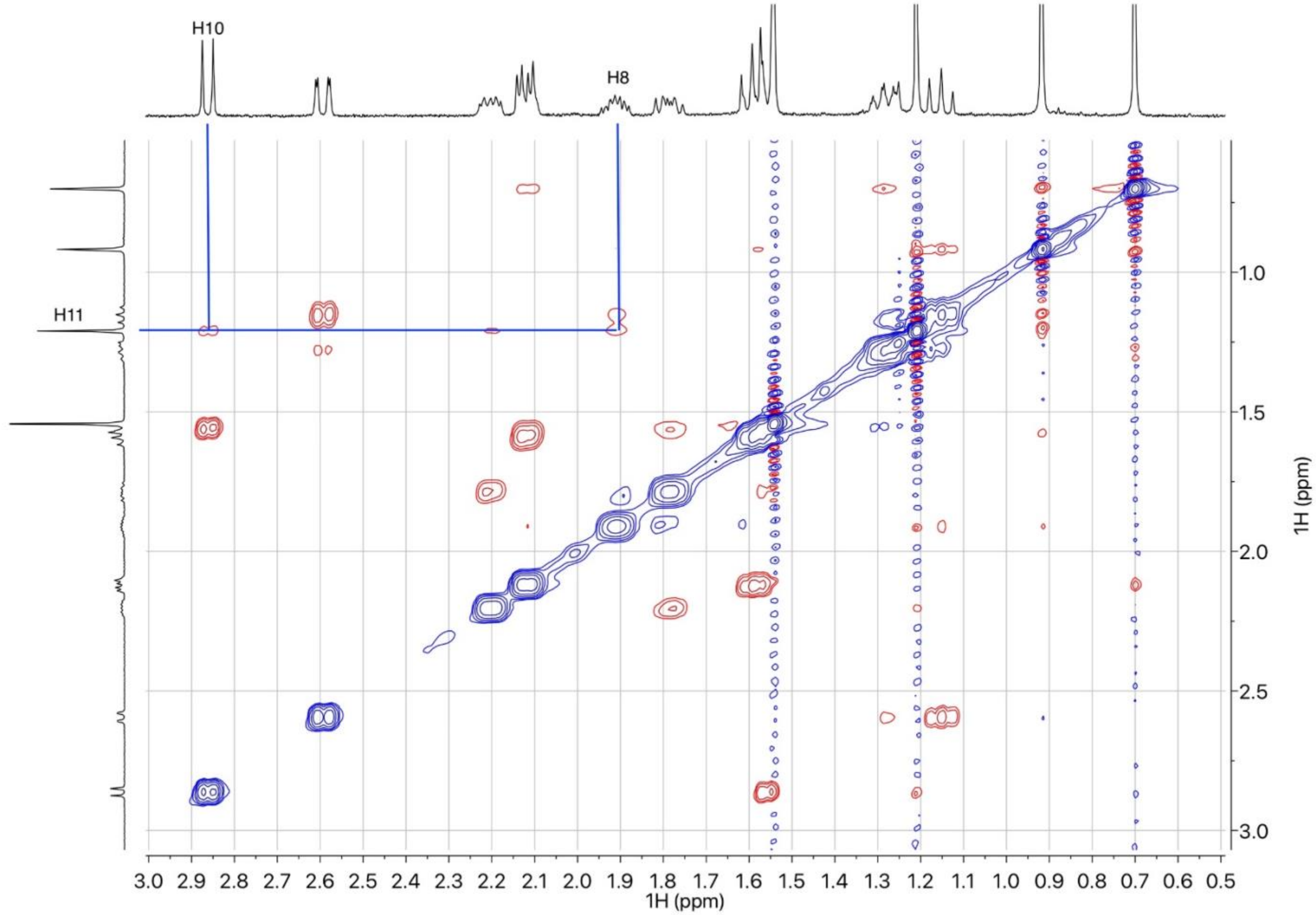


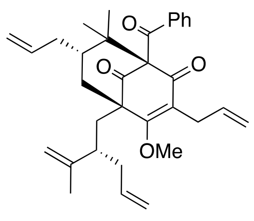


Partial NOESY Spectrum of **17** (500 MHz), Key ^{1}H-^{13}C Correlations Highlighted



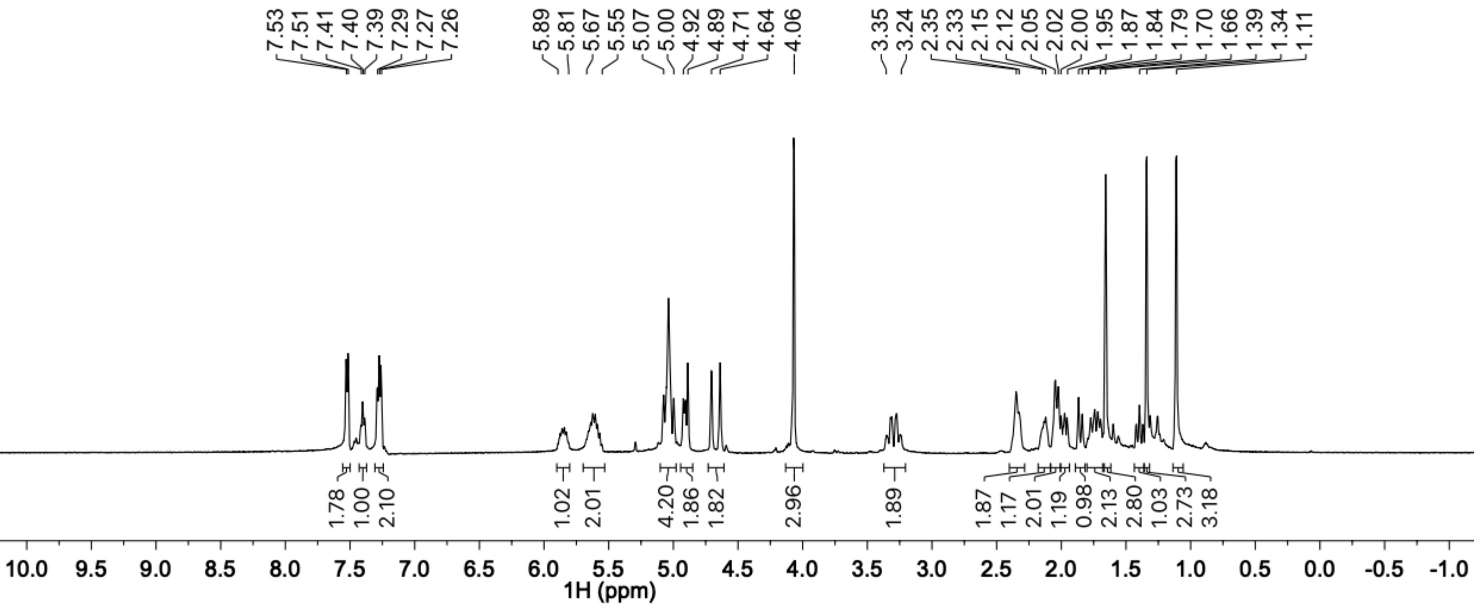




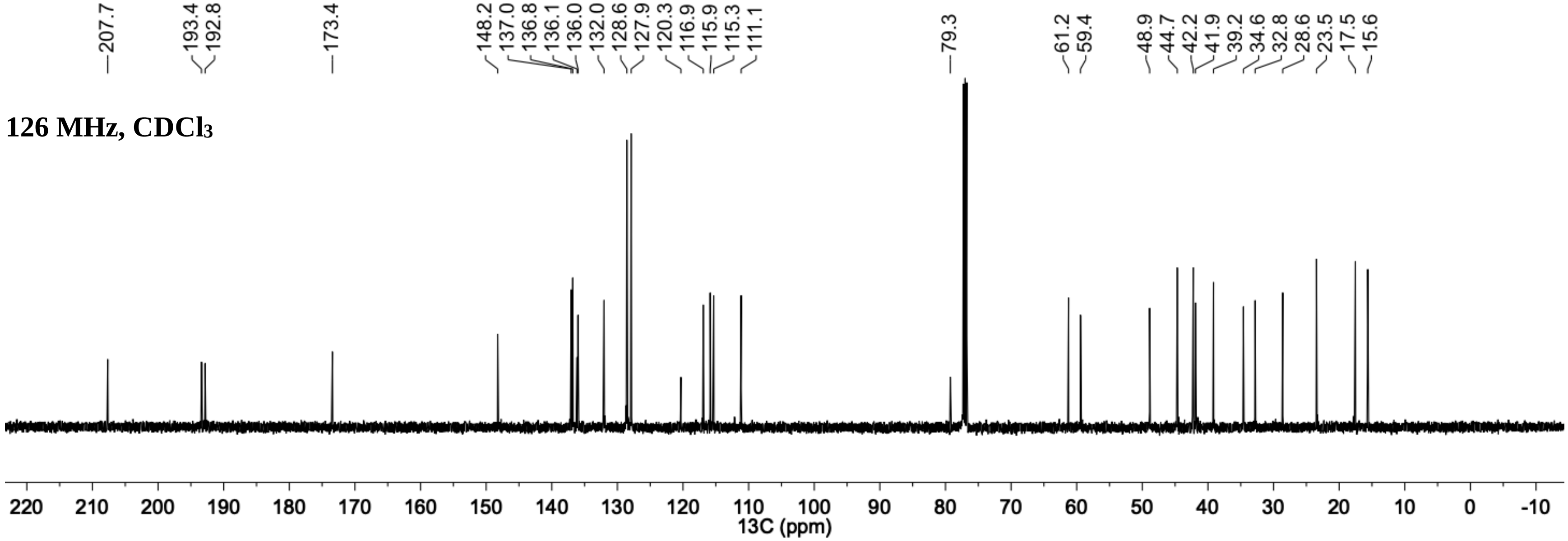


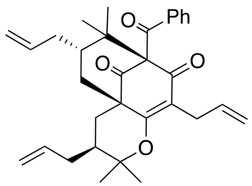
18

500 MHz, CDCl3



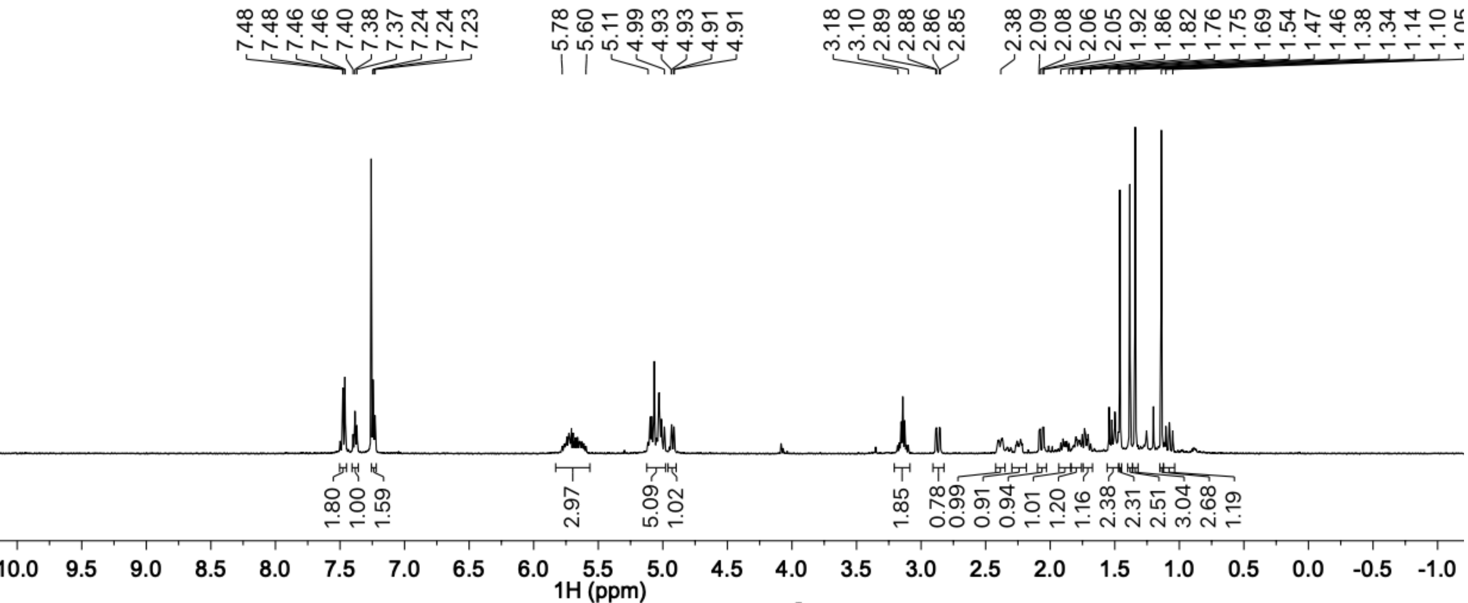
126 MHz, CDCl3



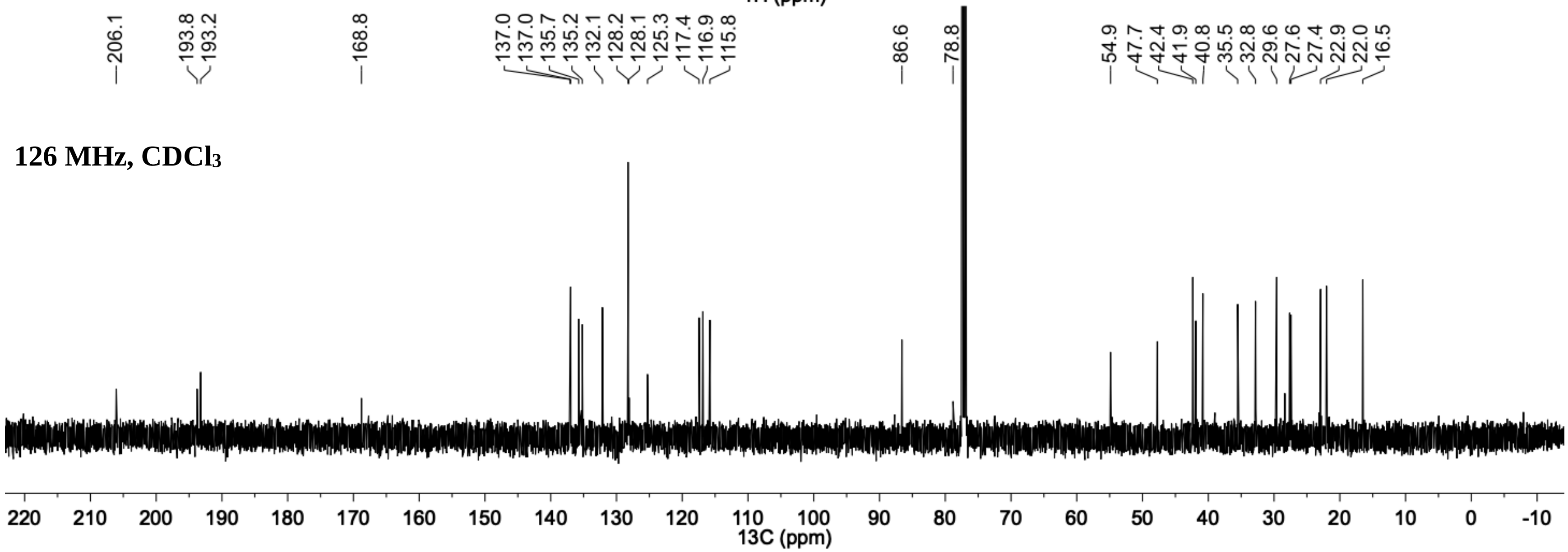


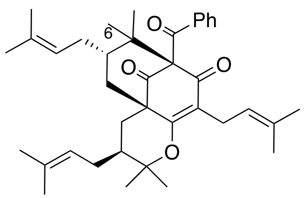
19

500 MHz, CDCl3



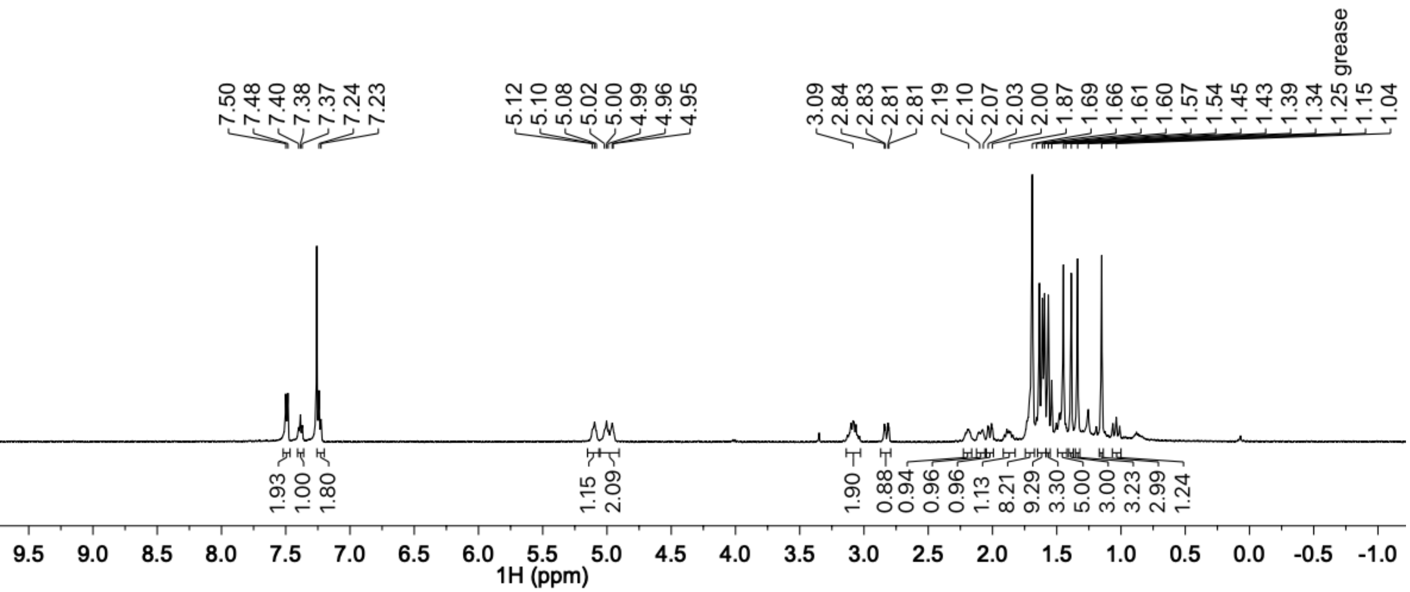
126 MHz, CDCl3



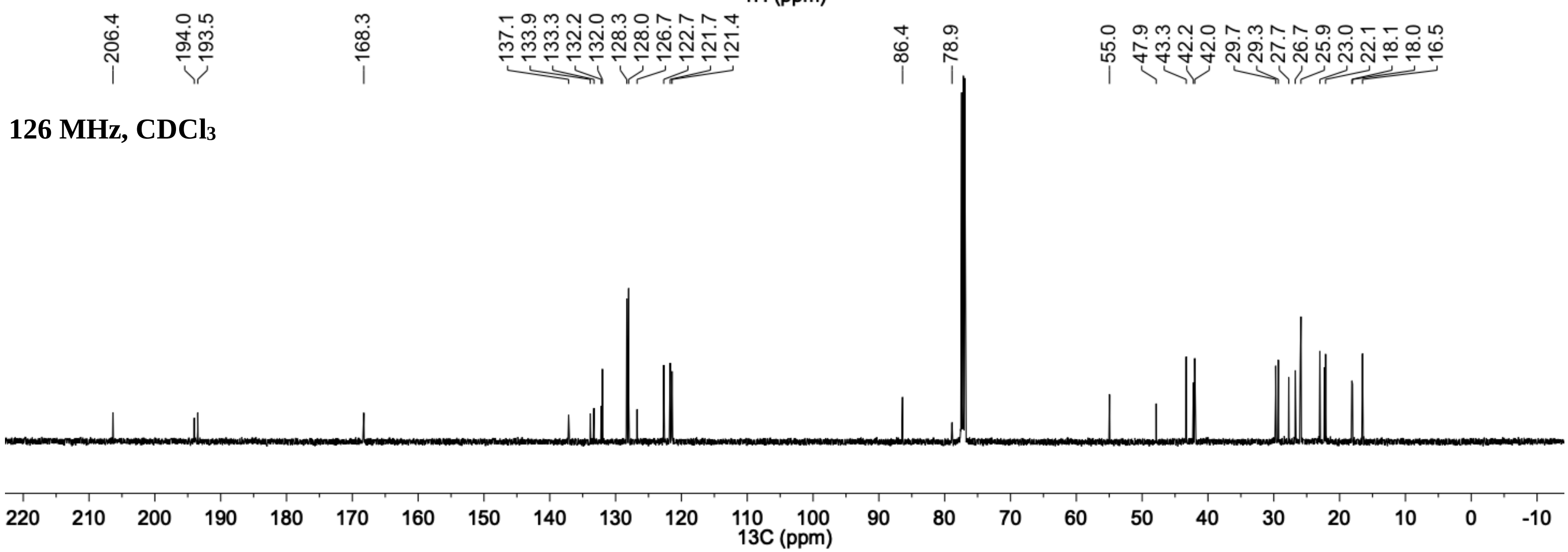


20 (–)-6-*epi*-garcimultiflorone A

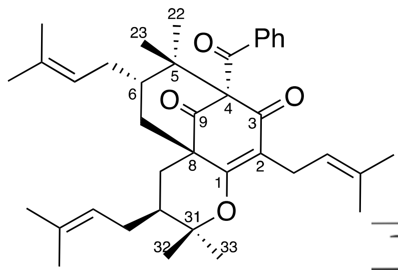
500 MHz, $CDCl_3$

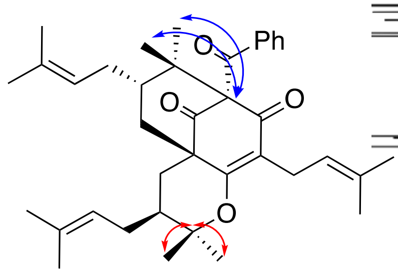


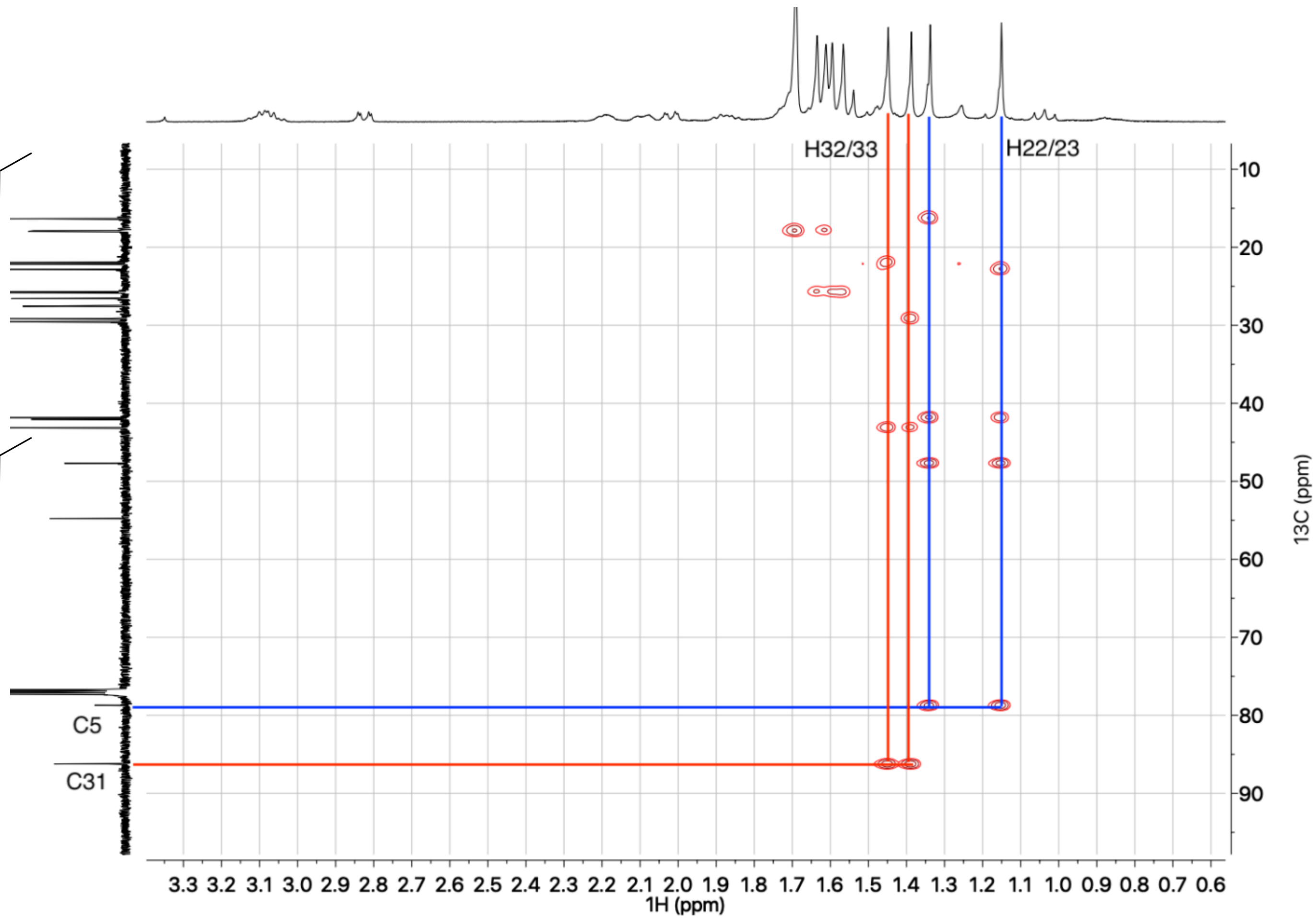
126 MHz, $CDCl_3$

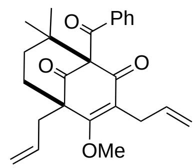


Partial gHMBC Spectrum of **20** (500/126 MHz), Key ^{1}H-^{13}C Correlations Highlighted



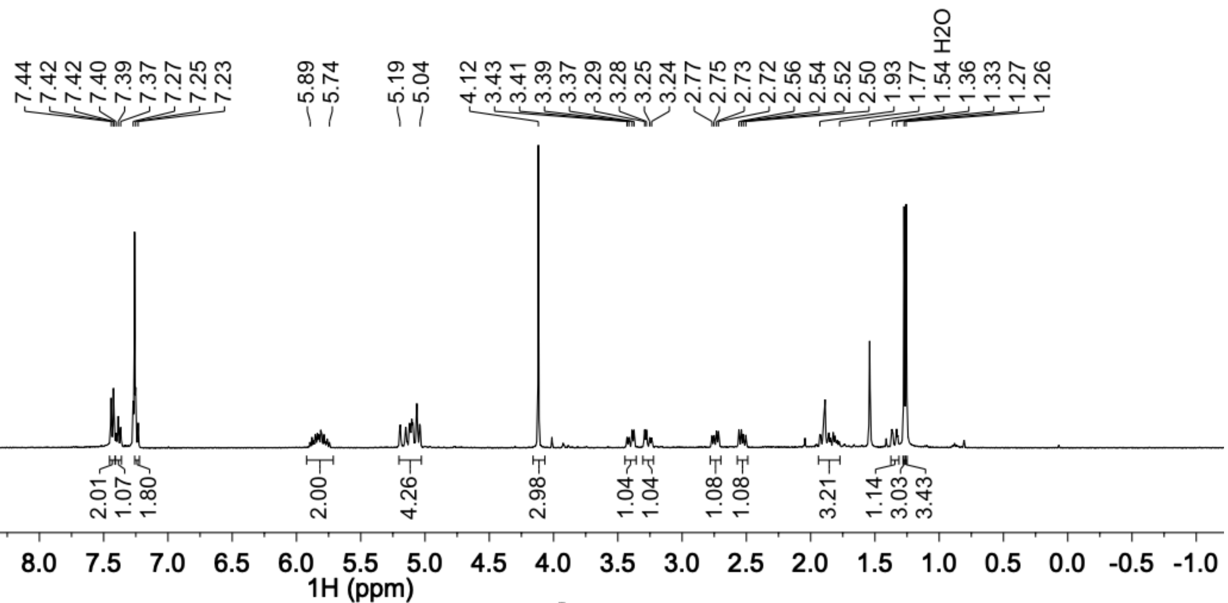




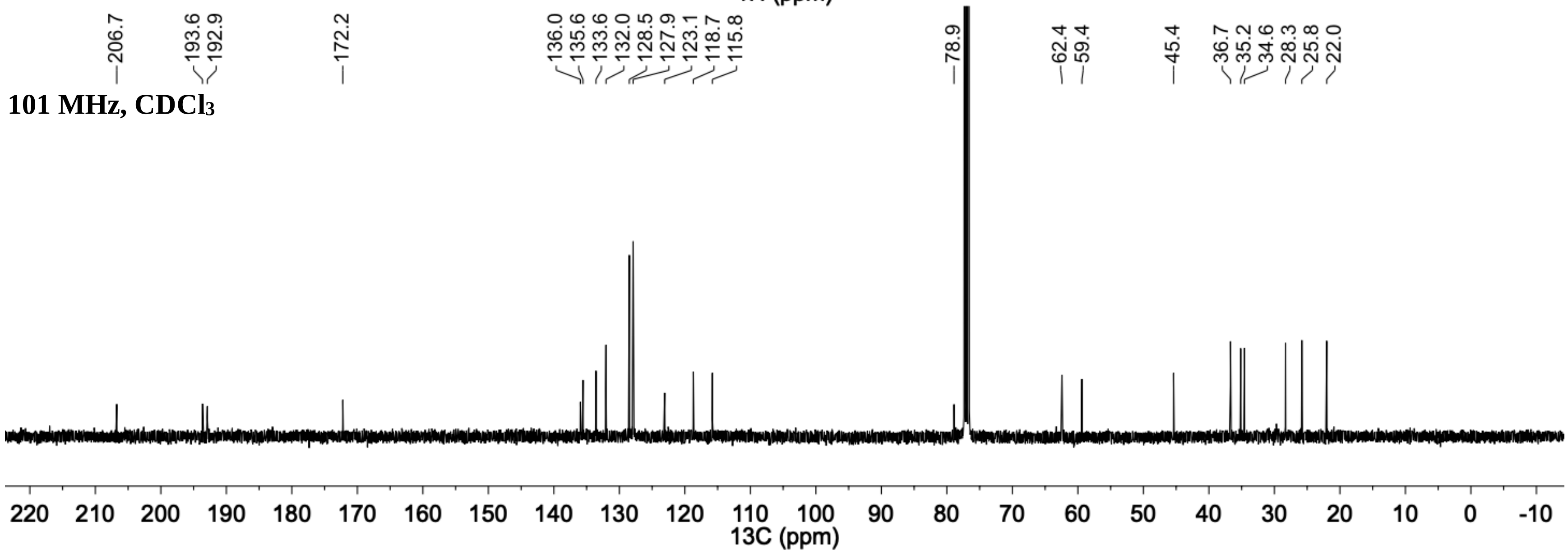


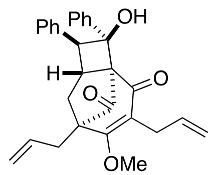
23

400 MHz, CDCl$_3$



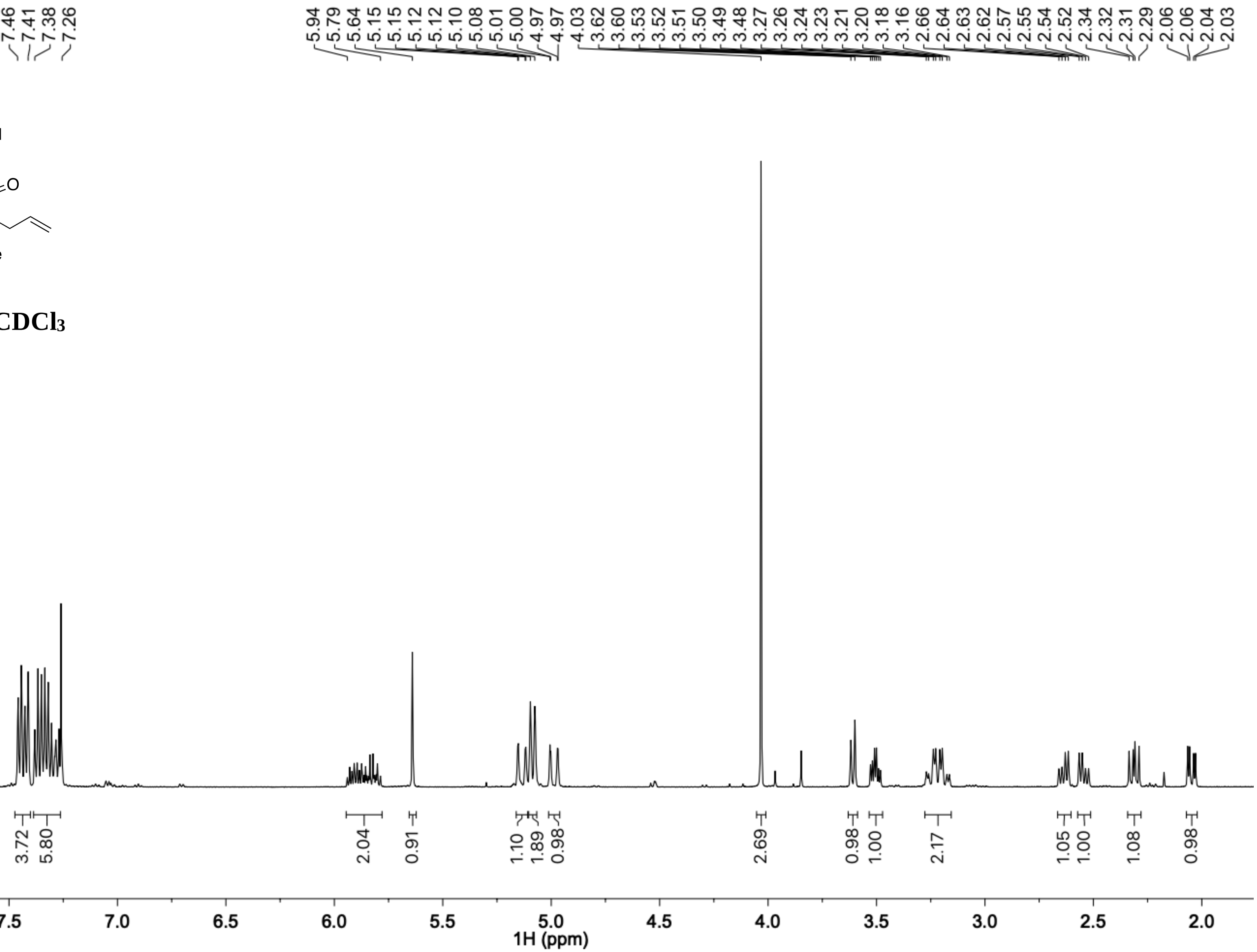
101 MHz, CDCl$_3$

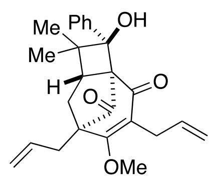




26

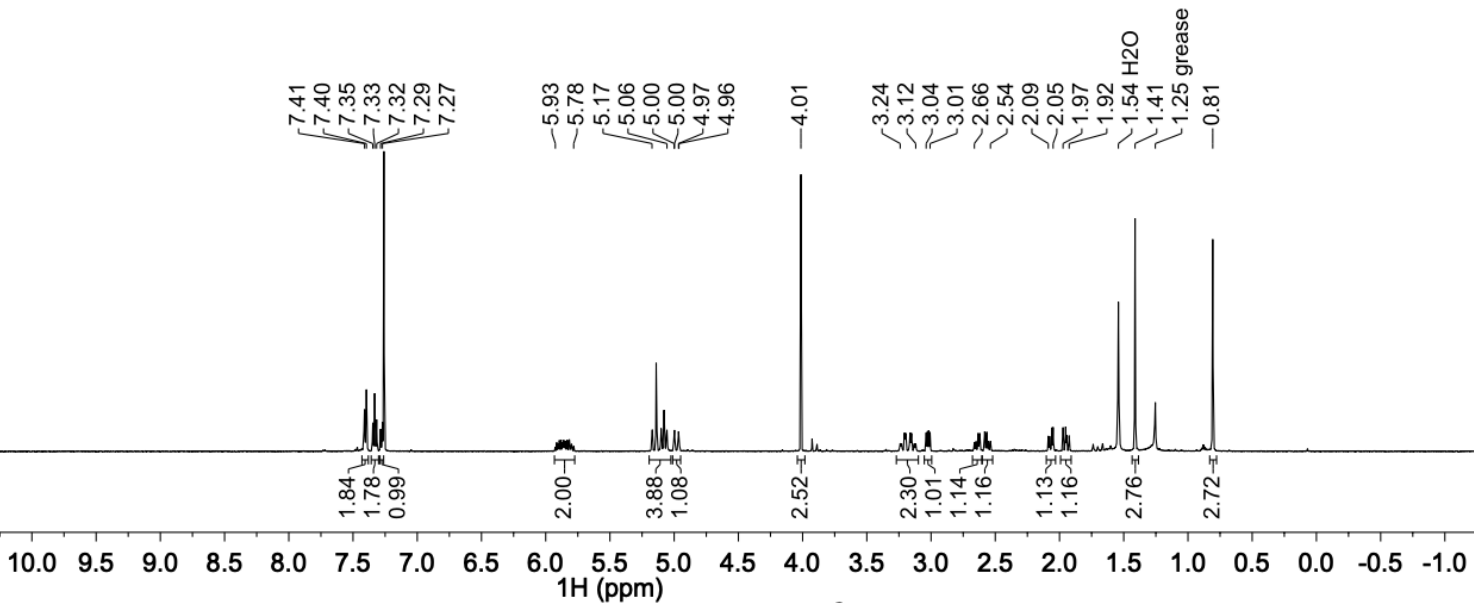
500 MHz, $CDCl_3$



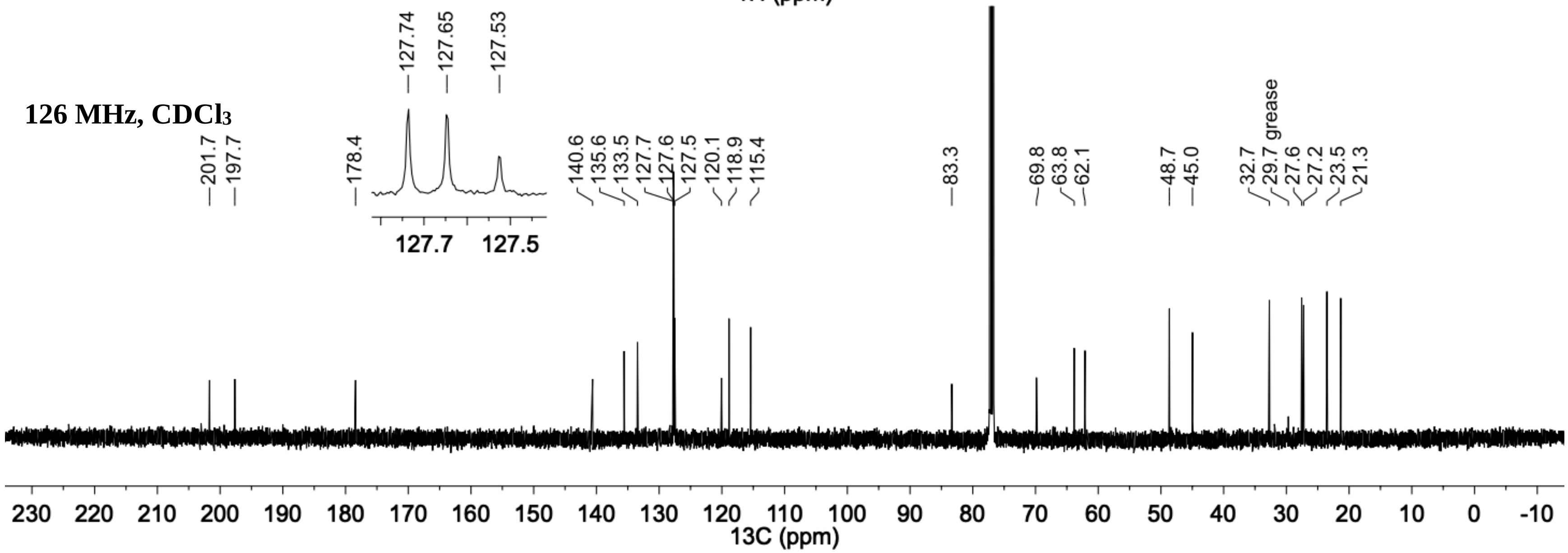


28

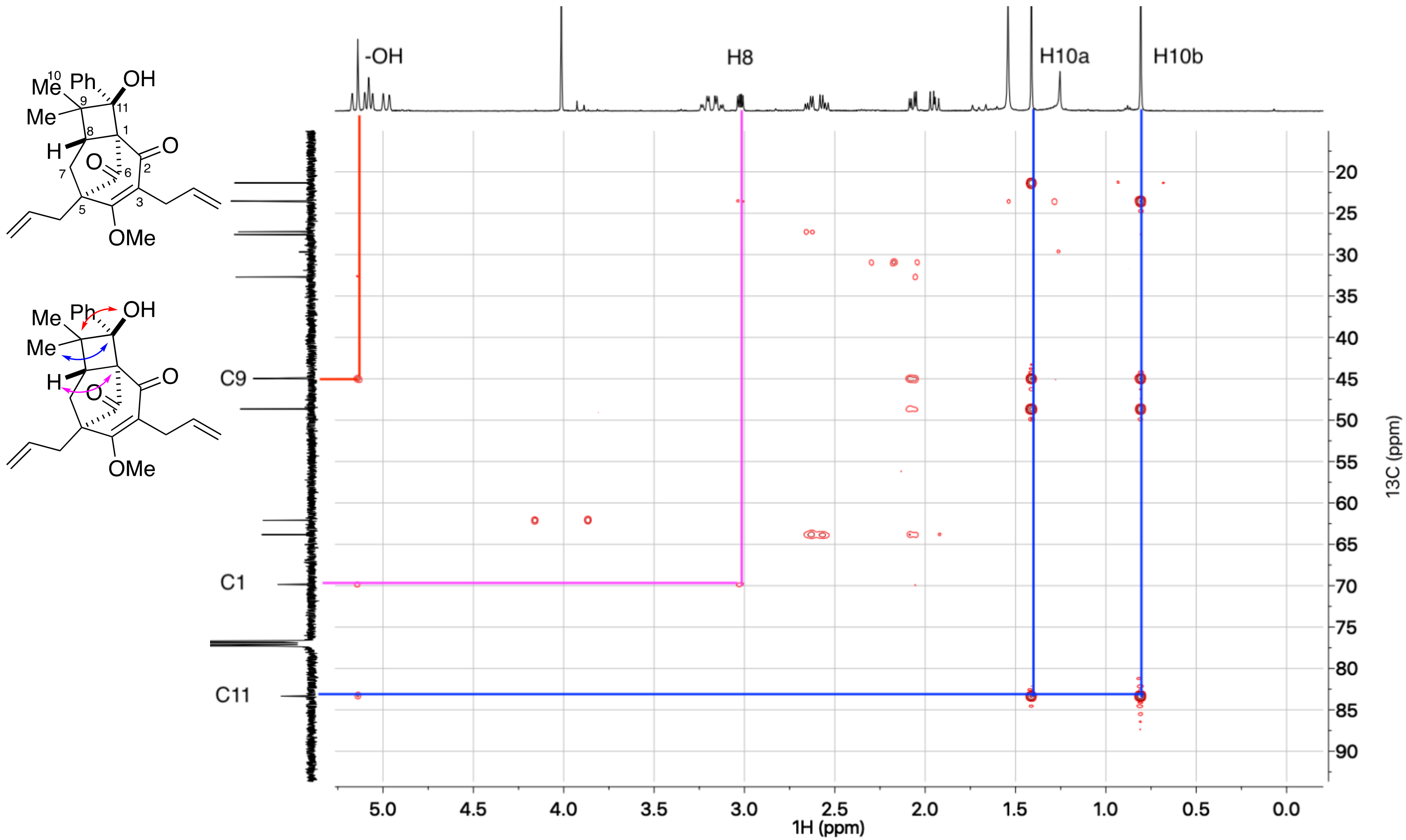
500 MHz, $CDCl_3$

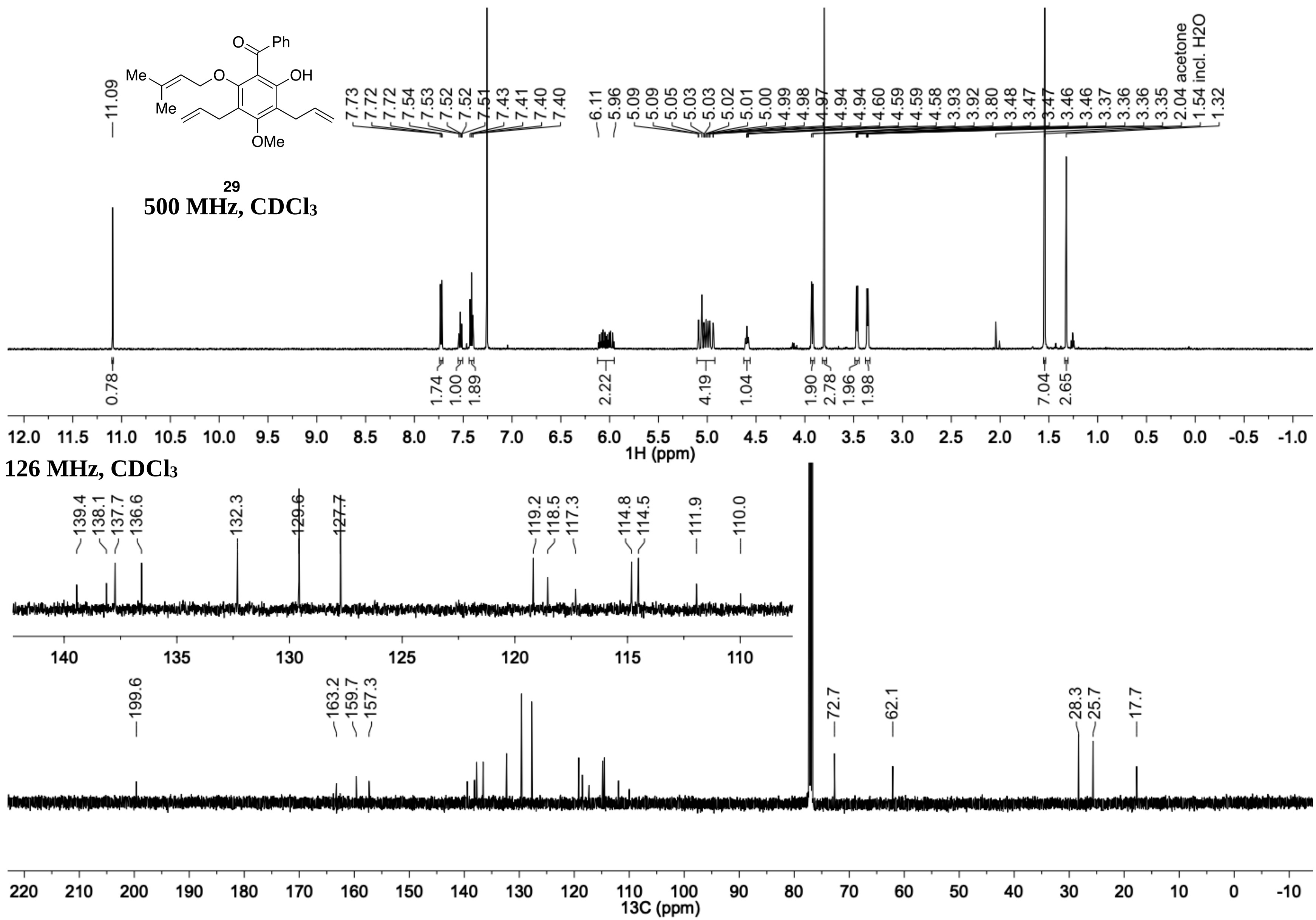


126 MHz, $CDCl_3$

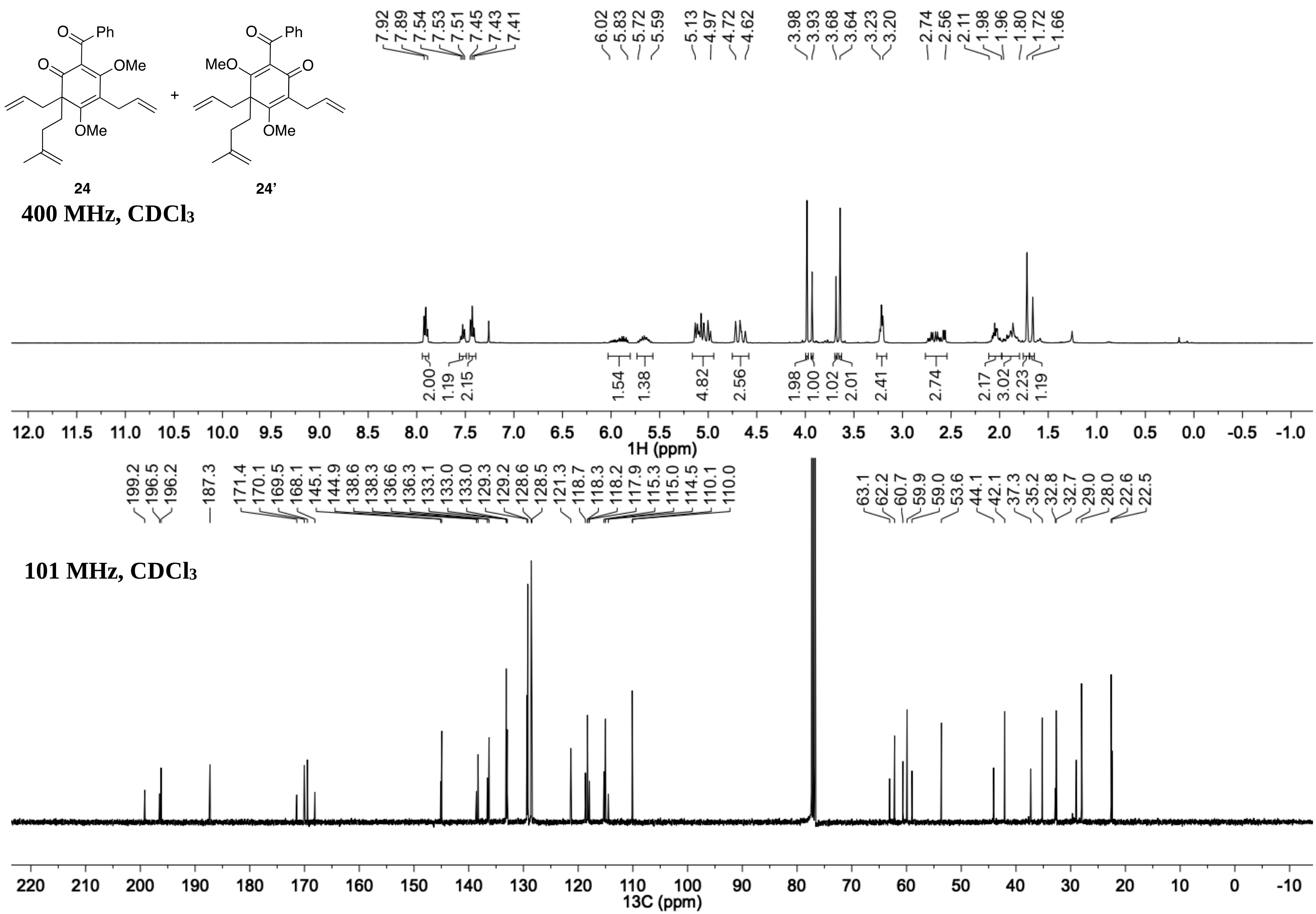


Partial gHMBC Spectrum of **28** (500/126 MHz), Key ^{1}H-^{13}C Correlations Highlighted





O
Ph
OH
Me
Me
O
OMe
29
500 MHz, CDCl3
11.09
7.73
7.72
7.72
7.54
7.53
7.52
7.52
7.51
7.43
7.41
7.40
7.40
6.11
5.96
5.09
5.09
5.05
5.03
5.03
5.02
5.01
5.00
4.99
4.98
4.97
4.94
4.94
4.60
4.59
4.59
4.58
3.93
3.92
3.80
3.48
3.47
3.47
3.46
3.46
3.37
3.36
3.36
3.35
2.04 acetone
1.54 incl. H2O
1.32
0.78
1.74
1.00
1.89
2.22
4.19
1.04
1.90
2.78
1.96
1.98
7.04
2.65
1H (ppm)
126 MHz, CDCl3
139.4
138.1
137.7
136.6
132.3
129.6
127.7
119.2
118.5
117.3
114.8
114.5
111.9
110.0
199.6
163.2
159.7
157.3
72.7
62.1
28.3
25.7
17.7
13C (ppm)


24
24'
400 MHz, CDCl3
1H (ppm)
101 MHz, CDCl3
13C (ppm)