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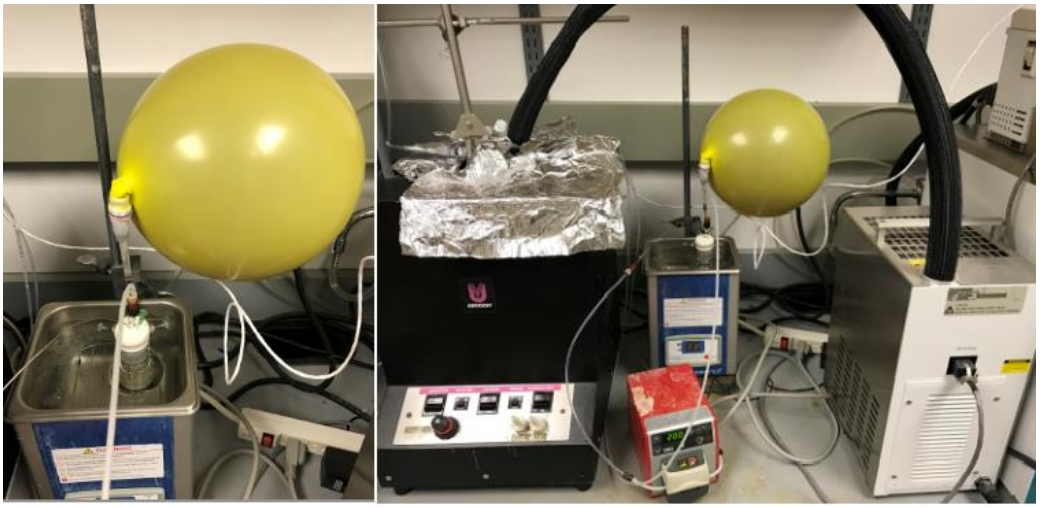
I. General Information

^{1}H NMR spectra were recorded at 400 or 500 MHz at ambient temperature with $CDCl_3$ (Cambridge Isotope Laboratories, Inc.) as the solvent unless otherwise stated. ^{13}C NMR spectra were recorded at 100 or 125 MHz at ambient temperature with $CDCl_3$ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to $CDCl_3$ (^{1}H, δ 7.26; ^{13}C, δ 77.16). Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (br = broad, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants. All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer. High-resolution mass spectra were obtained 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). 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, Water 2996 PDA (PhotoDiode

Array) detector, and ELSD (Evaporative Light Scattering Detector). An Acquity UPLC BEH C18 1.7µm column was used for analytical UPLC-MS. Preparative HPLC was performed on a Gilson PLC2020 using a Waters SunFire™ Prep C18 OBD™ 5µm 19X50 mm column. Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica gel 60-F plates (Silicycle, Inc.). Flash chromatography was performed using 200-400 mesh silica gel (Sorbent Technologies, Inc.). Preparative TLC was conducted with glass backed 250 µm or 1000 µm silica gel 60-F plates (Silicycle, Inc.). Preparative HPLC was conducted using a PLC 2020 Personal Purification System (Gilson, Inc.). Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Photochemistry experiments were performed using a Rayonet RPR-100 photochemical reactor equipped with RPR-3500Å irradiation lamps ($\lambda > 330$ nm, $\lambda_{max} = 350$ nm). For the Rayonet photoflow reactor, a Rayonet RPR-100 photobox was used as light source and a Thermo Scientific™ Neslab CC65 Immersion Cooler was using as a cooling system. The PTFE Tubing (1/32"ID x 1/16"OD) (Cole-Parmer Instrument Company) twined around a 500 mL Pyrex graduated cylinder and connected to a peristaltic pump (Benchtop pump with 114DV flip top single channel pumphead, model: 120S, Waston Marlow Fluid Technology Group) using 2 conical adapter assemblies (IDEX Health & Science, P-798). Two needle adapters (IDEX Health & Science, Flangeless Ferrule Tefzel®, P-300X; Flangeless Short Nut, P-335X; Luer Adapters, P-655) were also installed to connect the reaction flask with the peristaltic pump and reaction tubing. For the purple-LED reactor, the LED strip was purchased from Amazon (Lumcrissy 12V Flexible LED Strip Lights Waterproof 3528 SMD 5M 300LED 300 Units LEDs Light Strip (Purple)). All other reactions were carried out in oven-dried glassware under an argon/nitrogen atmosphere unless otherwise noted. The Scilligence ELN Reaction Planner (Scilligence Corp.) was used for experimental procedure planning. Spectrophotometric solvents (Sigma-Aldrich®) were used whenever necessary unless or otherwise mentioned. UV quality fluorimeter cells (with range until 190 nm) were purchased from Luzchem®. Absorbance measurements were performed using a Carey 300 UV-Vis spectrophotometer. Emission spectra were recorded on a Horiba Scientific® Fluorolog 3 spectrometer (FL3-22) equipped with double-grating monochromators, dual lamp housing containing a 450-watt CW xenon lamp and a UV xenon flash lamp (FL-1040), Fluorohub/MCA/MCS electronics and R928 PMT detector. Emission and excitation spectra were corrected in all the cases for source intensity (lamp

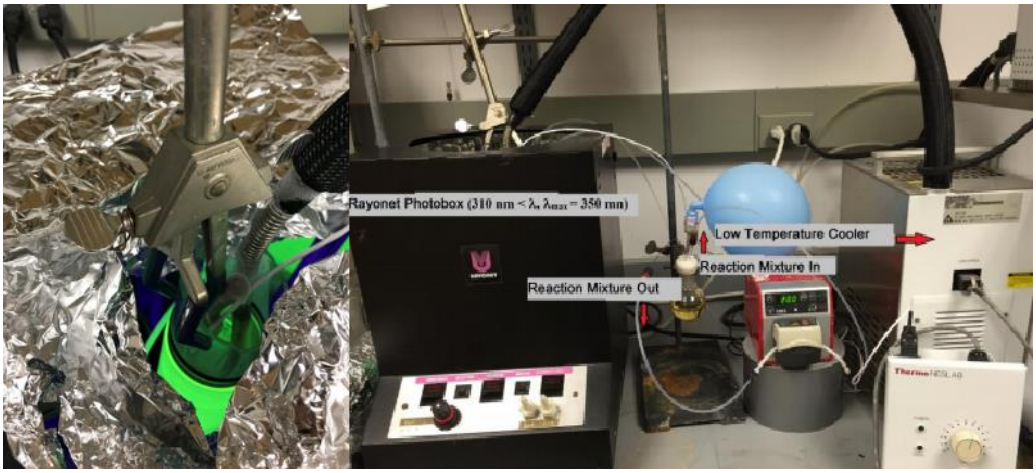
and grating) and emission spectral response (detector and grating) by standard instrument correction provided in the instrument software. Fluorescence emission spectra were processed by FluorEssence® software. Fluorescence lifetimes were determined by time correlated single photon counting using a pulsed diode (NanoLED) emitting at 263 nm and processed using DAS6® V6.4 software. Goodness-of-fit was assessed by minimizing the reduced chi squared function and was further judged by the symmetrical distribution of the residuals. Cyclic voltammetry was performed using HPLC grade acetonitrile as the solvent on a CH instrument. HPLC grade tetrahydrofuran, methylene chloride, diethyl ether, toluene, acetonitrile, and benzene were purchased from Fisher and VWR and were purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology, Inc.). Reagents were purchased from Sigma Aldrich, Oakwood, and Alfa Aesar and were used as received.

II. GRAPHICAL DESCRIPTION OF PHOTOREACTION SETUPS

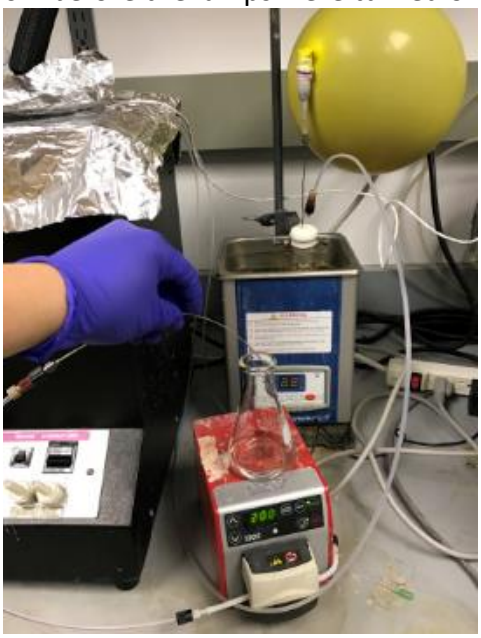


After starting materials and reaction solvents were added, the reaction flask was connected to a Rayonet photoflow reactor (reactor volume = 56 mL; flow rate = 57 mL/min) and the chiller was set to -20 °C to maintain the reaction at low temperature. The reaction flask was immersed in a sonicator with an ice-bath (an ice-bath was used to prevent solvent evaporation during degassing). The sonicator was turned on and an argon balloon with a long needle was used for

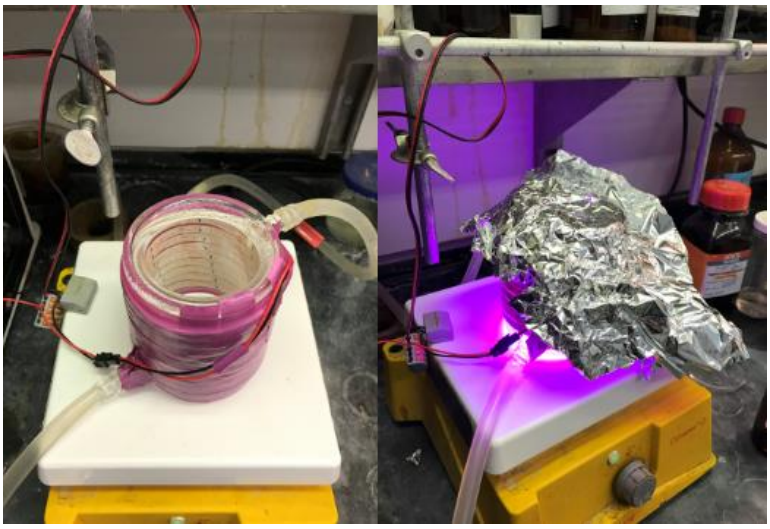
bubbling argon into the reaction to degas the reaction mixture. The duration of the degassing process was approximately 10 to 20 min.



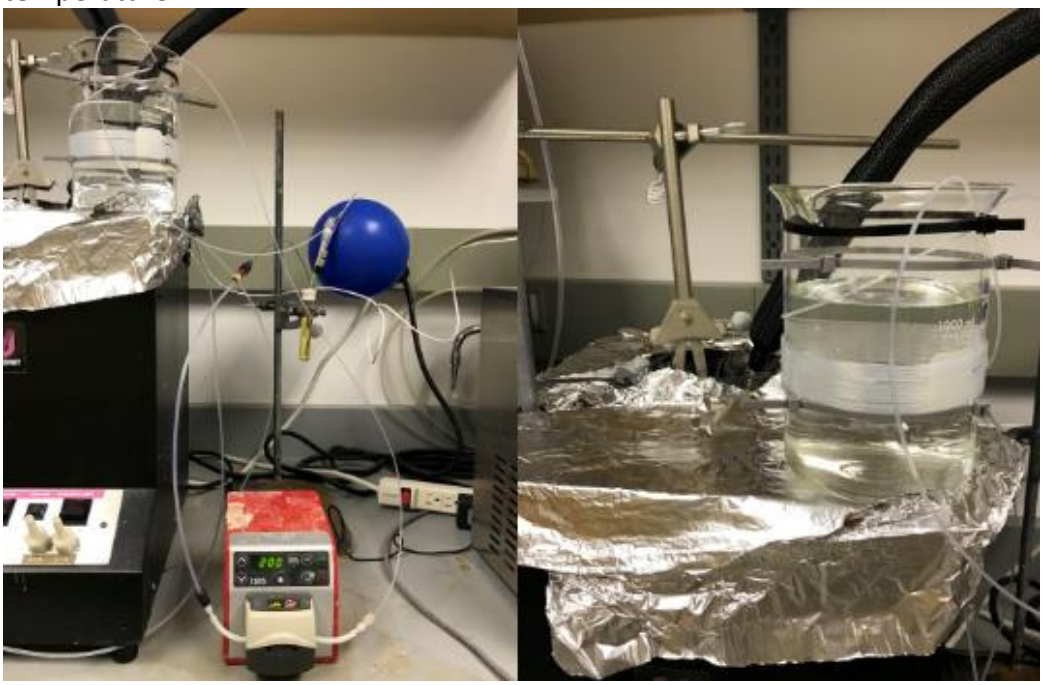
Upon completion of degassing, the UV lamps were turned on. A strong green fluorescence emission was observed. The reaction mixture was circulated for 5-6 h before the lamps were turned off.



When the reaction was complete, the reaction mixture was recollected back into the reaction flask. Subsequently, an additional 100 mL of CH_2Cl_2 was pumped through to rinse any residue present inside the tubing.



When a commercially available purple-LED (395 nm) was chosen as the light source for selective excitation of 3-HF for photocycloaddition experiments, the previously described apparatus was used. When the LED's were turned on, a water circulation system was used to maintain the reaction at room temperature.

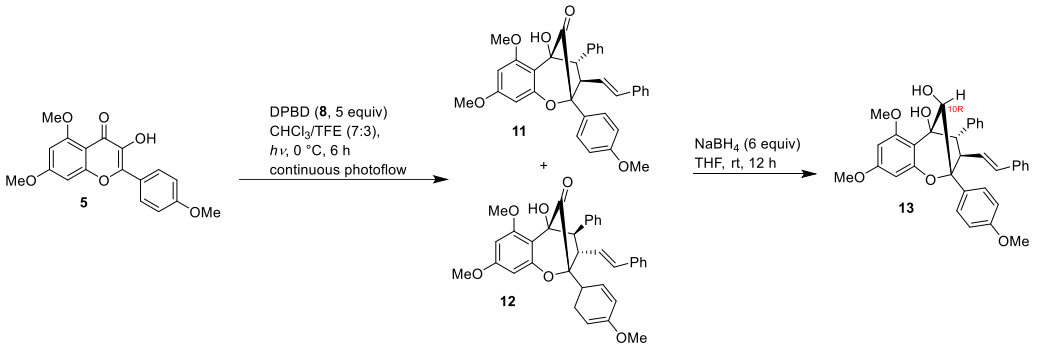


When small scale photoreactions were attempted, the photoflow reactor was switched to the setup indicated above (reaction volume = 5.4 mL; flow rate = 5 mL/min).

Use of a traditional UV-lamp (such as a Rayonet) will create significant heat which makes the photocycloaddition at -78 °C very hard to maintain. Accordingly, to overcome this problem, a UV-LED (λ_{max} = 365 nm) was chosen as a light source. This new photoreaction setup allows us to separate the photoreaction tube from the light source. A dewar with an optical window for light permeation allows us to run ESIPT photocycloaddition at -78 °C very conveniently.

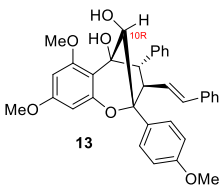
III. Experimental Procedures and Compound Characterization

Reaction Details and Additional Experiments:

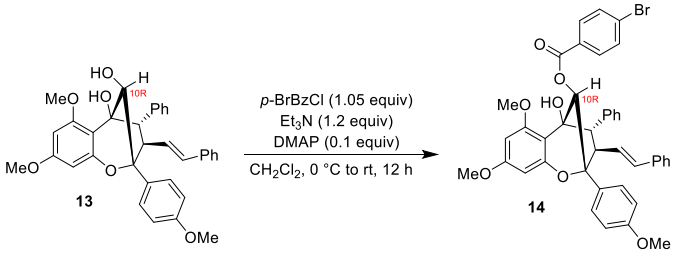


***Endo-10R*-aglain 13:** A 100 mL round bottom flask was charged with 3-hydroxyflavone **5** (500 mg, 1.52 mmol, 1 equiv), DPBD **8** (1.57 g, 7.61 mmol, 5 equiv), and 75 mL of a $CHCl_3$/TFE(7:3) mixture (0.02 M for 3-HF **5**). The flask was connected with the continuous photoflow reactor and placed into a sonicator with an ice-bath. Subsequently, the peristaltic pump was turned on to circulate the reaction mixture and argon bubbling with sonication was continued for an additional 20 min before the UV-lamp (Rayonet, λ_{max} = 350 nm) was turned on. After 6 h, the reaction mixture was collected back to the flask and concentrated *in vacuo*. Purification *via* flash chromatography using a gradient of hexanes/EtOAc (10:1 to 3:1) afforded cyclopenta[*bc*]benzopyrans **11-12** as a mixture of isomers which were used in next step without further purification. The isomeric ratio (**11** : **12**) was determined by ^{1}H NMR analysis to be 5:1 (545 mg, 67% yield, 1.02 mmol).

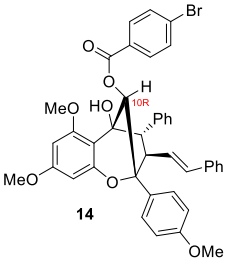
A flame-dried 100 mL flask was charged with a mixture of **11** and **12** (545 mg, 1.02 mmol, 1 equiv) and THF (6.8 mL, 0.15 M). Subsequently, $NaBH_4$ (232 mg, 6.12 mmol, 6 equiv) was added to the reaction at rt in one portion. The resulting mixture was then stirred for 12 h and was quenched with ice-cooled saturated ammonium chloride. The mixture was extracted with CH_2Cl_2 (10 mL $\times$ 3), washed with saturated sodium bicarbonate, and dried over sodium sulfate. The filtrate was concentrated *in vacuo* and ^{1}H NMR analysis of the crude extract was obtained. NMR analysis indicated that the reduction was diastereoselective to favor the *10R*-isomer (d.r.=5:1). Column chromatography purification using hexanes/EtOAc (5:1 to 3:1) afforded the aglain derivative **13** (360 mg, 44% over 2 steps) as a white solid. After recrystallization from EtOAc, trace amounts of impurities were removed and 276 mg of **13** (33%) was obtained.



13: R_f: 0.41 (hexanes: EtOAc = 1:1). m.p. = 223 °C (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.9 Hz, 2H), 7.18 (m, 3H), 7.10 (m, 3H), 6.97 (m, 2H), 6.94 (d, J = 8.9 Hz, 2H), 6.90 (m, 2H), 6.28 (d, J = 2.3 Hz, 1H), 5.98 (d, J = 15.6 Hz, 1H), 5.87 (d, J = 2.3 Hz, 1H), 5.49 (dd, J_1 = 15.6 Hz, J_2 = 8.7 Hz, 1H), 5.42 (s, 1H, OH), 4.75 (d, J = 4.8 Hz, 1H), 3.796 (s, 3H), 3.793 (s, 3H), 3.48 (dd, J_1 = 9.4 Hz, J_2 = 8.7 Hz, 1H), 3.28 (d, J =9.4 Hz, 1H), 2.36 (d, J = 4.8 Hz, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 160.3, 159.2, 153.4, 137.0, 136.7, 130.1, 129.6, 129.6, 128.7, 128.2, 128.2, 127.7, 127.0, 126.9, 126.1, 113.8, 104.0, 94.0, 92.9, 86.8, 82.0, 73.3, 61.6, 55.5, 55.4, 55.3, 53.7; IR υ_{max} (film): 3498, 2968, 1618, 1456, 1254, 1148, 1101, 831 cm^{-1}. HRMS-ESI (m/z) calculated $[M+Na]^+$ $C_{34}H_{32}O_6Na$, 559.2097, found 559.2091.



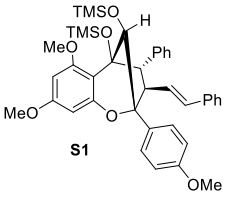
***Para*-bromobenzoate 14:** To a flame dried test tube were added aglain **13** (120 mg, 0.22 mmol, 1 equiv), Et_3N (37 μL, 0.27 mmol, 1.2 equiv), DMAP (2.7 mg, 0.02 mmol, 0.1 equiv), and dry CH_2Cl_2 (7.5 mL, 0.1 M) at 0 °C. Subsequently, 4-bromobenzoyl chloride (51.5 mg, 0.23 mmol, 1.05 equiv) was added in one portion. The resulting mixture was allowed to warm to room temperature and was stirred for 12 h before being quenching with 10 mL of saturated $NaHCO_3$ (aq.). The mixture was extracted with CH_2Cl_2 (5 mL × 3), washed with saturated NaCl (aq.), and dried over sodium sulfate. Column chromatography purification using hexanes/EtOAc (7:1 to 4:1) afforded the *para*-bromobenzoate **14** (121 mg, 75% yield) as a white solid.



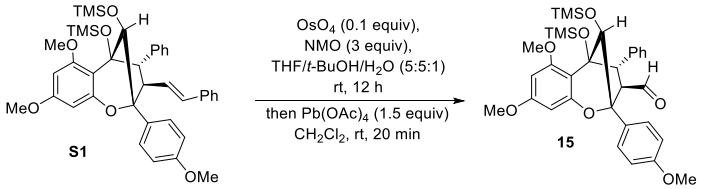
14: R_f: 0.61 (hexanes: EtOAc = 3:1). m.p. = 244 °C (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H), 7.42 (d, J = 8.7 Hz, 2H), 7.20 (m, 3H), 7.10 (m, 3H), 7.01 (m, 2H), 6.91 (m, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.50 (s, 1H), 6.36 (d, J = 2.4 Hz, 1H), 6.51 (d, J = 15.6 Hz, 1H), 5.86 (d, J = 2.4 Hz, 1H), 5.53 (dd, J_1 = 8.4 Hz, J_2 = 15.6 Hz, 1H), 5.32 (s, 1H, OH), 3.86 (s, 3H), 3.74 (s, 3H), 3.54 (dd, J_1 = 9.4 Hz, J_2 = 8.4 Hz, 1H), 3.49 (d, J = 9.4 Hz, 1H), 3.06 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 160.7, 159.7, 159.2, 153.6, 136.9, 136.3, 131.5, 131.5, 130.5, 129.2, 129.0, 128.7, 128.7, 128.2, 128.1,

127.7, 127.5, 127.1, 127.0, 126.1, 113.8, 104.6, 93.9, 92.5, 86.5, 81.4, 72.6, 61.6, 55.5, 55.4, 55.2, 54.5; IR υ_{max} (film): 3499, 2918, 1726, 1617, 1589, 1266, 1148, 1099, 1012, 753 cm^{-1}. HRMS-ESI (m/z) calculated $[M+Na]^+$ $C_{41}H_{36}O_7Br$ 719.1644, found 719.1643.

TMS-aglain S1: A flame dried test tube was charged with aglain **13** (200 mg, 0.37 mmol, 1 equiv) and dry CH_2Cl_2 (2.5 mL, 0.15 M). The solution was cooled to -78 °C before Et_3N (130 μL, 0.93 mmol, 2.5 equiv) and TMSOTf (148 μL, 0.82 mmol, 2.2 equiv) were added. The resulting mixture was stirred at -78 °C for an additional 10 min before warming up to 0 °C. After 1 h, the reaction was quenched with 5 mL of saturated $NaHCO_3$ (aq.). The mixture was extracted with CH_2Cl_2 (3 mL × 3), washed with saturated NaCl (aq.), and dried over sodium sulfate. Column chromatography purification using hexanes/EtOAc (20:1 to 15:1) afforded TMS-aglain **S1** (249 mg, 98% yield) as a colorless oil.

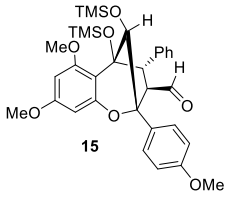


S1: R_f: 0.67 (hexanes: EtOAc = 4:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.9 Hz, 2H), 7.11 (m, 5H), 7.05 (m, 1H), 7.00 (m, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.19 (d, J = 2.4 Hz, 1H), 5.92 (d, J = 15.9 Hz, 1H), 5.73 (d, J = 2.4 Hz, 1H), 5.50 (dd, J_1 = 15.9 Hz, J_2 = 7.4 Hz, 1H), 4.60 (s, 1H, OH), 3.82 (s, 3H), 3.80 (s, 3H), 3.39 (d, J = 10.7 Hz, 1H), 3.33 (dd, J_1 = 10.7 Hz, J_2 = 7.4 Hz, 1H), 2.94 (s, 3H), 0.04 (s, 9H), -0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 192.7, 163.2, 160.1, 159.4, 159.0, 136.5, 136.2, 135.3, 130.4, 129.7, 128.4, 128.2, 127.8, 127.3, 126.4, 125.5, 123.9, 115.0, 114.5, 98.0, 94.4, 91.7, 62.1, 56.1, 55.7, 55.2, 52.0; IR υ_{max} (film): 2937, 2848, 1696, 1607, 1512, 1456, 1403, 1260, 1155, 1104, 830, 751, 698 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{40}H_{49}O_6Si_2$, 681.3068, found 681.3069.

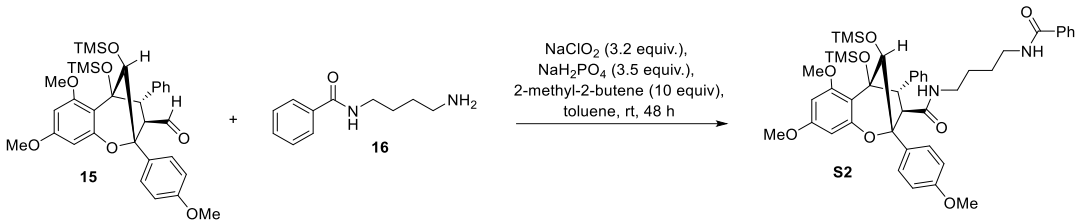


***Endo*-10*R*-TMS-aldehyde 15:** A test tube was charged with TMS-aglain **S1** (249 mg, 0.37 mmol, 1 equiv), THF (4.7 mL) and *t*-BuOH (4.7 mL). Subsequently, 0.93 mL OsO_4 (aq., 10 mg/mL) (9.3 mg, 0.036 mmol, 0.1 equiv) was added to the solution followed by addition of N-methylmorpholine oxide (NMO) (128.5 mg,

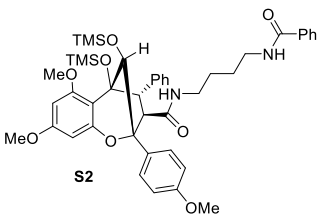
1.1 mmol, 3 equiv). The resulting mixture was stirred at room temperature for 12 h before 10 mL of saturated NaCl (aq.) was added. The mixture was extracted with Et_2O (5 mL × 3), washed with saturated NaCl (aq.), and dried over sodium sulfate. The filtrate was concentrated *in vacuo* to afford the diol compound as a brown oil which was subjected to next step without further purification. The brown oil was dissolved in a test tube with 10 mL of CH_2Cl_2. Subsequently, $Pb(OAc)_4$ (243 mg, 0.55 mmol, 1.5 equiv) was added. The resulting solution was stirred at room temperature for 20 min before 20 mL saturated $Na_2S_2O_3$ was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (10 mL × 3), washed with saturated NaCl (aq.), and dried over sodium sulfate. Column chromatography purification using hexanes/EtOAc (15:1 to 10:1) afforded *endo*-TMS-aldehyde **15** (158 mg, 71% yield) as a colorless oil.



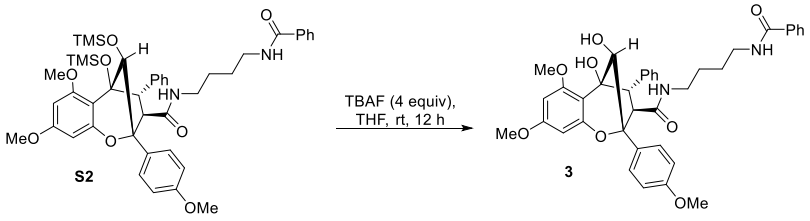
15: R_f: 0.35 (hexanes:EtOAc = 3:17). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (d, J = 2.8 Hz, 1H), 7.54 (d, J = 8.8 Hz, 2H), 7.11 (m, 3H), 6.98 (d, J = 8.8 Hz, 2H), 6.92 (m, 2H), 6.21 (d, J = 1.2 Hz, 1H), 5.76 (d, J = 1.2 Hz, 1H), (d, J = 1.2 Hz, 1H), 4.53 (s, 1H, OH), 3.88 (d, J = 10.6 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.52 (dd, J_1 = 10.6 Hz, J_2 = 2.8 Hz, 1H), 2.94 (s, 3H), 0.04 (s, 9H), -0.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 160.0, 158.9, 154.1, 137.6, 137.3, 130.8, 130.1, 130.0, 128.9, 128.1, 127.7, 126.84, 126.77, 126.2, 126.0, 113.1, 106.7, 92.7, 91.4, 86.2, 83.4, 78.7, 59.7, 55.3, 55.1, 53.9, 52.4, 2.1, 1.3; IR υ_{max} (film): 2957, 1721, 1613, 1587, 1516, 1465, 1250, 1195, 1151, 1110, 1035, 899, 839, 743, 696 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{33}H_{43}O_7Si_2$, 607.2547, found 607.2556.



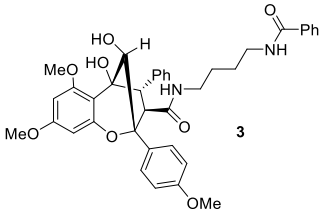
TMS-foveoglin A S2: A flame-dried test tube was charged with *endo*-TMS-aldehyde **15** (150 mg, 0.25 mmol, 1 equiv), amine **16**[S1] (238 mg, 1.24 mmol, 5 equiv) and dry toluene (2.5 mL, 0.1 M) under argon. The mixture was stirred at room temperature for 5 min before NaH_2PO_4 (104 mg, 0.87 mmol, 3.5 equiv), 2-methyl-2-butene (0.26 mL, 2.5 mmol, 10 equiv) and $NaClO_2$ (72 mg, 0.79 mmol, 3.2 equiv) were consecutively added. The resulting heterogeneous mixture was stirred for 48 h at room temperature. The reaction mixture was then filtered to remove insoluble inorganic salts and the filtrate was concentrated *in vacuo.* Column chromatography purification using hexanes/EtOAc (6:1 to 3:1) afforded TMS-foveoglin A **S2** (147 mg, 71% yield) as a colorless oil.



S2: R_f: 0.37 (hexanes: EtOAc = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.58 (d, J = 8.8 Hz, 2H), 7.50 (m, 1H), 7.44 (m, 2H), 7.08 (m, 3H), 6.92 (m, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.64 (t, J = 5.8 Hz, 1H, NH), 6.15 (d, J = 2.5 Hz, 1H), 5.73 (d, J = 2.5 Hz, 1H), 5.23 (t, J = 5.7 Hz, 1H, NH), 4.65 (s, 1H, OH), 4.02 (d, J = 10.2 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.25 (m, 1H), 3.12 (m, 1H), 3.07 (d, J = 10.2 Hz, 2H), 2.93 (s, 3H), 2.74 (m, 1H), 2.49 (m, 1H), 1.07 (m, 2H), 0.84 (m, 2H), 0.03 (s, 9H), -0.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 167.4, 160.8, 160.0, 159.3, 153.5, 137.6, 134.6, 131.3, 130.2, 128.9, 128.4, 128.0, 127.0, 126.9, 126.3, 113.0, 107.0, 92.8, 91.8, 84.7, 83.1, 78.5, 58.8, 55.4, 55.1, 53.9, 39.4, 38.9, 26.23, 26.21, 2.1, 1.2; IR υ_{max} (film): 3308, 2958, 2904, 1642, 1614, 1615, 1520, 1151, 1112, 1040, 905, 839, 696 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{44}H_{57}N_2O_8Si_2$, 797.3653, found 797.3659.

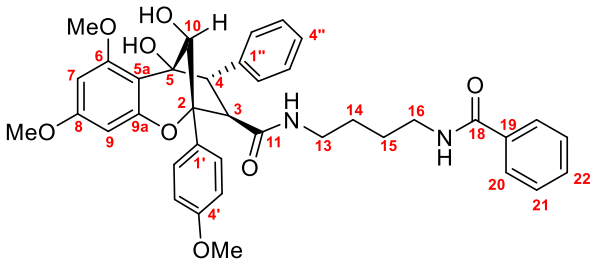


Foveoglin A 3: A flame dried test tube was charged with TMS-foveoglin A **S2** (120 mg, 0.15 mmol, 1 equiv) and dry THF (2 mL). Subsequently, TBAF (1 M THF solution, 0.36 mL, 0.36 mmol, 2.4 equiv) was added dropwise. The resulting mixture was stirred for 12 h before 5 mL of saturated NaCl (aq.) was added to quench the reaction. The mixture was extracted with EtOAc (5 mL $\times$ 3), washed with saturated NaCl (aq.), and dried over sodium sulfate. The filtrate was concentrated *in vacuo.* Column chromatography purification using hexanes/EtOAc (2:1 to 1:2) afforded foveoglin A **3** (94 mg, 96% yield) as an amorphous solid.



3: R_f: 0.51 (EtOAc). m.p. = 153 °C (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 8.9 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.16 (m, 3H), 6.93 (m, 2H), 6.89 (d, J = 8.9 Hz, 2H), 6.47 (brt, J = 5.7 Hz, 1H, NH), 6.25 (d, J = 2.3 Hz, 1H), 5.85 (d, J = 2.3 Hz, 1H), 5.54 (brt, J = 5.9 Hz, 1H, NH), 5.43 (s, 1H, OH), 4.91 (d, J = 5.5 Hz, 1H), 4.00 (d, J = 9.0 Hz, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.29 (m, 1H), 3.23 (d, J = 9.0 Hz, 1H), 3.15 (m, 1H), 3.10 (s, 3H), 2.92 (m, 1H), 2.60 (m, 1H), 2.31 (d, J = 5.5 Hz, 1H, OH), 1.14 (m, 2H), 0.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 167.4, 160.8, 160.3, 159.3, 152.9, 136.9, 134.6, 131.4, 129.2, 128.6, 128.5, 128.0, 127.7, 127.0, 126.9, 113.5, 104.3, 94.0, 93.0, 85.6, 81.8, 73.5, 59.0, 57.1, 55.5,

55.4, 39.4, 39.0, 26.3, 26.2; IR υ_{max} (film): 3375, 2955, 1641, 1618, 1517, 1492, 1458, 1305, 1254, 1148, 1105, 1037, 833 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{38}H_{41}N_2O_8$, 653.2863, found 653.2858.



(±)-foveoglin A (3)

^{1}H NMR

Positions	natural (–)-**3** δ lit[S2] ($CDCl_3$) (J_{H-H} in Hz)	synthetic (±)-**3** (this work) δ (500 MHz, $CDCl_3$) (J_{H-H} in Hz)
2		
3	3.22, d (9.0)	3.23, d (9.0)
4	4.00, d (9.0)	4.00, d (9.0)
5		
5-OH	5.44, s	5.43, s
5a		
6		
7	5.86, d (2.2)	5.85, d (2.3)
8		
9	6.26, d (2.2)	6.25, d (2.3)
9a		
10	4.91, s	4.91, d (5.5)
10-OH		2.31, d (5.5)
11		
NH-12	5.49, brt (5.5)	5.54, brt (5.7)
13	2.93, m 2.61, m	2.92, m 2.60, m
14	0.98, m	0.96, m
15	1.16, m	1.14, m
16	3.29, m 3.16, m	3.29, m 3.15, m
NH-17	6.46, brt (5.5)	6.47, brt (5.7)
18		
19		
20, 24	7.82, d (8.0)	7.81, d (7.5)
21, 23	7.47, t (7.7)	7.47, t (7.8)
22	7.53, t (7.2)	7.52, t (7.3)

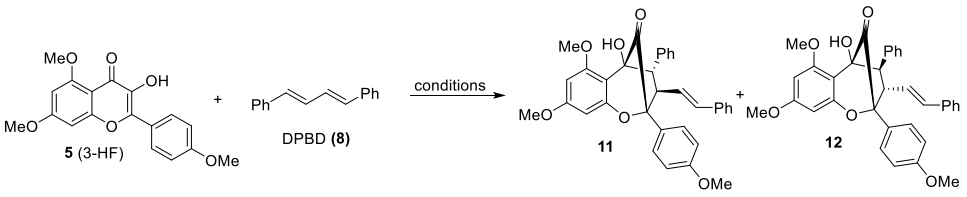
1’		
2’, 6’	7.62, d (8.9)	7.61, d (8.9)
3’, 5’	6.89, d (8.7)	6.89, d (8.9)
4’		
1’’		
2’’, 6’’	6.93, m	6.93 m
3’’, 5’’	7.16, m	7.16, m
4’’	7.16, m	7.16, m
OCH_3-6	3.11, s	3.10, s
OCH_3-8	3.79, s	3.78, s
OCH_3-4’	3.77, s	3.77, s

^{13}C NMR

	natural (–)-**3**	synthetic (±)-**3** (this work)
Positions	δ lit.[S2] ($CDCl_3$)	δ (125 MHz, $CDCl_3$)
2	85.6	85.6
3	59.0	59.0
4	57.1	57.1
5	81.8	81.8
5-OH		
5a	104.2	104.3
6	160.3	160.3
7	93.0	93.0
8	160.8	160.8
9	93.9	94.0
9a	152.8	152.9
10	73.5	73.5
10-OH		
11	170.0	170.0
NH-12		
13	39.0	39.0
14	26.2	26.2
15	26.3	26.3
16	39.4	39.4
NH-17		
18	167.5	167.4
19	134.5	134.6
20, 24	127.0	127.0
21, 23	128.6	128.6
22	131.5	131.4
1’	129.2	129.2

2’, 6’	128.0	128.0
3’, 5’	113.6	113.5
4’	159.3	159.3
1’’	136.8	140.7
2’’, 6’’	128.6	128.5
3’’, 5’’	127.7	127.7
4’’	127.0	127.0
OCH_3-6	55.5	55.5
OCH_3-8	55.4	55.4
OCH_3-4’	55.4	55.4

Condition Optimization for ESIPT Photocycloaddition of 5 and 8.

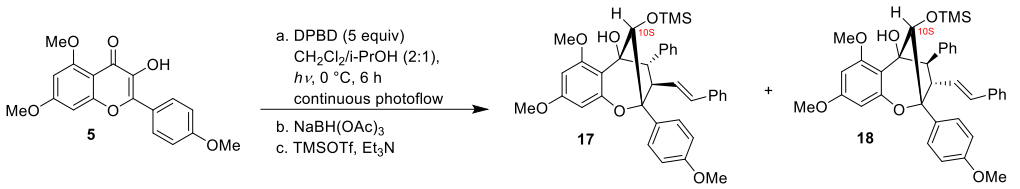


Entry	Solvent	Temp. Time	Additive	Outcome (**11**:**12**)[a]
1	CH_2Cl_2	0 °C, 6 h	N.A.	48%, 2:1 d.r.
2	CH_2Cl_2/MeOH (3:1)	0 °C, 6 h	N.A.	43%, 3:1 d.r.
3	CH_2Cl_2	0 °C, 6 h	p-TsOH	37%, 3:1 d.r.
4	CH_2Cl_2/*i*-PrOH (2:1)	0 °C, 6 h	N.A.	51%, 1:1 d.r.
5	CH_2Cl_2	0 °C, 6 h	benzophenone	50%, 2:1 d.r.
6	CH_3CN/MeOH (1:1)	0 °C, 6 h	N.A.	47%, 2:1 d.r.
7	THF	0 °C, 6 h	N.A.	47%, 3:1 d.r.
8	$CHCl_3$/TFE (7:3)	0°C, 6 h	N.A.	67%, 5:1 d.r.

[a] Diastereoselectivity determined by ^{1}H NMR analysis; isolated yield obtained for the mixture of diastereomers.

A 10 mL round bottom flask was charged with 3-hydroxyflavone **5** (30 mg, 0.09 mmol, 1 equiv), DPBD **8** (94 mg, 0.46 mmol, 5 equiv), and 9 mL of the indicated

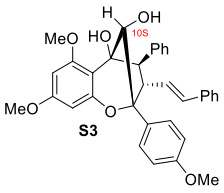
solvent mixture (0.01 M for 3-HF **5**). The flask was connected with the continuous photoflow reactor setup and placed into a sonicator with an ice-bath. Subsequently, the peristaltic pump was turned on to circulate the reaction mixture and the argon bubbling with sonication was continued for an additional 15 min before the UV-lamp (Rayonet, λ_{max} = 350 nm) was turned on. After 6 h, the reaction mixture was collected back into the flask and concentrated under vacuum. Purification *via* flash chromatography using a gradient of hexanes/EtOAc (10:1 to 3:1) afforded cyclopenta[*bc*]benzopyrans **11** and **12** as mixture of isomers.



***Exo-10S*-TMS-aglain 18:** A 100 mL round bottom flask was charged with 3-hydroxyflavone **5** (500 mg, 1.52 mmol, 1 equiv) and DPBD **8** (1.57 g, 7.61 mmol, 5 equiv) in 75 mL of CH_2Cl_2/*i*-PrOH (2:1) (0.02 M for 3-HF **5**). The flask was connected with the continuous photoflow reactor followed by degassing with argon gas for 10 min. Subsequently, the peristaltic pump was turned on to circulate the reaction mixture and the argon gas was kept for another 10 min before the UV-lamp (Rayonet, λ > 315 nm) was turned on. After 6 h, the reaction mixture was collected back into the flask and was concentrated under vacuum. Purification *via* flash chromatography using a gradient of hexanes/EtOAc (10:1 to 3:1) afforded cyclopenta[*bc*]benzopyrans **11** and **12** as mixture of isomers which were used in next step without further purification. The isomeric ratio was determined using ^{1}H NMR analysis to be 1:1 (426 mg, 52% yield, 0.8 mmol). A flame-dried 100 mL flask was charged with $NaBH(OAc)_3$ (1.01 g, 4,78 mmol, 6 equiv) and HOAc (0.27 mL, 4.78 mmol) in $PhCF_3$ (20 mL) at rt under argon. The mixture was then sonicated briefly and stirred at rt for 10 min. A mixture of **11** and **12** (426 mg, 0.8 mmol, 1 equiv) in 20 mL of $PhCF_3$ (0.02 M) was then added at rt at one portion under argon. The resulting mixture was then stirred for 14 h and was quenched with saturated ammonium chloride. The mixture was extracted with CH_2Cl_2, washed with saturated sodium bicarbonate, dried over sodium sulfate, and the filtrate concentrated *in vacuo.* ^{1}H NMR analysis of the crude extract indicated that the reduction was diastereoselective in favor of the *10S*-isomer (d.r.= 10:1). Column chromatography purification using hexanes/EtOAc (5:1) afforded an inseparable mixture of isomeric aglains (4

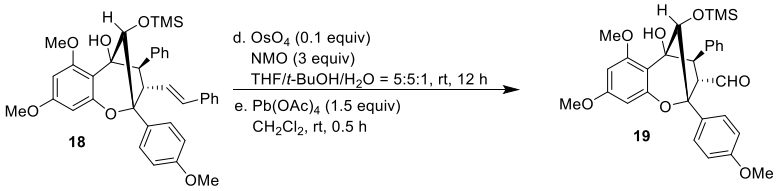
isomers combined, 406 mg, 95% yield) which was used in the next step without further purification. Preparative thin layer chromatography purification of 20 mg mixture material using hexanes/EtOAc (9:1) afforded pure *exo*-aglain compound **S3** (15 mg, 0.028 mmol).

To a flame dried test tube were added the mixture of isomeric aglains (406 mg, 0.76 mmol, 1 equiv), Et_3N (0.33 mL, 2.39 mmol, 3 equiv) and CH_2Cl_2 (7.5 mL, 0.1 M). After the resulting mixture was cooled to -78 °C, TMSOTf (290 μL, 1.6 mmol, 2 equiv) was added dropwise before the temperature was raised to 0 °C for 1 h. Ice-cooled saturated sodium bicarbonate was added to quench the reaction and CH_2Cl_2 (5 mL × 2) was employed for extraction. The combined organic layer was washed with saturated sodium chloride and dried over sodium sulfate. The filtrate was concentrated *in vacuo* and purified by column chromatography using a gradient of hexanes/Et_2O (30:1 to 20:1). *Exo-10S*-TMS-aglain **18** (186 mg, 0.35 mmol) was obtained in 23% yield from 3-HF **5** as a colorless oil. *Endo-10S*-TMS-aglain **17** (190 mg, 0.35 mmol) was also obtained in 23% yield from 3-HF **5**.



S3

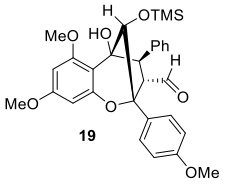
S3: R_f: 0.30 (hexanes: EtOAc = 7:3). ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 9.0 Hz, 2H), 7.49 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.3 Hz, 2H), 7.28 (d, J = 7.3 Hz, 1H), 7.20 (m, 4H), 7.12 (m, 1H), 6.96 (d, J = 9.0 Hz, 2H), 6.83 (dd, J_1 = 16 Hz, J_2 = 8.3 Hz, 1H), 6.28 (d, J = 2.3 Hz, 1H), 6.25 (d, J = 16 Hz, 1H), 6.14 (d, J = 2.3 Hz, 1H), 5.18 (s, 1H, OH), 4.40 (s, 1H, OH), 4.37 (dd, J_1 = 8.3 Hz, J_2 = 7.7 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.65 (d, J = 7.7 Hz, 1H), 2.90 (s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 159.3, 155.9, 153.9, 140.4, 137.2, 132.1, 130.2, 130.1, 128.8, 128.2, 128.1, 127.8, 127.1, 126.7, 126.2, 113.6, 113.3, 94.2, 92.3, 88.3, 81.6, 79.7, 64.9, 57.2, 56.1, 55.5, 55.2; IR υ_{max} (film): 3497, 3027, 2939, 1615, 1589, 1515, 1456, 1253, 1150, 1097, 1050, 830, 749, 698 cm^{-1}. HRMS-ESI (m/z) calculated $[M+Na]^+$ $C_{34}H_{32}O_6Na$, 559.2097, found 559.2095.



18 19

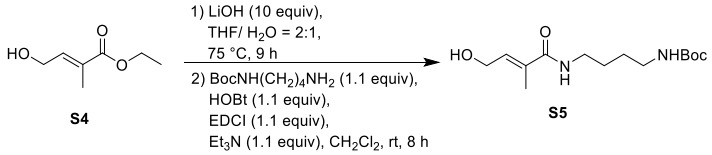
***Exo-10S*-TMS-aglain aldehyde 19:** A flame dried test tube was charged with **18** (150 mg, 0.25 mmol, 1 equiv), *N*-methylmorpholine-*N*-oxide (86.6 mg, 0.74 mmol, 3 equiv) and mixture of THF/*t*-BuOH (1:1) (6.4 mL, 0.04 M). After formation of a homogeneous solution, 0.64 mL OsO_4 (10 wt.% aq., 6.4 mg, 0.025 mmol, 0.1 equiv) aqueous solution was added. The solution immediately turned brown and was stirred for 12 h before 5 mL of saturated sodium chloride was

added to quench the reaction. The reaction mixture was extracted with Et_2O (5 mL × 3), the combined organic layer was washed with 10 mL of saturated sodium chloride, and dried over sodium sulfate. The filtrate was concentrated *in vacuo*. The crude diol product was used in the next step without further purification. Subsequently, the crude diol product was dissolved in 5 mL of CH_2Cl_2. $Pb(OAc)_4$ (164 mg, 0.37 mmol, 1.5 equiv) was added. The resulting mixture was stirred for 0.5 h before 5 mL of saturated $Na_2S_2O_3$ was added to quench the reaction. The combined organic layer from extraction with CH_2Cl_2 (3 mL × 3) was washed with 10 mL of saturated sodium chloride and dried over sodium sulfate. The filtrate was concentrated *in vacuo* and purified by column chromatography using a gradient of hexanes/CH_2Cl_2/EtOAc (20:1:1 to 15:1:1) to afford the *exo-10S*-TMS-aglain aldehyde **19** (95.4 mg, 0.18 mmol, 73% yield) as a colorless oil.



19

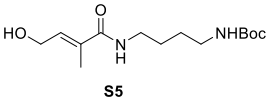
19: R_f: 0.19 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (d, J = 0.8 Hz, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.14 (d, J = 2.3 Hz, 1H), 6.13 (d, J = 2.3 Hz, 1H), 5.04 (s, 1H, OH), 4.34 (d, J = 6.2, 1H), 4.24 (dd, J_1 = 6.2 Hz, J_2 = 0.8 Hz, 1H), 4.19 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.77 (s, 3H), -0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.1, 160.4, 159.6, 156.4, 153.1, 140.9, 130.6, 129.6, 128.7, 127.8, 126.5, 113.5, 113.2, 93.8, 93.0, 88.7, 82.99, 92.96, 80.5, 66.2, 56.1, 55.5, 55.3, -0.26; IR υmax (film): 3502, 2927, 2856, 1728, 1617, 1515, 1459, 1253, 1152, 1089, 840 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{30}H_{35}O_7Si$, 535.2152, found 535.2144.



S4 **S5**

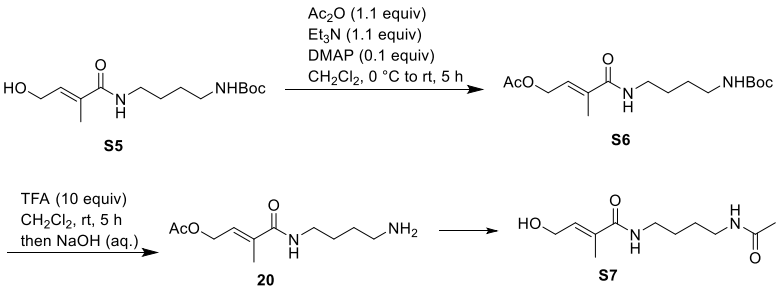
Boc-protected hydroxytiglic amide S5: Compound **S4** was prepared using the reported procedure.[S3] Subsequently, a 100 mL round bottom flask was charged with compound **S4** (2.0 g, 13.9 mmol, 1 equiv), LiOH (3.32g, 139 mmol, 10 equiv), and 50 mL of THF/H_2O (2:1) as solvent. The mixture was stirred for 9 h at 75 °C. After the reaction was cooled to room temperature, 1M HCl (aq.) was added to acidify the pH of the solution to 4. The mixture was then extracted with EtOAc (20 mL × 3). The combined organic layers were washed with saturated sodium chloride and dried over sodium sulfate. After concentration *in vacuo*, the crude material was purified by column chromatography using a gradient of hexanes/EtOAc (1:1 to 1:4). The hydroxytiglic acid (1.6 g, quantitative) was obtained as a white solid. Next, a 50 mL flame-dried flask was charged with hydroxytiglic acid (1.6, 8.5 mmol, 1 equiv), HOBt (1.26 g, 9.35 mmol, 1.1 equiv),

EDCI (1.79 g, 9.35 mmol, 1.1 equiv), *mono*-Boc-protected diaminobutane (1.09 g, 9.35 mmol, 1.1 equiv), Et_3N (1.3 mL, 9.35 mmol, 1.1 equiv), and CH_2Cl_2 (57 mL, 0.15 M). The resulting mixture was stirred at room temperature for 8 h. Then, 50 mL of saturated ammonium chloride was added to quench the reaction. The reaction mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was washed with saturated sodium chloride and dried over sodium sulfate. After concentration *in vacuo*, purification by column chromatography using a gradient of hexanes/EtOAc (1:2 to 1:5) afforded compound **S5** (2.25 g, 7.86 mmol) in 92% yield as a white solid.



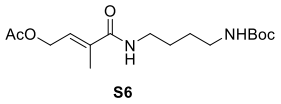
S5

S5: R_f: 0.19 (EtOAc). m.p. = 80 °C (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (td, J_1 = 6.1 Hz, J_2 = 1.1 Hz, 1H), 6.22 (brs, 1H, NH), 4.73 (brs, 1H, NH), 4.29 (d, J = 6.1 Hz, 2H), 3.31 (m, 2H), 3.11 (m, 2H), 1.84 (d, J = 1.1 Hz, 3H), 1.53 (m, 4H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 156.2, 133.9, 132.4, 79.3, 59.3, 40.1, 39.4, 28.4, 27.6, 26.6, 13.0; IR υ_{max} (film): 3338, 2934, 1690, 1621, 1533, 1366, 1281, 1169, 1017 cm^{-1}. HRMS-ESI (m/z) calculated $[M+Na]^+$ $C_{14}H_{26}O_4N_2Na$, 309.1790, found 309.1799.



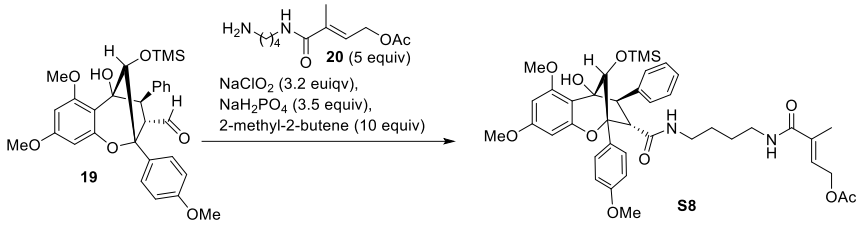
Tiglic amide acetate 20: A 50 mL flame-dried round bottom flask was charged with compound **S5** (2.0 g, 7.0 mmol, 1 equiv), Et_3N (1.1 mL, 7.7 mmol, 1.1 equiv), DMAP (85 mg, 0.7 mmol, 0.1 equiv), and CH_2Cl_2 (47 mL, 0.15 M). After the mixture was cooled to 0 °C by ice bath, Ac_2O (0.75 mL, 7.7 mmol, 1.1 equiv) was added dropwise. The reaction was warmed to rt and stirred for 5 h before 20 mL of saturated sodium bicarbonate was added. The mixture was extracted with CH_2Cl_2 (50 mL × 3), washed with saturated sodium chloride (50 mL), and dried over anhydrous sodium sulfate. Purification by column chromatography using a gradient of hexanes/EtOAc (1:1 to 1:3) afforded compound **S6** (2.1 g, 6.4 mmol) as a white solid (92% yield). Subsequently, compound **S6** (2.1 g, 6.4 mmol, 1 equiv) was redissolved by CH_2Cl_2 (43 mL, 0.15 M) in a 25 mL flame-dried round bottom flask. Trifluoroacetic acid (4.9 mL, 64 mmol, 10 equiv) was then added dropwise to the solution and the reaction was stirred for 5 h. The reaction

mixture was concentrated *in vacuo*. The remaining TFA was removed by azeotrope with benzene (15 mL × 3). The material was reconstituted with 50 mL of EtOAc and washed with sat. sodium chloride and aqueous 1M NaOH . After the aqueous layer was discarded, the organic layer was washed with saturated sodium chloride (50 mL) and dried over sodium sulfate to afford tiglic amide acetate **20** (1.05 g, 4.6 mmol, 72% yield) as a colorless oil. Compound **20** was found to undergo acyl transfer to afford amide **S7**. Accordingly, compound **20** was used in the next step without further purification.

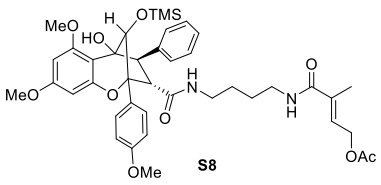


S6

S6: R_f: 0.19 (EtOAc/hexanes = 1:1). m.p. = 64 °C (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.30 (brs, 1H, NH), 6.23 (td, J_1 = 6.3 Hz, J_2 = 1.3 Hz, 1H), 4.80 (brs, 1H, NH), 4.63 (d, J = 6.3 Hz, 2H), 3.26 (m, 2H), 3.05 (m, 2H), 1.99 (s, 3H), 1.83 (d, J = 1.3 Hz, 3H), 1.47 (m, 4H), 1.35 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 156.2, 133.9, 132.4, 79.3, 59.3, 40.1, 39.4, 28.4, 27.6, 26.6, 13.0; IR υ_{max} (film): 3338, 2933, 1694, 1627, 1529, 1365, 1228, 1168, 1028 cm^{-1}. HRMS-ESI (m/z) calculated $[M+Na]^+$ $C_{16}H_{28}O_5N_2Na$, 351.1896, found 351.1901.

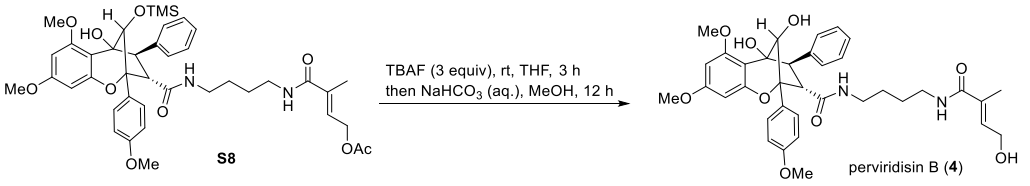


Silyl-protected perviridisin B S8: A flame-dried test tube was charged with aldehyde **19** (95.4 mg, 0.18 mmol, 1 equiv) and amine **20** (259 mg, 0.9 mmol, 5 equiv), and 2 mL of dry toluene (0.09 M). After stirring for 5 min, $NaClO_2$ (52 mg, 0.57 mmol, 3.2 equiv), NaH_2PO_4 (75 mg, 0.62 mmol, 3.5 equiv) and 2-methyl-2-butene (0.19 mL, 1.78 mmol, 10 equiv) were added. The resulting mixture was stirred for 48 h at room temperature before filtration to remove solids. The filtrate was concentrated *in vacuo* and purified by column chromatography using a gradient of hexanes/EtOAc (2:1 to 1:2) to afford silyl-protected perviridisin B **S8** (111 mg, 0.15 mmol, 82%) as a colorless oil.

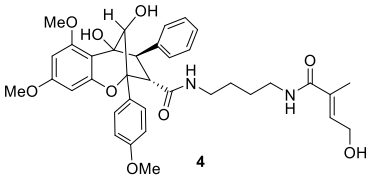


S8: R_f: 0.2 (EtOAc/hexanes = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.31 (m, 2H), 7.22 (m, 1H), 6.98 (d, J = 8.7 Hz, 2H), 6.28 (td, J_1 = 6.5 Hz, J_2 = 1.3 Hz, 1H), 6.15 (d, J = 2.6 Hz, 1H), 6.12 (d, J = 2.6 Hz, 1H), 5.94 (brs, 1H, NH), 5.22 (brt, J = 5.8 Hz, 1H, NH), 4.99 (s, 1H, OH), 4.70 (d, J = 6.5 Hz, 2H), 4.34 (d, J

= 6.8 Hz, 1H), 4.14 (s, 1H), 4.12 (d, J = 6.8 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.19 (m, 3H), 2.87 (m, 1H), 2.08 (s, 3H), 1.86 (d, J = 1.3 Hz, 3H), -0.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 169.8, 168.4, 160.2, 159.5, 156.4, 153.1, 141.5, 134.9, 130.6, 130.2, 128.6, 128.2, 128.1, 127.7, 126.4, 113.6, 113.5, 93.9, 92.7, 88.0, 83.3, 80.1, 60.8, 60.7, 58.5, 56.1, 55.4, 39.4, 38.5, 27.2, 25.9, 20.8, 13.1, -0.2; IR υ_{max} (film): 3506, 3416, 3346, 2957, 1742, 1619, 1516, 1458, 1253, 1152, 1091, 839 cm^{-1}. HRMS-ESI (m/z) calculated $[M+Na]^+$ $C_{41}H_{52}O_{10}N_2SiNa$, 783.3289, found 783.3279.

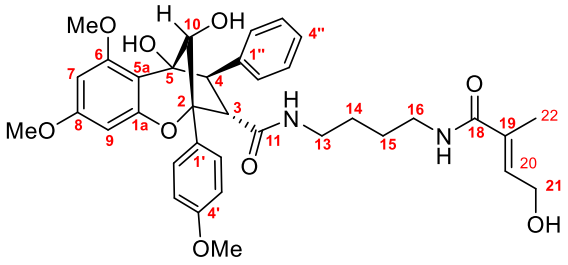


Perviridisin B 4: A flame dried test tube was charged with compound **S8** (111 mg, 0.15 mmol, 1 equiv), 1 mL THF and tetra-*n*-butylammonium fluoride (1M solution in THF, 0.44 mL, 0.44 mmol, 3 equiv). The resulting solution was stirred for 3 h. 3 mL of saturated sodium chloride and 10 mL EtOAc then was added to form a bilayer mixture and the aqueous layer was discarded. The organic layer was washed with 5 mL saturated sodium chloride and dried over sodium sulfate. The filtrate was concentrated *in vacuo* and was redissolved in 2 mL of MeOH which was followed by addition of 0.2 mL of saturated sodium bicarbonate. The mixture was stirred for 12 h and concentrated *in vacuo*. Purification by preparative TLC using EtOAc as solvent afforded perviridisin B **4** (86 mg, 0.12 mmol, 82% yield) as a white solid.



4: R_f: 0.11 (EtOAc). m.p. = 269 - 271 °C (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.28 (m, 1H), 7.04 (d, J = 8.5 Hz, 2H), 6.26 (td, J_1 = 6.5 Hz, J_2 = 1.5 Hz, 1H), 6.16 (d, J = 2.5 Hz, 1H), 6.14 (d, J = 2.5 Hz, 1H), 6.09 (brs, 1H), 5.22 (s, 1H, OH), 5.22 (brt, d = 6.4 Hz, 1H, NH), 4.39 (d, J = 6.5 Hz, 1H), 4.28 (d, J = 6.5 Hz, 1H), 4.26 (d, J = 5.1 Hz, 2H), 4.19 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.77 (s, 3H), 3.26 (m, 2H), 3.16 (m, 1H), 2.85 (m, 1H), 2.61 (s, 1H, OH), 1.81 (d, J = 1.5 Hz, 3H), 1.64 (m, 2H), 1.31 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 169.1, 160.4, 150.6, 156.1, 153.0, 140.6, 133.1, 132.9, 129.9, 129.6, 128.2, 126.8, 114.0, 112.1, 94.0, 92.6, 87.1, 82.4, 79.8, 60.3, 59.4, 58.1, 55.4, 39.3, 38.6, 27.3, 25.7, 13.0; IR υ_{max} (film): 3408, 2937, 1669, 1619,

1591, 1516, 1459, 1440, 1255, 1252, 1201, 1152, 1098, 1034, 834, 755 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{36}H_{43}O_9N_2$, 647.2969, found 647.2970.



(±)-perviridisin B (4)

^{1}H NMR

Positions	natural (+)-**4** δ lit[S4] ($CDCl_3$) (J_{H-H} in Hz)	synthetic (±)-**4** (this work) δ (500 MHz, $CDCl_3$) (J_{H-H} in Hz)
2		
3	4.28, d (6.7)	4.28, d (6.5)
4	4.40, d (6.5)	4.39, d (6.5)
5		
5-OH	5.23, s	5.22, s
5a		
6		
7	6.14, d (2.1)	6.14, d (2.5)
8		
9	6.16, d (2.2)	6.16, d (2.5)
9a		
10	4.20, s	4.19, s
10-OH	2.97, brs	2.98, brs
11		
NH-12	5.21, brt (6.4)	5.22, brt (6.4)
13	2.86, m 3.17, m	2.85, m 3.16, m
14	1.33, m	1.31, m
15	1.60, m	1.64, m
16	3.26, m	3.26, m
NH-17	6.10, brt (5.2)	6.09, brs
18		
19		
20	6.27, brt (6.0)	6.26, td (6.5, 1.5
21	4.27	4.26
22	1.82, s	1.81, d (1.5)

1′		
2′, 6′	7.84, d (8.9)	7.84, d (8.5)
3′, 5′	7.05, d (8.9)	7.04, d (8.5)
4′		
1′′		
2′′, 6′′	7.52, d (7.3)	7.52 d (7.5)
3′′, 5′′	7.36, t (7.4)	7.35, t (7.5)
4′′	7.29 (overlapped)	7.28 (overlapped)
OCH_3-6	3.89, s	3.89, s
OCH_3-8	3.77, s	3.77, s
OCH_3-4′	3.87, s	3.87, s

^{13}C NMR

	natural (+)-**4**	synthetic (±)-**4** (this work)
Positions	δ lit.[S4] ($CDCl_3$)	δ (125 MHz, $CDCl_3$)
2	87.1	87.1
3	60.3	60.3
4	58.1	58.1
5	79.9	79.8
5-OH		
5a	112.0	112.1
6	156.2	156.1
7	92.6	92.6
8	160.4	160.4
9	94.0	94.0
9a	153.0	153.0
10	82.4	82.4
10-OH		
11	169.5	169.5
NH-12		
13	38.5	38.6
14	27.3	27.3
15	25.6	25.7
16	39.4	39.3
NH-17		
18	169.1	169.1
19	133.0	133.0
20	133.1	133.1
21	59.4	59.4
22	13.0	13.0
1′	129.6	129.6

2’, 6’	128.3	128.2
3’, 5’	114.0	114.0
4’	159.6	159.6
1’’	140.7	140.7
2’’, 6’’	129.9	129.9
3’’, 5’’	128.3	128.3
4’’	126.8	126.8
OCH_3-6	56.2	56.2
OCH_3-8	55.4	55.4
OCH_3-4’	55.5	55.5

IV. Asymmetric ESIPT Photocycloaddition

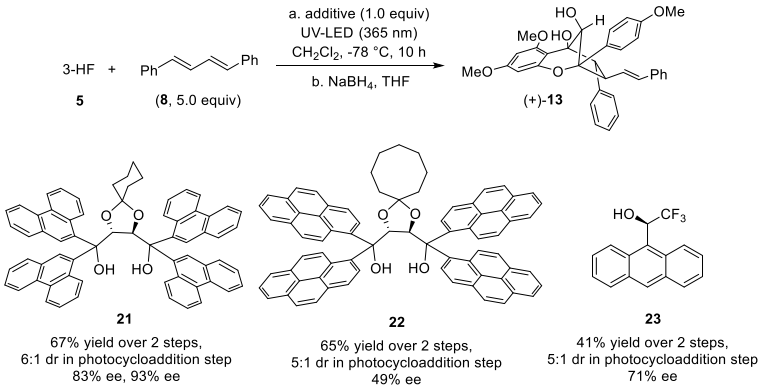


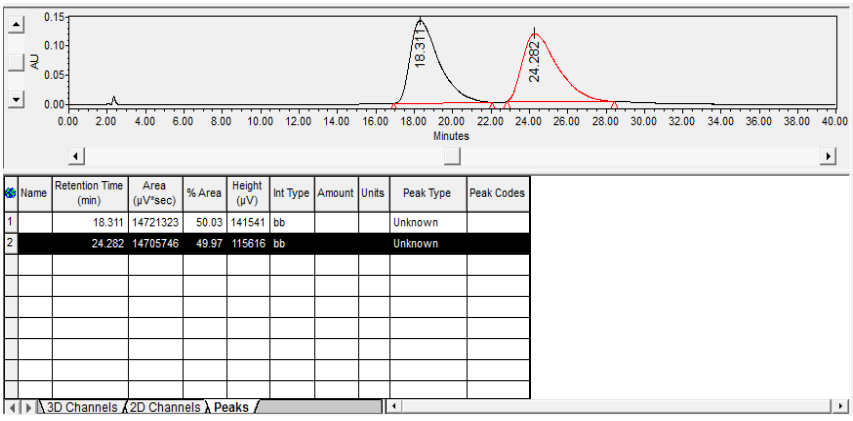
Table S1. Select Conditions for Optimization of the Asymmetric Photocycloaddition

entry	time, temperature	light source	solvent	chiral additive	yield, enantiomeric excess
1	12 h, -70 °C	Rayonet	PhMe/CH_2Cl_2 (1:2)	**21**	49% yield, 52% ee
2	12 h, -70 °C	Rayonet	PhMe/CH_2Cl_2 (1:2)	**22**	51% yield, 45% ee
3	12 h, -70 °C	Rayonet	CH_2Cl_2	**21**	56% yield, 69% ee
4	12 h, -70 °C	Rayonet	CH_2Cl_2	**23**	30% yield, 49% ee
5	2 h, -30 °C	Rayonet Photoflow	CH_2Cl_2	**21**	67% yield, 31% ee
6	10 h, -78 °C	UV-LED	CH_2Cl_2	**22**	65% yield, 49% ee
7	10 h, -78 °C	UV-LED	PhMe/CH_2Cl_2 (1:2)	**21**	31% yield, 71% ee
8	10 h, -78 °C	UV-LED	CH_2Cl_2	**21**	67% yield, 83% ee
9	10 h, -78 °C	UV-LED	CH_2Cl_2	**23**	41% yield, 71% ee

General procedure for asymmetric ESIPT photocycloaddition of 3-HF 5 with DPBD 8:

A flame-dried 100 mL photoreaction tube was charged with 3-hydroxyflavone **5** (50 mg, 0.15 mmol, 1 equiv), DPBD **8** (1.57 g, 7.61 mmol, 5 equiv) and 1.0 equivalent of hydrogen-bonding additive in 30 mL of dry CH_2Cl_2 (0.005 M for 3-HF **5**). Subsequently, the reaction mixture was degassed by argon gas bubbling combined with sonication for 10 min. During degassing, the reaction mixture was placed in an ice bath to prevent solvent evaporation. In order to conduct low temperature photochemistry experiments, a UV-LED (λ_{max} = 365 nm) was used as light source and a special dewar flask with a transparent window was used as temperature control.[S5] The dewar was filled with dry ice and isopropanol to cool the reaction to -78 °C and then the reaction tube was inserted into the dry ice bath. Due to the low solubility of DPBD **8** at -78 °C, the reaction mixture was diluted to 0.005 M instead of the previously described 0.03 M concentration. The reaction was then irradiated for 10 h. The solvent was concentrated *in vacuo* and redissolved in 10 mL of dry THF. Subsequently, $NaBH_4$ (29 mg, 0.76 mmol, 5 equiv) was then added to directly reduce the mixture. After 5 h, saturated NH_4Cl (aq.) was added to the reaction mixture to quench the reaction. The reaction was extracted with EtOAc (30 mL × 3), washed with saturated NaCl (aq.) and dried with anhydrous Na_2SO_4. The filtrate was then concentrated *in vacuo* and was finally purified by column chromatography using a gradient of hexanes/EtOAc (20:1 to 10:1 to remove DPBD and hydrogen-bonding additive, then 8:1 to 3:1). Aglain derivative (+)-**13** was obtained as a white solid. The enantioselectivity was determine using analytical chiral HPLC. $[\alpha]_D^{23}$= + 71.4° (*c* = 1.0, $CHCl_3$). (+)-**13** was further converted to (+)-**14** using the previously described method (*cf.* page S7). $[\alpha]_D^{23}$= + 92.3° (*c* = 1.0, $CHCl_3$)

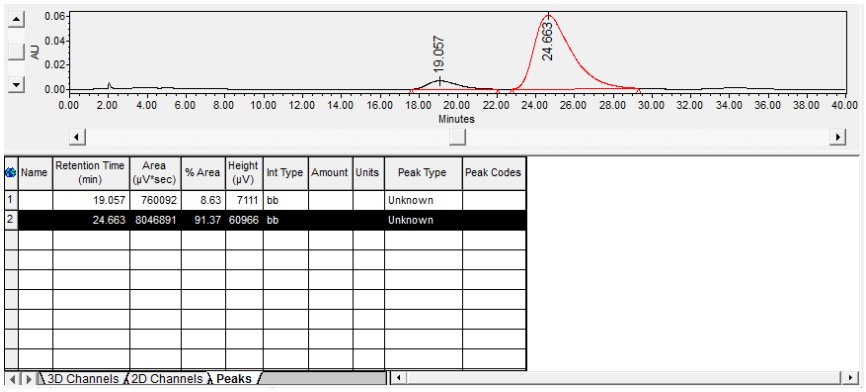
Chiral HPLC Analysis of aglain (±)-**13**: *Chiralcel OD* column with an isocratic mobile phase of isopropanol/hexanes (10:90), with a flow rate of 1.0 mL/min for 40 min.



	Name	Retention Time (min)	Area (µV*sec)	% Area	Height (µV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.311	14721323	50.03	141541	bb			Unknown	
2		24.282	14705746	49.97	115616	bb			Unknown	

3D Channels | 2D Channels | Peaks

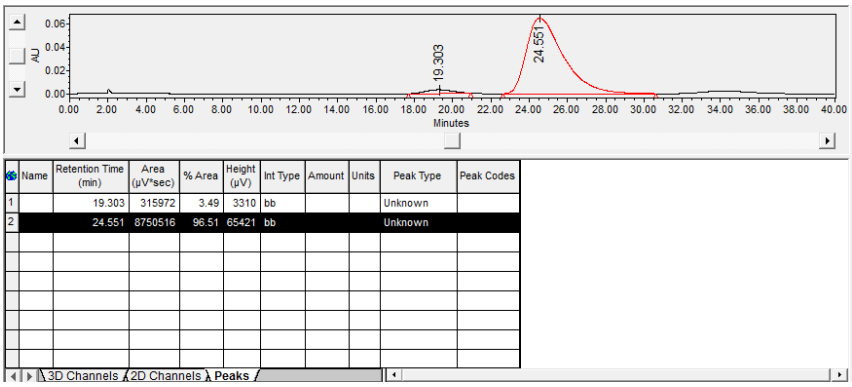
Chiral HPLC analysis of **13** obtained using TADDOL **21**:



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		19.057	760092	8.63	7111	bb			Unknown	
2		24.663	8046891	91.37	60966	bb			Unknown	

3D Channels | 2D Channels | Peaks

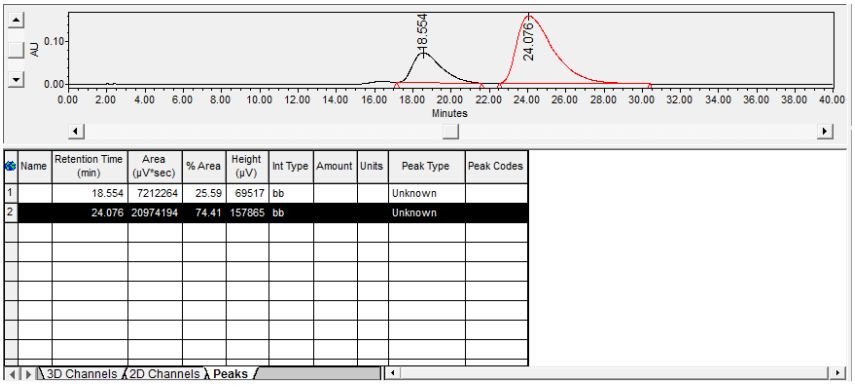
Enantiomeric excess after recrystallization of aglain (+)-**13** obtained from photoreaction with TADDOL **21**:



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		19.303	315972	3.49	3310	bb			Unknown	
2		24.551	8750516	96.51	65421	bb			Unknown	

3D Channels | 2D Channels | Peaks

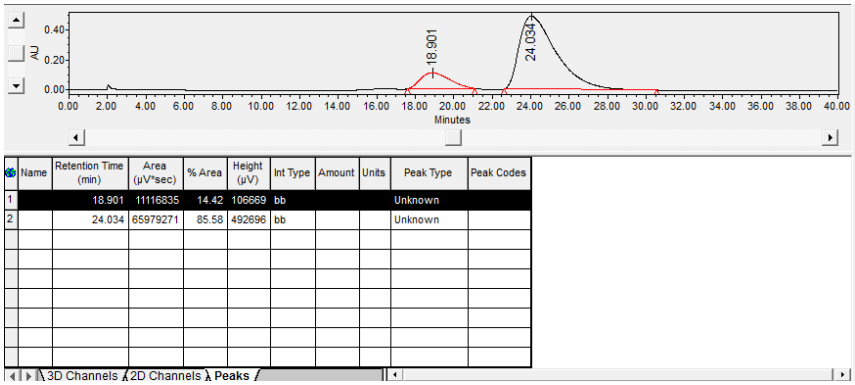
Chiral HPLC analysis of **13** obtained using TADDOL **22**:



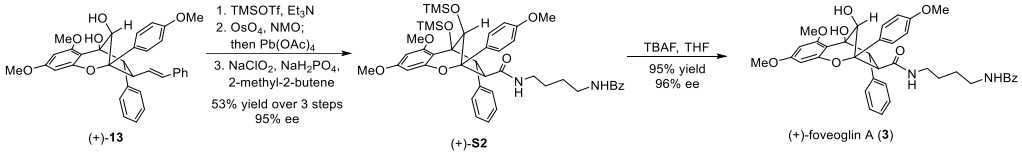
	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.554	7212264	25.59	69517	bb			Unknown	
2		24.076	20974194	74.41	157865	bb			Unknown	

3D Channels | 2D Channels | Peaks

Chiral HPLC analysis of **13** obtained using Pirkle's alcohol **23**:

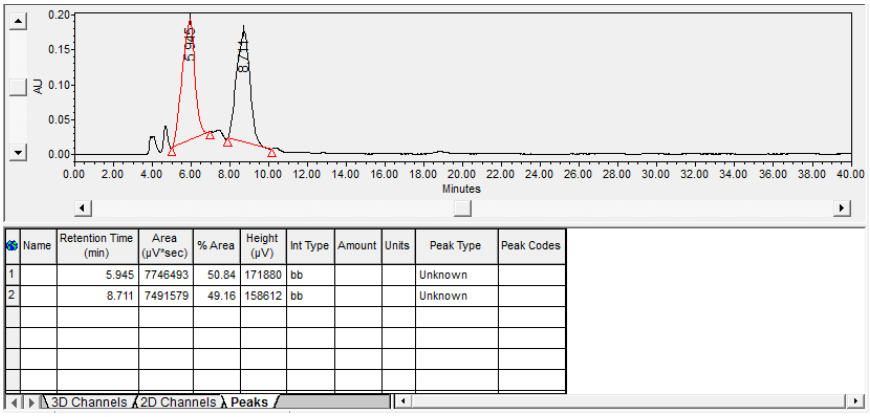


	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		18.901	11116835	14.42	106669	bb			Unknown	
2		24.034	65979271	85.58	492696	bb			Unknown	



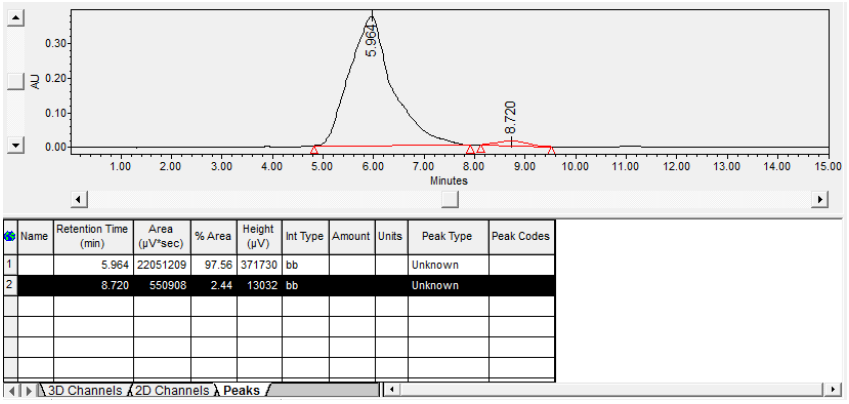
With (+)-**13** in hand, silylation, oxidative cleavage of the double bond, and oxidative amidation was performed using the previously described procedure (*cf.* page S9-S10) to furnish the core of foveoglin A in 53% yield and 95% ee, $[\alpha]_D^{20}$ +43.1 (c 0.1, $CHCl_3$). Silyl group deprotection by TBAF provided us (+)-foveoglin A **3** in 95% yield and 96% ee, $[\alpha]_D^{23}$ +25.3 (c 0.16, $CHCl_3$).

Chiral HPLC Analysis of aglain **S2**: *Chiralpak AD* column with an isocratic mobile phase of isopropanol/hexanes (5:95), with a flow rate of 1.0 mL/min for 40 min.



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.945	7746493	50.84	171880	bb			Unknown	
2		8.711	7491579	49.16	158612	bb			Unknown	

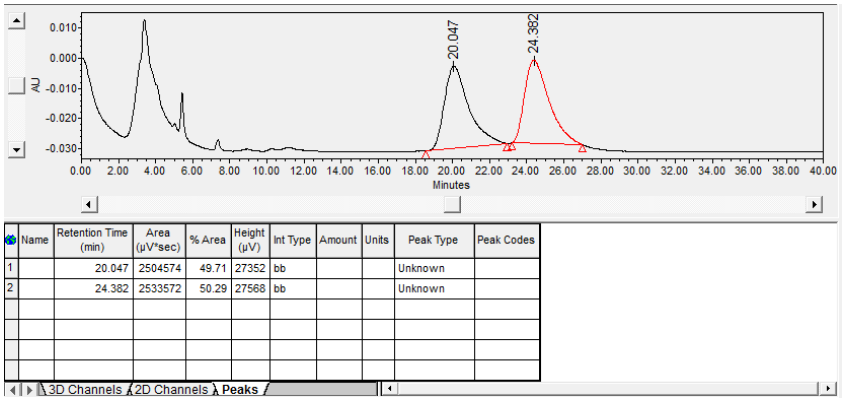
Enantiomeric excess of (+)-**S2**:



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		5.964	22051209	97.56	371730	bb			Unknown	
2		8.720	550908	2.44	13032	bb			Unknown	

3D Channels | 2D Channels | Peaks

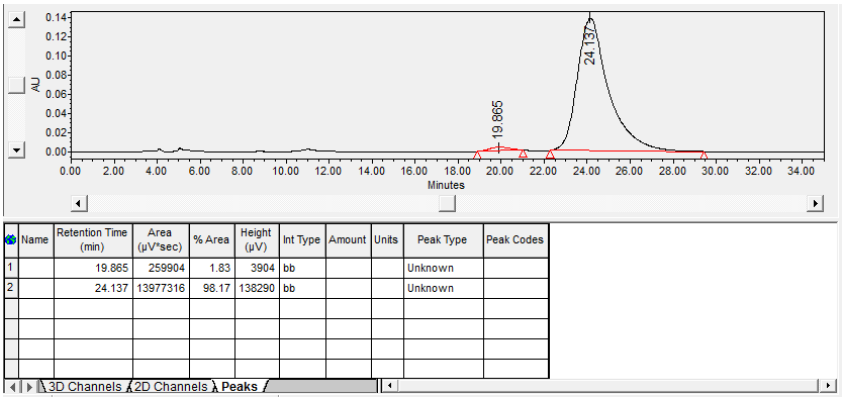
Chiral HPLC Analysis of (±)-foveoglin A **3**: *Chiralpak AD* column with an isocratic mobile phase of isopropanol/hexanes (20:80), with a flow rate of 1.0 mL/min for 40 min.



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		20.047	2504574	49.71	27352	bb			Unknown	
2		24.382	2533572	50.29	27568	bb			Unknown	

3D Channels | 2D Channels | Peaks

Enantiomeric excess of (+)-foveoglin A **3**:



	Name	Retention Time (min)	Area (μV*sec)	% Area	Height (μV)	Int Type	Amount	Units	Peak Type	Peak Codes
1		19.865	259904	1.83	3904	bb			Unknown	
2		24.137	13977316	98.17	138290	bb			Unknown	

3D Channels | 2D Channels | Peaks

As phenanthrenyl or pyrenyl groups are incorporated in TADDOL additives **21** and **22**, UV-Vis absorption spectra were recorded.

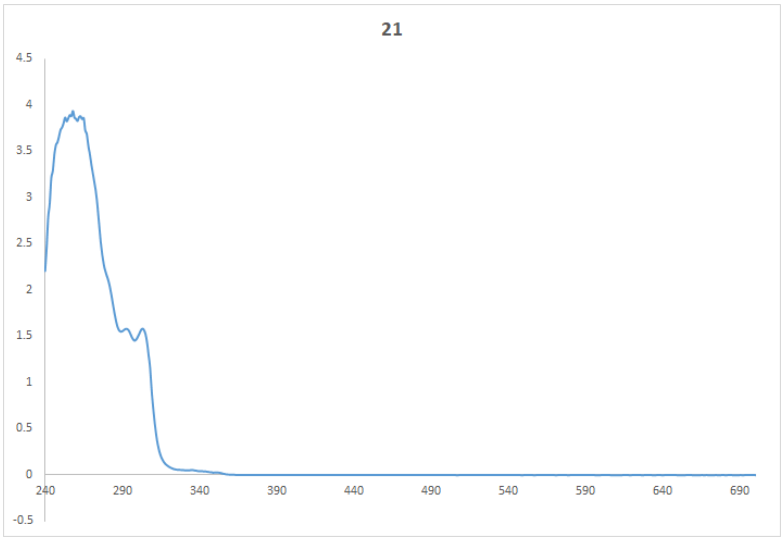


Figure S1. Absorption Spectrum of TADDOL **21**

(Concentration: 1.08 mM in $CHCl_3$)

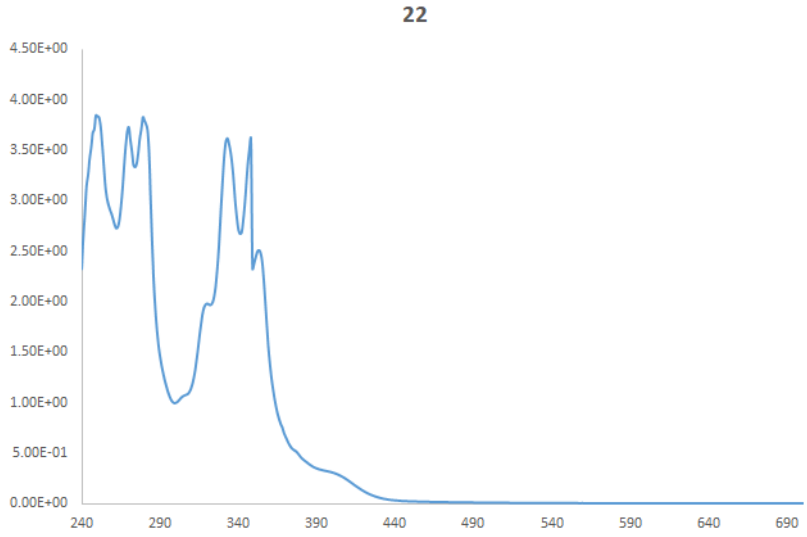


Figure S2. Absorption Spectrum of TADDOL **22**

(Concentration: 1.16 mM in $CHCl_3$)

From the absorption spectra, we can see that TADDOL **21** would not be photoexcited by 365 nm light; in comparison, TADDOL **22** could be photo excited by 365 nm light.

Determination of absolute configuration of *para*-bromo benzoate (+)-14 by VCD (vibrational circular dichroism):

Experimental VCD:

VCD and IR spectra for (+)-**14** were recorded using a KBr pellet on a Bruker FT-IR TENSOR II spectrometer with 8 cm^{-1} spectral resolution, polarization modulation efficiency set to 1300 cm^{-1}, and a 1900 cm^{-1} optical filter used to improve the signal-to-noise ratio. The VCD spectrum was collected from 1950 to 800 cm^{-1} at six different orientations of the tablet in the holder, with a 20 minutes acquisition time for each orientation. An averaged spectrum was calculated for the six orientations.

Predicted VCD:

Theoretical VCD calculations were performed using the "VCD Workflow" in Schrodinger, Inc.'s Maestro software.[S 6] Conformers were generated *via* a Macromodel conformational search (force field: OPLS 2005, mixed torsional/low-mode sampling, 5 kcal/mol MM energy window) followed by quantum mechanical screening for conformer retention (0.5 Angstrom deviation, 5.0 kcal/mol QM energy window), followed by DFT geometry optimizations (B3LYP/LACVP**) and VCD/IR spectrum predictions on the retained conformers. DFT calculations were performed in the absence of solvent. From the VCD Workflow module, seven conformers were obtained with final gas phase energies within 2.7 kcal/mol of the lowest energy conformer. The conformers and their gas phase energies are depicted in **Figure S3**. Due to the highly rigid fused bicyclic structure of **14**, the differences in conformers mainly arose from bond rotations at the aryl methoxy groups and the styrenyl substituent. The VCD workflow was also repeated on the enantiomer of **14**, with seven similar enantiomeric conformers also obtained (*not shown*). Single-point energy calculations with vibrational frequencies and VCD prediction were then performed on the enantiomeric sets of seven conformers querying alternative functional and basis set combinations. It was determined that B3PW91/TZV** gave the best agreement with the experimental IR/VCD spectra with respect to signal location and intensities.

VCD Analysis:

Following the DFT calculations, average computed VCD and IR spectra for the seven output conformers (B3PW91/TZV*) were generated using Boltzmann weighting based on calculated gas phase energies, with a Lortentzian line shape

at 8 cm^{-1} resolution.[7] For the purpose of visual comparison, the experimental IR and VCD intensities have been scaled by 1,000-fold and 10,000-fold, respectively, and the predicted IR and VCD frequencies have been offset by -20.0 cm^{-1}, based on a direct comparison of the predicted and experimental IRs (**Figure S2A/B**).[S8] A qualitative assessment of the measured vs. predicted VCD spectra for **14** (**Figure S2C/D**) and **ent-14** (**Figure S2E/F**) strongly supports the assignment of absolute stereochemistry for **14**.

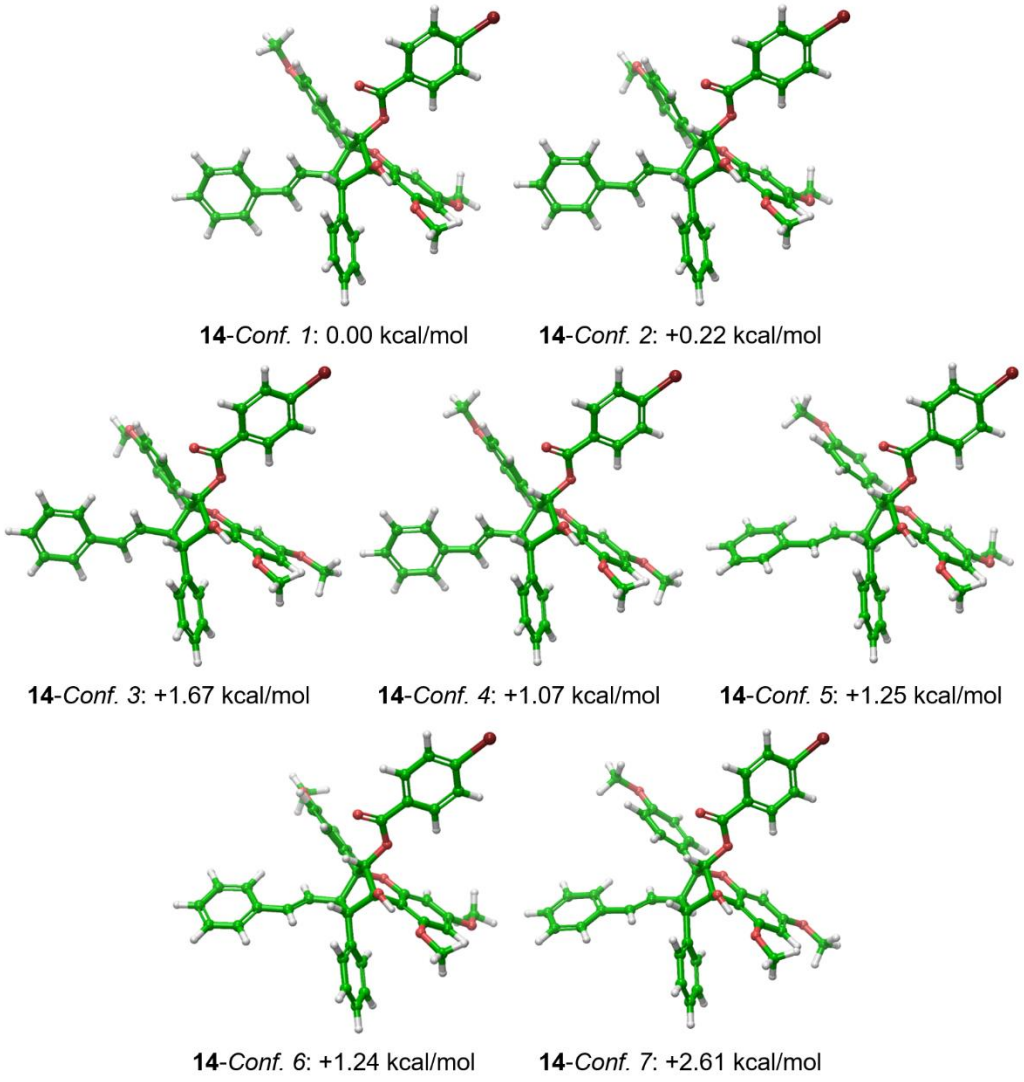


Figure S3. Seven conformers and relative gas phase energies (B3PW91/TZV**) obtained for compound **14** using Schrodinger's Jaguar VCD workflow.

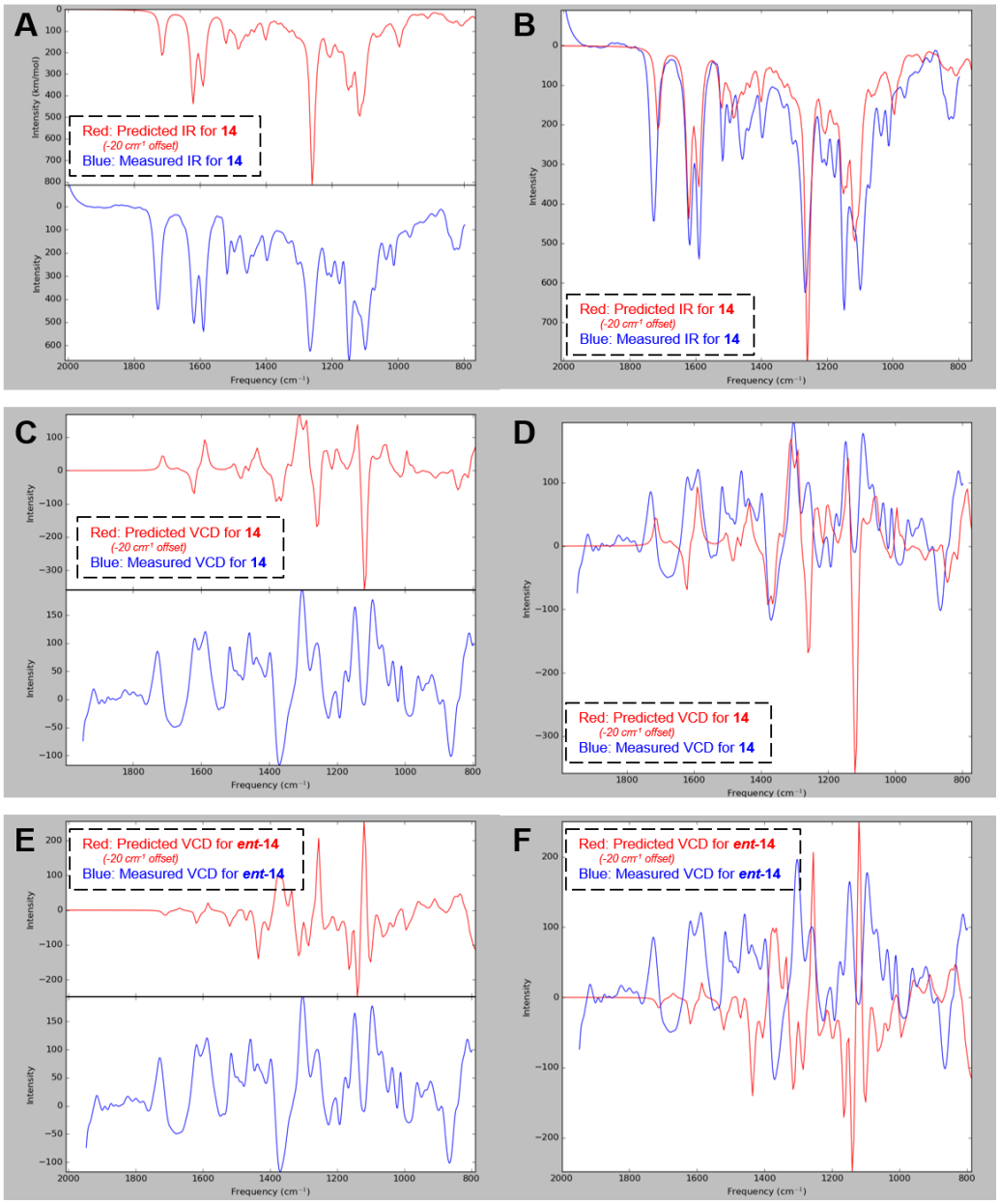


Figure S4. Predicted (red) and measured (blue) IR and VCD spectra comparisons for **14** and ***ent*-14**. All predicted spectra are offset by 20 cm^{-1} based on the IR comparisons. **A**) IR comparisons, stacked; **B**) IR comparisons, overlaid; **C**) VCD comparisons for **14**, stacked; **D**) VCD comparisons for **14**, overlaid; **E**) VCD comparisons for ***ent*-14**, stacked; **F**) VCD comparisons for ***ent*-14**, overlaid.

V. Mechanistic Studies

(1) Photophysical Measurements:

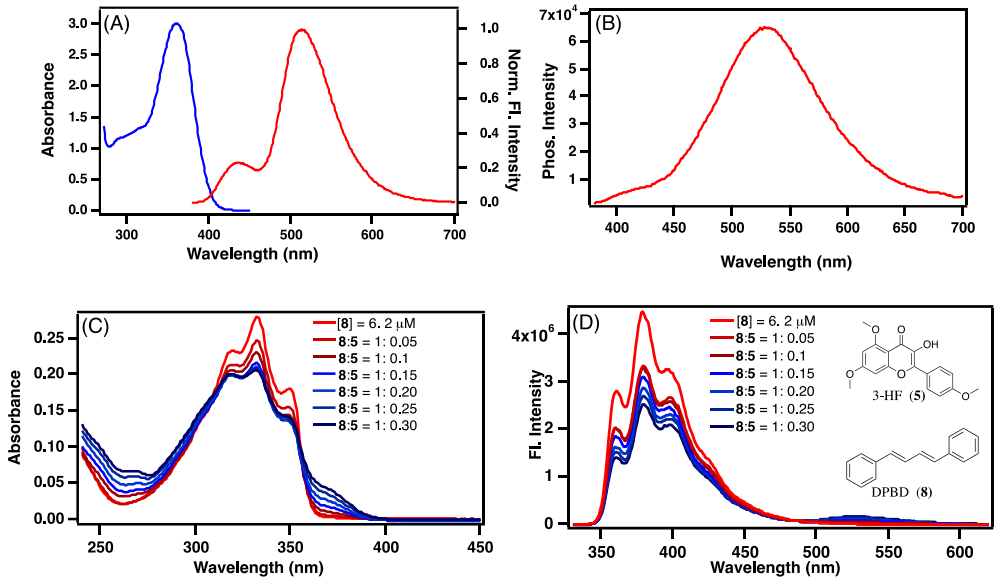


Figure S5. Photophysical Studies to Probe Excited State Reactivity of 3-Hydroxyflavone **5**. **A**) Absorbance (*blue*) of **5** in 2,2,2-trifluoroethanol (TFE) [**5**] =2.35 μM. Fluorescence (*red*) of **5** in TFE with λ_{exc}=360 nm. **B**) Phosphorescence of **5** recorded in TFE glass, λ_{exc}=360 nm. **C**) Absorbance of **8** (6.2 M) with addition of **5** at various equivalents (0 to 1.9 μM) recorded in a mixture of $CHCl_3$:EtOH (7:3) **D**) Fluorescence of **8** with addition of **5** at various equivalents (0 to 1.9 M) recorded in a mixture of $CHCl_3$:EtOH (7:3); λ_{exc}=320 nm; λ_{emiss}=330-620 nm.

Literature supports the ESIPT process for 3-hydroxyflavones. In polar protic solvents (*e.g.* trifluoroethanol), dual fluorescence emission (fluorescence of the normal state N centered at 439 nm and tautomer state T centered at 527 nm) was observed for **5** at both room temperature and 77 K (**Figure S5 A**). The phosphorescence spectrum of **5** recorded in TFE glass (**Figure S5 B**) shows a λ_{max} for phosphorescence emission (528 nm) indicating a triplet energy (E_T) of 54.2 kcal/mol. Based on the fact that the singlet energy of DPBD ($\lambda_{absorption}$ < 370 nm, E_S > 77 kcal/mol)[S9] is higher than the singlet energy of 3-HF **5** ($\lambda_{emission}$ > 390 nm, E_S < 73 kcal/mol), transfer of the singlet energy of 3-HF **5** to the ground state of DPBD **8** is forbidden.

Based on a literature report,[S10] the triplet energy of DPBD is 42 kcal/mol, which indicate that the possibility of a triplet energy transfer mechanism cannot be ruled out when taking into consideration that the triplet energy of 3-HF **5** is 55 kcal/mol based on the λ_{max} = 520 nm observed in the phosphorescence

spectrum of **5**. As the singlet state of normal and tautomeric forms of **5** are close (based on the fluorescence spectra; **Figure S5-A**), we expect their corresponding triplet states to be close to each other. Hence for calculating the feasibility of photo-induced transfer using Rhem-Wellller equation[S11] from the triplet excited state (*cf.* **Section (3)**; **Page S38**), we will employed the observed phosphorescence (**Figure S5-B**) to calculate the triplet energy.

Based on the computed free energy from Rehm-Weller equation[S11] for **5** and **8** and the absorptivity of the reactants under the concentrations employed for photoreactions, deciphering the nature of the excited reactant initiating the (3+2) photocycloaddition became vital. To address this point, Absorption and emission studies were performed with **5** and **8** at varying concentrations (**Figure S5 C-D**). Examination of **Figure S5 C** shows that the structured absorption of **8** centered at 332 nm undergoes a hypochromic shift upon addition of **5** indicating that there is likely a distortion of diene geometry in the presence of **5**. Similarly, the fluorescence intensity of **8** centered at 379 nm was lowered upon addition of **5**. This is likely due to the reduction in the absorptivity (hypochromic effect) of **8** by addition of **5**. Additionally, rise of an emission band centered at 530 nm was observed which matched the emission of the phototautomer of **5** (*cf.* **Figure S5 A**). These observations indicated that upon excitation of the reaction mixture at 320 nm, both the diene **8** and the 3-hydroxyflavone **5** are excited.

We subsequently attempted to record the transient absorption of 3-hydroxyflavone **5** both in the presence and absence of various dipolarophiles. Chou, Itoh, and others have suggested that the transient absorption of the parent 3-hydroxyflavone is complicated by overlapping absorptions from both the singlet and triplet excited states of the normal and the photo-tautomerized species.[S12] Unfortunately, attempts to record transient absorptions of both **5** met with similar complications as previously investigated, namely the aforementioned overlapping absorptions of differing excited states not to mention the low stability of the 3-hydroxflavone **5** under laser irradiation. These characteristics ruled out the use of transient absorption studies to gain useful information regarding the quenching of the presumed triplet excited states with various dipolarophiles.

(2) Selective UV photoexcitation experiments:

As the absorption spectrum of DPBD **8** (λ_{max} = 329 nm) overlapped with the absorption spectrum of 3-hydroxyflavone (λ_{max} = 360 nm), identification of the excited species upon photo irradiation is crucial for the mechanistic study. From the measurements, we are able to determine an optical window for selective excitation of 3-HF **5** (**Figure S5 D**).

Choice of the appropriate light source (purple LED, 395 nm to 405 nm) to selectively irradiate 3-HF **5** served to help identify the reactant being excited during photocycloadditions. To ensure that upon this LED light source irradiation only 3-hydroxyflavone **5** is being photoexcited, we conducted fluorescence measurements at excitation wavelengths of both 385 nm and 390 nm. At 385 nm excitation, we still can see trace amount of fluorescence signal coming from DPBD, and however, at 395 nm excitation, only fluorescence of 3-HF **5** can be seen, which indicates that the selection of the light source will certify that only 3-hydroxyflavone can be photoexcited.

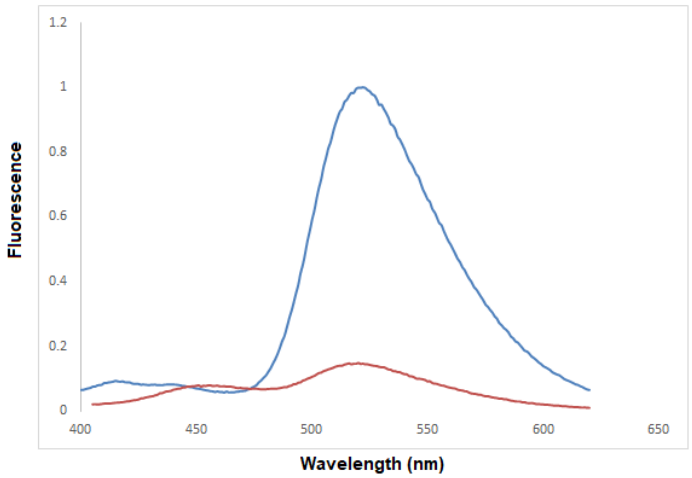
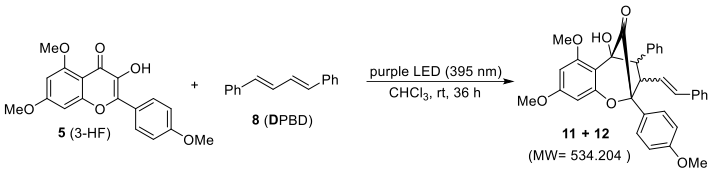
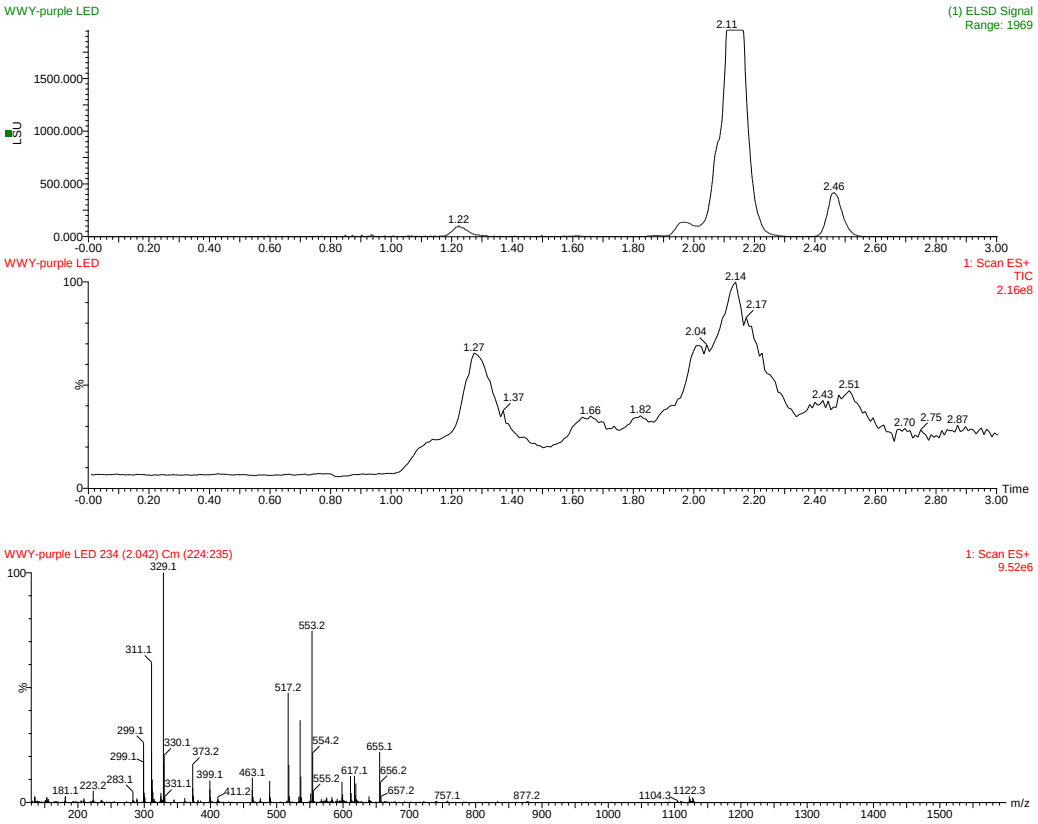


Figure S6. Fluorescence Spectra of a Mixture of 3-HF **5** and DPBD **8**

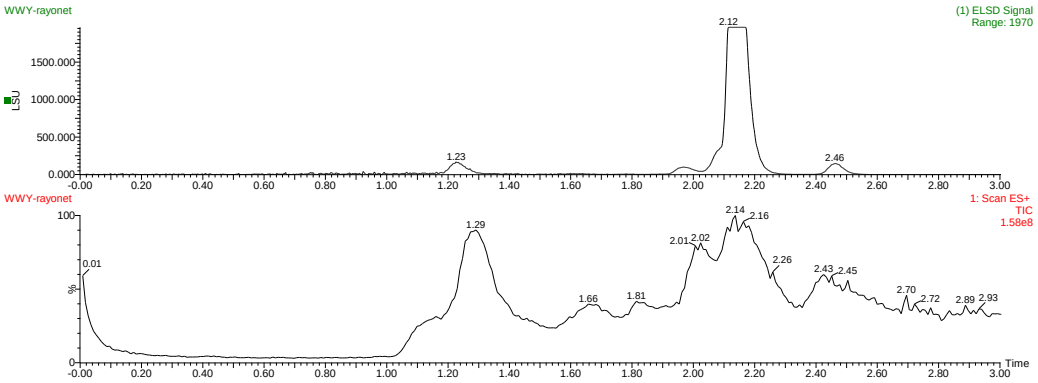


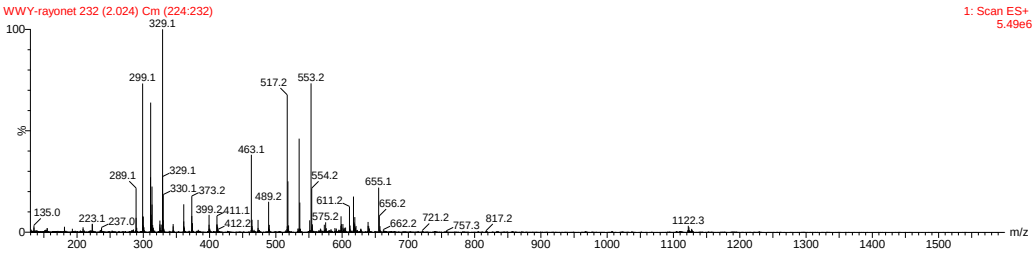
A flame dried test tube was charged with 3-HF **5** (30 mg, 0.09 mmol, 1 equiv.), DPBD **8** (94.3 mg, 0.46 mmol, 5 equiv), and $CHCl_3$/TFE 7:3 mixture (4.5 mL, 0.02 M). The resulting mixture was degassed by argon bubbling with sonication for 15 min. Subsequently, the reaction tube was introduced into a purple LED chamber (395 nm) and was irradiated for 36 h. The reaction mixture was concentrated *in vacuo* and used for the UPLC analysis for detection of the photocycloadducts mass. The mass clearly showed the mass of the photocycloadducts as a hydrate. The relative long irradiation for the production of photocycloadducts also demonstrated the low absorption efficiency from the UV-absorption spectrum.

UPLC trace for the Purple LED reaction (photocycloadducts retention time: 2.04 min. Mass (M+1) of the photocycloadduct shown is 553.2 which is the hydrate of the bridgehead ketone:



UPLC trace of a comparison experiment conducted under Rayonet irradiation as a control experiment (5 h):





Although the efficiency of the photoreaction using purple-LED irradiation was significantly decreased (based on the absorption spectra, the absorption efficiency of 3-HF **5** at 395 nm is low), this experiment confirmed that upon photoirradiation, excitation of 3-HF **5** is crucial to produce photocycloadducts.

(3) Studies of Photoinduced Electron Transfer (PET) Mechanism.

To study the photoinduced electron transfer mechanism, a calculation using the Rehm-Weller Equation was used to determine feasibility.

$$\Delta G^0 = E_{ox} - E_{red} - E_{00} - e^2/\varepsilon d$$

E_{ox} = oxidation potential of donor

E_{red} = reduction potential of acceptor

E_{00} = excitation Energy of donor

ε = dielectric constant of water

d = distance between donor and acceptor

All redox values were taken in MeCN as the solvent. Glassy carbon was used as the working electrode for *trans-trans*-1,4-diphenyl-1,3-butadiene **8**, pentafluoro-DPBD **27**, and 3-hydroxyflavone (**5**). A platinum (Pt) electrode was used for **5**. The reference electrode employed was Ag/AgCl and Ag wire pseudo-electrode, respectively. Tertbutylammonium-hexafluorophosphate (TBAHFP) was used as the supporting electrolyte. In all cases, ferrocene was used as internal standard. The singlet (3.08 eV) and triplet (2.35 eV) state energies of energy of **5** were computed from the fluorescence and phosphorescence spectra, respectively.

Table S2: Concentrations used to obtain electrochemical data.

Entry	Compound	Conc. (mM)	Electrolyte (M)
1	**5**	0.1	0.1
2	**8**	1.65	0.07
3	**27**	0.67	0.88

Table S3: Redox potentials of compounds under investigation

entry	Compound	E_{ox} (V)	E_{red} (V)
1	**5**	1.22	-1.79
2	**8**	1.38	-0.96
3	**27**	1.49	-0.90

Table S4: Free energy of electron transfer from triplet excited **5** as donor (E_{exc} = 2.35 eV; $E_{D/D+}$ = 1.22)

entry	Acceptor	$E(A/A^{-})$ (V)	ΔG (eV)	ΔG (kcal/mol)
1	**8**	-0.96	-0.23	-5.3
2	**27**	-0.90	-0.28	-6.6

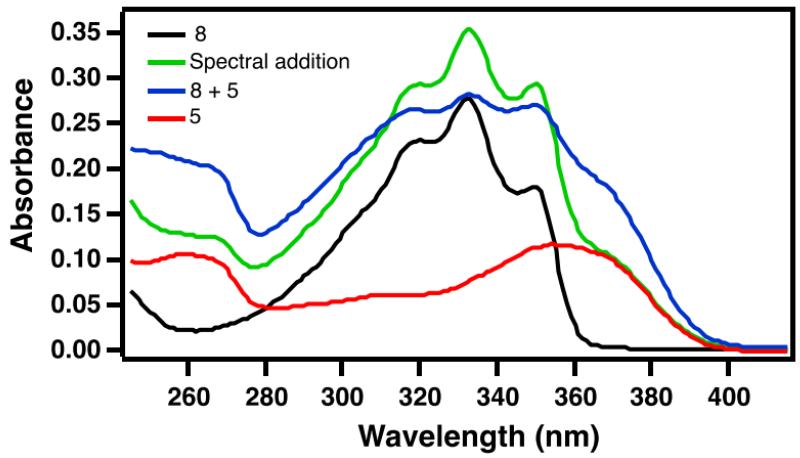


Figure S7. Absorption Spectra of a Mixture of 3-HF **5** and DPBD **8** in Comparison with Mathematically Added Spectrum

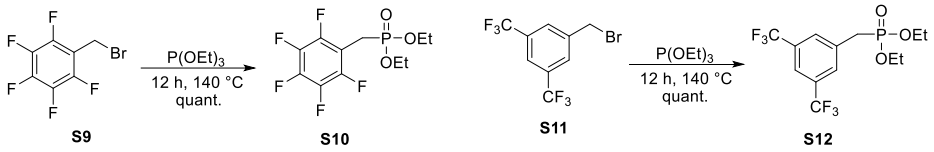
The absorption spectra of **8** (black), **5** (red) and a mixture of **8** and **5** (blue) along with the spectral addition of **8** and **5** (green) shows that there is no new electron donor-acceptor (EDA) complex formation (or at the very least the complex does not have sufficient absorptivity) under our experimental conditions (**Figure S7**). Nevertheless, the spectral addition (green) and experimental absorption of the mixture of **8** and **5** (blue) cannot rule out the interaction between **8** and **5** due to the change in absorptivity. Based on this, electron donor–acceptor (EDA) complex between **5** and **8** in the ground state is not observable under our experimental conditions *i.e.* no new complex was observed spectrophotometrically. In addition, the electron transfer pathway is initiated

from the triplet excited state of **5** leading to the observed photoproduct. Our data does not demonstrate an emissive EDA formation. However, we cannot rule out a non-emissive EDA.

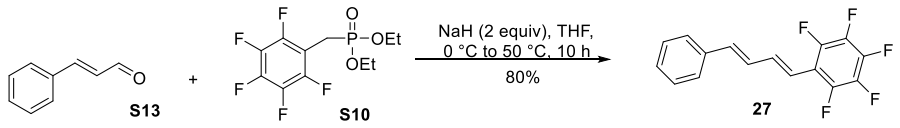
(4) Further studies of the ESIPT photocycloaddition of 5 with other substituted dipolarophiles.

To further study the ESIPT photocycloaddition of 3-HF **5** with diphenylbutadienes, we synthesized several additional substituted dipolarophiles. Evaluation of these dipolarophiles in the photoreaction should impart understanding regarding the electronic effects of the ESIPT photocycloaddition and serve to elucidate additional donor-acceptor effects.

Synthetic route to substituted stilbenes or diphenylbutadienes:

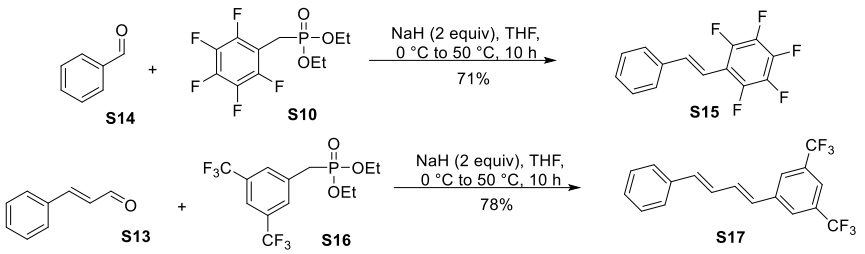


The phosphate derivatives **S10** and **S12** were prepared by reactions of benzyl bromide **S9** and **S11** (1 equiv.) with triethyl phosphite (3 equiv.) at 140 °C for 12 h. The remaining phosphite was remove under reduced pressure and the phosphate products were used in the subsequent olefination without further purification.[S13]



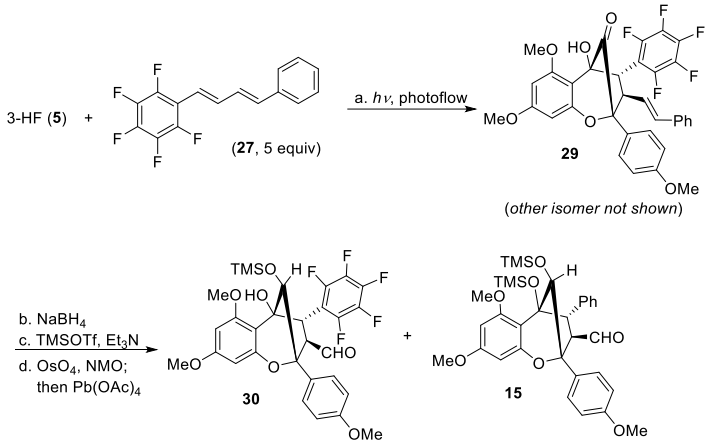
A flame-dried round bottom flask was charged with pentafluorobenzyl phosphate **S10** (5g, 15.71 mmol, 1 equiv) and dry THF (105 mL, 0.15 M). The solution was cooled to 0 °C before NaH (60% in mineral oil, 1.26 g, 31.43 mmol, 2 equiv) was added. After stirring for 5 min, cinnamaldehyde **S13** (2.08 g, 15.71 mmol, 1 equiv) was added. The resulting mixture was allowed to warm to room temperature and was subsequently heated to 50 °C for 10 h. The reaction mixture was then poured into ice-cooled saturated NH_4Cl (aq.). After extraction with CH_2Cl_2, the combined organic layer was washed with saturated NaCl (aq.), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Further purification *via* recrystallization in EtOAc afforded DPBD **27** as a white solid (3.72 g, 80% yield). Characterization data for this compound are in agreement with a previous

report.[S14]



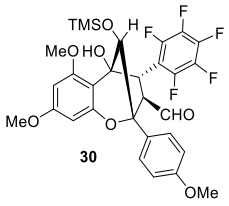
Using a similar synthetic strategy, dipolarophiles **S15** and **S17** were synthesized. Characterization data for these compounds were in agreement with previous reports. [S15, S16, S17, S18]

General procedure for mechanistic validation reactions:



A 100 mL round bottom flask was charged with 3-hydroxyflavone **5** (300 mg, 0.91 mmol, 1 equiv), pentafluoro-DPBD **27** (1.35 g, 4.6 mmol, 5 equiv), and 90 mL of CH_2Cl_2 (0.01 M for 3-HF **5**). The flask was connected with the continuous photoflow reactor followed by degassing of the reaction at 0 °C with argon bubbling for 5 min with sonication. Subsequently, the peristaltic pump was turned on to circulate the reaction mixture and argon bubbling with sonication was continued for an additional 15 min before the UV-lamp (Rayonet, λ_{max} = 350 nm) was turned on. After 6 h, the reaction mixture was collected back into the flask and was concentrated *in vacuo*. Purification *via* flash chromatography using a gradient of hexanes/EtOAc (10:1 to 3:1) afforded the cyclopenta[*bc*]benzopyran products as a mixture of isomers (cycloadducts were identified based on a ^{1}H NMR spectrum of the crude product) which were used in the next step without further purification. A flame-dried 100 mL flask was charged with the mixture of compounds (338 mg, 0.54 mmol, 1 equiv) and THF (4 mL, 0.14 M) was added. Subsequently, $NaBH_4$ (123 mg, 3.25 mmol, 6 equiv) was added at rt in one portion. The resulting mixture was then stirred for 12 h and was quenched with ice-cooled saturated ammonium chloride. The mixture was extracted with CH_2Cl_2 (10 mL × 3), washed with saturated sodium

bicarbonate, and dried over sodium sulfate. The filtrate was concentrated *in vacuo*. Column chromatography purification using hexanes/EtOAc (5:1 to 3:1) afforded an inseparable mixture of aglain products (321.6 mg), which was redissolved in CH_2Cl_2 (5 mL) and cooled to -78 °C. Subsequently, Et_3N (188 μL, 1.35 mmol, 2.5 equiv) and TMSOTf (210 μL, 1.14 mmol, 2.1 equiv) were added. The resulting mixture was stirred at -78 °C for an additional 10 min and was then to warmed to 0 °C for another 20 min before 10 mL of saturated Na_2CO_3 (aq.) was added to quench the reaction. The reaction mixture was further extracted with CH_2Cl_2 (3 mL × 3). The combined organic layer was washed with 10 mL saturated NaCl (aq.), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Subsequently, the crude compound mixture was redissolved in 13 mL of THF/*t*-BuOH (1:1). Subsequently, 1.3 mL OsO_4 (10 mg/mL, aq., 0.1 equiv) solution was added followed by addition of NMO (190 mg, 1.62 mmol, 3 equiv). The resulting mixture was stirred at room temperature for 12 h, before being extracted with Et_2O (5mL × 3). The combined organic layers were washed with saturated NaCl (aq.), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The obtained brown oil was redissolved in CH_2Cl_2 (5 mL) and $Pb(OAc)_4$ (360 mg, 0.81 mmol, 1.5 equiv) was added. The reaction mixture was stirred at room temperature for 20 min before 10 mL of saturated $Na_2S_2O_3$ (aq.) was added to quench the reaction. The reaction mixture was extracted with CH_2Cl_2 (5 mL × 3), washed with 10 mL saturated NaCl (aq.), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. Purification *via* column chromatography purification using hexanes/EtOAc (20:1 to 6:1) afforded pentafluoro-aglain aldehyde **30** (126 mg, 25% overall yield) as a colorless oil and aldehyde **15** (45.3 mg, 8.2 % overall yield) (for characterization data for **15**, see page S9).



30

30: R_f: 0.37 (EtOAc/hexanes = 1:4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.01 (d, J = 1.5 Hz, 1H), 7.50 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 6.30 (d, J = 1.1 Hz, 1H), 5.97 (d, J = 1.1 Hz, 1H), 5.54 (s, 1H, OH), 4.55 (s, 1H), 4.34 (d, J = 4.7 Hz, 1H), 4.01 (dd, J_1 = 4.7 Hz, J_2 = 1.5 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.48 (s, 3H), 0.002 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 160.9, 159.6, 158.9, 154.3, 147.6, 145.2, 138.5, 136.0, 127.9, 127.4, 114.2, 111.0, 103.8, 94.3, 92.5, 84.4, 81.4, 73.6, 58.5, 55.8, 55.32, 55.30, 44.2, 0.6; IR υ_{max} (film): 3497, 2959, 1720, 1619, 1496, 1378, 1253, 1149, 1098, 1098, 1029, 875, 841 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{30}H_{29}F_5O_7Si$, 647.2969, found 647.2970.

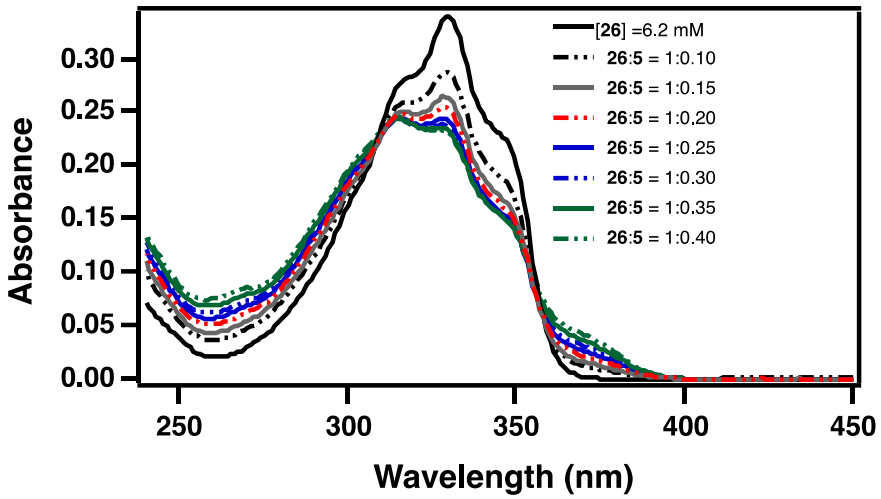


Figure S8. Absorbance of **27** (6.2 μM) with addition of **5** (0 to 2.5 μM) at various equivalence recorded in a mixture of $CHCl_3$:EtOH (7:3)

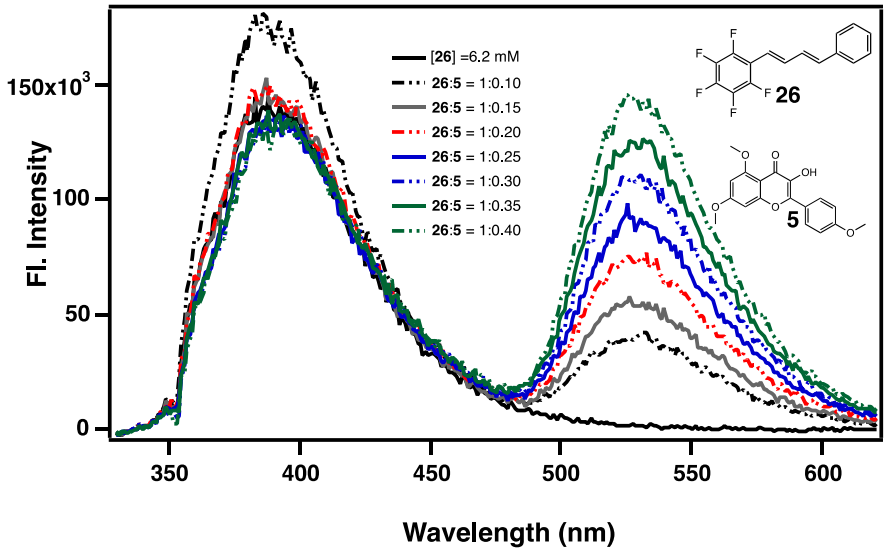
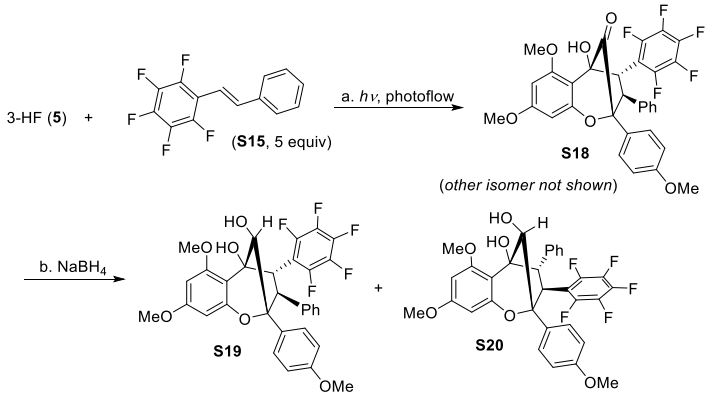
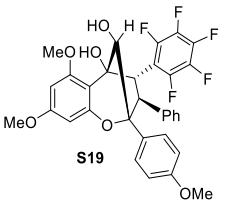


Figure S9. Fluorescence of **27** with addition of **5** at various equivalents (0 to 2.5 μM) recorded in a mixture of $CHCl_3$:EtOH (7:3); λ_{exc} = 320 nm; λ_{emiss} = 330 - 620 nm.



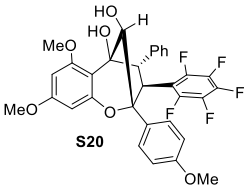
The previously mentioned general procedure for mechanistic validation

reactions was employed using 3-HF **5** (300 mg, 0.91 mmol, 1 equiv.) and stilbene **S15** (1.23 g, 4.6 mmol, 5 equiv.). After photocycloaddition, the inseparable mixture was purified *via* flash column chromatography using a gradient of hexanes/EtOAc (10:1 to 3:1) to afford 252 mg of a white solid. The crude product was reduced with $NaBH_4$ (96 mg, 2.52 mmol, 6 equiv.) in THF. Purification *via* flash column chromatography using a gradient of hexanes/EtOAc (9:1 to 4:1) afforded a mixture of compounds **S19** and **S20**. The mixture was further purified *via* preparative thin layer chromatography using hexanes/EtOAx/CH_2Cl_2 (7:1.5:1.5) afforded compound **S19** (142 mg, 26 % overall yield) as a white solid and **S20** (51 mg, 9.3 % overall yield) as a colorless oil.



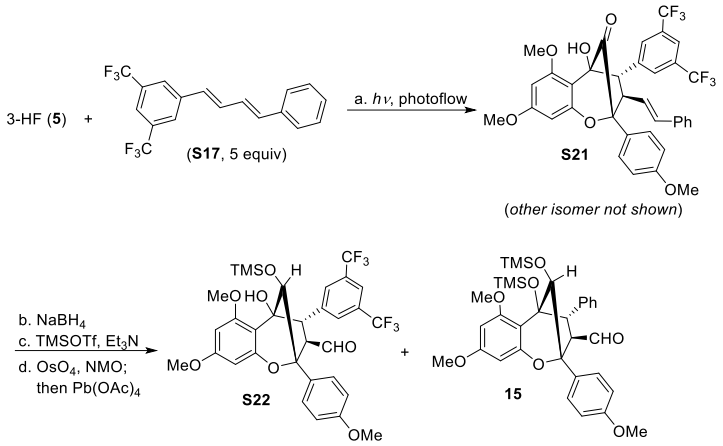
S19

S19: R_f: 0.13 (EtOAc/hexanes = 3:7). m.p. = 224 - 225 °C (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, J = 8.7 Hz, 2H), 7.01 (t, J = 7.2 Hz, 2H), 6.95 (t, J = 7.2 Hz, 1H), 6.90 (d, J = 7.2 Hz, 2H), 6.68 (d, J = 8.7 Hz, 2H), 6.31 (d, J = 2.1 Hz, 1H), 6.04 (d, J = 2.1 Hz, 1H), 5.63 (s, 1H, OH), 4.92 (d, J = 3.3 Hz, 1H), 4.39 (d, J = 10.6 Hz, 1H), 4.10 (d, J = 10.6 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.51 (s, 3H), 2.63 (brs, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 159.3, 158.8, 154.4, 147.5, 140.7, 139.3, 138.2, 136.2, 129.0, 128.9, 128.5, 128.2, 126.8, 113.2, 110.8, 102.8, 94.6, 92.8, 87.7, 81.5, 73.0, 55.7, 55.5, 55.1, 54.5, 54.3; IR υ_{max} (film): 3495, 2944, 1713, 1617, 1519, 1493, 1375, 1146, 1097, 998, 828, 701, 652 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{32}H_{26}F_5O_6$, 601.1650, found 601.1659.

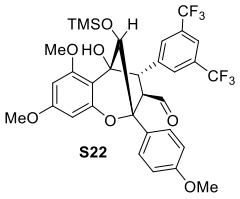


S20

S20: R_f: 0.13 (EtOAc/hexanes = 3:7). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.6 Hz, 2H), 7.19 (m, 3H), 7.00 (m, 2H), 6.80 (d, J = 8.6 Hz, 2H), 6.28 (d, J = 2.2 Hz, 1H), 5.89 (d, J = 2.2 Hz, 1H), 5.48 (s, 1H, OH), 5.17 (s, 1H), 4.45 (d, J = 10.9 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.74 (d, J = 10.9 Hz, 1H), 3.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.0, 160.3, 159.4, 153.2, 145.4, 143.4, 140.8, 138.3, 135.9, 135.4, 128.7, 128.1, 127.9, 127.5, 144.0, 113.5, 103.1, 94.3, 93.2, 86.6, 82.2, 72.1, 58.7, 55.43, 55.37, 55.21, 55.16, 45.7; IR υ_{max} (film): 3498, 2960, 2843, 1722, 1619, 1589, 1518, 1383, 1378, 1174, 1134, 1100, 1027, 875, 844 cm^{-1}. IR υ_{max} (film): 3495, 2944, 1713, 1617, 1519, 1493, 1375, 1146, 1097, 998, 828, 701, 652 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{32}H_{26}F_5O_6$, 601.1650, found 601.1655.



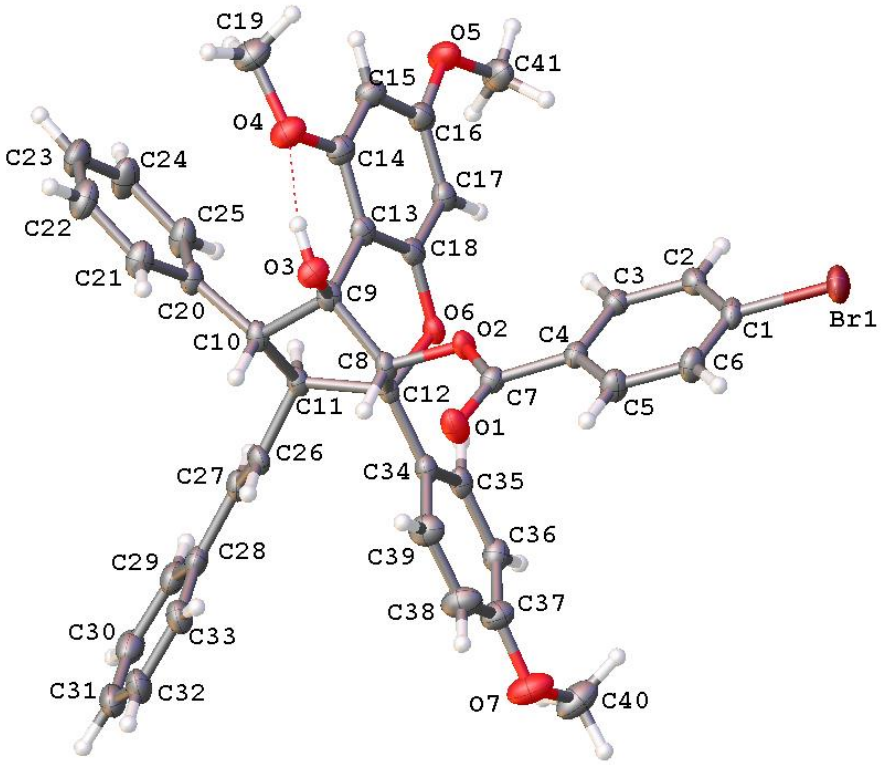
The previously mentioned general procedure for mechanistic validation reactions was employed using 3-HF **5** (300 mg, 0.91 mmol, 1 equiv.) and DPBD **S17** (1.56 g, 4.6 mmol, 5 equiv.). Aldehyde **S22** (132 mg, 22 % overall yield) was isolated as a colorless oil and compound **15** (39 mg, 7.5 % overall yield) was isolated as a minor product (for characterization data for **15**, see page S10).



S22: R_f: 0.43 (EtOAc/hexanes = 1:4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (d, J = 1.8 Hz, 1H), 7.69 (s, 1H), 7.52 (d, J = 8.8 Hz, 2H), 7.35 (s, 2H), 6.99 (d, J = 8.8 Hz, 2H), 6.33 (d, J = 2.2 Hz, 1H), 5.83 (d, J = 2.2 Hz, 1H), 5.42 (s, 1H, OH), 4.59 (s, 1H, OH), 3.97 (d, J = 9.0 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.57 (dd, J_1 = 9 Hz, J_2 = 1.8 Hz, 1H), 3.14 (s, 3H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 161.0, 159.6, 159.1, 153.0, 140.0, 130.8, 128.6, 127.7, 127.4, 124.3, 122.2, 120.7, 114.2, 103.5, 94.6, 94.5, 92.3, 84.2, 82.0, 74.4, 61.2, 55.4, 55.3, 55.2, 52.7, 0.6; IR υ_{max} (film): 3498, 2960, 2843, 1722, 1619, 1589, 1518, 1383, 1378, 1174, 1134, 1100, 1027, 875, 844 cm^{-1}. HRMS-ESI (m/z) calculated $[M+H]^+$ $C_{32}H_{33}F_6O_7Si_2$, 671.1900, found 671.1906.

VI. X-Ray Crystallographic Data

X-ray crystallographic data for compound 14:



Crystals of compound **14** suitable for X-ray analysis were obtained by slow evaporation from dichloromethane/hexanes. Crystallographic data have been deposited with the Cambridge Cystallograhic Data Centre (CCDC#1523489). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computing details

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL* (Sheldrick, 2008); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

References

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Bruker (2006). *SAINT*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Bruker (2006). *APEX2*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Dolmanov, O. V., *et al.* (2009). OLEX2: A complete structure solution, refinement and analysis program. J. Appl. Cryst. 42, 339-341 (2009).

(Compound 14)

Crystal data

$C_{41}H_{35}BrO_7$	$F(000) = 2976$
$M_r = 719.60$	$D_x = 1.411$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 22.603$ (2) Å	Cell parameters from 9408 reflections
$b = 20.3183$ (19) Å	$\theta = 3.9$–$66.7°$
$c = 14.8174$ (13) Å	$\mu = 2.08$ mm^{-1}
$\beta = 95.493$ (4)°	$T = 100$ K
$V = 6773.6$ (11) Å^3	Bar, colorless
$Z = 8$	0.22 × 0.09 × 0.08 mm

Data collection

Bruker Proteum-R diffractometer	11948 independent reflections
Radiation source: rotating anode	10807 reflections with $I > 2\sigma(I)$
Multilayer monochromator	$R_{int} = 0.055$
ϕ & ω scans	$\theta_{max} = 66.8°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan *SADABS* (Sheldrick, 1997)	$h = -26\rightarrow26$
$T_{min} = 0.646$, $T_{max} = 0.753$	$k = -24\rightarrow24$
133915 measured reflections	$l = -17\rightarrow17$

Refinement

Refinement on F^2	932 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.055$	H-atom parameters constrained
$wR(F^2) = 0.150$	$w = 1/[\sigma^2(F_o^2) + (0.0923P)^2 + 7.6376P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.002$
11948 reflections	$\Delta\rangle_{max} = 2.89$ e Å^{-3}
891 parameters	$\Delta\rangle_{min} = -0.70$ e Å^{-3}

Special details

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

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for compound **14***

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1A	0.97710 (2)	0.53306 (2)	-0.20398 (2)	0.04010 (12)
Br1	0.51754 (2)	0.44864 (2)	0.69611 (2)	0.03416 (11)
O2A	0.87551 (7)	0.55160 (9)	0.21092 (11)	0.0232 (4)
O6A	0.95160 (8)	0.55620 (10)	0.35916 (12)	0.0288 (4)
O3A	0.79380 (7)	0.65392 (9)	0.27061 (11)	0.0239 (4)
H3A	0.8002	0.6944	0.2659	0.036*
O4A	0.85823 (8)	0.76389 (10)	0.29108 (13)	0.0318 (4)
O5A	1.07190 (9)	0.74106 (13)	0.35515 (15)	0.0475 (6)
O7A	0.91566 (10)	0.25004 (11)	0.37981 (16)	0.0473 (6)
O1A	0.79113 (9)	0.51226 (13)	0.13760 (14)	0.0430 (5)
O2	0.63002 (7)	0.43773 (8)	0.28899 (11)	0.0214 (4)
O6	0.55489 (7)	0.43391 (8)	0.13652 (11)	0.0205 (3)
O3	0.71734 (8)	0.34668 (9)	0.22227 (12)	0.0259 (4)
H3	0.7165	0.3056	0.2154	0.039*
O4	0.66788 (8)	0.23558 (9)	0.15981 (14)	0.0332 (4)
O5	0.45908 (8)	0.22425 (9)	0.10366 (14)	0.0348 (4)
O7	0.55952 (10)	0.74087 (10)	0.16014 (16)	0.0455 (5)
O1	0.70742 (8)	0.49126 (10)	0.36401 (12)	0.0300 (4)
C1A	0.93542 (12)	0.53365 (14)	-0.09829 (17)	0.0292 (6)
C2A	0.88247 (14)	0.49994 (19)	-0.0993 (2)	0.0434 (8)

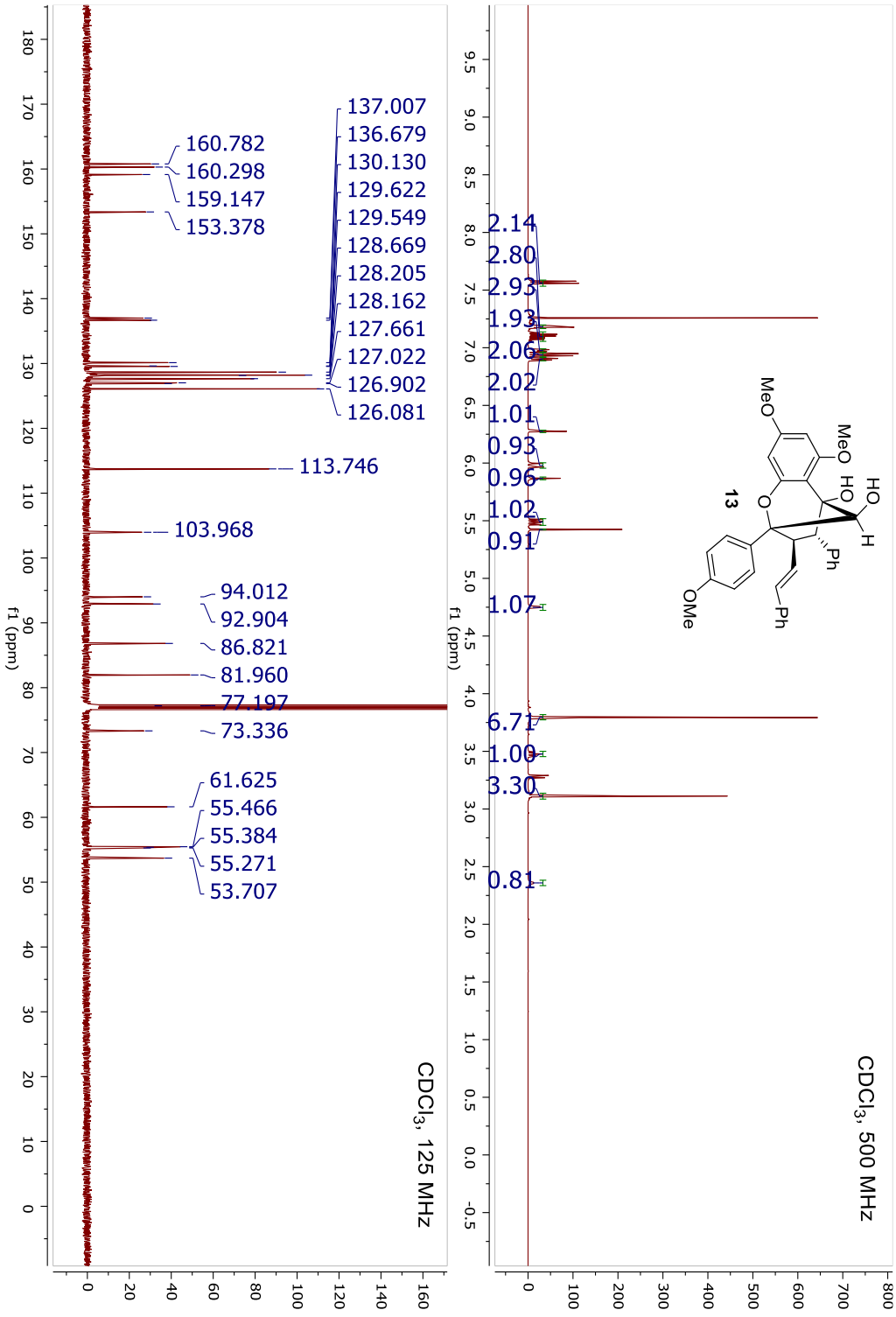
H2A	0.8670	0.4769	-0.1521	0.052*
C3A	0.85220 (13)	0.50006 (19)	-0.0225 (2)	0.0440 (8)
H3AA	0.8152	0.4777	-0.0232	0.053*
C4A	0.87541 (11)	0.53266 (13)	0.05584 (17)	0.0253 (5)
C7A	0.84201 (12)	0.53033 (13)	0.13736 (18)	0.0257 (5)
C8A	0.84965 (11)	0.55479 (13)	0.29565 (16)	0.0229 (5)
H8A	0.8115	0.5297	0.2924	0.027*
C12A	0.89412 (11)	0.52826 (14)	0.37171 (17)	0.0263 (6)
C11A	0.87237 (12)	0.56072 (14)	0.46042 (17)	0.0273 (6)
H11A	0.9064	0.5877	0.4882	0.033*
C26A	0.85717 (13)	0.51332 (15)	0.53201 (18)	0.0326 (6)
H26A	0.8827	0.4764	0.5417	0.039*
C27A	0.81306 (12)	0.51653 (14)	0.58286 (18)	0.0306 (6)
H27A	0.7859	0.5520	0.5721	0.037*
C28A	0.80180 (11)	0.46959 (14)	0.65585 (18)	0.0281 (6)
C29A	0.76281 (12)	0.48665 (14)	0.71995 (18)	0.0293 (6)
H29A	0.7436	0.5283	0.7162	0.035*
C30A	0.75187 (12)	0.44329 (15)	0.78920 (18)	0.0328 (6)
H30A	0.7246	0.4551	0.8314	0.039*
C31A	0.78042 (13)	0.38309 (16)	0.7969 (2)	0.0364 (6)
H31A	0.7734	0.3540	0.8449	0.044*
C5A	0.92904 (11)	0.56607 (13)	0.05532 (17)	0.0244 (5)
H5A	0.9452	0.5884	0.1084	0.029*
C6A	0.95912 (12)	0.56712 (14)	-0.02190 (18)	0.0297 (6)
H6A	0.9955	0.5905	-0.0224	0.036*
C18A	0.95274 (11)	0.62277 (15)	0.34670 (16)	0.0285 (6)
C13A	0.90073 (11)	0.66008 (14)	0.32741 (16)	0.0258 (5)
C9A	0.84085 (11)	0.62479 (13)	0.32637 (16)	0.0229 (5)
C10A	0.82361 (11)	0.61011 (13)	0.42431 (16)	0.0241 (5)
H10A	0.7850	0.5857	0.4178	0.029*
C32A	0.81955 (13)	0.36527 (16)	0.7339 (2)	0.0360 (6)
H32A	0.8397	0.3242	0.7393	0.043*
C33A	0.82910 (12)	0.40769 (15)	0.66296 (19)	0.0314 (6)
H33A	0.8545	0.3945	0.6188	0.038*
C20A	0.81465 (12)	0.67072 (14)	0.47981 (16)	0.0266 (5)
C21A	0.86134 (13)	0.71121 (16)	0.51519 (18)	0.0362 (6)
H21A	0.9012	0.6990	0.5080	0.043*

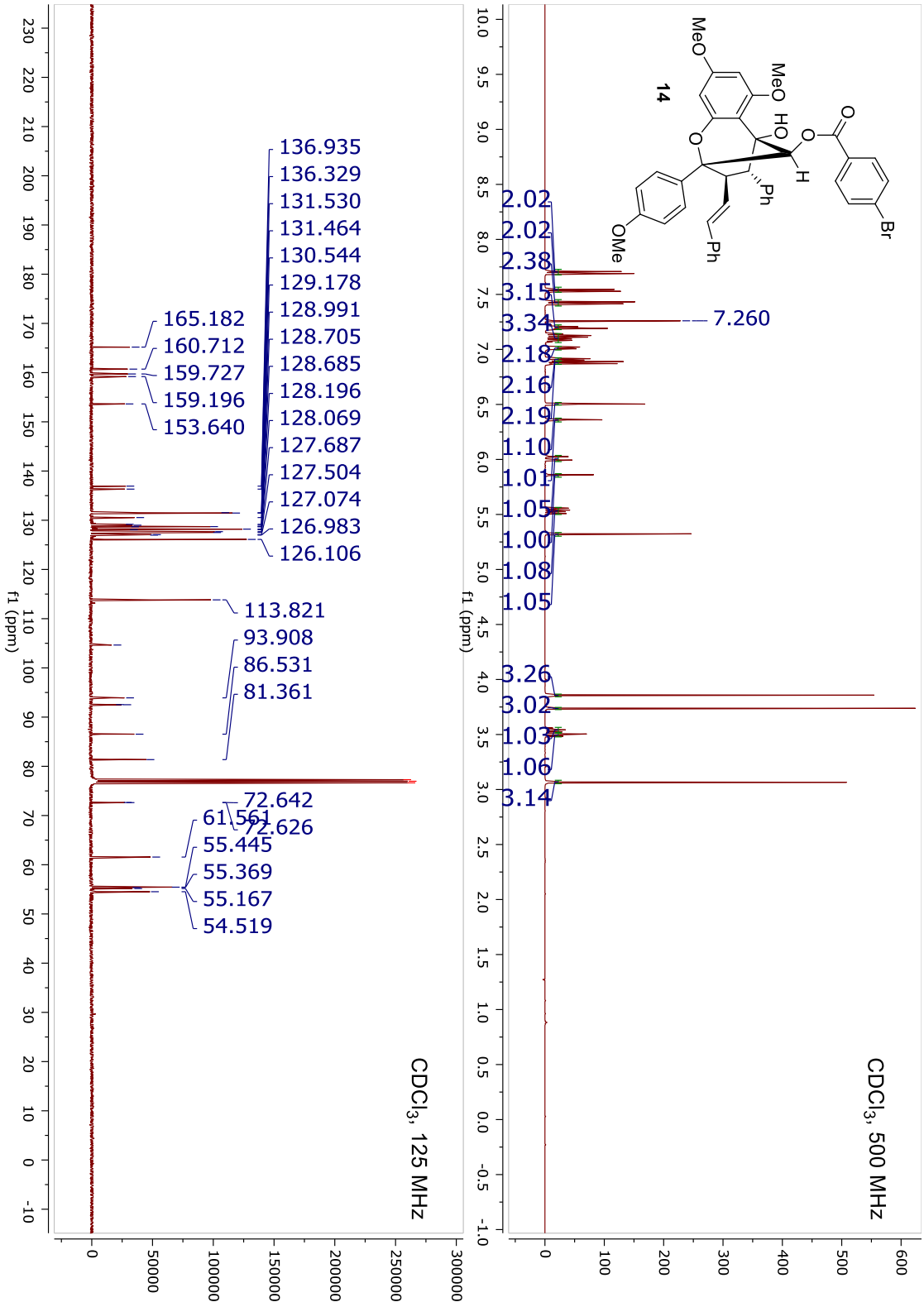
C22A	0.85007 (16)	0.76905 (16)	0.5607 (2)	0.0431 (7)
H22A	0.8821	0.7962	0.5841	0.052*
C23A	0.79223 (16)	0.78704 (16)	0.57198 (19)	0.0429 (8)
H23A	0.7846	0.8265	0.6032	0.051*
C24A	0.74603 (15)	0.74796 (16)	0.5382 (2)	0.0400 (7)
H24A	0.7063	0.7604	0.5461	0.048*
C25A	0.75686 (13)	0.69018 (15)	0.49239 (18)	0.0324 (6)
H25A	0.7244	0.6635	0.4693	0.039*
C14A	0.90889 (11)	0.72741 (15)	0.31388 (17)	0.0283 (6)
C19A	0.86490 (13)	0.82991 (15)	0.2582 (2)	0.0383 (7)
H19A	0.8787	0.8588	0.3089	0.057*
H19B	0.8265	0.8458	0.2300	0.057*
H19C	0.8940	0.8301	0.2133	0.057*
C15A	0.96509 (12)	0.75720 (16)	0.32294 (18)	0.0338 (6)
H15A	0.9692	0.8033	0.3152	0.041*
C16A	1.01493 (12)	0.71736 (17)	0.34367 (18)	0.0365 (7)
C41A	1.07965 (13)	0.8102 (2)	0.3543 (2)	0.0499 (9)
H41A	1.0622	0.8279	0.2963	0.075*
H41B	1.1222	0.8205	0.3623	0.075*
H41C	1.0599	0.8299	0.4038	0.075*
C17A	1.00901 (12)	0.65061 (17)	0.35386 (18)	0.0347 (6)
H17A	1.0432	0.6237	0.3657	0.042*
C34A	0.90172 (12)	0.45486 (15)	0.37292 (17)	0.0287 (6)
C39A	0.95644 (13)	0.42596 (16)	0.40050 (17)	0.0337 (6)
H39A	0.9899	0.4532	0.4170	0.040*
C38A	0.96302 (13)	0.35773 (16)	0.40435 (18)	0.0370 (7)
H38A	1.0006	0.3390	0.4236	0.044*
C37A	0.91483 (14)	0.31731 (16)	0.3802 (2)	0.0379 (7)
C40A	0.97115 (15)	0.21840 (18)	0.4014 (2)	0.0483 (8)
H40A	0.9994	0.2331	0.3594	0.072*
H40B	0.9659	0.1706	0.3962	0.072*
H40C	0.9865	0.2296	0.4636	0.072*
C36A	0.85988 (13)	0.34547 (16)	0.3525 (2)	0.0409 (7)
H36A	0.8266	0.3181	0.3357	0.049*
C35A	0.85365 (12)	0.41311 (16)	0.3494 (2)	0.0364 (7)
H35A	0.8158	0.4316	0.3309	0.044*
C1	0.56037 (12)	0.45366 (13)	0.59212 (18)	0.0254 (5)

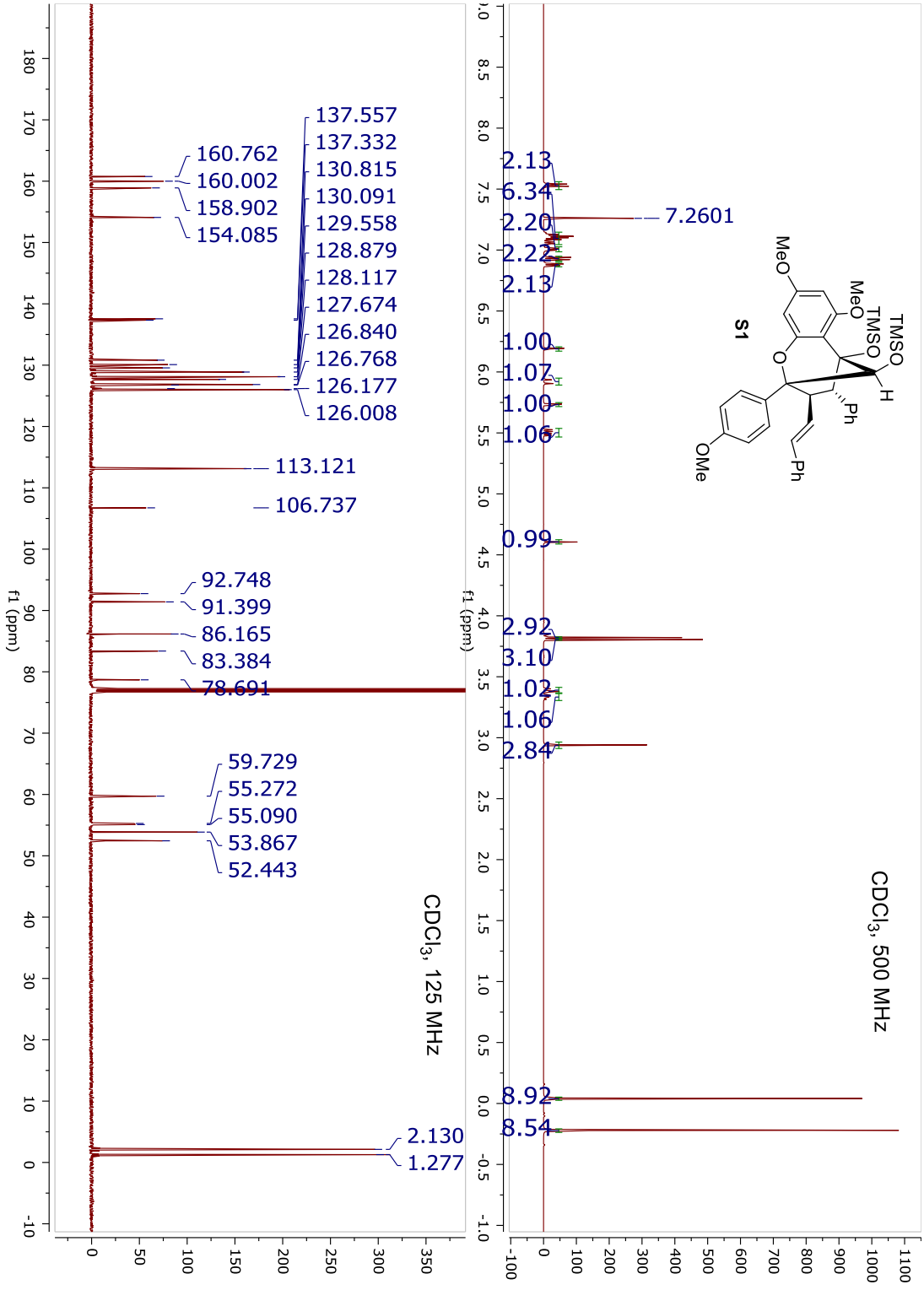
C6	0.61621 (12)	0.48257 (14)	0.59970 (18)	0.0299 (6)
H6	0.6326	0.5001	0.6561	0.036*
C5	0.64780 (12)	0.48566 (14)	0.52427 (18)	0.0280 (6)
H5	0.6860	0.5056	0.5288	0.034*
C4	0.62389 (11)	0.45977 (12)	0.44203 (17)	0.0203 (5)
C7	0.65918 (11)	0.46523 (12)	0.36280 (17)	0.0205 (5)
C8	0.65590 (11)	0.44216 (12)	0.20495 (16)	0.0202 (5)
H8	0.6922	0.4705	0.2115	0.024*
C12	0.61051 (11)	0.46915 (12)	0.13144 (16)	0.0200 (5)
C11	0.63722 (11)	0.44790 (12)	0.04082 (16)	0.0206 (5)
H11	0.6057	0.4247	0.0009	0.025*
C26	0.66014 (11)	0.50423 (13)	-0.01067 (17)	0.0242 (5)
H26	0.6955	0.5251	0.0148	0.029*
C27	0.63548 (11)	0.52715 (13)	-0.08810 (17)	0.0251 (5)
H27	0.5995	0.5070	-0.1123	0.030*
C28	0.65858 (12)	0.58148 (13)	-0.14130 (17)	0.0270 (5)
C29	0.62960 (13)	0.59710 (13)	-0.22570 (18)	0.0302 (6)
H29	0.5942	0.5746	-0.2470	0.036*
C30	0.65237 (15)	0.64563 (14)	-0.2790 (2)	0.0375 (7)
H30	0.6330	0.6552	-0.3372	0.045*
C31	0.70264 (14)	0.67977 (15)	-0.2479 (2)	0.0381 (7)
H31	0.7183	0.7124	-0.2849	0.046*
C3	0.56806 (11)	0.43017 (12)	0.43620 (17)	0.0223 (5)
H3B	0.5518	0.4120	0.3802	0.027*
C2	0.53612 (11)	0.42692 (12)	0.51107 (18)	0.0254 (5)
H2	0.4981	0.4066	0.5069	0.030*
C18	0.55909 (11)	0.36621 (12)	0.13964 (15)	0.0217 (5)
C13	0.61362 (11)	0.33457 (13)	0.15492 (16)	0.0229 (5)
C9	0.67001 (11)	0.37548 (12)	0.16646 (16)	0.0215 (5)
C10	0.68705 (10)	0.39772 (13)	0.07198 (16)	0.0215 (5)
H10	0.7250	0.4230	0.0823	0.026*
C32	0.73053 (14)	0.66647 (15)	-0.1625 (2)	0.0374 (7)
H32	0.7645	0.6911	-0.1400	0.045*
C33	0.70884 (13)	0.61737 (14)	-0.11013 (19)	0.0336 (6)
H33	0.7285	0.6080	-0.0520	0.040*
C20	0.69847 (11)	0.34031 (13)	0.01135 (17)	0.0249 (5)
C25	0.65643 (12)	0.31261 (15)	-0.05128 (19)	0.0332 (6)

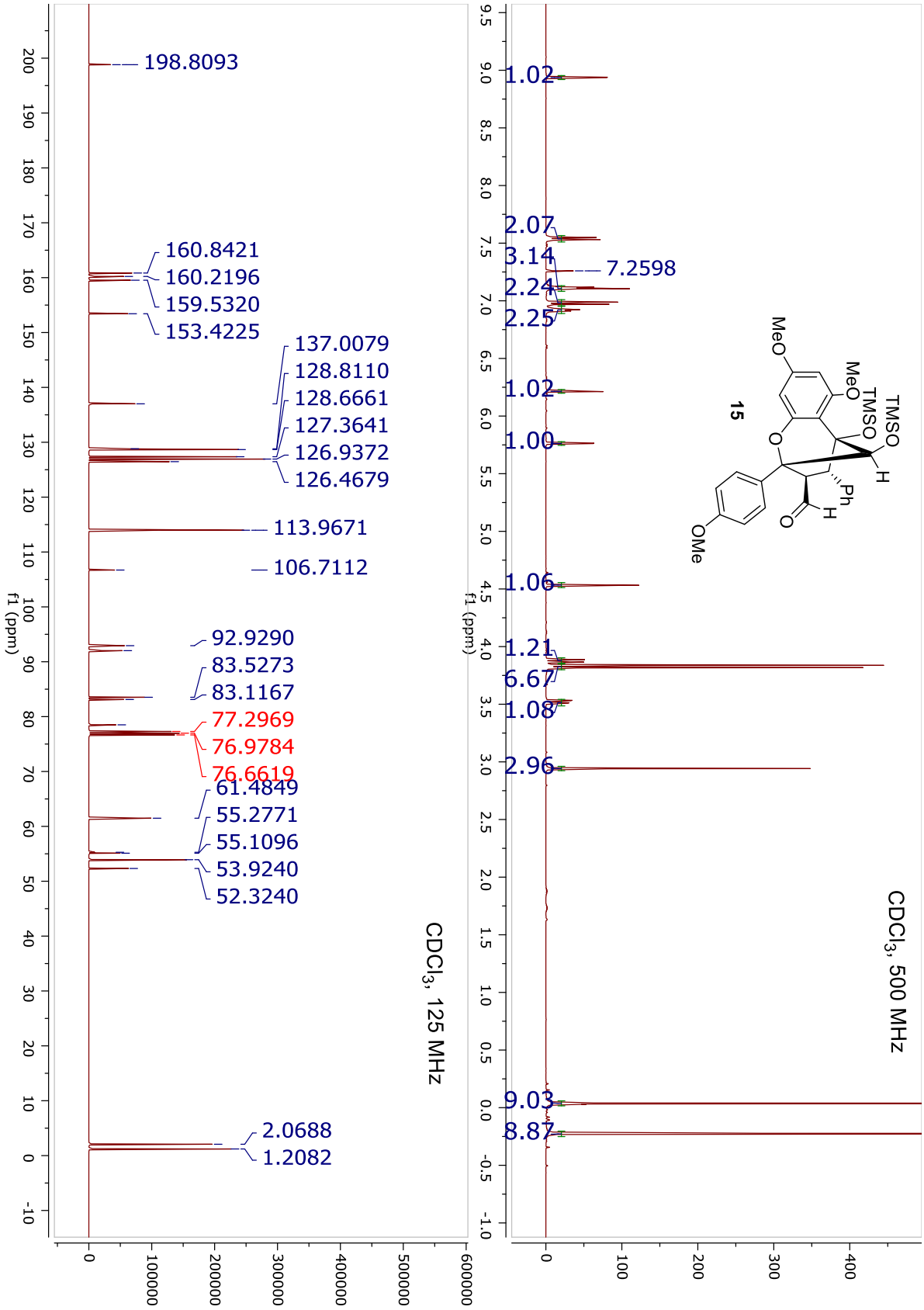
H25	0.6188	0.3332	-0.0637	0.040*
C24	0.66873 (13)	0.25466 (16)	-0.0964 (2)	0.0390 (7)
H24	0.6395	0.2364	-0.1395	0.047*
C23	0.72293 (14)	0.22360 (15)	-0.0789 (2)	0.0373 (7)
H23	0.7305	0.1832	-0.1080	0.045*
C22	0.76610 (14)	0.25189 (16)	-0.0187 (2)	0.0376 (7)
H22	0.8039	0.2315	-0.0073	0.045*
C21	0.75418 (12)	0.31008 (15)	0.02508 (19)	0.0312 (6)
H21	0.7844	0.3298	0.0652	0.037*
C14	0.61349 (12)	0.26527 (13)	0.15020 (17)	0.0269 (5)
C19	0.66994 (14)	0.16698 (14)	0.1368 (2)	0.0382 (7)
H19D	0.6513	0.1411	0.1821	0.057*
H19E	0.7114	0.1532	0.1358	0.057*
H19F	0.6486	0.1599	0.0769	0.057*
C15	0.56102 (12)	0.23043 (13)	0.13503 (18)	0.0292 (6)
H15	0.5616	0.1837	0.1338	0.035*
C16	0.50743 (12)	0.26422 (13)	0.12160 (17)	0.0277 (6)
C41	0.40269 (12)	0.25516 (15)	0.0917 (2)	0.0392 (7)
H41D	0.3967	0.2815	0.1454	0.059*
H41E	0.3716	0.2216	0.0830	0.059*
H41F	0.4008	0.2838	0.0383	0.059*
C17	0.50532 (11)	0.33243 (13)	0.12380 (16)	0.0238 (5)
H17	0.4686	0.3553	0.1148	0.029*
C34	0.59630 (11)	0.54114 (12)	0.13893 (17)	0.0221 (5)
C39	0.63764 (12)	0.58551 (14)	0.1799 (2)	0.0322 (6)
H39	0.6756	0.5701	0.2037	0.039*
C38	0.62410 (13)	0.65139 (14)	0.1862 (2)	0.0379 (7)
H38	0.6526	0.6809	0.2149	0.046*
C37	0.56861 (13)	0.67483 (13)	0.15044 (19)	0.0329 (6)
C40	0.50080 (15)	0.76470 (16)	0.1374 (2)	0.0454 (8)
H40D	0.4907	0.7611	0.0718	0.068*
H40E	0.4985	0.8109	0.1558	0.068*
H40F	0.4728	0.7385	0.1690	0.068*
C36	0.52761 (12)	0.63166 (13)	0.10826 (17)	0.0269 (5)
H36	0.4900	0.6472	0.0828	0.032*
C35	0.54172 (11)	0.56536 (13)	0.10331 (16)	0.0230 (5)
H35	0.5132	0.5358	0.0748	0.028*

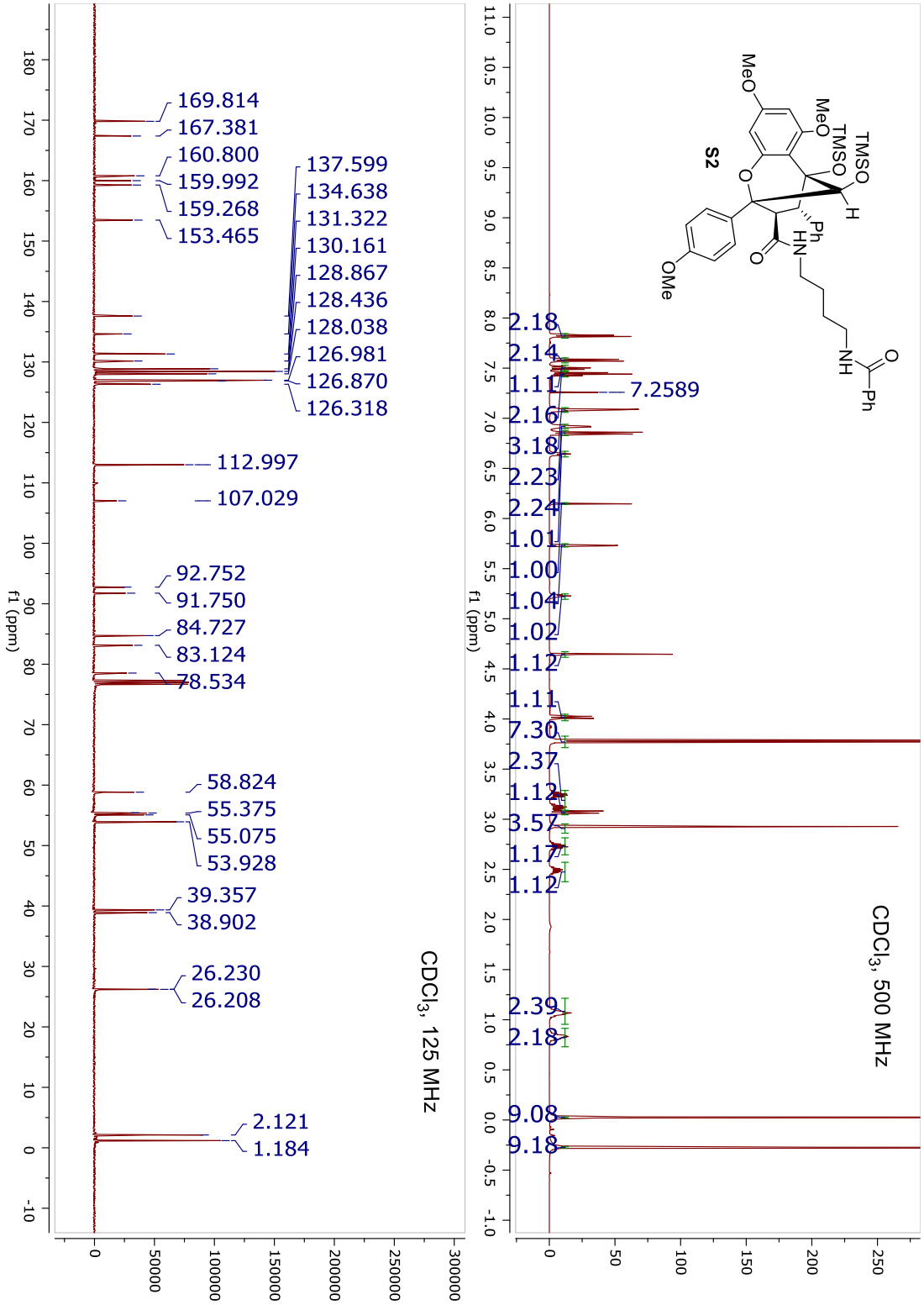
VII. SELECT SPECTRA

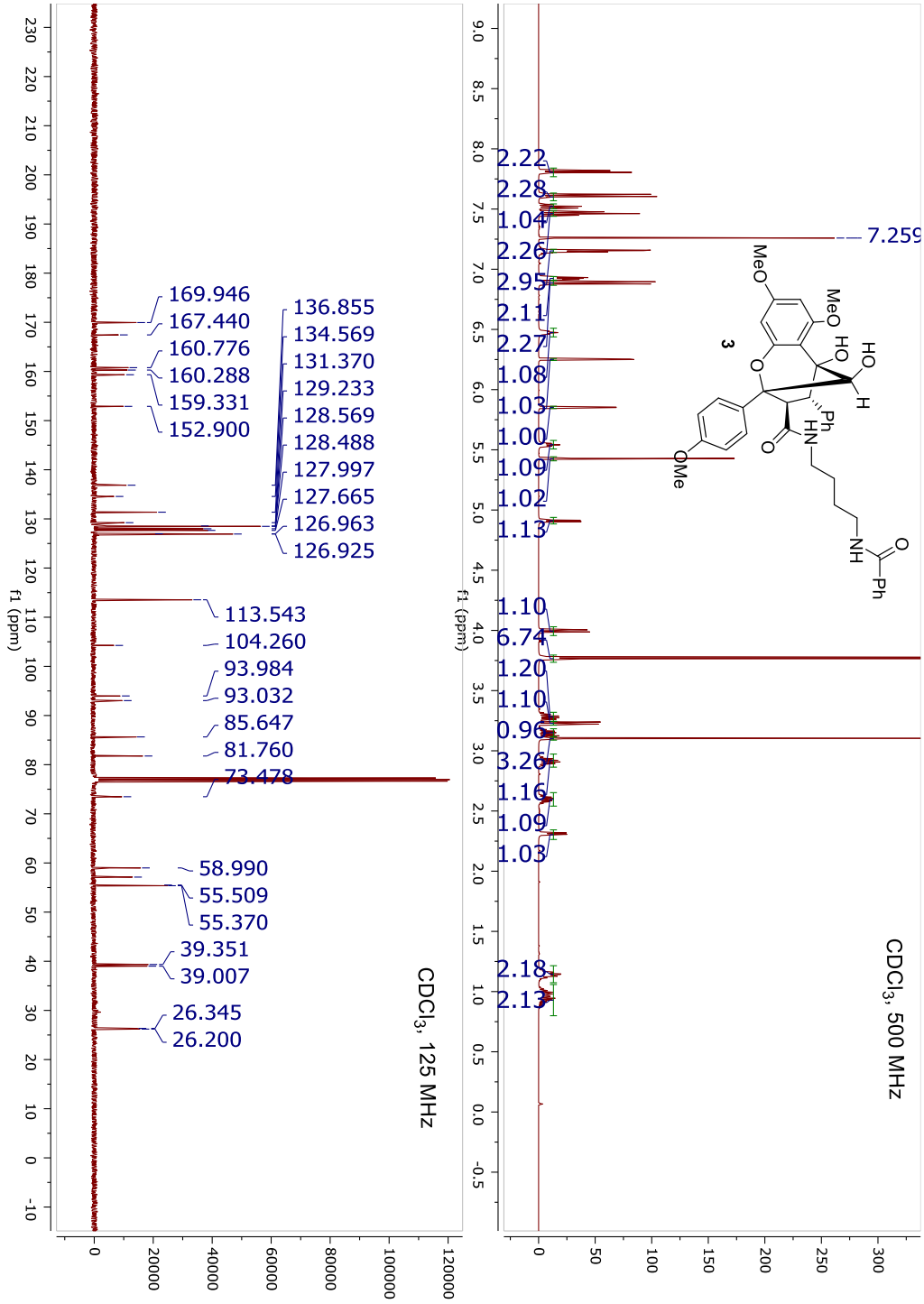


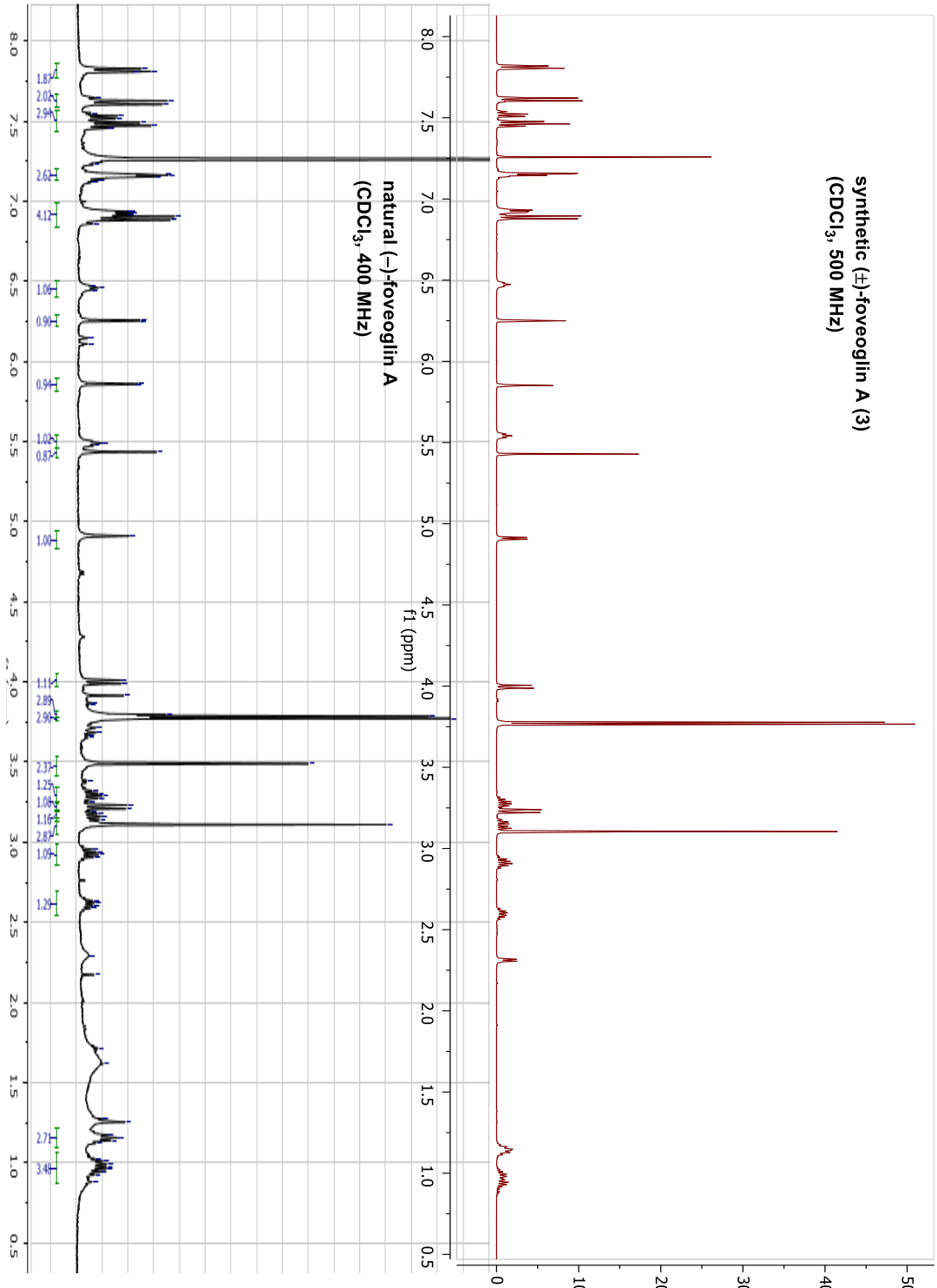

14
MeO
MeO
HO
O
O
H
Ph
Ph
OMe
Br
2.02
2.02
2.38
3.15
3.34
2.18
2.16
2.19
1.10
1.01
1.05
1.00
1.08
1.05
3.26
3.02
1.03
1.06
3.14
7.260
CDCl3, 500 MHz
f1 (ppm)
136.935
136.329
131.530
131.464
130.544
129.178
128.991
128.705
128.685
128.196
128.069
127.687
127.504
127.074
126.983
126.106
165.182
160.712
159.727
159.196
153.640
113.821
93.908
86.531
81.361
72.642
72.626
61.561
55.445
55.369
55.167
54.519
CDCl3, 125 MHz
f1 (ppm)

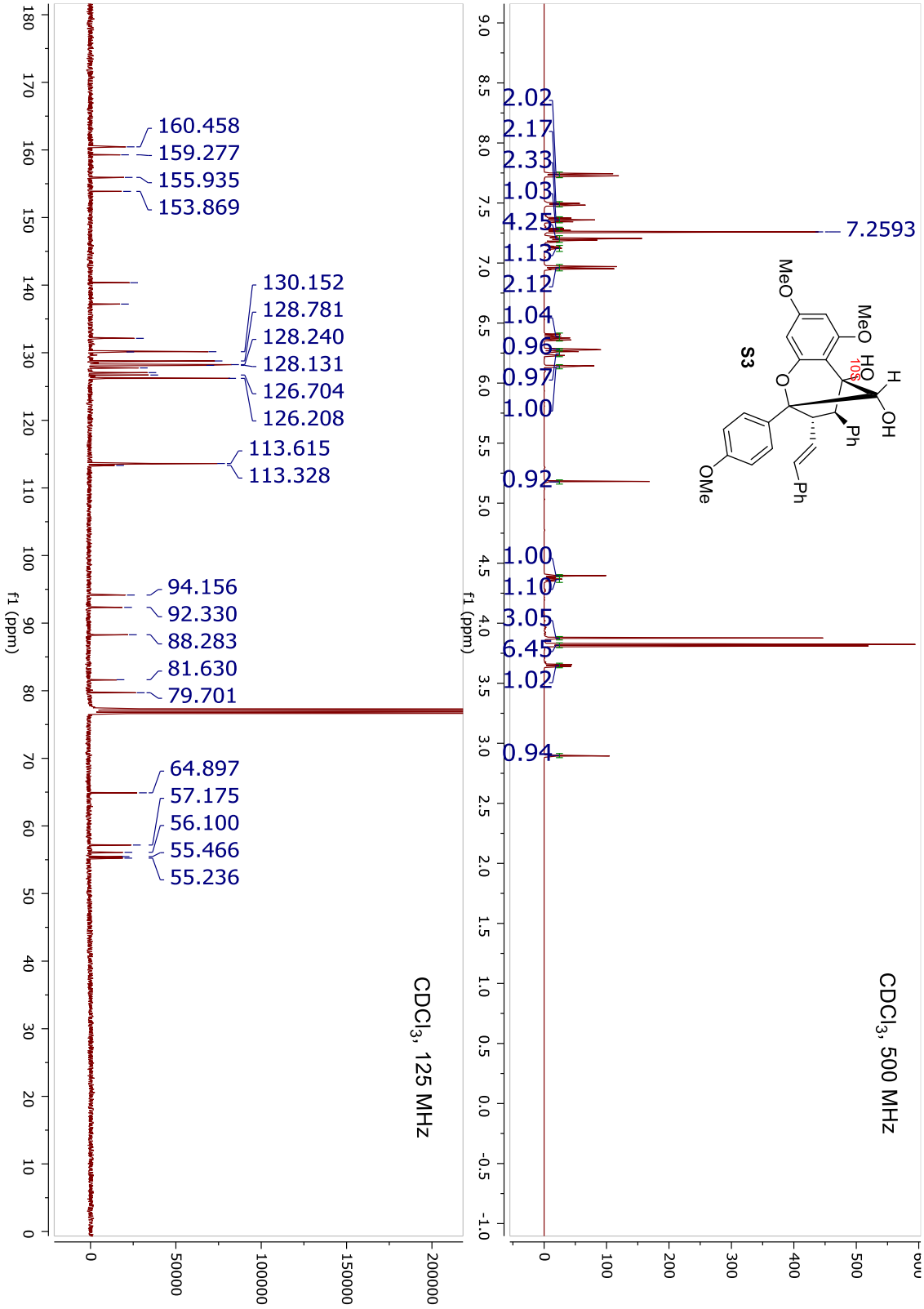

137.557
137.332
130.815
130.091
129.558
128.879
128.117
127.674
126.840
126.768
126.177
126.008
160.762
160.002
158.902
154.085
113.121
106.737
92.748
91.399
86.165
83.384
78.691
59.729
55.272
55.090
53.867
52.443
2.130
1.277
CDCl3, 125 MHz
f1 (ppm)
2.13
6.34
2.20
2.22
2.13
7.2601
1.00
1.07
1.00
1.06
0.99
2.92
3.10
1.02
1.06
2.84
8.92
8.54
CDCl3, 500 MHz
f1 (ppm)
S1
MeO
MeO
TMSO
H
Ph
Ph
OMe
O

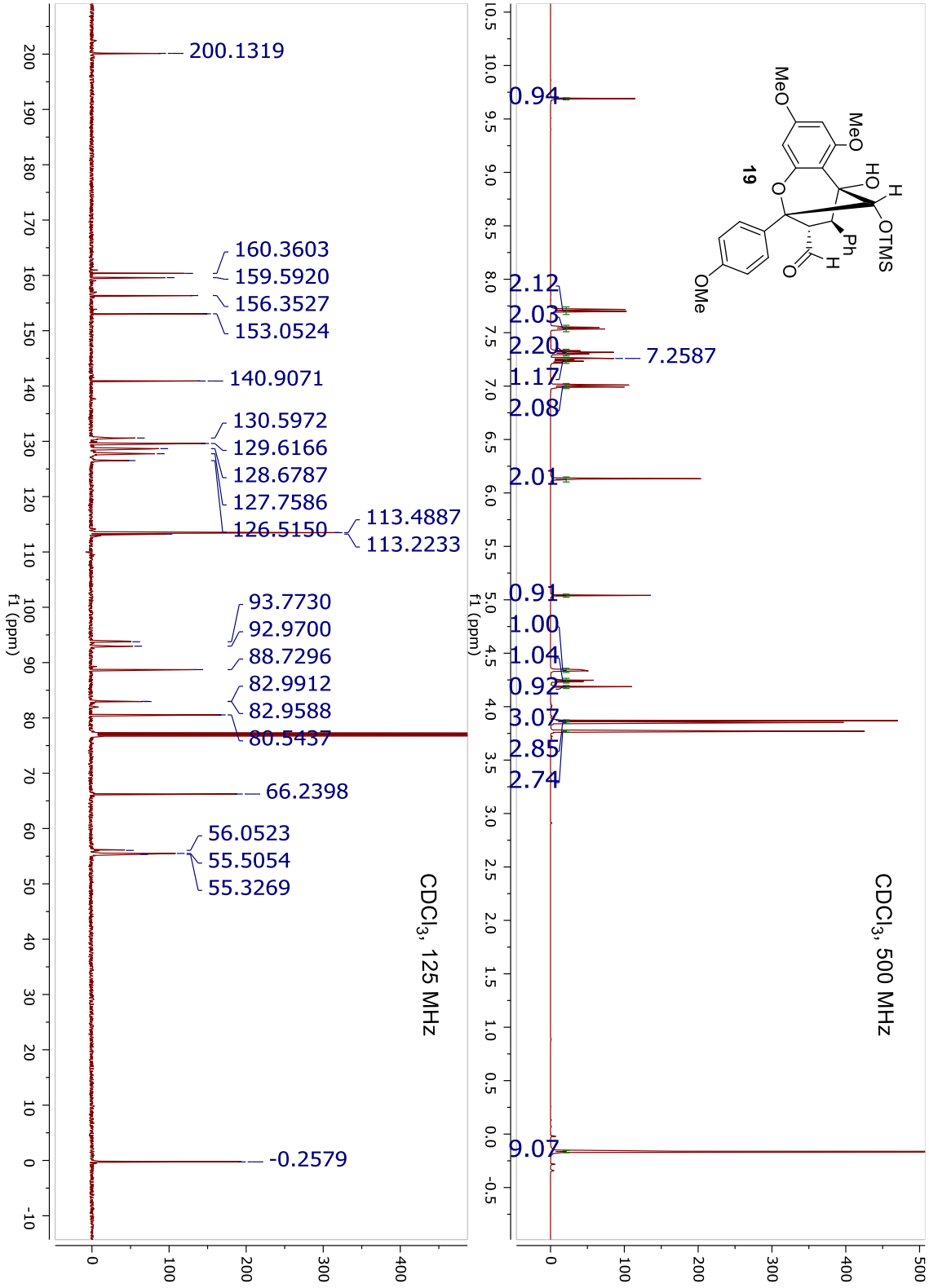

198.8093
160.8421
160.2196
159.5320
153.4225
137.0079
128.8110
128.6661
127.3641
126.9372
126.4679
113.9671
106.7112
92.9290
83.5273
83.1167
77.2969
76.9784
76.6619
61.4849
55.2771
55.1096
53.9240
52.3240
2.0688
1.2082
CDCl3, 125 MHz
f1 (ppm)
1.02
2.07
3.14
7.2598
2.24
2.25
1.02
1.00
1.06
1.21
6.67
1.08
2.96
9.03
8.87
CDCl3, 500 MHz
f1 (ppm)
MeO
MeO
TMSO
TMSO
15
O
Ph
H
H
O
OMe

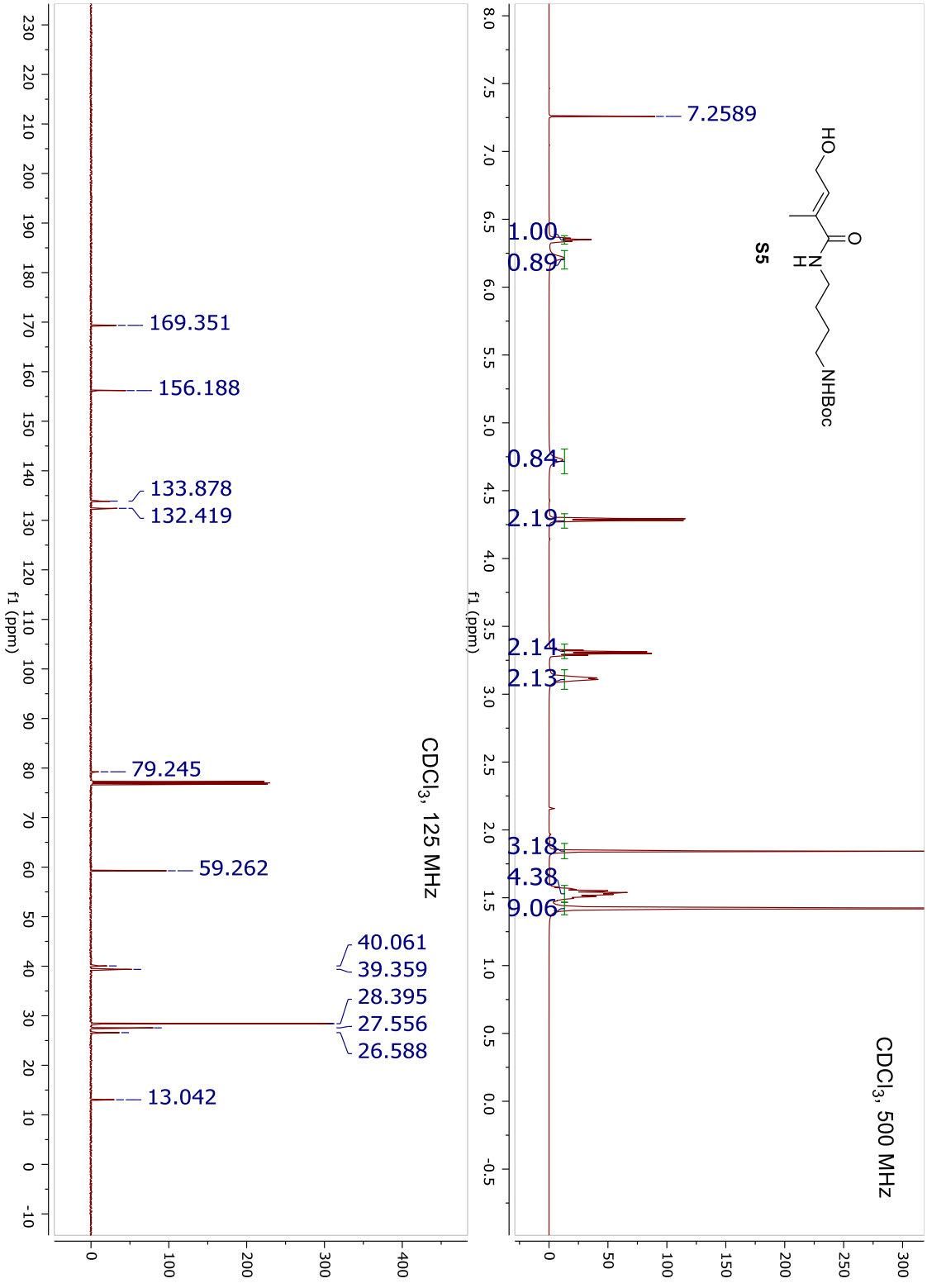

S2
MeO
MeO
TMSO
TMSO
H
Ph
HN
O
NH
O
Ph
OMe
CDCl3, 500 MHz
2.18
2.14
1.11
7.2589
2.16
3.18
2.23
2.24
1.01
1.00
1.04
1.02
1.12
1.11
7.30
2.37
1.12
3.57
1.17
1.12
2.39
2.18
9.08
9.18
CDCl3, 125 MHz
169.814
167.381
160.800
159.992
159.268
153.465
137.599
134.638
131.322
130.161
128.867
128.436
128.038
126.981
126.870
126.318
112.997
107.029
92.752
91.750
84.727
83.124
78.534
58.824
55.375
55.075
53.928
39.357
38.902
26.230
26.208
2.121
1.184
f1 (ppm)

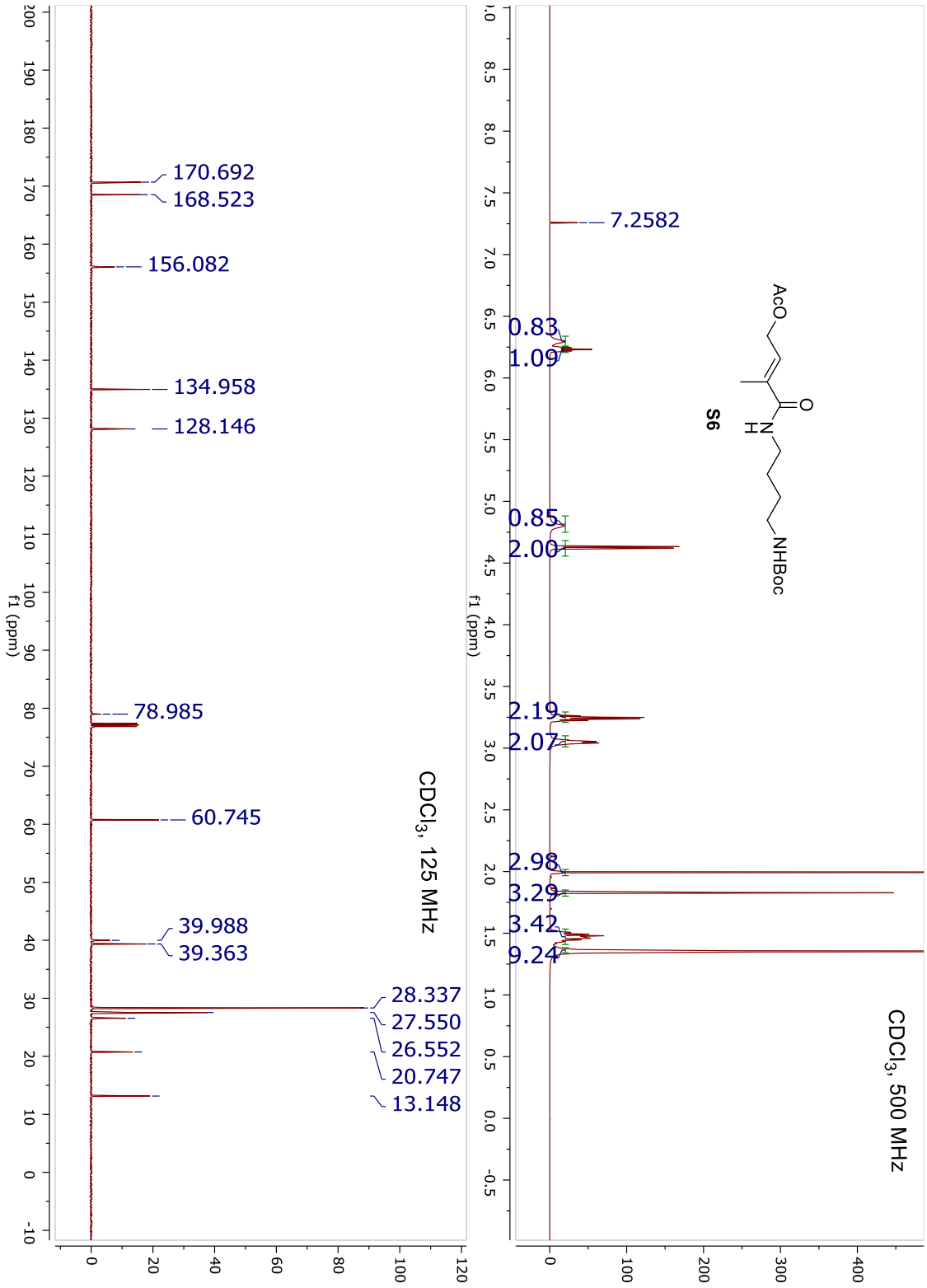

169.946
167.440
160.776
160.288
159.331
152.900
136.855
134.569
131.370
129.233
128.569
128.488
127.997
127.665
126.963
126.925
113.543
104.260
93.984
93.032
85.647
81.760
73.478
58.990
55.509
55.370
39.351
39.007
26.345
26.200
CDCl3, 125 MHz
f1 (ppm)
2.22
2.28
1.04
7.259
2.26
2.95
2.11
2.27
1.08
1.03
1.00
1.09
1.02
1.13
1.10
6.74
1.20
1.10
0.96
3.26
1.16
1.09
1.03
2.18
2.13
CDCl3, 500 MHz
f1 (ppm)
MeO
MeO
HO
HO
H
3
O
Ph
HN
O
OMe
NH
O
Ph

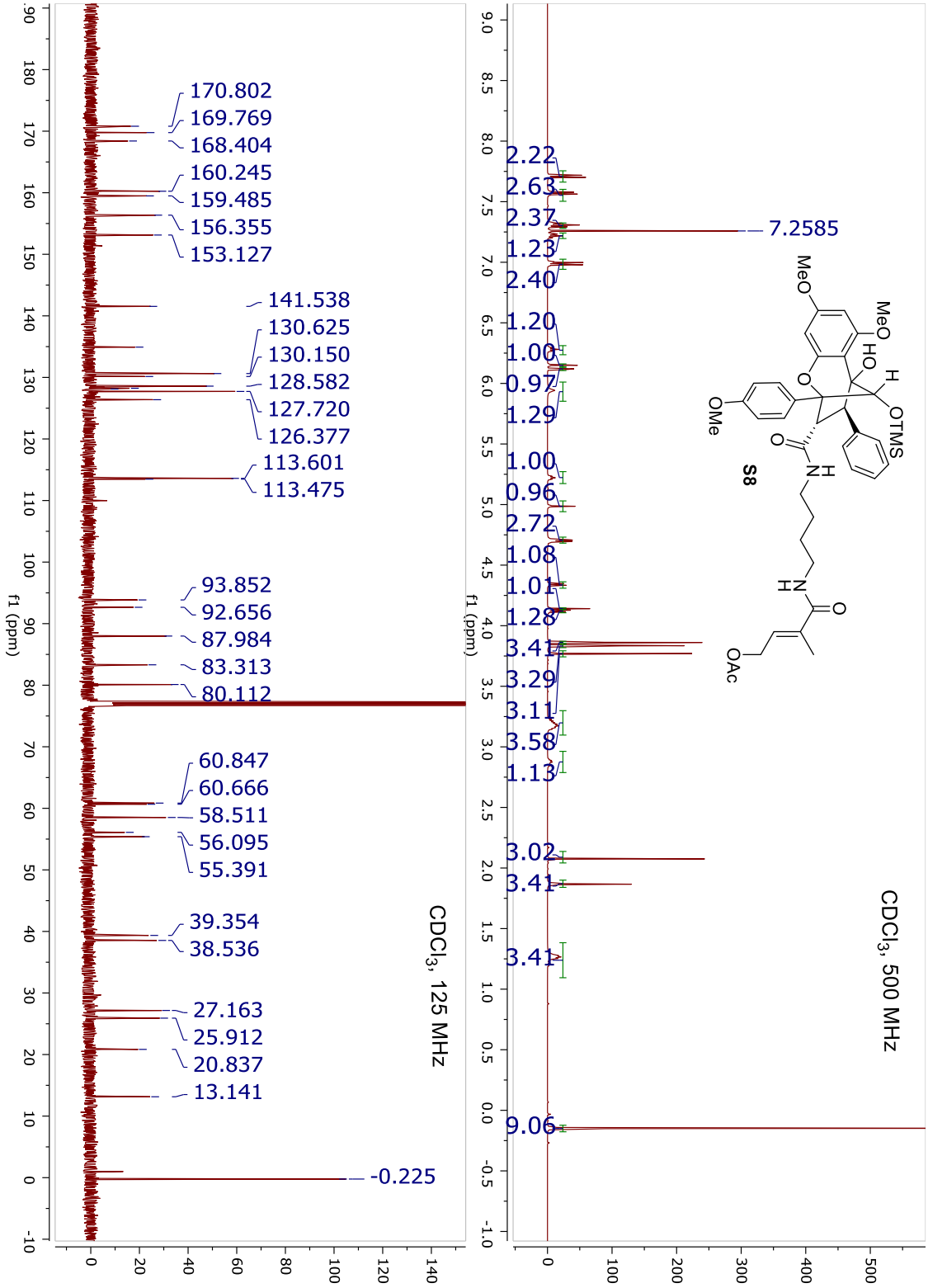

synthetic (±)-foveoglin A (3)
(CDCl3, 500 MHz)
natural (–)-foveoglin A
(CDCl3, 400 MHz)
f1 (ppm)

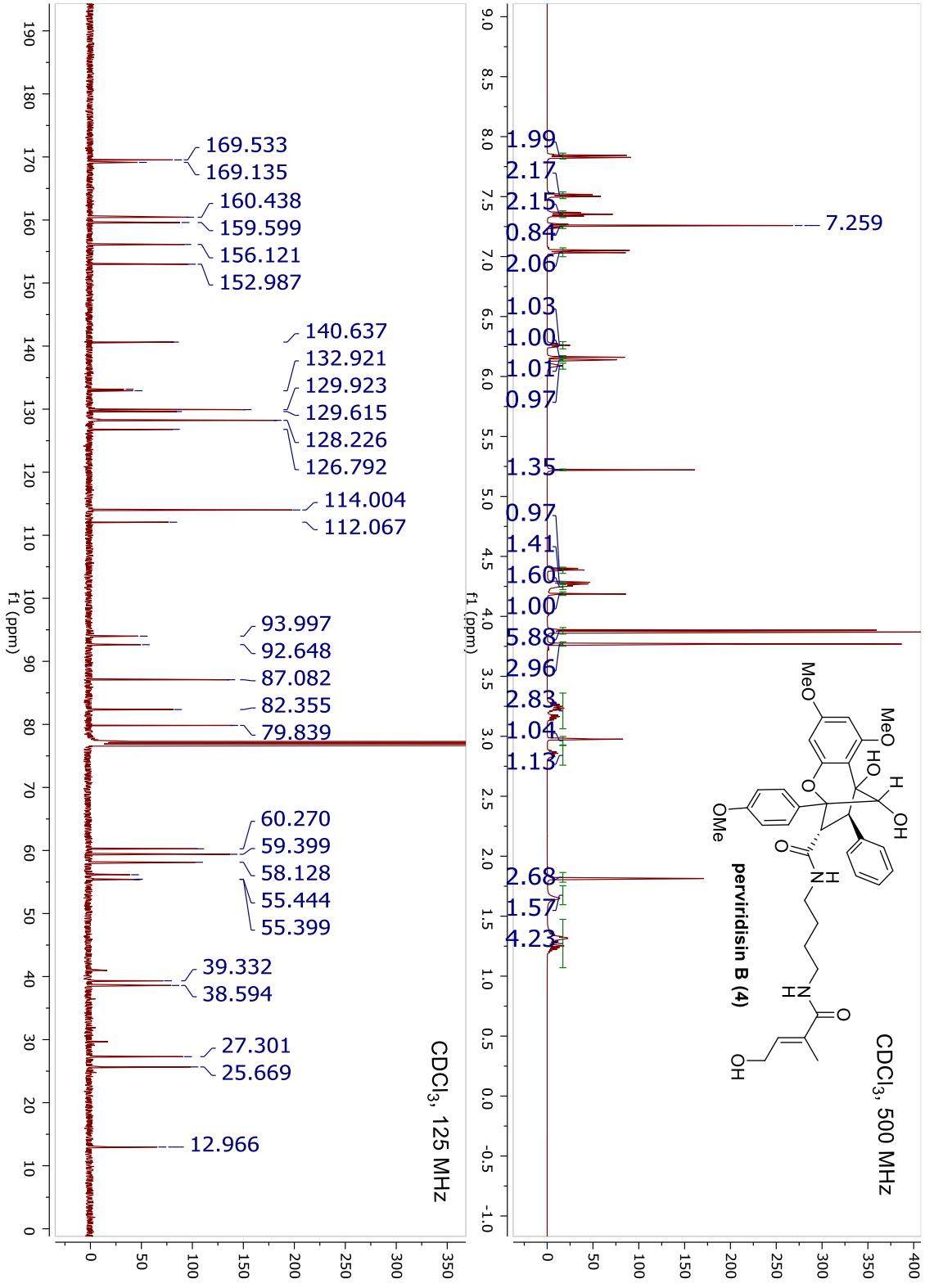

160.458
159.277
155.935
153.869
130.152
128.781
128.240
128.131
126.704
126.208
113.615
113.328
94.156
92.330
88.283
81.630
79.701
64.897
57.175
56.100
55.466
55.236
CDCl3, 125 MHz
f1 (ppm)
2.02
2.17
2.33
1.03
4.25
1.13
2.12
1.04
0.96
0.97
1.00
0.92
1.00
1.10
3.05
6.45
1.02
0.94
7.2593
CDCl3, 500 MHz
f1 (ppm)
MeO
MeO
HO
H
OH
O
Ph
Ph
OMe
S3

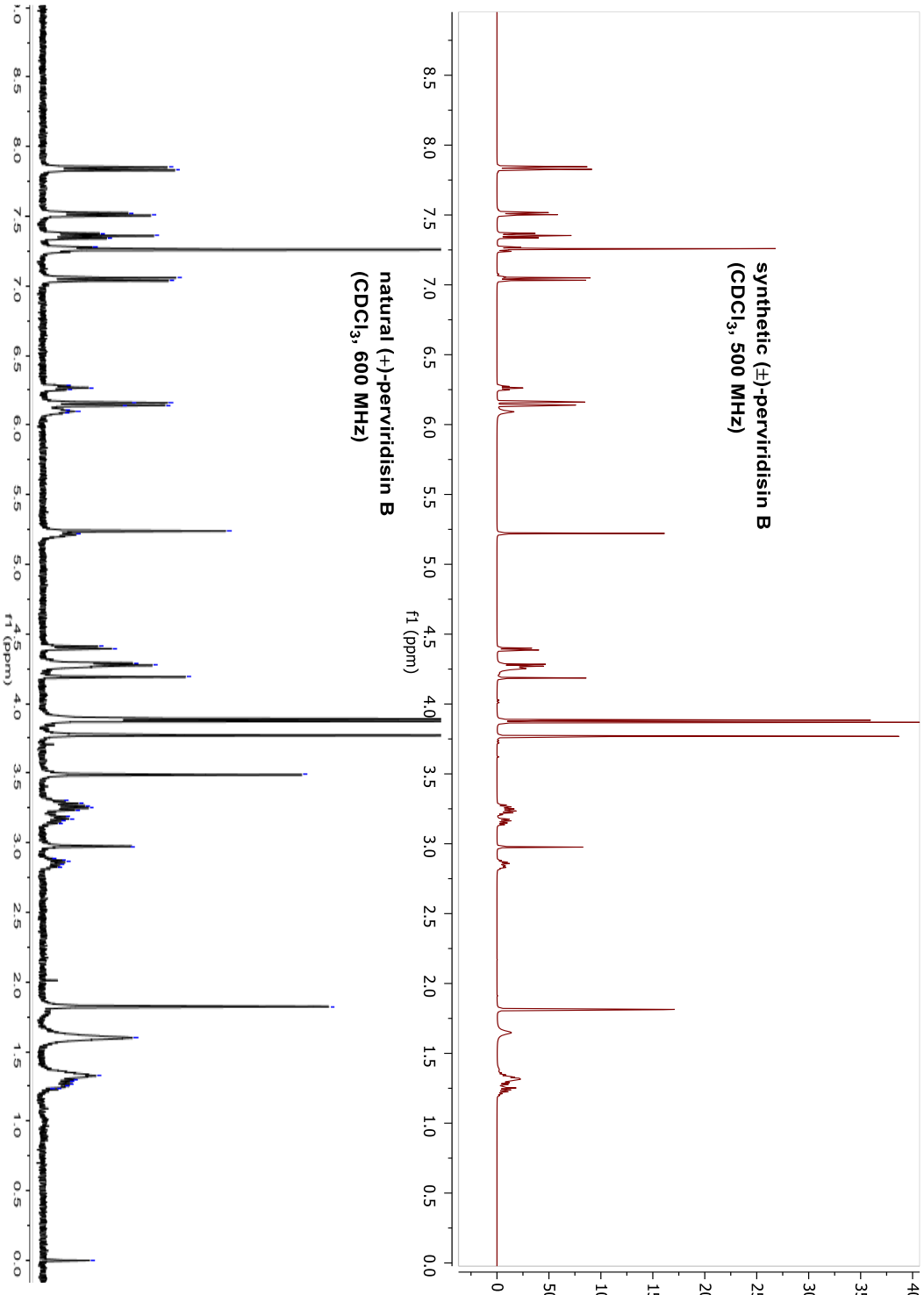

200.1319
160.3603
159.5920
156.3527
153.0524
140.9071
130.5972
129.6166
128.6787
127.7586
126.5150
113.4887
113.2233
93.7730
92.9700
88.7296
82.9912
82.9588
80.5437
66.2398
56.0523
55.5054
55.3269
-0.2579
f1 (ppm)
CDCl3, 125 MHz
0.94
2.12
2.03
2.20
7.2587
1.17
2.08
2.01
0.91
1.00
1.04
0.92
3.07
2.85
2.74
9.07
f1 (ppm)
CDCl3, 500 MHz
MeO
MeO
HO
H
OTMS
19
O
Ph
H
O
OMe

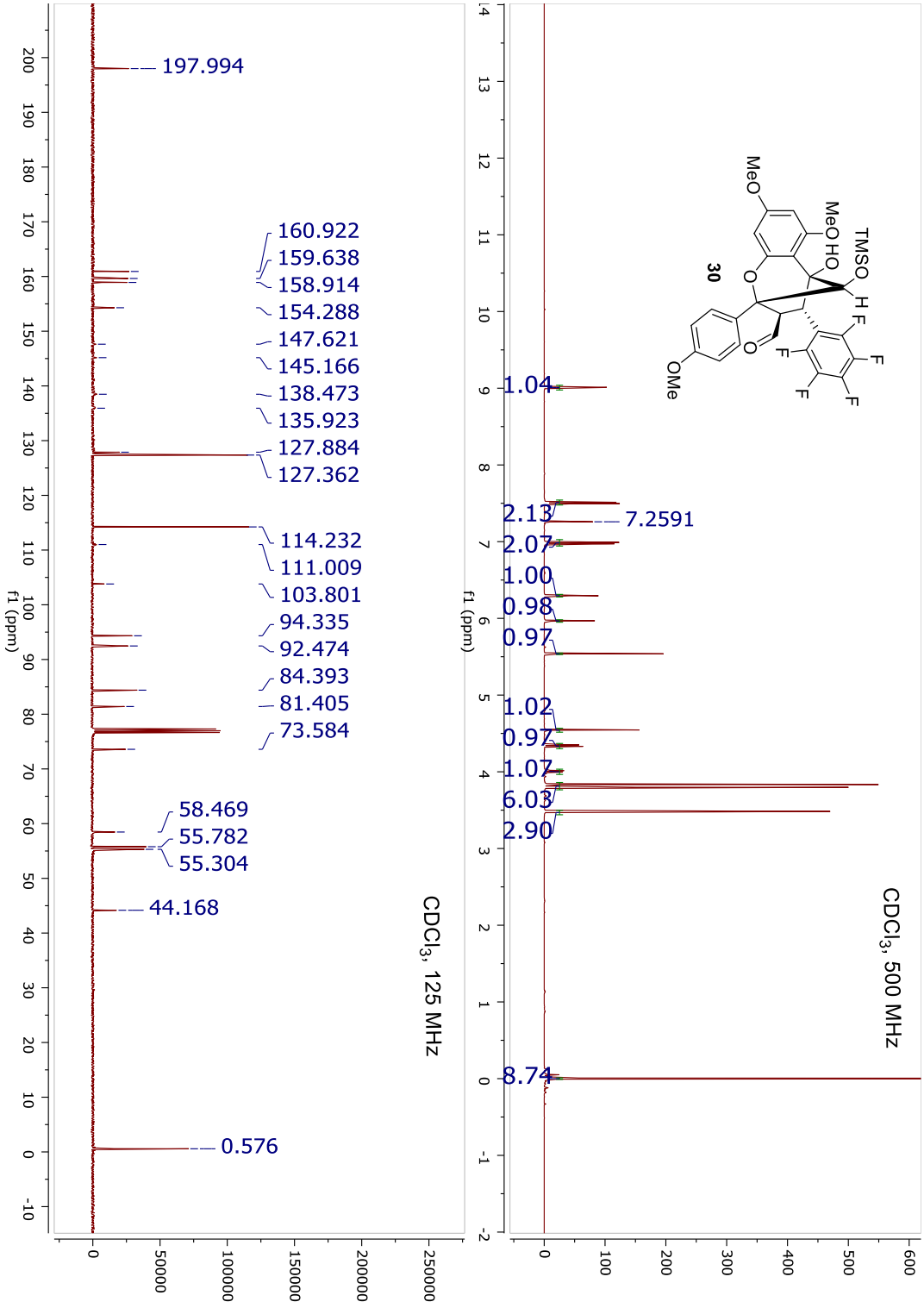

7.2589
1.00
0.89
0.84
2.19
2.14
2.13
3.18
4.38
9.06
S5
HO
O
N
H
NHBoc
CDCl3, 500 MHz
f1 (ppm)
169.351
156.188
133.878
132.419
79.245
59.262
40.061
39.359
28.395
27.556
26.588
13.042
CDCl3, 125 MHz
f1 (ppm)


170.692
168.523
156.082
134.958
128.146
78.985
60.745
39.988
39.363
28.337
27.550
26.552
20.747
13.148
CDCl3, 125 MHz
f1 (ppm)
7.2582
0.83
1.09
0.85
2.00
2.19
2.07
2.98
3.29
3.42
9.24
CDCl3, 500 MHz
f1 (ppm)
S6
AcO
O
N
H
NHBoc

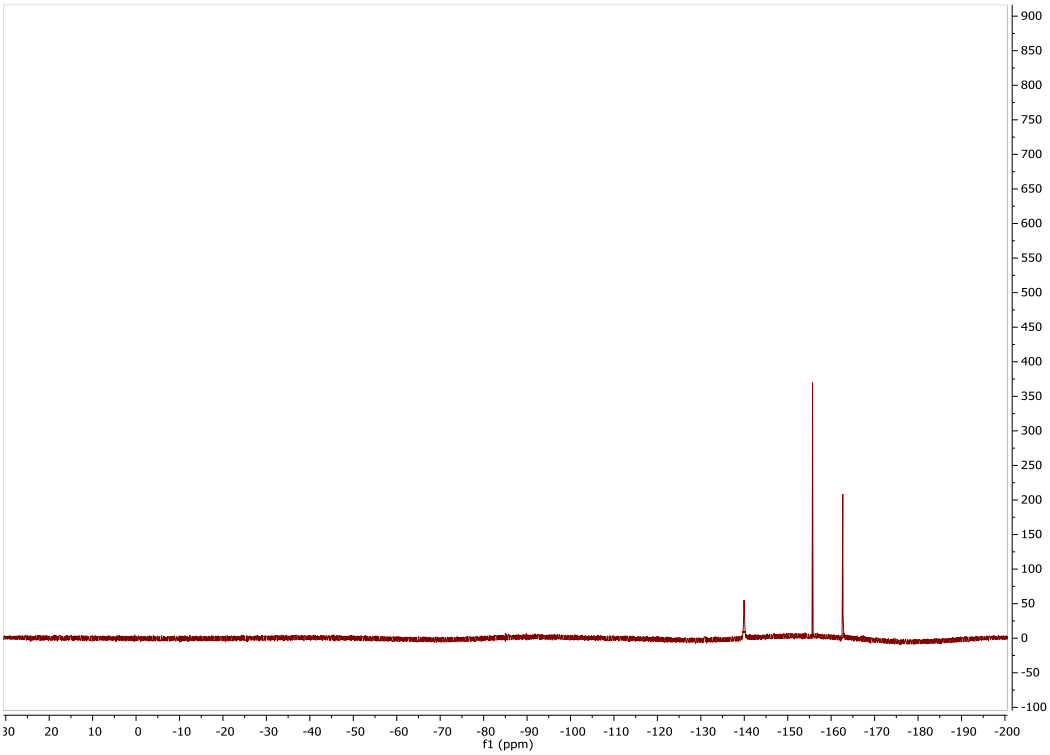

170.802
169.769
168.404
160.245
159.485
156.355
153.127
141.538
130.625
130.150
128.582
127.720
126.377
113.601
113.475
93.852
92.656
87.984
83.313
80.112
60.847
60.666
58.511
56.095
55.391
39.354
38.536
27.163
25.912
20.837
13.141
-0.225
CDCl3, 125 MHz
f1 (ppm)
2.22
2.63
2.37
1.23
2.40
1.20
1.00
0.97
1.29
1.00
0.96
2.72
1.08
1.01
1.28
3.41
3.29
3.11
3.58
1.13
3.02
3.41
3.41
9.06
7.2585
CDCl3, 500 MHz
f1 (ppm)
MeO
MeO
HO
H
OTMS
OMe
O
N
H
S8
N
H
O
OAc


169.533
169.135
160.438
159.599
156.121
152.987
140.637
132.921
129.923
129.615
128.226
126.792
114.004
112.067
93.997
92.648
87.082
82.355
79.839
60.270
59.399
58.128
55.444
55.399
39.332
38.594
27.301
25.669
12.966
CDCl3, 125 MHz
f1 (ppm)
1.99
2.17
2.15
7.259
0.84
2.06
1.03
1.00
1.01
0.97
1.35
0.97
1.41
1.60
1.00
5.88
2.96
2.83
1.04
1.13
2.68
1.57
4.23
CDCl3, 500 MHz
f1 (ppm)
MeO
MeO
HO
H
OH
O
OMe
O
N
H
N
H
O
OH
periviridisin B (4)

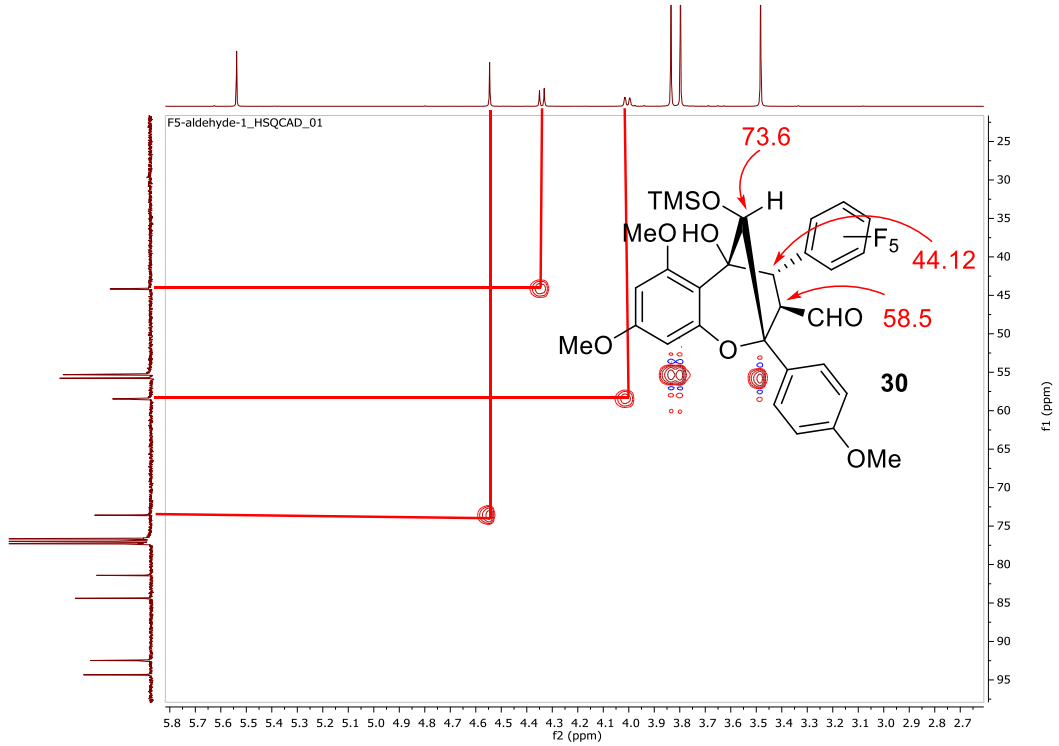

synthetic (±)-perviridisin B
(CDCl3, 500 MHz)
natural (+)-perviridisin B
(CDCl3, 600 MHz)
f1 (ppm)


197.994
160.922
159.638
158.914
154.288
147.621
145.166
138.473
135.923
127.884
127.362
114.232
111.009
103.801
94.335
92.474
84.393
81.405
73.584
58.469
55.782
55.304
44.168
0.576
CDCl3, 125 MHz
f1 (ppm)
1.04
2.13
7.2591
2.07
1.00
0.98
0.97
1.02
0.97
1.07
6.03
2.90
8.74
CDCl3, 500 MHz
f1 (ppm)
MeO
MeO
HO
TMSO
H
F
F
F
F
F
O
O
O
OMe
30

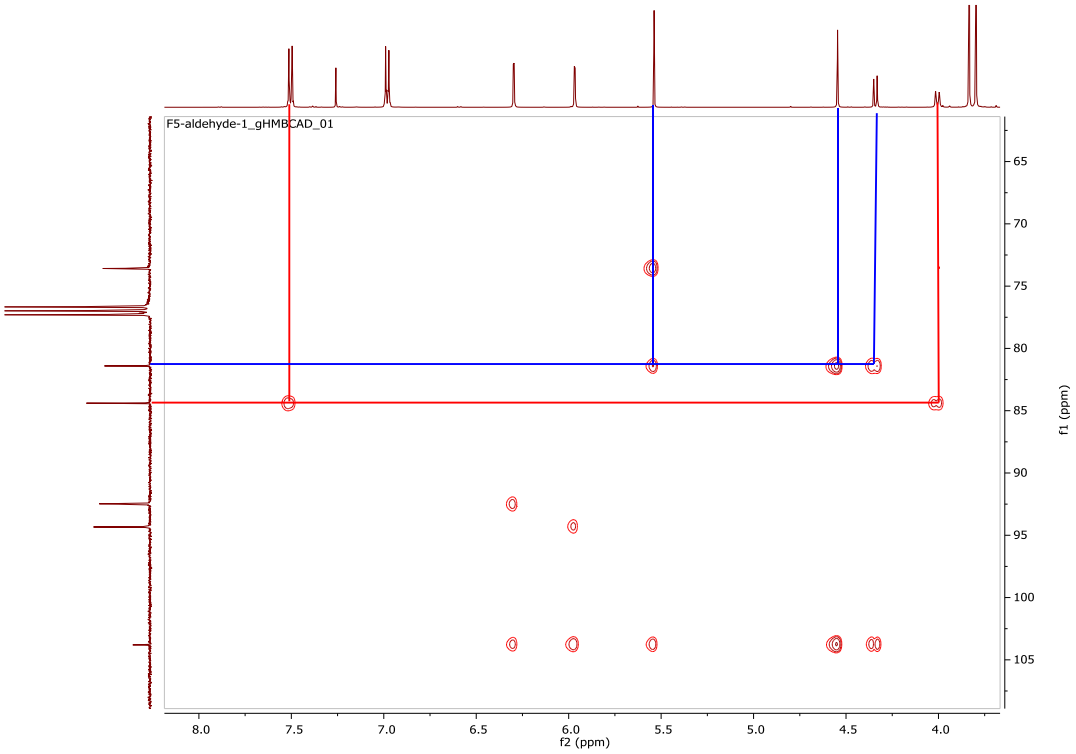
^{19}F NMR for compound **30**, $CDCl_3$, 375 MHz.

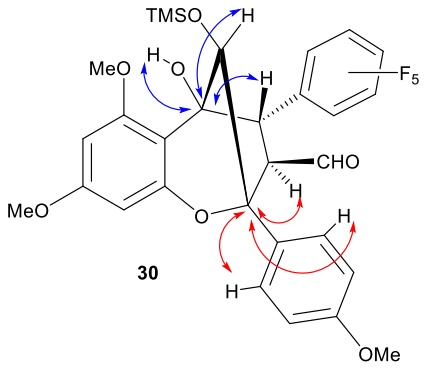


HSQC



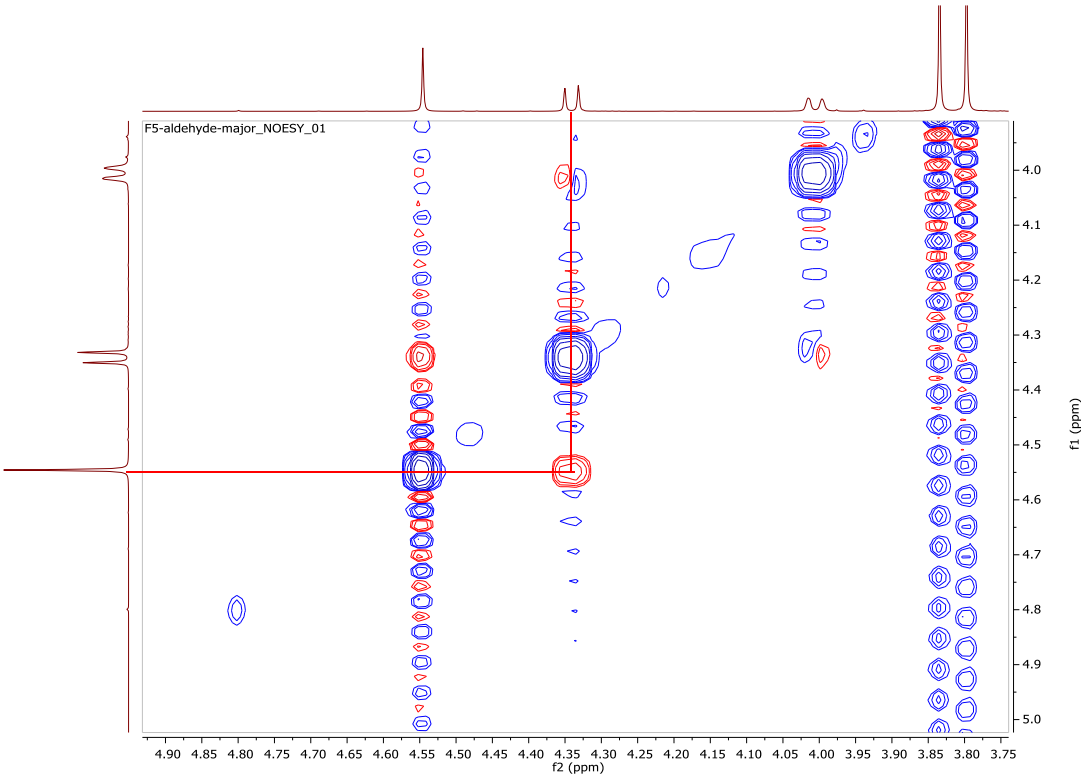
HMBC (compound **30**):

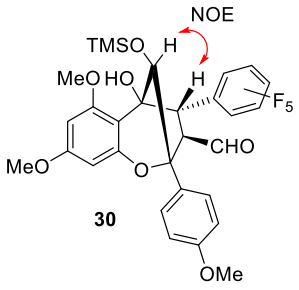




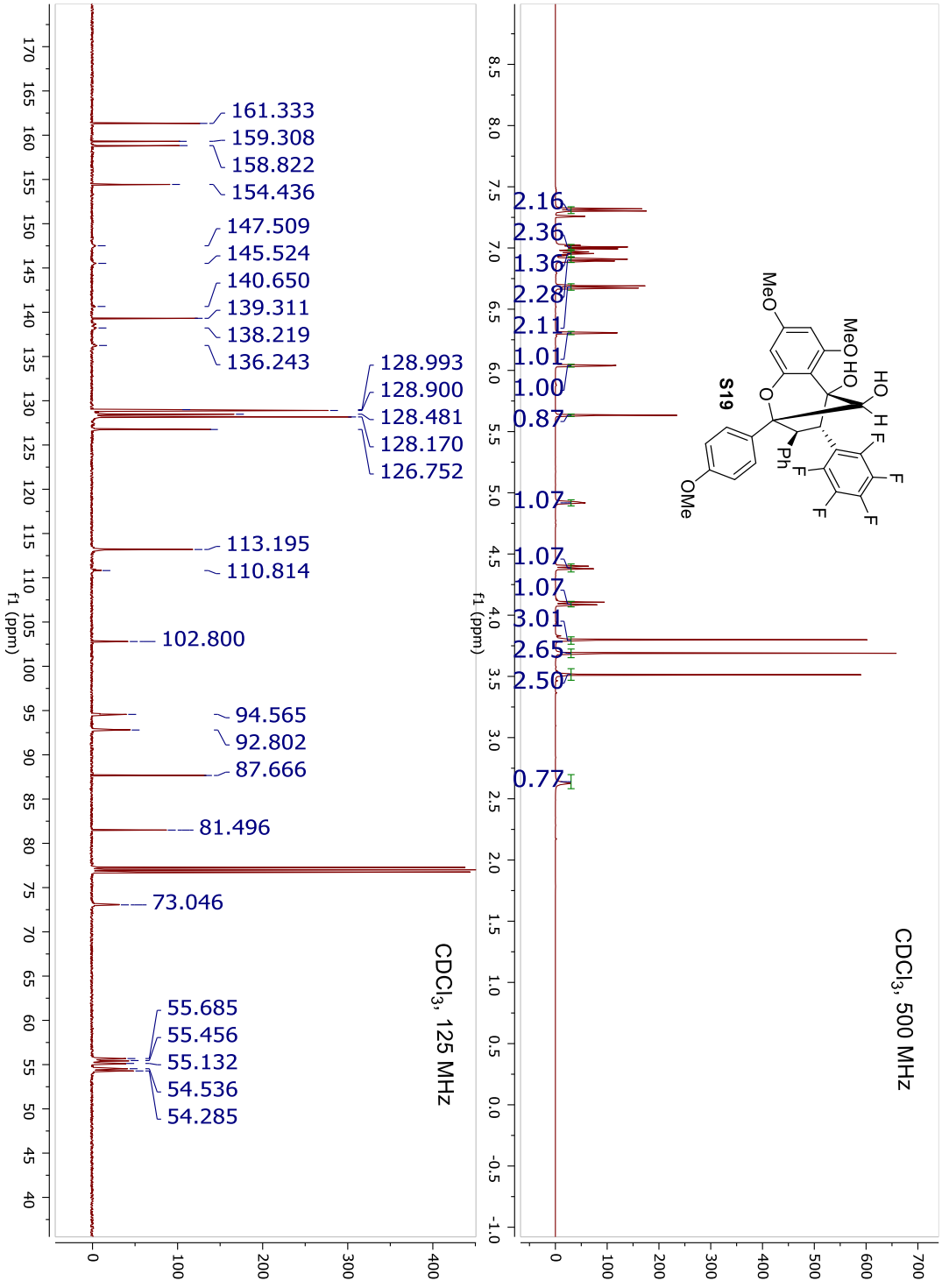
30

NOESY (compound **30**):

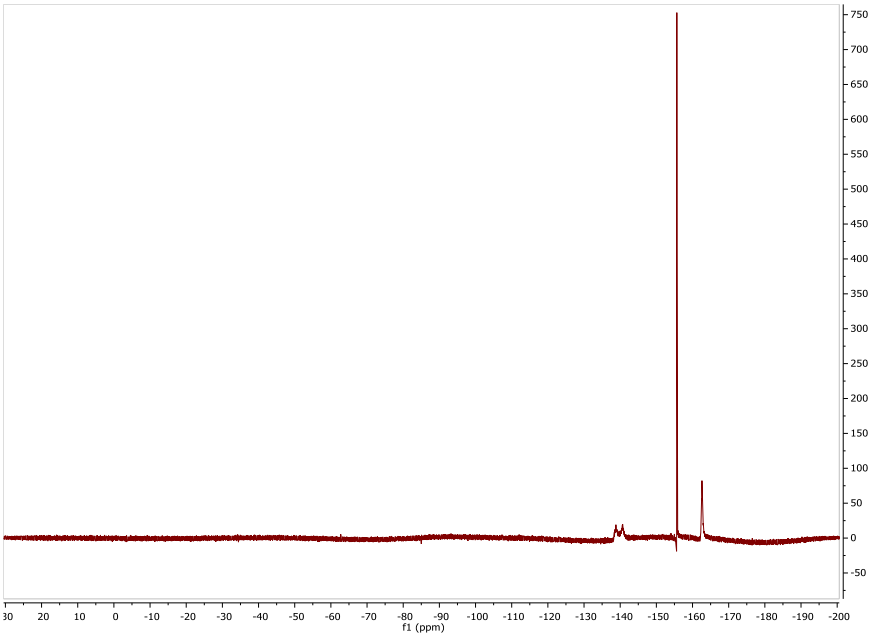




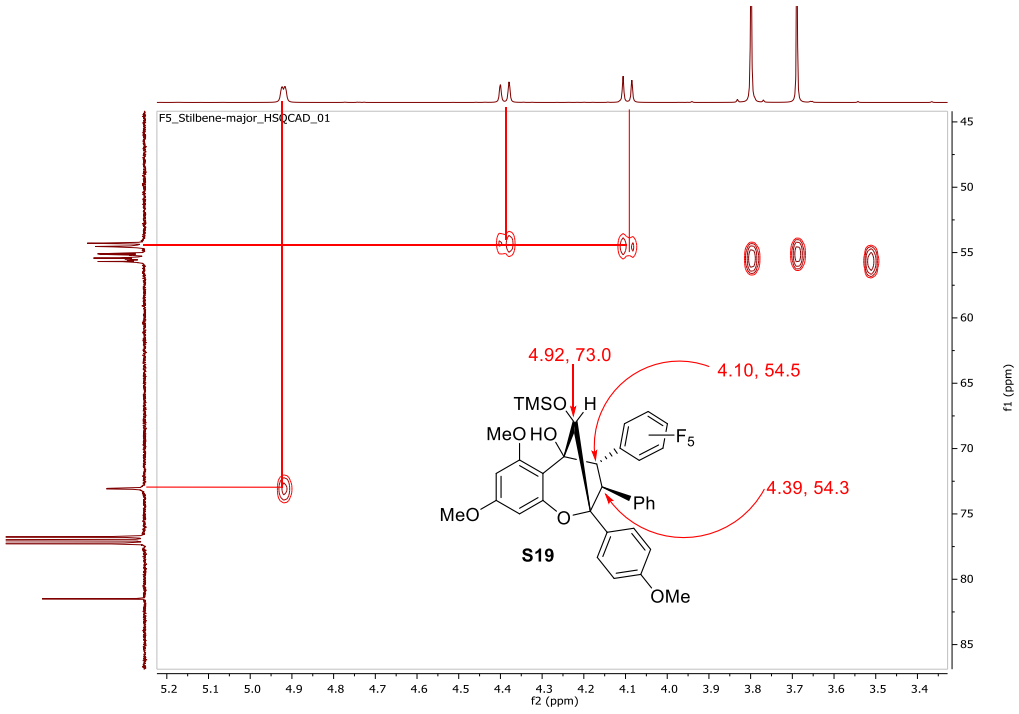
30


161.333
159.308
158.822
154.436
147.509
145.524
140.650
139.311
138.219
136.243
128.993
128.900
128.481
128.170
126.752
113.195
110.814
102.800
94.565
92.802
87.666
81.496
73.046
55.685
55.456
55.132
54.536
54.285
CDCl3, 125 MHz
f1 (ppm)
2.16
2.36
1.36
2.28
2.11
1.01
1.00
0.87
1.07
1.07
1.07
3.01
2.65
2.50
0.77
CDCl3, 500 MHz
S19
MeO
MeO
HO
HO
H
F
F
F
F
F
Ph
O
OMe

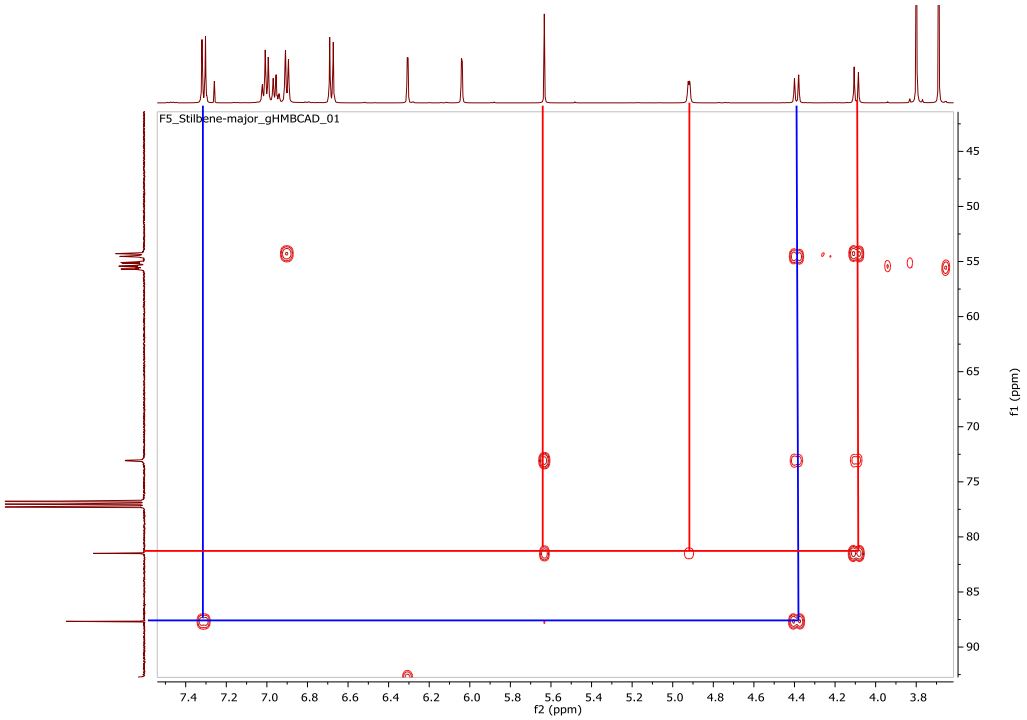
^{19}F NMR for compound **S19**, $CDCl_3$, 375 MHz.

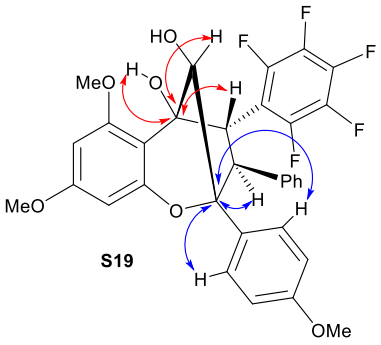


HSQC (compound **S19**):



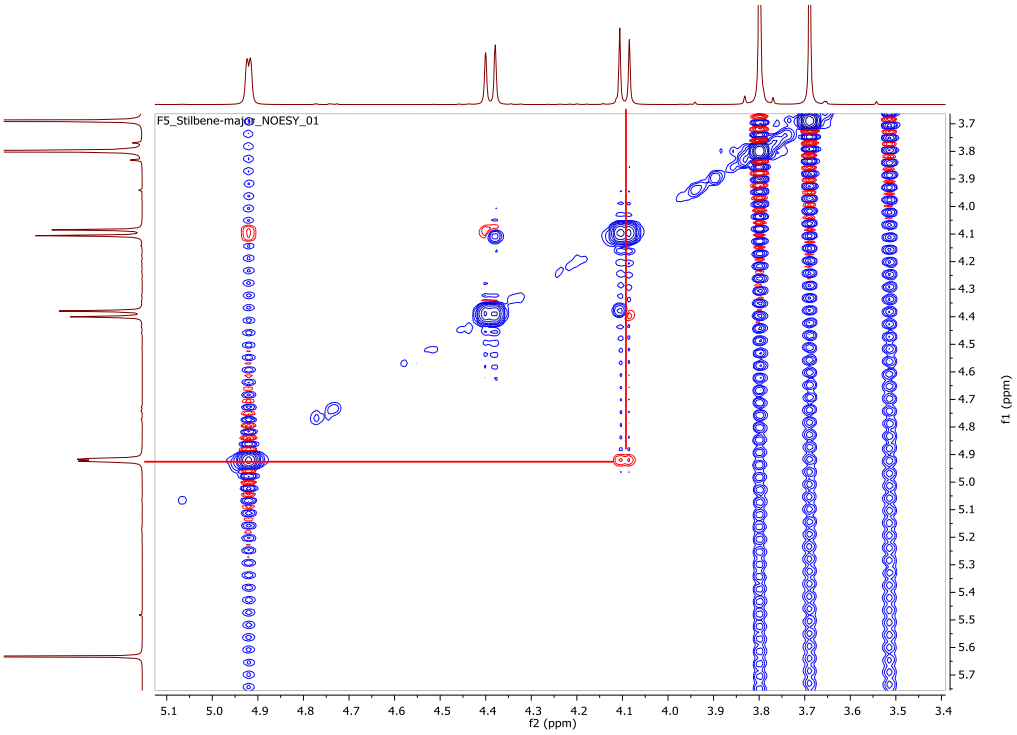
HMBC (compound **S19**):

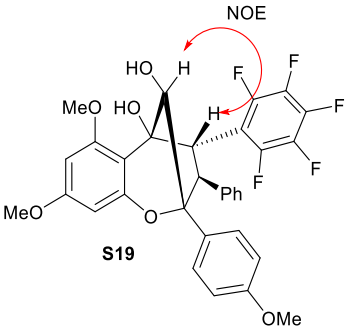




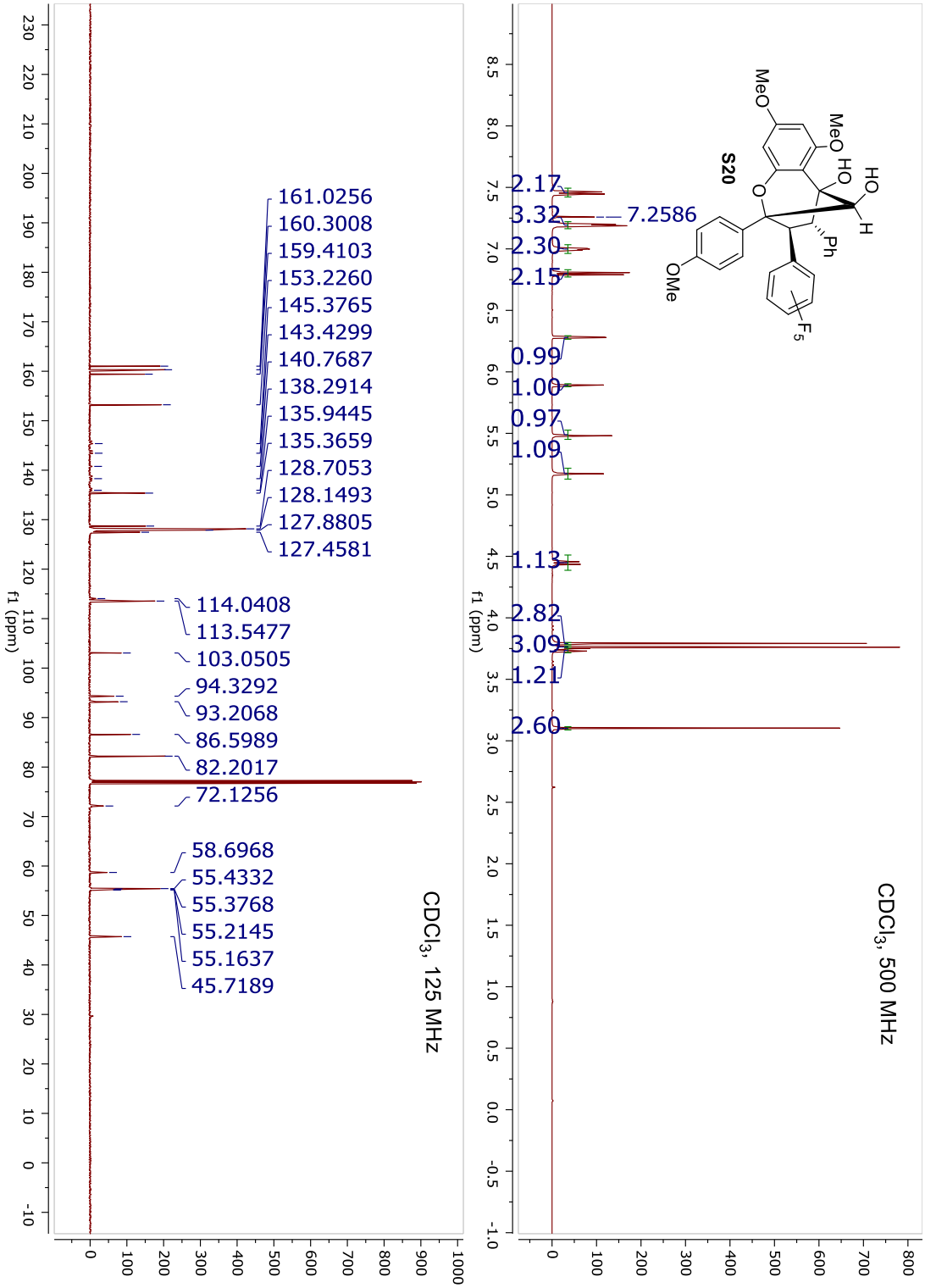
S19

NOESY (compound **S19**):

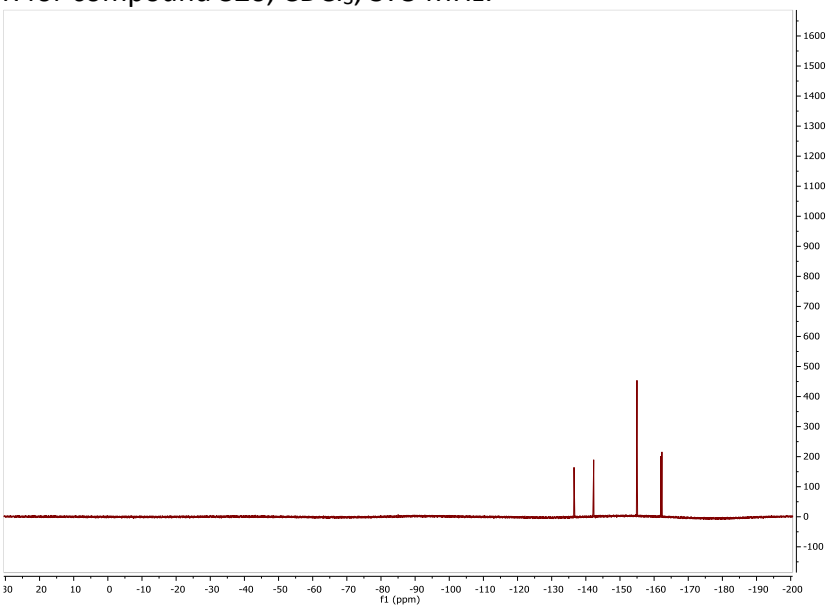




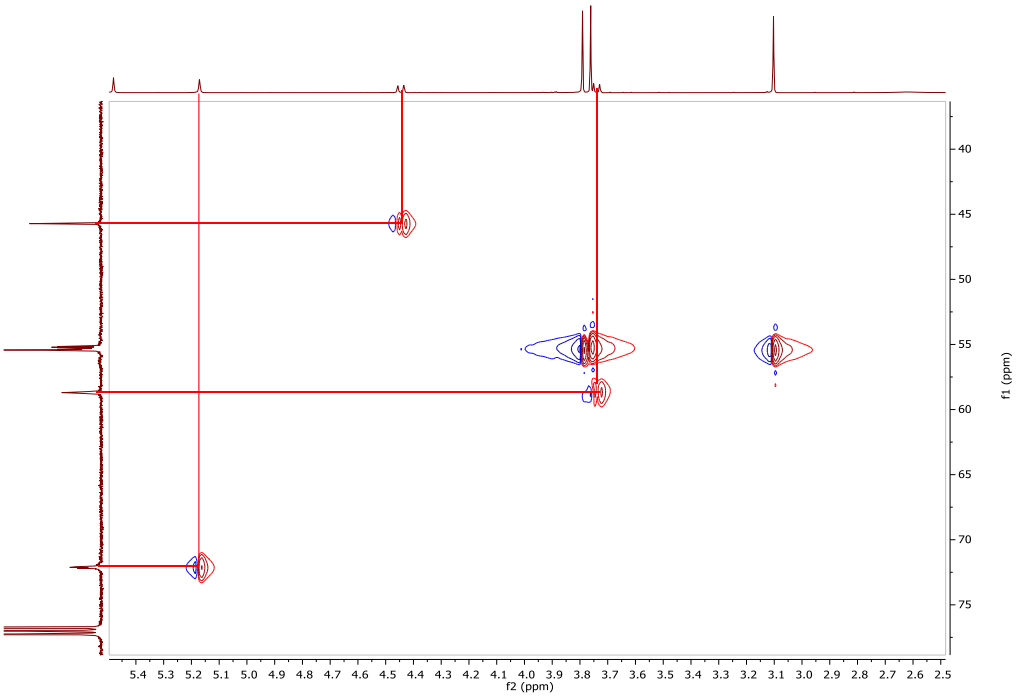
S19

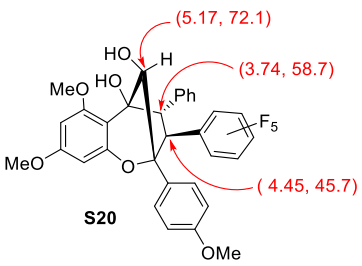

S20
MeO
MeO
HO
HO
H
Ph
OMe
F5
2.17
3.32
7.2586
2.30
2.15
0.99
1.00
0.97
1.09
1.13
2.82
3.09
1.21
2.60
CDCl3, 500 MHz
f1 (ppm)
161.0256
160.3008
159.4103
153.2260
145.3765
143.4299
140.7687
138.2914
135.9445
135.3659
128.7053
128.1493
127.8805
127.4581
114.0408
113.5477
103.0505
94.3292
93.2068
86.5989
82.2017
72.1256
58.6968
55.4332
55.3768
55.2145
55.1637
45.7189
CDCl3, 125 MHz
f1 (ppm)

^{19}F NMR for compound **S20**, $CDCl_3$, 375 MHz.



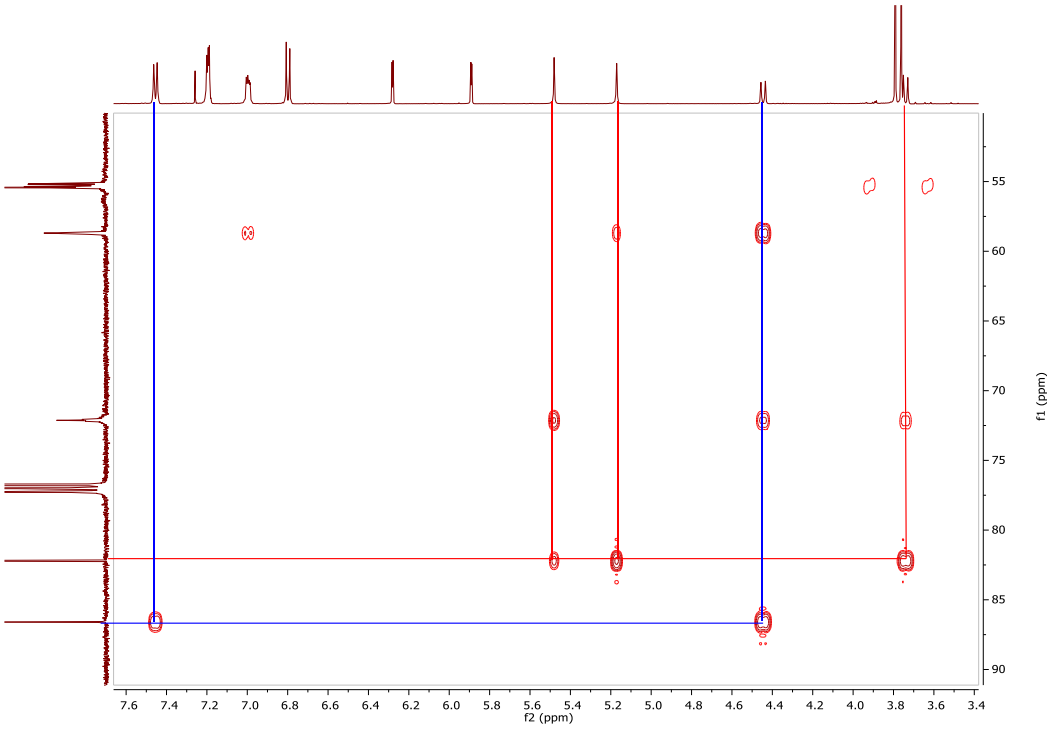
HSQC (compound **S20**):

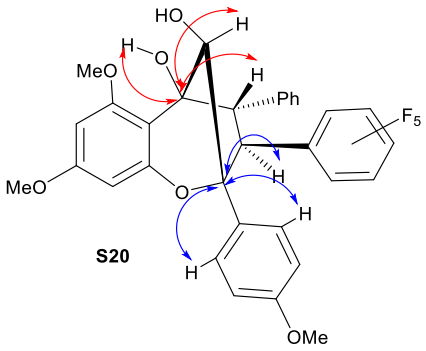




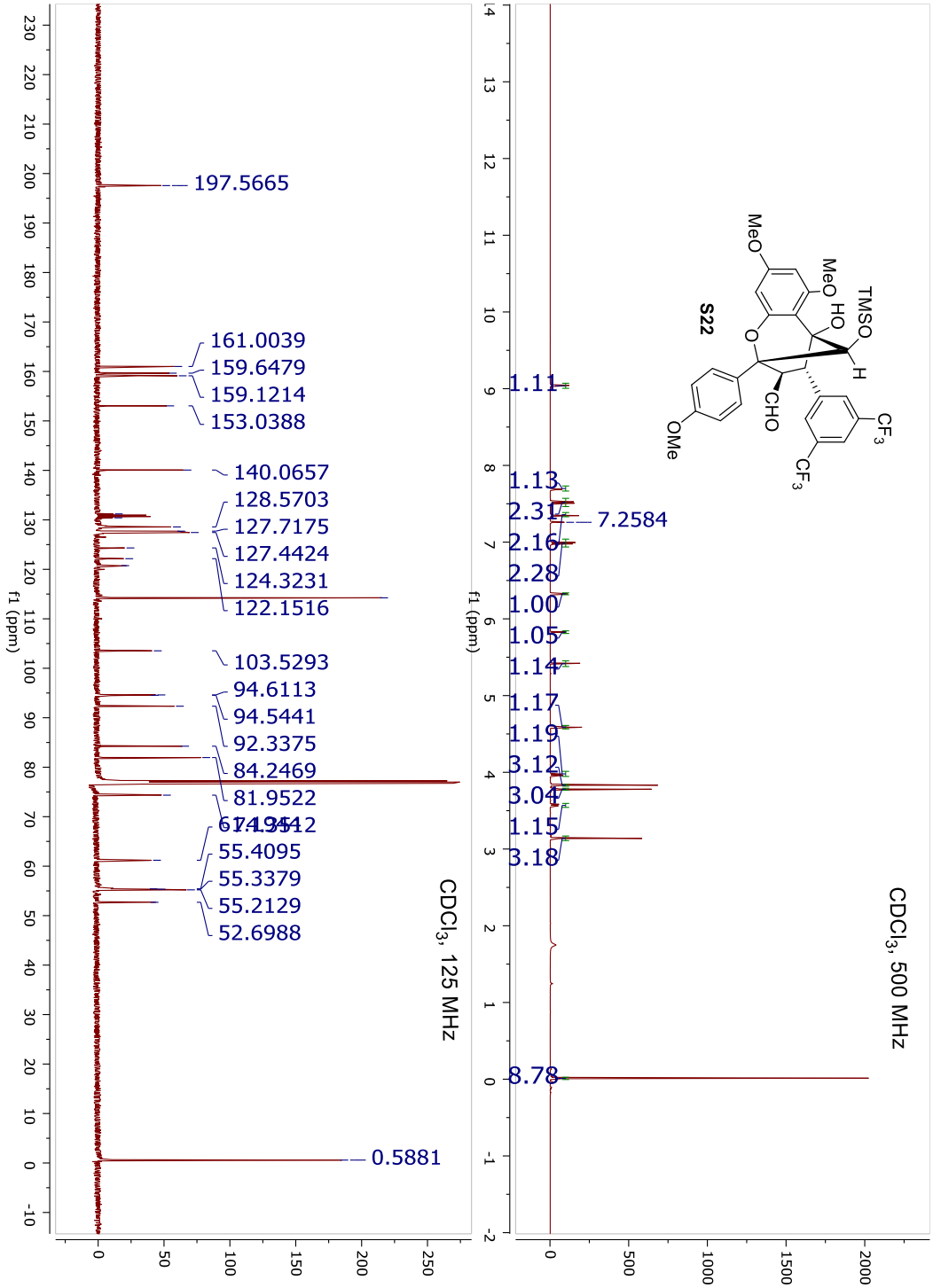
S20

HMBC (compound **S20**):

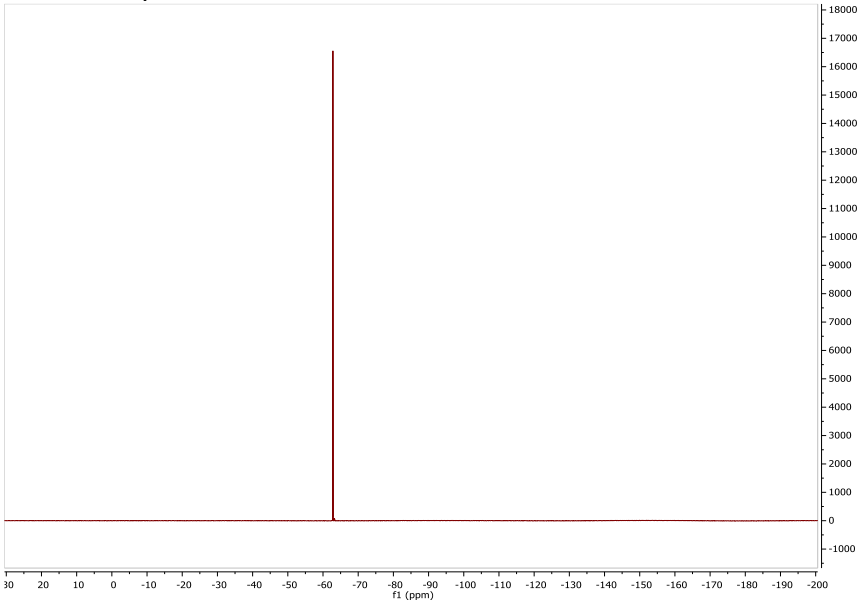




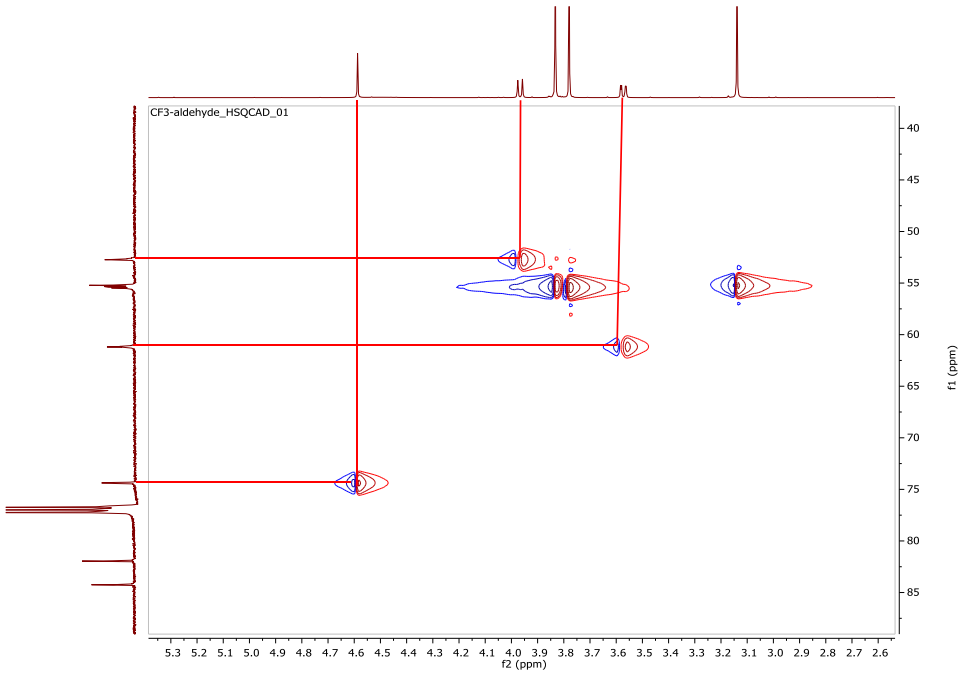
S20

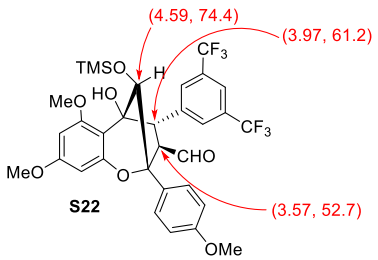

S22
MeO
MeO
HO
TMSO
H
O
CHO
OMe
CF3
CF3
CDCl3, 500 MHz
1.11
1.13
2.31
7.2584
2.16
2.28
1.00
1.05
1.14
1.17
1.19
3.12
3.04
1.15
3.18
8.78
CDCl3, 125 MHz
197.5665
161.0039
159.6479
159.1214
153.0388
140.0657
128.5703
127.7175
127.4424
124.3231
122.1516
103.5293
94.6113
94.5441
92.3375
84.2469
81.9522
55.4095
55.3379
55.2129
52.6988
0.5881
f1 (ppm)

^{19}F NMR for compound **S22**, $CDCl_3$, 375 MHz.

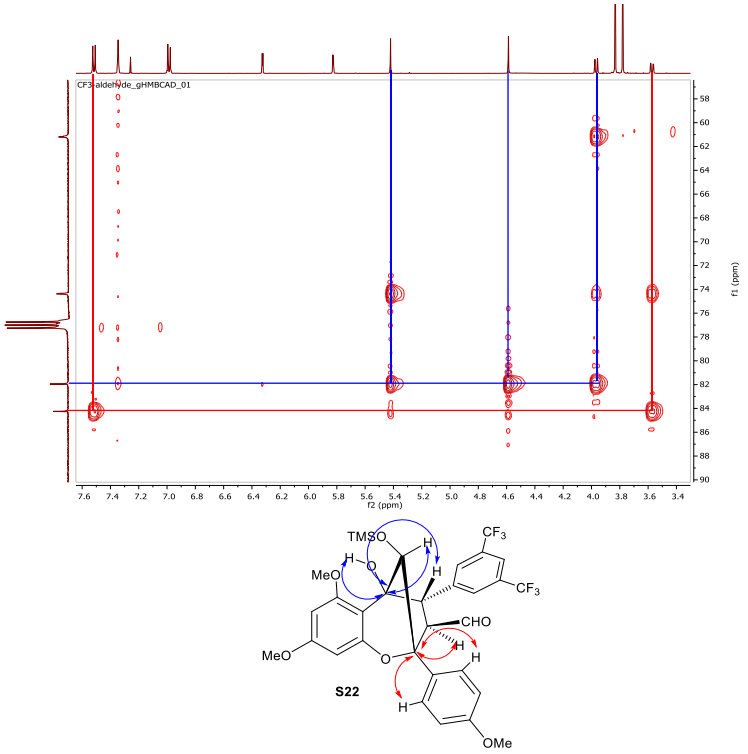


HSQC (compound **S22**):

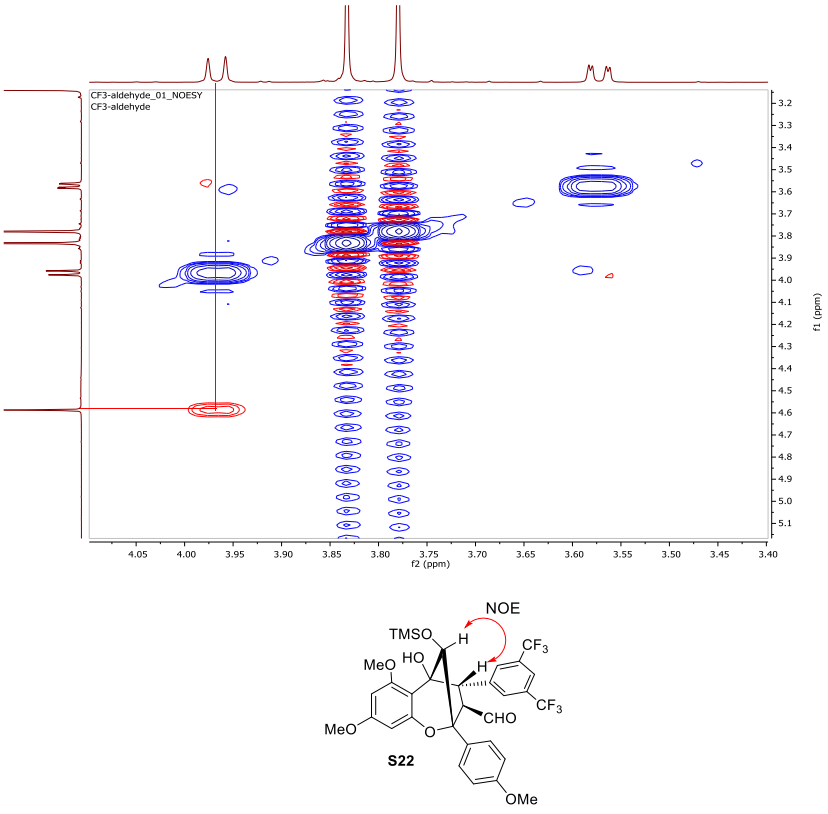




HMBC (compound **S22**):



NOESY (compound **S22**):



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