"The Total Synthesis of (–)-Cyanthiwigin F via Double Catalytic Enantioselective Alkylation"

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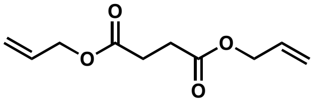
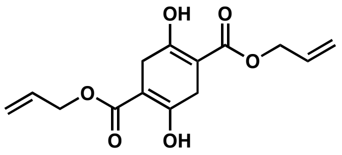
Supplementary Methods. All reactions were performed at ambient temperature (22 °C) unless otherwise noted. Reactions requiring external heat were modulated to the specified temperatures indicated by using an IKAmag temperature controller. All reactions were performed in glassware flame-dried under vacuum and allowed to cool under nitrogen or argon. Solvents were dried by passage over a column of activated alumina with an overpressure of argon gas. Tetrahydrofuran was distilled directly over benzophenone and sodium. All other chemicals and reagents were used as received. Grubbs' ruthenium catalyst **13** was donated by Materia Inc., and used without further purification. (*S*)-*t*-BuPHOX (**12**),[31] 4-iodo-2-methyl-1-butene,[32] and vinyl boronate ester **14**[33] were prepared according to known methods. Compounds purified by flash chromatography utilized ICN silica gel (particle size 0.032-0.063 mm) or SiliCycle® Silia*Flash*® P60 Academic Silica Gel (particle size 40-63 μm; pore diameter 60 Å). Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV, *p*-anisaldehyde, or alkaline permanganate staining. NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C) or a Varian Inova 500 (at 500 MHz for ^{1}H NMR and 125 for ^{13}C) instrument, and are reported relative to residual $CHCl_3$ (δ 7.26 for ^{1}H NMR, δ 77.16 for ^{13}C) or C_6H_6 (δ 7.16 for ^{1}H NMR, δ 128.37 for ^{13}C). The following format is used for the reporting of ^{1}H NMR data: chemical shift (δ ppm), multiplicity, coupling constant

(Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Spectrum Paragon 1000 spectrometer, and data are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the Caltech Mass Spectral Facility. Analytical chiral gas chromatography was performed with an Agilent 6850 GC using a G-TA (30 m x 0.25 mm) column (1.0 mL/min carrier gas flow). Analytical achiral gas chromatography was performed with an Agilent 6850 GC using a DB-WAX (30 x 0.25 mm) column (1.0 mL/min carrier gas flow). Preparatory reverse-phase HPLC was performed on a Waters HPLC with Waters Delta-Pak 2 x 100 mm, 15 μm column equipped with a guard, employing a flow rate of 1 mL/min and a variable gradient of acetonitrile and water as eluent. HPLC visualization was performed by collecting 1 mL fractions after initial injection and analyzing each fraction via TLC. Optical rotations were measured with a Jasco P-1010 polarimeter using a 100 mm path-length cell.



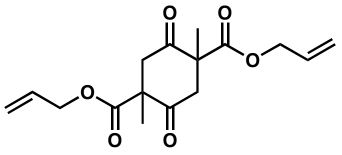
8

Diallyl succinate (8): To a solution of succinic acid (40.0 g, 338.7 mmol) in benzene (300 mL) was added TsOH • H_2O (0.21 g, 1.2 mmol, 0.003 equiv). After brief mixing, 70 mL of allyl alcohol (1.01 mol, 3.0 equiv) was added to the reaction, and the flask was fitted with a Dean–Stark trap and reflux condenser under nitrogen. The reaction was heated to 105 °C and allowed to reflux over 12 h. After collection of 13 mL H_2O from the Dean–Stark trap, the reaction was allowed to cool to room temperature and was quenched by slow treatment with saturated $NaHCO_3$ (*aq*) until gas evolution halted. The phases were separated, and the organic layer was washed with saturated $NaHCO_3$ (*aq*) (2 x 40 mL) and brine (2 x 30 mL). The combined organic layers were dried over $MgSO_4$, and solvent was removed in vacuo. The resulting colorless oil was dried under high vacuum to afford diallyl succinate (**8**) (59.8196 g, 89.1% yield). This material was carried into the next step without further purification: ^1H NMR ($CDCl_3$) δ 5.90 (ddt, *J* = 17.3, 10.5, 5.6 Hz, 2H), 5.31 (ddt, *J* = 17.0, 1.6, 1.3 Hz, 2H), 5.23 (ddt, *J* = 10.4, 1.3, 1.1 Hz, 2H), 4.60 (ddd, *J* = 5.9, 1.3, 1.3 Hz, 4H), 2.67 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 172.0, 132.1, 118.5, 65.5, 29.2; IR (Neat Film, NaCl) 3086, 2942, 1738, 1649, 1413, 1377, 1271, 1157, 990, 932 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{14}O_4$ $[M]^+$: 198.0892, found 198.0888.



SI-1

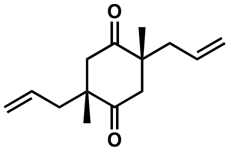
Diallyl succinylsuccinate (SI-1):[34] To a flame-dried flask under argon was added 25.0 g of 60% NaH (630.6 mmol, 2.5 equiv) and toluene (125 mL). To this was added, dropwise, 4.14 mL of allyl alcohol (70.6 mmol, 0.28 equiv) with vigorous stirring. After gas evolution had ceased, 50.0 g (252.2 mmol) diallyl succinate (**8**) was added dropwise and the reaction was heated to 95 °C. The reaction flask was fitted with a reflux condenser, and reaction was allowed to proceed over 10 h. After ca. 15 min., an additional 125 mL of toluene was added to the reaction to ensure fluidity of the mixture. Once the reaction had completed by TLC, the flask was cooled to room temperature, and the solvent was removed in vacuo. The crude solid was immediately suspended in CH_2Cl_2, and then acidified by addition of 2 N HCl (*aq*) (350 mL). The biphasic mixture was allowed to stir over 2 h, after which time all solids had dissolved. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and solvent was removed in vacuo to yield a crude orange solid. The crude residue was recrystallized twice from a mixture of petroleum ether and acetone to afford diallyl succinylsuccinate (**SI-1**) as a flakey white solid (26.97 g, 76.3% yield): ^{1}H NMR ($CDCl_3$) δ 12.11 (s, 2H), 5.95 (dddd, *J* = 17.1, 10.7, 5.7, 5.7 Hz, 2H), 5.35 (ddt, *J* = 17.3, 1.6, 1.3 Hz, 2H), 5.27 (ddt, *J* = 10.4, 1.3, 1.3 Hz, 2H), 4.69 (ddd, *J* = 5.3, 1.3, 1.3 Hz, 4H), 3.22 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 170.8, 168.8, 131.7, 118.4, 93.1, 65.2, 28.5; IR (Neat film, NaCl) 1666, 1647, 1684, 1451, 1389, 1329, 1219, 1204, 1133, 1061, 961, 843, 783 cm^{-1}; HRMS (EI) *m*/*z* calc'd for $C_{14}H_{16}O_6$ $[M]^+$: 280.0947, found 280.0948.



7

Bis(β-ketoester) 7: Prior to use in the reaction, acetone was dried by allowing to settle over anhydrous calcium suflate, and then was passed over a short plug of silica. Potassium carbonate (5.8 g, 43.9 mmol, 4.1 equiv) and diallyl succinylsuccinate (3.0 g, 10.7 mmol, 1.0 equiv) were suspended in acetone (21.3 mL). After addition of solvent to the solids, the reaction mixture was fitted with a reflux condenser and then was heated to 50 °C. To this mixture was added methyl iodide (3.40 mL, 54.5 mmol, 5.1 equiv). The reaction was stirred vigorously to ensure completion (Note: If reaction is not stirred, or if stirring is not efficient, potassium carbonate will collect into a solid aggregate and the reaction will halt. Breaking up these solid collections with a spatula is typically enough to reinitiate reaction, though in some cases additional methyl iodide may be required). After 6 h, the reaction was allowed to cool, and then was passed through filter paper. The remaining solids were then washed with additional CH_2Cl_2 to ensure complete solvation of any precipitated product trapped within the potassium carbonate. The collected organic layers were combined and concentrated to yield an amorphous semi-solid, which was purified over silica gel using 15% → 20% ethyl acetate in hexanes as eluent. Compound **7** was afforded as two diastereomers in a 1:1 ratio. The less polar diastereomer (by TLC analysis with 20% ethyl acetate in hexane) was obtained as a white, fluffy solid, and the more polar diastereomer was obtained as a thick, yellow oil (1.4 g for each diastereomer, 2.8 g for combined diastereomers, 85% yield). Less polar diastereomer: ^{1}H NMR ($CDCl_3$) δ 5.84 (dddd,*J* = 17.3, 10.4, 5.8, 5.8 Hz, 2H), 5.30 (app. dq, *J* = 17.3, 1.3 Hz, 2H), δ 5.26 (app. dq, *J* = 10.4, 1.3 Hz, 2H), δ 4.60 (app. ddd, *J* = 5.9, 1.3, 1.3 Hz, 4H), δ 3.14 (d, *J* = 15.2 Hz, 2H), δ 2.80 (d, *J* = 15.2

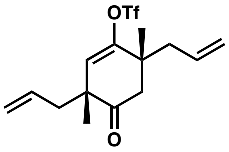
Hz, 2H), δ 1.43 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 201.8, 170.6, 131.0, 119.7, 66.8, 57.6, 48.1, 20.8; IR (Neat Film, NaCl) 2988, 2940, 1749, 1708, 1420, 1375, 1281, 1227, 1132, 1076, 911, 809, 744 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{20}O_6$ [M^+]: 308.1260, found 308.1263. [More polar diastereomer: ^{1}H NMR ($CDCl_3$) δ 5.88 (dddd, *J* = 17.1, 10.4, 5.7, 5.7 Hz, 2H), δ 5.31 (app. dq, *J* = 17.2, 1.5 Hz, 2H), δ 5.27 (app. dq, *J* = 10.3, 1.5, 2H), δ 4.62 (app. ddd, *J* = 5.4, 1.5, 1.5 Hz, 4H), δ 3.47 (d, *J* = 15.6 Hz, 2H), δ 2.63 (d, *J* = 15.9 Hz, 2H), δ 1.46 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 202.5, 169.9, 131.1, 119.1, 66.7, 56.6, 47.1, 21.5; IR (Thin Film, NaCl) 3088, 2984, 2940, 1747, 1722, 1649, 1454, 1422, 1381, 1275, 1233, 1196, 1110, 984, 934 cm^{-1}]



6

Diketone 6: A flame-dried round bottom flask cooled under argon was charged with bis(3,5-dimethoxydibenzylideneacetone)palladium(0) ($Pd(dmdba)_2$, 0.268 g, 0.33 mmol, 0.05 equiv) and (*S*)-*t*-BuPHOX (**12**) (0.140 g, 0.362 mmol, 0.055 equiv). The flask was purged under vacuum briefly, and then backfilled with argon. The solids were dissolved in Et_2O (500 mL), and the resulting solution was stirred at 25 °C for 30 min. After precomplexation, neat **7** (2.0 g, 6.59 mmol) was added to the reaction. The solution was vigorously stirred at 25 °C for 10 h (Note: continual stirring is necessary due to the apparent low solubility of $Pd(dmdba)_2$ in Et_2O.), after which time solvent was removed in vacuo. The crude oil was purified over silica gel using 3% ethyl acetate in hexanes as eluent to afford **6** as a colorless oil (1.07 g, 78% yield, 4.4 : 1 d.r., 99% ee). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (dddd, *J* = 18.3, 10.2, 6.9, 6.9 Hz, 2H), 5.17–5.09 (comp. m, 3H), 5.07–5.04 (m, 1H), 2.82 (d, *J* = 14.7 Hz, 2H), 2.38 (d, *J* = 15 Hz, 2H), 2.34

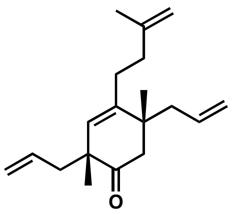
(app. ddt, *J* = 13.2, 6.9, 1.0 Hz, 2H), 2.09 (app. ddt, *J* = 13.5, 7.8, 0.9 Hz, 2H), 1.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.8, 132.4, 120.0, 49.4, 48.4, 43.8, 24.3; IR (Thin film, NaCl) 3078, 2978, 1712, 1640, 1458, 1378, 1252, 1129, 1101, 998, 921 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{20}O_2$ $[M]^+$: 220.1463, found 220.1466. $[\alpha]^{25}_{D}$ –163.1 (*c* 0.52, CH_2Cl_2). Chiral GC assay (GTA column): 100 °C isothermal method over 90 min. Retention times: 67.7 min (Major enantiomer, C_2 diastereomer, 81.7%), 74.1 min (Minor enantiomer, C_2 diastereomer, 0.6%), 77.4 min (*meso* diastereomer, 17.6%). Achiral GC assay (DB-Wax column): 100 °C isotherm over 2.0 min, ramp 5 °C/min to 190 °C, then 190 °C isotherm for 10.0 min. Retention times: 18.5 min (C_2 diastereomer, 81.0%), 18.7 min (*meso* diastereomer, 19.0%).



SI-2

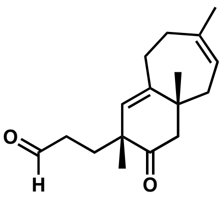
Triflate SI-2: A flask was charged with potassium bis(trimethylsilyl)amide (1.49 g, 7.49 mmol, 1.1 equiv) in the glovebox, and then was transferred to a manifold line outside of the glovebox under argon. The solids were dissolved in THF (180 mL), and the resulting solution was stirred while being cooled to –78 °C. To this alkaline solution was added, dropwise, neat **6** (1.5 g, 6.80 mmol). The solution immediately turned yellow, and viscosity increased. Deprotonation was allowed over 30 min, after which time the anionic solution was transferred by cannula into a solution of *N*-phenyl bis(trifluoromethane)sulfonimide (2.91 g, 8.17 mmol, 1.2 equiv) in THF (60 mL) at –78 °C. Reaction was allowed to proceed at this temperature over 6 h, after which time the mixture was brought to room temperature. The anionic reaction was quenched with brine. The phases were separated, and the aqueous layer was extracted with diethyl ether (3 x

100 mL) and ethyl acetate (1 x 100 mL). The combined organic layers were washed with brine (2 x 50 mL), dried over $MgSO_4$, filtered, and solvent was removed in vacuo. The crude oil obtained was loaded onto a silica gel column and eluted with 2% Et_2O in pentane. This afforded **SI-2** as a colorless oil (1.75 g, 73% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 5.77–5.58 (comp. m, 2H), 5.63 (s, 1H), 5.22–5.03 (comp. m, 4H), 2.71 (d, *J* = 14.3 Hz, 1H), 2.40 (d, *J* = 14.4 Hz, 1H), 2.49-2.30 (comp. m, 2H), 2.24 (app. ddt, *J* = 13.5, 6.9, 1.3 Hz, 1H), 2.09 (app. ddt, *J* = 13.8, 8.24, 1.2 Hz, 1H), 1.22 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.6, 152.0, 132.6, 132.1, 122.9, 120.6, 119.7, 49.2, 48.9, 43.8, 43.0, 42.1, 25.2, 24.6; IR (Neat Film, NaCl) 3081, 2980, 2934, 1721, 1673, 1641, 1457, 1416, 1214, 1141, 1010, 923.6, 895.2, 836.2 cm^{-1}. HRMS *m/z* calc'd for $C_{15}H_{19}O_4SF_3$ [M^+]: 352.0956, found 352.0949. $[\alpha]^{25}_D$ –6.5 (*c* 1.15, CH_2Cl_2).



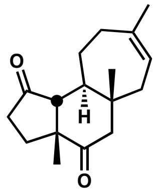
4

Tetraene 4: To a flame-dried Schlenk flask backfilled with argon was added powdered Zn metal (3.20 g, 48.9 mmol, 7.5 equiv). After brief vacuum purging and backfilling the flask with argon, the metal was suspended in THF (45 mL). To this suspension was cannula transferred a prepared solution of 1,2-dibromoethane (0.675 mL, 7.83 mmol, 1.2 equiv) and trimethylsilyl chloride (0.271 mL, 2.13 mmol, 0.33 equiv) in THF (22.5 mL). The reaction vessel was sealed, then heated to 65 °C for 15 min. After this time had elapsed, the reaction was cooled to room temperature, and a solution of 4-iodo-2-methyl-1-butene (1.92 g, 9.79 mmol, 1.5 equiv) in THF (22.5 mL) was cannula transferred into the suspension of activated Zn metal. The reaction vessel was sealed once again, and then was heated to 65 °C for 2 h. After this time had elapsed, the reaction was cooled to room temperature, and a prepared solution of triflate **SI-2** (2.3 g, 6.53 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (0.377g, 0.33 mmol, 0.05 equiv) in THF (45 mL) was added to the alkyl zinc solution via cannula. The reaction was sealed and heated to 65 °C for 3 h. After reaction had completed by TLC, it was cooled to room temperature and filtered over a Celite pad with copious washing with Et_2O. The filtrate then was diluted with brine and extracted with Et_2O (4 x 100 mL). The combined organic layers were washed with brine, then saturated $Na_2S_2O_3$ (*aq*) to removed colored impurities. The washed organic layers were dried over $MgSO_4$, filtered, and then solvent was removed in vacuo. The crude material obtained was then purified over silica gel using 0.5% → 1.0% → 1.5% → 3.0% Et_2O in petroleum ether as eluent. This afforded tetraene **4** as a colorless oil (1.40 g, 78.8%). ^1H NMR (300 MHz, $CDCl_3$) δ 5.77–5.61 (comp. m, 2 H), 5.20 (s, 1H), 5.10–4.97 (comp. m, 4H), 4.74 (d, J = 8.8 Hz, 2H), 2.56 (d, J = 13.5 Hz, 1H), 2.40-2.13 (comp. m, 8H), 2.05–1.98 (m, 1H), 1.77 (s, 3H), 1.09 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) d 214.4, 145.5, 142.5, 134.1, 134.0, 128.6, 118.6, 117.9, 110.1, 49.5, 48.7, 44.4, 44.3, 43.2, 36.5, 28.6, 26.5, 24.7, 22.7; IR (Neat Film, NaCl) 3076, 2996, 2928, 2360, 1715, 1639, 1455, 1376, 1320, 1298, 1261, 1229, 1138, 1093, 996, 916, 887 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{19}H_{28}O$ [M^+]: 272.2140, found 272.2138. $[\alpha]^{25}_D$ –72.4 (*c* 0.22, CH_2Cl_2).



15

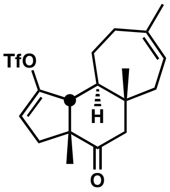
Bicyclic aldehyde 15: The following reaction was preformed in a glovebox under an atmosphere of nitrogen. To a flame-dried flask was added tetraene **4** (0.100 g, 0.37 mmol, 1.0 equiv) and PhH (10 mL). The solution was treated with Grubbs' ruthenium catalyst **13** (0.023 g, 0.037 mmol, 0.1 equiv) and was heated to 40 °C for 30 min. After this time had elapsed vinyl boronate ester **14**[35] (0.283g, 1.84 mmol, 5.0 equiv) was added via syringe and the temperature was maintained at 40 °C for 20 h. The reaction was then cooled to –20 °C briefly and treated with ethyl vinyl ether (ca. 200 μL) to quench the remaining catalyst. At this stage, the reaction was removed from the glovebox. Solvent was removed in vacuo, and the crude mixture was passed over a short plug of silica gel using 20% ethyl acetate in hexanes as eluent to remove all remaining catalyst and various ruthenium byproducts. The oil obtained was then redissolved in THF (10 mL) and treated with water (10 mL). A single portion of $NaBO_3$•H_2O (0.220 g, 2.20 mmol, 6.0 equiv) was added, and the reaction was allowed to stir for 1 h.[36] After complete consumption of the boronate was observed via TLC, the phases were separated, and the aqueous phase was extracted with ethyl acetate (4 x 20 mL). The combined organics were washed with brine, dried over $MgSO_4$, filtered, and then solvent was removed in vacuo. The crude material was purified over silica gel using 5.0% → 7.5% ethyl acetate in hexanes as eluent to afford bicyclic aldehyde **15** as a colorless oil (0.048 g, 51.0%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.71 (app. t, *J* = 1.3 Hz, 1H), 5.38–5.31 (m, 1H), 5.15 (s, 1H), 2.70 (d, *J* = 13.6 Hz, 1H), 2.59–2.32 (comp. m, 5H), 2.12 (d, *J* = 13.8 Hz, 1H), 2.24–2.04 (comp. m, 2 H), 1.89–1.64 (comp. m, 3 H), 1.67 (s, 3H), 1.12 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.5, 201.6, 146.4, 138.7, 129.0, 120.1, 51.6, 47.7, 39.9, 37.6, 37.2, 33.1, 29.6, 27.8, 25.9, 23.9; IR (Neat Film, NaCl) 2960, 2927, 2360, 2341, 1711-1710 (overlapping peaks), 1452, 1374, 1296, 1163 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{17}H_{24}O_2$ [M^+]: 260.1776, found 260.1784. $[\alpha]^{25}_{D}$ –83.5 (*c* 1.09, CH_2Cl_2).



16

Tricyclic diketone 16: To a flame-dried Schlenk flask was added bicyclic aldehyde **15** (0.600g, 2.32 mmol, 1.0 equiv). Dry PhH (5 mL) was added, then evaporated under vacuum. This azeotropic drying procedure was repeated two additional times, and the resulting material was then dried under high vacuum and backfilled with argon. To this was added *t*-butyl thiol (0.78 mL, 6.91 mmol, 3.0 equiv), AIBN (0.568 g, 3.46 mmol, 1.5 equiv), and PhH (20 mL). The reaction was freeze-pump-thawed thrice, and afterward was backfilled with argon. The reaction vessel was sealed and the reaction was heated to 80 °C and allowed to react over 22 h. After this time, the reaction was cooled to room temperature and solvent was removed in vacuo. The crude material was purified over silica gel using a gradient of 5.0% → 7.5% → 10.0% ethyl acetate in hexanes as eluent to afford the material as an amorphous solid (0.342 g, 57%); mp 94–96 °C. An analytically pure sample was prepared via reverse-phase HPLC purification using 30% acetonitrile in water. X-ray diffraction samples were grown via diffusion crystallization of the amorphous solid from acetonitrile and water. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.33 (ddq, *J* = 5.13, 5.13, 1.71 Hz, 1 H), 2.65 (d, *J* = 14.5 Hz, 1H), 2.55–2.49 (m, 1H), 2.41–2.28 (m, 2H), 2.27–2.21

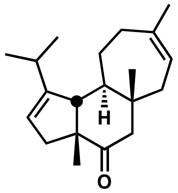
(m, 1H), 2.20–2.12 (m, 1H), 2.02 (d, J = 14.5 Hz, 1H), 2.01–1.93 (m, 2H), 1.89 (dd, J = 12.2, 1.2 Hz, 1H), 1.83–1.72 (m, 3H), 1.74 (s, 3H), 1.09 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 218.0, 212.8, 142.6, 121.0, 63.2, 52.6, 51.0, 47.8, 42.3, 40.1, 34.4, 32.4, 31.4, 25.4, 24.1, 21.7, 17.3; IR (Neat Film, NaCl) 2961, 2926, 2868, 1735, 1705, 1576, 1453, 1380, 1149 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{17}H_{24}O_2$ [M$^+$]: 260.1777, found 260.1776. $[\alpha]^{25}_{D}$ –158.6 (*c* 0.925, CH_2Cl_2).



SI-3

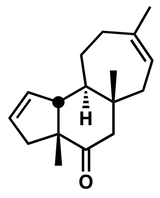
Tricyclic triflate SI-3: To a flame-dried flask under argon was added tricyclic diketone **16** (0.250 g, 0.960 mmol, 1.0 equiv). Dry PhH (5 mL) was added, then evaporated under vacuum. This azeotropic drying procedure was repeated two additional times, and the resulting material was then dried under high vacuum briefly, then dissolved in THF (10 mL). A separate flame-dried flask under argon was charged with potassium bis(trimethylsilyl)amide (0.211 g, 1.06 mmol, 1.1 equiv) and THF (10 mL). The flask containing diketone **16** was cooled to –78 °C, and the basic solution was cannula transferred to the cooled solution under a positive pressure of argon. Deprotonation was allowed over 30 min. After this time had elapsed, a solution of *N*-phenyl bis(trifluoromethane)sulfonimide (0.395 g, 1.10 mmol, 1.15 equiv) in THF (10 mL) was cannula transferred to the anionic solution under a positive pressure of argon. After 3 h, the reaction was quenched via addition of a solution of saturated sodium bicarbonate (*aq*). The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed, sequentially, with 2 N NaOH (*aq*) (30 mL), 2 N HCl (*aq*)

(30 mL), and brine (2 x 30 mL). The organic layers were then dried over $MgSO_4$, filtered, and solvent was removed in vacuo. The crude material was purified over silica gel using 0.5% → 1.0% ethyl acetate in hexanes as eluent to afford triflate **SI-3** as a white solid (0.226 g, 60%). ^{1}H NMR (500 MHz, C_6D_6) δ 5.16 (ddq, *J* = 5.1, 1.7, 1.7 Hz, 1H), 5.08 (dd, *J* = 3.0, 2.0 Hz, 1H), 2.07 (dd, *J* = 10.7, 2.2 Hz, 1H), 2.02 (br. t, *J* = 13.3 Hz, 1 H), 1.94–1.86 (m, 3H), 1.90 (s, 1H), 1.85 – 1.79 (m, 1H), 1.74 (app. ddt, *J* = 14.8, 6.8, 1.5 Hz, 1H), 1.59 (s, 3H), 1.57 (d, *J* = 3.4 Hz, 1H), 1.54 (d, *J* = 3.4 Hz, 1H), 1.38–1.31 (m, 1H), 1.35 (dd, *J* = 14.4, 8.5 Hz, 1H), 1.23 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.8, 153.2, 141.9, 121.4, 116.0, 57.6, 54.1, 54.0, 51.2, 41.6, 38.1, 36.5, 32.5, 26.2, 25.0, 23.6, 16.8; IR (Neat Film, NaCl) 2932, 1709, 1656, 1423, 1382, 1245, 1211, 1141, 1097, 927 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{17}H_{23}F_3O_4S$ [M^+]: 392.1269, found 392.1273. $[\alpha]^{25}_D$ –101.9 (*c* 0.63, CH_2Cl_2).



Cyanthiwigin F (1)

Cyanthiwigin F (1):[37] To a flame-dried 1 dram vial under argon was added 3.8 mg of CuCN (0.04 mmol, 1.5 equiv), followed by 0.5 mL of THF. This suspension was cooled to –78 °C, and to this was added, dropwise, 40 μl of *i*-PrMgCl (0.08 mmol, 3.0 equiv, 1.91 M solution in THF). After complete addition, the reaction was warmed to 0 °C and allowed to remain at this temperature until a homogeneous pale pink solution was obtained (~10 min). A separate solution was then prepared, consisting of 3.0 mg Pd(dppf)Cl_2 (0.005 mmol, 0.15 equiv) and 10 mg (0.025 mmol) of triflate species **SI-2** dissolved in 0.5 mL of THF. The solution containing **SI-2** was treated with the organocuprate solution via dropwise cannula addition at 0 °C. This was allowed to react at 0 °C for 3 h, after which time the reaction was quenched with a 1:1 mixture of NH_4Cl (*aq*) and NH_4OH (*aq*). The phases were separated, and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and then solvent was removed in vacuo. The crude material was purified over silica gel using 1% Et_2O in petroleum ether as eluent to afford 4.4 mg of colorless crystals (63% yield, 1.8 : 1 mixture of **1** : **17**). An analytically pure sample of **1** was prepared via reverse-phase HPLC purification using a gradient of 15% → 30% acetonitrile in water. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (app. q, *J* = 1.6 Hz, 1H), 5.34 (ddq, *J* = 5.1, 1.5, 1.5 Hz, 1H), 2.60 (d, *J* = 16.1 Hz, 1H), 2.50 (d, *J* = 13.7 Hz, 1H), 2.47 (app. t, *J* = 6.4 Hz, 1H), 2.24 (app. t, *J* = 13.3 Hz, 1H), 2.19–2.17 (m, 1H), 2.15 (d, *J* = 10.3 Hz, 1 H), 1.99 (app. ddt, *J* = 14.6, 6.8, 1.5 Hz, 1H), 1.98 (d, *J* = 14.1 Hz, 1H), 1.89 (dd, *J* = 16.1, 2.4 Hz, 1H), 1.84 (app. ddt, *J* = 14.2, 6.8, 2.5 Hz, 1H), 1.74 (s, 3H), 1.73 (app. dd, *J* = 14.6, 8.3 Hz, 1H), 1.61 (dt, *J* = 11.0, 2.9 Hz, 1H), 1.25 (m, 1H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.09 (s, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.5, 156.5, 141.8, 121.4, 119.9, 59.8, 55.2, 54.7, 54.3, 42.7, 42.2, 37.8, 33.2, 30.3, 26.4, 25.1, 22.8, 22.4, 21.6, 17.3; IR (Thin Film, NaCl) 2961, 2924, 1703, 1444, 1380, 1294, 1144, 912, 858, 810 cm^{-1}. HRMS (EI) *m*/*z* calc'd for $C_{20}H_{30}O_2$ [M$^+$]: 286.2297, found 286.2292. $[\alpha]^{25}_D$ –125.4 (*c* 0.025, MeOH).



17

Reduction byproduct (17): This material was obtained as a side product from the reaction employed to synthesize cyanthiwigin F (**1**), presumably as a result of reduction of the triflate moiety of **SI-2**. Compound **17** was later synthesized directly by the following method: To a flame dried vial containing 22 mg of **SI-2** was added 7 mg of dppp and 5 mg of $PdCl_2$(dppf). The solids were dissolved in 0.5 mL of DMF, and the resulting solution was treated with 114 μL of Bu_3N and 11 μL of formic acid (Note: Upon addition of the formic acid, the reaction evolves white smoke). The reaction mixture was heated to 95 °C for 4 h, after which time all of the starting triflate was observed to be consumed by TLC. The reaction was quenched by the addition of 1 mL of brine, followed by dilution with 2 mL of Et_2O. The aqueous and organic phases were separated, and the aqueous phase was thereafter extracted with Et_2O (3 x 10 mL). The combined organic phases were washed with 2 N HCl to remove any residual amine, then washed with brine. The collected organic phases were dried over $MgSO_4$, filtered, and then purified over silica gel using 2% Et_2O in petroleum ether to afford 4.0 mg (29.2% yield) of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00–5.94 (m, 1H), 5.72–5.68 (m, 1H), 5.39–5.30 (m, 1H), 2.55 (ddd, *J* = 16.6, 4.4, 2.2 Hz, 1H), 2.39 (d, *J* = 14.9, 1H), 2.23 (t, *J* = 13.5 Hz, 1H), 2.18–2.12 (comp. m, 1H), 2.08 (dd, *J* = 2.7, 1.1 Hz, 1H), 2.03 (dd, *J* = 2.7, 1.2 Hz, 1H), 2.02 (d, *J* = 14.7 Hz, 1H), 2.01 (dddd, *J* = 14.6, 6.9, 1.5, 1.5 Hz 1H), 1.99 (d, *J* = 14.6 Hz, 1H), 1.97–1.94 (m, 1H), 1.75 (s, 3H), 1.61 (s, 1H), 1.43–1.35 (m, 1H), 1.12 (s, 3H), 0.7 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.7, 142.0, 134.9, 128.0, 121.5, 59.4, 55.8, 54.9, 51.9, 43.8, 41.9, 37.5, 33.1, 26.6, 25.3, 23.8, 16.8; IR (Thin Film, NaCl) 2961, 2927, 1702, 1559, 1441, 1380, 1293, 1257, 1140, 856, 726 cm^{-1}. HRMS (EI) *m/z* calc'd for $C_{17}H_{24}O$ [M^+]: 244.1827, found 244.1821. $[\alpha]^{25}_{D}$ –238.4 (*c* 0.02, MeOH).

Supplementary Table 1. Comparison of ^{1}H NMR data for synthetic and natural cyanthiwigin F.

Synthetic[a] (ppm)	Multiplicity	Natural Sample[b] (ppm)	Multiplicity	Δ
5.38	app. q	5.35	br	0.03
5.34	ddq	5.31	m	0.03
2.6	d	2.56	d	0.04
2.5	d	2.48	d	0.02
2.46	app. t	2.45	m	0.01
2.24	app. t	2.21	m	0.03
2.18	m	2.11	m	0.07
2.15	d	2.13	d	0.02
1.99	app. ddt	1.98	m	0.01
1.98	d	1.95	d	0.03
1.89	dd	1.87	dd	0.02
1.84	app. ddt	1.81	m	0.03
1.74	s (3H)	1.71	s (3H)	0.03
1.73	app. dd	1.7	m	0.03
1.61	dt	1.58	dt	0.03
1.25	m	1.22	m	0.03
1.15	d (3H)	1.12	d (3H)	0.03
1.09	s (3H)	1.07	s (3H)	0.02
0.99	d (3H)	0.96	d (3H)	0.03
0.7	s (3H)	0.67	s (3H)	0.03
			Δ Average =	0.03

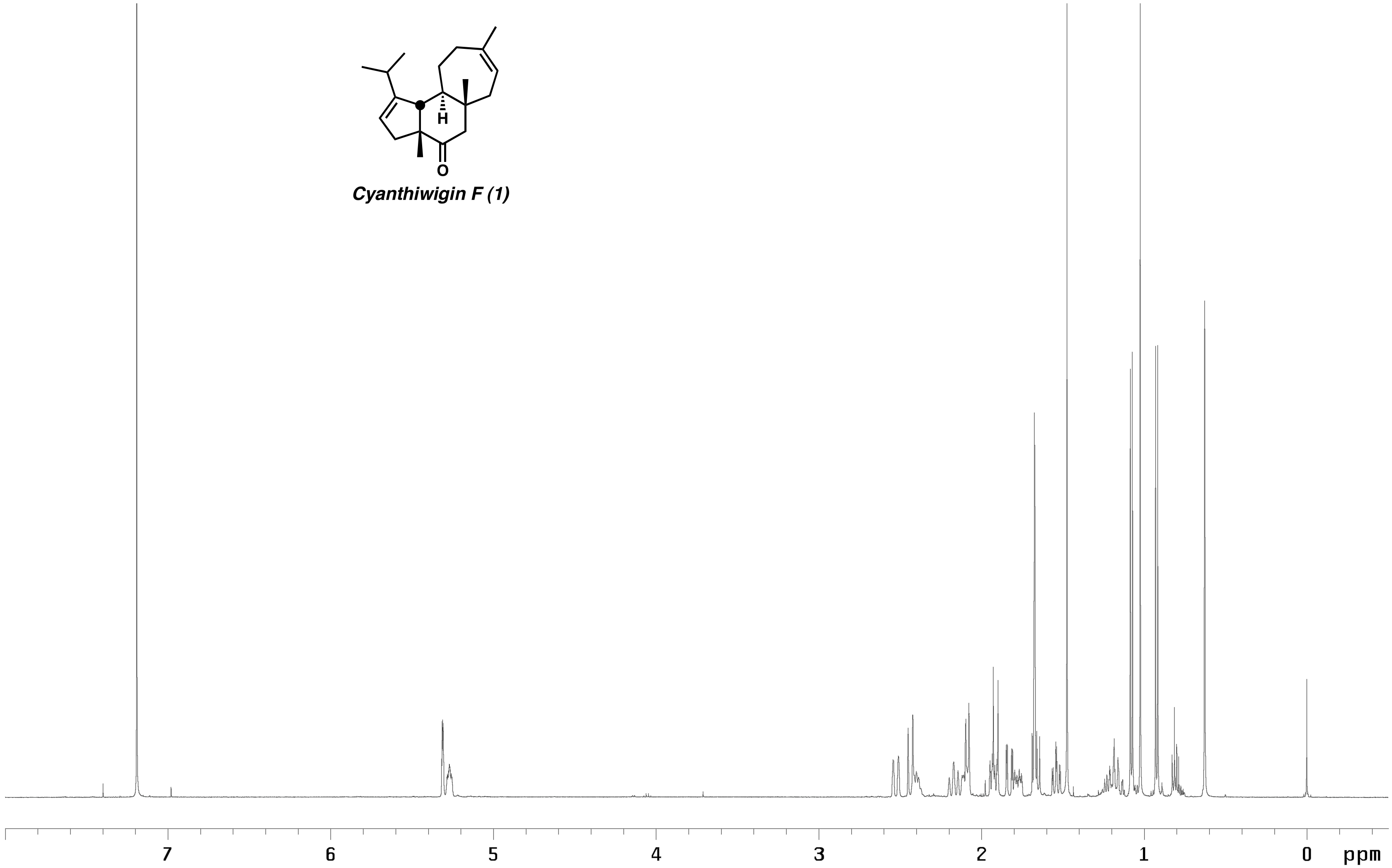
a. ^{1}H NMR data measured at 500 MHz in $CDCl_3$.

b. ^{1}H NMR data was reported at 400 MHz in $CDCl_3$.[38]

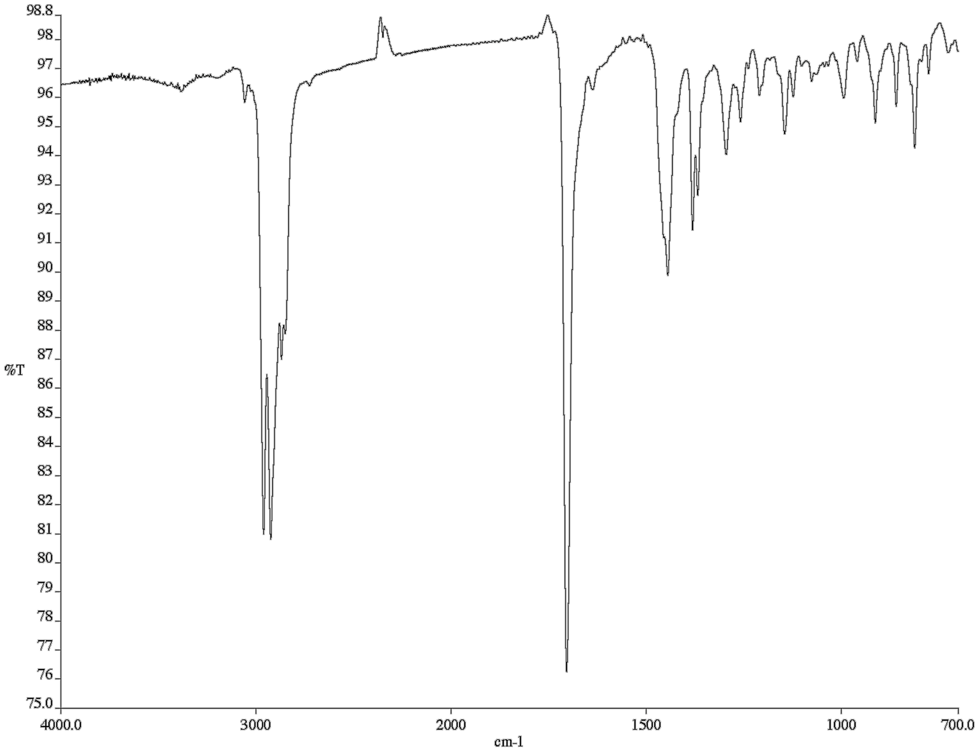
Supplementary Table 2. Comparison of synthetic and natural cyanthiwigin F ^{13}C NMR data.

Synthetic[a] (ppm)	Natural Sample[b] (ppm)	Δ
215.5	215.8	0.3
156.5	156.9	0.4
141.8	142.1	0.3
121.4	121.8	0.4
119.9	120.3	0.4
59.8	60.2	0.4
55.2	55.6	0.4
54.7	55.0	0.3
54.3	54.7	0.4
42.7	43.1	0.4
42.2	42.6	0.4
37.8	38.1	0.3
33.2	33.6	0.4
30.3	30.7	0.4
26.4	26.8	0.4
25.1	25.5	0.4
22.8	23.2	0.4
22.4	22.81	0.4
21.6	22.03	0.4
17.3	17.7	0.4
	Δ Average =	0.4

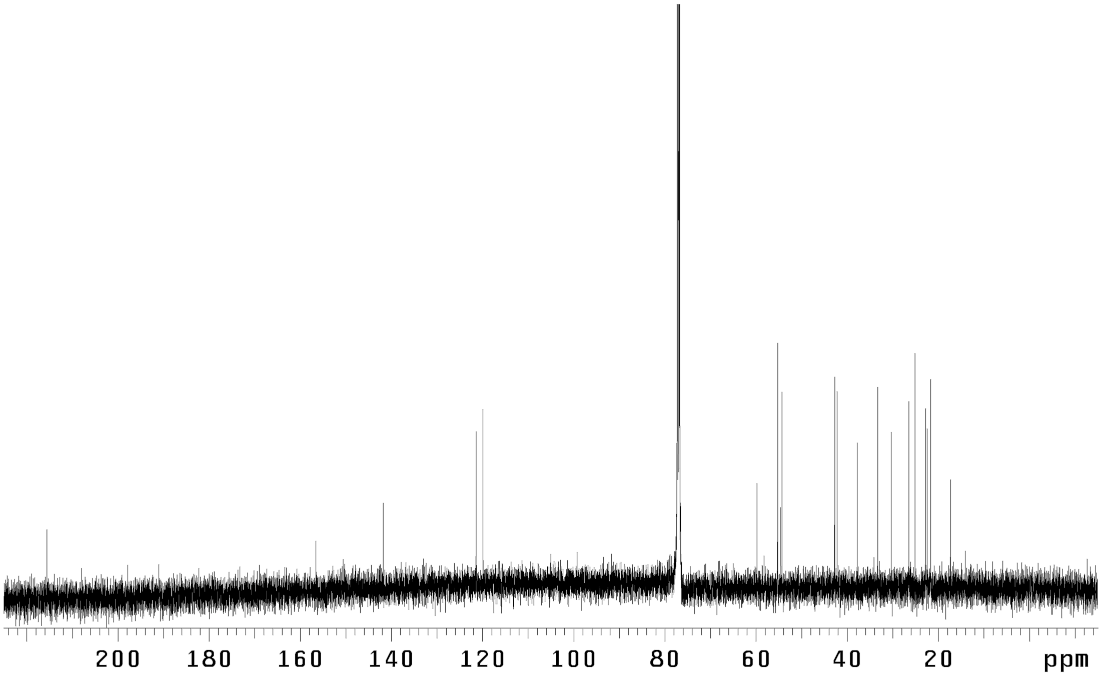
a. ^{13}C NMR data measured at 125 MHz in $CDCl_3$.
b. ^{13}C NMR data was reported at 100 MHz in $CDCl_3$.[5]



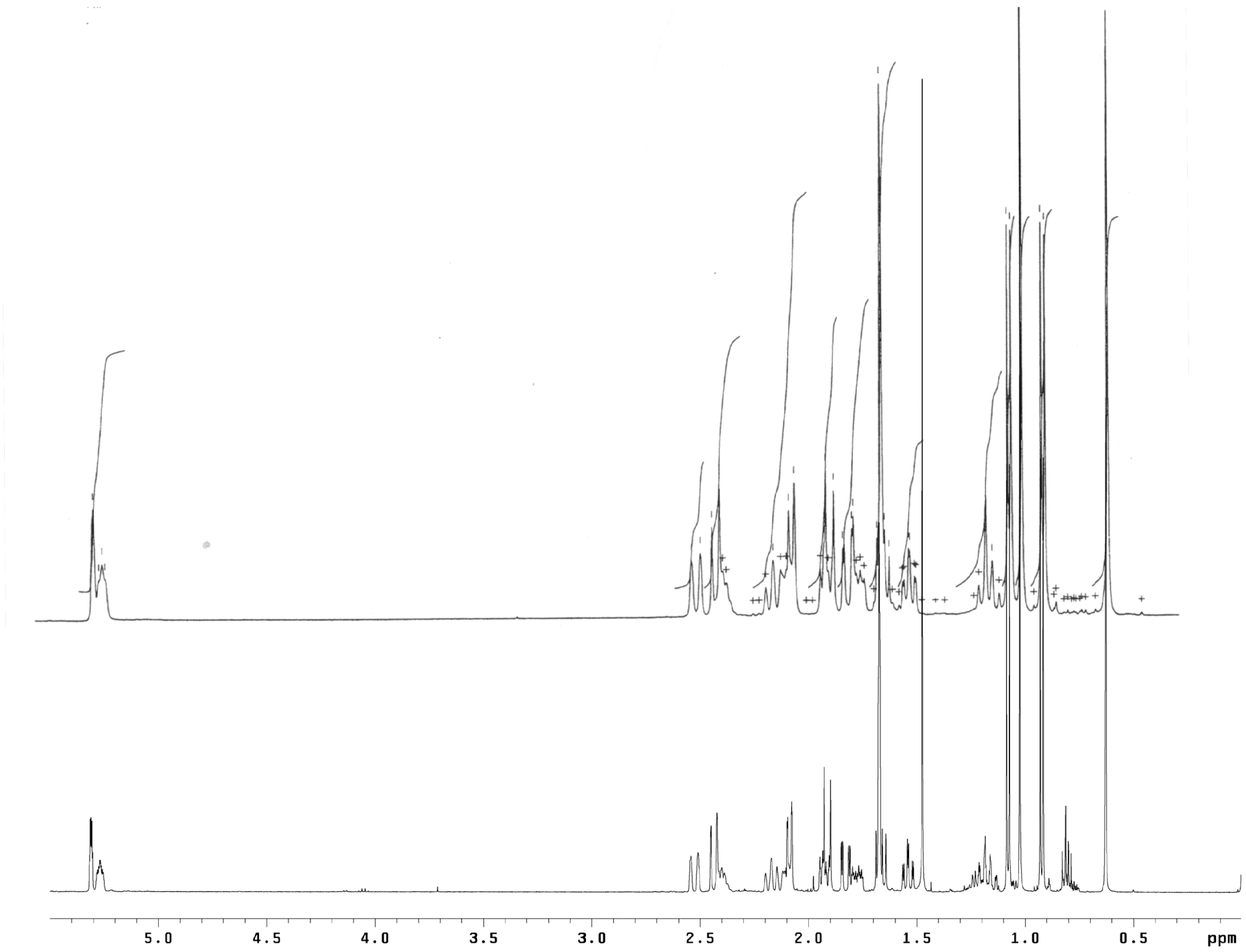
Supplementary Figure 1: ^{1}H NMR spectrum of synthetic cyanthiwigin F (**1**) in $CDCl_3$ (500 MHz).



Supplementary Figure 2: IR spectrum of synthetic cyanthiwigin F (**1**) (Thin Film, NaCl).



Supplementary Figure 3: ^{13}C NMR spectrum of synthetic cyanthiwigin F (**1**) in CDCl$_3$ (125 MHz).



Supplementary Figure 4: ^{1}H NMR comparison of natural[5] (above, 400 MHz) and synthetic (below, 500 MHz) cyanthiwigin F (**1**) in $CDCl_3$.

Supplementary Table 3. Crystal data and structure refinement for diketone **16** (CCDC 664430).

Empirical formula	$C_{17}H_{24}O_2$
Formula weight	260.36
Crystallization Solvent	Water/acetonitrile
Crystal Habit	Fragment
Crystal size	0.39 x 0.28 x 0.09 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	1.54178 Å CuKα
Data Collection Temperature	100(2) K
θ range for 5024 reflections used in lattice determination	4.12 to 65.79°
Unit cell dimensions	a = 7.4937(2) Å b = 9.0345(2) Å c = 21.4487(5) Å
Volume	1452.12(6) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.191 Mg/m^3
F(000)	568
Data collection program	Bruker SMART v5.630
θ range for data collection	4.12 to 65.79°
Completeness to θ = 65.79°	96.1 %
Index ranges	$-7 \le h \le 8$, $-10 \le k \le 8$, $-21 \le l \le 24$
Data collection scan type	ω scans at 7 φ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	7914
Independent reflections	2344 [R_{int}= 0.0753]
Absorption coefficient	0.593 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9486 and 0.8017

Supplementary Table 3 (cont.)

Structure solution and Refinement

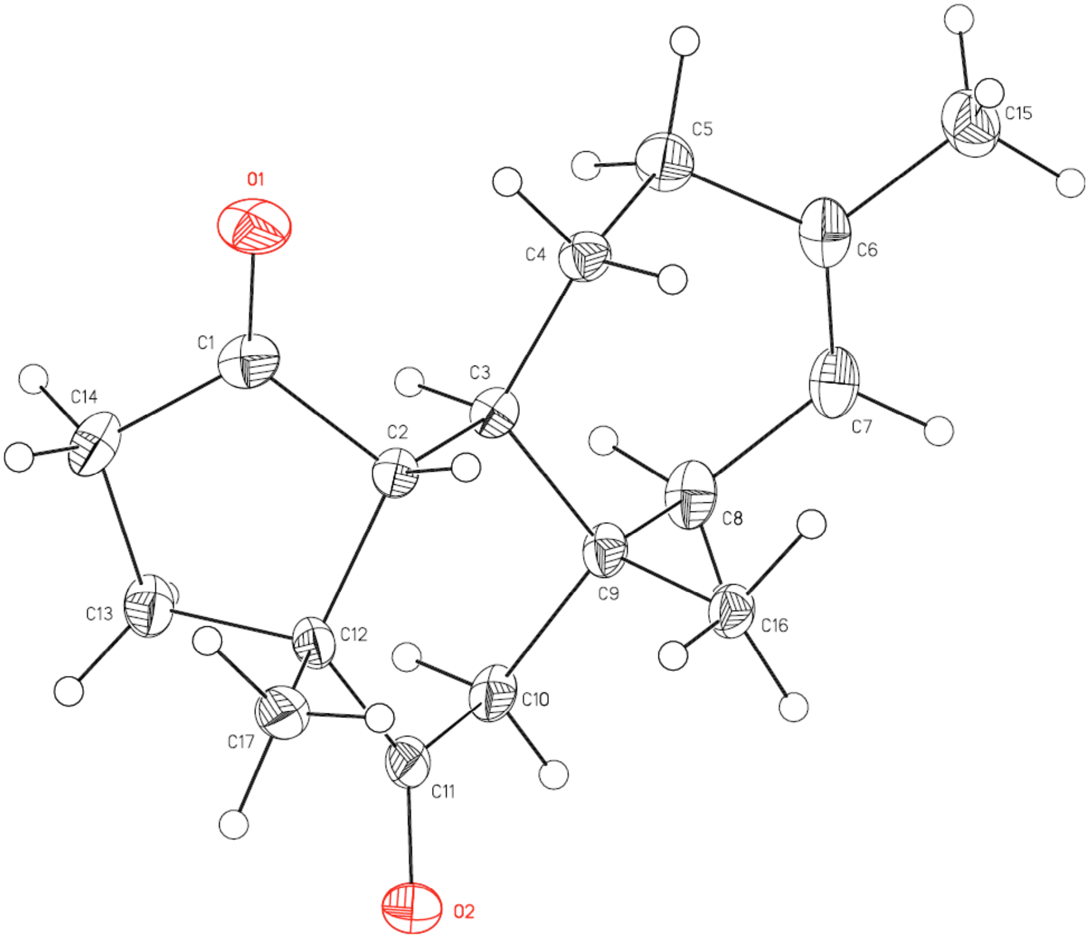
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	2344 / 0 / 268
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.394
Final R indices [$I>2\sigma(I)$, 2083 reflections]	R1 = 0.0335, *w*R2 = 0.0669
R indices (all data)	R1 = 0.0391, *w*R2 = 0.0686
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	0.2(2)
Largest diff. peak and hole	0.142 and -0.155 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

X-ray crystallographic structure of diketone 16



Supplementary Figure 5. ORTEP drawing of diketone **16** (shown with 50% probability ellipsoids).

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 664430.

Supplementary Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for diketone **16** (CCDC 664430). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	8369(2)	2053(2)	7466(1)	32(1)
O(2)	13478(2)	3487(2)	5446(1)	29(1)
C(1)	9211(2)	2001(2)	6981(1)	21(1)
C(2)	10059(2)	3336(2)	6653(1)	15(1)
C(3)	8595(2)	4237(2)	6306(1)	15(1)
C(4)	7465(3)	5062(2)	6791(1)	18(1)
C(5)	5740(3)	5787(2)	6542(1)	25(1)
C(6)	6041(2)	7246(2)	6214(1)	23(1)
C(7)	7053(3)	7331(2)	5712(1)	24(1)
C(8)	7949(3)	6025(2)	5407(1)	22(1)
C(9)	9420(3)	5246(2)	5792(1)	17(1)
C(10)	10444(3)	4224(2)	5340(1)	20(1)
C(11)	11962(2)	3449(2)	5658(1)	20(1)
C(12)	11518(2)	2593(2)	6244(1)	17(1)
C(13)	10651(3)	1092(2)	6049(1)	22(1)
C(14)	9615(3)	599(2)	6620(1)	24(1)
C(15)	5143(3)	8573(3)	6497(1)	30(1)
C(16)	10728(3)	6397(2)	6053(1)	19(1)
C(17)	13190(3)	2308(2)	6637(1)	23(1)

Supplementary Table 5. Bond lengths [Å] and angles [°] for diketone **16** (CCDC 664430).

O(1)-C(1)	1.219(2)	C(12)-C(2)-C(3)	116.84(14)
O(2)-C(11)	1.224(2)	C(1)-C(2)-H(2)	108.8(9)
C(1)-C(14)	1.514(3)	C(12)-C(2)-H(2)	111.2(9)
C(1)-C(2)	1.533(2)	C(3)-C(2)-H(2)	107.8(9)
C(2)-C(12)	1.554(2)	C(4)-C(3)-C(2)	108.61(14)
C(2)-C(3)	1.556(2)	C(4)-C(3)-C(9)	114.51(15)
C(2)-H(2)	0.972(16)	C(2)-C(3)-C(9)	111.44(14)
C(3)-C(4)	1.534(3)	C(4)-C(3)-H(3)	107.6(9)
C(3)-C(9)	1.559(2)	C(2)-C(3)-H(3)	106.6(9)
C(3)-H(3)	1.050(16)	C(9)-C(3)-H(3)	107.7(8)
C(4)-C(5)	1.544(3)	C(3)-C(4)-C(5)	115.75(16)
C(4)-H(4A)	1.008(19)	C(3)-C(4)-H(4A)	111.3(11)
C(4)-H(4B)	0.995(18)	C(5)-C(4)-H(4A)	107.4(11)
C(5)-C(6)	1.511(3)	C(3)-C(4)-H(4B)	108.6(10)
C(5)-H(5A)	0.994(19)	C(5)-C(4)-H(4B)	107.8(10)
C(5)-H(5B)	1.06(2)	H(4A)-C(4)-H(4B)	105.5(14)
C(6)-C(7)	1.320(3)	C(6)-C(5)-C(4)	113.95(17)
C(6)-C(15)	1.503(3)	C(6)-C(5)-H(5A)	109.1(11)
C(7)-C(8)	1.507(3)	C(4)-C(5)-H(5A)	106.3(11)
C(7)-H(7)	0.99(2)	C(6)-C(5)-H(5B)	108.4(12)
C(8)-C(9)	1.547(3)	C(4)-C(5)-H(5B)	107.8(11)
C(8)-H(8A)	1.046(19)	H(5A)-C(5)-H(5B)	111.3(15)
C(8)-H(8B)	1.013(19)	C(7)-C(6)-C(15)	122.73(18)
C(9)-C(16)	1.535(2)	C(7)-C(6)-C(5)	121.05(18)
C(9)-C(10)	1.543(2)	C(15)-C(6)-C(5)	116.21(18)
C(10)-C(11)	1.500(3)	C(6)-C(7)-C(8)	124.41(19)
C(10)-H(10A)	1.008(19)	C(6)-C(7)-H(7)	121.8(11)
C(10)-H(10B)	0.94(2)	C(8)-C(7)-H(7)	113.8(11)
C(11)-C(12)	1.514(2)	C(7)-C(8)-C(9)	116.25(16)
C(12)-C(17)	1.532(3)	C(7)-C(8)-H(8A)	109.8(11)
C(12)-C(13)	1.561(3)	C(9)-C(8)-H(8A)	108.7(11)
C(13)-C(14)	1.518(3)	C(7)-C(8)-H(8B)	110.5(10)
C(13)-H(13A)	0.966(18)	C(9)-C(8)-H(8B)	105.5(10)
C(13)-H(13B)	0.973(19)	H(8A)-C(8)-H(8B)	105.5(15)
C(14)-H(14A)	0.99(2)	C(16)-C(9)-C(10)	108.47(16)
C(14)-H(14B)	1.00(2)	C(16)-C(9)-C(8)	109.99(15)
C(15)-H(15A)	1.00(2)	C(10)-C(9)-C(8)	106.98(15)
C(15)-H(15B)	1.01(2)	C(16)-C(9)-C(3)	112.96(14)
C(15)-H(15C)	0.96(2)	C(10)-C(9)-C(3)	106.99(14)
C(16)-H(16A)	1.03(2)	C(8)-C(9)-C(3)	111.19(15)
C(16)-H(16B)	1.000(19)	C(11)-C(10)-C(9)	111.79(15)
C(16)-H(16C)	1.036(19)	C(11)-C(10)-H(10A)	107.4(10)
C(17)-H(17A)	1.00(2)	C(9)-C(10)-H(10A)	110.6(10)
C(17)-H(17B)	1.01(2)	C(11)-C(10)-H(10B)	110.2(12)
C(17)-H(17C)	0.95(2)	C(9)-C(10)-H(10B)	109.6(12)
		H(10A)-C(10)-H(10B)	107.0(15)
O(1)-C(1)-C(14)	124.84(18)	O(2)-C(11)-C(10)	121.45(17)
O(1)-C(1)-C(2)	125.15(17)	O(2)-C(11)-C(12)	121.84(17)
C(14)-C(1)-C(2)	109.99(15)	C(10)-C(11)-C(12)	116.70(15)
C(1)-C(2)-C(12)	102.14(14)	C(11)-C(12)-C(17)	111.27(16)
C(1)-C(2)-C(3)	109.78(14)	C(11)-C(12)-C(2)	113.80(14)

C(17)-C(12)-C(2)	109.74(15)	C(6)-C(15)-H(15B)	110.4(12)
C(11)-C(12)-C(13)	108.17(14)	H(15A)-C(15)-H(15B)	106.7(18)
C(17)-C(12)-C(13)	110.00(16)	C(6)-C(15)-H(15C)	114.4(14)
C(2)-C(12)-C(13)	103.55(15)	H(15A)-C(15)-H(15C)	112.7(19)
C(14)-C(13)-C(12)	104.54(15)	H(15B)-C(15)-H(15C)	102.7(17)
C(14)-C(13)-H(13A)	110.1(10)	C(9)-C(16)-H(16A)	109.4(11)
C(12)-C(13)-H(13A)	110.7(11)	C(9)-C(16)-H(16B)	111.8(11)
C(14)-C(13)-H(13B)	111.8(11)	H(16A)-C(16)-H(16B)	111.5(15)
C(12)-C(13)-H(13B)	112.1(12)	C(9)-C(16)-H(16C)	107.7(10)
H(13A)-C(13)-H(13B)	107.6(15)	H(16A)-C(16)-H(16C)	107.4(15)
C(1)-C(14)-C(13)	105.56(16)	H(16B)-C(16)-H(16C)	108.8(14)
C(1)-C(14)-H(14A)	113.1(12)	C(12)-C(17)-H(17A)	110.3(11)
C(13)-C(14)-H(14A)	111.2(12)	C(12)-C(17)-H(17B)	112.1(12)
C(1)-C(14)-H(14B)	109.3(12)	H(17A)-C(17)-H(17B)	108.9(16)
C(13)-C(14)-H(14B)	112.8(12)	C(12)-C(17)-H(17C)	111.9(11)
H(14A)-C(14)-H(14B)	105.1(17)	H(17A)-C(17)-H(17C)	109.2(16)
C(6)-C(15)-H(15A)	109.6(13)	H(17B)-C(17)-H(17C)	104.2(15)

Supplementary Table 6. Anisotropic displacement parameters ($Å^2$x 10^4) for diketone **16** (CCDC 664430). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	372(9)	382(9)	203(8)	136(6)	113(6)	108(7)
O(2)	332(8)	252(8)	275(8)	-7(6)	149(6)	2(7)
C(1)	202(11)	268(11)	149(10)	90(8)	-25(8)	30(8)
C(2)	203(10)	152(10)	94(10)	-6(7)	-6(7)	-11(7)
C(3)	175(10)	170(10)	115(10)	12(7)	-25(7)	-14(8)
C(4)	183(11)	195(11)	170(11)	27(9)	1(8)	1(8)
C(5)	173(11)	242(12)	320(13)	9(9)	-27(10)	14(9)
C(6)	199(12)	187(10)	317(12)	2(9)	-117(9)	9(8)
C(7)	306(12)	175(11)	231(12)	53(8)	-85(9)	15(9)
C(8)	312(11)	188(11)	165(11)	37(8)	-69(9)	3(9)
C(9)	252(11)	141(10)	124(10)	15(7)	-2(8)	-2(8)
C(10)	332(12)	160(11)	98(10)	17(8)	33(8)	-30(9)
C(11)	296(12)	142(11)	163(11)	-59(7)	66(8)	-34(8)
C(12)	211(11)	130(10)	157(10)	1(7)	5(7)	26(7)
C(13)	340(12)	174(11)	160(11)	-5(8)	4(9)	-7(9)
C(14)	308(13)	197(11)	213(12)	38(8)	-22(9)	-82(9)
C(15)	233(12)	241(12)	421(15)	3(11)	-34(10)	51(9)
C(16)	244(11)	150(10)	178(11)	-20(8)	16(8)	-29(9)
C(17)	212(12)	212(12)	262(12)	30(9)	28(9)	30(9)

Supplementary Table 7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for diketone **16** (CCDC 664430).

	x	y	z	U_{iso}
H(2)	10590(20)	3978(18)	6967(7)	5(4)
H(3)	7760(20)	3463(18)	6085(7)	7(4)
H(7)	7290(20)	8280(20)	5503(9)	29(5)
H(4A)	8180(20)	5860(20)	7005(8)	21(5)
H(5A)	5210(20)	5070(20)	6242(9)	24(5)
H(8A)	8490(30)	6340(20)	4977(9)	33(5)
H(10A)	9630(20)	3440(20)	5166(8)	22(5)
H(13A)	9850(20)	1230(20)	5701(9)	19(5)
H(14A)	8530(30)	40(20)	6501(9)	33(6)
H(15A)	5460(30)	9480(30)	6252(10)	46(7)
H(16A)	11750(30)	5860(20)	6279(9)	31(6)
H(17A)	14160(30)	1860(20)	6372(9)	30(5)
H(4B)	7120(20)	4350(20)	7125(8)	16(5)
H(5B)	4880(30)	5970(20)	6926(10)	41(6)
H(8B)	7040(20)	5230(20)	5307(8)	17(5)
H(10B)	10870(20)	4780(20)	5001(9)	26(5)
H(13B)	11540(30)	360(20)	5925(9)	24(6)
H(14B)	10310(30)	-90(20)	6890(10)	36(6)
H(15B)	5590(30)	8740(20)	6937(9)	34(6)
H(16B)	10120(20)	7120(20)	6333(8)	26(5)
H(17B)	12940(30)	1620(20)	7000(9)	37(6)
H(15C)	3890(30)	8470(30)	6556(10)	43(6)
H(16C)	11280(20)	6960(20)	5679(9)	22(5)
H(17C)	13620(20)	3190(20)	6827(8)	17(5)

Supplementary Notes:

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