Supporting Information for:

The Catalytic Enantioselective, Protecting Group-Free Total Synthesis of (+)-Dichroanone

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Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (either freshly distilled or passed through activated alumina columns). Chloroform, stabilized with ethanol was stored in the dark over oven-dried 4Å molecular sieves. Methanol and *N,N*-dimethyl acetamide were used as purchased. 2,2,6-Trimethylcyclohexanone **(9)** was used as received or prepared according to the procedure reported herein. All other commercially obtained reagents were used as received, unless specified otherwise. IBX was prepared by the method of Santagostino.[1] (*S*)-*t*-Bu-PHOX ligand was prepared according to known methods.[2] Reaction temperatures were controlled using an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized using direct visualization, UV at 254nm or 356nm, *p*-anisaldehyde, ceric ammonium molybdate, potassium permanganate, and iodine vapor over sand. TLC data include R_f, eluent, and method of visualization. ICN silica gel (particle size 0.032-0.063 mm) was used for flash column chromatography. Analytical chiral HPLC analyses were performed with an Agilent 1100 Series HPLC using a chiralcel AD normal-phase column (250 x 4.6 mm) employing 0.3–4.0% ethanol in hexane isocratic elution and a flow rate of 0.1 mL/min with visualization at 254nm. Analytical chiral GC analysis was performed with an Agilent 6850 GC using a GT-A column (0.25m x 30.00m) employing an 80 °C isotherm and a flow rate of 1.0 mL/min. ^{1}H NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz) or a Varian Inova 500 (at 500 MHz) and are reported relative to the residual

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[1] Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537-4538.

[2] a.) Peer, M.; de Jong, J. C.; Kiefer, M.; Langer, T.; Riech, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahedron* **1996**, *52*, 7547-7583. b.) Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 15044-15045.

solvent peak (δ 7.26 for $CDCl_3$ and δ 7.15 for C_6D_6). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz)[3] and integration. ^{13}C NMR spectra were recorded on a Varian Mercury 300 (at 75 MHz), or a Varian Inova 500 (at 125 MHz) and are reported relative the residual solvent peak (δ 77.2 for $CDCl_3$ and δ 128.4 for C_6D_6). Data for ^{13}C NMR spectra are reported in terms of chemical shift. ^{19}F NMR spectra were recorded on a Varian Mercury 300 (at 282 MHz) and are reported in terms of chemical shift without the use of a reference peak. IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer and are reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-1010 polarimeter, using a 100 mm path-length cell. High-resolution mass spectra were obtained from the California Institute of Technology Mass Spectral Facility. UV-Vis spectra were collected on an Agilent 8453 UV-Vis spectroscopy system and are reported as follows: λ_{max} (nm) then log(ε) ($M^{-1} \cdot cm^{-1}$). Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Boiling points are measured directly during distillation and are uncorrected. 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 293604.

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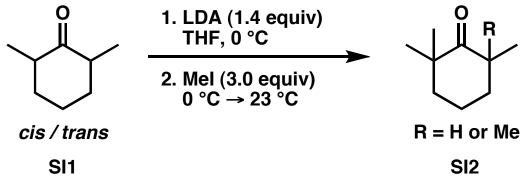
[3] When a subscript is shown with the coupling constant, it indicates what type of splitting the constant is associated with. For example (td, J_t = 5.0 Hz, J_d = 3.3 Hz, 1H) indicates that the triplet splitting has a 5.0 Hz coupling constant and the doublet has a 3.3 Hz coupling constant.



Ketone Mixture SI2. To a solution of *i*-Pr_2NH (16.6 mL, 119 mmol), (freshly distilled from CaH_2) in THF (400 mL) was added *n*-BuLi (44.4 mL, 2.55 M in hexanes, 113.2 mmol) in a dropwise fashion at 0 °C. After 30 min, a solution of 2,6-dimethylcyclohexanone (**SI1**) (10.0 g, 79.3 mmol), (fractionally distilled from $CaSO_4$ under N_2 at ambient pressure), (mixture of *cis* and *trans* isomers) in THF (10 mL) was added. After 1 h, MeI (14.8 mL, 237.9 mmol) was added quickly,[4] and the reaction was warmed to 23 °C. After 1 h, the reaction was poured into a flask containing saturated aqueous NH_4Cl (100 mL) and H_2O (100 mL). After stirring 10 min, the reaction was diluted with H_2O (75 mL) and pentanes (75 mL). The aqueous layer was extracted with pentanes (3 x 100 mL). All organic layers were combined, washed with brine (100 mL), dried (Na_2SO_4), filtered, concentrated, and distilled under N_2 at ambient pressure, affording ketone mixture **SI2** (9.57 g) as a clear, fragrant oil, which used without further characterization.

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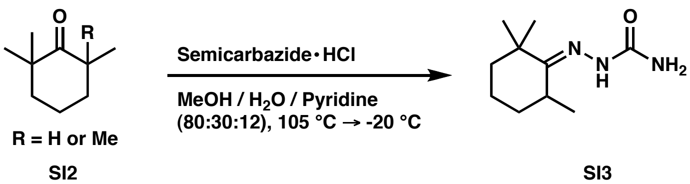
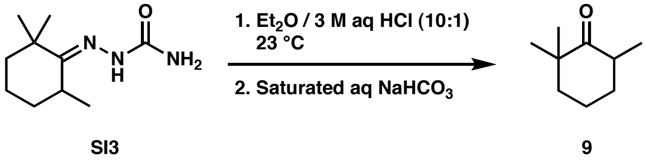
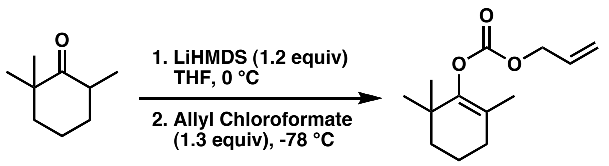
[4] Slow addition of MeI over 1 h led to a dark yellow solution that gave decomposition during distillation. The same outcome occurred when the reaction was stirred for more than 2 hours at 23 °C after MeI addition.



Semicarbozone SI3. To a solution of ketone mixture **SI2** (9.56 g), in MeOH (160 mL), water (60 mL), and pyridine (24 mL) was added semicarbazide hydrochloride (14.0g, 126.1 mmol). The reaction was refluxed at 105 °C for 30 min, and then the heating was turned off, and the reaction was allowed to cool to 23 °C in the oil bath. Then the reaction was cooled to –20 °C for 36 hours. The white crystals that formed were filtered and washed with water, then dried in vacuo over P_2O_5, giving **SI3** (10.8 g, 69% over 2 steps from **SI1**) as a white, crystalline solid. R_f 0.45 (1:9 MeOH/DCM), (I_2/Sand); mp 203-205 °C (water); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (s, broad, 1H), 6.05 (s, broad, 1H), 5.67 (s, broad, 1H), 2.92-2.79 (m, 1H), 1.84-1.66 (m, 1H), 1.64-1.31 (m, 5H), 1.13 (s, 3H), 1.13 (d, J = 7.7 Hz, 3H), 1.12 (s, 3H), 1.11-1.08 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.7, 158.8, 40.3, 38.0, 31.7, 29.6, 29.2, 28.3, 18.0, 17.1; IR (KBr): 3463, 3186, 2970, 2931, 2868, 2856, 1689, 1577, 1465, 1384, 1110, 1086 cm^{-1}; HRMS-FAB$^+$ (*m*/*z*): $[M+H]^+$ calc'd for $C_{10}H_{20}N_3O$, 198.1606; found, 198.1602.

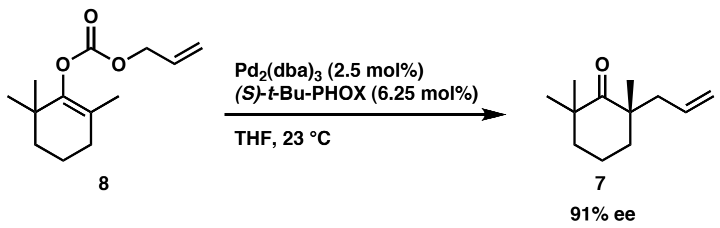


Ketone 9. To a suspension of semicarbazone **SI3** (10.9 g, 55.0 mmol) in Et_2O (400 mL) and water (20 mL) was added aqueous 6 M HCl (20 mL) in a dropwise fashion. The biphasic mixture was stirred vigorously at 23 °C for 3 h. Then saturated aqueous $NaHCO_3$ (300 mL) was added cautiously at 0 °C. After 30 min, the organic phase was collected. The aqueous phase was extracted with Et_2O (2 x 100 mL). All organic layers were combined, dried (Na_2SO_4), filtered, and concentrated. The residue was distilled at ambient pressure under N_2, affording ketone **9** (6.51 g, 82% yield) as a clear, fragrant oil. R_f 0.48 (1:9 EtOAc/hexane), (*p*-Anisaldehyde); bp 178-180 °C (760 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.54 (app. septet, J = 6.6 Hz, 1H), 1.99-1.88 (m, 1H), 1.77 (tdd, J_t = 26.7 Hz, J_d = 13.2 Hz, 3.8 Hz, 1H), 1.65 (app. dq, J_d = 13.2 Hz, J_q = 2.8 Hz, 1H), 1.52 (app. dddd, J = 13.7 Hz, 6.6 Hz, 4.1 Hz, 2.9 Hz, 1H), 1.42 (app. td, J_t = 13.2 Hz, J_d = 4.1 Hz, 1H), 1.19 (app. ddd, J = 26.1 Hz, 13.2 Hz, 3.9 Hz, 1H), 1.06 (s, 3H), 0.91 (s, 3H), 0.86 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 217.1, 45.1, 41.8, 40.7, 36.7, 25.6, 25.2, 21.5, 14.9; IR (NaCl/$CDCl_3$): 2967, 2930, 2869, 2853, 1707, 1471, 1455, 1384, 1376, 1127, 1019, 993, 957, 857 cm^{-1}; HRMS-EI$^+$ (*m/z*): [M]$^+$ calc'd for $C_9H_{16}O$, 140.1201; found, 140.1203.

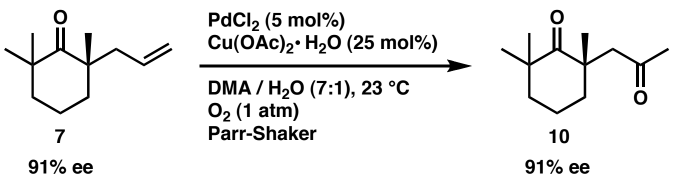


9 → 8

Enol Carbonate 8. A solution of LiHMDS (57.5 mL, 1.0M in THF, 57.5 mmol) in THF (300 mL) was cooled to 0 °C and a solution of ketone **9** (6.67 g, 47.6 mmol) in THF (10 mL) was added. The reaction was stirred at 0 °C for 1 h, then cooled to –78 °C and fitted with an addition funnel, which was charged with a solution of allyl chloroformate (6.56 mL, 61.8 mmol) in THF (200 mL). The solution was added dropwise over 30 min. Then the reaction was warmed to 23 °C. After 13 h, the reaction was poured into a mixture of saturated aqueous NH_4Cl (100 mL), water (100 mL), and hexane (100 mL). After 10 min, the organic phase was collected and the aqueous phase extracted with Et_2O (3 x 75 mL). All organic layers were combined, washed with brine (100 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography on silica gel (2:98 Et_2O/hexane eluent), affording enol carbonate **8** (9.19 g, 86% yield) as a clear oil. R_f 0.43 (1:9 EtOAc/hexane), (*p*-Anisaldehyde); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.96 (app. ddt, J_d = 17.1 Hz, 10.7 Hz, J_t = 5.8 Hz, 1H), 5.38 (app. ddq, J_d = 17.3 Hz, 8.3 Hz, J_q = 1.4 Hz, 1H), 5.28 (app. ddq, J_d = 10.5 Hz, 4.4 Hz, J_q = 1.1 Hz, 1H), 4.65 (app. ddt, J_d = 10.2 Hz, 5.7 Hz, J_t = 1.4 Hz, 2H), 2.05 (t, J = 5.5 Hz, 2H), 1.77-1.52 (m, 4H), 1.50 (s, 3H), 1.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 148.1, 131.8, 120.9, 119.1, 68.7, 39.4, 35.1, 31.4, 26.9, 19.3, 16.7; IR (NaCl/$CDCl_3$): 2965, 2934, 2868, 2838, 1759, 1459, 1363, 1271, 1238, 1138, 1025, 993, 937 cm^{-1}; HRMS-EI$^+$ (*m/z*): $[M]^+$ calc'd for $C_{13}H_{20}O$, 224.1413; found, 224.1408.



Allyl Ketone 7. A 100 mL round bottom flask was flame-dried under argon and charged with Pd$_2$dba$_3$ (24.2 mg, 0.0264 mmol) and (*S*)-*t*-Bu-PHOX (25.6 mg, 0.0661 mmol). The system was evacuated with vacuum and back-filled with argon (3x). Then THF (31.7 mL) was introduced. The red mixture was stirred for 30 min at 25 °C. Then **8** (237 mg, 1.057 mmol) was added, and the reaction immediately turned yellow-green, and around 25 min became orange. After 30 min, the orange reaction was concentrated and benzene (ca. 2 mL) was added. After concentrating a second time, more benzene (ca. 2 mL) was added. The residue was purified by flash chromatography on silica gel (2:98 hexane/Et$_2$O eluent), affording **7** (158 mg, 83% yield) as a clear oil in 91% ee as determined by chiral GC analysis. R_f 0.48 (1:9 EtOAc/hexane), (I$_2$/sand); ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.64 (dddd, J = 17.1 Hz, 10.5 Hz, 7.7 Hz, 6.9 Hz, 1H), 5.05 (app. ddt, J_d = 6.3 Hz, 2.2 Hz, J_t = 1.1 Hz, 1H), 4.98 (app. ddt, J_d = 13.8 Hz, 2.5 Hz, J_t = 1.4 Hz, 1H), 2.26 (AB spin system, app. dddt, J_{dAB} = 47.6 Hz, J_d = 13.8 Hz, 6.9 Hz, J_t = 1.4 Hz, 2H), 1.87-1.47 (m, 6H), 1.15 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 219.8, 134.7, 118.0, 47.7, 44.6, 44.0, 39.9, 37.0, 28.0, 27.3, 25.7, 17.9; IR (NaCl/CDCl$_3$): 3077, 2979, 2964, 2933, 2869, 1697, 1463, 1382, 999, 914 cm^{-1}; HRMS-EI$^+$ (*m/z*): [M]$^+$ calc'd for C$_{12}$H$_{20}$O, 180.1514; found, 180.1506; $[\alpha]^{24}_D$ –36.34° (*c* 0.140, CHCl$_3$), 91% ee.



Diketone 10. A 500 mL Parr Flask was charged with $PdCl_2$ (74.5 mg, 0.420 mmol), $Cu(OAc)_2 \cdot H_2O$ (381 mg, 2.10 mmol), *N*,*N*-dimethyl acetamide (17.5 mL), and water (2.5 mL). Then **7** (1.51 g, 8.39 mmol) was introduced. The system was cooled to –78 °C then evacuated with vacuum and back-filled from a balloon of O_2 (3x). The mixture was warmed to 23 °C and placed on a Parr Shaker for 24 h under a balloon of O_2.[5] The reaction was then directly loaded onto a silica gel column and purified by flash chromatography (15:85 Et_2O:pentane → 25:75 Et_2O:pentane eluent), affording **10** (1.27 g, 77% yield) as a clear oil. R_f 0.44 (1:4 EtOAc:hexane), ($KMnO_4$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.79 (AB spin system, app. dd, J_{dAB} = 281.1 Hz, J_d = 18.4 Hz, 2H), 2.05 (s, 3H), 2.00-1.72 (m, 3H), 1.71-1.53 (m, 2H), 1.47 (app. ddd, J = 12.0 Hz, 5.4 Hz, 2.8 Hz, 1H), 1.16 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 220.7, 206.9, 55.7, 45.0, 44.4, 38.9, 36.9, 30.2, 27.9, 27.8, 27.0, 18.2; IR (NaCl/$CDCl_3$): 2965, 2943, 2924, 2868, 1715, 1694, 1463, 1394, 1379, 1360, 1147, 1034 cm^{-1}; HRMS-EI$^+$ (*m/z*): $[M]^+$ calc'd for $C_{12}H_{20}O_2$, 196.1463; found, 196.1456; $[\alpha]^{27}_D$ +71.96° (*c* 0.200, $CHCl_3$), 91% ee.

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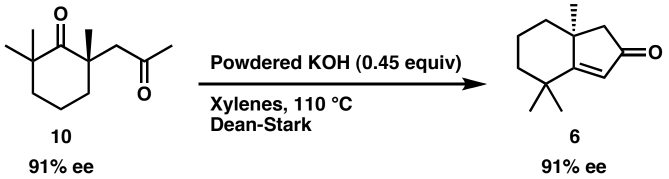
[5] When the reaction was run without the Parr Shaker (i.e. magnetic stirring only) on this scale or larger, the reaction would stall at incomplete conversion.



Bicyclic Enone 6. To a solution of **10** (1.21 g, 6.15 mmol) in xylenes (25 mL) was added freshly powdered KOH (155 mg, 2.76 mmol). The reactor was fitted with a Dean-Stark trap and heated to 110 °C for 11 h.[6] The reaction was cooled to 23 °C and directly loaded onto a column of silica gel and purified by flash chromatography (pentane → 5:95 Et_2O/pentane → 50:50 Et_2O/pentane eluent), affording **6** (1.06 g, 96% yield) as a clear, fragrant oil, which was fully characterized after enantioenrichment; $[\alpha]^{25}_{D}$ –87.21° (*c* 0.280, $CHCl_3$), 91% ee.

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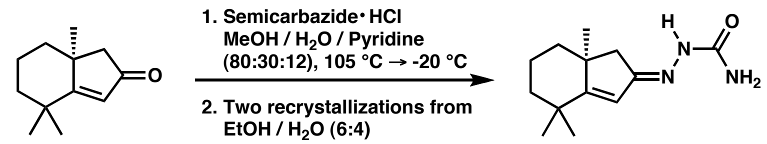
[6] Although xylenes do not reflux at this temperature, the xylene-water azeotrope does, and can be removed. Refluxing at greater than 110 °C was avoided as it led to decomposition.



6
83% ee

SI4
97% ee

Enantioenriched Semicarbazone SI4. To a suspension of enone **6** (1.70 g, 9.51 mmol)[7] in MeOH (27.1 mL), water (10.2 mL), and pyridine (4.07 mL) was added semicarbazide hydrochloride (1.91 g, 17.1 mmol). The reaction was refluxed at 105 °C for 2 h. Then the reaction was cooled to –20 °C for 36 h. The crystals that formed were filtered and washed with water, then suspended in absolute EtOH (115 mL). The suspension was heated to 95 °C, at which point it became a solution. Water was added dropwise until cloudiness persisted for 30 seconds even with stirring (76.6 mL). EtOH (200 μL) was added to remove the clouding. Then the heat was turned off, and the reaction was allowed to cool in the oil bath to 23 °C.[8] After 10 h, the crystals were filtered and suspended in EtOH (100 mL). The suspension was heated to 100 °C and water (72 mL) was added dropwise as before followed by EtOH (200 μL). The white, flaky crystals were grown in the same way, then collected by filtration, washed with water, and dried over P_2O_5 in vacuo, giving enantioenriched semicarbazone **SI4** (1.43 g, 64%) as a single imine geometric isomer (^{1}H NMR, nOesy) in 97% ee as determined by chiral HPLC analysis. R_f 0.46 (1:9 MeOH/DCM), (UV, 254 nm); mp 227-229 °C (water); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (s, broad, 1H), 5.86 (s, 1H), 5.80 (s, broad, 1H), 5.12 (s, broad, 1H), 2.36 (AB spin system, app. dd, J_{dAB} = 38.2 Hz, J_{d} = 16.8 Hz, 2H), 1.89 (app. d, J = 12.9 Hz, 1H), 1.78 (app. tt, J = 13.8 Hz, 3.0 Hz, 1H), 1.61-1.48 (m, 2H), 1.37-1.30 (m, 1H), 1.28 (s, 1H), 1.29-1.23 (m, 1H), 1.17 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$)[9]: δ 46.6 (broad), 44.8 (broad), 41.7, 41.0, 36.0 (broad), 31.4, 29.9, 27.7, 26.7, 19.5; IR (KBr): 3469, 3235 (broad), 3191 (broad), 3137 (broad), 2998, 2984, 2958, 2938, 2911, 2863, 1692, 1661, 1572, 1477, 1460, 1420, 1093 cm^{-1}; HRMS-FAB$^+$ (*m/z*): $[M+H]^+$ calc'd for $C_{13}H_{22}N_3O$, 236.1761; found, 236.1763; $[\alpha]^{25}_{D}$ –103.70° (*c* 0.100, $CHCl_3$), 97% ee.

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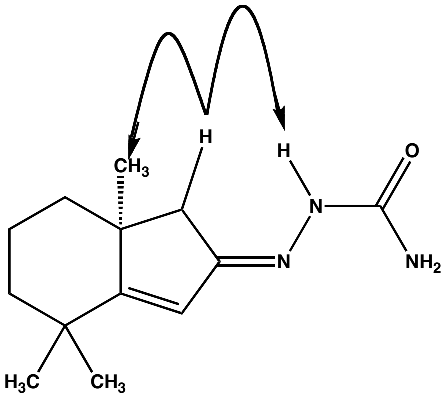
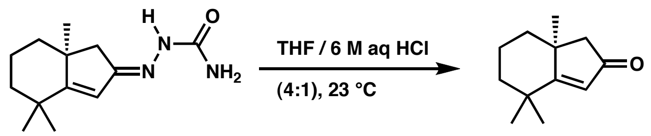
[7] The sample of bicyclic enone used in this recrystallization sequence was a combination of several lots of enone product and had a net ee of 83%.

[8] Cooling the system to 0 °C gave much less enantioenrichment per recrystallization than if the minimum temperature was kept at 23 °C.

[9] $CDCl_3$ was the only NMR solvent capable of solvating **SI4** at 23 °C (ca. 1 mg in 1 mL), making ^{13}C NMR spectroscopy challenging.

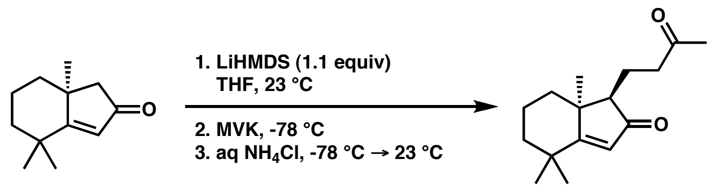


nOe's detected for SI4



SI4 97% ee → **6** 97% ee

Enantioenriched Enone 6. To a suspension of enantioenriched semicarbazone **SI4** (1.30 g, 5.53 mmol) in THF (120 mL) was added aqueous 6 M HCl (30 mL) in a dropwise fashion. After stirring vigorously for 12 h at 23 °C, the biphasic mixture was cooled to 0 °C, and saturated aqueous $NaHCO_3$ (72 mL) was added cautiously. After stirring for 10 min, the reaction was diluted with water (75 mL) and hexane (75 mL), and the organic phase was collected. The aqueous phase was extracted with Et_2O (3 x 75 mL). All organic layers were combined, washed with brine (75 mL), dried (Na_2SO_4), filtered, and concentrated, giving enantioenriched enone **6** (944 mg, 96% yield) as a clear, fragrant oil. R_f 0.37 (1:4 EtOAc/hexane), (UV, 254 nm); mp 9-11 °C (Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.82 (s, 1H), 2.29 (app. s, 2.29, 2H), 1.93 (app. dq, J_d = 10.5 Hz, J_q = 2.8 Hz, 1H), 1.83 (app. tt, J = 13.5 Hz, 3.3 Hz, 1H), 1.71-1.54 (m, 2H), 1.40 (app. ddd, J = 12.4 Hz, 8.0 Hz, 3.9 Hz, 1H), 1.36 (app. ddd, J = 8.0 Hz, 3.3 Hz, 2.0 Hz, 1H), 1.35 (s, 3H), 1.25 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.1, 194.4, 126.4, 54.7, 44.3, 41.5, 40.6, 36.5, 31.3, 27.4, 26.2, 19.1; IR (NaCl/$CDCl_3$): 2997, 2987, 2960, 2929, 2868, 2847, 1712, 1696, 1600, 1459, 1261, 1166 cm^{-1}; HRMS-EI$^+$ (*m/z*): $[M]^+$ calc'd for $C_{12}H_{18}O$, 178.1358; found, 178.1356; $[\alpha]^{24}_D$ –102.40° (*c* 0.200, $CHCl_3$), 97% ee.

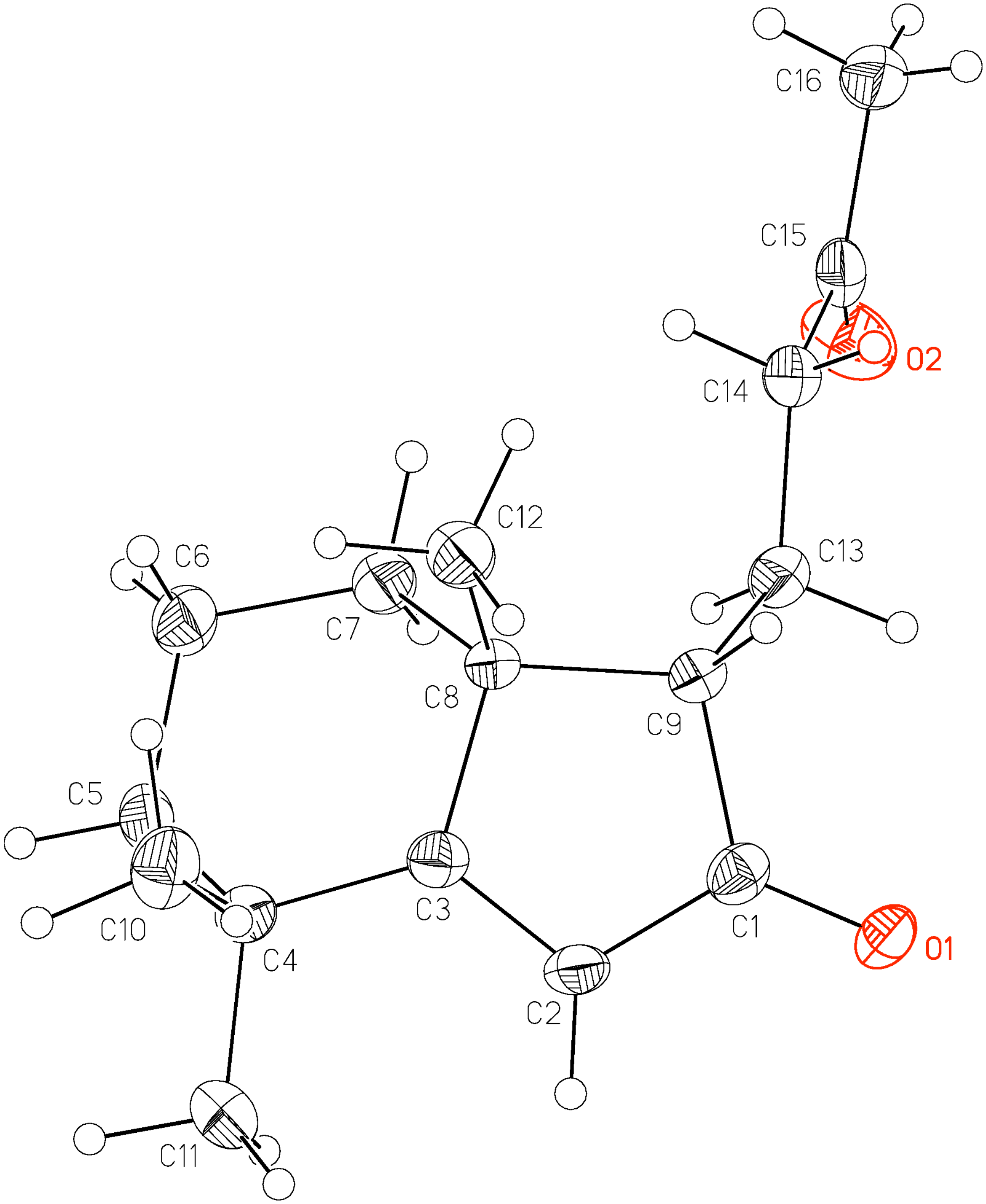


6
97% ee

11
98% ee, 10.7 : 1.0 dr

Keto-Enone 11. To a solution of LiHMDS (3.27 mL, 0.943M in THF, 3.09 mmol) in THF (29 mL) at 23 °C was added a solution of enantioenriched enone **6** (981 mg, 5.51 mmol) in THF (12 mL) in a dropwise fashion over 3 min. After 1 h, the reaction was cooled to –78 °C and methyl vinyl ketone (257 μL, 3.09 mmol) was added quickly. After 5 min, the reaction was quenched with a 1:1 mixture of saturated aqueous NH_4Cl (5 mL) and water (5mL) at –78 °C. Then the reaction was warmed to room temperature and diluted with hexanes (20 mL) and water (20 mL). After collecting the organic phase, the aqueous phase was extracted with Et_2O (3 x 15 mL). All organic layers were combined, washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography on silica gel (1:9 Et_2O/pentane → 2:8 Et_2O/pentane → 4:6 Et_2O/pentane eluent), affording starting material **6** (49.3 mg, 10% yield) as a clear oil, and keto-enone **11** (500 mg, 72% yield) as a clear oil which formed pale yellow crystals from the melt under reduced pressure. The solid was of 98% ee as determined by chiral HPLC analysis. Two separate crystals of racemic **11** were analyzed by X-ray diffraction; each proved to be the same diastereomer (relative stereochemistry is depicted in the product above). R_f 0.20 (1:4 EtOAc/hexane), (UV, 254 nm); mp 67-69 °C (Et_2O/pentane), (98% ee), mp 62-64 °C (Et_2O/pentane), (83% ee) mp 42-44 °C (Et_2O/pentane), (0% ee); ^{1}H NMR (300 MHz, $CDCl_3$), (major diastereomer): δ 5.76 (s, 1H), 2.89 (qd, J_q = 9.1 Hz, J_d = 5.2 Hz, 1H), 2.70 (ddd, J = 18.2 Hz, 8.8 Hz, 6.6 Hz, 1H), 1.99 (dd, J = 10.7 Hz, 5.0 Hz, 1H), 2.16 (s, 3H), 1.94-1.78 (m, 2H), 1.72-1.49 (m, 4H), 1.45 (dd, J = 13.2 Hz, 3.9 Hz, 1H), 1.35 (s, 3H), 1.33 (app. dd, J = 14.1 Hz, 4.4 Hz, 1H), 1.25 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), (major diastereomer): δ 211.0, 208.9, 193.1, 124.8, 58.1, 47.2, 41.7, 41.4, 36.7, 35.2, 31.2, 30.2, 28.3, 26.4, 21.3, 18.8; IR (KBr): 3009, 2958, 2943, 2897, 2871, 1710, 1691, 1598, 1460, 1420, 1381, 1372, 1357, 1269, 1161 cm^{-1}; HRMS-EI$^+$ (*m/z*): $[M]^+$ calc'd for $C_{16}H_{24}O_2$, 248.1776; found, 248.1774; $[\alpha]^{27}_D$ –15.79° (*c* 0.220, $CHCl_3$), 98% ee.

Crystal Structure of Racemic 11[10]



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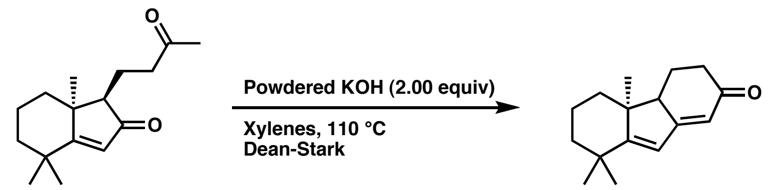
[10] The *depicted* absolute configuration of this molecule is enantiomeric to the actual structure of **11**. Although the data reveals the relative stereochemistry, the absolute configuration of this molecule within the unit cell is unknown.



11
98% ee, 10.7 : 1.0 dr

12
98% ee, 5.6 : 1.0 dr

Tricyclic Enone 12. To a solution of **11** (457 mg, 1.60 mmol) in xylenes (18 mL) was added freshly powdered KOH (207 mg, 3.69 mmol). The reactor was fitted with a Dean-Stark trap and heated to 110 °C for 14 h[11] in the dark. The reaction was cooled to 23 °C and directly loaded onto a column of silica gel and purified by flash chromatography (pentane → 2:8 Et_2O:pentane → 6:4 Et_2O:pentane eluent), affording tricyclic enone **12** (336 mg, 80% yield) as a yellow oil. The product was a mixture of two diastereomers as determined by ^{1}H NMR. R_f 0.28 (1:4 EtOAc/hexane), (UV, 254 nm), (first diastereomer) R_f 0.19 (1:4 EtOAc/hexane), (UV 254 nm), (second diastereomer);[12] ^{1}H NMR (300 MHz, $CDCl_3$), (major diastereomer): δ 6.05 (s, 1H), 5.76 (d, *J* = 2.5 Hz, 1H), 2.52 (app. ddd, *J* = 14.3 Hz, 5.5 Hz, 2.5 Hz, 1H), 2.50 (app. ddd, *J* = 14.9 Hz, 3.6 Hz, 2.8 Hz, 1H), 2.29 (ddd, *J* = 17.0 Hz, 13.5 Hz, 5.2 Hz, 1H), 1.98-1.72 (m, 4H), 1.56 (app. d, *J* = 12.4H, 2H), 1.39-1.24 (m, 2H), 1.16 (s, 6H), (1.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$), (major diastereomer): δ 200.1, 179.3, 171.7, 122.9, 117.2, 55.3, 49.1, 41.2, 40.1, 37.9, 35.7, 31.3, 27.7, 23.9, 22.4, 19.1; IR (NaCl/$CDCl_3$): 2930, 2868, 2847, 1659, 1652, 1619, 1616, 1585, 1457, 1418, 1385, 1372, 1320, 1273, 1244, 1194, 1181, 970, 887 cm^{-1}; HRMS-EI$^+$ (*m/z*): $[M]^+$ calc'd for $C_{16}H_{22}O$, 230.1671; found, 230.1668; $[\alpha]^{25}_D$ –224.40° (*c* 0.550, $CHCl_3$), 98% ee.

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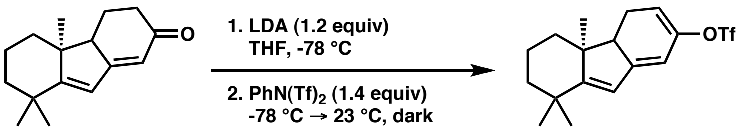
[11] Although xylenes do not reflux at this temperature, the xylene-water azeotrope does, and can be removed. Refluxing at greater than 110 °C was avoided as it led to decomposition.

[12] Under all conditions tested, these diastereomers were chromatographically inseparable.



12
98% ee, 5.6 : 1.0 dr

13
98% ee, 4.8 : 1.0 dr

Enol Triflate 13. A solution of *i*-Pr_2NH (186 μL, 1.33 mmol), (freshly distilled from CaH_2) in THF (17 mL) was cooled to 0 °C and *n*-BuLi (482 μL, 2.55 M in hexanes, 1.23 mmol) was added dropwise. After 30 min, the reaction was cooled to –78 °C and a solution of tricyclic enone **12** (236 mg, 1.03 mmol) in THF (3 mL) was added dropwise over 5 min. After 30 min, a solution of *N*-phenyl triflimide (513 mg, 1.44 mmol) in THF (6 mL) was added. 30 min later, the reaction was wrapped in foil and warmed to 23 °C. After 5 h, the reaction was diluted with Et_3N (5 mL) and concentrated to ca. 5 mL total volume. Then hexane (10 mL) and more Et_3N (2 mL) were added, and the reaction was concentrated to ca. 5 mL a second time. The reaction was filtered through a 5-inch plug of silica that had been pre-eluted with Et_3N/Et_2O/hexane (5:20:75)[13] then eluted with the same solvent mixture. The eluate was concentrated, giving crude, unstable enol triflate **13** (yield not determined) as an orange gel, which was immediately used in the next reaction. ^1H NMR revealed the product to be an inseparable mixture of diastereomers. R_f 0.80 (2:8:1 EtOAc/hexane/Et_3N, TLC plate is pre-eluted),[14] (Ceric Ammonium Molybdate), (both diastereomers); ^1H NMR (300 MHz, C_6D_6): δ 5.67 (s, 1H), 5.59 (app. dd, J = 2.5 Hz, 2.2 Hz, 1H), 5.32 (app. dtd, J_{d1} = 6.6 Hz, J_t = 2.2 Hz, J_{d2} = 1.1 Hz, 1H), 1.94 (ddd, J = 50.6 Hz, 19.8 Hz, 2.8 Hz, 1H), 1.96 (ddd, J = 29.2 Hz, 20.0 Hz, 2.5 Hz, 1H), 1.65 (app. dt, J_d = 14.8 Hz, J_t = 6.9 Hz, 1H), 1.62-1.44 (m, 2H), 1.34-1.18 (m, 2H), 1.12 (app. dd, J = 12.7 Hz, 3.0 Hz, 1H), 0.98 (s, 6H), 0.97-0.81 (m, 1H), 0.78 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ 172.7, 153.0, 149.1, 132.3, 131.4, 130.3, 122.5, 111.2, 107.7, 50.1, 48.7, 41.0, 40.2, 35.6, 31.8, 27.7, 23.1, 20.9, 19.6; ^{19}F NMR (282 MHz, C_6D_6): δ -71.6[15], -74.4 (major diastereomer), -74.5 (minor diastereomer); IR (NaCl/hexane): 2961, 2931, 2868, 2848, 1649, 1579, 1445, 1420, 1246, 1209, 1144, 1096, 1059, 907, 880, 862 cm^{-1}; HRMS-EI^+ (*m/z*): $[M]^+$ calc'd for $C_{17}H_{21}F_3O_3S$, 362.1164; found, 362.1166; $[\alpha]^{25}_D$ –11.24° (*c* 0.700, hexane), 98% ee.

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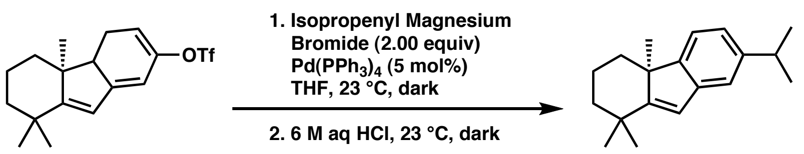
[13] If the crude enol triflate is exposed to silica that has not been basified, it decomposes to the starting material.

[14] If the plate is not pre-soaked in eluent, the product will be cleaved to starting material during plate development, giving the false appearance of an incomplete reaction.

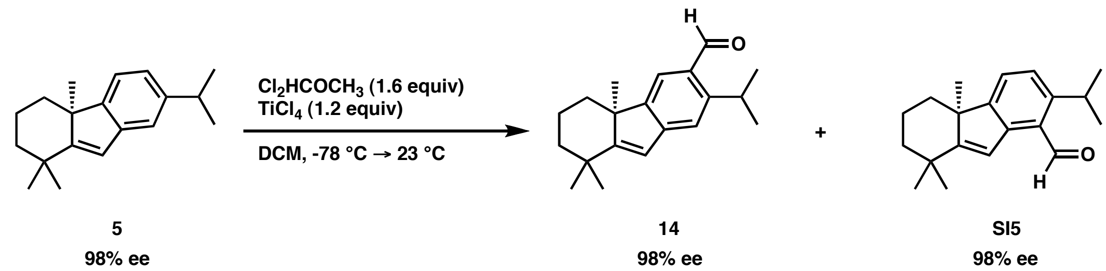
[15] This peak may arise from the fluorines of *N*-phenyl triflimide, which is also visible in the ^1H NMR.



13
98% ee, 4.8 : 1.0 dr

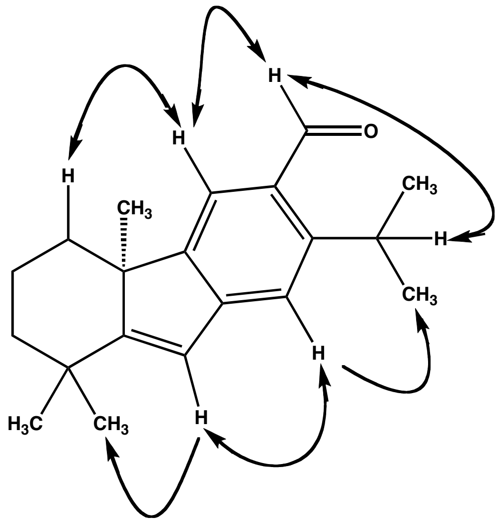
5
98% ee

Arene 5. To a solution of crude **13** (ca. 371 mg, 1.03 mmol) in THF (50 mL) was added isopropenyl magnesium bromide (4.12 mL, 0.5 M in THF, 2.06 mmol), and the flask was immediately covered in foil. Then a solution of $Pd(PPh_3)_4$ (29.5 mg, 0.0515 mmol, weighed in glovebox) in THF (5 mL) was promptly added at 23 °C. After 1 h, aqueous 6 M HCl (5.5 mL) was added in a dropwise manner. After 16 h at 23 °C, the reaction was diluted with water (40 mL) and hexane (40 mL), and the organic phase was collected. The aqueous phase was extracted with Et_2O (3 x 30 mL). All organic layers were combined, washed with brine (30 mL), dried (Na_2SO_4), filtered, and adsorbed onto silica gel. The adsorbed product was purified by flash chromatography on silica gel (hexane eluent), affording arene **5** (170 mg, 65% yield from bicyclic enone **12**) as a clear oil. R_f 0.43 (hexane), (UV 254 nm); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21 (d, J = 1.4 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 7.04 (dd, J = 7.7 Hz, 1.4 Hz, 1H), 6.40 (s, 1H), 2.96 (septet, J = 6.9 Hz, 1H), 2.18 (ddd, J = 12.7 Hz, 4.7 Hz, 3.0 Hz, 1H), 2.00 (app. qt, J_q = 13.8 Hz, J_t = 4.3 Hz, 1H), 1.74-1.60 (m, 2H), 1.41 (s, 3H), 1.35 (s, 3H), 1.32 (d, J = 6.9 Hz, 6H), 1.29 (s, 3H), 1.15 (td, J_t = 12.9 Hz, J_d = 3.7 Hz, 1H), 1.05 (td, J_t = 13.2 Hz, J_d = 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.4, 152.9, 147.2, 142.4, 122.4, 121.0, 120.8, 118.6, 50.8, 42.8, 38.3, 35.7, 34.3, 31.5, 25.5, 24.54, 24.51, 23.7, 20.0; IR (NaCl/$CDCl_3$): 3061, 2995, 2959, 2928, 2866, 2845, 1616, 1479, 1458, 1382, 1369, 1362, 886, 820 cm^{-1}; HRMS-EI$^+$ (m/z): $[M]^+$ calc'd for $C_{19}H_{26}$, 254.2035; found, 254.2046; $[\alpha]^{24}_D$ –80.74° (c 0.320, $CHCl_3$), 98% ee.

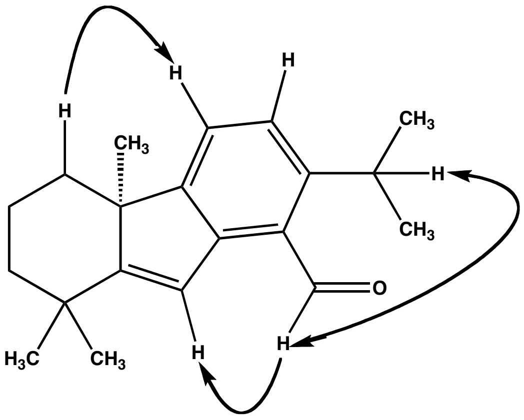


Aldehyde 14. A solution of **5** (156 mg, 0.614 mmol) in DCM (15 mL) was cooled to –78 °C and α,α-dichloromethyl, methyl ether (89.0 μL, 0.982 mmol) was introduced, followed by $TiCl_4$ (81.0 μL, 0.736 mmol). After 1 h, the deep red mixture was warmed to 23 °C, and 1 h later the reaction was poured onto a slurry of crushed ice (40 mL) and DCM (10 mL). After stirring vigorously for 1 h, the organic phase was collected. The aqueous phase was extracted with DCM (3 x 20 mL). All organic layers were combined, washed with water (20 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL), then dried (Na_2SO_4), filtered, and adsorbed onto silica gel. The adsorbed products were separated by flash chromatography on silica gel (1:99 Et_2O/hexane → 2:98 Et_2O/hexane → 5:95 Et_2O/hexane eluent), affording desired aldehyde **14** (137 mg, 79% yield) as a clear oil. The structure was elucidated by ^1H NMR nOesy experiments. R_f 0.40 (1:9 EtOAc/hexane), (UV 254 nm); ^1H NMR (300 MHz, $CDCl_3$): δ 10.39 (s, 1H), 7.73 (s, 1H), 7.33 (s, 1H), 6.42 (s, 1H), 3.96 (septet, $J = 6.9$ Hz, 1H), 2.20 (app. d, $J = 12.9$ Hz, 1H), 1.96 (app. qt, $J_q = 13.2$ Hz, $J_t = 3.3$ Hz, 1H), 1.56-1.72 (m, 2H), 1.39 (s, 3H), 1.33 (d, $J = 6.9$ Hz, 3H), 1.32 (d, $J = 6.9$ Hz, 3H), 1.31 (s, 3H), 1.25 (s, 3H), 1.10 (td, $J_t = 13.2$ Hz, $J_d = 3.9$ Hz, 1H), 0.99 (td, $J_t = 13.5$ Hz, $J_d = 3.9$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 170.2, 152.6, 151.4, 148.5, 129.2, 122.6, 121.1, 117.9, 51.3, 42.6, 37.9, 36.1, 31.3, 27.7, 25.1, 24.4, 24.3, 23.2, 19.7; IR (NaCl/$CDCl_3$): 3066, 2995, 2962, 2930, 2867, 2847, 2801, 2753, 2717, 2252, 1690, 1674, 1613, 1552, 1472, 1459, 1420, 1383, 1370, 1267, 1180, 1163, 906, 891 cm^{-1}; HRMS-EI^+ (*m/z*): $[M]^+$ calc'd for $C_{20}H_{26}O$, 282.1984; found, 282.1991; $[\alpha]^{24}_D$ –109.22° (*c* 1.205, $CHCl_3$), 98% ee. Undesired aldehyde **SI5** (13.3 mg, 8% yield) was also isolated as a clear oil. The structure was elucidated by ^1H NMR nOesy experiments. R_f 0.48 (1:9 EtOAc/hexane), (UV 356 nm); ^1H NMR (300 MHz, $CDCl_3$): δ 10.71 (s, 1H), 7.37 (d, $J = 7.7$ Hz, 1H), 7.19 (s, 1H), 7.17 (d, $J = 7.7$ Hz, 1H), 3.89 (septet, $J = 6.9$ Hz, 1H), 2.17 (app. dd, $J = 12.9$ Hz, 1.7 Hz, 1H), 1.97 (app. qt, $J_q = 14.0$ Hz, $J_t = 3.9$ Hz, 1H), 1.74-1.58 (m, 2H), 1.37 (s, 3H), 1.35 (s, 3H), 1.33 (d, $J = 6.9$ Hz, 3H), 1.32 (d, $J = 6.9$ Hz, 3H), 1.26 (s, 3H), 1.11 (td, $J_t = 12.9$ Hz, $J_d = 3.9$ Hz, 1H), 0.96 (td, $J_t = 13.2$

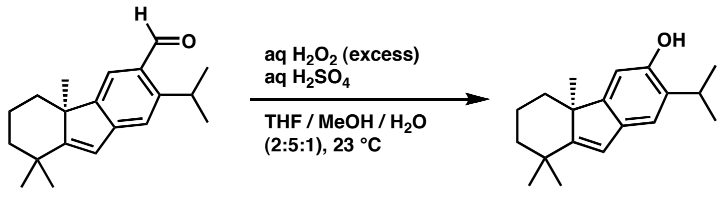
Hz, J_d = 3.6 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 192.8, 169.3, 154.3, 149.7, 144.3, 125.9, 125.7, 121.6, 120.1, 50.0, 42.7, 37.9, 36.1, 31.4, 28.2, 25.2, 24.60, 24.55, 23.1, 19.8; IR (NaCl/CDCl$_3$): 2994, 2962, 2930, 2867, 2846, 2777, 2754, 1682, 1591, 1571, 1456, 1417, 1254, 1183, 1176, 1109, 882, 828 cm^{-1}; HRMS-EI$^+$ (*m/z*): [M]$^+$ calc'd for $C_{20}H_{26}O$, 282.1984; found, 282.1990; $[\alpha]^{26}_D$ +1.15° (*c* 0.665, CHCl$_3$), 98% ee.



nOe's detected for 14



nOe's detected for SI5



14
98% ee

15
98% ee

Phenol 15. To a solution of **14** (135 mg, 0.478 mmol) in THF (5.4 mL) and MeOH (13.5 mL) at 23 °C was added 30% aqueous H_2O_2 (2.70 mL, 23.8 mmol) immediately followed by concentrated aqueous H_2SO_4 (245 μL). After 1 h, the reaction was cautiously added to an ice-cold mixture of $NaHSO_3$ (1.62 g, 15.6 mmol), water (54 mL), and Et_2O (20 mL). After 5 min, the reaction was diluted with water (10 mL) and hexane (20 mL), and the organic phase was collected. The aqueous phase was extracted with Et_2O (3 x 40 mL). All organic layers were combined, washed with brine (20 mL), dried (Na_2SO_4), filtered, and adsorbed on silica gel. The adsorbed product was purified by flash chromatography on silica gel (2:98 Et_2O/hexane → 10:90 Et_2O/hexane eluent), affording phenol **15** (95.0 mg, 74% yield) as a white, unstable powder. R_f 0.56 (1:4 EtOAc/hexane), (UV 254 nm); mp 105-106 °C dec (Et_2O/hexane); ^1H NMR (300 MHz, $CDCl_3$):[16] δ 7.11 (s, 1H), 6.68 (s, 1H), 6.29 (s, 1H), 4.57 (s, 1H),[17] 3.19 (app. quintet, J = 6.9 Hz, 1H), 2.07 (app. d, J = 12.4, 1H), 1.94 (app. qt, J_q = 13.5 Hz, J_t = 3.3 Hz, 1H), 1.62 (app. s, 1H), 1.58 (app. s, 1H), 1.34 (s, 3H), 1.28 (s, 3H), 1.27 (d, J = 6.9 Hz, 3H), 1.26 (d, J = 6.9 Hz, 3H), 1.22 (s, 3H), 1.10 (td, J_t = 13.2 Hz, J_d = 3.6 Hz, 1H), 1.01 (td, J_t = 13.2 Hz, J_d =3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0, 154.3, 150.0, 135.5, 132.4, 120.5, 117.9, 109.4, 50.9, 42.8, 38.2, 35.5, 31.4, 27.2, 25.6, 23.8, 23.1, 20.0; IR (KBr): 3393 (broad), 3057, 2988, 2965, 2934, 2909, 2868, 2837, 1459, 1431, 1382, 1362, 1286, 1166, 1076, 1004, 894, 856 cm^{-1}; HRMS-EI^+ (*m/z*): $[M]^+$ calc'd for $C_{19}H_{26}O$, 270.1984; found, 270.1993; $[\alpha]^{24}_D$ –73.23° (*c* 0.080, $CHCl_3$), 98% ee.

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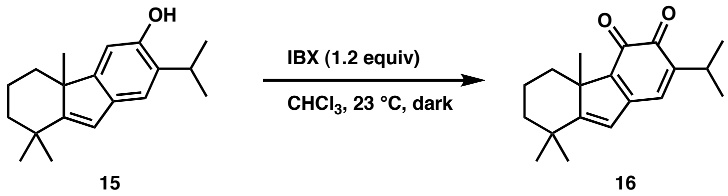
[16] The $CDCl_3$ was degassed with argon for 10 min before solvating the purified product. This reduced decomposition during spectral acquisition.

[17] When a drop of D_2O was added to the NMR sample, the singlet at δ 4.57 vanished.



Racemic *Ortho*-Quinone 16. To a rapidly stirred solution of racemic phenol **15** (25 mg, 0.0925 mmol) in $CHCl_3$ (5 mL) wrapped in foil was added IBX (30.5 mg, 0.102 mmol) in nine portions over a 9 h period at 23 °C. After 11 h, the reaction was filtered through glass frits with the aid of $CHCl_3$. 80% (by volume) of the solution was carried onward; the remaining 20% was saved. The 80% of maroon filtrate to be processed was diluted with hexane (15 mL), then concentrated to approx. 4 mL total volume. More hexane was added (20 mL), and the solution was concentrated again to approx. 4 mL. This process was repeated two more times; then the solution was purified by flash chromatography on silica gel (1:9 Et_2O/hexane eluent), affording unstable *o*-quinone **16** (4.3 mg, 20% yield based on 80% of starting material)[18] as a purple powder. The compound was suitable for partial characterization: R_f 0.55 (1:4 EtOAc/hexane), (Visible, purple); ^1H NMR (300 MHz, $CDCl_3$): δ 6.86 (s, 1H), 6.15 (s, 1H), 2.98 (app. quintet, J = 6.9 Hz, 1H), 2.41 (app. dd, J = 12.4 Hz, 1.7 Hz, IH), 1.95-2.20 (m, 1H), 1.89 (app. qt, J_q = 13.2 Hz, J_t = 2.5 Hz, 1H), 1.72 (app. d, J = 12.7 Hz, 1H), 1.60 (s, 3H), 1.43 (s, 3H), 1.24 (s, 3H), 1.11-1.21 (m, 1H), 1.12 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H), 1.00-1.08 (m, 1H); IR (NaCl/CH_2Cl_2): 3418 (broad), 3035, 2961, 2932, 2869, 1959, 1682, 1631, 1580, 1517, 1464, 1433, 1403, 1369, 1287, 1230, 1172, 1009 cm^{-1}; HRMS-FAB$^+$ (*m/z*): $[M+H]^+$ calc'd for $C_{19}H_{25}O$, 285.1855; found, 285.1851. The following experiment was employed for determining actual yield: To a rapidly stirred solution **15** (25.4 mg, 0.0940 mmol) in $CHCl_3$ (5 mL) in the dark was added IBX (30.2 mg, 0.1018 mmol) in one portion. After 15 h, the reaction was filtered through glass frits with the aid of $CHCl_3$. The filtrate was partially concentrated and $CDCl_3$ was added; this was repeated iteratively until there was less than 2% $CHCl_3$ by volume and approx. 3 mL total volume of solution. The solution was transferred to a 5.00 mL volumetric flask, and EtOAc (51.0 μL, 0.522 mmol, internal standard) was added. The flask was diluted to 5 mL using $CDCl_3$, giving a solution of unknown that was 0.0188 M in **16** (assuming a 100% yield) and

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[18] When the crude *o*-quinone is flashed, a substantial amount decomposes on the silica gel, making accurate yield determination by isolation difficult.

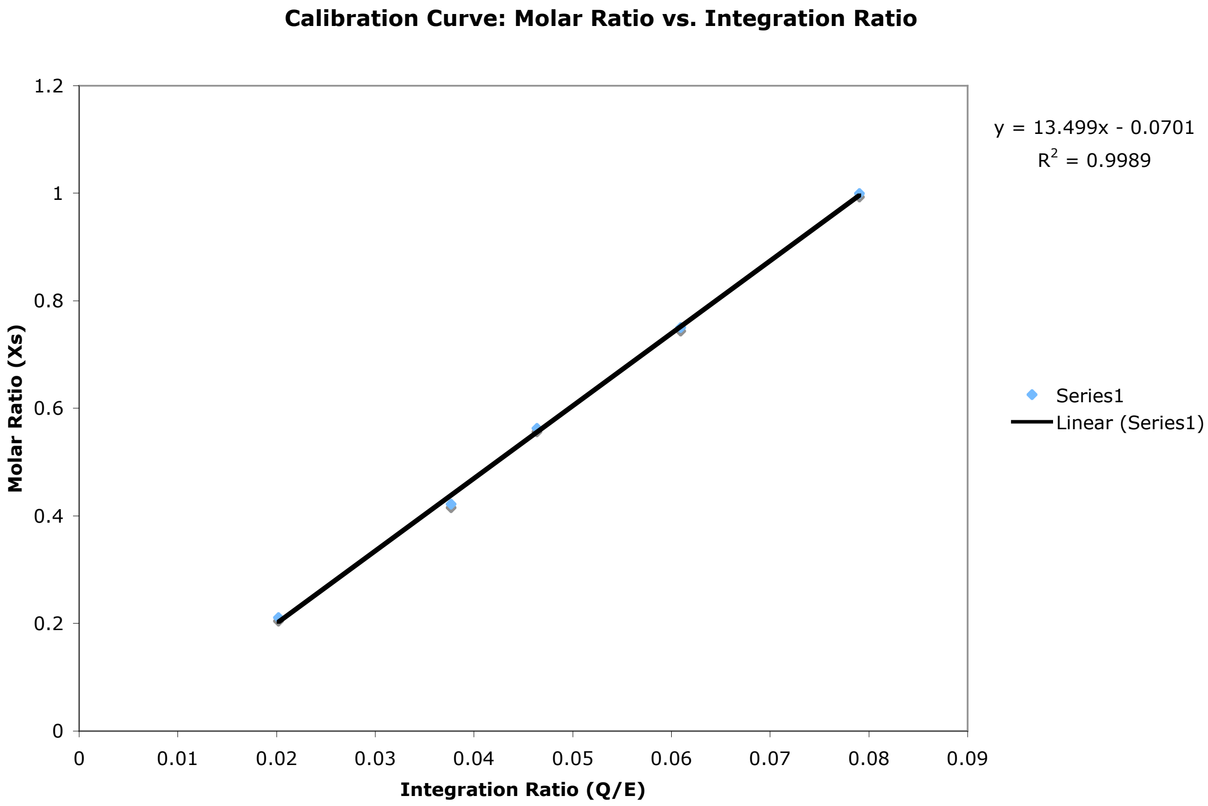
0.104 M in EtOAc, with a theoretical molar ratio, X_T, of 1:5.55 (maximum theoretical analyte: internal standard). In a separate 2.00 mL volumetric flask, analytically pure racemic *o*-quinone **16** (4.3 mg, 0.0151 mmol) from earlier in this procedure was dissolved in 2.0 mL of a stock solution of EtOAc (20.5 μL, 0.209 mmol, internal standard) and $CDCl_3$ (5.00 mL), giving a solution with a molar ratio X_S of 1:5.55 (analyte/internal standard). This analyte solution was serially diluted with the stock internal standard solution, giving four more solutions with molar ratios of $0.750X_S$, $0.563X_S$, $0.422X_S$, and $0.211X_S$. These four solutions, along with the original $1.000X_S$ solution, were analyzed by ^{1}H NMR, and the peak integration ratios δ 6.86 (analyte): δ4.08 (internal standard) were determined. A calibration curve of molar ratio vs. integration ratio was prepared. The unknown was also analyzed by ^{1}H NMR to obtain its integration ratio. The value of X_T (molar ratio) for the unknown was extrapolated from the equation of the least-squares best-fit line for the calibration curve, and was found to be $0.363X_S$. This corresponds to a 36% yield of racemic *o*-quinone **16**.

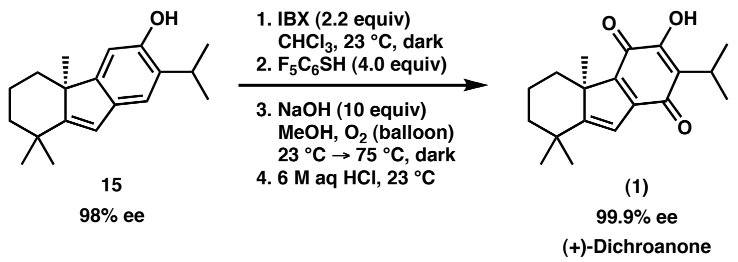
Calibration Curve and Extrapolation Data for *o*-Quinone 16 Yield Assay

AnalQInt6.86	AnalEInt4.08	AnalQ/E	Yield (X_S)
5.37	67.95	0.0790	1.00
4.46	73.20	0.0609	0.750
3.62	78.07	0.0464	0.563
2.99	79.35	0.0377	0.422
1.72	85.11	0.0202	0.211

UnkQInt6.86	UnkEInt4.08	UnknQ/E	Yield (X_T)
2.50	78.00	0.0321	0.363

Calibration Curve for *o*-Quinone 16 Yield Assay





(*R*)-(+)-Dichroanone (1). Phenol **15** (79.8 mg, 0.295mmol) was dissolved in $CHCl_3$ (16 mL) that had been degassed with argon for 10 min, then shaken over oven-dry MS4Å. IBX (99.0 mg, 0.354 mmol) was added under argon with vigorous stirring in the dark at 23 °C. At 19 h, the reaction was filtered through glass frits with the aid of $CHCl_3$. The filtrate, which contained enantioenriched *o*-quinone **16** (36% yield by ^{1}H NMR), was immediately used without further purification. To this solution was added pentafluorothiophenol (157 μL, 1.18 mmol) at 23 °C in the dark. After 2 h, the maroon reaction had become yellow-orange, and TLC revealed complete consumption of the *o*-quinone **16**. At this time, a solution of powdered NaOH (118 mg, 2.95 mmol) in MeOH (16 mL) was introduced. An O_2 balloon was attached and the reaction became deep red over the next 2 h. Then the mixture was refluxed under a balloon of O_2 at 75 °C in the dark for another 3 h. After cooling to 23 °C, the O_2 balloon was removed and substituted for an N_2 atmosphere. Aqueous 6 M HCl (1.60 mL) was added dropwise and stirring was continued at 23 °C as the reaction became bright orange-red, and a white precipitate formed. After 30 min, the reaction was diluted with water (20 mL) then hexane (20 mL), and the organic phase was collected. The aqueous phase was extracted with Et_2O (3 x 20 mL). All organic layers were combined, washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated to approx. 2 mL total volume. This suspension was purified by flash chromatography on silica gel (2:98 Et_2O/hexane eluent), affording semipure (+)-dichroanone (**1**) as an oily, unpleasant-smelling, red solid.[19] The residue was dissolved in hexane and adsorbed onto silica gel. The material was purified by flash chromatography on a second column of silica gel (2:98 Et_2O/hexane eluent), affording (*R*)-(+)-dichroanone (**1**) (31.0 mg, 35% yield from phenol **15**, 99% yield from *o*-qunione **16**) as an odorless, amorphous red solid. The product had a 99.9% ee as determined by chiral HPLC. The compound had the same spectroscopic and physical properties as the natural sample, and bore the opposite sense of optical rotation, establishing the absolute stereochemistry

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[19] The major residual impurities present after the first flash column were bis-(pentafluorophenyl) disulfide, pentafluorothiophenol, and 2-iodobenzoic acid.

of natural dichroanone to be (*S*). R_f 0.61 (1:4 EtOAc/hexane), (Visible orange-red); mp 119-120 °C (benzene); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 (s, 1H), 6.44 (s, 1H), 3.21 (septet, J = 7.2 Hz, 1H), 2.37 (app. ddd, J = 13.2 Hz, 5.0 Hz, 2.8 Hz, 1H), 1.92 (app. qt, J_q = 13.8 Hz, J_t = 3.3 Hz, 1H), 1.70 (app. dq, J_d = 13.2 Hz, J_q = 2.5 Hz, 1H), 1.62 (app. dddd, J = 14.2 Hz, 6.6 Hz, 3.9 Hz, 2.7 Hz, 1H), 1.45 (s, 3H), 1.28 (s, 3H), 1.24 (d, J = 7.2 Hz, 3H), 1.23 (d, J = 7.2 Hz, 3H), 1.23 (s, 3H), 1.11 (app. dt, J_d = 13.2 Hz, J_t = 4.4 Hz, 1H), 1.07 (app. dt, J_d = 13.2 Hz, J_t = 4.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.9, 178.4, 177.2, 152.6, 149.0, 147.9, 122.9, 118.1, 55.5, 43.5, 37.5, 37.1, 31.1, 24.9, 24.1, 20.3, 20.2, 19.2; IR (KBr): 3326, 2959, 2925, 2868, 1628, 1519, 1459, 1367, 1357, 1287, 1170, 1127, 1107, 992, 966 cm^{-1} (NaCl/$CHCl_3$): 3350, 2960, 2932, 2873, 1637, 1527, 1470, 1368, 1358, 1317, 1242, 1104, 990, 966 cm^{-1}; HRMS-EI$^+$ (*m/z*): [M]$^+$ calc'd for $C_{19}H_{24}O_3$, 300.17255; found, 300.17265; UV-Vis λ_{max} nm (log ε): 253(4.0), 332 (3.9); $[\alpha]^{27}_D$ +99.60° (*c* 0.0055, dioxane), 99.9% ee.

Comparison of Natural (*S*)-(–)-Dichroanone (1) and Synthetic (*R*)-(+)-Dichroanone (1)

^{1}H NMR of Dichroanone, CDCl$_3$[20]			
Synthetic (+), 300 MHz		Natural (–), 300 MHz[21]	
Shift (ppm)	**Multiplicity/Coupling (Hz)**	**Shift (ppm)**	**Multiplicity/Coupling (Hz)**
7.31	s	7.31	s
6.44	s	6.45	s
3.21	septet, 7.2	3.22	septet, 7.0
2.37	ddd, 13.2, 5.0, 2.8	2.38	br. dd, ca. 13, ca. 2
1.92	qt, q= 13.8, t = 3.3	1.93	m
1.7	dq, d = 13.2, q = 2.5	1.71	ddd, 7.5, 2.5, 2.5
1.62	dddd, 14.2, 6.6, 3.9, 2.7	ca. 1.6	m
1.45	s	1.46	s
1.28	s	1.29	s
1.24	d, 7.2	1.25	d, 7.0
1.23	d, 7.2	1.24	d, 7.0
1.23	s	1.24	s
1.11	dt, d = 13.2, t = 4.4	ca. 1.1	m
1.07	dt, d = 13.2, t = 4.4	ca. 1.1	m

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[20] Note that the chemical shifts of the synthetic (+)-Dichroanone **(1)** are uniformly 0.01 ppm upfield relative to the shifts for natural (–)-Dichroanone (**1**). This could be due to the reference value used by the isolation chemists. The chemical shift reference for the synthetic material was δ 7.26 ppm in accord with Cambridge Isotopes Laboratory, Inc.

[21] ^{1}H NMR, ^{13}C NMR, IR, UV-Vis, and optical rotation data have been reproduced from the isolation paper. See: Kawazoe, K.; Yamamoto, M.; Takaishi, Y.; Honda, G.; Fujita, T.; Sezik, E.; Yesilada, E. *Phytochemistry* **1999**, *50*, 493-497.

Comparison of Natural (*S*)-(–)-Dichroanone (1) and Synthetic (*R*)-(+)-Dichroanone (1)

^{13}C NMR of Dichroanone (1), $CDCl_3$	
Synthetic (+), 75 MHz	Natural (–), 75 MHz
Shift (ppm)	Shift (ppm)
185.9	185.8
178.4	178.3
177.2	177.3
152.6	152.6
149.0	149.0
147.9	148.0
122.9	123.0
118.1	118.1
55.5	55.5
43.5	43.6
37.5	37.5
37.1	37.1
31.1	31.0
24.9	24.9
24.1	24.1
20.3	20.3
20.2	20.2
-	20.2
19.2	19.2

IR of Dichroanone (1), KBr	
Synthetic (+)	Natural (–)
Wavenumber (cm^{-1})	Wavenumber (cm^{-1})
3326	3324
2959	2958
2925	-
2868	-
1628	1627
1519	1520
1459	1457
1367	-
1357	-
1287	1288
1170	-
1127	-
1107	-
992	-
966	-

UV-Vis Spectrum of Dichroanone (1)	
Synthetic (+)	Natural (–)
λ_{max} (nm), (log ε)	λ_{max} (nm), (log ε)
253 (4.0)	253 (4.0)
332 (3.9)	332 (4.0)

Specific Optical Rotation of Dichroanone (1)	
Synthetic (+)	Natural (–)
$[\alpha]^{27}_{D}$, (c 0.0055)	$[\alpha]^{25}_{D}$, (c 0.67)[22]
(in dioxane, 99.9%ee)	(in dioxane, 100%ee)
+99.60°	–99.3°

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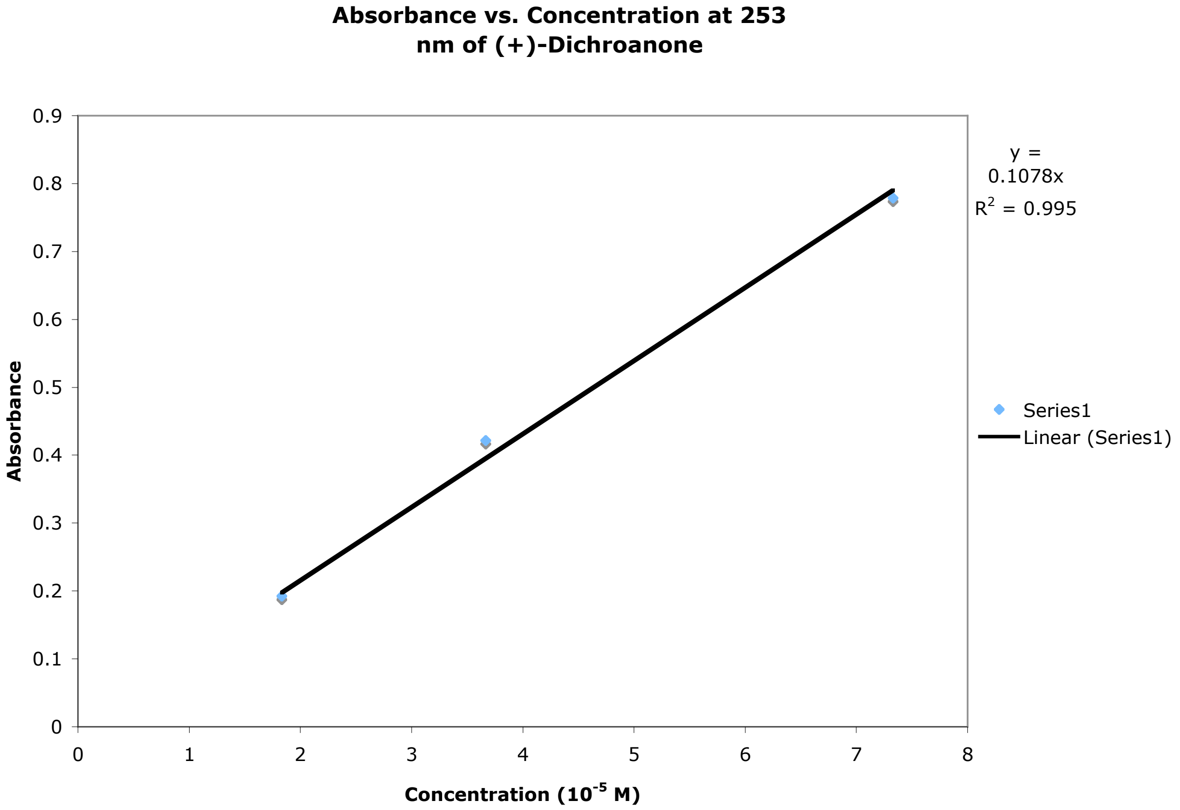
[22] An attempt was made to measure the specific optical rotation of synthetic (–) dichroanone (**1**) at c = 0.67 as reported by the isolation chemists; however, due to the cell path length used (100 mm) on the polarimeter, no sodium-D (589 nm) light was transmitted through the orange-red solution, making an accurate measurement difficult. To circumvent this issue, a lower concentration was employed.

Determination of Absorption Maxima and Extinction Coefficients for (*R*)-(+)-Dichroanone (1). A sample of (+)-Dichroanone (**1**) (11.0 mg, 0.0366 mmol) was dissolved in dioxane (2.00 mL) in a volumetric flask, giving a 0.183 M solution. This solution was serially diluted to the following concentrations (10^{-5} M): 7.329, 4.217, and 1.925. UV-Vis spectra of the three diluted samples were obtained using a 1-cm path length quartz cuvette, and absorbances at 253 nm and 332 nm were measured. A least-squares line of absorbance vs. concentration (constrained to fit the origin) was calculated for both 253 nm and 332 nm absorbance sets. The slope of the least-squares-fit line gave the molar extinction coefficients: λ_{max} nm (log ε): 253(4.0), 332 (3.9).

Data Points for UV-Vis Spectra of (*R*)-(+)-Dichroanone (1)

Concentration (10^{-5}M)	Abs at 253 nm	Abs at 332 nm
7.329	0.7783	0.5974
3.665	0.4217	0.3369
1.832	0.1925	0.1542

UV-Vis Data for (*R*)-(+)-Dichroanone (1)



ε_{253} = 10780 L / (mol • cm); log (ε_{253}) = 4.0[23]

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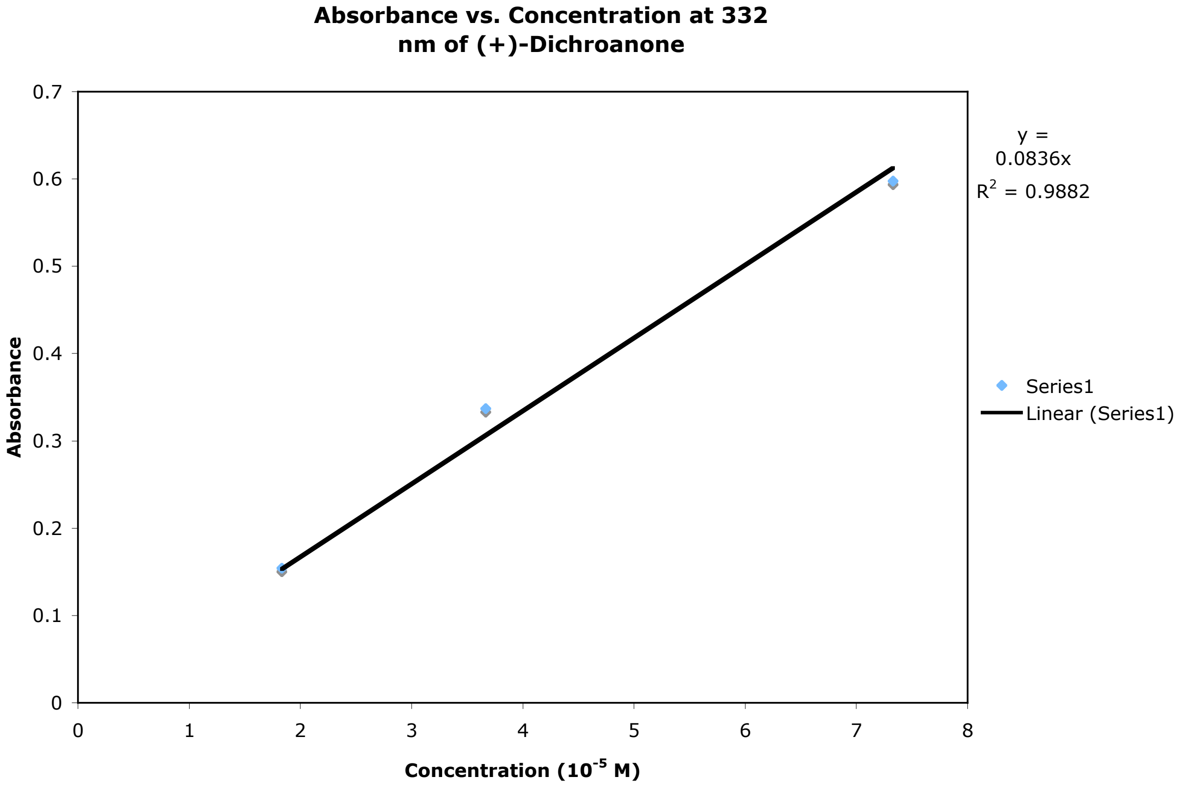
[23] For this graph, the equation of best fit is equivalent to Beer's Law, A = εlc, where l is a constant (1 cm, the path length of the sample in the quartz cuvette), and ε is the slope of the least squares line, constrained to run through the origin. Thus, ε is in units of [cm^{-1} • $(10^{-5}\ \text{M})^{-1}$] or more simply, ε = 100000 • (slope) • L / (mol • cm). Hence, ε_{253} = 10780 L / (mol • cm), and log(ε_{253}) = 4.0.

UV-Vis Data for (*R*)-(+)-Dichroanone SI19



ε_{332} = 8360 L / (mol • cm); log (ε_{332}) = 3.9[24]

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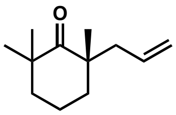
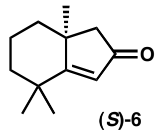
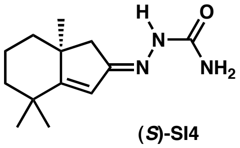
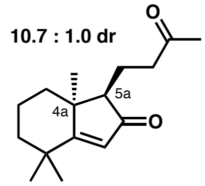
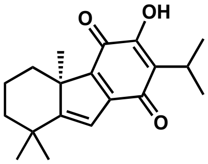
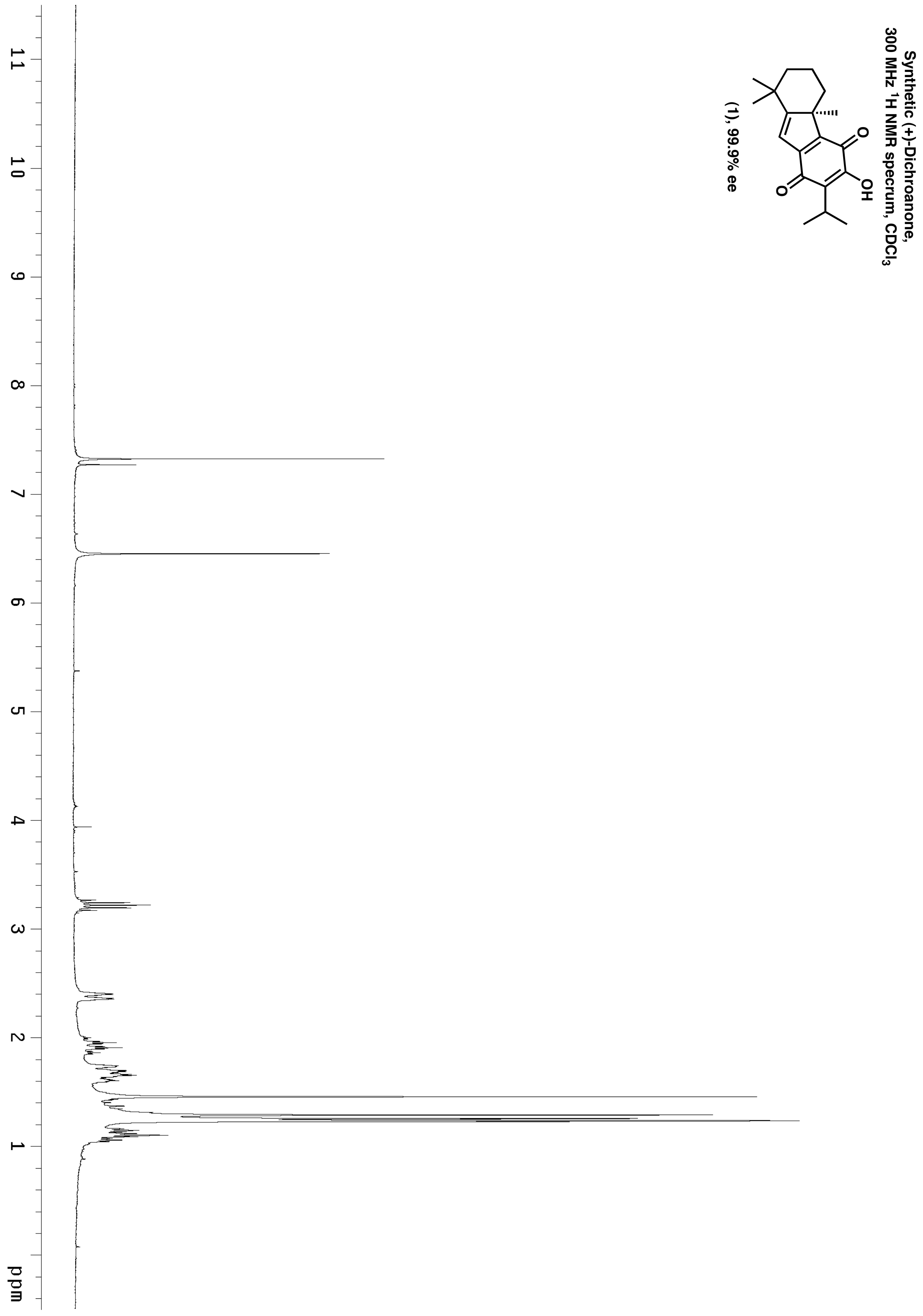
[24] For this graph, the equation of best fit is equivalent to Beer's Law, A = εlc, where l is a constant (1 cm, the path length of the sample in the quartz cuvette), and ε is the slope of the least squares line, constrained to run through the origin. Thus, ε is in units of [cm^{-1} • $(10^{-5}\text{ M})^{-1}$] or more simply, ε = 100000 • (slope) • L / (mol • cm). Hence, ε_{332} = 8360 L / (mol • cm), and log(ε_{332}) = 3.9.

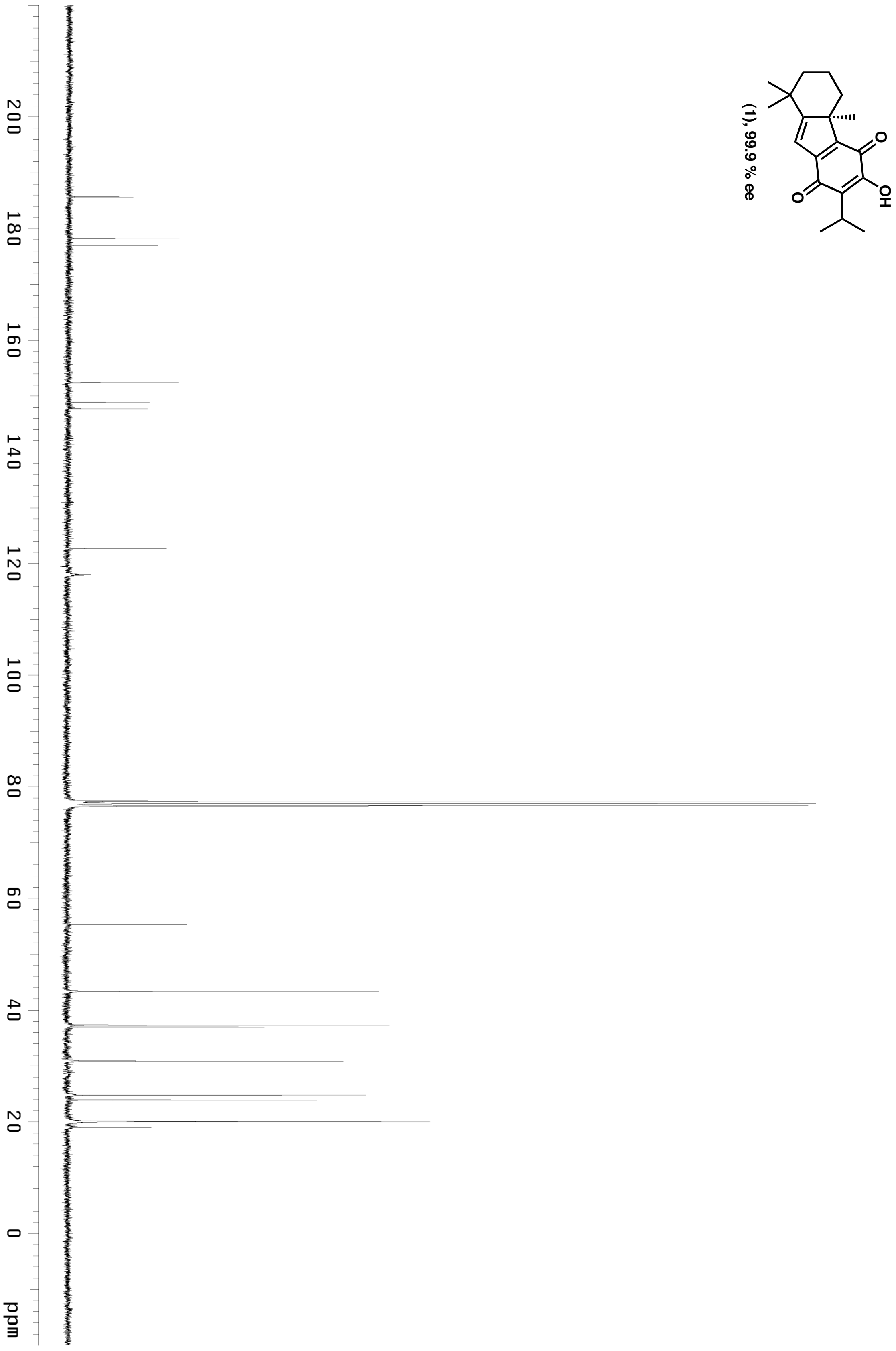
Methods for the Determination of Enantiomeric Excess

Entry	Substrate	Assay	Column	Method	Retention Time (min)	
1.	 **(*S*)-9**	*Enantiomeric Excess*	Chiral GC	80 °C isotherm	Major (***S***)	29.1
			Agilent GT-A Column	40 min	Minor (***R***)	30.5
2.	 **(*S*)-6**	*Enantiomeric Excess*	Chiral HPLC	3%EtOH/Hex monitor@254nm	Minor (***R***)	9.1
			Chiralcel AD Column	20 min	Major (***S***)	10.2
3.	 **(*S*)-SI4**	*Enantiomeric Excess*	Chiral HPLC	10%EtOH/Hex monitor@254nm	Minor (***R***)	9.3
			Chiralcel AD Column	20 min	Major (***S***)	12.1
4.	 **10.7 : 1.0 dr** **Major Diasteromer: (4a*S*, 5a*R*)-11**	*Enantiomeric Excess*	Chiral HPLC	4%EtOH/Hex monitor@254nm	Minor **(4a*S*, 5a*R*)**	17.6
			Chiralcel AD Column	40 min	Major **(4a*R*, 5a*S*)**	28.5
5.	 **(*R*)-(+)-Dichroanone-(1)**	*Enantiomeric Excess*	Chiral HPLC	0.3%EtOH/Hex monitor@254nm	Minor (***S***)	18.3
			Chiralcel AD Column	30 min	Major (***R****)*	21.1



Synthetic (+)-Dichroanone, 300 MHz ^{1}H NMR specrum, CDCl$_3$

(1), 99.9% ee



Synthetic (+)-Dichroanone,
75 MHz ^{13}C NMR specrum, $CDCl_3$

(1), 99.9 % ee

Crystal Structure Data for Compound 11.

Table 1. Crystal data and structure refinement for RMM01 (CCDC 293604).

Empirical formula	$C_{16}H_{24}O_2$
Formula weight	248.35
Crystallization Solvent	From melt
Crystal Habit	Plate
Crystal size	0.36 x 0.27 x 0.03 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 3103 reflections used in lattice determination	2.82 to 27.84°	
Unit cell dimensions	a = 7.2276(13) Å	
	b = 9.3724(17) Å	β= 92.231(3)°
	c = 10.3744(18) Å	
Volume	702.2(2) Å^3	
Z	2	
Crystal system	Monoclinic	
Space group	$P2_1$	
Density (calculated)	1.175 Mg/m^3	
F(000)	272	
Data collection program	Bruker SMART v5.630	
θ range for data collection	1.96 to 27.87°	
Completeness to θ = 27.87°	93.6 %	
Index ranges	$-9 \leq h \leq 9$, $-11 \leq k \leq 12$, $-13 \leq l \leq 13$	
Data collection scan type	ω scans at 3 ϕ settings	
Data reduction program	Bruker SAINT v6.45A	
Reflections collected	6194	
Independent reflections	2968 [R_{int}= 0.0422]	
Absorption coefficient	0.075 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9977 and 0.9734	

Table 1 (cont.)

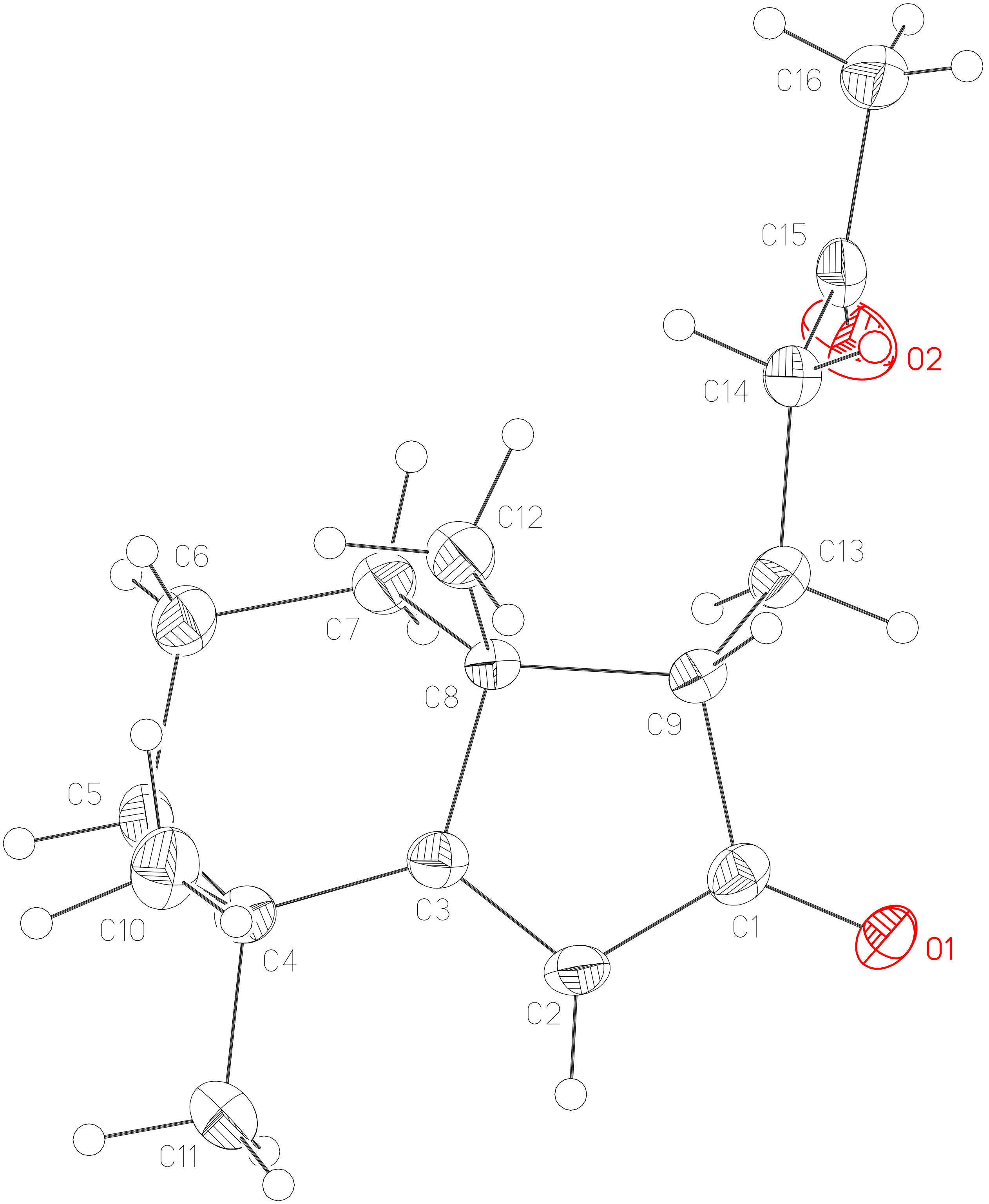
Structure solution and Refinement

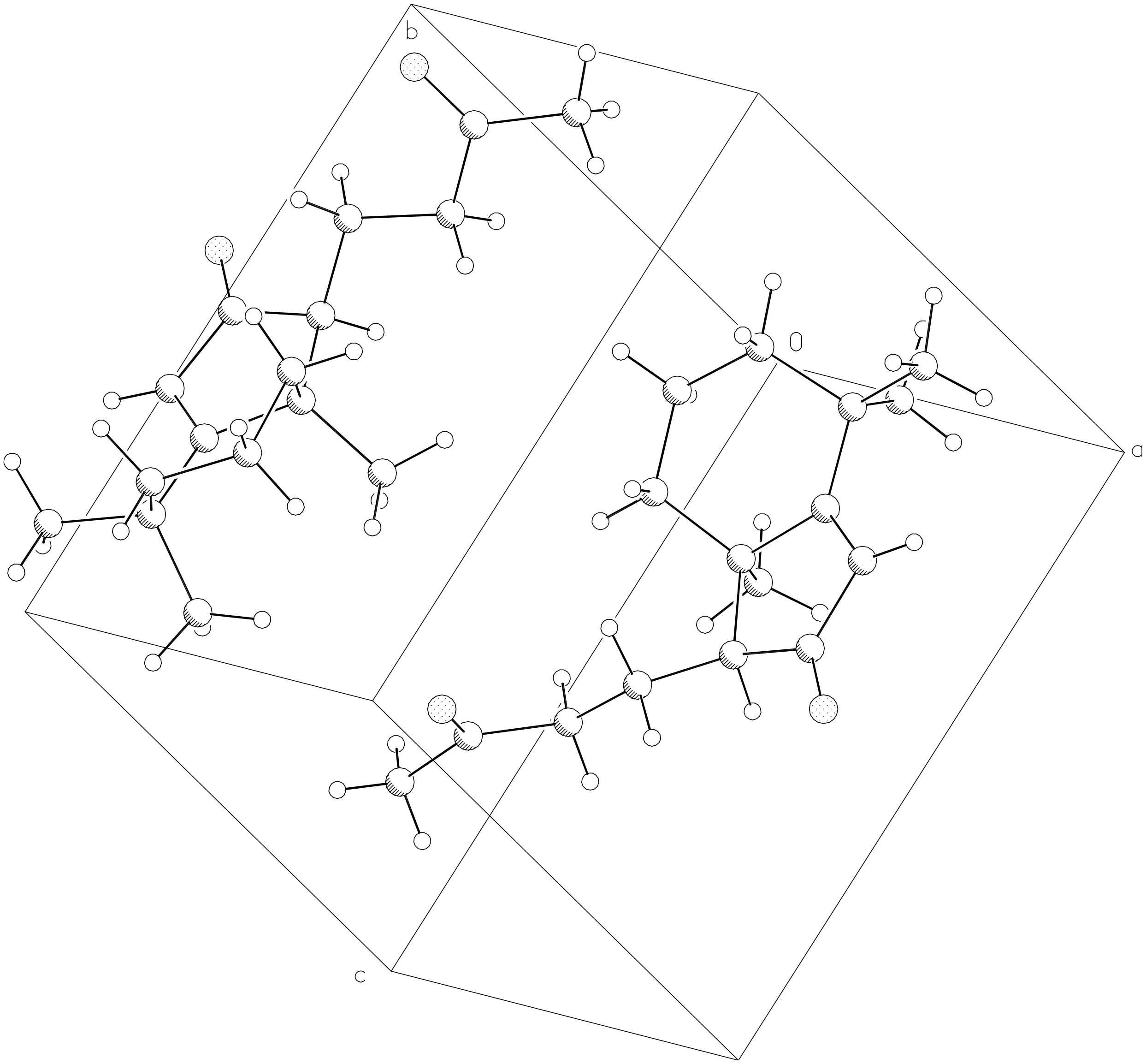
Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	2968 / 1 / 259
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.379
Final R indices [$I>2\sigma(I)$, 2464 reflections]	R1 = 0.0417, *w*R2 = 0.0708
R indices (all data)	R1 = 0.0528, *w*R2 = 0.0729
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	Not able to determine
Absolute structure parameter	-0.5(12)
Largest diff. peak and hole	0.279 and -0.197 e.Å^{-3}

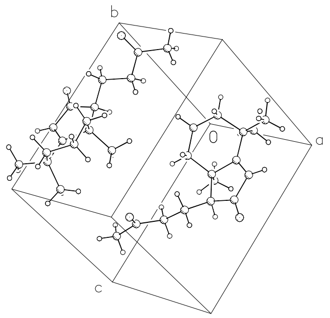
Special Refinement Details

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.


C16
C15
O2
C14
C12
C13
C6
C7
C8
C9
C5
C10
C4
C3
C1
O1
C2
C11


b
a
c


b
0
a
c

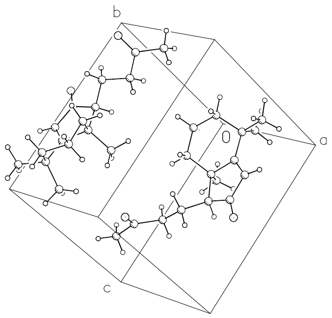

b
0
a
c

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for RMM01 (CCDC 293604). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	-2410(2)	8958(1)	3790(1)	26(1)
O(2)	3287(2)	11505(2)	1446(1)	43(1)
C(1)	-1126(2)	8961(2)	4599(2)	22(1)
C(2)	-1246(2)	9098(2)	5978(2)	24(1)
C(3)	438(2)	9136(2)	6569(2)	21(1)
C(4)	845(2)	9489(2)	7970(2)	24(1)
C(5)	2195(3)	10768(2)	7999(2)	25(1)
C(6)	3847(3)	10570(2)	7160(2)	30(1)
C(7)	3246(3)	10291(2)	5743(2)	25(1)
C(8)	1987(2)	8962(2)	5616(2)	19(1)
C(9)	904(2)	8804(2)	4288(2)	22(1)
C(10)	1666(3)	8214(2)	8718(2)	33(1)
C(11)	-912(3)	9929(3)	8641(2)	37(1)
C(12)	3162(3)	7620(2)	5848(2)	28(1)
C(13)	1425(3)	9737(2)	3163(2)	25(1)
C(14)	3226(3)	9280(2)	2556(2)	26(1)
C(15)	3946(3)	10329(2)	1605(2)	27(1)
C(16)	5601(3)	9861(3)	880(2)	32(1)

Table 3. Bond lengths [Å] and angles [°] for RMM01 (CCDC 293604).

O(1)-C(1)	1.2264(18)	C(2)-C(3)-C(8)	112.01(14)
O(2)-C(15)	1.209(2)	C(4)-C(3)-C(8)	121.71(14)
C(1)-C(2)	1.442(2)	C(3)-C(4)-C(11)	111.34(16)
C(1)-C(9)	1.522(2)	C(3)-C(4)-C(10)	111.95(16)
C(2)-C(3)	1.342(2)	C(11)-C(4)-C(10)	106.99(18)
C(2)-H(2)	0.934(16)	C(3)-C(4)-C(5)	106.74(15)
C(3)-C(4)	1.508(2)	C(11)-C(4)-C(5)	108.48(17)
C(3)-C(8)	1.531(2)	C(10)-C(4)-C(5)	111.33(16)
C(4)-C(11)	1.528(3)	C(6)-C(5)-C(4)	113.88(17)
C(4)-C(10)	1.532(3)	C(6)-C(5)-H(5B)	111.9(11)
C(4)-C(5)	1.546(3)	C(4)-C(5)-H(5B)	108.7(11)
C(5)-C(6)	1.516(3)	C(6)-C(5)-H(5A)	112.0(10)
C(5)-H(5B)	1.02(2)	C(4)-C(5)-H(5A)	109.7(10)
C(5)-H(5A)	0.975(18)	H(5B)-C(5)-H(5A)	99.7(14)
C(6)-C(7)	1.539(3)	C(5)-C(6)-C(7)	111.68(17)
C(6)-H(6B)	1.01(2)	C(5)-C(6)-H(6B)	114.1(11)
C(6)-H(6A)	0.98(2)	C(7)-C(6)-H(6B)	107.2(11)
C(7)-C(8)	1.545(3)	C(5)-C(6)-H(6A)	107.9(11)
C(7)-H(7A)	0.974(19)	C(7)-C(6)-H(6A)	106.5(12)
C(7)-H(7B)	0.939(19)	H(6B)-C(6)-H(6A)	109.3(16)
C(8)-C(12)	1.532(3)	C(6)-C(7)-C(8)	111.21(16)
C(8)-C(9)	1.565(2)	C(6)-C(7)-H(7A)	113.1(11)
C(9)-C(13)	1.518(3)	C(8)-C(7)-H(7A)	108.5(11)
C(9)-H(9)	1.02(2)	C(6)-C(7)-H(7B)	109.4(11)
C(10)-H(10A)	1.03(2)	C(8)-C(7)-H(7B)	110.4(11)
C(10)-H(10B)	0.96(2)	H(7A)-C(7)-H(7B)	104.0(15)
C(10)-H(10C)	1.05(2)	C(3)-C(8)-C(12)	113.62(16)
C(11)-H(11A)	0.96(2)	C(3)-C(8)-C(7)	107.62(16)
C(11)-H(11C)	1.03(2)	C(12)-C(8)-C(7)	109.11(14)
C(11)-H(11B)	1.02(2)	C(3)-C(8)-C(9)	103.04(12)
C(12)-H(12C)	1.00(2)	C(12)-C(8)-C(9)	108.39(16)
C(12)-H(12B)	0.97(2)	C(7)-C(8)-C(9)	115.09(15)
C(12)-H(12A)	1.009(19)	C(13)-C(9)-C(1)	112.16(15)
C(13)-C(14)	1.529(3)	C(13)-C(9)-C(8)	119.48(16)
C(13)-H(13A)	1.04(2)	C(1)-C(9)-C(8)	104.92(14)
C(13)-H(13B)	1.006(19)	C(13)-C(9)-H(9)	103.6(11)
C(14)-C(15)	1.500(3)	C(1)-C(9)-H(9)	105.4(10)
C(14)-H(14B)	0.975(18)	C(8)-C(9)-H(9)	110.6(11)
C(14)-H(14A)	0.967(17)	C(4)-C(10)-H(10A)	114.3(12)
C(15)-C(16)	1.503(3)	C(4)-C(10)-H(10B)	108.7(14)
C(16)-H(16B)	0.90(3)	H(10A)-C(10)-H(10B)	112.0(18)
C(16)-H(16C)	0.96(2)	C(4)-C(10)-H(10C)	107.4(12)
C(16)-H(16A)	0.97(2)	H(10A)-C(10)-H(10C)	104.8(18)
		H(10B)-C(10)-H(10C)	109.3(19)
O(1)-C(1)-C(2)	127.29(15)	C(4)-C(11)-H(11A)	113.8(14)
O(1)-C(1)-C(9)	124.39(15)	C(4)-C(11)-H(11C)	106.3(11)
C(2)-C(1)-C(9)	108.32(14)	H(11A)-C(11)-H(11C)	108.7(18)
C(3)-C(2)-C(1)	111.57(15)	C(4)-C(11)-H(11B)	110.4(12)
C(3)-C(2)-H(2)	124.9(10)	H(11A)-C(11)-H(11B)	112.6(19)
C(1)-C(2)-H(2)	123.5(10)	H(11C)-C(11)-H(11B)	104.5(17)
C(2)-C(3)-C(4)	125.86(16)	C(8)-C(12)-H(12C)	110.1(10)

C(8)-C(12)-H(12B)	108.4(14)	C(13)-C(14)-H(14B)	112.2(10)
H(12C)-C(12)-H(12B)	106.1(17)	C(15)-C(14)-H(14A)	108.8(11)
C(8)-C(12)-H(12A)	108.9(11)	C(13)-C(14)-H(14A)	111.8(11)
H(12C)-C(12)-H(12A)	110.9(15)	H(14B)-C(14)-H(14A)	104.9(16)
H(12B)-C(12)-H(12A)	112.3(18)	O(2)-C(15)-C(14)	122.82(18)
C(9)-C(13)-C(14)	113.31(16)	O(2)-C(15)-C(16)	120.97(19)
C(9)-C(13)-H(13A)	108.5(10)	C(14)-C(15)-C(16)	116.17(19)
C(14)-C(13)-H(13A)	112.1(10)	C(15)-C(16)-H(16B)	107.5(13)
C(9)-C(13)-H(13B)	105.7(11)	C(15)-C(16)-H(16C)	109.2(12)
C(14)-C(13)-H(13B)	109.2(11)	H(16B)-C(16)-H(16C)	111(2)
H(13A)-C(13)-H(13B)	107.7(14)	C(15)-C(16)-H(16A)	111.7(14)
C(15)-C(14)-C(13)	114.19(17)	H(16B)-C(16)-H(16A)	107.1(19)
C(15)-C(14)-H(14B)	104.2(11)	H(16C)-C(16)-H(16A)	110.2(18)

Table 4. Anisotropic displacement parameters (Å^{2}x 10^4) for RMM01 (CCDC 293604). 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)	180(6)	311(7)	286(7)	-27(7)	-40(5)	-6(6)
O(2)	528(10)	395(9)	366(9)	77(7)	117(7)	126(8)
C(1)	197(9)	186(9)	286(10)	-22(10)	-10(7)	-15(9)
C(2)	158(9)	286(11)	280(10)	-46(9)	48(8)	-18(9)
C(3)	198(8)	187(10)	235(9)	-13(8)	25(7)	-10(8)
C(4)	194(9)	276(11)	245(11)	-31(8)	19(8)	-18(8)
C(5)	275(11)	285(12)	188(11)	-24(9)	-14(9)	-29(9)
C(6)	274(12)	334(13)	283(12)	-24(10)	12(9)	-113(10)
C(7)	229(11)	262(11)	253(11)	-14(9)	23(10)	-34(9)
C(8)	155(8)	232(9)	182(9)	-7(9)	19(6)	-2(9)
C(9)	165(9)	281(11)	216(10)	-13(9)	3(7)	10(9)
C(10)	356(14)	334(13)	304(13)	45(10)	-32(11)	-83(11)
C(11)	333(13)	531(16)	245(12)	-85(11)	59(10)	-24(12)
C(12)	284(13)	285(12)	257(12)	15(10)	6(11)	65(10)
C(13)	204(10)	305(12)	242(11)	9(9)	-16(8)	13(9)
C(14)	220(10)	350(13)	197(10)	-4(9)	-5(8)	19(9)
C(15)	263(11)	354(13)	181(10)	-50(9)	-51(8)	21(9)
C(16)	247(12)	456(14)	253(12)	20(12)	25(10)	-38(11)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for RMM01 (CCDC 293604).

	x	y	z	U_{iso}
H(12C)	3900(30)	7703(19)	6684(19)	18(5)
H(14B)	4240(20)	9170(20)	3197(17)	24(5)
H(2)	-2360(20)	9190(20)	6393(15)	17(4)
H(16B)	5270(30)	9080(30)	420(20)	55(7)
H(5B)	1470(30)	11670(20)	7763(19)	31(6)
H(14A)	3110(20)	8356(19)	2145(16)	11(4)
H(5A)	2570(20)	10993(18)	8889(18)	17(5)
H(6B)	4700(30)	9760(20)	7443(19)	31(5)
H(9)	1030(20)	7790(20)	3938(18)	26(5)
H(13A)	1470(20)	10800(20)	3472(16)	20(5)
H(7A)	4290(30)	10165(18)	5186(17)	21(5)
H(16C)	6600(30)	9650(20)	1480(20)	35(6)
H(6A)	4550(30)	11460(20)	7172(18)	25(5)
H(7B)	2630(20)	11100(20)	5405(17)	20(5)
H(10A)	2990(30)	7960(20)	8490(20)	44(6)
H(11A)	-1810(30)	9180(30)	8690(20)	55(7)
H(12B)	2340(30)	6820(30)	5940(20)	45(7)
H(12A)	4000(30)	7490(20)	5104(19)	28(6)
H(11C)	-500(30)	10220(20)	9560(20)	33(5)
H(11B)	-1450(30)	10830(30)	8240(20)	44(6)
H(16A)	5970(30)	10580(20)	270(20)	42(6)
H(10B)	840(30)	7420(30)	8610(20)	46(7)
H(13B)	370(30)	9650(20)	2503(19)	26(5)
H(10C)	1770(30)	8500(20)	9690(20)	54(7)