ELECTRONIC SUPPLEMENTARY INFROMATION FOR:

Formal Total Synthesis of Triptolide

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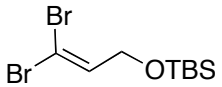
General Methods

^{1}H NMR spectra were recorded at 298K in $CDCl_3$ using a 500 MHz or a 300 MHz spectrometer. Residual chloroform (δ 7.26 ppm) was used as an internal reference. ^{13}C NMR spectra were recorded at 298 K in $CDCl_3$ at 125 MHz or 75 MHz with residual chloroform (δ 77.1 ppm) as an internal reference. IR spectra were recorded as neat films on NaCl plates for oils or as KBr pellets for solid products. Low resolution mass spectra were recorded on an ion trap mass spectrometer using electron impact (EI) ionisation mode at 40 or 70 eV. Low resolution electrospray ionisation spectra were recorded on an ion trap mass spectrometer. High resolution mass spectra were recorded on a mass spectrometer operating at 70 eV. Melting points are uncorrected. Analytical TLC was performed with silica gel plates, precoated with silica gel 60 F254 (0.2 mm). Flash chromatography employed 230–400 mesh silica gel. Enantiomer ratios were determined by chiral GC (SGE CYDEX column, 25 m × 0.22 mm ID, 0.25 μ film). Reactions were conducted under a positive pressure of dry argon or nitrogen. Benzene, diethyl ether, toluene and THF were dried over sodium wire and distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Commercially available chemicals were purified by standard procedures or used as purchased.

3,3-Dibromo-1-[(*tert*-butyldimethylsilyl)oxy]-prop-2-ene (**8**)

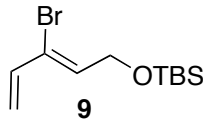


8

The title compound was prepared according to modified literature procedures.[1] To a stirred solution of triphenyl phosphine (11.0 g, 40 mmol, 4.0 equiv) in dichloromethane (35 mL) at 0 °C under argon was added a solution of carbon tetrabromide (6.95 g, 20 mmol, 2 equiv) in dichloromethane (15 mL) over 45 min, *via* cannula. The reaction mixture was stirred at RT for 30 min, NEt_3 (1.46 mL, 10 mmol, 1.0 equiv) was added before the mixture was cooled to 0 °C. A solution of [(*tert*-butyldimethylsilyl)oxy]acetaldehyde[2,3] (1.83 g, 10 mmol, 1.0 equiv) in dichloromethane (5 mL) was added dropwise. The reaction mixture was warmed to RT and stirring was continued for a further 30 min. To the reaction mixture was added hexanes and the resulting precipitate was filtered. The filtrate was concentrated under reduced pressure. After column chromatography (hexanes/diethyl ether 97:3),

dibromoalkene **8** (1.98 g, 6 mmol, 57%) was obtained as a colourless oil. Characterisation data was consistent with that reported in the literature.[1]

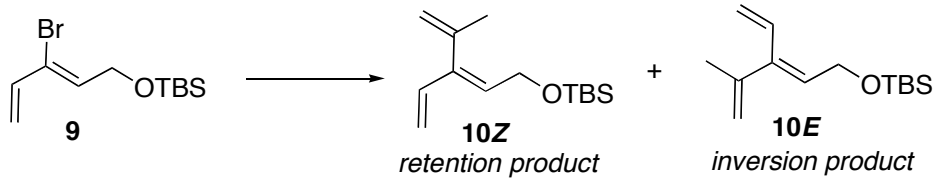
(2*Z*)-3-Bromo-1-[(*tert*-butyldimethylsilyl)oxy]-penta-2,4-diene (**9**)



9

The title compound was prepared according to modified literature procedures.[1] To a stirred solution of dibromide **8** (750 mg, 2.27 mmol, 1.0 equiv) and tributylvinylstannane (756 mg, 2.38 mmol, 1.05 equiv) in tetrahydrofuran (12 mL) was added tris(dibenzylideneacetone)dipalladium(0) (26 mg, 0.03 mmol, 0.0125 equiv) and triphenylarsine (70 mg, 0.23 mmol, 0.1 equiv). The mixture was freeze thaw degassed (× 2) then heated to 55 °C and stirring was continued for 18 h. The mixture was cooled and diluted with diethyl ether (50 mL), then washed with sat. aq. NH_3 soln. (2 × 20 mL). The aqueous layer was extracted with diethyl ether (50 mL). The combined organic layers were washed with sat. brine, dried and concentrated *in vacuo*. Column chromatography gave **9** (436 mg, 1.49 mmol, 66%) as a colourless oil. Characterisation data was consistent with that reported in the literature.[1]

Stille reaction of (2*Z*)-3-Bromo-1-[(*tert*-butyldimethylsilyl)oxy]-penta-2,4-diene (**9**) with tributyl(prop-1-en-2-yl)stannane.



9 **10*Z*** *retention product* **10*E*** *inversion product*

Method A

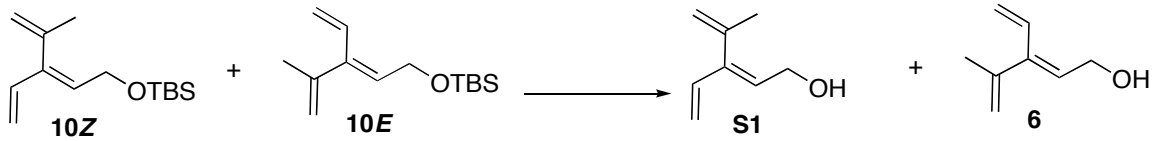
To a stirred solution of bromodiene **9** (200 mg, 0.69 mmol, 1.0 equiv) and tributyl(prop-1-en-2-yl)stannane (250 mg, 0.76 mmol, 1.1 equiv) in acetonitrile (4 mL) was added palladium acetate (7.7 mg, 0.03 mmol, 0.05 equiv) and triphenyl phosphine (18 mg, 0.06 mmol, 0.1 equiv). The mixture was freeze/thaw degassed (× 2) then heated to 60 °C for 18 h. The mixture was diluted with diethyl ether (20 mL) and washed with aq. NH_3 (2 × 20 mL). The aqueous layer was extracted with diethyl ether (2 ×

20 ml). The combined organic layers were washed with sat. brine, dried and concentrated *in vacuo*. Column chromatography gave a mixture of trienes **10*Z*** and **10*E*** as a colourless oil (1:1, 70 mg, 0.29 mmol, 42%).

Method B

To a stirred solution of bromodiene **9** (51 mg, 0.18 mmol, 1.0 equiv) and tributyl(prop-1-en-2-yl)stannane (122 mg, 0.37 mmol, 2.0 equiv) in DMF (200 μL) was added CsF (56 mg, 0.37 mmol, 2.0 equiv). The mixture was freeze/thaw degassed (× 2). CuI (4.2 mg, 0.02 mmol, 0.12 equiv), $PdCl_2$ (2.0 mg, 0.01 mmol, 0.06 equiv) and tBu$_3$P (5.8 mg, 0.02 mmol, 0.12 equiv) were added and the mixture was heated to 45 °C for 18 h. The mixture was filtered through a pad of celite with dichloromethane (50 mL). The filtrate was washed with sat. brine, dried and concentrated *in vacuo*. Column chromatography (hexanes/dichloromethane 90:10) gave a mixture of **10*Z*** and **10*E*** as a colourless oil (1:1, 22 mg, 0.09 mmol, 44%).

Deprotection of triene silyl ethers **10*Z*** and **10*E***



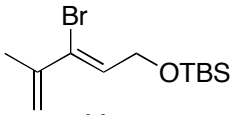
To a stirred solution of **10*Z*** and **10*E*** (1:1, 70 mg, 0.29 mmol, 1.0 equiv) in tetrahydrofuran (4 mL) at RT was added TBAF (1.0 M THF soln., 590 μL, 0.59 mmol, 2.0 equiv). Stirring was continued for 30 min before the mixture was diluted with diethyl ether (20 mL). The mixture was washed with sat. aqueous NH_4Cl (20 mL), sat. brine (20 mL), dried and concentrated *in vacuo*. Column chromatography (dichloromethane) gave a mixture of **S1** and **6** as a colourless oil (1:1, 16 mg, 0.12 mmol, 43%).

(2*E*)-3-(Prop-1-en-2-yl)penta-2,4-dien-1-ol (**6**):

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.40 (1H, dd, J = 17.5, 10.9 Hz), 5.74 (1H, t, J = 6.7 Hz), 5.36 (1H, ddd, J = 10.9, 2.1, 0.8 Hz), 5.15 (1H, dd, J = 17.5, 2.1 Hz), 5.03 (1H, bs), 5.01 (1H, bs), 4.35 (2H, d, J = 6.7 Hz), 1.92 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.4, 142.6, 132.5, 127.2, 119.5, 115.2,

60.1, 21.5 ppm. IR (thin film): ν = 3395, 2918, 2849 cm^{-1}. EIMS (70 eV) *m/z* (%): 124 (7), 123 (10), 43 (100); HRMS: calcd for $C_8H_{11}O$ [M–H]$^+$: 123.0810; found: 123.0810.

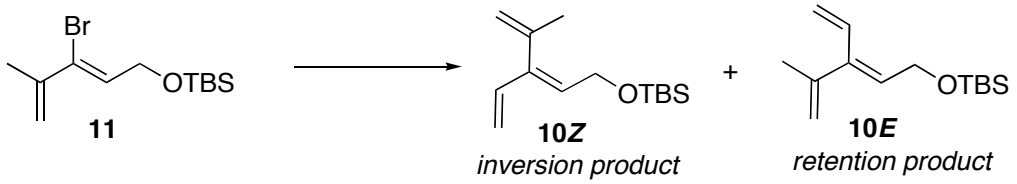
(2*Z*)-3-Bromo-1-[(*tert*-butyldimethylsilyl)oxy]-4-methylpenta-2,4-diene (**11**)



11

To a stirred solution of zinc bromide (1.12 g, 5.0 mmol, 1.1 equiv) in THF (5 mL) at 0 °C was added a solution of isopropenyl magnesium bromide (0.26 M solution in THF, 17.5 mL, 4.5 mmol, 1.0 equiv). The resulting mixture was warmed to RT before the dropwise addition of a solution of dibromide **8** (1.5 g, 4.5 mmol, 1.0 equiv) and $Pd(PPh_3)_4$ (263 mg, 0.23 mmol, 0.05 equiv) in THF (15 mL). The reaction mixture was stirred at RT for 45 min before being diluted with hexane (100 mL) and filtered. The filtrate was concentrated *in vacuo* and after column chromatography (hexane/ethyl acetate 99:1), triene **11** (1.03 g, 3.5 mmol, 78%) was obtained as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.16 (1H, t, *J* = 5.1 Hz), 5.49 (1H, m), 5.13 (1H, m), 4.43 (2H, d, *J* = 5.1 Hz), 2.00 (3H, m), 0.92 (9H, s), 0.10 (3H, s) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.2, 131.8, 125.3, 118.4, 64.6, 26.0, 20.8, 18.4, –5.1 ppm . IR (thin film): ν = 2955, 2930, 2886, 2858, 1609 cm^{-1}. EIMS (70 eV) *m/z* (%): 290 (20), 249 (30), 235 (28), 115 (50), 75 (100); HRMS: calcd for $C_8H_{14}OSiBr$ [M]$^+$: 232.9997; found: 232.9994.

Stille reaction of (2*Z*)-3-bromo-1-[(*tert*-butyldimethylsilyl)oxy]-4-methylpenta-2,4-diene (**11**) and tributylvinylstannane



11 **10*Z*** *inversion product* **10*E*** *retention product*

Method A

To a stirred solution of **11** (84 mg, 0.29 mmol, 1.0 equiv) and tributylvinylstannane (110 mg, 0.34 mmol, 1.2 equiv) in DMF (500 μL) was added CsF (87 mg, 0.58 mmol, 2.0 equiv). The mixture was

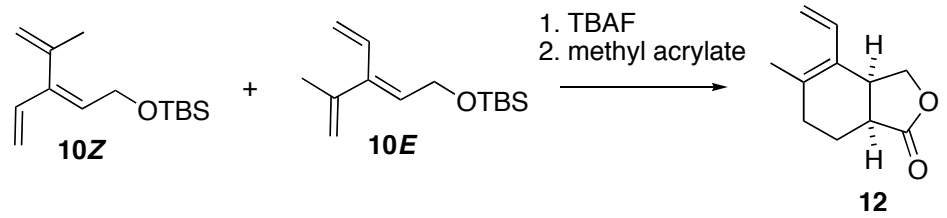
freeze/thaw degassed (× 2). CuI (4 mg, 0.02 mmol, 0.08 equiv), $PdCl_2$ (2.0 mg, 0.01 mmol, 0.04 equiv) and tBu$_3$P (4.7 mg, 0.02 mmol, 0.08 equiv) were added and the mixture was heated to 45 °C for 18 h. The mixture was filtered through a pad of celite with dichloromethane (50 mL). The filtrate was washed with sat. brine, dried and concentrated *in vacuo*. Column chromatography (hexanes/ethyl acetate 99:1) gave a mixture of **11, 10*Z*** and **10*E*** (50% conversion, 28 mg of **11** and 34 mg of **10*Z*** and **10*E*** (91:9), 69% based on recovered **11**). Column chromatography of this mixture (hexanes/dichloromethane 90:10) gave a mixture of triene silyl ethers **10*Z*** and **10*E*** (91:9) as a colourless oil.

(2*Z*)-1-[(*tert*-Butyldimethylsilyl)oxy]-4-methyl-3-vinylpenta-2,4-diene (**10*Z***):
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.31 (1H, dd, J = 17.4, 10.5 Hz), 5.55 (1H, t, J = 6.4 Hz), 5.16 (1H, bs), 5.15 (1H, d, J = 17.4 Hz), 5.07 (1H, d, J = 10.5 Hz), 4.72 (1H, bs), 4.26 (2H, d, J = 6.4 Hz), 1.85 (3H, s), 0.91 (9H, s), 0.08 (6H, s) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 141.1, 138.0, 130.3, 115.7, 114.9, 60.9, 26.1, 23.0, 18.5, –5.0 ppm. IR (thin film): ν = 2957, 2929, 2857 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 238 (2), 223 (2), 181 (55), 75 (100); HRMS: calcd for $C_{10}H_{17}OSi$ $[M–C_4H_9]^+$: 181.1049; found: 181.1050.

Method B

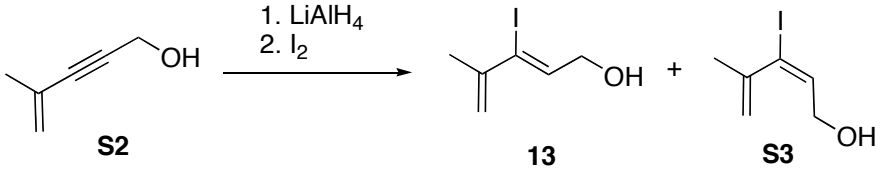
A solution of **11** (300 mg, 1.03 mmol, 1.0 equiv) and tributylvinylstannane (448 mg, 2.06 mmol, 2.0 equiv) in acetonitrile (4 mL) was freeze/thaw degassed (× 2). Triphenyl phosphine (24 mg, 0.10 mmol, 0.10 equiv) and palladium acetate (14 mg, 0.05 mmol, 0.05 equiv) were added and the mixture was heated to 60 °C for 18 h. The mixture was diluted with diethyl ether (20 mL) and washed with sat. aq. NH_3 (2 × 20 mL). The aqueous layer was extracted with diethyl ether (2 × 20 ml). The combined organic layers were washed with brine, dried and concentrated *in vacuo*. Column chromatography gave a mixture of triene silyl ethers **10*Z*** and **10*E*** (28:72, 113 mg, 0.47 mmol, 46%) as a colourless oil.

(±)-(3a*S*,7a*S*)-3,3a,7,7a-Tetrahydro-5-methyl-4-vinylisobenzofuran-1(6*H*)-one (**12**)



To a stirred solution of **10*Z*** and **10*E*** (28:72, 113 mg, 0.47 mmol, 1.0 equiv) in tetrahydrofuran (5 mL) was added TBAF (1.0 M sol, 2.5 mL, 2.5 mmol, 5.2 equiv). Stirring was continued for 2 h before the mixture was diluted with diethyl ether (20 mL). The mixture was washed with sat. aq. NH_4Cl (20 mL), sat. brine (20 mL), dried and concentrated *in vacuo*. Column chromatography (dichloromethane) gave a mixture of **S1** and **6** (28:72). Toluene (2 mL) and methyl acrylate (2 mL) were added and the mixture was heated in a sealed tube at 100 °C for 18 h. Concentration *in vacuo* followed by column chromatography (hexanes/ethyl acetate 75:25) gave **12** colourless oil. (18 mg, 0.10 mmol, 30% based on **10*E***). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.74 (1H, dd, J = 17.7, 11.3 Hz), 5.04 (1H, d, J = 11.3 Hz), 4.95 (1H, d, J = 17.8 Hz), 4.52 (1H, dd, J = 9.0, 7.5 Hz), 4.06 (1H, dd, J = 9.0, 4.9 Hz), 3.42 (1H, m), 2.86 (1H, m), 2.23–1.90 (3H, m), 1.81 (3H, s), 1.77 (1H, m) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.3, 136.8, 133.2, 126.5, 111.8, 72.5, 38.3, 34.8, 29.6, 20.5, 19.9 ppm . IR (thin film): ν = 3087, 2919, 1772 cm^{-1}. EIMS (70 eV) *m/z* (%): 178 (65), 163 (15), 134 (28), 105 (100); HRMS: calcd for $C_{11}H_{14}O_2$ [M]$^+$: 178.0994; found: 178.0999.

(2*Z*)-3-Iodo-4-methylpenta-2,4-dien-1-ol (**13**) and (2*E*)-3-iodo-4-methylpenta-2,4-dien-1-ol (**S3**)



The title compounds were prepared according to modified literature procedures.[4] To a suspension of $LiAlH_4$ (1.81 g, 48 mmol, 1.2 equiv) in diethyl ether (40 mL) at 0 °C was added a solution of **S2**[5,6] (3.82 g, 40 mmol, 1.0 equiv) in diethyl ether (8 mL). The mixture was stirred at RT for 1 h then cooled to 0 °C. EtOAc (4.7 mL, 48 mmol, 1.2 equiv) was added dropwise and stirring was continued at this temperature for 1 h. The mixture was cooled to –78 °C and solid I_2 (20 g, 79 mmol, 2.0 equiv) was

added in portions. The reaction was stirred at –78 °C for 1 h, 0 °C for 1 h then warmed to RT. Sat. aq. sodium thiosulfate solution (50 mL) was added and the mixture was filtered. The mixture was extracted with ether (2 × 100 mL). The combined organic layers were washed with sodium thiosulfate solution (50 mL), brine (50 mL) and dried. Concentration *in vacuo* followed by column chromatography (hexanes/ethyl acetate 85:15) gave **13** and **S3** (3.79 g, 17 mmol, 42%) as a 2.75:1 ratio of *Z*/*E* isomers as a colourless oil. For characterisation purposes, the two isomers were separated by normal phase preparative HPLC eluting with hexanes/ethyl acetate 88:12.

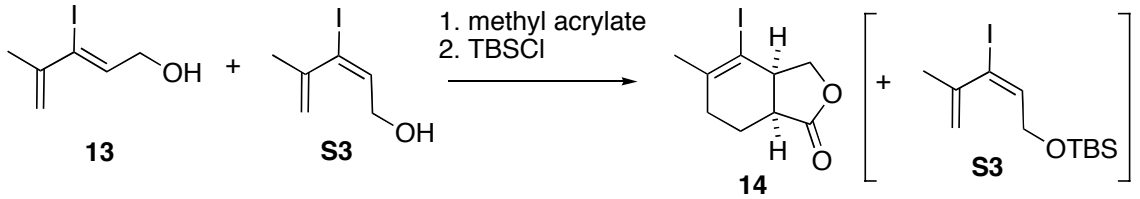
(2*Z*)-3-Iodo-4-methylpenta-2,4-dien-1-ol (**13**):

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.15 (1H, t, J = 5.5 Hz), 5.40 (1H, bs), 5.18 (1H, bs), 4.36 (2H, t, J = 4.8 Hz), 2.05 (3H, m), 1.83 (1H, bs) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.9, 135.9, 121.5, 108.9, 68.5, 20.8 ppm. IR (thin film): ν = 3319, 2922 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 224 (10), 127 (8), 97 (90), 41 (100); HRMS: calcd for $C_6H_9O^{127}I$ $[M]^+$: 223.9698; found: 223.9695.

(2*E*)-3-Iodo-4-methylpenta-2,4-dien-1-ol (**S3**):

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.39 (1H, t, J = 5.8 Hz), 5.00 (1H, m), 4.97 (1H, m), 41.2 (2H, d, J = 6.7 Hz), 1.91 (3H, dd, J = 1.5, 0.8 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.6, 139.9, 115.5, 104.3, 61.3, 22.4 ppm. IR (thin film): ν = 3306, 2945 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 224 (25), 195 (10), 127 (8), 97 (60), 41 (100); HRMS: calcd for $C_6H_9O^{127}I$ $[M]^+$: 223.9698; found: 223.9695.

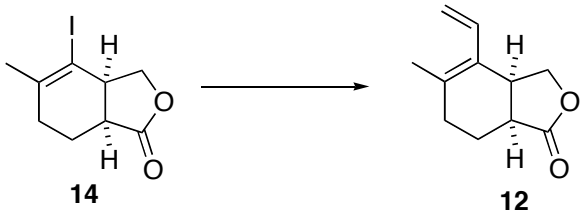
(±)-(3a*R*,7a*S*)-3,3a,7,7a-Tetrahydro-4-iodo-5-methylisobenzofuran-1(6*H*)-one (**14**)



A solution of **13** and **S3** (2.75:1 mixture of *Z*/*E* isomers, 3.79 g, 17 mmol, 1.0 equiv) in methyl acrylate (15 mL) and toluene (10 mL) was heated at 100 °C for 18 h. The mixture was concentrated *in vacuo* and the residue was dissolved in CH_2Cl_2 (15 mL). Imidazole (1.73 g, 25 mmol, 1.5 equiv), TBSCl (2.55 g, 17 mmol, 1.0 equiv) and DMAP (378 mg, 3.4 mmol, 0.2 equiv) were added at RT. Stirring was

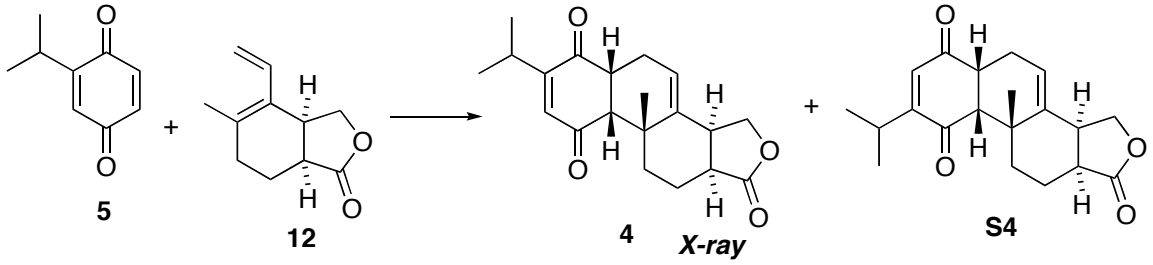
continued for 4 h. Water (20 mL) was added and the mixture was extracted with ether (100 mL). The organic layer was washed with sat. brine, dried and concentrated *in vacuo*. Column chromatography (hexanes/ethyl acetate 85:15) gave **14** as a colourless oil (2.10 g, 7.6 mmol, 61% from **13**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.38 (1H, ddd, J = 9.4, 6.5, 1.4 Hz), 4.32 (1H, ddd, J = 9.4, 3.7, 1.2 Hz), 3.47 (1H, bs), 2.81 (1H, dd, J = 12.4, 5.4 Hz), 2.27–2.06 (3H, m), 1.90 (3H, s), 1.90 (1H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.9, 142.7, 97.0, 73.5, 47.6, 40.7, 30.0, 29.3, 26.9, 20.7 ppm . IR (thin film): ν = 2917, 1769, 1646 cm^{-1}. EIMS (70 eV) *m/z* (%): 278 (95), 233 (30), 220 (28), 151 (12), 93 (100); HRMS: calcd for $C_9H_{11}O_2{}^{127}I$ $[M]^+$: 277.9804; found: 277.9803.

(±)-(3a*S*,7a*S*)-3,3a,7,7a-Tetrahydro-5-methyl-4-vinylisobenzofuran-1(6*H*)-one (**12**)



A solution of **14** (500 mg, 1.79 mmol, 1.0 equiv) and tributylvinylstannane (1.14 g, 3.60 mmol, 2.0 equiv) in toluene (10 mL) was freeze/thaw degassed (× 2). $Pd_2(dba)_3$ (41 mg, 0.04 mmol, 0.025 equiv) and tri-2-furylphosphine (63 mg, 0.27 mmol, 0.15 equiv) were added and the mixture was heated to 60 °C for 24 h. The mixture was diluted with diethyl ether (20 mL) and washed with sat. aq. NH_3 (50 mL). The aqueous layer was extracted with diethyl ether (20 mL). The combined organic layers were washed with sat. brine, dried and concentrated *in vacuo*. Column chromatography (hexanes to hexanes/ethyl acetate 85:15) gave **12** (277 mg, 1.55 mmol, 86%) as a colourless oil. Characterisation data was identical to that obtained by the Diels–Alder reaction between trienol **6** and methyl acrylate.

Diels–Alder reaction between diene **12** and quinone **5**



A solution of semicyclic diene **12** (890 mg, 4.99 mmol, 1.0 equiv) and quinone **5**[7] (1.10 g, 7.32 mmol, 1.5 equiv) in dichloromethane (3 mL) was compressed at 19 kbar at RT for 7 days. The solution was concentrated *in vacuo*. ^{1}H NMR analysis of the crude product mixture indicated the presence of an 83:17 mixture of **4** and **S4**. Column chromatography (hexanes/ethyl acetate 75:25) gave desired tetracycle **4** (819 mg, 2.49 mmol, 50%) as a colourless solid. A pure sample of **S4** (also obtained as a colourless solid) was obtained by preparative HPLC, eluting with hexanes/ethyl acetate 75:25.

(±)-(3a*S*,5a*R*,9a*R*,9b*R*,11a*S*)-3,3a,5,5a,9b,10,11,11a-Octahydro-7-isopropyl-9b-methylphenanthro[2,1-*c*]furan-1,6,9(9a*H*)-trione (**4**):

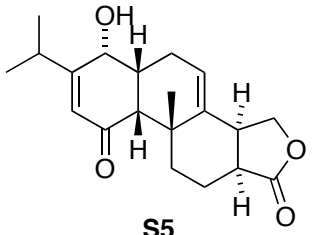
Recrystallisation from heptane/dichloromethane gave colourless crystals, m.p. 167–170 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.42 (1H, s), 5.42 (1H, t, J = 3.7 Hz), 4.30 (1H, t, J = 9.2 Hz), 4.09 (1H, dd, J = 11.2, 9.2 Hz), 3.54 (1H, ddd, J = 10.5, 7.2, 4.9 Hz), 3.29 (1H, dd, J = 19.0, 8.8 Hz), 3.03 (1H, d, J = 4.8 Hz), 2.92 (1H, dsept. J = 6.8, 1.0), 2.77 (1H, ddd, J = 12.4, 8.1, 6.1 Hz), 2.63 (1H, dt, J = 13.3, 3.5 Hz), 2.36 (1H, ddd, J = 19.0, 7.2, 3.9 Hz), 2.09 (1H, ddd, J = 19.0, 10.5, 3.5 Hz), 2.05 (1H, m), 1.81 (1H, ddd, J = 26.6, 13.3, 3.5 Hz), 1.29 (1H, dt, J = 13.3, 3.7 Hz), 1.26 (3H, s), 1.10 (3H, d, J = 6.8 Hz), 1.06 (3H, d, J = 6.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.1, 199.3, 179.3, 155.1, 136.7, 135.5, 123.2, 71.6, 58.1, 45.6, 41.8, 40.2, 35.0, 31.2, 28.3, 26.6, 21.3, 20.9, 20.0 ppm. IR (thin film): ν = 2962, 1768, 1673 cm^{-1}. EIMS (70 eV) *m/z* (%): 328 (80), 285 (19), 177 (24), 152 (100); HRMS: calcd for $C_{20}H_{24}O_4$ [M]$^+$: 328.1675; found: 328.1682.

(±)-(3a*S*,5a*R*,9a*R*,9b*R*,11a*S*)-3,3a,5,5a,9b,10,11,11a-Octahydro-8-isopropyl-9b-methylphenanthro[2,1-*c*]furan-1,6,9(9a*H*)-trione (**S4**):

Recrystallisation from heptane/dichloromethane gave colourless crystals, m.p. 146–152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.21 (1H, s), 5.38 (1H, t, J = 4.1 Hz), 4.28 (1H, t, J = 9.2 Hz), 4.07 (1H, dd, J = 11.1, 9.2 Hz), 3.46 (1H, dddd, J = 12.1, 6.7, 5.1, 1.3 Hz), 3.30 (1H, dd, J = 19.3, 8.9 Hz), 3.04 (1H, d, J

= 4.8 Hz), 2.91 (1H, dsept. *J* = 6.9, 1.0), 2.74 (1H, ddd, *J* = 12.6, 8.3, 6.2 Hz), 2.47 (1H, dt, *J* = 13.0, 3.4 Hz), 2.37 (1H, ddd, *J* = 19.2, 7.1, 3.6 Hz), 2.08–1.92 (2H, m), 1.80 (1H, ddd, *J* = 26.6, 13.4, 3.6 Hz), 1.27 (1H, m), 1.22 (3H, s), 1.09 (3H, d, *J* = 6.9 Hz), 1.02 (3H, d, *J* = 6.9 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.6, 199.9, 179.2, 162.3, 136.2, 129.8, 122.9, 71.6, 59.2, 45.1, 41.7, 40.2, 34.6, 31.0, 28.2, 26.7, 21.3, 20.5, 19.9 ppm. IR (thin film): ν = 2969, 2928, 1776, 1796, 1674 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 328 (70), 285 (10), 177 (5), 152 (40), 84 (100); HRMS: calcd for $C_{20}H_{24}O_4$ [M]$^+$: 328.1675; found: 328.1676.

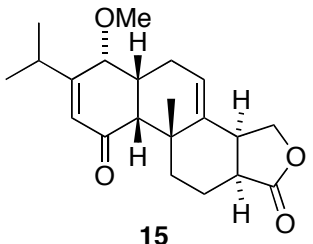
(±)-(3a*S*,5a*R*,6*R*,9a*R*,9b*R*,11a*S*)-3,3a,5a,6,9b,10,11,11a-octahydro-6-hydroxy-7-isopropyl-9b-methylphenanthro[2,1-*c*]furan-1,9(5*H*,9a*H*)-dione (**S5**)



S5 ***X-ray***

To a stirred solution of **4** (270 mg, 0.83 mmol, 1.0 equiv) in tetrahydrofuran (14 mL) at 0 °C was added a solution of $NaBH_4$ (25 mg, 0.66 mmol, 0.8 equiv) in water (2 mL). Stirring was continued for 30 min before the reaction was quenched by the addition of sat. aq. NH_4Cl soln. (20 mL). The mixture was extracted with ethyl acetate (20 mL × 2). The combined organic phases were dried and concentrated *in vacuo* to give **S5** as a colourless solid (270 mg, 0.83 mmol, 100%). Recrystallisation gave **S5** as colourless crystals, m.p. 176–178 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.70 (1H, bs), 5.36 (1H, t, *J* = 3.2 Hz), 4.88 (1H, d, *J* = 3.2 Hz), 4.28 (1H, t, *J* = 9.2 Hz), 4.06 (1H, dd, *J* = 11.1, 9.2 Hz), 3.25 (1H, q, *J* = 8.8 Hz), 3.19 (1H, m), 2.98 (1H, dt, *J* = 13.7, 3.9 Hz), 2.78 (1H, sept., *J* = 6.9 Hz), 2.75 (1H, ddd, *J* = 12.6, 8.0, 5.9 Hz), 2.41 (1H, d, *J* = 3.9 Hz), 2.18 (1H, ddd, *J* = 19.2, 6.3, 4.7 Hz), 2.01–1.97 (2H, m), 1.78 (1H, dq, *J* = 13.4, 3.6 Hz), 1.28–1.23 (1H, m), 1.26 (3H, s), 1.14 (3H, d, *J* = 6.9 Hz), 1.09 (3H, d, *J* = 6.9 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5, 180.0, 165.7, 136.6, 124.3, 123.9, 71.9, 71.6, 56.9, 41.8, 40.3, 38.5, 35.8, 31.3, 29.1, 29.0, 23.1, 22.0, 20.4, 20.0 ppm. IR (thin film): ν = 3469, 2965, 2872, 1762, 1668 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 330 (12), 178 (54), 150 (50), 111 (100); HRMS: calcd for $C_{20}H_{26}O_4$ [M]$^+$: 330.1831; found: 330.1834.

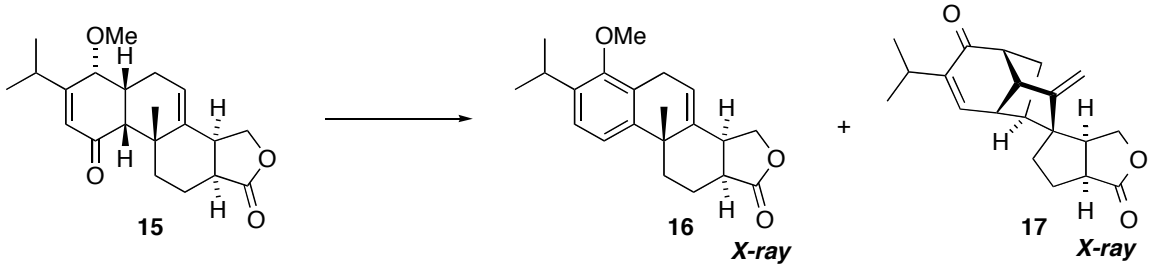
(±)-(3a*S*,5a*R*,6*R*,9a*R*,9b*R*,11a*S*)-3,3a,5a,6,9b,10,11,11a-Octahydro-7-isopropyl-6-methoxy-9b-methylphenanthro[2,1-*c*]furan-1,9(5*H*,9a*H*)-dione (**15**)



15 ***X-ray***

A solution of **S5** (40 mg, 0.12 mmol, 1.0 equiv) and Ag_2O (280 mg, 1.21 mmol, 10 equiv) in methyl iodide (5 mL) was heated to reflux for 18 h. The solution was diluted with dichloromethane (20 mL), filtered through celite and concentrated *in vacuo*. Column chromatography (hexanes/ethyl acetate 70:30) gave **15** as a colourless solid (41 mg, 0.12 mmol, 99%). Recrystallisation (heptane/dichloromethane) gave colourless needles, m.p. 88–90 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.68 (1H, bs), 5.36 (1H, t, J = 3.7 Hz), 4.30 (1H, dd, J = 4.7, 2.1 Hz), 4.27 (1H, t, J = 9.1 Hz), 4.06 (1H, dd, J = 11.2, 9.1 Hz), 3.49 (3H, s), 3.37 (1H, m), 3.25 (1H, q, J = 8.7 Hz), 3.00 (1H, dt, J = 13.0, 3.6 Hz), 2.79–2.72 (2H, m), 2.34 (1 H, d, J = 3.8 Hz), 2.09–1.95 (3H, m), 1.79 (1H, dq, J = 13.3, 3.8 Hz), 1.29 (3H, s), 1.27 (1H, dt, J = 13.3, 3.8 Hz), 1.07 (3H, d, J = 6.7 Hz), 1.05 (3H, d, J = 6.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.4, 179.8, 165.0, 136.6, 124.5, 123.9, 80.3, 71.8, 57.1, 56.3, 41.9, 40.3, 36.0, 33.6, 31.4, 29.1, 29.0, 23.0, 21.8, 20.3, 20.1 ppm. IR (thin film): ν = 2925, 1778, 1672 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 344 (9), 312 (25), 178 (45), 125 (100); HRMS: calcd for $C_{21}H_{28}O_4$ $[M]^+$: 344.1988; found: 344.1996. Anal. Calcd for $C_{21}H_{28}O_4$: C, 73.23; H, 8.19. Found: C, 73.12; H, 7.97.

Reaction of (±)-(3a*S*,5a*R*,6*R*,9a*R*,9b*R*,11a*S*)-3,3a,5a,6,9b,10,11,11a-octahydro-7-isopropyl-6-methoxy-9b-methylphenanthro[2,1-*c*]furan-1,9(5*H*,9a*H*)-dione (**15**) with triflic anhydride and 2,6-di-*tert*-butyl-4-methyl pyridine.



15 **16** ***X-ray*** **17** ***X-ray***

To a stirred solution of **15** (133 mg, 0.39 mmol, 1.0 equiv) in dichloromethane (2 mL) at –78 °C was added 2,6-di-*tert*-butyl-4-methyl pyridine (95 mg, 0.46 mmol, 1.2 equiv) and triflic anhydride (71 μL, 0.42 mmol, 1.1 equiv). The mixture was gradually warmed to RT and stirring was continued for 72 h. The mixture was diluted with dichloromethane (20 mL) and washed with sat. aq. $NaHCO_3$ (10 mL). The aqueous layer was extracted with dichloromethane (10 mL). The combined organic layers were washed with sat. brine (10 mL), dried and concentrated *in vacuo*. Column chromatography (hexanes/diethyl ether 60:40) gave **16** (55 mg, 0.17 mmol, 43%) and **17** (21 mg, 0.07 mmol, 17%) as colourless solids.

(±)-(3a*S*,9b*S*,11a*S*)-3,3a,9b,10,11,11a-hexahydro-7-isopropyl-6-methoxy-9b-methylphenanthro[2,1-*c*]furan-1(5*H*)-one (**16**):

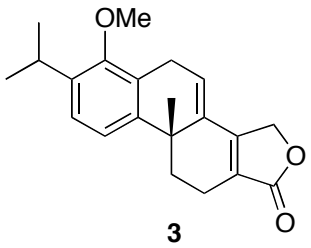
Recrystallisation (heptane/dichloromethane) gave colourless needles, m.p. 142–144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (1H, d, J = 8.4 Hz), 7.10 (1H, d, J = 8.4 Hz), 5.95 (1H, dd, J = 6.4, 2.3 Hz), 4.43 (1H, t, J = 9.3 Hz), 4.27 (1H, dd, J = 11.7, 9.3 Hz), 3.75 (3H, s), 3.64 (1H, dd, J = 21.6, 6.1 Hz), 3.45 (1H, q, J = 9.2 Hz), 3.32 (1H, sept., J = 6.8 Hz), 3.14 (1H, d, J = 21.1 Hz), 2.57 (1H, m), 2.35 (1H, ddd, J = 13.4, 4.2, 3.1 Hz), 2.13 (1H, m), 1.88 (1H, ddd, J = 26.3, 13.4, 2.7 Hz), 1.75 (1H, dt, J = 13.3, 2.7 Hz), 1.30 (3H, s), 1.26 (3H, d, J = 6.8 Hz), 1.20 (3H, d, J = 6.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.5, 154.2, 144.4, 138.8, 136.2, 127.6, 126.2, 124.8, 119.8, 72.0, 61.1, 42.3, 40.2, 37.5, 34.9, 29.1, 26.3, 24.5, 24.2, 23.7, 20.5 ppm. IR (thin film): ν = 2961, 2868, 2823, 1777 cm^{-1}. EIMS (70 eV) *m/z* (%): 326 (35), 311 (55), 269 (100); HRMS: calcd for $C_{21}H_{26}O_3$ [M]$^+$: 326.1882; found: 326.1883.

Rearranged pentacycle **17**:

Recrystallisation (heptane/dichloromethane) gave colourless needles, m.p. 65–67 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.56 (1H, dd, J = 6.7, 1.0 Hz), 5.09 (1H, s), 4.57 (1H, s), 4.38 (1H, dd, J = 9.6, 7.7 Hz), 4.30 (1H, dd, J = 9.6, 2.1 Hz), 3.20 (1H, ddd, J = 10.0, 8.4, 6.2 Hz), 3.02–2.97 (2H, m), 2.84 (1H, d, J = 6.4 Hz), 2.74 (1H, sept., J = 6.8 Hz), 2.56 (1H, d, J = 7.4 Hz), 2.09–2.03 (3H, m), 1.93 (1H, ddd, J = 13.1, 14.9, 7.6 Hz), 1.75 (1H, ddd, J = 19.8, 13.4, 6.7 Hz), 1.61 (1H, dd, J = 14.0, 7.9 Hz), 1.49 (1H, ddd, J = 14.0, 5.0, 1.7 Hz), 1.01 (3H, d, J = 6.8 Hz), 0.96 (3H, d, J = 6.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.6, 180.2, 154.2, 144.5, 139.4, 108.1, 69.8, 62.3, 60.3, 51.8, 50.8, 46.0, 46.0, 42.0,

27.3, 27.0, 26.1, 21.6, 21.6 ppm. IR (thin film): ν = 2959, 1771, 1675 cm^{-1}. EIMS (70 eV) *m/z* (%): 312 (100), 297 (39), 269 (44); HRMS: calcd for $C_{20}H_{24}O_3$ [M]$^+$: 312.1725; found: 312.1719.

(±)-(9b*S*)-10,11-Dihydro-7-isopropyl-6-methoxy-9b-methylphenanthro[2,1-*c*]furan-1(3*H*,5*H*,9b*H*)-one (**3**)

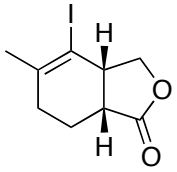


3

To a solution of **16** (25 mg, 0.08 mmol, 1.0 equiv) in CD_2Cl_2 (500 μL) at 0 °C was added triethylamine (43 μL, 0.30 mmol, 4.0 equiv) and TIPSOTf (62 μL, 0.23 mmol, 3.0 equiv). After 15 min, more triethylamine (43 μL, 0.30 mmol, 4.0 equiv) and TIPSOTf (62 μL, 0.23 mmol, 3.0 equiv) were added. After another 15 min, additional triethylamine (43 μL, 0.30 mmol, 4.0 equiv) and TIPSOTf (62 μL, 0.23 mmol, 3.0 equiv) were added. After 15 min, PhSeCl (176 mg, 0.91 mmol, 12.0 equiv) was added. After 1 h, the solution was diluted with dichloromethane (10 mL) and washed with sat. aq. $NaHCO_3$ (5 mL). The solution was concentrated *in vacuo* and the residue was dissolved in dichloromethane (10 mL) and cooled to 0 °C. H_2O_2 (30% aq. solution, 2 mL) was added and the mixture was stirred for 2 h at 0 °C. The organic layer was collected, dried and concentrated *in vacuo*. Column chromatography (hexanes/diethyl ether 60:40) gave **3** (18 mg, 0.06 mmol, 72%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (2H, s), 6.17 (1H, dd, *J* = 5.6, 2.3 Hz), 5.02 (1H, dt, *J* = 16.0, 2.6 Hz), 4.93 (1H, dd, *J* = 16.0, 3.1 Hz), 3.81 (1H, dd, *J* = 23.0, 5.5 Hz), 3.77 (3H, s), 3.39 (1H, d, *J* = 23.0 Hz), 3.32 (1H, sept., *J* = 7.1 Hz), 2.64–2.44 (2H, m), 1.80 (1H, m), 1.27 (3H, d, *J* = 7.1 Hz), 1.21 (3H, d, *J* = 7.1 Hz), 1.19 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 155.0, 154.4, 142.4, 139.2, 135.3, 126.3, 126.0, 125.1, 123.8, 120.6, 69.3, 61.1, 37.0, 32.8, 27.3, 26.3, 25.0, 24.2, 23.7, 18.0 ppm . IR (thin film): ν = 2962, 2869, 1755 cm^{-1}. EIMS (70 eV) *m/z* (%): 324 (40), 309 (35), 281 (20), 267 (65), 43 (100); HRMS: calcd for $C_{21}H_{24}O_3$: 324.1725; found: 324.1728. Characterisation data for **3** was consistent with that reported in the literature.[8]

Enantioselective Diels–Alder Reactions

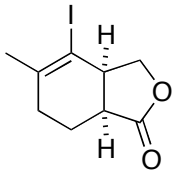
Table 1, Entry 1



(3*R*,4*S*)-14

To a stirred solution of (*S*)-2,2'-dihydroxy-1,1'-binapthyl (86 mg, 0.30 mmol, 1.0 equiv) in CH_2Cl_2 (6 mL) at RT was added powdered 4 Å molecular sieves (1.2 g) and a solution of $TiCl_2(OiPr)_2$ (0.3 M in toluene, 1.0 mL, 0.30 mmol, 1.0 equiv). After 1 h a solution of diene **13** (as a 63:37 *Z*/*E* mixture with **S3**, 68 mg, 0.30 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added. After a further 15 min, methyl acrylate (406 μL, 4.51 mmol, 15.0 equiv) was added. After 48 h at RT, hexane (20 mL) and Et_3N (2 mL) were added and the mixture was filtered through celite then concentrated *in vacuo*. Column chromatography (CH_2Cl_2/Et_3N, 99:1) gave iodolactone **14** [40 mg, 0.14 mmol, 75% from **13**, (3*S*,4*R*):(3*R*,4*S*) = 3:97] as a colourless oil. $[\alpha]_D = -130.5$ (*c* = 1.04, $CHCl_3$).

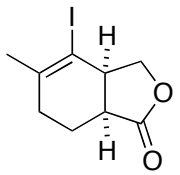
Table 1, Entry 2



(3*S*,4*R*)-14

To a stirred solution of diene **13** (as a 63:37 *Z*/*E* mixture with **S3**, 68 mg, 0.30 mmol, 1.0 equiv) and (*R*)-2,2'-dihydroxy-1,1'-binapthyl (86 mg, 0.30 mmol, 1.0 equiv) in CH_2Cl_2 (8 mL) at RT was added $TiCl_2(OiPr)_2$ (0.3 M in toluene, 1.0 mL, 0.30 mmol, 1.0 equiv). After 15 min, methyl acrylate (406 μL, 4.51 mmol, 15.0 equiv) was added. After 48 h at RT, hexane (20 mL) and Et_3N (2 mL) were added and the mixture was filtered through celite then concentrated *in vacuo*. Column chromatography (CH_2Cl_2/Et_3N, 99:1) gave iodolactone **14** [47 mg, 0.17 mmol, 89% from **13**, (3*S*,4*R*):(3*R*,4*S*) = 97:3] colourless oil. $[\alpha]_D = +139.3$ (*c* = 0.70, $CHCl_3$).

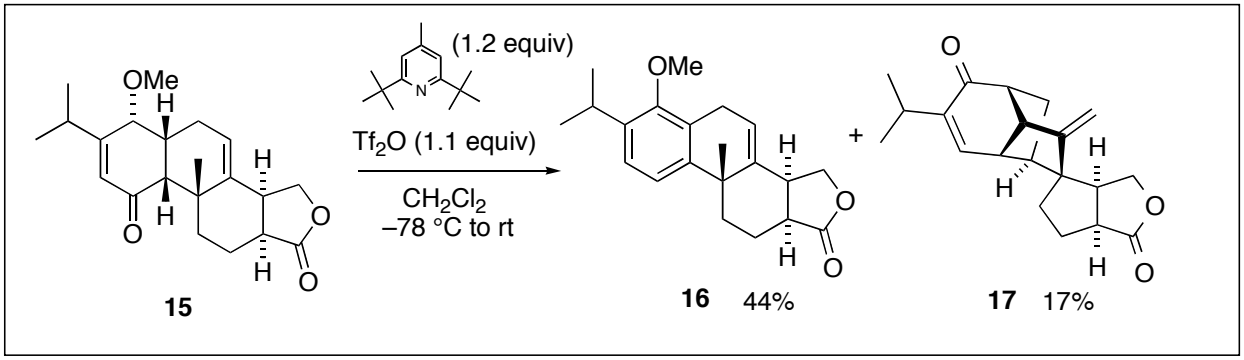
Table 1, Entry 3



(3*S*,4*R*)-14

To a stirred solution of (*R*)-2,2'-dihydroxy-1,1'-binapthyl (86 mg, 0.30 mmol, 0.10 equiv) in CH_2Cl_2 (6 mL) at RT was added powdered 4 Å molecular sieves (1.2 g) and a solution of $TiCl_2(OiPr)_2$ (0.3 M in toluene, 1.0 mL, 0.30 mmol, 0.10 equiv). After 1 h, a solution of diene **13** (as a 63:37 *Z*/*E* mixture with **S3**, 680 mg, 3.00 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added. After a further 15 min, methyl acrylate (4.06 mL, 45.1 mmol, 15.0 equiv) was added. After 48 h, hexane (20 mL) and Et_3N (2 mL) were added and the mixture was filtered through celite then concentrated *in vacuo*. Column chromatography (CH_2Cl_2/Et_3N, 99:1) iodolactone **14** [483 mg, 1.73 mmol, 91% from **13**, (3*S*,4*R*):(3*R*,4*S*) = 89:11] colourless oil.

Proposed mechanism for the conversion of **15** into **16** and **17**



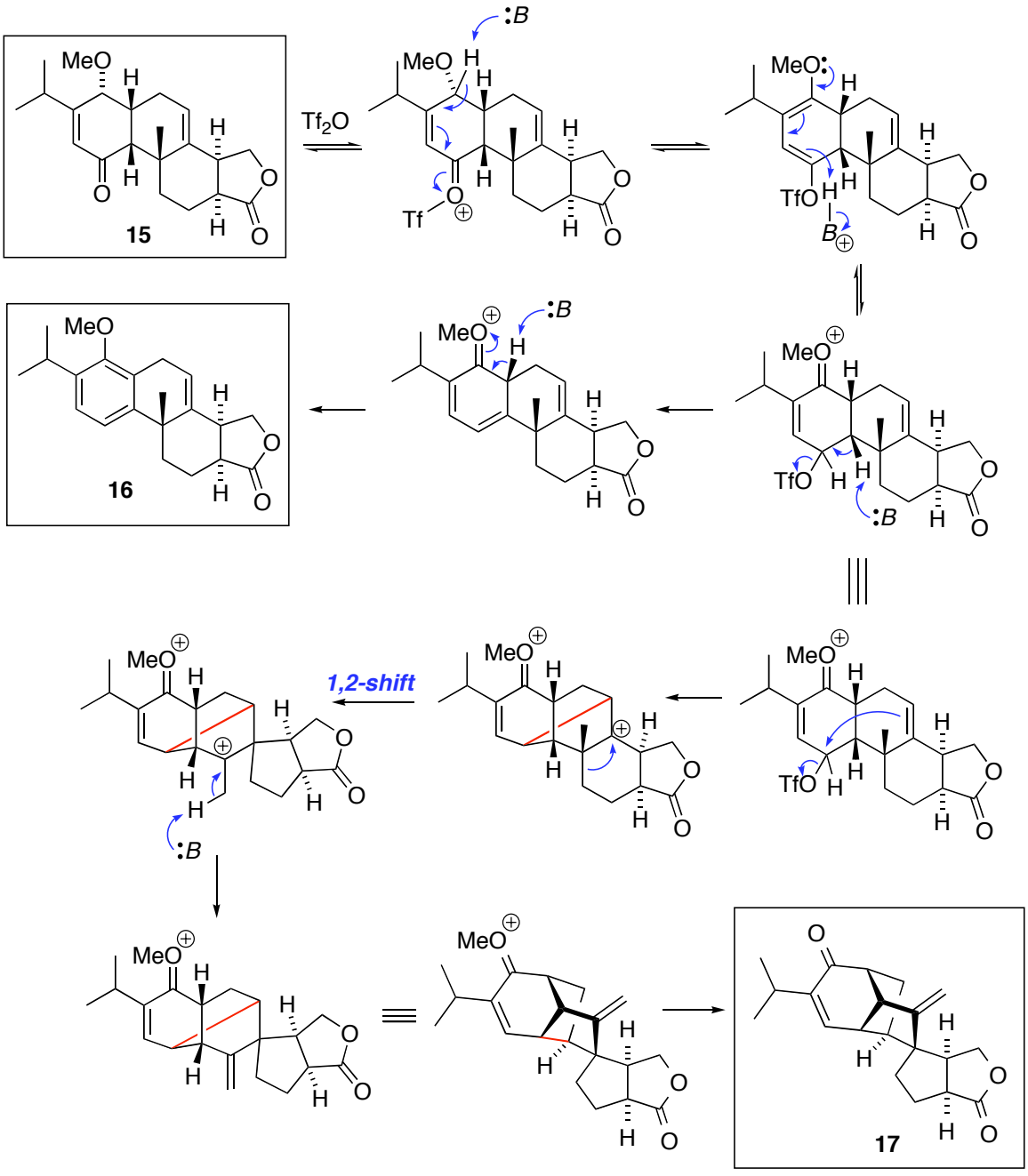


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Table S1 X-ray crystallographic data for compounds **4**, **S5** and **15**–**17**.

	4	**S5**[a]		**15**	**16**	**17**
		Orthorhombic form	Monoclinic form			
CCDC No.	658577	658578	669352	658574	658575	658576
Formula	$C_{20}H_{24}O_4$	$C_{20}H_{26}O_4$	$C_{20}H_{26}O_4$	$C_{21}H_{28}O_4$	$C_{21}H_{26}O_3$	$C_{20}H_{24}O_3$
M	328.41	330.42	330.42	344.45	326.44	312.41
Crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monolinic	monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$C2/c$	$P2_1/a$	$P2_1/c$	$P2_1/a$
a/Å	8.9554(2)	6.8313(1)	30.8694(6)	17.8410(3)	9.6828(3)	22.0658(4)
b/Å	9.8045(3)	10.1677(2)	6.9089(1)	6.4751(1)	10.5296(5)	6.9171(1)
c/Å	10.6568(3)	25.1585(4)	17.0770(4)	17.9281(3)	35.1809(15)	24.1734(4)
α/°	102.9314(13)	–	–	–	–	–
β/°	113.3780(16)	–	102.9197(12)	118.2156(8)	97.868(2)	115.5026(8)
γ/°	91.0740(17)	–	–	–	–	–
V/Å^3	831.03(4)	1747.47(5)	3549.87(12)	1825.00(5)	3553.1(3)	3330.12(10)
Z	2	4	8	4	8	8
T/K	200	200	200	200	200	200
Measured reflections	16625	18576	41222	36062	29916	54540
Independent reflections	3765	1806	4060	4190	6212	5856
Reflections in refinement	2983	1522	2406	2939	2641	3109
	[$I > 3.0\sigma(I)$]	[$I > 1.5\sigma(I)$]	[$I > 2.0\sigma(I)$]	[$I > 3.0\sigma(I)$]	[$I > 1.5\sigma(I)$]	[$I > 2.0\sigma(I)$]
R	0.0373	0.0336	0.0321	0.0320	0.0534	0.0410
Rw	0.0413	0.0403	0.0380	0.0379	0.0494	0.0356
S	1.1107	1.0504	1.1124	1.0680	1.1722	1.1332

[a] Crystals of two forms were obtained from the one sample of $C_{20}H_{26}O_4$, one orthorhombic and the other monoclinic.

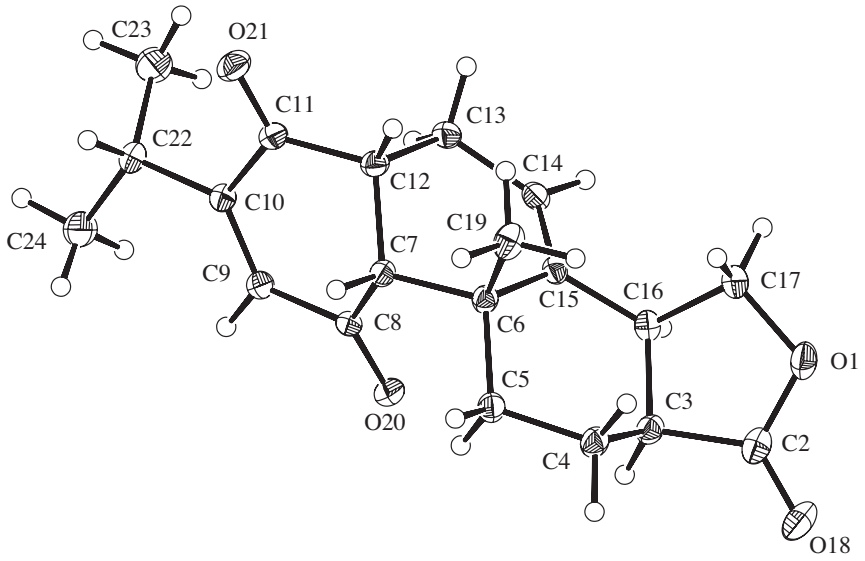

Figure S1. Anisotropic displacement ellipsoid plot of compound **4** (CCDC-658577) with labeling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

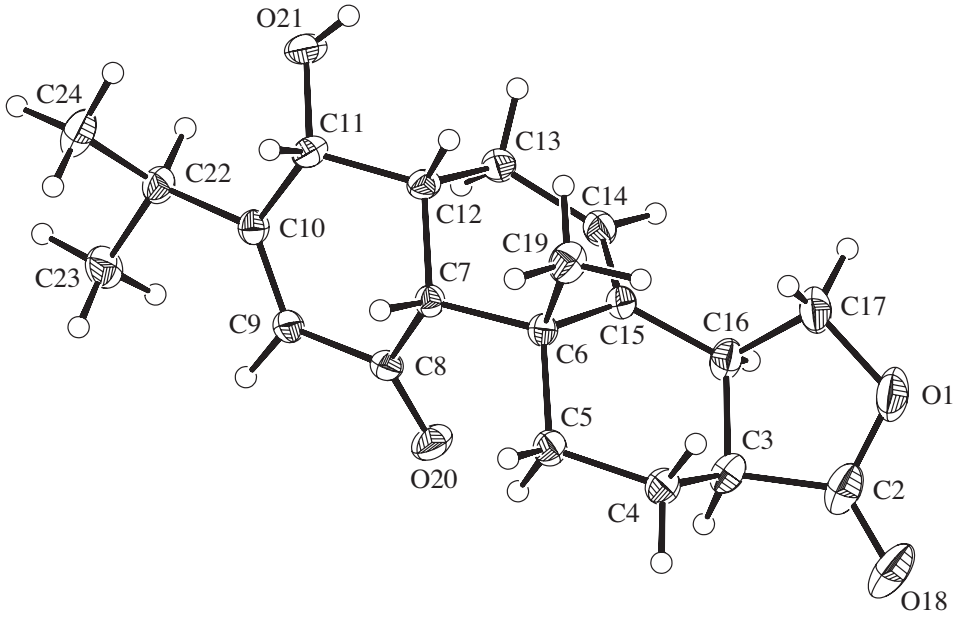

Figure S2. Anisotropic displacement ellipsoid plot of the orthorhombic form of compound **S5** (CCDC-658578) with labeling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

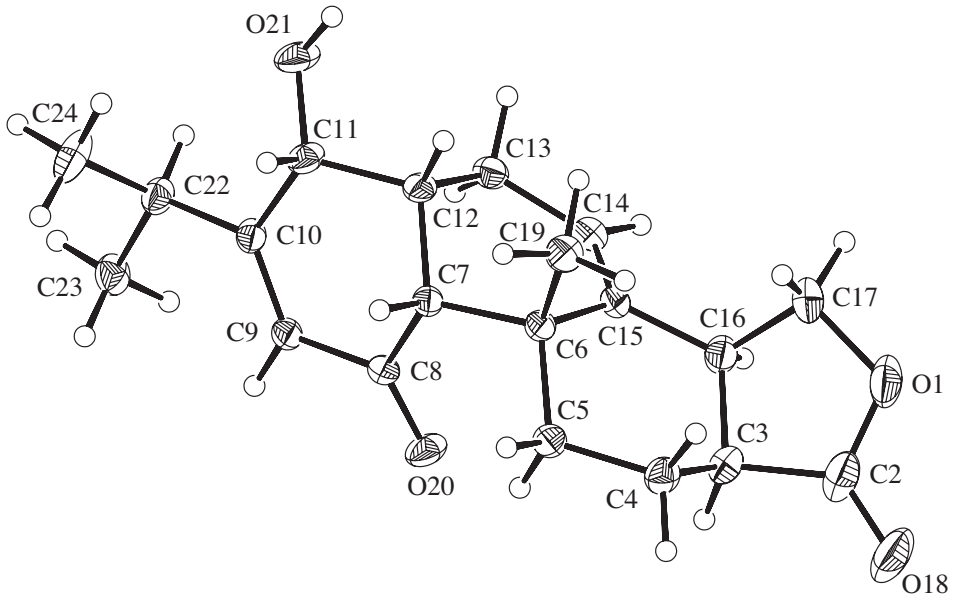

Figure S3. Anisotropic displacement ellipsoid plot of the monoclinic form of compound **S5** (CCDC-669352) with labeling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

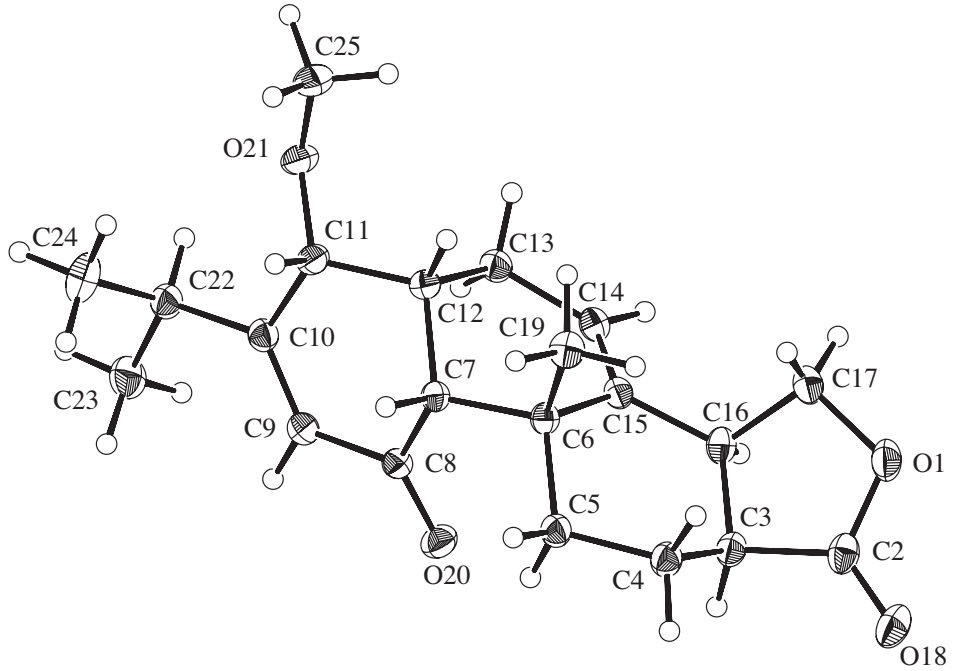

Figure S4. Anisotropic displacement ellipsoid plot of compound **15** (CCDC-658574) with labeling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

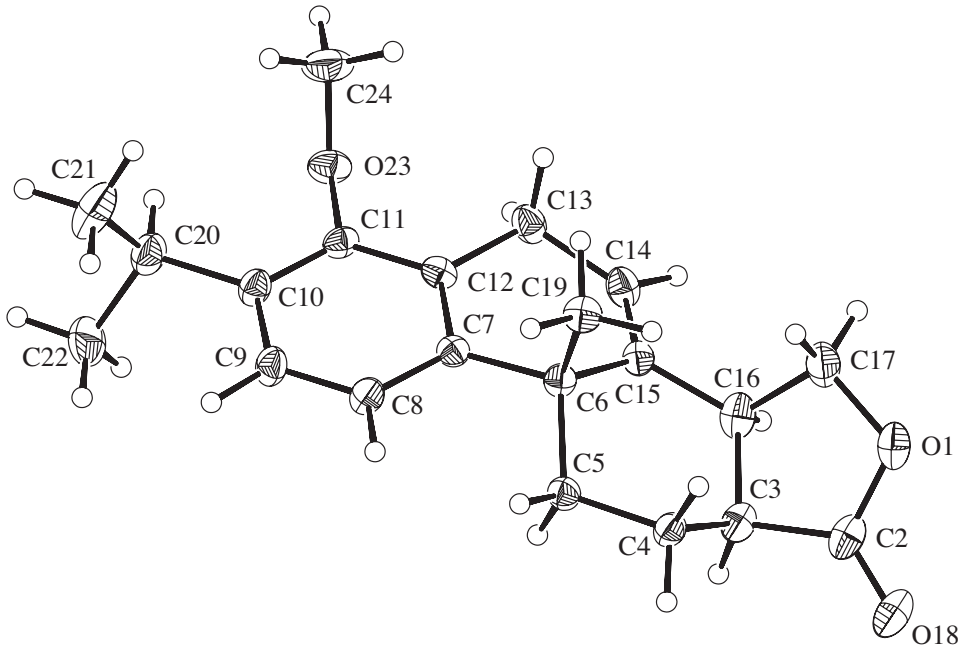

Figure S5. Anisotropic displacement ellipsoid plot of molecule one of compound **16** (CCDC-658575) with labeling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

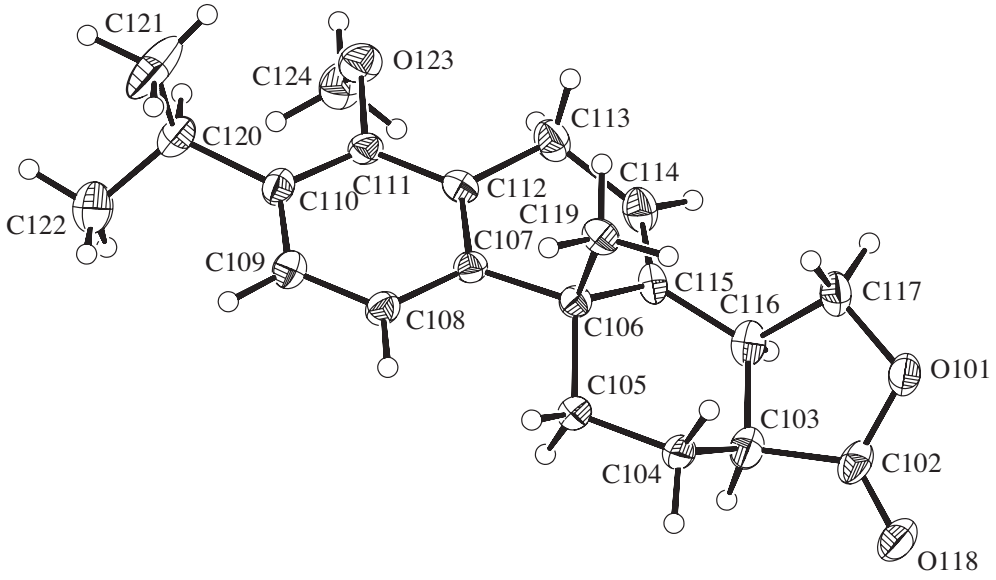

Figure S6. Anisotropic displacement ellipsoid plot of molecule two of compound **16** (CCDC-658575) with labeling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

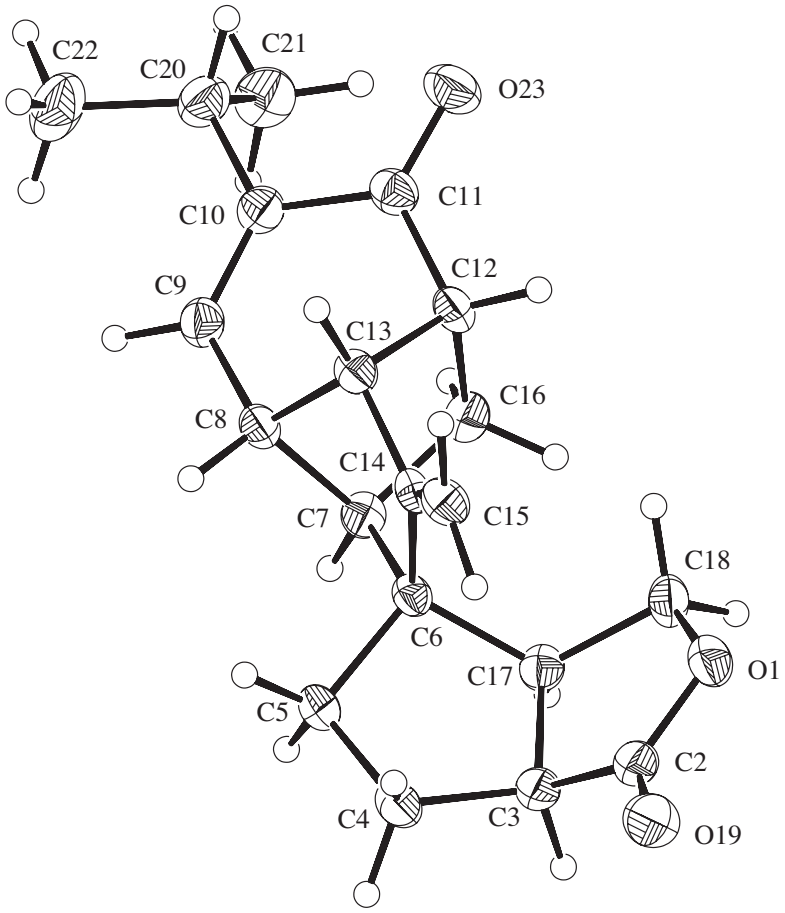

Figure S7. Anisotropic displacement ellipsoid plot of molecule one of compound **17** (CCDC-658576) with labeling of selected atoms. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

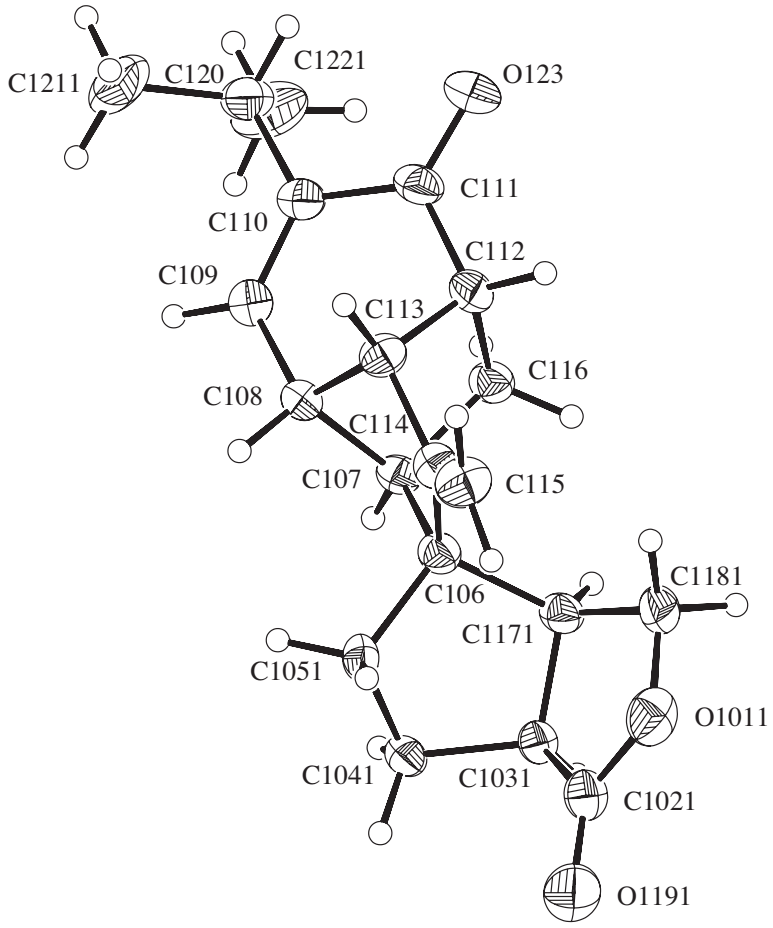

Figure S8. Anisotropic displacement ellipsoid plot of molecule two of compound **17** (CCDC-658576) with labeling of selected atoms. Only the major sites of disordered atoms are displayed. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

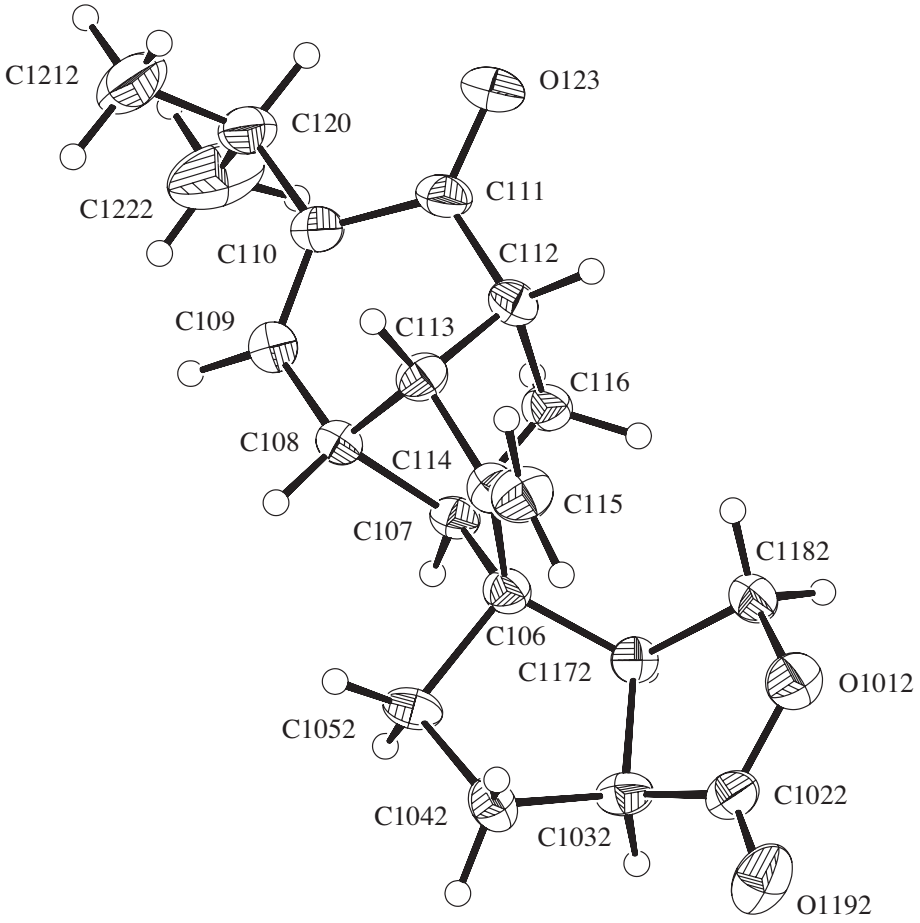

Figure S9. Anisotropic displacement ellipsoid plot of molecule two of compound **17** (CCDC-658576) with labeling of selected atoms. Only the minor sites of disordered atoms are displayed. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

Supplementary Material (ESI) for Chemical Communications
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                                                      Inj Volume : Manually
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check
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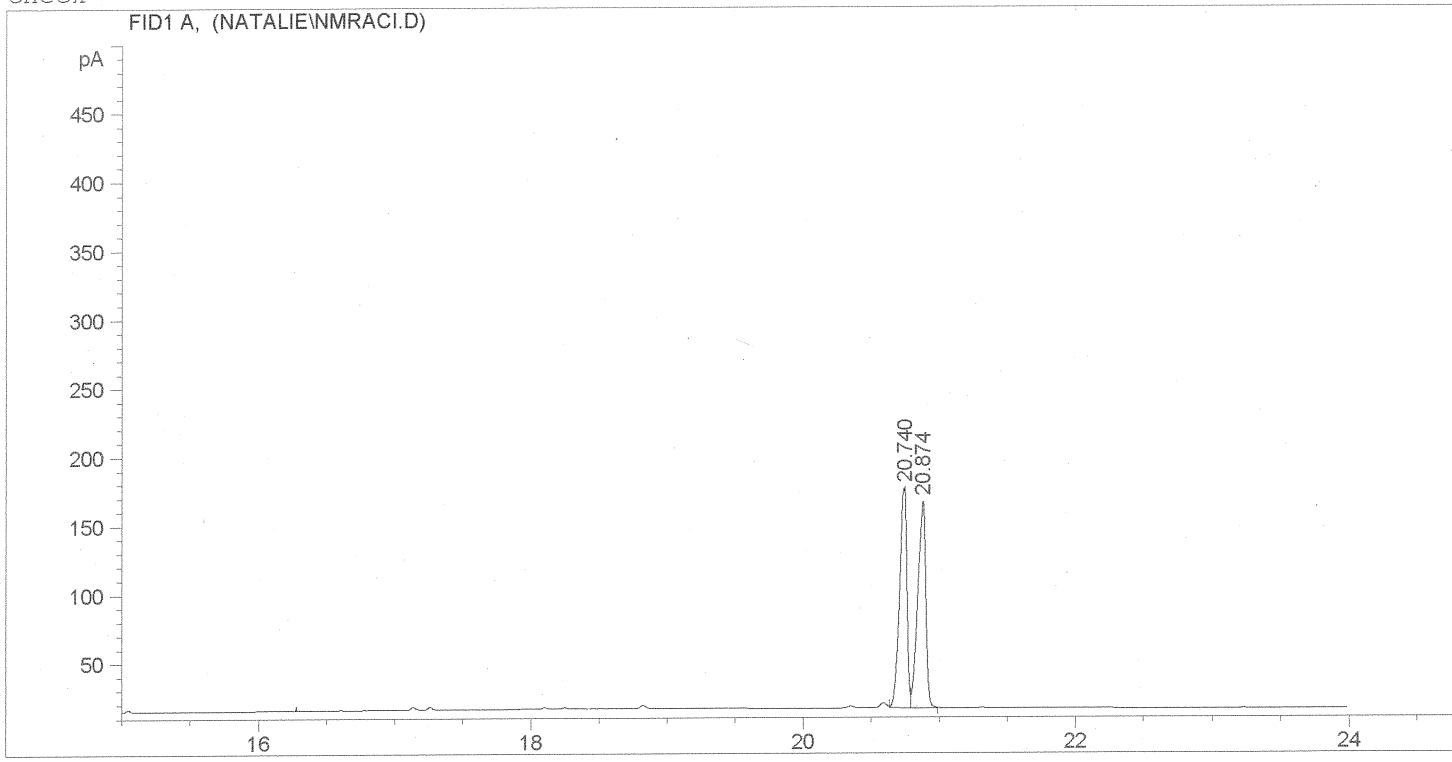


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Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
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 Results obtained with enhanced integrator!
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Figure S9. Racemic **14** (Scheme 2).

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                                                 Inj Volume : Manually

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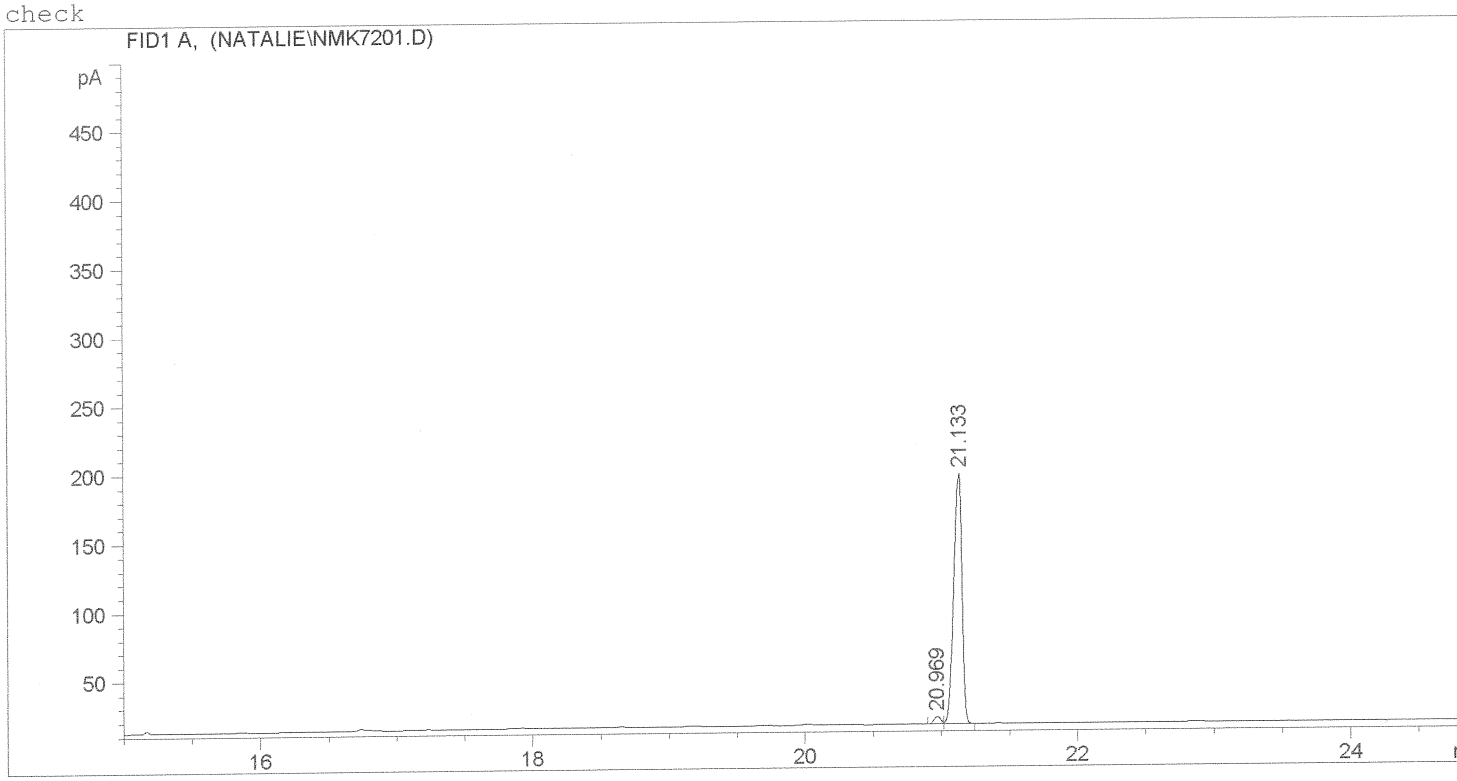


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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----|-------|----|-------|----------|----------|--------|
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   2  21.133 VP    0.0609  763.84985  182.14059 97.55958

Totals :                   782.95727  187.41187

 Results obtained with enhanced integrator!

                        *** End of Report ***
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Figure S10. (3*R*,4*S*)-**14** (Table 2, Entry 1).

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                                                 Inj Volume : Manually
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Last changed    : 7/20/2007 3:12:19 PM by Natalie
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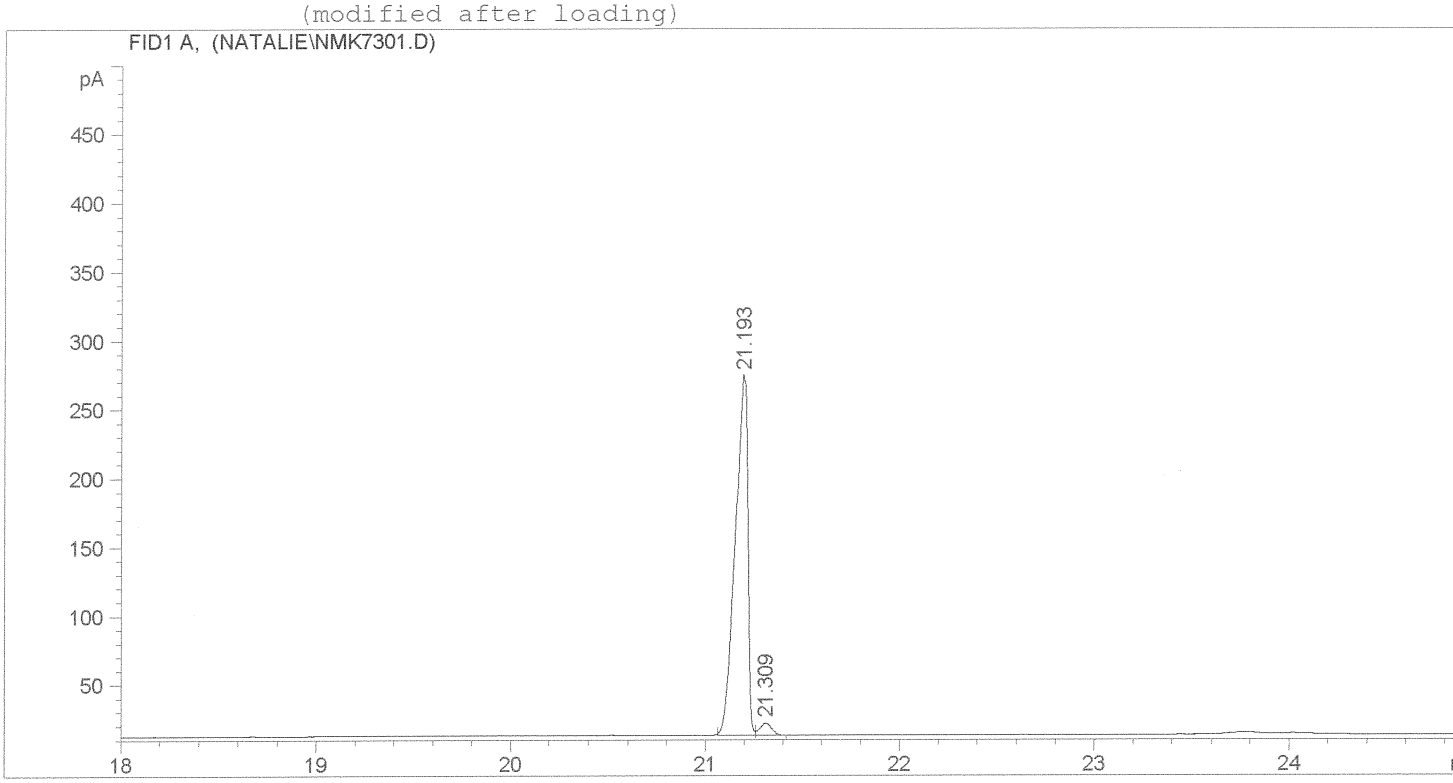


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                          Area Percent Report

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  21.193 BV    0.0671 1166.31836  261.27350 96.97012
   2  21.309 VB    0.0615   36.44219    8.58648  3.02988

Totals :                  1202.76055  269.85998

 Results obtained with enhanced integrator!

                          *** End of Report ***
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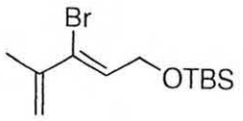
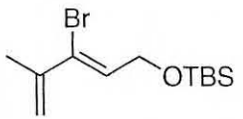
Figure S11. **(3*S*,4*R*)-14** (Table 2, Entry 2).



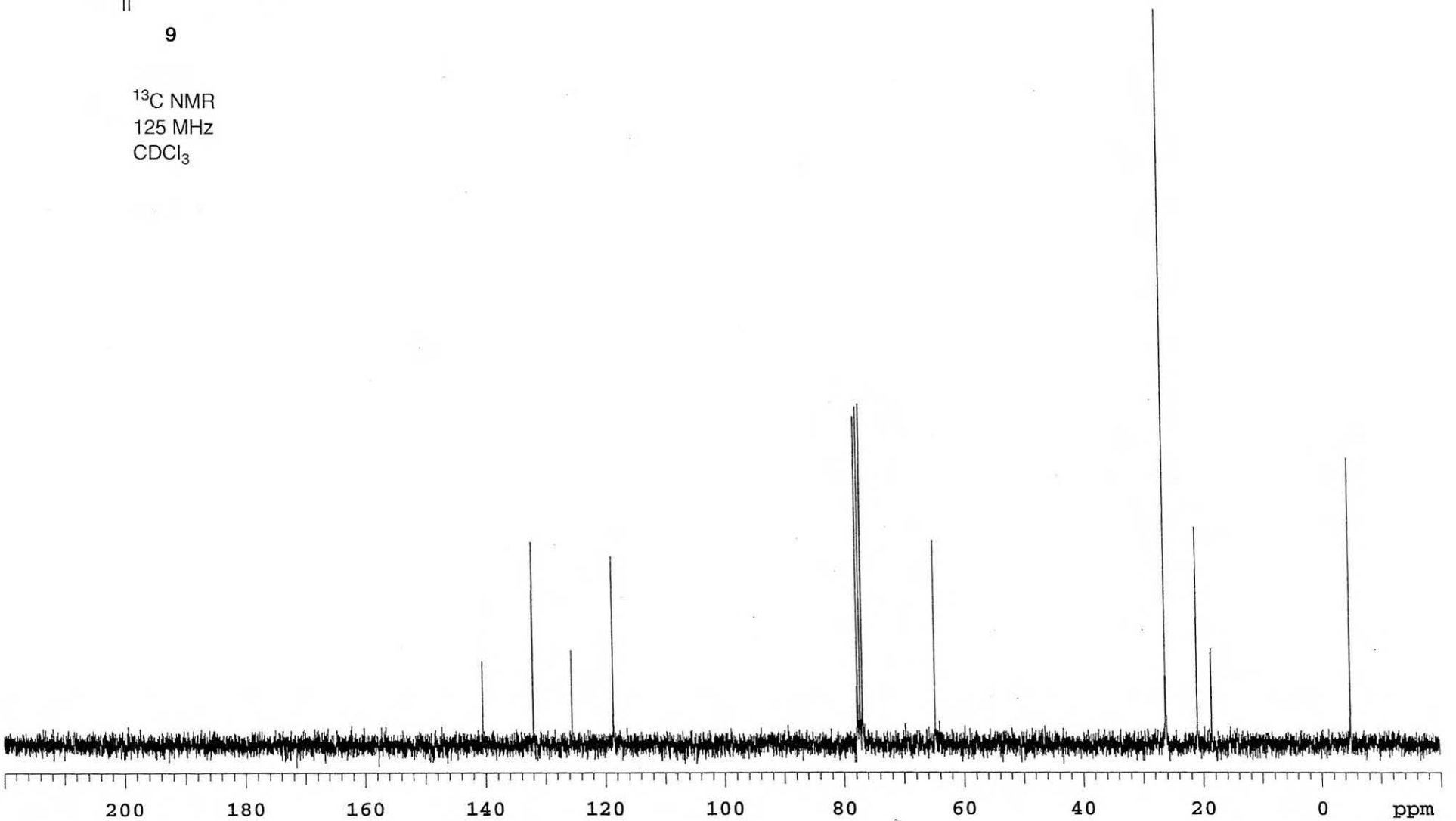
9

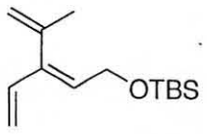
^{1}H NMR
500 MHz
$CDCl_3$



9

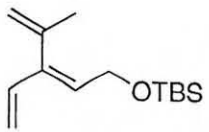
^{13}C NMR
125 MHz
$CDCl_3$





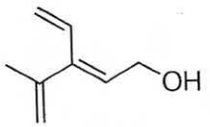
10*Z*

^{1}H NMR
300 MHz
$CDCl_3$



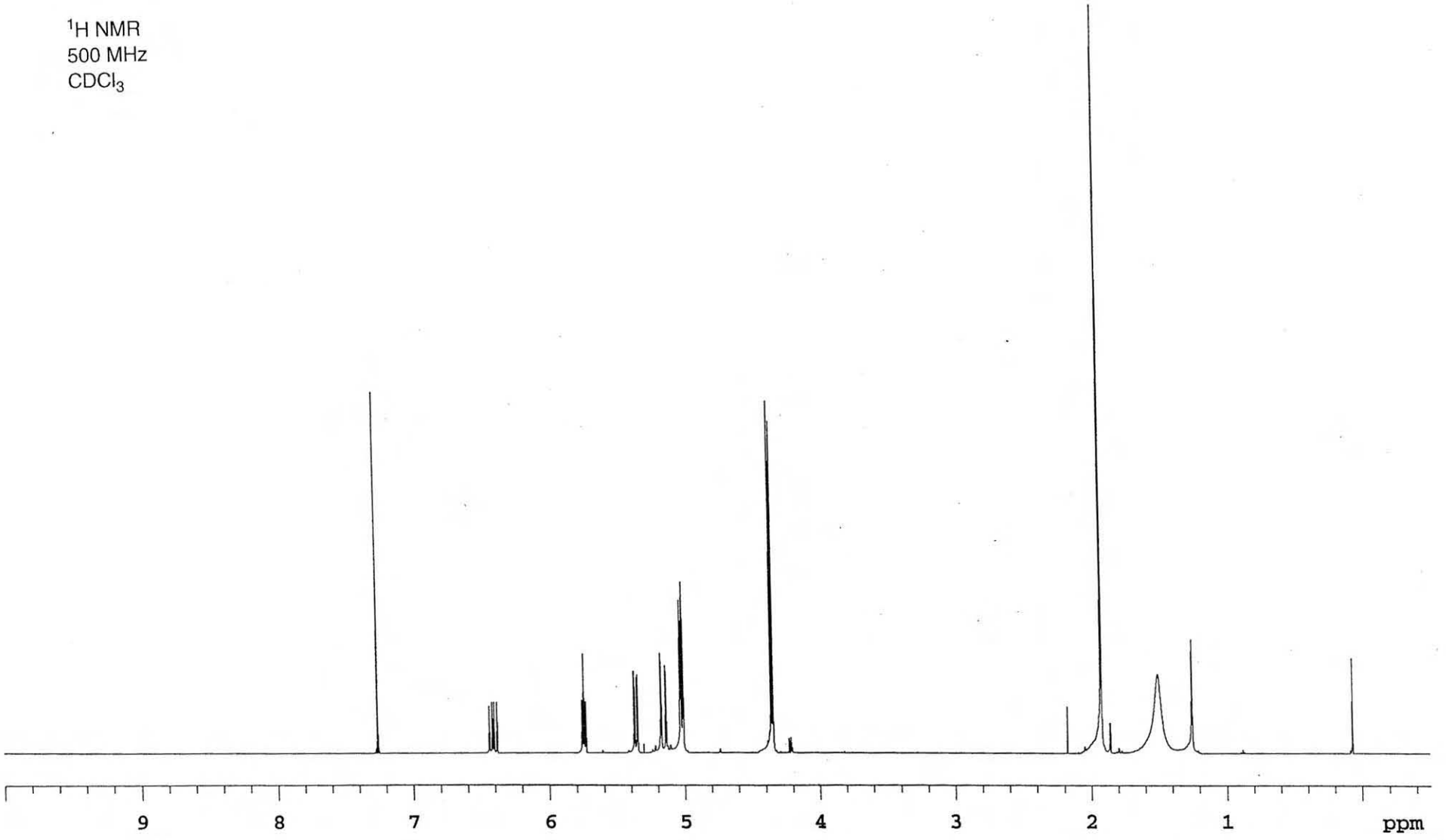
10*Z*

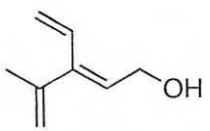
^{13}C NMR
75 MHz
$CDCl_3$



6

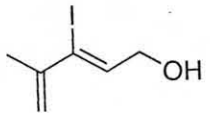
^{1}H NMR
500 MHz
$CDCl_3$





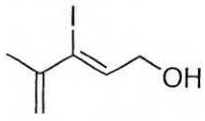
6

^{13}C NMR
125 MHz
$CDCl_3$



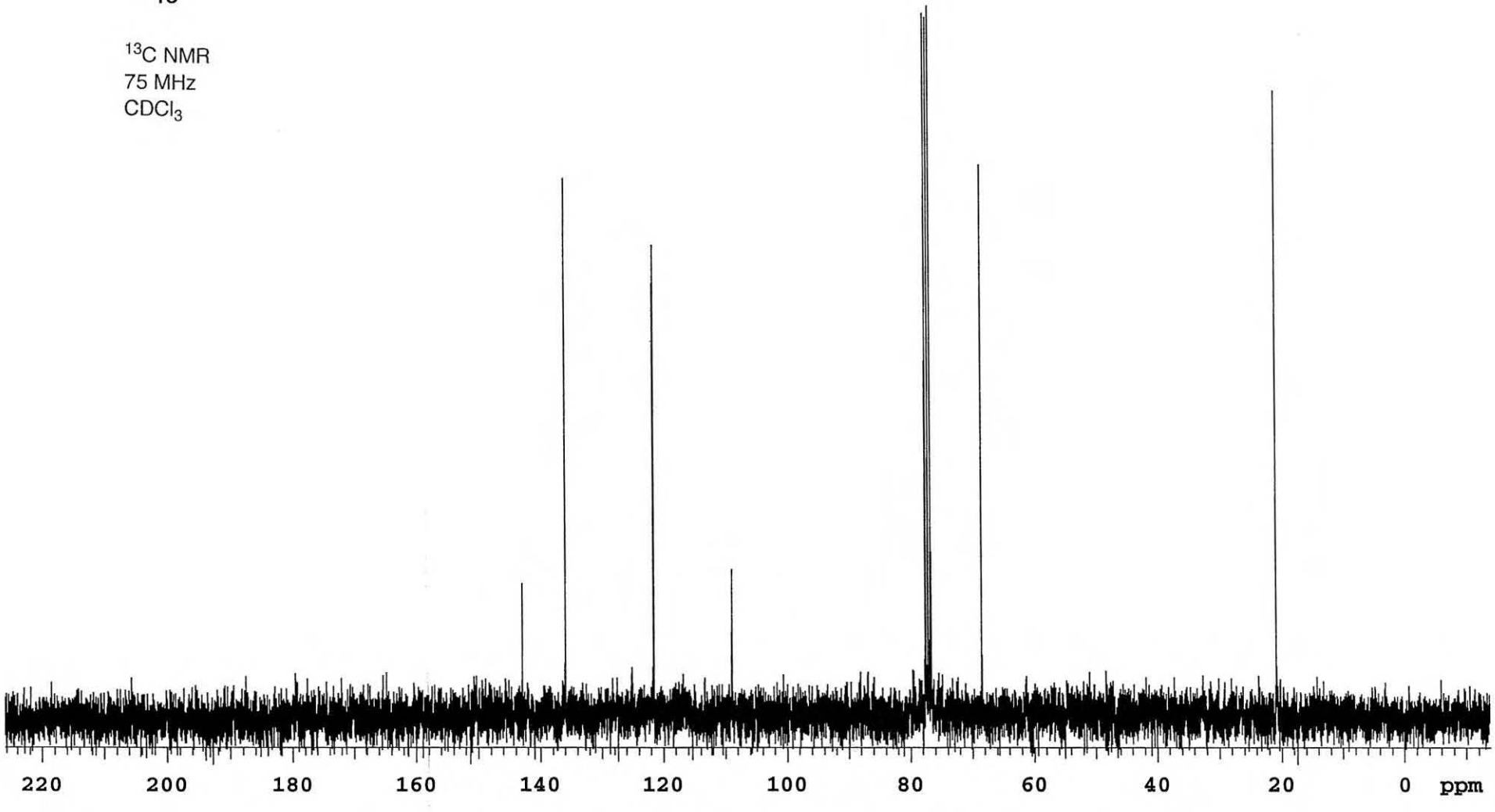
13

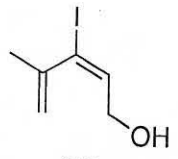
^{1}H NMR
300 MHz
$CDCl_3$



13

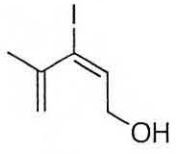
^{13}C NMR
75 MHz
$CDCl_3$





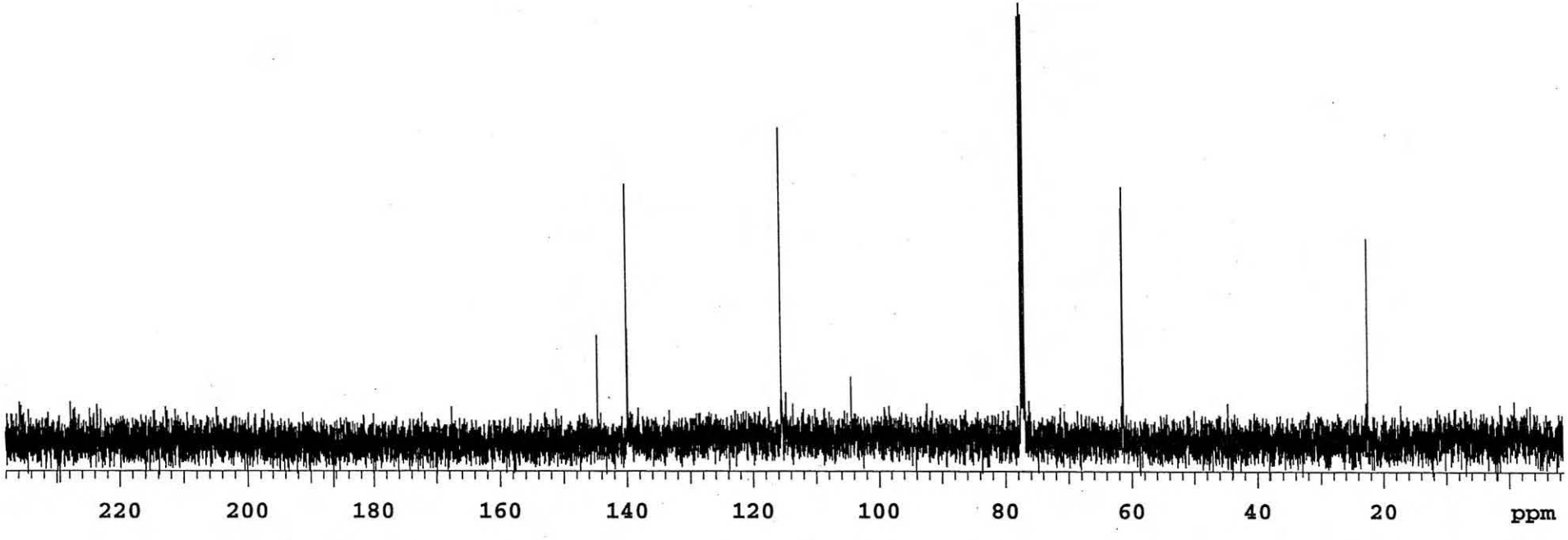
S3

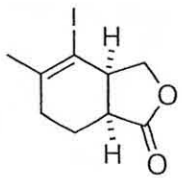
^{1}H NMR
300 MHz
$CDCl_3$



S3

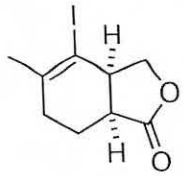
^{13}C NMR
75 MHz
$CDCl_3$





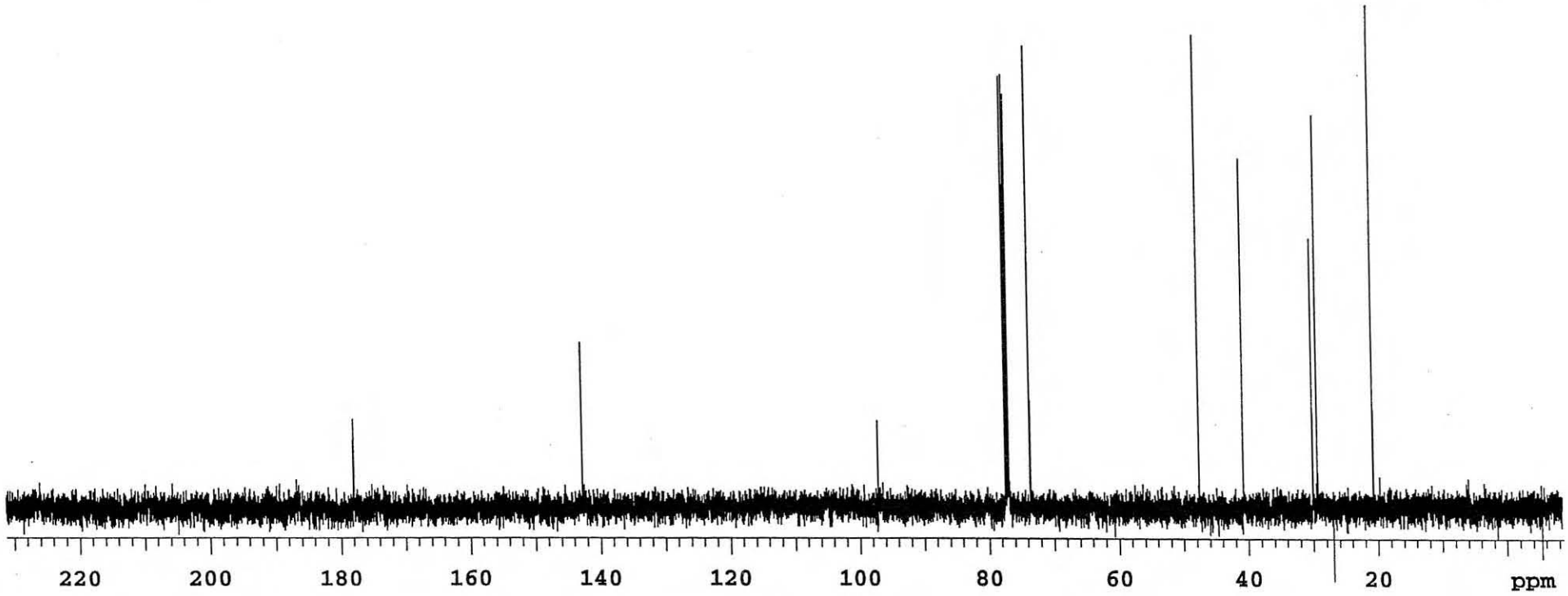
14

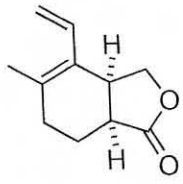
^{1}H NMR
500 MHz
$CDCl_3$



14

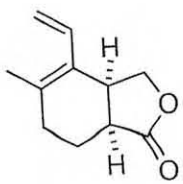
^{13}C NMR
125 MHz
$CDCl_3$





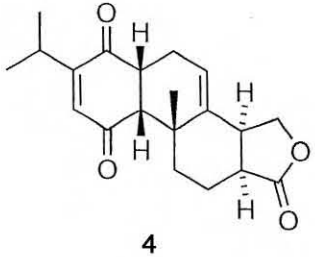
12

^{1}H NMR
500 MHz
$CDCl_3$



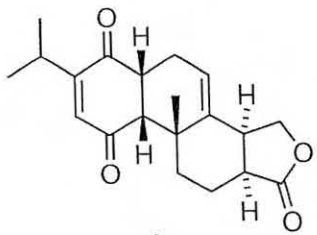
12

^{13}C NMR
125 MHz
$CDCl_3$



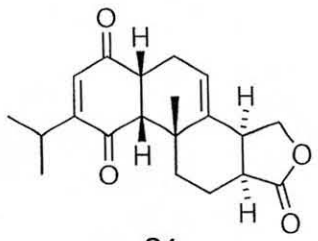
4

^{1}H NMR
500 MHz
$CDCl_3$



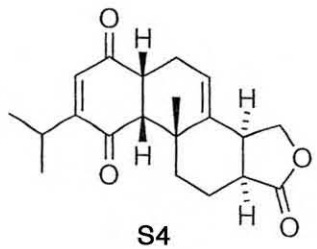
4

^{13}C NMR
125 MHz
$CDCl_3$



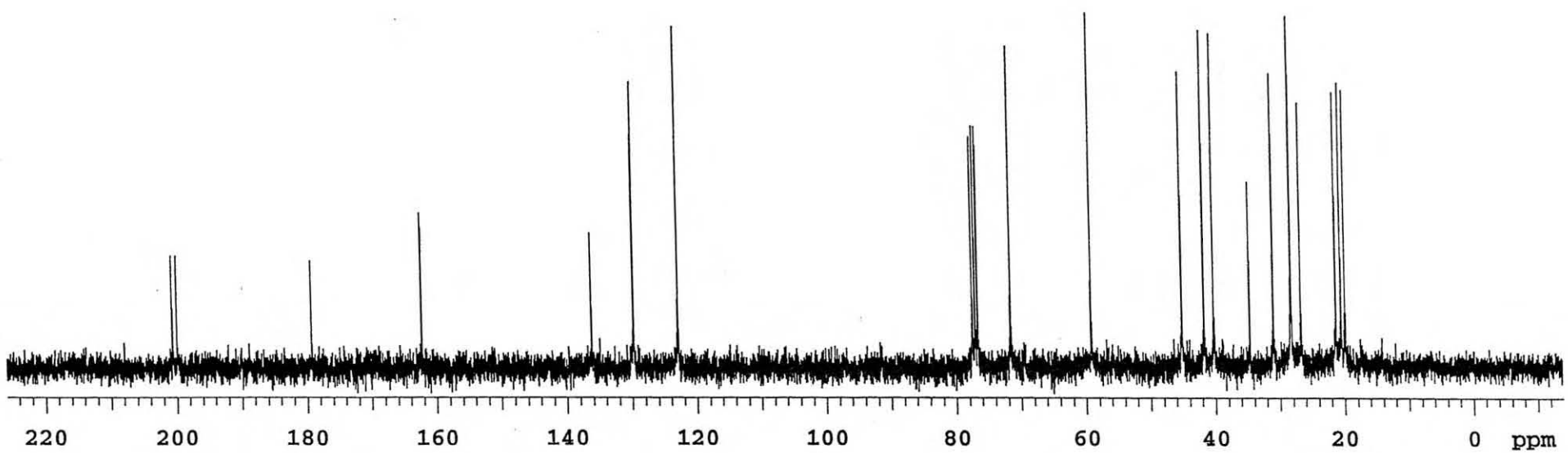
S4

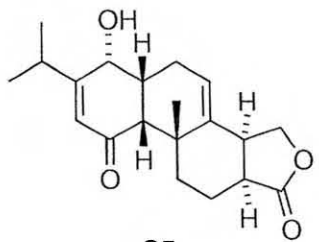
^{1}H NMR
300 MHz
$CDCl_3$



S4

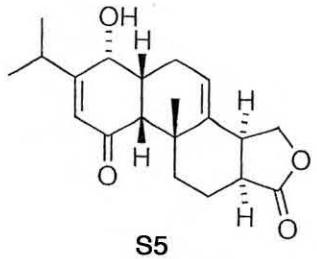
^{13}C NMR
75 MHz
$CDCl_3$





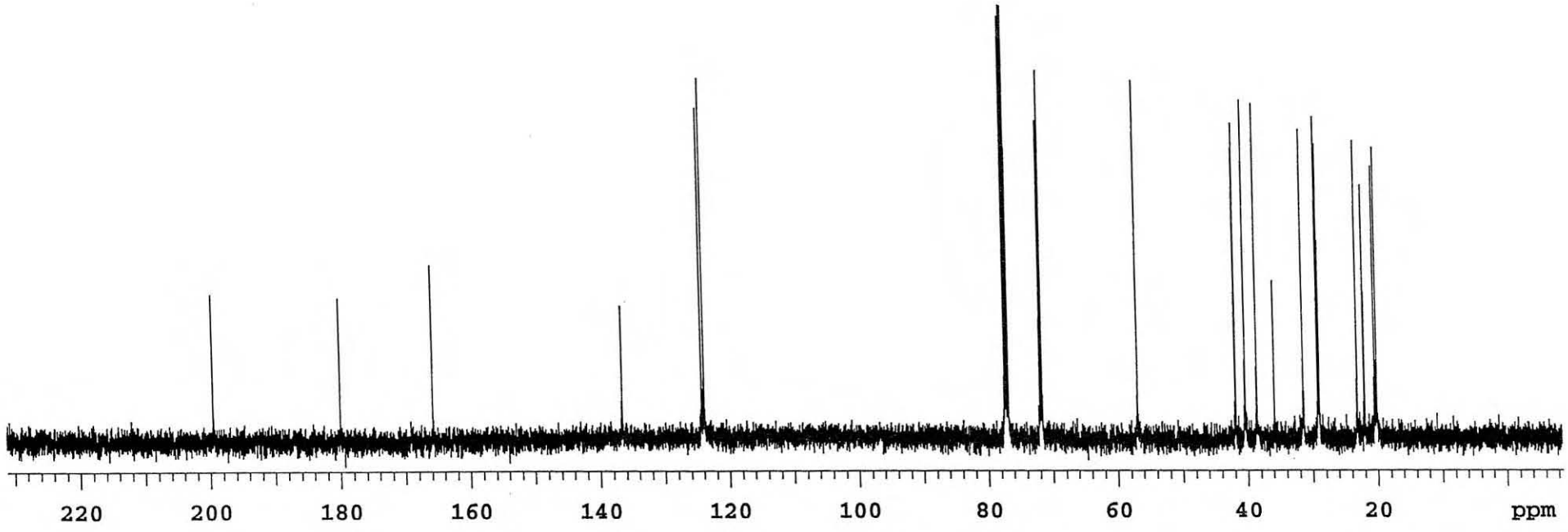
S5

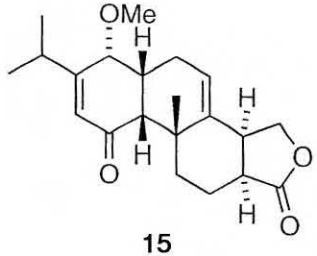
^{1}H NMR
500 MHz
$CDCl_3$



S5

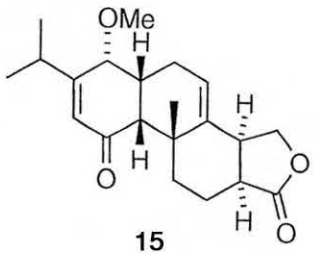
^{13}C NMR
125 MHz
$CDCl_3$





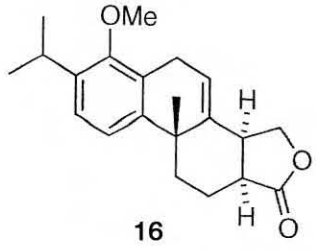
15

^{1}H NMR
500 MHz
$CDCl_3$



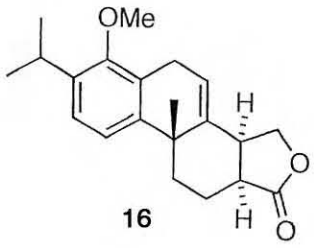
15

^{13}C NMR
125 MHz
$CDCl_3$



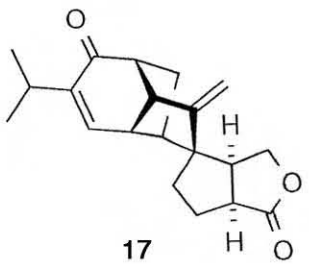
16

^{1}H NMR
500 MHz
$CDCl_3$



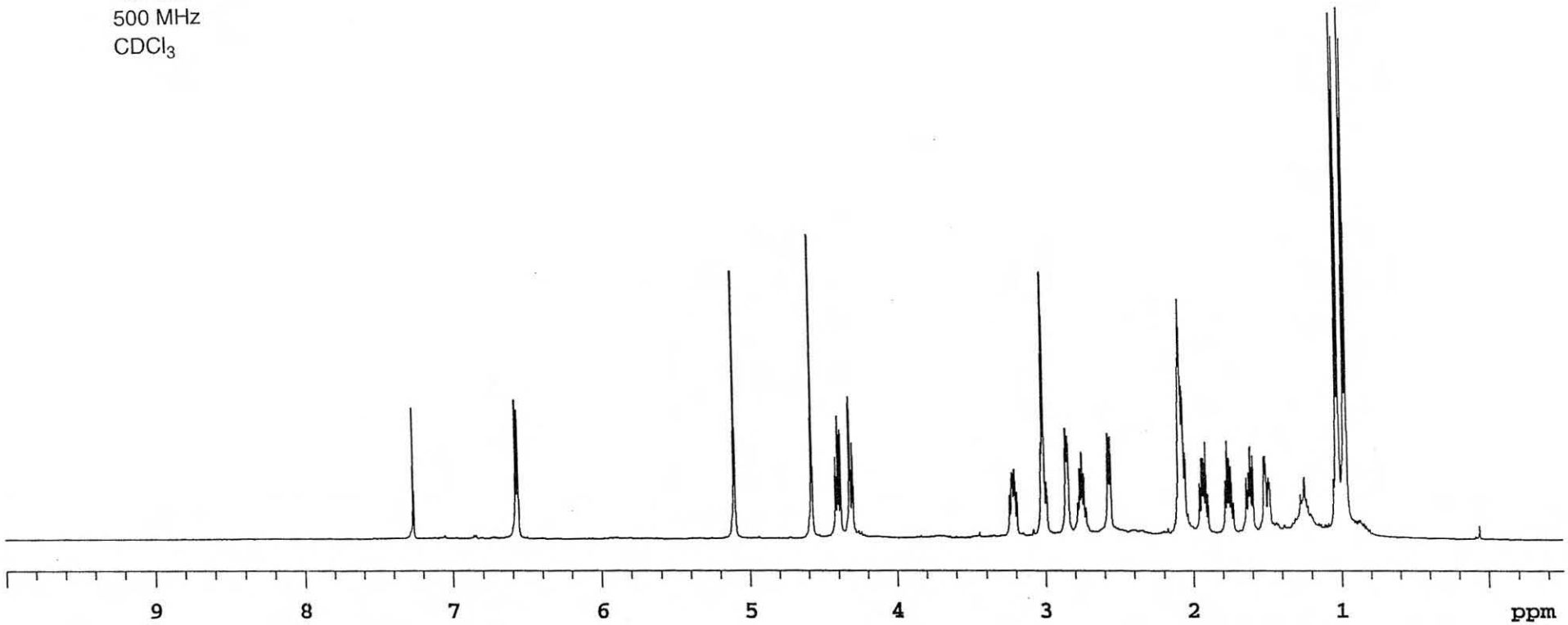
16

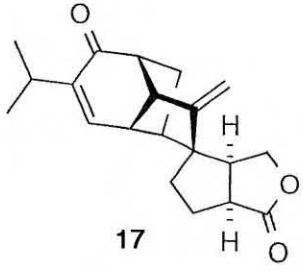
^{13}C NMR
125 MHz
$CDCl_3$



17

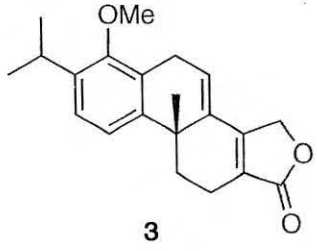
^{1}H NMR
500 MHz
$CDCl_3$





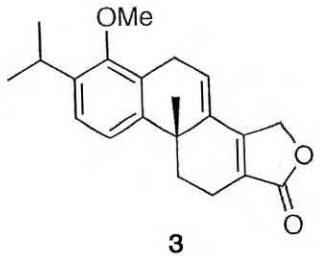
17

^{13}C NMR
125 MHz
$CDCl_3$



3

^{1}H NMR
500 MHz
$CDCl_3$



3

^{13}C NMR
125 MHz
$CDCl_3$