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Supporting Information

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Chiral Dendralenes for Rapid Access to Enantiomerically Pure Polycycles

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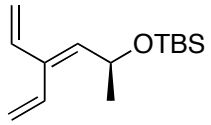
General Methods

NMR spectra were recorded at 298K using a 500 MHz, 400 MHz or a 300 MHz spectrometer. Residual acetone (δ 2.04 ppm), acetonitrile (δ 1.96 ppm), benzene (δ 7.15 ppm), chloroform (δ 7.26 ppm), and methanol (δ 3.31 ppm) were used as internal references for ^{1}H NMR spectra measured in these solvents. Residual acetone (δ 29.8 ppm, 206.8 ppm), acetonitrile (δ 1.3 ppm, 118.3 ppm), benzene (δ 128.1 ppm), chloroform (δ 77.1 ppm), and methanol (δ 49.0 ppm) were used as internal references for ^{13}C NMR spectra. 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 a ion trap mass spectrometer using electron impact (EI) ionization mode at 40 or 70 eV. Low resolution electrospray ionization spectra were recorded on a 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.

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.

(2*S*)-2-(*tert*-butyldimethylsilyl)oxy-4-vinylhexa-3,5-diene (4) by indium mediated coupling



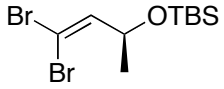
4

To a stirred solution of aldehyde **1**[1,2] (500 mg, 2.7 mmol, 1.0 equiv) and (*E*)-1-bromobuta-1,3-diene **2** (463 mg, 3.2, mmol, 1.2 equiv) in dry DMF (1.5 mL) was added indium metal (336 mg, 2.9 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 16 h. The reaction was quenched with sat. NH_4Cl solution (5 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organics were washed with brine (20 mL), dried and concentrated in vacuo. Column chromatography (hexanes/ethyl acetate 96:4) gave **3** (366 mg, 1.42 mmol, 54%) as a 1:1 mixture of diastereomers.

To a stirred solution of **3** (143 mg, 0.56 mmol, 1.0 equiv) in tetrahydrofuran (3 mL) was added triphenylphosphine (293 mg, 1.12 mmol, 2.0 equiv) and DEAD (176 μL, 1.12 mmol, 2.0 equiv). The mixture was heated at 60 ºC for 3.25 h before being concentrated in vacuo. Column chromatography (hexanes/ethyl acetate 99:1) gave **4** (61 mg, 0.26 mmol, 46%) as a colorless oil. R_f = 0.25 (hexanes). [α] = –24.3 (*c* = 0.77, dichloromethane). ^{1}H NMR (400 MHz, C_6D_6): δ 6.36 (1H, dd, *J* = 17.6, 11.3 Hz), 6.30 (1H, dd, *J* = 17.1, 10.8 Hz), 5.67 (1H, d, *J* = 8.8 Hz), 5.29 (1H, dd, *J* = 17.6, 2.0 Hz), 5.17 (1H, dd, *J* = 17.2, 2.0 Hz,), 5.13 (1H, dd, *J* = 10.3, 2.0 Hz), 4.97 (1H, dd, *J* = 10.3, 1.5 Hz), 4.73 (1H, dq, *J* = 8.8, 6.4 Hz), 1.22 (3H, d, *J* = 6.4 Hz), 0.96 (9H, s), 0.06 (3H, s), 0.05 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 136.8, 135.1, 131.9, 118.4, 115.1, 65.7, 26.0, 24.7, 18.3, –4.3, –4.6 ppm. IR (thin film): ν 2956, 2928, 2894, 2857cm^{-1}. EIMS (70 eV) *m/z* (%): 181 (40), 75 (100). HRMS: calcd for $C_{10}H_{17}OSi$ $[M–C_4H_9]^+$: 181.1049; found 181.1048

1,1-Dibromo[(3*S*)-(*tert*-butyldimethylsilyl)oxy]-1-butene (5)

This compound was prepared according to the procedure outlined by Trost.[2] To a stirred solution of triphenyl phospine (56.9 g, 217 mmol, 4.0 equiv) in dichloromethane (200 mL) at 0 °C under argon, was added a solution



5

of carbon tetrabromide (35.98 g, 108 mmol, 2 equiv) in dichloromethane (80 mL) over 45 min, via cannula. The reaction mixture was stirred at RT for 30 min before being cooled to 0 °C. A solution of aldehyde **1**[1,2] (10.22 g, 54 mmol, 1.0 equiv) in dichloromethane (40 mL) was added dropwise. The reaction mixture was warmed to RT and stirring continued for a further 30 min. To the reaction mixture was added hexanes and the resulting precipitate was filtered. The filtrate was then concentrated under reduced pressure. After column chromatography (hexanes) **5** (14.15 g, 41 mmol, 76%) was obtained as a colorless oil. ^{1}H NMR data was consistent with that reported in the literature.[2]

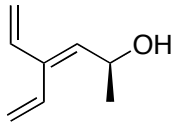
(2*S*)-2-(*tert*-butyldimethylsilyl)oxy-4-vinylhexa-3,5-diene (4) by Stille coupling

To a stirred solution of dibromoalkene **5** (1.0 g, 2.9 mmol, 1.0 equiv) and tributyl vinyl stannane (2.54 g, 7.3 mmol, 2.5 equiv) in acetonitrile (10 mL) under argon was added palladium(II) acetate (33 mg, 5 mol%) and triphenyl phosphine (76 mg, 10 mol%). The mixture was stirred at 60 ºC for 20 h before the addition of a further amount of palladium(II) acetate (15 mg, 2.5 mol%) and triphenyl phosphine (40 mg, 5 mol%). The reaction mixture was stirred at 60 ºC for a further 5 h. The mixture was diluted with diethyl ether (100 mL) and partitioned against aqueous ammonia solution (30% v/v, 2 × 80 mL). The organic layer was washed with brine (100 mL), dried and concentrated in vacuo. After column chromatography on silica (hexanes) **4** (419 mg, 1.76 mmol, 61%) was obtained as a colorless oil.

(2*S*)-2-(*tert*-butyldimethylsilyl)oxy-4-vinylhexa-3,5-diene (4) by Negishi coupling

To a stirred solution of vinyl magnesium bromide (1.0 M soln in THF, 14.5 mL, 14.5 mmol, 3.33 equiv) in THF (5 mL) at 0 °C was added zinc bromide (3.4 g, 15 mmol, 3.47 equiv). After 5 min a solution of **5** (1.5 g, 4.4 mmol, 1.0 equiv) and tetrakis(triphnylphosphine)palladium(0) (161 mg, mmol, 0.032 equiv) in THF (8 mL) was added dropwise via canula. Stirring was continued for 2 h before the mixture was diluted with hexane and filtered. The filtrate was concentrated in vacuo. After column chromatography (hexanes) **4** (693 mg, 2.9 mmol, 67%) was obtained as a colorless oil.

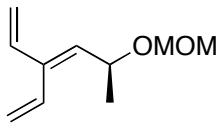
(2*S*)-4-vinylhexa-3,5-dien-2-ol (6)



6

To a stirred solution of **4** (863 mg, 3.62 mmol, 1.0 equiv) in THF at 0 ºC under argon, was added TBAF (1M solution in THF, 7.25 mL, 7.25 mmol, 2.0 equiv). Stirring was continued at this temperature for 10 min before being warmed to RT. After 2.5 h the reaction mixture was diluted in diethyl ether (50 mL) and partitioned against saturated NH_4Cl (25 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried and concentrated in vacuo. After column chromatography on silica (hexanes/ethyl acetate 85:15) the title compound **6** (389 mg, 3.13 mmol, 86%) was obtained as a colorless oil. R_f = 0.30 (hexanes/ethyl acetate 70:30). [α] = –31.2 (*c* = 1.65, dichloromethane) ^{1}H NMR (400 MHz, C_6D_6): δ 6.34 (1H, dd, *J* = 17.7, 11.4 Hz), 6.31 (1H, dd, *J* = 10.9, 17.2 Hz), 5.54 (1H, d, *J* = 8.8 Hz), 5.30 (1H, dd, *J* = 17.1, 1.5 Hz), 5.20 (1H, dd, *J* = 17.6, 1.5 Hz), 5.11 (1H, dd, *J* = 10.8, 1.5 Hz), 4.99 (1H, dd, *J* = 10.8, 1.5 Hz), 4.55 (1H, dq, *J* = 8.8, 6.4 Hz), 1.76 (1H, s), 1.14 (3H, d, *J* = 6.4 Hz) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ 138.0, 137.3, 136.2, 132.1, 118.6, 115.5, 64.4, 23.7 ppm. IR (thin film): ν 3329 (OH), 3088, 2972, 1603, 1452, 1424, 1368, 1293 cm^{-1}. EIMS (70 eV) *m/z* (%): 124 (10), 109 (20), 43 (100). HRMS: calcd for $C_8H_{12}O$ $[M]^+$: 124.0888; found 124.0892.

(*S*)-5-(methoxymethoxy)-3-vinylhexa-1,3-diene (7)

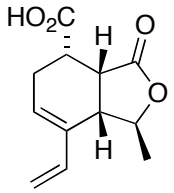


7

To a stirred solution of **6** (25 mg, 0.20 mmol, 1.0 equiv) in dichloromethane (2 mL) was added *i*Pr_2NEt (346 μL, 1.98 mmol, 10.0 equiv) and MOM-Cl (79 μL, 0.99 mmol, 5.0 equiv). Stirring was continued for 18 h before the reaction was quenched with sat. $NaHCO_3$ (5 mL). Ethyl acetate (10 mL) was added and the organic layer was washed with 2 M HCl (5 mL), $NaHCO_3$ (5 mL) and brine (5 mL) before being dried and concentrated in vacuo. Column chromatography of the crude material (hexane/ethyl acetate 96:4) yielded **7** (20 mg, 0.11 mmol, 55%) as a colorless oil. $[\alpha]_D^{25}$ = –166.8 (*c* = 0.61, chloroform). ^{1}H NMR (300

MHz, $CDCl_3$): δ 6.49 (1H, dd, *J* = 17.8, 11.6 Hz), 6.39 (1H, ddd, *J* = 17.3, 10.7, 0.9 Hz), 5.48 (1H, d, *J* = 9.7 Hz), 5.36 (1H, m), 5.33–5.24 (2H, m), 5.12 (1H, dd, *J* = 10.8, 1.9 Hz), 4.67 (1H, dq, *J* = 9.2, 6.4 Hz), 4.63 (1H, d, *J* = 6.5 Hz), 4.53 (1H, d, *J* = 6.5 Hz), 3.36 (3H, s), 1.29 (3H, d, *J* = 6.5 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 137.3, 132.6, 131.6, 118.9, 115.9, 93.8, 67.8, 55.3, 21.5 ppm. IR (thin film): ν = 2919, 2850, 1996 cm^{-1}. EIMS (70 eV) *m/z* (%): 167.0 (28), 149 (100), 57 (92); HRMS: calcd for $C_{10}H_{16}O_2$ $[M]^+$: 168.1150; found: 168.1143.

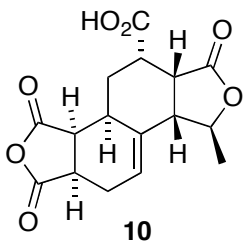
(1*S*,3a*R*,4*S*,7a*S*)-1-methyl-3-oxo-7-vinyl-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylic acid (9)



9

To a solution of [3]dendralene **6** (44.8 mg, 0.36 mmol, 1.0 equiv) in [D_6]benzene (1.2 mL) was added maleic anhydride (35.4 mg, 0.36 mmol, 1.0 equiv). The mixture was left at RT for 48 h. The product was filtered to give **9** (66.5 mg, 0.30 mmol, 83%) as a white solid. mp = 163–165 °C. [α] = +150 (*c* = 0.88, methanol). ^{1}H NMR (400 MHz, [D_6]acetone): δ 6.35 (1H, dd, *J* = 18.1, 11.3 Hz), 5.97 (1H, dd, *J* = 6.4, 2.5 Hz), 5.08 (1H, d, *J* = 11.3 Hz), 5.02 (1H, d, *J* = 18.1 Hz), 4.50 (1H, q, *J* = 6.4 Hz), 3.87 (1H, ddd, *J* = 8.3, 3.9, 1.0 Hz), 3.29 (1H, dm, *J* = 8.3 Hz), 2.72 (1H, ddd, *J* = 11.7, 5.4, 3.9 Hz), 2.49–2.30 (2H, m), 1.49 (3H, d, *J* = 6.9 Hz) ppm. ^{13}C NMR (100 MHz, [D_6]acetone): δ 176.3, 173.4, 138.4, 136.4, 131.4, 115.2, 80.5, 42.4, 39.7, 37.3, 24.3, 20.5 ppm. IR (KBr disc): ν 2993, 1770, 1700, 1644, 1452, 1419 cm^{-1}. ESIMS (positive ion) *m/z* (%): 467 (100), 246 (87), 224 (55). HRMS: calcd for $C_{12}H_{14}O_4$ $[M]^+$: 222.0892; found 222.0891.

Tetracycle 10

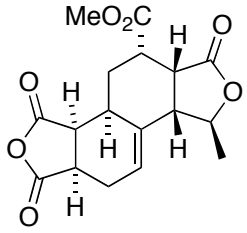


10

To a solution of **6** (27 mg, 0.22 mmol, 1.0 equiv) in deuterated acetonitrile (1 mL) was added maleic anhydride (43 mg, 0.44

mmol, 2.0 equiv). The mixture was left at RT for 60 h before being concentrated in vacuo to give **10** (70 mg, 0.22 mmol, 100%) as a colorless solid of approximately 90% purity. $[\alpha]_D^{25}$ = –4.34 (*c* = 1.66, chloroform). ^{1}H NMR (500 MHz, CD_3CN): δ 5.88 (1H, m), 4.49 (1H, dq, *J* = 6.4, 6.2 Hz), 3.55–3.48 (2H, m), 3.26 (1H, m), 3.15 (1H, dd, *J* = 12.2, 6.4 Hz), 2.98 (1H, m), 2.66 (1H, dd, *J* = 15.1, 7.0 Hz), 2.49 (1H, m), 2.38 (1H, ddd, *J* = 14.1, 11.2, 3.4 Hz), 2.29–2.15 (2H, m), 1.49 (3H, d, *J* = 6.4 Hz) ppm. ^{13}C NMR (125 MHz, CD_3CN): δ 178.1, 175.8, 174.7, 174.1, 132.7, 123.0, 83.2, 45.4, 43.1, 41.9, 41.8, 39.9, 32.8, 26.3, 25.36, 22.5 ppm. IR (thin film): ν = 2926, 2855, 1846, 1773, 1712, 1630 cm^{-1}. EIMS (70 eV) *m/z* (%): 320 (10), 230 (100); HRMS: calcd for $C_{16}H_{16}O_7$ $[M]^+$: 320.0896; found: 320.0895.

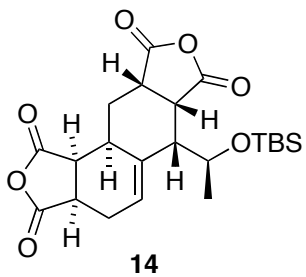
Tetracycle 11



11

To a solution of **16** (17.7 mg, 0.07 mmol, 1.0 equiv) in [D_6]benzene (1 mL) was added maleic anhydride (7.4 mg, 0.07mmol, 1.0 equiv). The mixture was heated at reflux for 3.5 h before additional maleic anhydride (3.7 mg, 0.04 mmol 0.5 equiv) was added. The mixture was heated at reflux for a further 14 h. The mixture was cooled to room temperature and the product was filtered to give **11** (16.9 mg, 0.05 mmol, 67%) as a white solid. The product was recrystallized from heptane/dichloromethane to give colorless crystals. mp 176–179 °C. [α] = –11.72 (*c* = 0.51, methanol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86–5.81 (1H, m), 4.55 (1H, q, *J* = 6.4 Hz), 3.69 (3H, s), 3.48–3.44 (2H, m), 3.11 (1H, dd, *J* = 12.2, 6.4 Hz), 2.99–2.90 (1H, m), 2.80 (1H, ddd, *J* = 15.7, 7.3, 1.5 Hz), 2.50 (1H, ddd, *J* = 13.2, 10.8, 3.4), 2.41–2.32 (1H, m), 2.32–2.16 (2H, m), 1.54 (3H, d, *J* = 6.4 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 173.5, 173.1, 172.0, 139.6, 122.4, 82.5, 52.4, 44.6, 42.6, 41.1, 40.8, 39.3, 32.4, 25.9, 24.9, 22.6 ppm. IR (KBr disc): ν 2988, 2360, 2339, 1772, 1717 cm^{-1}. EIMS (70 eV) *m/z* (%): 334 (20), 302 (40), 230 (95), 157 (70), 129 (100). HRMS: calcd for $C_{17}H_{18}O_7$ $[M]^+$: 334.1052; found 334.1055.

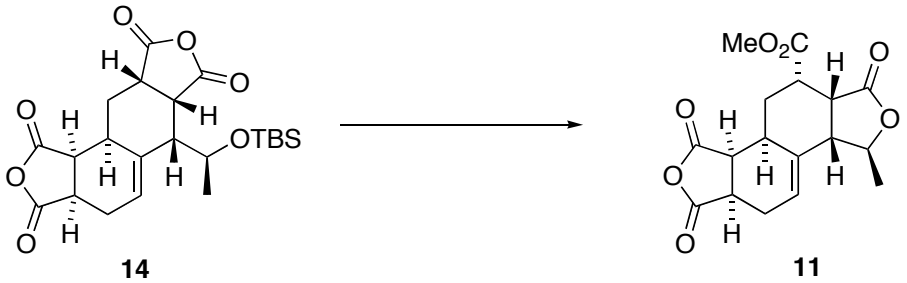
Tetracycle 14



14

To a solution of **4** (44 mg, 0.18 mmol, 1.0 equiv) in deuterated benzene (1 mL) at RT was added maleic anhydride (39 mg, 0.37 mmol, 1.0 equiv). After 115 h the reaction mixture was concentrated in vacuo to give **14** (78 mg, 0.18 mmol, 97%) as a colorless solid. mp 80–83 °C. $[\alpha]_D^{25}$ = +21.9 (*c* = 0.77, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.72 (1H, m), 4.36 (1H, dq, *J* = 9.9, 5.5 Hz), 4.01 (1H, dd, *J* = 10.6, 4.8 Hz), 3.58 (1H, ddd, *J* = 11.0, 6.4, 2.2 Hz), 3.43 (1H, ddd, *J* = 9.5, 7.4, 1.7 Hz), 3.38 (1H, dd, *J* = 9.6, 5.4 Hz), 2.84 (1H, dd, *J* = 15.7, 7.7 Hz), 2.73 (1H, ddd, *J* = 13.8, 13.8, 6.1 Hz), 2.43 (1H, m), 2.33 (1H, ddd, *J* = 14.4, 4.6, 1.9 Hz), 2.18 (2H, m), 1.23 (3H, d, *J* = 5.8 Hz), 0.88 (9 H, s), 0.15 (3H, s), 0.11 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 173.3, 171.3, 171.0, 138.2, 123.4, 65.4, 46.5, 44.0, 40.4, 40.0, 34.1, 26.0, 25.0, 23.8, 23.5, 18.1, –4.0, –4.9 ppm. IR (thin film): ν = 2930, 1850, 1777 cm^{-1}. EIMS (70 eV) *m/z* (%): 419 (10), 377 (100), 75 (80); HRMS: calcd for $C_{18}H_{21}O_7Si$ [M–C_4H_7]: 377.1057; found: 377.1056. Anal. Calcd for $C_{22}H_{30}O_7Si$: C, 60.81; H, 6.96. Found: C, 60.98; H, 7.09.

Conversion of Tetracycle 14 to Tetracycle 11

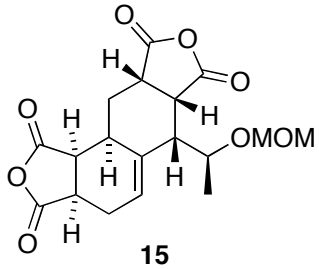


14 **11**

To a stirred solution of **14** (47 mg, 0.11 mmol, 1.0 equiv) in dichloromethane (2 mL) was added trifluoroacetic acid (250 μL, 3.2 mmol, 30 equiv). Stirring was continued for 16 h before the reaction mixture was concentrated in vacuo. The crude residue was dissolved in tetrahydrofuran (5 mL) and cooled to –78 °C with stirring. An ethereal solution of

diazomethane was added dropwise until tlc confirmed the reaction had gone to completion. Excess diazomethane was removed by bubbling N_2 gas through the solution. The solution was concentrated in vacuo. Recrystallization from heptane/dichloromethane gave **11** (29.7 mg, 0.09 mmol, 81%) as colorless crystals.

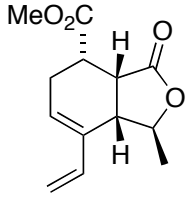
Tetracycle 15



15

To a stirred solution of **7** (12 mg, 0.07 mmol, 1.0 equiv) in deuterated benzene (1 mL) was added maleic anhydride (14 mg, 0.14 mmol, 2.0 equiv). The reaction mixture was allowed to stand at RT for 48 h before being concentrated in vacuo. Recrystallization from benzene/dichloromethane yielded **15** (26 mg, 0.07 mmol, 100%) as colorless crystals. mp 194–195 °C. $[\alpha]_D^{25}$ = –48.1 (*c* = 0.185, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.74 (1H, m), 4.87 (1H, d, *J* = 6.7 Hz), 4.74 (1 H, d, *J* = 6.7 Hz), 4.13 (1H, dq, *J* = 6.0, 4.2 Hz), 4.05 (1H, dd, *J* = 10.8, 5.0 Hz), 3.58 (1H, ddd, *J* = 10.7, 6.3, 2.3 Hz), 3.45 (1H, ddd, *J* = 9.4, 7.4, 1.5 Hz), 3.40 (3H, s), 3.38 (1H, dd, *J* = 9.7, 5.3 Hz), 2.86 (1H, dd, *J* = 15.9, 7.7 Hz), 2.72 (1H, dt, *J* = 13.9, 6.5 Hz), 2.53 (1H, m), 2.35 (1H, ddd, *J* = 14.4, 4.6, 2.6 Hz), 2.24–2.14 (2H, m), 1.30 (3H, d, *J* = 6.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 173.2, 171.4, 171.3, 137.9, 123.6, 96.9, 71.2, 56.0, 45.1, 44.1, 40.4, 40.2, 39.9, 34.0, 25.0, 23.7, 20.9 ppm. IR (thin film): ν = 2956, 1845, 1774 cm^{-1}. EIMS (70 eV) *m/z* (%): 364 (1), 333 (10), 319 (15), 302 (20), 45 (100); HRMS: calcd for $C_{18}H_{20}O_8$ $[M]^+$: 364.1158; found: 364.1154.

Methyl (1*S*,3a*R*,4*S*,7a*S*)-1-methyl-3-oxo-7-vinyl-1,3,3a,4,5,7a-hexahydro-2-benzofuran-4-carboxylate (16)

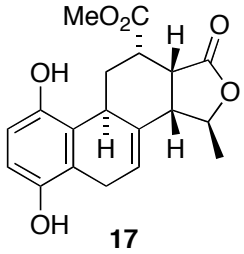


16

To a stirred solution of **9** (28.6 mg, 0.13 mmol, 1.0 equiv) in THF (3 mL) at –78 °C was added a solution of diazomethane. After 15 min the reaction mixture was concentrated in vacuo. Purification by column

chromatography on silica (hexanes/ethyl acetate 85:15) gave **16** (21.3 mg, 0.09 mmol, 70%) as a colorless solid. mp 74–75 °C. [α] = +120.0 (*c* = 0.20, dichloromethane) ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (1H, dd, *J* = 17.9, 11.0 Hz), 5.94 (1H, dd, *J* = 5.9, 2.9 Hz), 5.06 (1H, d, *J* = 11.0 Hz), 4.91 (1H, d, *J* = 17.9 Hz), 4.56 (1H, q, *J* = 6.6 Hz), 3.79 (3H, s), 3.17 (1H, d, *J* = 8.4 Hz), 2.66 (1H, ddd, *J* = 11.0, 5.9, 4.0 Hz), 2.49–2.37 (2H, m), 1.49 (3H, d, *J* = 6.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 172.6, 137.4, 134.9, 130.7, 112.0, 80.1, 52.2, 41.6, 39.2, 37.1, 23.4, 20.6 ppm. IR (KBr disc): ν 2359, 1772, 1726, 1644, 1432 cm^{-1}. EIMS (70 eV) *m/z* (%): 236 (45), 176 (70), 131 (50), 117 (80), 105 (100), 91 (35), 77 (40). HRMS: calcd for $C_{13}H_{16}O_4$ $[M]^+$: 236.1049; found 236.1048.

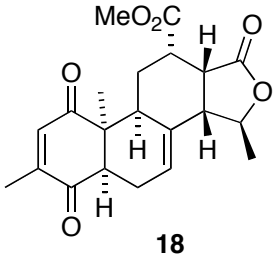
Tetracycle 17



17

To a solution of **16** (51 mg, 0.22 mmol, 1.0 equiv) in $[D_6]$benzene (1.00 mL) was added benzoquinone (23 mg, 0.22 mmol, 1.0 equiv). The mixture was heated at reflux for 48 h before being cooled to RT and concentrated in vacuo. After column chromatography on silica gel (hexanes/ethyl acetate 60:40) **17** (52 mg, 0.15 mmol, 70%) was obtained as an off-white solid. mp 127–130 °C. [α] = +62.3 (*c* = 0.26, methanol). ^{1}H NMR (400 MHz, acetone): δ 7.77 (1H, s), 7.62 (1H, s), 6.56 (2H, dd, *J* = 8.3, 2.0 Hz), 5.85 (1H, m), 4.68 (1H, dq, *J* = 7.8, 6.4 Hz), 3.67 (3H, s), 3.57–3.47 (1H, m), 3.30–3.24 (2H, m), 3.24–3.16 (2H, m), 3.00 (1H, dd, *J* = 9.8, 7.8 Hz), 2.91–2.84 (1H, m), 1.58 (1H, ddd, *J* = 13.2, 11.3, 5.9 Hz), 1.39 (3H, d, *J* = 6.4 Hz) ppm. ^{13}C NMR (100 MHz, acetone): δ 177.6, 174.7, 148.5, 148.2, 125.4, 122.0, 121.7, 113.4, 113.2, 79.6, 52.1, 51.7, 42.4, 41.0, 35.1, 28.4, 25.9, 19.9 ppm. IR (KBr disc): ν 3200, 2973, 1743, 1490 cm^{-1}. EIMS (70 eV) *m/z* 344 (100), 312 (90), 284 (55), 239 (50), 211 (90); HRMS: calcd for $C_{19}H_{20}O_6$ $[M]^+$: 344.1260; found: 344.1262.

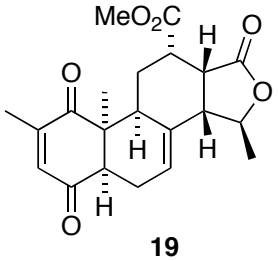
Tetracycle 18



18

To a stirred solution of **16** (30 mg, 0.13 mmol, 1.0 equiv) in deutereated toluene (1 mL) was added 2,5-dimethyl benzoquinone (21 mg, 0.15 mmol, 1.2 equiv). The mixture was heated to reflux for 125 h before being cooled to RT and concentrated in vacuo. HPLC of the crude material (hexane/ethyl acetate, 55:45) yielded **18** (37 mg, 0.10 mmol, 78%) as a yellow oil. $[\alpha]_D^{25}$ = +78.4 (*c* = 0.37, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.54 (1H, m), 5.65 (1H, m), 4.49 (1H, dq, *J* = 8.1, 6.0 Hz), 3.71 (3H, s), 3.16 (1H, dt, *J* = 7.6, 6.0 Hz), 3.08 (1H, dd, *J* = 10.6, 7.6 Hz), 2.90 (1H, dd, *J* = 6.6, 3.3 Hz), 2.81–2.73 (2H, m), 2.15 (1H, ddt, *J* = 18.5, 6.8, 2.5 Hz), 2.07 (1H, m), 2.02 (3H, d, *J* = 1.5 Hz), 1.89 (1H, dt, *J* = 13.8, 5.4 Hz), 1.55 (1H, ddd, *J* = 13.8, 11.6, 5.9 Hz), 1.39 (3H, d, *J* = 6.3 Hz), 1.38 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 199.7, 176.9, 173.3, 150.1, 137.2, 132.6, 122.1, 79.5, 52.5, 51.0, 50.8, 50.6, 41.7, 40.2, 39.2, 30.1, 24.2, 21.1, 19.8, 16.3 ppm. IR (thin film): ν = 2931, 1766, 1735, 1676, 1625 cm^{-1}. EIMS (70 eV) *m/z* (%): 372 (30), 341 (10), 312 (10), 32 (100); HRMS: calcd for $C_{21}H_{24}O_6$ $[M]^+$: 372.1573; found: 372.1573.

Tetracycle 19

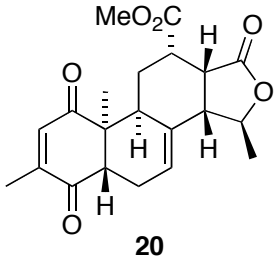


19

To a stirred solution of **16** (47 mg, 0.20 mmol, 1.0 equiv) in deuterated toluene (1 mL) was added 2,6-dimethylbenzoquinone (33 mg, 0.23 mmol, 1.2 equiv). The reaction mixture was heated to reflux for 109 h before being cooled to RT and concentrated in vacuo. After column chromatography (hexane/ethyl acetate, 55:45) **19** (56 mg, 0.15 mmol, 76%) was obtained as a yellow oil. $[\alpha]_D^{25}$ = +72.0 (*c* = 0.35, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.59 (1H, dd, *J* = 3.0, 1.5 Hz), 5.62 (1H, m), 4.45 (1H, dq, *J* = 7.8, 6.3 Hz), 3.71 (3H, s), 3.17 (1H, dt, *J* = 6.9, 5.9 Hz), 3.10 (1H, dd, *J* = 10.3, 7.3 Hz), 2.88 (1H, dd, *J* = 6.6, 4.2 Hz), 2.79 (1H, dd, *J* = 10.1, 7.9 Hz), 2.72 (1H, ddt, *J* = 18.5, 4.8, 1.8 Hz), 2.15 (1H, m), 2.08 (1H, m), 2.01 (3H, d, *J* = 1.4 Hz),

1.78(1H, dt, J = 13.6, 5.6 Hz), 1.69 (1H, ddd, J = 13.6, 11.0, 5.6 Hz), 1.40 (3H, s), 1.38 (3H, d, J = 6.3 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.3, 198.8, 176.8, 173.2, 149.9, 136.6, 132.8, 122.2, 79.7, 52.5, 51.6, 50.6, 50.4, 41.7, 40.1, 39.4, 29.5, 24.3, 22.5, 19.9, 16.6 ppm. IR (thin film): ν = 2930, 1769, 1735, 1678 cm^{-1}. EIMS (70 eV) m/z (%): 372 (100), 340 (40), 312 (45); HRMS: calcd for $C_{21}H_{24}O_6$ $[M]^+$: 372.1573; found: 372.1570.

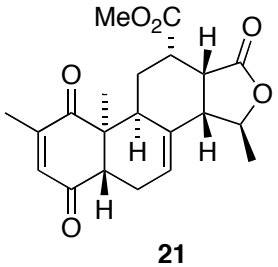
Tetracycle 20



20

To a stirred solution of **18** (10 mg, 0.03 mmol, 1.0 equiv) in chloroform (4 mL) was added dry silica (2.5 g). Stirring was continued for 8 h before the reaction mixture was filtered. The silica was rinsed with ethyl acetate (2 × 10 mL) and the filtrate concentrated in vacuo to give **20** (10 mg, 0.03 mmol, 100%). Recrystallization (heptane/dichloromethane/chloroform) gave colorless needles. mp 110–112 °C. $[\alpha]_D^{25}$ = +132.4 (c = 0.18, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.48 (1H, q, J = 1.4 Hz), 5.66 (1H, d, J = 4.9 Hz), 4.43 (1H, dq, J = 6.4, 3.8 Hz), 3.77 (3H, s), 3.48 (1H, dd, J = 10.4, 5.0 Hz), 2.89 (1H, dd, J = 8.3, 5.3 Hz), 2.87 (1H, dd, J = 6.1, 3.3 Hz), 2.74 (1H, dd, J = 7.4, 4.8 Hz), 2.73 (1H, dd, J = 7.4, 5.2 Hz), 2.50 (1H, m), 2.47–2.38 (2H, m), 2.33 (1H, ddt, J = 18.5, 11.0, 1.9 Hz), 2.01 (3H, d, J = 1.5 Hz), 1.41 (3H, d, J = 6.4 Hz), 1.37 (1H, m), 1.08 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0, 200.3, 176.3, 173.1, 150.3, 136.2, 135.8, 121.7, 79.9, 52.4, 51.0, 50.5, 45.7, 41.2, 38.8, 37.1, 29.0, 22.1, 21.7, 21.5, 16.2 ppm. IR (thin film): ν = 2927, 1766, 1736, 1674 cm^{-1}. EIMS (70 eV) m/z (%): 372 (50), 312 (60), 69 (100); HRMS: calcd for $C_{21}H_{24}O_6$ $[M]^+$: 372.1573; found: 372.1577.

Tetracycle 21

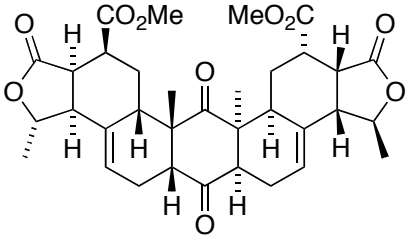


21

To a stirred solution of **19** (8 mg, 0.02 mmol, 1.0 equiv) in chloroform (4 mL) was added dry silica (2 g). Stirring was

continued for 4 h before the reaction mixture was filtered. The silica was rinsed with ethyl acetate (15 mL × 2) to give **21** (8 mg, 0.02 mmol, 100%). Recrystallization (heptane/ethyl acetate) gave colorless needles. mp 180–182 °C. $[\alpha]_D^{25}$ = +214.0 (*c* = 0.83, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.64 (1H, ddd, *J* = 2.8, 1.5, 1.5 Hz), 5.68 (1H, dd, *J* = 5.0, 1.7 Hz), 4.44 (1H, dq, *J* = 6.4, 3.5 Hz), 3.79 (3H, s), 3.51 (1H, dd, *J* = 10.3, 4.6 Hz), 2.92 (1H, m), 2.88 (1H, m), 2.74 (1H, ddd, *J* = 9.8, 7.3, 4.8 Hz), 2.61–2.40 (2H, m), 2.30 (1H, ddt, *J* = 2.0,m 11.0, 19 Hz), 2.01 (3H, d, *J* = 1.5 Hz), 1.43 (3H, d, *J* = 6.4 Hz), 1.36 (1H, m), 1.10 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 199.3, 176.2, 173.0, 148.4, 137.1, 135.9, 121.7, 79.9, 52.4, 50.7, 50.5, 45.7, 41.1, 38.7, 37.0, 28.9, 22.1, 21.8, 21.5, 16.5 ppm. IR (thin film): ν = 2933, 1764, 1737, 1680, 1628 cm^{-1}. EIMS (70 eV) *m/z* (%): 372 (100), 341 (25), 312 (80); HRMS: calcd for: $C_{21}H_{24}O_6$ $[M]^+$: 372.1573; found: 372.1576.

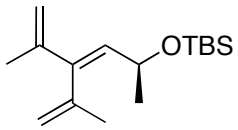
Heptacycle 22



22

To a solution of **16** (160 mg, 0.68 mmol, 1.0 equiv) in dichloromethane (3 mL) was added 2,6-dimthylbenzoquinone (46 mg, 0.34 mmol, 0.5 equiv). The reaction mixture was compressed at 19 kbar for 72 h then concentrated in vacuo. After column chromatography **22** (176 mg, 0.29, 85%) was obtained. Recrystallization (heptane/dichloromethane) gave colorless needles. mp 132–135 °C. $[\alpha]_D^{25}$ = +4.24 (*c* = 0.66, chloroform). ^{1}H NMR (500 MHz, C_6D_6): δ 5.17 (2H, m), 4.47 (2H, dq, *J* = 8.8, 6.2 Hz), 3.31 (6 H, s), 2.97 (2H, m), 2.88 (2H, dd, *J* = 17.6, 6.1 Hz), 2.50 (2H, dd, *J* = 10.7, 7.8 Hz), 2.24 (2H, d, *J* = 5.9 Hz), 2.19 (2H, t, *J* = 9.6 Hz), 2.00 (2H, d, *J* = 12.2 Hz), 1.84 (2H, dt, *J* = 12.5, 4.1 Hz), 1.68 (2H, dd, *J* = 17.3, 6.6 Hz), 1.11 (6H, s), 1.04 (6H, d, *J* = 6.2 Hz), 1.06–0.09 (2H, m) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 215.8, 208.0, 175.8, 173.1, 133.9, 122.4, 79.2, 52.1, 49.8, 49.6, 49.0, 41.7, 41.1, 40.17, 31.9, 26.3, 22.5, 19.7 ppm. IR (thin film): ν = 2974, 2892, 1768, 1734, 1701 cm^{-1}. EIMS (70 eV) *m/z* (%): 608 (100), 576 (50), 372 (40), 277 (45), 243 (70), 171 (95); HRMS: calcd for: $C_{34}H_{40}O_{10}$ $[M]^+$: 608.2621; found: 608.2624.

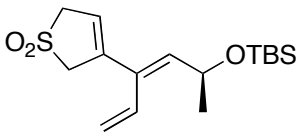
(2*S*)-2-(*tert*-butyldimethylsilyl)oxy-5-methyl-4-(prop-1-en-2-yl)hexa-3,5-diene (23)



23

To a stirred solution of zinc bromide (360 mg, 1.60 mmol, 5.5 equiv) in tetrahydrofuran (2 mL) was added a solution of isopropenyl magnesium bromide (3.8 mL of a 0.38 M solution in THF, 1.45 mmol, 5.0 equiv). After 30 min the solution was cooled to –78 °C and a solution of **5** (100 mg, 0.29 mmol, 1.0 equiv) and tetrakis(triphnylphosphine)palladium(0) (17 mg, 0.015 mmol, 0.05 equiv) in THF (2 mL) was added dropwise via canula. Stirring was continued at RT for 18 h before the mixture was diluted with hexane and filtered. The filtrate was concentrated in vacuo. After column chromatography (hexanes) **23** (64 mg, 0.24 mmol, 83%) was obtained as a colorless oil. $[\alpha]_D^{25}$ = –70.5 (*c* = 2.46, chloroform). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.49 (1H, d, *J* = 8.4 Hz), 5.13 (1H, bs), 4.99 (2H, m), 4.69 (1H, bs), 4.53 (1H, dq, *J* = 8.4, 6.3 Hz), 1.89 (3H, bs), 1.82 (3H, bs), 1.21 (3H, d, *J* = 6.2 Hz), 0.87 (9H, s), 0.03 (3H, s), 0.02 (3H, s) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 142.1, 141.8, 131.5, 115.6, 114.7, 67.2, 26.0, 25.5, 23.5, 20.6, 18.2, –4.2, –4.5 ppm. IR (thin film): ν = 3080, 2956, 2929, 2894, 2857 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 245 (35), 209 (50), 171 (20), 135 (22), 75 (100); HRMS: calcd for $C_{12}H_{21}OSi$ [M–C_4H_9]: 209.1362; found: 209.1362.

(2*S*,3*Z*)-2-(*tert*-butyldimethylsilyl)oxy-4-(1,1-dioxo-2,5-dihydrothiene-3-yl)hexa-3,5-diene (25)

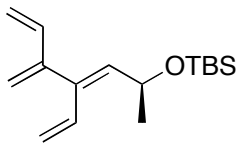


25

To a stirred solution of **24**[3] (172 mg, 0.59 mmol, 1.0 equiv) and 3-(tributylstannyl)-3-sulfolene (289 mg, 0.71 mmol, 1.02 equiv) in acetonitrile (5 mL) under argon was added palladium(II) acetate (4 mg, 0.02 mmol, 5 mol%) and triphenyl phosphine (9 mg, 0.03 mmol, 10 mol%). The reaction mixture was stirred at 60 °C for 48 h. The mixture was diluted in diethyl ether (50 mL) and partitioned against aqueous ammonia solution (30% v/v, 2 × 40 mL). The organic layer was washed with brine (40 mL), dried and concentrated in vacuo. After column chromatography on silica (hexanes/ethyl acetate 90:10) **25** (174 mg, 0.53 mmol, 90%) was obtained as a colorless oil. $[\alpha]_D^{25}$ = –45.1 (*c* =

3.4, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (1H, dd, *J* = 18.0, 11.3 Hz), 5.94 (1H, m), 5.46 (1H, ddd, *J* = 11.2, 1.7, 0.7 Hz), 5.44 (1H, d, *J* = 8.3 Hz), 5.21 (1H, dd, *J* = 17.7, 1.6 Hz), 4.65 (1H, dq, *J* = 8.3, 6.2 Hz), 3.93–3.84 (4H, m), 1.23 (3H, d, *J* = 6.5 Hz), 0.86 (9H, s), 0.02 (3H, s), 0.00 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.7, 136.9, 132.2, 130.7, 121.3, 120.0, 65.8, 57.5, 56.3, 25.9, 24.6, 18.2, –4.4, –4.6 ppm. IR (thin film): ν = 2955, 2928, 2856 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 271 (20), 207 (100), 133 (70), 75 (95); HRMS: calcd for $C_{12}H_{19}O_3SiS$ [M–C_4H_9]: 271.0824; found: 271.0824.

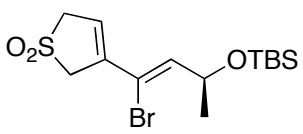
(2*S*,3*E*)-2-(*tert*-butyldimethylsilyl)oxy-5-methylene-4-vinylhepta-3,6-diene (26)



26

A solution of (2*S*,3*Z*)-4-bromo-2-(*tert*-butyldimethylsilyl)oxy-hexa-3,5-diene **25** (34 mg, 0.10 mmol, 1.0 equiv) in chlorobenzene (10 mL) was heated at reflux for 1.5 h before being concentrated in vacuo. After column chromatography (hexanes/ethyl acetate 98:2) **26** (19 mg, 0.07 mmol, 69%) was obtained as a colorless oil. $[\alpha]_D^{25}$ = +14.3 (*c* = 0.86, chloroform). ^{1}H NMR (500 MHz, C_6D_6): δ 6.60 (1H, dd, *J* = 17.5, 11.2 Hz), 6.34 (1H, dd, *J* = 17.3, 10.3 Hz), 5.63 (1H, d, *J* = 8.4 Hz), 5.30 (2H, ddd, *J* = 17.4, 11.9, 1.7 Hz), 5.11–5.02 (4H, m), 4.80 (1H, dq, *J* = 8.3, 6.4 Hz), 1.24 (3H, d, *J* = 6.4 Hz), 0.98 (9H, s), 0.10 (3H, s), 0.09 (3H, s) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 147.9, 138.8, 137.5, 136.2, 131.7, 118.1, 118.0, 116.6, 65.3, 26.1, 25.0, 18.3, –4.2, –4.5 ppm. IR (thin film): ν = 2957, 2929, 2857 cm^{-1}. EIMS (70 eV) *m*/*z* (%): 264 (2), 207 (60), 159 (15), 75 (100); HRMS: calcd for $C_{16}H_{28}OSi$ [M]: 264.1909; found: 264.1905.

(2*S*,3*Z*)-4-bromo-2-(*tert*-butyldimethylsilyl)oxy-4-(1,1-dioxo-2,5-dihydrothiene-3-yl)but-3-ene (27)

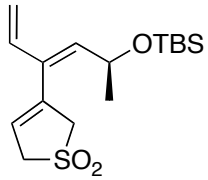


27

To a stirred solution of **5** (1.50 g, 4.36 mmol, 1.0 equiv) and 3-(tributylstannyl)-3-sulfolene (1.80 g, 4.40 mmol, 1.0 equiv) in

toluene (40 mL) was added tris(dibenzylideneacetone)dipalladium(0) (99 mg, 0.11 mmol, 2.5 mol%) and trifurylphosphine (151 mg, 0.65 mmol, 15 mol%). The reaction mixture was heated at 55 °C for 16 h before cooling to RT and diluting with diethyl ether (50 mL). The organic layer was treated with ammonia solution (2 × 50 mL), washed with brine (50 mL) and concentrated in vacuo. After column chromatography (hexanes/ethyl acetate 90:10) **27** (895 mg, 2.34 mmol, 54%) was obtained as a yellow oil. $[\alpha]_D^{25} = +1.28$ (*c* = 1.8, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.39 (1H, m), 5.92 (1H, d, *J* = 6.9 Hz), 4.76 (1H, dq, *J* = 6.6, 6.6 Hz), 4.02–3.94 (4H, m), 1.26 (3H, d, *J* = 6.4 Hz), 0.88 (9H, s), 0.08 (3H, s), 0.05 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 133.9, 123.6, 117.2, 69.4, 57.6, 56.4, 25.9, 23.0, 18.2, –4.5, –4.7 ppm. IR (thin film): ν = 2955, 2929, 2887, 2857 cm^{-1}. EIMS (70 eV) *m/z* (%): 325 (5), 323 (6), 281 (55), 279 (53), 261 (60), 259 (65), 181 (100); HRMS: calcd for $C_{10}H_{16}O_3SiS^{81}Br$ [M–C_4H_9]: 324.9752; found: 324.9736.

(2*S*,3*E*)-2-(*tert*-butyldimethylsilyl)oxy-4-(1,1-dioxo-2,5-dihydrothiene-3-yl)hexa-3,5-diene (28)

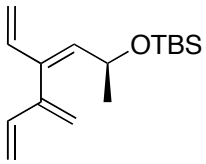


28

A solution of **27** (78 mg, 0.2 mmol, 1.0 equiv) and vinyltributyl tin (107 mg, 0.41 mmol, 2.0 equiv) in acetonitrile (2 mL) was degassed by the freeze/thaw method (× 2). To the resulting solution was added palladium(II) acetate (2 mg, 0.01 mmol, 5 mol%) and triphenyl phosphine (5 mg, 0.02 mmol, 10 mol%). The solution was then heated at 60 °C for 4 h before cooling to RT and dilution with diethyl ether (50 mL). The organic layer was treated with ammonia solution (2 × 50 mL), washed with brine (50 mL) and concentrated in vacuo. After column chromatography (hexanes/ethyl acetate 90:10) **28** (62 mg, 0.19 mmol, 92%) was obtained as a colorless oil. $[\alpha]_D^{25} = -10.7$ (*c* = 2.9, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.27 (1H, dd, *J* = 17.7, 10.7 Hz), 5.82 (1H, m), 5.66 (1H, d, *J* = 8.8 Hz), 5.14 (1H, d, *J* = 10.8, 5.1 Hz), 5.10 (1H, d, *J* = 17.4 Hz), 4.45 (1H, dq, *J* = 8.6, 6.3 Hz), 3.93 (2H, m), 3.77 (2H, dq, *J* = 16.6, 1.6 Hz), 1.22 (3H, d, *J* = 6.3 Hz), 0.86 (9H, s), 0.03 (3H, s), 0.01 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ

139.6, 136.9, 134.3, 133.0, 122.9, 116.2, 66.1, 57.5, 56.6, 25.8, 25.2, 18.2, –4.3, –4.4 ppm. IR (thin film): ν = 2956, 2929, 2857 cm^{-1}. EIMS (70 eV) *m/z* (%): 271 (70), 208 (40), 207 (100), 133 (50); HRMS: calcd for $C_{12}H_{19}O_3SiS$ [M–C_4H_9]: 271.0824; found: 271.0818.

(2*S*,3*Z*)-2-(*tert*-butyldimethylsilyl)oxy-5-methylene-4-vinylhepta-3,6-diene (29)



29

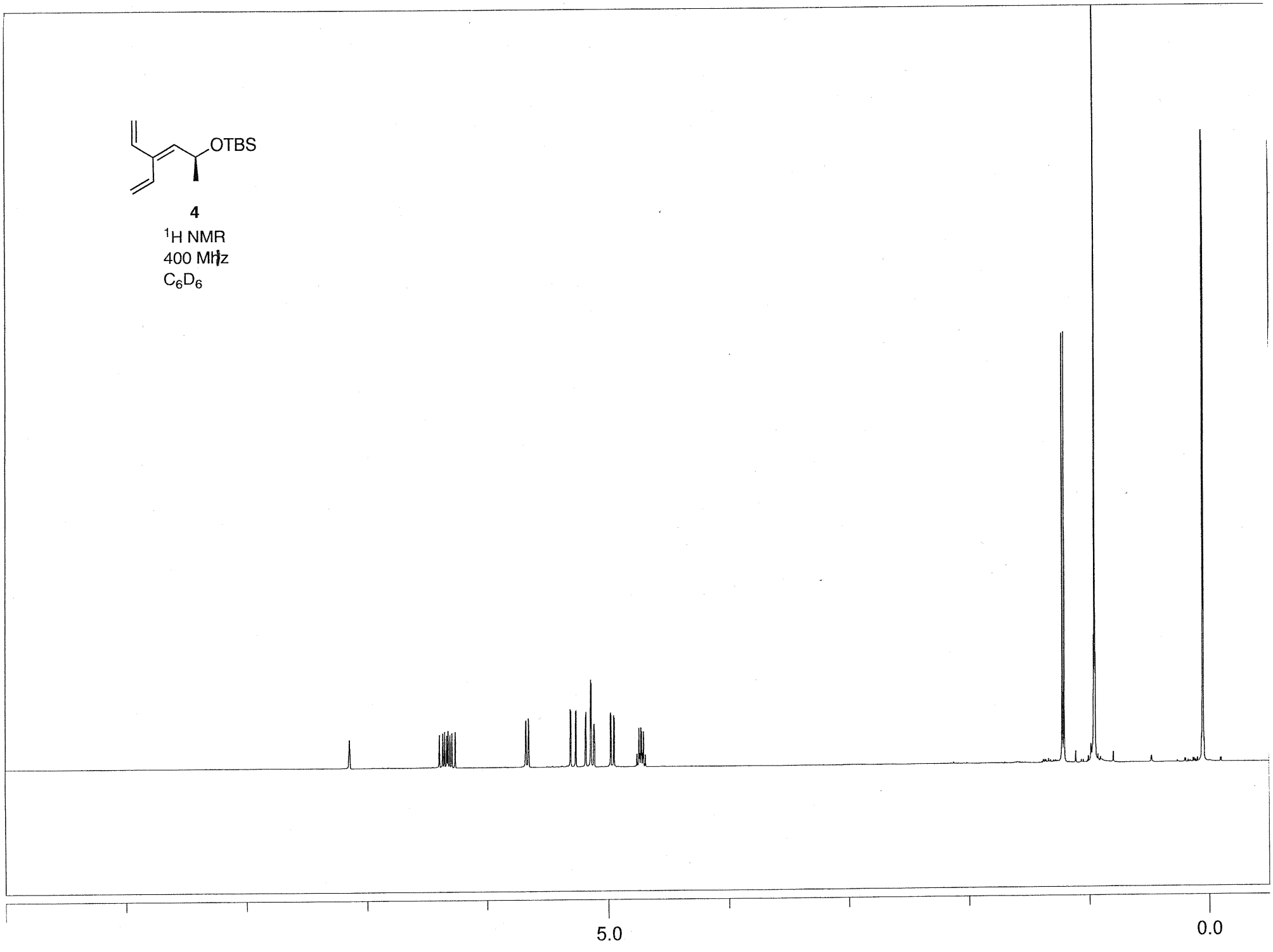
A solution of **28** (29 mg, 0.088 mmol, 1.0 equiv) in chlorobenzene (10 mL) was heated at reflux for 1.5 h before being concentrated in vacuo. After column chromatography (hexanes/ethyl acetate 98:2) **29** (21 mg, 0.079 mmol, 90%) was obtained as a colorless oil. $[\alpha]_D^{25}$ = –10.7 (*c* = 0.97, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.30 (1H, ddd, *J* = 17.1, 10.4, 0.6 Hz), 6.27 (1H, dd, *J* = 16.6, 10.4 Hz), 5.72 (1H, d, *J* = 8.3 Hz), 5.22 (1H, ddd, *J* = 5.1, 1.5, 0.5 Hz), 5.18 (1H, ddd, *J* = 5.4, 1.5, 0.7 Hz), 5.16 (1H, m), 4.99 (1H, dm, *J* = 10.5 Hz), 4.96 (1H, ddd, *J* = 10.5, 1.5, 0.7 Hz), 4.92 (1H, m), 4.50 (1H, dq, *J* = 8.4, 6.3 Hz), 1.23 (3H, d, *J* = 6.4 Hz), 0.99 (9H, s), 0.08 (3H, s), 0.06 (3H, s) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 144.3, 139.0, 138.3, 137.5, 137.1, 119.2, 117.2, 115.4, 67.0, 26.1, 25.1, 18.3, –4.0, –4.3 ppm. IR (thin film): ν = 2958, 2857 cm^{-1}. EIMS (70 eV) *m/z* (%): 221 (20), 207 (35), 159 (34), 75 (100); HRMS: calcd for $C_{12}H_{19}OSi$ [M–C_4H_9]: 207.1205; found: 207.1203.

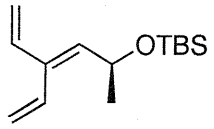
References

(1) J. A. Marshall, S. Xie, *J. Org. Chem.* **1995**, *60*, 7230–7237.

(2) B. M. Trost, T. J. J. Müller, J. Martinez, *J. Am. Chem. Soc.* **1995**, *117*, 1888–1899.

(3) T. N. Cayzer, L. S.-M. Wong, P. Turner, M. N. Paddon-Row, M. S. Sherburn, *Chem. Eur. J.* **2002**, *8*, 739–750.


OTBS
4
1H NMR
400 MHz
C6D6
5.0
0.0
ppm (f1)

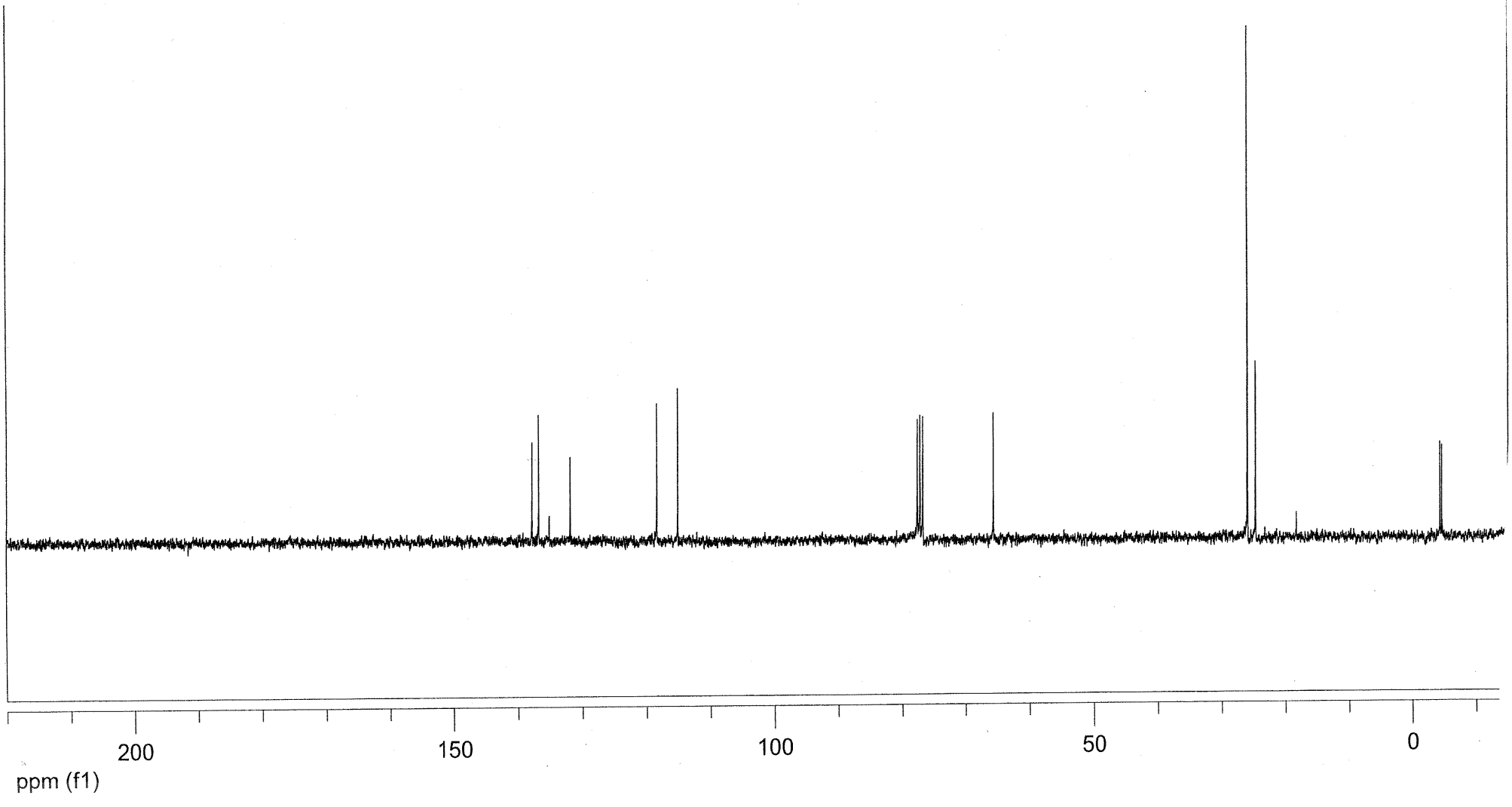


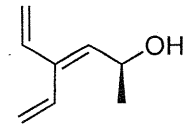
4

^{13}C NMR

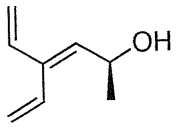
100 MHz

$CDCl_3$

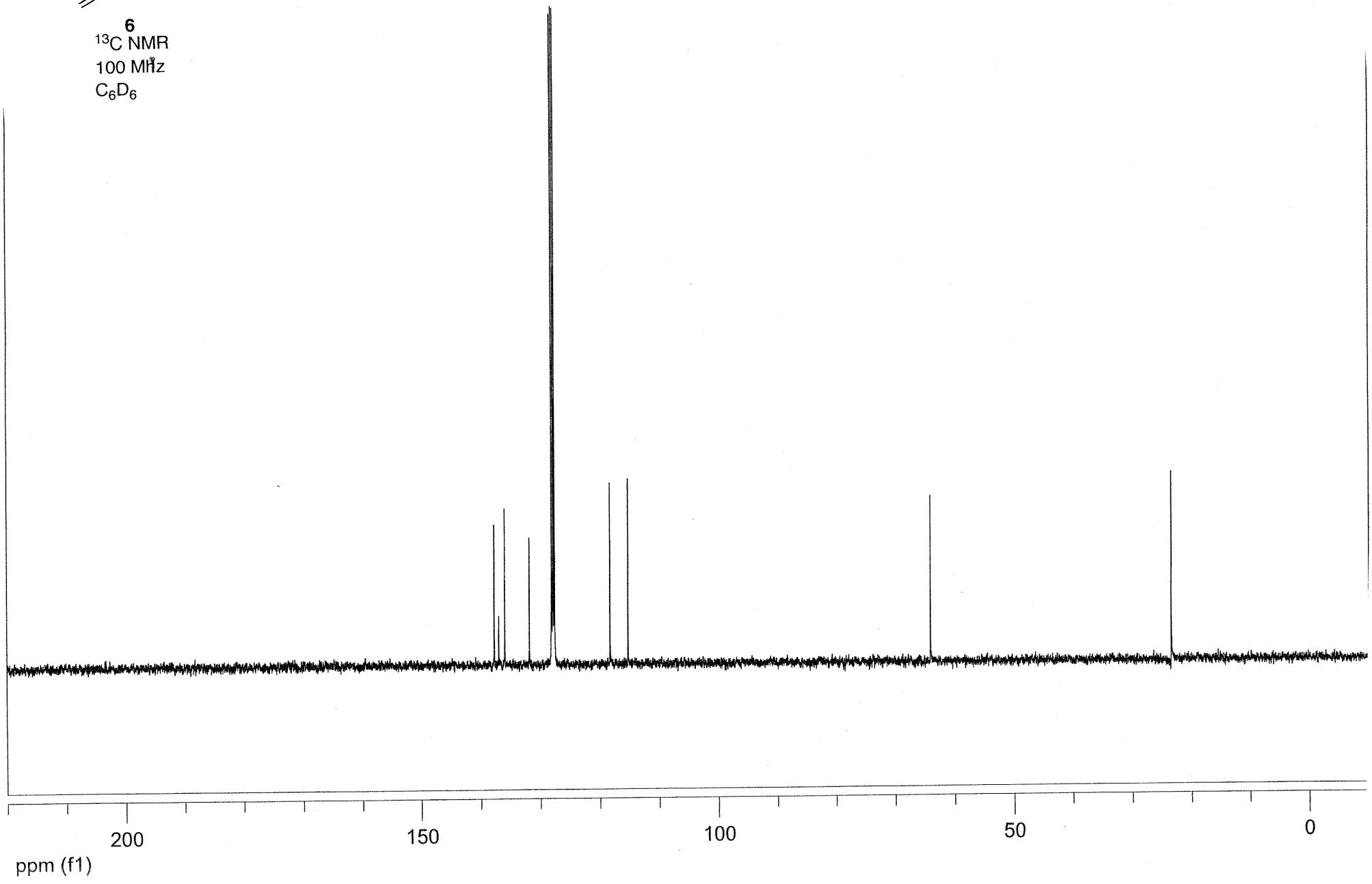


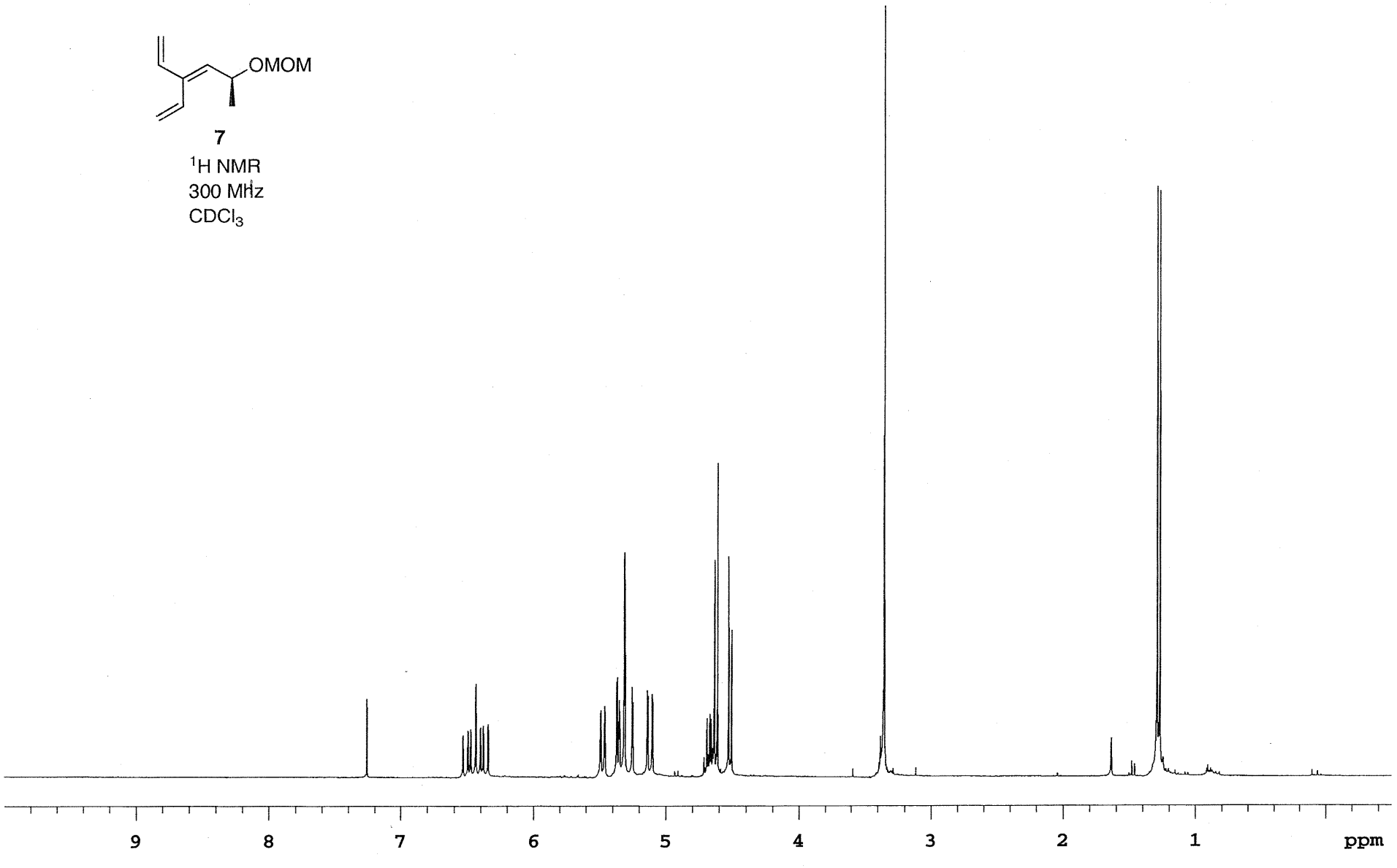


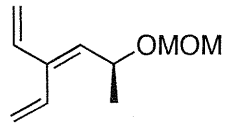
6
^{1}H NMR
400 MHz
C_6D_6



6
^{13}C NMR
100 MHz
C_6D_6

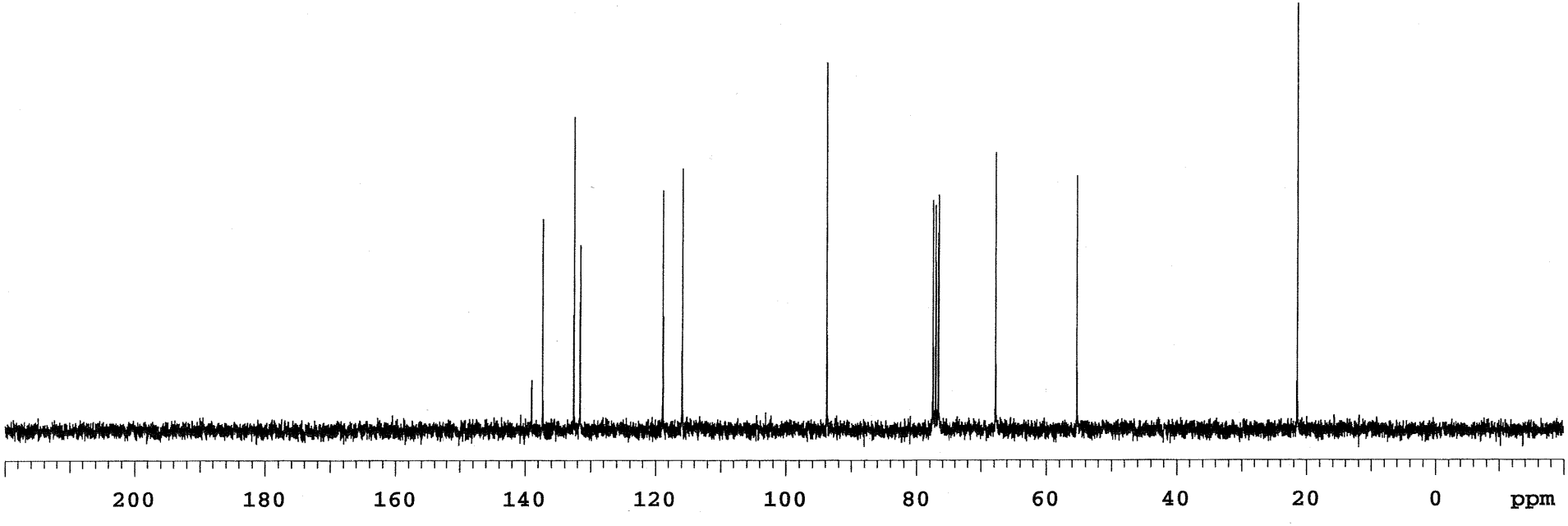


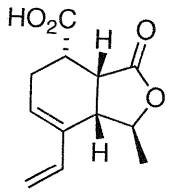

OMOM
7
1H NMR
300 MHz
CDCl3
9
8
7
6
5
4
3
2
1
ppm



7

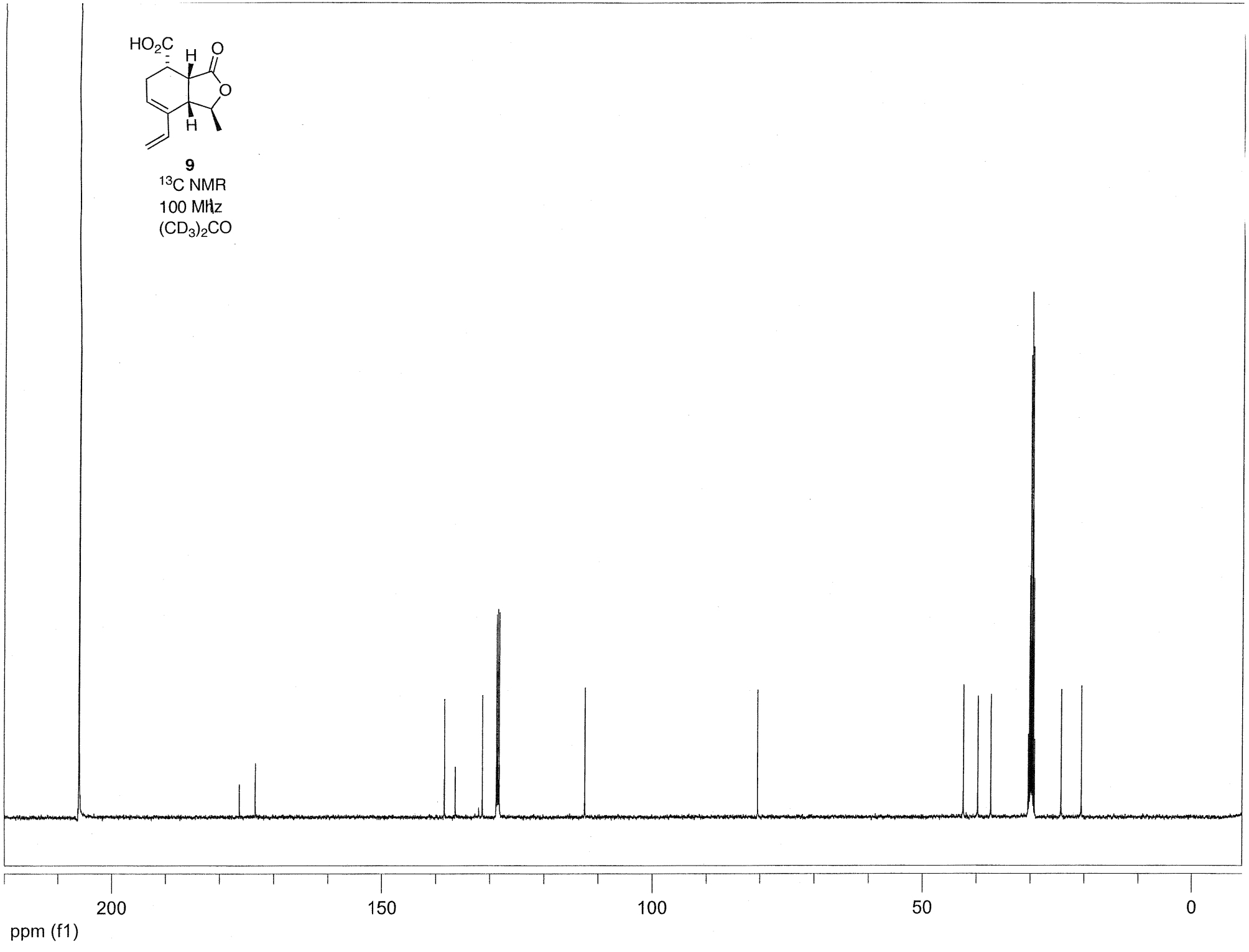
^{13}C NMR
75 MHz
$CDCl_3$

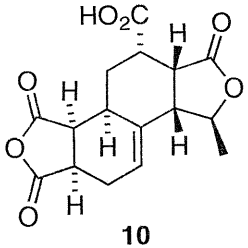




9

^{1}H NMR
400 MHz
$(CD_3)_2CO$


HO2C
H
O
O
H
9
13C NMR
100 MHz
(CD3)2CO
200
150
100
50
0
ppm (f1)

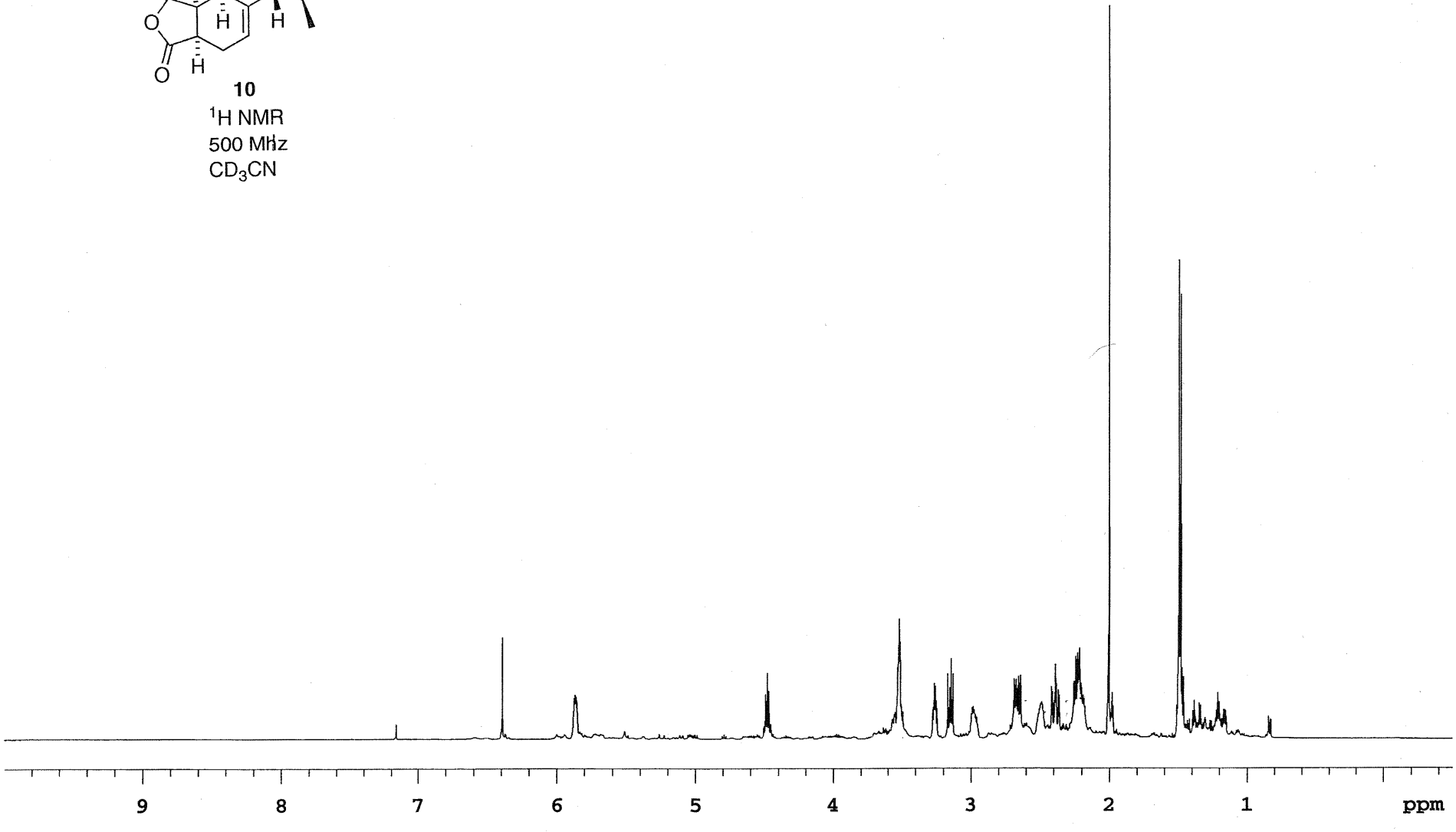


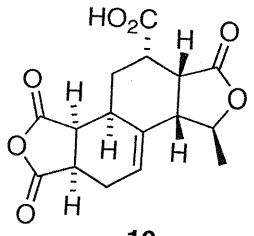
10

^{1}H NMR

500 MHz

CD_3CN



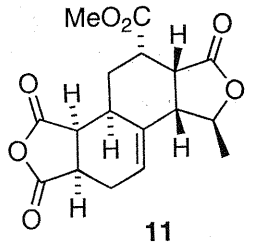


10

^{13}C NMR

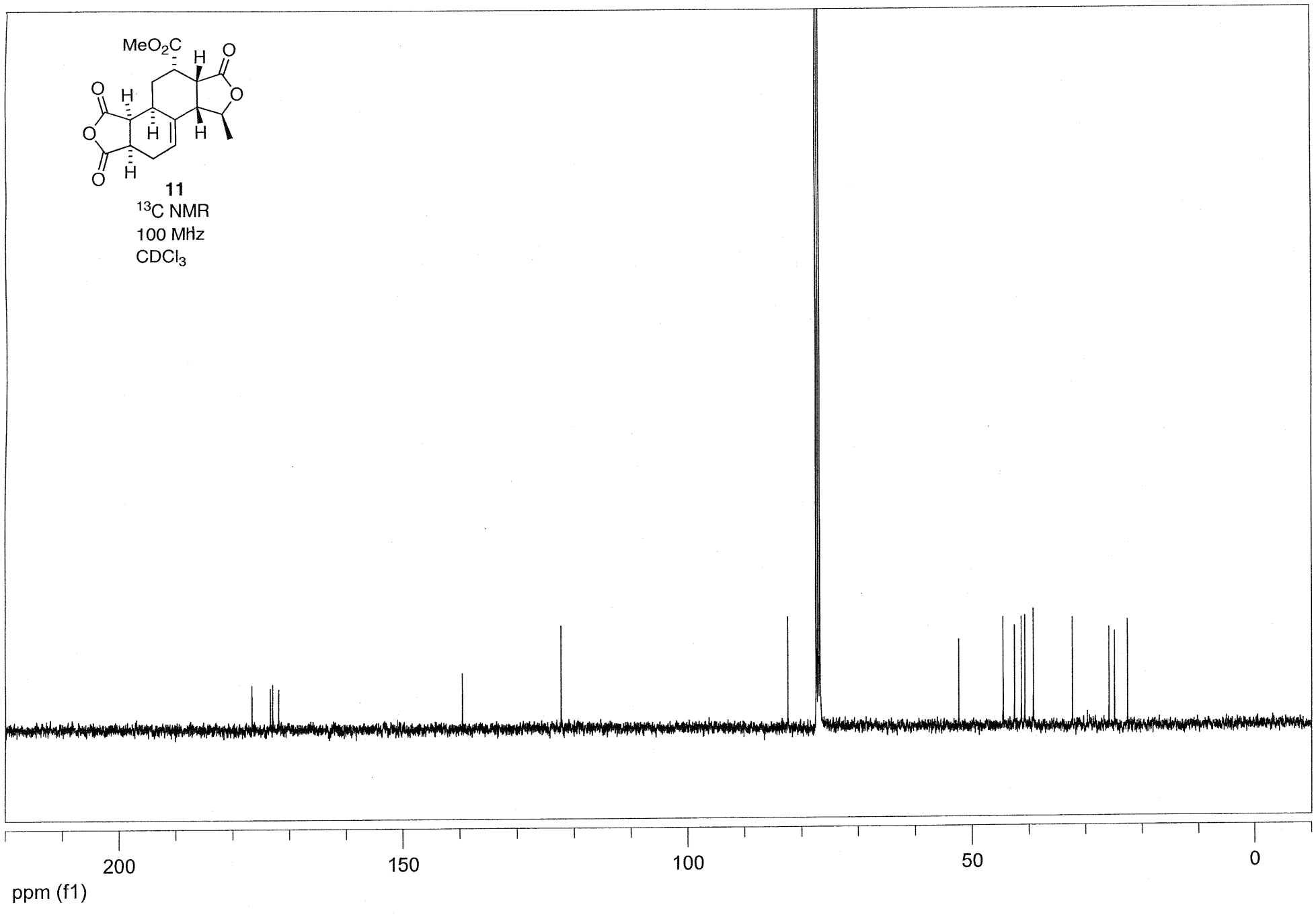
125 MHz

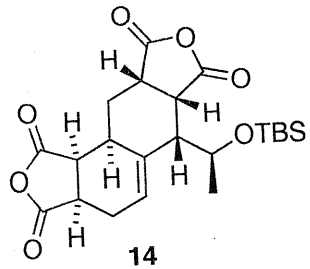
CD_3CN



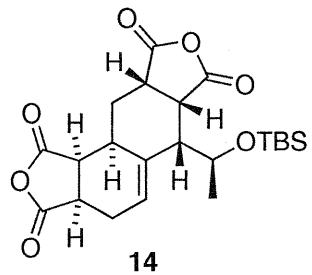
11

^{1}H NMR
400 MHz
$CDCl_3$


MeO2C
H
O
O
H
O
O
H
H
H
O
O
H
11
13C NMR
100 MHz
CDCl3
200
150
100
50
0
ppm (f1)



14
^{1}H NMR
500 MHz
$CDCl_3$

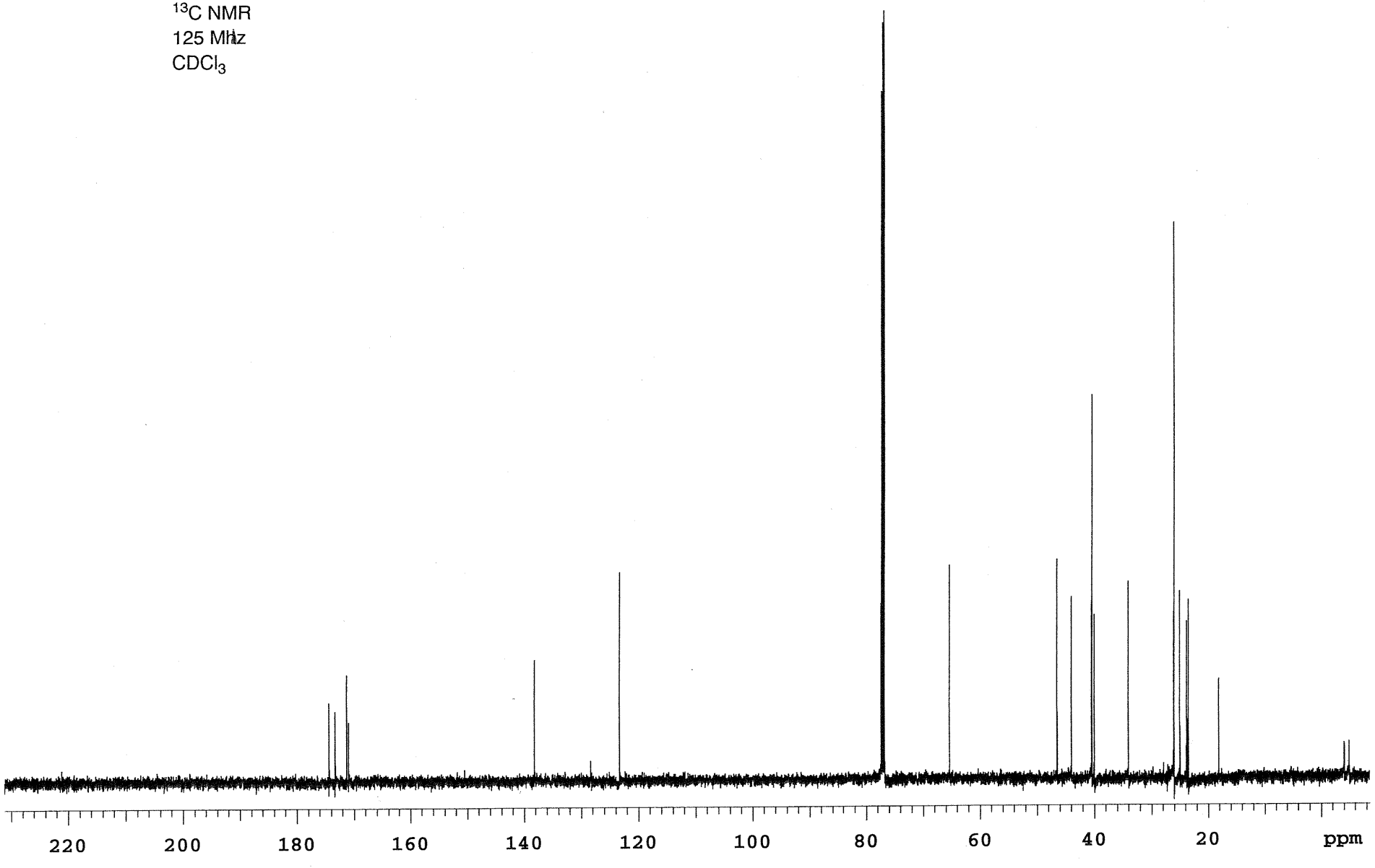


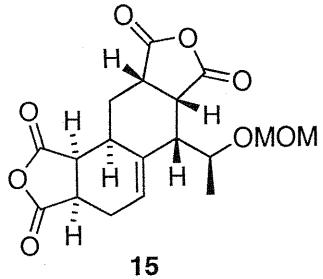
14

^{13}C NMR

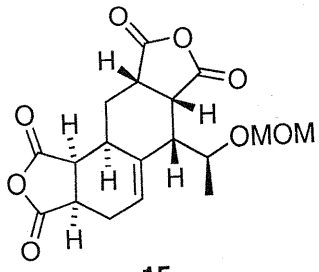
125 Mhz

$CDCl_3$





15
^{1}H NMR
500 MHz
$CDCl_3$

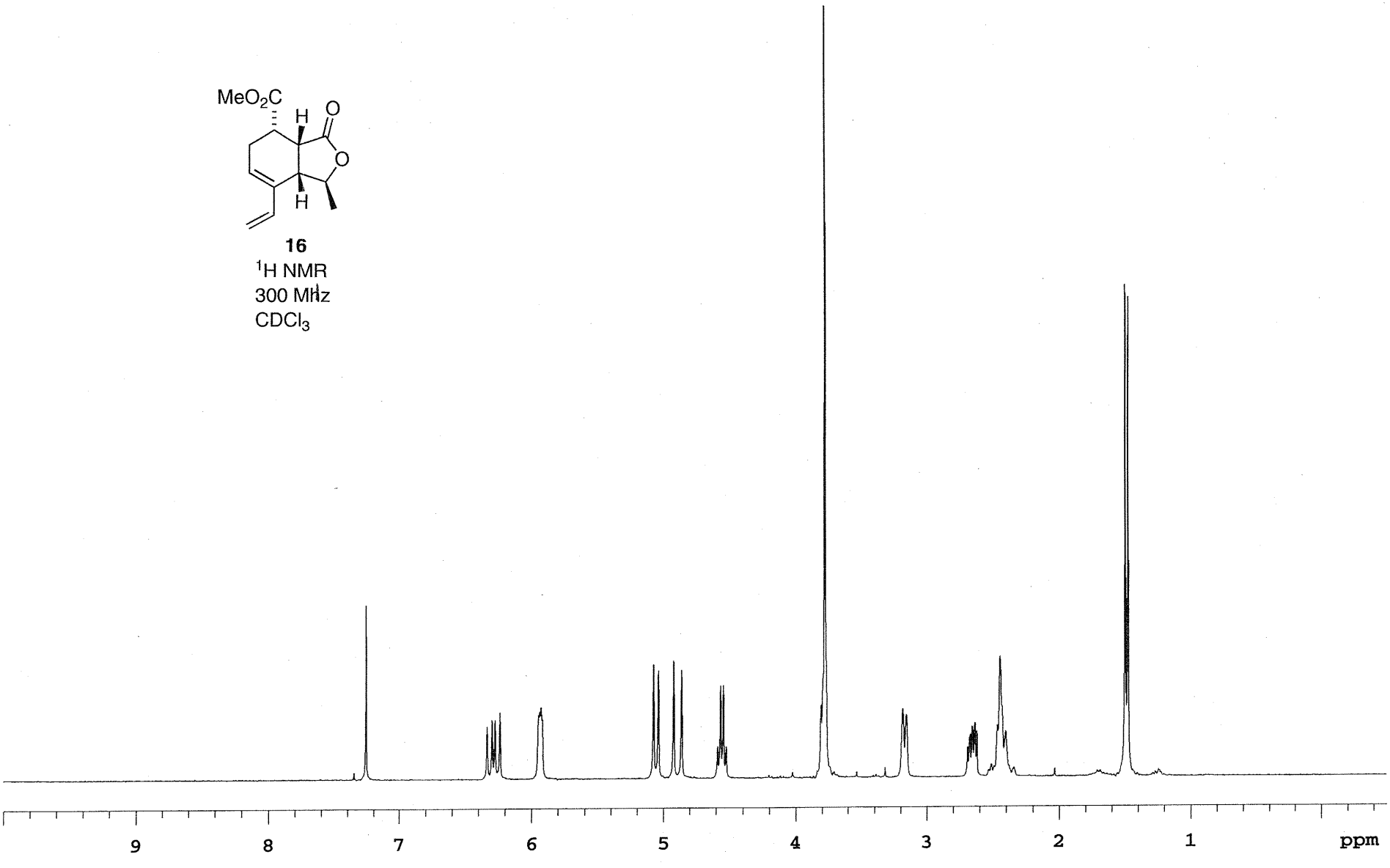


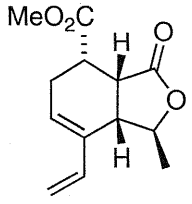
15

^{13}C NMR

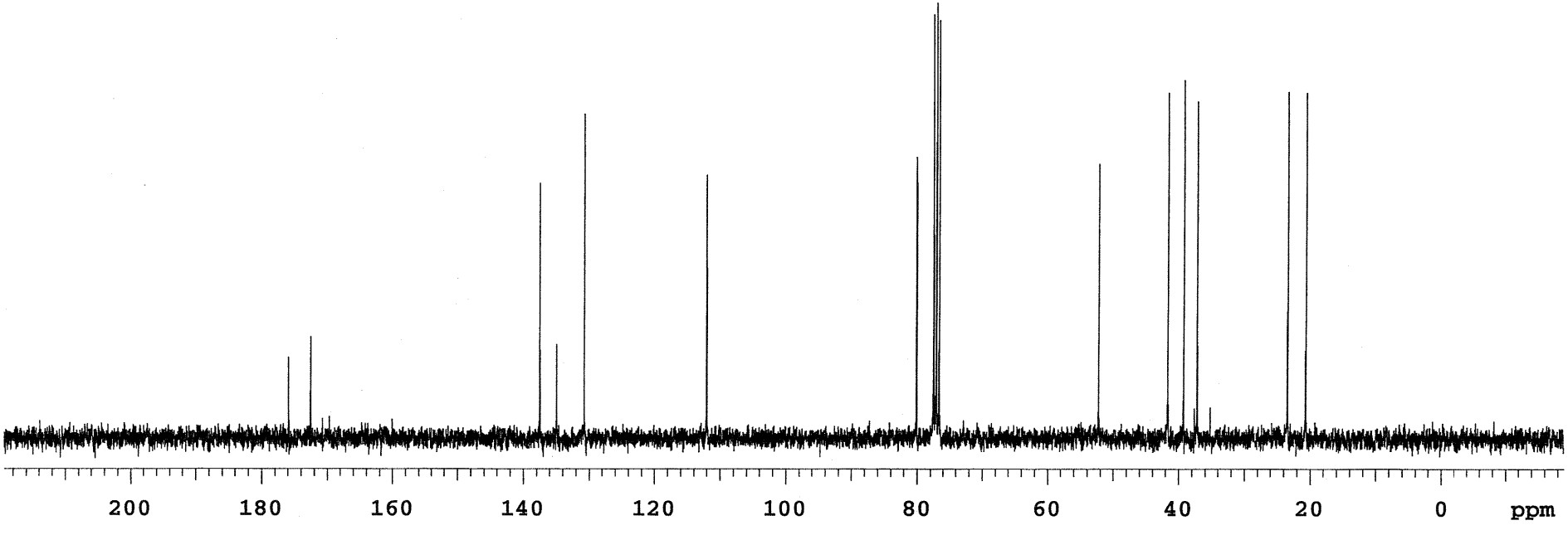
125 MHz

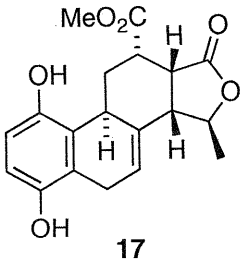
$CDCl_3$


MeO2C
H
O
O
H
16
1H NMR
300 MHz
CDCl3
9
8
7
6
5
4
3
2
1
ppm

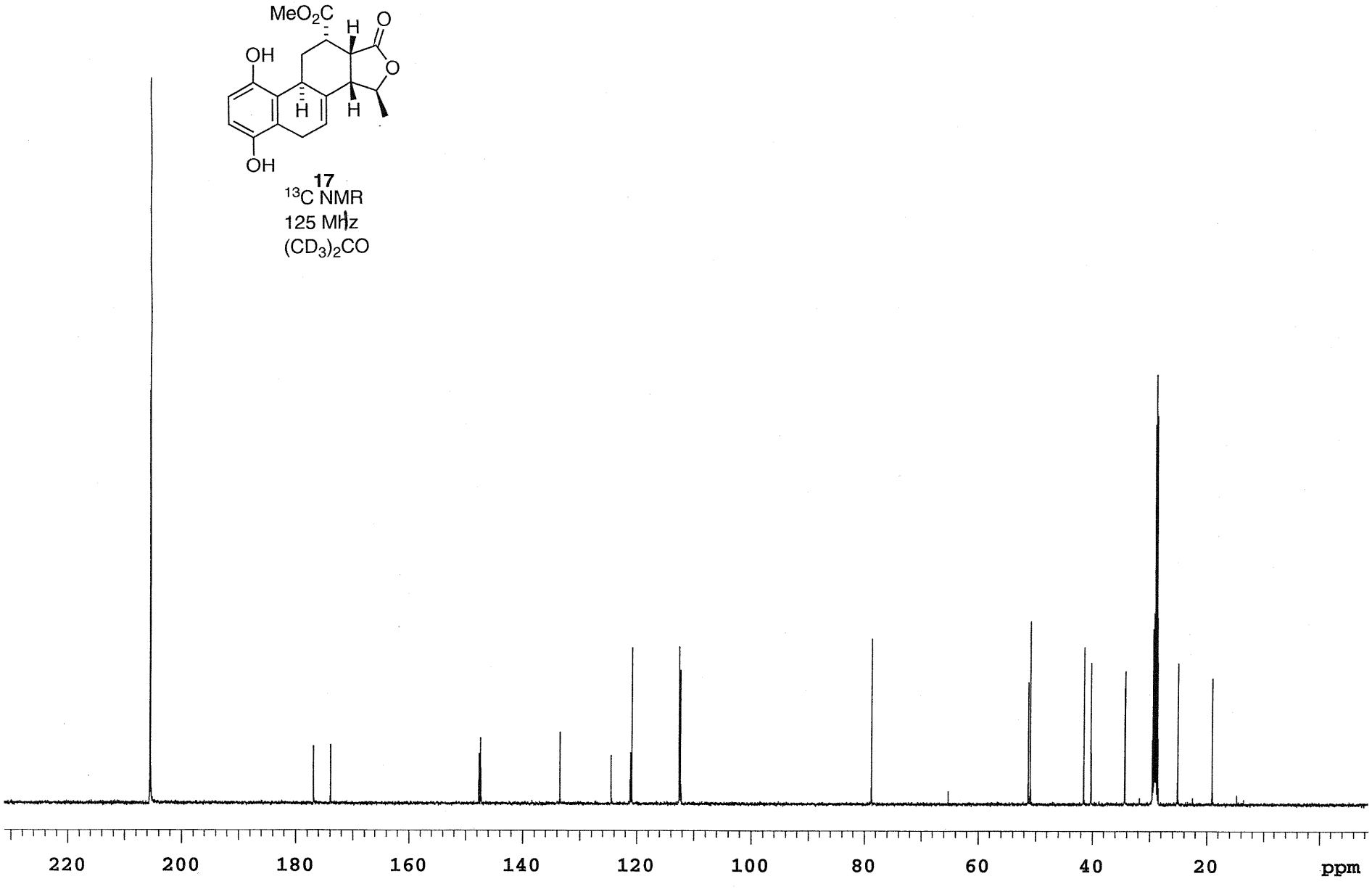


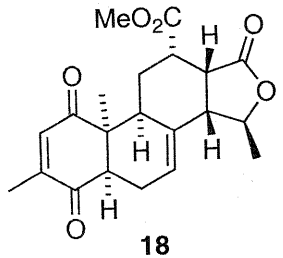
16
^{13}C NMR
75 MHz
$CDCl_3$





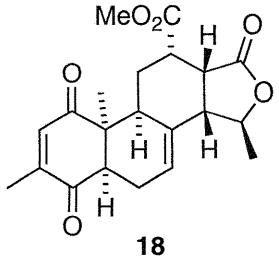
17
^{1}H NMR
300 MHz
$(CD_3)_2CO$


MeO2C
H
O
OH
O
H
H
OH
17
13C NMR
125 MHz
(CD3)2CO
220
200
180
160
140
120
100
80
60
40
20
ppm



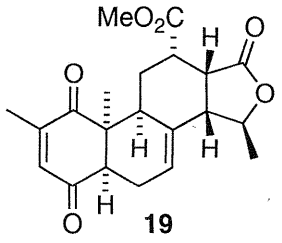
18

^{1}H NMR
500 MHz
$CDCl_3$



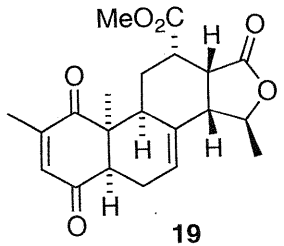
18

^{13}C NMR
125 MHz
$CDCl_3$



19

^{1}H NMR
500 MHz
$CDCl_3$

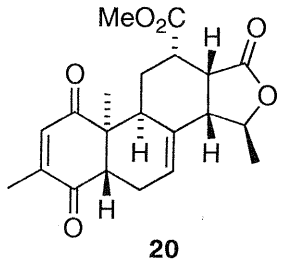


19

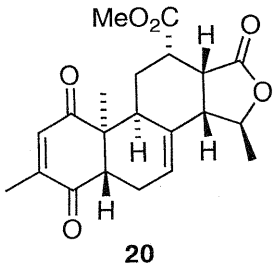
^{13}C NMR

125 MHz

$CDCl_3$



20
^{1}H NMR
500 MHz
$CDCl_3$

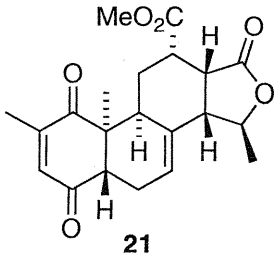


20

^{13}C NMR

125 MHz

$CDCl_3$

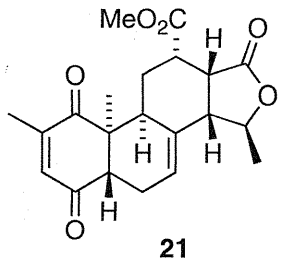


21

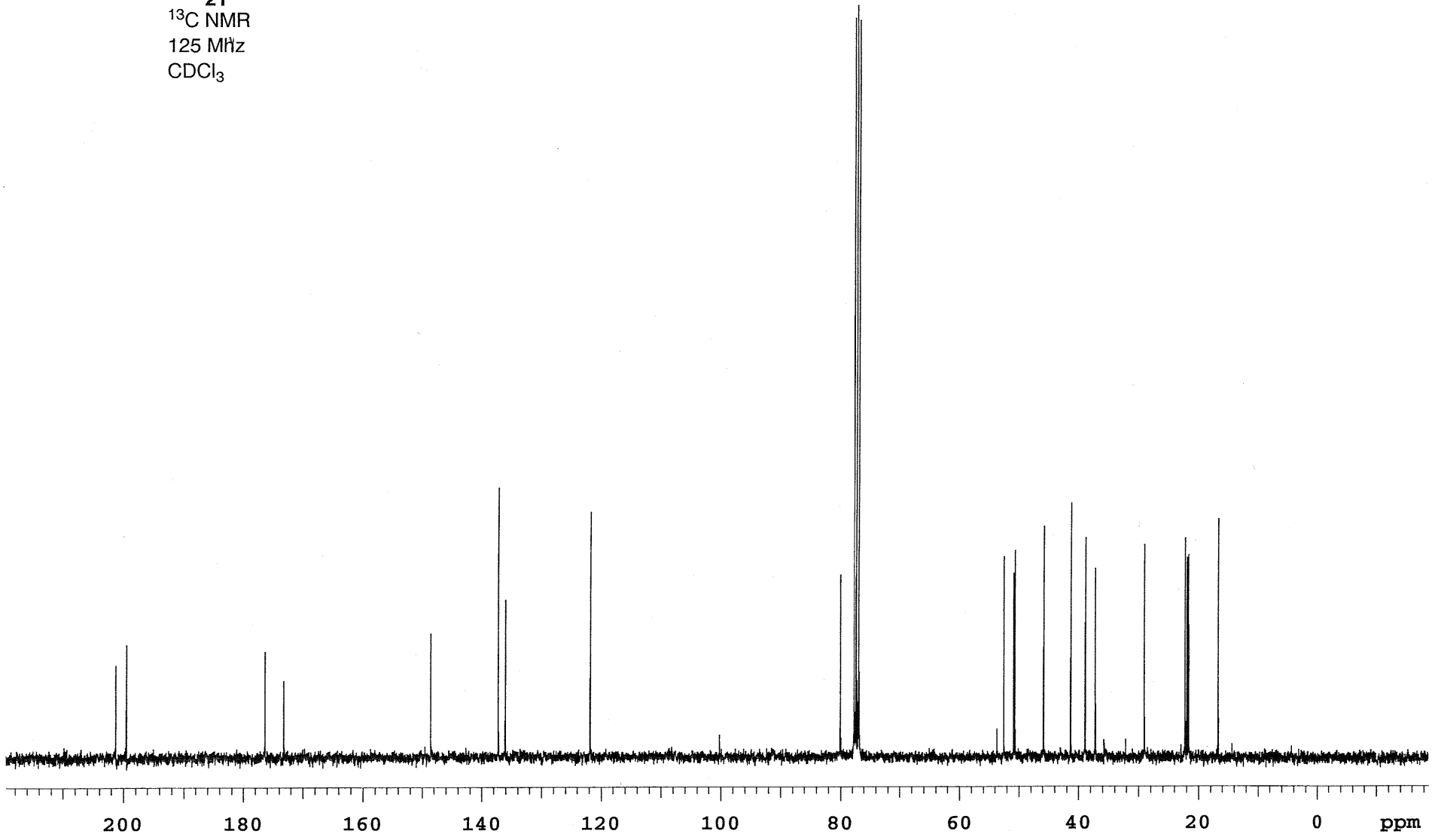
^{1}H NMR

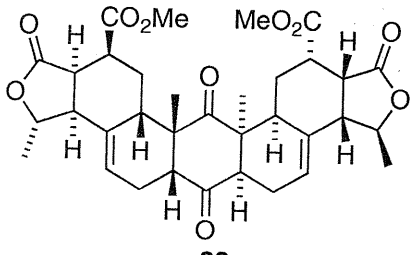
500 MHz

$CDCl_3$



21
^{13}C NMR
125 MHz
$CDCl_3$



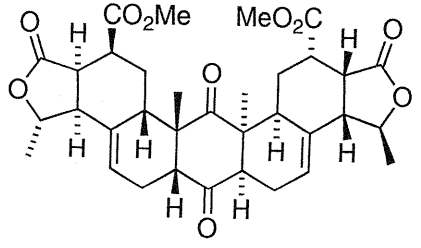


22

^{1}H NMR

500 MHz

C_6D_6

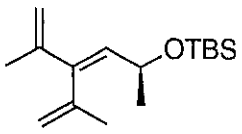


22

^{13}C NMR

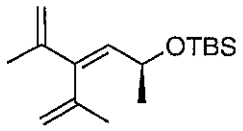
125 MHz

C_6D_6



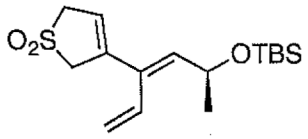
23

^{1}H NMR
300 MHz
$CDCl_3$

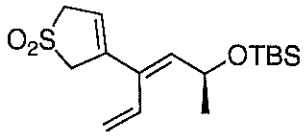


23

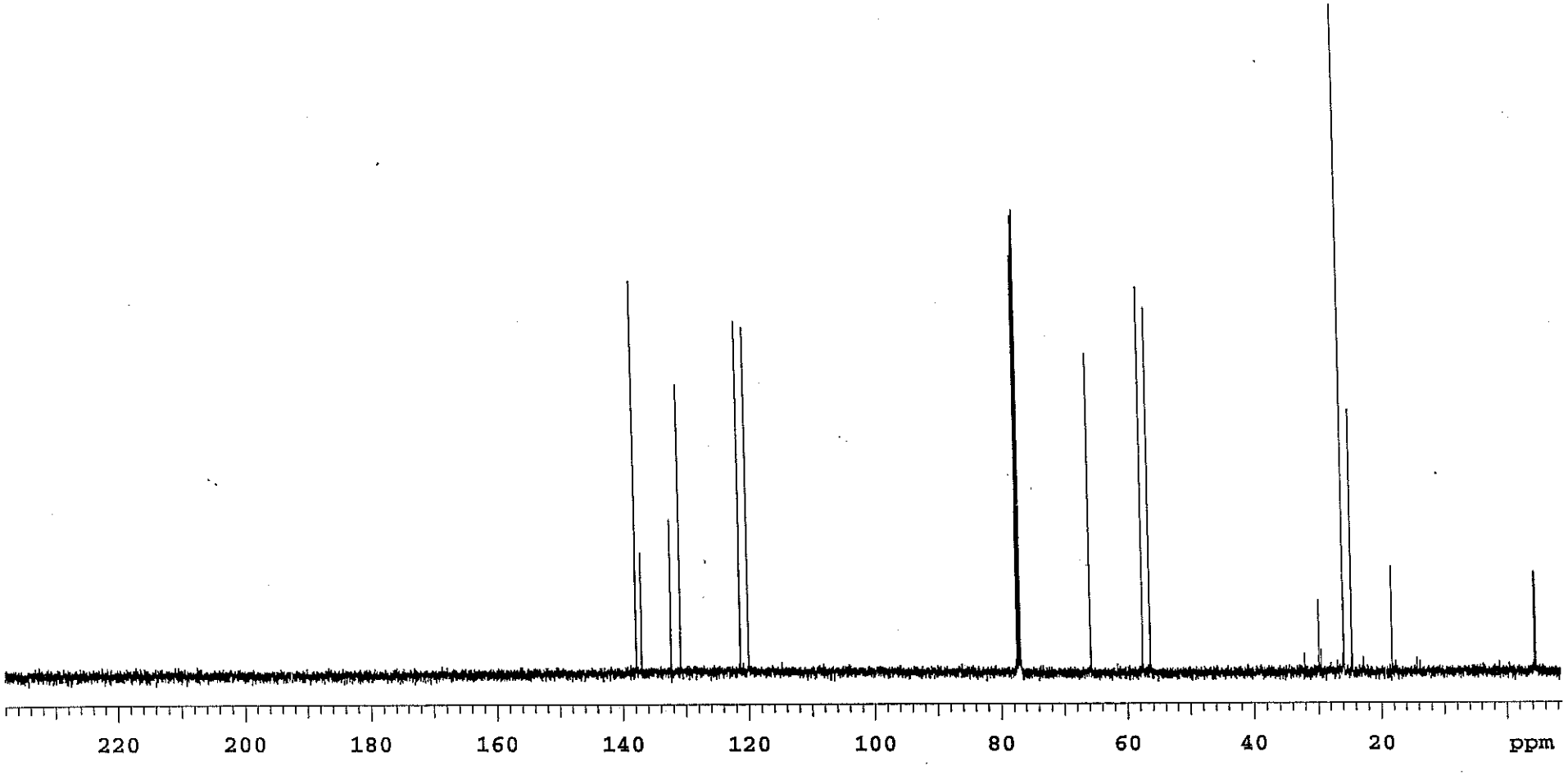
^{13}C NMR
100 MHz
$CDCl_3$

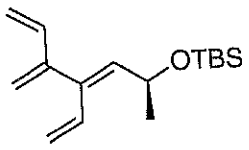


25
^{1}H NMR
500 MHz
$CDCl_3$



25
^{13}C NMR
125 MHz
$CDCl_3$



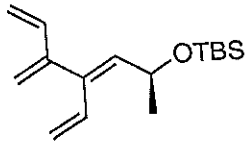


26

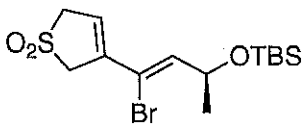
^{1}H NMR

500 MHz

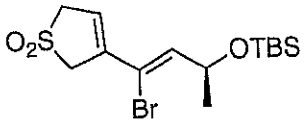
C_6D_6



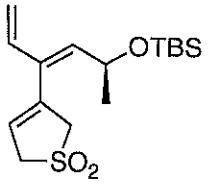
26
^{13}C NMR
125 MHz
C_6D_6



27
^{1}H NMR
500 MHz
$CDCl_3$

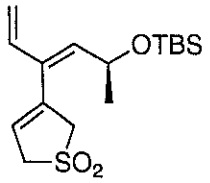


27
^{13}C NMR
125 MHz
$CDCl_3$



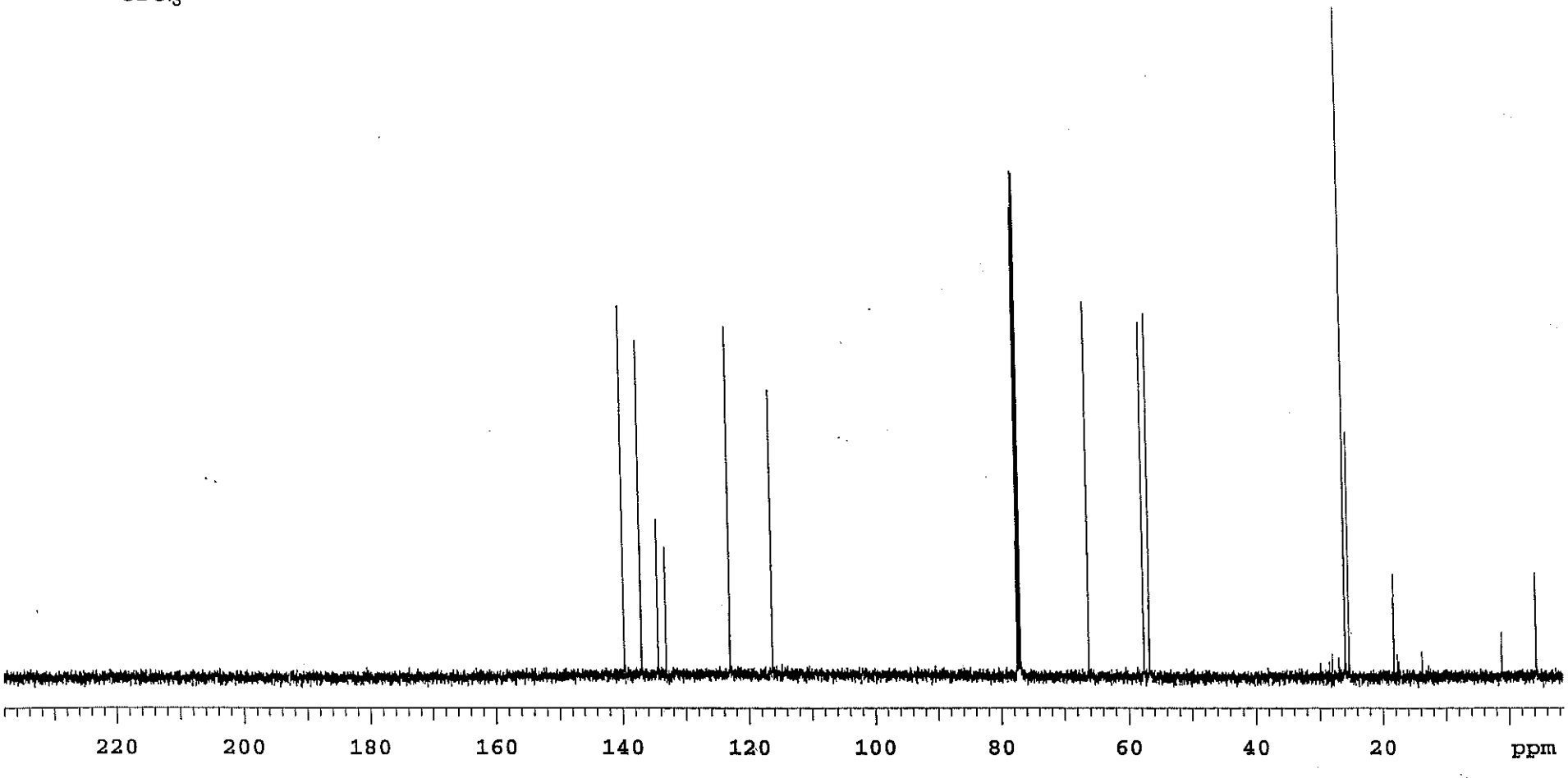
28

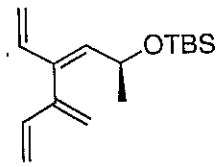
^{1}H NMR
500 MHz
$CDCl_3$



28

^{13}C NMR
125 MHz
$CDCl_3$



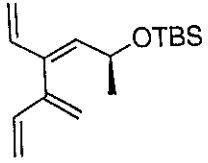


29

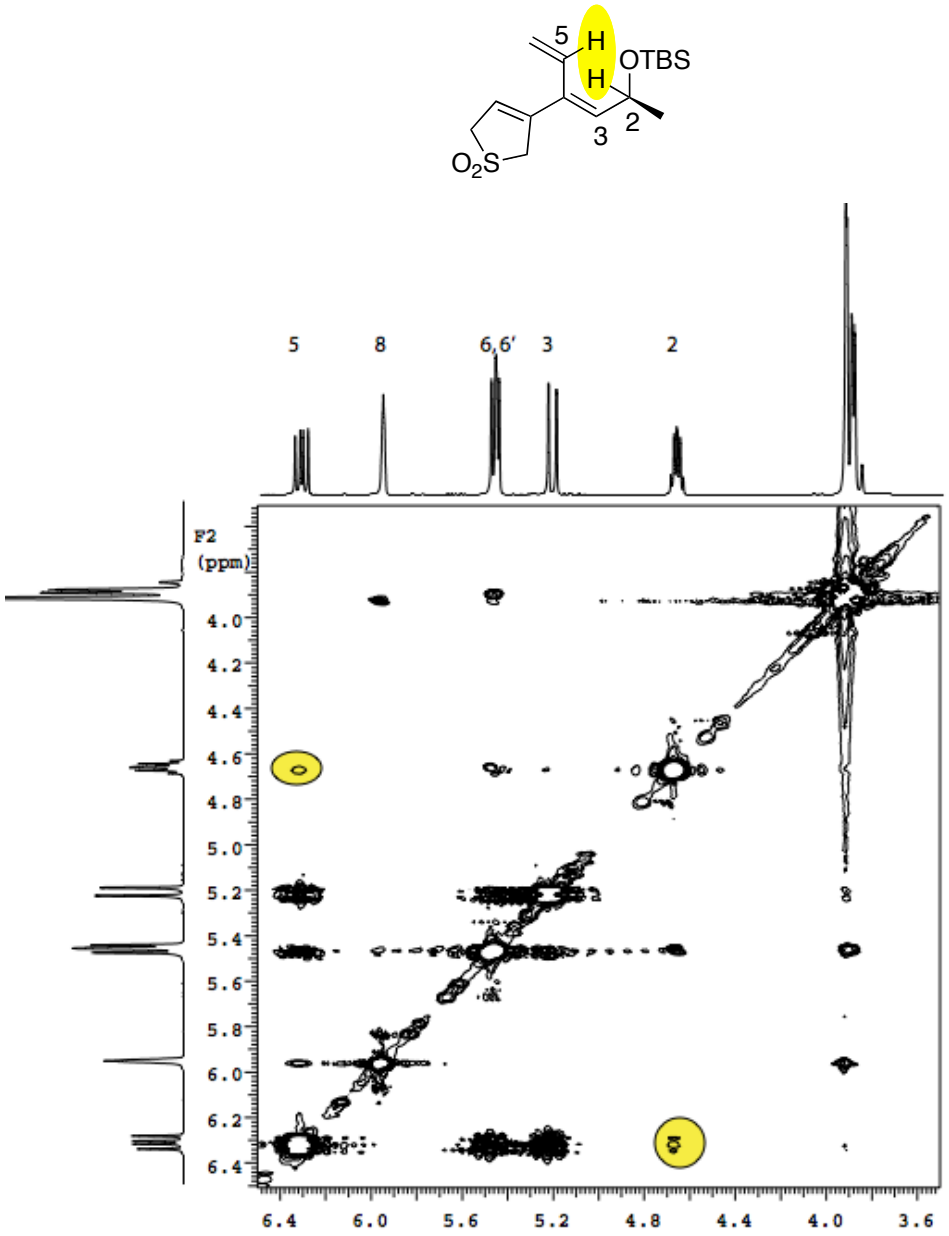
^{1}H NMR

500 MHz

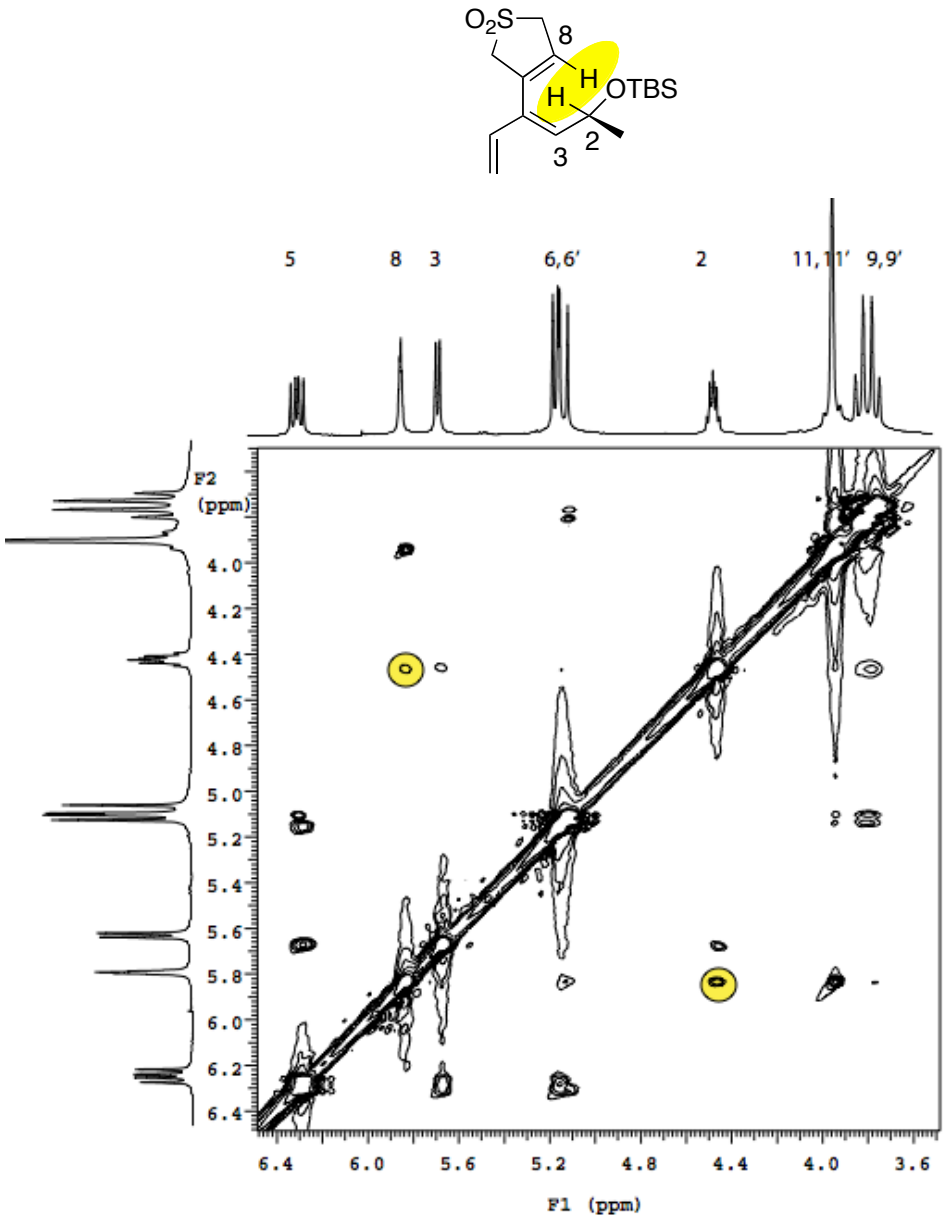
C_6D_6



29
^{13}C NMR
125 MHz
C_6D_6



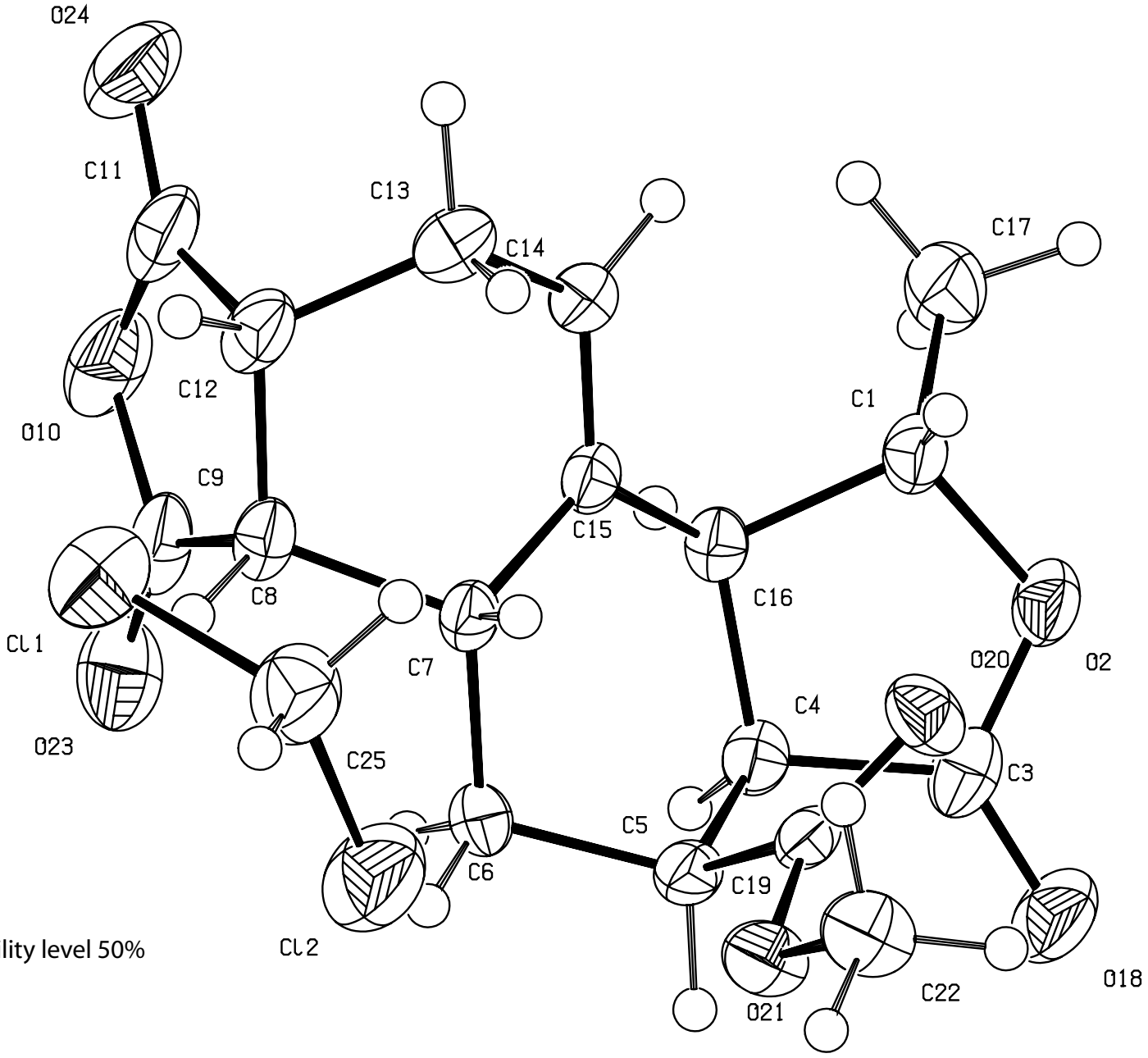
NOESY spectrum of [4]dendralene precursor **25**.



NOESY spectrum of [4]dendralene precursor **28**.

Compound **11**

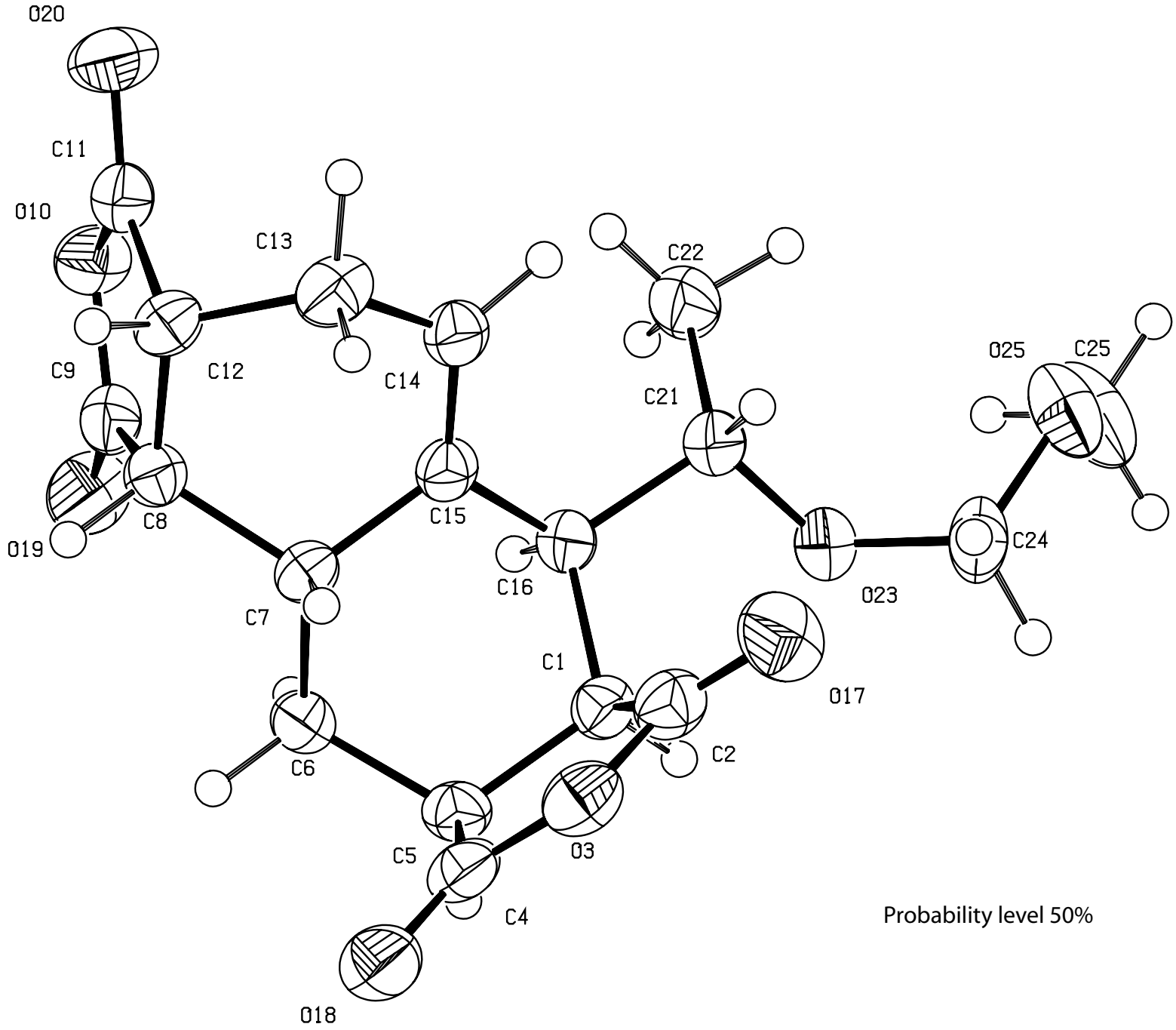
CCDC-609960



Probability level 50%

Compound **15**

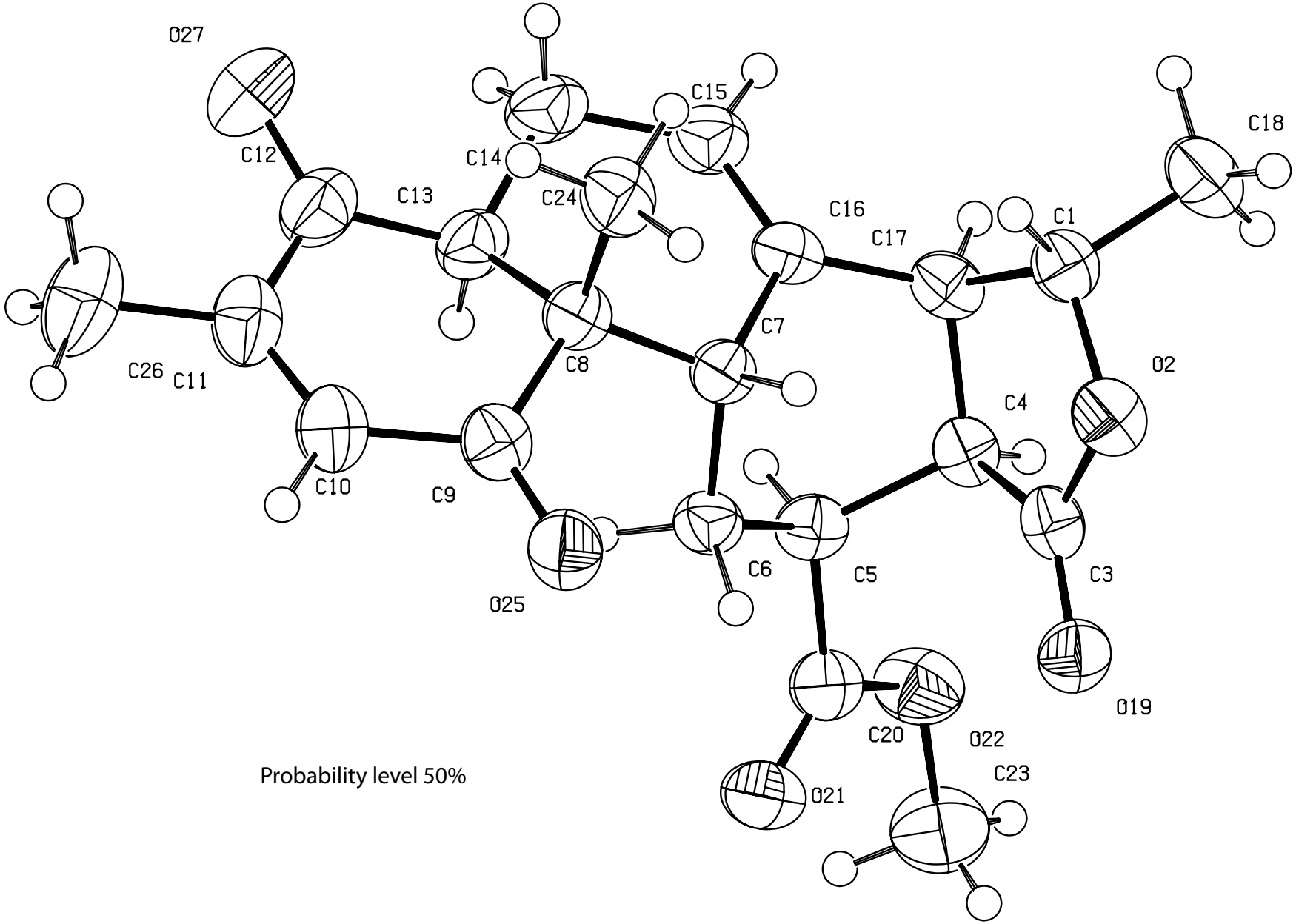
CCDC-609961



Probability level 50%

Compound **20**

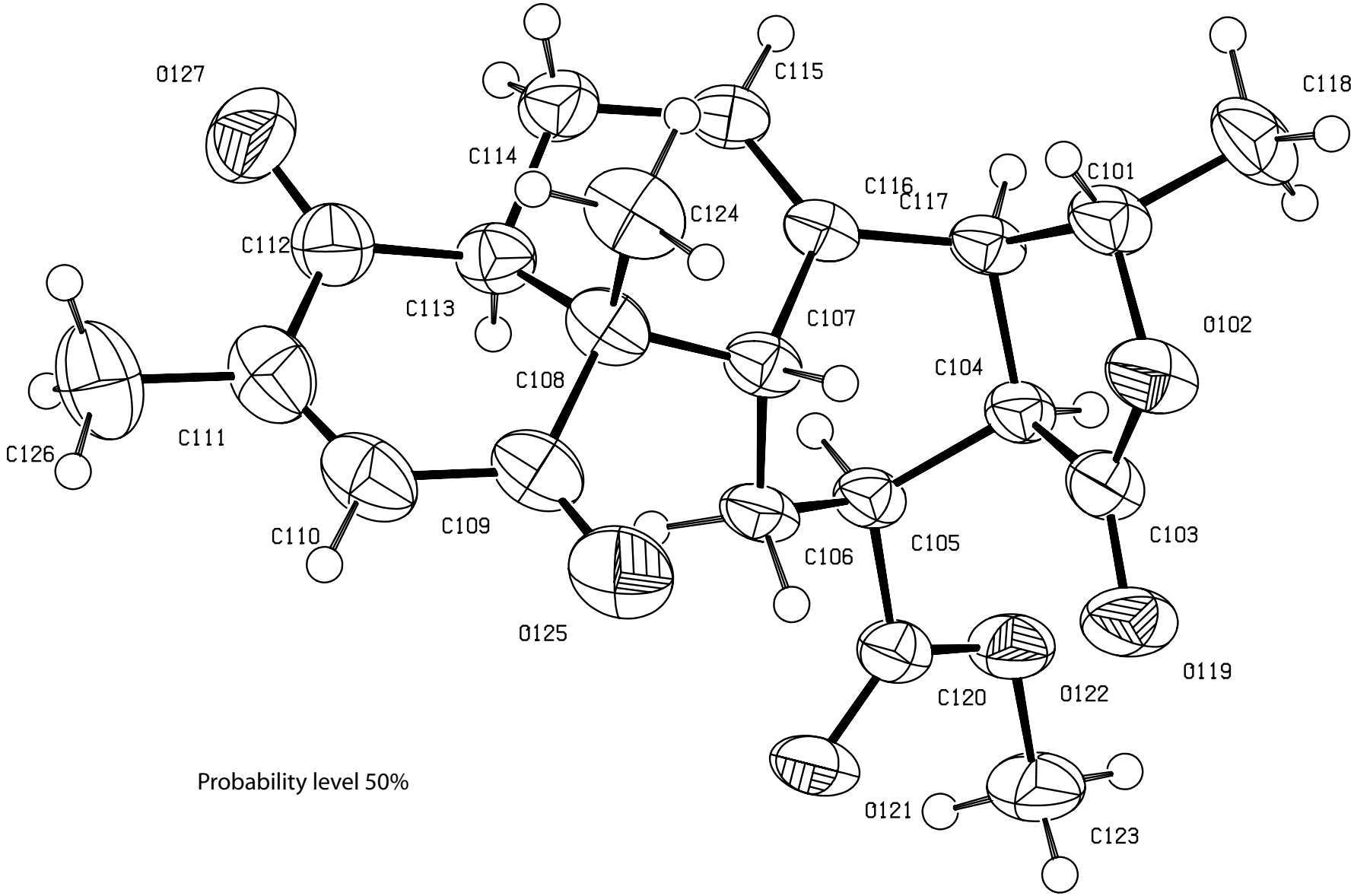
CCDC-609963



Probability level 50%

Compound **20**

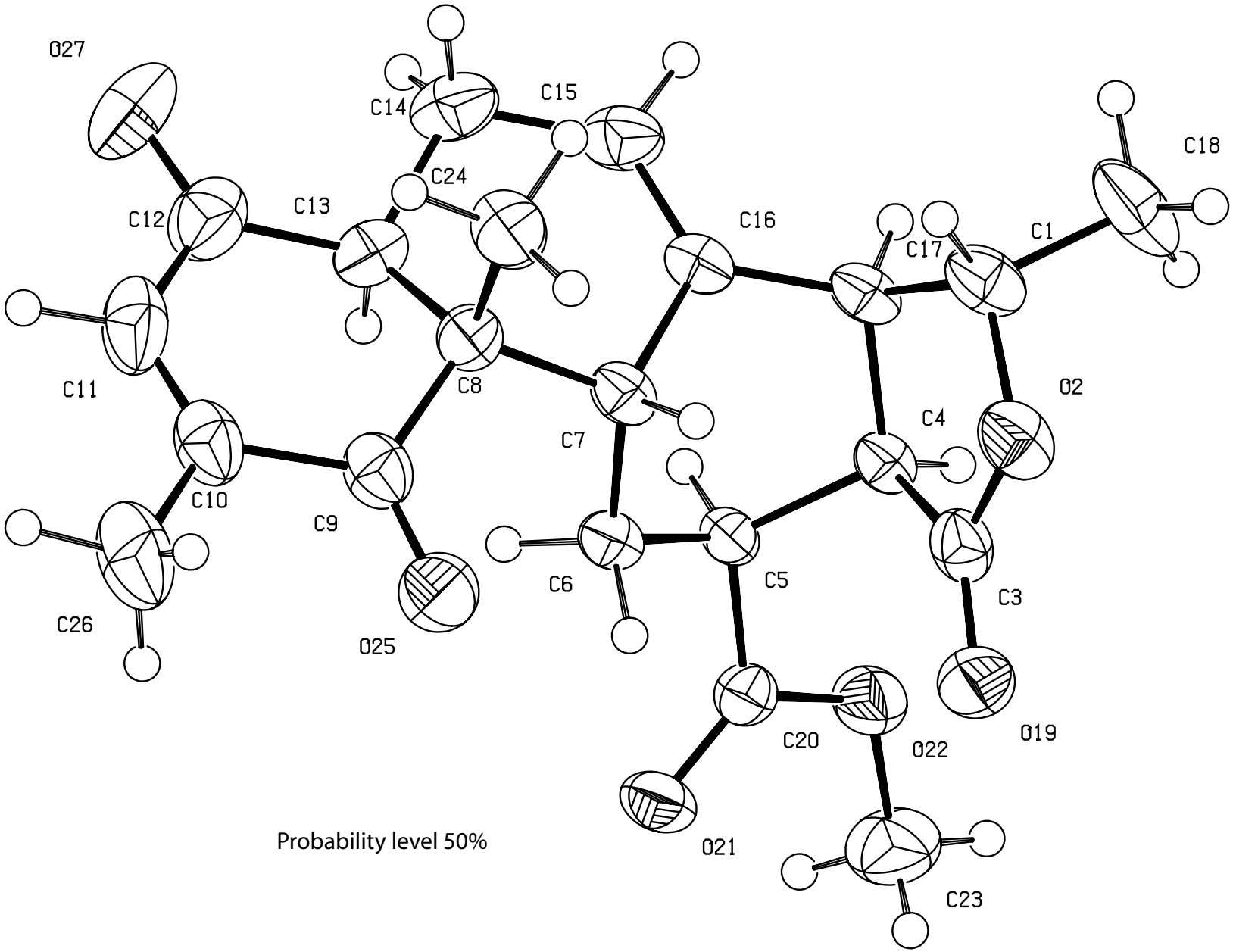
CCDC-609963



Probability level 50%

Compound **21**

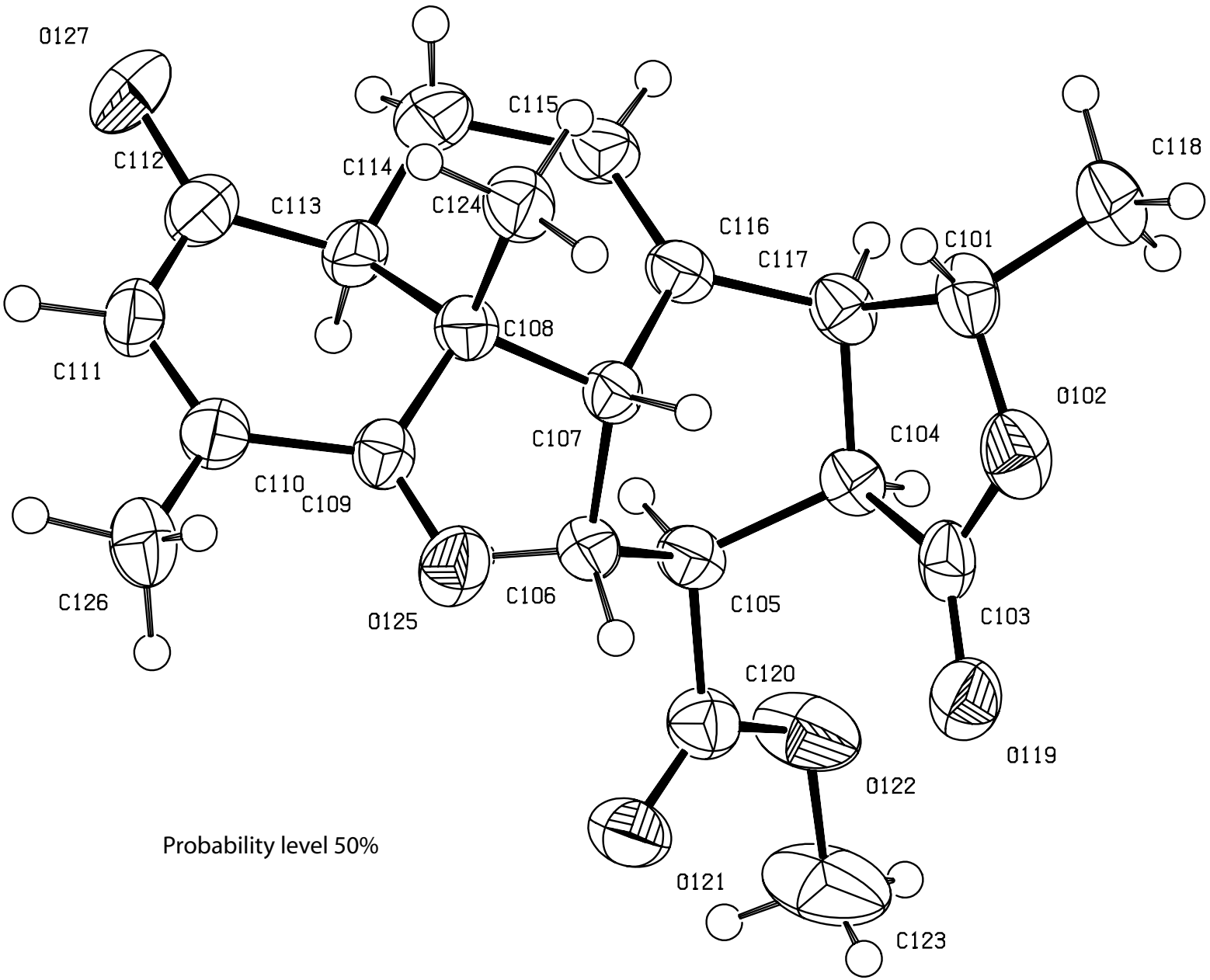
CCDC-609962



Probability level 50%

Compound **21**

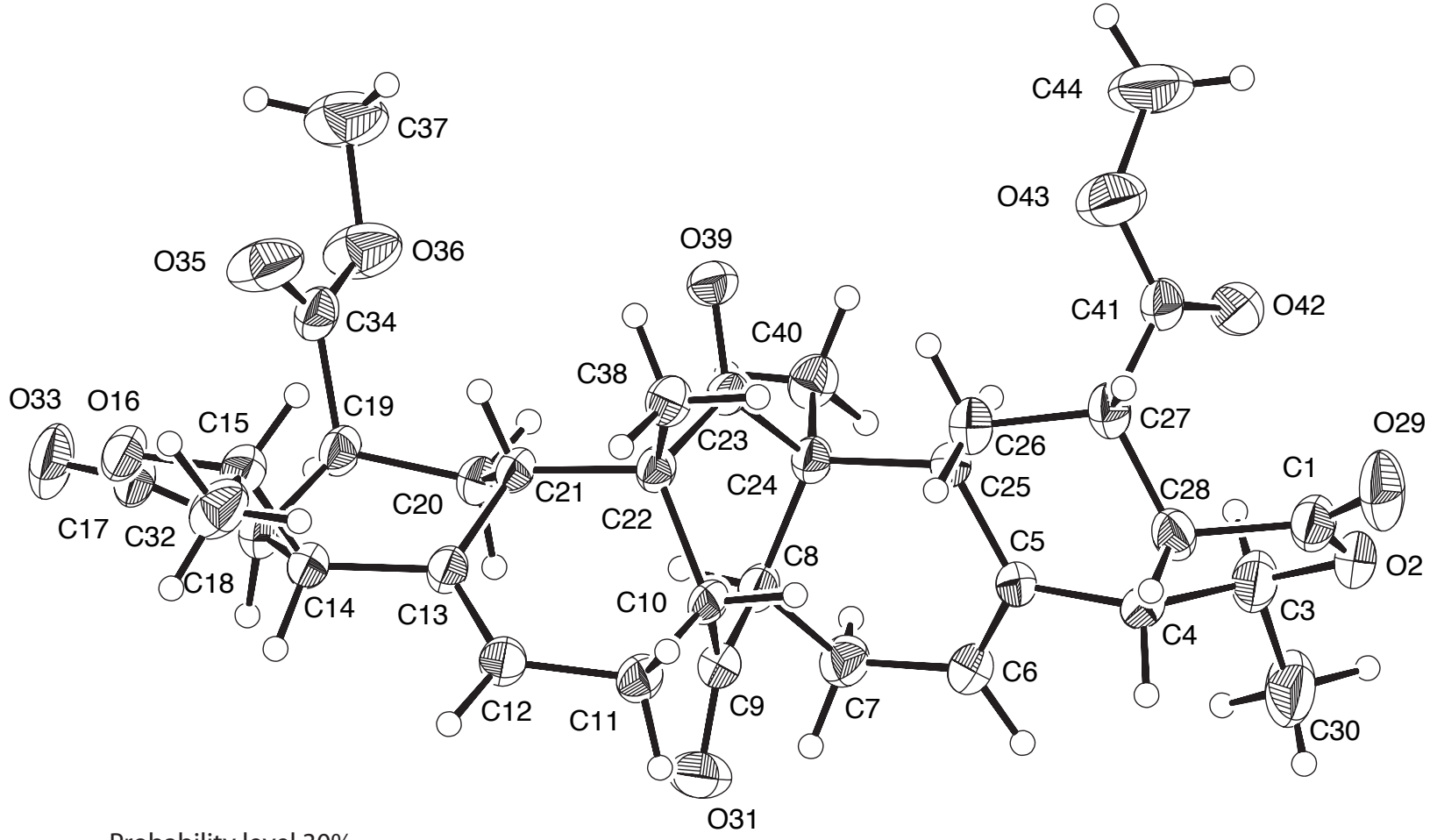
CCDC-609962



Probability level 50%

Compound **22**

CCDC-609964



Probability level 30%