Supporting Information

Total Synthesis and Absolute Stereochemical Assignment of Kibdelone C

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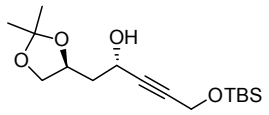
I. General Information: ^{1}H NMR spectra were recorded at 400 MHz or 500 MHz at ambient temperature with $CDCl_3$, MeOD, or CD_3CN (Cambridge Isotope Laboratories, Inc.) as solvents unless otherwise stated. Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, br = broad, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants. ^{13}C NMR spectra were recorded at 125.0 MHz at ambient temperature with the same solvents unless otherwise stated. Chemical shifts are reported in parts per million relative to $CDCl_3$ (^{1}H, δ 7.26; ^{13}C, δ 77.0), C_6D_6 (^{1}H, δ 7.15;), DMSO-D_6 (^{1}H, δ 2.49; ^{13}C, δ 39.4) or CD_3OD (^{1}H, δ 3.35, 4.78; ^{13}C, δ 49.3). All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer. High-resolution mass spectra were obtained in the Boston University Chemical Instrumentation Center using a Waters Q-TOF mass spectrometer. Melting points were recorded on a Mel-temp (Laboratory Devices). Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 200-400 mesh silica gel (Scientific Absorbents, Inc.). Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise noted. The Arthur™ Suite Reaction Planner (Symyx Technologies, Inc.) was used for experimental procedure planning.

Analytical LC-MS experiments were performed using a Waters Acquity UPLC (Ultra Performance Liquid Chromatography) with a Binary solvent manager, SQ mass spectrometer, Water 2996 PDA (PhotoDiode Array) detector, and Evaporative Light Scattering Detector (ELSD). An Acquity UPLC BEH C18 1.7 µm column was used for analytical UPLC-MS. HPLC grade tetrahydrofuran, methylene chloride, diethyl ether, toluene, acetonitrile, and benzene were purchased from Fisher and VWR and were purified and dried by passing through a PURE SOLV® solvent purification system (Innovative Technology, Inc.). Other ACS grade solvents for chromatography were purchased from Clean Harbors. All other reagents and relevant catalysts were purchased from Sigma-Aldrich, Acros, Alfa Aesar, and Strem Chemicals. Zinc bromide was fused using a torch under high vacuum prior to dissolution in diethyl ether. Magnesium iodide (98% from Sigma Aldrich) was dried in a vacuum oven overnight at 110 °C. Optically pure (4*S*)-(+)-4-(2-Hydroxyethyl)-2,2-dimethyl-1,3-dioxolane was purchased from Sigma-Aldrich. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm and are recorded as $[\alpha]^{22}$ D (concentration in grams/100 mL solvent). Electronic ^{1}H and ^{13}C NMR spectra of natural kibdelone C **3**, were kindly provided to us by Prof. Capon of the University of Queensland.

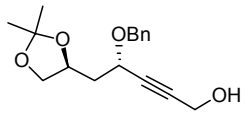
II. Experimental Procedures and Compound Characterization



26

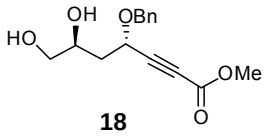
Propargylic alcohol 26. To a 3 L 3-necked round bottom flask equipped with mechanical stirrer was added *tert*-Butyldimethyl(2-propynyloxy)silane (32.7 mL, 156 mmol) and 1 L of anhydrous toluene. The solution was degassed under nitrogen, cooled to 0 °C, and 2.3 M butyllithium (65.0 mL, 149 mmol) was added slowly *via* cannula. After stirring 30 minutes, 287 mL of a 1.0 M solution of zinc dibromide in diethyl ether was added and the solution was slowly cooled to -78 °C. A solution of [(4S)-2,2-dimethyl-1,3-dioxolan-4-yl]acetaldehyde[S1] **16** (6.57 g, 45.6 mmol) in 100 mL of anhydrous toluene was slowly added to the reaction *via* cannula, the reaction was warmed to -40°C, and allowed to stir at that temperature overnight. The reaction was quenched with 500 mL saturated NH_4Cl and warmed to rt. The organic layer was separated, washed with brine, dried over sodium sulfate, and concentrated *in vacuo.* Purification on silica gel provided 10.53 g (74%) of **26** as a yellow oil. ^{1}H NMR (400 MHz, ($CDCl_3$) δ ppm 4.63 (brs, 1H), 4.55-4.45 (m, 2H), 4.35 (d, *J* = 1.61 Hz, 1H), 4.10 (dd, *J* = 8.13, 6.12 Hz, 1H), 3.64-3.56 (m, 1H), 2.87 (d, *J* = 6.68 Hz, 1H), 2.04-1.84 (m, 2H), 1.42 (s, 3H), 1.36 (s, 3H), 0.90 (s, 9H), 0.11 (s, 6H) ^{13}C NMR (100.0 MHz, $CDCl_3$) δ ppm 100.9, 85.1, 83.3, 72.9, 69.2, 59.5, 51.5, 40.7, 26.7, 25.6, 25.5, 18.1, -5.3. IR (oil) νmax: 3446, 2986, 2954, 2930, 2858, 2884, 1472, 1370, 1253, 1138, 1069, 834, 777. HR-MS: *m/z* Calcd. For $[C_{16}H_{30}O_4Si+Na]+$ 337.1811, Found 337.1800 (-3.2623 ppm). $[\alpha]_D^{23}$ = -17.6° (c = 0.50, $CHCl_3$).

[S1] Lebar, M.D.; Baker, B.J., *Tetrahedron Lett.* **2007**, *48* 8009–8010.



17

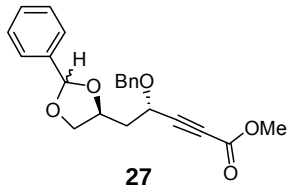
Propargylic alcohol 17. To a degassed mixture of **26** (10.53 g, 33.5 mmol) in 100 mL of anhydrous THF at 0 °C was added sodium hydride (60% dispersion in mineral oil) (2.66 g, 66.5 mmol). After hydrogen gas evolution had ceased, benzyl bromide (4.94 mL, 42 mmol) was added and the solution was heated to 45 °C overnight. The reaction was quenched with ice, the aqueous layer extracted 1 x 100 mL of EtOAc, and the combined organics washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The crude yellow residue was dissolved in 100 mL of anhydrous THF, cooled to 0 °C and the flask was charged with 35 mL of a 1.0 M solution of tetrabutylammonium fluoride and stirred for 30 minutes. The reaction was quenched with 100 mL of saturated NH_4Cl, the aqueous layer extracted with 1 x 100 mL of EtOAc, and the combined organics washed with brine, dried over sodium sulfate, filtered, and concentrated *in vacuo*. Purification on silica gel (10-40 % EtOAc in hexane) provided 6.80 g (68%) of **17** as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38 -7.27 (m, 5H), 4.64 (dd, *J* = 115.94, 11.63 Hz, 2H), 4.31 (s, 2H), 4.03 (dd, *J* = 13.00, 6.96 Hz, 1H), 3.09-4.04 (m, 1H), 3.57 (t, *J* = 7.64, 7.64 Hz, 1H), 2.09 -1.96 (m, 2H), 1.80 (brs, 1H), 1.39 (s, 3H), 1.34 (s, 3H) ^{13}C NMR (100.0 MHz, $CDCl_3$) δ ppm 137.5, 128.2, 127.7, 127.6, 108.4, 84.4, 83.7, 72.5, 70.7, 69.4, 65.6, 50.5, 40.1, 26.8, 25.5 IR (oil) νmax: 3390, 3031, 2986, 2935, 2870 1496, 1454, 1371, 1330, 1214, 1114, 1063, 1027, 832, 738, 697 HR-MS: *m/z* Calcd. for $[C_{17}H_{22}O_4+Na]+$ 313.1416, Found 313.1416 $[\alpha]_D^{23}$ = -7.2° (c = 1.0, $CHCl_3$).



18

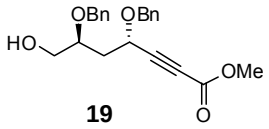
Ynoate diol 18. A 250 mL round bottom flask equipped with magnetic stir bar was charged with propargylic alcohol **17** (6.80 g, 23.4 mmol) and 80 mL of ethyl acetate. The solution was charged with IBX (13.1 g, 46.8 mmol), the flask was equipped with a reflux condenser, and heated to reflux for 3 h. The solution was cooled to 0 °C and the white solids were removed by filtration through Celite. The solvents were evaporated *in vacuo* and the clear residue (propargylaldehyde) was dissolved in 200 mL of a 1:1 mixture of 2-methyl-2-butene and *t*-butanol. The solution was cooled to 0 °C and a solution of sodium chlorite (13.2 g, 117 mmol) and sodium-phosphate monobasic monohydrate (16.2 g, 117 mmol) in 100 mL water was added dropwise *via* addition funnel over 20 minutes. The solution was allowed to stir for 2 h, quenched with 150 mL 1.0 M HCl, and extracted 2 x 200 mL with EtOAc. The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated *in vacuo*. The pale yellow residue was dissolved in 100 mL of methanol, cooled to 0 °C, and 15 mL of concentrated sulfuric acid added dropwise. The solution was slowly warmed to rt and allowed to stir at that temperature for 4 h. The reaction was diluted with 500 mL EtOAc, neutralized with 500 mL concentrated aq. $NaHCO_3$, and the aqueous layer extracted 1 x 200 mL EtOAc. The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated *in vacuo*. Purification on silica gel (0-50% EtOAc : CH_2Cl_2) afforded 4.91 g (75 %) of ynoate diol **18** as a white solid. mp 44-46 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$) 7.36-7. (m, 5H), 4.68 (dd, *J* = 165.81, 11.58 Hz, 2H), 4.54-4.52 (m, 1H), 4.12-4.06 (m, 1H), 3.81 (s, 3H), 3.65 (dd, *J* = 11.17, 3.44 Hz, 1H), 3.47 (dd, *J* = 11.17, 6.41 Hz, 1H), 2.02-1.88 (m, 2H) 1.52-1.49 (m, 1H), 1.33-1.28 (m, 1H) δ ppm ^{13}C NMR (125.0 MHz, $CDCl_3$) δ ppm 153.5,

136.7, 128.4, 127.9, 85.6, 77.4, 71.3, 68.2, 66.2, 65.5, 52.7, 38.0. IR (solid) νmax: 3417, 3030, 2954, 2873, 2235, 1715, 1497, 1454, 1434, 1250, 1074, 748, 698 HR-MS: *m/z* Calcd. for $[C_{15}H_{18}O_5+Na]+$301.1052, Found 301.1050 (-0.6642 ppm). $[\alpha]_D^{23}$ = -75.2° (c = 1.0, MeOH).



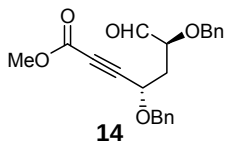
27

Ynoate Acetal 27. To a solution of diol **18** (4.90 g, 17.6 mmol) in anhydrous THF was added *p*-toluenesulfonic acid (280 mg, 1.6 mmol) and benzaldehyde dimethyl acetal (3.6 mL, 24 mmol). The solution was degassed under argon, equipped with a reflux condenser, and was heated to reflux overnight. The solvents were concentrated *in vacuo.* Purification on silica gel (0-5% EtOAc : CH_2Cl_2) provided 5.52 g (86%) of **27** as a colorless resin isolated as a 4:5 mixture of acetal diastereomers. Underlined shifts correspond to the major diastereomer as determined by integration. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.47-7.29 (m, 10H), 5.90 (s, 1H), 5.78 (s, 1H), 4.83 (dd, *J* = 11.38, 1.58 Hz, 2H), 4.51 (dd, *J* = 11.38, 1.46 Hz, 2H), 4.48-4.45 (m, 2H), 4.42 (dd, *J* = 12.87, 6.56 Hz, 2H), 4.27 (dd, *J* = 8.27, 6.22 Hz, 1H), 4.13 (dd, *J* = 7.99, 6.74 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.76 (dd, *J* = 8.02, 6.23 Hz, 1H), 3.66 (dd, *J* = 8.31, 6.87 Hz, 1H), 2.18-2.15 (m, 2H), 2.09 (ddd, *J* = 14.31, 9.93, 4.45 Hz, 2H) ^{13}C NMR (125.0 MHz, $CDCl_3$) δ ppm 153.6 153.5, 138.3, 137.7, 137.2, 137.1, 129.4, 129.2, 128.5, 128.4, 128.1, 126.7, 126.5, 104.0, 103.0, 86.0, 85.8, 77.63, 77.60, 73.2, 72.6, 71.6, 70.7, 70.2, 65.5, 65.5, 52.9, 52.9, 39.7, 39.2 νmax: 3032, 2954, 2871, 2234, 1715, 1454, 1434, 1380, 1248, 1088, 1069, 1026, 974, 915, 848, 749, 697 HR-MS: *m/z* Calcd. for $[C_{22}H_{22}O_5+K]+$ 405.1104, Found 405.1104 $[\alpha]_D^{23}$ = -67.2° (c = 1.0, $CHCl_3$).



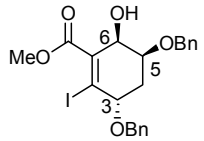
19

Bis-benzyl ether 19. A solution of acetal **27** (5.50 g, 15.0 mmol) in 60 mL of anhydrous CH_3CN was degassed with argon, cooled to 0 °C, and was charged with sodium cyanoborohydride (2.36 g, 27.5 mmol). Chlorotrimethylsilane (9.52 mL, 75.0 mmol was added in one portion, and after gas evolution ceased, the flask was quickly transferred to a preheated oil bath at 50°C and heated for an additional 15 minutes. The reaction was quenched with ice and the aqueous layer extracted 2 x 100 mL with EtOAc. The combined organics were washed with brine, dried over sodium sulfate, filtered, and concentrated *in vacuo*. Purification on silica gel (0-30% EtOAc : CH_2Cl_2) afforded 4.67 g, (84 %) of alcohol **19** as a colorless resin. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.36-7.27 (m, 8H), 7.24-7.21 (m, 2H), 4.65 (dd, *J* = 122.13, 11.43 Hz, 2H), 4.42-4.36 (m, 3H), 3.80 (s, 3H), 3.75 (td, *J* = 8.16, 3.66, 3.66 Hz, 1H), 3.51 (ddd, *J* = 11.48, 7.07, 4.41 Hz, 1H), 2.12 (ddd, *J* = 14.56, 8.87, 3.49 Hz, 1H), 2.00 (ddd, *J* = 14.56, 9.71, 3.72 Hz, 1H), 1.76 (dd, *J* = 6.99, 5.44 Hz, 1H) ^{13}C NMR (125.0 MHz, $CDCl_3$) δ ppm 153.5, 138.0, 136.9, 128.4, 128.2, 128.0, 127.8, 127.7, 86.3, 77.3, 75.5, 71.9, 71.2, 52.7, 37.6 IR (oil); 3436, 3031, 2952, 2871, 2234, 1715, 1496, 1454, 1434, 1250, 1052, 1027, 745, 697 νmax: HR-MS: *m/z* Calcd. for $[C_{22}H_{24}O_5+Na]+$ 391.1521, Found 391.1532 (-2.8122 ppm). $[\alpha]_D^{23}$ = -76.0° (c = 1.0, $CHCl_3$).



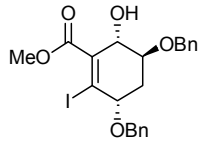
14

Ynoate aldehyde 14. A solution of *bis*-benzyl ether **19** (4.63 g, 12.6 mmol) in 100 mL ethyl acetate in a 250 mL round bottom flask equipped with magnetic stir bar was degassed under argon, charged with IBX (7.92 g, 28.3 mmol), and heated to reflux for 3 h. The solution was cooled to °C and the solids were filtered through a small pad of silica topped with Celite®. The organics were evaporated *in vacuo* to provide 4.31 g (94%) of **14** as a yellow resin. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.64 (d, *J* = 1.56 Hz, 1H), 7.36-7.27 (m, 8H), 7.26-7.23 (m, 2H), 4.69 (dd, *J* = 81.02, 11.42 Hz, 2H), 4.44 (dd, *J* = 9.94, 3.29 Hz, 1H), 4.36 (dd, *J* = 11.43, 4.93 Hz, 2H), 4.04 (ddd, *J* = 9.92, 3.33, 1.52 Hz, 1H), 3.79 (s, 3H), 2.24 (ddd, *J* = 14.42, 9.94, 3.39 Hz, 1H), 2.01 (ddd, *J* = 14.42, 9.91, 3.31 Hz, 1H) ^{13}C NMR (125.0 MHz, $CDCl_3$) δ ppm 201.7, 153.1, 136.8, 136.5, 128.2, 128.1, 127.9, 127.8, 85.2, 77.4, 72.5, 71.0, 63.6, 52.5, 35.4 IR (thin film); νmax: 3422, 3063, 3032, 2951, 2871, 2235, 1715, 1496, 1454, 1434, 1251, 1089, 1027, 747, 697 HR-MS: *m/z* $[C_{22}H_{22}O_5+Na]^+$ 389.1365, Found 389.1350 (-3.8547 ppm). $[\alpha]_D^{23}$ = -200° (c = 0.10, $CHCl_3$).



20

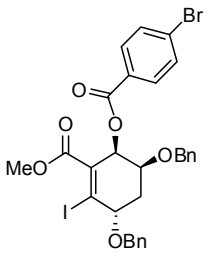
(3R,5R,6R) 2-Iodo-1-cyclohexenecarboxylate 20. To a 500 mL round bottom flask equipped with magnetic stir bar and argon balloon was added powdered magnesium iodide (7.36 g, 26.5 mmol) and 250 mL of anhydrous CH_2Cl_2. The solution was sonicated for 15 minutes and was then cooled to -78 °C. A solution of ynoate aldehyde **14** (4.31 g, 11.8 mmol), in 20 mL of anhydrous CH_2Cl_2 was added *via* cannula and the reaction was slowly warmed to -20°C and allowed to stir for 24 h. The reaction was quenched with 300 mL of a 1:1 solution of 1.0 M HCl and 1M citric acid and diluted with 500 mL EtOAc. The organics were washed 1 x 100 mL with water and 5 % sodium potassium tartrate followed by brine, dried over sodium sulfate, filtered, and concentrated *in vacuo.* Purification on silica gel (2 x 0-15% EtOAc : CH_2Cl_2) afforded 4.45 g (78%) of **20** as a pale yellow resin. ^{1}H NMR (500 MHz, C_6D_6) δ ppm 7.32-7.14 (m, 4H), 7.13-7.02 (m, 6H), 4.55 (brs, 1H), 4.27 (dd, *J* = 55.96, 11.39 Hz, 2H), 4.08-4.00 (m, 2H), 3.94 (t, *J* = 4.71, 4.71 Hz, 1H), 3.55 (ddd, *J* = 9.72, 3.76, 2.80 Hz, 1H), 2.54 (s, 1H), 1.95 (ddd, *J* = 13.85, 9.69, 4.42 Hz, 1H), 1.54 (dddd, *J* = 13.58, 5.04, 2.73, 0.69 Hz, 1H) ^{13}C NMR (125.0 MHz, $CDCl_3$) δ ppm 167.2, 140.4, 137.3, 137.2, 128.3, 128.1, 127.9, 127.8, 127.7, 107.5, 79.5, 72.5, 72.2, 71.0, 67.2, 52.2, 29.3 IR (thin film); νmax: 3495, 3087, 3061, 2948, 2868, 1727, 1632, 1496, 1453, 1433, 1395, 1241, 1065, 1027, 739, 698 HR-MS: *m/z* Calcd. for $[C_{22}H_{23}IO_5+Na]^+$ 517.0488, Found 517.0480 (-1.5472 ppm). $[\alpha]_D^{23}$ = -98° (c = 0.20, $CHCl_3$).



21

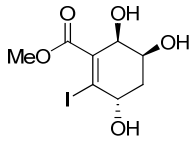
(3R,5R,6S) 2-Iodo-1-cyclohexenecarboxylate 21. Isolated as a minor product in above reaction to afford 535 mg (9%)of **21** as a clear resin. ^{1}H NMR (500 MHz, C_6D_6) δ ppm 7.31-7.26 (m, 2H), 7.20-7.04 (m, 8H), 4.42-4.39 (m, 1H), 4.34 (dd, *J* = 23.80, 11.79 Hz, 2H), 4.25 (dd, *J* = 11.78, 2.94 Hz, 2H), 3.94 (t, *J* = 4.53, 4.53 Hz, 1H), 3.64 (ddd, *J* = 9.74, 6.36, 3.04 Hz, 1H), 3.44 (s, 3H), 2.18 (d, *J* = 5.92 Hz, 1H), 1.92 (ddd, *J* = 13.64, 4.66, 3.19 Hz, 1H), 1.45 (ddd, *J* = 13.72, 9.96, 4.48 Hz, 1H) ^{13}C NMR (125.0 MHz, $CDCl_3$) δ 167.3, 141.5, 138.0, 137.5, 128.4, 128.3, 128, 127.9, 127.8, 127.7, 80.1, 75.2, 72.8, 72.4, 71.7, 52.3, 31.0 ppm 3449, 3085, 3030, 2949, 2868, 1726, 1496, 1453, 1251, 1060, 1027, 953, 878, 735, 697 IR

(thin film); νmax: 3495, 3087, 3061, 2948, 2868, 1727, 1632, 1496, 1453, 1433, 1395, 1241, 1065, 1027, 739, 698 HR-MS: *m/z* Calcd. for $[C_{22}H_{23}IO_5+Na]+$ 517.0488, Found 517.0471 (-3.2879 ppm). $[\alpha]_D^{23}$ = +20° (c = 0.20, $CHCl_3$).



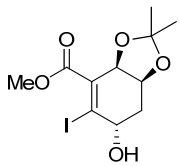
22

Bromobenzoate 22. To a solution of iodocyclohexene carboxylate **20** (50.0 mg, 0.102 mmol) in 3 mL of degassed anhydrous DMF in a 10 mL round bottom flask equipped with magnetic stir bar was added sodium hydride (60% dispersion in mineral oil, 8.09 mg, 0.204 mmol) After hydrogen gas evolution ceased, 4-bromobenzoyl chloride (33.6 mg, 0.153 mmol) was added and the solution was heated to 60 °C for 1 h. The solution was then cooled to 0 °C, quenched with ice, diluted with 20 mL EtOAc, washed 4 x 5 mL water, followed by brine, dried over sodium sulfate, filtered, and concentrated in *in vacuo.* Purification on silica gel (0-5% EtOAc : hexanes) provided 47 mg (68%) of **22** as a white solid. mp = 117-119°C (CH_2Cl_2). Crystals of **22** suitable for X-ray analysis were grown by slow evaporation from CH_2Cl_2:MeOH. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.81 (d, *J* = 8.71 Hz, 1H), 7.50 (d, *J* = 8.73 Hz, 1H), 7.32-7.24 (m, 4H), 7.18 (m, 6H), 6.10-6.08 (m, 1H), 4.62 (d, *J* = 11.81 Hz, 1H), 4.58 (s, 3H), 4.41 (d, *J* = 11.81 Hz, 1H), 4.32 (t, *J* = 3.66, 3.66 Hz, 1H), 3.99 (td, *J* = 11.53, 3.40, 3.40 Hz, 1H), 3.69 (s, 3H), 2.22 (ddd, *J* = 13.61, 11.50, 4.22 Hz, 1H), 2.03 (dtd, *J* = 13.64, 3.22, 3.19, 1.11 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.3, 164.7, 137.7, 137.2, 136.4, 131.7, 131.4, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 111.5 81.6, 73.2, 71.5, 70.4, 67.1, 52.6, 30.5 IR (solid); νmax: 3063, 3030, 2949, 2865, 1725, 1588, 1483, 1453, 1433, 1397, 1308, 1259, 1092, 1066, 1011, 1027, 960, 920, 846, 751, 753, 697, 682 HR-MS: *m/z* Calcd. For $[C_{29}H_{26}BrIO_5+Na]+$ 698.9855, Found 698.965 (-1.4306 ppm). $[\alpha]_D^{23}$ = -264° (c = 0.10, $CHCl_3$).



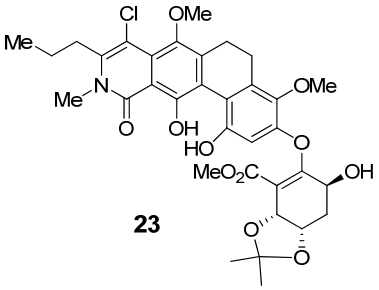
28

Triol 28. Iodocyclohexene carboxylate **20** (3.20 g, 6.50 mmol) was dissolved in 150 mL of CH_2Cl_2 in a 500 mL round bottom flask equipped with magnetic stir bar. The reaction mixture was degassed with argon and cooled to -78°C. A 1.0 M solution of boron trichloride in CH_2Cl_2 (24.0 mL) was added and the solution was stirred for 1 h. The reaction was quenched by addition of 50 mL methanol, slowly warmed to rt, and was allowed to stir at that temperature for 3 h. The solvents were concentrated *in vacuo* and the clear residue azeotroped with toluene (2 x 10 mL) to provide the triol as a tan solid which was taken into the acetonide formation without further purification. A small portion was purified by silica gel chromatography (5-15% MeOH:CH_2Cl_2) for characterization. Mp = 45-47°C (toluene). ^{1}H NMR (500 MHz, CD_3OD) δ ppm 4.35-4.30 (m, 2H), 4.00 (td, *J* = 9.22, 3.16, 3.16 Hz, 1H), 3.76 (s, 3H), 3.27 (td, *J* = 3.28, 1.65, 1.65 Hz, 1H), 2.25 (ddd, *J* = 14.12, 9.29, 4.69 Hz, 1H), 1.76 (ddd, *J* = 8.15, 5.73, 2.84 Hz, 1H) ^{13}C NMR (125 MHz, CD_3OD) δ ppm 169.8, 142.6, 111.1, 73.4, 70.0, 66.9, 52.7, 36.8 ; IR (thin film) νmax cm^{-1} 3401, 2955, 2878, 1078, 1723, 1434, 1041, 1334, 1267, 1207, 1135, 1060, 1070, 1023, 949, 917, 871, 834, 774, 624; HR-MS: calculated for: $[C_8H_{11}O_5+Na]^+$ 336.9549, found: 336.9562 (-3.8581 ppm). $[\alpha]_D^{23}$ = +32° (c = 0.10, MeOH).



13

***Iodocyclohexene acetonide* 13.** The crude triol **28** from the previous experiment (~2.1 g, 6.5 mmol) was dissolved in 100 mL of CH_2Cl_2 and 2,2-dimethoxypropane (1.90 mL, 16.20 mmol) was added. The reaction mixture was sonicated to break up the large chunks of solids. To the slurry was added (±)-10-camphorsulfonic acid (75 mg, 0.324 mmol) and the reaction mixture was heated at reflux until all of the solid triol had dissolved (~ 1 h). The solvents were removed *in vacuo.* Purification on silica gel (0-20 % EtOAc in CH_2Cl_2) provided 1.87 g (87%) of iodocyclohexene acetonide **13** as a white solid after azeotroping with toluene. Mp = 64-66 °C (toluene); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.77 (dd, *J* = 5.08, 1.70 Hz, 1H), 4.45 (dt, *J* = 4.74, 4.66, 2.58 Hz, 1H), 4.29 (dd, *J* = 8.51, 5.82 Hz, 1H), 3.78 (s, 3H), 3.26 (s, 1H), 2.54 (td, *J* = 14.22, 4.85, 4.85 Hz, 1H), 1.84 (ddd, *J* = 14.21, 9.39, 2.55 Hz, 1H), 1.30 (d, *J* = 5.71 Hz, 6H) ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 167.3, 137.9, 115.2, 109.7, 74.0, 71.9, 68.0, 52.5, 33.4, 27.5, 26.4; IR (solid) νmax 3381, 2982, 2948, 2359, 1725, 1604, 1431, 1382, 1365, 1340, 1303, 1233, 1213, 1200, 1143, 1063, 1026, 970, 936, 867, 847, 789 cm^{-1}; HR-MS: calculated for: $[C_{11}H_{15}O_5+Na]^+$ 376.9862, found: 376.9866 (-1.0610 ppm). $[\alpha]_D^{23}$ = +176° (c = 0.20, $CHCl_3$).

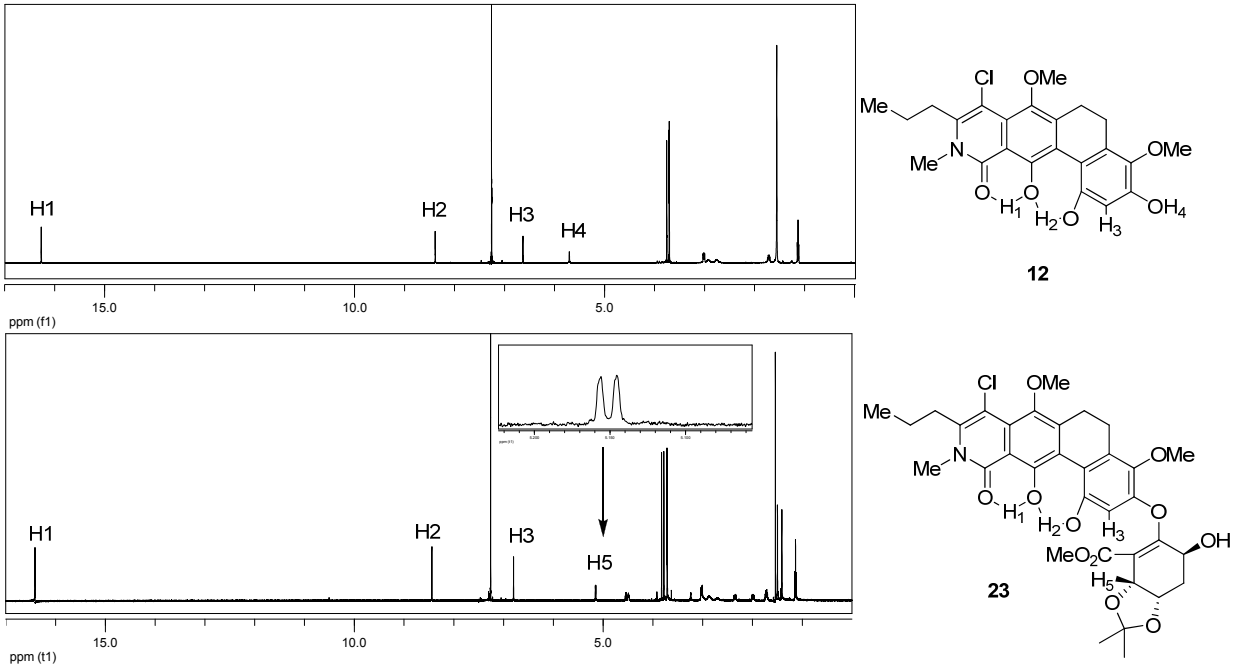


23

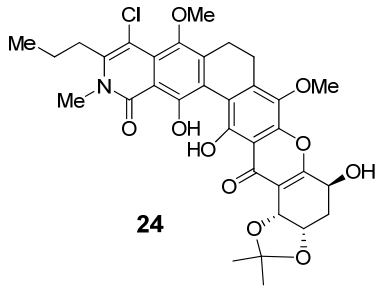
Vinylogous carbonate 23. To an oven dried 10 mL round bottom flask equipped with magnetic stir bar was added dihydrophenanthrene **12**,[S2] (157 mg, 0.353 mmol), iodocyclohexene acetonide **13** (200 mg, 0.282 mmol), and K_3PO_4 (180 mg, 0.847 mmol). The flask was degassed with argon, charged with 3.0 mL of anhydrous DMSO, and the reaction mixture was degassed further by vacuum and was heated to 50°C overnight. The dark solution was diluted with 150 mL EtOAc, cooled to 0 °C, and carefully acidified with 0.5 M $KHSO_4$. The organics were washed water (2 x 20 mL), brine, dried over sodium sulfate, filtered, concentrated *in vacuo,* and the residue purified on silica gel (5-30 % Et_2O in CH_2Cl_2) to provide 82 mg (44%) of **23** as a yellow solid. Mp. = 115-117 °C (CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 16.41 (s, 1H), 8.44 (s, 1H), 6.80 (s, 1H), 5.15 (d, *J* = 5.24 Hz, 1H), 4.54 (dt, *J* = 6.16, 6.12, 3.24 Hz, 1H), 4.51-4.47 (m, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H), 3.24 (brs, 1H), 3.05-2.99 (m, 2H), 2.87 (brs, 2H), 2.71 (brs, 2H), 2.38- ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 166.1, 165.7, 159.8, 152.0, 151.6, 148.6, 143.7, 142.4, 141.4, 140.1, 134.2, 126.9, 120.2, 117.4, 113.9, 110.2, 109.6, 109.3, 109.2, 73.2, 80.0, 62.7, 62.5, 62.0, 52.0, 33.4, 32.6, 32.0, 28.1, 26.2, 23.5, 22.1, 20.9, 14.1; IR (thin film) νmax 3052, 2963, 2836, 1658, 1619, 1603, 1479, 1465, 1258, 1108, 1069, 802 cm^{-1}; HRMS $[M+Na]^+$ calculated for $[C_{34}H_{38}NO_{11}+Na]^+$: 694.2031, found: 694.2051 (-2.8810 ppm). $[\alpha]_D^{23}$ = -88° (c = 0.20, $CHCl_3$).

[S2] Sloman, D.L.; Mitasev, B.; Scully, S.S.; Beutler, J.A.; Porco, J. A., Jr., *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 2511-2515.

Figure S1. ^{1}HNMR ($CDCl_3$) analysis of vinylogous carbonate **23**.



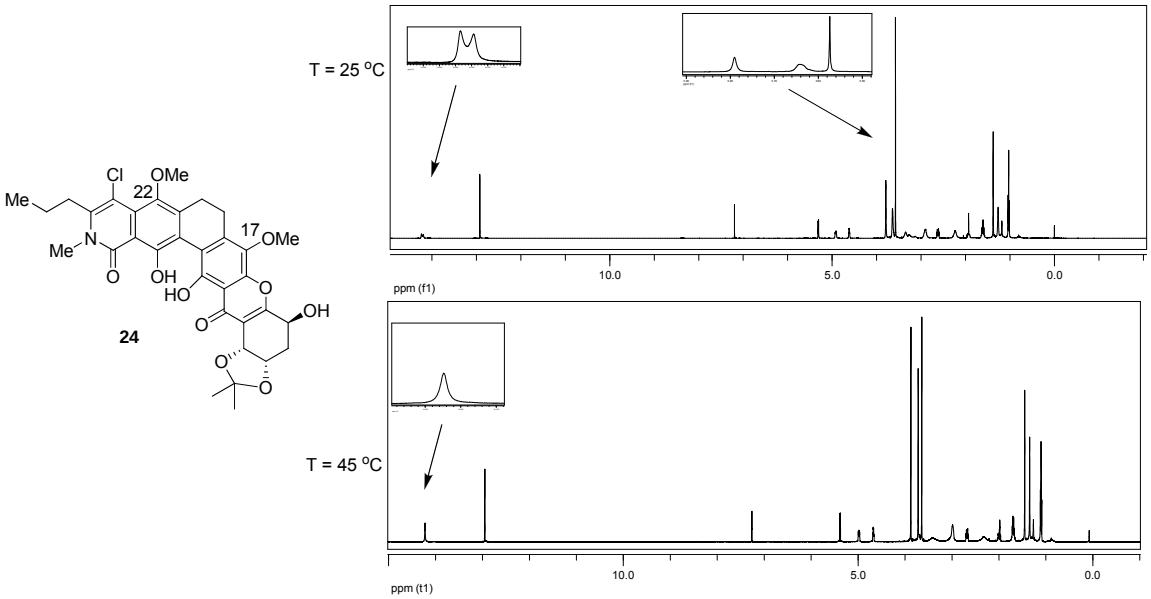
Extensive 2D NMR studies were unable to unambiguously assign the connectivity of *oxa*-Michael product **23**. However, strong evidence from ^{1}H NMR spectra suggested the desired isomer **23** to be plausible (Figure S1). The proton shifts for the three phenols of dihydrophenanthrene **12** were very distinct, with the strongly hydrogen bound H-1 occurring downfield at 16.3 ppm, H-2 at 8.4 ppm, and H-4 at 5.7 ppm. Analysis of the ^{1}H NMR spectrum of *oxa*-Michael product **23** showed the disappearance of the H-4 phenol shift, with chemical shifts for H-1 and H-2 being comparable.



Tetrahydroxanthone 24. *Oxa*-Michael product **23** (100.0 mg, 0.15 mmol) was dissolved in 5.0 mL of 1,4-dioxane and a solution of lithium hydroxide monohydrate (52.0 mg, 1.23 mmol) in 2 mL of water was added. The flask was heated to 75 °C and the reaction was monitored by UPLC-MS. The reaction was cooled to 0 °C and was carefully neutralized with a 0.5 M $KHSO_4$ solution. The mixture was extracted 2 x 10 mL with EtOAc, washed with brine, dried over sodium sulfate, filtered, and concentrated *in vacuo*. The crude residue was dissolved in 5 mL of 1,2-dichloroethane and treated with pyridine (60 µL, 0.745 mmol) followed by cyanuric chloride (34.3 mg, 0.186 mmol). The mixture was stirred for 5 min at rt. and was then heated in an oil bath to 75 °C for 1 h. The reaction was allowed to cool to rt, was quenched with ice, and finally diluted with 5 mL of cold 1.0 N HCl and 20 mL CH_2Cl_2. A precipitate formed which was removed by filtration through Celite®. The combined organics were washed with brine and dried over sodium sulfate. The crude

product was purified by silica gel chromatography (10-50% EtOAc:CH_2Cl_2) to afford 37 mg of **24** (39%, 2 steps) as an orange solid. Mp = 94-96 °C (EtOAc); ^{1}H NMR 45°C (See figure S1) (500 MHz, $CDCl_3$) δ ppm 14.22 (s, 1H), 12.95 (s, 1H), 5.38 (d, *J* = 6.07 Hz, 1H), 4.98 (dd, *J* = 9.57, 5.14 Hz, 1H), 4.70-4.65 (m, 1H), 3.87 (s, 3H), 3.72 (s, 3H), 3.64 (s, 3H), 3.41 (s, 2H), 2.99 (s, 1H), 2.68 (td, *J* = 13.77, 4.68, 4.68 Hz, 1H), 2.32 (s, 2H), 1.99 (ddd, *J* = 13.65, 10.18, 5.25 Hz, 1H), 1.75-1.64 (m, 2H), 1.45 (s, 3H), 1.34 (s, 3H), 1.10 (t, *J* = 7.34, 7.34 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 45°C δ ppm 182.2, 165.6, 164.8, 155.4, 153.6, 148.1, 142.3, 141.7, 141.3, 141.1, 135.7, 127.1, 117.8, 115.8, 115.1, 109.9, 109.7, 109.4, 109.0, 70.8, 69.1, 63.0, 62.5, 62.0, 34.5, 32.6, 31.7, 29.7, 27.5, 25.4, 23.4, 20.9, 13.9; IR (solid) νmax 3428, 2917, 2849, 1706, 1635, 1598, 1570, 1465, 1418, 1251, 1207, 1161, 1056, 1032, 967, 861, 823 cm^{-1}; CIHRMS $[M+H]^+$ calculated for $[C_{33}H_{34}ClNO_{10}+Na]$: 662.1769; found: 662.1775. (-0.9061 ppm). $[\alpha]_D^{23}$ = +300° (c = 0.10, $CHCl_3$).

Figure S.2 ^{1}H NMR ($CDCl_3$) analysis of tetrahydroxanthone acetonide **24**.



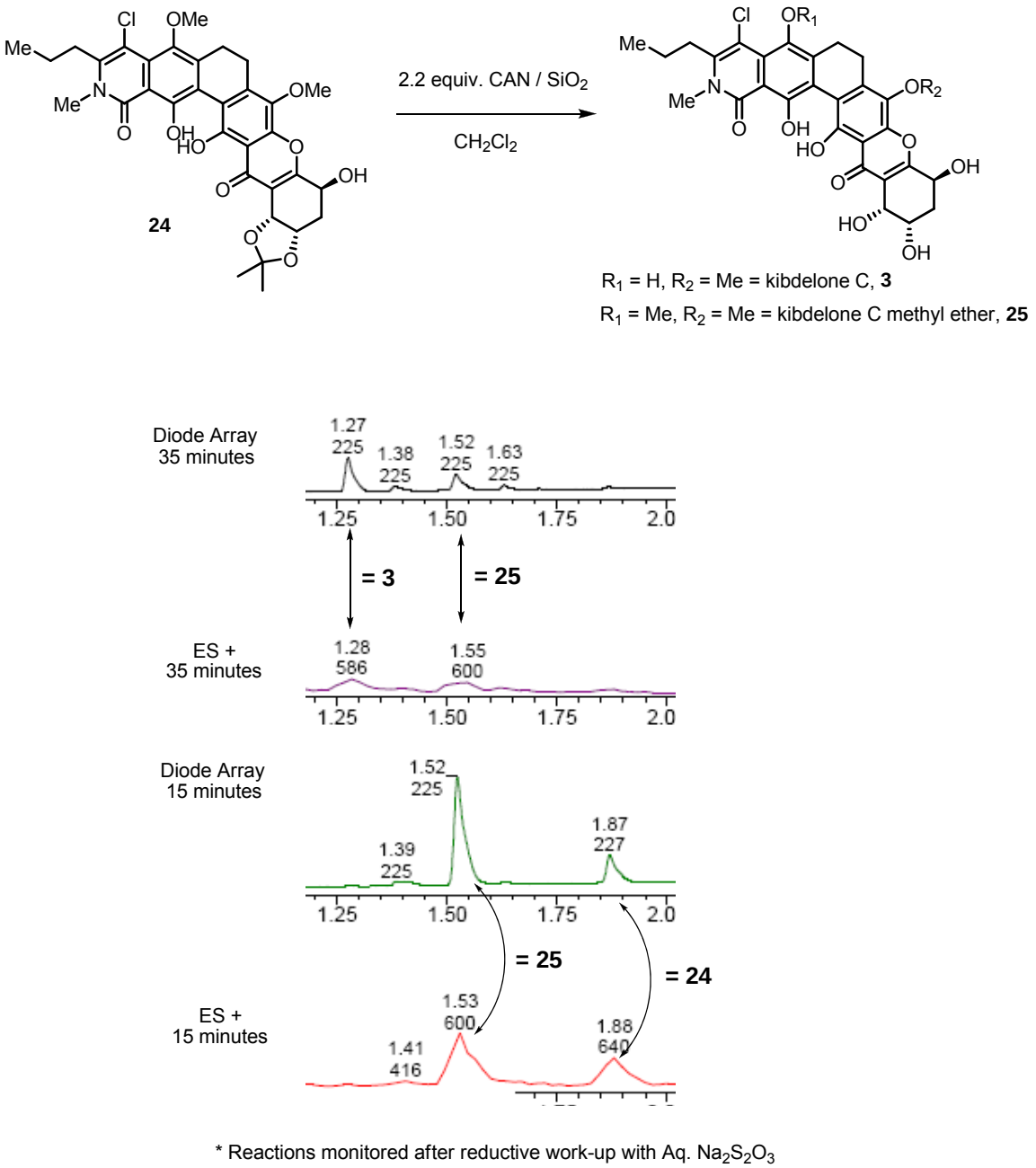
When the ^{1}H NMR spectrum of **24** was taken at rt, chemical shifts were broadened for the C-17 and C-22 methyl-ethers as well as for the hydrogen-bonded phenol, likely due to slowly interconverting hydrogen-bonded conformers. When the ^{1}H NMR was run at 45°C, coalescence of the hydrogen bonded phenol was observed, as well as sharpening of the shifts for C-17 and C-22 methyl ethers.

Our intial attempts at oxidative demethylation of **24** (followed by in-situ reductive quench with aqueous sodium dithionite) utilized aqueous CAN in acetonitrile. These conditions led to mixtures of demethylated products. We then utilized CAN adsorbed on silica gel[S3] in CH_2Cl_2 which provided kibdelone C **3** as the major product. Careful monitoring of the reaction revealed that the acetonide was being cleaved prior to oxidation

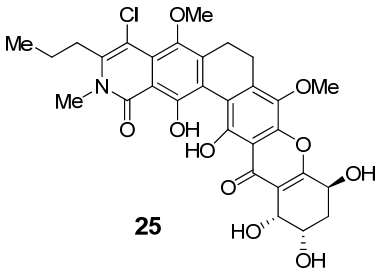
[S3] Ali, M.H.; Niedbalski, M.; Bohnert, G.; Bryant, D. *Synth. Comm.* **2006**, *36*, 1751-1759.

(Figure S3). This observation led us to target kibdelone C methyl ether **25** as a preferred substrate for oxidative demethylation.

Figure S3. UPLC Reaction Monitoring of CAN/silica oxidation of **24**

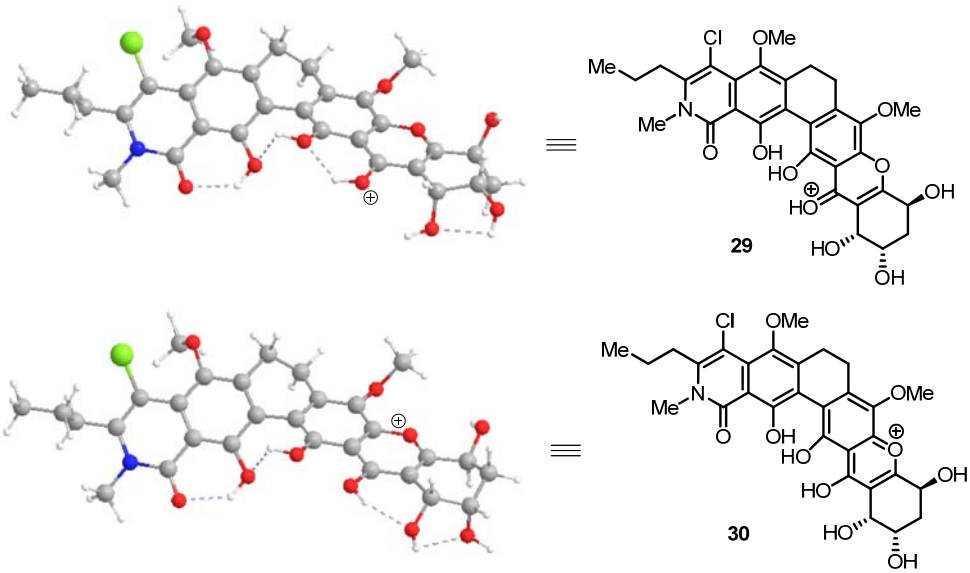


* Reactions monitored after reductive work-up with Aq. $Na_2S_2O_3$

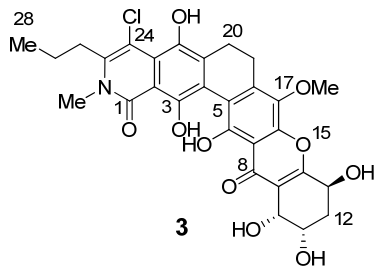


Kibdelone C methyl ether 25. Compound **24** (47.4 mg, 0.0687 mmol) was dissolved in 5.0 mL of anhydrous THF and 1.0 mL 3.0 N HCl and was degassed under argon. The solution was heated in an oil bath at 40 °C for 4 h. The reaction was diluted with 30 mL EtOAc, washed with brine, dried over sodium sulfate, filtered, and the solvents were concentrated *in vacuo* to afford 39 mg (95%) of **25** as a pale orange solid. Mp 165-167 °C (EtOAc); ^{1}H NMR (500 MHz, DMSO-D_6) δ ppm 14.32 (s, 1H), 13.18 (s, 1H), 5.99 (d, *J* = 6.36 Hz, 1H), 4.96 (d, *J* = 8.29 Hz, 1H), 4.74 (brd, *J* = 5.89 Hz, 1H), 4.72-4.70 (dd, 4.0, 3.5 1H), 4.69-4.66 (m, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 3.67 (s, 3H), 3.63 (s, 3H), 3.17 (brd, *J* = 5.00 Hz, 2H), 3.05-2.95 (dd, 8.0, 8.0 2H), 2.42-2.29 (m, 1H), 2.29-2.20 (ddd, 13.0, 12.5, 4.5 1H), 1.77 (brd, *J* = 13.33 Hz, 1H), 1.65 (m, 2H), 1.06 (t, *J* = 7.29, 7.29 Hz, 3H) ^{13}C NMR (125 MHz, $CDCl_3$) 184.3, 165.7, 163.90, 155.4, 153.2, 148.4, 142.4, 142.4, 142.3, 141.4, 141.2, 135.9, 127.3, 117.7, 115.8, 115.7, 109.9, 109.5, 66.0, 65.8, 64.5, 62.6, 62.1, 34.1, 32.6, 31.8, 29.7, 23.5, 21.0, 14.0 IR (solid) νmax 3403, 2929, 2360, 1634, 1570, 1467, 1417, 1251, 1222, 1196, 1137, 1035, 1016, 954, 904, 824 cm^{-1}; CIHRMS $[M+H]^+$ calculated for $[C_{30}H_{30}ClNO_{10}+H]$: 600.1636, found: 600.1615 (-3.4990 ppm). $[\alpha]_D^{23}$ = +90° (c = 0.20, $CHCl_3$).

Figure S4. Minimum Energy Conformers of Protonated Xanthones



A conformer search of the above protonated xanthone species (Spartan 2008, Semi-empirical AM1) revealed that hydrogen-bonding interactions of the D ring phenol are altered which may be responsible for an increased propensity for oxidation of the B ring. Additionally, the electron poor, positively charged xanthone E ring may reduce the propensity for oxidation of the D ring.



3

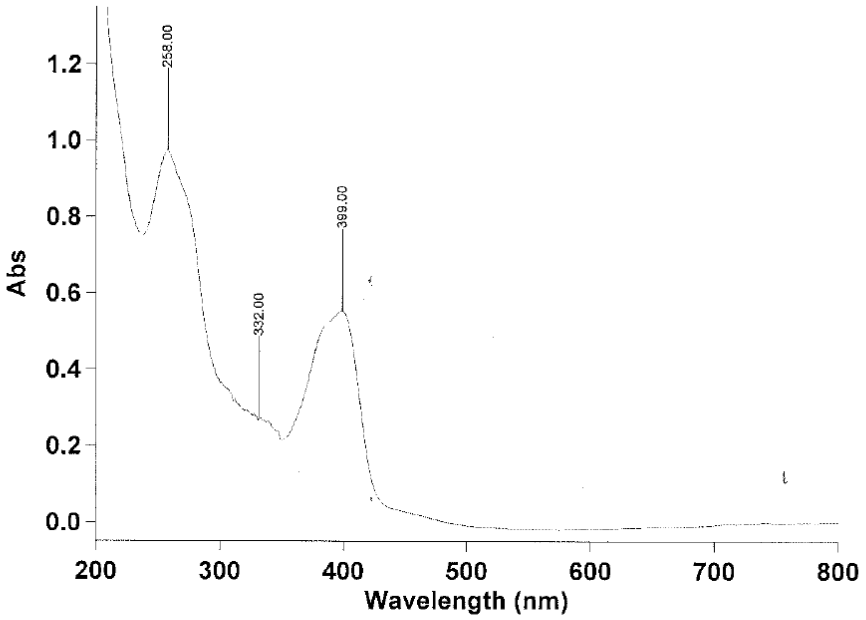
Kibdelone C 3. Kibdelone C methyl ether **25** (12.0 mg, 0.0200 mmol) was added to a 10 mL round bottom flask which was evacuated under argon. The reaction vessel was charged with 6 mL of CH_3CN and 120 uL of a 10% aq. acetic acid solution. To the bright yellow solution was added CAN (24.7 mg, 0.045 mmol) dissolved in 1.5 mL of water. The solution quickly turned dark red and was quenched after 2 minutes with a solution of sodium dithionite (105.8 mg, 0.517 mmol) in 1.0 mL water. The dark red solution slowly turned bright yellow and was allowed to stir for 20 minutes. The solution was diluted with 25 mL of ethyl acetate and the organics were washed 1 x 5 mL water, followed by brine, dried over sodium sulfate, filtered and concentrated *in vacuo* to give a pale orange residue which was purified by preparative HPLC C_{18}, 35-75% CH_3CN in water. The fractions were frozen and lyophilized to provide 7.3 mg (62%) of **3** as a yellow solid. Mp 265-267 $^{\circ}$C (benzene) (Nat. prod measured side by side = 265-267 $^{\circ}$C). ^{1}H NMR (500 MHz, DMSO-D_6) ^{13}C NMR (125.0 MHz, DMSO-D_6) (See below) IR (solid); νmax: 3346, 2934, 2862, 2360, 2342, 1681, 1628, 1514, 1464, 1365, 1301, 1247, 1199, 1174, 1138, 1036, 991, 953, 916, 828, 801, 723 CIHRMS $[M+H]^+$ calculated for $[C_{29}H_{28}ClNO_{10}+H]$: 586.1480, found 586.1497, (-2.9003 ppm) $[\alpha]_D^{23}$ = +48° (c = 0.50, $CHCl_3$).

Table S1 Natural *vs* Synthetic NMR Comparisons

Atom	**Natural Sample** [S4]		**Synthetic Sample**	
No.	^{1}H δH (m, J(Hz))	C^{13}	^{1}H δH (m, J(Hz))	C^{13}
1		165		165.0
2		108.8		108.7
3		152.6		152.5
4		116.8		116.8
5		114.7		114.7
6		152.3		152.3
7		108.6		108.5
8		182.4		182.4
9		117.9		117.8
10	4.70 (dd, 4.2, 3.8)	61.4	4.70 (dd, 4.5, 3.5)	61.4
11	3.93 (m)	64.1	3.93 (m)	64.0
12a	2.24 (ddd, 13.0, 12.5, 4.2)	33.8	2.24 (ddd, 13.0, 12.5, 4.5)	33.8
12b	1.77 (brd, 13.0)		1.77 (brd, 13.5)	
13	4.67 (m)	65.1	4.67 (m)	65.1
14		164.9		164.8
15[O]				
16		147.8		147.8
17		135.2		135.2
18		141.3		141.2
19a	2.24 (m)	23.09	2.24 (m)	23.03
19b	2.14 (m)		2.14 (m)	
20a	3.39 (brd, 13.0)	23.05	3.40 (brm)	23.0
20b	3.29 (brd, 13.0)		3.29 (brm)	
21		137.4		137.3
22		138		138
23		124.1		124.0
24		109.5		109.5
25		140.6		140.5
26	2.96 (dd, 8.2, 8.0)	31.8	2.96 (dd, 8.1, 8.0)	31.7
27	1.63 (m)	20.3	1.63 (m)	20.2
28	1.04 (t,7.2)	13.8	1.05 (t,7.3)	13.7
17-OMe	3.84 (s)	61.5	3.85 (s)	61.4
N-Me	3.61 (s)	31.6	3.61 (s)	31.6
3 OH	13.99 (s)		13.99 (s)	
6 OH	13.14 (s)		13.14 (s)	
10 OH	4.95 (brs)		4.95 (brs)	
11 OH	4.74 (d, 6.3))		4.75 (d, 6.4	
14 OH	5.99 (d, 6.5)		6.0 (d, 6.5)	
22 OH	8.42(s)		8.42 (s)	

[S4] Ratnayake, R.; Lacey, E.; Tennant, S.; Gill, J. H.; Capon, R. J., *Chem. Eur. J.* **2007,** *13*, 1610-1619.

Figure S5. UV Spectrum for Synthetic Kibdelone C



Scan Analysis Report

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Operator:
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Figure S6. Low-Resolution Mass Trace Comparison

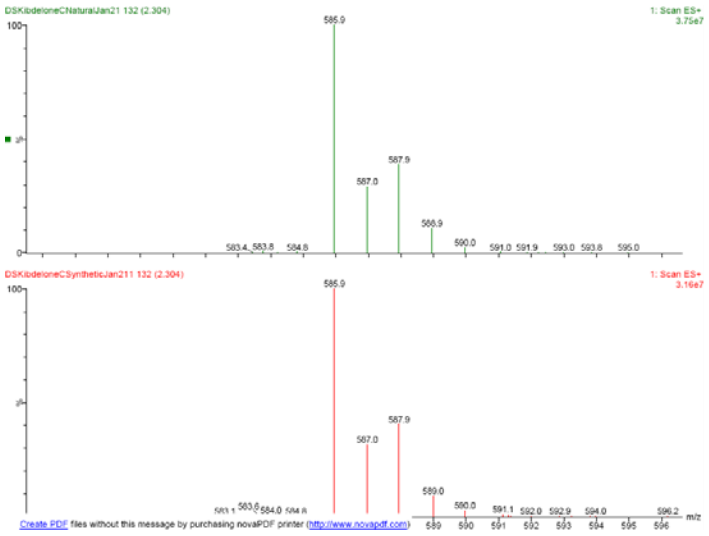


Figure S7. UPLC Co-Injections

Natural + Synthetic Co-Inject-Diode Array

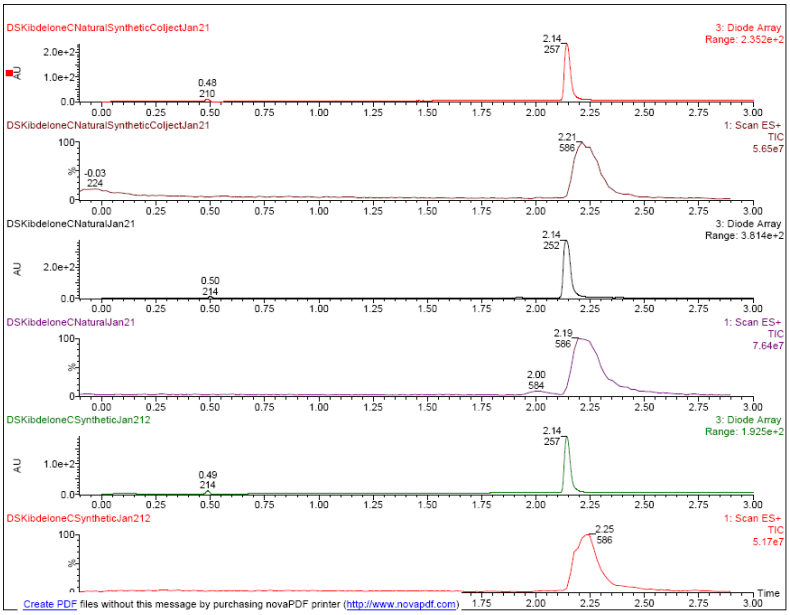
Natural + Synthetic Co-Inject ES+

Natural – Diode Array

Natural - ES+

Synthetic - Diode Array

Synthetic - ES+



III. X-Ray Crystallographic Data for Compounds 22 and 25

Crystals of compound **22** suitable for X-ray analysis were obtained by slow evaporation from CH_2Cl_2/MeOH. Crystallographic data have been deposited with the Cambridge Cystallograhic Data Centre (CCDC 815424). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Figure S8. ORTEP for iodocyclohexene carboxylate **22**

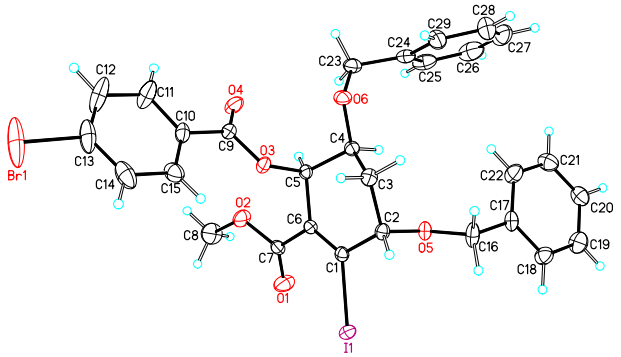


Table S2. Crystal data and structure refinement for **22**

Identification code	**22**	
Empirical formula	C29 H26 Br I O6	
Formula weight	677.31	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 10.8945(6) Å	α= 90°.
	b = 9.8099(5) Å	β= 110.216(3)°.
	c = 13.8138(9) Å	γ = 90°.
Volume	1385.39(14) $Å^3$	
Z	2	
Density (calculated)	1.624 Mg/m^3	
Absorption coefficient	2.638 mm^{-1}	
Crystal size	0.40 x 0.15 x 0.05 mm^3	
Theta range for data collection	1.57 to 32.65°.	
Index ranges	-16<=h<=16, -14<=k<=14, -20<=l<=20	
Reflections collected	37226	
Independent reflections	9879 [R(int) = 0.0317]	
Completeness to theta = 32.65°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8794 and 0.4184	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9879 / 1 / 335	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0713	
R indices (all data)	R1 = 0.0397, wR2 = 0.0752	
Absolute structure parameter	0.006(6)	
Largest diff. peak and hole	1.377 and -1.919 e.$Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **22**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	7308(1)	-2445(1)	2749(1)	27(1)

Br(1)	12041(1)	-9323(1)	-220(1)	92(1)
O(1)	5365(2)	-4487(2)	1262(1)	43(1)
O(2)	5976(2)	-6599(2)	1074(1)	35(1)
O(3)	8419(1)	-7388(2)	2621(1)	22(1)
O(4)	7482(2)	-9446(2)	2163(1)	34(1)
O(5)	7575(1)	-4321(2)	4897(1)	23(1)
O(6)	8560(1)	-8368(2)	4529(1)	26(1)
C(1)	7576(2)	-4485(2)	3228(1)	20(1)
C(2)	8442(2)	-4593(2)	4348(1)	21(1)
C(3)	9055(2)	-5998(2)	4620(2)	24(1)
C(4)	8008(2)	-7071(2)	4218(2)	21(1)
C(5)	7425(2)	-6991(2)	3051(2)	19(1)
C(6)	7028(2)	-5552(2)	2660(1)	19(1)
C(7)	6041(2)	-5449(2)	1599(1)	22(1)
C(8)	5012(3)	-6625(3)	52(2)	51(1)
C(9)	8291(2)	-8611(2)	2161(2)	24(1)
C(10)	9262(2)	-8780(2)	1635(2)	28(1)
C(11)	9431(3)	-10052(3)	1286(2)	50(1)
C(12)	10298(3)	-10237(4)	759(3)	65(1)
C(13)	10959(2)	-9128(4)	582(2)	52(1)
C(14)	10867(2)	-7871(3)	982(2)	47(1)
C(15)	10007(2)	-7693(3)	1516(2)	36(1)
C(16)	8203(2)	-3726(3)	5878(2)	34(1)
C(17)	7290(2)	-3805(2)	6475(2)	27(1)
C(18)	6766(2)	-2642(3)	6730(2)	32(1)
C(19)	5949(2)	-2718(3)	7308(2)	39(1)
C(20)	5649(2)	-3965(3)	7621(2)	34(1)
C(21)	6139(2)	-5129(3)	7347(2)	38(1)
C(22)	6962(2)	-5054(3)	6782(2)	35(1)
C(23)	7660(2)	-9322(2)	4684(2)	28(1)
C(24)	7435(2)	-9116(2)	5687(2)	27(1)
C(25)	6178(2)	-9061(3)	5721(2)	39(1)
C(26)	5977(3)	-8939(3)	6651(3)	52(1)
C(27)	7015(3)	-8852(3)	7544(2)	53(1)
C(28)	8277(3)	-8891(3)	7530(2)	47(1)
C(29)	8482(2)	-9016(3)	6599(2)	34(1)

Crystals of compound **25** suitable for X-ray analysis were obtained by slow evaporation from CH_2Cl_2/EtOH. Crystallographic data have been deposited with the Cambridge Cystallograhic Data Centre (CCDC 822438). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Figure S9. ORTEP for kibdelone C methyl ether **25**

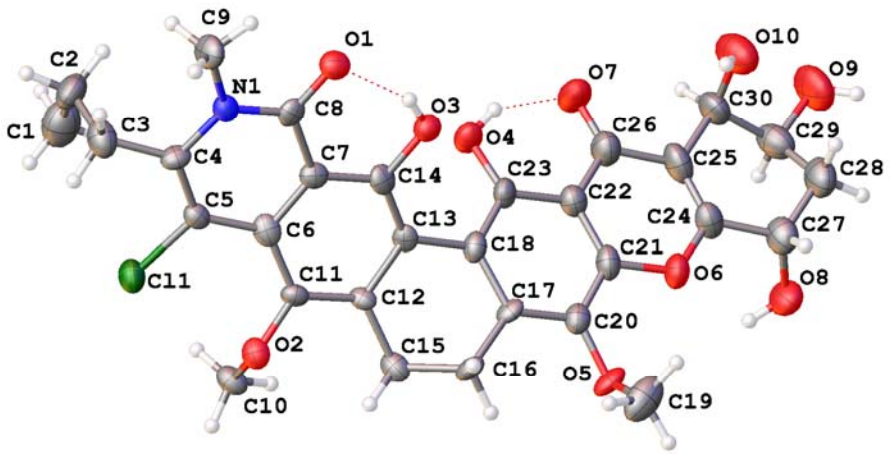


Table S4 Crystal data for **25**

$2(C_{30}H_{30}ClNO_{10})\cdot CO$	V = 3271.8 (11) Å^3
M_r = 1228.01	Z = 2
Monoclinic, $P2_1$	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 17.753 (4) Å	μ = 1.51 mm^{-1}
b = 8.1082 (16) Å	T = 100 K
c = 23.170 (5) Å	0.11 × 0.09 × 0.03 mm
β = 101.19 (3)°	
Bruker Proteum-R diffractometer	9928 independent reflections
Absorption correction: multi-scan TWINABS (Sheldrick, 1997)	8070 reflections with $I > 2s(I)$
T_{min} = 0.658, T_{max} = 0.753	R_{int} = 0.0636
9928 measured reflections	

$R[F^2 > 2s(F^2)] = 0.085$	H-atom parameters constrained
$wR(F^2) = 0.247$	$D\rangle_{max} = 0.82$ e Å^{-3}
$S = 1.04$	$D\rangle_{min} = -0.62$ e Å^{-3}
9928 reflections	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
791 parameters	Flack parameter: 0.05 (3)
8 restraints	

Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997).

$C_{30}H_{30}ClNO_{10}\cdot 0.5CO$	$F(000) = 1284$
$M_r = 1228.01$	$D_x = 1.251$ Mg m^{-3}
Monoclinic, $P2_1$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Hall symbol: P 2yb	Cell parameters from 9894 reflections
$a = 17.753$ (4) Å	$\theta = 2.5–65.5°$
$b = 8.1082$ (16) Å	$\mu = 1.51$ mm^{-1}
$c = 23.170$ (5) Å	$T = 100$ K
$\beta = 101.19$ (3)°	Plate, colorless
$V = 3271.8$ (11) Å^3	0.11 × 0.09 × 0.03 mm
$Z = 4$	$Z' = 2$

Bruker Proteum-R diffractometer	9928 independent reflections
Radiation source: rotating anode	8070 reflections with $I > 2s(I)$
graphite	$R_{int} = 0.0000$
ϕ & ω scans	$\theta_{max} = 66.3°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan TWINABS (Sheldrick, 1997)	$h = -20\rightarrow20$
$T_{min} = 0.658$, $T_{max} = 0.753$	$k = -9\rightarrow9$
9928 measured reflections	$l = -27\rightarrow27$

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.085$	H-atom parameters constrained
$wR(F^2) = 0.247$	$w = 1/[\sigma^2(F_o^2) + (0.1228P)^2 + 11.1908P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(D/\sigma)_{max} = 0.012$
9928 reflections	$D\rangle_{max} = 0.82$ e Å^{-3}
791 parameters	$D\rangle_{min} = -0.62$ e Å^{-3}
8 restraints	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.05 (3)

Special details

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

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

Notes on crystallographic anomalies and refinement:

The structure presented here represents the best available crystalline sample of compound N. Numerous attempts at growing crystals suitable for x-ray crystallography were unsuccessful. Over twenty solvent systems were screened the only system yielding crystals was a slow evaporation from ethanol/CH_2Cl_2.

The crystals obtained gave only weak diffraction, and data collection resulted in a low resolution data set with many missing reflections. Analysis of the frames collected, simulated precession photographs, and output from the programs ADDSYM [S5] and

[S5] ADDSYM, a component of PLATON, a multipurpose crystallographic tool. Spek, A.L. *Acta Cryst*. **2009**, *D65*, 148-155.

cell_now [S6] revealed that an apparent long axis (c = 46.34 Angstroms) was actually due to non-merohedral twinning through a rotation of 180 degrees about an axis at fractional coordinates of 1/4, 0, 0. The data was integrated as a two component twin, and data reduction with TWINABS indicated that the two components were present in a ratio of 0.676:0.324. A de-twinned hkl file was generated containing the single and fractional composite reflections of the major twin component. A file for HKLF5 refinement, containing de-twinned reflections due to both components, was also generated.

The structure was solved in space group P2(1) with two molecules in the asymmetric unit (Z' = 2). Refinement using the de-twinned major component data only revealed the entire skeletal structure of compound N in both independent molecules, as well as electron density peaks that appeared to correspond to two hydrogen bonded methanol molecules, one bonded to each independent molecule of N.

Examination of the crystal packing revealed a void space in the independent part of the unit cell, with diffuse electron density at its edges likely due to additional disordered solvent of partial occupancy. The interior part of the void contained only low electron density in difference maps.

Two types of refinements were attempted. The first, using only data from the major component (HKLF4 refinement), allowed the use of SQUEEZE [S7] to account for the diffuse electron density due to disordered, partial occupancy solvent. The second type, a refinement using the full data set with both components (HKLF5 refinment) is usually the preferred method for twins of this type, but the two component reflection file is incompatible with SQUEEZE.

The HKLF5 refinement was unsuccessful at accounting for the missing and disordered solvent. Although the two methanol molecules mentioned above could be found and refined isotropically, many additional 'lone' peaks of significant density (>0.8 electrons per cubic Angstrom) appeared in the difference maps, and could not be resolved into additional molecules of methanol or CH_2Cl_2. This unmodeled density limited the refinement to an R1 value of approximately 13.5%.

For the HKLF4 refinement, the structure was modeled as the two independent molecules of N, each with a hydrogen bonded methanol molecule of half occupancy. This model was input to SQUEEZE, which found a total void volume of 518 cubic Angstroms containing an electron count of 103. SQUEEZE then generated a modified HKL file with the contributions of this electron density removed.

After applying this correction, the nonhydrogen atoms in the four independent molecules were refined anisotropically. The two half-occupancy methanol molecules were refined isotropically, and their hydrogen atoms were not added, since none could be located in difference maps. The refinement converged at an R1 value of 0.0853, and is the refinement reported here.

[S6] G. Sheldrick, Cell_Now, Bruker-AXS, Inc., Madison, WI, **2004**.
[S7] SQUEEZE, a component of PLATON, a multipurpose crystallographic tool. Spek, A.L. *Acta Cryst*. **2009**, *D65*, 148-155.
[S8] Thompson, A.L., Watkin, D.J. *Tetrahedron: Asymmetry* **2009**, *20*, 712-717.

Suitability for Publication:

Despite the adverse characteristics of the sample and data set, the structures of the two independent molecules of N are unambiguously resolved. The absolute configuration is also unambiguously determined here, as shown by the agreement of all stereochemical refinement indicators[S8]: (Flack x = 0.05 (3), Hooft y = 0.041 (10), P2(true) = 1.000, P3(true) = 1.000, P3(false) = 0.000, G = 0.918 (19)).

CheckCIF Alerts and Explanations:

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full Low ·····. 0.93

Explanation: The measured fraction is low due to the weak diffraction of the sample, which was the best available sample for the experiment. This weak diffraction is probably due to the near-complete loss of solvent revealed during the refinement.

PLAT602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure !

Explanation: Voids in the unit cell were found to be due to disordered solvent of low occupancy.

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds (x 1000) Ang .. 11

Explanation: The low bond precision is due to the weakness of the diffraction, which resulted in many unobserved data at high resolution.

PLAT417_ALERT_2_B Short Inter D-H..H-D H8 .. H9A .. 2.09 Ang.
PLAT420_ALERT_2_B D-H Without Acceptor O8A - H8A ··· ?
PLAT420_ALERT_2_B D-H Without Acceptor O9 - H9 ··· ?

Explanation: The position of the hydrogen atoms, refined using a riding model, were nevertheless determined to poor resolution due to the overall low resolution of the data set.

PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ··· 3.47 Ratio
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ··· 3.53 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for O6A – C24A .. 5.80 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C6A – C7A .. 5.80 su
PLAT234_ALERT_4_C Large Hirshfeld Difference C1 – C2 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C16A – C17A .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C25A – C30A .. 0.16 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C1 - C2 ··· 1.41 Ang.

Explanation: These alerts provide further indication of the low resolution of this weak data set. Though the model shows some anomalous anisotropic displacement ellipsoids and low C-C bond precision, the skeletal structure and stereochemistry are unambiguous, and are the structural characteristics important to this investigation.

PLAT309_ALERT_2_C Single Bonded Oxygen (C-O .GT. 1.3 Ang) ·····.. O1SA
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O .GT. 1.3 Ang) ·····.. O1S

Explanation: These alerts arise because hydrogen atoms were not found, and therefore not

refined, for the two half-occupancy methanol molecules in the structure.

Table S5. Fractional atomic coordinates

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.76221 (12)	-0.4377 (2)	1.09276 (7)	0.0394 (5)	
Cl1A	0.21087 (11)	0.5343 (2)	-0.09076 (7)	0.0375 (4)	
O5A	0.2740 (3)	0.4874 (6)	0.3312 (2)	0.0371 (13)	
O6A	0.4210 (3)	0.4059 (6)	0.3809 (2)	0.0361 (13)	
O3	0.8916 (3)	-0.6226 (6)	0.8616 (2)	0.0321 (12)	
H3	0.9226	-0.6838	0.8839	0.048*	
C15A	0.2132 (4)	0.4966 (8)	0.1478 (3)	0.0273 (16)	
H15A	0.2132	0.3752	0.1525	0.033*	
H15B	0.1611	0.5304	0.1276	0.033*	
O9A	0.6976 (4)	0.1190 (8)	0.4899 (3)	0.0626 (18)	
H9A	0.6981	0.0212	0.5019	0.094*	
C16	0.6242 (4)	-0.4940 (9)	0.7968 (3)	0.0298 (16)	
H16C	0.6223	-0.6144	0.8035	0.036*	
H16D	0.5741	-0.4600	0.7729	0.036*	
O2	0.6636 (3)	-0.4454 (6)	0.97991 (18)	0.0320 (11)	
O2A	0.1724 (3)	0.5432 (6)	0.02325 (18)	0.0290 (10)	
O7A	0.5873 (3)	0.3334 (8)	0.2832 (2)	0.0474 (15)	
O10A	0.6796 (4)	0.3902 (9)	0.4171 (3)	0.0605 (17)	
H10	0.6674	0.4658	0.3922	0.091*	
C15	0.6367 (4)	-0.4062 (8)	0.8551 (3)	0.0318 (17)	
H15C	0.6334	-0.2856	0.8485	0.038*	
H15D	0.5959	-0.4382	0.8766	0.038*	
C16A	0.2314 (4)	0.5765 (8)	0.2080 (3)	0.0263 (15)	
H16A	0.2254	0.6976	0.2040	0.032*	
H16B	0.1953	0.5360	0.2324	0.032*	
O1	0.9665 (3)	-0.7350 (6)	0.9551 (2)	0.0343 (12)	

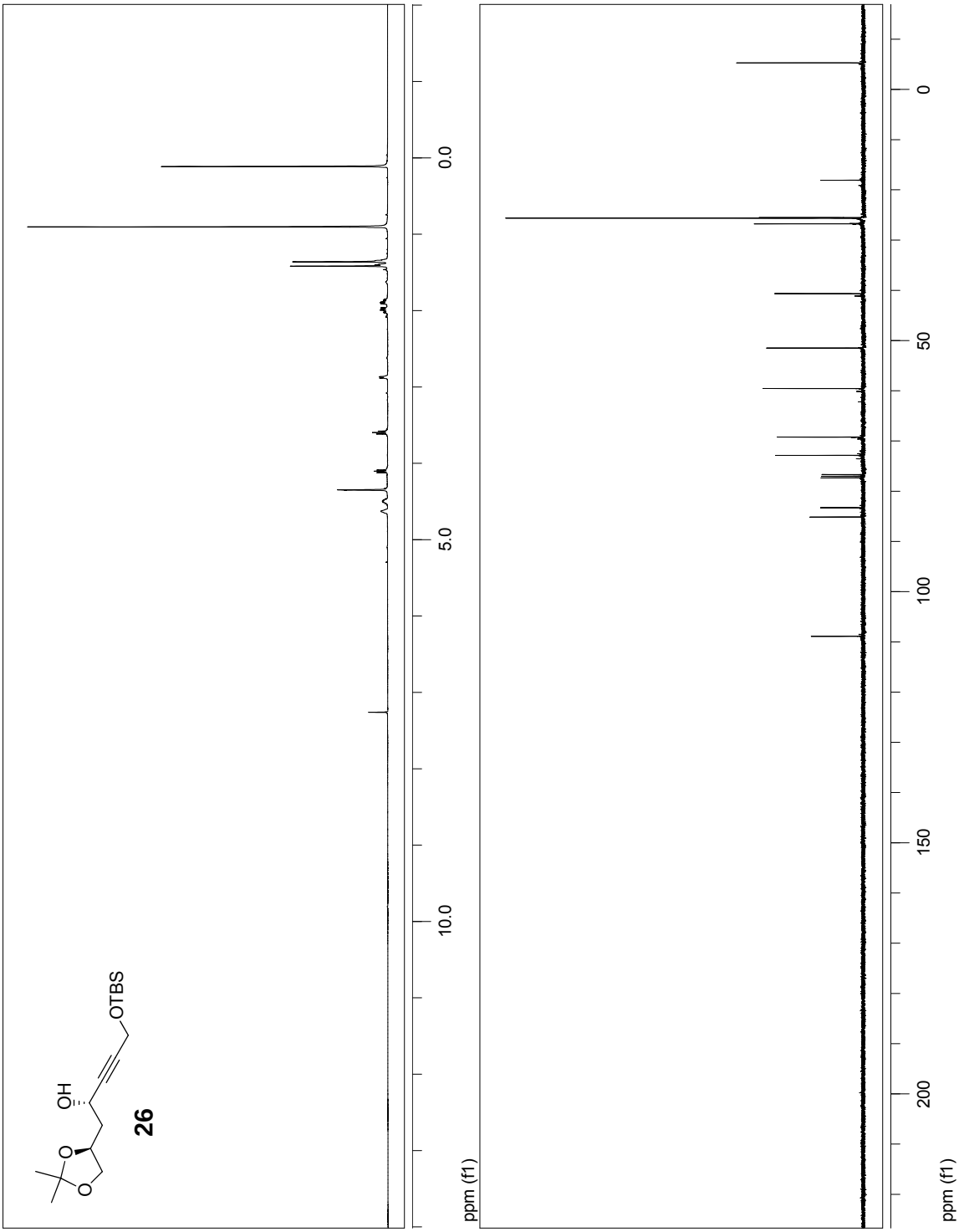
O7	0.9290 (4)	-0.2444 (10)	0.7081 (3)	0.064 (2)	
O4A	0.4908 (3)	0.4284 (7)	0.1914 (2)	0.0363 (12)	
H4A	0.5258	0.3683	0.2100	0.054*	
O3A	0.4633 (3)	0.7175 (6)	0.1388 (2)	0.0336 (12)	
H3A	0.4901	0.7509	0.1151	0.050*	
O5	0.5982 (3)	-0.4391 (7)	0.67083 (19)	0.0360 (12)	
O1A	0.4882 (3)	0.8280 (6)	0.0443 (2)	0.0332 (12)	
O6	0.7180 (3)	-0.3747 (7)	0.6159 (2)	0.0416 (14)	
O4	0.8881 (3)	-0.3339 (7)	0.8037 (2)	0.0399 (13)	
H4	0.9184	-0.3090	0.7814	0.060*	
C8A	0.4270 (4)	0.7657 (8)	0.0168 (3)	0.0269 (16)	
O8A	0.4534 (4)	0.1559 (7)	0.4712 (2)	0.0500 (15)	
H8A	0.4626	0.1165	0.5053	0.075*	
O8	0.6843 (4)	-0.2129 (9)	0.5071 (2)	0.0581 (17)	
H8	0.6632	-0.1987	0.5362	0.087*	
C11A	0.2504 (4)	0.5649 (8)	0.0499 (3)	0.0237 (14)	
N1A	0.4069 (4)	0.7822 (7)	-0.0425 (2)	0.0318 (14)	
N1	0.9304 (4)	-0.6887 (7)	1.0429 (2)	0.0277 (13)	
C7A	0.3754 (4)	0.6749 (7)	0.0470 (3)	0.0240 (15)	
C11	0.7240 (4)	-0.4696 (8)	0.9523 (3)	0.0248 (14)	
C12A	0.2706 (4)	0.5443 (8)	0.1104 (3)	0.0262 (15)	
C17	0.6863 (4)	-0.4568 (8)	0.7638 (3)	0.0246 (14)	
C14A	0.3968 (4)	0.6562 (7)	0.1088 (3)	0.0239 (15)	
C8	0.9202 (4)	-0.6688 (8)	0.9840 (3)	0.0274 (16)	
C6A	0.3026 (4)	0.6223 (7)	0.0163 (2)	0.0184 (13)	
C14	0.8406 (4)	-0.5587 (8)	0.8918 (3)	0.0295 (17)	
C7	0.8509 (4)	-0.5807 (8)	0.9532 (3)	0.0275 (15)	
C13A	0.3461 (4)	0.5732 (8)	0.1394 (3)	0.0243 (15)	
C17A	0.3123 (4)	0.5361 (9)	0.2374 (3)	0.0307 (16)	
C18	0.7612 (4)	-0.4431 (9)	0.7979 (3)	0.0291 (15)	
C21A	0.4052 (5)	0.4424 (8)	0.3218 (3)	0.0306 (17)	
C6	0.7964 (5)	-0.5257 (8)	0.9856 (3)	0.0311 (17)	
C4	0.8826 (4)	-0.6146 (8)	1.0769 (3)	0.0292 (16)	

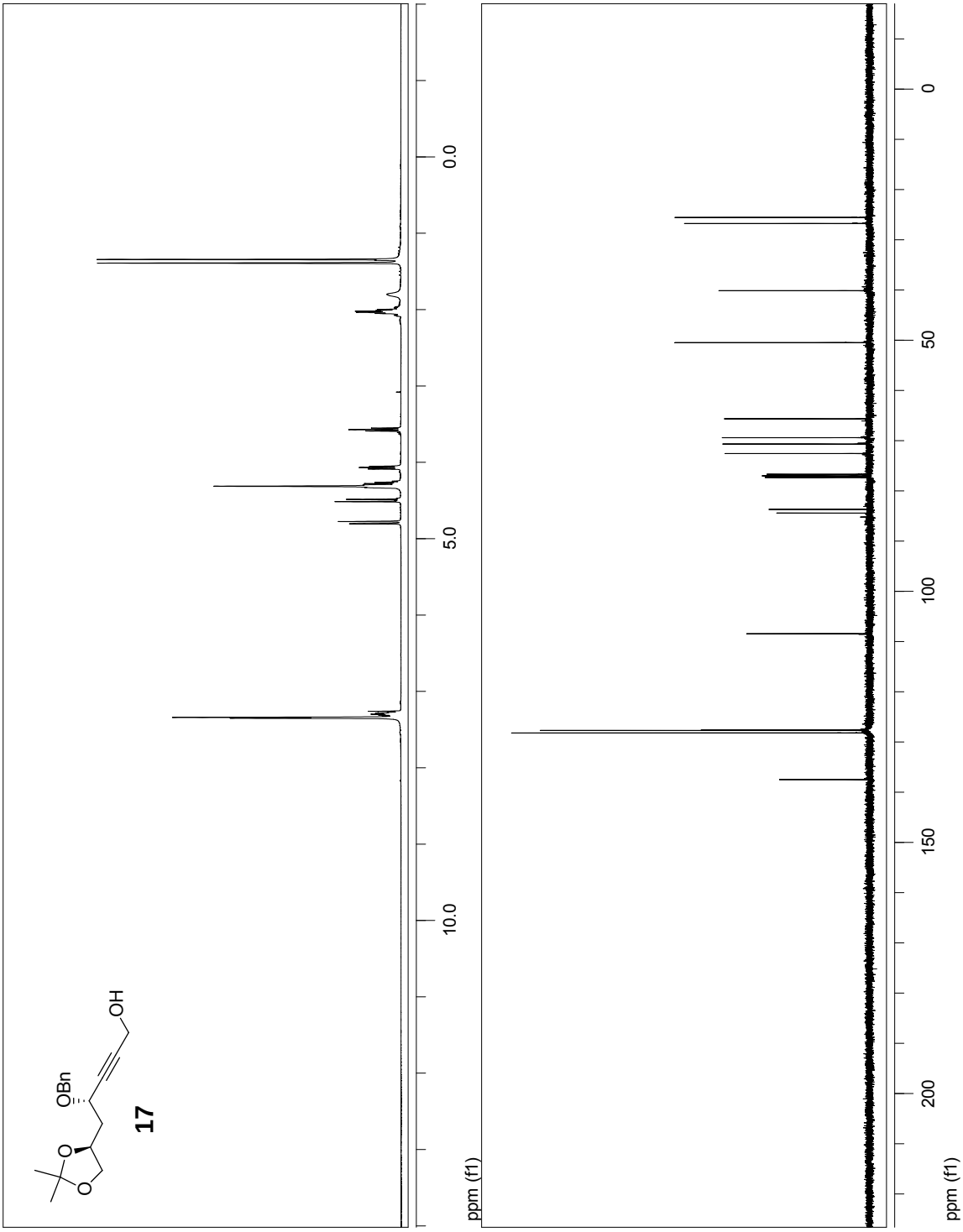
C20A	0.3312 (5)	0.4940 (8)	0.2977 (3)	0.0307 (17)	
C4A	0.3404 (5)	0.7078 (9)	-0.0757 (3)	0.0359 (19)	
C18A	0.3687 (4)	0.5294 (8)	0.2024 (3)	0.0234 (14)	
C5	0.8183 (4)	-0.5379 (8)	1.0484 (3)	0.0271 (16)	
C13	0.7762 (4)	-0.4817 (7)	0.8619 (3)	0.0243 (15)	
C20	0.6723 (5)	-0.4332 (9)	0.7026 (3)	0.0330 (17)	
C5A	0.2896 (4)	0.6327 (8)	-0.0480 (3)	0.0299 (16)	
C23	0.8210 (5)	-0.3817 (9)	0.7714 (3)	0.0325 (17)	
C26A	0.5359 (5)	0.3574 (9)	0.3127 (3)	0.0345 (18)	
C23A	0.4401 (4)	0.4642 (9)	0.2259 (3)	0.0300 (16)	
C24A	0.4929 (4)	0.3434 (9)	0.4044 (3)	0.0305 (17)	
C24	0.7732 (5)	-0.3229 (10)	0.5878 (3)	0.043 (2)	
C21	0.7335 (5)	-0.3883 (9)	0.6771 (3)	0.0370 (19)	
C10A	0.1461 (5)	0.3726 (9)	0.0167 (3)	0.0379 (19)	
H10A	0.1779	0.3111	-0.0061	0.057*	
H10B	0.0924	0.3700	-0.0039	0.057*	
H10C	0.1504	0.3222	0.0556	0.057*	
C3A	0.3322 (5)	0.7051 (10)	-0.1412 (3)	0.0355 (18)	
H3AA	0.3454	0.8151	-0.1549	0.043*	
H3AB	0.2781	0.6816	-0.1594	0.043*	
C22A	0.4607 (5)	0.4237 (9)	0.2866 (3)	0.0345 (18)	
C26	0.8645 (6)	-0.2907 (11)	0.6804 (3)	0.048 (2)	
C22	0.8066 (5)	-0.3565 (9)	0.7093 (3)	0.0360 (18)	
O10	0.9562 (5)	-0.3406 (11)	0.5776 (3)	0.082 (2)	
H10D	0.9422	-0.4267	0.5927	0.123*	
C27A	0.4987 (5)	0.2991 (11)	0.4692 (3)	0.042 (2)	
H27	0.4780	0.3918	0.4900	0.050*	
C9	0.9901 (5)	-0.8083 (11)	1.0701 (3)	0.045 (2)	
H9B	1.0163	-0.8526	1.0399	0.068*	
H9C	0.9660	-0.8987	1.0880	0.068*	
H9D	1.0276	-0.7525	1.1005	0.068*	
C25A	0.5463 (5)	0.3200 (9)	0.3736 (3)	0.0330 (17)	
C10	0.6423 (5)	-0.2782 (9)	0.9861 (3)	0.0350 (18)	

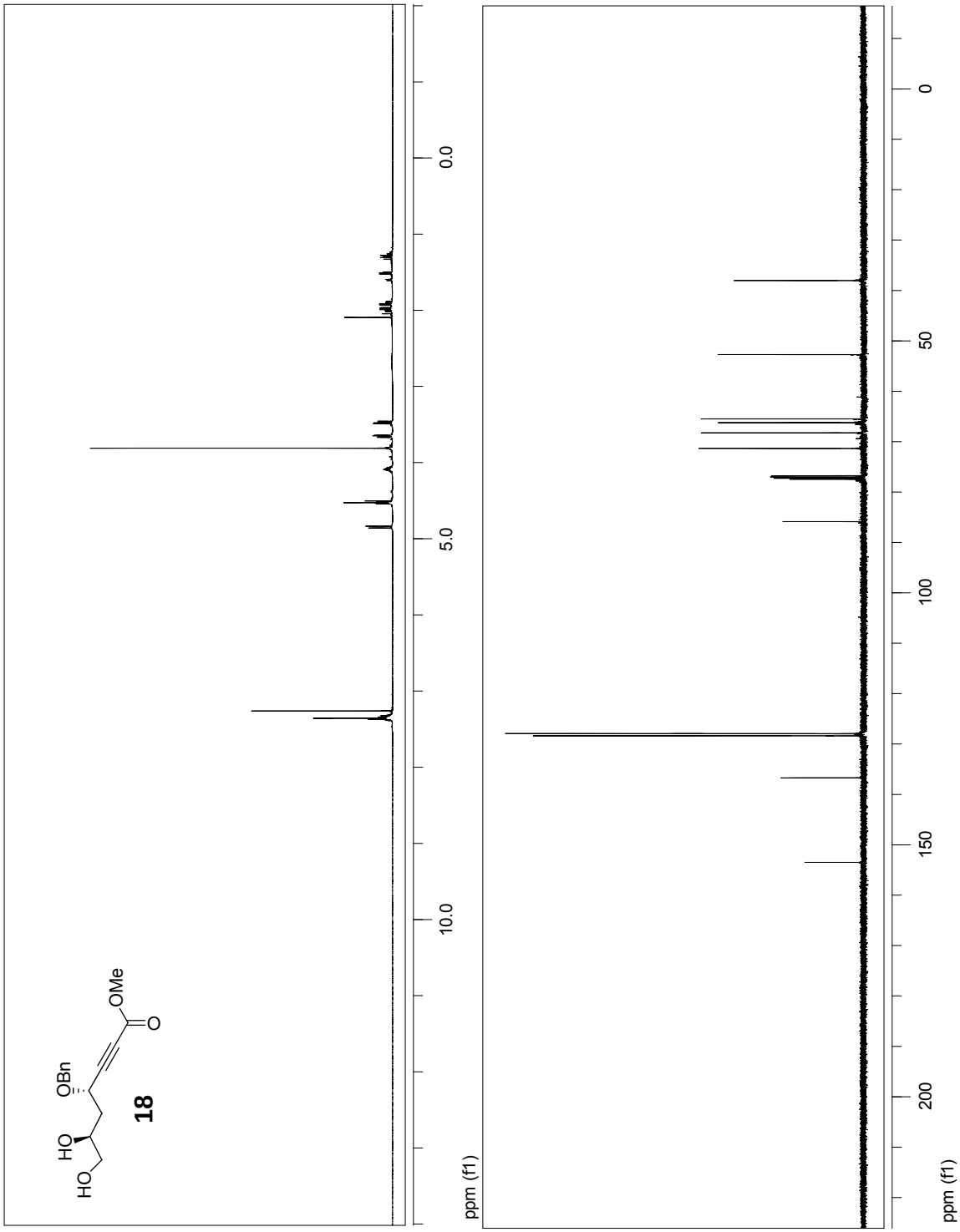
H10E	0.6822	-0.2229	1.0148	0.052*	
H10F	0.5935	-0.2741	0.9998	0.052*	
H10G	0.6366	-0.2222	0.9480	0.052*	
C28A	0.5797 (6)	0.2653 (12)	0.4980 (3)	0.051 (2)	
H28A	0.5804	0.2076	0.5357	0.061*	
H28B	0.6073	0.3712	0.5067	0.061*	
C25	0.8419 (6)	-0.2740 (12)	0.6152 (4)	0.053 (3)	
C30	0.9028 (6)	-0.2064 (14)	0.5830 (3)	0.054 (2)	
H30A	0.9309	-0.1127	0.6056	0.065*	
C30A	0.6266 (6)	0.2561 (11)	0.4035 (3)	0.049 (2)	
H30	0.6458	0.1792	0.3759	0.059*	
C9A	0.4516 (5)	0.8986 (9)	-0.0711 (3)	0.0344 (17)	
H9AA	0.4180	0.9872	-0.0898	0.052*	
H9AB	0.4737	0.8403	-0.1010	0.052*	
H9AC	0.4930	0.9458	-0.0416	0.052*	
C29	0.8620 (6)	-0.1477 (13)	0.5231 (4)	0.059 (3)	
H29A	0.8295	-0.0499	0.5280	0.070*	
C3	0.9109 (6)	-0.6157 (11)	1.1422 (3)	0.048 (2)	
H3B	0.9330	-0.7254	1.1543	0.058*	
H3C	0.8669	-0.5976	1.1621	0.058*	
C27	0.7493 (6)	-0.3219 (12)	0.5234 (4)	0.051 (2)	
H27A	0.7313	-0.4358	0.5111	0.061*	
O9	0.9205 (5)	-0.0985 (12)	0.4900 (3)	0.085 (3)	
H9	0.9085	-0.1338	0.4554	0.128*	
C29A	0.6206 (6)	0.1617 (11)	0.4599 (4)	0.052 (2)	
H29	0.5907	0.0581	0.4489	0.063*	
C2A	0.3849 (5)	0.5728 (11)	-0.1614 (3)	0.047 (2)	
H2AA	0.3865	0.5909	-0.2034	0.056*	
H2AB	0.4378	0.5861	-0.1385	0.056*	
C1A	0.3578 (6)	0.3986 (12)	-0.1535 (4)	0.059 (3)	
H1AA	0.3591	0.3776	-0.1117	0.089*	
H1AB	0.3916	0.3201	-0.1683	0.089*	
H1AC	0.3052	0.3852	-0.1756	0.089*	

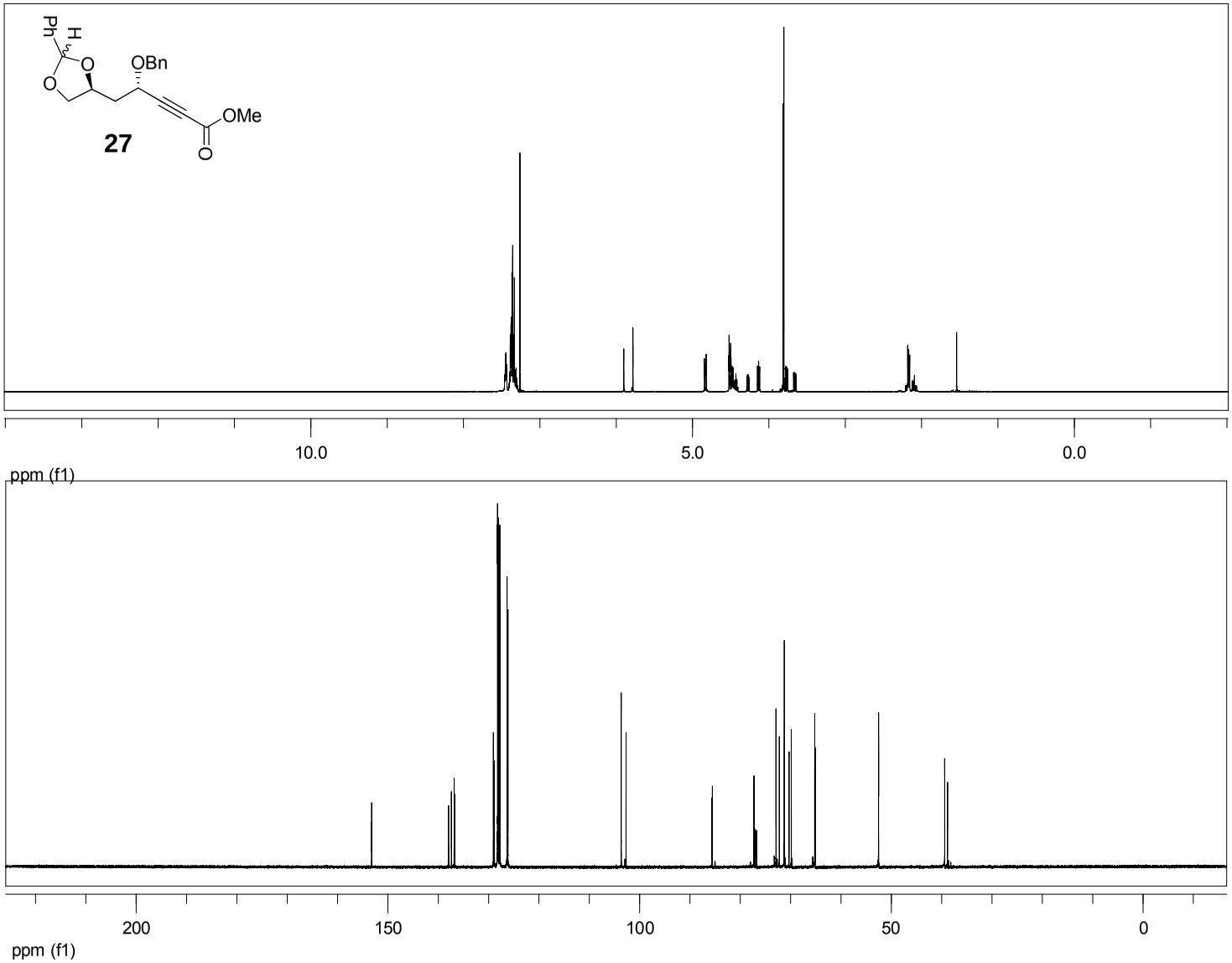
C1	0.9433 (8)	-0.3195 (15)	1.1566 (5)	0.077 (3)	
H1A	0.9216	-0.2972	1.1152	0.116*	
H1B	0.9849	-0.2413	1.1707	0.116*	
H1C	0.9031	-0.3073	1.1800	0.116*	
C19A	0.2543 (7)	0.6439 (12)	0.3523 (4)	0.065 (3)	
H19A	0.2941	0.6780	0.3856	0.097*	
H19B	0.2049	0.6356	0.3649	0.097*	
H19C	0.2504	0.7257	0.3207	0.097*	
C28	0.8122 (6)	-0.2803 (14)	0.4915 (4)	0.061 (3)	
H28C	0.7898	-0.2431	0.4512	0.073*	
H28D	0.8435	-0.3799	0.4886	0.073*	
C2	0.9723 (6)	-0.4817 (12)	1.1625 (4)	0.053 (2)	
H2A	0.9959	-0.5015	1.2042	0.064*	
H2B	1.0132	-0.4923	1.1391	0.064*	
C19	0.5693 (7)	-0.5998 (11)	0.6519 (4)	0.065 (3)	
H19D	0.6048	-0.6536	0.6302	0.098*	
H19E	0.5187	-0.5888	0.6262	0.098*	
H19F	0.5647	-0.6666	0.6862	0.098*	
C12	0.7147 (4)	-0.4496 (8)	0.8916 (3)	0.0222 (13)	
O1S	0.9390 (8)	-0.6443 (15)	0.6237 (6)	0.060 (3)*	0.50
O1SA	0.6224 (8)	0.7069 (16)	0.3931 (5)	0.056 (3)*	0.50
C1S	0.9642 (16)	-0.660 (3)	0.6874 (11)	0.085 (7)*	0.50
C1SA	0.6393 (18)	0.789 (4)	0.3397 (12)	0.104 (9)*	0.50

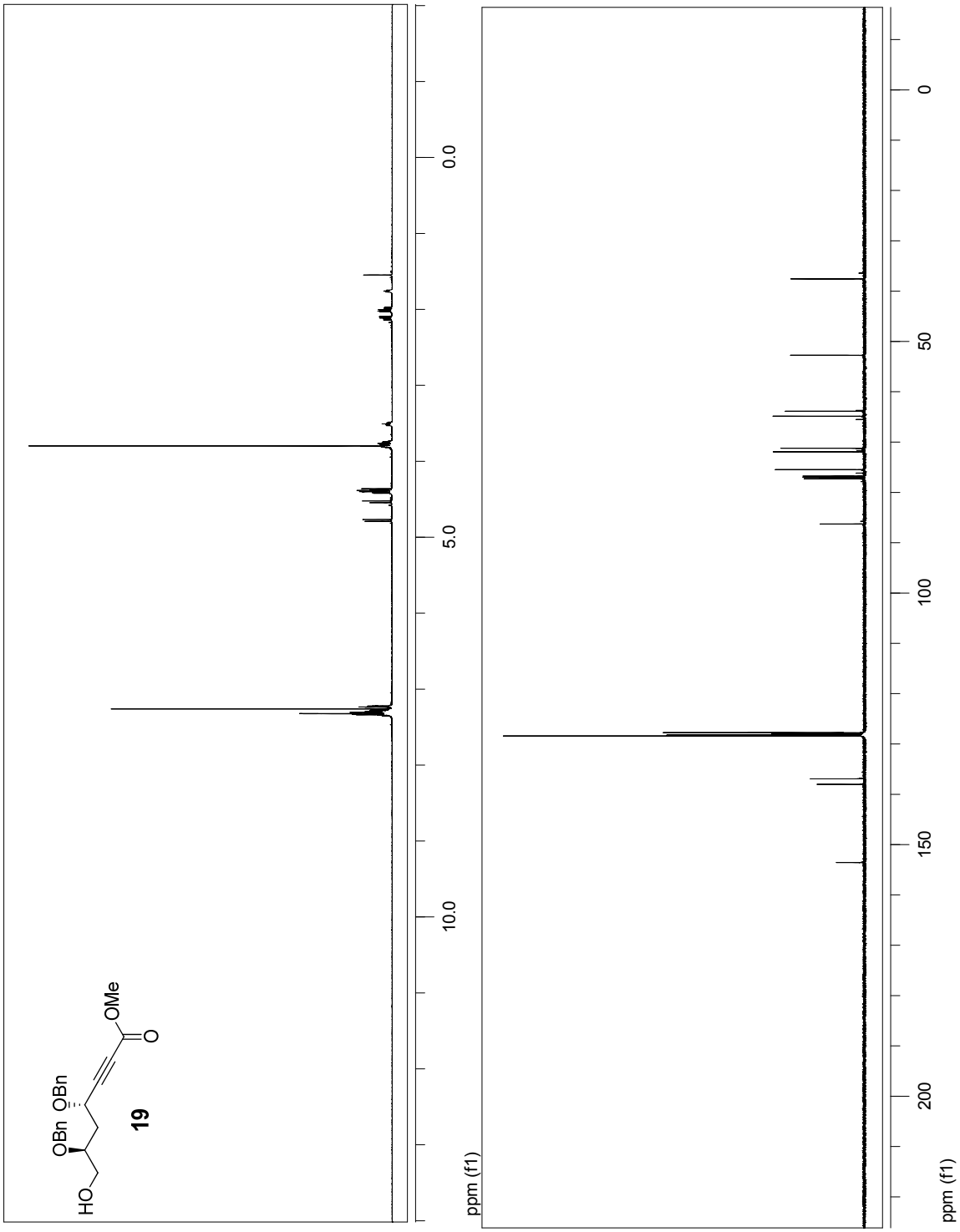
IV. ^{1}H and ^{13}C NMR Spectra

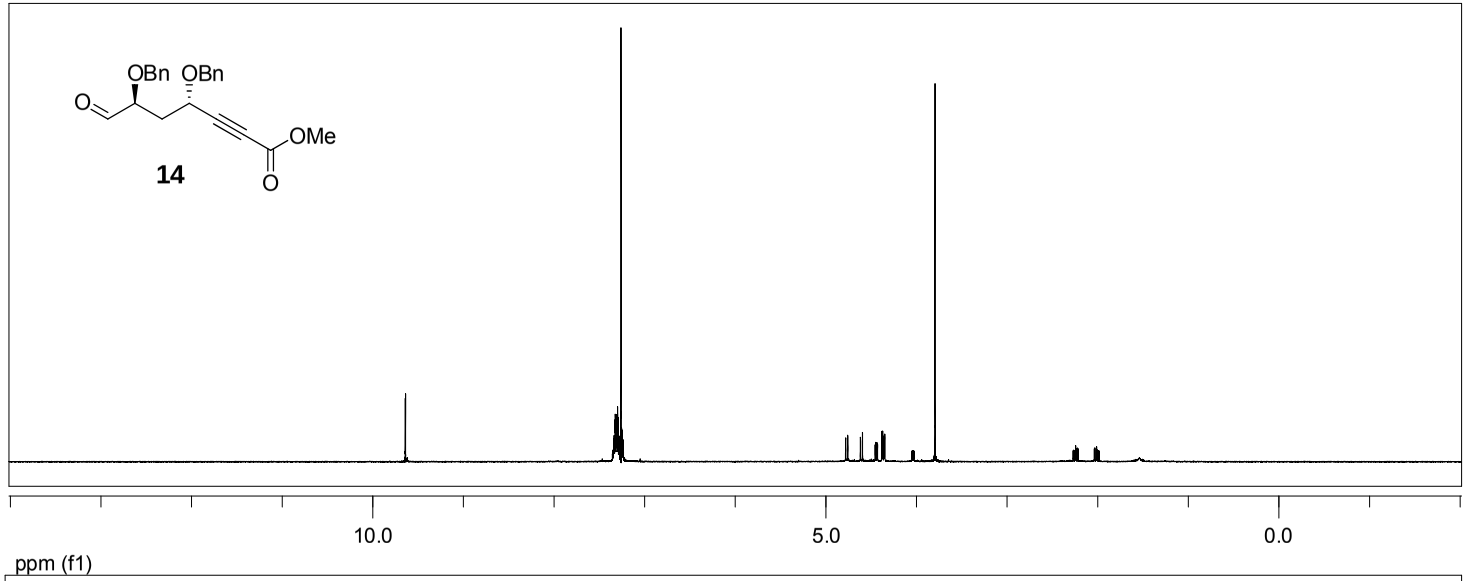


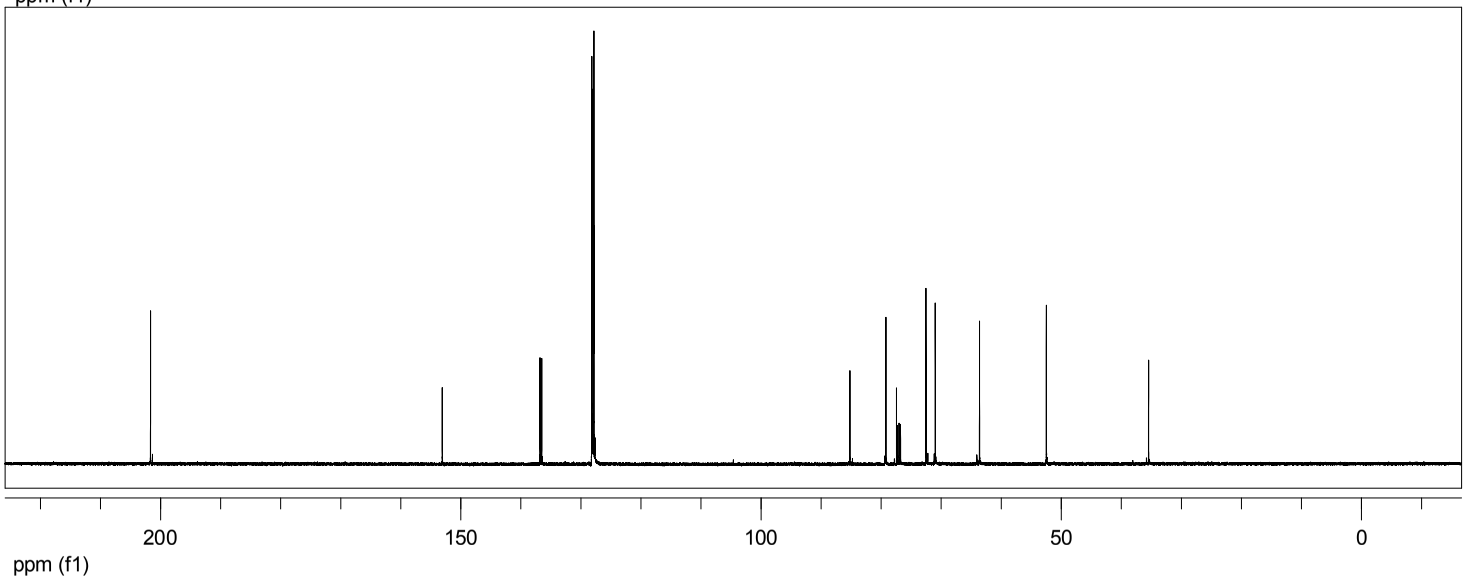

OH
OBn
O
O
17
10.0
5.0
0.0
ppm (f1)
0
50
100
150
200
ppm (f1)

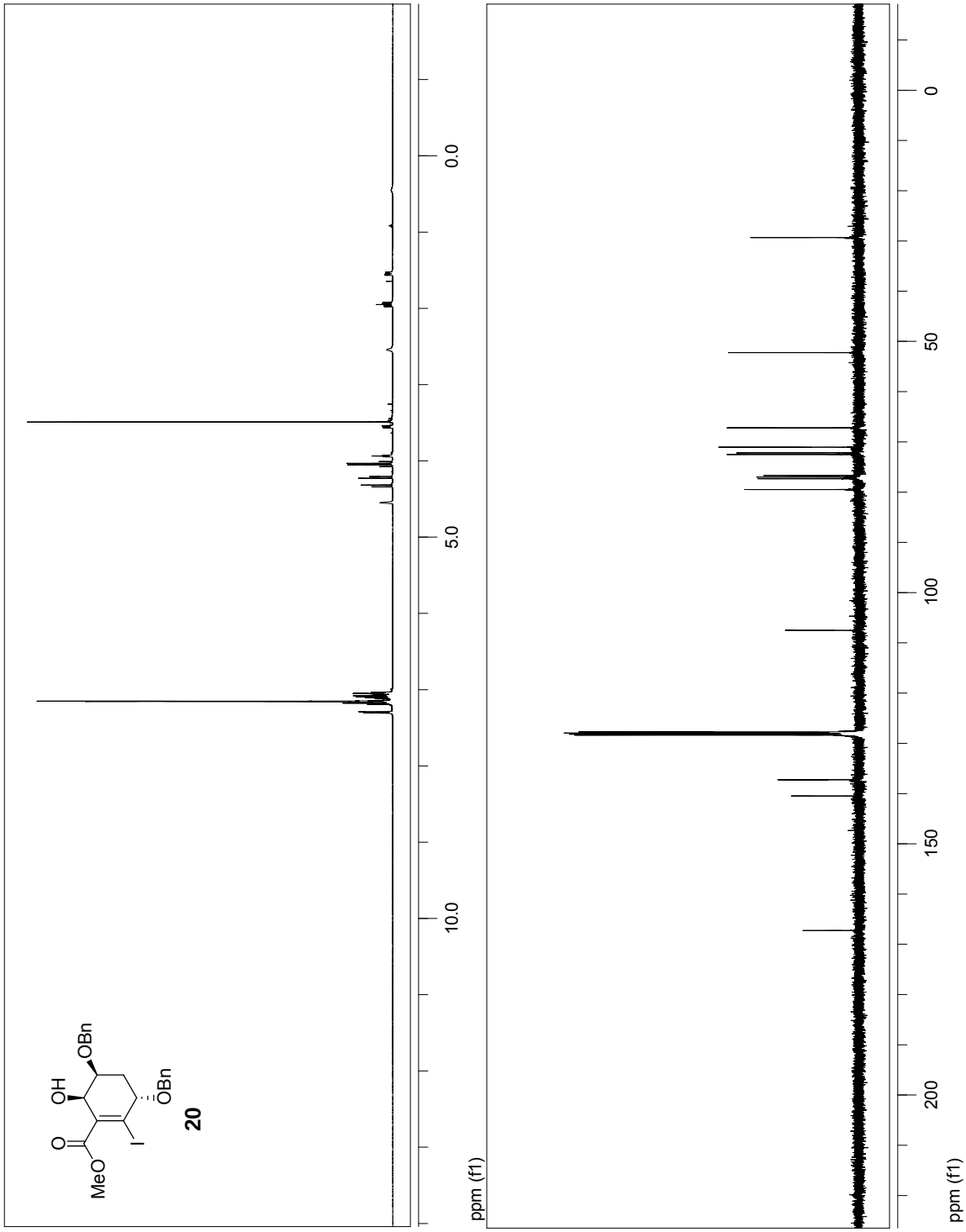

HO
HO
OBn
OMe
O
18
10.0
5.0
0.0
ppm (f1)
0
50
100
150
200
ppm (f1)

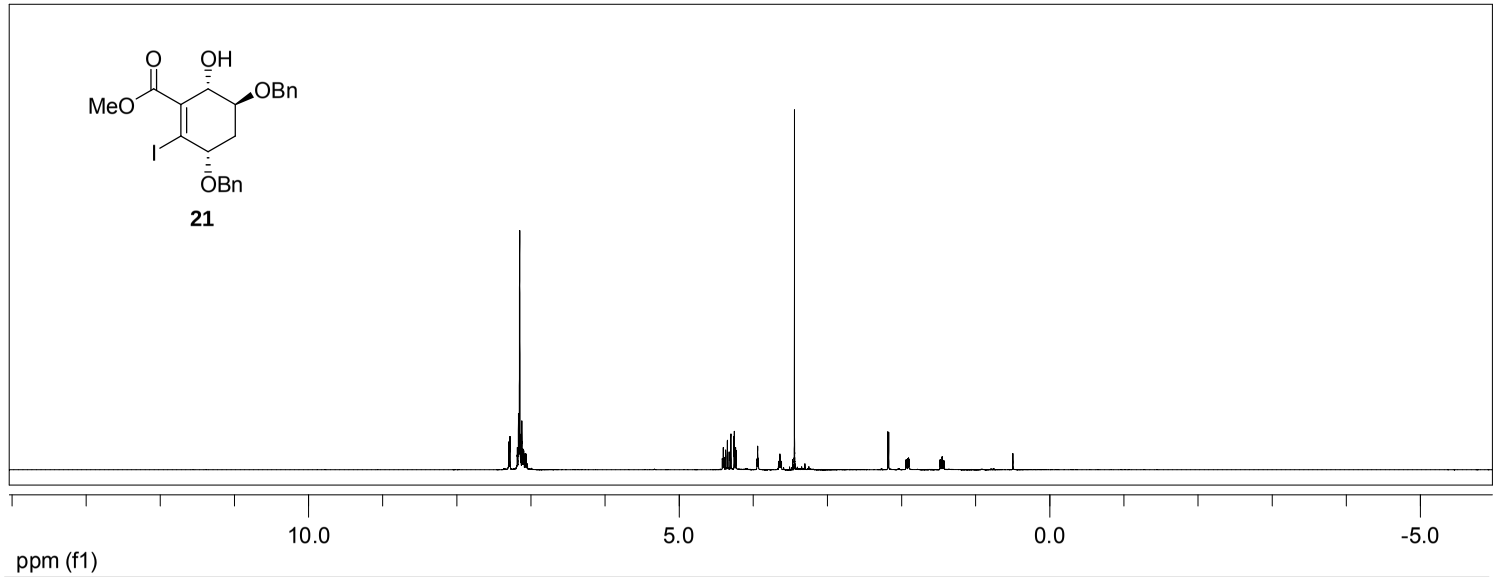

Ph
H
O
O
OBn
OMe
O
27
10.0
5.0
0.0
ppm (f1)
200
150
100
50
0
ppm (f1)

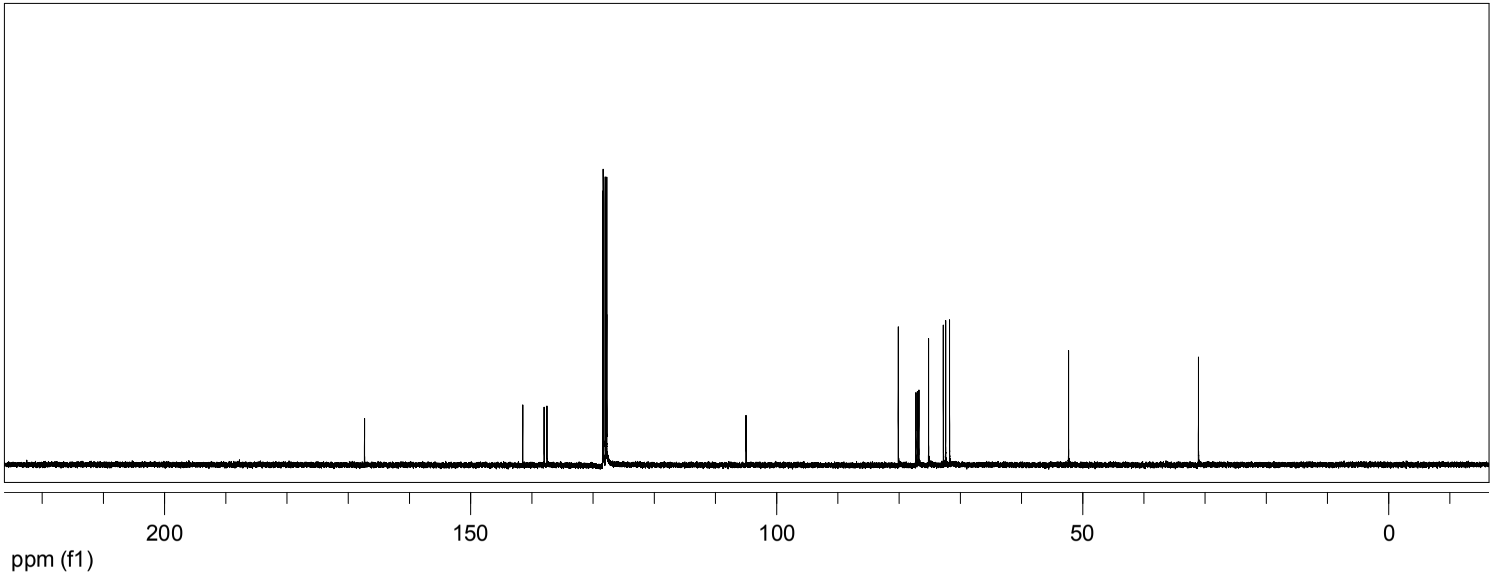

HO
OBn
OBn
19
OMe
O
10.0
5.0
0.0
ppm (f1)
0
50
100
150
200
ppm (f1)

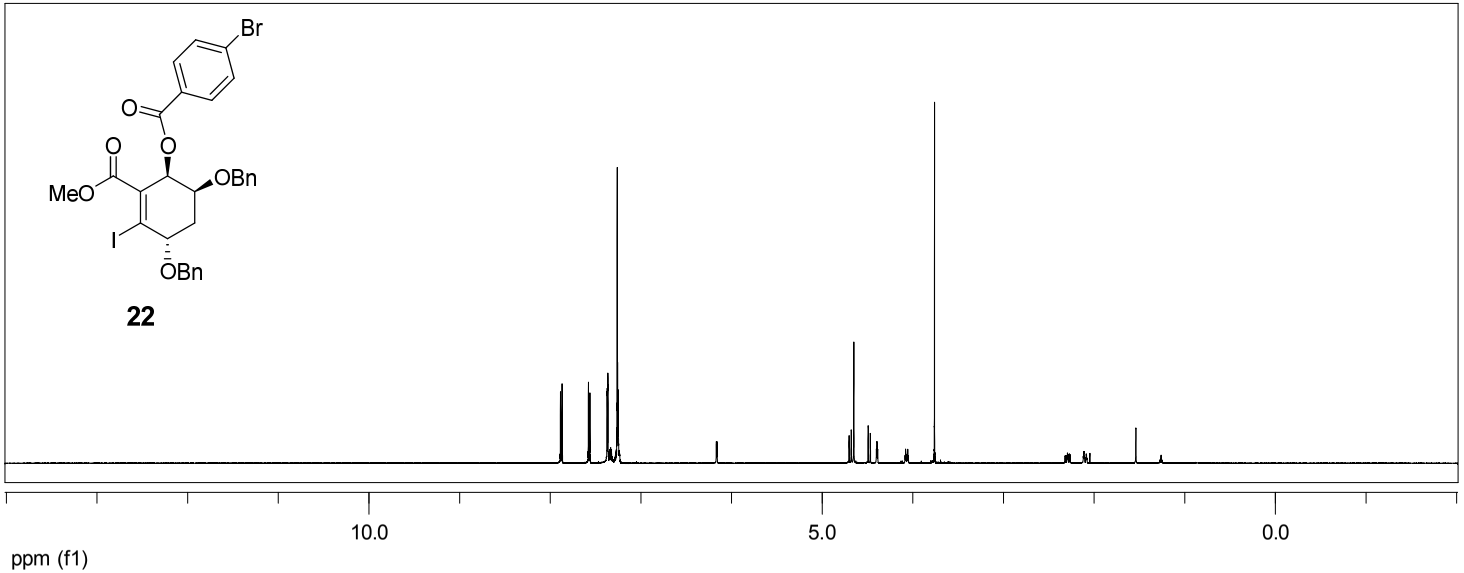

OBn
OBn
O
OMe
O
14
10.0
5.0
0.0
ppm (f1)

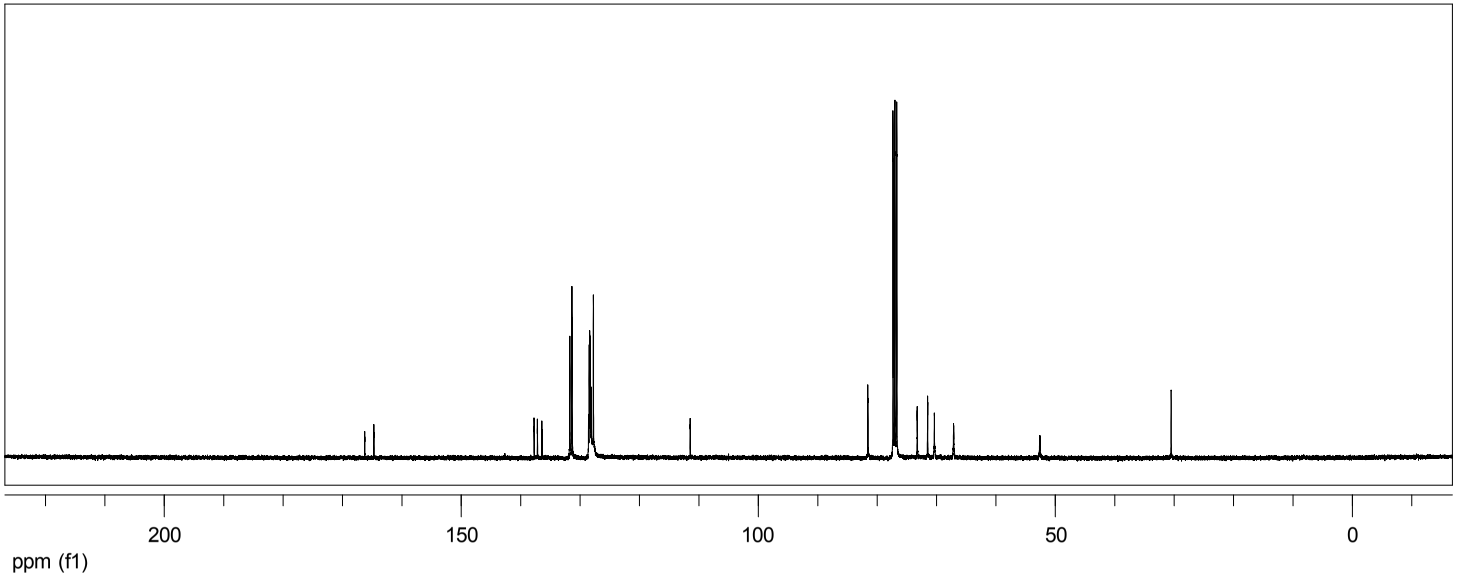

200
150
100
50
0
ppm (f1)

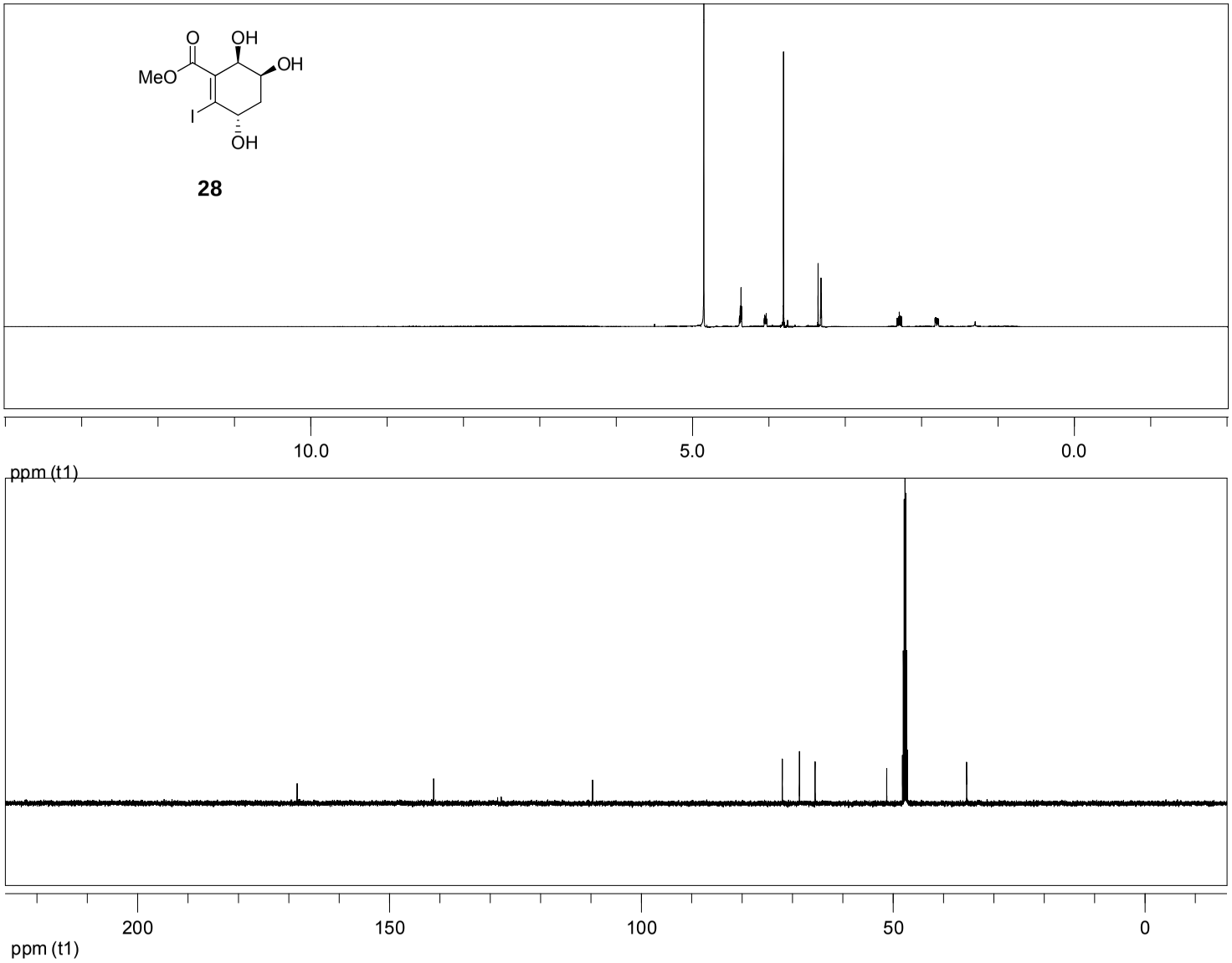

MeO
O
OH
OBn
OBn
I
20
10.0
5.0
0.0
ppm (f1)
150
100
50
0
ppm (f1)

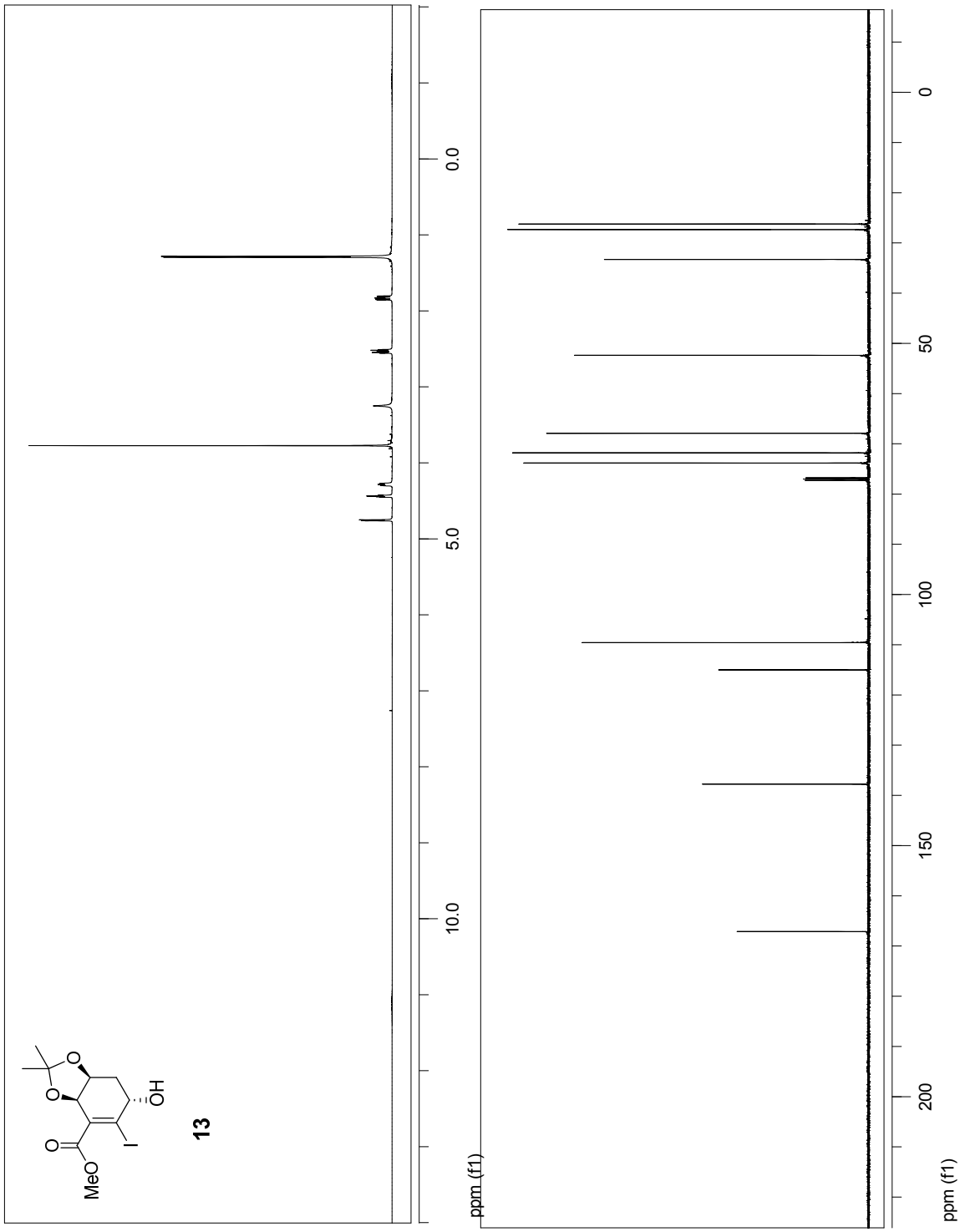

O
OH
MeO
OBn
I
OBn
21
10.0
5.0
0.0
-5.0
ppm (f1)

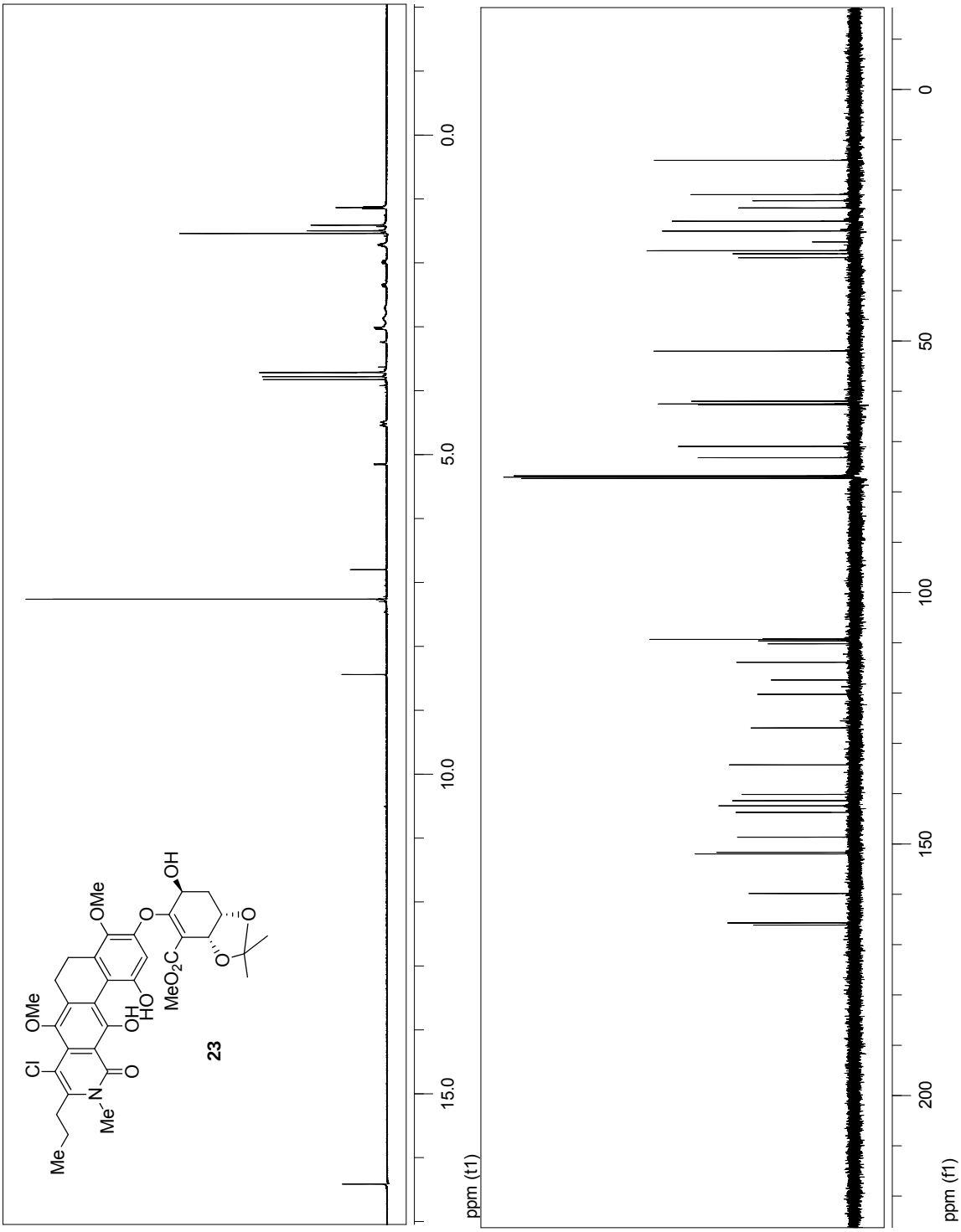

200
150
100
50
0
ppm (f1)

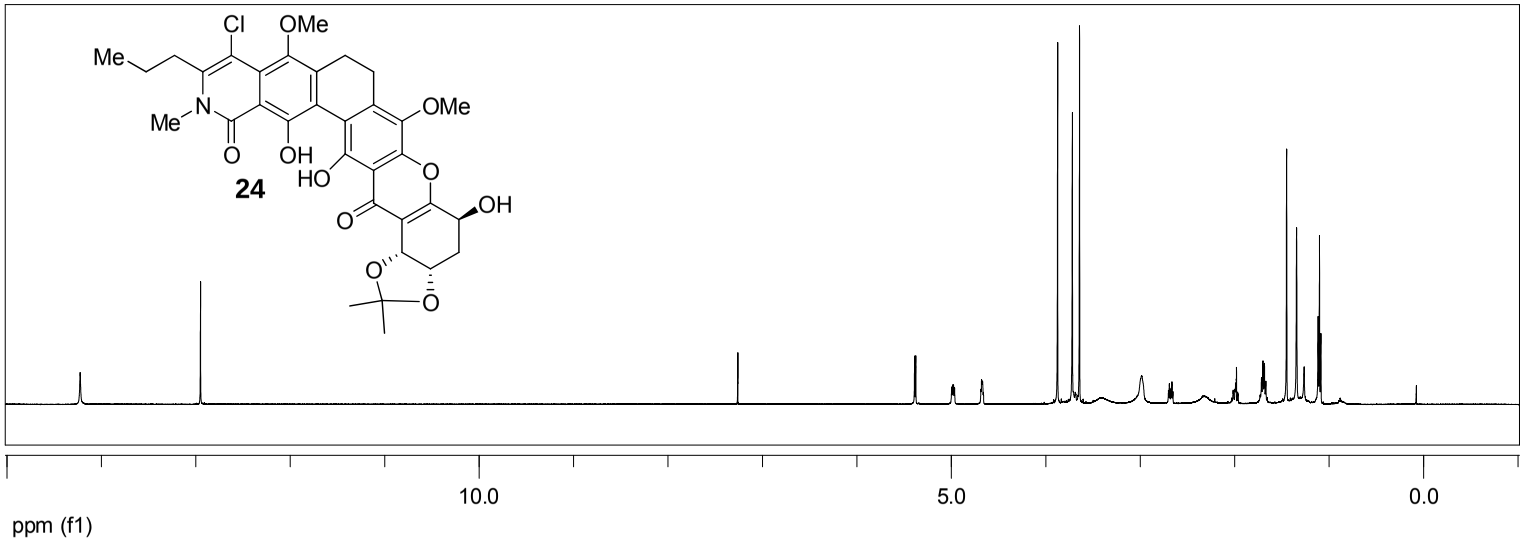

Br
O
O
O
MeO
OBn
I
OBn
22
10.0
5.0
0.0
ppm (f1)

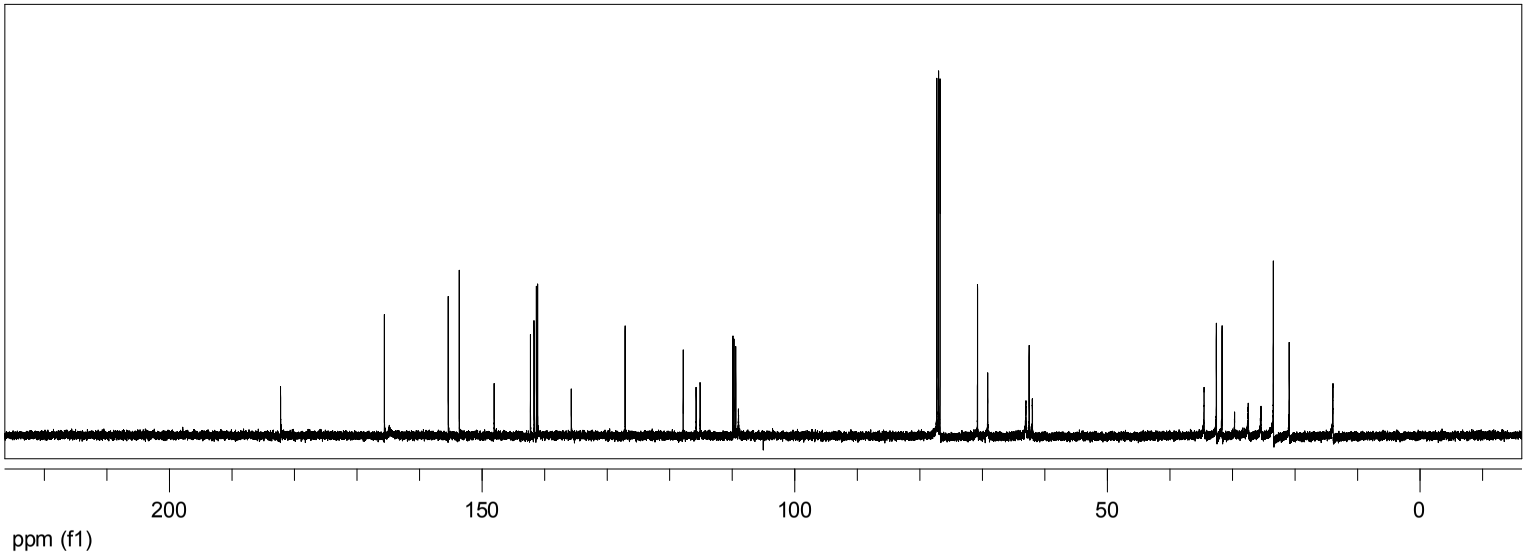

200
150
100
50
0
ppm (f1)

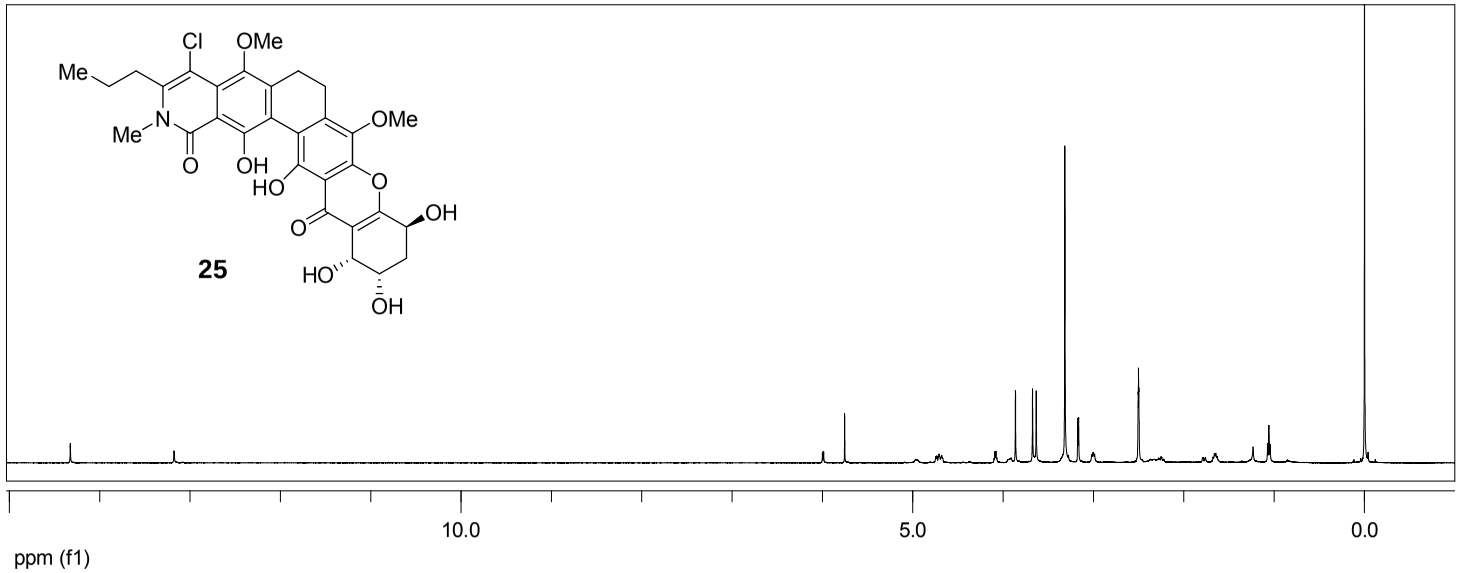

O
OH
OH
MeO
I
OH
28
10.0
5.0
0.0
ppm (t1)
200
150
100
50
0
ppm (t1)

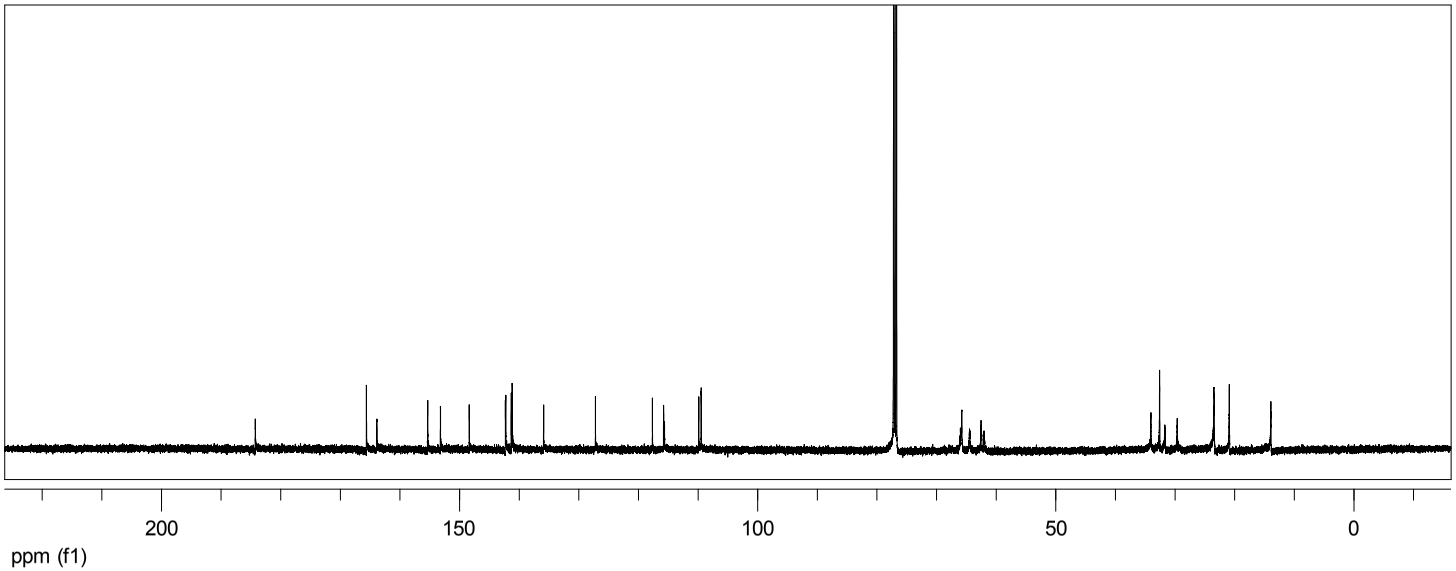

MeO
O
O
O
OH
I
13
10.0
5.0
0.0
ppm (f1)
200
150
100
50
0
ppm (f1)

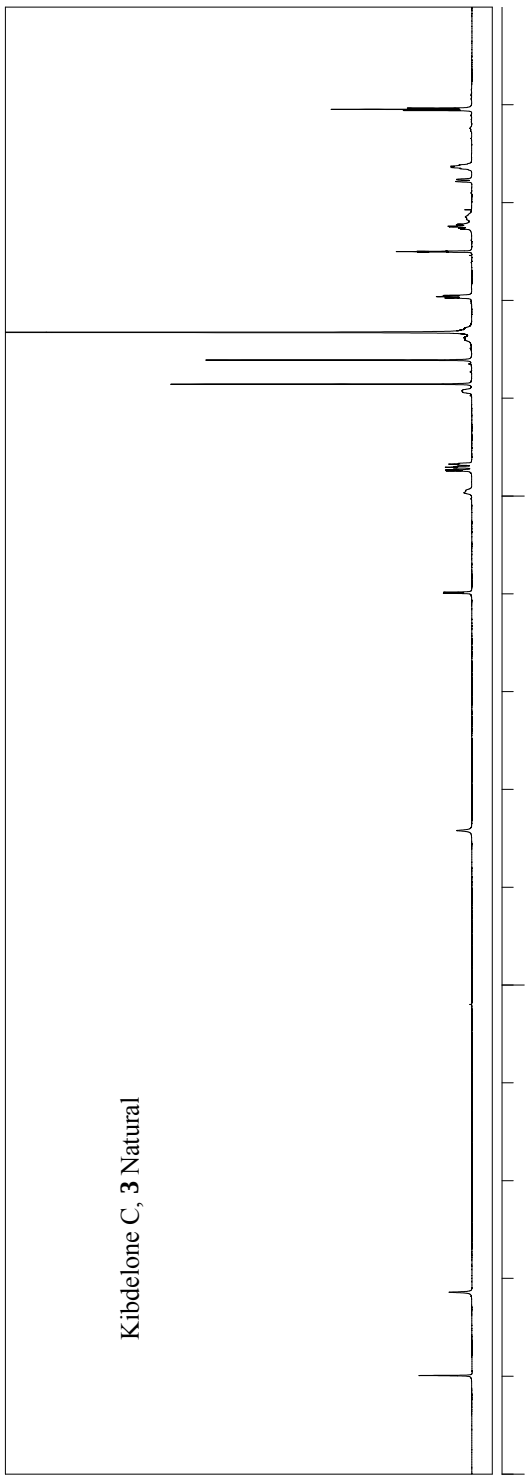

23
Cl
OMe
OMe
Me
N
Me
O
OH
HO
O
MeO2C
OH
O
O
15.0
10.0
5.0
0.0
ppm (t1)
200
150
100
50
0
ppm (f1)

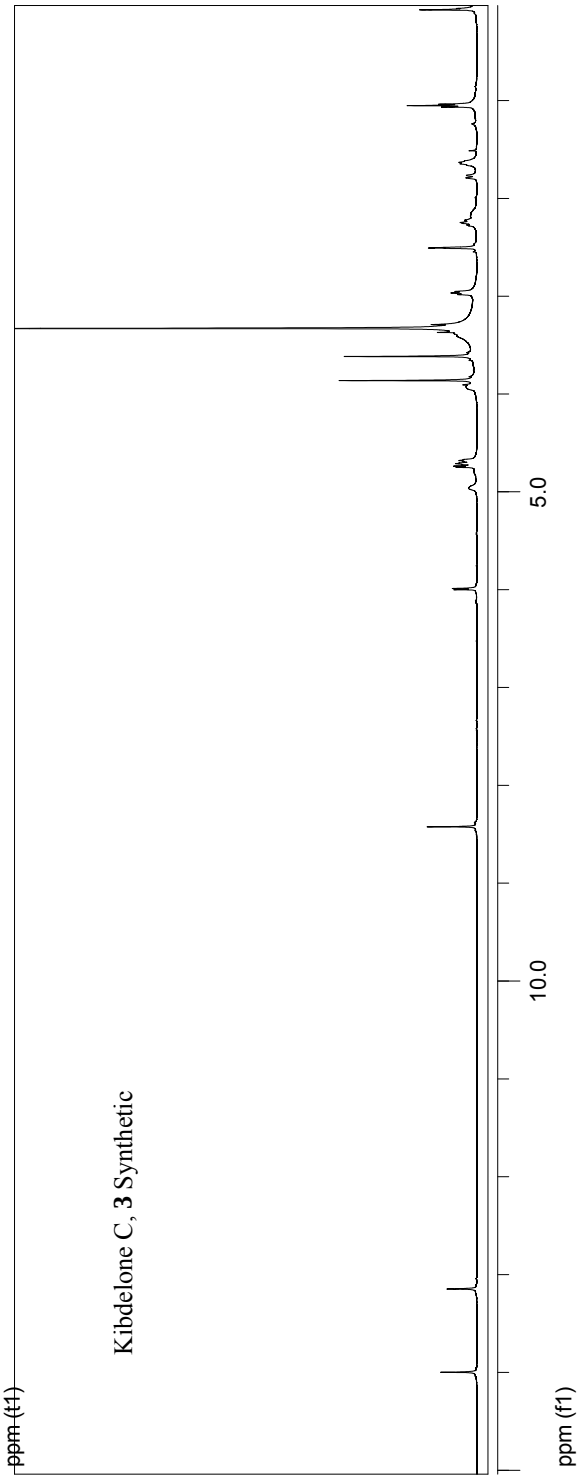

Cl
OMe
Me
N
Me
O
OH
HO
OMe
O
OH
O
O
O
24
10.0
5.0
0.0
ppm (f1)

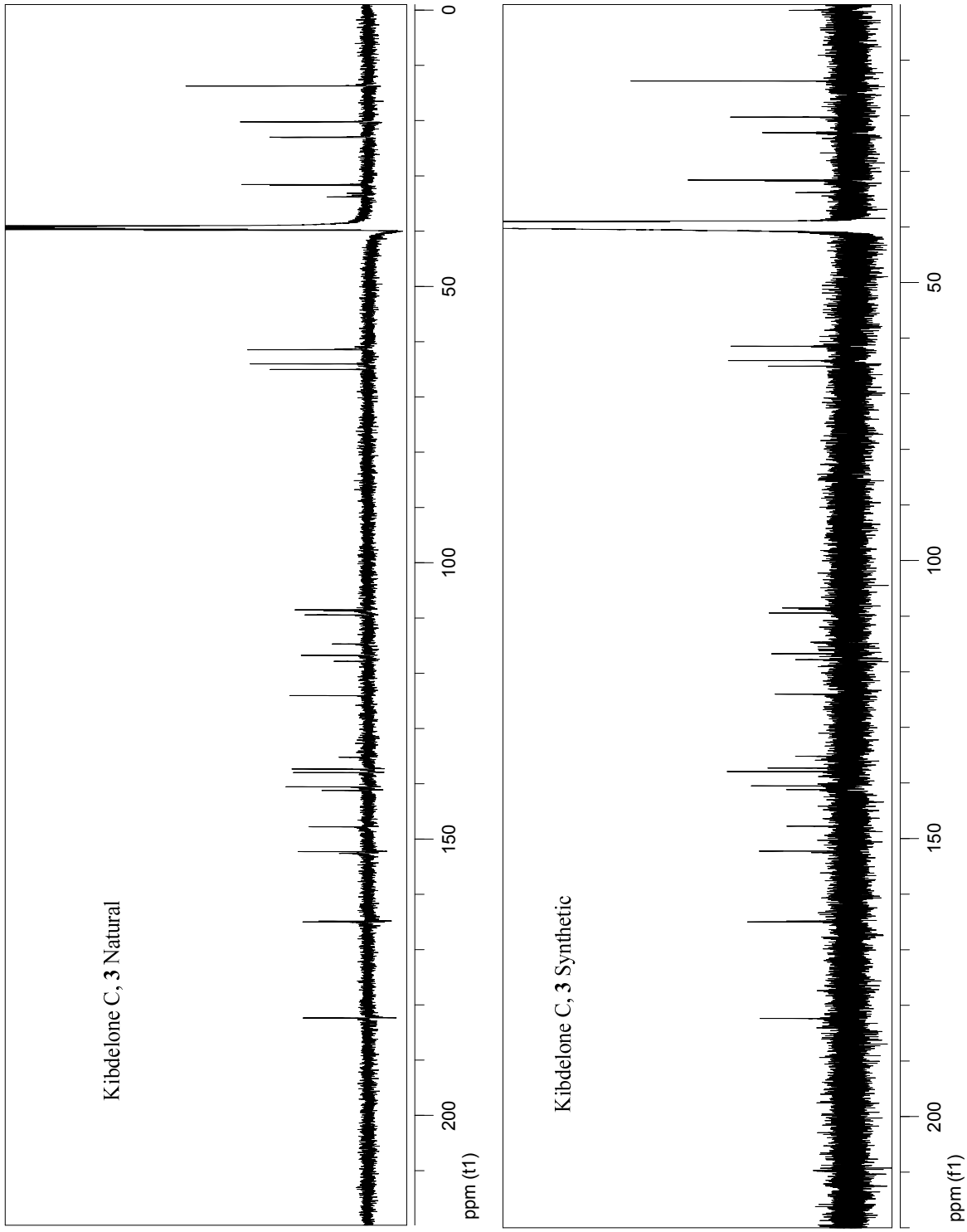

200
150
100
50
0
ppm (f1)


Cl
OMe
Me
N
Me
O
OH
HO
OMe
O
O
OH
HO
OH
25
10.0
5.0
0.0
ppm (f1)


200
150
100
50
0
ppm (f1)


Kibdelone C, 3 Natural
10.0
5.0
ppm (f1)


Kibdelone C, 3 Synthetic
10.0
5.0
ppm (f1)


Kibdelone C, 3 Natural
Kibdelone C, 3 Synthetic
200
150
100
50
0
ppm (t1)
ppm (f1)