Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Enantioselective Total Synthesis of (+)-Brazilin, (–)-Brazilein and (+)-Brazilide A

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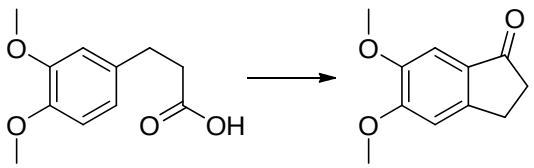
General Experimental: Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on Bruker Avance 300 and 400 spectrometer at 300 and 400 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was recorded on Bruker Avance 300 and 400 spectrometer at 75 and 100 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. Low-resolution Mass spectra were recorded on a VG Auto Spec-3000 magnetic sector MS spectrometer. High Resolution Mass spectra were taken on AB QSTAR Pulsar mass spectrometer. The infrared (IR) spectra were acquired as thin films on a FT-IR spectrometer and the absorption frequencies are reported in cm^{-1}. Chiral HPLC analyses were performed on Agilent 1100 series with a tunable UV detector at wavelength λ = 254 nm. Melting points were determined on a capillary melting point apparatus and are uncorrected. Optical rotations were obtained on a UV-210A spectrometer. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated. THF and diethyl ether used in the reactions were dried by distillation over metallic sodium and benzophenone; dichloromethane were distilled over P_2O_5. Unless otherwise stated, all reactions were conducted in dried glassware under a positive pressure of dry nitrogen or argon. Silica gel (Qingdao, 300-400 mesh) was used for column chromatography.

Synthesis of compound 12



11 **12**

5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-one

$C_{11}H_{12}O_3$ Mol. Wt.: 192.08

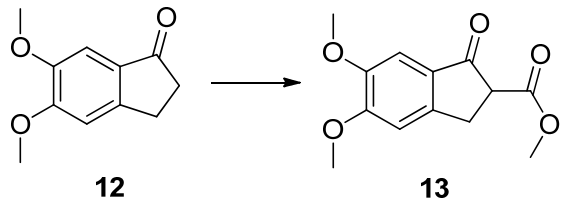
To a solution of 3-(3,4-dimethoxyphenyl)propanoic acid **11** (21 g, 0.1 mol) in anhydrous dichloromethane (300 mL) and DMF (0.5 mL) was added oxalyl chloride (24 mL, 0.25 mol) dropwise over a period of 1 hour. The mixture was then stirred at room temperature overnight. The resulting mixture was concentrated under reduced pressure and the crude aryl propionyl chloride was redissolved in anhydrous dichloromethane (300 mL) at 0 °C. To the solution of aryl propionyl

chloride was added portionwise a powder of $AlCl_3$ (16 g, 0.12 mol). The reaction mixture was then stirred at room temperature for 2 h. Ice (20 g) was added slowly at 0 °C (to quench the excess $AlCl_3$) followed by ice-water (100 mL). The organic phase was separated, and the aqueous phase was extracted with dichloromethane (3 × 100 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, decolorized with activated carbon, filtered, and concentrated to afford the product (**12**, 18.6 g , 97%) as pale yellow solid.[1]

Ref. 1: S. R. Haadsma-Svensson, K. A. Cleek, D. M. Dinh, J. N. Duncan, C. L. Haber, R. M. Huff, M. E. Lajiness, N. F. Nichols, M. W. Smith, K. A. Svensson, M. J. Zaya, A. Carlsson, C. H. Lin, *J. Med. Chem.* **2001,** *44*, 4716.

m.p.: 116-118 °C. IR: ν_{max} (KBr) cm^{-1}: 3055, 2928, 2849, 1699, 1592, 1497, 1450, 1313, 1258, 1116, 1037, 896, 851, 813, 708. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.17 (1H, *s*), 6.89 (1H, *s*), 3.96 (3H, *s*), 3.90 (3H, *s*), 3.05 (2H, *t*, *J* = 5.4 Hz), 2.68-2.65 (2H, *m*). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 205.77, 155.39, 150.43, 149.37, 129.91, 107.47, 104.16, 56.23, 56.09, 36.53, 25.58. ES+ *m/z* (%): 192 (M^+, 100), 177 (27), 164 (12), 149 (32), 135 (13), 121 (67), 107 (34), 91 (47), 77 (81), 63 (59), 51 (69). HRMS *m/z* Found: 192.0793, Calcd. for $C_{11}H_{12}O_3$ $(M)^+$: 192.0786.

Synthesis of compound 13



12 **13**

methyl 5,6-dimethoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate

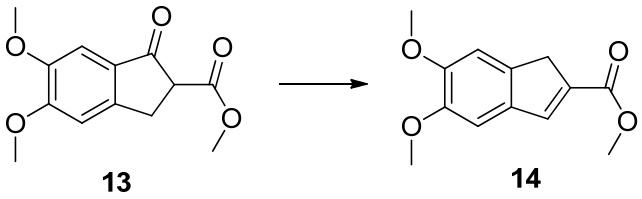
$C_{13}H_{14}O_5$ Mol. Wt.: 250.08

To a silution of 1-indanone **12** (9.6 g, 50 mmol) in dimethylcarbonate (80 mL) was added NaH (3.42 g, 100 mmol, 70% in paraffin), and the mixture was stirred at 90 °C for 3-4 h. The resulting solid was cooled with an ice-water bath at 0 °C. Dichloromethane (200 mL) was added, followed by aqueous solution of HCl (6M, 18 mL) and H_2O (100 mL). The organic phase was separated, and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated. The desired product (**13**, 11.5 g, 92%) was obtained as pale yellow solid by flash column chromatography (Hexane : EtOAc = 8 :1→4 : 1) on silica gel.[2]

Ref. 2: C. X. Pan, X. H. Zeng, Y. F. Guan, X. L. Jiang, L. Li, H. Zhang, *Synlett*, **2011**, 425.

m.p.: 161-162 °C. IR: ν_{max} (KBr) cm^{-1}: 3068, 2929, 2848, 1704, 1591, 1506, 1452, 1314, 1264, 1207, 1115, 1025, 956, 876, 723. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.16 (1H, *s*), 6.90 (1H, *s*), 3.96 (3H, *s*), 3.89 (3H, *s*), 3.77 (3H, *s*), 3.71 (1H, *dd*, *J* = 3.4, 7.9 Hz), 3.44 (1H, *dd*, *J* = 3.3, 17.0 Hz), 3.26 (1H, *dd*, *J* = 7.9, 17.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 197.94, 169.90, 156.11, 149.78, 149.27, 127.92, 107.26, 104.83, 56.34, 56.15, 53.41, 52.76, 30.02. ES+ *m/z* (%): 250 (M^+, 16), 218 (18), 190 (34), 175 (11), 125 (15), 111 (28), 97 (38), 85 (40), 83 (40), 77 (18), 71 (52), 57 (100), 55 (72). HRMS *m/z* Found: 250.0852, Calcd. for $C_{13}H_{14}O_5$ $(M)^+$: 250.0841.

Synthesis of compound 14



13 **14**

methyl 5,6-dimethoxy-1*H*-indene-2-carboxylate

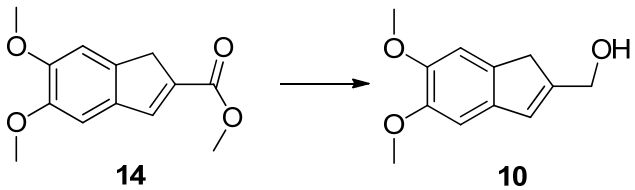
$C_{13}H_{14}O_4$ Mol. Wt.: 234.09

1-Indanone-2-carboxylic acid methyl ester **13** (5.0 g, 20 mmol) was dissolved in dichloromethane (100 mL) and methanol (10 mL). $NaBH_4$ (912 mg, 24 mmol) was added portionwise at 0 °C and the mixture was stirred at room temperature for 1 h. A solution of aqueous HCl (1 M, 30 mL) was added. The organic phase was separated and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was re-dissolved in toluene (100 mL) and PPTS (Pyridinium *p*-toluenesulfonate, 0.5 g, 2 mmol) was added. The resulting mixture was stirred at reflux with a Dean-Stark trap for 3-6 h. The reaction progress was monitored by TLC. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (250 mL) and washed with brine, dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : DCM = 1:1) afforded the product (**14**, 3.51 g, 75%) as white solid.[2]

Ref. 2: C. X. Pan, X. H. Zeng, Y. F. Guan, X. L. Jiang, L. Li, H. Zhang, *Synlett*, **2011**, 425.

m.p.: 122-123 °C. IR: ν_{max} (KBr) cm^{-1}: 3065, 2949, 2838, 1696, 1604, 1558, 1485, 1438, 1320, 1229, 1092, 989, 849, 737. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.64 (1H, *s*), 7.06 (1H, *s*), 7.02 (1H, *s*), 3.92 (3H, *s*), 3.91 (3H, *s*), 3.82 (3H, *s*), 3.61 (2H, *s*). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 165.37, 149.77, 148.69, 141.48, 138.32, 135.35, 135.25, 107.54, 105.95, 56.12, 51.50, 38.37. ES+ *m/z* (%): 234 (M^+, 76), 219 (24), 203 (24), 191 (16), 175 (52), 160 (26), 145 (20), 131 (93), 117 (58), 89 (100), 83 (81), 75 (27), 63 (72), 59 (67). HRMS *m/z* Found: 234.0893, Calcd. for $C_{13}H_{14}O_4$ $(M)^+$: 234.0892.

Synthesis of compound 10



14 **10**

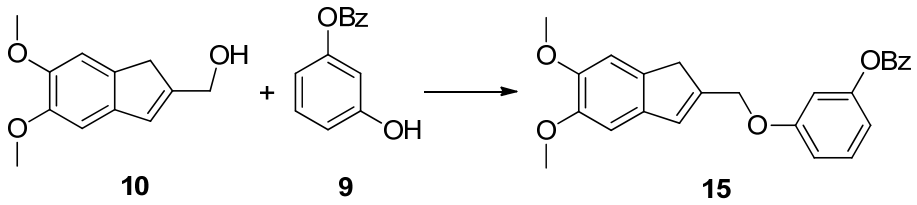
(5,6-dimethoxy-1*H*-inden-2-yl)methanol

$C_{12}H_{14}O_3$ Mol. Wt.: 206.09

To a solution of methyl ester **14** (5.0 g, 21.4 mmol) in dichloromethane (100 mL) at –78 °C under argon was added dropwise a solution of DIBAL-H (31.4 mL, 1.5 M in toluene, 47.1 mmol). After 3 h, the reaction was quenched slowly with MeOH (5.0 mL) at –78 °C followed by addition of a saturated aqueous solution of $NaHCO_3$ (27 mL). The reaction mixture was allowed to reach room temperature and filtered through celite. The organic phase was separated and the aqueous phase was extracted with dichloromethane (3 × 50 mL). The combined organic phases were washed with brine (80 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : DCM = 2:1) afforded product **10** (4.01 g, 91%) as white solid.

m.p.: 105-106 °C. IR: ν_{max} (KBr) cm^{-1}: 3356, 3064, 2927, 2837, 1610, 1485, 1320, 1267, 1215, 1101, 1026, 992, 856, 759. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 6.99 (1H, *s*), 6.87 (1H, *s*), 6.61 (1H, *s*), 4.51 (2H, *s*), 3.87 (6H, *s*), 3.33 (2H, *s*), 2.05 (1H, br, *s*). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 148.19, 147.36, 147.01, 137.22, 135.84, 127.54, 108.09, 104.54, 61.75, 56.24, 56.11, 38.93. ES+ *m/z* (%): 206 (M^+, 67), 191 (22), 175 (37), 161 (27), 145 (36), 131 (52), 115 (80), 103 (78), 91 (100), 83 (44), 77 (74), 63 (87), 51 (70). HRMS *m/z* Found: 206.0945, Calcd. for $C_{12}H_{14}O_3$ $(M)^+$: 206.0943.

Synthesis of compound 15



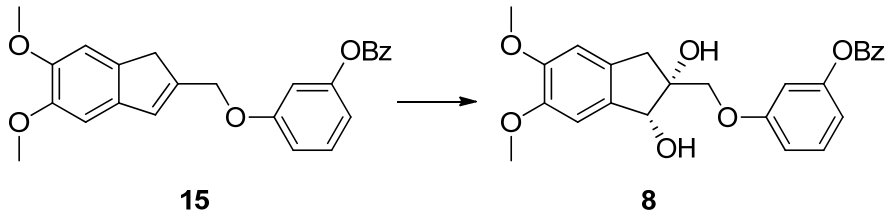
3-((5,6-dimethoxy-1*H*-inden-2-yl)methoxy)phenyl benzoate

$C_{25}H_{22}O_5$ Mol. Wt.: 402.15

1-Indene-2-methanol **10** (1.03 g, 5.0 mmol), triphenylphosphine (1.58 g, 6.0 mmol) and 3-hydroxyphenyl benzoate **9** (1.18 g, 5.5 mmol) were dissolved in dry THF (80 mL) then cooled to –78 °C. To this mixture was added dropwise a solution of diethyl azodicarboxylate (1.0 mL, 6.0 mmol) in dry THF (5 mL) over 30 min. The resulting yellow solution was then allowed to warm up and stirred at room temperature for 1 h. The reaction progress was monitored by TLC. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Hexane : DCM = 3:1→1:1) to give the product (**15**, 1.21 g, 60%) as white solid.

m.p.: 121-122 °C. IR: ν_{max} (KBr) cm^{-1}: 3064, 2991, 2932, 2831, 1736, 1603, 1487, 1313, 1261, 1144, 1100, 1012, 878, 778, 707. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.21 (2H, *d*, *J* = 7.2 Hz), 7.64 (1H, *t*, *J* = 7.2 Hz), 7.52 (2H, *t*, *J* = 7.8 Hz), 7.33 (1H, *t*, *J* = 8.2 Hz), 7.05 (1H, *s*), 6.93 (1H, *s*), 6.89 (1H, *dd*, *J* = 2.0, 8.4 Hz), 6.86 (1H, *t*, *J* = 2.0 Hz), 6.83 (1H, *dd*, *J* = 2.0, 8.4 Hz), 6.78 (1H, *s*), 4.95 (2H, *s*), 3.90 (6H, *s*), 3.46 (2H, *s*). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 165.12, 159.71, 151.90, 148.27, 147.29, 142.46, 136.96, 136.00, 133.64, 130.20, 129.93, 129.77, 129.53, 128.60, 114.14, 112.54, 108.60, 108.04, 104.71, 67.01, 56.26, 56.13, 39.37. ES+ *m/z* (%): 402 (M^+, 5), 250 (10), 234 (23), 206 (100), 191 (50), 175 (60), 161 (33), 145 (41), 131 (59), 117 (36), 105 (49), 91 (66), 77 (68), 63 (46). HRMS *m/z* Found: 402.1478, Calcd. for $C_{25}H_{22}O_5$ $(M)^+$: 402.1467.

Synthesis of compound 8



3-(((1*R*,2*R*)-1,2-dihydroxy-5,6-dimethoxy-2,3-dihydro-1*H*-inden-2-yl)methoxy)phenyl benzoate

$C_{25}H_{24}O_7$ Mol. Wt.: 436.15

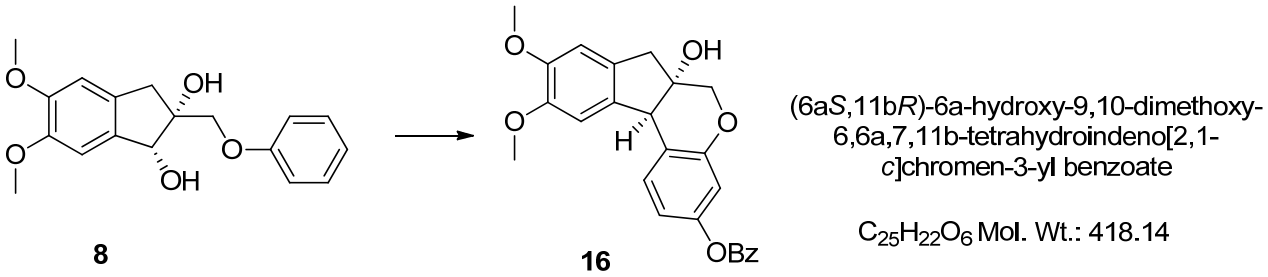
A 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 1.4 g AD-mix-β [3] and methanesulfonylamide (98 mg, 1.0 mmol). *tert*-Butanol (10 mL) and water (10 mL) were added and the slurry was

stirred at room temperature until all solids dissolved. The orange solution was then cooled to 0 °C. The 1-indene-2-benzoate (**15**, 402 mg, 1 mmol) and 3-hydroxyphenyl benzoate (**9**, 214 mg, 1.0 mmol) in dichloromethane (1 mL) were added. A solution of OsO_4 (0.13 mL, 20 mg/mL, 1% mmol) was added and the resulting mixture was vigorously stirred at room temperature for 3 days. The reaction progress was monitored by TLC. Saturated aqueous solution of $Na_2S_2O_3$ (13 mL) was added and the reaction was stirred for 15 min. The mixture was then extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with brine (15 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 3:1→2:1) afforded the product (**8**, 370 mg, 85%) as a yellow syrup. 80.5% ee, determined by HPLC on a Chiracel AS column using 2-propanol in hexane (30%) as the eluent.

Ref. 3: K. B. Sharpless, W. Amberg, Y. L. Bennani, G. A. Crispino, J. Hartung, K. S. Jeong, H. L. Kwong, K. Morikawa, Z. M. Wang, D. Xu, X. L. Zhang, *J. Org. Chem.*, **2011**, *57*, 2768.

IR: ν_{max} (KBr) cm^{-1}: 3443, 3072, 2924, 2848, 1732, 1603, 1497, 1455, 1320, 1264, 1143, 990, 872, 766, 708. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.19 (2H, *d*, *J* = 7.6 Hz), 7.64 (1H, *t*, *J* = 7.2 Hz), 7.51 (2H, *t*, *J* = 7.6 Hz), 7.34 (1H, *t*, *J* = 8.0 Hz), 6.96 (1H, *s*), 6.87-6.84 (3H, m), 6.75 (1H, *s*), 5.09 (1H, *d*, *J* = 6.9 Hz), 4.15 (1H, *d*, *J* = 9.3 Hz), 4.10 (1H, *d*, *J* = 9.2 Hz), 3.88 (3H, *s*), 3.87 (3H, *s*), 3.20 (1H, *s*), 3.08 (1H, *d*, *J* = 16.2 Hz), 3.05 (1H, *d*, *J* = 16.2 Hz), 2.80 (1H, *d*, *J* = 6.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 165.17, 159.37, 151.90, 149.96, 148.90, 133.73, 133.39, 131.16, 130.19, 130.09, 129.37, 128.62, 114.61, 112.36, 108.53, 108.01, 107.76, 80.67, 77.25, 72.28, 56.07, 40.87. ES+ *m/z* (%): 436 (M^+, 92) , 418 (14), 400 (5), 277 (18), 222 (11), 205 (22), 189 (33), 151 (9), 105 (100), 91 (6), 77 (58). HRMS *m/z* Found: 436.1529, Calcd. for $C_{25}H_{24}O_7$ $(M)^+$: 436.1522.

Synthesis of compound 16

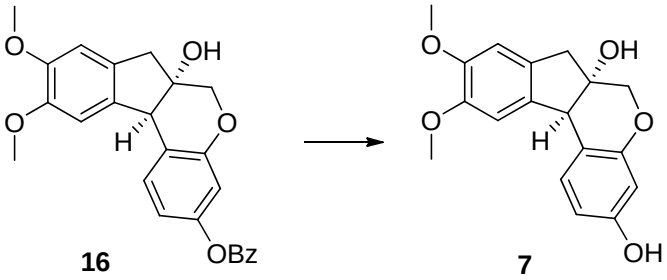


To a solution of diol **8** (930 mg, 2.13 mmol) in toluene (25 mL) was added pyridinium *p*-toluenesulfonate (PPTS, 643 mg, 2.56 mmol). The resulting mixture was stirred at 90 ºC for 2 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (100 mL) and washed with brine (20 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 3:1→2:1) afforded the product (**16**, 713 mg, 80%) as yellow plates.

m.p.: 130-131 °C. IR: ν_{max} (KBr) cm^{-1}: 3509, 3052, 2926, 2836, 1716, 1599, 1499, 1454, 1319, 1274, 1130, 1032, 960, 889, 710. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.20 (2H, *d*, *J* = 7.8 Hz), 7.64 (1H, *t*, *J* = 7.4 Hz), 7.52 (2H, *t*, *J* = 7.6 Hz), 7.45 (1H, *d*, *J* = 8.4 Hz), 6.94 (1H, *dd*, *J* = 2.0, 8.4 Hz), 6.82 (1H, *dd*, *J* = 2.0, 7.2 Hz), 6.81 (1H, *s*), 6.75 (1H, *s*), 4.21 (1H, *s*), 4.08 (1H, *d*, *J* = 11.2 Hz), 3.87 (1H, *d*, *J* = 11.2 Hz), 3.86 (3H, *s*), 3.84 (3H, *s*), 3.28 (1H, *d*, *J* = 15.6 Hz), 2.91 (1H, *d*, *J* =

15.6 Hz), 2.51 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 165.15, 154.31, 150.35, 148.86, 148.46, 135.42, 133.69, 131.15, 130.58, 130.22, 129.41, 128.60, 119.99, 115.28, 110.94, 108.46, 107.64, 70.33, 56.15, 56.08, 50.78, 41.33. ES+ m/z (%): 418 (M^+, 22), 400 (9), 295 (4), 267 (8), 239 (5), 211 (6), 194 (86), 165 (61), 118 (100), 105 (27). HRMS m/z Found: 418.1408, Calcd. for $C_{25}H_{22}O_6$ $(M)^+$ 418.1416.

Synthesis of compound 7



16 **7**

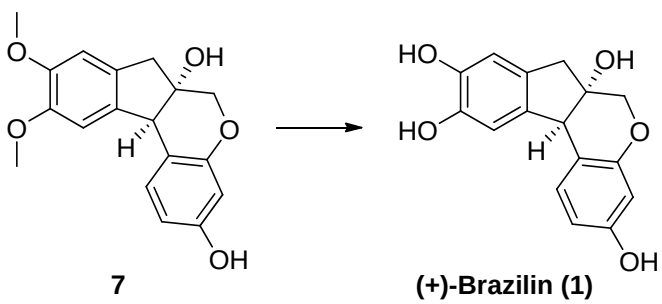
(6a*S*,11b*R*)-9,10-dimethoxy-6,6a,7,11b-tetrahydroindeno[2,1-*c*]chromene-3,6a-diol

$C_{18}H_{18}O_5$ Mol. Wt.: 314.12

To a solution of benzoate **16** (667 mg, 1.6 mmol) in THF (25 mL) was added a solution of LiOH (12.5 mL, 1.0 M in methol, 20 mmol). The reaction mixture was then stirred at room temperature for 30 min until TLC showed complete conversion. After removal of the solvents, the residue was then diluted with EtOAc (50 mL), aq. HCl (19 mL, 1.0 M) and brine (30 mL) and the organic phase was then separated. The aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic phases were washed with brine (30 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 1:1) afforded the product (**7**, 462 mg, 92%) as yellow crystals. After recrystallization (311 mg, 67%), the isomeric purity of phenol **7** was 99.8% ee, as determined by HPLC on a Chiracel AS column using 2-propanol in hexane (35%) as the eluent.

m.p.: 186-188 °C. $[\alpha]_D^{20}$ +125.5 (*c* 1.00, MeOH). IR: ν_{max} (KBr) cm^{-1}: 3359, 3259, 3011, 2925, 2840, 1608, 1500, 1466, 1287, 1224, 1148, 1037, 960, 841, 764. ^{1}H-NMR (400 MHz, MeOD) δ: 7.25 (1H, *d*, *J* = 8.3 Hz), 6.86 (1H, *s*), 6.80 (1H, *s*), 6.49 (1H, *dd*, *J* = 1.4, 8.3 Hz), 6.30 (1H, *s*), 4.03 (1H, *s*), 3.94 (1H, *d*, *J* = 11.3 Hz), 3.77 (3H, *s*), 3.76 (3H, *s*), 3.70 (1H, *d*, *J* = 11.3 Hz), 3.08 (1H, *d*, *J* = 15.8 Hz), 2.89 (1H, *d*, *J* = 15.8 Hz). ^{13}C-NMR (100 MHz, MeOD) δ: 156.62, 154.40, 148.72, 148.35, 137.03, 131.37, 130.78, 113.86, 108.76, 108.69, 108.22, 102.94, 76.79, 69.41, 55.29, 55.21, 50.03, 41.70. ES+ *m/z* (%): 314 (M^+, 7), 279 (3), 237 (7), 191 (4), 177 (6), 153 (17), 149 (31), 137 (29), 125 (12), 83 (17), 71 (46), 57 (100). HRMS *m/z* Found: 314.1148, Calcd. for $C_{18}H_{18}O_5$ $(M)^+$: 314.1154.

Synthesis of (+)-Brazilin (1)



7 **(+)-Brazilin (1)**

(6a*S*,11b*R*)-9,10-dihydroxy-6,6a,7,11b-tetrahydroindeno[2,1-*c*]chromene-3,6a-diol

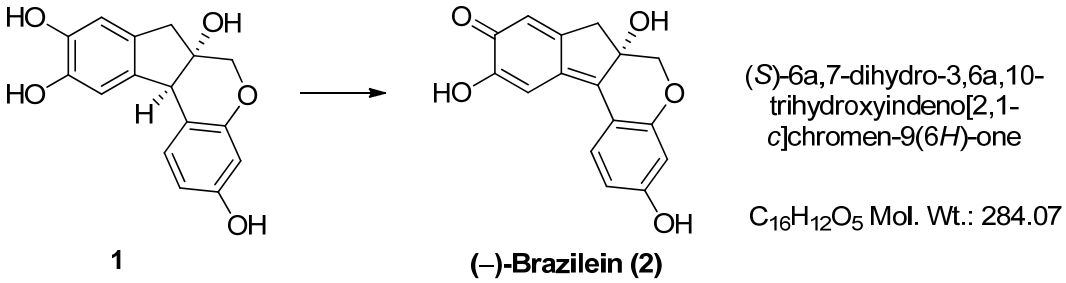
$C_{16}H_{14}O_5$ Mol. Wt.: 286.08

To a solution of compound **7** (30 mg, 0.1 mmol) in dry dichloromethane (10 mL) at –78 °C was added dropwise a solution of boron tribromide (0.09 mL, 4 N solution in dichloromethane, 0.35 mmol). The reaction mixture was then stirred at –78 °C for 2 h and stirred at room temperature overnight. The reaction was quenched by the addition of methanol (0.6 mL), then diluted with water (5 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (5 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 1:1) afforded the natural product (**1**, 22 mg, 81%) as yellow solid.[4]

m.p.: 68-69 °C. $[\alpha]_D^{20}$ +76.1 (*c* 1.00, MeOH), IR: ν_{max} (KBr) cm^{-1}: 3364, 2966, 2913, 1614, 1505, 1462, 1306, 1236, 1163, 1119, 1034, 979, 844, 771. ^{1}H-NMR (400 MHz, MeOD) δ: 7.19 (1H, *d*, *J* = 8.3 Hz), 6.71 (1H, *s*), 6.60 (1H, *s*), 6.47 (1H, *dd*, *J* = 2.4, 8.3 Hz), 6.30 (1H, *d*, *J* = 2.4 Hz), 3.96 (1H, *s*), 3.93 (1H, *d*, *J* = 11.3 Hz), 3.69 (1H, *d*, *J* = 11.3 Hz), 3.02 (1H, *d*, *J* = 15.6 Hz), 2.78 (1H, *d*, *J* = 15.6 Hz). ^{13}C-NMR (100 MHz, MeOD) δ: 157.84, 155.71, 145.64, 145.32, 137.45, 132.23, 131.37, 115.59, 112.89, 112.47, 109.97, 104.27, 78.08, 70.86, 51.07, 42.90. ES+ *m/z* (%): 286 (M^+, 39), 268 (16), 229 (6), 163 (3), 147 (3), 105 (6), 84 (82), 77 (5), 66 (100), 57 (18). HRMS *m/z* Found: 286.0844, Calcd. for $C_{16}H_{14}O_5$ $(M)^+$: 286.0841.

Ref. 4: a) C. F. J. Yamahara, T. Shimokawa, J. Kinjo, T. Tomimatsu, T. Nohara, *Phytochemistry* **1985**, *24*, 2403; b) D. S. Kim, N. Baek, S. P. Oh, K. Y. Jung, I. S. Lee, H.-K. Lee, *Phytochemistry* **1997**, *46*, 177.

Synthesis of (–)-Brazilein (2)

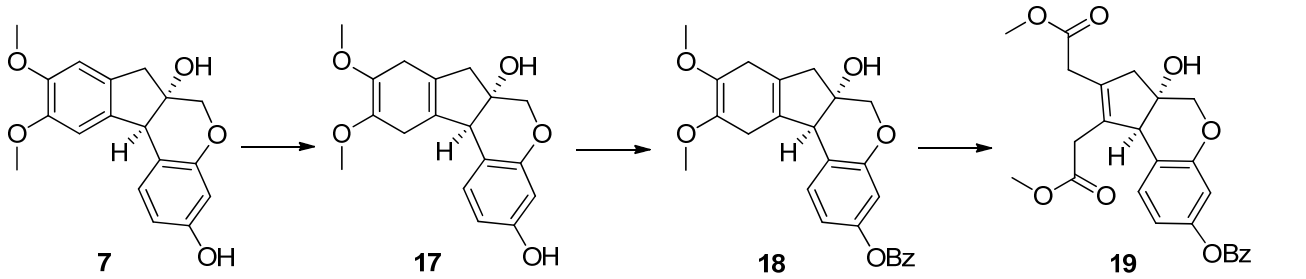


To a solution of (+)-Brazilin (**1**, 14.3 mg, 0.05 mmol) in anhydrous THF (3 mL) at 0 °C was added IBD (iodobenzene diacetate, 16.1 mg, 0.05 mmol). The reaction mixture was stirred for 10 min. The reaction progress was monitored by TLC. After removal of the solvent, the residue was chromatographed on silica gel ($CHCl_3$: MeOH = 5:1) to afford the product (**2**, 10.8 mg, 76%) as brown solid.

m.p.: 260-262 °C. $[\alpha]_D^{20}$ –871.0 (*c* 1.20, MeOH), ^{1}H-NMR (300 MHz, DMSO) δ: 7.81 (1H, *d*, *J* = 8.7 Hz), 7.10 (1H, *s*), 6.56 (1H, *dd*, *J* = 2.1, 8.7 Hz), 6.35 (1H, *d*, *J* = 2.1 Hz), 6.32 (1H, *s*), 5.66 (1H, br, *s*), 4.45 (1H, *d*, *J* = 11.7 Hz), 4.00 (1H, *d*, *J* = 11.7 Hz), 2.85 (2H, *s*). ^{13}C-NMR (75 MHz, DMSO) δ: 179.29, 162.33, 158.92, 157.73, 152.34, 151.60, 130.53, 126.03, 117.48, 110.11, 110.81, 104.12, 102.88, 74.21, 72.94, 39.65.

Ref. 4: D. S. Kim, N. Baek, S. P. Oh, K. Y. Jung, I. S. Lee, H.-K. Lee, *Phytochemistry* **1997**, *46*, 177.

Synthesis of compounds 17, 18 and 19



(6a*S*,11b*R*)-9,10-dimethoxy-6,6a,7,8,11,11b-hexahydroindeno[2,1-*c*]chromene-3,6a-diol

$C_{18}H_{20}O_5$ Mol. Wt.: 316.13

(6a*S*,11b*R*)-6a-hydroxy-9,10-dimethoxy-6,6a,7,8,11,11b-hexahydroindeno[2,1-*c*]chromen-3-yl benzoate

$C_{25}H_{24}O_6$ Mol. Wt.: 420.16

dimethyl 2,2'-((3a*S*,9b*R*)-7-(benzoyloxy)-3a-hydroxy-3,3a,4,9b-tetrahydrocyclopenta[*c*]chromene-1,2-diyl)diacetate

$C_{25}H_{24}O_8$ Mol. Wt.: 452.15

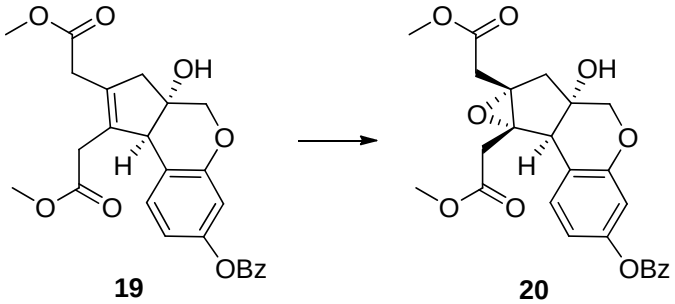
To a mixtute of compound **7** (500 mg, 1.59 mmol), anhydrous THF (5 mL), anhydrous EtOH (5 mL), and liquid ammonia (150 mL) at –78 °C under nitrogen was added lithium metal (445 mg, 63.6 mmol) in small pieces. The reaction mixture was stirred for 12 h at –78 °C and then warmed to room temperature with evaporation of ammonia. Ice water (20 mL) was added slowly. The mixture was then extracted with EtOAc (4 × 10 mL), and the combined organic phases were washed with brine (20 mL), and concentrated to afford the product **17** as a yellow syrup. This diene product (**17**) was then dissolved in dry dichloromethane (20 mL) and Et_3N (0.44 mL, 3.18 mmol), DMAP (4-dimethylamiopryidine, 19 mg, 0.159 mmol) and BzCl (0.22 mL, 1.91 mmol) were introduced at 0 °C. The reaction mixture was stirred for 20 min and the solvent was then removed under reduced pressure. After flash column chromatography on silica gel (Hexane : EtOAc = 3:1), the benzoate (**18**) was obtained as a yellow oil. The benzoate **18** was quickly dissolved in EtOAc (90 mL) and divided into three portions (30 mL/part). Each portion was diluted with EtOAc (10 mL) and MeOH (4 mL) then treated with pyridinium *p*-toluenesulfonate (PPTS, 133 mg, 0.53 mmol) at 0 °C. Ozone (O_3) was then bubbled through the mixture at 0 °C. The reaction progress was monitored by TLC. After ozonolysis, the three reaction mixtures were combined and treated with dimethyl sulfide (4 mL, 54.7 mmol) overnight at room temperature. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Hexane : EtOAc = 8:1→5:1→3:1) to afford product **19** (359 mg, 50% for 3 steps) as a yellow oil.

Compound 17: ^{1}H-NMR (300 MHz, MeOD) δ: 6.98 (1H, *d*, *J* = 8.1 Hz), 6.42 (1H, *dd*, *J* = 2.4, 8.4 Hz), 6.32 (1H, *d*, *J* = 2.4 Hz), 3.84 (1H, *d*, *J* = 11.1 Hz), 3.77 (1H, *d*, *J* = 11.1 Hz), 3.56 (7H, overlap, *s*), 2.95-2.86 (1H, *m*), 2.79-2.66 (3H, *m*), 2.53 (1H, *d*, *J* = 16.2 Hz), 2.31 (1H, *d*, *J* = 16.2 Hz). ^{13}C-NMR (75 MHz, MeOD) δ: 160.36, 159.32, 140.39, 140.17, 137.20, 134.31, 132.85, 117.09, 112.52, 107.13, 80.15, 74.70, 60.39, 60.19, 56.68, 48.49, 31.81, 30.95.

Compound 18: ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.18 (2H, *d*, *J* = 7.2 Hz), 7.63 (1H, *t*, *J* = 7.4 Hz), 7.50 (2H, *t*, *J* = 7.5 Hz), 7.17 (1H, *d*, *J* = 7.8 Hz), 6.83 (1H, *d*, *J* = 7.8 Hz), 6.81 (1H, *s*), 3.97 (1H, *d*, *J* = 11.1 Hz), 3.90 (1H, *d*, *J* = 11.1 Hz), 3.69 (1H, s), 3.62 (3H, *s*), 3.61 (3H, *s*), 2.93-2.78 (4H, *m*), 2.66 (1H, *d*, *J* = 16.2 Hz), 2.64 (1H, *s*), 2.33 (1H, *d*, *J* = 16.2 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 165.13, 155.16, 150.10, 136.36, 136.12, 133.63, 132.79, 130.64, 130.19, 129.74, 129.46, 128.57, 119.49, 114.93, 110.95, 76.81, 71.46, 57.57, 57.25, 53.45, 44.25, 28.60, 27.66.

Compound 19: $[\alpha]_D^{20}$ +28.0 (*c* 1.13, Acetone), IR: ν_{max} (KBr) cm^{-1}: 3458, 3060, 2949, 2844, 1733, 1601, 1497, 1441, 1311, 1257, 1149, 1047, 887, 800, 709. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.18 (2H, *d*, *J* = 7.8 Hz), 7.63 (1H, *t*, *J* = 7.4 Hz), 7.51 (2H, *t*, *J* = 7.7 Hz), 7.29 (1H, *d*, *J* = 8.2 Hz), 6.82 (1H, *dd*, *J* = 1.8, 8.4 Hz), 6.80 (1H, s), 4.02 (1H, *d*, *J* = 11.2 Hz), 3.96 (1H, *d*, *J* = 11.6 Hz), 3.93 (1H, s), 3.68 (3H, s), 3.66 (3H, s), 3.21-3.07 (4H, *m*), 2.85 (1H, *d*, *J* = 16.2 Hz), 2.56 (1H, *d*, *J* = 4.1 Hz), 2.42 (1H, *d*, *J* = 16.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 170.94, 170.64, 165.09, 155.16, 150.38, 134.79, 133.65, 131.48, 131.35, 130.20, 129.43, 128.58, 118.46, 114.88, 110.84, 75.29, 70.57, 53.14, 52.13, 52.07, 44.68, 34.17, 31.98. ES+ *m/z* (%): 452 (M^+, 6), 434 (15), 374 (5), 118 (11), 105 (24), 83 (100), 77 (13). HRMS *m/z* Found: 452.1482, Calcd. for $C_{25}H_{24}O_8$ $(M)^+$: 452.1471.

Synthesis of compound 20

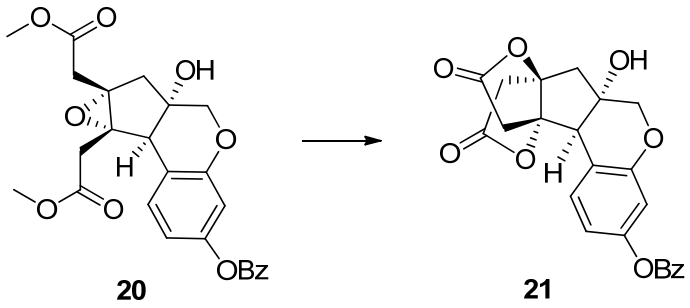


$C_{25}H_{24}O_9$ Mol. Wt.: 468.14

To a solution of compound **19** (42 mg, 0.093 mmol) in dry dichloromethane (3 mL) was added *m*-CPBA (3-chloroperoxybenzoic acid, 25 mg, 77%, 0.112 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C then at room temperature overnight. Saturated aqueous solution of $NaHSO_3$ (8 mL) was added. The mixture was extracted with dichloromethane (3 × 10 mL), and the combined organic phases were washed with saturated aqueous solution of $NaHCO_3$ (8 mL) and brine (8 mL), and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 3:1) afforded the product (**20**, 40 mg, 92%) as a colorless oil.

$[\alpha]_D^{20}$ +46.1 (*c* 2.88, Acetone). IR: ν_{max} (KBr) cm^{-1}: 3514, 3068, 2952, 1737, 1602, 1496, 1437, 1348, 1254, 1152, 1039, 939, 887, 708. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.17 (2H, *d*, *J* = 7.5 Hz), 7.64 (1H, *t*, *J* = 7.4 Hz), 7.51 (2H, *t*, *J* = 7.7 Hz), 7.30 (1H, *d*, *J* = 8.4 Hz), 6.85 (1H, *dd*, *J* = 2.3, 8.4 Hz), 6.82 (1H, *d*, *J* = 2.3 Hz), 4.02 (1H, *d*, *J* = 10.7 Hz), 3.74 (3H, s), 3.68 (1H, *d*, *J* = 10.7 Hz), 3.61 (3H, *s*), 2.71 (1H, *s*), 3.05 (1H, *d*, *J* = 17.1 Hz), 2.71 (2H, s), 2.55 (1H, *d*, *J* = 17.1 Hz), 2.54 (1H, *d*, *J* = 14.9 Hz), 2.30 (1H, *d*, *J* = 14.9 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 170.10, 169.33, 164.96, 156.10, 150.62, 133.73, 130.47, 130.18, 129.31, 128.62, 118.01, 115.42, 111.43, 75.25, 70.95, 69.05, 52.33, 52.13, 51.67, 41.00, 35.99, 34.31. ES+ *m/z* (%): 468 (M^+, 6), 268 (7), 256 (4), 239 (5), 156 (9), 139 (11), 125 (17), 118 (100), 111 (33), 105 (76), 97 (59). HRMS *m/z* Found: 468.1425, Calcd. for $C_{25}H_{24}O_9$ $(M)^+$: 468.1420.

Synthesis of compound 21

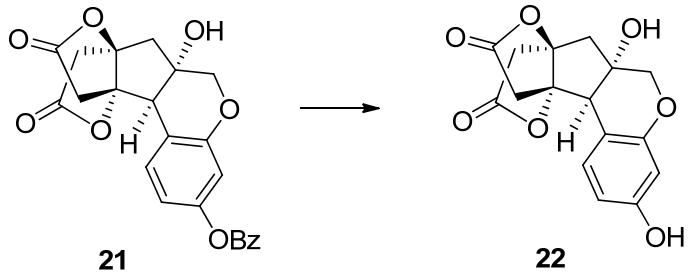


$C_{23}H_{18}O_8$ Mol. Wt.: 422.10

To a solution of epoxide **20** (22 mg, 0.047 mmol) in dry dichloromethane (1 mL) was added a solution of $BF_3{\cdot}Et_2O$ (boron trifluoride-diethyl etherate, 0.24 mL, 0.1 M in dichloromethane, 0.024 mmol) at 0 °C under nitrogen. The reaction mixture was then stirred for 30 min at 0 °C before stirring at room temperature overnight. A saturated aqueous solution of $NaHCO_3$ (5 mL) was added. The mixture was then extracted with dichloromethane (3 × 5 mL). The combined organic phases were washed with brine (5 mL) and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 3:1→2:1) afforded the product (**21**, 16.7 mg, 84%) as white solid.

m.p.: 133-135 °C. $[\alpha]_D^{20}$ –16.8 (*c* 1.14, Acetone), IR: ν_{max} (KBr) cm^{-1}: 3431, 3056, 2933, 1793, 1736, 1601, 1497, 1442, 1397, 1263, 1151, 1053, 992, 888, 814, 709. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.17 (2H, *d*, *J* = 7.9 Hz), 7.66 (1H, *t*, *J* = 7.3 Hz), 7.53 (2H, *t*, *J* = 7.7 Hz), 7.22 (1H, *d*, *J* = 8.4 Hz), 6.95 (1H, *dd*, *J* = 1.6, 8.4 Hz), 6.89 (1H, *s*), 3.94 (1H, *d*, *J* = 11.8 Hz), 3.73 (1H, *d*, *J* = 11.8 Hz), 3.58 (1H, *s*), 3.34 (1H, *d*, *J* = 19.1 Hz), 3.16 (1H, *d*, *J* = 19.1 Hz), 2.88 (1H, br, *s*), 2.77 (1H, *d*, *J* = 19.6 Hz), 2.61 (1H, *d*, *J* = 14.4 Hz), 2.56 (1H, *d*, *J* = 19.2 Hz), 2.50 (1H, *d*, *J* = 15.3 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 173.01, 172.15, 165.19, 154.50, 151.32, 134.03, 130.63, 130.27, 128.92, 128.73, 117.26, 116.95, 111.80, 97.58, 92.36, 76.16, 70.61, 55.44, 45.21, 42.04, 38.60. ES+ *m/z* (%): 422 (M^+, 3), 219 (2), 178 (4), 149 (4), 105 (84), 83 (100), 77 (31), 66 (30), 57 (32). HRMS *m/z* Found: 422.0996, Calcd. for $C_{23}H_{18}O_8$ $(M)^+$: 422.1022.

Synthesis of *C-10,11*-epimer of Brazilide A (22)



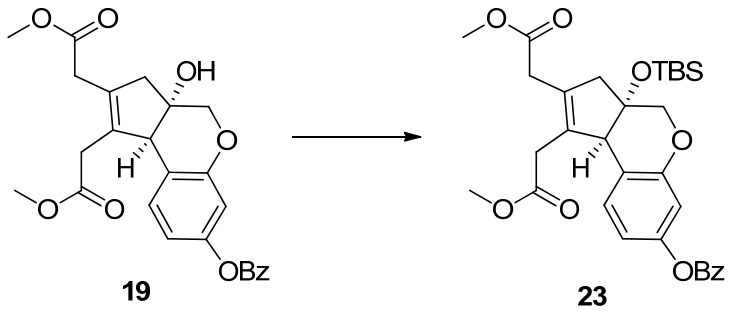
***C-10,11*-epimer Brazilide A (22)**

$C_{16}H_{14}O_7$ Mol. Wt.: 318.07

To a solution of bis-lactone **21** (19 mg, 0.045 mmol) in acetic acid (2 mL) was added 65% H_2SO_4 solution (0.14 mL). The reaction mixture was then stirred at 110 °C for 5 h, by which time TLC analysis showed no remaining starting material. After cooling to room temperature, EtOAc (5 mL) and water (5 mL) was added. After separation of the organic phase, the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine (8 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 3:1→2:1) afforded the product (**22**, 12.7 mg, 90%) as white solid.

m.p.: 127-128 °C. $[\alpha]_D^{20}$ +4.4 (*c* 1.30, Acetone), IR: ν_{max} (KBr) cm^{-1}: 3407, 3077, 2987, 2931, 1782, 1621, 1507, 1462, 1401, 1324, 1250, 1154, 1041, 994, 845, 639. ^{1}H-NMR (400 MHz, Acetone-d_6) δ: 7.00 (1H, *d*, *J* = 8.4 Hz), 6.57 (1H, *dd*, *J* = 1.4, 8.3 Hz), 6.40 (1H, *s*), 3.89 (1H, *d*, *J* = 11.6 Hz), 3.76 (1H, *d*, *J* = 11.6 Hz), 3.55 (1H, *s*), 3.44 (1H, *d*, *J* = 18.8 Hz), 3.16 (1H, *d*, *J* = 18.8 Hz), 2.80 (1H, *d*, *J* = 19.3 Hz), 2.64 (1H, *d*, *J* = 14.8 Hz), 2.56 (1H, *d*, *J* = 19.3 Hz), 2.47 (1H, *d*, *J* = 14.8 Hz). ^{13}C-NMR (100 MHz, Acetone-d_6) δ: 174.08, 173.37, 158.78, 156.15, 131.69, 112.17, 111.21, 104.56, 98.65, 93.59, 76.84, 71.15, 55.97, 46.02, 42.44, 39.10. ES+ m/z (%): 318 (M^+, 6), 192 (5), 161 (18), 147 (4), 131 (3), 118 (100), 105 (12), 97 (9). HRMS m/z Found: 318.0743, Calcd. for $C_{16}H_{14}O_7$ $(M)^+$: 318.0740.

Synthesis of compound 23



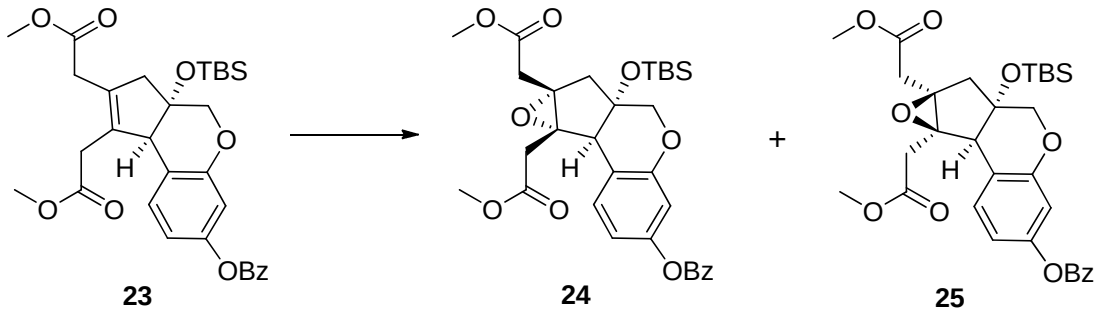
dimethyl 2,2'-((3a*S*,9b*R*)-7-(benzoyloxy)-3a-(*tert*-butyldimethylsilyloxy)-3,3a,4,9b-tetrahydrocyclopenta[*c*]chromene-1,2-diyl)diacetate

$C_{31}H_{38}O_8Si$ Mol. Wt.: 566.23

To a solution of compound **19** (240 mg, 0.53 mmol) in anhydrous dichloromethane (20 mL) at 0 °C under nitrogen was added a solution of 2,6-Lutidine (0.31 mL, 2.65 mmol) followed by addition of *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf, 0.52 mL, 2.12 mmol). The reaction mixture was then warmed up to room temperature and stirred at room temperature overnight. The reaction mixture was then cooled to 0 °C and quenched with brine (10 mL). The aqueous phase was extracted with dichloromethane (3 × 15 mL). The combined organic phases were washed with brine (15 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 8:1) afforded the product (**23**, 255 mg, 85%) as a yellow oil.

$[\alpha]_D^{20}$ +46.2 (*c* 1.24, Acetone), IR: ν_{max} (KBr) cm^{-1}: 3064, 2944, 2856, 1738, 1606, 1496,1442, 1317, 1256, 1150, 1010, 939, 832, 777, 709. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.16 (2H, *d*, *J* = 7.8 Hz), 7.60 (1H, *t*, *J* = 7.2 Hz), 7.47 (2H, *t*, *J* = 7.5 Hz), 7.22 (1H, *d*, *J* = 7.8 Hz), 6.77 (1H, *d*, *J*= 8.7 Hz), 6.74 (1H, s), 3.96-3.89 (3H, *m*), 3.65 (3H, s), 3.63 (3H, s), 3.18-3.02 (4H, m), 2.78 (1H, *d*, *J* = 16.2 Hz), 2.37 (1H, *d*, *J* = 16.2 Hz), 0.79 (9H, s), 0.02 (3H, s), – 0.03 (3H, s). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 170.92, 170.57, 165.01, 155.54, 150.29, 135.09, 133.49, 131.11, 130.14, 129.65, 128.53, 118.80, 114.11, 110.35, 70.69, 53.67, 51.95, 46.17, 34.29, 31.95, 25.63, 17.99, –2.85, –2.99. ES+ *m/z* (%): 565 (M^+–1, 10), 551 (40), 535 (52), 509 (27), 477 (8), 449 (8), 375 (15), 285 (3). 271 (5), 211 (4), 105 (100), 77 (35). HRMS *m/z* Found: 566.2330, Calcd. for $C_{31}H_{38}O_8Si$ $(M)^+$: 566.2336.

Synthesis of compounds 24 and 25



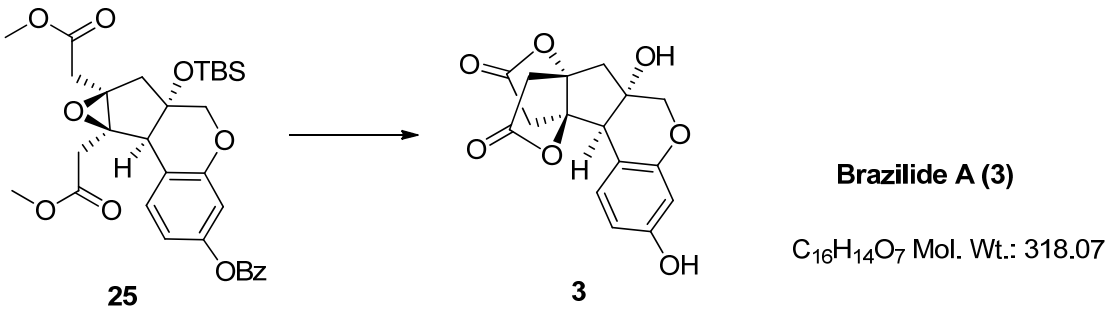
$C_{31}H_{38}O_9Si$ Mol. Wt.: 582.23 $C_{31}H_{38}O_9Si$ Mol. Wt.: 582.23

To a solution of compound **23** (246 mg, 0.435 mmol) in anhydrous dichloromethane (30 mL) was added *m*-CPBA (3-chloroperoxybenzoic acid, 97 mg, 77%, 0.435 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C then warmed up to 32 °C. The reaction mixture was then stirred at 32 °C for 3 days and during this period further *m*-CPBA was added every 12 h (6 × 49 mg, 77%, 6 × 0.22 mmol). Saturated aqueous solution of $NaHSO_3$ (20 mL) was added. The mixture was extracted with dichloromethane (3 × 25 mL), and the combined organic phases were washed with saturated aqueous solution of $NaHCO_3$ (15 mL), brine (15 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : Acetone = 30:1→20:1) afforded the epooxides (**24**, 160 mg, 63%; **25**, 54 mg, 22%) as colorless oil.

Compound 24: $[\alpha]_D^{20}$ +11.9 (*c* 1.51, Acetone), IR: ν_{max} (KBr) cm^{-1}: 3068, 2946, 2844, 1738, 1606, 1497, 1440, 1321, 1256, 1150, 1049, 939, 832, 777, 708. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.17 (2H, *d*, *J* = 7.7 Hz), 7.63 (1H, *t*, *J* = 7.4 Hz), 7.50 (2H, *t*, *J* = 7.7 Hz), 7.27 (1H, *d*, *J* = 8.3 Hz), 6.82 (1H, *dd*, *J* = 2.2, 8.3 Hz), 6.76 (1H, *s*), 4.08 (1H, *d*, *J* = 11.2 Hz), 3.76 (1H, *d*, *J* = 11.2 Hz), 3.69 (3H, *s*), 3.52 (3H, *s*), 3.44 (1H, *s*), 2.81 (1H, *d*, *J* = 17.1 Hz), 2.75 (1H, *d*, *J* = 16.3 Hz), 2.61 (1H, *d*, *J* = 16.3 Hz), 2.55 (1H, *d*, *J* = 17.1 Hz), 2.39 (1H, *d*, *J* = 14.6 Hz), 2.28 (1H, *d*, *J* = 14.6 Hz), 0.79 (9H, *s*), 0.07 (3H, *s*), 0.06 (3H, *s*). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 169.98, 169.90, 164.92, 155.76, 150.77, 133.63, 131.66, 130.15, 129.46, 128.59, 117.35, 114.72, 110.49, 78.90, 71.10, 70.84, 68.22, 52.05, 51.59, 42.57, 36.95, 34.76, 25.61, 18.01, –2.65, –2.74. ES+ *m/z* (%): 582 (M^+, 12), 581 (M^+–1, 23), 567 (82), 525 (100), 509 (18), 493 (25), 465 (21), 433 (32), 373 (25), 325 (25), 173 (18), 105 (53), 89 (12), 77 (34). HRMS *m/z* Found: 582.2274, Calcd. for $C_{31}H_{38}O_9$ Si $(M)^+$: 582.2285.

Compound 25: $[\alpha]_D^{20}$ –8.1 (*c* 1.51, Acetone), IR: ν_{max} (KBr) cm^{-1}: 3068, 2948, 2856, 1739, 1608, 1498, 1442, 1317, 1256, 1148, 1049, 1017, 833, 778, 708. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.20 (2H, *d*, *J* = 7.6 Hz), 7.63 (1H, *t*, *J* = 7.4 Hz), 7.51 (2H, *t*, *J* = 7.7 Hz), 7.28 (1H, *d*, *J* = 8.4 Hz), 6.84 (1H, *dd*, *J* = 2.2, 8.4 Hz), 6.79 (1H, *d*, *J* = 2.2 Hz), 4.00 (1H, *d*, *J* = 11.4 Hz), 3.93 (1H, *d*, *J* = 11.4 Hz), 3.81 (3H, *s*), 3.74 (3H, *s*), 3.43 (1H, *s*), 3.39 (1H, *d*, *J* = 16.7 Hz), 2.84 (1H, *d*, *J* = 16.3 Hz), 2.70 (1H, *d*, *J* = 16.3 Hz), 2.39 (1H, *d*, *J* = 16.7 Hz), 2.32 (1H, *d*, *J* = 14.7 Hz), 2.27 (1H, *d*, *J* = 14.7 Hz), 0.79 (9H, *s*), 0.00 (3H, *s*), – 0.01 (3H, *s*). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 169.95, 169.88, 165.03, 155.64, 150.47, 133.57, 130.87, 130.19, 129.57, 128.56, 115.48, 114.25, 110.49, 73.32, 73.06, 67.10, 64.34, 52.30, 52.05, 46.47, 41.30, 36.19, 34.63, 25.59, 17.93, –2.95, –3.15. ES+ *m/z* (%): 582 (M^+, 9), 581 (M^+–1, 16) .567 (17), 559 (22), 525 (43), 505 (21), 495 (59), 463 (100), 435 (38), 421 (18), 391 (9), 375 (14), 330 (13), 313 (21), 271 (13), 192 (16), 105 (67), 77 (24). HRMS *m/z* Found: 582.2285, Calcd. for $C_{31}H_{38}O_9Si$ $(M)^+$: 582.2285.

Synthesis of (+)-Brazilide A (3)



To a stirred solution of epoxide **25** (37 mg, 0.064 mmol) in anhydrous dichloromethane (5 mL) was added a solution of $BF_3{\cdot}Et_2O$ (boron trifluoride-diethyl etherate, 0.32 mL, 0.1 M in dichloromethane, 0.032 mmol) at 0 °C under nitrogen. The reaction mixture was stirred for 30 min at 0 °C then stirred at room temperature overnight. A saturated aqueous solution of $NaHCO_3$ (8 mL) was added. The resulting mixture was extracted with dichloromethane (3 × 15 mL), and the combined organic phases were washed with brine (8 mL) and concentrated. The residue was re-dissolved in acetic acid (3 mL), and a solution of 65% H_2SO_4 (0.2 mL) was added. The reaction mixture was stirred at 110 °C for 5 h, by which time TLC analysis showed no remaining starting material. After cooling to room temperature, EtOAc (5 mL) and water (5 mL) was added. The organic phase was separated. The aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (8 mL), dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (Hexane : EtOAc = 3:1→2:1) afforded the product (**2**, 16.6 mg, 82%) as white solid.[5]

m.p.: 252-253 °C. $[\alpha]_D^{20}$ +3.4 (*c* 1.36, Acetone), IR: ν_{max} (KBr) cm^{-1}: 3389, 2921, 2854, 1792, 1622, 1507, 1457, 1328, 1283, 1219, 1161, 1096, 1037, 996, 842, 713. ^{1}H-NMR (400 MHz, Acetone-d_6) δ: 7.12 (1H, *d*, *J* = 8.6 Hz), 6.46 (1H, *dd*, *J* = 2.4, 8.5 Hz), 6.31 (1H, *d*, *J* = 2.4 Hz), 3.90 (1H, *d*, *J* = 10.9 Hz), 3.82 (1H, *d*, *J* = 10.9 Hz), 3.67 (1H, *s*), 3.53 (1H, *d*, *J* = 18.7 Hz), 3.23 (1H, *d*, *J* = 18.7 Hz), 3.00 (1H, *d*, *J* = 19.2 Hz), 2.65 (1H, *d*, *J* = 19.2 Hz), 2.62 (1H, *d*, *J* = 15.4 Hz), 2.43 (1H, *d*, *J* = 15.6 Hz). ^{13}C-NMR (100 MHz, Acetone-d_6) δ: 174.12, 173.73, 158.47, 155.77, 134.52, 110.13, 109.51, 104.00, 96.52, 94.63, 78.52, 69.80, 54.30, 46.02, 44.45, 42.94. ES+ *m/z* (%): 318 (100), 300 (10), 232 (5), 174 (5), 163 (26), 147 (15), 105 (20), 91 (16), 77 (16), 57 (16). HRMS *m/z* Found: 318.0740, Calcd. for $C_{16}H_{14}O_7$ $(M)^+$: 318.0740.

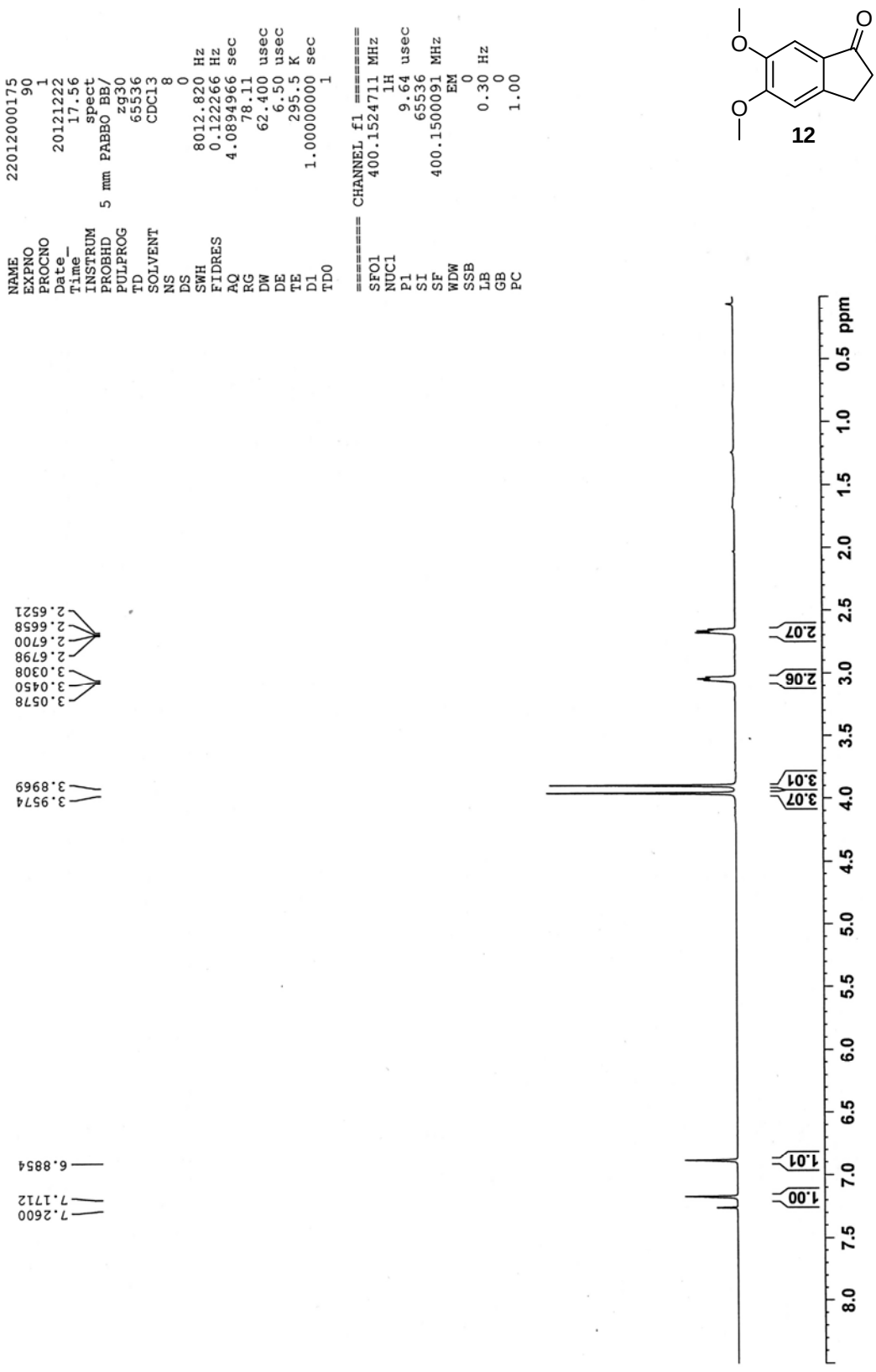
Ref. 5: B. O. Yang, C.-Q. Ke, Z.-S. He, Y.-P. Yang, Y. Ye, *Tetrahedron Lett*. **2002**, *43*, 1731.

Spectrum for

Enantioselective Total Synthesis of (+)-Brazilin, (–)-Brazilein and (+)-Brazilide A

Xuequan Wang, Hongbin Zhang, Xiaodong Yang*, Jingfeng Zhao, and Chengxue Pan*

Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, School of Chemical Science and Technology, Yunnan University, Kunming, Yunnan 650091, P. R. China Fax: 86-871-5035538. E-mail: zhanghb@ynu.edu.cn; xdyang@ynu.edu.cn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FIDRES 0.122266 Hz
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RG 78.11
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DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
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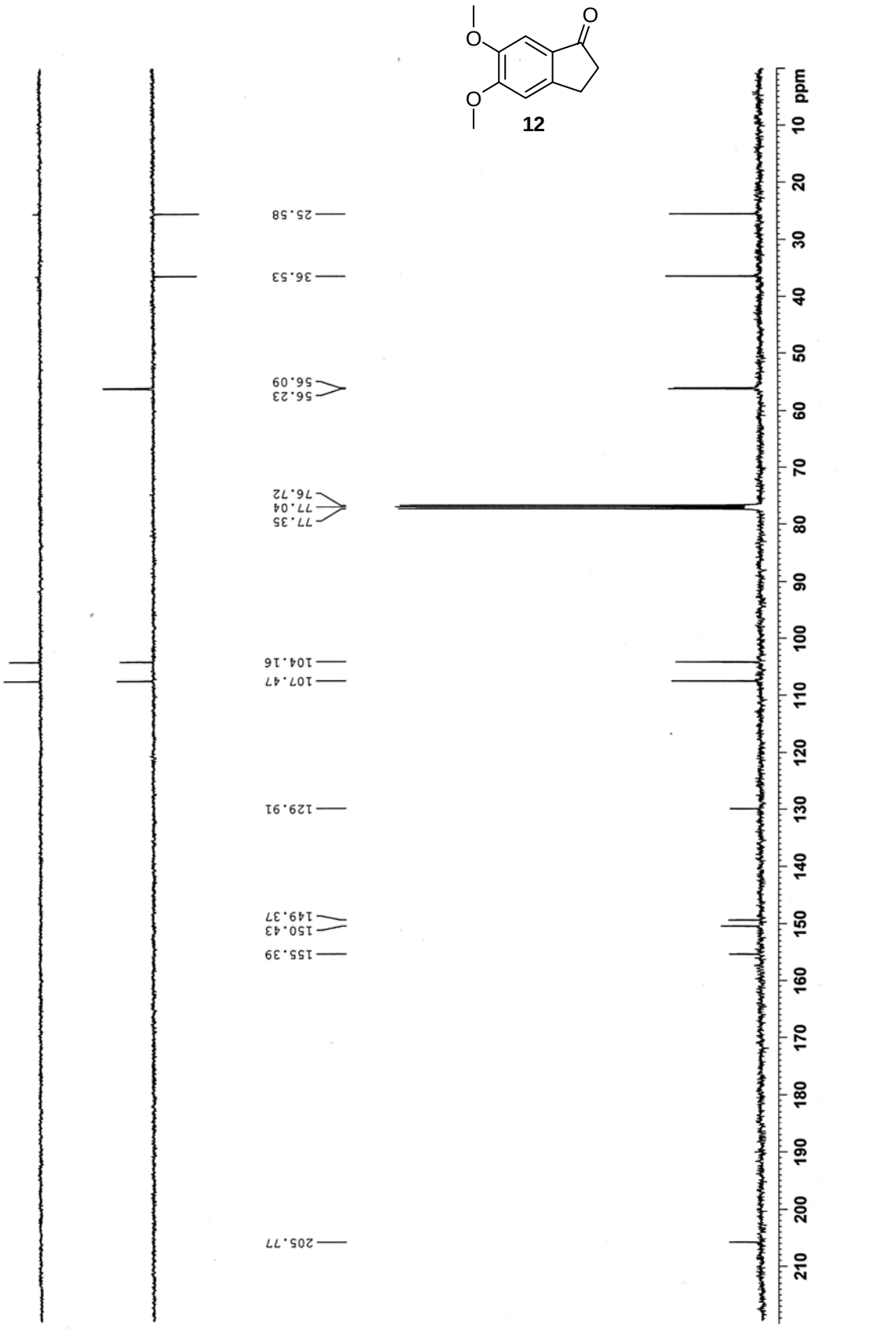
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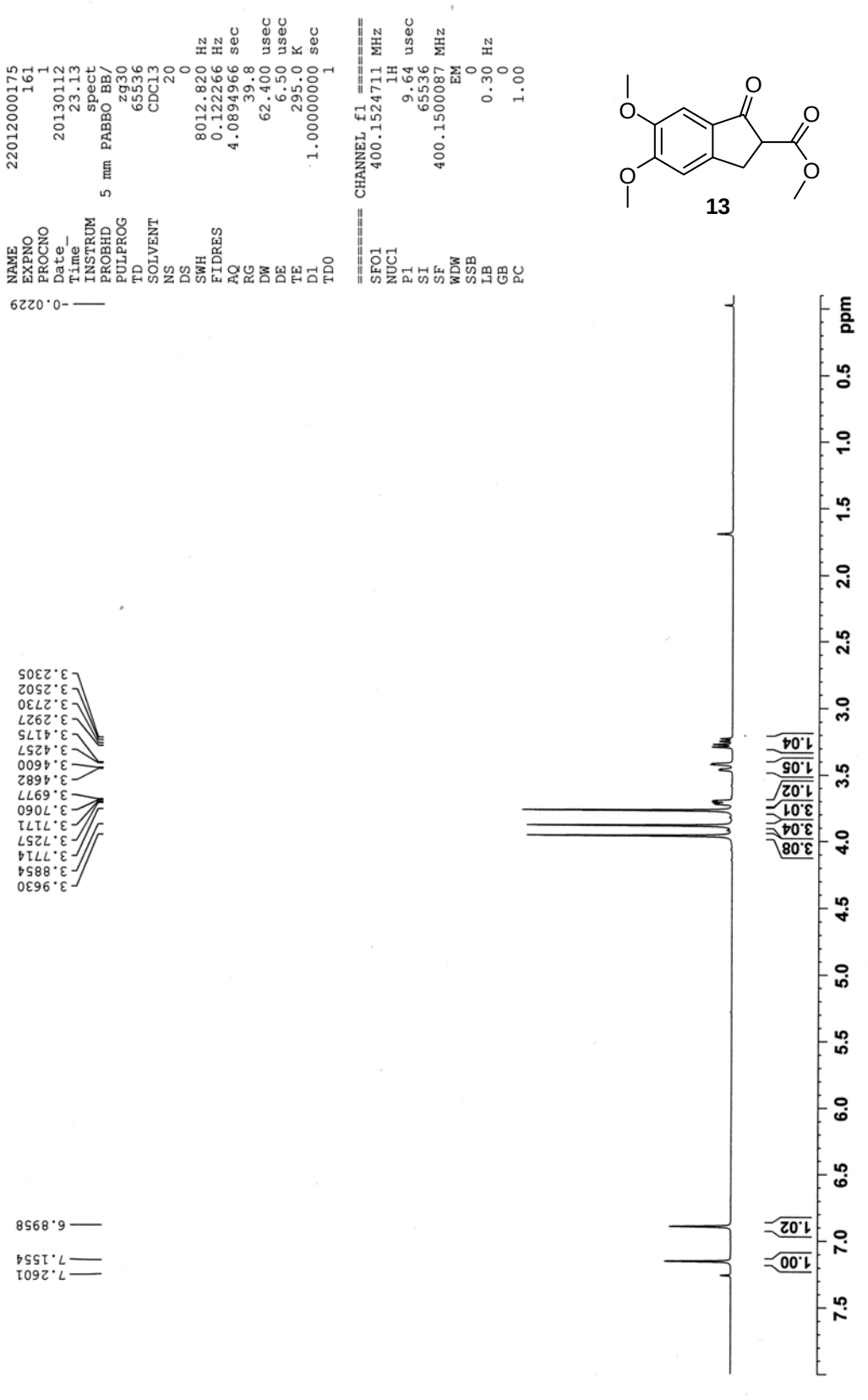
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DE 6.50 usec
TE 295.0 K
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P1 9.64 usec
SI 65536
SF 400.1500087 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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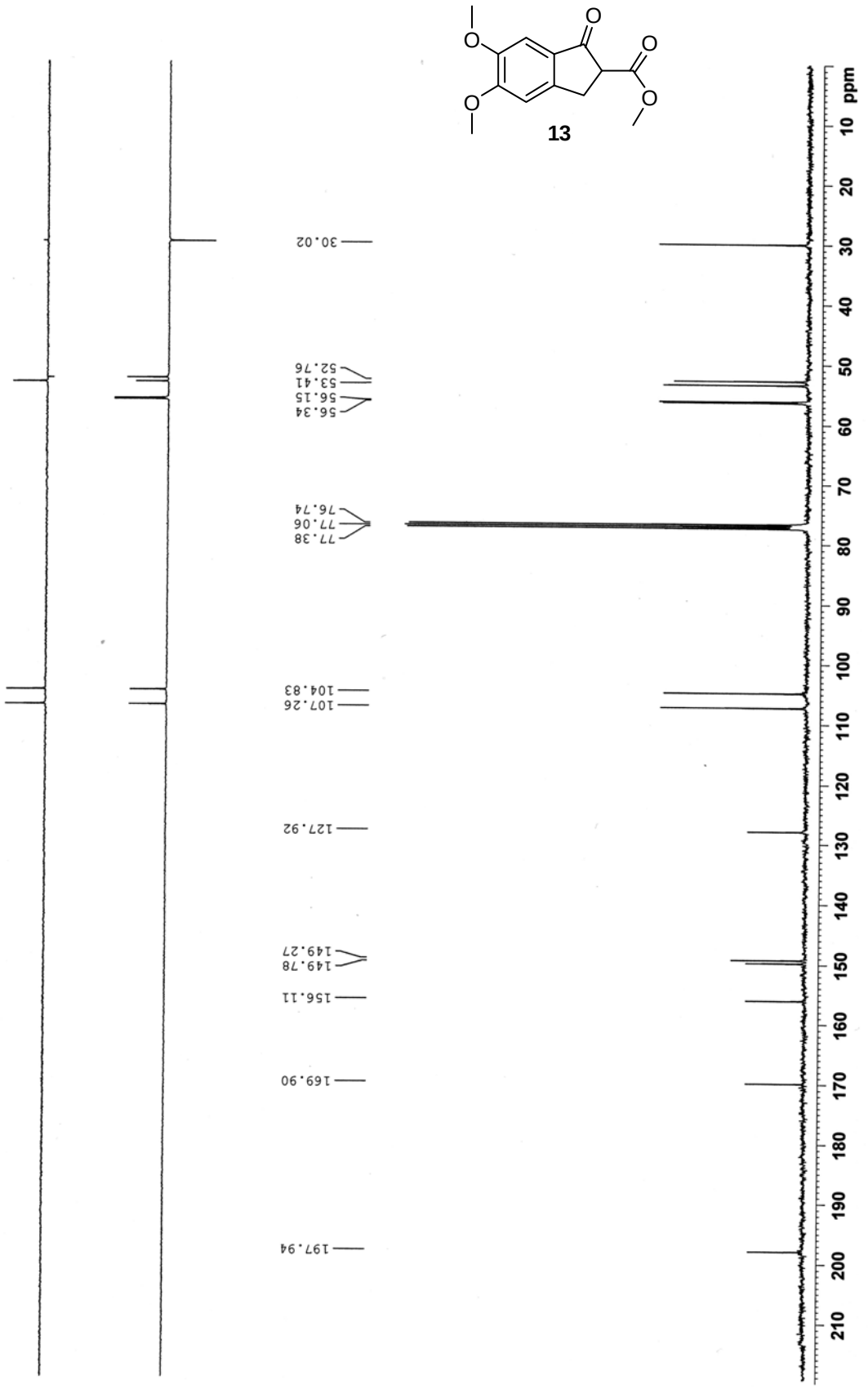
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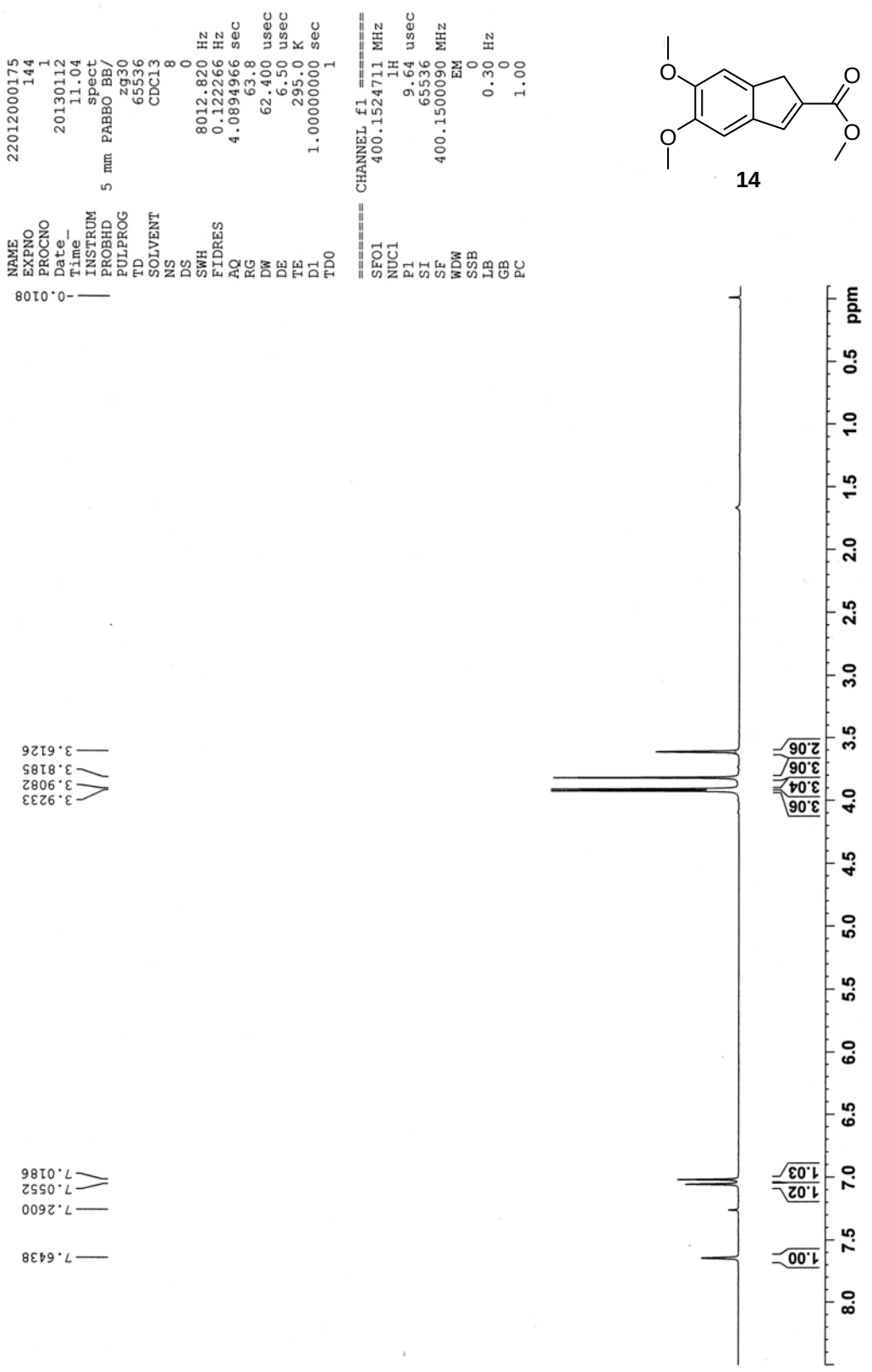
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LB 0.30 Hz
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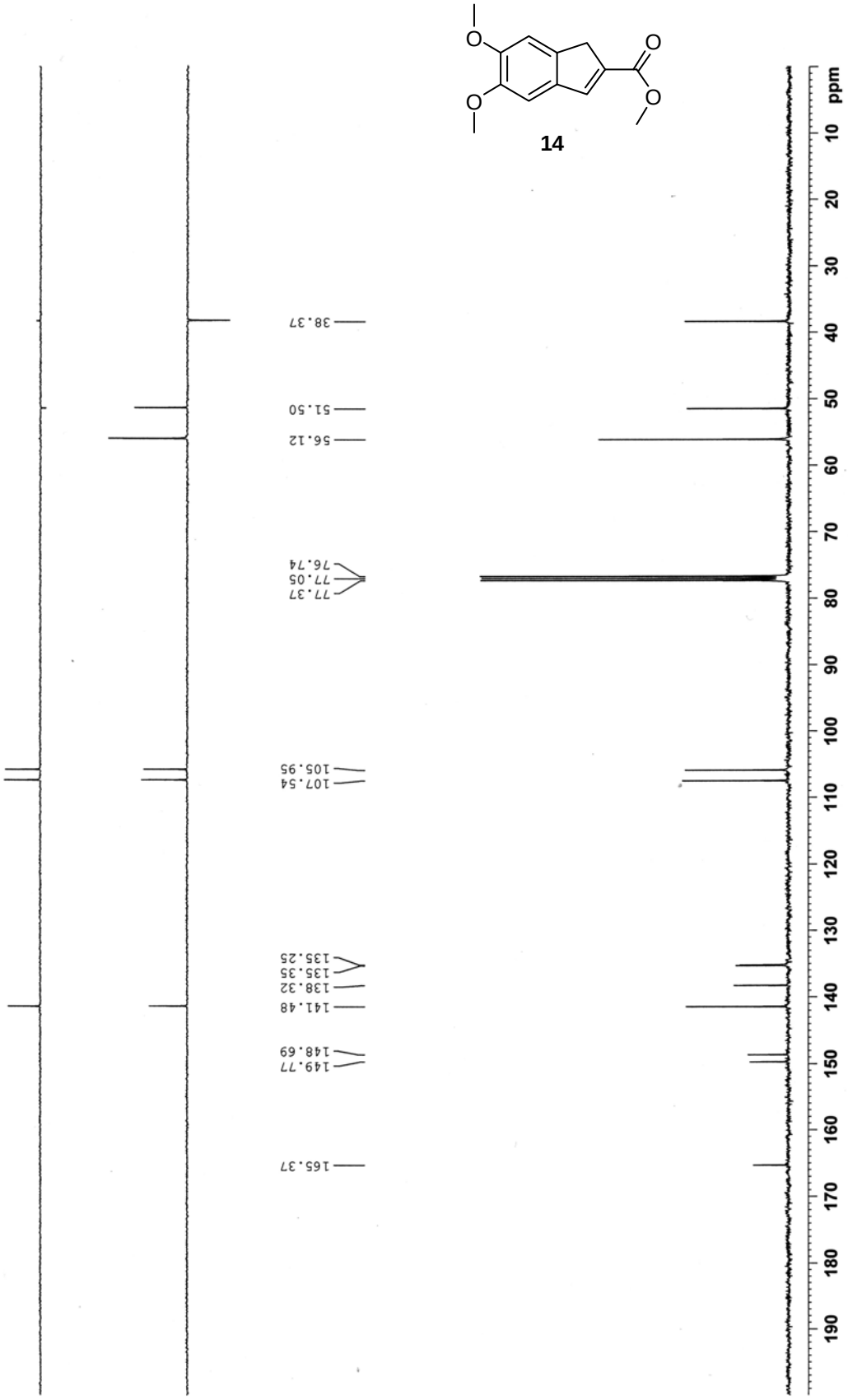

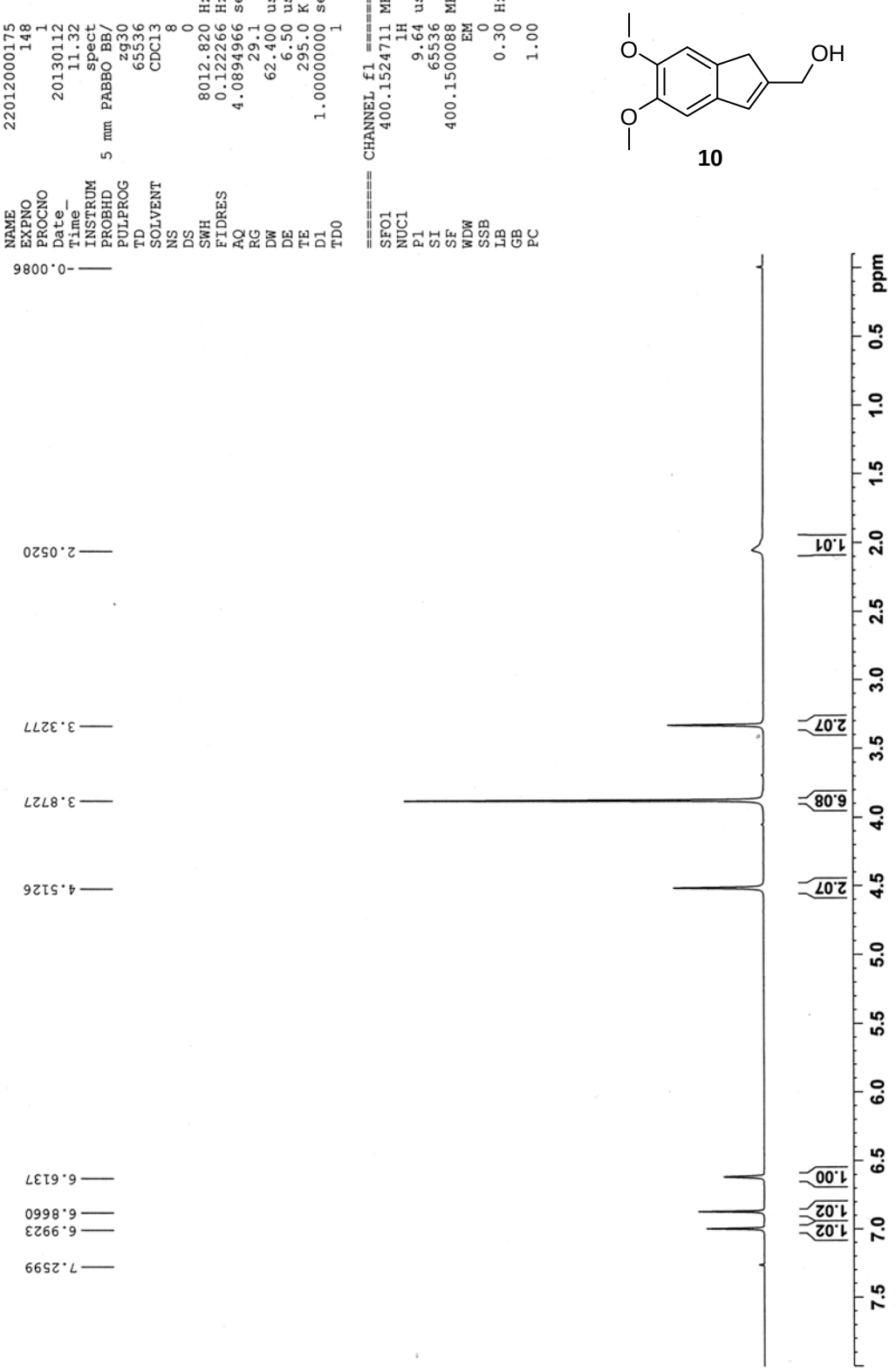
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SOLVENT CDC13
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FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 29.1
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
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NUC1 1H
P1 9.64 usec
SI 65536
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LB 0.30 Hz
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1.02
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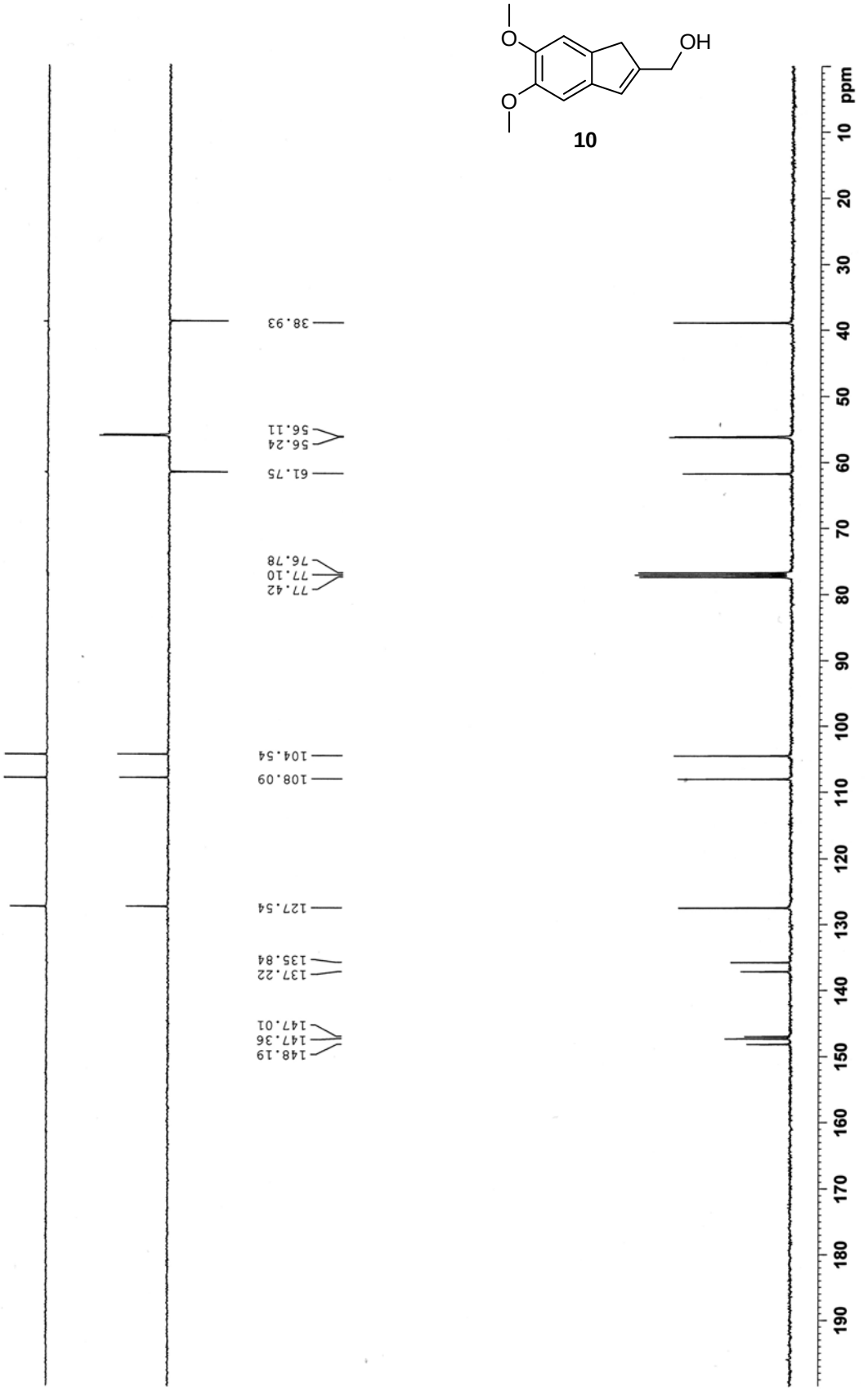
7.0
7.5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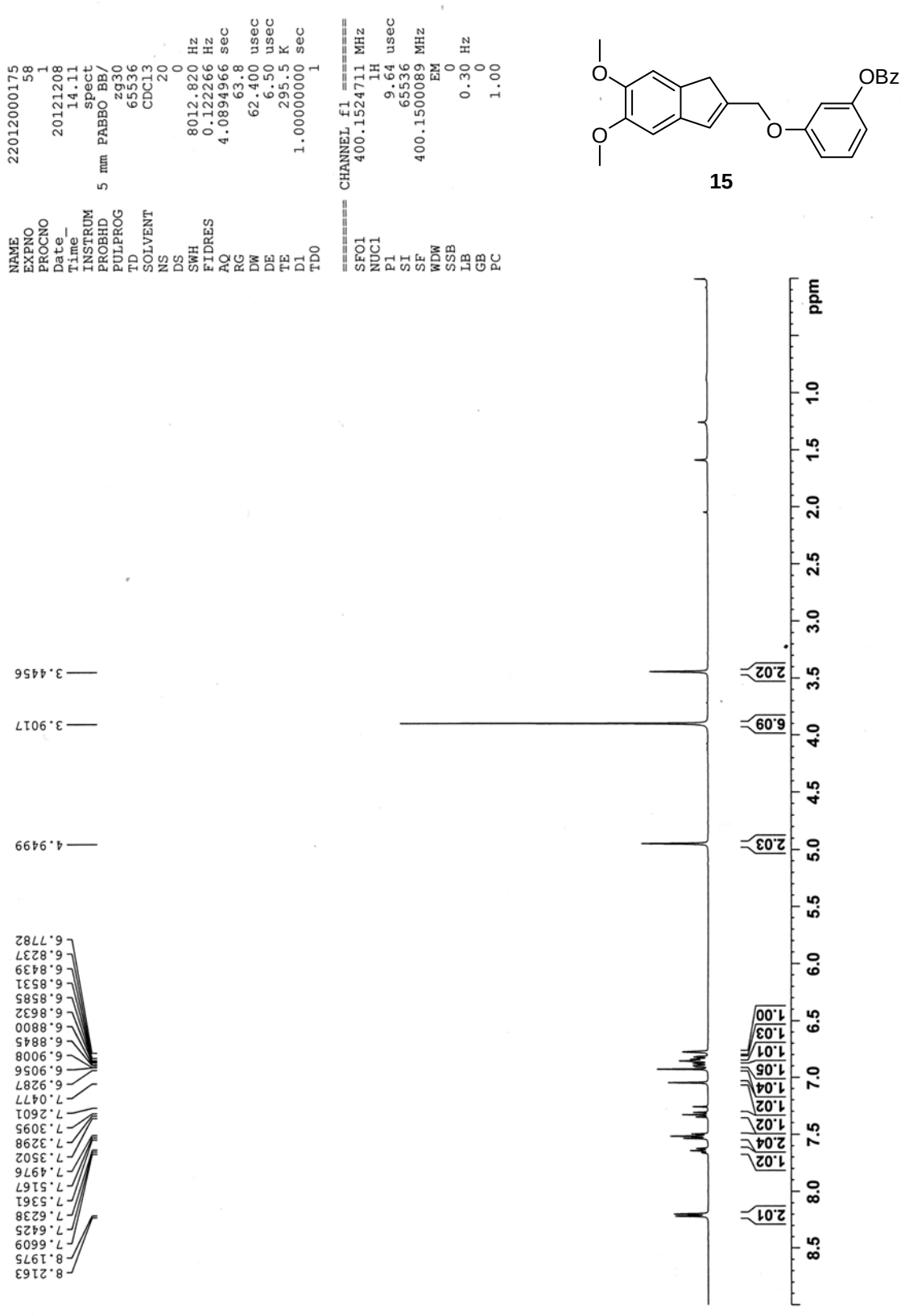
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FIDRES 0.122266 Hz
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RG 63.8
DW 62.400 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TDO 1
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NUC1 1H
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SI 65536
SF 400.1500089 MHz
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LB 0.30 Hz
GB 0
PC 1.00
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O
O
OBz
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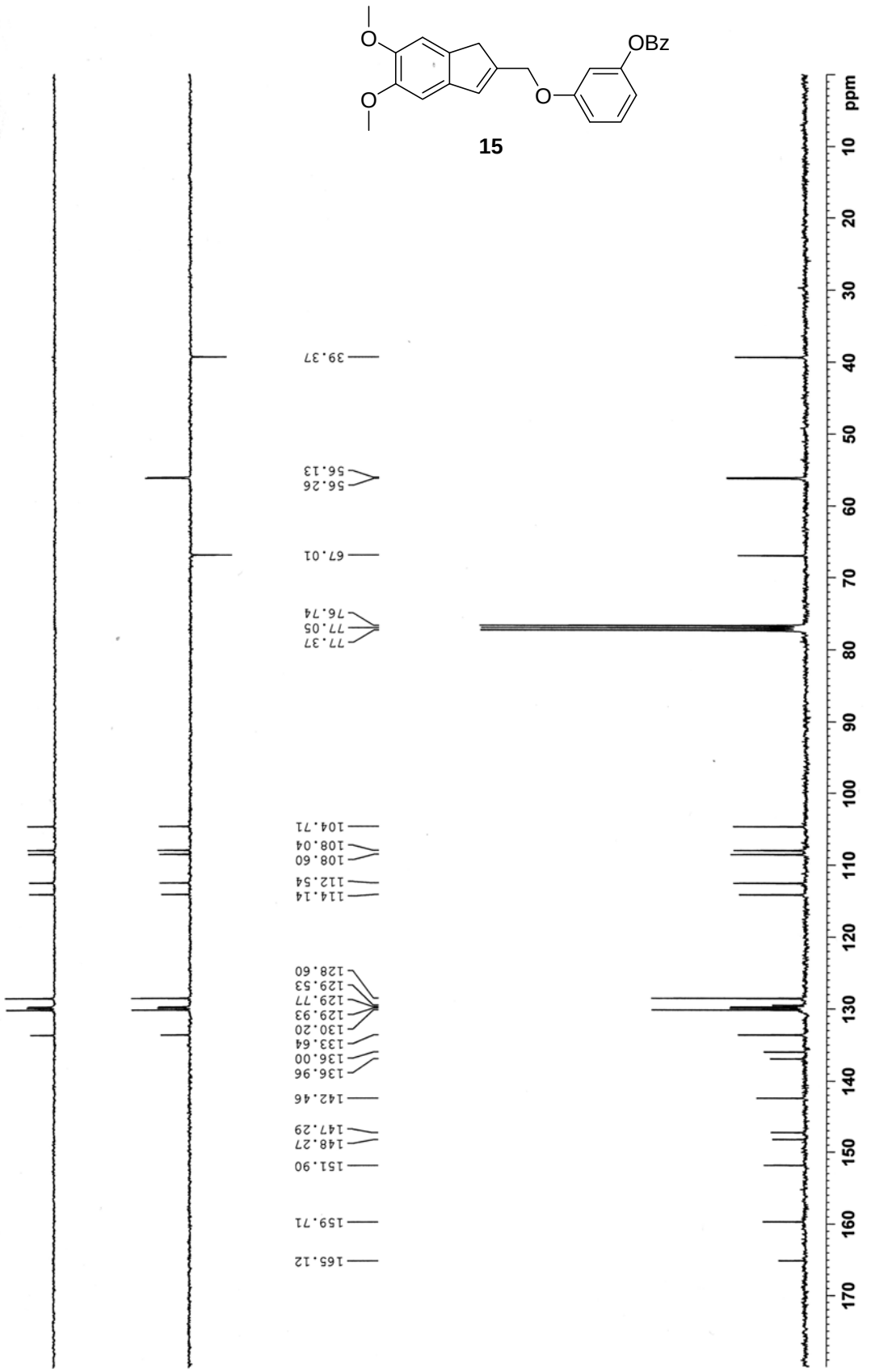
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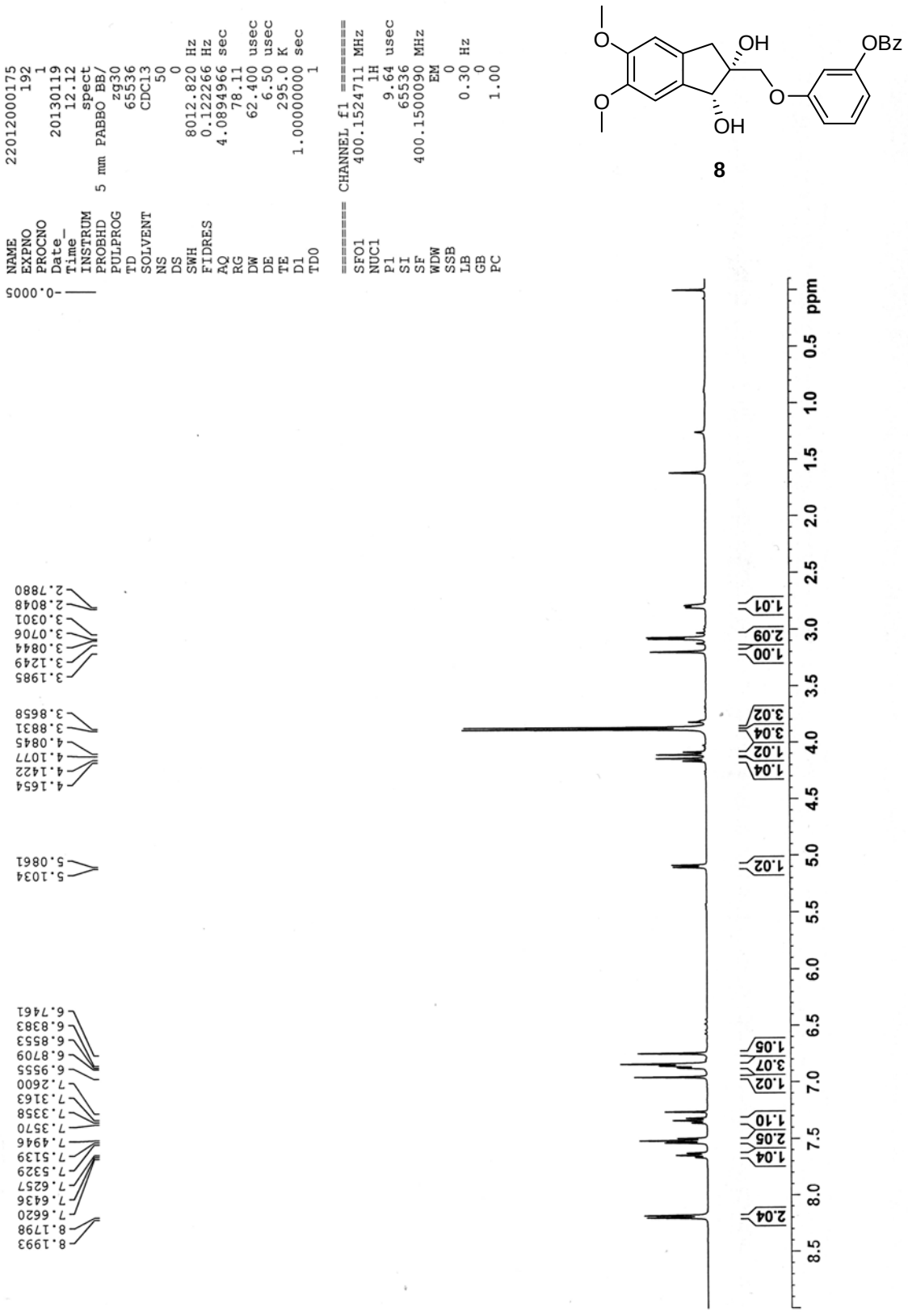
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FIDRES 0.122266 Hz
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RG 78.11
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
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NUC1 1H
P1 9.64 usec
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LB 0.30 Hz
GB 0
PC 1.00
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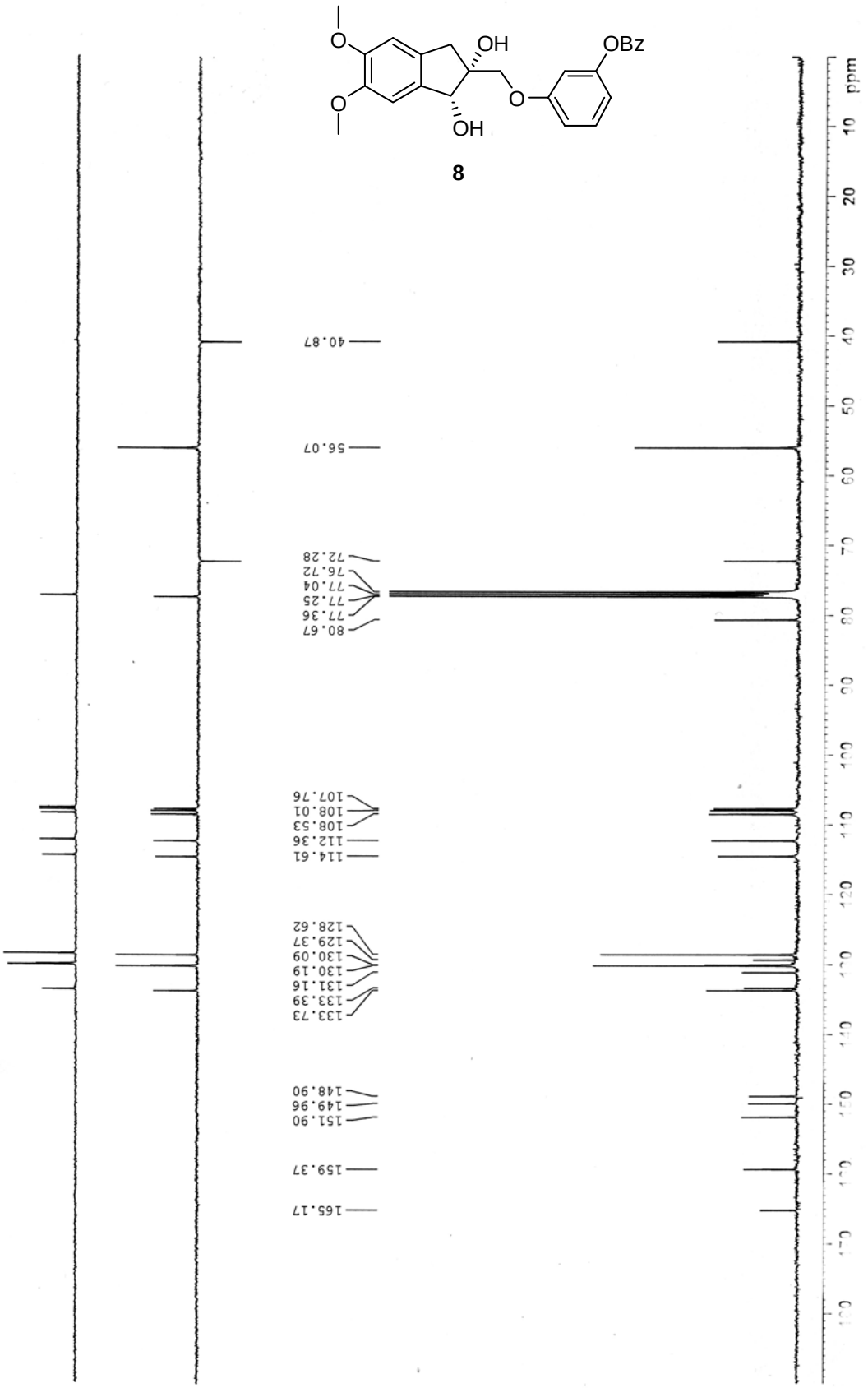
OBz
OH
8
ppm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108.53
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114.61
128.62
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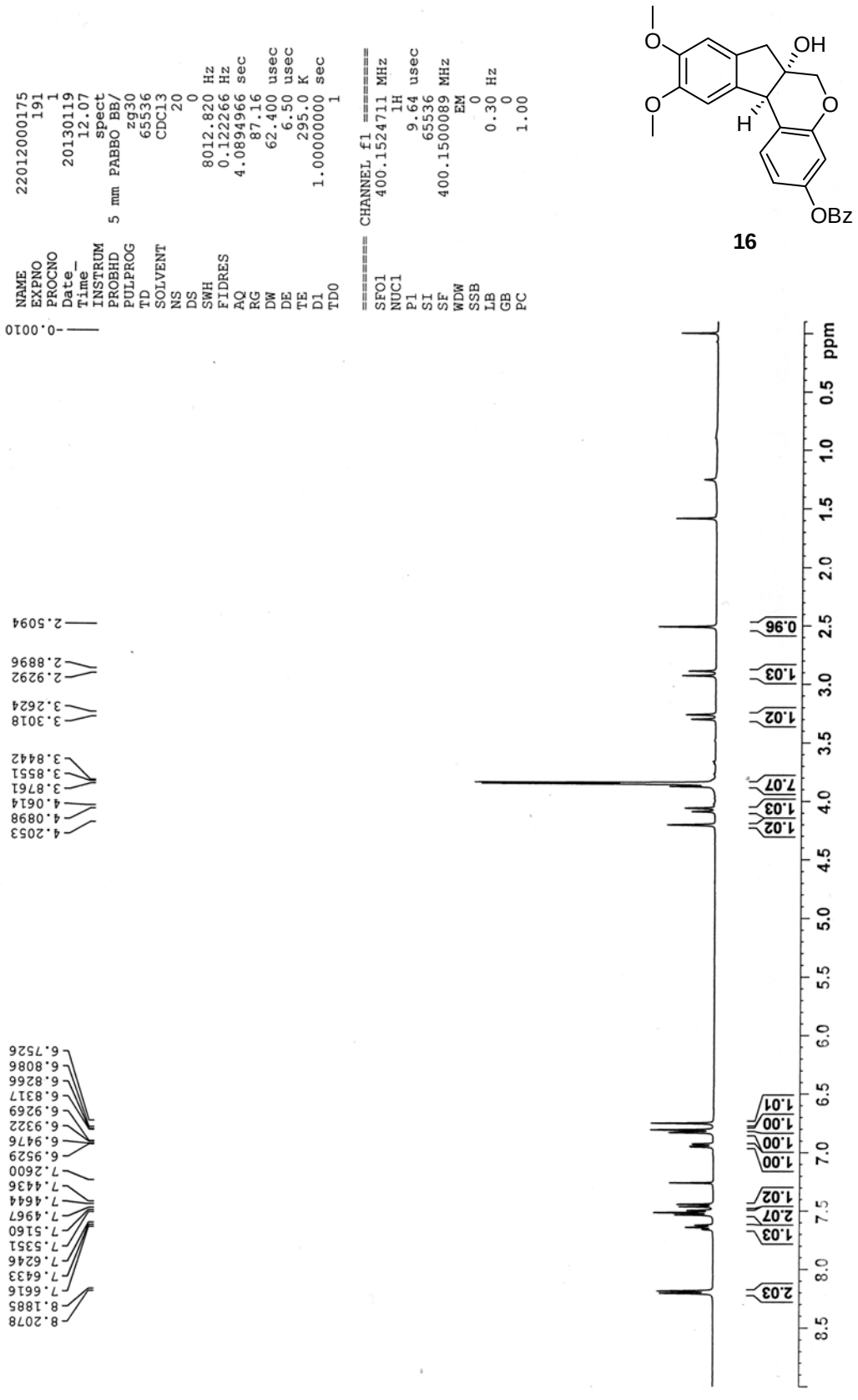
165.17
ppm

8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PROCNO 1
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Time 12.07
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PULPROG zg30
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SOLVENT CDCl3
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FIDRES 0.122266 Hz
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TE 295.0 K
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NUC1 1H
P1 9.64 usec
SI 65536
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LB 0.30 Hz
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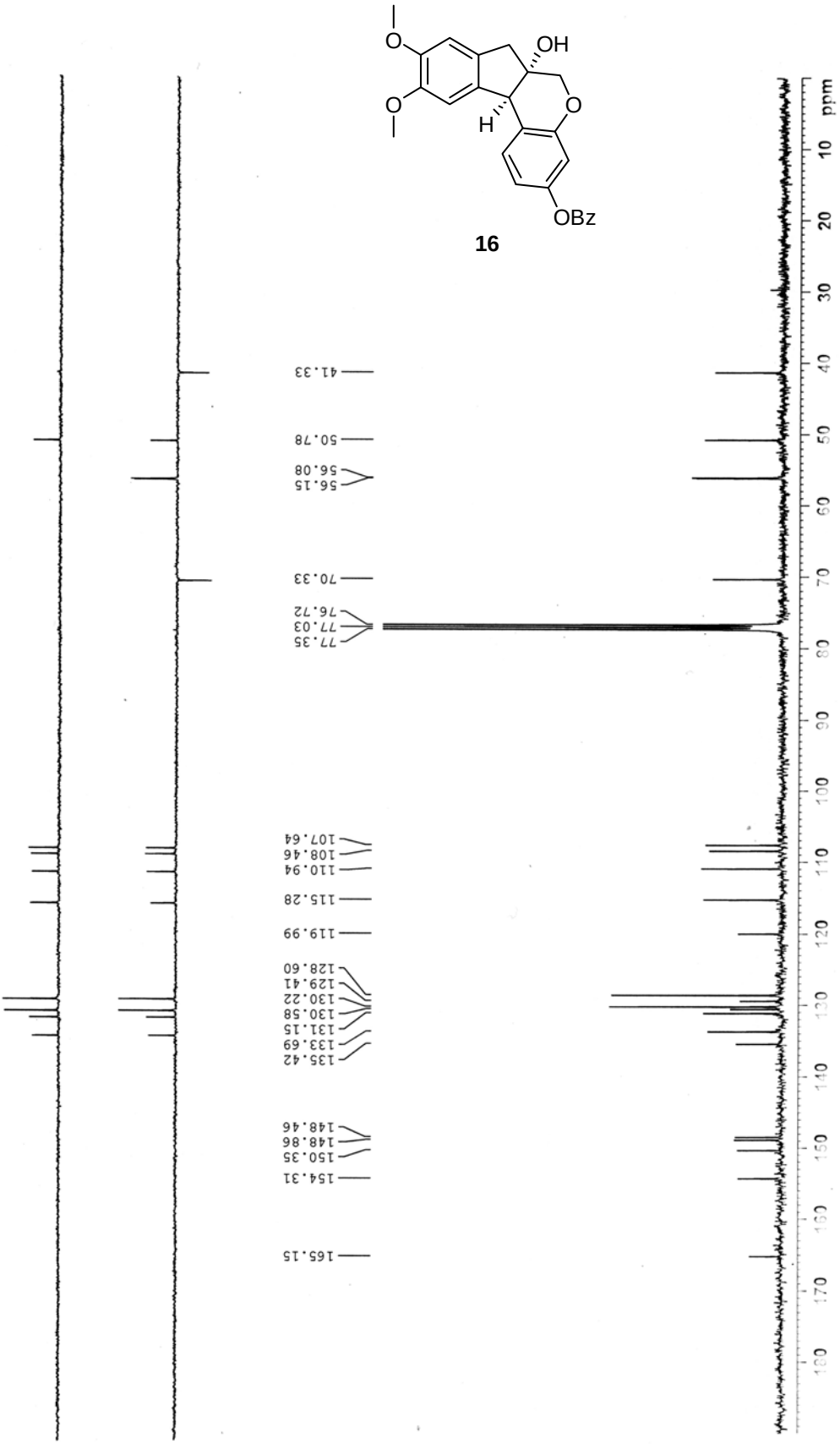
O
OBz
16
ppm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56.15
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76.72
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108.46
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115.28
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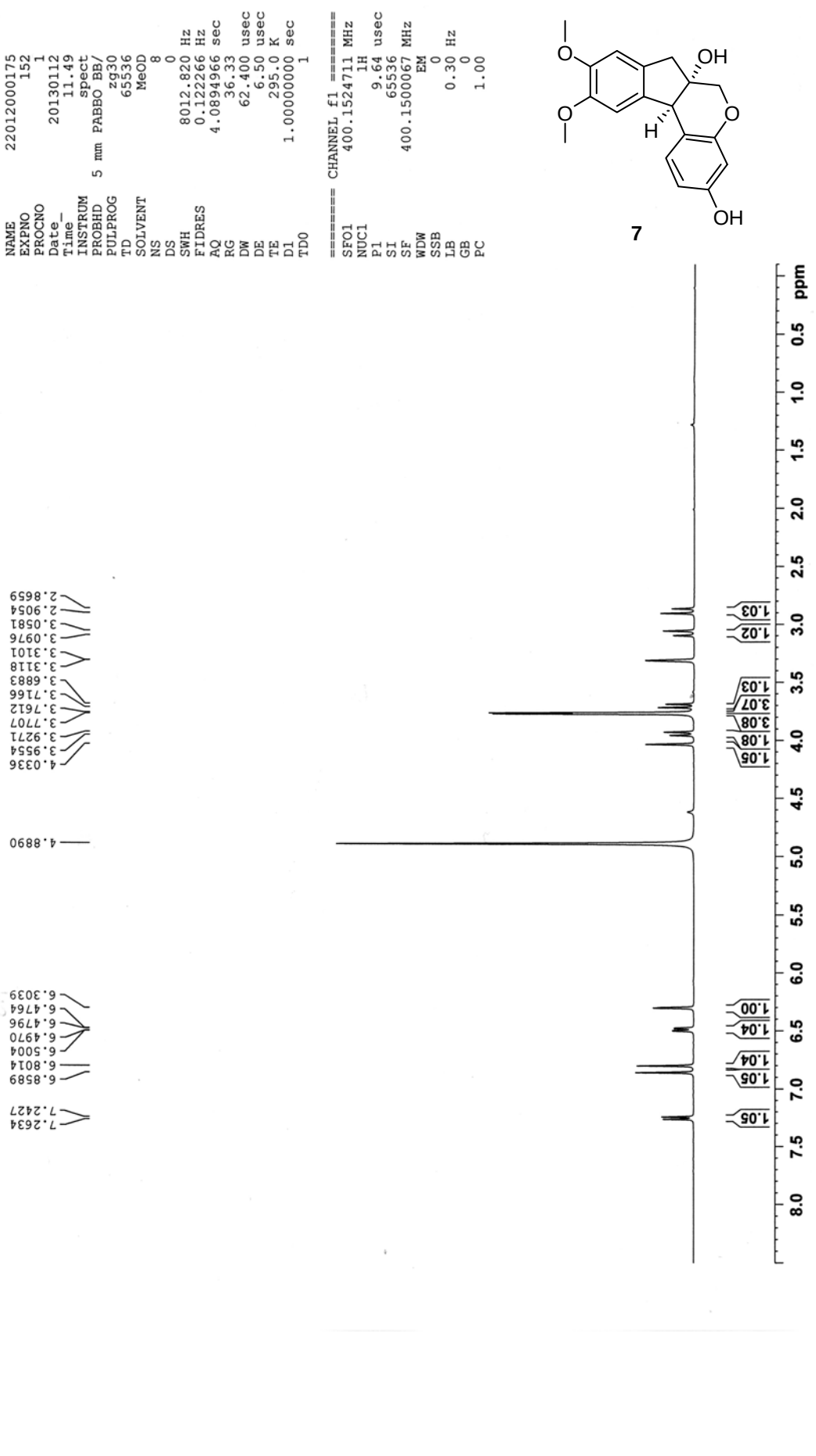
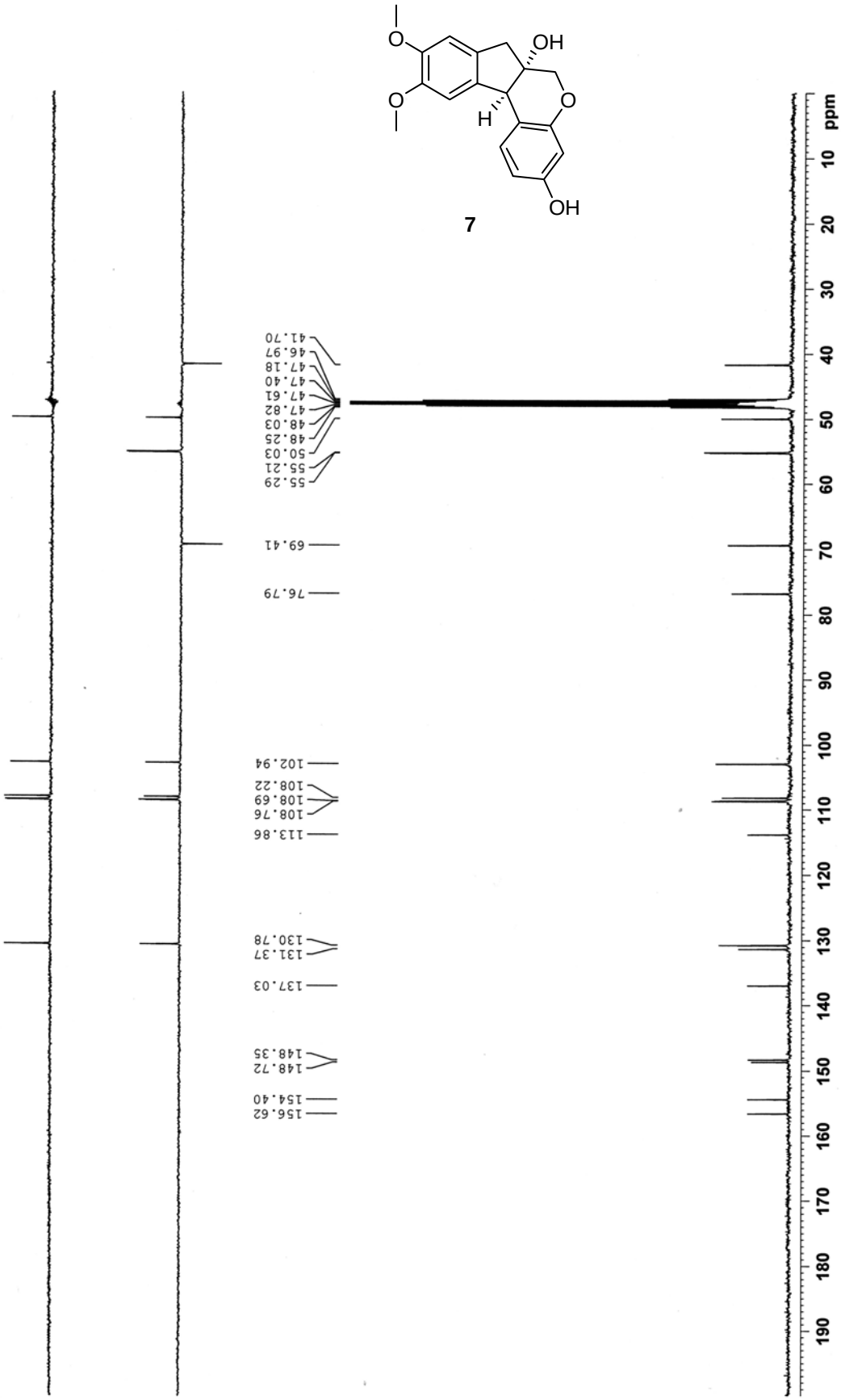
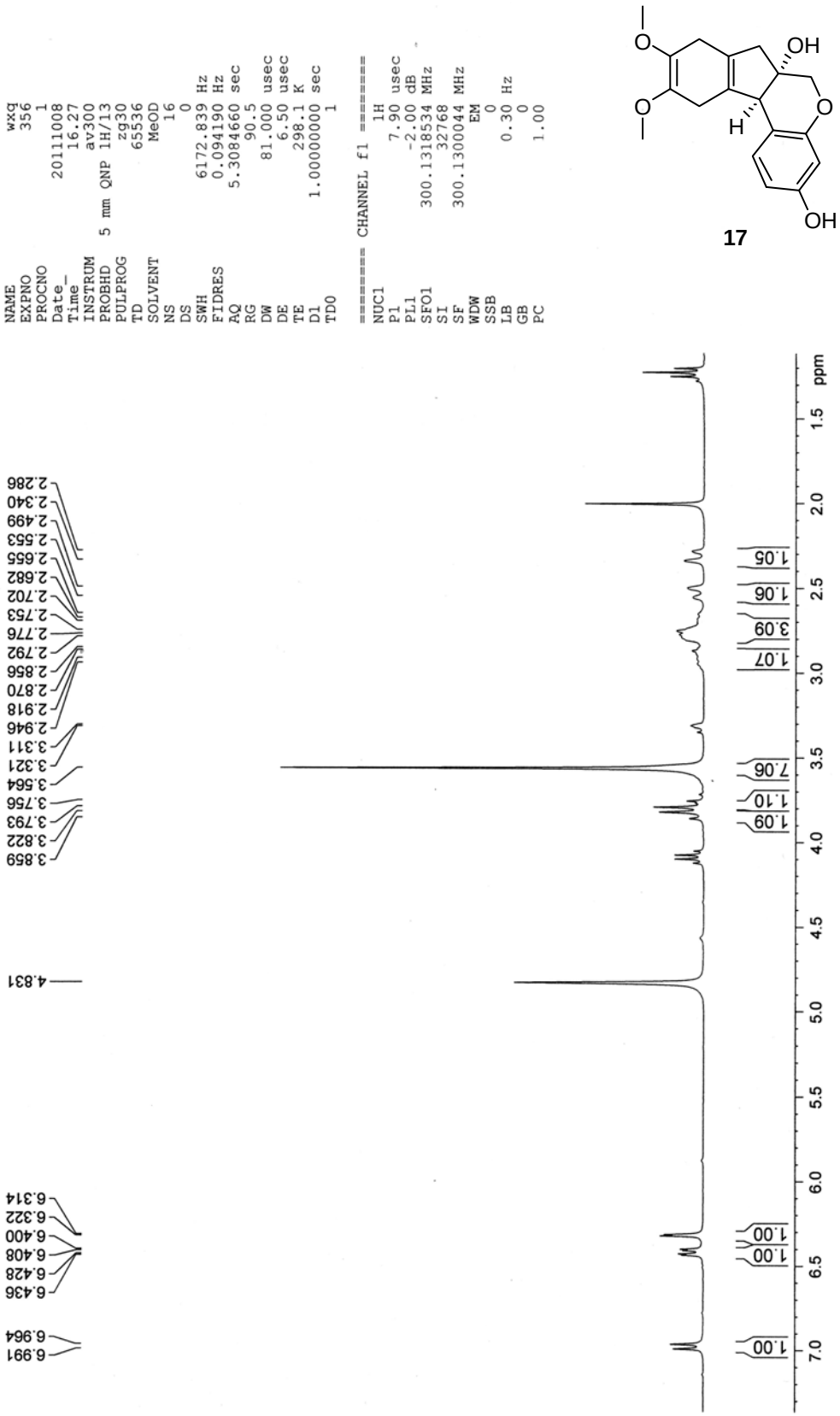
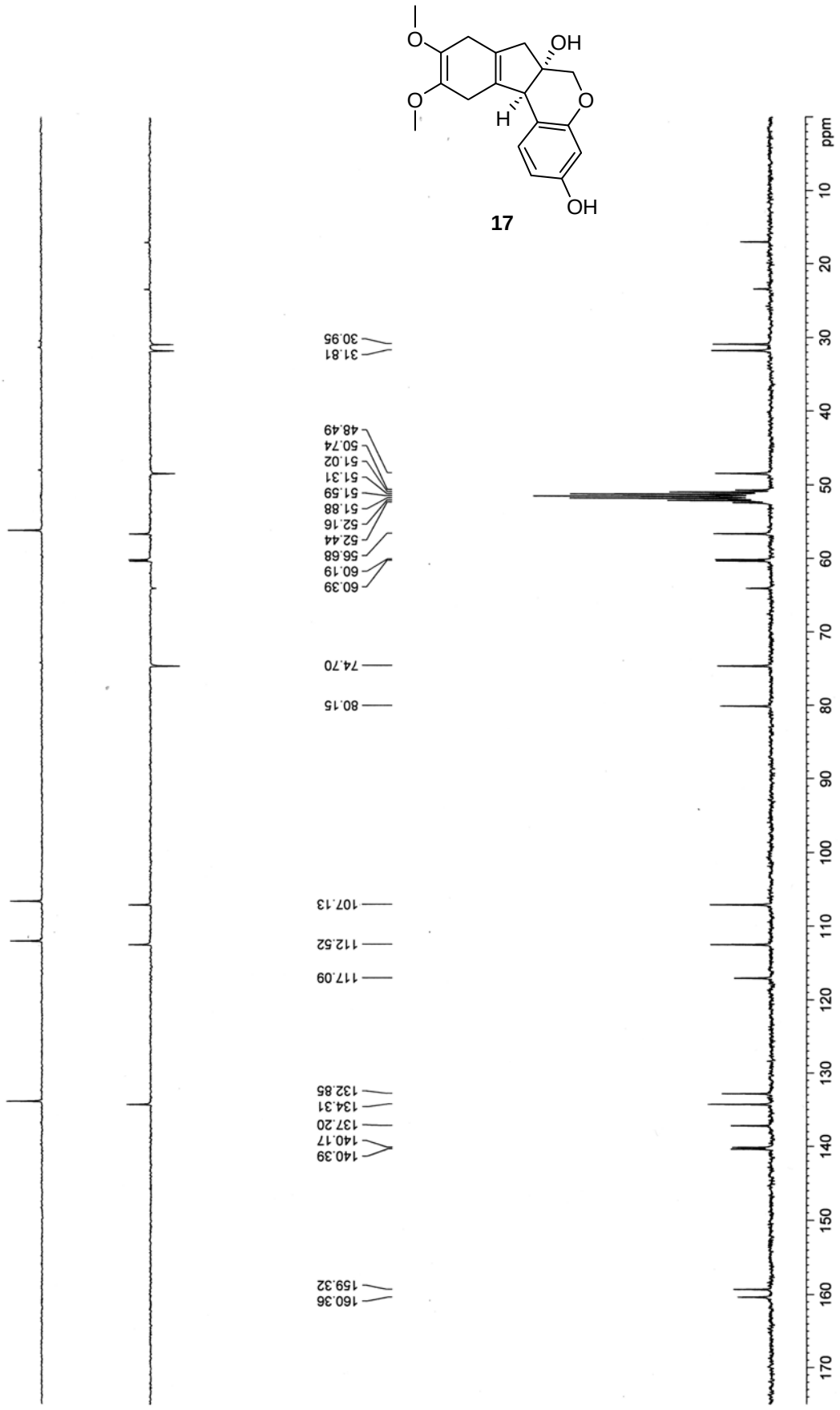
ppm

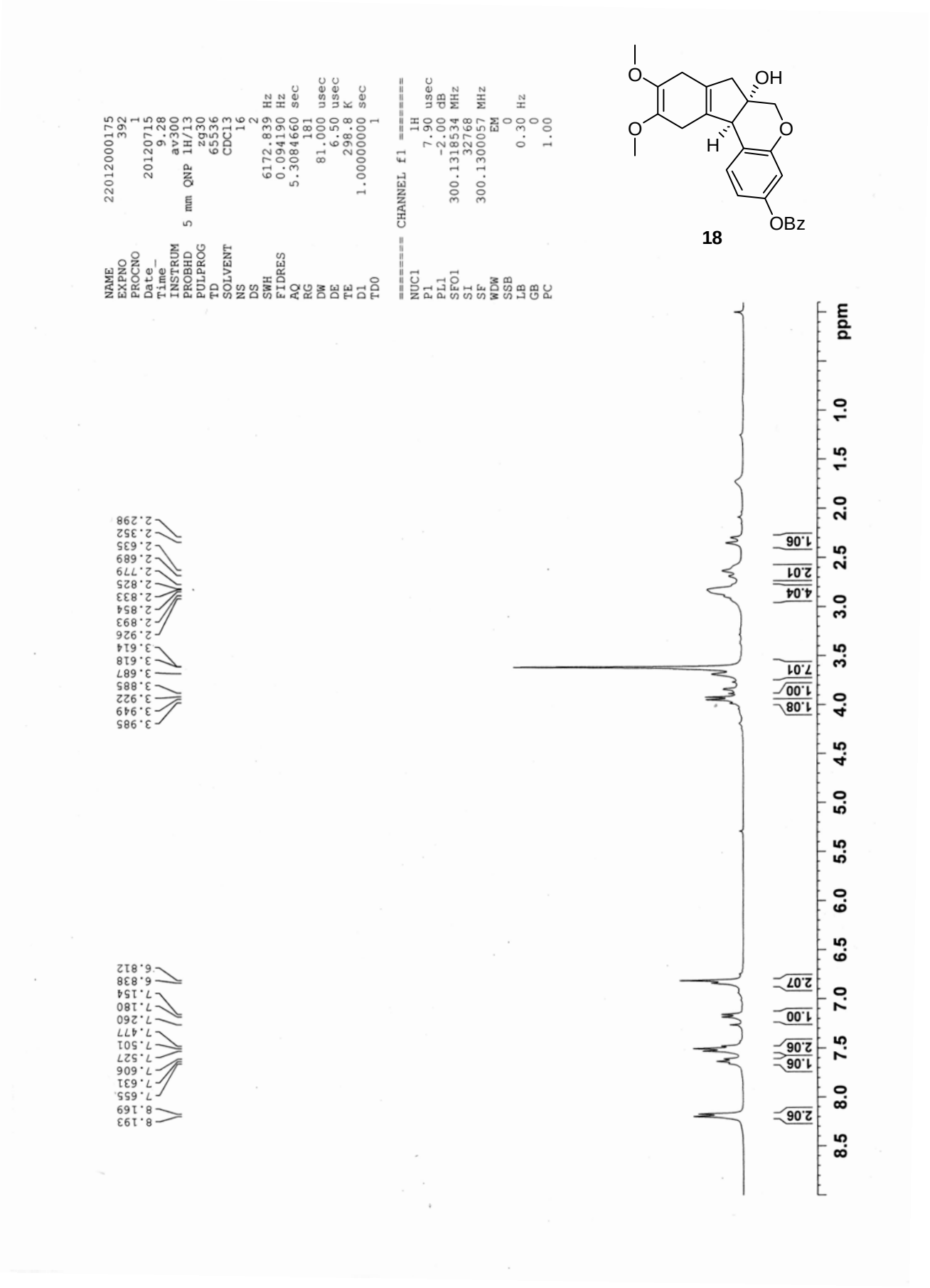


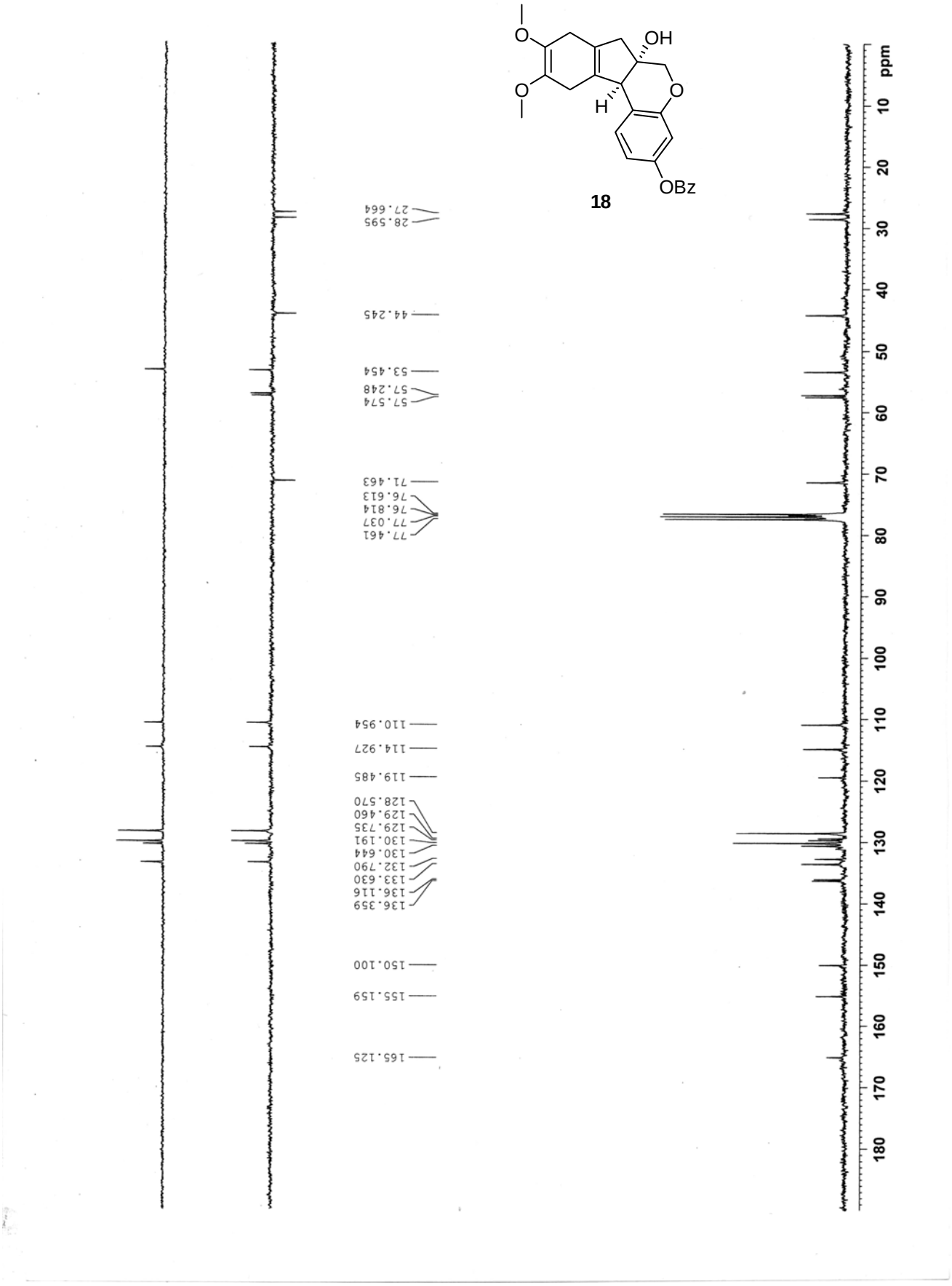

O
O
OH
H
O
OH
7
41.70
46.97
47.18
47.40
47.61
47.82
48.03
48.25
50.03
55.21
55.29
69.41
76.79
102.94
108.22
108.69
108.76
113.86
130.78
131.37
137.03
148.35
148.72
154.40
156.62
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

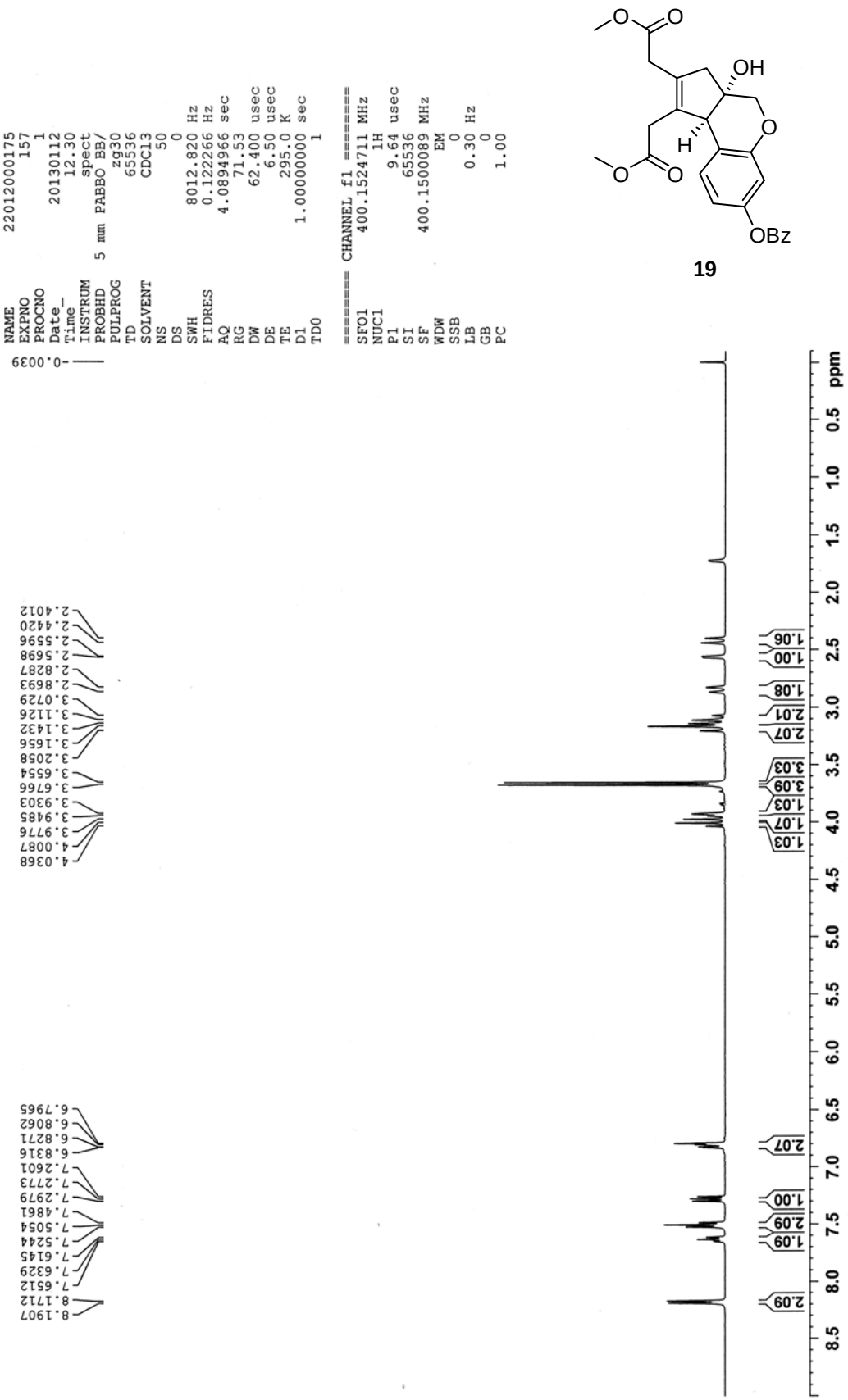

wxq
356
1
20111008
16.27
av300
5 mm QNP 1H/13
zg30
65536
MeOD
16
0
6172.839 Hz
0.094190 Hz
5.3084660 sec
90.5
81.000 usec
6.50 usec
298.1 K
1.00000000 sec
1
======== CHANNEL f1 ========
1H
7.90 usec
-2.00 dB
300.1318534 MHz
32768
300.1300044 MHz
EM
0
0.30 Hz
0
1.00
NAME
EXPNO
PROCNO
Date_
Time_
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
TD0
======== NUC1
P1
PL1
SFO1
SI
SF
WDW
SSB
LB
GB
PC
O
O
H
OH
O
OH
17
2.286
2.340
2.499
2.553
2.655
2.682
2.702
2.753
2.776
2.792
2.856
2.870
2.918
2.946
3.311
3.321
3.564
3.756
3.793
3.822
3.859
4.831
6.314
6.322
6.400
6.408
6.428
6.436
6.964
6.991
1.05
1.06
3.09
1.07
7.06
1.10
1.09
1.00
1.00
1.00
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0



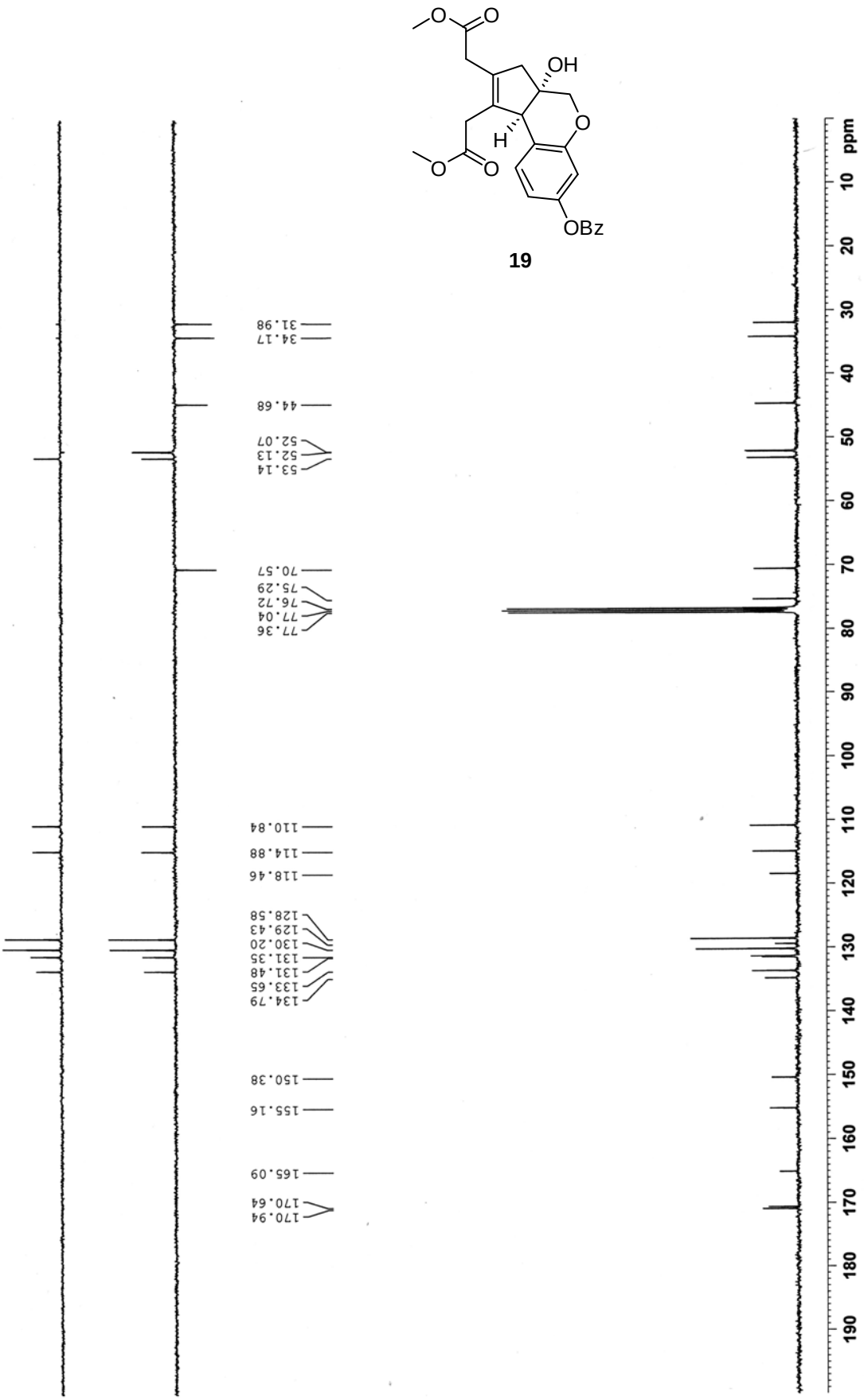
17


NAME 220120000175
EXPNO 392
PROCNO 1
Date_ 20120715
Time_ 9.28
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
O
O
H
O
OBz
18
ppm
1.06
2.01
4.04
7.01
1.00
1.08
2.07
1.00
1.06
2.06
2.06

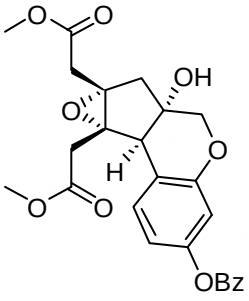

O
O
OH
H
O
OBz
18
27.664
28.595
44.245
53.454
57.248
57.574
71.463
76.613
76.814
77.037
77.461
110.954
114.927
119.485
128.570
129.460
129.735
130.191
130.644
132.790
133.630
136.116
136.359
150.100
155.159
165.125
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


NAME 22012000175
EXPNO 157
PROCNO 1
Date_ 20130112
Time_ 12.30
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 50
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 71.53
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1524711 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1500089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
-0.0039
8.1907
8.1712
7.6512
7.6329
7.6145
7.5244
7.5054
7.4861
7.2979
7.2773
7.2601
6.8316
6.8271
6.8062
6.7965
4.0368
4.0087
3.9776
3.9485
3.9303
3.6766
3.6554
3.2058
3.1656
3.1432
3.1126
3.0729
2.8693
2.8287
2.5698
2.5596
2.4420
2.4012
2.09
1.09
2.09
1.00
2.07
2.09
1.03
1.07
1.03
3.09
3.03
2.07
2.01
1.08
1.00
1.06
ppm

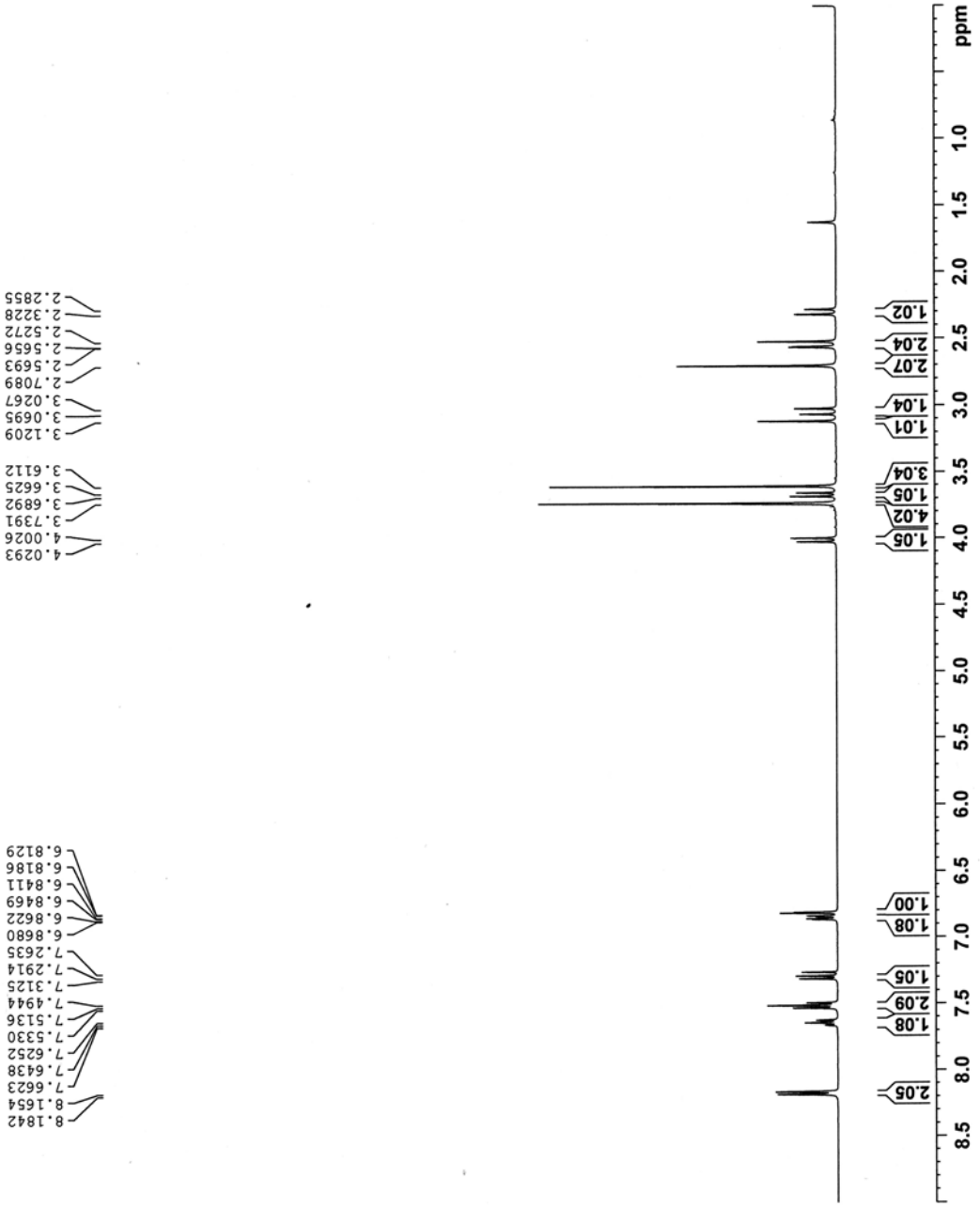
19

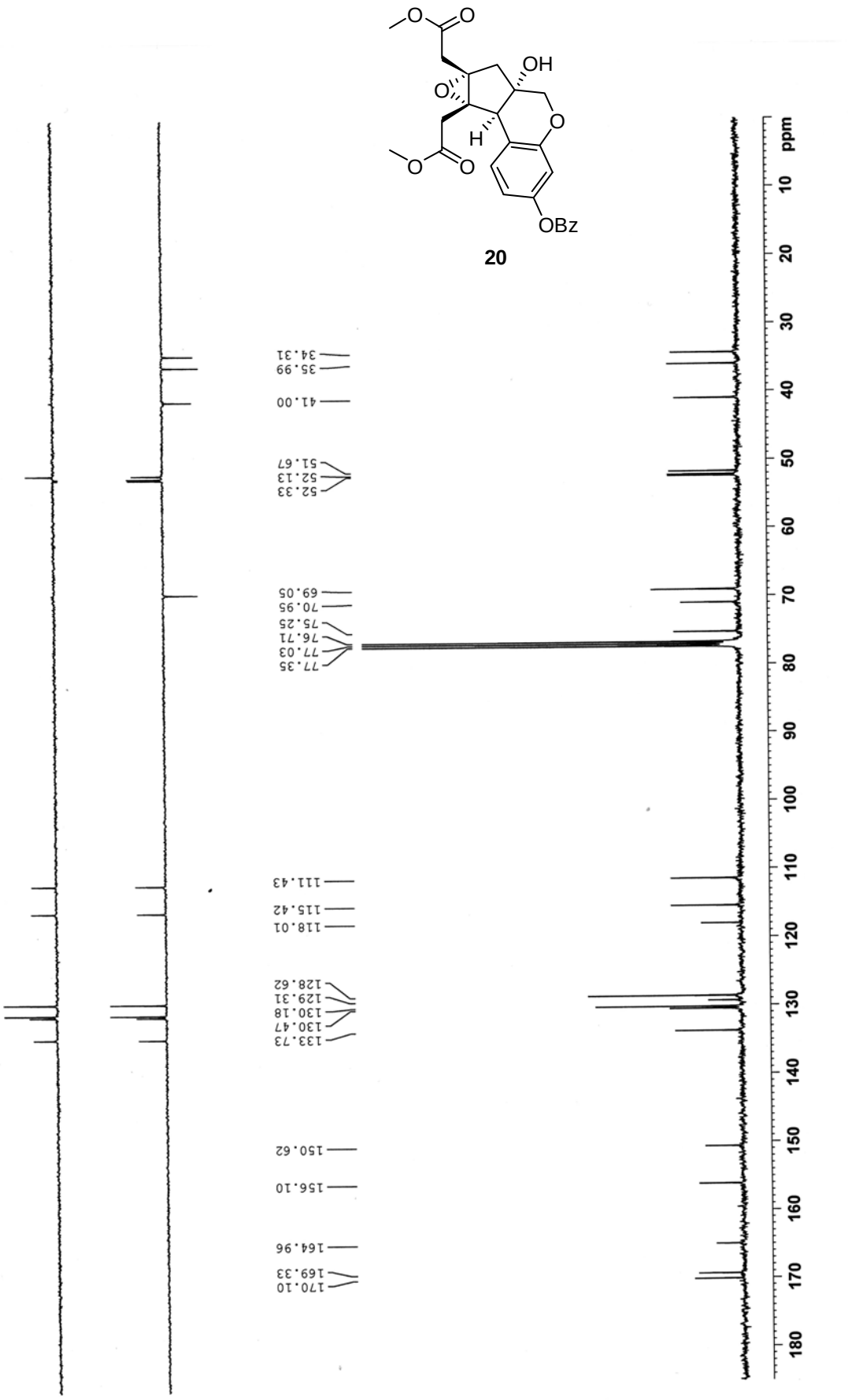

OH
O
H
OBz
31.98
34.17
44.68
52.07
52.13
53.14
70.57
75.29
76.72
77.04
77.36
110.84
114.88
118.46
128.58
129.43
130.20
131.35
131.48
133.65
134.79
150.38
155.16
165.09
170.64
170.94
ppm

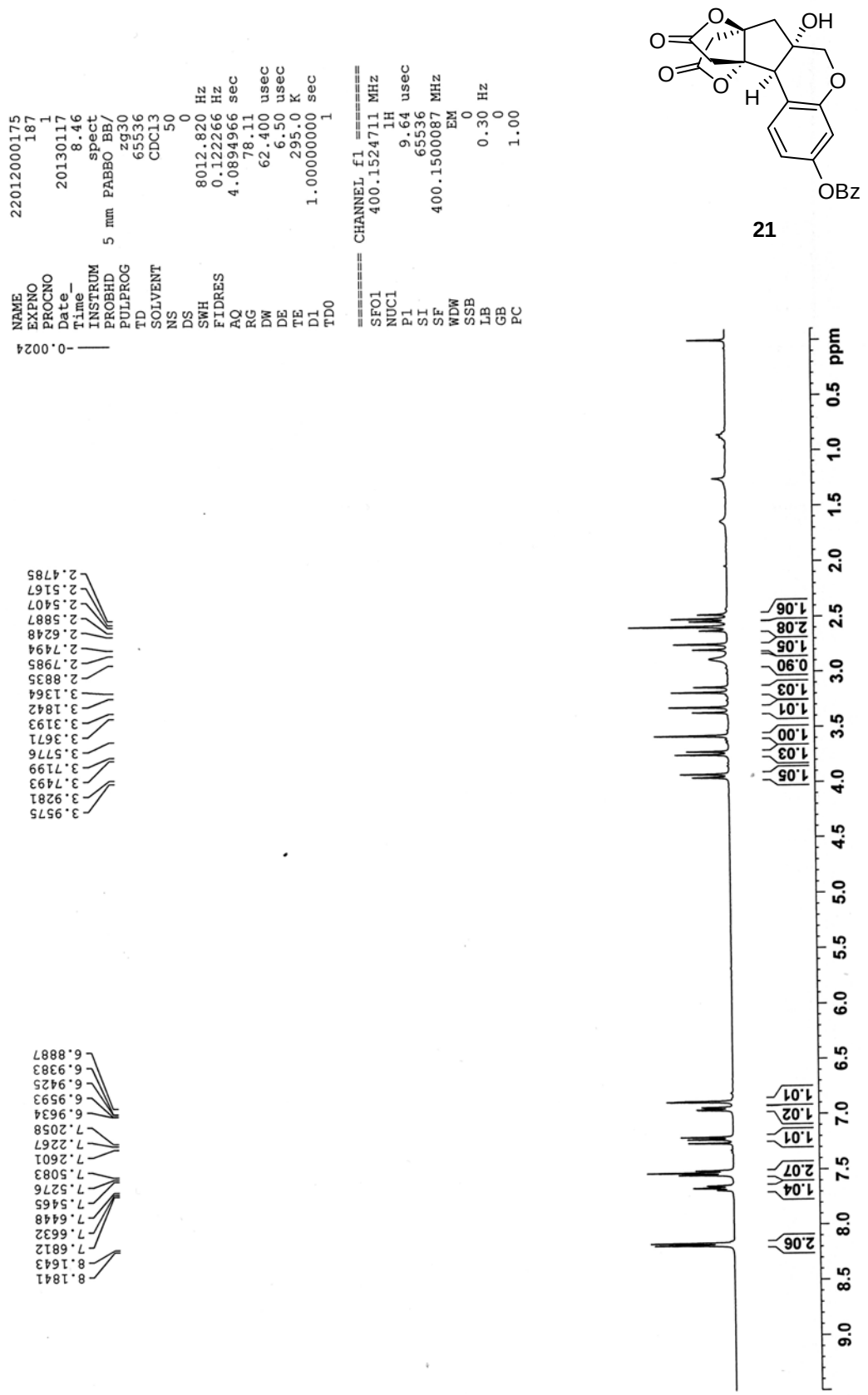
19


O
O
OH
O
O
H
O
O
OBz

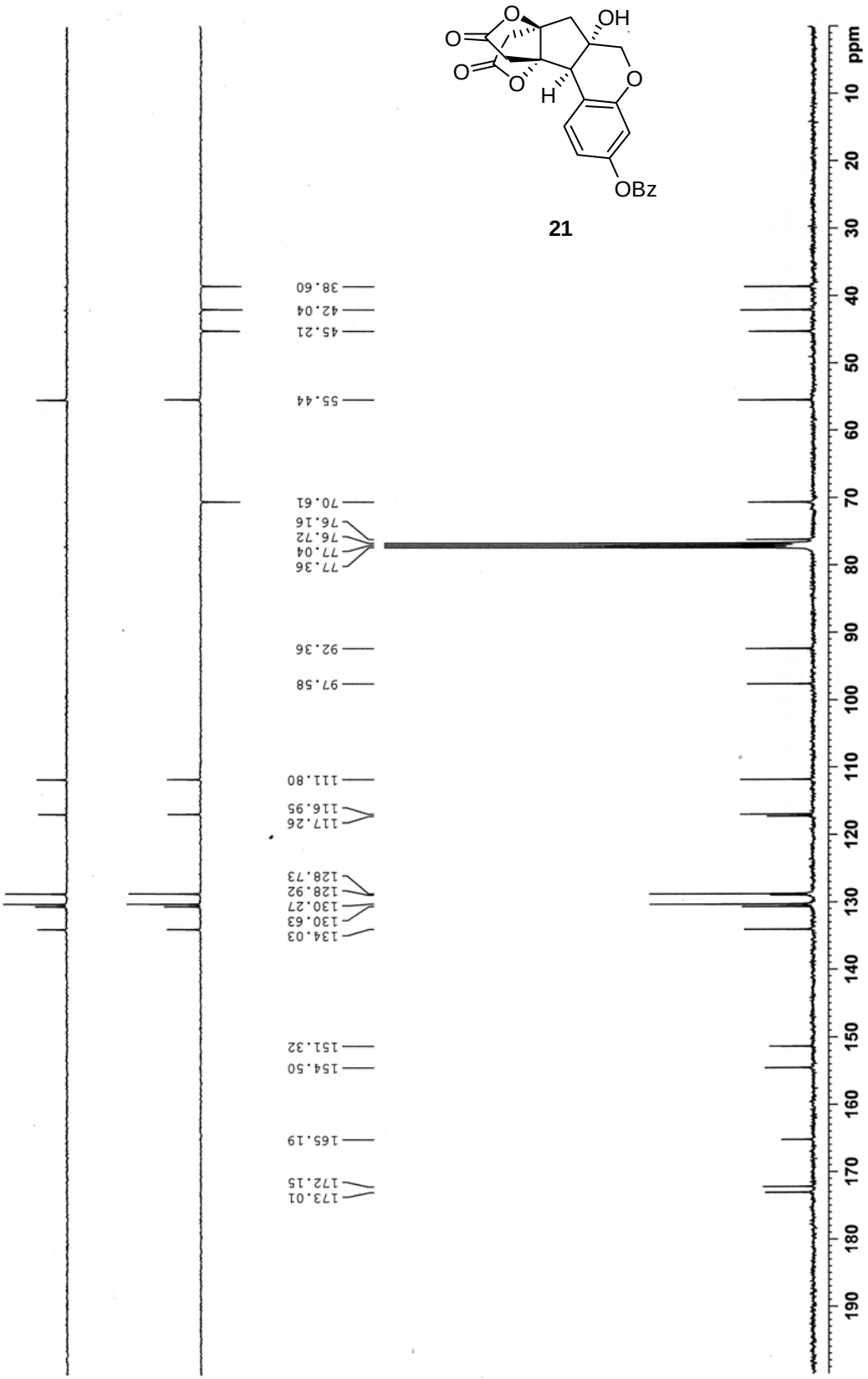
20

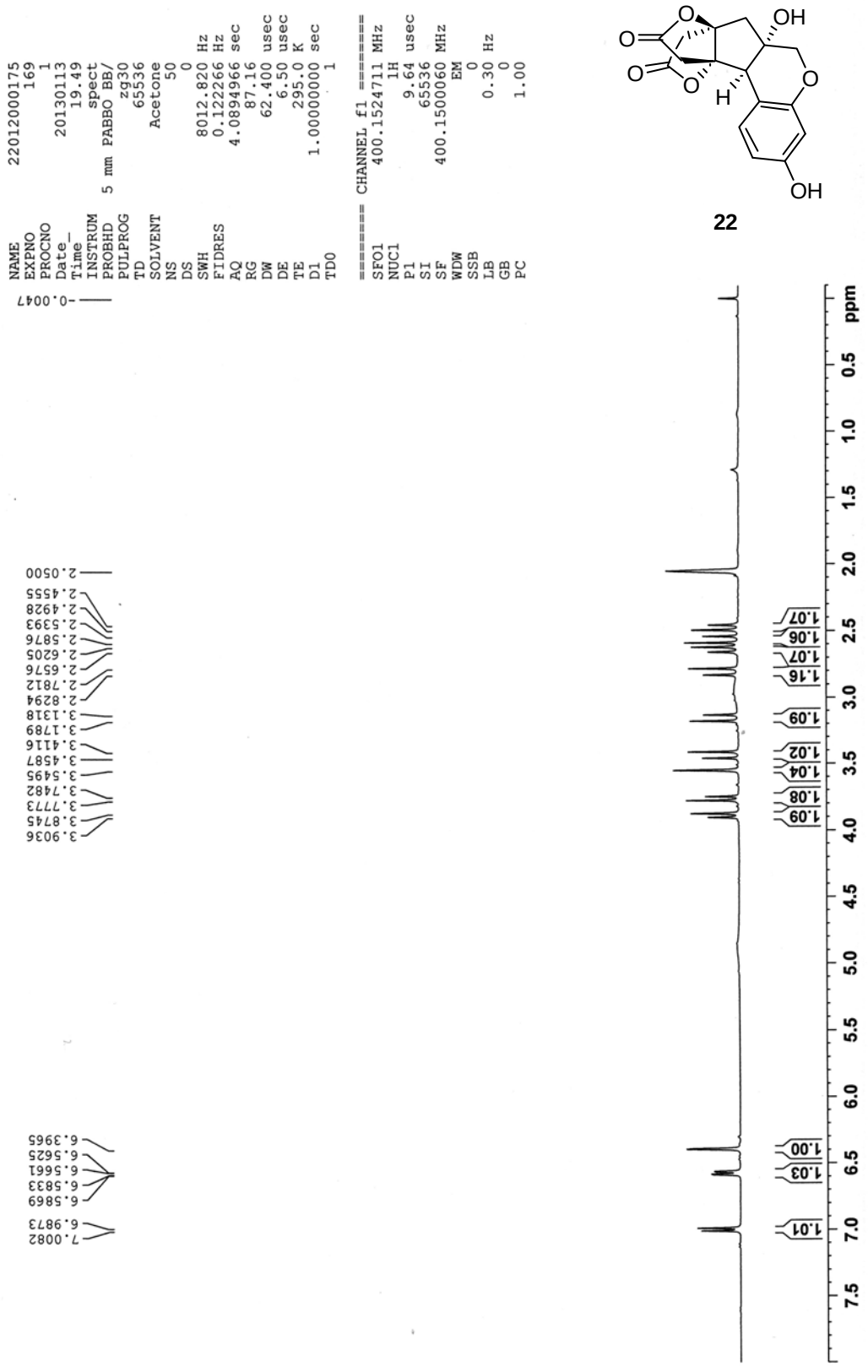

NAME 22012000175
EXPNO 125
PROCNO 1
Date_ 20130101
Time_ 19.43
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 15
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 71.53
DW 62.400 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1524711 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1500076 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.1842
8.1654
7.6623
7.6438
7.6252
7.5330
7.5136
7.4944
7.3125
7.2914
7.2635
6.8680
6.8622
6.8469
6.8411
6.8186
6.8129
4.0293
4.0026
3.7391
3.6892
3.6625
3.6112
3.1209
3.0695
3.0267
2.7089
2.5693
2.5556
2.5272
2.3228
2.2855
1.00
1.08
1.05
2.09
1.08
2.05
1.05
4.02
1.04
3.04
1.01
1.04
2.07
2.04
1.02
ppm


OH
O
O
H
O
O
O
O
OBz
20
34.31
35.99
41.00
51.67
52.13
52.33
69.05
70.95
75.25
76.71
77.03
77.35
111.43
115.42
118.01
128.62
129.31
130.18
130.47
133.73
150.62
156.10
164.96
169.33
170.10
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


NAME 22012000175
EXPNO 187
PROCNO 1
Date_ 20130117
Time 8.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 50
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 78.11
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1524711 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1500087 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
-0.0024
2.4785
2.5167
2.5407
2.5887
2.6248
2.7494
2.7985
2.8835
3.1364
3.1842
3.3193
3.3671
3.5776
3.7199
3.7493
3.9281
3.9575
6.8887
6.9383
6.9425
6.9593
6.9634
7.2058
7.2267
7.2601
7.5083
7.5276
7.5465
7.6448
7.6632
7.6812
8.1643
8.1841
1.06
2.08
1.05
0.90
1.03
1.01
1.03
1.00
1.03
1.05
1.01
1.02
1.01
2.07
1.04
2.06
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
O
O
O
O
OH
H
O
OBz

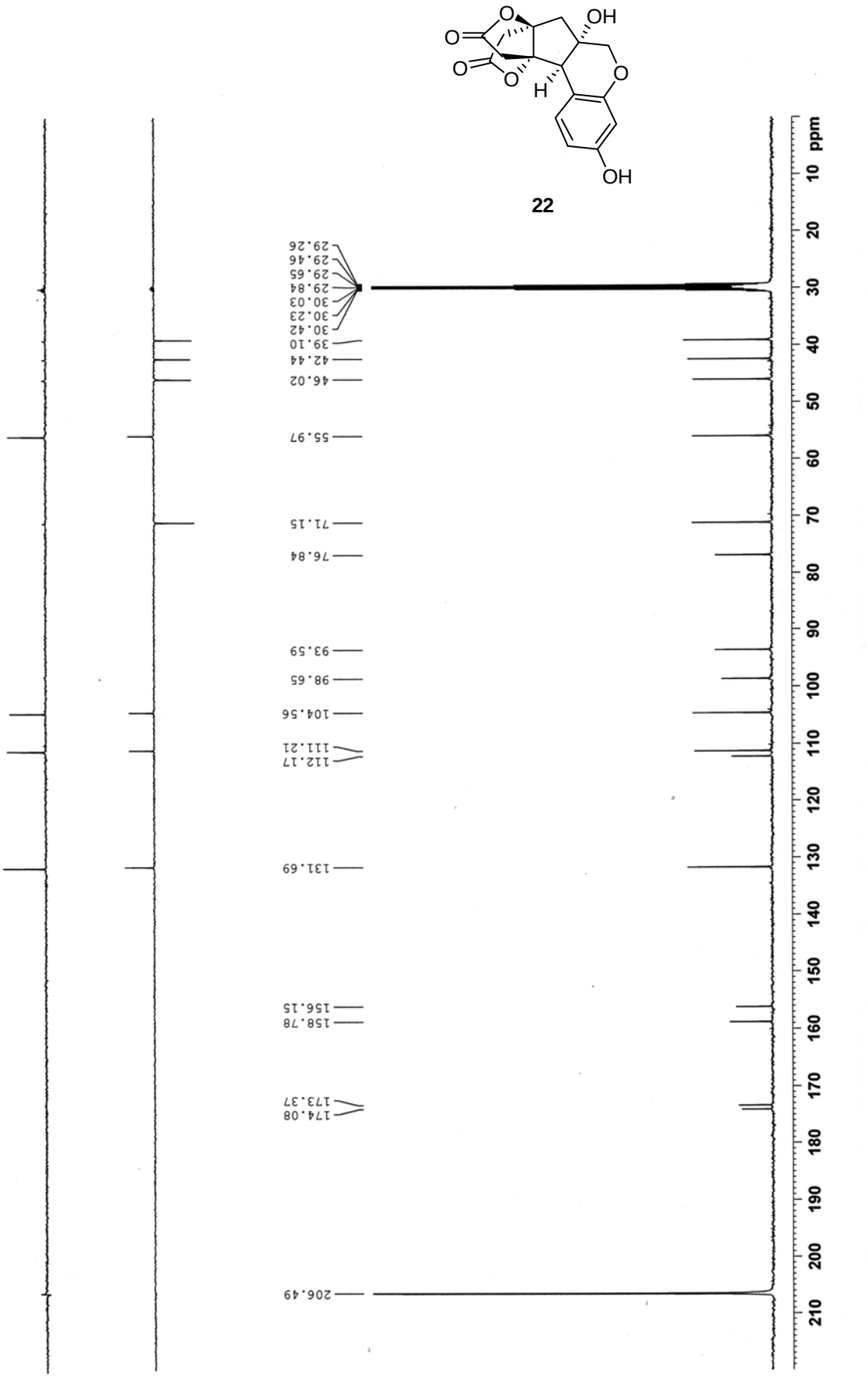
21

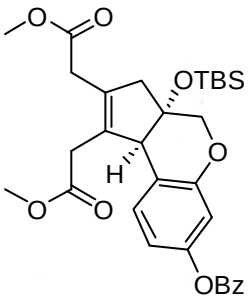

OH
O
O
O
O
H
O
OBz
21
38.60
42.04
45.21
55.44
70.61
76.16
76.72
77.04
77.36
92.36
97.58
111.80
116.95
117.26
128.73
128.92
130.27
130.63
134.03
151.32
154.50
165.19
172.15
173.01
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190


NAME 22012000175
EXPNO 169
PROCNO 1
Date_ 20130113
Time_ 19.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 50
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 87.16
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1524711 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1500060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
-0.0047
2.0500
2.4555
2.4928
2.5393
2.5876
2.6205
2.6576
2.7812
2.8294
3.1318
3.1789
3.4116
3.4587
3.5495
3.7482
3.7773
3.8745
3.9036
6.3965
6.5625
6.5661
6.5833
6.5869
6.9873
7.0082
1.07
1.06
1.07
1.16
1.09
1.02
1.04
1.08
1.09
1.00
1.03
1.01
ppm

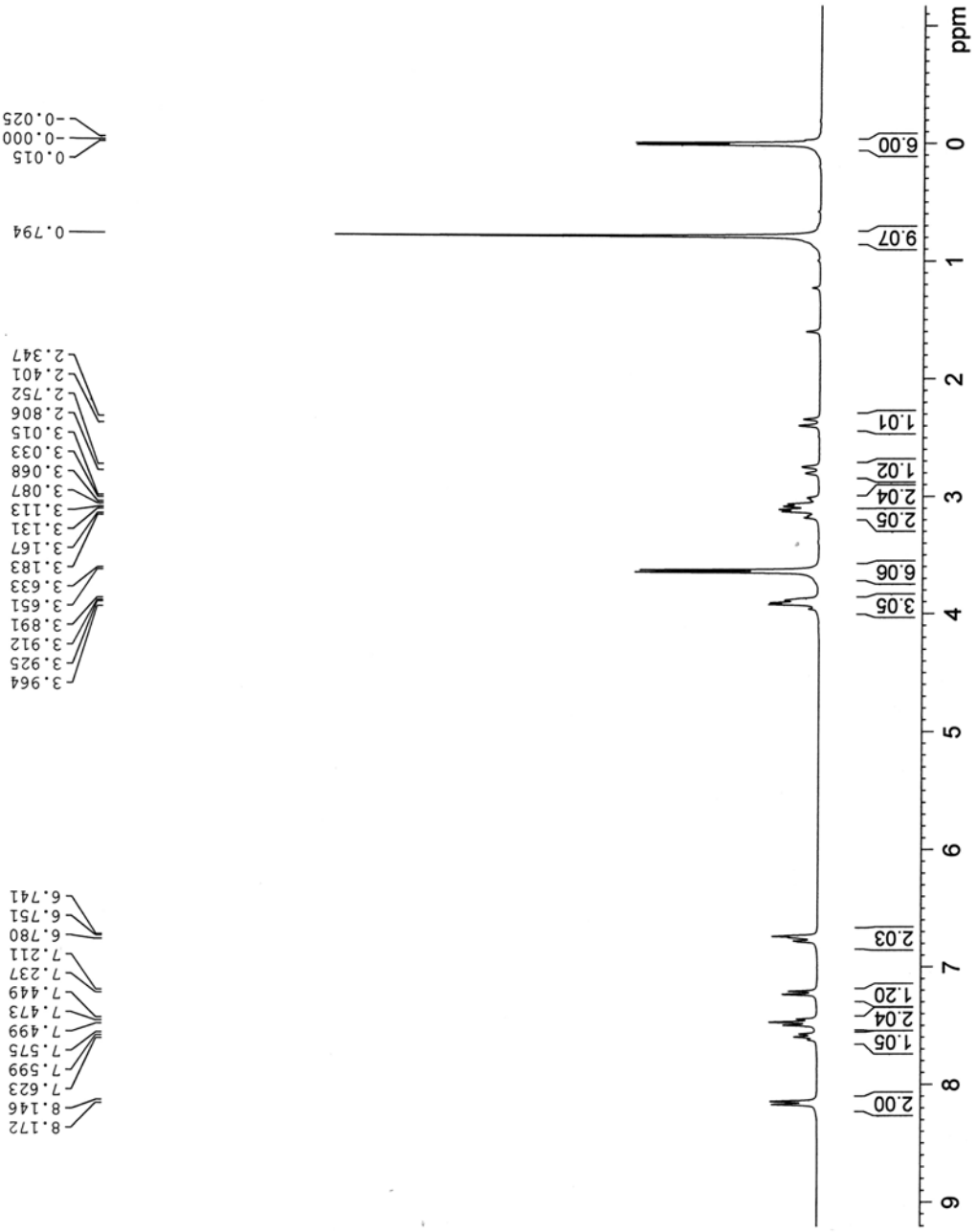
O
O
O
O
OH
H
O
OH

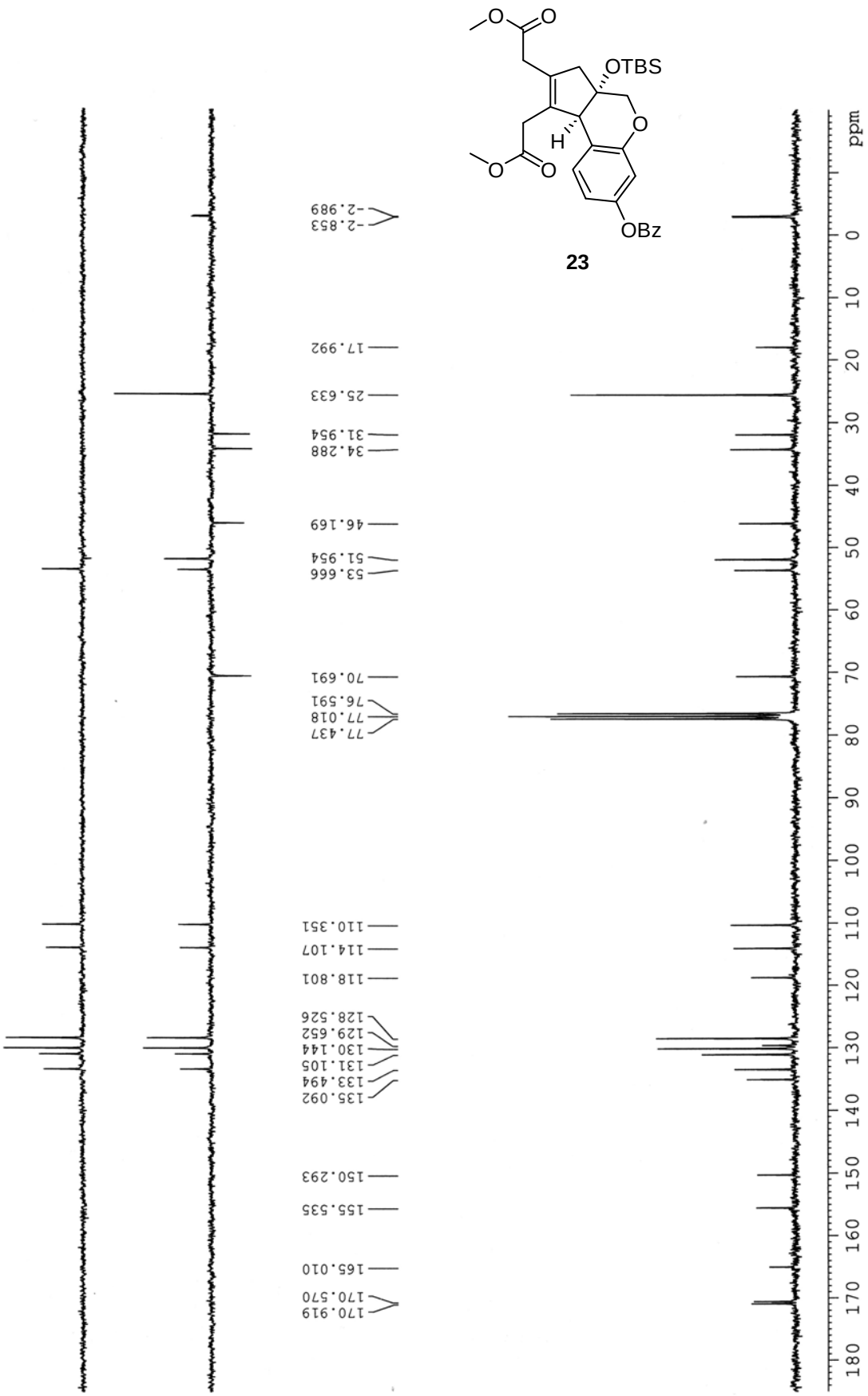
22


O
OH
O
O
O
H
O
OH
22
29.26
29.46
29.65
29.84
30.03
30.23
30.42
39.10
42.44
46.02
55.97
71.15
76.84
93.59
98.65
104.56
111.21
112.17
131.69
156.15
158.78
173.37
174.08
206.49
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

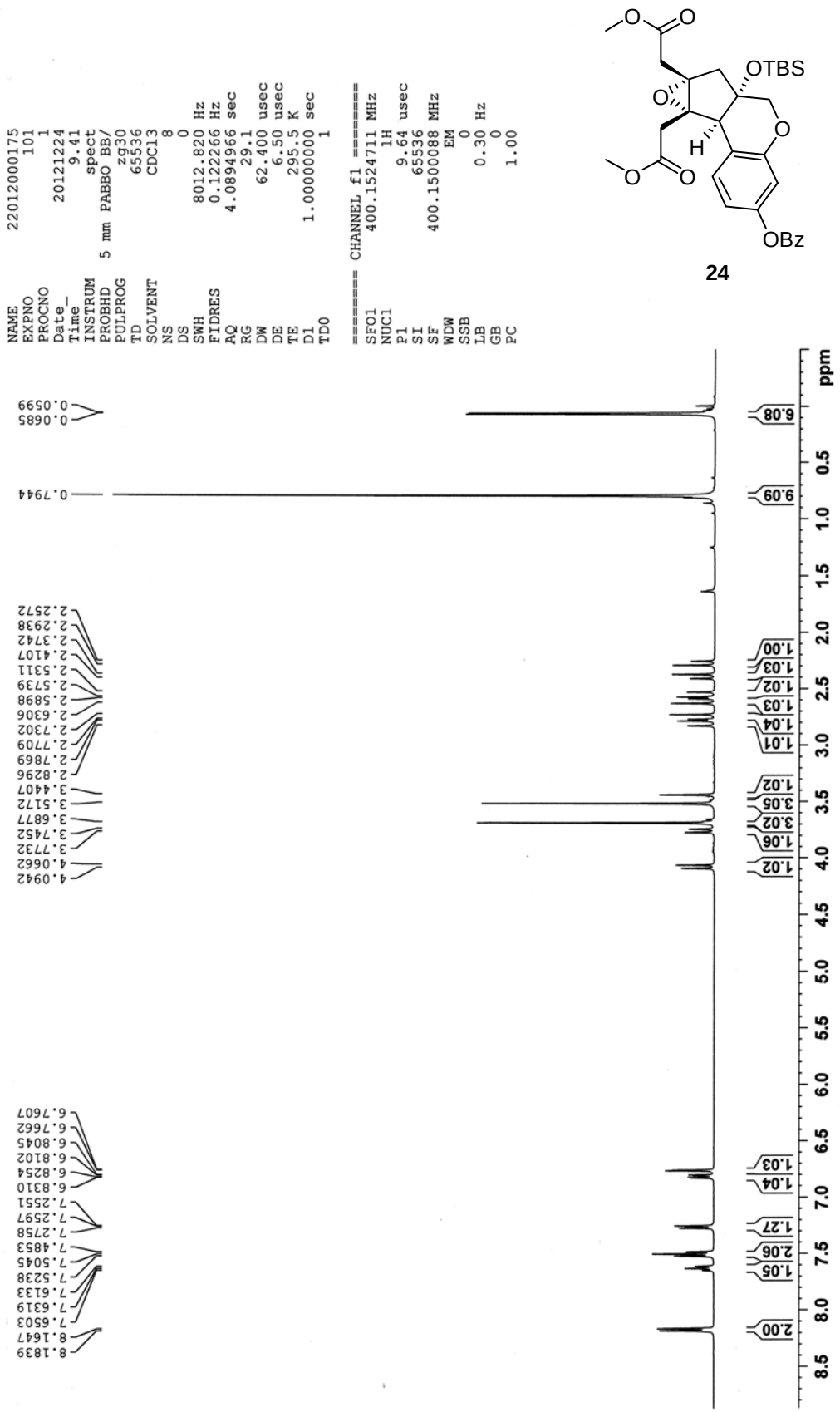

O
O
OTBS
H
O
O
O
OBz

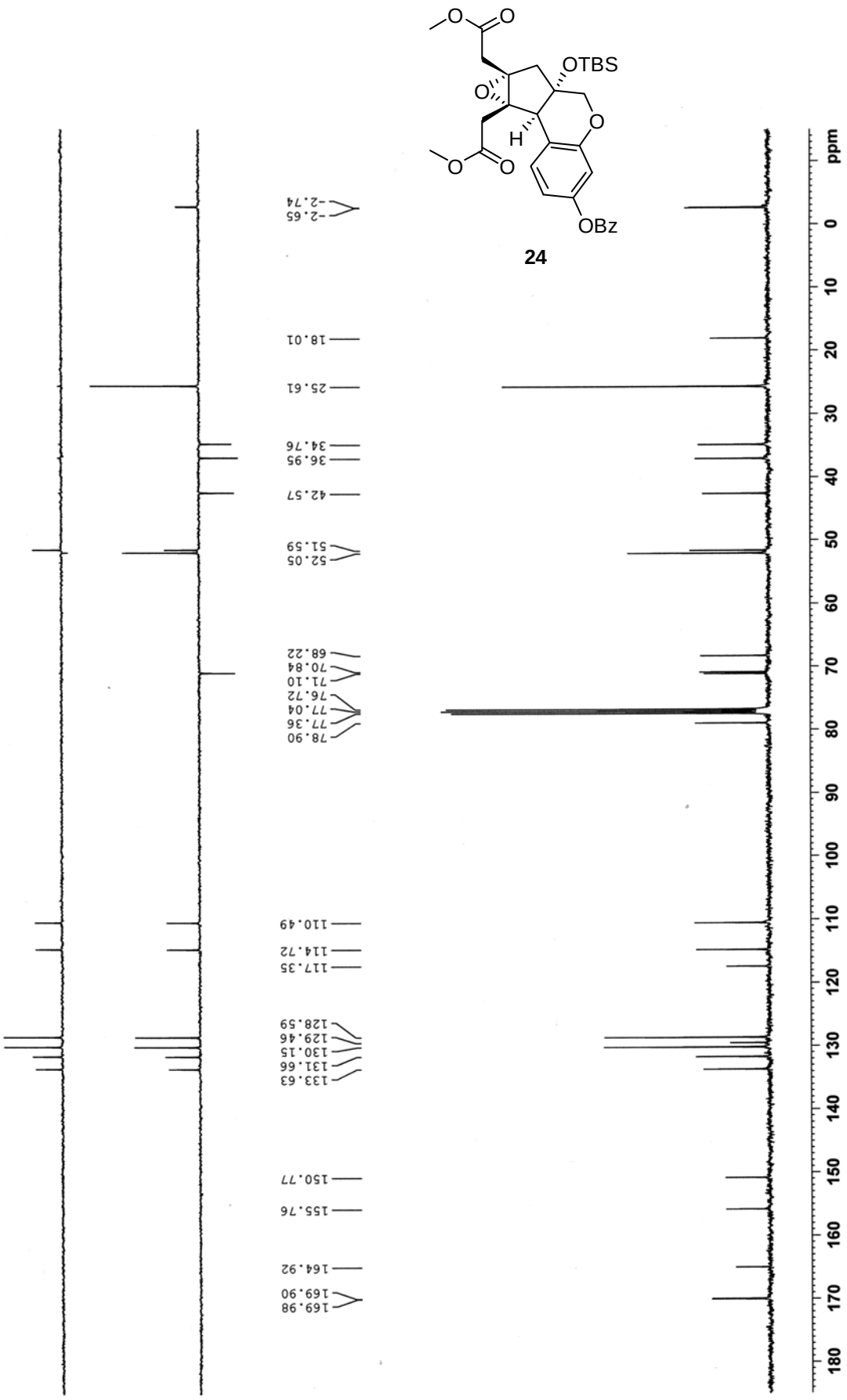
23


NAME yxd-n
EXPNO 388
PROCNO 1
Date_ 20120712
Time_ 10.07
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300135 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.172
8.146
7.623
7.599
7.575
7.499
7.473
7.449
7.237
7.211
6.780
6.751
6.741
3.964
3.925
3.912
3.891
3.651
3.633
3.183
3.167
3.131
3.113
3.087
3.068
3.033
3.015
2.806
2.752
2.401
2.347
0.794
0.015
0.000
-0.025
6.00
9.07
1.01
1.02
2.04
2.05
6.06
3.05
2.03
1.20
2.04
1.05
2.00
ppm

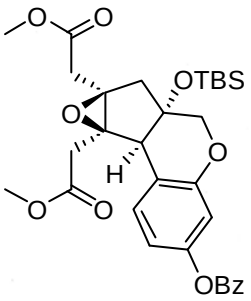

OTBS
O
H
O
O
O
O
OBz
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
-2.989
-2.853
17.992
25.633
31.954
34.288
46.169
51.954
53.666
70.691
76.591
77.018
77.437
110.351
114.107
118.801
128.526
129.652
130.144
131.105
133.494
135.092
150.293
155.535
165.010
170.570
170.919

23

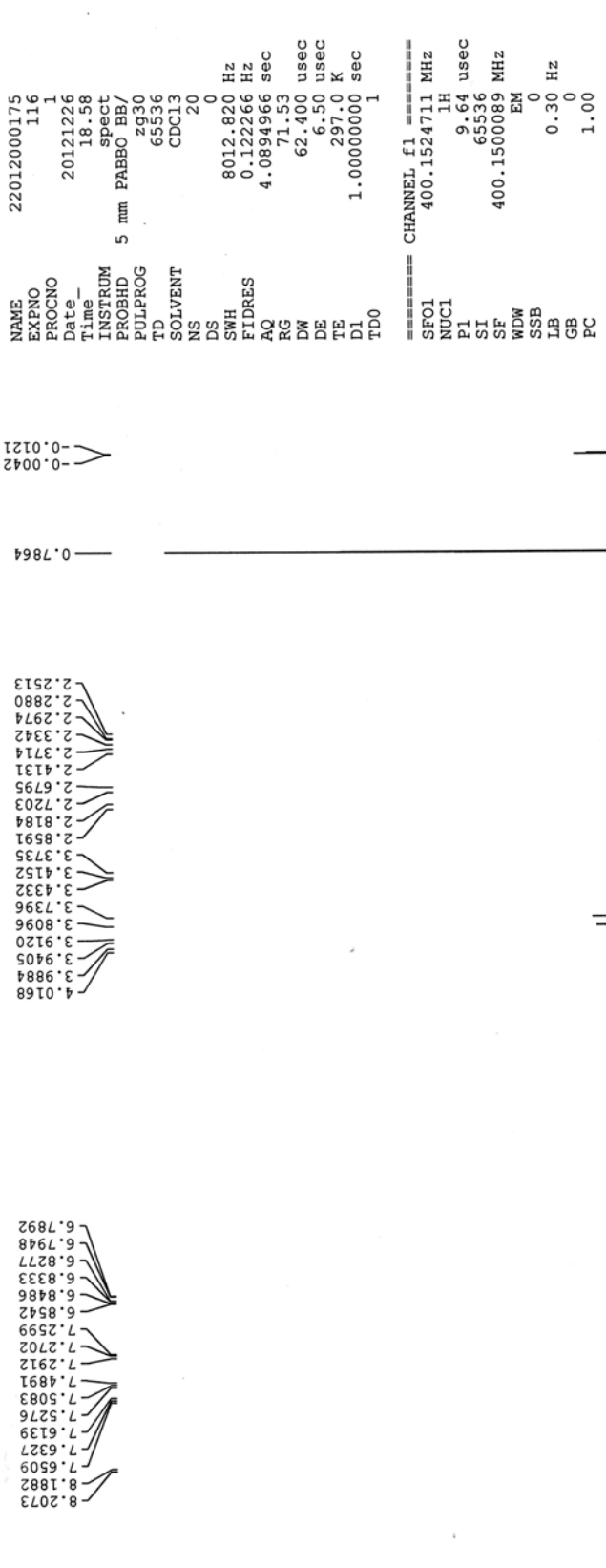

NAME 22012000175
EXPNO 101
PROCNO 1
Date_ 20121224
Time 9.41
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 29.1
DW 62.400 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1524711 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1500088 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OTBS
OBz
H
O
24
ppm

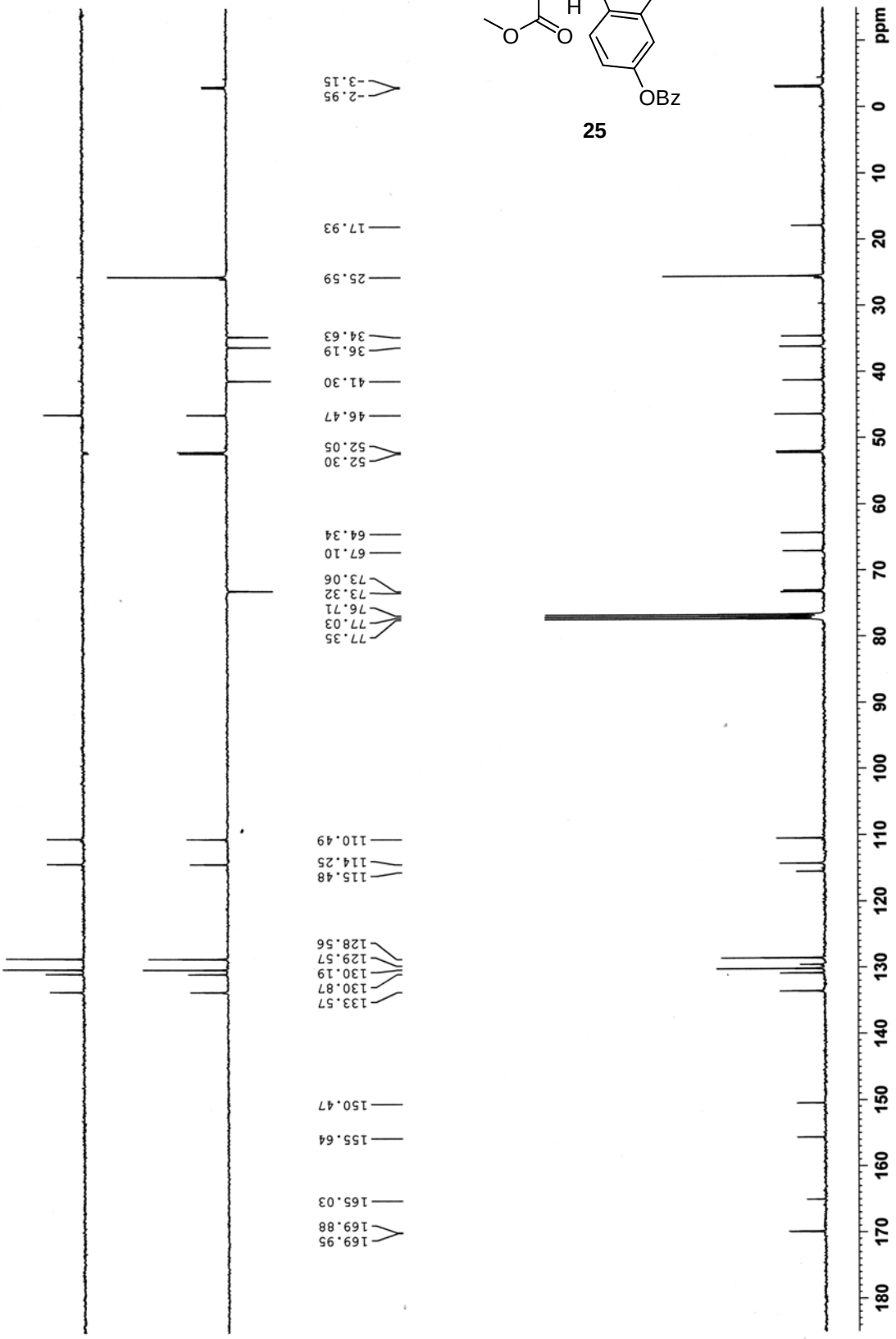


24

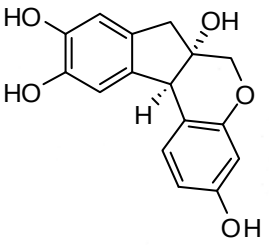

OTBS
OBz
H

25


NAME 22012000175
EXPNO 116
PROCNO 1
Date_ 20121226
Time 18.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 71.53
DW 62.400 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1524711 MHz
NUC1 1H
P1 9.64 usec
SI 65536
SF 400.1500089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

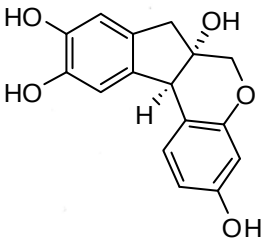

OTBS
OBz
H
O
O
O
O
O
O
-3.15
-2.95
17.93
25.59
34.63
36.19
41.30
46.47
52.05
52.30
64.34
67.10
73.06
73.32
76.71
77.03
77.35
110.49
114.25
115.48
128.56
129.57
130.19
130.87
133.57
150.47
155.64
165.03
169.88
169.95
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

25


HO
HO
OH
H
O
OH

(+)-Brzilin (**1**)

NAME 22012000175
EXPNO 20
PROCNO 1
Date_ 20121116
Time_ 13.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 36.33
DW 62.400 usec
DE 6.50 usec
TE 298.4 K
D1 1.00000000 sec
TDO 1
======== CHANNEL f1 ========
SFO1 400.1524711 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1500069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.1971
7.1763
6.7110
6.6037
6.4854
6.4794
6.4647
6.4587
6.2985
6.2926
4.8598
3.9642
3.9444
3.9159
3.7046
3.6763
3.3100
3.0381
2.9991
2.7956
2.7565
1.07
1.04
1.05
1.09
1.05
1.00
1.06
1.07
1.07
1.06
ppm


HO
HO
OH
H
O
OH

(+)-Brzilin (**1**)

42.90
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48.79
49.00
49.21
49.43
49.64
51.07
70.86
78.08
104.27
109.97
112.47
112.89
115.59
131.37
132.23
137.45
145.32
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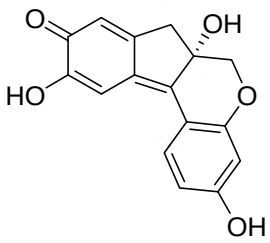
170
180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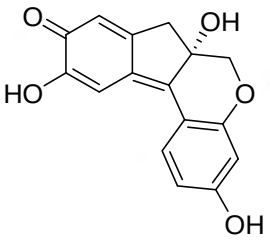
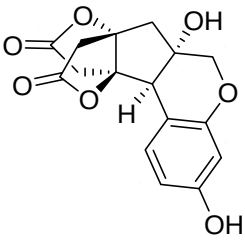
HO
O
OH

(-)-Brazilein (2)

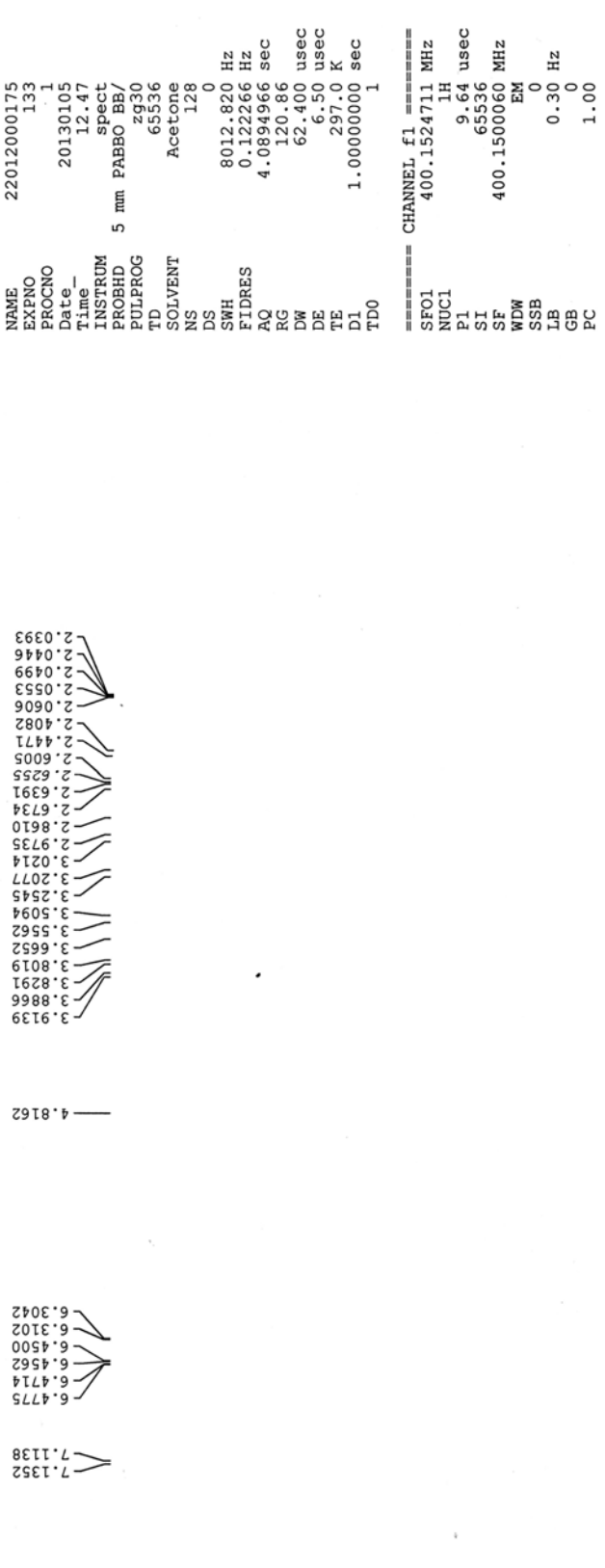
NAME 22012000175
EXPNO 64
PROCNO 1
Date_ 20130201
Time_ 17.08
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 36
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 6.50 usec
TE 297.3 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300012 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.07
1.06
1.03
1.02
0.97
0.99
1.07
1.07
1.05
1.11
ppm

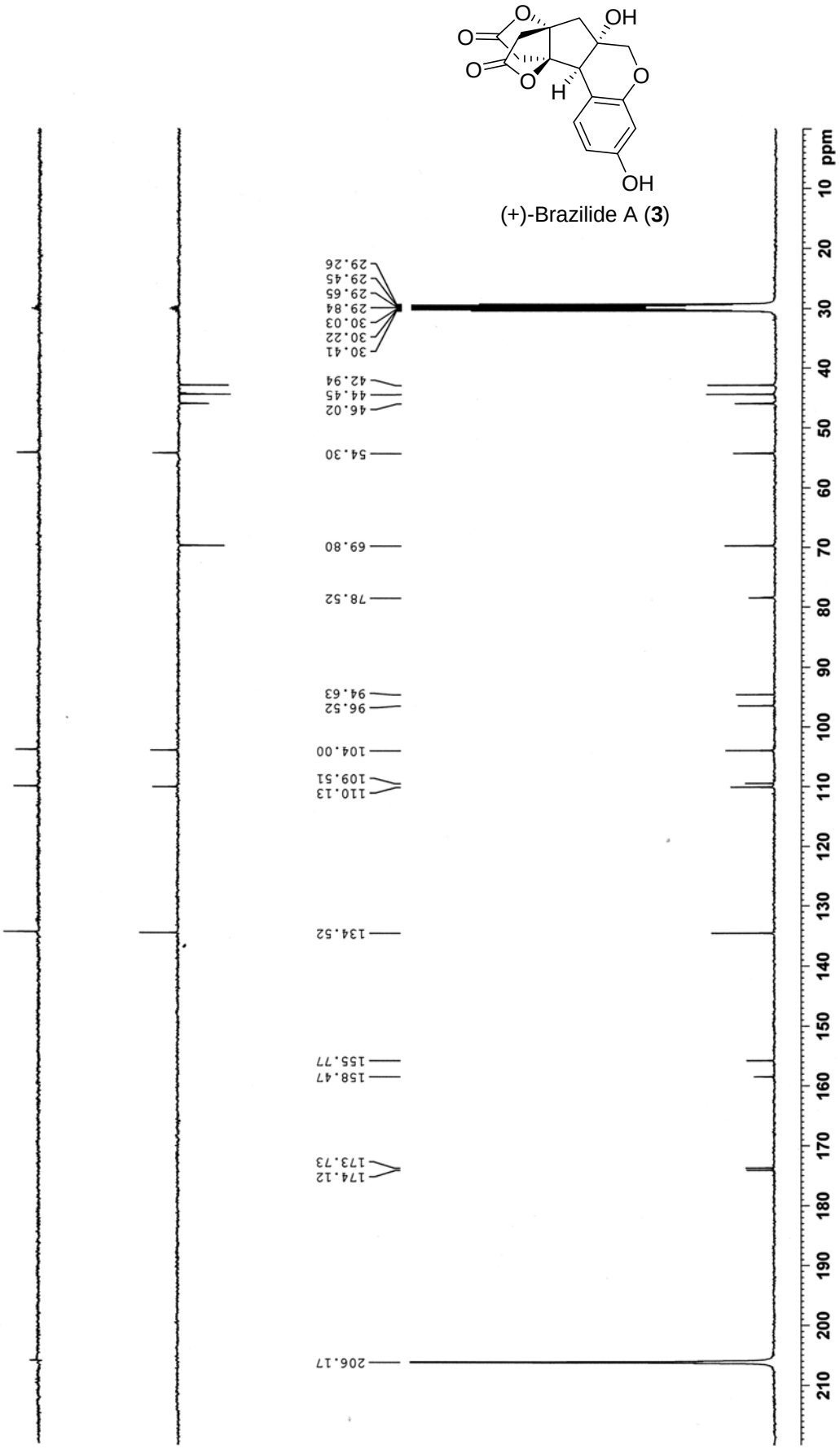


(-)-Brazilein (2)



(+)-Brazilide A (**3**)





Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\SXF00038.D Sample Name: zero

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Sample Name     : zero                          Location :   -
Acq. Operator   : 1
Acq. Method     : C:\HPCHEM\1\METHODS\ZYY.M\01.M
Last changed    : 2012-7-5 20:20:29 下午 by 1
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\ZYY.M\01.M
Last changed    : 2012-6-21 18:27:25 下午 by 1
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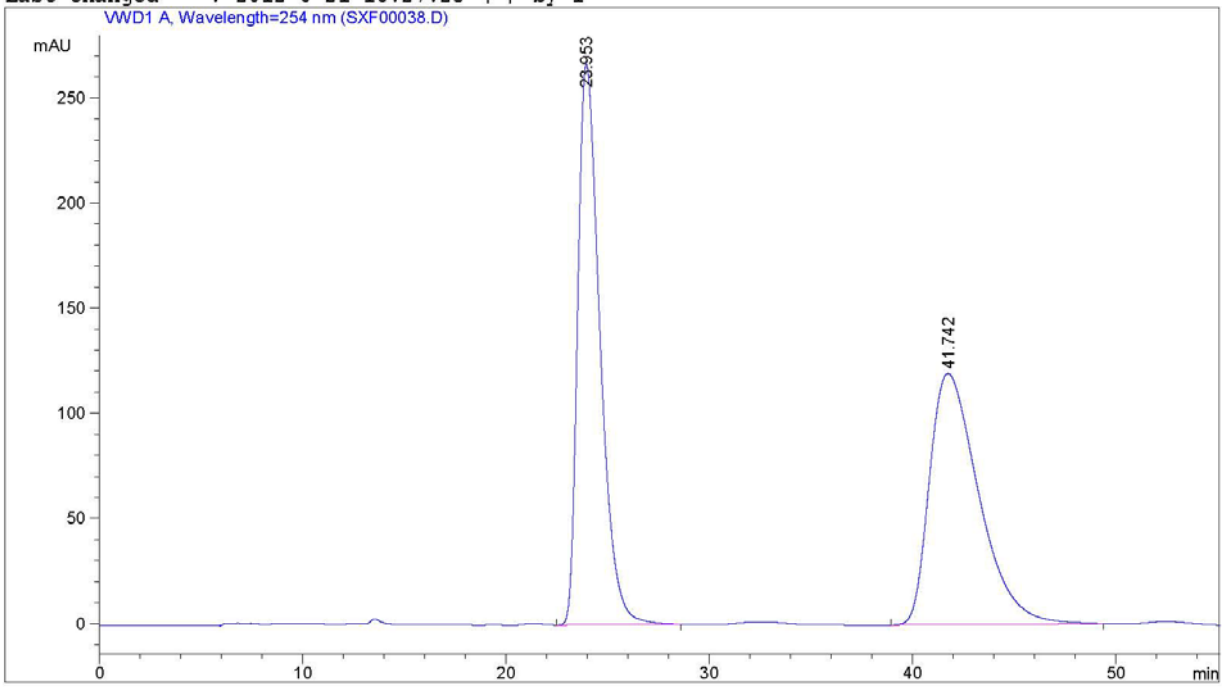



```
==================================================================
                        Area Percent Report
==================================================================

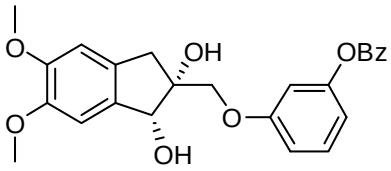
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  23.953 VB    1.1658 2.02632e4   266.74408  50.1289
   2  41.742 PB    2.6088 2.01590e4   119.49933  49.8711

Totals :                  4.04223e4   386.24341

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```



8

Instrument 1 2012-7-5 23:05:09 下午 1 Page 1 of 1

Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\WXQ00002.D Sample Name: zero

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==================================================================
Injection Date  : 2012-9-5 16:11:36 下午
Sample Name     : zero                          Location :   -
Acq. Operator   :
Method          : C:\HPCHEM\1\METHODS\CQ.M
Last changed    : 2012-9-5 14:00:57 下午 by 1
                  (modified after loading)
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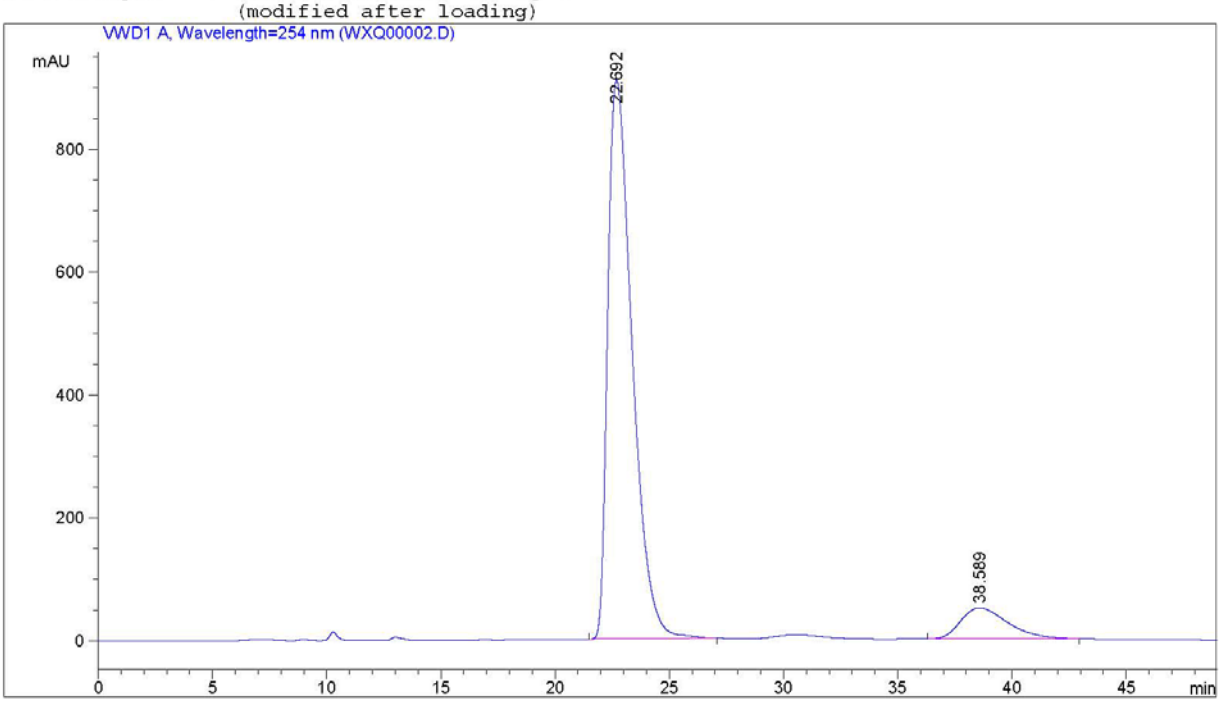



```
==================================================================
                      Area Percent Report
==================================================================

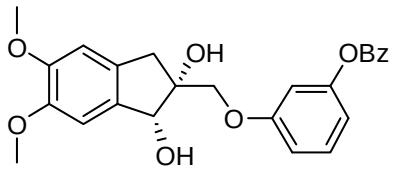
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  22.692 BB    1.1317 6.72658e4   910.06598  90.2326
   2  38.589 VB    2.0693 7281.29785   50.85722   9.7674

Totals :                  7.45471e4   960.92320

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```



8

Instrument 1 2012-9-5 17:01:15 下午 Page 1 of 1

Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\WXQ00056.D Sample Name: zero

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Injection Date   : 2013-1-19 15:22:48 下午
Sample Name      : zero                          Location :   -
Acq. Operator    : 1
Method           : C:\HPCHEM\1\METHODS\1.M
Last changed     : 2013-1-19 9:50:30 下午 by 1
                   (modified after loading)
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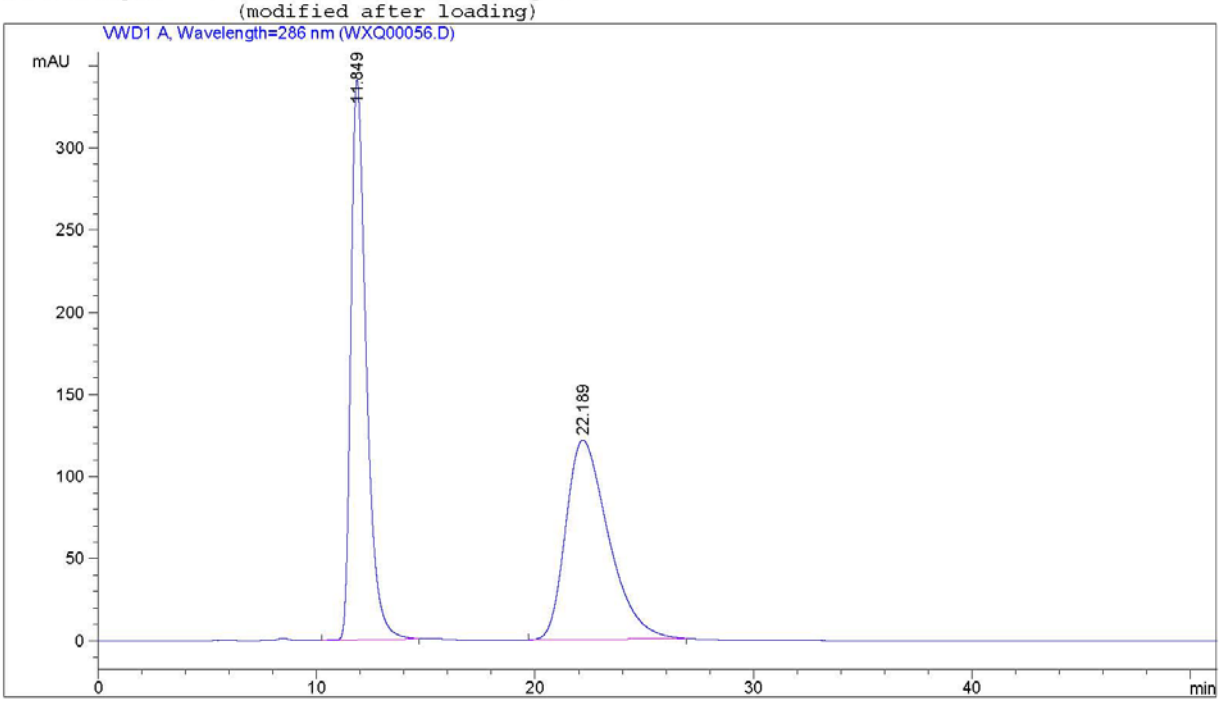



```
==================================================================
                      Area Percent Report
==================================================================

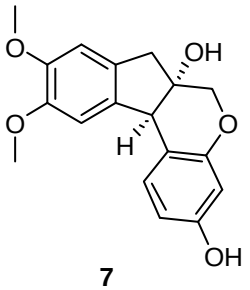
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000

Signal 1: VWD1 A, Wavelength=286 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.849 BB    0.7432 1.66939e4   340.88220  50.3205
   2  22.189 BB    2.0087 1.64812e4   121.19862  49.6795

Totals :                  3.31751e4   462.08083

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```



7

Instrument 1 2013-1-19 16:13:55 下午 1 Page 1 of 1

Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\WXQ00053.D Sample Name: zero

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==================================================================
Injection Date  : 2013-1-19 13:18:28 下午
Sample Name     : zero                          Location :   -
Acq. Operator   : 1
Method          : C:\HPCHEM\1\METHODS\1.M
Last changed    : 2013-1-19 9:50:30 下午 by 1
                  (modified after loading)
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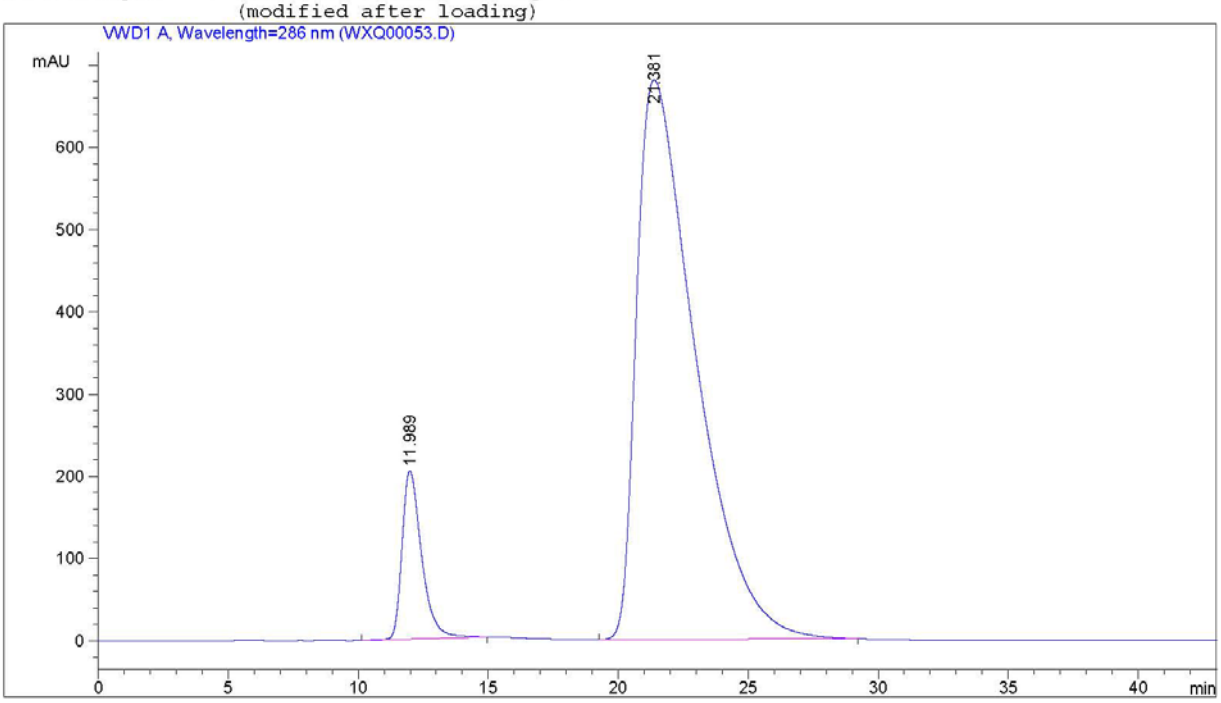



```
==================================================================
                      Area Percent Report
==================================================================

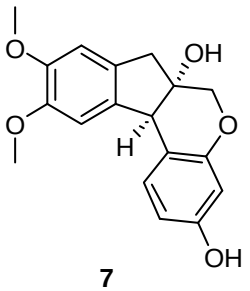
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=286 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.989 PB    0.8016 1.07707e4   204.72748   9.1332
   2  21.381 BB    2.3459 1.07158e5   680.28156  90.8668

Totals :                  1.17929e5   885.00903

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```



7

Instrument 1 2013-1-19 14:04:04 下午 1 Page 1 of 1

Data File C:\HPCHEM\1\VERIFY\DEFAULT.VAL\WXQ00052.D Sample Name: zero

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==================================================================
Injection Date  : 2013-1-19 12:36:36 下午
Sample Name     : zero                          Location :   -
Acq. Operator   : 1
Method          : C:\HPCHEM\1\METHODS\1.M
Last changed    : 2013-1-19 9:50:30 下午 by 1
                  (modified after loading)
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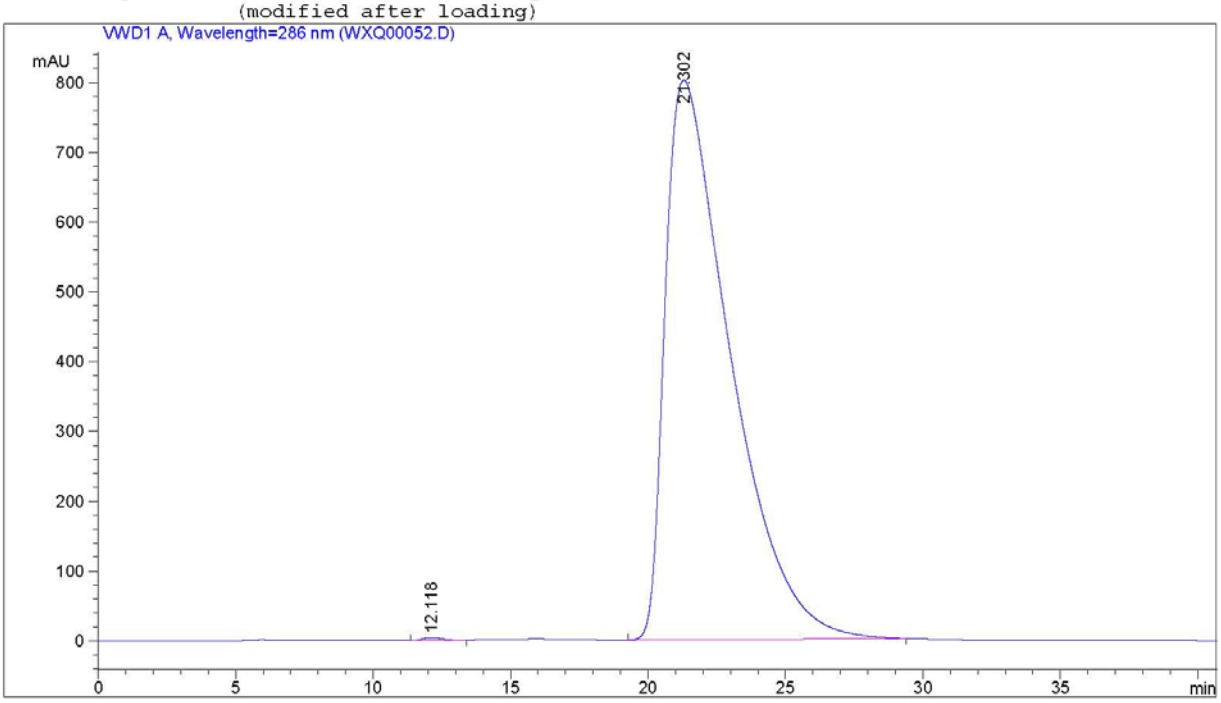


```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=286 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.118 PP    0.6813  165.04034    3.60430   0.1247
   2  21.302 BB    2.4032 1.32183e5   802.06293  99.8753

Totals :                  1.32348e5   805.66723

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
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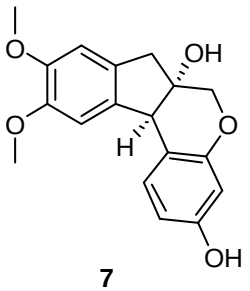

7

Instrument 1 2013-1-19 13:19:33 下午 1 Page 1 of 1

Compound 21 crystal structure analysis

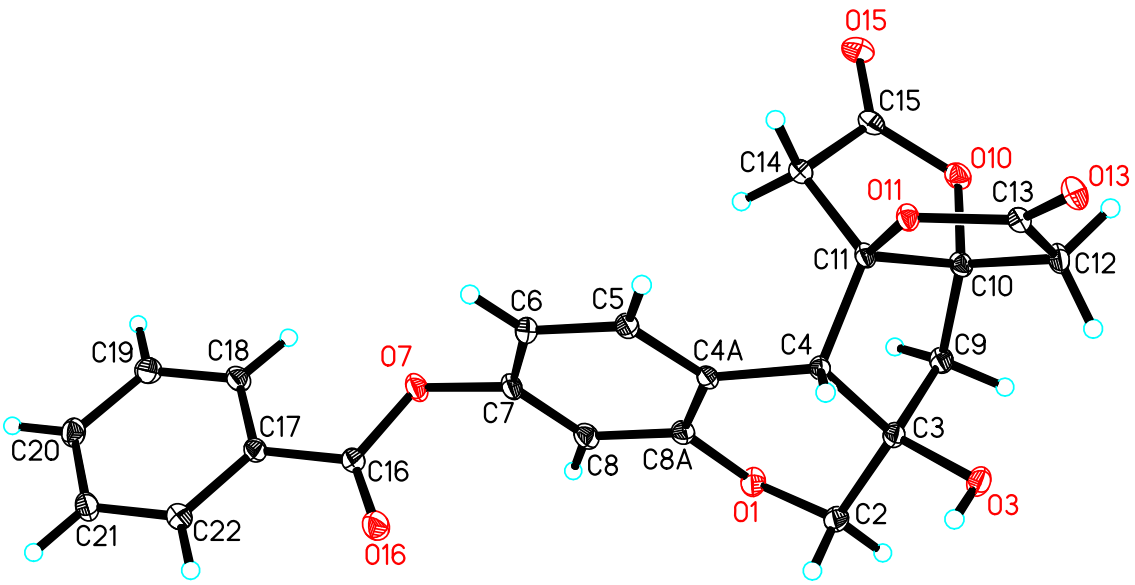

Figure 1 X-crystal structure of compound 21 (zhb_yxd_1)

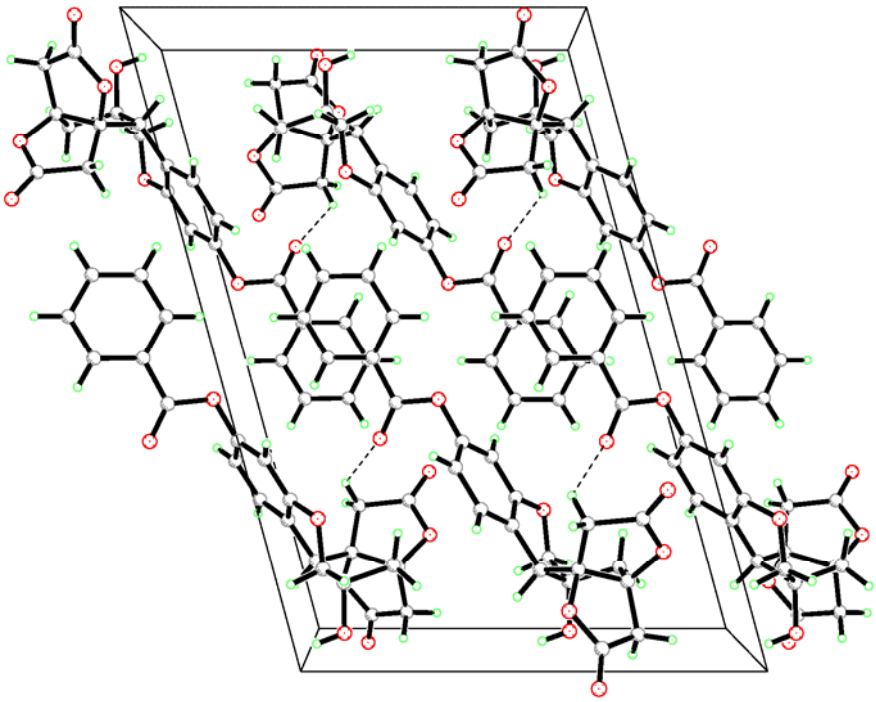

Table 1. Crystal data and structure refinement for zhb_yxd_1.

Identification code	mo_zhb_yxd_1_0m
Empirical formula	C23 H18 O8
Formula weight	422.37
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 19.082(4) A alpha = 90 deg. b = 8.1761(16) A beta = 105.231(3) deg. c = 12.919(3) A gamma = 90 deg.
Volume	1944.8(6) A^3
Z, Calculated density	4, 1.443 Mg/m^3
Absorption coefficient	0.110 mm^-1
F(000)	880
Crystal size	0.67 x 0.37 x 0.13 mm
Theta range for data collection	1.11 to 30.45 deg.
Limiting indices	-26<=h<=26, -11<=k<=10, -18<=l<=17
Reflections collected / unique	19227 / 5453 [R(int) = 0.0482]
Completeness to theta = 30.45	92.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9858 and 0.9298
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5453 / 0 / 281
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1263
R indices (all data)	R1 = 0.0675, wR2 = 0.1455
Largest diff. peak and hole	0.473 and -0.329 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for zhb_yxd_1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(15)	7204(1)	7023(2)	6197(1)	29(1)
O(7)	5938(1)	2554(2)	10477(1)	24(1)
O(13)	10069(1)	7429(1)	8758(1)	22(1)
O(11)	9007(1)	6537(1)	8924(1)	17(1)
O(10)	8183(1)	5421(1)	6553(1)	22(1)
O(1)	7734(1)	774(1)	8784(1)	23(1)
O(16)	6574(1)	1470(2)	12043(1)	28(1)
O(3)	9577(1)	2268(1)	8969(1)	22(1)
C(15)	7654(1)	6277(2)	6844(1)	21(1)
C(14)	7736(1)	6115(2)	8036(1)	18(1)
C(11)	8464(1)	5294(2)	8473(1)	15(1)
C(4)	8541(1)	3832(2)	9266(1)	15(1)
C(4A)	7863(1)	3446(2)	9615(1)	16(1)
C(5)	7584(1)	4591(2)	10201(1)	19(1)
C(6)	6949(1)	4300(2)	10503(1)	21(1)
C(7)	6598(1)	2830(2)	10210(1)	21(1)
C(16)	6000(1)	1873(2)	11457(1)	20(1)
C(17)	5288(1)	1746(2)	11715(1)	18(1)
C(18)	4640(1)	2205(2)	10992(1)	22(1)
C(19)	3997(1)	2152(2)	11300(1)	24(1)
C(20)	4002(1)	1618(2)	12323(1)	24(1)
C(13)	9558(1)	6521(2)	8449(1)	18(1)
C(10)	8670(1)	4633(2)	7465(1)	18(1)
C(12)	9435(1)	5259(2)	7575(1)	20(1)
C(9)	8552(1)	2799(2)	7496(1)	19(1)
C(3)	8801(1)	2377(2)	8689(1)	18(1)
C(8A)	7491(1)	1972(2)	9350(1)	19(1)
C(2)	8506(1)	760(2)	8974(1)	22(1)
C(8)	6853(1)	1657(2)	9643(1)	21(1)
C(21)	4644(1)	1118(2)	13031(1)	24(1)
C(22)	5291(1)	1185(2)	12733(1)	22(1)

Table 3. Bond lengths [A] and angles [deg] for zhb_yxd_1.

O(15)-C(15)	1.1949(19)
O(7)-C(16)	1.3592(19)
O(7)-C(7)	1.4102(18)
O(13)-C(13)	1.2077(18)
O(11)-C(13)	1.3502(17)
O(11)-C(11)	1.4591(16)
O(10)-C(15)	1.3600(19)
O(10)-C(10)	1.4461(17)
O(1)-C(8A)	1.3741(18)
O(1)-C(2)	1.4293(19)
O(16)-C(16)	1.2032(18)
O(3)-C(3)	1.4309(17)
O(3)-H(3)	0.8400
C(15)-C(14)	1.512(2)
C(14)-C(11)	1.512(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(11)-C(10)	1.5539(19)
C(11)-C(4)	1.555(2)
C(4)-C(4A)	1.5113(19)
C(4)-C(3)	1.553(2)
C(4)-H(4)	1.0000
C(4A)-C(8A)	1.394(2)
C(4A)-C(5)	1.395(2)
C(5)-C(6)	1.387(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.380(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.371(2)
C(16)-C(17)	1.484(2)
C(17)-C(18)	1.391(2)
C(17)-C(22)	1.392(2)
C(18)-C(19)	1.387(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.390(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.383(2)
C(20)-H(20)	0.9500
C(13)-C(12)	1.502(2)
C(10)-C(12)	1.517(2)
C(10)-C(9)	1.518(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(9)-C(3)	1.528(2)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(3)-C(2)	1.519(2)
C(8A)-C(8)	1.391(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(8)-H(8)	0.9500
C(21)-C(22)	1.387(2)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500

C(16)-O(7)-C(7)	115.41(12)
C(13)-O(11)-C(11)	111.57(11)
C(15)-O(10)-C(10)	111.72(11)
C(8A)-O(1)-C(2)	112.99(12)
C(3)-O(3)-H(3)	109.5
O(15)-C(15)-O(10)	121.17(14)
O(15)-C(15)-C(14)	128.37(15)
O(10)-C(15)-C(14)	110.46(12)
C(11)-C(14)-C(15)	105.04(12)
C(11)-C(14)-H(14A)	110.7
C(15)-C(14)-H(14A)	110.7
C(11)-C(14)-H(14B)	110.7
C(15)-C(14)-H(14B)	110.7
H(14A)-C(14)-H(14B)	108.8
O(11)-C(11)-C(14)	108.98(11)
O(11)-C(11)-C(10)	105.52(10)
C(14)-C(11)-C(10)	104.54(11)
O(11)-C(11)-C(4)	109.76(11)
C(14)-C(11)-C(4)	120.40(11)
C(10)-C(11)-C(4)	106.53(11)
C(4A)-C(4)-C(3)	112.94(11)
C(4A)-C(4)-C(11)	114.64(11)
C(3)-C(4)-C(11)	105.03(11)
C(4A)-C(4)-H(4)	108.0
C(3)-C(4)-H(4)	108.0
C(11)-C(4)-H(4)	108.0
C(8A)-C(4A)-C(5)	118.14(13)
C(8A)-C(4A)-C(4)	121.83(12)
C(5)-C(4A)-C(4)	120.02(13)
C(6)-C(5)-C(4A)	121.53(14)
C(6)-C(5)-H(5)	119.2
C(4A)-C(5)-H(5)	119.2
C(7)-C(6)-C(5)	117.97(14)
C(7)-C(6)-H(6)	121.0
C(5)-C(6)-H(6)	121.0
C(8)-C(7)-C(6)	122.81(14)
C(8)-C(7)-O(7)	118.96(14)
C(6)-C(7)-O(7)	118.20(14)
O(16)-C(16)-O(7)	122.69(14)
O(16)-C(16)-C(17)	125.17(14)
O(7)-C(16)-C(17)	112.11(12)
C(18)-C(17)-C(22)	120.36(14)
C(18)-C(17)-C(16)	122.32(14)
C(22)-C(17)-C(16)	117.30(13)
C(19)-C(18)-C(17)	119.74(14)
C(19)-C(18)-H(18)	120.1
C(17)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	119.81(14)
C(18)-C(19)-H(19)	120.1
C(20)-C(19)-H(19)	120.1
C(21)-C(20)-C(19)	120.34(14)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
O(13)-C(13)-O(11)	120.14(13)
O(13)-C(13)-C(12)	128.62(13)
O(11)-C(13)-C(12)	111.23(12)
O(10)-C(10)-C(12)	108.89(12)
O(10)-C(10)-C(9)	113.16(12)
C(12)-C(10)-C(9)	118.46(13)

O(10)-C(10)-C(11)	106.11(11)
C(12)-C(10)-C(11)	104.65(11)
C(9)-C(10)-C(11)	104.40(11)
C(13)-C(12)-C(10)	105.02(12)
C(13)-C(12)-H(12A)	110.7
C(10)-C(12)-H(12A)	110.7
C(13)-C(12)-H(12B)	110.7
C(10)-C(12)-H(12B)	110.7
H(12A)-C(12)-H(12B)	108.8
C(10)-C(9)-C(3)	103.94(12)
C(10)-C(9)-H(9A)	111.0
C(3)-C(9)-H(9A)	111.0
C(10)-C(9)-H(9B)	111.0
C(3)-C(9)-H(9B)	111.0
H(9A)-C(9)-H(9B)	109.0
O(3)-C(3)-C(2)	108.01(12)
O(3)-C(3)-C(9)	107.20(12)
C(2)-C(3)-C(9)	113.82(13)
O(3)-C(3)-C(4)	111.49(12)
C(2)-C(3)-C(4)	111.40(12)
C(9)-C(3)-C(4)	104.88(12)
O(1)-C(8A)-C(8)	116.99(13)
O(1)-C(8A)-C(4A)	121.77(13)
C(8)-C(8A)-C(4A)	121.24(14)
O(1)-C(2)-C(3)	112.51(12)
O(1)-C(2)-H(2A)	109.1
C(3)-C(2)-H(2A)	109.1
O(1)-C(2)-H(2B)	109.1
C(3)-C(2)-H(2B)	109.1
H(2A)-C(2)-H(2B)	107.8
C(7)-C(8)-C(8A)	118.30(14)
C(7)-C(8)-H(8)	120.9
C(8A)-C(8)-H(8)	120.9
C(20)-C(21)-C(22)	120.23(15)
C(20)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.9
C(21)-C(22)-C(17)	119.48(14)
C(21)-C(22)-H(22)	120.3
C(17)-C(22)-H(22)	120.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for zhb_yxd_1.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(15)	33(1)	27(1)	25(1)	9(1)	5(1)	4(1)
O(7)	19(1)	33(1)	23(1)	9(1)	10(1)	0(1)
O(13)	21(1)	23(1)	23(1)	0(1)	9(1)	-7(1)
O(11)	18(1)	15(1)	20(1)	-3(1)	9(1)	-3(1)
O(10)	27(1)	23(1)	16(1)	2(1)	7(1)	0(1)
O(1)	27(1)	15(1)	32(1)	-6(1)	15(1)	-4(1)
O(16)	21(1)	39(1)	27(1)	11(1)	9(1)	5(1)
O(3)	20(1)	26(1)	23(1)	-1(1)	9(1)	4(1)
C(15)	23(1)	17(1)	22(1)	3(1)	7(1)	-3(1)
C(14)	19(1)	17(1)	20(1)	2(1)	7(1)	0(1)
C(11)	17(1)	14(1)	17(1)	-1(1)	8(1)	-3(1)
C(4)	17(1)	13(1)	17(1)	-1(1)	8(1)	-1(1)
C(4A)	20(1)	15(1)	17(1)	2(1)	9(1)	0(1)
C(5)	23(1)	16(1)	20(1)	0(1)	10(1)	0(1)
C(6)	24(1)	21(1)	21(1)	2(1)	12(1)	4(1)
C(7)	18(1)	25(1)	21(1)	6(1)	10(1)	0(1)
C(16)	21(1)	18(1)	21(1)	2(1)	9(1)	1(1)
C(17)	20(1)	16(1)	21(1)	1(1)	9(1)	-1(1)
C(18)	22(1)	23(1)	22(1)	4(1)	8(1)	-2(1)
C(19)	20(1)	25(1)	29(1)	4(1)	6(1)	0(1)
C(20)	22(1)	26(1)	29(1)	0(1)	12(1)	-1(1)
C(13)	18(1)	17(1)	19(1)	3(1)	8(1)	0(1)
C(10)	22(1)	17(1)	15(1)	0(1)	8(1)	-1(1)
C(12)	22(1)	20(1)	23(1)	-2(1)	14(1)	-3(1)
C(9)	22(1)	16(1)	19(1)	-3(1)	9(1)	-2(1)
C(3)	19(1)	16(1)	21(1)	-1(1)	10(1)	1(1)
C(8A)	23(1)	15(1)	20(1)	0(1)	10(1)	0(1)
C(2)	26(1)	14(1)	30(1)	0(1)	14(1)	2(1)
C(8)	22(1)	19(1)	24(1)	2(1)	9(1)	-4(1)
C(21)	28(1)	27(1)	21(1)	1(1)	12(1)	0(1)
C(22)	23(1)	23(1)	21(1)	2(1)	7(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for zhb_yxd_1.

	x	y	z	U(eq)
H(3)	9735	2189	9638	33
H(14A)	7729	7204	8369	22
H(14B)	7340	5440	8176	22
H(4)	8937	4101	9922	18
H(5)	7835	5594	10400	23
H(6)	6761	5089	10898	25
H(18)	4638	2553	10289	26
H(19)	3554	2480	10813	29
H(20)	3563	1596	12538	29
H(12A)	9793	4360	7774	24
H(12B)	9477	5753	6895	24
H(9A)	8846	2209	7088	22
H(9B)	8034	2519	7195	22
H(2A)	8646	-123	8544	27
H(2B)	8730	517	9740	27
H(8)	6600	654	9455	26
H(21)	4642	729	13722	29
H(22)	5732	849	13221	26

Table 6. Torsion angles [deg] for zhb_yxd_1.

C(10)-O(10)-C(15)-O(15)	179.27(14)
C(10)-O(10)-C(15)-C(14)	-0.80(17)
O(15)-C(15)-C(14)-C(11)	-170.30(16)
O(10)-C(15)-C(14)-C(11)	9.77(16)
C(13)-O(11)-C(11)-C(14)	-121.79(12)
C(13)-O(11)-C(11)-C(10)	-10.01(14)
C(13)-O(11)-C(11)-C(4)	104.41(13)
C(15)-C(14)-C(11)-O(11)	98.48(13)
C(15)-C(14)-C(11)-C(10)	-13.95(14)
C(15)-C(14)-C(11)-C(4)	-133.48(13)
O(11)-C(11)-C(4)-C(4A)	122.46(12)
C(14)-C(11)-C(4)-C(4A)	-5.23(18)
C(10)-C(11)-C(4)-C(4A)	-123.77(12)
O(11)-C(11)-C(4)-C(3)	-112.99(12)
C(14)-C(11)-C(4)-C(3)	119.32(13)
C(10)-C(11)-C(4)-C(3)	0.79(14)
C(3)-C(4)-C(4A)-C(8A)	-5.07(19)
C(11)-C(4)-C(4A)-C(8A)	115.19(15)
C(3)-C(4)-C(4A)-C(5)	176.14(13)
C(11)-C(4)-C(4A)-C(5)	-63.60(17)
C(8A)-C(4A)-C(5)-C(6)	-1.1(2)
C(4)-C(4A)-C(5)-C(6)	177.72(13)
C(4A)-C(5)-C(6)-C(7)	0.4(2)
C(5)-C(6)-C(7)-C(8)	0.3(2)
C(5)-C(6)-C(7)-O(7)	-177.59(13)
C(16)-O(7)-C(7)-C(8)	93.40(17)
C(16)-O(7)-C(7)-C(6)	-88.64(17)
C(7)-O(7)-C(16)-O(16)	-2.9(2)
C(7)-O(7)-C(16)-C(17)	175.36(13)
O(16)-C(16)-C(17)-C(18)	-178.66(17)
O(7)-C(16)-C(17)-C(18)	3.1(2)
O(16)-C(16)-C(17)-C(22)	3.0(2)
O(7)-C(16)-C(17)-C(22)	-175.15(14)
C(22)-C(17)-C(18)-C(19)	2.1(2)
C(16)-C(17)-C(18)-C(19)	-176.13(14)
C(17)-C(18)-C(19)-C(20)	-1.0(2)
C(18)-C(19)-C(20)-C(21)	-0.9(3)
C(11)-O(11)-C(13)-O(13)	-176.90(13)
C(11)-O(11)-C(13)-C(12)	1.69(16)
C(15)-O(10)-C(10)-C(12)	-120.47(13)
C(15)-O(10)-C(10)-C(9)	105.58(14)
C(15)-O(10)-C(10)-C(11)	-8.31(15)
O(11)-C(11)-C(10)-O(10)	-101.08(12)
C(14)-C(11)-C(10)-O(10)	13.80(14)
C(4)-C(11)-C(10)-O(10)	142.28(11)
O(11)-C(11)-C(10)-C(12)	13.99(14)
C(14)-C(11)-C(10)-C(12)	128.87(12)
C(4)-C(11)-C(10)-C(12)	-102.65(13)
O(11)-C(11)-C(10)-C(9)	139.13(11)
C(14)-C(11)-C(10)-C(9)	-105.98(13)
C(4)-C(11)-C(10)-C(9)	22.50(14)
O(13)-C(13)-C(12)-C(10)	-174.01(15)
O(11)-C(13)-C(12)-C(10)	7.56(16)
O(10)-C(10)-C(12)-C(13)	100.22(13)
C(9)-C(10)-C(12)-C(13)	-128.62(14)

C(11)-C(10)-C(12)-C(13)	-12.90(15)
O(10)-C(10)-C(9)-C(3)	-152.30(11)
C(12)-C(10)-C(9)-C(3)	78.48(15)
C(11)-C(10)-C(9)-C(3)	-37.38(14)
C(10)-C(9)-C(3)-O(3)	-80.42(13)
C(10)-C(9)-C(3)-C(2)	160.20(12)
C(10)-C(9)-C(3)-C(4)	38.20(14)
C(4A)-C(4)-C(3)-O(3)	-142.38(12)
C(11)-C(4)-C(3)-O(3)	92.00(13)
C(4A)-C(4)-C(3)-C(2)	-21.64(17)
C(11)-C(4)-C(3)-C(2)	-147.26(12)
C(4A)-C(4)-C(3)-C(9)	101.93(13)
C(11)-C(4)-C(3)-C(9)	-23.69(14)
C(2)-O(1)-C(8A)-C(8)	-150.22(14)
C(2)-O(1)-C(8A)-C(4A)	30.27(19)
C(5)-C(4A)-C(8A)-O(1)	-179.30(13)
C(4)-C(4A)-C(8A)-O(1)	1.9(2)
C(5)-C(4A)-C(8A)-C(8)	1.2(2)
C(4)-C(4A)-C(8A)-C(8)	-177.61(13)
C(8A)-O(1)-C(2)-C(3)	-58.59(17)
O(3)-C(3)-C(2)-O(1)	176.51(12)
C(9)-C(3)-C(2)-O(1)	-64.58(17)
C(4)-C(3)-C(2)-O(1)	53.75(17)
C(6)-C(7)-C(8)-C(8A)	-0.2(2)
O(7)-C(7)-C(8)-C(8A)	177.66(13)
O(1)-C(8A)-C(8)-C(7)	179.92(14)
C(4A)-C(8A)-C(8)-C(7)	-0.6(2)
C(19)-C(20)-C(21)-C(22)	1.6(3)
C(20)-C(21)-C(22)-C(17)	-0.5(2)
C(18)-C(17)-C(22)-C(21)	-1.4(2)
C(16)-C(17)-C(22)-C(21)	176.94(14)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for zhb_yxd_1 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(13)#1	0.84	2.03	2.8460(17)	163.4

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,-y+1,-z+2

(+)-Brazilide A (3) crystal structure analysis

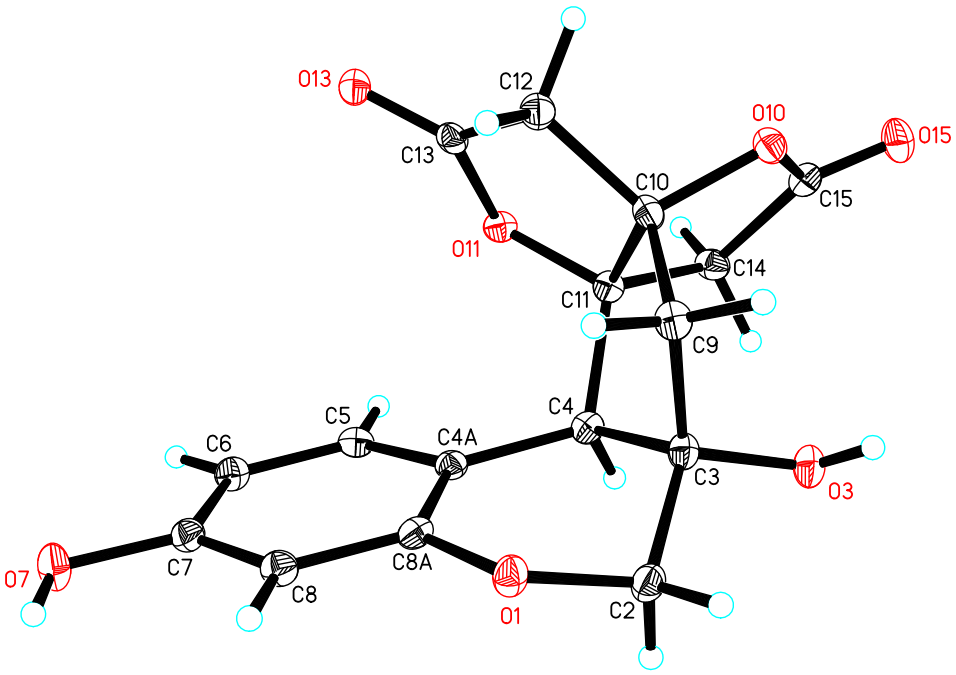

Figure 1 Absolute configuration of (+)-Brazilide A (3) (zhb_w_1)

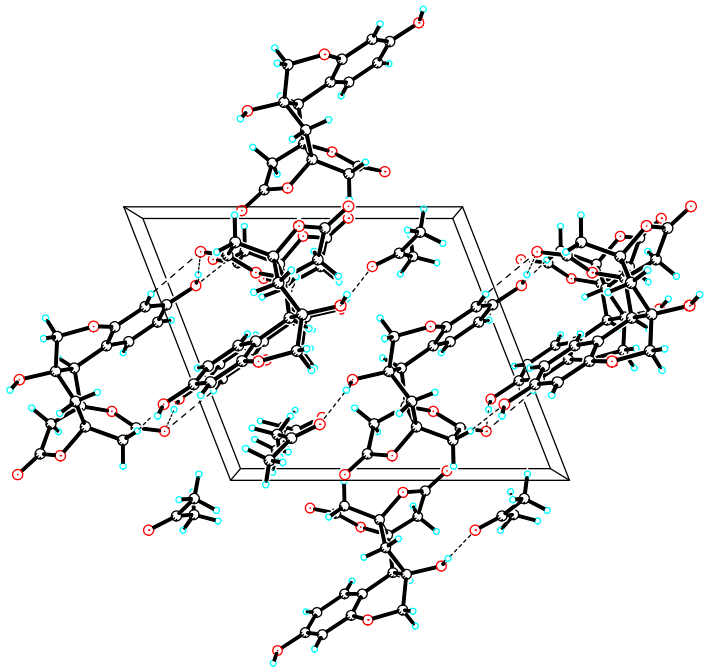

Table 1. Crystal data and structure refinement for zhb_w_1.

Identification code	cu_zhb_w_1_0m
Empirical formula	C19 H20 O8
Formula weight	376.35
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 10.9939(2) A alpha = 90 deg. b = 6.73910(10) A beta = 111.3280(10) deg. c = 12.6864(3) A gamma = 90 deg.
Volume	875.55(3) A^3
Z, Calculated density	2, 1.428 Mg/m^3
Absorption coefficient	0.949 mm^-1
F(000)	396
Crystal size	0.64 x 0.32 x 0.08 mm
Theta range for data collection	3.74 to 68.19 deg.
Limiting indices	-12<=h<=12, -7<=k<=6, -15<=l<=14
Reflections collected / unique	7274 / 2361 [R(int) = 0.0330]
Completeness to theta = 68.19	92.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9280 and 0.5819
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2361 / 1 / 248
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0278, wR2 = 0.0718
R indices (all data)	R1 = 0.0279, wR2 = 0.0719
Absolute structure parameter	0.36(14)
Largest diff. peak and hole	0.153 and -0.225 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for zhb_w_1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(7)	2793(1)	619(2)	-1066(1)	29(1)
O(15)	9962(1)	1142(2)	6618(1)	30(1)
O(3)	6345(1)	3139(2)	5247(1)	25(1)
O(1)	4370(1)	4420(2)	2308(1)	24(1)
O(11)	7614(1)	-811(2)	3127(1)	21(1)
O(13)	8380(1)	-738(2)	1727(1)	24(1)
O(10)	9188(1)	2664(2)	4949(1)	22(1)
O(8)	2077(1)	1003(2)	3292(1)	35(1)
C(7)	3524(2)	793(3)	57(1)	21(1)
C(6)	4170(2)	-898(3)	621(1)	22(1)
C(5)	4927(2)	-789(3)	1757(1)	20(1)
C(4A)	5081(2)	989(3)	2373(1)	18(1)
C(4)	5931(2)	1087(3)	3622(1)	19(1)
C(11)	7388(2)	538(3)	3923(1)	20(1)
C(14)	8077(2)	-243(3)	5119(1)	23(1)
C(15)	9175(2)	1188(3)	5678(1)	22(1)
C(10)	8112(2)	2497(3)	3868(1)	20(1)
C(9)	7135(2)	4153(3)	3737(1)	22(1)
C(3)	6032(2)	3240(3)	4052(1)	20(1)
C(2)	4742(2)	4315(3)	3512(1)	23(1)
C(8A)	4376(2)	2624(3)	1796(1)	20(1)
C(8)	3621(2)	2554(3)	647(1)	22(1)
C(12)	8630(2)	2166(3)	2924(1)	23(1)
C(13)	8218(2)	101(3)	2509(1)	20(1)
C(17)	817(2)	2130(4)	1451(2)	42(1)
C(18)	1561(2)	602(3)	2295(2)	29(1)
C(19)	1629(2)	-1443(4)	1862(2)	37(1)

Table 3. Bond lengths [A] and angles [deg] for zhb_w_1.

O(7)-C(7)	1.3627(19)
O(7)-H(7)	0.8400
O(15)-C(15)	1.192(2)
O(3)-C(3)	1.4284(19)
O(3)-H(3)	0.8400
O(1)-C(8A)	1.375(2)
O(1)-C(2)	1.4323(18)
O(11)-C(13)	1.347(2)
O(11)-C(11)	1.446(2)
O(13)-C(13)	1.209(2)
O(10)-C(15)	1.362(2)
O(10)-C(10)	1.4535(19)
O(8)-C(18)	1.214(2)
C(7)-C(8)	1.386(3)
C(7)-C(6)	1.395(3)
C(6)-C(5)	1.379(2)
C(6)-H(6)	0.9500
C(5)-C(4A)	1.407(3)
C(5)-H(5)	0.9500
C(4A)-C(8A)	1.392(2)
C(4A)-C(4)	1.521(2)
C(4)-C(3)	1.539(3)
C(4)-C(11)	1.550(2)
C(4)-H(4)	1.0000
C(11)-C(14)	1.522(2)
C(11)-C(10)	1.556(2)
C(14)-C(15)	1.505(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(10)-C(9)	1.516(3)
C(10)-C(12)	1.519(2)
C(9)-C(3)	1.536(2)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(3)-C(2)	1.517(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(8A)-C(8)	1.391(2)
C(8)-H(8)	0.9500
C(12)-C(13)	1.498(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(17)-C(18)	1.496(3)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.495(3)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

C(7)-O(7)-H(7)	109.5
C(3)-O(3)-H(3)	109.5
C(8A)-O(1)-C(2)	114.32(13)
C(13)-O(11)-C(11)	111.49(14)

C(15)-O(10)-C(10)	112.16(12)
O(7)-C(7)-C(8)	122.60(16)
O(7)-C(7)-C(6)	117.55(15)
C(8)-C(7)-C(6)	119.85(14)
C(5)-C(6)-C(7)	119.56(16)
C(5)-C(6)-H(6)	120.2
C(7)-C(6)-H(6)	120.2
C(6)-C(5)-C(4A)	122.05(16)
C(6)-C(5)-H(5)	119.0
C(4A)-C(5)-H(5)	119.0
C(8A)-C(4A)-C(5)	116.77(14)
C(8A)-C(4A)-C(4)	121.83(15)
C(5)-C(4A)-C(4)	121.34(14)
C(4A)-C(4)-C(3)	110.38(13)
C(4A)-C(4)-C(11)	115.73(13)
C(3)-C(4)-C(11)	101.70(13)
C(4A)-C(4)-H(4)	109.6
C(3)-C(4)-H(4)	109.6
C(11)-C(4)-H(4)	109.6
O(11)-C(11)-C(14)	109.25(14)
O(11)-C(11)-C(4)	113.76(12)
C(14)-C(11)-C(4)	115.01(13)
O(11)-C(11)-C(10)	106.36(12)
C(14)-C(11)-C(10)	105.11(13)
C(4)-C(11)-C(10)	106.59(14)
C(15)-C(14)-C(11)	105.73(14)
C(15)-C(14)-H(14A)	110.6
C(11)-C(14)-H(14A)	110.6
C(15)-C(14)-H(14B)	110.6
C(11)-C(14)-H(14B)	110.6
H(14A)-C(14)-H(14B)	108.7
O(15)-C(15)-O(10)	120.94(15)
O(15)-C(15)-C(14)	128.38(16)
O(10)-C(15)-C(14)	110.68(13)
O(10)-C(10)-C(9)	110.37(13)
O(10)-C(10)-C(12)	110.18(13)
C(9)-C(10)-C(12)	118.41(14)
O(10)-C(10)-C(11)	106.13(13)
C(9)-C(10)-C(11)	106.04(13)
C(12)-C(10)-C(11)	104.79(14)
C(10)-C(9)-C(3)	105.72(15)
C(10)-C(9)-H(9A)	110.6
C(3)-C(9)-H(9A)	110.6
C(10)-C(9)-H(9B)	110.6
C(3)-C(9)-H(9B)	110.6
H(9A)-C(9)-H(9B)	108.7
O(3)-C(3)-C(2)	109.07(13)
O(3)-C(3)-C(9)	112.78(13)
C(2)-C(3)-C(9)	112.81(15)
O(3)-C(3)-C(4)	106.85(13)
C(2)-C(3)-C(4)	110.76(14)
C(9)-C(3)-C(4)	104.33(14)
O(1)-C(2)-C(3)	111.28(13)
O(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2A)	109.4
O(1)-C(2)-H(2B)	109.4
C(3)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
O(1)-C(8A)-C(8)	114.91(15)

O(1)-C(8A)-C(4A)	123.07(14)
C(8)-C(8A)-C(4A)	122.02(16)
C(7)-C(8)-C(8A)	119.63(16)
C(7)-C(8)-H(8)	120.2
C(8A)-C(8)-H(8)	120.2
C(13)-C(12)-C(10)	105.15(14)
C(13)-C(12)-H(12A)	110.7
C(10)-C(12)-H(12A)	110.7
C(13)-C(12)-H(12B)	110.7
C(10)-C(12)-H(12B)	110.7
H(12A)-C(12)-H(12B)	108.8
O(13)-C(13)-O(11)	120.96(17)
O(13)-C(13)-C(12)	127.35(16)
O(11)-C(13)-C(12)	111.68(13)
C(18)-C(17)-H(17A)	109.5
C(18)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(18)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(8)-C(18)-C(19)	121.38(18)
O(8)-C(18)-C(17)	121.3(2)
C(19)-C(18)-C(17)	117.37(17)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for zhb_w_1.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(7)	36(1)	25(1)	19(1)	-2(1)	4(1)	3(1)
O(15)	33(1)	28(1)	21(1)	0(1)	1(1)	2(1)
O(3)	32(1)	24(1)	18(1)	-2(1)	9(1)	-5(1)
O(1)	28(1)	20(1)	21(1)	-2(1)	7(1)	5(1)
O(11)	21(1)	18(1)	25(1)	0(1)	10(1)	-1(1)
O(13)	25(1)	28(1)	20(1)	-3(1)	7(1)	0(1)
O(10)	22(1)	23(1)	20(1)	0(1)	6(1)	-4(1)
O(8)	42(1)	35(1)	26(1)	0(1)	10(1)	5(1)
C(7)	21(1)	24(1)	21(1)	-1(1)	9(1)	-1(1)
C(6)	24(1)	18(1)	26(1)	-4(1)	10(1)	-2(1)
C(5)	19(1)	18(1)	26(1)	2(1)	9(1)	0(1)
C(4A)	17(1)	20(1)	20(1)	1(1)	9(1)	-2(1)
C(4)	22(1)	17(1)	20(1)	2(1)	10(1)	-2(1)
C(11)	21(1)	18(1)	20(1)	0(1)	8(1)	0(1)
C(14)	20(1)	25(1)	23(1)	5(1)	7(1)	0(1)
C(15)	24(1)	22(1)	22(1)	0(1)	10(1)	2(1)
C(10)	20(1)	22(1)	17(1)	1(1)	4(1)	-4(1)
C(9)	26(1)	19(1)	22(1)	2(1)	8(1)	-2(1)
C(3)	23(1)	21(1)	17(1)	0(1)	7(1)	-1(1)
C(2)	26(1)	23(1)	22(1)	-3(1)	10(1)	1(1)
C(8A)	21(1)	18(1)	23(1)	-2(1)	12(1)	-1(1)
C(8)	22(1)	21(1)	23(1)	2(1)	9(1)	2(1)
C(12)	24(1)	24(1)	22(1)	0(1)	9(1)	-3(1)
C(13)	16(1)	23(1)	18(1)	3(1)	3(1)	2(1)
C(17)	34(1)	61(2)	33(1)	16(1)	14(1)	1(1)
C(18)	26(1)	38(1)	28(1)	2(1)	14(1)	-1(1)
C(19)	35(1)	47(1)	32(1)	-9(1)	15(1)	-5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for zhb_w_1.

	x	y	z	U(eq)
H(7)	2399	1691	-1304	43
H(3)	6719	4193	5549	38
H(6)	4088	-2118	225	27
H(5)	5358	-1951	2135	25
H(4)	5545	232	4065	23
H(14A)	7467	-289	5532	27
H(14B)	8421	-1595	5102	27
H(9A)	6792	4646	2948	27
H(9B)	7547	5273	4247	27
H(2A)	4056	3610	3698	28
H(2B)	4818	5674	3825	28
H(8)	3175	3706	269	27
H(12A)	8251	3143	2308	28
H(12B)	9593	2289	3212	28
H(17A)	793	3373	1845	63
H(17B)	-77	1661	1050	63
H(17C)	1247	2359	908	63
H(19A)	776	-2088	1661	56
H(19B)	2287	-2218	2451	56
H(19C)	1870	-1363	1192	56

Table 6. Torsion angles [deg] for zhb_w_1.

O(7)-C(7)-C(6)-C(5)	179.58(14)
C(8)-C(7)-C(6)-C(5)	-1.6(2)
C(7)-C(6)-C(5)-C(4A)	-0.4(2)
C(6)-C(5)-C(4A)-C(8A)	3.2(2)
C(6)-C(5)-C(4A)-C(4)	-179.41(14)
C(8A)-C(4A)-C(4)-C(3)	-8.3(2)
C(5)-C(4A)-C(4)-C(3)	174.53(14)
C(8A)-C(4A)-C(4)-C(11)	-123.04(16)
C(5)-C(4A)-C(4)-C(11)	59.7(2)
C(13)-O(11)-C(11)-C(14)	-120.47(14)
C(13)-O(11)-C(11)-C(4)	109.51(15)
C(13)-O(11)-C(11)-C(10)	-7.50(16)
C(4A)-C(4)-C(11)-O(11)	-27.1(2)
C(3)-C(4)-C(11)-O(11)	-146.74(13)
C(4A)-C(4)-C(11)-C(14)	-154.18(15)
C(3)-C(4)-C(11)-C(14)	86.19(17)
C(4A)-C(4)-C(11)-C(10)	89.77(16)
C(3)-C(4)-C(11)-C(10)	-29.86(14)
O(11)-C(11)-C(14)-C(15)	111.29(15)
C(4)-C(11)-C(14)-C(15)	-119.38(15)
C(10)-C(11)-C(14)-C(15)	-2.49(17)
C(10)-O(10)-C(15)-O(15)	-177.25(15)
C(10)-O(10)-C(15)-C(14)	2.82(18)
C(11)-C(14)-C(15)-O(15)	-179.95(17)
C(11)-C(14)-C(15)-O(10)	-0.02(18)
C(15)-O(10)-C(10)-C(9)	110.13(15)
C(15)-O(10)-C(10)-C(12)	-117.25(15)
C(15)-O(10)-C(10)-C(11)	-4.33(17)
O(11)-C(11)-C(10)-O(10)	-111.75(13)
C(14)-C(11)-C(10)-O(10)	4.05(17)
C(4)-C(11)-C(10)-O(10)	126.55(13)
O(11)-C(11)-C(10)-C(9)	130.85(13)
C(14)-C(11)-C(10)-C(9)	-113.35(14)
C(4)-C(11)-C(10)-C(9)	9.15(15)
O(11)-C(11)-C(10)-C(12)	4.85(16)
C(14)-C(11)-C(10)-C(12)	120.64(14)
C(4)-C(11)-C(10)-C(12)	-116.85(14)
O(10)-C(10)-C(9)-C(3)	-98.92(14)
C(12)-C(10)-C(9)-C(3)	132.82(15)
C(11)-C(10)-C(9)-C(3)	15.60(15)
C(10)-C(9)-C(3)-O(3)	80.68(17)
C(10)-C(9)-C(3)-C(2)	-155.19(13)
C(10)-C(9)-C(3)-C(4)	-34.90(15)
C(4A)-C(4)-C(3)-O(3)	156.44(12)
C(11)-C(4)-C(3)-O(3)	-80.21(14)
C(4A)-C(4)-C(3)-C(2)	37.76(17)
C(11)-C(4)-C(3)-C(2)	161.11(13)
C(4A)-C(4)-C(3)-C(9)	-83.89(15)
C(11)-C(4)-C(3)-C(9)	39.46(14)
C(8A)-O(1)-C(2)-C(3)	52.17(18)
O(3)-C(3)-C(2)-O(1)	-178.82(13)
C(9)-C(3)-C(2)-O(1)	55.0(2)
C(4)-C(3)-C(2)-O(1)	-61.50(18)
C(2)-O(1)-C(8A)-C(8)	159.11(13)
C(2)-O(1)-C(8A)-C(4A)	-21.0(2)

C(5)-C(4A)-C(8A)-O(1)	175.92(13)
C(4)-C(4A)-C(8A)-O(1)	-1.4(2)
C(5)-C(4A)-C(8A)-C(8)	-4.1(2)
C(4)-C(4A)-C(8A)-C(8)	178.53(14)
O(7)-C(7)-C(8)-C(8A)	179.50(14)
C(6)-C(7)-C(8)-C(8A)	0.8(2)
O(1)-C(8A)-C(8)-C(7)	-177.83(14)
C(4A)-C(8A)-C(8)-C(7)	2.2(2)
O(10)-C(10)-C(12)-C(13)	112.83(15)
C(9)-C(10)-C(12)-C(13)	-118.83(16)
C(11)-C(10)-C(12)-C(13)	-0.95(16)
C(11)-O(11)-C(13)-O(13)	-173.07(14)
C(11)-O(11)-C(13)-C(12)	7.19(17)
C(10)-C(12)-C(13)-O(13)	176.61(15)
C(10)-C(12)-C(13)-O(11)	-3.67(17)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for zhb_w_1 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(8)#1	0.84	2.00	2.7983(18)	159.4
O(7)-H(7)...O(13)#2	0.84	1.92	2.7580(19)	174.6

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1 #2 -x+1,y+1/2,-z