Supporting Information

Total Synthesis of Bisabosqual A

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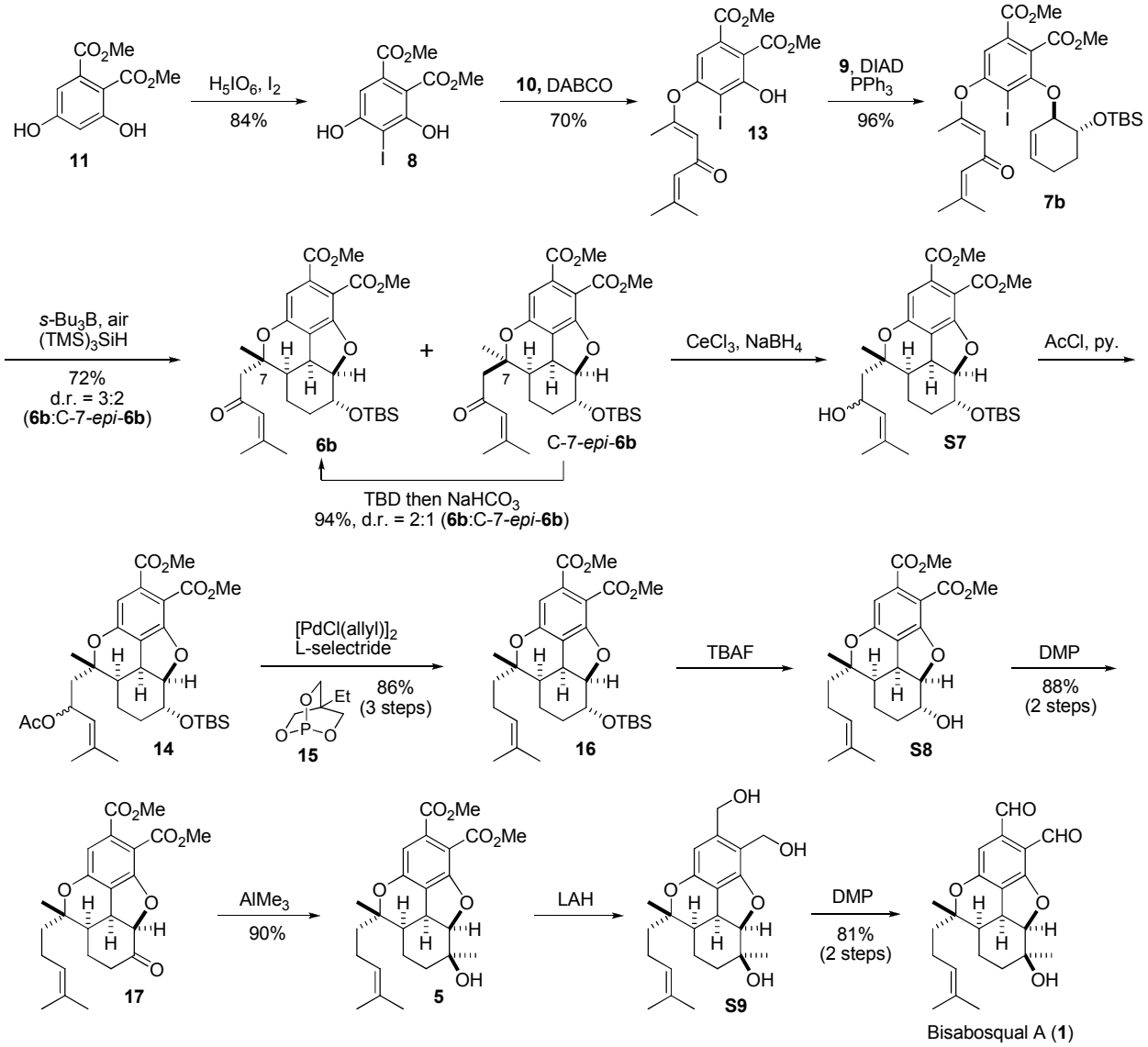
Contents:

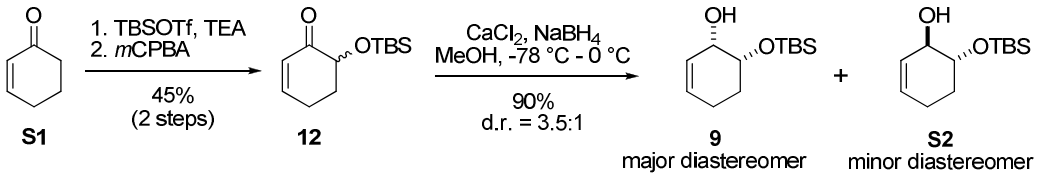
General Methods

Unless otherwise stated, all air and moisture-sensitive reactions were performed in oven-dried glassware under nitrogen. Unless otherwise stated, all commercially available chemicals, reagents and solvents were used as received. Reactions were monitored by thin layer chromatography (TLC) performed on Analtech, Inc. silica gel GF 250 µm plates and were visualized with ultraviolet (UV) light (254 nm) and/or $KMnO_4$ staining or by UPLC-MS (Waters Acquity, ESCI (ESI +/-, APCI +/-)). Gas chromatography – mass spectrometry (GC-MS) was performed with an Agilent 5890 GC Oven and an Agilent 5973 Mass Selective Detector. Silica gel flash chromatography was performed with RediSep®Rf normal phase silica flash columns on a CombiFlash Rf system from Teledyne Isco, Inc. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian-Inova 400 (400 MHz and 101 MHz, respectively), a Bruker 400 (400 MHz and 101 MHz, respectively), or a Bruker 500 (500 MHz and 126 MHz, respectively) spectrometer. Chemical shifts are reported in ppm relative to $CHCl_3$ (^{1}H, δ = 7.26 and ^{13}C NMR δ = 77.0). The peak shapes are denoted as follows: s, singlet; d, doublet; t, triplet; q, quartet; spt, septet; m, multiplet; br s, broad singlet. Infrared (IR) spectra were recorded with a Thermo-Nicolet Avatar 360 FT-IR. High-resolution mass spectra (HRMS) were acquired on an Agilent model 6220 MS(TOF).

Scheme S1

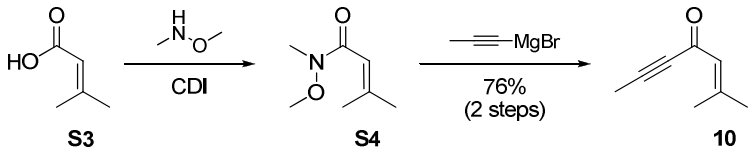

11
H5IO6, I2
84%
8
10, DABCO
70%
13
9, DIAD
PPh3
96%
7b
s-Bu3B, air
(TMS)3SiH
72%
d.r. = 3:2
(6b:C-7-epi-6b)
6b
C-7-epi-6b
CeCl3, NaBH4
S7
AcCl, py.
TBD then NaHCO3
94%, d.r. = 2:1 (6b:C-7-epi-6b)
14
[PdCl(allyl)]2
L-selectride
86%
(3 steps)
15
16
TBAF
S8
DMP
88%
(2 steps)
17
AlMe3
90%
5
LAH
S9
DMP
81%
(2 steps)
Bisabosqual A (1)

Scheme S2



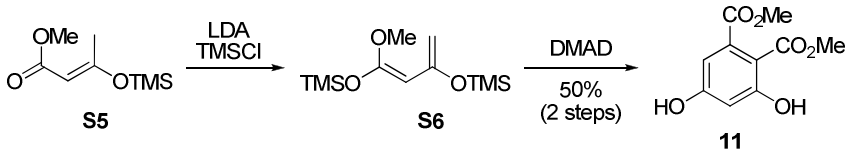
S1 **12** **9** major diastereomer **S2** minor diastereomer

Scheme S3



S3 **S4** **10**

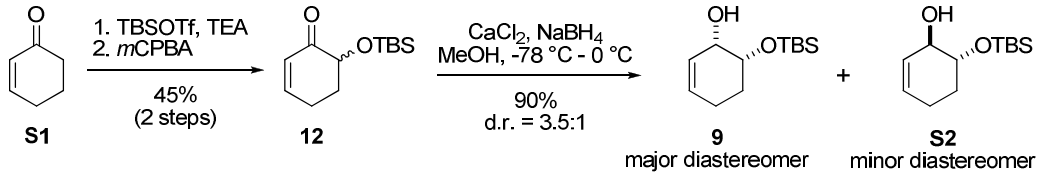
Scheme S4



S5 **S6** **11**

Experimental Procedures and Characterization

Compound **9**



To a stirred solution of **12** (6.00 g, 26.5 mmol) in MeOH (150 mL) was added $CaCl_2$ (4.40 g, 39.8 mmol, 1.5 equiv.). The mixture was cooled to -78 °C and $NaBH_4$ (1.20 g, 31.8 mmol, 1.2 equiv.) was added in portions over a period of 20 minutes. The mixture was stirred at -78 °C for 6 hours and then the mixture was allowed to slowly warm to 0 °C and stirred for 1 hour. Saturated aqueous $NaHCO_3$ was added and the resulting mixture was extracted with CH_2Cl_2 (4x). The combined organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The ^1H NMR spectrum of the crude product indicated a 3.5:1 mixture of diastereomers favoring **9.** The mixture was purified via silica gel flash chromatography (EtOAc/Heptane) to afford **9** (4.11 g, 68% yield) as a colorless oil and **S2** (1.34 g, 22% yield) as a colorless oil.

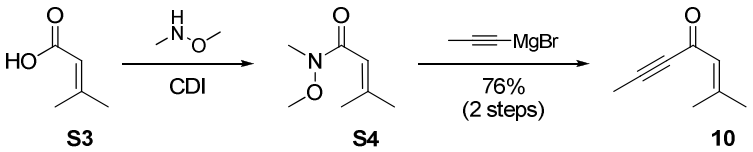
9: ^1H NMR (400MHz, $CDCl_3$) δ 5.88 - 5.81 (m, 1H), 5.75 - 5.69 (m, 1H), 4.05 - 3.97 (m, 1H), 3.89 - 3.82 (m, 1H), 2.54 (br s, 1H), 2.25 - 2.13 (m, 1H), 2.06 - 1.94 (m, 1H), 1.89 - 1.77 (m, 1H), 1.64 - 1.53 (m, 1H), 0.91 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (101MHz, $CDCl_3$): δ 130.8, 127.0, 70.3, 66.5, 26.1, 25.8, 23.8, 18.1, -4.5, -4.9 ppm. FTIR (cm^{-1}) = 3559, 3029, 2952, 2929, 2886, 2857, 1463, 1252, 1094. HRMS (ESI) calculated for $C_{12}H_{24}O_2SiNa$ $[M+Na]^+$ 251.1438, found 251.1444.

S2: ^1H NMR (400MHz, $CDCl_3$) δ 5.74 - 5.66 (m, 1H), 5.62 - 5.56 (m, 1H), 4.07 - 3.99 (m, 1H), 3.64 (ddd, *J*=3.5, 7.0, 10.8 Hz, 1H), 2.17 - 2.08 (m, 2H), 2.06 (d, *J*=3.7 Hz, 1H), 1.86 - 1.77 (m, 1H), 1.69 - 1.57 (m, 1H), 0.90 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (101MHz, $CDCl_3$) δ 128.8, 127.8, 74.2, 73.1, 29.1, 25.8, 24.6, 18.1, -4.3, -4.6 ppm. FTIR (cm^{-1}) = 3364, 3028, 2929, 2890, 2856, 1463. HRMS (ESI) calculated for $C_{12}H_{24}O_2SiNa$ $[M+Na]^+$ 251.1438, found 251.1443.

12[1]: ^1H NMR (400MHz, $CDCl_3$) δ 6.91 - 6.85 (m, 1H), 6.01 - 5.94 (m, 1H), 4.16 (dd, *J*=4.9, 11.3 Hz, 1H), 2.57 - 2.35 (m, 2H), 2.20 - 2.11 (m, 1H), 2.11 - 1.97 (m, 1H), 0.90 (s, 9H), 0.15 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (101MHz, $CDCl_3$) δ 198.6, 149.4, 128.4, 74.1, 32.4, 25.7, 25.2, 18.4, -4.5, -5.4 ppm.

[1] Synthesis of compound **12** was previously described. Draghici, C.; Brewer, M. *J. Am. Chem. Soc.* **2008**, *130*, 3766.

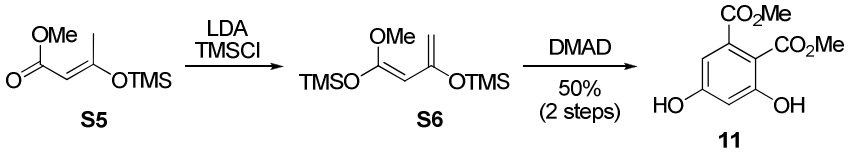
Compound **10**[2]



10: ^{1}H NMR (500MHz, $CDCl_3$) δ 6.13 (spt, *J*=1.3 Hz, 1H), 2.20 (d, *J*=1.5 Hz, 3H), 2.01 (s, 3H), 1.92 (d, *J*=1.2 Hz, 3H). ^{13}C NMR (101MHz, $CDCl_3$) δ 176.8, 157.5, 126.0, 88.3, 82.5, 27.8, 21.0, 4.1 ppm. FTIR (cm^{-1}) = 2978, 2213, 1650, 1607, 1440, 1378. HRMS (ESI) calculated for $C_8H_{11}O$ $[M+H]^+$ 123.0804, found 123.0807

S4: ^{1}H NMR (400MHz, $CDCl_3$) δ 6.02 (br. s., 1H), 3.58 (s, 3H), 3.10 (s, 3H), 2.04 (d, *J*=1.4 Hz, 2H), 1.81 (d, *J*=1.4 Hz, 2H), ^{13}C NMR (101MHz, $CDCl_3$) δ 167.8, 152.8, 114.1, 61.1, 35.9, 27.3, 19.9 ppm. FTIR (cm^{-1}) = 2972, 2937, 1652, 1445, 1366. HRMS (ESI) calculated for $C_7H_{14}NO_2$ $[M+H]^+$ 144.1019, found 144.1023.

Compound **11**[3]



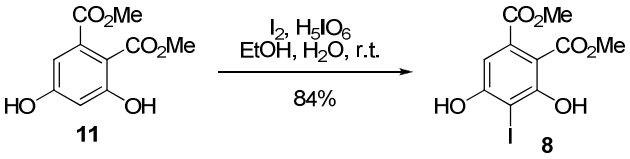
11: ^{1}H NMR (500MHz, $CDCl_3$) δ 10.97 (s, 1H), 7.25 (s, 1H), 6.46 (d, *J*=2.4 Hz, 1H), 6.41 (d, *J*=2.4 Hz, 1H), 3.89 (s, 3H), 3.87 ppm (s, 3H). ^{13}C NMR (101MHz, $CDCl_3$) δ 170.3, 169.0, 163.6, 161.4, 137.1, 108.1, 104.9, 102.7, 53.0, 52.7 ppm. FTIR (cm^{-1}) = 3349, 2955, 1709, 1668, 1618, 1590, 1463. HRMS (ESI) calculated for $C_{10}H_{11}O_6$ $[M+H]^+$ 227.0550, found 227.0555.

S6: ^{1}H NMR (400MHz, $CDCl_3$) δ 4.47 (s, 1H), 4.14 (d, *J*=1.4 Hz, 1H), 3.94 (d, *J*=1.4 Hz, 1H), 3.55 (s, 3H), 0.24 (s, 9H), 0.21 (s, 9H). ^{13}C NMR (101MHz, $CDCl_3$) δ 158.7, 153.5, 89.4, 77.8, 55.1, 0.6, 0.4 ppm

[2] Synthesis of compound **10** was previously described. Jacobi, P. A.; Armacost, L. M.; Brielmann, H. L.; Cann, R. O.; Kravitz, J. I.; Martinelli, M. J. *J Org. Chem.* **1994**, *59*, 5292.

[3] Synthesis of compound **11** was previously described. Yamamoto, K.; Suzuki, S.; Tsuji, J. *Chemistry Letters.* **1978**, 649.

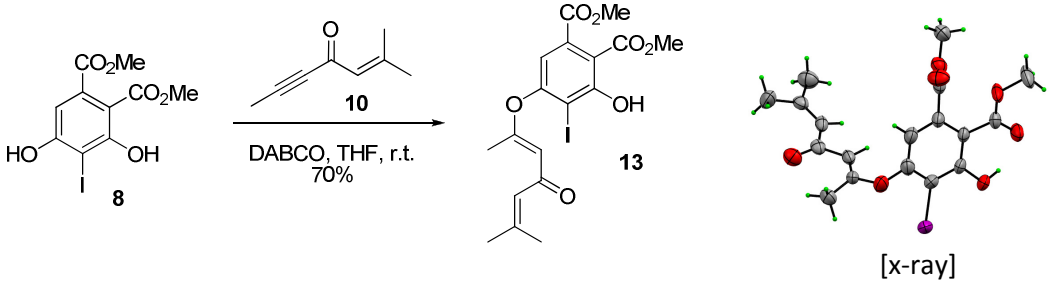
Compound **8**



To a stirred solution of **11** (5.2 g, 0.023 mol) in EtOH (150 mL) was added I_2 (3.5 g, 0.0138 mol, 0.6 equiv.) in one portion followed by H_5IO_6 (1.05 g, 4.6 mmol, 0.2 equiv.) as a solution in water (4 mL). The reaction mixture was stirred at room temperature for 6 hours and then it was concentrated under reduced pressure. EtOAc was added and the resulting mixture was washed with 10% aqueous $Na_2S_2O_3$ and brine. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/Heptane) to afford **8** (6.8 g, 84% yield) as a white solid.

8: ^{1}H NMR (400MHz, $CDCl_3$) δ 12.00 (s, 1H), 6.63 (s, 1H), 6.19 (s, 1H), 3.91 (s, 3H), 3.88 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 168.8, 162.1, 160.4, 137.3, 106.7, 102.7, 78.3, 53.1, 52.9. FTIR (cm^{-1}) = 3219, 1691, 1665, 1595, 1438, 1409, 1331, 1251 cm^{-1}. HRMS (ESI) calculated for $C_{10}H_{10}IO_6$ $[M+H]^+$ 352.9515, found 352.9517.

Compound **13**

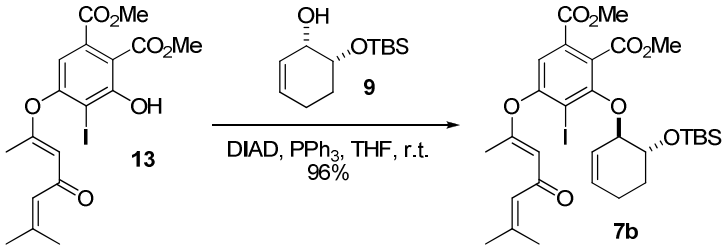


[x-ray]

To a stirred solution of **8** (8.00 g, 22.7 mmol) and **10** (4.2 g, 34 mmol, 1.5 equiv.) in THF (150 mL) was added DABCO (0.51g, 4.5 mmol, 0.2 equiv.) in one portion at room temperature. The mixture was stirred at room temperature for 80 hours and then CH_2Cl_2 was added followed by water. The aqueous layer was carefully adjusted to pH 3 with a 1N aqueous solution of $KHSO_4$ and extracted with CH_2Cl_2 (2x). The organic layer was dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by silica gel chromatography (EtOAc/Heptane) to afford **13** (7.52 g, 70% yield, 84% yield based on recovered starting material) of a white solid.

13: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 11.70 (s, 1 H), 6.70 (s, 1 H), 5.83-5.80 (m, 1 H), 5.30 (s, 1 H), 3.95 (s, 3 H), 3.89 (s, 3 H), 2.52 (s, 3 H), 2.14 (d, *J*=1.2 Hz, 3 H), 1.83 (d, , *J*=1.2 Hz, 3 H). ^{13}C NMR (101MHz, $CDCl_3$) δ 189.5, 168.6, 168.5, 167.9, 162.4, 158.8, 154.9, 136.9, 126.3, 112.8, 108.4, 107.1, 84.5, 53.4, 52.9, 27.7, 20.6, 18.4 ppm. FTIR (cm^{-1}) = 2953, 1737, 1675, 1621, 1584, 1438, 1390, 1323, 1252, 1191, 1161, 1100, 1056. HRMS (ESI) calculated for $C_{18}H_{20}IO_7$ $[M+H]^+$ 475.0248, found 475.0238.

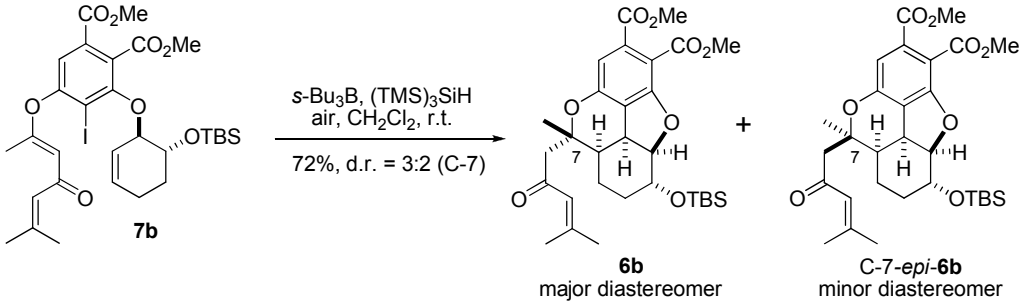
Compound **7b**



To a stirred solution of **13** (1.66 g, 3.50 mmol), **9** (0.96 g, 4.2 mmol, 1.2 equiv.) and PPh_3 (1.38 g, 5.25 mmol, 1.5 equiv.) in THF (35 mL) at room temperature was added DIAD (1.06 g, 5.25 mmol, 1.5 equiv.) dropwise over a period of 10 minutes. After stirring an additional 6h, the reaction mixture was quenched by the addition of water and the resulting mixture was extracted with EtOAc. The combined organic solution was dried with anhydrous $MgSO_4$ and then concentrated under reduced pressure. The crude residue was purified by silica gel flash chromatography (EtOAc/Heptane) to afford **7b** (2.30 g, 96% yield) as a colorless gum.

7b: ^{1}H NMR (400MHz, $CDCl_3$) δ 7.41 (s, 1H), 5.98 (dt, *J*=3.5, 10.0 Hz, 1H), 5.84 - 5.78 (m, 1H), 5.64 - 5.55 (m, 1H), 5.15 (s, 1H), 4.72 - 4.65 (m, 1H), 4.23 (dt, *J*=2.9, 6.2 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 2.55 (s, 3H), 2.30 - 2.16 (m, 1H), 2.13 (d, *J*=0.8 Hz, 3H), 2.11 - 2.02 (m, 1H), 2.01 - 1.92 (m, 1H), 1.82 (d, *J*=1.0 Hz, 3H), 1.77 - 1.67 (m, 1H), 0.84 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (101MHz, $CDCl_3$) δ 189.6, 169.6, 166.2, 164.6, 157.0, 155.3, 154.6, 133.8, 130.3, 127.7, 126.4, 122.2, 118.7, 107.0, 96.7, 81.4, 68.7, 52.9, 52.9, 27.6, 26.6, 25.7, 21.7, 20.6, 18.5, 18.1, -4.7, -4.8 ppm. FTIR (cm^{-1}) = 2951, 2855, 1732, 1620, 1572, 1382, 1278, 1250, 1096. HRMS (ESI) calculated for $C_{30}H_{41}IO_8SiNa$ $[M+Na]^+$ 707.1507, found 707.1492.

Compound **6b**

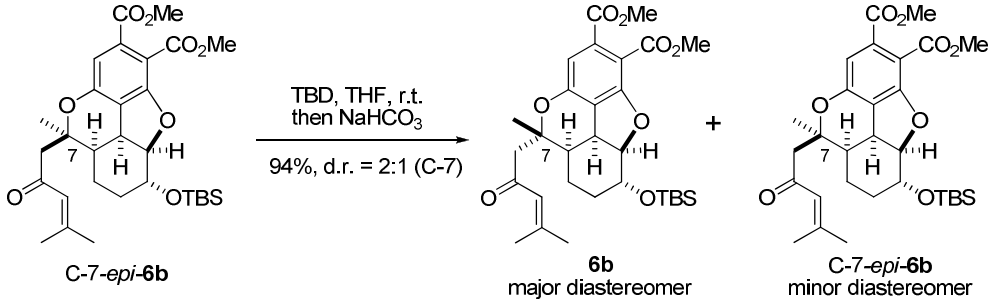


To a stirred solution of **7b** (2.30 g, 3.36 mmol) and $(TMS)_3SiH$ (1.25g, 3.36 mmol, 1.5 equiv.) in CH_2Cl_2 at room temperature was simultaneously added *s*-Bu_3B (3.36 mL, 1M in THF, 3.36 mmol, 1 equiv.) and air via a syringe (10 mL). The addition procedure took place over a period of 30 min. The mixture was stirred an additional 15 minutes at room temperature and then the mixture was concentrated under reduced pressure. The crude ^{1}H NMR spectrum indicated a 3:2 mixture of diastereomers about C-7, favoring **6b**. The crude residue was subjected to silica gel flash chromatography (EtOAc/Heptane) to afford 1.36 g (72% yield) of a 3:2 (**6b**:C-7-*epi*-**6b**) mixture of diastereomers as a pale yellow foam. Separation of diastereomers was performed by preparative HPLC (5-100% EtOH in Heptane,

Phenomenex Cellulose-2, 250 x 21.2mm 5µ, Flow = 28 mL/min) to afford **6b** (0.79 g, 42%) as a white solid and C-7-*epi*-**6b** (0.41 g, 22%) as a pale yellow solid.

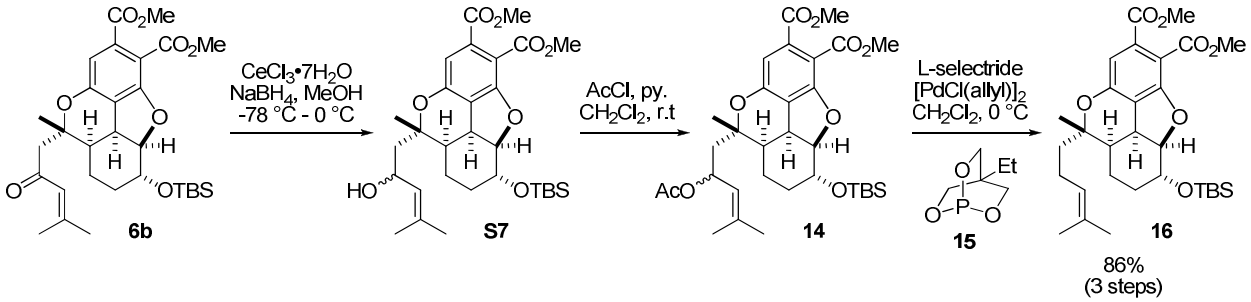
6b: ^{1}H NMR (400MHz, $CDCl_3$) δ 6.69 (s, 1H), 6.01 (s, 1H), 4.90-4.84 (m, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.61 (t, *J*=7.3 Hz, 1H), 3.25-3.17 (m, 1H), 2.77-2.62 (m, 2H), 2.47-2.39 (m, 1H), 2.15 (s, 3H), 1.88 (s, 3H), 1.80-1.71 (m, 1H), 1.70-1.62 (m, 1H), 1.52 (s, 3H), 1.32-1.19 (m, 1H), 0.85 (s, 9H), 0.92-0.79 (m, 1H), 0.04 (s, 3H), -0.07 ppm (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 197.3, 168.4, 165.4, 159.6, 157.5, 153.0, 135.3, 124.5, 114.5, 109.7, 108.0, 95.9, 81.5, 72.5, 52.7, 52.2, 51.5, 35.6, 35.3, 30.8, 27.9, 25.7, 23.5, 20.9, 20.1, 17.9, -4.9, -5.2 ppm. FTIR (cm^{-1}) = 2950, 1727, 1683, 1622, 1432, 1377. HRMS (ESI) calculated for $C_{30}H_{43}O_8Si$ $[M+H]^+$ 559.2722, found 559.2718.

C-7-*epi*-**6b:** ^{1}H NMR (500MHz, $CDCl_3$) δ 6.66 (s, 1H), 6.15 - 6.13 (m, 1H), 4.86 (dd, *J*=6.7, 8.2 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.63 (t, *J*=7.3 Hz, 1H), 3.20 (ddd, *J*=4.4, 6.8, 11.7 Hz, 1H), 2.98 - 2.81 (m, 2H), 2.52 - 2.43 (m, 1H), 2.15 (d, *J*=1.2 Hz, 3H), 1.91 (d, *J*=1.2 Hz, 3H), 1.65 - 1.54 (m, 2H), 1.41 (s, 3H), 1.30 - 1.17 (m, 1H), 0.84 (s, 9H), 0.87 - 0.75 (m, 1H), 0.03 (s, 3H), -0.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 168.5, 165.5, 159.5, 156.9, 152.7, 135.3, 124.3, 114.7, 109.9, 107.7, 95.8, 81.8, 72.5, 52.7, 52.1, 51.5, 35.6, 34.6, 30.8, 27.9, 25.7, 24.3, 20.9, 20.7, 17.9, -4.9, -5.2. FTIR (cm^{-1}) = 2950, 1725, 1686, 1620, 1433, 1377. HRMS (ESI) calculated for $C_{30}H_{43}O_8Si$ $[M+H]^+$ 559.2722, found 559.2720.



To a stirred solution of C-7-*epi*-**6b** (50 mg, 0.089 mmol) in THF (1 mL) at room temperature was added 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (18.7 mg, 0.13 mmol, 1.5 equiv.) in one portion. The resulting mixture was stirred at room temperature for 20 minutes and then saturated aqueous $NaHCO_3$ (1 mL) was added followed by CH_2Cl_2 (1 mL). The mixture was allowed to stir at room temperature for 2 hours and then it was extracted with CH_2Cl_2 (3x). The combined organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The ^{1}H NMR of the crude product indicated a 2:1 mixture of diastereomers about C-7, favoring **6b**. The crude residue was purified via flash chromatography (EtOAc/Heptane) to afford a mixture of **6b** and C-7-*epi*-**6b** (47 mg, 94% yield as a 2:1 (**6b**:C-7-*epi*-**6b**) mixture of diastereomers) as a colorless gum.

Compound **16**



To a stirred solution of **6b** (250 mg, 0.45 mmol) and cerium chloride heptahydrate (333 mg, 0.89 mmol, 2 equiv.) in MeOH (10 mL) at -78 °C was added $NaBH_4$ (25 mg, 0.67 mmol, 1.5 equiv.) in one portion. The mixture was allowed to warm to 0 °C. After stirring for 1h, the mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (3x). The combined organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure to provide 250 mg of a white foam as a mixture of diastereomers at C-9 (~5:1). The residue was used directly in the next step. To a stirred solution of **S7** in CH_2Cl_2 (8 mL) at 0 °C was added pyridine (72 µL, 0.89 mmol, 2 equiv.) followed by acetyl chloride (38 µL, 0.54 mmol, 1.2 equiv.) dropwise over a period of 5 minutes. The mixture was stirred at 0 °C for 30 minutes after which TLC indicated the consumption of starting material. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL) and extracted with CH_2Cl_2 (3x). The combined organic solution was washed with 0.1 N aqueous $KHSO_4$, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to provide 268 mg (99% crude yield) of a white solid as a mixture of diastereomers at C-9. A portion of the crude residue was used directly in the next step: to a stirred solution of **14** (180 mg, 0.30 mmol) in THF (15mL) at room temperature was added allylpalladium (II) chloride dimer (5.5 mg, 0.015 mmol, 0.05 equiv.) and phosphite **15** (9.7 mg, 0.06 mmol, 0.2 equiv.). The solution was cooled to 0 °C and L-selectride (0.6 mL, 1.0 M in THF, 0.6 mmol, 2 equiv.) was added in one portion and stirred at 0 °C until TLC indicated consumption of starting material (15 min). The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL) and the resulting mixture was diluted with water and then extracted with CH_2Cl_2 (3x). The combined organic solution was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was subjected to silica gel flash chromatography (EtOAc/Heptane) to afford **16** (140 mg, 86% yield for 3 steps) as a colorless gum.

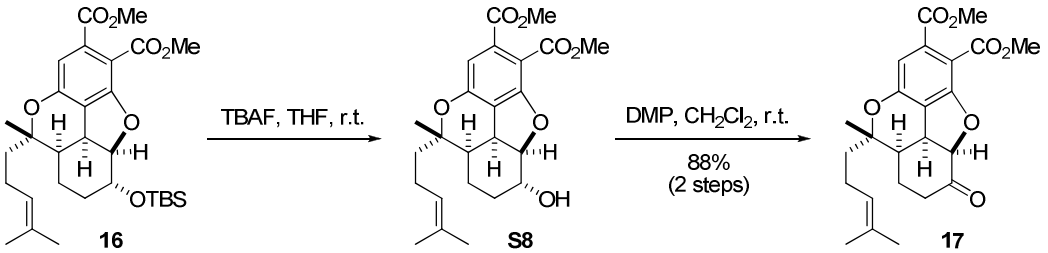
16: ^{1}H NMR (400MHz, $CDCl_3$) δ 6.66 (s, 1H), 5.05 - 4.96 (m, 1H), 4.85 (dd, *J*=6.8, 7.8 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.61 (t, *J*=7.3 Hz, 1H), 3.26 - 3.16 (m, 1H), 2.10 - 1.93 (m, 3H), 1.77 - 1.66 (m, 1H), 1.63 (s, 3H), 1.65 - 1.57 (m, 1H), 1.55 (s, 3H), 1.53 - 1.44 (m, 1H), 1.39 (s, 3H), 1.29 - 1.18 (m, 2H), 0.84 (s, 9H), 0.88 - 0.81 (m, 1H), 0.04 (s, 3H), -0.06 - -0.09 (m, 3H). ^{13}C NMR (101MHz, $CDCl_3$): δ 168.5, 165.5, 159.4, 153.5, 135.2, 132.3, 123.1, 114.3, 109.8, 107.4, 95.6, 82.6, 72.5, 52.6, 52.1, 38.4, 36.5, 35.1, 30.9, 25.7, 25.6, 22.3, 22.2, 20.4, 17.9, 17.6, -4.9, -5.3 ppm. FTIR (cm^{-1}) = 2951, 1723, 1624, 1432, 1377. HRMS (ESI) calculated for $C_{30}H_{45}O_7Si$ $[M+H]^+$ 545.2929, found 545.2940.

S7: (crude NMR, data extracted from major diastereomer): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.71 (s, 1H), 5.17-5.10 (m, 1H), 4.87 (dd, *J*=8.2, 6.7 Hz, 1H), 4.75-4.67 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.67-3.61 (m, 1H), 3.23 (ddd, *J*=11.8, 6.7, 4.7 Hz, 1H), 2.08-1.99 (m, 1H), 1.98-1.90 (m, 2H), 1.80-1.72 (m, 1H), 1.69 (s, 3H), 1.69 (s, 3H), 1.60 (s, 1H), 1.53 (s, 3H), 1.55-1.49 (m, 1H), 1.31-1.17 (m, 1H) 0.94-0.80 ppm (m, 1H), 0.85

(s, 9H), 0.84-0.86 (m, 1H), 0.04 (s, 3H), -0.06 ppm (s, 3H). HRMS (ESI) calculated for $C_{30}H_{45}O_8Si$ $[M+H]^+$ 561.2878, found 561.2876.

14: (crude NMR, data extracted from major diastereomer): ^{1}H NMR (400MHz, $CDCl_3$) δ 6.65 (s, 1H), 5.77 (dt, *J*=3.5, 8.9 Hz, 1H), 5.10 - 5.03 (m, 1H), 4.87 (dd, *J*=6.6, 8.3 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.64 - 3.57 (m, 1H), 3.22 (ddd, *J*=4.6, 6.7, 11.8 Hz, 1H), 2.13 - 2.05 (m, 1H), 2.04 - 1.96 (m, 1H), 1.96 (s, 3H), 1.76 (d, *J*=1.2 Hz, 3H), 1.69 (d, *J*=1.2 Hz, 3H), 1.68 - 1.63 (m, 2H), 1.44 (s, 3H), 1.47 - 1.40 (m, 1H), 1.32 - 1.18 (m, 1H), 0.86 (s, 9H), 0.91 - 0.79 (m, 1H), 0.04 (s, 3H), -0.06 (s, 3H). HRMS (ESI) calculated for $C_{32}H_{46}O_9Si$ Na $[M+Na]^+$ 625.2803, found 625.2797.

Compound **17**

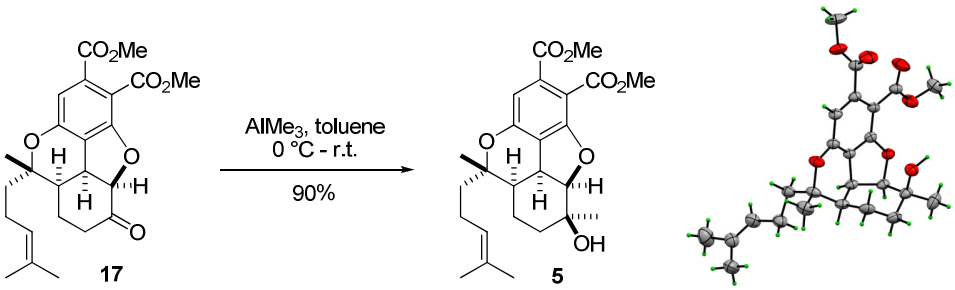


To a stirred solution of **16** (80 mg, 0.15 mmol) in THF (3 mL) at 0 °C was added TBAF (0.49 mL, 1.0 M in THF, 0.49 mmol, 1.5 equiv.) dropwise over a period of 5 minutes. The reaction mixture was warmed to room temperature and stirred until TLC indicated consumption of starting material (1 h). The reaction mixture was diluted with CH_2Cl_2 and the resulting solution was washed with water (3x) and brine (2x) and then dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to yield **S8** as white solid (62mg). The crude residue was used directly in the next step. To a stirred solution of **S8** (62 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) at room temperature was added Dess-Martin periodinane (91 mg, 0.21 mmol, 1.5 equiv.) in one portion. The reaction mixture was stirred at room temperature until TLC indicated consumption of starting material (20 min). A 1:1 mixture of saturated aqueous $NaHCO_3$ and 10% aqueous $Na_2S_2O_3$ (3 mL) was added and the resulting mixture was stirred at room temperature for 15 minutes and then extracted with CH_2Cl_2, (3x). The combined organic solution was washed with a 1:1 mixture of saturated aqueous $NaHCO_3$ and 10% aqueous $Na_2S_2O_3$, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to silica gel flash chromatography (EtOAc/Heptane) to afford **17** (54 mg, 88% yield over 2 steps) as a white solid.

S8: ^{1}H NMR (400MHz, $CDCl_3$) δ 6.69 (s, 1H), 5.04 - 4.98 (m, 1H), 4.90 (dd, *J*=7.0, 8.2 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.65 (t, *J*=7.2 Hz, 1H), 3.33 (ddd, *J*=4.3, 7.1, 12.0 Hz, 1H), 2.12 - 2.00 (m, 3H), 1.86 - 1.75 (m, 2H), 1.65 (s, 3H), 1.68 - 1.59 (m, 1H), 1.57 (s, 3H), 1.55 - 1.47 (m, 1H), 1.41 (s, 3H), 1.32 - 1.18 (m, 1H), 0.98 (s, 1H), 0.95 - 0.84 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 165.7, 159.3, 153.5, 134.9, 132.4, 123.1, 114.3, 110.0, 107.6, 95.4, 82.7, 71.7, 52.6, 52.4, 38.5, 36.4, 35.0, 29.1, 25.6, 22.3, 22.2, 20.6, 17.6. FTIR (cm^{-1}) = 3394, 2952, 1715, 1623, 1433, 1377. HRMS (ESI) calculated for $C_{24}H_{31}O_7$ $[M+H]^+$ 431.2070, found 431.2073.

17: ^{1}H NMR (400MHz, $CDCl_3$) δ 6.68 (s, 1H), 5.22 (d, *J*=8.6 Hz, 1H), 5.03 (t, *J*=7.0 Hz, 1H), 4.08 (t, *J*=6.8 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 2.47 - 2.25 (m, 3H), 2.16 - 2.02 (m, 3H), 1.65 (s, 3H), 1.73 - 1.62 (m, 1H), 1.59 (s, 3H), 1.44 (s, 3H), 1.30 - 1.16 (m, 2H). ^{13}C NMR (101MHz, $CDCl_3$): δ 205.4, 168.0, 165.0, 159.9, 153.4, 135.6, 132.6, 122.8, 111.1, 110.1, 107.4, 88.3, 82.4, 52.6, 52.5, 38.5, 38.5, 38.5, 36.3, 25.6, 22.6, 22.5, 22.2, 17.6 ppm. FTIR (cm^{-1}) = 2951, 1722, 1621, 1432, 1375. HRMS calculated for $C_{24}H_{29}O_7$ $[M+H]^+$ 429.1908, found 429.1914.

Compound **5**

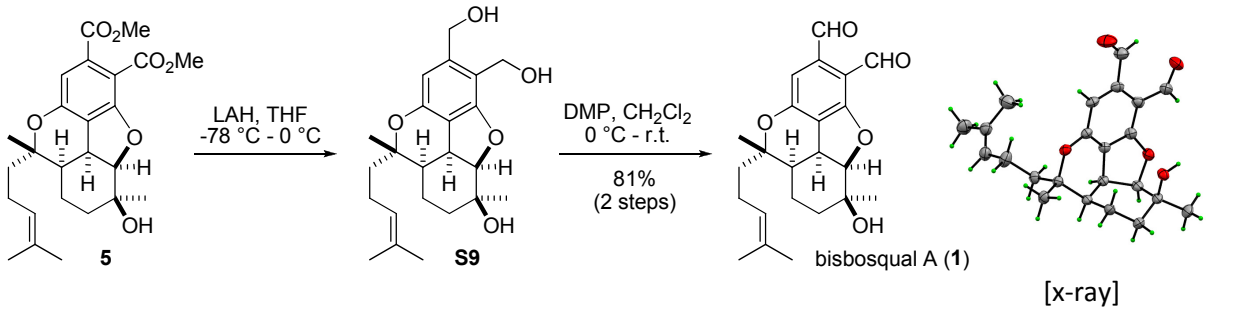


[x-ray]

To a stirred solution of **17** (52 mg, 0.12 mmol) in toluene (3 mL) at 0 °C was added $AlMe_3$ (0.09 mL, 2.0 M in heptane, 0.18 mmol, 1.5 equiv.) dropwise over a period of 5 minutes. The reaction mixture was allowed to warm to room temperature and then stir until TLC indicated consumption of starting material (30 min). The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and the resulting mixture was extracted with CH_2Cl_2 (4x). The combined organic solution was filtered through Celite and concentrated under reduced pressure. The residue was subjected to silica gel flash chromatography (EtOAc/Heptane) to afford **5** (49 mg, 90% yield) as a white solid.

5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 4.99-5.06 (m, 1H), 4.86 (d, *J*=8.98 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.62-3.69 (m, 1H), 2.02-2.11 (m, 2H), 1.93-2.01 (m, 1H), 1.73-1.81 (m, 1H), 1.65 (s, 3H), 1.61-1.71 (m, 1H), 1.58 (s, 3H), 1.56 (br. s., 1H), 1.47-1.55 (m, 2H), 1.42 (s, 3H), 1.27 (s, 3H), 1.25-1.33 (m, 1H), 1.12-1.24 (m, 1H). ^{13}C NMR (101MHz, $CDCl_3$) δ 168.0, 166.1, 161.0, 153.3, 133.6, 132.3, 123.3, 114.7, 110.3, 106.1, 92.0, 82.5, 69.1, 52.5, 52.3, 38.5, 36.2, 34.8, 33.7, 29.8, 25.6, 22.2, 22.2, 17.6, 16.3 ppm. FTIR (cm^{-1}) = 2956, 1627, 1433, 1376, 1289, 1263. HRMS (ESI) calculated for $C_{25}H_{33}O_7$ $[M+H]^+$ 445.2221, found 445.2224.

Compound **1**: Bisabosqual A



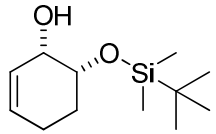
To a stirred solution of **5** (25.1 mg, 0.0565 mmol) in THF (3 mL) at -78 °C was added LAH (0.14 mL, 1.0 M in THF, 0.14 mmol, 2.5 equiv.) dropwise over a period of 10 minutes. The reaction mixture was allowed to warm to 0 °C and stirred at this temperature until TLC analysis indicated the reaction to be complete (30 min). The reaction mixture was carefully quenched with $Na_2SO_4 \cdot 10H_2O$ and the resulting mixture was filtered through Celite and then concentrated under reduced pressure. The crude residue was used immediately in the subsequent step without purification. To a stirred solution of crude **S9** (from above) in CH_2Cl_2 (3 mL) at 0 °C was added Dess-Martin periodinane (59 mg, 0.14 mmol, 2.5 equiv.) in one portion. The reaction mixture was warmed to room temperature and then stirred until TLC indicated consumption of starting material (45 min). Then a 1:1 mixture of saturated aqueous $NaHCO_3$ and 10% aqueous $Na_2S_2O_3$ (3 mL) was added and the resulting mixture was stirred at room temperature for 30 minutes. The reaction mixture was extracted with CH_2Cl_2, (3x). The combined organic solution was washed with a 1:1 mixture of saturated aqueous $NaHCO_3$ and 10% aqueous $Na_2S_2O_3$, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to silica gel flash chromatography (EtOAc/Heptane) to afford **1** (17.5 mg, 81% yield over 2 steps) as a white solid.

1: ^{1}H NMR (400MHz, $CDCl_3$) δ 10.47 (s, 1H), 10.37 (s, 1H), 6.93 (s, 1H), 5.03 (tdt, *J*=1.4, 2.9, 7.1 Hz, 1H), 4.97 (d, *J*=8.8 Hz, 1H), 3.69 - 3.63 (m, 1H), 2.13 - 2.05 (m, 2H), 2.09 - 2.00 (m, 1H), 1.83 - 1.76 (m, 1H), 1.72 - 1.64 (m, 1H), 1.65 (s, 3H), 1.59 (s, 3H), 1.59 - 1.56 (m, 1H), 1.57 (br. s, 1H), 1.56 - 1.53 (m, 1H), 1.46 (s, 3H), 1.32 (s, 3H), 1.32 - 1.26 (m, 1H), 1.25 - 1.17 (m, 1H). ^{13}C NMR (101MHz, $CDCl_3$): δ 192.2, 188.1, 165.5, 155.7, 139.3, 132.5, 123.1, 117.3, 113.8, 112.4, 92.7, 83.5, 69.2, 38.7, 36.0, 34.9, 33.3, 29.6, 25.6, 22.2, 22.1, 17.7, 16.4. FTIR (cm^{-1}) = 3469, 2967, 1685, 1618, 1382. HRMS (ESI) calculated for $C_{23}H_{29}O_5$ $[M+H]^+$ 385.2010, found 385.2007.

Comparison of Natural and Synthetic Bisabosqual A:

Position	Authentic (^{1}H)	Synthetic (^{1}H)	Authentic (^{13}C)	Synthetic (^{13}C)
1	1.55 (m, 1H), 1.28 (m, 1H)	1.55 (m, 1H), 1.29 (m, 1H)	16.33	16.4
2	1.79 (m, 1H), 1.21 (m, 1H)	1.80 (m, 1H), 1.21 (m, 1H)	34.93	34.9
3	-	-	69.14	69.2
4	4.97 (d, *J*=8.8 Hz, 1H)	4.97 (d, *J*=8.8 Hz, 1H)	92.77	92.7
5	3.66 (dd, *J*=8.8, 6.6 Hz, 1H)	3.66 (m, 1H)	33.27	33.3
6	2.05 (m, 1H)	2.05 (m, 1H)	35.94	36.0
7	-	-	83.52	83.5
8	1.67 (m, 1H), 1.57 (m, 1H)	1.68 (m, 1H), 1.58 (m, 1H)	38.71	38.7
9	2.08 (m, 2H)	2.09 (m, 2H)	22.21	22.2
10	5.03 (m, 1H)	5.03 (tdt, *J*=7.1,2.9,1.4, 1H)	123.08	123.1
11	-	-	132.47	132.5
12	1.65 (br. s, 3H)	1.65 (s, 3H)	25.57	25.6
13	1.59 (br. s, 3H)	1.59 (s, 3H)	17.63	17.7
14	1.46 (s, 3H)	1.46 (s, 3H)	22.11	22.1
15	1.31 (s, 3H)	1.32 (s, 3H)	29.53	29.6
1’	-	-	117.31	117.3
2’	-	-	165.69	165.5
3’	-	-	112.08	112.4
4’	-	-	139.26	139.3
5’	6.93 (s, 1H)	6.93 (s, 1H)	113.67	113.8
6’	-	-	155.71	155.7
7’	10.46 (s, 1H)	10.47 (s, 1H)	188.27	188.1
8’	10.36 (s, 1H)	10.37 (s, 1H)	192.24	192.2
3-OH	1.55 (br. s, 1H)	1.57 (br. s, 1H)	-	-

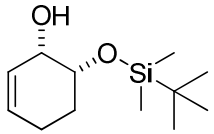
Acquisition Time (sec)	2.5625	***Comment***			
Date	05 Aug 2012 14:20:48	***Date Stamp***	05 Aug 2012 14:20:48		
File Name					
Frequency (MHz)	399.54	***Nucleus***	1H	***Number of Transients***	16
Origin	spect	***Original Points Count***	16384	***Owner***	FCNGRO-BRKOA
Points Count	16384	***Pulse Sequence***	zg30	***Receiver Gain***	57.00
SW(cyclical) (Hz)	6393.86	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	2384.9451
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6393.47	***Temperature (degree C)***	25.148



9

^{1}HNMR (400 MHz) in $CDCl_3$

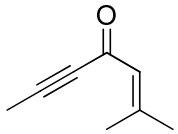
Acquisition Time (sec)	1.4680	***Comment***	00701217-D-161	***Date***	Jun 17 2012	***Date Stamp***	Jun 17 2012
File Name						***Frequency (MHz)***	100.64
Nucleus	13C	***Number of Transients***	512	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	40.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	10063.0557	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	22321.43	***Temperature (degree C)***	25.000



9

^{13}CNMR (100 MHz) in $CDCl_3$

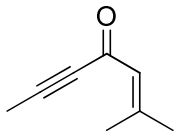
Acquisition Time (sec)	2.9464	***Comment***	00701217-E293-P			***Date***	Jun 17 2012
Date Stamp	Jun 17 2012	***File Name***	\\UNITYI.PFIZER.COM\SAMBA\120617\0201.FID\FID			***Frequency (MHz)***	499.58
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	23552	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	44.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2992.8242	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	7993.60	***Temperature (degree C)***	25.000



10

^{1}HNMR (500 MHz) in $CDCl_3$

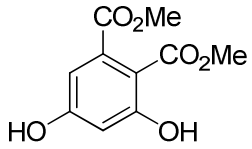
Acquisition Time (sec)	1.4680	***Comment***	00701217-E-293	***Date***	Jun 17 2012	***Date Stamp***	Jun 17 2012
File Name	\\UNITYH.PFIZER.COM\AUTO\2012\20120617\00701217-E-293_20120617_03\CARBON_01.FID\FID					***Frequency (MHz)***	100.64
Nucleus	13C	***Number of Transients***	512	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	40.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	10061.6934	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	22321.43	***Temperature (degree C)***	25.000



10

^{13}CNMR (100 MHz) in $CDCl_3$

Acquisition Time (sec)	2.9464	***Comment***	00701217-E215-P			***Date***	Jun 17 2012
Date Stamp	Jun 17 2012	***File Name***	\\UNITYI.PFIZER.COM\SAMBA\120617\0101.FID\FID			***Frequency (MHz)***	499.58
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	23552	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	42.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2993.0684	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	7993.60	***Temperature (degree C)***	25.000



11

^{1}HNMR (500 MHz) in $CDCl_3$

Acquisition Time (sec)	1.4680	***Comment***	00701217-E-215	***Date***	Jun 17 2012	***Date Stamp***	Jun 17 2012
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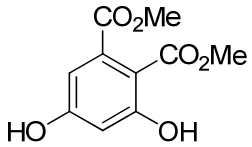
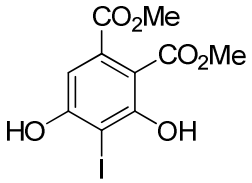
Nucleus	13C	***Number of Transients***	512	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	40.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	10061.0127	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	22321.43	***Temperature (degree C)***	25.000



11

^{13}CNMR (100 MHz) in $CDCl_3$

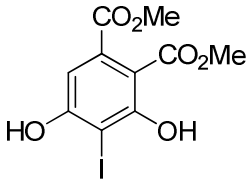
Acquisition Time (sec)	3.6815	***Date***	Aug 22 2010	***Date Stamp***	Aug 22 2010		
File Name	\\UNITYF.PFIZER.COM\SAMBA\100822\0401.FID\FID			***Frequency (MHz)***	399.83	***Nucleus***	1H
Number of Transients	16	***Original Points Count***	23552	***Points Count***	32768	***Pulse Sequence***	s2pul
Receiver Gain	48.00	***Solvent***	CHLOROFORM-d			***Spectrum Offset (Hz)***	2411.4619
Sweep Width (Hz)	6397.44	***Temperature (degree C)***	25.000				



8

^{1}HNMR (400 MHz) in $CDCl_3$

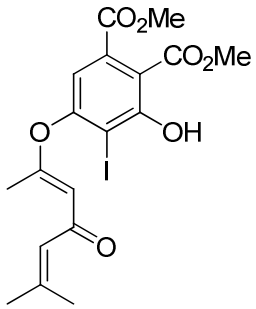
Acquisition Time (sec)	1.0871	***Comment***	00701217-C139	Very long C-13 for dilute sample		***Date***	Jul 5 2012
Date Stamp	Jul 5 2012	***File Name***	\\UNITYI.PFIZER.COM\SAMBA\120705\4002.FID\FID			***Frequency (MHz)***	125.63
Nucleus	13C	***Number of Transients***	8192	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	12529.5928	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	30143.18	***Temperature (degree C)***	25.000



8

^{13}CNMR (125 MHz) in $CDCl_3$

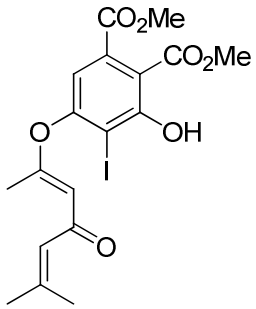
Acquisition Time (sec)	3.6815	***Comment***	00701217-D159			***Date***	Mar 18 2011
Date Stamp	Mar 18 2011	***File Name***	\\UNITYF.PFIZER.COM\SAMBA\110318\1601.FID\FID			***Frequency (MHz)***	399.83
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	23552	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	48.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2411.8523	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6397.44	***Temperature (degree C)***	25.000



13

^{1}HNMR (400 MHz) in $CDCl_3$

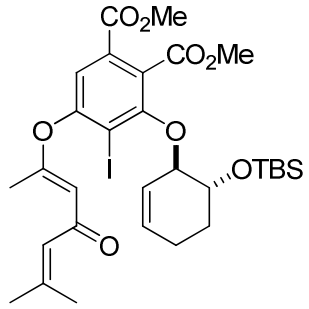
Acquisition Time (sec)	1.3582	***Comment***	00701217-D159 Longer C-13 for more dilute sample			***Date***	Mar 18 2011
Date Stamp	Mar 18 2011	***File Name***	\\UNITYF.PFIZER.COM\SAMBA\110318\9002.FID\FID			***Frequency (MHz)***	100.55
Nucleus	13C	***Number of Transients***	2048	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	10033.0625	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	24125.45	***Temperature (degree C)***	25.000



13

^{13}CNMR (100 MHz) in $CDCl_3$

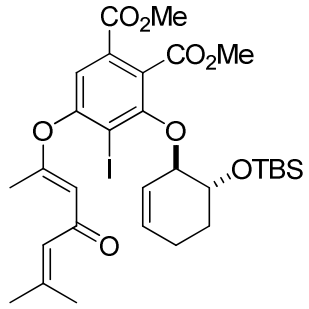
Acquisition Time (sec)	3.6815	***Date***	Nov 22 2010	***Date Stamp***	Nov 22 2010		
File Name	\\UNITYF.PFIZER.COM\SAMBA\101122\1601.FID\FID			***Frequency (MHz)***	399.83	***Nucleus***	1H
Number of Transients	16	***Original Points Count***	23552	***Points Count***	32768	***Pulse Sequence***	s2pul
Receiver Gain	42.00	***Solvent***	CHLOROFORM-d			***Spectrum Offset (Hz)***	2411.6570
Sweep Width (Hz)	6397.44	***Temperature (degree C)***	25.000				



7b

^{1}HNMR (400 MHz) in $CDCl_3$

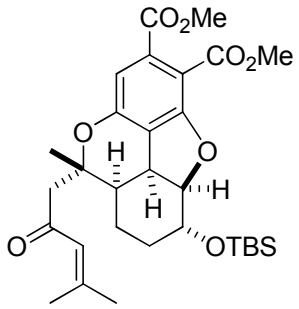
Acquisition Time (sec)	1.3582	***Date***	Nov 23 2010	***Date Stamp***	Nov 23 2010		
File Name	\\UNITYF.PFIZER.COM\SAMBA\101122\9102.FID\FID			***Frequency (MHz)***	100.55	***Nucleus***	13C
Number of Transients	2048	***Original Points Count***	32768	***Points Count***	32768	***Pulse Sequence***	s2pul
Receiver Gain	60.00	***Solvent***	CHLOROFORM-d			***Spectrum Offset (Hz)***	10517.7051
Sweep Width (Hz)	24125.45	***Temperature (degree C)***	25.000				



7b

^{13}CNMR (100 MHz) in $CDCl_3$

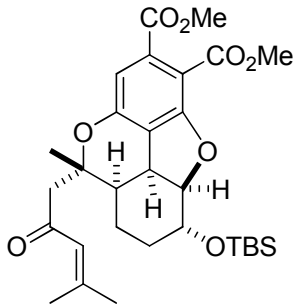
Acquisition Time (sec)	2.5625	***Comment***			
Date	13 Apr 2012 09:52:00	***Date Stamp***	13 Apr 2012 09:52:00		
File Name	\\AMRGROB10025582.AMER.PFIZER.COM\BKDATA:.DATA\AMENDC01\NMR\00701217-E239\2\PDATA\1\1r				
Frequency (MHz)	399.54	***Nucleus***	1H	***Number of Transients***	16
Origin	spect	***Original Points Count***	16384	***Owner***	FCNGRO-BRKOA
Points Count	65536	***Pulse Sequence***	zg30	***Receiver Gain***	114.00
SW(cyclical) (Hz)	6393.86	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	2385.2864
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6393.76	***Temperature (degree C)***	25.152



6b

^{1}HNMR (400 MHz) in $CDCl_3$

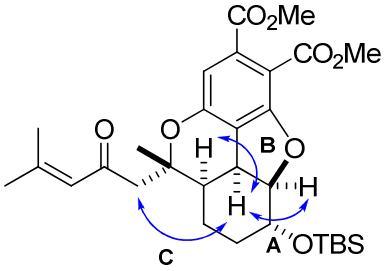
Acquisition Time (sec)	1.2788	***Comment***	00701217-E-239	***Date***	Sep 20 2012	***Date Stamp***	Sep 20 2012
File Name	\\UNITYH.PFIZER.COM\AUTO\2012\20120920\00701217-E-239_20120920_01\CARBON_01.FID\FID					***Frequency (MHz)***	100.64
Nucleus	13C	***Number of Transients***	16384	***Original Points Count***	28544	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	40.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	10063.0029	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	22321.43	***Temperature (degree C)***	25.000



6b

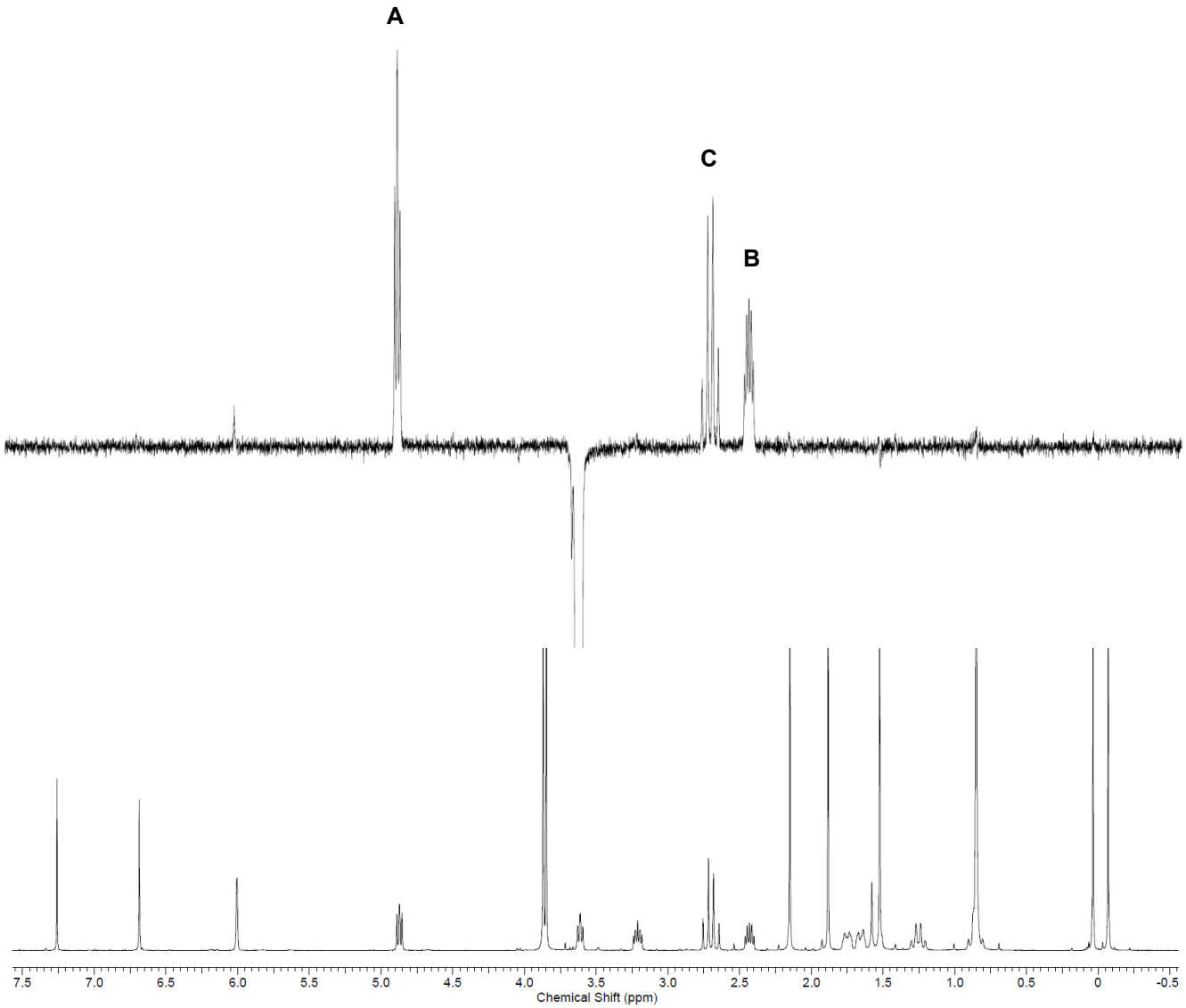
^{13}CNMR (100 MHz) in $CDCl_3$

Acquisition Time (sec)	2.5559	***Comment***	00701217-E239-361	***Date***	Jun 19 2012	***Date Stamp***	Jun 19 2012
File Name	C:\DOCUME~1\AMENDC01\LOCALS~1\TEMP\GAINS9192.TMP\PRODUCTION\UNITYH\AMENDC01\00701217-E239-361_2012171110916.FID\FID						
Frequency (MHz)	400.20	***Nucleus***	1H	***Number of Transients***	64	***Original Points Count***	16384
Points Count	16384	***Pulse Sequence***	NOESY1D	***Receiver Gain***	30.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2401.1633	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6410.26	***Temperature (degree C)***	25.000

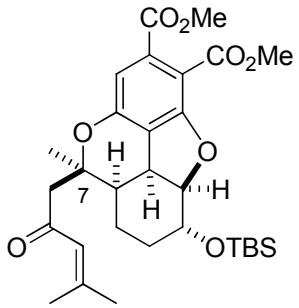


6b

NOE 3.61 ppm



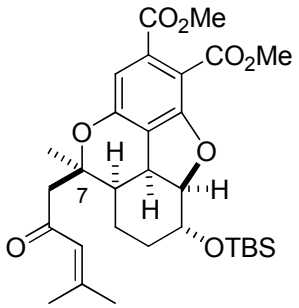
Acquisition Time (sec)	2.9464	***Comment***	00701217-E239-364			***Date***	Jul 28 2012
Date Stamp	Jul 28 2012	***File Name***	\\UNITYI.PFIZER.COM\SAMBA\120728\0401.FID\FID			***Frequency (MHz)***	499.58
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	23552	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	42.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2992.8242	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	7993.60	***Temperature (degree C)***	25.000



C-7-*epi*-**6b**

^{1}HNMR (500 MHz) in $CDCl_3$

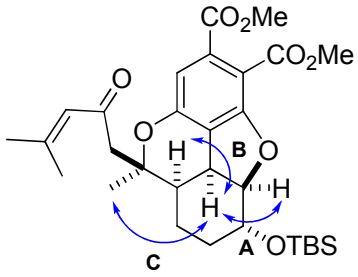
Acquisition Time (sec)	1.3631	***Comment***			5
Date	01 Aug 2012 00:22:24	***Date Stamp***	01 Aug 2012 00:22:24		
File Name	\\AMRGROB10025582.AMER.PFIZER.COM\BKDATA:.DATA\AMENDC01\NMR\00701217-E239-CNMR\1\FID				
Frequency (MHz)	100.46	***Nucleus***	13C	***Number of Transients***	8192
Origin	spect	***Original Points Count***	32768	***Owner***	FCNGRO-BRKOA
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	228.00
SW(cyclical) (Hz)	24038.46	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	10046.9531
Spectrum Type	STANDARD	***Sweep Width (Hz)***	24037.73	***Temperature (degree C)***	25.152



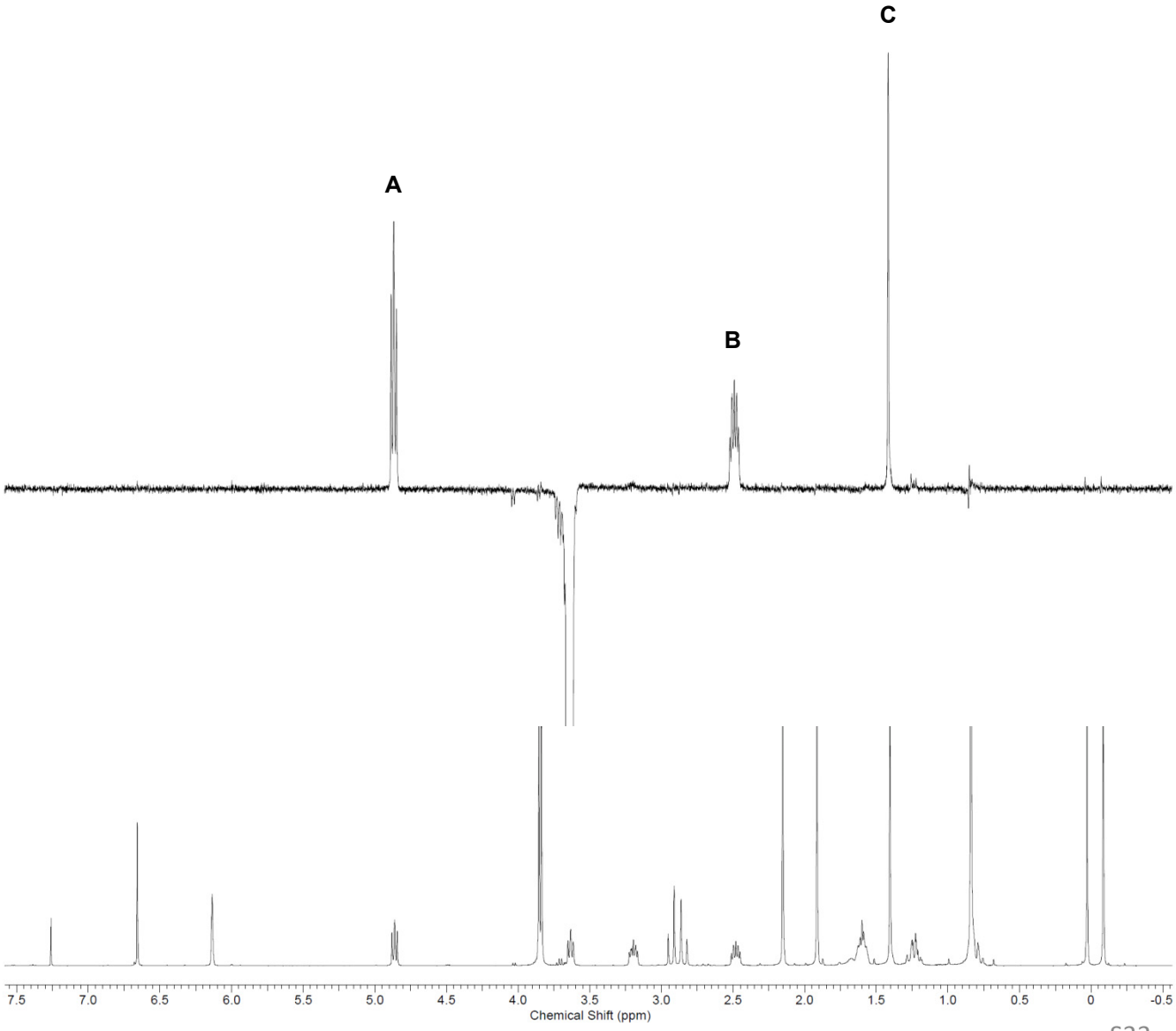
C-7-*epi*-**6b**

^{13}CNMR (100 MHz) in $CDCl_3$

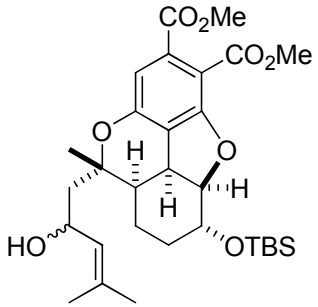
Acquisition Time (sec)	2.5559	***Comment***	00701217-E239-363	***Date***	Jul 31 2012	***Date Stamp***	Jul 31 2012
File Name	C:\DOCUME~1\AMENDC01\LOCALS~1\TEMP\GAINS19712.TMP\PRODUCTION\UNITYH\AMENDC01\00701217-E239-363_2012213110542.FID\FID						
Frequency (MHz)	400.20	***Nucleus***	1H	***Number of Transients***	64	***Original Points Count***	16384
Points Count	16384	***Pulse Sequence***	NOESY1D	***Receiver Gain***	30.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2401.1633	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6410.26	***Temperature (degree C)***	25.000



C-7-*epi*-**6b**
NOE 3.63 ppm



Acquisition Time (sec)	5.1118	***Comment***	00701217-F53-long			***Date***	Sep 17 2012
Date Stamp	Sep 17 2012	***File Name***	\\UNITYH.PFIZER.COM\AUTO\2012\20120917\00701217-F53-LONG_20120917_01\PROTON_01.FID\FID				
Frequency (MHz)	400.20	***Nucleus***	1H	***Number of Transients***	80	***Original Points Count***	32768
Points Count	32768	***Pulse Sequence***	s2pul	***Receiver Gain***	30.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	2401.1633	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6410.26	***Temperature (degree C)***	25.000

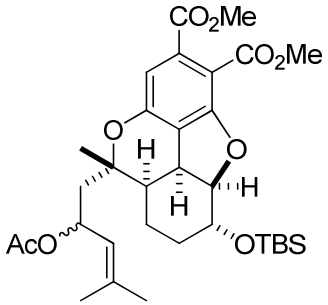


S7

(crude NMR)

^{1}HNMR (400 MHz) in $CDCl_3$

Acquisition Time (sec)	5.1118	***Comment***	00701217-E-83	***Date***	Sep 28 2011	***Date Stamp***	Sep 28 2011
File Name	\\UNITYH.PFIZER.COM\AUTO\2011\20110928\00701217-E-83_20110928_01\PROTON_01.FID\FID					***Frequency (MHz)***	400.20
Nucleus	1H	***Number of Transients***	192	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	30.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2401.6167	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6410.26	***Temperature (degree C)***	25.000

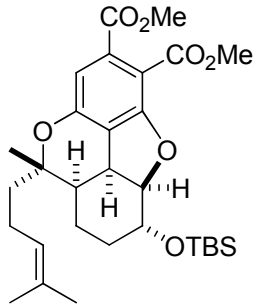


14

(crude NMR)

^{1}HNMR (400 MHz) in $CDCl_3$

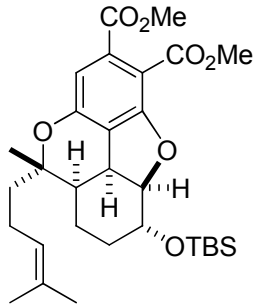
Acquisition Time (sec)	3.6841	***Comment***	00701217-E91-pure			***Date***	Oct 1 2011
Date Stamp	Oct 1 2011	***File Name***	\\UNITYG.PFIZER.COM\SAMBA\111001\0201.FID\FID			***Frequency (MHz)***	399.54
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	23552	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	26.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2401.5022	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6392.84	***Temperature (degree C)***	25.000



16

^{1}HNMR (400 MHz) in $CDCl_3$

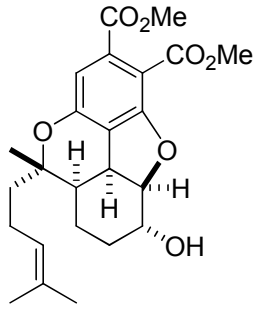
Acquisition Time (sec)	1.4680	***Comment***	00701217-E91-pure			***Date***	Oct 1 2011
Date Stamp	Oct 1 2011	***File Name***	\\UNITYH.PFIZER.COM\AUTO\2011\20111001\00701217-E91-PURE_20111001_01\CARBON_01.FID\FID				
Frequency (MHz)	100.64	***Nucleus***	13C	***Number of Transients***	512	***Original Points Count***	32768
Points Count	32768	***Pulse Sequence***	s2pul	***Receiver Gain***	40.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	10555.1309	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	22321.43	***Temperature (degree C)***	25.000



16

^{13}CNMR (100 MHz) in $CDCl_3$

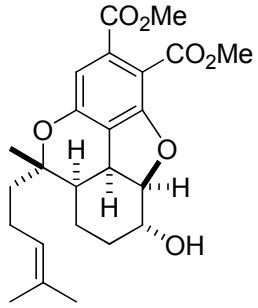
Acquisition Time (sec)	2.5625	***Comment***			
Date	09 Jul 2012 19:04:32	***Date Stamp***	09 Jul 2012 19:04:32		
File Name	\\AMRGROB10025582.AMER.PFIZER.COM\BKDATA:.DATA\AMENDC01\NMR\00701217-E97-NOE\2\FID				
Frequency (MHz)	399.54	***Nucleus***	1H	***Number of Transients***	16
Origin	spect	***Original Points Count***	16384	***Owner***	FCNGRO-BRKOA
Points Count	16384	***Pulse Sequence***	zg30	***Receiver Gain***	203.00
SW(cyclical) (Hz)	6393.86	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	2384.5544
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6393.47	***Temperature (degree C)***	25.146



S8

^{1}HNMR (400 MHz) in $CDCl_3$

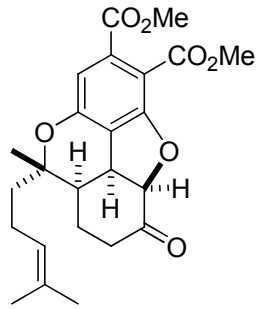
Acquisition Time (sec)	1.3631	***Comment***			
Date	09 Jul 2012 20:27:44	***Date Stamp***	09 Jul 2012 20:27:44		
File Name	\\AMRGROB10025582.AMER.PFIZER.COM\BKDATA:.DATA\AMENDC01\NMR\00701217-E97-NOE\3\FID				
Frequency (MHz)	100.46	***Nucleus***	13C	***Number of Transients***	2048
Origin	spect	***Original Points Count***	32768	***Owner***	FCNGRO-BRKOA
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	362.00
SW(cyclical) (Hz)	24038.46	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	10048.4209
Spectrum Type	STANDARD	***Sweep Width (Hz)***	24037.73	***Temperature (degree C)***	25.149



S8

^{13}CNMR (100 MHz) in $CDCl_3$

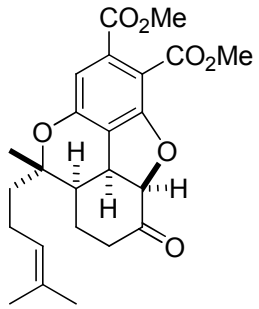
Acquisition Time (sec)	3.6841	***Comment***	00701217-E109-pure			***Date***	Oct 20 2011
Date Stamp	Oct 20 2011	***File Name***	\\UNITYG.PFIZER.COM\SAMBA\111020\0201.FID\FID			***Frequency (MHz)***	399.54
Nucleus	1H	***Number of Transients***	16	***Original Points Count***	23552	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	36.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	2397.1536	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	6392.84	***Temperature (degree C)***	25.000



17

^{1}HNMR (400 MHz) in $CDCl_3$

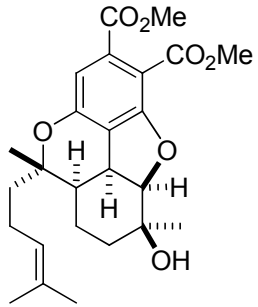
Acquisition Time (sec)	1.3591	***Comment***	00701217-E109-pure Quick C-13 for concentrated sample			***Date***	Oct 20 2011
Date Stamp	Oct 20 2011	***File Name***	\\UNITYG.PFIZER.COM\SAMBA\111020\0202.FID\FID			***Frequency (MHz)***	100.47
Nucleus	13C	***Number of Transients***	256	***Original Points Count***	32768	***Points Count***	32768
Pulse Sequence	s2pul	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	10046.3643	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	24110.91	***Temperature (degree C)***	25.000



17

^{13}CNMR (100 MHz) in $CDCl_3$

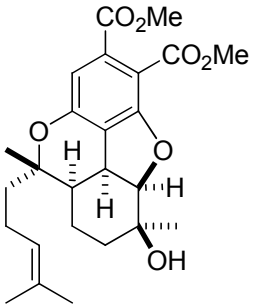
Acquisition Time (sec)	2.5625	***Comment***			
Date	12 Jul 2012 13:44:32	***Date Stamp***	12 Jul 2012 13:44:32		
File Name	\\AMRGROB10025582.AMER.PFIZER.COM\BKDATA:.DATA\AMENDC01\NMR\00701217-E281-3\2\FID				
Frequency (MHz)	399.54	***Nucleus***	1H	***Number of Transients***	16
Origin	spect	***Original Points Count***	16384	***Owner***	FCNGRO-BRKOA
Points Count	16384	***Pulse Sequence***	zg30	***Receiver Gain***	256.00
SW(cyclical) (Hz)	6393.86	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	2384.5544
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6393.47	***Temperature (degree C)***	25.152



5

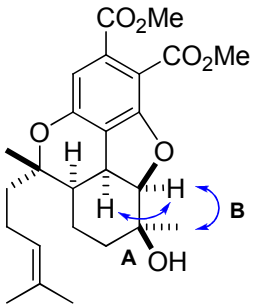
^{1}HNMR (400 MHz) in $CDCl_3$

Acquisition Time (sec)	1.3631	***Comment***			
Date	07 Jul 2012 17:17:52	***Date Stamp***	07 Jul 2012 17:17:52		
File Name	\\AMRGROB10025582.AMER.PFIZER.COM\BKDATA:.DATA\AMENDC01\NMR\00701217-E281-NOE\3\FID				
Frequency (MHz)	100.46	***Nucleus***	13C	***Number of Transients***	2048
Origin	spect	***Original Points Count***	32768	***Owner***	FCNGRO-BRKOA
Points Count	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	144.00
SW(cyclical) (Hz)	24038.46	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	10047.6865
Spectrum Type	STANDARD	***Sweep Width (Hz)***	24037.73	***Temperature (degree C)***	25.149



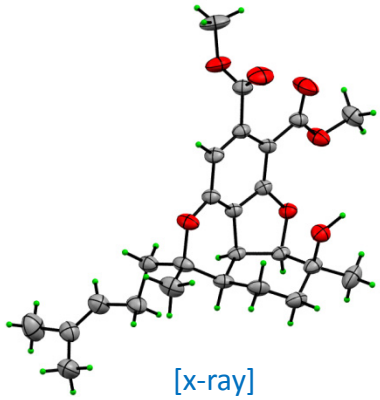
5

^{13}CNMR (100 MHz) in $CDCl_3$



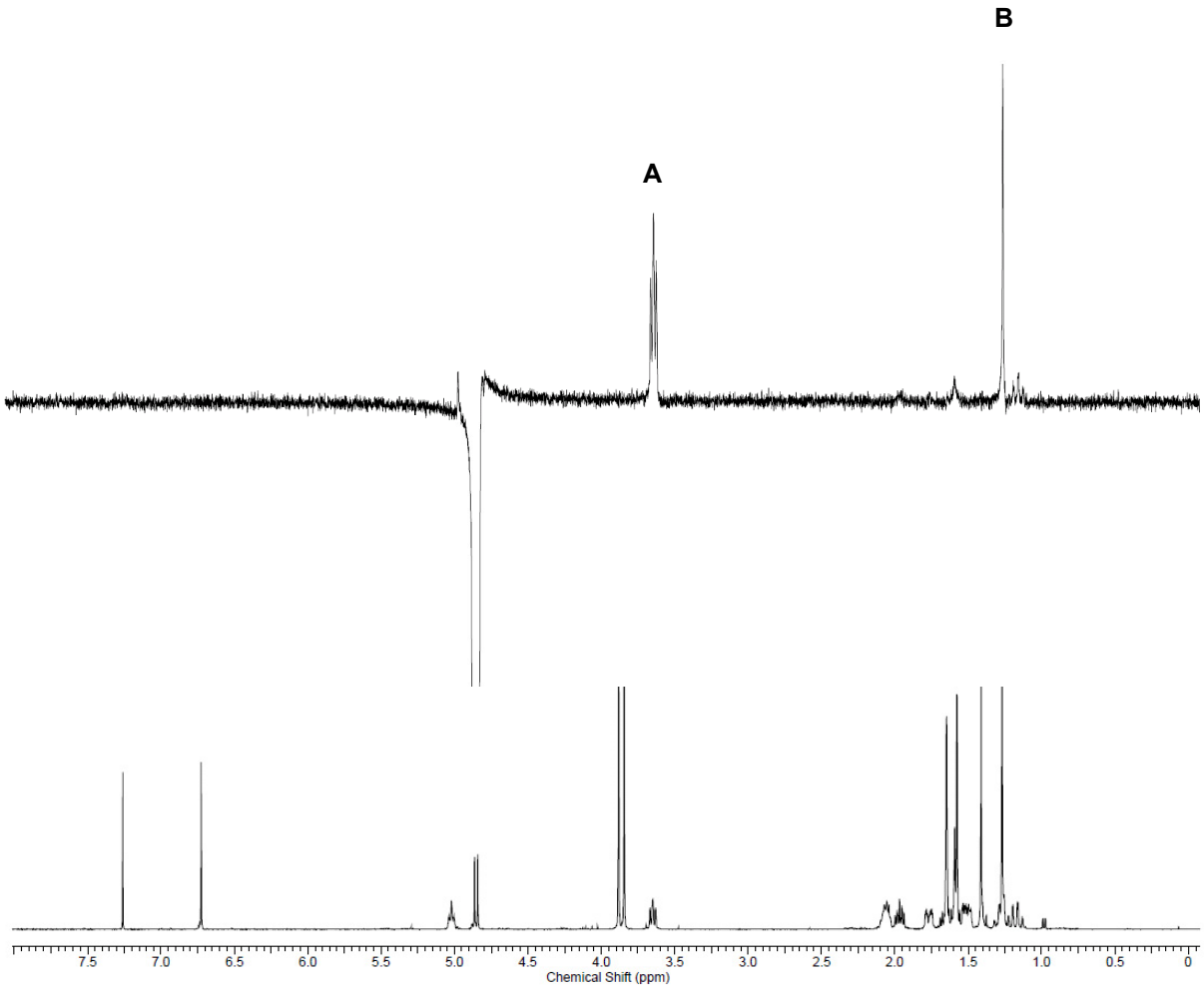
5

NOE 4.85 ppm

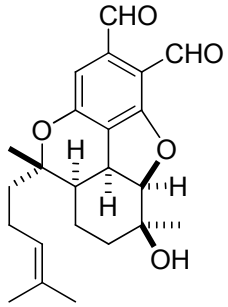


[x-ray]

Acquisition Time (sec)	2.5559	*Comment*	00701217-E281-485	*Date*	Jul 8 2012	*Date Stamp*	Jul 8 2012
File Name	C:\DOCUME~1\AMENDC01\LOCALS~1\TEMP\GAINS9193.TMP\PRODUCTION\UNITYH\AMENDC01\00701217-E281-485_2012190115707.FID\FID						
Frequency (MHz)	400.20	*Nucleus*	1H	*Number of Transients*	64	*Original Points Count*	16384
Points Count	16384	*Pulse Sequence*	NOESY1D	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2401.1633	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6410.26	*Temperature (degree C)*	25.000



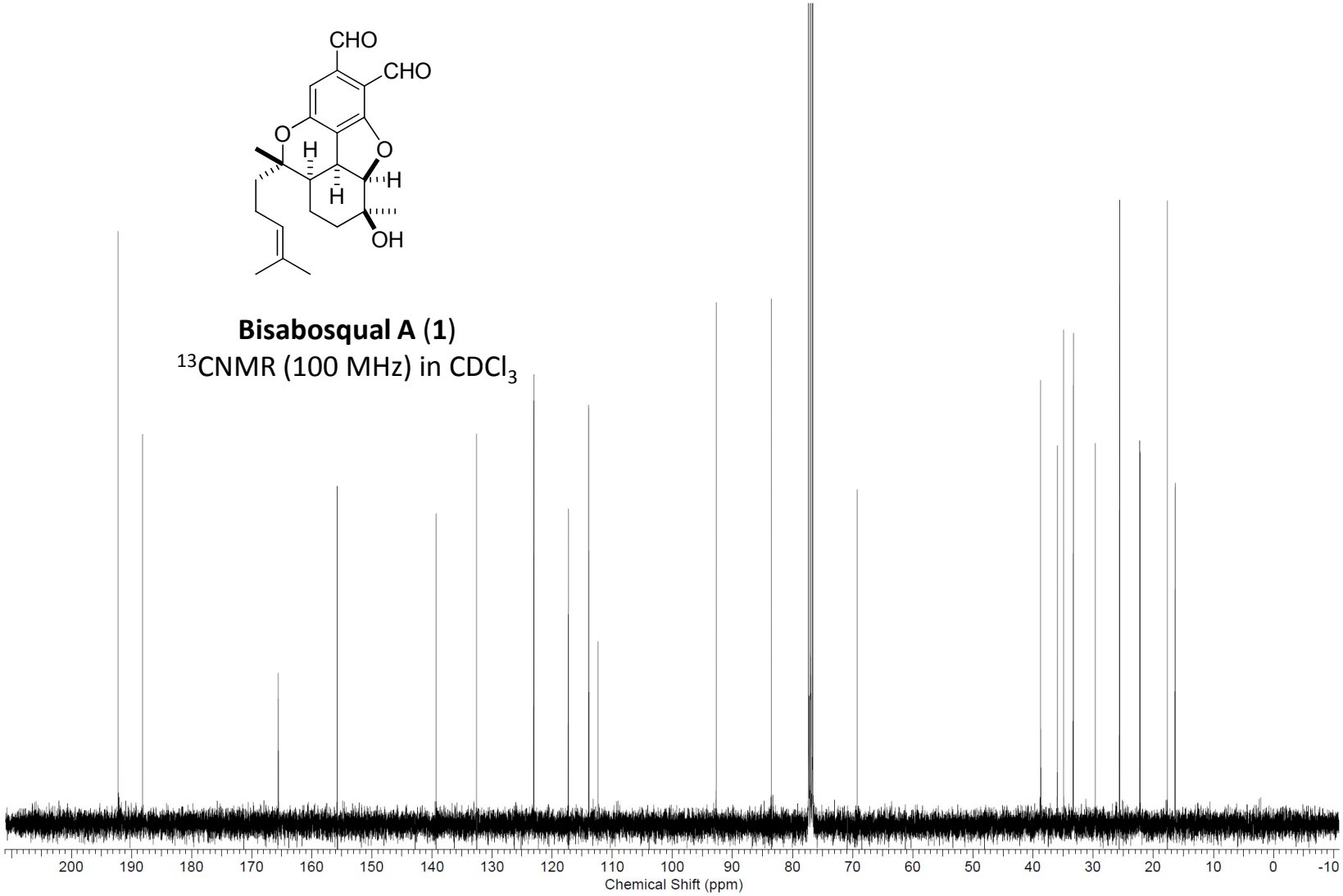
Acquisition Time (sec)	2.5625	***Comment***			
Date	18 Sep 2012 14:12:16	***Date Stamp***	18 Sep 2012 14:12:16		
File Name	\\AMRGROB10025582.AMER.PFIZER.COM\BKDATA:.DATA\AMENDC01\NMR\00701217-BISABOSQUAL\1\FID				
Frequency (MHz)	399.54	***Nucleus***	1H	***Number of Transients***	256
Origin	spect	***Original Points Count***	16384	***Owner***	FCNGRO-BRKOA
Points Count	16384	***Pulse Sequence***	zg30	***Receiver Gain***	322.00
SW(cyclical) (Hz)	6393.86	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	2385.7253
Spectrum Type	STANDARD	***Sweep Width (Hz)***	6393.47	***Temperature (degree C)***	25.150



Bisabosqual A (1)

^{1}HNMR (400 MHz) in $CDCl_3$

Acquisition Time (sec)	1.2788	***Comment***	00701217-Bis-pure			***Date***	Sep 18 2012
Date Stamp	Sep 18 2012	***File Name***	\\UNITYH.PFIZER.COM\AUTO\2012\20120918\00701217-BIS-PURE_20120918_01\CARBON_01.FID\FID				
Frequency (MHz)	100.64	***Nucleus***	13C	***Number of Transients***	16384	***Original Points Count***	28544
Points Count	32768	***Pulse Sequence***	s2pul	***Receiver Gain***	40.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	10063.7373	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	22321.43	***Temperature (degree C)***	25.000



Bisabosqual A (1)

^{13}CNMR (100 MHz) in $CDCl_3$