A Wharton-Fragmentation-Based Approach to the Carbocyclic Core of the Phomoidrides

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Supporting Information

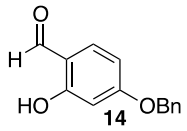
Contents

1. General Experimental Methods

The NMR data are reported as follows: chemical shift in ppm on the δ scale, multiplicity (app = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, coupling constants (Hz), and integration. ^{1}H NMR spectra were either recorded at ambient temperature at 300 MHz or 400 MHz. ^{13}C NMR spectra were recorded at ambient temperature at 100 MHz. For ^{1}H NMR spectra acquired in $CDCl_3$, chemical shifts are reported as δ values in ppm and are calibrated according to internal $CHCl_3$ (7.26 ppm). For ^{1}H NMR spectra acquired in DMSO-**d**$_6$, chemical shifts are reported as δ values in ppm and are calibrated according to internal DMSO (2.50 ppm). For ^{13}C NMR spectra, chemical shifts are reported as δ values in ppm relative to chloroform and DMSO. Infrared spectra (IR) were obtained on an FTIR spectrophotometer and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra were acquired on electrospray ionization (ESI) spectrometer and were obtained by peak matching. Single-crystal X-ray analyses were performed by Susie Miller or Brian Newell of Colorado State University.

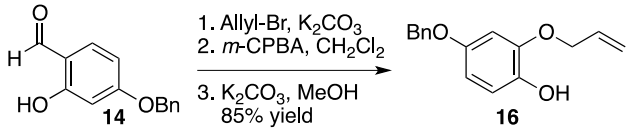
Analytical thin-layer chromatography (TLC) was performed using 0.25 mm precoated silica gel plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on silica gel (SiO_2) 60 Å (200-400 mesh). Unless otherwise noted all reactions were carried out using flame-dried or oven-dried glassware and inert atmosphere operations were conducted under N_2 (g) passed through a Drierite drying tube. CEM Discover Microwave was utilized for reactions performed under microwave irradiation. Anhydrous tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), toluene, and diethyl ether (Et_2O) were filtered through two columns of activated basic alumina and transferred under Ar (g) according to the method described by Grubbs.[1] Anhydrous toluene wasfiltered through one column of activated basic alumina and one column of Q5 reactant, copper (II) oxide oxygen scavenger. Anhydrous acetonitrile (CH_3CN), dimethylsulfoxide (DMSO), and 1,2-dichloroethane were purchased from Aldrich and used without further purification. Triethylamine (Et_3N) was dried by distillation from CaH_2 under nitrogen. Zinc (II) chloride ($ZnCl_2$) was purchased as a 0.5 M solution in THF. All other commercial reagents were used as received, unless noted otherwise. Single-crystal X-ray analyses were performed by Susie Miller or Brian Newell of Colorado State University.

2. Experimental Details



4-Benzyloxy-2-(hydroxy)benzaldehyde (14) To a stirred solution of 2,4-dihydroxy benzaldehyde (20.0 g, 145 mmol, 1 equiv) in acetone (290 mL, 0.5 M) at room temperature was added K_2CO_3 (18.0 g, 130 mmol, 0.9 equiv) and benzyl bromide (10.3 mL, 86.9 mmol. 0.6 equiv) and the resulting mixture heated at reflux until TLC analysis (30% EtOAc / hexanes) indicated the consumption of benzyl bromide. The reaction mixture was cooled to room temperature and the solids were removed by filtration through celite. The filtrate was concentrated under reduced pressure and the resulting oil purified by gravity column chromatography (5, 10 then 20% EtOAc / hexanes until the product is recovered) to afford **14** (16.5 g, 83% based on benzyl bromide) as a purple solid.

1: R_f 0.59 (20% EtOAc / hexanes); IR (CH_2Cl_2 cast) 2833, 1643, 1626, 1576, 1371, 1338, 1228, 1215, 1121 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.48 (s, 1H), 9.72 (s, 1H), 7.46 – 7.32 (m, 6H), 6.62 (dd, J = 8.8, 2.2 Hz, 1H), 6.52 (d, J = 2.2 Hz, 1H), 5.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 166.0, 164.6, 135.8, 135.4, 128.9, 128.6, 127.7, 115.5, 109.1, 101.8, 70.6; HRMS (ESI) calcd for $C_{14}H_{13}O_3$ [M+H^+] 229.0859; found 229.0857.



2-Allyloxy-4-(benzyloxy)benzaldehyde To a stirred solution of **14** (16.5 g, 72.3 mmol, 1 equiv) in acetone (145 mL, 0.5 M) at room temperature was added K_2CO_3 (20.0 g, 145 mmol, 2.0 equiv) and allyl bromide (8.0 mL, 94.0 mmol, 1.3 equiv) and the resulting mixture heated at reflux for 6 hours, at which time NMR analysis of a crude reaction aliquot indicated the consumption of **14**. The reaction mixture was cooled to room temperature and the solids were removed by filtration through celite. The celite was rinsed with EtOAc (2 x 50 mL) and the filtrate was concentrated under reduced pressure to afford the allyl ether as a crude oil. This was carried forward in the next step without additional purification.

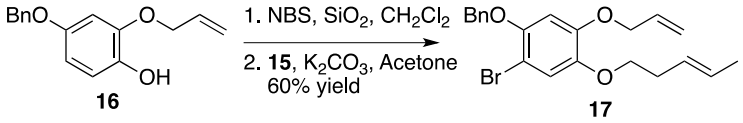
2-Allyloxy-4-(benzyloxy)phenol (16) Crude allyl ether was suspended in CH_2Cl_2 (580 mL, 0.125 M) and to this was added *m*-CPBA (25.0 g, 101 mmol, 1.4 equiv, 70%

pure). The resulting reaction mixture was heated at reflux until for 6 hours, at which time NMR analysis of a crude reaction aliquot indicated the consumption of starting material. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. This was re-suspended in EtOAc (500 mL), added to a 2L separatory funnel and washed successively with saturated aqueous $NaHCO_3$ solution (6x150 mL), eventually resulting in the aqueous layer being clear and colorless. A sample of the organic layer was concentrated and analyzed by NMR analysis, which showed complete removal of the *m*-CBA by-product from the desired formate ester.

Into the separptory funnel containing the organic layer was then added MeOH (75 mL) and saturated aqueous K_2CO_3 solution (50 mL), and this was shook for ca. 10 minutes. A sample of the resulting dark colored organic layer was concentrated and analyzed by NMR analysis, which indicated complete cleavage of the formate ester (as indicated by the loss of the formate ester peak). To the separatory funnel was then added water (600 mL) and the resulting bi-layer separated. The organic layer was then washed with brine, dried over magnesium sulfate, filtered and concentrated. Phenol **16** was recovered as a brown solid (15.8 g, 85% over three steps), and was sufficiently pure for use in the subsequent reaction without additional purification.

Allyl Ether: R_f 0.59 (20% EtOAc / hexanes); IR (CH_2Cl_2 cast) 2849, 1677, 1600, 1499, 1454, 1259, 1182 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.46 – 7.30 (m, 5H), 6.61 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.51 (d, *J* = 2.1 Hz, 1H), 6.12 – 5.96 (m, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.09 (s, 2H), 4.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 165.4, 162.8, 136.2, 132.5, 130.7, 129.0, 128.6, 127.8, 119.5, 118.3, 107.1, 100.1, 70.6, 69.3; HRMS (ESI) calcd for $C_{17}H_{17}O_3$ $[M+H^+]$ 269.1172; found 269.1170.

16: R_f 0.59 (20% EtOAc / hexanes); IR (thin film/NaCl) 3327 (bs), 3088 (w), 3035 (w), 2911 (w), 2861 (w), 1836 (w), 1621 (m), 1513 (s), 1453 (s), 1423 (m), 1404 (m), 1378 (m), 1360 (m), 1266 (s), 1235 (m), 1219 (m), 1176 (s), 1125 (s), 1027 (s), 999 (m) cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.43 – 7.31 (m, 5H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 6.48 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.04 (ddd, *J* = 22.6, 10.6, 5.5 Hz, 1H), 5.39 (dd, *J* = 17.3, 1.3Hz, 1H), 5.31 (dd, *J* = 10.5, 1.2 Hz, 2H), 4.99 (s, 2H), 4.56 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDC1_3$) δ 152.5, 145.9, 140.1, 137.1, 132.6, 128.5, 127.9, 127.5, 118.4, 114.2, 106.0 101.6, 70.8, 69.8; HRMS (FAB) calcd for $C_{16}H_{16}O_3$ $[M^+]$ 256.1099; found 256.1099.



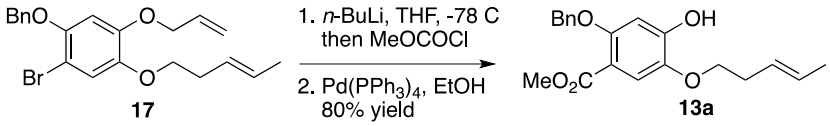
2-Allyloxy-4-benzyloxy-5-bromophenol To a stirred solution of **16** (12.0 g, 46.8 mmol, 1.0 equiv) in CH_2Cl_2 (470 mL, 0.1 M) at room temperature was added SiO_2 (11.3 g, 187 mmol, 4.0 equiv) and NBS (10.0 mL, 56.2 mmol, 1.2 equiv) and the resulting mixture stirred overnight at room temperature at which time NMR analysis of a crude reaction aliquot indicated the consumption of **16**. The reaction was then filtered through celite and washed with EtOAc (2 x 100 mL), and the filtrate concentrated under reduced

pressure. The crude oil was purified by column chromatography (30% EtOAc / hexanes until the product was recovered) to afford the bromophenol (13.3 g, 85%) as a red oil.

To a stirred solution of bromophenol (32.5 g, 97.0 mmol, 1.0 equiv) in acetone (250 mL, 0.4 M) at room temperature was added K_2CO_3 (33.5 g, 242 mmol, 2.5 equiv) and alkyl iodide **15** (47.5 g, 242.0 mmol, 2.5 equiv) and the resulting mixture heated at reflux for 48 hours, at which time TLC analysis (20% EtOAc / hexanes) indicated the near consumption of bromophenol. The reaction mixture was cooled to room temperature, and to it was added EtOAc (400 mL) and water (400 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 200 mL). The combined organic extracts were washed with water, brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (5, 10 then 20% EtOAc / hexanes until the product was recovered) to afford **17** (27.3 g, 70%, 76% BRSM) and recovered bromophenol (2.7g).

Bromophenol: R_f 0.44 (30% EtOAc / hexanes); IR (CH_2Cl_2 cast) 3032, 2834, 1627, 1504, 1454, 1335, 1289, 1216, 1117 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 5H), 7.13 (s, 1H), 6.53 (s, 1H), 5.98 (ddt, J = 16.1, 10.8, 5.4 Hz, 1H), 5.34 (d, J = 17.6 Hz, 1H), 5.30 (d, J = 10.8 Hz, 1H), 5.05 (s, 2H), 4.50 (d, J = 5.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 145.1, 141.3, 136.9, 132.4, 128.7, 128.1, 127.5, 118.94, 118.87, 104.2, 102.5, 72.8, 70.4; HRMS (ESI) calcd for $C_{16}H_{14}BrO_3$ $[M–H]^-$ 333.0132; found 333.0128.

17: R_f 0.61 (20% EtOAc / hexanes); IR (CH_2Cl_2 cast) 3029, 2932, 1503, 1454, 1397, 1211, 1020 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.20 (m, 5H), 7.00 (s, 1H), 6.50 (s, 1H), 5.92 (ddt, J = 16.6, 10.4, 5.1 Hz, 1H), 5.58 – 5.34 (m, 2H), 5.27 (d, J = 17.2 Hz, 1H), 5.16 (d, J = 10.4 Hz, 1H), 4.99 (s, 2H), 4.42 (d, J = 4.0 Hz, 2H), 3.86 (t, J = 7.0 Hz, 2H), 2.40 (app q, J = 6.4 Hz, 2H), 1.60 (d, J = 5.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 148.6, 144.4, 136.8, 133.3, 128.7, 128.1, 127.9, 127.4, 126.7, 119.4, 117.9, 104.4, 103.3, 72.3, 70.7, 70.1, 32.8, 18.2; HRMS (ESI) calcd for $C_{21}H_{24}BrO_3$ $[M+H^+]$ 403.09033; found 403.09016.



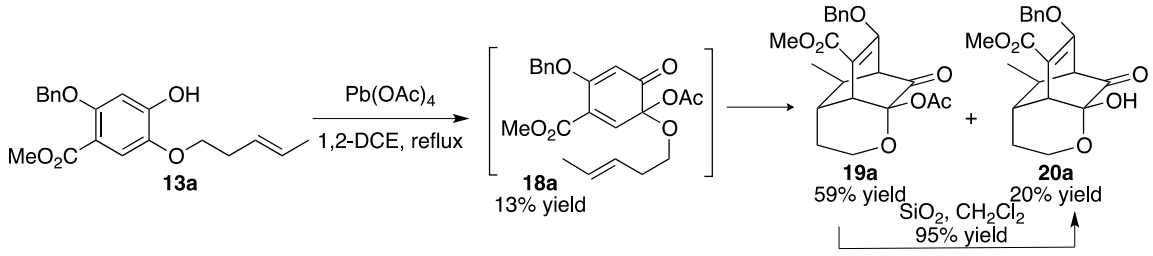
Methyl Ester Aryl bromide **17** was dried by azeotropic distillation with toluene until a constant weight (10.8 g, 26.8 mmol, 1.0 equiv) was achieved. To the flask was then added THF (270 mL, 0.1 M) and the resulting solution cooled to -78 ºC. To this was added *n*-BuLi (22.0 mL, 34.8 mmol, 1.3 equiv, 1.6 M in hexanes) and the reaction mixture was stirred at -78 ºC for 8 minutes, after which methyl chloroformate (12.4 mL, 161 mmol, 6.0 equiv) was rapidly added. The reaction was stirred for an additional 30 minutes at -78 ºC at which time TLC analysis (30% EtOAc / hexanes) indicated the consumption of **5**. The reaction mixture was warmed to room temperature, and to it was added EtOAc (200 mL) and water (200 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 200 mL). The combined organic extracts were

washed with water, brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (5, 15 then 30% EtOAc / hexanes until the product was recovered) to afford the methyl ester (8.2 g, 80%) as an oil.

Phenol 13a A stirred solution of methyl ester (60 mg, 0.16 mmo1, 1.0 equiv) in absolute EtOH (1.6 mL) was heated to reflux. $Pd(PPh_3)_4$ (16 mg, 0.016 mmol, 0.1 equiv) was then added, and the reaction was refluxed for 3 h. EtOH solvent was evaporated under reduced pressure and the residue chromatographed on silica gel (gradient elution, 4% to 14% EtOAc in hexanes) to afford **13a** as a pale yellow amorphous solid (54 mg, 100% yield).

Methyl Ester: R_f 0.48 (30% EtOAc / hexanes); IR (thin film/NaCl) 3027 (w), 2924 (m), 2857 (w), 1723 (s), 1697 (m), 1606 (m), 1585 (w), 1513 (s), 1453 (m), 1438 (s), 1412 (m), 1384 (s), 1247 (s), 1214 (s), 1079 (m), 1023 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.29 (m, 6H), 6.54 (s, 1H), 6 (ddd, *J* = 22.4, 10.5, 5.1 Hz, 1H), 5.61 – 5.48 (m, 2H), 5.38 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.27 (dd, *J* =10.6, 1.3Hz, 1H), 5.13 – 5.11 (m, 2H), 4.56 (d, *J* = 5.2 Hz, 2H), 3.99 (q, *J* = 7 Hz, 2H), 3.87 (s, 3H), 2.49 (dd, *J* = 13.6, 6.8, Hz, 2H), 1.68 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 166.5, 154.8, 153.4, 143.2, 137.4, 133.0, 129.2, 128.9, 128.2, 127.5, 127.0, 118.4, 117.7, 112.7, 103.0, 72.7, 70.2, 70.1, 52.2, 33.1, 18.5; HRMS (EI) calcd for $C_{23}H_{26}O_5$ [M^+] 382.1780; found 382.1767.

13a: R_f 0.46 (30% EtOAc / hexanes);IR (thin film/NaC1) 3390 (bs), 3028 (w), 2947 (m), 2879 (w), 1722 (m), 1691 (m), 1587 (m), 1513 (s), 1445 (s), 1383 (m), 1249 (s), 1216 (s), 1173 (s), 1078 (m), 1025 (m) cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.51-7.3 (m, 6H), 6.64 (s, 1H), 6.04 (s, 1H), 5.59-5.45 (m, 2H), 5.11 (s, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.87 (s, 3H), 2.46 (dd, *J* = 6.5, 13.1 Hz, 2H), 1.69 (dd, *J* = 1.2, 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDC1_3$) δ 166.7, 155.4, 151.4, 140, 137.3, 128.9, 128.3, 128.1, 127.8, 127.6, 127.3, 126.8, 116.2, 111.5, 102.3, 71.8, 69.9, 52.3, 32.9, 18.5; HRMS (EI) calcd for $C_{20}H_{22}O_5$ [$M+H^+$] 343.1545; found 343.1549.



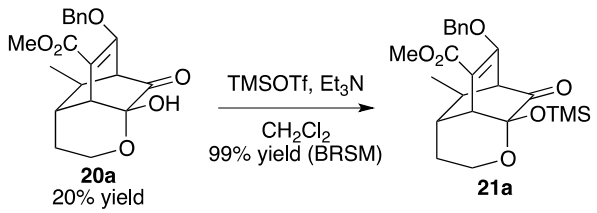
Phenolic Oxidation / Diels-Alder Sequence To a stirred solution of **7** (200 mg, 0.58 mmol, 1.0 equiv) in 1,2-dichloroethane (21 mL) heated to reflux was added lead tetraacetate (340 mg, 0.77 mmol, 1.3 equiv), and the mixture was allowed to reflux for 48 h. At this point, solids were removed by filtration over a celite plug rinsing with CH_2C1_2, and solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel to afford **18a** as a pale red oil (31 mg, 13% yield), **19a** as a pale yellow oil (138 mg, 59% yield), and **20a** as a pale yellow oil (47 mg, 20% yield).

Hemiketal 19a To a solution of **19a** (6.6 g, 13.9 mmol, 1.0 equiv) in CH_2Cl_2 (139 mL, 0.1 M) was added SiO_2 (26.4 g, 4 g / g of **19a**) and the reaction mixture stirred overnight at room temperature, at which time TLC analysis (50% EtOAc / hexanes) indicated the consumption of **19a**. The reaction mixture was passed through a plug of silica, eluting with 50% EtOAc / hexanes, which afforded hemi-ketal **20a** (5.6 g, 95%) as a yellow oil.

18a: R_f 0.44 (30% EtOAc / hexanes); IR (thin film/NaCl) 3066 (w), 3030 (w), 2953 (w), 2856 (w), 1742 (s), 1674 (s), 1580 (m), 1499 (w), 1454 (w), 1346 (w), 1405 (w), 1368 (m), 1279 (s), 1235 (s), 1191 (m), 1127 (m), 1075 (m), 1043 (w), 1012 (m), 976 (m) cm^{-1}; ^1H NMR (500 MHz, $CDC1_3$) δ 7.41 – 7.30 (m, 5H), 6.84 (s, 1H), 5.62 (s, 1H), 5.53 – 5.47 (m, 1H), 5.39 – 5.33 (m, 1H), 5.05 (dd, *J* = 31.9, 12.0 Hz, 2H), 3.8 (s, 3H), 3.79 – 3.65 (m, 2H), 2.32 – 2.22 (m, 2H), 2.12 (s, 3H), 1.64 – 1.60 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.0, 169.9, 165.2, 164.1, 141.3, 134.8, 130.3, 129.1, 128.9, 128.1, 127.6, 126.7, 101.2, 93.0, 71.7, 64.8, 53.0, 33.4, 21.0, 18.4; HRMS (FAB) calcd for $C_{22}H_{24}O_7$ [M^+] 423.1420; found 423.1437

19a: R_f 0.21 (30% EtOAc / hexanes); IR (thin film/NaCl) 2954 (w), 2927 (w), 1747 (s), 1719 (m), 1690 (m), 1623 (m), 1437 (m), 1372 (m), 1233 (s), 1284 (w), 1233 (s), 1191 (s), 1129 (m), 1110 (w), 1089 (s), 1060 (m), 1043 (s), 1015 (m), 982 (m) cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.43 – 7.30 (m, 5H), 5.13 (dd, *J* = 48.5, 12.0 Hz, 2H), 4.08 (ddd, *J* = 12.5, 6.0, 2.6 Hz, 1H), 3.79 (d, *J* = 3.4 Hz, 1H), 3.75 (m, 3H), 3.68 (dt, *J* = 17.9, 6.0, 3.8 Hz, 1H), 3.53 (d, 1H), 2.08 – 2.01 (m, 2H), 1.99 (s, 3H), 1.9 (dddd, *J* = 3.4, 3.4, 3.4, 3.4 Hz, 1H), 1.62 (dddd, *J* = 13.6, 3.0, 3.0, 2.9 Hz, 1H), 1.56 (s, OH), 1.01 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 169.0, 165.2, 163.1, 136.4, 129.0, 128.7, 127.8, 105.7, 94.1, 72.7, 62.3, 58.0, 52.0, 42.7, 38.1, 36.5, 29.1, 21.4, 21.0; HRMS (FAB) calcd for $C_{22}H_{25}O_7$ [M+H^+] 401.1600; found 401.1610.

20a: R_f 0.21 (50% EtOAc / hexanes); IR (thin film/NaCl) 2954 (w), 2927 (w), 1747 (s), 1719 (m), 1690 (m), 1623 (m), 1437 (m), 1372 (m), 1233 (s), 1284 (w), 1233 (s), 1191 (s), 1129 (m), 1110 (w), 1089 (s), 1060 (m), 1043 (s), 1015 (m), 982 (m) cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.40 – 7.31 (m, 5H), 5.11 (s, 2H), 3.91 (dd, *J* =12.2, 5.3 Hz, 1H), 3.75 (s, 3H), 3.58 (ddd, *J* = 12.2, 12.2, 2.3 Hz, 1H), 3.41 (d, *J* = 2.7 Hz, 1H), 3.30 (d, *J* = 3.4 Hz, 1H), 2.15 – 2.10 (m, 1H), 2.05 – 1.96 (m, 1H), 1.92 (t, *J* = 3.4 Hz, 1H), 1.62 (dd, *J* = 13.6, 2.1 Hz, 1H), 1.05 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, CDC13) δ 205.9, 163.7, 159.2, 134.8, 127.6, 127.4, 126.3, 108.1, 89.4, 71.3, 60.3, 56.4, 50.7, 42.0, 36.7, 33.9, 28.2, 19.4; HRMS (FAB) calcd for $C_{20}H_{23}O_6$ [M+H^+] 359.1495; found 359.1506.



Small-Scale:

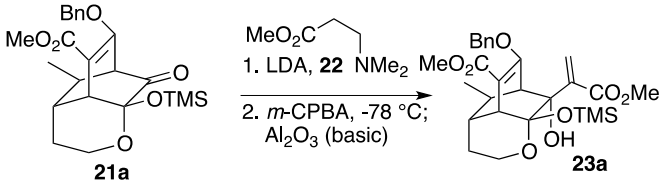
TMS Ketal 21a Hemi-ketal **20a** (23 mg, 0.066 mmol, 1.0 equiv) was dissolved in TMSCN (100 μL, 0.73 mmol, 11 equiv) and the reaction was stirred for 5 min. Solvent (CAUTION: TMSCN liberates HCN gas upon reaction with water) was evaporated under reduced pressure to afford pure **21a** (28 mg, 99% yield).

Large-Scale:

TMS Ketal 21a To a stirred solution of **20a** (2.9 g, 8.1 mmol, 1 equiv) in CH_2Cl_2 (81 mL, 0.1 M) at -78 ºC was added Et_3N (1.5 mL, 10.5 mmol, 1.3 equiv) followed by TMSOTf (1.6 mL, 8.9 mmol, 1.1 equiv) and the resulting mixture stirred at -78 ºC for 5 minutes, at which time TLC analysis (50% EtOAc / hexanes) indicated the consumption of **9**. The reaction quenched by the addition of saturated $NaHCO_3$ solution (40 mL), EtOAc (100 mL) and water (100 mL), and allowed to warm to room temperature. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic extracts were washed with water, brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (50% EtOAc / hexanes until the product was recovered) to afford **21a** (1.9 g, 55% yield, 99% BRSM) as a yellow oil and recovered **20a** (1.3 g).

Note: A common side product observed when employing TMSCN in large-scale reactions was the cyanohydrin product. This has been partially characterized: ^{1}H NMR shows two TMS signals; HRMS (TOF LCMS) calcd for $C_{27}H_{39}NO_6Si_2$ [M+Na^+] 552.23159, found 562.23032.

21a: R_f 0.21 (50% EtOAc / hexanes); IR (thin film/NaCl) 2955 (s), 2873 (w), 1748 (s), 1694 (s), 1622 (s), 1498 (w), 1454 (m), 1437 (m), 1376 (m), 1333 (w), 1283 (w), 1248 (s), 1195 (s), 1152 (s), 1038 (s), 980 (m), 945 (m), 846 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.06 (s, 2H), 3.87 (dd, *J* = 12.6, 5.6 Hz, 1H), 3.76 (s, 3H), 3.53 (td, *J* = 12.7, 2.9 Hz, 1H), 3.34 (d, *J* = 2.8 Hz, 1H), 3.18 (d, *J* = 3.4 Hz, 1H), 2.08 (qdd, *J* =10.2, 6.8, 3.3 Hz, 1H), 1.98 – 1.90 (m, 1H), 1.84 (t, *J* = 3.3 Hz, 1H), 1.54 (dd, *J* = 13.6, 1.4 Hz, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDC1_3$) δ 206.0, 164.9, 160.5, 136.1, 128.6, 128.2, 127.3, 109.0, 92.3, 72.2, 61.3, 58.0, 51.3, 45.7, 37.8, 35.3, 29.2, 20.5, 1.5; HRMS (EI) calcd for $C_{23}H_{31}O_6Si$ [M+H^+] 431.1900; found 431.1889



Enolate of 22 To a solution of diisopropylamine (210 μL, 1.47 mmol, 1.5 equiv) in THF (920 μL) at –20 ºC was added *n*-BuLi (730 μL, 1.17 mmol, 1.2 equiv, 1.6 M

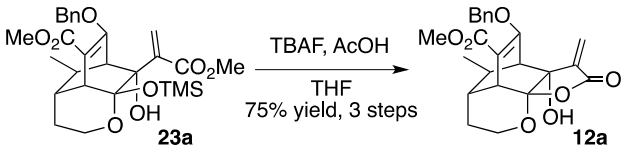
hexanes solution) dropwise over five minutes. The resultant mixture was stirred at –20 ºC for five minutes, and then cooled to –78 ºC for thirty minutes. To this mixture was added methyl-3-(dimethylamino)propionate **22** (140 μL, 0.98 mmol) dropwise over five minutes. The reaction mixture was stirred at –78 ºC for thirty minutes; warmed to 0 ºC and stirred for 15 min; warmed to room temperature and stirred for 15 min. This resulted in a orange / yellow slurry that was employed in the subsequent transformation. Any other consistency in the enolate mixture was found to be ineffective in the reaction.

Tertiary Amine A A solution of TMS ether ketone **21a** (120 mg, 0.28 mmol) in THF (2.8 mL + 1 mL) was added to enolate of **22** (0.95 mL, 0.98 mmol, 3.5 equiv, 0.5M solution) dropwise over 1 min at –78 °C. The solution was slowly warmed from –78 ºC to 0 ºC over three hours. At which point the reaction mixture was cooled to –78 ºC and treated with 1M AcOH in THF (5mL) and allowed to warm to room temperature. At which point the reaction mixture was treated with water (5mL) and ethyl acetate (5mL). The aqueous layer was extracted with EtOAc (2 x 10mL), and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification via silica gel chromatography (10% methanol / CH_2Cl_2) furnished **tertiary amine A** (140 mg, 89%) as an orange oily residue.

Unsaturated Ester 23a Tertiary amine (102 mg, 0.18 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (2 mL) and cooled to –78 ºC at which point mCPBA (61 mg, 0.27 mmol, 1.5 equiv) was added. The reaction was stirred at –78 ºC for 20 min at which time basic Alumina (200 mg) was added and the cold reaction mixture was quickly transferred to a short basic alumina column and filtered eluting with 10% Methanol / CH_2Cl_2. The collected fractions contain both the desired unsaturated ester **23a** and the intermediate *N*-oxide. Upon slow rotary evaporation with warming, the *N*-oxide is converted to the desired compound. Purification via silica gel chromatography (40% EtOAc / Hexanes) furnished **23a** (88 mg, 95% yield) as a clear oily residue.

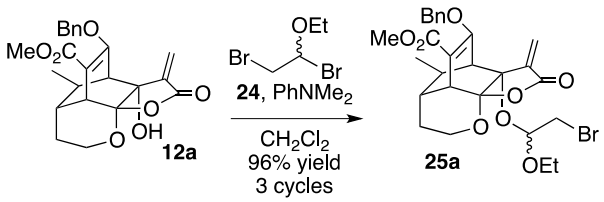
Tertiary Amine: FTIR (NaCl/thin film) 2951 (m), 1701 (s), 1624 (m), 1454 (m), 1435 (m), 1390 (m), 1375 (m), 1351 (m), 1331 (m), 1315 (w), 1295 (m), 1258 (m), 1246 (s), 1194 (m), 1182 (m), 1159 (m), 1125 (w), 1107 (w), 1089 (w), 1058 (w), 1043 (w), 1031 (w), 1013 (w), 991 (w), 956 (w), 930 (w), 911 (w), 900 (w), 864 (m), 842 (m), 791 (w), 783 (w), 757 (w), 735 (w), 697 (w), 668 (w), 649 (w), 612 (w), 594 (w), 572 (w), 557 (w), 538 (w), 524 (w), 512 (w), 504 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 5H), 5.10 (d, *J* = 11.8 Hz, 1H), 4.92 (d, *J* = 11.8 Hz, 1H), 4.56 (td, *J* = 12.3, 4.0 Hz, 1H), 3.92 (dd, *J* = 11.7, 6.4 Hz, 1H), 3.75 (s, 3H), 3.52 (s, 3H), 3.07 (t, *J* = 10.5 Hz, 1H), 2.95 (dd, *J* = 10.2, 3.5 Hz, 1H), 2.92 (d, *J* = 2.9 Hz, 1H), 2.81 (br, 1H), 2.66 (d, *J* = 2.3 Hz, 1H), 2.42 (ddd, *J* = 7.0, 4.7, 2.3 Hz, 1H), 2.20 (s, 6H), 1.89 (tdd, *J* = 13.1, 6.8, 3.9 Hz, 1H), 1.62 (dt, *J* = 3.4, 3.2 Hz, 1H), 1.47 (t, *J* = 3.7 Hz, 1H), 0.91 (d, J = 7.1 Hz, 3H), 0.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 165.7, 165.3, 137.0, 128.6, 128.0, 127.3, 106.0, 99.7, 80.6, 72.1, 63.2, 59.8, 54.6, 51.6, 51.3, 49.8, 47.9, 46.2, 38.9, 29.3, 28.9, 21.9, 2.2; HRMS (TOF LCMS) calcd for $C_{29}H_{44}NO_8Si$ $[M+H^+]$ 562.28362; found 562.28324.

23a: FTIR (NaCl/thin film) 3445 (br), 2954 (m), 1703 (s), 1622 (m), 1453 (m), 1437 (m), 1394 (m), 1352 (m), 1324 (m), 1293 (m), 1280 (m), 1258 (m), 1246 (m), 1194 (m), 1162 (m), 1124 (m), 1116 (m), 1088 (m), 1058 (m), 1037 (m), 1022 (m), 990 (m), 957 (m), 913 (m), 864 (m), 842 (m), 814 (m), 784 (m), 735 (m), 696 (m), 661 (m), 636 (m), 608 (m), 559 (m), 538 (m), 529 (m), 512 (m), 505 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 5.85 (s, 1H), 5.80 (s, 1H), 5.48 (s, 1H), 5.40 (d, *J* = 11.9 Hz, 1H), 4.92 (d, *J* = 11.9 Hz, 1H), 4.63 (td, *J* = 12.1, 4.3 Hz, 1H), 3.92 (dd, *J* = 11.8, 6.2 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.92 (d, *J* = 2.8 Hz, 1H), 2.89 (d, *J* = 2.2 Hz, 1H), 2.52 (ddd, *J* = 7.0, 4.8, 2.2 Hz, 1H), 1.91 (tdd, *J* = 12.8, 6.9, 4.0 Hz, 1H), 1.67 (dt, *J* = 13.3, 3.0 Hz, 1H), 1.54 (t, *J* = 3.6 Hz, 1H), 1.00 (d, *J* = 7.1 Hz, 3H), 0.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 164.6, 163.7, 141.8, 135.4, 127.0, 126.6, 126.1, 118.9, 104.8, 97.9, 79.8, 72.2, 61.4, 51.9, 50.3, 49.7, 46.0, 38.4, 27.6, 27.5, 20.2, 0.0; HRMS (TOF LCMS) calcd for $C_{27}H_{37}O_8Si$ [M+H^+] 517.22577; found 517.22379.



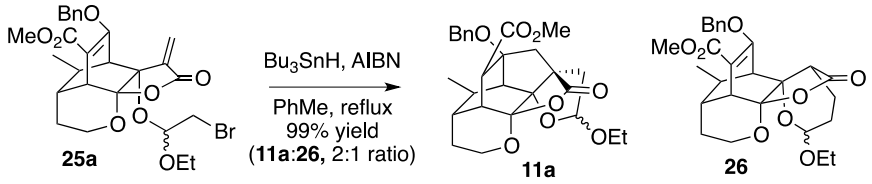
Exo-Methylene Lactone 12a To a solution of TMS-ether **23a** (43mg, 0.083 mmol) in THF (1 mL) was added glacial AcOH (24 μL, 0.416 mmol, 5 equiv) and TBAF (420 μL, 0.416 mmol, 5 equiv, 1.0 M THF solution) at 0 ºC. The mixture was stirred at 0 ºC for 30 min, allowed to warm to room temperature for 2.5 h. At this time, additional equivalences of TBAF were added at hourly intervals until reaction was complete by TLC. The reaction was quenched by the addition of water (2 mL) and diluted with EtOAc (5 mL). The aqueous layer was extracted with EtOAc (2 x 5mL), and the combined organic layers were washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. Purification via silica gel chromatography (50% EtOAc / Hexanes) furnished **12a** (30 mg, 88%) as a white foam.

12a: R_f 0.26 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 3409 (br), 2953 (w), 2924 (w), 1772 (s), 1686 (m), 1619 (m), 1454 (m), 1438 (m), 1401 (m), 1376 (m), 1317 (m), 1286 (m), 1260 (m), 1222 (m), 1194 (m), 1151 (m), 1125 (m), 1101 (m), 1083 (m), 1041 (m), 1006 (m), 986 (m), 961 (m), 911 (m), 733 (m), 697 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.45 (m, 5H), 6.28 (s, 1H), 5.76 (s, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 12.0 Hz, 1H), 4.39 (ddd, *J* = 13.1, 9.7, 4.9 Hz, 1H), 4.11 (ddd, *J* = 11.4, 6.4, 4.7 Hz, 1H), 3.70 (s, 3H), 3.41 (br, 1H), 3.35 (d, *J* = 3.0, 1H), 3.08 (d, *J* = 2.3 Hz, 1H), 2.30 (ddd, *J* = 7.0, 4.6, 2.4 Hz, 1H), 1.98-2.10 (m, 1H), 1.66-1.78 (m, 1H), 0.97 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.4, 164.7, 141.1, 136.3, 128.8, 128.5, 127.5, 126.6, 104.6, 103.6, 76.2, 72.6, 64.1, 52.5, 51.8, 42.5, 39.1, 31.7, 29.0, 21.3; HRMS (TOF LCMS) calcd for $C_{23}H_{25}O_7$ [M+H^+] 413.16003; found 413.15974.



Bromoacetal 25a Alcohol **12a** (1.32 g, 3.25 mmol) was dissolved in CH_2Cl_2 (32.5 mL, 0.1 M) and treated with $PhNMe_2$ (8.3 mL, 65.0 mmol, 20 equiv) and **24** (4.35 mL, 32.5 mmol, 10 equiv) at room temperature. The solution stirred at room temperature for 16 h. The reaction was diluted with EtOAc (50 mL) and washed with 1N aqueous HCl (3 x 30 mL), followed by water and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was loaded onto silica and purified by column chromatography (30 then 50% EtOAc / hexanes until the products were recovered) to yield **25a** (950 mg wet) as an orange oil, and recovered **12a** (835 mg). The recovered starting material was re-subjected to the reaction conditions to afford, after a total of 3 cycles, **25a** (1.48 g, 96% BRSM) and **12a** (0.18 g).

12a: R_f 0.51 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 2972 (w), 2953 (w), 2926 (w), 1774 (s), 1703 (m), 1691 (m), 1621 (m), 1453 (m), 1438 (m), 1398 (m), 1376 (m), 1316 (m), 1286 (m), 1257 (m), 1221 (m), 1194 (m), 1150 (m), 1126 (m), 1084 (m), 1072 (m), 1055 (m), 1038 (m), 1014 (m), 913 (w), 735 (m), 697 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (1.3:1 mixture of diastereomers) δ 7.43 – 7.30 (m, 11.5H), 6.53 (s, 1.3H), 6.44 (s, 1.0H), 5.87 (s, 1.3H), 5.62 (s, 1.0H), 5.11 – 4.97 (m, 4.6H), 4.77 – 4.70 (m, 2.3H), 4.58 (td, *J* = 12.4, 3.9 Hz, 1.0H), 4.44 (td, *J* = 11.8, 4.1 Hz, 1.3H), 4.10 – 4.00 (m, 2.3H), 3.71 (s, 3.0H), 3.71 (s, 3.9H), 3.55 – 3.35 (m, 9.2H), 3.21 (m, 2.6H), 3.15 (d, *J* = 2.9 Hz, 1.0H), 2.97 (d, *J* = 2.2 Hz, 1.0H), 2.48 – 2.38 (m, 2.3H), 2.11 – 1.95 (m, 2.3H), 1.82 – 1.65 (m, 4.6H), 1.19 (t, *J* = 7.0 Hz, 3.9H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3.9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 166.0, 164.9, 164.8, 164.7, 164.6, 136.5, 136.3, 136.2, 135.8, 129.0, 128.7, 128.5, 128.4, 127.7, 127.3, 126.4, 105.5, 105.0, 103.8, 97.9, 97.0, 82.0, 81.4, 73.7, 72.9, 63.6, 63.4, 62.6, 61.4, 53.8, 53.3, 51.8, 45.2, 44.3, 40.4, 39.8, 32.5, 32.3, 29.8, 29.2, 28.8, 28.7, 21.5, 21.4, 15.2, 15.0; HRMS (TOF LCMS) calcd for $C_{27}H_{32}BrO_8$ $[M+H^+]$ 563.12806, found 563.12756.

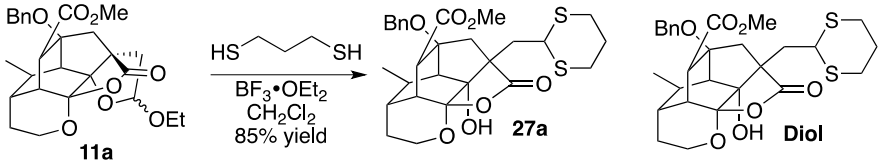


Ethyl Acetal 11a Bromide **25a** (177 mg, 0.315 mmol) was dissolved in toluene (10 mL) and to this was added Bu_3SnH (210 μL, 0.787 mmol, 2.5 equiv) followed by AIBN (155 mg, 0.945 mmol, 3.0 equiv). The mixture was placed in a 115 ºC oil bath and stirred at reflux for one hour, at which time TLC analysis (50% EtOAc / hexanes) indicated the consumption of starting material. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography (10, 25 then 40% EtOAc / Hexanes until the product

was recovered) to yield **11a** (101 mg, 66%) as an oil and cyclization byproduct **26** (52 mg, 33%).

11a: R_f 0.48 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 2953 (m), 2923 (m), 2912 (m), 2359 (m), 2342 (m), 2331 (m), 1786 (s), 1731 (m), 1454 (m), 1435 (m), 1360 (m), 1327 (m), 1299 (m), 1275 (m), 1255 (m), 1245 (m), 1206 (m), 1173 (m), 1142 (m), 1133 (m), 1109 (m), 1071 (m), 1051 (m), 1030 (m), 1003 (m), 986 (m), 961 (m), 934 (m), 914 (m), 886 (w), 734 (w), 697 (w), 677 (w), 668 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (~1:1 mixture of diastereomers) δ 7.26–7.37 (m, 10H), 5.48 (dd, *J* = 5.7, 2.3 Hz, 1H), 5.32 (d, *J* = 4.1 Hz, 1H), 4.49-4.59 (m, 4H), 4.19-4.30 (m, 2H), 3.90-4.05 (m, 2H), 3.75-3.84 (m, 2H), 3.71 (s, 3H), 3.70 (s, 3H), 3.50-3.57 (m, 3H), 3.31-3.40 (m, 1H), 2.83 (d, *J* = 8.8 Hz, 2H), 2.77 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.65-2.72 (m, 2H), 2.56 (d, *J* = 1.8 Hz, 1H), 2.53 (d, *J* = 1.8 Hz, 1H), 2.02-2.28 (m, 6H), 1.90 (dd, *J* = 12.9, 4.2 Hz, 1H), 1.55-1.75 (m, 6H), 1.31 (d, *J* = 7.1 Hz, 3H), 1.29 (d, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 176.8, 176.1, 171.8, 138.5, 128.5, 127.5, 127.0, 126.9, 109.8, 107.5, 106.9, 106.2, 95.2, 94.6, 86.1, 84.7, 66.4, 66.2, 64.1, 63.0, 62.6, 62.3, 56.7, 56.1, 54.0, 53.2, 52.4, 51.2, 44.2, 43.9, 43.1, 42.8, 41.2, 41.1, 40.9, 39.9, 30.8, 30.7, 27.7, 27.5, 20.9, 20.8, 15.4, 14.6; HRMS (TOF LCMS) calcd for $C_{27}H_{33}O_8$ $[M+H^+]$ 485.21754, found 485.21763.

26: R_f 0.40 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 2971, 1781, 1701, 1623, 1439, 1379, 1128, 1087, 1012 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.20 (m, 5H), 5.22 (d, *J* = 12.4 Hz, 1H), 4.96 (d, *J* = 12.4 Hz, 1H), 4.62 (dd, *J* = 4.6, 4.3 Hz, 1H), 4.41 (ddd, *J* = 12.3, 12.3, 3.8 Hz, 1H), 3.95 (dd, *J* = 12.0, 6.6 Hz, 1H), 3.87 (dt, *J* = 8.9, 7.2 Hz, 1H), 3.67 (s, 3H), 3.45 (dt, *J* = 9.0, 7.0 Hz, 1H), 3.12 (d, *J* = 2.7 Hz, 1H), 3.01 (d, *J* = 1.9 Hz, 1H), 2.32 (m, 1H), 2.25 (m, 1H), 2.02 – 1.88 (m, 2H), 1.70 (m, 1H), 1.63 (m, 1H), 1.52 – 1.37 (m, 3H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 165.3, 164.5, 136.3, 128.9, 128.6, 127.5, 106.0, 104.7, 97.2, 81.4, 72.6, 64.3, 63.2, 51.5, 50.4, 43.9, 43.0, 40.3, 29.7, 28.5, 26.8, 21.6, 18.5, 15.1; HRMS (ESI) calcd for $C_{27}H_{33}O_8$ $[M+H^+]$ 485.2170; found 485.2173.

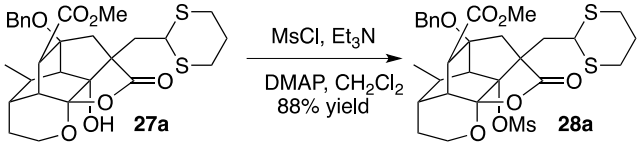


Dithiane 27a Acetal **11a** (35 mg, 0.072 mmol) was dissolved in CH_2Cl_2 (750 μL, 0.1 M), cooled to 0 °C and treated with BF_3•OEt_2 (27 μL, 0.18 mmol, 2.5 equiv) and propanedithiol (18 μL, 0.18 mmol, 2.5 equiv). The reaction mixture was stirred at 0 °C for 45 min at which time TLC analysis (50% EtOAc / hexanes) indicated the consumption of starting material. The reaction was quenched with aqueous saturated $NaHCO_3$ (2 mL) and diluted with EtOAc (10 ml). The aqueous layer was separated and washed with EtOAc (2 x 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (20, 40 then 50% EtOAc / Hexanes until the product

was recovered) to yield **27a** (33 mg, 85%) as a white film and a trace of **diol** as a white foam.

27a: R_f 0.44 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 3451 (br), 2925 (s), 1779 (s), 1735 (s), 1322 (m), 1139 (m), 1081 (m), 983 (m), 669 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 5H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.48 (t, *J* = 6.5 Hz, 1H), 4.35 (td, *J* = 11.5, 4.5 Hz, 1H), 4.07 (ddd, *J* = 11.7, 6.4, 2.6 Hz, 1H), 3.71 (s, 3H), 3.31 (d, *J* = 4.8 Hz, 1H), 3.21 (d, *J* = 13.6 Hz, 1H), 2.94 – 2.80 (m, 5H), 2.55 (d, *J* = 2.0 Hz, 1H), 2.44 – 2.32 (m, 3H), 2.15 (dd, *J* = 15.3, 6.4 Hz, 1H), 2.11 – 1.97 (m, 3H), 1.96 – 1.82 (m, 2H), 1.65 – 1.60 (m, 1H), 1.29 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 171.6, 138.7, 128.5, 127.5, 127.0, 105.5, 83.9, 80.7, 66.1, 63.9, 53.2, 52.5, 52.1, 51.2, 42.1, 41.3, 41.0, 40.4, 39.0, 30.4, 30.2, 27.9, 25.4, 20.8; HRMS (TOF LCMS) calcd for $C_{28}H_{35}O_7S_2$ $[M+H^+]$ 547.18242; found 547.18182.

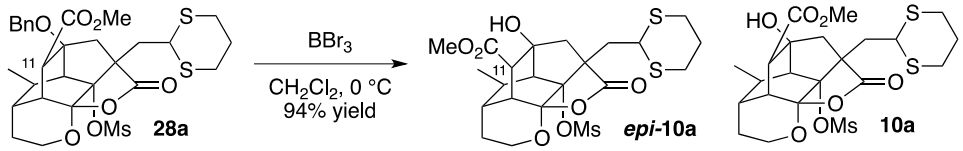
Diol: R_f 0.12 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 3461 (br), 2953 (s), 2910, 1771 (s), 1454, 1435, 1267, 1243, 1204, 1072, 983 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.46 (t, *J* = 6.3 Hz, 1H), 4.34 (ddd, *J* = 11.7, 11.7, 3.4 Hz, 1H), 4.07 (m, 1H), 3.75 (s, 3H), 3.38 (br. s, 1H), 2.92 – 2.78 (m, 5H), 2.48 (s, 1H), 2.37 (t_{AB}, *J* = 16.0 Hz, 2H), 2.30 (dd, *J* = 15.7, 6.3 Hz, 1H), 2.19 (s, 1H), 2.11 (dd, *J* = 15.2, 6.3 Hz, 1H), 2.07 – 1.92 (m, 4H), 1.92 – 1.79 (m, 3H), 1.55 (m, 1H), 1.27 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 171.4, 105.6, 84.8, 76.6, 63.8, 54.9, 54.0, 52.6, 51.3, 47.5, 42.1, 40.8, 38.8, 38.7, 30.3, 30.2, 28.4, 25.4, 20.9; HRMS (ESI) calcd for $C_{21}H_{29}O_7S_2$ $[M+H^+]$ 457.1349; found 457.1352.



Mesylate 28a Alcohol **27a** (705 mg, 1.29 mmol) was dissolved in CH_2Cl_2 (13 mL, 0.1 M), cooled to 0 °C and treated with Et_3N (1.8 mL, 12.9 mmol, 10 equiv), DMAP (315 mg, 2.6 mmol, 2.0 equiv) and then MsCl (752 μL, 9.68 mmol, 7.5 equiv). The solution was allowed to stir and warm to room temperature overnight at which time TLC analysis (50% EtOAc / hexanes) indicated the consumption of starting material. The reaction was quenched with aqueous saturated $NaHCO_3$ (15 mL) and diluted with EtOAc (20 mL). The aqueous layer was extracted with EtOAc (2 x 15 mL). The combined organic layer was washed with water, brine, dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (40% EtOAc / hexanes until the product was recovered) to provide mesylate **28a** (710 mg, 88%) as a white foam.

28a: R_f 0.53 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 2924 (ms), 1781 (m), 1735 (m), 1323 (m), 1185 (m), 1134 (m), 1081 (m), 981 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.36 (m, 5H), 4.85 (dd, *J* = 8.5, 3.4 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.55 (d, *J* = 11.7 Hz, 1H), 4.38 (td, *J* = 12.3, 3.8 Hz, 1H), 4.03 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.72 (s, 3H), 3.35 (d, *J* = 2.3 Hz, 1H), 3.35 (d, *J* = 13.5 Hz, 1H), 3.24 (s, 3H), 2.94 (td, *J* = 27.1, 2.3 Hz, 1H), 2.94 (dt, *J* = 28.3, 2.4 Hz, 1H), 2.85 (s, 1H), 2.74-2.84 (m, 2H), 2.62 (dd, *J* =

13.5, 1.4 Hz, 1H), 2.49-2.58 (m, 3H), 2.25 (dd, *J* = 14.6, 3.4 Hz, 1H), 1.90-2.15 (m, 4H), 1.60-1.66 (m, 1H), 1.31 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 171.2, 138.2, 128.5, 127.6, 127.1, 105.1, 98.0, 81.0, 66.2, 62.7, 52.6, 51.5, 51.4, 50.8, 42.1, 41.6, 40.9, 40.8, 40.5, 40.2, 31.3, 30.6, 30.1, 27.3, 25.5, 20.7; HRMS (TOF LCMS) calcd for $C_{29}H_{37}O_9S_3$ [M+H$^+$] 625.15997; found 625.15963.

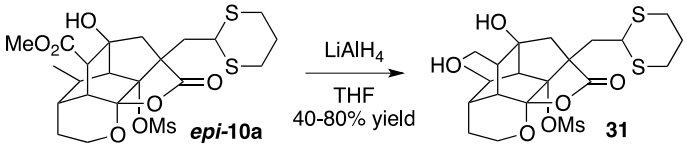


Tertiary alcohols epi-10a and 10a Benzyl ether **28a** (389 mg, 0.62 mmol) was dissolved in CH_2Cl_2 (16 mL, 0.04M) and cooled to 0 °C. To this was added successive portions of BBr_3 (59 μL, 0.62 mmol, 1.0 equiv), and the reaction monitored by TLC (20% EtOAc / benzene) after each portion of BBr_3. Upon consumption of starting material the reaction was quenched by addition of aqueous saturated $NaHCO_3$ (10 mL) and diluted with EtOAc (15 mL). The aqueous layer was separated and washed with EtOAc (2 x 15mL). The combined organic extracts were washed with water, brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (20, 40 then 60% EtOAc/hexanes unitl the products were recovered) to provide alcohol ***epi*-10a** (315 mg, 94%) as a white foam as well as **10a** (12 mg, 4%) as a pale oil.

***epi*-10a**: R_f 0.33 (20% EtOAc/benzene); FTIR (NaCl/thin film) 3848 (w), 2932 (w), 1777 (s), 1770 (s), 1746 (m), 1731 (m), 1722 (m), 1712 (m), 1698 (m), 1680 (m), 1650 (m), 1469 (m), 1462 (m), 1453 (m), 1441 (m), 1434 (m), 1427 (m), 1416 (m), 1337 (s), 1221 (m), 1185 (m), 1151 (s), 1075 (m), 1024 (m), 1000 (m), 969 (m), 958 (m), 916 (m), 883 (m), 845 (m), 814 (m), 778 (m), 735 (m), 701 (m), 631 (w), 579 (w), 527 (w), 505 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (s, 1H), 4.75 (dd, *J* = 8.6, 4.2 Hz, 1H), 4.38 (td, *J* = 12.2, 4.0 Hz, 1H), 4.04 (dd, *J* = 12.4, 5.7 Hz, 1H), 3.77 (s, 3H), 3.26 (s, 3H), 3.05 (d, *J* = 2.3 Hz, 1H), 2.95 (td, *J* = 25.3, 2.6 Hz, 1H), 2.95 (dt, *J* = 25.0, 2.7 Hz, 1H), 2.78-2.87 (m, 2H), 2.73 (d, *J* = 3.2 Hz, 1H), 2.67 (d, *J* = 13.6 Hz, 1H), 2.48-2.56 (m, 2H), 2.32 (dd, *J* = 14.7, 4.2 Hz, 1H), 2.21-2.28 (m, 2H), 2.04-2.14 (m, 1H), 1.79-1.98 (m, 3H), 1.56-1.65 (m, 1H), 1.29 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 173.4, 104.7, 98.4, 73.9, 62.8, 53.0, 52.4, 51.8, 51.4, 46.3, 42.9, 42.4, 40.9, 39.8, 31.8, 31.1, 30.5, 29.6, 26.5, 25.5, 19.7; HRMS (TOF LCMS) calcd for $C_{22}H_{31}O_9S_3$ [M+H$^+$] 535.11302; found 535.11563.

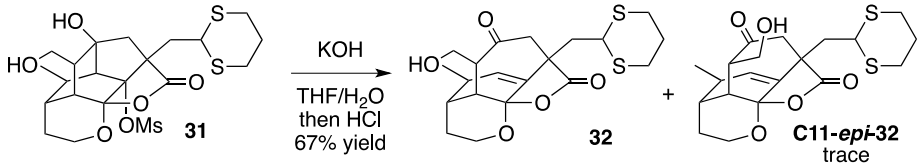
10a: R_f 0.15 (20% EtOAc/benzene); FTIR (NaCl/thin film) 3494, 2928, 1778, 1735, 1337, 1184, 1144, 1107, 1081 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (dd, *J* = 8.5, 3.6 Hz, 1H), 4.29 (ddd, *J* = 12.4, 12.4, 3.8 Hz, 1H), 3.96 (dd, *J* = 12.1, 6.2 Hz, 1H), 3.69 (s, 3H), 3.18 (s, 3H), 3.12 (d, *J* = 2.3 Hz, 1H), 2.96 – 2.78 (m, 2H), 2.77 – 2.66 (m, 3H), 2.56 – 2.39 (m, 4H), 2.37 (d, *J* = 2.7 Hz, 1H), 2.15 (dd, *J* = 14.7, 3.6 Hz, 1H), 2.08 – 1.75 (m, 4H), 1.54 (m, 1H), 1.25 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 170.8, 105.0, 98.2, 76.8, 62.5, 53.8, 52.6, 51.8, 51.4, 46.7, 42.0, 40.9, 40.6, 39.9, 39.5, 31.1,

30.4, 30.0, 27.6, 25.4, 20.7; HRMS (ESI) calcd for $C_{22}H_{30}O_9S_3Na$ [M+Na^+] 557.0944; found 557.0943.



Diol 31 To a stirred solution of ***epi*-10a** (19 mg, 0.035 mmol, 1 eq) in THF (1.8 mL, 0.02 M) was added $LiAlH_4$ (1.2 mg, 0.032 mmol, 0.9 eq) and the mixture was vigorously stirred at RT for up to 15 minutes while monitoring by TLC (80% EtOAc / hexanes). Upon consumption of starting material the reaction was quenched according to the Fieser & Fieser protocol, filtered through celite and concentrated by rotary evaporation. The product was purified by column chromatography (30, 50, then 80% EtOAc / hexanes until the product was recovered) to afford **31** (14 mg, 78%) as a white foam. The yield of this transformation is variable, and typically falls within 40-80%.

31: R_f 0.45 (80% EtOAc / hexanes); IR (CH_2Cl_2 cast) 3448 br., 2926, 1773, 1336, 1079, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.77 (dd, *J* = 8.6, 3.6 Hz, 1H), 4.34 (ddd, *J* = 12.2, 12.2, 3.8 Hz, 1H), 4.13 (ddd, *J* = 10.4, 10.4, 3.8 Hz, 1H), 3.99 (dd, *J* = 12.1, 6.0 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.22 (s, 3H), 3.13 (s, 1H), 3.01 (s, 1H), 3.00 – 2.86 (m, 2H), 2.80 – 2.75 (m, 2H), 2.56 – 2.44 (m, 2H), 2.31 (d, *J* = 12.6 Hz, 1H), 2.25 (d, *J* = 14.7, 3.6 Hz, 1H), 2.14 (dd, *J* = 5.1, 5.1 Hz, 1H), 2.12 – 2.03 (m, 1H), 1.94 – 1.75 (m, 4H), 1.55 (m, 1H), 1.30 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 105.3, 98.5, 75.2, 63.1, 62.6, 54.2, 52.3, 51.5, 43.7, 42.5, 42.1, 40.9, 40.1, 31.3, 31.3, 30.6, 29.9, 26.8, 25.6, 20.1 ; HRMS (TOF LCMS) calcd for $C_{21}H_{30}O_8S_3Na$ [M+Na^+] 529.0995; found 529.0994.

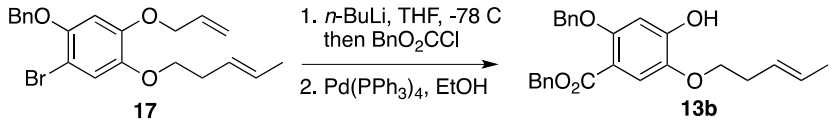


Fragmentation Products 32 and epi-32 To a stirred solution of **31** (13 mg, 0.026 mmol, 1 eq) in THF (1.3 mL, 0.02M) and water (6 μL, 0.5μL/mg) at RT was added solid KOH (5.0 mg, 0.090 mmol, 3.5 eq) and the mixture was vigorously stirred overnight while monitoring by TLC (10% MeOH / CH_2Cl_2). Upon consumption of starting material the reaction was quenched with 200μL of 1N HCl and stirred for 30 minutes. This was then diluted with EtOAc (10 mL) and water (10 mL) and the layers separated. The aqueous layer was then extracted EtOAc (2 x 5 mL) and the combined organic extracts washed with water, bride and dried over magnesium sulfate. This was filtered and concentrated by rotary evaporation. The product was purified by column chromatography (1, 2, 4 then 6% MeOH / CH_2Cl_2 until the product was recovered) to afford **32** (7.0 mg, 67 %) as an oil, as well as a trace of ***epi*-32**.

32: R_f 0.51 (10% MeOH / CH_2Cl_2); IR (CH_2Cl_2 cast) 3371 br., 2926, 1771, 1697, 1424, 1337, 1226, 1117 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.54 (d, *J* = 3.6 Hz, 1H), 4.30 (br. s, 1H), 4.15 (dd, *J* = 8.3, 8.3 Hz, 1H), 3.93 – 3.65 (m, 4H), 3.00 (d, *J* = 3.4 Hz, 1H), 2.93 (m, 1H), 2.88 – 2.67 (m, 5H), 2.83 (d, *J* = 15.1 Hz, 1H), 2.50 (d, *J* = 15.2 Hz, 1H), 2.36 (ddd, *J* = 7.4, 7.4, 3.4 Hz, 1H), 2.13 (dd, *J* = 14.2, 9.4 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.96 – 1.87 (m, 1H), 1.83 – 1.74 (m, 2H), 1.48 (ddd, *J* = 8.7, 8.5, 4.1 Hz, 1H), 1.08 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 177.4, 141.8, 133.9, 107.5, 61.6, 60.3, 59.5, 52.9, 49.8, 47.9, 43.4, 38.7, 38.2, 37.8, 34.7, 29.1, 28.8, 25.5, 19.4; HRMS (ESI) calcd for $C_{20}H_{27}O_5S_2$ [$M+H^+$] 411.1294; found 411.1294.

***epi*-32**: R_f 0.70 (10% MeOH / CH_2Cl_2); IR (CH_2Cl_2 cast) 3371 br., 2926, 1771, 1697, 1424, 1337, 1226, 1117 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (s, 1H), 4.01 (dd, *J* = 10.0, 6.6 Hz, 1H), 3.97 – 3.81 (m, 2H), 3.78 – 3.68 (m, 2H), 2.99 – 2.85 (m, 3H), 2.69 (m, 1H), 2.63 (d, *J* = 11.5 Hz, 1H), 2.62 – 2.49 (m, 2H), 2.45 (d, *J* = 11.3 Hz, 1H), 2.37 (d, *J* = 5.8 Hz, 1H), 2.23 (dd, *J* = 14.7, 6.6 Hz, 1H), 2.18 (m, 1H), 2.11 (s, 1H), 2.00 – 1.89 (m, 3H), 1.75 – 1.70 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 174.6, 138.4, 132.1, 105.0, 61.5, 60.9, 60.5, 55.6, 50.5, 43.1, 40.6, 39.5, 37.0, 35.5, 32.8, 27.6, 27.0, 25.4, 23.6; HRMS (ESI) calcd for $C_{20}H_{27}O_5S_2$ [$M+H^+$] 411.1294; found 411.1297.

Benzyl Ester Series:



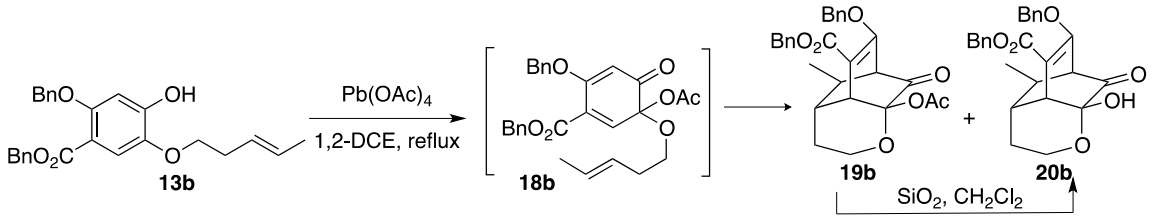
Benzyl Ester Following the procedure for the synthesis of **13a**, compound **17** (1.85g, 5.0 mmol, 1eq) was converted to **benzyl ester** using benzyl chloroformate (2.6 mL, 17.8 mmol, 3.0 eq). The resulting crude product was purified by column chromatography (5, 10 then 20% EtOAc / hexanes until the product was recovered) to afford **benzyl ester** (2.44 g, 89%) as a yellow oil.

Phenol 13b Following the procedure for the synthesis of **13a**, compound **benzyl ester** (2.44 g, 5.31 mmol, 1eq) was converted to **13b**. The resulting crude product was purified by column chromatography (10, 20 then 30% EtOAc / hexanes until the product was recovered) to afford **13b** (2.15 g, 97%) as a clear, colorless oil.

Benzyl Ester: R_f 0.68 (30% EtOAc / hexanes); IR (thin film/NaCl) 3031, 2935, 1720, 1694, 1608, 1514, 1454, 1421, 1383, 1240, 1210, 1024 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52-7.27 (m, 11H), 6.54 (s, 1H), 5.98 (ddd, *J* = 17.2, 10.4, 5.2 Hz, 1H), 5.63 – 5.44 (m, 2H), 5.38 (dd, J_{AB} = 17.0 Hz, 1H), 5.34 (s, 2H), 5.27 (d, *J* = 11.1 Hz, 1H), 5.09 (s, 2H), 4.57 (d, *J* = 5.1 Hz, 2H), 3.98 (t, *J* = 7.1 Hz, 2H), 2.48 (q, *J* = 7.0 Hz, 2H), 1.67 (d, *J* = 5.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 165.9, 154.6, 153.2, 142.8, 136.9, 136.5, 132.8, 128.7, 128.6, 128.3, 128.1, 127.9, 127.4, 127.2, 126.7, 118.1, 117.8, 112.3,

102.4, 72.3, 69.95, 69.88, 66.6, 32.7, 18.2; HRMS (ESI) calcd for $C_{29}H_{30}O_5$ [M+Na^+] 481.1986; found 481.1986.

13b: R_f 0.61 (30% EtOAc / hexanes);IR (thin film/NaC1) 3353 (bs), 2921 (m), 1686 (m), 1586 (m), 1512 (s), 1439 (s), 1382 (m), 1217 (s), 1173 (s), 1025 (m) cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.51 – 7.28 (m, 10H), 6.65 (s, 1H), 6.05 (s, 1H), 5.66 – 5.41 (m, 2H), 5.33 (s, 2H), 5.08 (s, 2H), 4.04 (t, J = 6.6 Hz, 2H), 2.45 (q, J = 6.4 Hz, 2H), 1.69 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDC1_3$) δ 166.1, 155.2, 151.2, 139.7, 136.8, 136.6, 128.7, 128.3, 128.1, 127.9, 127.4, 126.6, 116.3, 111.3, 101.8, 71.6, 69.7, 66.7, 32.7, 18.2; HRMS (ESI) calcd for $C_{26}H_{26}O_5Na$ [M+Na^+] 441.16725; found 441.16735.



Phenolic Oxidation / Diels-Alder Sequence Following the procedure for the synthesis of **19a** from **13a**, compound **13b** (1.36 g, 3.25 mmol, 1eq) was converted to compounds **19b** and **18b**. The crude product was purified by column chromatography (20, 30 then 40% EtOAc / hexanes until the product was recovered) to afford **19b** (1.09 g, 71%) and **18b** (177 mg, 11%).

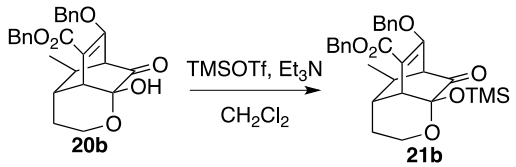
Hemiketal 20b Following the procedure for the synthesis of **20a** from **19a**, compound **19b** (5.45 g, 11.4 mmol, 1eq) was converted to compound **20b**. The crude product was purified by column chromatography (10, 20, 30 then 40% EtOAc / hexanes until the product was recovered) to afford **20b** (3.8 g, 76%) and recovered **19b** (1.4 g, 23%).

18b: R_f 0.41 (30% EtOAc / hexanes); IR (thin film/NaCl) 3033, 2949, 1741, 1673, 1580, 1499, 1456, 1366, 1236, 1126, 1070, 1012 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.36 – 7.21 (m, 10H), 6.84 (s, 1H), 5.61 (s, 1H), 5.56 – 5.41 (m, 1H), 5.37 – 5.27 (m, 1H), 5.18 (q, J_{AB} = 12.3 Hz, 2H), 4.97 (q, J_{AB} = 12.1 Hz, 2H), 3.81 – 3.72 (m, 1H), 3.70 – 3.61 (m, 1H), 2.21 (q, J = 7.1 Hz, 2H), 2.09 (s, 3H), 1.61 (dd, J = 6.2, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 169.7, 165.1, 163.6, 141.2, 135.2, 134.4, 130.3, 128.9, 128.8, 128.7, 128.6, 127.8, 126.5, 125.5, 100.9, 92.8, 71.7, 67.8, 64.5, 64.1, 33.2, 20.9, 18.2; HRMS (ESI) calcd for $C_{28}H_{28}O_7Na$ [M+Na^+] 499.1727; found 499.1722.

19b: R_f 0.21 (30% EtOAc / hexanes); IR (thin film/NaCl) 3032, 2957, 1747, 1682, 1621, 1454, 1406, 1368, 1240, 1189, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.39 – 7.27 (m, 10H), 5.21 (q, J_{AB} = 13.1 Hz, 2H), 5.17 (d, J_{AB} = 11.5 Hz, 1H), 5.05 (d, J_{AB} = 11.5 Hz, 1H), 4.07 (ddd, J = 12.2, 6.2, 2.6 Hz, 1H), 3.81 (d, J = 3.4 Hz, 1H), 3.67 (ddd, J = 12.0, 12.0, 3.6 Hz, 1H), 3.57 (d, J = 2.4 Hz, 1H), 2.11 – 1.98 (m, 2H), 1.91 (m, 1H), 1.84 (s, 3H), 1.58 (dddd, J = 13.8, 6.4, 3.2, 3.2 Hz, 1H), 0.95 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 168.8, 164.4, 163.4, 136.4, 136.1, 128.8, 128.7, 128.5, 128.3,

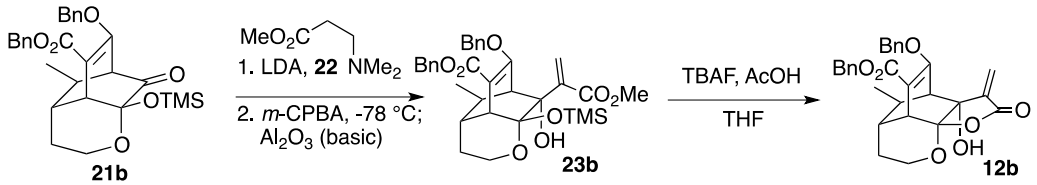
128.2, 127.8, 105.1, 94.9, 72.5, 62.3, 62,1, 57.7, 42.6, 37.9, 36.4, 28.9, 20.9, 20.8; HRMS (ESI) calcd for $C_{28}H_{28}O_7Na$ [M+Na^+] 499.1727; found 499.1732.

20b: R_f 0.08 (30% EtOAc / hexanes); IR (thin film/NaCl) 3390, 2957, 2925, 2871, 1741, 1689, 1617, 1455, 1403, 1363, 1323, 1250, 1176, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.38 – 7.21 (m, 10H), 5.21 (s, 2H), 5.03 (s, 2H), 3.88 (dd, *J* = 12.3, 4,9 Hz, 1H), 3.55 (ddd, *J* = 12.2, 12.2, 3.4 Hz, 1H), 3.47 (br. s, 1H), 3.44 (d, *J* = 2.8 Hz, 1H), 3.33 (d, *J* = 3.4 Hz, 1H), 2.11 (m, 1H), 1.97 (m, 1H), 1.89 (m, 1H), 1.58 (m, 1H), 1.03 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, CDC13) δ 207.2, 164.5, 160.6, 136.3, 135.8, 128.8, 128.7, 128.5, 128.2, 128.1, 127.7, 108.9, 90.7, 72.5, 66.6, 61.6, 57.4, 43.3, 37.9, 35.2, 29.4, 20.6; HRMS (ESI) calcd for $C_{26}H_{26}O_6Na$ [M+Na^+] 457.16216; found 457.16237.



TMS Ketal 21b Following the procedure for the synthesis of **21a** from **20a**, compound **20b** (70 mg, 0.16 mmol, 1eq) was converted to compound **21b**. The crude product was purified by column chromatography (10, 20 then 30% EtOAc / hexanes until the product was recovered) to afford **21b** (66 mg, 81%) as an oil.

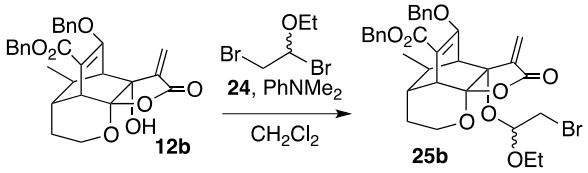
21b: R_f 0.45 (30% EtOAc / hexanes); IR (thin film/NaCl) 2957, 1747, 1693, 1621, 1455, 1402, 1248, 1194, 1093, 1037 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 10H), 5.20 (d, J_{AB} = 12.8 Hz, 1H), 5.16 (d, J_{AB} = 12.8 Hz, 1H), 4.99 (q, J_{AB} = 11.7 Hz, 2H), 3.81 (dd, *J* = 12.7, 5.4 Hz, 1H), 3.48 (ddd, *J* = 12.7, 12.7, 2.4 Hz, 1H), 3.34 (d, *J* = 2.9 Hz, 1H), 3.17 (d, *J* = 3.4 Hz, 1H), 2.03 (m, 1H), 1.88 (m, 1H), 1.80 (m, 1H), 1.47 (m, 1H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDC1_3$) δ 206.1, 164.5, 160.8, 136.5, 135.9, 128.7, 128.6, 128.3, 128.1, 127.9, 127.5, 108.8, 92.4, 72.1, 66.1, 61.4, 57.9, 45.8, 37.8, 35.4, 29.3, 20.6, 1.6; HRMS (ESI) calcd for $C_{29}H_{34}O_6SiNa$ [M+Na^+] 529.20224; found 529.20206.



Tertiary Amine B, Unsaturated Ester 23b and Exo-Methylene Lactone 12b Following the procedure for the synthesis of **12a,** compound **21b** (2.6 g, 5.1 mmol, 1eq) was carried through the exact three-step synthesis, affording **12b** (1.8 g, 73%) as a white foam.

23b: FTIR (NaCl/thin film) 3441, 2955, 1701, 1625, 1439, 1400, 1317, 1247, 1190, 1088, 1057, 1035, 864 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 10H), 5.85 (s, 1H), 5.82 (s, 1H), 5.48 (s, 1H), 5.30 (d, J_{AB} = 12.0 Hz, 1H), 5.22 (d, J_{AB} = 12.4 Hz, 1H), 5.18 (d, J_{AB} = 12.4 Hz, 1H), 4.93 (d, J_{AB} = 11.8 Hz, 1H), 4.59 (ddd, *J* = 11.9, 11.9, 4.5 Hz, 1H), 3.92 (dd, *J* = 11.2, 6.0 Hz, 1H), 3.76 (s, 3H), 2.95 (m, 2H), 2.52 (ddd, *J* = 7.2, 5.1, 2.3 Hz, 1H), 1.89 (dddd, *J* = 12.0, 12.0, 6.8, 4.2 Hz, 1H), 1.68 (m, 1H), 1.56 (m, 1H), 1.00 (d, *J* = 7.1 Hz, 3H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 166.1, 165.0, 143.5, 136.9, 136.5, 128.7, 128.3, 128.2, 127.7, 120.7, 106.4, 99.6, 81.5, 73.5, 66.2, 63.0, 53.3, 52.0, 47.6, 40.0, 29.4, 29.3, 21.9, 1.6; HRMS (ESI) calcd for $C_{33}H_{40}O_8SiNa$ [M+Na^+] 615.23847; found 615.23902.

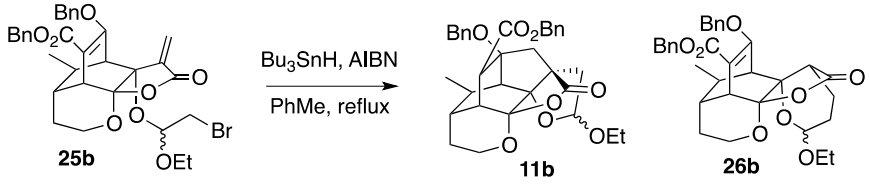
12b: R_f 0.40 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 3423, 2956, 2925, 1773, 1686, 1619, 1455, 1408, 1286, 1260, 1193, 1125, 1083, 1007 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.15 (m, 10H), 6.24 (s, 1H), 5.72 (s, 1H), 5.14 (d, J_{AB} = 12.8 Hz, 1H), 5.06 (d, J_{AB} = 12.8 Hz, 1H), 4.95 (d, J_{AB} = 11.7 Hz, 1H), 4.89 (d, J_{AB} = 11.7 Hz, 1H), 4.33 (ddd, *J* = 11.7, 11.7, 4.9 Hz, 1H), 4.04 (m, 1H), 3.64 (s, 1H), 3.34 (d, *J* = 2.8, 1H), 3.07 (d, *J* = 2.1 Hz, 1H), 2.27 (ddd, *J* = 6.8, 4.4, 2.4 Hz, 1H), 1.97 (m, 2H), 1.68 (m, 1H), 0.92 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.6, 164.3, 141.3, 136.3, 136.1, 128.8, 128.7, 128.5, 128.1, 127.6, 127.5, 126.6, 104.6, 103.5, 76.2, 72.5, 64.2, 52.3, 42.6, 39.1, 31.7, 29.0, 21.3; HRMS (ESI) calcd for $C_{29}H_{28}O_7Na$ [M+Na^+] 511.17327; found 511.17332.



Bromoacetal 25b Following the procedure for the synthesis of **25a** from **12a**, compound **12b** (1.92 g, 3.93 mmol, 1eq) was converted to compound **25b**. The crude product was purified by column chromatography (20, 30, 40 then 50% EtOAc / hexanes until the product was recovered) to afford **25b** (1.59 g, 63%) and recovered **12b** (0.81 g) after the first cycle.

25b: R_f 0.58 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 2924, 2854, 1773, 1682, 1621, 1454, 1406, 1285, 1192, 1084 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (1.2:1 mixture of diastereomers) δ 7.40 – 7.20 (m, 10H), 6.50 (s, 0.5H), 6.47 (s, 0.5H), 5.89 (s, 0.5H), 5.64 (s, 0.5H), 5.22 (d, J_{AB} = 12.4 Hz, 1H), 5.14 (d, J_{AB} = 12.4 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.75 (dd, *J* = 5.1, 5.1 Hz, 0.5H), 4.73 (dd, *J* = 3.6, 3.6, 0.5H), 4.59 (ddd, *J* = 11.8, 11.8, 4.3 Hz, 0.5H), 4.44 (ddd, *J* = 11.6, 11.6, 4.1 Hz, 0.5H), 4.12 – 4.01 (m, 1H), 3.56 – 3.37 (m, 4H), 3.28 (d, *J* = 2.8 Hz, 0.5H), 3.27 (d, *J* = 2.2 Hz, 0.5H), 3.25 (d, *J* = 2.8 Hz, 0.5H), 3.01 (d, *J* = 2.2 Hz, 0.5H), 2.46 (m, 1H), 2.06 (m, 1H), 1.84 – 1.66 (m, 2H), 1.21 (t, *J* = 7.0 Hz, 1.5H), 1.13 (t, *J* = 7.0 Hz, 1.5H), 1.04 (d, *J* = 7.0 Hz, 1.5H), 1.02 (d, *J* = 7.0 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 166.0, 165.2, 165.0, 164.2, 164.1, 136.4, 136.3, 136.2, 136.0, 129.0, 128.8, 128.7, 128.5, 128.4, 128.1, 127.8, 127.5, 126.5, 105.6, 105.1, 103.7, 97.9, 97.1, 82.1, 81.5, 73.7, 72.9, 63.7, 63.5, 62.7, 61.5, 53.8, 53.2, 45.2,

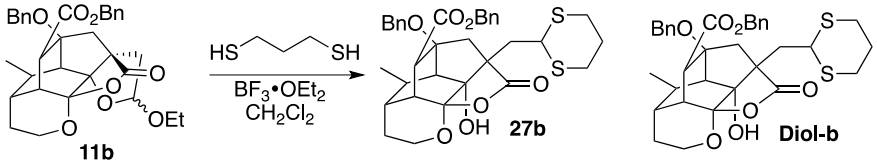
44.4, 40.4, 39.8, 32.6, 32.4, 29.9, 29.3, 28.8, 28.7, 21.4, 15.3, 15.1; HRMS (ESI) calcd for $C_{33}H_{35}BrO_8Na$ [M+Na^+] 661.14075; found 661.14033.



Ethyl Acetal 11b and byproduct 26b Following the procedure for the synthesis of **11a** from **25a**, compound **25b** (2.40 g, 3.75 mmol, 1eq) was converted to compounds **11b** and **26b**. The crude product was purified by column chromatography (10, 20, 30, 40 then 50% EtOAc / hexanes until the product was recovered) to afford **11b** (1.09 g, 52%) and cyclization byproduct **26b** (882 mg, 39%).

11b: R_f 0.60 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 2972, 2925, 1785, 1734, 1454, 1275, 1197, 1174, 1072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (~1:1 mixture of diastereomers) δ 7.33 – 7.12 (m, 10H), 5.50 (dd, J = 5.8, 2.1 Hz, 0.5H), 5.34 (d, J = 4.0 Hz, 0.5H), 5.20 (d, J_{AB} = 12.0 Hz, 1H), 5.09 (d, J_{AB} = 12.0 Hz, 0.5H), 5.08 (d, J_{AB} = 12.0 Hz, 0.5H), 4.44 (d, J_{AB} = 11.6 Hz, 1H), 4.39 (d, J_{AB} = 11.6 Hz, 1H), 4.18 (m, 1H), 3.96 – 3.83 (m, 1H), 3.80 – 3.67 (m, 1H), 3.52 – 3.41 (m, 1H), 3.35 – 3.25 (m, 1H), 2.79 (d, J = 9.4 Hz, 1H), 2.72 (dd, J = 14.2, 6.0 Hz, 0.5H), 2.66 – 2.59 (m, 0.5H), 2.57 (m, 0.5H), 2.53 (m, 0.5H), 2.21 – 2.13 (m, 1H), 2.09 – 1.80 (m, 4H), 1.52 – 1.44 (m, 1H), 1.22 (app t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.0 Hz, 1.5H), 1.08 (t, J = 7.0 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) 176.8, 176.1, 171.2, 138.5, 135.7, 135.6, 128.9, 128.8, 128.6, 128.5, 127.6, 127.0, 126.9, 109.8, 107.6, 106.9, 106.3, 95.3, 94.7, 86.2, 84.8, 67.3, 66.4, 66.2, 64.1, 63.0, 62.7, 62.3, 56.7, 56.1, 54.0, 53.1, 51.5, 51.4, 44.3, 43.9, 43.1, 42.7, 41.3, 41.2, 40.9, 39.9, 30.7, 30.7, 27.8, 27.6, 20.9, 20.8, 15.4, 14.7; HRMS (ESI) calcd for $C_{33}H_{36}O_8Na$ [M+Na^+] 583.23024; found 583.22974.

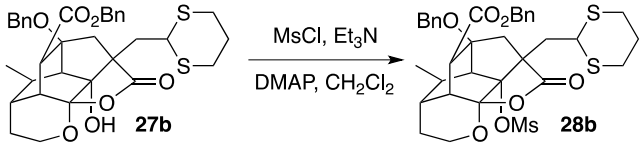
26b: R_f 0.48 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 2968, 2912, 1780, 1690, 1454, 1377, 1255, 1127, 1088, 1043 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 10H), 5.26 – 5.20 (m, 2H), 5.16 (d, J_{AB} = 12.7 Hz, 1H), 4.95 (d, J_{AB} = 12.2 Hz, 1H), 4.66 (dd, J = 4.6, 4.6 Hz, 1H), 4.46 (ddd, J = 12.4, 12.4, 3.8 Hz, 1H), 4.01 (dd, J = 11.7, 6.6 Hz, 1H), 3.92 (dq, J = 9.1, 7.0 Hz, 1H), 3.50 (dq, J = 9.0, 7.0 Hz, 1H), 3.24 (d, J = 2.8 Hz, 1H), 3.05 (d, J = 2.0 Hz, 1H), 2.39 (dd, J = 7.4, 4.6, 1H), 2.31 (m, 1H), 2.08 – 1.96 (m, 2H), 1.77 (m, 1H), 1.66 (m, 1H), 1.58 – 1.41 (m, 3H), 1.23 (t, J = 7.0 Hz, 3H), 1.07 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 165.6, 164.0, 136.3, 136.2, 128.9, 128.7, 128.6, 128.1, 127.7, 106.1, 104.8, 97.4, 81.5, 72.9, 66.3, 64.4, 63.3, 50.6, 44.1, 43.1, 40.4, 29.8, 28.6, 26.9, 21.8, 18.6, 15.2; HRMS (ESI) calcd for $C_{33}H_{36}O_8Na$ [M+Na^+] 561.24829; found 561.24695.



Dithiane 27b Following the procedure for the synthesis of **27a** from **11a**, compound **11b** (1.06 g, 1.89 mmol, 1eq) was converted to compounds **27b**. The crude product was purified by column chromatography (15, 30 then 45% EtOAc / hexanes until the product was recovered) to afford **27b** (920 mg, 78%) as a white foam as well as a trace amount of **Diol-b**.

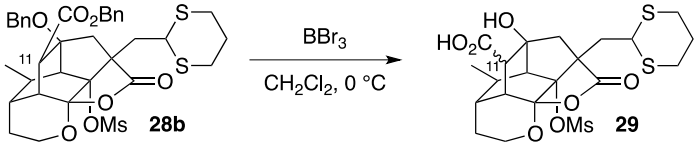
27b: R_f 0.59 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 3445, 3031, 2908, 1775, 1733, 1454, 1368, 1258, 1203, 1165, 1072, 983 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.13 (m, 10H), 5.13 (d, J_{AB} = 12.2 Hz, 1H), 5.03 (d, J_{AB} = 12.2 Hz, 1H), 4.49 – 4.38 (m, *3*H), 4.28 (ddd, *J* = 11.5, 11.5, 4.5 Hz, 1H), 3.99 (ddd, *J* = 11.3, 6.1, 2.8 Hz, 1H), 3.26 (s, 1H), 3.11 (d, *J* = 13.6 Hz, 1H), 2.87 – 2.73 (m, 5H), 2.47 (d, *J* = 2.1 Hz, 1H), 2.33 (d, *J* = 13.6 Hz, 1H), 2.30 (d, *J* = 2.6 Hz, 1H), 2.29 (dd, *J* = 15.2. 6.6 Hz, 1H), 2.08 (dd, *J* = 15.1, 6.4 Hz, 1H), 2.04 – 1.88 (m, 3H), 1.87 – 1.75 (m, 2H), 1.54 – 1.44 (m, 1H), 1.21 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 171.0, 138.6, 135.5, 128.8, 128.7, 128.5, 128.4, 127.4, 127.0, 105.5, 83.9, 80.8, 67.3, 66.0, 63.8, 53.0, 52.3, 51.1, 42.1, 41.2, 40.8, 40.4, 39.0, 30.3, 30.2, 27.9, 25.4, 20.7; HRMS (ESI) calcd for $C_{34}H_{38}O_7S_2Na$ [M+Na^+] 645.19512; found 645.19493.

Diol-b: R_f 0.31 (50% EtOAc / hexanes); FTIR (NaCl/thin film) 3466, 2909, 1773, 1454, 1242, 1168, 1072, 1026, 909 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.29 (m, 5H), 5.20 (d, J_{AB} = 12.1 Hz, 1H), 5.09 (d, J_{AB} = 12.1 Hz, 1H), 4.45 (t, *J* = 6.4 Hz, 1H), 4.32 (ddd, *J* = 11.5, 11.5, 4.2 Hz, 1H), 4.02 (ddd, *J* = 11.2, 6.2, 2.2 Hz, 1H), 3.45 (br. s, 1H), 2.94 – 2.78 (m, 5H), 2.48 (d, *J* = 2.6 Hz, 1H), 2.41 (d, J_{AB} = 14.3 Hz, 1H), 2.35 (d, J_{AB} = 14.3 Hz, 1H), 2.31 (dd, *J* = 15.1, 6.2 Hz, 1H), 2.20 (d, *J* = 2.6 Hz, 1H), 2.11 (dd, *J* = 15.3, 6.6 Hz, 1H), 2.07 – 1.79 (m, 5H), 1.53 (m, 1H), 1.26 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 170.9, 135.3, 129.0, 128.9, 128.7, 105.6, 84.9, 76.6, 67.6, 63.7, 54.8, 54.0, 51.1, 47.2, 42.1, 40.7, 38.8, 38.7, 30.3, 30.2, 28.1, 25.4, 20.9; HRMS (ESI) calcd for $C_{27}H_{32}O_7S_2Na$ [M+Na^+] 555.14817; found 555.14797.



Mesylate 27b Following the procedure for the synthesis of **17a** from **27a**, compound **27b** (385 mg, 0.618 mmol, 1eq) was converted to compound **28b**. The crude product was purified by column chromatography (5, 10 then 20% EtOAc / benzene until the product was recovered) to afford **28b** (270 mg, 62%) as a white foam, and recovered **27b** (97 mg, 25%).

28b: R_f 0.53 (20% EtOAc / benzene); FTIR (NaCl/thin film) 2926, 1781, 1732, 1455, 139, 1184, 1150, 1081, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 10H), 5.20 (d, J_{AB} = 12.1 Hz, 1H), 5.09 (d, J_{AB} = 12.1 Hz, 1H), 4.83 (dd, J = 8.6, 3.0 Hz, 1H), 4.54 – 4.42 (m, 2H), 4.36 (ddd, J = 12.6, 12.6, 3.8 Hz, 1H), 4.00 (ddd, J = 12.1, 12.1, 6.4 Hz, 1H), 3.35 – 3.24 (m, 2H), 3.23 (s, 3H), 3.05 – 2.71 (m. 5H), 2.63 – 2.45 (m, 3H), 2.23 (dd, J = 14.3, 3.0 Hz, 1H), 2.12 – 1.76 (m, 5H), 1.66 (m, 1H), 1.28 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 170.7, 138.2, 135.4, 129.0, 128.8, 128.7, 128.5, 127.6, 127.1, 105.2, 98.1, 81.2, 67.6, 66.2, 62.7, 51.8, 51.5, 50.7, 42.2, 41.4, 41.0, 40.7, 40.5, 40.3, 31.4, 30.7, 30.1, 27.4, 25.6, 20.7; HRMS (ESI) calcd for $C_{35}H_{40}O_9S_3Na$ [M+Na^+] 723.17267; found 723.17141.

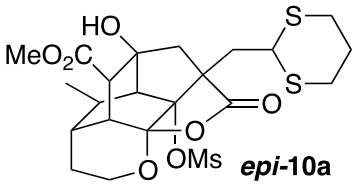


Acids 29 Benzyl ether **28b** (40 mg, 0.057 mmol) was dissolved in CH_2Cl_2 (1 mL, 0.06M) and cooled to 0 °C. To this was added successive portions of BBr_3 (5.0 μL, 0.57 mmol, 1.0 equiv), and the reaction monitored by TLC (20% EtOAc / benzene) after each portion of BBr_3. Upon consumption of starting material the reaction was quenched by addition of aqueous saturated $NaHCO_3$ (10 mL) and diluted with EtOAc (10 mL). The aqueous layer was separated and washed with EtOAc (2 x 15mL). The combined organic extracts were washed with water, brine and concentrated *in vacuo*. The residue was purified by column chromatography (0 then 10% MeOH/CH_2Cl_2 until the products were recovered) to provide a epimeric mixture of acids **29** (23 mg, 77%) as a white foam.

Acid: R_f 0.51 (10% MeOH/CH_2Cl_2); HRMS (ESI) calcd for $C_{21}H_{27}O_9S_3Na$ [M+Na^+] 543.0793; found 543.0828.

In order to assure that the products were the acids, they were subjected to ethereal CH_2N_2 and the newly formed products isolated. Both were found to be identical to compounds **10a** and ***epi*-10a** by NMR spectroscopy.

3. X-ray Data



***epi*-10a**

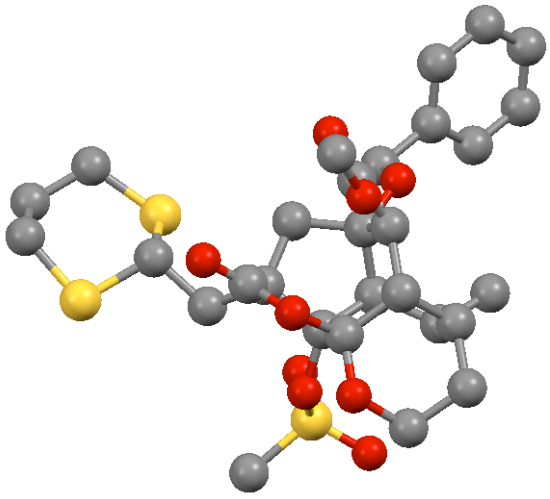


Table 1. Crystal data and structure refinement for **wood02 (C11-*epi-10a)*.**

Identification code	wood02	
Empirical formula	C22 H30 O9 S3	
Formula weight	534.64	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.0924(3) Å	α= 107.430(2)∞.
	b = 9.1537(4) Å	β= 91.471(2)∞.
	c = 14.5615(6) Å	γ = 96.663(2)∞.
Volume	1146.15(8) $Å^3$	
Z	2	
Density (calculated)	1.549 Mg/m^3	
Absorption coefficient	0.377 mm^{-1}	
F(000)	564	
Crystal size	0.30 x 0.25 x 0.15 mm^3	
Theta range for data collection	2.35 to 33.23°.	
Index ranges	-12<=h<=13, -14<=k<=14, -22<=l<=22	
Reflections collected	32393	
Independent reflections	8602 [R(int) = 0.0344]	
Completeness to theta = 33.23∞	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9463 and 0.8953	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8602 / 0 / 311	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.1118	
R indices (all data)	R1 = 0.0569, wR2 = 0.1210	
Largest diff. peak and hole	0.987 and -0.428 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (≈^{2}x 10^3) for wood02. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8564(2)	-505(2)	1244(1)	19(1)
C(2)	8447(2)	-1887(2)	1637(1)	19(1)
C(3)	8340(2)	-1436(2)	2719(1)	16(1)
C(4)	6818(2)	1088(2)	2649(1)	13(1)
C(5)	5383(2)	1778(2)	2960(1)	13(1)
C(6)	5070(1)	3277(2)	2759(1)	11(1)
C(7)	6210(2)	4636(2)	3301(1)	13(1)
C(8)	3950(2)	5596(2)	3639(1)	12(1)
C(9)	3556(1)	3801(2)	3128(1)	10(1)
C(10)	4916(2)	3157(2)	1675(1)	12(1)
C(11)	3616(2)	4045(2)	1574(1)	11(1)
C(12)	2492(1)	3547(2)	2238(1)	11(1)
C(13)	4097(2)	5845(2)	1994(1)	13(1)
C(14)	3427(2)	6470(2)	2968(1)	13(1)
C(15)	1163(2)	4464(2)	2459(1)	12(1)
C(16)	3863(2)	6661(2)	1248(1)	15(1)
C(17)	2606(2)	8415(2)	728(1)	21(1)
C(18)	93(2)	4162(2)	1571(1)	17(1)
C(19)	1718(2)	6210(2)	2918(1)	13(1)
C(20)	1218(2)	6874(2)	3934(1)	15(1)
C(21)	1899(2)	6152(2)	4640(1)	15(1)
C(22)	2326(2)	1338(2)	4812(1)	25(1)
O(1)	7528(1)	4720(1)	3320(1)	17(1)
O(2)	5539(1)	5874(1)	3782(1)	15(1)
O(3)	3497(1)	6141(1)	4567(1)	14(1)
O(4)	2987(1)	3581(1)	620(1)	15(1)
O(5)	4588(2)	6496(1)	554(1)	25(1)
O(6)	2830(1)	7601(1)	1434(1)	19(1)
O(7)	3052(1)	3141(1)	3871(1)	12(1)
O(8)	2008(1)	463(1)	2919(1)	19(1)
O(9)	380(1)	2233(1)	3838(1)	22(1)

S(1)	6910(1)	441(1)	1349(1)	16(1)
S(2)	6712(1)	-529(1)	3147(1)	16(1)
S(3)	1814(1)	1717(1)	3753(1)	12(1)

Table 3. Bond lengths [≈] and angles [∞] for wood02.

C(1)-C(2)	1.531(2)
C(1)-S(1)	1.8086(15)
C(2)-C(3)	1.514(2)
C(3)-S(2)	1.8146(15)
C(4)-C(5)	1.5361(19)
C(4)-S(1)	1.8130(15)
C(4)-S(2)	1.8275(14)
C(5)-C(6)	1.5409(19)
C(6)-C(7)	1.5218(19)
C(6)-C(10)	1.5510(19)
C(6)-C(9)	1.5659(19)
C(7)-O(1)	1.1908(17)
C(7)-O(2)	1.3618(18)
C(8)-O(3)	1.3846(17)
C(8)-O(2)	1.4366(16)
C(8)-C(14)	1.534(2)
C(8)-C(9)	1.5803(19)
C(9)-O(7)	1.4486(17)
C(9)-C(12)	1.5408(18)
C(10)-C(11)	1.5387(19)
C(11)-O(4)	1.4095(16)
C(11)-C(12)	1.5477(19)
C(11)-C(13)	1.580(2)
C(12)-C(15)	1.5365(19)
C(13)-C(16)	1.516(2)
C(13)-C(14)	1.532(2)
C(14)-C(19)	1.5410(19)
C(15)-C(18)	1.5344(19)
C(15)-C(19)	1.553(2)
C(16)-O(5)	1.2003(19)
C(16)-O(6)	1.3253(18)
C(17)-O(6)	1.4626(18)
C(19)-C(20)	1.525(2)
C(20)-C(21)	1.533(2)

C(21)-O(3)	1.4610(17)
C(22)-S(3)	1.7431(16)
O(7)-S(3)	1.5839(10)
O(8)-S(3)	1.4296(12)
O(9)-S(3)	1.4333(12)

C(2)-C(1)-S(1)	113.96(11)
C(3)-C(2)-C(1)	113.22(13)
C(2)-C(3)-S(2)	114.52(10)
C(5)-C(4)-S(1)	112.43(9)
C(5)-C(4)-S(2)	102.50(9)
S(1)-C(4)-S(2)	111.49(8)
C(4)-C(5)-C(6)	120.34(12)
C(7)-C(6)-C(5)	111.37(11)
C(7)-C(6)-C(10)	110.73(11)
C(5)-C(6)-C(10)	114.66(11)
C(7)-C(6)-C(9)	103.72(11)
C(5)-C(6)-C(9)	112.96(11)
C(10)-C(6)-C(9)	102.57(10)
O(1)-C(7)-O(2)	120.52(13)
O(1)-C(7)-C(6)	128.35(13)
O(2)-C(7)-C(6)	111.11(11)
O(3)-C(8)-O(2)	102.75(10)
O(3)-C(8)-C(14)	113.01(12)
O(2)-C(8)-C(14)	109.74(11)
O(3)-C(8)-C(9)	115.86(11)
O(2)-C(8)-C(9)	105.73(11)
C(14)-C(8)-C(9)	109.20(11)
O(7)-C(9)-C(12)	117.95(11)
O(7)-C(9)-C(6)	111.72(10)
C(12)-C(9)-C(6)	107.64(11)
O(7)-C(9)-C(8)	106.22(10)
C(12)-C(9)-C(8)	108.62(10)
C(6)-C(9)-C(8)	103.74(10)
C(11)-C(10)-C(6)	105.51(11)
O(4)-C(11)-C(10)	111.82(11)

O(4)-C(11)-C(12)	109.69(11)
C(10)-C(11)-C(12)	102.08(11)
O(4)-C(11)-C(13)	113.35(11)
C(10)-C(11)-C(13)	110.75(11)
C(12)-C(11)-C(13)	108.51(11)
C(15)-C(12)-C(9)	113.24(11)
C(15)-C(12)-C(11)	115.88(11)
C(9)-C(12)-C(11)	98.64(10)
C(16)-C(13)-C(14)	117.12(12)
C(16)-C(13)-C(11)	111.81(11)
C(14)-C(13)-C(11)	109.82(11)
C(13)-C(14)-C(8)	107.84(11)
C(13)-C(14)-C(19)	114.03(12)
C(8)-C(14)-C(19)	106.17(11)
C(18)-C(15)-C(12)	112.53(12)
C(18)-C(15)-C(19)	111.97(12)
C(12)-C(15)-C(19)	110.01(11)
O(5)-C(16)-O(6)	122.83(14)
O(5)-C(16)-C(13)	122.31(14)
O(6)-C(16)-C(13)	114.83(13)
C(20)-C(19)-C(14)	108.05(11)
C(20)-C(19)-C(15)	113.33(12)
C(14)-C(19)-C(15)	109.56(11)
C(19)-C(20)-C(21)	111.45(11)
O(3)-C(21)-C(20)	112.37(12)
C(7)-O(2)-C(8)	113.07(11)
C(8)-O(3)-C(21)	115.30(10)
C(16)-O(6)-C(17)	115.51(12)
C(9)-O(7)-S(3)	127.24(8)
C(1)-S(1)-C(4)	100.44(7)
C(3)-S(2)-C(4)	103.16(7)
O(8)-S(3)-O(9)	117.05(7)
O(8)-S(3)-O(7)	111.17(6)
O(9)-S(3)-O(7)	109.70(6)
O(8)-S(3)-C(22)	111.46(8)
O(9)-S(3)-C(22)	108.93(9)

O(7)-S(3)-C(22)	96.62(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^3) for wood02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

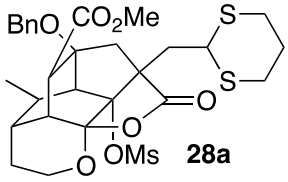
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	18(1)	24(1)	20(1)	9(1)	6(1)	11(1)
C(2)	21(1)	18(1)	19(1)	6(1)	3(1)	9(1)
C(3)	15(1)	18(1)	21(1)	10(1)	2(1)	8(1)
C(4)	12(1)	14(1)	13(1)	6(1)	2(1)	3(1)
C(5)	12(1)	14(1)	15(1)	7(1)	2(1)	3(1)
C(6)	9(1)	12(1)	12(1)	4(1)	1(1)	2(1)
C(7)	15(1)	12(1)	12(1)	5(1)	-1(1)	1(1)
C(8)	9(1)	13(1)	12(1)	3(1)	1(1)	1(1)
C(9)	10(1)	11(1)	10(1)	4(1)	1(1)	1(1)
C(10)	12(1)	15(1)	11(1)	4(1)	2(1)	4(1)
C(11)	12(1)	13(1)	10(1)	4(1)	1(1)	4(1)
C(12)	10(1)	12(1)	10(1)	3(1)	0(1)	2(1)
C(13)	14(1)	14(1)	15(1)	6(1)	4(1)	4(1)
C(14)	14(1)	11(1)	14(1)	4(1)	3(1)	3(1)
C(15)	10(1)	15(1)	13(1)	5(1)	1(1)	2(1)
C(16)	17(1)	14(1)	17(1)	6(1)	4(1)	3(1)
C(17)	26(1)	26(1)	17(1)	13(1)	4(1)	9(1)
C(18)	14(1)	22(1)	16(1)	6(1)	-2(1)	5(1)
C(19)	12(1)	14(1)	15(1)	6(1)	4(1)	5(1)
C(20)	14(1)	16(1)	15(1)	2(1)	4(1)	7(1)
C(21)	14(1)	18(1)	13(1)	4(1)	4(1)	6(1)
C(22)	34(1)	22(1)	20(1)	12(1)	-5(1)	-7(1)
O(1)	12(1)	19(1)	22(1)	7(1)	2(1)	2(1)
O(2)	11(1)	13(1)	18(1)	2(1)	-1(1)	0(1)
O(3)	14(1)	16(1)	9(1)	1(1)	0(1)	2(1)
O(4)	15(1)	22(1)	10(1)	6(1)	1(1)	4(1)
O(5)	33(1)	24(1)	23(1)	11(1)	14(1)	13(1)
O(6)	23(1)	23(1)	17(1)	12(1)	6(1)	12(1)
O(7)	12(1)	12(1)	11(1)	5(1)	1(1)	0(1)
O(8)	19(1)	16(1)	18(1)	0(1)	5(1)	-2(1)
O(9)	13(1)	20(1)	32(1)	8(1)	7(1)	2(1)

S(1)	17(1)	20(1)	14(1)	7(1)	3(1)	8(1)
S(2)	16(1)	18(1)	19(1)	11(1)	4(1)	6(1)
S(3)	12(1)	13(1)	12(1)	4(1)	2(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($\approx^2$x 10^3) for wood02.

	x	y	z	U(eq)
H(1A)	8783	-860	556	23
H(1B)	9409	258	1595	23
H(2A)	7559	-2615	1321	22
H(2B)	9328	-2431	1466	22
H(3A)	9236	-719	3032	20
H(3B)	8338	-2374	2925	20
H(4)	7701	1859	2952	15
H(5A)	5354	1963	3665	16
H(5B)	4543	975	2651	16
H(10A)	5840	3626	1474	15
H(10B)	4703	2064	1272	15
H(12)	2126	2422	1959	13
H(13)	5194	5981	2140	16
H(14)	3784	7597	3250	15
H(15)	601	4109	2951	15
H(17A)	3556	8963	637	32
H(17B)	1903	9158	961	32
H(17C)	2209	7669	112	32
H(18A)	599	4538	1084	26
H(18B)	-772	4705	1759	26
H(18C)	-231	3051	1304	26
H(19)	1333	6787	2499	16
H(20A)	122	6679	3922	18
H(20B)	1515	8005	4157	18
H(21A)	1704	6739	5307	18
H(21B)	1412	5078	4510	18
H(22A)	1581	557	4925	37
H(22B)	2391	2290	5355	37
H(22C)	3292	955	4753	37
H(4A)	3652	3666	242	23

Table 6. Torsion angles [∞] for wood02.



28a

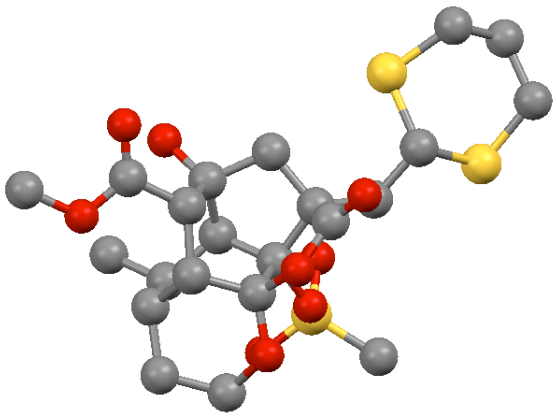


Table 1. Crystal data and structure refinement for **wood13 (28a).**

Identification code	wood13	
Empirical formula	C31 H40 Cl4 O9 S3	
Formula weight	794.61	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6413(4) Å	α= 93.135(2)°.
	b = 12.5011(5) Å	β= 100.872(2)°.
	c = 16.1465(7) Å	γ = 111.766(2)°.
Volume	1758.25(13) $Å^3$	
Z	2	
Density (calculated)	1.501 Mg/m^3	
Absorption coefficient	0.567 mm^{-1}	
F(000)	828	
Crystal size	0.62 x 0.18 x 0.06 mm^3	
Theta range for data collection	2.05 to 28.45°.	
Index ranges	-12<=h<=12, -16<=k<=16, -21<=l<=21	
Reflections collected	30817	
Independent reflections	8600 [R(int) = 0.0288]	
Completeness to theta = 28.45°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9668 and 0.7202	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8600 / 0 / 424	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0905	
R indices (all data)	R1 = 0.0550, wR2 = 0.0990	
Largest diff. peak and hole	0.566 and -0.568 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\approx^2$x 10^3) for wood13. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2065(2)	8750(2)	-173(1)	14(1)
C(2)	3924(2)	8329(2)	-1178(1)	20(1)
C(3)	3508(3)	9087(2)	-1803(1)	24(1)
C(4)	3250(2)	10092(2)	-1383(1)	24(1)
C(5)	702(2)	8242(2)	259(1)	14(1)
C(6)	5311(2)	10575(2)	4084(2)	25(1)
C(7)	3770(2)	8752(2)	3274(1)	14(1)
C(8)	2370(2)	5336(2)	1687(1)	17(1)
C(9)	4343(2)	4696(2)	2490(1)	20(1)
C(10)	1769(2)	3293(2)	2034(1)	20(1)
C(11)	4780(3)	3866(2)	2870(2)	28(1)
C(12)	2210(3)	2462(2)	2402(2)	28(1)
C(13)	3715(3)	2751(2)	2824(2)	29(1)
C(14)	2833(2)	4414(2)	2070(1)	14(1)
C(15)	1795(2)	6967(2)	2214(1)	12(1)
C(16)	2292(2)	7620(2)	1469(1)	13(1)
C(17)	2221(2)	7734(2)	3085(1)	12(1)
C(18)	3258(3)	5359(2)	4348(2)	29(1)
C(19)	313(3)	9047(2)	6160(2)	38(1)
C(20)	1821(2)	9462(2)	1679(1)	15(1)
C(21)	1163(2)	8226(2)	1221(1)	12(1)
C(22)	131(2)	8428(2)	2474(1)	12(1)
C(23)	-2340(2)	7728(2)	2847(1)	16(1)
C(24)	-1730(2)	7167(2)	3561(1)	17(1)
C(25)	-408(2)	6868(2)	3375(1)	14(1)
C(26)	844(2)	7997(2)	3240(1)	12(1)
C(27)	-3687(2)	7027(2)	-222(1)	20(1)
C(28)	12(2)	6460(2)	1910(1)	11(1)
C(29)	-182(2)	7569(2)	1642(1)	11(1)
C(30)	-903(2)	5945(2)	2577(1)	13(1)
C(31)	-804(2)	4794(2)	2792(1)	17(1)

Cl(1)	5006(1)	6588(1)	4613(1)	36(1)
Cl(2)	1984(1)	5456(1)	4978(1)	38(1)
Cl(3)	516(1)	7749(1)	5873(1)	50(1)
Cl(4)	-1450(1)	9058(1)	5612(1)	38(1)
O(1)	4853(2)	8778(1)	2990(1)	21(1)
O(2)	3838(2)	9603(1)	3838(1)	20(1)
O(3)	2434(2)	6122(1)	2394(1)	14(1)
O(4)	2788(2)	10296(1)	1513(1)	24(1)
O(5)	1198(2)	9536(1)	2355(1)	14(1)
O(6)	-1117(2)	8674(1)	2612(1)	14(1)
O(7)	-1648(1)	7458(1)	1128(1)	12(1)
O(8)	-2075(2)	5747(1)	109(1)	19(1)
O(9)	-3949(2)	5678(1)	960(1)	23(1)
S(1)	2413(1)	7550(1)	-656(1)	17(1)
S(2)	1570(1)	9640(1)	-934(1)	20(1)
S(3)	-2854(1)	6327(1)	503(1)	13(1)

Table 3. Bond lengths [≈] and angles [∞] for wood13.

C(1)-C(5)	1.546(3)
C(1)-S(2)	1.8160(19)
C(1)-S(1)	1.8209(19)
C(2)-C(3)	1.520(3)
C(2)-S(1)	1.812(2)
C(3)-C(4)	1.518(3)
C(4)-S(2)	1.810(2)
C(5)-C(21)	1.537(3)
C(6)-O(2)	1.450(2)
C(7)-O(1)	1.207(2)
C(7)-O(2)	1.336(2)
C(7)-C(17)	1.523(3)
C(8)-O(3)	1.441(2)
C(8)-C(14)	1.505(2)
C(9)-C(14)	1.388(3)
C(9)-C(11)	1.388(3)
C(10)-C(12)	1.384(3)
C(10)-C(14)	1.386(3)
C(11)-C(13)	1.379(3)
C(12)-C(13)	1.383(3)
C(15)-O(3)	1.424(2)
C(15)-C(16)	1.543(3)
C(15)-C(17)	1.552(3)
C(15)-C(28)	1.562(2)
C(16)-C(21)	1.549(2)
C(17)-C(26)	1.539(2)
C(18)-Cl(1)	1.766(3)
C(18)-Cl(2)	1.769(2)
C(19)-Cl(3)	1.754(3)
C(19)-Cl(4)	1.767(3)
C(20)-O(4)	1.197(2)
C(20)-O(5)	1.355(2)
C(20)-C(21)	1.519(2)
C(21)-C(29)	1.555(3)

C(22)-O(6)	1.400(2)
C(22)-O(5)	1.435(2)
C(22)-C(26)	1.523(3)
C(22)-C(29)	1.580(3)
C(23)-O(6)	1.455(2)
C(23)-C(24)	1.518(3)
C(24)-C(25)	1.530(3)
C(25)-C(26)	1.538(3)
C(25)-C(30)	1.555(3)
C(27)-S(3)	1.750(2)
C(28)-C(30)	1.537(3)
C(28)-C(29)	1.541(2)
C(29)-O(7)	1.450(2)
C(30)-C(31)	1.531(2)
O(7)-S(3)	1.5967(13)
O(8)-S(3)	1.4248(14)
O(9)-S(3)	1.4286(15)

C(5)-C(1)-S(2)	107.28(12)
C(5)-C(1)-S(1)	108.45(12)
S(2)-C(1)-S(1)	113.55(10)
C(3)-C(2)-S(1)	114.30(14)
C(4)-C(3)-C(2)	113.44(18)
C(3)-C(4)-S(2)	113.59(15)
C(21)-C(5)-C(1)	114.61(15)
O(1)-C(7)-O(2)	122.90(18)
O(1)-C(7)-C(17)	124.88(17)
O(2)-C(7)-C(17)	112.10(16)
O(3)-C(8)-C(14)	106.09(15)
C(14)-C(9)-C(11)	120.34(19)
C(12)-C(10)-C(14)	120.49(19)
C(13)-C(11)-C(9)	120.1(2)
C(13)-C(12)-C(10)	120.1(2)
C(11)-C(13)-C(12)	119.9(2)
C(10)-C(14)-C(9)	119.11(18)
C(10)-C(14)-C(8)	121.29(18)

C(9)-C(14)-C(8)	119.57(18)
O(3)-C(15)-C(16)	113.72(15)
O(3)-C(15)-C(17)	103.92(14)
C(16)-C(15)-C(17)	115.79(15)
O(3)-C(15)-C(28)	114.64(14)
C(16)-C(15)-C(28)	101.56(14)
C(17)-C(15)-C(28)	107.45(14)
C(15)-C(16)-C(21)	105.25(14)
C(7)-C(17)-C(26)	116.93(15)
C(7)-C(17)-C(15)	115.07(15)
C(26)-C(17)-C(15)	110.55(15)
Cl(1)-C(18)-Cl(2)	111.34(13)
Cl(3)-C(19)-Cl(4)	112.05(14)
O(4)-C(20)-O(5)	121.12(17)
O(4)-C(20)-C(21)	127.56(18)
O(5)-C(20)-C(21)	111.29(15)
C(20)-C(21)-C(5)	109.24(15)
C(20)-C(21)-C(16)	110.71(15)
C(5)-C(21)-C(16)	113.93(15)
C(20)-C(21)-C(29)	104.14(14)
C(5)-C(21)-C(29)	115.13(15)
C(16)-C(21)-C(29)	103.17(14)
O(6)-C(22)-O(5)	103.07(13)
O(6)-C(22)-C(26)	111.98(15)
O(5)-C(22)-C(26)	109.75(14)
O(6)-C(22)-C(29)	115.91(15)
O(5)-C(22)-C(29)	106.24(14)
C(26)-C(22)-C(29)	109.44(14)
O(6)-C(23)-C(24)	112.06(15)
C(23)-C(24)-C(25)	111.36(16)
C(24)-C(25)-C(26)	107.75(15)
C(24)-C(25)-C(30)	112.94(15)
C(26)-C(25)-C(30)	109.45(15)
C(22)-C(26)-C(25)	106.71(15)
C(22)-C(26)-C(17)	111.67(15)
C(25)-C(26)-C(17)	109.07(14)

C(30)-C(28)-C(29)	112.75(14)
C(30)-C(28)-C(15)	116.37(15)
C(29)-C(28)-C(15)	98.61(13)
O(7)-C(29)-C(28)	118.40(14)
O(7)-C(29)-C(21)	111.66(14)
C(28)-C(29)-C(21)	107.78(14)
O(7)-C(29)-C(22)	106.45(13)
C(28)-C(29)-C(22)	108.29(14)
C(21)-C(29)-C(22)	103.13(14)
C(31)-C(30)-C(28)	112.56(15)
C(31)-C(30)-C(25)	112.95(15)
C(28)-C(30)-C(25)	109.80(15)
C(7)-O(2)-C(6)	115.19(16)
C(15)-O(3)-C(8)	117.74(14)
C(20)-O(5)-C(22)	112.40(14)
C(22)-O(6)-C(23)	115.92(13)
C(29)-O(7)-S(3)	125.76(11)
C(2)-S(1)-C(1)	100.74(9)
C(4)-S(2)-C(1)	99.98(9)
O(8)-S(3)-O(9)	118.18(9)
O(8)-S(3)-O(7)	110.30(8)
O(9)-S(3)-O(7)	107.91(8)
O(8)-S(3)-C(27)	111.11(10)
O(9)-S(3)-C(27)	109.51(10)
O(7)-S(3)-C(27)	97.88(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^3) for wood13. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	15(1)	15(1)	15(1)	5(1)	5(1)	8(1)
C(2)	18(1)	29(1)	19(1)	7(1)	8(1)	12(1)
C(3)	21(1)	40(1)	18(1)	14(1)	9(1)	14(1)
C(4)	20(1)	28(1)	26(1)	16(1)	9(1)	9(1)
C(5)	13(1)	15(1)	15(1)	4(1)	4(1)	6(1)
C(6)	20(1)	19(1)	26(1)	-5(1)	2(1)	0(1)
C(7)	16(1)	15(1)	13(1)	2(1)	1(1)	8(1)
C(8)	26(1)	16(1)	15(1)	1(1)	5(1)	14(1)
C(9)	16(1)	19(1)	24(1)	3(1)	5(1)	6(1)
C(10)	16(1)	16(1)	26(1)	-1(1)	2(1)	5(1)
C(11)	21(1)	35(1)	30(1)	4(1)	-1(1)	18(1)
C(12)	34(1)	13(1)	34(1)	3(1)	6(1)	8(1)
C(13)	44(1)	24(1)	29(1)	7(1)	5(1)	24(1)
C(14)	18(1)	14(1)	13(1)	1(1)	5(1)	10(1)
C(15)	14(1)	12(1)	13(1)	1(1)	4(1)	8(1)
C(16)	14(1)	14(1)	14(1)	3(1)	4(1)	8(1)
C(17)	13(1)	13(1)	13(1)	2(1)	3(1)	7(1)
C(18)	27(1)	37(1)	28(1)	5(1)	7(1)	18(1)
C(19)	41(2)	28(1)	42(2)	-9(1)	3(1)	13(1)
C(20)	14(1)	14(1)	19(1)	1(1)	4(1)	7(1)
C(21)	12(1)	11(1)	15(1)	3(1)	5(1)	6(1)
C(22)	12(1)	10(1)	14(1)	1(1)	4(1)	5(1)
C(23)	13(1)	18(1)	19(1)	1(1)	6(1)	8(1)
C(24)	17(1)	20(1)	15(1)	2(1)	6(1)	9(1)
C(25)	14(1)	15(1)	13(1)	2(1)	5(1)	7(1)
C(26)	12(1)	14(1)	12(1)	0(1)	2(1)	7(1)
C(27)	22(1)	21(1)	17(1)	2(1)	-4(1)	11(1)
C(28)	13(1)	10(1)	12(1)	0(1)	3(1)	6(1)
C(29)	10(1)	10(1)	11(1)	1(1)	1(1)	5(1)
C(30)	12(1)	12(1)	15(1)	2(1)	4(1)	5(1)
C(31)	21(1)	13(1)	17(1)	4(1)	6(1)	7(1)

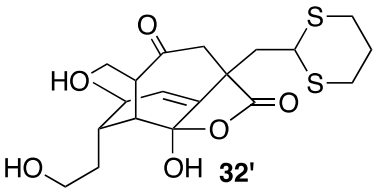
Cl(1)	29(1)	40(1)	40(1)	6(1)	10(1)	13(1)
Cl(2)	31(1)	62(1)	26(1)	8(1)	10(1)	20(1)
Cl(3)	64(1)	37(1)	47(1)	-12(1)	-10(1)	32(1)
Cl(4)	43(1)	35(1)	40(1)	-5(1)	10(1)	20(1)
O(1)	14(1)	23(1)	26(1)	-2(1)	6(1)	6(1)
O(2)	15(1)	18(1)	22(1)	-6(1)	2(1)	3(1)
O(3)	20(1)	14(1)	12(1)	0(1)	3(1)	12(1)
O(4)	22(1)	14(1)	34(1)	0(1)	14(1)	1(1)
O(5)	15(1)	8(1)	17(1)	0(1)	4(1)	4(1)
O(6)	14(1)	15(1)	19(1)	0(1)	5(1)	9(1)
O(7)	11(1)	11(1)	14(1)	-1(1)	0(1)	5(1)
O(8)	21(1)	17(1)	18(1)	-4(1)	1(1)	10(1)
O(9)	19(1)	23(1)	18(1)	1(1)	4(1)	-3(1)
S(1)	18(1)	17(1)	19(1)	4(1)	8(1)	8(1)
S(2)	20(1)	21(1)	24(1)	12(1)	9(1)	11(1)
S(3)	13(1)	12(1)	13(1)	1(1)	1(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for wood13.

	x	y	z	U(eq)
H(1A)	2998	9251	268	17
H(2A)	4841	8826	-738	24
H(2B)	4201	7758	-1486	24
H(3A)	4341	9400	-2109	29
H(3B)	2564	8598	-2229	29
H(4A)	3147	10613	-1810	28
H(4B)	4163	10544	-925	28
H(5A)	59	8704	161	17
H(5B)	67	7437	-19	17
H(6A)	5254	11151	4500	37
H(6B)	5574	10933	3581	37
H(6C)	6098	10297	4340	37
H(8A)	3083	5753	1336	21
H(8B)	1320	4985	1325	21
H(9A)	5082	5461	2518	24
H(10A)	729	3094	1754	24
H(11A)	5813	4066	3161	33
H(12A)	1478	1692	2366	33
H(13A)	4016	2182	3081	35
H(16A)	2224	7071	983	16
H(16B)	3360	8201	1648	16
H(17A)	2348	7211	3514	15
H(18A)	3463	4649	4434	35
H(18B)	2775	5295	3739	35
H(19A)	1165	9710	6034	46
H(19B)	379	9150	6781	46
H(23A)	-2910	7133	2343	19
H(23B)	-3064	8032	3030	19
H(24A)	-2568	6449	3633	20
H(24B)	-1371	7705	4101	20

H(25A)	18	6565	3880	16
H(26A)	1176	8590	3755	15
H(27A)	-4485	6446	-670	31
H(27B)	-2899	7557	-478	31
H(27C)	-4143	7470	74	31
H(28A)	-312	5865	1397	13
H(30A)	-2004	5775	2321	15
H(31A)	-1121	4249	2267	25
H(31B)	-1482	4463	3175	25
H(31C)	253	4932	3071	25

Table 6. Torsion angles [∞] for wood13.



32'

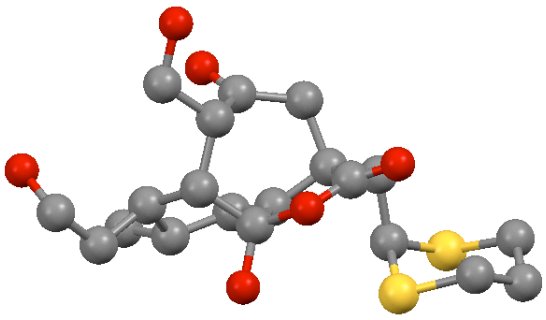


Table 1. Crystal data and structure refinement for **wood16 (32)**.

Identification code	wood16	
Empirical formula	C20 H29 O6 S2	
Formula weight	429.55	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)/c	
Unit cell dimensions	a = 12.5635(17) Å	α= 90∞.
	b = 6.5271(10) Å	β= 90.859(7)∞.
	c = 23.877(3) Å	γ = 90∞.
Volume	1957.7(5) $Å^3$	
Z	4	
Density (calculated)	1.457 Mg/m^3	
Absorption coefficient	0.308 mm^{-1}	
F(000)	916	
Crystal size	0.24 x 0.08 x 0.07 mm^3	
Theta range for data collection	2.34 to 20.86°.	
Index ranges	-12<=h<=12, -6<=k<=6, -23<=l<=22	
Reflections collected	18741	
Independent reflections	2043 [R(int) = 0.1376]	
Completeness to theta = 20.86∞	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9797 and 0.9303	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2043 / 168 / 131	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0683, wR2 = 0.1703	
R indices (all data)	R1 = 0.1038, wR2 = 0.1937	
Largest diff. peak and hole	1.151 and -0.653 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($\approx^2$x 10^3) for wood16. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1475(5)	957(10)	8698(3)	22(1)
C(2)	855(5)	-550(9)	9057(3)	22(1)
C(3)	1028(5)	-2764(10)	8892(3)	22(1)
C(4)	1218(5)	-1637(10)	7767(3)	22(1)
C(5)	2386(5)	-2287(10)	7680(3)	22(1)
C(6)	2984(5)	-828(10)	7304(3)	22(1)
C(7)	3375(5)	1078(10)	7606(3)	22(1)
C(8)	2407(5)	62(10)	6805(3)	22(1)
C(9)	2735(5)	2262(10)	6742(3)	22(1)
C(10)	3987(5)	-1908(10)	7058(3)	22(1)
C(11)	4314(5)	-1148(10)	6480(3)	22(1)
C(12)	4531(5)	1126(9)	6383(3)	22(1)
C(13)	5343(5)	1553(10)	5939(3)	22(1)
C(14)	3478(5)	2370(10)	6253(3)	22(1)
C(15)	2852(5)	1644(10)	5710(3)	22(1)
C(16)	1957(5)	-842(10)	6360(3)	22(1)
C(17)	1813(5)	404(10)	5835(3)	22(1)
C(18)	2583(5)	3465(9)	5331(3)	22(1)
C(19)	3486(5)	4284(10)	4998(3)	22(1)
C(20)	1491(5)	-932(10)	5328(3)	22(1)
O(1)	3774(3)	1176(6)	8066(2)	22(1)
O(2)	3295(3)	2760(6)	7271(2)	22(1)
O(3)	1930(3)	3741(6)	6669(2)	22(1)
O(4)	4411(3)	-2371(6)	6099(2)	22(1)
O(5)	6346(4)	750(8)	6064(2)	47(2)
O(6)	3824(4)	2744(7)	4623(2)	35(1)
S(1)	1033(1)	1021(2)	7972(1)	22(1)
S(2)	495(1)	-3417(3)	8199(1)	23(1)

Table 3. Bond lengths [≈] and angles [∞] for wood16.

C(1)-C(2)	1.526(9)
C(1)-S(1)	1.813(6)
C(2)-C(3)	1.515(9)
C(3)-S(2)	1.825(6)
C(4)-C(5)	1.545(8)
C(4)-S(2)	1.808(7)
C(4)-S(1)	1.818(6)
C(5)-C(6)	1.516(9)
C(6)-C(8)	1.501(9)
C(6)-C(7)	1.517(9)
C(6)-C(10)	1.566(9)
C(7)-O(1)	1.202(7)
C(7)-O(2)	1.362(7)
C(8)-C(16)	1.335(8)
C(8)-C(9)	1.502(9)
C(9)-O(3)	1.408(7)
C(9)-O(2)	1.472(7)
C(9)-C(14)	1.507(9)
C(10)-C(11)	1.528(9)
C(11)-O(4)	1.218(7)
C(11)-C(12)	1.527(9)
C(12)-C(13)	1.509(9)
C(12)-C(14)	1.579(9)
C(13)-O(5)	1.393(8)
C(14)-C(15)	1.580(9)
C(15)-C(18)	1.529(9)
C(15)-C(17)	1.568(9)
C(16)-C(17)	1.503(9)
C(17)-C(20)	1.540(9)
C(18)-C(19)	1.495(9)
C(19)-O(6)	1.416(8)
C(2)-C(1)-S(1)	113.7(4)
C(3)-C(2)-C(1)	113.1(5)

C(2)-C(3)-S(2)	114.0(4)
C(5)-C(4)-S(2)	112.8(4)
C(5)-C(4)-S(1)	115.1(4)
S(2)-C(4)-S(1)	113.1(3)
C(6)-C(5)-C(4)	112.8(5)
C(8)-C(6)-C(5)	118.4(5)
C(8)-C(6)-C(7)	102.1(5)
C(5)-C(6)-C(7)	113.1(6)
C(8)-C(6)-C(10)	105.0(5)
C(5)-C(6)-C(10)	110.4(5)
C(7)-C(6)-C(10)	106.9(5)
O(1)-C(7)-O(2)	121.4(6)
O(1)-C(7)-C(6)	127.4(6)
O(2)-C(7)-C(6)	111.1(5)
C(16)-C(8)-C(6)	130.9(6)
C(16)-C(8)-C(9)	117.1(6)
C(6)-C(8)-C(9)	108.6(5)
O(3)-C(9)-O(2)	106.8(5)
O(3)-C(9)-C(8)	118.1(5)
O(2)-C(9)-C(8)	104.7(5)
O(3)-C(9)-C(14)	108.9(5)
O(2)-C(9)-C(14)	111.1(5)
C(8)-C(9)-C(14)	107.2(5)
C(11)-C(10)-C(6)	114.9(5)
O(4)-C(11)-C(12)	120.2(6)
O(4)-C(11)-C(10)	119.5(6)
C(12)-C(11)-C(10)	120.2(6)
C(13)-C(12)-C(11)	114.2(5)
C(13)-C(12)-C(14)	109.9(5)
C(11)-C(12)-C(14)	112.2(5)
O(5)-C(13)-C(12)	113.5(5)
C(9)-C(14)-C(12)	110.5(5)
C(9)-C(14)-C(15)	108.3(5)
C(12)-C(14)-C(15)	114.4(5)
C(18)-C(15)-C(17)	109.7(5)
C(18)-C(15)-C(14)	110.8(5)

C(17)-C(15)-C(14)	113.9(5)
C(8)-C(16)-C(17)	118.1(6)
C(16)-C(17)-C(20)	112.1(5)
C(16)-C(17)-C(15)	110.3(5)
C(20)-C(17)-C(15)	110.7(5)
C(19)-C(18)-C(15)	115.5(5)
O(6)-C(19)-C(18)	108.7(5)
C(7)-O(2)-C(9)	110.9(5)
C(1)-S(1)-C(4)	101.3(3)
C(4)-S(2)-C(3)	100.7(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^3) for wood16. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2} U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

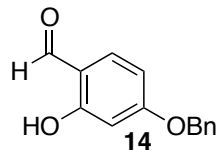
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(2)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(3)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(4)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(5)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(6)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(7)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(8)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(9)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(10)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(11)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(12)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(13)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(14)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(15)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(16)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(17)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(18)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(19)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
C(20)	9(1)	31(1)	24(1)	-1(1)	-10(1)	2(1)
O(1)	10(2)	32(2)	25(2)	-2(1)	-12(1)	-2(1)
O(2)	10(2)	32(2)	25(2)	-2(1)	-12(1)	-2(1)
O(3)	5(2)	29(3)	32(3)	1(2)	-10(2)	2(2)
O(4)	10(2)	32(2)	25(2)	-2(1)	-12(1)	-2(1)
O(5)	23(3)	54(4)	63(4)	-9(3)	-15(3)	0(3)
O(6)	24(3)	43(3)	38(3)	-5(3)	3(2)	-6(2)
S(1)	10(1)	28(1)	28(1)	0(1)	-14(1)	2(1)
S(2)	10(1)	33(1)	25(1)	1(1)	-11(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10 ^{3}) for wood16.

	x	y	z	U(eq)
H(1A)	2238	584	8713	26
H(1B)	1404	2347	8859	26
H(2A)	1074	-369	9454	26
H(2B)	87	-230	9025	26
H(3A)	691	-3659	9173	26
H(3B)	1802	-3053	8900	26
H(4)	874	-1747	7388	26
H(5A)	2755	-2358	8049	26
H(5B)	2398	-3676	7513	26
H(8)	1728	350	7003	26
H(10A)	4593	-1710	7322	26
H(10B)	3845	-3398	7034	26
H(12)	4831	1679	6743	26
H(13A)	5085	968	5579	26
H(13B)	5406	3054	5889	26
H(14)	3680	3838	6199	26
H(15)	3335	720	5498	26
H(16)	1734	-2231	6374	26
H(17)	1227	1409	5899	26
H(18A)	2005	3050	5069	26
H(18B)	2304	4587	5567	26
H(19A)	3254	5513	4786	26
H(19B)	4082	4681	5251	26
H(20A)	2043	-1964	5265	32
H(20B)	1413	-66	4995	32
H(20C)	814	-1616	5403	32
H(3)	1403	3424	6863	33
H(5)	6405	-410	5915	70
H(6)	4289	3226	4411	52

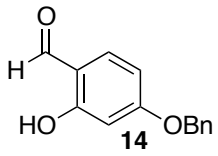
Table 6. Torsion angles [∞] for wood16.

4. Spectra

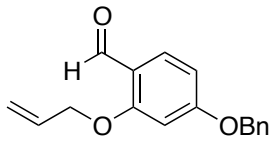


14

RNT-1-172
14/RNT-1-172_20100816_02/CARBON_01
July 18, 2012 3:24 PM



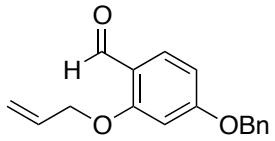
14



Allyl Ether

^{13}C OBSERVE

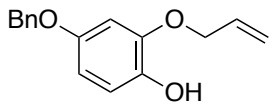
188.422
165.378
162.837
136.151
132.458
130.660
128.964
128.585
127.784
118.306
107.089
100.058
70.552
69.324



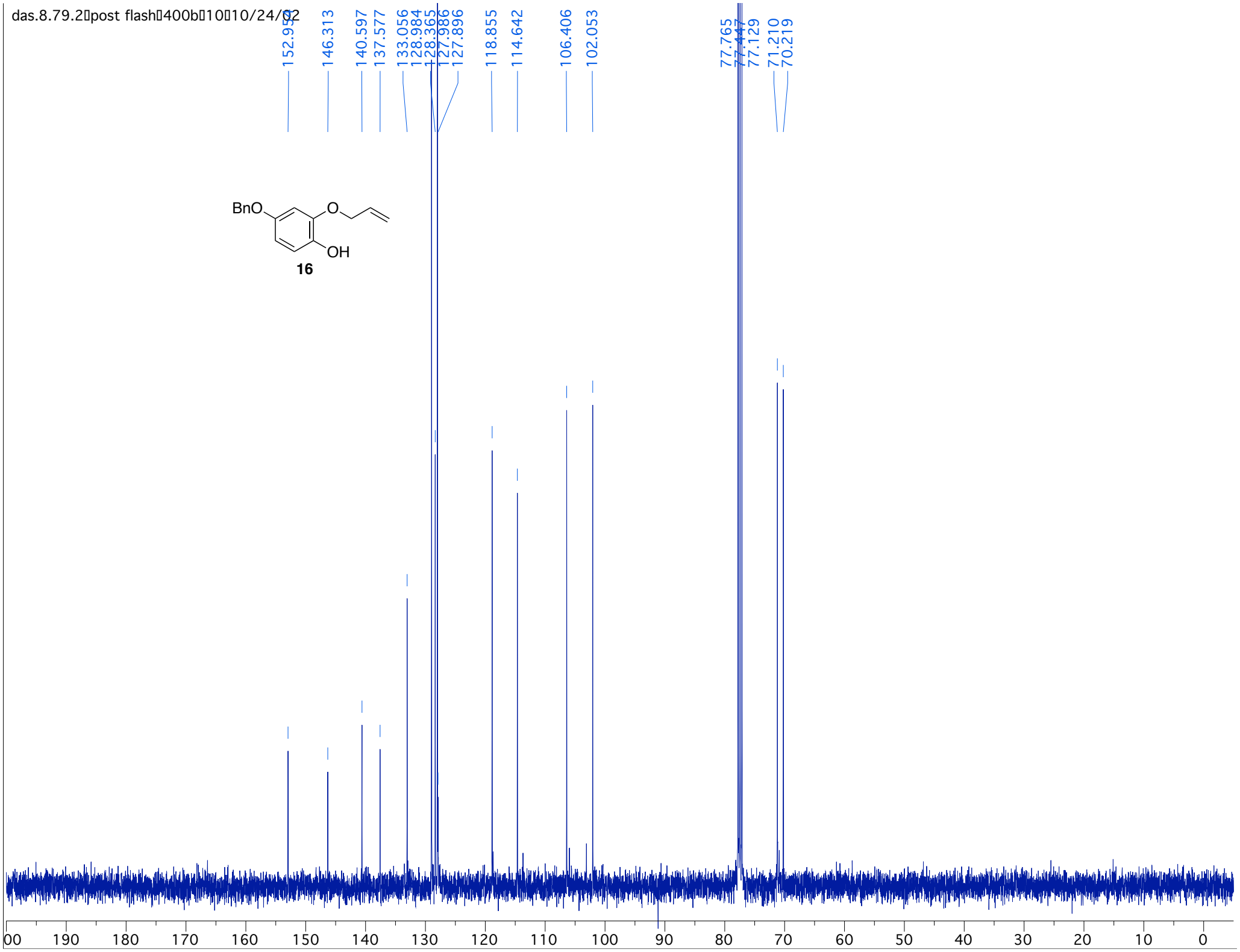
Allyl Ether

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

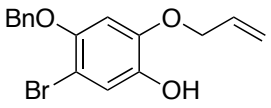
das.8.79.2 post flash 400b 10 10/24/02



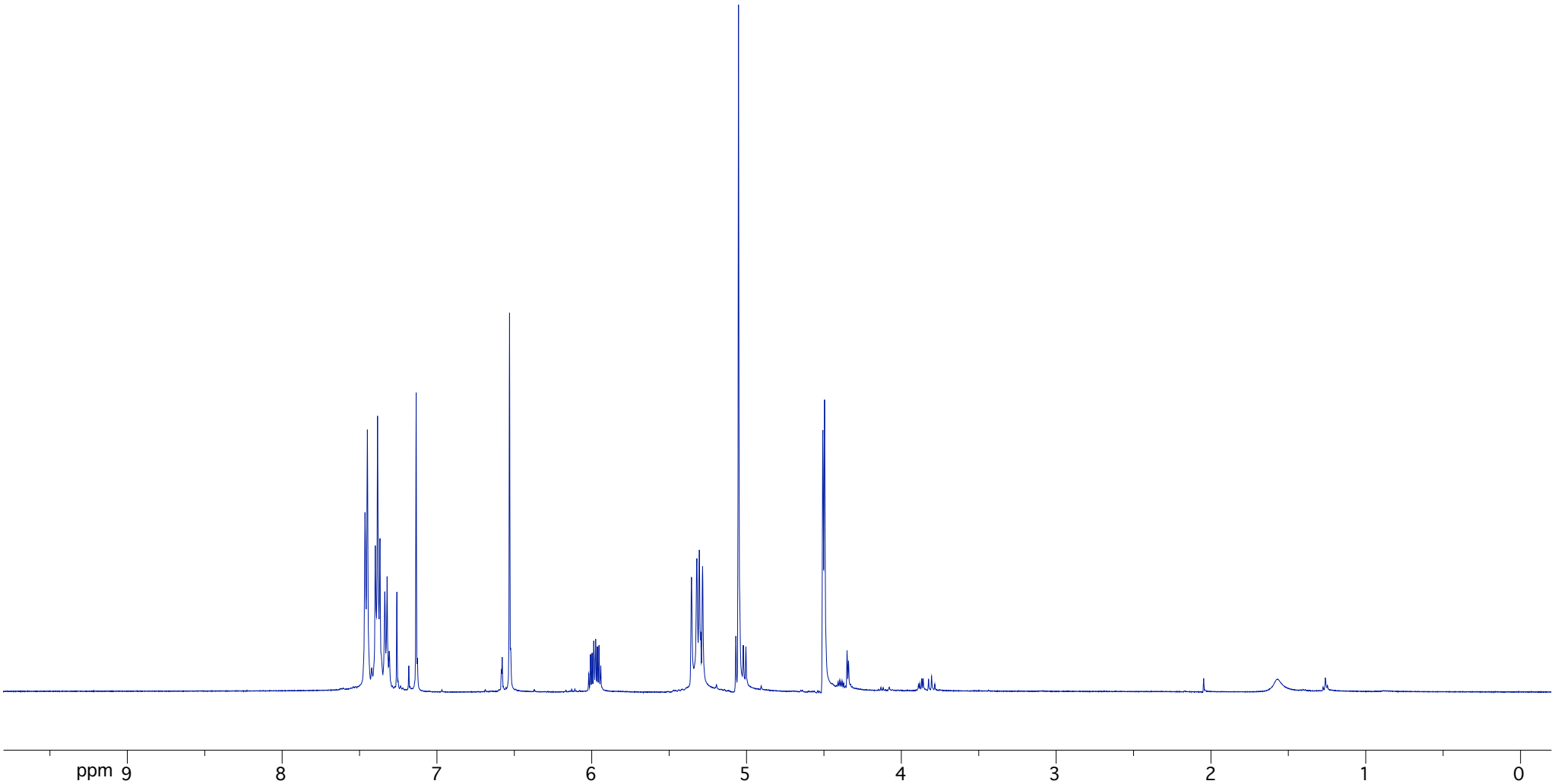
16


das.8.79.2 post flash 400b 10 10/24/12
152.955
146.313
140.597
137.577
133.056
128.984
128.365
127.986
127.896
118.855
114.642
106.406
102.053
77.765
77.442
77.129
71.210
70.219
BnO
O
OH
16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

GKM-4-098p
Bromophenol/GKM-4-098p_20100813_01/PROTON_01
July 18, 2012 1:18 PM

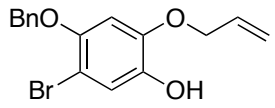


Bromophenol

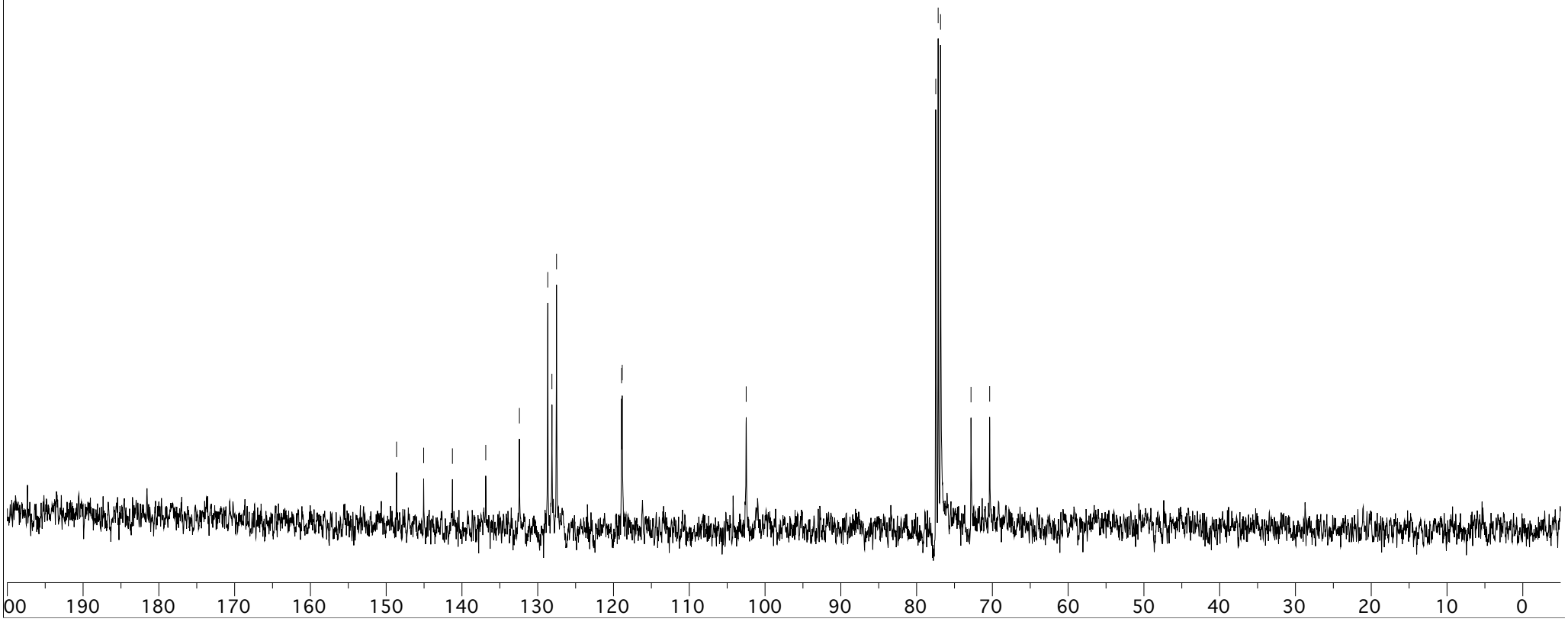


GKM-4-098 Bromination product
FIDs/Bromophenol/GKM-4-098C
July 18, 2012 1:19 PM

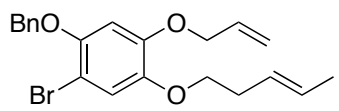
148.633
145.054
141.258
136.859
132.417
128.675
128.128
127.520
118.929
118.849
102.490
77.473
77.154
76.838
72.820
70.356



Bromophenol



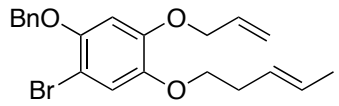
STANDARD ^{1}H OBSERVE
FIDs/17/GKM-10-064H
July 18, 2012 1:21 PM



17

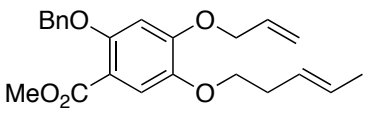
GKM-10-064 Side chain alkylation product
FIDs/17/GKM-10-064C
July 18, 2012 1:22 PM

149.621
148.641
136.897
133.326
128.893
128.736
128.280
128.156
128.024
127.500
126.786
119.413
117.923
104.516
103.405
77.548
77.232
76.912
72.409
70.738
70.147
32.824
18.238



17

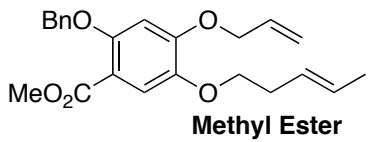
VIP number 1230966□das.8.303□plst w/u□500□1/4/03□20□PROTON_WOOD $CDCl_3$ usr2 spiegel 1
Methyl Ester/DAS.8.303/20
July 18, 2012 1:27 PM



Methyl Ester

VIP number 1230966 das.8.303 plst w/ 500 124/938 30°C CDCl3 usr2 spiegel 1
Methyl Ester/DAS.8.303/21
July 18, 2012 1:25 PM

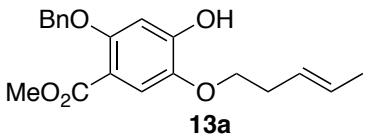
166.534
154.765
153.350
143.204
137.364
133.044
129.152
128.922
128.239
128.139
127.512
127.032
118.365
117.713
112.718
103.034
77.679
77.425
77.171
72.701
70.231
70.097
52.236
33.052
18.458



Methyl Ester

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

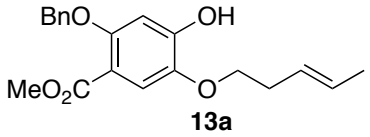
das.9.59.1 post flash 400b 1/9/03 40
13a/DAS.9.59.1/40
July 18, 2012 1:31 PM



13a

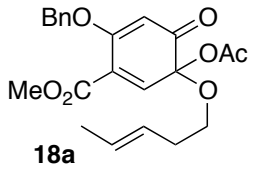
das.9.59.1 carbon 51 post flash 400b 1/9/03
13a/DAS.9.59.1/51
July 18, 2012 1:32 PM

166.673
155.353
151.347
139.979
137.263
129.123
128.910
128.847
128.253
128.138
127.765
127.621
127.303
126.826
116.202
111.485
102.298
77.798
77.480
77.162
71.764
69.875
52.254
32.933
18.466



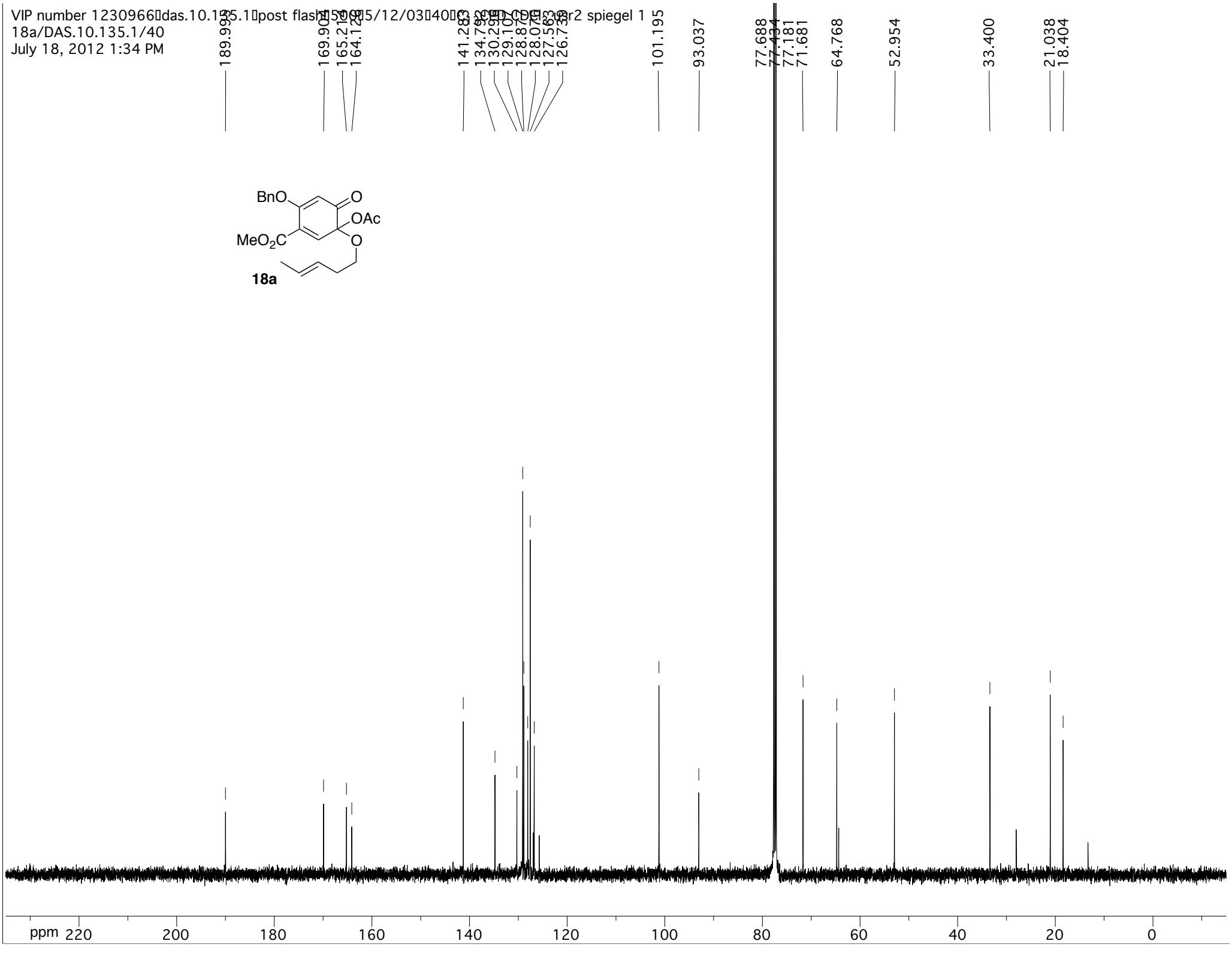
13a

VIP number 1230966 das.10.135.1 post flash 500 5/12/03 20 PROTON_PEAK $CDCl_3$ usr2 spiegel 2
18a/DAS.10.135.1/20
July 18, 2012 1:34 PM

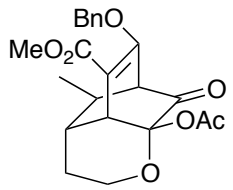


18a

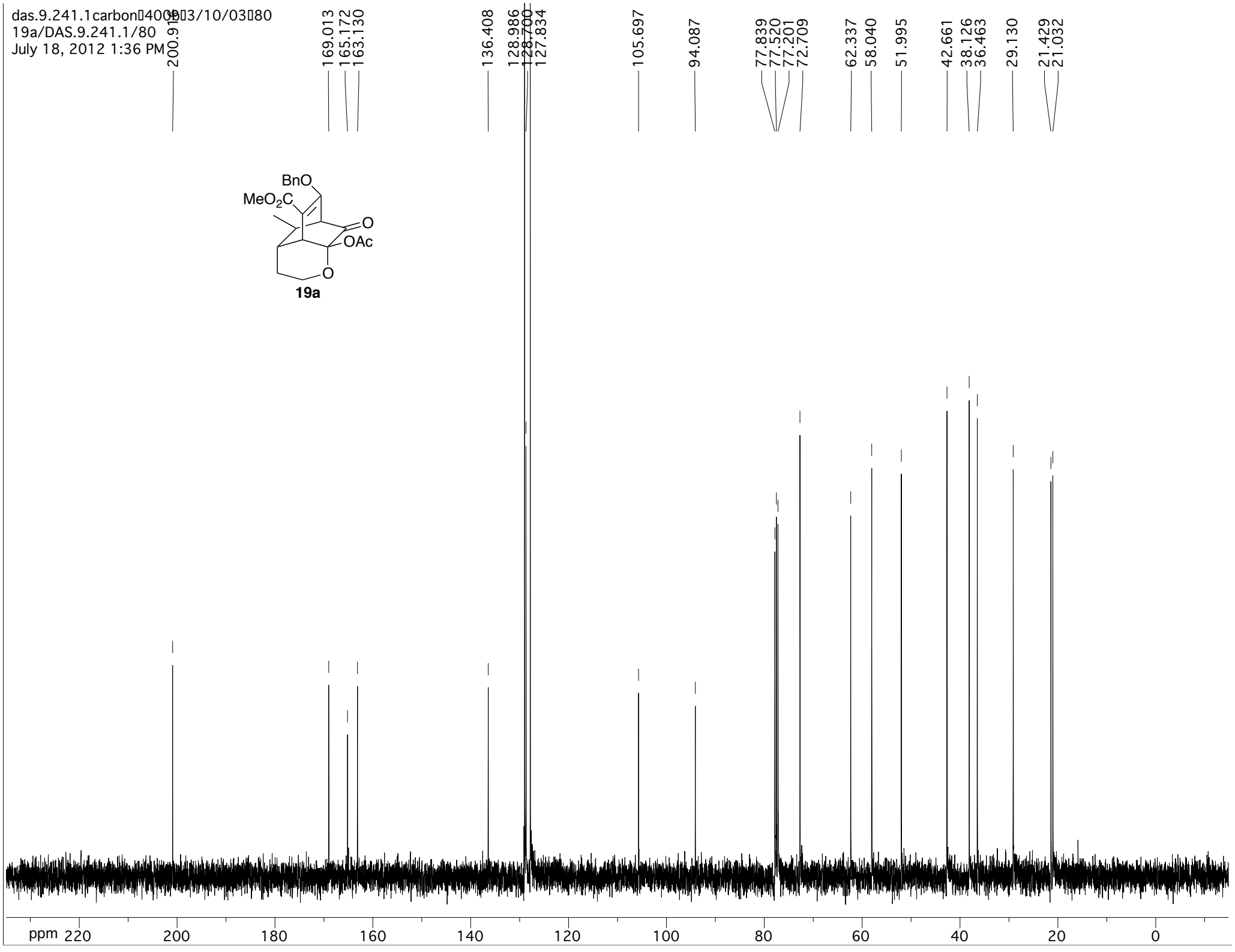
VIP number 1230966 das.10.135.1 post flash 1 500 15/12/03 40 13 2 CDCl3 cr2 spiegel 1
18a/DAS.10.135.1/40
July 18, 2012 1:34 PM



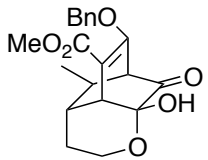
das.9.241.1 flash 400b 3/10/03 70
19a/DAS.9.241.1/70
July 18, 2012 1:35 PM



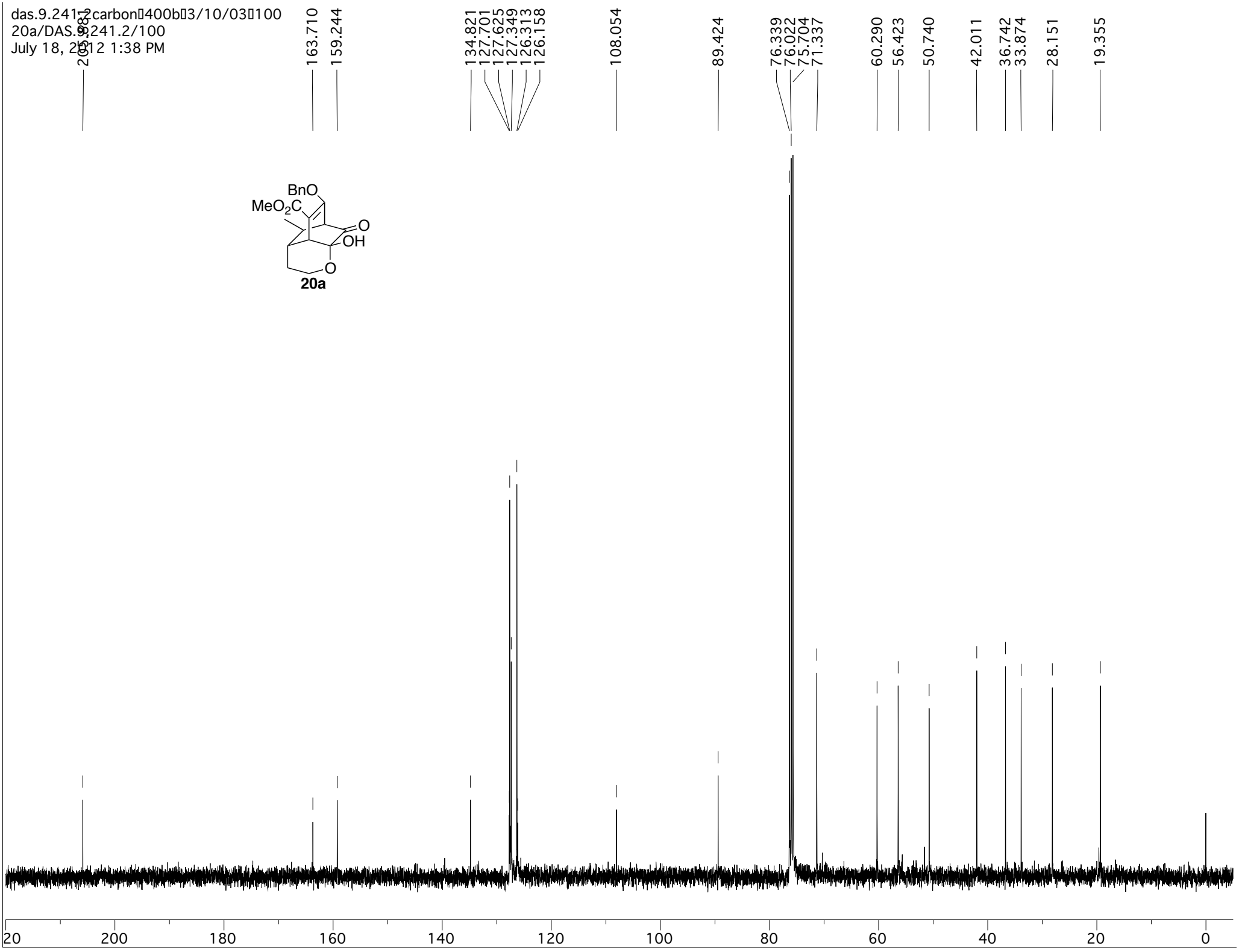
19a


das.9.241.1carbon 40 3/10/03 80
19a/DAS.9.241.1/80
July 18, 2012 1:36 PM
200.913
169.013
165.172
163.130
136.408
128.986
128.700
127.834
105.697
94.087
77.839
77.520
77.201
72.709
62.337
58.040
51.995
42.661
38.126
36.463
29.130
21.429
21.032
BnO
MeO2C
O
OAc
O
19a
ppm
220
200
180
160
140
120
100
80
60
40
20
0

das.9.249.2 post flash 400b 3/10/03 90
20a/DAS.9.241.2/90
July 18, 2012 1:37 PM



20a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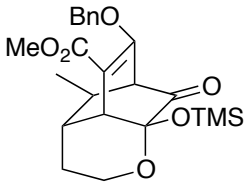
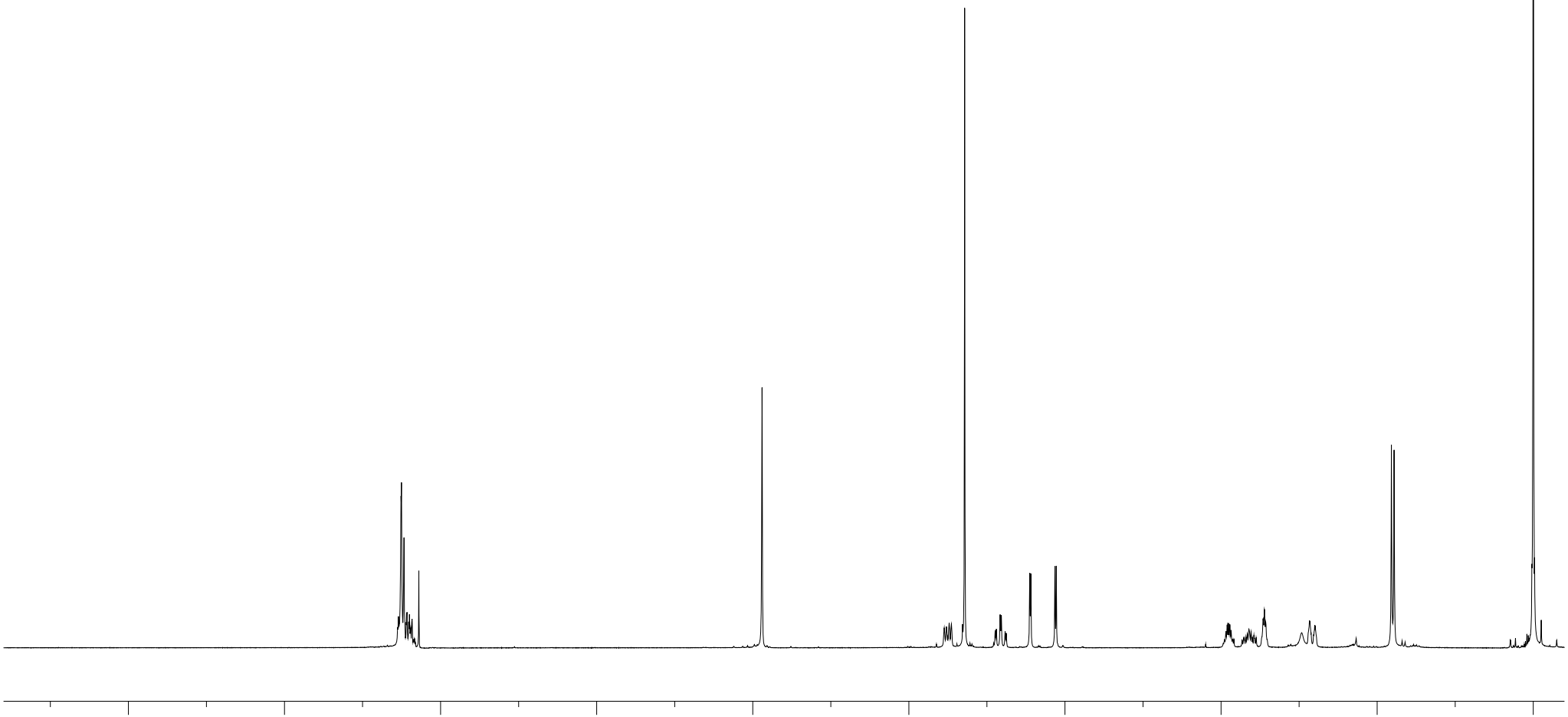
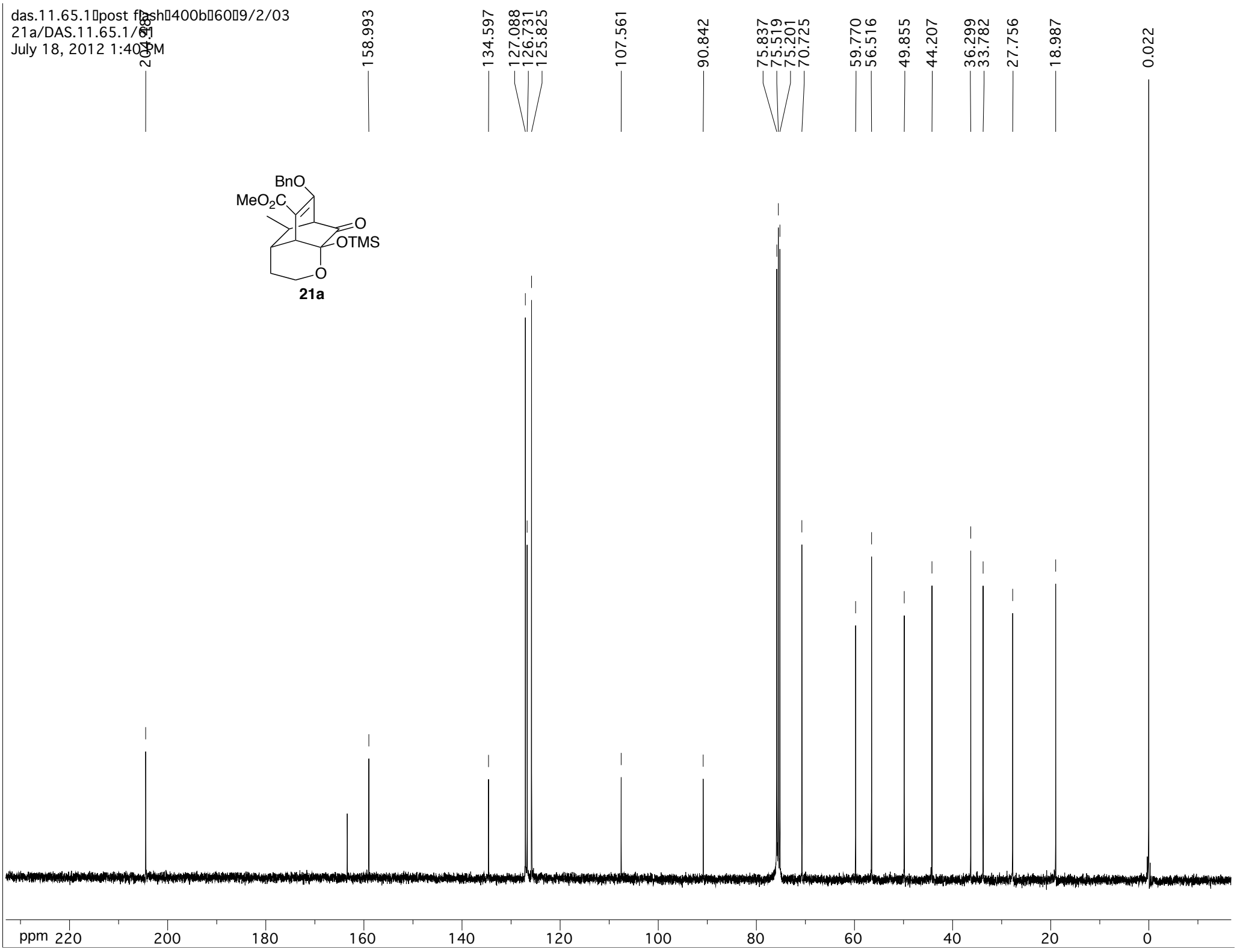
20a/DAS.9.241.2/100
July 18, 2012 1:38 PM
198.981
163.710
159.244
134.821
127.701
127.625
127.349
126.313
126.158
108.054
89.424
76.339
76.022
75.704
71.337
60.290
56.423
50.740
42.011
36.742
33.874
28.151
19.355
BnO
MeO2C
O
OH
O
20a
200
180
160
140
120
100
80
60
40
20
0

das.11.65.1 post flash 400b 60 9/2/03
21a/DAS.11.65.1/60
July 18, 2012 1:39 PM

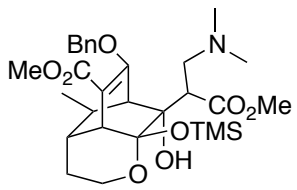


21a




das.11.65.1 post flash 400b 60 9/2/03
21a/DAS.11.65.1/61
July 18, 2012 1:40 PM
200.188
158.993
134.597
127.088
126.731
125.825
107.561
90.842
75.837
75.519
75.201
70.725
59.770
56.516
49.855
44.207
36.299
33.782
27.756
18.987
0.022
BnO
MeO2C
O
OTMS
O
21a
ppm
220
200
180
160
140
120
100
80
60
40
20
0

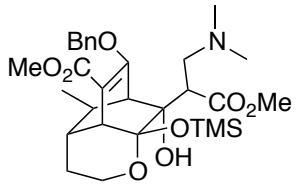
bmt6-2_30May2008
Tertiary Amine a/TAA/PROTON
July 18, 2012 1:41 PM



Tertiary Amine A

bmt6-2_30May2008
Tertiary Amine a/TAA/CARBON
July 18, 2012 1:41 PM

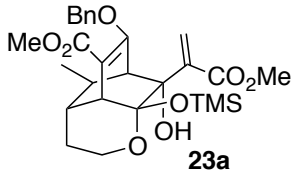
163.952
134.809
126.385
125.832
125.113
103.791
97.496
78.438
75.312
74.994
74.675
69.899
60.986
57.618
52.471
49.420
49.138
47.670
45.674
44.074
36.673
27.082
26.724
19.777
0.005



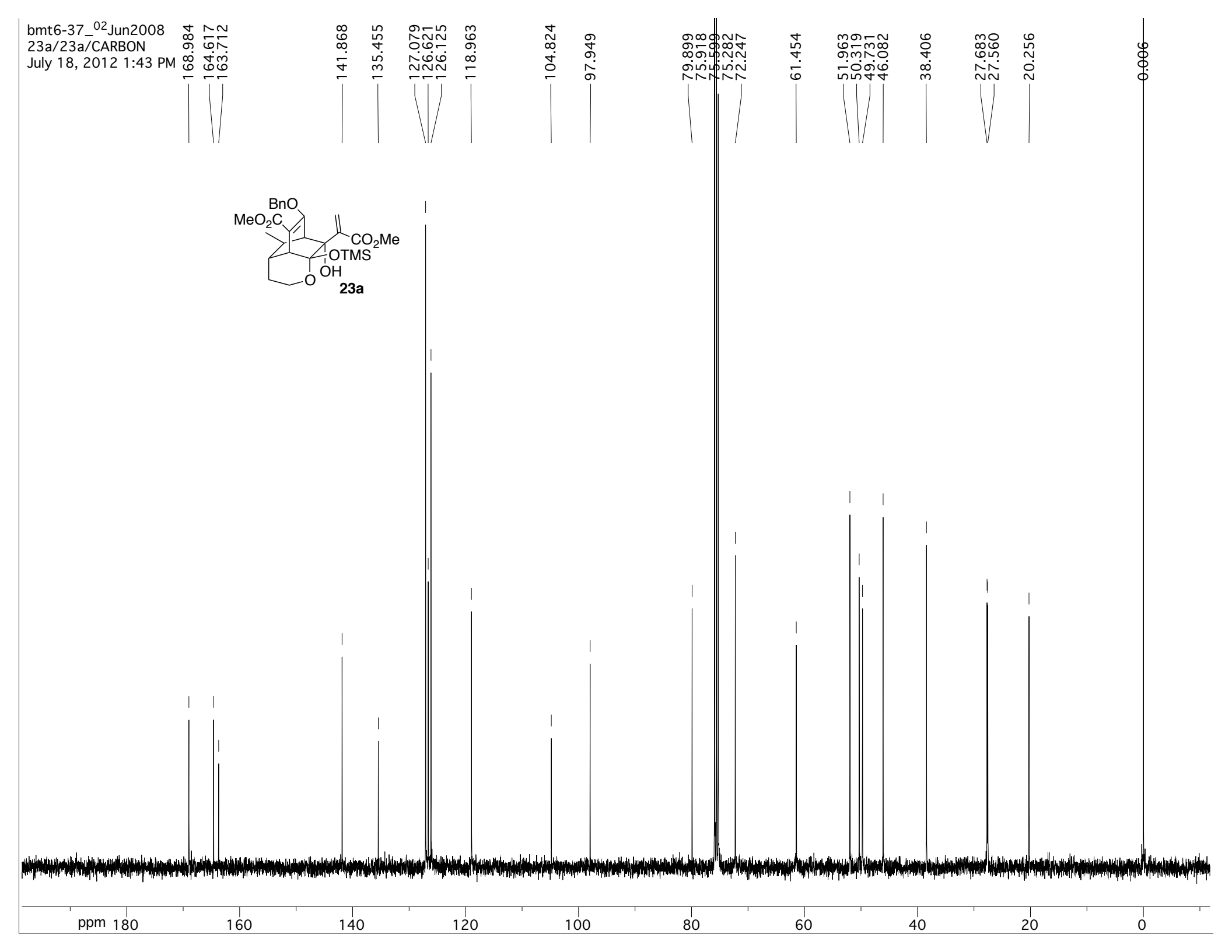
Tertiary Amine A

ppm 180 160 140 120 100 80 60 40 20 0

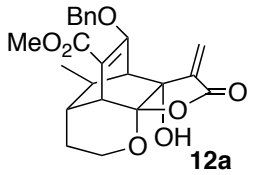
bmt6-37_[02]Jun2008
23a/23a/PROTON
July 18, 2012 1:42 PM



23a


bmt6-37_02Jun2008
23a/23a/CARBON
July 18, 2012 1:43 PM
168.984
164.617
163.712
141.868
135.455
127.079
126.621
126.125
118.963
104.824
97.949
79.899
75.918
75.599
75.282
72.247
61.454
51.963
50.319
49.731
46.082
38.406
27.683
27.560
20.256
0.006
BnO
MeO2C
CO2Me
OTMS
OH
O
23a
ppm
180
160
140
120
100
80
60
40
20
0

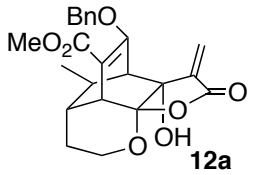
STANDARD ^{1}H OBSERVE
FIDs/12a/12aH
July 18, 2012 1:45 PM



12a

^{13}C OBSERVE
FIDs/12a/12a
July 18, 2012 1:46 PM

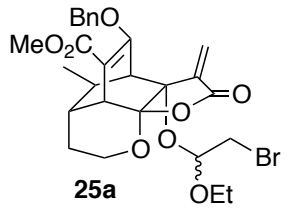
166.396
165.442
164.714
141.110
136.365
128.826
128.517
127.550
126.658
104.623
103.608
77.589
77.273
76.958
76.254
72.688
64.199
52.584
51.890
42.584
42.531
39.122
39.095
31.785
29.068
21.351



12a

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

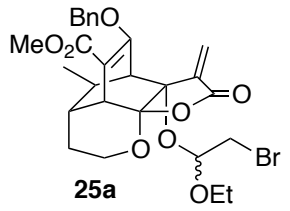
STANDARD ^{1}H OBSERVE
FIDs/25a/25a
July 18, 2012 1:47 PM



25a

^{13}C OBSERVE
FIDs/25a/25aC
July 18, 2012 1:47 PM

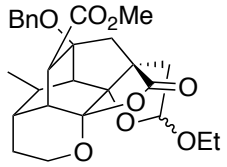
166.084
164.906
164.830
164.773
164.628
136.512
136.346
136.293
135.859
129.025
128.798
128.553
128.473
127.786
127.388
126.478
105.588
105.084
103.807
97.909
97.056
82.063
81.463
77.426
73.724
72.959
63.683
63.460
62.634
61.471
53.878
53.357
51.872
45.246
44.386
40.406
39.842
32.568
32.384
29.892
29.259
28.843
28.764
21.425
15.266
15.087



25a

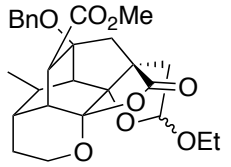
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

bmt6-91_[01]Jul2008
11a/11a/PROTON
July 18, 2012 1:48 PM



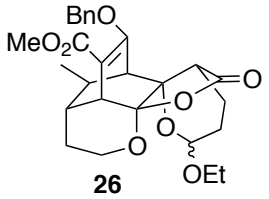
11a

^{13}C OBSERVE
FIDs/11a/11a C
July 18, 2012 1:48:58 PM



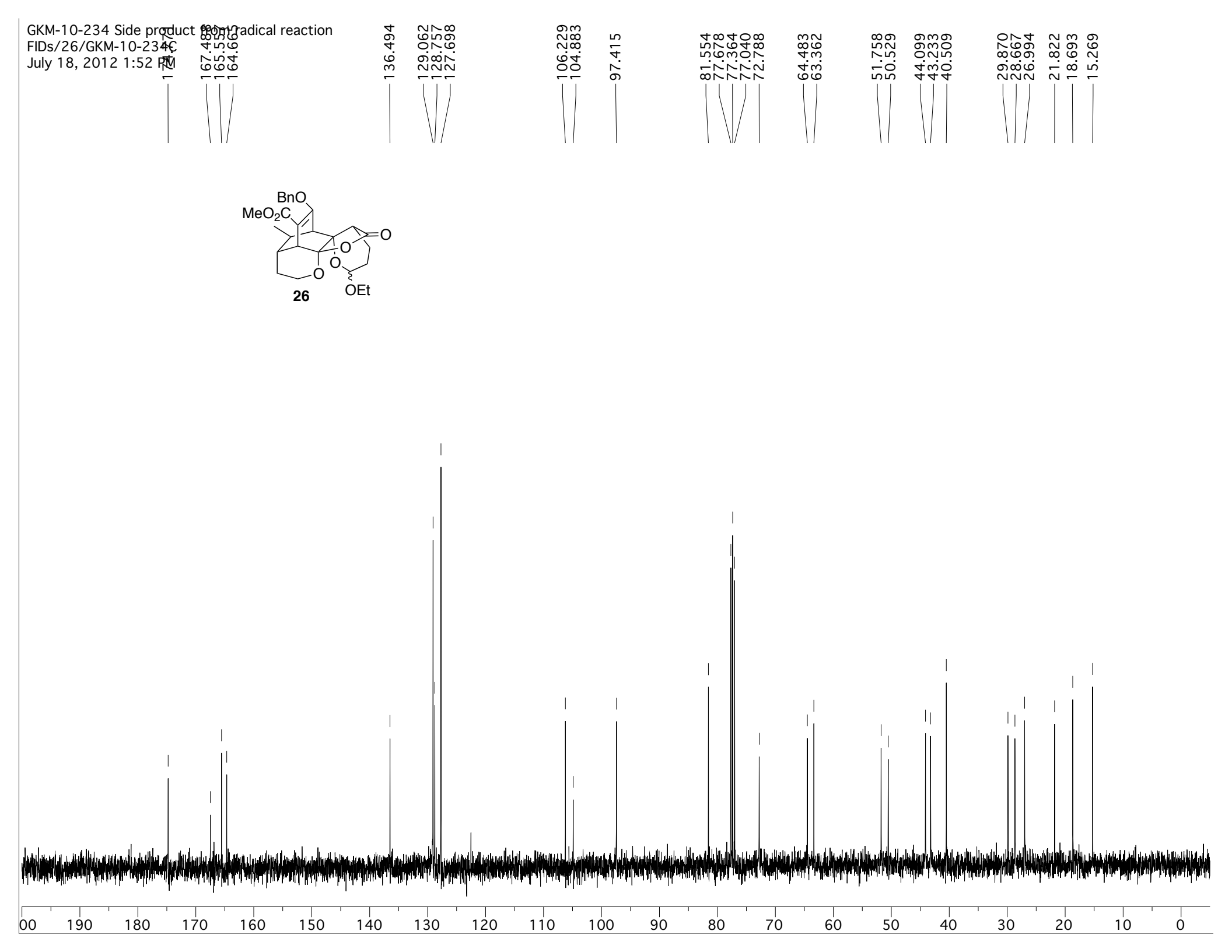
11a

GKM-20-234sp
26/GKM-10-234sp_20100817_01/PROTON_01
July 18, 2012 1:50 PM

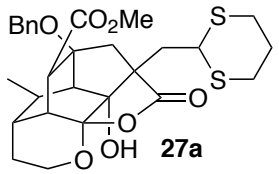


26

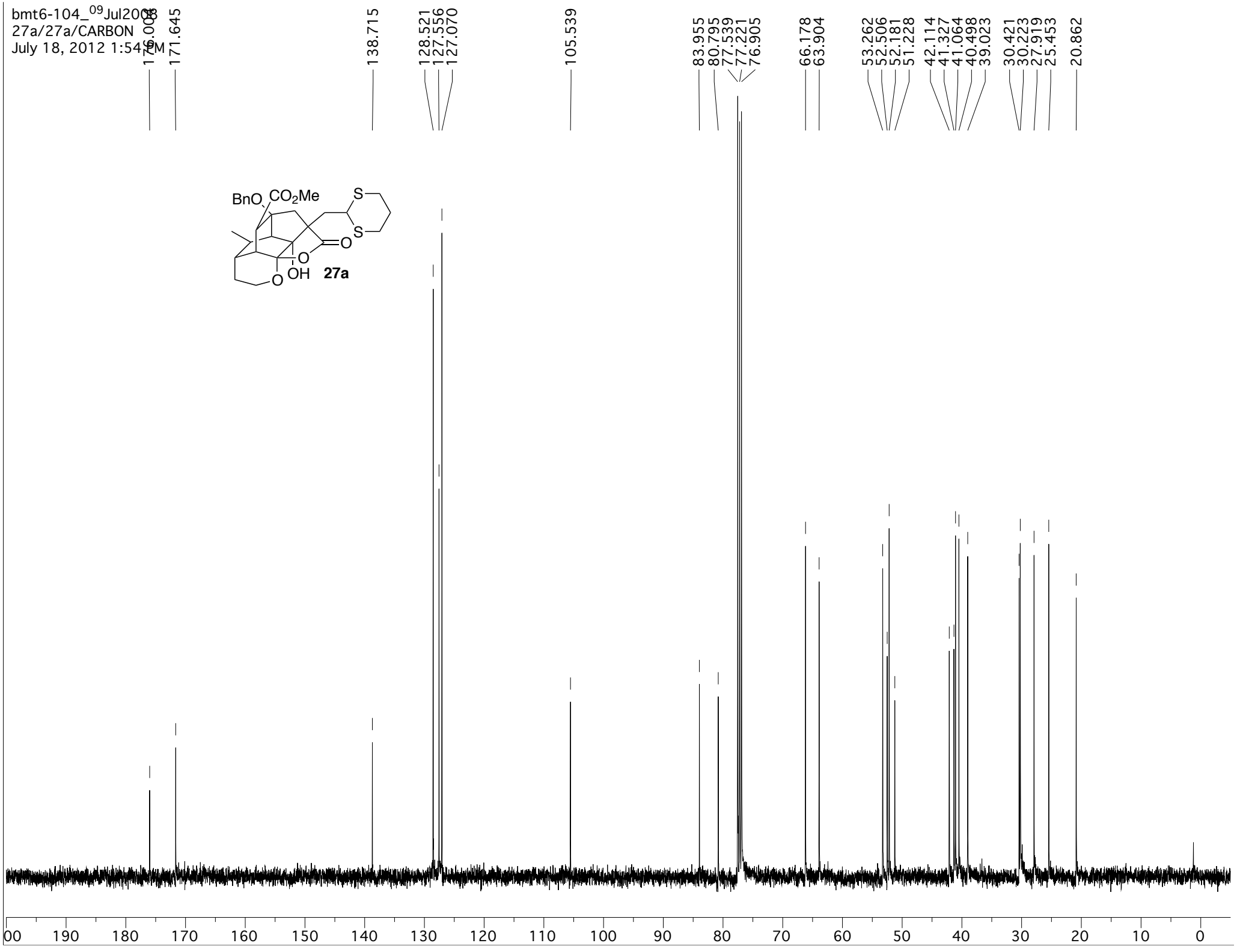
GKM-10-234 Side product from radical reaction
FIDs/26/GKM-10-234C
July 18, 2012 1:52 PM



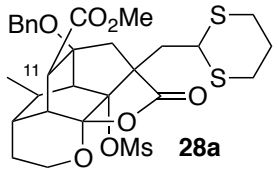
bmt6-104_09Jul2008
27a/27a/PROTON
July 18, 2012 1:53 PM



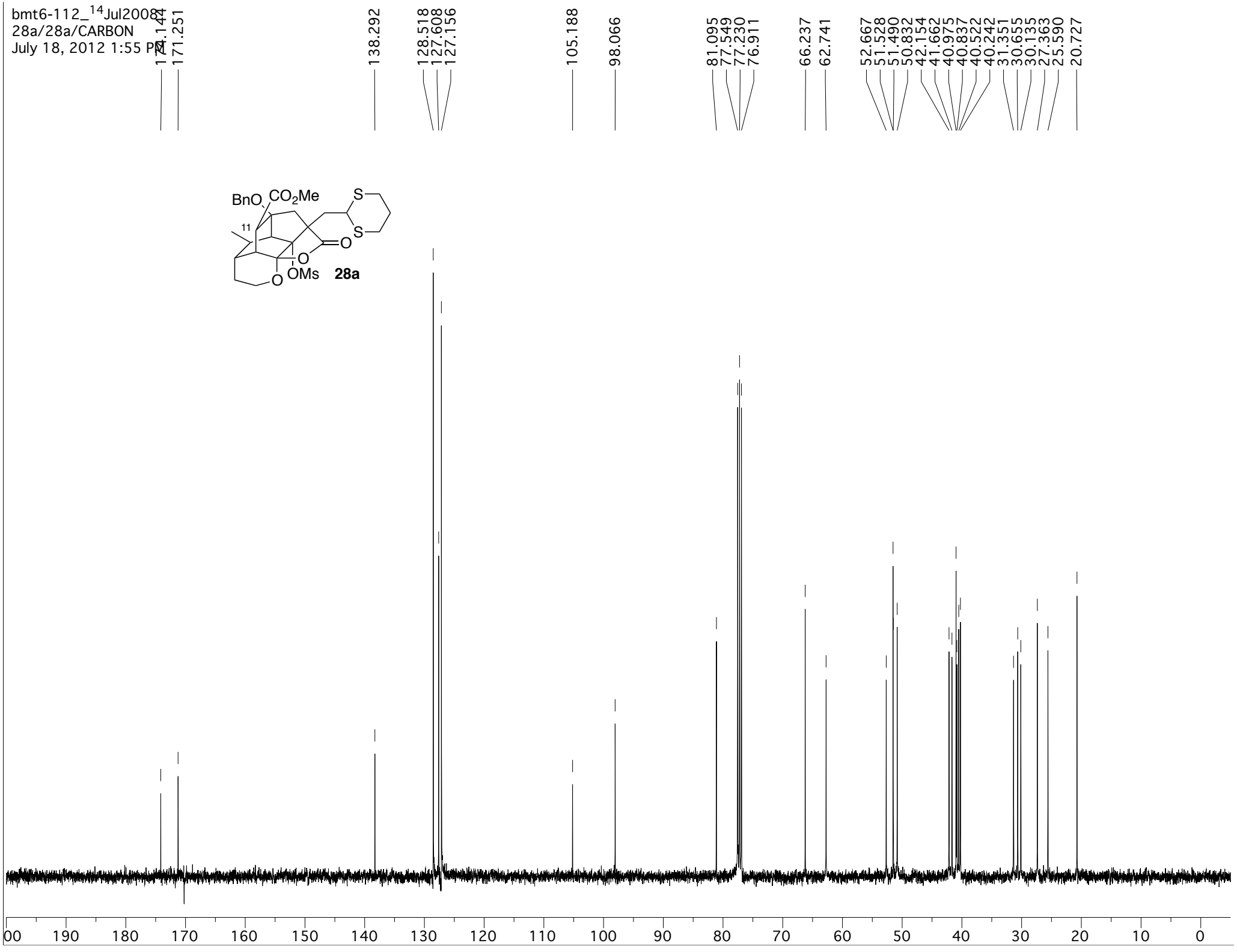
27a


bmt6-104_09Jul2012
27a/27a/CARBON
July 18, 2012 1:54:17 PM
170.008
171.645
138.715
128.521
127.556
127.070
105.539
83.955
80.795
77.539
77.221
76.905
66.178
63.904
53.262
52.506
52.181
51.228
42.114
41.327
41.064
40.498
39.023
30.421
30.223
27.919
25.453
20.862
BnO
CO2Me
S
S
O
O
O
OH
27a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

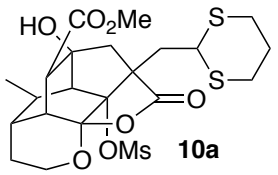
bmt6-112_[14]Jul2008
28a/28a/PROTON
July 18, 2012 1:55 PM



28a

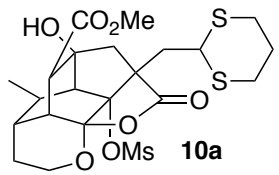

bmt6-112_ 14Jul2008
28a/28a/CARBON
July 18, 2012 1:55 PM
171.144
171.251
138.292
128.518
127.608
127.156
105.188
98.066
81.095
77.549
77.230
76.911
66.237
62.741
52.667
51.528
51.490
50.832
42.154
41.662
40.975
40.837
40.522
40.242
31.351
30.655
30.135
27.363
25.590
20.727
BnO
CO2Me
11
S
S
O
O
O
OMs
28a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

GKM-9-022 Side product, low Rf, from BBr_3 reaction
FIDs/10a/GKM-9-022H_sp
July 18, 2012 2:00 PM



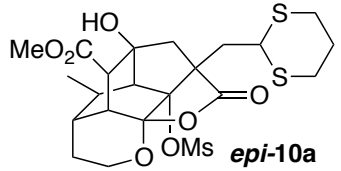
10a

GKM-10-240 Side products from BBr_3 reaction
FIDs/10a/GKM-10-240C.esp
July 18, 2012 1:59 PM



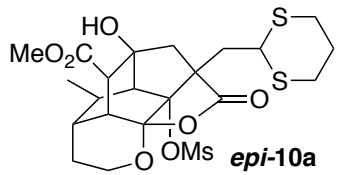
10a

bmt6-121-2_[20]Jul2008
epi10a/epi 10a/PROTON
July 18, 2012 2:01 PM



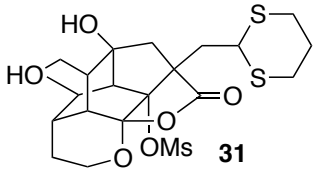
***epi*-10a**

bmt6-121-2_ ^{20}Jul2012
epi10a/epi 10a/CARBON
July 18, 2012 2:00 PM



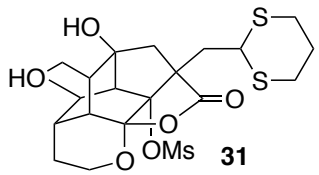
***epi*-10a**

$LiAlH_4$ reduction product
31/GKM-7-232_14Aug2009/PROTON
July 18, 2012 2:03 PM



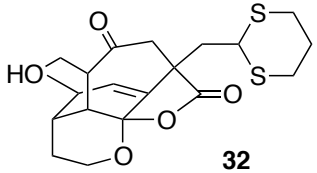
31

GKM-7-232 $LiAlH_4$ reduction product
FIDs/31/GKM-7-232C
July 18, 2012 2:03 PM



31

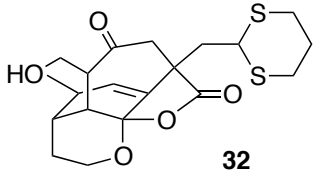
GKM-9-020_13Jan2010
32/GKM-9-020_13Jan2010/PROTON
July 18, 2012 2:06 PM



32

GKM-9-020 Fragmentation product
FIDs/32/GKM-9-020C.
July 18, 2012 2:06 PM

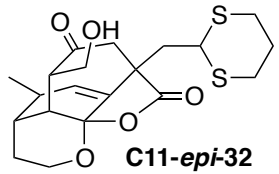
206.699
177.449
141.864
133.985
107.560
77.526
77.204
76.891
61.686
60.340
59.556
52.981
49.881
47.958
43.420
38.725
38.287
37.813
34.751
29.144
28.821
25.578
19.530



32

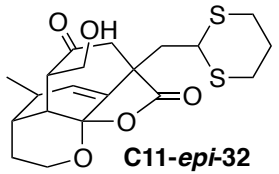
240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40

GKM-9-176_spt1_ ^{26}Feb2010
epi-30/GKM-9-176_spt1_26Feb2010/PROTON
July 18, 2012 2:08 PM



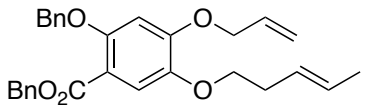
C11-*epi*-32

GKM-9-176 Spot 1 from Var. Frag product purification
FIDs/epi-30/GKM-9-176C_spt1
July 18, 2012 2:08 PM

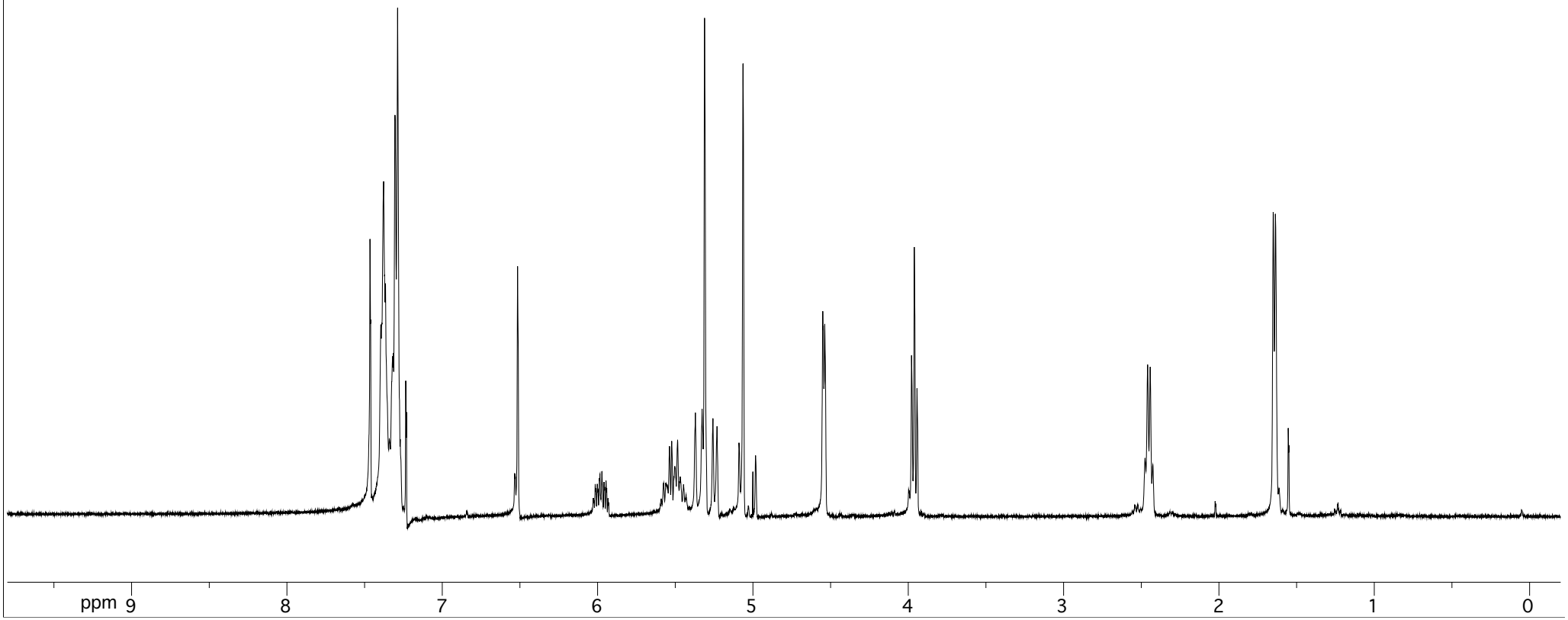


C11-*epi*-32

GKM-3-276 Bn Ester formation
FIDs/Benzyl Ester/GKM-3-276H_p
July 18, 2012 2:10 PM

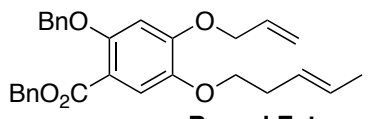


Benzyl Ester



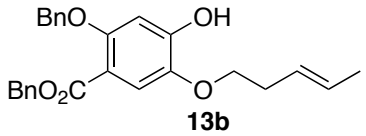
GKM-3-276 Bn Ester formation
FIDs/Benzyl Ester/GKM-3-276C
July 18, 2012 2:10 PM

165.603
154.667
153.265
142.863
136.970
136.531
132.814
128.791
128.696
128.353
128.154
128.020
127.976
127.462
126.802
118.181
117.812
112.329
102.444
77.547
77.225
76.911
72.325
70.009
69.924
66.675
32.807
18.260



Benzyl Ester

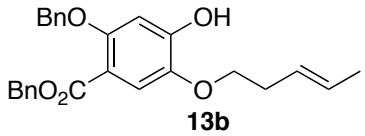
GKM-3-278 Allyl deprotection
FIDs/13b/GKM-3-278H_p2
July 18, 2012 2:15 PM



13b

GKM-3-278 Deallylation product
FIDs/13b/GKM-3-278C_1
July 18, 2012 2:15 PM

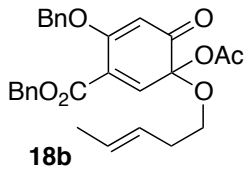
166.067
155.213
151.190
139.682
136.840
136.547
128.668
128.336
128.118
127.944
127.364
126.591
116.243
111.272
101.823
77.404
76.694
76.552
71.559
69.718
66.676
32.692
29.909
18.219



13b

240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40

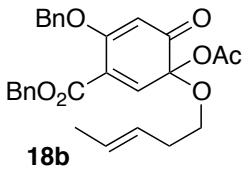
GKM-3-282 Fraction 10, phenolic oxidation product
FIDs/18b/GKM-3-282H_f10
July 18, 2012 2:15 PM



18b

GKM-3-282 Fraction 10, phenolic oxidation product
FIDs/18b/GKM-3-282C_f10_1
July 18, 2012 2:15 PM

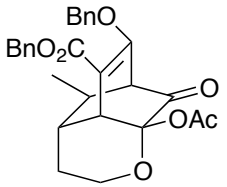
189.805
169.703
165.033
163.607
141.223
135.182
134.400
130.255
128.901
128.752
128.682
128.626
127.897
127.768
126.766
126.495
125.475
100.938
92.805
77.601
77.283
76.964
71.652
67.827
64.544
64.141
33.188
27.779
20.859
18.235



18b

240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40

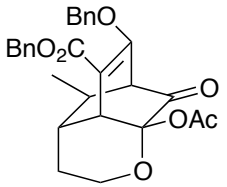
GKM-3-282 Fraction 16, Oxidation/DA product, acetate
FIDs/19b/GKM-3-282H_f16
July 18, 2012 2:14 PM



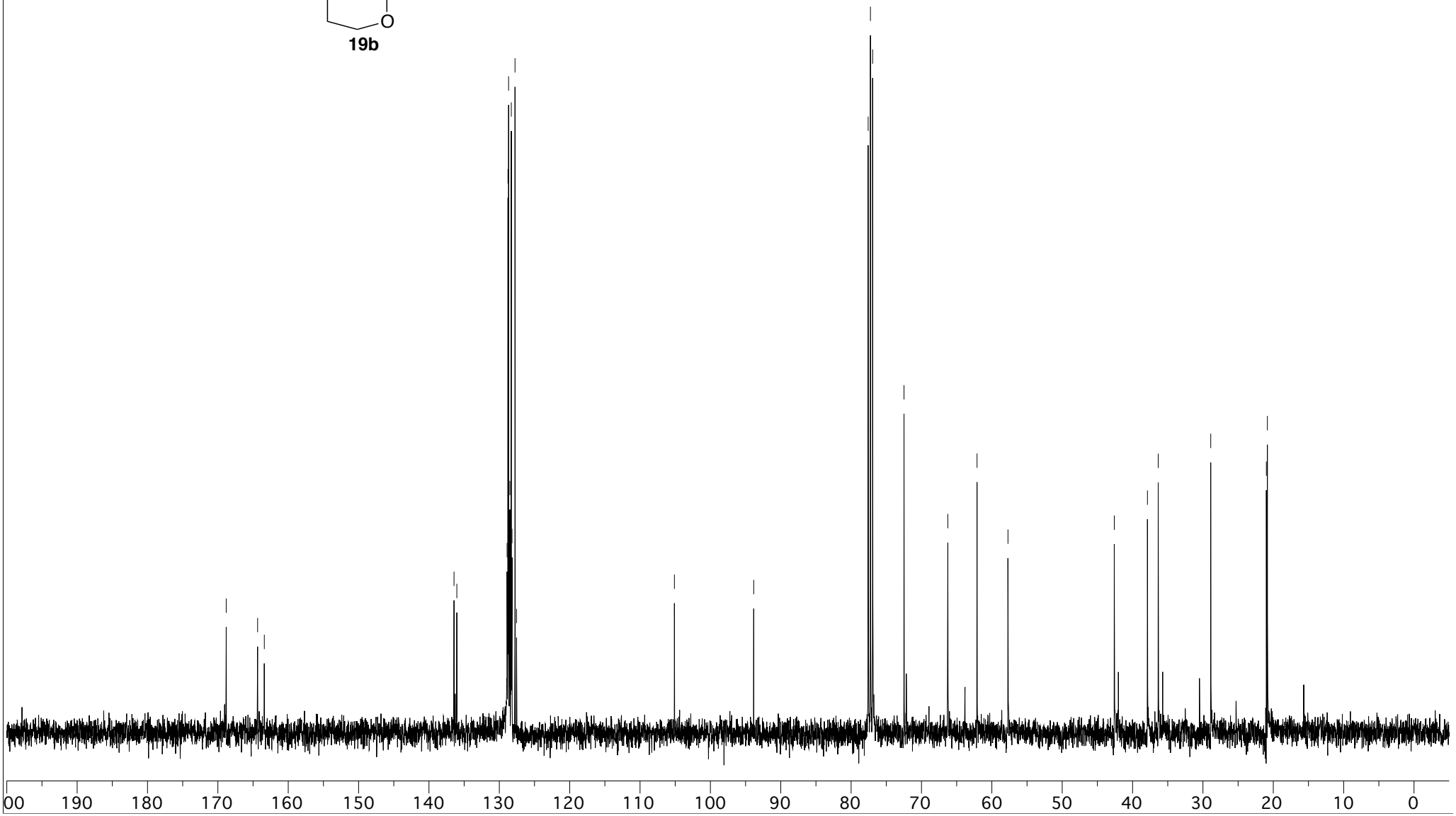
19b

GKM-3-282 Fraction 16, Oxidation/DA product, acetone
FIDs/19b/GKM-3-282C_F16
July 18, 2012 2:14 PM

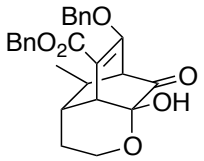
168.115
164.355
163.400
136.436
136.039
128.899
128.773
128.681
128.569
128.497
128.371
128.298
128.196
127.770
127.553
105.116
93.846
77.579
77.257
76.943
72.485
66.259
62.104
57.709
42.598
37.887
36.356
28.890
20.986
20.841



19b

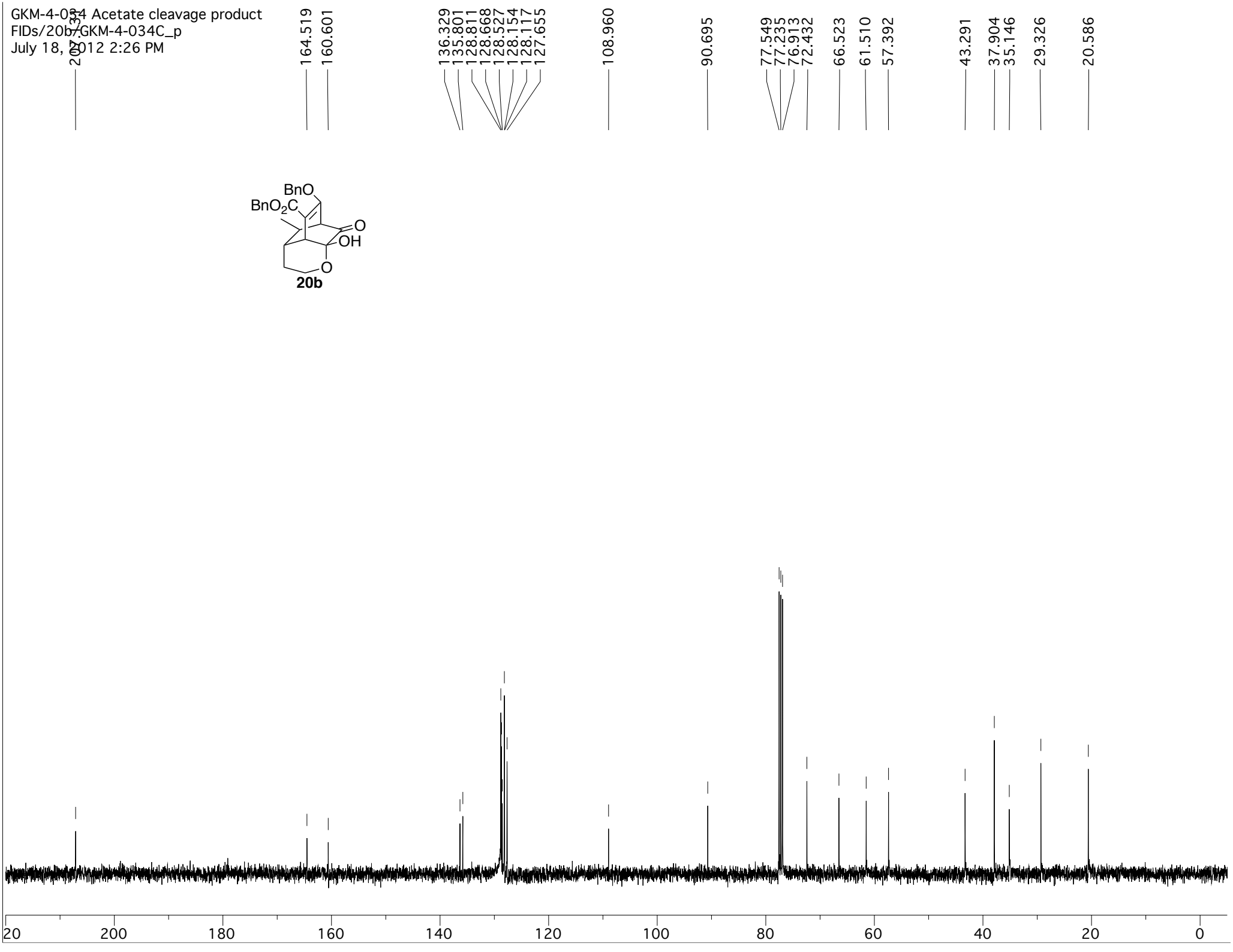


GKM-4-034-2_[21]Oct2008
20b/GKM-4-034-2_21Oct2008/PROTON
July 18, 2012 2:26 PM

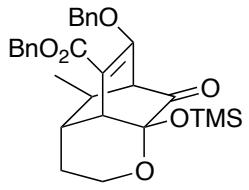


20b

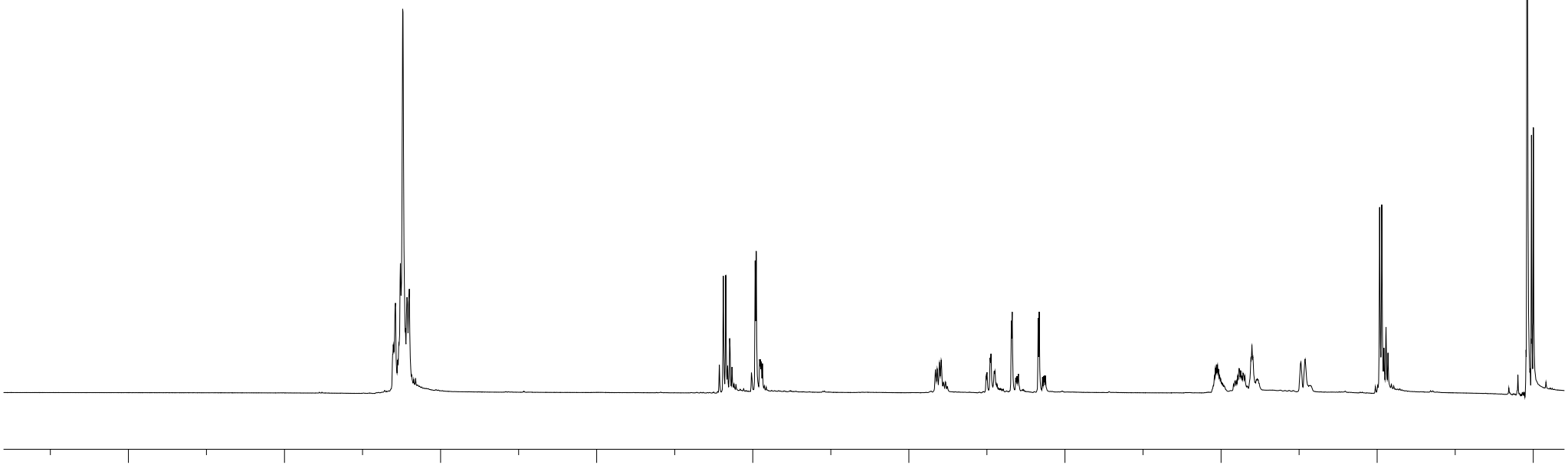
GKM-4-034 Acetate cleavage product
FIDs/20b/GKM-4-034C_p
July 18, 2012 2:26 PM



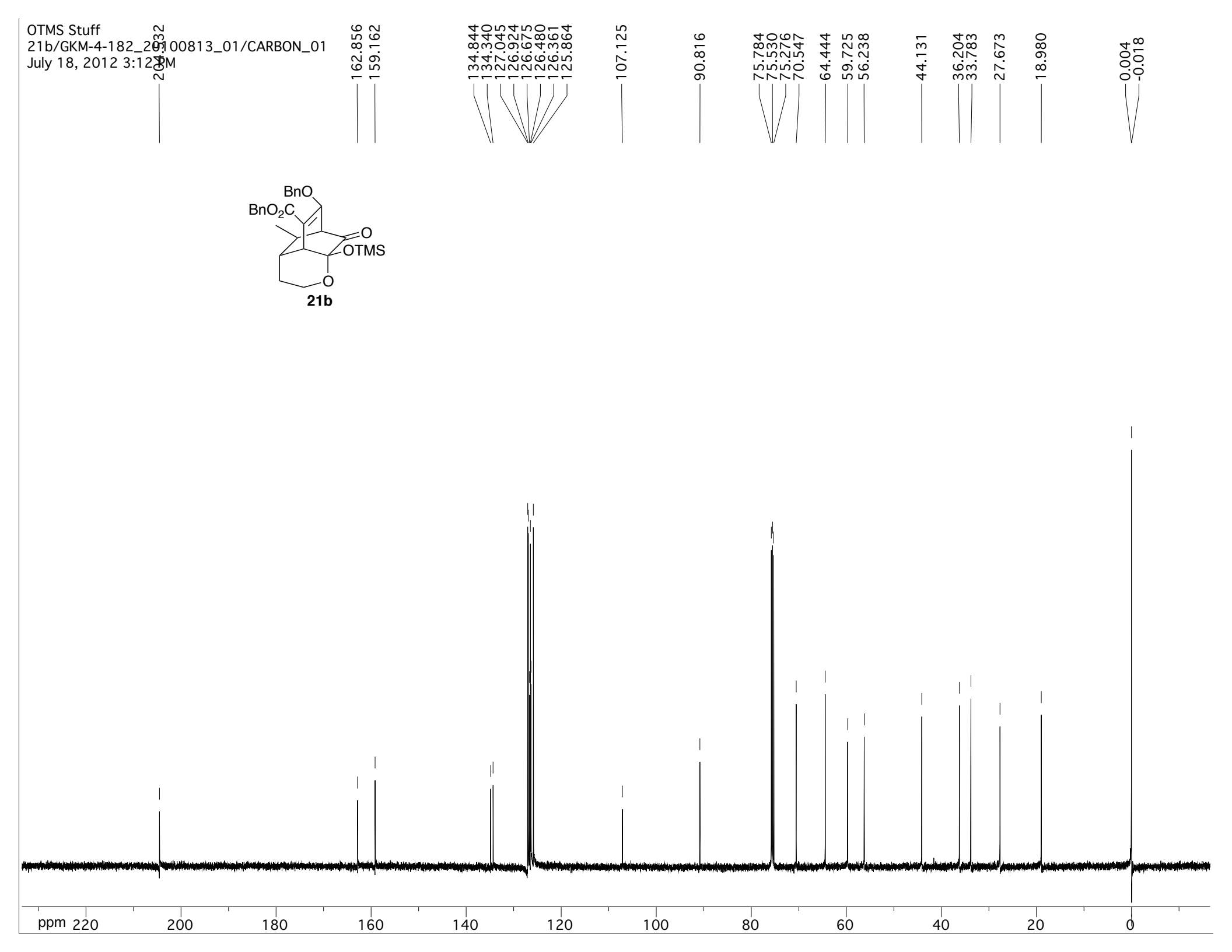
OTMS Stuff
21b/GKM-4-182_20100813_01/PROTON_01
July 18, 2012 2:26 PM



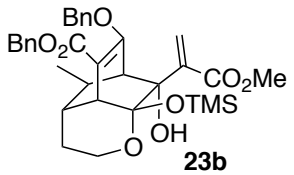
21b



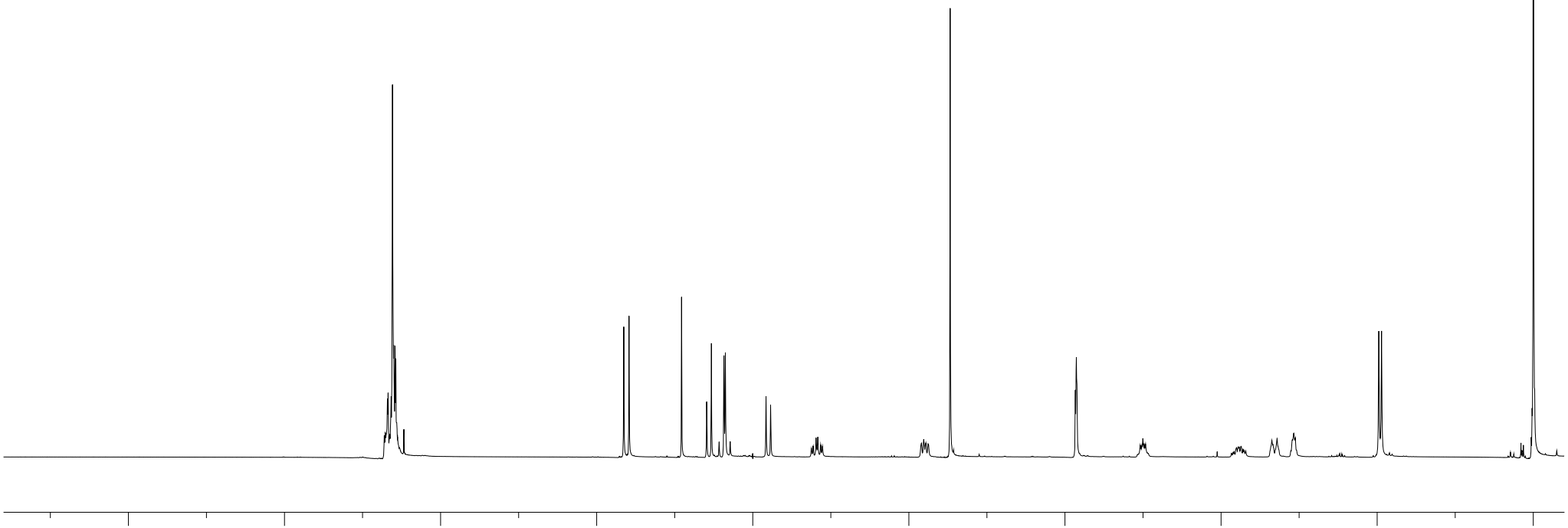
OTMS Stuff
21b/GKM-4-182_20100813_01/CARBON_01
July 18, 2012 3:12:



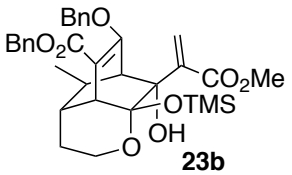
GKM-4-230 Cope elimination product
FIDs/23b/GKM-4-230H_p
July 18, 2012 2:28 PM



23b

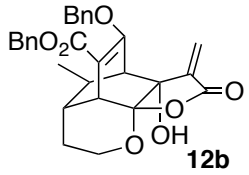


GKM-4-230 Cope elimination product
FIDs/23b/GKM-4-230C_
July 18, 2012 2:28 PM

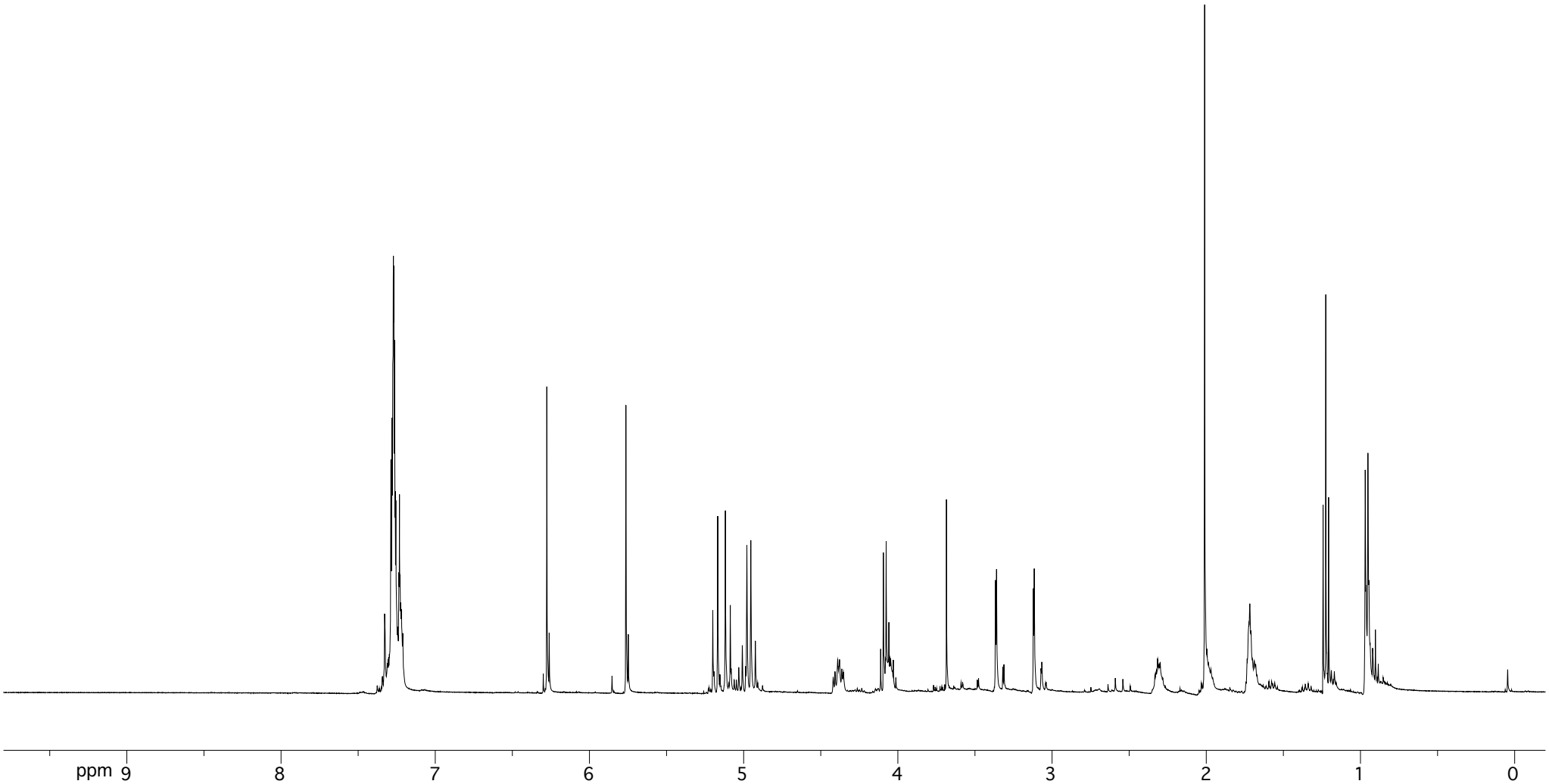


23b

GKM-4-038 Lactone closure product
FIDs/12b/GKM-4-038H
July 18, 2012 2:38 PM

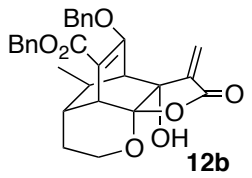


12b



GKM-4-038 Lactone closure product
FIDs/12b/GKM-4-038C_p
July 18, 2012 2:38 PM

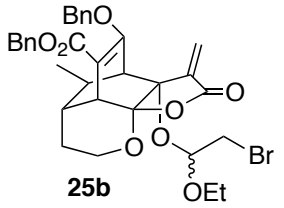
166.347
165.577
164.243
141.245
136.363
136.110
128.773
128.662
128.463
127.697
127.607
127.516
126.586
104.609
103.443
77.564
77.242
76.927
76.244
72.521
66.385
64.166
52.253
42.598
39.052
31.694
28.964
21.296



12b

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

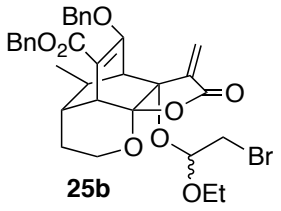
GKM-4-214 Bromoacetal product
FIDs/25b/GKM-4-214H_p
July 18, 2012 2:38 PM



25b

GKM-4-214 Bromoacetal product
FIDs/25b/GKM-4-214C_p
July 18, 2012 2:38 PM

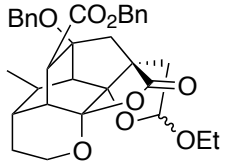
166.109
165.138
164.972
136.351
136.307
136.147
135.981
128.954
128.777
128.716
128.682
128.517
128.444
128.099
127.789
127.460
126.495
105.572
103.731
97.958
97.085
82.083
81.514
77.429
73.667
72.887
66.438
63.691
63.473
62.705
61.520
53.775
53.164
45.242
44.371
40.361
39.789
32.594
32.404
29.964
29.327
28.817
28.739
21.424
15.269
15.102



25b

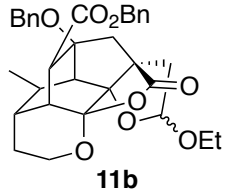
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

GKM-4-224 Radical reaction product, isomer mixture
FIDs/11b/GKM-4-224H_p
July 18, 2012 2:37 PM



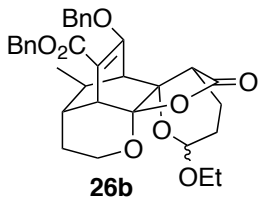
11b

GKM-4-224 Radical reaction product, isomer mixture
FIDs/11b/GKM-4-224C
July 18, 2012 2:37:?M

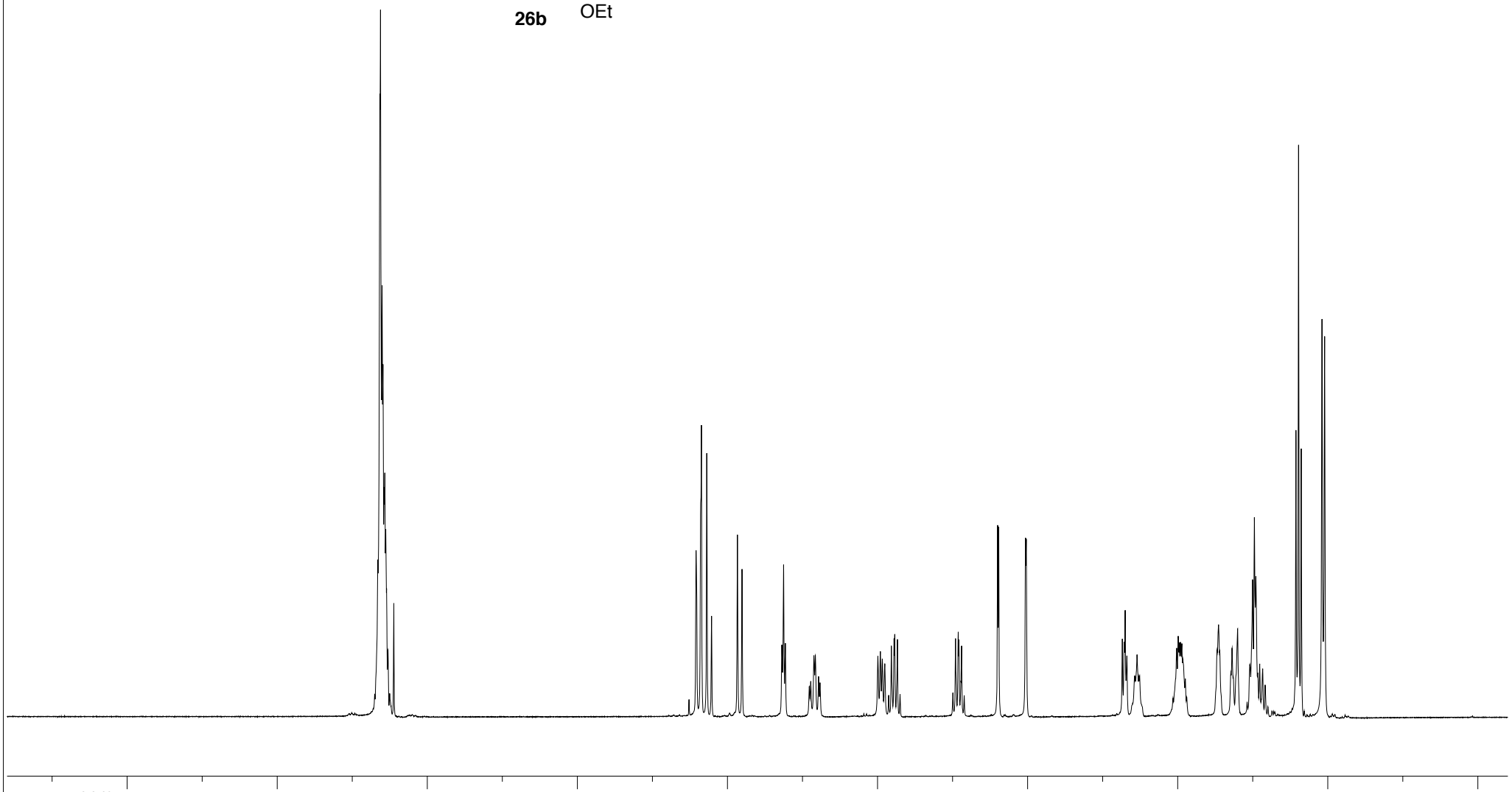


11b

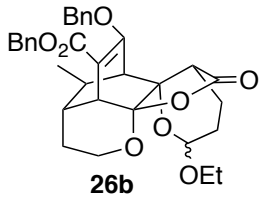
GKM-2-250 Side product, Bn ether cleavage on Dithiane
FIDs/26b/GKM-4-246H_sp
July 18, 2012 2:37 PM



26b

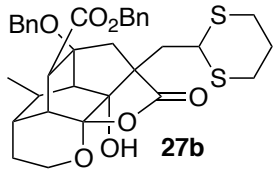


GKM-2-250 Side product, Bn ether cleavage on Dithiane
FIDs/26b/GKM-4-246c_sp
July 18, 2012 2:37 PM



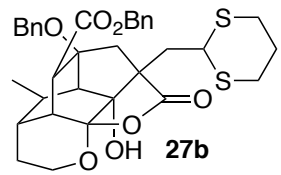
26b

GKM-4-226 Dithiane product
FIDs/27b/GKM-4-226H_p
July 18, 2012 2:45 PM



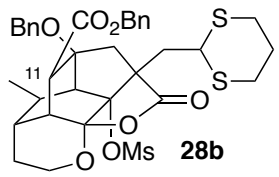
27b

GKM-4-226 dithiane product
FIDs/27b/GKM-4-226C_1_9
July 18, 2012 2:45 PM



27b

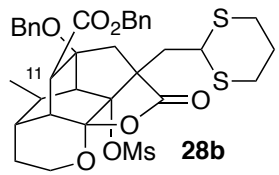
GKM-4-234 Mesylate product
FIDs/28b/GKM-4-234H_p
July 18, 2012 2:44 PM



28b

GKM-4-234 Mesylate product
FIDs/28b/GKM-4-234C_1
July 18, 2012 2:45 PM

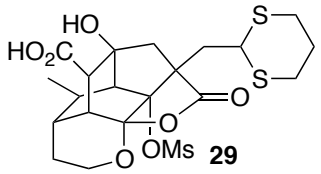
171.330
170.336
138.224
135.435
129.009
128.955
128.828
128.664
128.499
127.588
127.148
126.936
98.089
81.194
67.587
66.166
62.709
51.783
51.470
50.652
42.163
41.438
40.967
40.691
40.483
40.240
31.362
30.648
30.041
27.396
25.596
20.653



28b

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

GKM-4-198 Debenzylation reaction product
FIDs/29/GKM-4-198H
July 18, 2012 2:44 PM



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