Supporting Information

Manganese(III)-Mediated Transformations of Phloroglucinols: A Formal Oxidative [4+2] Cycloaddition Leading to Bicyclo[2.2.2]octadiones

Branko Mitasev and John A. Porco, Jr.*

Department of Chemistry and Center for Chemical Methodology and Library Development (CMLD-BU), Boston University, Boston, MA 02215

E-mail: porco@bu.edu

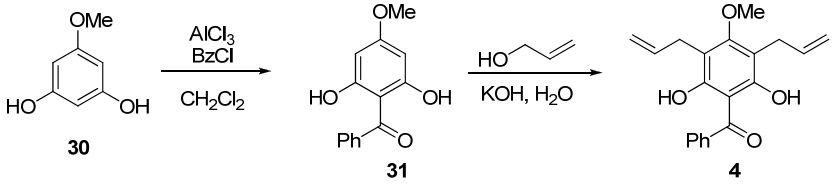
Table of Contents

I. General Information

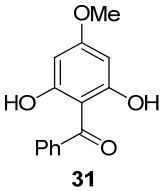
^{1}H NMR spectra were recorded at either 300 MHz or 400 MHz (as noted) at ambient temperature with $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded either at 75.0 MHz or 100.0 MHz (as noted) at ambient temperature with $CDCl_3$ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to $CDCl_3$ (^{1}H, δ 7.27; ^{13}C, δ 77.0). Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants. All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer. High-resolution mass spectra were obtained in the Boston University Chemical Instrumentation Center using a Waters Q-TOF mass spectrometer. Melting points were recorded on a Mel-temp apparatus (Laboratory Devices). Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 200-400 mesh silica gel (Scientific Absorbents, Inc.). Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. All other reagents were purchased from Sigma-Aldrich, Lancaster, Alfa Aesar, and Strem Chemicals. Methylene chloride, tetrahydrofuran, benzene, and hexane were purified by passing through two packed columns of neutral alumina (Innovative Technology, Inc, Newburyport, MA). All reactions were carried out in flame-dried glassware under an argon atmosphere unless otherwise noted. The Arthur™ Suite Reaction Planner (Symyx Technologies, Inc.) was used for experimental procedure planning.

II. Experimental Procedures and Compound Characterization

Preparation of Compound 4:



30 31 4



31

(2,6-Dihydroxy-4-methoxyphenyl)(phenyl)methanone (31). 3-Methoxyresorcinol **30** (12.0 g, 85.6 mmol) was placed in a flame-dried round-bottom flask, and CH_2Cl_2 (130.0 mL) was added under argon atmosphere. The suspension was cooled at 0 ºC and $AlCl_3$ (22.8 g, 171.0 mmol) was added. Stirring was continued until the suspension turned into a clear, yellowish solution (typically 10-15 min). Benzoyl chloride (14.9 mL, 128.0 mmol) was added dropwise over 5 minutes. The reaction solution was allowed to warm to ambient temperature over 2h, then quenched by pouring it carefully into an ice/water mixture. The aqueous layer was extracted three times with CH_2Cl_2, the organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by flash chromatography to afford **31** (13.9 g, 67%) as a yellow solid.

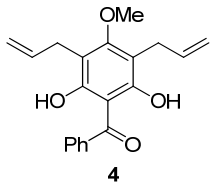
Mp = 129-130 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 2H), 7.68-7.65 (m, 2H), 7.64-7.59 (m, 1H), 7.56-7.52 (m, 2H), 6.05 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (100.0 MHz, $CDCl_3$) δ 197.4, 167.0, 162.4, 139.7, 132.4, 129.2, 127.8, 104.5, 95.0, 55.6.

IR νmas (film): 3312.8, 1630.2, 1591.3, 1318.8, 1154.7 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{14}H_{12}O_4$ 244.0736 found 267.0631 (M+Na).



4

(3,5-Diallyl-2,6-dihydroxy-4-methoxyphenyl)(phenyl)methanone (4). To a suspension of phloroglucinol **31** (8.9 g, 36.4 mmol) in water (66.0 mL) at 0 °C was added KOH (4.3 g, 76.6 mmol). The suspension was stirred under sonication until **31** was completely dissolved. Allyl bromide (6.9 mL, 79.7 mmol) was added dropwise over 10 minutes. The resulting mixture was stirred at 0 ^{o}C for 3 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted three times with ethyl acetate.

The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification on silica gel (hexane: ethyl acetate = 20: 1 to 10 : 1) provided compound **4** (2.40 g, 20%) as a yellow solid.

Mp = 52.0-53.0 °C.

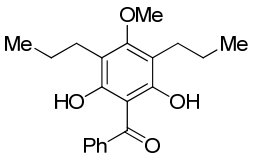
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (s, 2H), 7.70-7.66 (m, 2H), 7.61-7.53 (m, 1H), 7.52-7.46 (m, 2H), 6.02 (ddt, *J* = 15.3, 9.3, 5.7 Hz, 2H), 5.12-5.05 (m, 4H), 3.78 (s, 3H), 3.41 (dt, *J* = 6.0, 1.5 Hz, 4H).

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 199.0, 163.6, 157.8, 140.1, 136.5, 132.4, 128.8, 128.2, 115.3, 112.1, 107.5, 62.1, 27.9.

IR νmas (film): 3076.3, 2929.8, 1733.8, 1674.7, 1652.1, 1612.1, 1361.6, 1222.6 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{20}H_{22}O_4$ 324.1362 found 347.1284 (M+Na).

(2,6-Dihydroxy-4-methoxy-3,5-dipropylphenyl)(phenyl)-methanone (21). To a solution of compound **4** (1.02 g, 3.15 mmol) in EtOH (35 mL) was added Pd/C (10% wt, 83.9 mg, 0.08 mmol) at ambient temperature under an argon atmosphere. The reaction vessel was sealed with a rubber septum, and the atmosphere replaced with hydrogen *via* a balloon and needle by applying three vacuum cycles. After complete consumption of starting material according to TLC analysis (typically 1 h), the septum was removed and the remaining hydrogen gas was flushed using a gentle stream of nitrogen. The reaction mixture was filtered over a plug of Celite ® eluting with ethyl acetate and solvents were removed *in vacuo.* The crude residue was purified on silica gel (hexane: ethyl acetate = 20: 1 to 10 : 1) to afford **21** (823 mg, 80 %) as a yellow solid.



21

Mp = 74.3-75.7 °C.

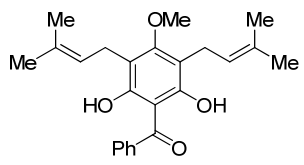
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (s, 2H), 7.72-7.68 (m, 2H), 7.65-7.59 (m, 1H), 7.57-7.51 (m, 2H), 3.81 (s, 3H), 2.54 (t, *J* = 7.8 Hz, 4H), 1.56 (tq, *J* = 7.8, 7.2 Hz, 4H), 0.97 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 198.5, 164.3, 157.2, 139.7, 132.6, 129.2, 128.1, 115.3, 107.1, 61.72, 25.8, 22.9, 14.4.

IR ν_{max} (film): 3521.9, 2960.3, 1616.8, 1596.2, 1576.5, 1120.9 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{20}H_{24}O_4$ 328.1675 found 329.1744 (M+1).

(2,6-Dihydroxy-4-methoxy-3,5-bis(3-methylbut-2-enyl)-phenyl)(phenyl) methanone (32). To a suspension of phloroglucinol **31** (8.8 g, 36.0 mmol) in water (71.0 mL) was added KOH (4.0 g, 72.0 mmol) at 0 °C under argon. The suspension was stirred under sonication until phloroglucinol **31** was completely dissolved. Prenyl bromide (8.3 mL, 72.0 mmol) was added dropwise over 10 minutes.



32

The resulting mixture was stirred at 0 °C for 4 h. The reaction mixture was quenched with satd. aqueous NH_4Cl and extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification on silica gel (hexane: ethyl acetate = 20:1 to 10:1) provided compound **32** (2.8 g, 20%) as a viscous yellow liquid that solidified upon refrigeration.

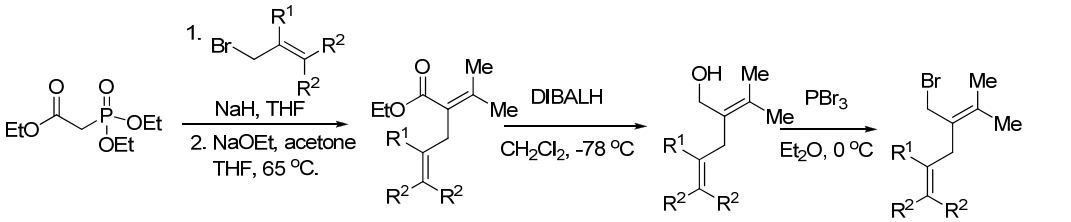
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 2H), 7.71-7.67 (m, 2H), 7.59-7.54 (m, 1H), 7.51-7.44 (m, 2H), 5.20 (ts, *J* = 6.6, 1.5 Hz, 2H), 3.76 (s, 3H), 3.34 (d, *J* = 6.6 Hz, 4H), 1.77 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 199.1, 162.9, 157.5, 140.3, 133.3, 132.1, 128.5, 128.3, 122.5, 113.7, 107.7, 61.6, 25.7, 22.7, 17.9.

IR νmas (film): 3513.3, 2913.7, 1619.3, 1596.8, 1096.9 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{24}H_{28}O_4$ 380.1988 found 403.1888 (M+Na).

Preparation of allylic bromides 5, 33, and 34.



To a solution of triethylphosphonoacetate (6.9 mL, 31.0 mmol) in THF (60.0 mL) was added NaH (60% in mineral oil, 1.4 g, 34.0 mmol) at 0 °C under an argon atmosphere. After 30 minutes, allyl bromide (2.9 mL, 34.0 mmol) was added dropwise over 5 min. The reaction mixture was stirred overnight, allowing it to warm to ambient temperature. The reaction was quenched with saturated aqueous NH_4Cl and the volatiles were removed *in vacuo*. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solvents were removed *in vacuo* and the crude allyltriethylphosphonoacetate (8.0 g) was used in the next step without further purification.[S1] Sodium metal (766 mg, 33 mmol) was added to EtOH (60 mL) at 0 °C under Ar. The reaction mixture was stirred until visible evolution of hydrogen gas ceased. The crude allyltriethylphosphonoacetate (8.0 g, 30.3 mmol) was added as a solution in THF (60 mL). After 15 min, acetone (10.0 mL) was added, and the reaction mixture was refluxed at 65 °C for 16 h. After cooling to ambient

[S1] Janecki, T.; Baszczyk, E.; Studzian, K.; Ralski, M.; Krajewska, U.; Janecka, A. *J. Med. Chem*. **2002**, *45*, 1142–1145

temperature, the reaction mixture was diluted with Et_2O, and washed consecutively with satd. aq NH_4Cl and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and the solvents removed *in vacuo* using a rotary evaporator with an ice bath cooled to 8 ºC. The crude residue was purified by silica gel chromatography (hexane : Et_2O, 10 : 1) to afford ester **5A** (2.3 g, 45%) as a colorless liquid.

5A: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83-5.66 (m, 1H), 5.01 (dt, *J* = 16.8, 0.4 Hz, 1H), 4.97 (dt, *J* = 8.4, 0.4 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.05 (d, *J* = 6.0 Hz, 2H), 2.02 (s, 3H), 1.81 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100.0 MHz, $CDCl_3$) δ 169.1. 144.2, 135.4, 125.2, 114.9, 60.0, 34.0, 23.0, 21.0, 14.2.

IR νmas (film): 2980.4, 2933.2, 1713.6, 1199.6 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{10}H_{16}O_2$ 169.1228 found 191.1048 (M+Na).

To a solution of ester **5A** (0.50 g, 2.97 mmol) in CH_2Cl_2 (20 mL) was added DIBAL-H (1.0M solution in hexane, 10.4 mL, 10.4 mmol) at -78 ºC over 3 min. The reaction mixture was stirred at -78 ºC for 2 h, and then ethyl acetate (1.0 mL) and satd. aq. NH_4Cl (3.0 mL) were added consecutively. After 1h, the mixture was filtered over a plug of Celite ¥® using a Büchner funnel and rinsed extensively with Et_2O. The solvent was removed *in vacuo* and the crude residue was purified by silica gel chromatography (hexane : Et_2O, 10 : 1 to 1 : 1) to afford alcohol **5B** (0.35 g, 93%) as a colorless liquid.

5B: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.2, 10.0, 6.4 Hz, 1H), 5.03 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.00 (dq, *J* = 10.0, 1.6 Hz, 1H), 4.15 (d, *J* = 5.2 Hz, 2H), 2.93 (d, *J* = 6.4 Hz, 2H), 1.79 (s, 3H), 1.72 (s, 3H).

^{13}C NMR (100.0 MHz, $CDCl_3$) δ 136.8, 131.8, 129.7, 115.1, 62.5, 35.4, 20.8, 20.4.

IR νmas (film): 3331.2, 2931.9, 997.6, 911.4 cm^{-1}.

To a solution of alcohol **5B** (130.0 mg, 1.03 mmol) in Et_2O (10 mL) was added pyridine (8.3 μL, 0.1 mmol), followed by PBr_3 (67.8 μL, 0.72 mmol) at 0 ºC under Ar. Formation of a white precipitate was observed immediately. After 30 min, the solvent was removed *in vacuo* to a volume of ca. 1 mL, hexane (5 mL) was added, and the mixture was filtered over a plug of silica gel eluting with hexane : Et_2O (20 : 1). The solvents were removed *in vacuo* using a rotary evaporator with an ice bath cooled to 10 ºC. The crude bromide **5** (145 mg, 75%) was used in the next step without further purification. Allylic bromide **5** was stored frozen and used as a solution in benzene (ca. 450 mg/mL).

5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (ddt, *J* = 16.8, 10.4, 6.4 Hz, 1H), 5.03 (dq, *J* = 16.8, 1.6 Hz, 1H), 5.02 (dq, *J* = 10.4, 1.6 Hz, 1H), 4.08 (s, 2H), 2.94 (d, *J* = 6.4 Hz, 2H), 1.81 (s, 3H), 1.74 (s, 3H).

^{13}C NMR (100.0 MHz, $CDCl_3$) δ 135.5, 135.4, 126.9, 115.5, 35.2, 34.8, 21.0, 20.5.

IR νmas (film): 2925.3, 1441.1, 1200.8, 914.5 cm^{-1}.

Allylic bromides **33** and **34** were prepared in an analogous manner as described for **5**.

33A: Triethylphosphonoacetate (3.1 mL, 15.6 mmol), NaH (60% in mineral oil, 0.7 g, 17.0 mmol), prenyl bromide (2.0 mL, 17.2 mmol); Na (0.37 g, 16.18 mmol), acetone (5 mL). Obtained **33A** (820 mg, 28%).

33B: **353** (0.35 g, 1.76 mmol), DIBALH (1.0M solution in hexane, 4.8 mL, 4.8 mmol). Obtained **33B** (0.22 g, 82%).

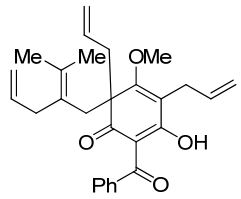
33: **33B** (0.20 g, 1.27 mmol), pyridine (10.3 μL, 0.1 mmol), PBr_3 (83.6 μL, 0.9 mmol); Obtained **35** (0.26 g, 94%).

34A: Triethylphosphonoacetate (1.8 mL, 9.0 mmol), NaH (60% in mineral oil, 0.4 g, 9.9 mmol), methallyl bromide (1.0 mL, 9.9 mmol). Na (0.21 g, 9.0 mmol), acetone (2.5 mL). Obtained **34A** (360 mg, 22%).

34B : **34A** (0.21 g, 1.15 mmol), DIBALH (1.0M solution in hexane, 2.5 mL, 2.5 mmol). Obtained **34B** (0.14 g, 86%).

34 : **34B** (0.13 g, 0.93 mmol), pyridine (7.5 μL, 0.9 mmol), PBr_3 (61.0 μL, 0.65 mmol); Obtained **34** (0.17 g, 90%).

General Procedure A for alkylative dearomatization of phloroglucinol derivatives with allylic bromides:

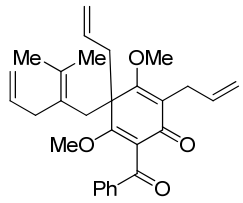


3

4,6-Diallyl-2-benzoyl-3-hydroxy-5-methoxy-6-(2-(propan-2-ylidene)pent-4-enyl)cyclohexa-2,4-dienone (3). To a solution of **4** (0.150 g, 0.462 mmol) in THF (5 mL) was added KHMDS (0.5 M solution in toluene, 1.850 mL, 0.925 mmol) at 0 ºC under Ar. After 2 min, bromide **5** (0.114 mg, 0.601 mmol) was added dropwise as a solution in benzene (450 mg/mL). After 20 min, the reaction was poured into saturated aqueous NH_4Cl and mixture extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by silica gel chromatography (hexane: ethyl acetate = 20: 1 to 3 : 1) to afford **3** (164 mg, 82%) as a colorless to light brown oil.

For spectroscopic characterization, compound **3** was converted to the methylated deriative **36** by the following procedure. To a solution of **3** (0.021 g, 0.048 mmol) in CH_3CN/MeOH (9 : 1, 1.1 mL) was added trimethylsilyldiazomethane (2.0 M solution in Et_2O, 0.24 mL, 0.48 mmol) at 0 ºC under Ar. After 10 min, solvents were evaporated *in vacuo*, and the

crude residue purified by preparative TLC (hexanes : ethyl acetate) to afford **36** (15 mg, 69%) as a colorless oil.



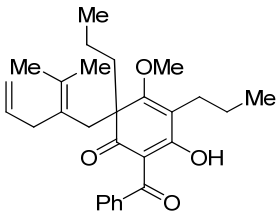
36

36: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.53 (tt, *J* = 7.6, 2.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.86 (ddt, *J* = 16.8, 11.6, 6.0 Hz, 1H), 5.72-5.62 (m, 2H), 5.13 (d, *J* = 11.6 Hz, 1H), 5.12 (d, *J* = 16.8 Hz, 1H), 5.03-4.91 (m, 4H), 4.03 (s, 3H), 3.62 (s, 3H), 3.21 (ddt, 1/2AB, *J* = 16, 5.6, 2.0 Hz, 2H), 2.80-2.68 (m, 6H), 1.69 (s, 3H), 1.68 (s, 3H).

^{13}C NMR (75.0 MHz, $CDCl_3$) δ196.3, 187.4, 170.8, 169.2, 138.4, 136.4, 136.3, 133.2, 133.1, 131.8, 129.1, 128.6, 125.7, 119.5, 118.2, 117.5, 114.9, 114.3, 62.0, 59.3, 54.1, 42.3, 39.6, 36.3, 28.3, 21.0, 20.8.

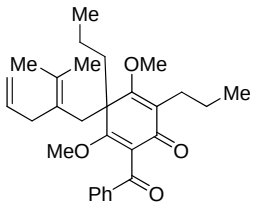
IR ν_{max} (film): 3076.4, 2928.4, 1733.7, 1674.8, 1651.7, 1612.6, 16362.0, 1223.1cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{29}H_{34}O_4$ 446.2457 found 469.2323 (M+Na).



12

2-Benzoyl-3-hydroxy-5-methoxy-6-(2-(propan-2-ylidene)pent-4-enyl)-4,6-dipropylcyclohexa-2,4-dienone (12). Prepared according to general procedure A using: **21** (0.054 g, 0.164 mmol), **5** (0.040 g, 0.214 mmol), NaHMDS (1.0 M solution in THF, 0.34 mL, 0.34 mmol), THF (3.5 mL). Obtained compound **12** (60 mg, 83%) as a colorless oil. Methylation: **12** (0.016 g, 0.037 mmol), (2.0 M trimethylsilyldiazomethane solution in Et_2O, 0.18 mL, 0.36 mmol). Obtained compound **37** (10 mg, 60%).



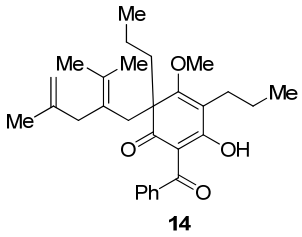
37

37: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.68 (ddt, *J* = 15.6, 9.2, 6.4 Hz, 1H), 4.96-4.91 (m, 2H), 3.97 (s, 3H), 3.60 (s , 3H), 2.81-2.67 (m, 4H), 2.40-2.27 (m, 2H), 1.96-1.84 (m, 2H), 1.68 (s, 6H), 1.65-1.48 (m, 2H), 1.40-1.10 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 196.8, 188.2, 170.431, 169.9, 138.5, 136.2, 133.0, 131.3, 129.1, 128.6, 126.1, 123.6, 117.5, 114.3, 61.6, 59.3, 54.1, 40.3, 39.9, 36.2, 26.2, 22.4, 20.9, 20.8, 18.1, 14.5, 14.2;

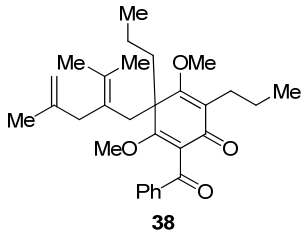
IR ν_{max} (film): 2958.9, 1677.8, 1649.1, 1611.9, 1363.9, 1221.7 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{29}H_{38}O_4$ 450.2770 found 473.2686 (M+Na).



14

2-Benzoyl-3-hydroxy-5-methoxy-6-(4-methyl-2-(propan-2-ylidene)pent-4-enyl)-4,6-dipropylcyclohexa-2,4-dienone (14). Prepared according to general procedure A using: **21** (0.060 g, 0.183 mmol), **34** (0.055 g, 0.271 mmol), NaHMDS (1.0 M solution in THF, 0.402 mL, 0.402 mmol). Obtained **14** (64 mg, 78%) as a colorless oil. Methylation: **14** (0.016 g, 0.035 mmol), (2.0 M trimethylsilyldiazomethane solution in Et_2O, 0.18 mL, 0.36 mmol). Obtained compound **38** (10 mg, 60%).



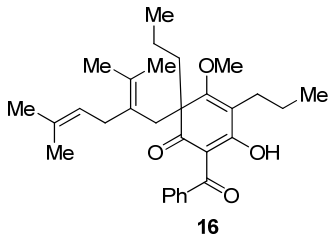
38

38: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.53 (tt, *J* = 5.7, 0.9 Hz, 1H), 7.44 (t, *J* = 6.0 Hz, 2H), 4.71 (app sex, *J* = 0.9 Hz, 1H), 4.55 (s, 1H), 3.96 (s, 3H), 3.60 (s, 3H), 2.76-2.64 (m, 4H), 2.40-2.28 (m, 2H), 1.96-1.81 (m, 2H), 1.71 (s, 3H), 1.66 (s, 3H), 1.65 (s, 3H), 1.57-1.51 (m, 1H), 1.40-1.33 (m, 1H), 1.28-1.24 (m, 1H), 1.23-1.10 (m, 1H), 0.92 (t, *J* = 5.4 Hz, 3H), 0.92 (t, *J* = 5.4 Hz, 3H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 196.9, 188.3, 170.6, 170.0, 143.6, 138.5, 133.0, 132.0, 129.1, 128.6, 127.6, 126.0, 123.6, 109.6, 61.6, 59.3, 54.2, 40.3, 40.1, 39.7, 26.3, 22.9, 22.4, 21.1, 20.9, 18.2, 14.6, 14.2;

IR ν_{max} (film): 2960.6, 1674.6, 1650.3, 1615.2, 1448.8, 1363.9, 1221.8 cm^{-1}.

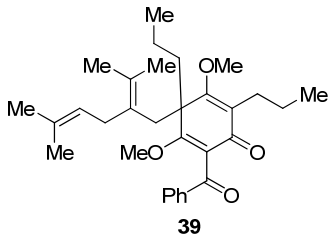
HRMS (ESI+) m/z calculated for $C_{30}H_{40}O_4$ 464.2927 found 487.2825 (M+Na).



16

2-Benzoyl-3-hydroxy-5-methoxy-6-(5-methyl-2-(propan-2-ylidene)hex-4-enyl)-4,6-dipropylcyclohexa-2,4-dienone (16). Prepared according to general procedure A, using: **21** (0.030 g, 0.091 mmol), **35** (0.024 g, 0.110 mmol), NaHMDS (1.0 M solution in THF, 0.201 mL, 0.201 mmol). Obtained **12** (41 mg, 96%) as a colorless oil. Methylation: **16** (0.020 g, 0.043 mmol), (2.0 M

trimethylsilyldiazomethane solution in Et_2O, 0.215 mL, 0.43 mmol). Obtained compound **39** (11 mg, 53%).

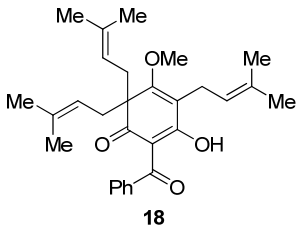


39

39: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.56-7.50 (m, 1H), 7.46-7.41 (m, 2H), 4.94 (tsept, *J* = 6.6, 1.5 Hz, 1H), 3.97 (s, 3H), 3.60 (s, 3H), 2.76 (d, *J* = 13.2 Hz, 1H), 2.70-2.66 (m, 3H), 2.36-2.30 (m 2H), 1.94-1.88 (m, 2H), 1.68 (s, 6H), 1.65 (s, 3H), 1.60 (s, 3H), 1.61-1.54 (obsc m, 1H), 1.40-1.10 (m, 3H), 0.93 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 196.9, 188.3, 170.5, 169.9, 138.5, 133.0, 131.0, 130.1, 129.1, 128.6, 128.3, 123.7, 123.4, 117.5, 61.6, 59.3, 54.2, 40.8, 40.2, 31.4, 26.4, 25.8, 22.4, 21.0, 20.8, 18.2, 17.8, 14.63, 14.2;

HRMS (ESI+) m/z calculated for $C_{31}H_{42}O_4$ 487.3083 found 501.2985 (M+Na).



18

2-Benzoyl-3-hydroxy-5-methoxy-4,6,6-tris(3-methylbut-2-enyl)cyclohexa-2,4-dienone (18). Prepared according to general procedure A using: **32** (0.056 g, 0.147 mmol), prenyl bromide (0.017 mL, 0.147 mmol), and KHMDS (0.50 M solution in toluene, 0.598 mL, 0.294 mmol). Obtained compound **18** (61 mg, 92%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 18.26 (s, 1H)*, 16.10 (s, 0.6H)**, 7.51-5.44 (m, 5H), 7.41-7.34 (m, 3H), 5.13 (tsept, *J* = 6.0, 1.6 Hz, 1H)*, 5.05 (tsept, *J* = 6.0, 1.6 Hz, 0.6H)**,4.90-4.86 (m, 3.2H), 4.02 (s, 3H), 3.94 (s, 1.8H), 3.30 (d, *J* = 6.0 Hz, 2H)*, 3.17 (d, J = 6.0 Hz, 1.2H)**, 2.80 (dd, *J* = 14.0, 7.6 Hz, 1.2H)**, 2.71-2.64 (m, 3.2H), 2.52 (dd, *J* = 14.0, 7.2 Hz, 1.2H)*, 1.79 (s, 6H)*, 1.71 (s, 2H)**, 1.70 (s, 2H)**, 1.69 (s, 6H)*, 1.66 (s, 4H)**, 1.63 (s, 10H);

* denotes major enol tautomer

** denotes minor enol tautomer

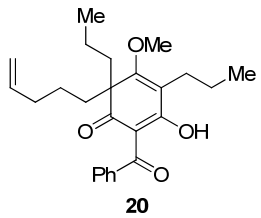
^{13}C NMR (100.0 MHz, $CDCl_3$) δ 199.2, 196.8, 195.0, 191.6, 189.6, 184.7, 175.7, 167.6, 139.0, 138.7, 135.4, 134.4, 132.7, 131.6, 131.1, 128.1, 127.9, 127.7, 127.6, 124.1, 122.7, 122.2, 118.7, 117.9, 62.3, 61.7, 59.3, 54.0, 37.7, 36.1, 25.9, 25.8, 25.7, 25.6, 23.0, 22.9,

18.1, 18.0 (two overlapping peaks), 17.9;

IR ν_{max} (film): 2967.9, 2913.8, 1639.2 (br), 1517.0, 1446.3, 1231.5 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{29}H_{36}O_4$ 448.2614 found 471.2516 (M+Na).

General procedure B for alkylative dearomatization of phloroglucinol derivatives employing alkyl triflates.



20

2-Benzoyl-3-hydroxy-5-methoxy-6-(pent-4-enyl)-4,6-dipropyl-cyclohexa-2,4-dienone (20). Preparation of 4-pentenyl trifluoromethanesulfonate: to a solution of 4-penten-1-ol (0.069 mL, 0.685 mmol) in hexane / benzene (3 : 1) was added *N,N*-disopropylethylamine (0.159 mL, 0.914 mmol) at 0 ºC under Ar. Trifluoromethanesulfonic anhydride (0.115 mL, 0.685 mmol) was added dropwise over one minute. After 5 min, the white suspension was collected into a syringe, and filtered over a plug of cotton. The solvents were removed *in vacuo* to an approximate volume of 0.5 mL and this solution was used in the next step without further purification.

To a solution of **21** (0.075 g, 0.228 mmol) in THF / benzene (3 : 1, mL) was added NaHMDS (1.0 M solution in THF, 0.457 mL, 0.457 mmol) at 0 ºC under Ar. After 2 min, the previously prepared triflate solution was added dropwise over 1 min). After 15 min, the reaction solution was poured into saturated aqueous NH_4Cl and the mixture extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude residue was purified by silica gel chromatography (hexane: ethyl acetate = 20: 1 to 3 : 1) to afford compound **20** (60 mg, 66%) as a colorless oil.

1.2 : 1 mixture of tautomers

^{1}H NMR (400 MHz, $CDCl_3$) δ 18.46 (s, 1H)*, 16.38 (s, 0.8H)**, 7.53-7.38 (m, 9H), 5.78-5.67 (m, 1.8H), 5.01-4.92 (m, 3.6H), 4.04 (s, 3H)*, 3.94 (s, 2.4H)**, 2.57-2.53 (m, 2H)*, 2.44-2.34 (m, 1.6H)**, 2.04-1.83 (m, 7.2H), 1.78-1.41 (m, 7.2H), 1.26-1.08 (m, 7.2H), 1.03 (t, *J* = 7.2 Hz, 3H)*, 0.94 (t, *J* = 7.2 Hz, 2.4H)**, 0.88 (t, *J* = 7.2 Hz, 2.4H)**, 0.83 (t, *J* = 7.2 Hz, 3H)*;

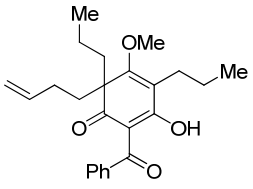
* denotes major enol tautomer

** denotes minor enol tautomer

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 199.5, 197.1, 195.6, 192.2, 190.1, 184.7, 175.4, 167.5, 139.0, 138.8, 138.1, 137.9, 131.7, 131.0, 128.0, 127.7, 127.6, 125.8, 119.4, 115. 1, 114.9, 113.2, 108.9, 62.2, 61.9, 59.6, 53.9, 41.7, 40.1, 38.7, 37.3, 33.8, 33.6, 26.0, 25.8, 24.3, 23.9, 22.9, 22.5, 18.3, 18.0, 14.4, 14.3, 14.1;

IR ν_{max} (film): 2959.4, 2932.7, 1640.8, 1436.0, 1228.6 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{25}H_{32}O_4$ 396.2301 found 397.2381 (M+1).



22

2-Benzoyl-6-(but-3-enyl)-3-hydroxy-5-methoxy-4,6-dipropyl-cyclohexa-2,4-dienone (22). Prepared according to general procedure B using: **21** (0.060 g, 0.183 mmol), 3-buten-1-ol (0.036 mL, 0.420 mmol), *N*,*N*-disopropylethylamine (0.095 mL, 0.548 mmol), Tf_2O (0.070 mL, 0.420 mmol), and NaHMDS (1.0 M solution in THF, 0.365 mL, 0.365 mmol). Obtained compound **22** (45 mg, 64%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 18.48 (s, 1H)*, 16.38 (s, 0.8H)**, 7.53-7.39 (m, 9H), 5.80-5.66 (m, 1.8H), 5.02-4.91 (m, 3.6H), 4.08 (s, 3H)*, 3.98 (s, 2.4H)**, 2.61-2.57 (m, 2H)*, 2.48-2.43 (m, 1.6H)**, 2.16-1.45 (m, 14.4H), 1.23-1.13 (m, 3.6H), 1.09 (t, *J* = 7.2 Hz, 3H)*, 0.99 (t, *J* = 7.2 Hz, 2.4H)**, 0.93 (t, *J* = 7.2 Hz, 2.4H)**, 0.88 (t, *J* = 7.2 Hz, 3H)*;

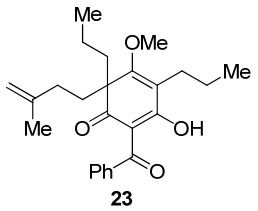
* denotes major enol tautomer

** denotes minor enol tautomer

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 199.4, 197.2, 195.3, 191.9, 190.1, 184.6, 175.1, 167.1, 139.0, 138.8, 137.7, 137.3, 131.7, 131.1, 128.0, 127.7, 127.6, 126.0, 119.5, 115.1, 114.8, 113.3, 109.0, 62.3, 61.9, 59.4, 53.7, 41.7, 40.2, 38.2, 36.8, 29.2, 29.0, 26.1, 25.9, 22.9, 22.5, 18.2, 18.0, 14.4, 14.3, 14.1;

IR ν_{max} (film): 2960.3, 1640.8, 1520.9, 1436.0, 1229.5 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{24}H_{30}O_4$ 382.2144 found 405.2049 (M+Na).



23

2-Benzoyl-3-hydroxy-5-methoxy-6-(3-methylbut-3-enyl)-4,6-di-propylcyclohexa-2,4-dienone (23). Prepared according to general procedure B using: **21** (0.110 g, 0.335 mmol), 3-methyl-3-buten-1-ol (0.10 mL, 1.05 mmol), *N*,*N*-disopropylethylamine (0.233 mL, 1.34 mmol), Tf_2O (0.170 mL, 1.05 mmol) and NaHMDS (1.0 M solution in THF, 0.77 mL, 0.77 mmol). Obtained compound **23** (84 mg, 63%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 18.47 (s, 1H)*, 16.40 (s, 0.8H)**, 7.53-7.46 (m, 5H), 7.43-7.38 (m, 4H), 4.72 (s, 0.8H)**, 4.69 (s, 1H)*, 4.68 (s, 0.8H)**, 4.64 (s, 1H)*, 4.08 (s, 3H)*, 3.98 (s, 2.4H)**, 2.60 (dd, *J* = 7.6, 5.6 Hz, 1H)*, 2.47 (dd, *J* = 7.6, 5.6 Hz, 1H)**, 2.21-1.48 (m, 14.4H), 1.73 (s, 2.4H)**, 1.70 (s, 3H)**, 1.25-1.13 (m, 3.6H), 1.08 (t, J = 7.6 Hz, 3H),* 0.99 (t, J = 7.6 Hz, 2.4H),** 0.93 (t, J = 7.6 Hz, 2.4H),** 0.88 (t, J = 7.6 Hz, 3H)*.

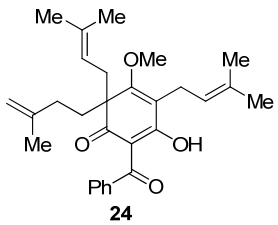
* denotes major enol tautomer

** denotes minor enol tautomer

^{13}C NMR (100.0 MHz, $CDCl_3$) δ 199.5, 197.1, 195.3, 192.0, 190.0, 184.7, 175.2, 167.2, 145.0, 144.7, 139.0, 138.8, 131.7, 131.1, 128.0, 127.7, 125.9, 119.5, 113.3, 110.3, 110.1, 108.9, 62.2, 61.9, 59.4, 53.7, 41.7, 40.2, 37.4, 35.9, 32.8, 32.7, 26.0, 25.9, 22.9, 22.5 (three peaks overlapping), 18.3, 18.0, 14.4, 14.3, 14.1 ;

IR ν_{max} (film): 2960.6, 1643.6, 1600.1, 1520.9, 1447.7, 1229.1 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{25}H_{32}O_4$ 396.2301 found 397.2369 (M+1).



24

2-Benzoyl-3-hydroxy-5-methoxy-4,6-bis(3-methylbut-2-enyl)-6-(3-methylbut-3-enyl)cyclohexa-2,4-dienone (24). Prepared according to general procedure B using: **32** (0.245 g, 0.643 mmol), 3- methyl-3-buten-1-ol (0.150 mL, 1.481 mmol), *N*,*N*-disopropylethylamine (0.336 mL, 1.932 mmol), Tf_2O (0.250 mL, 0.481 mmol), and NaHMDS (1.0 M solution in THF, 1.48 mL, 1.48 mmol). Obtained compound **24** (164 mg, 56%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 18.34 (s, 1H)*, 16.24 (s, 0.6H)**, 7.50-7.36 (m, 8H), 5.19 (tq, *J* = 6.4, 1.6 Hz, 1H)*, 5.09 (tq, *J* = 6.4, 1.6 Hz, 0.6H)**, 4.96 (t, *J* = 6.4 Hz, 1H)*,

4.88 (t, J = 6.4 Hz, 0.6H)**, 4.73 (s, 0.6H)**, 4.68 (s, 0.6H)**, 4.67 (s, 1H)*, 4.62 (s, 1H)*, 4.06 (s, 3H)*, 3.97 (s, 1.8H)**, 3.32 (d, J = 6.4 Hz, 2H)*, 3.18 (d, J = 6.4 Hz, 1.2H)**, 2.77 (dd, J = 14.0, 8.0 Hz, 0.6H)**, 2.68 (dd, J = 14.0, 8.0 Hz, 0.6H)**, 2.64 (dd, J = 14.4, 7.6 Hz, 1H)*, 2.53 (dd, J = 14.4, 7.6 Hz, 1H)*,2.27-2.11 (m, 2.4H), 1.94-1.76 (m, 4H), 1.80-1.61 (m, 24H corresponding to C-CH_3 from both enol tautomers).

* denotes major enol tautomer

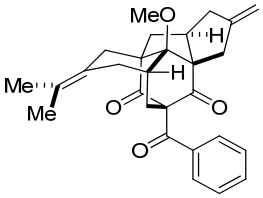
** denotes minor enol tautomer

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 199.2, 196.6, 194.9, 191.5, 189.6, 184.5, 175.4, 167.4, 145.1, 144.8, 138.9, 138.6, 135.6, 134.6, 132.9, 131.9, 131.7, 131.2, 128.2, 127.9, 127.7, 127.6, 124.5, 122.5, 122.0, 118.4, 118.4, 118.3, 117.6, 110.3, 109.8, 109.0, 62.5, 61.9, 59.2, 53.8, 38.7, 37.1, 36.4, 35.0, 32.9 (two peaks ovrlp), 25.9 (two peaks ovrlp), 25.7, 25.6, 23.1, 23.0, 22.5, 18.1, 18.0 (two peaks ovrlp), 17.9.

IR ν_{max} (film):2966.0, 1683.8, 1652.5, 1558.9, 1436.8, 1232.8 cm^{-1}.

LRMS (ESI+) m/z for $C_{29}H_{36}O_4$ found 449.6 (M+1)

General Procedure C for Mn (III)-mediated oxidative cyclization:



6

Polycyclic compound 6. A Schlenk tube equipped with a magnetic stir bar was charged with $Mn(OAc)_3(H_2O)_2$ (0.047 g, 0.175 mmol) and $Cu(OAc)_2(H_2O)$ (0.017 g, 0.083 mmol) and the atmosphere flushed with nitrogen three times. Degassed[S2] glacial acetic acid (0.5 mL), was added at ambient temperature. A solution of **3** (0.036 g, 0.083 mmol) in acetic acid (2.0 mL) was added *via* cannula and the reaction mixture was stirred at ambient temperature for 3h. The dark blue solution was poured into water and extracted two times with ethyl acetate. The organic layers were combined, washed with water then satd. aq. $NaHCO_3$, dried over anhydrous Na_2SO_4, and filtered. The solvents were removed *in vacuo*, and the crude residue purified by silica gel chromatography (hexanes : ethyl acetate, 10 : 1) to afford **6** (27 mg, 76%) as a white crystalline solid.

Mp = 172-174 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.53-7.48 (m, 1H), 7.38 (t, J = 7.6 Hz,

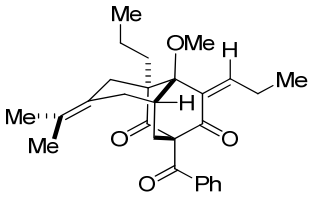
[S2] Glacial acetic acid was degassed by bubbling argon *via* a needle for 10 min.

2H), 4.90 (s, 1H), 4.84 (s, 1H), 3.56 (s, 3H), 3.26 (d, *J* = 8.8 Hz, 1H), 3.00 (d, *J* = 13.2 Hz, 1H), 2.96-2.91 (m, 2H), 2.87-2.79 (m, 1H), 2.63 (d, *J* = 17.6 Hz, 1H), 2.55 (d, *J* = 14.0 Hz, 1H), 2.45-2.41 (m, 1H), 2.38-2.29 (m, 3H), 2.28 (d, *J* = 13.2 Hz, 1H), 2.17 (d, *J* = 14.0 Hz, 1H), 2.01 (dd, *J* = 12.8, 6.4 Hz, 1H), 1.94 (dd, *J* = 14.0, 2.4 Hz, 1H), 1.66 (s, 3H), 1.61 (s, 3H).

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 209.6, 205.6, 194.8, 151.6, 135.9, 132.9, 129.7, 128.6, 128.2, 121.7, 104.9, 85.6, 72.9, 71.9, 67.7, 51.8, 47.2, 42.00, 40.5, 33.1, 31.3, 31.1, 30.6, 27.7, 20.7, 20.5;

IR ν_{max} (film): 2938.4, 1737.1, 1703.8, 1679.5, 1448.7, 1265.4 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{28}H_{30}O_4$ 430.2144 found 453.2045 (M+Na).



13

Bicyclo[2.2.2]octadione 13. Prepared according to general procedure C employing substrate **12** (0.026 g, 0.060 mmol), $Mn(OAc)_3(H_2O)_2$ (0.036 g, 0.125 mmol), and $Cu(OAc)_2(H_2O)$ (0.012 g, 0.060 mmol). Obtained compound **13** (12 mg, 82%) as a white, crystalline solid.

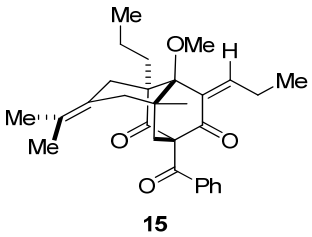
Mp = 173-176 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.47 (m, 3H), 7.40-7.35 (m, 2H), 6.35 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.43 (s, 3H), 2.90 (dd, *J* = 14.4, 2.4 Hz, 1H), 2.84 (app sex, *J* = 7.6 Hz, 1H), 2.76-2.72 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.70 (app sex, *J* = 7.6 Hz, 1H), 2.53 (app dt, *J* = 13.2, 3.2 Hz, 1H), 2.39 (dd, *J* = 14.0, 11.2 Hz, 1H), 2.23-2.18 (m, 2H), 1.83 (dd, *J* = 14.0, 3.6 Hz, 1H), 1.66 (s, 3H), 1.62 (s, 3H), 1.55-1.59 (obsc m, 2H), 1.45-1.36 (m, 2H), 1.14 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 206.9, 195.2, 193.5, 147.1, 135.7, 132.7, 131.8, 129.1, 128.7, 128.1, 122.5, 80.9, 74.0, 58.2, 50.4, 35.3, 32.1, 30.8, 30.5, 29.5, 22.6, 20.4, 20.1, 17.1, 15.0, 13.8;

IR ν_{max} (film): 2922.1, 1724.2, 1685.9, 1260.8 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{28}H_{34}O_4$ 434.2457 found 457.2360 (M+Na).



15

Bicyclo[2.2.2]octadione 15. Prepared according to general procedure C, using: **14** (0.015 g, 0.033 mmol), $Mn(OAc)_3(H_2O)_2$ (0.019 g, 0.070 mmol) and $Cu(OAc)_2(H_2O)$ (0.006 g, 0.033 mmol). Obtained **15** (12 mg, 82%) as a white, crystalline solid.

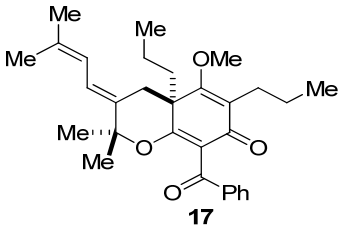
Mp = 141-143 °C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.46 (m, 3H), 7.39-7.34 (m, 2H), 6.35 (t, *J* = 7.8 Hz, 1H), 3.64 (s, 3H), 2.94 (dd, *J* = 13.2, 1.8 Hz, 1H), 2.87-2.70 (m, 2H), 2.40 (dd, *J* = 13.8, 1.8 Hz, 1H), 2.24 (d, *J* = 13.5 Hz, 1H), 2.15 (d, *J* = 14.4 Hz, 1H), 1.99 (d, 1/2AB, *J* = 14.1 Hz, 1H), 1.90 (d, 1/2AB, *J* = 14.1 Hz, 1H), 1.65 (s, 3H), 1.61 (s, 3H), 1.51-1.45 (m, 4H), 1.25 (s, 3H), 1.15 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 6.5 Hz, 3H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 205.8, 195.2, 193.1, 147.4, 135.8, 132.7, 131.6, 129.0, 128.0, 127.8, 124.1, 83.6, 74.4, 58.6, 54.9, 39.7, 39.5, 38.7, 36.2, 32.0, 29.2, 22.6, 20.4, 20.1, 17.6, 15.1, 13.9;

IR ν_{max} (film): 2957.5, 2916.9, 1724.2, 1686.4, 1623.8, 1447.9, 1261.9 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{29}H_{36}O_4$ 448.2614 found 471.2514 (M+Na).



17

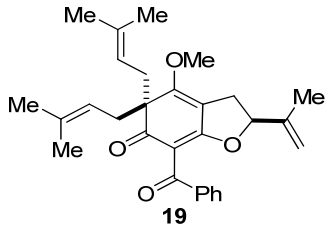
(*E*)-8-Benzoyl-5-methoxy-2,2-dimethyl-3-(3-methylbut-2-enylidene)-4a,6-dipropyl-4,4a-dihydro-2H-chromen-7(3H)-one (17). Prepared according to general procedure C using: **16** (0.017 g, 0.037 mmol), $Mn(OAc)_3(H_2O)_2$ (0.021 g, 0.077 mmol) and $Cu(OAc)_2(H_2O)$ (0.008 g, 0.037 mmol). Obtained compound **17** (12 mg, 70%) as a colorless, viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.83 (m, 2H), 7.52 (tt, *J* = 7.2, 2.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 6.36 (dd, *J* = 11.1, 1.8 Hz, 1H), 6.10 (d, *J* = 11.2 Hz, 1H), 3.99 (s, 3H), 3.24 (d, *J* = 14.1 Hz, 1H), 2.43 (t, *J* = 8.1 Hz, 2H), 2.40 (obsc d, *J* = 14.1 Hz, 1H), 1.90 (s, 3H), 1.82 (s, 3H), 1.87-1.75 (obsc m, 1H), 1.72-1.62 (m, 1H), 1.56-1.46 (obsc m, 2H), 1.50 (s, 3H), 1.26 (s, 3H), 1.24-1.10 (m, 2H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 194.5, 186.9, 170.3, 169.0, 138.7, 137.7, 133.5, 132.9, 129.0, 128.3, 125.1, 124.5, 121.9, 119.2, 86.2, 62.0, 47.9, 38.6, 31.7, 30.3, 28.5, 26.7, 26.6, 26.0, 22.4, 18.4, 17.5, 14.5, 14.0;

IR ν_{max} (film): 2960.1, 2930.1, 1676.4, 1653.2, 1618.5, 1374.1, 1222.9, 1111.5 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{30}H_{38}O_4$ 462.2770 found 485.2684 (M+Na).



19

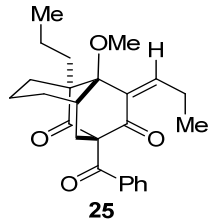
7-Benzoyl-4-methoxy-5,5-bis(3-methylbut-2-enyl)-2-(prop-1-en-2-yl)-2,3-dihydrobenzofuran-6(5H)-one (19). Prepared according to general procedure C using: **18** (0.037 g, 0.082 mmol), $Mn(OAc)_3(H_2O)_2$ (0.046 g, 0.173 mmol) and $Cu(OAc)_2(H_2O)$ (0.016 g, 0.082 mmol). Reaction time, 15 min at 65 ºC. Obtained compound **19** (28 mg, 76%) as a colorless, viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.47 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.39-7.34 (m, 2H), 5.23 (dd, *J* = 9.2, 5.2 Hz, 1H), 5.00 (tsept, *J* = 7.6, 1.6 Hz, 1H), 4.98 (d, *J* = 0.8 Hz, 1H), 4.93 (tsept, *J* = 7.2, 1.6 Hz, 1H), 4.89 (t, J = 1.2 Hz, 1H), 4.02 (s, 3H), 3.46 (dd, *J* = 15.2, 9.2 Hz, 1H), 3.04 (dd, *J* = 4.8 Hz, 1H), 2.68 (dd, J = 14, 7.2 Hz, 1H), 2.62 (dd, *J* = 13.6, 8.0 Hz, 1H), 2.50 (dd ovrlp, *J* = 13.6, 7.2 Hz, 2H), 1.70 (s, 3H), 1.68 (s, 6H), 1.60 (s, 6H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 196.3, 193.3, 176.9, 167.0, 142.4, 138.8, 134.4, 134.2, 132.3, 129.1, 128.0, 118.9, 118.8, 113.6, 104.5, 87.9, 58.8, 58.1, 39.1, 38.0, 31.3, 25.9 (two peaks ovrlp), 18.0 (two peaks ovrlp), 16.6;

IR ν_{max} (film): 2970.8, 2913.3, 1663.4, 1569.6, 1448.0, 1383.1, 1233.5 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{29}H_{34}O_4$ 446.2457 found 447.2529 (M+1).



25

Bicyclo[2.2.2]octadione 25. Prepared according to general procedure C using: **20** (0.016 g, 0.041 mmol), $Mn(OAc)_3(H_2O)_2$ (0.023 g, 0.087 mmol), and $Cu(OAc)_2(H_2O)$ (0.008 g, 0.041 mmol). Reaction time 4 h at 35 ºC. Obtained compound **25** (12 mg, 72%) as a white, crystalline solid.

Mp = 135-137 °C

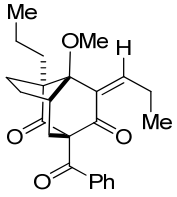
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.53 (m, 2H), 7.51 (tt, *J* = 7.2, 0.8 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 6.33 (dd, J = 8.0, 6.8 Hz, 1H), 3.38 (s, 3H), 2.85 (dq, 1/2AB, *J* = 15.6, 7.6 Hz, 1H), 2.70 (dq, 1/2AB, *J* = 15.6, 7.6 Hz, 1H), 2.67-2.63 (obsc m, 1H), 2.43 (dd, *J* = 14.4,

11.6 Hz, 1H), 2.14 (dd, *J* = 14.4, 3.2 Hz, 1H), 1.91 (br d, *J* = 12.8 Hz, 1H), 1.84-1.73 (m, 2H), 1.62-1.45 (m, 3H), 1.38-1.29 (m, 4H), 1.13 (t, *J* = 7.6 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H);

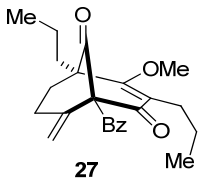
^{13}C NMR (75.0 MHz, $CDCl_3$) δ 208.2, 195.3, 193.4, 147.1, 135.9, 132.7, 129.0, 128.0, 80.8, 74.5, 56.4, 50.2, 35.4, 29.5, 29.2, 27.2, 25.6, 22.5, 16.9, 16.8, 15.0, 13.8;;

IR ν_{max} (film): 2958.9, 2871.4, 1720.6, 1686.0, 1448.8, 1261.8, 1094.2 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{25}H_{30}O_4$ 394.2144 found 417.2054 (M+Na).



26



27

Bicyclo[2.2.2]octadione 26 and bicyclo[3.3.1]nonane 27 Prepared according to general procedure C using: **22** (0.035 g, 0.091 mmol), $Mn(OAc)_3(H_2O)_2$ (0.051 g, 0.192 mmol), and $Cu(OAc)_2(H_2O)$ (0.018 g, 0.091 mmol). Obtained **26** (8 mg, 23%) as a white, crystalline solid and **27** (21 mg, 60%) as a viscous liquid.

26: Mp = 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.52 (tt, *J* = 7.6, 1.2Hz, 1H), 7.49-7.37 (m, 2H), 6.43 (dd, *J* = 8.0, 7.2 Hz, 1H), 3.36 (s, 3H), 2.91 (dd, *J* = 9.6, 6.4 Hz, 1H), 2.79 (app sept, *J* = 8.0 Hz, 1H), 2.72 (app sept, *J* = 8.0 Hz, 1H), 2.39 (dd, *J* = 14.8, 10.4 Hz, 1H), 2.18-2.09 (m, 1H), 2.07 (d, *J* = 14.8 Hz, 1H), 2.02 (dd, *J* = 12.8, 4.8 Hz, 1H), 1.96 (dd, *J* = 12.0, 5.2 Hz, 1H), 1.92-1.88 (m, 1H), 1.64-1.46 (m, 2H), 1.36-1.25 (m, 2H), 1.13 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 209.5, 195.4, 192.5, 148.5, 136.2, 132.7, 130.1, 129.3, 128.0, 87.4, 73.6, 65.1, 51.3, 34.9, 33.7, 33.2, 31.8, 30.4, 22.8, 19.0, 15.2, 13.7;

IR ν_{max} (film): 2960.7, 1723.6, 1689.1, 1625.1, 1449.0, 1262.2 1099.2 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{24}H_{28}O_4$ 380.1988 found 403.1885 (M+Na).

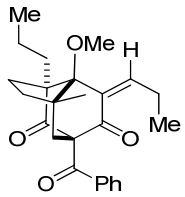
27: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 3H), 7.35-7.31 (m, 2H), 5.61 (d, *J* = 1.6 Hz, 1H), 5.29 (t, *J* = 1.6 Hz, 1H), 4.09 (s, 3H), 2.66-2.53 (m, 2H), 2.45-2.35 (m, 2H), 2.16 (ddd, *J* = 13.2, 6.0, 4.8 Hz, 1H), 1.94 (ddd, *J* = 13.6, 12.0, 4.4 Hz, 1H), 1.84 (ddd, *J* = 13.2, 10.0, 6.0 Hz, 1H), 1.75 (ddd, *J* = 13.6, 12.0, 4.4 Hz, 1H), 1.47-1.36 (m, 3H), 1.32-1.23 (m, 1H), 0.96 (t, *J* = 7.2, 3H), 0.94 (t, *J* = 7.2, 3H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 205.9, 193.4, 192.1, 173.3, 140.5, 136.9, 132.1, 128.6,

128.0, 124.8, 117.1, 79.5, 62.3, 58.0, 37.3, 34.4, 30.6, 26.2, 22.1, 18.3, 14.7, 14.1;

IR ν_{max} (film): 2960.0, 1727.9, 1699.5, 1655.6, 1596.2, 1447.3, 1227.7 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{24}H_{28}O_4$ 380.1988 found 403.1885 (M+Na).



28

Bicyclo[2.2.2]octadione 28. Prepared according to general procedure C using: **23** (0.030 g, 0.076 mmol), $Mn(OAc)_3(H_2O)_2$ (0.043 g, 0.160 mmol) and $Cu(OAc)_2(H_2O)$ (0.015 g, 0.076 mmol). Obtained **28** (21 mg, 69%) as a white, crystalline solid.

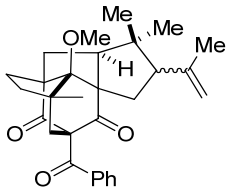
Mp = 142-144 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.54-7.49 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 6.45 (t, *J* = 7.6 Hz, 1H), 3.64 (s, 3H), 2.80-2.71 (m, 2H), 2.15 (d, *J* = 14.0 Hz, 1H), 2.05-1.86 (m, 3H), 1.92 (d, *J* = 14.0 Hz, 1H), 1.78-1.70 (m, 1H), 1.64-1.54 (m, 3H), 1.35-1.23 (m, 1H), 1.19 (s, 3H), 1.12 (t, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (75.0 MHz, $CDCl_3$) δ 209.0, 195.5, 192.1, 148.9, 136.8, 132.6, 130.6, 129.4, 127.8 88.5, 75.0, 66.0, 54.8, 46.9, 42.2, 37.8, 34.9, 34.5, 23.8, 22.8, 19.3, 15.1, 13.8;

IR ν_{max} (film): 2960.7, 1725.3, 1684.6, 1261.4 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{25}H_{30}O_4$ 395.2222 found 417.2052 (M+Na).



29

Polycyclic compound 29. Prepared according to general procedure C using: **24** (0.114 g, 0.254 mmol), $Mn(OAc)_3(H_2O)_2$ (0.140 g, 0.530 mmol), and $Cu(OAc)_2(H_2O)$ (0.051 g, 0.350 mmol). Obtained compound **29** (84 mg, 74%) as a 3 : 1 mixture of diastereomers. Crystallization from hexane afforded a sample enriched with diastereomer **29a** in a 9 : 1 ratio.

Mp = 161.5-162.0 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 4.92 (s, 1H), 4.71 (s, 1H), 3.79 (s, 3H), 2.93 (dd, *J* = 9.6, 8.4 Hz, 1H), 2.49-2.39 (m, 3H), 2.23 (app t, *J* = 12.8 Hz, 1H), 2.12-1.91 (m, 7H), 1.78 (s, 3H), 1.42 (s, 3H), 1.06 (s, 3H), 0.82 (s, 3H);

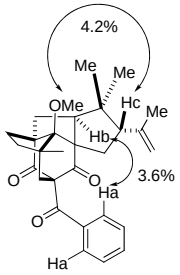
^{13}C NMR (75.0 MHz, $CDCl_3$) δ 212.1, 203.6, 195.2, 143.7, 137.0, 132.8, 128.3, 128,2,

112.9, 95.6, 79.0, 72.4, 68.0, 62.7, 59.5, 55.8, 46.6, 45.5, 43.5, 40.3, 29.9, 28.3, 26.9, 25.7, 25.2, 23.6, 18.3;

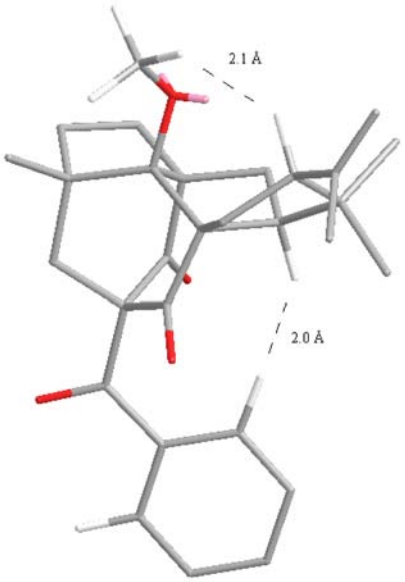
IR ν_{max} (film): 2955.6, 1736.2, 1704.8, 1682.9, 148.6, 1249.7 cm^{-1}.

HRMS (ESI+) m/z calculated for $C_{29}H_{34}O_4$ 447.2535 found 469.2364 (M+Na).

selected nOe enhacements used in assigning the relative stereochemistry of 29a

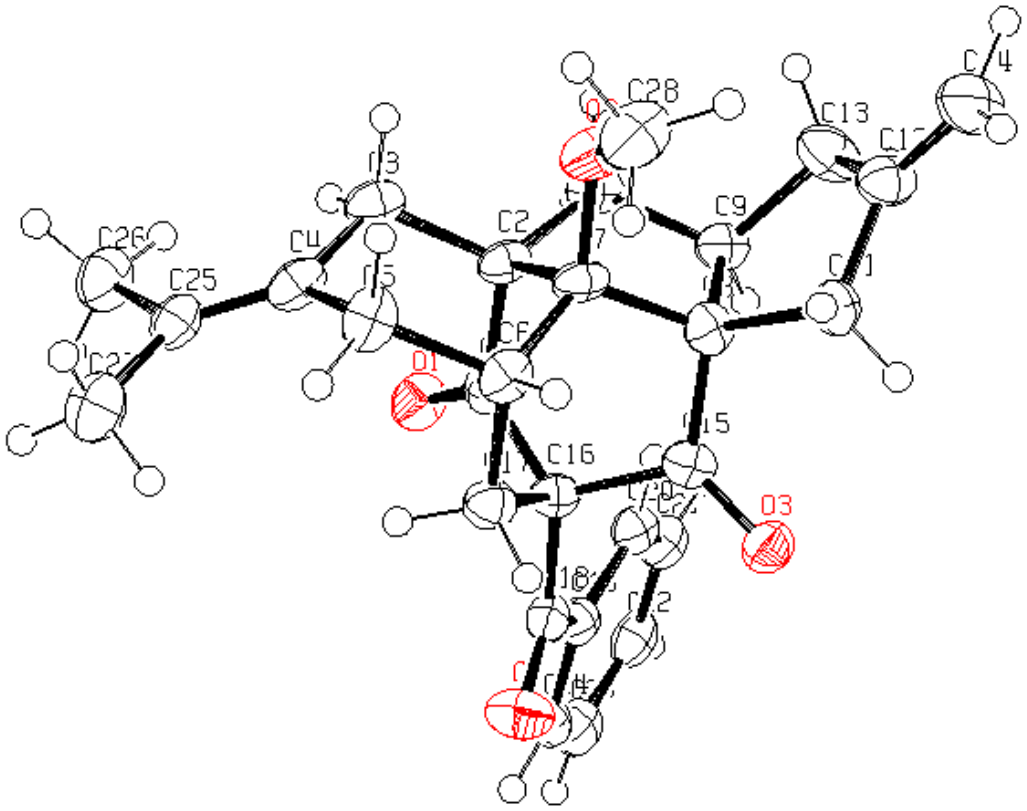


29a



III. X-Ray Crystallographic Data

X-ray crystallographic data for compound 6



Crystals of compound **6** suitable for x-ray analysis were obtained by slow evaporation from a solution in EtOH/H_2O (3 : 1). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 704796). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Table 1. Crystal data and structure refinement for compound **6**.

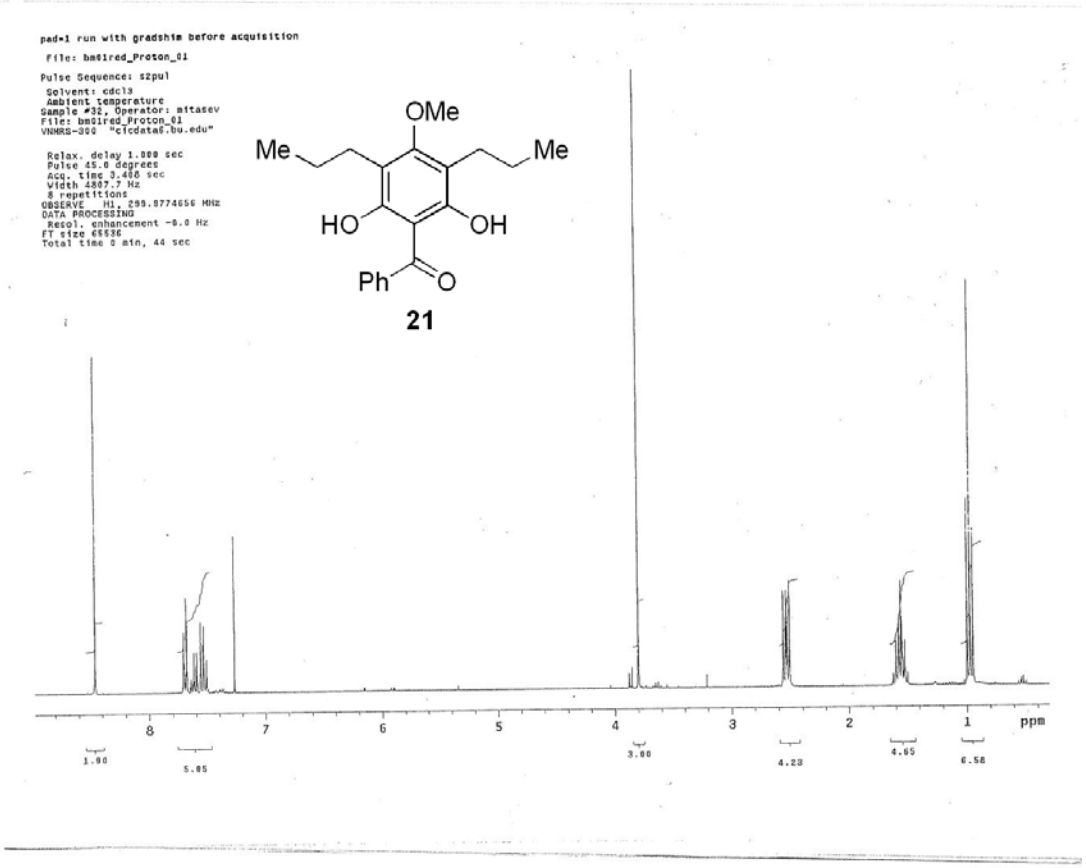
Identification code	compound **6**	
Empirical formula	C28 H30 O4	
Formula weight	430.52	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pca2(1)	
Unit cell dimensions	a = 24.138(3) Å	α= 90°.
	b = 8.8059(8) Å	β= 90°.
	c = 10.1770(11) Å	γ = 90°.
Volume	2163.2(4) $Å^3$	
Z	4	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	920	
Crystal size	0.20 x 0.10 x 0.02 mm^3	
Theta range for data collection	1.69 to 23.27°.	
Index ranges	-26<=h<=25, -9<=k<=7, -11<=l<=11	
Reflections collected	7891	
Independent reflections	1662 [R(int) = 0.0711]	
Completeness to theta = 23.27°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9983 and 0.9828	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1662 / 1 / 300	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.0874	
R indices (all data)	R1 = 0.0625, wR2 = 0.0958	
Absolute structure parameter	0(10)	
Largest diff. peak and hole	0.185 and -0.162 $e.Å^{-3}$	

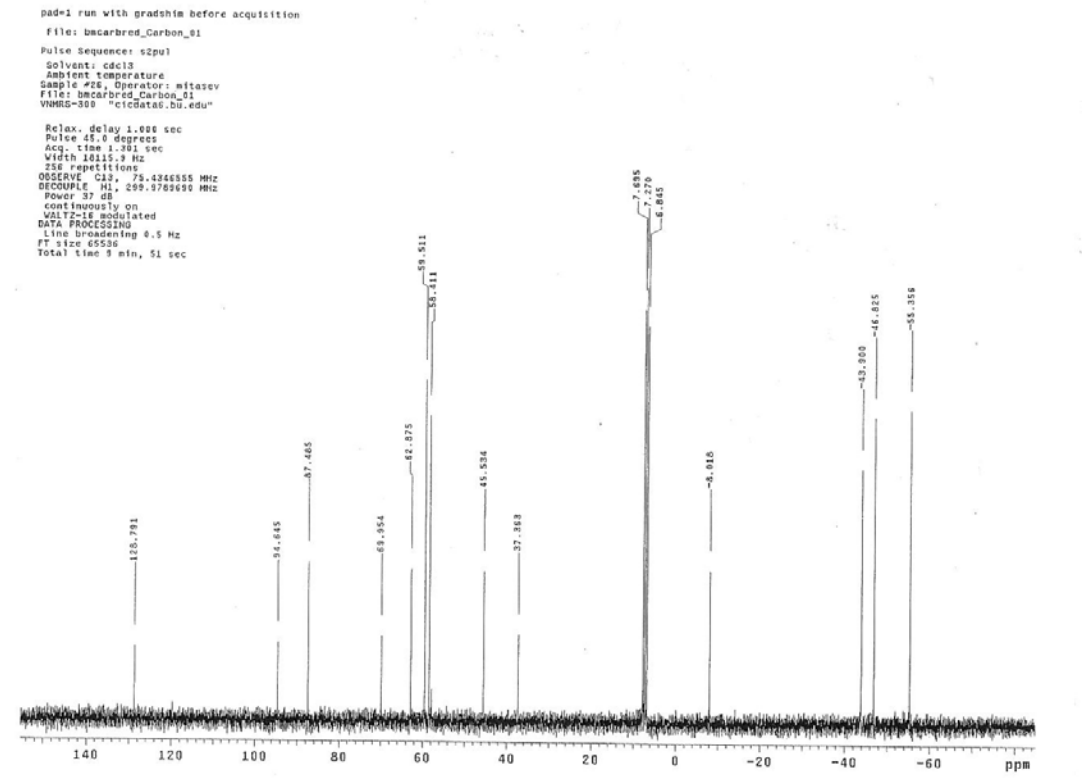
Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

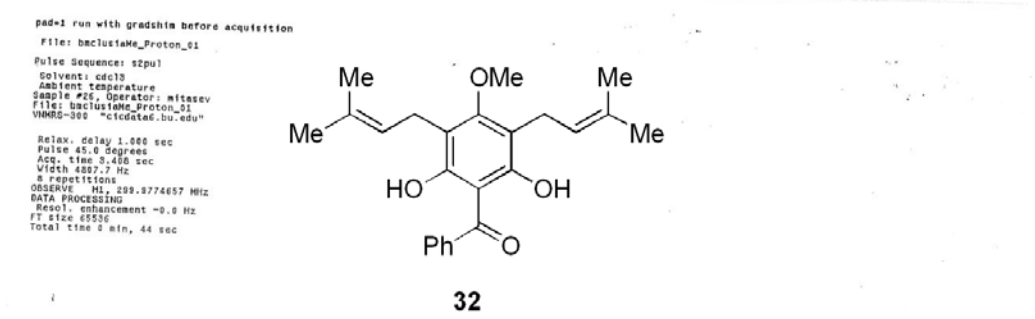
	x	y	z	U(eq)
O(1)	3861(1)	-2915(2)	84(3)	37(1)
O(2)	3109(1)	2040(2)	241(3)	36(1)
O(3)	4953(1)	1110(2)	-1073(3)	34(1)
O(4)	5335(1)	-1563(3)	928(3)	44(1)
C(1)	3903(1)	-1549(4)	55(4)	28(1)
C(2)	3401(1)	-489(3)	19(4)	27(1)
C(3)	2992(1)	-991(4)	1094(4)	34(1)
C(4)	3242(2)	-858(4)	2442(4)	33(1)
C(5)	3503(2)	702(4)	2688(4)	35(1)
C(6)	3902(1)	1173(4)	1589(3)	28(1)
C(7)	3603(1)	1146(3)	267(4)	28(1)
C(8)	3961(1)	1447(3)	-961(4)	29(1)
C(9)	3621(2)	634(4)	-2092(3)	30(1)
C(10)	3200(2)	-413(4)	-1405(4)	32(1)
C(11)	4045(2)	3083(3)	-1454(4)	32(1)
C(12)	3587(2)	3402(4)	-2403(4)	35(1)
C(13)	3374(2)	1906(4)	-2943(4)	43(1)
C(14)	3395(2)	4760(4)	-2727(5)	48(1)
C(15)	4504(2)	649(4)	-733(4)	27(1)
C(16)	4456(1)	-724(3)	167(4)	25(1)
C(17)	4401(1)	54(4)	1534(4)	31(1)
C(18)	4977(1)	-1705(4)	91(4)	29(1)
C(19)	5055(1)	-2795(4)	-1014(4)	29(1)
C(20)	4736(2)	-2758(4)	-2152(3)	29(1)
C(21)	4845(2)	-3727(4)	-3173(4)	35(1)
C(22)	5263(2)	-4798(4)	-3063(4)	37(1)
C(23)	5572(2)	-4871(4)	-1929(4)	42(1)
C(24)	5482(2)	-3860(4)	-919(4)	32(1)
C(25)	3235(2)	-1943(4)	3369(4)	31(1)
C(26)	2937(2)	-3435(4)	3189(4)	44(1)
C(27)	3499(2)	-1775(4)	4709(4)	47(1)

C(28)	3122(2)	3563(4)	758(4)	47(1)

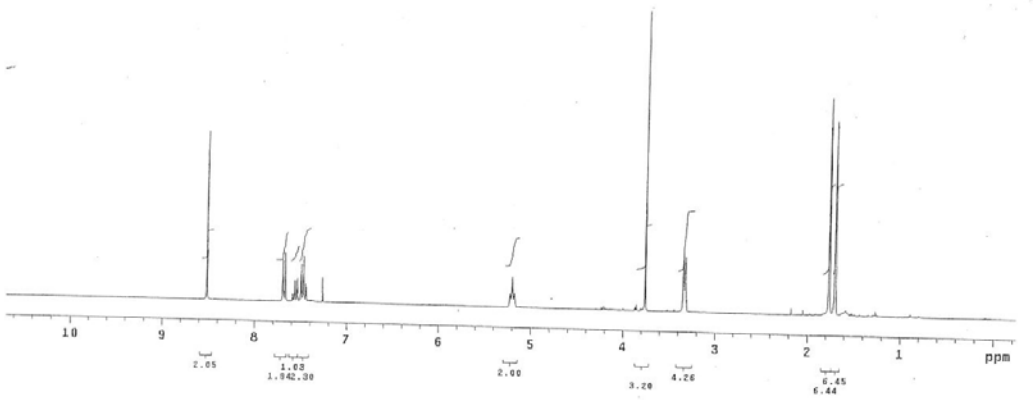
IV. Select NMR Spectra

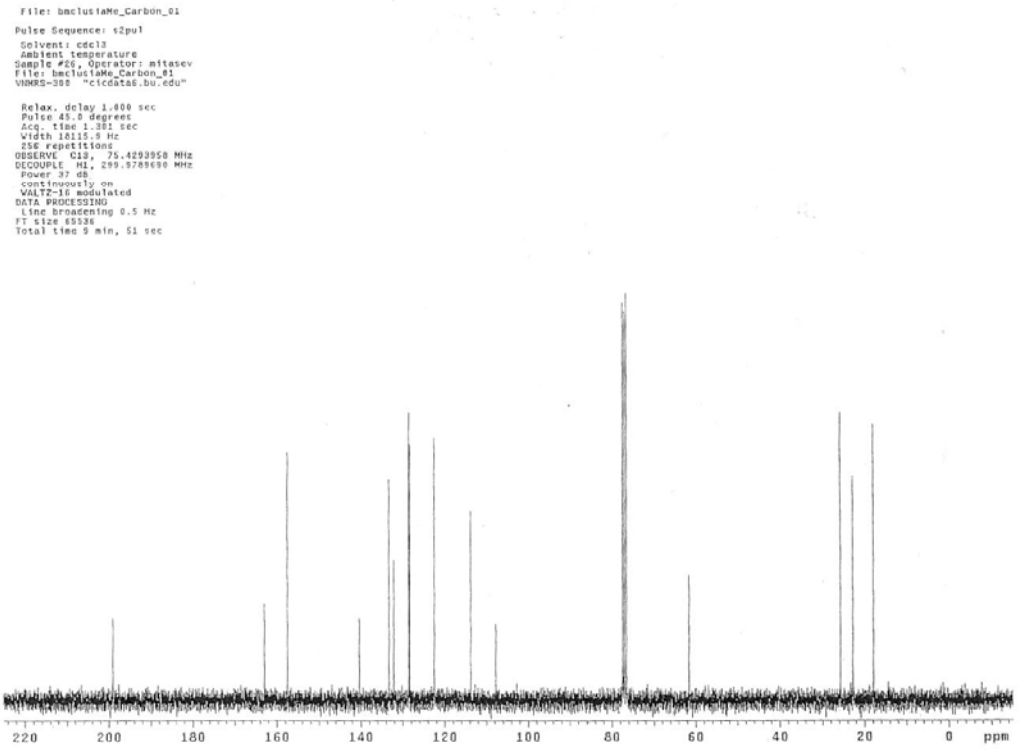

pad=1 run with gradshim before acquisition
File: bm01red_Proton_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #32, Operator: mitasev
File: bm01red_Proton_01
VNMRS-300 "cicdata6.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.466 sec
Width 4807.7 Hz
8 repetitions
OBSERVE H1, 299.8774656 MHz
DATA PROCESSING
Resol. enhancement -0.8 Hz
FT size 65536
Total time 0 min, 44 sec
OMe
Me
Me
HO
OH
Ph
O
21
8
7
6
5
4
3
2
1
ppm
1.00
5.05
3.00
4.23
4.65
6.58

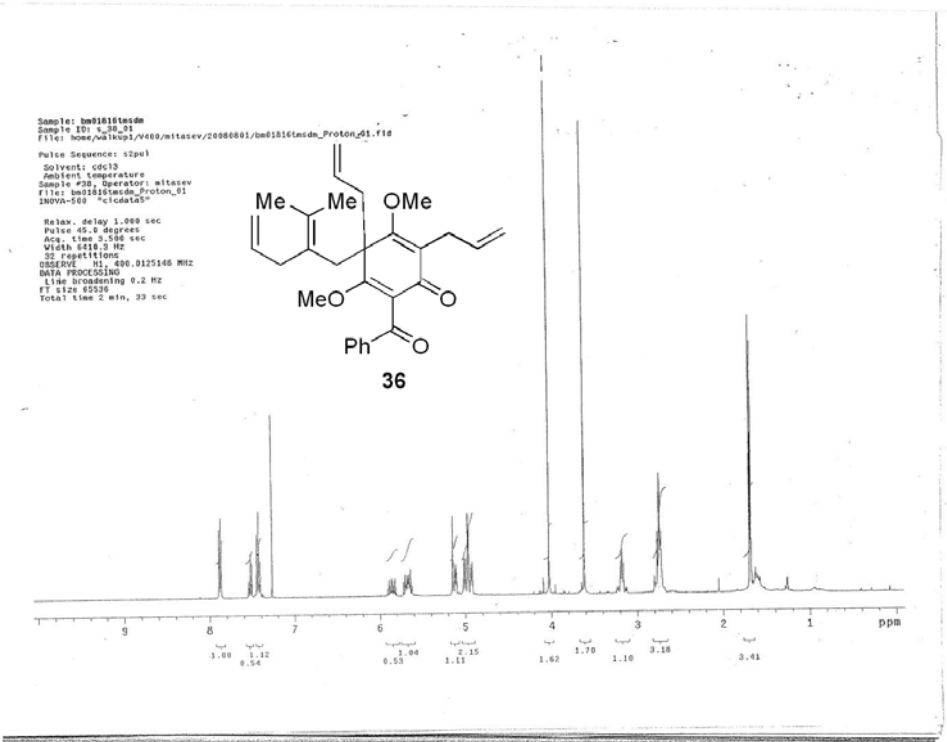

pad=1 run with gradshim before acquisition
File: bmcarbred_Carbon_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #26, Operator: mitasev
File: bmcarbred_Carbon_01
VNMRS-300 "cicdata6.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
256 repetitions
OBSERVE C13, 75.4246555 MHz
DECOUPLE H1, 299.9789690 MHz
Power 37 dB
continuously ON
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
128.791
94.645
87.485
69.454
62.875
59.511
58.111
45.534
37.363
7.695
7.679
6.845
-8.016
-43.900
-46.825
-55.356
140
120
100
80
60
40
20
0
-20
-40
-60
ppm

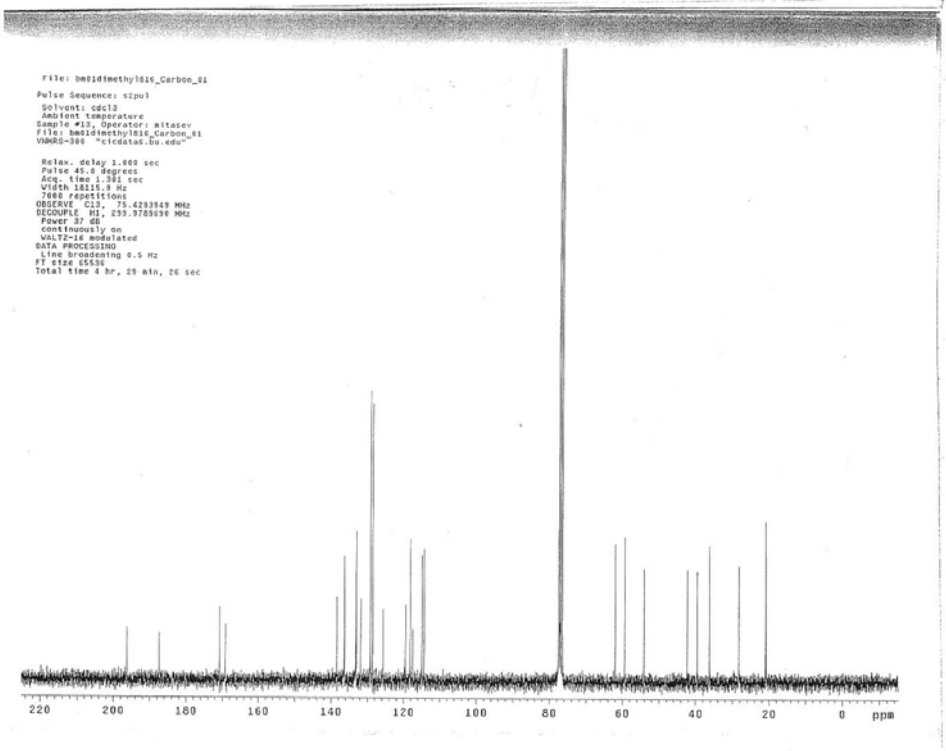

pad=1 run with gradshim before acquisition
File: bmclusiaMe_Proton_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #26, Operator: mitasev
File: bmclusiaMe_Proton_01
VNMRS-300 "cicdata6.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.406 sec
Width 4807.7 Hz
8 repetitions
OBSERVE H1, 299.8774657 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 44 sec
Me
OMe
Me
Me
Me
HO
OH
Ph
O

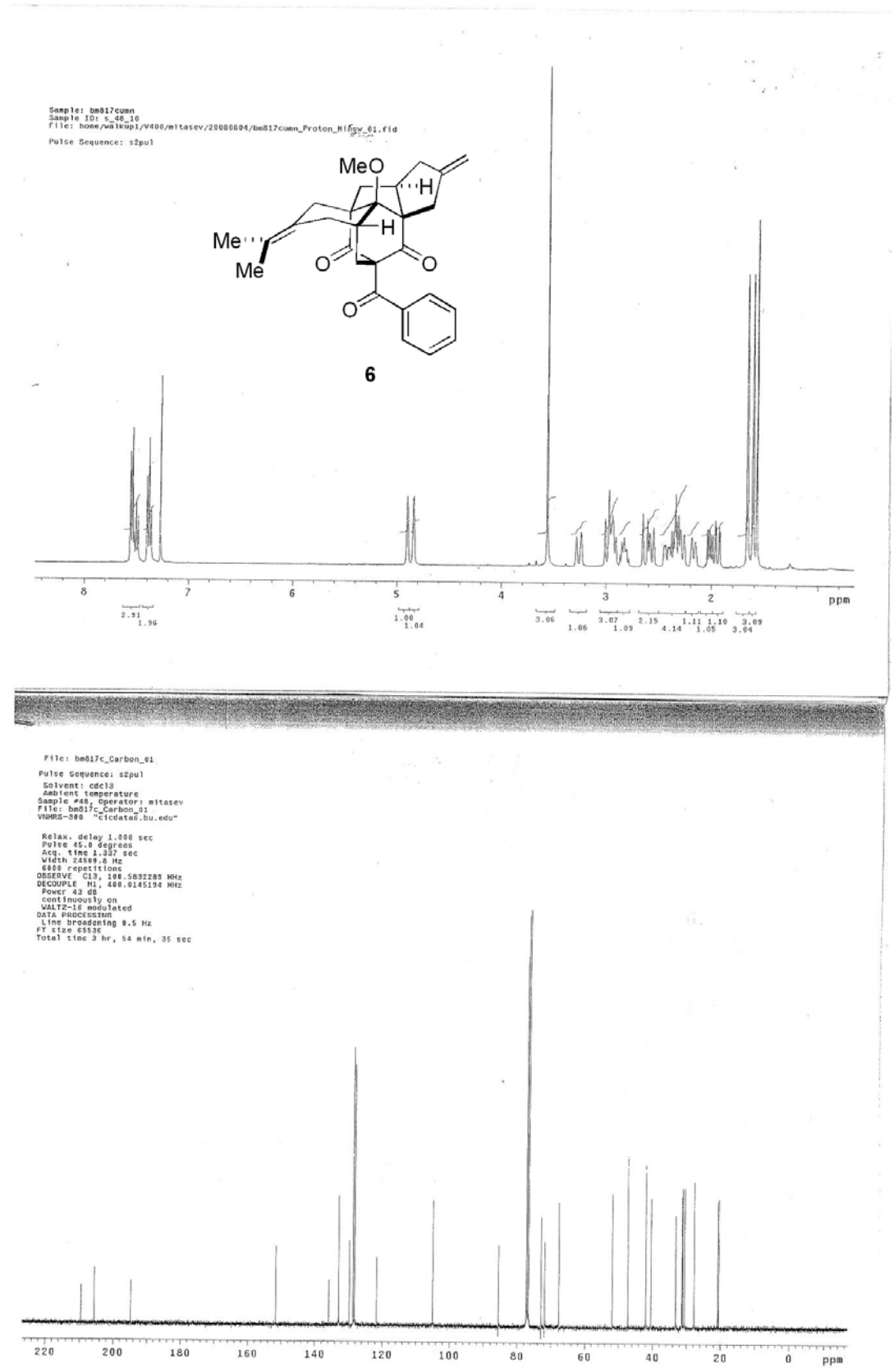
32

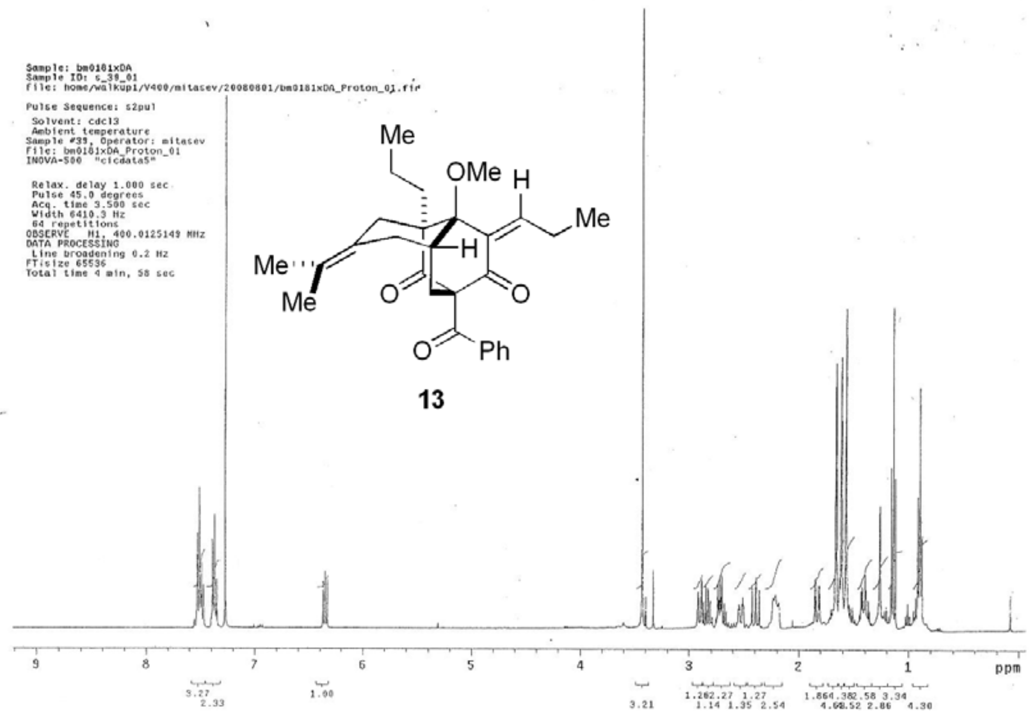

10
9
8
7
6
5
4
3
2
1
ppm
2.05
1.03
1.942.30
2.00
3.20
4.26
6.45
6.44

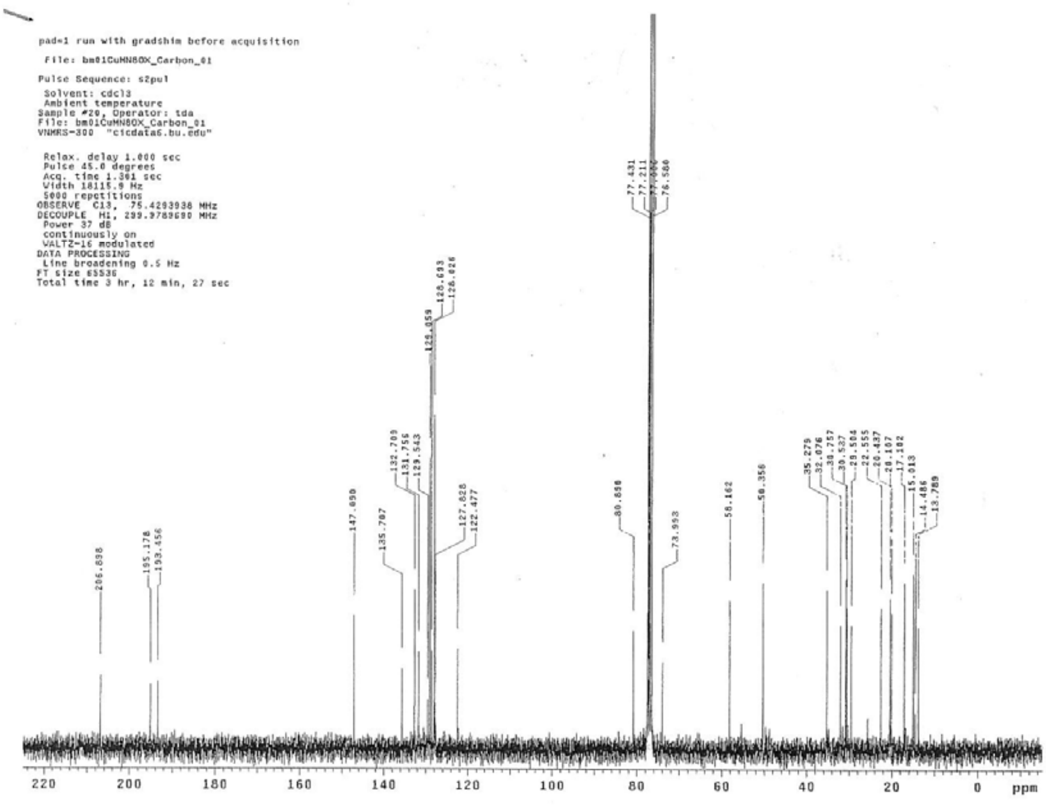

File: bmclusiaMe_Carbon_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #26, Operator: mitasev
File: bmclusiaMe_Carbon_01
VNMRS-300 "cicdata6.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.381 sec
Width 18115.9 Hz
256 repetitions
OBSERVE C13, 75.4293958 MHz
DECOUPLE H1, 299.9789690 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 min, 51 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

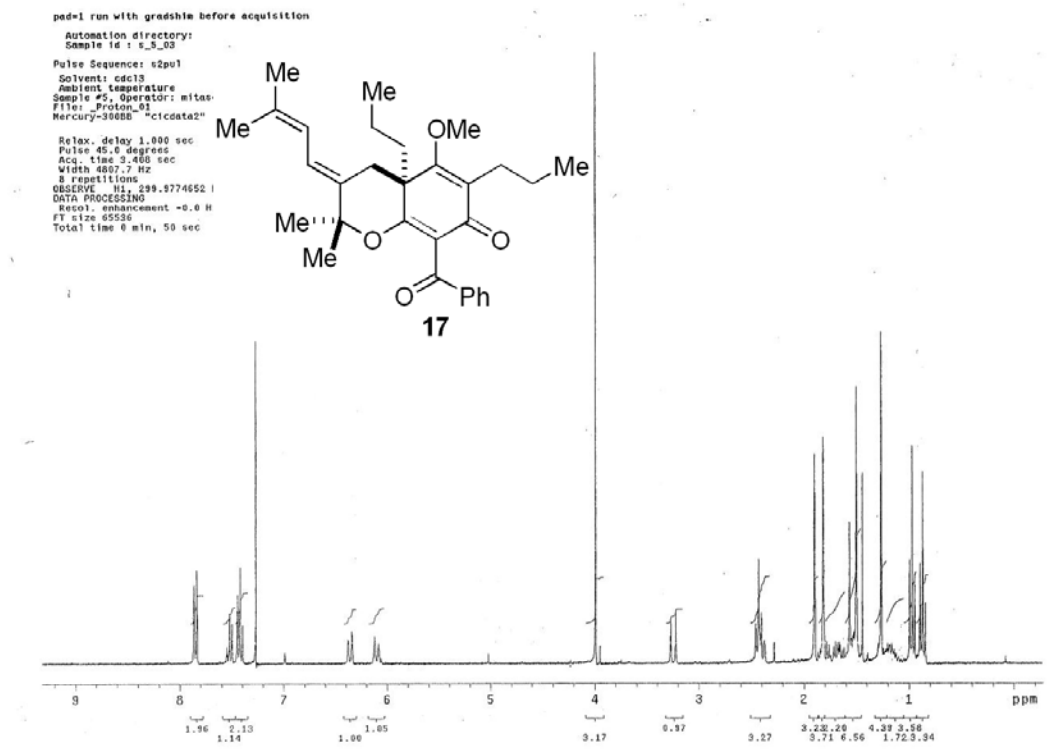

Sample: bm01816tmsdm
Sample ID: s_30_01
File: home/walkup1/v400/mitasev/20060801/bm01816tmsdm_Proton_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #30, Operator: mitasev
File: bm01816tmsdm_Proton_01
INOVA-500 "cicdata5"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6418.3 Hz
32 repetitions
OBSERVE H1, 499.8125146 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 min, 33 sec
Me
Me
OMe
MeO
O
Ph
O
36
ppm
1.00
1.12
0.54
1.04
0.53
2.15
1.11
1.62
1.70
1.10
3.18
3.41

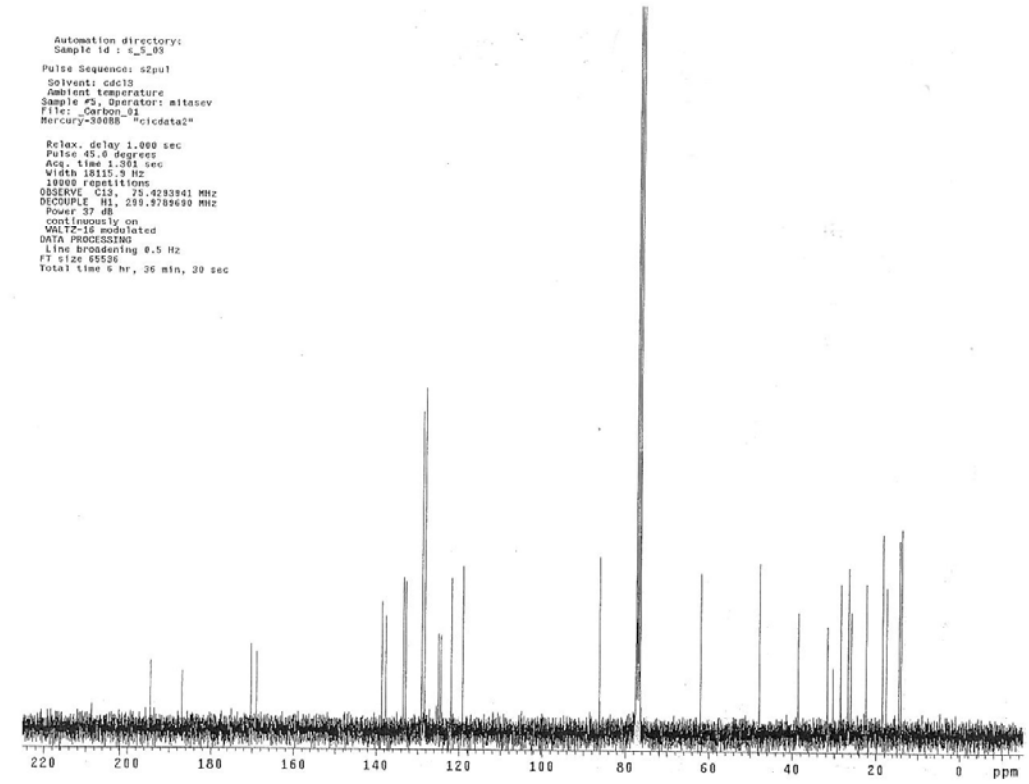

File: bm01dimethyl816_Carbon_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #13, Operator: mitasev
File: bm01dimethyl816_Carbon_01
VNMRS-300 "cicdata6.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.381 sec
Width 18115.9 Hz
7000 repetitions
OBSERVE C13, 75.4283949 MHz
DECOUPLE H1, 299.9785630 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 4 hr, 29 min, 26 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

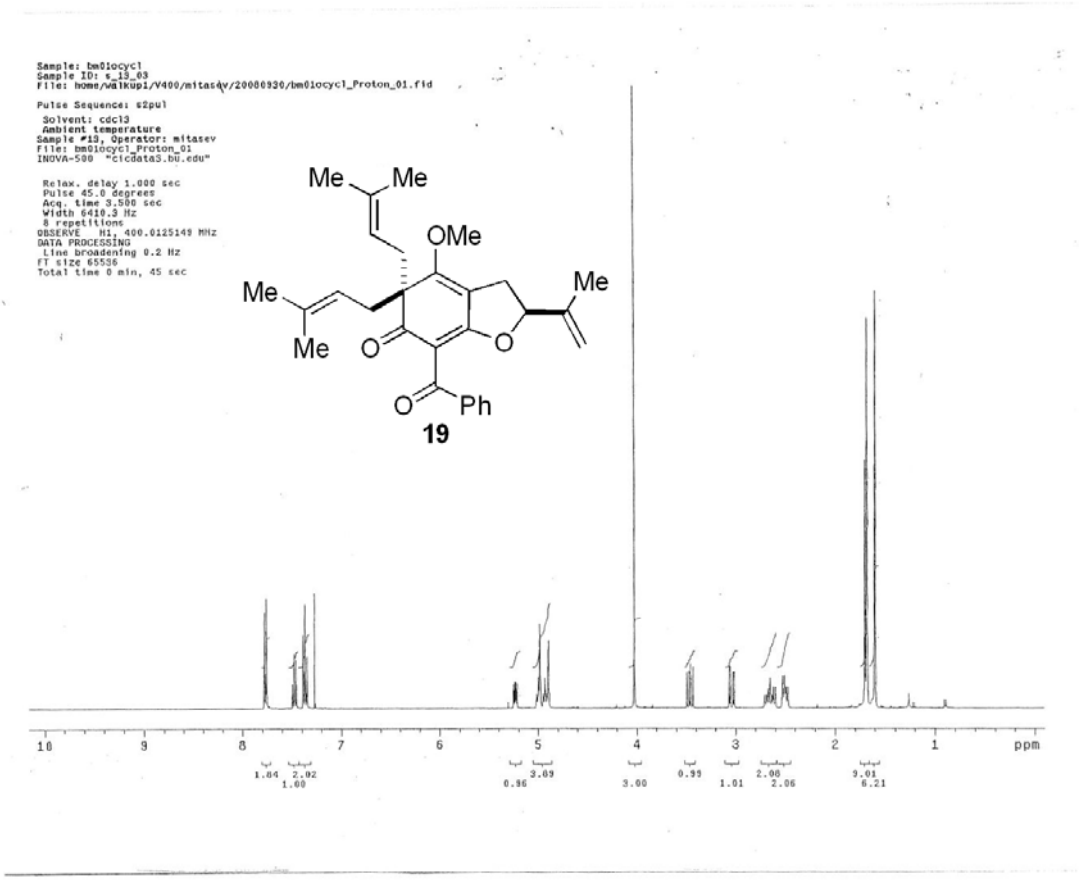

Sample: bm817cumn
Sample ID: s_48_10
File: home/walkup1/V400/mitasev/20080804/bm817cumn_Proton_Hifsw_01.fid
Pulse Sequence: s2pul
MeO
H
H
Me
Me
O
O
O
6
ppm
File: bm817c_Carbon_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #48, Operator: mitasev
File: bm817c_Carbon_01
VNMRS-300 "cicdata6.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.337 sec
Width 24509.8 Hz
6000 repetitions
OBSERVE C13, 100.5832285 MHz
DECOUPLE H1, 400.0145194 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 54 min, 35 sec
ppm

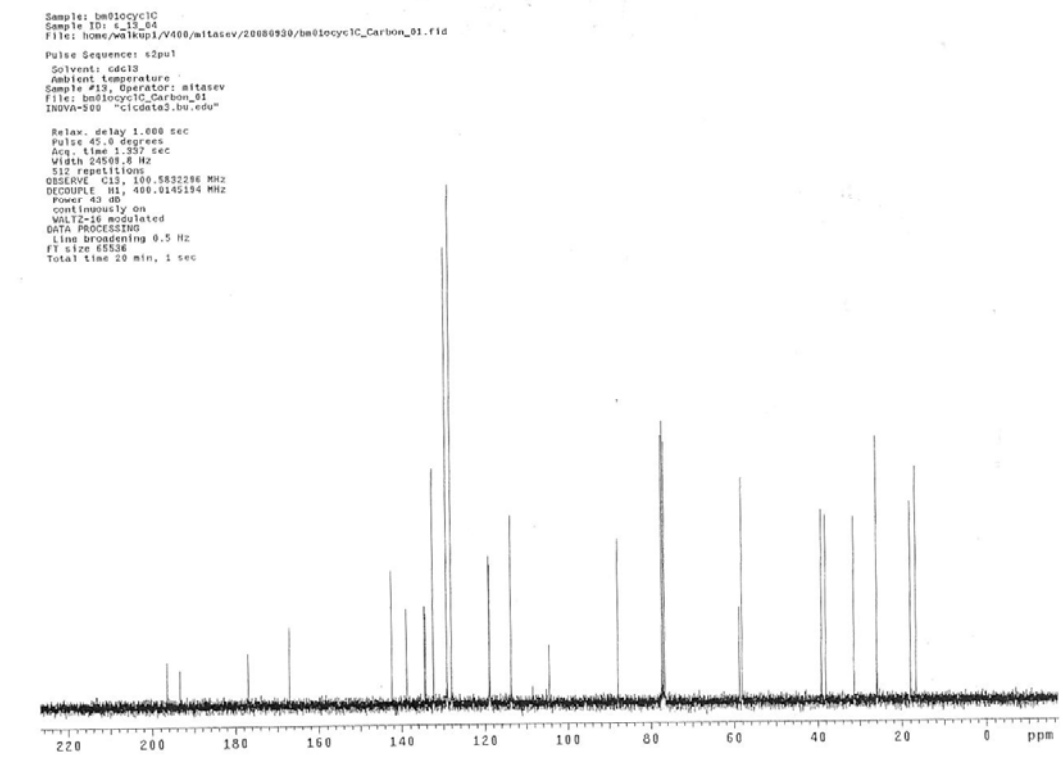

Sample: bm0181xDA
Sample ID: s_39_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
64 repetitions
OBSERVE H1, 400.0125149 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 4 min, 58 sec
Me
OMe
H
Me
H
Me
Me
O
O
O
Ph
13
ppm

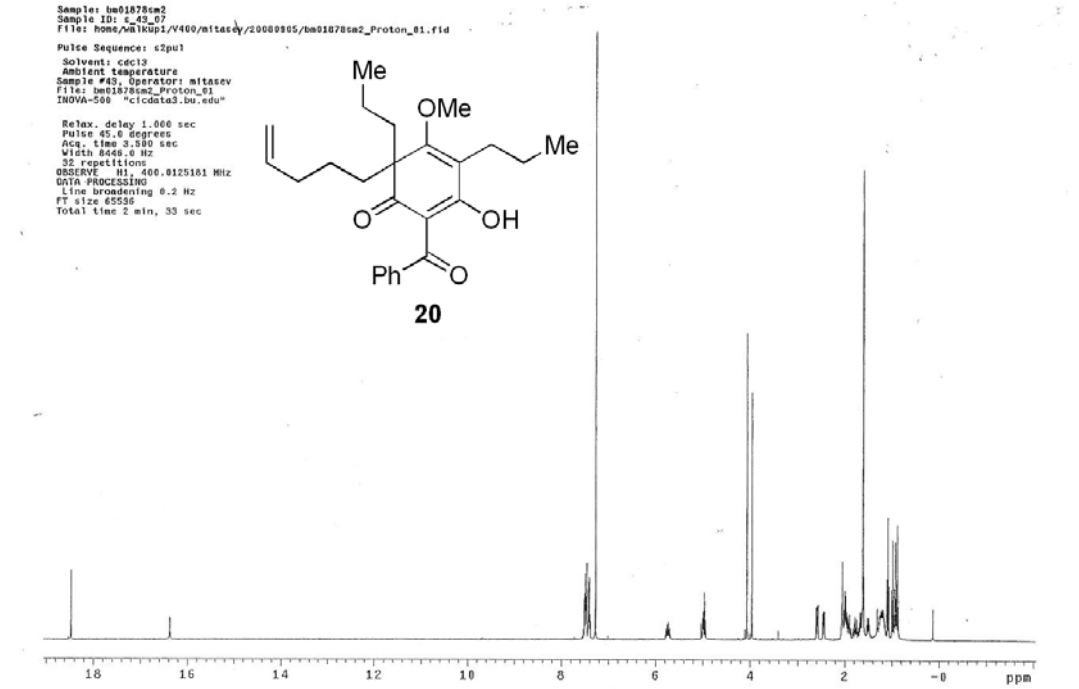

pad=1 run with gradshim before acquisition
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
5000 repetitions
OBSERVE C13, 75.4293938 MHz
DECOUPLE H1, 299.9789690 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 12 min, 27 sec
ppm

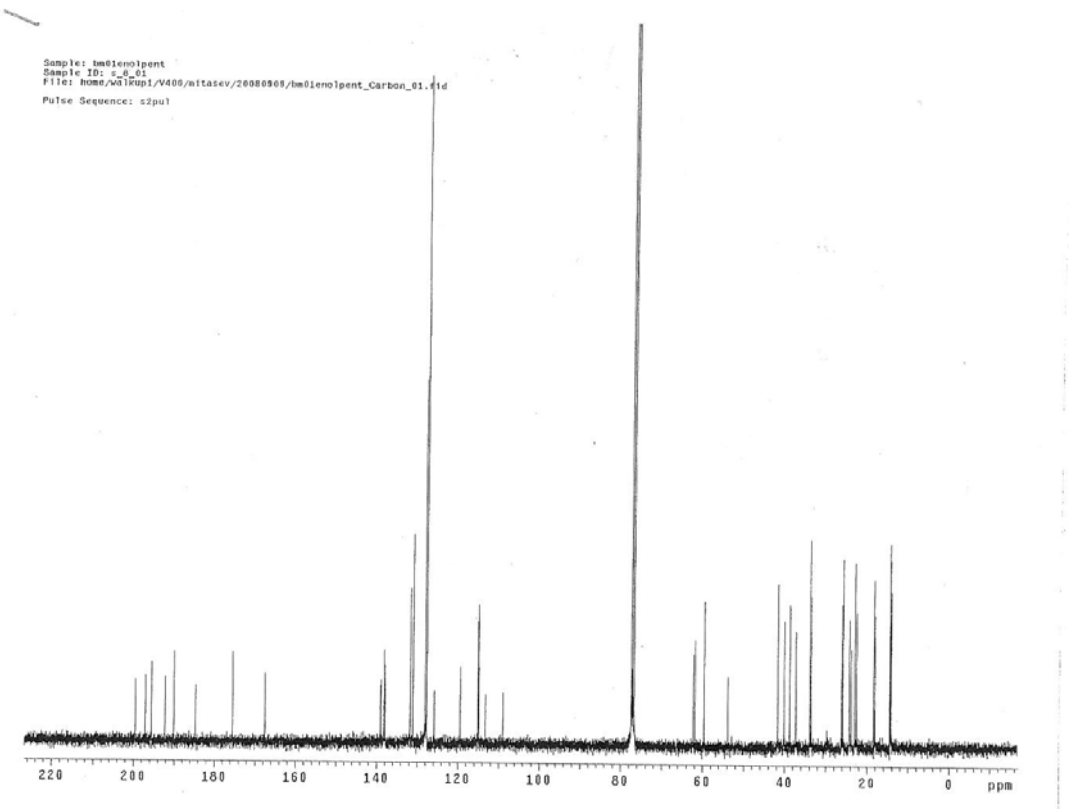

pad=1 run with gradshim before acquisition
Automation directory:
Sample id : s_S_03
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #5, Operator: mitas
File: _Proton_01
Mercury-300BB "cicdata2"
Relax. delay 1.000 sec
Pulse 45.6 degrees
Acq. time 3.408 sec
Width 4807.7 Hz
8 repetitions
OBSERVE H1, 299.9774652
DATA PROCESSING
Resol. enhancement -0.0 H
FT size 65536
Total time 0 min, 50 sec
Me
Me
Me
OMe
Me
Me
Me
O
O
O
Ph
17
9
8
7
6
5
4
3
2
1
ppm
1.96
2.13
1.14
1.00
1.05
3.17
0.97
3.27
3.22
3.20
3.71
6.56
4.39
3.56
1.72
3.34

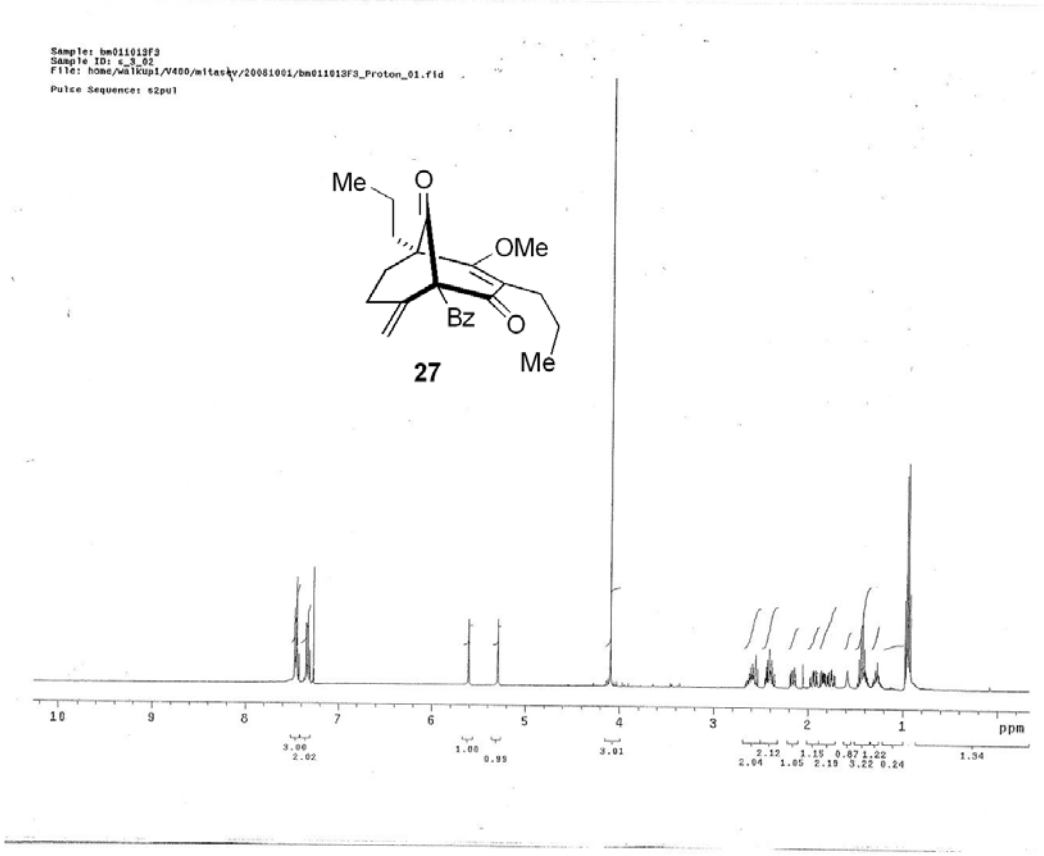

Automation directory:
Sample id : s_S_03
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #5, Operator: mitasev
File: _Carbon_01
Mercury-300BB "cicdata2"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
19000 repetitions
OBSERVE C13, 75.4293941 MHz
DECOUPLE H1, 299.9709690 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 6 hr, 36 min, 20 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

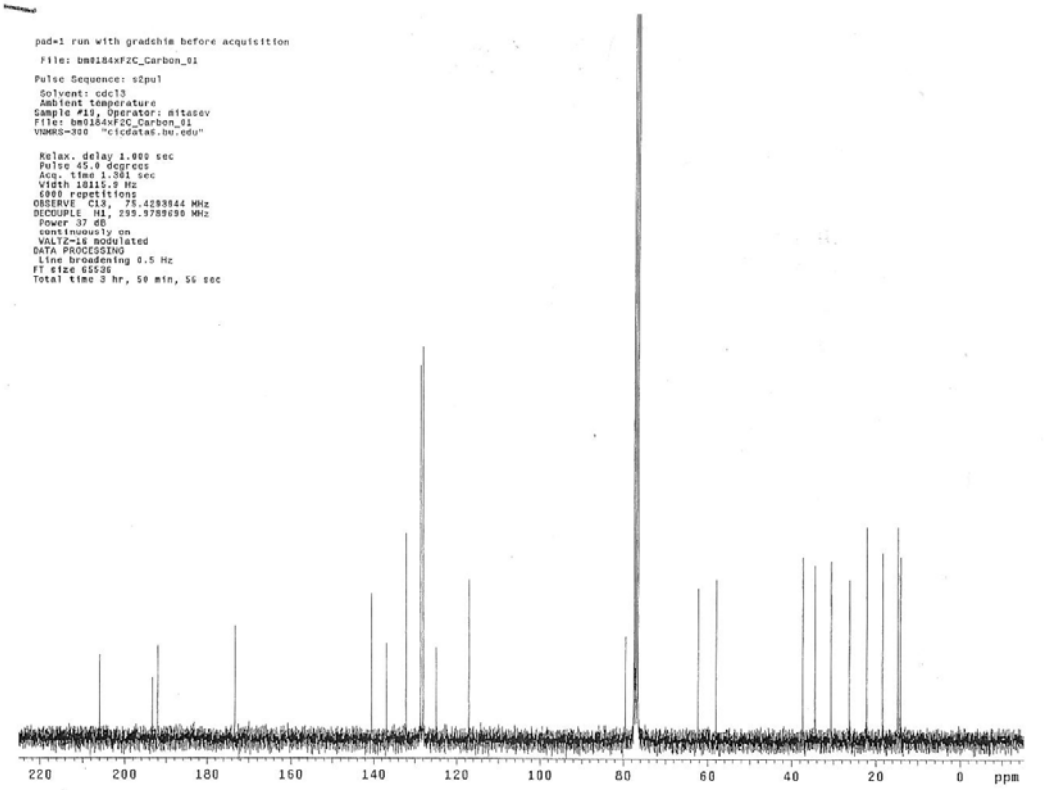

Sample: bm01ocycl
Sample ID: s_13_03
File: home/walkup1/V400/mitas4v/20080930/bm01ocycl_Proton_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #13, Operator: mitasev
File: bm01ocycl_Proton_01
INOVA-500 "cicdata3.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 400.0125149 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 45 sec
Me
Me
OMe
Me
Me
Me
O
O
O
Ph
19
10
9
8
7
6
5
4
3
2
1
ppm
1.84
2.02
1.00
0.86
3.09
3.00
0.99
1.01
2.08
2.06
9.01
6.21

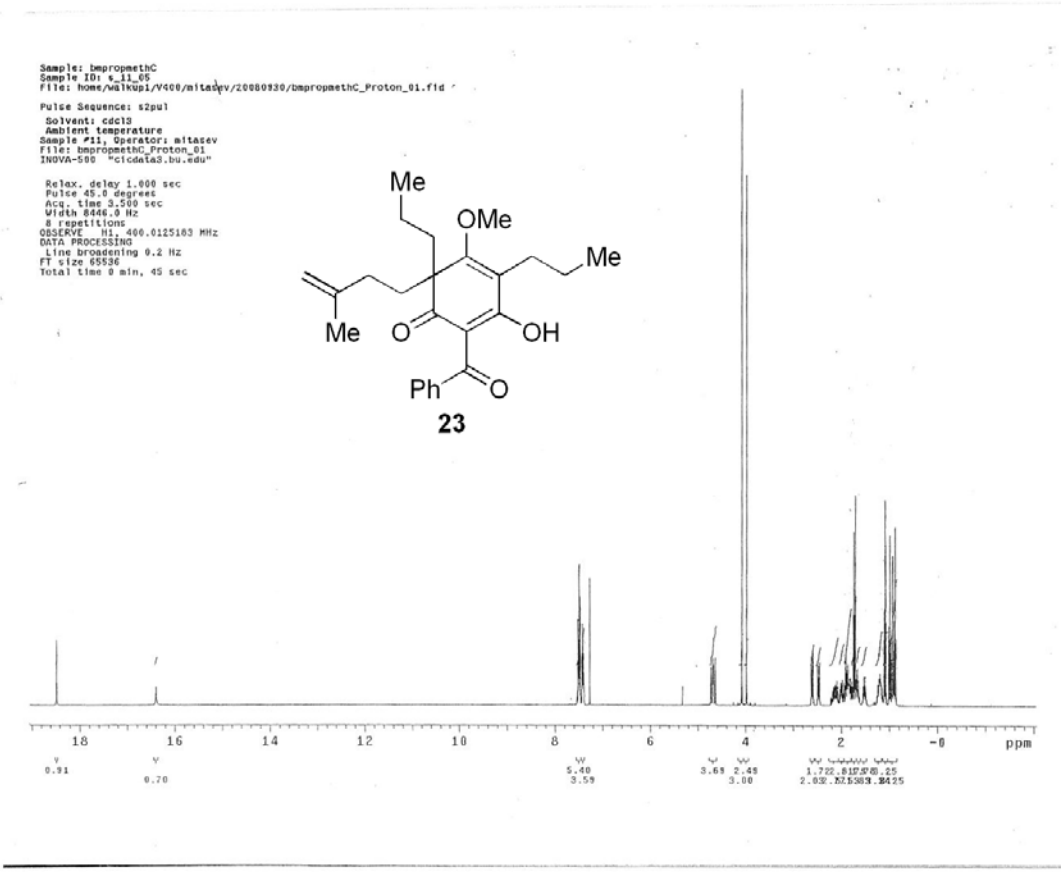

Sample: bm01ocyc1C
Sample ID: s_13_04
File: home/walkup1/V400/mitasev/20080930/bm01ocyc1C_Carbon_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #13, Operator: mitasev
File: bm01ocyc1C_Carbon_01
INOVA-500 "cicdata3.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.357 sec
Width 24508.8 Hz
512 repetitions
OBSERVE C13, 100.5832286 MHz
DECOUPLE H1, 400.0145194 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 20 min, 1 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

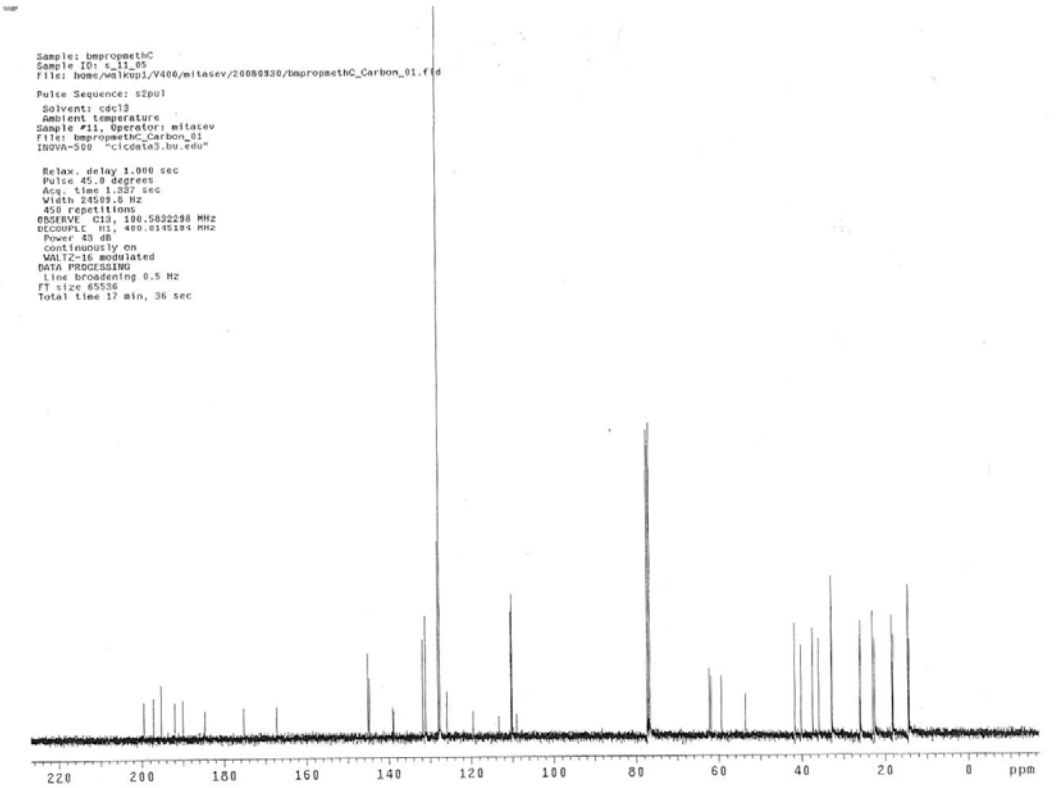

Sample: bm01878sm2
Sample ID: c_49_67
File: home/walkup1/V400/mitasev/20080905/bm01878sm2_Proton_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #49, Operator: mitasev
File: bm01878sm2_Proton_01
INOVA-500 "cicdata3.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8446.0 Hz
32 repetitions
OBSERVE H1, 400.0125181 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 min, 33 sec
Me
OMe
Me
O
OH
Ph
O
20
18
16
14
12
10
8
6
4
2
-0
ppm

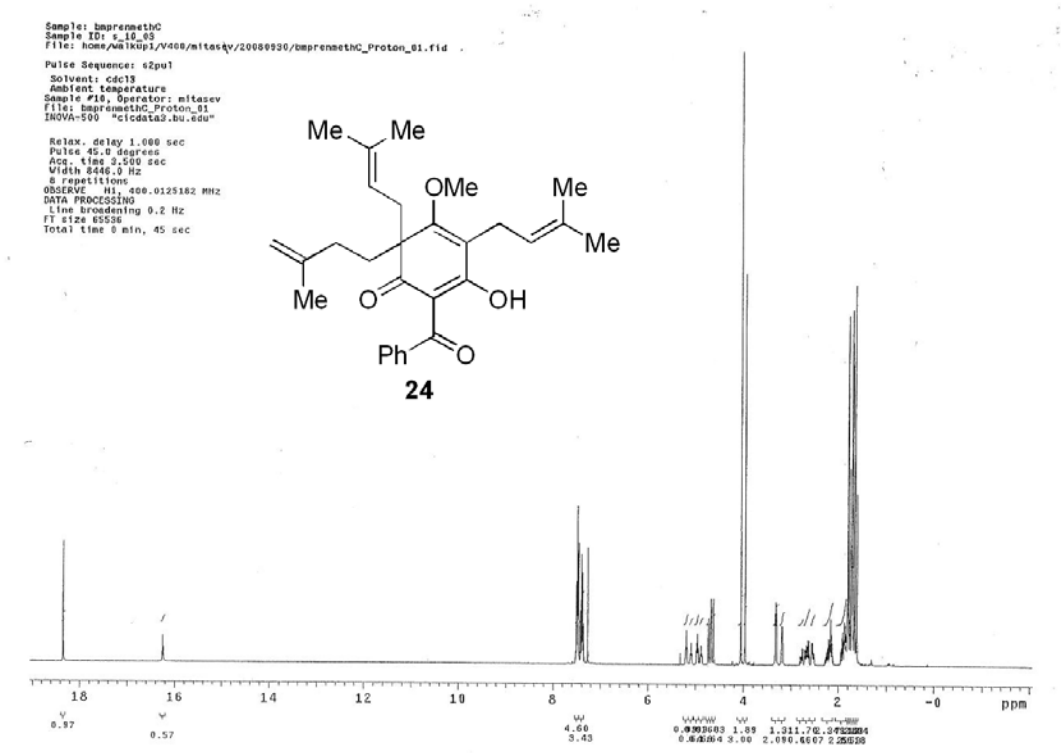

Sample: bm01enolpent
Sample ID: c_0_01
File: home/walkup1/V400/mitasev/20080909/bm01enolpent_Carbon_01.fid
Pulse Sequence: s2pul
220
200
180
160
140
120
100
80
60
40
20
0
ppm

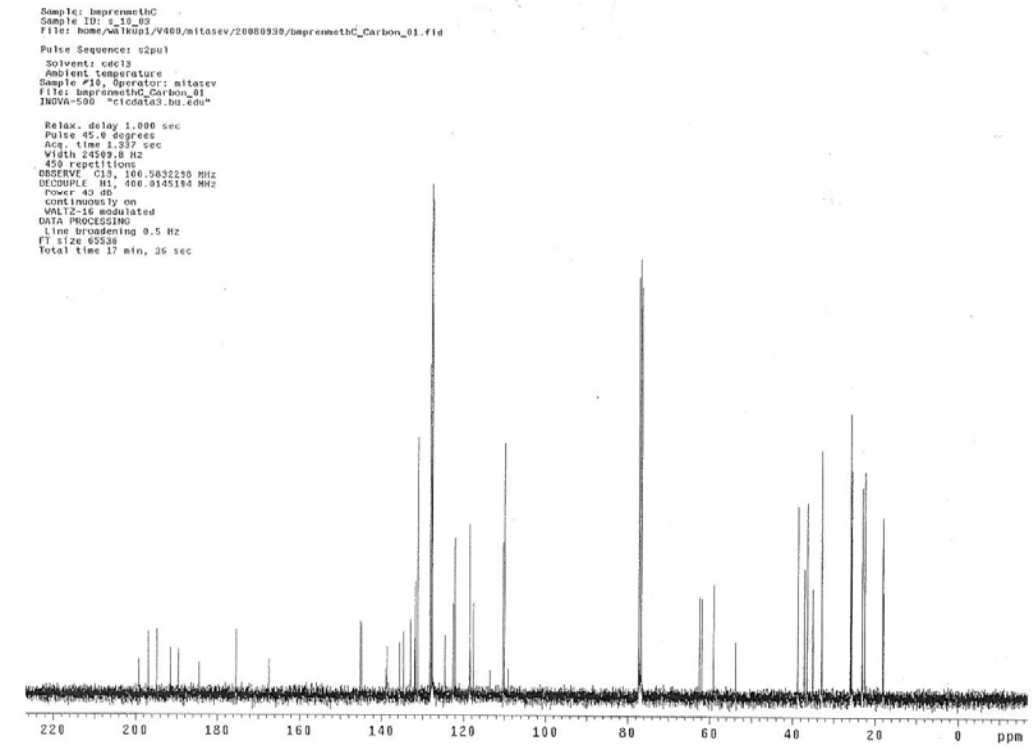

Sample: bm011013F3
Sample ID: 6_3_02
File: home/walkup1/V400/mitasev/20081001/bm011013F3_Proton_01.fid
Pulse Sequence: s2pul
Me
O
OMe
Bz
O
Me
27
10
9
8
7
6
5
4
3
2
1
ppm
3.00
2.02
1.00
0.99
3.01
2.12
1.15
0.67
1.22
2.04
1.05
2.19
3.22
0.24
1.34

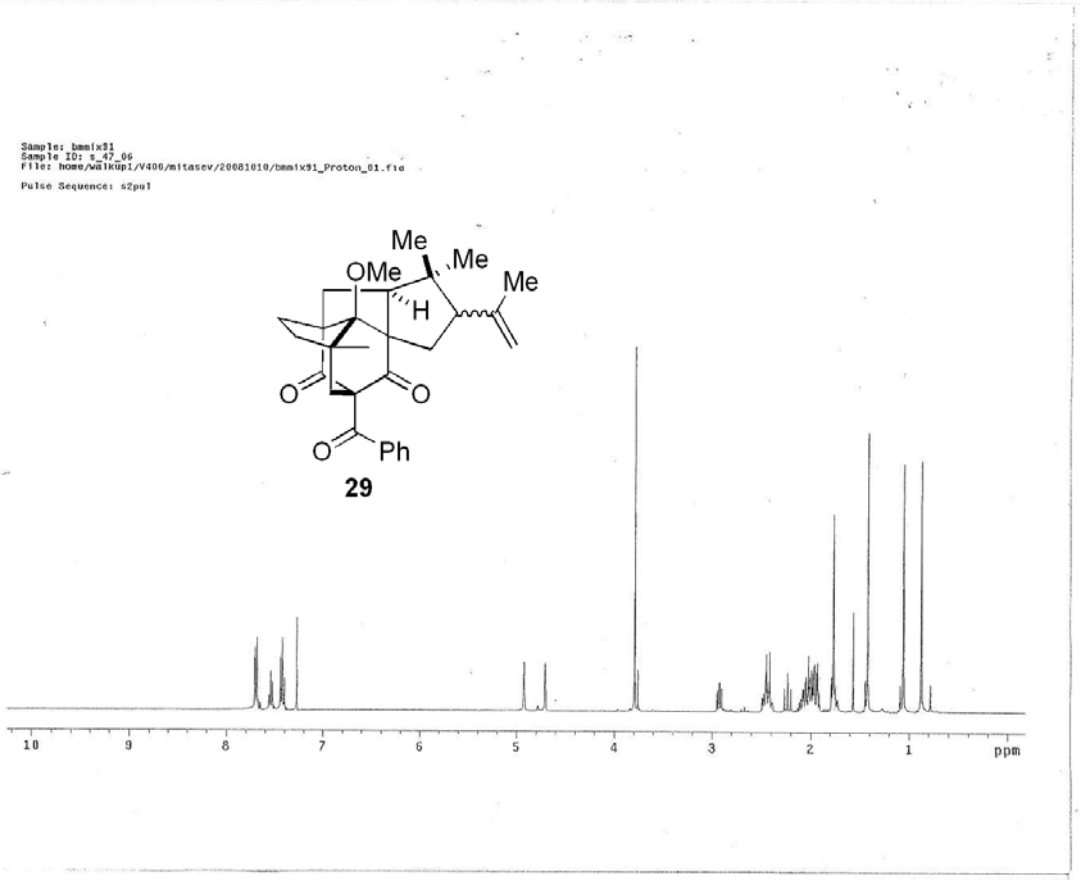

pad=1 run with gradshim before acquisition
File: bm0184xF2C_Carbon_01
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #19, Operator: mitasev
File: bm0184xF2C_Carbon_01
VNMRS-300 "cicdatas.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
6000 repetitions
OBSERVE C13, 75.4288844 MHz
DECOUPLE H1, 299.9789690 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 50 min, 56 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

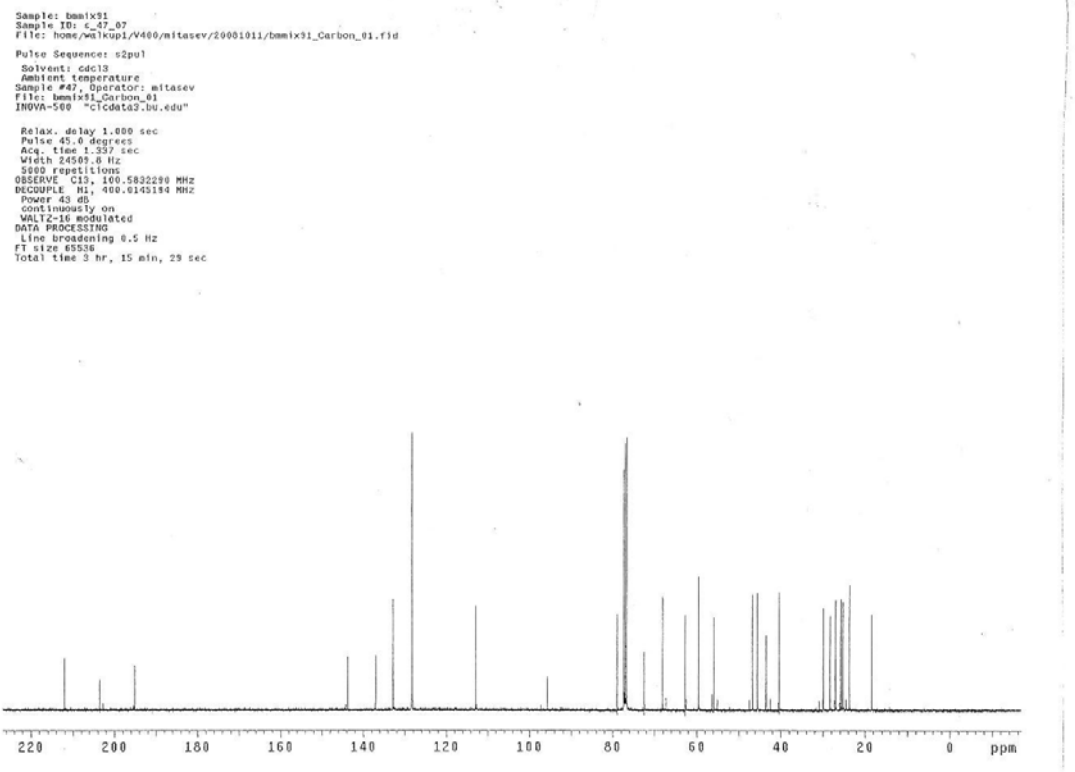

Sample: bmpropmethC
Sample ID: s_11_05
File: home/walkup1/V400/mitasev/20080930/bmpropmethC_Proton_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #11, Operator: mitasev
File: bmpropmethC_Proton_01
INOVA-500 "cicdata3.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8446.0 Hz
8 repetitions
OBSERVE H1, 400.0125163 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min, 45 sec
Me
OMe
Me
Me
O
OH
Ph
O
23
18
16
14
12
10
8
6
4
2
-0
ppm
0.91
0.70
5.40
3.59
3.68
2.48
3.00


Sample: bmpropmethC
Sample ID: s_11_05
File: home/walkup1/V400/mitasev/20080930/bmpropmethC_Carbon_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #11, Operator: mitasev
File: bmpropmethC_Carbon_01
INOVA-500 "cicdata3.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.327 sec
Width 24509.8 Hz
450 repetitions
OBSERVE C13, 100.5832298 MHz
DECOUPLE H1, 400.0145184 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 17 min, 36 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Sample: bmprenmethC
Sample ID: s_10_03
File: home/walkup1/V400/mitasev/20080930/bmprenmethC_Proton_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #10, Operator: mitasev
File: bmprenmethC_Proton_01
INOVA-500 "cicdata3.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6446.0 Hz
8 repetitions
OBSERVE H1, 400.0125182 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 8 min, 45 sec
Me
Me
OMe
Me
Me
O
Me
OH
Ph
O
24
18
16
14
12
10
8
6
4
2
-0
ppm
0.97
0.57
4.60
3.43
1.89
3.00


Sample: bmprenmethC
Sample ID: s_10_03
File: home/walkup1/V400/mitasev/20080930/bmprenmethC_Carbon_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #10, Operator: mitasev
File: bmprenmethC_Carbon_01
INOVA-500 "cicdata3.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.337 sec
Width 24509.8 Hz
450 repetitions
OBSERVE C13, 100.5632250 MHz
DECOUPLE H1, 400.0145184 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 17 min, 36 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Sample: bmmix91
Sample ID: s_47_06
File: home/walkup1/V400/mitasev/20081010/bmmix91_Proton_01.fid
Pulse Sequence: s2pul
Me
Me
Me
OMe
H
O
O
O
Ph
29
10
9
8
7
6
5
4
3
2
1
ppm


Sample: bmmix91
Sample ID: s_47_07
File: home/walkup1/V400/mitasev/20081011/bmmix91_Carbon_01.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #47, Operator: mitasev
File: bmmix91_Carbon_01
INOVA-500 "clcdata3.bu.edu"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.397 sec
Width 24509.8 Hz
5000 repetitions
OBSERVE C13, 100.5832290 MHz
DECOUPLE H1, 400.6143194 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 15 min, 29 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm