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Supporting Information

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Copper(I)-Catalyzed Conjugate Addition of Ethyl Propiolate

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General Experimental

All non aqueous reactions were carried out in oven dried glasswares under argon atomosphere using solvents that were dried by passage over two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; Macherey und Nagel; activated under a flow of N_2 at 300° over night; solvent drying system) under an argon atmosphere (H_2O content < 30 ppm, *Karl-Fischer* titration). For aqueous reactions, deionized water was used as solvent. For flash chromatography and extractions technical grade solvents were distilled prior to use.

All chemicals were purchased from suppliers and used as received unless noted otherwise. Achiral Meldrums acid derived acceptors were prepared according to literature procedures.[1] Ethyl propiolate was purchased from Acros (99%), copper(II) acetate monohydrate was purchased from Aldrich (98+%, ACS reagent grade), and (+)-L-sodium ascorbate was purchased from Fluka (>99%). Chromatographic purification was performed as flash chromatography (FC) using Merck silica 60 or Brunschwig Silica 60, with 0.7 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC glass plates and visualized with UV light and/or permanganate stain.

^{1}H-NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in the indicated solvent. All signals are reported in ppm with the internal solvent signal as standard. The data is reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration). ^{13}C-NMR spectra were recorded with 1H-decoupling on a VARIAN Mercury 75 MHz spectrometer in the indicated solvent, all signals are reported in ppm with the internal solvent signal as reference. Infrared spectra were recorded on a Perkin Elmer Spectrum RX-I FT-IR spectrophotometer as thin films or KBr pellets. The data is being reported as absorption maxima (?, cm-1) with corresponding characteristic intensity (w = weak, m = medium, s = strong, br = broad). Melting points were measured on a Buechi 510 melting point apparatus using open glass capillaries and are uncorrected. Opticals rotation [a]D T were measured by Jasco DID 1000 Polarimeter, 10 cm, 1 ml cell. Concentration (c, g/100 ml), solvent of the each sample are given in parentheses.

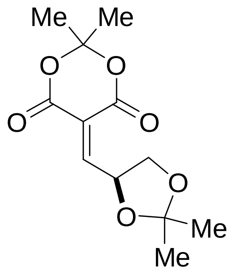
High resolution mass spectrometric measurements were performed by the mass spectrometry service of the Laboratorium für Organische Chemie at the ETH Zürich. EI measurements were performed on a VG Tribrid spectrometer, 70 eV. ESI measurements were performed on a TSQ 7000.

X-ray crystal structural analysis was performed by Dr. Bernd Schweizer at the X-ray crystallography group at the Organic Chemistry Laboratory, ETH Zurich.

[1] a) T. F. Knöpfel, E. M. Carreira, *J. Am. Chem. Soc.* **2003**, *125*, 6054-6055; b) T. F. Knöpfel, P. Zarotti, T. Ichikawa, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 9682-9683.

Experimental Procedures

General Procedure I: Preparation of Chiral Acceptors: (S)-5-((2,2-dimethyl-1,3-dioxolan-4-yl)methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (6a)



In a 100 mL round bottom flask were placed *R*-2,2-dimethyl-1,3-dioxolane-4-carboxaldehyde (1.30 g, 10 mmol, 1.2 equiv), toluene (10 mL), Meldrum's acid (1.20 g, 8.3 mmol) and sodium sulfate (10 g). To the stirring reaction mixture was added piperidine (50 μL, 0.5 mmol, 0.06 equiv). The reaction mixture was stirred at rt for 1 h. The reaction mixture was chromatographed (1/1 Hexane/EtOAc, 40 mm x 10 cm SiO_2) providing 1.30 g (5.0 mmol, 61%) of **6a** as white solid.

mp: 59 - 60 ^{o}C

$[a]_D^{21}$ +114 (c = 1.25, $CHCl_3$)

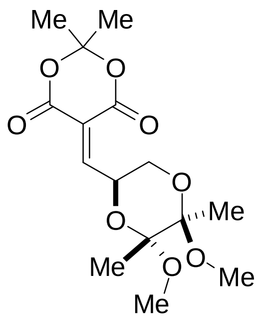
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, *J* = 6.3, 1 H), 5.54 (dt, *J* = 7.2, 6.3, 1 H) 4.56-4.51, 3.79-3.74 (ABX, 2 H) 1.76 (s, 3 H), 1.75 (s, 3 H), 1.50 (s, 3 H), 1.42 (s, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): 166.0, 160.3, 159.3, 117.7, 111.0, 105.4, 74.3, 68.8, 27.9, 27.6, 26.3, 25.2

IR ($CHCl_3$): 2990 (m), 1737 (s), 1634 (m), 1382 (m), 1283 (m), 1218 (m), 1153 (w), 1059 (m), 1020 (m)

HRMS: (HR-EI, positive): Calcd. for $C_{11}H_{13}O_6^+$ ($[M-CH_3]^+$) 241.0707, found 241.0705

5-(((2S,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl)methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione (6b)



Following the general procedure I using (2R,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane-2-carbaldehyde (3.57 g, 17.5 mmol). After chromatography, the residue was crystalized from Hexane/CH_2Cl_2 (9/1) to give 2.90 g (8.78 mmol, 50%) of **6b** as white solid.

mp: 99-100 ^{o}C

[a]$_D^{23}$ -106.2 (c = 1.6, $CHCl_3$)

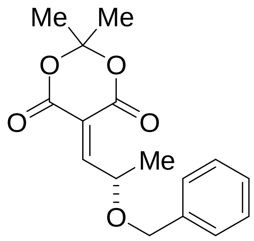
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 6.9, 1 H), 5.55 (m, 1 H), 3.77-3.59 (ABX, 2 H), 3.28 (s, 6 H), 1.75 (s, 3 H), 1.74 (s, 3 H), 1.32 (s, 6 H)

^{13}C NMR (75 MHz, $CDCl_3$): 160.9, 160.3, 158.8, 118.8, 105.3, 98.7, 97.7, 67.4, 58.6, 48.4, 48.3, 28.0, 27.7, 17.8, 17.6

IR ($CHCl_3$): 2994 (m), 2950 (m), 2835 (m), 1734 (s), 1646 (m), 1445 (m), 1361 (m), 1280 (m), 1204 (m), 1142 (m), 1115 (m), 1036 (m)

HRMS: (HR-ESI, positive): Calcd. for $C_{15}H_{22}O_8Na^+$ ($[M+Na]^+$) 353.1207, found 353.1200

(S)-5-(2-(benzyloxy)propylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (6c)



Following the general procedure I using (S)-2-(benzyloxy)propanal (3.12 g, 19.0 mmol). After chromatography of the crude oil, 3.25 g (11.2 mmol, 59%) of **6c** was obtained as clear oil.

[a]$_D^{25}$ +1.3 (c = 0.81, $CHCl_3$)

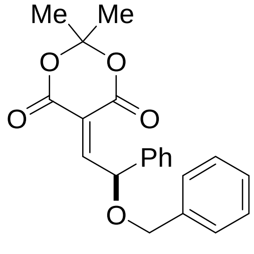
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.8, 1 H), 7.36 – 7.26 (m, 5 H), 5.23 (qd, *J* = 7.8, 6.6, 1 H), 4.53 (AB, 2 H), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.43 (d, *J* = 6.3, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): 168.9, 160.7, 159.1, 137.4, 128.3, 127.8, 127.7, 116.9, 72.9, 72.1, 27.7, 27.6, 19.2

IR (neat): 3031 (m), 2984 (m), 2936 (m), 2871 (m), 1738 (s), 1634 (m), 1496 (m), 1454 (m), 1394 (m), 1353 (m), 1281 (m), 1203 (m), 1074 (m), 1019 (m)

HRMS: (HR-EI, positive): Calcd. for $C_{13}H_{12}O_4^+$ ($[M-CH_3COCH_3]^+$) 232.0730, found 232.0739

(S)-5-(2-(benzyloxy)-2-phenylethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (6d)



Following the general procedure I using (R)-2-(benzyloxy)-2-phenylacetaldehyde (144 mg, 1.0 mmol). After chromatography of the crude oil, 180 mg (0.51 mmol, 51%) of **6d** was obtained as clear oil.

$[a]_D^{27}$ +88.6 (c = 1.0, $CHCl_3$)

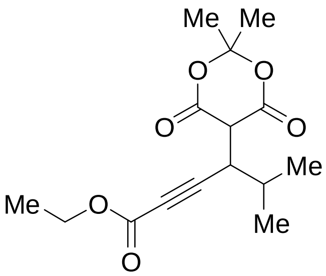
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.7, 1 H), 7.59 – 7.56 (m, 2 H), 7.41 – 7.25 (m, 8 H), 6.26 (d, *J* = 9.0, 1 H), 4.41 (AB, 2 H), 1.73 (s, 3 H), 1.62 (s, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): 163.1, 161.0, 159.5, 137.4, 137.2, 128.9, 128.8, 128.3, 127.8, 127.7, 127.5, 116.1, 105.0, 70.8, 27.8, 27.6

IR ($CHCl_3$): 3063 (m), 3039 (m), 2988 (m), 2942 (m), 2868 (m), 1766 (m), 1736 (s), 1635 (m), 1494 (m), 1455 (m), 1394 (m), 1355 (m), 1283 (s), 1221 (m), 1203 (m), 1082 (m), 1064 (m), 1028 (m)

HRMS: (HR-EI, positive): Calcd. for $C_{18}H_{14}O_4^+$ ($[M-CH_3COCH_3]^+$) 294.0887, found 294.0888

General Procedure II: Copper Mediated Conjugate Addition of Ethyl Propiolate: Ethyl 4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-5-methylhex-2-ynoate (2a)



In a test tube (100 x 12 mm) equipped with a stir bar was added $Cu(OAc)_2$ (20 mg, 0.10 mmol, 0.4 equiv) and deionized water (0.4 mL). To the stirring solution was added Na-(+)-ascorbate (40 mg, 0.20 mmol, 0.8 equiv). The reaction mixture was stirred for 5 min, and during this time the solution turns brown initially and changes its color to orange. To the reaction mixture was added ethyl propiolate (253 μL, 2.50 mmol, 10 equiv). The reaction mixture was stirred for 10 min, and during this time the color changes from orange to yellow. To the reaction mixture was then added **1a** (48 mg, 0.25 mmol), and the reaction mixture was stirred vigorously at rt for 48 h. The reaction mixture was diluted with saturated aqueous ammonium chloride (1 mL) and extracted with dichloromethane (10 mL x 3). The solution was dried over Na_2SO_4, passed through a pad of Celite (40 mm x 1 cm) and concentrated. The residue was purified by chromatography (20 mm x 7 cm SiO_2, 3/1 – 1/1 Hexane/EtOAc) to afford **2a** (68 mg, 92%) as white solid.

mp:67-68^{o}C

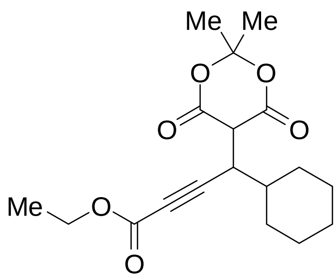
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.17 (q, *J* = 7.2, 2 H), 3.75 (d, *J* = 2.7, 1 H), 3.23 (dd, *J* = 10.5, 2.7, 1 H), 2.47 (m, 1 H), 1.80 (s, 3 H), 1.78 (s, 3 H) 1.27 (t, *J* = 7.2, 3 H), 1.18 (d, *J* = 5.1, 3 H), 0.97 (d, *J* = 6.6, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 164.0, 163.0, 153.1, 105.5, 86.1, 76.0, 62.0, 47.1, 38.7, 29.8, 28.5, 27.5, 21.9, 20.3, 14.1

IR ($CHCl_3$): 2970 (m), 2909 (m), 2874 (m), 2240 (m), 1786 (m), 1750 (s), 1710 (m), 1474 (m), 1385 (m), 1368 (m), 1334 (m), 1300 (m), 1259 (m), 1214 (m), 1139 (m), 1080 (m), 1067 (m), 1006 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{15}H_{19}O_6^-$ ($[M-H]^-$) 295.1187, found 295.1207

Ethyl 4-cyclohexyl-4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)but-2-ynoate (2b)



Following the General Procedure II using **1b** (60 mg, 0.25 mmol), 71 mg of **2b** (0.21 mmol, 84%) was obtained as white solid.

mp: 101-102 ^oC

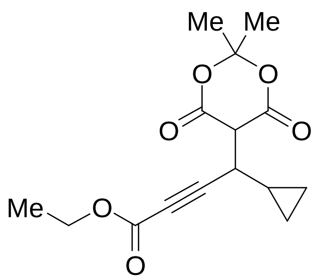
^{1}**H NMR** (300 MHz, $CDCl_3$): δ 4.18 (q, J = 6.9, 2 H), 3.78 (d, J = 2.4, 1 H), 3.29 (dd, J = 10.5, 2.7, 1 H), 2.26 – 2.05 (m, 2 H), 1.80 (s, 3 H), 1.78 (s, 3 H), 1.80 – 1.60 (m, 4 H), 1.27 (t, J = 7.2, 3 H), 1.33 – 0.88 (m, 5 H)

^{13}**C NMR** (75 MHz, $CDCl_3$): δ 164.0, 163.0, 153.1, 105.4, 86.2, 76.0, 61.9, 46.4, 38.2, 37.3, 32.3, 30.6, 28.4, 27.5, 26.0, 25.9, 14.1

IR ($CHCl_3$): 3022 (m), 2932 (m), 2855 (m), 2238 (m), 1785 (m), 1750 (s), 1709 (m), 1450 (m), 1396 (m), 1368 (m), 1333 (m), 1302 (m), 1260 (m), 1216 (m), 1108 (m), 1069 (m), 1010 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{18}H_{23}O_6^-$ ($[M-H]^-$) 335.1500, found 335.1496

Ethyl 4-cyclopropyl-4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)but-2-ynoate (2c)



Following the General Procedure II using **1c** (49 mg, 0.25 mmol), 48 mg of **2c** (0.16 mmol, 65%) was obtained as pale yellow oil which solidified upon standing.

mp: 89-90 ^oC

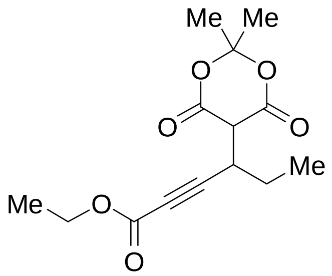
^{1}**H NMR** (300 MHz, $CDCl_3$): δ 4.21 (q, J = 7.2, 2 H), 3.78 (d, J = 2.4, 1 H), 2.91 (dd, J = 9.5, 2.4, 1 H), 1.81 (s, 6 H), 1.58 (m, 1 H), 1.29 (t, J = 6.9, 3 H), 0.75 – 0.31 (m, 4 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.4, 163.2, 153.3, 105.5, 85.4, 75.1, 62.0, 49.8, 35.7, 28.4, 27.3, 14.0, 13.2, 5.8, 5.0

IR ($CHCl_3$): 3021 (m), 2241 (m), 1785 (m), 1751 (s), 1709 (m), 1465 (w), 1385 (m), 1368 (m), 1336 (m), 1302 (m), 1259 (m), 1216 (m), 1111 (m), 1066 (m), 1013 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{18}H_{23}O_6^-$ ($[M-H]^-$) 293.1031, found 293.1033

Ethyl 4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)hex-2-ynoate (2d)



Following the General Procedure II using **1d** (46 mg, 0.25 mmol), 38 mg of **2d** (0.13 mmol, 54%) was obtained as clear oil.

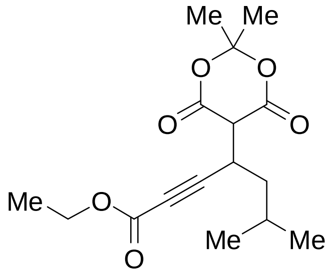
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.20 (q, J = 7.2, 2 H), 3.75 (d, J = 2.4, 1 H), 3.48 (m, 1 H), 2.03 (m, 1 H), 1.79 (s, 6 H), 1.66 (m, 1 H), 1.29 (t, J = 6.9, 3 H), 1.11 (t, J = 7.5, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0, 153.3, 105.4, 86.3, 75.6, 62.0, 49.2, 32.2, 28.4, 27.1, 24.5, 14.0, 12.5

IR (neat): 2959 (m), 2932 (m), 2873 (m), 2242 (m), 1789 (m), 1750 (s), 1711 (m), 1465 (m), 1395 (m), 1385 (m), 1305 (m), 1259 (m), 1205 (m), 1135 (m), 1065 (m), 1014 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{14}H_{17}O_6^-$ ($[M-H]^-$) 281.1031, found 281.1039

Ethyl 4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-6-methylhept-2-ynoate (2e)



Following the General Procedure II using **1e** (53 mg, 0.25 mmol), 70 mg of **2e** (0.23 mmol, 90%) was obtained as off white solid.

mp: 81-83 ^{o}C

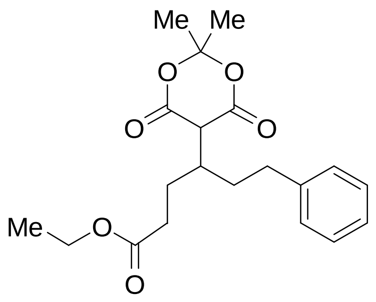
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.17 (q, J = 7.2, 2 H), 3.78 (d, J = 2.7, 1 H), 3.64 (m, 1 H), 2.03 (m, 1 H), 1.88 – 1.72 (m, 1 H), 1.79 (s, 3 H), 1.77 (s, 3 H), 1.28 (t, J = 6.9, 3 H), 1.27 – 1.18 (m, 1 H), 0.95 (d, J = 6.3, 3 H), 0.94 (d, J = 6.6, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0, 153.3, 105.4, 86.6, 75.2, 61.9, 49.5, 39.4, 28.3, 27.0, 26.1, 23.0, 21.1, 14.0

IR ($CHCl_3$): 3020 (m), 2963 (m), 2873 (m), 2242 (m), 1788 (m), 1752 (s), 1708 (m), 1468 (m), 1384 (m), 1369 (m), 1307 (m), 1259 (m), 1216 (s), 1065 (m), 1009 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{16}H_{21}O_6^-$ ($[M-H]^-$) 309.1416, found 309.1342

Ethyl 4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-6-phenylhexanoate (5f)



Following the General Procedure II using **1f** (65 mg, 0.25 mmol), crude **2f** was obtained as clear oil. The crude **2f** was dissolved in EtOAc (5 mL). To the solution was added 10% Pd/C (5 mg), and the reaction mixture was subjected to hydrogen atmosphere using a balloon at rt for 2 h. The reaction mixture was diluted with Hexane/EtOAc (1/1, 50 mL), passed through a pad of silica gel (40 mm x 1 cm) and concentrated under reduced pressure. The residue was chromatographed (Hexane/EtOAc, 3/1, 20 mm x 15 cm SiO_2) to afford 55 mg (0.15 mmol, 61%) of **5f** as clear oil.

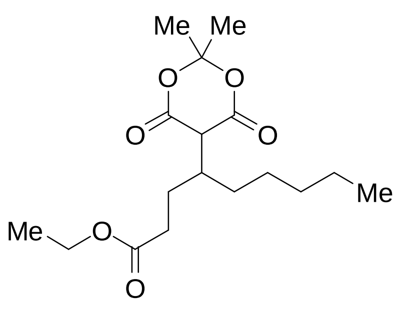
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.15 (m, 5 H), 4.12 (q, *J* = 7.2, 2 H), 3.62 (d, *J* = 2.4, 1 H), 2.82 – 2.35 (m, 4 H), 2.01 – 1.86 (m, 4 H), 1.81 (s, 3 H), 1.72 (s, 3 H), 1.25 (t, *J* = 7.2, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 173.0, 164.8, 141.3, 128.4, 128.2, 126.0, 104.7, 60.6, 48.4, 38.1, 34.4, 33.3, 32.9, 28.3, 27.1, 27.0, 14.3

IR (neat): 3026 (m), 2940 (w), 2244 (m), 1786 (m), 1750 (s), 1710 (m), 1496 (w), 1455 (m), 1384 (m), 1369 (m), 1306 (m), 1260 (m), 1216 (m), 1108 (m), 1069 (m), 1020 (m)

HRMS (HR-ESI, positive): Calcd. for $C_{20}H_{26}O_6Na^+$ ($[M+Na]^+$) 385.1622, found 385.1617

Ethyl 4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)nonanoate (5g)



Following the General Procedure II using **1g** (57 mg, 0.25 mmol), crude **2g** was obtained as pale yellow oil. The crude **2g** was dissolved in EtOAc (5 mL). To the solution was added 10% Pd/C (5 mg), and the reaction mixture was subjected to hydrogen atmosphere using a balloon at 0°C for 1 h. The reaction mixture was diluted with EtOAc (50 mL), passed through a pad of silica gel (40 mm x 1 cm) and concentrated under reduced pressure. The residue was chromatographed (Hexane/EtOAc, 3/1, 20 mm x 15 cm SiO_2) to afford 61 mg (0.19 mmol, 74%) of **5g** as clear oil.

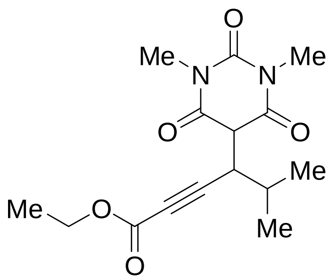
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.10 (q, *J* = 7.2, 2 H), 3.62 (d, *J* = 2.7, 1 H), 2.50 – 2.30 (m, 3 H), 1.94 – 1.82 (m, 2 H), 1.75 (s, 3 H), 1.73 (s, 3 H), 1.60 – 1.20 (m, 8 H), 1.23 (t, *J* = 7.2, 3 H), 0.87 (m, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 165.3, 104.8, 60.5, 48.2, 38.5, 32.9, 31.7, 31.6, 28.2, 27.4, 27.3, 27.0, 22.5, 14.2, 14.0

IR (neat): 2958 (m), 2932 (m), 2862 (m), 2257 (w), 1783 (m), 1747 (s), 1629 (w), 1460 (m), 1394 (m), 1383 (m), 1295 (m), 1206 (m), 1064 (m), 1027 (m)

HRMS (HR-ESI, positive): Calcd. for $C_{17}H_{27}O_6^-$ ([M-H]$^-$) 327.1813, found 327.1820

Ethyl 4-(1,3-dimethyl-2,4,6-trioxohexahydropyrimidin-5-yl)-5-methylhex-2-ynoate (4a)



Following the General Procedure II using **3a** (53 mg, 0.25 mmol), 58 mg of **4a** (0.19 mmol, 75%) was obtained as white solid after crystallization from hexanes.

mp: 131-133 °C

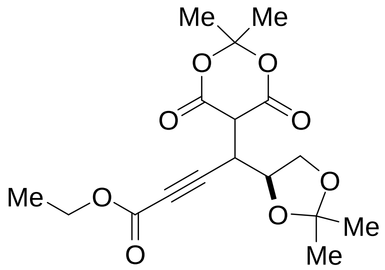
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.40 (d, *J* = 1.8, 1 H), 4.19 (q, *J* = 7.2, 2 H), 4.09 (dd, *J* = 2.8, 1.8, 1 H), 3.47 (s, 3 H), 3.32 (s, 3 H), 2.29 (m, 1 H), 1.30 (t, *J* = 7.1, 3 H), 1.01 (d, *J* = 7.1, 3 H), 0.97 (d, *J* = 6.9, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.4, 163.5, 159.9, 159.1, 151.1, 98.5, 88.1, 60.3, 51.3, 32.4, 30.1, 28.2, 18.7, 18.5, 14.2

IR ($CHCl_3$): 3020 (m), 2965 (m), 1694 (s), 1667 (s), 1513 (m), 1464 (m), 1390 (w), 1371 (m), 1325 (m), 1310 (m), 1216 (m), 1163 (m), 1036 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{15}H_{19}N_2O_5^-$ ([M-H]$^-$) 307.1230, found 307.1298

General Procedure III: Diastereoselective Conjugate Addition of Ethyl Propiolate: Ethyl 4-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)but-2-ynoate (7a)



In a test tube (100 x 12 mm) equipped with a stir bar was added $Cu(OAc)_2$ (10 mg, 0.05 mmol, 0.2 equiv) and deionized water (0.2 mL). To the stirring solution was added Na-(+)-ascorbate (20 mg, 0.10 mmol, 0.4 equiv). The reaction mixture was stirred for 5 min, and during this time the solution turns brown initially and changes its color to orange. To the reaction mixture was added ethyl propiolate (253 μL, 2.50 mmol, 10 equiv). The reaction mixture was stirred for 10 min, and during this time the color changes from orange to yellow. The reaction mixture was cooled to 0^{o}C using an ice bath. To the reaction mixture was then added **6a** (64 mg, 0.25 mmol), and the reaction mixture was stirred vigorously at 0 ^{o}C for 4 h. The reaction mixture was diluted with saturated aqueous ammonium chloride (1 mL) and extracted with dichloromethane (10 mL x 3). The solution was dried over Na_2SO_4, passed through a pad of Celite (40 mm x 1 cm) and concentrated. The residue was purified by chromatography (20 mm x 7 cm SiO_2, 1/1 Hexane/EtOAc) to afford **7a** (73 mg, 0.21 mmol, 82%) as white solid.

mp: 125 – 127 ^{o}C

[a]$_D^{20}$ +5.0 (c = 1.0, $CHCl_3$)

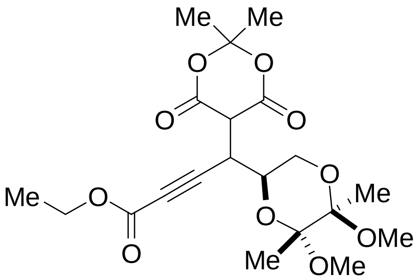
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.66 (q, *J* = 6.6, 1 H), 4.20 (q, *J* = 7.2, 2 H), 4.09 (m, 2 H), 3.90 (dd, *J* = 6.8, 3.2, 1 H), 3.79 (d, *J* = 3.3, 1 H), 1.79 (s, 6 H), 1.43 (s, 3 H), 1.34 (s, 3 H), 1.28 (t, *J* = 7.2, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.2, 162.6, 152.9, 110.3, 105.6, 83.0, 74.0, 66.9, 62.1, 46.3, 33.7, 30.1, 28.5, 27.2, 26.4, 25.2, 14.0

IR ($CHCl_3$): 3018 (m), 2986 (m), 2940 (m), 2906 (m), 2244 (m), 1824 (m), 1790 (m), 1750 (m), 1711 (s), 1456 (m), 1384 (m), 1260 (m), 1216 (s), 1151 (m), 1109 (m), 1071 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{17}H_{21}O_8^-$ ($[M-H]^-$) 353.1242, found 353.1247

Ethyl 4-((2S,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl)-4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)but-2-ynoate (7b)



Following General Procedure III using **6b** (84 mg, 0.25 mmol) at rt for 2 h, 85 mg (0.20 mmol, 79%) of **7b** was obtained as white solid.

mp: 97-98 ^{o}C

[a]$_D^{20}$ -92.8 (c = 0.8, $CHCl_3$)

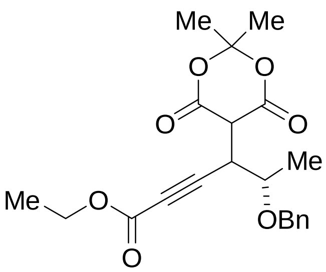
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.41 (m, 1 H), 4.19 (q, *J* = 7.2, 2 H), 4.03 (dd, *J* = 8.4, 2.1, 1 H), 3.85 – 3.75 (m, 2 H), 3.58 – 3.53 (m, 1 H), 3.25 (s, 3 H), 3.22 (s, 3 H), 1.78 (s, 6 H), 1.27 (t, *J* = 7.5, 3 H), 1.24 (s, 6 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.1, 152.9, 105.2, 100.0, 97.7, 83.1, 76.2, 65.1, 62.0, 60.8, 60.4, 48.3, 48.2, 45.6, 31.9, 27.2, 17.4, 14.0

IR ($CHCl_3$): 3019 (m), 2952 (m), 2836 (m), 2246 (m), 1790 (m), 1751 (s), 1711 (s), 1447 (m), 1376 (m), 1302 (m), 1259 (m), 1216 (s), 1145 (m), 1118 (m), 1037 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{20}H_{27}O_{10}^-$ ([M-H]$^-$) 427.1610, found 427.1614

(5S)-Ethyl 5-(benzyloxy)-4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)hex-2-ynoate (7c)



Following General Procedure III using **6c** (84 mg, 0.25 mmol) at 0^{o}C for 24 h, 65 mg (0.17 mmol, 67%) of **7c** was obtained as yellow oil.

[a]$_D^{20}$ +2.9 (c = 0.5, $CHCl_3$)

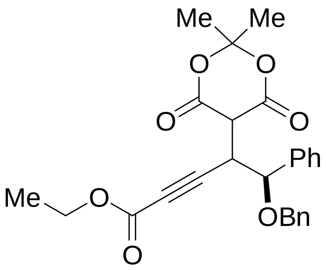
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 – 7.26 (m, 5 H), 4.58 (AB, 2 H), 4.21 (q, *J* = 7.2, 2 H), 4.21 – 4.16 (m, 1 H), 3.90 (dd, *J* = 7.2, 3.3, 1 H), 3.82 (d, *J* = 3.5, 1 H), 1.75 (s, 3 H), 1.70 (s, 3 H), 1.35 (d, *J* = 6.2, 3 H), 1.29 (t, *J* = 7.1, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.8, 163.0, 153.2, 137.6, 128.4, 128.0, 127.8, 105.4, 84.6, 73.9, 71.8, 62.0, 46.0, 36.2, 28.3, 27.1, 17.7, 14.0

IR ($CHCl_3$): 3019 (m), 2983 (m), 2939 (m), 1824 (m), 1714 (s), 1454 (m), 1372 (m), 1269 (m), 1216 (s), 1146 (m), 1096 (m), 1038 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{21}H_{23}O_7^-$ ([M-H]$^-$) 387.1449, found 387.1445

(5S)-ethyl 5-(benzyloxy)-4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-5-phenylpent-2-ynoate (7d)



Following General Procedure III using **6d** (88 mg, 0.25 mmol) at 0°C for 24 h, 95 mg (0.21 mmol, 84%) of **7d** was obtained as yellow oil.

$[\alpha]_D^{20}$ -28.7 (c = 1.8, $CHCl_3$)

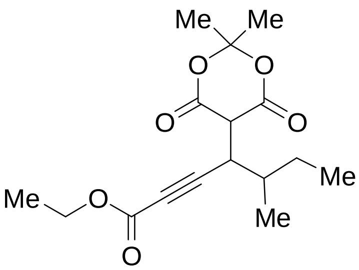
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.26 (m, 10 H), 5.17 (d, *J* = 10.2, 1 H), 4.45 (AB, 2 H), 4.23 (q, *J* = 7.2, 2 H), 3.90 (dd, *J* = 9.6, 2.7, 1 H), 3.06 (d, *J* = 2.4, 1 H), 1.72 (s, 3 H), 1.47 (s, 3 H), 1.30 (t, *J* = 6.9, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.3, 162.7, 153.2, 137.7, 137.5, 129.4, 129.2, 128.3, 127.8, 127.7, 127.6, 105.5, 84.9, 81.0 75.4, 71.6, 61.9, 47.3, 38.2, 28.4, 26.7, 14.0

IR (neat): 3065 (w), 3033 (m), 2988 (m), 2942 (m), 2876 (m), 2245 (m), 1789 (m), 1751 (s), 1711 (s), 1586 (m), 1496 (m), 1455 (m), 1384 (m), 1367 (m), 1302 (m), 1261 (s), 1205 (m), 1070 (m), 1012 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{26}H_{25}O_7^-$ ($[M-H]^-$) 449.1606, found 449.1609

Ethyl 4-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl)-5-methylhept-2-ynoate (7e)



Following the General Procedure II using racemic **6e** (53 mg, 0.25 mmol), 43 mg of **7e** (0.14 mmol, 55%) was obtained as clear oil.

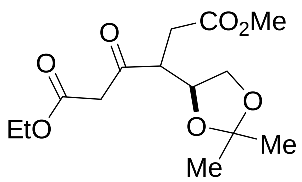
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.17 (q, *J* = 7.2, 2 H), 3.76 (d, *J* = 1.8, 1 H), 3.33 (d, *J* = 9.9, 2.1, 1 H of one diastereomer), 3.30 (dd, *J* = 10.8, 2.1, 1 H of the other diastereomer), 2.30 – 2.20 (m, 1 H), 1.93 – 1.83 (m, 1 H of one diastereomer), 1.79 (s, 3 H), 1.78 (s, 3 H), 1.50 – 1.42 (m, 1 H of the other diastereomer), 1.33 – 1.24 (m, 3 H), 1.13 (d, *J* = 6.9, 3 H of one diastereomer), 0.96 – 0.88 (m, 3 H and 3 H of the other diastereomer)

^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2, 163.2, 163.1, 153.2, 105.5, 86.3, 86.2, 76.1, 75.8, 61.9, 47.0, 46.8, 37.0, 35.4, 35.2, 28.3, 27.7, 27.4, 26.4, 17.5, 16.1, 13.9, 10.7, 10.6

IR (neat): 2969 (m), 2939 (m), 2879 (m), 2238 (m), 1786 (m), 1751 (s), 1709 (s), 1464 (m), 1396 (m), 1385 (m), 1367 (m), 1335 (m), 1301 (s), 1258 (s), 1206 (m), 1142 (m), 1073 (m), 1009 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{16}H_{21}O_6^-$ ($[M-H]^-$) 309.1344, found 309.1342

General Procedure IV: Synthesis of Ketoester 9: 6-Ethyl 1-methyl 3-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-oxohexanedioate (9a)



In a test tube (100 x 12 mm) equipped with a stir bar was added $Cu(OAc)_2$ (10 mg, 0.05 mmol, 0.2 equiv) and deionized water (0.2 mL). To the stirring solution was added Na-(+)-ascorbate (20 mg, 0.10 mmol, 0.4 equiv). The reaction mixture was stirred for 5 min, and during this time the solution turns brown initially and changes its color to orange. To the reaction mixture was added ethyl propiolate (253 μL, 2.50 mmol, 10 equiv). The reaction mixture was stirred for 10 min, and during this time the color changes from orange to yellow. To the reaction mixture was then added **6a** (64 mg, 0.25 mmol), and the reaction mixture was stirred vigorously at rt for 24 h. The reaction mixture was diluted with saturated aqueous ammonium chloride (1 mL) and extracted with dichloromethane (10 mL x 3). The solution was dried over Na_2SO_4, and concentrated. The crude oil was dissolved in methanol (1.6 mL) and the solution was cooled using dry ice/acetone bath at -78^{o}C. To the cold solution was added dropwise triethylamine (40 μL), and the reaction mixture was stirred for 3 h. The volatiles were removed under reduced pressure. The residue was purified by chromatography (1/1 Hexanes/EtOAc, 20 mm x 15 cm) to afford 40 mg (0.13 mmol, 53%) of **9a** as clear oil.

$[a]_D^{20}$ -57.4 (c = 1.0, $CHCl_3$)

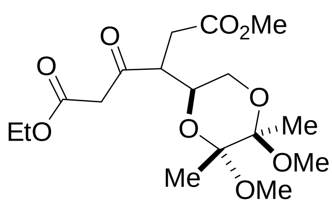
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.16 (q, *J* = 7.2, 2 H), 4.14 – 4.09 (m, 1 H), 4.04 – 3.98, 3.68 – 3.63 (ABX, 2 H), 3.70 (s, 2 H), 3.65 (s, 3 H), 3.30 (m, 1 H), 2.86 – 2.77, 2.34 – 2.27 (ABX, 2 H), 1.43 (s, 3 H), 1.31 (s, 3 H), 1.27 (t, *J* = 6.9, 3 H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 203.7, 171.7, 166.8, 109.8, 75.6, 67.4, 61.2, 52.0, 51.0, 50.5, 32.2, 26.4, 25.2, 14.1

IR (neat): 2988 (m), 1743 (s), 1658 (w), 1440 (m), 1372 (m), 1268 (m), 1159 (m), 1066 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{14}H_{22}O_7Na^+$ ($[M+Na]^+$) 325.1258, found 325.1257

6-ethyl 1-methyl 3-((2S,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl)-4-oxohexanedioate (9b)



Following the General Procedure IV using **6b** (84 mg, 0.25 mmol), 57 mg of **9b** (0.15 mmol, 61%) was obtained as clear oil.

[α**]$_D^{20}$** -123.5 (c = 2.0, $CHCl_3$)

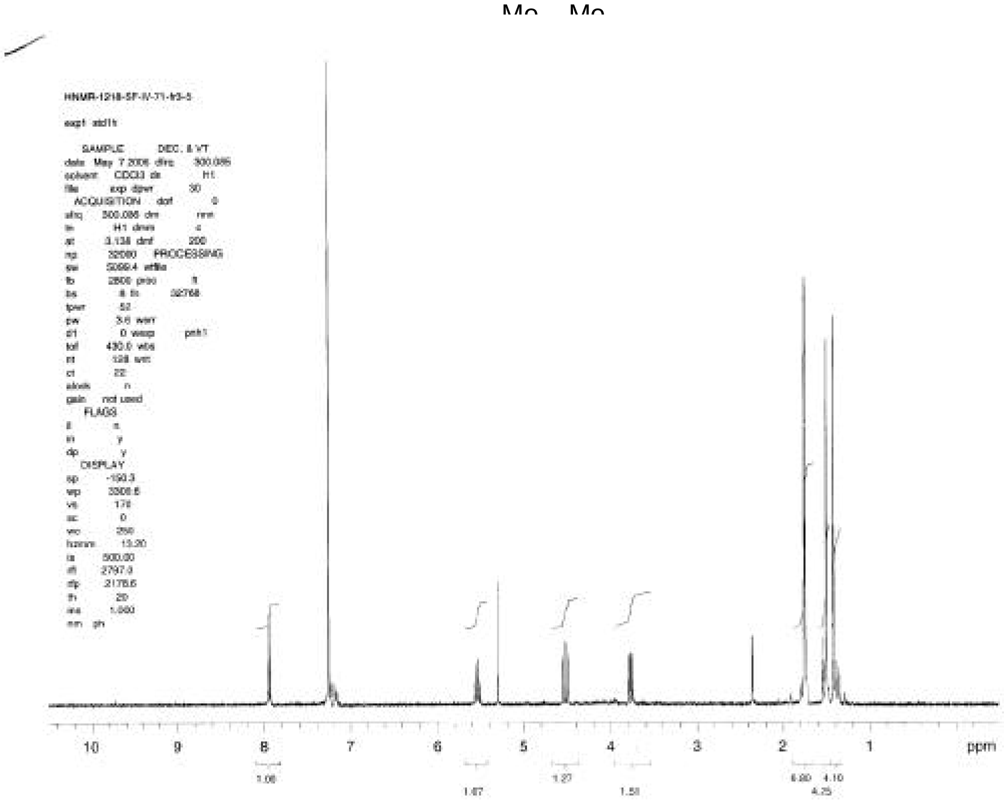
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.23 – 4.09 (m, 3 H), 3.99 – 3.91 (m, 1 H), 3.76 (AB, 2 H), 3.65 – 3.56, 3.42 – 3.37 (ABX, 2 H), 3.63 (s, 3 H), 3.24 (s, 3 H), 3.12 (s, 3 H), 2.82 – 2.73, 2.29 – 2.22 (ABX, 2 H), 1.25 (t, *J* = 7.1, 3 H), 1.24 (s, 6 H)

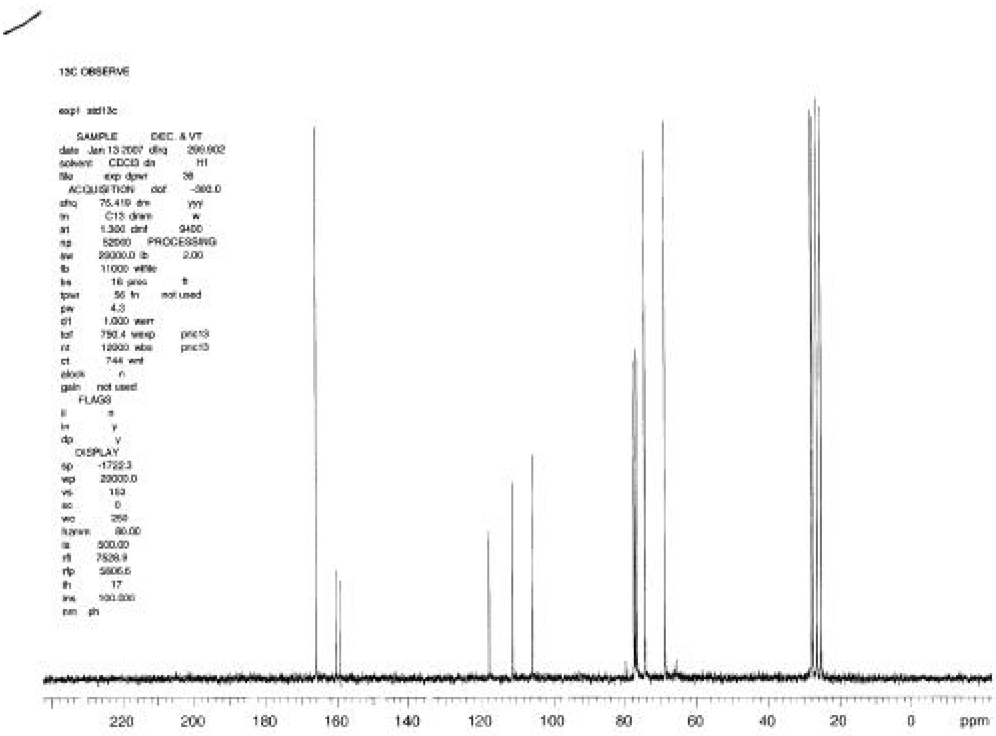
^{13}C NMR (75 MHz, $CDCl_3$): δ 204.7, 171.4, 166.8, 99.2, 98.1, 69.4, 61.5, 61.0, 52.3, 52.1, 48.2, 48.1, 48.0, 32.4, 17.6, 17.5, 14.2

IR (neat): 3018 (m), 2954 (m), 2837 (m), 1822 (w), 1739 (s), 1664 (w), 1440 (m), 1411 (m), 1376 (m), 1309 (m), 1216 (s), 1145 (m), 1118 (m), 1036 (m)

HRMS (HR-ESI, negative): Calcd. for $C_{14}H_{22}O_7Na^+$ ($[M+Na]^+$) 399.1626, found 399.1633

NMR Spectra of New Compounds





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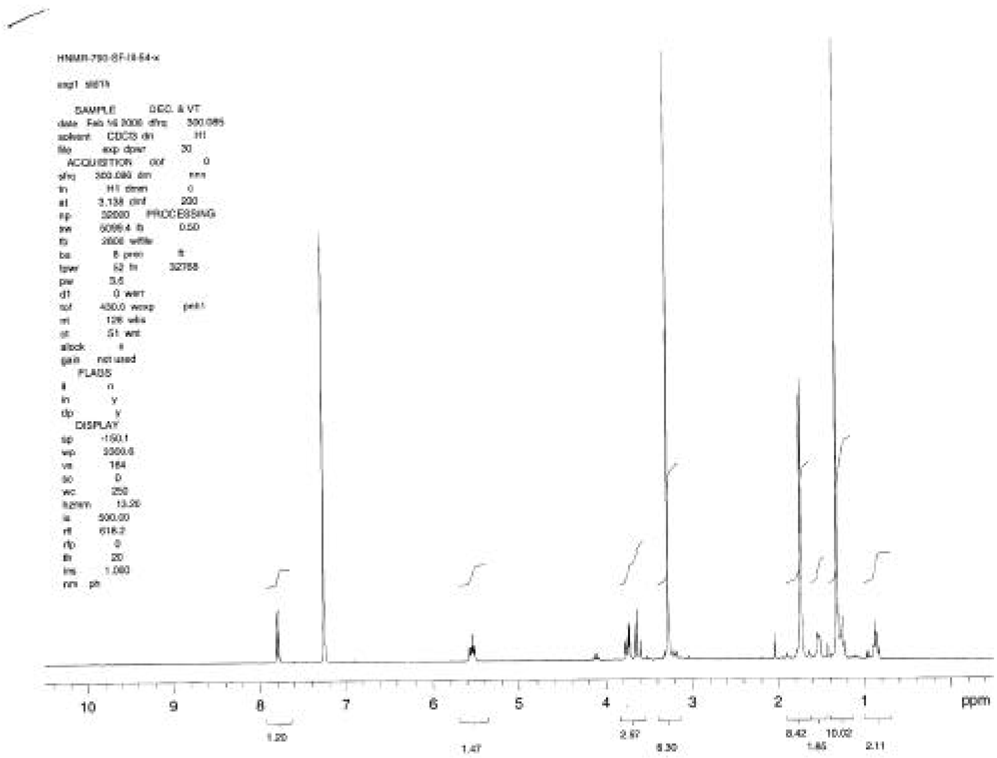

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7
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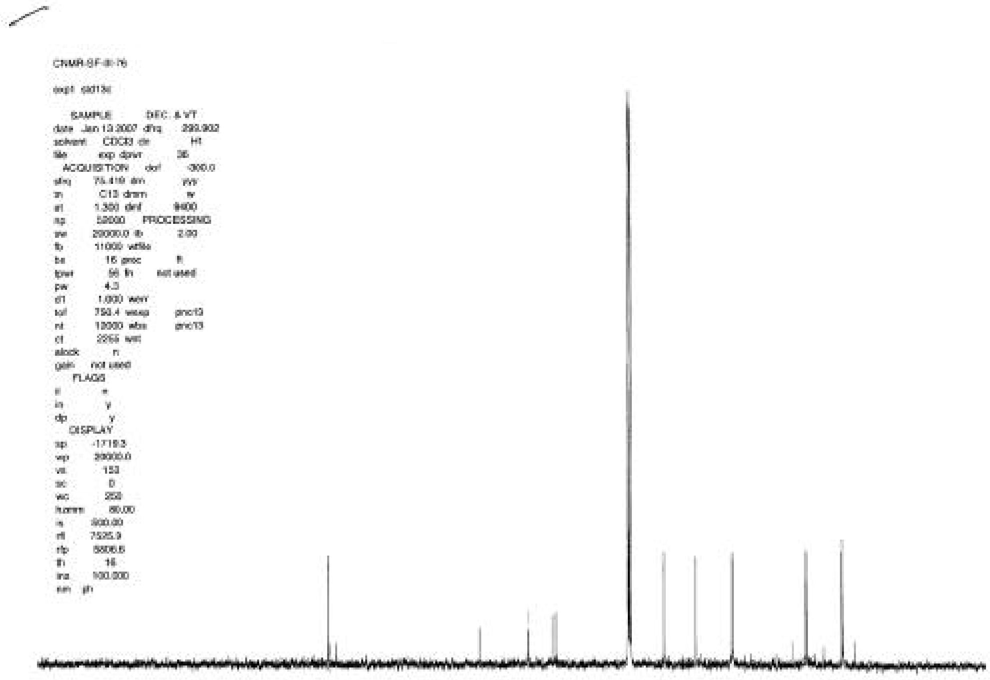
10.02
2.11



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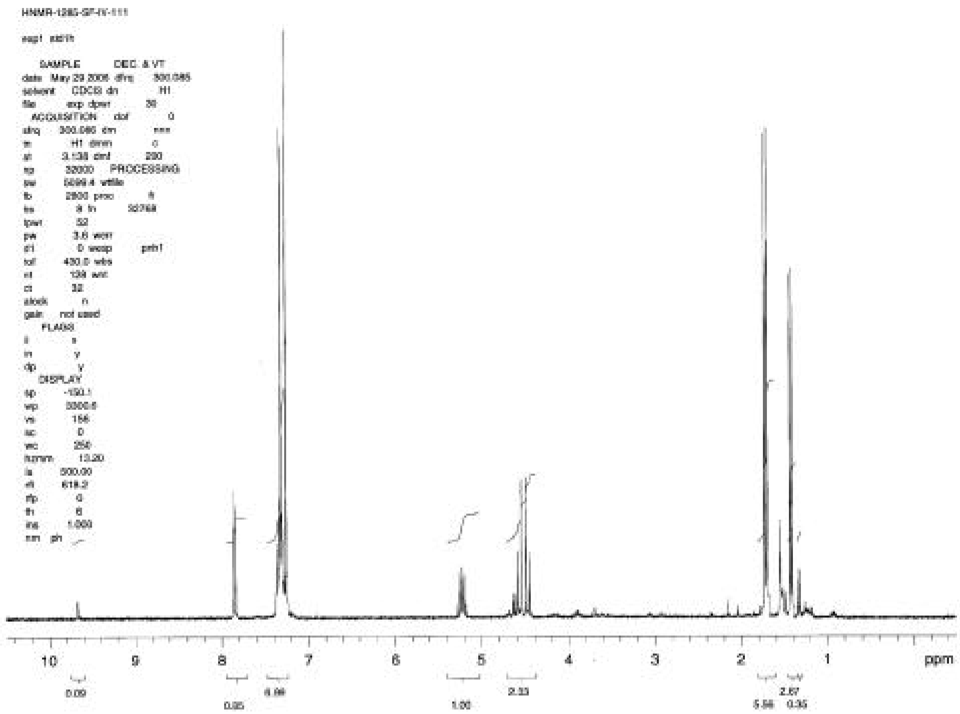
Me Me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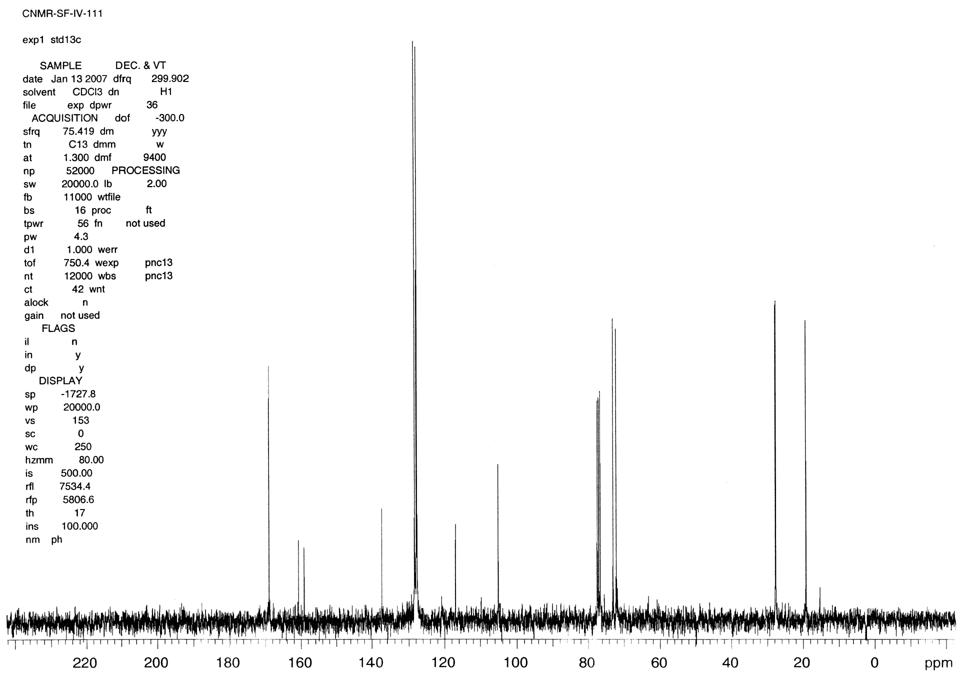
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pw 4.3
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ct 42 wnt
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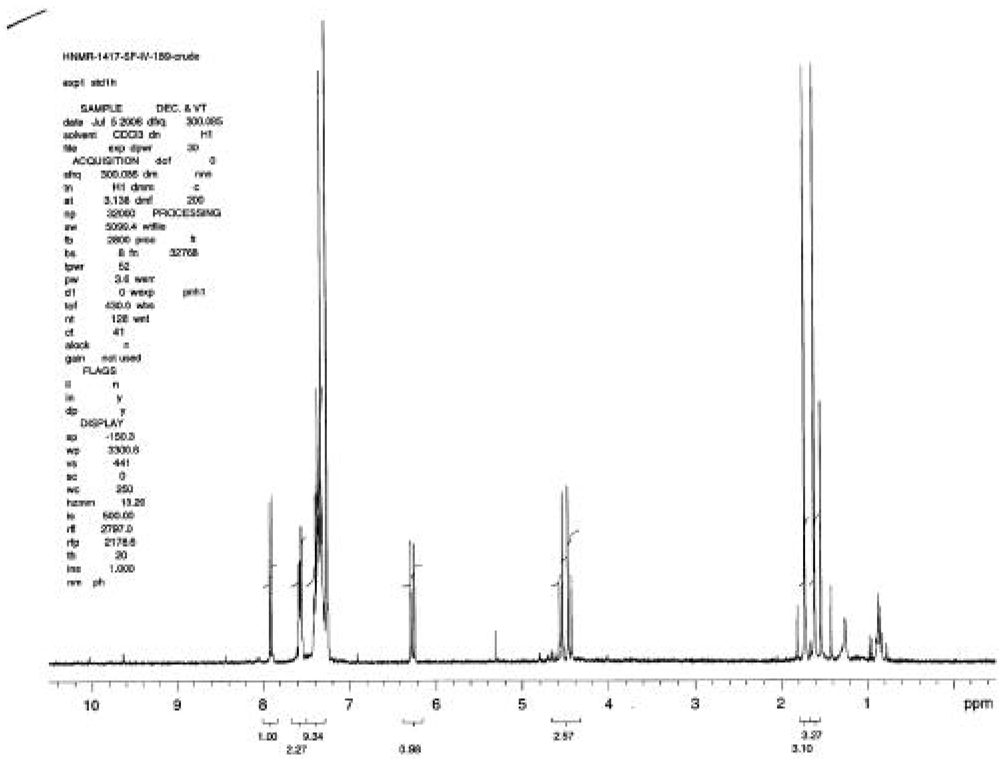
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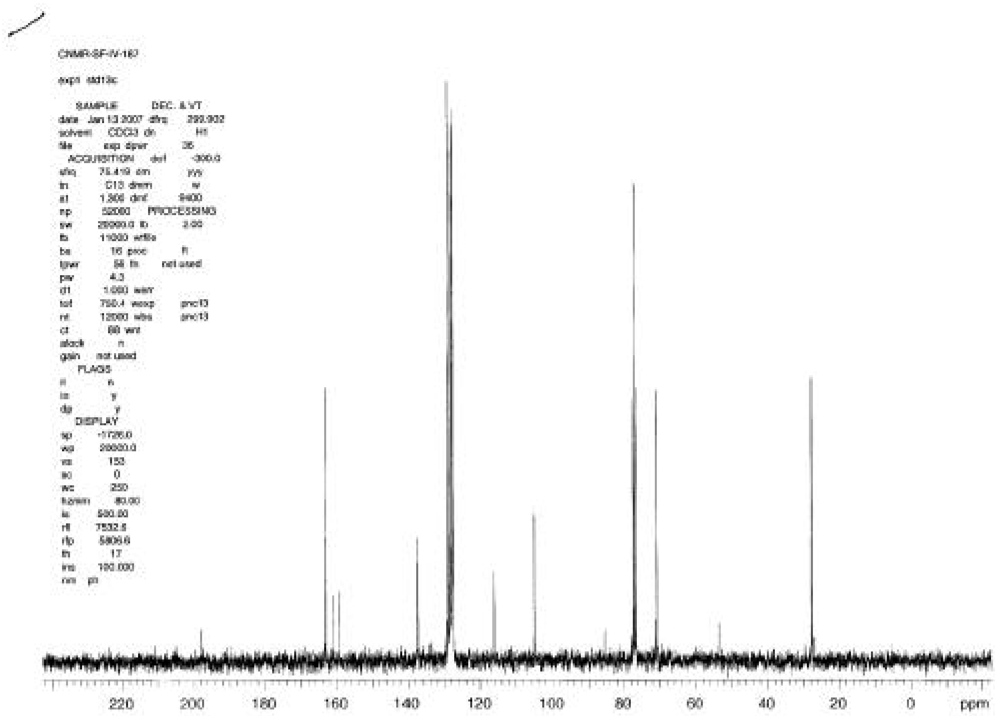
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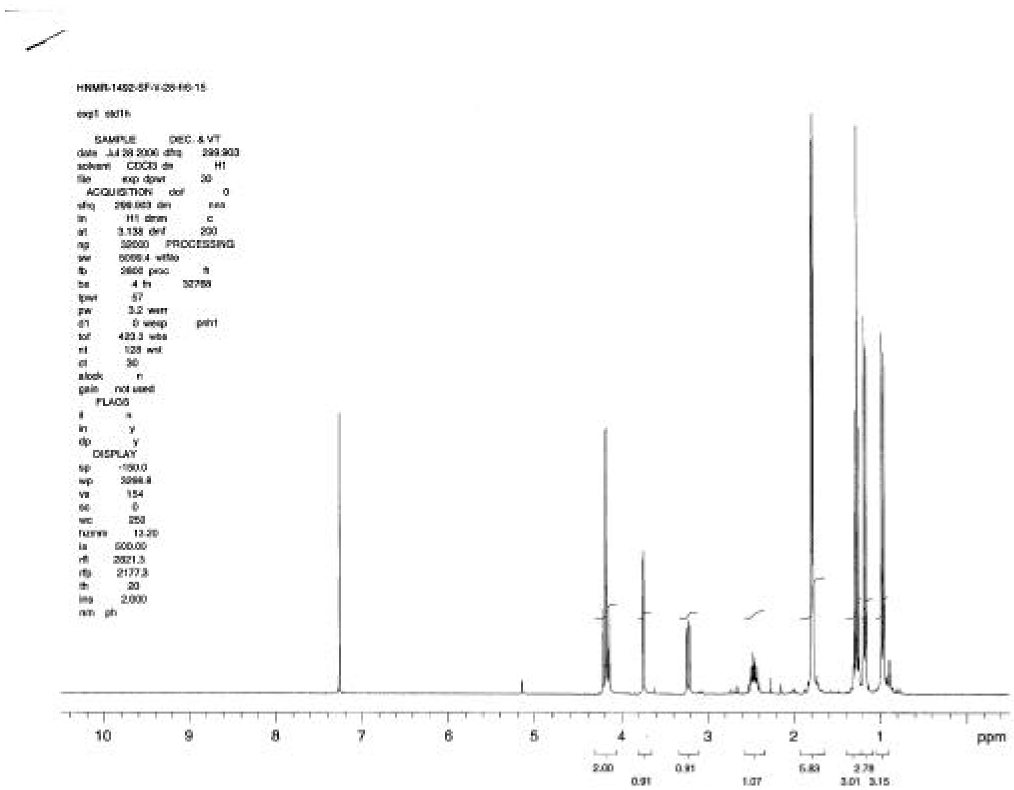

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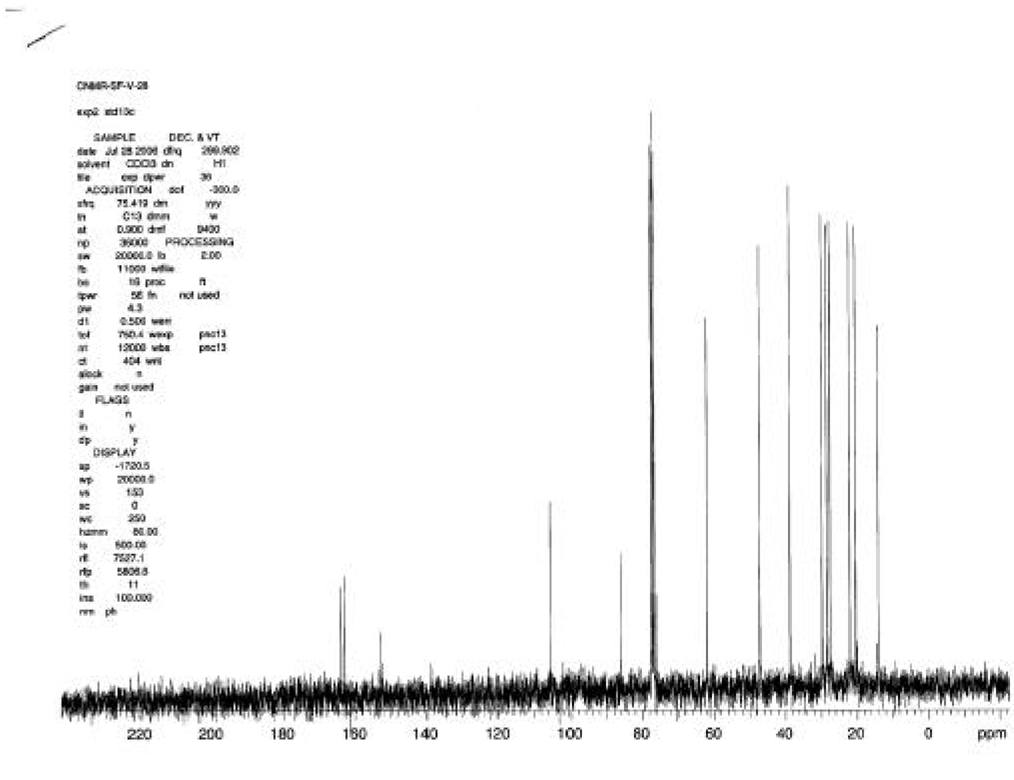

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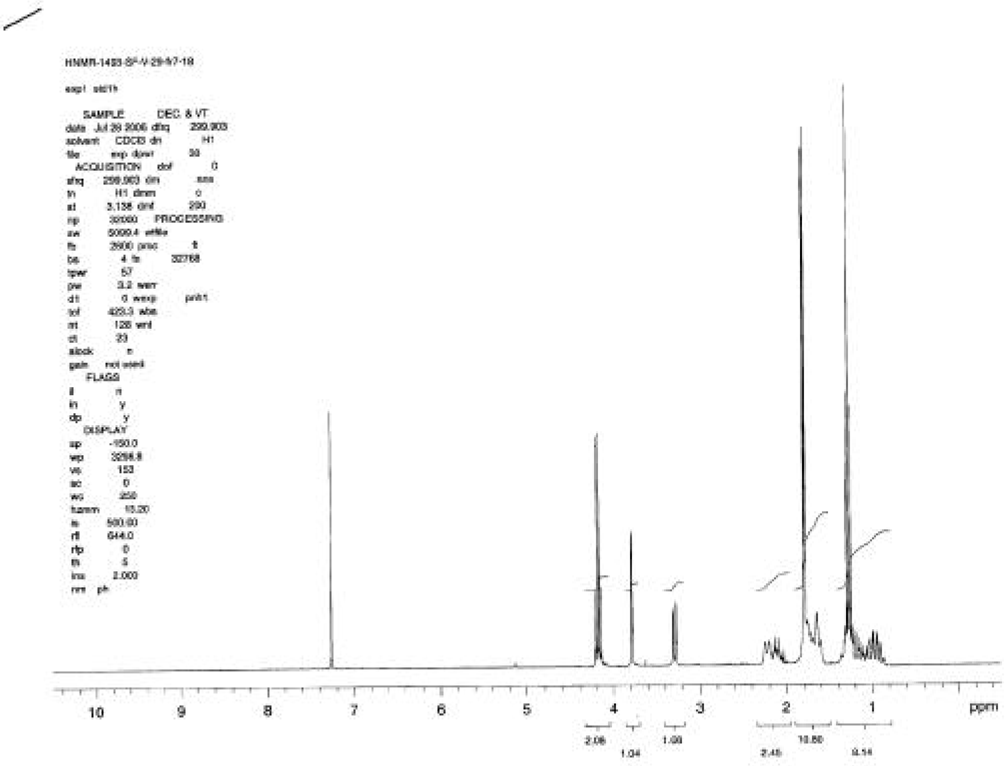
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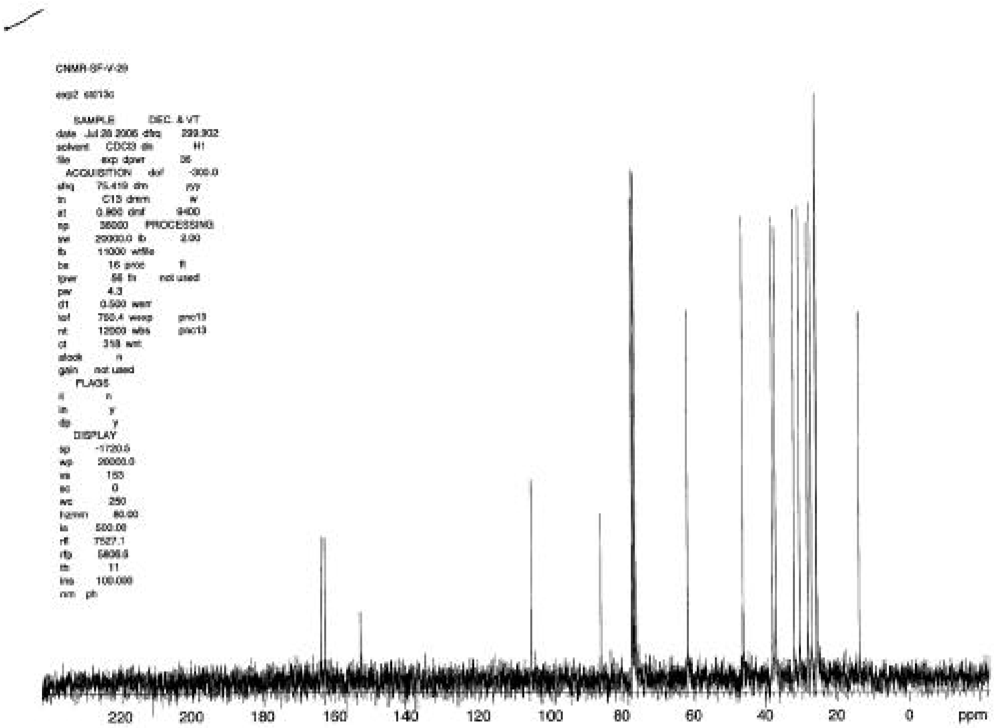
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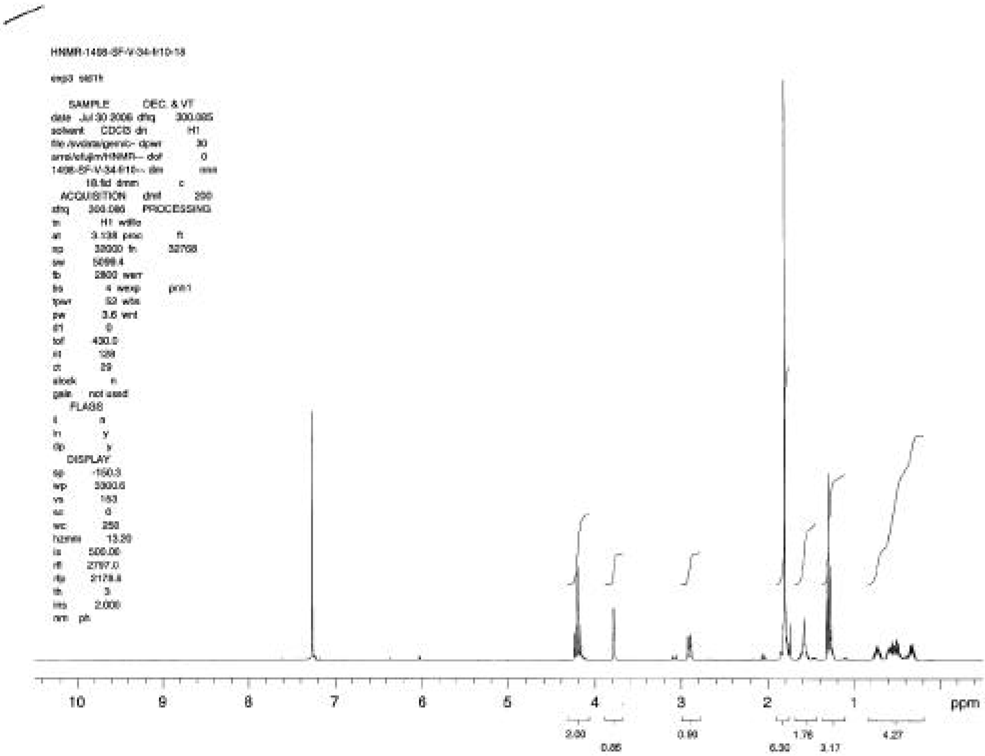
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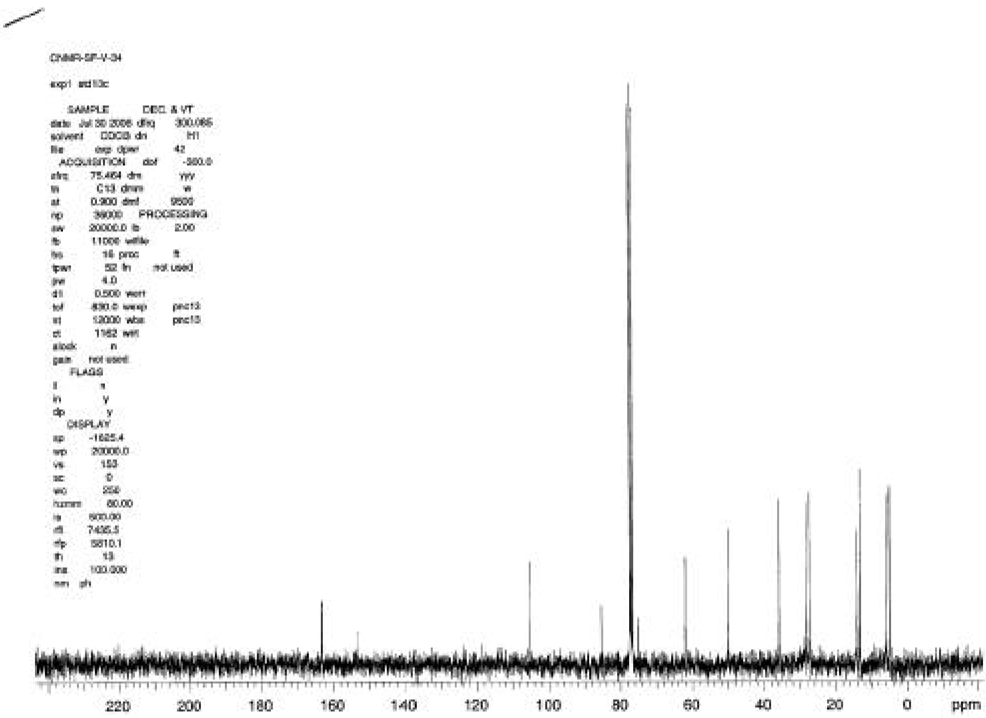
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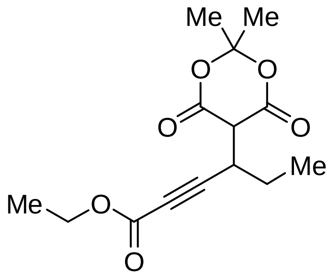
2d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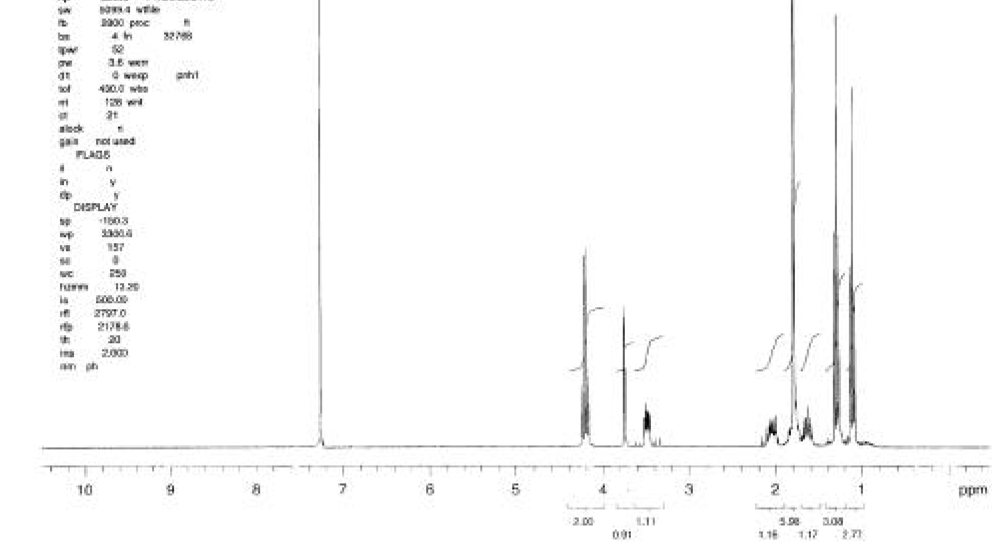
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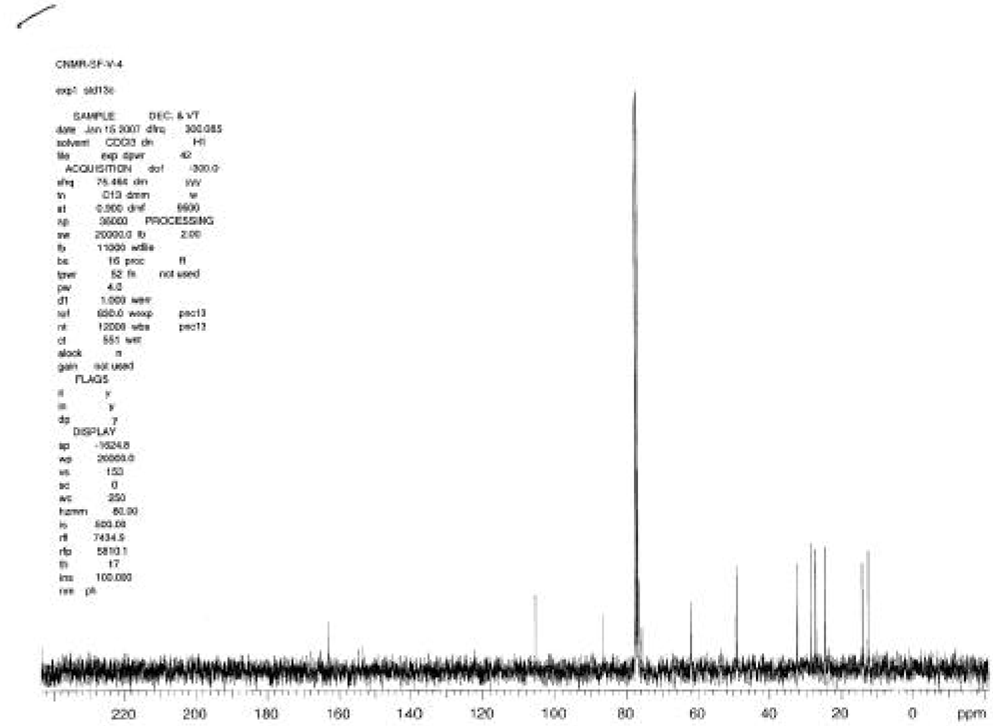
ppm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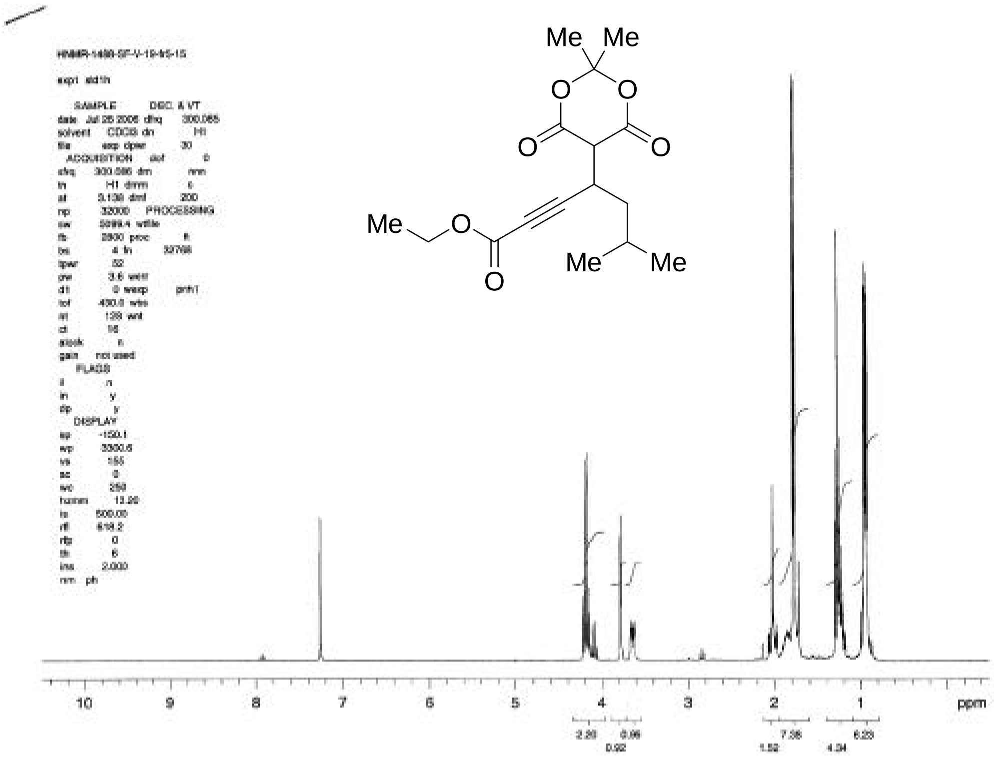
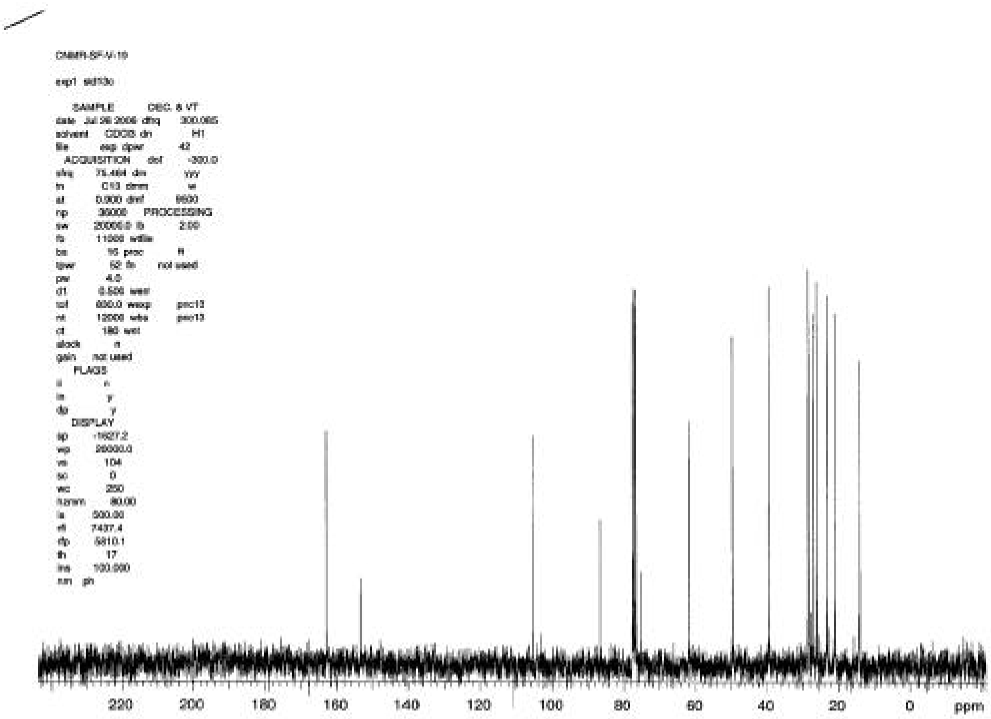
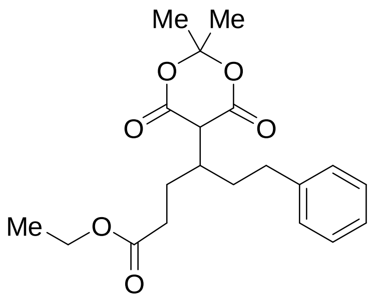
ppm

2e





5f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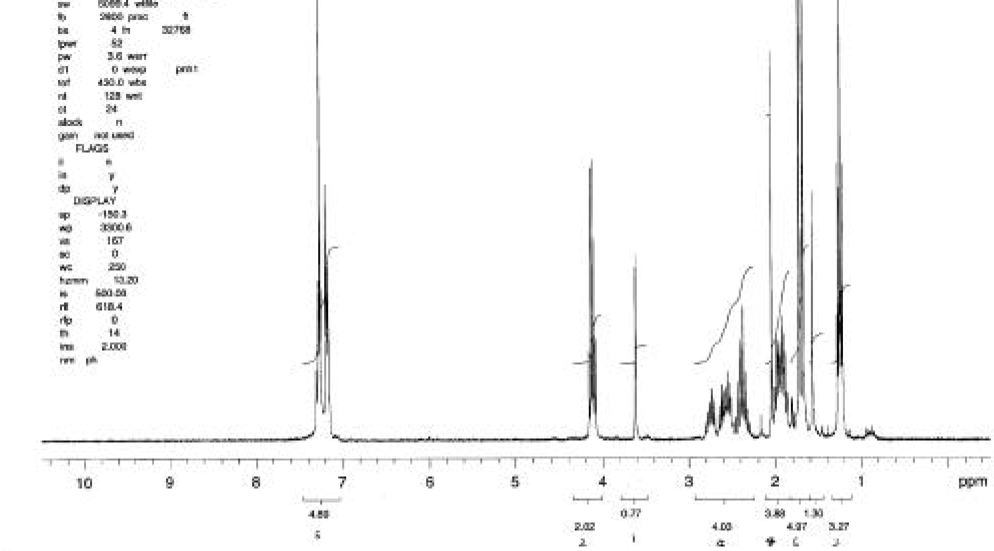
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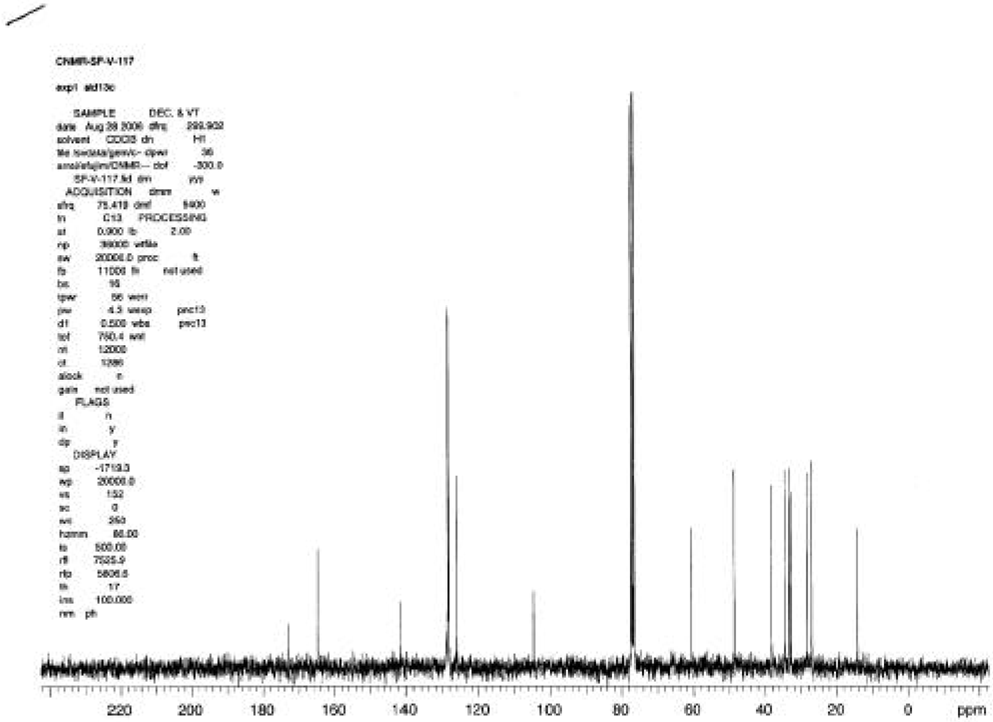
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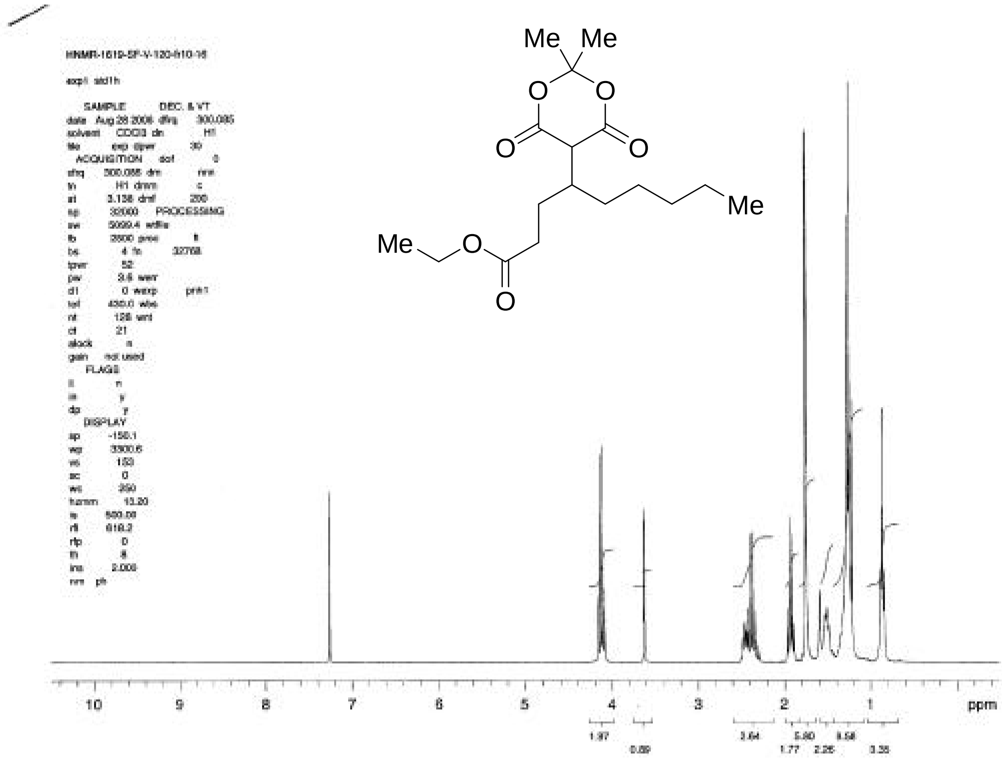

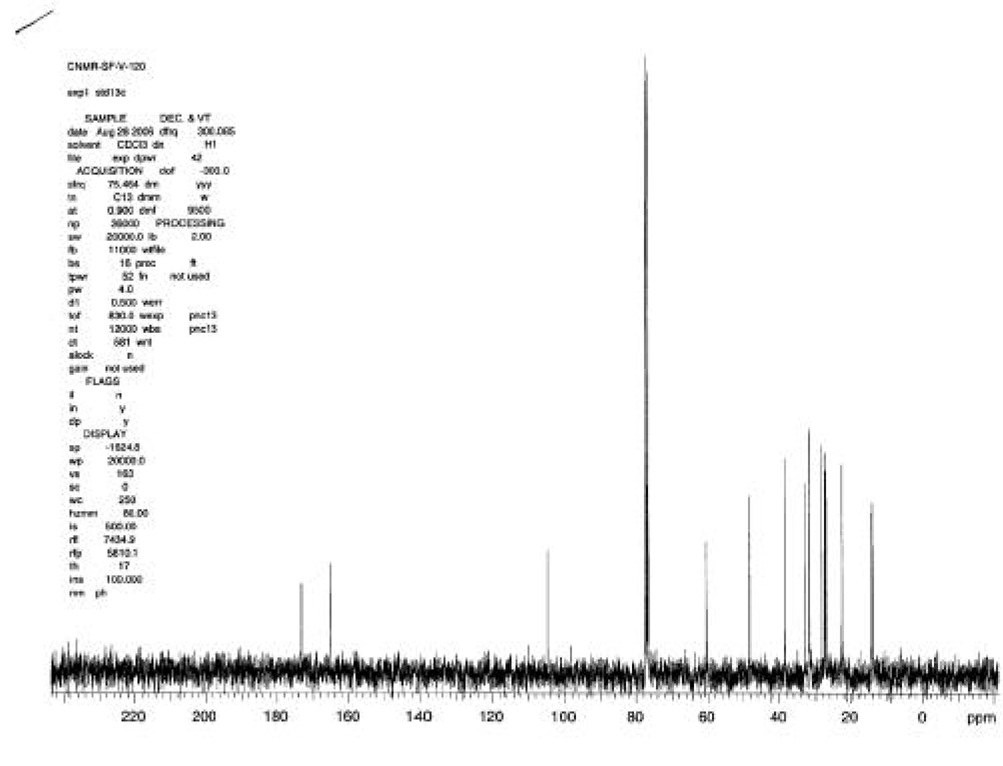

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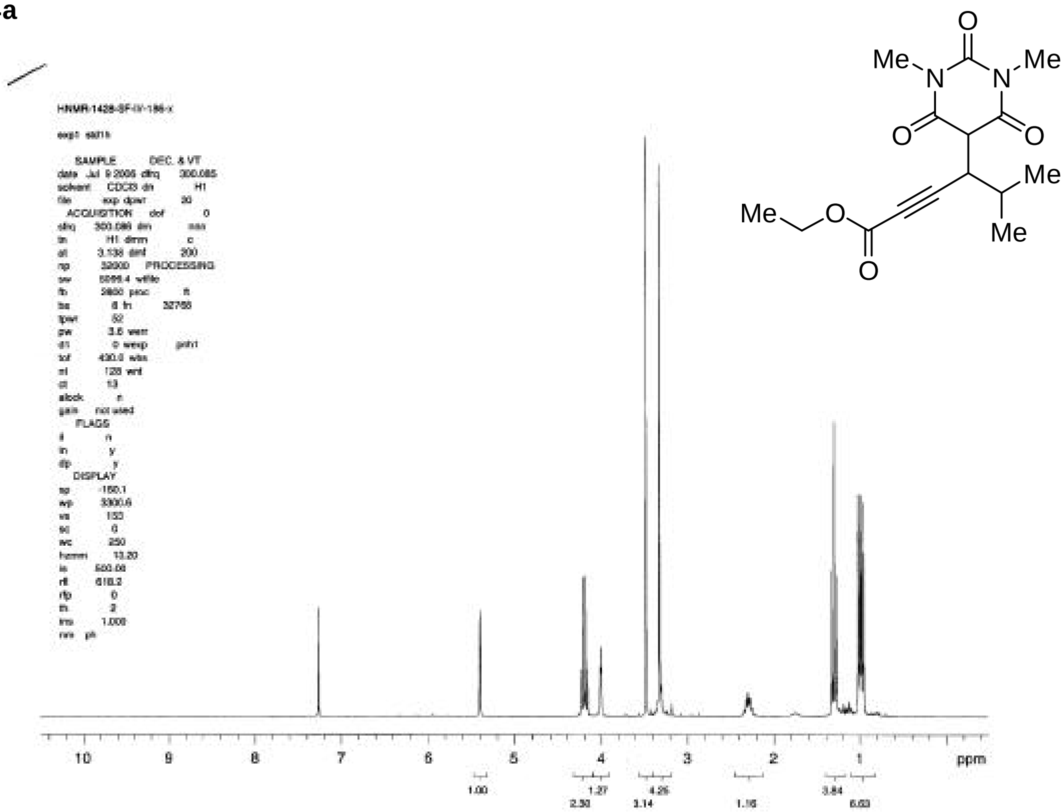

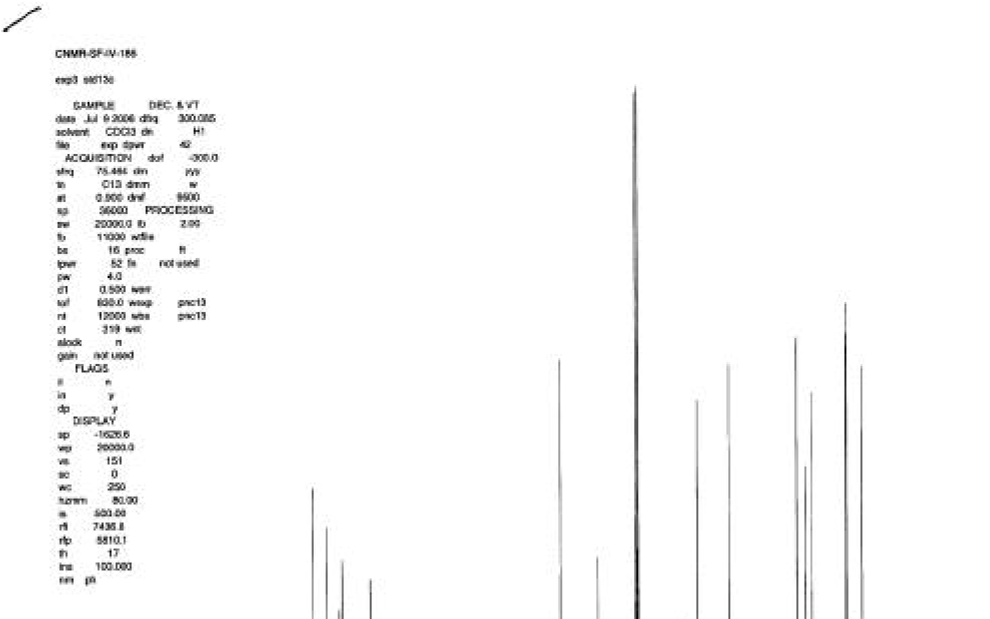

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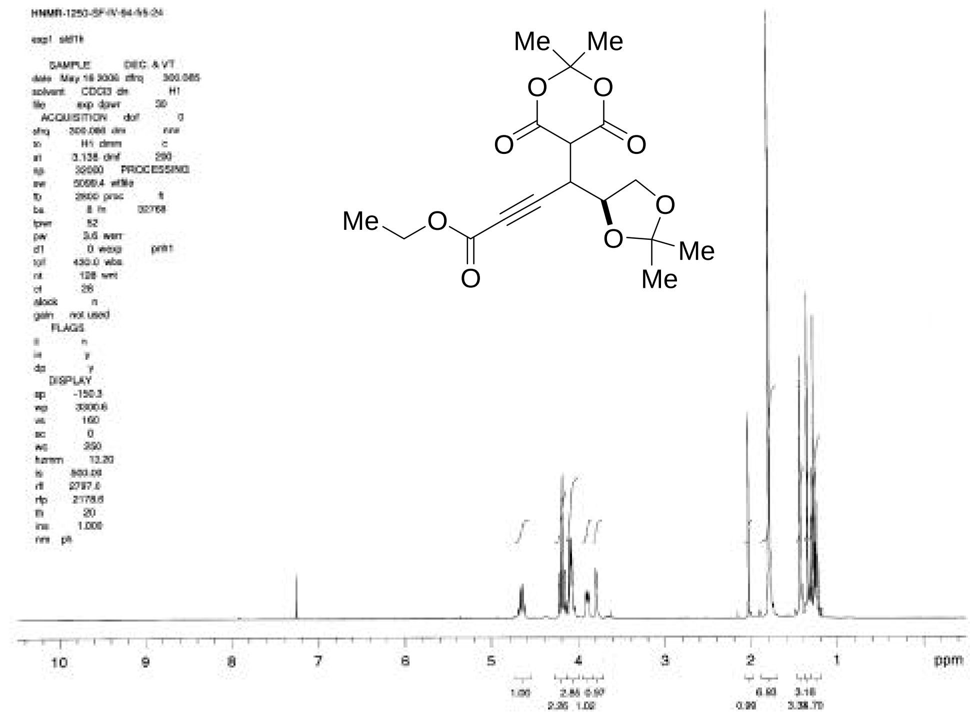

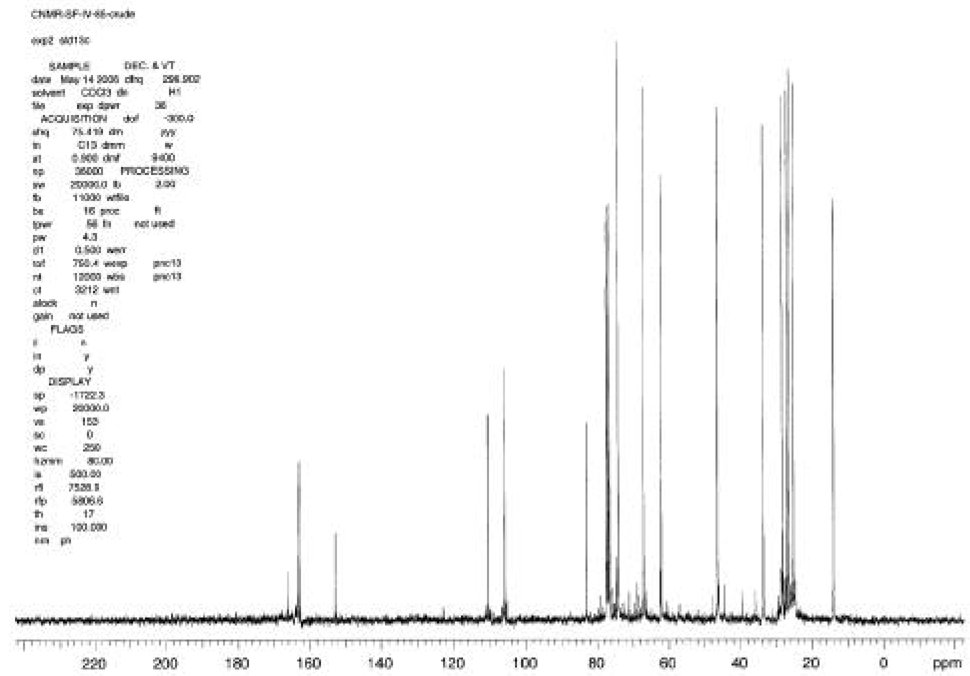

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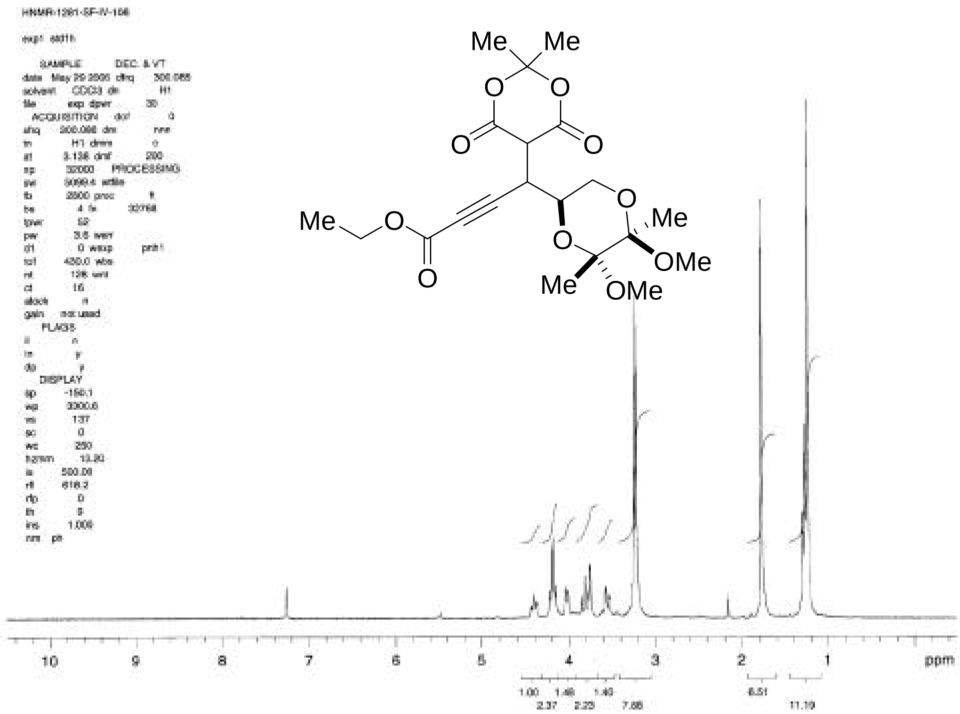

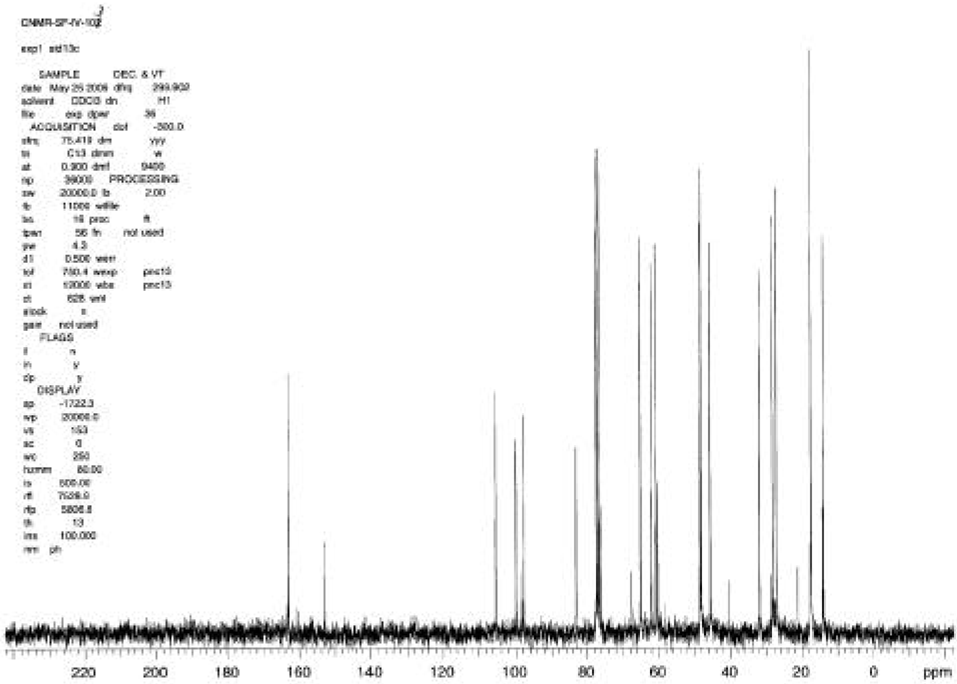

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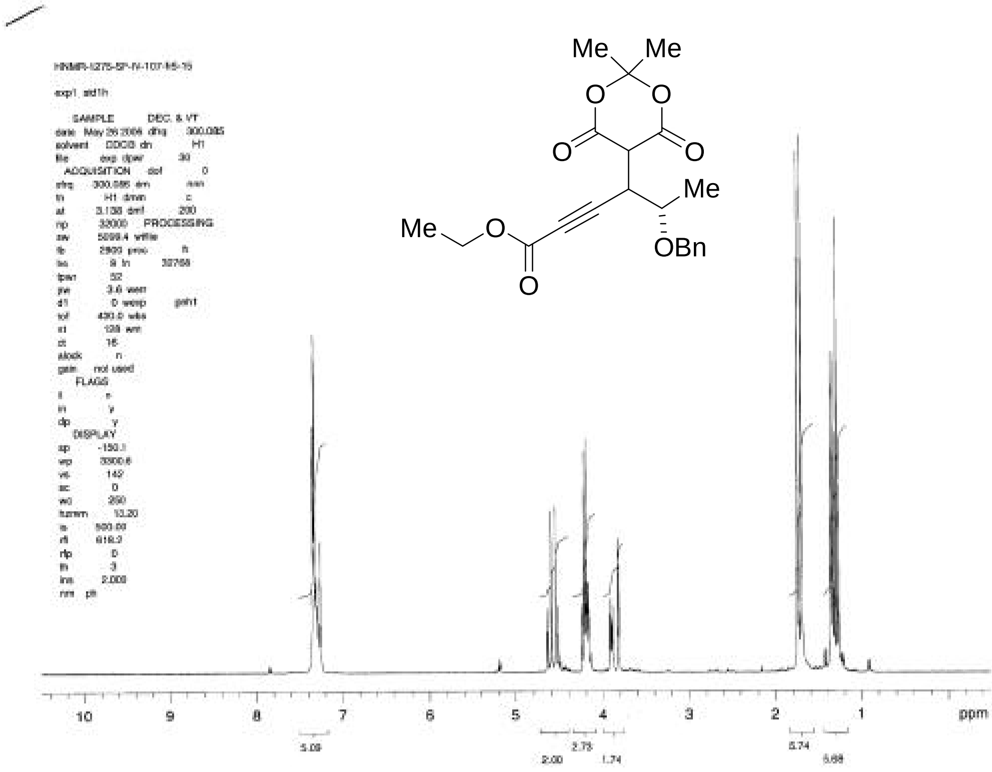

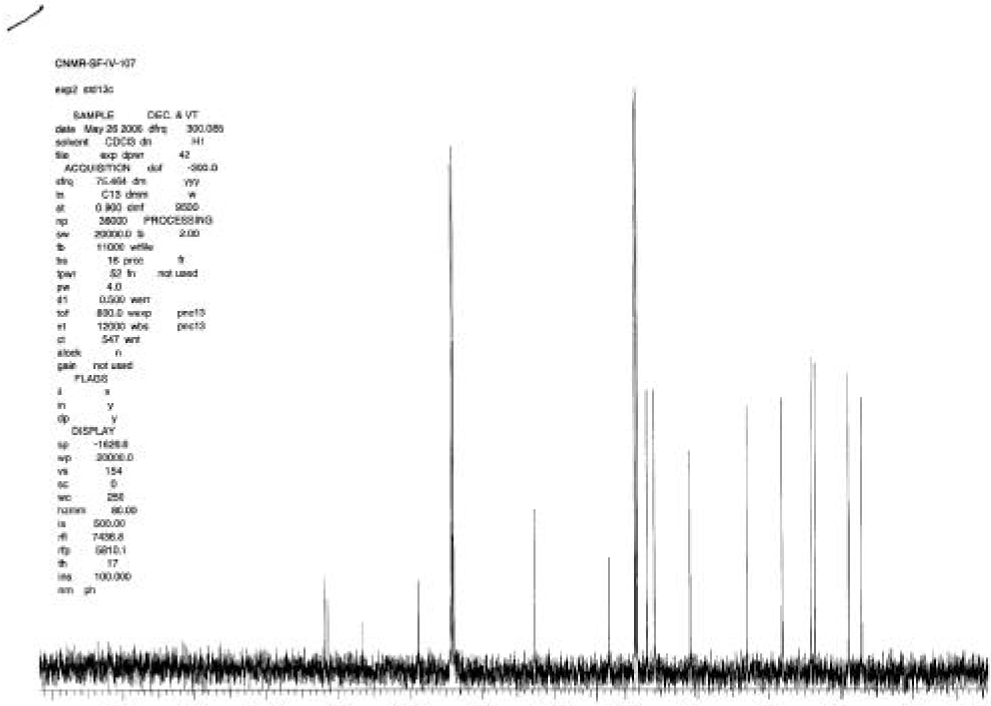

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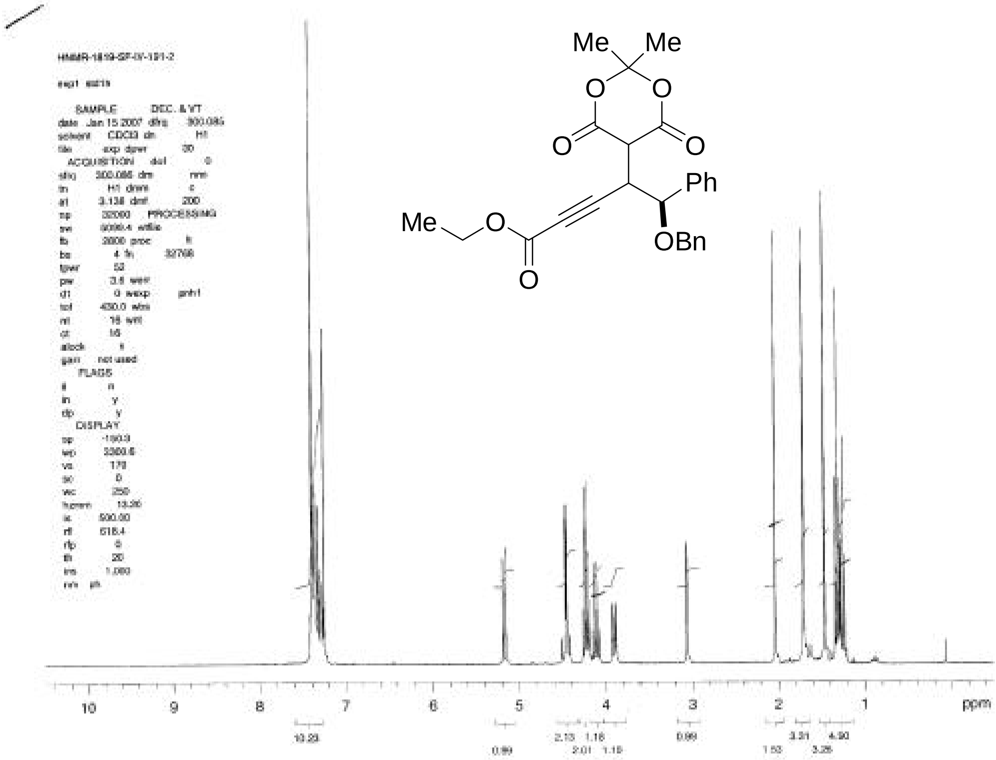

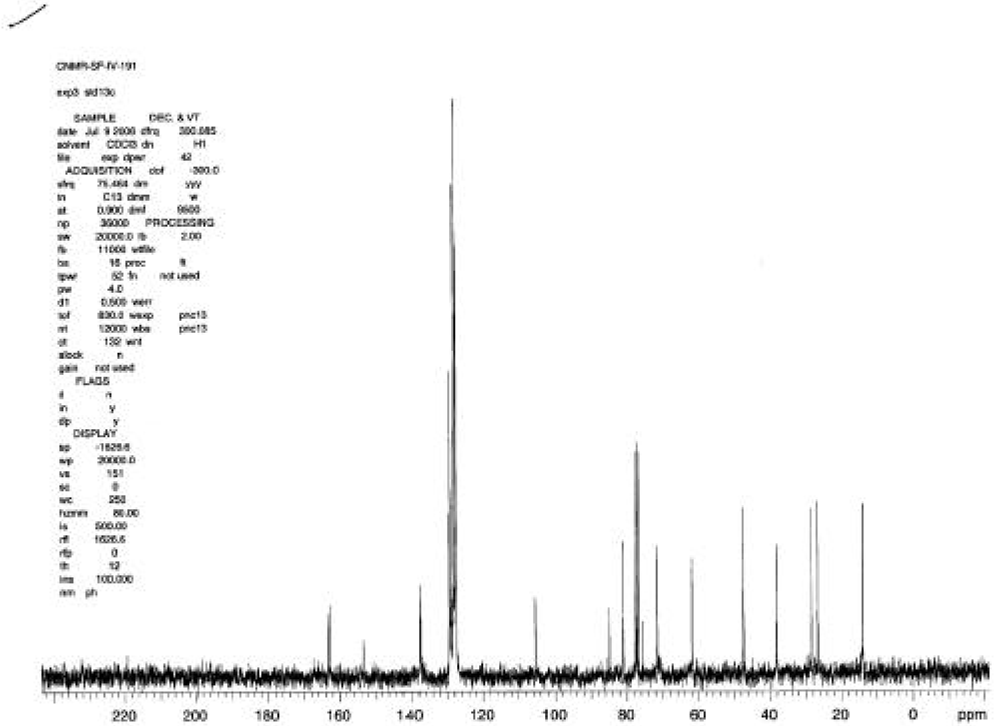

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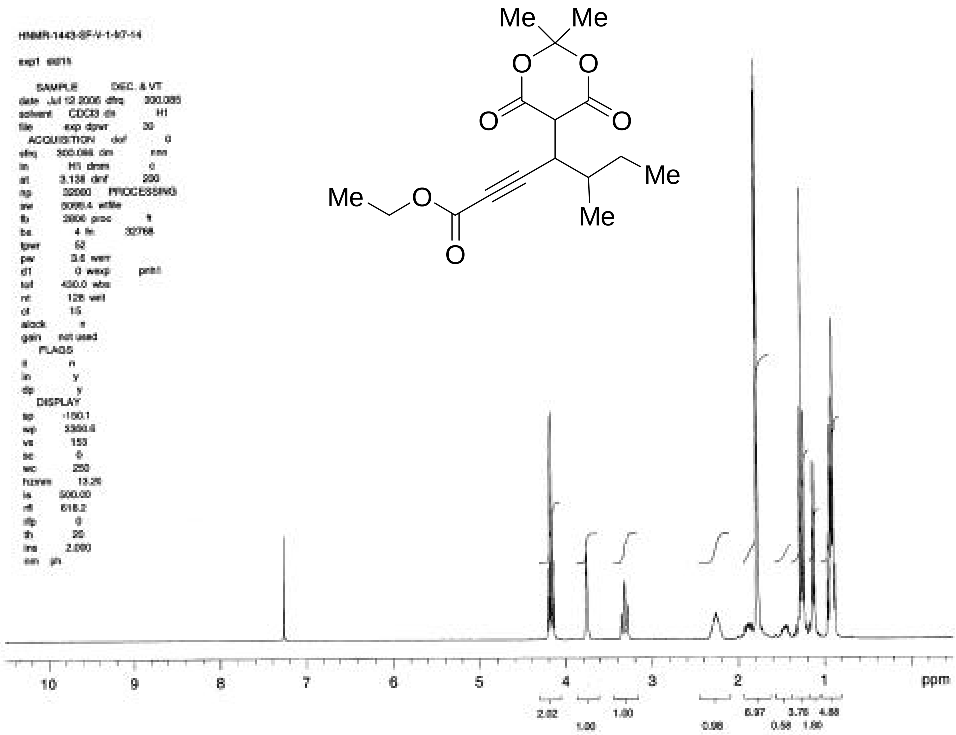

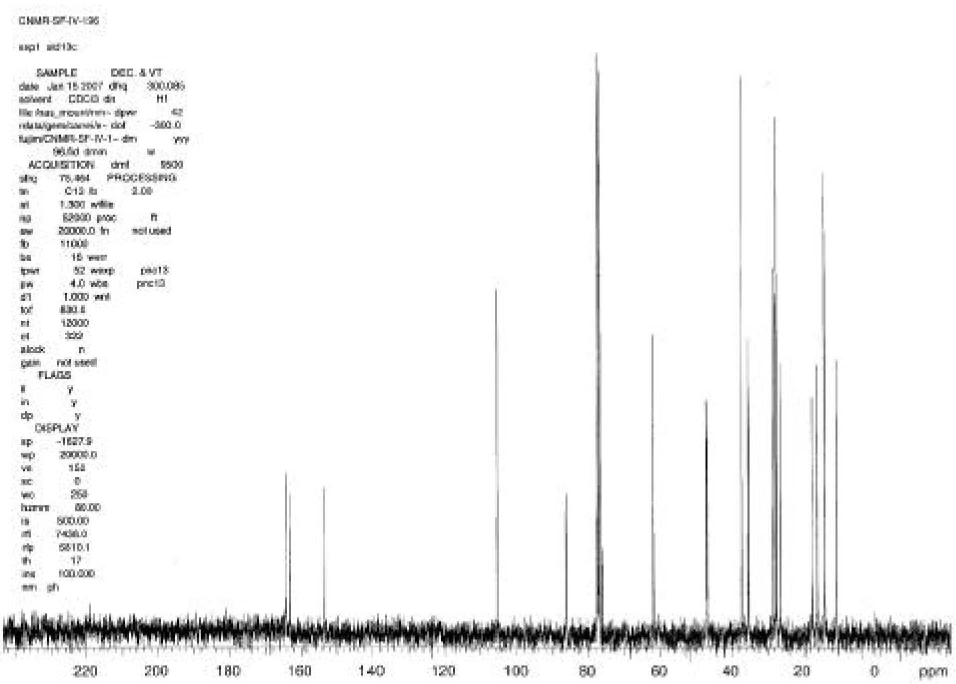

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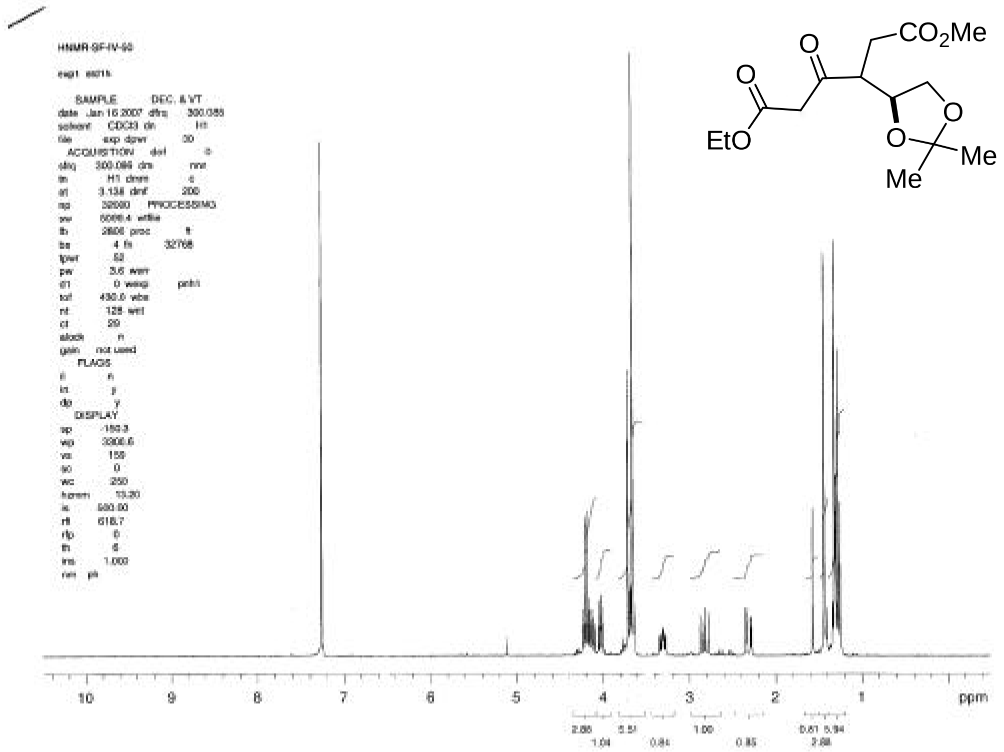

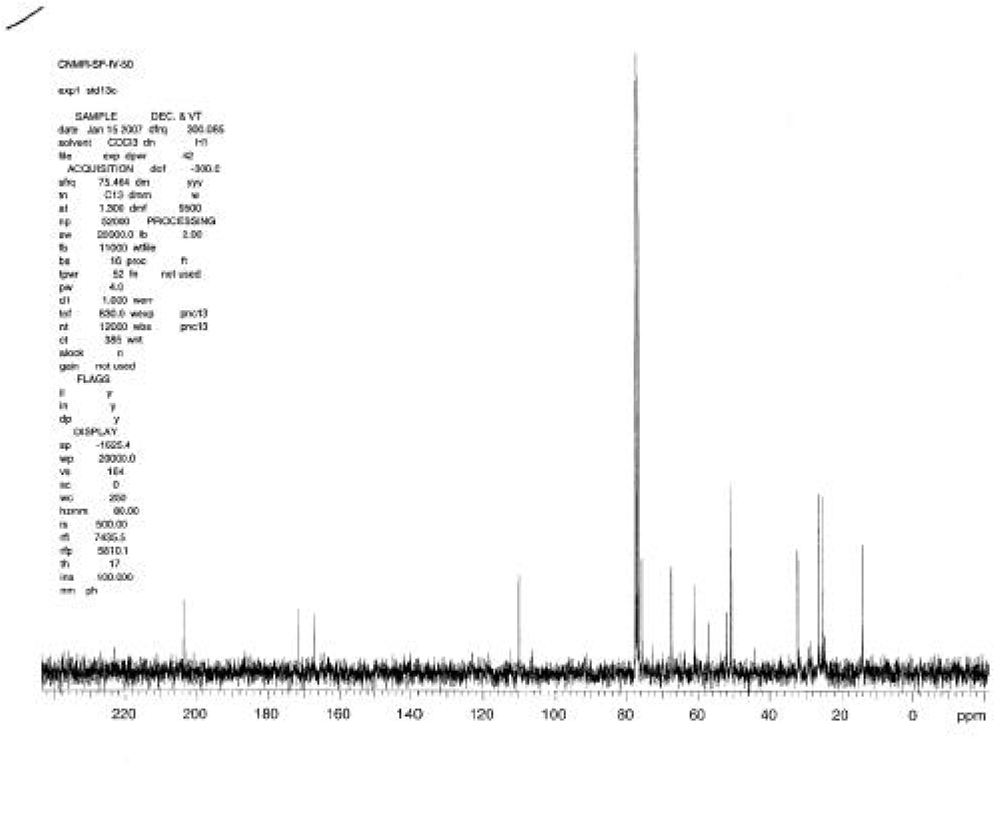

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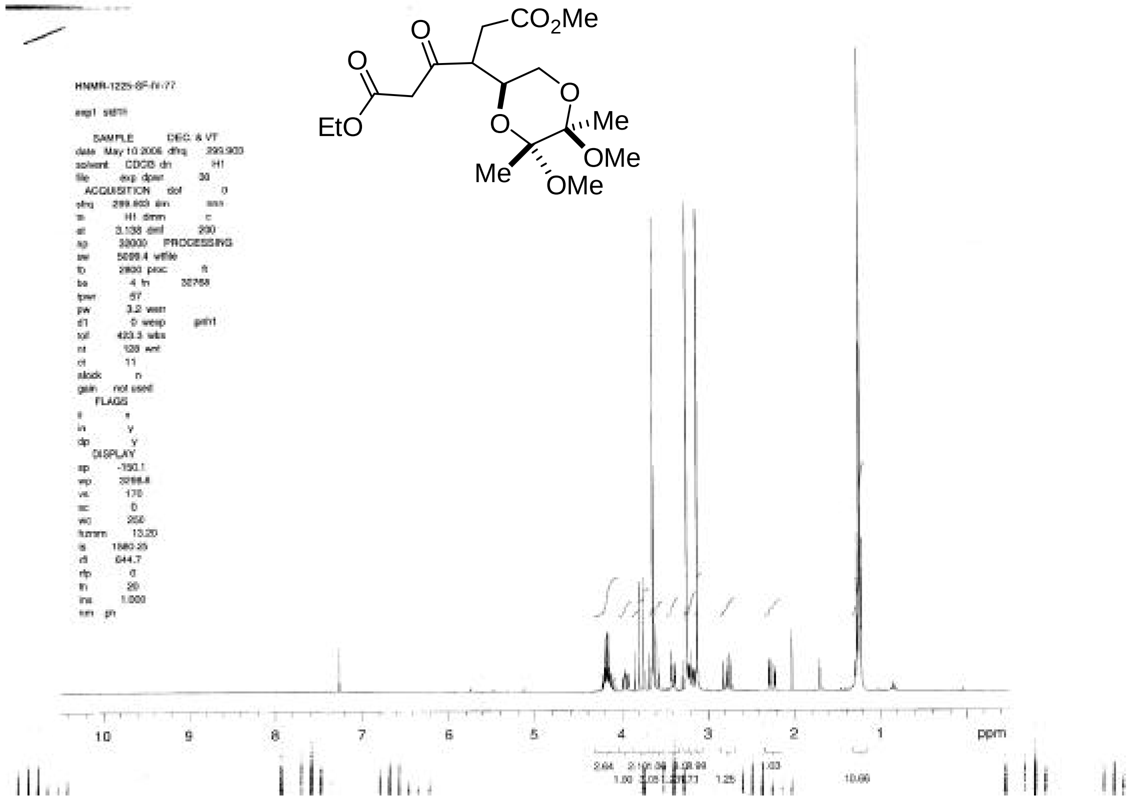
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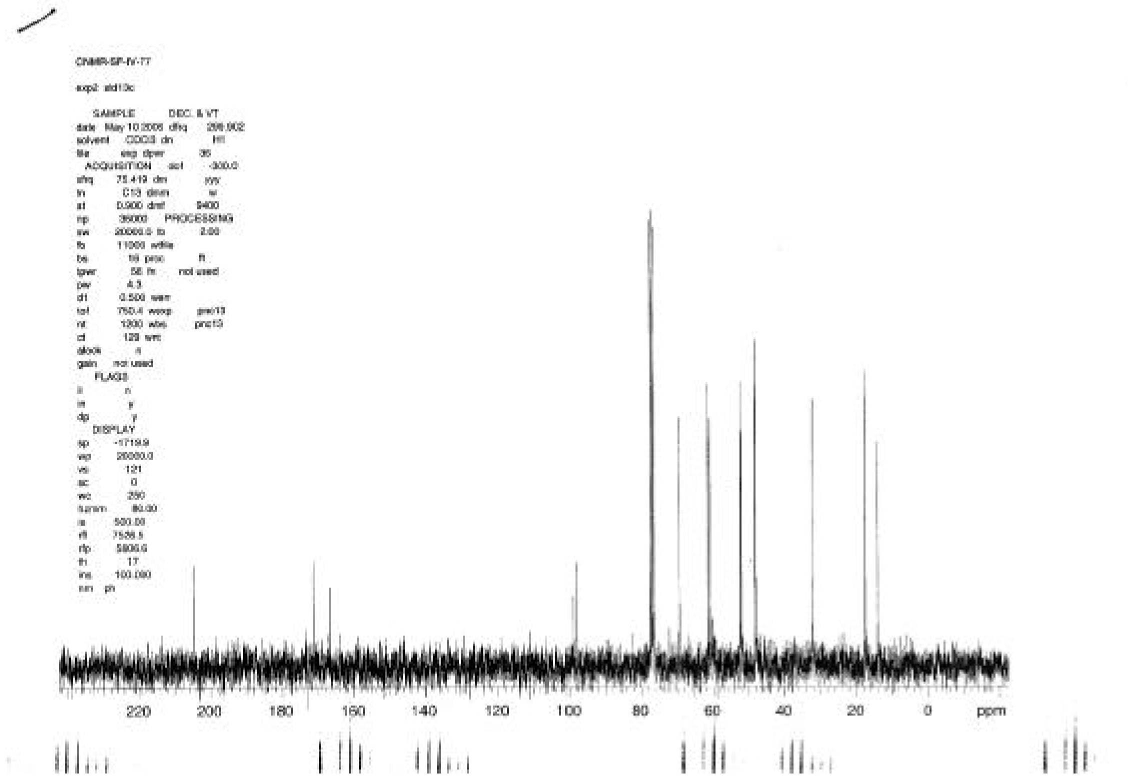
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X-ray crystal structure of *syn*-7b

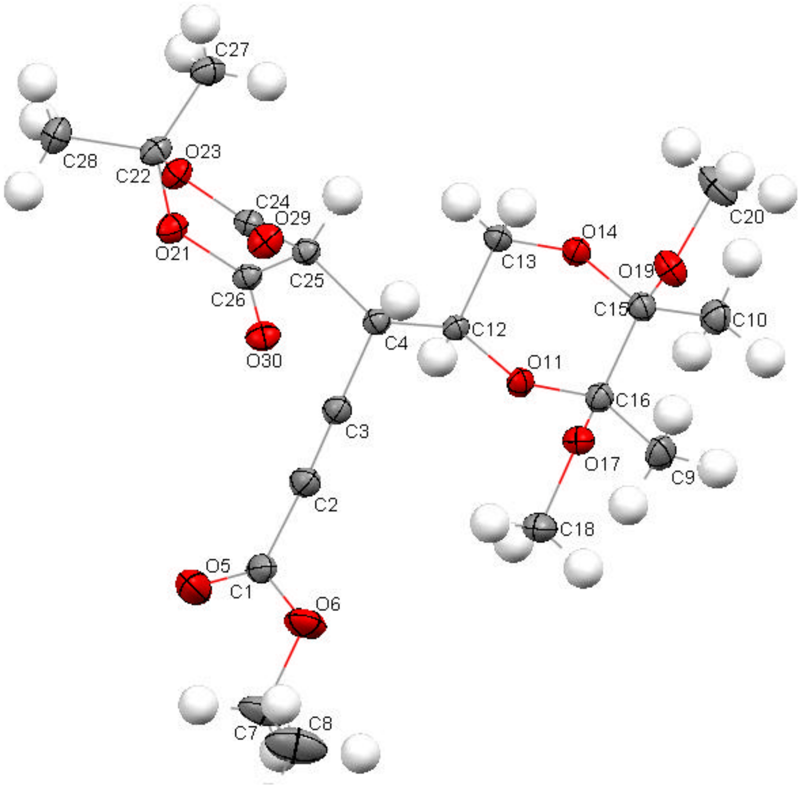

Figure 1. Crytal Structure of ***syn*-7b** (Ellipsoid probability level = 30%). Crystals were grown from hexanes/CH_2Cl_2 (1/1) by slow evaporation of the solvent.

Comment

The study of the titled structure (ethyl 4-((5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl)-4-(2,2-dimethyl -4,6-dioxo-1,3-dioxan-5-yl)but-2-ynoate) was undertaken to establish its three dimensional structure. Geometries are tabulated below. All diagrams and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan).

Experimental

Crystal data

$C_{20}H_{28}O_{10}$
$C_{20}H_{28}O_{10}$
M_r = 428.434
Orthorhombic
$P2_12_12_1$
a = 9.2671 (3)Å
b = 12.7312 (4)Å
c = 18.1005 (5)Å
α = 90.00°
β = 90.00°
γ = 90.00°
V = 2135.52 (11)$Å^3$
Z = 4

D_x = 1.333 Mg m^{-3}
F(000) = 912
Density measured by: not measured
fine-focus sealed tube
Mo $K\alpha$ radiation λ = 0.71073
Cell parameters from 7708 refl.
θ = 0.998—27.485 °
μ = 0.107 mm^{-1}
T = 233 K
Cube
0.4 x 0.2 x 0.16 mm
Colourless
Crystal source: Carreira laboratory

Data collection

KappaCCD CCD diffractometer
Absorption correction: none
4854 measured reflections
4835 independent reflections
4019 observed reflections
Criterion: >2sigma(I)

R_{int} = 0.033
θ_{max} = 27.51 °
h = -12 →12
k = -16 →16
l = -23 →23

Refinement

Refinement on F^2
fullmatrix least squares refinement
R(all) = 0.0661
R(gt) = 0.0487
wR(ref) = 0.1490
wR(gt)= 0.1287
S(ref) = 1.038
4835 reflections
363 parameters
0 restraints

mixed
Calculated weights $1/[\sigma^2(I_o)+(I_o+I_c)^2/900]$
Δ/σ_{max} = 0.028
$\Delta\rho_{max}$ = 0.357eÅ^3
$\Delta\rho_{min}$ = -0.355eÅ^3
Extinction correction: none
Atomic scattering factors from International Tables
Vol C Tables 4.2.6.8 and 6.1.1.4
Flack parameter = 0.4 (10)
Flack H D (1983), *Acta Cryst*. A39, 876-881

Data collection: KappaCCD
Cell refinement: HKL Scalepack (Otwinowski & Minor 1997)
Data reduction: Denzo and Scalepak (Otwinowski & Minor, 1997)
Program(s) used to solve structure: *SIR*97(Cascarano al.,*Acta Cryst*.,1996,A52,C-79)
Program(s) used to refine structure: *SHELXL*-97 (Sheldrick, 1997)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)*

$U_{eq} = 1/3 S_i S_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i.\boldsymbol{a}_j$.

	x	y	z	U_{eq}	Occ
O5	0.9051 (4)	-0.20934 (19)	0.49231 (13)	0.0740 (8)	1
O6	0.7600 (3)	-0.25894 (15)	0.58423 (13)	0.0565 (5)	1
O11	0.72655 (18)	0.09904 (12)	0.70711 (8)	0.0336 (4)	1
O14	0.81807 (19)	0.30542 (13)	0.72868 (9)	0.0347 (4)	1
O17	0.94189 (19)	0.11225 (14)	0.77309 (10)	0.0389 (4)	1
O19	0.6196 (2)	0.25819 (15)	0.80077 (10)	0.0432 (4)	1
O21	0.86975 (18)	0.21116 (14)	0.40103 (9)	0.0374 (4)	1
O23	0.61767 (18)	0.20436 (14)	0.38494 (9)	0.0361 (4)	1
O29	0.48934 (18)	0.11427 (15)	0.46533 (10)	0.0415 (4)	1
O30	0.96873 (17)	0.13986 (15)	0.49926 (10)	0.0389 (4)	1
C1	0.8200 (3)	-0.1891 (2)	0.54003 (13)	0.0429 (6)	1
C2	0.7704 (3)	-0.0833 (2)	0.55586 (14)	0.0414 (6)	1
C3	0.7366 (3)	0.00569 (19)	0.56576 (12)	0.0352 (5)	1
C4	0.6983 (3)	0.11628 (18)	0.57862 (12)	0.0301 (4)	1
C7	0.7981 (5)	-0.3688 (2)	0.5699 (3)	0.0695 (10)	1
C8	0.6836 (5)	-0.4342 (3)	0.5989 (3)	0.0940 (15)	1
C9	0.7181 (4)	0.0586 (2)	0.83375 (15)	0.0485 (7)	1
C10	0.8606 (3)	0.2857 (2)	0.85508 (14)	0.0444 (6)	1
C12	0.7798 (2)	0.15995 (17)	0.64602 (11)	0.0287 (4)	1
C13	0.7513 (3)	0.27498 (18)	0.66067 (12)	0.0337 (5)	1
C15	0.7697 (3)	0.24620 (19)	0.79082 (12)	0.0344 (5)	1
C16	0.7907 (3)	0.12706 (19)	0.77596 (12)	0.0346 (5)	1
C18	0.9891 (4)	0.0067 (2)	0.76110 (17)	0.0505 (7)	1
C20	0.5718 (4)	0.3607 (3)	0.8203 (2)	0.0605 (9)	1
C22	0.7467 (3)	0.2634 (2)	0.36794 (13)	0.0357 (5)	1
C24	0.5972 (2)	0.16290 (18)	0.45244 (12)	0.0311 (5)	1
C25	0.7168 (2)	0.18296 (18)	0.50822 (12)	0.0292 (4)	1
C26	0.8626 (2)	0.17525 (18)	0.47115 (12)	0.0299 (4)	1
C27	0.7376 (3)	0.3762 (2)	0.39346 (16)	0.0417 (6)	1

C28	0.7657 (4)	0.2540 (3)	0.28542 (14)	0.0492 (7)	1
H7A	0.8897	-0.3861	0.5940	0.083	1
H7B	0.8088	-0.3805	0.5166	0.083	1
H8A	0.6759	-0.4237	0.6518	0.141	1
H8B	0.7052	-0.5074	0.5888	0.141	1
H8C	0.5931	-0.4154	0.5755	0.141	1
H10A	0.845 (4)	0.362 (3)	0.864 (3)	0.079 (12)	1
H10B	0.968 (4)	0.267 (3)	0.8469 (17)	0.048 (8)	1
H28A	0.766 (4)	0.175 (3)	0.2707 (18)	0.053 (9)	1
H28B	0.684 (4)	0.288 (3)	0.257 (2)	0.067 (11)	1
H28C	0.861 (4)	0.294 (3)	0.272 (2)	0.064 (10)	1
H20	0.601 (6)	0.380 (4)	0.871 (3)	0.098 (15)	1
H4	0.598 (4)	0.120 (2)	0.5895 (17)	0.044 (8)	1
H9A	0.609 (5)	0.077 (3)	0.832 (2)	0.082 (13)	1
H12	0.886 (3)	0.149 (2)	0.6408 (13)	0.025 (6)	1
H13A	0.643 (3)	0.287 (2)	0.6660 (14)	0.033 (7)	1
H27	0.824 (3)	0.416 (2)	0.3741 (15)	0.034 (7)	1
H9B	0.719 (4)	-0.016 (3)	0.8184 (19)	0.063 (10)	1
H13B	0.794 (3)	0.319 (2)	0.6251 (17)	0.039 (7)	1
H18	0.939 (4)	-0.020 (3)	0.7185 (19)	0.054 (9)	1
H9C	0.768 (4)	0.074 (3)	0.884 (2)	0.067 (11)	1
H27B	0.730 (3)	0.381 (2)	0.4424 (18)	0.037 (7)	1
H10C	0.837 (4)	0.246 (3)	0.903 (2)	0.060 (10)	1
H20B	0.476 (5)	0.356 (4)	0.828 (2)	0.086 (14)	1
H25	0.706 (4)	0.261 (3)	0.5255 (18)	0.055 (9)	1
H20C	0.623 (6)	0.411 (4)	0.785 (3)	0.097 (15)	1
H18B	1.103 (5)	0.013 (3)	0.747 (2)	0.073 (11)	1
H18C	0.970 (5)	-0.034 (3)	0.804 (2)	0.076 (12)	1
H27C	0.656 (4)	0.407 (3)	0.375 (2)	0.067 (11)	1

Table 2. *Anisotropic displacement parameters (Å^2)*

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
O5	0.114 (2)	0.0179 (14)	0.0266 (14)	0.0489 (13)	0.0014 (11)	0.0596 (13)
O6	0.0687 (13)	0.0010 (9)	0.0097 (12)	0.0272 (9)	0.0037 (9)	0.0738 (13)
O11	0.0435 (9)	-0.0065 (7)	0.0038 (7)	0.0290 (8)	0.0014 (6)	0.0282 (7)
O14	0.0436 (9)	-0.0055 (7)	-0.0008 (7)	0.0276 (8)	-0.0015 (6)	0.0328 (7)
O17	0.0436 (9)	0.0064 (7)	0.0001 (7)	0.0344 (9)	0.0032 (7)	0.0387 (8)
O19	0.0391 (9)	-0.0011 (8)	0.0060 (8)	0.0424 (10)	-0.0131 (8)	0.0482 (9)
O21	0.0324 (8)	0.0031 (7)	0.0048 (7)	0.0415 (10)	0.0084 (7)	0.0384 (8)
O23	0.0357 (8)	-0.0044 (7)	-0.0041 (7)	0.0398 (9)	0.0043 (7)	0.0327 (7)
O29	0.0330 (9)	-0.0088 (7)	-0.0034 (7)	0.0456 (10)	0.0045 (8)	0.0460 (10)
O30	0.0313 (8)	0.0018 (7)	-0.0040 (7)	0.0408 (10)	0.0036 (7)	0.0447 (9)
C1	0.0611 (16)	0.0035 (11)	-0.0112 (12)	0.0321 (13)	-0.0015 (10)	0.0356 (11)
C2	0.0558 (15)	-0.0036 (11)	-0.0060 (11)	0.0305 (12)	-0.0008 (9)	0.0378 (12)
C3	0.0450 (13)	-0.0055 (10)	-0.0041 (10)	0.0290 (11)	0.0009 (8)	0.0314 (10)
C4	0.0326 (11)	-0.0010 (9)	0.0015 (9)	0.0263 (11)	0.0025 (8)	0.0314 (10)
C7	0.075 (2)	0.0058 (15)	0.002 (2)	0.0292 (15)	0.0002 (16)	0.104 (3)
C8	0.091 (3)	-0.0065 (19)	-0.004 (3)	0.0379 (19)	0.007 (2)	0.153 (5)
C9	0.0685 (19)	-0.0066 (14)	0.0125 (13)	0.0408 (15)	0.0045 (11)	0.0362 (12)
C10	0.0542 (16)	-0.0055 (13)	-0.0051 (11)	0.0423 (15)	-0.0037 (11)	0.0368 (11)
C12	0.0351 (11)	-0.0008 (9)	0.0013 (8)	0.0250 (10)	0.0022 (8)	0.0261 (9)
C13	0.0451 (13)	-0.0005 (10)	-0.0019 (10)	0.0253 (11)	-0.0003 (8)	0.0306 (10)
C15	0.0393 (12)	-0.0012 (9)	0.0024 (9)	0.0322 (11)	-0.0023 (9)	0.0318 (10)
C16	0.0409 (12)	-0.0028 (10)	0.0027 (9)	0.0333 (11)	0.0012 (9)	0.0297 (10)
C18	0.0612 (18)	0.0158 (14)	0.0049 (14)	0.0402 (15)	0.0064 (13)	0.0502 (15)
C20	0.0523 (18)	0.0122 (15)	0.0021 (16)	0.055 (2)	-0.0261 (18)	0.074 (2)
C22	0.0333 (11)	-0.0009 (10)	0.0008 (9)	0.0394 (12)	0.0093 (9)	0.0345 (11)
C24	0.0311 (11)	0.0023 (9)	-0.0006 (9)	0.0272 (11)	-0.0006 (9)	0.0350 (10)
C25	0.0299 (10)	-0.0012 (8)	-0.0012 (8)	0.0276 (11)	0.0007 (8)	0.0301 (9)

C26	0.0310 (10)	-0.0025 (8)	-0.0016 (9)	0.0260 (10)	0.0026 (8)	0.0328 (9)
C27	0.0438 (14)	0.0002 (11)	0.0018 (12)	0.0354 (13)	0.0098 (11)	0.0459 (14)
C28	0.0595 (17)	0.0020 (14)	0.0036 (12)	0.0553 (17)	0.0061 (11)	0.0326 (12)

Table 3 . *Geometric parameters (Å, °)*

O5—C1	1.198 (4)	C25—C26	1.511 (3)
O6—C1	1.319 (4)	C4—H4	0.95 (3)
O6—C7	1.465 (4)	C7—H7A	0.9800
O11—C16	1.426 (3)	C7—H7B	0.9800
O11—C12	1.438 (3)	C8—H8A	0.9700
O14—C15	1.426 (3)	C8—H8B	0.9700
O14—C13	1.431 (3)	C8—H8C	0.9700
O17—C16	1.415 (3)	C9—H9A	1.03 (5)
O17—C18	1.429 (3)	C9—H9B	0.99 (4)
O19—C15	1.412 (3)	C9—H9C	1.04 (4)
O19—C20	1.423 (4)	C10—H10A	0.99 (4)
O21—C26	1.351 (3)	C10—H10B	1.04 (3)
O21—C22	1.449 (3)	C10—H10C	1.03 (4)
O23—C24	1.344 (3)	C12—H12	1.00 (3)
O23—C22	1.446 (3)	C13—H13A	1.02 (3)
O29—C24	1.198 (3)	C13—H13B	0.94 (3)
O30—C26	1.196 (3)	C18—H18	0.96 (4)
C1—C2	1.452 (4)	C18—H18B	1.08 (5)
C2—C3	1.189 (4)	C18—H18C	0.94 (4)
C3—C4	1.470 (3)	C20—H20	0.99 (5)
C4—C12	1.539 (3)	C20—H20B	0.90 (5)
C4—C25	1.541 (3)	C20—H20C	1.02 (5)
C7—C8	1.447 (6)	C25—H25	1.04 (4)
C9—C16	1.518 (3)	C27—H27	1.01 (3)
C10—C15	1.521 (3)	C27—H27B	0.89 (3)
C12—C13	1.511 (3)	C27—H27C	0.92 (4)
C15—C16	1.553 (3)	C28—H28A	1.04 (4)
C22—C27	1.511 (4)	C28—H28B	1.02 (4)
C22—C28	1.509 (3)	C28—H28C	1.05 (4)
C24—C25	1.521 (3)		
C1—O6—C7	115.7 (3)	O19—C15—C16	104.5 (2)
C16—O11—C12	113.22 (17)	O14—C15—C16	109.91 (18)
C15—O14—C13	113.54 (17)	C10—C15—C16	112.7 (2)
C16—O17—C18	115.7 (2)	O17—C16—O11	110.32 (19)
C15—O19—C20	115.9 (2)	O17—C16—C9	112.8 (2)
C26—O21—C22	120.32 (18)	O11—C16—C9	105.9 (2)
C24—O23—C22	120.97 (17)	O17—C16—C15	105.09 (19)
O5—C1—O6	124.8 (3)	O11—C16—C15	110.11 (19)
O5—C1—C2	123.4 (3)	C9—C16—C15	112.7 (2)
O6—C1—C2	111.8 (2)	O23—C22—O21	108.93 (17)
C3—C2—C1	175.7 (3)	O23—C22—C27	112.5 (2)
C2—C3—C4	178.6 (3)	O21—C22—C27	110.7 (2)
C3—C4—C12	110.68 (19)	O23—C22—C28	105.4 (2)
C3—C4—C25	111.70 (18)	O21—C22—C28	106.3 (2)
C12—C4—C25	113.70 (18)	C27—C22—C28	112.6 (2)
O6—C7—C8	108.0 (3)	O29—C24—O23	119.8 (2)
O11—C12—C13	109.13 (18)	O29—C24—C25	124.4 (2)
O11—C12—C4	104.28 (17)	O23—C24—C25	115.73 (18)
C13—C12—C4	113.81 (19)	C26—C25—C24	110.24 (17)
O14—C13—C12	109.75 (19)	C26—C25—C4	115.53 (18)
O19—C15—O14	110.7 (2)	C24—C25—C4	112.04 (18)
O19—C15—C10	114.3 (2)	O30—C26—O21	119.1 (2)
O14—C15—C10	104.7 (2)	O30—C26—C25	124.81 (19)

O21—C26—C25	116.06 (18)
C3—C4—H4	108.5 (19)
C12—C4—H4	107.2 (19)
C25—C4—H4	104.6 (18)
O6—C7—H7A	110.1
C8—C7—H7A	110.1
O6—C7—H7B	110.1
C8—C7—H7B	110.1
H7A—C7—H7B	108.4
C7—C8—H8A	109.5
C7—C8—H8B	109.5
H8A—C8—H8B	109.5
C7—C8—H8C	109.5
H8A—C8—H8C	109.5
H8B—C8—H8C	109.5
C16—C9—H9A	106 (2)
C16—C9—H9B	111 (2)
H9A—C9—H9B	102 (3)
C16—C9—H9C	107 (2)
H9A—C9—H9C	115 (3)
H9B—C9—H9C	115 (3)
C15—C10—H10A	112 (3)
C15—C10—H10B	110.4 (18)
H10A—C10—H10B	113 (3)
C15—C10—H10C	111 (2)
H10A—C10—H10C	108 (3)
H10B—C10—H10C	102 (3)
O11—C12—H12	109.8 (15)
C13—C12—H12	108.7 (15)
C4—C12—H12	111.1 (14)
O14—C13—H13A	107.6 (15)
C12—C13—H13A	109.7 (17)
O14—C13—H13B	104.3 (18)
C12—C13—H13B	112.4 (18)
H13A—C13—H13B	113 (2)
O17—C18—H18	108 (2)
O17—C18—H18B	105 (2)
H18—C18—H18B	108 (3)
O17—C18—H18C	109 (3)
H18—C18—H18C	112 (3)
H18B—C18—H18C	114 (3)
O19—C20—H20	112 (3)
O19—C20—H20B	106 (3)
H20—C20—H20B	99 (4)
O19—C20—H20C	106 (3)
H20—C20—H20C	107 (4)
H20B—C20—H20C	126 (4)
C26—C25—H25	106 (2)
C24—C25—H25	106.8 (19)
C4—C25—H25	105.3 (19)
C22—C27—H27	109.4 (16)
C22—C27—H27B	111.9 (19)
H27—C27—H27B	112 (3)
C22—C27—H27C	110 (3)
H27—C27—H27C	108 (3)
H27B—C27—H27C	106 (3)
C22—C28—H28A	109.4 (18)
C22—C28—H28B	113 (2)
H28A—C28—H28B	107 (3)
C22—C28—H28C	107 (2)
H28A—C28—H28C	114 (3)
H28B—C28—H28C	107 (3)

C7—O6—C1—O5	-2.9 (5)
C7—O6—C1—C2	177.0 (3)
O5—C1—C2—C3	-10 (4)
O6—C1—C2—C3	170 (4)
C1—C2—C3—C4	-58 (13)
C2—C3—C4—C12	-34 (11)
C2—C3—C4—C25	93 (11)
C1—O6—C7—C8	-156.0 (4)
C16—O11—C12—C13	-58.6 (2)
C16—O11—C12—C4	179.45 (18)
C3—C4—C12—O11	-63.9 (2)
C25—C4—C12—O11	169.43 (18)
C3—C4—C12—C13	177.30 (19)
C25—C4—C12—C13	50.6 (3)
C15—O14—C13—C12	-58.3 (3)
O11—C12—C13—O14	57.5 (2)
C4—C12—C13—O14	173.48 (18)
C20—O19—C15—O14	-65.7 (3)
C20—O19—C15—C10	52.3 (3)
C20—O19—C15—C16	176.0 (2)
C13—O14—C15—O19	-60.0 (2)
C13—O14—C15—C10	176.3 (2)
C13—O14—C15—C16	54.9 (3)
C18—O17—C16—O11	-62.4 (3)
C18—O17—C16—C9	55.8 (3)
C18—O17—C16—C15	178.91 (19)
C12—O11—C16—O17	-59.8 (2)
C12—O11—C16—C9	177.8 (2)
C12—O11—C16—C15	55.7 (2)
O19—C15—C16—O17	-174.44 (18)
O14—C15—C16—O17	66.8 (2)
C10—C15—C16—O17	-49.7 (3)
O19—C15—C16—O11	66.8 (2)
O14—C15—C16—O11	-52.0 (2)
C10—C15—C16—O11	-168.5 (2)
O19—C15—C16—C9	-51.2 (3)
O14—C15—C16—C9	-170.0 (2)
C10—C15—C16—C9	73.5 (3)
C24—O23—C22—O21	41.1 (3)
C24—O23—C22—C27	-82.1 (3)
C24—O23—C22—C28	154.9 (2)
C26—O21—C22—O23	-44.7 (3)
C26—O21—C22—C27	79.5 (3)
C26—O21—C22—C28	-157.8 (2)
C22—O23—C24—O29	180.0 (2)
C22—O23—C24—C25	0.3 (3)
O29—C24—C25—C26	141.1 (2)
O23—C24—C25—C26	-39.2 (3)
O29—C24—C25—C4	11.0 (3)
O23—C24—C25—C4	-169.40 (19)
C3—C4—C25—C26	-52.8 (3)
C12—C4—C25—C26	73.4 (2)
C3—C4—C25—C24	74.6 (2)
C12—C4—C25—C24	-159.25 (19)
C22—O21—C26—O30	-174.2 (2)
C22—O21—C26—C25	6.1 (3)

C24—C25—C26—O30	-143.8 (2)	C24—C25—C26—O21	35.9 (3)
C4—C25—C26—O30	-15.5 (3)	C4—C25—C26—O21	164.15 (19)

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