



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 atmosphere 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 N₂ at 300° over night; solvent drying system) under an argon atmosphere (H₂O 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.

¹H-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). ¹³C-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 (ν, 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. Optical rotation [α]_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.

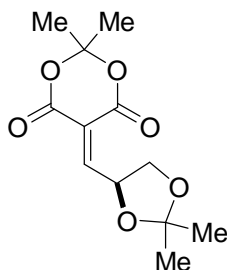
High resolution mass spectrometric measurements were performed by the mass spectrometry service of the Laboratorium für Organische Chemie at the ETH Zürich. EI measurements were performed on a VG Tribrid spectrometer, 70 eV. ESI measurements were performed on a TSQ 7000.

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 μ L, 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 SiO₂) providing 1.30 g (5.0 mmol, 61%) of **6a** as white solid.

mp: 59 – 60 °C

[α]_D²¹ +114 (*c* = 1.25, CHCl₃)

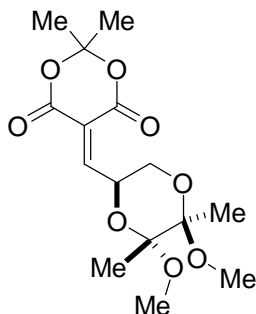
¹H NMR (300 MHz, CDCl₃): δ 7.94 (d, *J* = 6.3, 1 H), 5.54 (dt, *J* = 7.2, 6.3, 1 H) 4.56–4.51, 3.79–3.74 (ABX, 2 H) 1.76 (s, 3 H), 1.75 (s, 3 H), 1.50 (s, 3 H), 1.42 (s, 3 H)

¹³C NMR (75 MHz, CDCl₃): 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 (CHCl₃): 2990 (m), 1737 (s), 1634 (m), 1382 (m), 1283 (m), 1218 (m), 1153 (w), 1059 (m), 1020 (m)

HRMS: (HR-EI, positive): Calcd. for C₁₁H₁₃O₆⁺ ([M-CH₃]⁺) 241.0707, found 241.0705

5-(((2*S*,5*R*,6*R*)-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 (2*R*,5*R*,6*R*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane-2-carbaldehyde (3.57 g, 17.5 mmol). After chromatography, the residue was crystallized from Hexane/CH₂Cl₂ (9/1) to give 2.90 g (8.78 mmol, 50%) of **6b** as white solid.

mp: 99–100 °C

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

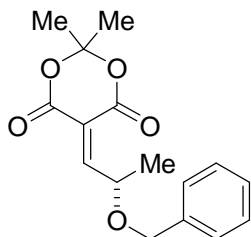
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.80 (d, $J = 6.9$, 1 H), 5.55 (m, 1 H), 3.77–3.59 (ABX, 2 H), 3.28 (s, 6 H), 1.75 (s, 3 H), 1.74 (s, 3 H), 1.32 (s, 6 H)

$^{13}\text{C NMR}$ (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 $\text{C}_{15}\text{H}_{22}\text{O}_8\text{Na}^+$ ($[\text{M}+\text{Na}]^+$) 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.

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

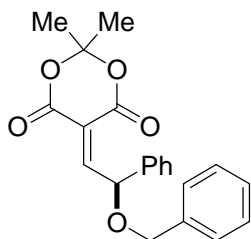
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.85 (d, $J = 7.8$, 1 H), 7.36 – 7.26 (m, 5 H), 5.23 (qd, $J = 7.8, 6.6$, 1 H), 4.53 (AB, 2 H), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.43 (d, $J = 6.3$, 3 H)

$^{13}\text{C NMR}$ (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 $\text{C}_{13}\text{H}_{12}\text{O}_4^+$ ($[\text{M}-\text{CH}_3\text{COCH}_3]^+$) 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.

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

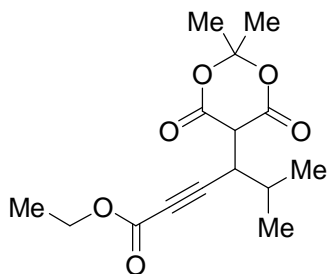
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.91 (d, $J = 8.7$, 1 H), 7.59 – 7.56 (m, 2 H), 7.41 – 7.25 (m, 8 H), 6.26 (d, $J = 9.0$, 1 H), 4.41 (AB, 2 H), 1.73 (s, 3 H), 1.62 (s, 3 H)

$^{13}\text{C NMR}$ (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 $\text{C}_{18}\text{H}_{14}\text{O}_4^+$ ($[\text{M}-\text{CH}_3\text{COCH}_3]^+$) 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 $\text{Cu}(\text{OAc})_2$ (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°C

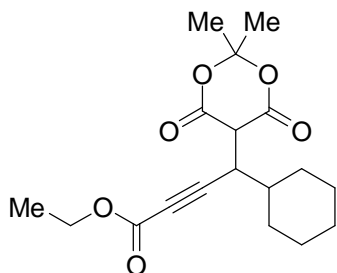
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 4.17 (q, $J = 7.2$, 2 H), 3.75 (d, $J = 2.7$, 1 H), 3.23 (dd, $J = 10.5$, 2.7, 1 H), 2.47 (m, 1 H), 1.80 (s, 3 H), 1.78 (s, 3 H), 1.27 (t, $J = 7.2$, 3 H), 1.18 (d, $J = 5.1$, 3 H), 0.97 (d, $J = 6.6$, 3 H)

$^{13}\text{C NMR}$ (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 (CHCl₃): 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 C₁₅H₁₉O₆⁻ ([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 °C

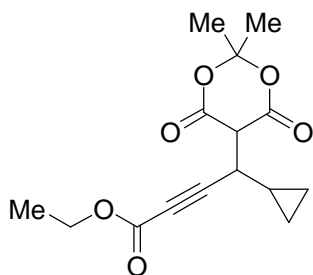
¹H NMR (300 MHz, CDCl₃): δ 4.18 (q, *J* = 6.9, 2 H), 3.78 (d, *J* = 2.4, 1 H), 3.29 (dd, *J* = 10.5, 2.7, 1 H), 2.26 – 2.05 (m, 2 H), 1.80 (s, 3 H), 1.78 (s, 3 H), 1.80 – 1.60 (m, 4 H), 1.27 (t, *J* = 7.2, 3 H), 1.33 – 0.88 (m, 5 H)

¹³C NMR (75 MHz, CDCl₃): 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 (CHCl₃): 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 C₁₈H₂₃O₆⁻ ([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 °C

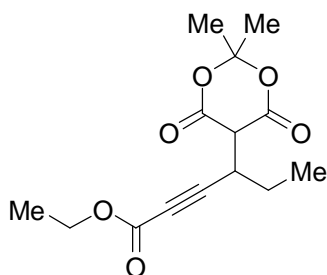
¹H NMR (300 MHz, CDCl₃): δ 4.21 (q, *J* = 7.2, 2 H), 3.78 (d, *J* = 2.4, 1 H), 2.91 (dd, *J* = 9.5, 2.4, 1 H), 1.81 (s, 6 H), 1.58 (m, 1 H), 1.29 (t, *J* = 6.9, 3 H), 0.75 – 0.31 (m, 4 H)

¹³C NMR (75 MHz, CDCl₃): 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 (CHCl₃): 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 C₁₈H₂₃O₆⁻ ([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.

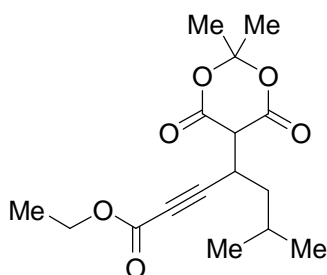
¹H NMR (300 MHz, CDCl₃): δ 4.20 (q, *J* = 7.2, 2 H), 3.75 (d, *J* = 2.4, 1 H), 3.48 (m, 1 H), 2.03 (m, 1 H), 1.79 (s, 6 H), 1.66 (m, 1 H), 1.29 (t, *J* = 6.9, 3 H), 1.11 (t, *J* = 7.5, 3 H)

¹³C NMR (75 MHz, CDCl₃): 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 C₁₄H₁₇O₆⁻ ([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 °C

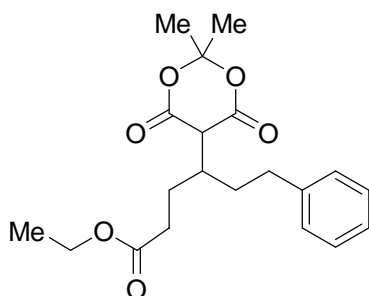
¹H NMR (300 MHz, CDCl₃): δ 4.17 (q, *J* = 7.2, 2 H), 3.78 (d, *J* = 2.7, 1 H), 3.64 (m, 1 H), 2.03 (m, 1 H), 1.88 – 1.72 (m, 1 H), 1.79 (s, 3 H), 1.77 (s, 3 H), 1.28 (t, *J* = 6.9, 3 H), 1.27 – 1.18 (m, 1 H), 0.95 (d, *J* = 6.3, 3 H), 0.94 (d, *J* = 6.6, 3 H)

¹³C NMR (75 MHz, CDCl₃): 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 (CHCl₃): 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 C₁₆H₂₁O₆⁻ ([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 SiO₂) to afford 55 mg (0.15 mmol, 61%) of **5f** as clear oil.

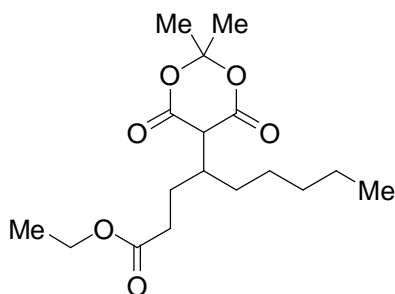
¹H NMR (300 MHz, CDCl₃): δ 7.30 – 7.15 (m, 5 H), 4.12 (q, *J* = 7.2, 2 H), 3.62 (d, *J* = 2.4, 1 H), 2.82 – 2.35 (m, 4 H), 2.01 – 1.86 (m, 4 H), 1.81 (s, 3 H), 1.72 (s, 3 H), 1.25 (t, *J* = 7.2, 3 H)

¹³C NMR (75 MHz, CDCl₃): 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 C₂₀H₂₆O₆Na⁺ ([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 SiO₂) to afford 61 mg (0.19 mmol, 74%) of **5g** as clear oil.

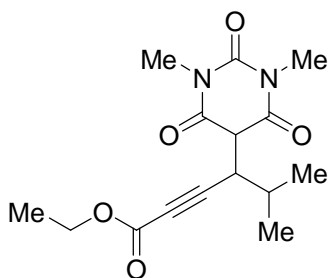
¹H NMR (300 MHz, CDCl₃): δ 4.10 (q, *J* = 7.2, 2 H), 3.62 (d, *J* = 2.7, 1 H), 2.50 – 2.30 (m, 3 H), 1.94 – 1.82 (m, 2 H), 1.75 (s, 3 H), 1.73 (s, 3 H), 1.60 – 1.20 (m, 8 H), 1.23 (t, *J* = 7.2, 3 H), 0.87 (m, 3 H)

¹³C NMR (75 MHz, CDCl₃): 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 C₁₇H₂₇O₆[−] ([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

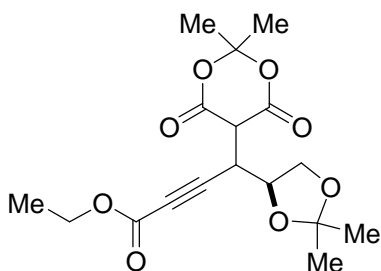
¹H NMR (300 MHz, CDCl₃): δ 5.40 (d, *J* = 1.8, 1 H), 4.19 (q, *J* = 7.2, 2 H), 4.09 (dd, *J* = 2.8, 1.8, 1 H), 3.47 (s, 3 H), 3.32 (s, 3 H), 2.29 (m, 1 H), 1.30 (t, *J* = 7.1, 3 H), 1.01 (d, *J* = 7.1, 3 H), 0.97 (d, *J* = 6.9, 3 H)

¹³C NMR (75 MHz, CDCl₃): 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 (CHCl₃): 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 C₁₅H₁₉N₂O₅[−] ([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 $\text{Cu}(\text{OAc})_2$ (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°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°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 $^\circ\text{C}$

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

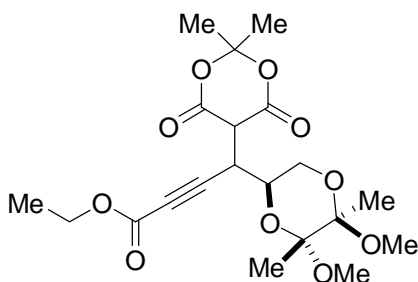
^1H NMR (300 MHz, CDCl_3): δ 4.66 (q, J = 6.6, 1 H), 4.20 (q, J = 7.2, 2 H), 4.09 (m, 2 H), 3.90 (dd, J = 6.8, 3.2, 1 H), 3.79 (d, J = 3.3, 1 H), 1.79 (s, 6 H), 1.43 (s, 3 H), 1.34 (s, 3 H), 1.28 (t, J = 7.2, 3 H)

^{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 $\text{C}_{17}\text{H}_{21}\text{O}_8^-$ ($[\text{M}-\text{H}]^-$) 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 °C

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

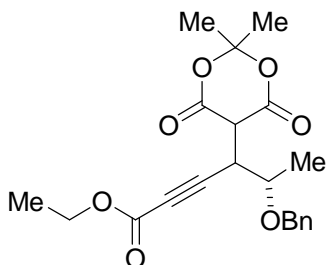
^1H NMR (300 MHz, CDCl_3): δ 4.41 (m, 1 H), 4.19 (q, $J = 7.2$, 2 H), 4.03 (dd, $J = 8.4$, 2.1, 1 H), 3.85 – 3.75 (m, 2 H), 3.58 – 3.53 (m, 1 H), 3.25 (s, 3 H), 3.22 (s, 3 H), 1.78 (s, 6 H), 1.27 (t, $J = 7.5$, 3 H), 1.24 (s, 6 H)

^{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 $\text{C}_{20}\text{H}_{27}\text{O}_{10}^-$ ($[\text{M}-\text{H}]^-$) 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°C for 24 h, 65 mg (0.17 mmol, 67%) of **7c** was obtained as yellow oil.

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

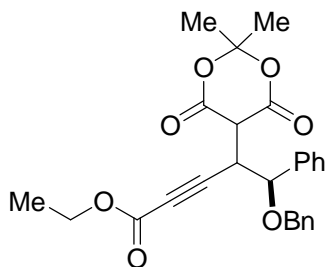
^1H NMR (300 MHz, CDCl_3): δ 7.35 – 7.26 (m, 5 H), 4.58 (AB, 2 H), 4.21 (q, $J = 7.2$, 2 H), 4.21 – 4.16 (m, 1 H), 3.90 (dd, $J = 7.2$, 3.3, 1 H), 3.82 (d, $J = 3.5$, 1 H), 1.75 (s, 3 H), 1.70 (s, 3 H), 1.35 (d, $J = 6.2$, 3 H), 1.29 (t, $J = 7.1$, 3 H)

^{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 $\text{C}_{21}\text{H}_{23}\text{O}_7^-$ ($[\text{M}-\text{H}]^-$) 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)

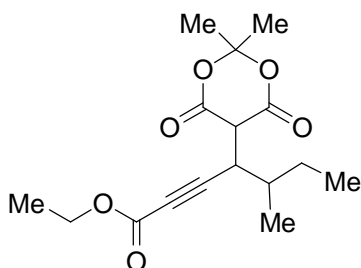
^1H NMR (300 MHz, CDCl_3): δ 7.42 – 7.26 (m, 10 H), 5.17 (d, $J = 10.2$, 1 H), 4.45 (AB, 2 H), 4.23 (q, $J = 7.2$, 2 H), 3.90 (dd, $J = 9.6$, 2.7, 1 H), 3.06 (d, $J = 2.4$, 1 H), 1.72 (s, 3 H), 1.47 (s, 3 H), 1.30 (t, $J = 6.9$, 3 H)

^{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 $\text{C}_{26}\text{H}_{25}\text{O}_7^-$ ($[\text{M}-\text{H}]^-$) 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.

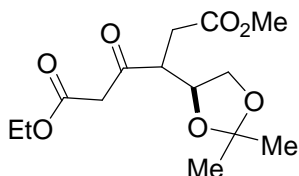
^1H NMR (300 MHz, CDCl_3): δ 4.17 (q, $J = 7.2$, 2 H), 3.76 (d, $J = 1.8$, 1 H), 3.33 (d, $J = 9.9$, 2.1, 1 H of one diastereomer), 3.30 (dd, $J = 10.8$, 2.1, 1 H of the other diastereomer), 2.30 – 2.20 (m, 1 H), 1.93 – 1.83 (m, 1 H of one diastereomer), 1.79 (s, 3 H), 1.78 (s, 3 H), 1.50 – 1.42 (m, 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 μ L, 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 $-78^\circ C$. To the cold solution was added dropwise triethylamine (40 μ L), 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, $CHCl_3$)

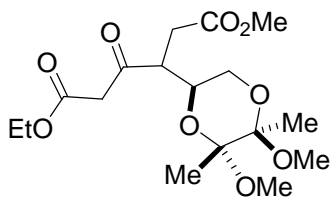
1H NMR (300 MHz, $CDCl_3$): δ 4.16 (q, J = 7.2, 2 H), 4.14 – 4.09 (m, 1 H), 4.04 – 3.98, 3.68 – 3.63 (ABX, 2 H), 3.70 (s, 2 H), 3.65 (s, 3 H), 3.30 (m, 1 H), 2.86 – 2.77, 2.34 – 2.27 (ABX, 2 H), 1.43 (s, 3 H), 1.31 (s, 3 H), 1.27 (t, J = 6.9, 3 H)

^{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.

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

^1H 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)

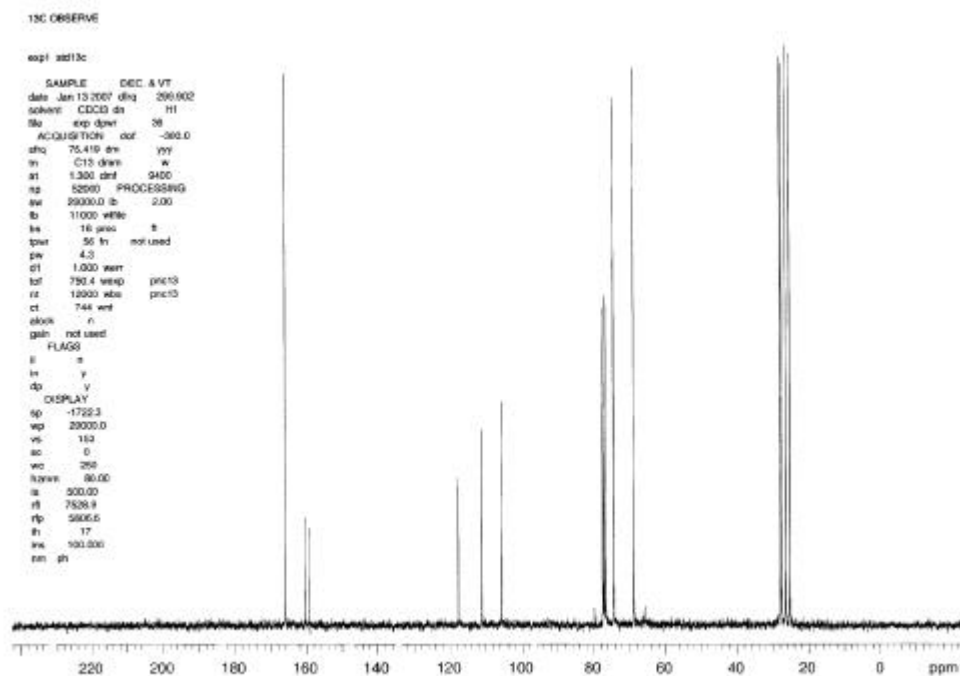
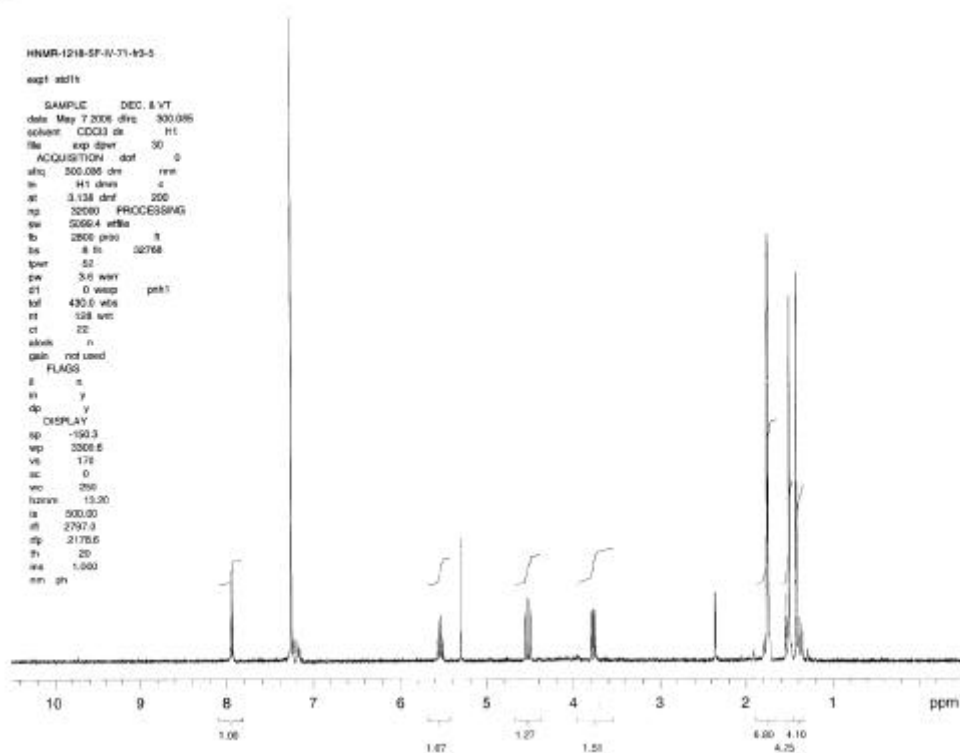
^{13}C NMR (75 MHz, CDCl_3): δ 204.7, 171.4, 166.8, 99.2, 98.1, 69.4, 61.5, 61.0, 52.3, 52.1, 48.2, 48.1, 48.0, 32.4, 17.6, 17.5, 14.2

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 $\text{C}_{14}\text{H}_{22}\text{O}_7\text{Na}^+$ ($[\text{M}+\text{Na}]^+$) 399.1626, found 399.1633

NMR Spectra of New Compounds

Me Me

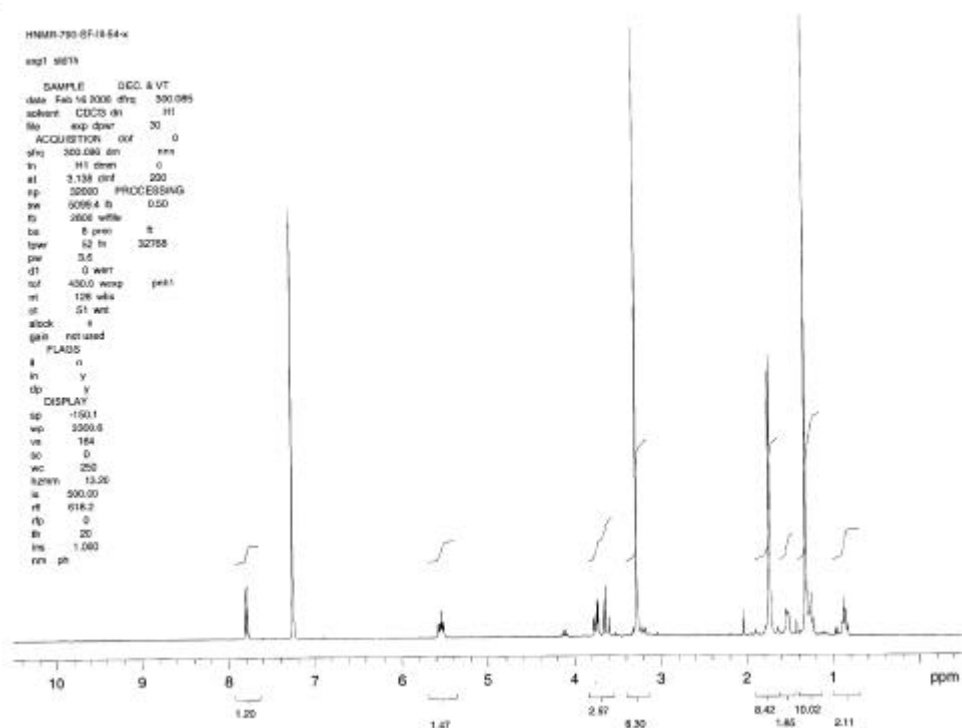


Me Me

HNMR-750-SF-18-64-x

exp1 9819

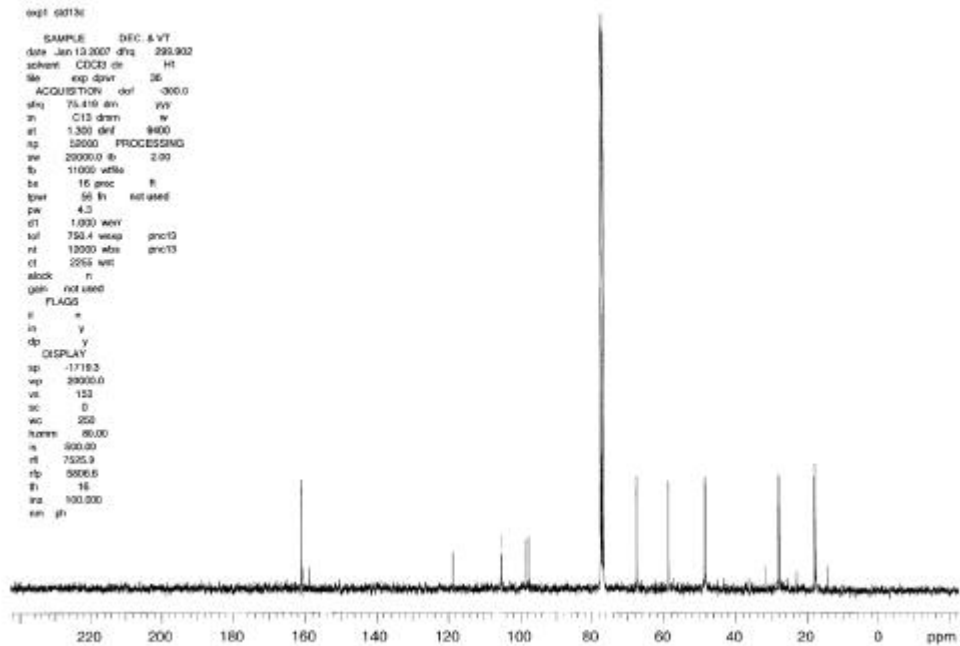
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solvent CDCl3 d1 H1
file exp dprvt 30
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sfreq 300.080 dm nns
in H1 dnm 0
at 3.138 dnf 200
ap 30000 PROCESSING
re 5000.4 ft 0.50
fs 3000 vella
bs 8 proc ft
tprv 52 ft 32758
pw 3.0
dt 0 wvt
ntf 430.0 wvnp pelt
nt 128 wla
ot 51 wvt
alock n
gain not used
f FLAGG
n
in y
dp y
DISPLAY
sp -150.1
wp 3000.0
vn 164
sc 0
wc 250
hnm 13.20
n 500.00
nt 616.2
dp 0
ft 20
ins 1.000
nm ph



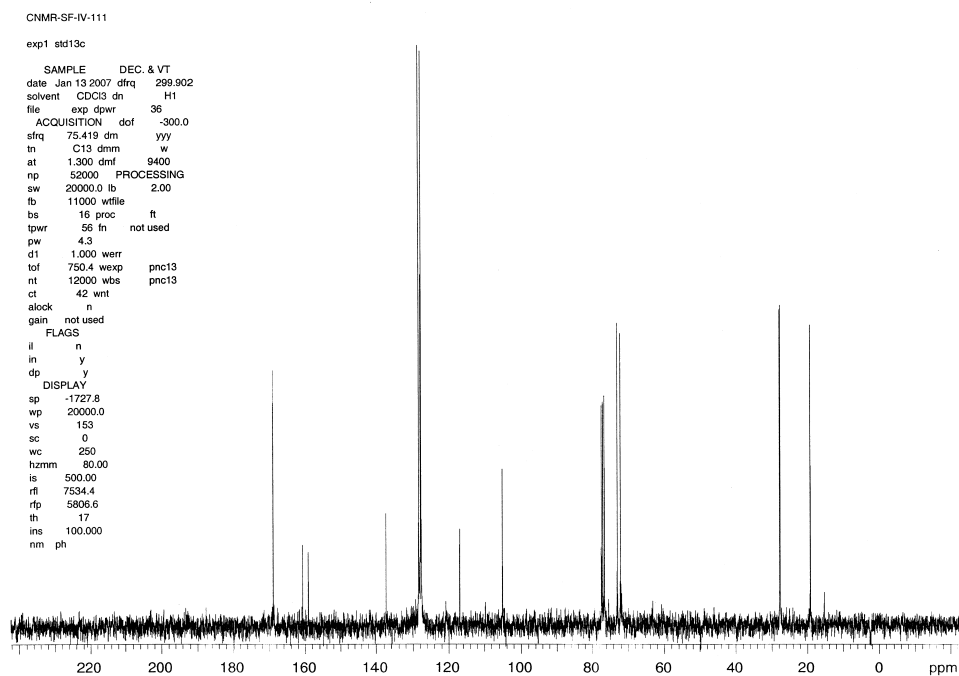
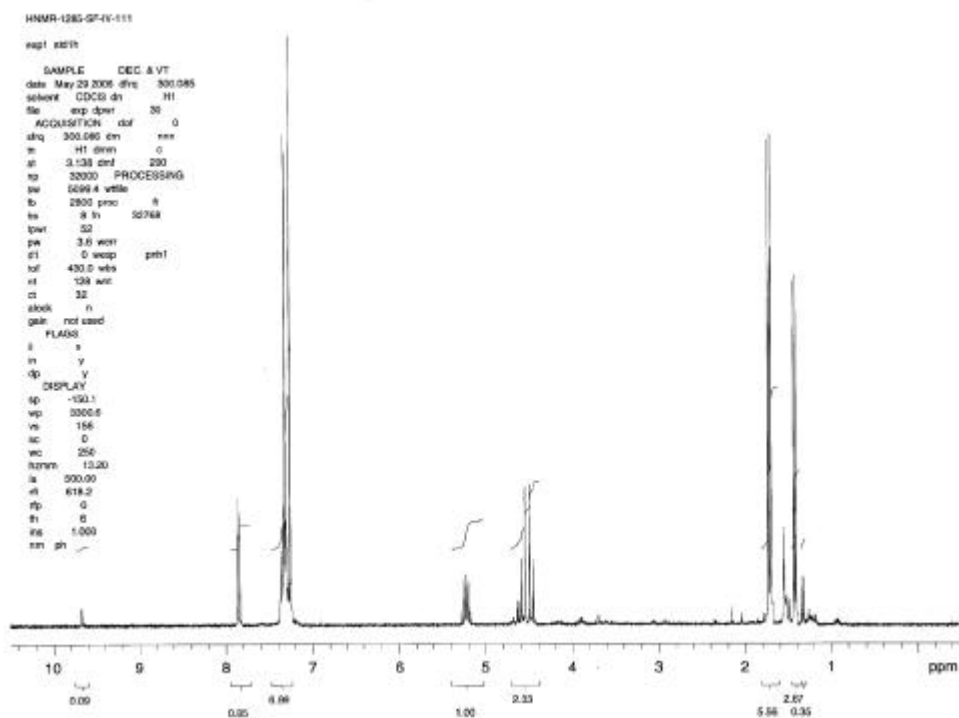
CNMR-SF-18-76

exp1 9813c

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solvent CDCl3 d1 H1
file exp dprvt 30
ACQUISITION d1 -300.0
sfreq 75.410 dm vvv
in C13 dnm w
at 1.300 dnf 9400
ap 50000 PROCESSING
re 20000.0 ft 2.00
fs 11000 vella
bs 16 proc ft
tprv 56 ft not used
pw 4.3
dt 1.000 wvt
ntf 750.4 wvnp pnc13
nt 10000 wla pnc13
ot 2556 wvt
alock n
gain not used
f FLAGG
n
in y
dp y
DISPLAY
sp -1718.3
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sc 0
wc 250
hnm 80.00
n 500.00
nt 7525.9
dp 5000.0
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ins 100.000
nm ph



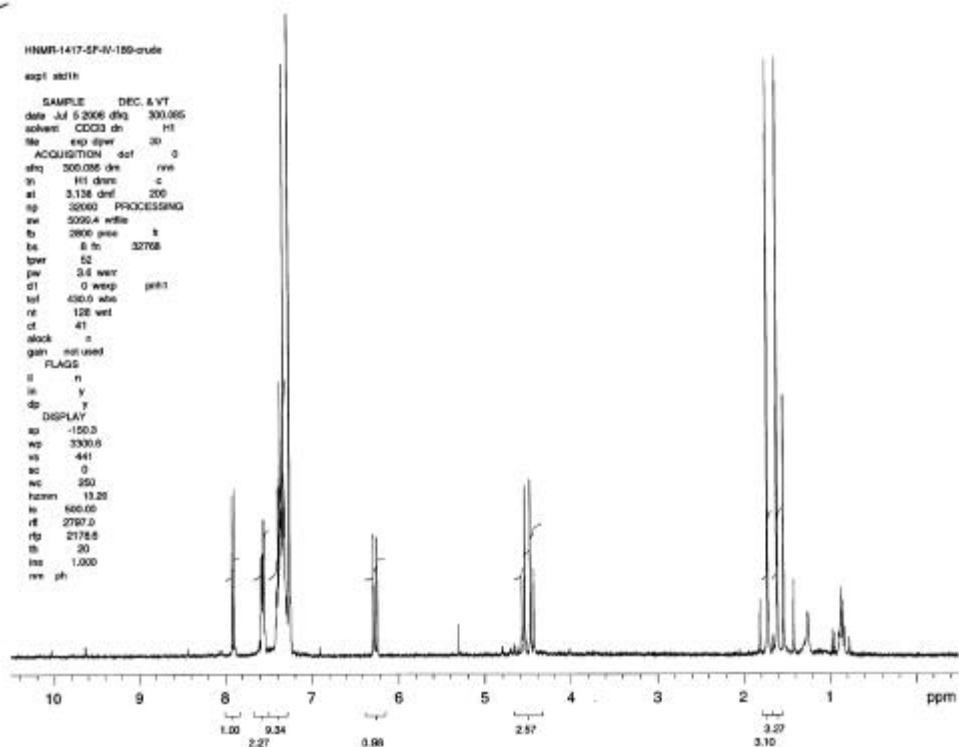
Me Me



HNMR-1417-SF-IV-189-crude

exp1 sdt1h

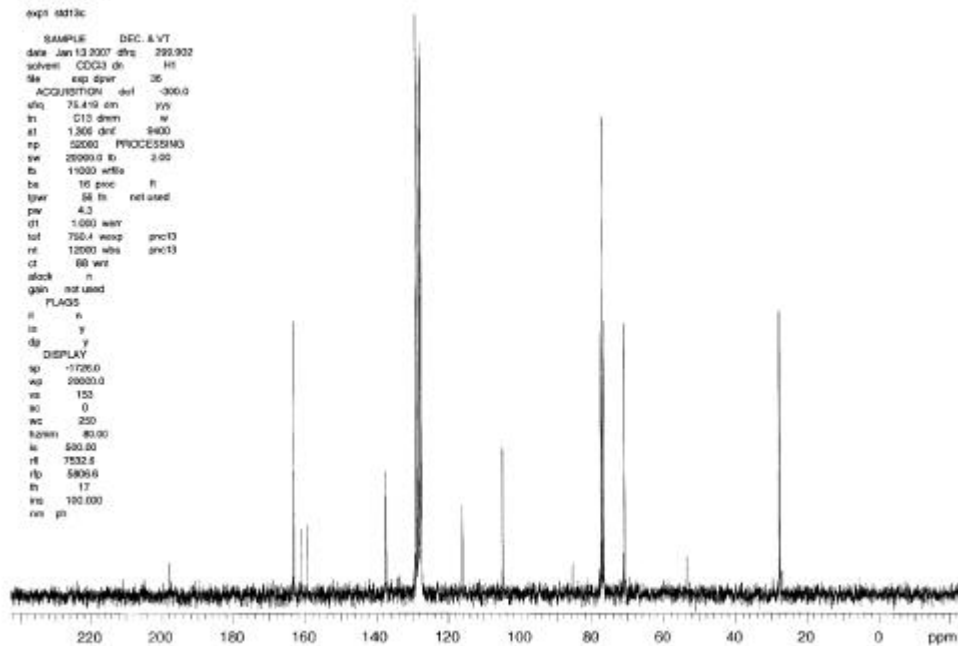
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date Jul 5 2006 dth 300.085
solvent CDCl3 dth H1
file exp dth 30
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dth 300.085 dth rve
in H1 dth z
at 3.138 dth 200
rp 32000 PROCESSING
sw 5000.4 vfile s
fs 2800 gms s
fs 8 fs 32708
tpr 52
pw 3.6 wsr
dt 0 wsr pnt
td 430.0 wsr
re 128 wsr
ct 41
stack n
gain not used
FLAGS
n y
n y
n y
DISPLAY
sp -150.0
wp 3300.0
vs 441
sc 0
wc 250
hznm 13.20
is 600.00
rf 2797.0
rp 2175.5
fs 30
is 1.000
re ph



CNMR-SF-IV-187

exp1 sdt1c

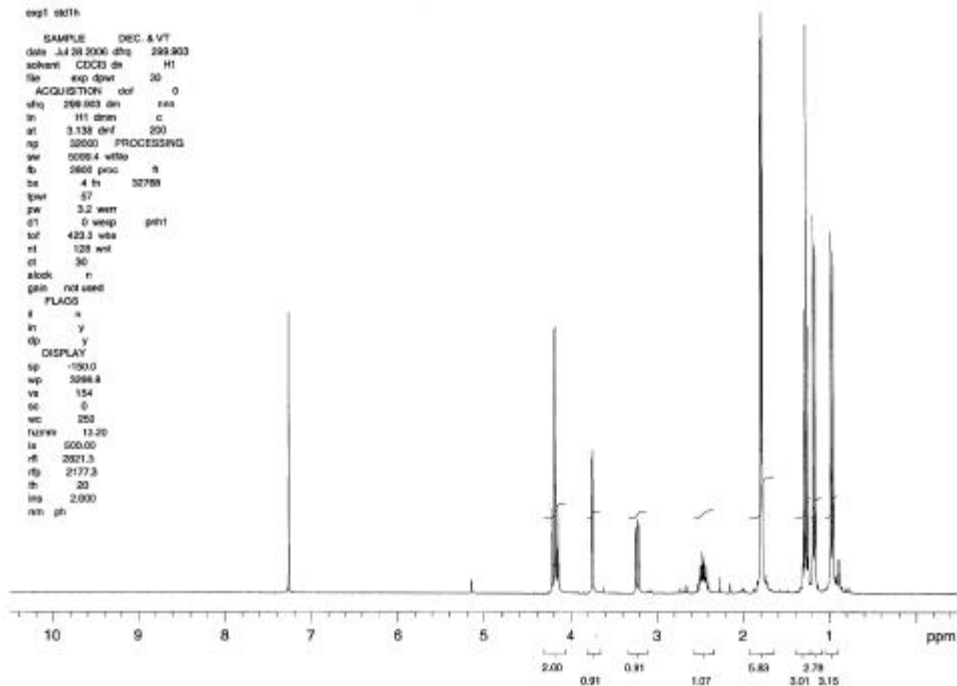
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date Jan 13 2007 dth 299.902
solvent CDCl3 dth H1
file exp dth 35
ACQUISITION dth -300.0
dth 299.902 dth rve
in C13 dth w
at 1.366 dth 9400
rp 32000 PROCESSING
sw 25000.0 fs 2.00
fs 10000 vfile s
fs 10 pnt fs
tpr 56 fs not used
pw 4.3
dt 1.000 wsr pnt
td 750.4 wsr pnt
re 12000 wsr pnt
ct 60 wsr
stack n
gain not used
FLAGS
n y
n y
n y
DISPLAY
sp -1726.0
wp 20000.0
vs 152
sc 0
wc 250
hznm 80.00
is 500.00
rf 7532.8
rp 5806.6
fs 17
is 100.000
re ph



HNMR-1450-2F-V-25-10-15

exp1 101h

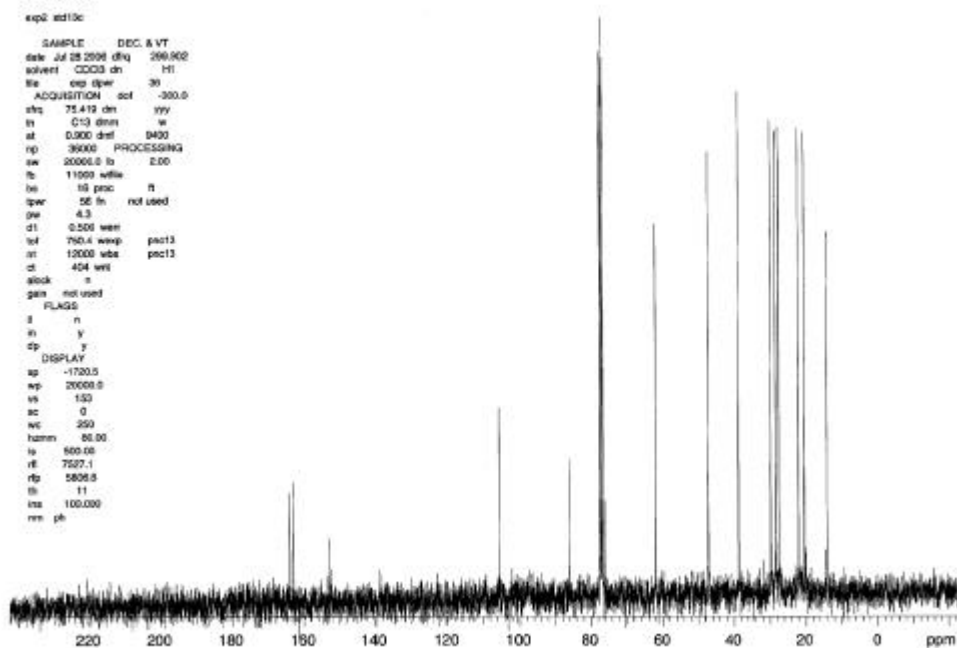
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solvent CDCl3 dn H1
file exp dpr 30
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in H1 dnm c
at 3.138 dref 500
np 30000 PROCESSING
sw 5000.4 wftlo
fs 2600 proc n
ts 4 fs 32780
dpr 57
pw 3.2 werr
dt 0 wexp pth1
sf 433.3 wba
nt 128 wnt
ct 30
ablock n
gain not used
FLAGS
s n
in y
dp y
DISPLAY
sp -100.0
wp 3098.8
vs 154
sc 0
wc 250
hzmm 13.20
ls 500.00
rf 2021.3
rp 2177.3
fs 20
lra 2.000
rm ph



HNMR-2F-V-28

exp2 101h

SAMPLE DEC & VT
date Jul 28 2006 dth 200.902
solvent CDCl3 dn H1
file exp dpr 30
ACQUISITION dcl -300.0
chq 75.412 dn rny
in C13 dnm w
at 0.000 dref 0400
np 30000 PROCESSING
sw 20000.0 fs 2.00
fs 11000 wftlo
ts 10 proc n
dpr 55 fs not used
pw 4.3
dt 0.500 werr
sf 750.4 wexp pnc13
nt 12000 wba pnc13
ct 404 wnt
ablock n
gain not used
FLAGS
s n
in y
dp y
DISPLAY
sp -1720.5
wp 20000.0
vs 150
sc 0
wc 250
hzmm 80.00
ls 500.00
rf 7527.1
rp 5836.8
fs 11
lra 100.000
rm ph

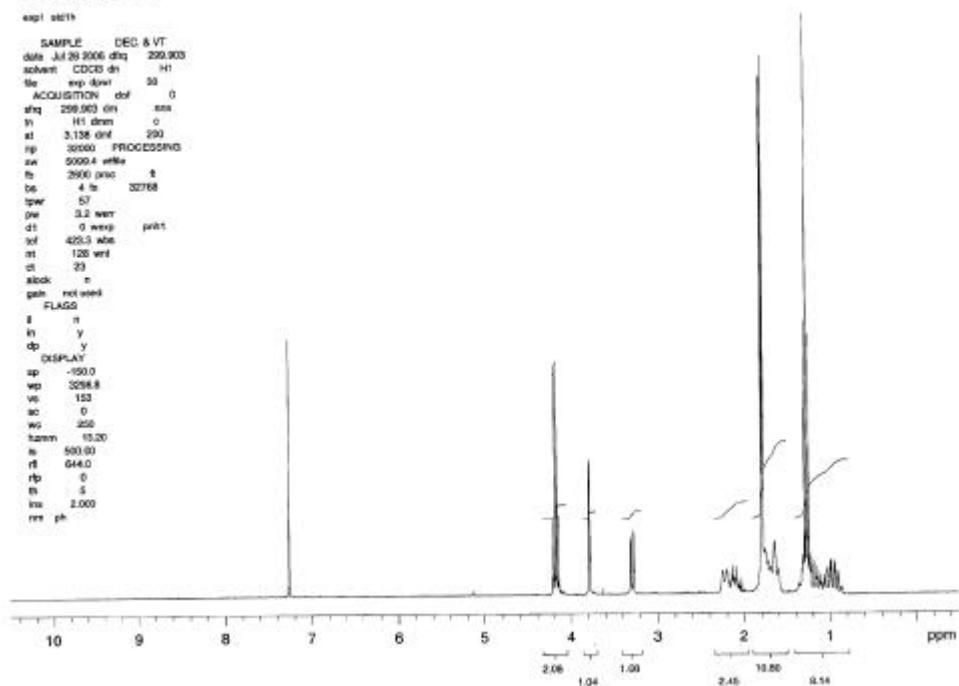


Mo Mo

HNMR-1400 SF-V-29-07-18

exp1 0015

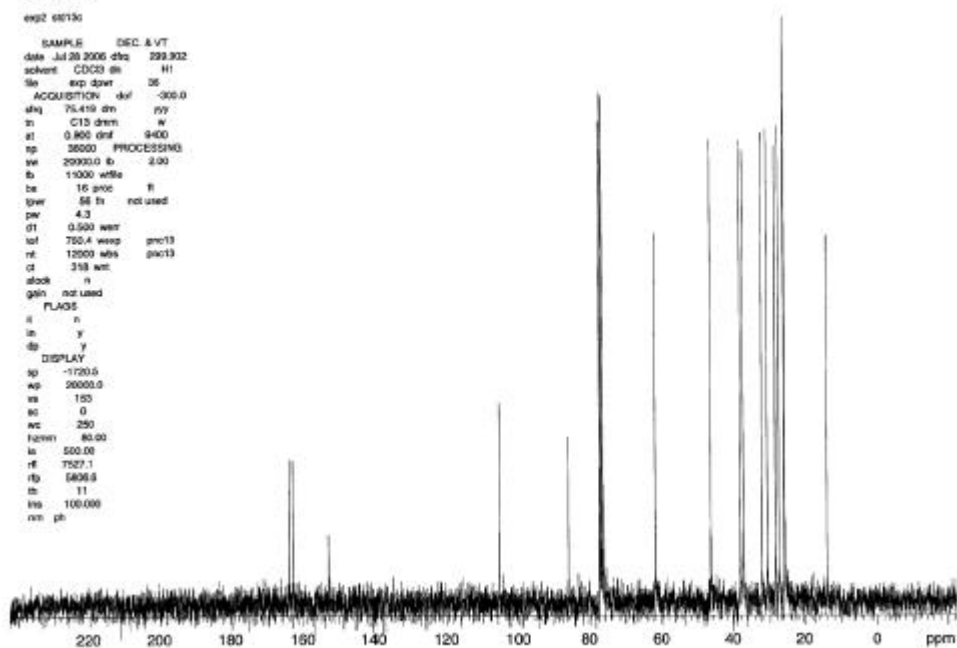
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date Jul 20 2006 dth 200.003
solvent CDCl3 dth H1
file exp dth 00
ACQUISITION dth 0
dth 250.003 dth 0
f1 101 dth 0
s1 3.156 dth 200
np 30000 PROCESSING
ze 5000.4 vfile
fs 2000 pnc
ds 4 fs 32768
pwr 57
pw 3.2 wnt
d1 0 wnt pnc
sf 400.3 wnt
nt 120 wnt
st 23
stock n
gain not used
FLAG
f n
fs y
dp y
DISPLAY
sp -150.0
wp 3200.0
vs 123
ac 0
wc 250
fzmm 15.20
ls 500.00
rf 644.0
rp 0
fs 5
fs 2.000
rm ph



CNMR SF-V-29

exp2 00150

SAMPLE DEC & VT
date Jul 20 2006 dth 200.002
solvent CDCl3 dth H1
file exp dth 00
ACQUISITION dth -300.0
dth 75.410 dth 0
f1 C13 dth 0
s1 0.800 dth 9400
np 30000 PROCESSING
ze 20000.0 fs 2.00
fs 15000 vfile
ds 16 pnc
pwr 56 fs not used
pw 4.3
d1 0.500 wnt
sf 750.4 wnt pnc13
nt 1200 wnt pnc13
st 318 wnt
stock n
gain not used
FLAG
f n
fs y
dp y
DISPLAY
sp -1720.0
wp 20000.0
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wc 250
fzmm 80.00
ls 500.00
rf 7527.1
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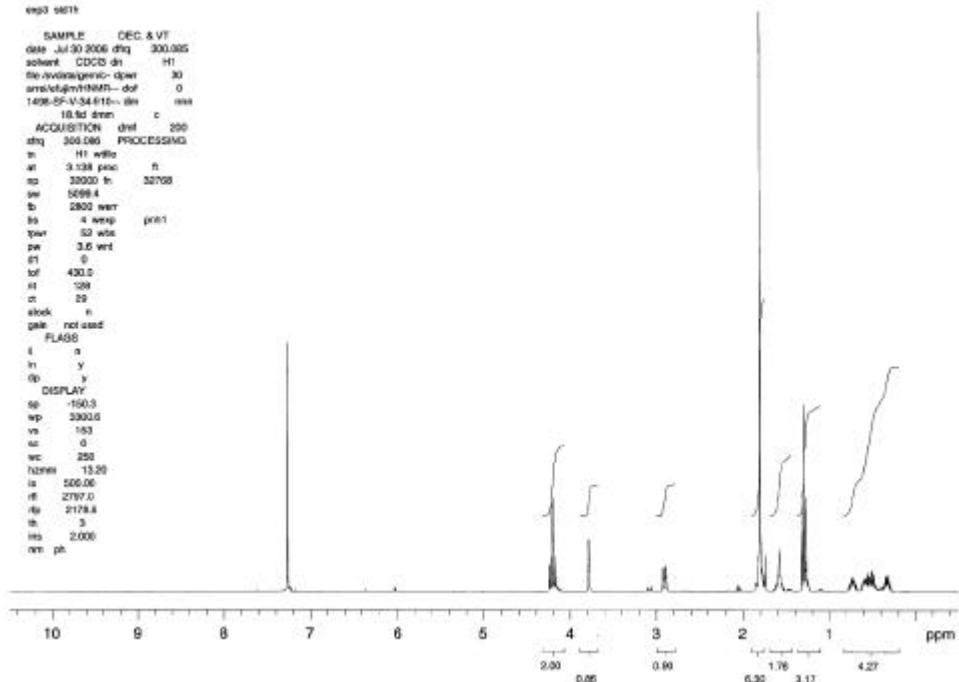


Me Me

HNMR-1405-SF-V-34-610-18

exp3 5815

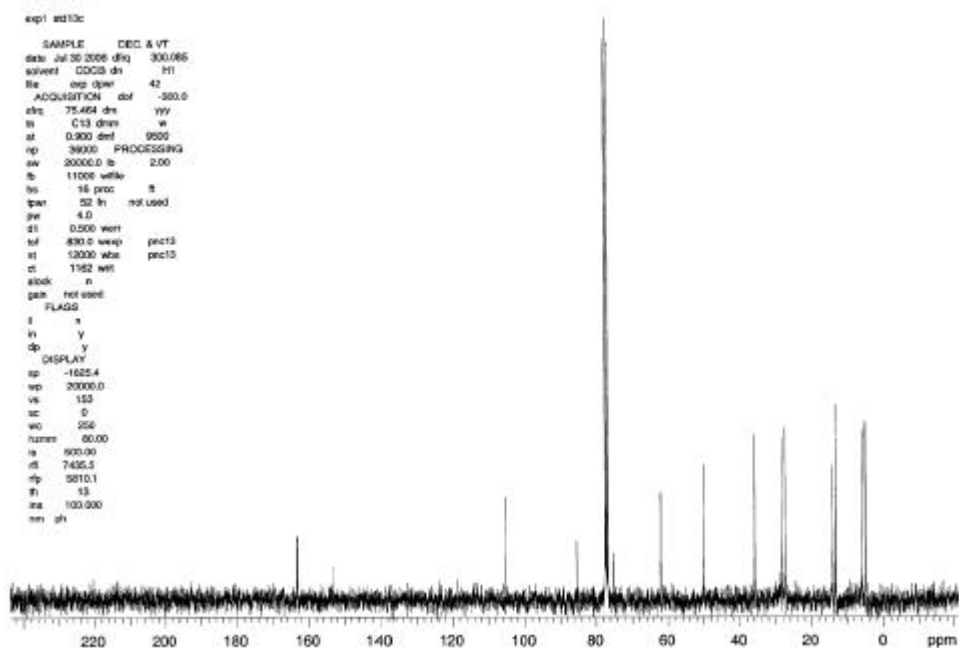
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1405-SF-V-34-610-...-d1et
18.1d d1et c
ACQUISITION d1et 200
dmq 300.085 PROCESSING
H1 w1e
w1 3.138 pasc n
w2 30000 f1 32708
w3 5098.4
f2 2800 werr
f3 4 werr pcr1
t1w1 52 w1e
w1 3.5 werr
d1 0
f1 430.0
f2 128
d1 20
clock n
gate not used
FLAG
f1 n
f2 y
dp y
DISPLAY
sp -150.3
wp 3000.0
vs 153
sc 0
wc 250
hzmax 15.20
ls 500.00
rf 2797.0
rp 2178.4
f1 3
f2 2.000
nm ph



HNMR-SF-V-34

exp1 5810c

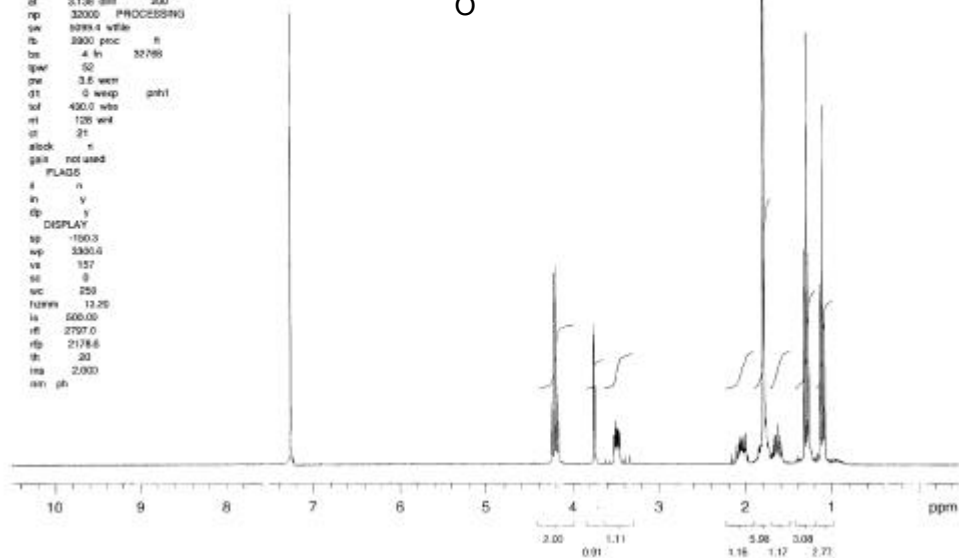
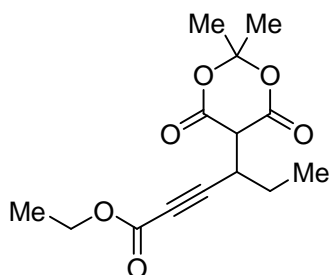
SAMPLE DEC & VT
date Jul 30 2006 dmq 300.085
solvent CDCl3 d1 H1
file exp d1et 42
ACQUISITION d1et 300.0
dmq 75.464 d1et w1
f1 C13 d1et w1
at 0.300 d1et 9500
rp 30000 PROCESSING
w1 20000.0 f1 2.00
f2 11000 werr
f3 16 pasc f1
t1w1 52 f1 not used
w1 4.0
d1 0.500 werr
f1 830.0 werr pcr13
f2 12000 werr pcr13
d1 1152 werr
clock n
gate not used
FLAG
f1 n
f2 y
dp y
DISPLAY
sp -1625.4
wp 20000.0
vs 153
sc 0
wc 256
hzmax 60.00
ls 900.00
rf 7465.3
rp 5810.1
f1 13
f2 100.000
nm ph



2d

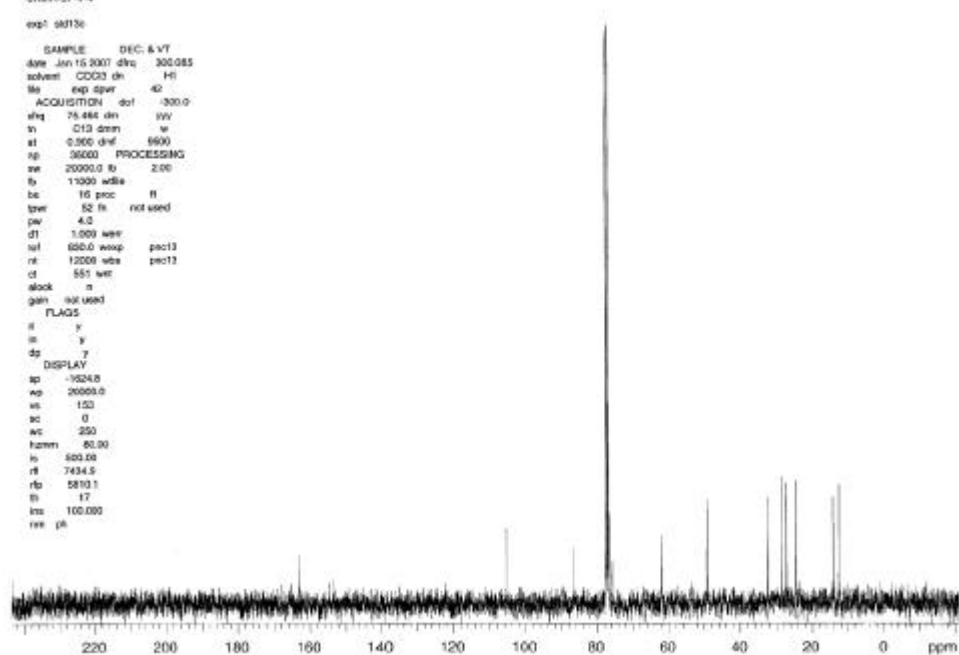
HNMR-1210-SF-V-4
exp1 0010

SAMPLE DEC: & VT
date Jan 15 2007 dno 300.085
solvent CDCl3 d1 H1
file exp dper 30
ACQUISITION dnt 0
drg 300.085 dm ann
in H1 dm c
at 5.136 dnt 300
np 32000 PROCESSING
sw 5099.4 wfile n
fs 3000 proc n
bs 4 fs 32785
tqwr 52
pw 3.5 wwr
dt 0 wwr pnt1
sol 400.0 wbs
nt 126 wnt
ct 21
stuck n
gain not used
FLAGS
f n
in y
cp 1
DISPLAY
sp -100.3
wp 3300.0
vs 157
ss 9
sc 250
fzmm 12.25
ls 600.00
rf 2797.0
rd 2178.6
ft 20
lra 2.000
ren ph

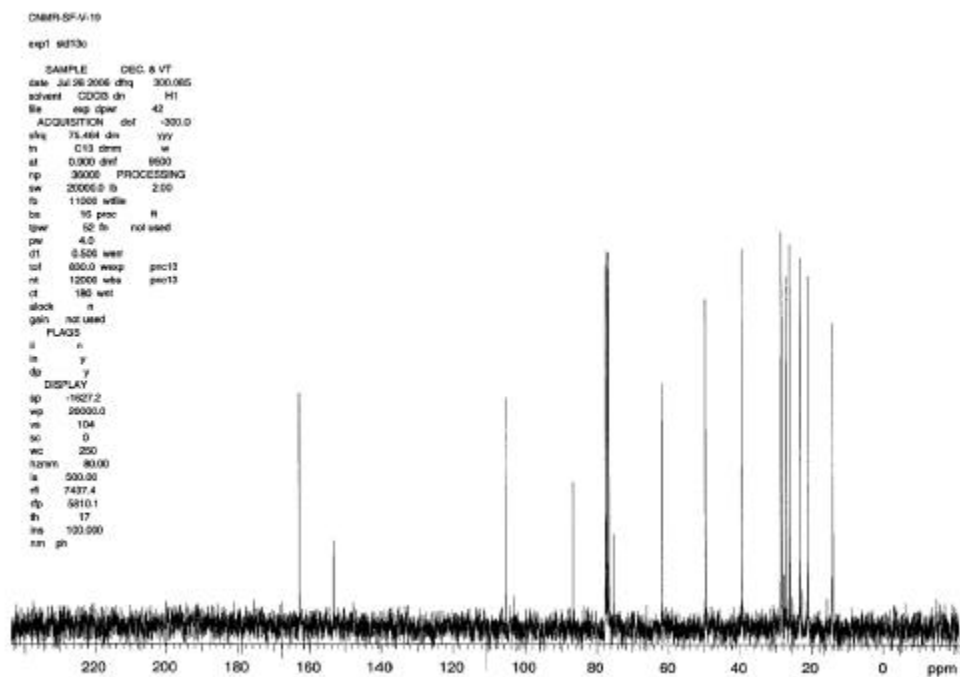
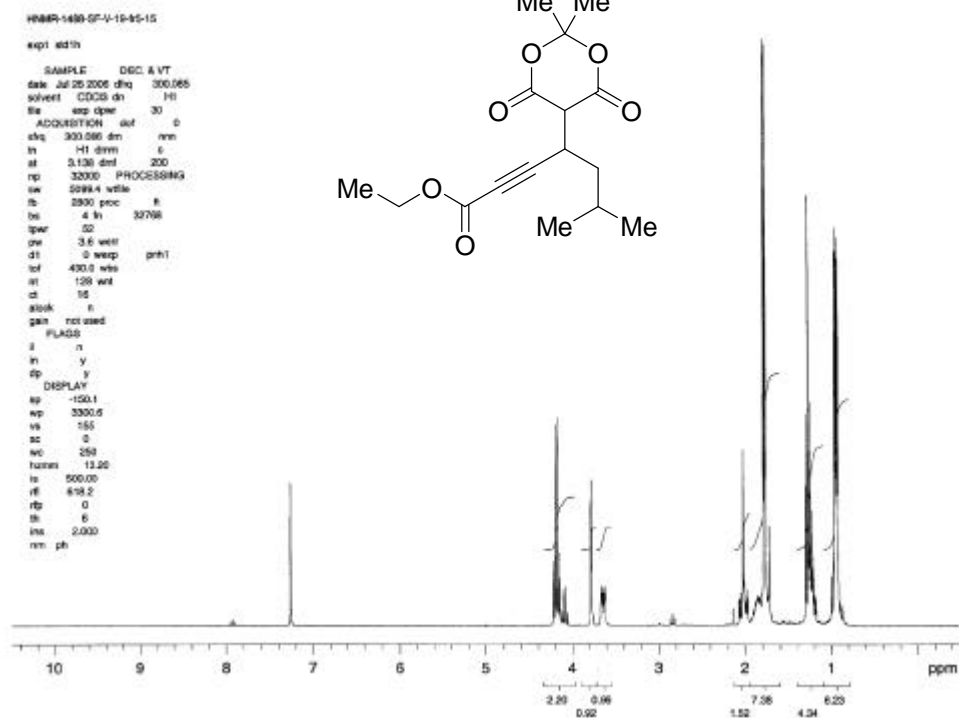


CNMR-SF-V-4
exp1 0010

SAMPLE DEC: & VT
date Jan 15 2007 dno 300.085
solvent CDCl3 d1 H1
file exp dper 40
ACQUISITION dnt 300.0
drg 75.484 dm wv
in C13 dm w
at 0.500 dnt 8600
np 36000 PROCESSING
sw 20000.0 fs 2.00
fs 11000 wfile n
bs 16 proc n
tqwr 52 fs not used
pw 4.3
dt 1.000 wwr
sol 600.0 wwr pnt13
nt 12000 wbs pnt13
ct 551 wnt
stuck n
gain not used
FLAGS
f y
in y
cp 7
DISPLAY
sp -100.3
wp 26000.0
vs 153
ss 0
sc 250
fzmm 60.00
ls 600.00
rf 7434.5
rd 5810.1
ft 17
lra 100.000
ren ph



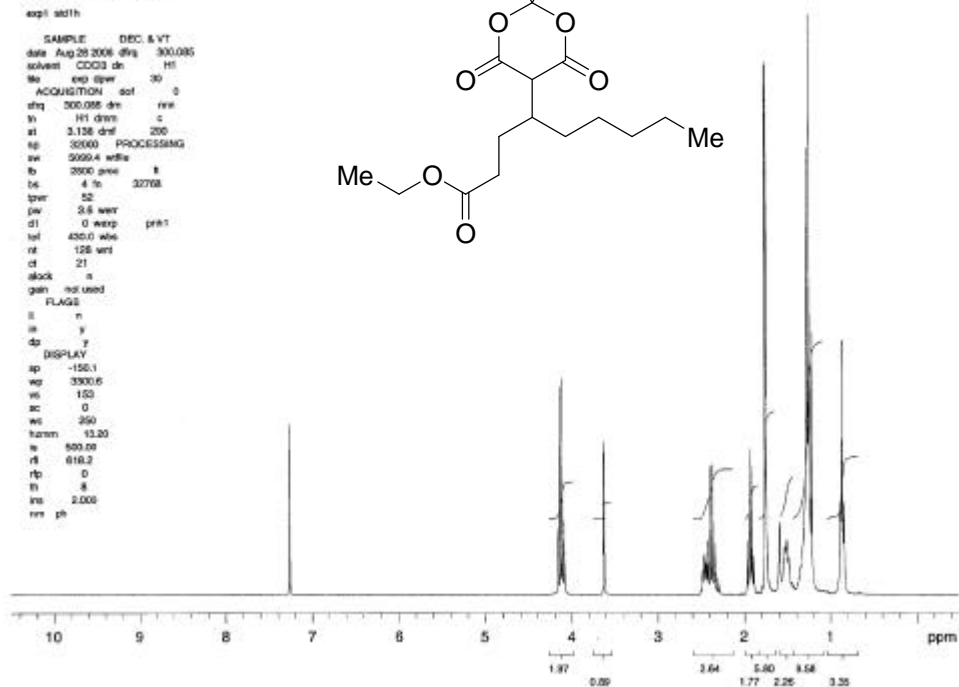
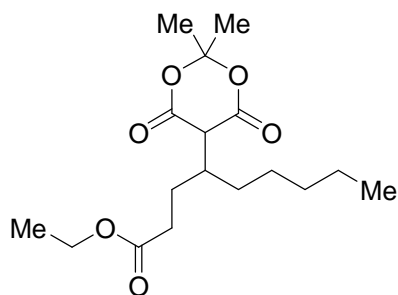
2e



5g

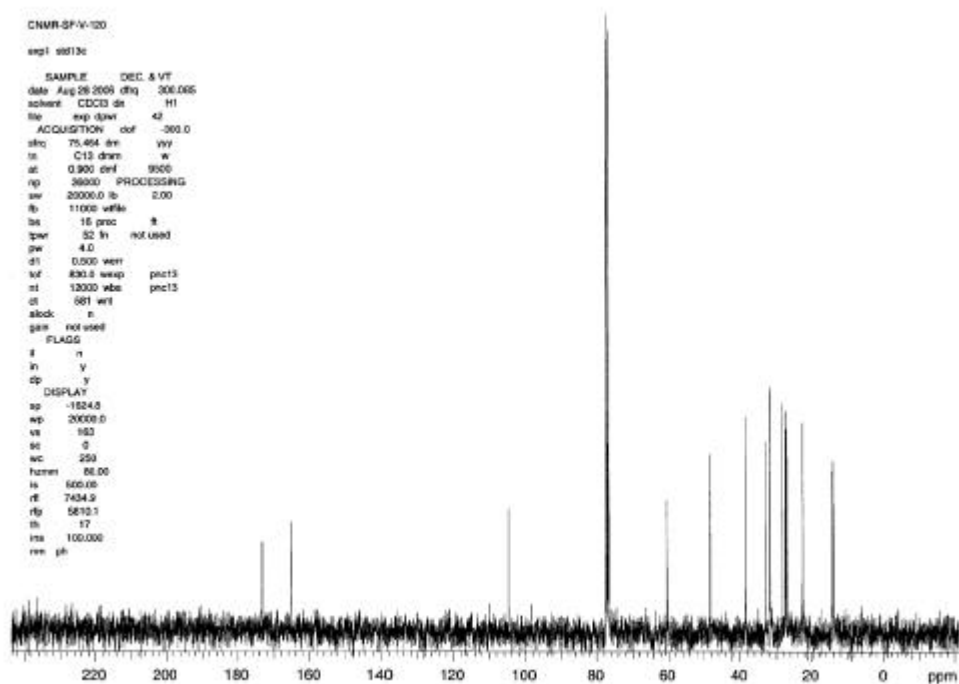
HNMR-1610-SF-V-120-610-18
exp1 sdt1h

SAMPLE DEC: & VT
date Aug 28 2009 dth 300.085
solvent CDCl3 dth H1
file exp dth 30
ACQUISITION sol 0
dth 300.085 dth rnm
in H1 dth c
at 3.138 dth 200
ap 30000 PROCESSING
wv 5000.4 wth
lb 2000 gth
bs 4 th 32768
pwr 52
pw 3.6 wth
d1 0 wth
sol 430.0 wth
nt 128 wth
ct 21
aback n
gain not used
FLAGS
f n
in y
dp y
DISPLAY
ap -150.1
wv 3000.6
wv 150
wv 0
wv 250
hnmn 13.20
w 500.00
rf 616.2
rfp 0
th 8
ms 2.000
rm ph



CNMR-SF-V-120
exp1 sdt13e

SAMPLE DEC: & VT
date Aug 28 2009 dth 300.085
solvent CDCl3 dth H1
file exp dth 42
ACQUISITION sol -300.0
dth 75.404 dth vvv
in C13 dth w
at 0.900 dth 9500
ap 30000 PROCESSING
wv 20000.0 lb 2.00
lb 11000 wth
bs 16 proc
pwr 52 th not used
pw 4.0
d1 0.000 wth
sol 430.0 wth pnc13
nt 13000 wth pnc13
ct 681 wth
aback n
gain not used
FLAGS
f n
in y
dp y
DISPLAY
ap -150.1
wv 20000.0
wv 163
wv 0
wv 250
hnmn 16.00
w 500.00
rf 7434.9
rfp 5610.1
th 17
ms 100.000
rm ph

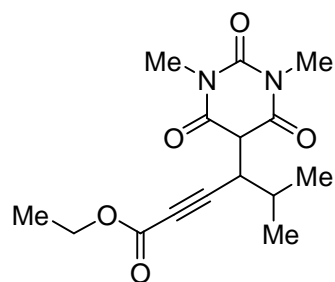
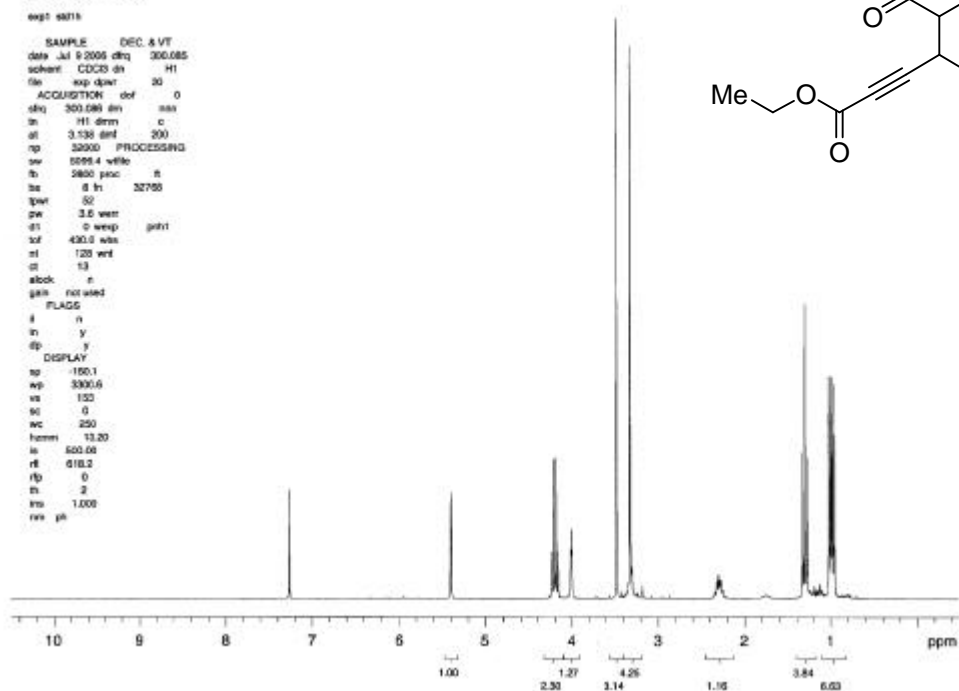


4a

HNMR-1428-SF-IV-188-x

exp1 48115

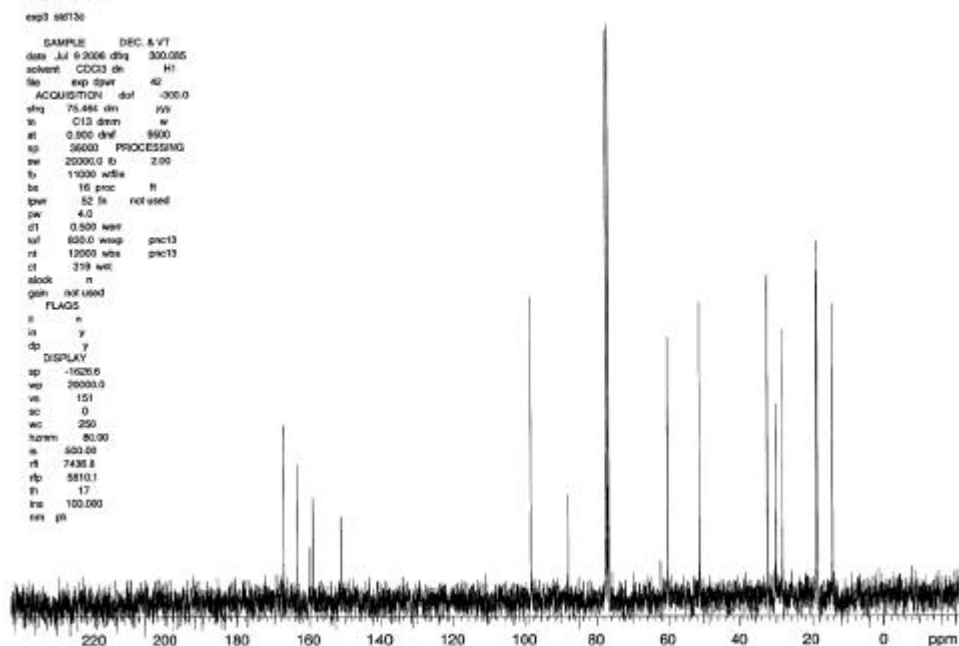
SAMPLE DEC & VT
 date Jul 9 2006 dmq 300.085
 solvent CDCl3 d1 H1
 file exp d1 30
 ACQUISITION d1 0
 dmq 300.085 d1 min
 in H1 d1 30
 at 3.136 d1 300
 np 32000 PROCESSING
 sw 5595.4 wfile
 fs 2860 proc H
 bs 8 fs 32768
 pwr 3.5 wett
 d1 0 wett gnt1
 sol 430.0 wds
 nt 120 wds
 ct 13
 block n
 gain not used
 FLAGG
 f n
 in y
 dp y
 DISPLAY
 np -150.1
 wp 3300.6
 vs 150
 bc 0
 wc 250
 hzmm 13.20
 is 600.00
 rf 018.2
 rp 0
 ft 3
 ins 1.000
 res ph



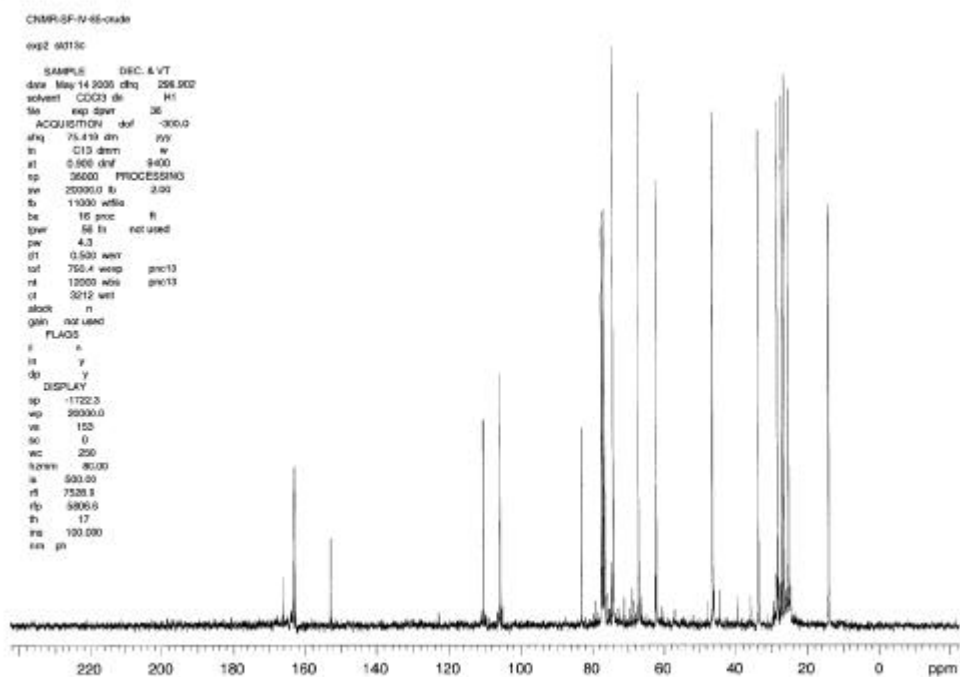
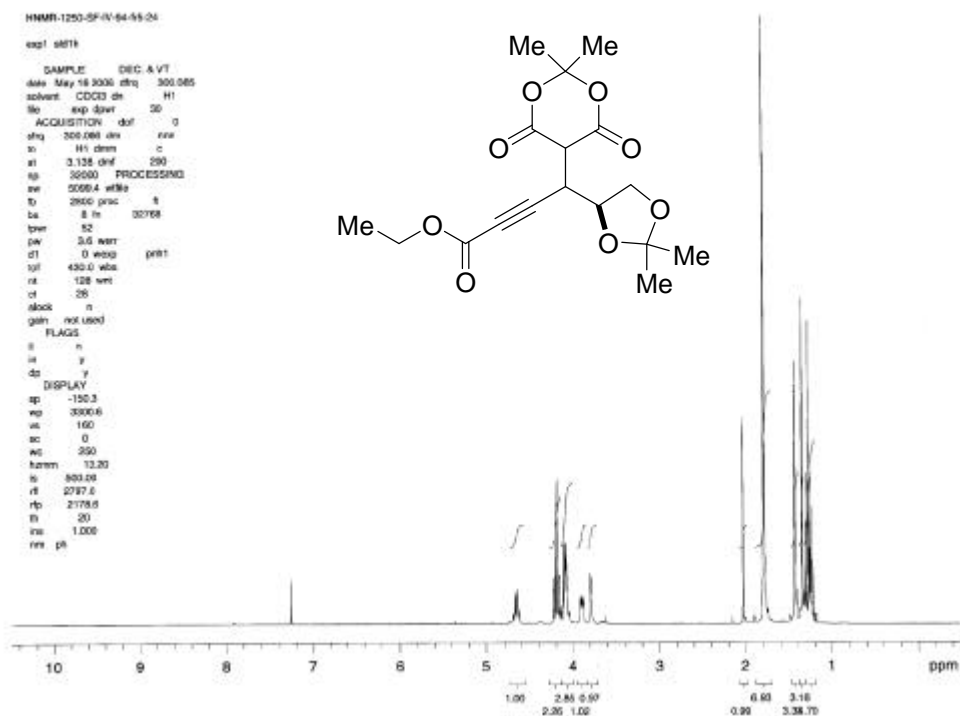
CNMR-SF-IV-188

exp3 48136

SAMPLE DEC & VT
 date Jul 9 2006 dmq 300.085
 solvent CDCl3 d1 H1
 file exp d1 40
 ACQUISITION d1 -300.0
 dmq 75.484 d1 pwr
 fs C13 d1 30
 at 0.500 d1 8600
 np 36000 PROCESSING
 sw 20000.0 fs 2.00
 fs 11000 wfile
 bs 16 proc H
 pwr 52 fs not used
 pwr 4.0
 d1 0.500 wett
 sol 600.0 wett pnc13
 nt 12000 wds pnc13
 ct 319 wds
 block n
 gain not used
 FLAGG
 f n
 in y
 dp y
 DISPLAY
 np -150.1
 wp 26000.0
 vs 151
 bc 0
 wc 250
 hzmm 80.00
 is 600.00
 rf 7435.8
 rp 5810.1
 ft 17
 ins 100.000
 res ph



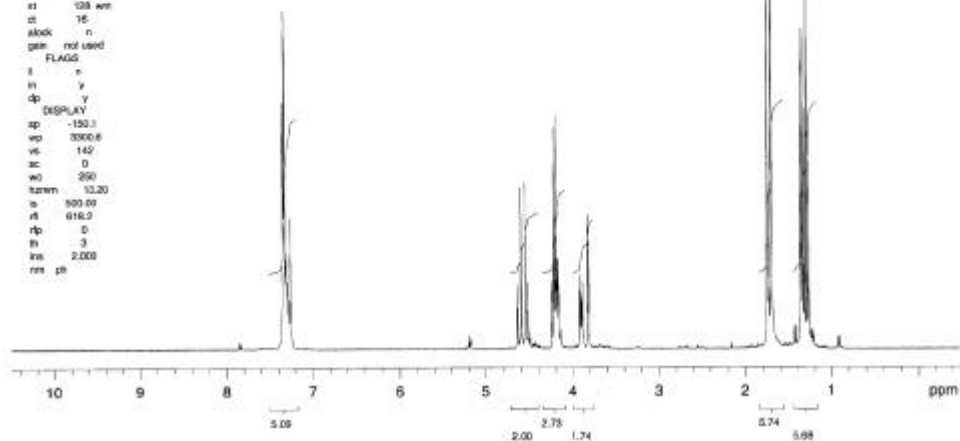
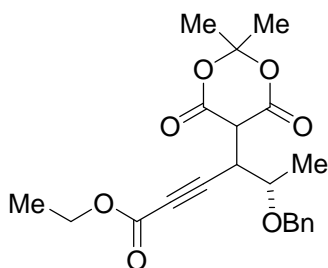
7a



7c

HNMR-1275-SF-V-107-15-15
exp1 std1h

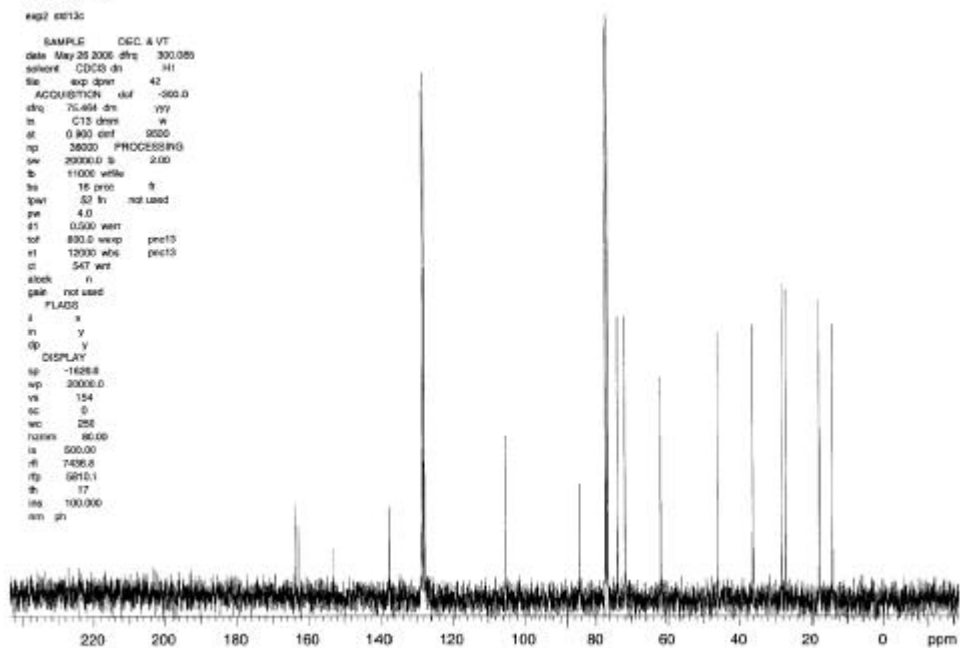
SAMPLE DEC & VT
date May 25 2006 dthg 300.085
solvent CDCl3 dth H1
file exp dthg 30
ACQUISITION dth 0
dthg 300.085 dm rsh
in H1 dthg C
at 3.130 dth 200
np 30000 PROCESSING
av 5099.4 vthg
ls 2900 pthg
ls 8 in 32768
dth 32
pw 3.6 wthg
d1 0 wthg gth1
vol 490.0 wthg
st 128 wthg
st 16
clock n
gain not used
FLAGG
i n
in y
dp y
DISPLAY
ap -150.1
vp 3000.0
vs 142
ac 0
wc 256
turn 13.20
ls 500.00
st 616.2
rp 0
th 3
res 2.008
nm ph



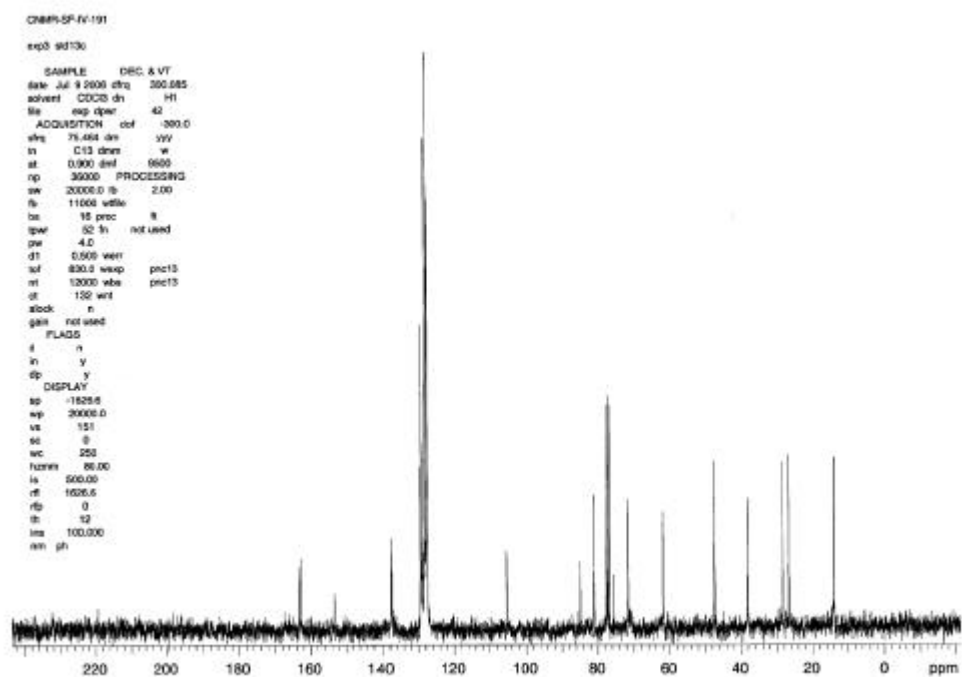
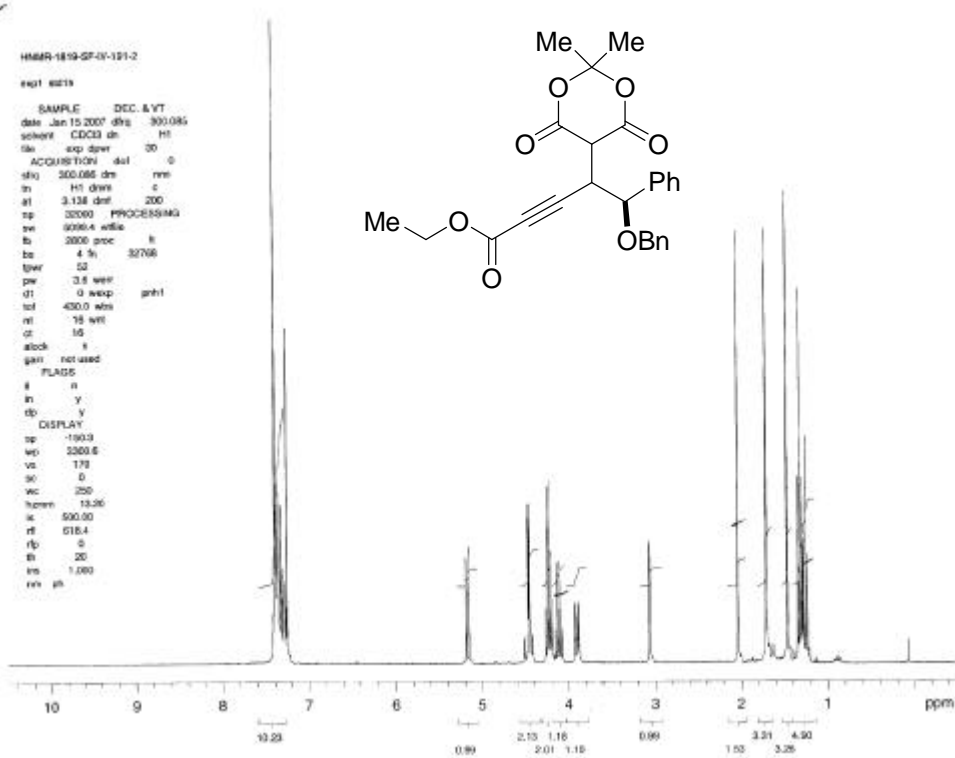
CNMR-SF-V-107

exp2 std13c

SAMPLE DEC & VT
date May 25 2006 dthg 300.085
solvent CDCl3 dth H1
file exp dthg 42
ACQUISITION dth -500.0
dthg 75.404 dm rsh
in C13 dthg w
at 0.800 dth 3000
np 30000 PROCESSING
av 20000.0 s 2.00
ls 11000 vthg
ls 16 pthg
ls 32 in not used
pw 4.0
d1 0.500 wthg
vol 890.0 wthg pth13
st 12000 wthg pth13
st 547 wthg
clock n
gain not used
FLAGG
i n
in y
dp y
DISPLAY
ap -1428.8
vp 30000.0
vs 154
ac 0
wc 256
turn 95.00
ls 500.00
st 7436.8
rp 6010.1
th 17
res 100.000
nm ph



7d

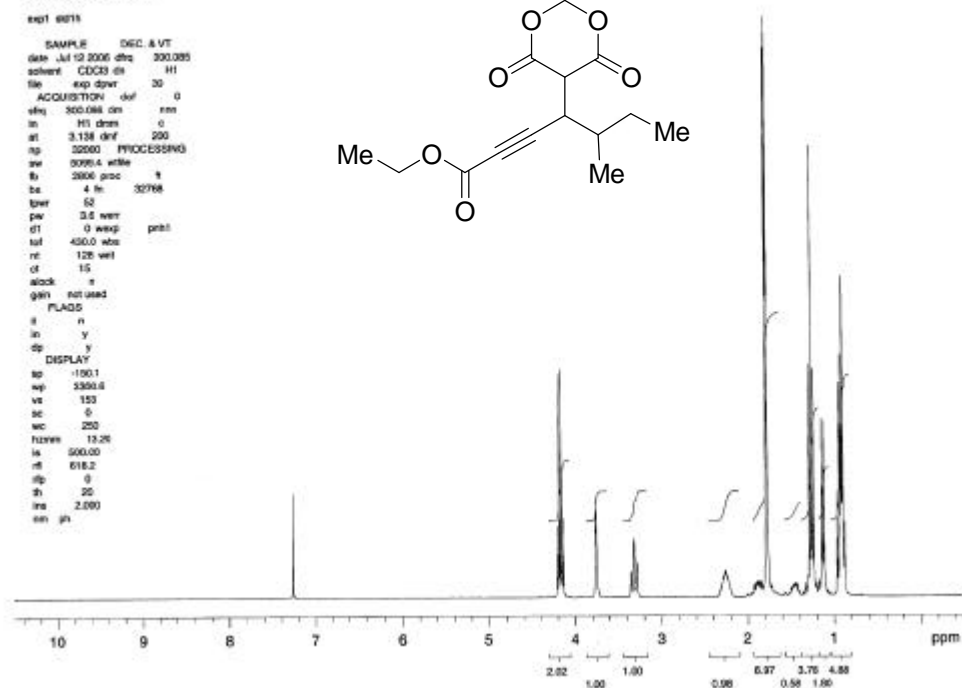
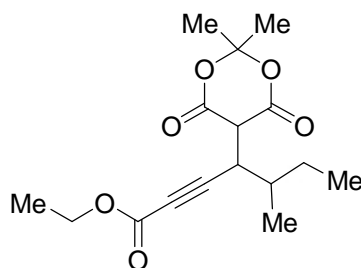


7e

HNMR-1443-SF-V-1-97-54
exp1 6015

SAMPLE DEC & VT
date Jul 12 2006 dmq 300.095
solvent CDCl3 d5 H1
file exp dprvt 30
ACQUISITION dmf 0
sfreq 300.086 dm nm
in 3.136 dmf 200
ap 32060 PROCESSING
aw 3099.4 wfile
fs 3806 proc
bs 4 in 32768
tprv 52
pw 3.5 wexp
d1 0 wexp
sol 430.0 wba
nt 128 wvt
ct 15
clock
gain not used
FLAOS
f n
in y
dp y

DISPLAY
sp -150.1
ap 3300.0
ve 153
sc 0
wc 200
hzmax 13.26
ls 500.00
rf 618.2
dp 0
sh 25
ms 2.000
em ph

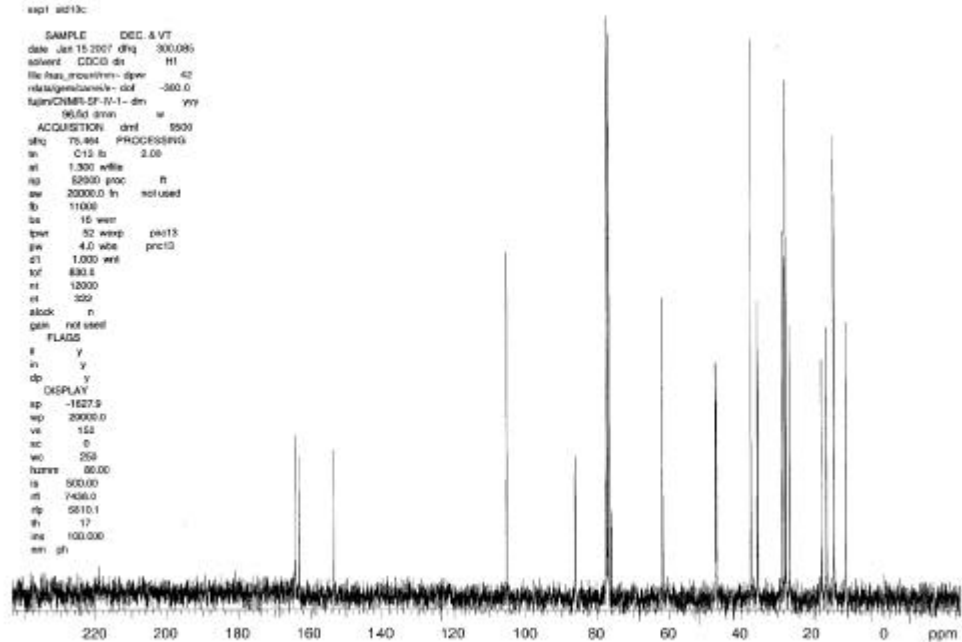


CNMR-SF-IV-126
exp1 6013c

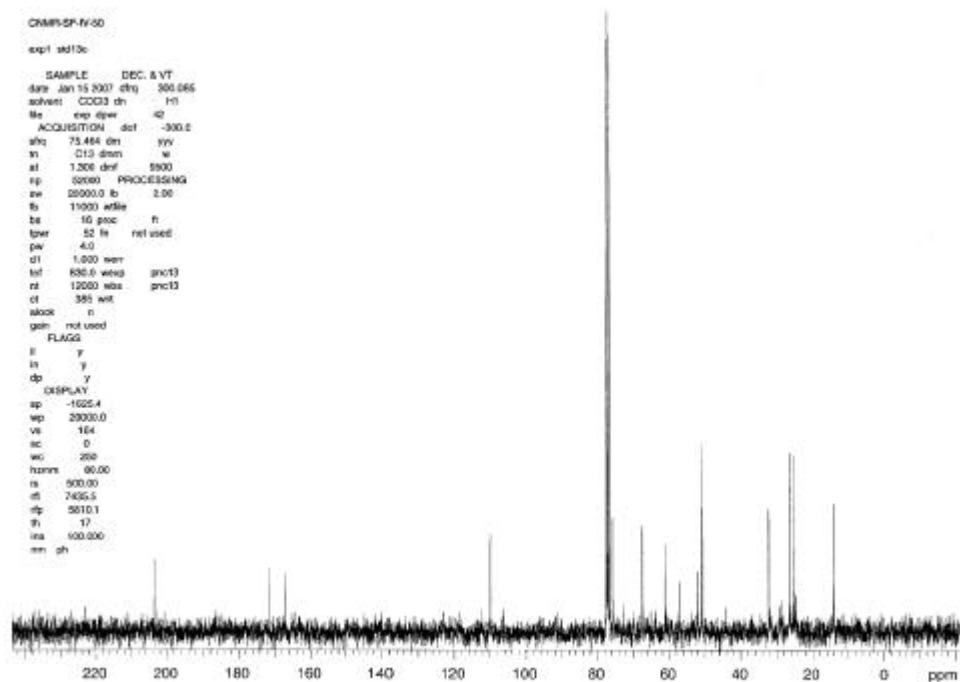
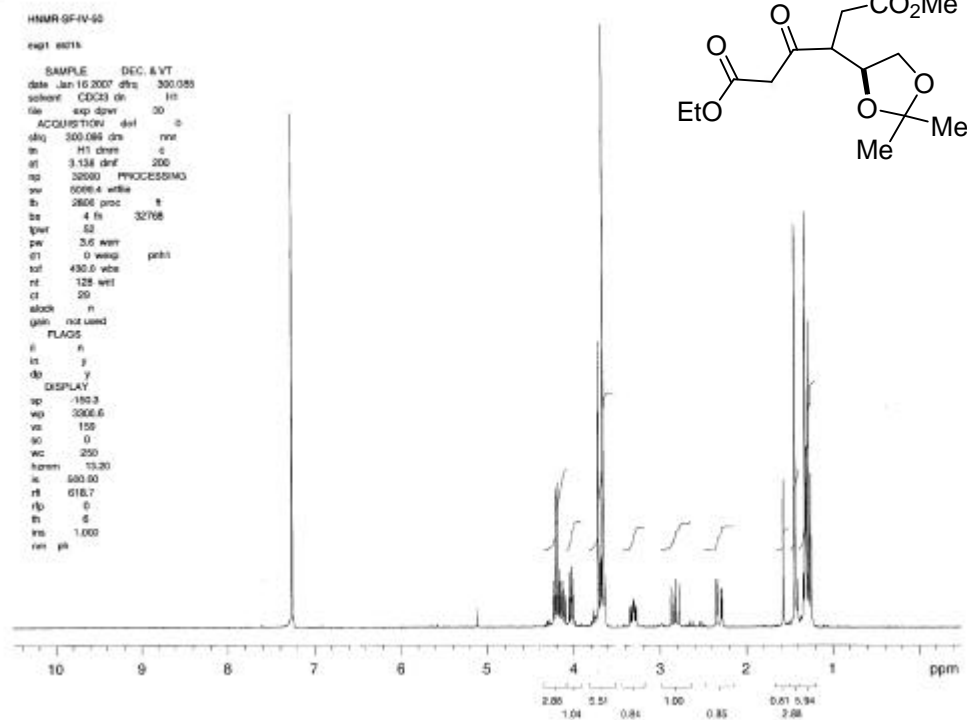
SAMPLE DEC & VT
date Jan 15 2007 dmq 300.095
solvent CDCl3 d5 H1
file data_incorrected.dpr 42
ntdata/gpmdata/cn- dmf -360.0
tupr/CNMR-SF-IV-1- dmf yyy
96.50 dmin w

ACQUISITION dmf 5000
sfreq 75.464 PROCESSING
in C-13 fs 2.00
at 1.300 wfile
ap 62900 proc
aw 20000.0 in not used
fs 11000
bs 15 wexp
tprv 52 wexp
pw 4.0 wba
d1 1.000 wvt
sol 830.1
nt 13000
ct 329
clock n
gain not used
FLAOS
f y
in y
dp y

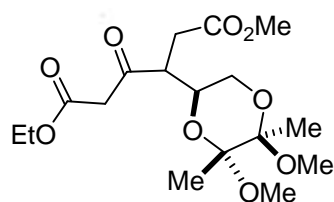
DISPLAY
sp -1627.9
ap 20000.0
ve 152
sc 0
wc 258
hzmax 60.00
ls 500.00
rf 7406.0
dp 2810.1
sh 17
ms 100.000
em ph



9a



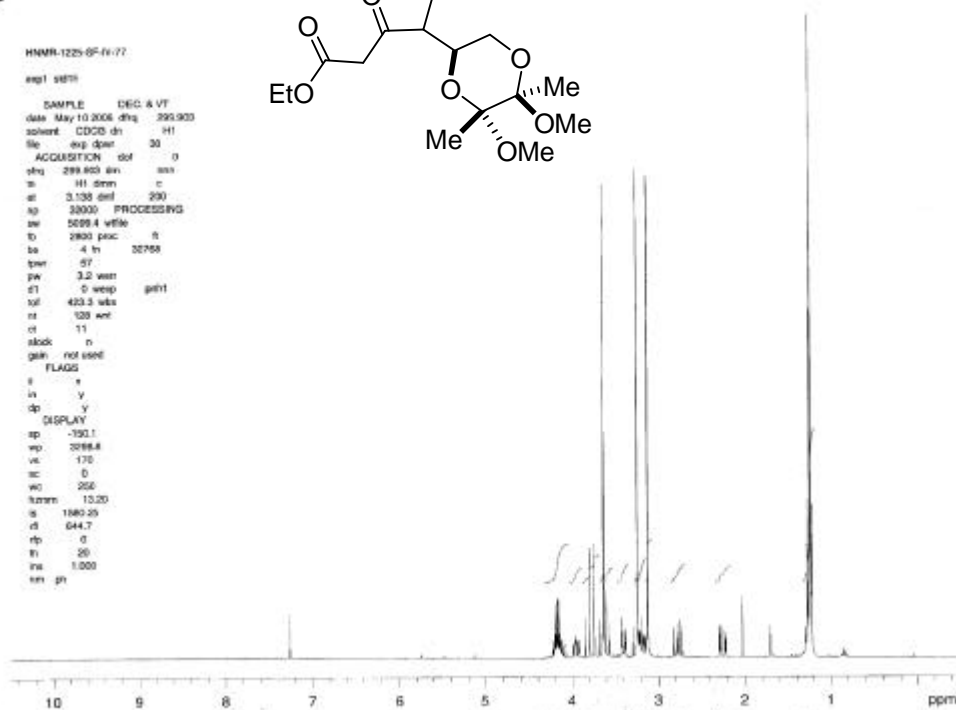
9b



HNMR-125-6F-14-77

exp1 s87f

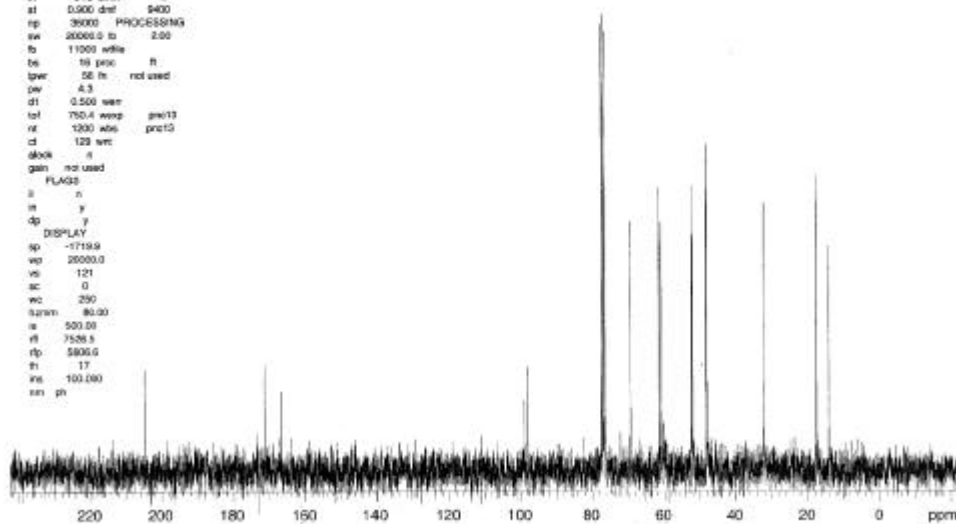
SAMPLE DEC & VT
 date May 10 2006 chg 205.903
 solvent CDCl3 ch H1
 file exp dpar 30
 ACQUISITION dot 0
 chg 299.803 sin ash
 in H1 dem c
 at 3.138 dnt 290
 ap 30000 PROCESSING
 aw 5099.4 vfile
 to 2900 proc ft
 ba 4 in 32768
 bwr 57
 pw 3.2 warr
 d1 0 wexp gph1
 xfl 423.3 wls
 nt 129 wrr
 ct 11
 clock n
 gain not used
 FLAGG
 il n
 in y
 dp y
 DISPLAY
 sp -190.1
 wp 32768.8
 vs 170
 ac 0
 mc 255
 turn 15.20
 s 1980.25
 d 644.7
 rp 0
 tn 20
 ms 1.000
 nm ph



CNMR-6F-14-77

exp2 s87f3c

SAMPLE DEC & VT
 date May 10 2006 chg 206.062
 solvent CDCl3 ch H1
 file exp dpar 35
 ACQUISITION dot -300.0
 chg 75.412 dm wv
 in C13 dem w
 at 0.000 dnt 5400
 ap 30000 PROCESSING
 aw 20000.0 to 2.00
 to 11000 wfile
 ba 16 proc ft
 bwr 56 in not used
 pw 4.3
 d1 0.500 warr
 xfl 750.4 wexp gph13
 nt 1200 wrr
 ct 129 wrr
 clock n
 gain not used
 FLAGG
 il n
 in y
 dp y
 DISPLAY
 sp -1719.9
 wp 20000.0
 vs 121
 ac 0
 mc 250
 turn 90.00
 s 500.00
 d 7526.5
 rp 5800.0
 tn 17
 ms 100.080
 nm ph



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

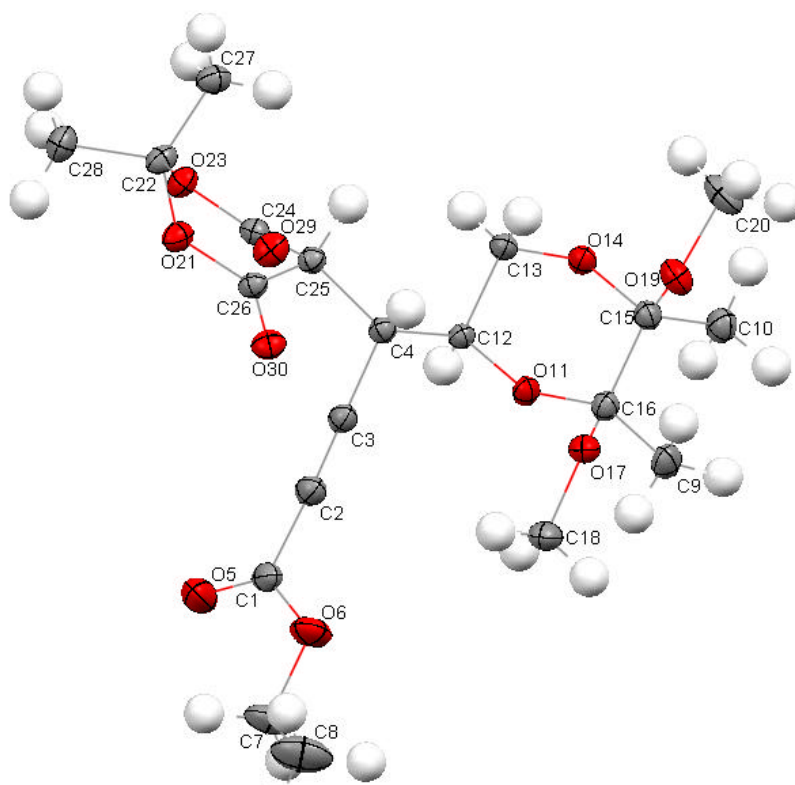


Figure 1. Crystal Structure of *syn-7b* (Ellipsoid probability level = 30%). Crystals were grown from hexanes/ CH_2Cl_2 (1/1) by slow evaporation of the solvent.

Comment

The study of the titled structure (ethyl 4-((5*R*,6*R*)-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

$\text{C}_{20}\text{H}_{28}\text{O}_{10}$
 $\text{C}_{20}\text{H}_{28}\text{O}_{10}$
 $M_r = 428.434$
Orthorhombic
 $P2_12_12_1$
 $a = 9.2671(3)\text{\AA}$
 $b = 12.7312(4)\text{\AA}$
 $c = 18.1005(5)\text{\AA}$
 $\alpha = 90.00^\circ$
 $\beta = 90.00^\circ$
 $\gamma = 90.00^\circ$
 $V = 2135.52(11)\text{\AA}^3$
 $Z = 4$

$D_x = 1.333\text{ Mg m}^{-3}$
 $F(000) = 912$
Density measured by: not measured
fine-focus sealed tube
Mo $K\alpha$ radiation $\lambda = 0.71073$
Cell parameters from 7708 refl.
 $\theta = 0.998\text{--}27.485^\circ$
 $\mu = 0.107\text{ mm}^{-1}$
 $T = 233\text{ K}$
Cube
 $0.4 \times 0.2 \times 0.16\text{ mm}$
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)

$R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 27.51^\circ$
 $h = -12 \rightarrow 12$
 $k = -16 \rightarrow 16$
 $l = -23 \rightarrow 23$

Refinement

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

mixed
Calculated weights $1/[\sigma^2(I_o) + (I_o + I_c)^2/900]$
 $\Delta/\sigma_{\text{max}} = 0.028$
 $\Delta\rho_{\text{max}} = 0.357\text{e}\text{\AA}^3$
 $\Delta\rho_{\text{min}} = -0.355\text{e}\text{\AA}^3$
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: *SIR97*(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 (\AA^2)

$$U_{eq} = 1/3 \sum_i \sum_j \mathbf{S}_{ij} U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

	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 (\AA^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)

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—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)

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)
C4—C25—C26—O30 -15.5 (3)

C24—C25—C26—O21 35.9 (3)
C4—C25—C26—O21 164.15 (19)

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