Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis of unprotected glyco-alkynones via molybdenum-catalyzed carbonylative Sonogashira cross-coupling reaction

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1. General methods

The solvents were purified by distillation or used without any purification in the case of HPLC-grade material. Acetonitrile HPLC-grade was used as received, 1,4-dioxane, toluene and THF were purified by distilling from sodium benzophenone ketyl. DIPEA and Et_3N were dried over CaH_2 and distilled before use. All reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, Oakwood or Fluorochem. Flash column chromatography was performed using silica gel 60 Å, 230-400 Mesh. Thin Layer Chromatography (TLC) was carried out using Merck TLC silica gel 60 F254 plates and for visualization, TLC plates were either placed under ultraviolet light, or stained with iodine or acidic vanillin solution. Compounds were all identified by usual analytical methods: ^{1}H NMR, ^{13}C NMR, IR, and HR-MS (ESI). ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$, CD_3OD or DMSO-d_6 in a Bruker DPX-300 instrument. Chemical shifts are referenced to the residual solvent signal. ^{1}H peaks are quoted to the nearest 0.01 Hz and ^{13}C peaks are quoted to the nearest 0.1 Hz. Multiplicity of the signals is reported as follows: s (singlet), d (dublet), t (triplet), dd (doublet of doublets) m (multiplet). High-resolution mass spectra (HRMS) were recorded on a Shimadzu LCMS-TOF, using ESI with 50% solution of acetonitrile/H_2O and 0.1% formic acid as ionization method. Infrared spectra were acquired on an Agilent Technologies Cary 630 and melting points were measured using a Buchi B-545 melting point apparatus. Optical rotations were registered using a 200 mm cell on an Anton Paar MCP 200 polarimeter at 589 nm. [α] is reported in deg.cm^3.g^{-1}.dm^{-1} and c is expressed in g/100 cm^3.

Single Crystal X-ray Study of 3a. A pale-yellow flat needle-like crystal of **3a**, $C_{16}H_{16}O_5$, was mounted on a 150 μm Mitegen loop with polybutenes (Aldrich, average Mn ~920). A Bruker D8 Quest Pho-ton 100 diffractometer system equipped with a Incoatex IμS High Brilliance microfocus X ray tube (Cu Kα, ν= 1.54178 Å) and a Incoatec Montel two-dimensional X ray optics monochromator collected the X-ray diffraction images at room temperature (~24 °C) using 0.5° φ or ω scans to a maximum θ angle of 72.26° (0.81 Å resolution). Bruker Saint[1] was used to integrate the images using a narrow-frame algorithm and SA-DABS[2] was used to perform the multi-scan adsorption correction. The structure was solved using the intrinsic phasing method and refined on F2 with all data using the Bruker SHELXTL Software Package,[3,4] using the monoclinic polar Sohncke space group P21, with Z = 4 (two molecules per asymmetric unit) for $C_{16}H_{16}O_5$. The polarity of the space group and absolute structure of the structure were determined by the resonance scattering effects. Table S1 contains the crystallographic information, derived parameters, atomic positions, thermal parameters, bond lengths and angles, torsion angles and hydrogen bond distances. Crystal Impact Diamond[5] was used for the preparation of the Figure S1, showing the ORTEP style molecular structure diagrams, packing diagram, and hydrogen bonding networks. Complete data are available under CCDC deposition number 2085190, www.ccdc.cam.ac.uk.

Table S1. Sample and crystal data for **3a**.

Identification code	**3a**
Chemical formula	$C_{16}H_{16}O_5$
Formula weight	288.29 g mol^{-1}
Temperature	297(2) K
Wavelength	1.54178 Å

1) Bruker AXS Inc. SAINT+ Integration Engine, V8.40A, Madison, Wisconsin, USA. Bruker AXS Inc., Madison, Wisconsin, USA.: Madison, WI, U.S.A. **2018**.

2) G. M. Sheldrick, SADABS, Version 2016/2. Bruker AXS Inc., Madison, Wisconsin, USA.: Madison, Wisconsin, USA. **2016**.

3) Bruker AXS Inc. SHELXTL XT, Version 2014/5 - Crystal Structure Solution, Madi-son, Wisconsin, USA. Bruker AXS Inc.: Madison, WI, U.S.A. **2014**.

4) Bruker AXS Inc. SHELXTL XL, Version 2018/3 - Crystal Structure Refinement, Madison, Wisconsin, USA. Bruker AXS Inc.: Madison, WI, U.S.A. **2018**.

5) K. Brandenburg, H. Putz, Diamond, Version 3.2k - Crystal and Molecular Structure Visualization. Crystal Impact GbR: Bonn, Germany **2016**.

Crystal size	0.021 × 0.052 × 0.414 mm	
Crystal habit	pale yellow flat needle	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.27541(14) Å	α= 90°
	b = 9.9710(2) Å	β = 91.2091(12)°
	c = 23.3558(6) Å	γ = 90°
Volume	1461.10(6) Å^3	
Z	4	
Density (calculated)	1.311 g cm^{-3}	
Absorption coefficient	0.813 mm^{-1}	
F(000)	608	

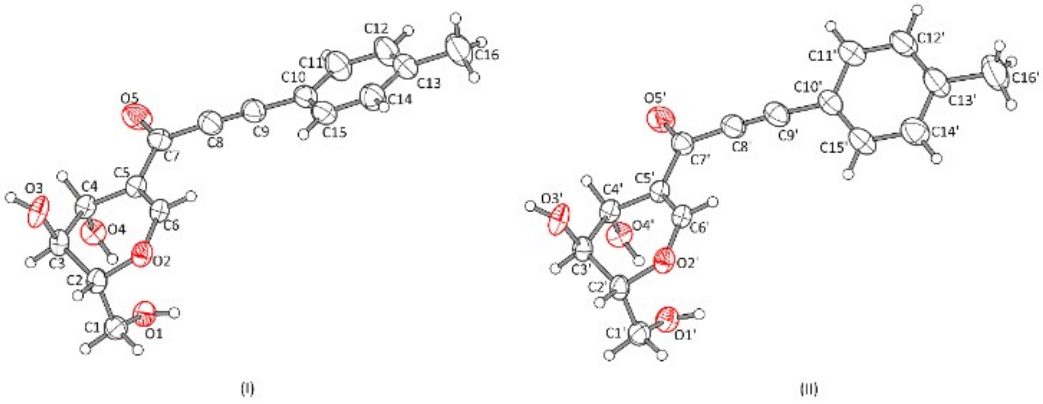
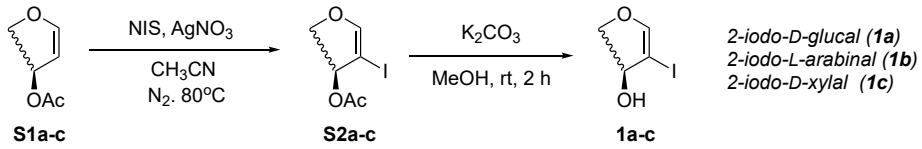


Figure S1. ORTEP-style molecular structure diagrams of **3a**.

2. Synthetic Procedures

2.1 Synthesis of 2-iodoglycals

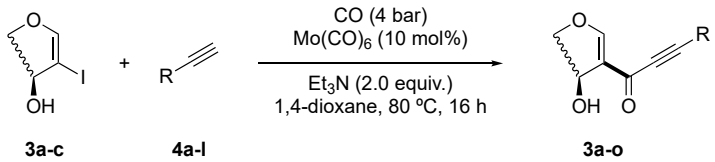


2-iodo-D-glucal (**1a**) and 2-iodo-D-xylal (**1c**) were synthesized following a published literature procedure.[6] 2-iodo-L-arabinal (**S2b**) was synthesized following a similar procedure:
To a 25-mL flame-dried reaction vial were added 3,4-di-*O*-acetyl-L-arabinal (**S1b**) (400 mg, 2.0 mmol, 1.0 equiv.), *N*-iodosuccinimide (540 mg, 2.40 mmol, 1.2 equiv.), $AgNO_3$ (70 mg, 0.40 mmol, 20 mol%) and HPCL-grade MeCN (6 mL). The mixture was stirred at 70 °C for 2 h under N_2 atmosphere and then filtered through a pad of celite. The resulting solution was evaporated under reduced pressure and the residue was purified by flash column chromatography using a gradient mixture of EtOAc (0% to 20%) in hexanes. The resulting product was transferred to a reaction flask and then K_2CO_3 (0.1 equiv.) was added followed by MeOH (6 mL/mmol of 2-iodoglycal). The mixture was stirred at RT for 2 h and then the solvent was removed under reduced pressure. The

[6] M. Malinowski, T. V. Tran, M.de Robichon, N. Lubin-Germain, A. Ferry, *Adv. Synth. Catal.* **2020**, *362*, 1184– 1189.

residue was purified byflash column chromatography using DCM/MeOH as eluent (0 to 10%) to give the 2-iodo-L-arabinal (**1b**) as a white solid (413.5 mg, 1.70 mmol, 85% over two steps).
^{1}H NMR (300 MHz, chloroform-d) δ 6.37 (s, 1H), 4.79 (d, *J* = 5.1 Hz, 1H), 4.63 (dd, *J* = 11.9, 4.3 Hz, 1H), 4.48 (t, *J* = 6.6 Hz, 1H), 3.83 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.1, 77.2, 68.7, 66.1, 63.4, 62.7; **m.p**. 139 – 141°C; **IR** (ν, cm^{-1}) = 3340, 2915, 1628, 1396, 1242, 1170, 1110, 1028; **HRMS** (ESI- TOF) calc. [$C_5H_7O_3I + Na^+$], 264.9332, found 264.9335. **$[\alpha]^{20}_D$** = – 173.0 (0.1, $CHCl_3$)

2.2 General Procedure A: Molybdenum-catalyzed carbonylative Sonogashira reaction of 2-iodoglycals with terminal alkynes

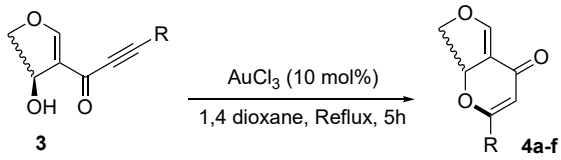


3a-c **4a-l** **3a-o**

To a 600-mL stainless steel reactor (**Figure S2**) were added a magnetic stir bar, the corresponding 2-iodoglycal (0.5 mmol, 1.0 equiv.), $Mo(CO)_6$ (13 mg, 0.05 mmol, 10 mol%), Et_3N (139 µL, 1.00 mmol, 2.0 equiv.), 1,4-dioxane (5 mL) and the corresponding terminal alkyne (0.75 mmol, 1.5 equiv.). The reactor was sealed, evacuated and backfilled with CO three times and then pressurized with 4 bar of CO. The equipment was placed in an oil bath at 80 °C and the reaction was stirred for 16 h. The resulting mixture was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography using DCM/MeOH [illegible] corresponding glyco-alkynone.

Figure S2. Stainless steel reactor.

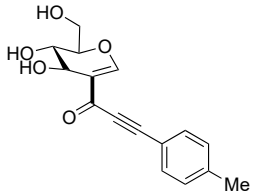
2.3 General Procedure B: Au-catalyzed cyclization of glyco-alkynones



To a 10-mL oven-dried reaction vial were added the correspondent glyco-alkynone (0.2 mmol, 1.0 equiv.) and $AuCl_3$ (6.0 mg, 10 mol%). The container was then sealed, evacuated and back-filled with N_2 three times followed by the addition dry 1,4-dioxane (2 mL). The mixture was stirred at 80 °C for 3 h in an oil bath and then, after cooling to RT, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography using a mixture of DCM/MeOH (0 to 10%) as eluent.

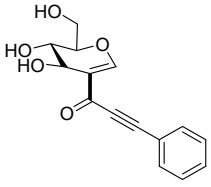
3. Characterization data

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(*p*-tolyl)-prop-2-yn-1-one (3a)



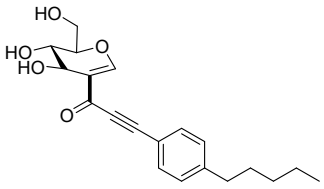
3a was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.5 mmol, 1.0 equiv.) and 4-ethynyltoluene (95 µL, 0.75 mmol, 1.5 equiv.) and was isolated as a white solid (112 mg, 0.39 mmol, 78%)..^{1}H NMR (300 MHz, CD_3OD) δ 8.12 (d, J = 1.7 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 4.48 (dd, *J* = 3.7, 1.6 Hz, 1H), 4.35 (s, 1H), 4.06 – 3.64 (m, 3H), 2.39 (s, 3H).^{13}C NMR (75 MHz, CD_3OD) δ 178.6, 163.5, 142.7, 133.8, 130.6, 120.2, 118.2, 91.7, 85.8, 83.7, 68.9, 63.7, 62.0, 21.7; m.p. 134– 136°C; IR (υ, cm^{-1}) 3227, 2820, 2756, 2125, 1562, 1270, 1177, 1156, 1032, 987, 789; HRMS (ESI- TOF) calc. [$C_{16}H_{16}O_5Na^+$], 311.0890, found 311.0894. $[\alpha]^{20}_D$ = +15.0 (0.1, $CHCl_3$).

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2H-pyran-5-yl)-3-phenylprop-2-yn-1-one (3b)



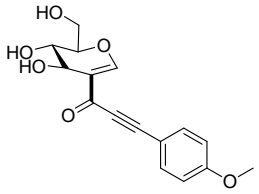
3b was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.500 mmol, 1.0 equiv.) and phenylacetylene (82 µL, 0.75 mmol, 1.5 equiv.) and was isolated as a yellow solid (71 mg, 0.26 mmol, 52%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.10 (s, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.49 (m, 3H), 5.30 (d, *J* = 17.9 Hz, 2H), 4.98 (s, 1H), 4.33 (s, 2H), 3.86 (s, 1H), 3.82 – 3.71 (m, 1H), 3.71 – 3.57 (m, 1H).^{13}C NMR (75 MHz, DMSO-d_6) δ 175.7, 161.5, 132.6, 130.6, 128.9, 119.5, 119.0, 88.5, 85.5, 83.0, 66.8, 60.8, 60.2; m.p. 112 – 114 °C; IR (υ, cm^{-1}) = 3298, 2853, 2129, 1557, 1443, 1272, 1160, 994, 735, 670. HRMS (ESI- TOF) calc.[$C_{15}H_{14}O_5Na^+$]297.0733,found297.0733; $[\alpha]^{20}_D$ = +24.0 (0.1, $CHCl_3$).

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(4-pentylphenyl)prop-2-yn-1-one (3c)



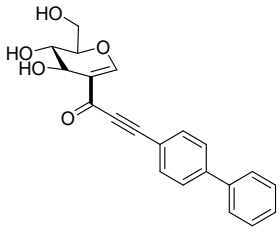
3cwas synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.500 mmol, 1.0 equiv.) and 1-ethynyl-4-pentylbenzene (146 µL, 0.750 mmol, 1.5 equiv.) and was isolated as a yellow solid (59 mg, 0.17 mmol, 34%). ^{1}H NMR (300 MHz, CD_3OD) δ 8.20 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 2H), 4.59 – 4.54 (m, 1H), 4.43 (s, 1H), 4.07 – 3.85 (m, 3H), 3.41 (d, *J* = 11.1 Hz, 2H), 2.72 (d, *J* = 7.8 Hz, 2H), 1.71 (t, *J* = 7.4 Hz, 2H), 1.47 – 1.38 (m, 4H), 0.98 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, MeOD) δ 178.6, 163.5, 147.6, 133.9, 130.0, 120.2, 118.5, 91.7, 85.8, 83.7, 68.9, 63.8, 62.0, 36.9, 32.5, 32.0, 23.5, 14.3; m.p. 154 – 155 °C; IR (υ, cm^{-1}) = 3210, 2842 2769, 2130, 1568, 1529, 1410, 1215, 1160, 960; HRMS (ESI- TOF) calc. [$C_{20}H_{24}O_5 + H^+$] 345.1697, found 345.1699; $[\alpha]^{20}_D$ = +36.0(0.1, $CHCl_3$).

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(4-methoxyphenyl)prop-2-yn-1-one (3d)



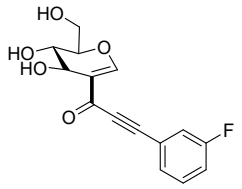
3d was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.5 mmol, 1.0 equiv.) and 4-ethynylanisole (97 µL, 0.75 mmol, 1.5 equiv.) and was isolated as a yellow solid (132 mg, 0.435 mmol, 87%).^{1}H NMR (300 MHz, DMSO-d_6) δ 8.05 (d, J = 2.5 Hz, 1H), 7.65 (d, J = 6.3 Hz, 2H), 7.18 – 6.92 (m, 2H), 5.39 – 5.11 (m, 2H), 4.93 (s, 1H), 4.56 – 4.13 (m, 2H), 3.81 (d, J = 2.4 Hz, 4H), 3.73 (d, J = 5.1 Hz, 1H), 3.66 – 3.56 (m, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 176.3, 161.6, 161.5, 135.2, 119.4, 115.1, 111.7, 89.9, 85.6, 83.4, 67.3, 61.3, 60.6, 55.9; m.p. 162 – 164°C; IR (υ, cm^{-1}) = 3227, 2834, 2747, 2117, 1549, 1534, 1460, 1253, 1212, 1156, 808. HRMS (ESI- TOF) calc. [$C_{16}H_{16}O_6$ + H^+] 345.1697, found 345.1691. $[\alpha]^{20}_D$ = +29.0 (0.1, $CHCl_3$).

3-([1,1'-Biphenyl]-4-yl)-1-((2*R*,3*S*,4*S*)-3,4-dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)prop-2-yn-1-one (3e)



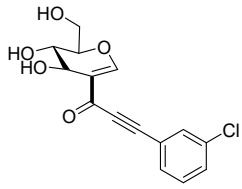
3e was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.500 mmol, 1.0 equiv.) and 4-ethynyl-1,1'-biphenyl (133 mg, 0.750 mmol, 1.5 equiv.) and was isolated as a yellow solid (126 mg, 0.359 mmol, 72%).^{1}H NMR (300 MHz, DMSO-d_6) δ 8.14 (s, 1H), 7.76 (m, 6H), 7.51 (t, J = 7.6 Hz, 2H), 7.43 (d, J = 7.2 Hz, 1H), 5.45 – 5.21 (m, 2H), 4.98 (s, 1H), 4.35 (d, J = 10.5 Hz, 2H), 3.95 – 3.84 (m, 1H), 3.83 – 3.71 (m, 1H), 3.65 (d, J = 12.6 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 176.1, 162.0, 142.6, 139.3, 133.8, 129.6, 128.7, 127.5, 127.3, 119.5, 119.00, 88.9, 86.7, 83.54, 67.3, 61.2, 60.7; m.p. 124 – 126 °C; IR (υ, cm^{-1}) = 3232, 2844, 2747, 2115, 1546, 1544, 1460, 1260, 1210, 1115, 810; HRMS (ESI- TOF) calc. [$C_{21}H_{18}O_5Na^+$] 373.1046, found 373,1042; $[\alpha]^{20}_D$ = +7.0 (0.05, $CHCl_3$).

1-((2*R*,3*S*,4*S*)-3,4-dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(3-fluorophenyl)prop-2-yn-1-one (3f)



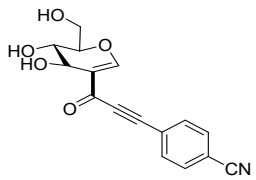
3f was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.5 mmol, 1.0 equiv.) and 1-ethynyl-3-fluorobenzene (87 µL, 0.75 mmol, 1.5 equiv.) and was isolated as a white solid (61 mg, 0.21 mmol, 42%).^{1}H NMR (300 MHz, CD_3OD) δ 8.26 (s, 1H), 7.63 – 7.56 (m, 2H), 7.51 (d, J = 9.4 Hz, 1H), 7.44 – 7.34 (m, 1H), 4.61 (d, J = 3.4 Hz, 1H), 4.51 (s, 1H), 4.15 – 3.93 (m, 3H), 3.47 (dd, J = 11.6, 8.9 Hz, 1H), 3.42 – 3.34 (m, 2H); ^{13}C NMR (75 MHz, CD_3OD) δ 178.1, 164.1, 163.1 (d, J = 144.1 Hz), 132.1 (d, J = 8.6 Hz), 130.0 (d, J = 3.1 Hz), 123.3 (d, J = 9.5 Hz), 120.4 (d, J = 9.0 Hz), 120.1, 119.1 (d, J = 21.5 Hz), 89.2, 86.5, 83.9, 68.9, 63.7, 62.1; m.p. 141.5 – 142.1 °C; IR (υ, cm^{-1}) = 3226, 2836, 2129, 1527, 1428, 1384, 1158, 979; HRMS (ESI- TOF) calc. [$C_{15}H_{13}FO_5Na^+$] 315.0639, found 315.0648; $[\alpha]^{20}_D$ = –143.0(0.1, $CHCl_3$).

3-(3-Chlorophenyl)-1-((2*R*,3*S*,4*S*)-3,4-dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)prop-2-yn-1-one (3g)



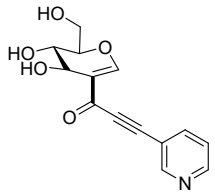
3g was synthesized according to General Procedure A and using 2-iodoglucal (136 mg, 0.500 mmol, 1.0 equiv.) and 3-chloro-1-ethynylbenzene (92 µL, 0.75 mmol, 1.5 equiv.) and was isolated as a white solid (74 mg, 0.24 mmol, 48%).^{1}H NMR (300 MHz, CD_3OD) δ 8.21 (s, 1H), 7.73 (s, 1H), 7.67 – 7.55 (m, 2H), 7.51 (d, J = 7.8 Hz, 1H), 4.56 (s, 1H), 4.44 (s, 1H), 4.06 – 3.87 (m, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ178.0, 163.9, 135.7, 133.2, 132.1, 131.9, 131.4, 123.2, 120.3, 88.9, 86.7, 83.8, 68.8, 63.6, 62.0.m.p. 134 – 135 °C; IR (υ, cm^{-1}) = 3255, 2831, 2132, 1426, 1363, 1272, 1162, 1061, 985, 763; HRMS (ESI- TOF) calc. [$C_{15}H_{13}ClO_5Na^+$] 331.0344, found 331.0346; $[\alpha]^{20}_D$ = –20.0 (0.1, $CHCl_3$).

4-(3-((2R,3S,4S)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2H-pyran-5-yl)-3-oxoprop-1-yn-1-yl)benzonitrila (3h)



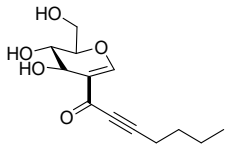
3h was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.5 mmol, 1.0 equiv.) and 4-ethynylbenzonitrile (95 mg, 0.75 mmol, 1.5 equiv.) and was isolated as a white solid (87 mg, 0.29 mmol, 58%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.14 (s, 1H), 7.91 (dd, J = 6.1 Hz, 4H), 5.34 – 5.28 (m, 1H), 5.26 – 5.23 (m, 1H), 4.92 (t, J = 5.6 Hz, 1H), 4.32 (s, 1H), 4.26 (s, 1H), 3.81 (s, 1H), 3.72 (q, J = 6.2 Hz, 1H), 3.64 – 3.56 (m, 1H);^{13}C NMR (75 MHz, DMSO-d_6)δ 175.2, 162.3, 133.3, 132.6, 124.5, 119.1, 118.1, 112.7, 88.0, 86.0, 83.2, 66.7, 60.5, 60.1; m.p. 151 – 152°C; IR (υ, cm^{-1}) = 3237, 3220, 2825, 2157, 1687, 1564, 1538, 1268, 1175, 985, 821;HRMS (ESI- TOF) calc. [$C_{16}H_{13}NO_5Na^+$] 322.0686, found 322.0683; $[\alpha]^{20}_D$ = +12.0 (0.1, $CHCl_3$).

1-((2R,3S,4S)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2H-pyran-5-yl)-3-(pyridin-3-yl)prop-2-yn-1-one (3i)



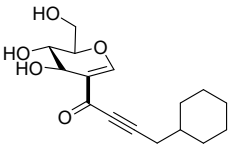
3i was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.500 mmol, 1.0 equiv.) and 3-ethynylpyridine (77 µL, 0.75 mmol, 1.5 equiv.) and was isolatedas a yellow solid (91 mg, 0.33 mmol, 66%).^{1}H NMR (300 MHz, DMSO-d_6) δ 8.89 (s, 1H), 8.67 (d, J = 4.8 Hz, 1H), 8.15 (s, 2H), 7.50 (s, 1H), 5.29 (dd, J = 22.0, 4.1 Hz, 2H), 4.91 (s, 1H), 4.30 (d, J = 12.8 Hz, 2H), 3.83 (s, 1H), 3.73 (d, J = 6.5 Hz, 1H), 3.64 – 3.55 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.8, 162.6, 153.3, 151.0, 140.5, 124.1, 119.5, 117.4, 88.4, 85.5, 83.6, 67.2, 61.1, 60.6; m.p. 137.8 – 138.4°C; IR (υ, cm^{-1}) = 3138, 2037, 1933, 1536, 1493, 1510, 1151, 987; HRMS (ESI- TOF) calc. [$C_{14}H_{13}NO_5$ +H$^+$] 276.0866, found 276.0867; $[\alpha]^{20}_D$ = –67.0 (0.1, $CHCl_3$).

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)hept-2-yn-1-one (3j)



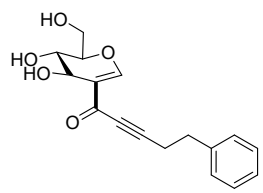
3j was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.500 mmol, 1.0 equiv.) and 1-hexyne (86 µL, 0.75 mmol, 1.5 equiv.) and was isolated as a white solid (26 mg, 0.10 mmol, 20%). ^{1}H NMR(300 MHz, CD_3OD) δ 8.05 (s, 1H), 6.77 (s, 1H), 4.49 (s, 1H), 4.37 (s, 1H), 4.04 – 3.95 (m, 3H), 3.93 – 3.86 (m, 2H), 2.53 (t, J = 7.0 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.55 (q, J = 7.4 Hz, 2H), 1.04 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 163.3, 149.0, 83.6, 81.1, 74.5, 70.9, 68.8, 63.7, 61.9, 31.1, 23.0, 19.1, 13.8; m.p. 111 – 112°C; IR (υ, cm^{-1}) = 3206, 2836, 2761, 2129, 1598, 1536, 1411, 1250, 1100, 980; HRMS (ESI- TOF) calc. [$C_{13}H_{18}O_5Na^+$] 277.1046, found 277.1040; $[\alpha]^{20}_D$ = +58.0 (0.05, $CHCl_3$).

4-Cyclohexyl-1-((2*R*,3*S*,4*S*)-3,4-dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)but-2-yn-1-one (3k)



3k was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.500 mmol, 1.0 equiv.) and 3-cyclohexylpropyne (108 µL, 0.750 mmol, 1.5 equiv.) and was isolated as a yellow solid (33 mg, 0.12 mmol, 23%).^{1}H NMR (300 MHz, CD_3OD) δ 8.05 (s, 1H), 4.50 (s, 1H), 4.38 (s, 1H), 4.05 – 3.83 (m, 5H), 2.42 (d, J = 6.4 Hz, 2H), 1.95 – 1.77 (m, 6H), 1.41 – 1.09 (m, 6H); ^{13}C NMR (75 MHz, CD_3OD) δ 178.9, 163.3, 120.2, 93.7, 83.6, 79.8, 68.8, 63.7, 62.0, 38.3, 33.8, 27.2, 27.2, 27.2; m.p. 109.2 – 112.4 °C; IR (υ, cm^{-1}) = 3209, 2823, 2757, 2136, 1566, 1529, 1402, 1259, 1177, 979, 806; HRMS (ESI- TOF) calc. [$C_{16}H_{22}O_5$+H$^+$] 295.1540, found 295.1546; $[\alpha]^{20}_D$ = +26.0 (0.05, $CHCl_3$).

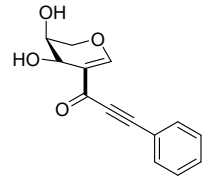
1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-5-phenylpent-2-yn-1-one (3l)



3l was synthesized according to General Procedure A using 2-iodoglucal (136 mg, 0.500 mmol, 1.0 equiv.) and 4-phenyl-1-butyne (105 µL, 0.750 mmol, 1.5 equiv.) and was isolated as a yellow solid (51 mg, 0.17 mmol, 34%).^{1}H NMR (300 MHz, DMSO-d_6) δ 7.68 (s, 1H), 7.35 – 7.23 (m, 5H), 5.17 (m, 2H), 4.88 (t, J = 5.6 Hz, 1H), 4.24 (s, 1H), 4.17 (s, 1H), 3.76 (s, 1H), 3.70 – 3.53 (m, 2H), 2.87 (t, J = 7.2 Hz, 2H), 2.77 (d, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.8, 160.9, 140.0, 128.4, 128.3, 126.3, 118.8, 91.4, 82.8, 78.4, 66.7, 60.5, 60.1, 33.1, 19.9; m.p. 127 – 128°C; IR (υ,

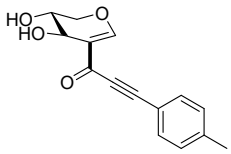
cm^{-1}) = 3204, 2835, 2767, 2133, 1564, 1533, 1412, 1250, 1170, 810; HRMS (ESI- TOF) calc. [$C_{17}H_{18}O_5Na^+$] 325.1046, found 325.1048; $[\alpha]^{20}_D$ = +62.0(0.1, $CHCl_3$).

1-((3*S*,4*S*)-3,4-Dihydroxy-3,4-dihydro-2*H*-pyran-5-yl)-3-phenylprop-2-yn-1-one (3m)



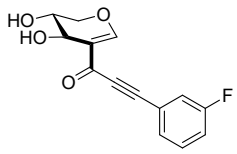
3m was synthesized according to General Procedure A using 2-iodo-L-arabinal (121 mg, 0.500 mmol, 1.0 equiv.) and phenylacetylene (82 μL, 0.75 mmol, 0.75 mmol, 1.5 equiv.) and was isolated as a yellow solid (50 mg, 0.21 mmol, 41%).^{1}H NMR (300 MHz, CD_3OD) δ 8.14 (s, 1H), 7.73 (m, 2H), 7.57 (m, 3H), 4.79 (m, 1H), 4.23 (m, 2H), 4.07 (m, 2H), 3.92 (m, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ 176.1, 163.7, 148.8, 132.5, 130.4, 128.5, 119.9, 89.8, 84.9, 69.8, 66.5, 64.2; m.p. 118 – 120 °C; IR (υ, cm^{-1}) = 3278, 2823, 2130, 1559, 1344, 1276, 1164, 1030, 959, 735);HRMS (ESI- TOF) calc. [$C_{14}H_{12}NO_4$ + H^+] 245.0808, found 245.0806; $[\alpha]^{20}_D$ = –159.0 (0.1, $CHCl_3$).

1-((3*R*,4*S*)-3,4-Dihydroxy-3,4-dihydro-2*H*-pyran-5-yl)-3-(p-tolyl)prop-2-yn-1-one (3n)



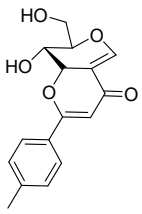
3n was synthesized according to General Procedure A and using 2-iodo-D-xylal (121 mg, 0.500 mmol, 1.0 equiv.) and 4-ethynyltoluene (95 μL, 0.75 mmol, 1.5 equiv.) and was isolated as a yellow solid (115 mg, 0.445 mmol, 89%).^{1}H NMR (300 MHz, CD_3OD) δ 8.26 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.59 (s, 1H), 4.49 – 4.28 (m, 2H), 4.00 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 178.6, 164.8, 142.8, 133.9, 130.7, 120.1, 118.3, 91.9, 86.0, 68.8, 67.2, 61.1, 21.8; m.p. 85.7 – 86.3°C; IR (υ, cm^{-1}) = 3274, 2123, 1551, 1203, 1166, 1015, 991, 966, 799; HRMS (ESI- TOF) calc. [$C_{15}H_{14}O_4Na^+$] 281.0784, found 281.0781; $[\alpha]^{20}_D$ = –194.0 (0.1, $CHCl_3$).

1-((3*R*,4*S*)-3,4-Dihydroxy-3,4-dihydro-2*H*-pyran-5-yl)-3-(3-fluorophenyl)prop-2-yn-1-one (3o)



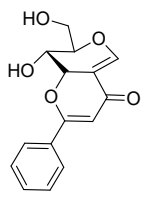
3o was synthesized according to General Procedure A and using 2-iodo-D-xylal (121 mg, 0.500 mmol, 1.0 equiv.) and 1-ethynyl-3-fluorobenzene (87μL, 0.75 mmol, 1.5 equiv.) and was isolated as a white solid (68 mg, 0.26 mmol, 52%). ^{1}H NMR (300 MHz, CD_3OD) δ 8.24 (s, 1H), 7.54 (s, 2H), 7.47 (d, *J* = 9.5 Hz, 1H), 7.38 – 7.30 (m, 1H), 4.55 (s, 1H), 4.32 (q, 2H), 3.96 (s, 1H); ^{13}C NMR (75 MHz, CD_3OD) δ178.1, 165.4, 163.7 (d, *J* = 246.5 Hz), 162.1, 131.9 (d, *J* = 8.6 Hz) 129.9 (d, *J* = 3,1 Hz) 123.3 (d, *J* = 9.5 Hz), 120.1 (d, *J* = 3.1 Hz),118.9 (d, *J* = 21.5 Hz), 89.2, 86.4, 68.7, 67.1, 61.0; m.p. 141.3 – 142.6°C; IR (υ, cm^{-1}) = 3265, 2130, 1536, 1440, 1380, 1275, 1210, 1156, 980, 860; HRMS (ESI- TOF) calc. [$C_{14}H_{11}FO_4$ + H^+] 263.0714, found 263.0717; $[\alpha]^{20}_D$ = –168.0.

(7*R*,8*S*,8a*R*)-8-Hydroxy-7-(hydroxymethyl)-2-(p-tolyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4a)



4a was synthesized according to General Procedure Band using **3a** (58 mg, 0.20 mmol, 1.0 equiv.) and $AuCl_3$ (6.0 mg, 0.02 mmol, 10 mol%) and was isolated as a white solid (43 mg, 0.15 mmol, 74%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.37 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.06 (s, 2H), 5.10 (d, *J* = 7.3 Hz, 1H), 4.90 (s, 1H), 4.13 – 3.96 (m, 2H), 3.80 (d, *J* = 17.3 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ 181.6, 168.0, 151.0, 142.2, 130.1, 129.8, 126.8, 108.9, 102.4, 80.8, 79.4, 64.7, 59.9, 21.5; m.p. 172.8 – 173.9°C; IR (υ, cm^{-1}) = 3306, 2829, 1600, 1538, 1460, 1341, 1210, 1143, 1095, 1026, 808;HRMS (ESI- TOF) calc. [$C_{16}H_{16}O_5$+ H^+] 289.1071, found 289.1072; $[\alpha]^{20}_D$ = –344.0 (0.1, $CHCl_3$).

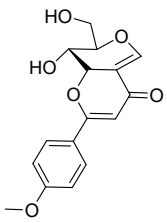
(7*R*,8*S*,8a*R*)-8-Hydroxy-7-(hydroxymethyl)-2-phenyl-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4b)



4b was synthesized according to General Procedure B using **3b** (55 mg, 0.20 mmol, 1.0 equiv.) $AuCl_3$ (6.0 mg, 0.02 mmol, 10 mol%) and was isolated as a white solid (31 mg, 0.11 mmol, 56%). ^{1}H NMR (300 MHz, CD_3OD) δ 8.42 (s, 1H), 7.67 (t, *J* = 10.6 Hz, 2H), 7.56 – 7.34 (m, 3H), 4.74 – 4.59 (m, 1H), 4.22 (m, 1H), 3.90 – 3.74 (m, 3H);^{13}C NMR (75 MHz, CD_3OD) δ 189.7, 159.5,

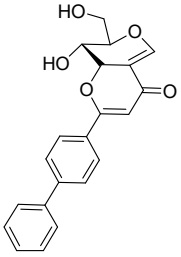
151.9, 134.2, 132.1, 130.0, 121.0, 105.8, 101.4, 69.3, 69.3, 65.9, 65.5; m.p. 157 – 159 °C; IR (υ, cm^{-1}) = 3308, 2836, 1605, 1542, 1466, 1344, 1200, 1140, 1015, 890;HRMS (ESI- TOF) calc. [$C_{15}H_{14}O_5$ + H^+]: 275.0914, found: 275.0920; $[\alpha]^{20}_D$ = –359.0 (0.1, $CHCl_3$).

(7*R*,8*S*,8a*R*)-8-Hydroxy-7-(hydroxymethyl)-2-(4-methoxyphenyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4c)



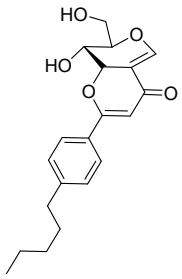
4c was synthesized according to General Procedure B and obtained using **3d**(61 mg, 0.20 mmol, 1.0 equiv.) $AuCl_3$ (6.0 mg, 0.02 mmol, 10 mol%) and was isolated as a yellow solid (47 mg, 0.15 mmol, 77%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.91 (d, *J* = 9.1 Hz, 2H), 7.50 (s, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.05 (s, 1H), 5.19 (d, *J* = 7.7 Hz, 1H), 4.35 – 4.26 (m, 1H), 4.09 (dd, *J* = 22.9, 10.7 Hz, 3H), 3.93 (s, 3H);^{13}C NMR (75 MHz, DMSO-d_6) δ181.1, 166.9, 150.6, 143.0, 138.9, 131.3, 129.0, 128.1, 127.0, 126.9, 126.8, 108.4, 102.5, 80.3, 79.0, 64.2, 59.4; m.p. 153.6 – 155.1°C; IR (υ, cm^{-1}) = 3306, 2829, 1600, 1538, 1460, 1341, 1210, 1143, 1095, 1026, 808;HRMS (ESI- TOF) calc. [$C_{16}H_{16}O_6$ + H^+]305.1020, found 305.1024; $[\alpha]^{20}_D$ = –194.0 (0.1, $CHCl_3$).

(7*R*,8*S*,8a*R*)-2-([1,1'-Biphenyl]-4-yl)-8-hydroxy-7-(hydroxymethyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4d)



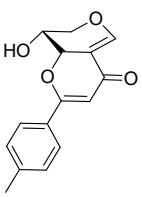
4d was synthesized according to General Procedure B and using **3e** (70 mg, 0.20 mmol, 1.0 equiv.) $AuCl_3$ (6.0 mg, 0.02 mmol, 10 mol%) and was isolatedas a yellow solid (44 mg, 0.13 mmol, 63%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.01 – 7.88 (m, 2H), 7.70 (m, 4H), 7.45 – 7.26 (m, 4H), 6.08 (s, 1H), 6.00 (s, 1H), 5.05 (d, J = 7.4 Hz, 1H), 4.81 (s, 1H), 3.99 (m, 2H), 3.78 (m, 2H);^{13}C NMR (75 MHz, DMSO-d_6) δ 181.6, 167.5, 151.2, 143.5, 139.4, 131.8, 129.5, 128.7, 127.5, 127.5, 127.3, 108.9, 103.1, 80.8, 79.5, 64.8, 59.9; m.p. 132 – 134 °C; IR (υ, cm^{-1}) = 3229, 2827, 2758, 1601,1538, 1367, 1210, 1032, 1022, 747, 676;HRMS (ESI- TOF) calc. [$C_{21}H_{18}O_5$+ H^+]351.1227, found 351.1227; $[\alpha]^{20}_D$ = –249.0 (0.1, $CHCl_3$).

(7*R*,8*S*,8a*R*)-8-Hydroxy-7-(hydroxymethyl)-2-(4-pentylphenyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4e)



4e was synthesized according to General Procedure B and using **3c** (68 mg, 0.20 mmol, 1.0 equiv.) $AuCl_3$ (6.0 mg, 0.02 mmol, 10 mol%) and was isolatedas a yellow solid (42 mg, 0.12 mmol, 61%). ^{1}H NMR (300 MHz, CD_3OD) δ 7.69 (d, J = 7.9 Hz, 2H), 7.33 (s, 1H), 7.19 (d, J= 7.9 Hz, 2H), 5.93 (s, 1H), 5.03 (d, J = 7.5 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.97 – 3.81 (m, 3H), 2.56 (t, J = 7.7 Hz, 2H), 1.53 (t, J = 7.8 Hz, 2H), 1.28 – 1.19 (m, 4H), 0.80 (t, J = 6.6 Hz, 3H);^{13}C NMR (75 MHz, CD_3OD) δ 185.0, 171.6, 152.9, 148.9, 131.3, 129.9, 127.9, 109.8, 102.6, 81.7, 80.6, 66.1, 61.2, 36.8, 32.6, 32.0, 23.5, 14.3; m.p. 146 – 148 °C; IR (υ, cm^{-1}) = 3215, 2829, 2762, 1603, 1540, 1369, 1208, 1030, 1018, 780; HRMS (ESI- TOF) calc. [$C_{20}H_{24}O_5$ + H^+]: 345.1697, found: 345.1691; $[\alpha]^{20}_D$ = –169.0 (0.1, $CHCl_3$).

(8*R*,8a*R*)-8-Hydroxy-2-(4-pentylphenyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4f)

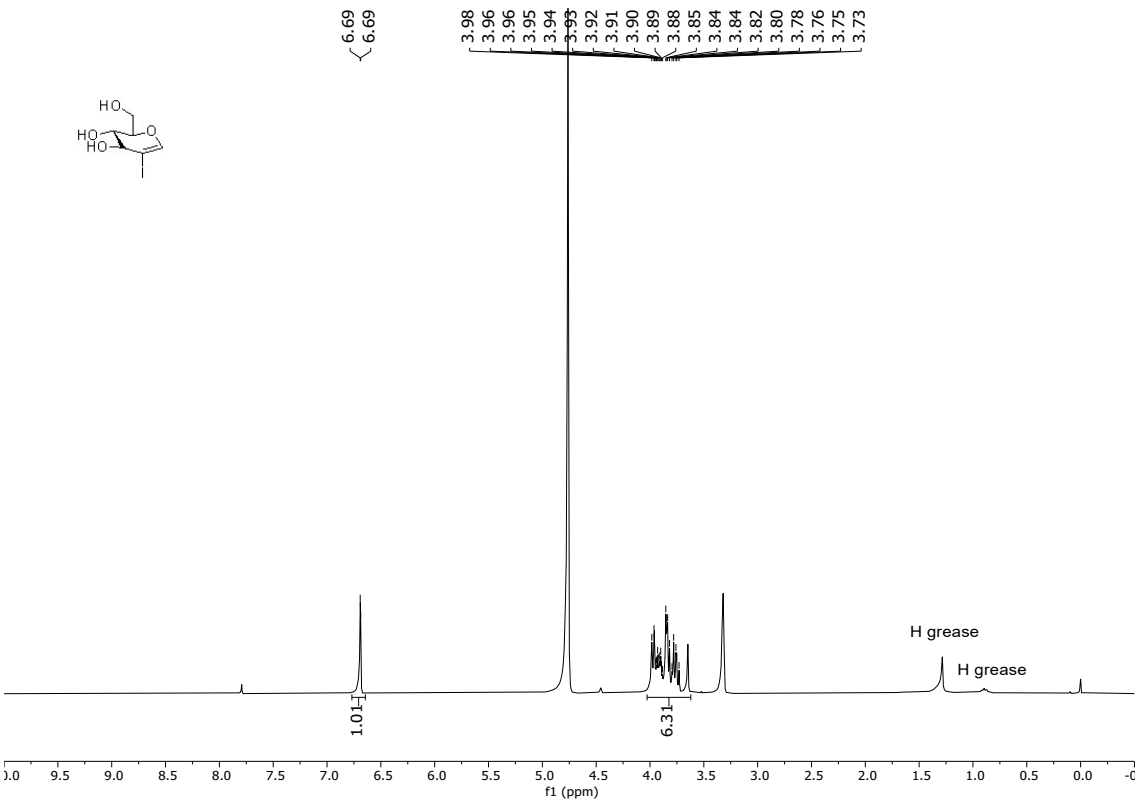


4f was synthesized according to General Procedure B and using **3n** (52 mg, 0.20 mmol, 1.0 equiv.) and $AuCl_3$ (6.0 mg, 0.02 mmol, 10 mol%) and was isolated as a yellow solid (23 mg, 0.09 mmol, 44%). ^{1}H NMR (300 MHz, CD_3OD) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.48 (s, 1H), 7.35 (d, *J* = 7.9 Hz,

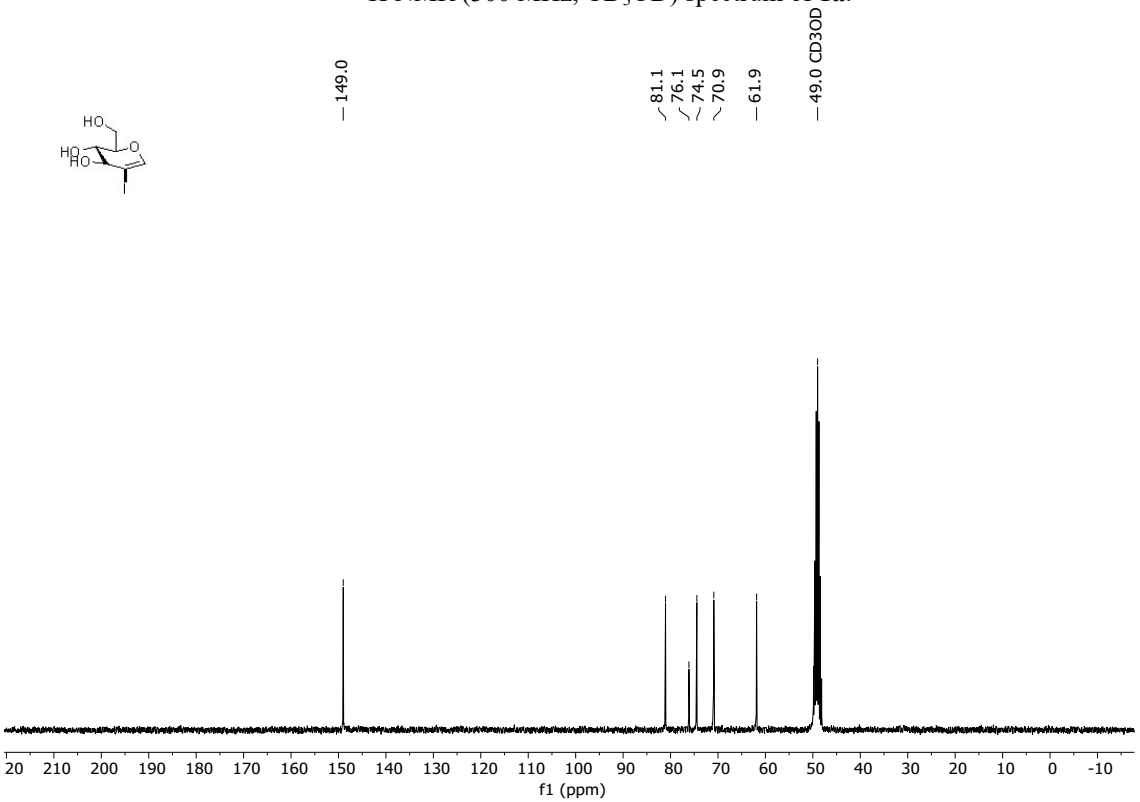
2H), 6.09 (s, 1H), 5.12 (d, J = 7.0 Hz, 1H), 4.47 – 4.27 (m, 2H), 4.01 (t, J = 10.8 Hz, 1H), 2.46 (s, 3H);^{13}C NMR (75 MHz, CD_3OD) δ 185.1, 171.5, 153.5, 144.0, 131.0, 130.5, 127.8, 109.8, 102.7, 80.0, 69.8, 66.2, 21.5; m.p. 91 – 93°C; IR (υ, cm^{-1}) = 3309, 2858, 1620, 1542, 1460, 1344, 1200, 1141, 1080, 810;HRMS (ESI- TOF) calc. [$C_{15}H_{14}O_4$+H^+] 259.0965, found 259.0964; $[\alpha]^{20}_D$ = –194.0 (0.1, $CHCl_3$).

4. ^{1}H and ^{13}C NMR spectra

(2*R*,3*S*,4*R*)-2-(Hydroxymethyl)-5-iodo-3,4-dihydro-2*H*-pyran-3,4-diol (1a)

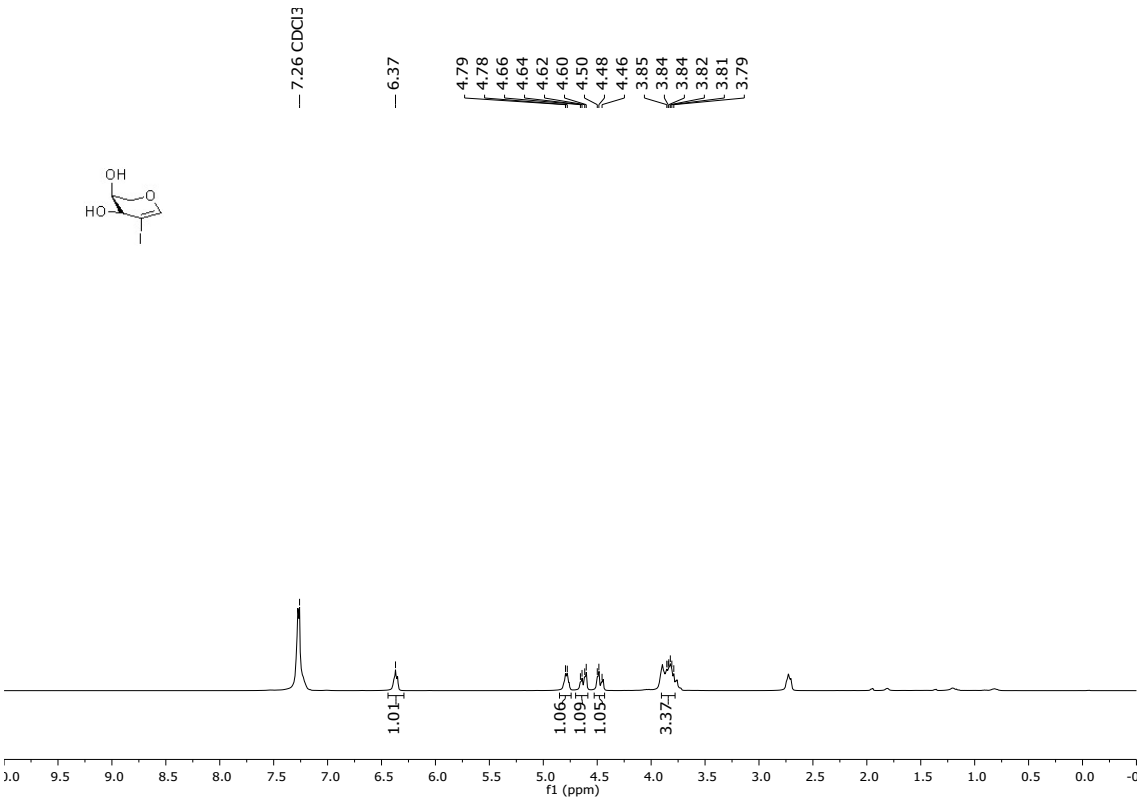


^{1}H NMR (300 MHz, CD_3OD) spectrum of **1a**.

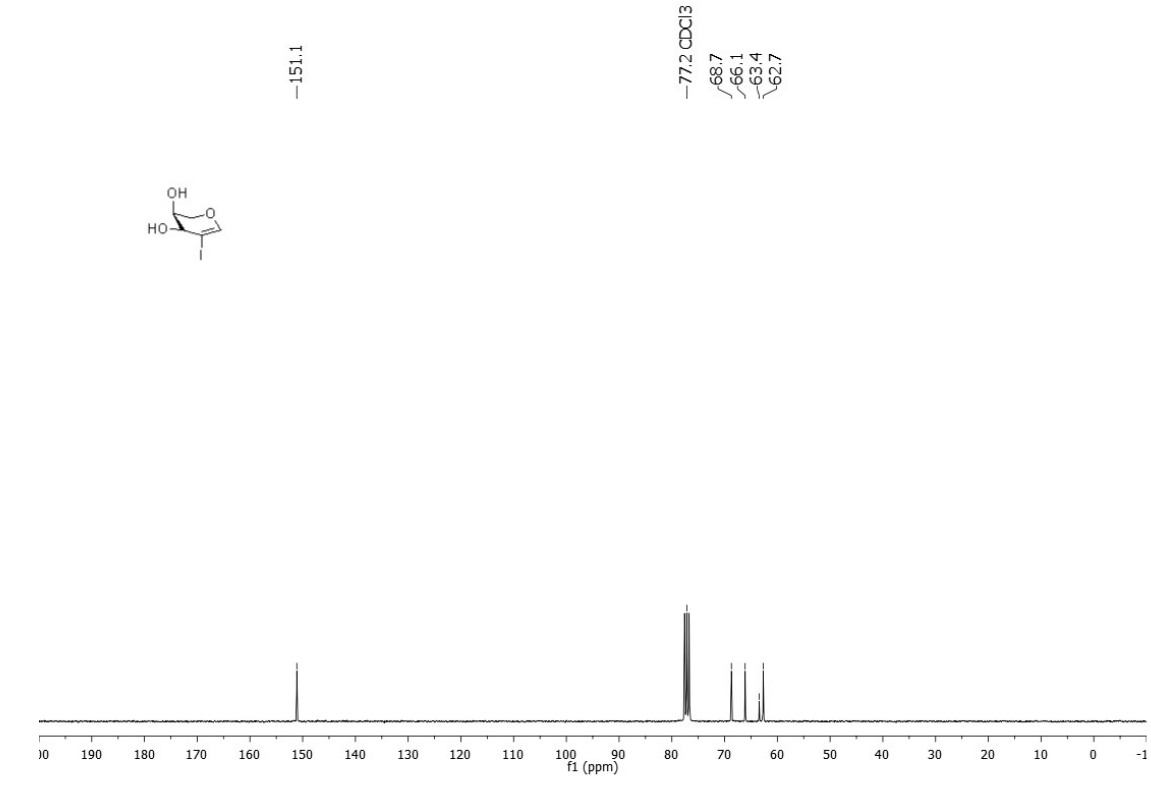


^{13}C NMR (75 MHz, CD_3OD) spectrum of **1a**.

(3*S*,4*R*)-5-iodo-3,4-dihydro-2*H*-pyran-3,4-diol (1b)

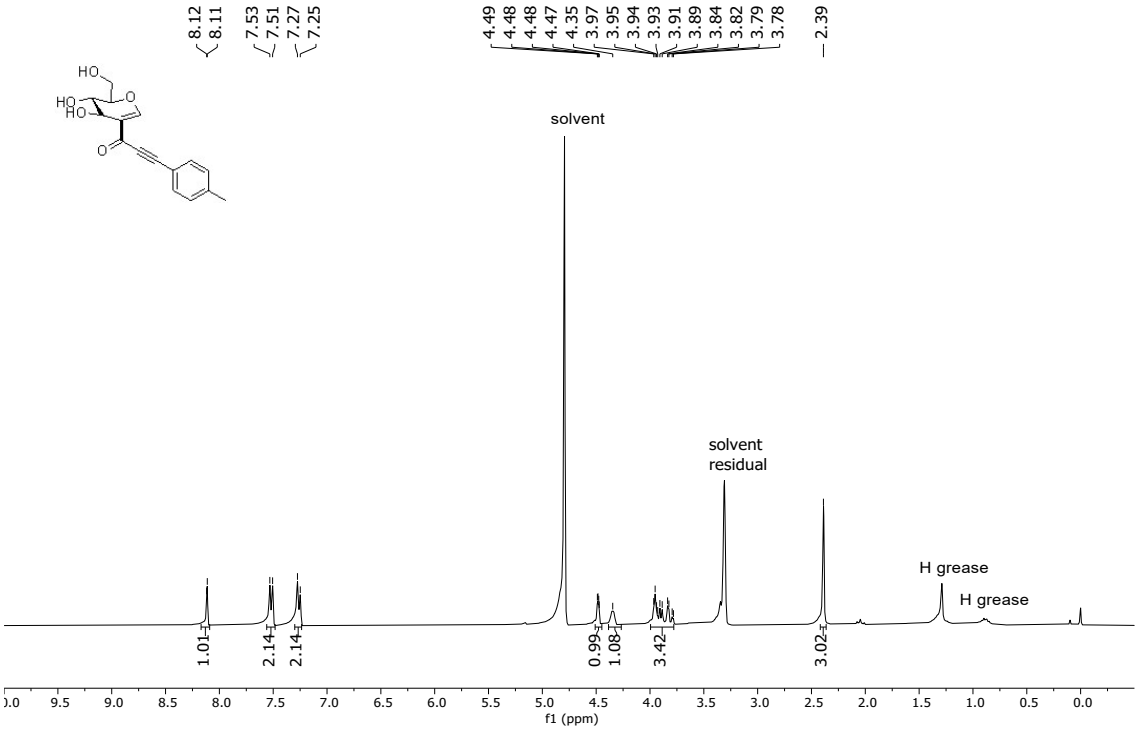


^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **1b**.

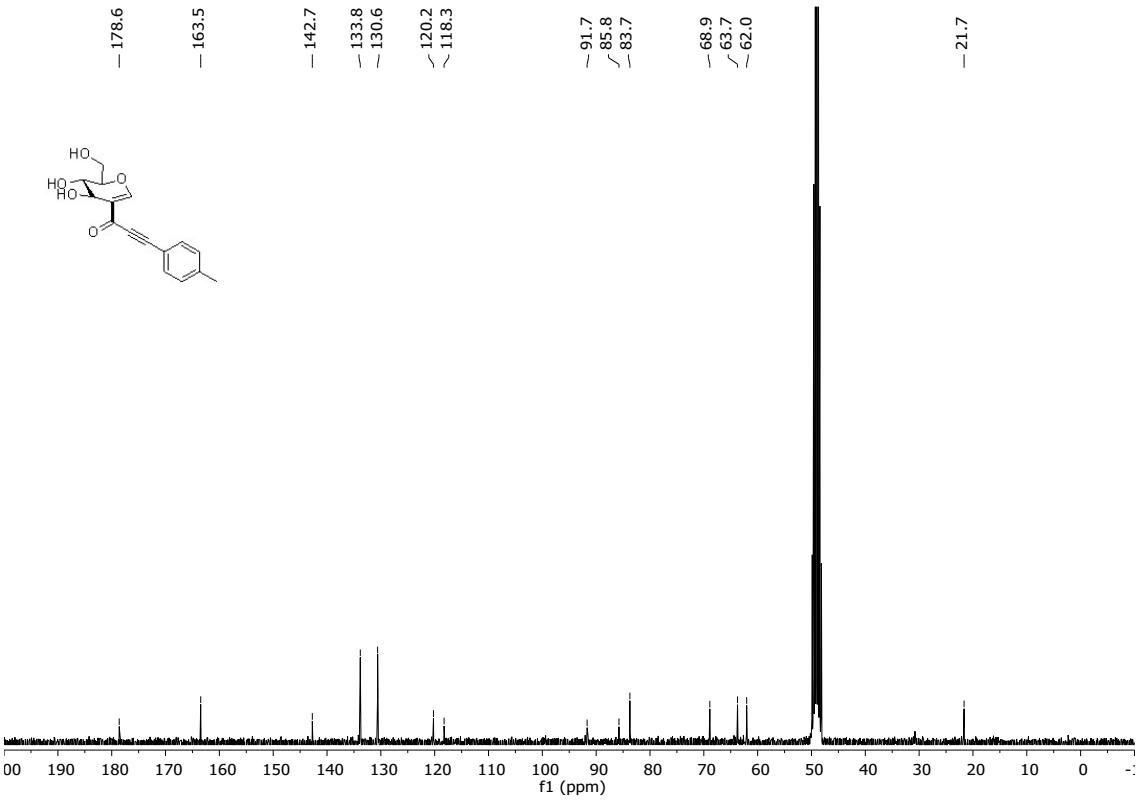


^{13}C NMR (75 MHz, $CDCl_3$) spectrum of **1b**

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(p-tolyl)-prop-2-yn-1-one (3a)

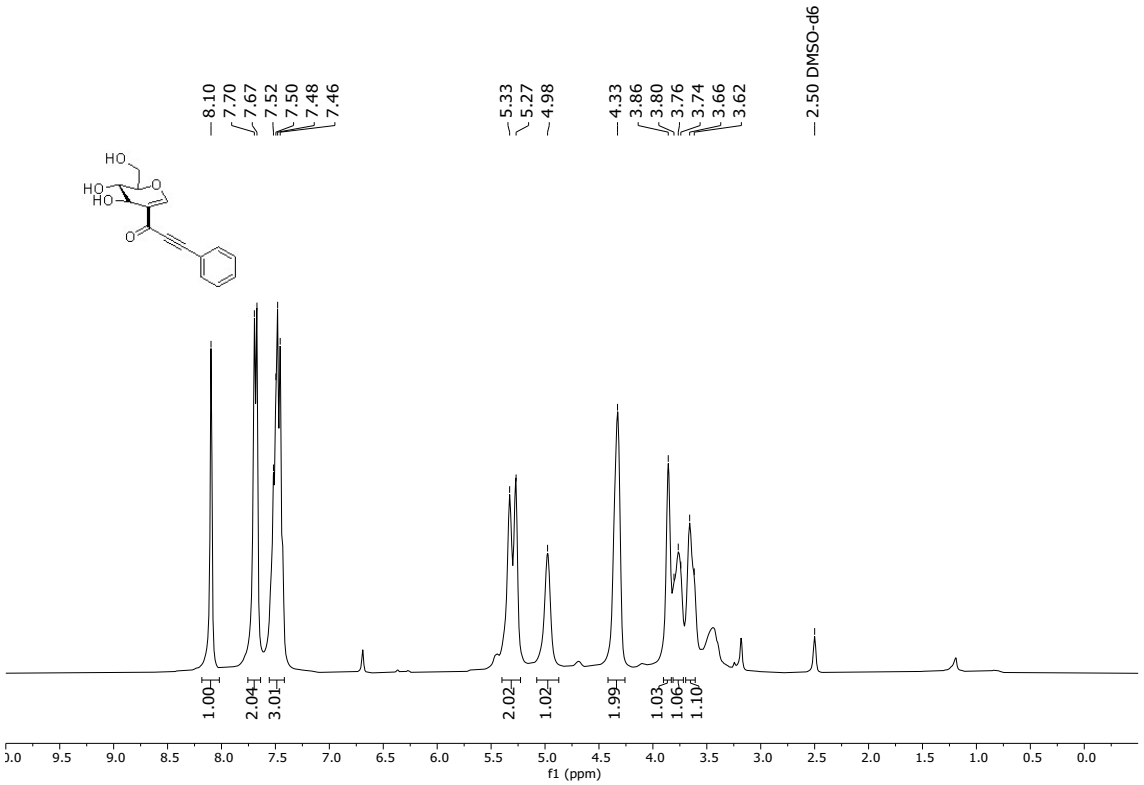


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3a**.

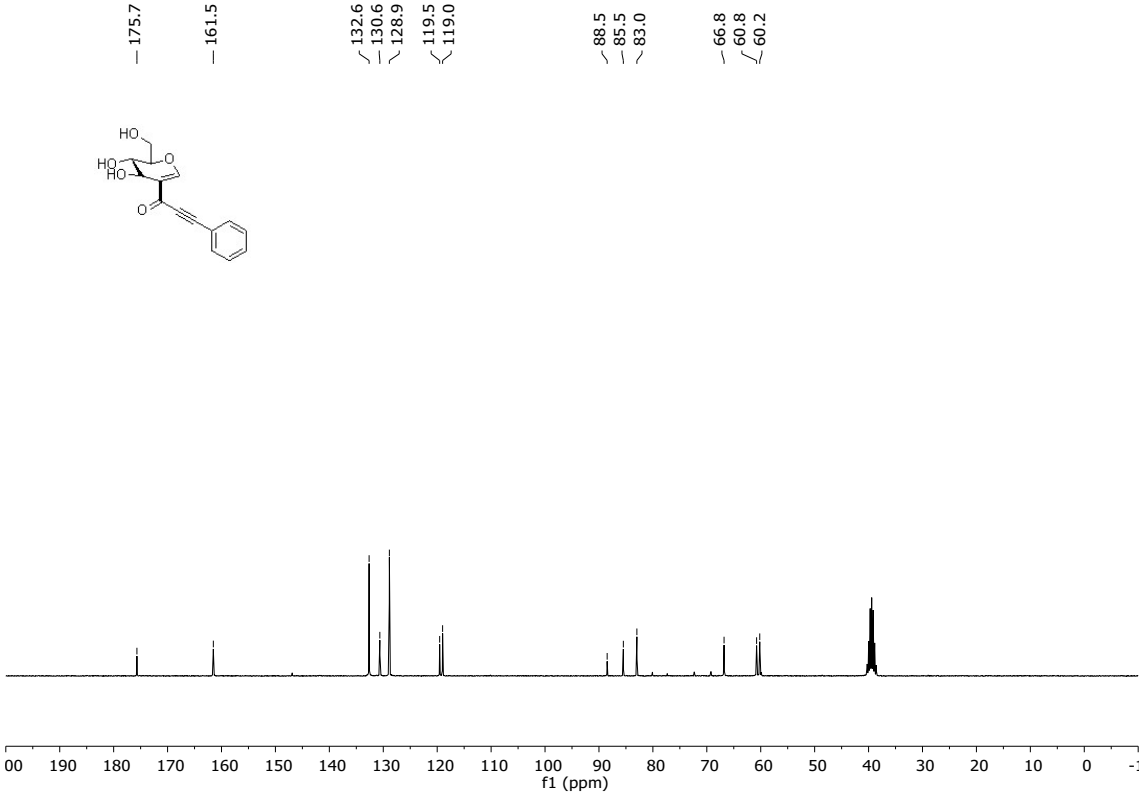


^{13}C NMR (75 MHz, CD_3OD) spectrum of **3a**.

1-((2R,3S,4S)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-phenylprop-2-yn-1-one (3b)

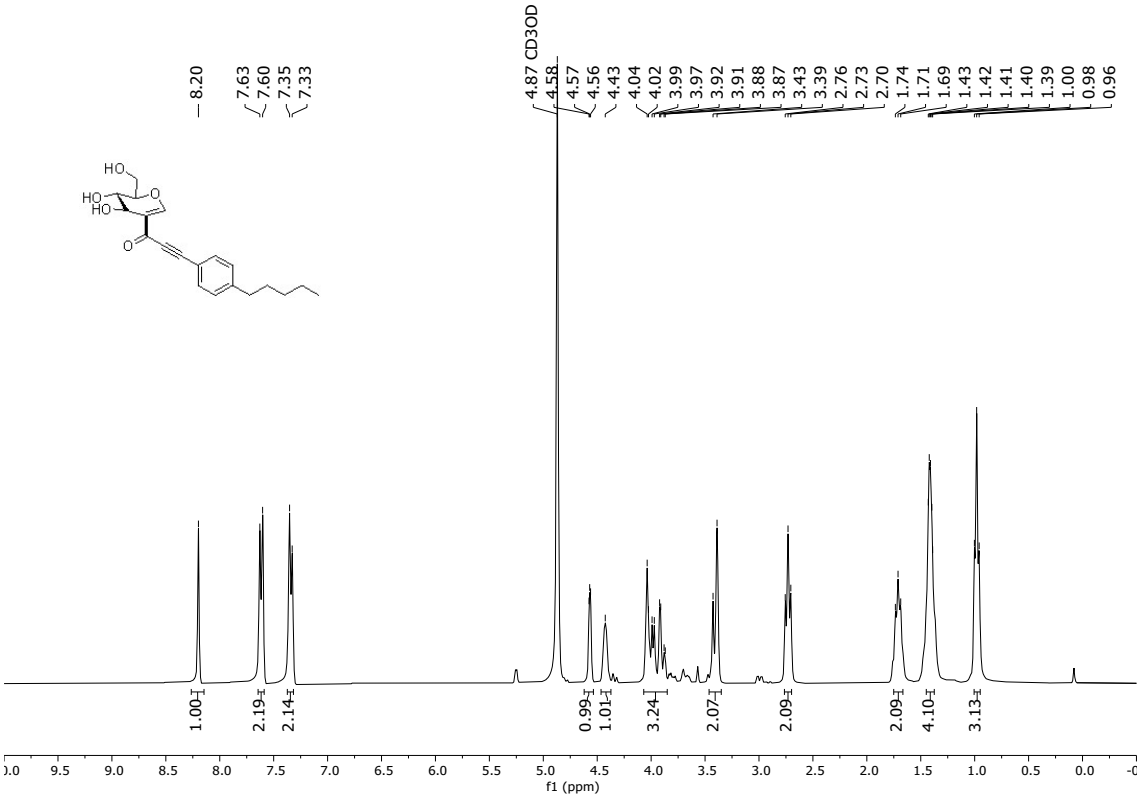


^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **3b**.

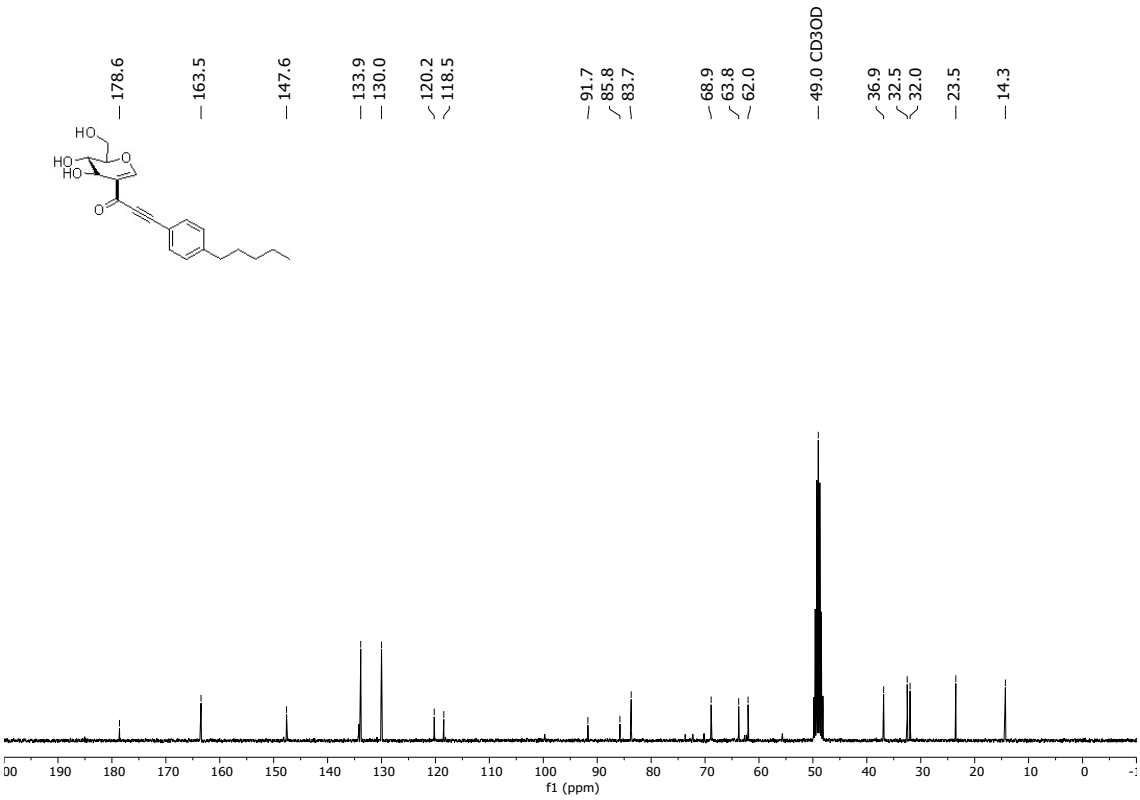


^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **3b**.

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(4-pentylphenyl)prop-2-yn-1-one (3c)

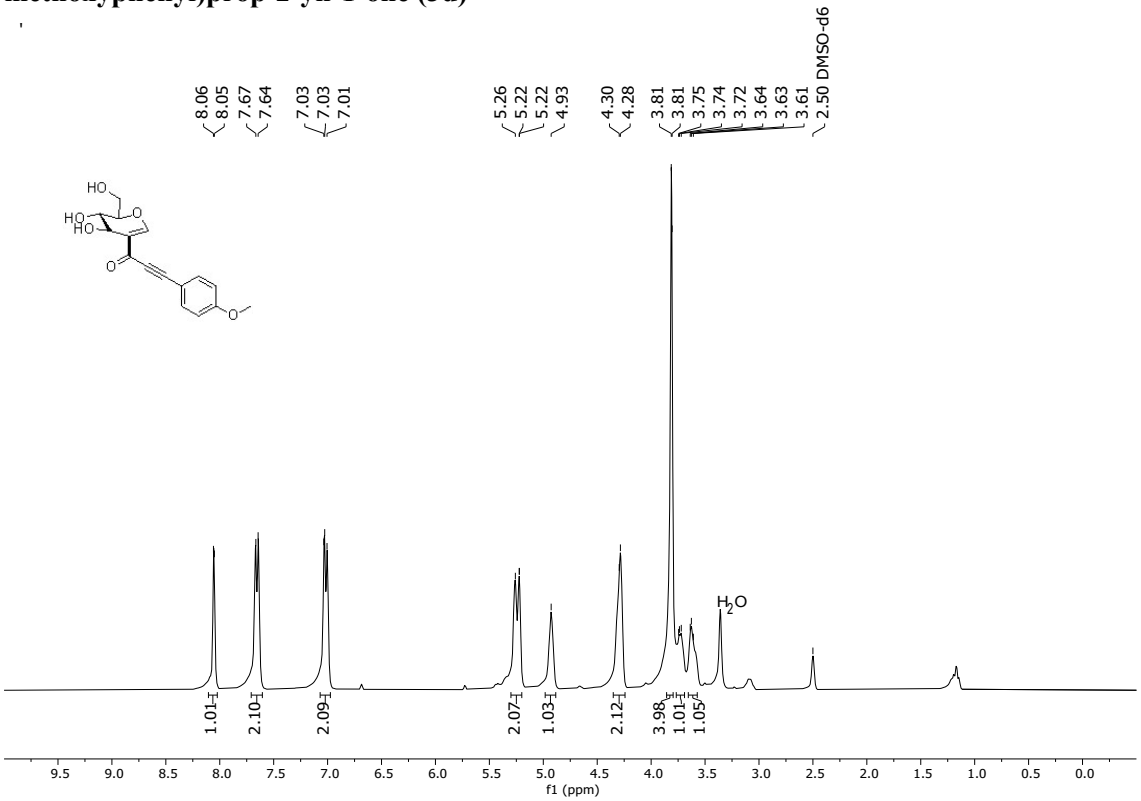


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3c**.

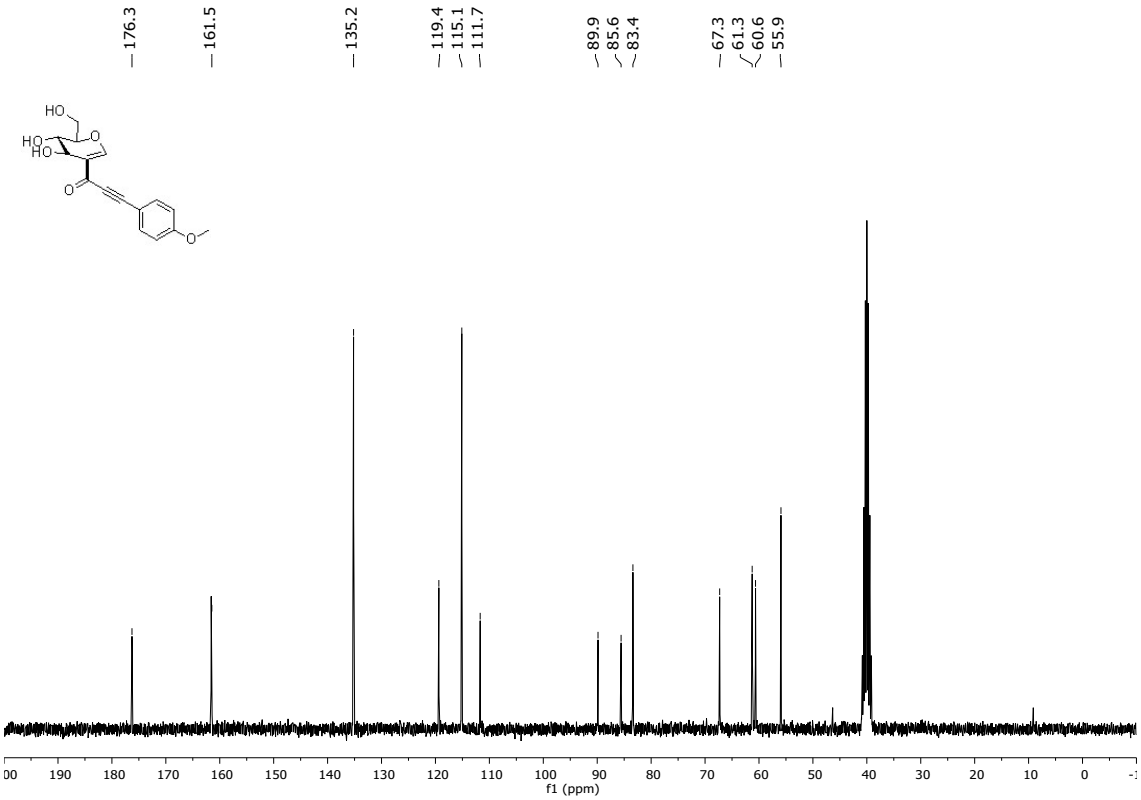


^{13}C NMR (75 MHz, CD_3OD) spectrum of **3c**.

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(4-methoxyphenyl)prop-2-yn-1-one (3d)

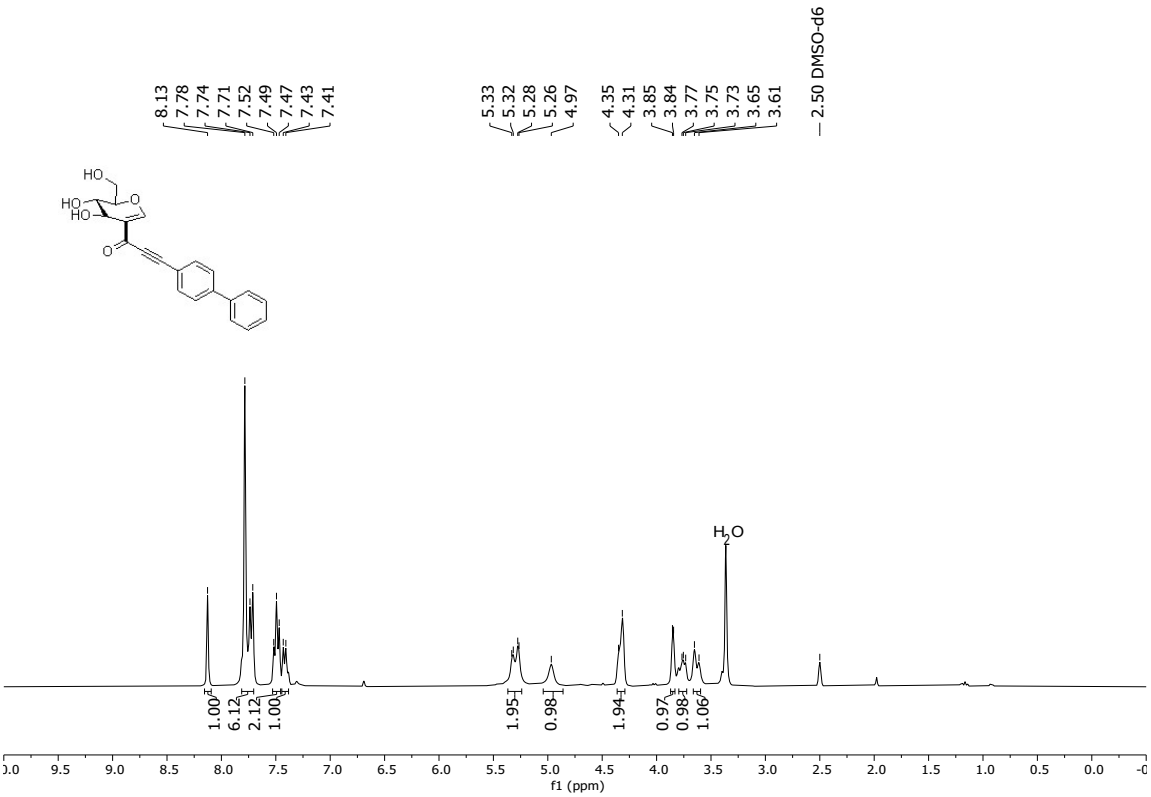


^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **3d**.

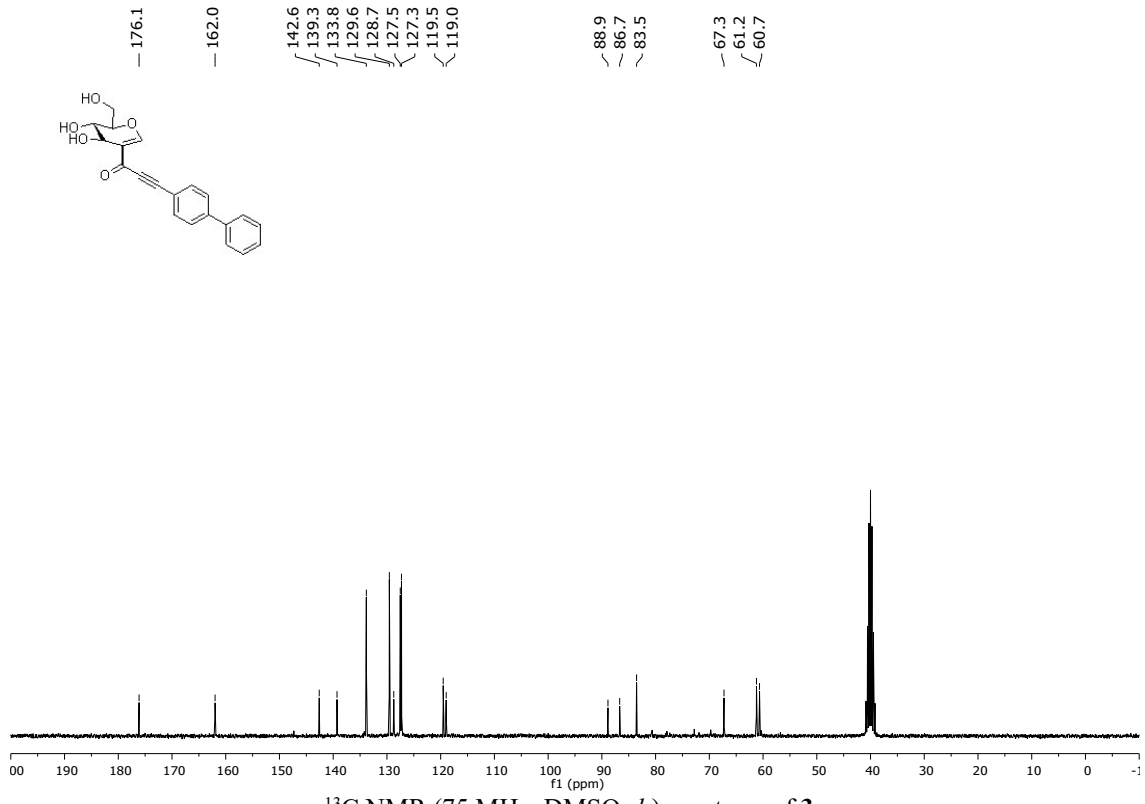


^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **3d**.

3-([1,1'-Biphenyl]-4-yl)-1-((2R,3S,4S)-3,4-dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)prop-2-yn-1-one (3e)

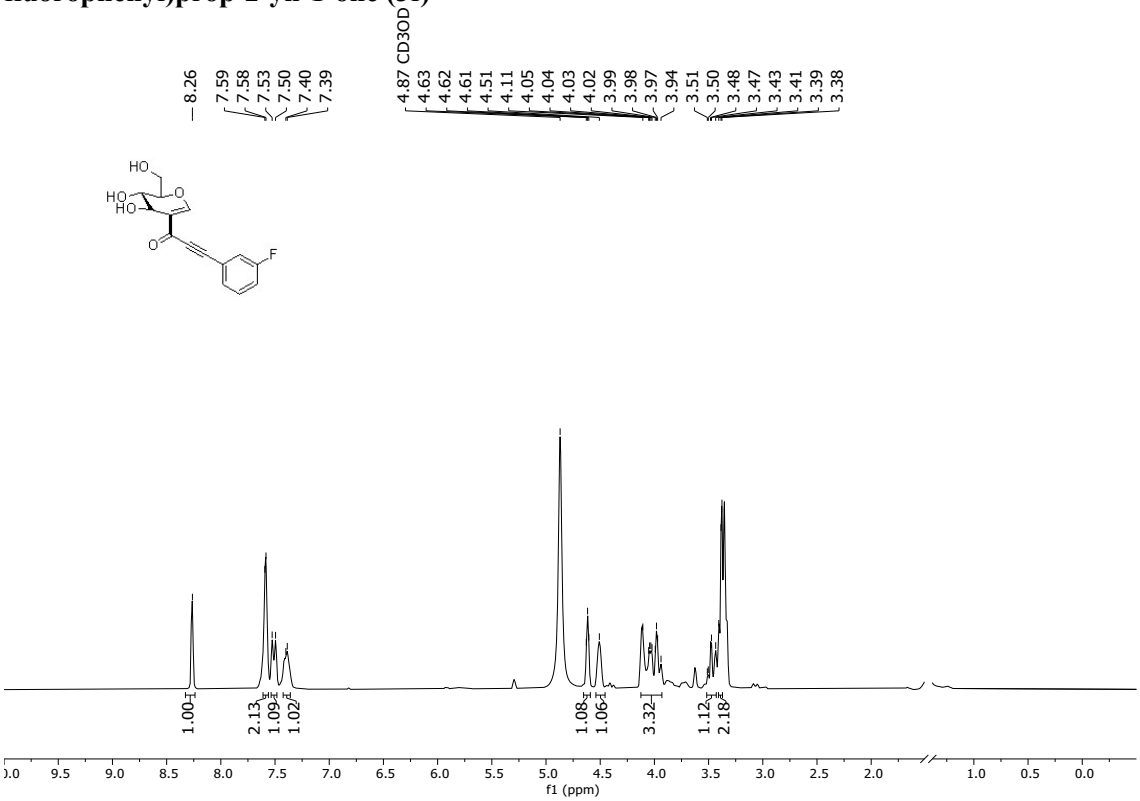


^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **3e**.

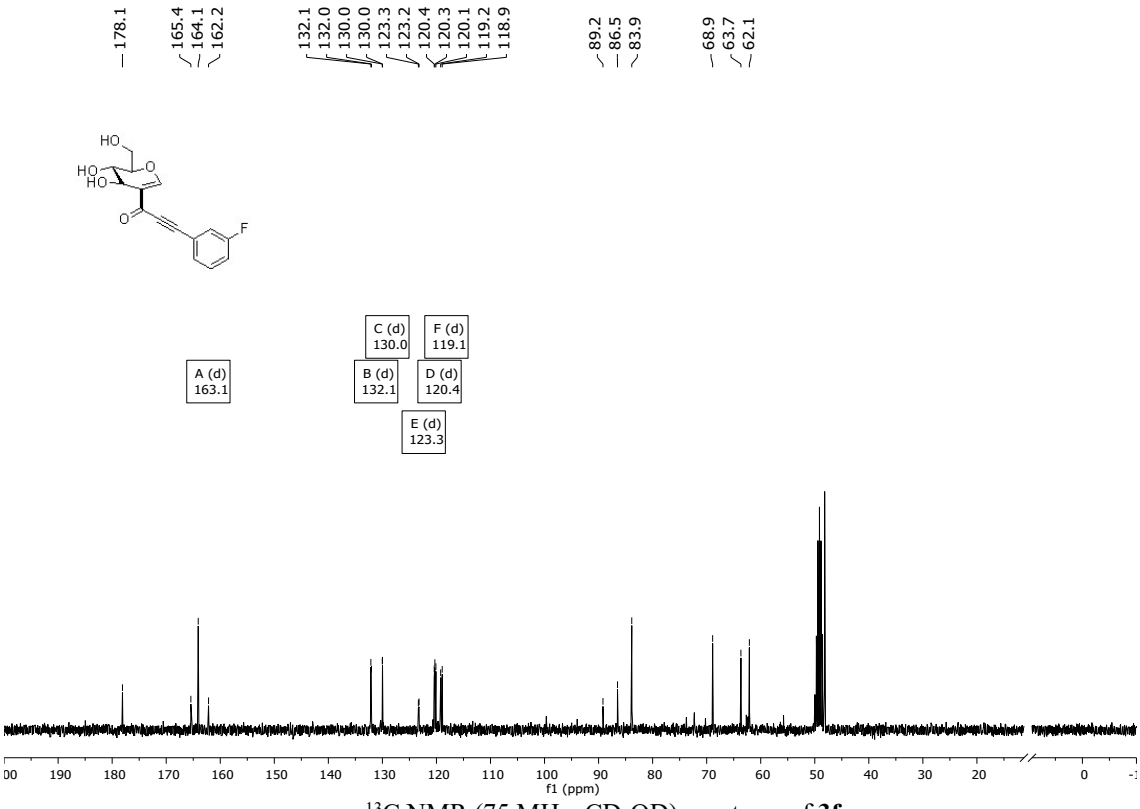


^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **3e**

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(3-fluorophenyl)prop-2-yn-1-one (3f)

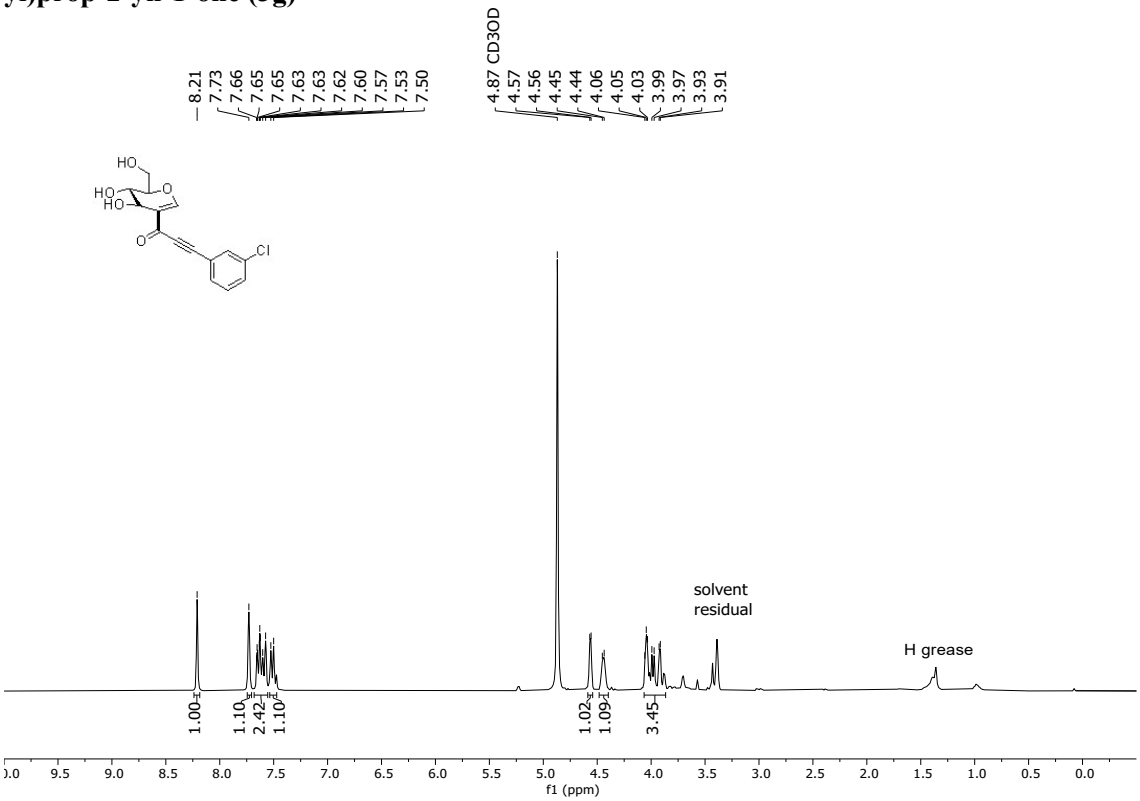


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3f**.

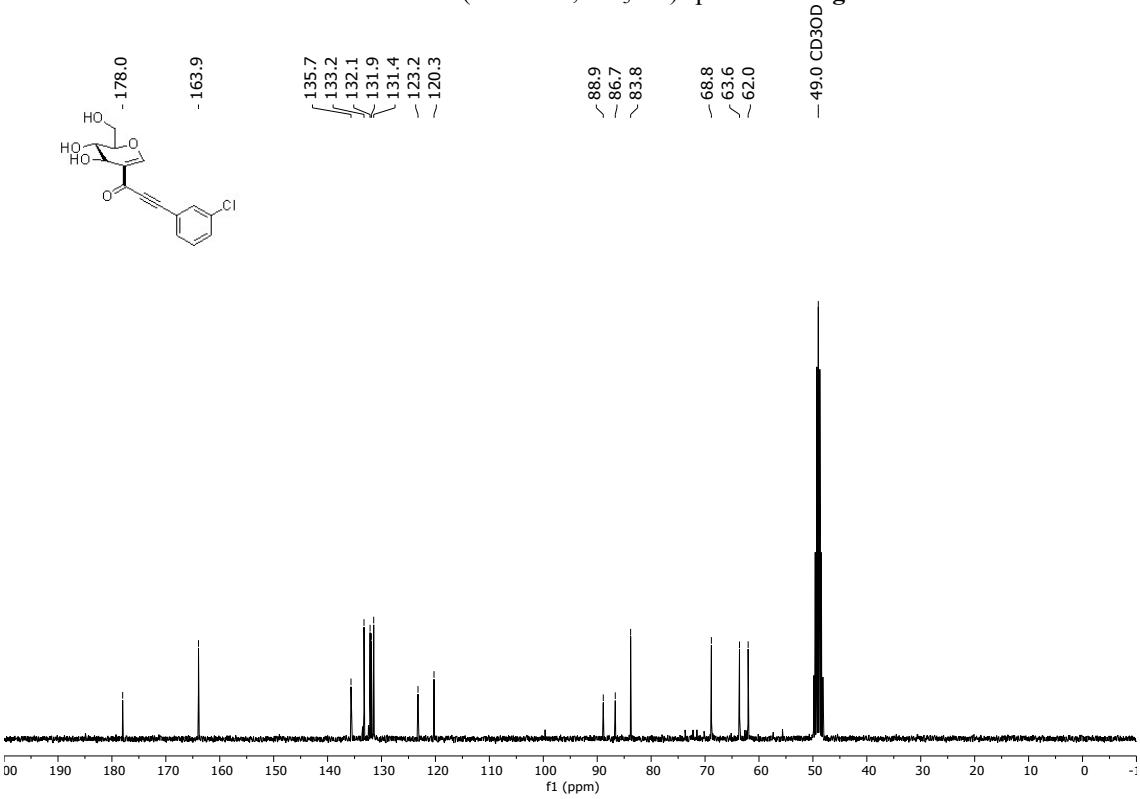


^{13}C NMR (75 MHz, CD_3OD) spectrum of **3f**.

3-(3-Chlorophenyl)-1-((2R,3S,4S)-3,4-dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)prop-2-yn-1-one (3g)

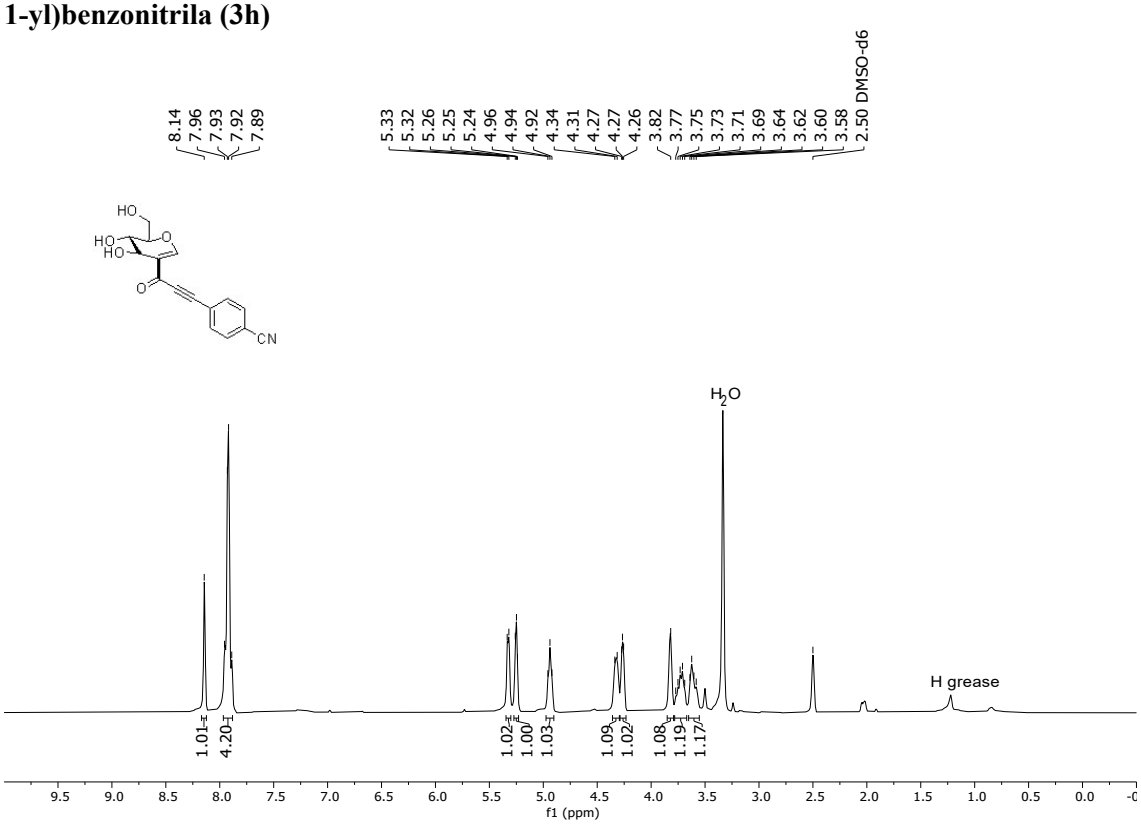


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3g**.

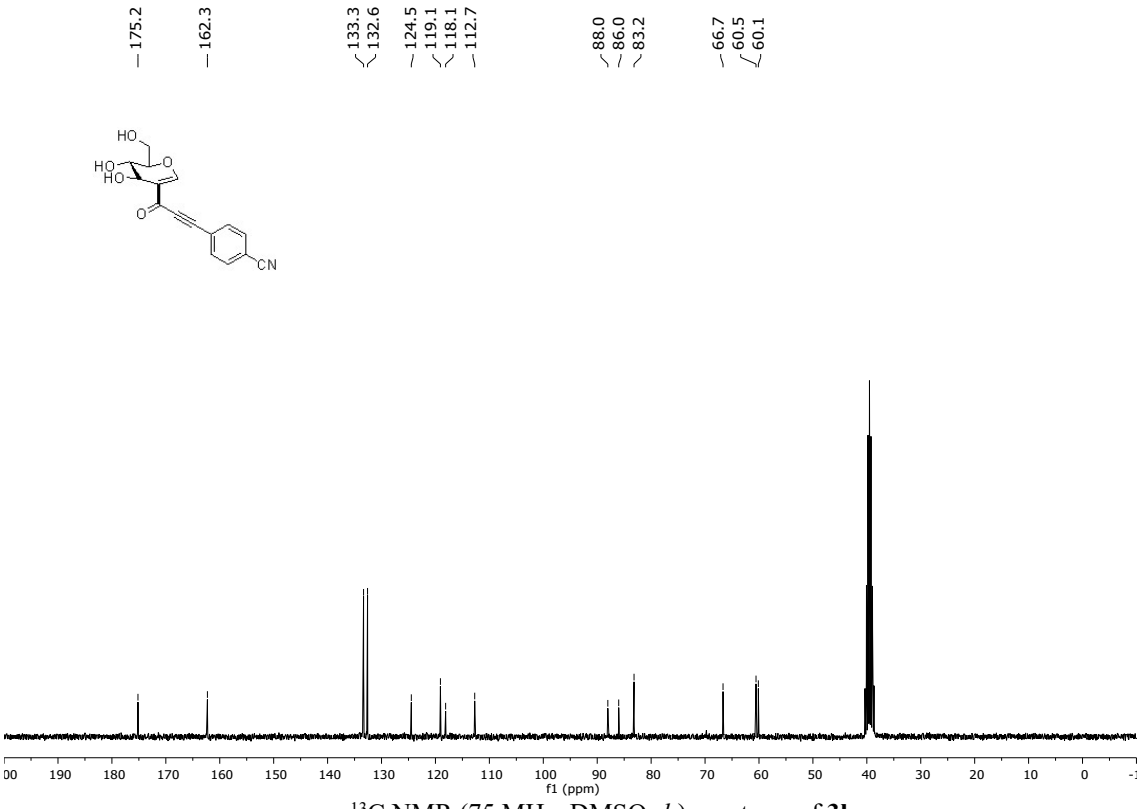


^{13}C NMR (75 MHz, CD_3OD) spectrum of **3g**.

4-(3-((2R,3S,4S)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-oxoprop-1-yn-1-yl)benzonitrila (3h)

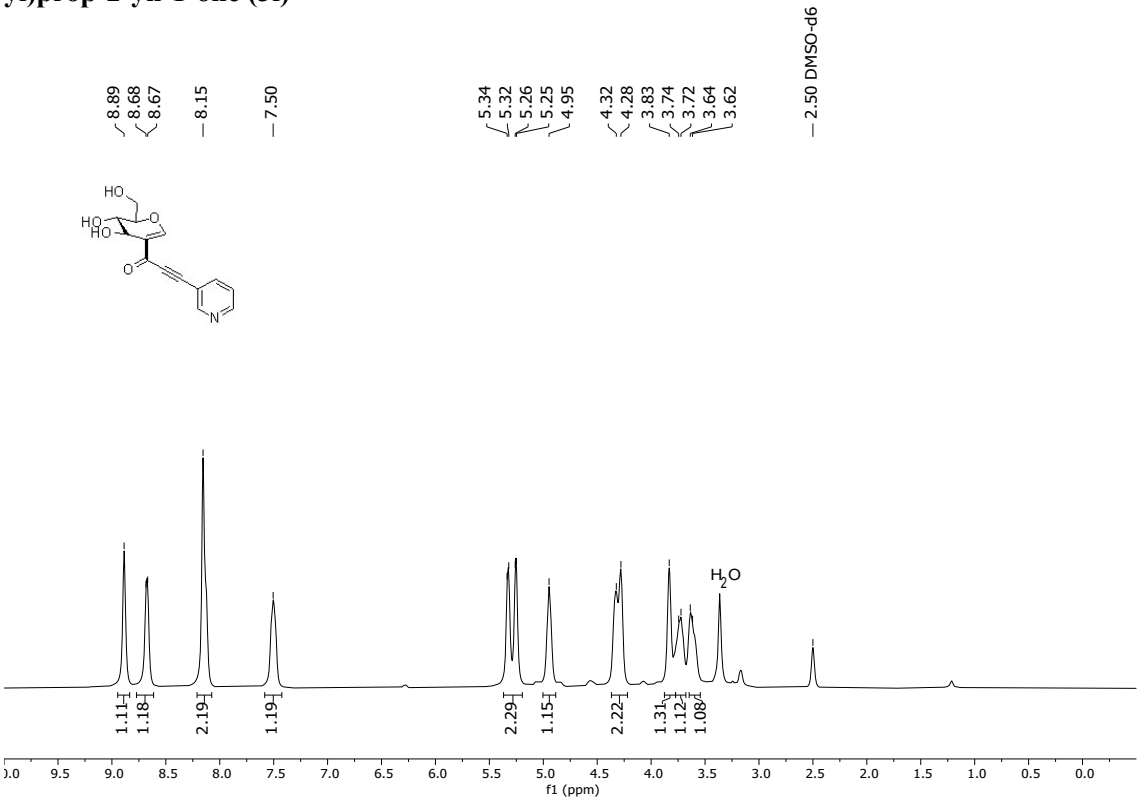


^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **3h**.

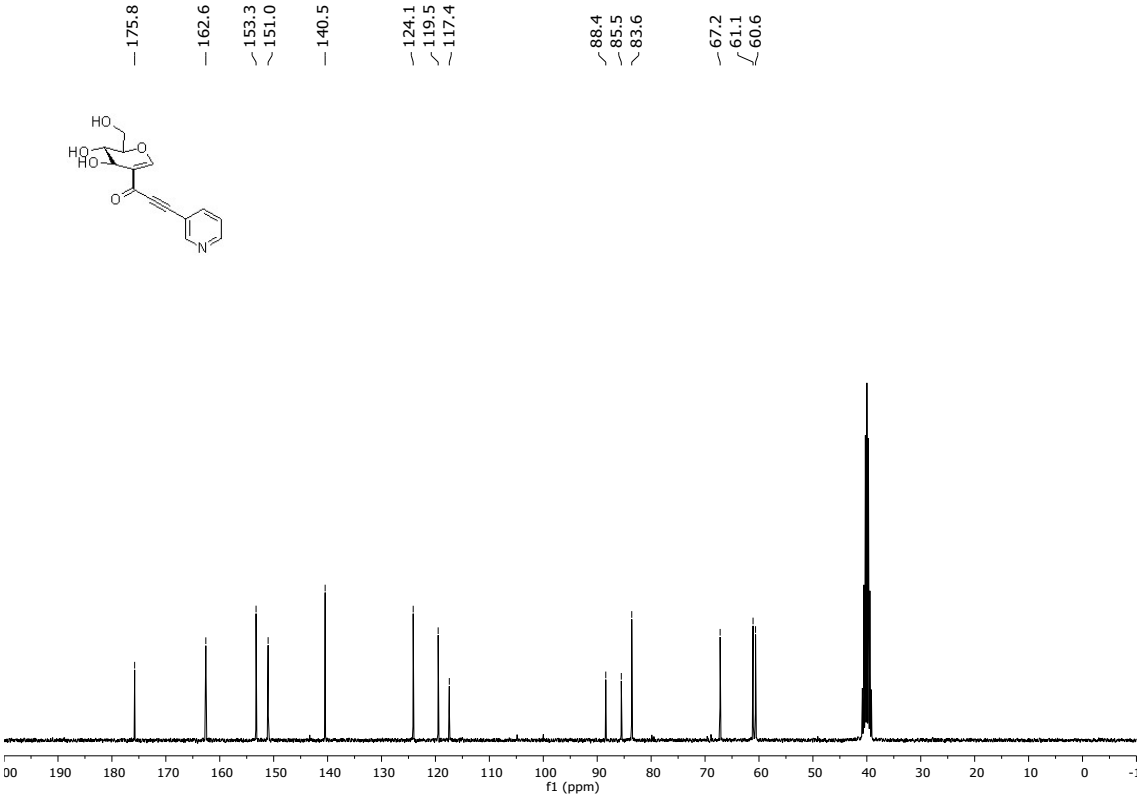


^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **3h**.

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-3-(pyridin-3-yl)prop-2-yn-1-one (3i)

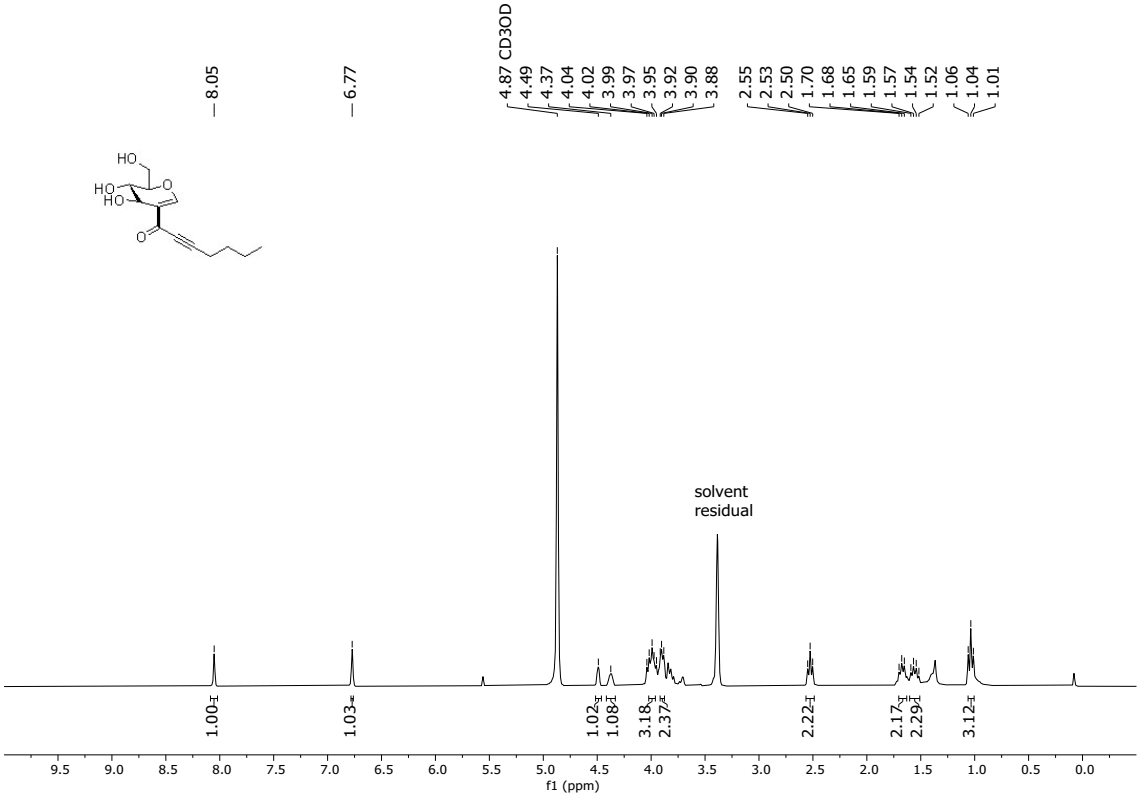


^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **3i**.

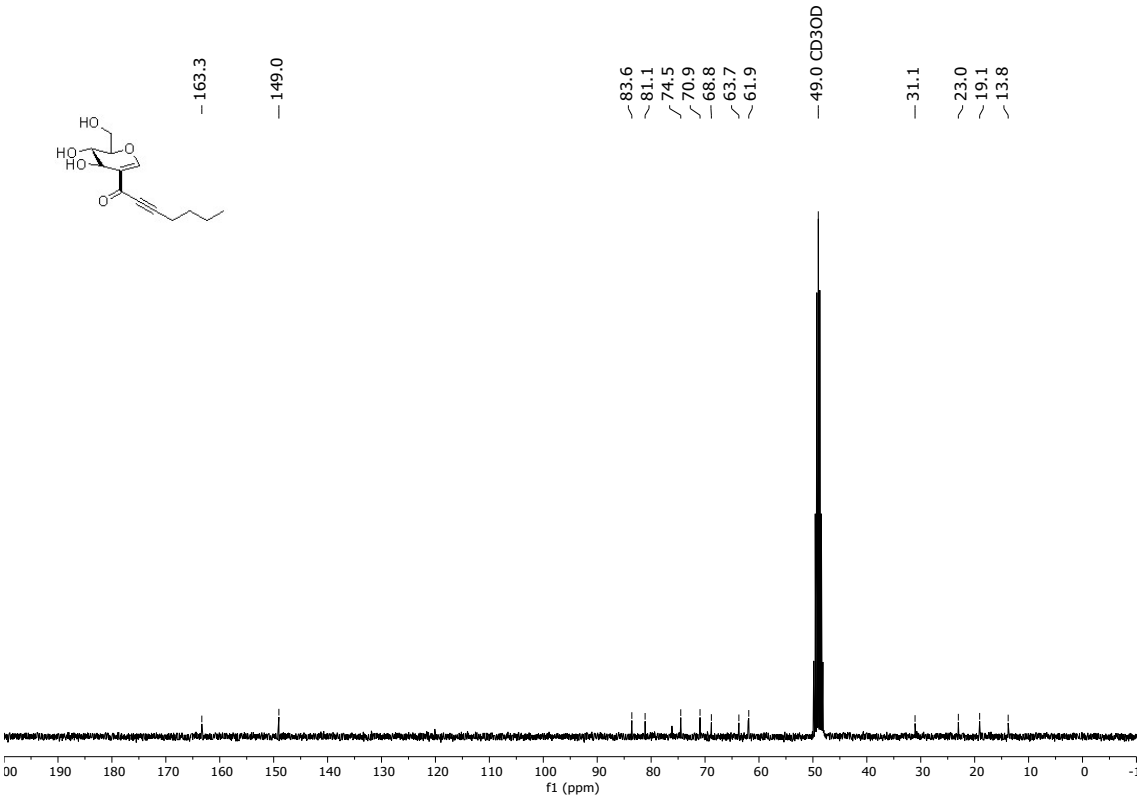


^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **3i**.

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)hept-2-yn-1-one (3j)

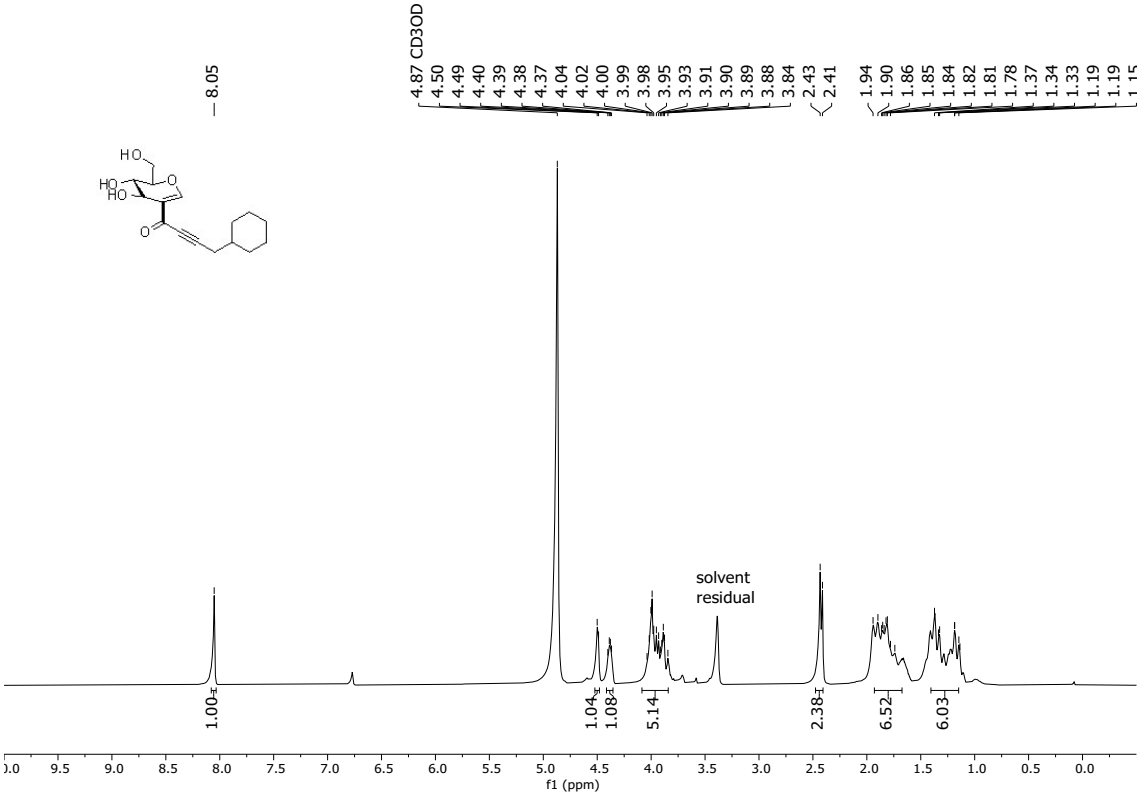


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3j**.

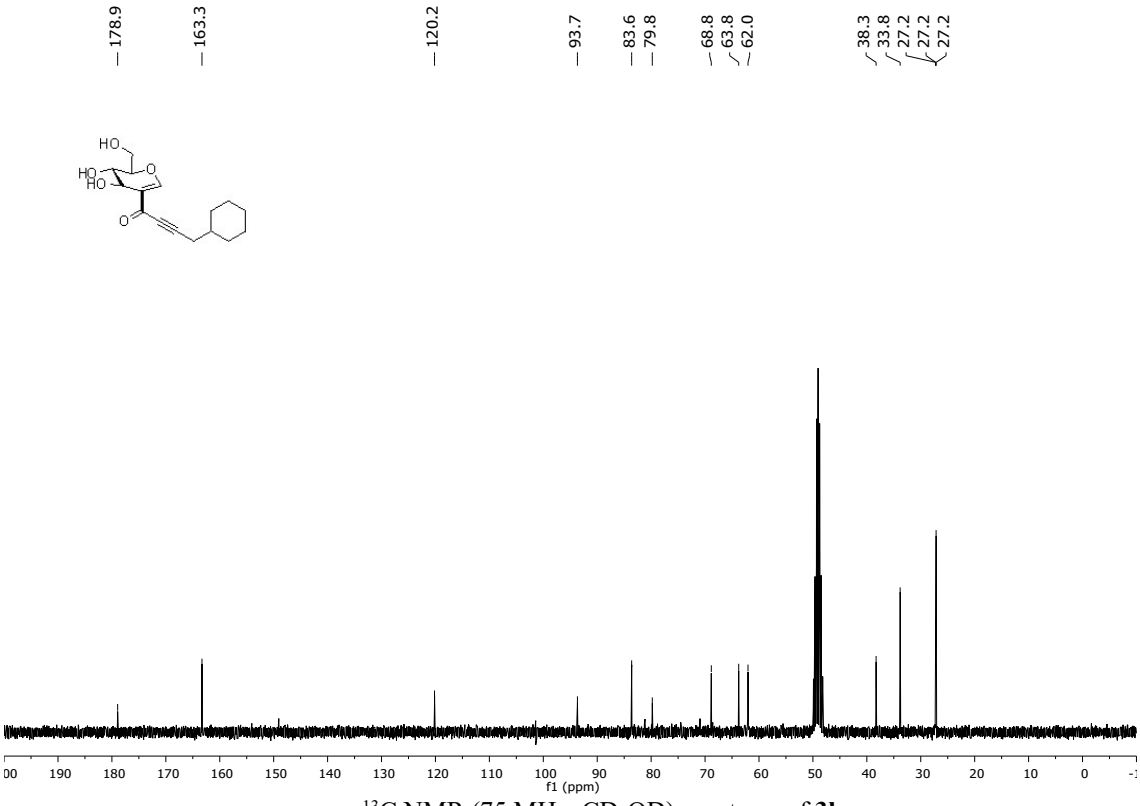


^{13}C NMR (75 MHz, CD_3OD) spectrum of **3j**.

4-Cyclohexyl-1-((2*R*,3*S*,4*S*)-3,4-dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)but-2-yn-1-one (3k)

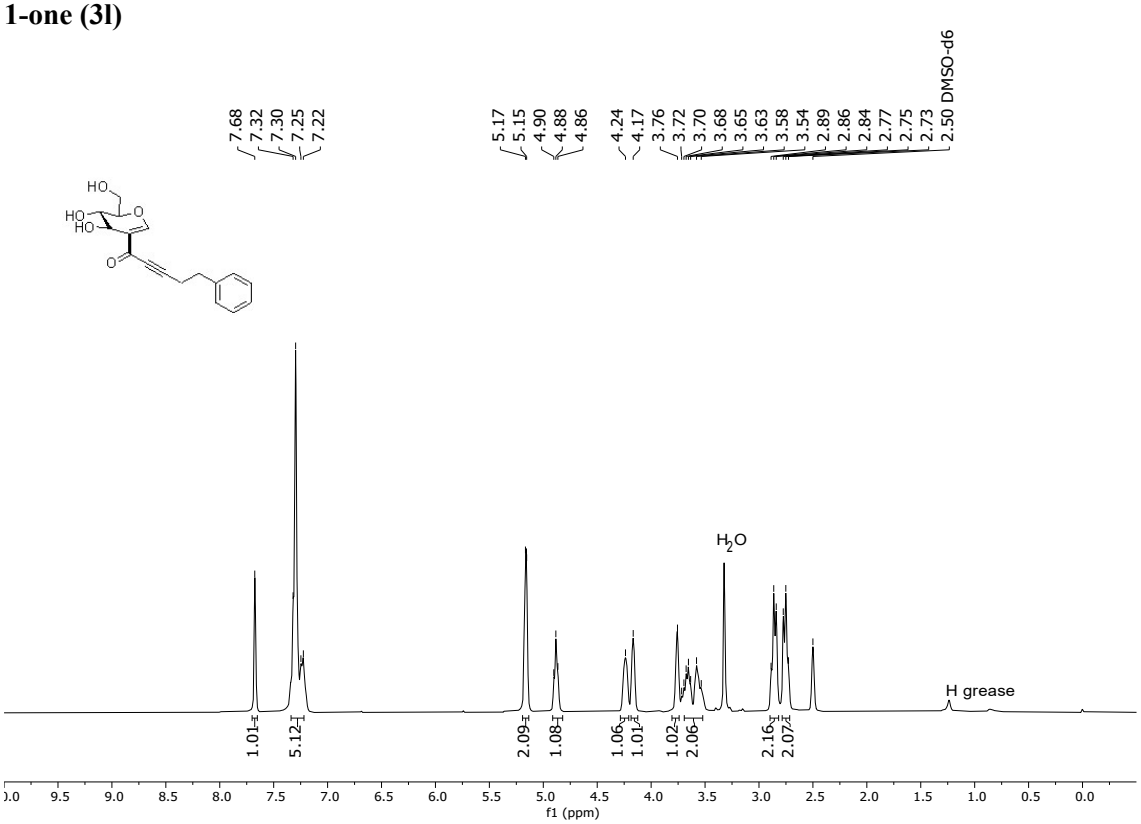


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3k**.

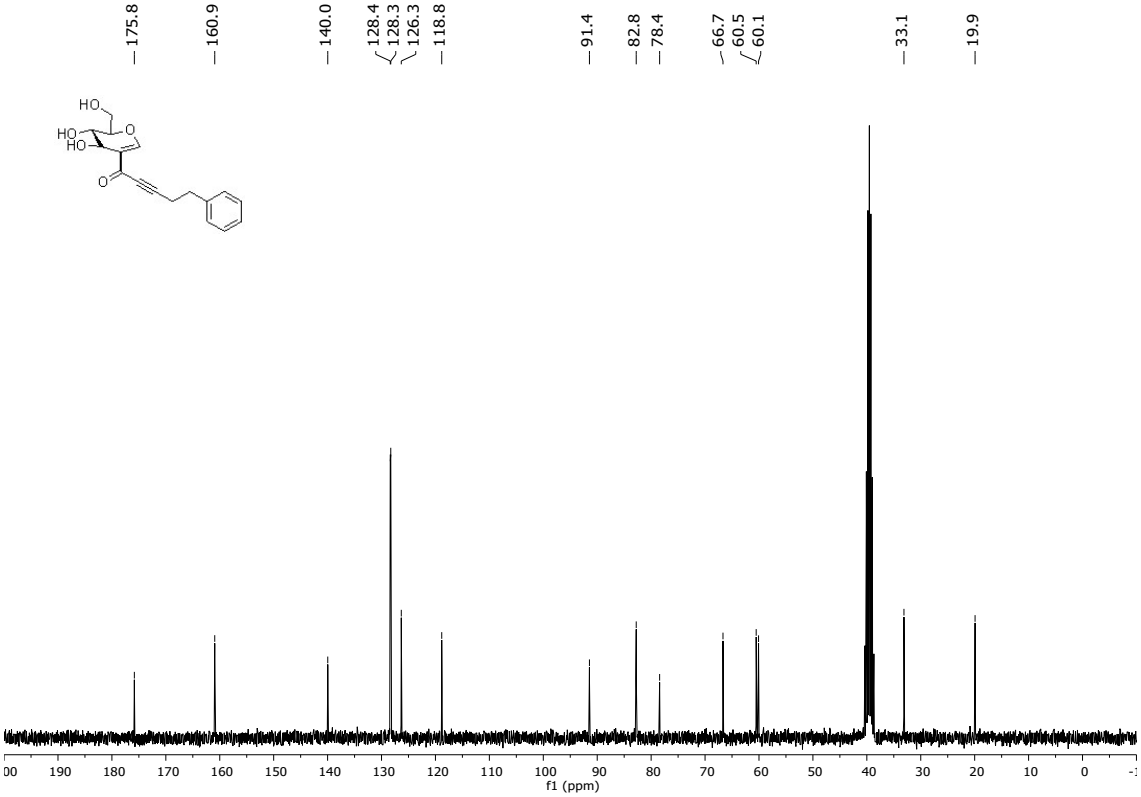


^{13}C NMR (75 MHz, CD_3OD) spectrum of **3k**.

1-((2*R*,3*S*,4*S*)-3,4-Dihydroxy-2-(hydroxymethyl)-3,4-dihydro-2*H*-pyran-5-yl)-5-phenylpent-2-yn-1-one (3l)

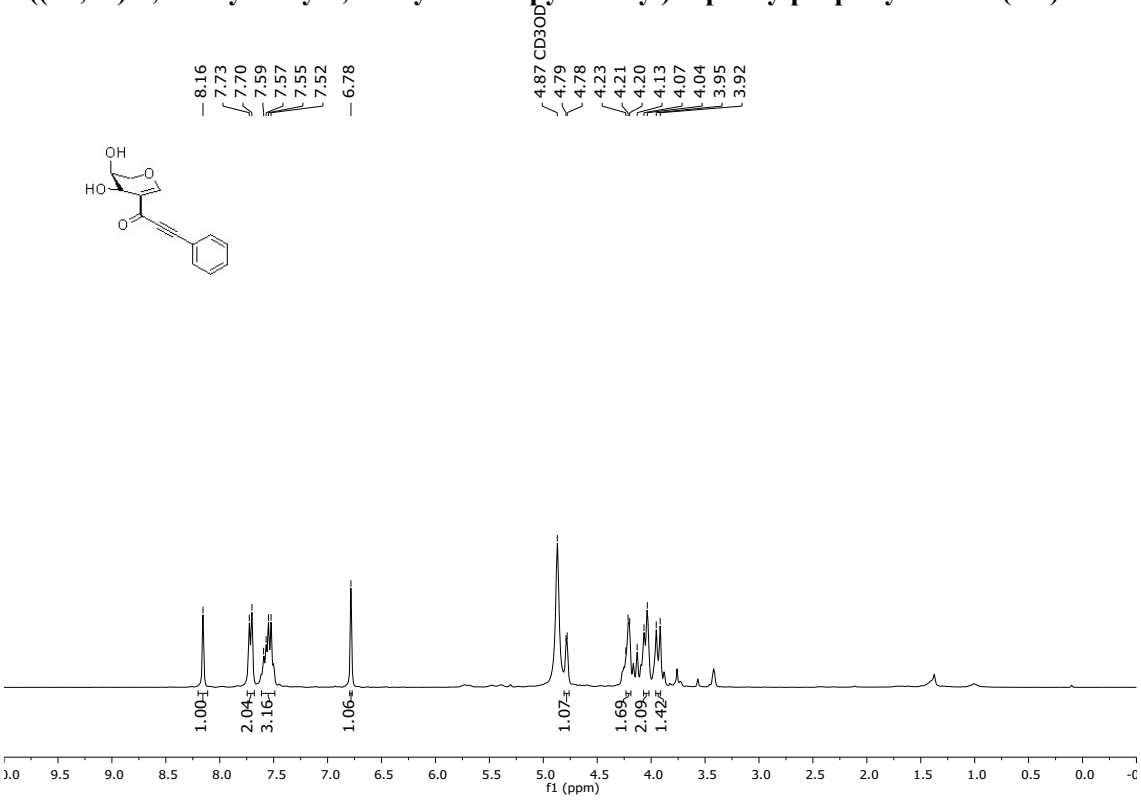


^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **3l**.

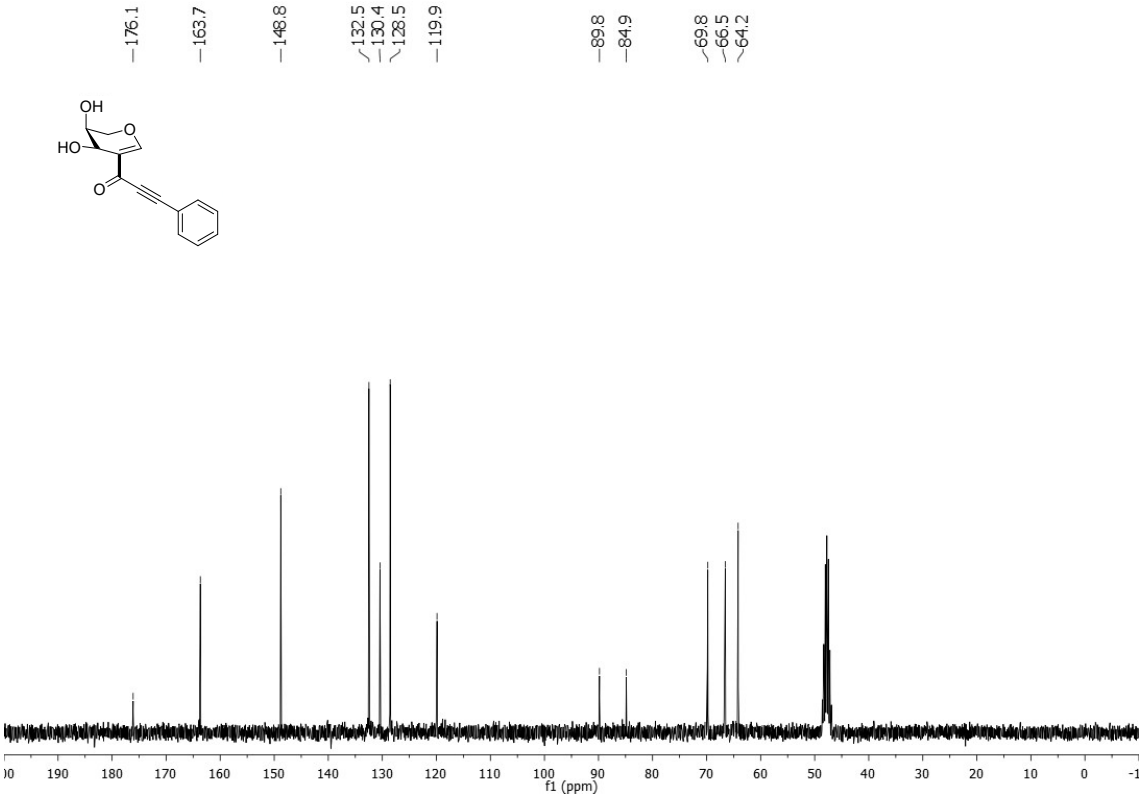


^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **3l**.

1-((3*S*,4*S*)-3,4-Dihydroxy-3,4-dihydro-2*H*-pyran-5-yl)-3-phenylprop-2-yn-1-one (3m)

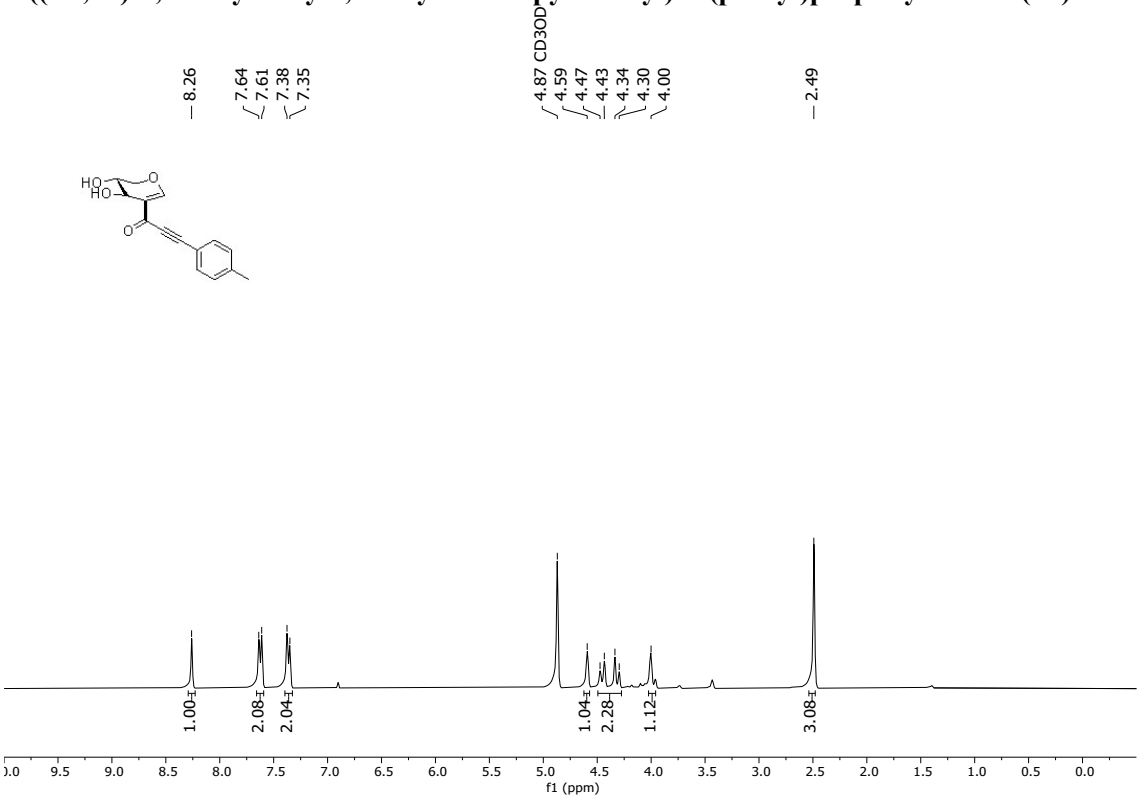


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3m**.

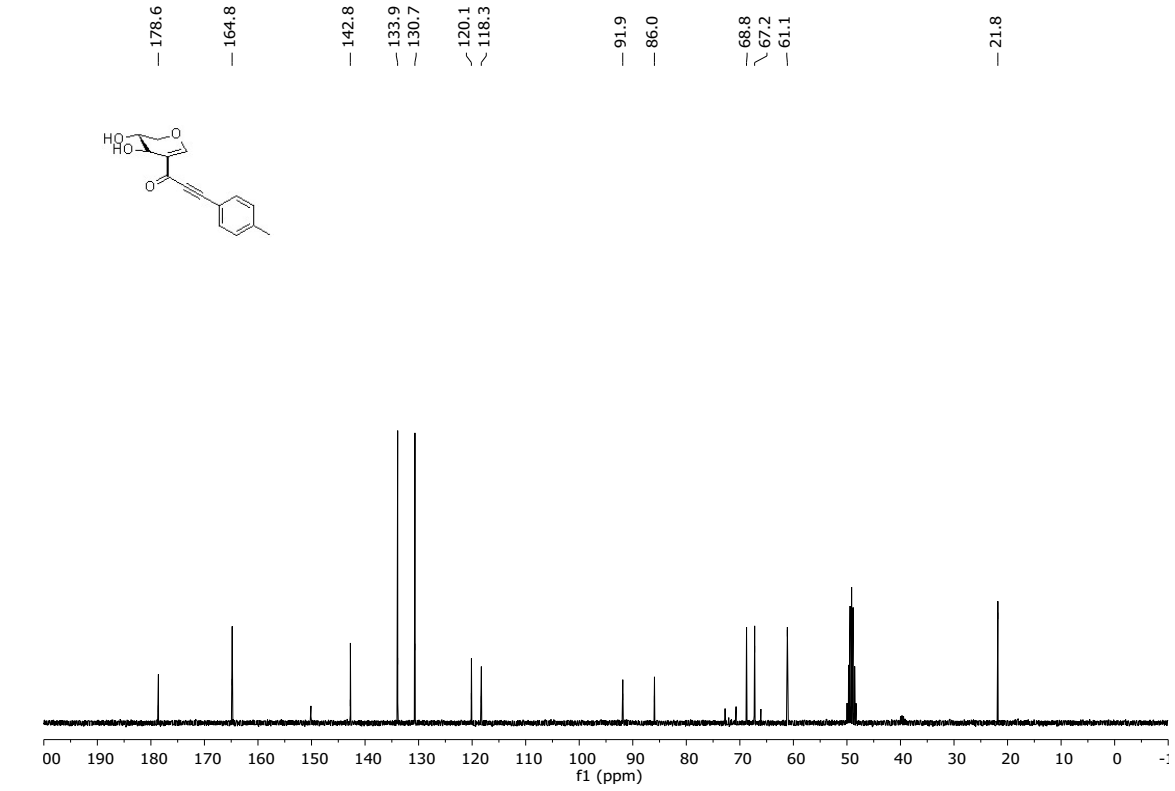


^{13}C NMR (75 MHz, CD_3OD) spectrum of **3m**.

1-((3*R*,4*S*)-3,4-Dihydroxy-3,4-dihydro-2*H*-pyran-5-yl)-3-(p-tolyl)prop-2-yn-1-one (3n)

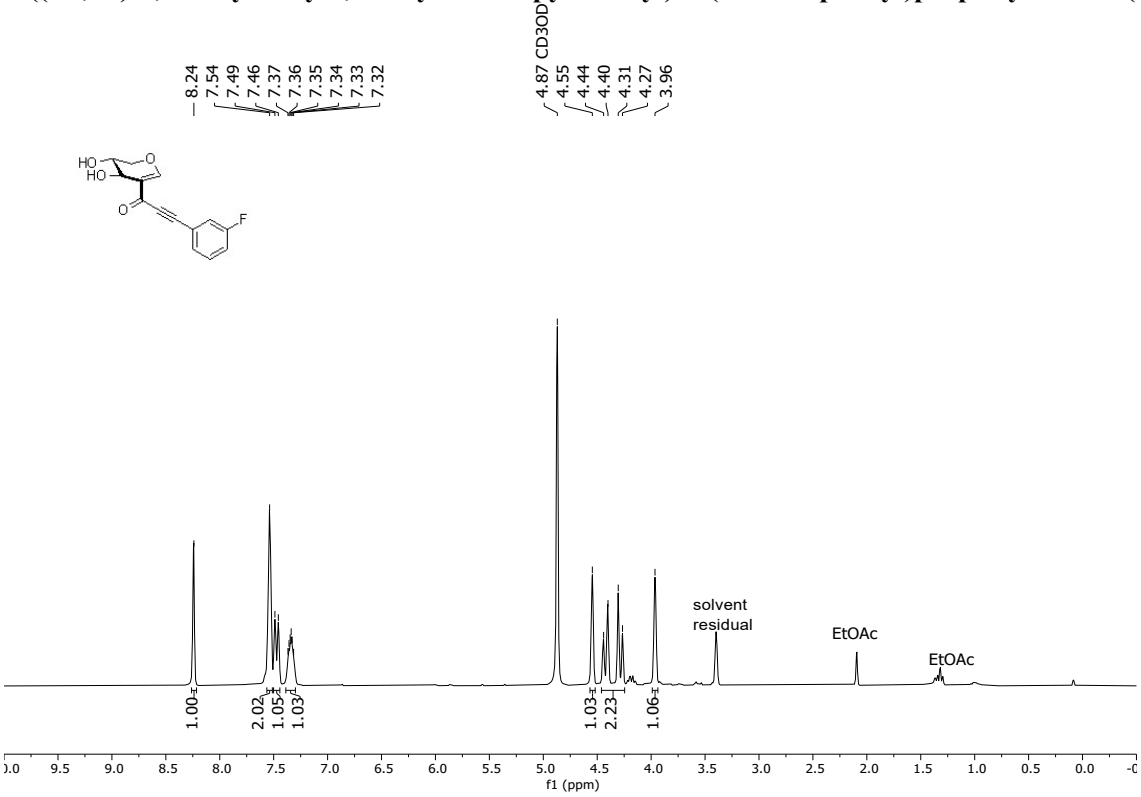


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3n**.

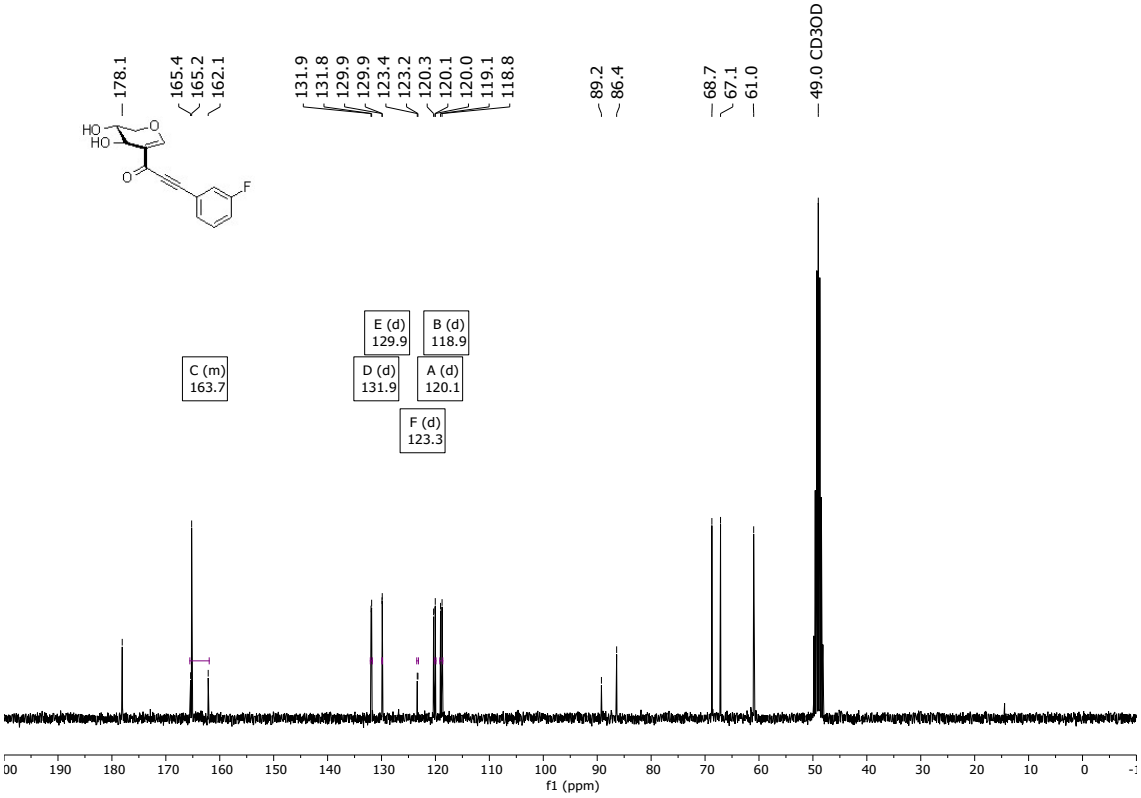


^{13}C NMR (75 MHz, CD_3OD) spectrum of **3n**.

1-((3*R*,4*S*)-3,4-Dihydroxy-3,4-dihydro-2*H*-pyran-5-yl)-3-(3-fluorophenyl)prop-2-yn-1-one (3o)

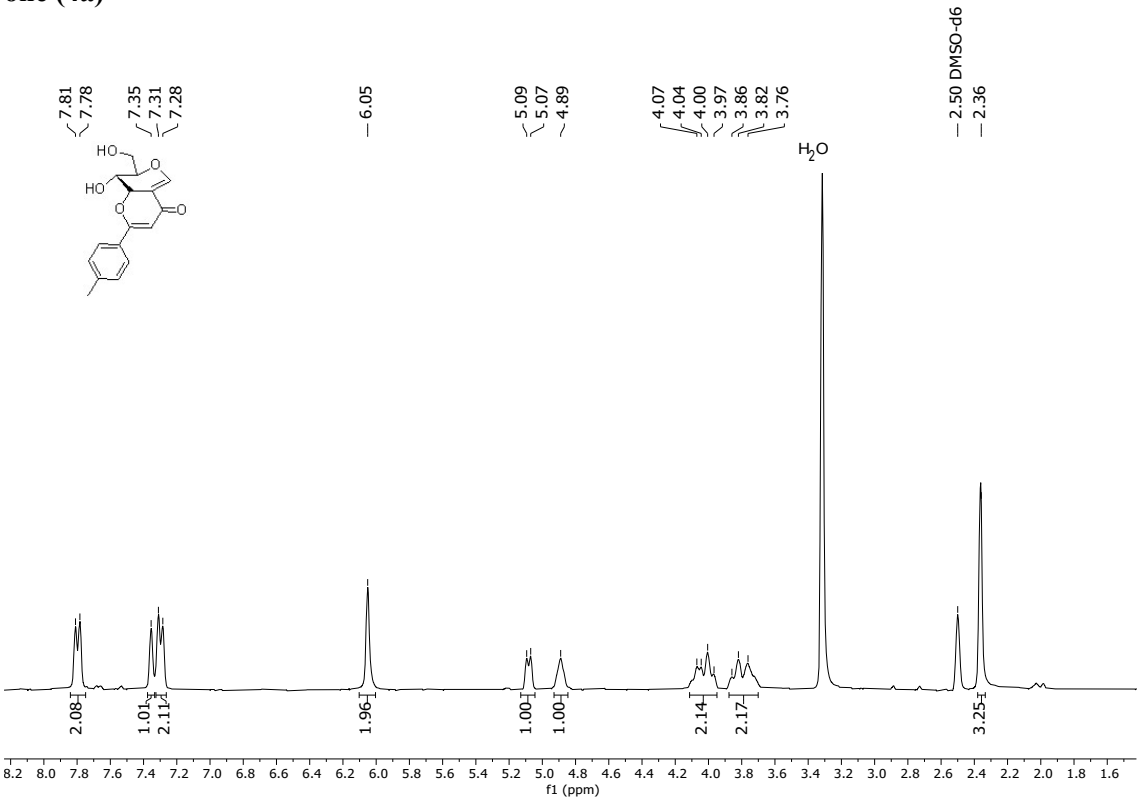


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3o**.

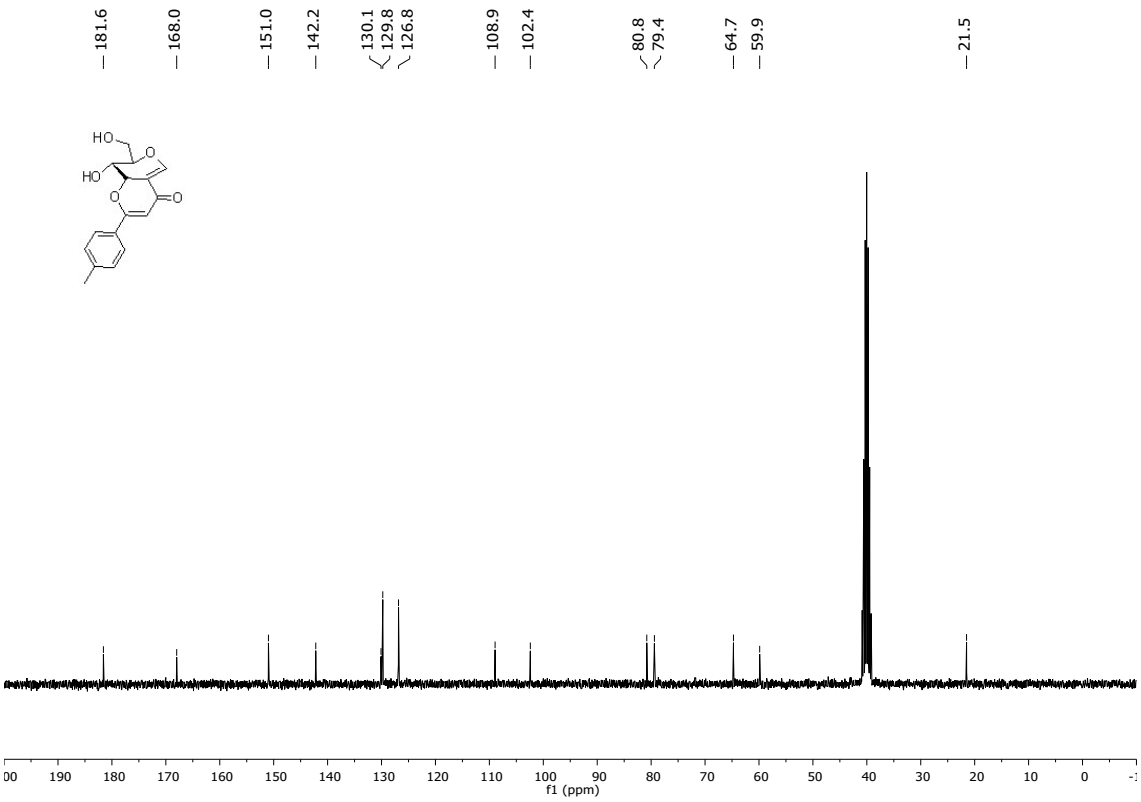


^{1}H NMR (300 MHz, CD_3OD) spectrum of **3o**.

(7*R*,8*S*,8a*R*)-8-Hydroxy-7-(hydroxymethyl)-2-(p-tolyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4a)

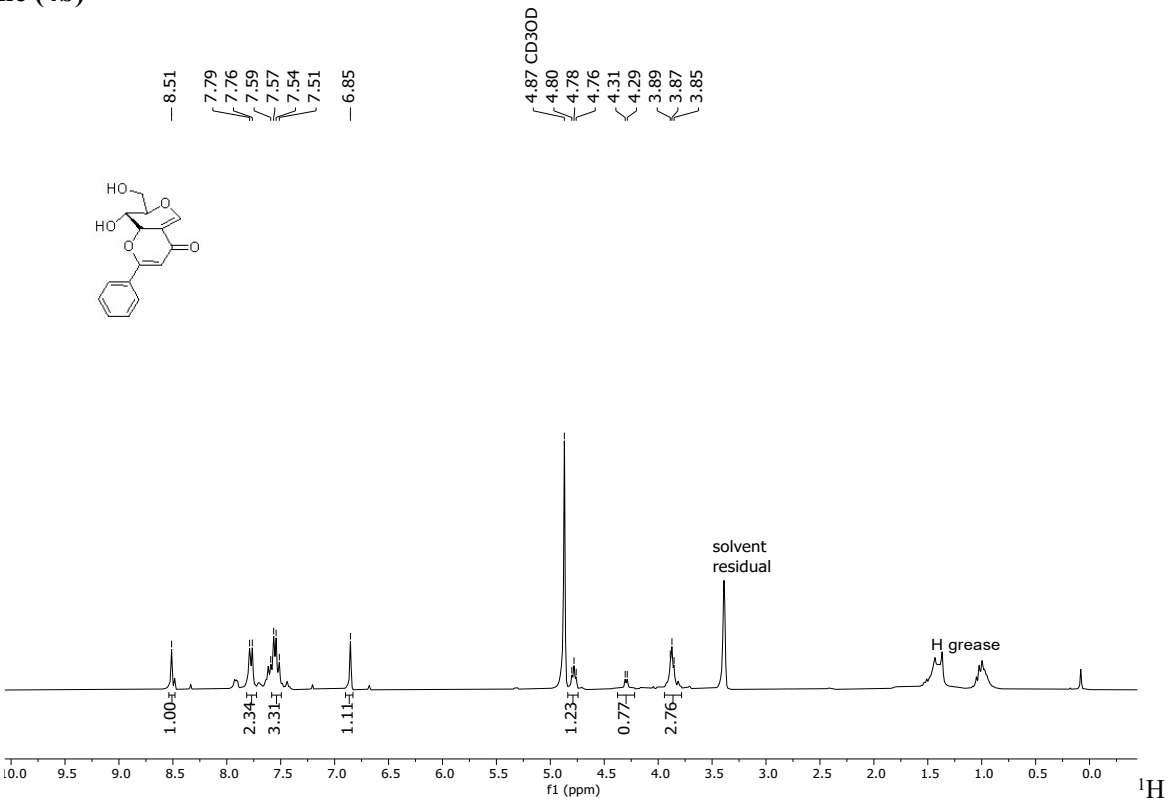


^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **4a**.

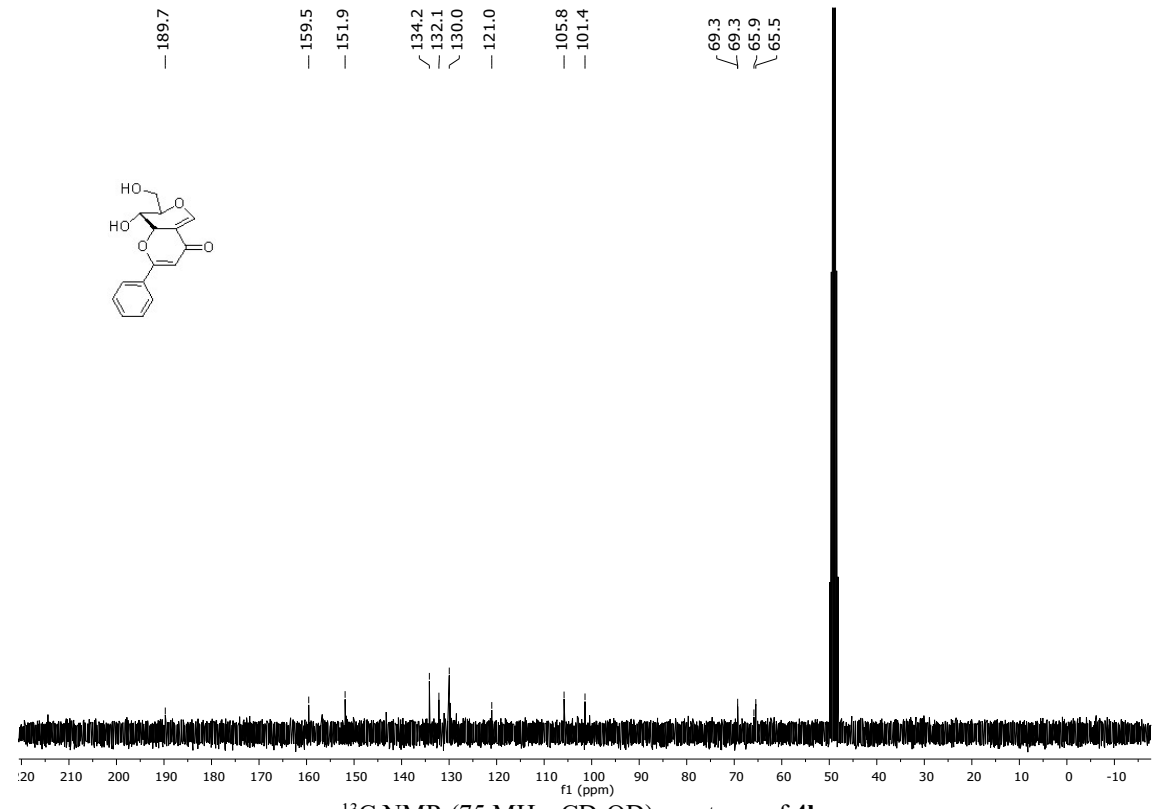


^{13}C NMR (75 MHz, DMSO-d_6) spectrum of **4a**.

(7*R*,8*S*,8a*R*)-8-Hydroxy-7-(hydroxymethyl)-2-phenyl-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4b)

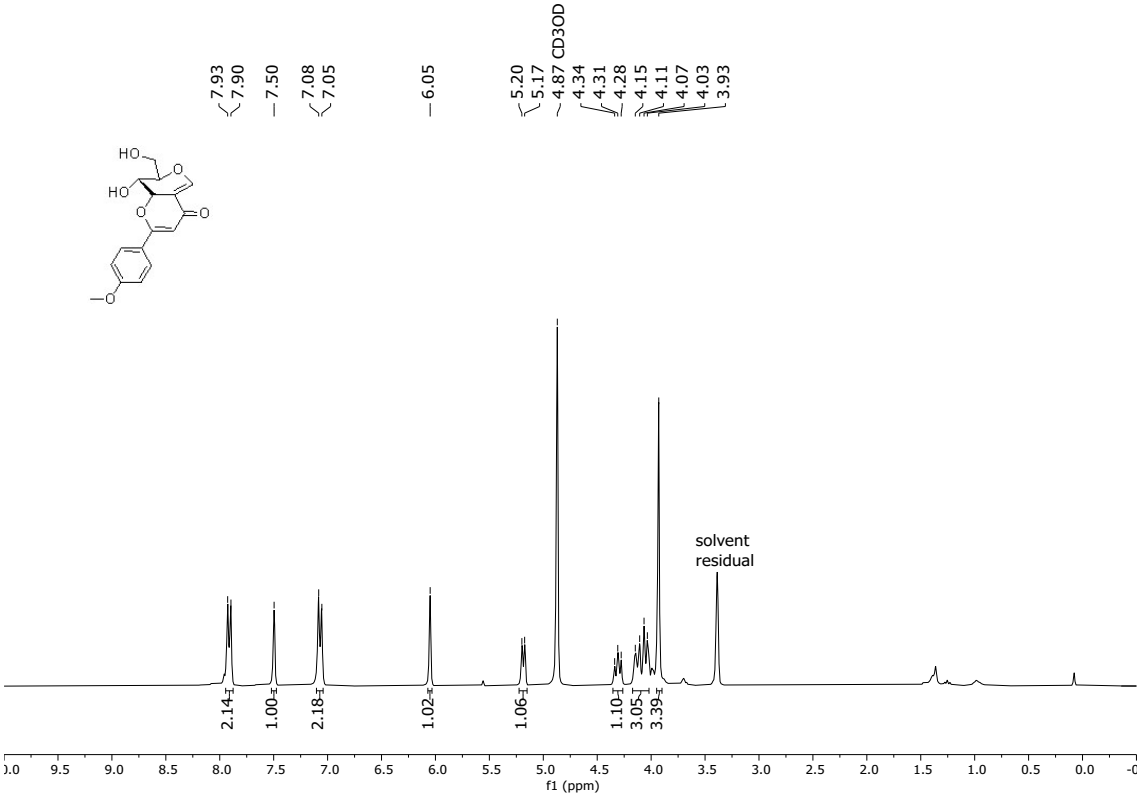


^{1}H NMR (300 MHz, CD_3OD) spectrum of **4b**.

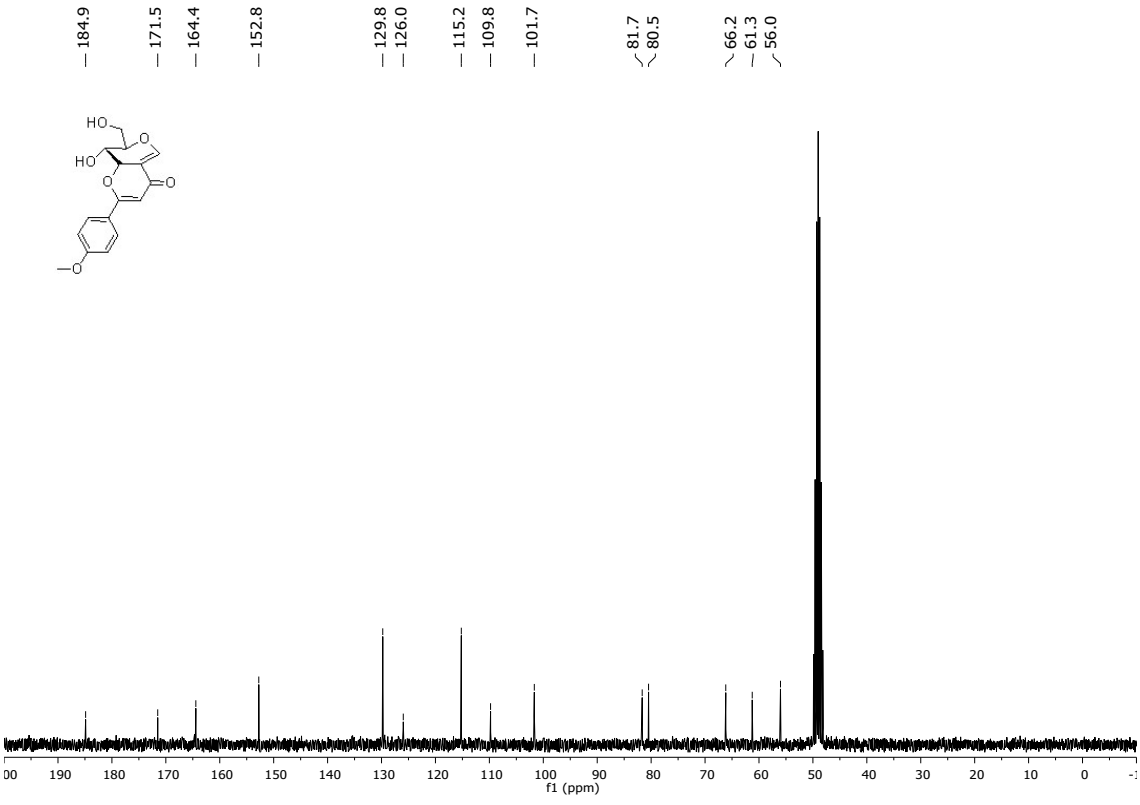


^{13}C NMR (75 MHz, CD_3OD) spectrum of **4b**.

(7*R*,8*S*,8a*R*)-8-Hydroxy-7-(hydroxymethyl)-2-(4-methoxyphenyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4c)

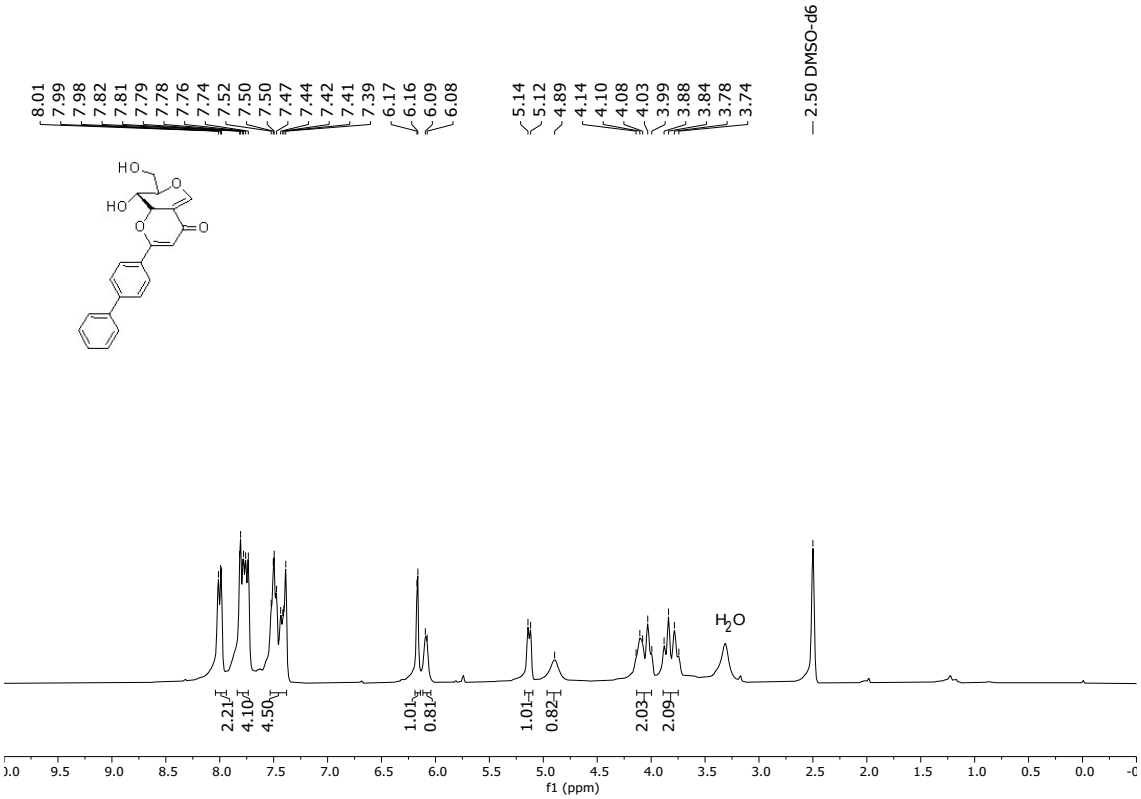


^{1}H NMR (300 MHz, CD_3OD) spectrum of **4c**.

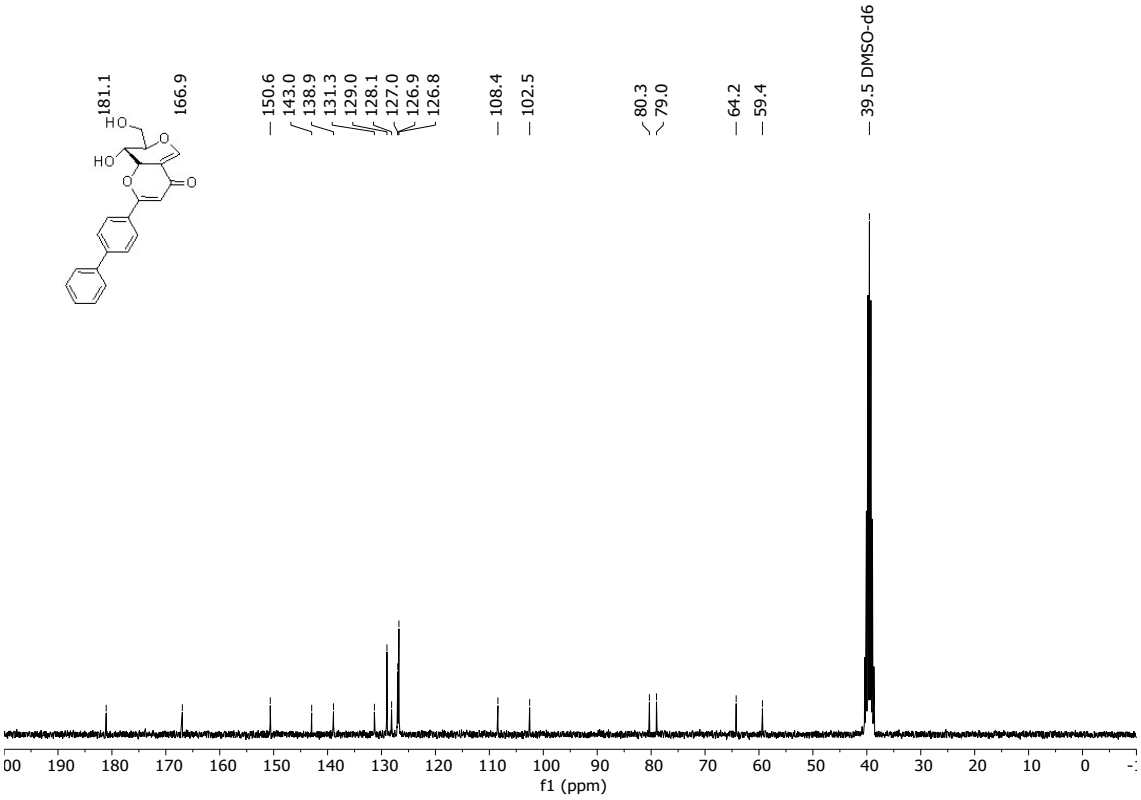


^{13}C NMR (75 MHz, CD_3OD) spectrum of **4c**.

(7*R*,8*S*,8a*R*)-2-([1,1'-Biphenyl]-4-yl)-8-hydroxy-7-(hydroxymethyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4d)

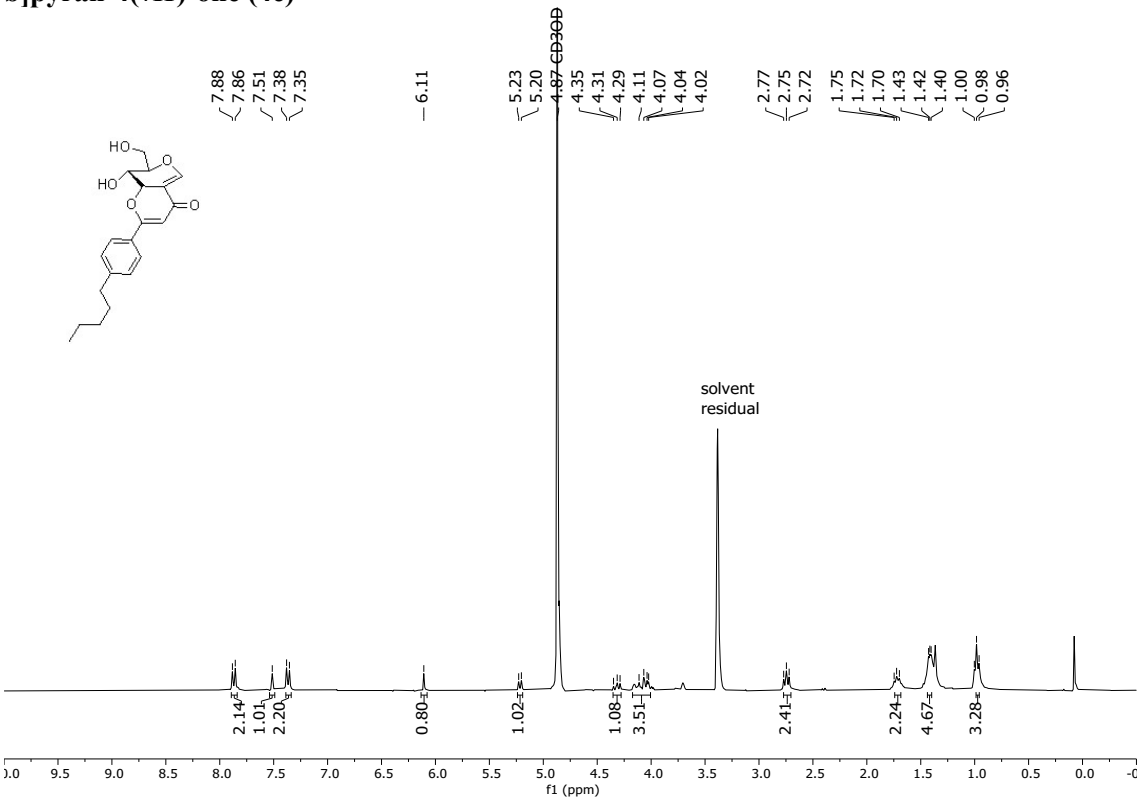


^{1}H NMR (300 MHz, DMSO-*d6*) spectrum of **4d**.

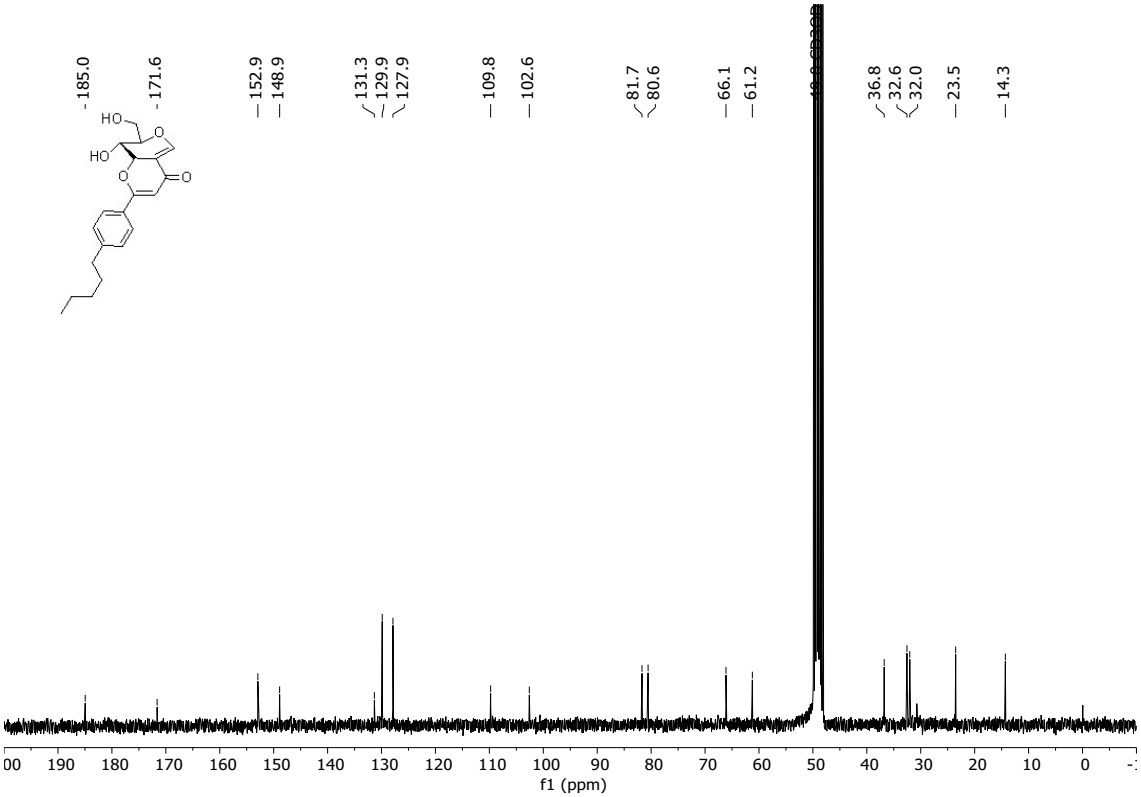


^{13}C NMR (75 MHz, DMSO-*d6*) spectrum of **4d**.

(7*R*,8*S*,8a*R*)-8-Hydroxy-7-(hydroxymethyl)-2-(4-pentylphenyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4e)

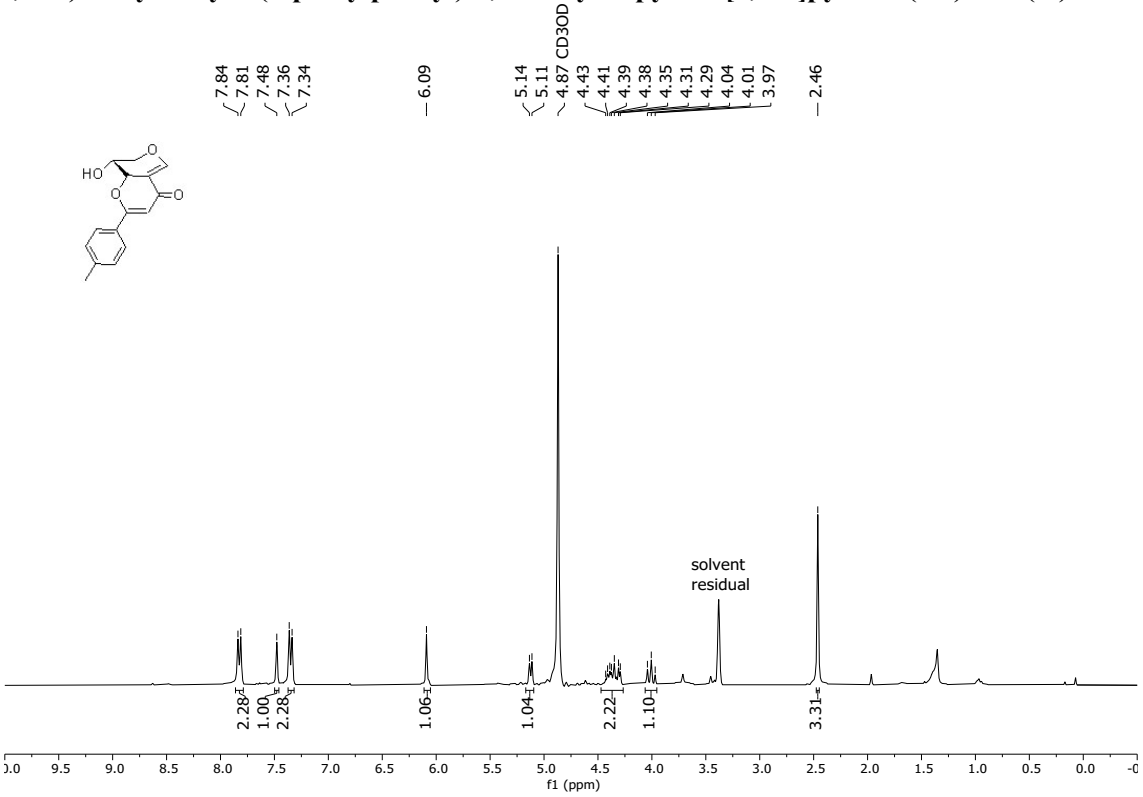


^{1}H NMR (300 MHz, CD_3OD) spectrum of **4e**.

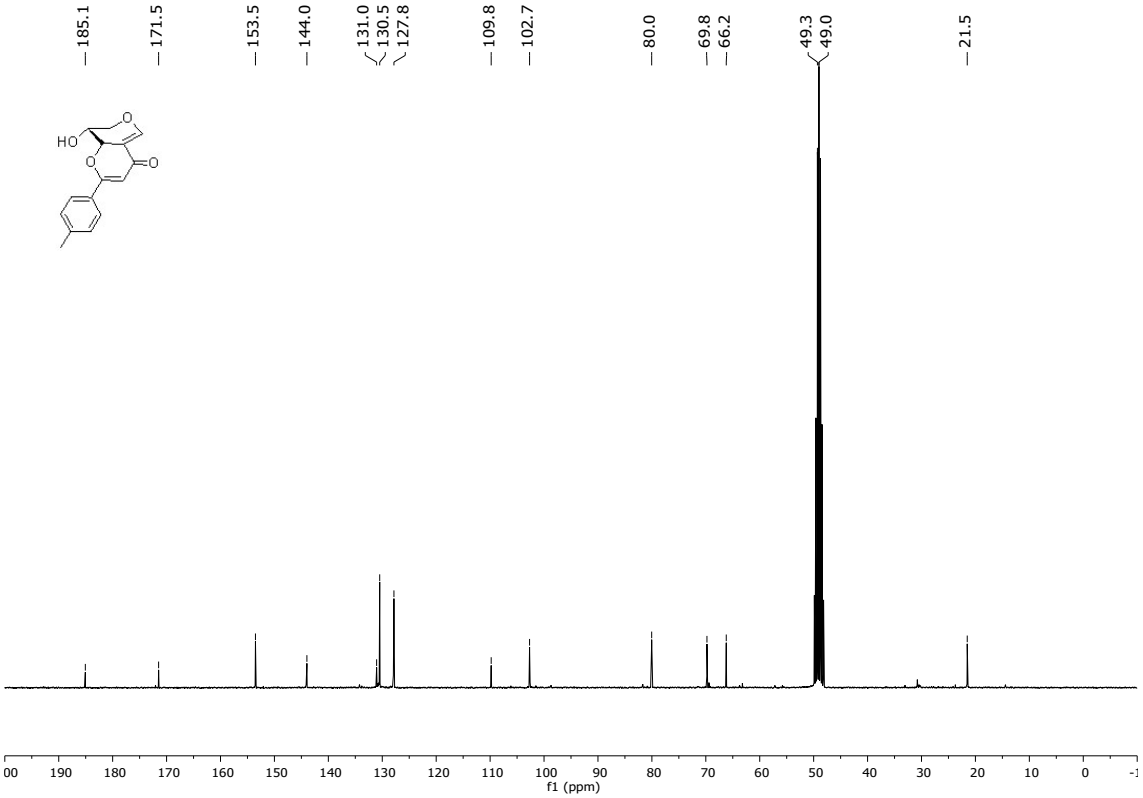


^{13}C NMR (75 MHz, CD_3OD) spectrum of **4e**.

(8*R*,8a*R*)-8-Hydroxy-2-(4-pentylphenyl)-8,8a-dihydropyrano[4,3-b]pyran-4(7*H*)-one (4f)



^{1}H NMR (300 MHz, CD_3OD) spectrum of **4f**.



^{13}C NMR (75 MHz, CD_3OD) spectrum of **4f**.