Synthesis of Phenols from Hydroxymethylfurfural (HMF)

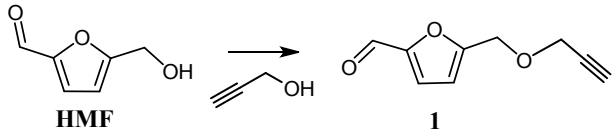
Svetlana Tšupova[a], Frank Rominger[a]†, Matthias Rudolph[a], A. Stephen K. Hashmi[a]

Supporting information

Experimental

Chemicals were purchased from commercial suppliers and used without further purification. HMF was purchased from Carbolution and used as recieved. NMR spectra were recorded at room temperature on the following spectrometers: BrukerAvance DRX-300, Bruker Avance III-300, Bruker Avance DRX-500, Bruker Avance III-500 and Bruker Avance III-600. Chemical shifts are given in ppm and coupling constants in Hz. ^{1}H and ^{13}C spectra were calibrated in relation to the deuterated solvents. The following abbreviations were used for ^{1}H NMR to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), bs (broad singlet). All ^{13}C NMR spectra were measured with ^{1}H decoupling. The multiplicities mentioned in the spectra [s (singlet, quaternary Carbon), d (doublet, CH group), t (triplet, CH_2-group), q (quartet, CH_3-group)] were determined by DEPT135 and HSQC. EI+ and FAB+ spectra were obtained using a JEOL JMD-700 spectrometer. For EI-MS electrons with energy of 70 eV were used. For the FAB-MS-matrix, 3-nitrobenzyl alcohol (NBA) or o-nitrophenyl octyl ether (NPOE) was used. For ESI+ and DART spectra, a Bruker ApexQe. FT-ICR-MSspectrometer was used. Infrared Spectroscopy (IR) was processed on a Bruker Lumos; Germanium ATR-Kristall spectrometer. The solvent or matrix is denoted in brackets. For the most significant bands, the wave number (cm-1) is given. Melting points were measured in open glass capillaries in a Büchi melting point apparatus and were not corrected. Flow reactions were performed using LATEK P-402 10 ml pump and steel column 4.6 X 250 mm, which was filled with Amberlyst ® 15 hydrogen form polymer beads, supplied by Sigma Aldrich. HPLC oven was used to heat the column. Flash column chromatography was accomplished using Silica gel 60 (0.04.0.063 mm/ 230-400 mesh ASTM purchased from MachereyNagel). Analytical Thin Layer Chromatography (TLC) was carried out on precoated aluminum sheets (Macherey-Nagel, ALUGRAM®Xtra SIL G/UV254). Components were detected under UV light 254 and were visualized by various dye solvents.

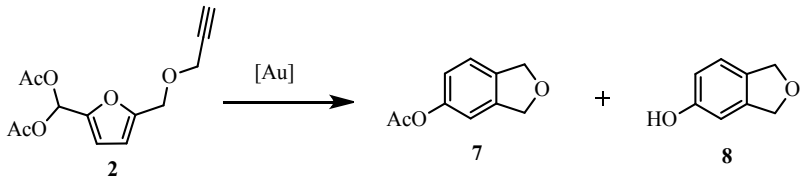
Screening tables



HMF **1**

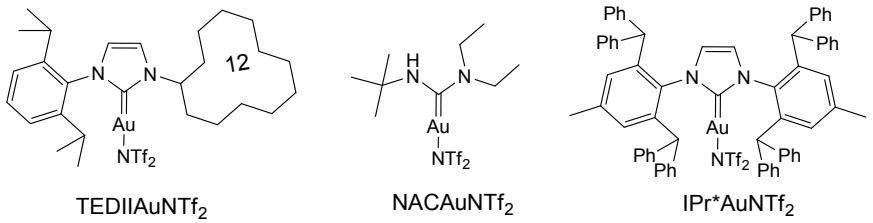
Entry	Alcohol	Catalyst (mol %)	Temp.	Solvent	Result
1	3 eqs.	*p*-TsOH (5)	60 °C	THF	nr
2	3 eqs.	*p*-TsOH (5)	60 °C	DMF	-[c]
3	3 eqs.	*p*-TsOH (5)	60 °C	Dioxane	-[c]
4	3 eqs.	*p*-TsOH (5)	60 °C	EA	33% [c,d]
5	-	*p*-TsOH (5)	60 °C	Propargyl alcohol	Full conv. [f]
6	2.5 eqs.	*p*-TsOH (5)	60 °C	Toluene	36% [c,d]
7	2.5 eqs.	*p*-TsOH (5)	60 °C	DCE	42% [c,d]
8	2.5 eqs.	*p*-TsOH (5)	60 °C	ACN	30% [c,d]
9	1 eq.	$Ph_3PAuNTf_2$ (5)[a]	60 °C	Toluene	-[b]
10	3 eqs.	$Ph_3PAuNTf_2$ (5)[a]	60 °C	Toluene	-[b]
11	5 eqs.	$Ph_3PAuNTf_2$ (5)[a]	60 °C	Toluene	-[b]
12	2.5 eqs.	$[P(OPh)_3]_4Pd$ (5)	80 °C	Toluene	Polymerisation
13	3 eqs.	$FeCl_3$ (5)	rt	ACN	Full conv.
14	3 eqs.	$FeCl_3$ (5)	rt	THF	nr
15	10 eqs.	$FeCl_3$ (5)	rt	ACN	Full conv. [f]
16	3 eqs.	$Fe(OTf)_3$ (5)	rt	ACN	30% [e]
17	3 eqs.	$Al(OTf)_3$ (5)	rt	ACN	nr
18	3 eqs.	$InBr_3$ (5)	rt	ACN	nr
19	3 eqs.	$BiBr_3$ (5)	rt	ACN	nr
20	3 eqs.	$C_6F_5B(OH)_2$ (5)	rt	ACN	nr
21	3 eqs.	$La(NO_3)_3{*}6H_2O$ (5)	rt	ACN	nr
22	-	Amberlyst 15, (100)	rt	Propargyl alcohol	54% [d]
23	-	Amberlyst 15, (100)	45 °C	Propargyl alcohol	69% [d]
24	-	Amberlyst 15, (100)	75 °C	Propargyl alcohol	80% [d]
25	-	Amberlyst 15, (100)	100 °C	Propargyl alcohol	3% [d]

Table 1. Formation of propargyl-HMF under batch conditions: 0.1 mmol of HMF in 0.5 ml of solvent. Nr – no reaction. a. activated in-situ. b. no conversion of HMF, all alcohol consumed. c. dimerization of HMF. d. NMR yield using 1,3,5-trimethoxybenzene as internal standard. e. isolated yields. f. isolated yields in upscale to 0.5-1 g of HMF: 28-52%



Catalyst	Conversion of **2**	Deprotection	Yield of **7**	Yield of **8**
$IPrAuNTf_2$	69 %	--	19 %	16 %
$Ph_3PAuNTf_2$	38 %		36 %	0 %
$TEDIIAuNTf_2$	76 %	--	29 %	23 %
$BrettPhosAuNTf_2$	100 %	--	46 %	34 %
$NACAuNTf_2$	59 %		0 %	0 %
$NaAuCl_4\,2H_2O$	7 %		0 %	0 %
$AuCl_3$	100 %	--	0 %	0 %
IPr^*AuNTf_2	61 %		0 %	0 %
t-$BuNCAuNTf_2$	1 %		0 %	0 %
t-$BuXPhosAuNTf_2$	100 %	--	45 %	32 %

Table 2. Catalyst screening for the cyclization of **2**. 0.1 mmol of 2 in 0.5 ml of $CDCl_3$, 1 mol% of catalyst, room temperature. Mesitylene was used as internal standard, NMR yields are reported.



$TEDIIAuNTf_2$ $NACAuNTf_2$ IPr^*AuNTf_2

Solvent	Conversion of **2**	Yield of **7**	Yield of **8**
Ethyl acetate	100 %	--	--
EtOH	100 % [a]	--	--
i-PrOH	100 %	--	--
Ac_2O	100 %	--	--
Acetone	100 %	--	--
THF	100 %	--	--
MTBE	100 %	--	--
Diethyl ether	100 %	--	--
Anisole	100 %	--	--
Sulfolane	100 %	--	23 % [b]
DCM [c]	100 %	37 %	43 %
BMIM PF_6	100 %	--	--
neat	100 %	--	--

Table 3. .Solvent screening for the cyclization of **2**. 0.1 mmol of 2 in 0.5 ml of solvent, 1% of $BrettPhosAuNTf_2$, room temperature. Mesitylene was used as internal standard, NMR yields are reported. a. triple bond hydration. b.in mixture with sulfolane. c. starting from 4 mmol of 2 and using $IPrAuNTf_2$ as a catalyst, isolated yields.

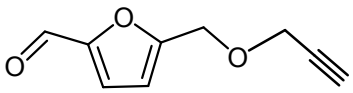
5-((prop-2-yn-1-yloxy)methyl)furan-2-carbaldehyde (1)

Representative procedure for the formation of **1** using p-TsOH as a catalyst.

HMF (604 mg, 4.8 mmol) was dissolved in propargyl alcohol (5 ml) and *p*-TsOH (46 mg, 0.23 mmol) was added. The obtained mixture was stirred at 70°C overnight. Volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent petroleum ether/ethyl acetate 5:1) resulting in 340 mg of yellowish oil (43% yield).

Representative procedure for the formation of **1** under flow conditions.

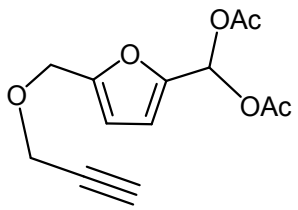
Stainless steel HPLC column was packed with dry Amberlyst 15 (2.3 g), connected to pump, washed with ethyl acetate and heated to 70°C. HMF (200 mg, 1.6 mmol) was dissolved in propargyl alcohol (1 ml, 17 mmol) and ethyl acetate (1 ml) was added. The resulting mixture was introduced into the column at the flow rate 1.5 ml/min and ethyl acetate was used to pump it through the column at the same 1.5 ml/min rate. The composition of the affluent was monitored by TLC (petroleum ether/ethyl acetate 5:1). After 15-20 minutes, only faint spots of HMF and propargyl-HMF were seen and the pumping was continued for additional 5 minutes. Volatiles were removed from the obtained solution resulting in yellowish oil. If necessary, purification might be achieved by filtration through silica gel using diethyl ether as eluent yielding to 228 mg (78% of the title compound and 15% of EMF) as yellowish oil.



Yellowish oil. R_f (petroleum ether/ethyl acetate 3:2) = 0.62. FTIR (neat) cm^{-1}: 3283, 3122, 2905, 2856, 2117, 1770, 1693, 1585, 1522, 1444, 1402, 1351, 1276, 1193, 1016, 970, 943, 910, 809, 784. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.56 (s, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 6.50 (d, *J* = 3.5 Hz, 1H), 4.58 (s, 2H), 4.16 (d, *J* = 2.4 Hz, 2H), 2.44 (t, *J* = 2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 177.74 (s), 157.31 (s), 152.73 (s), 121.66 (d), 111.77 (d), 78.60 (d), 75.48 (s), 63.27 (t), 57.72 (t). HRMS (EI+) [M+] calcd: 164.0473; found: 164.0461

(5-((prop-2-yn-1-yloxy)methyl)furan-2-yl)methylene diacetate (2)

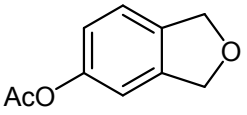
5-((prop-2-yn-1-yloxy)methyl)furan-2-carbaldehyde **1** (2.51 g, 15.3 mmol) was dissolved in acetic anhydride (2.8 ml, 30 mmol) and $La(NO_3)_3{*}6H_2O$ (132 mg, 0.31 mmol) was added. The obtained mixture was stirred overnight. Then 50 ml of diethyl ether were added and the obtained mixture was filtered through celite. Volatiles were removed yielding 4.2 g of brownish oil (quanititive yield, containts minor amount of acetic acid).



Brownish oil. R_f (petroleum ether/ethyl acetate 3:2) = 0.61. FTIR (neat) cm^{-1}: 1935, 1764, 1682, 1563, 1524, 1441, 1373, 1239, 1203, 1080, 1018, 969, 810. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.67 (s, 1H), 6.48 (d, *J* = 3.2 Hz, 1H), 6.36 (d, *J* = 3.2 Hz, 1H), 4.56 (s, 2H), 4.18 (d, *J* = 2.2 Hz, 2H), 2.47 (t, *J* = 1.9 Hz, 1H), 2.13 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 168.38 (s), 152.19 (s), 148.21 (s), 110.55 (d), 110.46 (d), 83.39 (d), 79.05 (s), 75.01 (t), 63.08 (t), 57.09 (t), 20.70 (q). HRMS (EI+) [M+] calcd: 266.0790; found: 266.0816

1,3-dihydroisobenzofuran-5-yl acetate (8)

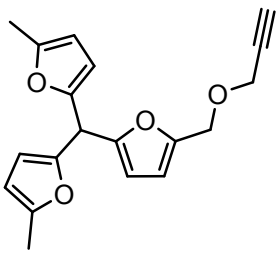
(5-((prop-2-yn-1-yloxy)methyl)furan-2-yl)methylene diacetate **2** (1.00 g, 3.76 mmol) was dissolved in DCM (25 ml) and *t*-BuXPhosAuNTf$_2$ (17 mg, 0.02 mmol) was added. The resulting mixture as stirred at room temperature overnight. Volatiles were removed and the residue was purified by column chromatigraphy on silica gel (eluent petroleum ether/ethyl acetate 5:1). 267 mg of colorless oil (**8**, 40% yield) and 190 mg of white solid (**9**, 37% yield) were isolated. Analytical data for 9 matches literature data.[i]



Colorless oil. R_f (petroleum ether/ethyl acetate 5:1) = 0.44. FTIR (neat) cm^{-1}: 3496, 3288, 3060, 3029, 3856, 2674, 2386, 2084, 1940, 1750, 1682, 1654, 1622, 1597, 1485, 1434, 1365, 1317, 1287, 1180, 1136, 1099, 1012, 949. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.8 Hz, 2H), 7.00 – 6.94 (m, 3H), 5.09 (s, 4H), 2.30 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.63 (s), 150.21 (s), 140.78 (s), 136.60 (s), 121.68 (d), 120.66 (d), 114.54 (d), 73.36 (t), 73.23 (t), 21.06 (q). HRMS (EI+) [M+] calcd: 178.0630; found: 178.0615

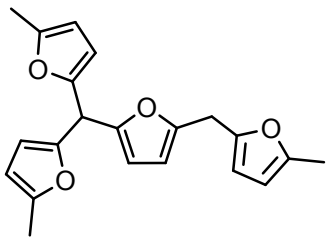
5,5'-((5-((prop-2-yn-1-yloxy)methyl)furan-2-yl)methylene)bis(2-methylfuran) (3)

5-((prop-2-yn-1-yloxy)methyl)furan-2-carbaldehyde **1** (100 mg, 0.61 mmol) was dissolved in acetonitrile and methylfuran (153 ul, 1.44 mmol) and $AuCl_3$ (0.12 ml, 0.05 M solution, 0.006 mmol) were added. The resulting mixture was stirred for 3 days. Volatiles were removed and the residue was purified by chromatography on silica gel (eluent petroleum ether/ethyl acetate 10:1) resulting in 25 mg (12% yield) of 5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran) and 126 mg (76% yield) of 5,5'-((5-((prop-2-yn-1-yloxy)methyl)furan-2-yl)methylene)bis(2-methylfuran).



Brownish oil. R_f (petroleum ether/ethyl acetate 10:1) = 0.34. FTIR (neat) cm^{-1}: 3131, 3105, 2980, 2948, 2922, 2885, 1676, 1614, 1561, 1450, 1383, 1359, 1271, 1217, 1020, 1000, 950, 772. ^1H NMR (400 MHz, $CDCl_3$) δ = 6.31 (d, *J* = 3.2 Hz, 1H), 6.06 (d, *J* = 3.1 Hz, 1H), 5.97 (d, *J* = 3.0 Hz, 2H), 5.89 (dd, *J* = 3.0, 0.9 Hz, 2H), 5.41 (s, 1H), 4.52 (s, 2H), 4.14 (d, *J* = 2.4 Hz, 2H), 2.43 (t, *J* = 2.4 Hz, 1H), 2.26 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.33 (s), 151.53 (s), 150.18 (s), 150.10 (s), 111.01 (d), 107.96 (d), 106.23 (d), 79.43 (s), 74.66 (s), 63.21 (t), 56.59 (t), 39.18 (d), 13.56 (q). HRMS (EI+) [M+] calcd: 310.1205; found: 310.1217.

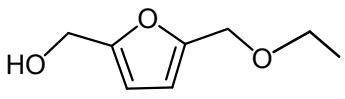
5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran)



Brownish oil. R_f (petroleum ether/ethyl acetate 10:1) = 0.68. FTIR (neat) cm^{-1}: 2981, 2948, 2922, 2885, 1771, 1707, 1613, 1562, 1450, 1384, 1359, 1218, 1175, 1022, 10001, 950, 776. ^1H NMR (400 MHz, $CDCl_3$) δ = 6.00 (q, *J* = 3.4 Hz, 2H), 5.96 (d, *J* = 2.9 Hz, 2H), 5.93 – 5.85 (m, 4H), 5.38 (s, 1H), 3.91 (s, 2H), 2.26 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.41 (s), 151.37 (s), 151.20 (s), 150.91 (s), 150.55 (s), 149.71 (s), 107.87 (d), 107.84 (d), 107.76 (d), 107.03 (d), 106.19 (d), 106.10 (d), 39.15 (d), 27.57 (t), 13.57(q), 13.47 (q). HRMS (EI+) [M+] calcd: 336.1362; found: 336.1368.

(5-(ethoxymethyl)furan-2-yl)methanol (5)

Ethoxymethylfurfural (889 mg, 5.77 mmol) was dissolved in methanol (10 ml) and $NaBH_4$ (622 mg, 16.4 mmol) was added by small portions. The obtained mixture was stirred for overnight. Volatiles were removed and the residue was purified by chromatography on silica gel (eluent petroleum ether/ethyl acetate 5:1) resulting in 774 mg (86%) of colorless oil.

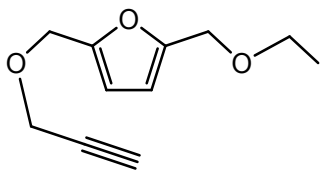


Colorless oil. R_f (petroleum ether/ethyl acetate 2:1) = 0.61. FTIR (neat) cm^{-1}: 3228, 2945, 2878, 1563, 1454, 1402, 1360, 1245, 1205, 1183, 1029, 999, 975, 923, 817. ^1H NMR (301 MHz, $CDCl_3$) δ = 6.28 – 6.20 (m, 2H), 4.59 (s, 2H), 4.42 (s, 2H), 3.54 (q, *J* = 7.0 Hz, 2H), 1.82 (s, 1H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.26 (s), 152.06 (s), 109.79 (d), 108.36 (d), 65.75 (t), 64.61 (t), 57.57 (t), 15.04 (q). HRMS (EI+) [M+] calcd: 156.0786; found: 156.0789

2-(ethoxymethyl)-5-((prop-2-yn-1-yloxy)methyl)furan (6)

(5-(ethoxymethyl)furan-2-yl)methanol **5** (750 mg, 4.81 mmol) was dissolved in toluene (5 ml) and K_2CO_3 (1.33 g, 9.62 mmol), KOH (940 mg, 16.8 mmol) and TBAHS (153 mg, 0.48 mmol) were added. The resulting mixture was stirred at room temperature overnight. Water was added and aqueous layer was

extracted with ether. Volatiles were removed and the residue was purified by column chromatography on silica gel (eluent petroleum ether/ethyl acetate 5:1) resulting in 927 mg (99%) of colorless liquid.

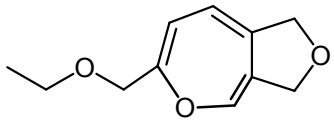


Colorless liquid. R_f (petroleum ether/ethyl acetate 5:1) = 0.48. FTIR (neat) cm^{-1}: 2976, 2929, 2858, 2115, 1714, 1609, 1557, 1484, 1442, 1372, 1348, 1254, 1219, 1197, 1169, 1070, 961, 929, 887, 843, 796. ^1H NMR (301 MHz, $CDCl_3$) δ = 6.32 (d, *J* = 3.1 Hz, 1H), 6.27 (d, *J* = 3.2 Hz, 1H), 4.54 (s, 2H), 4.42 (s, 2H), 4.17 (d, *J* = 2.4 Hz, 2H), 3.54 (d, *J* = 7.0 Hz, 2H), 2.46 (t, *J* = 2.4 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.74 (s), 150.92 (s), 110.71 (d), 109.64 (d), 79.30 (s), 74.76 (d), 65.73 (t), 64.61 (t), 63.22 (t), 56.79 (t), 15.05 (q). HRMS (EI+) [M+] calcd: 194.0943; found: 194.0943

Cycloizomerization of 2-(ethoxymethyl)-5-((prop-2-yn-1-yloxy)methyl)furan

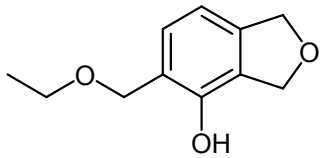
2-(ethoxymethyl)-5-((prop-2-yn-1-yloxy)methyl)furan **6** (200 mg, 1.03 mmol) was dissolved in ethyl acetate (5 ml) and $IPrAuNTf_2$ (6.8 mg, 0.007 mmol) was added. The resulting mixture was stirred at room temperature overnight. Volatiles were removed and the residue was purified by column chromatography on silica gel (eluent petroleum ether/ethyl acetate 10:1) resulting in 9.5 mg of 6-(ethoxymethyl)-1,3-dihydrofuro[3,4-c]oxepine (5%), 117 mg of 5-(ethoxymethyl)-1,3-dihydroisobenzofuran-4-ol **9** (59%), 20 mg of 1,3-dihydroisobenzofuran-5-ol **8** (20%) and 14 mg of the mixture of 4-(ethoxymethyl)-1,3-dihydroisobenzofuran-5-ol **10** and 6-(ethoxymethyl)-1,3-dihydroisobenzofuran-5-ol **11** (1:5 mixture, 7%).

6-(ethoxymethyl)-1,3-dihydrofuro[3,4-c]oxepine



Colorless oil. R_f (petroleum ether/ethyl acetate 10:1) = 0.29. FTIR (neat) cm^{-1}: 2976, 2857, 1939, 1765, 1686, 1617, 1592, 1490, 1442, 1411, 1392, 1365, 1303, 1264, 1250, 1201, 1174, 1148, 1100, 1076, 1047, 1000, 917, 901, 846, 817. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, *J* = 8.5 Hz, 1H), 7.02 – 6.83 (m, 2H), 5.21 (s, 2H), 5.12 – 4.98 (m, 4H), 3.74 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.25 (s), 140.74 (s), 132.22 (s), 121.60 (d), 115.81 (d), 108.90 (d), 93.52 (t), 73.54 (t), 73.22 (t), 64.26 (t), 15.10 (q). HRMS (EI+) [M+] calcd: 194.0943; found: 194.0941.

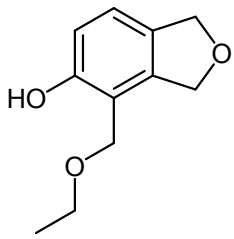
5-(ethoxymethyl)-1,3-dihydroisobenzofuran-4-ol (9)



Colorless solid. R_f (petroleum ether/ethyl acetate 10:1) = 0.17. FTIR (neat) cm^{-1}: 3354, 2976, 2895, 2868, 1737, 1632, 1598, 1487, 1463, 1441, 1378, 1349, 1327, 1281, 1263, 1233, 1153, 1121, 1088, 1044, 1008, 984, 937, 897, 803, 788. mp = 52.8-54.3 °C. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 5.13 (m, 2H), 5.08 (m, 2H), 4.74 (s, 2H), 3.62 (q, *J* = 7.0 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.86 (s), 141.33 (s), 127.56 (d), 126.46 (s), 120.82 (s), 111.97 (d), 73.84 (t), 72.17 (t), 71.73 (t), 66.30 (t), 15.02 (q). HRMS (EI+) [M+] calcd: 194.0943; found: 194.0940

1:5 Mixture of 4-(ethoxymethyl)-1,3-dihydroisobenzofuran-5-ol (10) and 6-(ethoxymethyl)-1,3-dihydroisobenzofuran-5-ol (11)

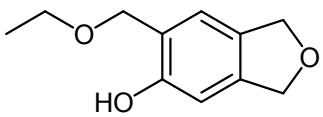
Colorless oil. R_f (petroleum ether/ethyl acetate 10:1) = 0.11. FTIR (neat) cm^{-1}: 3302, 2859, 1733, 1620, 1598, 1495, 1460, 1372, 1284, 1223, 1145, 1097, 1026, 943, 889, 855, 814, 761. HRMS (EI+) [M+] calcd: 194.0943; found: 194.0936



4-(ethoxymethyl)-1,3-dihydroisobenzofuran-5-ol (10)

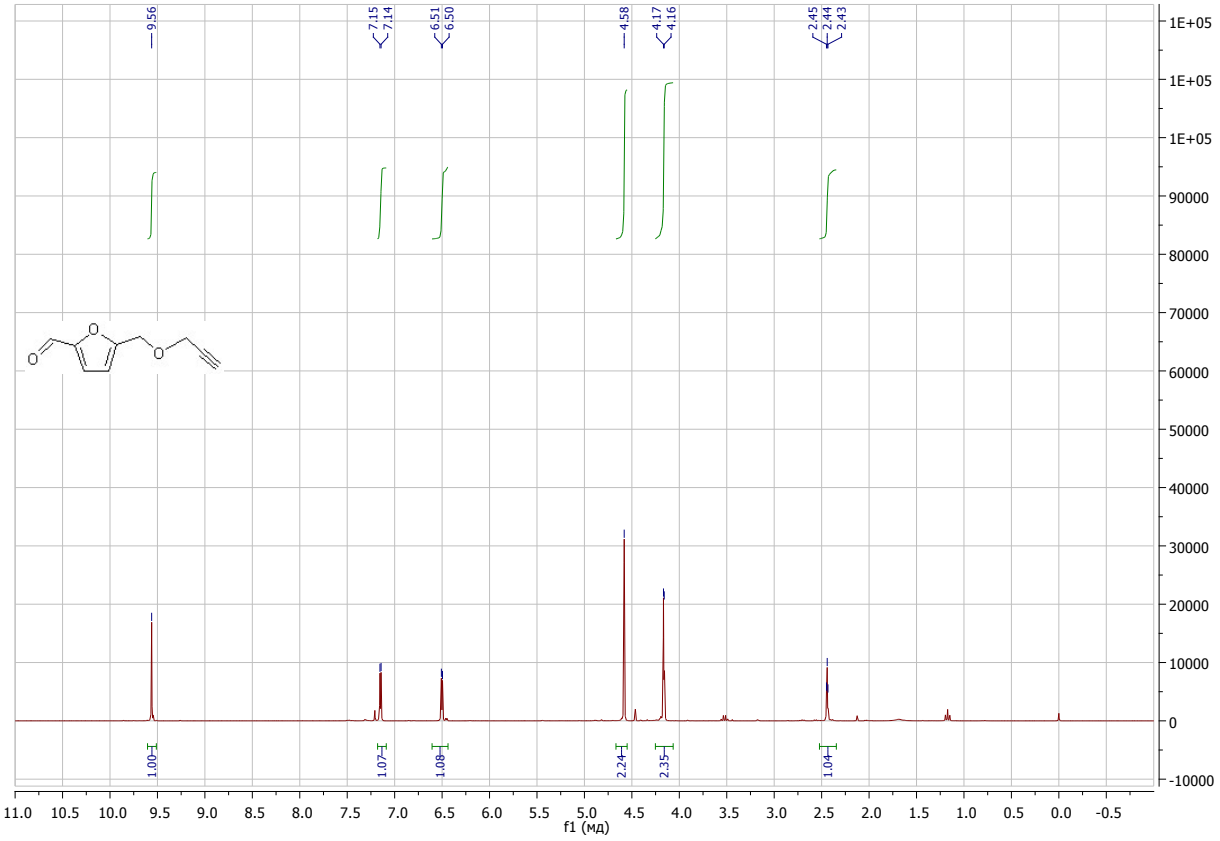
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.16 (s, 2H), 4.69 (s, 2H), 4.62 (s, 2H), 3.61 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.79 (s), 141.02 (s), 130.08 (s), 121.09 (d), 116.18 (d), 115.66 (s), 73.52 (t), 72.31 (t), 69.08 (t), 66.77 (t), 15.01 (q).

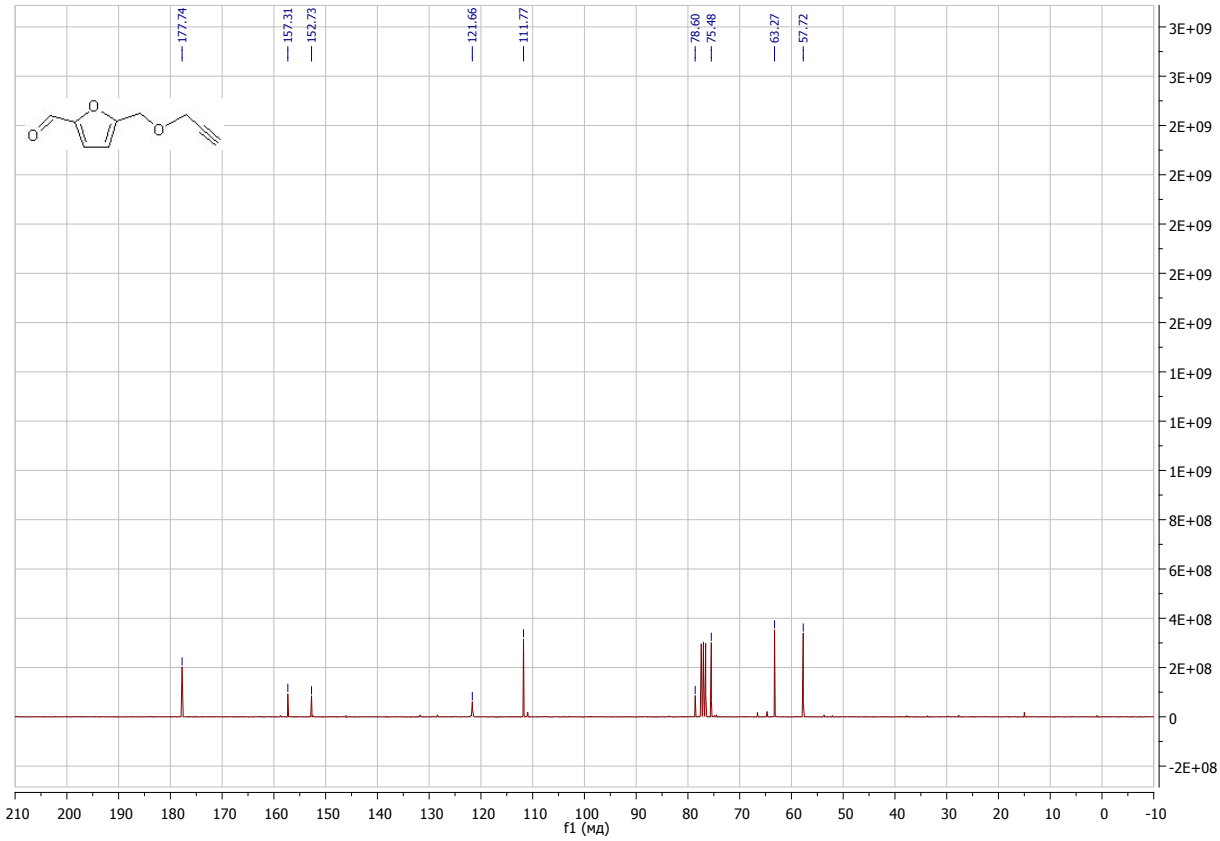
6-(ethoxymethyl)-1,3-dihydroisobenzofuran-5-ol (11)



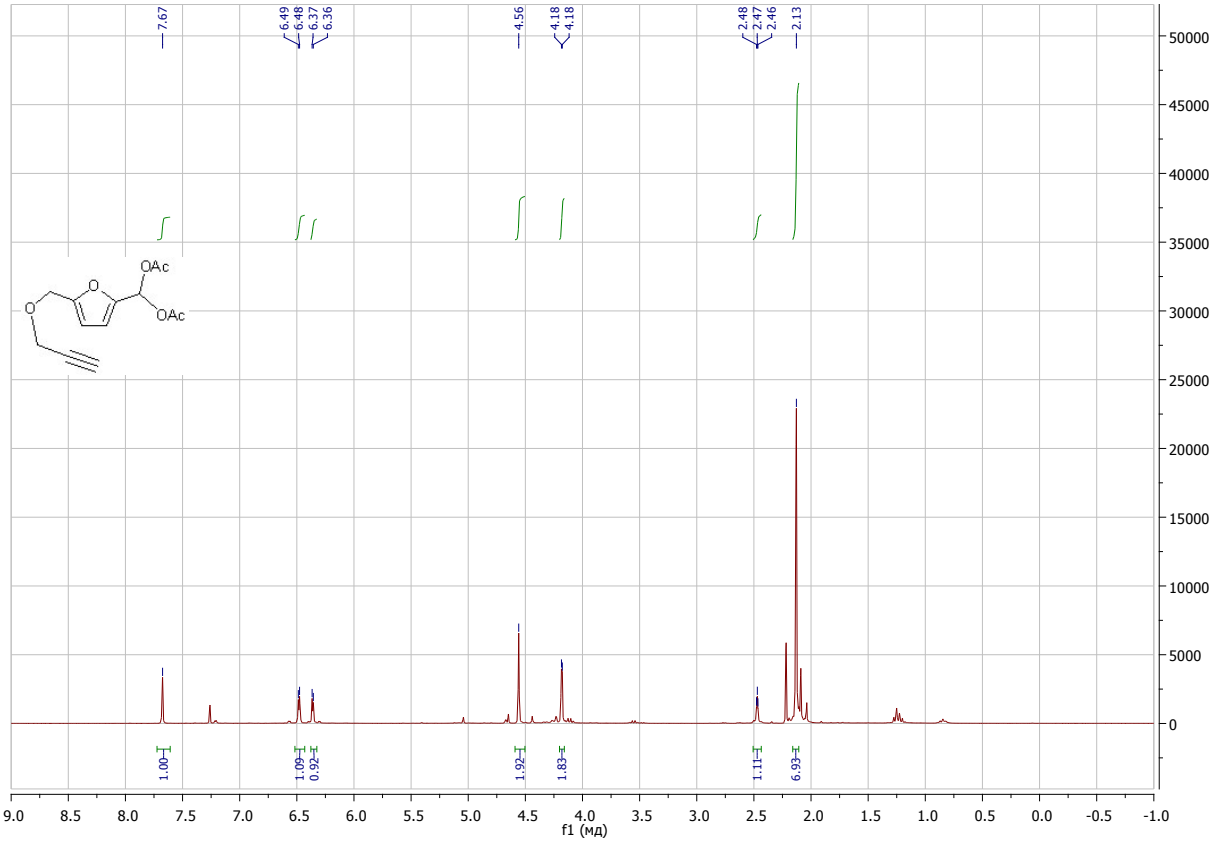
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (s, 1H), 6.87 (s, 1H), 6.76 (s, 1H), 5.04 (s, 4H), 4.69 (s, 2H), 3.61 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.08 (s), 137.62 (s), 131.07 (s), 121.59 (s), 120.25 (d), 109.01 (d), 73.47 (t), 73.12 (t), 72.15 (t), 66.19 (t), 15.01 (q).

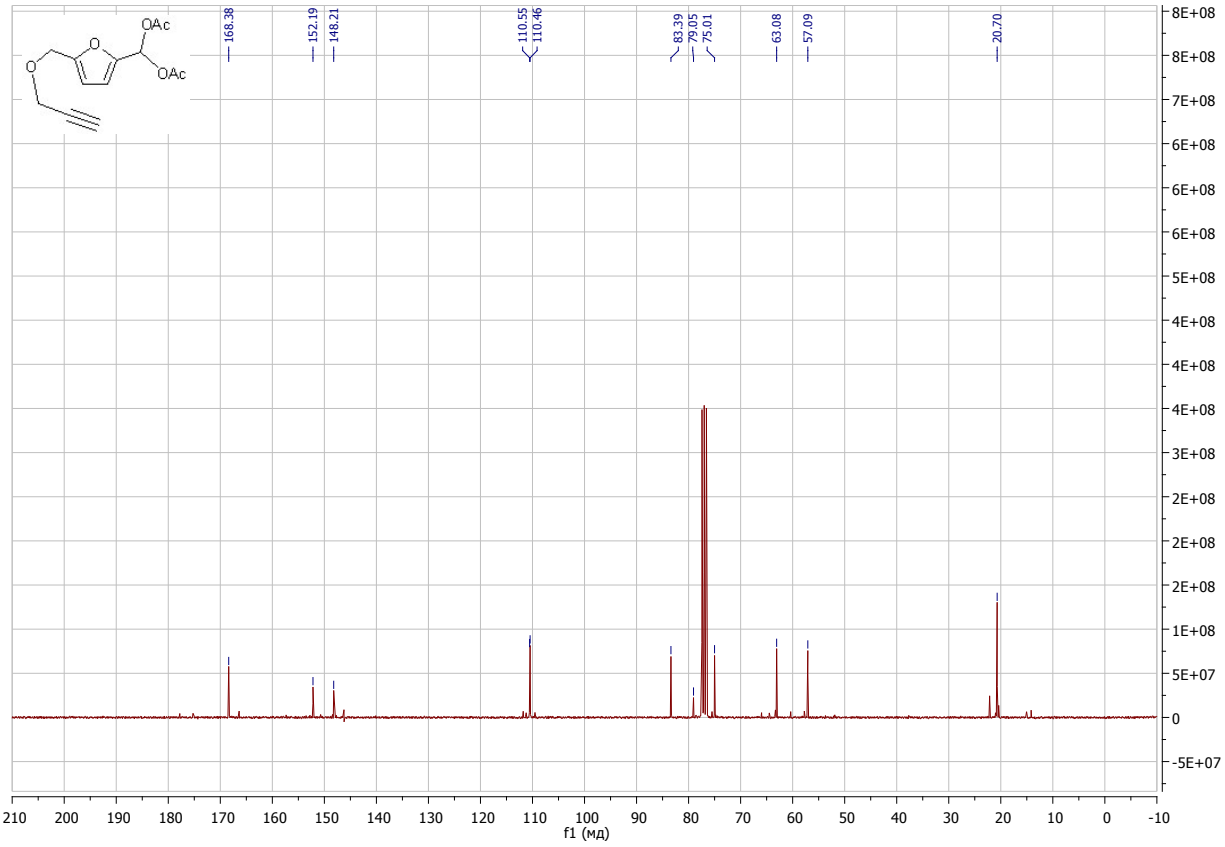
5-((prop-2-yn-1-yloxy)methyl)furan-2-carbaldehyde (1)



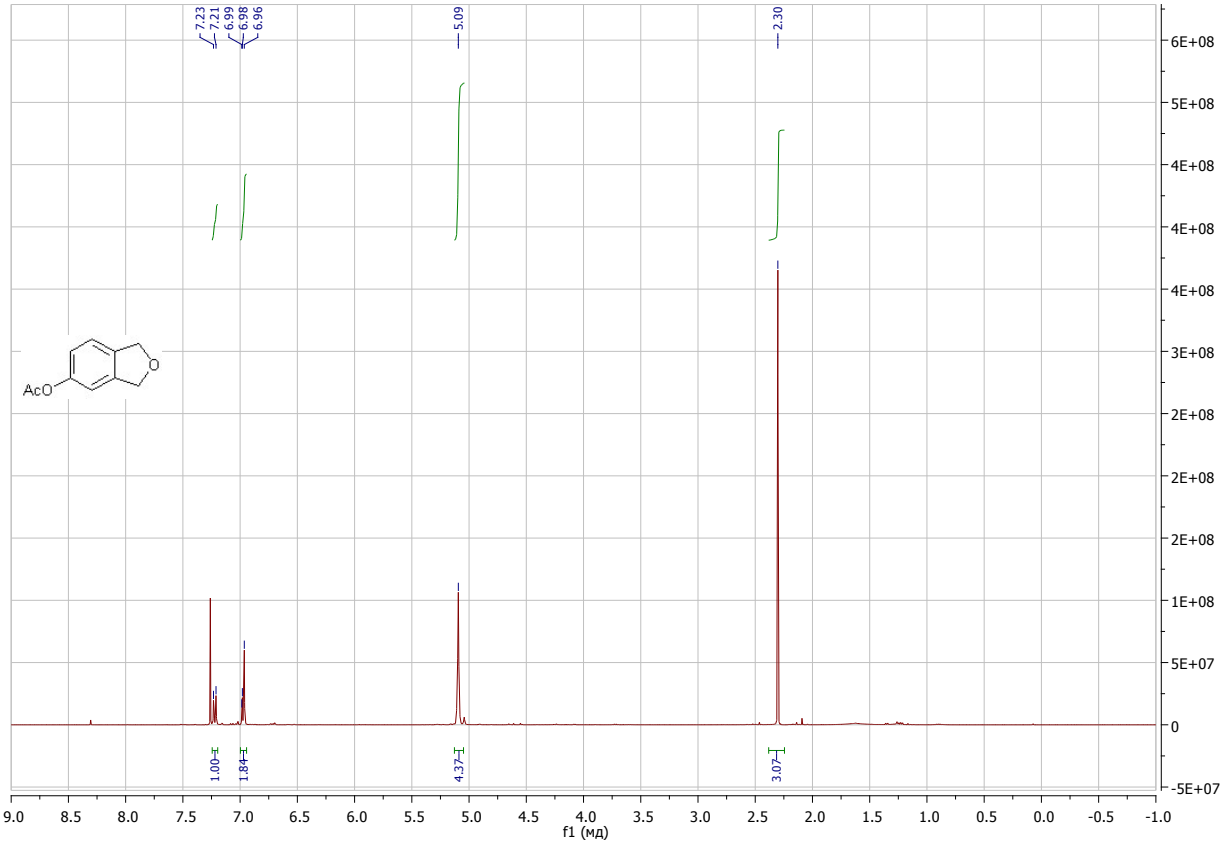


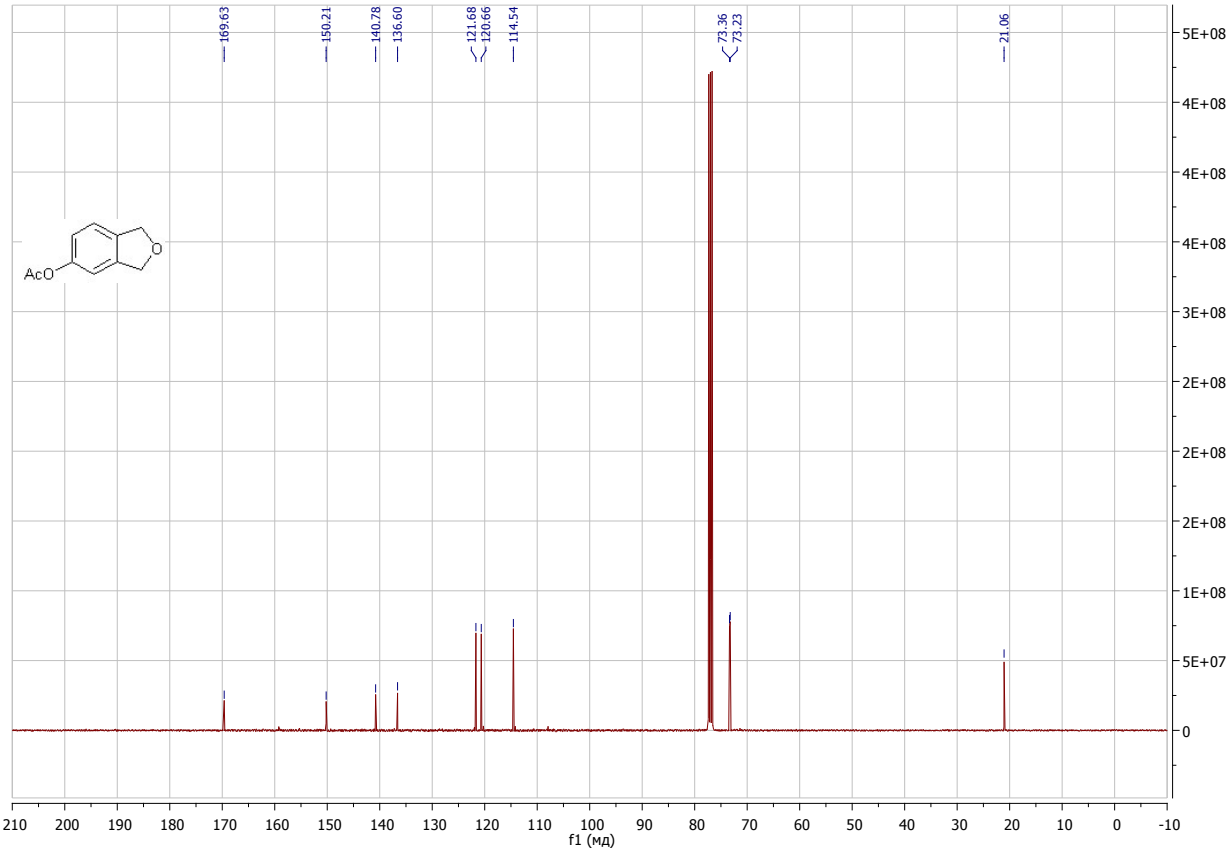
(5-((prop-2-yn-1-yloxy)methyl)furan-2-yl)methylene diacetate (2)



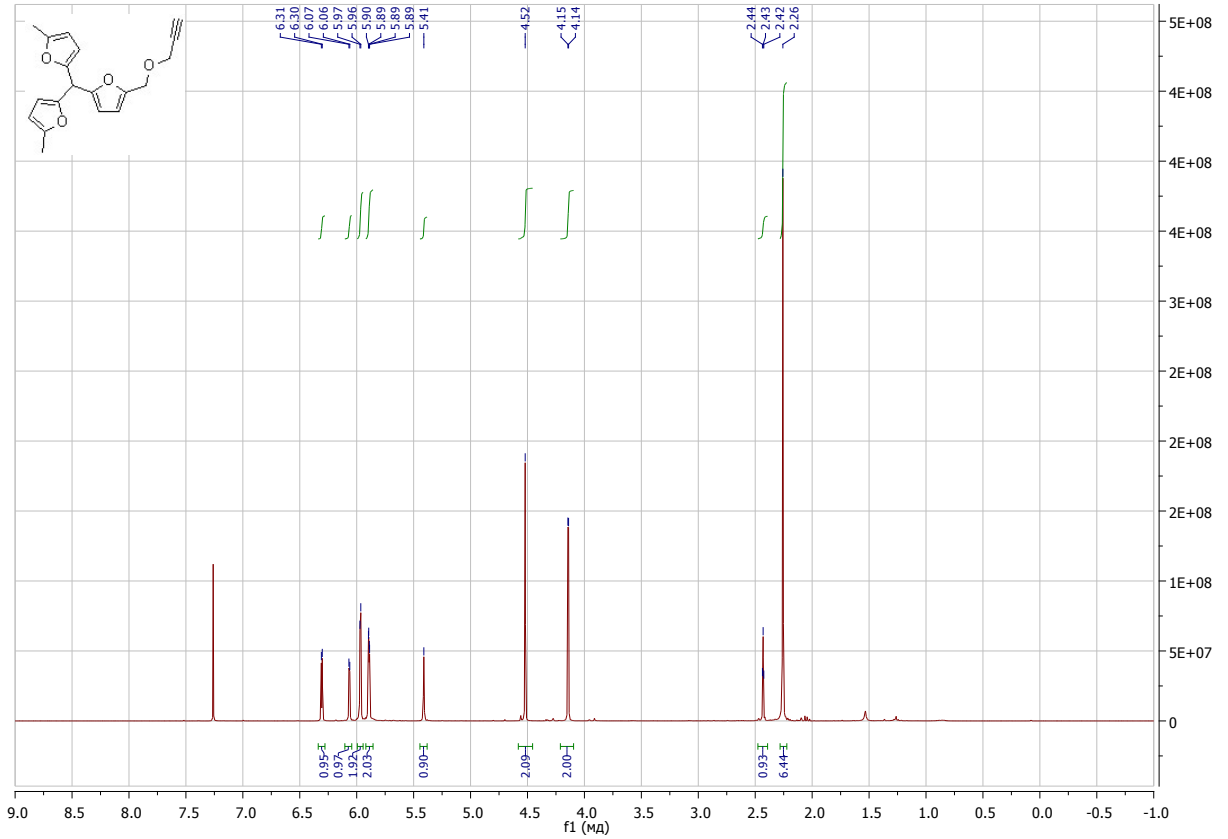


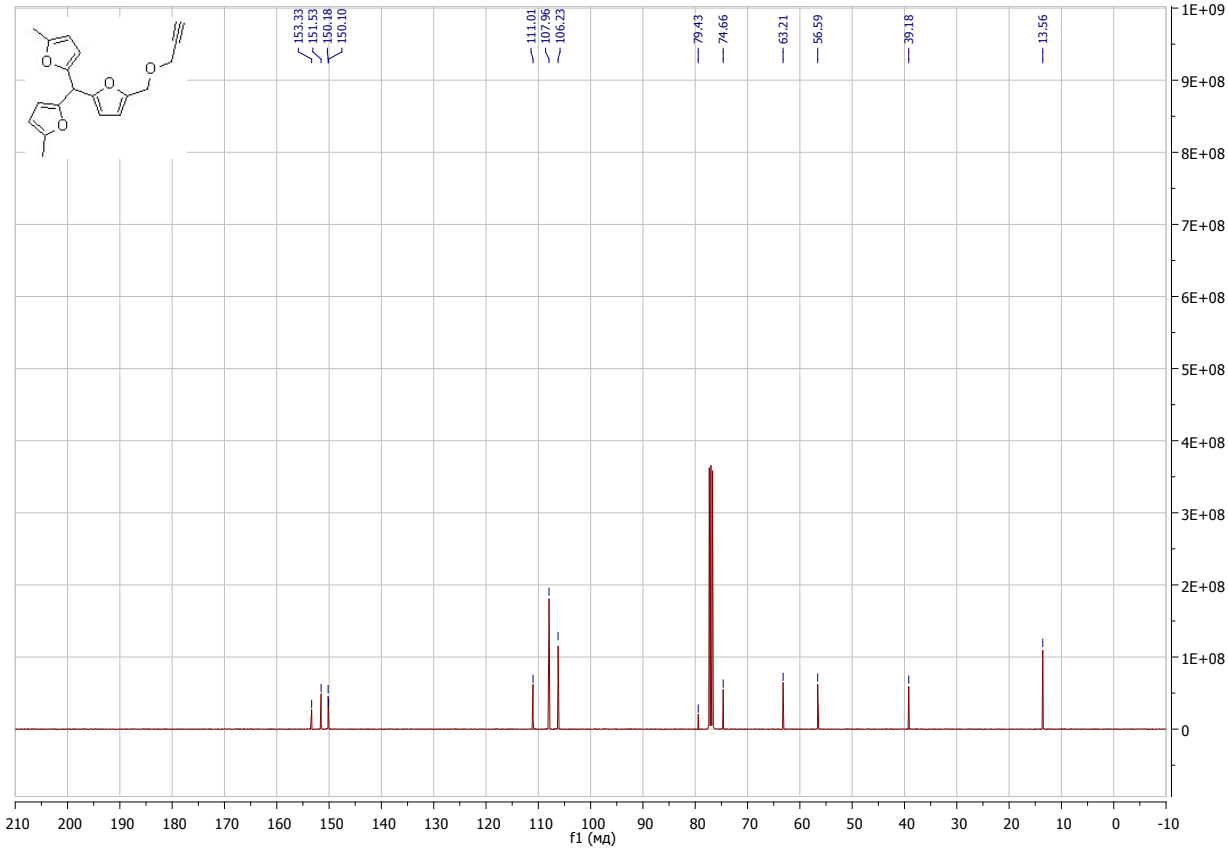
1,3-dihydroisobenzofuran-5-yl acetate (8)



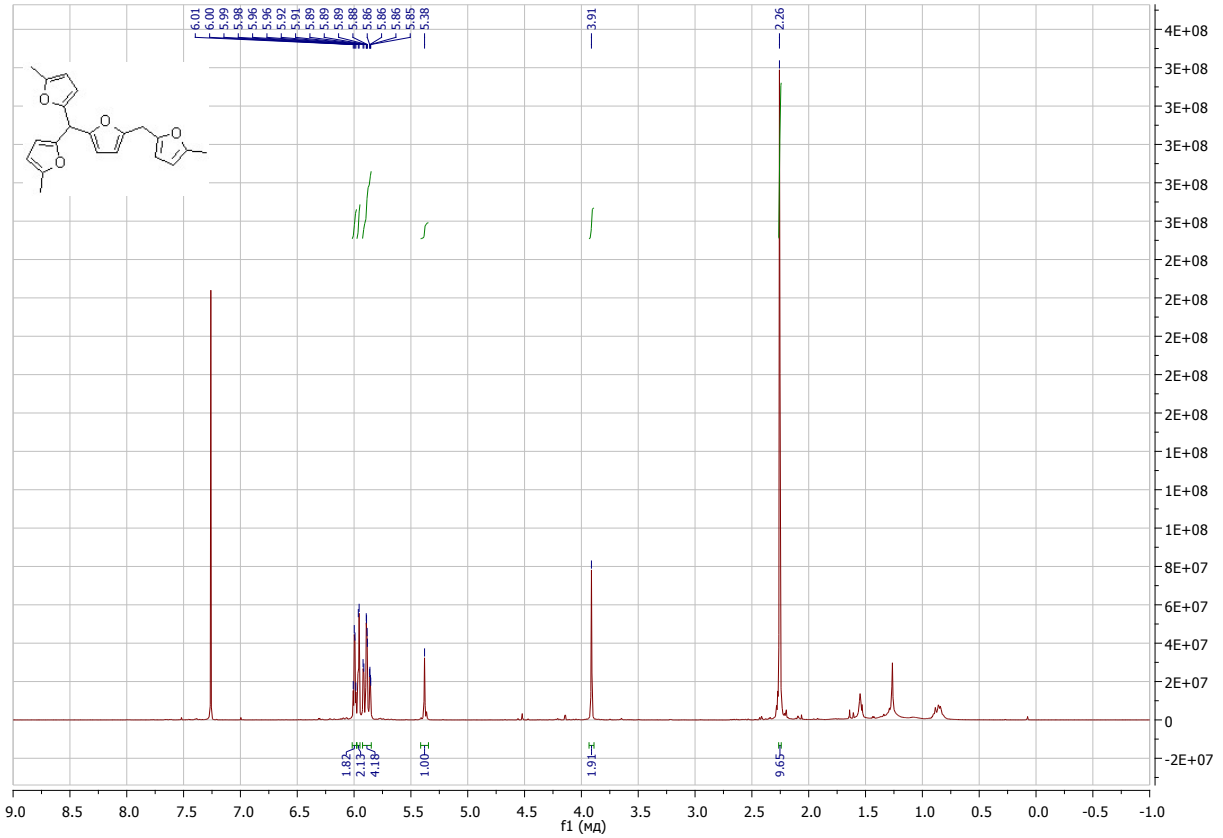


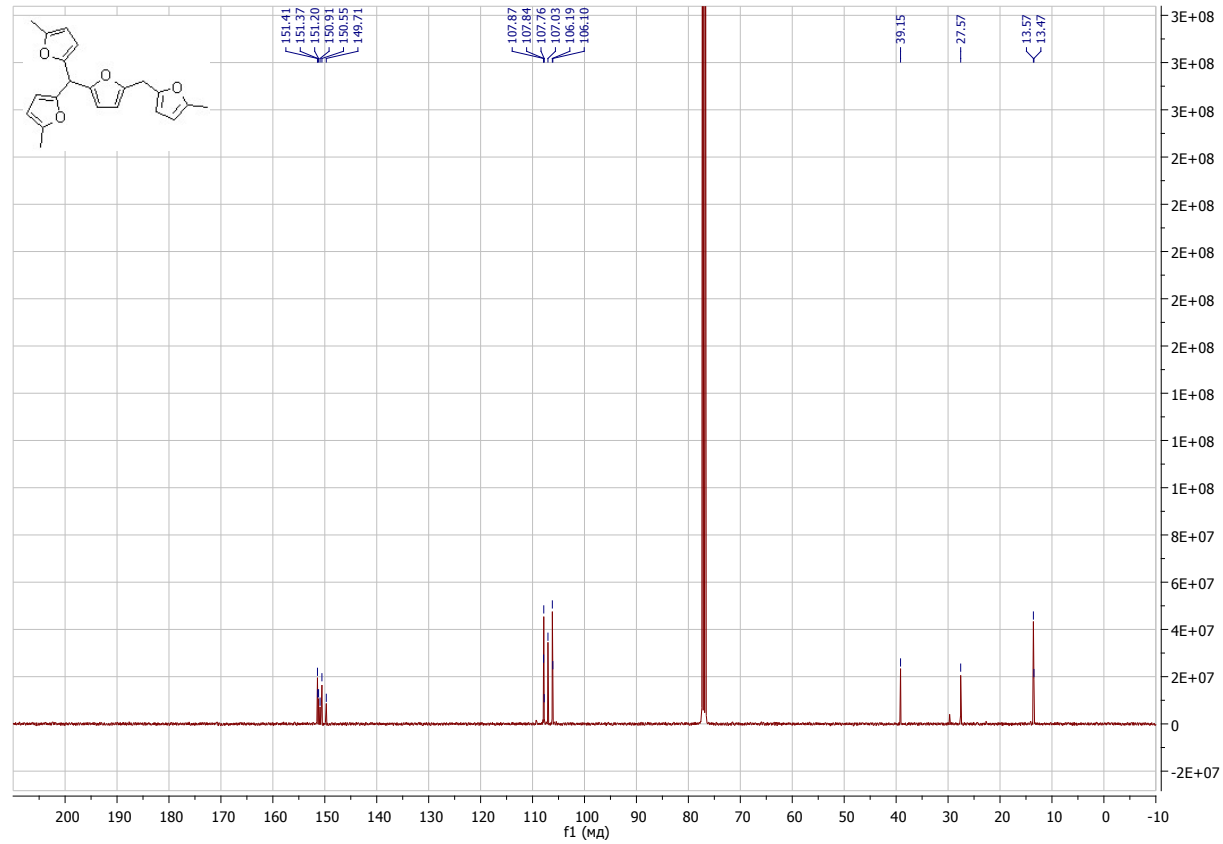
5,5'-((5-((prop-2-yn-1-yloxy)methyl)furan-2-yl)methylene)bis(2-methylfuran) (3)



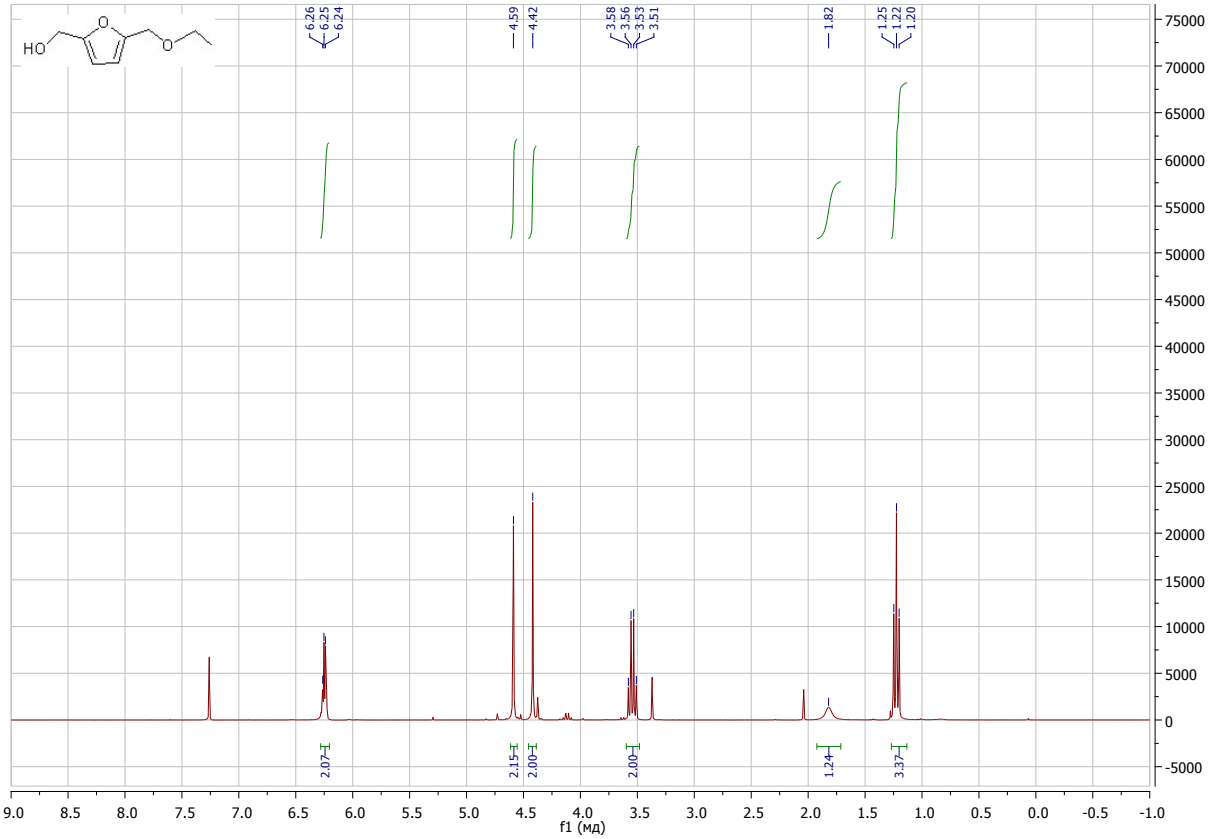


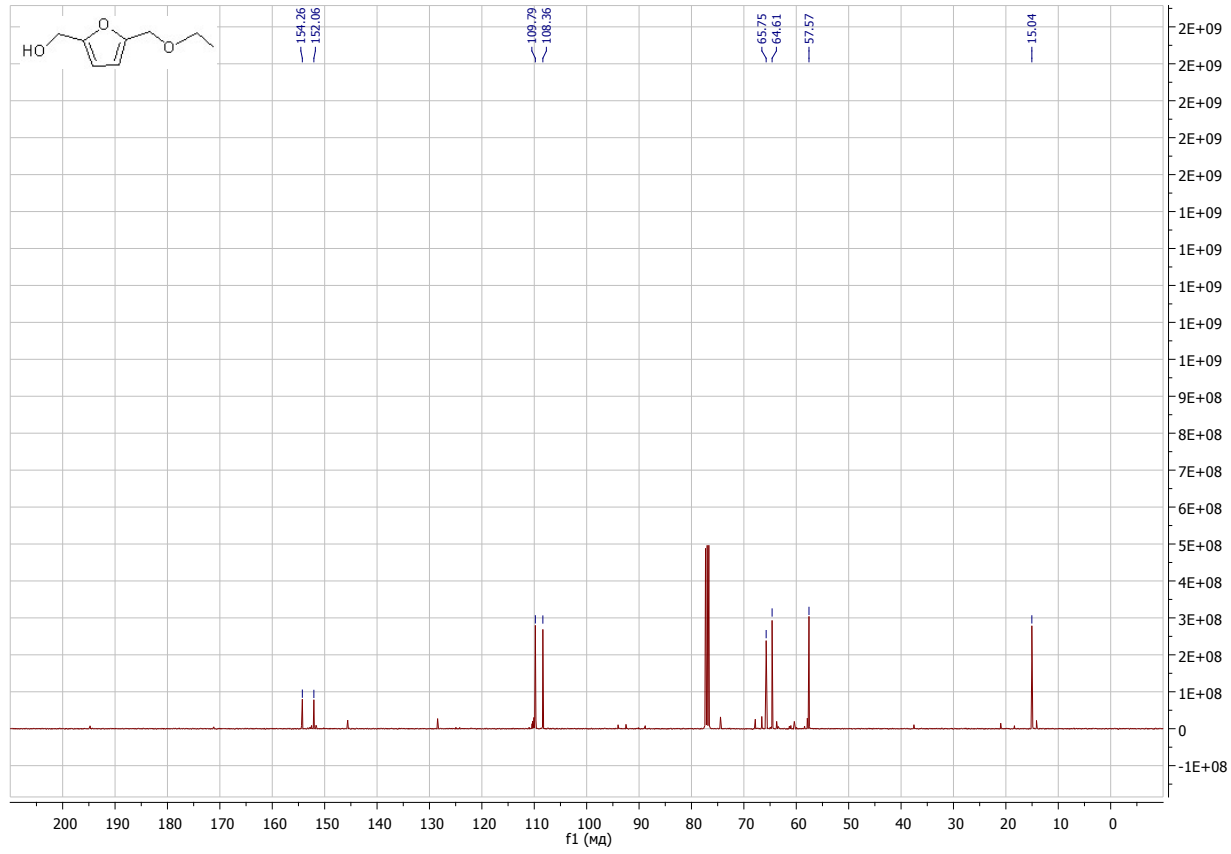
5,5'-((5-((5-methylfuran-2-yl)methyl)furan-2-yl)methylene)bis(2-methylfuran)



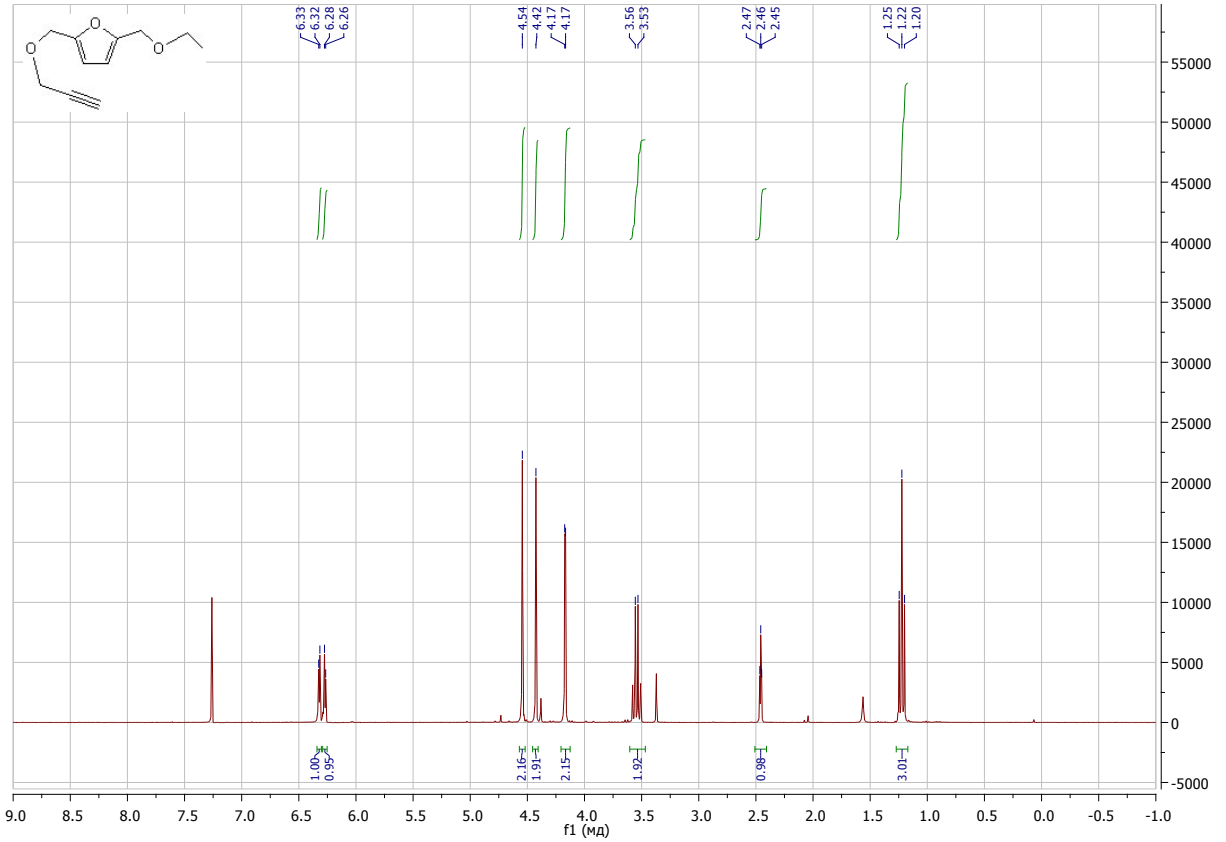


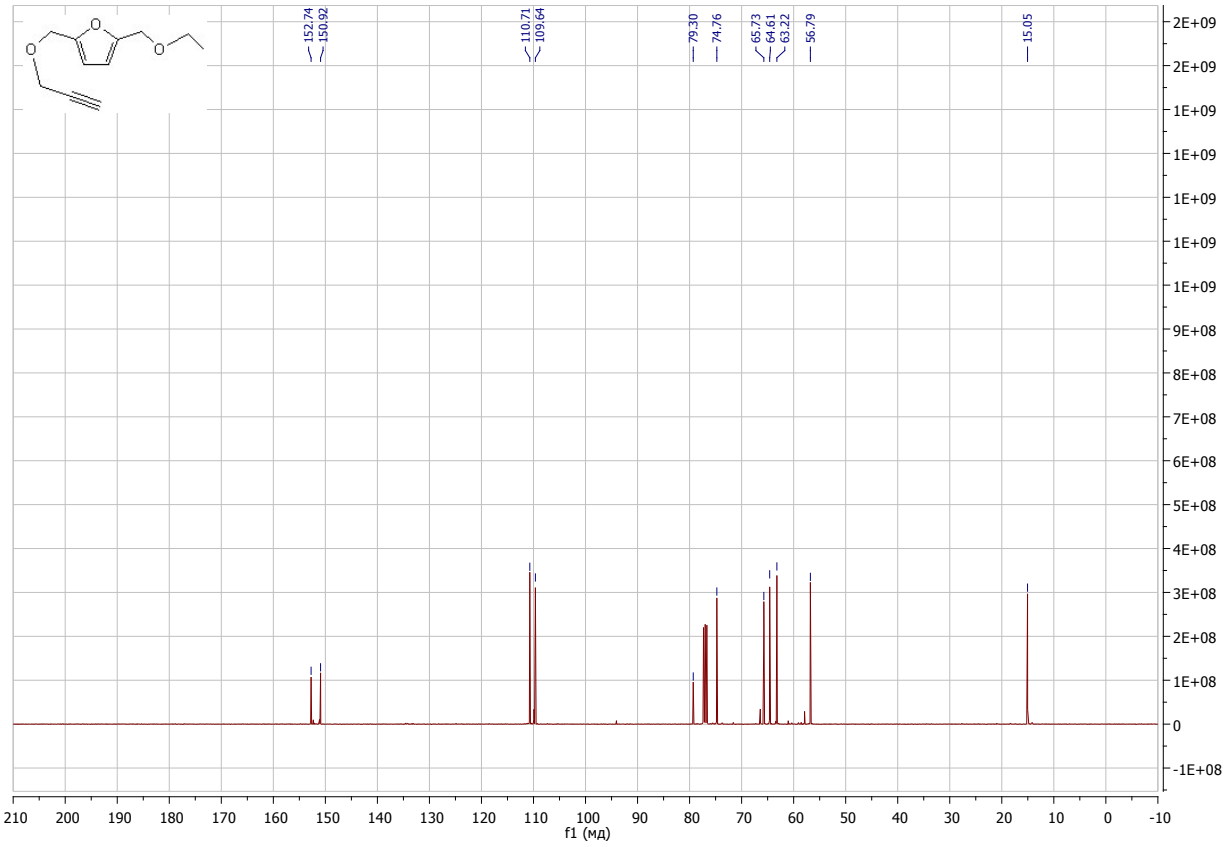
(5-(ethoxymethyl)furan-2-yl)methanol (5)



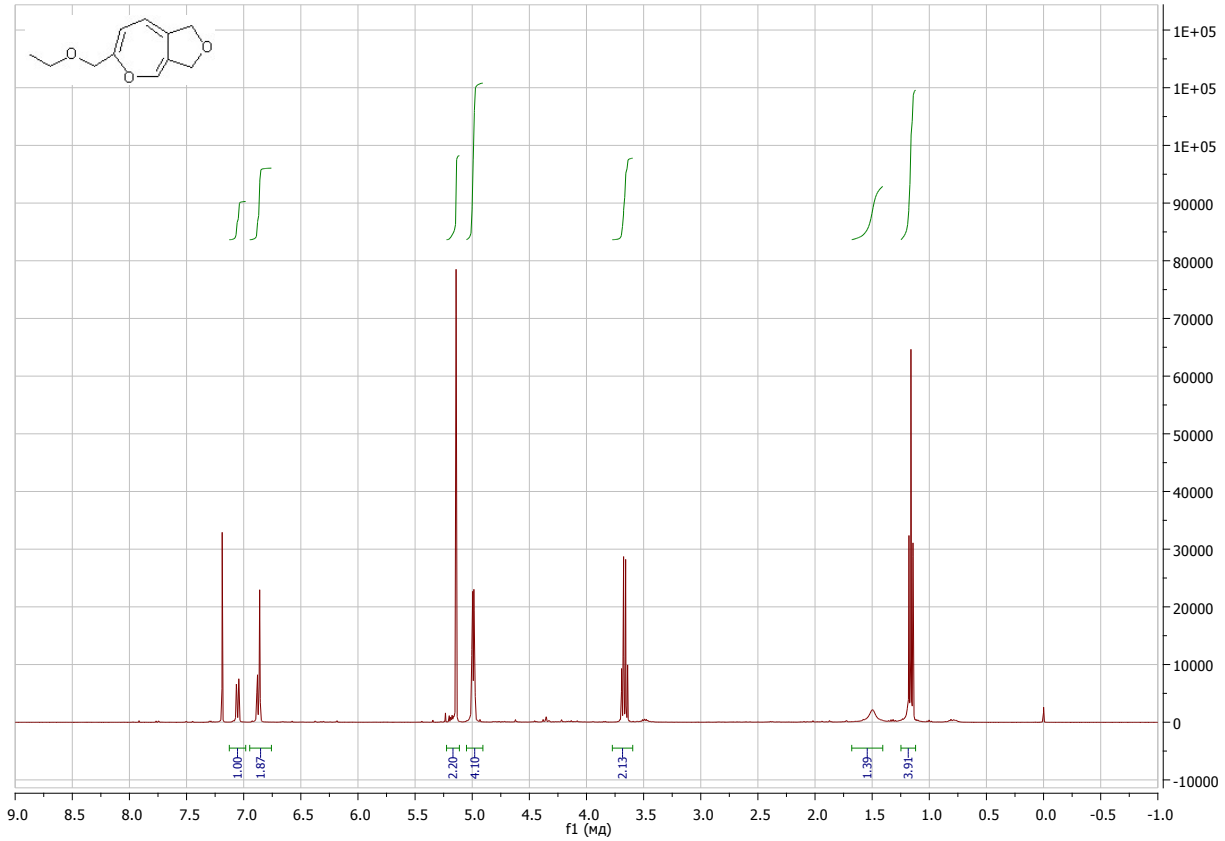


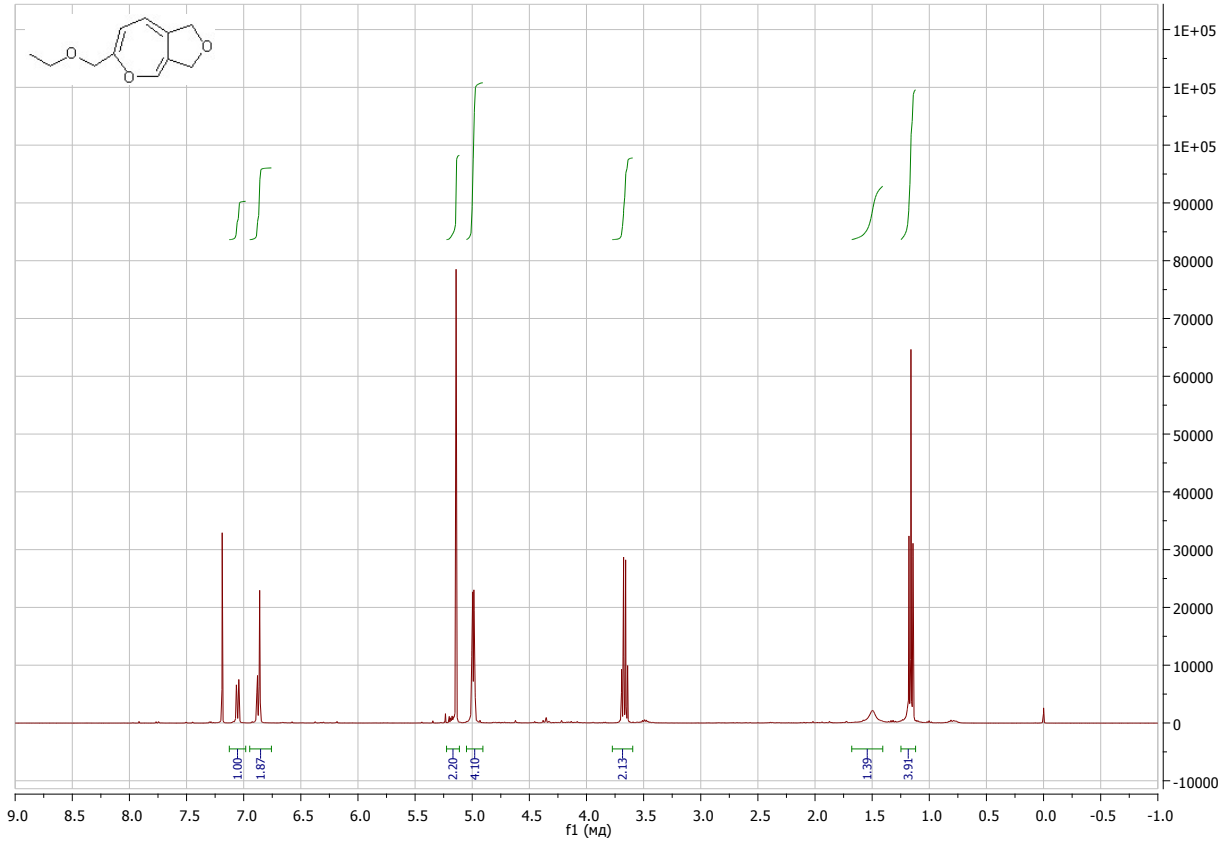
2-(ethoxymethyl)-5-((prop-2-yn-1-yloxy)methyl)furan (6)



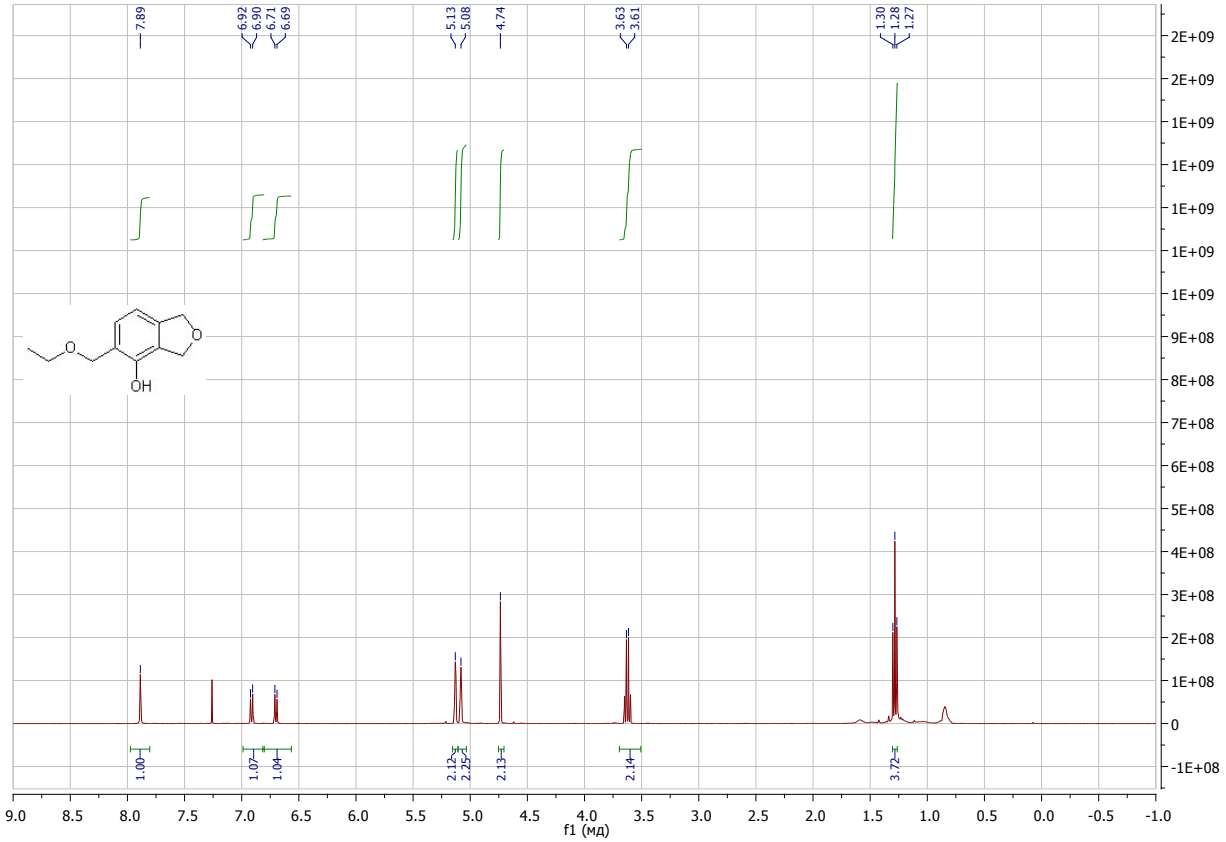


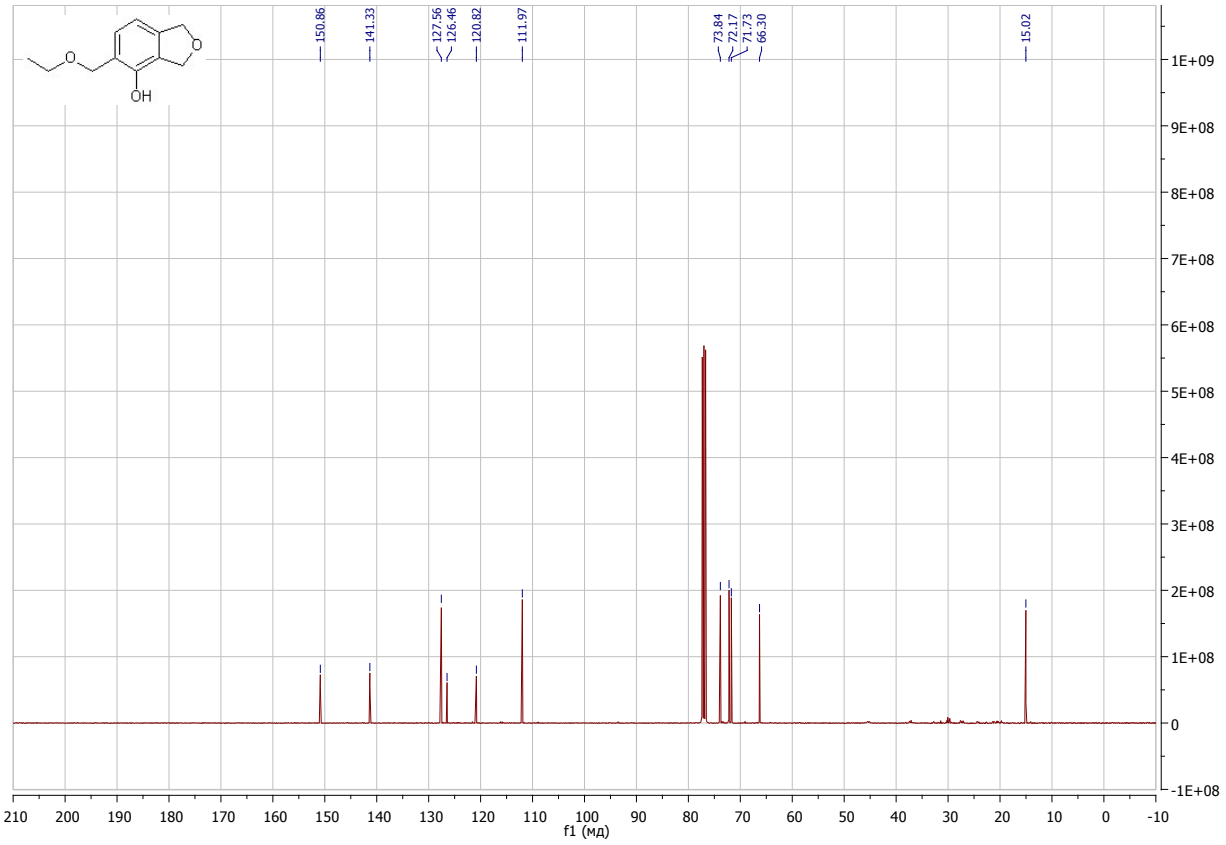
6-(ethoxymethyl)-1,3-dihydrofuro[3,4-c]oxepine



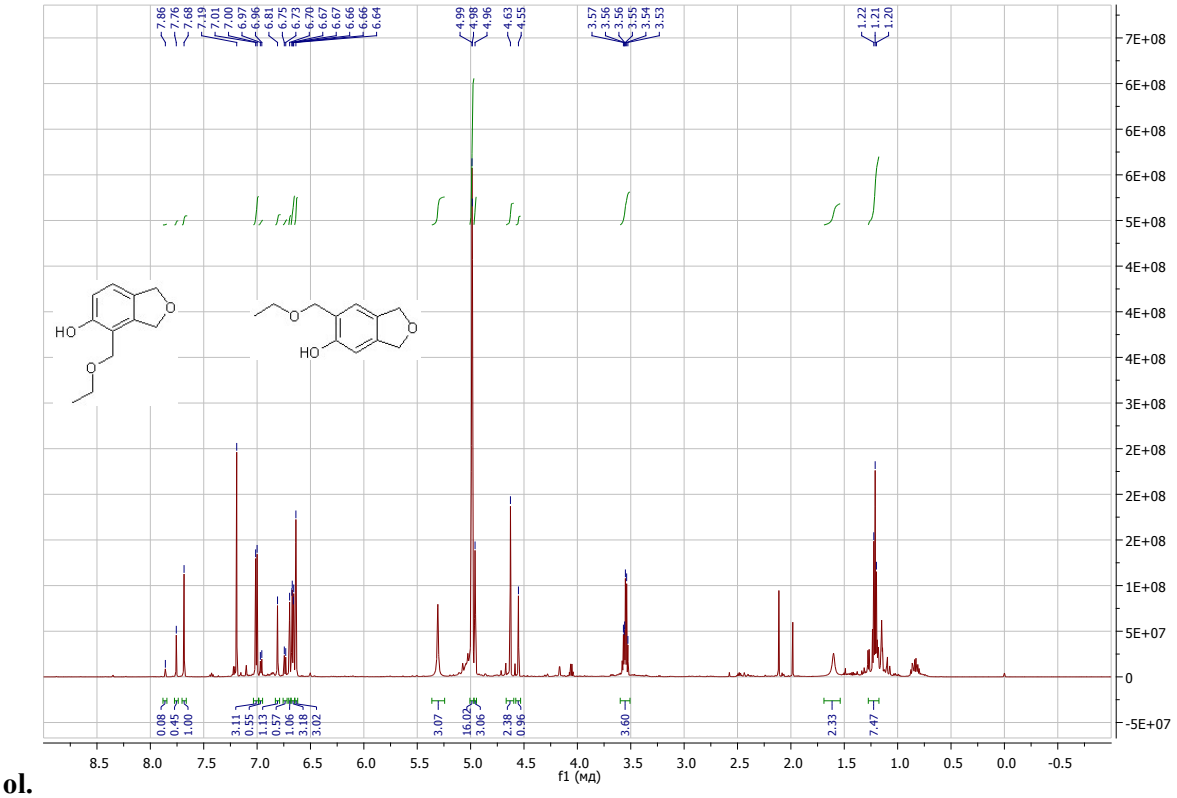


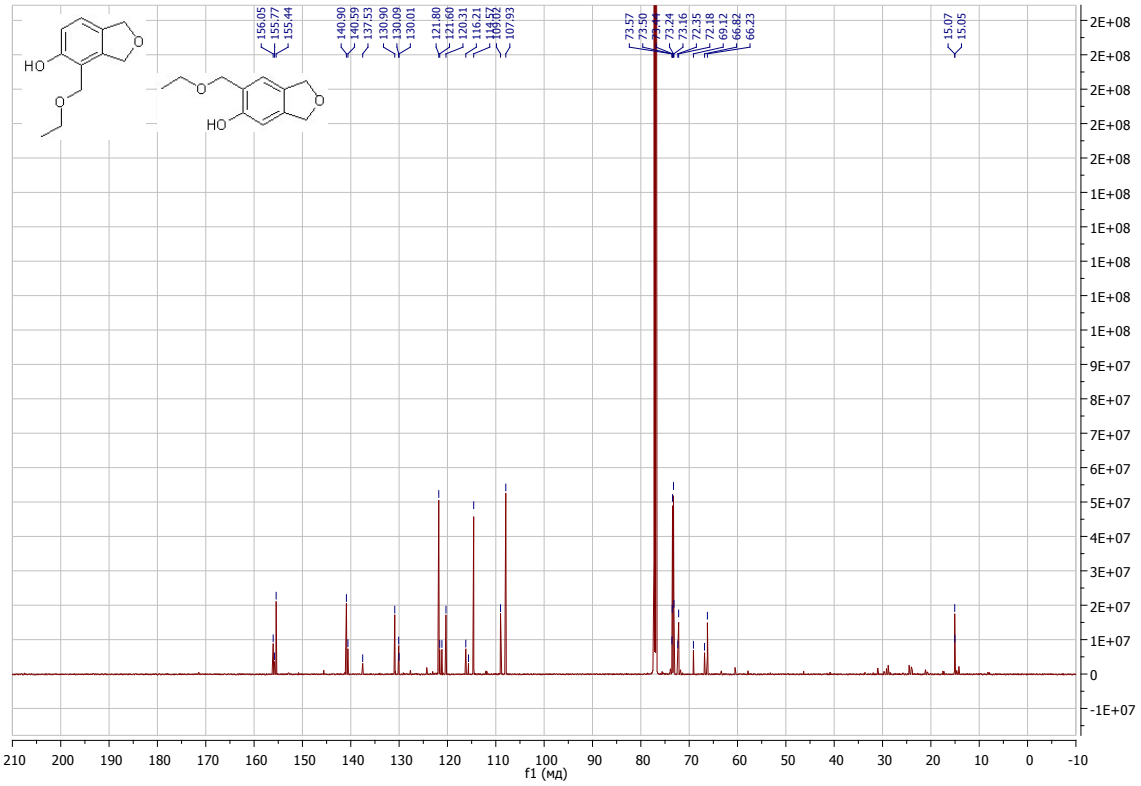
5-(ethoxymethyl)-1,3-dihydroisobenzofuran-4-ol (9)





4-(ethoxymethyl)-1,3-dihydroisobenzofuran-5-ol and 6-(ethoxymethyl)-1,3-dihydroisobenzofuran-5-ol.





Chemie : Svetlana Tsupova (AK Hashmi)
Probe : ST676
Dateinamen : sts9.*
Operateur : F. Rominger (AK Hofmann)
Gerät : Bruker APEX-II Quazar

Table 4: Kristalldaten und Strukturverfeinerung für sts9

Strukturkennzeichen	sts9
Summenformel	$C_8H_8O_2$
Molmasse	136.14
Temperatur	200(2) K
Wellenlänge	0.71073 Å
Kristallsystem	monoklin
Raumgruppe	P21/n
Z	4
Gitterkonstanten	a = 6.6884(5) Å α = 90 °
	b = 7.6318(6) Å β =100.414(2) °
	c = 12.9438(11) Å γ = 90 °
Zellvolumen	649.83(9) $Å^3$
Dichte (berechnet)	1.392 g/cm^3
Absorptionskoeffizient µ	0.100 mm^{-1}
Kristallform	polyhedron
Kristallgröße	0.110 x 0.090 x 0.090 mm^3
Kristallfarbe	colourless
Gemessener Theta-Bereich	3.112 bis 27.386 °
Indexgrenzen	$-8\leq h\leq 8$, $0\leq k\leq 9$, $0\leq l\leq 16$
Gemessene Reflexe	6490
Unabhängige Reflexe	1928 (R(int) = 0.0279)
Beobachtete Reflexe	1534 ($I > 2\sigma(I)$)
Absorptionskorrektur	Semi-empirical from equivalents
Max/min Transmission	0.96 and 0.89
Strukturverfeinerung	Full-matrix least-squares an F^2
Daten/Restraints/Parameter	1928 / 0 / 96
Goodness-of-fit an F^2	1.18
R-Werte (I>2sigma(I))	R1 = 0.042, wR2 = 0.131
Extinktionskoeffizient	n/a
Max/min Restelektronendichte	0.27 und -0.21 $eÅ^{-3}$

Table 5: Crystal data and structure refinement for sts9.

Identification code	sts9
Empirical formula	$C_8H_8O_2$
Formula weight	136.14
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Z	4
Unit cell dimensions	a = 6.6884(5) Å α = 90 deg.
	b = 7.6318(6) Å β =100.414(2) deg.
	c = 12.9438(11) Å γ = 90 deg.
Volume	649.83(9) $Å^3$
Density (calculated)	1.39 g/cm^3
Absorption coefficient	0.10 mm^{-1}
Crystal shape	polyhedron
Crystal size	0.110 x 0.090 x 0.090 mm^3

Crystal colour	colourless
Theta range for data collection	3.1 to 27.4 deg.
Index ranges	$-8 \le h \le 8$, $0 \le k \le 9$, $0 \le l \le 16$
Reflections collected	6490
Independent reflections	1928 (R(int) = 0.0279)
Observed reflections	1534 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.89
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1928 / 0 / 96
Goodness-of-fit on F^2	1.18
Final R indices (I>2sigma(I))	R1 = 0.042, wR2 = 0.131
Largest diff. peak and hole	0.27 and -0.21 $eÅ^{-3}$

Table 6: Atomkoordinaten und äquivalente isotrope Auslenkungsparameter ($Å^2$) für sts9. U_{eq} wird berechnet als ein Drittel der Spur des orthogonalen U_{ij} Tensors.
(Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for sts9. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.)

Atom	x	y	z	U_{eq}
O1	0.5410(3)	0.1069(2)	0.9001(1)	0.0355(5)
H1	0.450(5)	0.158(4)	0.925(3)	0.059(10)
C1	0.5312(3)	0.1489(3)	0.7965(2)	0.0256(5)
C2	0.6888(3)	0.0886(3)	0.7489(2)	0.0254(5)
H2	0.7953	0.0191	0.7867	0.030
C3	0.6861(3)	0.1330(3)	0.6446(2)	0.0230(5)
C4	0.5293(4)	0.2307(3)	0.5880(2)	0.0230(6)
C5	0.3701(4)	0.2870(3)	0.6350(2)	0.0264(5)
H5	0.2607	0.3520	0.5960	0.032
C6	0.3729(4)	0.2468(3)	0.7397(2)	0.0271(7)
H6	0.2658	0.2865	0.7731	0.033
O7	0.7701(3)	0.1885(2)	0.4810(1)	0.0362(5)
C7	0.8373(4)	0.0911(3)	0.5760(2)	0.0302(6)
H7A	0.9756	0.1280	0.6098	0.036
H7B	0.8387	-0.0361	0.5613	0.036
C8	0.5695(5)	0.2584(3)	0.4787(2)	0.0303(6)
H8A	0.4681	0.1954	0.4267	0.036
H8B	0.5648	0.3846	0.4607	0.036

Table 7: H-Atomkoordinaten und isotrope Auslenkungsparameter ($Å^2$) für sts9.
(Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for sts9.)

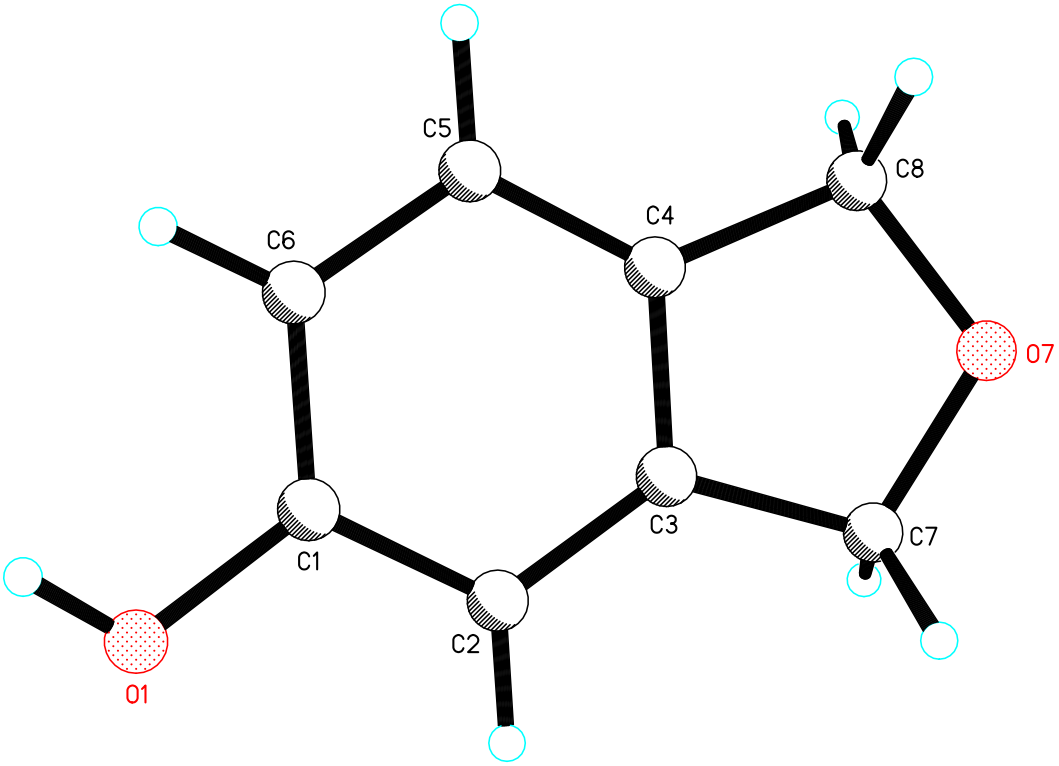
Atom	x	y	z	U_{eq}
H1	0.450(5)	0.158(4)	0.925(3)	0.059(10)
H2	0.7953	0.0191	0.7867	0.030
H5	0.2607	0.3520	0.5960	0.032
H6	0.2658	0.2865	0.7731	0.033
H7A	0.9756	0.1280	0.6098	0.036
H7B	0.8387	-0.0361	0.5613	0.036
H8A	0.4681	0.1954	0.4267	0.036
H8B	0.5648	0.3846	0.4607	0.036

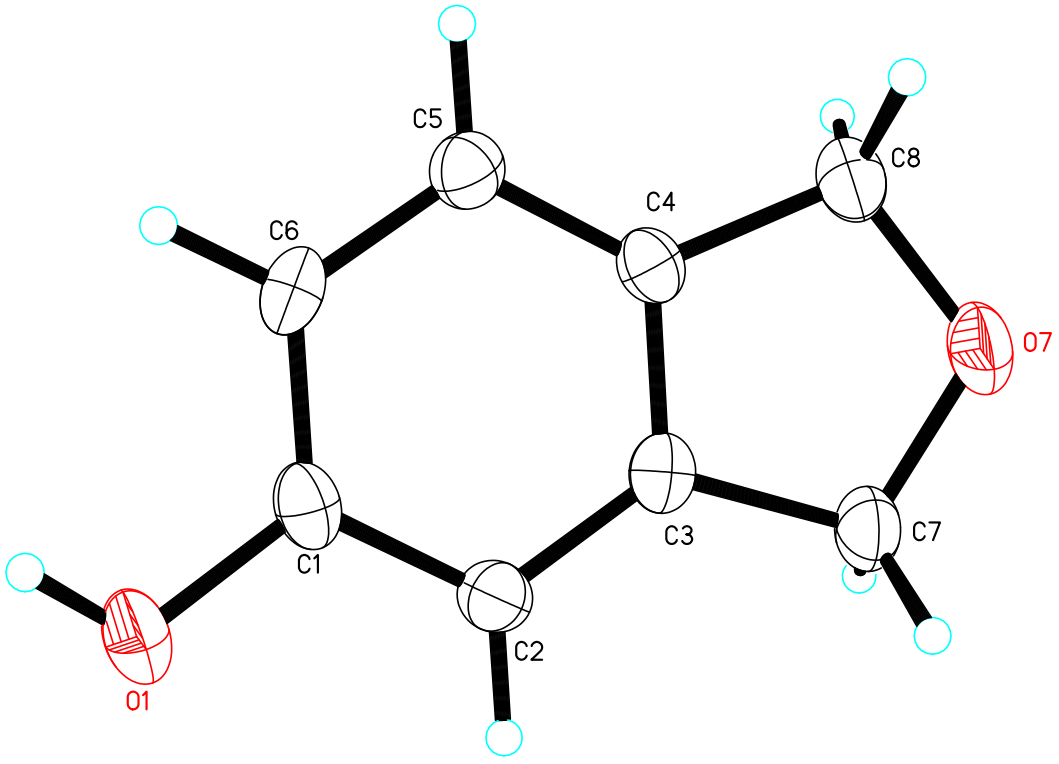
Table 8: Anisotrope Auslenkungsparameter (Å^2) für sts9. Der Exponent für den anisotropen Auslenkungsparameter hat die Form: -2 pi^2 (h^2 a^{*2} U_{11} + ... + 2 h k a* b* U_{12})
(Anisotropic displacement parameters (Å^2) for sts9. The anisotropic displacement factor exponent takes the form: -2 pi^2 (h^2 a^{*2} U_{11} + ... + 2 h k a* b* U_{12}))

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0424(11)	0.0446(11)	0.0220(9)	0.0014(7)	0.0126(8)	0.0030(8)
C1	0.0307(12)	0.0272(11)	0.0200(11)	-0.0035(9)	0.0076(9)	-0.0060(9)
C2	0.0264(11)	0.0256(11)	0.0238(11)	0.0008(9)	0.0036(9)	0.0013(9)
C3	0.0252(11)	0.0198(10)	0.0252(11)	-0.0033(8)	0.0080(8)	-0.0043(8)
C4	0.0263(13)	0.0212(11)	0.0219(13)	0.0004(8)	0.0052(10)	-0.0038(8)
C5	0.0252(12)	0.0254(11)	0.0293(14)	0.0012(10)	0.0064(10)	-0.0011(9)
C6	0.0236(14)	0.0295(14)	0.0313(16)	-0.0036(8)	0.0131(13)	-0.0002(8)
O7	0.0411(10)	0.0432(10)	0.0289(9)	0.0056(8)	0.0184(7)	0.0027(9)
C7	0.0319(12)	0.0340(12)	0.0276(13)	0.0004(9)	0.0130(10)	0.0009(10)
C8	0.0346(16)	0.0310(14)	0.0271(15)	0.0025(8)	0.0107(12)	-0.0015(9)

Table 9: Bindungslängen (Å) und -winkel (°) für sts9.
(Bond lengths (Å) and angles (deg) for sts9.)

O1-C1	1.369(3)	C1-C6-H6	119.7
O1-H1	0.83(4)	C7-O7-C8	110.84(17)
C1-C6	1.392(3)	O7-C7-C3	104.89(17)
C1-C2	1.392(3)	O7-C7-H7A	110.8
C2-C3	1.388(3)	C3-C7-H7A	110.8
C2-H2	0.9500	O7-C7-H7B	110.8
C3-C4	1.384(3)	C3-C7-H7B	110.8
C3-C7	1.496(3)	H7A-C7-H7B	108.8
C4-C5	1.386(3)	O7-C8-C4	104.7(2)
C4-C8	1.502(4)	O7-C8-H8A	110.8
C5-C6	1.387(4)	C4-C8-H8A	110.8
C5-H5	0.9500	O7-C8-H8B	110.8
C6-H6	0.9500	C4-C8-H8B	110.8
O7-C7	1.438(3)	H8A-C8-H8B	108.9
O7-C8	1.439(3)		
C7-H7A	0.9900		
C7-H7B	0.9900		
C8-H8A	0.9900		
C8-H8B	0.9900		
C1-O1-H1	111(2)		
O1-C1-C6	122.7(2)		
O1-C1-C2	116.8(2)		
C6-C1-C2	120.5(2)		
C3-C2-C1	118.19(19)		
C3-C2-H2	120.9		
C1-C2-H2	120.9		
C4-C3-C2	121.4(2)		
C4-C3-C7	109.2(2)		
C2-C3-C7	129.3(2)		
C3-C4-C5	120.2(2)		
C3-C4-C8	109.1(2)		
C5-C4-C8	130.7(2)		
C4-C5-C6	119.0(2)		
C4-C5-H5	120.5		
C6-C5-H5	120.5		
C5-C6-C1	120.6(2)		
C5-C6-H6	119.7		


C5
C8
C4
C6
O7
C3
C7
C1
C2
O1


C5
C8
C4
C6
O7
C3
C7
C1
C2
O1

sts9: colourless crystal (polyhedron), dimensions 0.110 x 0.090 x 0.090 mm^3, crystal system monoclinic, space group $P2_1/n$, Z=4, a=6.6884(5) Å, b=7.6318(6) Å, c=12.9438(11) Å, alpha=90 deg, beta=100.414(2) deg, gamma=90 deg, V=649.83(9) $Å^3$, rho=1.392 g/cm^3, T=200(2) K, $Theta_{max}$= 27.386 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.37and a completeness of 93.0% to a resolution of 0.77 Å, 6490 reflections measured, 1928 unique (R(int)=0.0279), 1534 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.10mm^{-1}, T_{min}=0.89, T_{max}=0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL (Version 2014-3) software [2], 96 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.18 for observed reflections, final residual values R1(F)=0.042, $wR(F^2)$=0.131 for observed reflections, residual electron density -0.21 to 0.27 $eÅ^{-3}$. CCDC ..... contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Lit. 1: (program SADABS 2012/1 for absorption correction)
G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin 2012

Lit. 2: (program SHELXL 2014-3 for structure refinement)
Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

Chemie : Svetlana Tsupova (AK Hashmi)
Probe : ST387
Dateinamen : sts24.*
Operateur : F. Rominger (AK Hofmann)
Gerät : Bruker APEX-II CCD

Table 10: Kristalldaten und Strukturverfeinerung für sts24

Strukturkennzeichen	sts24	
Summenformel	$C_{11}H_{14}O_3$	
Molmasse	194.22	
Temperatur	200(2) K	
Wellenlänge	0.71073 Å	
Kristallsystem	monoklin	
Raumgruppe	$P2_1/c$	
Z	4	
Gitterkonstanten	a = 4.5985(6) Å	α = 90 °
	b = 20.751(3) Å	β = 91.893(3) °
	c = 10.2612(13) Å	γ = 90 °
Zellvolumen	978.6(2) Å^3	
Dichte (berechnet)	1.318 g/cm^3	
Absorptionskoeffizient μ	0.095 mm^{-1}	
Kristallform	keil	
Kristallgröße	0.41 x 0.09 x 0.04 mm^3	
Kristallfarbe	colourless	
Gemessener Theta-Bereich	1.963 bis 25.179 °	
Indexgrenzen	$-5\leq h\leq 5$, $-24\leq k\leq 24$, $-11\leq l\leq 12$	
Gemessene Reflexe	6096	
Unabhängige Reflexe	1759 (R(int) = 0.0275)	
Beobachtete Reflexe	1484 ($I > 2\sigma(I)$)	
Absorptionskorrektur	Semi-empirical from equivalents	
Max/min Transmission	0.96 and 0.79	
Strukturverfeinerung	Full-matrix least-squares an F^2	
Daten/Restraints/Parameter	1759 / 0 / 129	
Goodness-of-fit an F^2	1.21	
R-Werte (I>2sigma(I))	R1 = 0.042, wR2 = 0.126	
Extinktionskoeffizient	n/a	
Max/min Restelektronendichte	0.19 und -0.22 eÅ^{-3}	

Table 11: Crystal data and structure refinement for sts24.

Identification code	sts24	
Empirical formula	$C_{11}H_{14}O_3$	
Formula weight	194.22	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Z	4	
Unit cell dimensions	a = 4.5985(6) Å	α = 90 deg.
	b = 20.751(3) Å	β = 91.893(3) deg.
	c = 10.2612(13) Å	γ = 90 deg.
Volume	978.6(2) Å^3	
Density (calculated)	1.32 g/cm^3	
Absorption coefficient	0.09 mm^{-1}	
Crystal shape	wedge	
Crystal size	0.410 x 0.090 x 0.040 mm^3	
Crystal colour	colourless	

Theta range for data collection	2.0 to 25.2 deg.
Index ranges	$-5 \le h \le 5$, $-24 \le k \le 24$, $-11 \le l \le 12$
Reflections collected	6096
Independent reflections	1759 (R(int) = 0.0275)
Observed reflections	1484 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.79
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1759 / 0 / 129
Goodness-of-fit on F^2	1.21
Final R indices (I>2sigma(I))	R1 = 0.042, wR2 = 0.126
Largest diff. peak and hole	0.19 and -0.22 $eÅ^{-3}$

Table 12: Atomkoordinaten und äquivalente isotrope Auslenkungsparameter ($Å^2$) für sts24. U_{eq} wird berechnet als ein Drittel der Spur des orthogonalen U_{ij} Tensors.
(Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for sts24. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.)

Atom	x	y	z	U_{eq}
C11	0.3818(4)	0.6850(1)	-0.0352(2)	0.0238(4)
O11	0.2995(3)	0.7374(1)	0.0349(1)	0.0321(4)
H11	0.1780	0.7260	0.0898	0.048
C12	0.5736(4)	0.6966(1)	-0.1353(2)	0.0229(4)
C13	0.6685(4)	0.6471(1)	-0.2125(2)	0.0273(5)
C14	0.5760(5)	0.5842(1)	-0.1940(2)	0.0352(5)
H14	0.6404	0.5500	-0.2476	0.042
C15	0.3865(5)	0.5731(1)	-0.0947(2)	0.0358(5)
H15	0.3218	0.5302	-0.0803	0.043
C16	0.2862(4)	0.6220(1)	-0.0145(2)	0.0297(5)
C17	0.7053(4)	0.7590(1)	-0.1769(2)	0.0265(5)
H17A	0.5529	0.7892	-0.2094	0.032
H17B	0.8154	0.7794	-0.1034	0.032
O17	0.8963(3)	0.7415(1)	-0.2794(2)	0.0368(4)
C18	0.8696(5)	0.6742(1)	-0.3101(2)	0.0332(5)
H18A	1.0618	0.6527	-0.3031	0.040
H18B	0.7881	0.6683	-0.3998	0.040
C19	0.0830(5)	0.6059(1)	0.0924(2)	0.0393(6)
H19A	-0.0675	0.6398	0.0982	0.047
H19B	-0.0156	0.5644	0.0732	0.047
O20	0.2441(3)	0.6015(1)	0.2125(1)	0.0342(4)
C21	0.0672(5)	0.5798(1)	0.3150(2)	0.0350(5)
H21A	-0.0074	0.5360	0.2952	0.042
H21B	-0.1011	0.6090	0.3239	0.042
C22	0.2480(6)	0.5789(1)	0.4396(2)	0.0515(7)
H22A	0.1312	0.5623	0.5103	0.077
H22B	0.3130	0.6228	0.4608	0.077
H22C	0.4178	0.5511	0.4290	0.077

Table 13: H-Atomkoordinaten und isotrope Auslenkungsparameter ($Å^2$) für sts24.
(Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for sts24.)

Atom	x	y	z	U_{eq}
H11	0.1780	0.7260	0.0898	0.048

H14	0.6404	0.5500	-0.2476	0.042
H15	0.3218	0.5302	-0.0803	0.043
H17A	0.5529	0.7892	-0.2094	0.032
H17B	0.8154	0.7794	-0.1034	0.032
H18A	1.0618	0.6527	-0.3031	0.040
H18B	0.7881	0.6683	-0.3998	0.040
H19A	-0.0675	0.6398	0.0982	0.047
H19B	-0.0156	0.5644	0.0732	0.047
H21A	-0.0074	0.5360	0.2952	0.042
H21B	-0.1011	0.6090	0.3239	0.042
H22A	0.1312	0.5623	0.5103	0.077
H22B	0.3130	0.6228	0.4608	0.077
H22C	0.4178	0.5511	0.4290	0.077

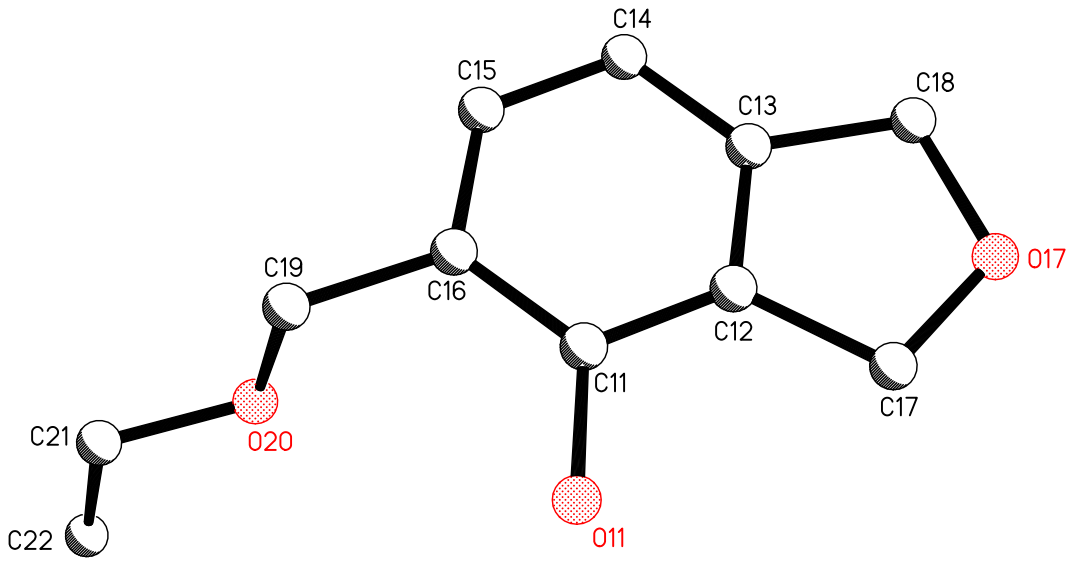
Table 14: Anisotrope Auslenkungsparameter ($Å^2$) für sts24. Der Exponent für den anisotropen Auslenkungsparameter hat die Form: $-2\,pi^2\,(h^2\,a^{*2}\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12})$
(Anisotropic displacement parameters ($Å^2$) for sts24. The anisotropic displacement factor exponent takes the form: $-2\,pi^2\,(h^2\,a^{*2}\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12})$)

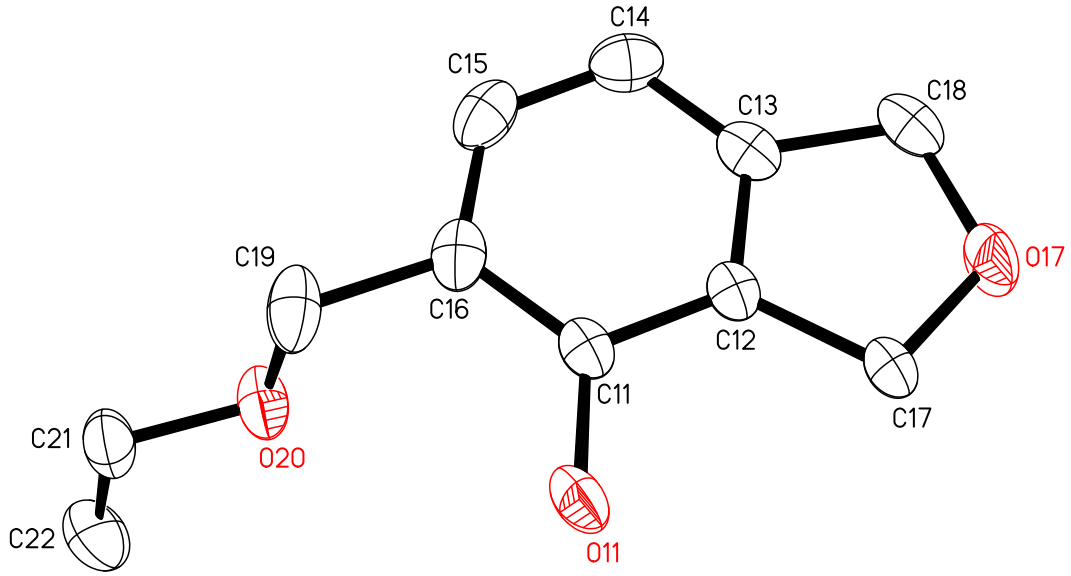
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C11	0.0188(9)	0.0330(11)	0.0196(9)	0.0025(8)	-0.0009(7)	0.0017(8)
O11	0.0290(8)	0.0431(9)	0.0248(8)	-0.0010(6)	0.0106(6)	0.0001(6)
C12	0.0186(9)	0.0297(11)	0.0202(9)	0.0031(8)	-0.0009(7)	0.0014(7)
C13	0.0217(10)	0.0371(12)	0.0229(10)	-0.0010(8)	-0.0027(8)	0.0068(8)
C14	0.0365(12)	0.0310(12)	0.0377(12)	-0.0050(9)	-0.0061(10)	0.0056(9)
C15	0.0351(12)	0.0294(12)	0.0422(13)	0.0087(9)	-0.0104(10)	-0.0061(9)
C16	0.0211(10)	0.0398(12)	0.0275(11)	0.0100(9)	-0.0066(8)	-0.0059(8)
C17	0.0255(10)	0.0334(11)	0.0209(10)	0.0012(8)	0.0055(8)	0.0003(8)
O17	0.0349(8)	0.0426(9)	0.0341(8)	0.0030(7)	0.0193(6)	-0.0010(7)
C18	0.0294(11)	0.0477(14)	0.0227(10)	-0.0027(9)	0.0038(8)	0.0064(9)
C19	0.0263(11)	0.0546(15)	0.0366(12)	0.0171(11)	-0.0036(9)	-0.0119(10)
O20	0.0273(8)	0.0479(9)	0.0274(8)	0.0092(6)	0.0028(6)	-0.0049(6)
C21	0.0369(12)	0.0311(12)	0.0378(12)	0.0069(9)	0.0146(9)	0.0021(9)
C22	0.0676(17)	0.0572(16)	0.0305(13)	0.0022(11)	0.0128(12)	-0.0034(13)

Table 15: Bindungslängen (Å) und -winkel (°) für sts24.
(Bond lengths (Å) and angles (deg) for sts24.)

C11-O11	1.363(2)	C18-H18B	0.9900
C11-C12	1.397(3)	C19-O20	1.420(3)
C11-C16	1.399(3)	C19-H19A	0.9900
O11-H11	0.8400	C19-H19B	0.9900
C12-C13	1.377(3)	O20-C21	1.424(2)
C12-C17	1.498(3)	C21-C22	1.502(3)
C13-C14	1.388(3)	C21-H21A	0.9900
C13-C18	1.496(3)	C21-H21B	0.9900
C14-C15	1.382(3)	C22-H22A	0.9800
C14-H14	0.9500	C22-H22B	0.9800
C15-C16	1.394(3)	C22-H22C	0.9800
C15-H15	0.9500	O11-C11-C12	116.39(17)
C16-C19	1.502(3)	O11-C11-C16	124.84(17)
C17-O17	1.440(2)	C12-C11-C16	118.76(18)
C17-H17A	0.9900	C11-O11-H11	109.5
C17-H17B	0.9900	C13-C12-C11	120.99(18)
O17-C18	1.436(3)	C13-C12-C17	110.06(17)
C18-H18A	0.9900	C11-C12-C17	128.95(17)

C12-C13-C14	121.26(19)
C12-C13-C18	108.58(18)
C14-C13-C18	130.16(19)
C15-C14-C13	117.4(2)
C15-C14-H14	121.3
C13-C14-H14	121.3
C14-C15-C16	122.9(2)
C14-C15-H15	118.6
C16-C15-H15	118.6
C15-C16-C11	118.69(19)
C15-C16-C19	119.7(2)
C11-C16-C19	121.6(2)
O17-C17-C12	104.61(15)
O17-C17-H17A	110.8
C12-C17-H17A	110.8
O17-C17-H17B	110.8
C12-C17-H17B	110.8
H17A-C17-H17B	108.9
C18-O17-C17	110.84(15)
O17-C18-C13	105.64(16)
O17-C18-H18A	110.6
C13-C18-H18A	110.6
O17-C18-H18B	110.6
C13-C18-H18B	110.6
H18A-C18-H18B	108.7
O20-C19-C16	109.20(16)
O20-C19-H19A	109.8
C16-C19-H19A	109.8
O20-C19-H19B	109.8
C16-C19-H19B	109.8
H19A-C19-H19B	108.3
C19-O20-C21	111.54(16)
O20-C21-C22	108.61(18)
O20-C21-H21A	110.0
C22-C21-H21A	110.0
O20-C21-H21B	110.0
C22-C21-H21B	110.0
H21A-C21-H21B	108.3
C21-C22-H22A	109.5
C21-C22-H22B	109.5
H22A-C22-H22B	109.5
C21-C22-H22C	109.5
H22A-C22-H22C	109.5
H22B-C22-H22C	109.5





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Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.09mm^{-1}, T_{min}=0.79, T_{max}=0.96, structure refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2014/7 (Sheldrick, 2014) software [2], 129 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.21 for observed reflections, final residual values R1(F)=0.042, wR(F^2)=0.126 for observed reflections, residual electron density -0.22 to 0.19 eÅ^{-3}. CCDC ..... contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

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Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

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[i] B. Martín-Matute, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2001**, *40*, 4754 – 4756.