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Supporting Information

Oxidative cyclization of alkenoic acids with AgOAc

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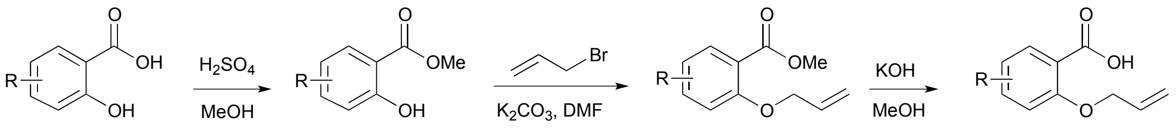
General Information

All reactions (except the hydrolysis of esthers Ic-XIVc) were carried out under a nitrogen atmosphere. MeOH, acetone, diethyl ether and DCM were dried by standard methods and freshly distilled prior to use. Dry DMSO, DMF, and DCE, were purchased from Aldrich. Comercial reagents were used as received without further purification. Silver salts were stored under N_2 atmosphere. Reactions containing silver salts were protected from light in order to prevent its decomposition. Thin layer chromatography was carried out using TLC Alugram G/UV254 0.20 mm. Chromatography purifications were performed using flash grade silica gel (SDS Chromatogel 60 Acc, 40-60 μm). NMR spectra were recorded at 25 ºC on a Jeol Eclipse 300 Mz, Bruker Avance 400 Mz and Varian Unity Inova 500 MHz spectrometers. Chemical shifts are reported in ppm. High resolution mass spectra (HRMS) were recorded and on a Jeol The Accutof JMS-T100LC spectrometer using plolyethylene glycol as internal standard. Melting points were determined using a Reichert microscope apparatus and were uncorrected.

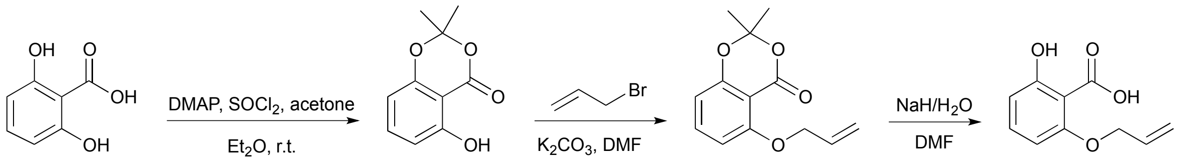
Synthesis of starting materials

The synthesis of alkenoic acids **1a**-**21a** was carried out according to Schemes 1- 6.



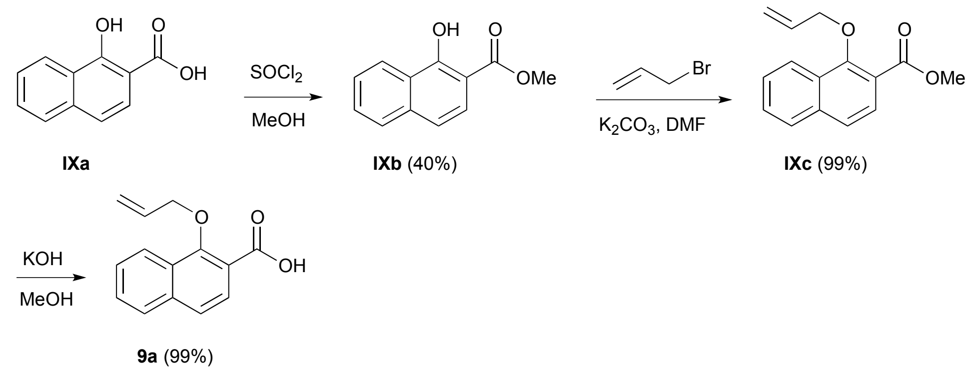
R = H (**Ia**);	R = H (**Ib**, 99%);	R = H (**Ic**, 98%)	R = H (**1a**, 90%)
R = 4-OMe (**IIa**);	R = 4-OMe (**IIb**, 98%);	R = 4-OMe (**IIc**, 64%);	R = 4-OMe (**2a**, 99%);
R = 4-Cl (**IIIa**);	R = 4-Cl (**IIIb**, 98%);	R = 4-Cl (**IIIc**, 87%);	R = 4-Cl (**3a**, 96%);
R = 3-Me (**IVa**);	R = 3-Me (**IVb**, 68%);	R = 3-Me (**IVc**, 89%);	R = 3-Me (**4a**, 99%);
R = 5-OMe (**Va**);	R = 5-OMe (**Vb**, 70%);	R = 5-OMe (**Vc**, 99%);	R = 5-OMe (**5a**, 82%);
R = 5-Cl (**VIa**);	R = 5-Cl (**VIb**, 87%);	R = 5-Cl (**VIc**, 98%);	R = 5-Cl (**6a**, 96%);
R = 5-NO_2 (**VIIa**);	R = 5-NO_2 (**VIIb**, 51%);	R = 5-NO_2 (**VIIc**, 75%);	R = 5-NO_2 (**7a**, 99%);

Scheme 1.

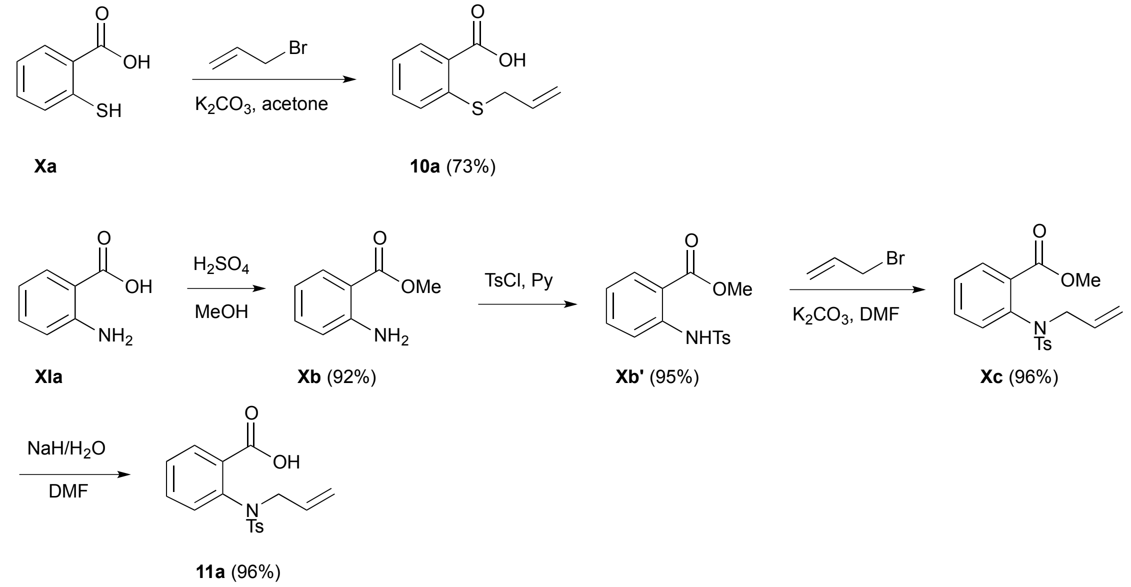


VIIIa **VIIIb** (63%) **VIIIc** (95%) **8a** (87%)

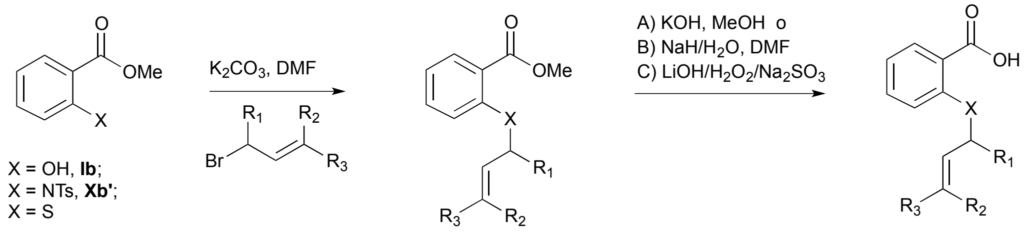
Scheme 2.



Scheme 3.



Scheme 4.

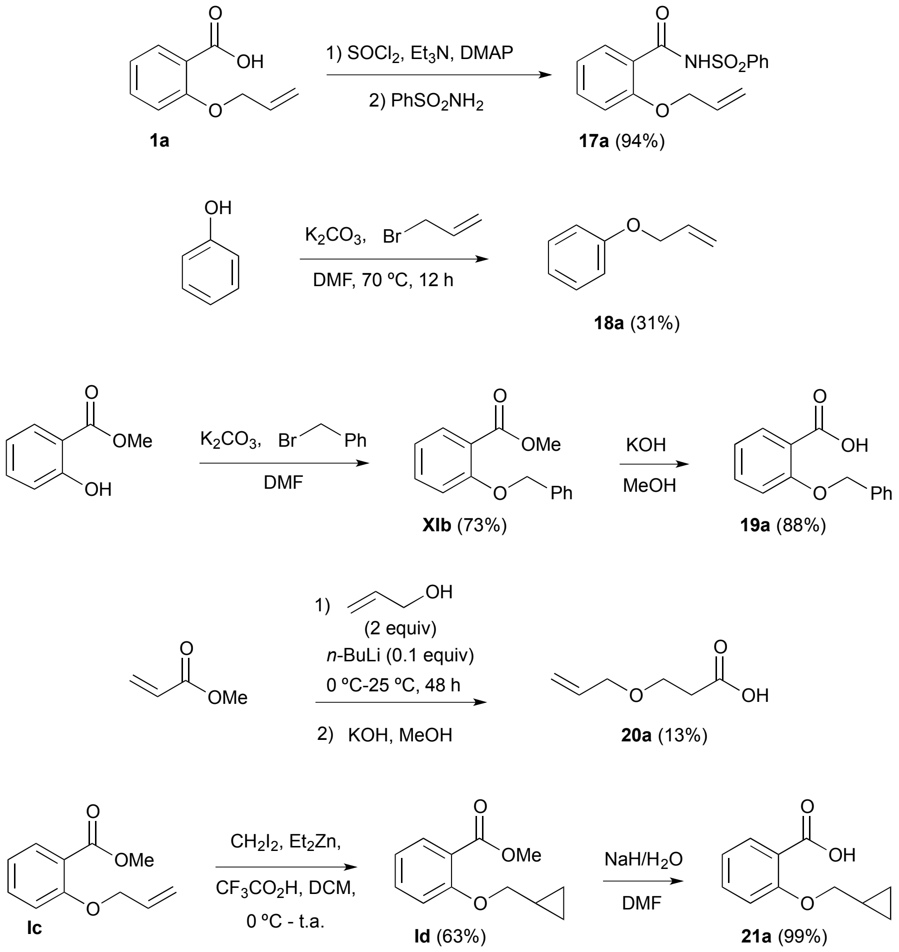


X = OH, **Ib**;
X = NTs, **Xb'**;
X = S

X =O, R_1 = CH_3, R_2=R_3= H (**XIc**, 37%);
X =S, R_1 = CH_3, R_2=R_3= H (**XIIc**,66%);
X = O, R_1 = H, R_2 = H, R_3= Ph (**XIIIc**, 92%);
X = O, R_1 = H, R_2=R_3= CH_3 (**XIVc**, 67%);
X = NTs, R_1 = H, R_2=R_3= CH_3 (**XVc**, 90%);

X = O, R_1 = CH_3, R_2=R_3= H (**12a**, 94%);
X = S, R_1 = CH_3, R_2=R_3= H (**13a**, 81%);
X = O, R_1 = H, R_2 = H, R_3= Ph (**14a**, 35%);
X = O, R_1 = H, R_2=R_3= CH_3 (**15a**, 76%);
X = NTs, R_1 = H, R_2=R_3= CH_3 (**16a**, 95%);

Scheme 5.



Scheme 6.

The following compounds were purchased from Aldrich and used as received:

Salicylic acid, 4-metoxysalicylic acid, 4-chlorosalicylic acid, 3-methylsalicylic acid, 5-chlorosalicylic acid, 5-nitrosalicylic acid, 5-methoxysalicylic acid, antranilic acid, 2,6-dihydroxybenzoic acid, 1-hydroxy-2-naphthalenecarboxylic acid, 2-thiosalicylic acid, methyl thiosalicylate, allyl bromide, 3,3-dimethylallyl bromide, but-3-en-2-ol, allylic alcohol, bencyl bromide, methyl acrylate, 4-dimethylaminopyridine, and benzenesulfonamide.

Esterification of carboxylic acids Ia-XIa:

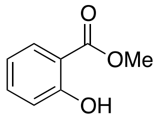
Method A:

The corresponding carboxylic acid (28.96 mmol) was dissolved in MeOH (60 mL) and H_2SO_4 (98%, 2 mL) was added dropwise to the solution. The reaction mixture was heated under reflux for 18 hours, subsequently it was cooled to 25 ºC and the solvent was removed under vacuum. The residue was diluted with water (50 mL), thereafter K_2CO_3 was added until pH = 5-6, and the aqueous solution was extracted with DCM (3 x 30 mL). Finally, the combined organic phases were dried over Na_2SO_4 and concentrated under vacuum to afford the desired compound with enough purity to be used in the next reaction without further purification.

Method B:

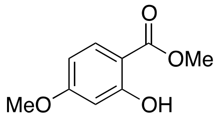
To a solution of the corresponding acid (21.87 mmol) in MeOH (35 mL) at 0 °C, $SOCl_2$ (15.86 mL, 218.75 mmol) was added dropwise over a period of 10 min. Once the addition was finished, the reaction was allowed to warm to rt and subsequently heated to 65°C for a period of 18 hours. After this time, MeOH and the excess of $SOCl_2$ were removed under vacuum. The residue obtained was dissolved in DCM and a saturated solution of $NaHCO_3$ (40 mL) was added until no evolution of gas was observed. The aqueous solution was extracted with DCM (3 x 40 mL), and the combined organic phases were dried over Na_2SO_4 and concentrated under vacuum, to afford the desired compound with enough purity to be used in the next reaction without further purification.

Methylsalicylate (Ib).[1]



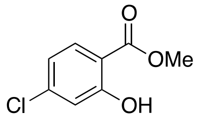
Method A. Colorless oil, (4.04 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.77 (s, 1H), 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.88 (t, *J* = 7.2 Hz, 1H), 3.95 (s, 3H).

Methyl 4-methoxysalicylate (IIb).[2]



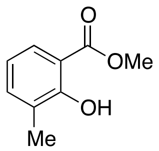
Method A. White solid, (2.655 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.98 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 6.56 – 6.32 (m, 2H), 3.90 (s, 3H), 3.81 (s, 3H).

Methyl 4-chlorosalicylate (IIIb).[3]



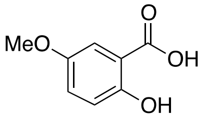
Method A. Pink oil, (2.12 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.08 - 6.95 (m, 1H), 6.94 - 6.76 (m, 1H), 3.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.12 (C), 162.23 (C), 141.56 (C), 131.01 (CH), 120.00 (CH), 117.86 (CH), 111.11 (C), 52.60 (CH_3).

Methyl 3-methylsalicylate (IVb).[4]



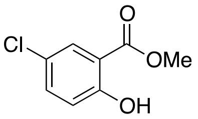
Method A. Yellow oil, (4.47 g, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.94 (s, 1H), 7.61 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 6.70 (t, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 2.19 (s, 3H).

Methyl 5-methoxysalicylate (Vb):[5]



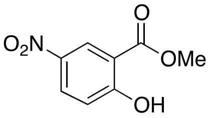
Method A. Yellowish oil, (0.42 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.28 (d, *J* = 3.1 Hz, 1H), 7.08 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.91 (d, *J* = 9.1 Hz, 1H), 3.95 (s, 3H), 3.78 (s, 3H).

5-Clorosalicilato de metilo/ Methyl 5-chlorosalicylate (VIb).[6]



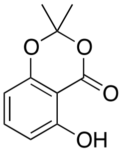
Method A. White solid, (4.67 g, 87%). ^{1}H NMR (301 MHz, $CDCl_3$) δ 10.62 (s, 1H), 7.74 (d, *J* = 2.7 Hz, 1H), 7.33 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 3.89 (s, 3H).

Methyl 5-Nitrosalicylate (VIIb):[7]



Method A. White solid, (0.30 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.44 (s, 1H), 8.79 (d, *J* = 2.8 Hz, 1H), 8.33 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.09 (d, *J* = 9.2 Hz, 1H), 4.03 (s, 3H).

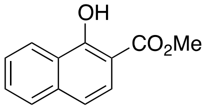
5-Hydroxy-2,2-dimethyl-4*H*-1,3-benzodioxin-4-one (VIIIb).[8]



To a solution of 2,6-dihydroxybenzoic acid (0.50 gr, 3.24 mmol) in anhydrous ether (2 mL) was added acetone (0.34 mL, 4.54 mmol) and 4-dimethylaminopyridine (0.019 gr, 0.16 mmol). The solution was cooled to 20 ºC and a solution of $SOCl_2$ (0.34 mL, 4.61 mmol) in ether (0.5 mL) was added dropwised over 10 min. The solution was stirred at r.t. for 48 h, then the solvent was removed under vacuum and the residue obtained was purified by column chromatography (hexane/EtOAc, 40:1).

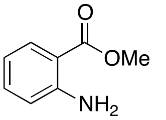
Colorless crystals, (0.39 gr, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.34 (s, 1H), 7.41 (ddd, *J* = 8.1, 0.4 Hz, 1H), 6.63 (dd, *J* = 8.5, 0.9 Hz, 1H), 6.44 (dd, *J* = 8.2, 0.9 Hz, 1H), 1.75 (s, 6H).

Methyl 1-hydroxy-2-naphthoate (IXb).[9]



Method B (reaction time: 48 h). Light yellow solid, (1.117 g, 35%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.00 (s, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 4.00 (s, 3H).

Methyl anthranilate (Xb).[10]

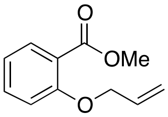


Method B. Yellowish oil, (2.87 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (ddd, *J* = 7.8, 1.6, 0.7 Hz, 1H), 7.26 (ddd, *J* = 8.3, 7.2, 1.6 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 5.58 (bs, 1H), 3.87 (s, 3H).

Synthesis of esters Ic-XVc and XIb:

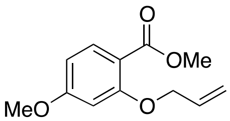
A mixture of the corresponding ester (9.85 mmol), K_2CO_3 (20 mmol) and the allylic bromide or bencyl bromide (12.8 mmol) was stirred in DMF at 25 ºC for 24 h. Then the reaction was diluted with water (20 mL) and extracted with DCM (3 x 20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. If necessary, the product was further purified by silica gel chromatography using mixtures of hexane/EtOAc as eluent.

Methyl 2-allyloxy-benzoate (Ic).[11]



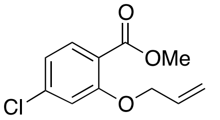
Yellowish oil, (0.448g, 99%). ^{1}H RMN (300 MHz, $CDCl_3$) δ 7.79 (ddd, *J* = 7.7, 1.8, 0.5 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.01 – 6.92 (m, 2H), 6.05 (ddt, *J* = 17.2, 10.6, 4.8 Hz, 1H), 5.50 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.29 (dq, *J* = 10.6, 1.6 Hz, 1H), 4.61 (dt, *J* = 4.8, 1.8 Hz, 2H), 3.88 (s, 3H).

Methyl 2-allyloxy-4-methoxybenzoate (IIc):[12]



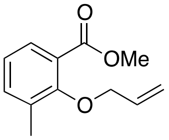
Yellowish oil, (0.23 g, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.6, 0.4 Hz, 1H), 6.49 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 6.06 (ddt, *J* = 17.2, 10.6, 4.8 Hz, 1H), 5.54 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.30 (dq, *J* = 10.6, 1.6 Hz, 1H), 4.59 (dt, *J* = 4.8, 1.7 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H).

Methyl 2-(allyloxy)-4-chlorobenzoate (IIIc):[3]



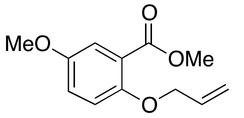
Yellowish solid, (0.14 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 8.0, 0.7 Hz, 1H), 6.97 – 6.92 (m, 2H), 6.03 (ddt, *J* = 17.2, 10.6, 4.8 Hz, 1H), 5.51 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.31 (dq, *J* = 10.6, 1.6 Hz, 1H), 4.59 (dt, *J* = 4.8, 1.7 Hz, 2H), 3.87 (s, 3H).^{13}C NMR (100 MHz, CDCl3) δ 165.84 (C), 158.78 (C), 139.22 (C), 132.90 (CH), 132.04 (CH), 120.65 (CH), 118.79 (C), 117.85 (CH_2), 114.09 (CH), 69.66 (CH_2), 52.09 (CH_3).

Methyl 2-allyloxy-3-methylbenzoate (IVc):[13]



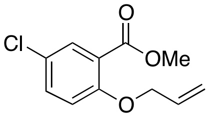
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (ddq, *J* = 7.8, 1.7, 0.5 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.11 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.40 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.28 – 5.23 (m, 1H), 4.44 (ddd, *J* = 5.7, 1.2 Hz, 2H), 3.90 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.99 (C), 157.00 (C), 135.07 (CH), 133.86 (CH), 132.96 (C), 129.13 (CH), 124.89 (C), 123.61 (CH), 117.56 (CH_2), 75.02 (CH_2), 52.15 (CH_3), 16.36 (CH_3). IR (neat): 2950, 2924, 1724, 1592, 1462, 1433 cm^{-1}. HRMS-DART calculated for $C_{12}H_{15}O_3$ [M+H]$^+$: 207.10212; found: 207.10247.

Methyl 2-allyloxy-5-methoxybenzoate (Vc):[14]



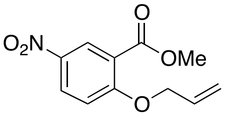
Yellowish oil, (0.242 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 3.1 Hz, 1H), 6.99 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 6.05 (ddt, *J* = 17.3, 10.6, 5.0 Hz, 1H), 5.46 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.27 (dq, *J* = 10.6, 1.5 Hz, 1H), 4.56 (dt, *J* = 5.0, 1.7 Hz, 2H), 3.89 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.71 (C), 153.45 (C), 152.54 (C), 133.29 (CH), 121.41 (C), 119.70 (CH), 117.41 (CH_2), 116.21 (CH), 115.89 (CH), 70.82 (CH_2), 55.93 (CH_3), 52.22 (CH_3). IR (neat): 2997, 2950, 2837, 1727, 1706, 1585, 1495 cm^{-1}. HRMS-DART calculated for $C_{12}H_{15}O_4$ [M+H]$^+$: 223.09703; found: 223.09687.

Methyl 2-allyloxy-5-chlorobenzoate (VIc):[3]



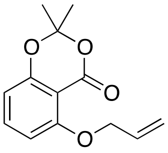
Pink oil, (0.447g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 2.8, 0.2 Hz, 1H), 7.37 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.03 (ddt, *J* = 17.2, 10.6, 4.8 Hz, 1H), 5.49 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.30 (dq, *J* = 10.6, 1.5 Hz, 1H), 4.60 (dt, *J* = 4.8, 1.7 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.57 (C), 156.85 (C), 133.15 (CH), 132.45 (CH), 131.56 (CH), 125.57 (C), 121.88 (C), 117.85 (CH$_2$), 115.20 (CH), 69.95 (CH$_2$), 52.36 (CH$_3$). IR (neat): 3082, 2993, 2950, 1730,1579, 1484 cm^{-1}. HRMS-DART calculated for $C_{11}H_{12}ClO_3$ [M+H]$^+$: 227.04750; found: 227.04816.

Methyl 2-allyloxy-5-nitrobenzoate (VIIc):



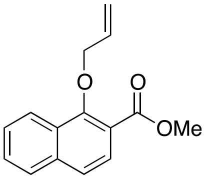
Yellow solid, (0.22 g, 75%), mp = 99-101 °C.^{1}H NMR (400 MHz, CDCl$_3$) δ 8.71 (d, *J* = 2.9 Hz, 1H), 8.33 (dd, *J* = 9.2, 2.9 Hz, 1H), 7.04 (d, *J* = 9.2 Hz, 1H), 6.05 (ddt, *J* = 17.3, 10.7, 4.8 Hz, 1H), 5.54 (dtd, *J* = 17.3, 1.8, 1.2 Hz, 1H), 5.37 (dq, *J* = 10.7, 1.5 Hz, 1H), 4.75 (dt, *J* = 4.9, 1.7 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.46 (C), 162.60 (C), 131.23 (CH), 128.72 (CH), 127.88 (CH), 120.78 (C), 118.57 (CH$_2$), 113.18 (CH), 70.05 (CH$_2$), 52.50 (CH$_3$). IR (neat): 3078, 2957, 1694, 1604, 1511, 1487 cm^{-1}. HRMS-DART calculated for $C_{11}H_{12}NO_5$ [M+H]$^+$: 238.07155; found: 238.07249.

2,2-Dimethyl-5-(2-propen-1-yloxy)-4*H*-1,3-benzodioxin-4-one (VIIIc).[8]



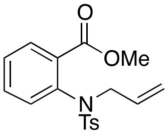
White solid, (0.88 gr, 95%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.41 (t, *J* = 8.4 Hz, 1H), 6.60 (dd, *J* = 8.5, 0.9 Hz, 1H), 6.54 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.08 (ddt, *J* = 17.2, 10.6, 4.8 Hz, 1H), 5.58 (dq, *J* = 17.2, 1.8 Hz, 1H), 5.33 (dq, *J* = 10.6, 1.6 Hz, 1H), 4.68 (dt, *J* = 4.8, 1.7 Hz, 2H), 1.70 (s, 6H).

Methyl 1-allyloxy-2-naphtoate (IXc):[15]

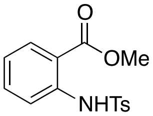


Yellowish oil, (0.14 g, 99%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.29 (ddt, *J* = 7.6, 1.6, 0.8 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.61 – 7.53 (m, 2H), 6.24 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.50 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.33 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.67 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.87 (C), 157.04 (C), 136.84 (C), 133.84 (CH), 128.98 (C), 128.46 (CH), 127.95 (CH), 126.78 (CH), 126.66 (CH), 123.90 (CH), 123.84 (CH), 119.69 (C), 118.06 (CH$_2$), 76.94 (CH$_2$), 52.37 (CH$_3$).

Methyl 2-{[(4-methylphenyl)sulfonyl]-2-propen-1-ylamino}benzoate (Xc):



Synthesis of methyl 2-{[(4-methylphenyl) sulfonyl]amino}benzoate (Xb').[16]

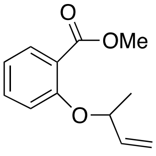


To a solution of methyl anthranilate (**IXb**) (1.5 g, 9.92 mmol) in DCM (11 mL) pyridine (0.96 mL, 11.91 mmol) was added dropwise. The reaction mixture was stirred at 25 ºC for 1 h before a solution of 4-methylbenzene-1-sufonyl chloride (2.27 g, 11.91 mmol) in DCM (8 mL) was slowly added. After stirring the reaction mixture at 25 ºC for 24 h a saturated aqueous solution of NH_4Cl was added. The organic phase was extracted with DCM (4 x 30 mL) dried over Na_2SO_4 and concentrated under vacuum. The solid obtained was further purified by column chromatography (hexane/EtOAc: 10:1). White solid: (2.87 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.61 (s, 1H), 7.91 (ddd, *J* = 8.0, 1.7, 0.4 Hz, 1H), 7.74(d, *J* = 8.3 Hz, 2H), 7.68 (ddd, *J* = 8.4, 1.1, 0.4 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.22 (dd, *J* = 8.6, 0.7 Hz, 2H), 7.02 (ddd, *J* = 8.0, 7.3, 1.2 Hz, 1H), 3.87 (s, 3H), 2.36 (s, 3H).

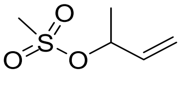
Methyl 2-{[(4-methylphenyl)sulfonyl]-2-propen-1-ylamino}benzoate (Xc):

Yellowish solid, (0.766 g, 97%), mp = 105-106 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 1H), 7.52 – 7.49 (m, 2H), 7.42 – 7.34 (m, 2H), 7.24 – 7.21 (m, 2H), 6.94 – 6.91 (m, 1H), 5.90 (ddt, *J* = 16.6, 10.7, 6.7 Hz, 1H), 5.04 (t, *J* = 2.6, 1.2 Hz, 1H), 5.01 (dq, *J* = 8.2, 1.3 Hz, 1H), 4.26 (dt, *J* = 6.7, 1.3 Hz, 2H), 3.78 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.64 (C), 143.30 (C), 137.97 (C), 136.90 (C), 133.43 (CH), 132.73 (C), 131.99 (CH), 131.32 (CH), 131.10 (CH), 129.50 (CH), 128.32 (CH), 127.63 (CH), 118.99 (CH_2), 54.70 (CH_2), 52.27 (CH_3), 21.59 (CH_3). IR (neat): 2948, 2923, 1717, 1595, 1489, 1449 cm^{-1}. HRMS-DART calculated for $C_{18}H_{20}NO_4S$ $[M+H]^+$: 346.11130; found: 346.11174.

Methyl 2-[(1-methyl-2-propen-1-yl)oxy]-benzoate (XIc):



Synthesis of but-3-en-2-yl methanesufonate:[17]

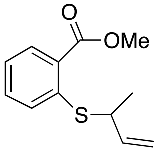


To a solution of but-3-en-2-ol (13.86 mmol) and Et_3N (20.8 mmol) in DCM (40 mL), was was added dropwise $MeSO_2Cl$ (17.33 mmol) at 0 ºC. The mixture was stirred at the same temperature for 2 h. Then a saturated solution of Na_2CO_3 (21 ml) was added to quench the reaction. After the separation of the organic layer, the aqueous layer was extracted with DCM (4 x20 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and concentrated under vaccum. The oil obtained (1.38 g, 74%), was used directly in the next step.

2-[(1-Metil-2-propen-1-il)oxi]-benzoato de metilo (XIc).

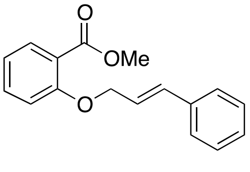
A mixture of methylsalicylate (1.31 mmol), K_2CO_3 (1.71 mmol) and but-3-en-2-yl methanesufonate was stirred in DMF (2.4 mL) at 25 °C for 24 h. Then water was added, and the aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and concentrated under vaccum. The residue obtained was purified by column chromatography hexane/EtOAc (50/1) to afford the product as a yellow oil, (0.93 g, 37%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (ddd, *J* = 7.7, 1.8, 0.4 Hz, 1H), 7.39 (ddd, *J* = 8.4, 7.3, 1.8 Hz, 1H), 6.99 – 6.93 (m, 2H), 5.94 (ddd, *J* = 17.3, 10.6, 6.0 Hz, 1H), 5.30 (dt, *J* = 17.3, 1.3 Hz, 1H), 5.17 (dt, *J* = 10.6, 1.3 Hz, 1H), 4.82 (q, *J* = 6.2 Hz, 1H), 3.88 (s, 3H), 1.47 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.99 (C), 157.51(C), 138.89 (CH), 132.94 (CH), 131.44 (CH), 121.62 (C), 120.45 (CH), 116.02 (CH), 115.83 (CH_2), 76.37 (CH), 51.87 (CH_3), 21.26 (CH_3). IR (neat): 2982, 2950, 1728, 1599, 1581, 1486 cm^{-1}. HRMS-DART calculated for $C_{12}H_{15}O_3$ $[M+H]^+$: 207.10212; found: 207.10146.

Methyl 2-[(1-methyl-2-propen-1-yl)thio]-benzoate (XIIc):



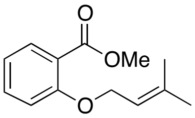
Colorless oil, (0.28 g, 62%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 -7.84 (m, 1H), 7.49 – 7.36 (m, 2H), 7.21 – 7.10 (m, 1H), 5.83 (ddd, *J* = 17.1, 10.2, 7.8 Hz, 1H), 5.21 - 5.00 (m, 2H), 4.01 – 3.97 (m, 1H), 3.90 (s, 3H), 1.45 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.29 (C), 139.71 (CH), 132.28 (C), 131.87 (CH), 131.31 (C), 130.92 (CH), 128.81 (CH), 124.74 (CH), 115.57 (CH_2), 52.24 (CH_3), 43.87 (CH), 20.30 (CH_3). IR (neat): 2951, 2925, 1712, 1461, 1433, 1285 cm.$^{-1}$ HRMS-DART calculated for $C_{12}H_{15}O_2S_1$ $[M+H]^+$: 223.07927; found: 223.07937.

Methyl 2-[(3-phenyl-2-propen-1-yl)oxy]benzoate (XIIIc):[18]



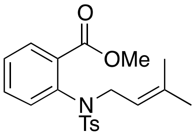
Yellow solid. Obtained: 0.487 g (92%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (ddd, *J* = 7.7, 1.9, 0.4 Hz, 1H), 7.53 – 7.24 (m, 6H), 7.05 – 6.96 (m, 2H), 6.81 (d, *J* = 16.2 Hz, 1H), 6.43 (dt, *J* = 15.9, 5.4 Hz, 1H), 4.81 (dd, *J* = 5.4, 1.6 Hz, 2H), 3.92 (s, 3H).

Methyl 2-[(3-methyl-2-butenyl)oxy]-benzoate (XIVc):



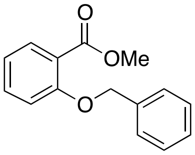
Colorless oil, (0.579 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 1H), 7.43 (ddd, J = 8.4, 7.3, 1.9 Hz, 1H), 7.01 – 6.92 (m, 2H), 5.50 (tdq, J = 7.0, 2.8, 1.4 Hz, 1H), 4.62 (d, J = 6.5 Hz, 2H), 3.88 (s, 3H), 1.78-1.76 (m, 3H), 1.74-1.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.80 (C), 158.44 (C), 137.54 (C), 133.27 (CH), 131.62 (CH), 120.68 (C), 120.14 (CH), 119.70 (CH), 113.88 (CH), 66.13 (CH_2), 51.94 (CH_3), 25.78 (CH_3), 18.31(CH_3). IR (neat): 2947, 2916, 1728, 1598, 1488, 1449 cm^{-1}. HRMS-DART calculated for $C_{13}H_{17}O_3$ $[M+H]^+$: 221.11777; found: 221.11841.

Methyl 2-{(3-methyl-2-buten-1-yl)[(4-methylphenyl)sulfonyl]amino}benzoate (XVc):[19]



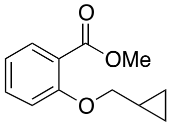
Colorless oil, (0.34 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.43 – 7.32 (m, 2H), 7.27 – 7.20 (m, 2H), 6.98 – 6.92 (m, 1H), 5.23 (tdq, J = 9.0, 2.8, 1.4 Hz, 1H), 4.26 (d, J = 7.3 Hz, 2H), 3.79 (s, 3H), 2.41 (s, 3H), 1.60 (d, J = 1.3 Hz, 3H), 1.39 (d, J = 1.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.81 (C), 143.11 (C), 138.27 (C), 137.45 (C), 137.27 (C), 132.87 (C), 131.90 (CH), 131.34 (CH), 131.24 (CH), 129.46 (CH), 128.20 (CH), 127.68 (CH), 119.20 (CH), 52.29 (CH_3), 49.55 (CH_2), 25.81 (CH_3), 21.65 (CH_3), 17.67 (CH_3). IR (neat): 2948, 2919, 1725, 1597, 1489 cm^{-1}. HRMS-DART calculated for $C_{20}H_{24}NO_4S$ $[M+H]^+$: 374.14260; found: 374.14377.

Methyl 2-benzyloxy-benzoate (XIb):[20]



White solid, (0.80 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (ddd, J = 7.5, 1.8, 0.6 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.47 – 7.24 (m, 4H), 7.03 – 6.97 (m, 2H), 5.19 (s, 2H), 3.91 (s, 3H).

Methyl 2-(cyclopropylmethoxy)benzoate (Id):[21]



To a solution of Et_2Zn[22] (3.12 mL, 1 M in hexane) in freshly distilled CH_2Cl_2 (4 mL) at 0 ºC was slowly added a solution of CF_3CO_2H (0. 24 mL, 3.12 mmol mmol) in DCM (2 mL). Upon stirring for 20 min, a solution of CH_2I_2 (0. 25 mL, 3.12 mmol) in DCM (2 mL) was added. After an additional 20 min of stirring, a solution of **Ic** (0. 30 gr, 1.56 mmol) in DCM (2 mL) was added, and the ice bath was removed. The reaction was stirred overnight at rt, then was quenched with a saturated aqueous solution of NH_4Cl, and the layers were separated. The aqueous layer was extracted with DCM (3 X 10 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue obtained was purified by column chromatography (hexane/EtOAc, 40/1) to afford the product as a colorless oil (0.20 gr, 62%).

^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (ddd, *J* = 7.7, 1.8, 0.5 Hz, 1H), 7.42 (ddd, *J* = 8.2, 7.5, 1H), 7.00 – 6.93 (m, 2H), 3.92 (d, *J* = 6.5 Hz, 2H), 3.89 (s, 3H), 1.38 – 1.22 (m, 1H), 0.66 – 0.59 (m, 2H), 0.45 – 0.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.04 (C), 158.72 (C), 133.40 (CH), 131.69 (CH), 120.99 (C), 120.43 (CH), 114.25 (CH), 73.63 (CH_3), 52.03 (CH_2), 10.31 (CH_2), 3.16 (CH). IR (neat): 3006, 2949, 2873, 1727, 1707, 1599, 1489 cm^{-1}. HRMS-FAB calculated for $C_{12}H_{14}O_3$ $[M+H]^+$: 207.1021; found: 207.1022.

Synthesis of alkenoic acids 1a-21a:

Method A:

To a solution of the corresponding esther (2.62 mmol) in EtOH (20 mL) a saturated aqueous solution of KOH (30 drops) was added. The homogeneous mixture was stirred at 25 ºC for 20 h. Later on, water (30 mL) was added and the resulting solution was acidified with HCl 10% until pH = 2. The aqueous layer was extracted with DCM (4 x 30 mL), the combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The desired alkenoic acids were obtained as a white or slightly colored powder. If necessary, the final alkenoic acids were further purified washing with pentane.

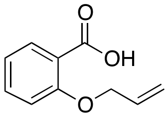
Method B:

To a suspension of NaH (60% in mineral oil, 0.55 mmol) in DMF (3 mL) at 0 ºC was added water (1.5 mmol). After stirring for 10 minutes, a solution of the corresponding esther (0.50 mmol) in DMF (3 mL) was added to the suspension. The reaction mixture was stirred from 0 ºC to 25 ºC until the esther was totally consumed, then HCl 10% was added until pH = 2. The organic phase was extracted with Et_2O (3 x 20 mL) and the combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. If necessary, the final alkenoic acids were further purified washing with pentane.

Method C:

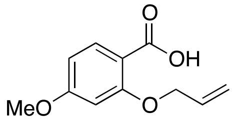
To a solution of $LiOH·H_2O$ (0.083 g, 1.99 mmol) in THF:H_2O (1:1, 4 mL) at 0 ºC was added H_2O_2 (30%, 1.99 mmol). This solution was dropped over a solution of the corresponding ester (0.99 mmol) in THF (2 mL) and stirred from 0 ºC to 25 ºC until the ester was totally consumed. Thereafter a solution of Na_2SO_3 (5.97 mmol) was added, and the reaction mixture was stirred for 15 minutes. The resulting solution was acidified to pH=3 and extracted with DCM (3 x 20 mL). Finally, the combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. If necessary, the final alkynoic acids were further purified washing with pentane or by column chromatography.

2-Allyloxybenzoic acid (1a):[23]



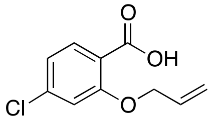
Method A. White solid, (0.99 g, 99%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.81 (br s, 1H), 8.16 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.53 (ddd, *J* = 8.5, 7.4, 1.8 Hz, 1H), 7.12 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.08 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.48 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.42 (dq, *J* = 10.5, 1.1 Hz, 1H), 4.78 (dt, *J* = 5.6, 1.3 Hz, 2H).

2-Allyloxy-4-methoxybenzoic acid (2a):[24]



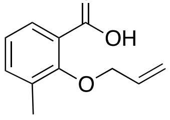
Method A. White solid, (0.05 g, 36%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.73 (br s, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 6.63 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.51 (d, *J* = 2.3 Hz, 1H), 6.08 (ddt, *J* = 17.2, 10.4, 5.6 Hz,1H), 5.48 (dq, *J* = 17.3, 1.5 Hz, 1H), 5.42 (dq, *J* = 10.5, 1.1 Hz, 1H), 4.75 (dt, *J* = 5.6, 1.3 Hz, 2H), 3.85 (s, 3H).

2-Allyloxy-4-chlorobenzoic acid (3a):[25]



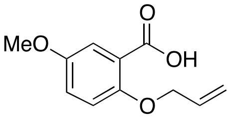
Method A. White solid, (0.08, 75%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.70 (br s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.04 (d, *J* = 1.9 Hz, 1H), 6.08 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.56 – 5.44 (m, 2H), 4.78 (dt, *J* = 5.6, 1.2 Hz, 2H).

2-Allyloxy-3-methylbenzoic acid (4a):[12]



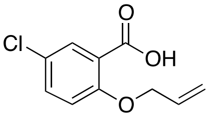
Method A. White solid, (0.43 g, 96%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 11.16 (br s, 1H), 7.99 – 7.94 (m, 1H), 7.47 – 7.40 (m, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.11 (ddt, *J* = 17.1, 10.3, 6.0 Hz, 1H), 5.47 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.39 (dq, *J* = 10.3, 1.1 Hz, 1H), 4.51 (ddd, *J* = 6.0, 1.4, 1.0 Hz, 2H), 2.37 (s, 3H).

2-Allyloxy-5-methoxybenzoic acid (5a):[21]



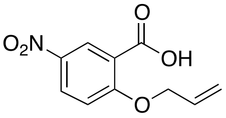
Method A. White solid, (0.18 g, 70%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 11.14 (s, 1H), 7.66 (d, *J* = 3.2 Hz, 1H), 7.09 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.99 (d, *J* = 9.1 Hz, 1H), 6.07 (ddt, *J* = 17.2, 10.5, 5.7 Hz,1H), 5.55 – 5.37 (m, 2H), 4.74 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.81 (s, 3H).

2-Allyloxy-5-chlorobenzoic acid (6a):[21]



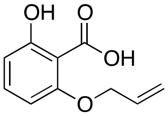
Method A. White solid, (0.43, 96%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.63 (br s, 1H), 8.13 (d, *J* = 2.8 Hz, 1H), 7.48 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.07 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.53 – 5.42 (m, 2H), 4.78 (dt, *J* = 5.6, 1.4 Hz, 2H).

2-Allyloxy-5-nitrobenzoic acid (7a):



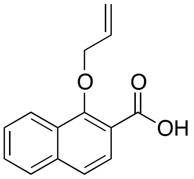
Method A. Orange solid, (0.10 g, 99%), mp = 134-135 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.64 (d, *J* = 2.9 Hz, 1H), 8.20 (dd, *J* = 9.2, 2.9 Hz, 1H), 6.96 (d, *J* = 9.2 Hz, 1H), 5.94 (ddt, *J* = 17.2, 10.6, 4.9 Hz, 1H), 5.43 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.24 (dq, *J* = 10.6, 1.4 Hz, 1H), 4.66 (dt, *J* = 4.9, 1.7 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.78 (C), 162.48 (C), 140.63 (C), 131.27 (CH), 128.39 (CH), 128.03 (CH), 121.62 (C), 118.51 (CH$_2$), 113.23 (CH), 70.03 (CH$_2$). IR (neat): 3417, 1709, 1611, 1517, 1488 cm^{-1}. HRMS-DART calculated for $C_{10}H_{10}NO_5$ [M+H]$^+$: 224.05590; found: 224.05566.

2-Allyloxy-6-hydroxybenzoic acid (8a):



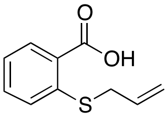
Method B. Pinkish solid, (0.22 gr, 87%), m.p.: 41-43 ºC. ^{1}H NMR (300 MHz, CDCl$_3$) δ 12.17 (s, 1H), 11.48 (s, 1H), 7.39 (t, *J* = 8.3 Hz, 1H), 6.72 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.49 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.09 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.55 – 5.44 (m, 2H), 4.77 (dt, *J* = 5.9, 1.3 Hz, 2H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 170.95 (C), 164.41 (C), 157.72 (C), 135.66 (CH), 130.62 (CH), 121.37 (CH$_2$), 112.60 (CH), 102.66 (CH), 102.02 (C), 71.40 (CH$_2$). IR (neat): 3214, 2883, 1688, 1619, 1528, 1457 cm^{-1}. HRMS-DART calculated for $C_{10}H_{11}O_4$ [M+H]$^+$: 195.06573; found: 195.06536.

1-Allyloxy-2-naphtoic acid (9a):[26]



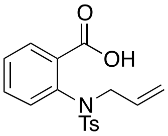
Method A. White solid, (0.29 g, 99%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.22 – 8.14 (m, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.91 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.69 – 7.57 (m, 2H), 6.23 (ddt, *J* = 17.1, 10.4, 5.9 Hz, 1H), 5.53 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.44 (dq, *J* = 10.4, 1.0 Hz, 1H), 4.76 (dt, *J* = 5.9, 1.2 Hz, 2H).

2-Allylthio-benzoic acid (10a):[27]



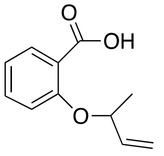
A mixture of 2-thiosalicylic (0.20 g, 1.29 mmol), K_2CO_3 (0.35 g, 2.59 mmol) and allyl bromide (0.17 mL, 1.95 mmol) in acetone (3 mL), was stirred at rt for 1h. Thereafter a saturated solution of NH_4Cl was added and the mixture was acidified with HCl 10%. until pH= 4. Thereafter, the crude mixture was extracted with DCM (3 x 5 mL),the combined organic phases were dried with anhydrous Na_2SO_4 and concentrated under vaccum. The white solid obtained was purified washing with pentane, (0.18 g, 73%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.2, 7.2, 1.6 Hz, 1H), 7.36 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.22 (ddd, *J* = 7.9, 7.3, 1.2 Hz, 1H), 5.94 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.33 (dq, *J* = 17.0, 1.4 Hz, 1H), 5.21 (dq, *J* = 10.1, 1.2 Hz, 1H), 3.63 (dt, *J* = 6.6, 1.2 Hz, 1H).

2-{[(4-Methylphenyl)sulfonyl]-2-propen-1-ylamino}benzoic acid (11a):[22]



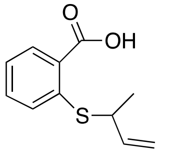
Method B. Yellow solid, (0.32 g, 96%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.58 (br s, 1H), 7.99 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.90 (m, 1H), 5.90 (ddt, *J* = 17.0, 10.4, 6.8 Hz, 1H), 5.11 - 5.06 (m, 1H), 5.04 (d, *J* = 10.0 Hz, 1H), 4.28 (br s, 2H), 2.39 (s, 3H).

2-[(1-methyl-2-propen-1-yl)oxy]-benzoic acid (12a):



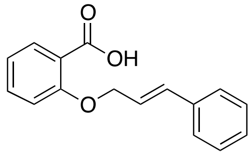
Method A. Colorless oil, (0.08 g, 94%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 11.04 (br s, 1H), 8.17 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.3, 1.0 Hz, 1H), 7.11 (ddd, *J* = 7.7, 7.3, 1.0 Hz, 1H), 7.07 – 7.03 (m, 1H), 5.94 (ddd, *J* = 17.3, 10.6, 6.2 Hz, 1H), 5.34 (dt, *J* = 17.3, 1.0 Hz, 1H), 5.30 (dt, *J* = 10.6, 1.0 Hz, 1H), 5.09 (p, *J* = 6.3 Hz, 1H), 1.59 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 165.60 (C), 156.70 (C), 136.84 (CH), 134.89 (CH), 133.79 (CH), 122.48 (CH), 118.54 (C), 118.10 (CH$_2$), 114.82 (CH), 78.25 (CH), 21.30 (CH$_3$). HRMS-DART calculated for $C_{11}H_{13}O_3$ [M+H]+: 193.08647; found: 193.08716. IR (neat): 3243, 3023, 2920, 1731, 1600 cm^{-1}.

2-[(1-methyl-2-propen-1-yl)thio]-benzoic acid (13a):



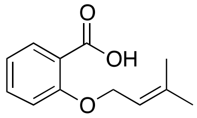
Method C. White solid, (0.15 g, 81%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.15 - 8.08 (m, 1H), 7.50 - 7.39 (m, 2H), 7.30 - 7.20 (m, 1H), 5.85 (ddd, *J* = 17.1, 10.1, 7.8 Hz, 1H), 5.21 - 5.00 (m, 2H), 4.01 - 3.87 (m, 1H), 1.48 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 170.85 (C), 139.29 (CH), 133.20 (C), 132.87 (CH), 132.54 (CH), 129.92 (C), 125.54 (CH), 124.85, 116.07 (CH$_2$), 44.84 (CH), 20.27 (CH$_3$). IR (neat): 2964, 2920, 2652, 2558, 1678, 1560, 1411 cm^{-1}. HRMS-DART calculated for $C_{11}H_{13}O_2S$ [M+H]+: 209.06362; found: 209.06349.

2-[(3-Phenyl-2-propen-1-yl)oxy]benzoic acid (14a):[17]



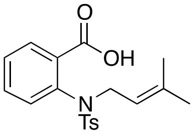
Method A. Yellowish solid, (0.03 g, 35%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.94 (br s, 1H), 8.22 (dd, *J*=7.8, 1.9 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.44 – 7.30 (m, 5H), 7.20 – 7.10 (m, 2H), 6.81 (d, *J* = 15.9 Hz, 1H), 6.43 (dt, *J*= 15.9, 6.3 Hz, 1H), 4.97 (d, *J* = 6.2 Hz, 2H).

2-[(3-Methyl-2-butenyl)oxy]-benzoic acid (15a):[21]



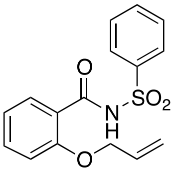
Method A. White solid, (0.85 g, 76%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.76 (br s, 1H), 8.17 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.54 (ddd, *J* = 8.4, 7.4, 1.9 Hz, 1H), 7.11 (ddd, *J* = 7.8, 7.4, 1.0 Hz, 1H), 7.05 (dd, *J* = 8.5, 1.0 Hz, 1H), 5.51 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.75 (d, *J* = 7.1 Hz, 2H), 1.83 – 1.80 (m, 3H), 1.78 – 1.75 (m, 3H).

2-{(3-methyl-2-buten-1-yl)[(4-methylphenyl)sulfonyl]amino} benzoic acid (16a):



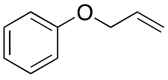
Method A. White solid, (0.40 g, 95%), mp = 135-136°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 1H), 7.62 – 7.54 (m, 2H), 7.46 – 7.40 (m, 2H), 7.31 – 7.27 (m, 2H), 6.93 – 6.87 (m, 1H), 5.14 (tdt, *J* = 7.4, 2.8, 1.3 Hz, 1H), 4.36 (bs, 1H), 4.11 (bs, 1H), 2.42 (s, 3H), 1.59 (d, *J* = 1.4 Hz, 3H), 1.40 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.55 (C), 144.21 (C), 139.21 (C), 138.02 (C), 135.07 (C), 132.62 (CH), 132.04 (CH), 130.00 (CH), 129.62 (CH), 128.72 (CH), 128.15 (CH), 117.54 (CH), 49.69 (CH_2), 25.65 (CH_3), 21.60 (CH_3), 17.58 (CH_3). HRMS-DART calculated for $C_{19}H_{22}NO_4S$ $[M+H]^+$: 360.12695; found: 360.12641. IR (KBr): 2918, 2854, 1704, 1675, 1595 cm^{-1}.

2-Allyloxy-*N*-(phenylsulfonyl)benzamide (17a):



A mixture of 2-allyloxybenzoic acid (0.23 g, 1.05 mmol) and $SOCl_2$ (3 mL, 16.27 mmol) was stirred at rt for 1 h. Then, the excess of $SOCl_2$ was removed under vacuum. The residue obtained was dissolved in toluene (1 mL) and added dropwise to a solution of benzenesulfonamide (0.15 g, 0.95 mmol), DMAP (0.06 g, 0.477 mmol) and Et_3N (0.33 mL, 2.38 mmol) in EtOAc (2 mL). The mixture was stirred a 50 °C for 1 h. Thereafter, a saturated solution of NH_4Cl was added and the aqueous phase was extracted with DCM (3 x 5 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated under vaccum. The residue obtained was purified by column chromatography (hexane/EtOAc: 2:1), to afford the product as a white solid, (0.28 g, 95%), mp = 76-78 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.54 (s, 1H), 8.18 – 8.13 (m, 1H), 8.06 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.56 – 7.52 (m, 2H), 7.49 (ddd, *J* = 8.4, 7.3, 1.9 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.99 (dd, *J* = 8.4, 0.9 Hz, 1H), 6.15 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.54 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.49 (dq, *J* = 10.5, 1.1 Hz, 1H), 4.75 (dt, *J* = 5.6, 1.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.17 (C), 156.87 (C), 138.97 (C), 134.98 (CH), 133.66 (CH), 132.59 (CH), 130.99 (CH), 128.77 (CH), 128.48 (CH), 121.93 (CH), 120.23 (CH_2), 119.06 (C), 113.04 (CH), 70.44 (CH_2). IR (neat): 3288, 3245, 3096, 1680, 1589 cm^{-1}. HRMS-DART calculated for $C_{16}H_{16}NO_4S$ $[M+H]^+$: 318.08000; found: 318.08070.

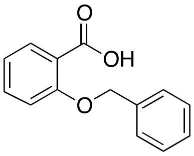
Allyl phenyl ether (18a):[28]



A mixture of phenol (1.00 gr, 10.62 mmol), K_2CO_3 (2.93 gr, 21.24 mmol) and allyl bromide (1.10 mL, 12.7 mmol) was stirred in DMF (27 mL) at 70 ºC for 12 h. Then the reaction was diluted with water (20 mL) and extracted with DCM (3 x 25 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under vacuum. The residue obtained was further purified by silica gel chromatography (hexane/EtOAc, 100:1).

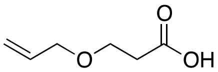
Yellowish oil, (0.435 g, 31 %) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.00 – 6.90 (m, 3H), 6.08 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.43 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.30 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.55 (dt, *J* = 5.3, 1.5 Hz, 2H).

2-Benzyloxy-benzoic acid (19a):[1]



Method A. White solid, (0.52 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.87 (s, 1H), 8.22 (ddd, *J* = 7.8, 1.9, 0.4 Hz, 1H), 7.56 (ddd, *J* = 8.3, 7.4, 1.9 Hz, 1H), 7.47 – 7.41 (m, 5H), 7.19 – 7.11 (m, 2H), 5.30 (s, 2H).

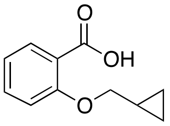
3-Allyloxypropionic acid (20a):[29]



To a Schlenk containing allylic alcohol (1.6 mL, 23.22 mmol) was added *n*-BuLi (0.73 mL, 1.16 mmol, 1. 6 M in hexane) at 0 ºC. After stirring for 10 min, methyl acrilate (1.04 mL, 11.61 mmol) was added at 0 ºC. The mixture was stirred from 0 ºC to 25 ºC for 48 h. Acidification with formic acid (0.2 mL) and concentration under vacuum, gave a suspension which was partially diluted in DCM and then filtered over a mixutre Celite-silica gel. After concentration under vacuum, the residue obtained was dissolved in EtOH (12 mL) and treated with a saturated solution of KOH (20 drops). The homogeneous mixture was stirred at 25 ºC for 48 h. Later on, DCM (10 mL) was added, and the organic phase was extracted with water (3 x 7 mL). The aqueous phase was then acidified with HCl 10% until pH = 3 and extracted with DCM (3 x 7 mL). Finally, the combined organic phases were dried over Na_2SO_4 and concentrated under vacuum.

Yellowish oil (0.19 g, 13%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.20 (ddt, *J* = 10.4, 1.7, 1.2 Hz, 1H), 4.01 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.65 (t, *J* = 6.3 Hz, 2H).

2-(Cyclopropyloxy)-benzoic acid (21a):[30]

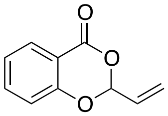


Method B. Colorless oil (0.20 g, 99%).^{1}H NMR (300 MHz, $CDCl_3$) δ 11. 22 (bs, 1H), 8.11 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.11 - 7.01 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.01 (d, *J* = 7.4 Hz, 2H), 1.58 - 1.14 (m, 1H), 0.88 - 0.57 (m, 2H), 0.48 - 0.07 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.58 (C), 157.66 (C), 135.09 (CH), 133.78 (CH), 122.32 (CH), 117.92 (C), 113.03 (CH), 75.57 (CH_2), 10.03 (CH), 3.66 (CH_2). IR (neat): 3246, 3082, 3009, 2943, 2882, 1729, 1601, 1456 cm^{-1}. HRMS-FAB calculated for $C_{11}H_{12}O_3$ $[M+H]^+$: 193.0865; found: 193.0859.

General method for the oxidative cyclization reactions of alkenoic acids:

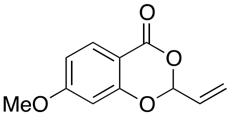
A mixture of the alkenoic acid (0.17 mmol), and AgOAc (0.51 mmol) was stirred in DMSO at 120 ºC for 18 h. After cooling to rt, a saturated solution of NH_4Cl (5 mL) was added, and the mixture was extracted with DCE (3 x 5 mL). The combined organic phases were dried with anhydrous Na_2SO_4 and concentrated under vaccum. The residue obtained was purified by column chromatography (hexane/EtOAc: 10:1).

2-Ethenyl-4*H*-1,3-benzodioxin-4-one (1b):[31]



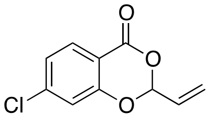
Yellowish oil, (0.023 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (ddd, *J* = 7.8, 1.7, 0.5 Hz, 1H), 7.58 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 7.19 (ddd, *J* = 7.9, 7.4, 1.0 Hz, 1H), 7.07 (ddd, *J* = 8.3, 1.1, 0.5 Hz, 1H), 6.12 (ddd, *J* = 17.3, 10.7, 4.8 Hz, 1H), 6.01 (dt, *J* = 4.8, 1.1 Hz, 1H), 5.77 (ddd, *J* = 17.3, 0.8 Hz, 1H), 5.60 (dt, *J* = 10.7, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.69 (C), 157.93 (C), 136.36 (CH), 130.65 (CH), 130.26 (CH), 123.53 (CH), 122.29 (CH_2), 116.83 (CH), 114.61 (C), 99.61 (CH). IR (neat): 3089, 2959, 2925, 2857, 1748, 1612, 1587 cm^{-1}. HRMS-DART calculated for $C_{10}H_9O_3$ $[M+H]^+$: 177.05517; found: 177.05562.

2-Ethenyl-7-methoxy-4*H*-1,3-benzodioxin-4-one (2b):



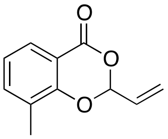
Yellowish oil, (0.013 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 1H), 6.73 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 6.12 (ddd, *J* = 17.3, 10.7, 4.8 Hz, 1H), 6.00 (dt, *J* = 4.8, 1.1 Hz, 1H), 5.77 (dt, *J* = 17.3, 0.9 Hz, 1H), 5.60 (dt, *J* = 10.7, 0.9 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.21 (C), 161.60 (C), 159.83 (C), 131.75 (CH), 130.77 (CH), 122.10 (CH_2), 111.43 (CH), 107.13 (C), 100.50 (CH), 99.56 (CH), 55.82 (CH_3). IR (neat): 3089, 2946, 2843, 1733, 1612, 1581 cm^{-1}. HRMS-DART calculated for $C_{11}H_{11}O_4$ $[M+H]^+$: 207.06573; found: 207.06575.

7-Chloro-2-ethenyl-4*H*-1,3-benzodioxin-4-one (3b):



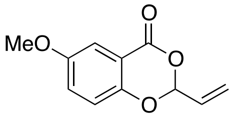
Yellowish oil, (0.022 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.17 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.11 (dd, *J* = 1.9, 0.4 Hz, 1H), 6.10 (ddd, *J* = 17.2, 10.6, 4.7 Hz, 1H), 6.02 (dt, *J* = 4.8, 1.0 Hz, 1H), 5.77 (ddd, *J* = 17.2, 0.7 Hz, 1H), 5.62 (ddd, *J* = 10.6, 0.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.99 (C), 158.42 (C), 142.56 (C), 131.49 (CH), 130.43 (CH), 124.48 (CH), 122.78 (CH_2), 117.43 (CH), 113.20 (C), 99.98 (CH). IR (neat): 3005, 2845, 2859, 1648, 1657 cm^{-1}. HRMS-DART calculated for $C_{10}H_8ClO_3$ [M+H]+: 211.01620; found: 211.01549.

2-Ethenyl-8-methyl-4*H*-1,3-benzodioxin-4-one (4b):



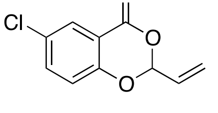
Yellowish oil, (0.019 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (ddq, *J* = 7.8, 1.7, 0.6 Hz, 1H), 7.42 (ddq, *J* = 7.5, 1.6, 0.8 Hz, 1H), 7.08 (ddd, *J* = 7.5, 0.4 Hz, 1H), 6.14 (ddd, *J* = 17.3, 10.7, 4.7 Hz, 1H), 6.00 (dt, *J* = 4.7, 1.1 Hz, 1H), 5.78 (ddd, *J* = 17.3, 0.8 Hz, 1H), 5.60 (dt, *J* = 10.7, 0.0 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.08 (C), 156.22 (C), 137.28 (CH), 130.88 (CH), 127.72 (CH), 126.38 (C), 122.91 (CH), 121.97 (CH_2), 114.26 (C), 99.32 (CH), 14.95 (CH_3). IR (neat): 2923, 2856, 1741, 1602, 1483 cm^{-1}. HRMS-DART calculated for $C_{11}H_{11}O_3$ [M+H]$^+$: 191.07082; found: 191.07149.

2-Ethenyl-6-methoxy-4*H*-1,3-benzodioxin-4-one (5b):



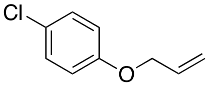
Yellowish oil, (0.018 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 1H), 6.71 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 6.09 (ddd, *J* = 17.3, 10.7, 4.8 Hz, 1H), 5.98 (dt, *J* = 4.8, 1.1 Hz, 1H), 5.75 (dt, *J* = 17.3, 1.0 Hz, 1H), 5.58 (dt, *J* = 10.7, 0.9 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.20 (C), 161.61 (C), 159.83 (C), 131.75 (CH) , 130.76 (CH), 122.12 (CH_2), 111.44 (CH), 107.11 (C), 100.49 (CH), 99.57 (CH), 55.83 (CH_3). IR (neat): 3005, 2912, 2838, 1741, 1489, 1428 cm^{-1}. HRMS-DART calculated for $C_{11}H_{11}O_4$ [M+H]$^+$: 207.06573; found: 207.06612.

6-Chloro-2-ethenyl-4*H*-1,3-benzodioxin-4-one (6b):



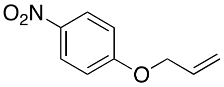
Yellowish oil, (0.009 g, 32 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 2.6, 0.4 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.04 (dd, *J* = 8.8, 0.4 Hz, 1H), 6.10 (ddd, *J* = 17.3, 10.7, 4.7 Hz, 1H), 6.00 (dt, *J* = 4.8, 1.0 Hz, 1H), 5.77 (ddd, *J* = 17.3, 0.7 Hz, 1H), 5.62 (dt, *J* = 10.7, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.67 (C), 156.50 (C), 136.52 (CH), 130.41 (CH), 129.75 (CH), 129.10 (C), 122.83 (CH_2), 118.64 (CH), 115.81 (C), 99.96 (CH). IR (neat): 2923, 2856, 1744, 1607, 1472, 1420 cm^{-1}. HRMS-DART calculated for $C_{10}H_8ClO_3$ $[M+H]^+$: 211.01620; found: 211.01663.

4-Allyloxy-1-chlorobenzene (6c).[32]



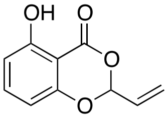
^1H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 2H), 6.87 – 6.81 (m, 2H), 6.03 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.40 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.29 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.51 (dt, *J* = 5.3, 1.5 Hz, 2H).

1-Allyloxy-4-nitrobenzene (7c).[33]



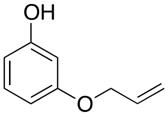
^1H NMR (300 MHz, $CDCl_3$) δ 8.24 – 8.17 (m, 2H), 7.03 – 6.92 (m, 2H), 6.04 (ddt, *J* = 17.1, 10.5, 5.3 Hz, 1H), 5.44 (dq, *J* = 17.3, 1.5 Hz, 1H), 5.35 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.64 (dt, *J* = 5.3, 1.5 Hz, 2H).

2-Ethenyl-5-hydroxy-4*H*-1,3-benzodioxin-4-one (8b):



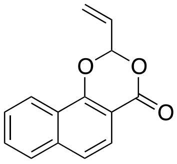
Yellowish oil, (0.002 g, 4 %). ^1H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 1H), 7.45 (t, *J* = 8.3 Hz, 1H), 6.70 (dd, *J* = 8.5, 0.9 Hz, 1H), 6.55 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.10 (ddd, *J* = 17.1, 10.6, 4.8 Hz, 1H), 6.03 (dt, *J* = 4.8, 0.9 Hz, 1H), 5.78 (dt, *J* = 17.1, 0.8 Hz, 1H), 5.62 (dt, *J* = 10.5, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.37 (C), 161.88 (C), 157.50 (C), 138.12 (CH), 130.33 (CH), 122.89 (CH), 111.72 (CH), 106.94 (CH), 100.68 (C), 100.20 (CH). IR (neat): 3255, 2987, 2856, 1704, 1632, 11587, 1485 cm^{-1}.

3-Allyloxy-phenol (8c):[34]



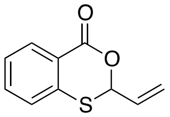
Yellowish oil, (0.003 g, 7 %). ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 1H), 6.51 (ddd, *J* = 8.3, 2.3, 1.0 Hz, 1H), 6.45 – 6.40 (m, 2H), 6.05 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.41 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.83 (bs, 1H), 4.51 (dt, *J* = 5.3, 1.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.97 (C), 156.65 (C), 133.17 (CH), 130.09 (CH), 117.68 (CH), 107.90 (CH), 107.22 (CH), 102.32 (CH), 68.82 (CH_2).

2-Ethenyl-4*H*-naphtho[1,2-*d*][1,3]dioxin-4-one (9b):



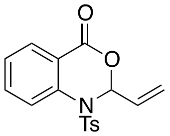
Yellowish oil, (0.05 g, 50%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.25 (ddt, *J* = 8.3, 1.4, 0.8 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.68 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.62 – 7.56 (m, 2H), 6.26 (ddd, *J* = 17.1, 10.6, 4.8 Hz, 1H), 6.19 (dt, *J* = 4.8, 1.0 Hz, 1H), 5.90 – 5.84 (m, 1H), 5.67 (dt, *J* = 10.5, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.02 (C), 156.41 (C), 137.41 (C), 130.71 (CH), 130.09 (CH), 128.08 (CH), 126.93 (CH), 123.75 (CH), 123.22 (C), 123.05 (CH), 122.86 (CH), 122.43 (CH$_2$), 108.87 (C), 99.88 (CH). IR (neat): 2923, 1738, 1630, 1579 cm^{-1}. HRMS-DART calculated for $C_{14}H_{11}O_3$ [M+H]$^+$: 227.07082; found: 227.07139.

2-Ethenyl-4*H*-3,1-benzoxathiin-4-one (10b):



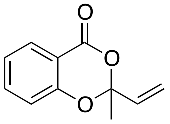
Pink oil, (0.025 g, 84%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (ddd, *J* = 7.8, 1.5, 0.8 Hz, 1H), 7.49 (ddd, *J* = 8.8, 7.1, 1.5 Hz, 1H), 7.35 – 7.30 (m, 2H), 6.16 – 6.02 (m, 2H), 5.71 – 5.63 (m, 1H), 5.50 – 5.44 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.64 (C), 137.95 (C), 133.72 (CH), 132.60 (CH), 131.21 (CH), 127.60 (CH), 126.81 (CH), 124.32 (C), 120.60 (CH$_2$), 81.64 (CH). IR (neat): 3063, 2921, 2852, 1723, 1589, 1440 cm^{-1}. HRMS-DART calculated for $C_{10}H_9O_2S$ [M+H]$^+$: 193.03232; found: 193.03262.

2-Ethenyl-1-[(4-methylphenyl)sulfonyl]-1*H*-benzo[d][1,3]oxazin-4(2*H*)-one (11b):



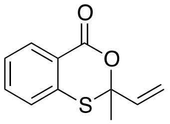
Yellowish oil, (0.013 g, 67%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (ddd, *J* = 4.0, 1.4, 0.5 Hz, 1H), 7.82 (ddd, *J* = 4.4, 1.4, 0.5 Hz, 1H), 7.66 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.38 – 7.33 (m, 1H), 7.17 – 7.13 (m, 1H), 6.80 (dt, *J* = 3.2, 2.0 Hz, 1H), 5.78 (ddd, *J* = 17.2, 10.7, 3.2 Hz, 1H), 5.44 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.30 (dd, *J* = 10.7, 2.1 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.66 (C), 145.40 (C), 137.12 (C), 135.10 (CH), 133.86 (C), 132.49 (CH), 129.99 (CH), 127.80 (C), 127.77 (CH), 126.57 (CH), 121.42 (CH$_2$), 121.34 (C), 86.07 (CH), 21.78 (CH$_3$). IR (neat): 3068, 2957, 2924, 2857, 1732, 1600 cm^{-1}. HRMS-DART calculated for $C_{17}H_{16}NO_4S$ [M+H]$^+$: 330.08000; found: 330.08084.

2-Ethenyl-2-methyl-4*H*-1,3-benzodioxin-4-one (12b):[35]



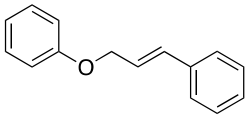
Yellowish oil, (0.015 g, 20%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.9, 1.7 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.14 – 7.06 (m, 1H), 7.02 – 6.95 (m, 1H), 5.90 (dd, J = 17.3, 10.8 Hz, 1H), 5.52 (d, J = 17.3 Hz, 1H), 5.32 (d, J = 11.0 Hz, 1H), 1.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.52 (C), 156.38 (C), 136.56 (C), 136.43 (CH), 129.77 (CH), 122.89 (CH), 119.78 (CH_2), 117.09 (CH), 114.63 (C), 105.33 (CH), 26.82 (CH_3). IR (neat): 3086, 2920, 2852, 1746, 1613, 1592 cm^{-1}. HRMS-DART calculated for $C_{11}H_{11}O_3$ [M+H]$^+$: 191.07082; found: 191.07091.

2-Ethenyl-2-methyl-4*H*-1,3-benzoxathiin-4-one (13b):[28]



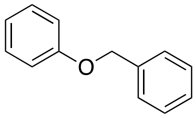
Yellowish (0.019 g, 47%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (ddd, J = 7.8, 1.5, 0.6 Hz, 1H), 7.45 (td, J = 7.5, 1.5 Hz, 1H), 7.31 - 7.18 (m, 2H), 5.95 (dd, J = 17.0, 10.7 Hz, 1H), 5.36 (d, J = 17.0 Hz, 1H), 5.14 (d, J = 10.7 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.88 (C), 138.55 (CH), 136.32 (C), 133.90 (CH), 132.06 (CH), 127.69 (CH), 126.59 (CH), 124.19 (C), 117.03 (CH_2), 87.34 (C), 28.20 (CH_3). IR (neat): 3066, 2986, 2927, 2852, 1719, 1589, 1440 cm^{-1}. HRMS-DART calculated for $C_{11}H_{11}O_2S$ [M+H]$^+$: 207.04797; found: 207.04800.

Cinnamyloxybenzene (14c).[36]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.39 – 7.23 (m, 5H), 7.03 – 6.94 (m, 3H), 6.75 (dt, J = 16.1, 1.5 Hz, 1H), 6.44 (dt, J = 16.0, 5.8 Hz, 1H), 4.71 (dd, J = 5.8, 1.5 Hz, 2H).

Benzyloxybenzene (19c).[37]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.27 (m, 7H), 7.08 – 6.95 (m, 3H), 5.08 (s, 2H).

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